

# Supporting Information

## Bimetallic Zinc Complex --- Active Species in Oxidative Coupling of Terminal Alkynes with Aldehydes

Jiwen Yuan,<sup>a</sup> Jing Wang,<sup>a</sup> Guanghui Zhang,<sup>a,b</sup> Chao Liu,<sup>\*a</sup> Xiaotian Qi,<sup>c</sup> Yu Lan,<sup>\*c</sup> Jeffrey T. Miller,<sup>b</sup>  
A. Jeremy. Kropf,<sup>b</sup> Emilio E. Bunel,<sup>b</sup> and Aiwen Lei<sup>\*a,b</sup>

<sup>a</sup> College of Chemistry and Molecular Sciences Wuhan University, Wuhan 430072, P. R. China

<sup>b</sup> Chemical Science, Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne,  
Illinois 60439, United States

<sup>c</sup> College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, P. R.  
China

E-mail: [aiwenlei@whu.edu.cn](mailto:aiwenlei@whu.edu.cn)

General information.....	S2
Completes Reference for Gaussian 09.....	S2
General procedure.....	S3
Substrate scope.....	S5
General ReactIR experimental details.....	S6
X-Ray Absorption Spectroscopy experimental details.....	S10
B3LYP Calculated Wavenumbers of Possible Forms of Bimetallic, Monometallic Zinc speciees.....	S12
Detail descriptions for products.....	S18
Copies of products <sup>1</sup> H NMR and <sup>13</sup> C NMR.....	S22
Reference.....	S35

## General information

All reactions were isolated from moisture and oxygen by a nitrogen atmosphere with a balloon fitted on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Toluene was purified by distillation with sodium. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp.60-90 °C). Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and biphenyl was added as internal standard. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. <sup>1</sup>H and <sup>13</sup>C NMR data were recorded with Varian Mercury (300, or 400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively. For the ReactIR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem. Data manipulation was carried out using the iC IR software, version 4.2.

## Completes Reference for Gaussian 09

Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

## General procedure for the oxidative coupling of Terminal Alkynes with Aldehydes

### Method A:

ZnI<sub>2</sub> (398.8 mg, 1.25 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then the tube was charged with nitrogen. Toluene (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, alkyne (0.50 mmol), triethylamine (126.3 mg, 1.25 mmol) and aldehyde (1.25 mmol) were consecutively added into the reaction tube. The reaction was then heated to 80 °C and stirred for 12 h. Upon completion, the reaction was quenched with dilute HCl solution (2.0 M) and extracted with ethyl ether (3 × 10 mL). The organic layers were washed by saturated NaHSO<sub>3</sub> solution and then combined. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate= 100:1).

### Method B:

ZnI<sub>2</sub> (398.8 mg, 1.25 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then the tube was charged with nitrogen. Toluene (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, alkyne (0.50 mmol), triethylamine (126.3 mg, 1.25 mmol) and aldehyde (1.25 mmol) were consecutively added into the reaction tube. The reaction was then heated to 60 °C and stirred for 24 h. Upon completion, the reaction was quenched with dilute HCl solution (2.0 M) and extracted with ethyl ether (3 × 10 mL). The organic layers were washed by saturated NaHSO<sub>3</sub> solution and then combined. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate= 100:1).

### Procedure for Eq. (2)

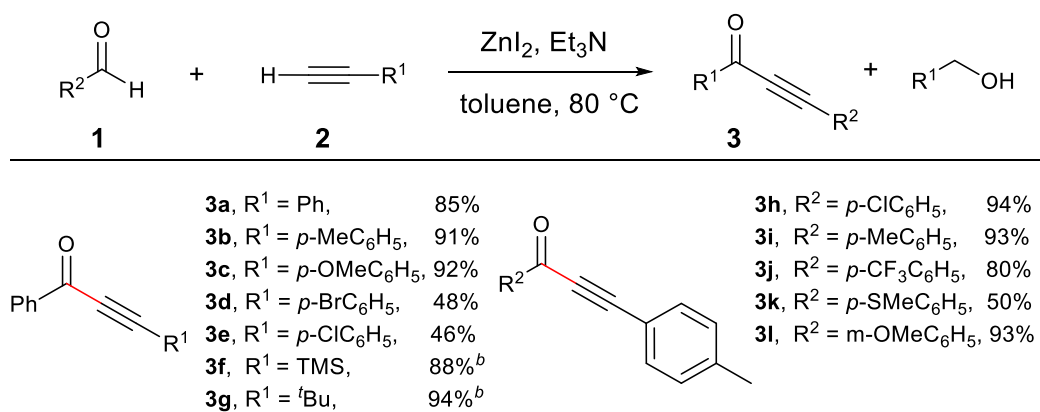
ZnI<sub>2</sub> (398.8 mg, 1.25 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then the tube was charged with nitrogen. Toluene (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, phenylacetylene (51.0 mg, 0.50 mmol), triethylamine (126.3 mg, 1.25 mmol) and benzaldehyde (53.0 mg, 0.5 mmol) were consecutively injected into the reaction tube. The reaction was

then heated to 80 °C and stirred for 0.5 h. The reaction was quenched with dilute HCl solution (2.0 M). The desired ynone was obtained with quantitative yield.

### **Procedure for Eq. (3)**

ZnI<sub>2</sub> (398.8 mg, 1.25 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then the tube was charged with nitrogen. Toluene (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, phenylacetylene (51.0 mg, 0.50 mmol), triethylamine (126.3 mg, 1.25 mmol) and benzaldehyde (53.0 mg, 0.5 mmol) were consecutively injected into the reaction tube. The reaction was then heated to 80 °C and stirred for 0.5h. Then, the reaction was cooled to room temperature and pivalaldehyde (64.6 mg, 0.75 mmol) was injected into the reaction tube. The reaction was then heated to 60 °C. Upon completion, the reaction was quenched with dilute HCl solution (2.0 M) and the yield was determined by GC analysis with 1,1'-biphenyl as the internal standard.

## Substrate scope



**Figure S1.** Synthesis of ynones **3** from different aldehydes **1** with terminal alkynes **2** through method A.

[b]: method B.

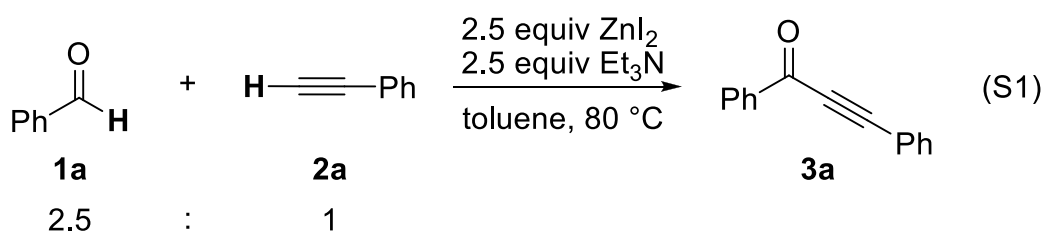
## General ReactIR experimental details

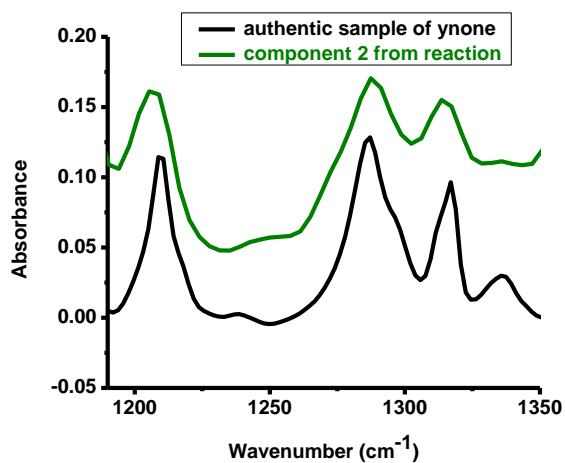
For the ReactIR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem. Data manipulation was carried out using the iC IR software, version 4.2.

The reaction was carried out as follows: a three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with solution of reactants. Operando IR spectra were recorded over the course of the reaction.

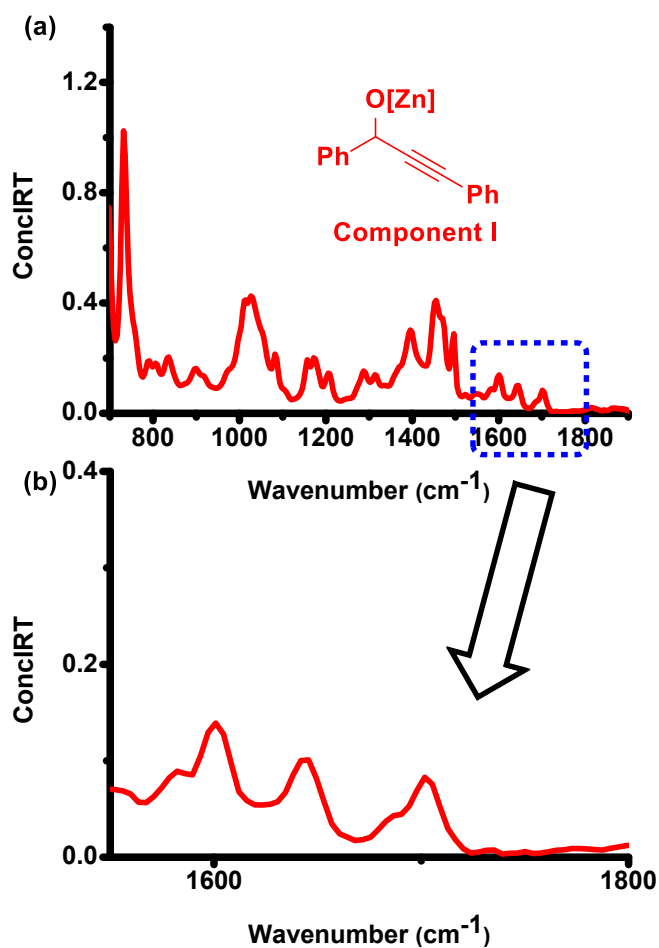
### The reaction between 1a and 2a

The reaction was carried out as follows:  $\text{ZnI}_2$  (398.8 mg, 1.25 mmol) was added to a three necked reaction vessel with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept in 80 °C. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with 2.0 mL toluene and the data collection was started, followed by sequential addition of phenylacetylene (51.0 mg, 0.50 mmol), triethylamine (126.3 mg, 1.25 mmol) and benzaldehyde (132.5 mg, 1.25 mmol). Operando IR spectra were recorded over the course of the reaction (eq S1).

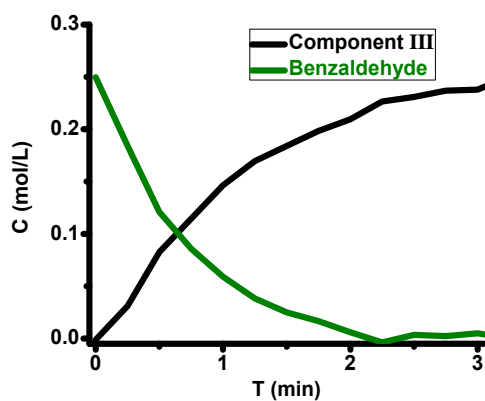
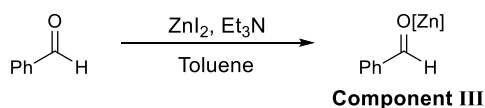




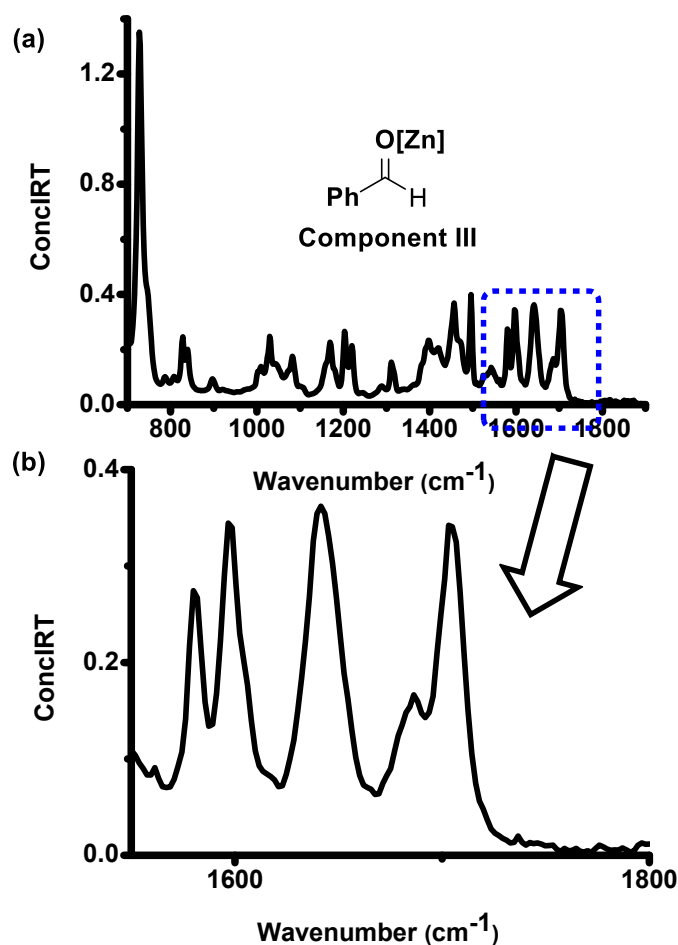
**Figure S1.** The black line: component II from reaction; the green line: authentic sample of ynone.



**Figure S2.** (a) The ConcIRT spectrum of component I (b) Amplification of the ConcIRT spectrum

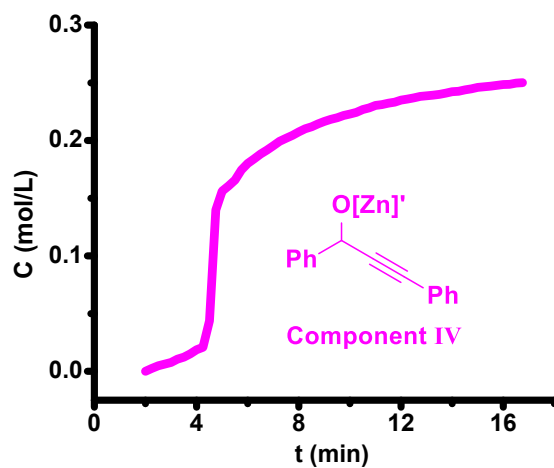


**Figure S3.** Kinetic profiles of the stoichiometric out and monitored by operando IR. The reaction vessel was first charged with Et<sub>3</sub>N, and ZnI<sub>2</sub> in toluene. As shown in Figure 3, after the addition of benzaldehyde, a new component III appeared reaction between 1a, Et<sub>3</sub>N, and ZnI<sub>2</sub>

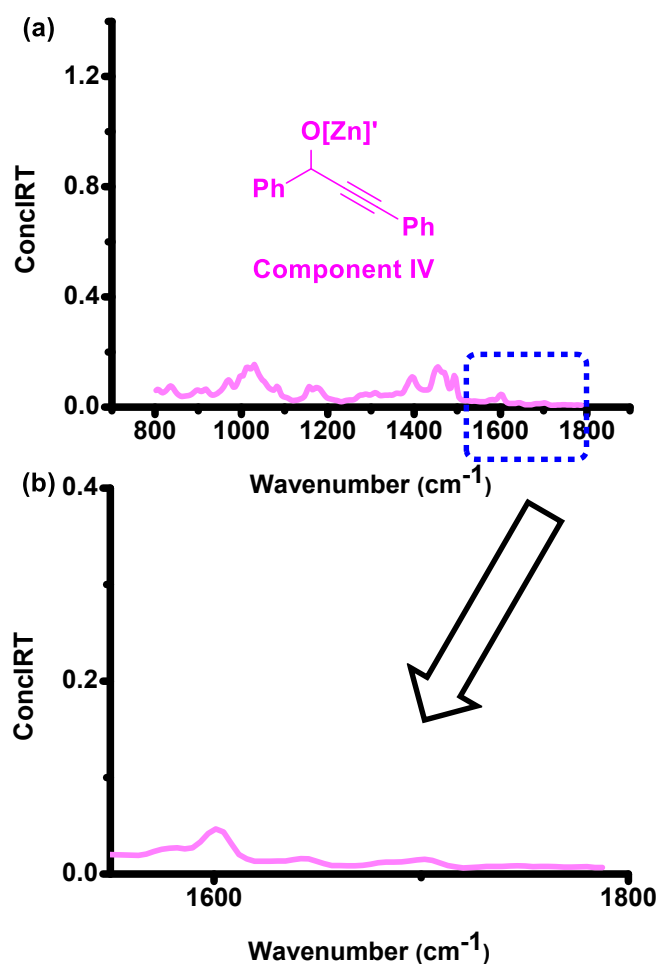


**Figure S4.** (a) The ConcIRT spectrum of component III; (b) Amplification of the ConcIRT spectrum.





**Figure S5.** Kinetic profiles of the reaction between **1a** and **2a** (the ratio of **1a** and **2a** was 1:1).



**Figure S6.** (a) The ConcIRT spectrum of component IV (b) Amplification of the ConcIRT spectrum

## X-Ray Absorption Spectroscopy experimental details

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data was collected in transmission quick scan mode. Insertion-device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point.

