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LIST OF ABBREVIATIONS

Ac	acetyl
Bn	benzyl
CI	chemical ionization
CuAAC	Cu catalyst azide-alkyne cycloaddition
DFT	density fuctional theory
DIAD	diisopropyl azodicarboxylate
DPPA	diphenylphosphoryl azide
DMF	*N*,*N*-dimethylformamide
EI	electron impact ionization
ESI	electrospray ionization
Et	ethyl
IR	infrared absorption spectrometry
i	iso
n	normal
t	tertiary
LHMDS	lithium hexamethyldisilazide
Me	methyl
MIP	2-methoxyisopropyl
MOM	methoxymethyl
Ms	methane sulfonyl
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
Nu	nucleophile
Ph	phenyl
Py	pyridine
R*f*	retention factor
SPAAC	strain-promoted azide-alkyne cycloaddition
T	temperature
TBAF	tetrabutylammonium fluoride
TBAI	tetrabutylammonium iodide
TBS	*t*-butyldimethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid

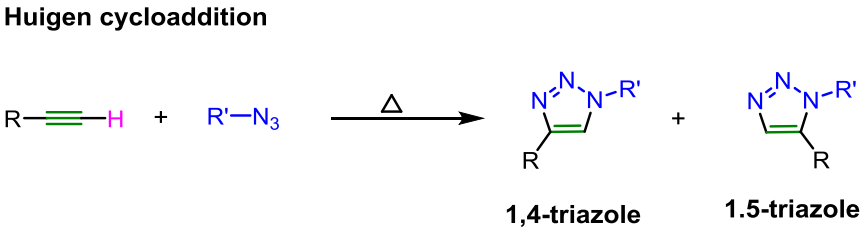
	tetrahydrofuran
THF	thin layer chromatography
TLC	trimethylsilyl
TMS	*p*-toluene sulfonyl
Ts	

Chapter 1 Introduction

1.1 Synthesis of 1,2,3-triazoles

1,2,3-triazoles have been studied for over a century as the important heterocyclic moiety and still attracted considerable attention due to their numerous applications. The conventional methodology to produce 1,2,3-triazole is [3+2] Azide-Alkyne Cycloaddition (AAC).

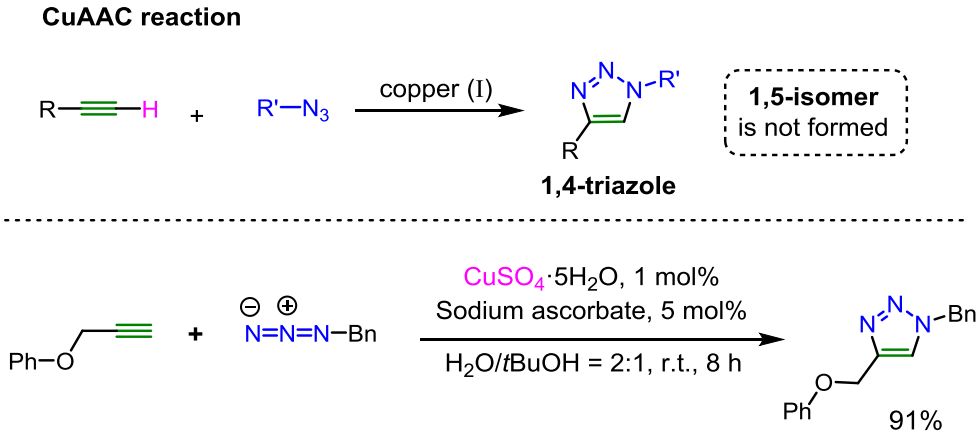
The first synthesis of 1,2,3-triazoles was demonstrated with diethyl acetylenedicarboxylate and phenyl azide reported by A. Michael in 1893.[1] In 1960s, Huisgen significantly pioneered the thermal conditions (Scheme 1). However, due to the high activation energy (ΔG = +26 kcal/mol), these cycloadditions require elevated temperature and long reaction time to accelerate the reaction (80~120°C for 12~24h), affording a mixture of 1,4 and 1,5 regioisomers (Scheme 1).[2]



Scheme 1. *Huisgen cycloaddition reaction.*

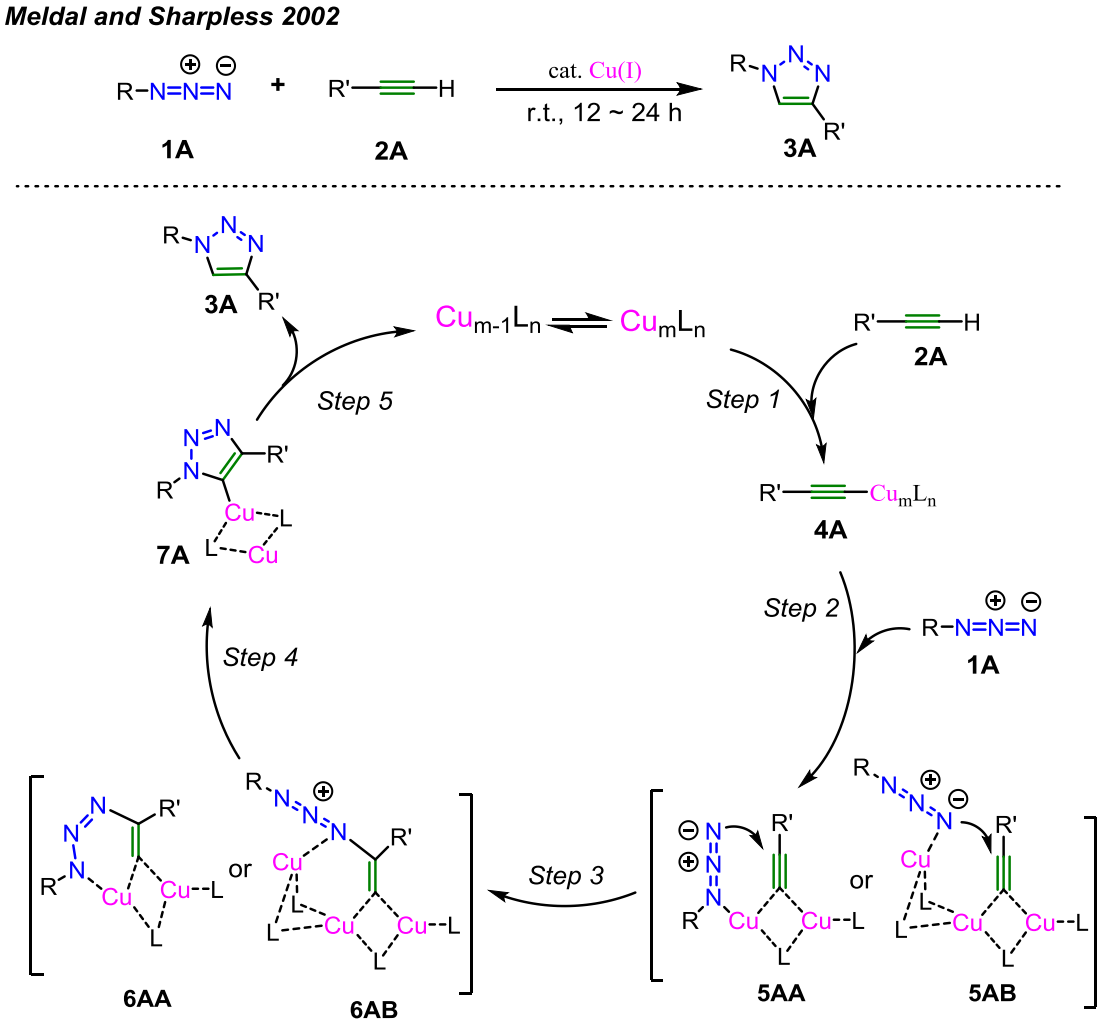
In the past decade, this cycloaddition reaction has been extensively developed to lower the activation barrier, since the copper-catalyzed conditions were reported. In 2002, the groups of Sharpless[3] and Meldal[4] independently developed the Cu(I)

catalysts dramatically accelerate the reaction of terminal alkynes with azides, to give the 1,4 disubstitutied triazoles regioselectively under mild conditions (Scheme 2).



Scheme 2. *Highly regioselective Cu catalyzed azide-alkyne cycloaddition reaction.*

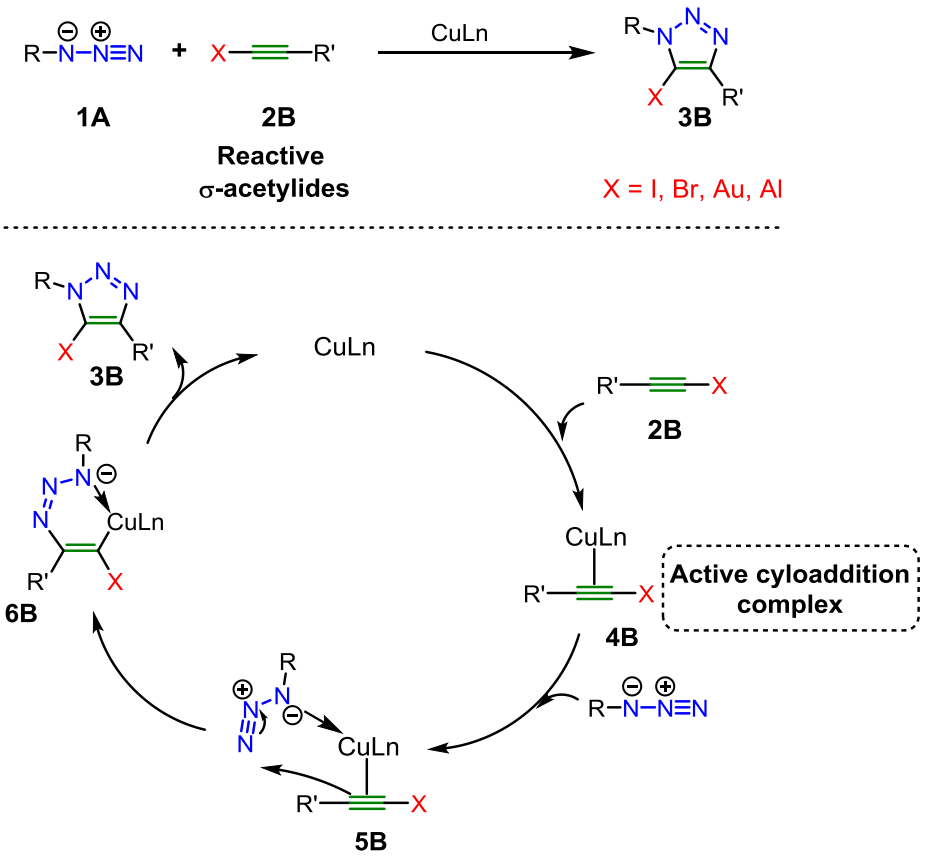
The proposed mechanism of CuAAC reaction has been investigated by many groups over the past decade, but still has not yet been completely proven, especially the complexation of the Cu(I)-species and the origin selectivity of the cycloaddition are still unknown. The copper catalysts in these transformation are Cu(I), in addition, Cu(II) salts can also be used as pre-catalysts which can be easily reduced to Cu(I) in the present of reducing agents (sodium ascorbate). Moreover, addition of base can significantly accelerate the transformation under Cu(I) catalyst conditions, comparing with Cu(II) case that no effect of base addition was observed.



Scheme 3. *Proposed mechanism for CuAAC reaction by kinetic studies.*

The mechanism of the CuAAC reaction has been investigated by kinetic studies and DFT calculation.[2,5-8] At first, in the present of base, the important intermediate Cu(I) acetylide **1A** (Scheme 3) was formed from Cu(I) and alkyne **1A**. The step 2 is the coordination of azide **1A** and to the Cu(I) acetylide to form the complex **6A**. It is suggested that complex **5A** can be presented as **5AA** or **5AB** that alkynyl **2A** and azide **1A** were coordinated to one Cu center or not. Structure **5AA** indicates that the

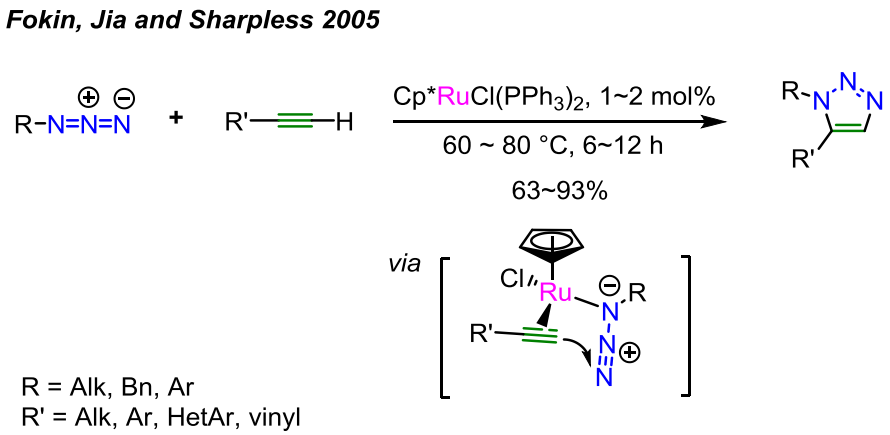
Cu(I) acetylide **4A** and azide **1A** coordinate to just one copper atom. On the other hand, structure **5AB** demonstrates that the coordination of the substrate to different copper atoms is possible. Through C-N bond formation to give the triazolide **7A**, finally 1,4-disubstituted 1,2,3-triazole **3A** is produced by protonolysis with the recovery of the copper catalyst.



Scheme 4. *Proposed mechanism for CuAAC reaction with reactive σ-acetylides.*

In the case of dipolar cycloadditions of 1-halo and 1-metalloalkynes with organic azides suggested that the copper catalyst effects the cycloaddition reaction through π-interactions with the formally internal alkyne (Scheme 4).[8,9] At first, the copper may

activate the reactive σ-acetylides through formation of π-complex intermediate **4B** to which organic azide coordinates leading complex **5B**. Then nucleophilic attack at N of the azide by β carbon of the acetylide forms the C-N bond, producing intermediate **6** which results the ring closure product **3B**.

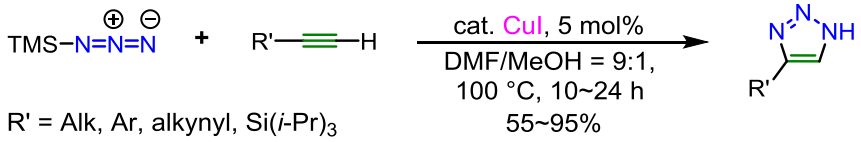


Scheme 5 *Ru-catalyzed Azide-Alkyne cycloaddition reaction.*

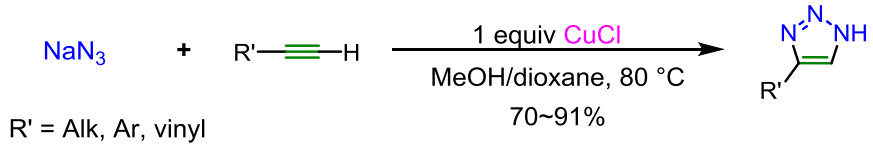
In 2005, Fokin, Jia and Sharpless demostrated the synthesis of 1,5-disubstituted 1,2,3-triazoles (Scheme 5).[10] These cycloadditions of terminal alkynes with organic azides were carried out in the present of Cp*Ru-catalyst forming 1,5-disubstituted triazoles in good yield with high regioselectivity, complementary to CuAAC producting 1,4-disubstituted triazoles.

Due to the high efficiency, this CuAAC reaction has been extensively developed and applied by many groups. Thus, Yamamoto's group reported the cycloaddition reaction with trimethylsilyl azide ($TMSN_3$) to prepare the *NH*-triazoles in good yields

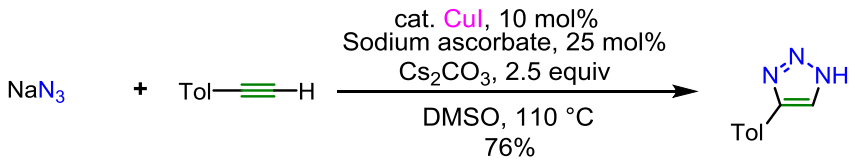
(Scheme 6).[11] The reaction proceed through the formation of Cu-acetylides followed by a cycloaddtion reaction with the in situ-formed hydrazoic acid. This protocol allows the preparation of a lot of substituted triazoles in good yields. Yang's group developed the Cu(I)-mediated cycloaddition reaction of terminal alkynes and sodium azide (NaN_3) to give the corresponding triazoles in good to excellent yields (Scheme 7).[12] More recently, Kuang and co-workers demonstrated that this CuAAC reaction of terminal alkyne and sodium azide could proceeded in the present of catalytic amount of Cu(I) and base (Scheme 8).[13]



Scheme 6. *CuAAC reaction with $TMSN_3$ by Yamamoto's group.*



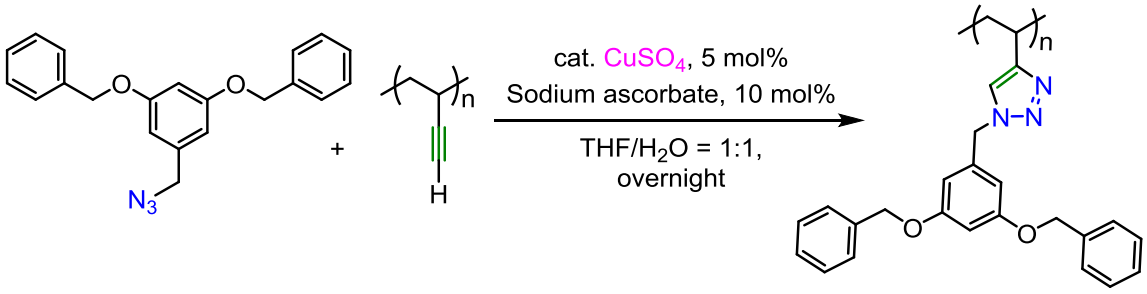
Scheme 7. *CuAAC reaction with $TMSN_3$ by Yang's group.*



Scheme 8. *CuAAC reaction with $TMSN_3$ by Kuang's group.*

These metal-catalyst variant of the Huisgen [3+2] cycloaddition have made an

enormous impact in chemical discipline, ranging from drug discovery, chemical biology, materials science, development of sensors, polymer chemistry to nanotechnology. In 2004, Fréchet and co-workers reported the application of this CuAAC reaction using poly(vinylacetylene) and dendritic benzyl azide for (Scheme 9).[14]



Scheme 9. *Application of CuAAC reaction for polymer chemistry.*

CuAAC also has been utilized to modifications of activity and selectivity of existing pharmaceuticals and natural products, and compatible with the complexity of these compound classes. Based on replacement of the central part of known HIV inhibitors, Brik et al. synthesized the novel compounds through CuAAC reaction, in which the triazole actively participated in the crucial binding to the water nucleophile (Figure 2).[15,16] In vitamin D synthesis,[17,18] advantage has been taken of the exquisite orthogonality and specificity of the of the triazole coupling and the triazole has been formed at last step of synthesis in the presence of unprotected functional groups. Under the standard CuAAC condition, the desired cycloaddition products were

isolated in good yields (70~100%) (Figure 3).

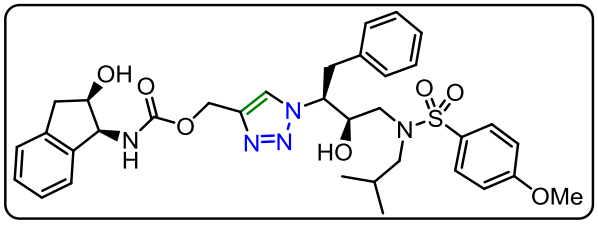


Figure 2. *Chemical structure of HIV-1 protease inhibitor.*

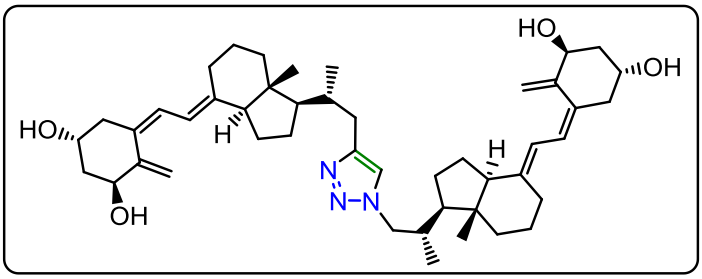


Figure 3. *Chemical structure of Vitamin D dimer.*

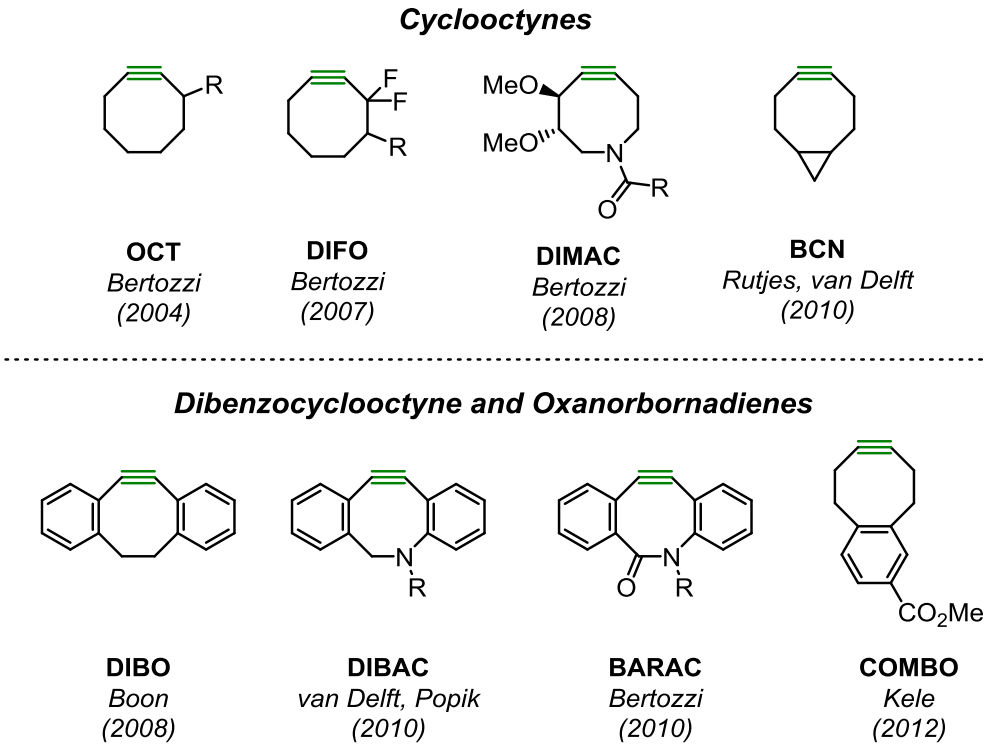
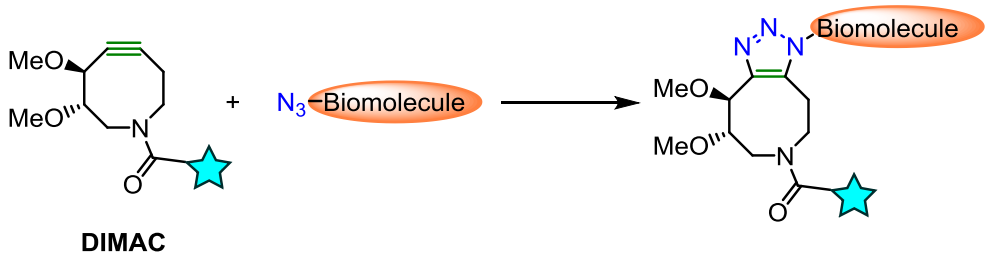


Figure 4. *Reagent development for Copper-free AAC reaction.*

Despite the power and versatility of CuAAC reaction, the requirement for the toxic

copper severely limits its application in cellular systems. And the scope of reaction materials is also limited due to the potential for residual traces of copper.[19] Thus, many groups have developed the mild, rapid and Cu-free triazolations.

As an catalyst-free alternative approach to lower the activation barrier for cycloaddition, Bertozzi, Boons and Alabugin, harnessing the reactivity of activated cyclooctynes (OCT), have developed strain-promoted azide-alkyne cycloadditions which has been well-utilized in chemical biology (Figure 4). In 2008, Bertozzi reported the synthesis of 6,7-dimethoxyazacyclooct-4-yne (DIMAC) which is biocompatible and feasible for detecting azide-labeled biomolecules via copper-free azide-alkyne cycloaddition reaction (Scheme 10).[20] During the past years, by Boons group the dibenzocyclooctynes (DIBO) has been tested as high potential compounds for copper-free azide-alkyne bioconjugations (Figure 4).

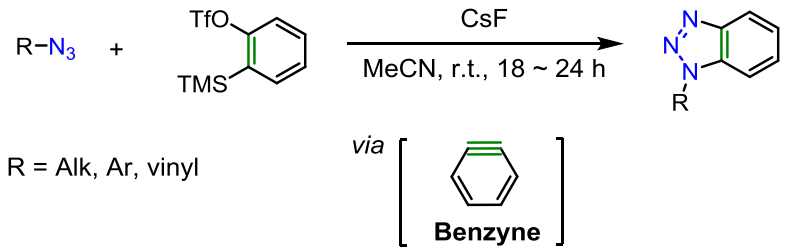


DIMAC

Scheme 10. *DIMAC for biolabeling study via copper-free AAC reaction.*

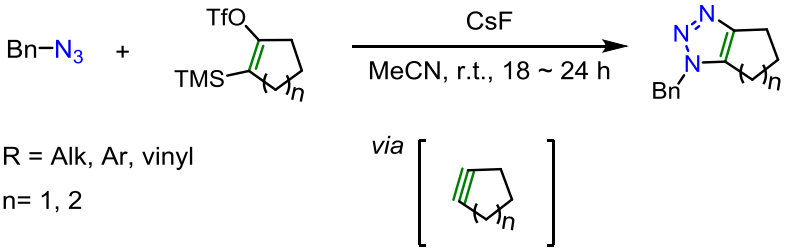
Moreover, Moses, Larock, Reddy, and Feringa reported separately that the [3+2] cycloadditions of benzynes and organic azides under mild conditions to form

benzotriazoles rapidly. Benzynes which can be formed from, for example, trimethylsilylphenyl *O*-triflate through fluoride-promoted *o*-elimination, reacted with various azides to afford the functional benzotriazoles (Scheme 11).[21]



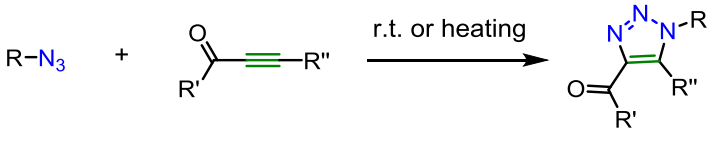
Scheme 11. *Synthesis of benzotriazoles from benzynes and azides.*

More recently, Garg and co-workers demonstrated that the cycloadditions of cyclohexynes and the more elusive intermediate, cyclopentyne, with organic azide to construct the new heterocyclic compounds (Scheme 12).[22]



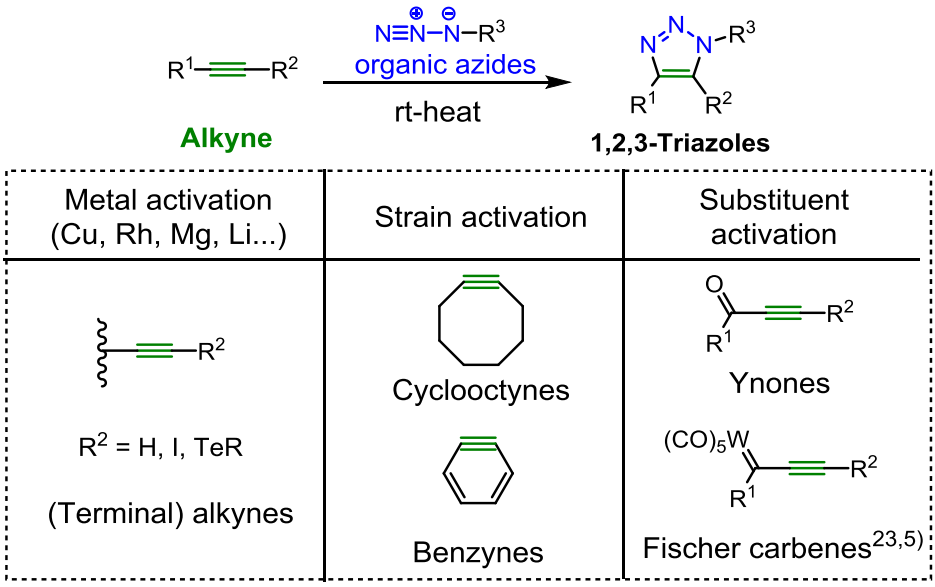
Scheme 12. *Cycloaddition of Cyclohexyne and Cyclopentyne.*

In additional, Curran, Maas, and others also reported that C-C triple bond activated by a carbonyl can accelerate the reaction,[23] affording the corresponding triazoles under mild conditions compared with general alkynes (Scheme 13).



Scheme 13. *AAC activation by carbonyl furnishes.*

However, metal-catalyst AAC are limited to mostly terminal alkynes (Scheme 14) and the toxicity of copper salts limits the utility for the in vivo applications. With the increasing of the reactivity, cyclooctyne became unstable that should be stored as a solid at 0 °C protected from light and oxygen (BARAC, Figure 4).[24] The lack of regioselectivity in the cycloadditions was also a disadvantage of strain-promoted azide-alkyne cycloaddtion reactions, preventing its application in drug design and peptidomimetics. Moreover, most of the reported methods require ambient or elevated temperature with long reaction time.



Scheme 14. *Strategies of Azide-Alkyne cycloadditions.*

Therefore, I was interested in development of the novel rapid triazole synthesis which can allow both internal- and terminal-alkyne to afford fully substituted 1,2,3-triazoles and multicomponent coupling reactions between ambient and low

temperature.

1.2 Organic azides

Organic azides are popular functionalities in organic chemistry, and in 1864 the first organic azide, phenyl azide, has been synthesized by Perter Grieβ.[25,26] After that, in more than 150 years, numerous applications of these energy-rich molecules have been investigated,[27] such as Curtius rearrangement that provide the isocyanates from appropriate acyl azides,[28] Staudinger reaction,[29] Schmidt reaction,[30,31] Huisgen reaction,[32,33] and so on.

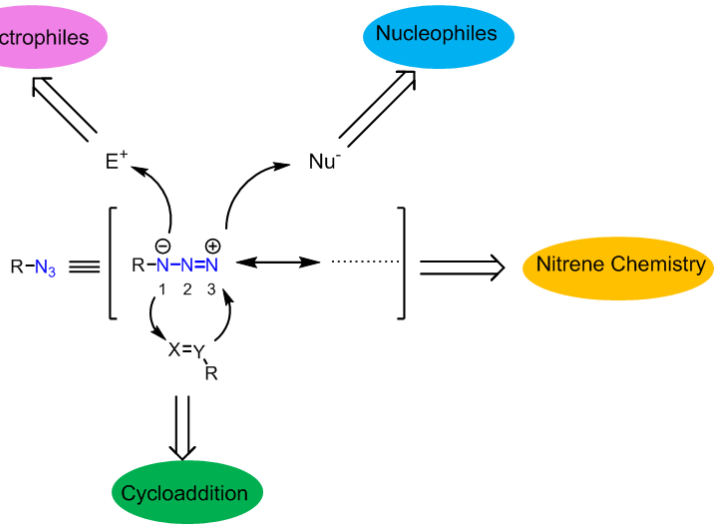


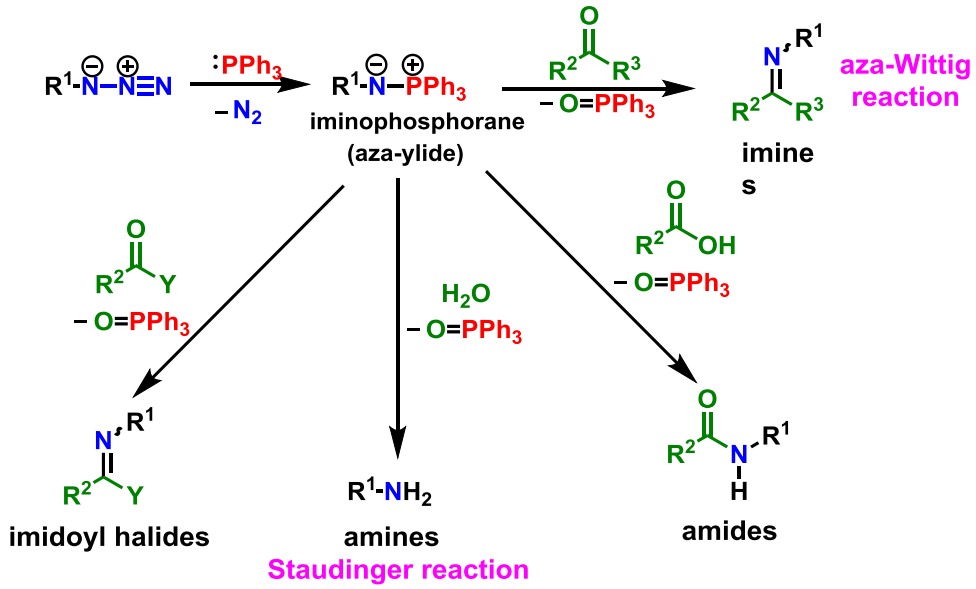
Figure 5 *Reactivity of organic azide.*

Organic azides involve three zwitterionic nitrogens and prove very different chemical reactivities (Figure 1). In principle, organic azide can work as a nucleophile at the N1 atom and as an electrophile the N3 atom. With the three zwitterionic nitrogens,

organic aizdes also work as 1,3-dipolar, reacting with dipolarophile for cycloaddition reaction. In addition, nitrenes can be produced from organic azides under thermal conditions or photoirradiations, and be utilized to aziridinations and C-H aminations.

1.2.1 Reactions as an electrophile

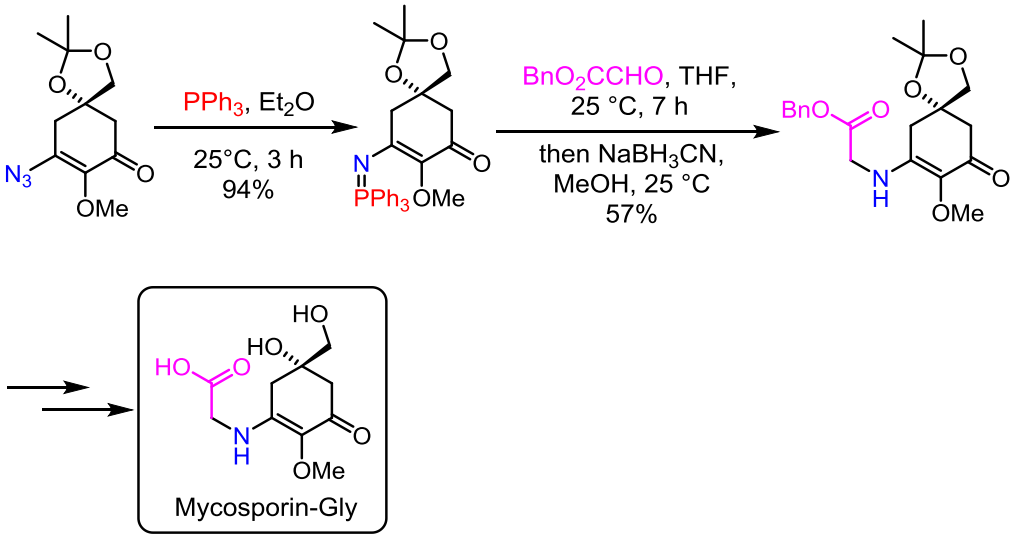
In 1919, Staudinger and Meyer reported the Staudinger reduction using phenyl azide and triphenylphosphine as procedure. This reaction involves the construction of iminophosphoranes which are important reagents and intermediates for variety of organic nitrogen compounds (Scheme 15).[34]



Scheme 15. *Nucleophilic addition to organic azide.*

In the present of water, this iminophosphorane can be hydrolyzed to the corresponding primary amine with formation of phosphine oxide; with carboxylic acid the aza-ylide can be converted to *N*-substituted amindes; and also condensation with

acyl halides can generate imydoyl halides. Moreover, the reaction of iminophosphoranes with various carbonyl compounds, called aza-Wittig reaction, has been frequently used for produce imines.[35-38] The product of the reaction is Schiff base. Due to its high synthetic potential, this methodology has been received considerable attention in the past decade for the generation of C=N bond containing heterocycles compounds.[15] In particular, the intramolecular aza-Wittig reaction is one of powerful tools for the prepartation of five-, six-, seven-, and eight-membered heterocycles.[39-43]

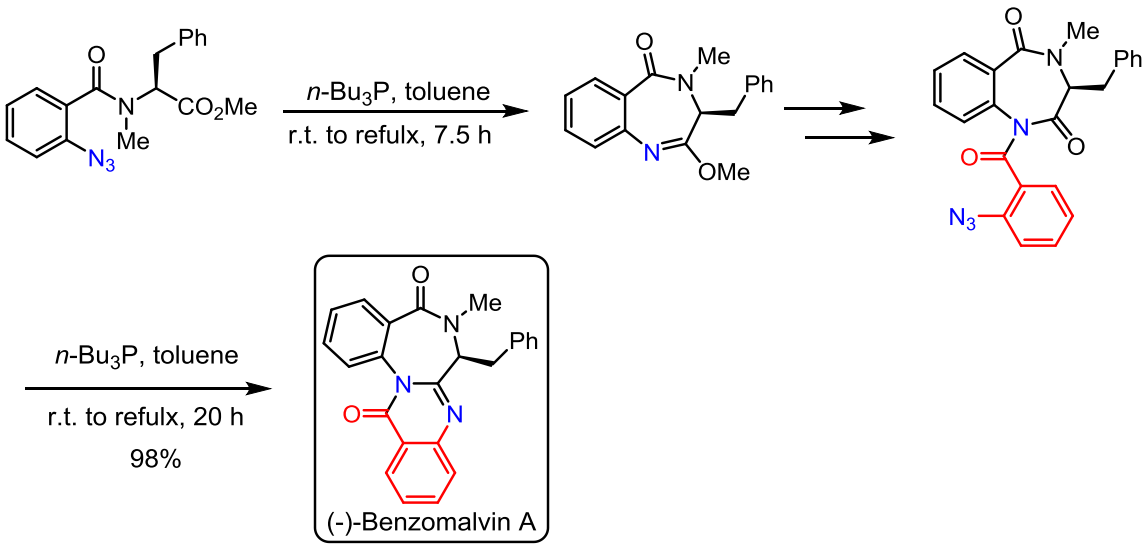


Scheme 16. *Total synthesis of Mycosporin-Gly by Staudinger reaction.*

In 1989, Staundinger reaction had been utilized to the enatioselective total synthesis of mycosporins (Scheme 16).[44] To elaborate the side chain, the cyclic vinyl azide was first converted to a stable vinyl iminophosphorane followed by reaction with benzyl glyoxylate to afford the Schiff base which was promptly reduced by sodium

cyanoborohydride.

The first total synthesis of (-)-benzomalvin A was achieved by Eguchi's group (Scheme 17). Both of the heterocycle skeletons were efficiently prepared by intramolecular aza-Wittig reaction.[45,46] Starting with L-phenylalanine, the azide derivative was reacted with tributylphosphine to generate the iminophosphorane followed by the intramolecular aza-Wittig cyclization to give the seven-member ring. The endgame of the synthetic route was accomplished by another intramolecular aza-Wittig cyclization reaction.



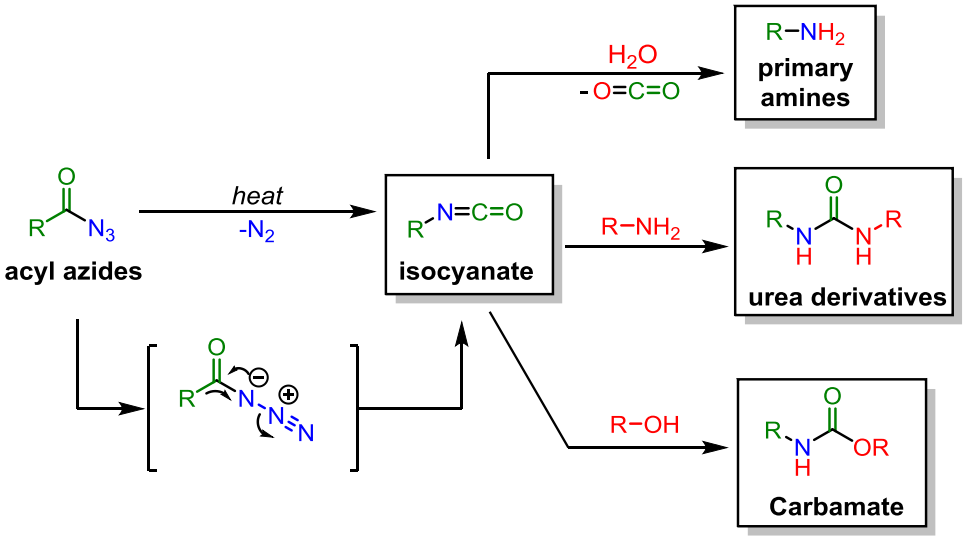
Scheme 17. *Total synthesis of (-)-benzomalvin A with aza-Wittig reaction.*

1.2.2 Nitrogen elimination-initiated reactions

Under thermolysis or photolysis conditions, azides can easily release nitrogen gas, and this promotes various rearrangements and addition reactions.[47,48] Nitrenes are one

of chemical species produced under these conditions. Although nitrenes are related to carbenes, they still have different properties.[49] The reactions of nitrenes were ranged from cycloaddition, rearrangement to insertion reactions.

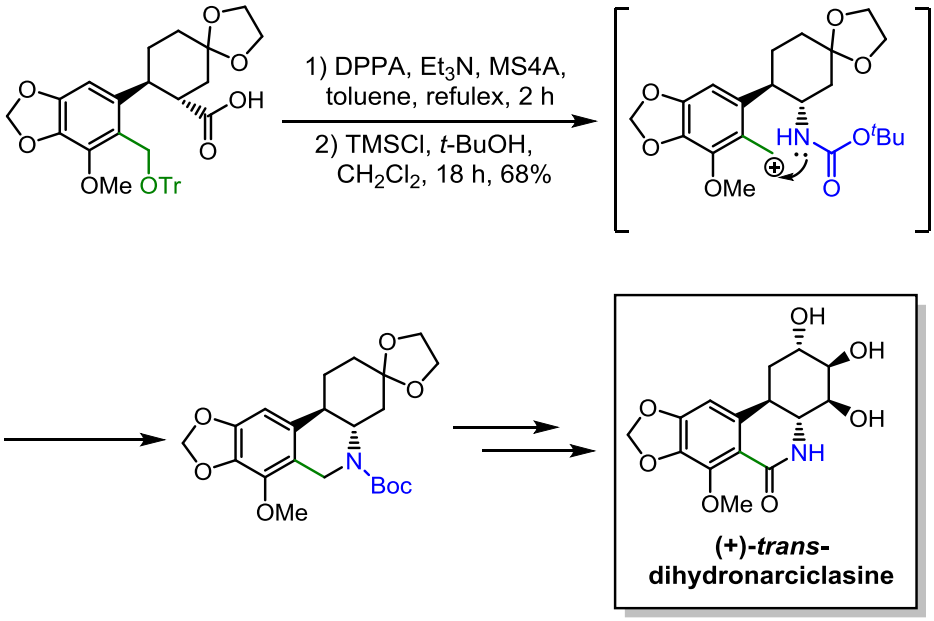
The Curtius rearrangement reaction is decomposition of acyl azides to afford the corresponding isocyanates (Scheme 18). If the generated isocyanate is treated with water, primary amine can be formed. When the reactions are carried out in the present of amines, the corresponding urea derivatives can be obtained. With alcohol, the isocyanates are converted to carbamate compounds.



Scheme 18. *Curtius rearrangement reaction.*

The total synthesis of *anti*-cancer alkaloid *trans*-dihydronarciclasine isolated from the Chinese medicinal plant *Zephyranthes candida* (Scheme 19) was achieved using Curtius rearrangement reaction.[50] Acylazide was generated from carboxylic acid with

diphenylphosphoryl azide (DPPA) and the producing isocyanate was generated with *tert*-butanol to give Boc-amine product. Through this reaction, the generated benzylic carbocation was trapped with the amide to constract the tricyclic compound, which was then transformed to the desired (+)-*trans*-dihydronarciclasine.

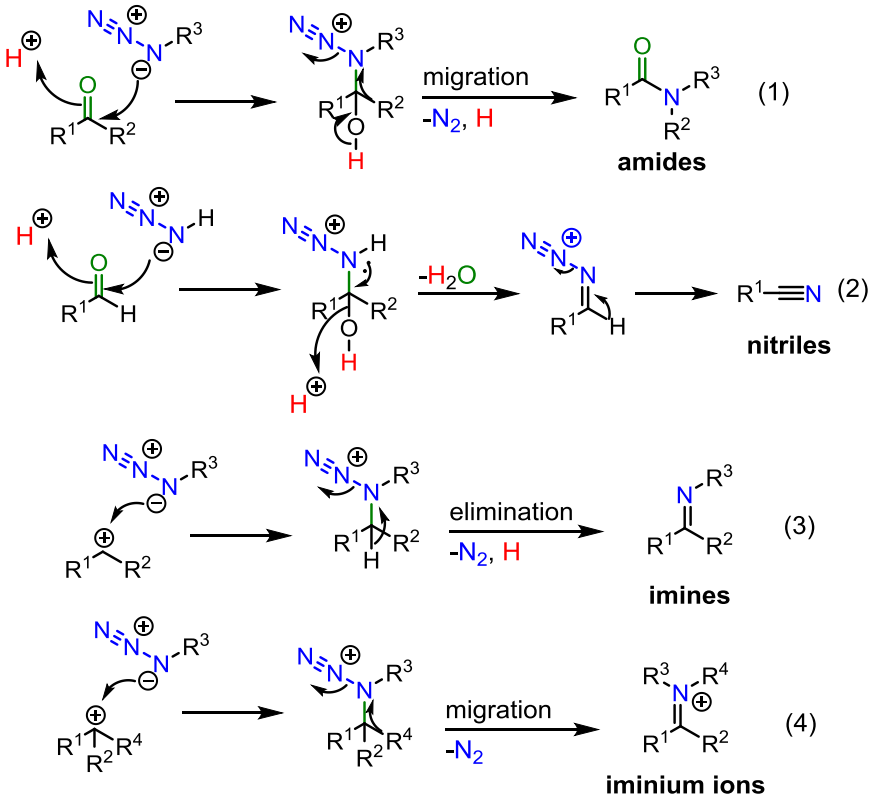


Scheme 19. *Total synthesis of* (+)-*trans*-dihydronarciclasine.

1.2.3 Reactions as a nucleophile

Normally, organoazides can react with suitable electron-deficient compounds (carbon electrophiles, protons, and boranes) to produce amine-substituted diazonium ions, which easily lose nitrogen. In 1923, Schmidt reported that under thermal conditions the reaction of hydrazoic acid with benzophenone produced the benzanilide.[51] This reaction was found to generality for ketones, aldehydes, and carboxylic acid, that undergo with alkylazides followed by rearrangement and loss of

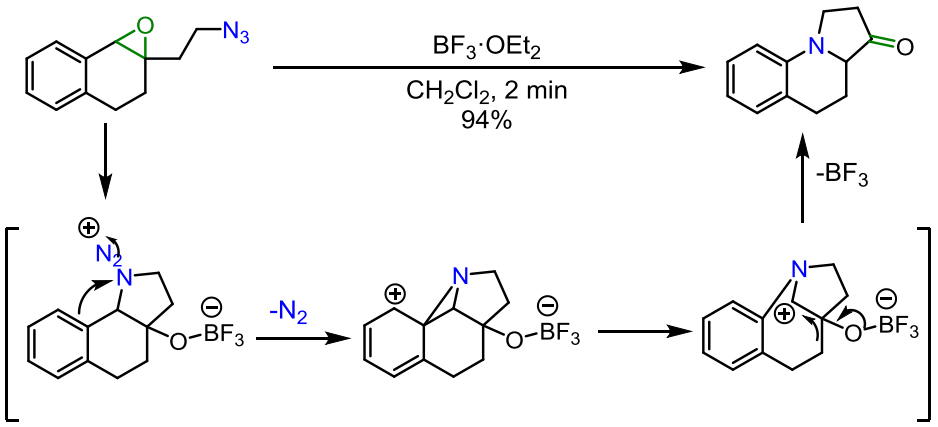
nitrogen in a concerted manner to give amides (Scheme 20, eq 1), nitriles (eq 2), imines (eq 3), and iminium ions (eq 4) in the presence of acids, respectively.[27,52]



Scheme 20. *Schmidt reactions.*

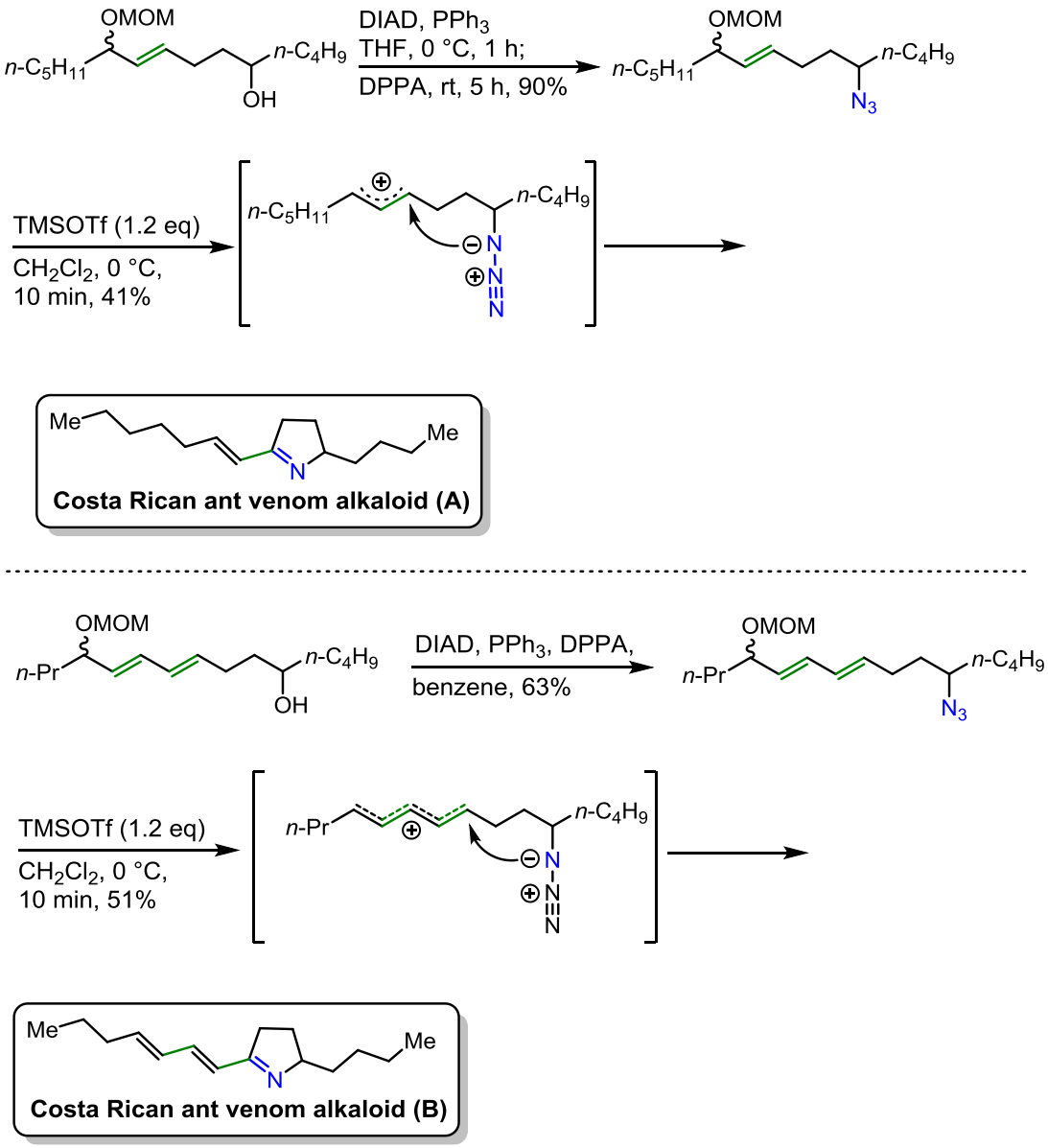
Since the intermolecular reactions end in low yields, Schmidt reaction has usually been demonstrated as intramolecular reactions with aliphatic azides and carbonyl compounds to provide lactams (Scheme 9).[53] Aubé[54] and Pearson[52,55,56] develop this intramolecular reaction and reported that Lewis acids can accelerate the Schmidt reaction and organic azides can react with ketones, which is also named Boyer reaction.[57] Besides ketones, azidoalkyl-substituted epoxides or carbenium ions can be transformed in an intramolecular reaction (Scheme 21).[58] In the presence of Lewis acid,

aliphatic azides efficiently reacted with ketones in good yields to obtained *N*-alkynlated amides or lactams, but it is limited to aliphatic ketones.



Scheme 21. *Boyer reaction with epoxide.*

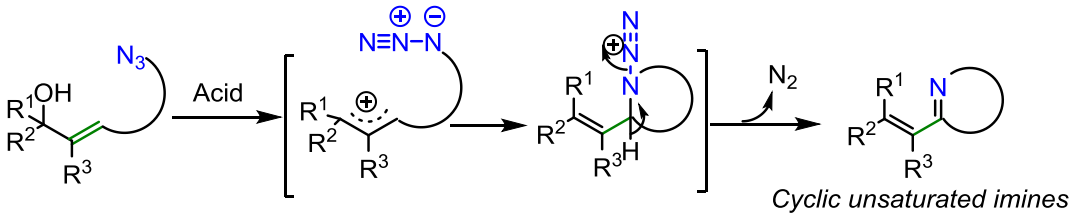
Despite Schmidt reactions require generation of carbocation, utilization of more reactive allyl cations was limited due to the difficulty of reaction control. Our group had developed the application of allyl cation generated from allylic alcohols and derivatives reacted with organic azide to provide α,β-unsaturated imines which have been difficult to prepare because of their instabilities (Scheme 22).[59] Using this novel strategy, total synthesis of Costa Rican ant venom alkaloids **A** and **B** possessing conjugated imine moieties were achieved.[59,60] The allyl/pentadienyl cation-mediated Schmidt reactions were set as the key steps at the last stag of syntheses, affording α,β- and α,β,γ,δ-unsaturated imine alkaloids.



Scheme 22. *Total synthesis of Costa Rican ant venom* ***A*** *and* ***B****.*

1.3 Design of synthetic route

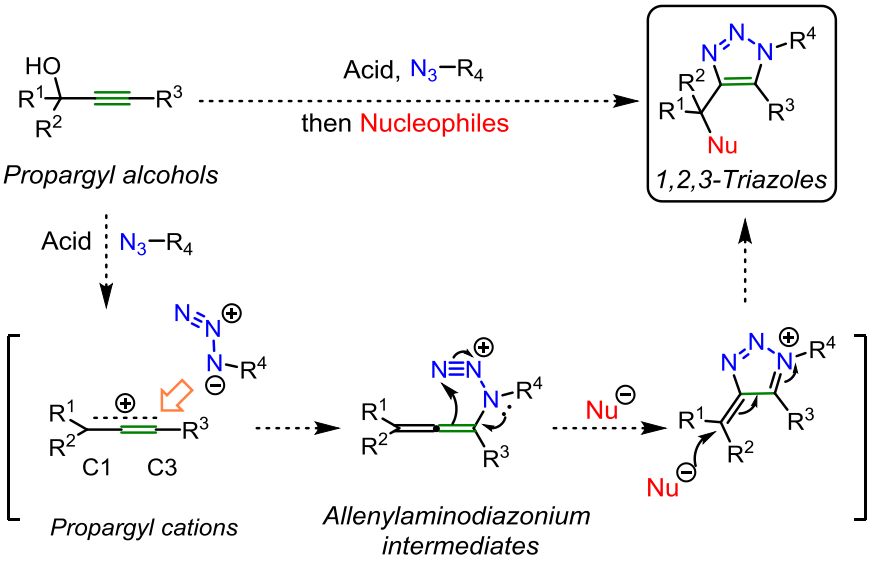
Recently, our group has developed the novel method to contract the unsaturated cyclic imines with allyl cations from allyl alcohols under acid condition with organic azides (Scheme 23).[59]



Scheme 23. *Allylic cation-mediated intermolecular cyclization reaction.*

Base on the same conjugated carbocation chemistry, I design the cyclization reaction of the propargyl cations and organic azides that the carbon-carbon triple bond is employed instead of double bond to afford the functional fully substituted 1,2,3-triazoles without metal catalysts under mild conditions (Scheme 24).

In the presence of acid, propargyl cations prepared from corresponding alcohols reacted with azides to generate the allenylaminodiazonium intermediates which have high potential enough to form triazole rings immediately. To the best of my knowledge, these diazonium compounds have not been reported, despite it is known that the triazoles can be generated from allenyl azides cyclization.[61] I expect that since these high reactive species such as propargyl cations and diazonium intermediates can achieve rapid transformations even at ambient temperature. The trisubstituted triazoles functionalized with additional nucleophiles can be obtained.

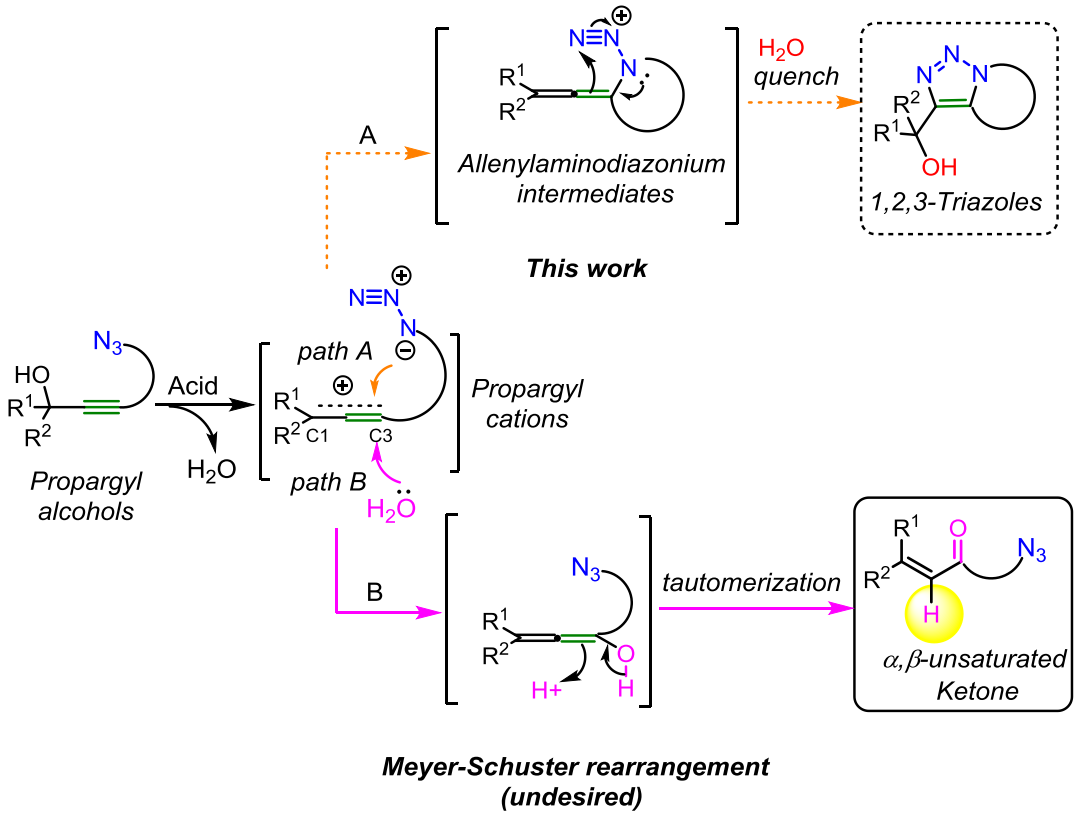


Scheme 24. *Propargyl cation-mediated cyclization reaction.*

Chapter 2 Carbocation-Mediated Azide-Alkyne Cycloaddition

2.1 Intramolecular [3+2] azide-alkyne cyclization reaction

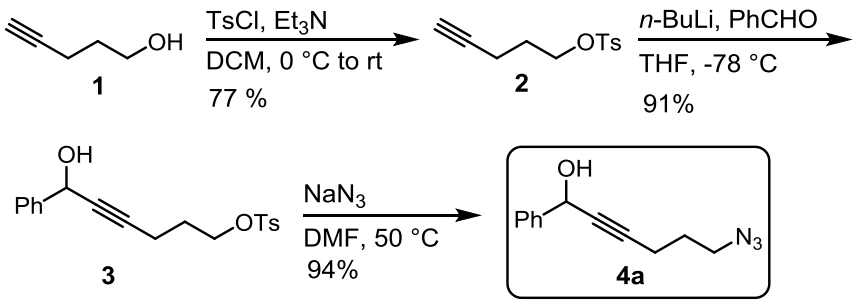
To realize my strategy to make fully substituted triazoles under mild condition, intramolecular [3+2] cyclization reaction can be investigated at first (Scheme 25). Under the acid conditions after performing the propargyl cation, the azide anion attached to the sp carbon C3 affords the unstable intermediate allenylaminodiazonium through pathway A. Through this intramolecular cyclization reaction, the bicycle triazoles can be obtained smoothly.



Scheme 25. *Preparation of propargyl alcohol.*

As the other pathway, enone products by Meyer-Schuster rearrangement can also be obtained through pathway B. Attack of a water molecule on the carbocation followed by tautomerization prior to the attack of azides would give the α,β-unsaturated carbonyl compounds (Scheme 25).

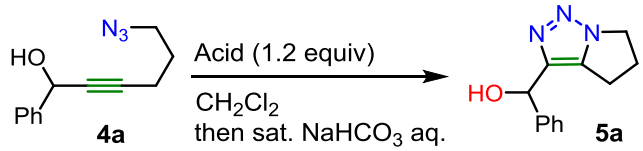
As alkyl propargyl alcohols required strong acid, phenyl propargyl alcohol **4** was chosen in order to use weaker acid. General procedure of preparation is shown in Scheme 26.



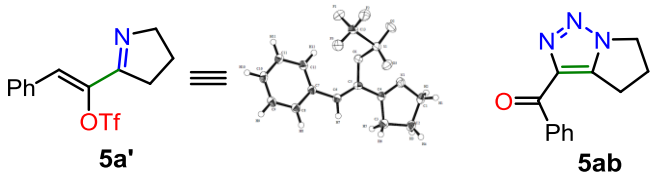
Scheme 26. *Preparation of propargyl alcohol.*

With 1.2 equiv of $TsOH \cdot H_2O$,[59] triazolyl alcohol compound **5a** was generated from propargyl alcohol **4a** at ambient temperature in 32% (entry 1, Table 1). On the other hand, TMSOTf could afford the desired triazolyl ketone **5ab** in 13% with an unexpected vinyl triflate compound **5a'** in 7%, which was confirmed by X-ray crystallographic analysis. The O-triflate group seemed to be derived from TMSOTf. Using $TsOH \cdot H_2O$, no vinyl tosylate product was observed. TfOH and $BF_3 \cdot OEt_2$ only gave complex mixture.

Table 1. *Investigation of intramolecular [3+2] with acids*

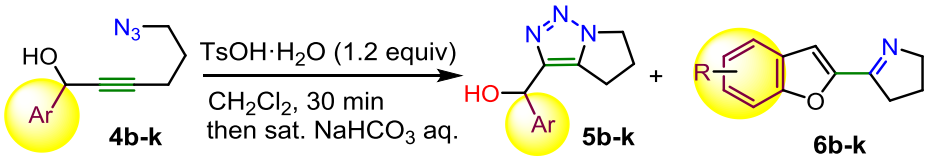


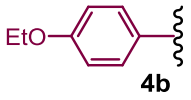
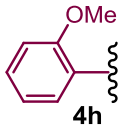
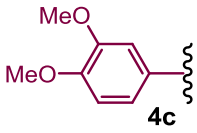
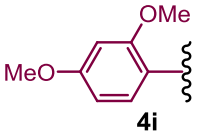
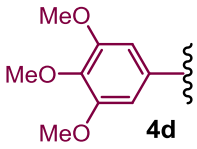
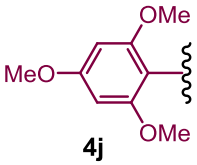
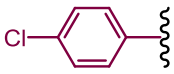
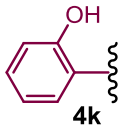
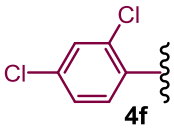
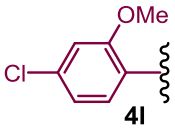
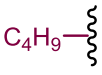
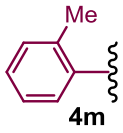
Entry	Acid	Products	
1	$TsOH \cdot H_2O$, rt	**5** / 32%	
2	TfOH, 0 °C	Complex mixture	
3	TMSOTf, 0 °C	**5a'** / 7%	**5ab** / 13%
4	$BF_3 \cdot OEt_2$, 0 °C	Complex mixture	



With this optimized condition in hand, I turned attention to the scope of this intramolecular [3+2] cyclization with substrates (Table 2). Considering the stability of carbocation, electron donating groups were mainly introduced to improve the yield. With electron donative substrates, the corresponding triazoles were obtained in good yields (entry 1-3). On the other hand, reducing the electron density of phenyl group, the yield of triazoles went down (entry 4-5). Because of the stability of carbocation, the alkyl propargyl alcohol did not afford any products, and only starting material was recovered (entry 6).

Table 2. *Scope of intramolecular [3+2] cyclization*



Entry	R	Yields (%) 5	Entry	R	Yields (%) 5	6
1	 4b	82	7	 4h	70	6
2	 4c	71	8[a]	 4i	53	0
3	 4d	74	9[b]	 4j	57	0
4	 4e	61	10	 4k	41	2
5	 4f	44	11	 4l	70	6
6	 4g	0	12	 4m	63	0

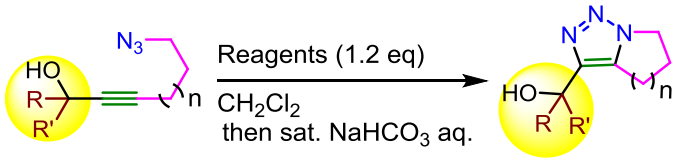
[a] With dichloroacetic acid. [b] With chloroacetic acid.

Moreover, I found that introducing nucleophilic function groups on appropriate position of phenyl moiety could provide bicyclic compounds through intramolecular substitution at α-position of imines. With prepared ortho-methoxy or ortho-hydroxy

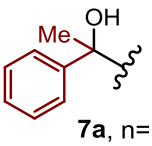
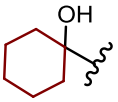
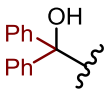
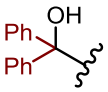
compounds, benzofurans **6h**, **6k** and **6l** were generated along with triazole compounds **5h**, **5k** and **5l** by $TsOH \cdot H_2O$ (entry 7, 10 and 11). With more electron donative substrates, only corresponding triazole products were observed.

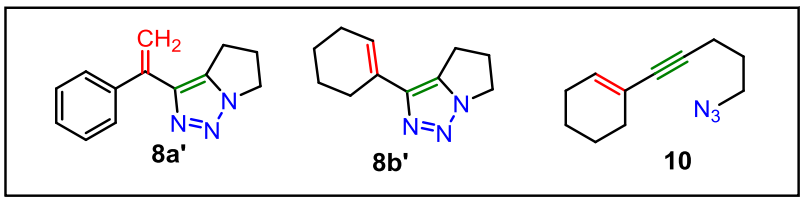
Furthermore, to improve the yield of triazoles, tertiary propargyl carbocations which are more stable and active than secondary carbocations were investigated for the cyclization reaction (Table 3). With methyl phenyl propargyl alcohol (**7a**), under the standard condition the corresponding triazole product **8a** was obtained in 54% with dehydroxyl triazole product **8a'** in 19% (entry 1). Due to the decreasing activity and stability of carbocation, with alkyl propargyl alcohol the dehydrated triazole product **8b'** was obtained in a moderate yield with dehydrated starting material **10** (entry 2). Then I continued to increase the reactivity, herein diphenyl propargyl alcohol was tested. Using diphenyl substrate **7c**, corresponding triazole product **8c** was given in a good to excellent yield. Even with weaker acid TFA, triazole **8c** was generated in 98% at room temperature in 30 min. Moreover, under -90 °C, the corresponding triazole was successfully produced in 91% with TMSOTf (entry 3). The same transformation toward 6-member ring were successfully completed with TFA and $TsOH \cdot H_2O$ at room temperature, and even -90 °C within 5min.

Table 3. *Intramolecular [3+2] cyclization with tertiary propargyl alcohols*



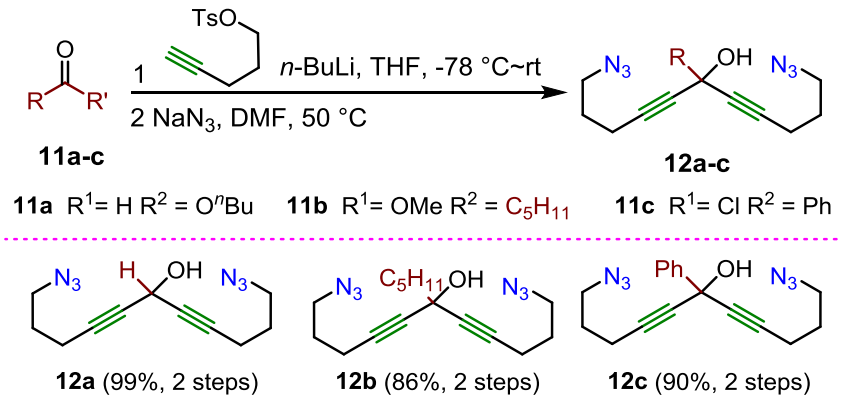
7a-d, n = 1,2 **8a-d,** n = 1,2

Entry	Ar	Reagents	Conditions	Yields	
				8	**Byproduct**
1	 **7a**, n=1	TsOH·H_2O	rt, 30 min	54%	**8a'** (19%)
2	 **7b**, n=1	TsOH·H_2O	Reflux, 30 min	0	**8b'** (50%) **10** (38%)
3	 **7c**, n=1	TFA	rt, 30 min	98%	no
		TsOH·H_2O	0 °C, 2 h	99%	
		TMSOTf	-90 °C, 5 min	91%	
4	 **7d**, n=2	TFA	rt, 30 min	92%	no
		TsOH·H_2O	rt, 20 min	90%	
		TMSOTf	-90 °C, 5 min	96%	



On the other hand, further development of this azide-alkyne [3+2] cyclization reaction, double intramolecular cyclization was investigated with dialkyne substrates. At first the dialkyne substrates were prepared as following procedure. The starting material **12a-c** could be easily prepared from the coupling reaction of tosylated pentynol with corresponding carbonyl compound followed by azidation using NaN_3

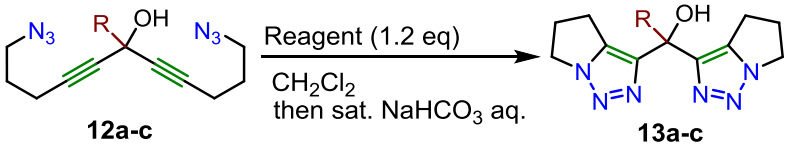
(Scheme 27).

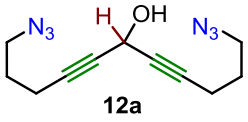
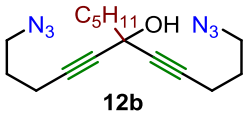
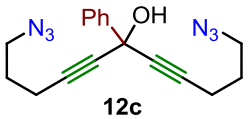


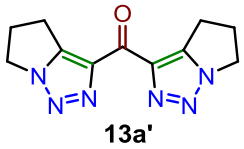
Scheme 27. *Preparation of bialkyne propargyl alcohols.*

Table 4 shows the investigation results of double cyclization reactions. Due to instability of the carbocation, **12a** gave **13a** only in the yield of 13% (entry 1). With alkyl bialkyne substrate **12b**, at ambient temperature triazole compound was obtained in 37% with dehydrated starting material **14** in 11% using $TsOH \cdot H_2O$. Employing stronger Lewis acid TMOTf, the yield of desired triazole was increasing to a moderated yield and the byproduct was observed in the yield of 10% (entry 2). In entry 3, phenyl dialkyne compound **12c** was studied with $TsOH \cdot H_2O$ at room temperature, and the double cyclization was completed in a good yield in 10 min, because of increased activity of carbocation.

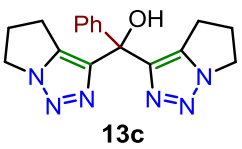
Table 4. *Intramolecular double [3+2] cyclization with bialkyne substrates*



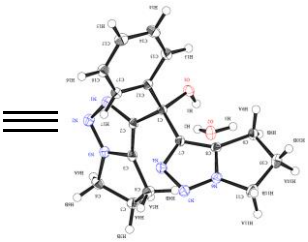
Entry	Substrates	Reagents	Conditions	Yields	
				13	**Byproduct**
1	 **12a**	$TsOH·H_2O$	rt, 30 min	no	**13a'**(13%)
2	 **12b**	$TsOH·H_2O$	rt, overnight	37%	**14** (11%)
		TMSOTf	-20 °C, 6 h	58%	**14** (10%)
3	 **12c**	$TsOH·H_2O$	rt, 10 min	79%	no

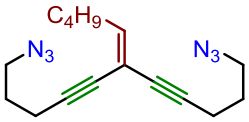


13a'



13c

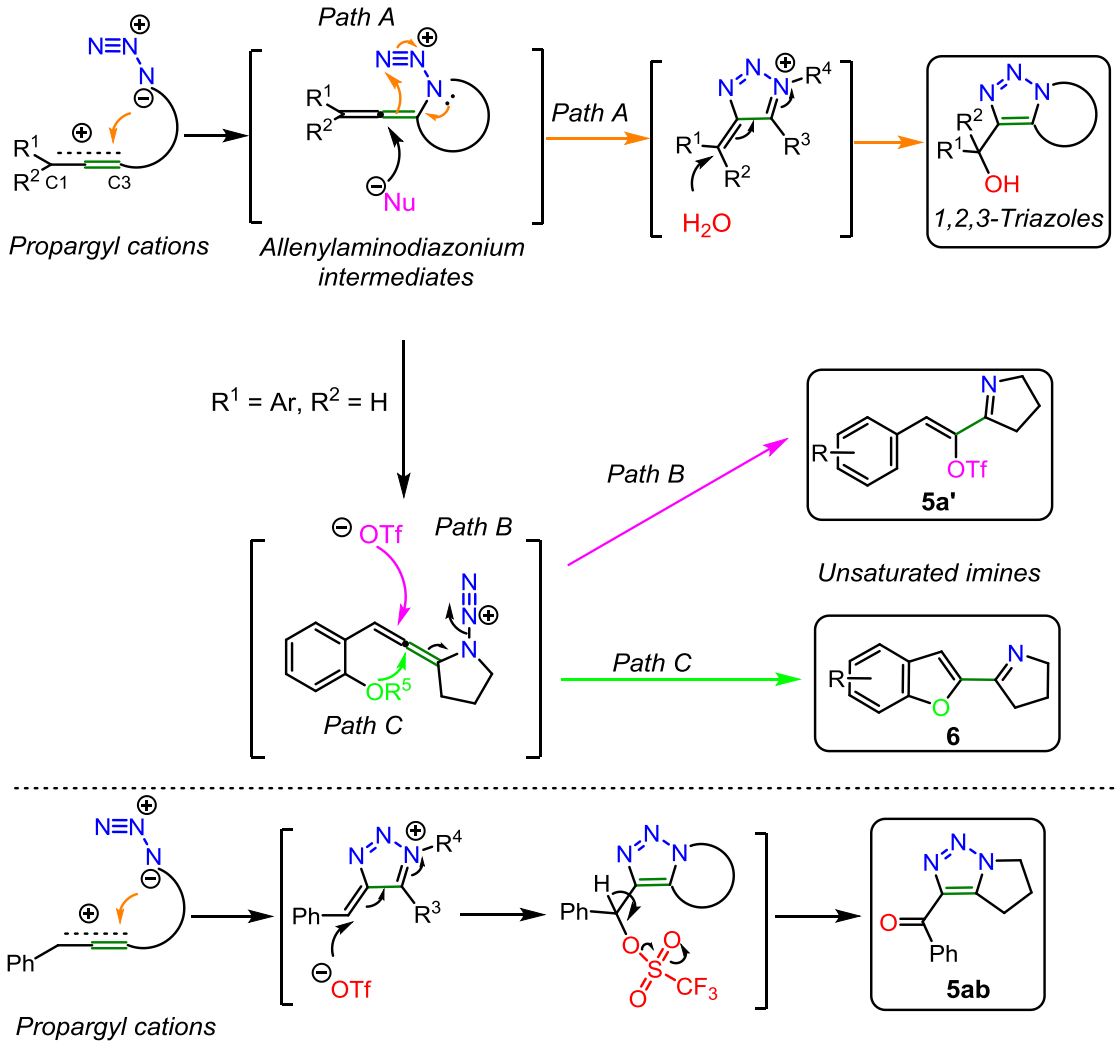




14

These intramolecular [3+2] cyclization reactions of azide with internal alkyne were highly accelerated by the propargyl cation effiently. According to the above results, the reaction possible mechanism is described in Scheme 28. Formation of the generated propargyl cations from corresponding alcohols under acid condition, after azide anions attached to the sp carbon, the unstable diazonium intermediates were produced. Then this active allenylaminodiazonium intermediates could be immediately transformed to the desired triazoles. On the other hand, diazo moiety in

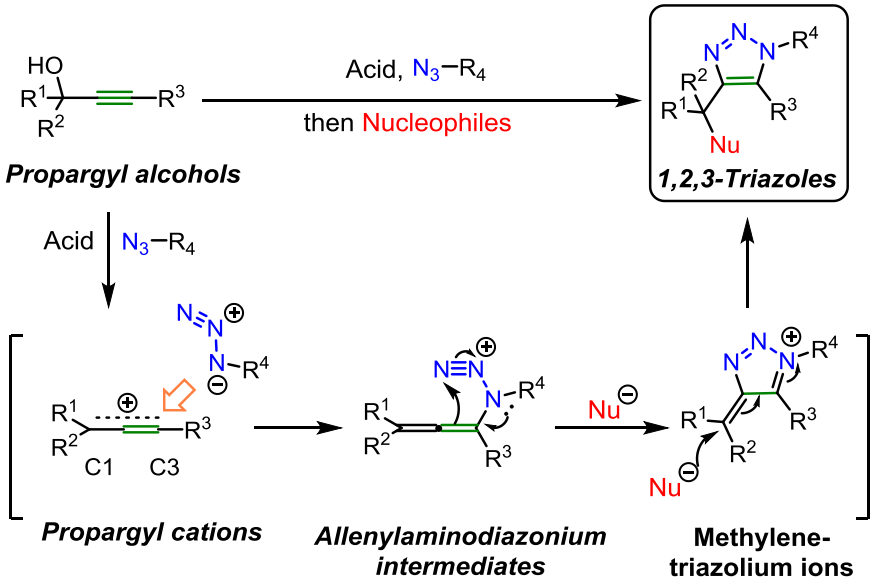
diazoallenamines is a good leaving group and the center carbon atom in allene could be a nucleophilic position. Thus, nucleophiles came to eliminate dinitrogen by S_N2' substitution. $TsOH \cdot H_2O$ was effective in most cases and when using TMSOTf, vinyl triflate compound **5a'** was obtained via umpolung. With ortho-substituted phenyl group, benzofuryl imines **6** were produced through intramolecular cyclizations.



Scheme28. *Preparation of bialkyne propargyl alcohols.*

2.2 Intermolecular [3+2] azide-alkyne cyclization reaction

After investigation of intramolecular [3+2] cyclization, I then turn my attention to intermolecular transformation which could be more widely used in organic chemistry, chemical biology and pharmaceuticals to produce synthetic precursors. By established conditions of intermolecular reactions, highly substituted 1*H*-1,2,3-triazoles could be obtained (Scheme 29).

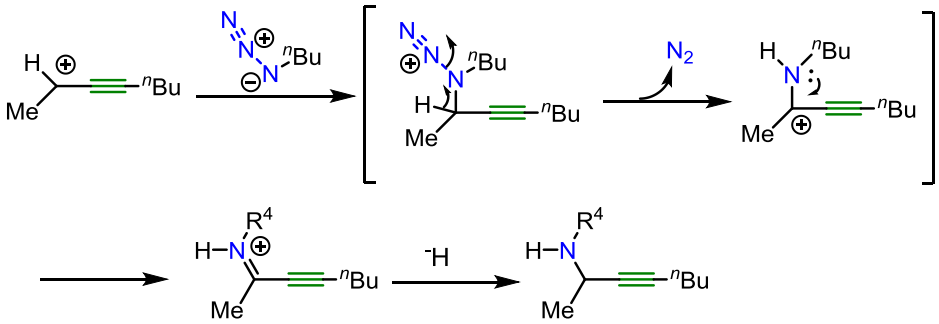


Scheme 29. *Generation of 1,2,3-triazoles via allenylaminodiazonium intermediates.*

Comparing with typical synthetic method, through this strategy both terminal and internal alkyne could be accepted under low temperature. Formation of the active allenylaminodiazonium intermediates followed by nucleophile addition to the Methylene-triazolium ions, the fully substituted 1,2,3-triazole could be demonstrated rapidly. Although concerted [3+2] reactions would deliver both 1*H*- and 3*H*-triazoles,

deactivation of the C2 position by a delocalized carbocation can avoid this pathway and yield products selectively.

This strategy is challenging from the follow points: (1) with azides, a sp^2 carbocation (C1) is more reactive than the desired sp carbocation (C3) to produce unsaturated imines by a Schmidt reaction or propargyl azides (Scheme 30);[7] (2) Meyer-Schuster rearrangement producing the enones would be competitive.

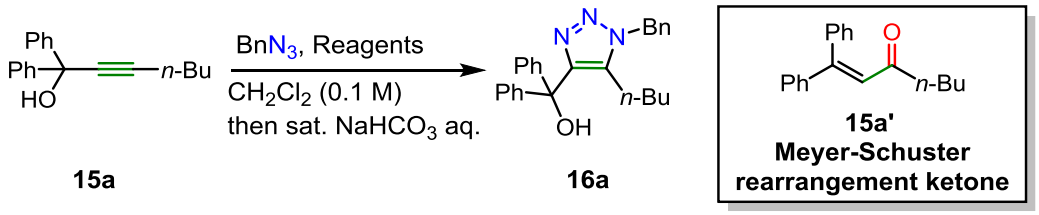


Scheme 30. *Intermolecular Schmidt reaction of azide with carbocation.*

2.2.1 Optimization of intermolecular azide-alkyne cyclization reaction

To avoid the reaction at C1 position by steric and electronic influence,[62] I designed diphenyl propargyl alcohol for the initial study of the reaction condition, and the reaction were quenched with a saturated sodium bicarbonate aqueous solution in order to produce triazolylalkanols, recently reported as new synthetic precursors (Table 5).[63]

Table 5. *Optimization of intermolecular [3+2] cyclization reaction*



15a **16a**

Entry	*BnN_3 (equiv)*	*Reagents (equiv)*	*Temp (°C)*	*Time (min)*	*Yield (%)*
1[a]	*2.5*	*$TsOH{\cdot}H_2O$ (1.2)*	*rt*	*20*	*11*
2	*1.5*	*MsOH (1.2)*	*rt*	*10*	*79*
3[b]	*1.5*	*TMSCl (1.2)*	*rt*	*120*	*0*
4[c]	*1.5*	*$FeCl_3$ (1.2)*	*rt*	*5*	*0*
5	*1.5*	*$Sc(OTf)_3$ (1.2)*	*rt*	*5*	*52*
6	*1.5*	*$Cu(OTf)_2$ (1.2)*	*rt*	*10*	*47*
7	*1.5*	*$BF_3{\cdot}OEt_2$ (1.2)*	*rt*	*1*	*90*
8	*1.5*	*$BF_3{\cdot}OEt_2$ (1.2)*	*-20*	*5*	*92*
9	*1.5*	*$BF_3{\cdot}OEt_2$ (1.2)*	*-60*	*5*	*80*
10	*1.5*	*TMSOTf (1.2)*	*-78*	*5*	*97*
11	*1.5*	*TMSOTf (1.2)*	*-90*	*5*	*99*
12	*1.2*	*TMSOTf (1.2)*	*-90*	*5*	*90*
13	*1.5*	*TMSOTf (1.05)*	*-90*	*5*	*94*
14	*1.5*	*TMSOTf (0.2)*	*-90*	*120*	*16*
15	*1.5*	*TBSOTf (1.2)*	*-90*	*5*	*60*
16[d]	*1.5*	*TMSOTf (1.2)*	*-90*	*5*	*88*
17[e]	*1.5*	*TMSOTf (1.2)*	*-90*	*5*	*97*

[a] **15a'** was obtained in 30%. [b] **15a'** was obtained in 90%. [b] **15a'** was obtained in 24%.

[d] Performed in toluene. [e] High dilution conditions (0.005M).

Tosylic acid gave a desired triazole **16a**, but the Meyer-Schuster rearrangement product was major probably due to its solubility and the presence of water of hydrates (entry 1). On the other hand, mesylic acid could produce **16a** in 10 min in good yield (entry 2). Although the conditions are effective at rt, further investigations on reagents

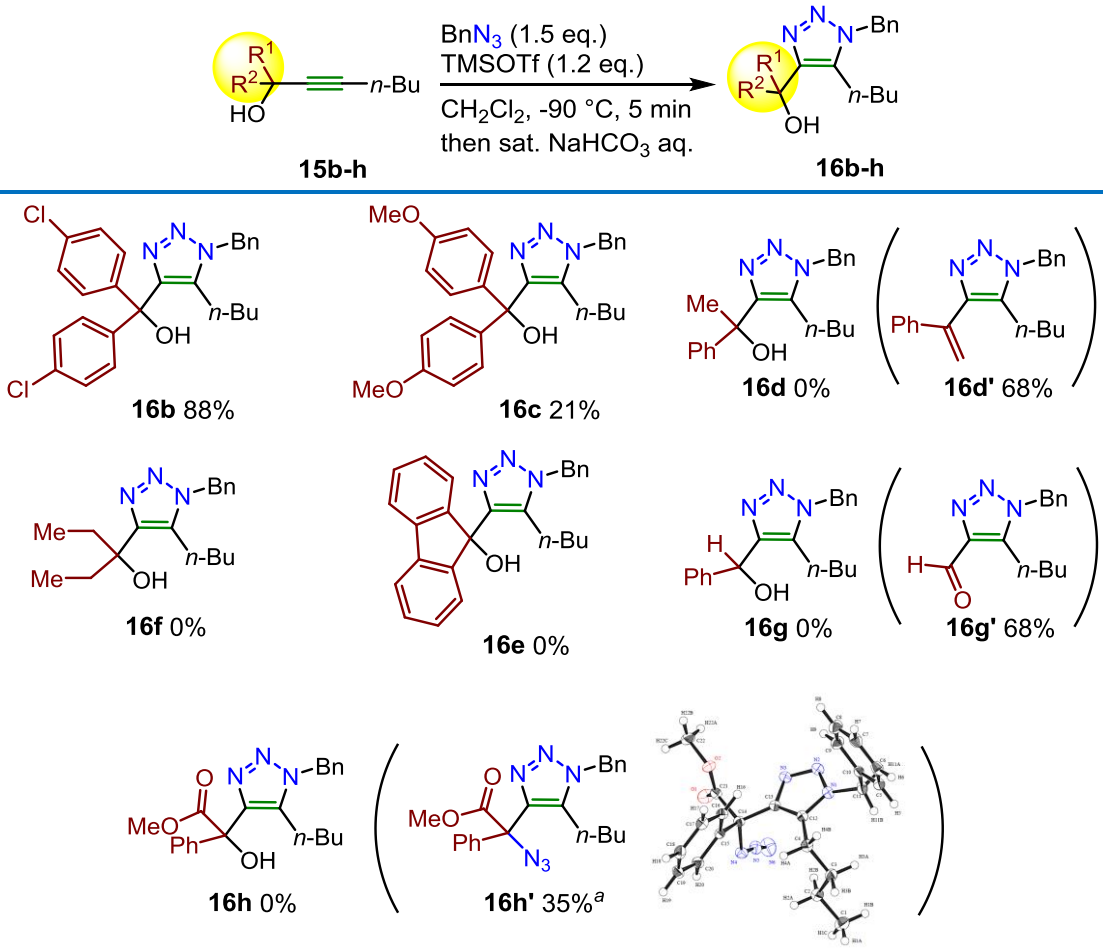
were continued to improve the reaction speed and availability under low temperatures. TMSCl and $FeCl_3$ only afforded the Meyer-Schuster rearrangement ketone **15a**' (entries 3-4). *$Sc(OTf)_3$* and *$Cu(OTf)_2$* worked to yield **16a** in moderate yield (entries 5-6), and *$BF_3{\cdot}OEt_2$* worked well resulting in an excellent yield (entry 7). This reagent could complete the reaction in 1 min and was powerful enough to perform the reaction at -60 °C (entries 8-9). Further cooling conditions were achieved with TMSOTf, and the desired transformation was successfully demonstrated even at -90 °C, close to the melting point of the solvent (entries 10-11). It should be noted that these reaction conditions could afford **16** in almost quantitative yield in only 5 min at -90 °C. Reducing the equivalence of benzyl azide and an acid reagent could also give similar results (entries 12-13). Unfortunately, catalytic conditions were ineffective probably due to the basicity of the resulting triazoles (entry 14). The use of TBSOTf also worked, but not as well as TMSOTf (entry 15). Instead of dichloromethane, toluene could work as an efficient solvent (entry 16). It is noteworthy that high dilution conditions did not reduce the efficiency of the reaction (entry 17). TfOH, $MgBr_2$, $Ti(OiPr)_4$, $TiCl_4$, or $Yb(OTf)_3$ were not effective. When using TfOH, the starting material directly converted into the unidentified polymeric materials. Whether $MgBr_2$ or $Ti(OiPr)_4$ could not afford the desired triazole product, only starting material recovered. $TiCl_4$ only afford the

Meyer-Schuster rearrangement ketone. $Yb(OTf)_3$ also could not gave the desired product, starting materials was recovered along with trace amount of Meyer-Schuster rearrangement product.

2.2.2 Scope of intermolecular azide-alkyne cyclization reaction

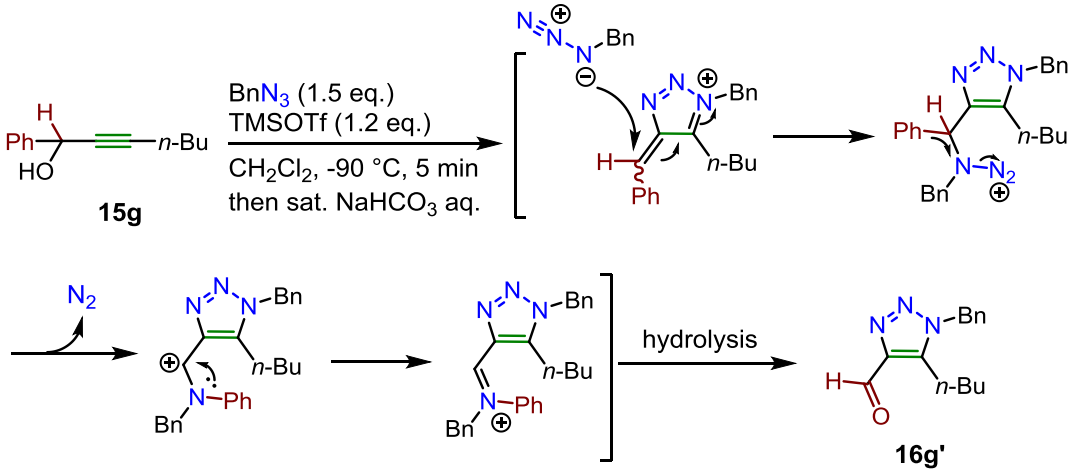
With optimized condition in hand, I pay attention to scope of substituents on the alkynes and azides. Herein, the cyclization reaction was carried out with TMSOTf in dichloromethane at -90 °C.

Table 6. *Scope of $R^1$and R^2 group study*



[a] 2.5 equiv of BnN_3 and 2.1 equiv of TMSOTf were used at room temperature.

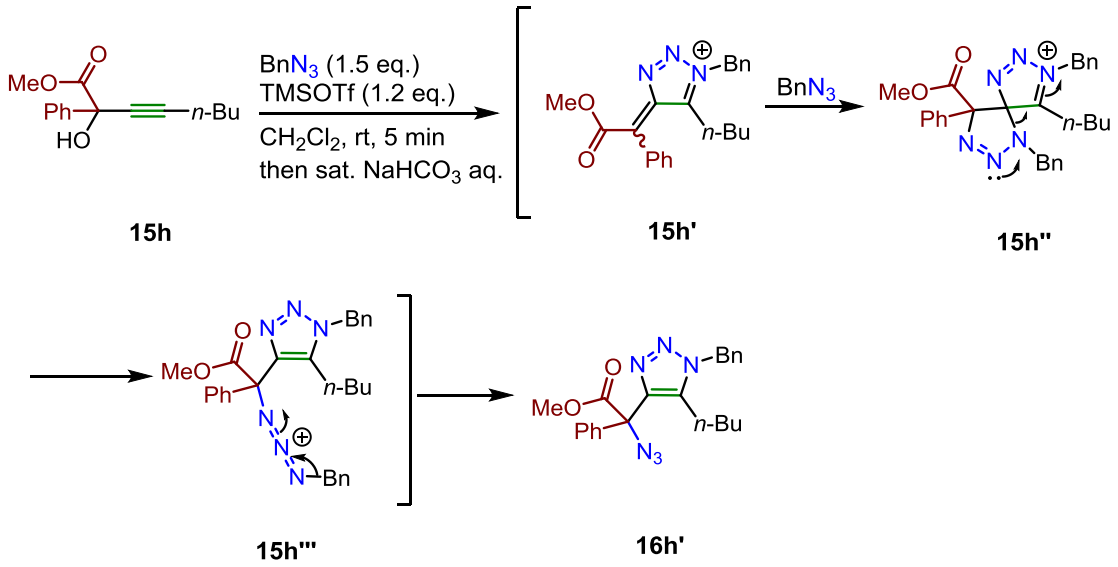
Firstly, investigation of substrates was performed with R^1 and R^2 group (Table 6). Electron deficient aryl **16b** was found to be effective as a phenyl group, despite the electron-donative aryl **16c** was obtained in low yield under this standard reaction condition. Methylphenyl propargyl alcohol **15d** gave **16d'** in a moderated yield as dehydrated product. In the case of benzyl alcohol **15g**, aldehyde **16g'** was obtained probably through [3+2] followed by Schmidt reaction-hydrolysis (Scheme 31).



Scheme 31. *Cyclization of Propargyl alcohol* ***15g****.*

Diethyl propargyl alcohol **15f** didn't afford the desired triazole product **15f** in this intermolecular cyclization reaction, only starting material was recovered after the reaction. And the fluorenyl substrate **15e** was labile under acid conditions. With electron withdrawing methoxycarbonyl group, propargyl alcohol **15h** was converted into azido triazole **16h'** at ambient temperature. In this case, the azidation was seemed to proceed on the C1 position. Because these types of azido triazoles were not found in other cases,

I described the possible mechanism in Scheme 32. The azide group in compound **16h'** may be introduced by the [3+2] cyclization of an additional benzyl azide to the unsaturated ester moiety of methylenetriazolium ions **15h'**, and the ring-opening of spirocyclic bistriazoline **15h''** would trigger the production of **16h'**. Generation of product **16h'** could be one of the evidence of formation of triazolium intermediate **15h'**.

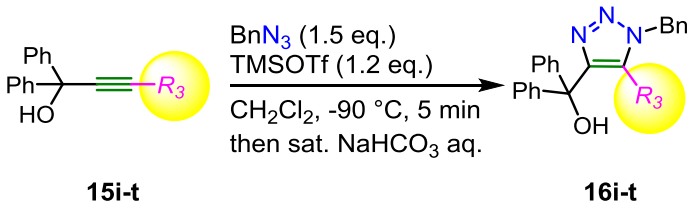


Scheme 32. *Cyclization of Propargyl alcohol **15h**.*

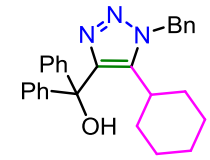
After that, I began to investigate the reaction with R^3 group on alkyne moiety (Table 7). Secondary cyclohexyl alkyne **15i**, alkoxyl methyl **15l-m** and methoxy carbonyl **15o** produced the corresponding triazoles **16i**, **16l-m**, and **16o** in good to excellent yields. Interestingly, transformation of terminal alkyne **15k** was also achieved in giving the desired disubstituted triazole **16k** in 90%. The propargylic alkyne in **15q** could selectively react with benzyl azide to afford the triazole **16q** in good to excellent yield. Even sterically bulky substrate **15r** could produce the cyclization product **16r** rapidly.

On the other hand, I also found that conjugated alkyne **15j** and propargyl acetate alkyne **15n** gave corresponding triazoles in fair yield. It was observed that the desired product **15j** was generated with unexpected byproduct benzazepine **15j'**. The plausible mechanism of **15j'** was described in Scheme 33. In the case of trityl compound **15s** (eq 2), triazolation followed by Fridel-Crafts reaction occurred to produce tricyclic product **16s'**. In addition, the cyclohexenyl alkyne was converted into cyclopentyl aldehyde **15t'** (eq 3). Probably, the benzyl azide selectively reacted with alkene group instead of alkyne to form triazoline followed by ring-contraction-hydrolysis to obtain the aldehyde **15t'** (Scheme 34).

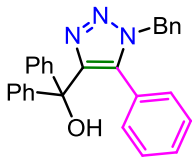
Table 7. *Scope of R^3 group study*



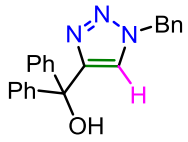
15i-t **16i-t**



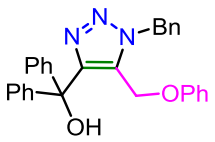
16i 96%



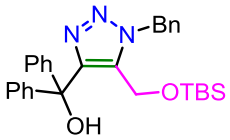
16j 22%



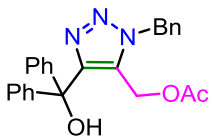
16k 90%[a]



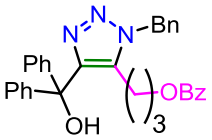
16l 91%



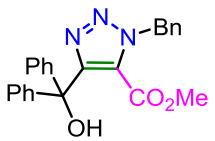
16m 91%[b]



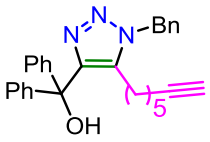
16n 22%



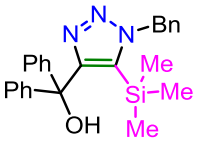
16o 93%



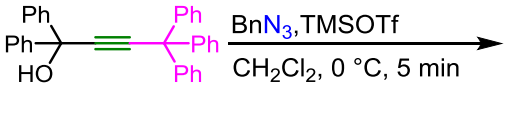
16p 57%[c]



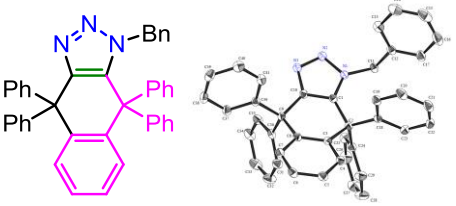
16q 98%



16r 93%[d]

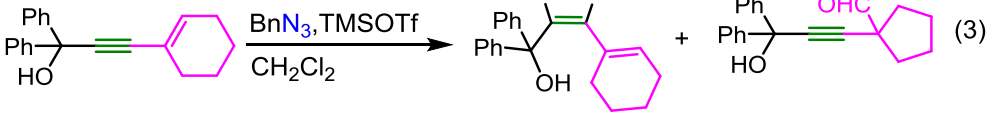


15s



16s' 48%

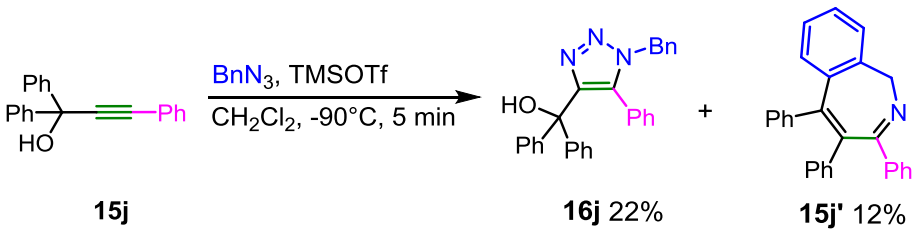
(2)



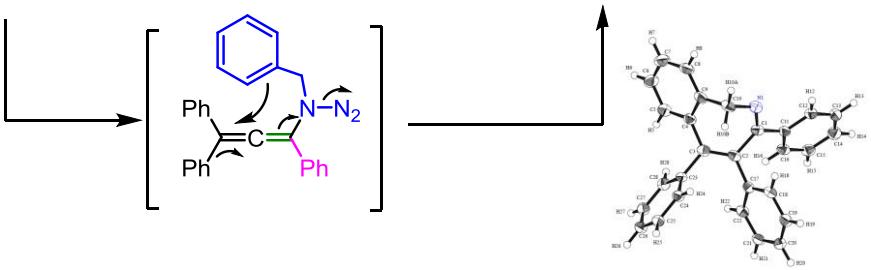
(3)

15t **16t** 0% **15t'**

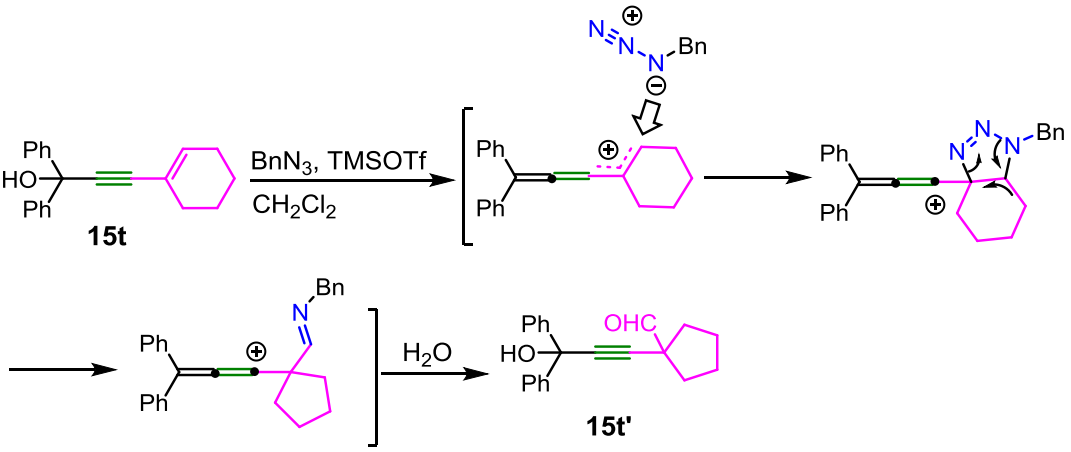
[a] 2.1 equiv of TMSOTf were used. [b] Along with 7% deTBS triazole. [c] Performed at -60 °C. [d] 10 min reaction.



15j **16j** 22% **15j'** 12%



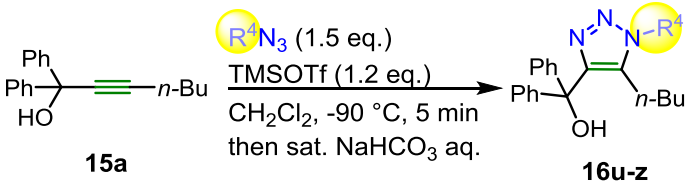
Scheme 33. *Paulisable mechanism of compound **15j'**.*

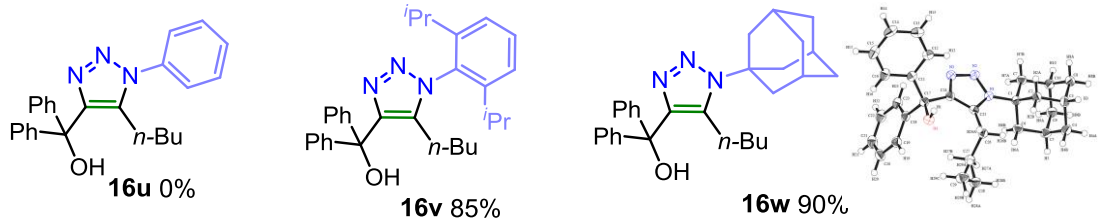


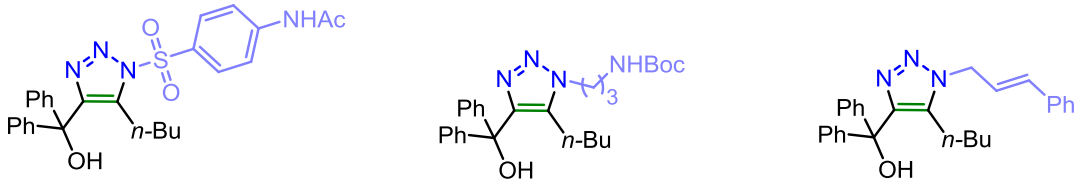
Scheme 34. *Paulisable mechanism of compound **15t'**.*

Furthermore, I investigated the substitutents of R^4 on organic azides (Table 8). In contrast to unreactive phenyl azide, the sterically hindered 2,6-diisopropylphenylazide successfully converted to desired triazole **16v** in good yield, due to the stronger nucleophilicity of its azide moiety comparing with phenyl azide as reported by Hosoya *et al*.[64] They reported that calculation of the transition state structure of the cyclization, the activation energy for the cyclization of cyclooctyne with 2,6-diisopropylphenylazide was estimated to be 2.5 kcal mol^{-1} lower than that with phenyl azide, providing a good agreement with the experimental result. It is revealed that although the less nucleophilic sulfonylazide could not give product **16x**, the primary azide (3-azidopropan-1-Boc protected amine, cinnamyl azide) and bulky tertiary azide (adamantyl azide) could generated the desired trisubstituted triazoles **16w** and **16y-z** in good yield. It should be noted that all triazoles were obtained as single isomer even in the case of ester **16p**.

Table 8. *Scope of R^4 group study*

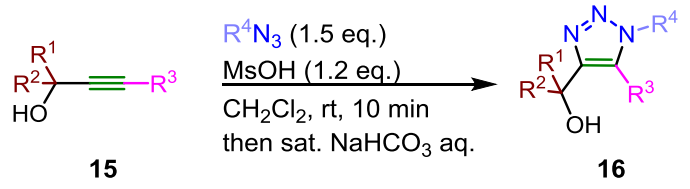


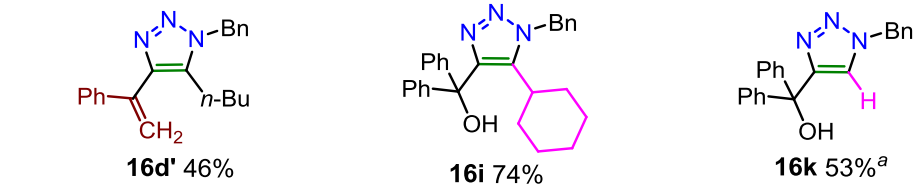


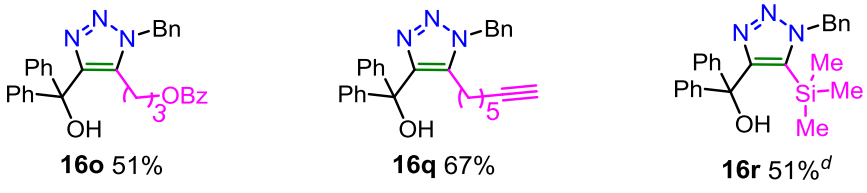


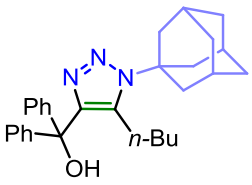
[a] 2.5 equiv of TMSOTf was used.

Table 9 *Scope of [3+2] cyclization at room temperature*

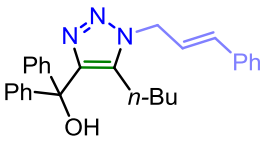








16w 44%



16z 64%

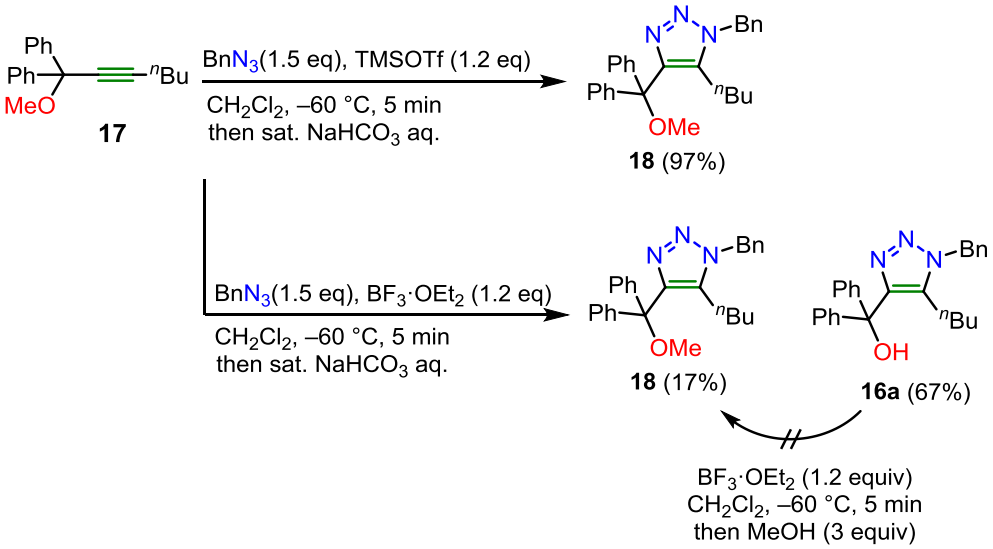
[a] 2.1 equiv of MsOH was used.

Moreover, to conduct this cyclization reaction at ambient temperature, the reactions were investigated with methanesulfonic acid (MsOH) (Table 9). The desired transformation was successfully demonstrated at room temperature in 10 min in moderate yields.

Chapter 3 Multicomponent Coupling Reaction

In the studies described, I mainly disclosed the introduction of hydroxyl group into the triazole products by quenching with aqueous media as nucleophiles. However, considering the proposed reaction mechanism (Scheme 29), the products could be functionalized using other additional nucleophiles instead of a hydroxyl group. Before testing the generality of multicomponent coupling reaction, I investigated the origin of the hydroxyl group to make sure the hydroxyl group's source (Scheme 35).

The treatment of methylation propargyl alcohol **17** with stoichiometric amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf), which were mainly used in previous work, only afforded the triazole possessing methoxy group **18** at both –90 and –60 °C, even after quenching with an aqueous medium.



Scheme 35. *Investigation of the origin of hydroxyl group.*

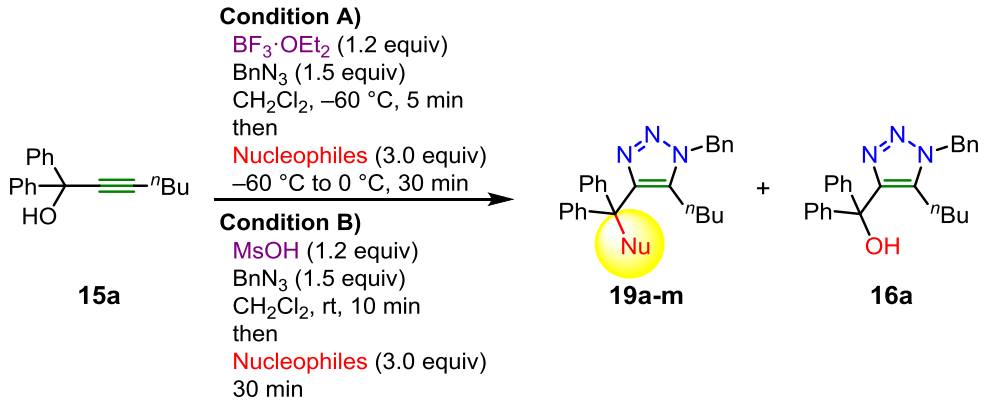
However, $BF_3 \cdot OEt_2$ gave hydroxy compound **16a** as the major product. This indicates that the origin of the hydroxy group depends on the acid used, and the resulting silanols or silyl ethers may be the source of hydroxy groups in the case of TMSOTf. With $BF_3 \cdot OEt_2$, the benzylic position was successfully substituted by external water.

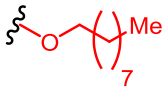
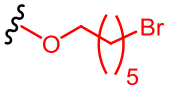
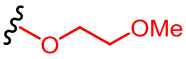
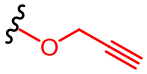
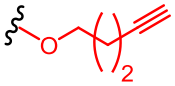
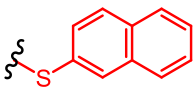
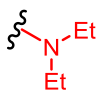
This results also indicate that $BF_3 \cdot OEt_2$ is a suitable acid for the substitution of triazolium intermediates with additional nucleophiles probably because hydroxy group donation activity of the resulting boronates or borinates are limited. For introduction of hydroxy groups, TMSOTf seems to be better reagent. Methyl ether **17** was not obtained from **16a** by acid treatments in the presence of methanol. Thus, the functionalization of the benzylic position should be performed as one-pot reactions.

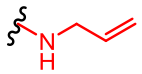
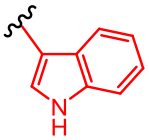
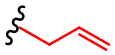
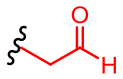
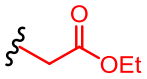
Based on these results, three-component reaction coupling reactions with various nucleophiles were investigated to functionalize the benzylic position with $BF_3 \cdot OEt_2$ (Table 10, Condition A). In order to avoid the quenching reaction by moisture, the reaction was carried out under nitrogen gas atmosphere. As nucleophiles, primary alcohols could produce the desired ether triazoles **19a-e** in good yields along with triazolyalkanol **16a** (entries 1-5). Although the reactions with secondary alcohols was failed to afford the coupling products, naphthalenethiol, diethylamine and allyl amine

were successfully introduced to the benzylic position to afford coupling product **19f-h** in good yields (entries 6-8). When azidotrimethylsilane ($TMSN_3$) was used as the nucleophile, azido compound **19i** was generated in good yield.

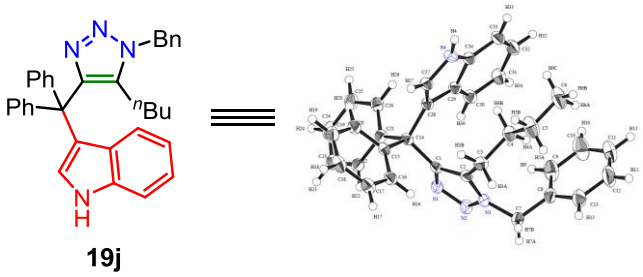
Table 10. *Scope of three-component reaction with nucleophiles*



Entry	Nucleophiles and products		Yield (%)			
			Condition A		Condition B	
			19	**16a**	**19**	**16a**
1		**19a**	80	10	69	trace
2		**19b**	73	11	58	11
3		**19c**	76	12	63	0
4		**19d**	74	12	53	trace
5		**19e**	77	10	61	0
6		**19f**	81	7	62	0
7		**19g**	78	11	55	0

8		**19h**	77	12	60	0
9[a]		**19i**	85	10	70	0
10		**19j**	65	0	42	0
11[b]		**19k**	69	3	54	trace
12[c]		**19l**	55	35	43	25
13[d]		**19m**	68	20	55	14

[a] Azidotrimethylsilane was used as the nucleophile. [b] Allyltributyltin was used as the nucleophile. [c] Ethyl vinyl ether was used as the nucleophile. [d] 1-Ethoxy-1-trimethylsilyloxyethylene was used as the nucleophile.



19j

Interestingly, through these three-component coupling reactions, not only heteroatom nucleophiles, but also carbon nucleophiles could achieve to form quaternary carbon centers. Indole selectively gave the corresponding coupling product **19j** in good yield (entry 9). The allyl group was successfully introduced with allyltributyltin to afford the **19k** (entry 10), while the allylsilanes was failed. These carbon-carbon bond formations also could be achieved by silyl enol ethers[65] to give obtain the desired

aldehyde **19l** and ethyl ester **19m** (entries 12 and 13). Addition of molecular sieves did not improve the results.

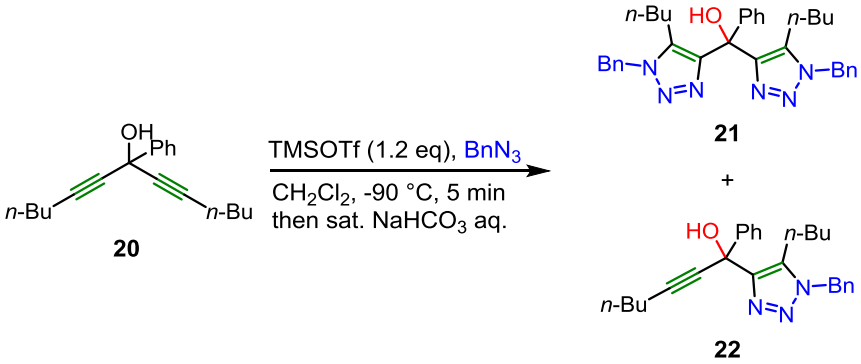
In addition, to achieve these three-component coupling reactions at ambient temperature, the same reactions were investigated with MsOH (Table 10, Condition B), and the desired coupling products were successfully obtained in 40 min. Interestingly, although the product yields were slightly lower than those obtained under condition A, lesser amount of byproduct **16a** were obtained. Considering the generation of **16a** in Scheme 46, boronic acids or borates were still active as nucleophiles, and water molecule generated by MsOH was relatively weaker nucleophiles than those acids.

Generation of three-component coupling reactions also indicated the presence of methylenetriaolium intermediates or carbocations of triazole (Scheme 29). In chapter 2 of scope of intermolecular cyclization, generation of azido triazole **16h** could be other evidence of the methylenetriazolium intermediates **15h'** from **15h** (Scheme 32).

To further develop the functionalization of triazoles by multicomponent coupling reactions, double [3+2] triazolation reactions were investigated. Based on the chapter 2 results, at first we investigated the cyclization reaction with dihexynyl alcohol **20** in the present of TMSOTf at -90 °C (Table 11). After 5 min, the reactions were quenched by saturated sodium bicarbonate aqueous solution to produce hydroxylated compound **21**.

With 2.5 equiv BnN_3, the corresponding double triazolation product **21** was obtained in 62% along with mono-cyclization product **22** in 7% (entry 1). Increasing the amount of BnN_3 to 3.0 equiv, the best yield of desired bistriazole product **21** was raised to 72% with trace amount of mono triazole **22** (entry 2). On the other hand, this cyclization reaction could be controlled to afford monotriazolation product **22** in moderate yield by reducing the amount of organic azide (entry 3).

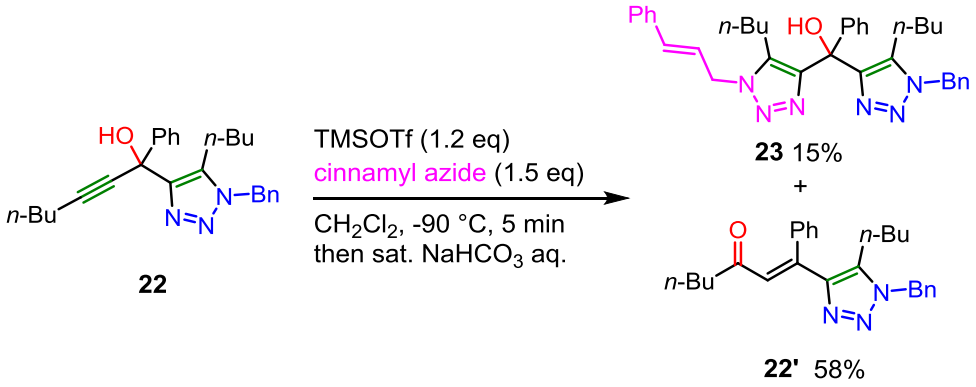
Table 11. *[3+2] cyclization reaction with dialkyne substrate.*



Entry	*BnN_3 (equiv)*	*Yields (%)*	
		21	***22***
1	*2.5*	*62*	*7*
2	*3.0*	*72*	*2*
3	*1.05*	*2*	*55*

Based on these successful results, I then conducted the four-component coupling reaction with two kinds of organic azide. Firstly, mono triazolation compound **22** was used to demonstrate the desired four-component coupling product (Scheme 36). Using cinnamyl azide, the mono substrate could convert into the corresponding double triazolation product **21** in 15% yield, but Meyer-Schuster rearrangement byproduct **22'**

was obtained in 58%. Thus, to effectively generate the four component coupling reaction product, this transformation should be performed as one-pot reactions.

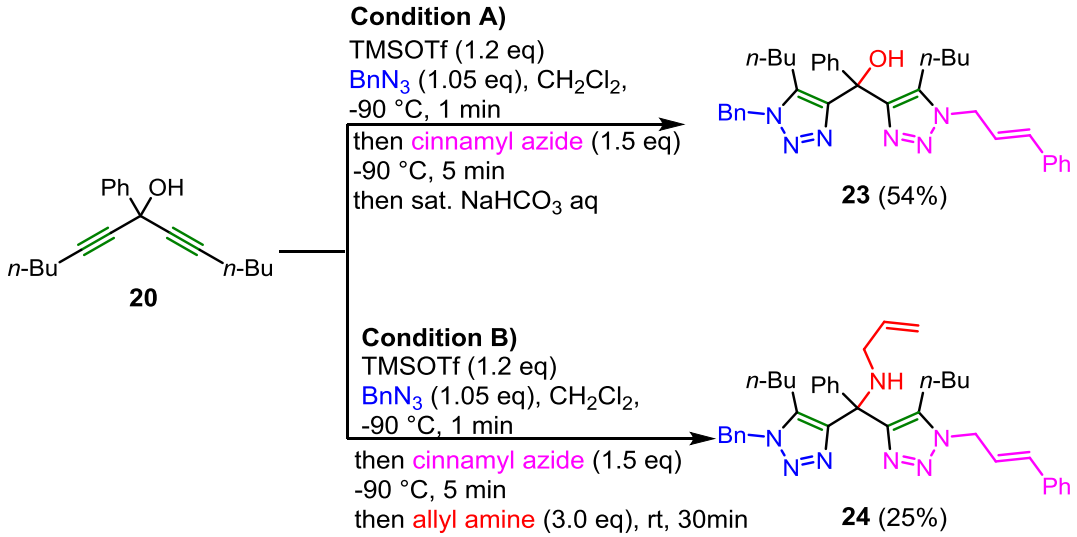


Scheme 36. *Cyclization reaction of mono triazolated compound.*

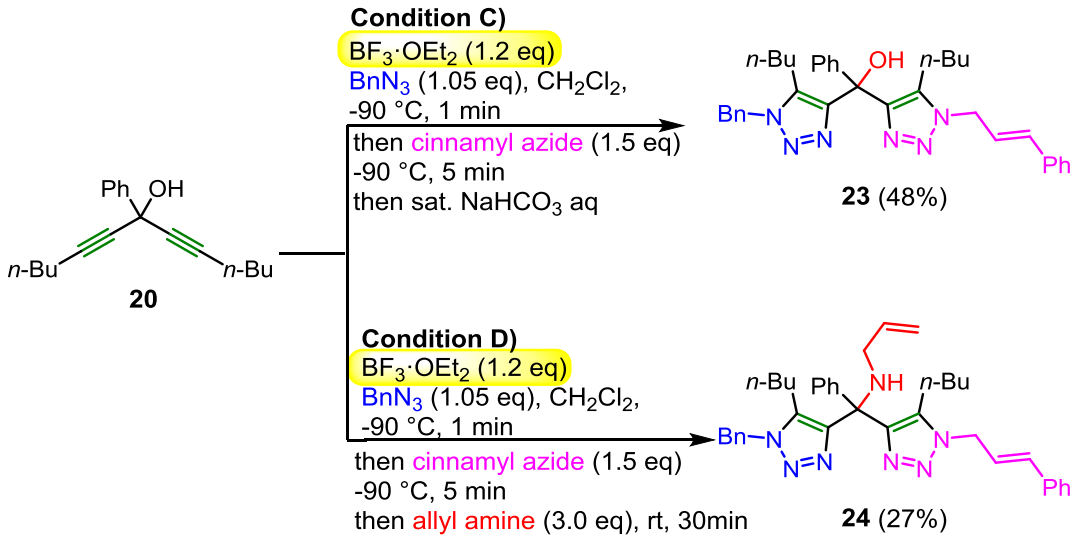
Controlling the reagent (Condition A), double [3+2] cyclization reaction was sequentially achieved to produce the desired hydroxylated triazole compound **23** in moderate yield (Scheme 37). In additional, not only hydroxyl group but also other functional group could be introduced by changing quenching method with other nucleophiles. For further functionalization, allylamine was used as a nucleophile, and the dialkyne **21** was successfully converted in to the corresponding four-component product **24** (Condition B).