The ionization chambers optimized for the maximum current with linear response ( $\sim 10^{10}$  photons detected/sec) with 10% absorption ( $N_2$ ) in the incident ion chamber and 70% absorption (50%  $N_2$  and 50% Ar) in the transmission detector. A Zn foil spectrum was acquired simultaneously with each measurement for energy calibration and multiple scans were taken to ensure spectrum reproducibility.

All samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting prevent exposure to air and water. The spectra of the intermediate were obtained at 80 °C in toluene solution; while spectra were taken at room temperature for all solid reference compounds. For solution samples, the Zn concentration was adjusted to be around 0.1M with a path length of 3.5 mm. The energy of the Zn XANES was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. Experimental phase-shift, backscattering-amplitudes for Zn-O, and Zn-I were obtained from reference compounds: ZnO (4 Zn-O at 1.98 Å)<sup>1</sup> and ZnI<sub>2</sub> (2 Zn-I at 2.62 Å)<sup>2</sup>, respectively.

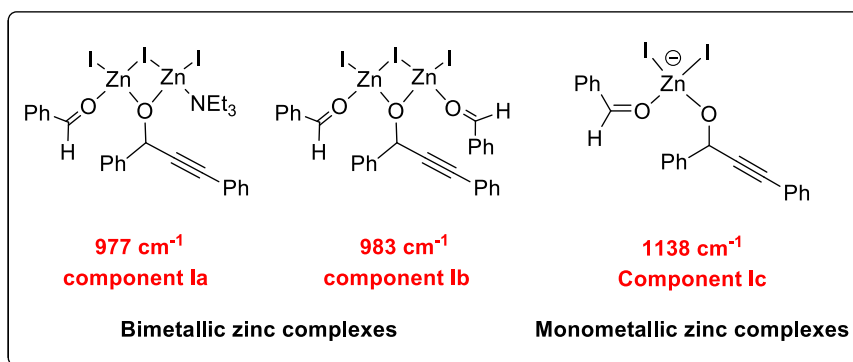
Background and normalization procedures were carried out using the Athena software package using standard methods.<sup>3</sup> Standard procedures based on WINXAS 3.2 software<sup>4</sup> were used to extract the EXAFS data. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor,  $k^2$ -weighted Fourier transform data. The data fit equally well with both  $k^1$  and  $k^3$  weightings.

Table S1 XANES edge energy and oxidation states

<b>Sample</b>	<b>Edge Energy (eV)</b>	<b>Oxidation State</b>	<b>Comments</b>
Zn foil	9659.0	0	XANES references for determination of oxidation states.
ZnO	9662.0	II	
ZnCl <sub>2</sub>	9662.4	II	
ZnBr <sub>2</sub>	9662.0	II	
ZnI <sub>2</sub>	9661.5	II	
ZnCl <sub>2</sub> -THF complex	9662.4	II	
Zn(acac) <sub>2</sub> xH <sub>2</sub> O	9663.2	II	
Ph <sub>2</sub> Zn	9662.5	II	
Reaction 1	9661.6	II	Observed Zn species under standard reaction conditions.
Reaction 2	9661.6	II	Observed Zn species in the reaction of phenyl acetylene with benzyl alcohol

## B3LYP Calculated Wavenumbers of Possible Forms of Bimetallic Zinc species

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. Density functional theory B3LYP with a standard 6-31G(d) basis set (SDD basis set for Zn and I) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies.



## B3LYP Geometries for the Optimized Compounds

### Component Ia

Zn	-0.14487000	-1.53358900	-0.18584100
I	-0.68564600	-3.97172800	0.28184400
I	1.41507100	-1.02283000	-2.42821100
Zn	2.08604200	0.81629700	-0.50849300
O	0.61988100	0.07040200	0.64954500
C	0.39206900	0.48387200	2.01372500
C	-0.81450900	1.32371800	2.08318100
C	-1.80560000	2.02516000	2.10151800
C	-2.98510900	2.83313600	2.11758000
C	-4.25725600	2.24016200	1.98734100
C	-2.89990000	4.23194200	2.26193600
C	-5.40676300	3.02758100	1.99761900
H	-4.32926200	1.16175100	1.88385000
C	-4.05409400	5.01197600	2.27217000
H	-1.92360300	4.69441600	2.37154100
C	-5.31019900	4.41449600	2.13943500

H	-6.38115400	2.55597000	1.90171000
H	-3.97331400	6.08944900	2.38715900
H	-6.20843500	5.02564600	2.15103800
C	-2.92519600	-1.37859700	-1.38363600
H	-2.74580500	-2.44439400	-1.59844700
O	-2.05130200	-0.72064200	-0.80736600
C	-4.21135500	-0.82478400	-1.79574300
C	-5.11276700	-1.65037600	-2.48897000
C	-4.55499100	0.50879500	-1.50442700
C	-6.34629900	-1.14681500	-2.89464200
H	-4.83965900	-2.68013600	-2.70649100
C	-5.78919100	1.00426500	-1.90672000
H	-3.85132800	1.12935200	-0.95930600
C	-6.68198100	0.17825800	-2.60280400
H	-7.04403500	-1.78117300	-3.43283700
H	-6.06176800	2.03050900	-1.67865400
H	-7.64541500	0.57084900	-2.91665900
I	4.44064900	0.63921300	0.53699300
N	1.66144800	2.83731700	-1.22274500
C	0.64482900	2.81635200	-2.32737000
H	0.63555700	3.81433200	-2.79461500
H	0.99719400	2.10453800	-3.07482400
C	1.13329500	3.68762700	-0.10205000
H	0.78070400	4.63644200	-0.53836700
H	0.26263900	3.17241500	0.30741000
C	2.93629200	3.43569800	-1.74186200
H	3.66339700	3.39086700	-0.93002800
H	2.74404800	4.49726900	-1.96679300
C	-0.77241400	2.43290000	-1.90691800
H	-0.79069600	1.51251100	-1.31861700
H	-1.26834000	3.21963200	-1.33077200
H	-1.36388600	2.26224500	-2.81324000
C	2.11163700	3.98749300	1.03322200
H	2.91364000	4.66805700	0.73431900
H	1.55521000	4.46972900	1.84456300
H	2.57342300	3.08009000	1.43341200
C	3.53245800	2.74480700	-2.96664100
H	4.51295100	3.18986300	-3.16705100
H	3.69008400	1.67596500	-2.79173700
H	2.92335400	2.86698500	-3.86664800
C	0.36767700	-0.70979400	2.96411300
C	-0.78869900	-1.11884300	3.63623300
C	1.56251600	-1.41994200	3.15997500
C	-0.75519900	-2.22585900	4.48740400
H	-1.71282100	-0.56536600	3.50019700

C	1.59340600	-2.52500900	4.00763600
H	2.46566600	-1.10654200	2.64233500
C	0.43359500	-2.93080000	4.67428800
H	-1.66051400	-2.53643600	5.00208100
H	2.52332500	-3.06869600	4.14912400
H	0.45851900	-3.79249300	5.33584600
H	1.25492100	1.10456800	2.29562400

**Component Ib**

Zn	-0.70337800	-1.91289300	-0.07666600
I	-0.96544100	-4.06596100	1.26659800
I	0.44211500	-1.55504000	-2.49197100
Zn	1.19173700	0.53986000	-0.85444500
I	1.27656100	2.93768700	-1.72439800
O	0.22306000	-0.31779100	0.62450500
C	-0.05307400	0.26880400	1.91134600
H	-0.43056800	-0.54413100	2.54863300
C	-1.10655600	1.28624100	1.79175700
C	-2.00231800	2.08736800	1.62423300
C	-3.05540300	3.02464800	1.38897500
C	-3.07891900	3.77563000	0.19597500
C	-4.08977400	3.20016000	2.32886100
C	-4.11654400	4.67416800	-0.04609200
H	-2.27786400	3.64681000	-0.52591600
C	-5.12058900	4.10342500	2.07903200
H	-4.07316000	2.62391700	3.24893500
C	-5.13945500	4.84150300	0.89210000
H	-4.12208200	5.24985200	-0.96774600
H	-5.91130400	4.23264500	2.81328100
H	-5.94329700	5.54780200	0.70232800
C	1.24193700	0.77718100	2.53609500
C	1.61286500	2.12588400	2.50024300
C	2.11043100	-0.15591000	3.12041600
C	2.83785900	2.53442100	3.03538300
H	0.94002500	2.85508200	2.05959000
C	3.33090300	0.25134200	3.65662100
H	1.82529700	-1.20503400	3.14927700
C	3.69845200	1.59996500	3.61402700
H	3.11280600	3.58552000	3.00545200
H	3.99200200	-0.48042900	4.11343200
H	4.64647600	1.92014200	4.03859200
C	-3.72923200	-1.77290800	-0.28693300
H	-3.71478500	-2.85848500	-0.09578600
O	-2.65939400	-1.15701100	-0.36801500
C	-5.03088900	-1.13197700	-0.41760500

C	-6.19004200	-1.92543800	-0.36158700
C	-5.13354400	0.26276800	-0.58162900
C	-7.44362700	-1.33095000	-0.47598300
H	-6.09997700	-3.00117800	-0.23028600
C	-6.38770700	0.85116200	-0.68653200
H	-4.22917600	0.86107300	-0.61084400
C	-7.53949800	0.05489700	-0.63692800
H	-8.34197800	-1.93961600	-0.43695700
H	-6.47080400	1.92794800	-0.79846600
H	-8.51842200	0.51930200	-0.72094600
O	3.18330200	-0.03363800	-0.42986600
C	4.18124200	0.69669700	-0.44280900
H	4.06628500	1.76553400	-0.68528600
C	5.52830500	0.21555500	-0.15981100
C	6.59734800	1.12631200	-0.20592400
C	5.76388700	-1.13732300	0.14914500
C	7.89377300	0.69030500	0.05533000
H	6.40457700	2.16894000	-0.44720500
C	7.05949100	-1.56672600	0.40860800
H	4.92463700	-1.82481900	0.17748900
C	8.12197600	-0.65426200	0.36196600
H	8.72278400	1.39066000	0.01977100
H	7.24939600	-2.60925600	0.64614500
H	9.13340300	-0.99577000	0.56500400

**Component Ic**

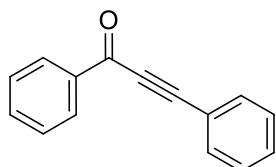
C	-1.86121100	-2.20782700	0.83443600
C	-0.82947200	-1.82906400	1.35197200
C	0.38910100	-1.26990700	1.99208900
H	0.14187900	-1.18579600	3.07233700
O	0.69626600	0.00425800	1.53927800
Zn	1.12859400	0.58723200	-0.23935100
I	0.72809100	-0.74473600	-2.46731700
C	1.56722200	-2.26471200	1.93512100
C	1.36978600	-3.64958700	1.99845000
C	2.87449300	-1.76853200	1.89515900
C	2.45802300	-4.52332200	2.01823200
H	0.35654200	-4.04318900	2.01387400

C	3.96415000	-2.64254200	1.91111100
H	3.02524900	-0.69511300	1.84400700
C	3.76144600	-4.02228600	1.97456800
H	2.28702100	-5.59730100	2.05658700
H	4.97377600	-2.24051500	1.86688300
H	4.61036700	-4.70259200	1.98122700
C	-3.03607000	-2.65047900	0.15352800
C	-4.13215200	-3.18346100	0.86081600
C	-3.11564300	-2.55773700	-1.25170600
C	-5.27242700	-3.61145300	0.18347200
H	-4.07505500	-3.25698100	1.94324100
C	-4.26091300	-2.98601700	-1.91947700
H	-2.26996200	-2.14734800	-1.79641800
C	-5.34274100	-3.51432300	-1.20869700
H	-6.10935800	-4.02157200	0.74436000
H	-4.30742600	-2.90715500	-3.00293400
H	-6.23365900	-3.84797600	-1.73552200
I	3.06284000	2.39703900	-0.16266000
O	-0.65616500	1.99994000	-0.26391300
C	-1.32735800	2.04296000	0.76386400
H	-1.04675600	1.39368100	1.60866300
C	-2.49504400	2.93124600	0.91915300
C	-3.21091800	2.91636500	2.12415000
C	-2.89265000	3.78574500	-0.12170400
C	-4.31707500	3.74867000	2.29164900
H	-2.89480900	2.24957600	2.92300100

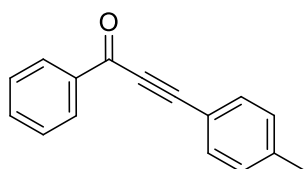


C	-3.99627700	4.61550600	0.04742900
H	-2.32154200	3.77883900	-1.04494300
C	-4.70836900	4.59727300	1.25318400
H	-4.87246000	3.73654000	3.22564500
H	-4.30645700	5.27825900	-0.75609300
H	-5.57074000	5.24696600	1.38170300

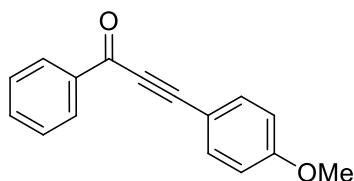
### Detail descriptions for products



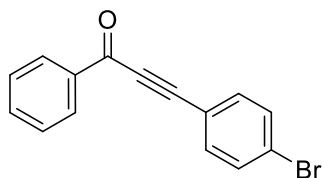
**1,3-Diphenylprop-2-yn-1-one (3a)**<sup>5</sup>: (Method A). Isolated yield = 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.23 (d, *J* = 8.0 Hz, 2H), 7.70-7.61 (m, 3H), 7.54-7.40 (m, 5H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 177.9, 136.8, 134.1, 133.0, 130.7, 129.5, 128.6, 128.5(5), 120.0, 93.0, 86.8 ppm.



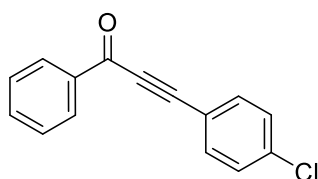
**Phenyl-3-(p-tolyl)prop-2-yn-1-one (3b)**<sup>5</sup>: (Method A). Isolated yield = 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.26 (d, *J* = 8.0 Hz, 2H), 7.63-7.53 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 178.0, 141.6, 137.0, 134.1, 133.1, 129.5, 129.5, 128.6, 117.0, 93.9, 86.9, 21.8 ppm.



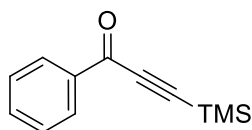
**3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (3c)**<sup>5</sup>: (Method A). Isolated yield = 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.13 (d, *J* = 8.0 Hz, 2H), 7.55-7.51 (m, 3H), 7.44-7.17 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 178.0, 161.7, 137.0, 135.1, 133.9, 129.5, 128.5, 114.4, 111.9, 94.3, 86.9, 55.4 ppm.