According to the successful results, I also tested $BF_3{\cdot}OEt_2$ to improve the yields of four-component coupling reactions (Scheme 38). Under condition C and D, double cyclization successfully gave the corresponding products **23** and **24** in moderate yields. It was noticed that, not only TMSOTf but also $BF_3{\cdot}OEt_2$, the desired triazoles was

obtained along with trace amount of Meyer-Schuster rearrangement product, hydroxy-subsituted compound and polymeric materials. In these cases, introduction of carbon nucleophiles like indole were unsuccessful, and hydroxylated compunds were produced.



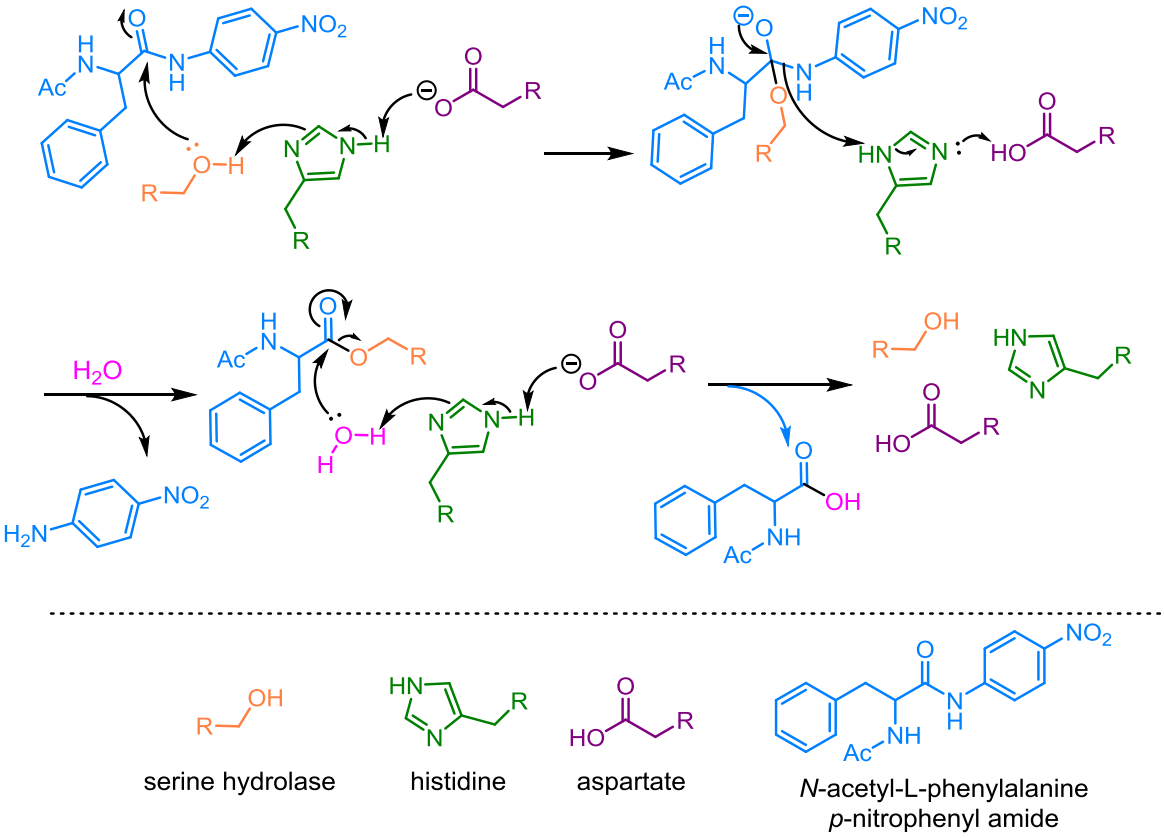
Scheme 37. *Investigation of four-component coupling reaction with TMSOTf.*



Scheme 38. *Investigation of four-component coupling reaction with $BF_3{\cdot}OEt_2$.*

Chapter 4 Synthesis of Serine Hydrolases Inhibitor and Its 5-Substituted Derivatives

Serine hydrolases are considered as one of the largest known and most diverse enzyme families. One characteristic defining feature of this family is the presence of an active site nucleophilic serine that is used for hydrolysis of the substrates.[66]

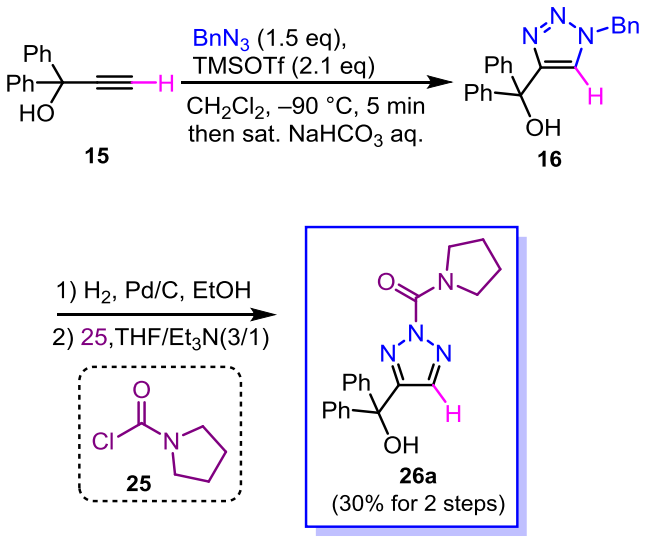


Scheme 39. *Hydrolization of activated serine hydrolase.*

The nucleophilic serine of these hydrolases is typically activated by a proton relay involving an acidic residue (aspartate or glutamate) and a basic residue (usually

histidine) (Scheme 39). *N*-acetyl-L-phenylalanine *p*-nitrophenyl amide enables to be used as substrate analogs for enzyme assays. This powerful nucleophilic serine residue attacked the unreactive carbonyl group forming an enzyme substrate intermediate. Then the peptide bond was cleaved followed by hydrolysis again. Along with histidine and aspartic acid, this serine residue constitutes the catalytic triad of the active site.

Due to the biological importance, serine hydrolases have been used as the targets of clinical drugs to treat various diseases such as diabetes and Alzheimer's disease.[67] However, the biochemical activities of these enzymes are yet to be understood. For this reason, it is important to produce efficient synthetic methods to prepare selective inhibitors of these enzymes and preparation of its derivatives as candidates of more active drug molecules. To develop the efficiency of this triazole synthesis for bioactive molecule synthesis, I carried out the synthesis of triazole urea **26a** reported as a serine hydrolase inhibitor by Cravatt *et al.*[68] and its 5-substituted derivatives. Cravatt's reported the serine hydrolase inhibitors can selectively inhibit enzymes from diverse branches of the serine hydrolase family, such as peptidases (aceyl-peptide hydrolase), lipases (platelet-activating factor acetylhydrolase-2), uncharacterized hydrolases (α,β-hydrolase-11, ABHD11). Here, my triazole products have the same core structure of AA32-1 and AA44-2 which selectively inhibit ABHD11.



Scheme 40. *Synthesis of Serine hydrolases inhibitor* ***26a.***

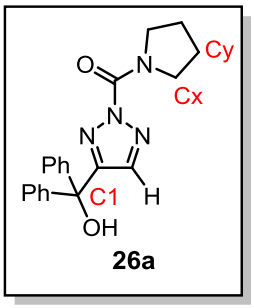
1,4-disubstituted **26a** were prepared from appropriate propargyl alcohols with TMSOTf followed by quenching with aqueous media (Scheme 40). The obtained *N*-benzyltriazoles were deprotected by hydrogenolysis, and the obtained unprotected triazoles were coupled with carbamoyl chloride **26** to afford serine hydrolase inhibitor triazole urea **26a** regioselectively.

To confirm the structure of synthesized triazole urea compound **26a**, same as the reported data, I compared the ^{1}H and ^{13}C NMR analysis in $CDCl_3$ along with other analytical data. However, the spectroscopic data of compound **26a** didn't match the reported data (Table 12). Then I noticed that the peak of benzylic carbon C1 (δ 77.2) was overlapped with the solvent peak ($CDCl_3$, δ 77.0) in ^{13}C NMR analysis. However, the split patterns of δ 53.8 and 25.2 (Cx and Cy) were quite different from mine and

C1 carbon peak at 91.1 was not recognized.

Table 12. *^{1}H and ^{13}C spectroscopic data of compound **26a** (in $CDCl_3$).*

Reported data ^{1}H-NMR (400MHz, $CDCl_3$)	**26a** ^{1}H-NMR (500MHz, $CDCl_3$)	Reported ^{13}C-NMR (100MHz, $CDCl_3$)	**26a** ^{13}C-NMR (126MHz, $CDCl_3$)
7.49 (s, 1H)	7.56 (s, 1H)	152.7	155.6
7.30-7.18 (m, 10H)	7.33-7.29 (m, 10H)	144.5	147.7
3.97 (t, *J* = 6.4Hz, 1H)	3.76 (t, *J* = 6.5Hz, 2H)	131.2	144.9
3.78 (t, *J* = 6.4Hz, 1H)	3.70 (t, *J* = 6.5Hz, 2H)	128.8	135.3
3.65 (m, 2H)	1.96-1.92 (m, 4H)	127.0	128.2
1.91 (m, 4H)		126.5	127.8
		123.3	127.1
		91.1	77.2
		53.8	50.1
		25.2	48.7
			26.4
			24.0



26a

Therefore, I changed solvent the $CDCl_3$ to CD_3OD and CD_2Cl_2. Then after discussion with Professor Adibekian one of the authors, he kindly gave me the NMR analysis data of CD_3OD. My ^{1}H NMR data almost matched to their corrected data (Figure 5, 6). For ^{13}C NMR, at first, they still have two incorrect assignments around δ100.0 and δ55.0 (Figure 7, yellow). They also miss assign two peaks (Figure 7, red). They think the peak of δ 78.0 from chloroform and δ 49.8 is another impurity. Finally, they agree with my NMR assignment and the incorrect NMR assignments were found in the reference article. The C1 was found at 78.0 and Cx were found at δ 51.5 and δ 49.8 which is

near with the solvent peak (CD_3OD, δ49.0). Finally, the NMR data of compound **26a** were identical to those in CD_3OD, which were newly provided by author (Table 13, Figure 6, 8).

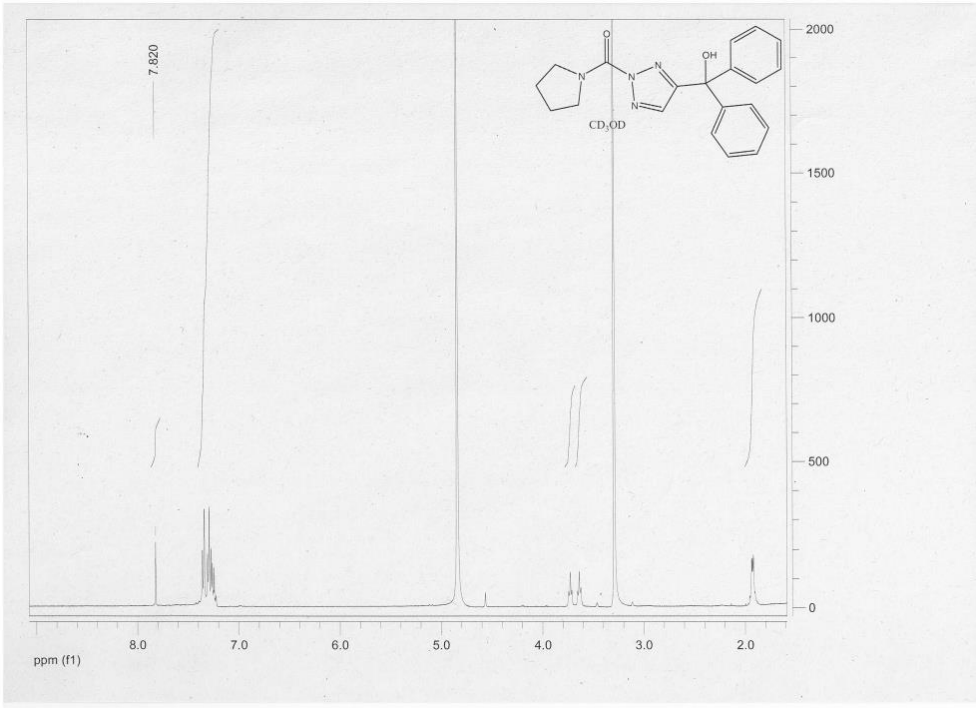


Figure 5. *^1H NMR spectroscopic data of **26a** provided by author (in CD_3OD).*

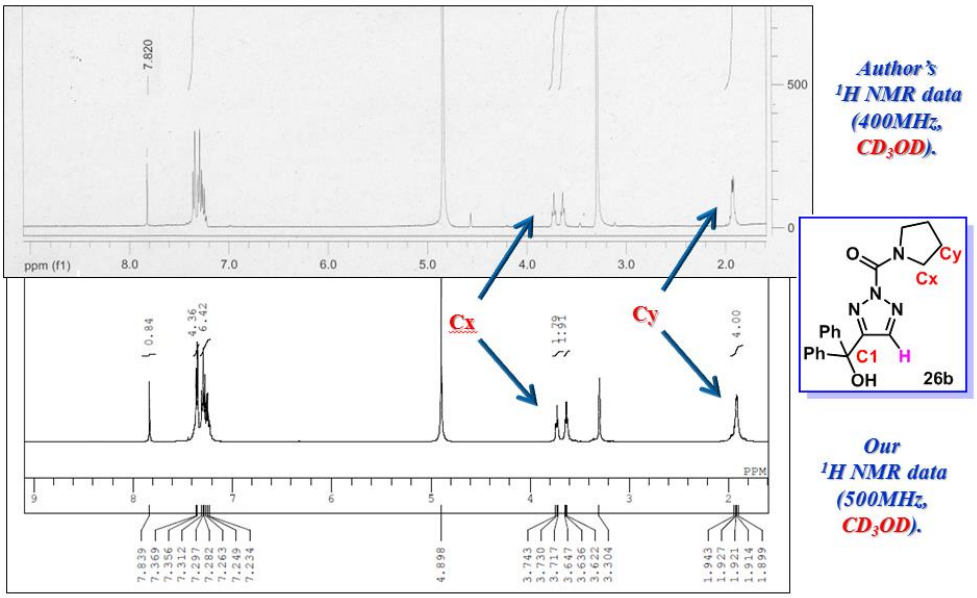


Figure 6. *^1H NMR spectroscopic data of **26a** provided by author (in CD_3OD).*

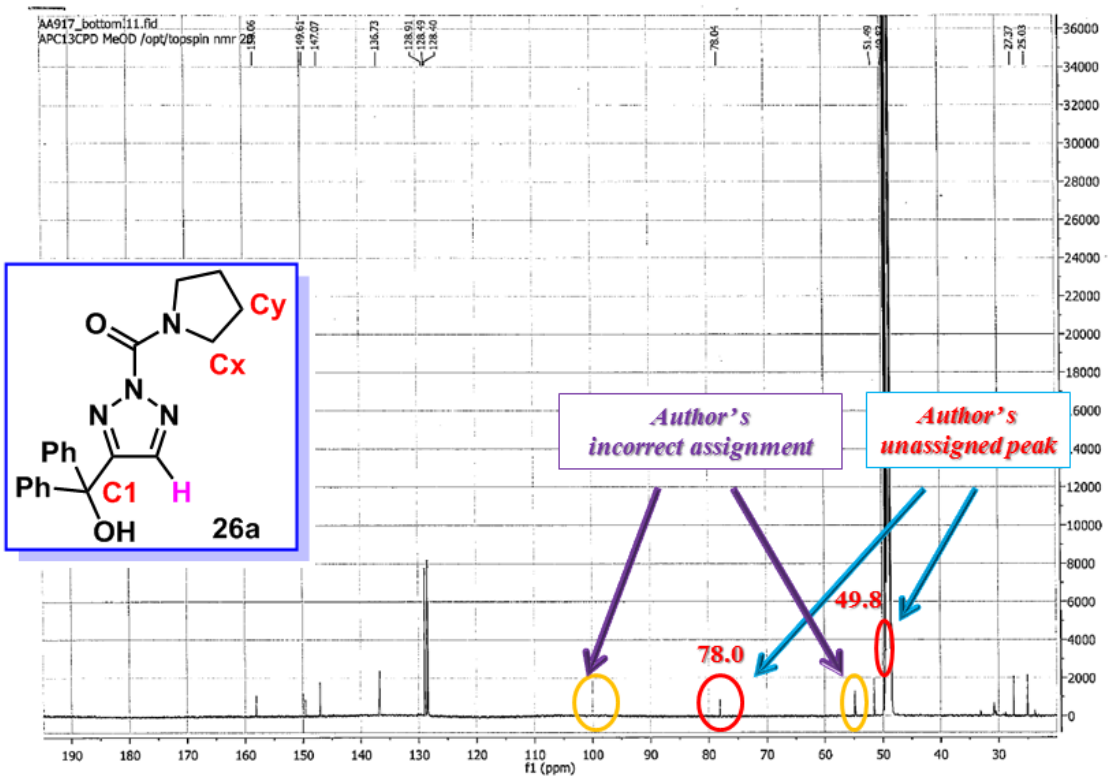


Figure 7. *^{1}H NMR spectroscopic data of **26a** provided by author (in CD_3OD).*

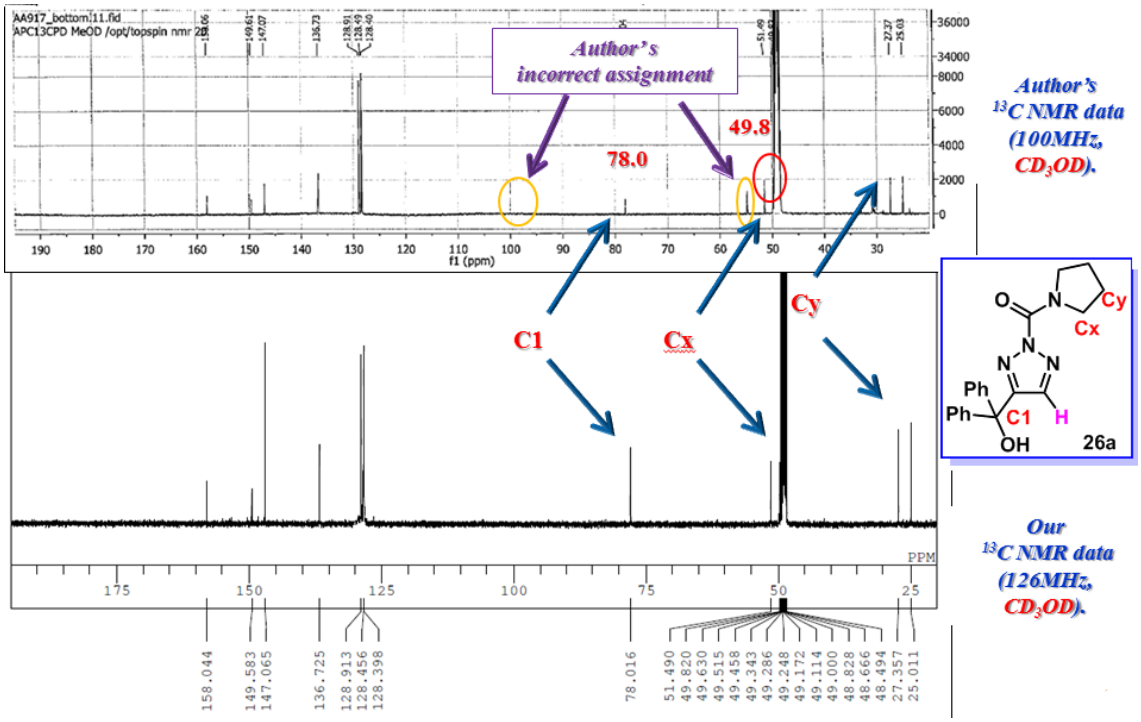
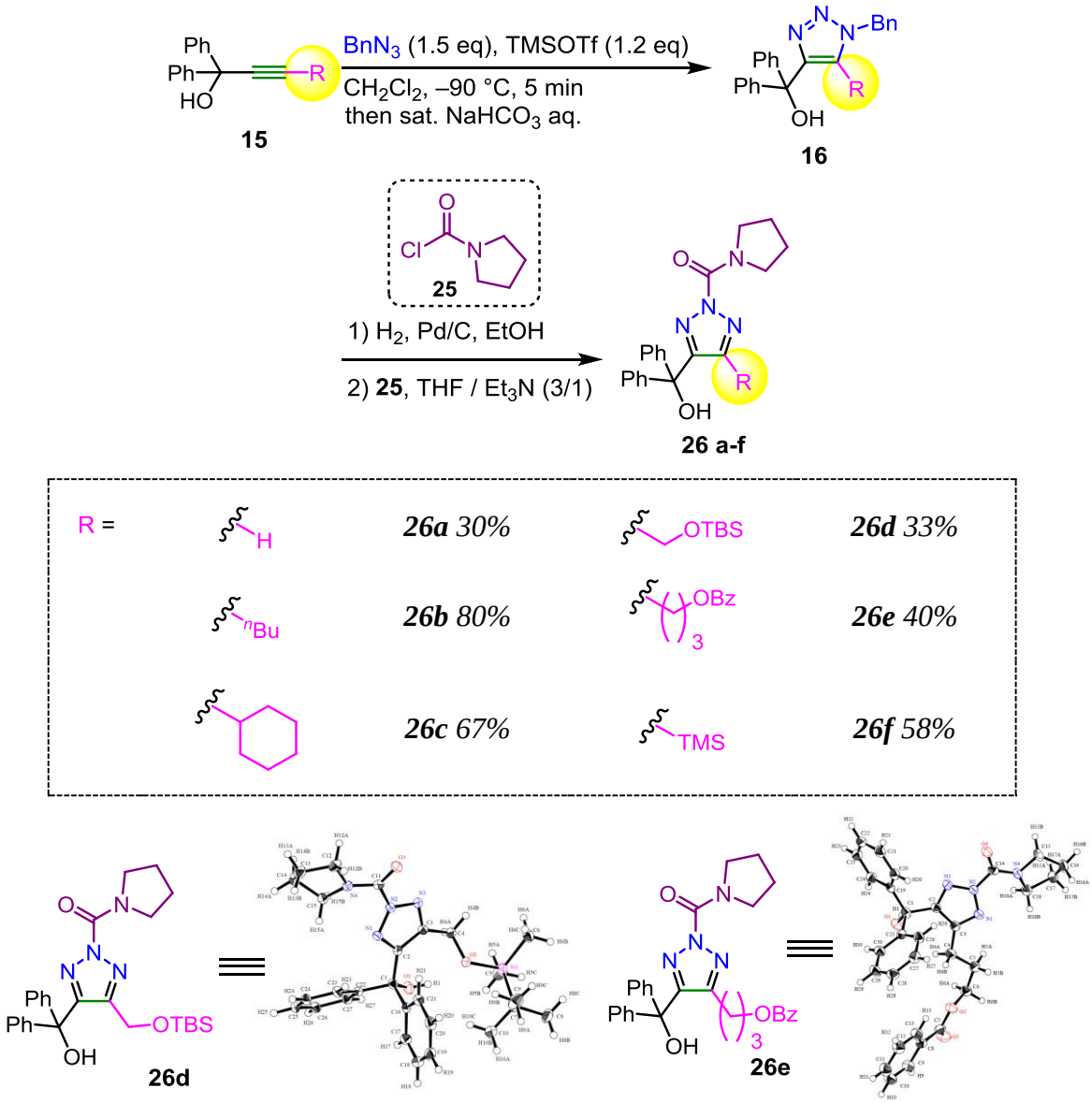


Figure 8. *^{1}H NMR spectroscopic data of **26a** provided by author (in CD_3OD).*

Table 13. *^{1}H and ^{13}C spectroscopic data of compound **26b** (in CD_3OD).*

26b ^{1}H-NMR (500M , CD_3OD)	Corrected data ^{13}C-NMR (100M , CD_3OD)	**26b** ^{13}C-NMR (125M , CD_3OD)
7.84(s, 1H)	158.0	158.0
7.23-7.37(m, 10H)	149.6	149.6
3.73(t, *J* = 6.0Hz, 2H)	147.1	147.1
3.64(t, *J* = 6.0Hz, 2H)	136.7	136.7
1.94-1.90(m, 4H)	128.9	128.9
	128.5	128.5
	128.4	128.4
	78.0	78.0
	51.5	51.5
	49.8	49.8
	27.4	27.4
	25.0	25.0

Then after comfirmation of the compound **26a**, I began to synthesize the its 5-subsitituted derivetives **26b-f** (Scheme 41). According to the sucessful result, 26b-f were obtained from corresponding propargyl alkyne under starding cyclization condition, followed by debenzylation and coupling with compound **25.** In all cases, desired 2*H*-triazole ureas **26a–f** were obtained regioselectively. Description of structures of **26d,e** were unambiguously confirmed by X-ray crystallographic analysis. Since it is difficult to prepare triazole ureas **26a,c–f** obtained from internal alkynes by CuAAC, this method could prove to be an efficient way to explore the property and activity of fully substituted triazole molecules.



Scheme 41. *Synthesis of serine hydrolases inhibitor and its 5-substituted derivatives.*

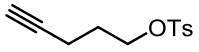
Chapter 5 Supporting Information

5.1 Experimental section

General information

^{1}H and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer (500MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated by residual solvent peak ($CDCl_3$, δ 7.26 for 1H NMR, δ 77.00 for ^{13}C NMR; CD_3OD, δ 3.31 for ^{1}H NMR, δ 49.00 for ^{13}C NMR; CD_2Cl_2, δ 5.32 for ^{1}H NMR, δ 53.8 for ^{13}C NMR) or tetramethylsilane (δ 0 for ^{1}H NMR). Abbreviations are following: s (singlet), d (doublet), t (triplet), q (quartet), br (broad peak), m (complex multiplet). Inflared spectra were measured on a JASCO FT/IR-4200 spectrometer. Mass spectra were recorded on a JEOL JMS-700 MStaion [EI (70 eV), CI, FAB and ESI]. X-ray crystallography was performed on Rigaku R-AXIS RAPID/S imaging plate diffractometer. Flush column chromatography was performed by MERCK Silica gel 60. The progress of reactions was monitored by silica gel thin layer chromatographyplates (MERCKTLC Silicagel 60 F_{254}). Phosphomolybdic acid ethanol solution, ninhydrin-acetic acid butanol solution and anisaldehyde-acetic acid-sulfuric acid ethanol solution were used as TLC stain. All reagents were purchased from Sigma-Aldrich, Wako pure chemical industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Nakalai Tesque. Used Dehydrated solvents —tetrahydrofuran, dichloromethane and toluene— were purchased from Kanto Chemical, Wako pure chemical industries, Ltd, and Nakalai Tesque. Sodium azide purchased from Nakalai Tesque was carefully handled, and transferred with plastic spatulas.

pent-4-yn-1-yl 4-methylbenzenesulfonate (2)



2

To a stirred solution of 4-pentyn-1-ol **1** (100.0 mg, 1.19 mmol) and TsCl (249.3 mg, 1.31 mmol) in dichloromethane (12 ml) was added dropwise triethylamine (0.2 mL, 1.43 mmol) at 0 °C, then reaction mixture was allowed to warm up to ambient temperature. After 2 h, the mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography (ethyl acetate / hexane = 1/10) gave tosylate **2** (220 mg, 77.7%) as a colorless oil.

Colorless oil; R_f value 0.53(ethyl acetate / hexane = 1/3);IR (NaCl, neat) ν_{max} = 3291, 2962, 1598, 1360, 1176 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 8.5 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 4.14 (t, 2H, *J* = 6.0 Hz), 2.45 (s, 3H), 2.25 (td, 2H, *J* = 6.5, 2.5 Hz), 1.88 (t, 1H, *J* = 2.5 Hz), 1.86 (tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR (126 MHz,

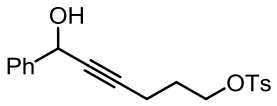
$CDCl_3$) δ 144.8, 132.9, 129.8, 127.9, 82.1, 69.4, 68.7, 27.7, 21.6, 14.7; HRMS (ESI) calcd for $C_{12}H_{14}O_3SNa$ $[M+Na]^+$ 261.0561, found 261.0561.

General Experimental Procedure of propargyl alcohols

To a stirred solution of tosylate **2** in dry THF under an atmosphere of nitrogen was added dropwise *n*-BuLi at -78 °C and the mixture was stirred for 10 min. Benzaldehyde was then added at same temperature. After 4h, the reaction was quenched with water. The mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$. The crude product can be used to the next step without further purification.

To a stirred solution of benzyl alcohols in DMF was added sodium azide at room temperature and the reaction mixture was heated to 50 °C. After 20 min, the reaction mixture was diluted with ether and was washed with water and brined. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography gave azide as colorless oil.

6-hydroxy-6-phenylhex-4-yn-1-yl 4-methylbenzenesulfonate (3)

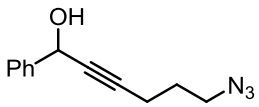


3

The reaction with tosylate **2** (146 mg, 0.612 mmol), *n*-BuLi (1.6 M in hexane, 0.44 mL, 0.706 mmol) and benzaldehyde (47.6 µL, 0.471 mmol) in TH F (4.8 mL) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1 / 5) gave benzyl alcohol **3** (148 mg, 91% based on benzaldehyde) as a colorless oil.

Colorless oil; R_f value 0.15(ethyl acetate / hexane = 1/3);IR (NaCl, neat) ν_{max} = 3524, 2960, 1598, 1189, 1175, 930 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2H, *J* = 8.0 Hz), 7.48 (d, 2H, *J* = 8.0 Hz), 7.30 – 7.38 (m, 3H), 5.36 (br, 1H), 4.14 (t, 2H, *J* = 6.5 Hz), 2.42 (s, 3H), 2.35 (td, 2H, *J* = 7.0, 2.0 Hz), 1.87 (tt, 2H, *J* = 7.0, 6.5 Hz) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 140.9, 132.8, 129.8, 128.5, 128.2, 127.8, 126.5, 84.2, 81.3, 68.9, 64.5, 27.6, 21.6, 15.1; HRMS (ESI) calcd for $C_{19}H_{20}O_4SNa$ $[M+Na]^+$ 367.0980, found 367.09800.

6-azido-1-phenylhex-2-yn-1-yl acetate (4a)

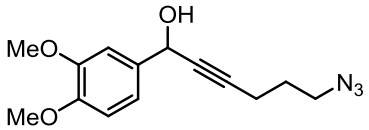


4a

To a stirred solution of benzyl alcohol **3** (780 mg, 2.02 mmol) in DMF (20 mL) was added sodium azide (170.6 mg, 2.62 mmol) at room temperature and the reaction mixture was heated to 50 °C. After 20 min, the reaction mixture was diluted with ether and was washed with water and brined. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 3) gave azide **4a** (487.9 mg, 94%) as a colorless oil.

Colorless oil; R_f value 0.45(ethyl acetate / hexane = 1/2); IR (NaCl, neat) ν_{max} = 2931, 2098, 1739, 1227 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, 2H, *J* = 7.0 Hz), 7.38 (m, 3H), 6.45 (br, 1H), 3.40 (t, 2H, *J* = 7.0 Hz), 2.40 (td, 2H, *J* = 2.0, 6.5 Hz), 2.10 (s, 3H), 1.80 (tt, 2H, *J* = 6.5, 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 137.2, 128.7, 128.5, 127.5, 86.1, 77.9, 65.7, 49.9, 27.4, 20.9, 16.0; HRMS (ESI) calcd for $C_{14}H_{15}N_3O_2Na$ $[M+Na]^+$ 280.1062, found 280.1061.

6-azido-1-(3,4-dimethoxyphenyl)hex-2-yn-1-ol(4c)



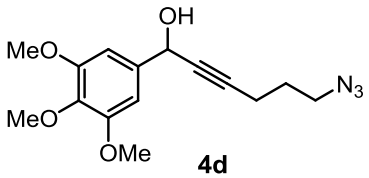
4c

The reaction with tosylate **2** (2.15 g, 9.03 mmol), *n*-BuLi (1.55 M in hexane, 6.41 mL, 9.93 mmol) and benzaldehyde (1 g, 6.02 mmol) in THF (60 mL) followed by collected the organic layer under vacuum affording the crude product 2.97g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (2.87g, 7.15 mmol) with sodium azide (0.511g, 7.86mmol) in DMF (25ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 5 to 1/2) gave azide **4c** (1.81 g, 92%) as a colorless oil.

Colorless oil; R_f value 0.34 (ethyl acetate / hexane = 1/2); IR (NaCl, neat) ν_{max} 3433, 2938, 2098, 1593, 1125 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.07(m, 2H), 6.86(d, 1H, *J* = 8.5 Hz), 5.41(m, 1H), 3.91(s, 3H), 3.89(s, 3H), 3.42(t, 2H, *J* = 7.0 Hz), 2.42(td, 2H, *J* = 6.5, 2.0 Hz), 2.18(d, 1H, OH, *J* = 5.5 Hz), 1.82(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 149.1, 133.7, 118.9, 110.9, 109.8, 85.4, 81.2, 64.6, 55.93, 55.86, 50.2, 27.7, 16.1; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1166.

6-azido-1-(3,4,5-trimethoxyphenyl)hex-2-yn-1-ol(4d)



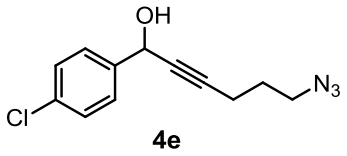
4d

The reaction with tosylate **2** (1.09 g, 4.59 mmol), *n*-BuLi (1.55 M in hexane, 3.26 mL, 5.05 mmol) and benzaldehyde (1 g, 3.06 mmol) in THF (31 mL) followed by collected the organic layer under vacuum affording the crude product 1.32g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (1.32 g, 3.04 mmol) with sodium azide (0.217 g, 3.34 mmol) in DMF (15 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/1) gave azide **4d** (0.897 g, 96%) as a colorless oil.

Colorless oil; R_f value 0.48(ethyl acetate/hexane = 1/1); IR (NaCl, neat) ν_{max} 3433, 2999, 2099, 1594, 1125 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.73(s, 2H), 5.34(t, 1H, *J* = 2.0 Hz), 3.84(s, 6H), 3.80(s, 3H), 3.39(t, 2H, *J* = 6.5 Hz), 2.37(td, 2H, *J* = 7.0, 2.0 Hz), 1.78(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 153.1, 137.6, 136.7, 103.4, 85.2, 81.1, 64.6, 60.7, 56.0, 50.0, 27.6, 16.0; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1273.

6-azido-1-(4-chlorophenyl)hex-2-yn-1-ol(4e)



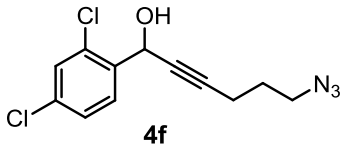
4e

The reaction with tosylate **2** (1.53 g, 6.40 mmol), *n*-BuLi (1.55 M in hexane, 4.54 mL, 7.04 mmol) and benzaldehyde (0.6 g, 4.27 mmol) in THF (42 mL) followed by collected the organic layer under vacuum affording the crude product 1.6g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (1.6 g, 6.40 mmol) with sodium azide (0.499 g, 7.68mmol) in DMF (32 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/3) gave azide **4e** (1.08 g, 99%) as a colorless oil.

Colorless oil; R_f value 0.52(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3388, 2936, 2099, 1488, 1255, 1089 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.45(m, 2H), 7.34(m, 2H), 5.41(s, 1H), 3.40(t, 2H, *J* = 6.0 Hz), 2.43(br, 1H, OH), 2.39(td, 2H, *J* = 7.0, 2.0 Hz), 1.80(tt, 2H, *J* = 7.0, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 139.5, 134.0, 128.7, 127.9, 85.9, 80.7, 63.9, 50.1, 27.6, 16.1; HRMS (ESI) calcd for $C_{12}H_{12}ClN_3ONa$ $[M+Na]^+$ 272.0567, found 272.0566.

6-azido-1-(2,4-dichlorophenyl)hex-2-yn-1-ol(4f)



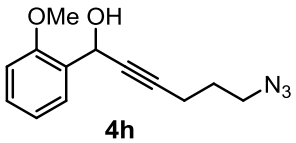
4f

The reaction with tosylate **2** (787.0 g, 1.7 mmol), *n*-BuLi (1.55 M in hexane, 2.27 mL, 1.85 mmol) and benzaldehyde (0.34 g, 1.94 mmol) in THF (20 mL) followed by collected the organic layer under vacuum affording the crude product 0.880 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (0.880 g, 2.13 mmol) with sodium azide (0.166 g, 2.55 mmol) in DMF (10 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 5) gave azide **4f** (0.461 g, 87%) as a colorless oil.

Colorless oil; R_f value 0.38(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3346, 2932, 2098, 1469, 1254 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.67(d, 1H, *J* = 8.5 Hz), 7.39(d, 1H, *J* = 1.5 Hz), 7.30(dd, 1H, *J* = 8.5, 1.5 Hz), 5.75(br, 1H), 3.40(t, 2H, *J* = 6.5 Hz), 2.40(br, 1H), 2.39(td, 2H, *J* = 7.0, 2.0 Hz), 1.80(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 136.9, 134.8, 133.2, 129.5, 129.0, 127.5, 85.9, 79.6, 61.5, 50.1, 27.6, 16.1; LRMS (EI) 255($[M-N_2]^+$, 5%), 220(86), 175(64), 110(100); HRMS (EI) calcd for $C_{12}H_{11}Cl_2NO$ $[M-N_2]^+$ 255.0218, found 255.0188.

6-azido-1-(2-methoxyphenyl)hex-2-yn-1-ol(4h)



4h

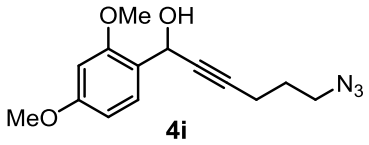
The reaction with tosylate **2** (3.94 g, 16.5 mmol), *n*-BuLi (1.55 M in hexane, 12.77 mL, 19.8 mmol) and benzaldehyde (1.5 g, 11.02 mmol) in THF (110 mL) followed by collected the organic layer under vacuum affording the crude product 3.12 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (3.12 g, 8.33 mmol) with sodium azide (0.65 g, 10 mmol) in DMF (8 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 2) gave azide **4h** (1.98 g, 97%) as a colorless oil.

Colorless oil; R_f value 0.36(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3417, 2938, 2098, 1244 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.56(dd, 1H, *J* = 7.5, 2.0 Hz), 7.31(ddd, 1H, *J* = 7.5, 7.5, 2.0 Hz), 6.99(dd, 1H, *J* = 7.5, 7.5 Hz), 6.92(d, 1H, *J* = 7.5 Hz), 5.70(td, 1H, *J* = 6.0, 2.0 Hz), 3.90(s, 3H), 3.43(t, 2H, *J* = 6.5 Hz), 3.00(d, 1H, OH, *J* = 6.0 Hz),

2.41(td, 2H, *J* = 7.0, 2.0 Hz), 1.82(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.7, 129.6, 128.9, 127.7, 120.8, 110.7, 85.0, 80.4, 61.2, 55.5, 50.2, 27.7, 16.2; HRMS (ESI) calcd for $C_{13}H_{15}N_3O_2Na$ $[M+Na]^+$ 268.1062, found 268.1061.

6-azido-1-(2,4-dimethoxyphenyl)hex-2-yn-1-ol(4i)

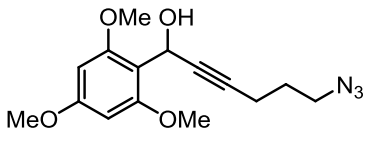


4i

To a stirred solution of 5-azidopent-1-yne (945.7 mg, 8.67 mmol) in dry THF (48 mL) under an atmosphere of nitrogen was added dropwise *n*-BuLi (1.58 M in hexane, 5.79 mL, 9.15 mmol) at -78 °C and the mixture was stirred for 60 min. Benzaldehyde (700.0 mg, 4.81 mmol) was then added at same temperature. After 8 h, the reaction was quenched with water. The mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1 / 5 to 1/3) gave desired benzyl alcohol **4i** (0.774 g, 67%) as a colorless oil.

Colorless oil; R_f value 0.33 (ethyl acetate / hexane = 1 / 2); IR (NaCl, neat) ν_{max} 3426, 2938, 2099, 1613, 1506, 1208 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.46(d, 1H, *J* = 9.0 Hz), 6.48(d, 1H, *J* = 2.5 Hz), 6.46(dd, 1H, *J* = 7.0, 2.5 Hz), 5.65(m, 1H), 3.85(s, 3H), 3.80(s, 3H), 3.42(t, 2H, *J* = 7.0 Hz), 2.83(d, 1H, OH, *J* = 6.0 Hz), 2.40(td, 2H, *J* = 7.0, 2.5 Hz), 1.81(tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 161.0, 157.1, 128.5, 121.8, 104.1, 98.7, 84.6, 80.7, 60.6, 55.5, 55.4, 50.2, 27.7, 16.1; LRMS (EI) 275(M^+, 100%), 216(71); HRMS (EI) calcd for $C_{14}H_{17}N_3O_3$ (M^+) 275.1270, found 275.1262.

6-azido-1-(2,4,6-trimethoxyphenyl)hex-2-yn-1-ol(4j)



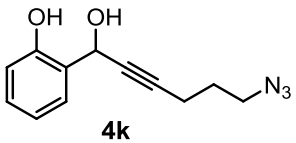
4j

To a stirred solution of 5-azidopent-1-yne (1.4 mg, 12.84 mmol) in dry THF (71 mL) under an atmosphere of nitrogen was added dropwise *n*-BuLi (1.58 M in hexane, 8.58 mL, 913.56 mmol) at -78 °C and the mixture was stirred for 60 min. Benzaldehyde (1.4 g, 7.14 mmol) was then added at same temperature. After 8 h, the reaction was quenched with water. The mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$ followed by silica gel

column chromatography (ethyl acetate / hexane = 1/10 to 1/6 to 1/3) gave desired benzyl alcohol **4j** (1.7 g, 80%) as a colorless oil.

Colorless oil; R_f value 0.33(ethyl acetate / hexane = 1/1); IR (NaCl, neat) ν_{max} 3427, 2938, 2098, 1593, 1233, 1125 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.13(s, 2H), 5.78(m, 1H), 3.85(s, 6H), 3.80(s, 3H), 3.37(t, 2H, *J* = 7.0 Hz), 2.30(t, 2H, *J* = 7.0 Hz), 1.74(tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 160.9, 158.0, 110.7, 91.1, 82.5, 81.2, 56.3, 55.8, 55.3, 50.1, 27.7, 16.1; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1273.

2-(6-azido-1-hydroxyhex-2-yn-1-yl)phenol(4k)



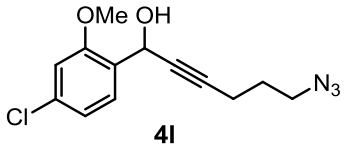
4k

The reaction with tosylate **2** (1.9 g, 7.98 mmol), *n*-BuLi (1.55 M in hexane, 5.67 mL, 19.8 mmol) and benzaldehyde (0.65 g, 5.32 mmol) in THF (50 mL) followed by collected the organic layer under vacuum affording the crude product 1.86 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol (1.86 g, 5.16 mmol) with sodium azide (0.402 g, 6.19 mmol) in DMF (10 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/8) gave desired azide **4k** (0.672 g, 57 %) as a colorless oil.

Colorless oil; R_f value 0.4(ethyl acetate / hexane = 1/1); IR (NaCl, neat) ν_{max} 3481, 2938, 2099, 1490, 1245, 755 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.32–7.33(m, 2H including OH), 7.24(ddd, 1H, *J* = 7.5, 7.5, 1.5 Hz), 6.89–6.91(m, 2H), 5.66(d, 1H, *J* = 5.5 Hz), 3.42(t, 2H, *J* = 7.0 Hz), 3.04(d, 1H, OH, *J* = 5.5 Hz), 2.42(td, 1H, *J* = 7.0, 2.0 Hz), 1.81(tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 155.1, 130.0, 127.5, 124.9, 120.2, 117.0, 87.2, 79.1, 64.0, 50.1, 27.6, 16.1; HRMS (ESI) calcd for $C_{12}H_{13}N_3O_2Na$ $[M+Na]^+$ 254.0906, found 254.0905.

6-azido-1-(4-chloro-2-methoxyphenyl)hex-2-yn-1-ol(4l)



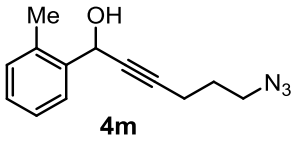
4l

The reaction with tosylate **2** (2.10 g, 8.79 mmol), *n*-BuLi (1.55 M in hexane, 6.74 mL, 9.67 mmol) and benzaldehyde (1.0 g, 5.86 mmol) in THF (59 mL) followed by collected the organic layer under vacuum affording the product 2.74 g. [silica gel

purification (ethyl acetate / hexane = 1 / 10 to 1/5 to 1/1)].
Colorless oil; R_f value 0.24(ethyl acetate / hexane = 1/3); IR (NaCl, neat) ν_{max} 3433, 2963, 2116, 1637, 1248, 1175 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.78(d, 2H, *J* = 8.5 Hz), 7.44(d, 1H, *J* = 8.0 Hz), 7.32(d, 2H, *J* = 8.5 Hz), 6.95(dd, 1H, *J* = 8.0, 1.5 Hz), 6.88(d, 1H, *J* = 2.0 Hz), 5.58(t, 1H, *J* = 2.0 Hz), 4.15(t, 2H, *J* = 6.0 Hz), 3.87(s, 3H), 2.43(s, 3H), 2.35(td, 2H, *J* = 6.5, 2.0 Hz), 1.87(tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 157.1, 144.8, 134.9, 132.9, 129.8, 128.6, 127.8, 127.6, 120.7, 111.5, 84.7, 80.2, 68.9, 60.2, 55.8, 27.7, 21.6, 15.1; HRMS (ESI) calcd for $C_{20}H_{21}ClO_5SNa$ $[M+Na]^+$ 431.0696, found 431.0699.

Then the crude benzyl alcohol (2.74 g, 6.7 mmol) with sodium azide (478.9 mg, 7.37 mmol) in DMF (39 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/8) gave azide **4l** (1.41 g, 86 %) as a colorless oil.
Colorless oil; R_f value 0.34(ethyl acetate / hexane = 1 / 3); IR (NaCl, neat) ν_{max} 3419, 2940, 2099, 1639, 1596, 1489, 1248 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.50(d, 1H, *J* = 8.0 Hz), 6.97(dd, 1H, *J* = 8.0, 1.5 Hz), 6.89(d, 1H, *J* = 1.5 Hz), 5.66(t, 1H, *J* = 1.5 Hz), 3.88(s, 3H), 3.41(t, 2H, *J* = 6.5 Hz), 2.40(td, 2H, *J* = 7.0, 1.5 Hz), 1.81(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 157.2, 135.0, 128.7, 127.7, 120.8, 111.5, 85.2, 80.1, 60.4, 55.8, 50.1, 27.7, 16.1; HRMS (ESI) calcd for $C_{13}H_{14}ClN_3O_2Na$ $[M+Na]^+$ 302.0672, found 302.0672.

6-azido-1-(o-tolyl)hex-2-yn-1-ol(4m)



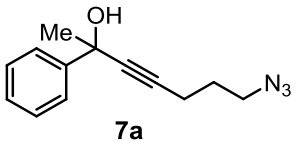
4m

The reaction with tosylate **2** (1.04 g, 4.37 mmol), *n*-BuLi (1.55 M in hexane, 2.95 mL, 4.66 mmol) and benzaldehyde (0.35 g, 2.91 mmol) in THF (59 mL) followed by collected the organic layer under vacuum affording the product 0.95 g. [silica gel purification (ethyl acetate / hexane = 1 / 8 to 1/2)].
Colorless oil; R_f value 0.30(ethyl acetate / hexane = 1 / 2); IR (NaCl, neat) ν_{max} 3433, 1644, 1360, 1175 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.78(d, 2H, *J* = 8.0 Hz), 7.59(m, 1H), 7.32(d, 2H, *J* = 8.0 Hz), 7.23(m, 2H), 7.17(m, 1H), 5.53(d, 1H, *J* = 2.0 Hz), 4.15(t, 2H, *J* = 6.0 Hz), 2.43(s, 3H), 2.41(s, 3H), 2.35(td, 2H, *J* = 6.5, 2.0 Hz), 1.87(tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.8, 138.6, 135.7, 132.9, 130.7, 129.8, 128.3, 127.9, 126.2, 126.1, 84.8, 81.0, 68.9, 62.2, 27.7, 21.6, 18.9, 15.2; HRMS (ESI)

calcd for $C_{20}H_{22}O_4SNa$ $[M+Na]^+$ 381.1137, found 381.1136.

Then the crude benzyl alcohol (0.95 g, 2.65 mmol) with sodium azide (0.189 g, 2.92mmol) in DMF (27 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 10 to 1/8) gave azide **4m** (0.579 g, 95 %) as a colorless oil.
Colorless oil; R_f value 0.45(ethyl acetate / hexane = 1 / 2); IR (NaCl, neat) ν_{max} 3420, 2098, 1646 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.63(m, 1H), 7.22–7.25(m, 2H), 7.18(m, 1H), 5.60(br, 1H), 3.40(t, 2H, *J* = 6.5 Hz), 2.44(s, 3H), 2.39(dt, 2H, *J* = 7.0, 2.0 Hz), 2.17(br, 1H, OH), 1.80(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 138.7, 135.7, 130.7, 128.3, 126.29, 126.23, 85.3, 80.8, 62.5, 50.2, 27.7, 18.9, 16.1; LRMS (EI) 200($[M-N_2-H]^+$, 47%), 186(51), 184(71), 115(100); HRMS (EI) calcd for $C_{13}H_{16}N_3O$ $[M+H]^+$ 230.12934, found 230.1299.

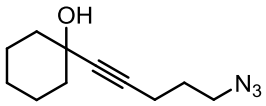
7-azido-2-phenylhept-3-yn-2-ol(7a)



7a

The reaction with tosylate **2** (1.40 g, 6.24 mmol), *n*-BuLi (1.55 M in hexane, 4.43 mL, 6.87 mmol) and ketone (0. 5 g, 4.16 mmol) in THF (42 mL) followed by followed by collected the organic layer under vacuum affording the crude product 0.95 g. The crude product can be used to the next step without further purification.
Then the crude benzyl alcohol with sodium azide (446.2 mg, 6.86mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1 / 20 to 1/10 to 1/5) gave azide **7a** (0.872 g, 91 %) as a colorless oil.
Colorless oil; R_f value 0.19(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3393, 2982, 2094, 1446 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.65(d, 2H, *J* = 6.5 Hz), 7.37(dd, 2H, *J* = 7.5, 7.5 Hz), 7.29(dd, 1H, *J* = 7.5, 7.5 Hz), 3.43(t, 2H, *J* = 6.5 Hz), 2.42(t, 2H, *J* = 6.5 Hz), 2.31(s, 1H, OH), 1.83(tt, 2H, *J* = 6.5, 6.5 Hz), 1.75(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.9, 128.3, 127.6, 124.8, 85.0, 83.7, 70.0, 50.2, 33.4, 27.8, 16.1; HRMS (ESI) calcd for $C_{13}H_{15}N_3ONa$ $[M+Na]^+$ 252.11128, found 252.11129.

1-(5-azidopent-1-yn-1-yl)cyclohexan-1-ol(7b)



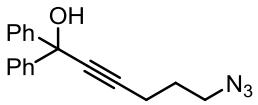
7b

The reaction with tosylate **2** (1.37 g, 6.11 mmol), *n*-BuLi (1.55 M in hexane, 3.62 mL, 5.60 mmol) and ketone (0.5 g, 5.09 mmol) in THF (50 mL) followed by followed by collected the organic layer under vacuum affording the crude product 1.71 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol with sodium azide (1.71 g, 5.08 mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **7b** (0.97 g, 85%) as a colorless oil.

Colorless oil; R_f value 0.58(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3383, 2933, 2856, 2097 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 3.42(t, 2H, *J* = 6.0 Hz), 2.35(t, 2H, *J* = 6.5 Hz), 1.80–1.89(m, 3H including OH), 1.78(tt, 2H, *J* = 6.5, 6.0 Hz), 1.68(m, 2H), 1.47–1.59(m, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 85.1, 82.7, 68.7, 50.2, 40.1, 27.9, 25.1, 23.4, 16.0; HRMS (ESI) calcd for $C_{11}H_{17}N_3ONa$ $[M+Na]^+$ 230.1269, found 230.1273.

6-azido-1,1-diphenylhex-2-yn-1-ol (7c)



7c

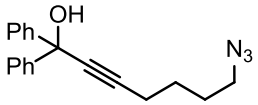
The reaction with tosylate **2** (0.543 g, 2.15 mmol), *n*-BuLi (1.58 M in hexane, 1.46 mL, 2.30 mmol) and ketone (0.28 g, 1.54 mmol) in THF (15 mL) followed by followed by collected the organic layer under vacuum affording the product 2.2 g. [silica gel purification (ethyl acetate / hexane = 1 / 8 to 1/4)].

Colorless oil; R_f value 0.25(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3502, 3060, 3029, 2958, 1598, 1491, 1449, 1360, 1175 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.75(d, 2H, *J* = 7.5 Hz), 7.53(m, 4H), 7.23–7.32(m, 8H), 4.15(t, 2H, *J* = 6.0 Hz), 2.76(s, 1H), 2.43(t, 2H, *J* = 6.5 Hz), 2.39(s, 3H), 1.90(tt, 2H, *J* = 6.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.1, 144.8, 132.8, 129.9, 128.2, 127.9, 127.6, 125.9, 85.5, 84.4, 74.3, 68.8, 27.7, 21.6, 15.2; LRMS (EI) 420(M^+, 0.8%), 403(5), 343(100), 220(53), 105(71); HRMS (EI) calcd for $C_{25}H_{24}O_4S$ (M^+) 420.1395, found 420.1397.

Then the crude benzyl alcohol with sodium azide (0.124 g, 1.9 mmol) in DMF (5 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **7c** (0.32 g, 70%) as a colorless oil.

Colorless oil; R_f value 0.50(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3426, 2933, 2099, 1490, 1449 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.59(m, 4H), 7.31(m, 4H), 7.27(m, 2H), 3.43(t, 2H, *J* = 6.5 Hz), 2.75(s, 1H), 2.48(t, 2H, *J* = 7.0 Hz), 1.85(tt, 2H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.2, 128.2, 127.6, 125.9, 86.2, 84.2, 74.4, 50.2, 27.7, 16.2; HRMS (CI) calcd for $C_{18}H_{18}N_3O$ $[M+H]^+$ 292.1450, found 292.1455.

7-azido-1,1-diphenylhept-2-yn-1-ol(7d)



7d

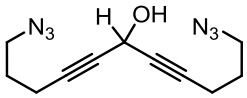
The reaction with tosylate (0.255 g, 1.07 mmol), *n*-BuLi (1.55 M in hexane, 0.729 mL, 1.15 mmol) and ketone (0.15 g, 0.823 mmol) in THF (8 mL) followed by followed by collected the organic layer under vacuum affording the product 0.45 g. [silica gel purification (ethyl acetate / hexane = 1 / 8 to 1/3)].

Colorless solid; R_f value 0.28(ethyl acetate/hexane = 1/3); m.p. 102.8–103.2 °C;IR (NaCl, neat) ν_{max} 3477, 1644, 1174, 933 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.78(d, 2H, *J* = 8.0 Hz), 7.60–7.57(m, 4H), 7.38–7.31(m, 6H), 7.28–7.25(m, 2H), 4.06(t, 2H, *J* = 6.5 Hz), 2.92(s, 1H, OH), 2.44(s, 3H), 2.34(t, 2H, *J* = 7.0 Hz), 1.82(tt, 2H, *J* = 6.5, 6.5 Hz), 1.63(tt, 2H, *J* = 6.5, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.4, 144.8, 132.9, 129.9, 128.2, 127.8, 127.5, 125.9, 86.9, 83.9, 74.4, 69.9, 28.0, 24.3, 21.6, 18.3; HRMS (ESI) calcd for $C_{26}H_{26}O_4SNa$ $[M+Na]^+$457.14495, found 457.14440.

Then the crude benzyl alcohol with sodium azide (83.47 mg, 1.28 mmol) in DMF (20 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5) gave azide **7d** (0.108 g, 43%) as a colorless oil.

Colorless oil; R_f value 0.47(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3421, 2935, 2096, 1489, 1449 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.60(m, 4H), 7.33(dd, 4H, *J* = 6.5, 6.5 Hz), 7.27(m, 2H), 3.31(t, 2H, *J* = 6.5 Hz), 2.76(s, 1H, OH), 2.40(t, 2H, *J* = 7.0 Hz), 1.66–1.76(m, 4H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.3, 128.2, 127.6, 125.9, 87.2, 83.7, 74.4, 50.9, 28.0, 25.6, 18.5,; HRMS (ESI) calcd for $C_{19}H_{19}N_3ONa$ $[M+Na]^+$ 328.1426, found 328.1424.

1,11-diazidoundeca-4,7-diyn-6-ol(12a)



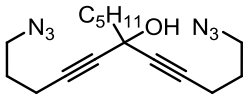
12a

The reaction with tosylate (1.54 g, 6.58 mmol), *n*-BuLi (1.55 M in hexane, 4.39 mL, 6.58 mmol) and aldehyde (0.28 g, 2.74 mmol) in THF (30 mL) followed by followed by collected the organic layer under vacuum affording the crude product 0.33 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol with sodium azide (94.38 mg, 1.45 mmol) in DMF (15 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/2) gave azide **12a** (0.128 g, 79%) as a colorless oil.

Colorless oil; R_f value 0.36(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3390, 2935, 2098, 1255 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 5.10(tt, 1H, *J* = 1.5, 1.5 Hz), 3.42(t, 4H, *J* = 7.0 Hz), 2.36(td, 4H, *J* = 6.5, 1.5 Hz), 2.19(m, 1H, OH), 1.80(tt, 4H, *J* = 7.0, 6.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 83.3, 78.9, 52.3, 50.1, 27.4, 16.0; HRMS (ESI) calcd for $C_{11}H_{14}N_6ONa$ $[M+Na]^+$ 269.1127, found 269.1123.

1,11-diazido-6-pentylundeca-4,7-diyn-6-ol(12b)



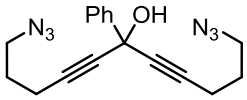
12b

The reaction with tosylate (0.915 g, 3.84 mmol), *n*-BuLi (1.55 M in hexane, 2.8 mL, 4.22 mmol) and ester (0.25 g, 1.92 mmol) in THF (20 mL) followed by followed by collected the organic layer under vacuum affording the crude product 1.10 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol with sodium azide (299.6 mg, 4.61 mmol) in DMF (38 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/15 to 1/5 to 1/1) gave azide **12b** (0.521 g, 86%) as a colorless oil.

Colorless oil; R_f value 0.45(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3420, 2930, 2098, 1254 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 3.40(t, 4H, *J* = 7.0 Hz), 2.45(s, 1H, OH), 2.35(t, 4H, *J* = 7.0 Hz), 1.83(m, 2H), 1.78(tt, 4H, *J* = 7.0, 7.0 Hz), 1.54(m, 2H), 1.31–1.35(m, 4H), 0.90(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 82.2, 81.9, 63.7, 50.1, 44.1, 31.4, 27.5, 24.3, 22.5, 16.0, 14.0; HRMS (ESI) calcd for $C_{16}H_{24}N_6ONa$ $[M+Na]^+$ 339.1909, found 339.1901.

1,11-diazido-6-phenylundeca-4,7-diyn-6-ol(12c)



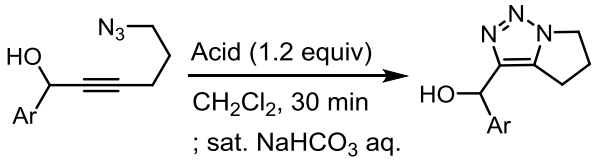
12c

The reaction with tosylate (1.19 g, 4.98 mmol), *n*-BuLi (1.55 M in hexane, 3.49 mL, 5.23 mmol) and chloride (0.35 g, 2.49 mmol) in THF (25 mL) followed by followed by collected the organic layer under vacuum affording the crude product 2.89 g. The crude product can be used to the next step without further purification.

Then the crude benzyl alcohol with sodium azide (388.5 mg, 5.98 mmol) in DMF (25 ml) followed by silica gel column chromatography (ethyl acetate / hexane = 1/20 to 1/10 to 1/2) gave azide **12c** (0.724 g, 90%) as a colorless oil.

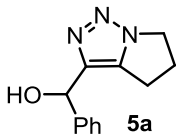
Colorless oil; R_f value 0.51(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3398, 2935, 2099, 1449, 1255 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.76(m, 2H), 7.35–7.41(m, 3H), 3.41(t, 4H, *J* = 7.0 Hz), 2.86(m, 1H, OH), 2.42(t, 4H, *J* = 7.0 Hz), 1.82(tt, 4H, *J* = 7.0, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.7, 83.9, 82.0, 65.0, 50.1, 27.5, 16.1; HRMS (ESI) calcd for $C_{17}H_{18}N_6ONa$ $[M+Na]^+$ 345.1440, found 345.1436.

General Experimental Procedure of triazolations



To the mixture of propargyl alcohol (1.0 equiv) in dichloromethane (0.1 M to alcohols) under nitrogen atmosphere, $TsOH \cdot H_2O$ (1.2 equiv) was added at ambient temperature. After 30 minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography afforded triazole.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(phenyl)methanol(5a)

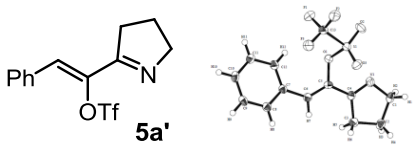


5a

The reaction with propargyl alcohol **4a** (50 mg, 0.232 mmol) and $TsOH \cdot H_2O$ (53.0 mg, 0.278 mmol) in dichloromethane (2.3 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to ethyl acetate) afforded triazole **5a** (16.1 mg, 32%) along with tosylated byproduct in 6%.

Colorless oil; R_f value 0.15(dichloromethane/mechanol = 20/1); IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.43(d, 2H, *J* = 7.0 Hz), 7.34(dd, 1H, *J* = 7.0, 7.5 Hz), 7.28(t, 2H, *J* = 7.5 Hz), 6.01(sd, 1H, *J* = 2.5 Hz), 4.20(t, 2H, *J* = 7.0 Hz), 4.12(sd, 1H, *J* = 3.0 Hz), 2.65-2.55(m, 2H), 2.48-2.42(m, 1H), 2.28-2.22(m, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 143.0, 141.8, 139.4, 128.3, 127.6, 126.1, 68.6, 46.2, 28.0, 20.6; HRMS (ESI) calcd for $C_{12}H_{11}NONa$ $[M+Na]^+$ 238.0956, found 238.0955.

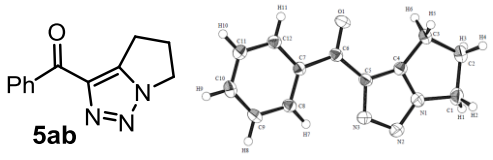
(*Z*)-1-(3, 4-dihydro-2*H*-pyrrol-5-yl)-2-phenylvinyl trifluoromethanesulfonate (5a')



To a stirred solution of propargyl alcohol **1** (68.0 mg, 0.316 mmol) in dichloromethane (3 mL) under an atmosphere nitrogen was added dropwise TMSOTf (68.5 μL, 0.379 mmol) at 0 °C. After 20 min, the reaction was quenched with saturated $NaHCO_3$ aqueous solution at 0 °C. The mixture was diluted with ethyl acetate and was washed with water and brine. Drying collected organic layer over $MgSO_4$ followed by silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/5 to 1/4) gave imine product **5a'** (7.1 mg, 7%) as a colorless solid along with triazole ketone **5ab** in 13%.

White crystal; R_f value 0.28(ethyl acetate/hexane = 1/3); m.p. 109.1–112.7 °C; IR (NaCl, neat) ν_{max} 3385, 3035, 2971, 1258, 1049, 740 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.56(d, 2H, *J* = 6.5 Hz), 7.41(m, 3H), 6.78(s, 1H), 4.15(t, 2H, *J* = 7.0 Hz), 2.85(t, 2H, *J* = 8.5 Hz), 2.09(tt, 2H, *J* = 7.0, 8.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 167.5, 142.5, 130.8, 129.9, 129.8, 128.7, 126.9, 118.2(q, *J* = 322 Hz), 61.9, 34.5, 23.2; HRMS (ESI) calcd for $C_{13}H_{12}F_3NONaS$ $[M+Na]^+$ 342.03877, found 342.03882.

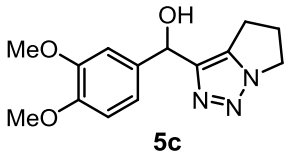
(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(phenyl)methanone(5ab)



White crystal; R_f value 0.13(ethyl acetate/hexane = 1/3); m.p. 141.7–146.7 °C; IR (NaCl, neat) ν_{max} 2958, 2871, 1694, 1263, 893, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 8.45(d, 2H, *J* = 8.0 Hz), 7.60(t, 1H, *J* = 7.0 Hz), 7.52(dt, 2H, *J* = 8.0, 7.0 Hz), 4.43(t, 2H, *J* = 7.0 Hz), 3.23(t, 2H, *J* = 7.5 Hz), 2.91(tt, 2H, *J* = 7.0, 7.5 Hz); ^{13}C NMR(126 MHz,

$CDCl_3$) δ 186.1, 148.6, 140.4, 136.6, 133.0, 130.5, 128.3, 46.7, 28.2, 22.4; HRMS (ESI) calcd for $C_{12}H_{11}NONa$ $[M\text{-}N_2+Na]^+$ 208.07383, found 208.07385.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4-dimethoxyphenyl)methanol(5c)

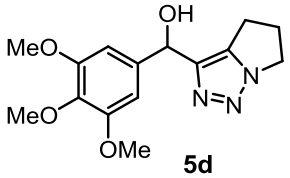


5c

The reaction with propargyl alcohol **4c** (150 mg, 0.545 mmol) and $TsOH\cdot H_2O$ (124.4 mg, 0.654 mmol) in dichloromethane (5 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to ethyl acetate) afforded triazole **5c** (106.7 mg, 71%).

White solid; R_f value 0.10(ethyl acetate/hexane = 1/1); m.p. 125.4–125.7 °C; IR (NaCl, neat) ν_{max} 3433, 1644, 1514, 1234, 1137 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.01(d, 1H, *J* = 2.0 Hz), 6.94(dd, 1H, *J* = 8.0, 2.0 Hz), 6.84(d, 1H, *J* = 8.0 Hz), 5.95(s, 1H), 4.24(t, 2H, *J* = 7.5 Hz), 2.77(br, 1H, OH), 2.63(m, 2H), 2.47(ddd, 1H, *J* = 15.1, 8.5, 6.0 Hz), 2.33(ddd, 1H, *J* = 15.1, 8.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 149.0, 148.5, 143.0, 139.2, 134.4, 118.4, 110.8, 109.3, 68.6, 55.9, 46.2, 28.0, 20.7; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1170.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4,5-trimethoxyphenyl)methanol(5d)

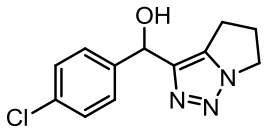


5d

The reaction with propargyl alcohol **4d** (200 mg, 0.655 mmol) and $TsOH\cdot H_2O$ (149.5 mg, 0.786 mmol) in dichloromethane (6.6 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1 to ethyl acetate then methanol/dichloromethane = 30/1 to 20/1) afforded triazole **5d** (106.7 mg, 71%).

White crystal; R_f value 0.22(dichloromethane/mechanol = 20/1); m.p. 137.8–138.2 °C; IR (NaCl, neat) ν_{max} 3433, 1233, 1124 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.66(s, 2H), 5.91(s, 1H), 4.17(t, 2H, *J* = 7.5 Hz), 3.78 (s, 6H), 3.77(s, 3H), 2.48–2.64(m, 3H), 2.29(ddd, 1H, *J* = 16.0, 9.5, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 153.0, 143.0, 139.2, 137.7, 137.0, 102.8, 68.3, 60.7, 56.0, 46.1, 27.9, 20.7; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1276.

(4-chlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol(5e)

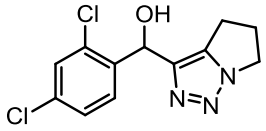


5e

The reaction with propargyl alcohol **4e** (200 mg, 0.801 mmol) and $TsOH \cdot H_2O$ (182.8 mg, 0.961 mmol) in dichloromethane (8 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/2 to 1/1 to 2/1) afforded triazole **5e** (121.7 mg, 61%).

White crystal; R_f value 0.2(ethyl acetate/hexane = 1/2); m.p. 142.8–142.9 °C; IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.38(d, 2H, *J* = 8.5 Hz), 7.32(d, 2H, *J* = 8.5 Hz), 6.00(s, 1H), 4.23(t, 2H, *J* = 7.5 Hz), 2.64(m, 2H), 2.47(ddd, 1H, *J* = 15.0, 8.5, 6.5 Hz), 2.29(ddd, 1H, *J* = 15.0, 9.0, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 142.6, 140.3, 139.3, 133.4, 128.5, 127.6, 68.0, 46.3, 28.0, 20.7; HRMS (ESI) calcd for $C_{12}H_{12}ClN_3ONa$ $[M+Na]^+$ 272.0567, found 272.0570.

(2,4-dichlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol(5f)

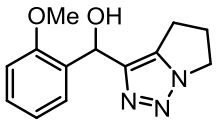


5f

The reaction with propargyl alcohol **4f** (150 mg, 0.528 mmol) and $TsOH \cdot H_2O$ (120.5 mg, 0.633 mmol) in dichloromethane (5 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to 2/1 to ethyl acetate then methanol / dichloromethane = 20/1) afforded triazole **5f** (44 mg, 44%).

White crystal; R_f value 0.1(ethyl acetate/hexane = 1/2); m.p. 176.8–170.0 °C; IR (NaCl, neat) ν_{max} 3224, 2879, 1589, 1035, 858 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.76(d, 1H, *J* = 8.5 Hz), 7.36(d, 1H, *J* = 1.0 Hz), 7.33(dd, 1H, *J* = 8.5, 1.0 Hz), 6.30(s, 1H), 4.43(br, 1H, OH), 4.25(t, 2H, *J* = 7.0 Hz), 2.65(tdd, 2H, *J* = 8.0, 7.5, 7.0 Hz), 2.37(td, 1H, *J* = 16.0, 7.5 Hz), 2.30(td, 1H, *J* = 16.0, 8.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 141.0, 139.3, 137.9, 133.9, 132.6, 129.0, 128.9, 127.4, 64.9, 46.3, 28.0, 20.5; HRMS (ESI) calcd for $C_{12}H_{11}Cl_2N_3ONa$ $[M+Na]^+$ 306.0177, found 306.0177.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(2-methoxyphenyl)methanol(5h)

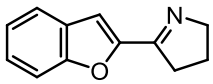


5h

The reaction with propargyl alcohol **4h** (80 mg, 0.326 mmol) and $TsOH \cdot H_2O$ (74.5 mg, 0.19 mmol) in dichloromethane (3 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1 to 2/1) afforded triazole **5h** (56.1 mg, 70%), along with imine **6h** (3.5mg, 6%).

White solid; R_f value 0.43(methaol/dichloromethane = 1/10); m.p. 119.1–119.4 °C; IR (NaCl, neat) ν_{max} 3340, 1490, 1240, 1028 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.47(dd, 1H, *J* = 7.5, 2.0 Hz), 7.27(ddd, 1H, *J* = 8.0, 7.5, 2.0 Hz), 6.98(dd, 1H, *J* = 8.0, 8.0 Hz), 6.87(d, 1H, *J* = 8.0 Hz), 6.23(d, 1H, *J* = 5.0 Hz), 4.23(t, 2H, *J* = 7.0 Hz), 3.80(s, 3H), 3.69(d, 1H, OH, *J* = 5.0 Hz), 2.63(tt, 2H, *J* = 7.5, 7.5 Hz), 2.38(td, 1H, *J* = 15.0, 7.5 Hz), 2.38(td, 1H, *J* = 15.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.2, 142.1, 139.2, 129.9, 128.7, 127.2, 120.7, 110.3, 64.7, 55.4, 46.1, 28.0, 20.6; HRMS (ESI) calcd for $C_{13}H_{15}N_3O_2$ $[M+Na]^+$ 268.1062, found 268.1062.

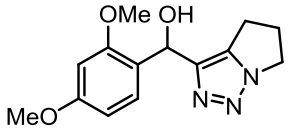
5-(benzofuran-2-yl)-3,4-dihydro-2H-pyrrole(6h)



6h

Colorless oil; R_f value 0.48 (methanol/dichloromethane = 1/10); IR (NaCl, neat) ν_{max} 3423, 1630, 824, 599 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.62(d, 1H, *J* = 8.0 Hz), 7.56(d, 1H, *J* = 7.5 Hz), 7.35(dd, 1H, *J* = 8.0, 7.5 Hz), 7.26(dd, 1H, *J* = 7.5, 7.5 Hz), 7.10(s, 1H), 4.14(t, 2H, *J* = 8.0 Hz), 2.97(t, 2H, *J* = 8.0 Hz), 2.07(tt, 2H, *J* = 8.0, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 164.7, 155.4, 151.3, 127.8, 126.2, 123.2, 121.9, 111.9, 109.2, 62.0, 35.0, 22.5; HRMS (ESI) calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0919, found 186.0918.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(2,4-dimethoxyphenyl)methanol(5i)



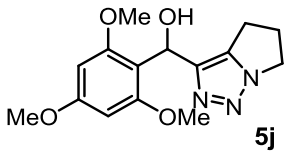
5i

The reaction with propargyl alcohol **4i** (127.3 mg, 0.462 mmol) and dichloroacetic acid

(0.045 mL, 0.555 mmol) in dichloromethane (4.6 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/6 to 1/2 to 1/1 to 2/1 then methanol / dichloromethane = 20/1 to 10/1) afforded triazole **5i** (56.1 mg, 70%).

White solid; R_f value 0.23(methaol/dichloromethane = 1/10); m.p. 124.4–124.6 °C; IR (NaCl, neat) ν_{max} 3433, 2097, 1646, 1030 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.33(d, 1H, *J* = 8.0 Hz), 6.48(dd, 1H, *J* = 8.0, 2.0 Hz), 6.44(d, 1H, *J* = 2.5 Hz), 6.14(s, 1H), 4.23(t, 2H, *J* = 7.5 Hz), 3.79(s, 3H), 3.76(s, 3H), 2.64(tt, 2H, *J* = 7.5, 7.5 Hz), 2.52(dt, 1H, *J* = 16.5, 7.5 Hz), 2.43(dt, 1H, *J* = 16.5, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 160.4, 157.4, 142.4, 139.1, 128.0, 122.6, 104.1, 98.4, 64.6, 55.4, 55.3, 46.1, 28.0, 20.7; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1177.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(2,4,6-trimethoxyphenyl)methanol(5j)

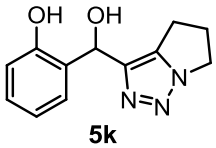


5j

The reaction with propargyl alcohol **4j** (117.7 mg, 0.386 mmol) and chloroacetic acid (43.7 mg, 0.463 mmol) in dichloromethane (3.8 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/1 to ethyl acetate then methanol / dichloromethane = 10/1) afforded triazole **5j** (67.7 mg, 57%).

White solid; R_f value 0.33(methaol/dichloromethane = 1/10); m.p. 139.3–139.9 °C; IR (NaCl, neat) ν_{max} 3445, 1607, 1205, 1150 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.30(s, 1H), 6.14(s, 2H), 4.22(t, 2H, *J* = 7.5 Hz), 3.74(s, 9H), 2.50–2.68(m, 4H), 2.06(br, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 160.8, 158.4, 142.9, 138.6, 110.2, 90.9, 62.3, 55.8, 55.3, 46.0, 28.1, 20.7; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1272.

2-((5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(hydroxy)methyl)phenol(5k)



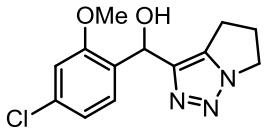
5k

The reaction with propargyl alcohol **4k** (65.0 mg, 0.281 mmol) and $TsOH \cdot H_2O$ (64.2 mg, 0.259 mmol) in dichloromethane (2 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to ethyl acetate then methanol/dichloromethane = 10/1)

afforded triazole **5k** (26.5 mg, 41%).

Colorless oil; R_f value 0.2(methaol/dichloromethane = 1/10); IR (NaCl, neat) ν_{max} 3196, 1456, 1240, 911, 755 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 8.92(br, 1H, OH), 7.21(dd, 1H, *J* = 8.0, 7.5 Hz), 7.02(d, 1H, *J* = 7.0 Hz), 6.94(d, 1H, *J* = 8.0 Hz), 6.84(dd, 1H, *J* = 7.5, 7.5 Hz), 6.17(s, 1H), 5.96(br, 1H, OH), 4.24(t, 2H, *J* = 8.0 Hz), 2.51–2.66(m, 3H), 2.14(m, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.2, 141.9, 140.0, 129.4, 127.6, 124.4, 119.8, 117.7, 69.3, 46.5, 27.9, 20.3; HRMS (ESI) calcd for $C_{12}H_{13}N_3O_2$ $[M+Na]^+$ 254.0906, found 254.0909.

(4-chloro-2-methoxyphenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol(5l)

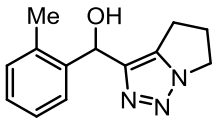


5l

The reaction with propargyl alcohol **4l** (74.1 mg, 0.265 mmol) and $TsOH·H_2O$ (60.5 mg, 0.318 mmol) in dichloromethane (2.7 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/5 to 2/1 ethyl acetate) afforded triazole **5l** (51.8 mg, 70%) along with benzofuran (6%).

White solid; R_f value 0.25(methaol/dichloromethane = 1/10); m.p. 154.9–155.1 °C; IR (NaCl, neat) ν_{max} 3422, 2065, 1645, 1244 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.45(d, 1H, *J* = 8.0 Hz), 6.98(dd, 1H, *J* = 8.0, 2.0 Hz), 6.86(d, 1H, *J* = 2.0 Hz), 6.20(s, 1H), 4.25(t, 2H, *J* = 8.0 Hz), 3.78(s, 3H), 2.67(tt, 2H, *J* = 8.0, 8.0 Hz), 2.50(td, 1H, *J* = 15.0, 7.5 Hz), 2.39(td, 1H, *J* = 15.0, 8.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.8, 141.8, 139.1, 134.1, 128.7, 128.1, 120.8, 111.1, 63.9, 55.7, 46.2, 28.1, 20.6; HRMS (ESI) calcd for $C_{13}H_{14}ClN_3O_2Na$ $[M+Na]^+$ 302.06722, found 302.0676.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(o-tolyl)methanol(5m)

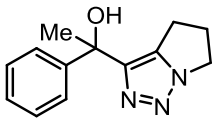


5m

The reaction with propargyl alcohol **4m** (188.7 mg, 0.823 mmol) and $TsOH·H_2O$ (187.9 mg, 0.988 mmol) in dichloromethane (8 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/2 to 1/1 to 2/1) afforded triazole **5m** (117.5 mg, 63%).

White solid; R_f value0.25(methaol/dichloromethane = 1/20); m.p. – °C; IR (NaCl, neat) ν_{max} 3420, 2064, 1646, 1031 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.67(d, 1H, *J* = 7.0 Hz), 7.26(dd, 1H, *J* = 8.0, 7.0 Hz), 7.20(ddd, 1H, *J* = 8.0, 7.0, 1.5 Hz), 7.13(d, 1H, *J* = 7.0 Hz), 6.20(s, 1H), 4.22(t, 2H, *J* = 7.0 Hz), 3.30(br, 1H, OH), 2.58(m, 2H), 2.35(ddd, 1H, *J* = 16.5, 9.0, 5.5 Hz), 2.21(s, 3H), 2.07(ddd, 1H, *J* = 16.5, 9.0, 6.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 142.1, 139.7, 139.5, 134.7, 130.3, 127.5, 126.1, 125.5, 65.7, 46.2, 28.0, 20.4, 19.1; LRMS (EI) 229(M^+, 100%), 184(57); HRMS (EI) calcd for $C_{13}H_{15}N_3O$ (M^+) 229.1215, found 229.1212.

1-(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)-1-phenylethan-1-ol(8a)

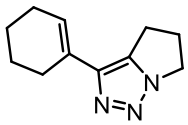


8a

The reaction with propargyl alcohol **7a** (154 mg, 0.671 mmol) and $TsOH \cdot H_2O$ (153 mg, 0.806 mmol) in dichloromethane (6.7 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to 2/1) afforded triazole **8a** (82.9 mg, 54%) along with byproduct (26.7 mg, 19%).

Colorless oil; R_f value 0.28(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3362, 2980, 1446, 1066, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.48(d, 2H, *J* = 8.0 Hz), 7.33(dd, 2H, *J* = 8.0, 7.5 Hz), 7.25(dd, 1H, *J* = 7.0, 6.5 Hz), 4.25(t, 2H, *J* = 7.5 Hz), 3.26(s, 1H, OH), 2.66(m, 2H), 2.49(m, 2H), 1.99(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 146.4, 146.2, 138.6, 128.1, 127.0, 125.2, 71.9, 46.2, 30.0, 28.1, 21.2,; HRMS (ESI) calcd for $C_{13}H_{15}N_3O$ $[M+Na]^+$ 252.1113, found 252.1118.

3-(cyclohex-1-en-1-yl)-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazole(8b')



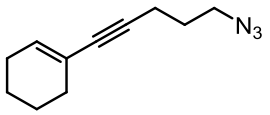
8b'

The reaction with propargyl alcohol (100 mg, 0.482 mmol) and $TsOH \cdot H_2O$ (110 mg, 0.579 mmol) in dichloromethane (4.8 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/4 to 1/2 to 1/1) afforded triazole **8b'** (51.7 mg, 50%) along with byproduct (30.1 mg, 30%).

Colorless oil; R_f value 0.13(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 2926, 1558 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.19(m, 1H), 4.30(t, 2H, *J* = 7.5 Hz), 2.96(t, 2H, *J* =

8.0 Hz), 2.80 (tt, 2H, *J* = 8.0, 7.5 Hz), 2.21-2.18(m, 2H), 1.78-1.73(m, 2H), 1.68-1.63(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 141.4, 137.2, 128.6, 124.2, 46.0, 28.3, 26.0, 25.3, 22.5, 22.2, 22.0; HRMS (ESI) calcd for $C_{11}H_{16}N_3$ $[M+H]^+$ 190.1344, found 190.1338.

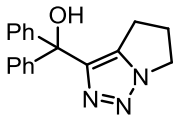
1-(5-azidopent-1-yn-1-yl)cyclohex-1-ene(10)



10

Colorless oil; R_f value 0.67(ethyl acetate/hexane = 1/2; IR (NaCl, neat) ν_{max} 2930, 2858, 2097, 1255, 917 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 6.02(m, 1H), 3.41(t, 2H, *J* = 7.0 Hz), 2.41(t, 2H, *J* = 7.0 Hz), 2.05–2.09(m, 4H), 1.78(tt, 2H, *J* = 7.0, 7.0 Hz), 1.53–1.64(m, 4H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 133.8, 120.6, 85.1, 83.4, 50.2, 29.4, 28.0, 25.5, 22.3, 21.5, 16.5; HRMS (ESI) calcd for $C_{11}H_{16}N_3$ $[M+H]^+$ 190.1344, found 190.1348.

(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)dip henylmethanol(8c)

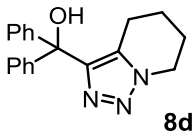


8c

The reaction with propargyl alcohol **7c** (42.0 mg, 0.144 mmol) and $TsOH\cdot H_2O$ (38.5 mg, 0.173 mmol) in dichloromethane (2 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/4 to 1/1) afforded triazole **8c** (41.8 mg, 99%).

White crystal; R_f value 0.24(ethyl acetate/hexane = 1/1); m.p. 113–114 °C; IR (NaCl, neat) ν_{max} 3378, 3059, 1491, 1448, 1316, 1168, 1021 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.25–7.34(m, 10H), 4.24(t, 2H, *J* = 7.5 Hz), 4.19(br-s, 1H, OH), 2.56(tt, 2H, *J* = 7.5, 7.5 Hz), 2.07(t, 2H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.5, 145.1, 140.2, 127.8, 127.34, 127.29, 76.6, 46.2, 27.9, 20.8; HRMS (ESI) calcd for $C_{18}H_{17}N_3ONa$ $[M+Na]^+$ 314.1269, found 314.1267.

diphenyl(4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-a]pyridin-3-yl)methanol(8d)



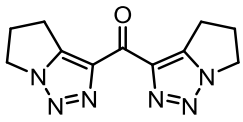
8d

The reaction with propargyl alcohol **7d** (62.0 mg, 0.203 mmol) and $TsOH\cdot H_2O$ (54.2

mg, 0.244 mmol) in dichloromethane (2 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/2 to 1/1) afforded triazole **8d** (62.0 mg, 99%).

Colorless oil; R_f value 0.11(ethyl acetate/hexane = 1/3); IR (NaCl, neat) ν_{max} 3376, 2953, 1490, 1447, 1016, 759, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.28–7.31(m, 10H), 4.34(t, 2H, *J* = 6.0 Hz), 4.28(br, 1H, OH), 2.00(t, 2H, *J* = 7.0 Hz), 1.93(m, 2H), 1.67(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 147.7, 145.2, 131.0, 127.9, 127.7, 127.5, 77.4, 46.6, 22.2, 20.6, 19.9; HRMS (ESI) calcd for $C_{19}H_{19}N_3ONa$ $[M+Na]^+$ 328.1426, found 328.1426.

bis(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanone (13a)

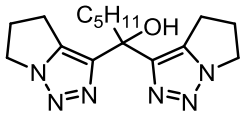


13a

The reaction with propargyl alcohol (150 mg, 0.610 mmol) and TMSOTf (0.132 mL, 0.731 mmol) in dichloromethane (6 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to ethyl acetate then methaol/dichloromethane = 1/10) afforded triazole **13a** (20.1 mg, 13%).

Colorless oil; R_f value 0.1(methaol/dichloromethane = 1/20); IR (NaCl, neat) ν_{max} 2961, 2098, 1645, 1572, 1195, 1644, 1571, 930 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 4.43(t, 4H, *J* = 7.5 Hz), 3.33(t, 4H, *J* = 7.5 Hz), 2.88(tt, 4H, *J* = 7.5, 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 177.5, 147.5, 139.0, 46.8, 28.0, 23.4; HRMS (ESI) calcd for $C_{11}H_{12}N_6ONa$ $[M+Na]^+$ 267.0970, found 267.0971.

1,1-bis(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)hexan-1-ol(13b)



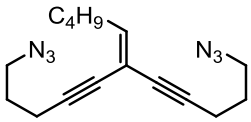
13b

The reaction with propargyl alcohol **12b** (117.6 mg, 0.372 mmol) and TMSOTf (0.081 mL, 0.446 mmol) in dichloromethane (4 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to ethyl acetate then methaol/dichloromethane = 1/30 to 1/20 to 1/10) afforded triazole **13b** (67.6mg, 58%).

White crystal; R_f value 0.1(methaol/dichloromethane = 1/20); m.p. 108.8–109.7 °C; IR (NaCl, neat) ν_{max} 3349, 2953, 2868, 1455, 1313, 911, 729 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 4.31(s, 1H, OH), 4.24(t, 4H, *J* = 7.5 Hz), 2.93(m, 4H), 2.71(tt, 4H, *J* = 7.5, 7.5

Hz), 2.19(m, 2H), 1.24(m, 6H), 0.81(m, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.7, 138.9, 71.3, 46.3, 41.4, 31.8, 28.1, 22.9, 22.5, 21.6, 14.0; HRMS (ESI) calcd for $C_{16}H_{24}N_6ONa$ $[M+Na]^+$ 339.1909, found 339.1903.

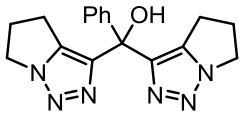
1-azido-6-(5-azidopent-1-yn-1-yl)undec-6-en-4-yne(14)



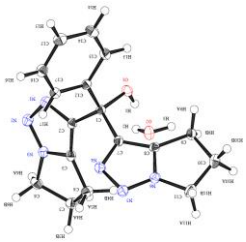
14

Colorless oil; R_f value 0.24(methaol/dichloromethane = 1/20); IR (NaCl, neat) ν_{max} 2931, 2097, 1255 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 6.19(t, 1H, *J* = 8.0 Hz), 3.41–3.45(m, 4H), 2.49(t, 2H, *J* = 6.5 Hz), 2.42(t, 2H, *J* = 6.5 Hz), 2.30(td, 2H, *J* = 8.0, 8.0 Hz), 1.78–1.85(m, 4H), 1.30–1.42(m, 4H), 0.90(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.0, 105.0, 91.5, 84.9, 80.0, 50.21, 50.19, 30.7, 30.3, 27.8, 27.7, 22.3, 16.8, 16.5, 13.9; HRMS (CI) calcd for $C_{16}H_{23}N_6$ $[M+H]^+$ 299.1984, found 299.1985.

bis(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(phenyl)methanol(13c)



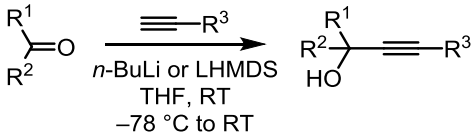
13c



The reaction with propargyl alcohol (117.6 mg, 0.372 mmol) and TMSOTf (0.081 mL, 0.446 mmol) in dichloromethane (4 ml) followed by silica gel column purification (ethyl acetate/hexane = 1/5 to 1/2 to 1/1 to ethyl acetate then methaol/dichloromethane = 1/30 to 1/20 to 1/10) afforded triazole **13c** (67.6mg, 58%).

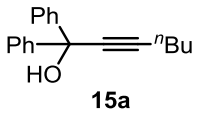
White crystal; R_f value 0.14(dichloromethane/methanol = 10/1); m.p. 157.7–157.8 °C; IR (NaCl, neat) ν_{max} 3284, 2965, 1448, 1171, 751 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.56(m, 2H), 7.29(m, 2H), 7.25(m, 1H), 5.72(s, 1H, OH), 4.18–4.30(m, 4H), 2.43–2.64(m, 8H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.8, 143.9, 140.2, 127.9, 127.4, 126.3, 71.9, 46.3, 27.9, 21.3; HRMS (ESI) calcd for $C_{17}H_{18}N_6ONa$ $[M+Na]^+$ 345.1440, found 345.1430.

General Procedure of Preparation of Starting Materials (15a–k, 15m, 15o–s)



To the mixture of corresponding terminal alkyne (1.3–2.0 equiv) in THF (0.2–0.1 M for ketone) was added *n*-butyllithium in hexane or lithium hexamethyldisilazide in THF (same to alkynes) was added dropwise at –78 °C. After 30 minutes, ketone or aldehyde (1 equiv) was added at the same temperature and the mixture was gradually warmed up to room temperature. Checking the consumption of ketone, saturated ammonium chloride aqueous solution was added. The mixture was extracted with ethyl acetate and washed with saturated ammonium chloride aqueous solution and brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography afforded propargyl alcohols for triazolations.

1,1-Diphenylhept-2-yn-1-ol (**15a**)

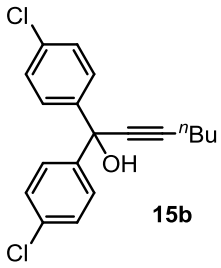


15a

The reaction with 1-hexyne (0.53 mL, 4.6 mmol), *n*-butyllithium (1.58 M in hexane, 3.13 mL, 4.94 mmol) and benzophenone (600 mg, 3.3 mmol) in THF (33 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/8) afforded **15a** (855 mg, 3.23 mmol, 98%).

Colorless oil; R_f value 0.45(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3446, 2957, 2931, 1449, 1002, 698 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.55(d, 4H, *J* = 8.0 Hz), 7.26(m, 4H), 7.19(m, 2H), 2.65(m, 1H, OH), 2.29(t, 2H, *J* = 7.0 Hz), 1.52(m, 2H), 1.40(m, 2H), 0.87(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.5, 128.1, 127.4, 125.9, 88.3, 82.9, 74.4, 30.6, 22.0, 18.6, 13.6; LRMS (EI) 264(M^+, 28%), 221(95), 208(46), 207(100), 187(79); HRMS (EI) calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found 264.1516.

1,1'-Bis(4-chlorophenyl)hept-2-yn-1-ol (**15b**)

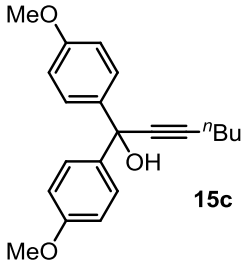


15b

The reaction with 1-hexyne (0.3 mL, 2.59 mmol), LHMDS (1.0 M in THF, 2.6 mL, 2.6 mmol) and 4,4'-dichlorobenzophenone (500 mg, 2.06 mmol) in THF (10 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/100 to 1/50 to 1/25) afforded **15b** (654.4 mg, 1.964 mmol, 99%).

Light yellow oil; R_f value 0.25(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3411, 2958, 2932, 2871, 2229, 1905, 1488, 1092, 1013, 815 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.50(d, 4H, *J* = 9.0 Hz), 7.28(d, 4H, *J* = 9.0 Hz), 2.70(s, 1H, OH), 2.33(t, 2H, *J* = 7.0 Hz), 1.56(tt, 2H, *J* = 7.5, 7.0 Hz), 1.43(qt, 2H, *J* = 7.5, 7.5 Hz), 0.93(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 143.7, 133.6, 128.4, 127.4, 89.1, 82.1, 73.5, 30.5, 22.0, 18.5, 13.6; LRMS (EI) 332(M^+, 13%), 299(29), 298(24), 297(94), 275(59), 221(86), 139(100); HRMS (EI) calcd for $C_{19}H_{18}Cl_2O$ (M^+) 332.0735, found 332.0734.

1,1'-Bis(4-methoxyphenyl)hept-2-yn-1-ol (**15c**):



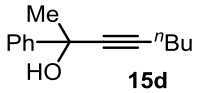
15c

The reaction with 1-hexyne (0.47 mL, 4.13 mmol), LHMDS (1.0 M in THF, 4.2 mL, 4.2 mmol) and 4,4'-dimethoxybenzophenone (500 mg, 2.06 mmol) in THF (10 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/20 to 1/15 to 1/10) afforded **15c** (669.5 mg, 2.064 mmol, 100%).

Light yellow oil; R_f value 0.36(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3462, 2956, 2932, 2836, 1507, 1248, 1173, 1033, 827 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.50(d, 2H, *J* = 9.0 Hz), 6.84(d, 2H, *J* = 9.0 Hz), 3.79(s, 6H), 2.70(s, 1H, OH), 2.33(t, 2H, *J* = 7.0 Hz), 1.57(tt, 2H, *J* = 7.5, 7.0 Hz), 1.45(qt, 2H, *J* = 7.5, 7.5 Hz), 0.94(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 158.8, 138.1, 127.2, 113.3, 87.8, 83.3, 73.8, 55.2, 30.7, 22.0, 18.6, 13.6; LRMS (EI) 324(22%, M^+), 281(14), 267(27), 135(21),

83(100); HRMS (EI) calcd for $C_{21}H_{24}O_3$ (M^+) 324.1725, found 324.1724.

2-Phenyloct-3-yn-2-ol (**15d**):

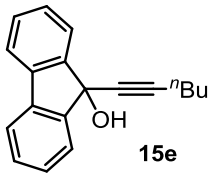


15d

The reaction with 1-hexyne (0.67 mL, 5.8 mmol), LHMDS (1.0 M in THF, 6.2 mL, 6.2 mmol) and acetophenone (486 mg, 4.16 mmol) in THF (42 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/20) afforded **15d** (549 mg, 2.71 mmol, 65%).

Colorless oil; R_f value 0.46(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3397, 2958, 1447, 921, 763, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.66(d, 2H, *J* = 7.5 Hz), 7.36(dd, 2H, *J* = 7.5, 8.0 Hz), 7.29(t, 1H, *J* = 8.0 Hz), 2.33(br, 1H), 2.29(t, 2H, *J* = 7.5 Hz), 1.75(s, 3H), 1.53(tt, 2H, *J* = 7.5, 7.5 Hz), 1.44(tq, 2H, *J* = 7.5, 7.5 Hz), 0.93(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 146.2, 128.2, 127.5, 124.9, 85.7, 83.7, 70.1, 33.5, 30.7, 22.0, 18.4, 13.6; HRMS (CI) calcd for $C_{14}H_{19}O$ $[M+H]^+$ 203.1436, found 203.1438.

9-(Hex-yn-1-yl)-9*H*-fluoren-9-ol (**1e**):

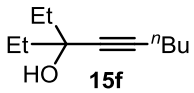


15e

The reaction with 1-hexyne (0.27 mL, 2.31 mmol), *n*-butyllithium (1.05 M in hexane, 2.4 mL, 2.50 mmol) and 9-fluorenone (300 mg, 1.67 mmol) in THF (9 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/80) afforded **15e** (265.6 mg, 1.012 mmol, 61%).

Yellow oil; R_f value 0.45(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3398, 3064, 3042, 2956, 2931, 1450, 1009, 768, 732 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.69(dd, 2H, *J* = 7.5, 1.0 Hz), 7.61(dd, 2H, *J* = 7.5, 1.0 Hz), 7.39(ddd, 2H, *J* = 7.5, 7.5, 1.0 Hz), 7.35(ddd, 2H, *J* = 7.5, 7.5, 1.0 Hz), 2.44(s, 1H, OH), 2.21(t, 2H, *J* = 7.0 Hz), 1.48(m, 2H), 1.37(m, 2H), 0.88(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 147.6, 138.9, 129.4, 128.5, 124.1, 120.1, 84.3, 79.8, 74.9, 30.5, 21.9, 18.5, 13.6; LRMS (EI) 262(M^+, 100%), 215(35); HRMS (EI) calcd for $C_{19}H_{18}O$ (M^+) 262.1358, found 262.1358.

3-Ethylnon-4-yn-3-ol (**1f**):

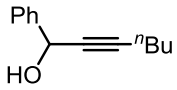


15f

The reaction with 1-hexyne (0.97 mL, 8.7 mmol), *n*-butyllithium (1.64 M in hexane, 5.3 mL, 8.7 mmol) and 3-pentanone (0.61 mL, 5.8 mmol) in THF (58 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/10) afforded **15f** (787 mg, 4.68 mmol, 81%).

Colorless oil; R_f value 0.49(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3389, 2965, 2935, 1460, 1143, 965 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 2.2(t, 2H, *J* = 7.0 Hz), 1.81(m, 1H, OH), 1.63(m, 4H), 1.48(tt, 2H, *J* = 7.5, 8.0 Hz), 1.40(tq, 2H, *J* = 7.5, 8.0 Hz), 1.01(t, 6H, *J* = 7.5 Hz), 0.90(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 84.9, 82.5, 72.2, 34.6, 30.9, 21.9, 18.3, 15.6, 8.6; HRMS (CI) calcd for $C_{11}H_{20}O$ $[M+H]^+$ 169.1592, found 169.1592.

1-Phenylhept-2-yn-1-ol (**15g**):

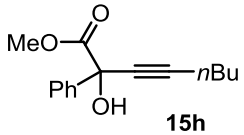


15g

The reaction with 1-hexyne (0.31 mL, 2.59 mmol), *n*-butyllithium (1.64 M in hexane, 1.7 mL, 2.8 mmol) and benzaldehyde (0.19 mL, 1.9 mmol) in THF (18 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/20 to 1/10) afforded **15g** (271 mg, 1.44 mmol, 77%).

Colorless oil; R_f value 0.48(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3332, 2957, 1454, 1001, 698 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.55(d, 2H, *J* = 6.5 Hz), 7.38(dd, 2H, *J* = 7.0, 6.5 Hz), 7.32(t, 1H, *J* = 7.0 Hz), 5.45(br-d, 1H, *J* = 4.0), 2.36(s, 1H, OH), 2.29(td, 2H, *J* = 7.0, 1.5 Hz), 1.54(tt, 2H, *J* = 7.0, 8.0 Hz), 1.44(tq, 2H, *J* = 7.0, 8.0 Hz), 0.93(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 141.2, 128.5, 128.1, 126.6, 87.6, 79.8, 64.7, 30.6, 21.9, 18.4, 13.5; LRMS (EI) 188(M^+, 100%), 145(63), 105(50), 77(62); HRMS (EI) calcd for $C_{13}H_{16}O$ (M^+) 188.1201, found 188.1202.

Methyl 2-hydroxy-2-phenyloct-3-ynoate (15h)

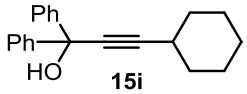


15h

To a stirred solution of 1-hexyne (0.487 mL, 4.26 mmol) in THF (31 mL) at 0 ºC under nitrogen atmosphere was added lithium bis(trimethylsilyl)amide (1.0 M in THF, 4.57 mL, 4.57 mmol) dropwise. After 30 min, methyl benzoylformate (500.0 mg, 3.05 mmol) was then added at the same temperature and the mixture was warmed up to room temperature. After 12 h, reaction mixture was quenched with saturated ammonium chloride aqueous solution. The mixture was diluted with ether and washed with water and brine. Then the collected organic layer was dried over magnesium sulfate and concentration *in vacuo* followed by silica gel column chromatography (ethyl acetate/hexane = 1/ 20 to 1/15) to give **15h** (344.8 mg, 46%).

Colorless oil; R_f value 0.29 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3496, 3029, 1736, 1256, 1063, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 2H, *J* = 6.5 Hz), 7.39–7.32 (m, 3H), 4.18 (s, 1H, OH), 3.76 (s, 3H), 2.33 (t, 2H, *J* = 7.5 Hz), 1.58 (tt, 2H, *J* = 7.5, 8.0 Hz), 1.46 (tq, 2H, *J* = 8.0, 7.5 Hz), 0.93 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 139.6, 128.5, 128.2, 126.2, 87.6, 78.1 72.8, 54.0, 30.3, 21.9, 18.4, 13.5; HRMS (CI) calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1334, found 247.1335.

3-Cyclohexyl-1,1-diphenylprop-2-yn-1-ol (**15i**)

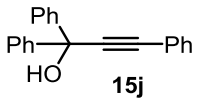


15i

The reaction with cyclohexylacetylene (0.2 mL, 1.531 mmol), LHMDS (1.0 M in THF, 1.9 mL, 1.9 mmol) and benzophenone (232.4 mg, 1.276 mmol) in THF(7 mL) afforded **15i** (368.4 mg, 1.269 mmol, 99%) by silica gel column purification (ethyl acetate/hexane = 1/80 to 1/50).

Light yellow oil; R_f value 0.31(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3455, 3060, 2929, 2853, 2231, 1490, 1448, 1031, 991, 765, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.71(m, 4H), 7.38(dd, 4H, *J* = 7.5, 7.5 Hz), 7.31(t, 2H, *J* = 7.5 Hz), 2.98(m, 1H, OH), 2.61(m, 1H), 1.94(m, 2H), 1.82(m, 2H), 1.59–1.65(m, 3H), 1.38–1.45(m, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.5, 128.0, 127.3, 125.8, 92.0, 83.0, 74.3, 32.4, 29.0, 25.8, 24.7; LRMS (EI) 290(M^+, 15%), 208(80), 207(100); HRMS (EI) calcd for $C_{21}H_{22}O$ (M^+) 290.1671, found 290.1670.

1,1,3-Triphenyl-2-propyn-1-ol (**15j**)

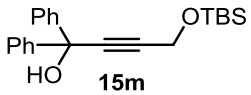


15j

The reaction with phenylacetylene (0.6 mL, 5.488 mmol), *n*-butyllithium (1.57 M in hexane 3.5 mL, 5.488 mmol) and benzophenone (500 mg, 2.744 mmol) in THF (14 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/20) afforded **15j** (763.5 mg, 2.685 mmol, 98%).

Light yellow oil; R_f value 0.54 (ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3545, 3435, 3060, 3029, 2224, 1598, 1489, 1448, 1335, 1164, 1045, 984, 916, 890, 755, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69(m, 4H), 7.52(m, 2H), 7.34–7.37(m, 7H), 7.29(m, 2H), 2.88(s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 131.8, 128.7, 128.3, 127.7, 128.3, 127.7, 126.0, 122.3, 91.8, 87.2, 74.8; LRMS (EI) 284(M^+, 83%), 267(12), 207(30), 206(55), 153(77), 136(54), 107(79), 89(60), 78(58), 77(100); HRMS (EI) calcd for $C_{21}H_{16}O$ (M^+) 284.1201, found 284.1201.

4-(*Tert*-butyldimethylsilyl)oxy-1,1-diphenylbut-2-yn-1-ol (**15m**)



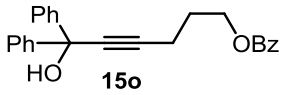
15m

The reaction with 1-(tert-butyldimethylsilyl)oxyprop-2-yne[1] (291.4 mg, 1.711 mmol), *n*-butyllithium (1.57 M in hexane, 1.5 mL, 0.2.355 mmol) and benzophenone (222.7 mg, 1.222 mmol) in THF (12 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/100 to 1/80 to 1/50) afforded **15m** (185.7 mg, 0.5267 mmol, 43%).

1) Karjalainen, O. K.; Koskinen, A. M. P. *Org. Biomol. Chem.* **2011**, *9*, 1231–1236.

White solid ; R_f value 0.30(ethyl acetate/hexane = 1/10); m.p. 83.0–84.5 °C; IR (NaCl, neat) ν_{max} 3387, 3060, 2930, 2857, 1449, 1352, 1254, 1044 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.61(d, 4H, *J* = 8.0 Hz), 7.33(dd, 4H, *J* = 8.0, 8.0 Hz), 7.27(t, 2H, *J* = 8.0 Hz), 4.48(s, 2H), 2.90(s, 1H), 0.93(s, 9H), 0.13(s, 3H), 0.12(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.7, 128.1, 127.6, 126.0, 87.1, 86.1, 74.3, 51.8, 25.7, 18.2, –5.2; HRMS (ESI) calcd for $C_{22}H_{28}O_2SiNa$ $[M+Na]^+$ 375.1756, found 375.1751.

6-Benzoyloxy-1,1-diphenylhex-2-yn-1-ol (**15o**)



15o

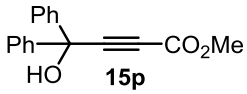
The reaction with 4-pentynyl benzoate[1] (568.1 mg, 0.3018 mmol), LHMDS (1.0 M in THF, 3.3 mL, 3.29 mmol) and benzophenone (500 mg, 2.744 mmol) in THF (12 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/20 to 1/10 to 1/6)

afforded **15o** (974.2 mg, 2.630 mmol, 84%).

1) Stevens, B. D.; Nelson, S. G. *J. Org. Chem.* **2005**, *70*, 4375–4379.

Light white crystal; R_f value 0.33(ethyl acetate/hexane = 1/4); m.p. 65.5–67.0 °C; IR (NaCl, neat) ν_{max} 3462, 3060, 2959, 2235, 1717, 1450, 1276, 1119, 752, 701 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 8.04(dd, 2H, *J* = 8.0, 1.0 Hz), 7.55–7.60(m, 5H), 7.44(dd, 2H, *J* = 8.0, 8.0 Hz), 7.31(m, 4H), 7.24(m, 2H), 4.46(t, 2H, *J* = 7.0 Hz), 2.82(m, 1H, OH), 2.55(t, 2H, *J* = 7.0 Hz), 2.07(tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 166.5, 145.2, 133.0, 130.1, 129.6, 128.4, 128.2, 127.6, 125.9, 86.5, 83.9, 74.4, 63.5, 27.7, 15.8; LRMS (EI) 370(M^+, 0.3%), 293(20), 105(100), 77(51); HRMS (EI) calcd for $C_{25}H_{22}O_3$ (M^+) 370.1569, found 370.1573.

Methyl 4-hydroxy-4-diphenylbut-2-ynoate (**15p**)

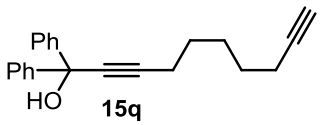


15p

The reaction with methyl propiolate (0.64 mL, 7.7 mmol), LHMDS (1.0 M in THF, 8.2 mL, 8.2 mmol) and benzophenone (1.0 g, 5.5 mmol) in THF (33 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/15 to 1/10) afforded **15p** (201 mg, 0.755 mmol, 14%).

Colorless oil; R_f value 0.26(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3393, 2954, 1701, 1439, 1267, 750, 696 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.57(d, 4H, *J* = 7.0 Hz), 7.36(dd, 4H, *J* = 7.0, 8.0 Hz), 7.31(t, 2H, *J* = 8.0 Hz), 3.80(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 153.8, 143.0, 128.5, 128.3, 126.0, 88.8, 78.3, 74.3, 52.9; LRMS (EI) 266(M^+, 12%), 234(68), 206(78), 178(85), 105(100); HRMS (EI) calcd for $C_{17}H_{14}O_3$ (M^+) 266.0943, found 266.0944.

1,1-Diphenyldeca-2,9-diyn-1-ol (**15q**)



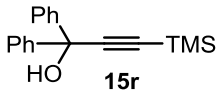
15q

The reaction with 1,8-nonadiyne (0.6 mL, 4.116 mmol), LHMDS (1.0 M in THF, 4.1 mL, 4.116 mmol) and benzophenone (500 mg, 2.744 mmol) in THF (14 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/40 to 1/20 to 1/15) afforded **15q** (703.3 mg, 2.326 mmol, 85%).

Colorless oil; R_f value 0.19(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3517, 3293, 2938, 2861, 2233, 2115, 1598, 1490, 1449, 1332, 1004, 767 cm^{-1}; ^1H NMR(500

MHz, $CDCl_3$) δ 7.60(d, 4H, *J* = 7.5 Hz), 7.32(dd, 4H, *J* = 7.5, 7.5 Hz), 7.25(t, 2H, *J* = 7.5 Hz), 2.72(m, 1H, OH), 2.36(t, 2H, *J* = 7.0 Hz), 2.20(m, 2H), 1.93(t, 1H, *J* = 2.5 Hz), 1.54(m, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.4, 128.1, 127.5, 125.9, 87.9, 84.4, 83.2, 74.4, 68.4, 27.97, 27.94, 27.86, 18.8, 18.3; HRMS (ESI) calcd for $C_{22}H_{22}NaO$ $[M+Na]^+$ 325.1568, found 325.1570.

1,1,-Diphenyl-3-trimethylsilyl-2-propyn-1-ol (**15r**)

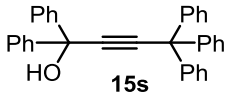


15r

The reaction with trimethylsilylacetylene (0.76 mL, 5.488 mmol), *n*-butyllithium (1.57 M in hexane, 3.5 mL, 5.488 mmol) and benzophenone (500 mg, 2.744 mmol) in THF (14 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/30 to 1/20) afforded **15r** (721.4 mg, 2.572 mmol, 94%).

Colorless oil; R_f value 0.27(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3548, 3454, 3060, 3029, 2959, 2170, 1599, 1491, 1449, 1251, 1057, 845 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.61(m, 4H), 7.33(m, 4H), 7.27(m, 2H), 2.77(s, 1H), 0.24(s, 9H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.7, 128.2, 127.6, 125.9, 107.6, 92.0, 74.6, –0.2, ,; LRMS (EI) 280(8%, M^+), 264(13), 263(15), 203(27), 191(22), 190(100), 189(46); HRMS (EI) calcd for $C_{18}H_{20}OSi$ (M^+) 280.1283, found 280.1281.

1,1,4,4,4-Pentaphenyl-2-butyn-1-ol (**15s**)



15s

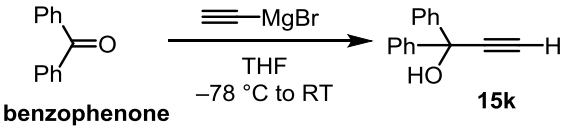
The reaction with 3-triphenylprop-1-yne[a] (1.10 g, 4.116 mmol), *n*-butyllithium (1.57 M, 2.80 mL, 4.390 mmol) and benzophenone (500 mg, 2.744 mmol) in THF (14 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/100 to 1/20 to 1/10) afforded **15s** (1.24 g, 0.266 mmol, 97%).

a) Karlen, S.D.; Ortiz, R.; Chapman, O. L.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 6554–6555.

White crystal; R_f value 0.25(ethyl acetate/hexane = 1/10); m.p. 128.5–130.0 °C; IR (NaCl, neat) ν_{max} 3541, 3437, 3084, 3060, 3027, 1598, 1490, 1447, 1326, 1216, 1033, 758, 698 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.76(m, 4H), 7.35–7.46(m, 21H), 3.10(br, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.1, 144.9, 129.1, 128.1, 128.0, 127.5, 126.8, 126.0, 93.3, 87.8, 74.7, 55.7; LRMS (EI) 450(M^+, 18%), 268(44), 267(43), 183(49),

105(100); HRMS (EI) calcd for $C_{34}H_{26}O$ (M^+) 450.1984, found 450.1983.

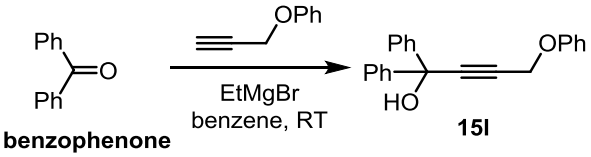
Preparation of terminal alkyne 15k (1,1-diphenylprop-2-yn-1-ol)



To the solution of benzophenone (1.0 g, 5.5 mmol) in THF (27 mL) was added ethynylmagnesium bromide (0.5 M in THF, 26 mL, 13.2 mmol) at –78 °C under nitrogen atmosphere, and the mixture was warmed up to room temperature. After 20 h, the mixture was diluted with ethyl acetate and was treated with saturated ammonium chloride aqueous solution and brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography (ethyl acetate/hexane = 1/25 to 1/20 to 1/15) afforded propargyl alcohols **15** (1.06 g, 93%) as a light yellow oil, which was slowly crystallized to light yellow solid.

Light yellow crystal; R_f value 0.52(ethyl acetate/hexane = 1/4); m.p. 48.5–49.0 °C; IR (NaCl, neat) ν_{max} 3543, 3438, 3286, 3060, 2115, 1956, 1599, 1490, 1449, 1335, 1167 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.62(m, 4H), 7.35(m, 4H), 7.28(m, 2H), 2.89(s, 1H, OH), 2.80(s, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 144.3, 128.3, 127.9, 125.9, 86.3, 75.5, 74.3; LRMS (EI) 208(M^+, 100%), 207(48), 191(17), 131(60), 130(29); HRMS (EI) calcd for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0889.

Preparation of phenyl ethers 15l (1,1-diphenyl-4-phenoxybut-2-yn-1-ol)



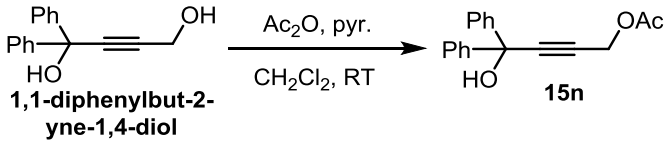
To the solution of 1-phenoxyprop-2-yne[b] (652.7 mg, 4.94 mmol) in benzene (10 mL) was added ethylmagnesium bromide (0.95M in THF, 6.7 mL, 6.37 mmol) dropwise at room temperature under nitrogen atmosphere. After 20 min, benzophenone (500 mg, 2.74 mmol) dissolved in 2 mL of THF was added dropwise to the mixture. After 6 h, the mixture was treated with saturated ammonium chloride aqueous solution and brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography (ethyl acetate / hexane = 1/30 to 1/25 to 1/10 to 1/8) afforded phenyl propargyl ether **15l** (814.5.4 mg, 94%) as viscous light-yellow oil.

b) Pastine, S. J.; Youn, S. W.; Sames, D. *Org. Lett.* **2003**, *5*, 1055–1058.

Light yellow oil; R_f value 0.45(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3433, 3060, 3029, 1597, 1492, 1449, 1214, 1032, 754, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$)

δ 7.53(d, 4H, *J* = 8.0 Hz), 7.24–7.34(m, 8H), 7.02–7.03(m, 3H), 4.85(s, 2H), 2.78(s, 1H, OH); ^{13}C NMR(126 MHz, $CDCl_3$) δ 157.5, 144.4, 129.5, 128.2, 127.8, 125.9, 121.6, 115.2, 89.8, 82.3, 74.4, 56.2; LRMS (EI) 314(M^+, 21%), 221(51), 203(49), 178(47), 143(50), 105(100); HRMS (EI) calcd for $C_{22}H_{18}O_2$ (M^+) 314.1307, found 314.1307.

Preparation of acetate 15n (4-acetoxy-1,1-diphenylbut-2-yn-1-ol)



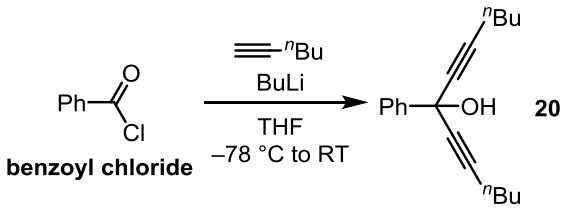
1,1-diphenylbut-2-yne-1,4-diol **15n**

To the dichloromethane solution (5mL) of known 1,1-diphenyl-but-2-yne-1,4-diol (111.1 mg, 0.4663 mmol), prepared by the same procedure for **1k**,[1] was added pyridine (188μL, 2.33 mmol) and acetic anhydride (220μL, 2.33 mmol) at room temperature. After 2 h, the mixture was treated with saturated ammonium chloride aqueous solution and brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography (ethyl acetate / hexane = 1/10 to 1/8) afforded acetate **15n** (127.7 mg, 98%) as white crystal.

1) Fiesselmann, H.; Sasse, K. *Chem. Ber.* **1956**, *89*, 1775–1791.

White solid; R_f value 0.62(ethyl acetate/hexane = 1/2); m.p. 79.0–80.5 °C; IR (NaCl, neat) ν_{max} 3448, 3060, 3029, 1743, 1449, 1229, 1030, 700 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.61(m, 4H), 7.35(m, 4H), 7.29(m, 2H), 4.81(s, 2H), 3.34(br, 1H, OH), 2.09(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 170.4, 144.4, 128.2, 127.7, 125.9, 89.1, 81.0, 74.2, 52.3, 20.6; LRMS (EI) 280(M^+, 5%), 220(83), 192(100), 115(81); HRMS (EI) calcd for $C_{18}H_{16}O_3$ (M^+) 280.1099, found 280.1097.

Preparation of dialkyne 20 (7-phenyltrideca-5,8-diyn-7-ol)



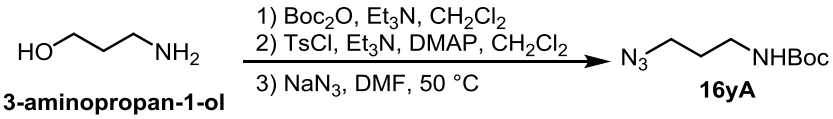
benzoyl chloride **20**

To the solution of 1-hexene (0.987 mL, 8.89 mmol) in THF (36 mL) was added *n*-Butyllithium (2.64 M in hexane, 3.37 mL, 8.89 mmol) at –78 °C under nitrogen atmosphere. After 30 min, benzoyl chloride (500 mg, 3.56 mmol) was added to the mixture and the mixture was warmed up to room temperature. After 3h, the mixture was diluted with ether, and was treated with saturated ammonium chloride aqueous solution

and brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography (Ethyl acetate/hexane= 1/20 to 1/15) afforded dipropargyl alcohol **20** (870 mg, 91%) as a colorless oil.

Colorless oil; R_f value 0.64(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3520, 2871, 1449, 995, 696 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.80(d, 2H, *J* = 7.5 Hz), 7.38(dd, 2H, *J* = 7.5, 7.5 Hz), 7.32(t, 1H, *J* = 7.5 Hz), 2.73(s, 1H, OH), 2.29(t, 4H, *J* = 7.0 Hz), 1.54(tt, 4H, *J* = 7.0, 7.5 Hz), 1.43(tq, 4H, *J* = 7.5, 7.5 Hz), 0.92(t, 6H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 142.9, 128.3, 128.2, 125.7, 85.8, 81.0, 65.2, 30.4, 21.9, 18.5, 13.6; HRMS (ESI) calcd for $C_{19}H_{24}NaO$ $[M+Na]^+$ 291.1725, found 291.1715.

Preparation of *tert*-butyl (3-azidopropyl)carbamate (16yA)



To a solution of 3-aminopropan-1-ol (300 mg, 0.152 mmol) in DCM (4ml) under an atmosphere of nitrogen was added triethylamine (0.337 mL, 2.4 mmol) at ambient temperature and the resulting solution was stirred for 5 min. Then Boc_2O (0.459 mL, 2.0 mmol) was added at the same temperature. After 10 h, the reaction was quenched with water. The reaction mixture was washed with water and brine. Drying collected organic layer over magnesium sulfate followed by concentration, the crude product was used to the next step without further purification.

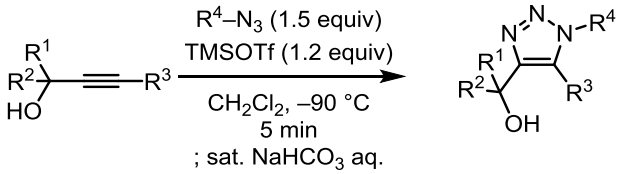
To a solution of *N*-Boc-3-aminopropan-1-ol (350 mg) in dichloromethane (3 mL) under nitrogen atmosphere was added triethylamine (0.336 ml, 0.239 mmol) and 4-toluenesulfonyl chloride (0.380 mg, 1.99 mmol) at ambient temperature. After 2.5 h, the reaction was quenched by water. The reaction mixture was washed with water and brine. Drying collected organic layer over magnesium sulfate followed by concentration, the crude product was used to the next step without further purification.

To a solution of crude material (430 mg) in DMF (6.5 mL) under nitrogen atmosphere was added sodium azide (93.4 mg, 1.44 mmol) at ambient temperature. Then the reaction mixture was heated at 50 °C for 2 h. The reaction was quenched with water and was extracted with ether. Drying collected organic layer over magnesium sulfate followed by concentration and silica gel chromatography (ethyl acetate/hexane = 1/10) gave *tert*-butyl (3-azidopropyl)carbamate **16yA** (244.7 mg, 94% for 3 steps) as a colorless oil.