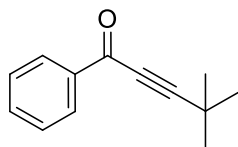
**3-(4-bromophenyl)-1-phenylprop-2-yn-1-one (3d)<sup>5</sup>:** (Method A). Isolated yield = 48%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.23 (d, *J* = 8.0 Hz, 2H), 7.69-7.53 (m, 7H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 177.8, 136.7, 134.4, 134.3, 132.1, 129.6, 128.7, 125.6, 119.0, 91.7, 87.7 ppm.



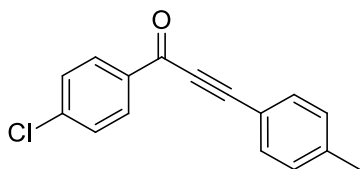
**3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (3e)<sup>5</sup>:** (Method A). Isolated yield = 46%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.23 (d, *J* = 8.0 Hz, 2H), 7.66-7.62 (m, 3H), 7.56-7.52 (m, 2H), 7.4-7.41 (m, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 177.8, 137.2, 136.7, 134.3, 134.2(9), 129.6, 129.2, 128.7, 118.6, 91.7, 87.6 ppm.



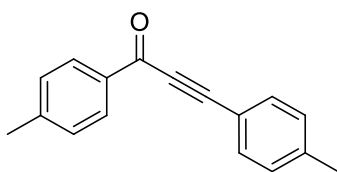
**1-Phenyl-3-(trimethylsilyl)prop-2-yn-1-one (3f)<sup>6</sup>:** (Method B). Isolated yield = 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.07 (d, *J* = 7.8 Hz, 2H), 7.54-7.43 (m, 1H), 7.41-7.39 (m, 2H), 0.25 (s, 9H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 178.0, 136.7, 134.5, 130.0, 128.8, 101.0, 100.9 ppm.



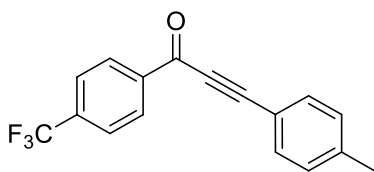
**4,4-Dimethyl-1-phenylpent-2-yn-1-one (3g)<sup>7</sup>:** (Method B). Isolated yield = 94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.51-7.49 (m, 1H), 7.39-7.36 (m, 2H), 1.29 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 178.3, 137.0, 133.8, 129.4, 128.4, 103.9, 78.1, 30.0 ppm.



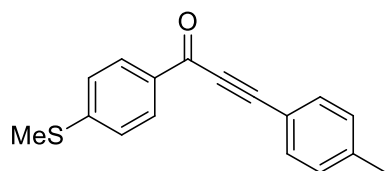
**1-(4-Chlorophenyl)-3-(p-tolyl)prop-2-yn-1-one (3h)<sup>8</sup>:** (Method A). Isolated yield = 94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.17(d, *J* = 8.0, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  176.7, 141.8, 140.6, 133.2, 129.6, 129.0, 116.7, 94.4, 86.5, 21.8 ppm.



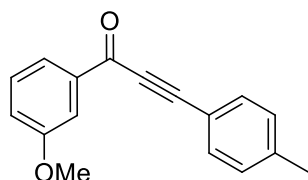
**1,3-Di-p-tolylprop-2-yn-1-one (3i)<sup>9</sup>:** (Method A). Isolated yield = 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.11 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H). ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 177.8, 145.1, 141.4, 134.7, 133.1, 129.7, 129.5, 129.3, 117.1, 93.3, 86.9, 21.9, 21.8 ppm. HRMS (ESI) calcd for C<sub>17</sub>H<sub>14</sub>O [M+H]<sup>+</sup>: 235.1078; found: 235.1120.



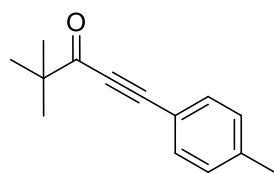
**3-(P-tolyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (3j):** (Method A). Isolated yield = 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.22 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 176.7, 142.1, 139.5, 135.0 (q, *J* = 32.6 Hz), 129.8, 129.6, 125.6 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.9 Hz), 116.5, 95.2, 86.6, 21.8 ppm. HRMS (ESI) calcd for C<sub>17</sub>H<sub>11</sub>F<sub>3</sub>O [M+H]<sup>+</sup>: 289.0796; found: 289.0837.



**1-(4-(Methylthio)phenyl)-3-(p-tolyl)prop-2-yn-1-one (3k):** (Method A). Isolated yield = 50%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.10 (d,  $J$  = 8.6 Hz, 2H), 7.56 (d,  $J$  = 8.1 Hz, 2H), 7.28 (d,  $J$  = 8.6 Hz, 2H), 7.21 (d,  $J$  = 7.9 Hz, 2H), 2.52 (s, 3H), 2.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 176.9, 147.4, 141.4, 133.4, 132.9, 129.7, 129.4, 124.6, 116.9, 93.3, 86.6, 21.7, 14.6 ppm. HRMS (APCI) calcd for  $\text{C}_{17}\text{H}_{14}\text{OS}$   $[\text{M}]^+$ : 266.0765; found: 266.0762.



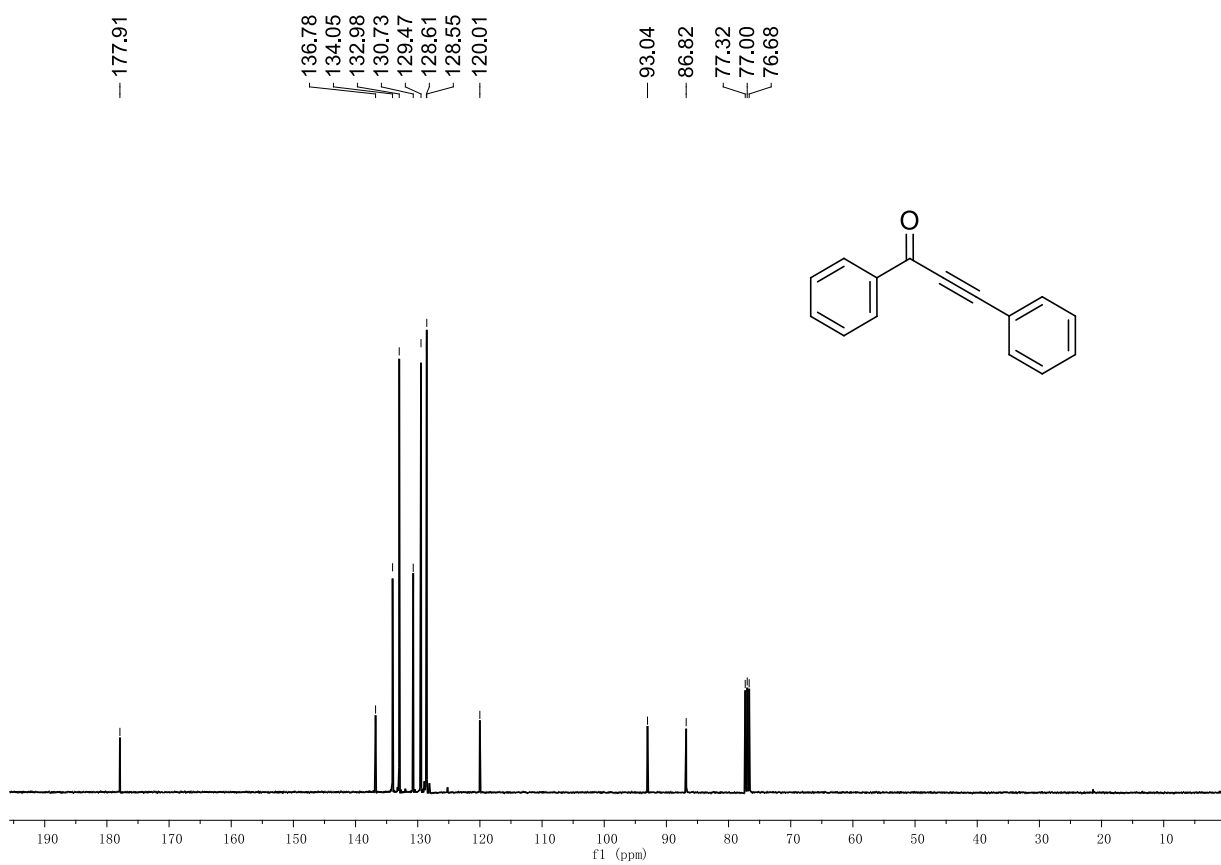
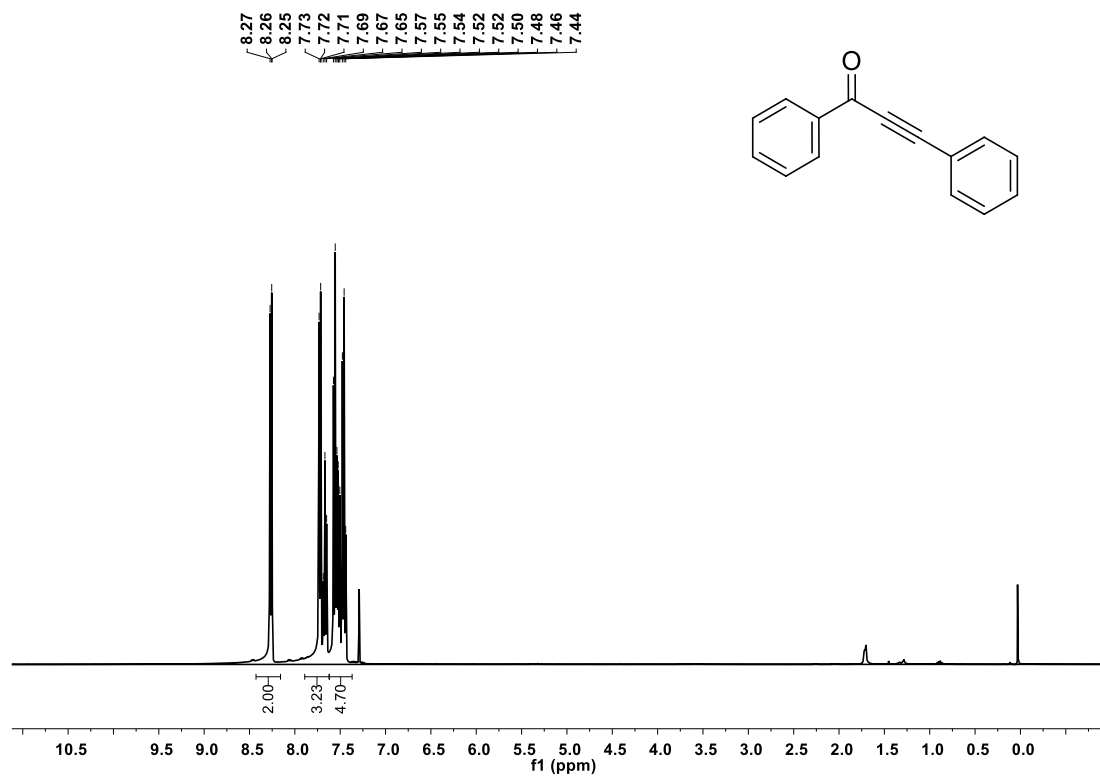
**1-(3-Methoxyphenyl)-3-(p-tolyl)prop-2-yn-1-one (3l):** (Method A). Isolated yield = 93%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.77 (d,  $J$  = 8.0 Hz, 1H), 7.61 (s, 1H), 7.49 (d,  $J$  = 8.0 Hz, 2H), 7.36-7.32 (m, 1H), 7.14-7.07 (m, 2H), 7.08 (dd,  $J_1$  = 8.1 Hz,  $J_2$  = 2.3, 1H) 3.79 (s, 3H), 2.31 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 177.7, 159.7, 141.5, 138.3, 133.0, 129.5, 129.4, 122.7, 120.7, 116.9, 112.8, 93.6, 86.8, 55.4, 21.7 ppm. HRMS (APCI) calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_2$   $[\text{M}]^+$ : 250.0994; found: 250.0996.