Colorless oil; R_f value 0.11(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3351, 2977, 2097, 1692, 1520, 1251, 1171 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 4.64(br, 1H, NH),

3.36(t, 2H, *J* = 7.0 Hz), 3.21(td, 2H, *J* = 6.5, 6.0 Hz), 1.77(tt, 2H, *J* = 6.5, 7.0 Hz), 1.44(s, 9H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 155.9, 79.4, 49.1, 38.0, 29.2, 28.4; HRMS (CI) calcd for $C_8H_{17}N_4O_2$ $[M+H]^+$ 201.1352, found 201.1349.

General Experimental Procedure of triazolations



To the mixture of propargyl alcohol (1 equiv), organic azide (1.5 equiv) in dichloromethane (0.1 M to alcohols) under nitrogen atmosphere, trimethylsilyl trifluoromethanesulfonate (1.2 equiv) was added at –90 °C dropwise. After five minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography afforded triazole.

In the case of three component coupling reactions, for dialkyne **20**, cinnamylazide was added at –90 °C, and then the mixture was treated as shown above after 5 min.

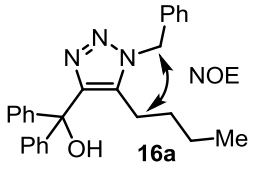
For coupling products **7a–d**, the reactions were performed at –60 °C for 5 min. Then, nucleophiles (3 equiv) were added at the same temperature and the mixture was wormed up to 0 °C. After 30 min, the mixture was treated as same as above to obtain three-component coupling products.

c) For cinnamylazide, see: Lal, S.; McNally, J.; White, A. J. P.; Díez-González, S. *Organometallics*, **2011**, *30*, 6225–6232.

d) For phenylazide, see: Cheng, H.; Wan, J.; Lin, M.-I; Liu, Y.; Lu, X.; Liu, J.;Xu, Y.; Chen, J.; Tu, Z.; Cheng, Y.-S. E.; Ding, K. *J. Med. Chem.* **2012**, *55*, 2144–2153.

e) For 2,6-diisopropylphenylazide, see: Pilyugina, T. S.; Schrock, R. R.; Hock, A. S.; Müller, P. *Organometallics*, **2005**, *24*, 1929–1937. Since this azide was gradually decomposed, it was used soon after purifications.

(1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**2a**):

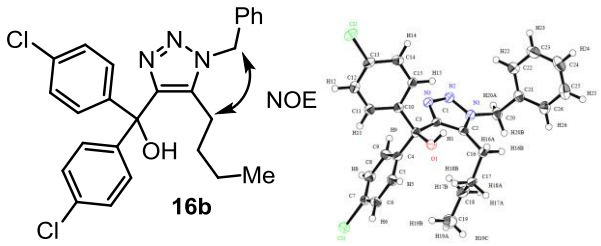


The reaction with **15a** (67.0 mg, 0.253 mmol), benzylazide (50.6 mg, 0.380 mmol) and

TMSOTf (55 μL, 0.304 mmol) in dichloromethane (2.5 mL) followed by silica gel column chromatography (ethyl acetate/hexane = 1/5) afforded **16a** (99.7 mg, 0.251 mmol, 99%).

Colorless oil; R_f value 0.19(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3419, 3060, 2957, 2870, 1494, 1448, 1013, 760 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.31–7.34(m, 3H), 7.24–7.30(m, 10H), 7.13(d, 2H, *J* = 7.5 Hz), 5.45(s, 2H), 4.29(s, 1H, OH), 1.92(m, 2H), 0.86(qt, 2H, *J* = 8.0, 7.5 Hz), 0.71(m, 2H), 0.58(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.9, 145.4, 135.1, 134.9, 128.9, 128.3, 127.9, 127.5, 127.0, 76.7, 51.9, 30.3, 22.7, 22.6, 13.3; LRMS (EI) 397(M^+, 78%), 320(41), 105(79), 91(100); HRMS (EI) calcd for $C_{26}H_{27}N_3O$ (M^+) 397.2154, found 397.2155.

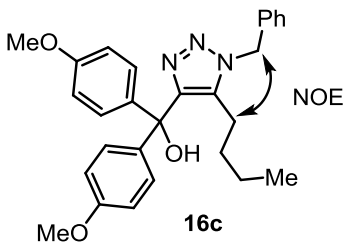
(1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)bis(4-chlorophenyl)methanol (**16b**) (CCDC 950501):



The reaction with **15b** (92.0 mg, 0.276 mmol), benzylazide (55.1 mg, 0.414 mmol), TMSOTf (60 μL, 0.331 mmol) in dichloromethane (2.8 mL) followed by silica gel column chromatography purification (ethyl acetate / hexane = 1/20 to 1/13 to 1/6)afforded **2b** (113.0 mg, 0.242 mmol, 88%).

White solid; R_f value 0.24(ethyl acetate/hexane = 1/4); m.p. 142.3–143.3 °C; IR (NaCl, neat) ν_{max} 3347, 2958, 2931, 2871, 1490, 1092, 1013, 911, 826, 731 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.33–7.37(m, 3H), 7.27(d, 4H, *J* = 8.0 Hz), 7.20(d, 4H, *J* = 8.0 Hz), 7.15(d, 2H, *J* = 7.5 Hz), 5.46(s, 2H), 4.33(m, 1H), 2.01(m, 2H), 0.94(tq, 2H, *J* = 7.5, 7.5 Hz), 0.76(m, 2H), 0.64(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, C_6D_6) δ 148.6, 144.8, 135.8, 135.0, 133.8, 129.8, 129.1, 128.5, 128.3, 127.3, 77.4, 51.8, 30.7, 23.0, 22.9, 13.6; HRMS (FAB) calcd for $C_{26}H_{24}Cl_2N_3O$ $[M–H]^+$ 465.1375, found 465.1374.

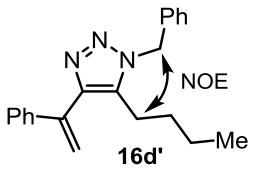
(1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)bis(4-methoxyphenyl)methanol (**2c**):



The reaction with **15c** (85.1 mg, 0.262 mmol), benzylazide (52.4 mg, 0.393 mmol), TMSOTf (57 µL, 0.315 mmol) in dichloromethane (2.6 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/20 to 1/4 to 1/3) afforded **16c** (24.7 mg, 0.206 mmol, 21%).

Yellow oil; R_f value 0.27(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3481, 2956, 1509, 1250, 1173, 1034, 830 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.30–7.36(m, 3H), 7.15–7.18(m, 6H), 6.81(dt, 4H, *J* = 9.0, 3.0 Hz), 5.46(s, 2H), 4.19(s, 1H, OH), 3.78(s, 6H), 1.96(m, 2H), 0.91(qt, 2H, *J* = 7.5, 7.5 Hz), 0.74(m, 2H), 0.61(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 158.8, 149.3, 137.9, 135.2, 134.7, 129.1, 128.9, 128.2, 127.0, 113.1, 77.1, 55.2, 51.9, 30.4, 22.7(2C), 13.4; HRMS (ESI) calcd for $C_{28}H_{31}N_3O_3Na$ $[M+Na]^+$ 480.2263, found 480.2261.

1-Benzyl-5-butyl-4-(1-phenylvinyl)-1*H*-1,2,3-triazole (**16d'**):

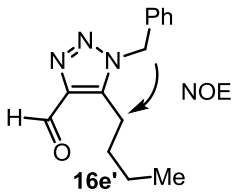


16d'

The reaction with **15d** (64.2 mg, 0.317 mmol), benzylazide (63.4 mg, 0.476 mmol), TMSOTf (69 µL, 0.381 mmol) in dichloromethane (3.2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5) afforded **16d'** (68.4 mg, 0. 215 mmol, 68%).

Colorless oil; R_f value 0.35(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2957, 1495, 1455, 1240, 1028, 702 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ7.26–7.33(m, 8H), 7.19 (d, 2H, *J* = 6.5 Hz), 5.63(dd, 2H, *J* = 21.0, 2.0 Hz), 5.52(s, 2H), 2.24(t, 2H, *J* = 8.0 Hz), 1.10(m, 2H), 0.99(tq, 2H, *J* = 7.0, 7.0 Hz), 0.64(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.0, 139.8, 139.8, 135.2, 134.8, 128.9, 128.2, 128.2, 127.9, 127.3, 127.0, 116.9, 51.9, 30.3, 22.5, 22.2, 13.3; HRMS (ESI) calcd for $C_{21}H_{23}N_3Na$ $[M+Na]^+$ 340.1790, found 340.1789.

1-benzyl-5-butyl-1*H*-1,2,3-triazole-4-carbaldehyde (**16g'**):

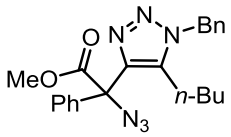


16e'

The reaction with **16g** (100.8 mg, 0.535 mmol), benzylazide (106.9 mg, 0.803 mmol), TMSOTf (116 µL, 0.642 mmol) in dichloromethane (5.4 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/20 to 1/10) afforded **16g'** (41.9 mg, 0. 172 mmol, 32%).

Colorless oil; R_f value 0.24(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 2958, 1696, 1472, 835, 717 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 10.2(s, 1H,CHO), 7.36–7.34(m, 3H), 7.20(m, 2H), 5.54(s, 2H), 2.85(t, 2H, *J* = 7.5 Hz), 1.32–1.27(m, 4H), 0.82(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 186.1, 144.1, 141.5, 134.1, 129.1, 128.7, 127.2, 51.8, 29.9, 22.9, 22.4, 13.5; HRMS (ESI) calcd for $C_{14}H_{17}N_3NaO$ $[M+Na]^+$ 266.1269, found 266.1269.

Methyl 2-azido-2-(1-benzyl-5-butyl-1H-1,2,3-triazol-4-yl)-2-phenylacetate (16h', CCDC 950507)

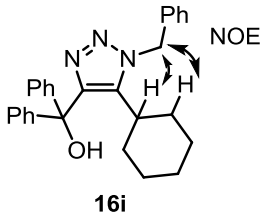


16h'

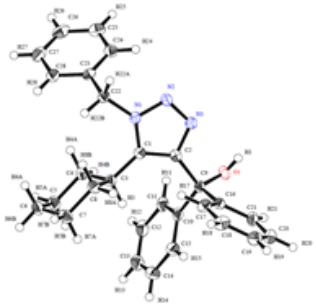
To a mixture of propargyl alcohol **16h** (68.3 mg, 0.277 mmol) and benzyl azide (55.4 mg, 0.416 mmol) in dichloromethane (2.8 mL) under nitrogen atmosphere, TMSOTf (110.2 µL, 0.610 mmol) was added at room temperature dropwise. After five minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Then the collected organic layer was dried over magnesium sulfate followed by concentration *in vacuo* and silica gel column chromatography (ethyl acetate / hexane = 1 / 5) to afford **16h'** (34.3 mg, 31%)

Colorless solid.; R_f value 0.18 (ethyl acetate/hexane = 1/5); m.p. 158.7–159.4 °C; IR (NaCl, neat) ν_{max} 2957, 2112, 1746, 1241 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.35–7.30 (m, 6H), 7.11 (d, 2H, *J* = 7.0 Hz), 5.54 (d, 1H, *J* = 16.0 Hz), 5.47 (d, 1H, *J* = 16.0 Hz), 3.89 (s, 3H), 2.19 (m, 1H), 2.02 (m, 1H), 1.06–0.84 (m, 4H), 0.62 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 143.3, 136.6, 136.2, 134.7, 129.0, 128.5, 128.3, 128.1, 127.4, 126.8, 71.1, 53.6, 52.1, 29.7, 22.5, 22.4, 13.2; HRMS (ESI) calcd for $C_{22}H_{24}N_6NaO_2$ $[M+Na]^+$ 427.1858, found 427.1856.

(1-Benzyl-5-cyclohexyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**16i**) (CCDC 950502)



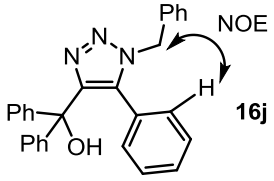
16i



The reaction with **15i** (55.0 mg, 0.189 mmol), benzylazide (35.8 mg, 0.269 mmol), TMSOTf (39 μL, 0.215 mmol) in dichloromethane (2 mL) afforded **16i** (76.6 mg, 0.181 mmol, 96%) by silica gel column purification (ethyl acetate/hexane = 1/6 to 1/5 to 1/4).

White solid; R_f value 0.18(ethyl acetate/hexane = 1/4); m.p. 112.9–114.0 °C; IR (NaCl, neat) ν_{max} 3446, 2928, 1448, 758, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.28–7.35(m, 13H), 7.07(d, 2H, *J* = 7.5 Hz), 5.62(s, 2H), 4.51(s, 1H, OH), 2.25(tt, 1H, *J* = 12.5, 2.5 Hz), 1.48–1.51(m, 3H), 1.25(dddd, 2H, *J* = 12.5, 12.5, 12.5, 2.5 Hz), 1.16(m, 2H), 0.95(dtt, 1H, *J* = 13.0, 13.0, 3.5 Hz), 0.72(ddddd, 2H, *J* = 13.0, 13.0, 13.0, 3.5, 3.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.8, 145.4, 138.4, 136.0, 128.8, 127.90, 127.89, 127.5, 126.4, 77.9, 53.1, 34.0, 30.3, 26.5, 25.5; LRMS (EI) 423(43%, M^+), 105(47), 91(100); HRMS (EI) calcd for $C_{28}H_{29}N_3O$ (M^+) 423.2311, found 423.2306.

(1-Benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**16j**)



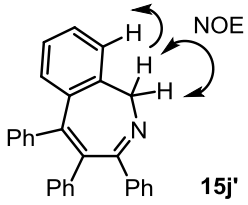
16j

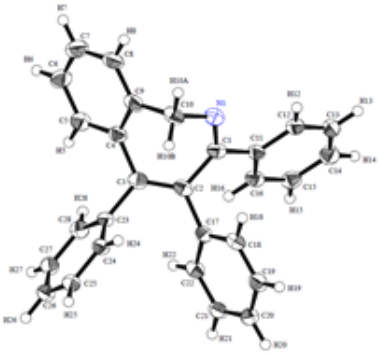
The reaction with **15j** (60.4 mg, 0.212 mmol), benzylazide (42.4 mg, 0.319 mmol) and TMSOTf (42 μL, 0.234 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/25 to 1/12 to 1/10 to 1/5) afforded **16j** (19.5 mg, 0.0467 mmol, 22%).

Light yellow solid; R_f value 0.23 (ethyl acetate/hexane = 1/4); m.p. 99.6–101.0 °C; IR (NaCl, neat) ν_{max} 3419, 3060, 3030, 1489, 1448, 1009, 757, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.20–7.26(m, 4H), 7.12–7.16(m, 10H), 7.04(dd, 2H, *J* = 8.0, 8.0 Hz), 6.94(dd, 2H, *J* = 8.0, 2.0 Hz), 6.55(dd, 2H, *J* = 8.0, 2.0 Hz), 5.26(s, 2H), 4.15(s, 1H, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 145.2, 135.1, 135.0, 129.9, 128.7, 128.6,

128.1, 128.0, 127.7, 127.6, 127.3, 126.9, 77.7, 52.1; HRMS (ESI) calcd for $C_{28}H_{23}N_3ONa$ $[M+Na]^+$ 440.1739, found 440.1739.

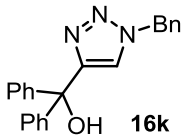
3,4,5-Triphenyl-1*H*-benzo[*c*]azepine(15j')

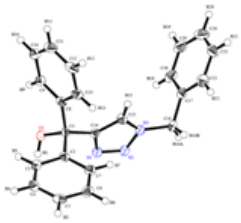




White solid; R_f value 0.33(ethyl acetate/hexane = 1/4); m.p. 138.6–140.0 °C; IR (NaCl, neat) ν_{max} 3057, 2957, 2835, 1489, 1444, 754, 697 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.50–7.53(m, 3H), 7.35(d, 1H, *J* = 8.0 Hz), 7.32(dd, 1H, *J* = 7.5, 7.5 Hz), 7.19–7.28(m, 9H), 6.93–7.03(m, 5H), 5.07(d, 1H, *J* = 10.0 Hz), 4.45(d, 1H, *J* = 10.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 167.4, 148.1, 140.6, 139.9, 139.4, 138.7, 138.20, 138.16, 130.6, 130.3, 129.5, 128.9, 128.7, 128.6, 127.9, 127.8, 127.5, 127.4, 127.1, 127.0, 126.6, 56.2; HRMS (ESI) calcd for $C_{28}H_{22}N$ $[M+H]^+$ 372.1752, found 372.1752.

(1-Benzyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**16k**) (CCDC 950503)

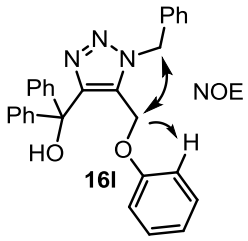




The reaction with **15k** (55.0 mg, 0.264 mmol), benzylazide (52.7 mg, 0.396 mmol) and TMSOTf (100 µL, 0.555 mmol) in dichloromethane (3 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/6 to 1/2 to 1/1) afforded **16k** (80.8 mg, 0.237 mmol, 90%).

White crystal; R_f value 0.40(ethyl acetate/hexane = 1/2); m.p. 140.5–140.9 °C; IR (NaCl, neat) ν_{max} 3393, 3056, 3030, 1490, 1446, 1173, 1016 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.40–7.56(m, 16H), 5.65(s, 2H), 4.04(s, 1H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 154.4, 145.6, 134.5 129.1, 128.7, 128.0, 127.8, 127.5, 127.1, 122.4, 76.7, 54.1; HRMS (ESI) calcd for $C_{22}H_{19}N_3ONa$ $[M+Na]^+$ 364.1426, found 364.1430.

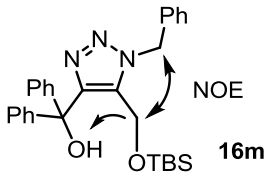
(1-Benzyl-5-phenoxymethyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**15l**)



The reaction with **15l** (64.0 mg, 0.204 mmol), benzylazide (40.7 mg, 0.305 mmol) and TMSOTf (44 µL, 0.244 mmol) in dichloromethane (2.0 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/10 to 1/9 to 1/8) afforded **16l** (83.1 mg, 0.186 mmol, 91%).

White solid; R_f value 0.20(ethyl acetate/hexane = 1/4) ; m.p. 122.0–123.2 °C; IR (NaCl, neat) ν_{max} 3420, 3061, 3033, 2246, 1599, 1495, 1233, 1173, 1031, 909, 754, 731, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.15–7.27(m, 13H), 7.10–7.14(m, 4H), 6.90(t, 1H, *J* = 7.5 Hz), 6.50(d, 2H, *J* = 8.5 Hz), 5.58(s, 2H), 4.24(s, 2H), 4.01(br, 1H, OH); ^{13}C NMR(126 MHz, $CDCl_3$) δ 157.3, 151.6, 144.8, 134.4, 129.6, 129.4, 128.9, 128.4, 128.0, 127.7, 127.6, 127.4, 121.6, 114.4, 77.8, 57.5, 52.8; HRMS (ESI) calcd for $C_{29}H_{25}N_3NaO_2$ $[M+Na]^+$ 470.1846, found 470.1851.

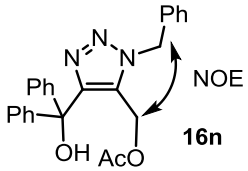
(1-Benzyl-5-((*tert*-butyldimethylsilyl)oxy)methyl-1*H*-1,2,3-triazol-4-yl)diphenyl-methanol (**16m**):



The reaction with **15m** (62.6 mg, 0.178 mmol), benzylazide (35.5 mg, 0.266 mmol), TMSOTf (39 µL, 0.213 mmol) in dichloromethane (2 mL) followed by silica gel column purification (ethyl acetate/hexane = 1/30 to 1/20 to 1/8 to 1/4) afforded **16m**(65.0 mg, 0. 134 mmol, 75%).

Yellow oil; R_f value 0.24(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3408, 3060, 3032, 2953, 2928, 2856, 1448, 1066, 838, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.16–7.35(m, 13H), 7.15(d, 2H, *J* = 7.0 Hz), 5.63(s, 2H), 4.60(s, 1H, OH), 4.07(s, 2H), 0.78(s, 9H), –0.18(s, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 150.9, 145.2, 134.9, 132.4, 128.9, 128.2, 127.9, 127.6, 127.5, 126.9, 77.6, 53.5, 52.5, 25.6, 18.0, –5.87, –5.89,; HRMS (ESI) calcd for $C_{29}H_{35}N_3O_2SiNa$ $[M+Na]^+$ 508.2396, found 508.2392.

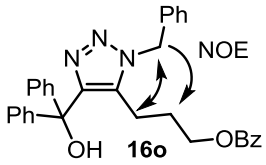
(5-Acetoxymethyl-1-benzyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol (**16n**):



The reaction with **15n** (127.7 mg, 0.456 mmol), benzylazide (91.0 mg, 0.683 mmol), TMSOTf (99 µL, 0.547 mmol) in dichloromethane (5 mL) afforded **16n** (41.3 mg, 0.100 mmol, 22%) by silica gel column purification (ethyl acetate/hexane = 1/20 to 1/10 to 1/6).

Yellow oil; R_f value 0.39(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3449, 3060, 3029, 1740, 1230, 1029, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.26–7.36(m, 13H), 7.15(d, 2H, *J* = 6.0 Hz), 5.60(s, 2H), 4.67(s, 2H), 4.40(s, 1H, OH), 1.70(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 170.4, 152.1, 145.1, 134.7, 129.0, 128.9, 128.4, 127.9, 127.6, 127.4, 127.0, 77.7, 53.6, 52.4, 20.2; HRMS (ESI) calcd for $C_{25}H_{23}NaN_3O_3$ $[M+Na]^+$ 436.1637, found 436.1637.

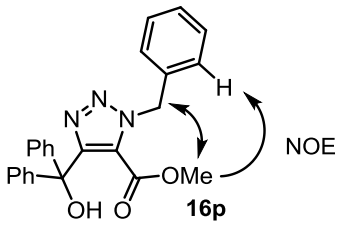
[5-(3-Benzoyloxyprop-1-)yl-1-benzyl-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16o**):



The reaction with **15o** (75.2 mg, 0.203 mmol), benzylazide (40.5 mg, 0.305 mmol) and TMSOTf (44 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/5 to 1/3 to 1/2) afforded **16o** (95.0 mg, 0.189 mmol, 93%).

Light yellow oil; R_f value 0.43(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3477, 3061, 2954, 2247, 1716, 1450, 1276, 714 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.93(d, 2H, *J* = 7.0 Hz), 7.59(t, 1H, *J* = 7.5 Hz), 7.45(dd, 2H, *J* = 7.5, 7.0 Hz), 7.25–7.29(m, 13H), 7.10(dd, 2H, *J* = 7.5, 2.5 Hz), 5.48(s, 2H), 4.15(m, 1H, OH), 3.88(t, 2H, *J* = 6.5 Hz), 2.23(m, 2H), 1.23(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 166.2, 149.4, 145.3, 134.9, 133.8, 133.1, 129.9, 129.4, 129.0, 128.4, 128.3, 128.0, 127.72, 127.66, 126.9, 77.8, 63.9, 52.0, 27.5, 20.1; HRMS (ESI) calcd for $C_{32}H_{29}N_3O_3$ $[M+Na]^+$ 526.2107, found 526.2107.

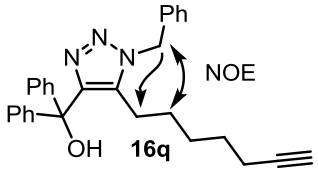
[1-benzyl-5-methoxycarbonyl-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16p**):



The reaction with **15p** (32.9 mg, 0.124 mmol), benzylazide (24.7 mg, 0.185 mmol), TMSOTf (47 μL, 0.26 mmol) in dichloromethane (1.3 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/15 to 1/10 to 1/5) afforded **16p** (28.2 mg, 0. 071 mmol, 57%).

Colorless oil; R_f value 0.32(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3413, 3056, 1702, 1449, 1265, 735, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.36–7.27(m, 13H), 7.18(d, 2H, *J* = 6.0 Hz), 5.86(s, 2H), 5.69(s, 1H, OH), 3.64(s, 3H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 159.7, 158.7, 144.7, 134.8, 128.9, 128.5, 127.8, 127.5, 127.34, 127.29, 124.8, 77.6, 55.0, 52.9; HRMS (ESI) calcd for $C_{24}H_{21}N_3O_3$ $[M+Na]^+$ 422.1481, found 422.1481.

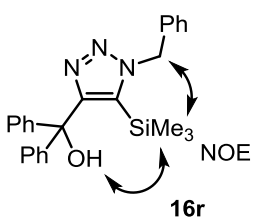
[1-Benzyl-5-(hept-6-yn-1-yl)-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16q**):

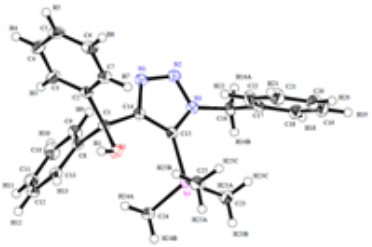


The reaction with **15q** (71.9 mg, 0.238 mmol), benzylazide (47.5 mg, 0.357 mmol) and TMSOTf (52 μL, 0.285 mmol) in dichloromethane (2.4 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/2) afforded **16q** (99.5 mg, 0.241 mmol, 93%).

Light yellow oil; R_f value 0.17(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3419, 3302, 2938, 1495, 1448, 1012, 907, 701 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.26–7.37(m, 13H), 7.16(d, 2H, *J* = 6.5 Hz), 5.47(s, 2H), 4.27(s, 1H, OH), 1.95–2.00(m, 4H), 1.93(t, 1H, *J* = 3.0 Hz), 1.16(tt, 2H, *J* = 7.5, 7.5 Hz), 0.94(tt, 2H, *J* = 7.5, 7.5 Hz), 0.71(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.9, 145.3, 135.1, 134.7, 129.0, 128.3, 127.9, 127.8, 127.6, 127.0, 84.2, 77.7, 68.3, 52.0, 28.5, 27.7, 27.6, 22.9, 18.0; HRMS (ESI) calcd for $C_{29}H_{29}N_3NaO$ $[M+Na]^+$ 458.2208, found 458.2208.

(1-Benzyl-5-trimethylsilyl-1*H*-1,2,3-triazol-4-yl)diphenylmethanol(**16r**) (CCDC 950504):

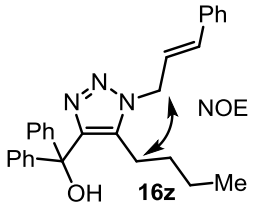




The reaction with **15r** (72.5 mg, 0.259 mmol), benzylazide (51.6 mg, 0.388 mmol) and TMSOTf (56 µL, 0.310 mmol) in dichloromethane (2.7 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10) afforded **16r** (99.5 mg, 0.241 mmol, 93%).

White crystal; R_f value 0.23(ethyl acetate/hexane = 1/4); m.p. 155–156 °C; IR (NaCl, neat) ν_{max} 3379, 3060, 3030, 2950, 2898, 1495, 1446, 1249, 847, 755, 699 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.19–7.28(m, 13H, 6.83(d, 2H, *J* = 7.0 Hz), 5.68(s, 2H), 2.96(s, 1H), 0.24(m, 9H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 160.8, 146.6, 136.9, 132.9, 128.7, 127.9, 127.7, 127.6, 127.4, 125.8, 79.1, 53.9, 1.1; HRMS (ESI) calcd for $C_{25}H_{27}N_3OSiNa$ $[M+Na]^+$ 436.1821, found 436.1822.

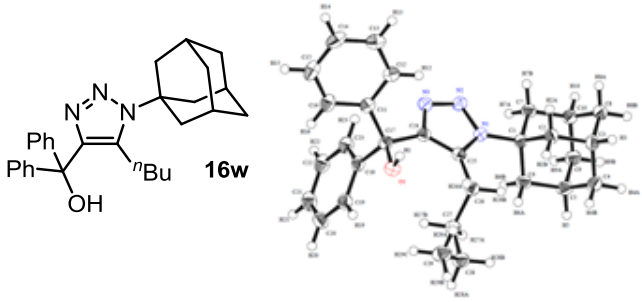
[4-Butyl-1-cinnamyl-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16z**):



The reaction with **15a** (55.1 mg, 0.208 mmol), azide (49.8 mg, 0.313 mmol), TMSOTf (45 µL, 0.25 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/5) afforded **16z** (78.2 mg, 0. 185 mmol, 89%).

Colorless oil; R_f value 0.18(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3481, 2957, 1448, 762 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.26(m, 15H), 6.43(d, 1H, *J* = 15.0 Hz), 6.29(dt, 1H, *J* = 15.0, 6.0 Hz), 4.99(d, 2H, *J* = 6.0 Hz), 4.29(s, 1H, OH), 2.06(t, 2H, *J* = 6.5 Hz), 0.94(m, 4H), 0.63(t, 3H, *J* = 5.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.7, 145.4, 135.5, 134.8, 133.7, 128.6, 128.3, 127.9, 127.5, 126.5, 122.7, 77.7, 50.3, 30.7, 22.7, 22.6, 13.4; HRMS (ESI) calcd for $C_{28}H_{29}N_3NaO$ $[M+Na]^+$ 446.2208, found 446.2208.

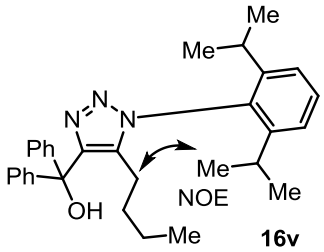
[1-Adamantyl-5-butyl-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16w**) (CCDC 950505):



The reaction with **15a** (70.8 mg, 0.268 mmol), azide (71.2 mg, 0.402 mmol), TMSOTf (58 μL, 0.32 mmol) in dichloromethane (2.7 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10) afforded **16w** (106.7 mg, 0. 242 mmol, 90%).

Colorless solid; R_f value 0.12(ethyl acetate/hexane = 1/5); m.p. 154.2–158.6 ℃; IR (NaCl, neat) ν_{max} 3509, 2963, 1473, 1000, 761, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ7.26–7.31(m, 10H), 4.40(s, 1H, OH), 2.37(d, 6H, *J* = 3.0 Hz), 2.29(t, 2H, *J* = 6.5 Hz), 2.25(s, 3H), 1.77(t, 6H, *J* = 13.5 Hz), 0.92–0.97(m, 4H), 0.68(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 149.2, 145.6, 134.9, 128.0, 127.8, 127.4, 78.0, 62.8, 35.9, 31.7, 29.7, 24.5, 22.8, 13.3; HRMS (ESI) calcd for $C_{29}H_{35}N_3NaO$ $[M+Na]^+$ 464.2678, found 464.2673.

[5-Butyl-1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16v**) :

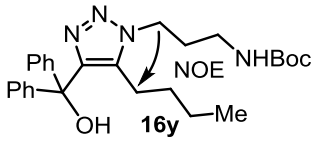


The reaction with **15a** (43.2 mg, 0.163 mmol), azide (49.9 mg, 0.245 mmol), TMSOTf (35 μL, 0.20 mmol) in dichloromethane (1.6 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/20 to 1/10) afforded **16v** (64.5 mg, 0.138 mmol, 85%).

Colorless oil; R_f value 0.19(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3504, 2963, 1447, 1000, 761, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.49(t, 1H, *J* = 7.5 Hz), 7.28–7.36(m, 12H), 4.44(s, 1H, OH), 2.16(qq, 2H, *J* = 7.0, 6.5 Hz), 1.83(t, 2H, *J* = 8.0 Hz), 1.19(d, 6H, *J* = 7.0 Hz), 1.16(d, 6H, *J* = 6.0 Hz), 0.72(m, 4H), 0.48(t, 3H, *J* = 6.5

Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.0, 146.3, 145.4, 136.8, 131.6, 130.8, 127.94, 127.88, 127.6, 123.9, 77.8, 30.2, 28.7, 25.7, 23.1, 22.6, 22.3, 13.2; HRMS (ESI) calcd for $C_{31}H_{38}N_3O$ $[M+H]^+$ 468.3015, found 468.3026.

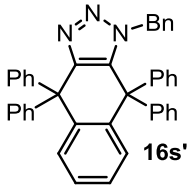
[1-(3-*tert*-butoxylcarbonylaminoprop-1-)yl-5-butyl-1*H*-1,2,3-triazol-4-yl]diphenylmethanol (**16y**) :

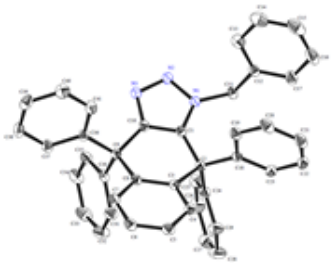


The reaction with **15a** (53.5 mg, 0.202 mmol), azide (60.8 mg, 0.306 mmol), TMSOTf (91 μL, 0.51 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/5 to 1/3) afforded**16y** (75.8 mg, 0.163 mmol, 81%).

Colorless oil; R_f value 0.35(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3338, 2960, 1692, 1168, 700 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ7.27–7.31(m, 10H), 4.90(s, 1H, OH), 4.25(s, 1H,NH), 4.22(t, 2H, *J* = 7.5 Hz),3.17–3.18(m, 2H), 2.03–2.10(m, 4H), 1.43(s, 9H), 0.91–1.02(m, 4H), 0.70(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 156.0, 148.5, 145.4, 134.7, 127.9, 127.8, 127.5, 79.4, 77.7, 45.1, 37.4, 30.8, 30.2, 28.3, 22.7, 13.5; HRMS (ESI) calcd for $C_{27}H_{36}N_4NaO_3$ $[M+Na]^+$ 487.2685, found 487.2680.

1-Benzyl-4,4,9,9-tetraphenyl-4,9-dihydro-1*H*-naphtho[2,3-*d*][1,2,3]triazole (**16s'**) (CCDC 950506):



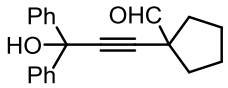


The reaction with **15s** (84.3 mg, 0.187 mmol), benzylazide (37.4 mg, 0.281 mmol) and TMSOTf (41 μL, 0.225 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10) and PTLC afforded **16s'** (50.5 mg, 0.0893 mmol, 48%).

White crystal; m.p. 206.0–207.2 °C; R_f value 0.16(ethyl acetate/hexane = 1/10); IR (NaCl, neat) ν_{max} 3060, 3029, 1597, 1495, 1445, 749, 697 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.04–7.20(m, 14H), 6.90–6.98(m, 9H), 6.83(d, 2H, *J* = 7.5 Hz), 6.74(d, 4H, *J*

= 8.5 Hz), 4.78(s, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 150.8, 144.8, 144.4, 142.4, 141.5, 137.2, 134.5, 131.4, 130.3, 129.8, 129.5, 128.0, 127.9, 127.7, 127.6, 127.4, 126.9, 126.5, 126.3, 126.1, 54.91, 54.87, 52.2; HRMS (ESI) calcd for $C_{41}H_{32}N_3$ $[M+H]^+$ 566.2596, found 566.2596.

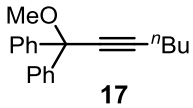
1-(3-Hydroxy-3,3-diphenylprop-1-yn-1-yl)cyclopentanecarbaldehyde(15t')



15t'

Yellow oil; R_f value 0.37(ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 3424, 2941, 1727, 1449, 698 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 9.55(s, 1H), 7.60(dd, 4H, *J* = 8.0, 1.0 Hz), 7.33(dd, 4H, *J* = 8.0, 8.0 Hz), 7.26(tt, 2H, *J* = 8.0, 1.0 Hz), 2.89(s, 1H), 2.18(m, 2H), 1.96(m, 2H), 1.80(m, 2H), 1.69(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 197.4, 145.0, 128.2, 127.6, 125.8, 87.7, 87.5, 74.4, 53.4, 35.2, 25.1; LRMS (EI) 304(M^+, 10%), 303(11), 287(37), 275(62), 207(56), 105(100); HRMS (EI) calcd for $C_{21}H_{20}O_2$ (M^+) 304.1463, found 304.1464.

1,1-Diphenyl-1-methoxyhept-2-yne(17)



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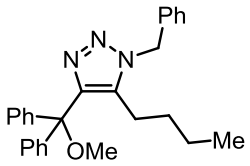
To a stirred solution of sodium hydride (39.4 mg, 0.983 mmol) in THF (3 mL) at 0 ºC under nitrogen atmosphere was added **15a** (0.200 g, 0.757 mmol) in THF (1 mL) dropwise and stirred for 30 min at the same temperature. After 30 min, iodomethane (0.141 mL, 2.27 mmol) was then added at same temperature and the mixture was warmed up to room temperature. After 2h, reaction mixture was quenched with water. The mixture was diluted with ethyl acetate and washed with water and brine. Then the collected organic layer was dried over magnesium sulfate and concentration *in vacuo* followed by silica gel column chromatography (ethyl acetate/hexane = 1/5) to give **17** (187.7 mg, 46%).

Colorless oil; R_f value 0.76 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2933, 1488, 1449, 1082, 763, 698 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.56–7.54 (m, 4H), 7.31–7.27 (m, 4H), 7.24–7.20 (m, 2H), 3.33 (s, 3H), 2.38 (t, 2H, *J* = 7.0 Hz), 1.60 (tt, 2H, *J* = 7.5, 7.0 Hz), 1.47 (tq, 2H, *J* = 7.0, 7.5 Hz), 0.94 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 128.0, 127.3, 126.6, 90.4, 80.9, 79.4, 52.2, 30.8, 22.0, 18.6,

13.6; LRMS (EI) 278 (M^+,27%), 247 (60), 221 (57), 201 (100); HRMS (EI) calcd for $C_{20}H_{22}O$ (M^+) 278.1670, found 278.1668.

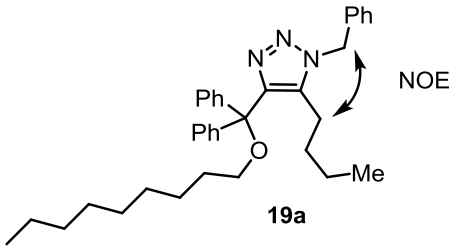
1-Benzyl-5-butyl-4-(methoxydiphenylmethyl)-1*H*-1,2,3-triazole(18)



18

To a mixture of propargyl ether **17** (34.7 mg, 0.125 mmol) and benzyl azide (24.9 mg, 0.187 mmol) in dichloromethane (1.5 mL) under nitrogen atmosphere, TMSOTf (27 µL, 0.150 mmol) was added at room temperature dropwise. After five minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Then the collected organic layer was dried over magnesium sulfate followed by concentration *in vacuo* and silica gel column chromatography (ethyl acetate/hexane = 1/5) to afford **18** (49.8 mg, 97%) as a colorless oil.; R_f value 0.19 (ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 2927, 2855, 1456, 1070, 744, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 4H, *J* = 7.0 Hz),7.19–7.10 (m, 7H), 7.03 (tt, 2H, *J* = 7.5, 7.0 Hz), 6.98 (d, 2H, *J* = 7.0 Hz), 5.33 (s, 2H), 2.91 (s, 3H), 1.96 (t, 2H, *J* = 8.0 Hz), 0.83–0.74 (m, 4H), 0.50 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 143.9, 136.9, 135.3, 128.9, 128.1, 127.8, 127.6, 126.9, 126.8, 82.6, 51.9, 51.8, 29.8, 22.8, 22.6, 13.4; LRMS (EI) LRMS (EI) 411(M^+,7%), 381(35), 105(12), 91(100); HRMS (EI) calcd for $C_{27}H_{29}N_3O$ (M^+) 411.2311, found 411.2314.

1-benzyl-5-butyl-4-((nonyloxy)diphenylmethyl)-1H-1,2,3-triazole (19a)



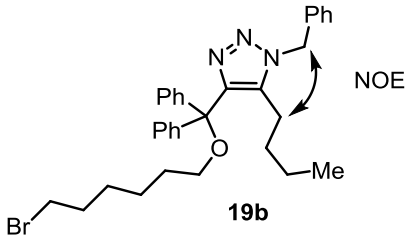
19a

The reaction of **19a** (85.9 mg, 82%) and **16a** (7.7 mg, 10%) from **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol) and $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/30 to 1/20 to 1/10).

Colorless oil ; R_f value 0.38 (ethyl acetate/hexane = 1/5); R_f value 0.38 (ethyl

acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2927, 2855, 1457, 1070, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, 4H, *J* = 7.0 Hz), 7.33–7.25 (m, 7H), 7.17 (dd, 2H, *J* = 6.0, 7.5 Hz), 7.11 (d, 2H, *J* = 6.0 Hz), 5.47 (s, 2H,) 3.09 (t, 2H, *J* = 7.0 Hz), 2.07 (t, 2H, *J* = 8.0 Hz), 1.54 (tt, 2H, *J* = 7.0, 8.0 Hz), 1.28–1.22 (m, 12H), 0.96–0.86 (m, 7H),0.65 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 144.4, 136.9, 135.4, 128.8, 128.1, 127.8, 127.5, 126.9, 126.7, 81.8, 63.7, 51.8, 31.9, 29.9, 29.52, 29.46, 29.2, 26.3, 22.9, 22.7, 22.6, 14.1, 13.5; HRMS (ESI) calcd for $C_{35}H_{45}N_3ONa$ $[M+Na]^+$ 546.34603, found 546.34558.

1-benzyl-4-(((6-bromohexyl)oxy)diphenylmethyl)-5-butyl-1*H*-1,2,3-triazole(19b)

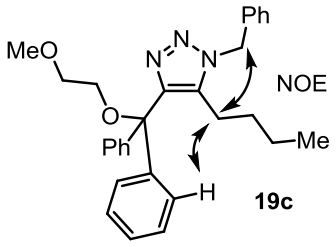


19b

The reaction of **19b** (81.5 mg, 73%) and **16a** (8.7 mg, 11%) from **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol) and $BF_3{\cdot}OEt_2$ (47% in ether, 65 μL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/15 to 1/10).

Colorless oil ; R_f value 0.29 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2933, 2868, 1456, 1071, 896, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, 4H, *J* = 8.0 Hz), 7.34–7.25 (m, 7H), 7.17 (dd, 2H, *J* = 7.5, 6.5 Hz), 7.12 (d, 2H, *J* = 6.5 Hz), 5.47 (s, 2H), 3.35 (t, 2H, *J* = 7.0 Hz), 3.11 (t, 2H, *J* = 6.5 Hz), 2.04 (t, 2H, *J* = 8.0 Hz), 1.80 (tt, 2H, *J* = 7.0, 6.5 Hz), 1.55 (tt, 2H, *J* = 6.5, 7.0 Hz), 1.35 (m, 4H), 0.96–0.86 (m, 4H), 0.65 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 144.3, 136.9, 135.3, 128.8, 128.1, 127.8, 127.4, 126.9, 126.7, 81.8, 63.4, 51.8, 33.8, 32.7, 29.9, 29.7, 27.9, 25.5, 22.8, 22.7, 13.4; LRMS (EI) ; HRMS (ESI) calcd for $C_{32}H_{38}BrN_3ONa$ $[M+Na]^+$ 582.20959, found 582.20950.

1-benzyl-5-butyl-4-((2-methoxyethoxy)diphenylmethyl)-1*H*-1,2,3-triazole(19c)

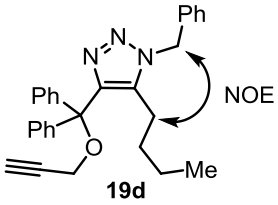


19c

The reaction of **19c** (105.7 mg, 76%) and **3a** (14.3 mg, 12%) from **4a** (80.5 mg, 0.196 mmol) and $BF_3{\cdot}OEt_2$ (47% in ether, 65 μL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/60 to 1/50 to 1/40 to 1/30 to 1/20 to 1/10).

Colorless oil; R_f value 0.18 (ethyl acetate/hexane = 1/4); IR (NaCl, neat) ν_{max} 2955, 2929, 1449, 1080, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, 4H, *J* = 8.0 Hz), 7.26–7.34 (m, 7H), 7.18 (dd, 2H, *J* = 7.5, 7.0 Hz), 7.14 (d, 2H, *J* = 7.5 Hz), 5.46 (s, 2H), 3.49 (t, 2H, *J* = 4.0 Hz), 3.30–3.31 (m, 5H), 2.13 (m, 2H), 0.89–1.02 (m, 4H), 0.67 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 143.8, 137.0, 135.3, 128.9, 128.1, 127.8, 127.7, 127.0, 126.8, 82.3, 72.0, 62.9, 58.7, 51.8, 30.0, 22.9, 22.7, 13.5; LRMS (EI) 455 (3%, M^+), 381 (26), 91 (100); HRMS (EI) calcd for $C_{29}H_{33}N_3O_2$ (M^+) 455.2573, found 455.2573.

1-Benzyl-5-butyl-4-(diphenyl(prop-2-yn-1-yloxy)methyl)-1*H*-1,2,3-triazole (**19d**):

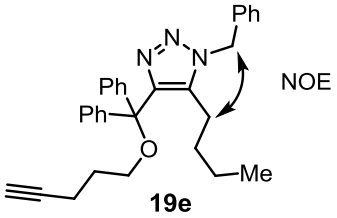


19d

The reaction with **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 μL, 0.24 mmol) in dichloromethane (2 mL) and additional propargyl alcohol (33.7 mg, 0.600 mmol) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/4) afforded **19d** (64.7 mg, 0.149 mmol, 72%) and **2a** (9.2 mg, 0.023 mmol, 12%).

Colorless oil; R_f value 0.34(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3438, 3293, 2957, 1490, 1449, 1058, 727 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.57(d, 4H, *J* = 7.0 Hz), 7.25–7.30(m, 7H), 7.19(t, 2H, *J* = 7.0 Hz), 7.13(d, 2H, *J* = 6.5 Hz), 5.44(s, 2H), 3.87(d, 2H, *J* = 3.0 Hz), 2.17(t, 1H, *J* = 3.0 Hz), 2.09(t, 2H, *J* = 8.0 Hz), 0.91–0.97(m, 4H), 0.64(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 145.6, 143.2, 137.3, 135.1, 128.8, 128.2, 127.9, 127.10, 127.08, 83.0, 80.4, 73.1, 52.7, 51.8, 30.0, 22.9, 22.7, 13.4; HRMS (ESI) calcd for $C_{29}H_{29}N_3ONa$ $[M+Na]^+$ 458.22083, found 458.22086.

1-benzyl-5-butyl-4-((pent-4-yn-1-yloxy)diphenylmethyl)-1*H*-1,2,3-triazole(19e)

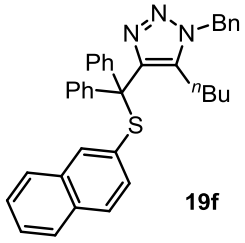


19e

The reaction of **19e** (71.8 mg, 77%) and **16a** (8.1 mg, 10%) from **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/4).

Colorless oil ; R_f value 0.29 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3448, 3303, 2956, 2871, 1449, 1071, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, 4H, *J* = 8.0 Hz), 7.33–7.25 (m, 7H), 7.18–7.12 (m, 4H), 5.46 (s, 2H), 3.22 (t, 2H, *J* = 6.5 Hz), 2.81 (t, 2H, *J* = 7.5 Hz), 2.03 (t, 2H, *J* = 8.5 Hz), 1.78–1.73 (m, 3H), 0.95–0.86 (m, 4H), 0.63 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 144.2, 137.0, 135.3, 128.9, 128.1, 127.8, 127.4, 126.9, 126.7, 83.8, 81.8, 68.4, 62.0, 51.8, 29.9, 29.0, 22.8, 22.6, 15.5, 13.4; HRMS (ESI) calcd for $C_{31}H_{33}N_3ONa$ $[M+Na]^+$ 486.25213, found 486.25226.

1-Benzyl-5-butyl-4-((naphthalen-2-ylthio)diphenylmethyl)-1*H*-1,2,3-triazole (19f)



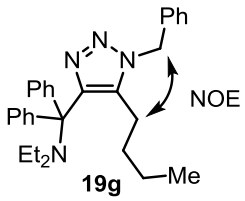
19f

The reaction of **19f** (87.8 mg, 81%) and **16a** (5.2 mg, 7%) from **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5).

Colorless oil; R_f value 0.28 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3054, 2975, 1495, 1455, 728, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, 1H, *J* = 8.0 Hz), 7.57 (d, 1H, *J* = 7.5 Hz), 7.54–7.53 (m, 2H), 7.48–7.43 (m, 6H), 7.32–7.22 (m, 10H), 7.04 (d, 2H, *J* =7.5 Hz), 5.49 (s, 2H), 2.18 (t, 2H, *J* = 8.5 Hz), 0.97 (tq, 2H, *J* = 7.5, 8.0 Hz), 0.73 (m, 2H), 0.64 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ147.1,

142.9, 135.9, 135.1, 133.9, 133.0, 132.3, 131.5, 131.1, 129.4, 128.7, 128.0, 127.7, 127.6, 127.4, 127.2, 126.9, 126.7, 126.1, 125.9, 64.0, 52.0, 29.0, 23.3, 22.7, 13.3; HRMS (ESI) calcd for $C_{36}H_{33}N_3SNa$ $[M+Na]^+$ 562.22929, found 562.22952.

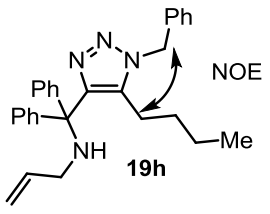
***N*-((1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)diphenylmethyl)-*N*-ethylethanamine (19g)**:



The reaction with **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) and additional diethylamine (63 µL, 0.600 mmol) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5) afforded **19g** (70.6 mg, 0.156 mmol, 78%) and **2a** (8.6 mg, 0.022 mmol, 11%).

Colorless oil; R_f value 0.23(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2960, 1594, 1456, 1025, 705 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.53(d, 4H, *J* = 8.0 Hz), 7.31–7.35(m, 3H), 7.25–7.29(m, 4H), 7.17(dd, 2H, *J* = 6.5, 7.0 Hz), 7.07(d, 2H, *J* = 7.0 Hz), 5.49(s, 2H), 2.45(q, 4H, *J* = 7.5 Hz), 2.30(t, 2H, *J* = 8.5 Hz), 1.07(m, 2H), 0.82(m, 2H), 0.74(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 146.6, 144.1, 135.6, 135.4, 129.1, 128.8, 128.0, 127.3, 126.6, 126.0, 74.4, 51.9, 47.2, 29.1, 23.6, 23.0, 16.1, 13.5; HRMS (ESI) calcd for $C_{30}H_{36}N_4Na$ $[M+Na]^+$ 475.2838, found 475.2828.

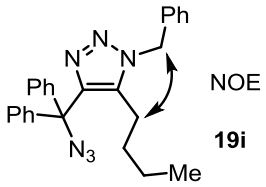
***N*-((1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)diphenylmethyl)prop-2-en-1-amine (19h)**



The reaction of **19h** (68.2 mg, 77%) and **16a** (9.4 mg, 12%) from **15a** (53.8 mg, 0.204 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/4).

Colorless oil; R_f value 0.29 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3320, 2957, 2870, 1491, 1456, 728, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, 4H, *J* = 7.0 Hz), 7.32–7.23 (m, 7H), 7.18 (dd, 2H, *J* = 7.0, 6.5 Hz), 7.10 (d, 2H, *J* = 7.0 Hz), 5.91 (ddt, 1H, *J* = 17.0, 10.5, 5.0 Hz), 5.43 (s, 2H), 5.18 (dd, 1H, *J* = 17.0, 1.5 Hz), 5.01 (dd, 1H, *J* = 10.5, 1.5 Hz), 2.92 (d, 2H, *J* = 5.0 Hz), 2.18 (t, 2H, *J* = 8.5 Hz), 2.07 (s, 1H, NH), 0.98 (td, 2H, *J* = 7.5, 7.0 Hz), 0.81–0.75 (m, 2H), 0.64 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 144.4, 137.0, 135.3, 135.1, 128.8, 128.3, 128.0, 127.7, 126.8, 126.5, 114.9, 66.6, 51.8, 46.6, 29.8, 22.9, 22.7, 13.4; HRMS (ESI) calcd for $C_{29}H_{32}N_4Na$ $[M+Na]^+$ 459.2525, found 459.2524.

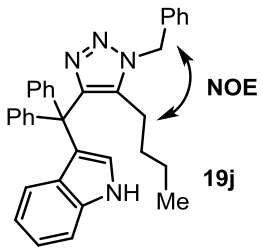
4-(Azidodiphenylmethyl)-1-benzyl-5-butyl-1*H*-1,2,3-triazole (**19i**):

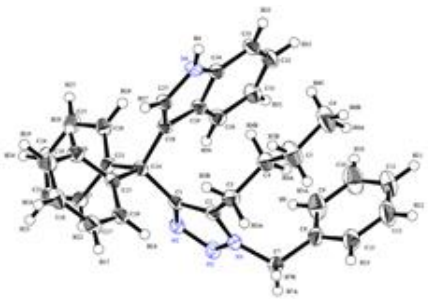


The reaction with **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 μL, 0.24 mmol) in dichloromethane (2 mL) and additional trimethylsilylazide (80 μL, 0.600 mmol) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5) afforded **19i** (72.1 mg, 0.171 mmol, 86%) and **16a** (7.6 mg, 0.019 mmol, 10%).

Colorless oil; R_f value 0.26(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2958, 2102, 1456, 1249,700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.29–7.37(m, 13H), 7.16(d, 2H, *J* = 7.0 Hz), 5.49(s, 2H), 2.17(t, 2H, *J* = 8.5 Hz), 0.99(tq, 2H, *J* = 7.5, 7.0 Hz), 0.86–0.92(m, 2H), 0.66(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 146.1, 141.8, 136.0, 135.0, 128.9, 128.23, 128.15, 128.1, 127.9, 126.9, 72.1, 51.9, 30.2, 22.8, 22.6, 13.4; HRMS (ESI) calcd for $C_{26}H_{26}N_6Na$ $[M+Na]^+$ 445.21166, found 445.21159.

3-((1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)diphenylmethyl)-1*H*-indole (**19j**) (CCDC 956342):

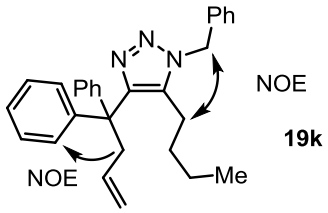




The reaction with **15a** (55.1 mg, 0.208 mmol), benzylazide (41.6 mg, 0.313 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 67 μL, 0.25 mmol) in dichloromethane (2 mL) and additional indole (73.3 mg, 0.625 mmol) dissolved in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/2) afforded **19j** (67.7 mg, 0.136 mmol, 65%).

Colorless solid; R_f value 0.23(ethyl acetate / hexane = 1 / 5); m.p. 228.2–229.4 °C; IR (KBr, neat) ν_{max} 3222, 2947, 2868, 1492, 1330, 1237, 704 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 8.66(s, 1H), 7.73–7.75(m, 4H), 7.61–7.71(m, 10H), 7.49–7.54(m, 3H), 7.26(m, 2H), 7.18(d, 1H, *J* = 2.5 Hz), 5.91(s, 2H), 2.27(t, 2H, *J* = 8.5 Hz), 1.16(td, 2H, *J* = 7.5, 7.0 Hz), 0.92(t, 3H, *J* = 7.5 Hz), 0.78(m, 2H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.3, 145.2, 136.9, 135.9, 135.6, 130.2, 128.8, 128.0, 127.5, 127.3, 126.6, 126.1, 124.6, 122.4, 121.8, 121.3, 119.2, 111.0, 53.8, 51.9, 28.7, 23.6, 22.8, 13.4; LRMS (EI) 496(M^+, 22%), 354(23), 281(47), 207(54), 129(54), 91(100); HRMS (EI) calcd for $C_{34}H_{32}N_4$ (M^+) 496.2627, found 496.2628.

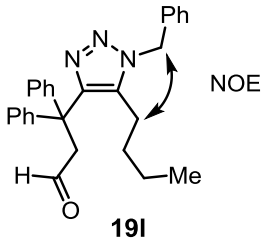
1-Benzyl-5-butyl-4-(1,1-diphenylbut-3-en-1-yl)-1*H*-1,2,3-triazole(19k)



The reaction of **19k** (57.9 mg, 69%) and **16a** (2.1 mg, 3%) from **15a** (53.0 mg, 0.200 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 μL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/15 to 1/10 to 1/4).

White solid; R_f value 0.28 (ethyl acetate/hexane = 1/5); m.p. 128.9–130.1 °C; IR (NaCl, neat) ν_{max} 3081, 2959, 1466, 907, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.38(m, 3H), 7.34–7.31 (m, 4H), 7.28–7.24 (m, 6H), 7.20 (t, 2H, *J* = 7.0 Hz), 6.02 (tdd, 1H, *J* = 17.0, 6.5, 7.5 Hz), 5.53 (s, 2H), 4.97–4.92 (m, 2H), 3.63 (d, 2H, *J* = 6.5 Hz), 1.90 (m, 2H), 0.89 (tt, 2H, *J* = 7.5, 7.5 Hz), 0.62 (t, 3H, *J* = 7.5 Hz), 0.51–0.45 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 144.6, 136.2, 135.4, 135.3, 128.9, 128.8, 128.1, 127.7, 126.8, 126.2, 117.0, 52.1, 51.8, 47.1, 29.1, 23.1, 22.7, 13.4; HRMS (ESI) calcd for $C_{29}H_{31}N_3Na$ $[M+Na]^+$ 444.24157, found 444.23930.

3-(1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)-3,3-diphenylpropanal (19l)

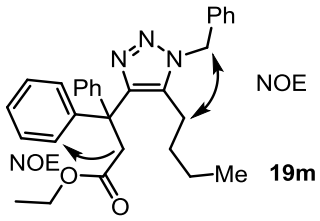


19l

The reaction of **19l** (45.8 mg, 55%) and **16a** (27.6 mg, 35%) from **15a** (52.4 mg, 0.198 mmol), benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/5 to 1/4).

Colorless oil; R_f value 0.14 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2957, 2858, 1715, 1455, 1023, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (t, 1H, *J* = 2.5 Hz), 7.56–7.51 (m, 3H), 7.49–7.41 (m, 6H), 7.35 (d, 2H, *J* = 7.0 Hz), 7.25 (d, 4H, *J* = 8.5 Hz), 5.65 (s, 2H), 3.80 (d, 2H, *J* = 2.5 Hz), 1.96 (t, 2H, *J* = 8.5 Hz), 0.95 (qt, 2H, *J* = 7.5, 7.5 Hz), 0.71 (t, 3H, *J* = 7.5 Hz), 0.59–0.53 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 148.0, 143.8, 135.8, 135.1, 129.0, 128.5, 128.4, 128.3, 127.0, 126.99, 55.2, 52.0, 49.7, 29.3, 23.0, 22.7, 13.3; HRMS (ESI) calcd for $C_{28}H_{29}N_3ONa$ $[M+Na]^+$ 446.22083, found 446.22063.

ethyl 3-(1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)-3,3-diphenylpropanoate(19m)



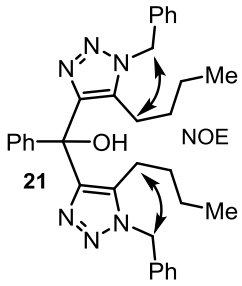
19m

The reaction of **19m** (63.1 mg, 68%) and **16a** (15.3 mg, 20%) from **15a** (52.5 mg, 0.199 mmol) , benzylazide (40.0 mg, 0.300 mmol), $BF_3{\cdot}OEt_2$ (47% in ether, 65 µL, 0.24 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification ethyl acetate/hexane = 1/80 to 1/70 to 1/50 to 1/30 to 1/20 to 1/4).

Colorless oil; R_f value 0.14 (ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2957, 2870, 1742, 1151, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 3H), 7.25–7.22 (m, 4H), 7.21–7.15 (m, 6H), 7.10 (d, 2H, *J* = 7.0 Hz), 5.42 (s, 2H), 3.95 (q, 2H, *J* = 7.0 Hz), 3.78 (s, 2H), 1.84 (t, 2H, *J* = 8.5 Hz), 1.06 (t, 3H, *J* = 7.0 Hz), 0.77 (qt, 2H, *J* = 7.0, 7.5 Hz), 0.51 (t, 3H, *J* = 7.5 Hz), 0.37–0.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 148.0, 144.2, 135.4, 135.2, 128.9, 128.7, 128.1, 127.9, 126.8, 126.5,

60.0, 51.9, 50.8, 46.9, 29.0, 23.3, 22.7, 13.9, 13.4; HRMS (ESI) calcd for $C_{30}H_{34}N_3O_2$ $[M+H]^+$ 468.26510, found 468.26574.

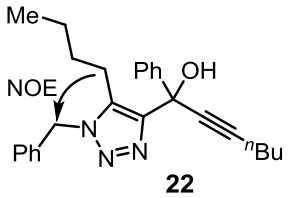
Bis(1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanol (**21**):



The reaction with **20** (55.0 mg, 0.205 mmol), benzylazide (81.9 mg, 0.615 mmol) and TMSOTf (44 µL, 0.25 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/3 to 2/1) afforded **20** (78.8 mg, 0.147 mmol, 72%).

Colorless oil; R_f value 0.25(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3471, 2957, 1456, 727, 698 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.29–7.34(m, 6H), 7.26(s, 5H), 7.17(d, 4H, *J* = 6.5 Hz), 5.49(d, 2H, *J* = 15.5 Hz), 5.43(d, 2H, *J* = 15.5 Hz), 5.28(s, 1H, OH), 2.35–2.53(m, 4H), 0.99–1.02 (m, 4H), 0.75–0.92 (m, 4H), 0.63(t, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.1, 144.6, 135.6, 135.1, 128.9, 128.2, 127.9, 127.7, 127.4, 127.1, 74.2, 51.9, 30.2, 23.0, 22.6, 13.4; HRMS (ESI) calcd for $C_{33}H_{38}N_6NaO$ $[M+Na]^+$ 557.3005, found 557.3004.

1-(1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)-1-phenylhept-2-yn-1-ol(22)

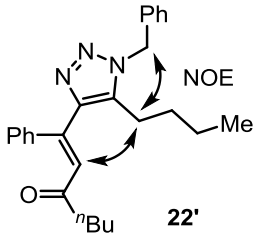


The reaction with **20** (77.0 mg, 0.261 mmol), benzylazide (36.5 mg, 0.274 mmol) and TMSOTf (57 µL, 0.0.313 mmol) in dichloromethane (2 mL) followed by silica gel column chromatography purification (ethyl acetate/hexane = 1/10 to 1/3 to 2/1) afforded **22** (57.9 mg, 55%).

Colorless oil; R_f value 0.29(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 3352, 2957, 1455, 1003, 733, 698 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.83(d, 2H, *J* = 7.5 Hz), 7.55(m, 6H), 7.35(d, 2H, *J* = 7.0 Hz), 5.67(d, 1H, *J* = 15.5 Hz), 5.64 (d, 1H, *J* = 15.5 Hz),4.63(s, 1H, OH), 2.59–2.61 (m, 1H), 2.52(td, 2H, *J* = 1.5, 7.0 Hz), 2.41–2.46(m,

1H), 1.75(tt, 2H, *J* = 7.5, 7.5 Hz), 1.62(tq, 2H, *J* = 7.5, 7.5 Hz), 1.24–1.27(m, 3H), 1.10(t, 3H, *J* = 7.5 Hz), 0.92–1.02(m, 1H), 0.89(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 147.8, 143.5, 134.9, 133.7, 128.9, 128.3, 128.1, 128.0, 127.1, 126.5, 88.2, 80.9, 69.7, 52.0, 30.5, 29.9, 22.6, 22.5, 22.0, 18.6, 13.6, 13.5; HRMS (ESI) calcd for $C_{26}H_{31}N_3NaO$ $[M+Na]^+$ 424.2365, found 424.2365.

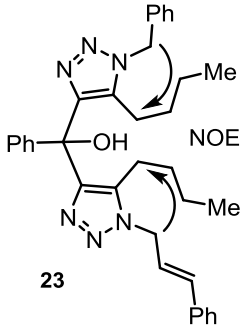
(*E*)-1-(1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)-1-phenylhept-1-en-3-one(22')



22'

Colorless oil; R_f value 0.34(ethyl acetate/hexane = 1/5); IR (NaCl, neat) ν_{max} 2957, 2871, 1684, 1456, 727, 698 cm^{-1}; ^{1}H NMR(500 MHz, $CDCl_3$) δ7.32–7.36(m, 6H), 7.22–7.24(m, 2H), 7.14(d, 2H, *J* = 8.0 Hz), 7.04(s, 1H), 5.45(s, 2H), 2.32(t, 2H, *J* = 7.5 Hz), 1.84(t, 2H, *J* = 9.5 Hz), 1.48(tt, 2H, *J* = 7.5, 7.0 Hz), 1.19(tq, 2H, *J* = 7.5, 7.5 Hz), 0.83–0.88(m, 4H) , 0.82(t, 3H, *J* = 7.5 Hz), 0.59(t, 3H, *J* = 7.0 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 202.0, 144.2, 142.7, 137.4, 137.1, 134.8, 129.0, 128.9, 128.6, 128.4, 128.3, 127.1, 126.5, 52.0, 43.4, 30.8, 26.2, 22.6, 22.4, 22.2, 13.8, 13.3; HRMS (ESI) calcd for $C_{26}H_{31}N_3NaO$ $[M+Na]^+$ 424.2365, found 424.2372.

(1-Benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)(5-butyl-1-cinnamyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanol (**23**):



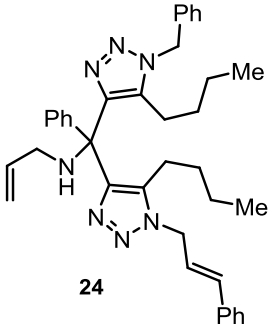
23

To the mixture of **20** (52.2 mg, 0.194 mmol), benzylazide (27.2 mg, 0.204 mmol) in dichloromethane (2.0 mL) was added TMSOTf (42.2 μL, 0.233 mmol) at –90 °C. After 1 min, cinnamylazide (46.4 mg, 0.291) dissolved in 0.5 mL of dichloromethane was added to the mixture. After five minutes, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column

chromatography (ethyl acetate/hexane = 1/20 to 1/10 to 1/3 to 1/2) afforded **23** (58.9 mg, 0.105 mmol, 54%)

Colorless oil; R_f value 0.17(ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 3366, 2956, 2929, 1456, 728, 698 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 7.29–7.36(m, 8H), 7.26–7.28(m, 5H), 7.18(d, 2H, *J* = 7.0 Hz), 6.51(d, 1H, *J* =7.0 Hz), 6.33(dt, 1H, *J* = 15.5, 6.5 Hz), 5.50(d, 2H, *J* = 15.5 Hz), 5.43(d, 2H, *J* = 15.5 Hz), 5.30(s, 1H), 5.03(dd, 2H, *J* = 5.0, 5.0 Hz), 2.59–2.64(m, 1H), 2.47–2.51(m, 2H), 2.38–2.43(m, 1H), 0.79–1.28(m, 8H), 0.69(t, 3H, *J* = 7.5 Hz), 0.63(t, 3H, *J* = 7.5 Hz); ^{13}C NMR(126 MHz, $CDCl_3$) δ 148.1, 144.6, 135.7, 135.5, 135.1, 133.8, 128.9, 128.6, 128.22, 128.18, 127.9, 127.8, 127.4, 127.1, 126.6, 122.8, 74.2, 51.9, 50.3, 30.5, 30.2, 23.1, 23.0, 22.7, 22.6, 13.52, 13.47; HRMS (ESI) calcd for $C_{35}H_{40}NaN_6O$ $[M+Na]^+$ 583.3161, found 583.3161.

N-((1-benzyl-5-butyl-1*H*-1,2,3-triazol-4-yl)(5-butyl-1-cinnamyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)prop-2-en-1-amine(24)



24

To a mixture of **20** (77.6 mg, 0.289 mmol), benzylazide (40.4 mg, 0.304 mmol) in dichloromethane (3.0 mL) was added boron trifluoride diethyl ether complex (101.3 μL, 0.376 mmol) at –60 °C. After 1 min, cinnamylazide (69.0 mg, 0.434 mmol) dissolved in 0.5 mL of dichloromethane was added to the mixture. After five minutes, allylamine (51.3 μL, 0.867 mmol) was added at the same temperature, and then warmed up to room temperature. After 30 min, the mixture the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Then the collected organic layer was dried over magnesium sulfate followed by concentration *in vacuo* and silica gel column chromatography (ethyl acetate/hexane = 1/12 to 1/10 to 1/5 to 1/3) to afford **24** (45.9 mg, 27%).

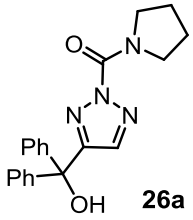
Colorless oil; R_f value 0.30 (ethyl acetate/hexane = 1/2); IR (NaCl, neat) ν_{max} 2957, 2931, 2870, 1456, 1241, 904, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, 2H, *J* = 7.5, 2.0 Hz), 7.39–7.25 (m, 11H), 7.16 (dd, 2H, *J* = 6.5, 1.5 Hz), 6.49 (d, 1H, *J* = 16.0 Hz), 6.33 (td, 1H, *J* =16.0, 6.5 Hz), 5.92 (ddt, 1H, *J* = 17.0, 10.0 Hz), 5.50 (s, 2H), 5.21 (dd, 1H, *J* = 17.0, 2.0 Hz), 5.06–5.02 (m, 3H), 3.01 (d, 2H, *J* = 4.0 Hz), 2.58–2.29 (m,

4H), 1.21–1.15 (m, 2H), 1.09–1.05 (m, 4H), 0.86–0.78 (m, 5H), 0.70 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 146.9, 142.9, 136.9, 135.7, 135.6, 135.3, 133.5, 128.8, 128.6, 128.4, 128.2, 128.1, 127.6, 126.9, 126.8, 126.5, 123.0, 114.8, 62.6, 51.8, 50.2, 46.4, 30.2, 29.8, 22.91, 22.87, 22.76, 22.67, 13.61, 13.55; HRMS (ESI) calcd for $C_{38}H_{45}NaN_7$ $[M+Na]^+$ 622.36341, found 622.36220.

General procedure of synthesis of triazole ureas:

A slurry of 30 wt% (based on starting material triazole) of 10% Pd/C in ethanol was added to a stirred solution of 1,4,5-trisubstituted triazoles under nitrogen and the resulting mixture was stirred under an atmosphere of hydrogen gas for 20 h. The reaction mixture was filtered through a plug of celite washing with methanol. The filtrate was evaporated under reduced pressure to give a white solid residue which was used to the next step without further purification. The crude unprotected triazoles (1.2 equiv), pyrrolidine carbonyl chloride **25** (1.0 equiv), and 4-dimethylaminopyridine (0.2 equiv) were dissolved in 5:1 THF/triethylamine (0.1 M based on triazoles), and the mixture was stirred for 10 h at 60 °C. The solvents were removed, and then the crude material was purified by silica gel chromatography to afford triazole ureas.

(4-(Hydroxydiphenylmethyl)-2*H*-1,2,3-triazol-2-yl)(pyrrolidin-1-yl)methanone (26a)



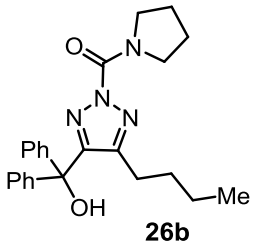
26a

17.9 mg (30%) for two steps from **16k** (70.0 mg, 0.206 mmol) [silica gel chromatography (hexane/ethyl acetate = 20:1 to 10:1 to 5/1 to 3/1 to 2/1 to 1/1 to ethyl acetate)].

White solid; R_f value 0.23 (ethyl acetate/hexane = 1/2); m.p. 156.7–157.7 °C; IR (NaCl, neat) ν_{max} 3363, 2917, 1697, 1264, 1058, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.33–7.29 (m, 10H), 3.76 (t, 2H, *J* = 6.5 Hz), 3.70 (t, 2H, *J* = 6.5 Hz), 1.96–1.92 (m, 4H); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 (s, 1H), 7.35–7.27 (m, 10H), 3.72 (t, 2H, *J* = 6.0 Hz), 3.63 (t, 2H, *J* = 6.0 Hz), 1.95–1.90 (m, 4H); ^{1}H NMR (500 MHz, CD_3OD) δ 7.84 (s, 1H), 7.37–7.23 (m, 10H), 3.73 (t, 2H, *J* = 6.0 Hz), 3.64 (t, 2H, *J* = 6.0 Hz), 1.94–1.90 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 147.7, 144.9, 135.3, 128.2, 127.8, 127.1, 77.2, 50.1, 48.7, 26.4, 24.0; ^{13}C NMR (126 MHz, CD_2Cl_2) δ 155.8, 147.9, 145.5, 135.4, 128.4, 128.1, 127.4, 77.4, 50.4, 48.9, 26.7, 24.4; ^{13}C NMR (126 MHz,

CD_3OD) δ 158.0, 149.6, 147.1, 136.7, 128.9, 128.5, 128.4, 78.0, 51.5, 49.8, 27.4, 25.0; HRMS (ESI) calcd for $C_{20}H_{20}N_4O_2Na$ $[M+Na]^+$ 371.14839, found 371.14822.

(4-Butyl-5-(hydroxydiphenylmethyl)-2*H*-1,2,3-triazol-2-yl)(pyrrolidin-1-yl)methanone (26b)

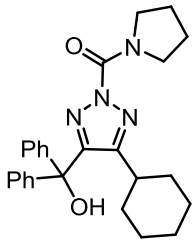


26b

121.7mg (0.300mmol, 80%) for two steps from **16a** (220.1 mg, 0.554mmol) [silica gel chromatography (hexane/ethyl acetate = 3:1 to 1:1, dichloromethane/methanol = 40:1)].

White solid; Rf value 0.45 (ethyl acetate/hexane = 1/2); m.p. 168.7–170.4 °C; IR (NaCl, neat) ν_{max} 3333, 2958, 2871, 1694, 1448, 1418, 1264, 1171, 941 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27–7.19 (m, 10H), 3.67 (s, 1H), 3.64–3.58 (m, 4H), 2.20 (t, 2H, *J* = 8.0 Hz), 1.83 (br, 4H), 1.27 (tt, 2H, *J* = 7.5, 8.0 Hz), 1.07 (tt, 2H, *J* = 7.5, 7.5 Hz), 0.66 (t, 3H, *J* = 7.5 Hz); 13C NMR (126 MHz, $CDCl_3$) δ 152.2, 148.9, 147.9, 144.4, 128.0, 127.8, 127.5, 77.9, 50.1, 48.6, 30.3, 26.5, 25.5, 24.0, 22.4, 13.6; HRMS (ESI) calcd for $C_{24}H_{28}N_4O_2Na$ $[M+Na]+$ 427.21099, found 427.21052.

(4-Cyclohexyl-5-(hydroxydiphenylmethyl)-2*H*-1,2,3-triazol-2-yl)(pyrrolidin-1-yl)methanone (26c)



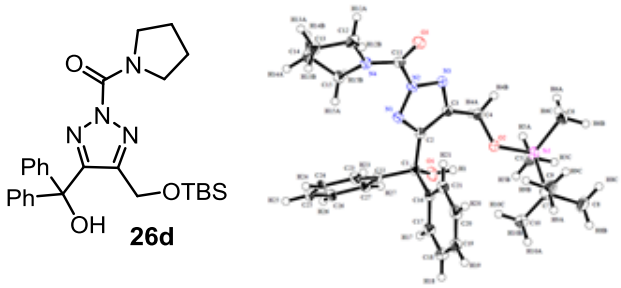
26c

152.0 mg (0.353 mmol, 67%) for two steps from **16i** (260.0 mg, 0.614 mmol) [silica gel chromatography (hexane/ethyl acetate = 5:1 to 3:1 to 1:1, dichloromethane/methanol = 40:1)].

White solid; R_f value 0.26 (ethyl acetate/hexane = 1/2); m.p. 226.8–227.0 °C; IR (NaCl, neat) ν_{max} 3334, 3061, 2925, 2854, 1694, 1423, 1340, 1260 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 10H), 3.73 (s, 1H), 3.72 (t, 2H, *J* = 7.0 Hz), 3.68 (t, 2H, *J* = 7.0Hz), 2.17–2.11 (m, 1H), 1.91 (m, 4H), 1.69–1.53 (m, 3H), 1.46–1.37 (m, 4H),

1.16–1.10 (m, 1H), 0.96–0.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 151.5, 148.0, 144.5, 128.0, 127.8, 127.7, 78.0, 50.1, 48.6, 35.2, 26.5, 26.3, 25.7, 24.0; HRMS (ESI) calcd for $C_{26}H_{30}N_4O_2Na$ $[M+Na]^+$ 453.22664, found 453.22670.

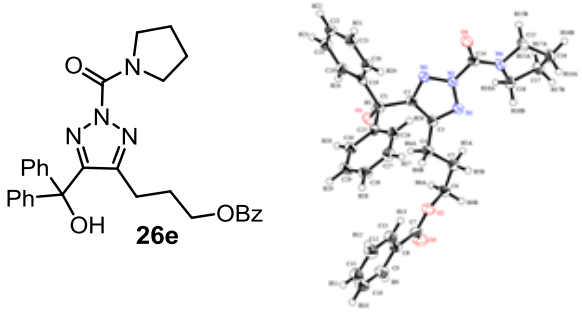
(4-(((tert-Butyldimethylsilyl)oxy)methyl)-5-(hydroxydiphenylmethyl)-2*H*-1,2,3-triazol-2-yl)(pyrrolidin-1-yl)methanone (26d, CCDC 1014155)



39.1 mg (0.079 mmol, 33%) for two steps from **16m** (139.6 mg, 0.287 mmol) [silica gel chromatography (hexane/ethyl acetate = 5:1 to 3:1 to 1:1)].

White solid; R_f value 0.2 (ethyl acetate/hexane = 1/2); m.p. 146.8–147.9 °C; IR (NaCl, neat) ν_{max} 3403, 2928, 2884, 1717, 1410, 1259, 1059, 993 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38–7.36 (m, 4H), 7.33–7.27 (m, 6H), 5.68 (s, 1H), 4.65 (s, 2H), 3.59 (t, 2H, *J* = 6.5 Hz), 3.54 (t, 2H, *J* = 6.5 Hz), 1.90–1.84 (m, 4H), 0.82 (s, 9H), –0.02(s, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.9, 147.9, 146.5, 145.3, 128.1, 127.7, 127.5, 76.9, 58.4, 50.4, 48.9, 26.7, 25.8, 24.4, 18.4, –5.7; HRMS (ESI) calcd for $C_{27}H_{36}N_4O_3SiNa$ $[M+Na]^+$ 515.24544, found 515.24415.

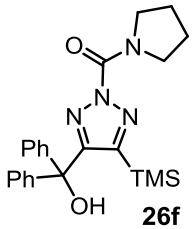
3-(5-(Hydroxydiphenylmethyl)-2-(pyrrolidine-1-carbonyl)-2*H*-1,2,3-triazol-4-yl)propyl benzoate (26e, CCDC 1014154)



117.7 mg (0.231 mmol, 40%) for two steps from **16o** (349.3 mg, 0.694 mmol) [silica gel chromatography (hexane/ethyl acetate = 5:1 to 3:1 to 2:1, dichloromethane / methanol = 60:1)].

White solid; R_f value 0.2 (ethyl acetate/hexane = 1/2); m.p. 184.7–185.5 °C; IR (NaCl, neat) ν_{max} 3403, 2928, 2884, 1717, 1410, 1259, 1059, 993 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ7.92 (dd, 2H, *J* = 8.0, 1.0 Hz), 7.53 (td, 1H, *J* = 7.0, 1.0 Hz), 7.39 (tt, 2H, *J* = 7.0, 8.0 Hz), 7.30–7.23 (m, 10H), 4.18 (t, 2H, *J* = 5.5 Hz), 3.63 (s, 1H), 3.64–3.60 (m, 4H), 2.52 (t, 2H, *J* = 7.5 Hz), 1.97–1.81 (m, 2H), 1.89–1.84 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 152.2, 147.81, 147.76, 144.3, 132.9, 130.1, 129.5, 128.3, 128.1, 127.9, 127.4, 77.9, 64.2, 50.1, 48.6, 27.1, 26.5, 24.0, 22.7; HRMS (ESI) calcd for $C_{30}H_{30}N_4O_4Na$ $[M+Na]^+$ 533.21647, found 533.21563.

(4-(Hydroxydiphenylmethyl)-5-(trimethylsilyl)-2*H*-1,2,3-triazol-2-yl)(pyrrolidin-1-yl)methanone (26f)



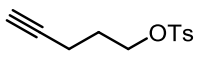
26f

82.1 mg (0.195 mmol, 58%) for two steps from **16r** (164.7 mg, 0.404 mmol) [silica gel chromatography (hexane/ethyl acetate = 5:1 to 3:1 to 2:1 to 1:1)].

White solid; R_f value 0.34 (ethyl acetate/hexane = 1/2); m.p. 168.7–169.4 °C; IR (NaCl, neat) ν_{max} 3350, 2959, 1697, 1252, 1048, 928, 761 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.28 (m, 10H), 3.66 (t, 2H, *J* = 7.0 Hz), 3.58 (t, 2H, *J* = 7.0 Hz), 2.88 (s, 1H), 1.92–1.84 (m, 4H), 0.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 148.6, 148.2, 145.6, 128.0, 127.7, 127.4, 78.7, 49.9, 48.4, 26.4, 24.1, –0.4; HRMS (ESI) calcd for $C_{23}H_{28}N_4O_2SiNa$ $[M+Na]^+$ 443.18792, found 443.18773.

Chapter 5 Supporting Information

5.2 NMR spectra



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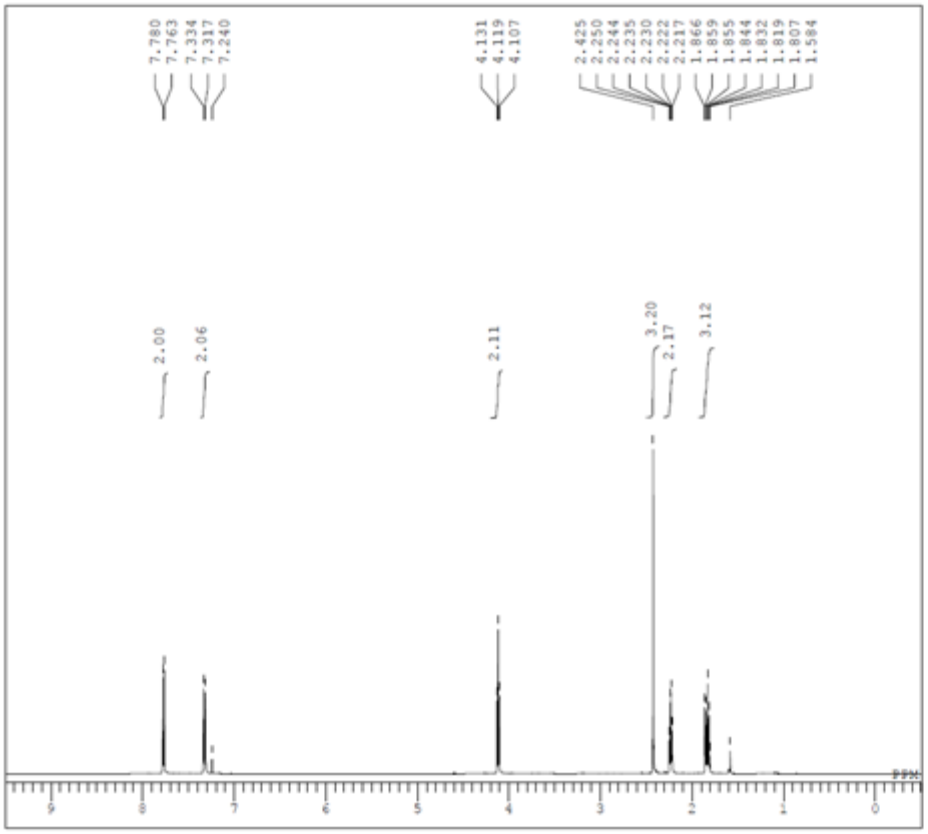


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OBFIN           6.01 Hz
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PD            4.0000 sec
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CTEMP           19.8 c
SLVNT   CDCL3
EXREF           7.24 ppm
BF              0.10 Hz
RGAIN             16
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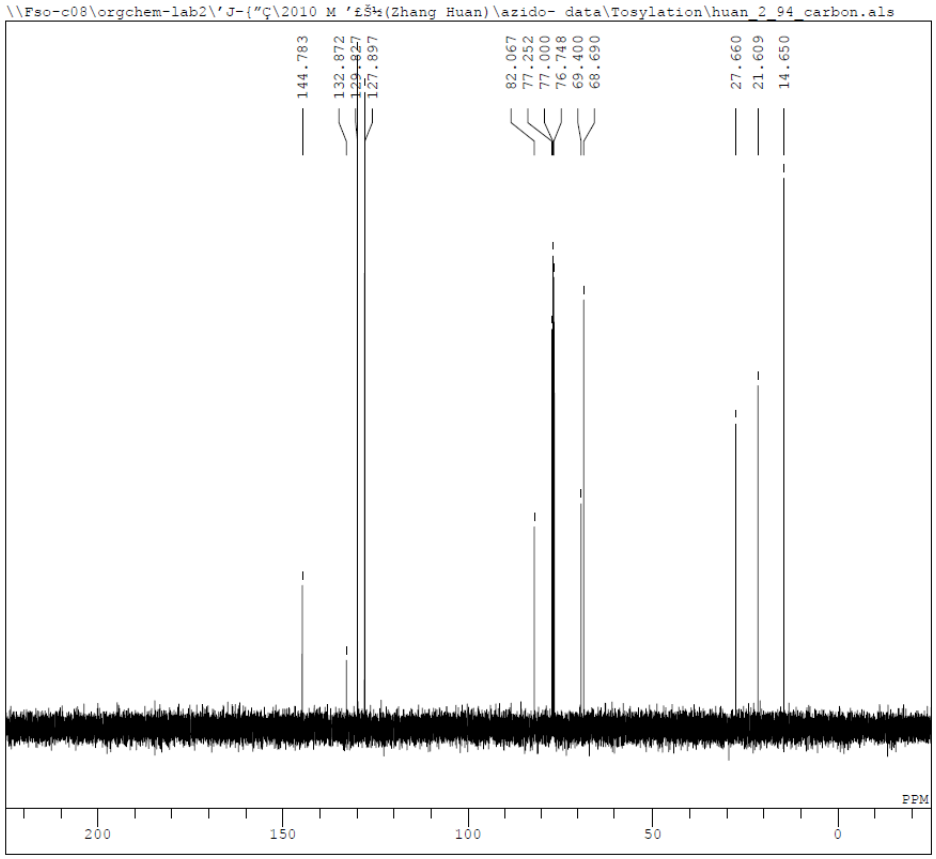
\\Fso-c08\orgchem-lab2\'J-{"Ç\2010 M 'ŁŠ½(Zhang Huan)\azido- data\Tosylation\huan_2_94_carbon.als

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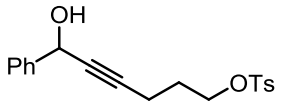

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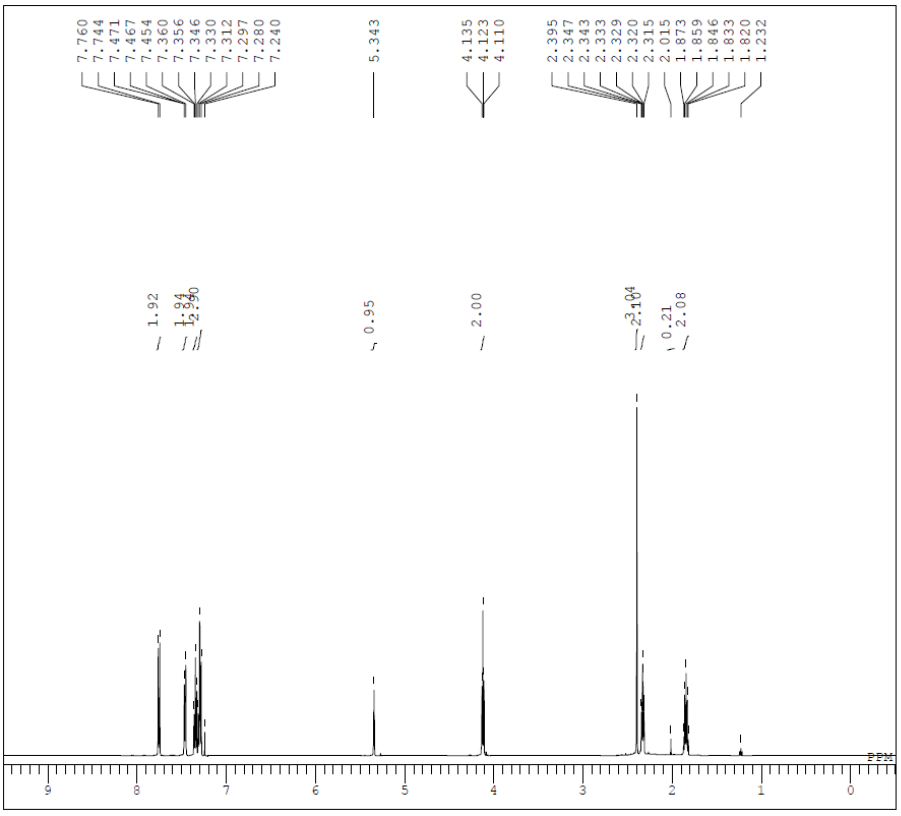


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CTEMP           20.3 c
SLVNT   CDCL3
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RGAIN             15
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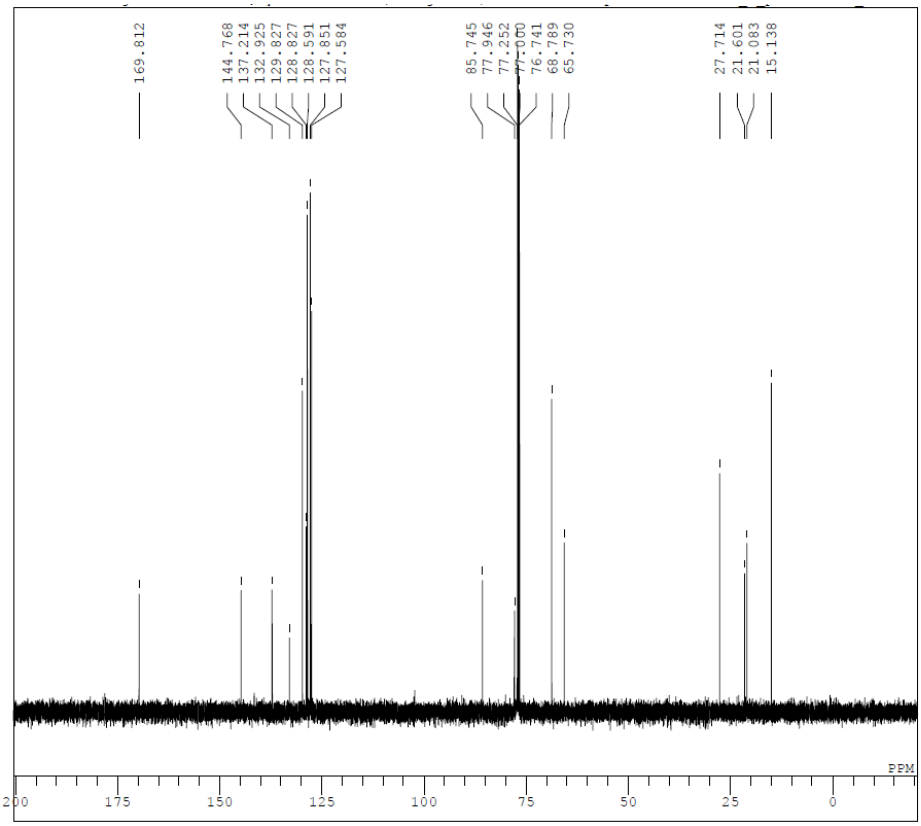


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PD            1.0000 sec
PW1             4.47 usec
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SLVNT   CDCL3
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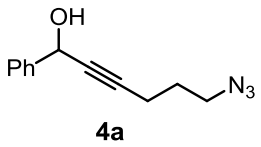
BF              0.10 Hz
RGAIN             30
```



4a

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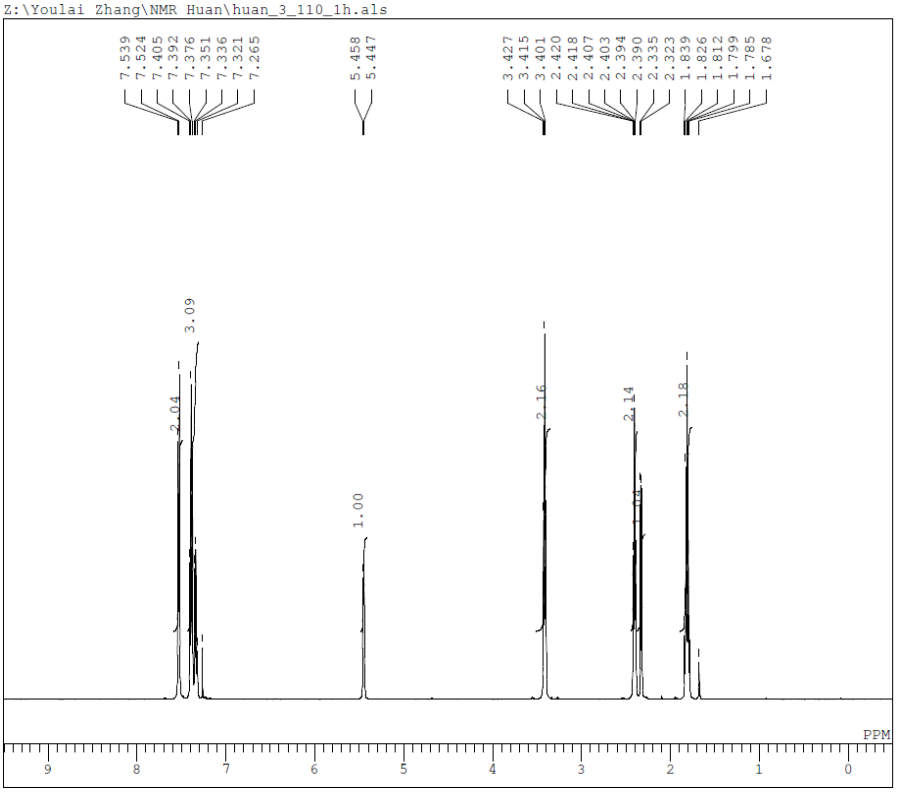


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IRNUC
CTEMP          20.2 c
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RGAIN            15
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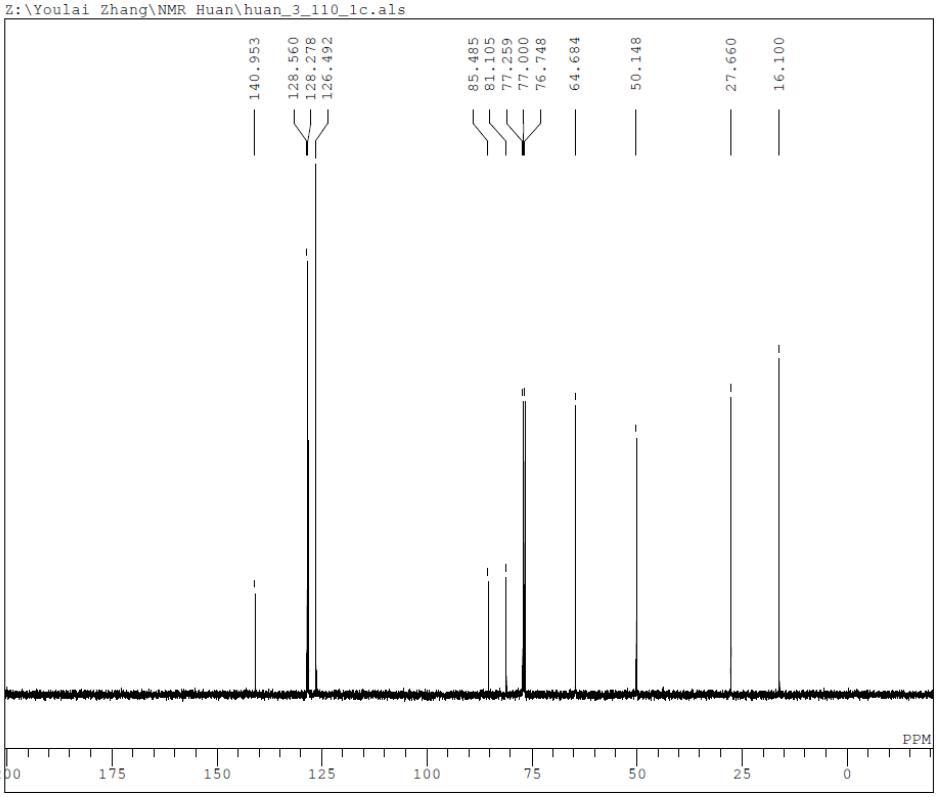
Z:\Youlai Zhang\NMR Huan\huan_3_110_1c.als

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PD           1.0000 sec
PW1            4.47 usec
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RGAIN            29
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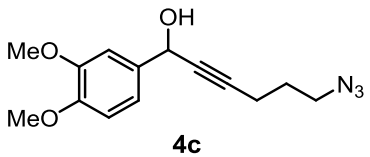

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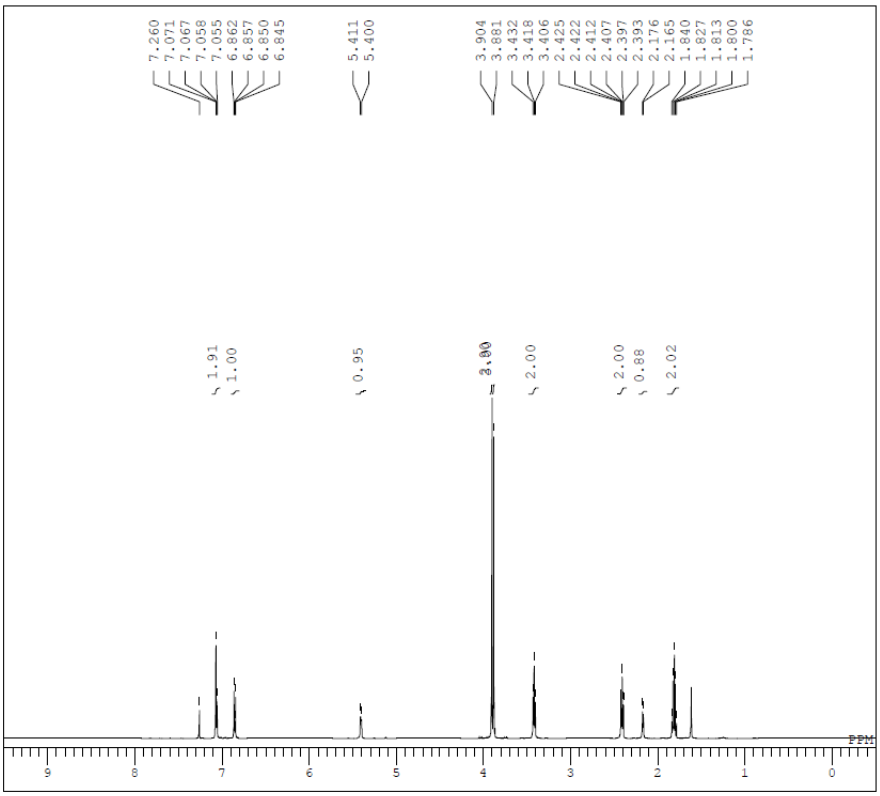


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CTEMP           20.7 c
SLVNT   CDCL3
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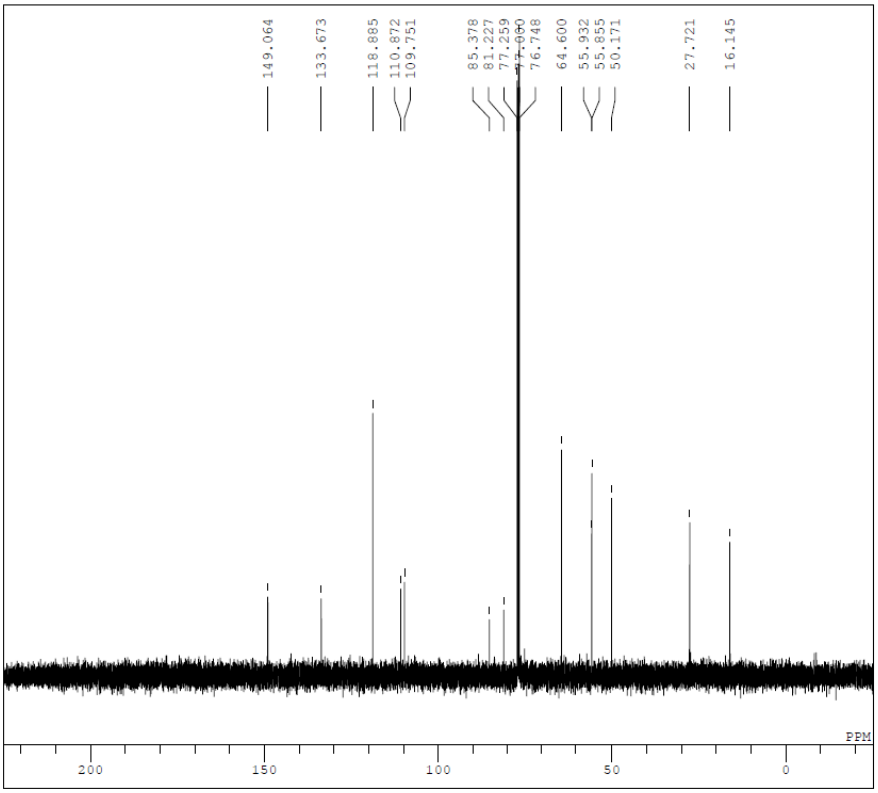
BF              0.10 Hz
RGAIN             19
```

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RGAIN             30
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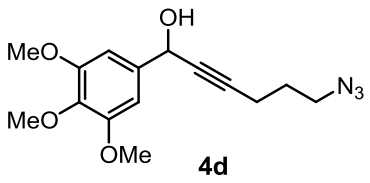

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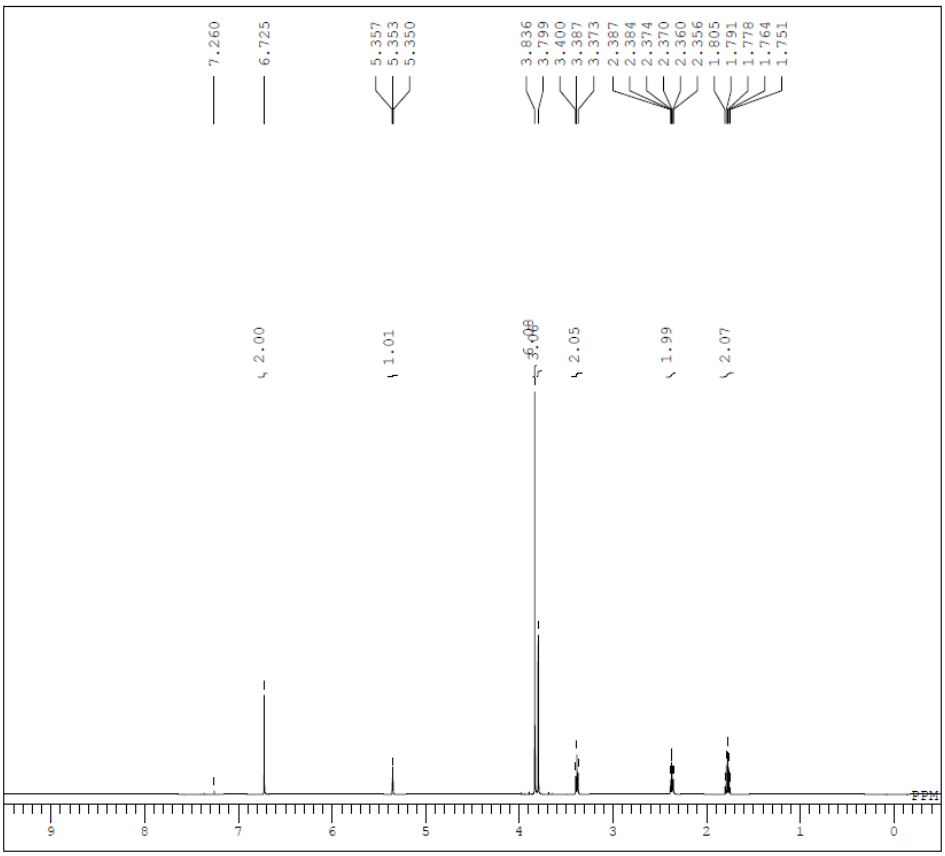


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EXREF           7.26 ppm
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RGAIN             13
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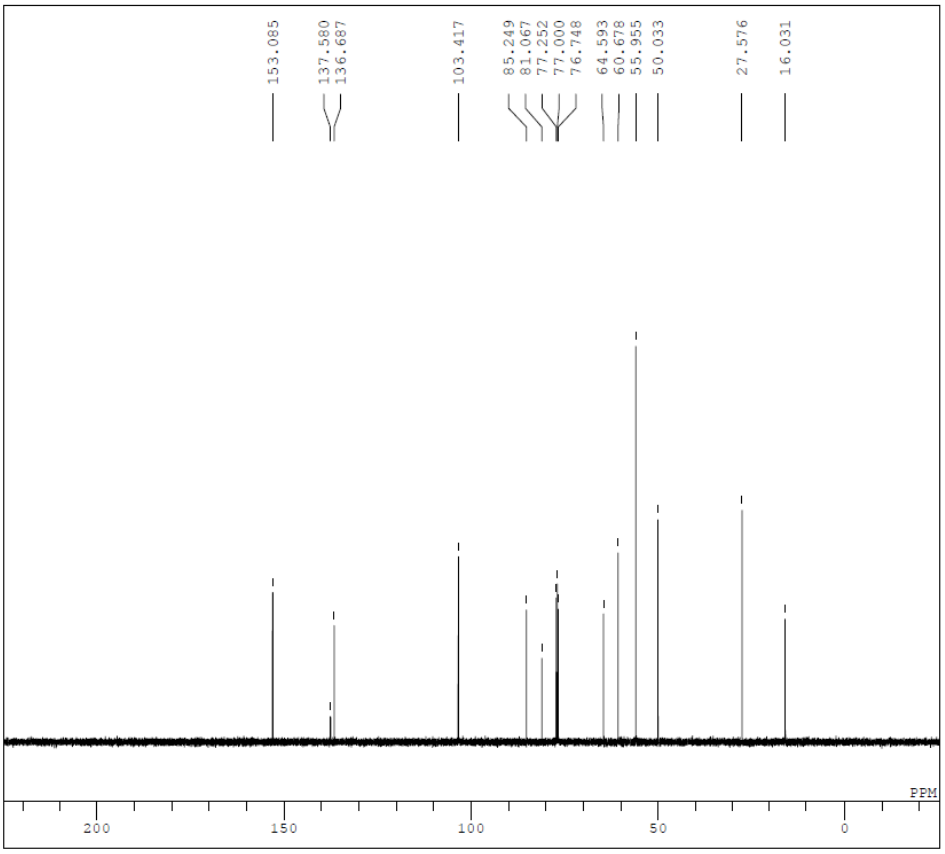


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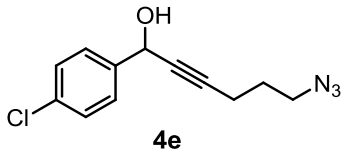

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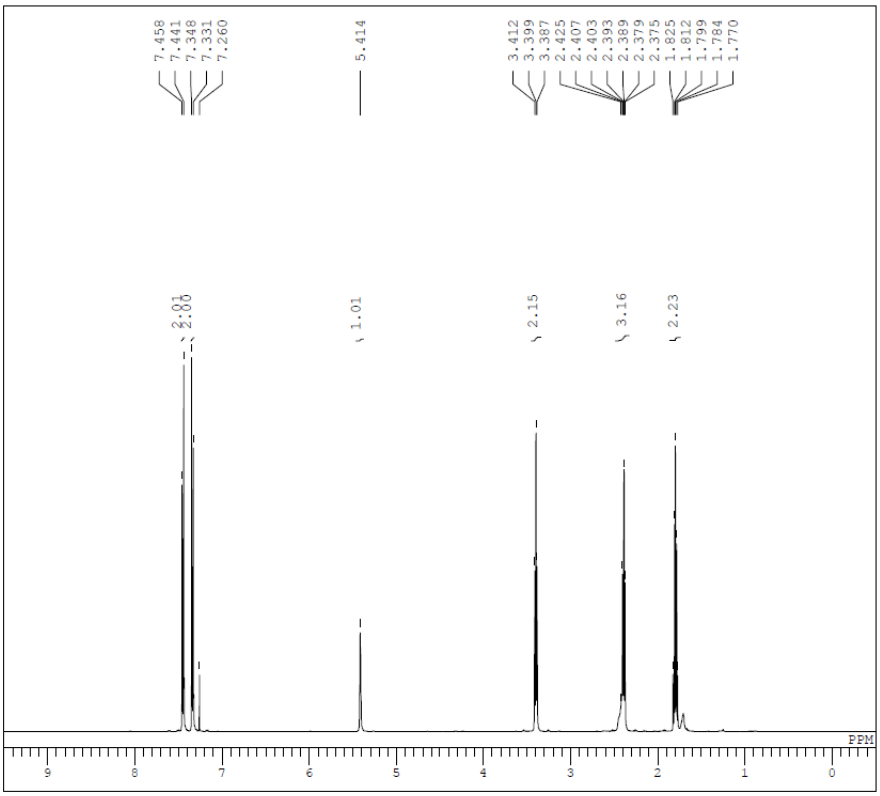


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POINT          16384
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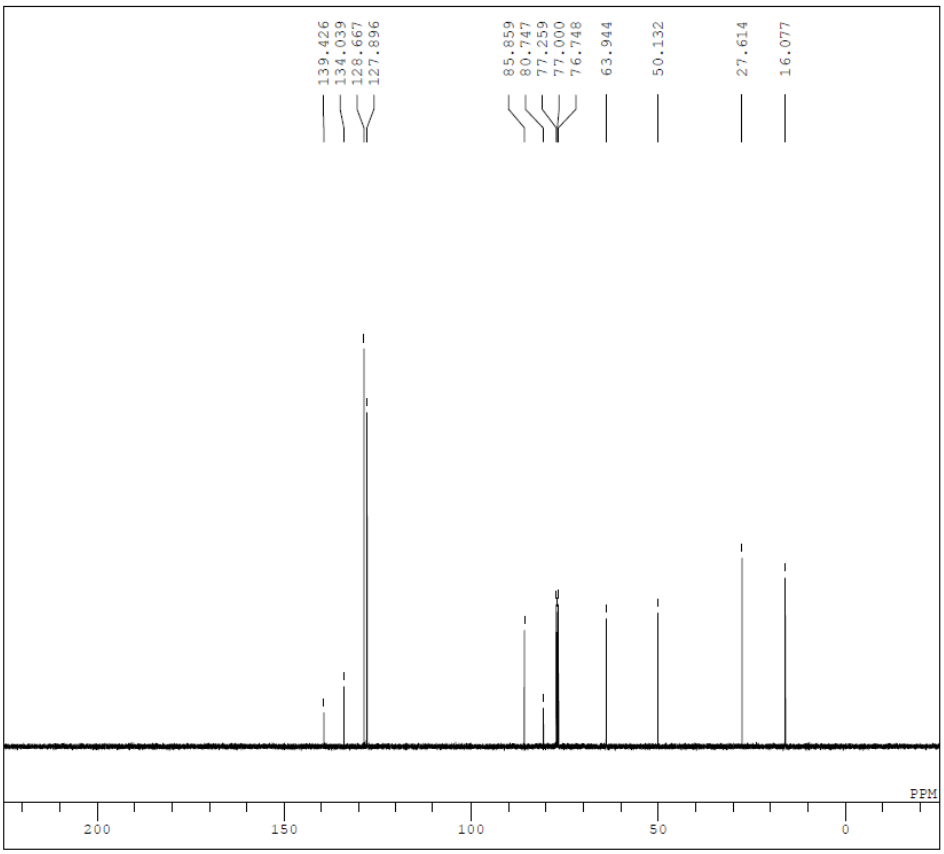
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           20.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             17
```

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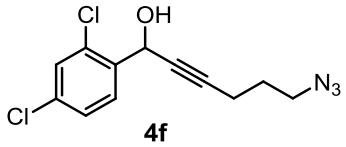
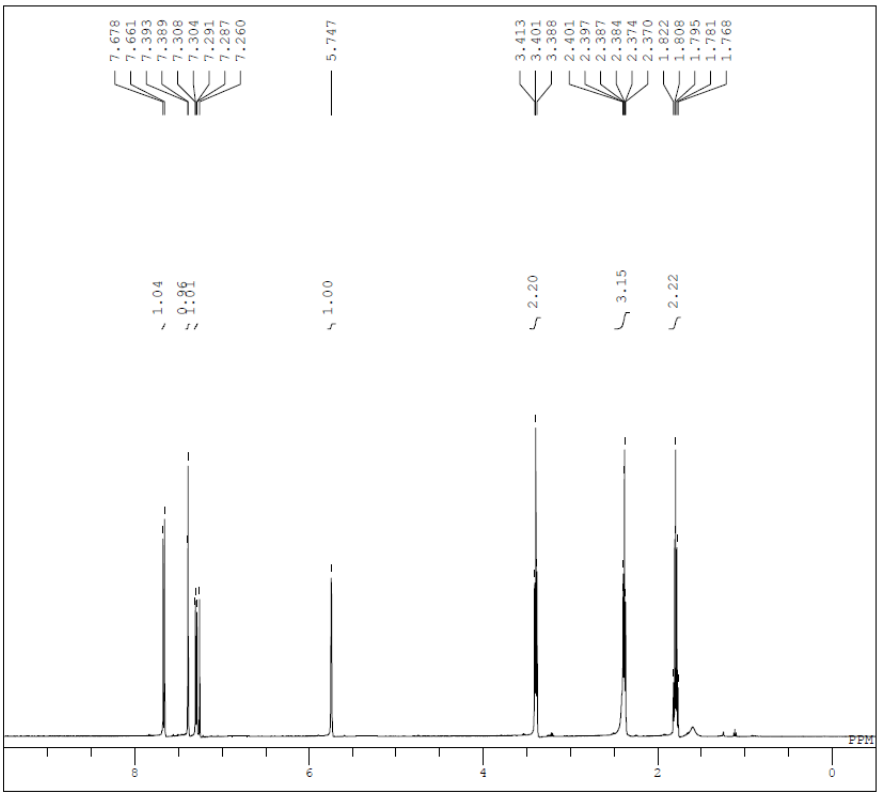
POINT          32768
FREQU       31446.54 Hz
SCANS            830
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           22.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



4f

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POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
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CTEMP           20.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             21
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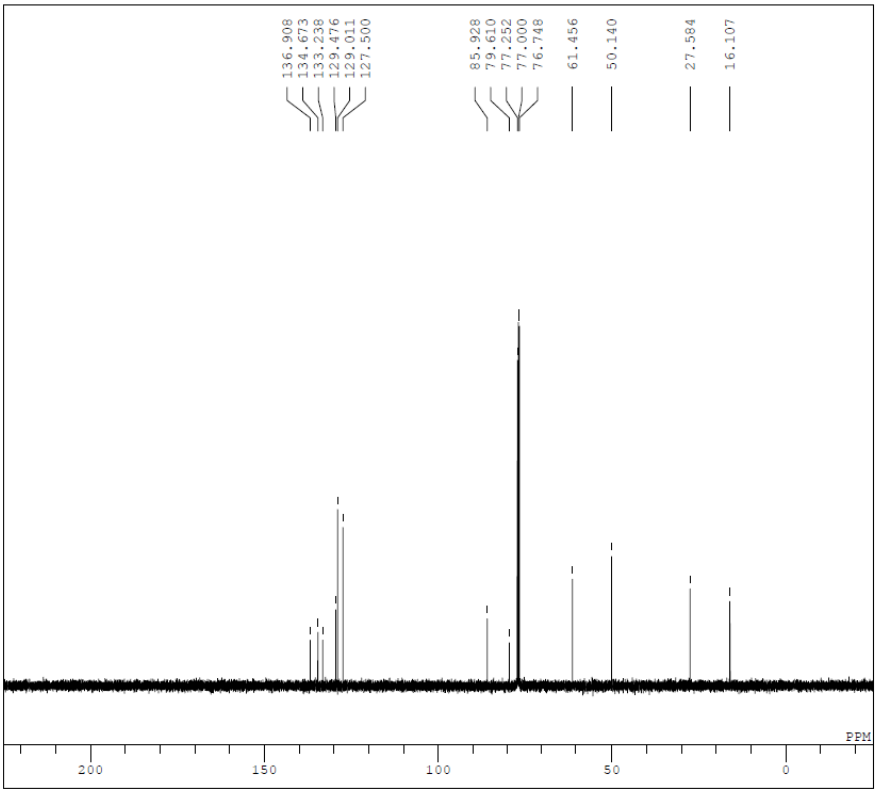


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FREQU       31446.54 Hz
SCANS            678
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PD            1.0000 sec
PW1             4.47 usec
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BF              0.10 Hz
RGAIN             30
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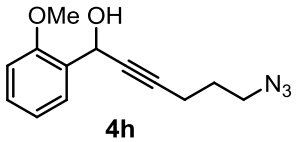

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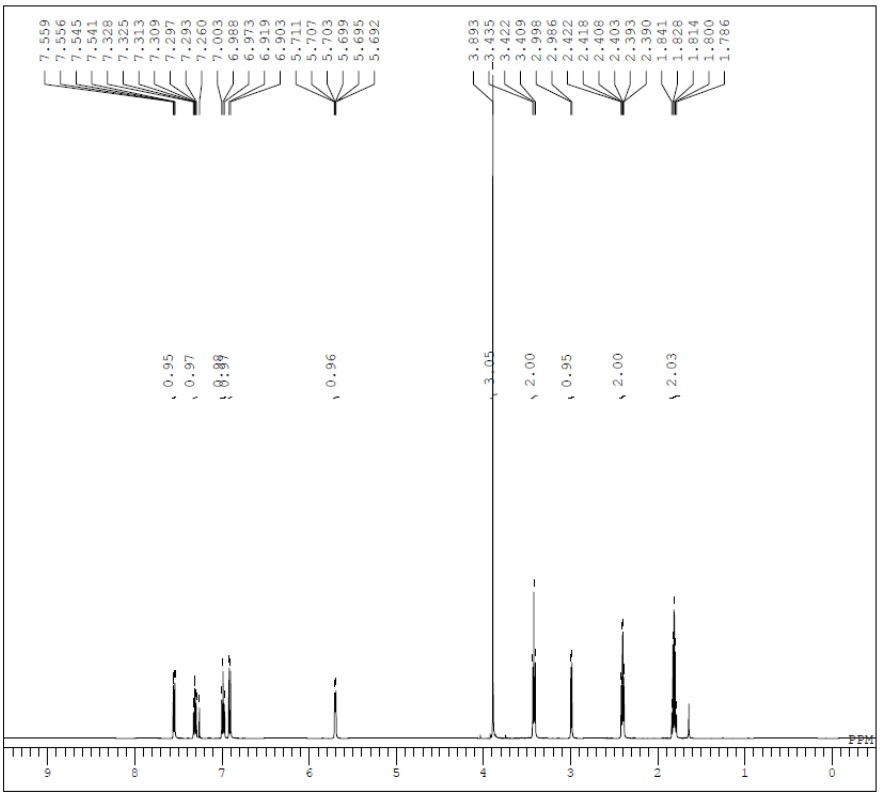


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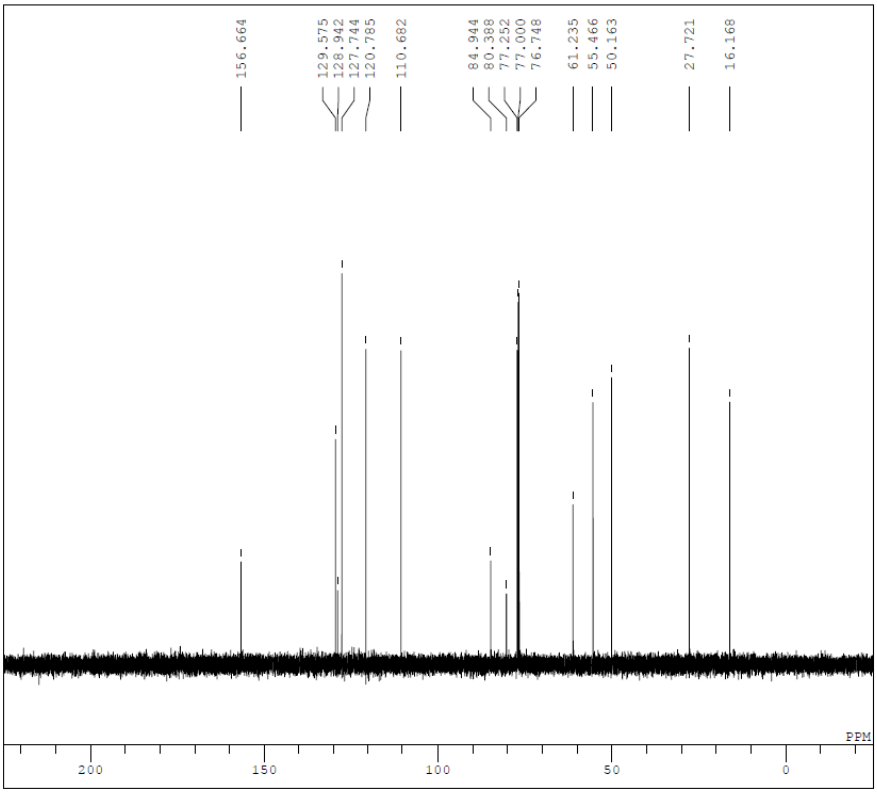
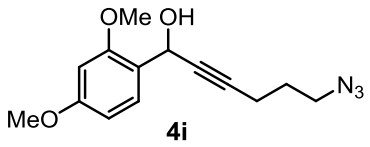
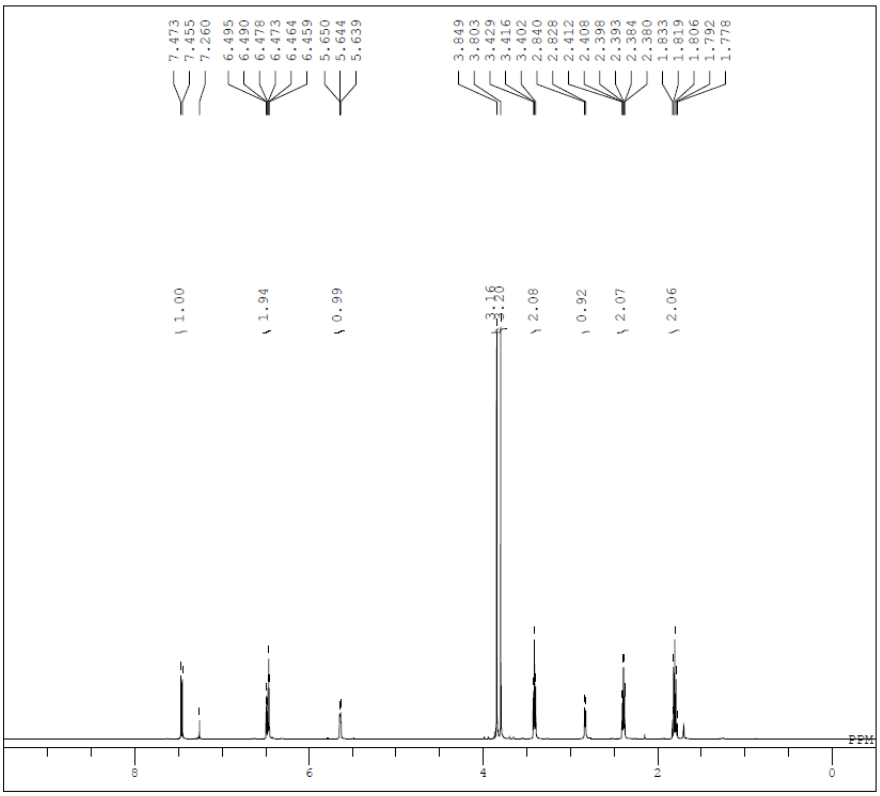
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           19.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             16
```