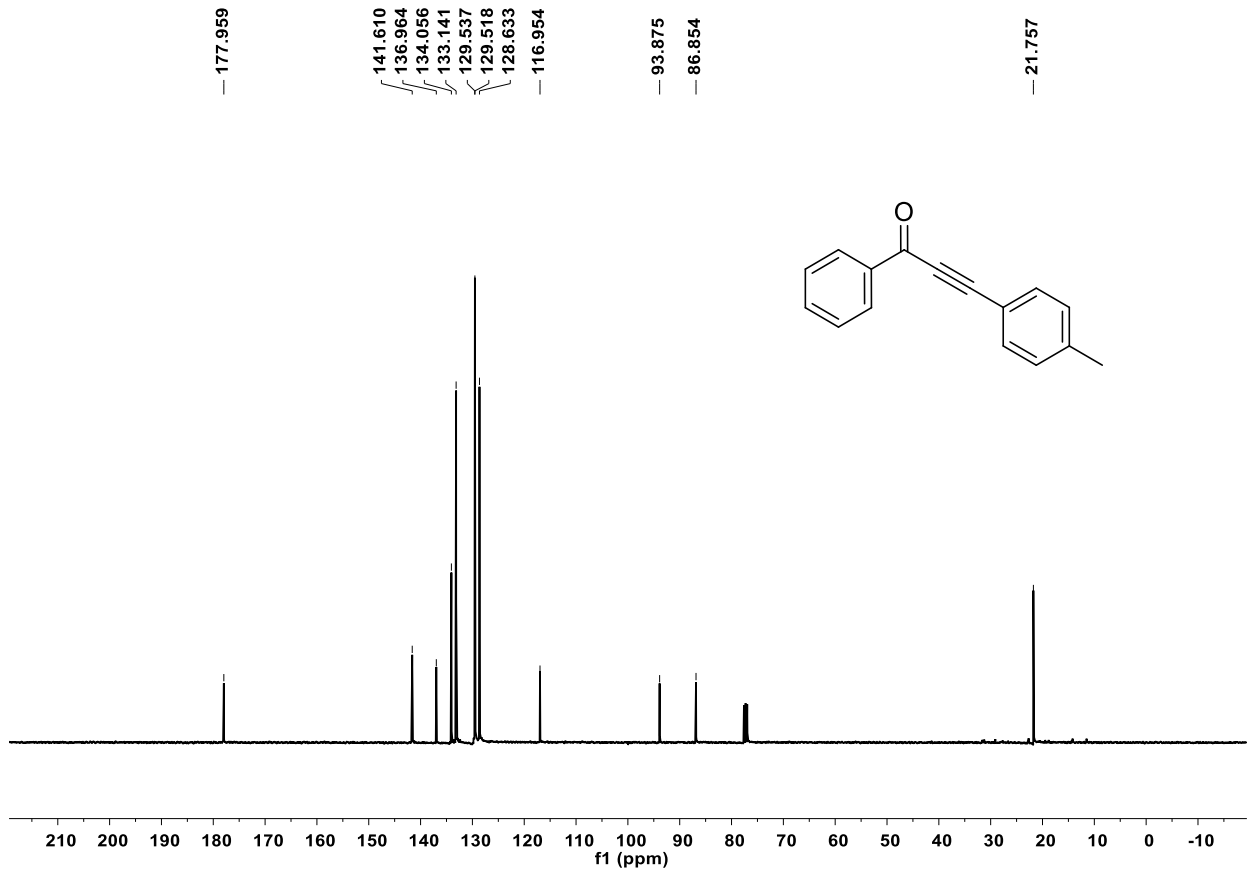
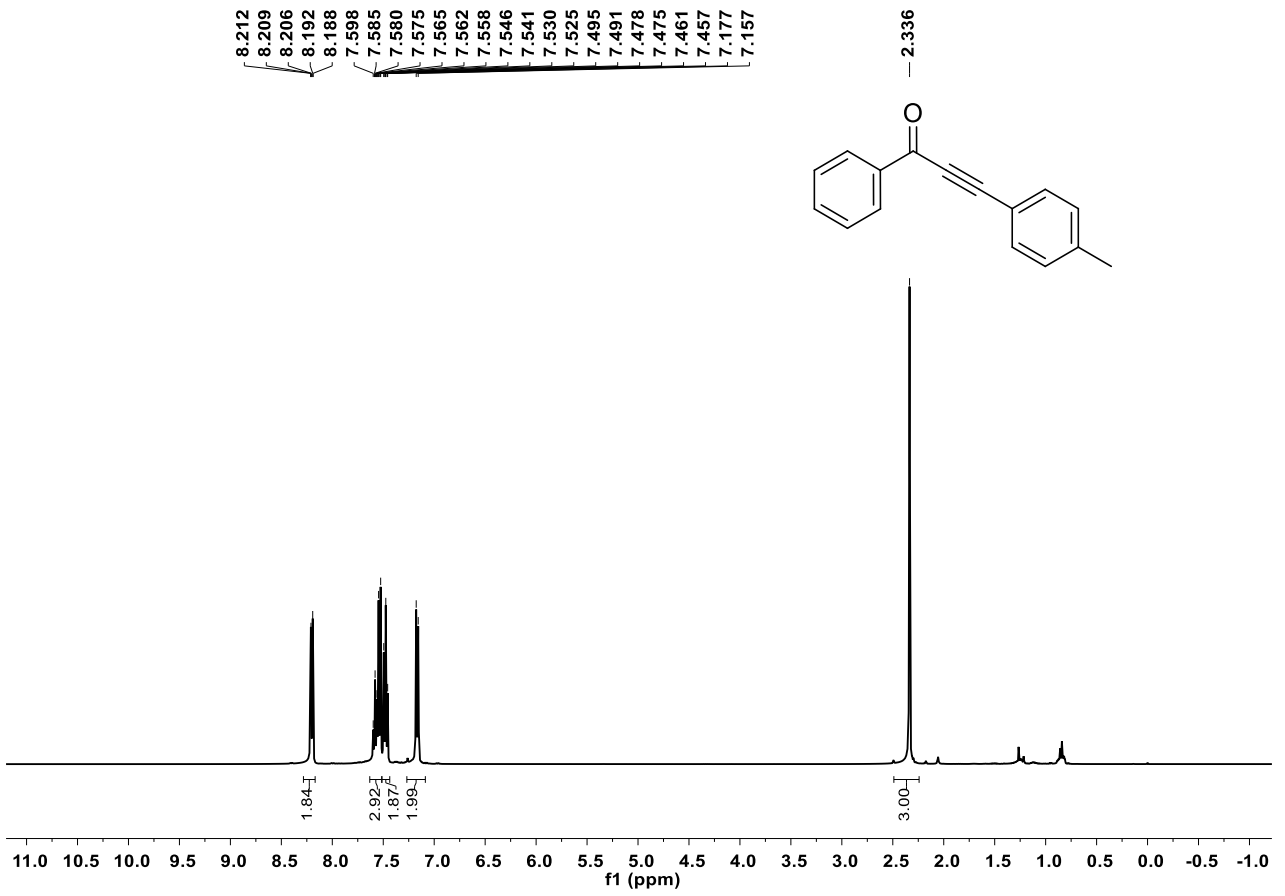
**4,4-Dimethyl-1-(p-tolyl)pent-1-yn-3-one (3m):** (Method B). Isolated yield = 72%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.48 (d,  $J$  = 8.1 Hz, 2H), 7.19 (d,  $J$  = 7.9 Hz, 2H), 2.39 (s, 3H), 1.28 (s, 9H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 194.4, 141.2, 133.0, 129.4, 117.1, 92.9, 85.8, 44.8, 26.2, 21.7 ppm. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{16}\text{O}$   $[\text{M}]^+$ : 200.1201; found: 200.1197.

# Copies of products $^1\text{H}$ NMR and $^{13}\text{C}$ NMR

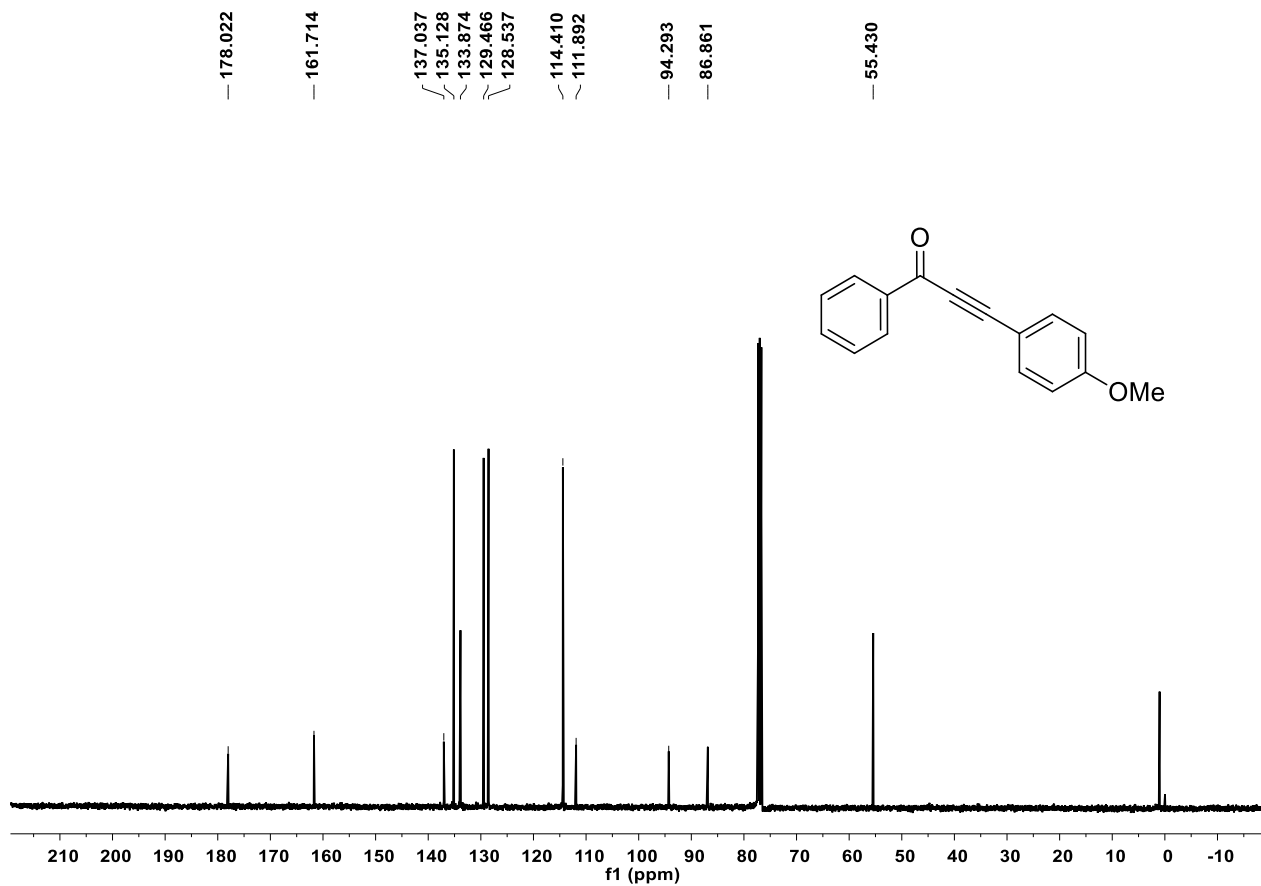
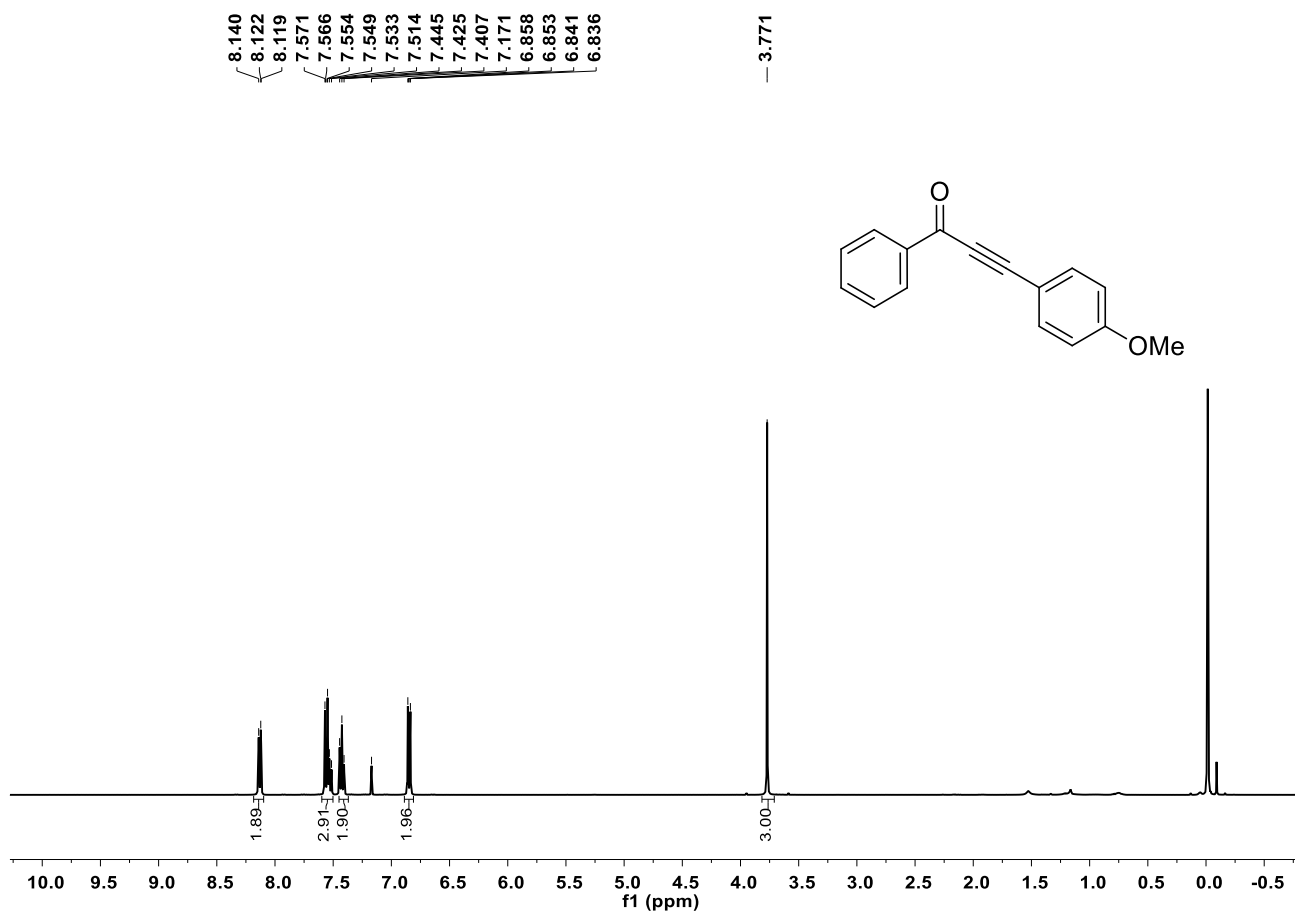
**3a**



3b



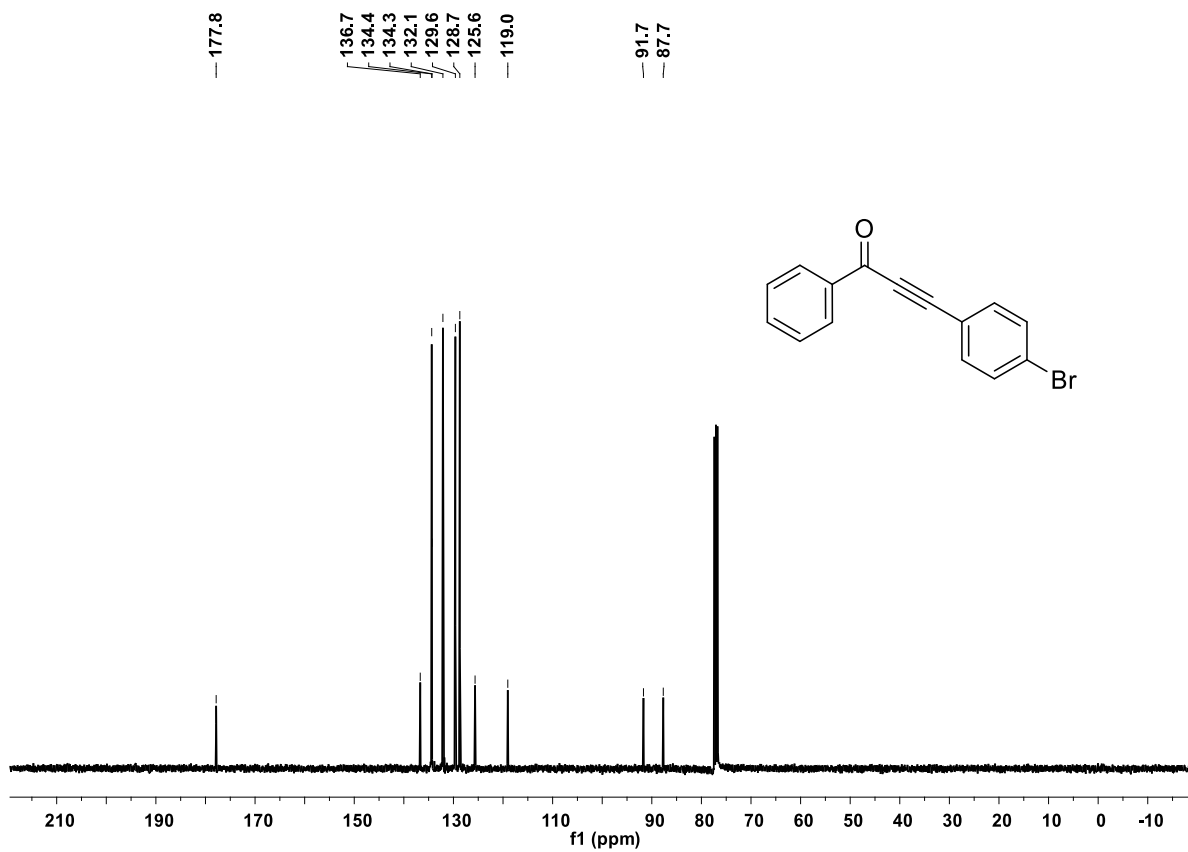
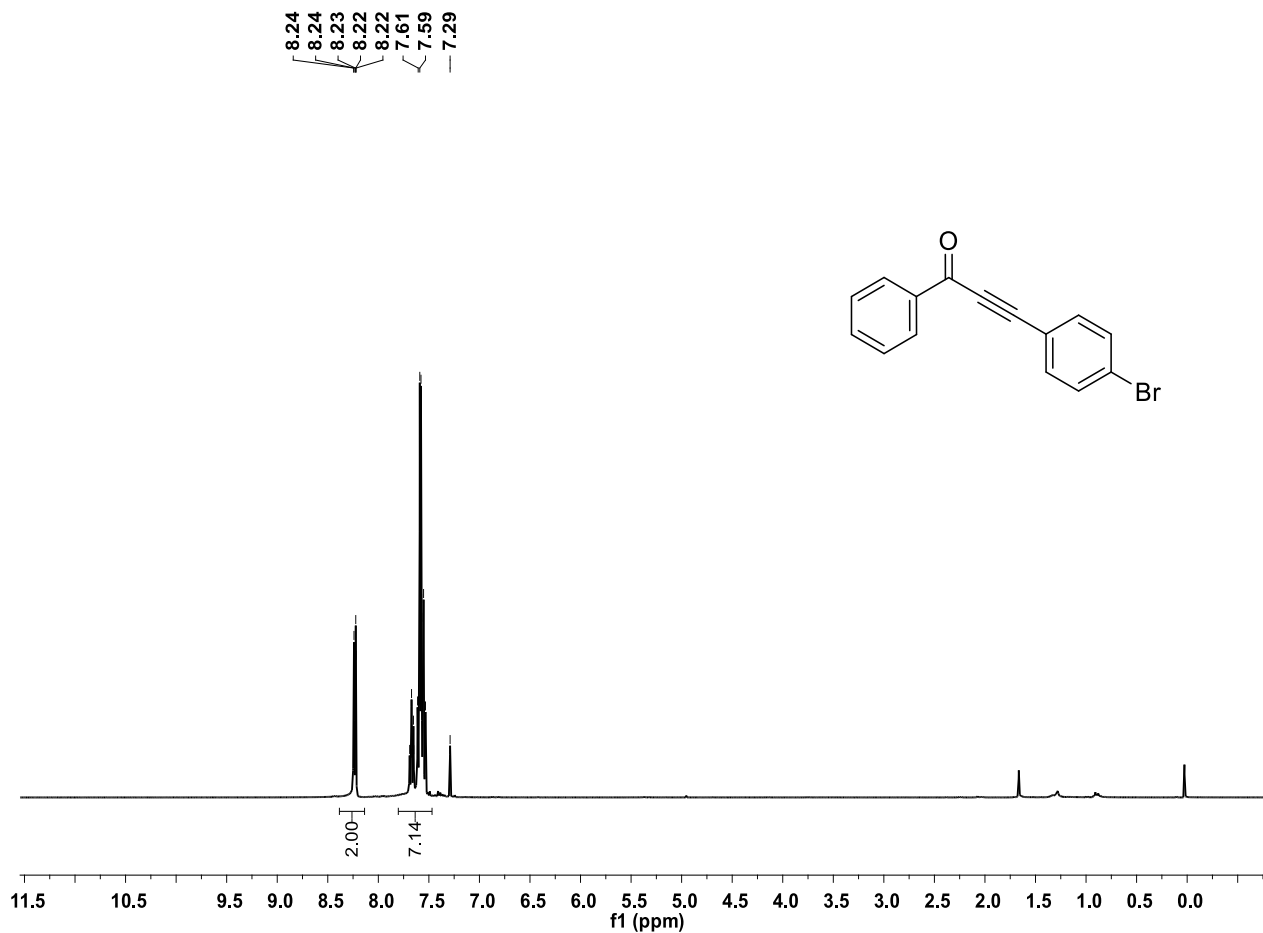
3c



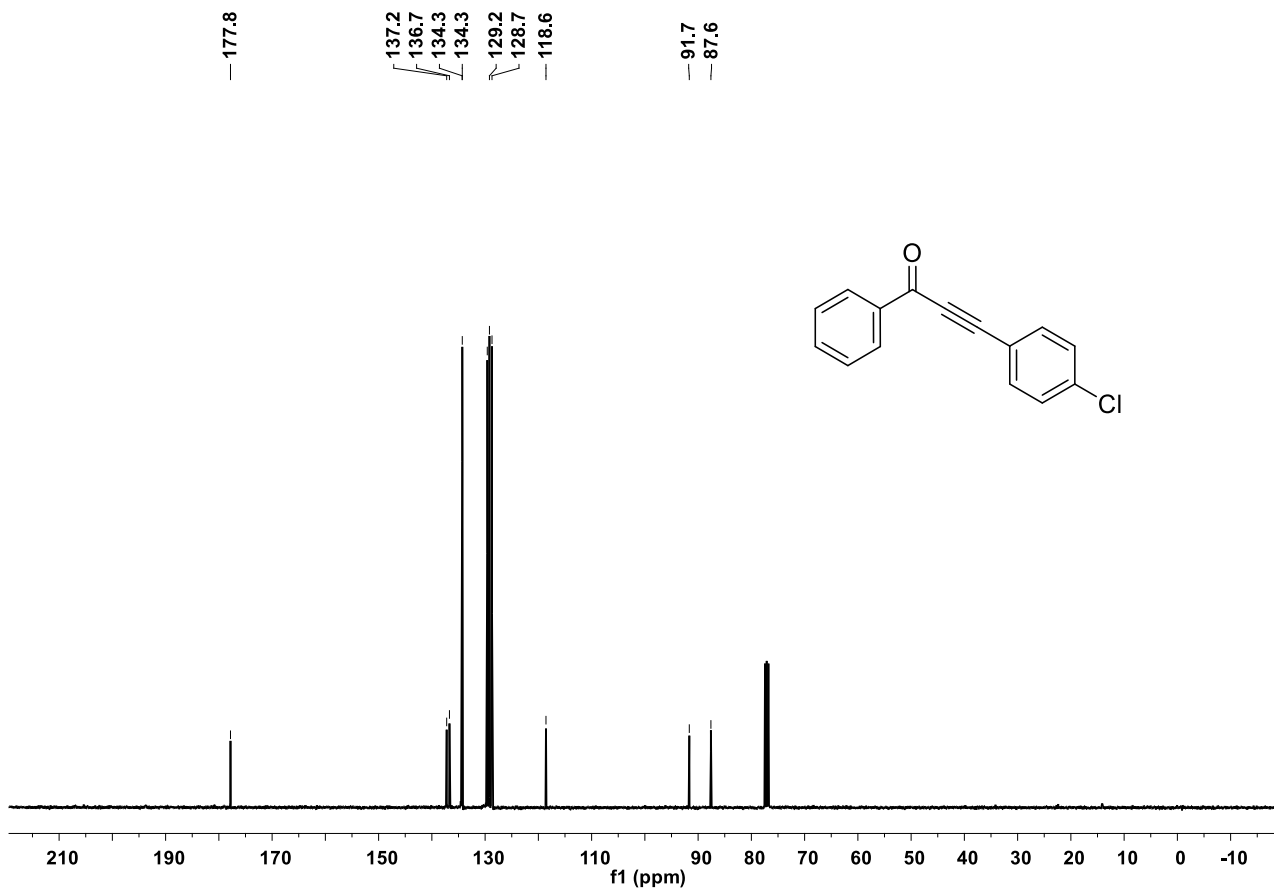
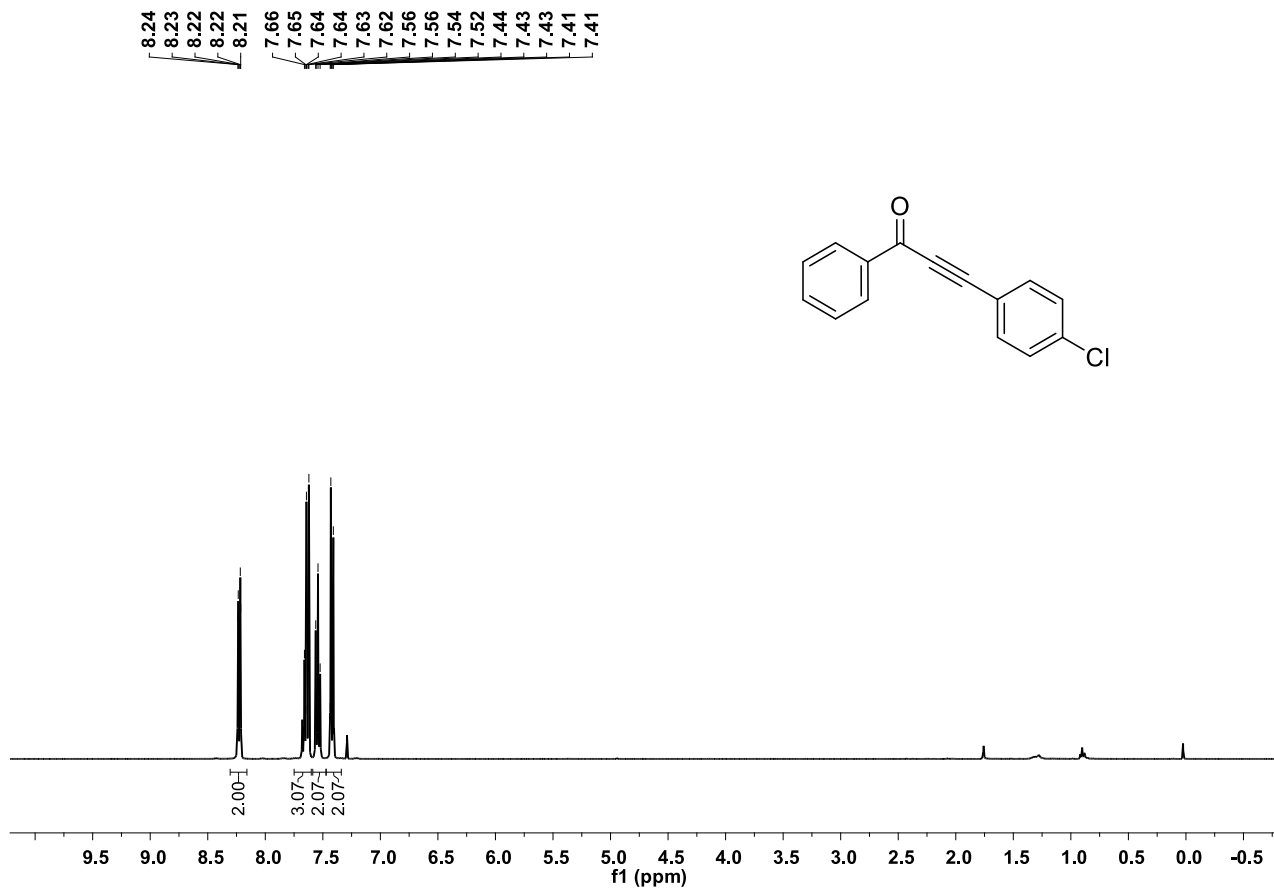
S24



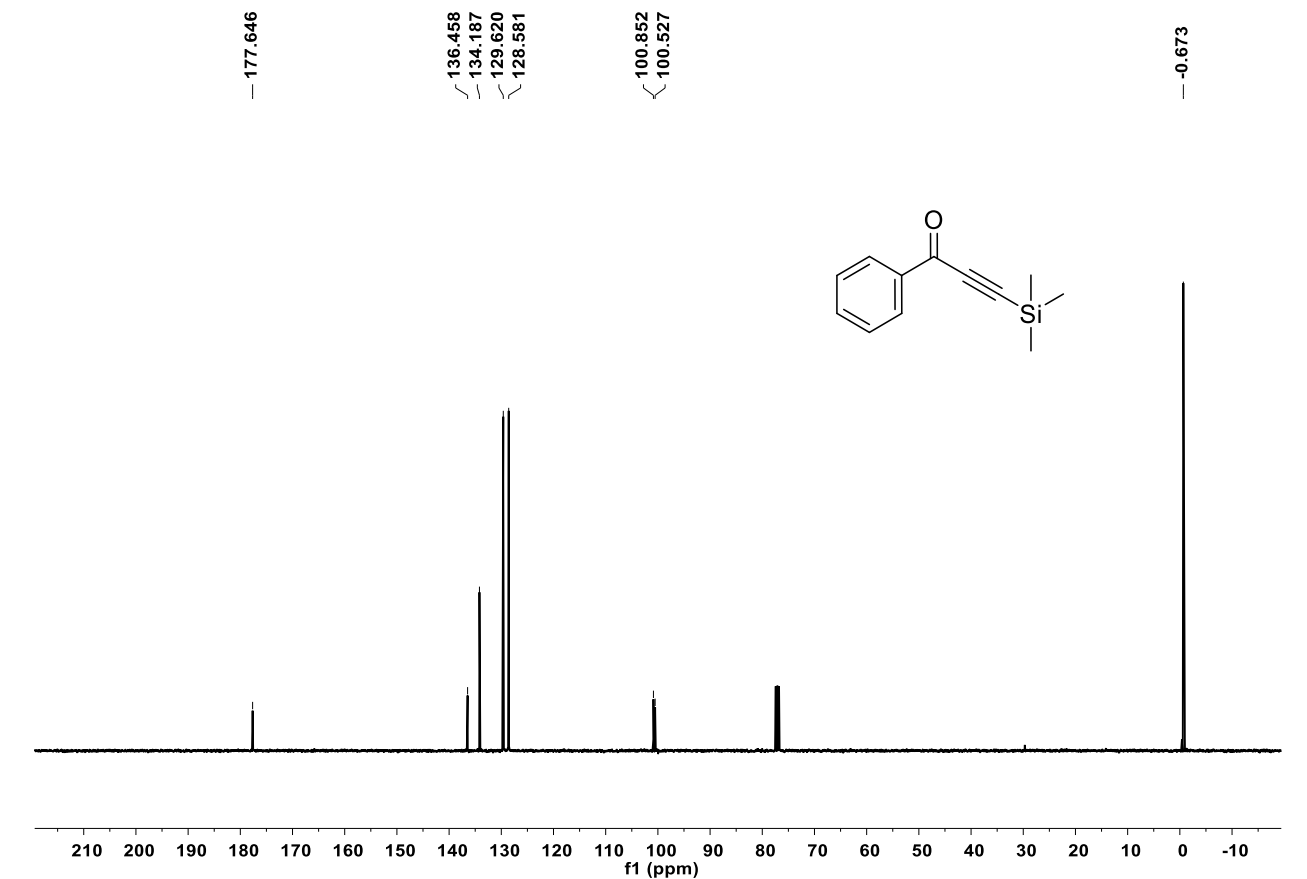
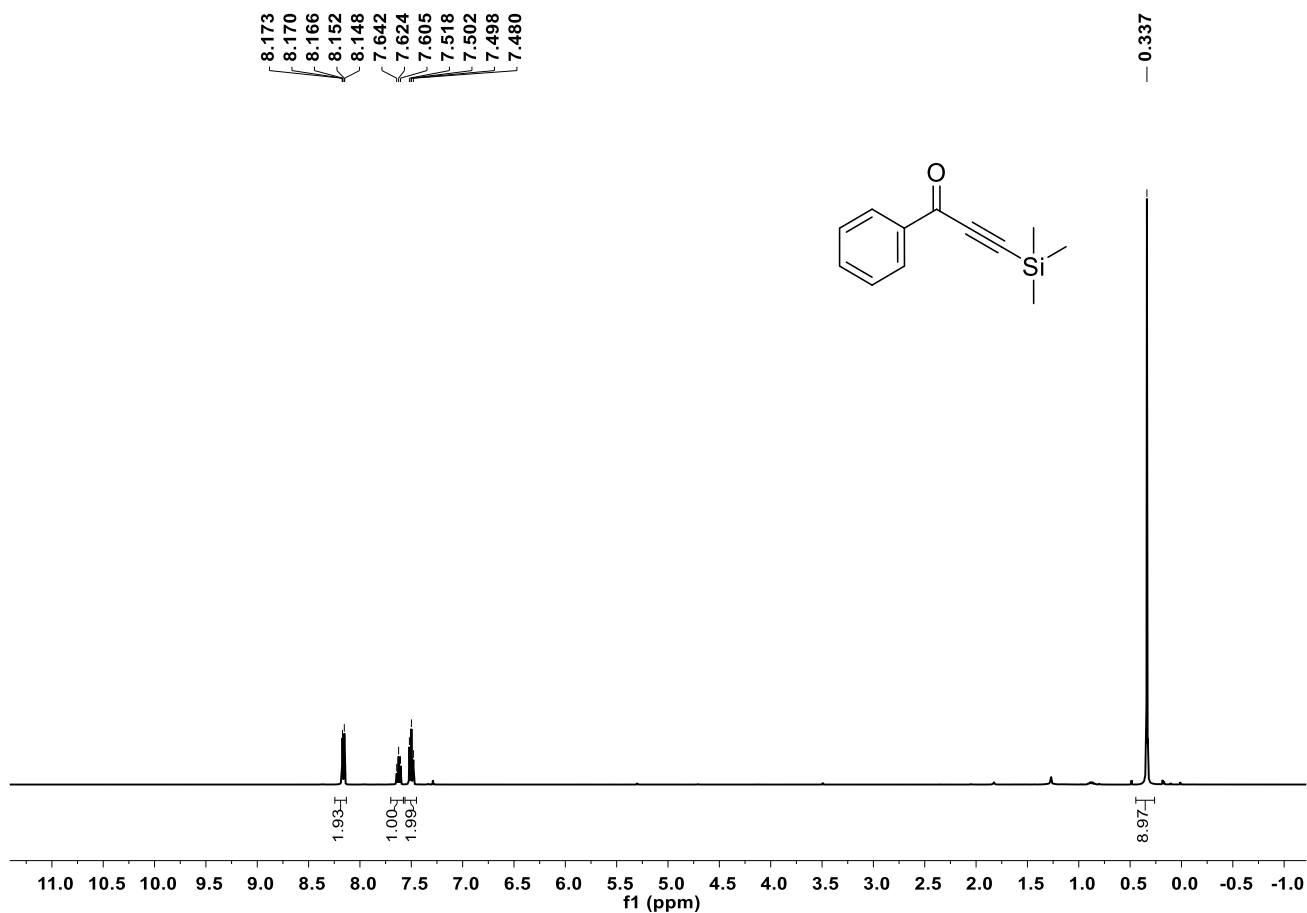
3d