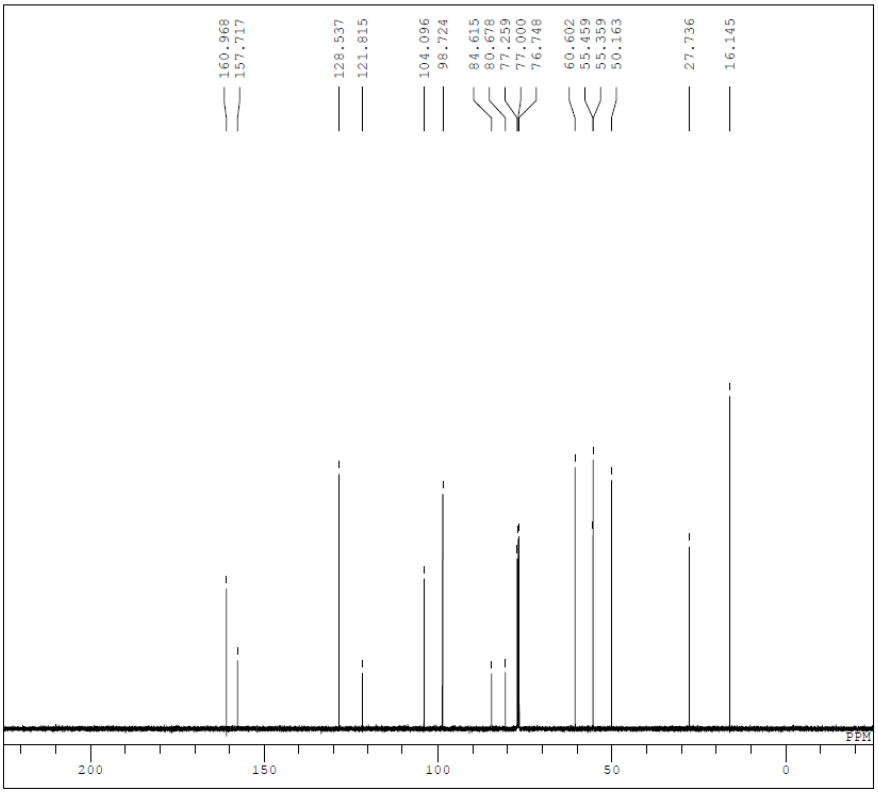

```
DFILE   huan_4_71_1_c13.als
COMNT   Single Pulse with Broadband Deco
DATIM   2012-05-08 11:32:46
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            200
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           19.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



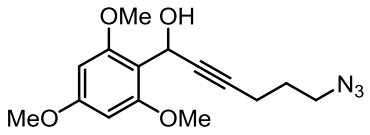
4i



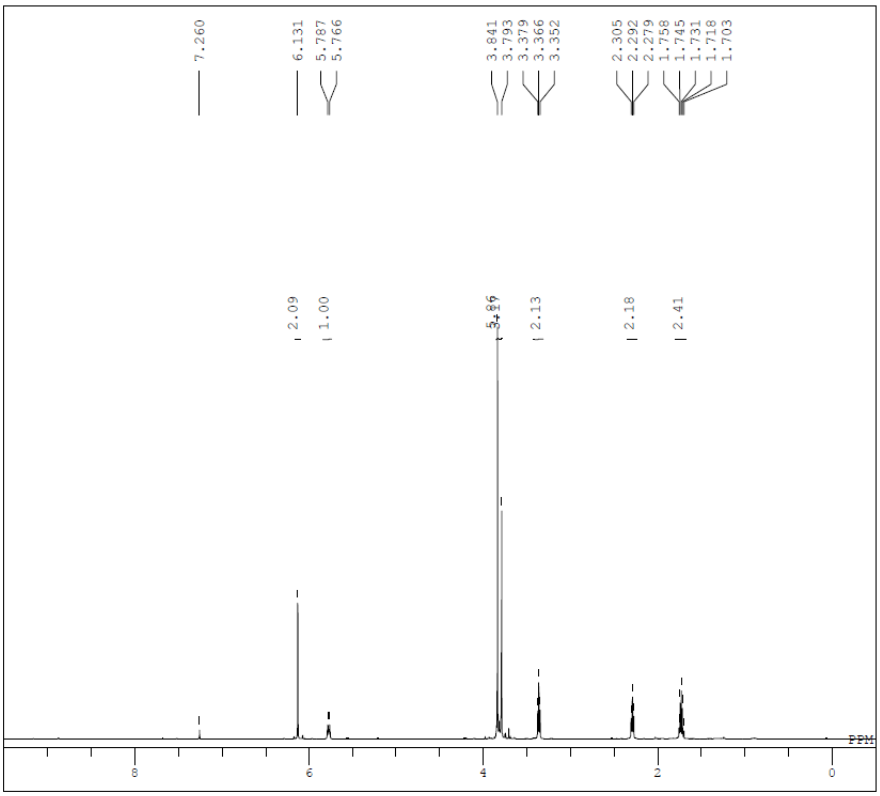

```
DFILE   huan_5_20_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-07-24 11:37:23
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC   1H
CTEMP           21.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             14
```



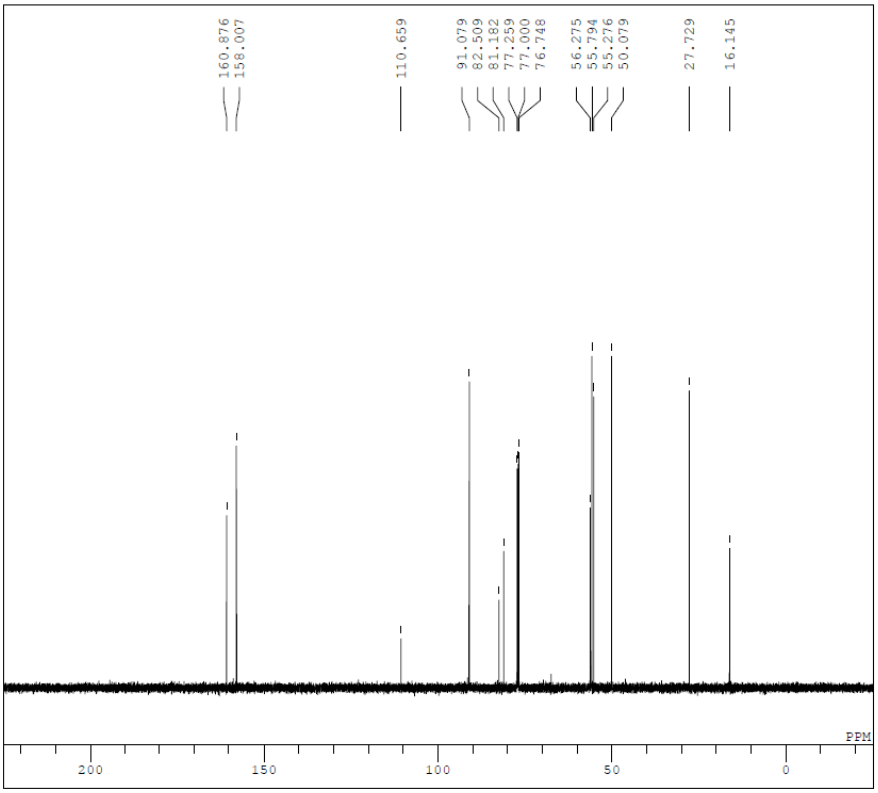

```
DFILE   huan_5_20_ic13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-07-24 12:30:57
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1200
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           23.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



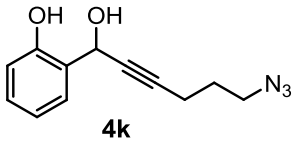
4j



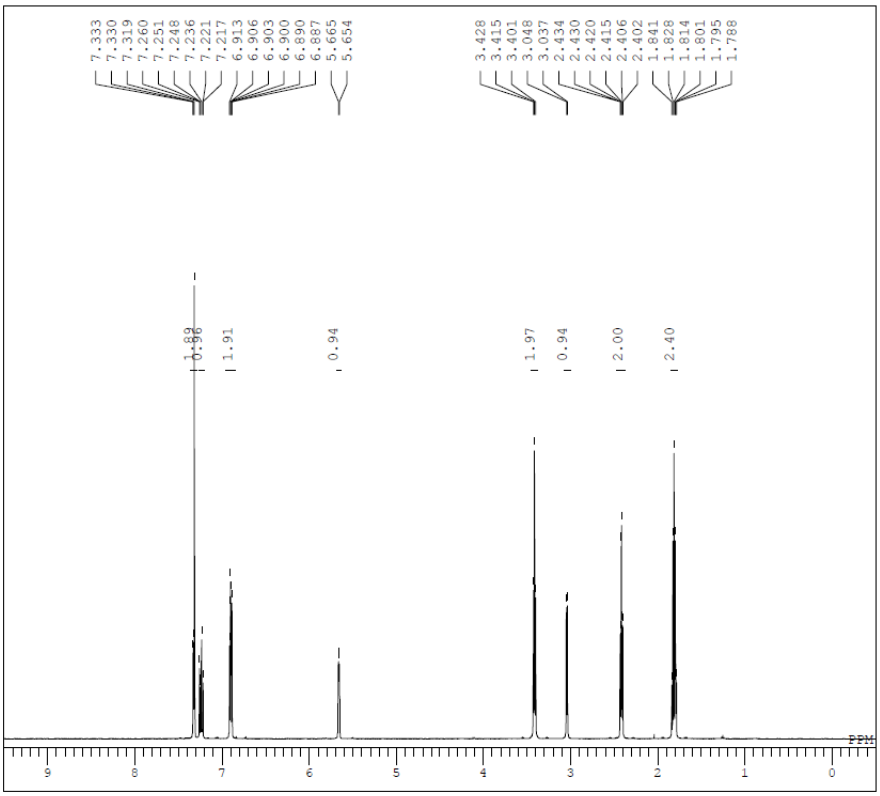

```
DFILE   huan_5_33_1_h.als
COMNT   Single Pulse Experiment
DATIM   2012-08-07 17:51:43
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC   1H
CTEMP           22.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             14
```



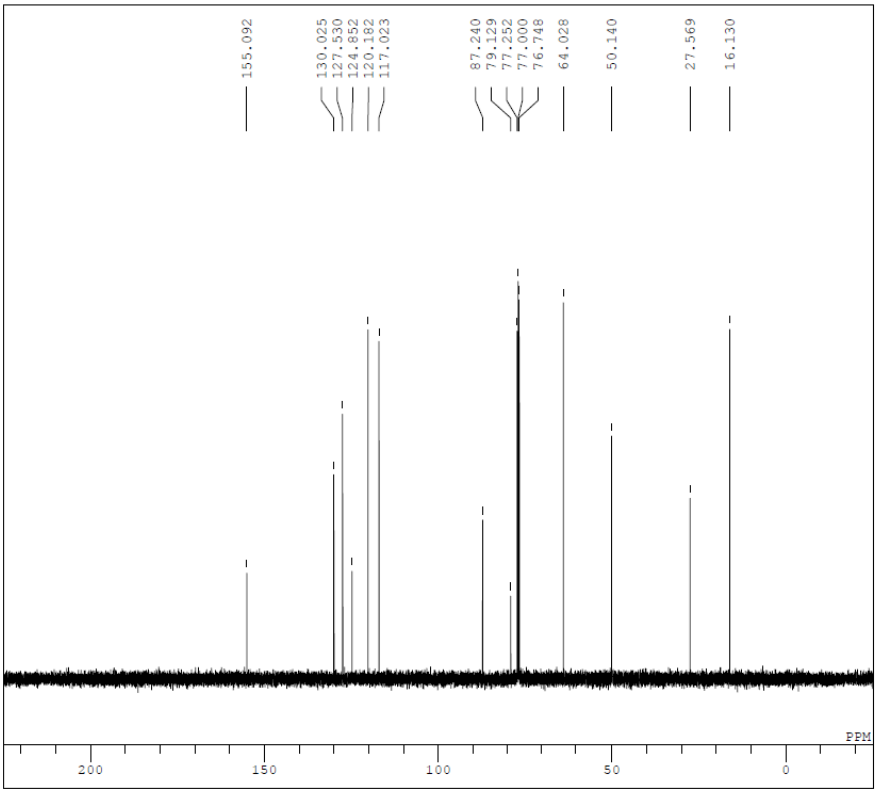

```
DFILE   huan_5_33_ic13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-08-07 18:23:34
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            395
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP           23.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



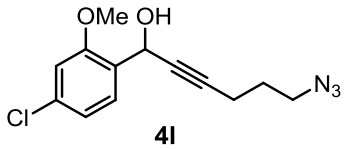
4k



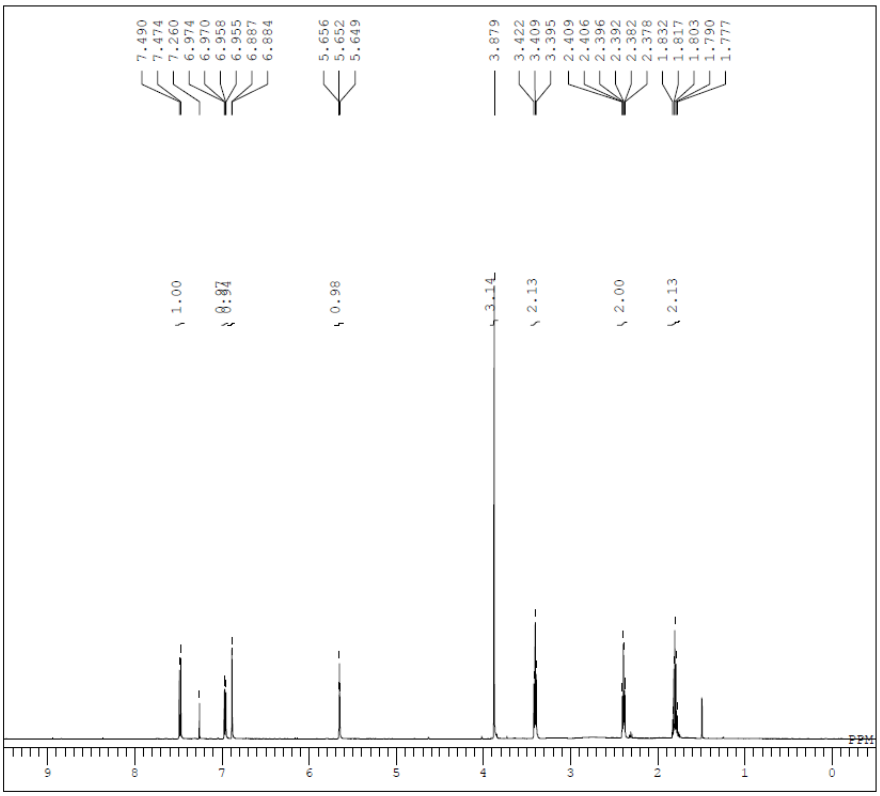

```
DFILE   huan_4_145_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-06-26 22:01:27
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           20.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             17
```



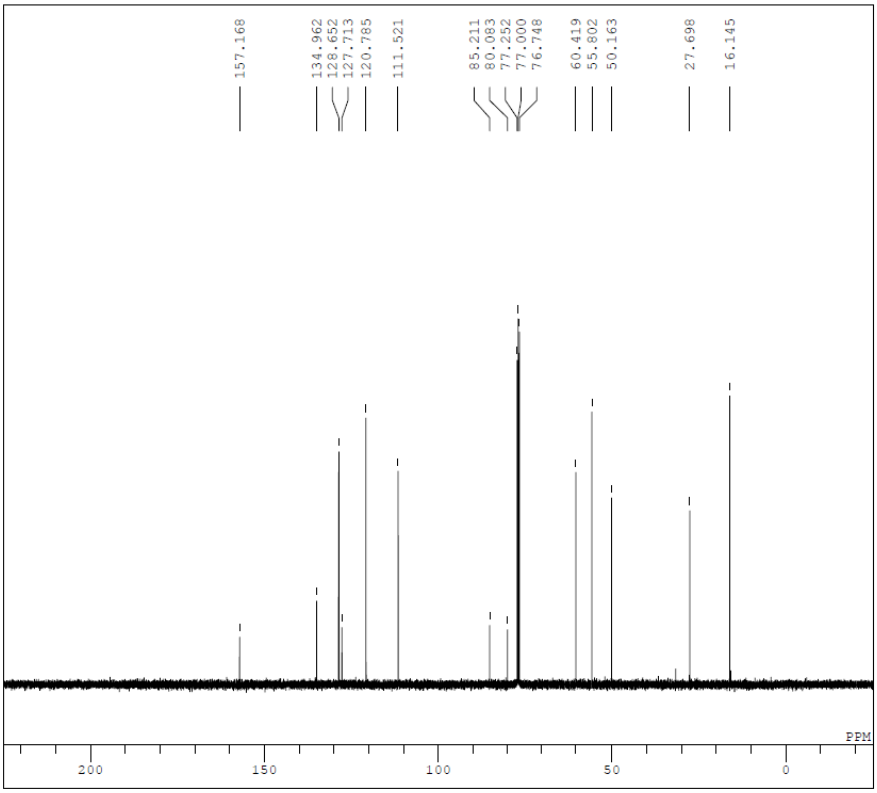

```
DFILE   huan_4_145_1C13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-06-26 22:27:10
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            416
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           22.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             29
```



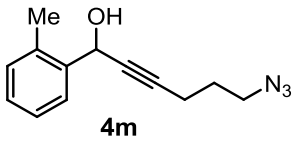
4l



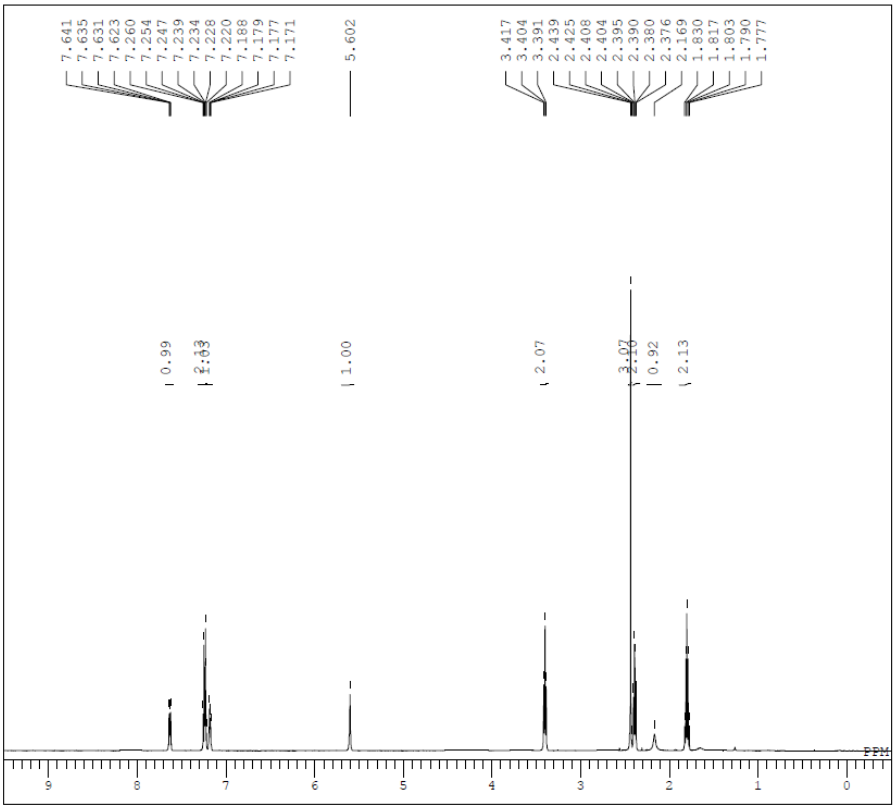

```
DFILE   huan_5_58_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-08-29 17:19:14
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC   1H
CTEMP           21.8 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             18
```



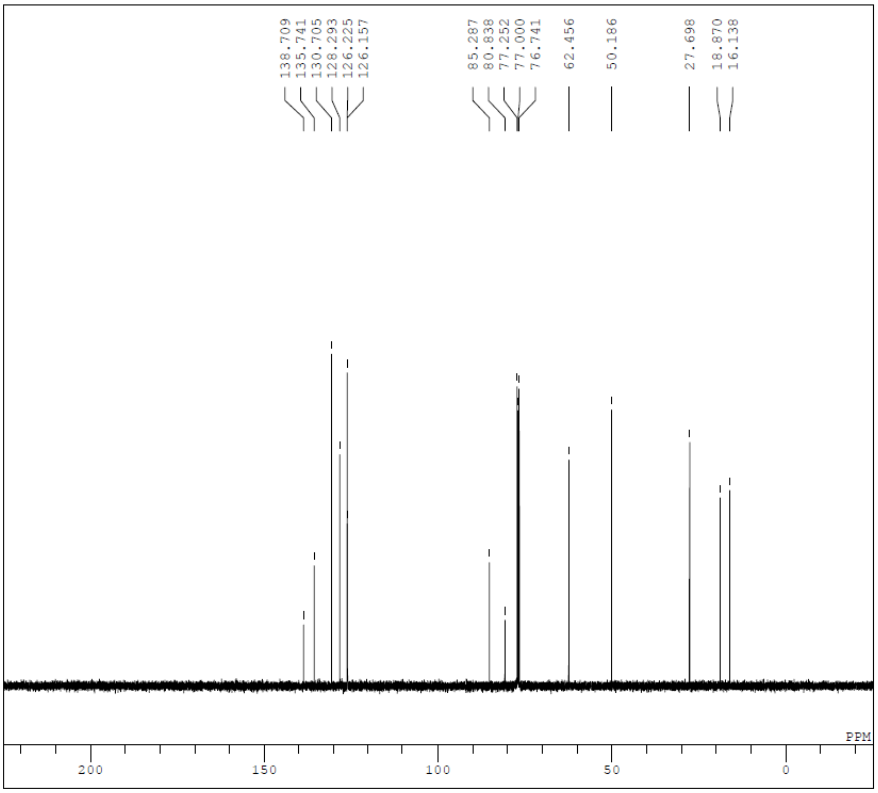

```
DFILE   huan_5_58_1c13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-08-29 18:10:36
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1055
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           23.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



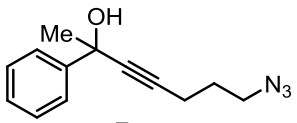
4m



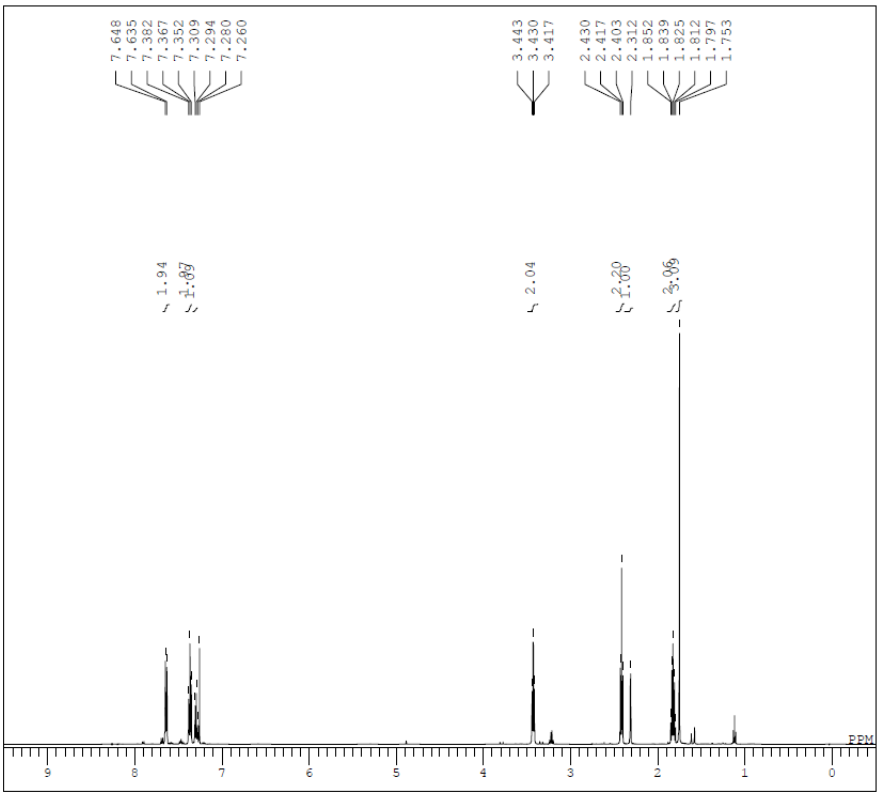

```
DFILE  huan_5_47_1h.als
COMNT  Single Pulse Experiment
DATIM  2012-08-21 17:21:32
OBNUC  1H
EXMOD  single_pulse.exp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU      10010.01 Hz
SCANS            16
ACQTM        1.6368 sec
PD           4.0000 sec
PW1            7.00 usec
IRNUC
CTEMP          22.3 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            17
```



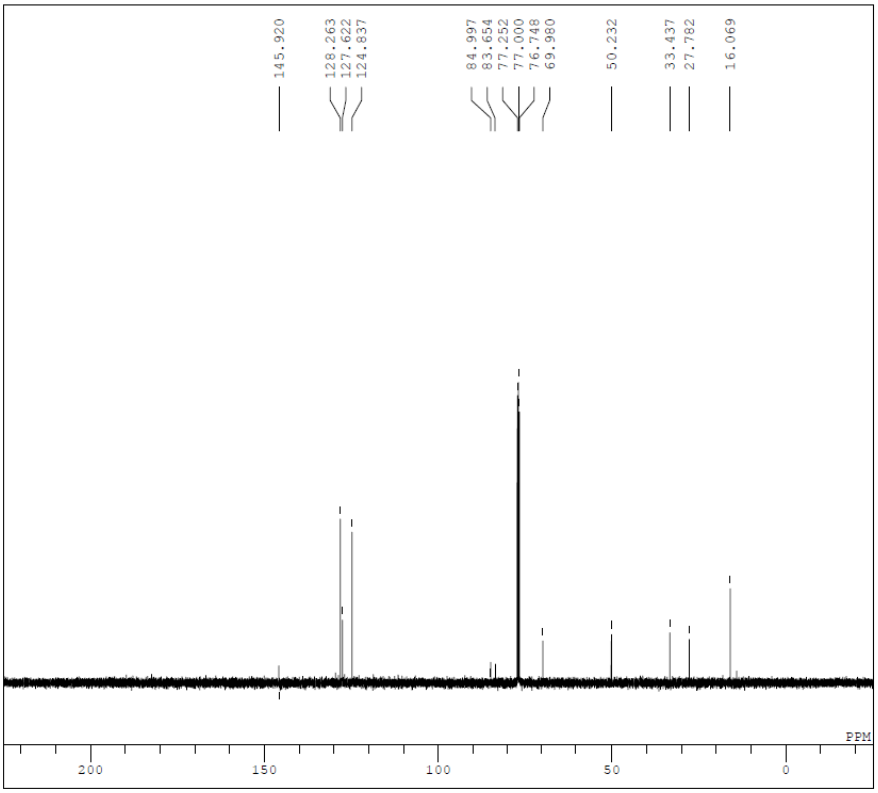

```
DFILE  huan_5_47_1c13.als
COMNT  Single Pulse with Broadband Decc
DATIM  2012-08-21 18:13:25
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32768
FREQU      31446.54 Hz
SCANS            906
ACQTM        1.0420 sec
PD           1.0000 sec
PW1            4.47 usec
IRNUC  1H
CTEMP          24.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            30
```



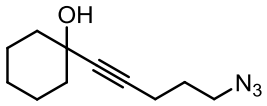
7a



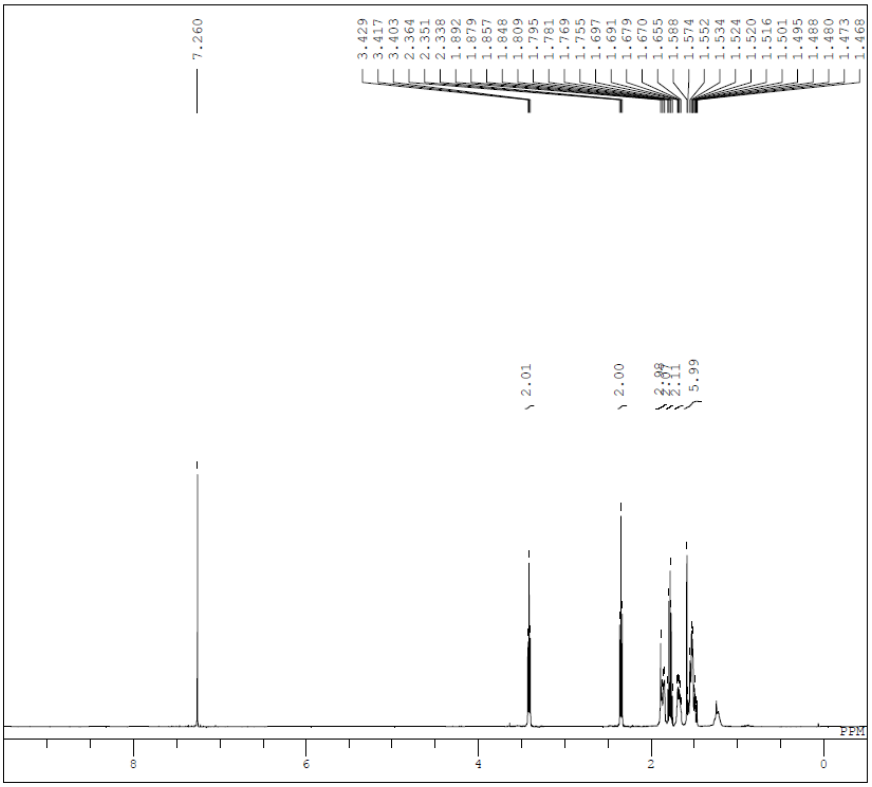

```
DFILE   huan_5_99_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-11-04 16:51:16
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           18.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             21
```



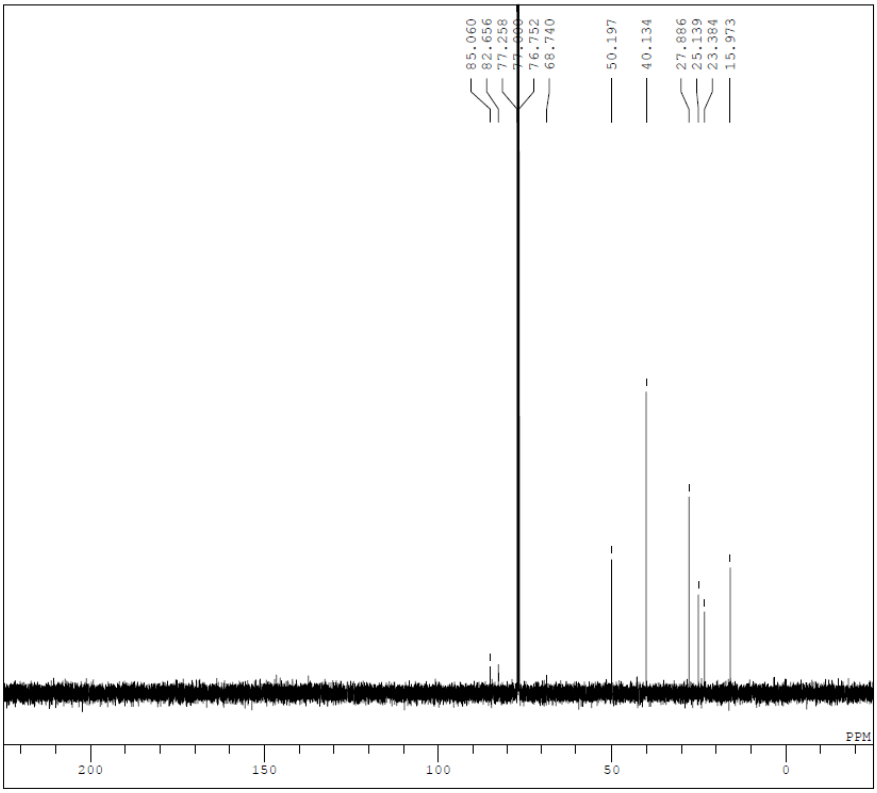

```
DFILE   huan_5_99_1c13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-11-04 17:17:21
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            736
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           19.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



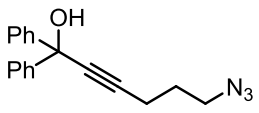
7b



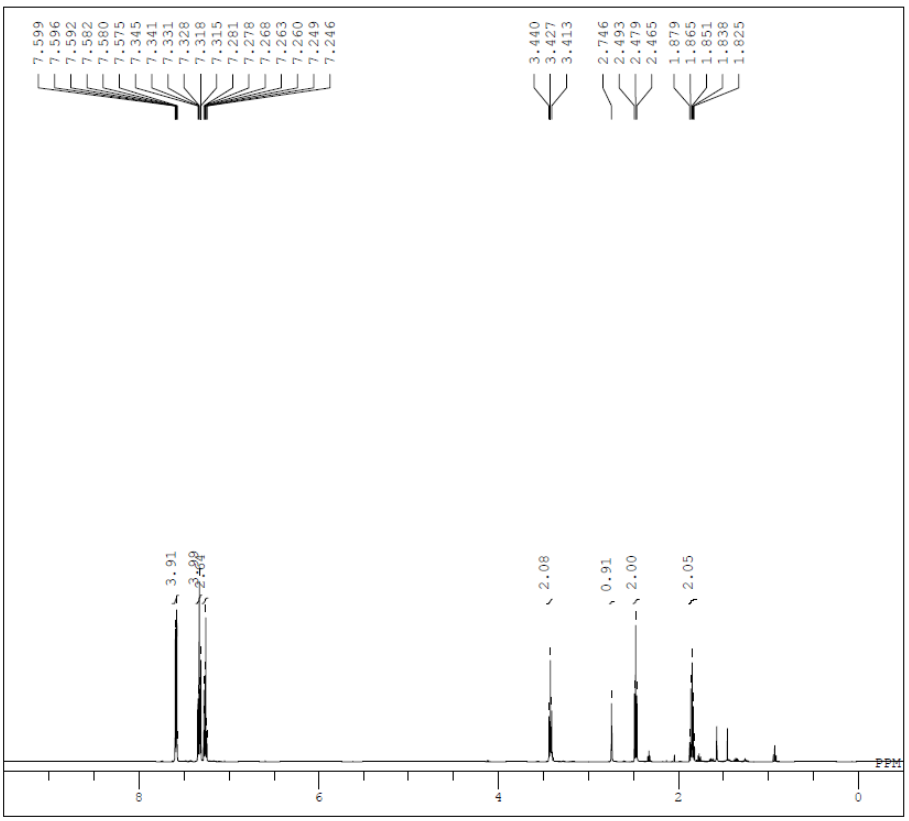

```
DFILE   huan_5_143_i_proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-01 22:31:59
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           15.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             44
```



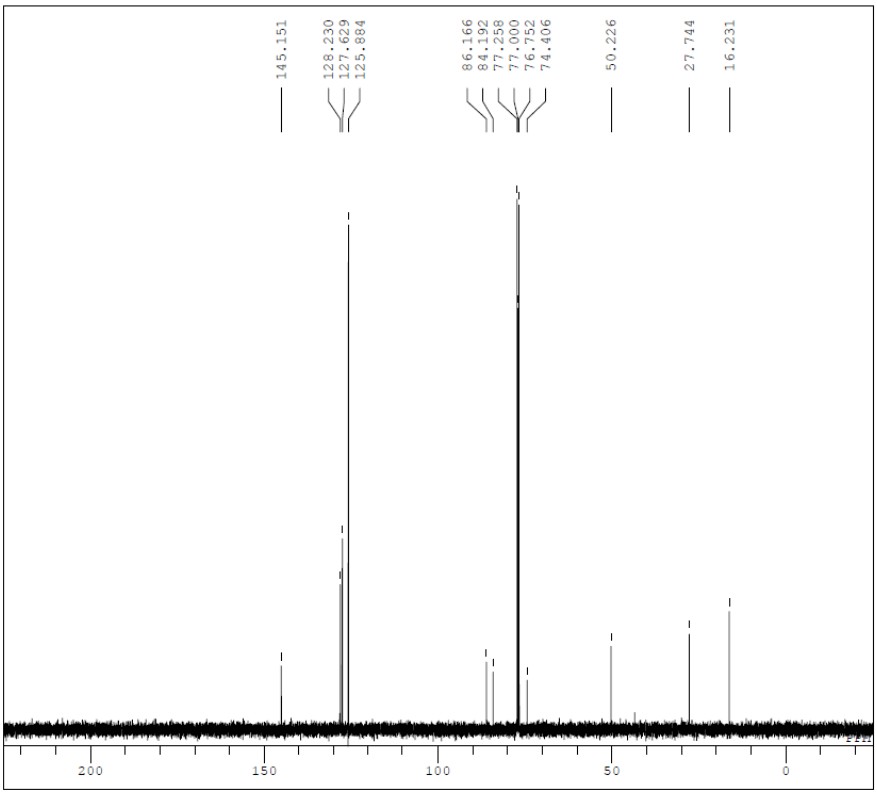

```
DFILE   huan_5_143_i_Carbon-1-1.als
COMNT   single_pulse_decoupled_gated_NOE
DATIM   2012-12-01 22:40:59
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU        31446.54 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           14.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             60
```



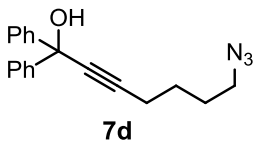
7c



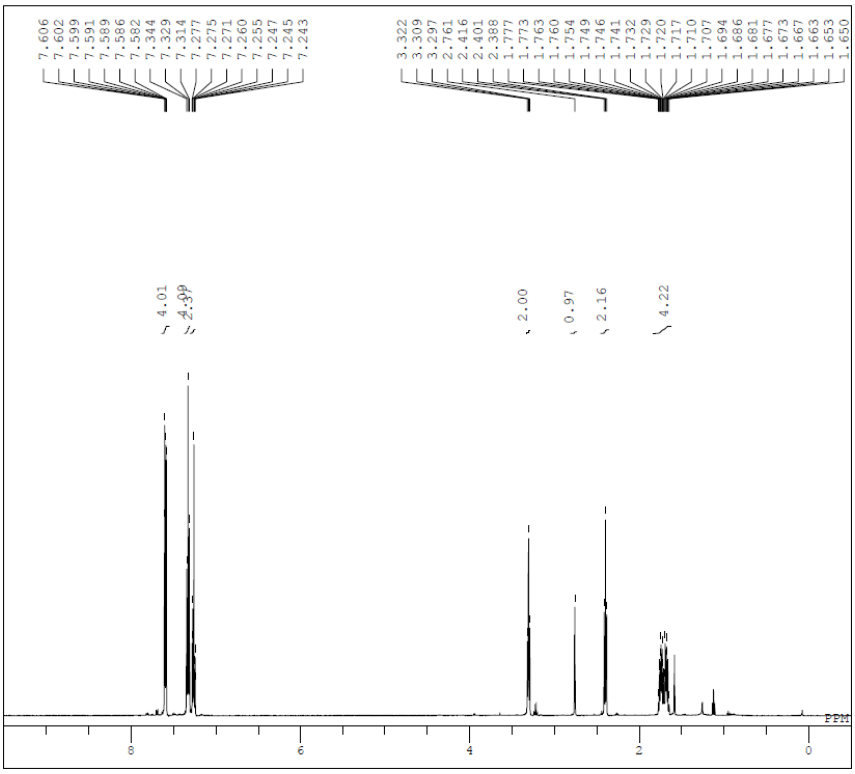

```
DFILE   HT5-47-1-1-1.jdf
COMNT   single_pulse
DATIM   2012-11-27 10:31:06
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            14.7 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              40
```



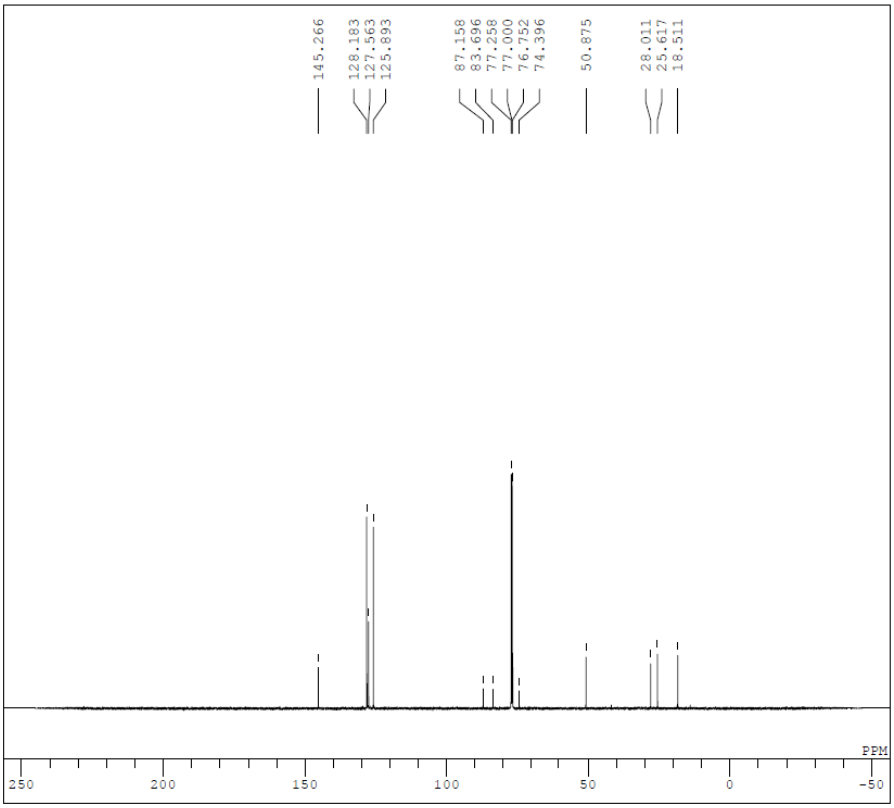

```
DFILE   HT5-47-1-2-1 carbon.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-27 10:33:25
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            107
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            15.2 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              60
```



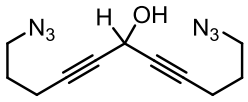
7d



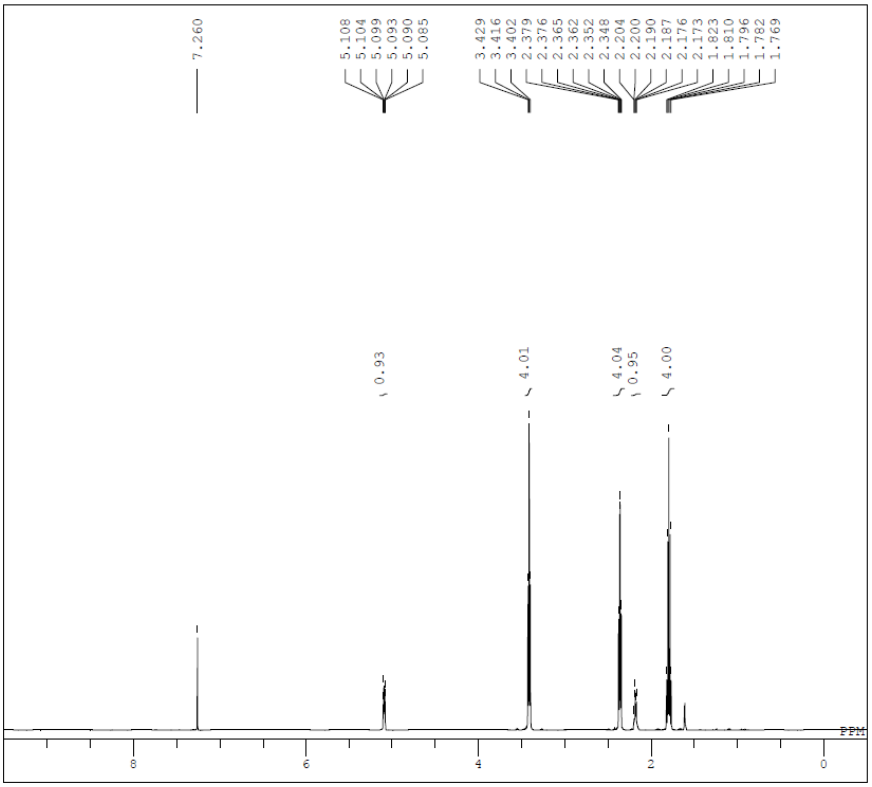

```
DFILE  huan_5_142_1_proton-1-2.als
COMNT  single_pulse
DATIM  2012-12-01 17:09:12
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          14.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            38
```



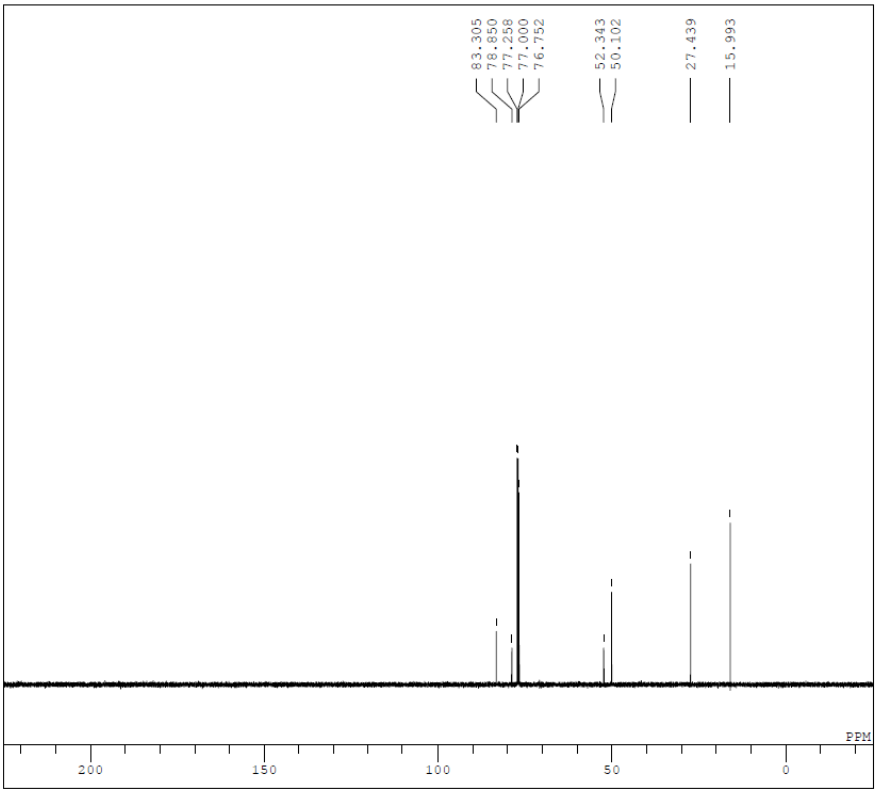

```
DFILE  huan_5_142_1_Carbon-1-2.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-01 17:30:11
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         40960
FREQU      49135.22 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC  1H
CTEMP          15.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



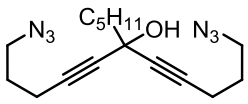
12a



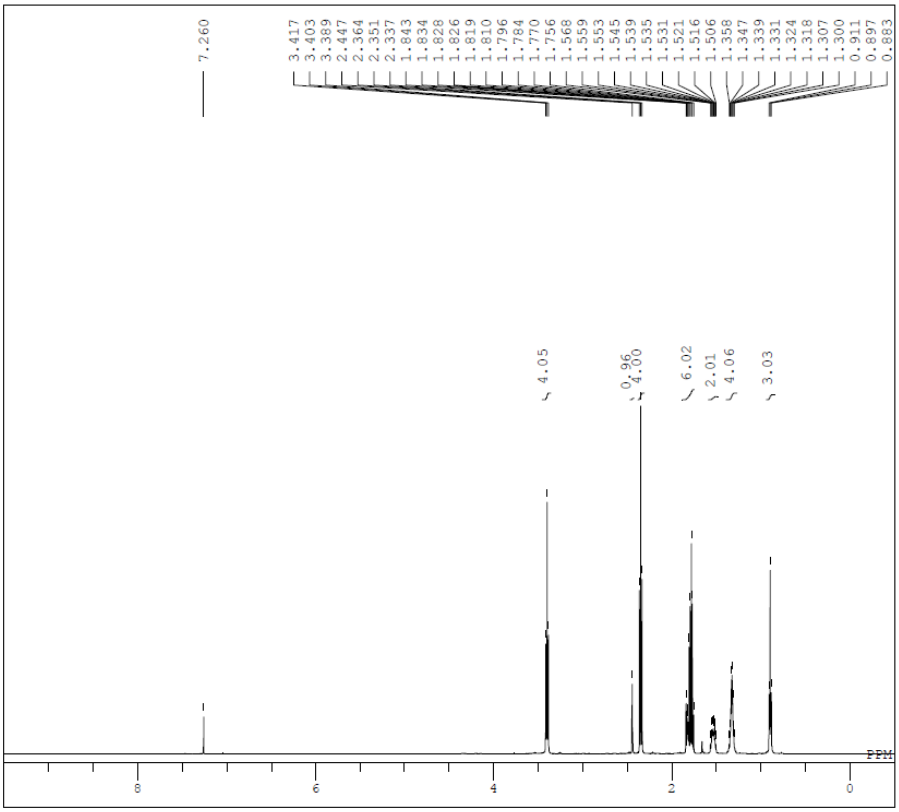

```
DFILE  huan_5_143_2_proton-1-1.als
COMNT  single_pulse
DATIM  2012-12-01 18:38:32
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          14.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            42
```



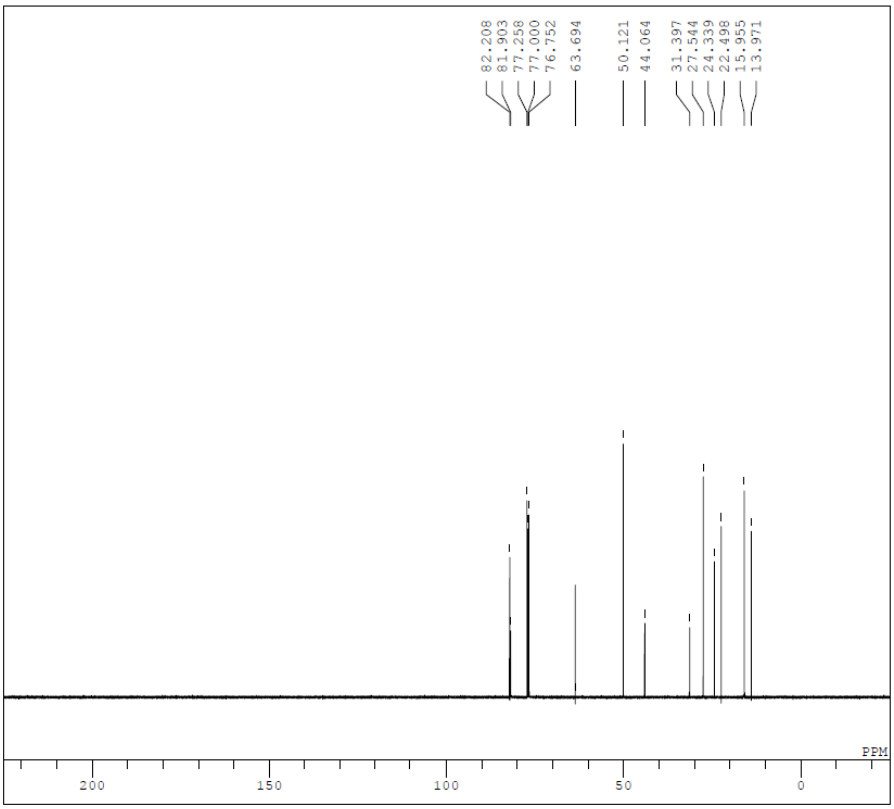

```
DFILE  huan_5_143_2_Carbon-1-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-01 18:54:09
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS           245
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC  1H
CTEMP          15.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



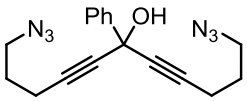
12b



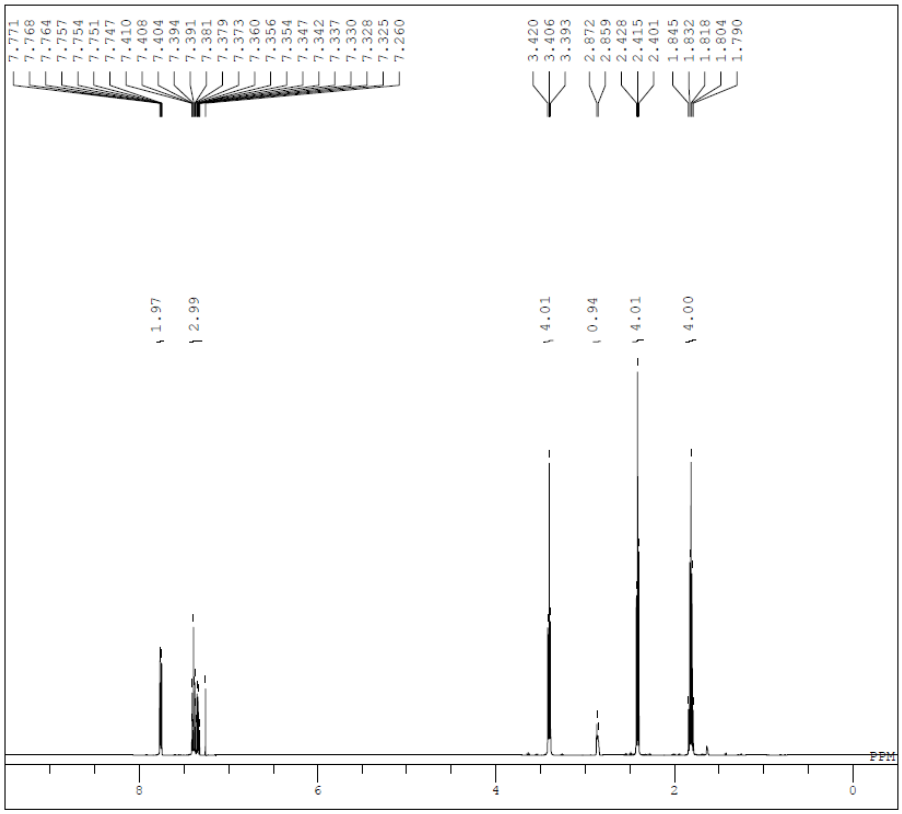

```
DFILE  huan_5_125_1h_proton-1-1.als
COMNT  single_pulse
DATIM  2012-11-24 12:22:17
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          15.2 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```



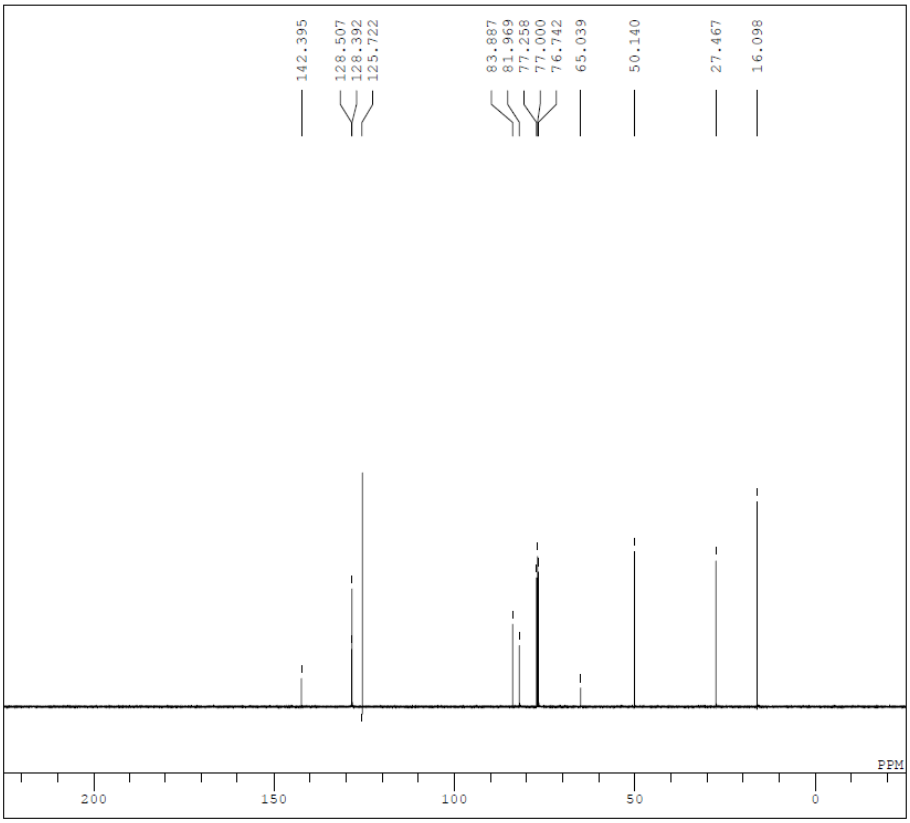

```
DFILE  huan_5_125_1h_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2012-11-24 12:53:53
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS           512
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          14.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



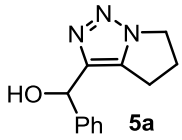
12c




```
DFILE   huan_5_122_1_proton-1-1.als
COMNT   single_pulse
DATIM   2012-11-21 11:56:34
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS               8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           16.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             34
```

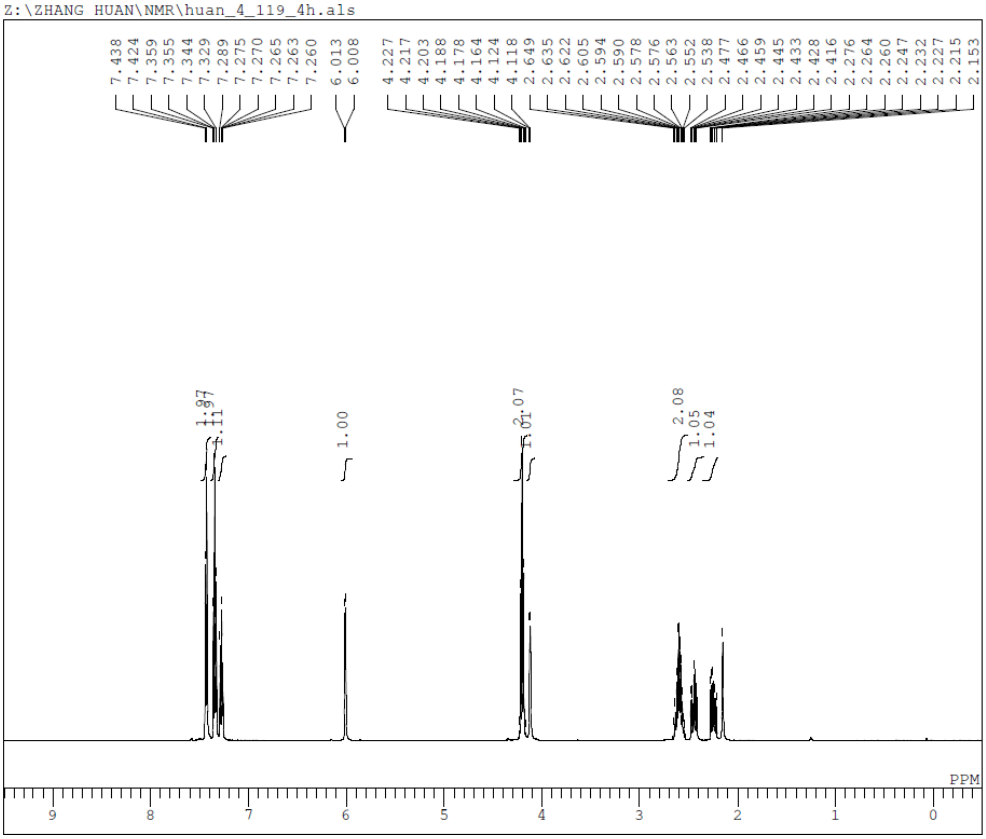



```
DFILE   huan_5_122_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-21 12:28:09
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           15.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             60
```



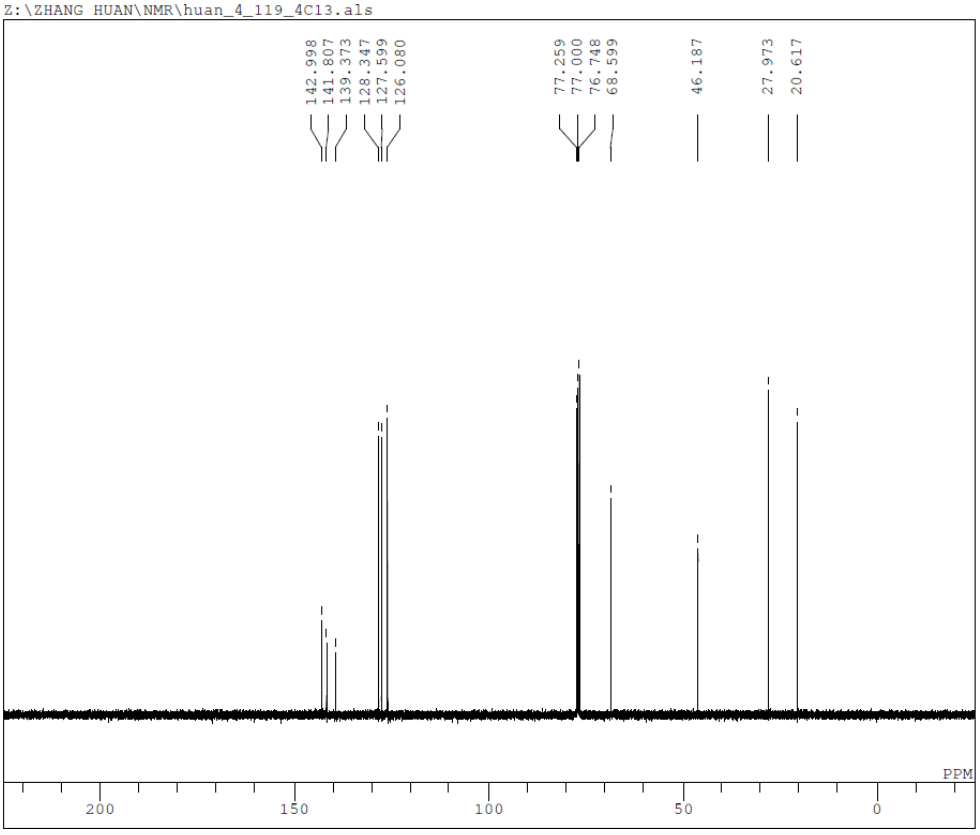
5a

Z:\ZHANG HUAN\NMR\huan_4_119_4h.als

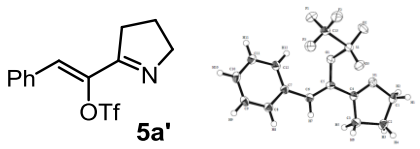



```
DFILE   huan_4_119_4h.als
COMNT   Single Pulse Experiment
DATIM   2012-06-04 21:50:03
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           20.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             17
```

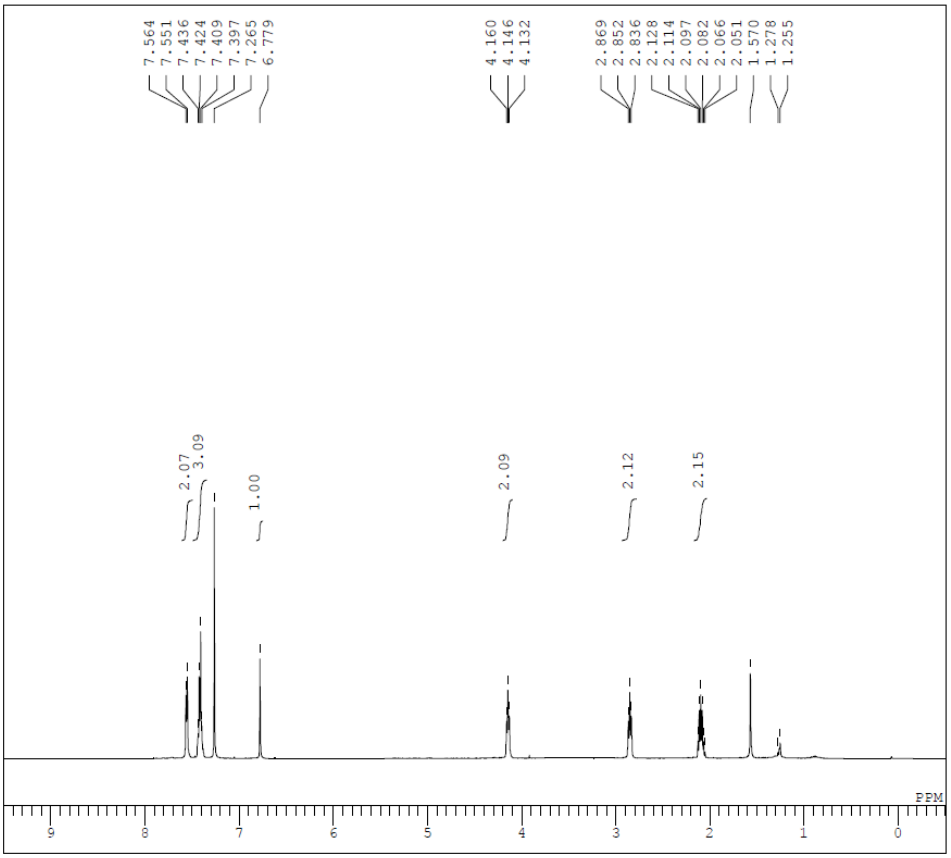
Z:\ZHANG HUAN\NMR\huan_4_119_4C13.als




```
DFILE   huan_4_119_4C13.als
COMNT   Single Pulse with Broadband De
DATIM   2012-06-05 11:28:01
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            844
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           22.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```

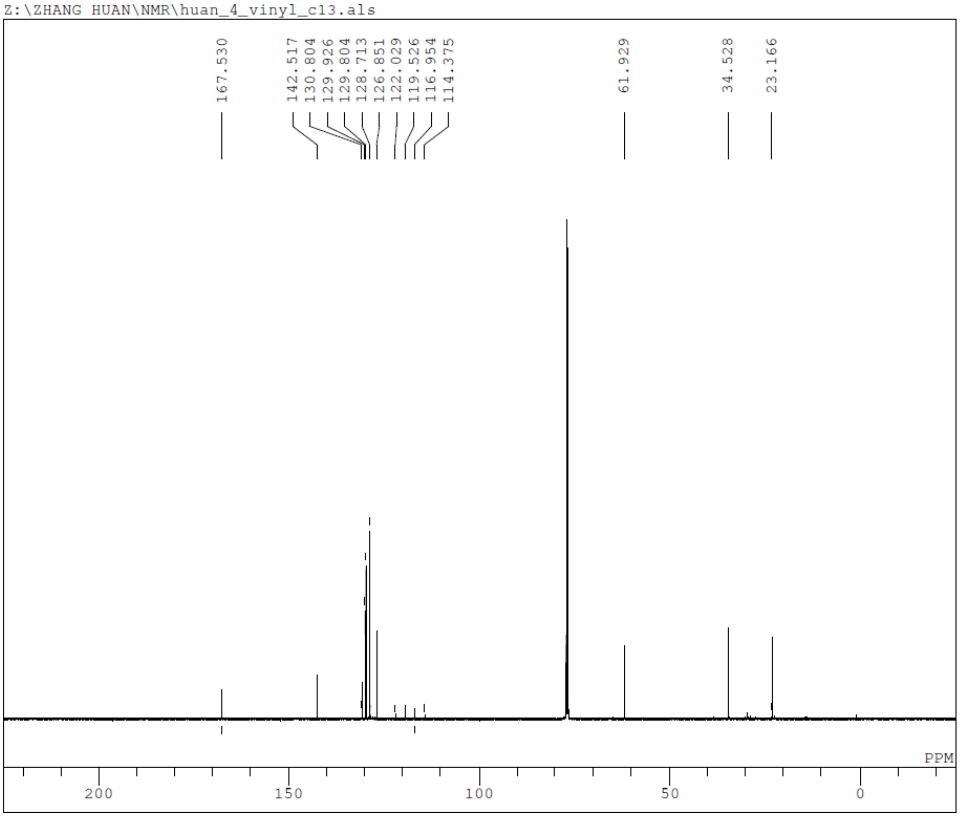


5a'

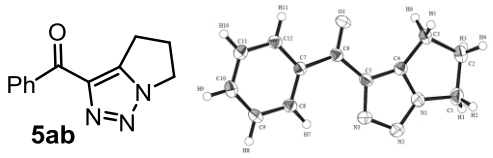


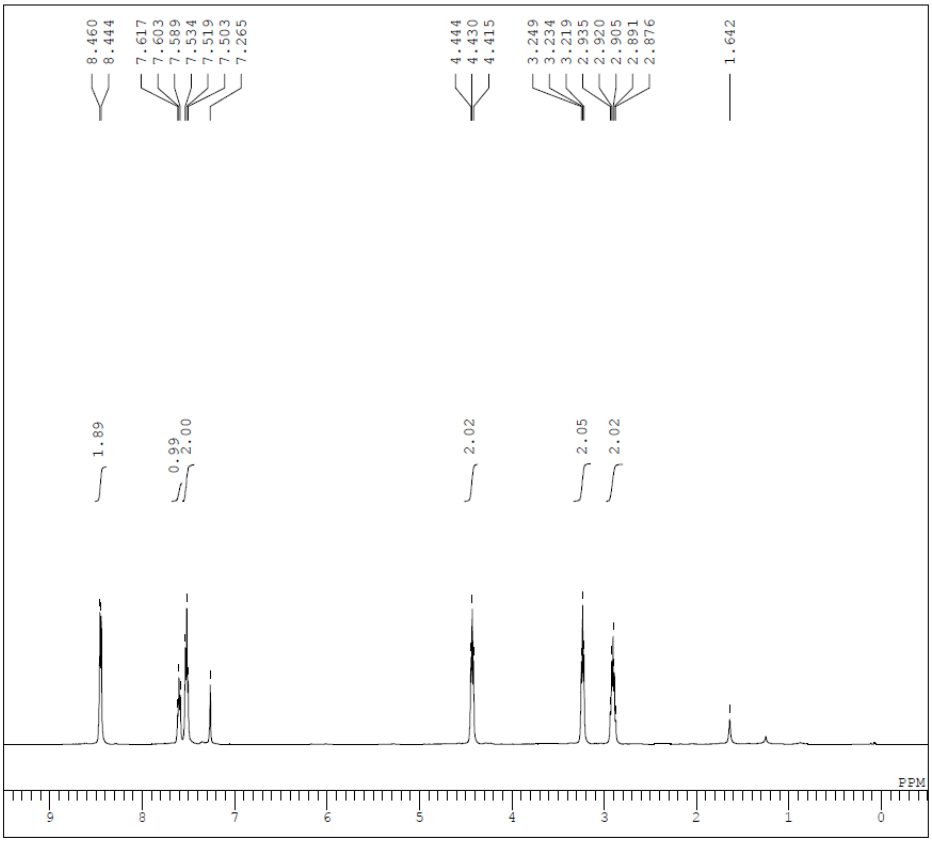

```
DFILE   huan_3_OTf_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-01-27 20:31:39
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             32
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            18.6 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               1.00 Hz
RGAIN              24
```

Z:\ZHANG HUAN\NMR\huan_4_vinyl_c13.als



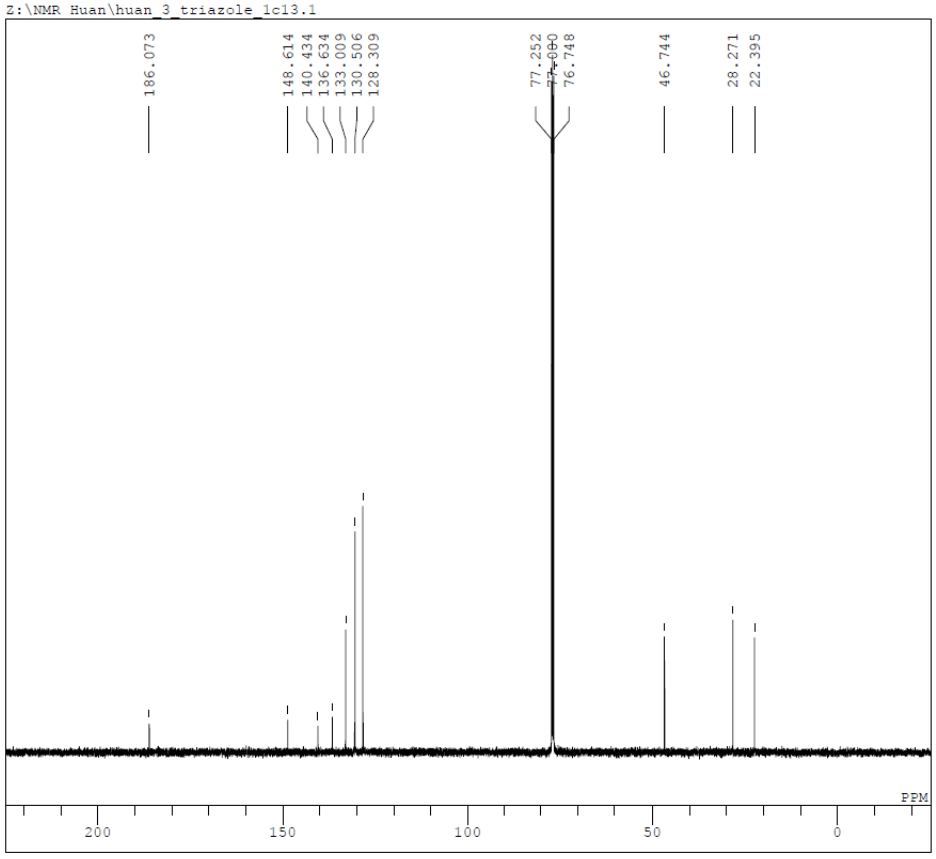

```
DFILE   huan_4_vinyl_c13.als
COMNT   Single Pulse with Broadband De
DATIM   2012-04-23 08:42:38
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS          60502
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            19.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              30
```



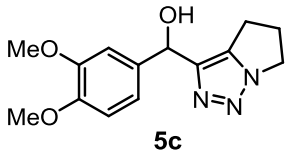



```
DFILE   huan_3_triazole_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-01-30 14:41:04
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           18.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              1.00 Hz
RGAIN             19
```

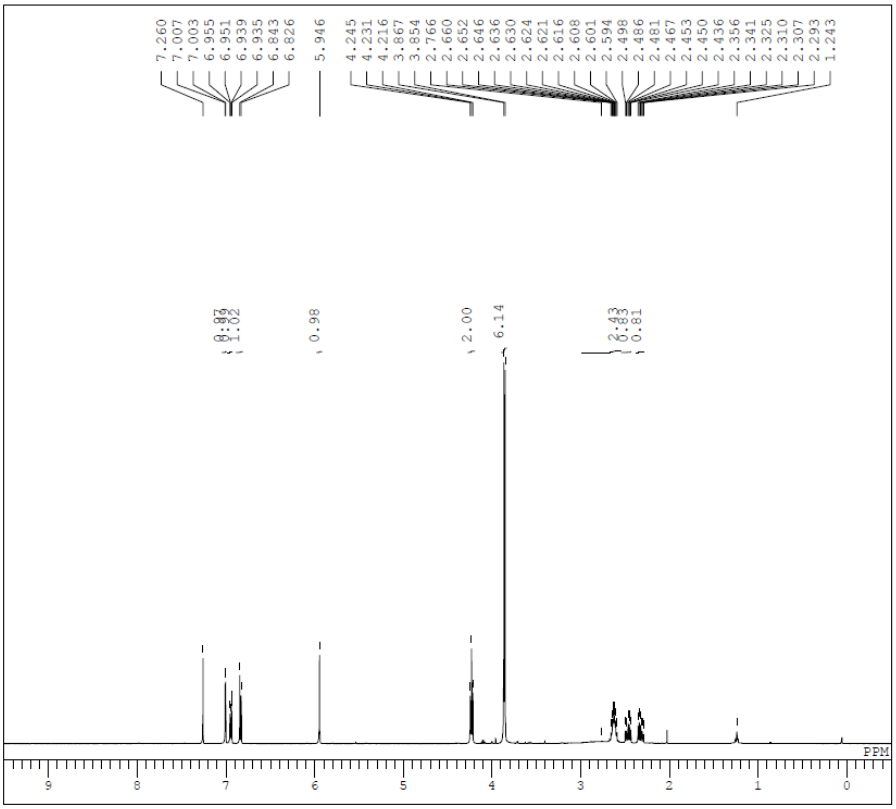
Z:\NMR Huan\huan_3_triazole_1c13.1



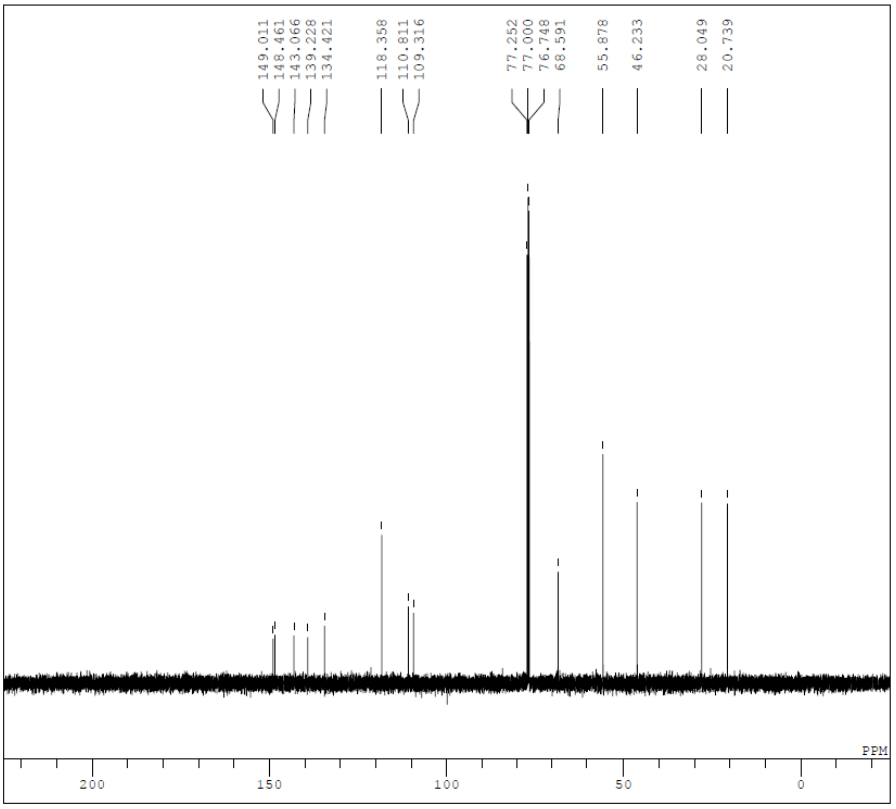

```
DFILE   huan_3_triazole_1c13.1
COMNT   Single Pulse with Broadband Decc
DATIM   2012-01-30 15:49:06
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1500
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           20.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              1.00 Hz
RGAIN             29
```



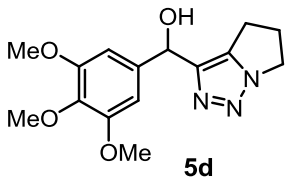
5c



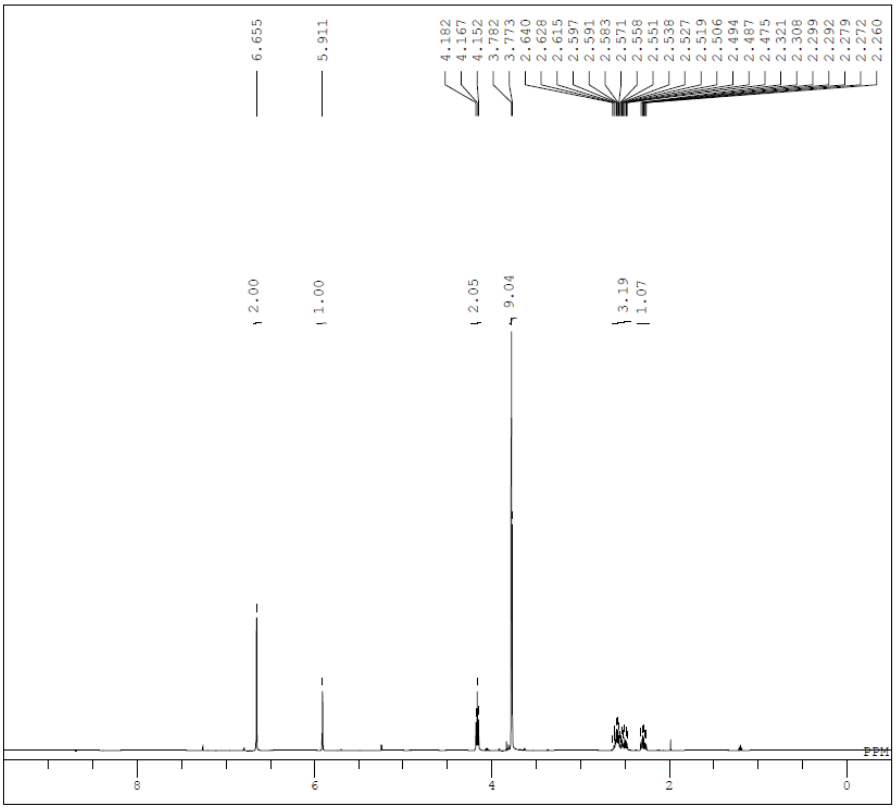

```
DFILE   huan_5_72_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-09-10 18:05:17
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC   1H
CTEMP           21.6 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             18
```



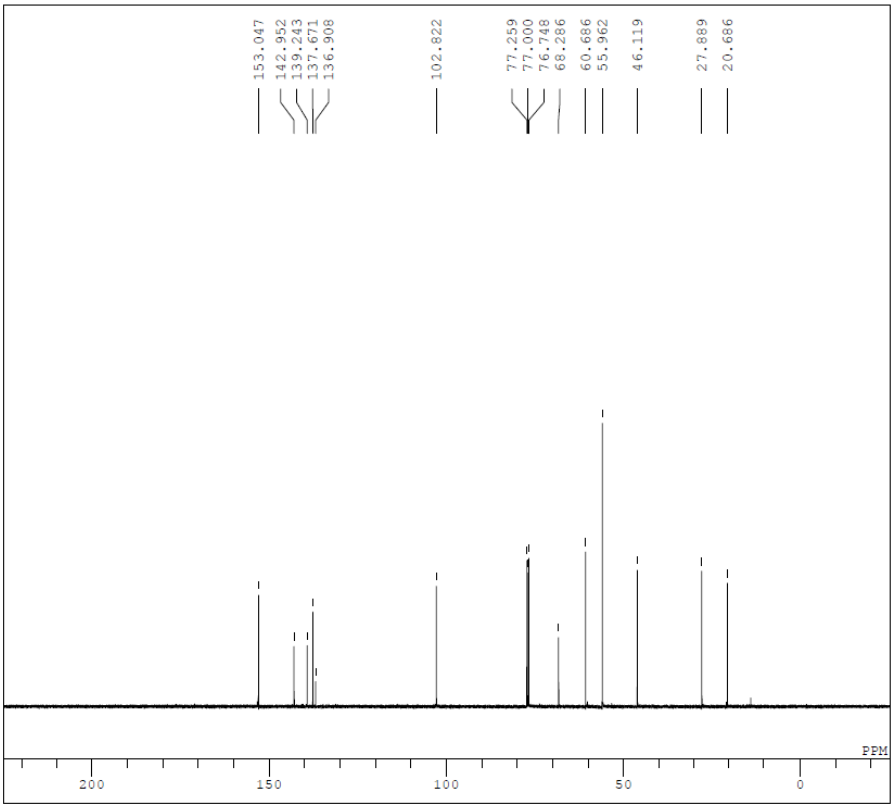

```
DFILE   huan_5_72_1c13.als
COMNT   Single Pulse with Broadband Deco
DATIM   2012-09-10 18:34:02
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            510
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           23.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



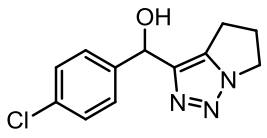
5d



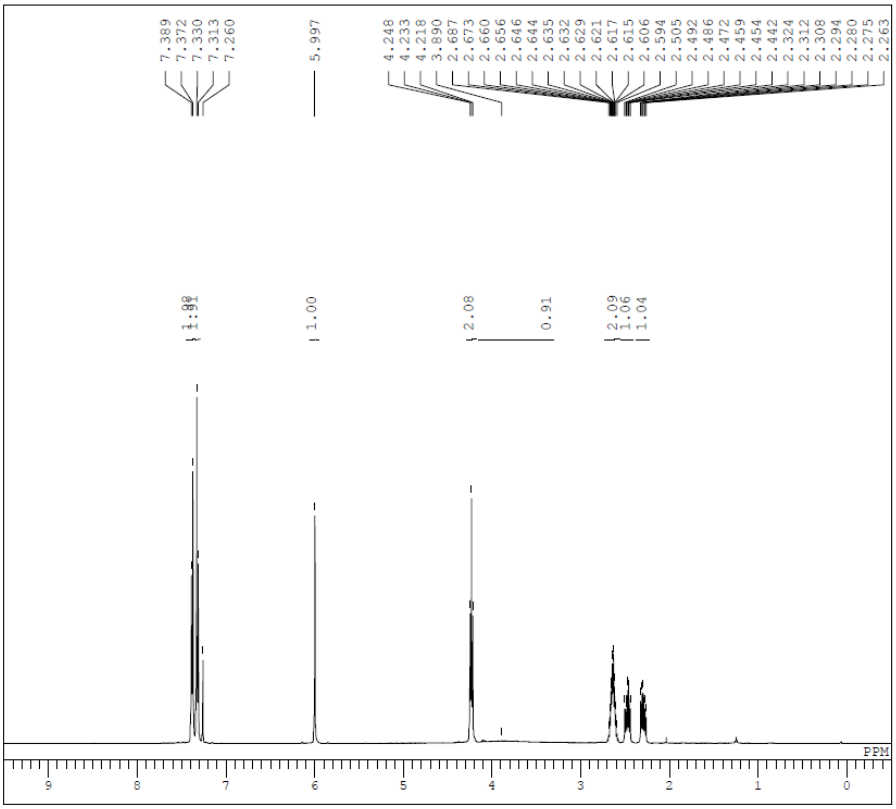

```
DFILE   huan_5_73_1.als
COMNT   Single Pulse Experiment
DATIM   2012-09-11 10:22:35
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC   1H
CTEMP           20.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             12
```



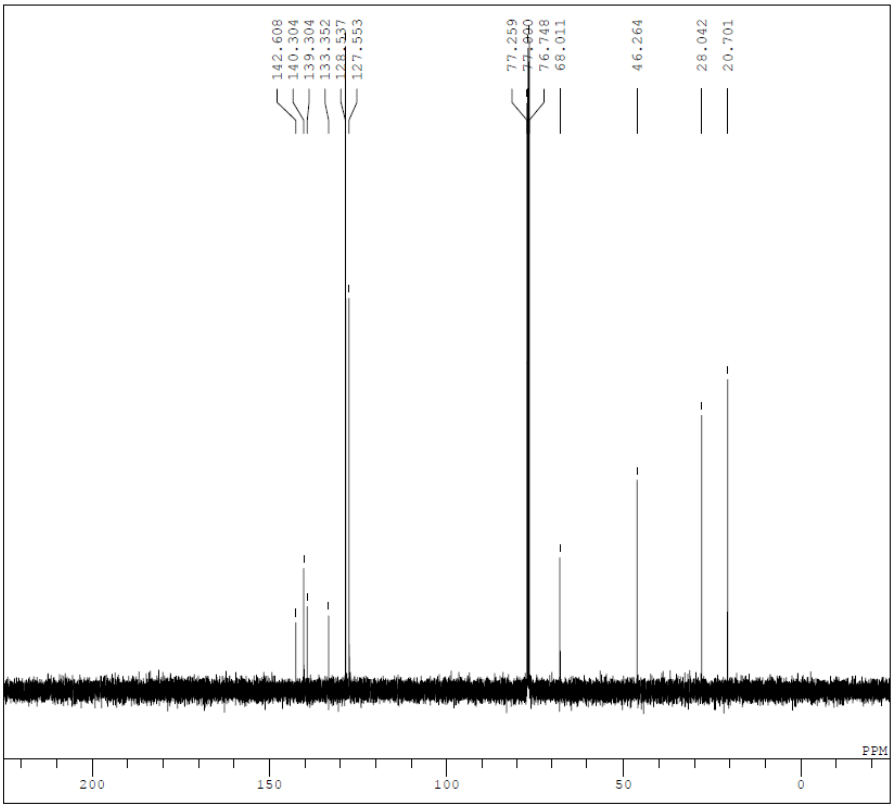

```
DFILE   huan_5_73_1c13.als
COMNT   Single Pulse with Broadband Deco
DATIM   2012-09-11 11:46:32
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1586
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           22.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



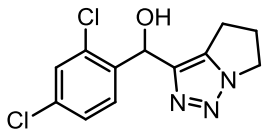
5e



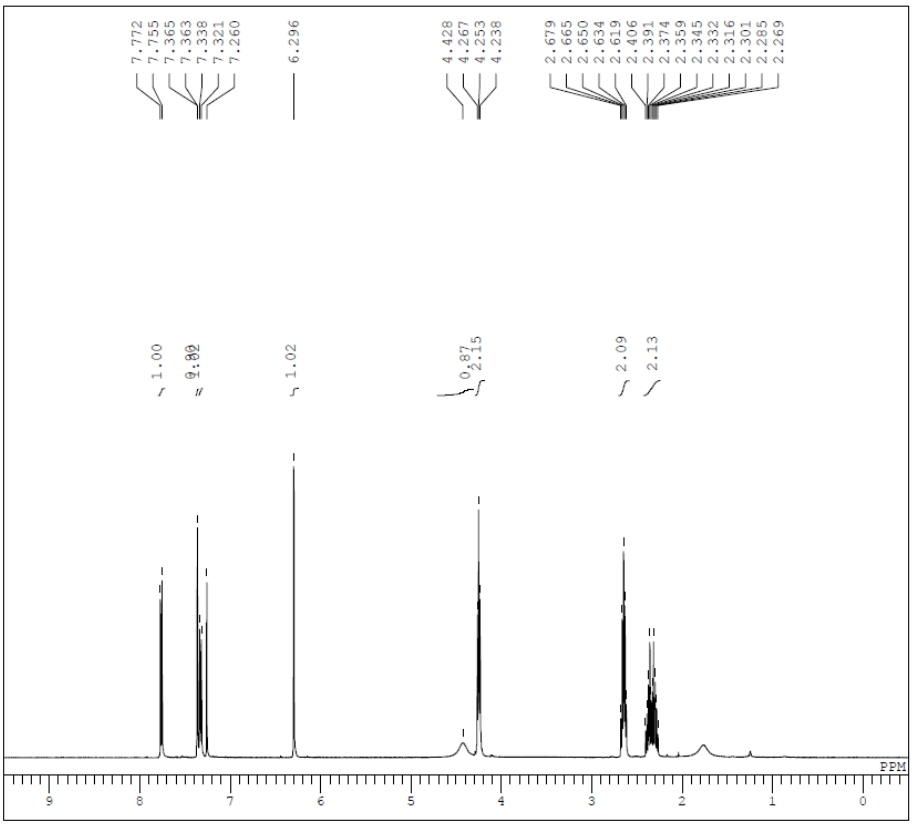

```
DFILE   huan_5_84_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-10-08 21:20:22
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           20.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             19
```



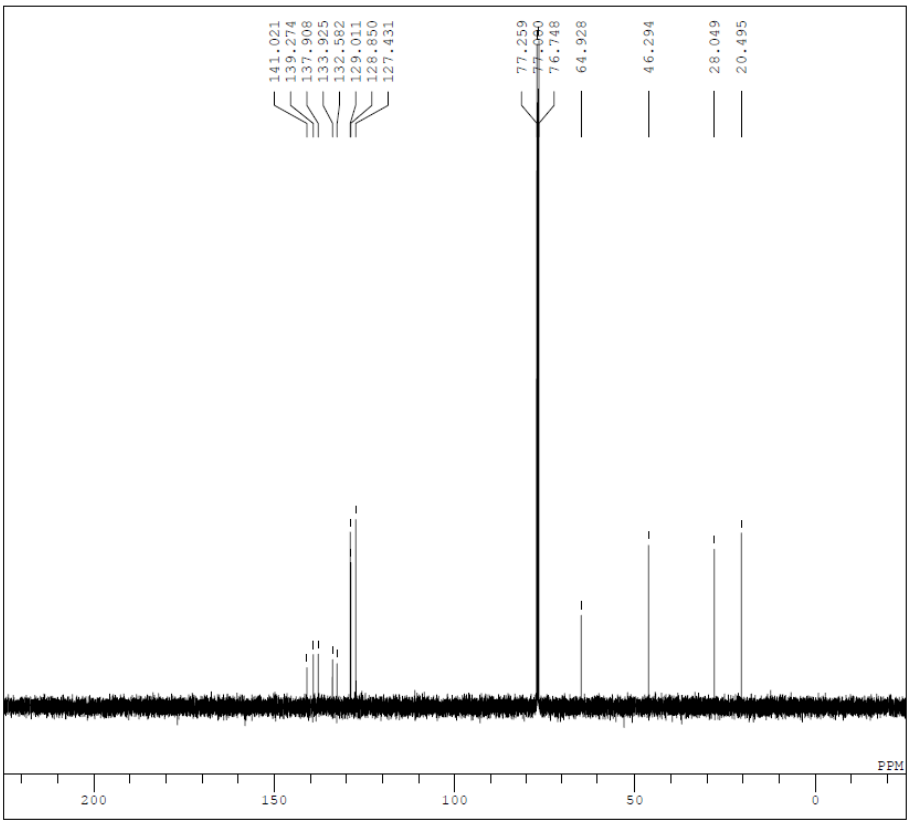

```
DFILE   huan_5_84_1c13.1
COMNT   Single Pulse with Broadband Deco
DATIM   2012-10-08 21:55:17
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            664
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           22.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



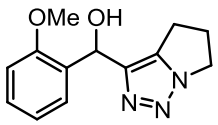
5f



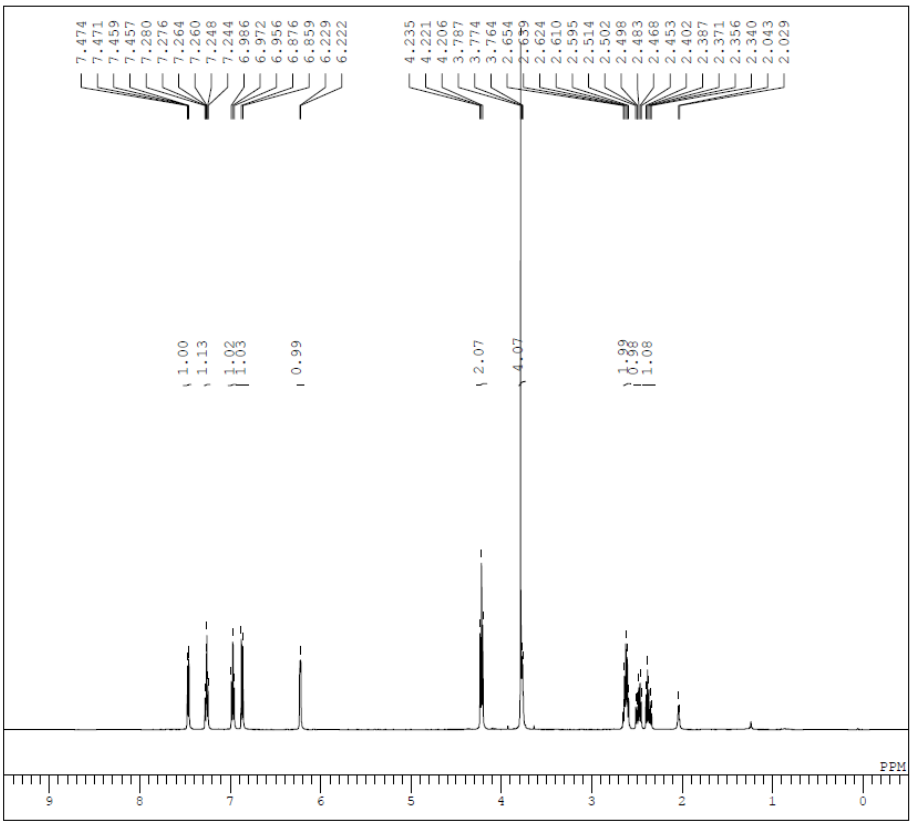

```
DFILE   huan_5_87_4h.als
COMNT   Single Pulse Experiment
DATIM   2012-10-17 17:14:00
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            20.1 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              21
```



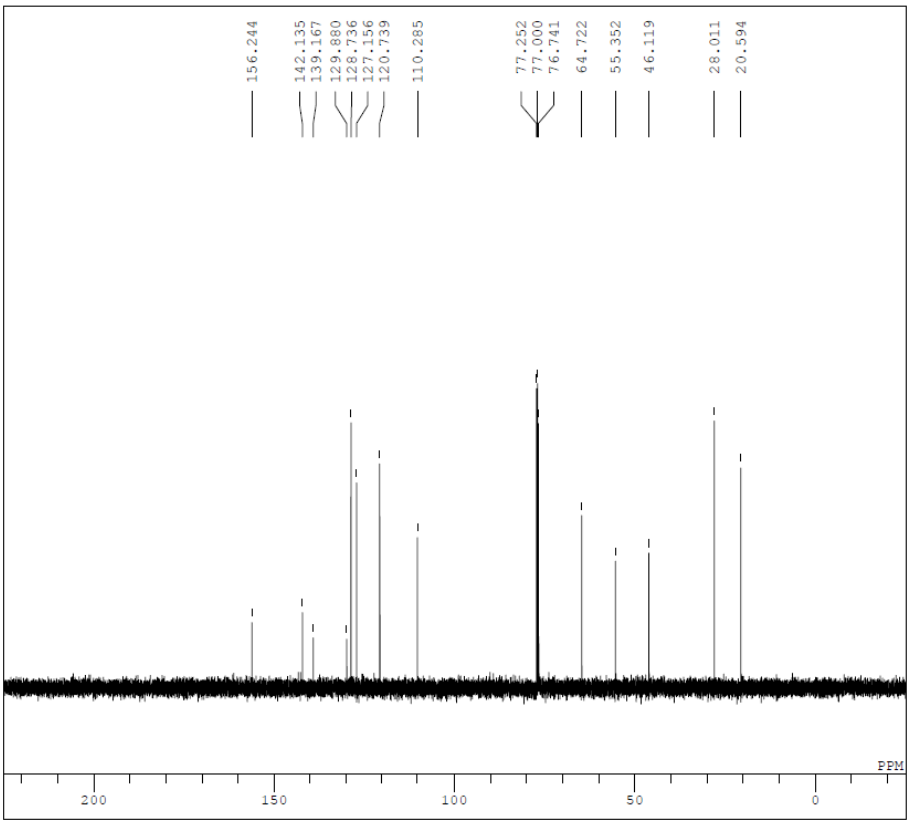

```
DFILE   huan_5_87_4c13.1
COMNT   Single Pulse with Broadband Decc
DATIM   2012-10-17 17:47:44
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            782
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            21.7 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              30
```



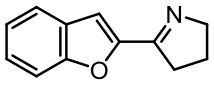
5h




```
DFILE   huan_4_102_2H.als
COMNT   Single Pulse Experiment
DATIM   2012-05-22 16:59:29
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            19.6 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              16
```

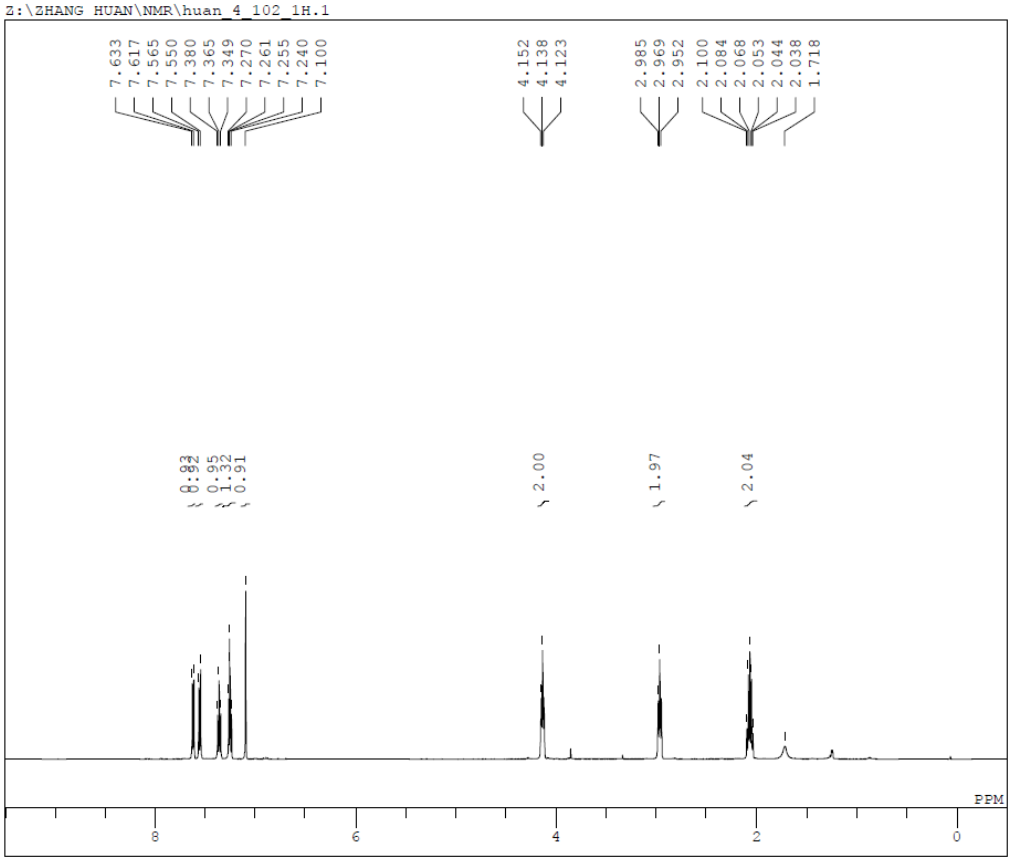



```
DFILE   huan_4_102_2C13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-05-22 17:21:03
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            200
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            20.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              29
```



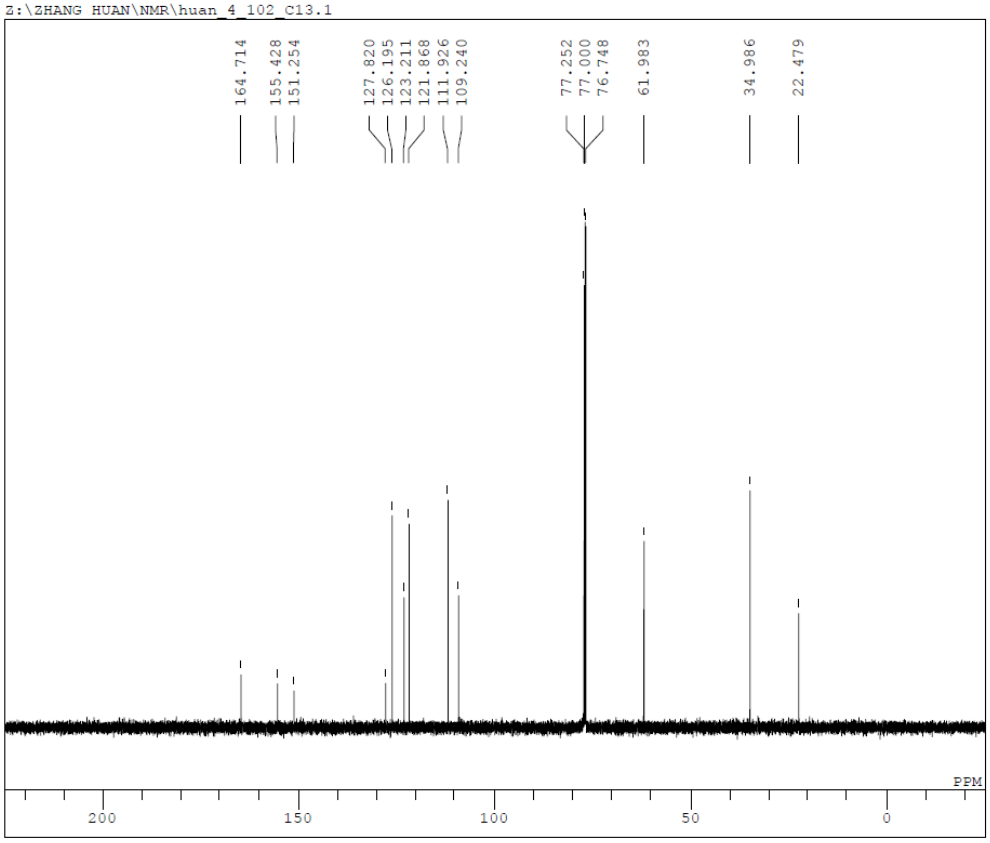
6h

Z:\ZHANG HUAN\NMR\huan_4_102_1H.1

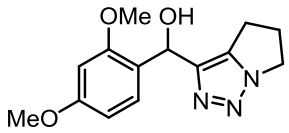



```
DFILE   huan_4_102_1H.1
COMNT   Single Pulse Experiment
DATIM   2012-05-22 11:17:44
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            19.2 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.12 Hz
RGAIN              19
```

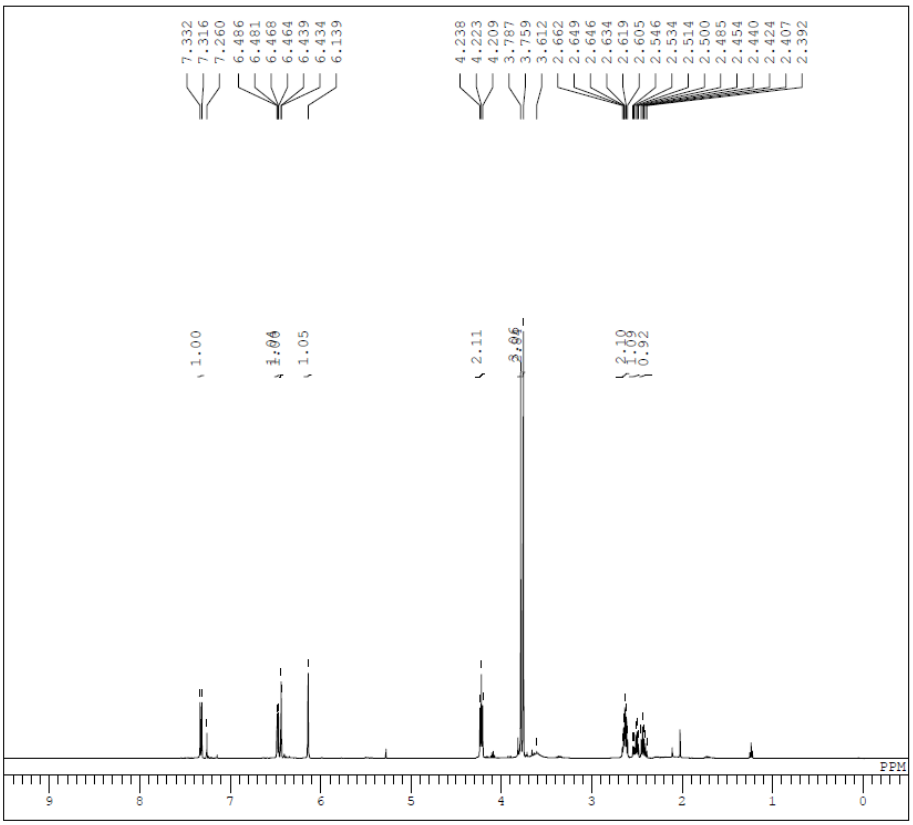
Z:\ZHANG HUAN\NMR\huan_4_102_C13.1



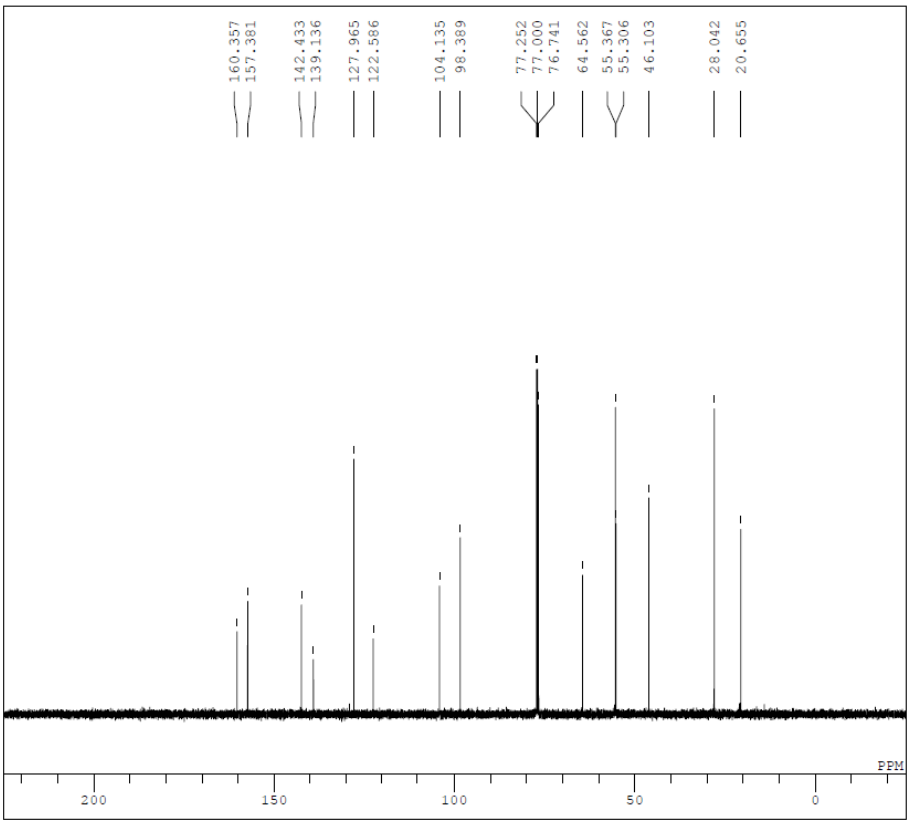

```
DFILE   huan_4_102_C13.1
COMNT   Single Pulse with Broadband Dec
DATIM   2012-05-22 12:16:16
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1116
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            21.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              29
```



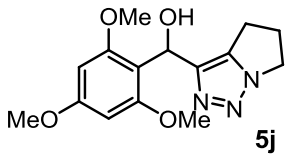
5i



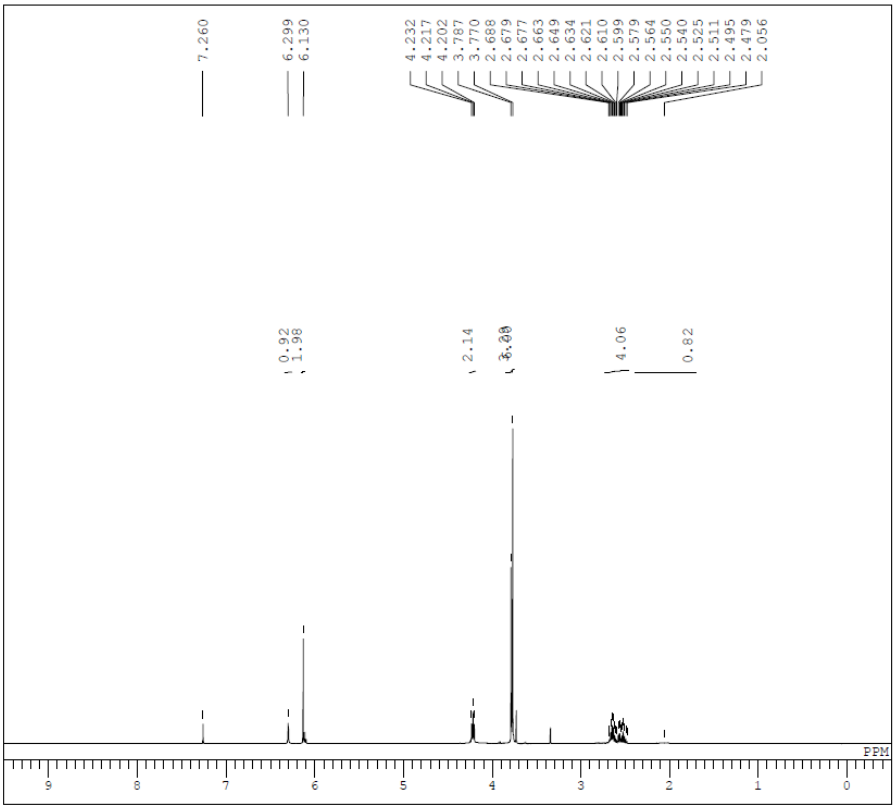

```
DFILE   huan_5_74_1h.als
COMNT   Single Pulse Experiment
DATIM   2012-09-13 10:23:26
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            21.0 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              15
```



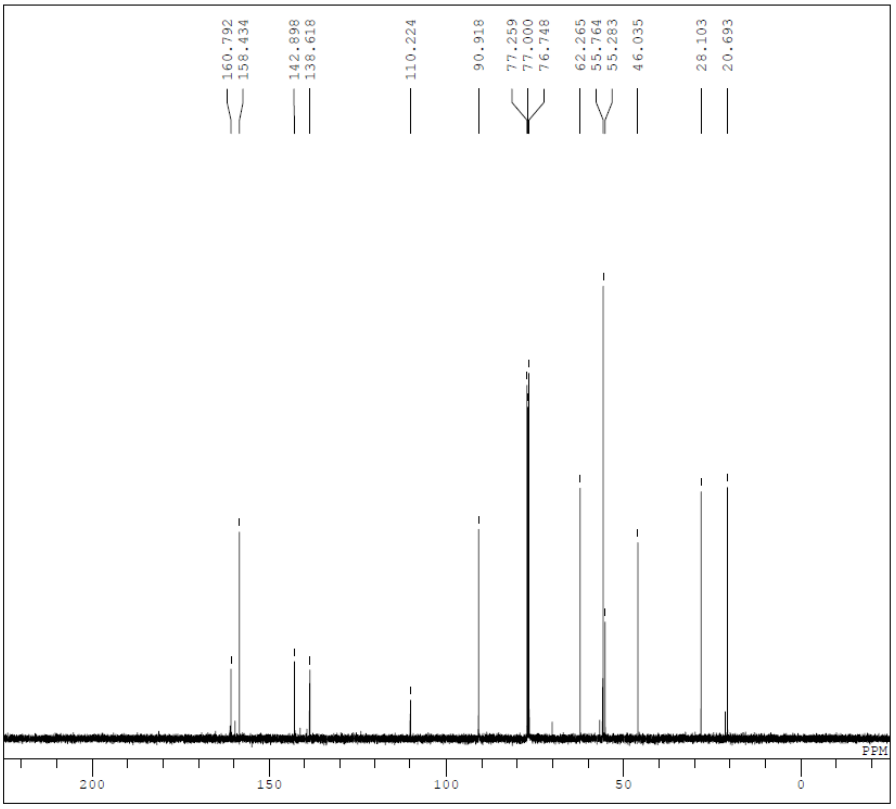

```
DFILE   huan_5_74_1c13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-09-13 11:04:04
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            916
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            23.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              30
```



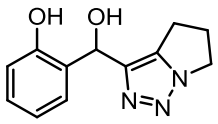
5j



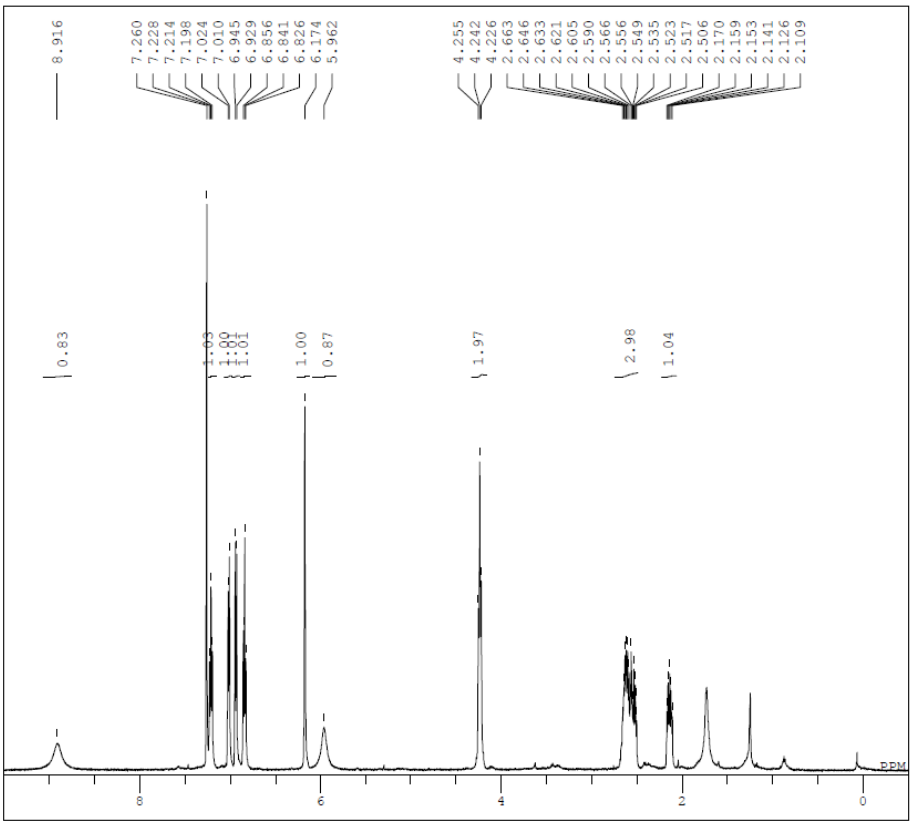

```
DFILE   huan_5_74_2h.als
COMNT   Single Pulse Experiment
DATIM   2012-09-13 14:47:50
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           21.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             15
```



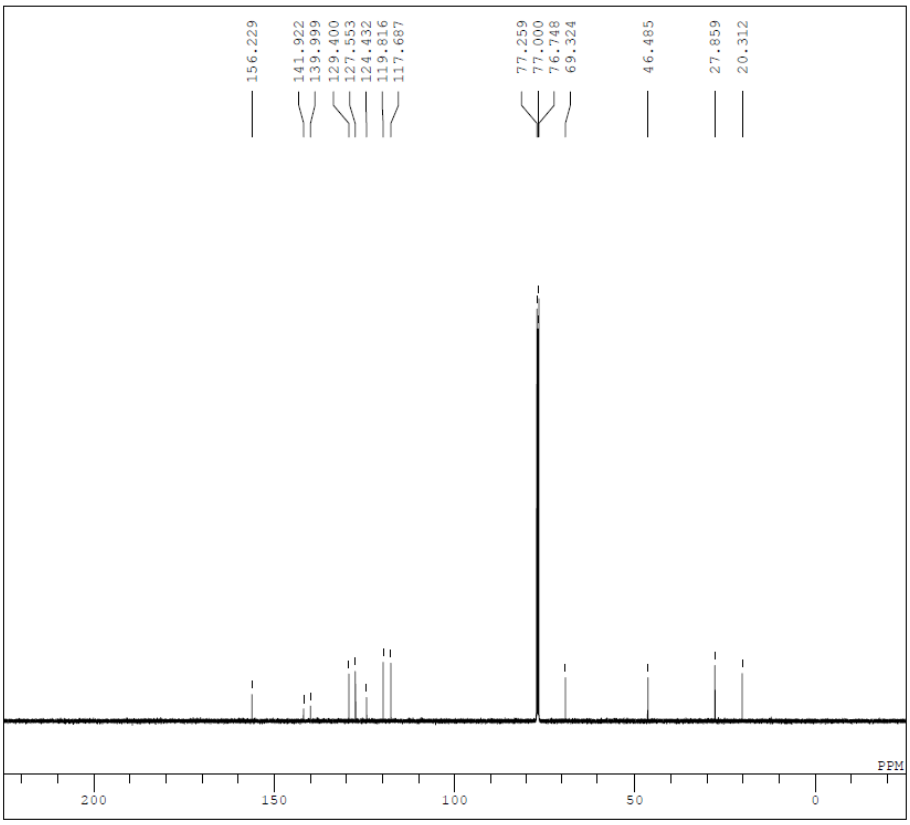

```
DFILE   huan_5_74_2c13.als
COMNT   Single Pulse with Broadband Deco
DATIM   2012-09-13 15:43:48
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1290
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           23.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



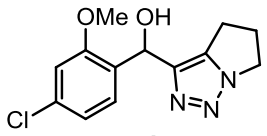
5k



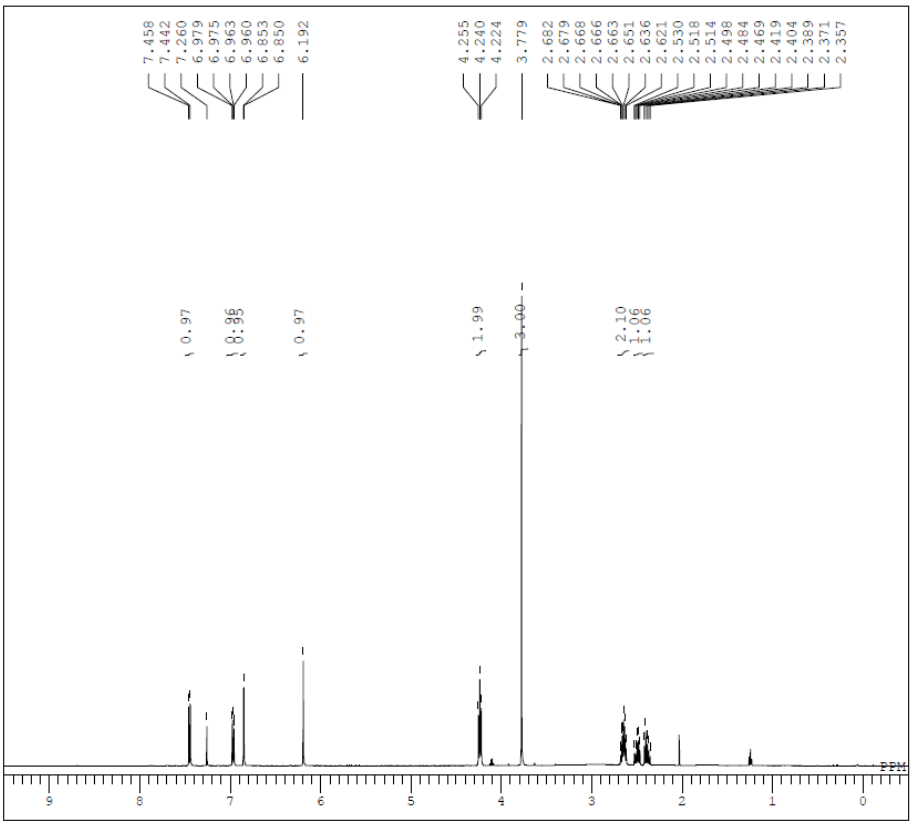

```
DFILE   huan_5_97_2hh.als
COMNT   Single Pulse Experiment
DATIM   2012-11-05 02:12:26
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM          1.6368 sec
PD             4.0000 sec
PW1              7.00 usec
IRNUC
CTEMP            18.0 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              23
```



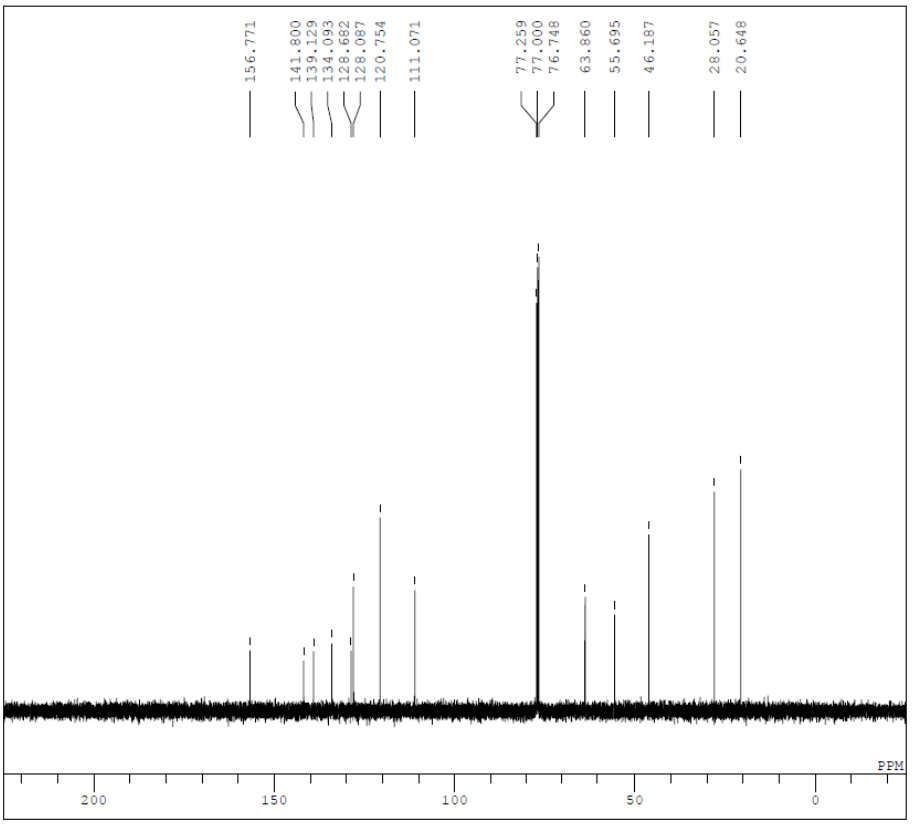

```
DFILE   huan_5_97_2c13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-11-05 07:46:07
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           9739
ACQTM          1.0420 sec
PD             1.0000 sec
PW1              4.47 usec
IRNUC   1H
CTEMP            19.5 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              30
```



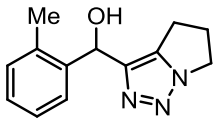
5l



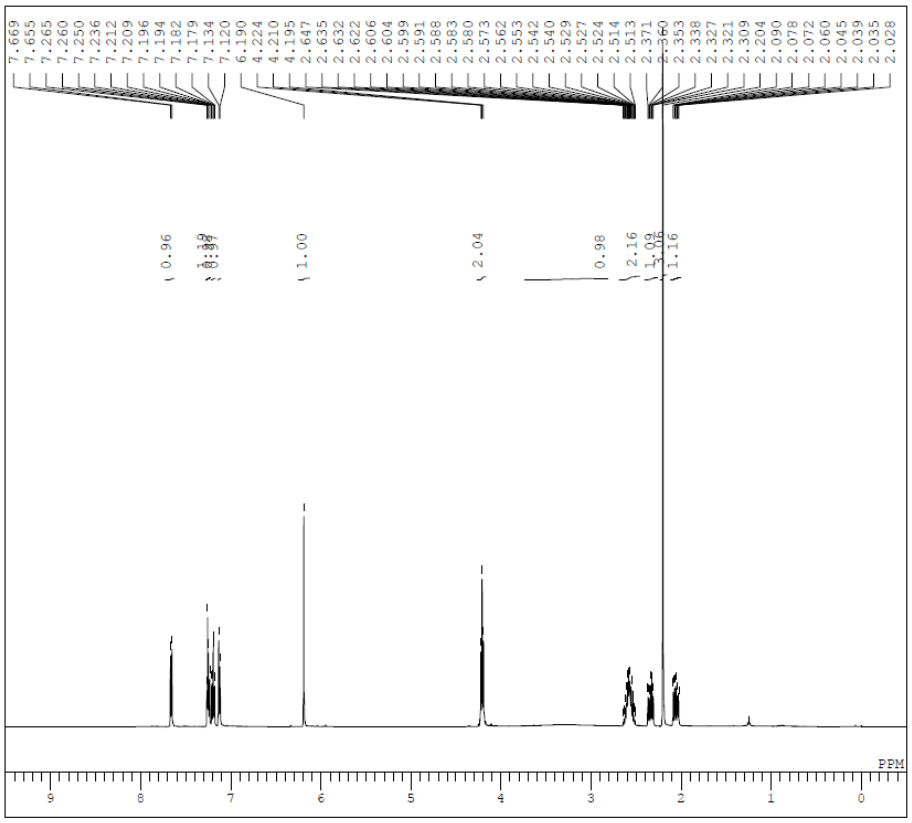

```
DFILE   huan_5_59_2h.als
COMNT   Single Pulse Experiment
DATIM   2012-08-29 22:18:55
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU      10010.01 Hz
SCANS            16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           21.8 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             19
```



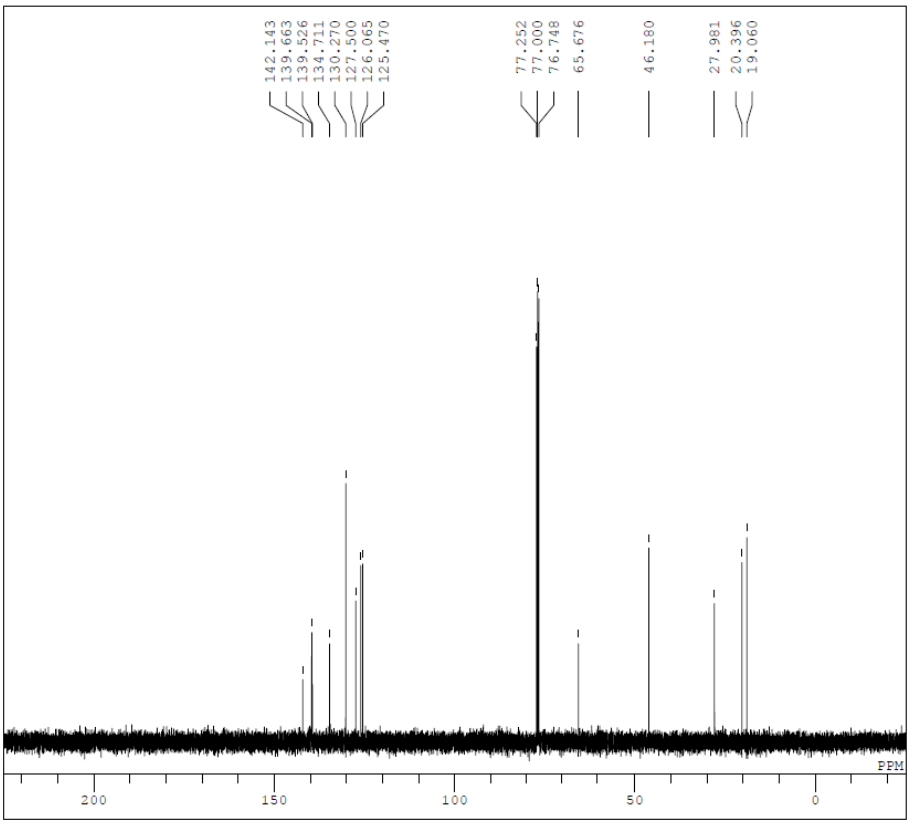

```
DFILE   huan_5_59_2c13.1
COMNT   Single Pulse with Broadband Decc
DATIM   2012-08-29 22:49:35
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32768
FREQU      31446.54 Hz
SCANS           418
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           23.5 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



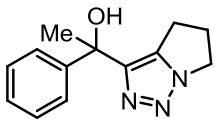
5m



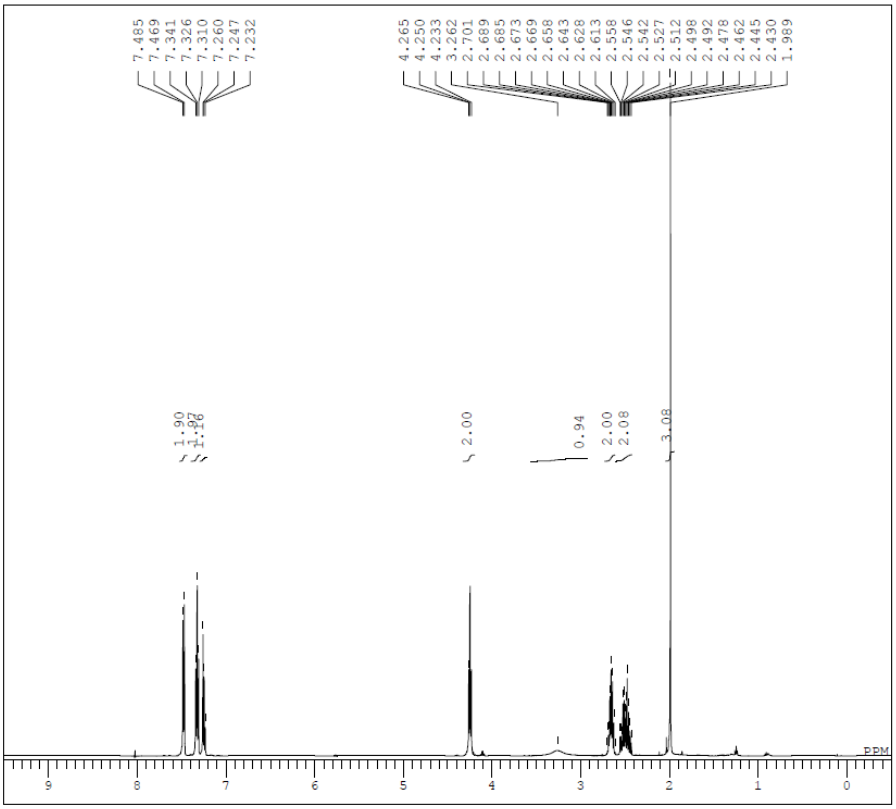

```
DFILE   huan_5_49_5.als
COMNT   Single Pulse Experiment
DATIM   2012-08-21 14:48:29
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           22.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             17
```



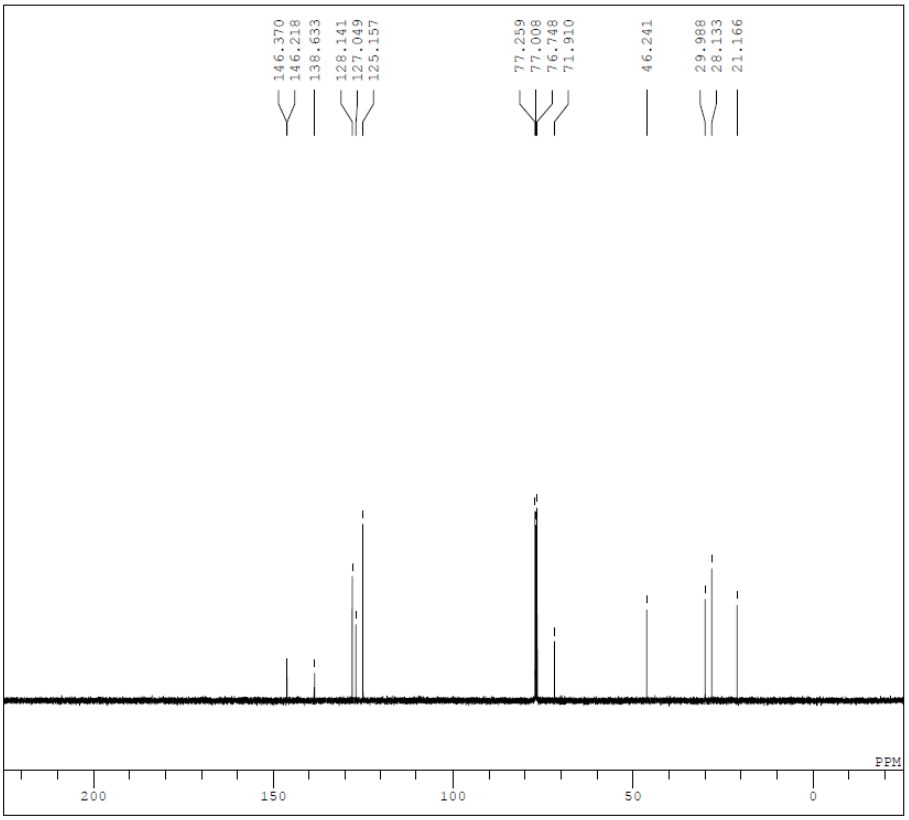

```
DFILE   huan_5_49_5_c13.als
COMNT   Single Pulse with Broadband Decc
DATIM   2012-08-21 15:21:41
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS            272
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           24.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



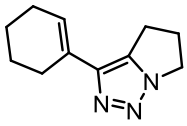
8a




```
DFILE   huan_5_100_3.als
COMNT   Single Pulse Experiment
DATIM   2012-11-01 09:13:43
OBNUC   1H
EXMOD   single_pulse.exp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU       10010.01 Hz
SCANS             16
ACQTM         1.6368 sec
PD            4.0000 sec
PW1             7.00 usec
IRNUC
CTEMP           18.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             18
```

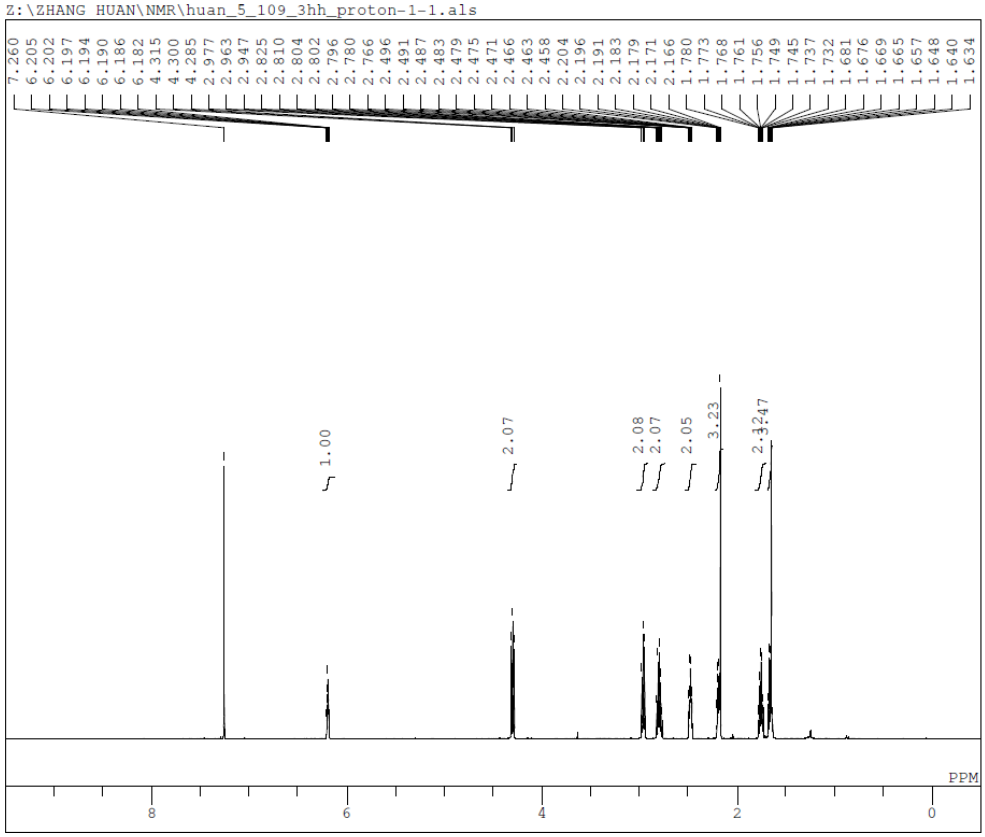



```
DFILE   huan_5_100_3c13.1
COMNT   triazole
DATIM   2012-11-01 13:18:47
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       31446.54 Hz
SCANS           1000
ACQTM         1.0420 sec
PD            1.0000 sec
PW1             4.47 usec
IRNUC   1H
CTEMP           20.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             30
```



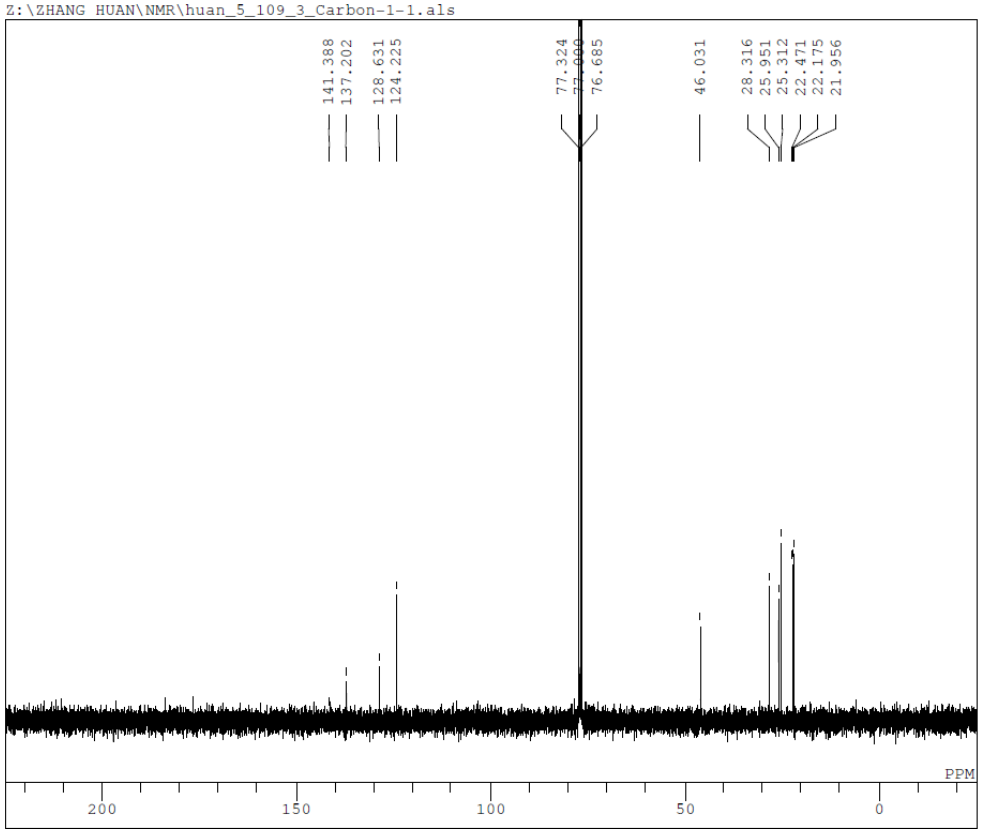
8b'

Z:\ZHANG HUAN\NMR\huan_5_109_3hh_proton-1-1.als

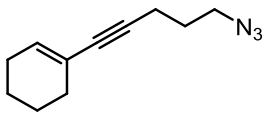



```
DFILE   huan_5_109_3hh_proton-1-1.als
COMNT   single_pulse
DATIM   2012-11-20 17:11:30
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           16.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             44
```

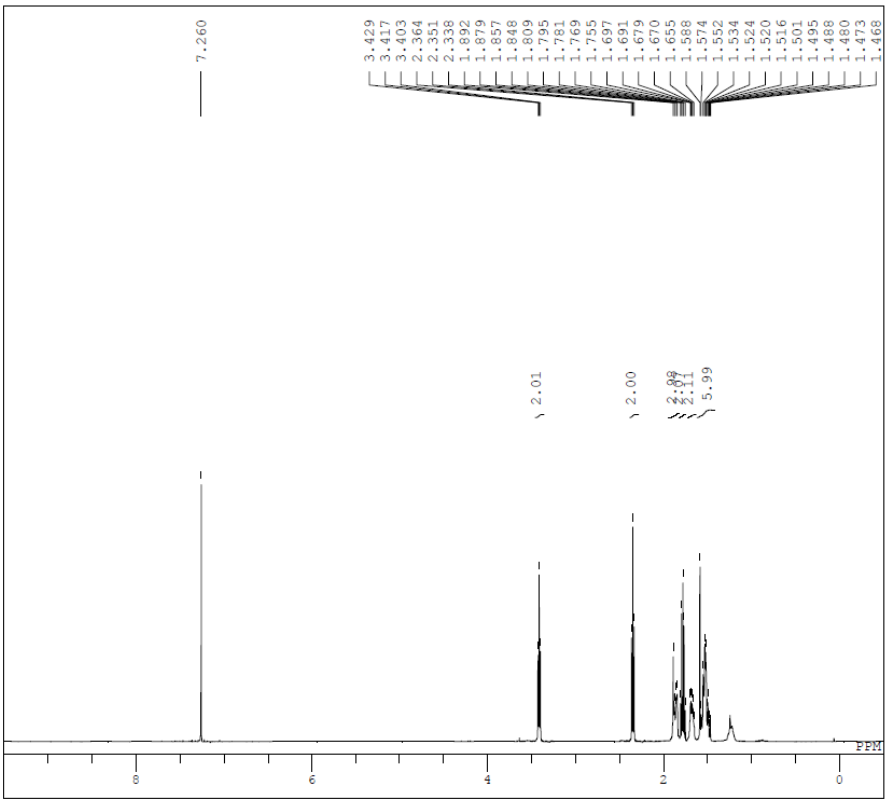
Z:\ZHANG HUAN\NMR\huan_5_109_3_Carbon-1-1.als



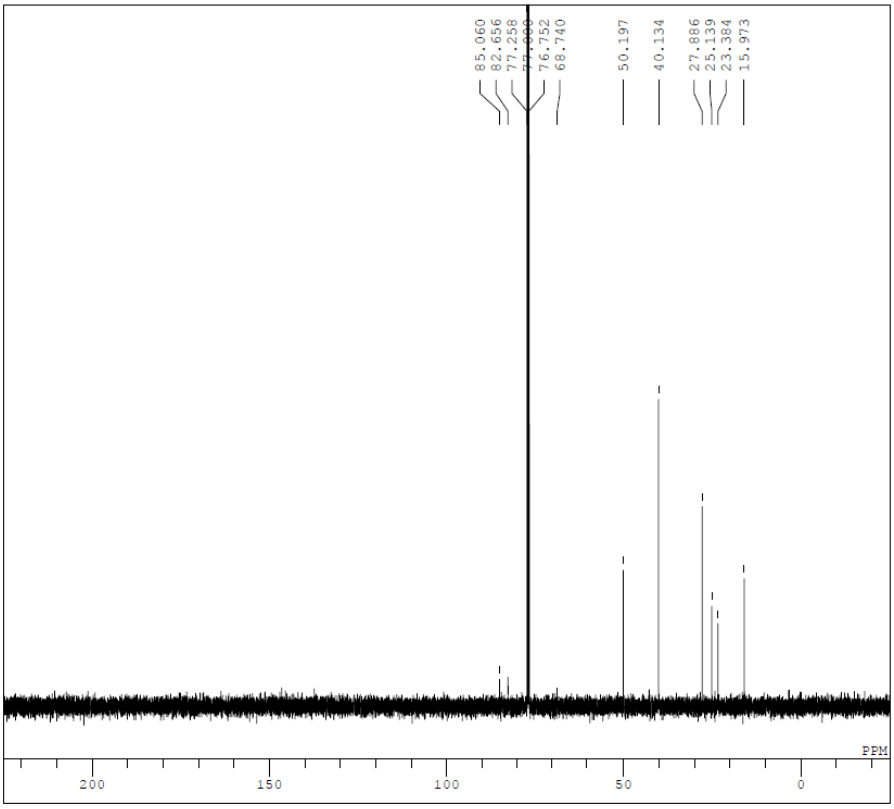

```
DFILE   huan_5_109_3_Carbon-1-1.als
COMNT   single pulse decoupled gated N
DATIM   2012-11-13 19:41:04
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            308
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.02 usec
IRNUC   1H
CTEMP           20.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             38
```



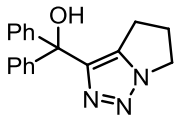
10



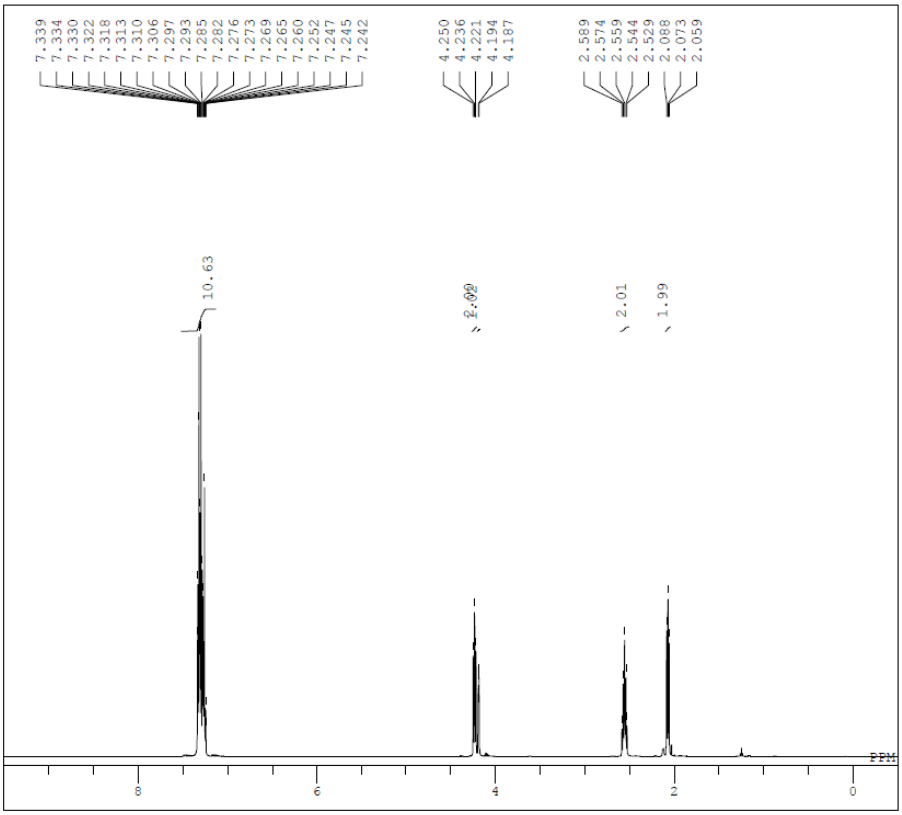

```
DFILE   huan_5_143_1_proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-01 22:31:59
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           15.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             44
```



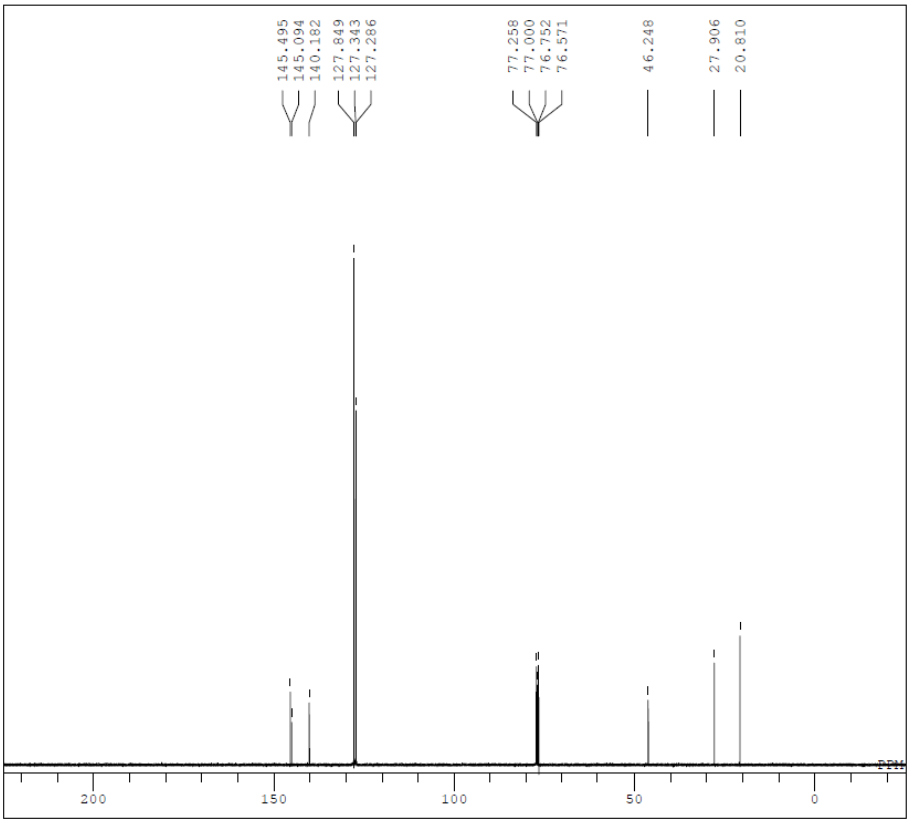

```
DFILE   huan_5_143_1_Carbon-1-1.als
COMNT   single_pulse decoupled gated NOE
DATIM   2012-12-01 22:40:59
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           14.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             60
```



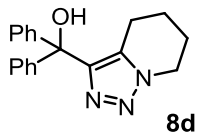
8c



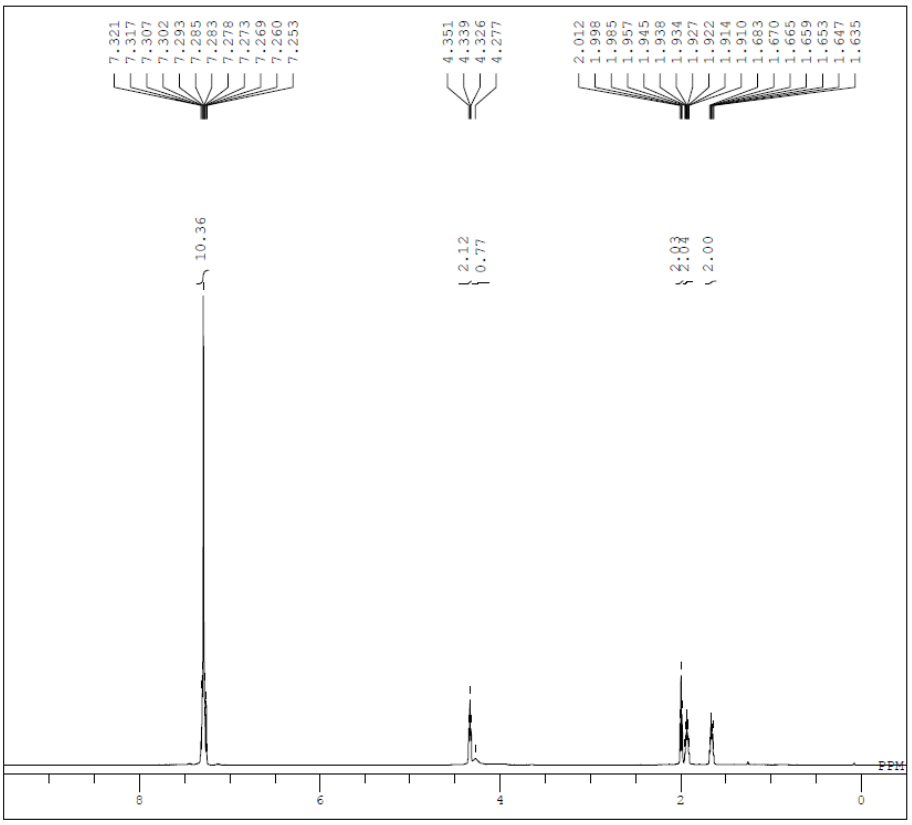

```
DFILE   HT5-48-1alkyne-1-1.jdf
COMNT   single_pulse
DATIM   2012-11-28 18:14:23
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           14.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             28
```



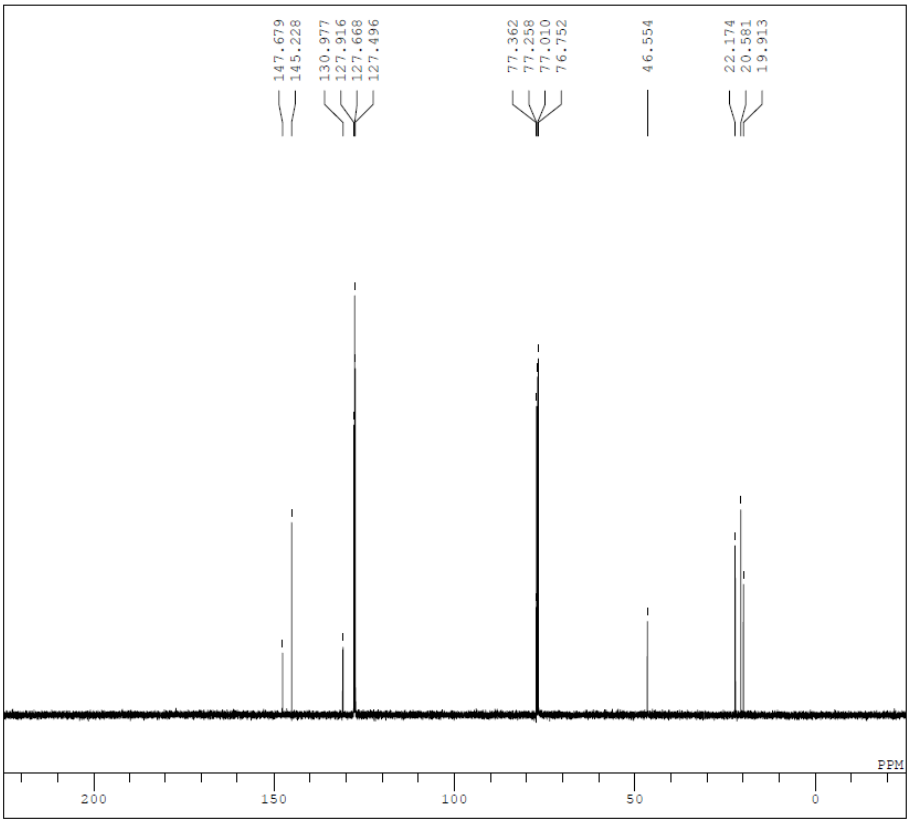

```
DFILE   HT5-48-1carbon13-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-28 18:16:47
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS            127
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           14.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



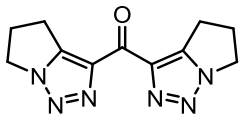
8d



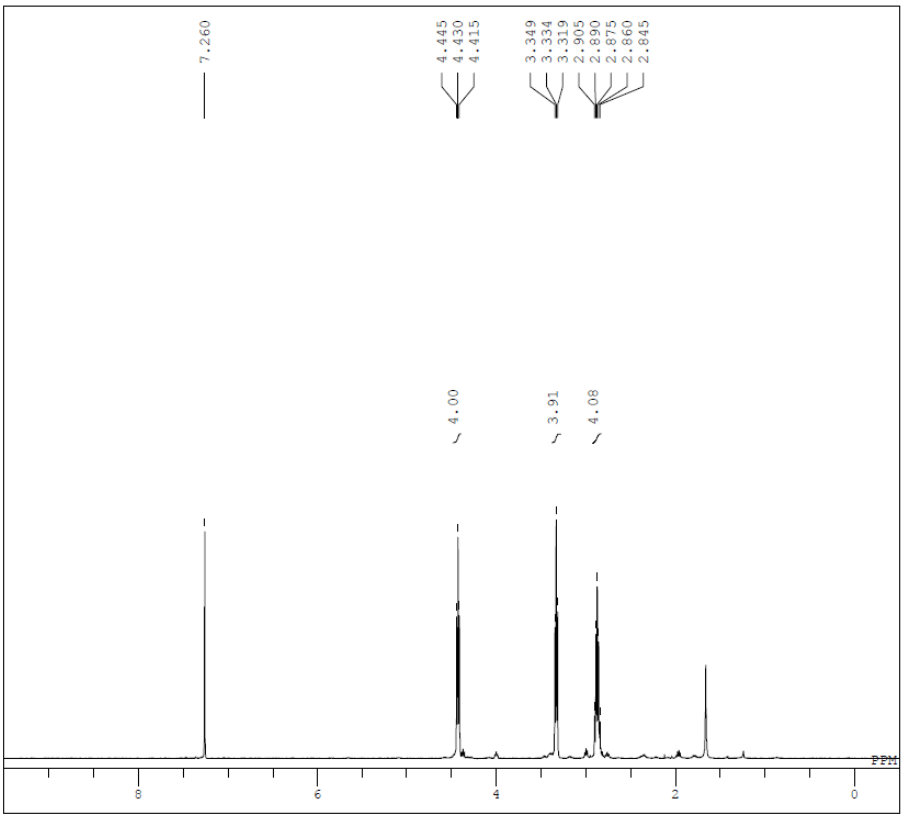

```
DFILE   huan_5_144__proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-03 23:13:03
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          15.3 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```



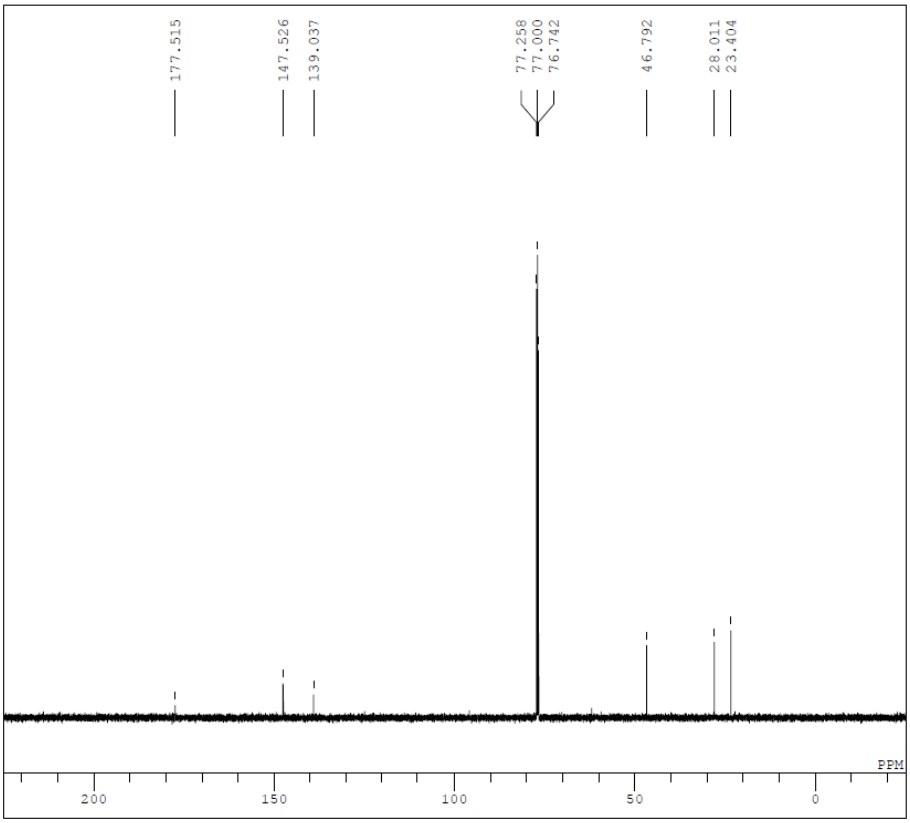

```
DFILE   huan_5_144_1h_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-05 14:56:52
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS            212
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          16.5 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            60
```



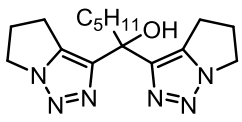
13a



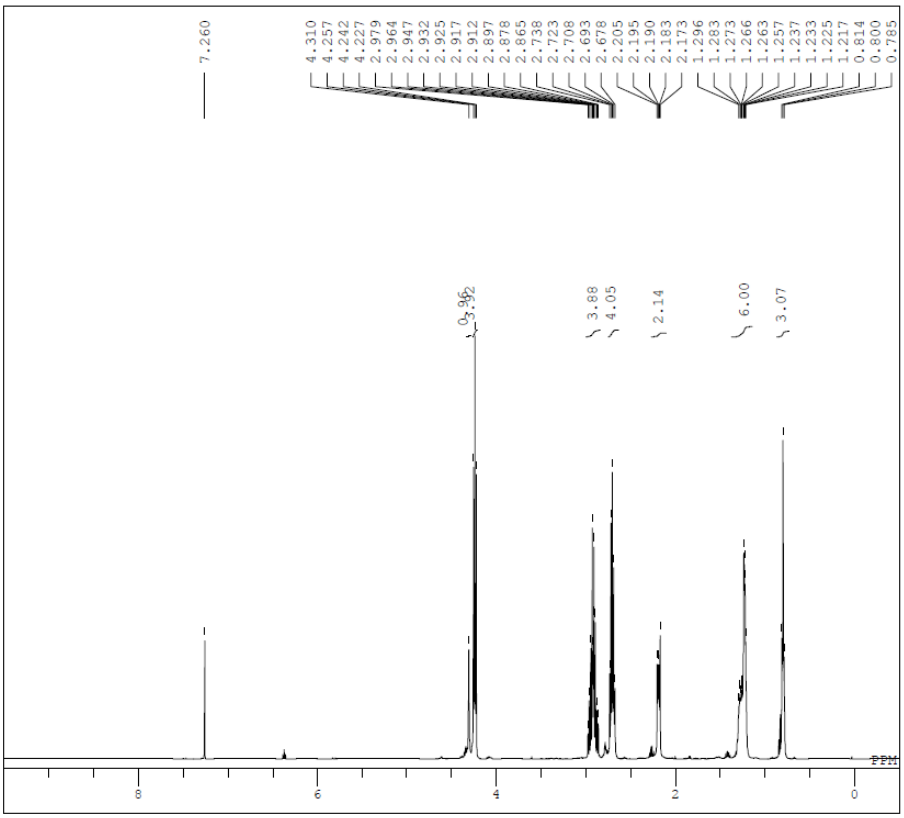

```
DFILE   huan_5_115_5_proton-1-1.als
COMNT   single_pulse
DATIM   2012-11-19 21:13:23
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS               8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           15.9 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             44
```



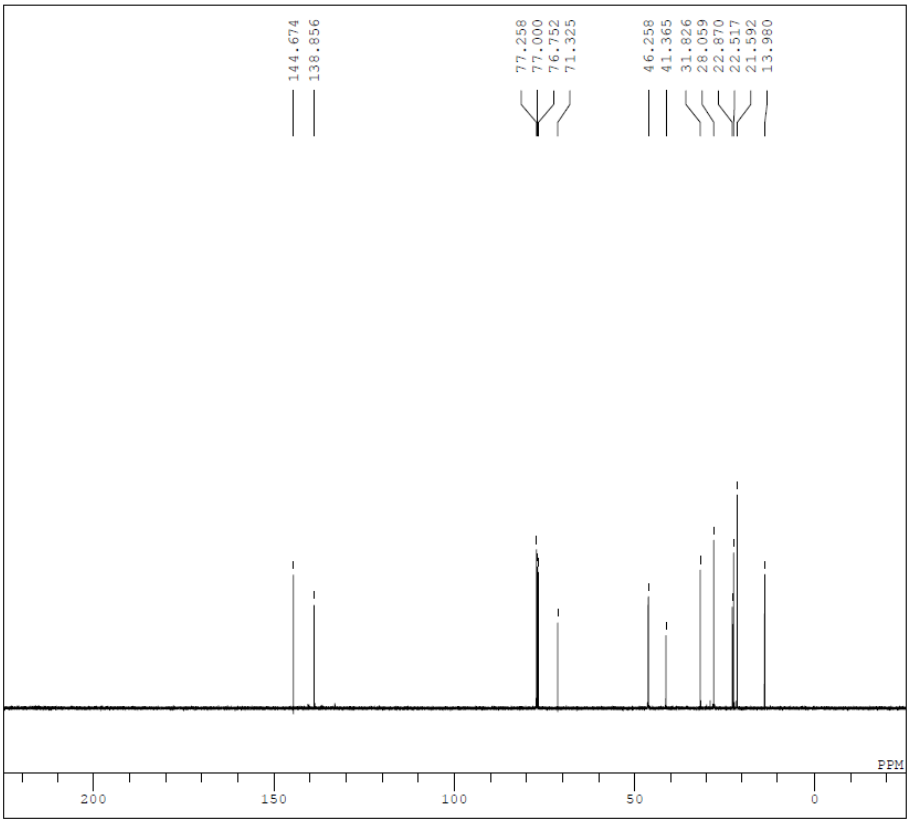

```
DFILE   huan_5_115_5_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-19 21:14:43
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            384
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           15.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



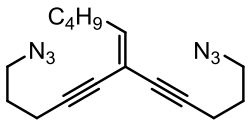
13b



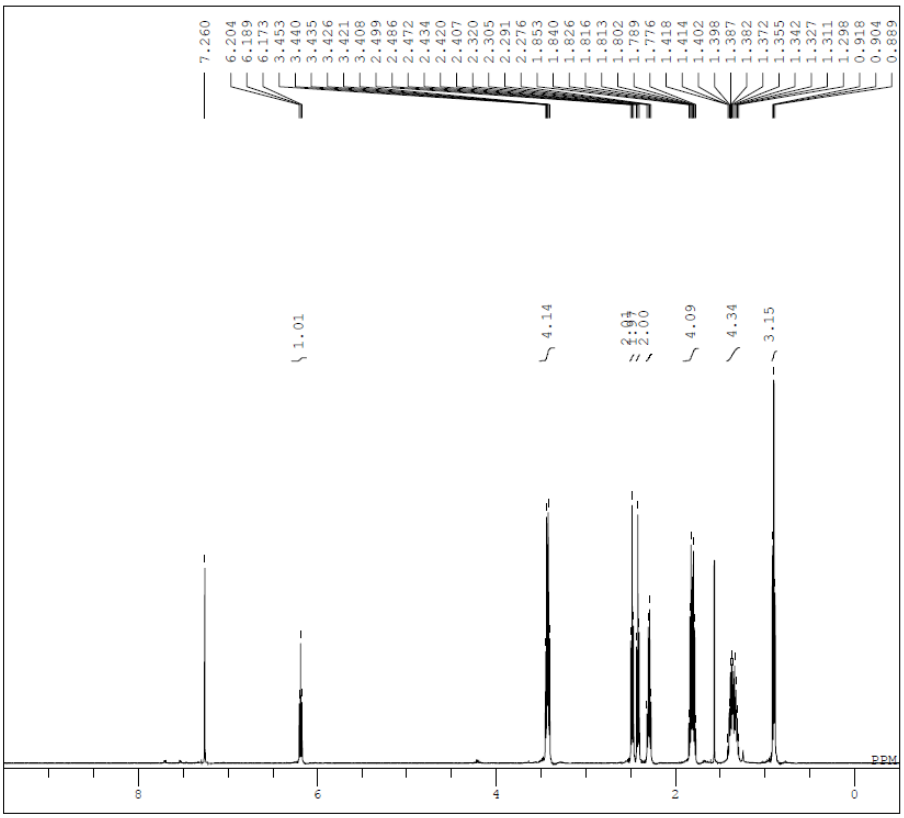

```
DFILE   huan_5_129_4_proton-1-1.als
COMNT   single_pulse
DATIM   2012-11-26 22:20:05
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           14.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             26
```



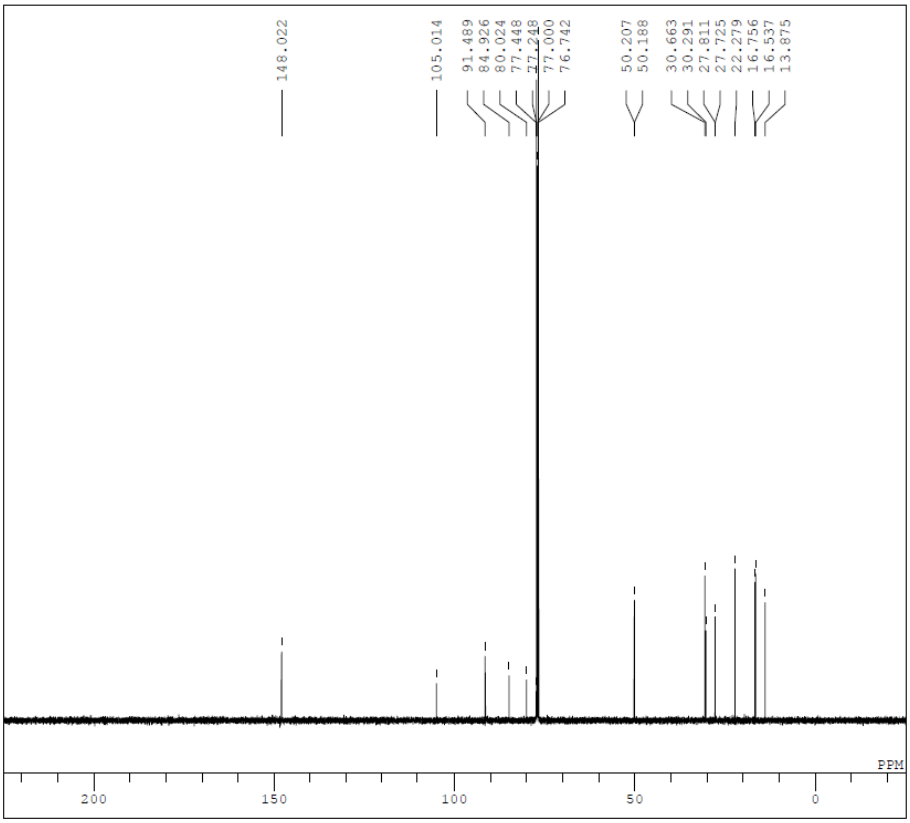

```
DFILE   huan_5_129_4_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-11-26 22:39:44
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            188
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           15.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



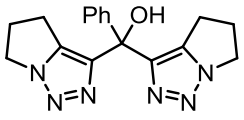
14



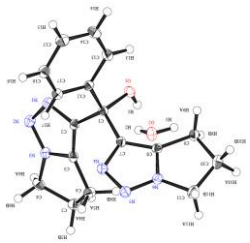

```
DFILE   huan_5_143_3_proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-01 20:33:27
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           15.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             42
```

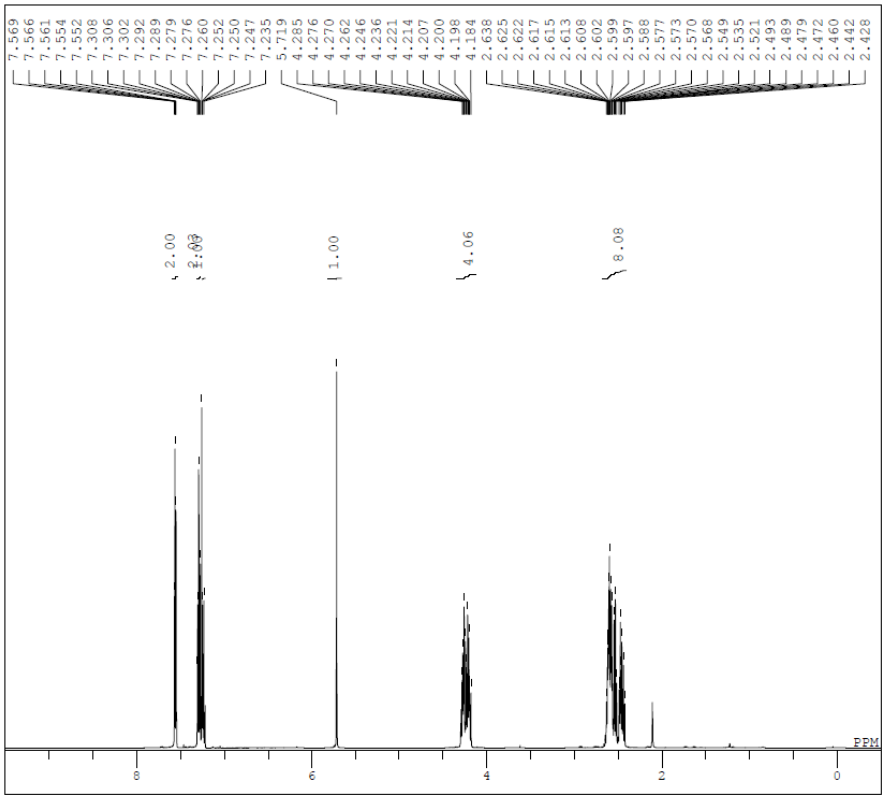



```
DFILE   huan_5_143_3_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-01 20:50:04
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            962
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           14.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             58
```

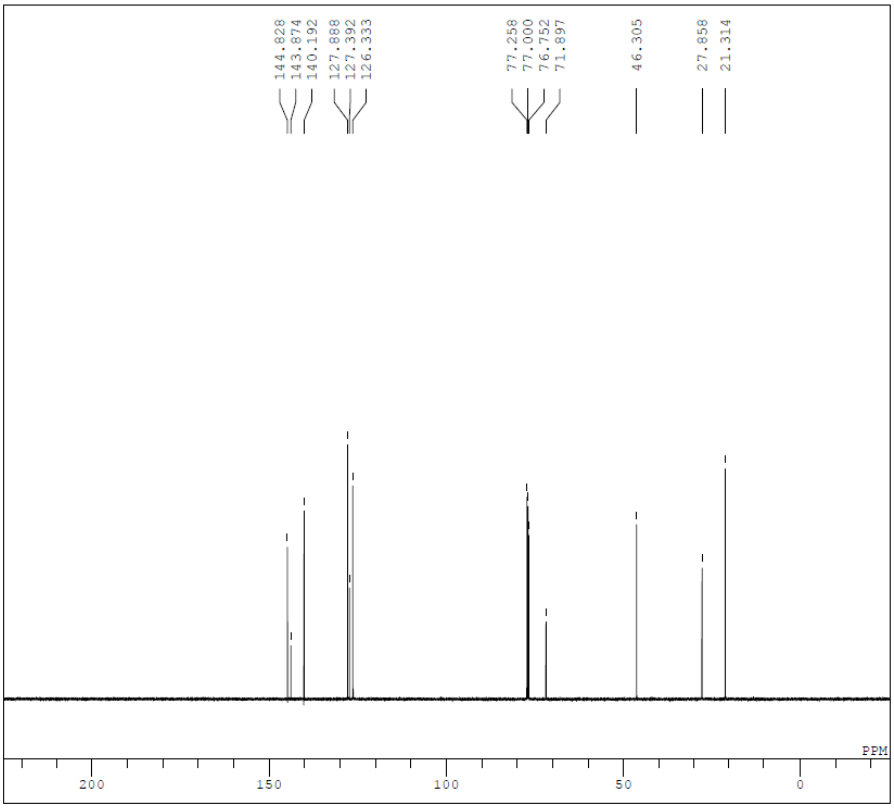


13c

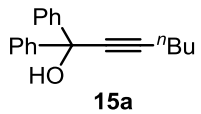




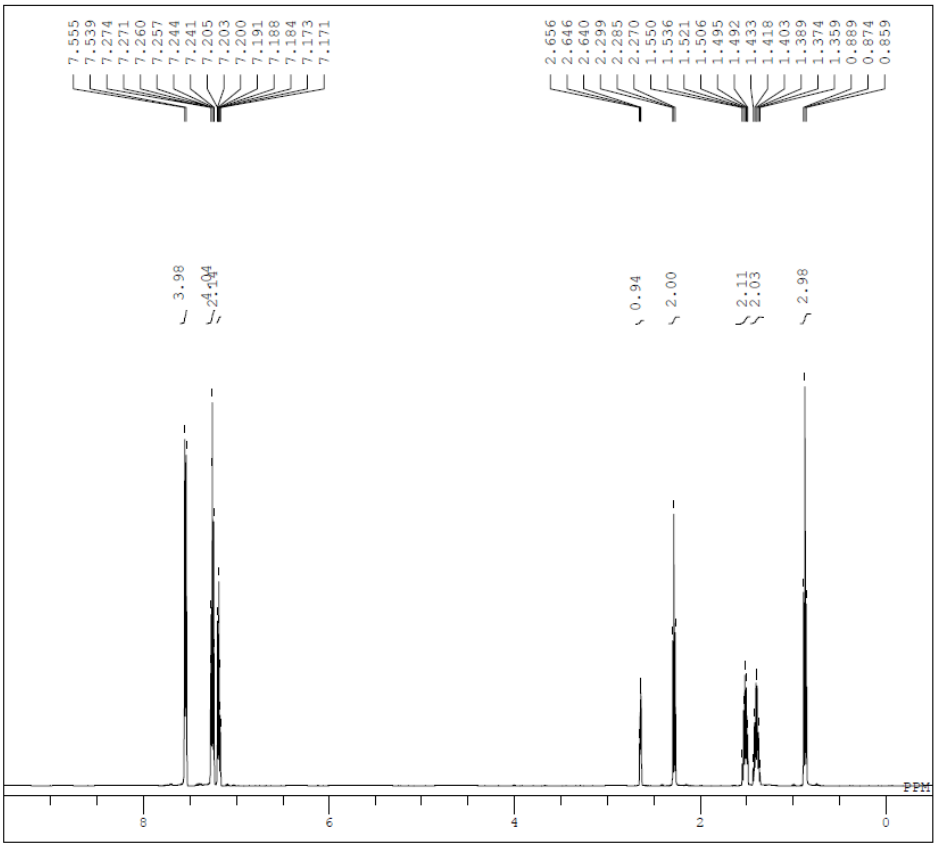

```
DFILE   huan_5_123_2_proton-1-1.als
COMNT   single_pulse
DATIM   2012-11-21 22:02:00
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           15.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             30
```



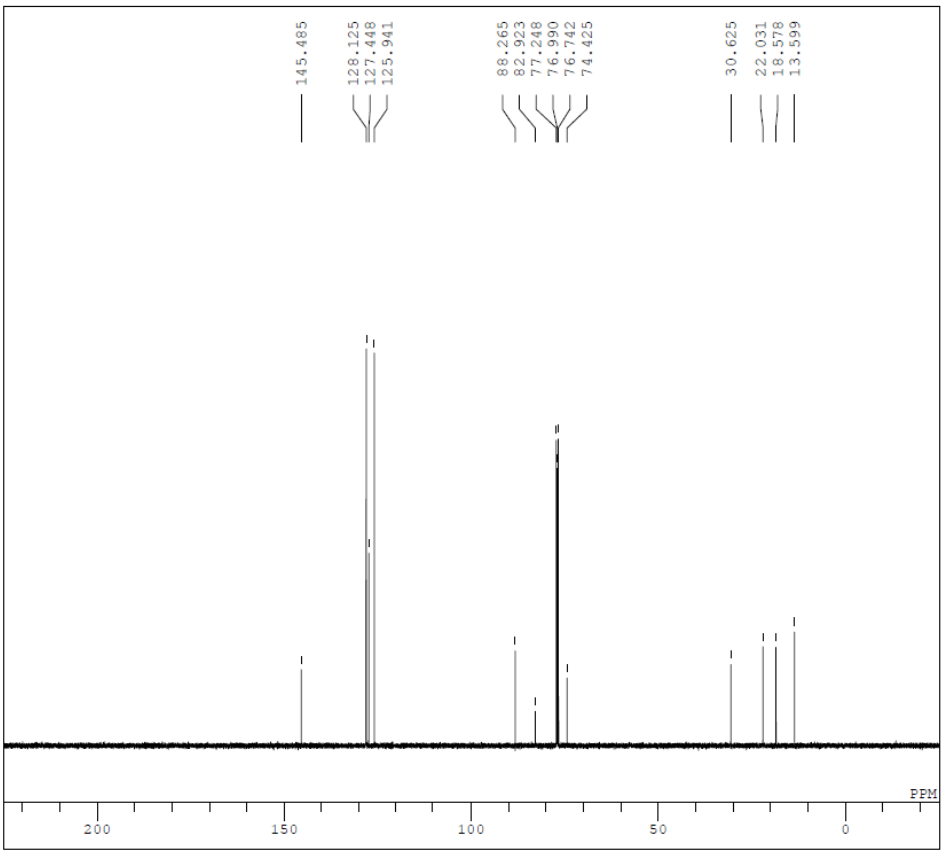

```
DFILE   huan_5_123_2_Carbon-1-1.als
COMNT   single_pulse decoupled gated NOE
DATIM   2012-11-21 22:33:36
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU        31446.54 Hz
SCANS            419
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           16.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             58
```



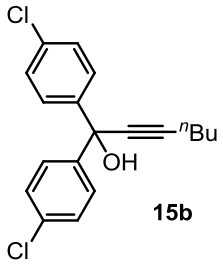
15a



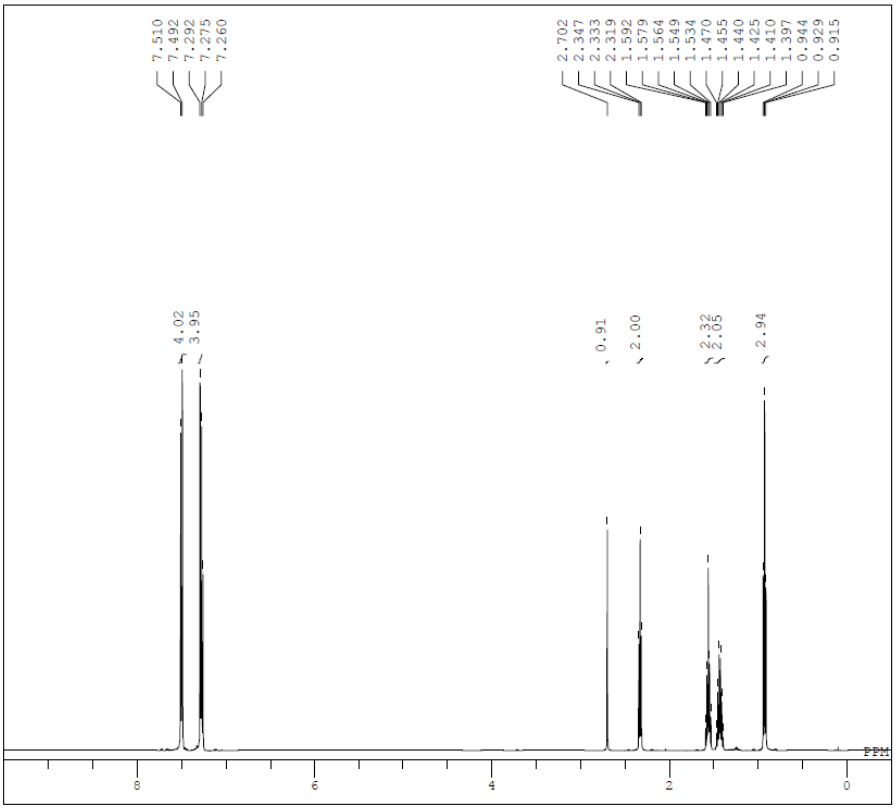

```
DFILE   huan_5_149_1_proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-10 20:25:55
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           17.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             36
```



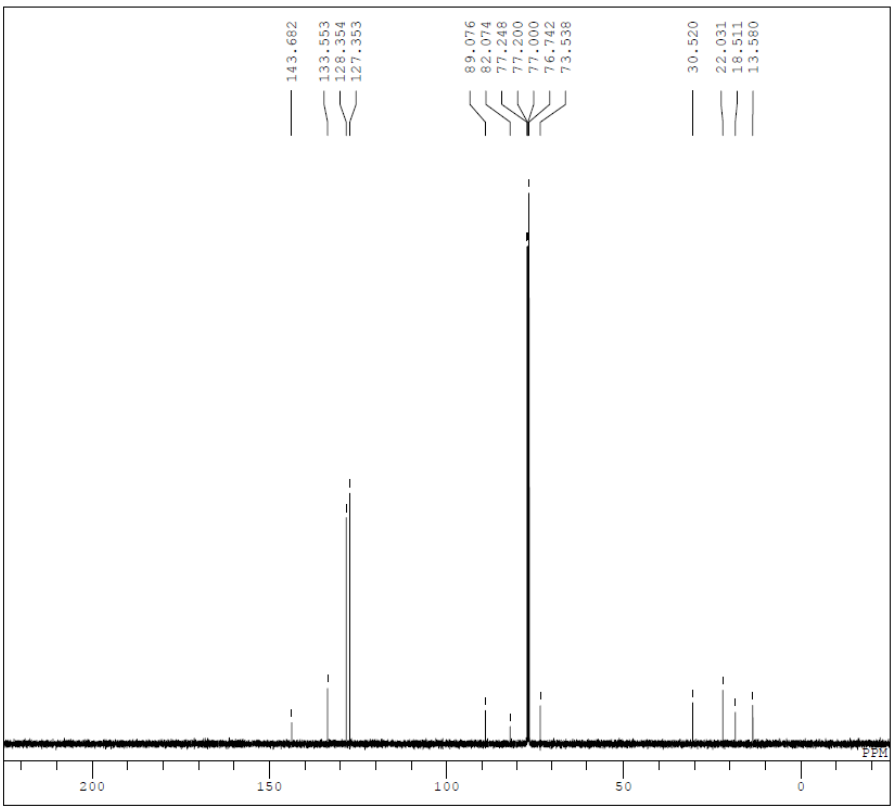

```
DFILE   huan_5_149_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-10 20:57:26
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            512
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



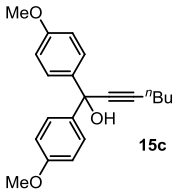
15b



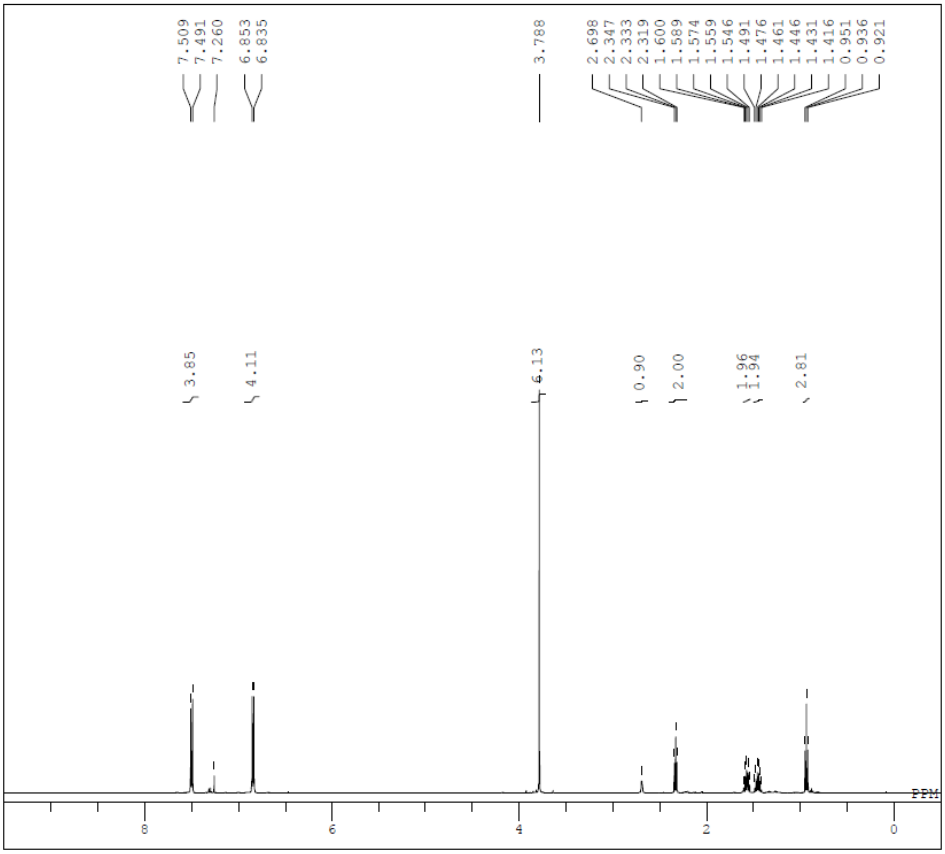

```
DFILE   HT5-98-2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-02-08 18:08:14
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             18
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            17.3 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              42
```



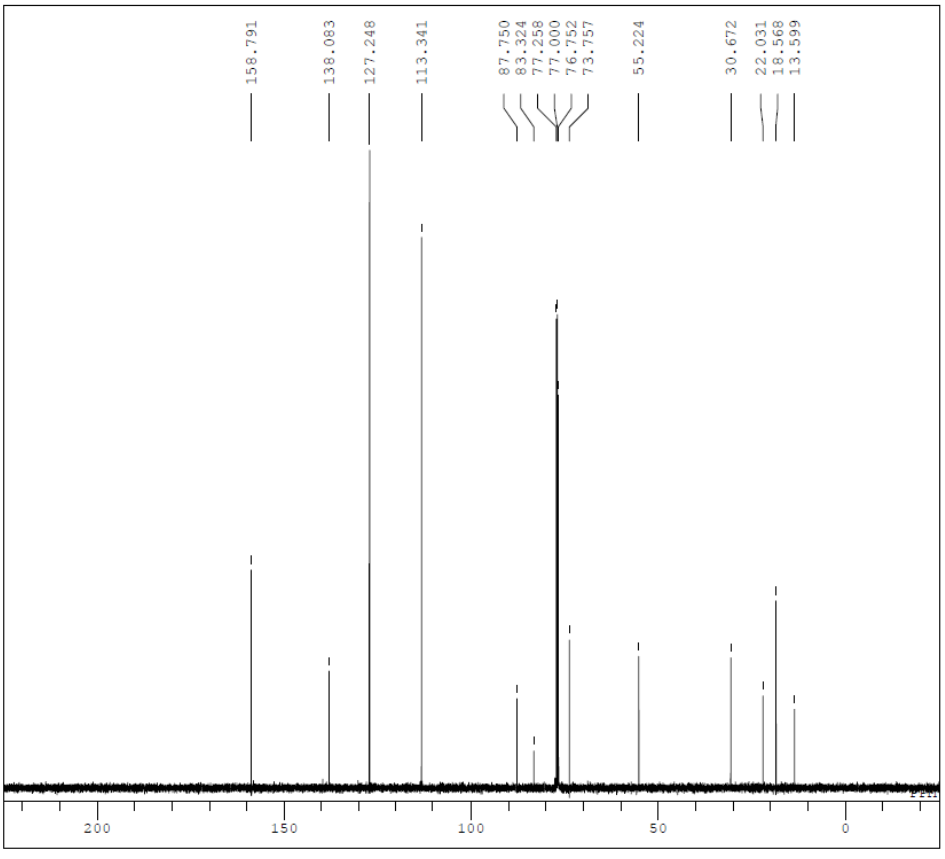

```
DFILE   HT5-98-2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-08 18:10:52
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            520
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            17.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              58
```



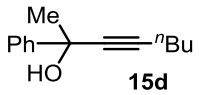
15c




```
DFILE   HT5-89-2_Proton-1-1.jdf
COMNT   single_pulse lower spot
DATIM   2013-02-01 10:51:35
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          19.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             30
```

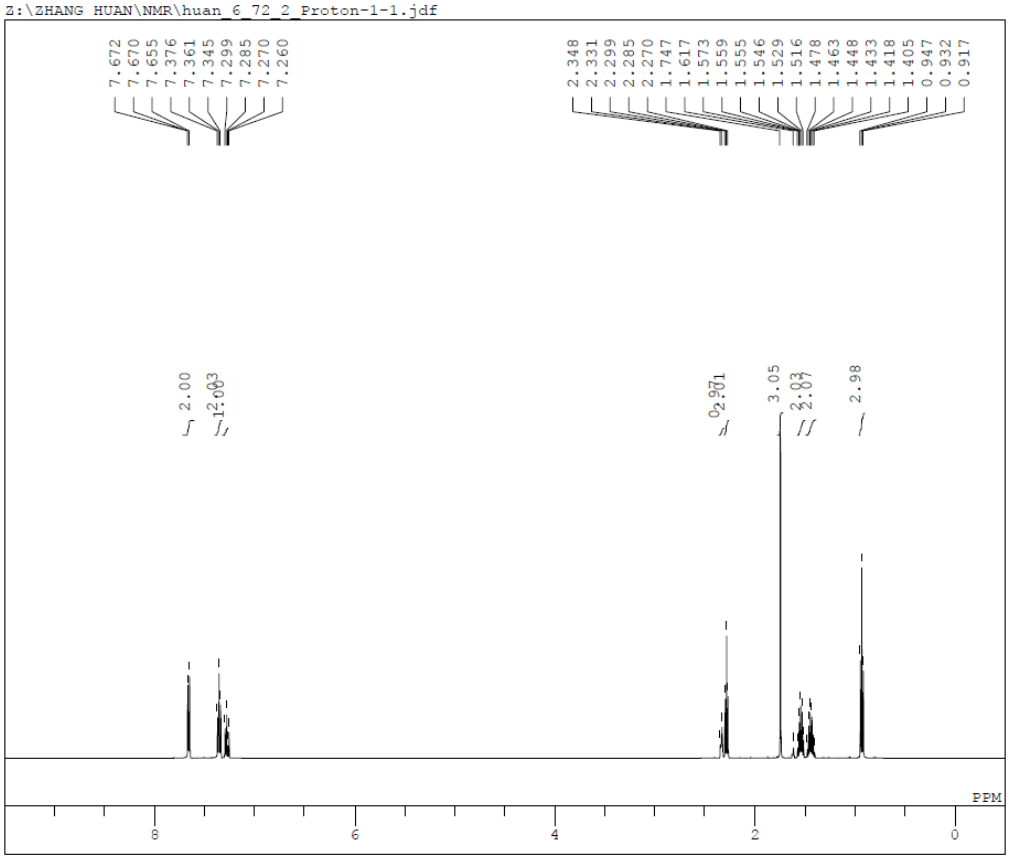



```
DFILE   HT5-89-2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-01 10:54:04
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            297
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             56
```



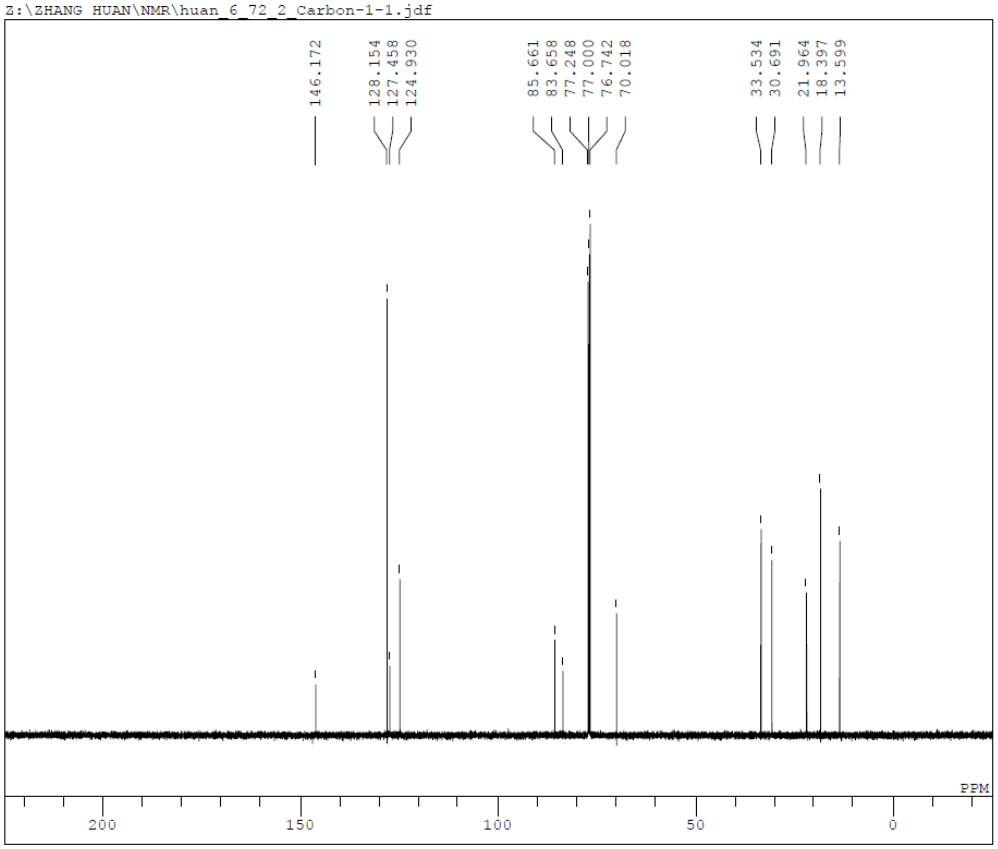
15d

Z:\ZHANG HUAN\NMR\huan_6_72_2_Proton-1-1.jdf

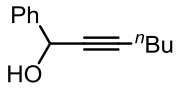



```
DFILE   huan_6_72_2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-24 14:07:06
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS                8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             32
```

Z:\ZHANG HUAN\NMR\huan_6_72_2_Carbon-1-1.jdf

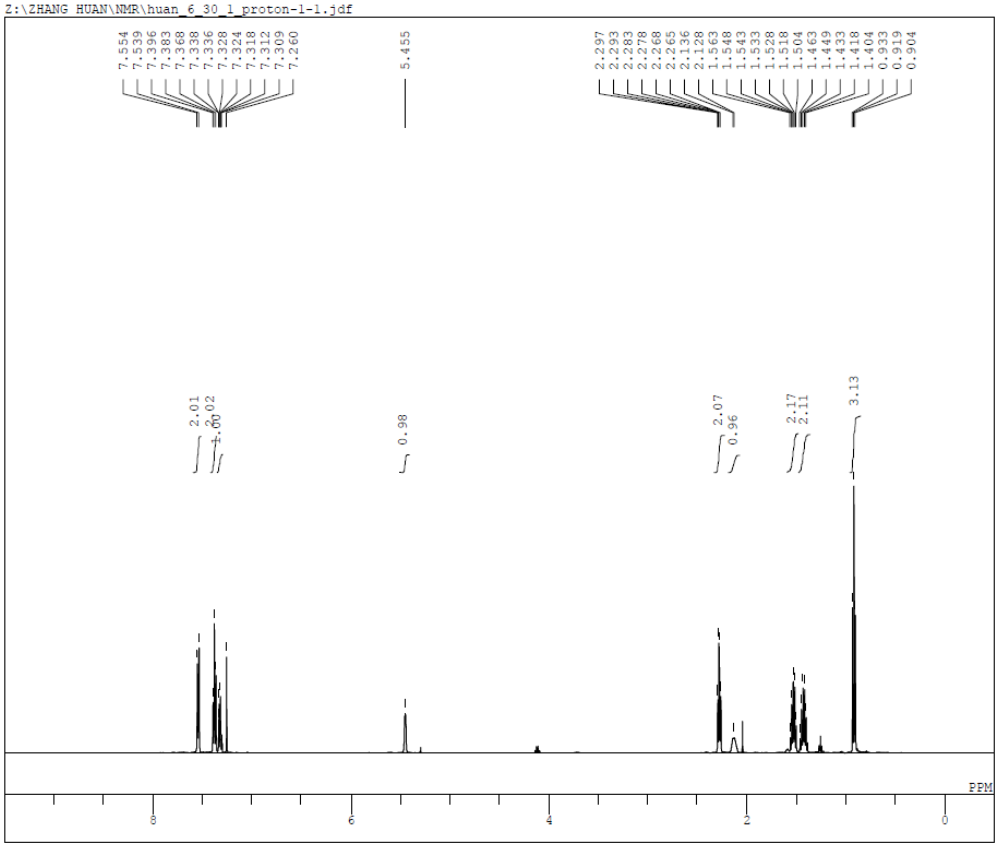



```
DFILE   huan_6_72_2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-24 14:08:36
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             56
```



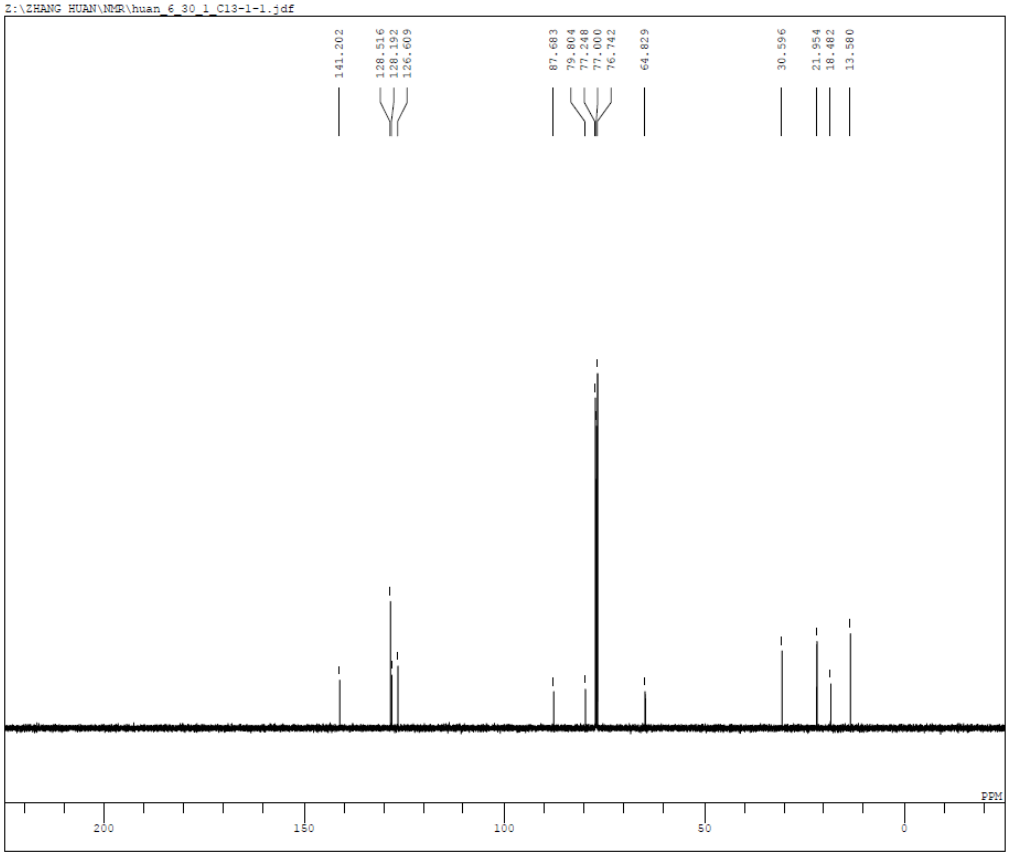
15g

Z:\ZHANG HUAN\NMR\huan_6_30_1_proton-1-1.jdf

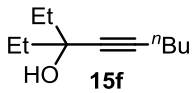



```
DFILE  huan_6_30_1_proton-1-1.jdf
COMNT  single_pulse
DATIM  2013-05-07 21:09:04
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          16.0 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            38
```

Z:\ZHANG HUAN\NMR\huan_6_30_1_C13-1-1.jdf

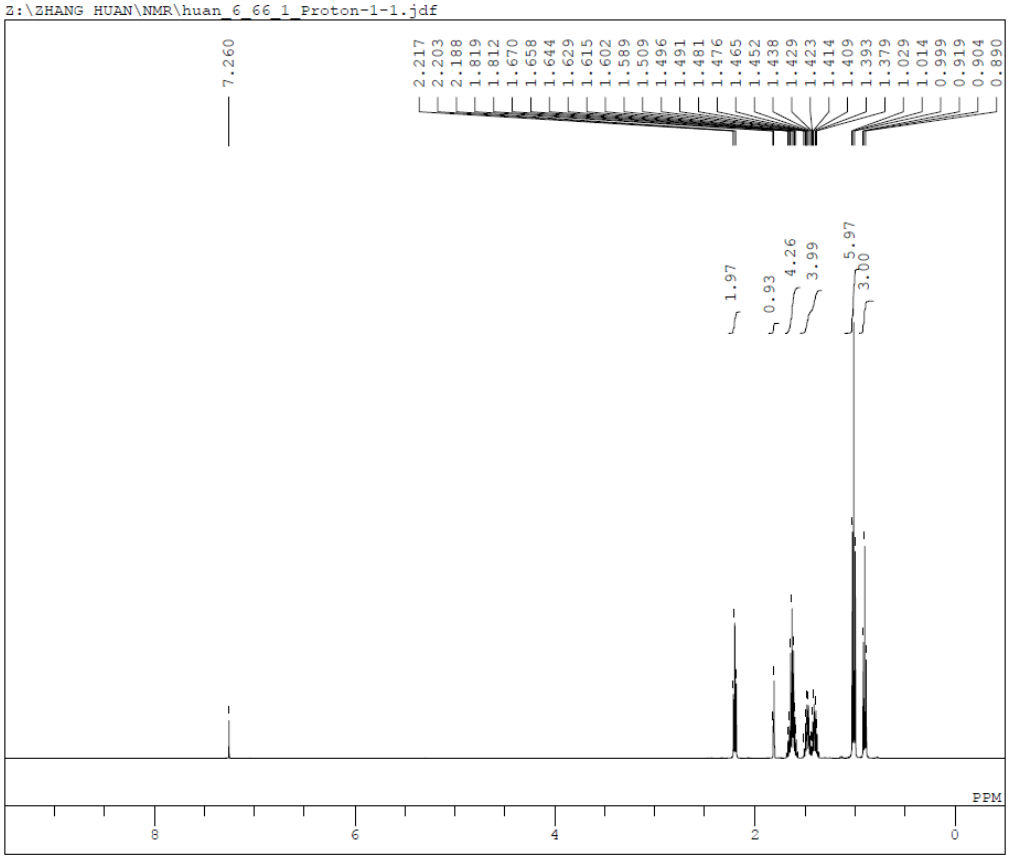



```
DFILE  huan_6_30_1_C13-1-1.jdf
COMNT  single_pulse decoupled gated NOE
DATIM  2013-05-09 22:03:38
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS           256
ACQTM        0.8336 sec
PD           2.0000 sec
PW1             3.12 usec
IRNUC  1H
CTEMP          18.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            56
```



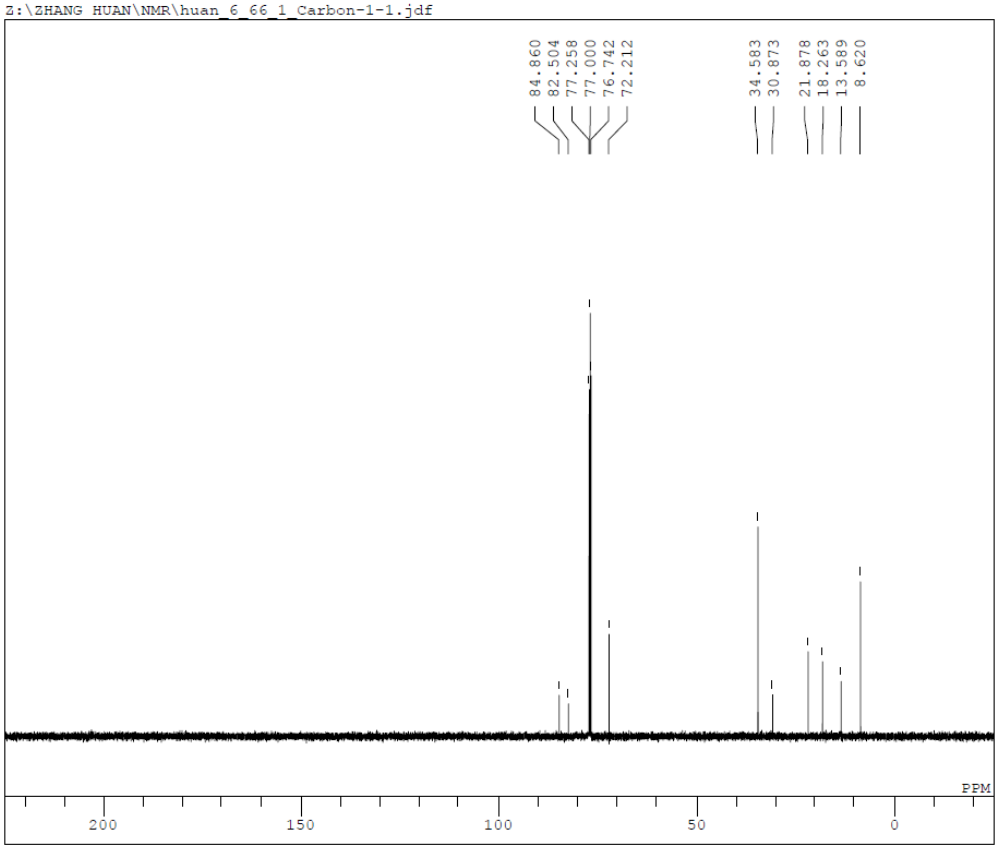
15f

Z:\ZHANG HUAN\NMR\huan_6_66_1_Proton-1-1.jdf

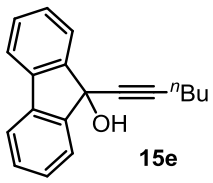



```
DFILE   huan_6_66_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-21 22:51:08
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS                8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.2 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            34
```

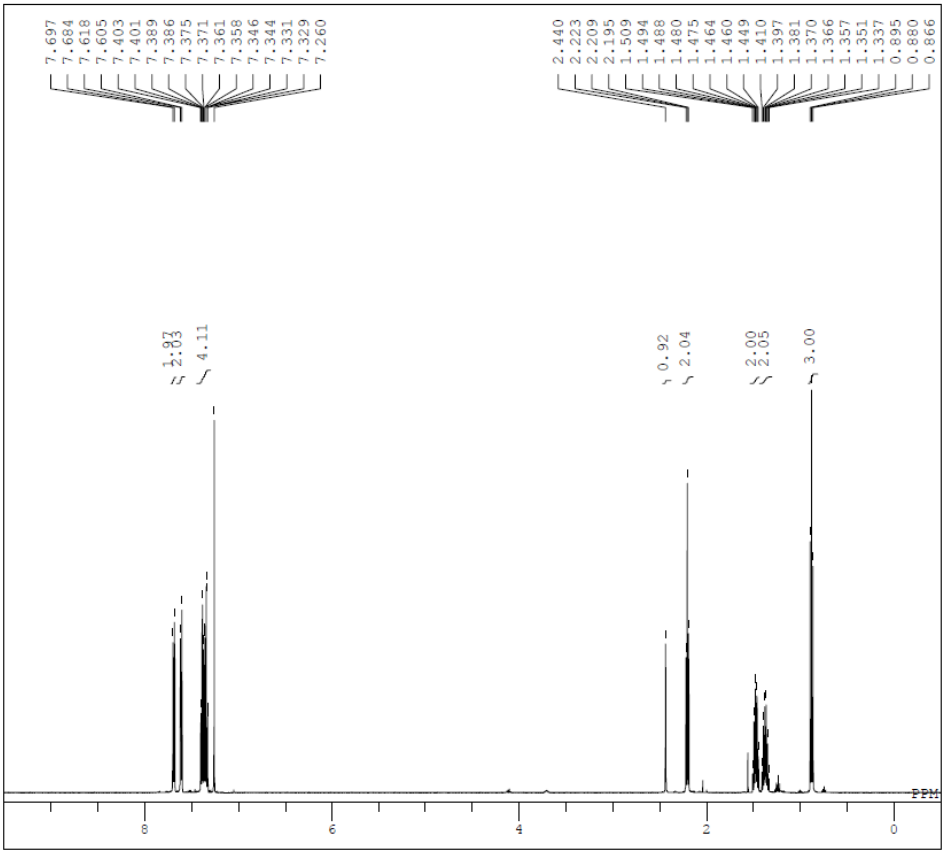
Z:\ZHANG HUAN\NMR\huan_6_66_1_Carbon-1-1.jdf



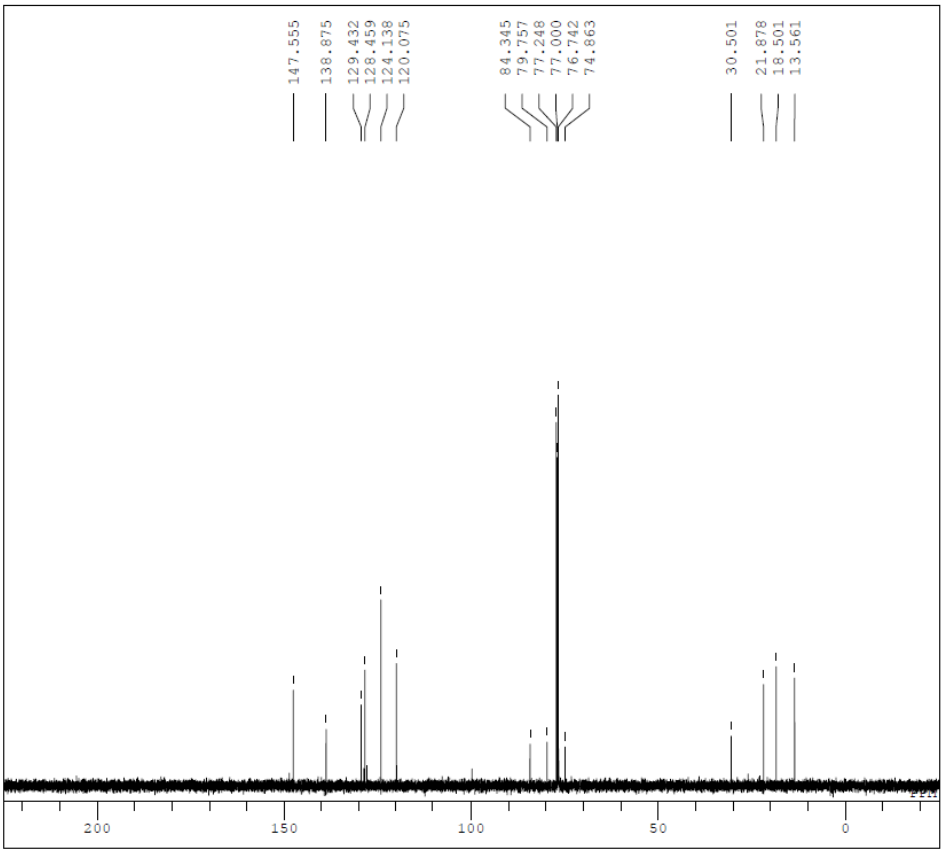

```
DFILE   huan_6_66_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-21 22:52:39
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             256
ACQTM         0.8336 sec
PD            2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP          18.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



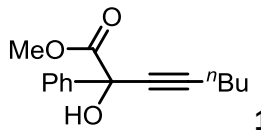
15e




```
DFILE   HT5-86-3_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-01-31 03:14:43
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             40
```

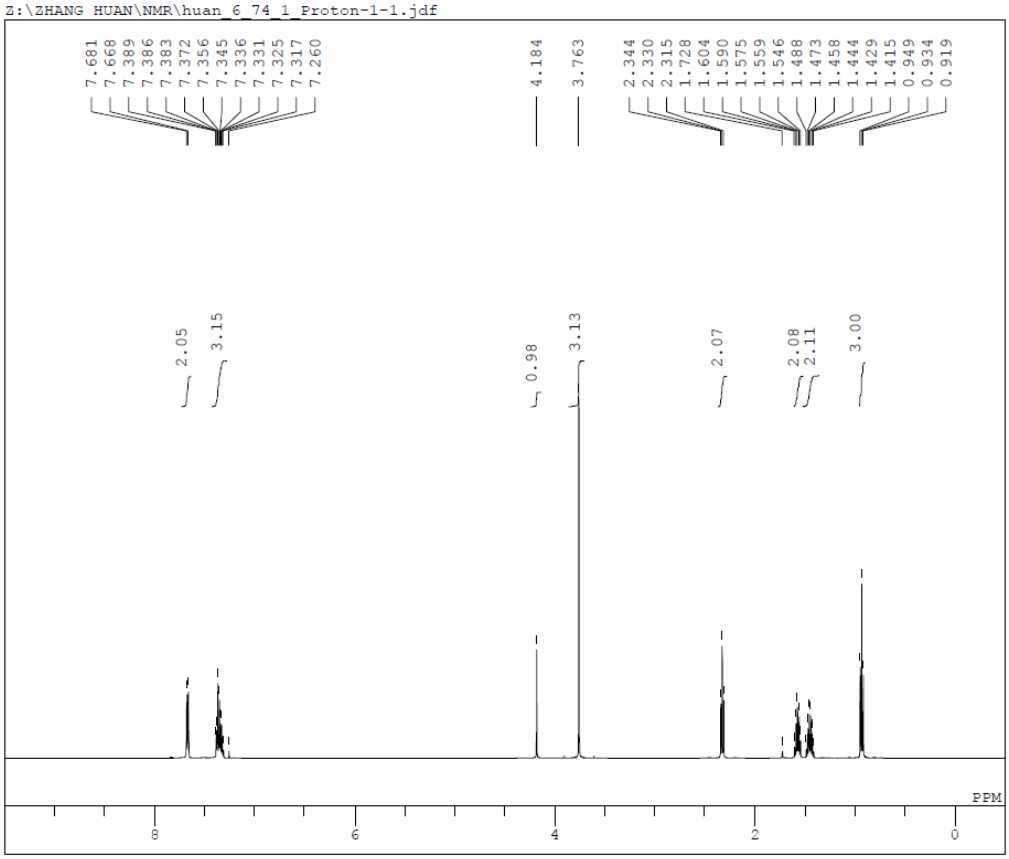



```
DFILE   HT5-86-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-30 18:02:38
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             73
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



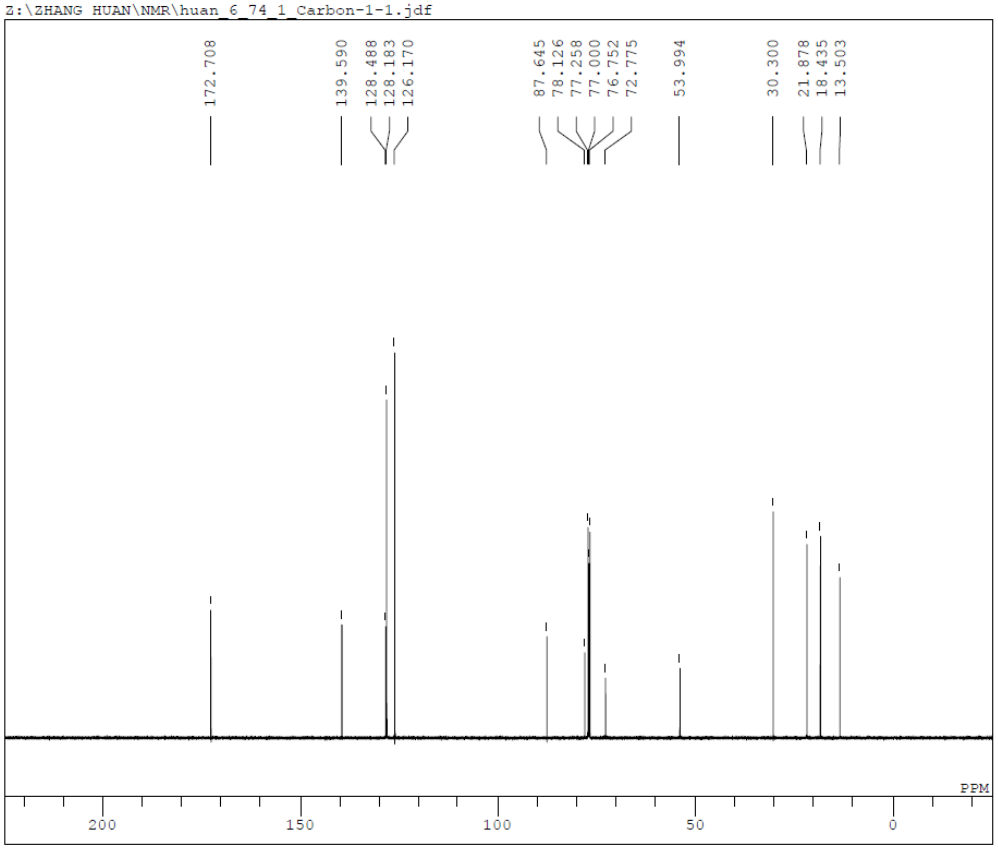
15h

Z:\ZHANG HUAN\NMR\huan_6_74_1_Proton-1-1.jdf

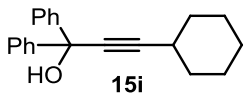



```
DFILE   huan_6_74_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-24 17:36:57
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS                8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             22
```

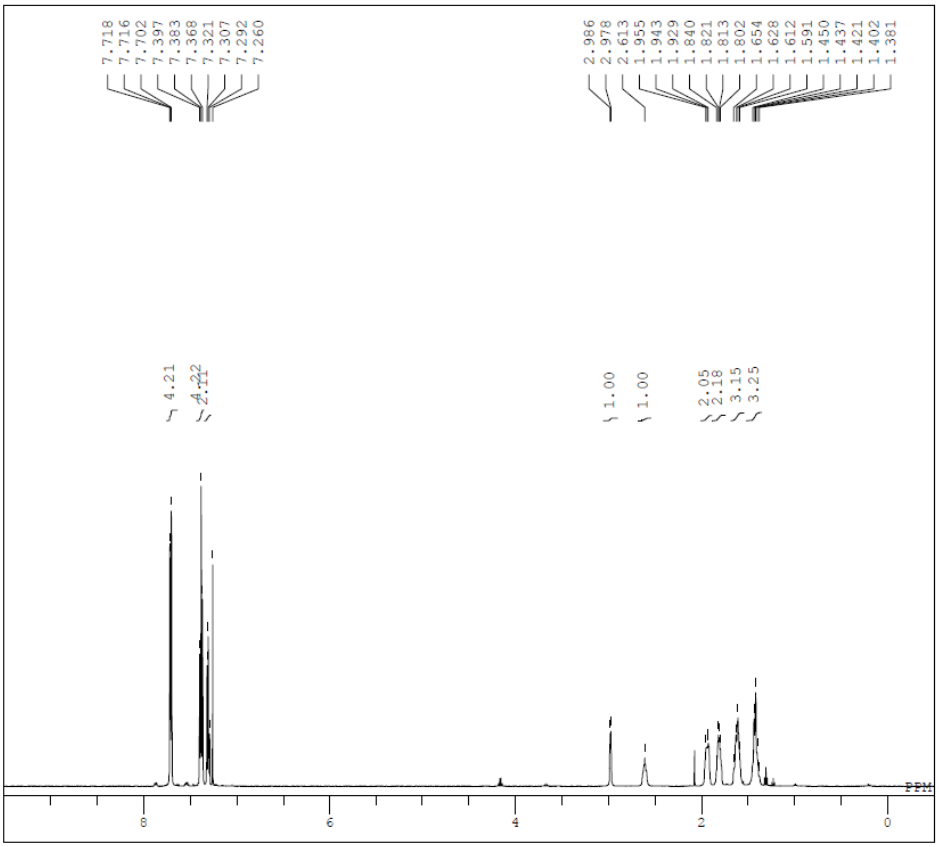
Z:\ZHANG HUAN\NMR\huan_6_74_1_Carbon-1-1.jdf



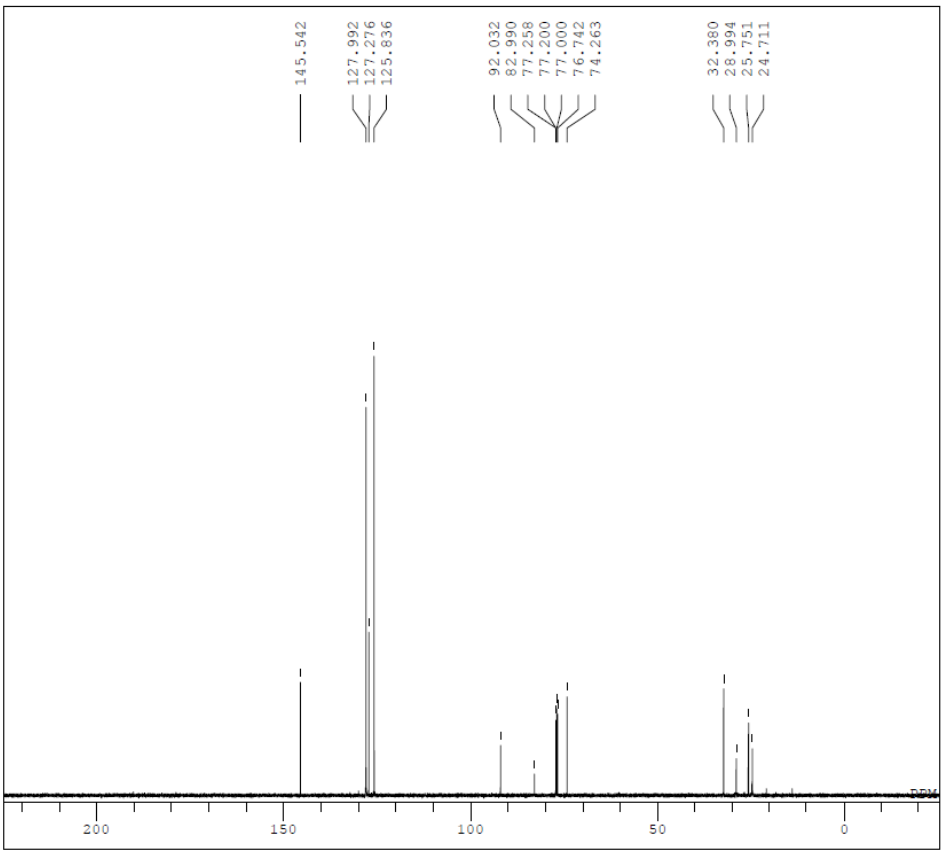

```
DFILE   huan_6_74_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-24 17:38:28
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



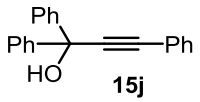
15i



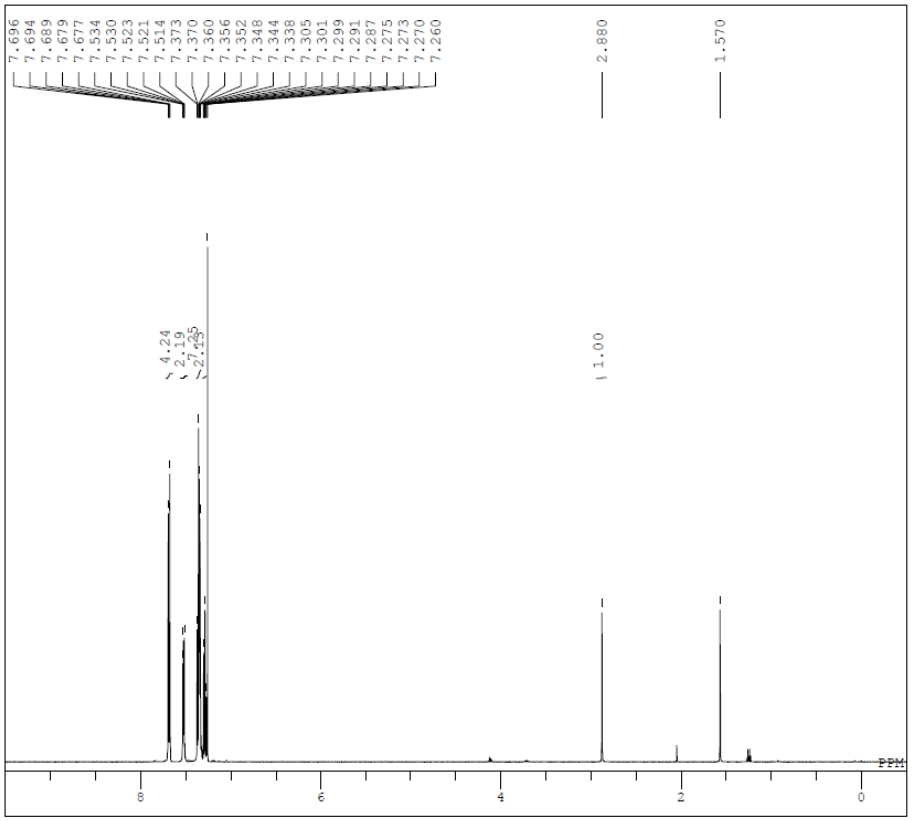

```
DFILE   HT5-115-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-03-09 01:15:34
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           16.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             18
```



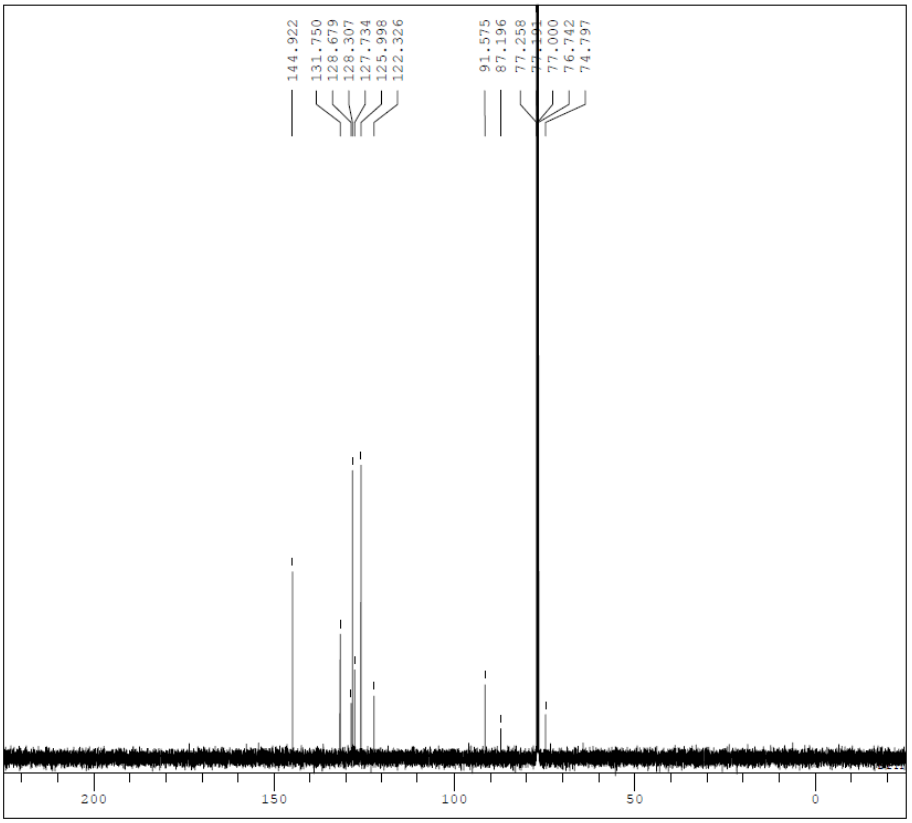

```
DFILE   HT5-115-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-03-09 01:17:04
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             69
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           16.3 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             56
```



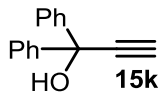
15j



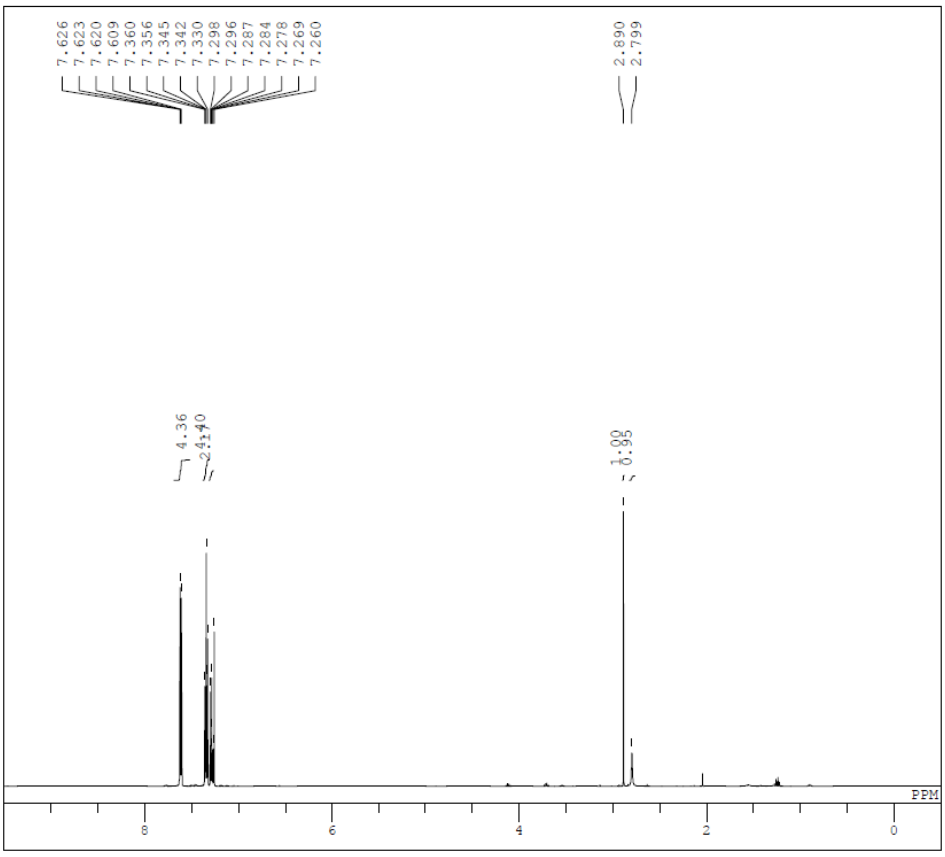

```
DFILE   HT5-56-1 alkyne-1-1.jdf
COMNT   single_pulse
DATIM   2012-12-15 19:05:50
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           14.7 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             44
```



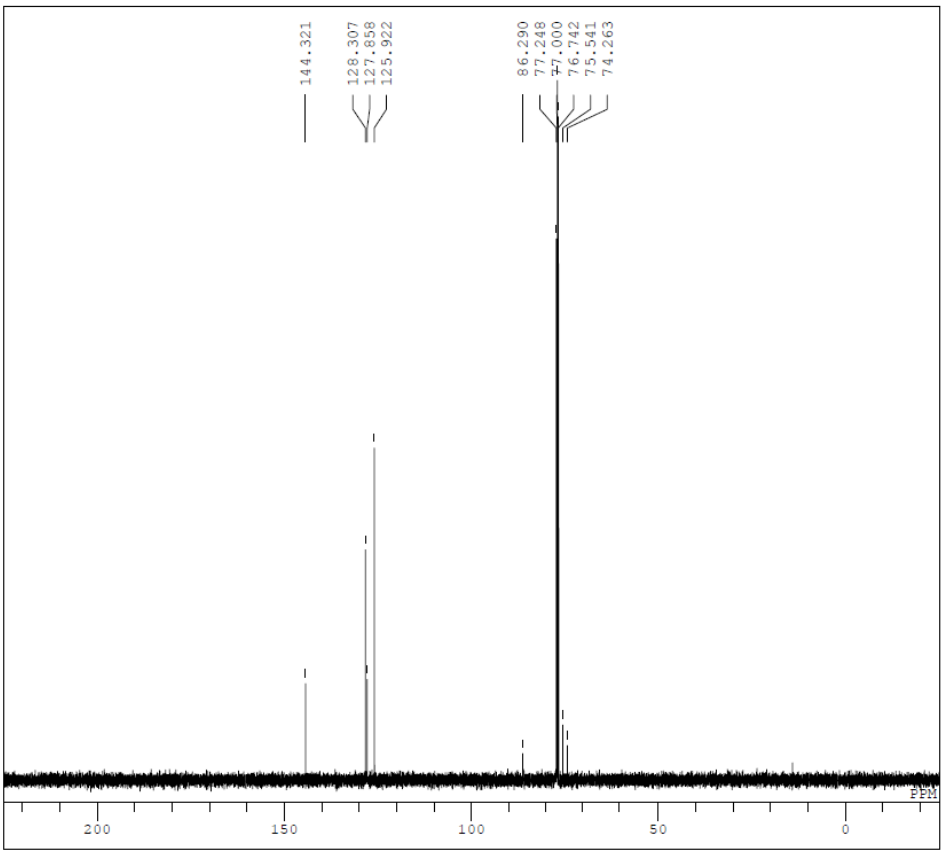

```
DFILE   HT5-56-1 13C-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-15 19:08:15
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           15.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



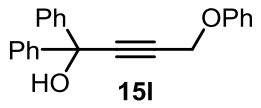
15k



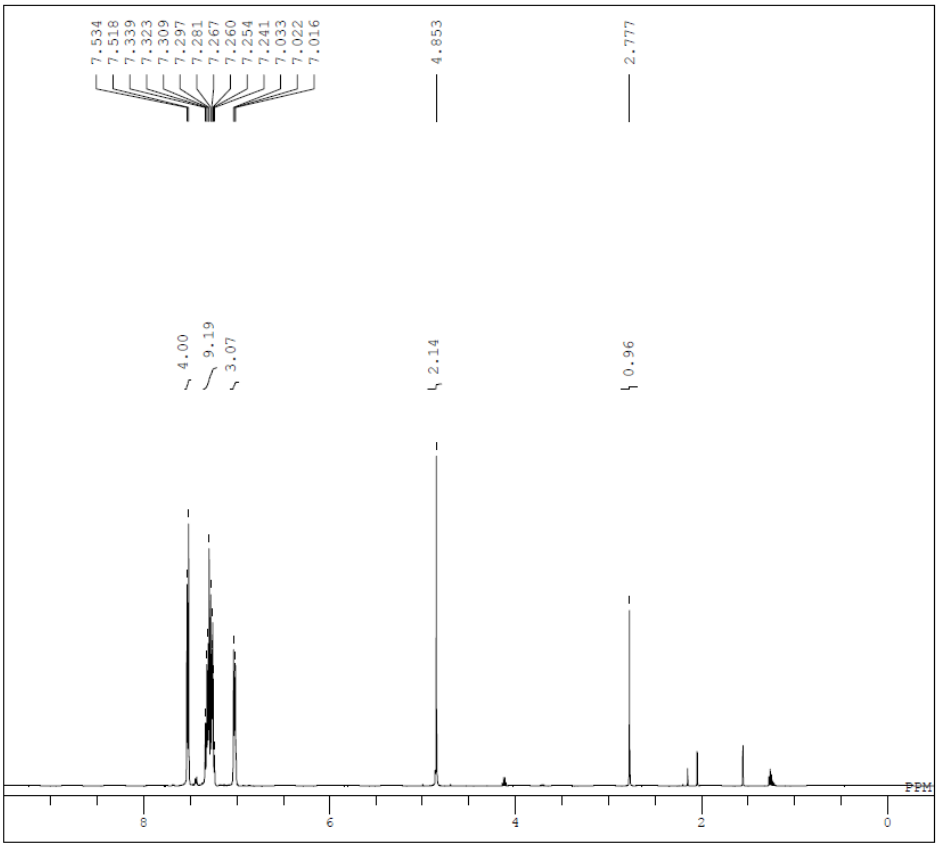

```
DFILE   HT5-52-3 proton-1-1.jdf
COMNT   single_pulse
DATIM   2012-12-04 21:36:49
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.8 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            44
```



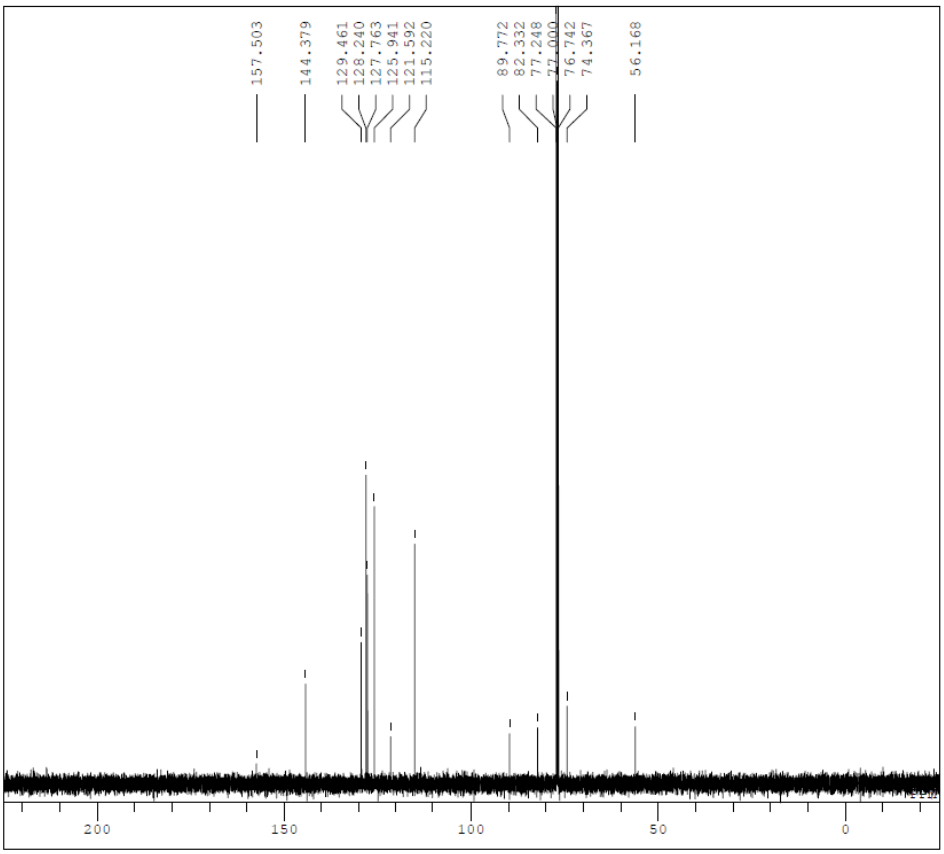

```
DFILE   HT5-52-1 alkyne 13C-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-04 20:09:24
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            207
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          17.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.10 Hz
RGAIN            60
```



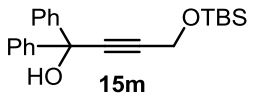
15l



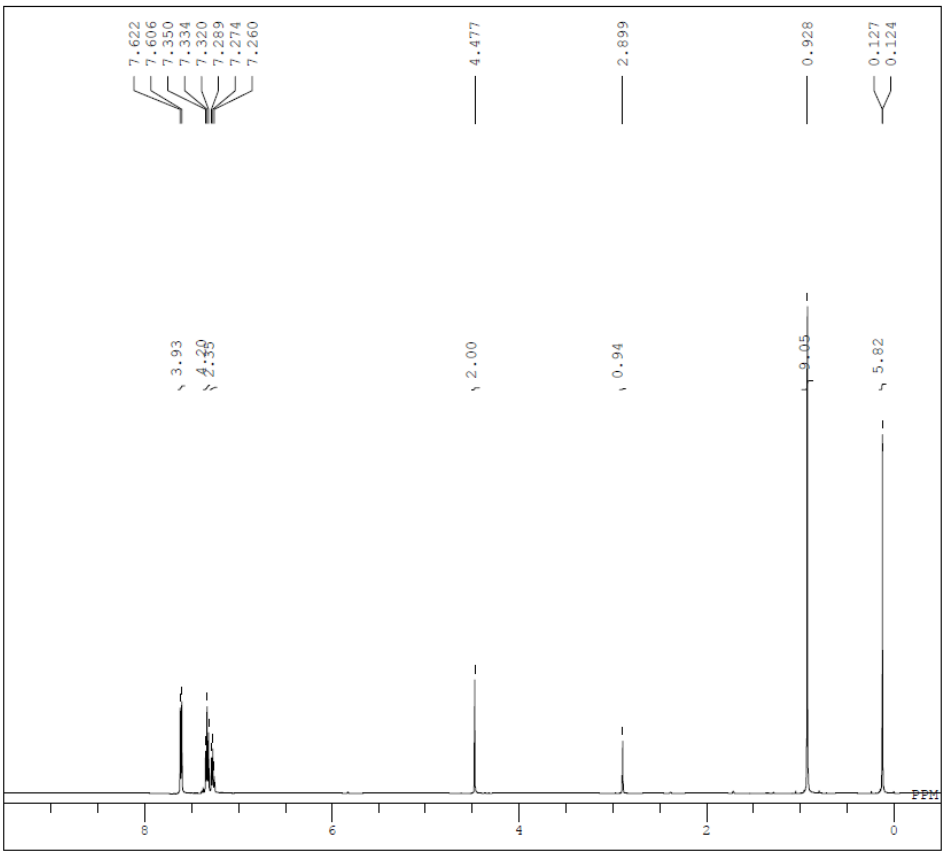