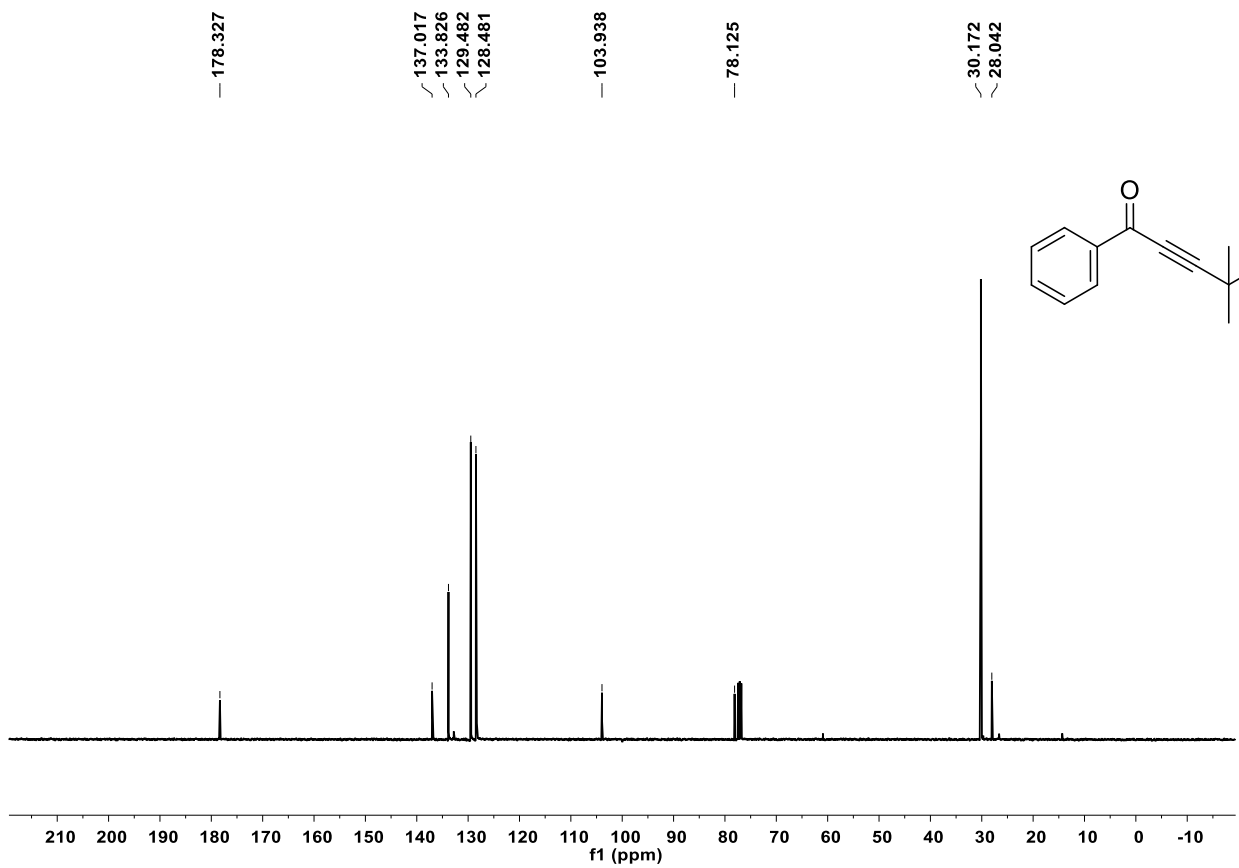
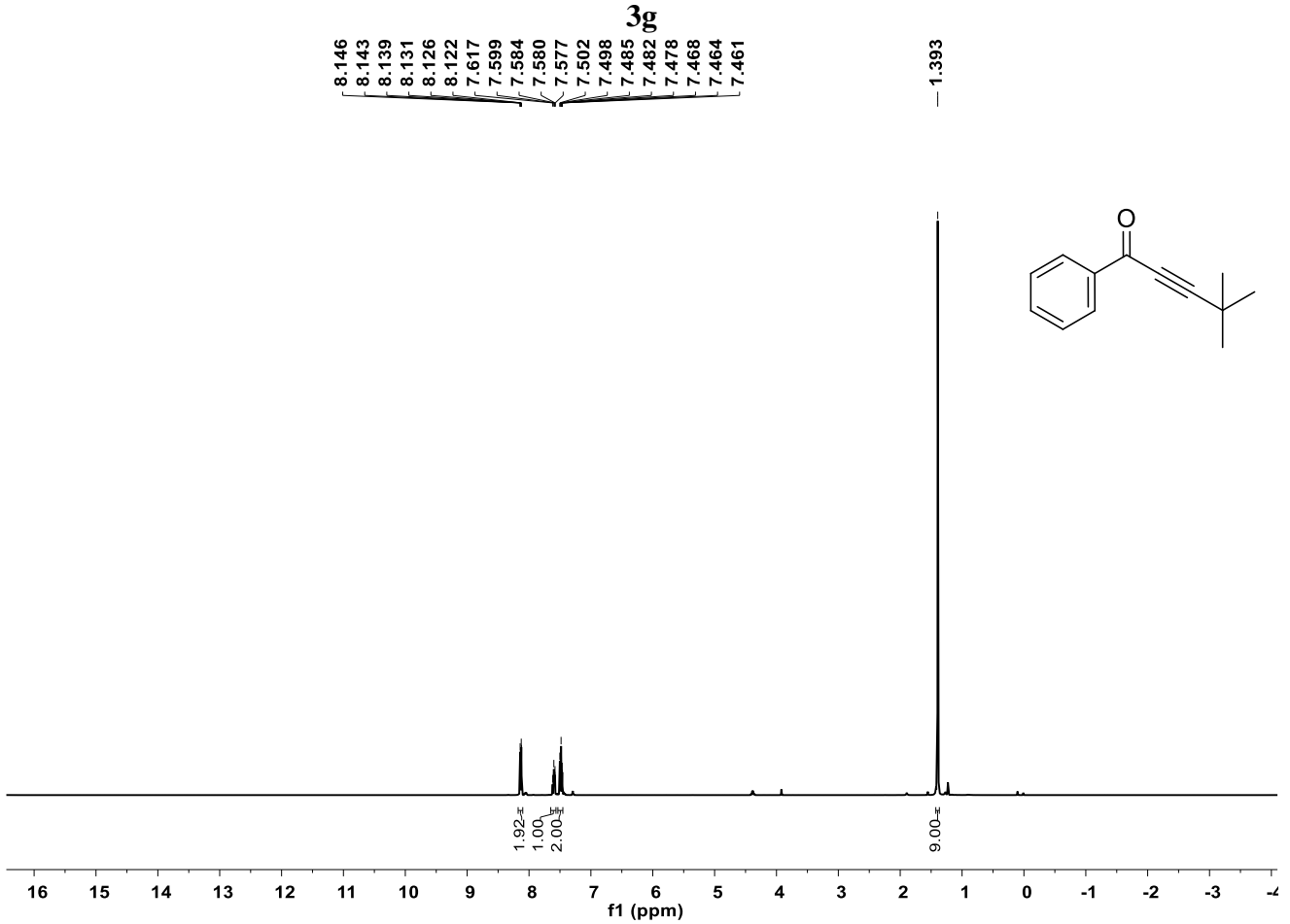


3e

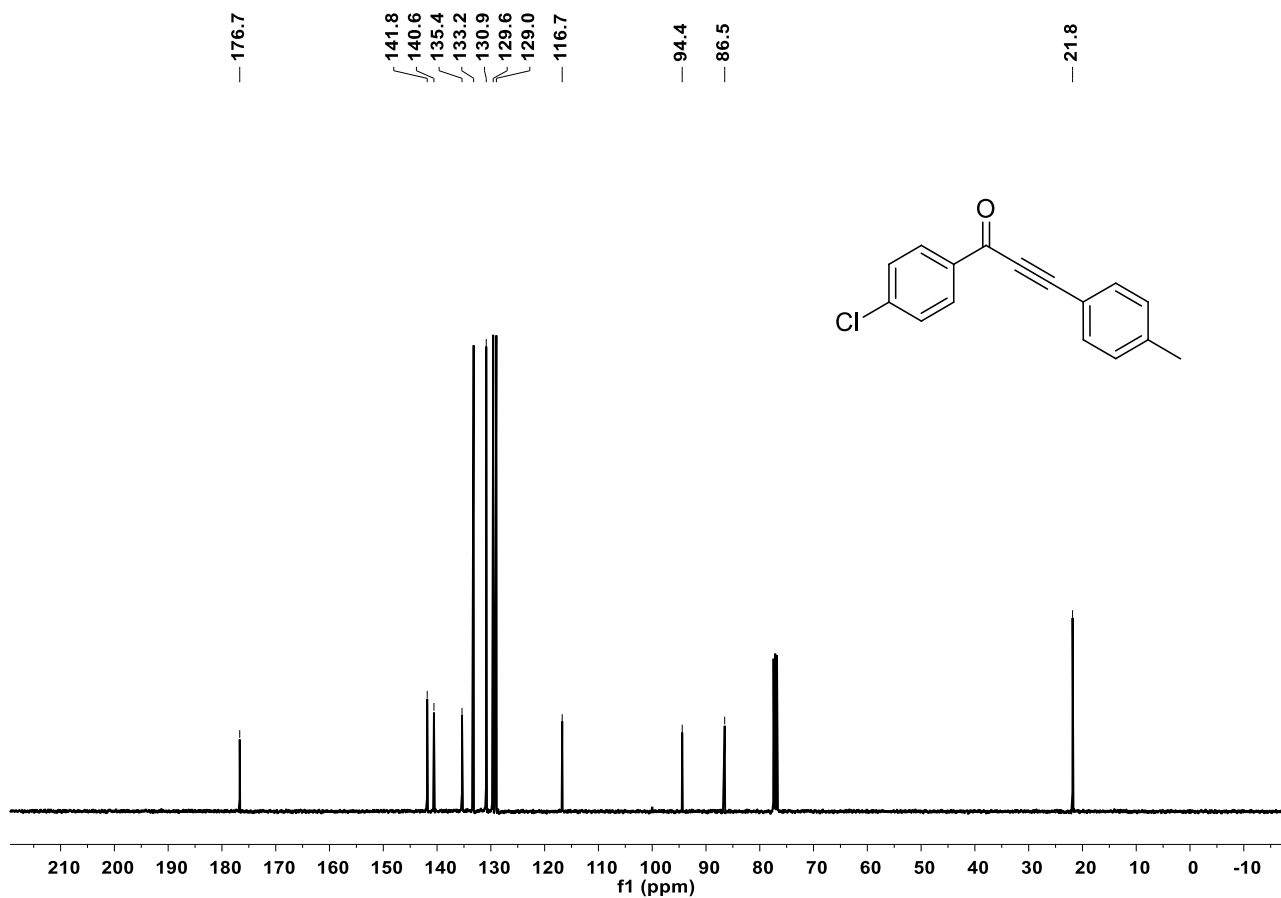
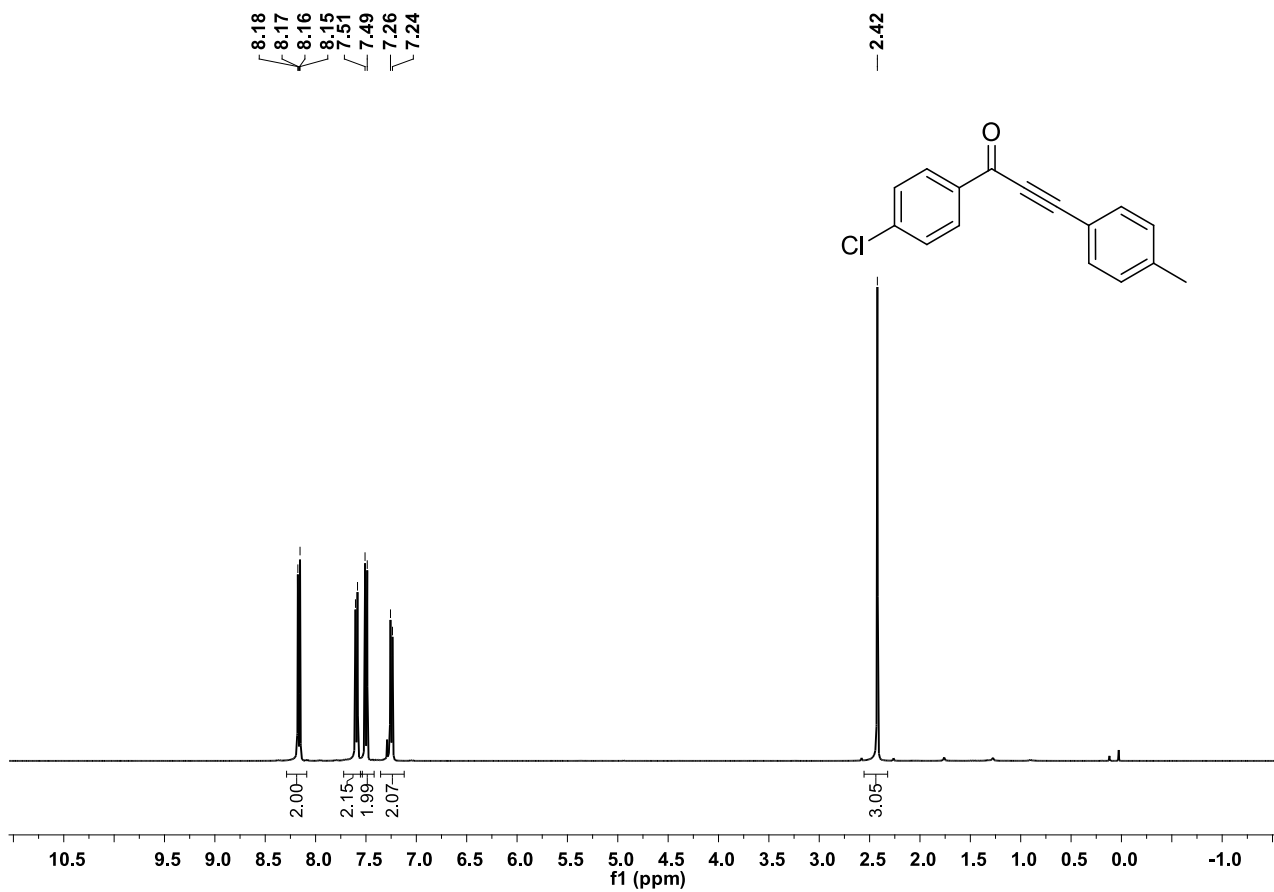