```
DFILE   HT5-108-2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-02-28 22:40:27
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             42
```



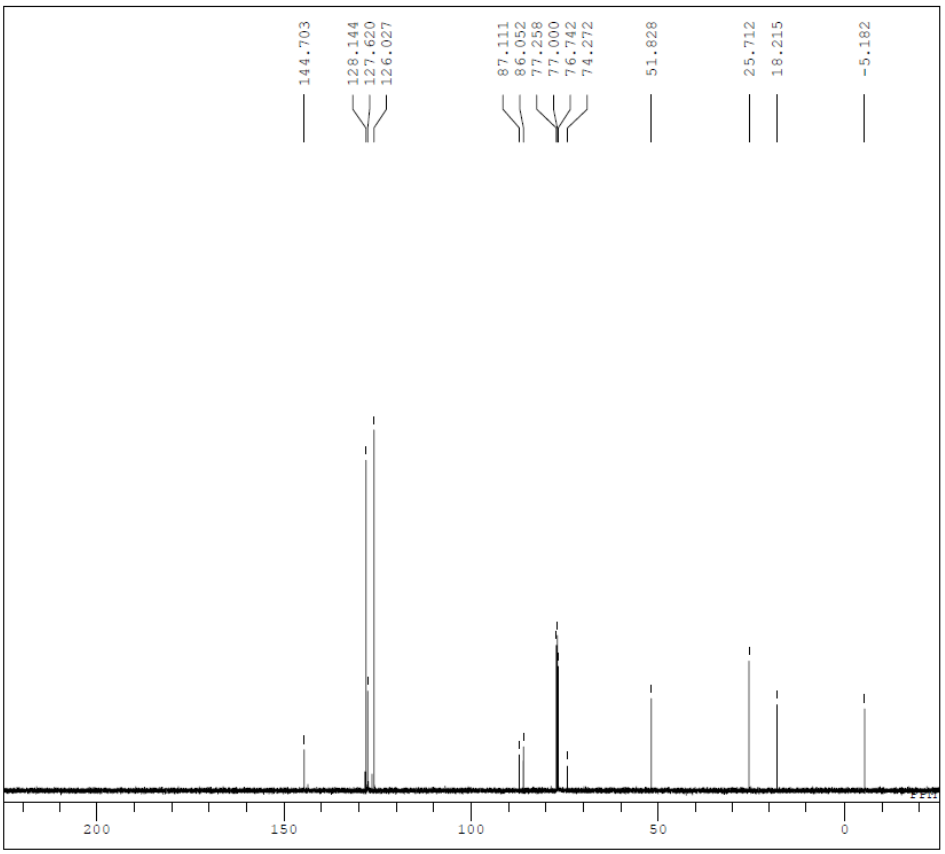

```
DFILE   HT5-108-2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-28 22:45:50
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            152
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             58
```



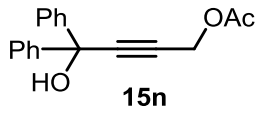
15m



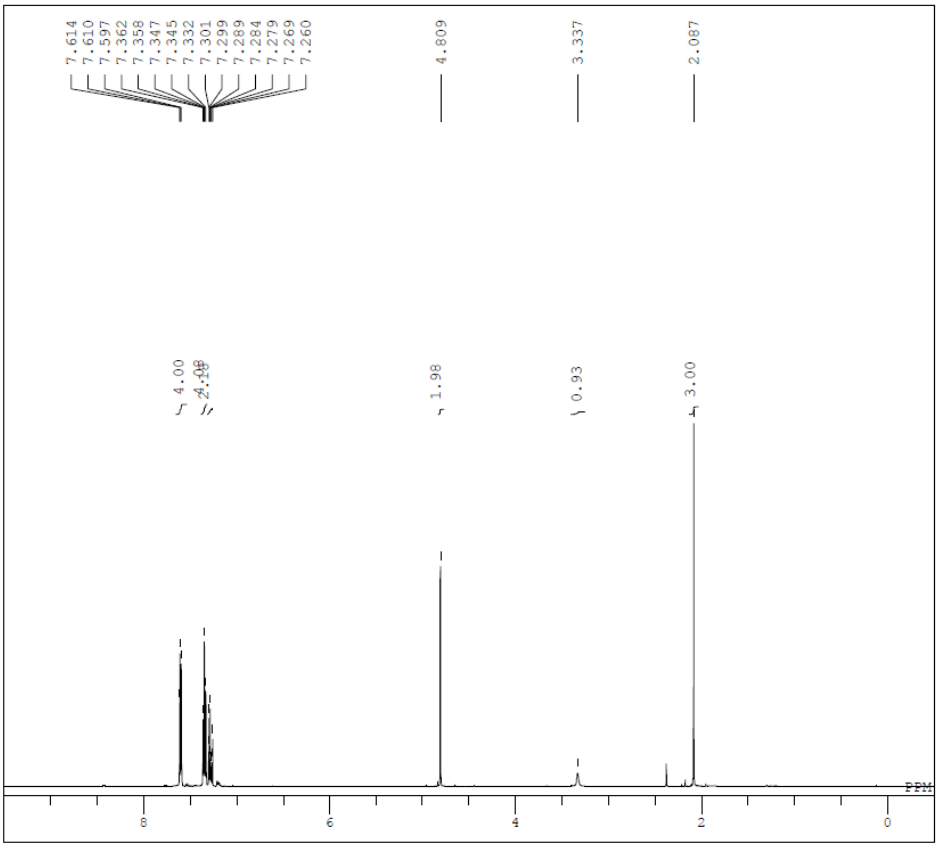

```
DFILE   HT5-75-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-01-24 16:31:54
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          14.1 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            24
```



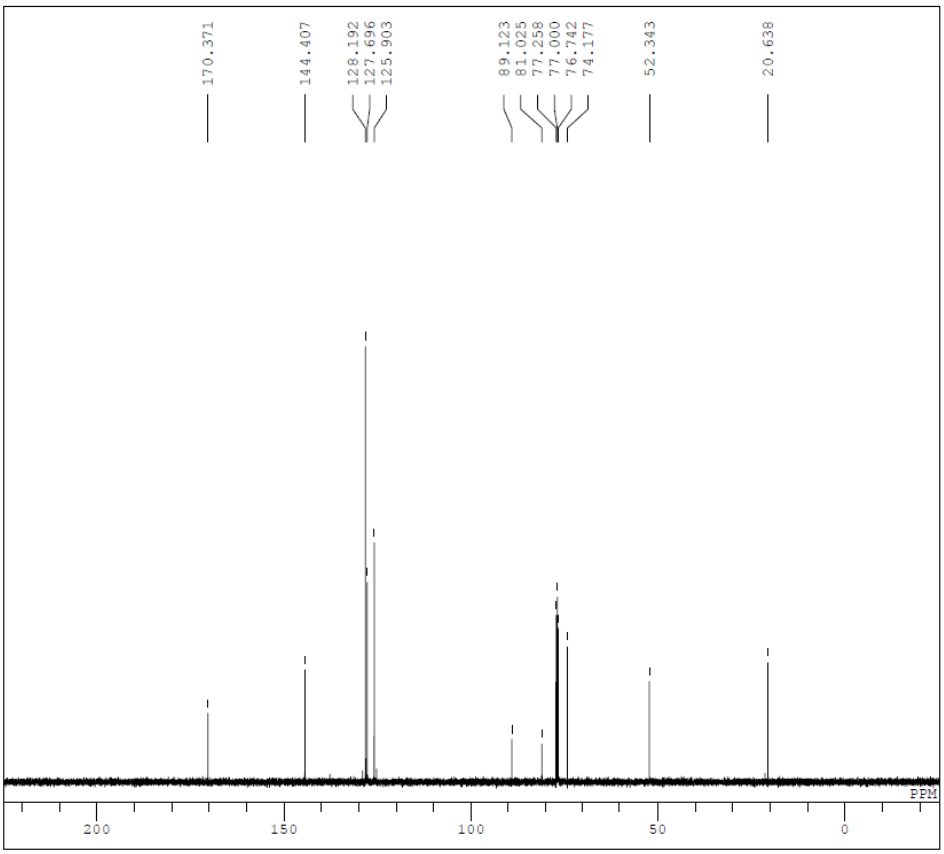

```
DFILE   HT5-75-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-24 16:34:19
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             72
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          14.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.10 Hz
RGAIN            56
```



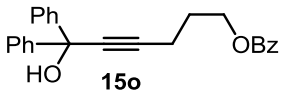
15n



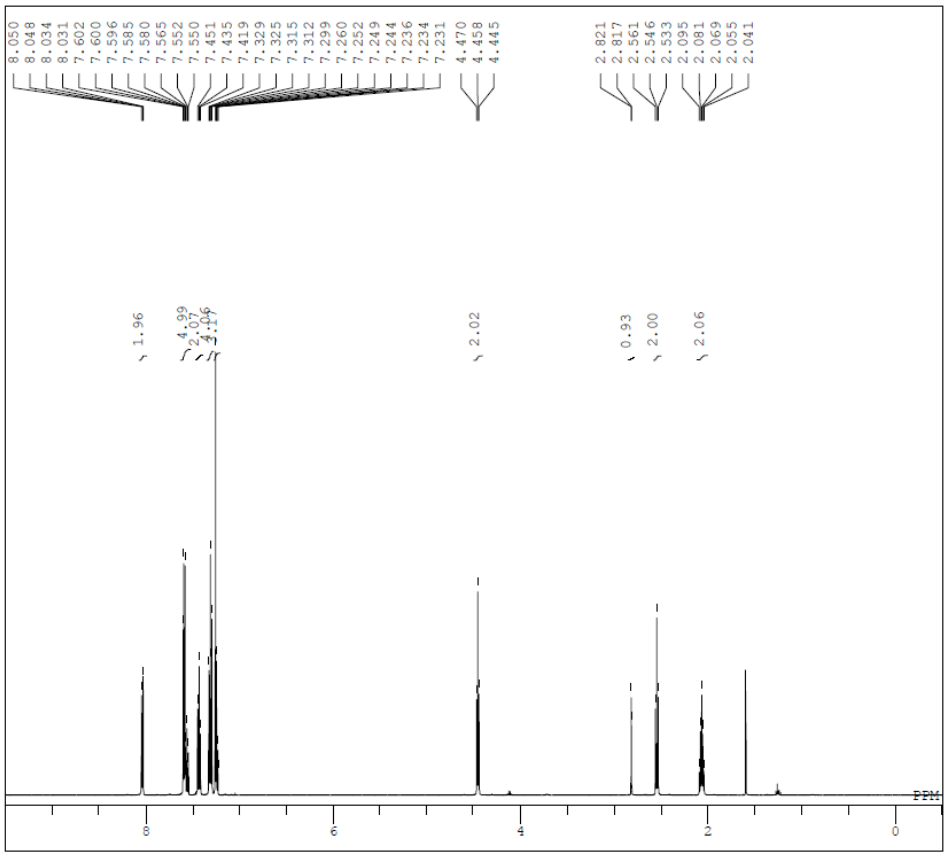

```
DFILE   HT5-111-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-02-23 19:56:10
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           17.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             24
```



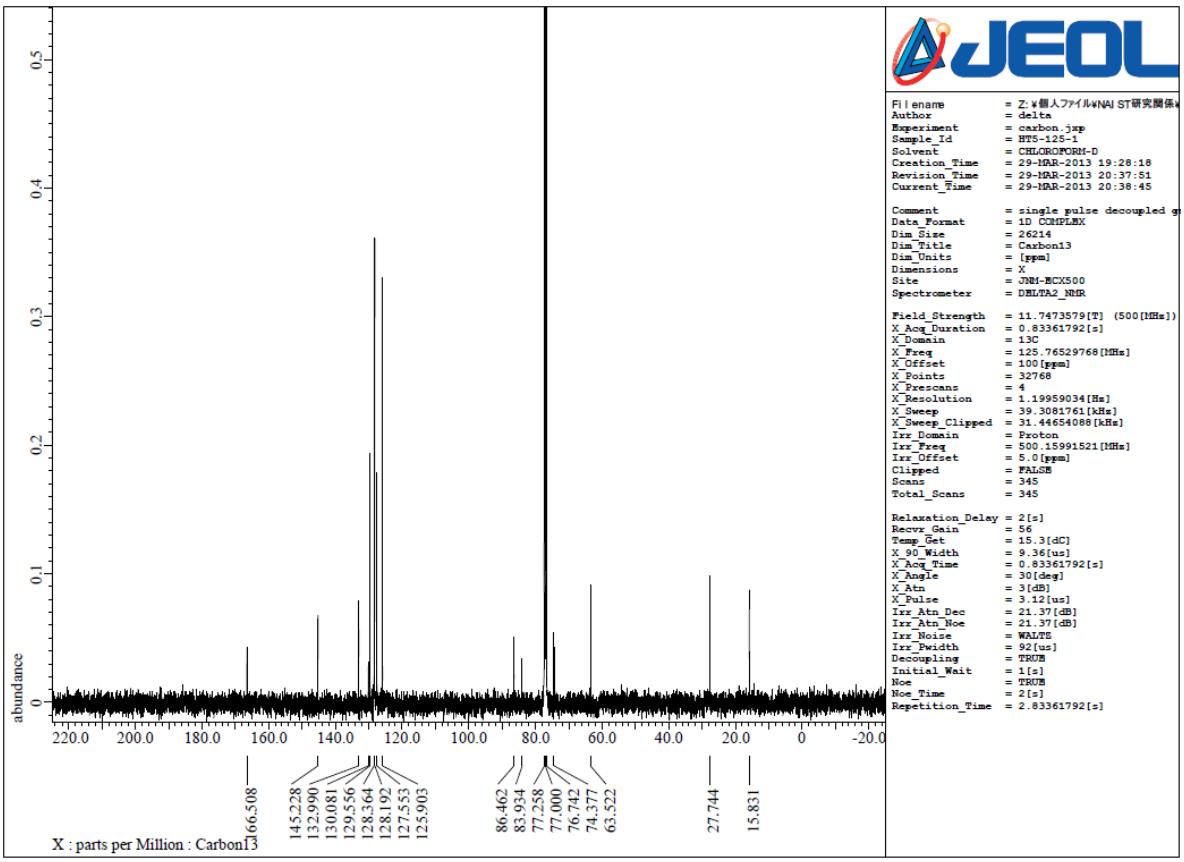

```
DFILE   HT5-111-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-23 19:57:40
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             47
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           17.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             56
```



15o




```
DFILE   HT5-125-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-03-29 19:26:49
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           15.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             42
```

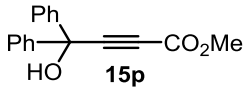



```
Filename          = Z:¥個人ファイル¥NAI ST研究関係¥
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = HT5-125-1
Solvent           = CHLOROFORM-D
Creation_Time     = 29-MAR-2013 19:28:18
Revision_Time     = 29-MAR-2013 20:37:51
Current_Time      = 29-MAR-2013 20:38:45

Comment           = single pulse decoupled g
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

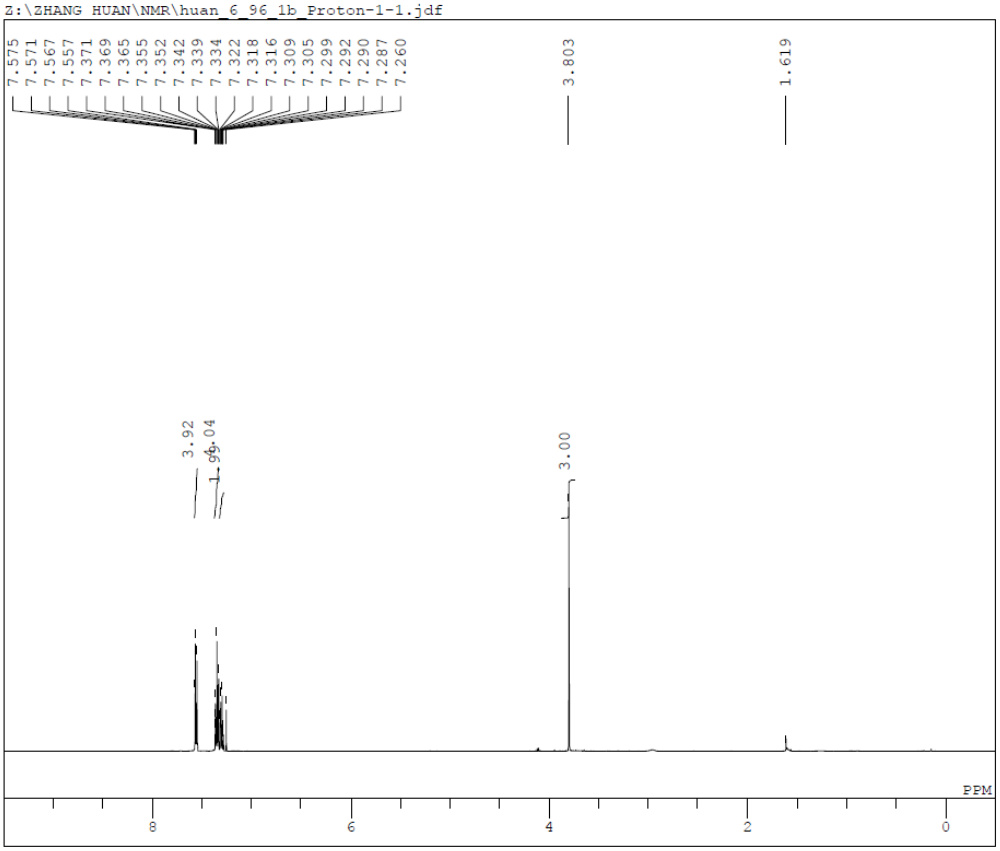
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 345
Total_Scans       = 345

Relaxation_Delay  = 2[s]
Recvr_Gain        = 56
Temp_Get          = 15.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 21.37[dB]
Irr_Atn_Noe       = 21.37[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



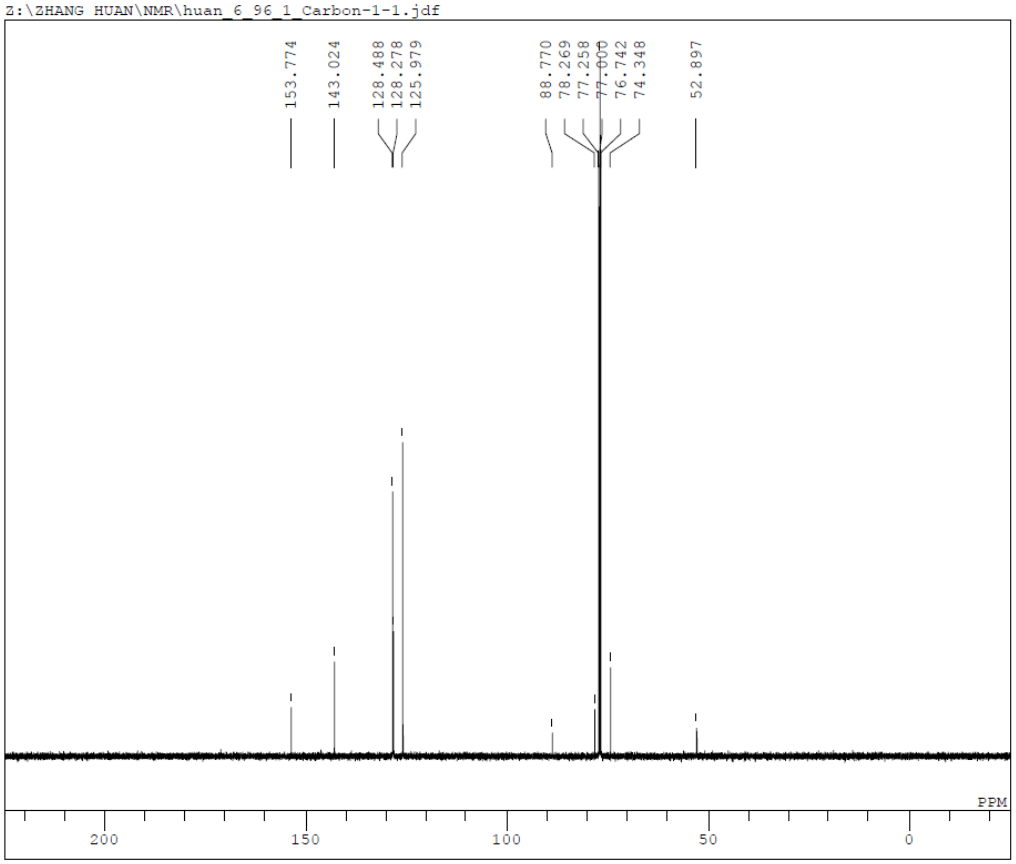
15p

Z:\ZHANG HUAN\NMR\huan_6_96_1b_Proton-1-1.jdf

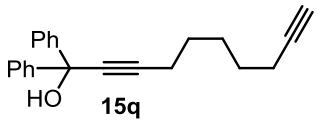



```
DFILE   huan_6_96_1b_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-06-06 12:09:20
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             40
```

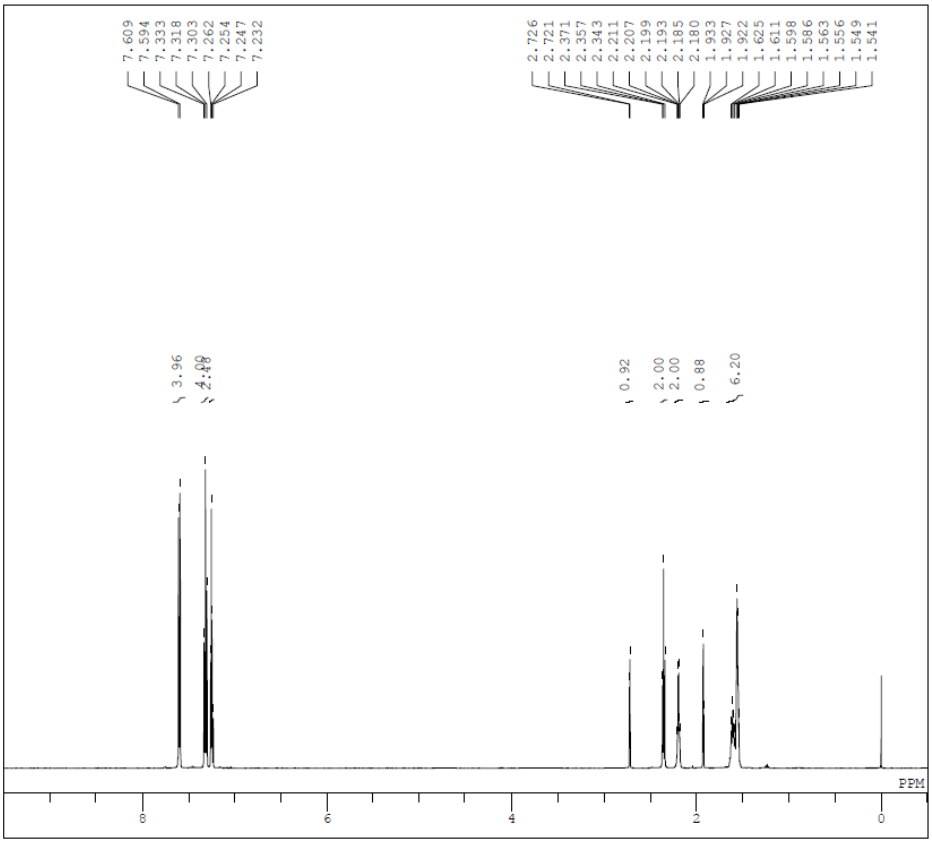
Z:\ZHANG HUAN\NMR\huan_6_96_1_Carbon-1-1.jdf



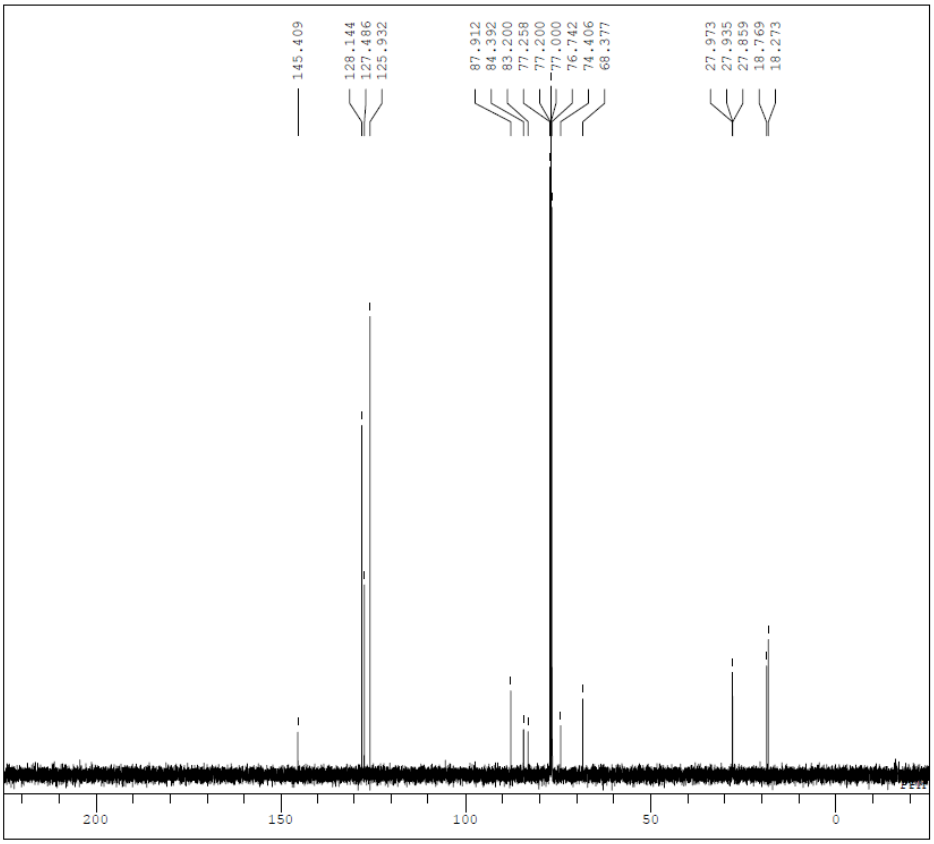

```
DFILE   huan_6_96_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-05 18:26:05
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS            1024
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           21.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



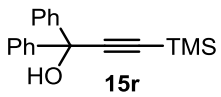
15q



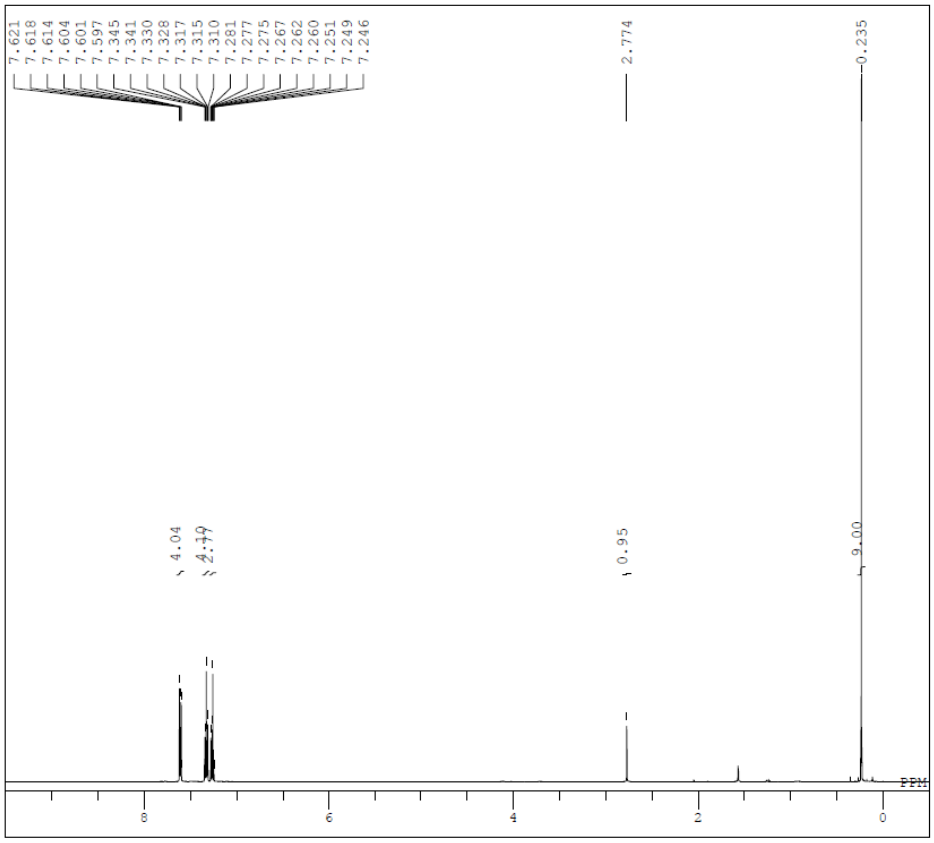

```
DFILE   HT5-127-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-04-04 20:31:04
OBNUC   1H
EXMOD   proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC   1H
CTEMP         15.5 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.10 Hz
RGAIN           36
```



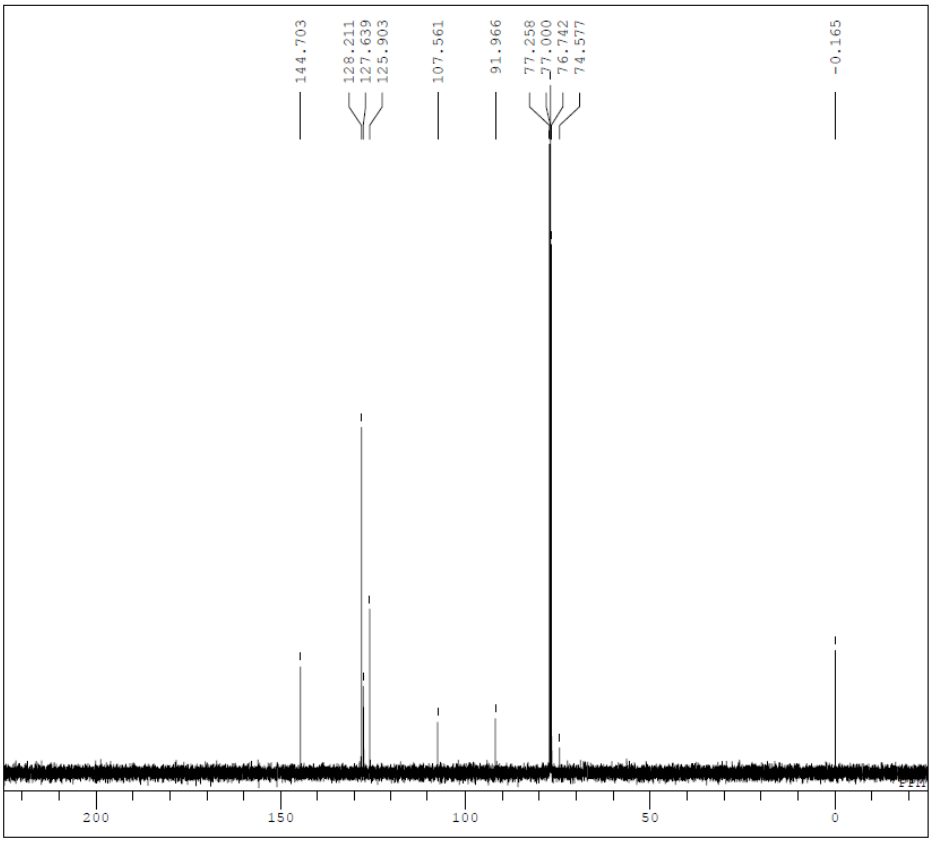

```
DFILE   HT5-127-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-04-04 20:32:33
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS          108
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC   1H
CTEMP         15.9 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            0.10 Hz
RGAIN           56
```



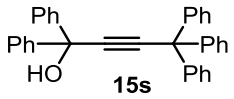
15r



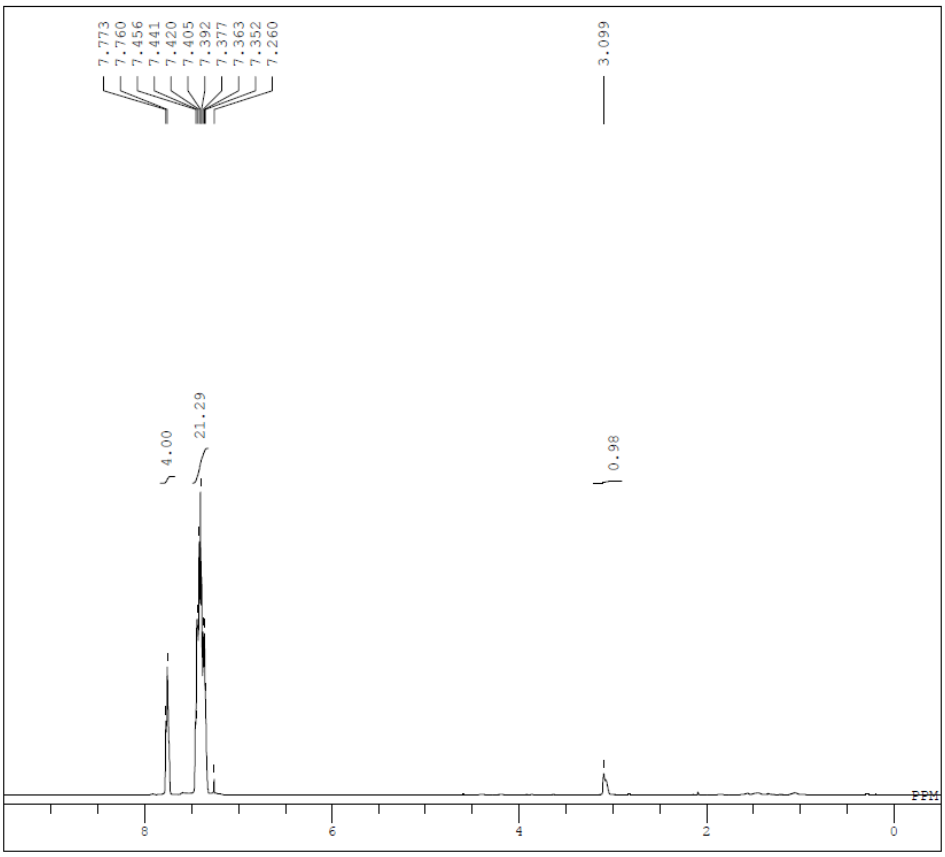

```
DFILE   HT5-59-1 proton-1-1.jdf
COMNT   HT5-59-1 coupling TMSacetylene
DATIM   2012-12-19 20:33:23
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            13.8 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              40
```



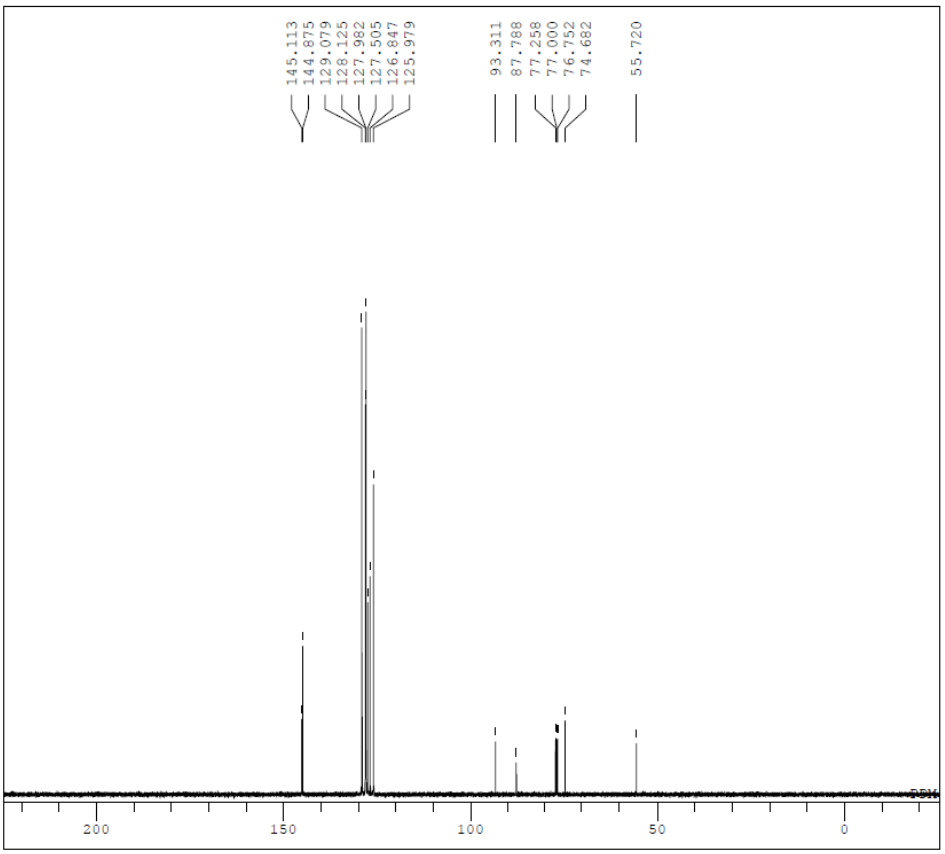

```
DFILE   HT5-59-1 13C-1-1.jdf
COMNT   HT5-59-1 13C NMR
DATIM   2012-12-19 16:38:55
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            114
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            14.2 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              52
```



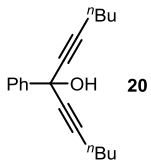
15s




```
DFILE   HT5-65-1_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-01-08 17:13:33
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            18.3 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              20
```

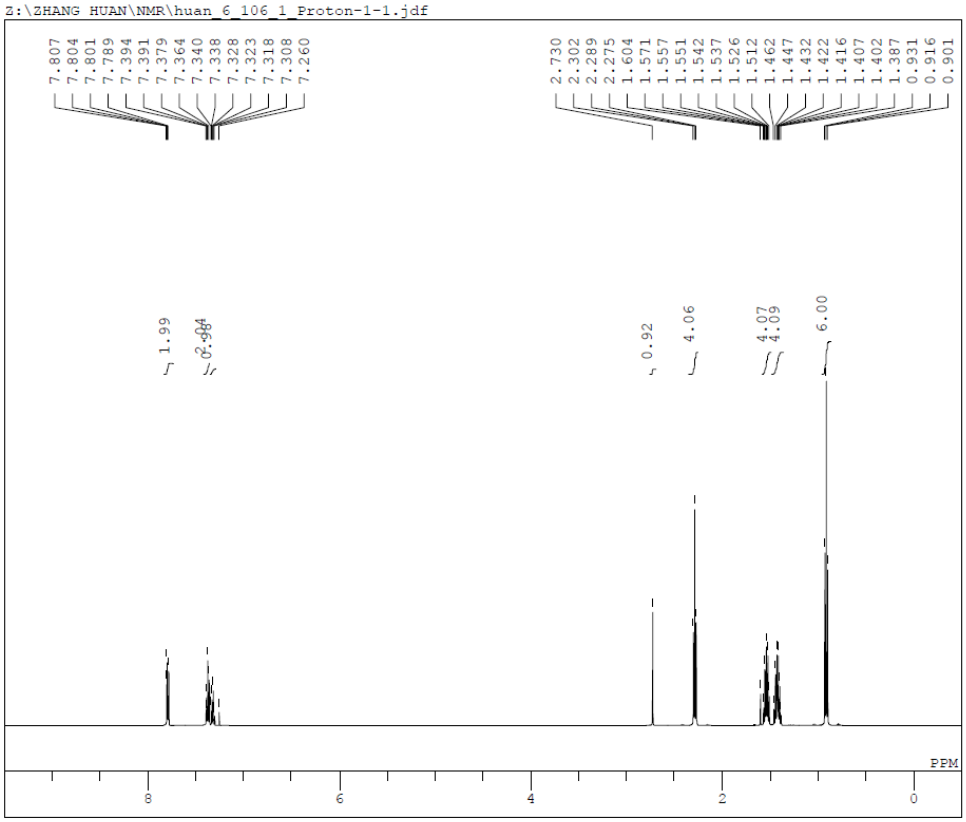



```
DFILE   HT5-65-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-08 17:15:51
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             97
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            18.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              60
```



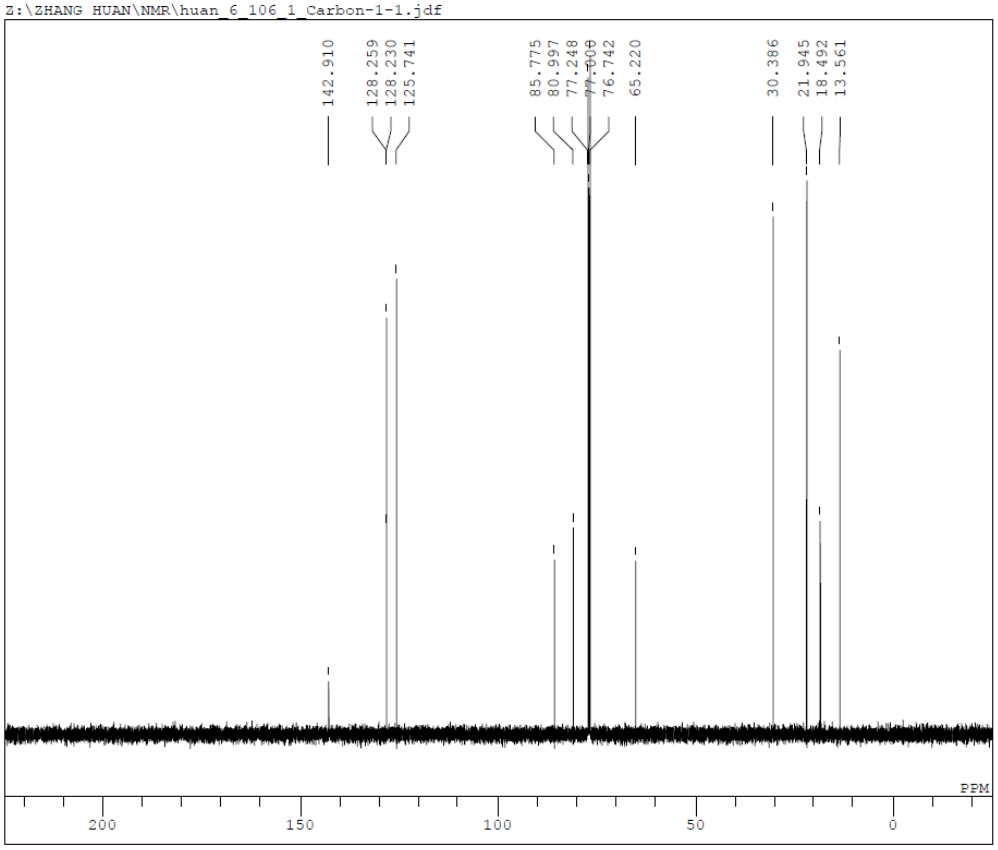
20

Z:\ZHANG HUAN\NMR\huan_6_106_1_Proton-1-1.jdf

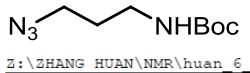



```
DFILE   huan_6_106_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-06-12 23:55:46
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             30
```

Z:\ZHANG HUAN\NMR\huan_6_106_1_Carbon-1-1.jdf

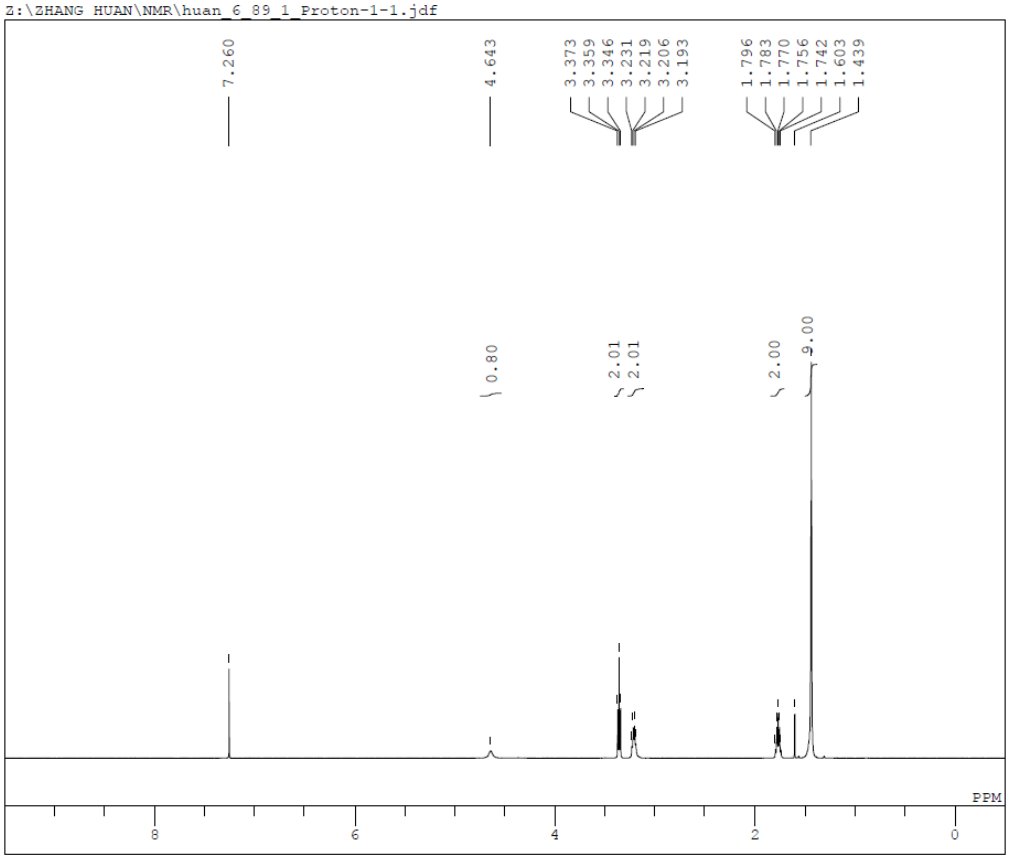



```
DFILE   huan_6_106_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-12 23:57:15
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            138
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           19.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



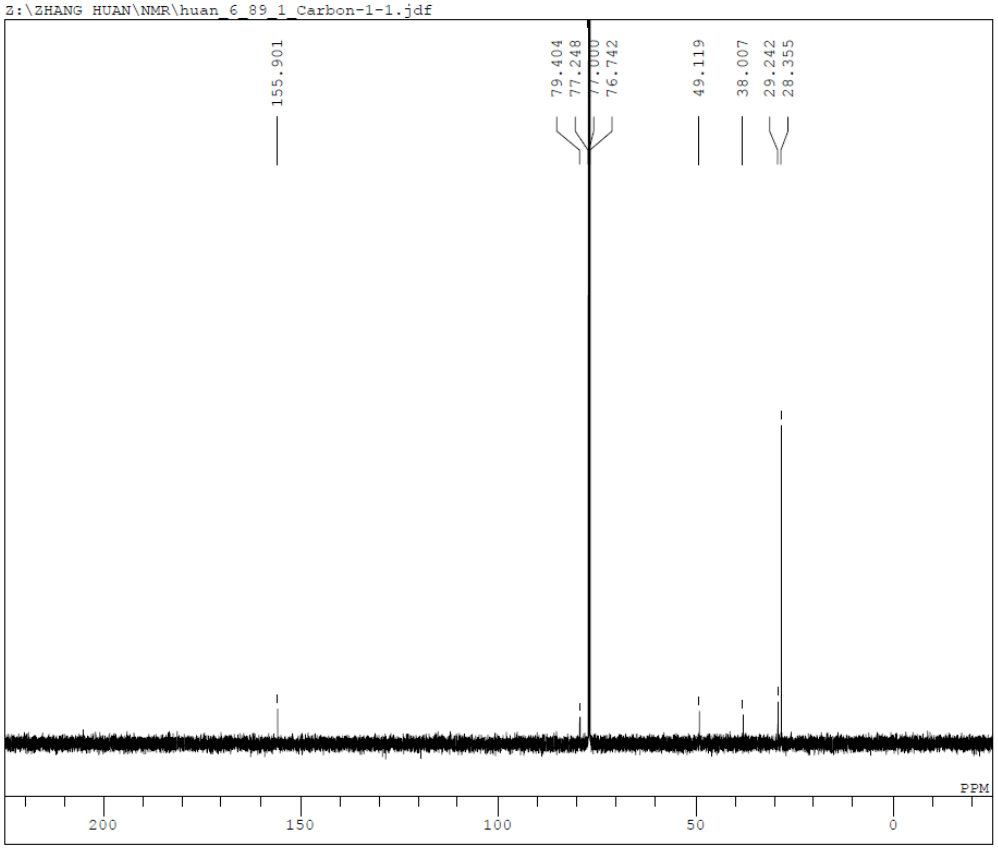
16yA

Z:\ZHANG HUAN\NMR\huan_6_89_1_Proton-1-1.jdf

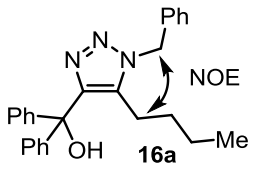



```
DFILE   huan_6_89_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-06-02 23:24:02
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS               8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          19.1 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            42
```

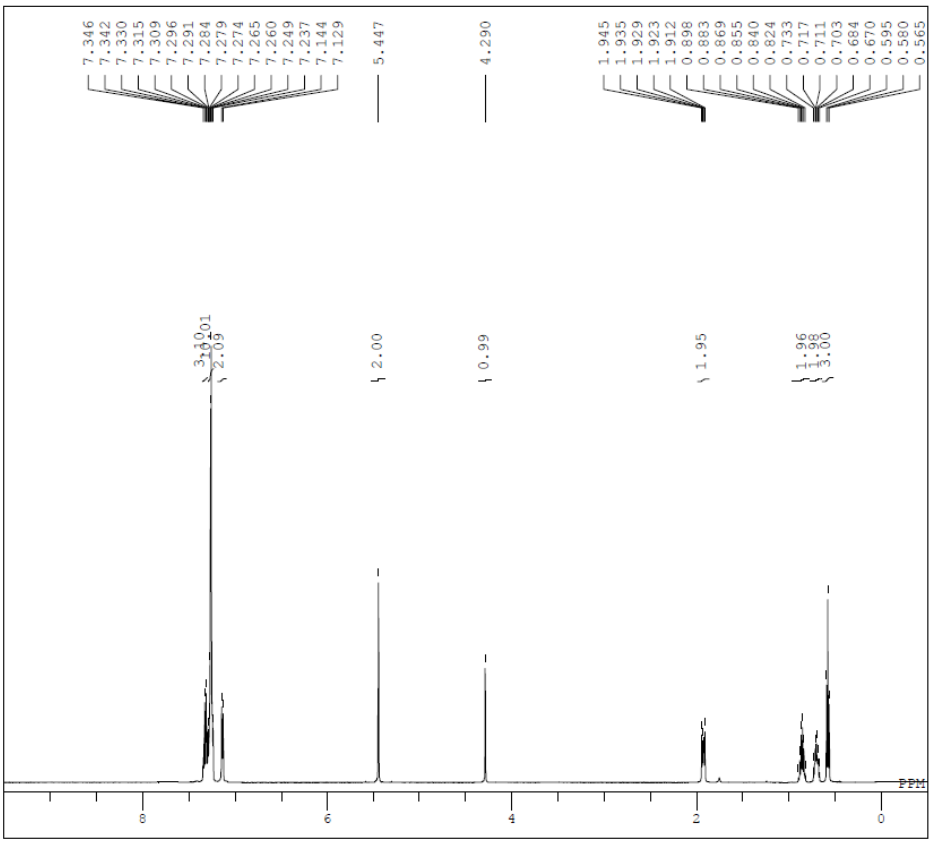
Z:\ZHANG HUAN\NMR\huan_6_89_1_Carbon-1-1.jdf



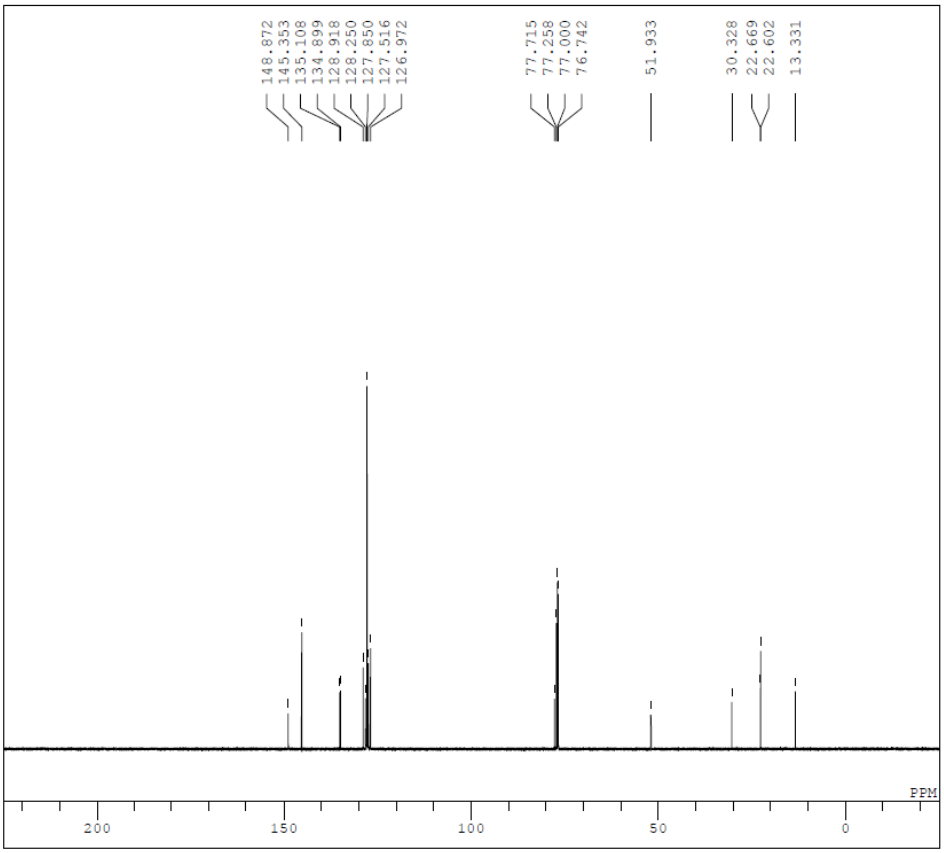

```
DFILE   huan_6_89_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-02 23:25:31
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.9 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            58
```



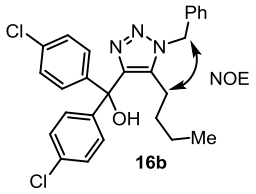
16a



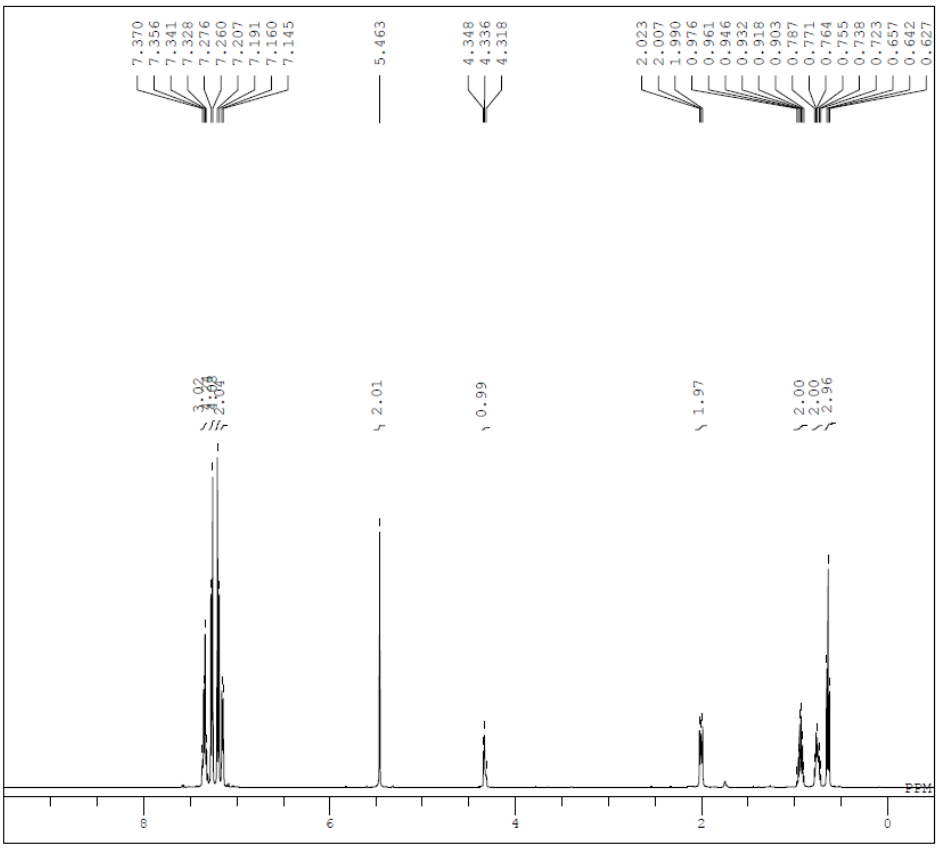

```
DFILE   huan_6_6_1_proton-1-1.als
COMNT   single_pulse
DATIM   2012-12-11 21:37:49
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             30
```



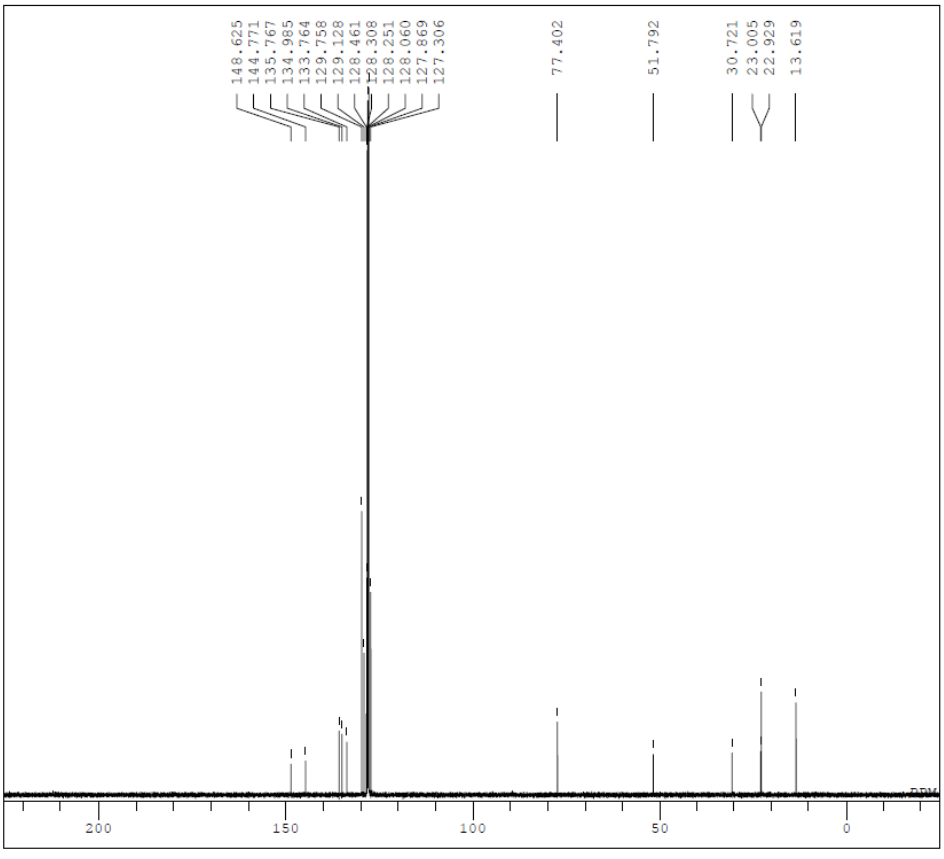

```
DFILE   huan_6_6_1_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-11 22:40:18
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            407
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



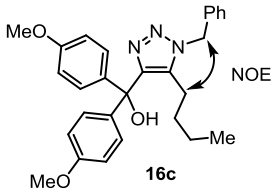
16b



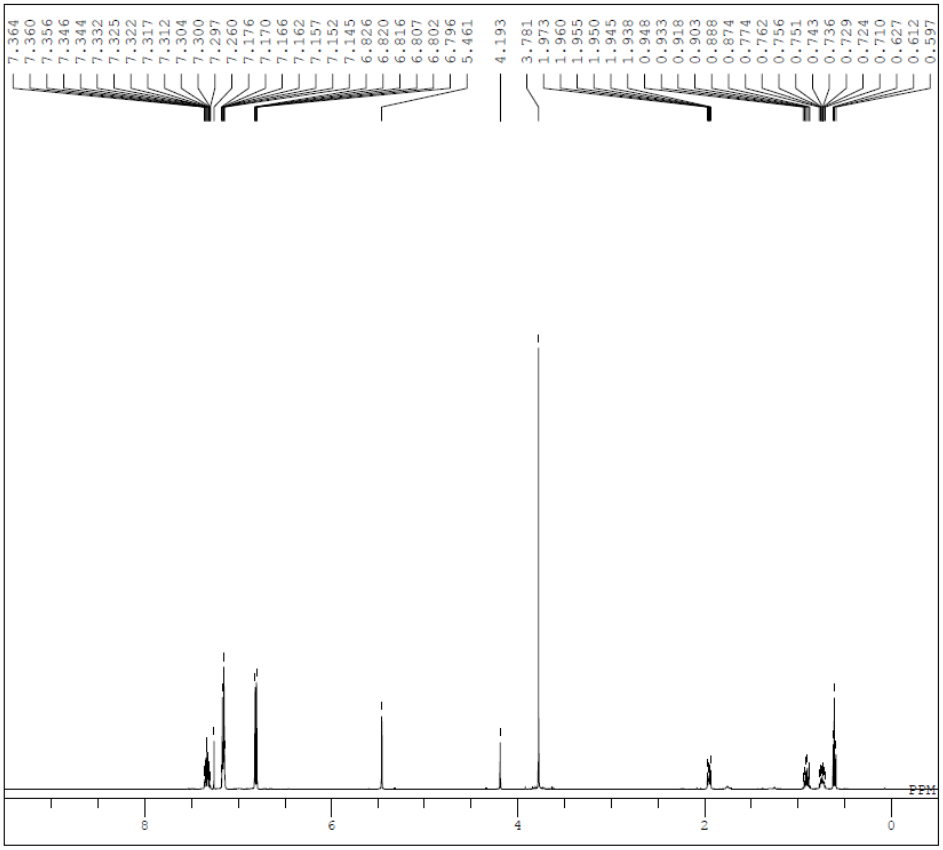

```
DFILE   HT5-101-1_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-02-13 20:53:01
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           17.9 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             30
```



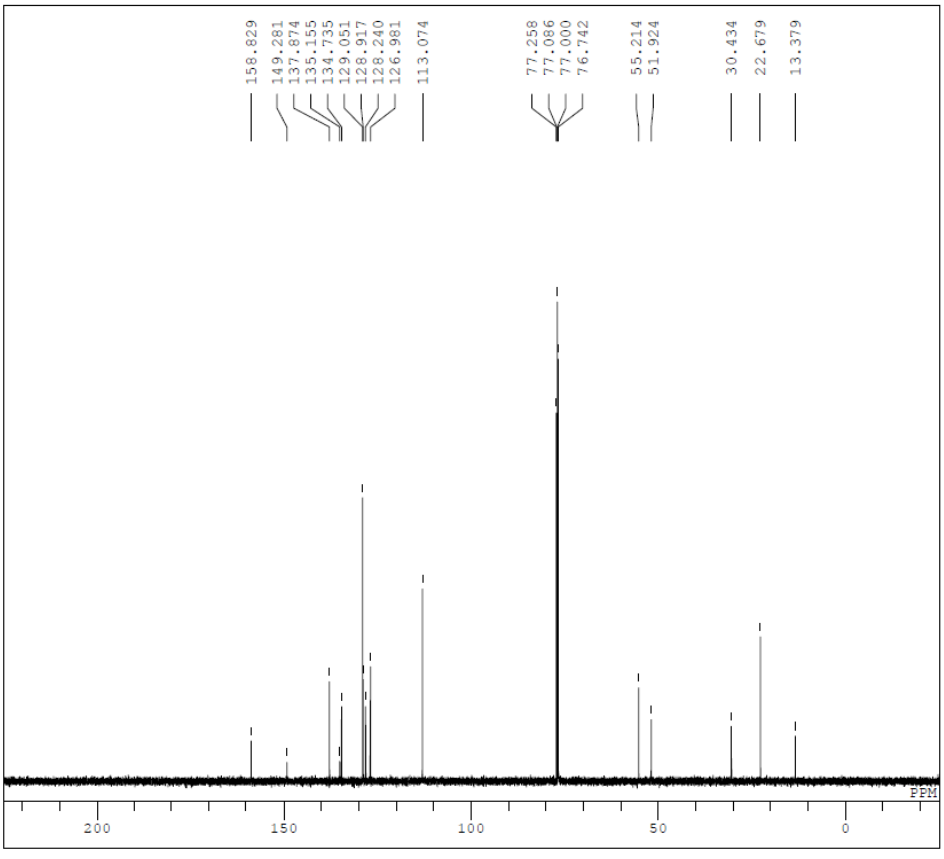

```
DFILE   HT5-101-2_Carbon-1-1 (2).jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-16 00:18:21
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             84
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           15.2 c
SLVNT   C6D6
EXREF         128.06 ppm
BF              0.10 Hz
RGAIN             58
```



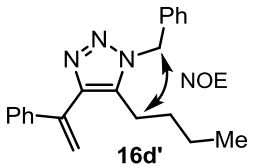
16c




```
DFILE  HT5-91-2_Proton-1-1.jdf
COMNT  single_pulse lower spot
DATIM  2013-02-04 19:18:43
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS            16
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          15.2 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```

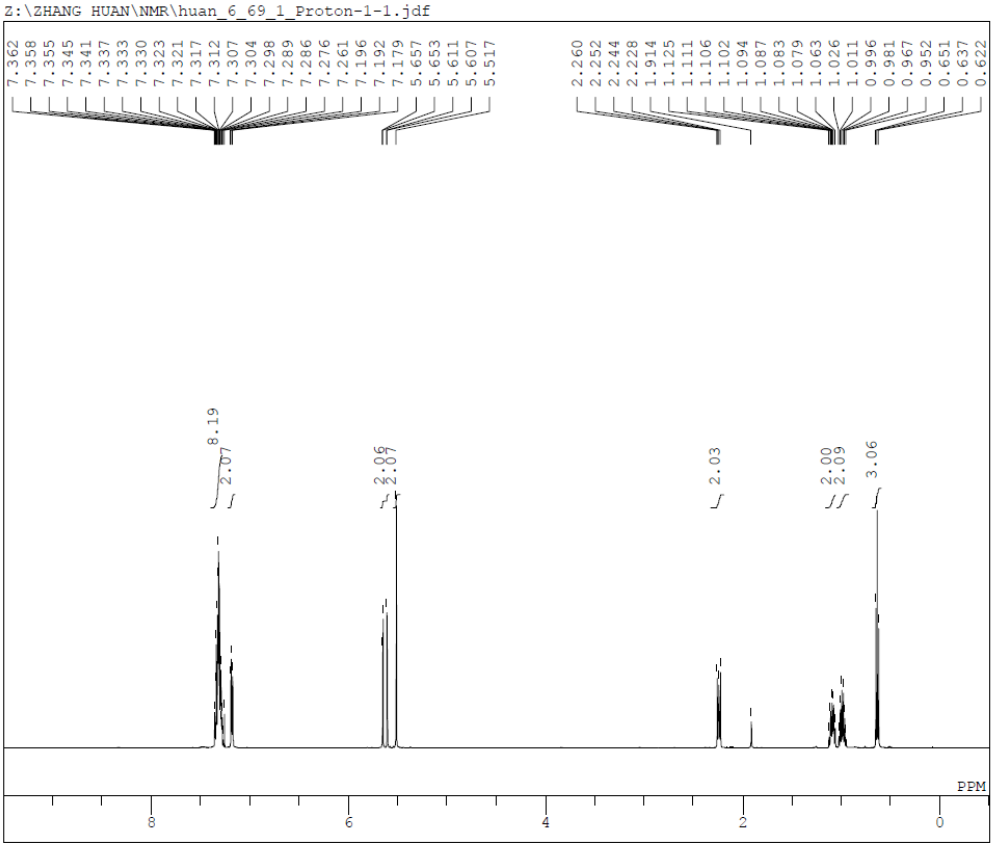



```
DFILE  HT5-91-2_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2013-02-04 19:21:08
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS           227
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          15.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            58
```



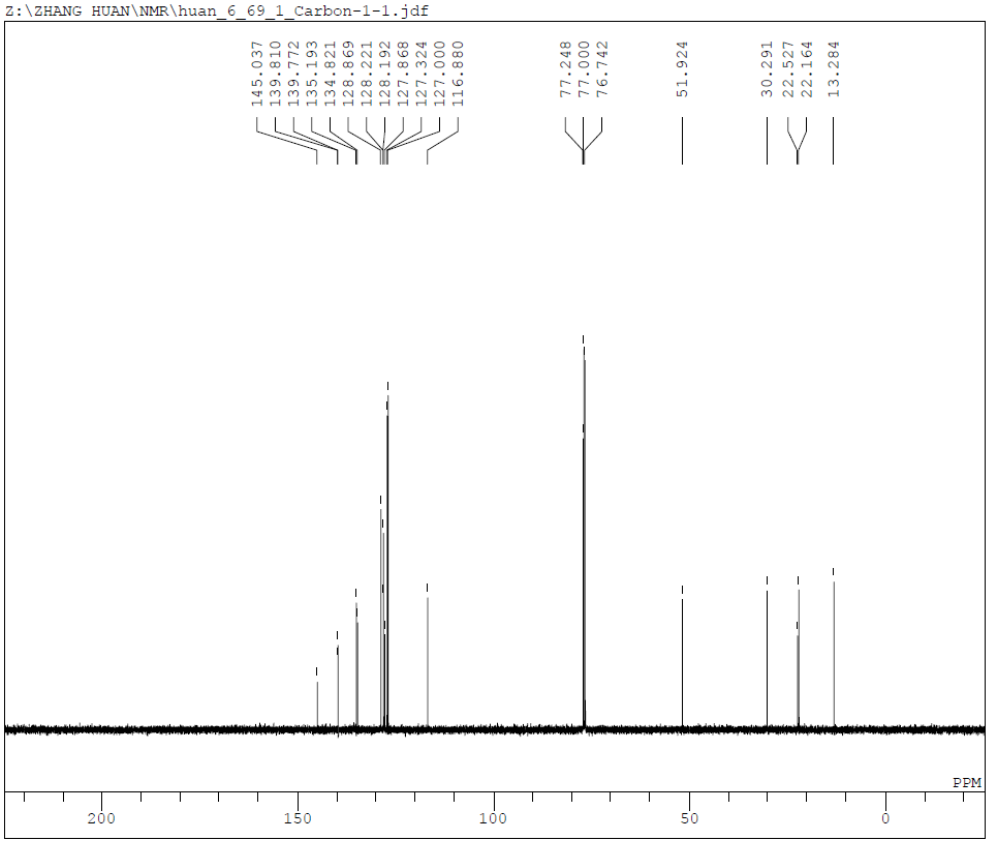
16d'

Z:\ZHANG HUAN\NMR\huan_6_69_1_Proton-1-1.jdf

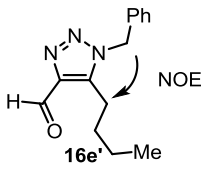



```
DFILE   huan_6_69_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-21 21:35:18
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.5 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            28
```

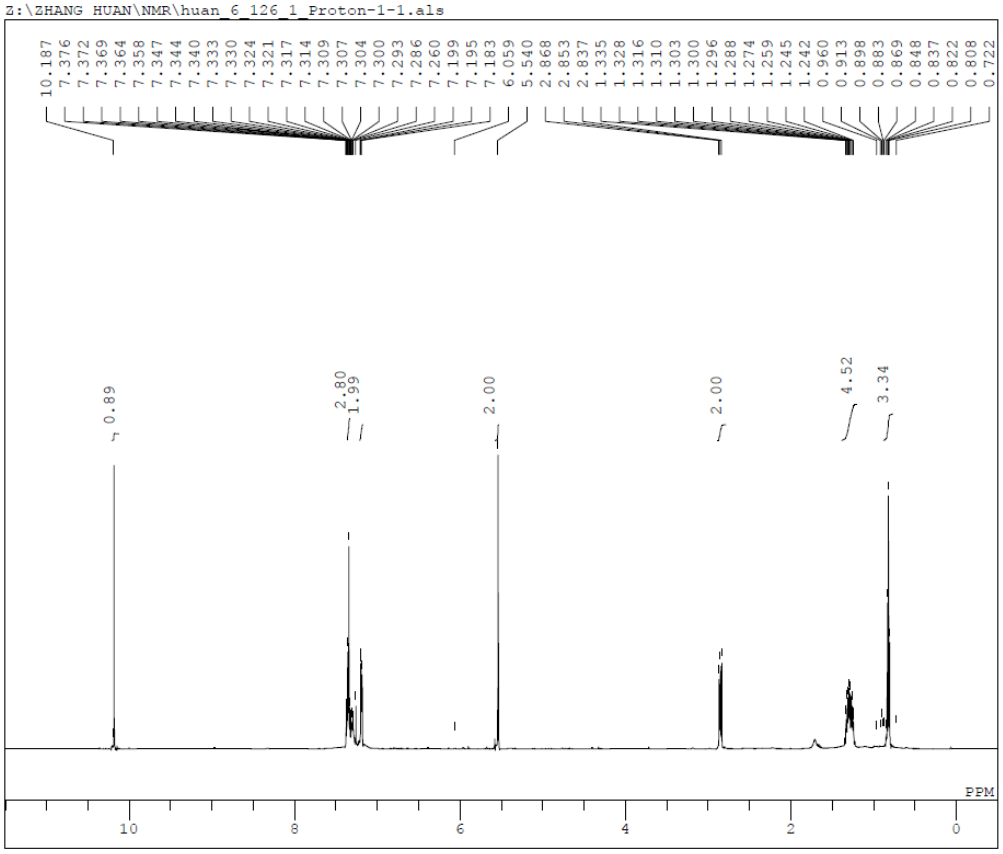
Z:\ZHANG HUAN\NMR\huan_6_69_1_Carbon-1-1.jdf




```
DFILE   huan_6_69_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-21 21:36:49
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            178
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```

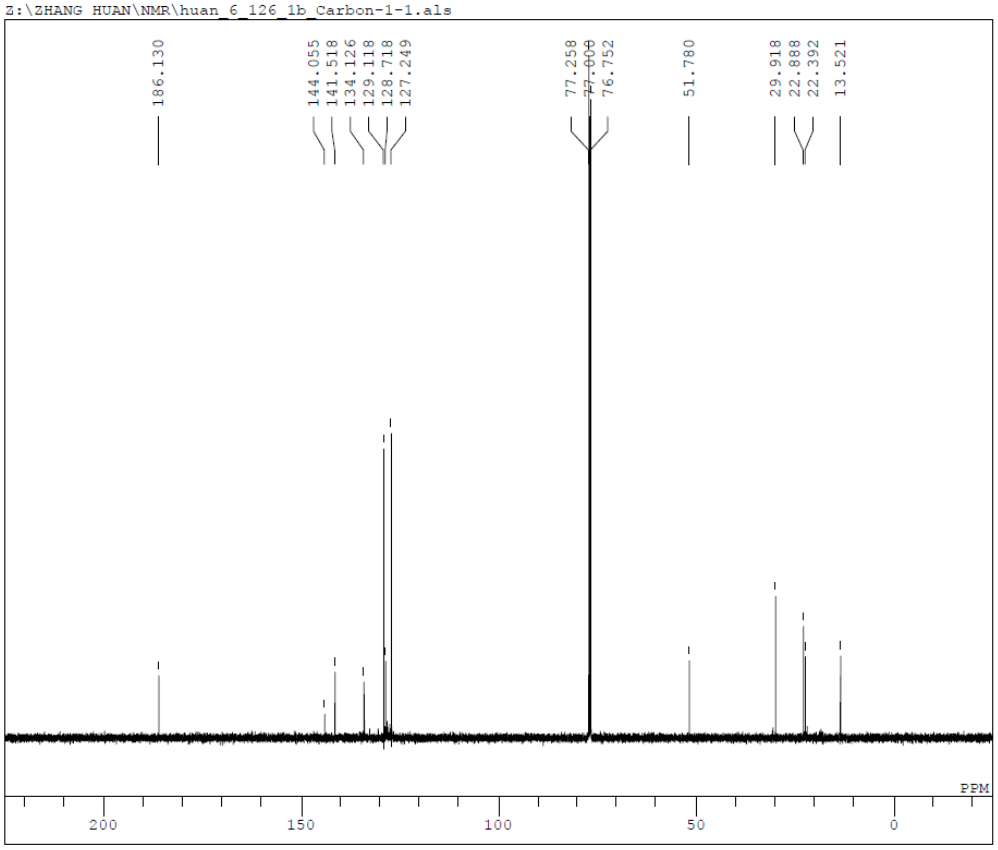


Z:\ZHANG HUAN\NMR\huan_6_126_1_Proton-1-1.als

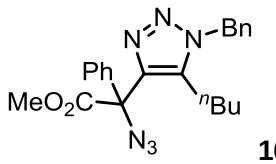



```
DFILE   huan_6_126_1_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-06-26 21:25:28
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.6 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            34
```

Z:\ZHANG HUAN\NMR\huan_6_126_1b_Carbon-1-1.als

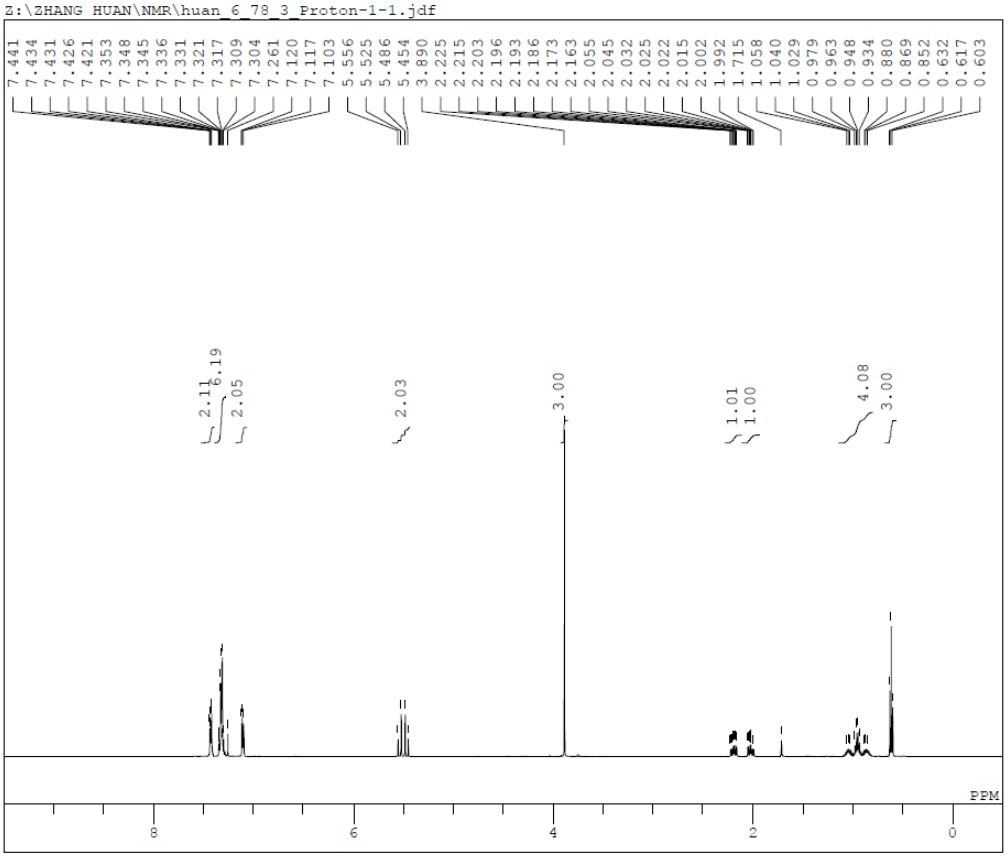



```
DFILE   huan_6_126_1b_Carbon-1-1.als
COMNT   single pulse decoupled gated NO
DATIM   2013-06-27 10:18:36
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            604
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.1 c
SLVNT   NONE
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



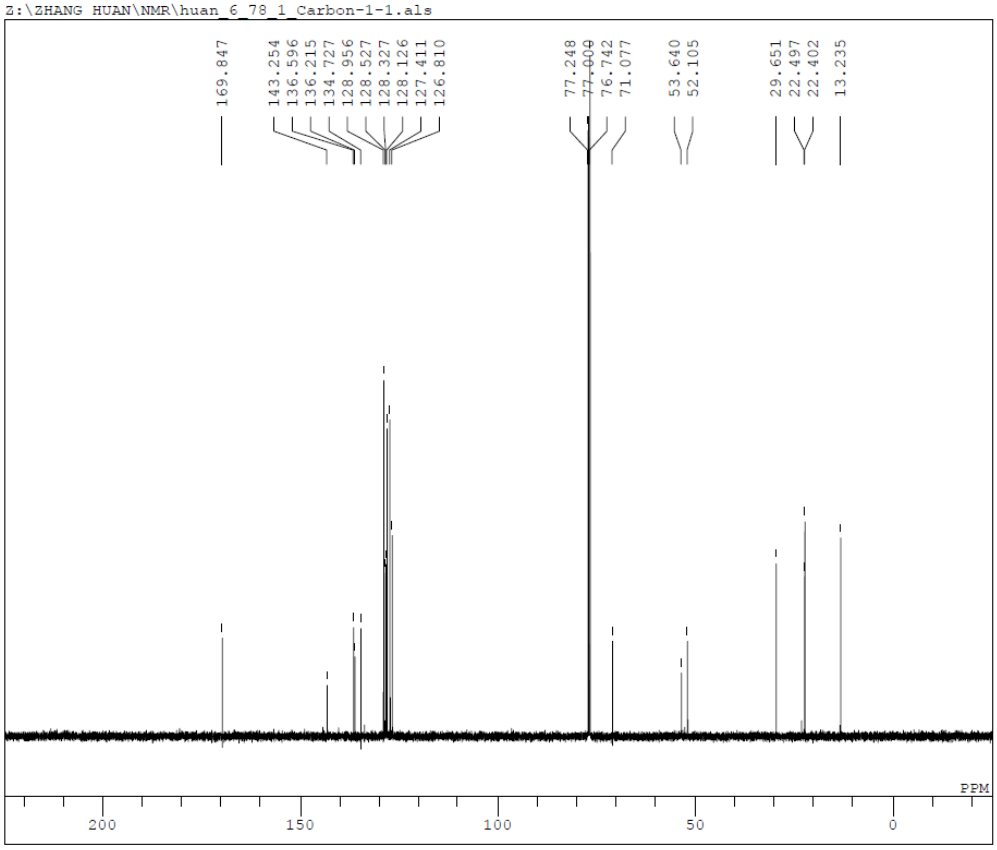
16h'

Z:\ZHANG HUAN\NMR\huan_6_78_3_Proton-1-1.jdf

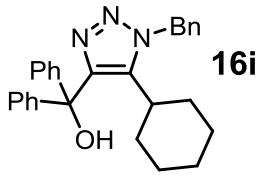



```
DFILE   huan_6_78_3_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-29 13:31:42
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             30
```

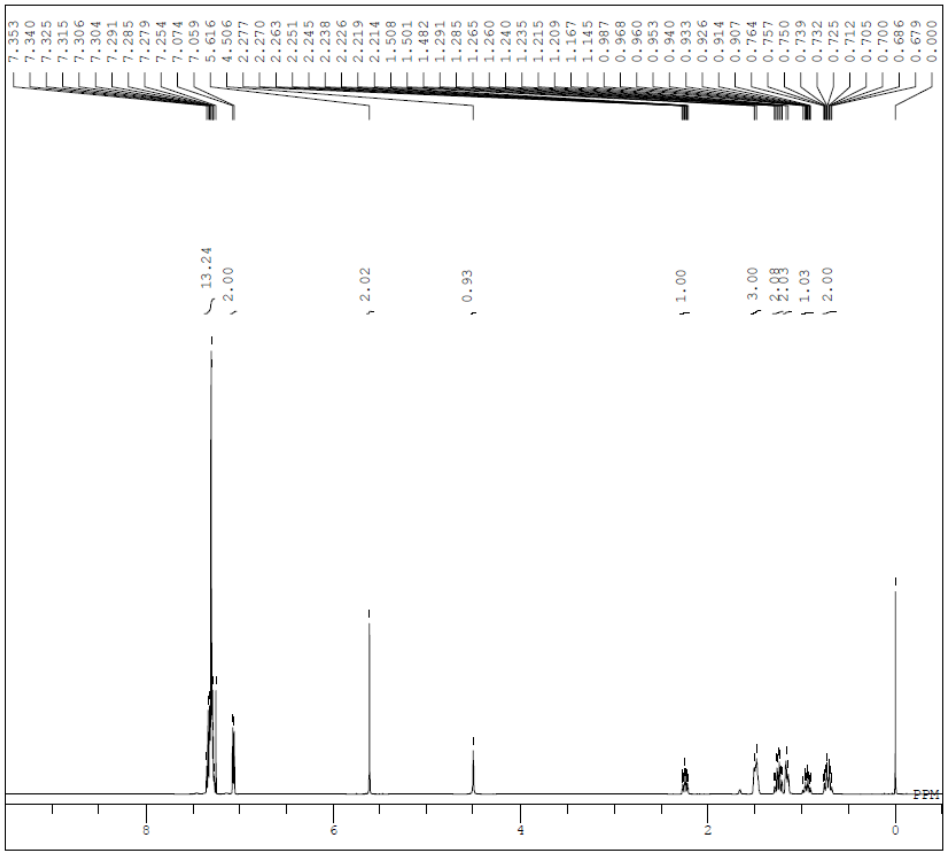
Z:\ZHANG HUAN\NMR\huan_6_78_1_Carbon-1-1.als



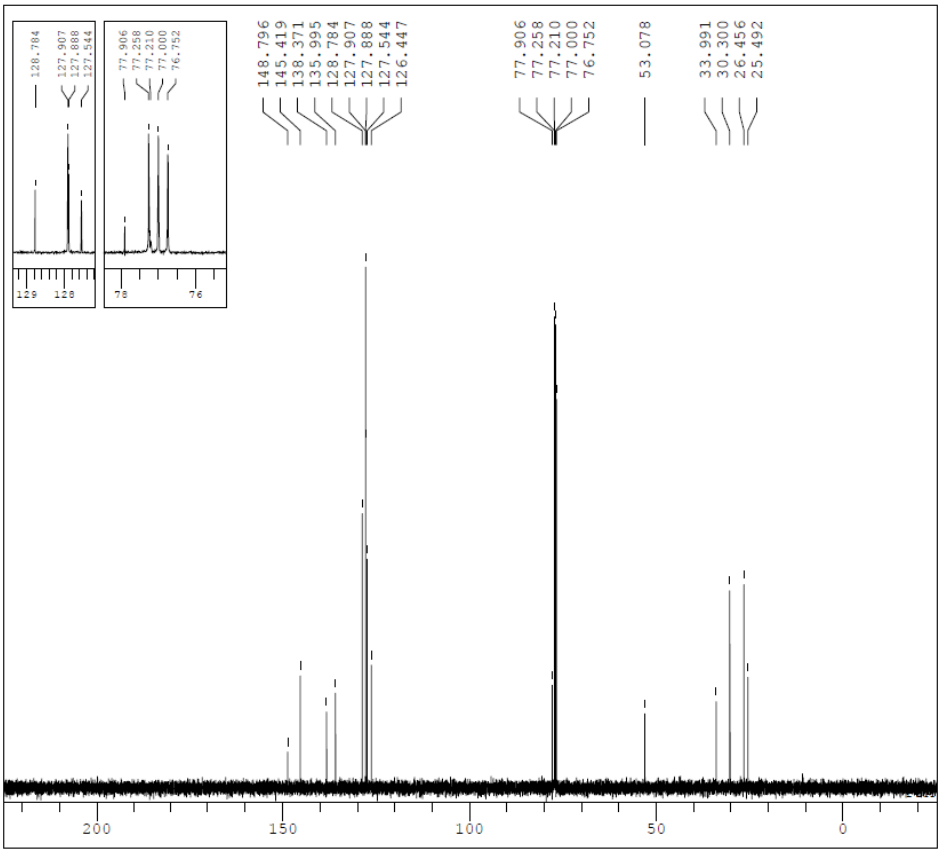

```
DFILE   huan_6_78_1_Carbon-1-1.als
COMNT   single pulse decoupled gated NO
DATIM   2013-05-27 21:40:26
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



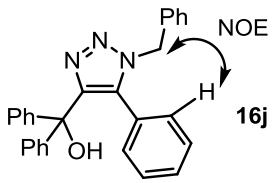
16i



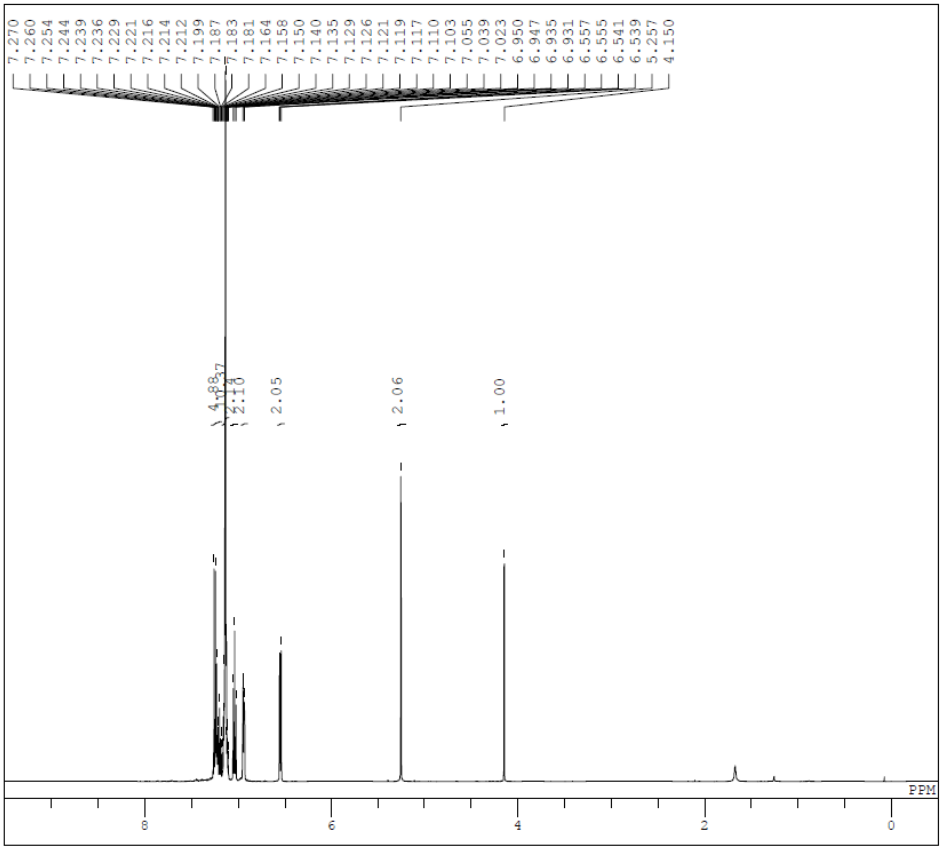

```
DFILE   HT5-116-2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-03-11 21:00:22
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS              8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.8 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.10 Hz
RGAIN             32
```



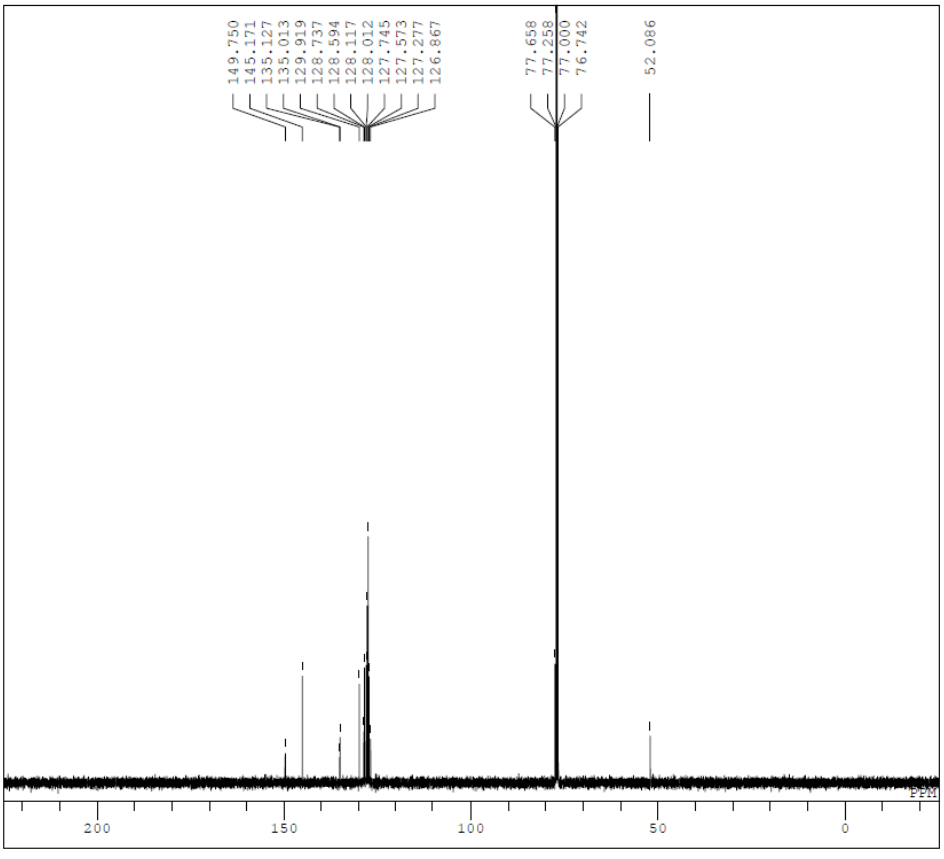

```
DFILE   HT5-116-1_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2013-03-11 18:30:57
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS             81
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           19.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



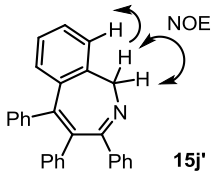
16j



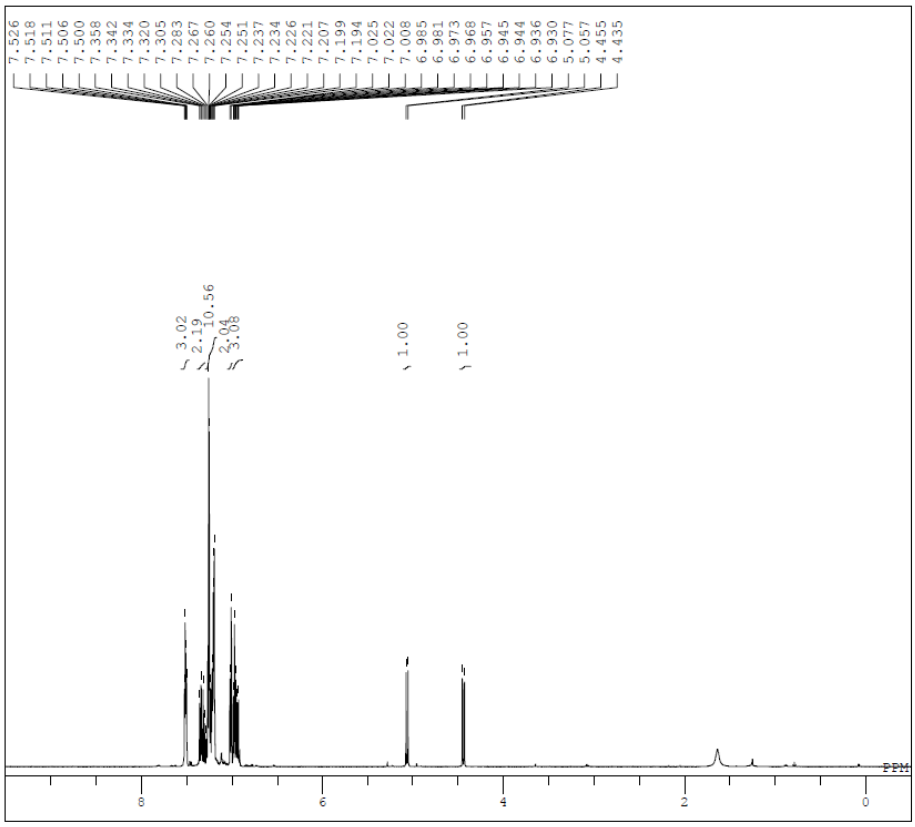

```
DFILE   HT5-57-4 alkyne-1-1.als
COMNT   HT5-57-4 4th spot
DATIM   2012-12-17 21:59:17
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          15.3 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            38
```



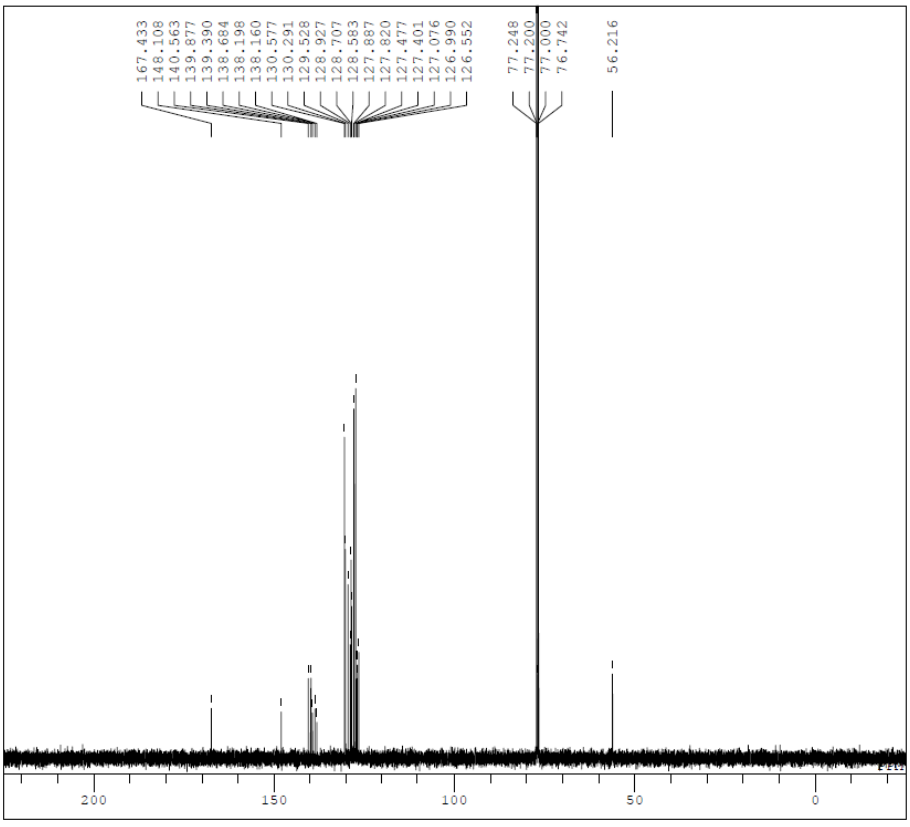

```
DFILE   HT5-57-4 13C-1-1.als
COMNT   HT5-57-4 4th spot 13C
DATIM   2012-12-17 22:43:35
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            432
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          15.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.10 Hz
RGAIN            58
```



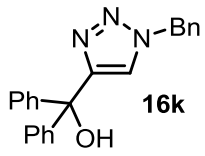
15j'



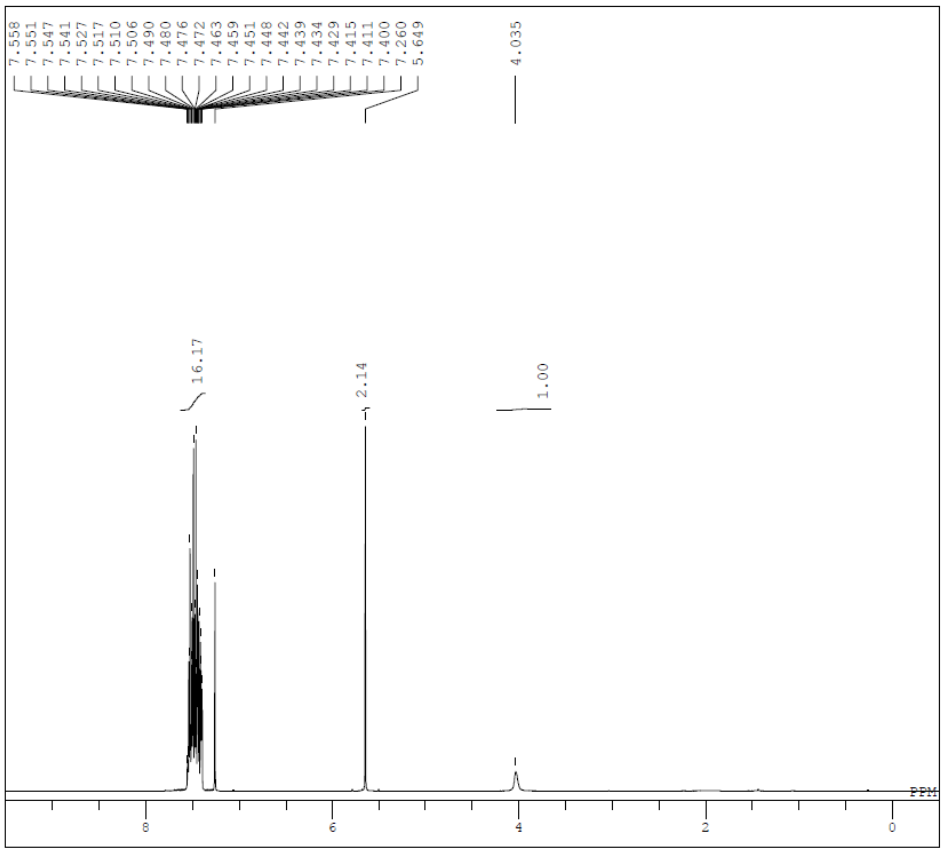

```
DFILE   HT5-57-3-2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2012-12-22 15:11:28
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             32
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            14.3 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              42
```



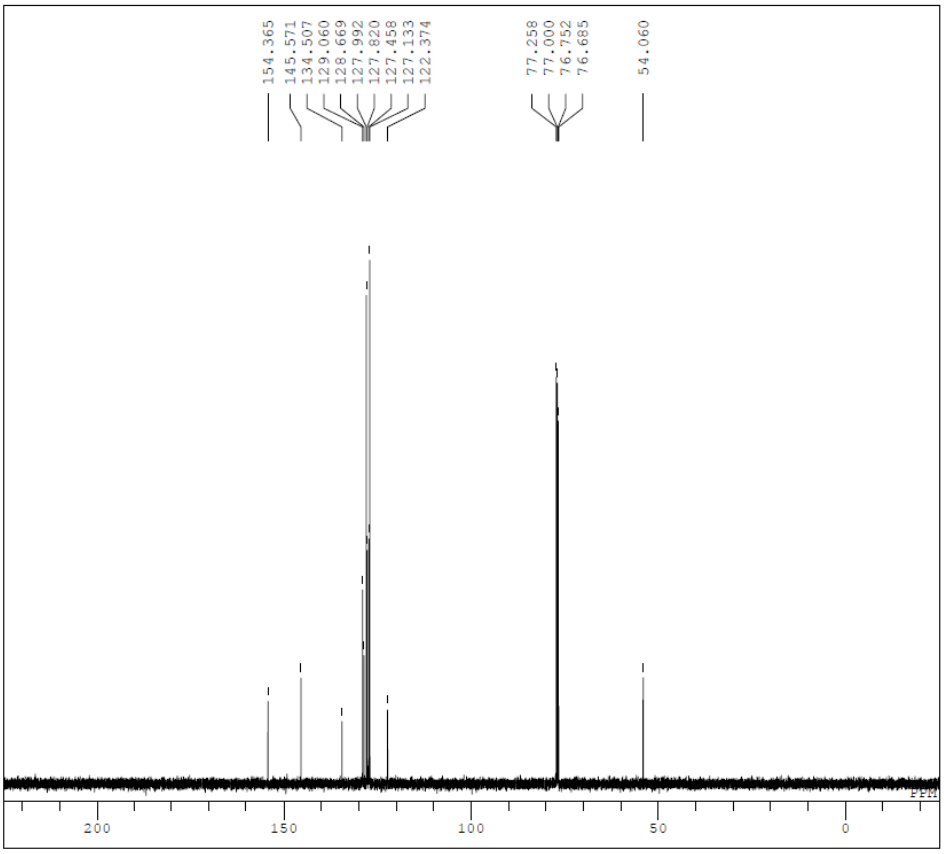

```
DFILE   HT5-57-3-2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-22 15:15:34
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            730
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            14.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              60
```



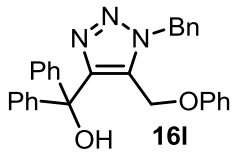
16k



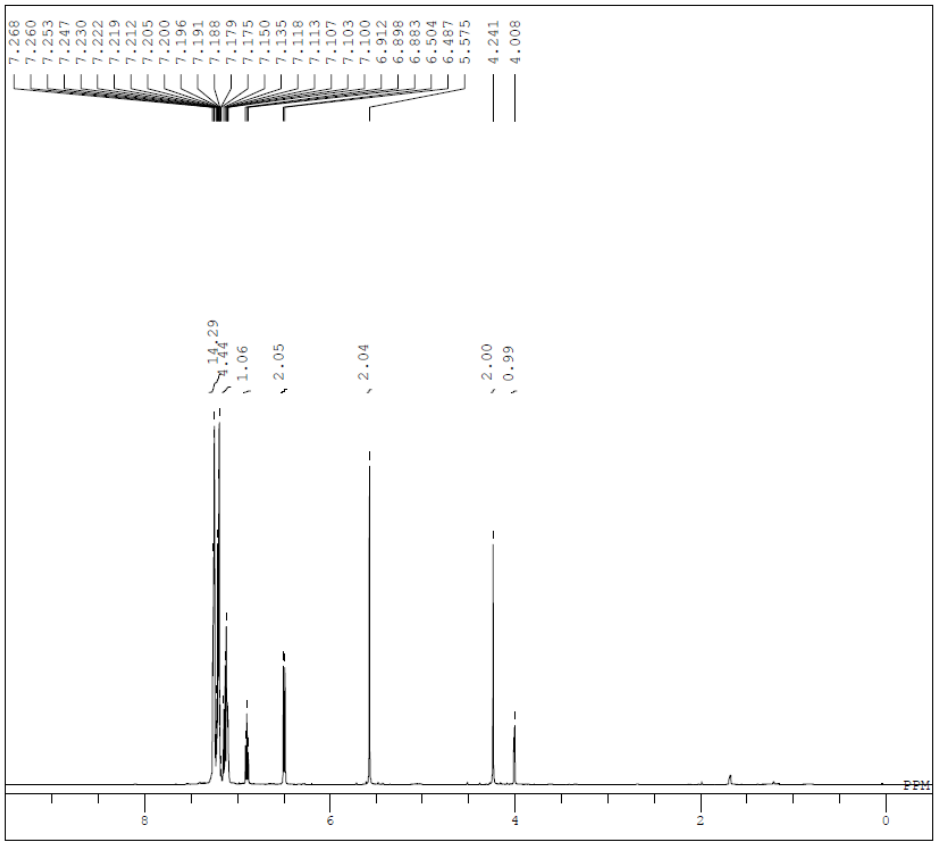

```
DFILE   HT5-53-1 alkyne-1-1.jdf
COMNT   single_pulse
DATIM   2012-12-11 23:42:52
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             36
```



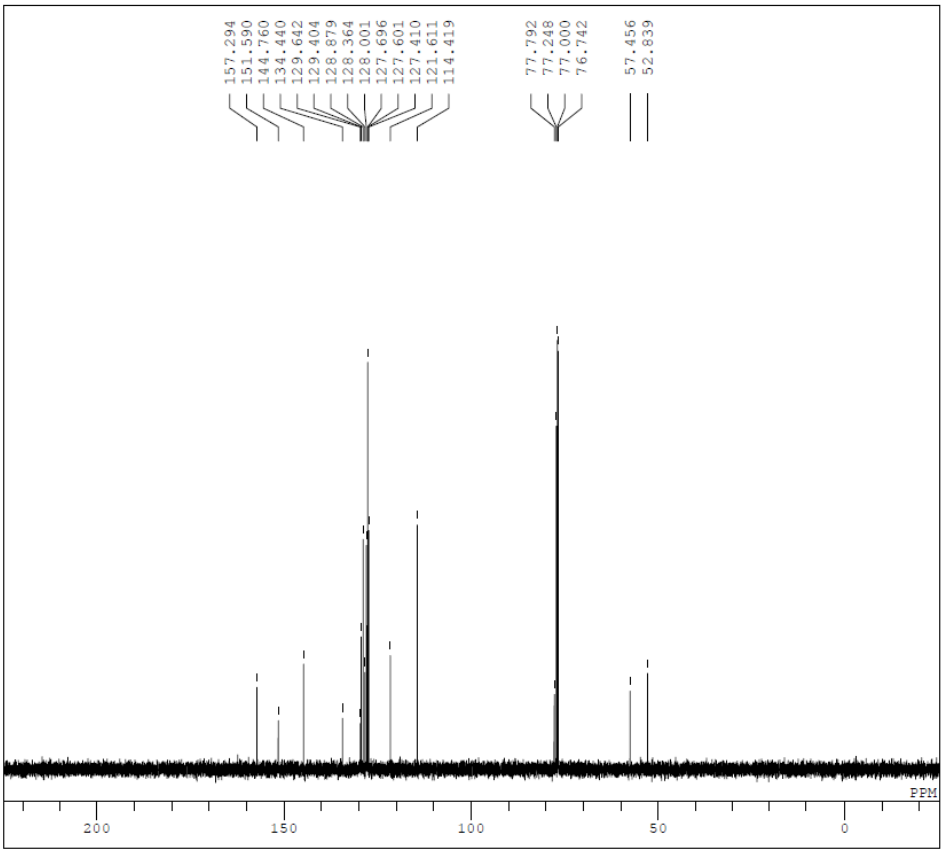

```
DFILE   HT5-53-1 alkyne 13C-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2012-12-11 23:45:10
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            133
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             60
```



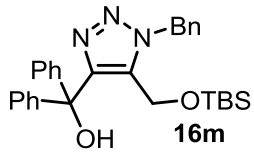
16l



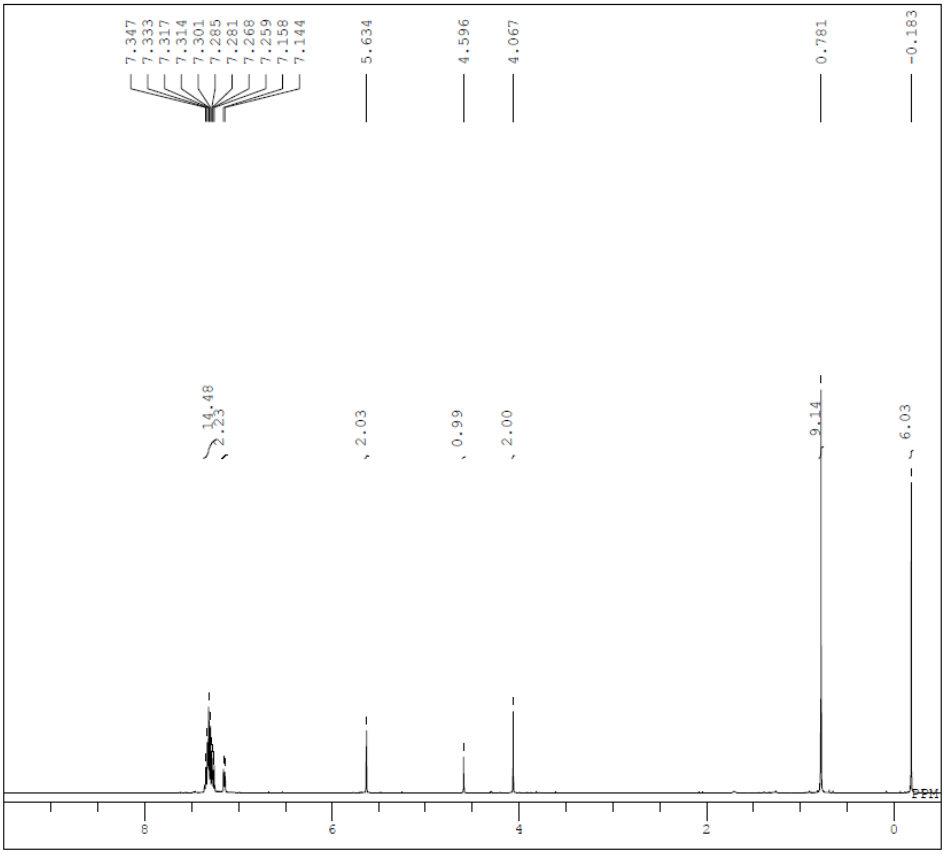

```
DFILE  HT5-114-1_Proton-1-1.jdf
COMNT  single_pulse
DATIM  2013-03-01 19:26:55
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP         14.9 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```



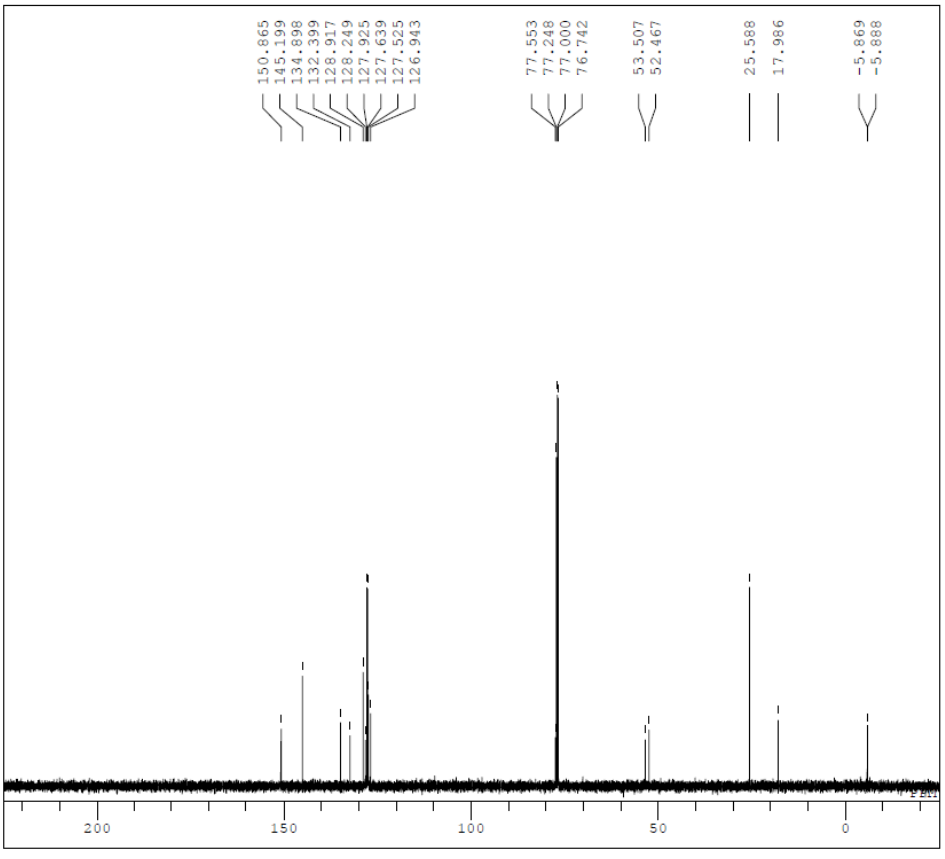

```
DFILE  HT5-114-1_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2013-03-01 19:28:33
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS            58
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP         15.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            58
```



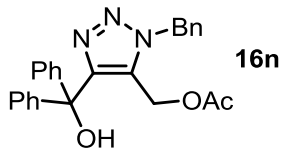
16m



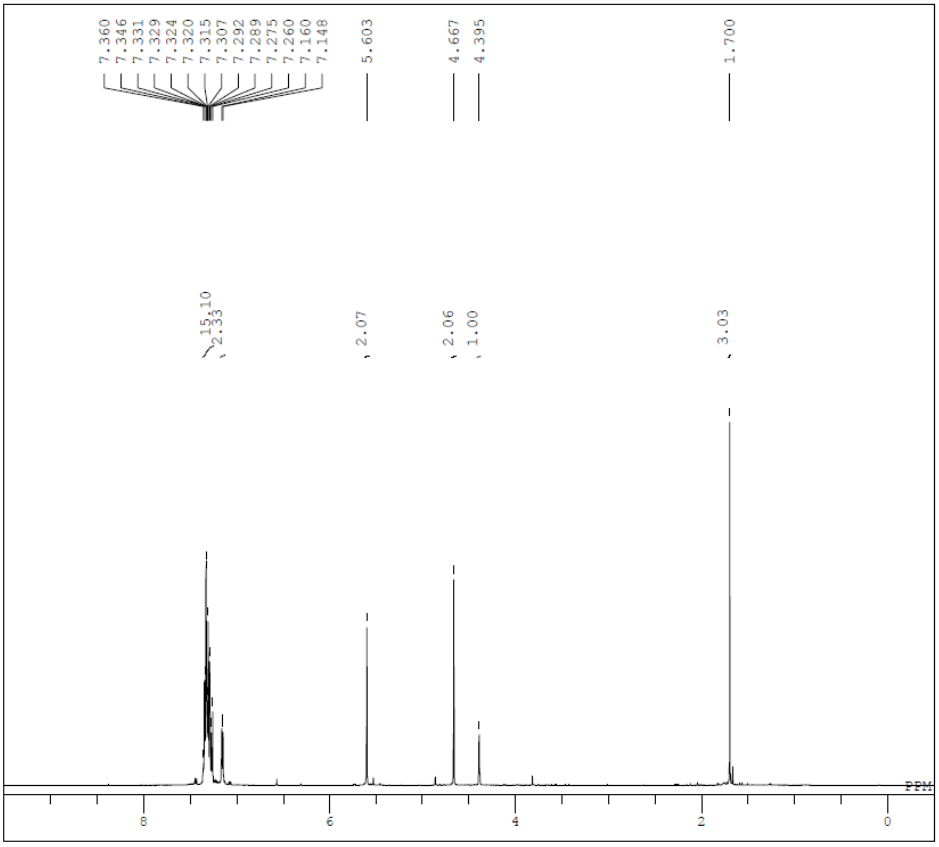

```
DFILE  HT5-84-1_Proton-1-1.jdf
COMNT  single_pulse
DATIM  2013-01-28 22:14:03
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         16384
FREQU       9384.38 Hz
SCANS            16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          17.2 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```



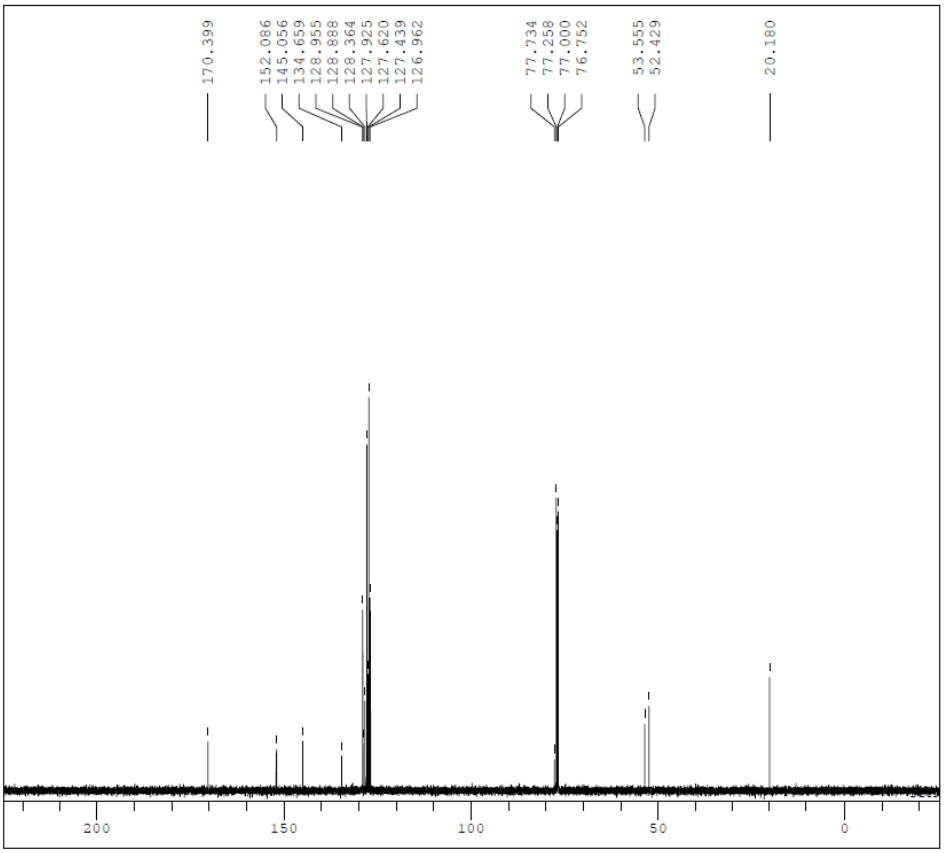

```
DFILE  HT5-84-1_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NOE
DATIM  2013-01-28 22:16:28
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS           103
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC  1H
CTEMP          17.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            58
```



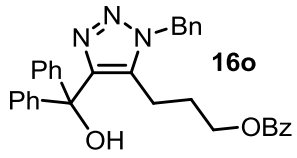
16n



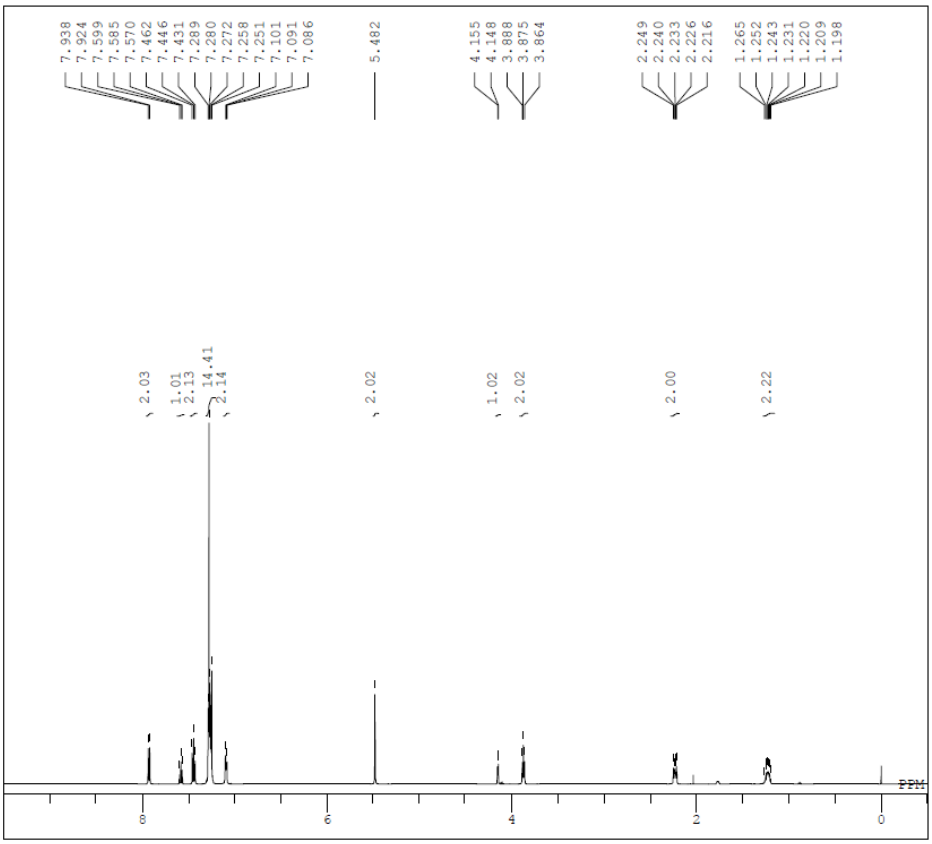

```
DFILE   HT5-112-3_Proton-1-1.jdf
COMNT   lower spot single_pulse
DATIM   2013-02-28 10:41:16
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          14.4 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            30
```



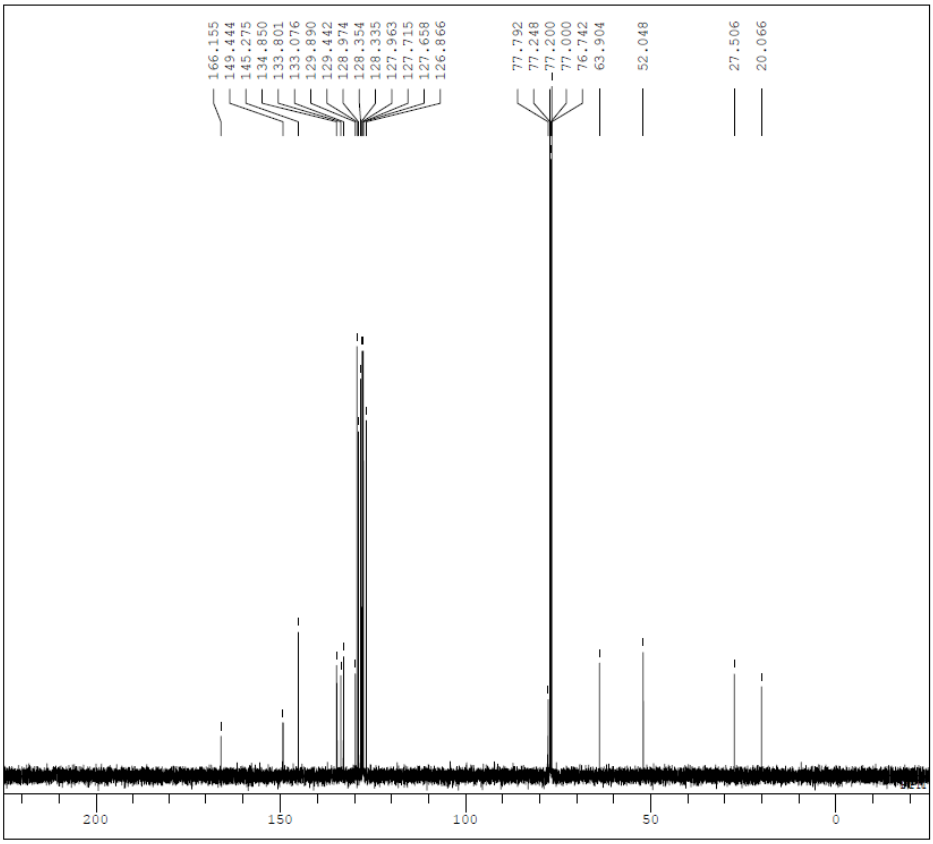

```
DFILE   HT5-112-3_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-02-28 10:43:25
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS             86
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          14.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.10 Hz
RGAIN            56
```



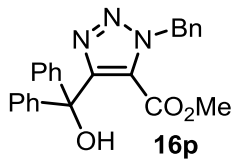
16o




```
DFILE   HT5-126-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-04-01 21:16:54
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.10 Hz
RGAIN            30
```

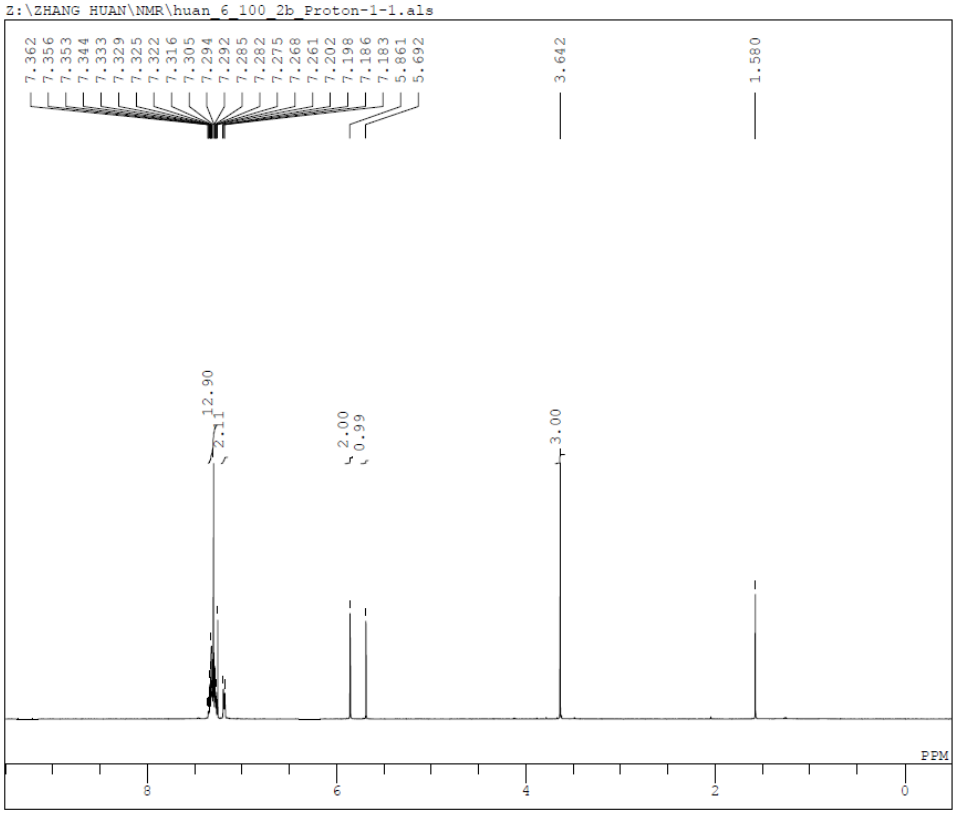



```
DFILE   HT5-126-1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-04-01 21:18:23
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS            151
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.0 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            58
```



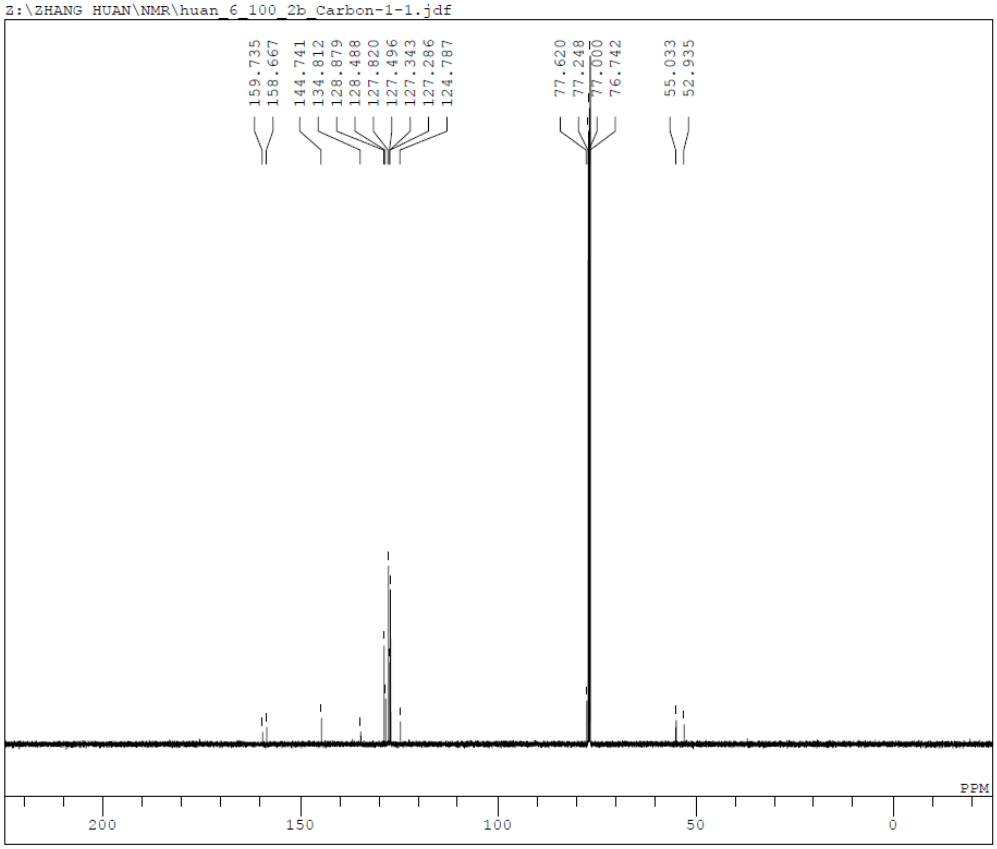
16p

Z:\ZHANG HUAN\NMR\huan_6_100_2b_Proton-1-1.als

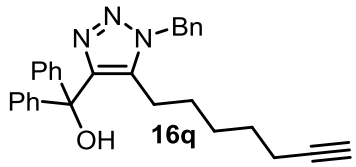


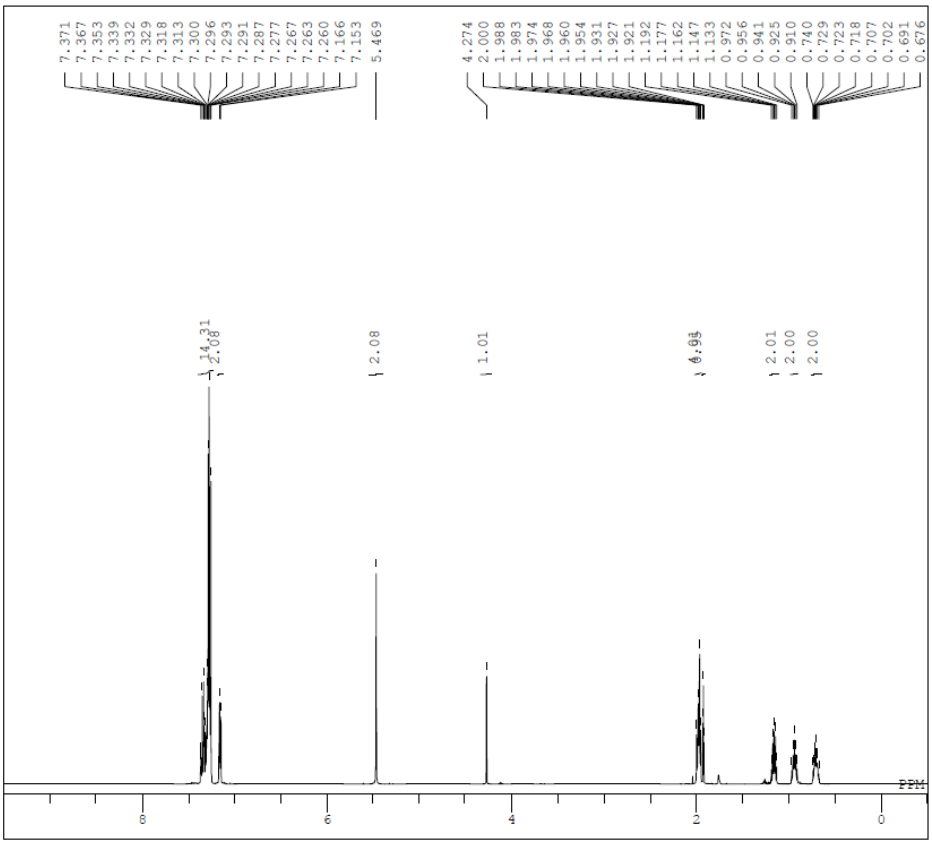

```
DFILE   huan_6_100_2b_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-06-08 11:22:39
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS                8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.6 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             42
```

Z:\ZHANG HUAN\NMR\huan_6_100_2b_Carbon-1-1.jdf

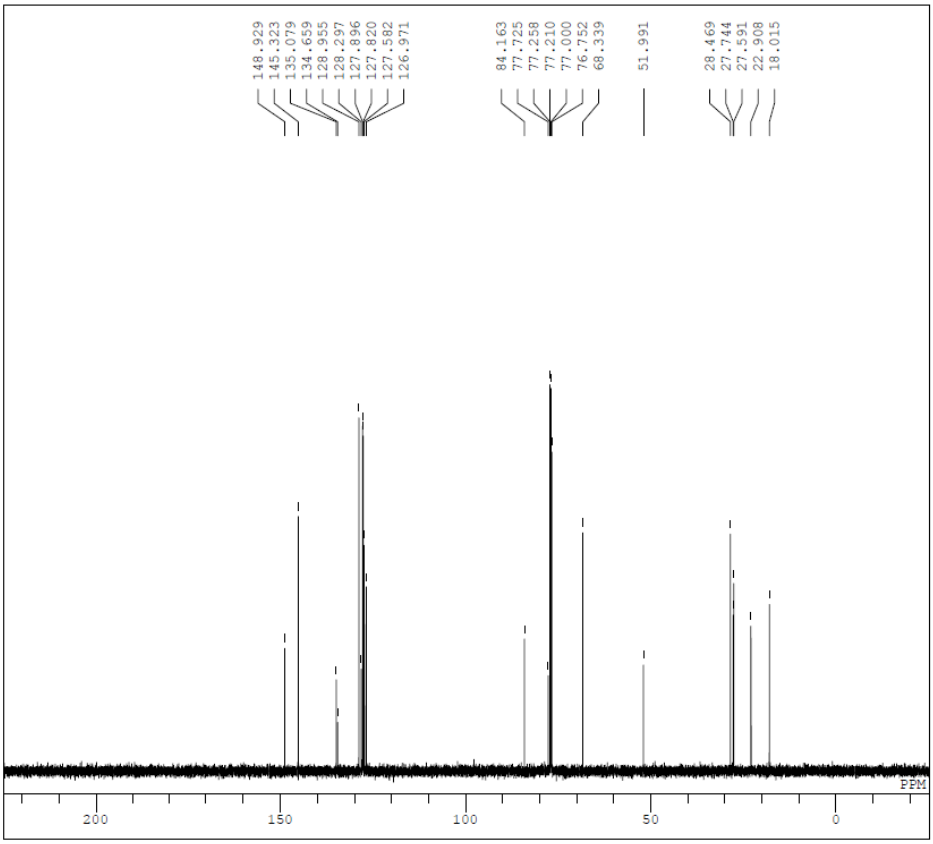



```
DFILE   huan_6_100_2b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-08 11:24:10
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1240
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             56
```

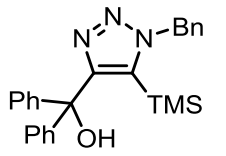




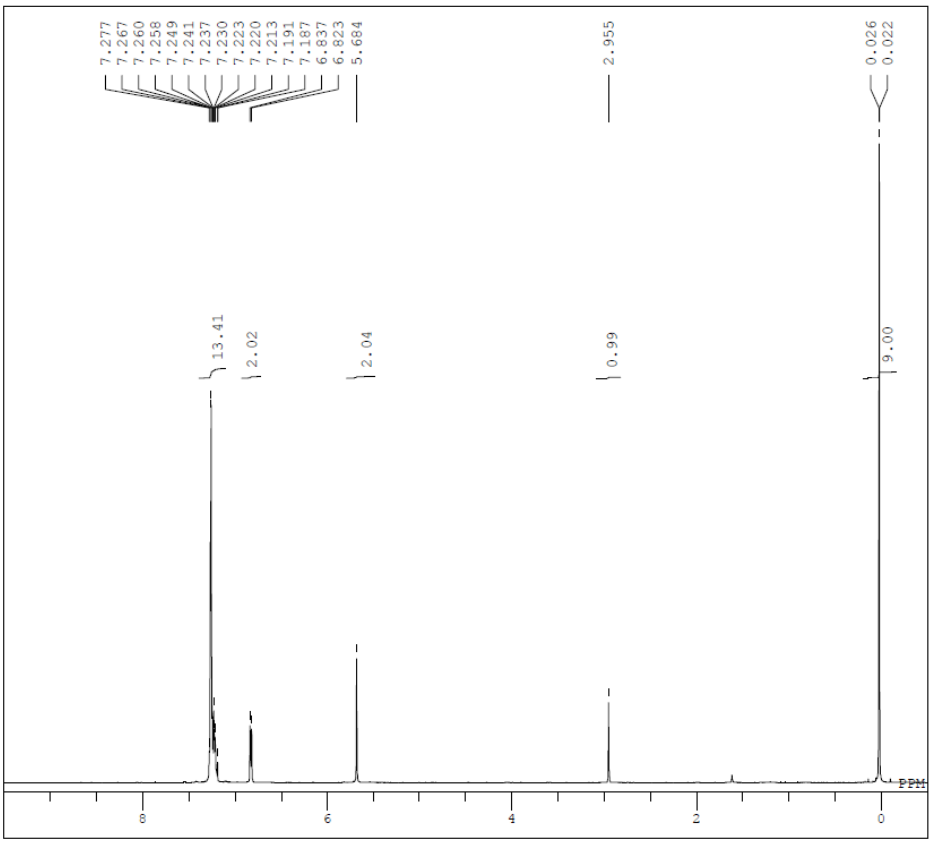
DFILE HT5-130-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-04-06 17:40:26
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.22 usec
IRNUC 1H
CTEMP 16.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.10 Hz
RGAIN 30



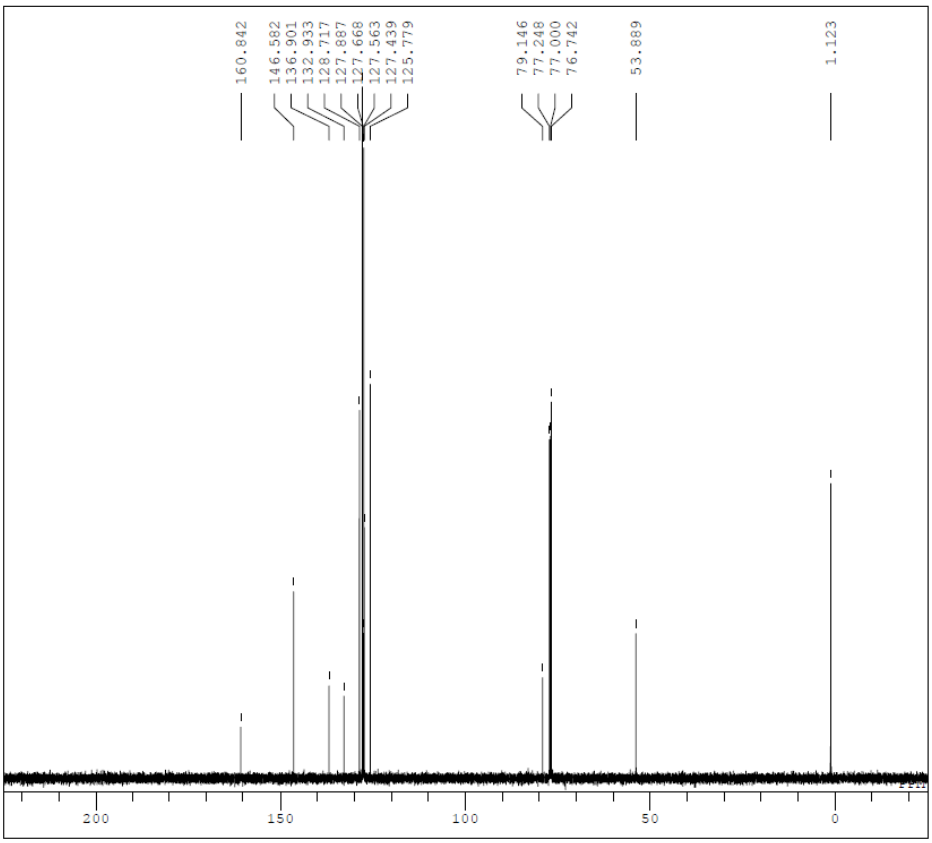
DFILE HT5-130-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-04-06 17:41:57
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39308.18 Hz
SCANS 92
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.12 usec
IRNUC 1H
CTEMP 16.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 60



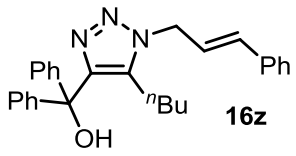
16r




```
DFILE   HT5-61-1 alkyne-1-1.jdf
COMNT   HT5-61-1 [3+2] TMS-alkyne
DATIM   2012-12-20 21:49:49
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP            17.7 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              30
```

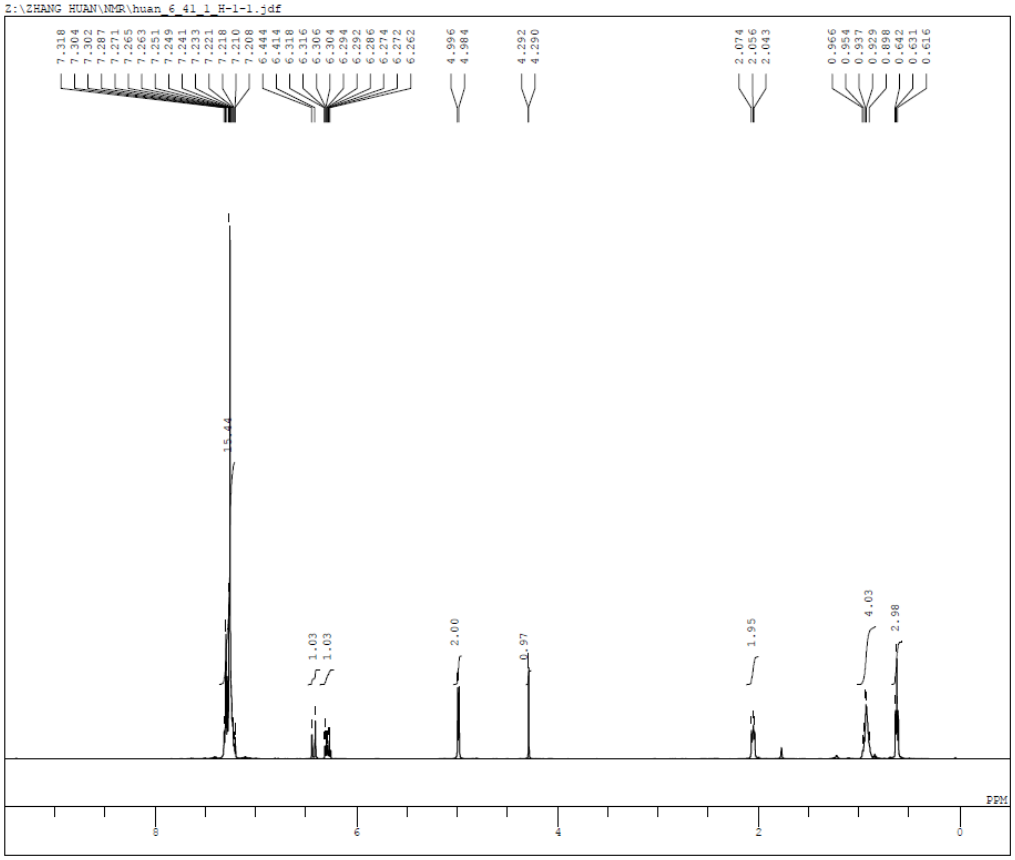



```
DFILE   HT5-61-1 13C-1-1.jdf
COMNT   HT5-61-1 13C
DATIM   2012-12-20 21:52:12
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            103
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP            18.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.10 Hz
RGAIN              60
```



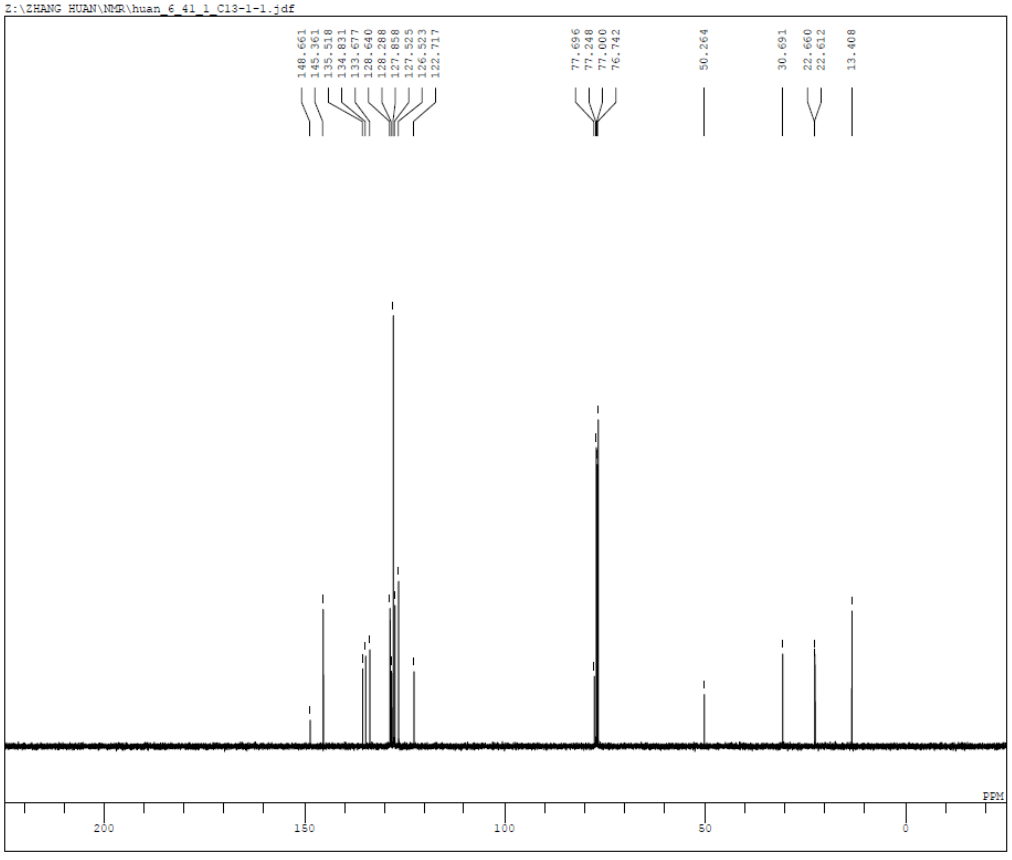
16z

Z:\ZHANG HUAN\NMR\huan_6_41_1_H-1-1.jdf

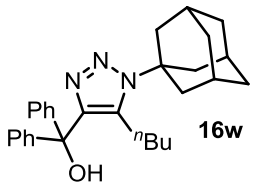



```
DFILE   huan_6_41_1_H-1-1.jdf
COMNT   single_pulse
DATIM   2013-05-10 11:20:04
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.4 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF              0.10 Hz
RGAIN             26
```

Z:\ZHANG HUAN\NMR\huan_6_41_1_C13-1-1.jdf

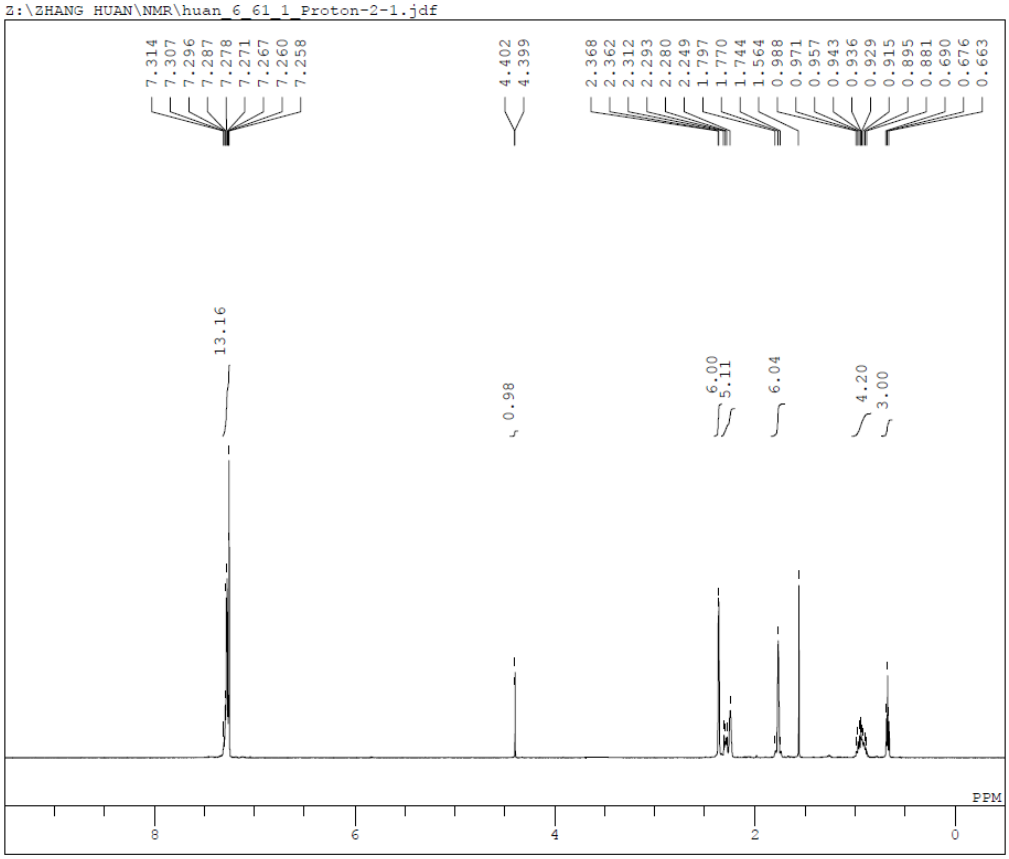



```
DFILE   huan_6_41_1_C13-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-05-10 11:21:30
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            258
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          17.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



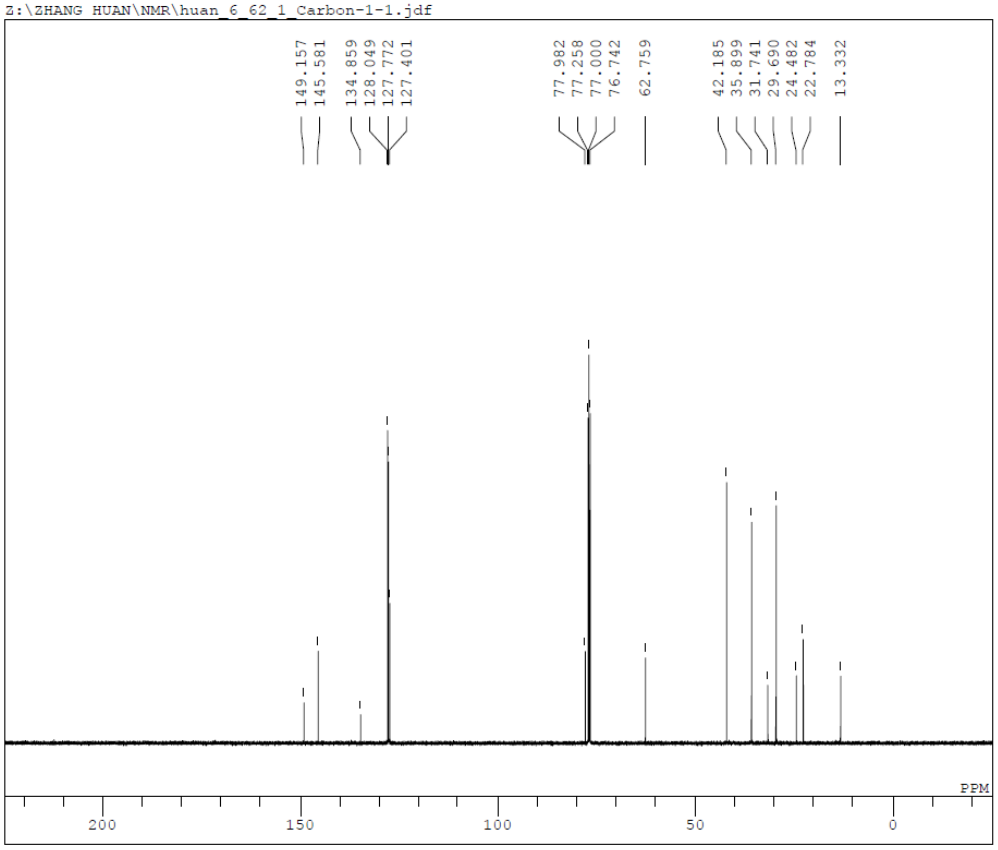
16w

Z:\ZHANG HUAN\NMR\huan_6_61_1_Proton-2-1.jdf

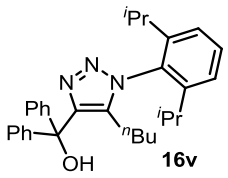



```
DFILE   huan_6_61_1_Proton-2-1.jdf
COMNT   single_pulse
DATIM   2013-05-17 16:34:18
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.8 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             46
```

Z:\ZHANG HUAN\NMR\huan_6_62_1_Carbon-1-1.jdf

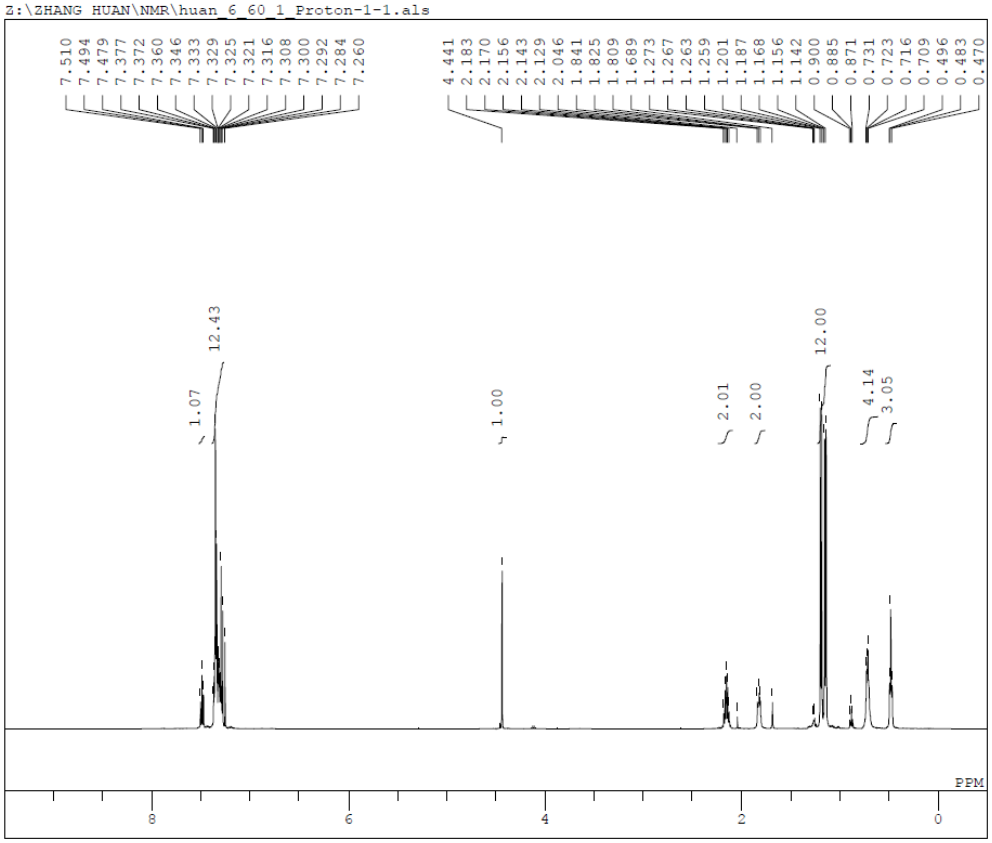



```
DFILE   huan_6_62_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-20 21:50:35
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



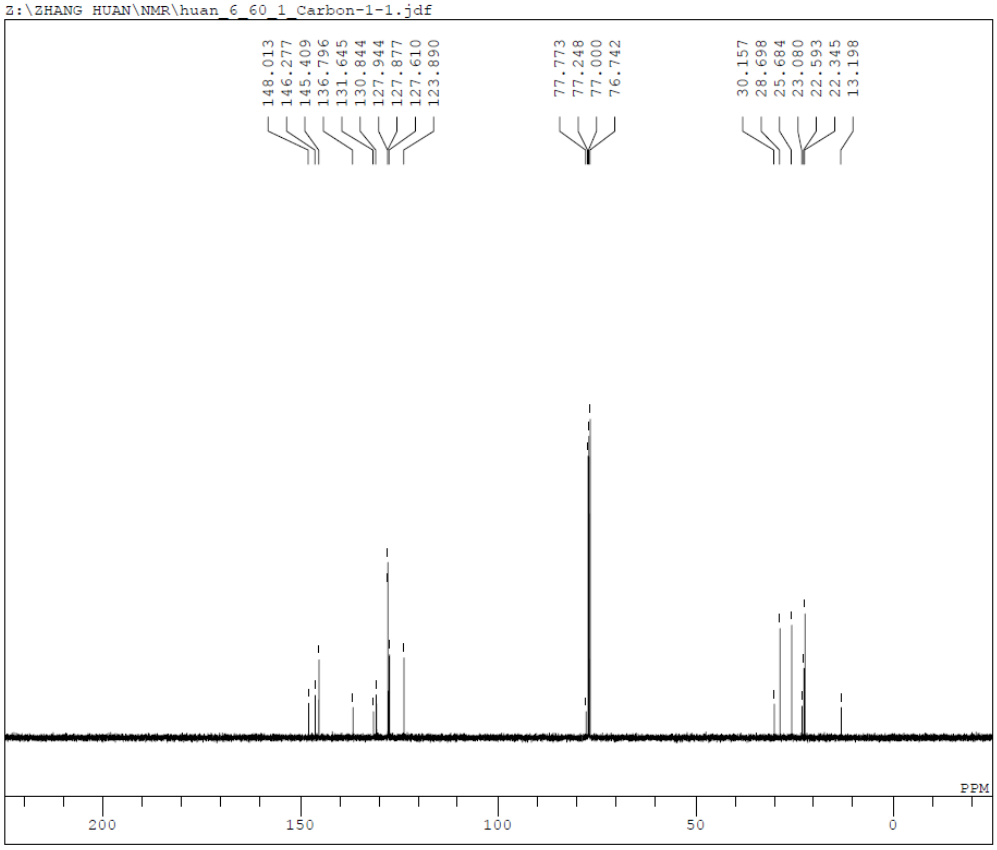
16v

Z:\ZHANG HUAN\NMR\huan_6_60_1_Proton-1-1.als

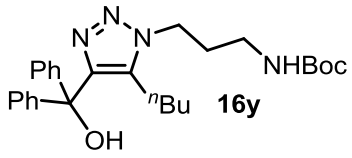


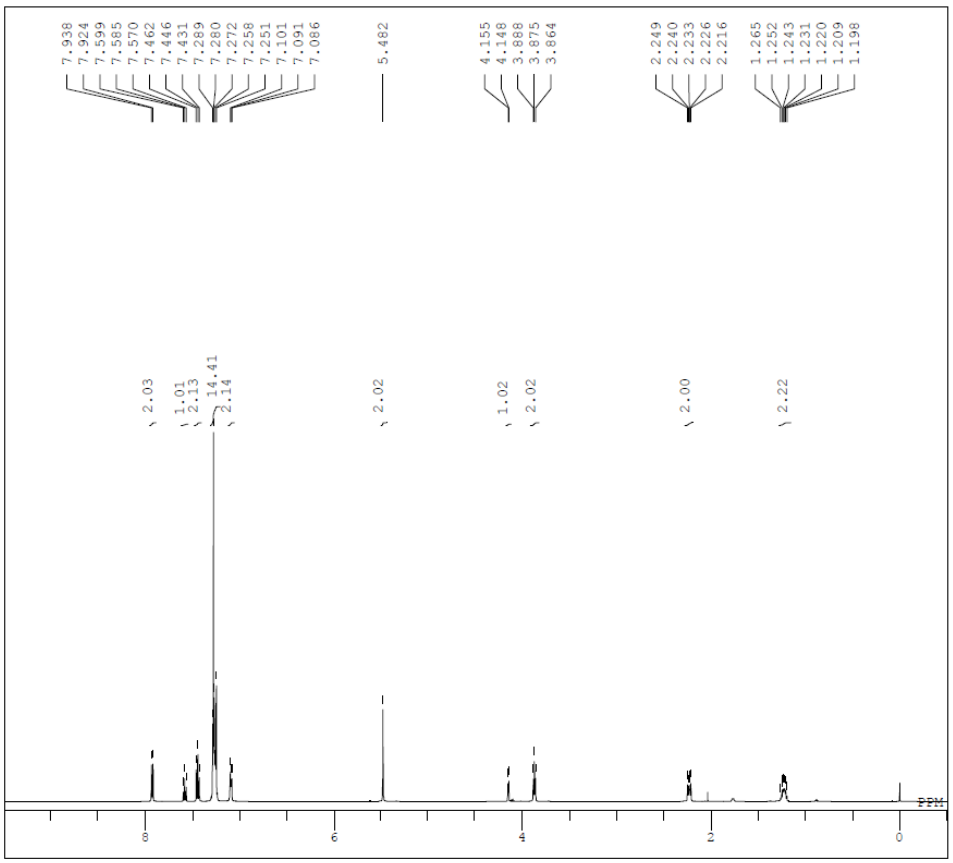

```
DFILE   huan_6_60_1_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-05-16 23:43:46
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.1 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             30
```

Z:\ZHANG HUAN\NMR\huan_6_60_1_Carbon-1-1.jdf

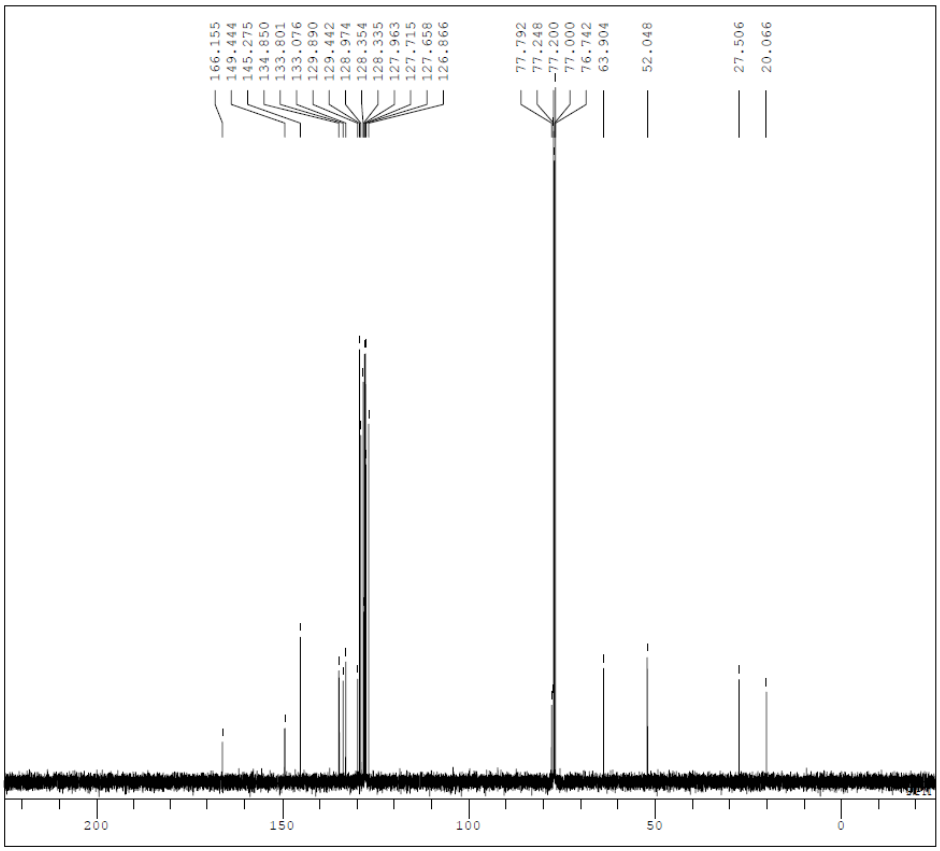



```
DFILE   huan_6_60_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-05-16 23:45:17
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            198
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.1 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```

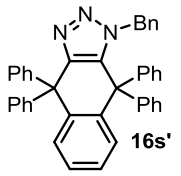




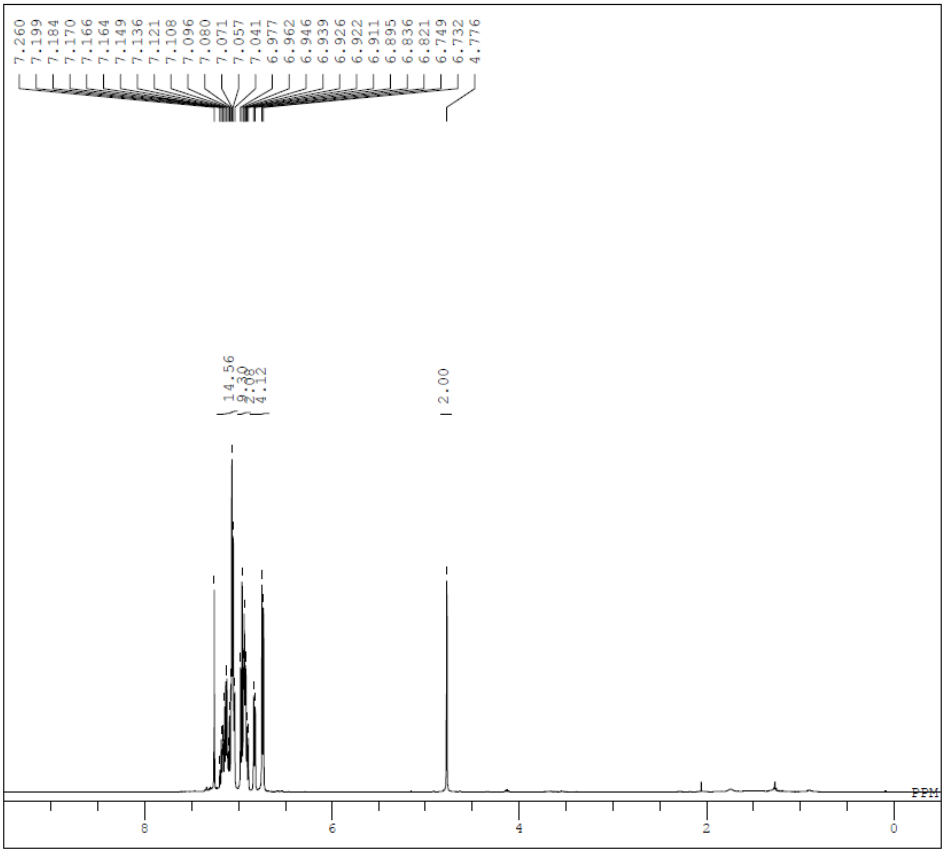
DFILE HT5-126-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2013-04-01 21:16:54
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 9384.38 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.22 usec
IRNUC 1H
CTEMP 17.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 30



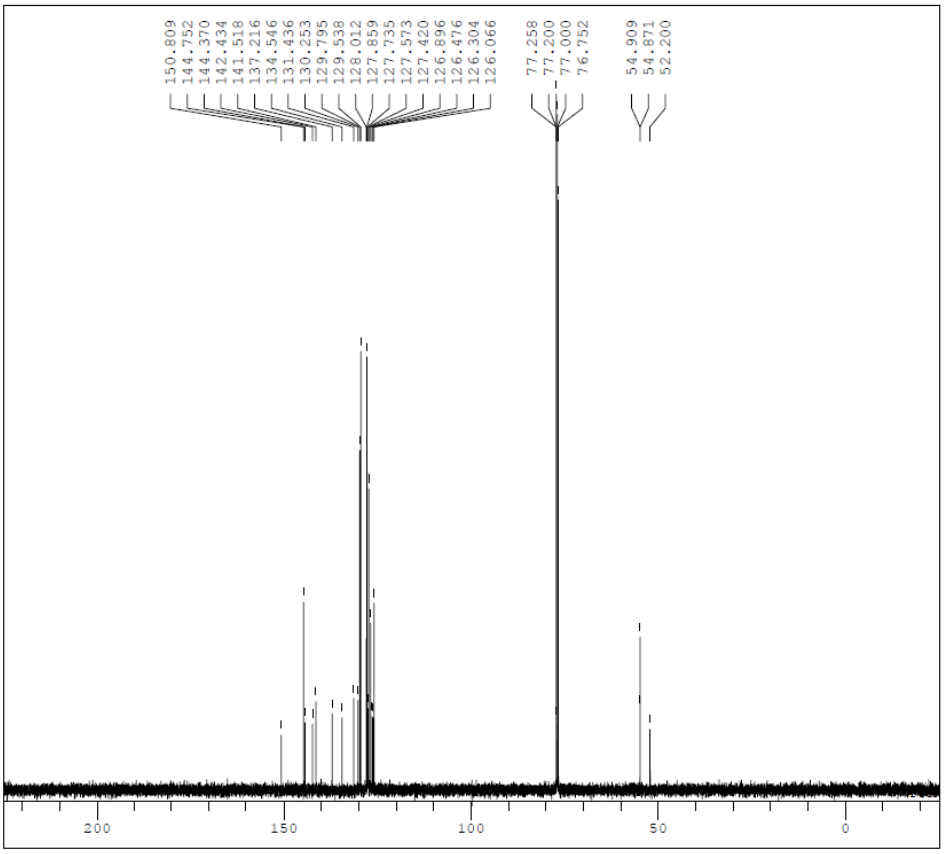
DFILE HT5-126-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2013-04-01 21:18:23
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39308.18 Hz
SCANS 151
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.12 usec
IRNUC 1H
CTEMP 18.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 58



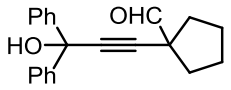
16s'



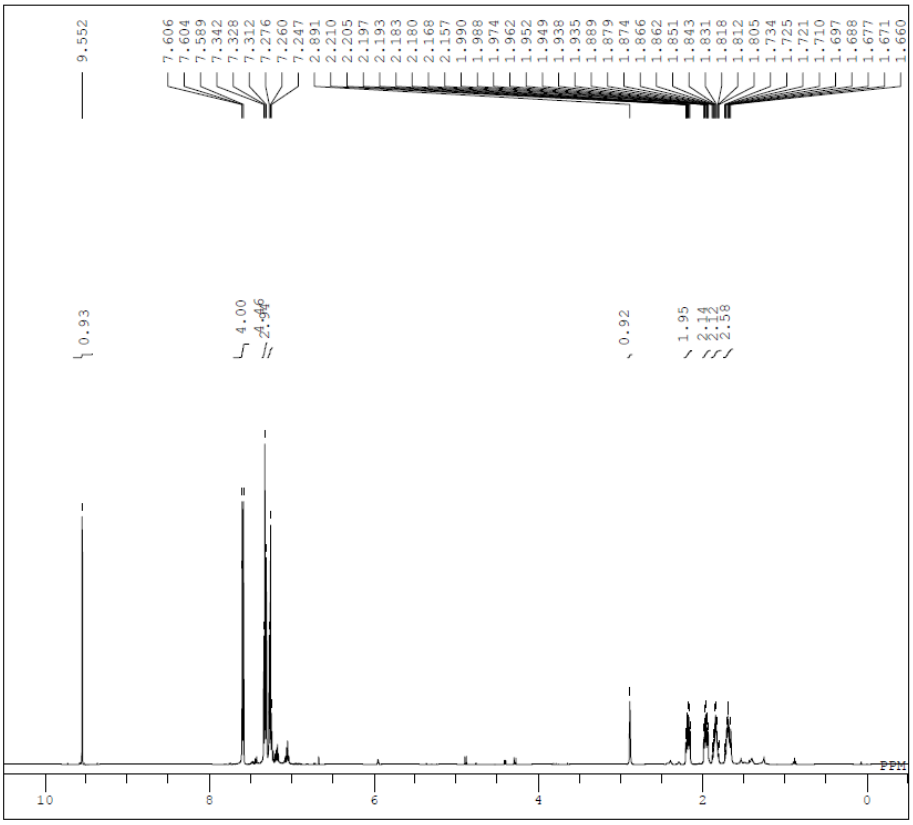

```
DFILE   HT5-70-1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-01-11 00:12:01
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           17.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             30
```



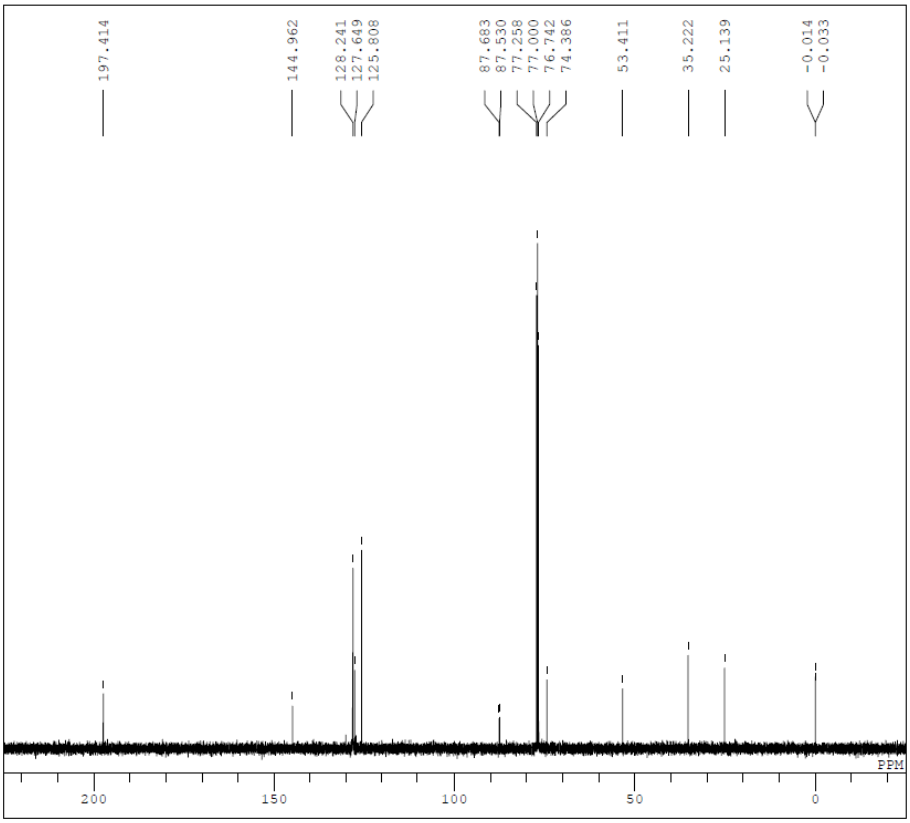

```
DFILE   HT5-70-1_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-11 00:15:15
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            269
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           17.4 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



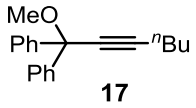
15t'




```
DFILE   HT5-68-3_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-01-23 22:53:27
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             16
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           13.8 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             38
```

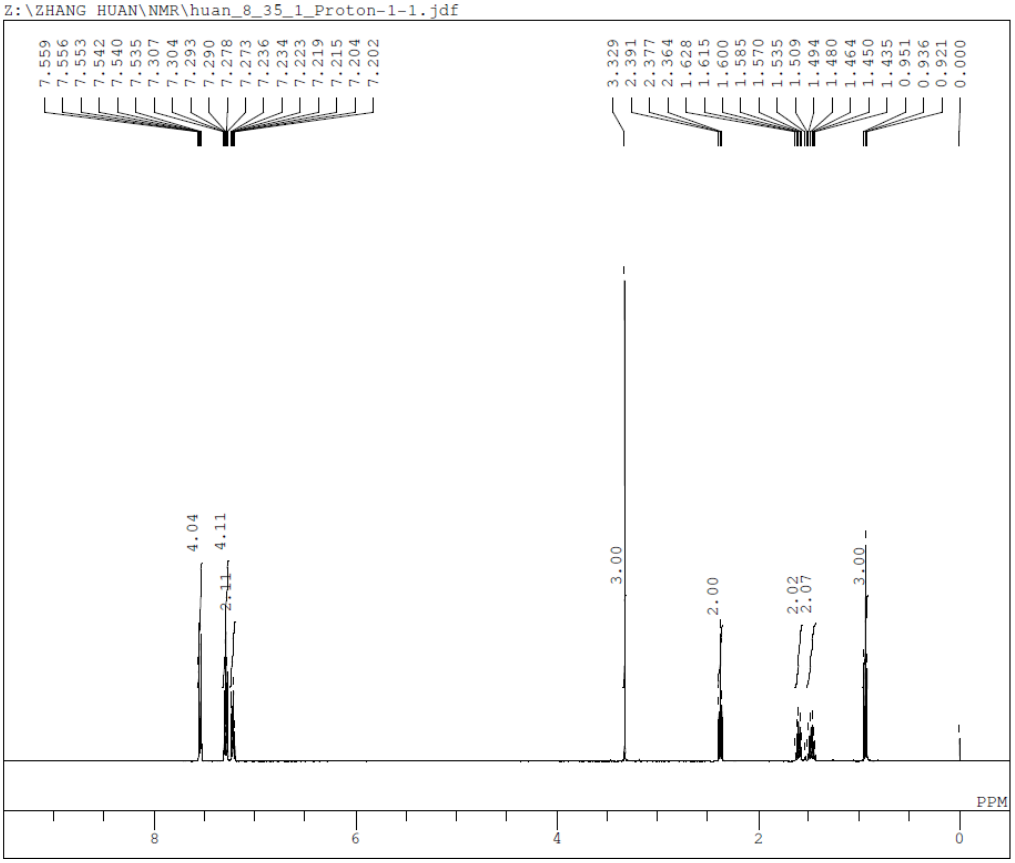



```
DFILE   HT5-68-1_Carbon-1-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2013-01-17 18:38:28
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            159
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.10 Hz
RGAIN             58
```



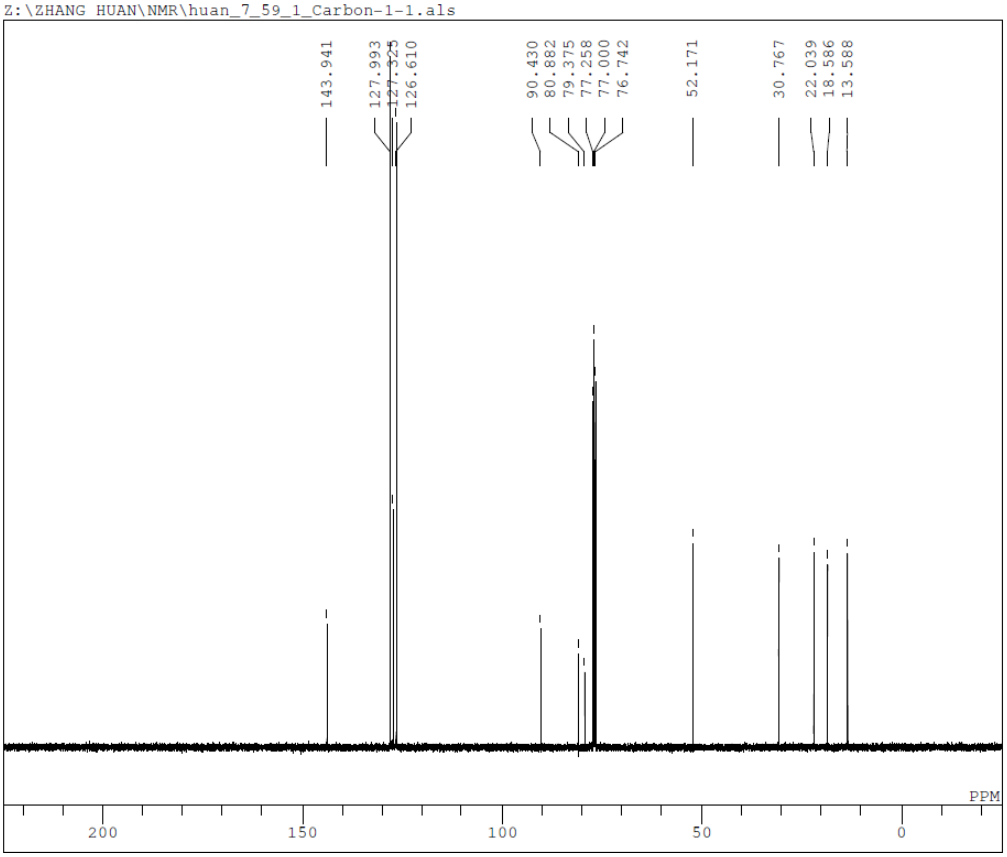
17

Z:\ZHANG HUAN\NMR\huan_8_35_1_Proton-1-1.jdf

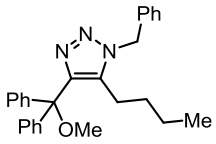



```
DFILE   huan_8_35_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2014-06-23 12:18:47
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.3 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             30
```

Z:\ZHANG HUAN\NMR\huan_7_59_1_Carbon-1-1.als

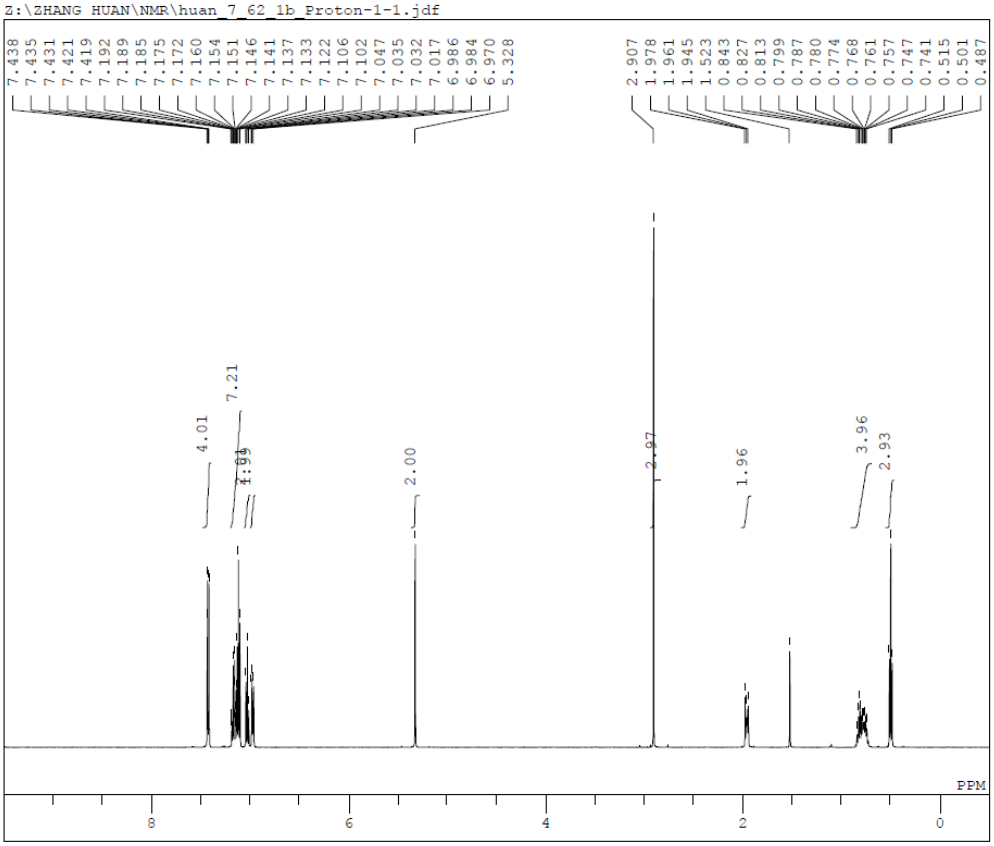



```
DFILE   huan_7_59_1_Carbon-1-1.als
COMNT   single pulse decoupled gated N
DATIM   2013-09-20 22:31:35
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



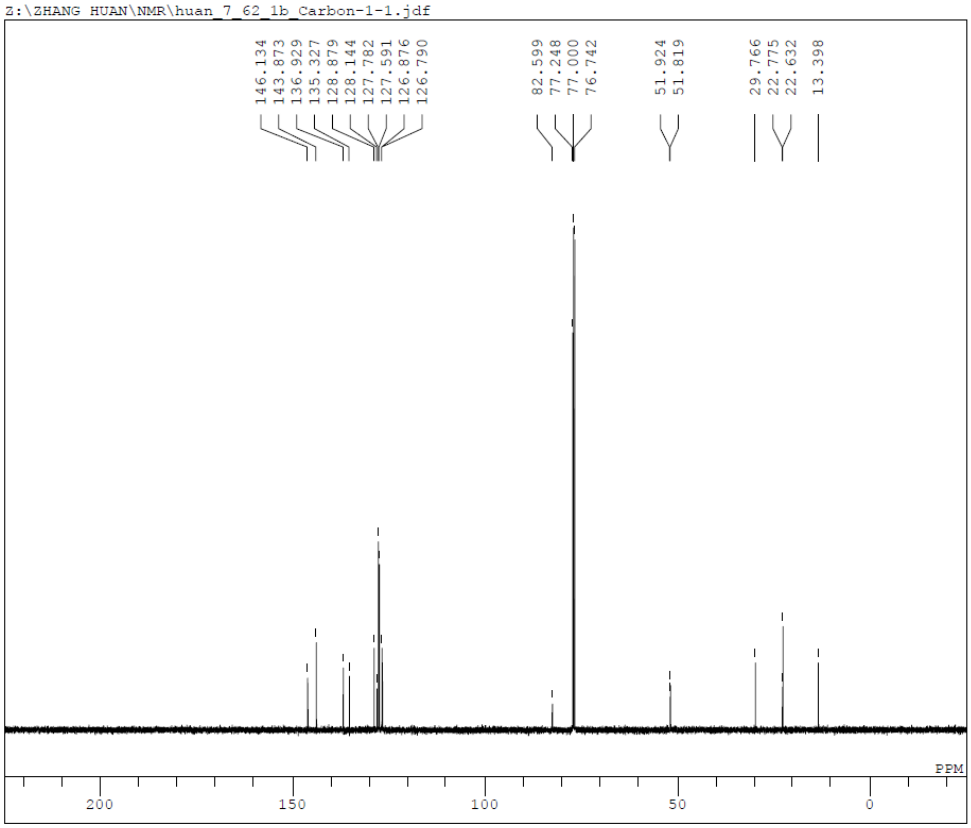
18

Z:\ZHANG HUAN\NMR\huan_7_62_1b_Proton-1-1.jdf

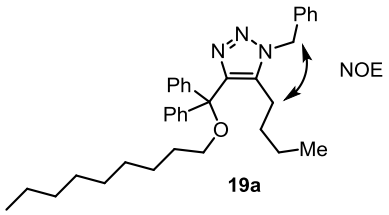



```
DFILE   huan_7_62_1b_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-09-24 19:49:07
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          19.7 c
SLVNT   CDCL3
EXREF          1.52 ppm
BF             0.12 Hz
RGAIN            32
```

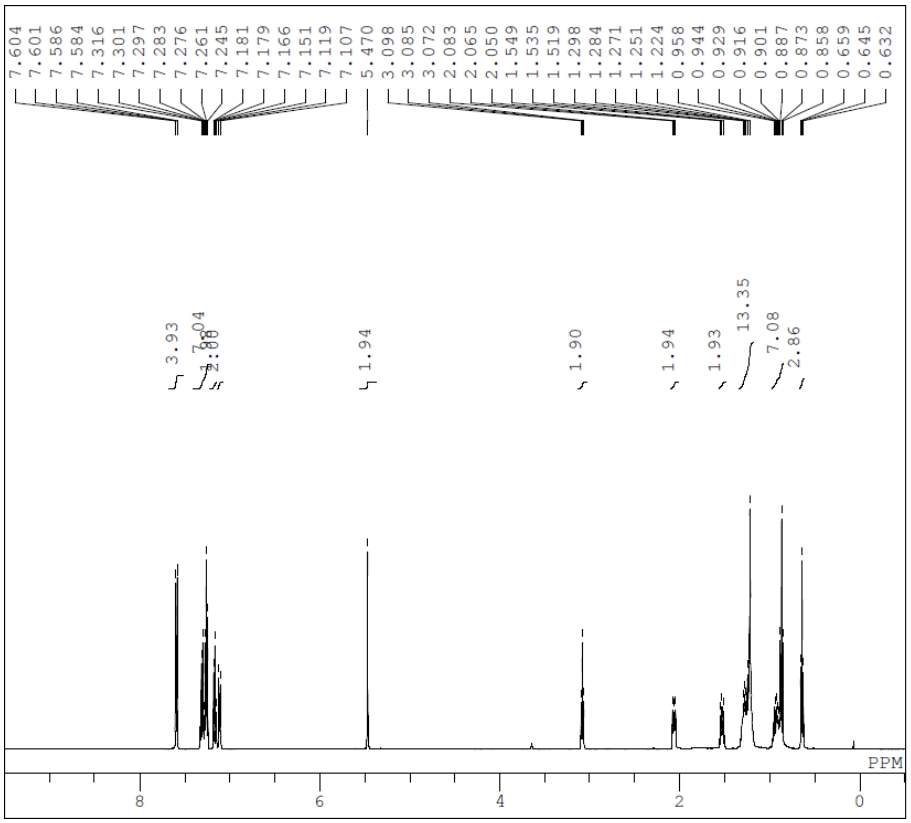
Z:\ZHANG HUAN\NMR\huan_7_62_1b_Carbon-1-1.jdf




```
DFILE   huan_7_62_1b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-09-24 19:50:36
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             512
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```

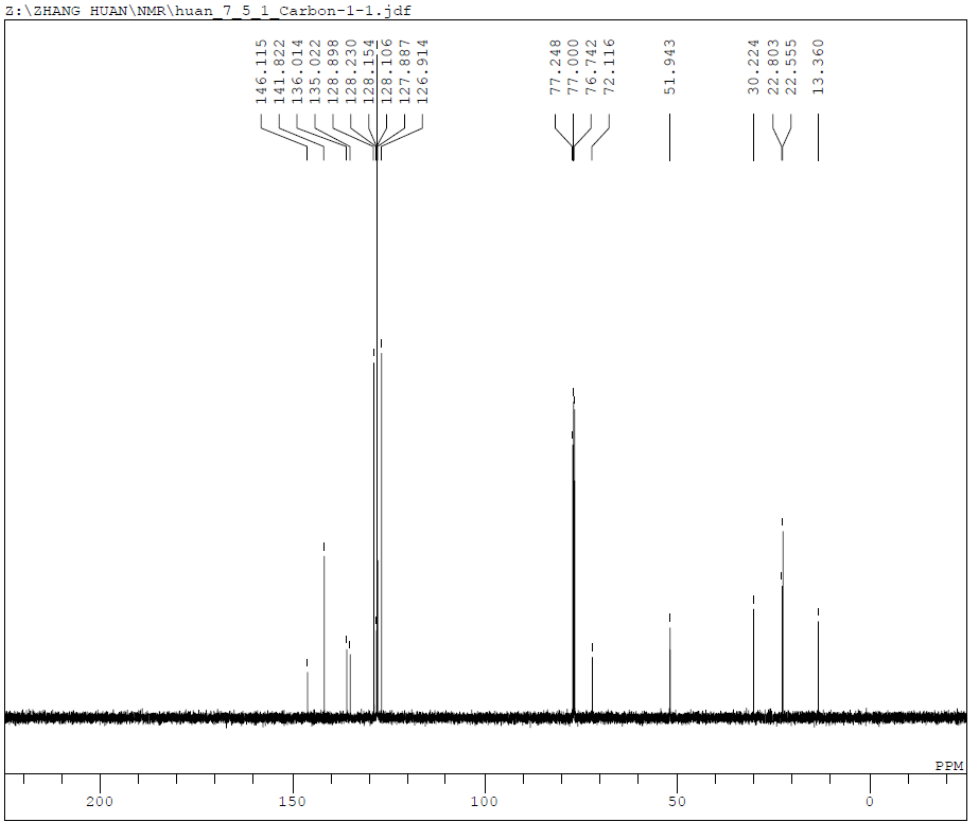


19a

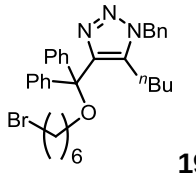



```
DFILE   huan_6_151_1_Proton-1-1.a
COMNT   single_pulse
DATIM   2013-07-23 21:39:04
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS               8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           19.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             28
```

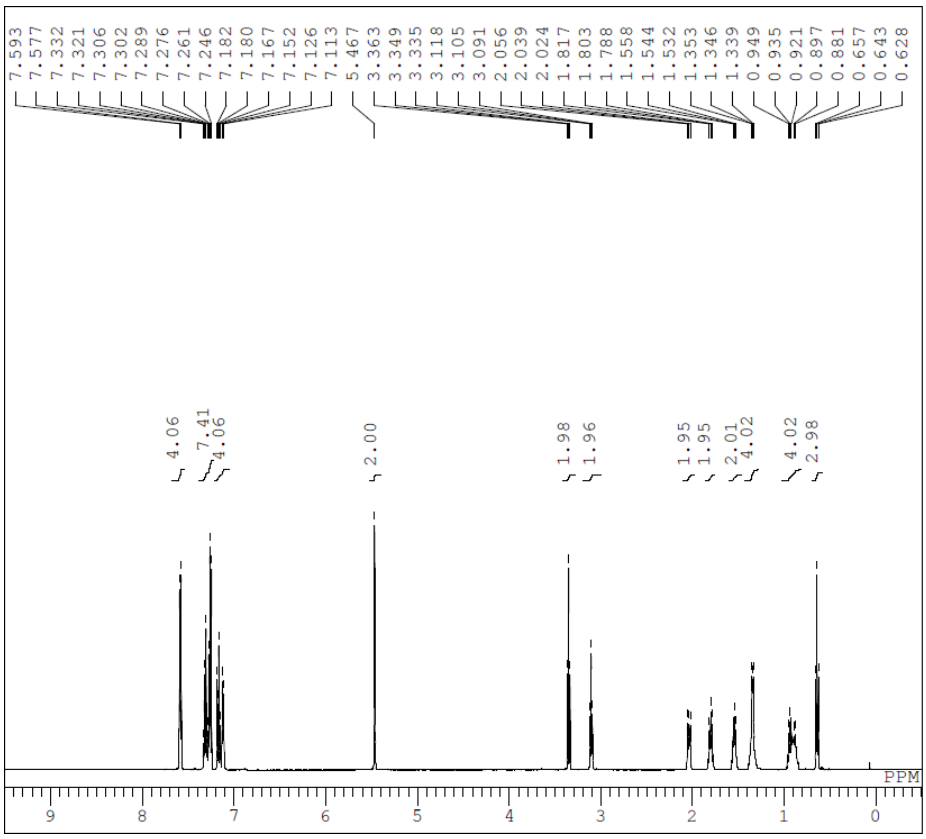
Z:\ZHANG HUAN\NMR\huan_7_5_1_Carbon-1-1.jdf




```
DFILE   huan_7_5_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-28 19:38:13
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            130
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           19.5 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             58
```

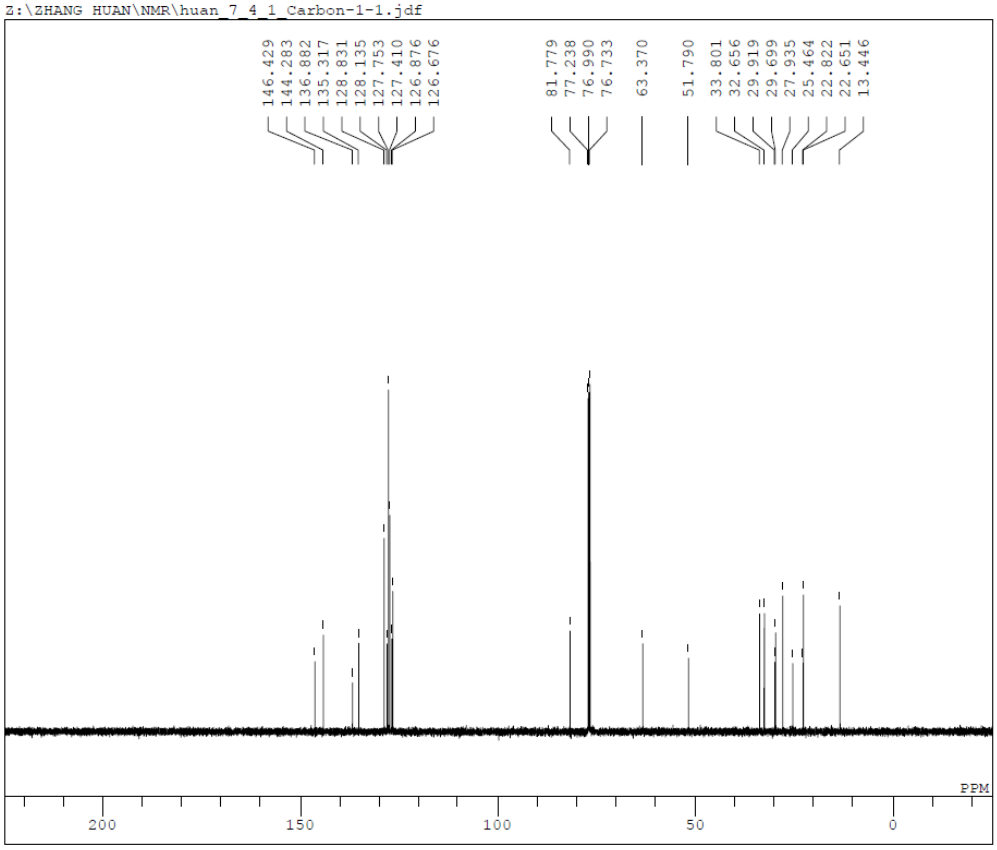


19b

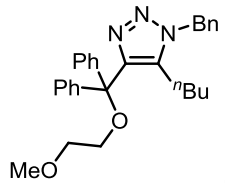



```
DFILE  huan_7_4_1_Proton-1-1.als
COMNT  single_pulse
DATIM  2013-07-26 22:35:24
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          19.0 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            28
```

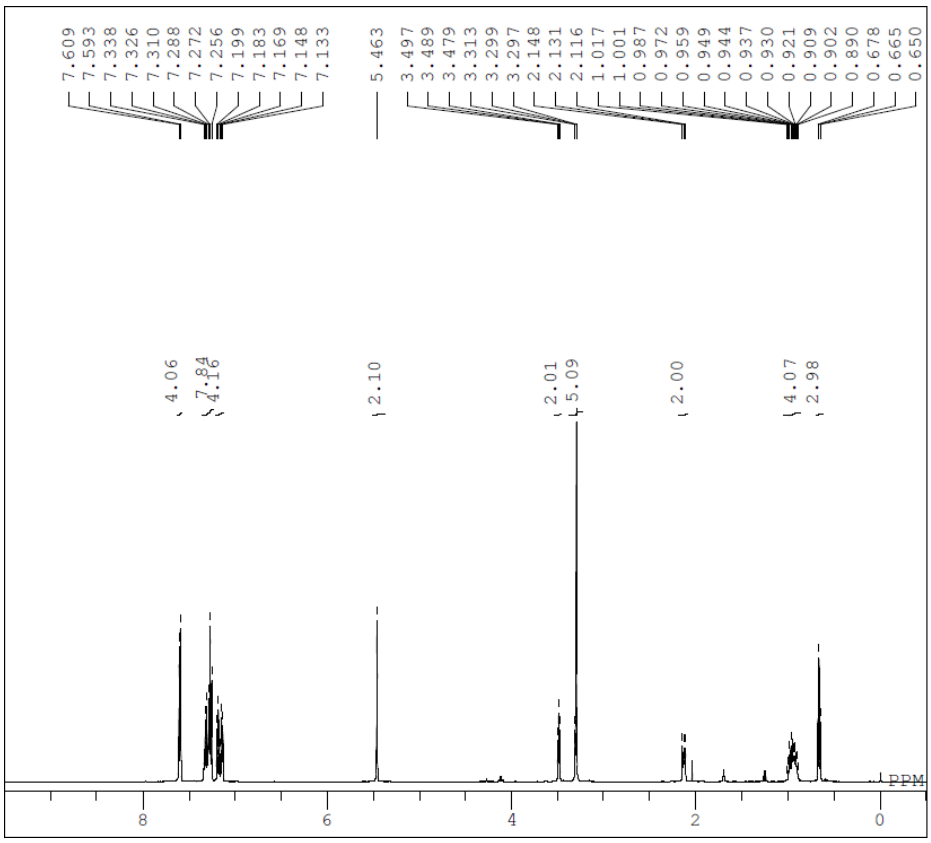
Z:\ZHANG HUAN\NMR\huan_7_4_1_Carbon-1-1.jdf



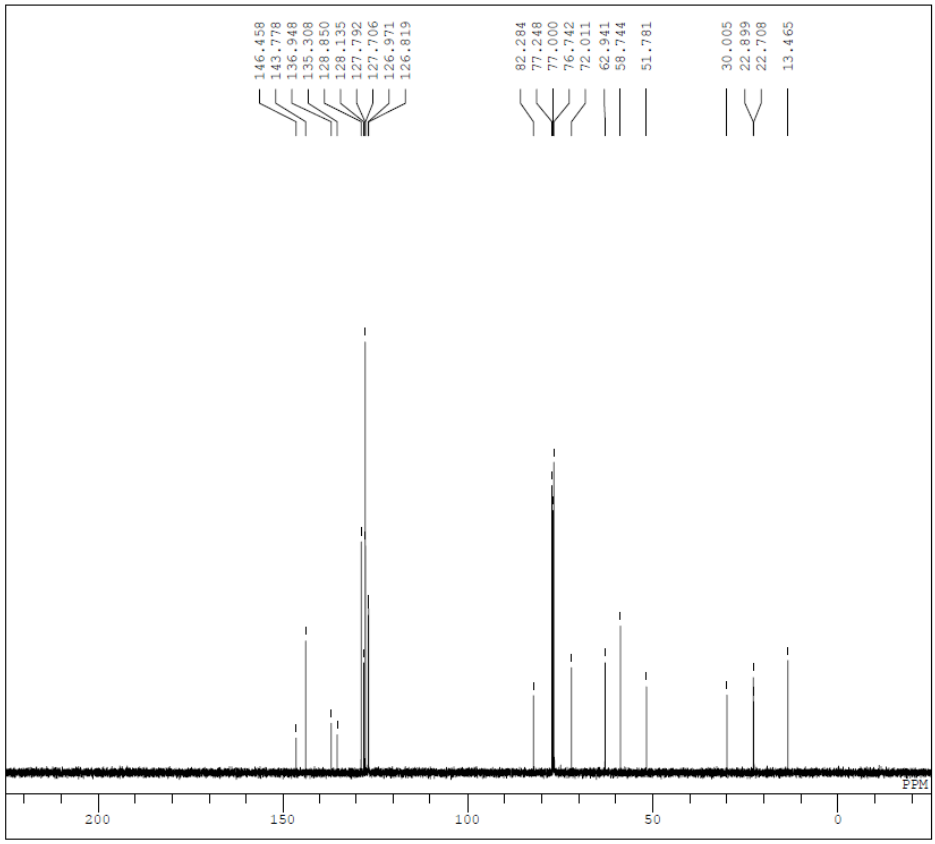

```
DFILE  huan_7_4_1_Carbon-1-1.jdf
COMNT  single pulse decoupled gated NO
DATIM  2013-07-26 22:36:54
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU       39308.18 Hz
SCANS            351
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          19.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            56
```



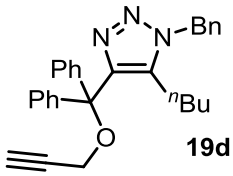
19c




```
DFILE   HT5-129-2_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-04-22 17:46:29
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS               8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.0 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.10 Hz
RGAIN             30
```

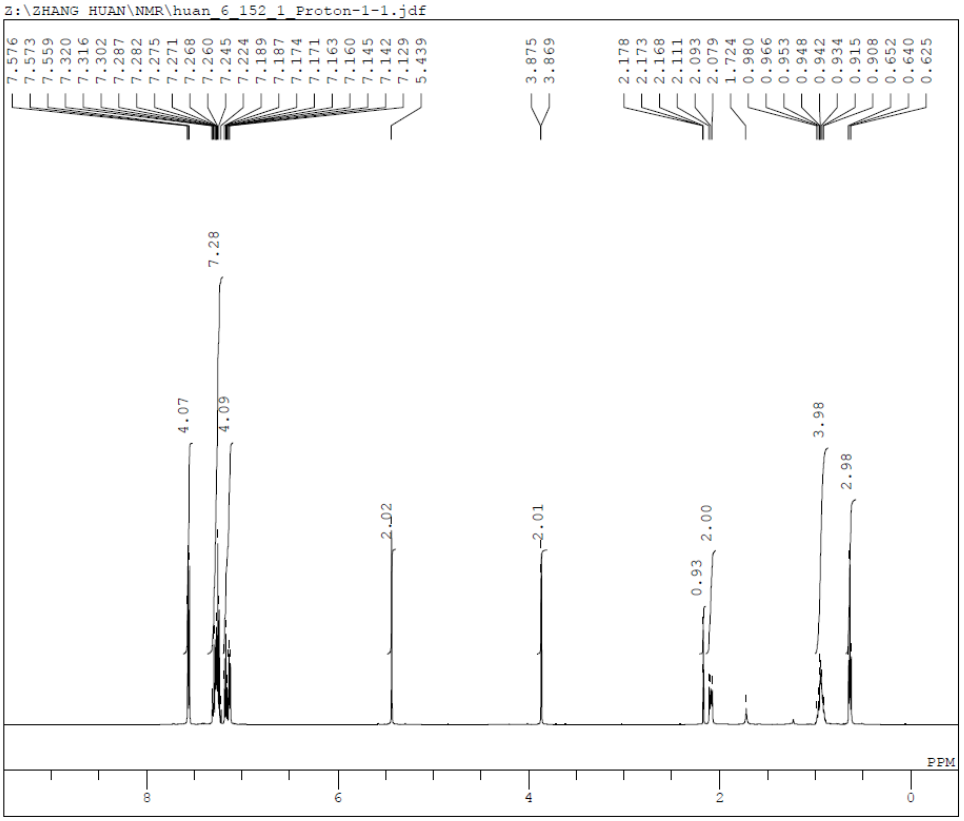



```
DFILE   HT5-129-2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-04-22 17:49:06
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            126
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.7 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             60
```



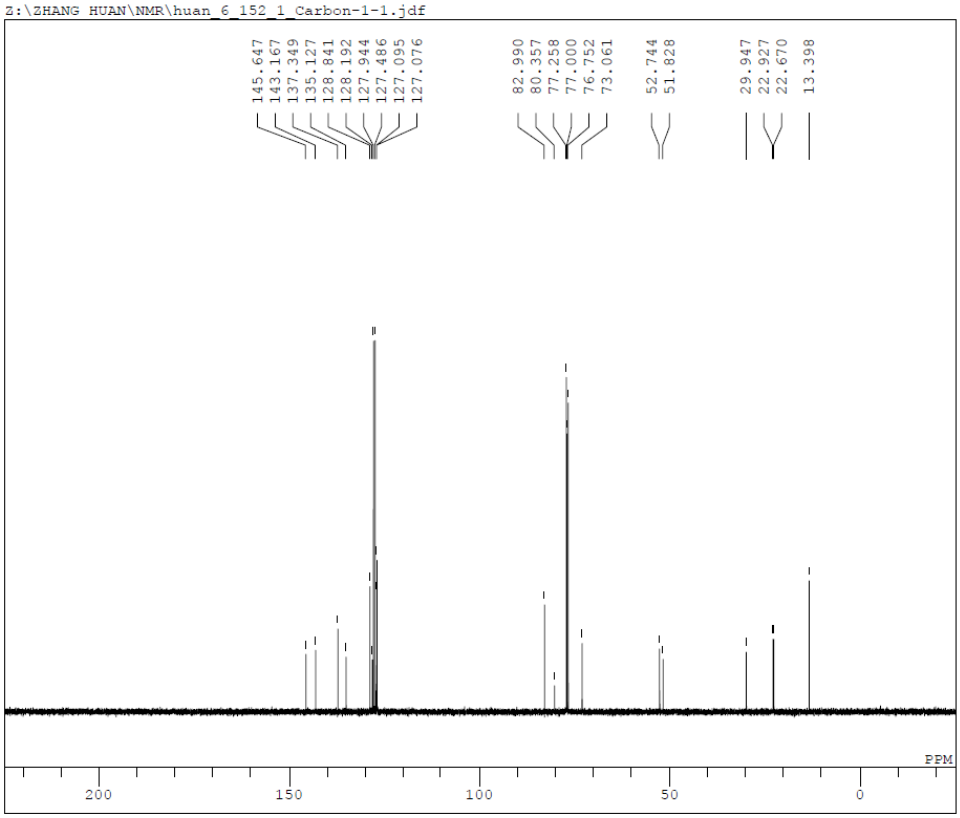
19d

Z:\ZHANG HUAN\NMR\huan_6_152_1_Proton-1-1.jdf

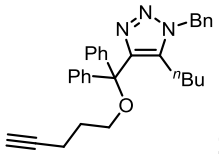



```
DFILE   huan_6_152_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-24 20:35:18
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             30
```

Z:\ZHANG HUAN\NMR\huan_6_152_1_Carbon-1-1.jdf

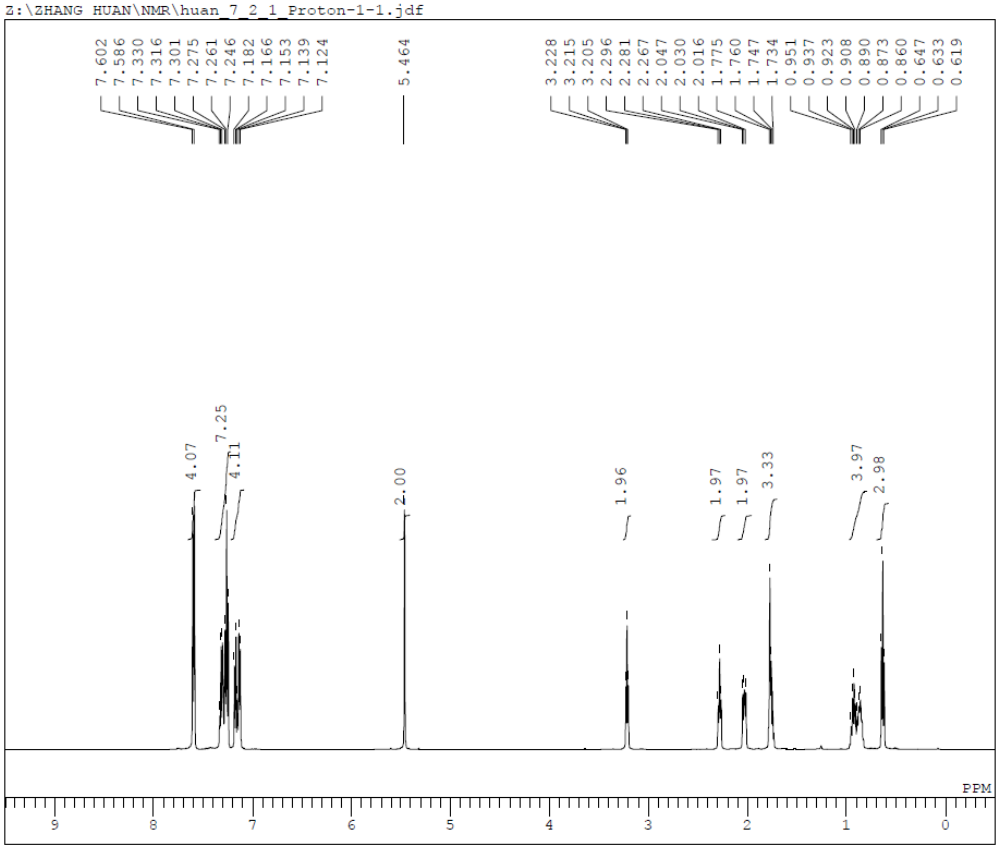



```
DFILE   huan_6_152_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-24 20:36:48
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            482
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



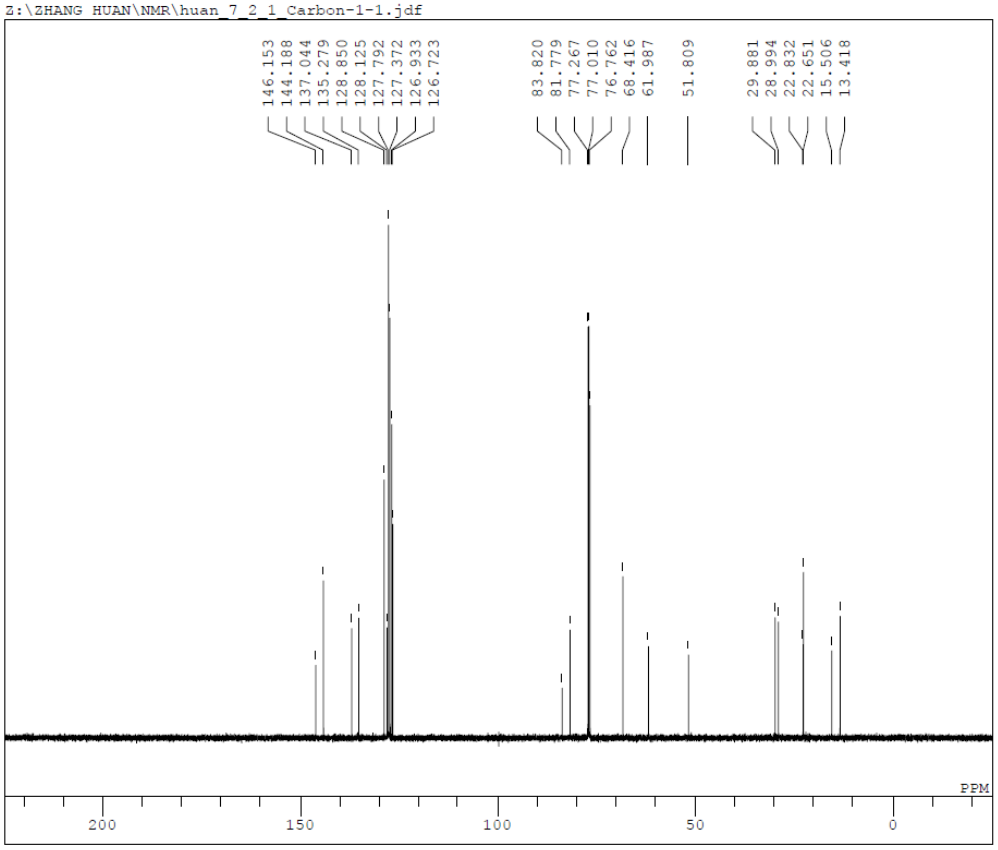
19e

Z:\ZHANG HUAN\NMR\huan_7_2_1_Proton-1-1.jdf

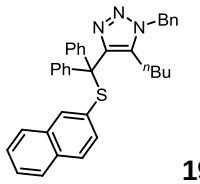



```
DFILE   huan_7_2_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-26 20:51:19
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.10 Hz
RGAIN             26
```

Z:\ZHANG HUAN\NMR\huan_7_2_1_Carbon-1-1.jdf

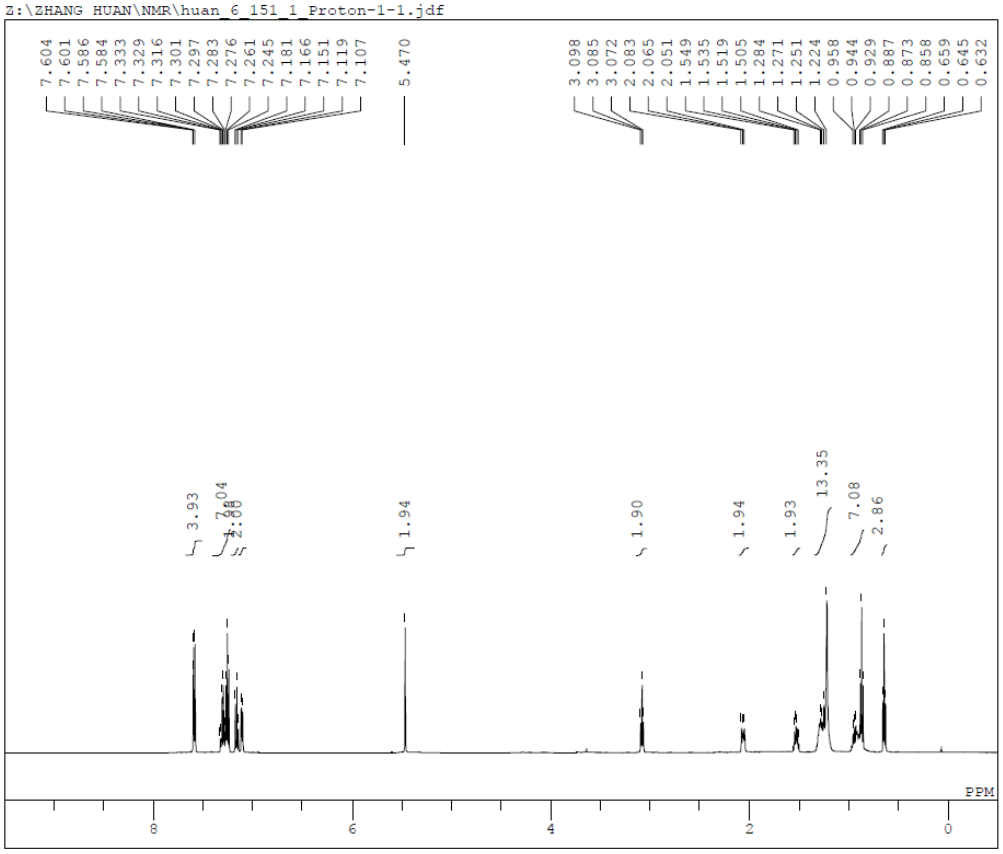



```
DFILE   huan_7_2_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-26 20:52:50
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            454
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.10 Hz
RGAIN             58
```



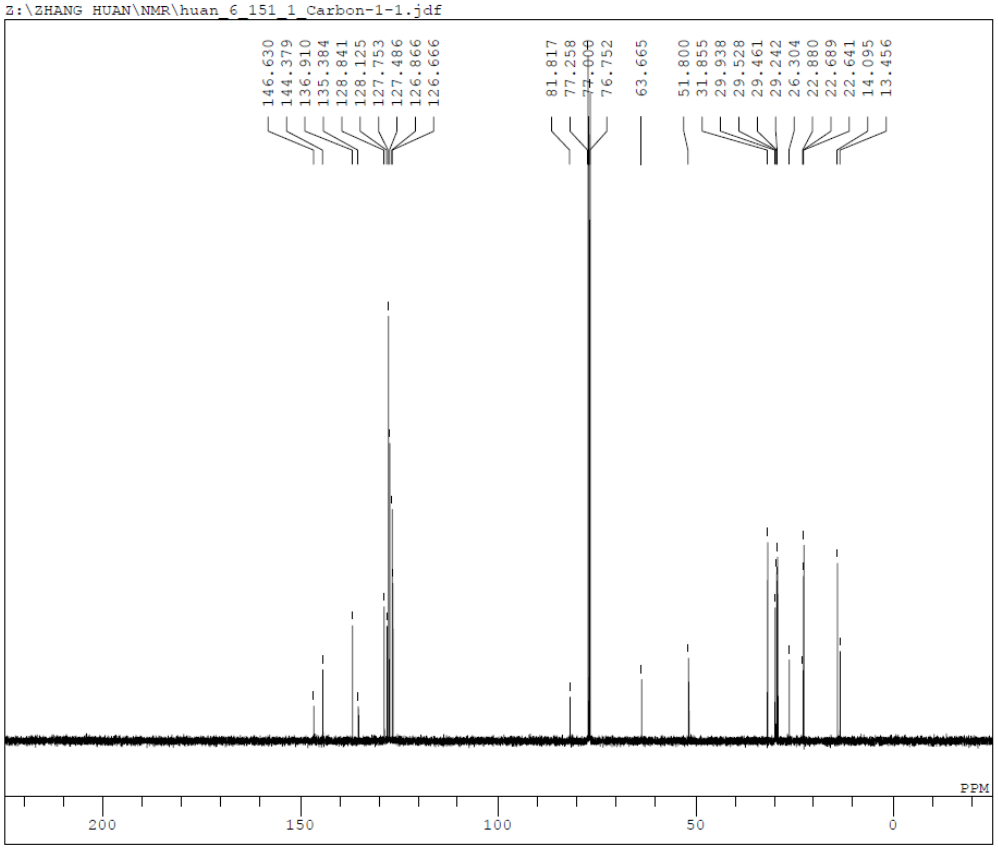
19f

Z:\ZHANG HUAN\NMR\huan_6_151_1_Proton-1-1.jdf

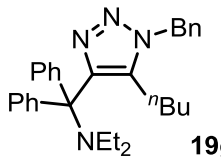



```
DFILE   huan_6_151_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-23 21:39:04
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             28
```

Z:\ZHANG HUAN\NMR\huan_6_151_1_Carbon-1-1.jdf

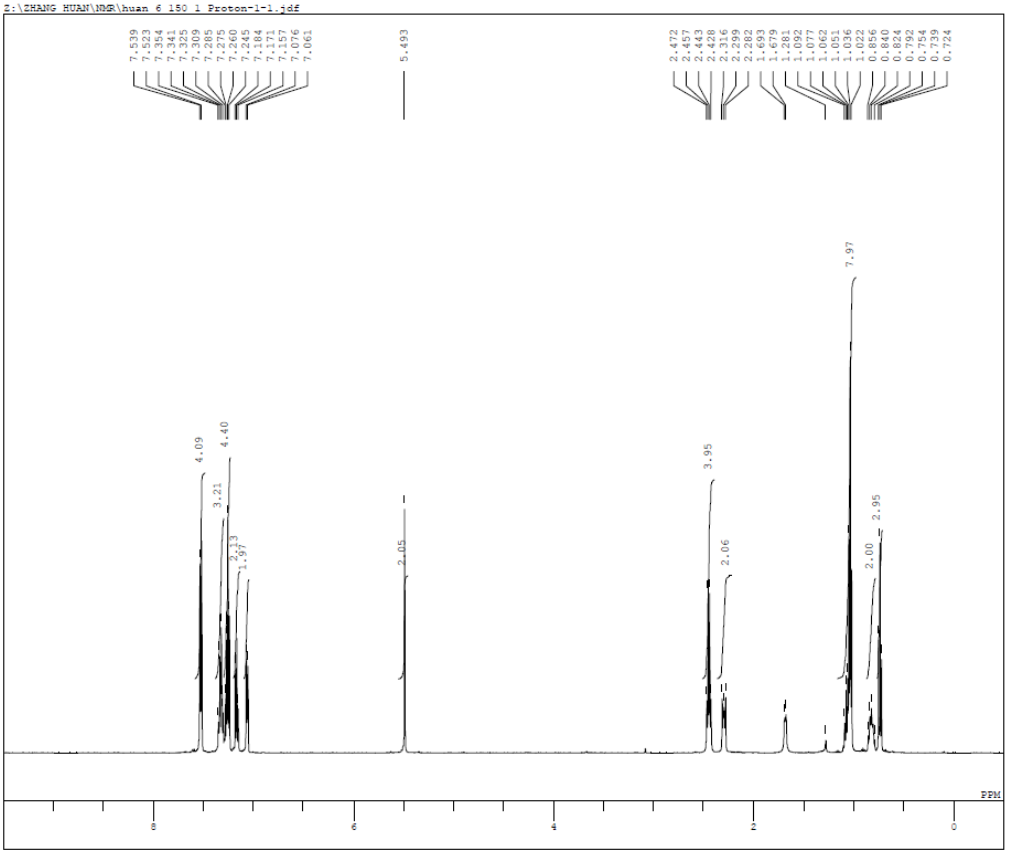



```
DFILE   huan_6_151_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-23 21:40:35
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            591
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.3 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



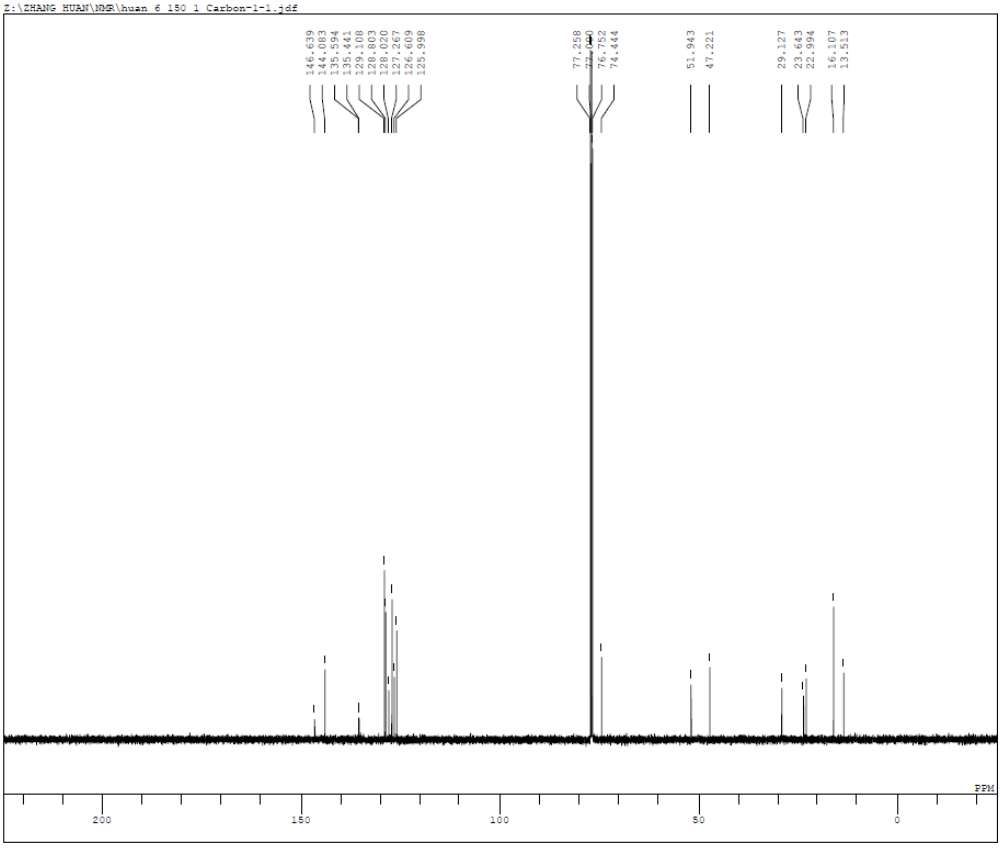
19g

Z:\ZHANG HUAN\NMR\huan 6 150 1 Proton-1-1.jdf

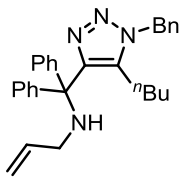



```
DFILE   huan_6_150_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-23 15:47:59
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.36 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           19.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             36
```

Z:\ZHANG HUAN\NMR\huan 6 150 1 Carbon-1-1.jdf

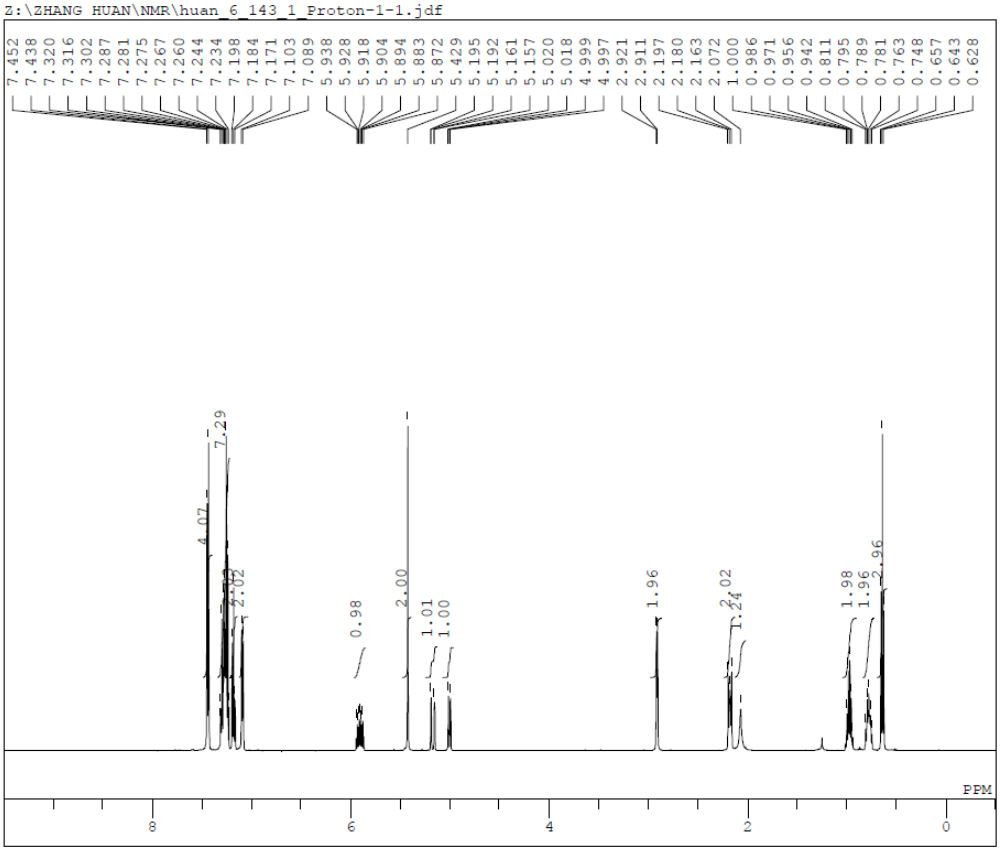



```
DFILE   huan_6_150_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2013-07-23 15:49:35
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.16 Hz
SCANS            809
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              9.12 usec
IRNUC   1H
CTEMP           19.9 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



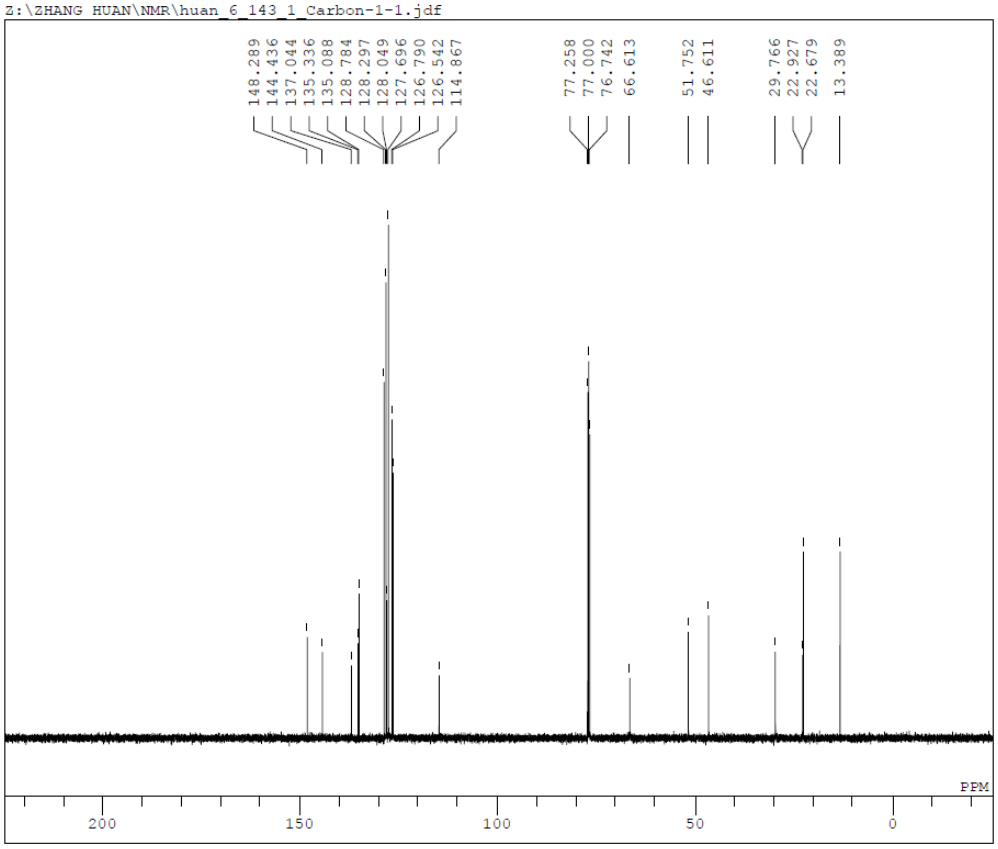
19h

Z:\ZHANG HUAN\NMR\huan_6_143_1_Proton-1-1.jdf

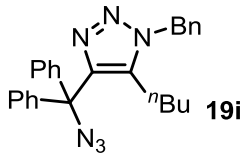



```
DFILE   huan_6_143_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-17 18:17:46
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          19.0 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            24
```

Z:\ZHANG HUAN\NMR\huan_6_143_1_Carbon-1-1.jdf

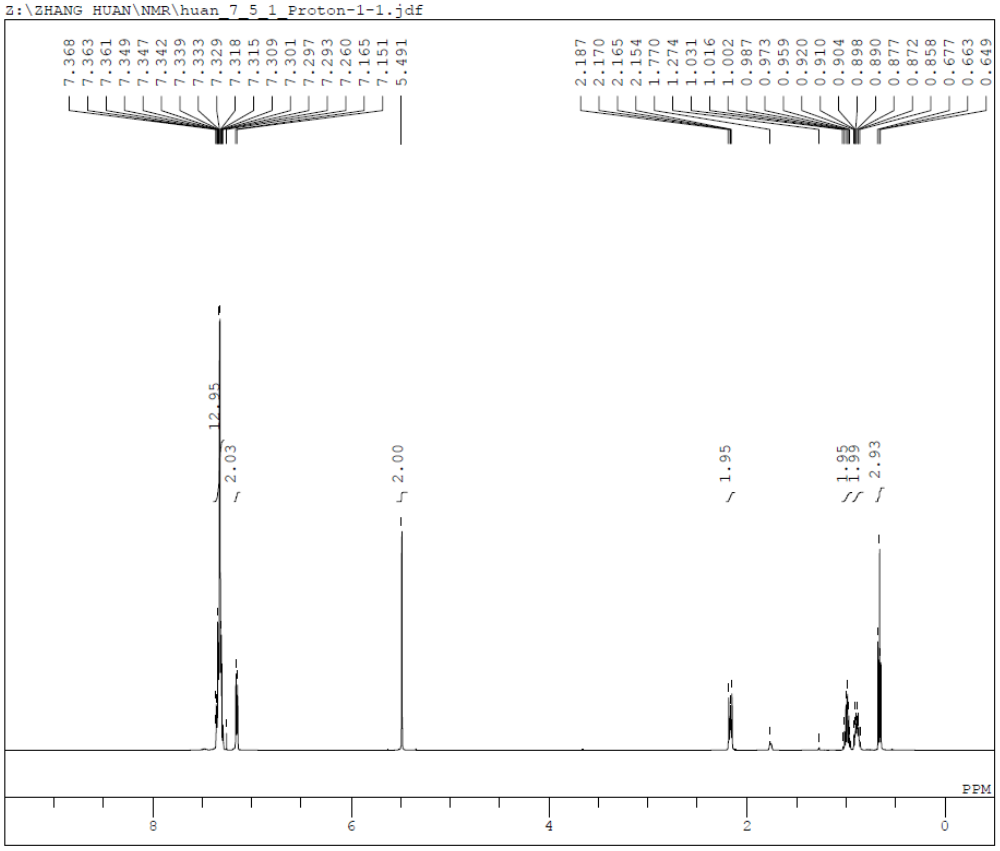



```
DFILE   huan_6_143_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-17 18:42:20
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            193
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.3 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



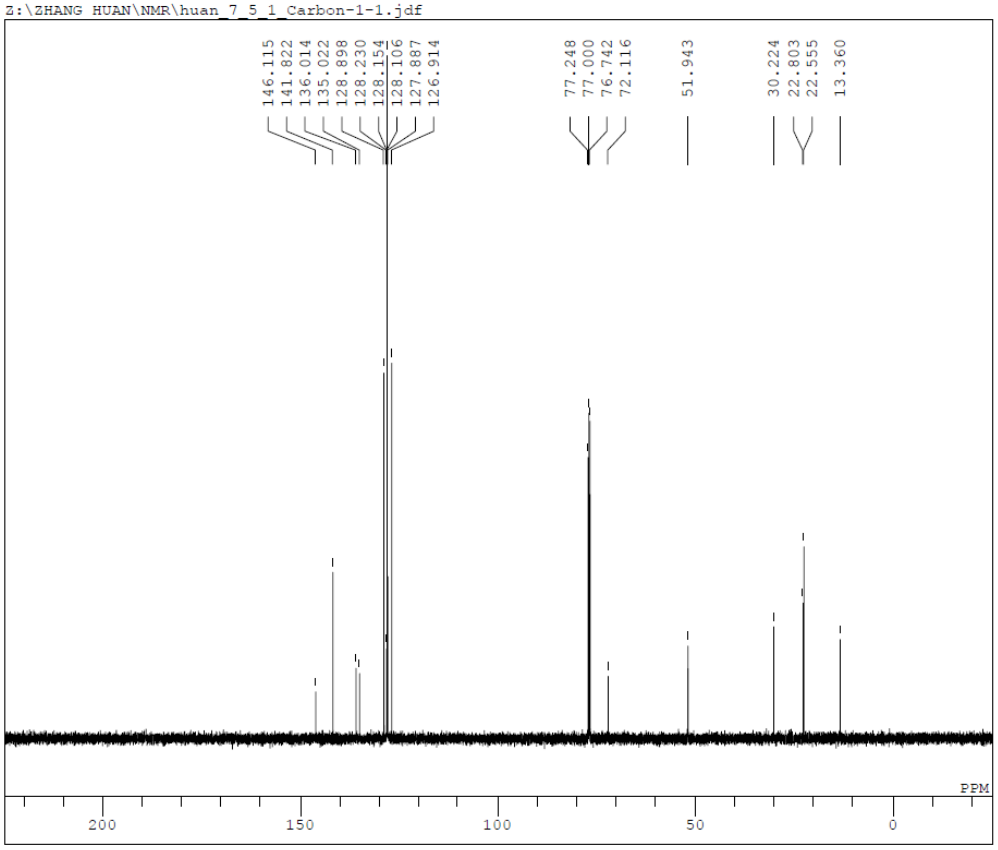
19i

Z:\ZHANG HUAN\NMR\huan_7_5_1_Proton-1-1.jdf

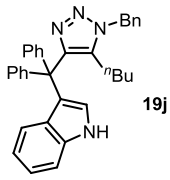



```
DFILE   huan_7_5_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-07-27 16:16:39
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.9 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            28
```

Z:\ZHANG HUAN\NMR\huan_7_5_1_Carbon-1-1.jdf

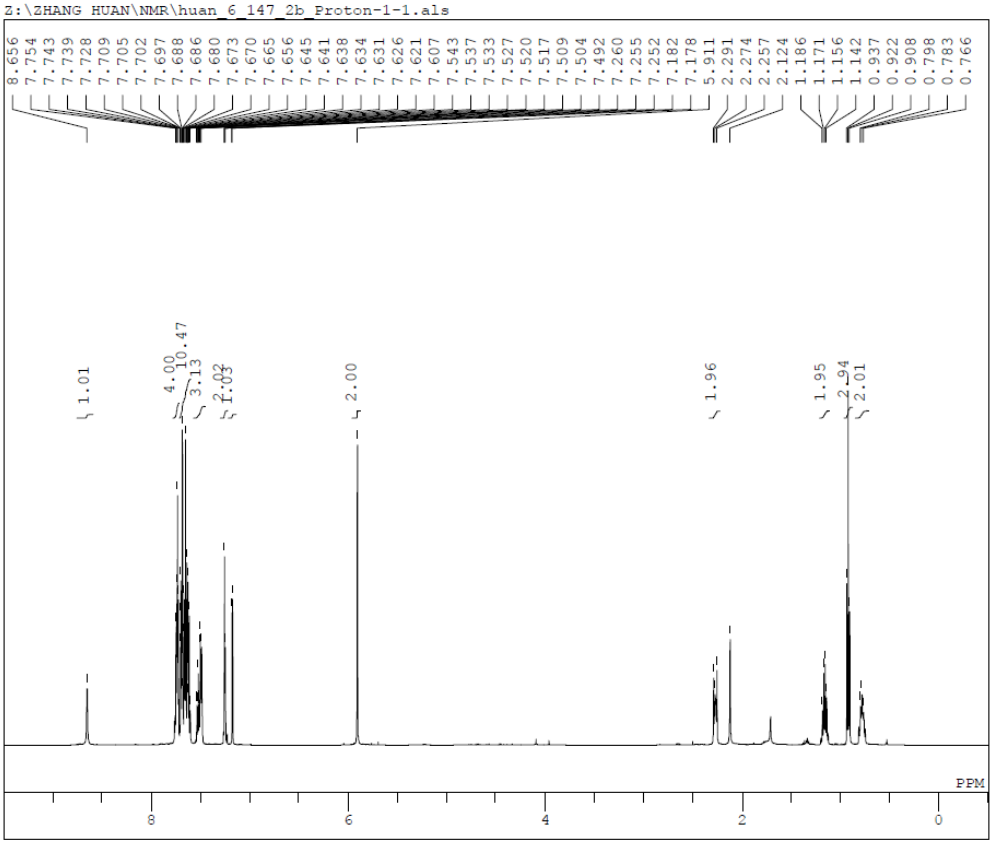



```
DFILE   huan_7_5_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-28 19:38:13
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            130
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.5 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.10 Hz
RGAIN            58
```



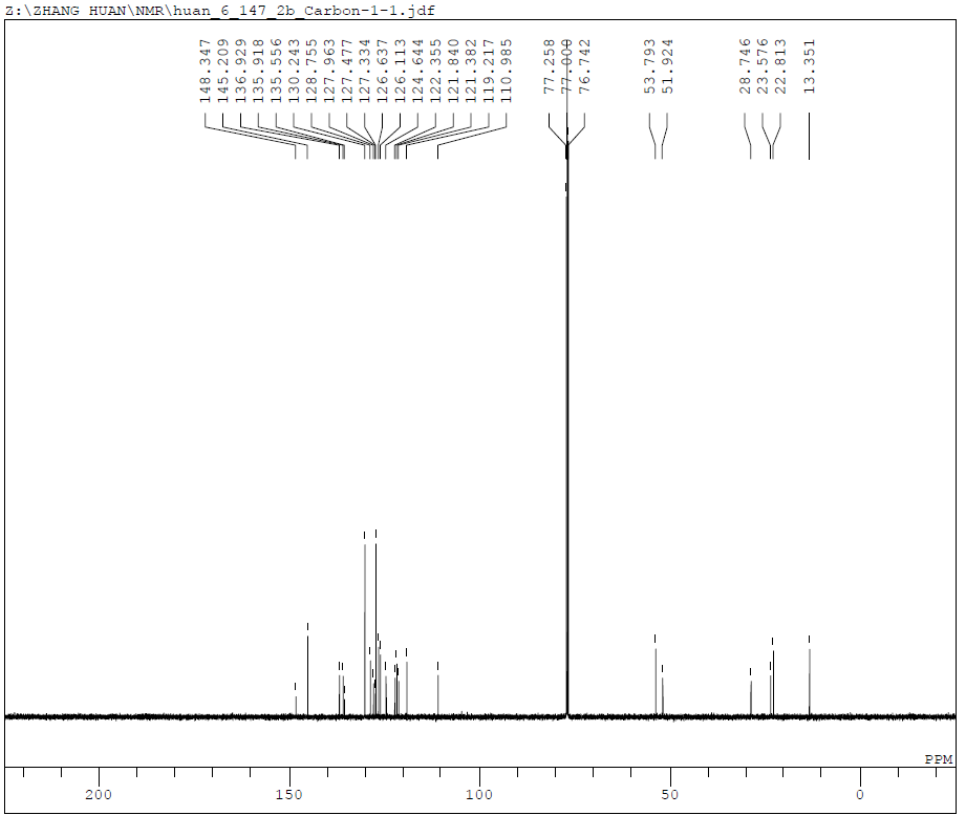
19j

Z:\ZHANG HUAN\NMR\huan_6_147_2b_Proton-1-1.als

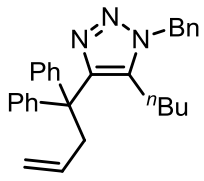



```
DFILE   huan_6_147_2b_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-07-21 17:23:54
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.6 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            36
```