3f

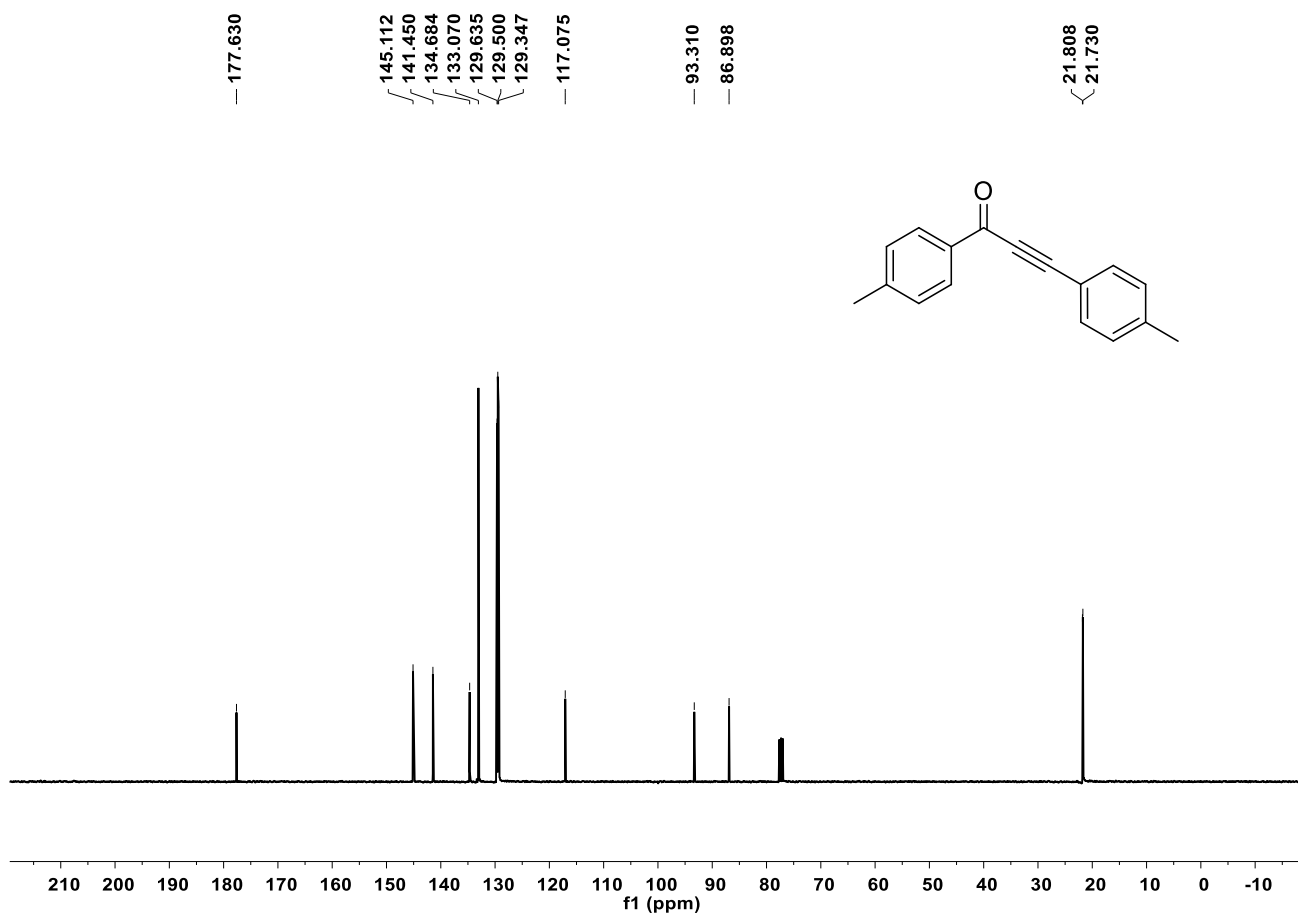
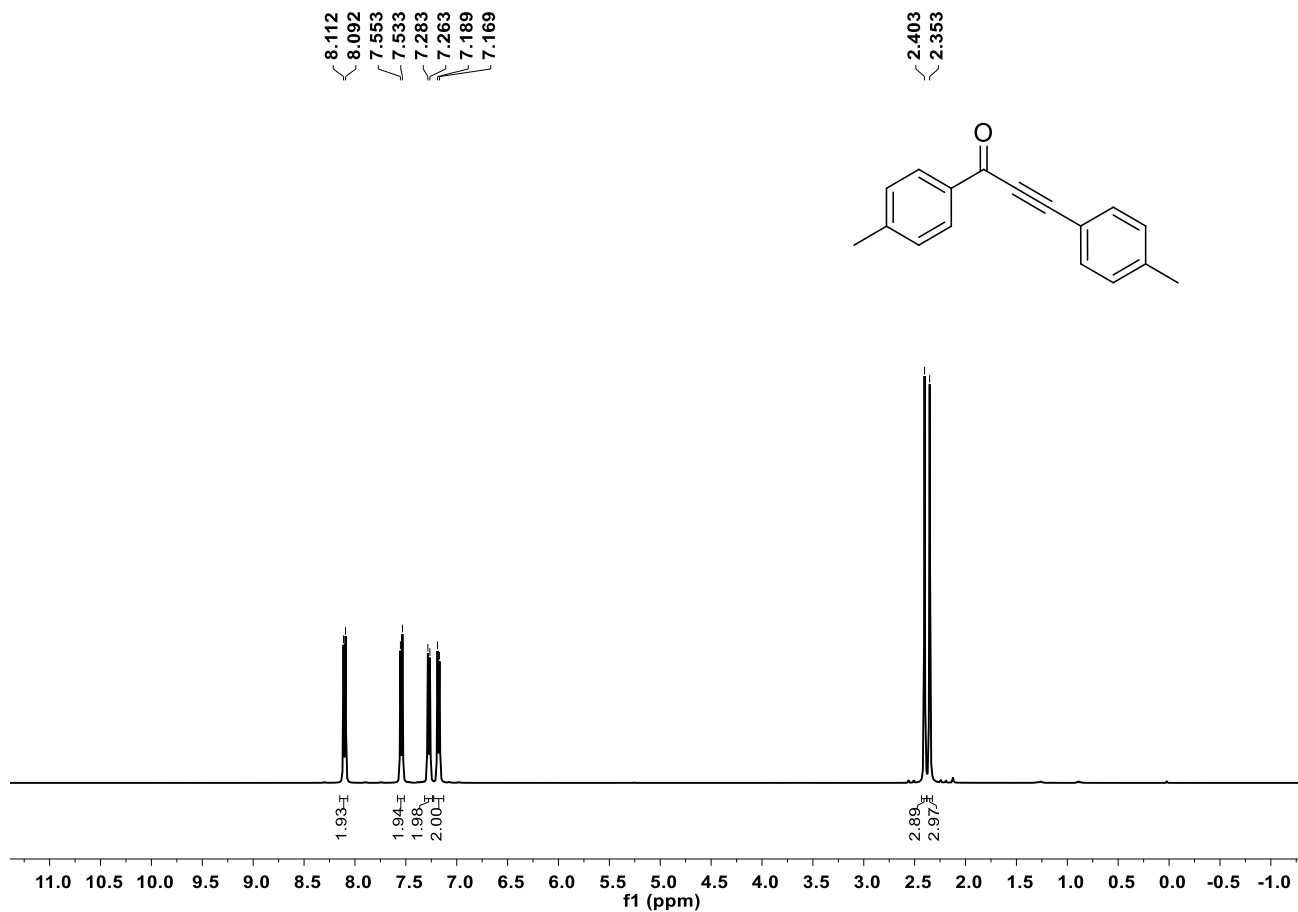




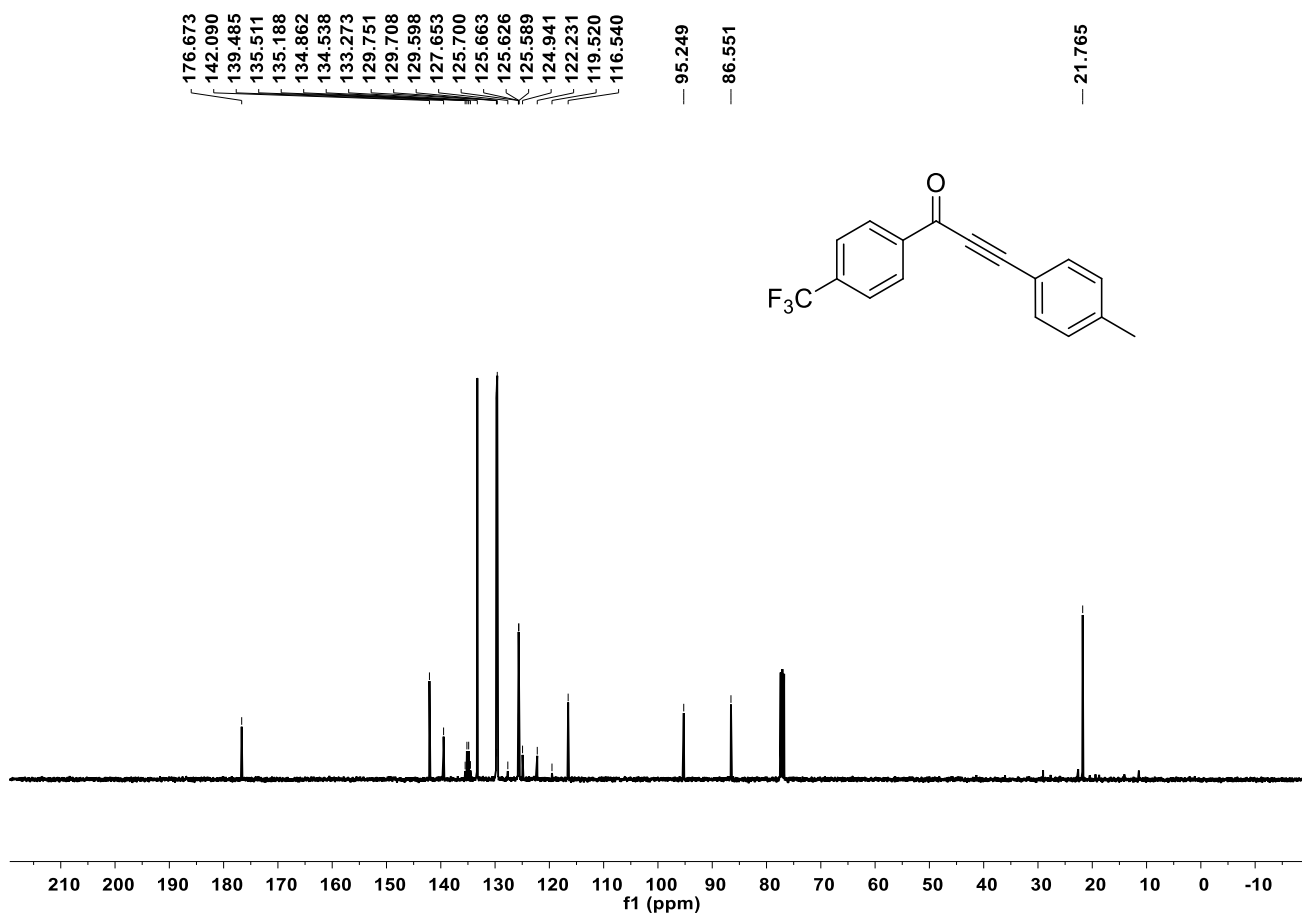
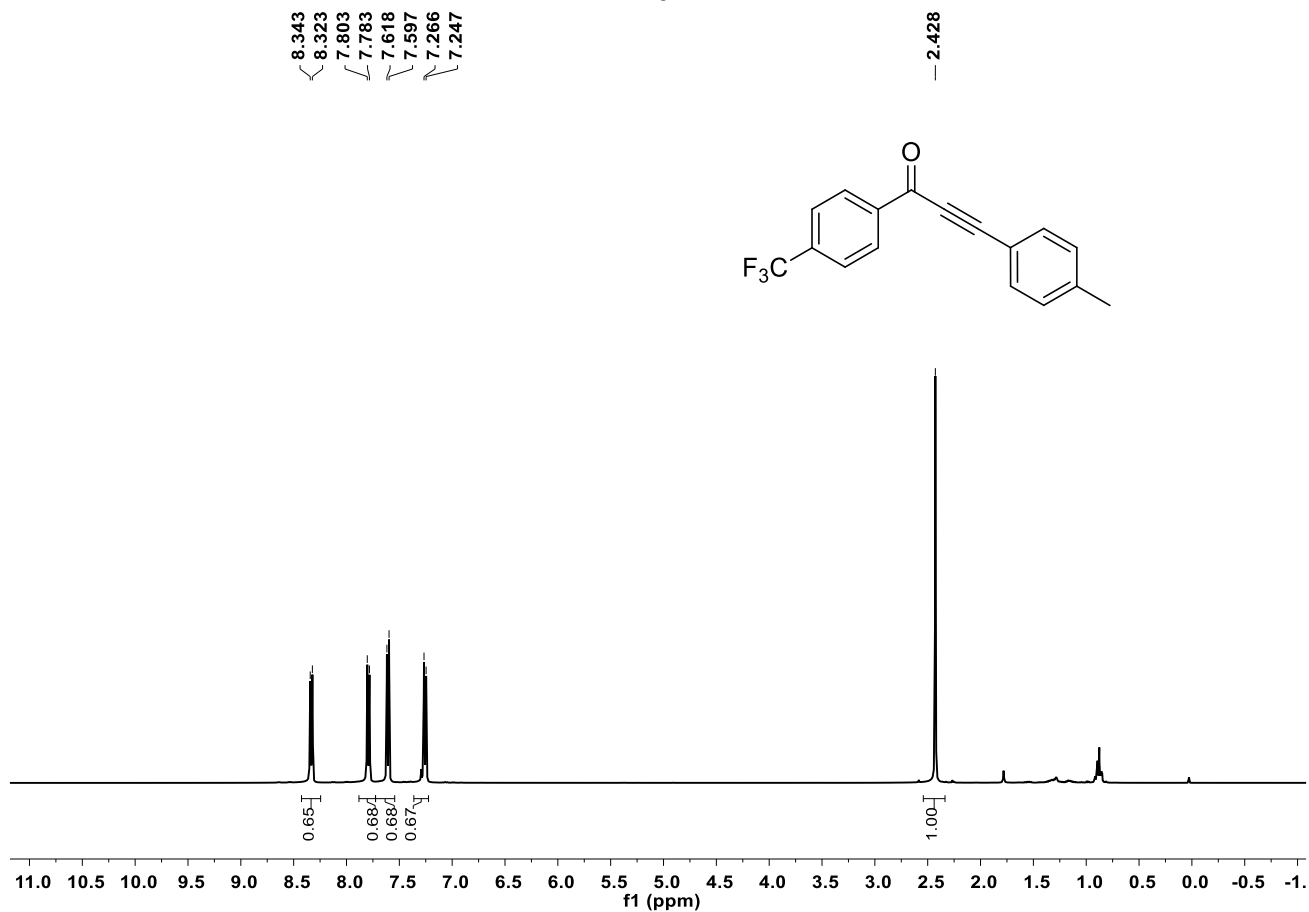
3h