Z:\ZHANG HUAN\NMR\huan_6_147_2b_Carbon-1-1.jdf

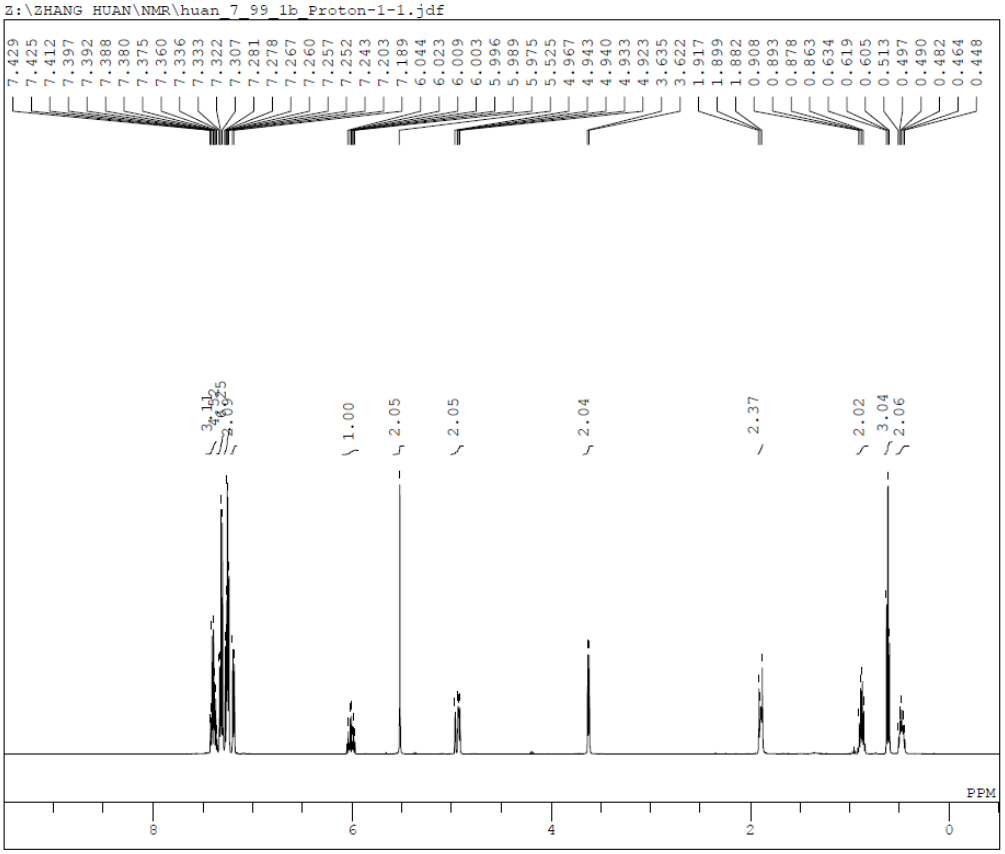



```
DFILE   huan_6_147_2b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-21 17:25:25
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1171
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.8 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



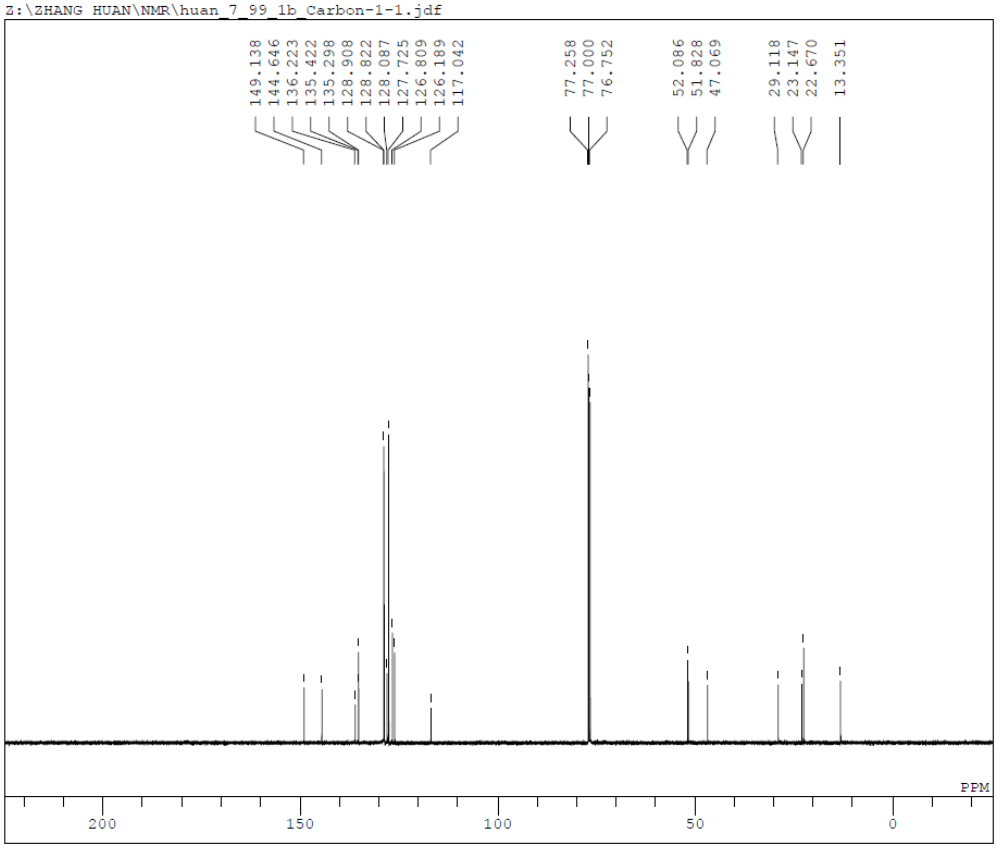
19k

Z:\ZHANG HUAN\NMR\huan_7_99_1b_Proton-1-1.jdf

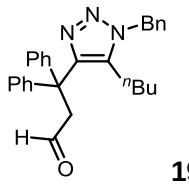



```
DFILE   huan_7_99_1b_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-11-05 11:52:27
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          16.9 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            28
```

Z:\ZHANG HUAN\NMR\huan_7_99_1b_Carbon-1-1.jdf

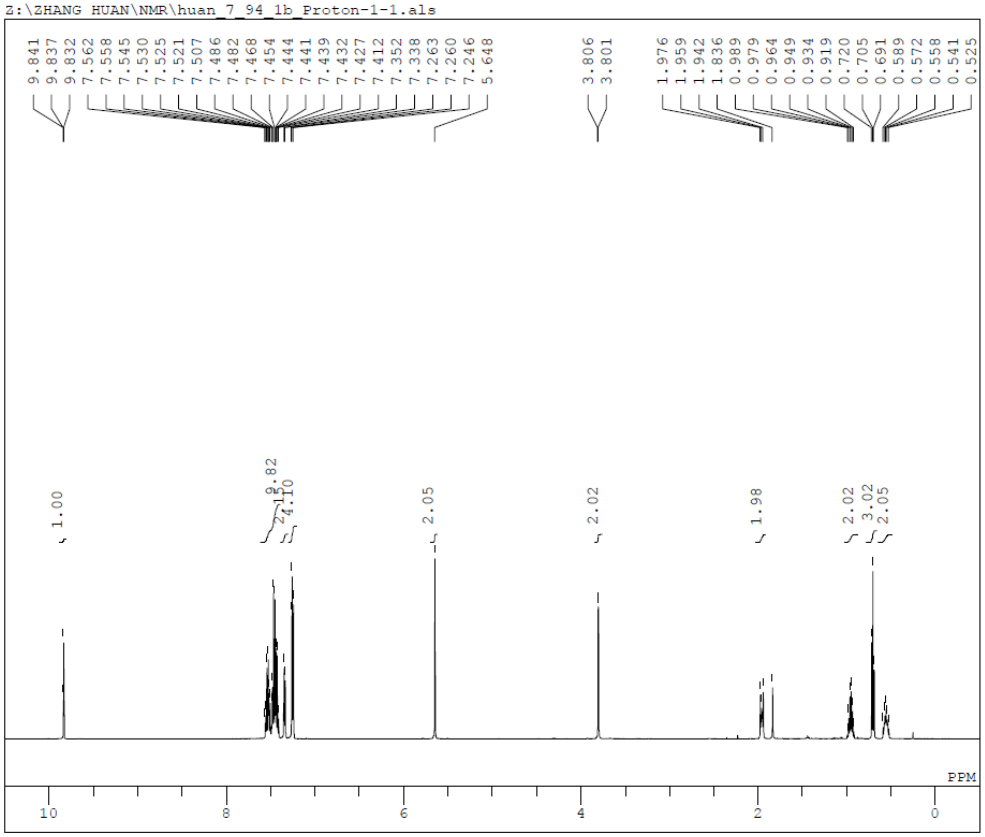



```
DFILE   huan_7_99_1b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-11-05 11:53:58
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            718
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          16.5 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            54
```



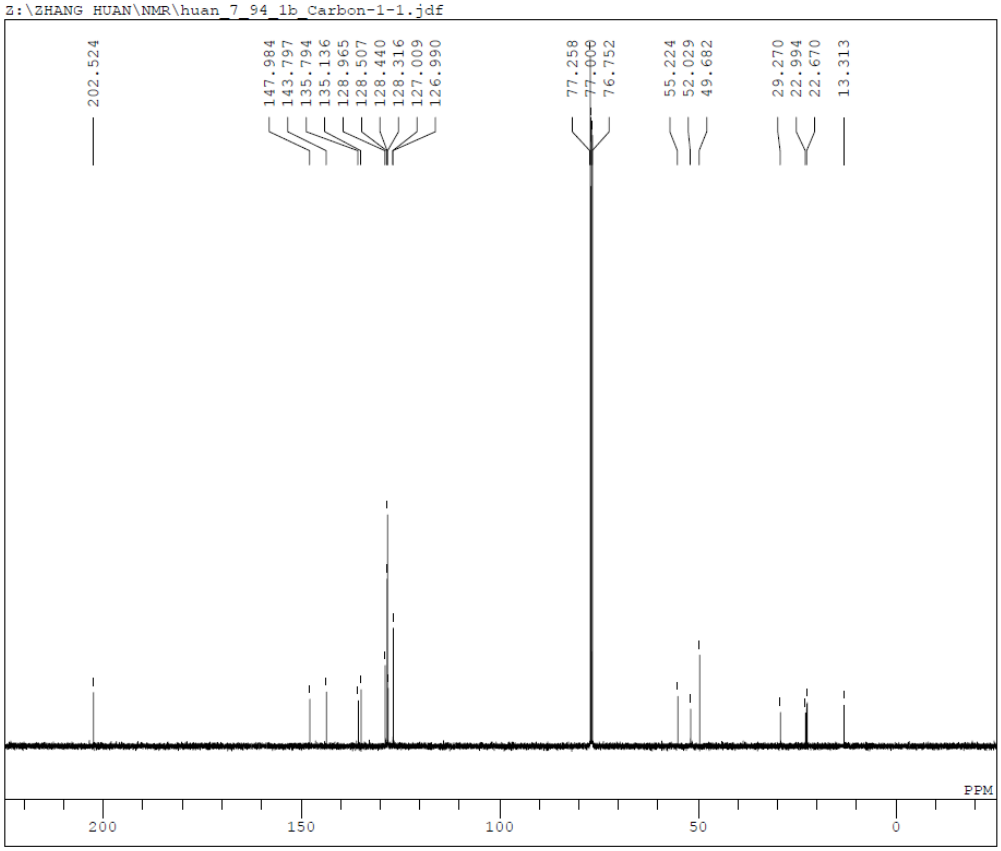
19l

Z:\ZHANG HUAN\NMR\huan_7_94_1b_Proton-1-1.als

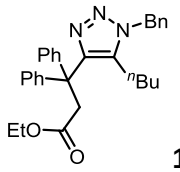



```
DFILE   huan_7_94_1b_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-10-31 11:45:44
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           17.4 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             36
```

Z:\ZHANG HUAN\NMR\huan_7_94_1b_Carbon-1-1.jdf

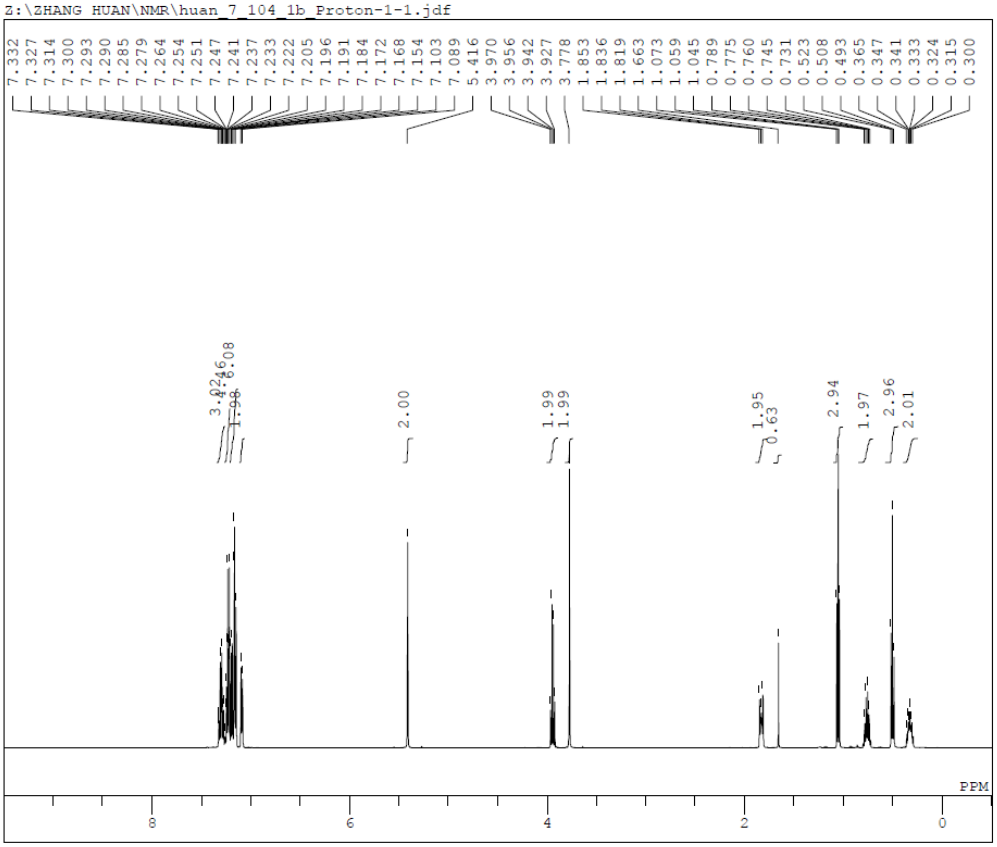



```
DFILE   huan_7_94_1b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-10-31 11:47:15
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS             903
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           18.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```



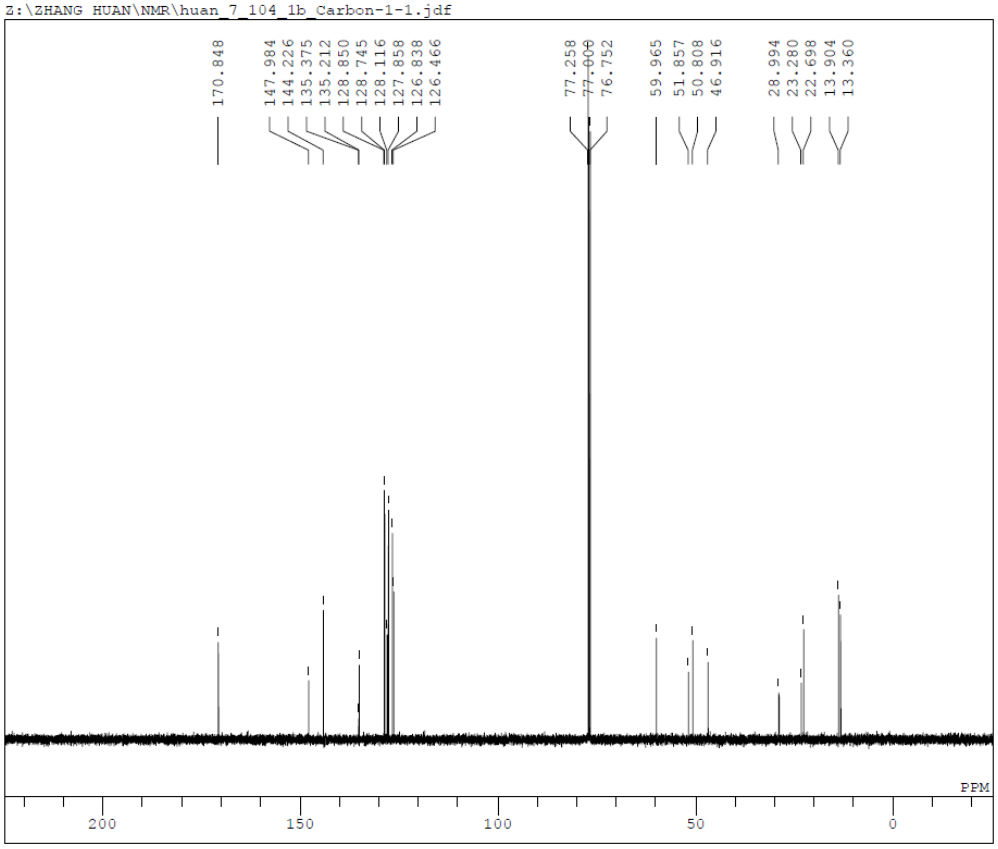
19m

Z:\ZHANG HUAN\NMR\huan_7_104_1b_Proton-1-1.jdf

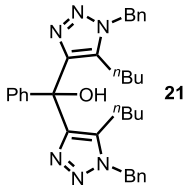



```
DFILE   huan_7_104_1b_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-11-07 16:16:31
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          17.6 c
SLVNT   CDCL3
EXREF          5.42 ppm
BF             0.12 Hz
RGAIN            36
```

Z:\ZHANG HUAN\NMR\huan_7_104_1b_Carbon-1-1.jdf

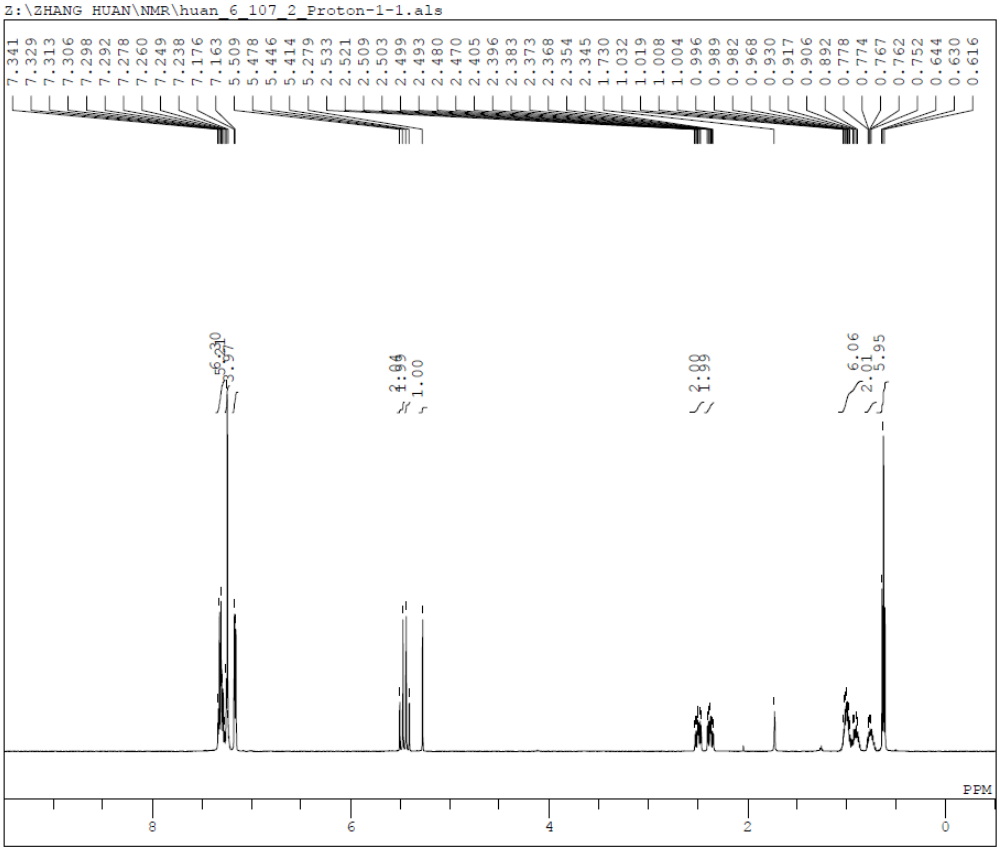



```
DFILE   huan_7_104_1b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-11-07 16:18:02
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            679
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          17.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            58
```



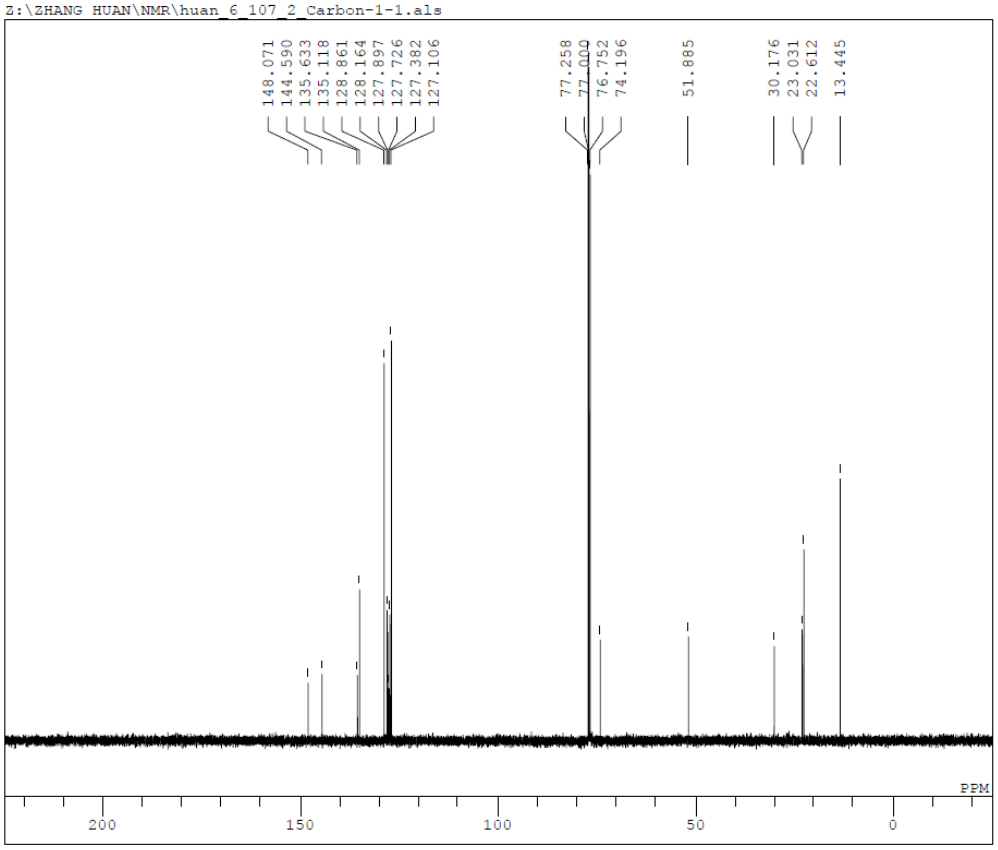
21

Z:\ZHANG HUAN\NMR\huan_6_107_2_Proton-1-1.als

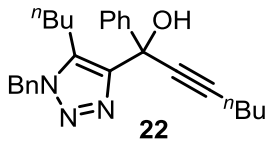



```
DFILE   huan_6_107_2_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-06-12 22:01:51
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             30
```

Z:\ZHANG HUAN\NMR\huan_6_107_2_Carbon-1-1.als

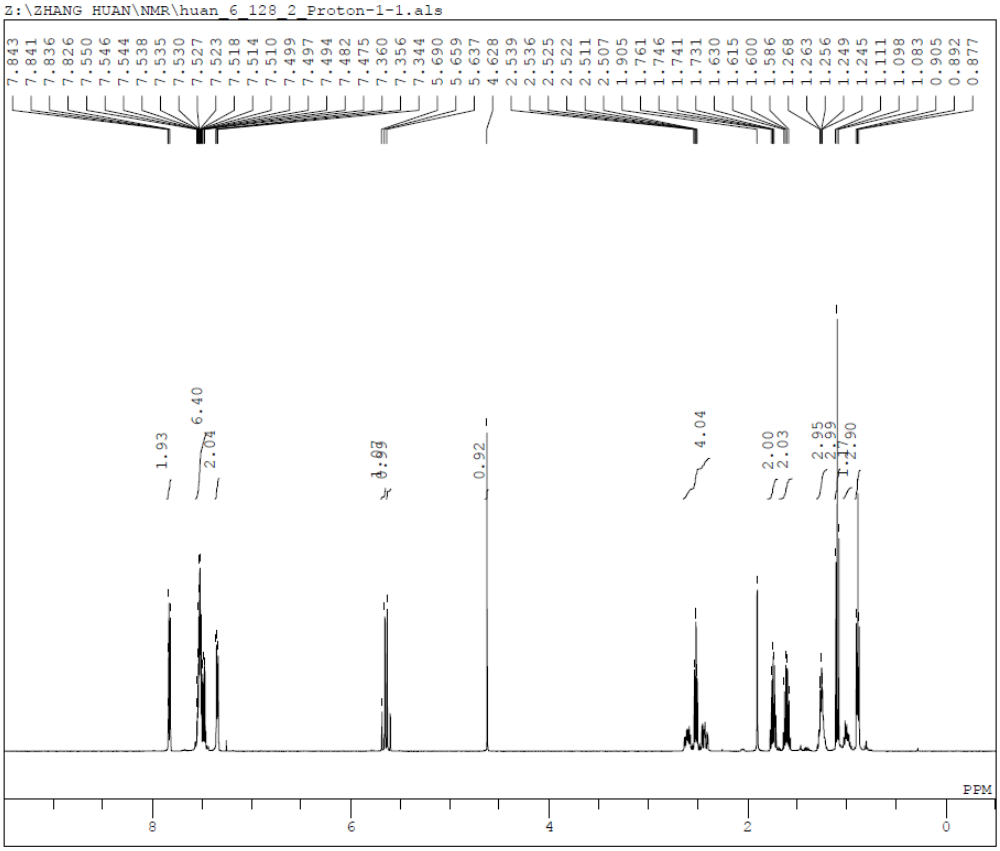



```
DFILE   huan_6_107_2_Carbon-1-1.als
COMNT   single pulse decoupled gated NO
DATIM   2013-06-12 22:03:22
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.54 Hz
SCANS            362
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.8 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              0.12 Hz
RGAIN             58
```



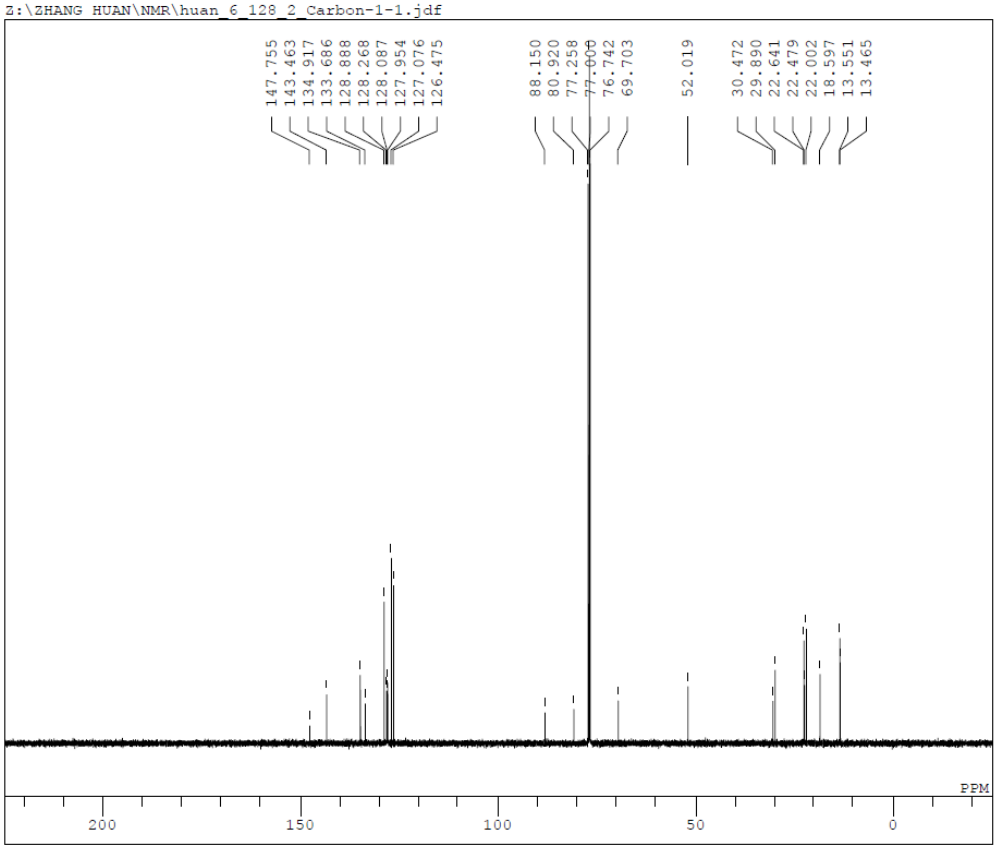
22

Z:\ZHANG HUAN\NMR\huan_6_128_2_Proton-1-1.als

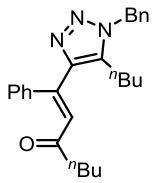



```
DFILE   huan_6_128_2_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-06-27 16:41:12
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.3 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            34
```

Z:\ZHANG HUAN\NMR\huan_6_128_2_Carbon-1-1.jdf

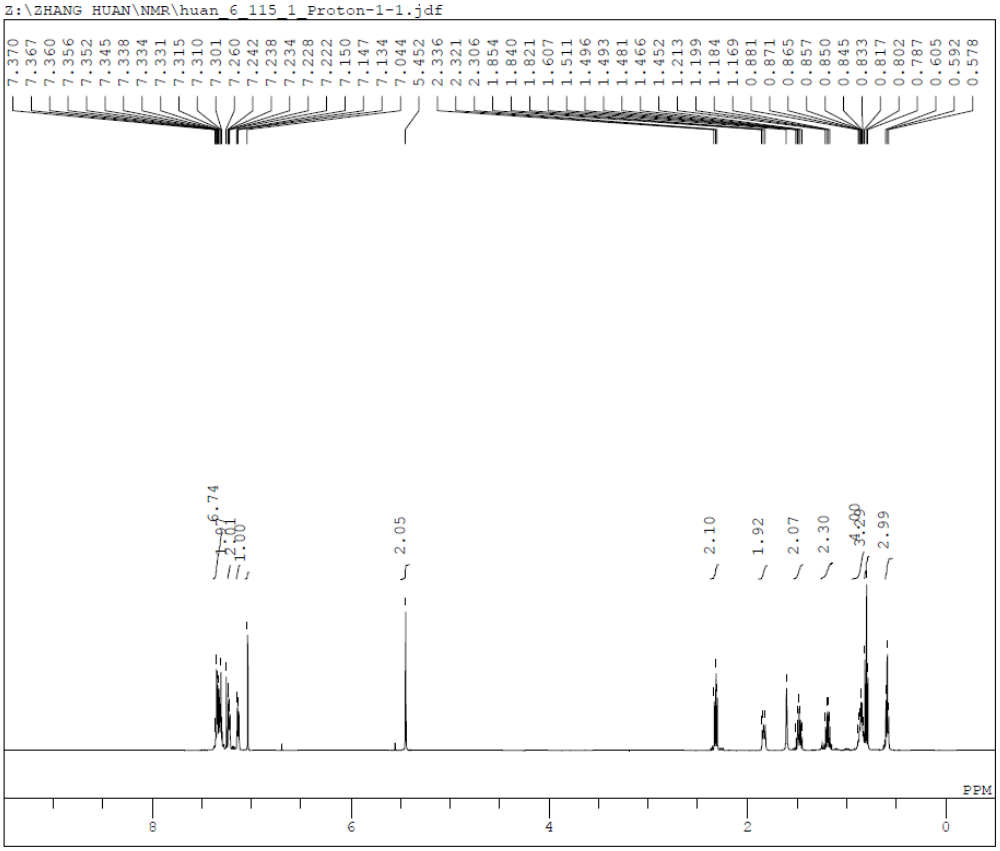



```
DFILE   huan_6_128_2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-27 16:42:42
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            897
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            58
```



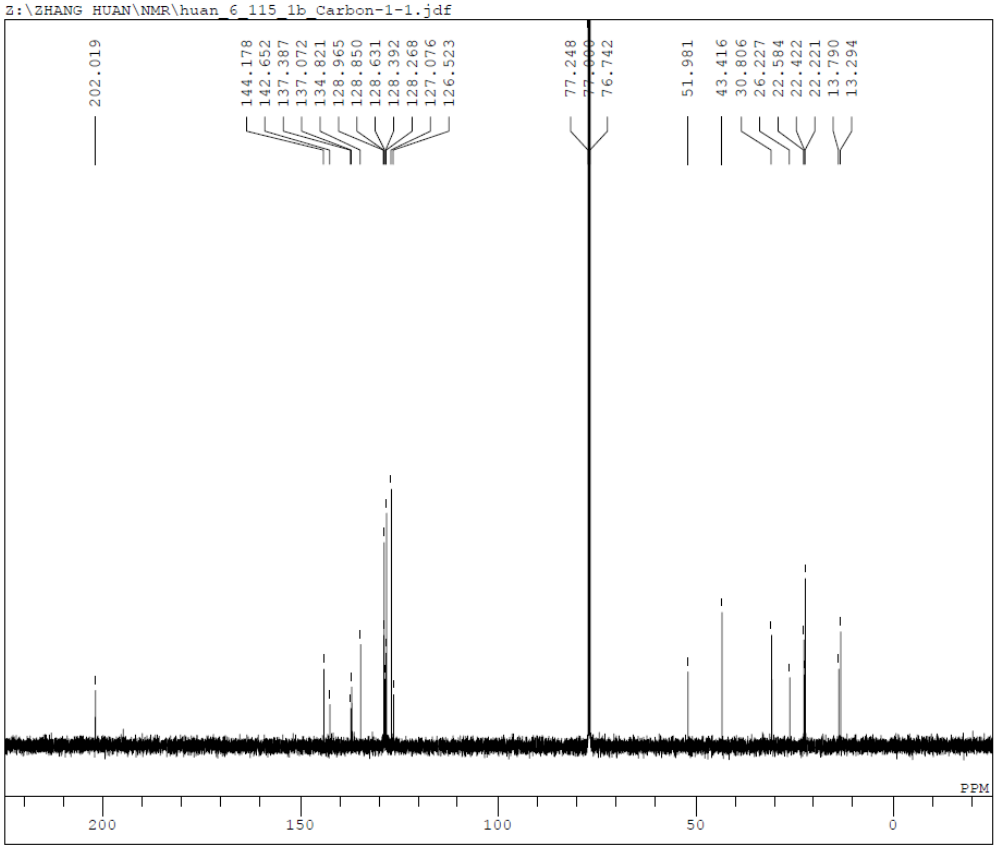
22'

Z:\ZHANG HUAN\NMR\huan_6_115_1_Proton-1-1.jdf

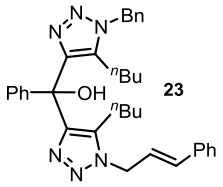



```
DFILE   huan_6_115_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-06-19 21:13:29
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             42
```

Z:\ZHANG HUAN\NMR\huan_6_115_1b_Carbon-1-1.jdf

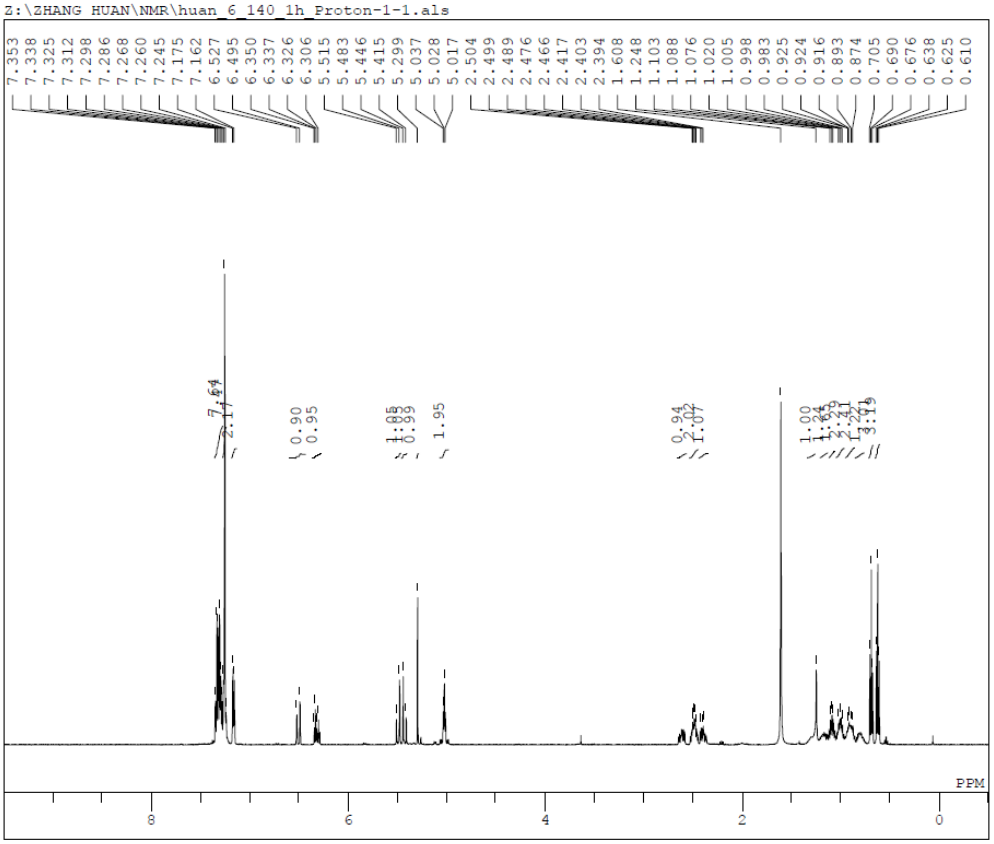



```
DFILE   huan_6_115_1b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-06-21 13:54:03
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           2029
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           18.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             56
```



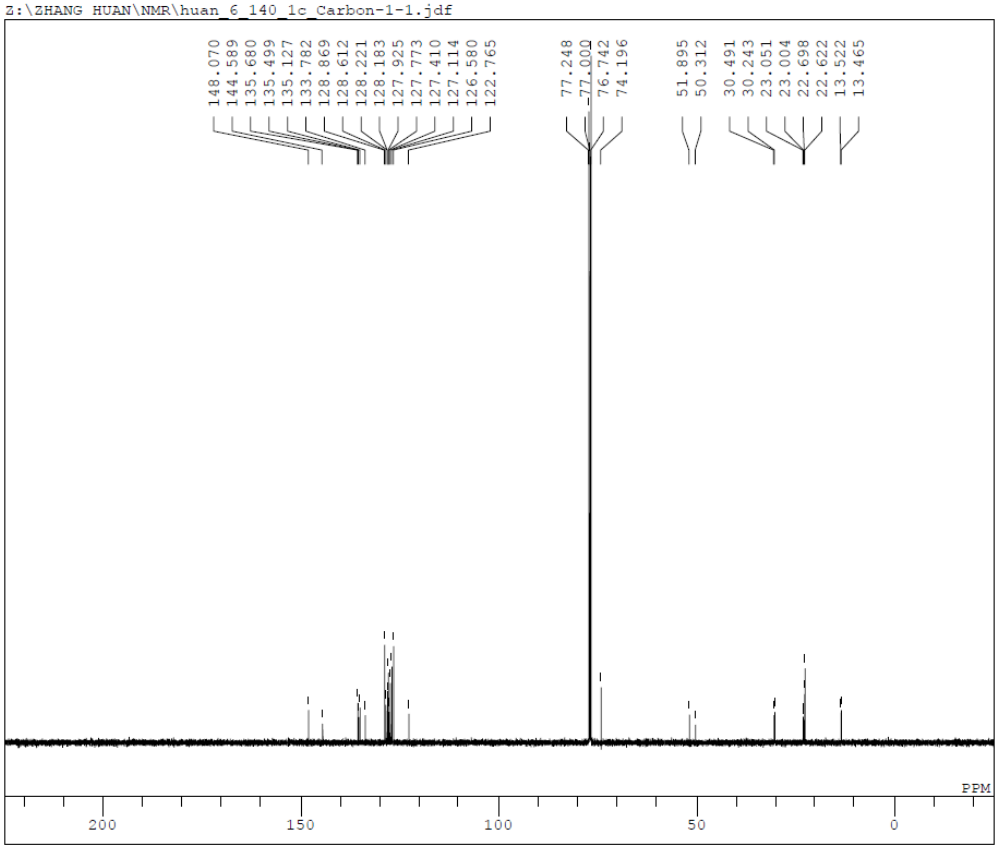
23

Z:\ZHANG HUAN\NMR\huan_6_140_1h_Proton-1-1.als

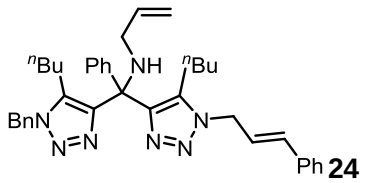



```
DFILE   huan_6_140_1h_Proton-1-1.als
COMNT   single_pulse
DATIM   2013-07-16 09:48:33
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS             8
ACQTM          1.7459 sec
PD             5.0000 sec
PW1              6.22 usec
IRNUC   1H
CTEMP           18.9 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             44
```

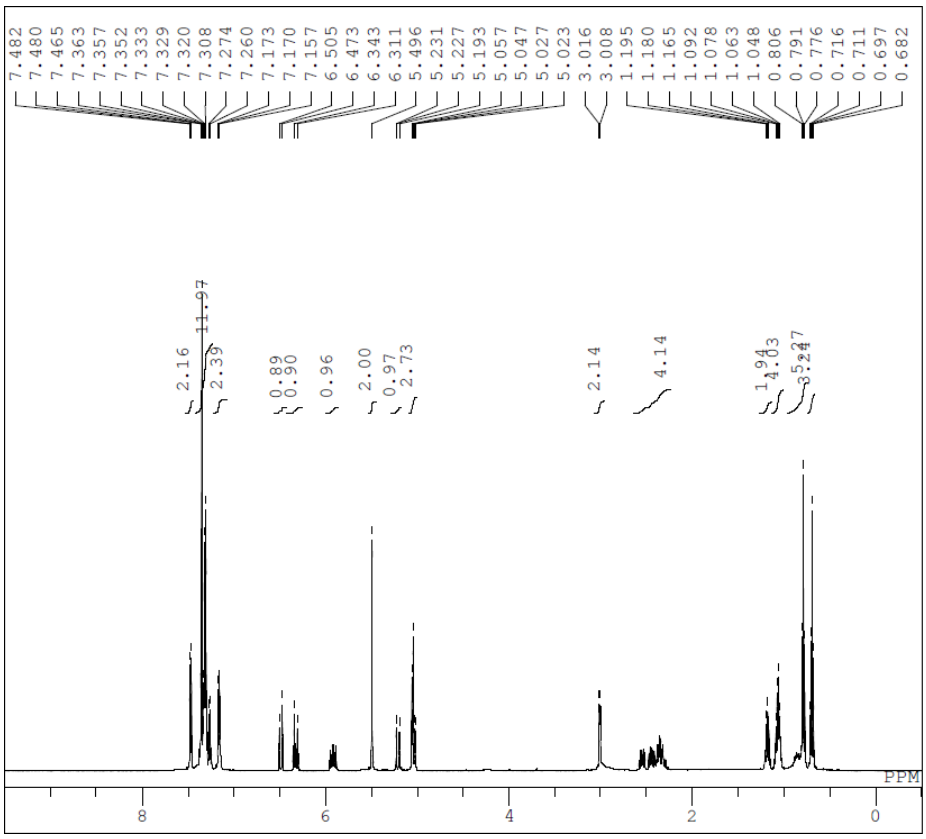
Z:\ZHANG HUAN\NMR\huan_6_140_1c_Carbon-1-1.jdf




```
DFILE   huan_6_140_1c_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-07-13 14:28:25
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1024
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              3.12 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```

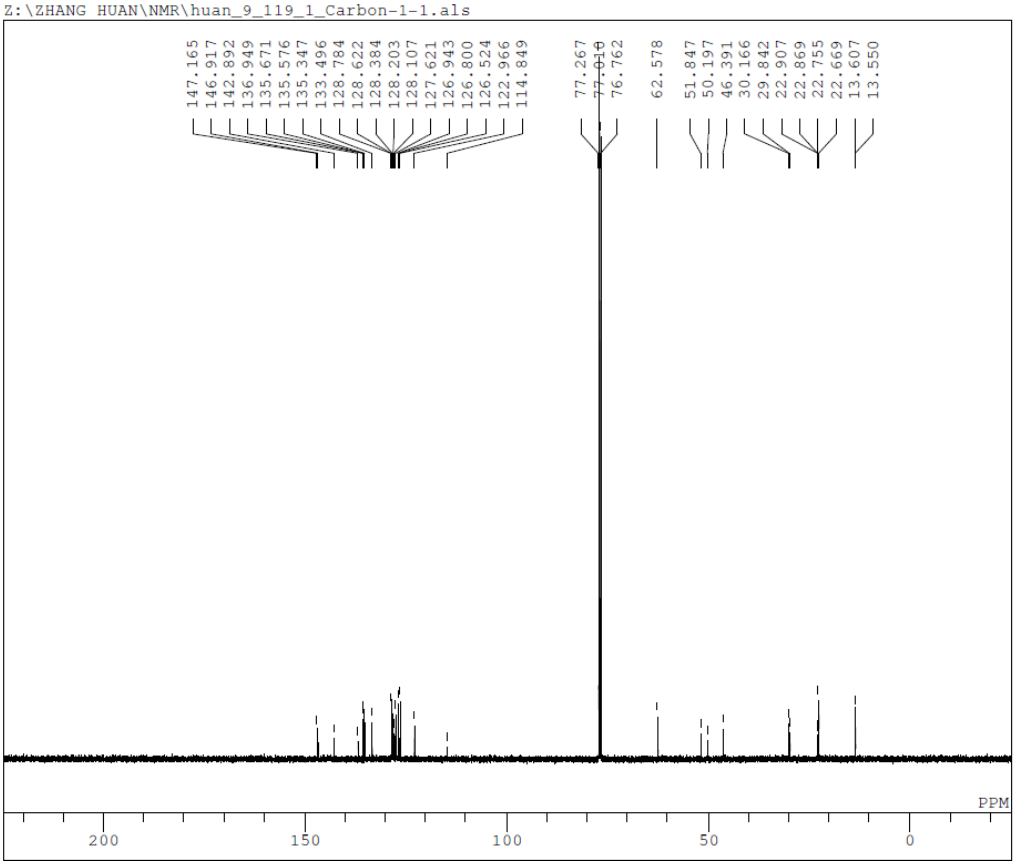


24

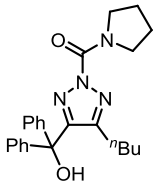



```
DFILE  huan_7_119_1_Proton-1-1.a
COMNT  single_pulse
DATIM  2013-11-25 21:23:04
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC  1H
CTEMP          16.1 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            34
```

Z:\ZHANG HUAN\NMR\huan_9_119_1_Carbon-1-1.als

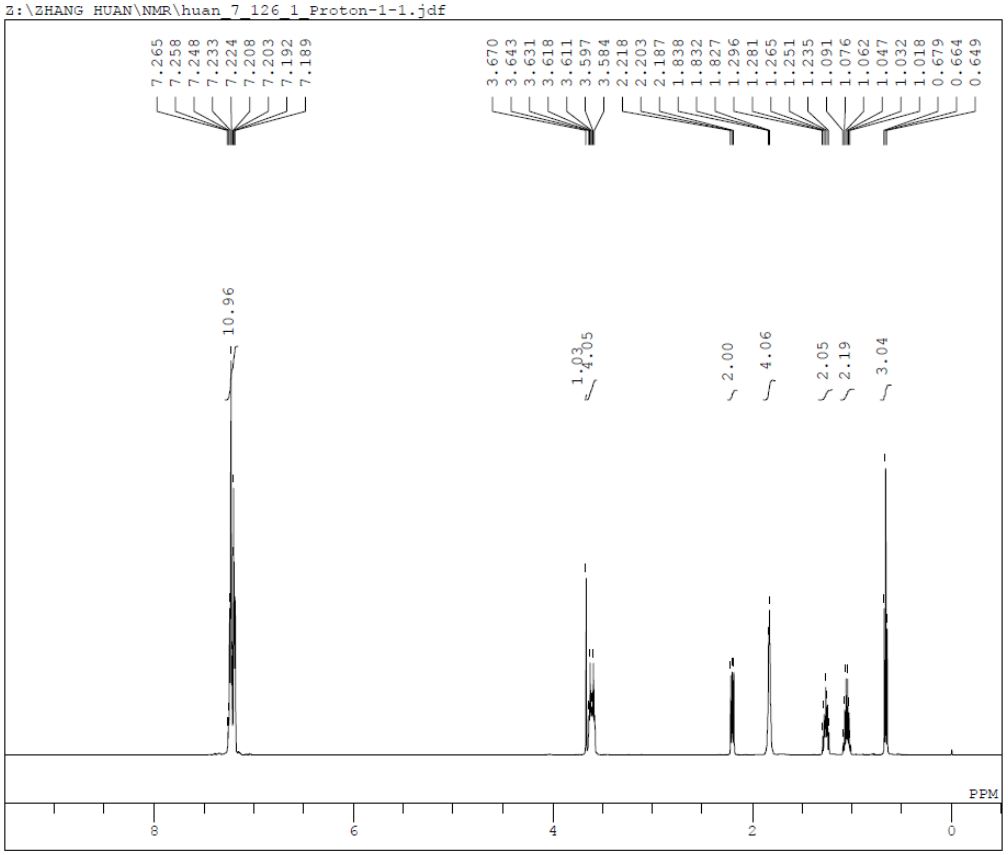



```
DFILE  huan_9_119_1_Carbon-1-1.als
COMNT  single pulse decoupled gated N
DATIM  2013-11-25 21:24:35
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.54 Hz
SCANS          1024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1             3.12 usec
IRNUC  1H
CTEMP          15.9 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



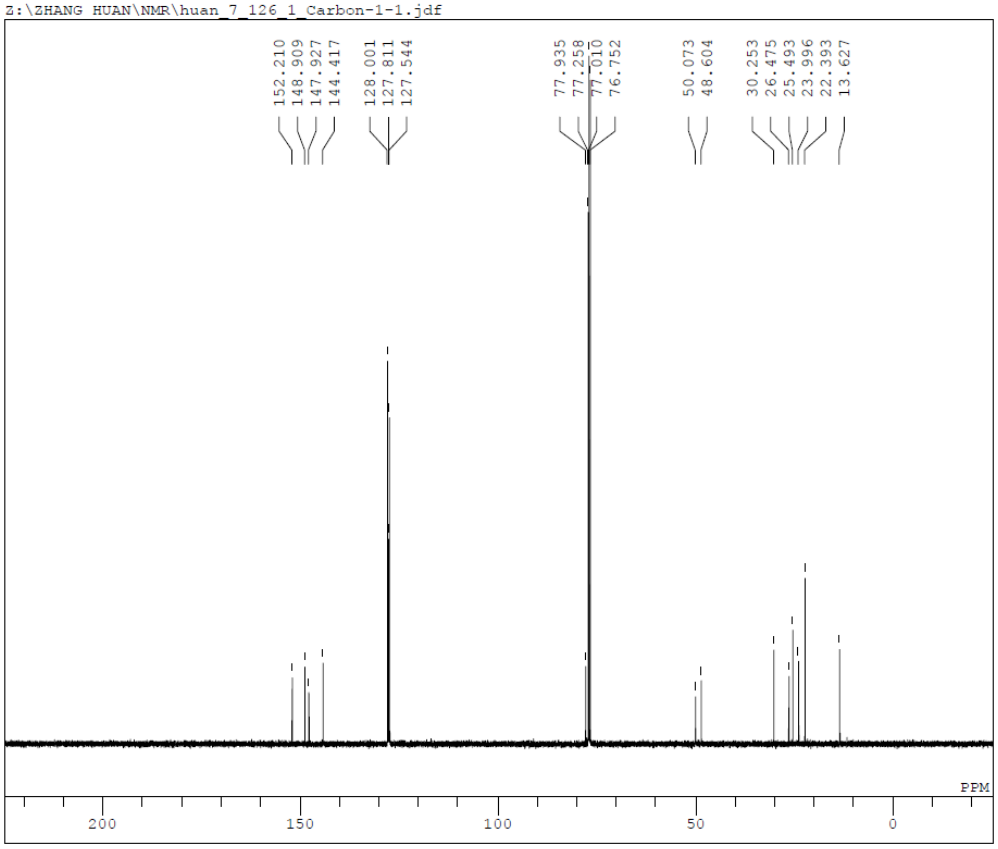
26b

Z:\ZHANG HUAN\NMR\huan_7_126_1_Proton-1-1.jdf

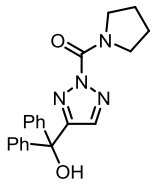



```
DFILE   huan_7_126_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-12-16 12:13:42
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             30
```

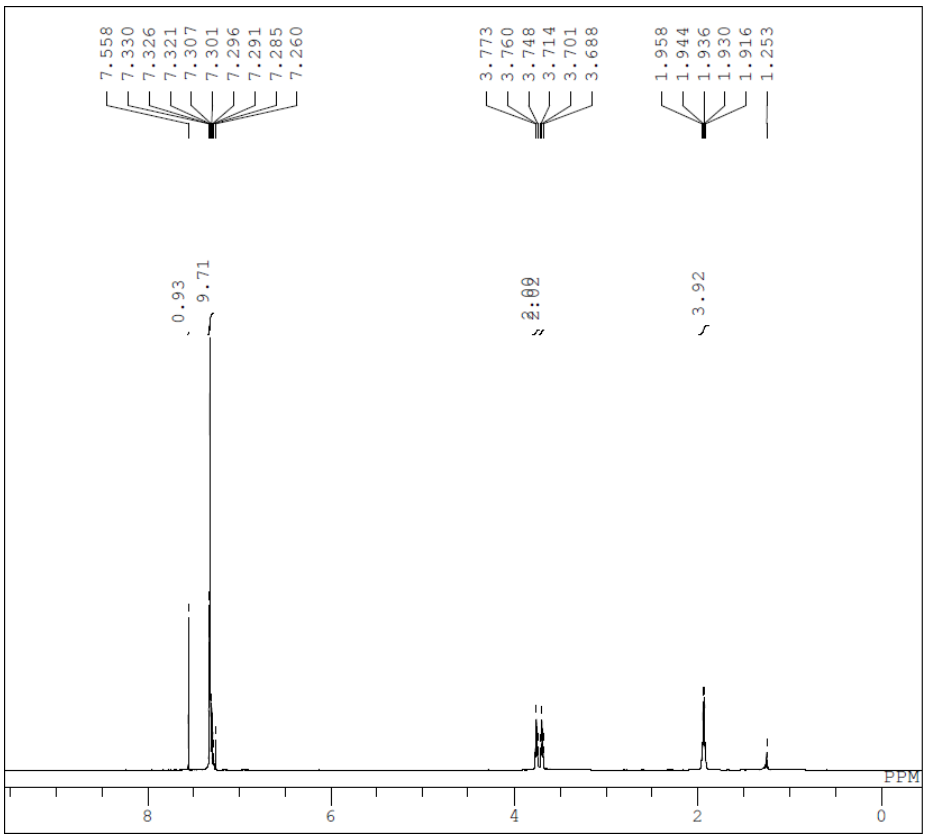
Z:\ZHANG HUAN\NMR\huan_7_126_1_Carbon-1-1.jdf




```
DFILE   huan_7_126_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-12-16 12:15:13
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             56
```

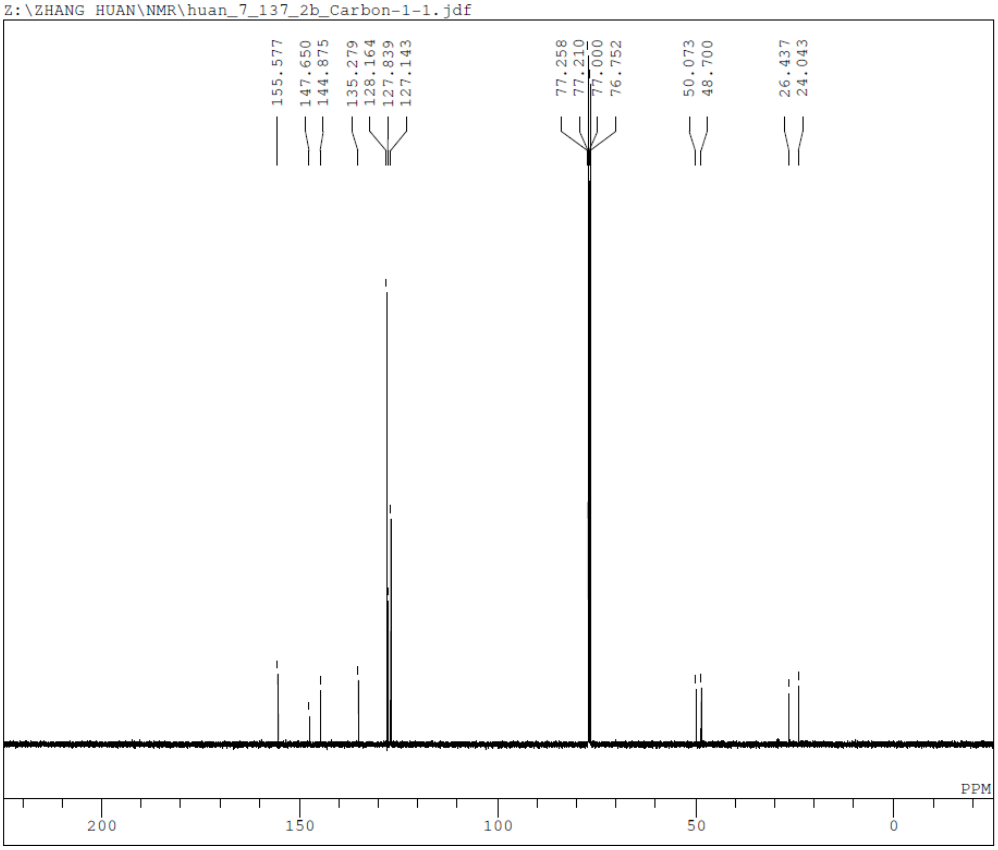


26a in $CDCl_3$

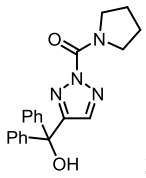



```
DFILE  huan_7_137_2_Proton-1-1.a
COMNT  single_pulse
DATIM  2014-01-16 10:36:57
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          19.4 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            38
```

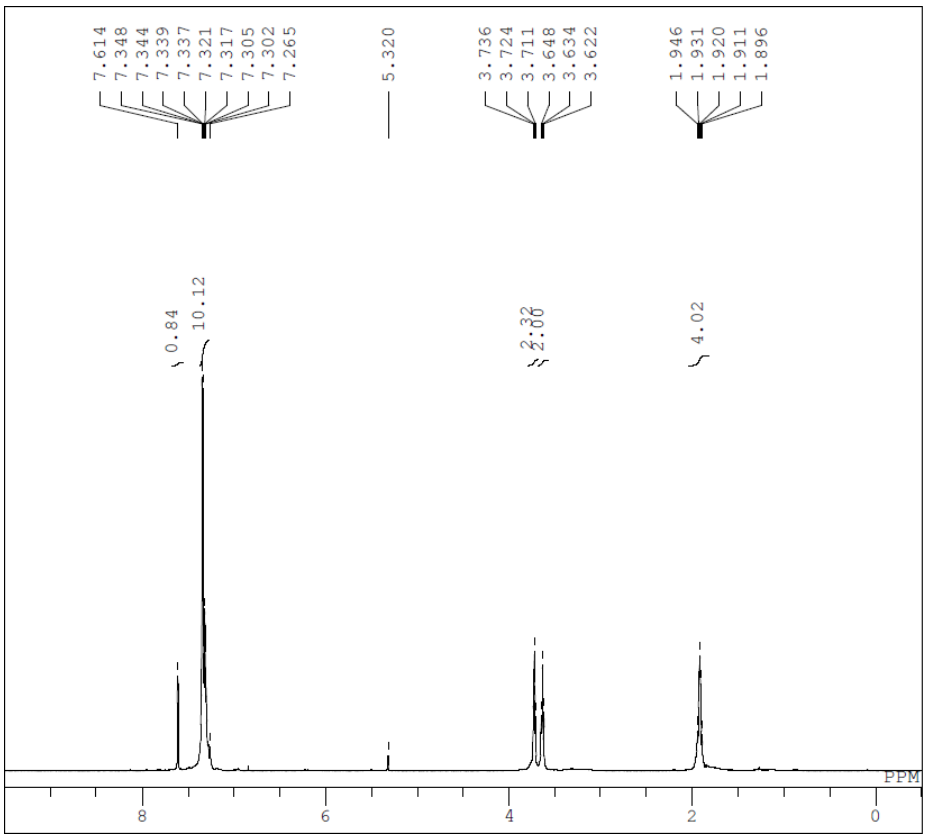
Z:\ZHANG HUAN\NMR\huan_7_137_2b_Carbon-1-1.jdf




```
DFILE  huan_7_137_2b_Carbon-1-1.jdf
COMNT  single pulse decoupled gated N
DATIM  2014-01-17 12:12:58
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS          1024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          19.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```

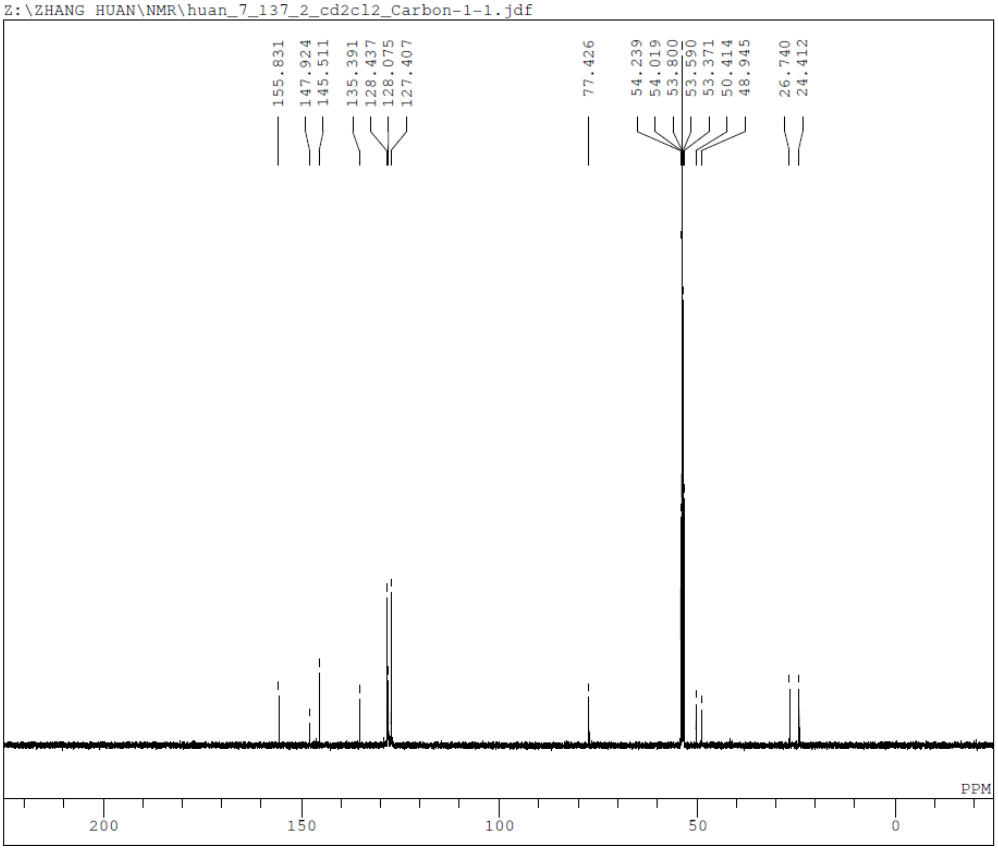


26a in CD_2Cl_2

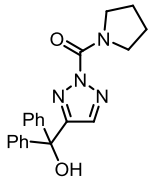



```
DFILE  huan_7_137_2_cd2cl2_Protc
COMNT  single_pulse
DATIM  2014-06-09 12:10:49
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          18.6 c
SLVNT  CD2CL2
EXREF          5.32 ppm
BF             0.12 Hz
RGAIN            34
```

Z:\ZHANG HUAN\NMR\huan_7_137_2_cd2cl2_Carbon-1-1.jdf

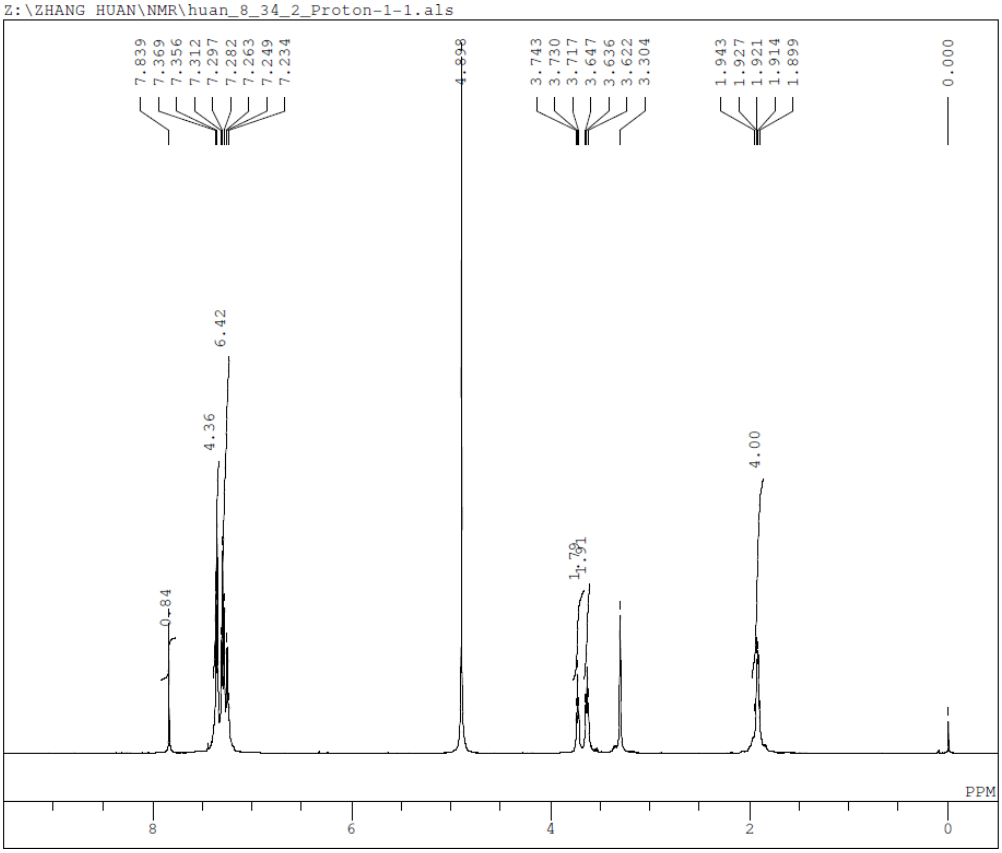



```
DFILE  huan_7_137_2_cd2cl2_Carbon-1-1
COMNT  single pulse decoupled gated N
DATIM  2014-06-09 12:12:19
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS          2024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          19.4 c
SLVNT  CD2CL2
EXREF         53.80 ppm
BF             0.12 Hz
RGAIN            58
```



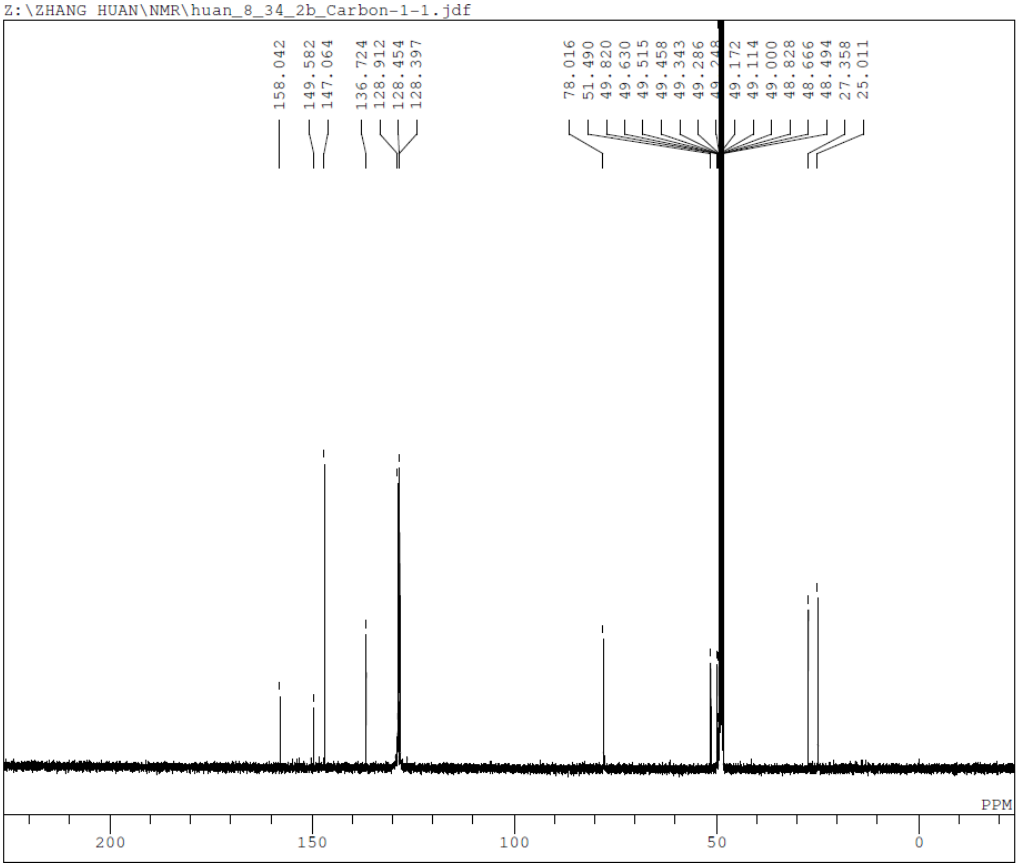
26a in CD_3OD

Z:\ZHANG HUAN\NMR\huan_8_34_2_Proton-1-1.als

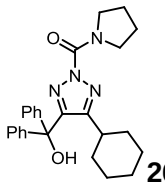



```
DFILE   huan_8_34_2_Proton-1-1.als
COMNT   single_pulse
DATIM   2014-06-20 19:59:49
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          13107
FREQU        7507.51 Hz
SCANS              8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          18.4 c
SLVNT   CD3OD
EXREF          0.00 ppm
BF             0.10 Hz
RGAIN            36
```

Z:\ZHANG HUAN\NMR\huan_8_34_2b_Carbon-1-1.jdf

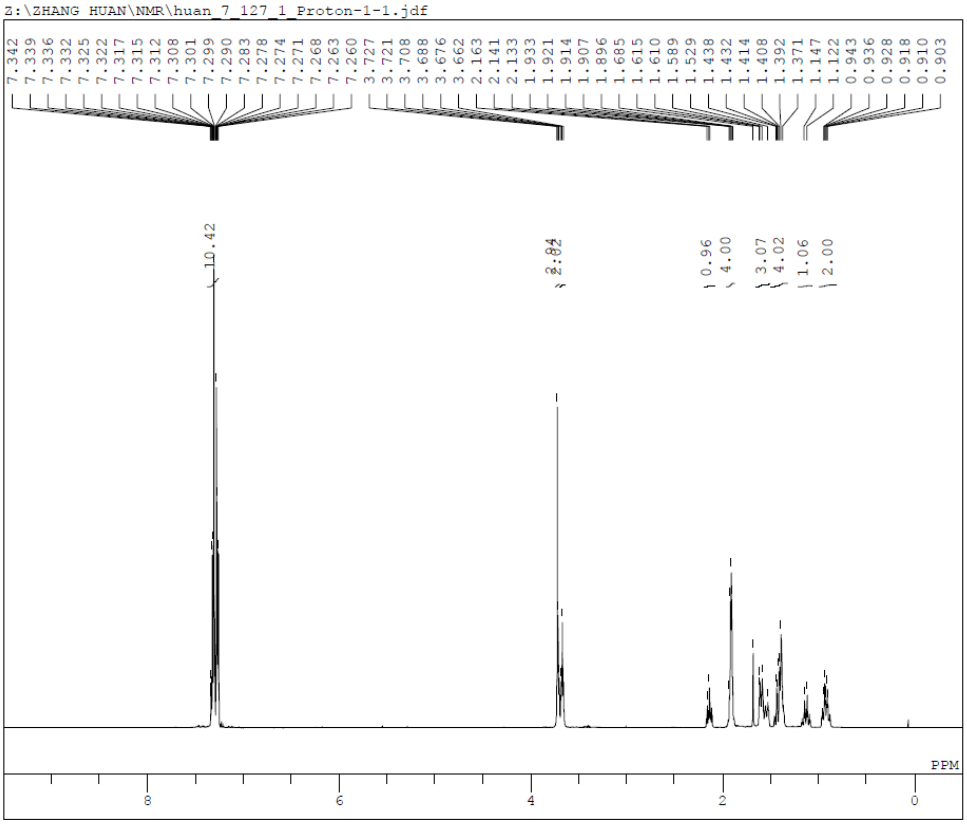



```
DFILE   huan_8_34_2b_Carbon-1-1.jdf
COMNT   single pulse decoupled gated N
DATIM   2014-06-21 17:42:10
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU        39308.18 Hz
SCANS            50529
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          18.8 c
SLVNT   CD3OD
EXREF          49.00 ppm
BF              0.12 Hz
RGAIN             58
```



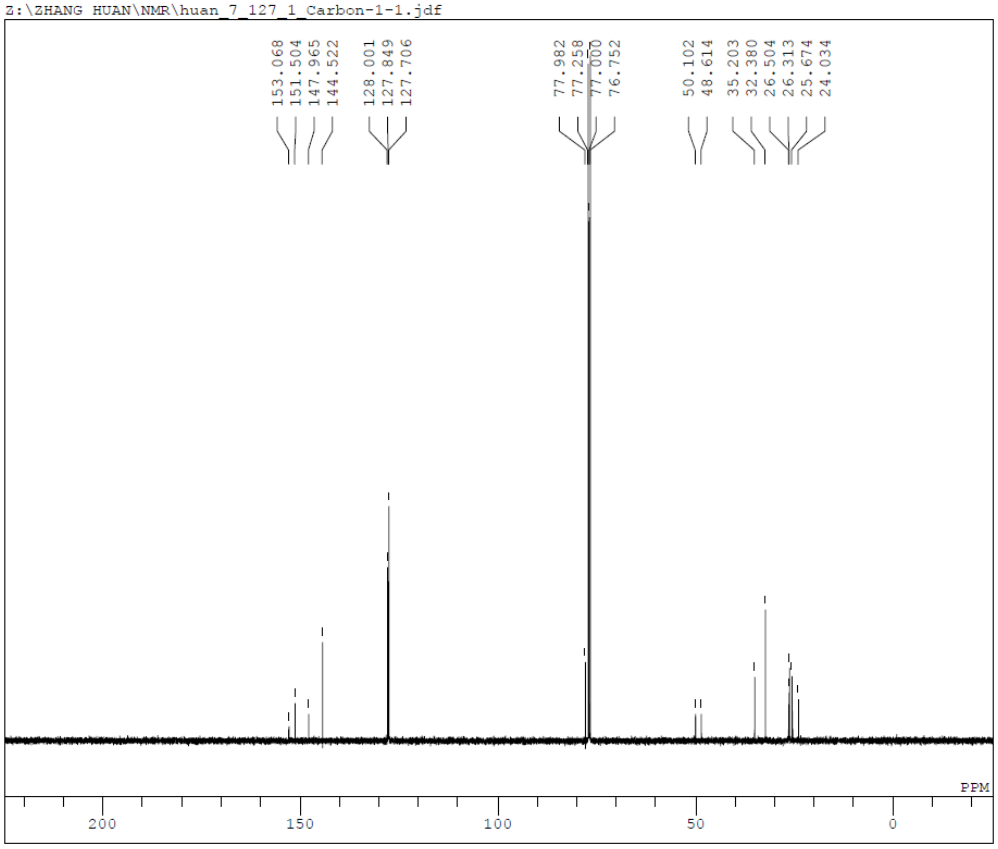
26c

Z:\ZHANG HUAN\NMR\huan_7_127_1_Proton-1-1.jdf

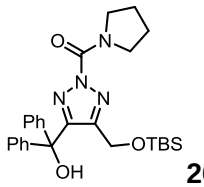



```
DFILE   huan_7_127_1_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-12-16 19:40:51
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP          19.3 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            36
```

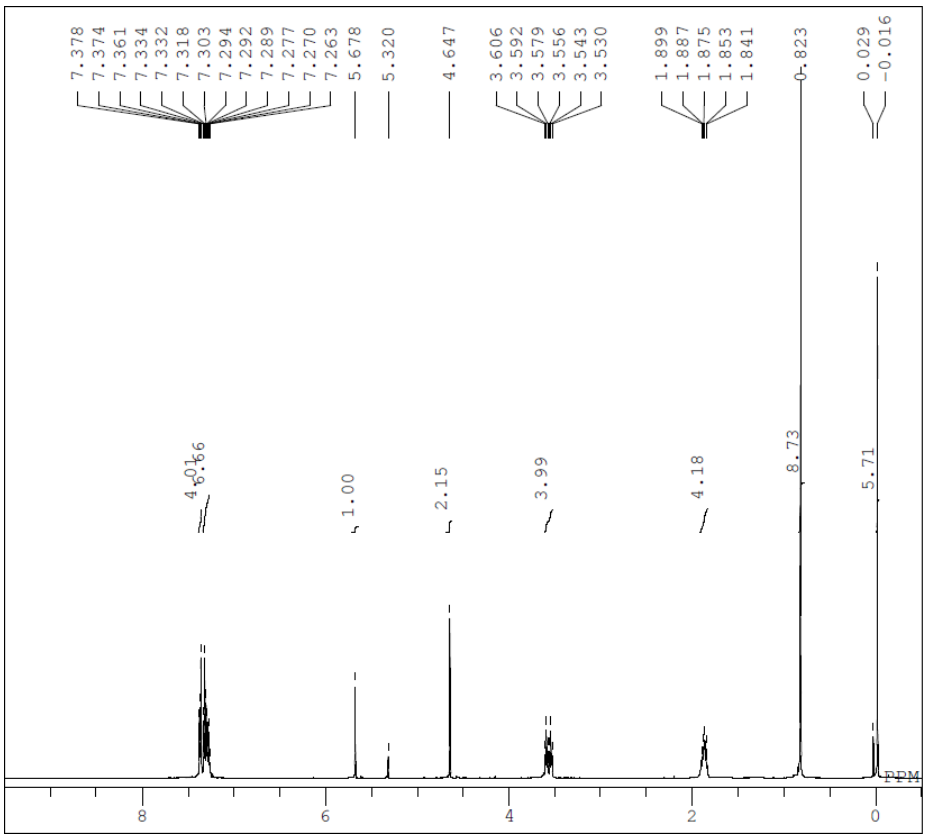
Z:\ZHANG HUAN\NMR\huan_7_127_1_Carbon-1-1.jdf




```
DFILE   huan_7_127_1_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NO
DATIM   2013-12-16 19:42:22
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS            789
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP          19.7 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            56
```

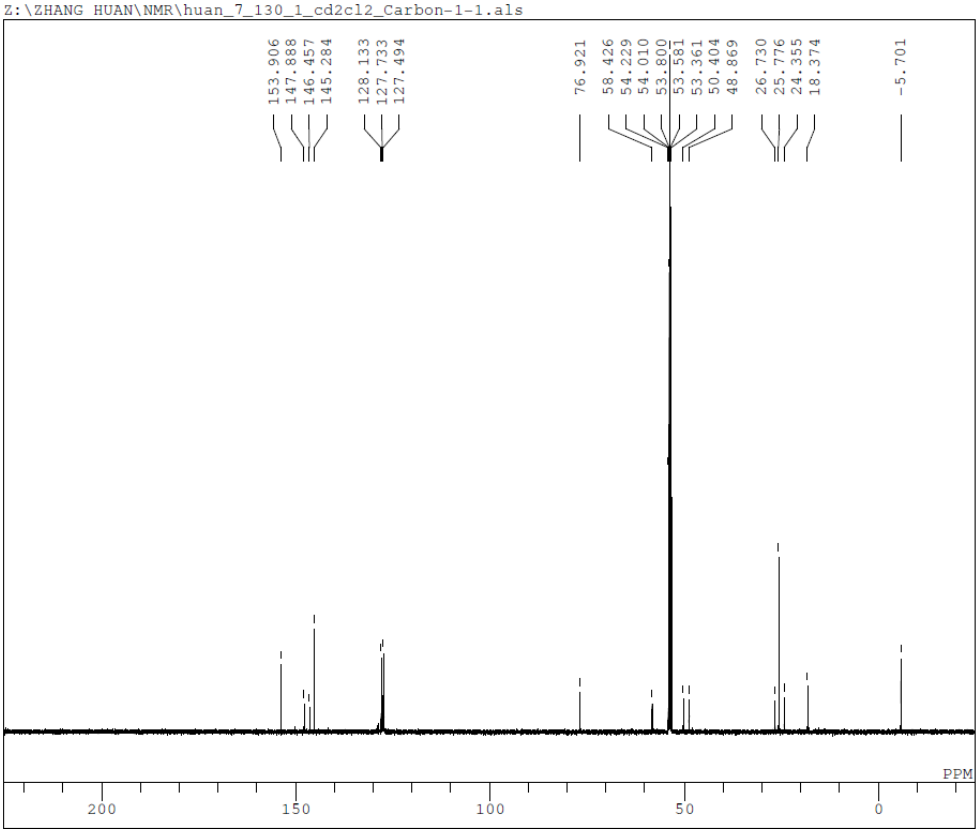


26d

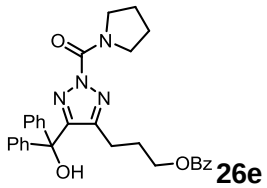



```
DFILE  huan_7_130_1_cd2cl2_Protc
COMNT  single_pulse
DATIM  2014-06-09 18:19:41
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          18.2 c
SLVNT  CD2CL2
EXREF          5.32 ppm
BF             0.10 Hz
RGAIN            30
```

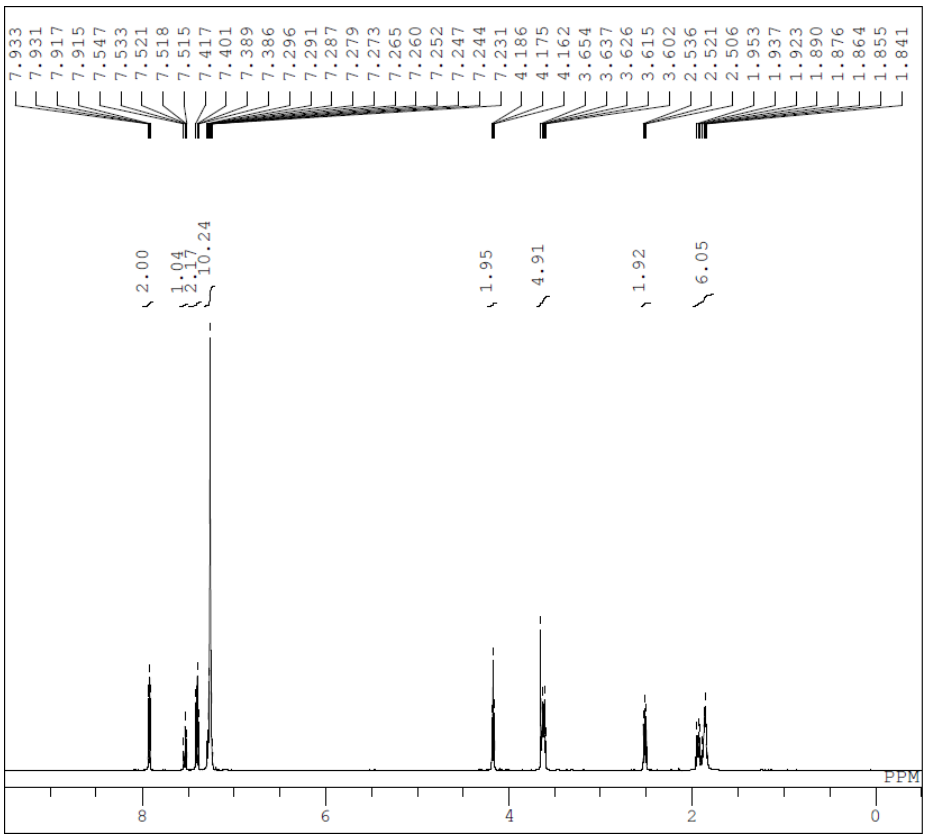
Z:\ZHANG HUAN\NMR\huan_7_130_1_cd2cl2_Carbon-1-1.als




```
DFILE  huan_7_130_1_cd2cl2_Carbon-1-1
COMNT  single pulse decoupled gated N
DATIM  2014-06-09 18:21:11
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.54 Hz
SCANS          2024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          18.8 c
SLVNT  CD2CL2
EXREF         53.80 ppm
BF             0.12 Hz
RGAIN            58
```

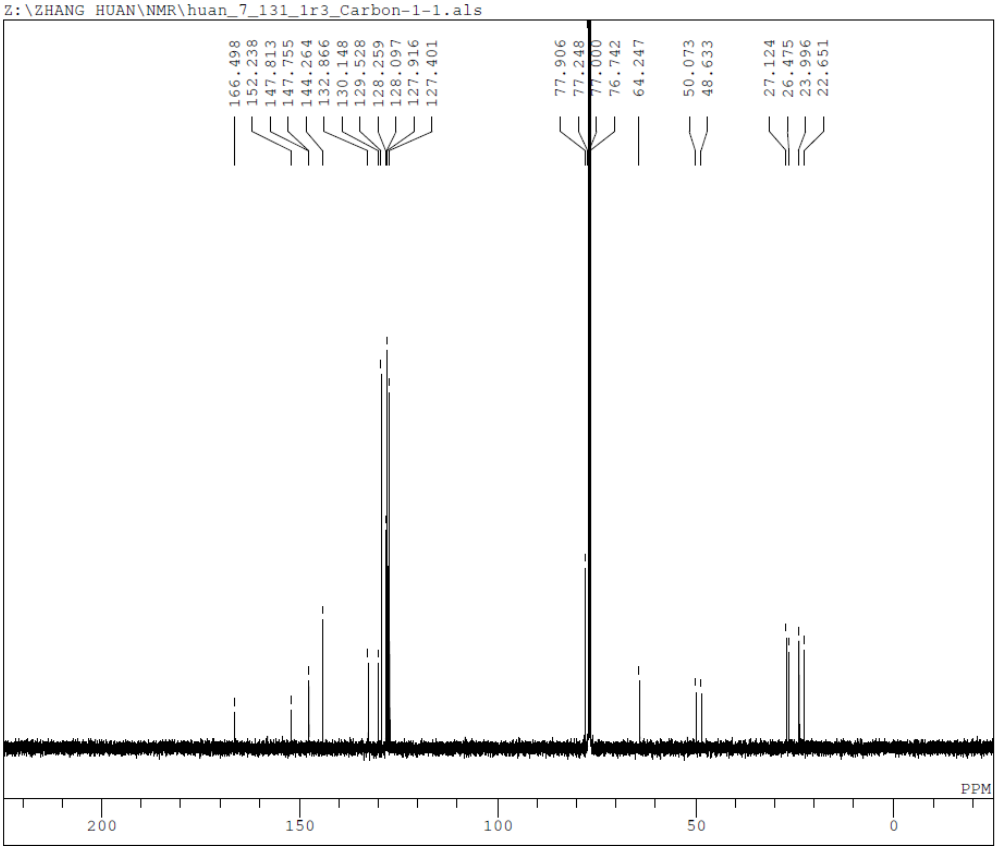


26e

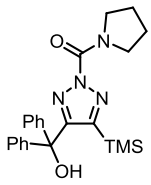



```
DFILE  huan_7_131_1_Proton-1-1.a
COMNT  single_pulse
DATIM  2013-12-20 17:35:48
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.51 Hz
SCANS             8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.22 usec
IRNUC  1H
CTEMP          18.9 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            30
```

Z:\ZHANG HUAN\NMR\huan_7_131_1r3_Carbon-1-1.als

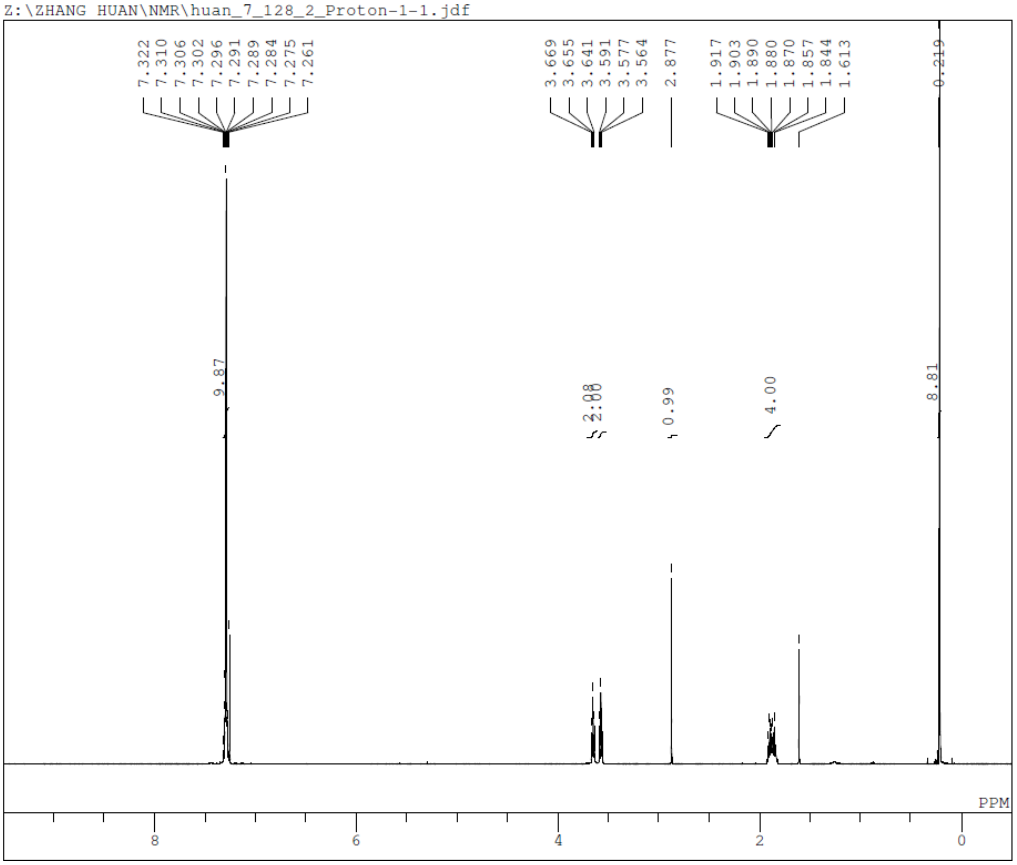



```
DFILE  huan_7_131_1r3_Carbon-1-1.als
COMNT  single pulse decoupled gated N
DATIM  2014-05-09 11:50:28
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         32767
FREQU      39308.18 Hz
SCANS          2906
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.12 usec
IRNUC  1H
CTEMP          17.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            58
```



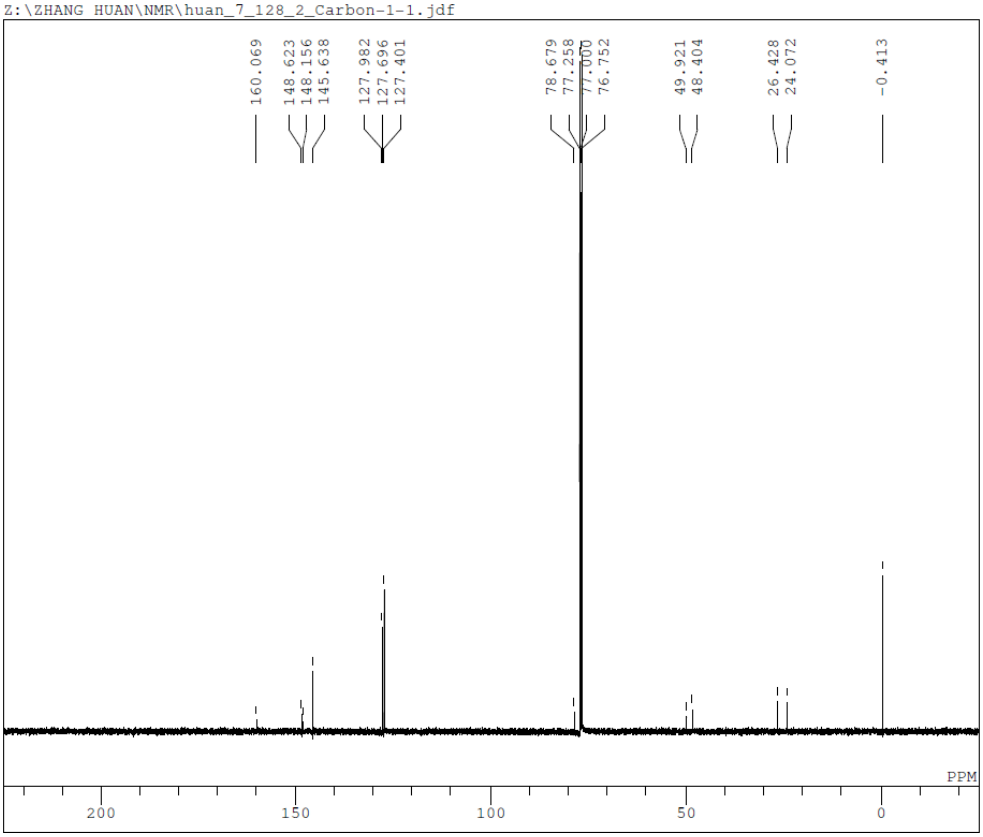
26f

Z:\ZHANG HUAN\NMR\huan_7_128_2_Proton-1-1.jdf



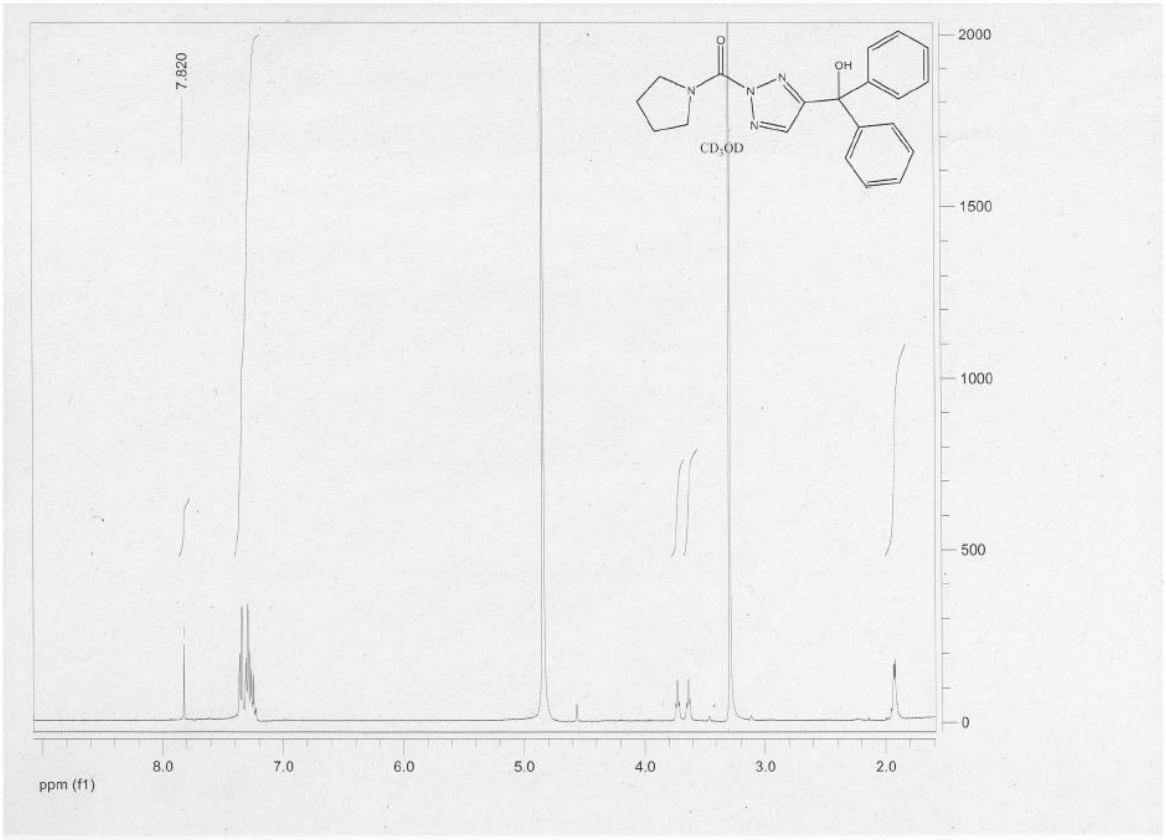

```
DFILE   huan_7_128_2_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2013-12-20 12:16:27
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.22 usec
IRNUC   1H
CTEMP           18.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             40
```

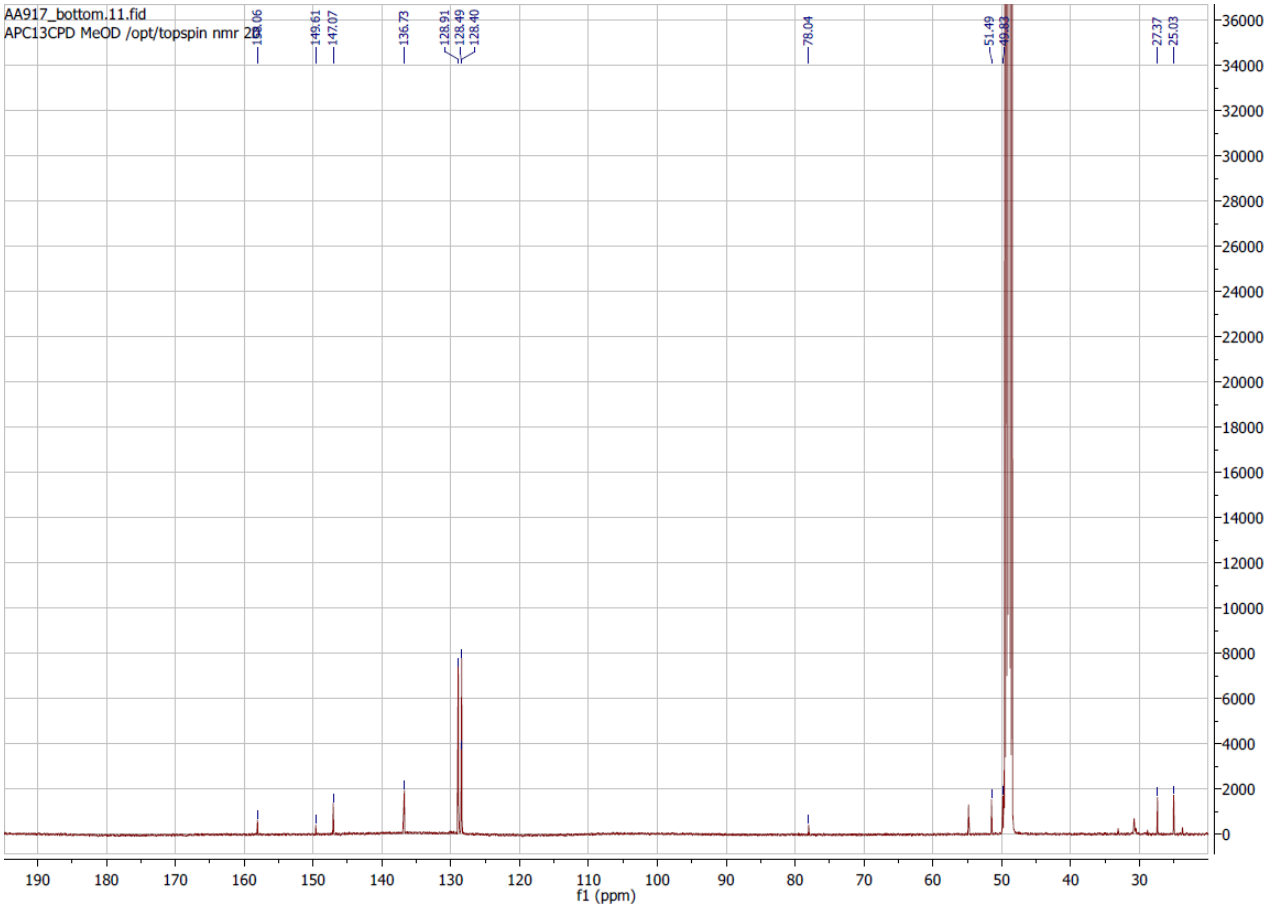
Z:\ZHANG HUAN\NMR\huan_7_128_2_Carbon-1-1.jdf




```
DFILE   huan_7_128_2_Carbon-1-1.jdf
COMNT   single pulse decoupled gated N
DATIM   2013-12-20 12:17:58
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32767
FREQU       39308.18 Hz
SCANS           1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.12 usec
IRNUC   1H
CTEMP           19.0 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             58
```

Provided ^{1}H and ^{13}C NMR Spectra of **26b** recorded in CD_3OD.



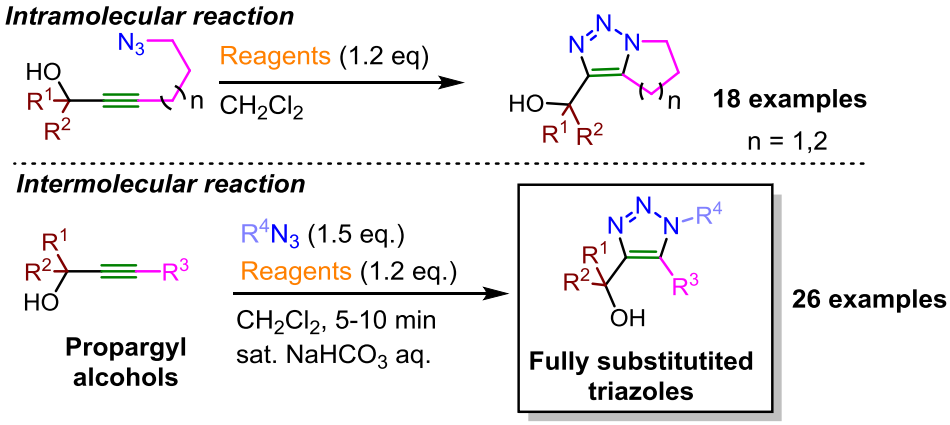


Chapter 6 Conclusion

The applications of triazoles produced azide-alkyne cycloadditions range from drug discovery, chemical biology, materials science, development of sensors, polymer chemistry, to other molecular science. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) to produce these functional cores is the most famous method, which is arguably the most widely utilized in "click chemistry". Because of its various efficiencies in research area, many groups have recently reported the rapid, mild, and Cu-free triazolations, such as using strained alkyne and substituent activation. However, CuAAC is limited to mostly terminal alkynes and the toxicity of copper salts limits the utility for *in vivo* applications. In addition, most of the reported methods including classic Huisgen reactions require room or high temperature with a long reaction time. With three zwiterionic nitrogens, organic azides not only can be used as 1,3-dipolars for cycloadditions but also electrophiles and nucleophiles.

In chapter 2, based on the previous results for synthesis of cylclic unsaturated imines with allyl cations and organic azides, I investigated the intramolecular [3+2] cycloaddition of benzyl propargyl alcohols with azide under acid conditions to afford triazoles. According to these successful results, intermolecular triazole formations were examined. Through optimization, the internal reactions were also demonstrated with

organic azide in the present of TMSOTf, and the desired transformation was preceded in good to excellent yield even at -90 °C. With optimized condition, various fully substituted functional triazoles were successfully produced within 10 min (Scheme 52). The reaction results indicate that: 1) for R^1 and R^2 group, electron deficient aryl was found to be effective as diphenyl group; 2) both terminal and internal alkyne can afford the desired triazole product; 3) strong nucleophilic azides were favorite to this transformation; 4) this cyclization reaction proceed regioselectively to produce triazoles was generated as single isomer; 5) the transformation can be carried out not only at ambient but also low temperature, even at -90 °C; 6) the presence of methylenetriazolium was indicated.



Scheme 52. *Intra- and inter- molecular azide-alkyne cycloaddition reactions.*

In chapter 3, to develop the efficiency of this carbocation-mediated azide-alkyne cycloaddition reaction, I conducted various types of multicomponent coupling reactions in one-pot. According to the proposed mechanism, not only a hydroxyl group, but also other functional groups could be introduced by changing quenching methods. Investigation of the origin of the hydroxyl group to make sure the hydroxyl groups source indicated that $BF_3 \cdot OEt_2$ is a suitable acid for the substitution of triazolium intermediates with additional nucleophiles, such as alcohols, amines, thiol, carbon nucleophiles and so on. Moreover, controlling of the amount of the reagents and the reactivity of substrates, four-component coupling reaction was achieved by double [3+2] reaction followed by substitution with nucleophile with dialkyne substrates (Figure 6).

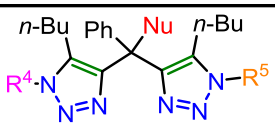


Figure 6. Four-component coupling triazole

In chapter 4, to further demonstrate the efficiency of the method toward bioactive molecule synthesis, I carried out the synthesis of triazole urea reported as a serine hydrolase inhibitor along with its 5-substituted derivatives (Figure 7). Serine hydrolases have been used as the targets of clinical drugs to treat

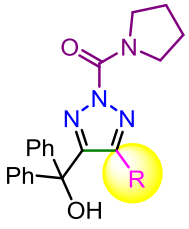


Figure 7. Cravatt's serine hydrolase inhibitor (R = H) and its derivatives

various diseases such as diabetes and Alzheimer's disease.The 1,4-disustituted and 1,4,5 trisubstituted *N*-benzyltriazoles prepared by the developed method were deprotected followed by carbamoylation to afford serine hydrolase inhibitor triazole urea and its 5-substituted derivatives, which were difficult to prepared by traditional methods. Moreover, I also suggested the errata and incorrect assignment of analycal data of the reported inhibitor compound.

I successfully developed the rapid regioselective synthesis of fully substituted 1,2,3-triazoles mediated by propargyl cations formed from propargyl alcohols, accepting both terminal and internal alkynes at low and ambient temperature in good yields. Various types of one-pot multicomponent coupling reactions, including double triazolations and functionalizations of triazoles with additional nucleophiles, were demonstrated. The synthesized triazoles were successfully converted to serine hydrolase inhibitor triazole urea and its derivatives. Our method can provide new preparation method of highly substituted triazoles and exploration of their uses in synthetic organic chemistry and pharmaceutical research.

Reference

1. Michael, A. *J. Prakt. Chem.* **1893**, *48*, 94.
2. Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 210-216.
3. Rostovtsev, V. V.; Green, L. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596-2599.
4. Tornoe, C. W.; Christensen, C,; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057-3064.
5. Rodionov, V. O. Presolski, V. I.; Diaz, D. D.; Fokin, V. V.; Finn, M. G. *J. Am. Chem. Soc.* **2007**, *129*, 12705.
6. Hein, J. E.; Fokin, V. V. *Chem. Soc. Rev.* **2010**, *39*, 1302.
7. Ahlquist, M.; Fokin, V. V. *Organometallics* **2007**, *26*, 4389.
8. Worrell, B. T.; Malik, J. A.; Fokin, V. V. *Science* **2013**, *340*, 457-460.
9. 1) Hein, J. E.; Tripp, J. C.; Krasnova, L. B.; Sharpless, K. B. Fokin. V. V. *Angew. Chem., Int. Ed.* **2009**, *48*, 8018-8021. 2) Zhou. Y.; Lecourt, T.; Micouin, L. *Angew. Chem., Int. Ed.* **2010**, *42*, 2607-2610.
10. Zhang, L.; Chen, X. G.; Xue, P.; Sun, H. H. Y.; Williams, I. D.; Sharpless, K. B.; Fokin, V. V. and Jia, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 15998-15999.
11. Jin, T.; Kamijo, S.; Yamamoto, Y. *Eur. J. Org. Chem.* **2004**, 3789.
12. Lu, L.-H.; Wu, J.-H.; Yang, C.-H. *J. Chin. Chem. Soc. (Taipei, Taiwan)* **2008**, *55*, 414.
13. Jiang, Y.; Kuang, C.; Yang, Q. *Synthesis* **2010**, 4256.
14. Helms, B.; Mynar, J. L.; Hawker, C. J. and Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020-15021.
15. Brik, A,; Muldoon, J.; Lin, Y. C.; Elder, J. H.; Goodsell, D. S.; Olson, A. J.; Fokin, V. V.; Sharpless, K. B.;.Wong, C. H. *ChemBioChem* **2003**, *4*, 1246.
16. Brik, A,; Muldoon, J.; Lin, Y. C.; Elder, J. H.; Olson, A. J.; Goodsell, D. S.;.Wong, C. H. *ChemBioChem* **2005**, *6*, 1167.
17. Suarez, P. L.; Gándara, Z.; Gómez, G.; Fall, Y. *Tetrahedron Lett.* **2004**, *45*, 4619.
18. Suh, B. C.; Jeon, H.; Poser, G. H.; Silverman, S. M. *Tetrahedron Lett.* **2004**, *45*, 4623.
19. Prescher, J. A.; Bertozzi, C. R. *Nat. Chem. Biol.* **2005**, *1*, 13-21.
20. Codelli, J. A.; Baskin, J. M.; Agard, N. J.; and Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 11486-11493.
21. 1) Zhang, F. Z.; and Moses, J. E. *Org. Lett.* **2009**, *11*, 1587-1590. 2) Shi, F.; Waldo, J. P.; Chen, Y. and Larock, R. C. *Org. Lett.* **2008**, *10*, 2409-2412. 3) Chandrasekhar, S.;

Seenaiah, M.; Rao, C. L.; Reddy, C. R. *Tetrahedron*, **2008**, *64*, 11325-11327.
22. Medina, J. M. McMahon, T. C.; Jiménez-Osés, G.; Houk, K. N.; Garg. N. K. *J. Am. Chem. Soc*. **2014**, *136*, 14706-14709.
23. 1) Merling, E.; Lamm, V.; Geib, S. J.; Lacôote, E.; Curran, D. P. *Org. Lett.* **2012**, *14*, 2690–2693. 2) Weingäartner, W.; Maas, G. *Eur. J. Org. Chem.* **2012**, 6372–6382. 3) Yanai, H.; Taguchi, T. *Tetrahedron Lett.* **2005**, *46*, 8639–8643. 4) Journet, M.; Cai, D.; Kowal, J. J.; Larsen, R. D. *Tetrahedron Lett.* **2001**, *42*, 9117–9118. 5) Sawoo, S.; Dutta, P.; Charkraborty, A.; Mukhopadhyay, R.; Bouloussa, O.; Sarkar, A. *Chem. Commun*. **2008**, 5957-5959.
24. Gold, B.; Shevchenko, N. E.; Bonus, N.; Budley, G. B. Alabugin, I. V. *J. Org. Chem.* **2012**, *77*, 75-89.
25. 1)Griess, P. *Proc. R. Soc. London* **1864**, *13*, 375. 2)Bräse, S.; Banert, K. Organic Azides, Syntheses and Applications; John Wiley & Sons, Ltd.: Chichester, U.K., 2010.
26. Bräse, S.; Gil C.; Knepper K.; Zimmermann V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188-5240.
27. Tanimoto, H.; Kakiuchi, K. *Nat. Prod. Commun.* **2013**, *8*, 1021-1034.
28. Cultius, T. *Berichte der deutschen chemischen Gesellschaft*. **1890**, *23*, 3023-3033.
29. Staudinger, H.; Meyer, J. *Helv. Chim. Acta*. **1919**, *2*, 635-646.
30. Schmidt, K. F. Z. *Angew. Chem.* **1923**, *36*, 511.
31. Pearson, W. H.; Fang, W.-K. *J. Org. Chem.* **1995**, *60*, 4960-4961.
32. Huisgen, R.; Szeimies, G.; Mobius, L. *Chem. Ber.* **1967**, *100*, 2494-2507.
33. Huisgen, R. *Angew. Chem., Int. Ed.* **1963**, *2*, 565-632.
34. Gololobov, G. V.; Kasukhin, L. F., *Tetrahedron*, **1992**, *48*, 1353-1381.
35. Kurosawa, W.; Kan, T.; Fukuyama, T. *J. Am. Chem. Soc*. **2003**, *125*, 8112-8113.
36. Molina, P.; Vilaplana, M. J. *Synthesis* **1994**, 1197-1218.
37. Wamhoff, H.; Richardt, G.; Stolben, S. *Adv. Heterocycl. Chem.* **1995**, *33*, 159-249.
38. Fresneda, P. M.; Molina, P. *Synlett* **2004**, 1-17.
39. Luheshi, A.-B. N.; Salem, S. M.; Smalley, R. K.; Kennewell, P. D.; Westwood, R. *Tetrahedron Lett.* **1990**, *31*, 6561-6564.
40. Takeuchi, H.; Matsushita, Y.; Eguchi, S. *Tetrahedron* **1991**, *47*, 1535-1537.
41. Takeuchi, H.; Hagiwara, S.; Eguchi, S. *Tetrahedron* **1989**, *45*, 6375-6386.
42. Alajarín, M.; Molina, P.; Vidal, A.; Tovar, F. *Synlett* **1998**, 1288-1290.
43. Cledera, P.; Avendaño, C.; Menédez, J. C. *Tetrahedron* **1998**, *54*, 12349-12360.
44. White, J. D.; Cammack, J. H.; Sakuma, J. H. *J. Am. Chem. Soc*. **1989**, *111*, 8970-8972.

45. Sugimori, T.; Okawa, T.; Eguchi, S.; Yashima, E.; Okamoto, Y. *Chem. Lett.* **1997**, 869-870.
46. Sugimori, T.; Okawa, T.; Eguchi, S.; Kakehi, A.; Yashima, E.; Okamoto, Y. *Tetrahedron* **1998**, *54*, 7997-8008
47. Schuster, M. S.; Platz, M. S. *Adv. Photochem*. **1992**, *18*, 69-143.
48. Gritsan, N. P.; Pritchina, E. A. *Russ. Chem. Rev.* **1992**, *61*, 500-516.
49. Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487-492.
50. Yamada, K.; Mogi, Y.; Mhomed, M. A.; Takasu, K.; Tomioka, K. *Org. Lett.* **2012**, *14*, 5868-5871.
51. Schmidt, K. F. *Angew. Chem.* **1923**, *35*, 511.
52. Pearson, W. H. *J. Heterocycl. Chem.* **1996**, *33*, 1489-1496.
53. Lang, S.; Kennedy, A. R.; Murphy, J. A.; Payne, A. H. *Org. Lett.* **2003**, *5*, 3655-3658.
54. 1) Aubé, J.; Milligan, G. L. *J. Am. Chem. Soc.* **1991**, *113*, 8965-8966. 2) Aubé, J.; Milligan, G. L.; Mossman, C. J. *J. Org. Chem.* **1992**, *57*, 1635–1637. 3) Milligan, G. L. Mossman, C. J.; Aubé, J. *J. Am. Chem. Soc*. **1995**, *117*, 10449-10459. 4) Wrobleski, A.; Aubé, J. *J. Org. Chem.* **2001**, *66*, 886-889.
55. Fresneda, PM.; Molina, P.; Delgado, S. *Tetrahedron Letters*, **1999**, *40*, 7275.
56. 1) Pearson, W. H.; Schkeryantz, J. M.; *Tetrahedron Lett.* **1992**, *33*, 5291-5294. 2) Pearson, W. H.; Fang, W.-K. *J. Org. Chem.* **2000**, *65*, 7158-7174.
57. Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc*. **1955**, *77*, 951-954.
58. Lang, S.; Kennedy, A. R.; Murphy, J. A.; Payne, A. H. *Org. Lett.* **2003**, *5*, 3655-3658.
59. Hayashi, K.; Tanimoto, H.; Zhang, H.; Morimoto, T.; Nishiyama, Y.; Kakiuchi, K. *Org. Lett.* **2012**, *14*, 5728-5731.
60. Zhang, H.; Tanimoto, H.; Morimoto, T.; Nishiyama, Y.; Kakiuchi, K. *Tetrahedron*, **2014**, *70*, 9828-9835.
61. 1) Fotsing, J. R.; Banert, K. *Eur. J. Org. Chem.* **2005**, 3704–3714. 2) Banert, K. *Liebigs Ann./Recueil* **1997**, 2005–2018. 3) Banert, K. *Chem. Ber*. **1989**, *122*, 911–918. 4) Banert, K.; Hagedorn, M. *Angew. Chem., Int. Ed. Engl*. **1989**, *25*, 1675–1676.
62. 1) Yan, W.; Ye, X.; Weise, K.; Petersen, J.; Shi, X. *Chem. Commun.* **2012**, *48*, 3521–3523. 2) Yin, G.; Zhu, Y.; Zhang, L.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 940–943. 3) Ishikawa, T.; Okano, M.; Aikawa, T.; Saito, S. *J. Org. Chem*. **2001**, *66*, 4635–4642. 4) Grecian, S.; Desai, P.; Mossman, C.; Poutsma, J. L.; Aubé, J. *J. Org. Chem.* **2007**, *72*, 9439–9447.

63. 1) Selander, N.; Worrell, B. T.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2012**, *51*, 13054–13057. 2) Miura, T.; Funakoshi, Y.; Morimoto, M.; Biyajima, T.; Murakami, M. *J. Am. Chem. Soc.* **2012**, *134*, 17440–17443.
64. Yoshida, S.; Shiraishi, A.; Kanno, K.; Matsushita, T.; Johmoto, K.; Uekusa, H.; Hosoya, T. *Sci. Rep*. **2011**, *1*, 82.
65. Zhan, Z.; Cai, X.; Wang, S.; Yu, J.; Liu, H.; Cui, Y. *J. Org. Chem.* **2007**, *72*, 9838-9841.
66. Simon, G. M. and Cravatt, B. F. *J. Biol. Chem*. **2010**, *285*, 11051-11055.
67. a) Henness, S. and Perry, C. M. *Drugs* **2006**, *66*, 1625-1656. b) Thornberry, N. A. and Weber, A. E. *Curr. Top. Med. Chem.* **2007**, *7*, 557-568. c) Kluge, A. F. and Petter, R. C. **2010**, *14*, 421-427. d) Racchi, M.; Mazzucchelli, M.; Porrello, E.; Lanni, C.; Govoni, S. *Pharmacol. Res.* **2004**, *50*, 441.
68. Adibekian, A.; Martin, B. R.; Wang, C.; Hsu, K.-L.; Bachovchin, D. A.; Niessen, S.; Hoover, H.; Cravatt, B. F. *Nat. Chem. Biol.* **2011**, *7*, 469-478

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LIST OF PUBLICATIONS

学位論文の主たる部分を公表した論文

(1) Huan Zhang, Hiroki Tanimoto, Tsumoru Morimoto, Yasuhiro Nishiyama, Kiyomi Kakiuchi, "Regioselective Rapid Synthesis of Fully-substituted 1,2,3-Triazoles Mediated by Propargyl Cations", *Org. Lett.* **2013**, *15*, 5222–5225.

(2) Huan Zhang, Hiroki Tanimoto, Tsumoru Morimoto, Yasuhiro Nishiyama, Kiyomi Kakiuchi, "Acid-mediated Synthesis of Fully Substituted 1,2,3-Triazoles: Multicomponent Coupling Reactions, Mechanistic Study, Synthesis of Serine Hydrolase Inhibitor and Its Derivatives", *Tetrahedron* **2014**, *70*, 9828–9835.

参考論文

(1) Kyohei Hayashi, Hiroki Tanimoto, Huan Zhang, Tsumoru Morimoto, Yasuhiro Nishiyama, Kiyomi Kakiuchi, "Efficient Synthesis of α,β-Unsaturated Alkylimines Performed with Allyl Cations and Azides: Application to the Synthesis of an Ant Venom Alkaloid", *Org. Lett.* **2012**, *14*, 5728–5731.

(2) Huan Zhang, Kyohei Hayashi, Hiroki Tanimoto, Tsumoru Morimoto, Yasuhiro Nishiyama, Kiyomi Kakiuchi, "Total synthesis of unsaturated imine venom alkaloids of Costa Rican ant by way of Schmidt reaction via allyl/pentadienyl cations", *Tetrahedron* **2014**, *70*, 8600–8605.

(3) Qijian Ni, Huan Zhang, André Grossmann, Charles C. J. Loh, Carina Merkens, Dieter Enders, "Asymmetric Synthesis of Pyrroloindolones by N-Heterocyclic Carbene Catalyzed [2+3] Annulation of α-Chloroaldehydes with Nitrovinylindoles", *Angew. Chem., Int. Ed.* **2014**, *52*, 13562–13566.

学会発表

国際会議発表

(1) Huan Zhang, Hiroki Tanimoto, Yasuhiro Nishiyama, Tsumoru Morimoto,Kiyomi kakiuchi, “Synthesis of α-substituted α,β-unsaturated imine from propargyl alcohol and azide”,19th International Conference on Organic Synthesis in conjunction with The 24th Royal Australian Chemical Institute Organic Conference (ICOS-19), ポスター番号: 243 (Melbourne Convention Centre), Melbourne, Australia, Jul/1‐6/2012 (Presentation on Jul/3‐4).

(2) Huan Zhang, Hiroki Tanimoto, Tsumoru Morimoto, Yasuhiro Nishiyama, Kiyomi Kakiuchi, “Development of Carbocation Mediated Azide-Alkyne Cyclization Reactions”, International Symposium on Catalysis and Fine Chemicals 2013 (C&FC 2013), OPP-10 (Renmin University), Beijing, China, Dec 1-5, 2013, 118 (Short Talk and Poster Presentation OPP-10, Presentation on Dec/3).

国内会議発表

(1) 張歓, 谷本裕樹, 垣内喜代三, 「プロパルギルカチオンを利用した迅速な 3 置換トリアゾール類の合成法の開発(Regioselective Rapid Synthesis of Fully Substituted 1,2,3-Triazoles Mediated by Propargyl Cations)」(英語講演), 3A3-07, 日本化学会第 94 春季年会(日本化学会主催), 2C2-50(B 講演), 名古屋大学・東山キャンパス(愛知), (2013 年 3 月 27–30 日, 29 日発表) **[日本化学会第 94 春季年会学生講演賞]**

(2) ○張歓, 谷本裕樹, 西山靖浩, 森本積, 垣内喜代三, 「アルキルアジドを用いたプロパルギルアルコールの変換反応に関する研究(Study on the transformation reaction of propargyl alcohol by alkyl azide)」(英語講演), 日本

化学会第 92 春季年会(日本化学会主催), 講演番号：3E3-30, 慶應義塾大学理工学部(神奈川), (2012 月 3 月、27 日発表)