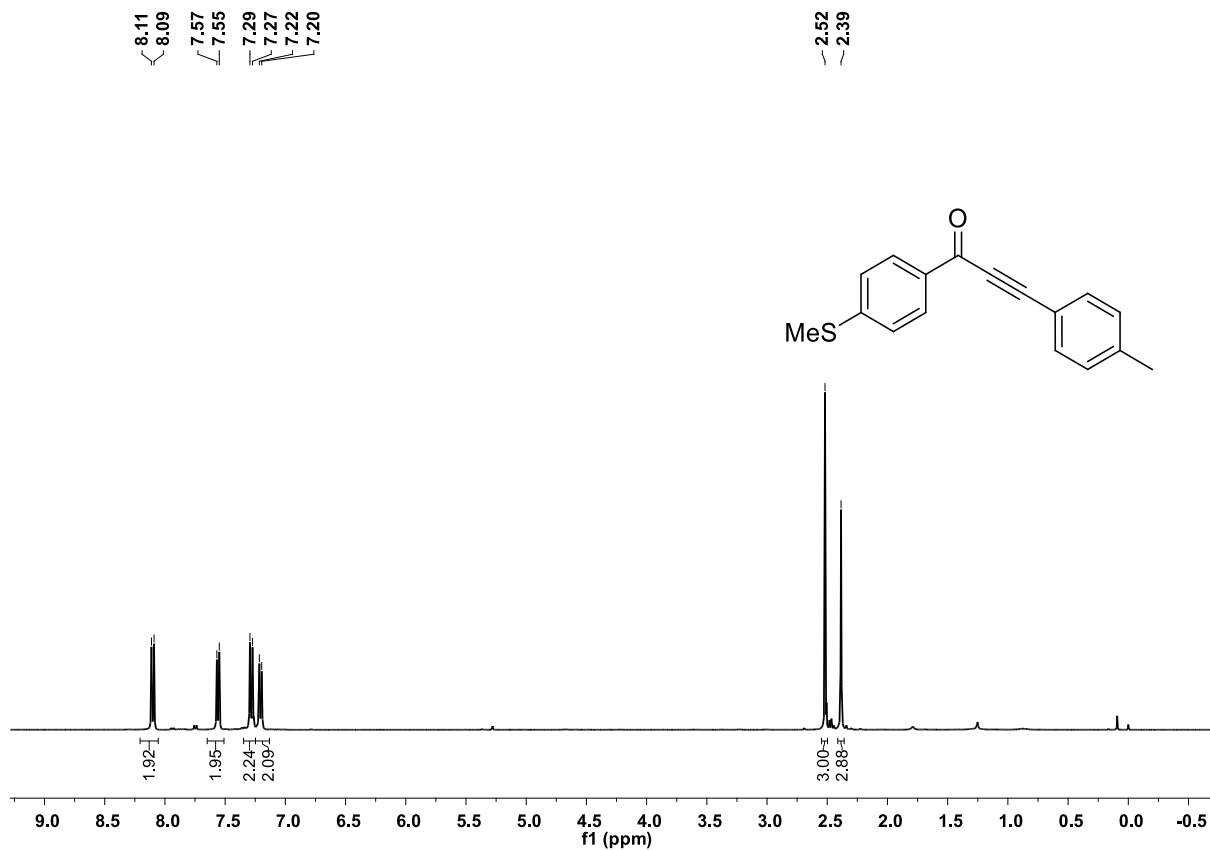
3i



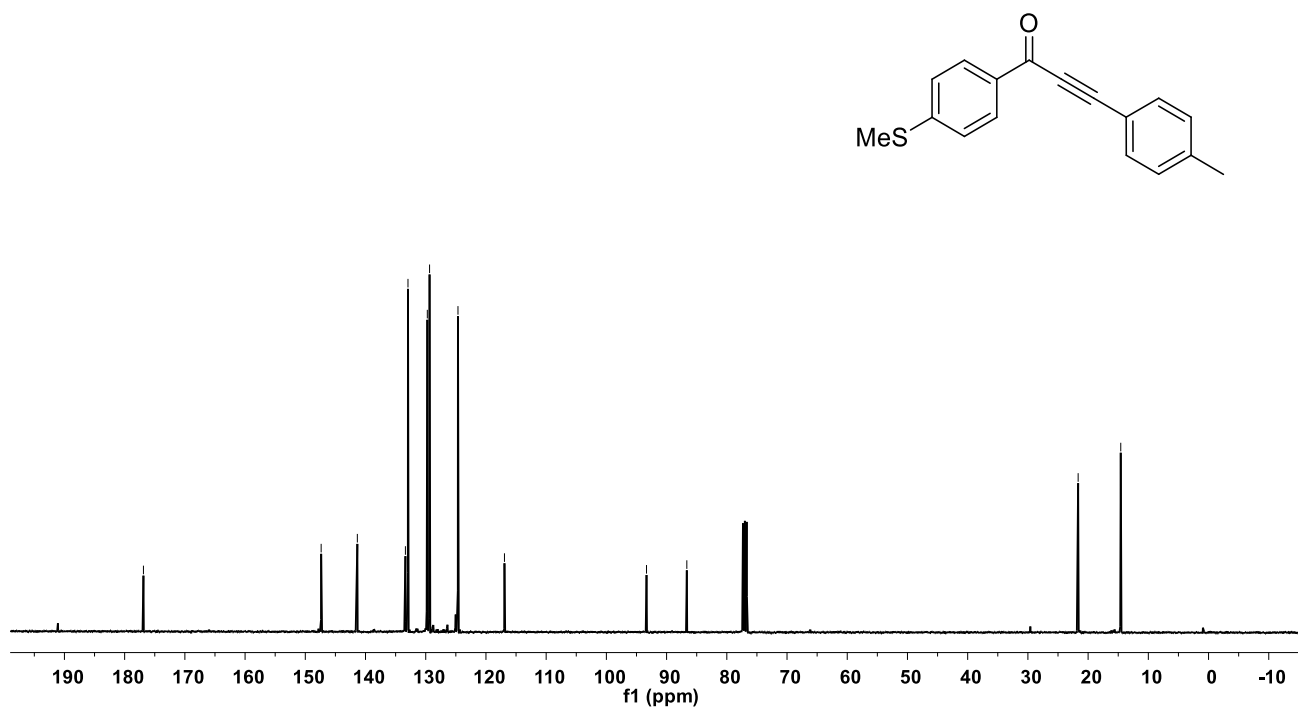
3j



3k

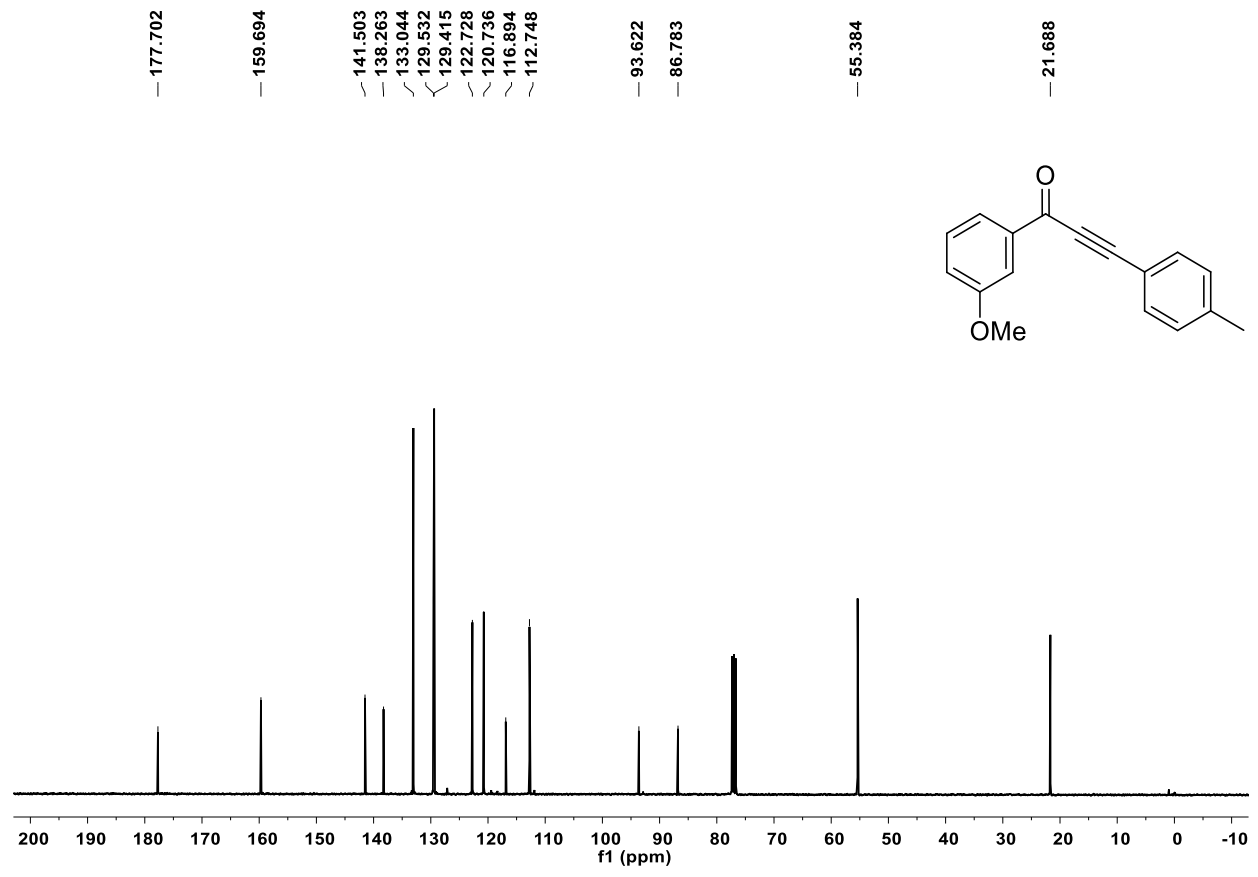
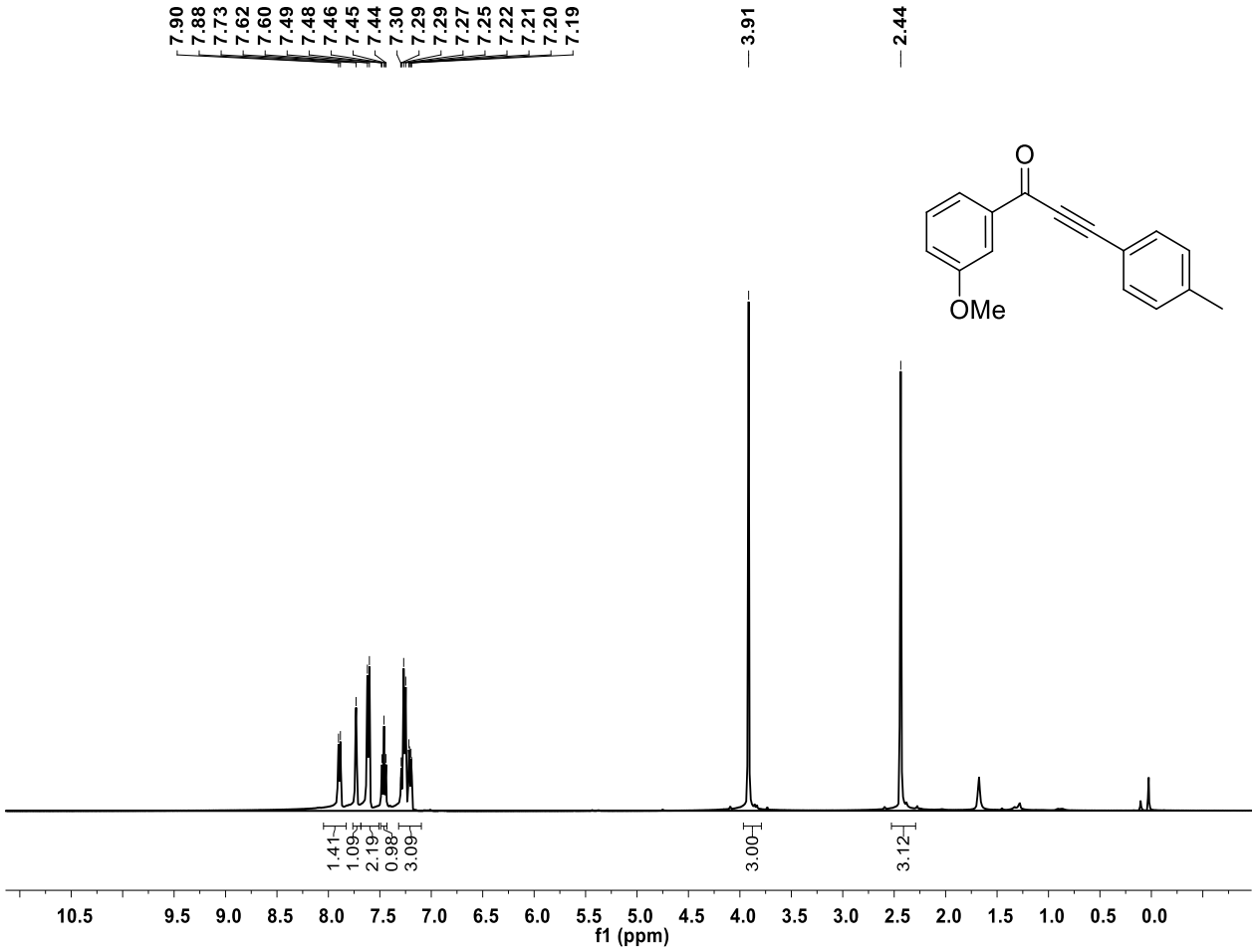


- 176.879
- 147.368
- 141.357
- 132.947
- 129.737
- 129.364
- 124.645
- 116.926
- 93.335
- 86.640
- 21.656
- 14.577

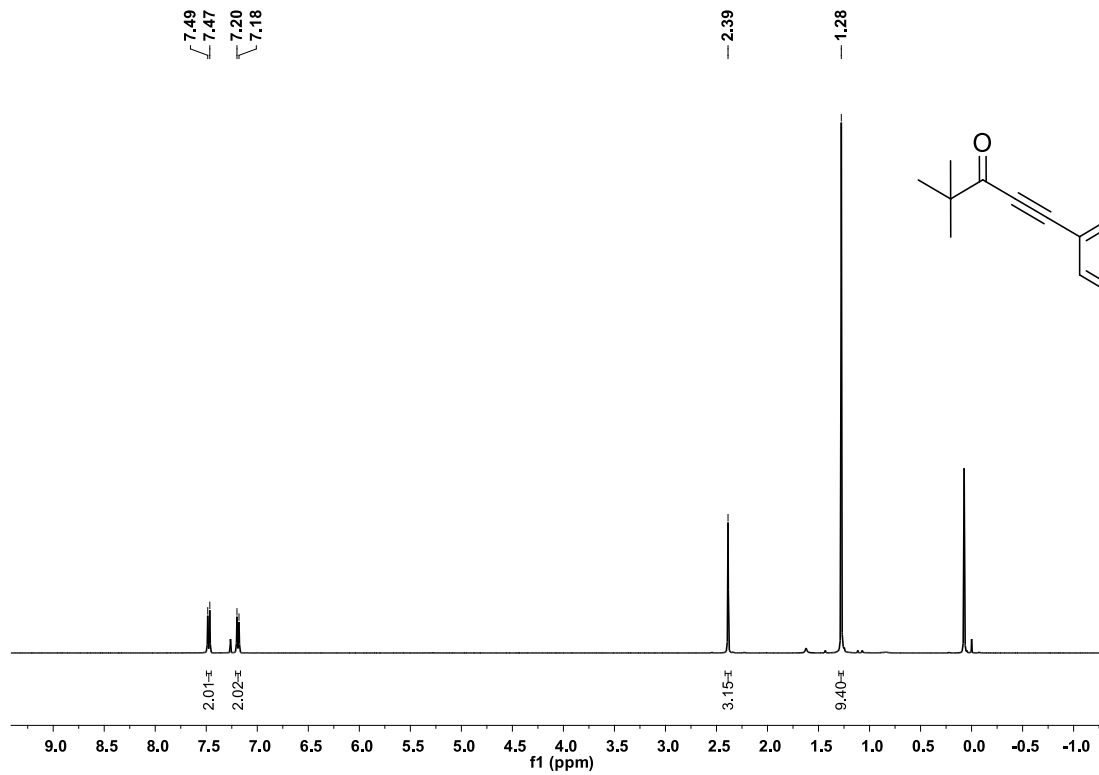




3l



### 3m



194.367

141.201

132.962

129.362

117.121

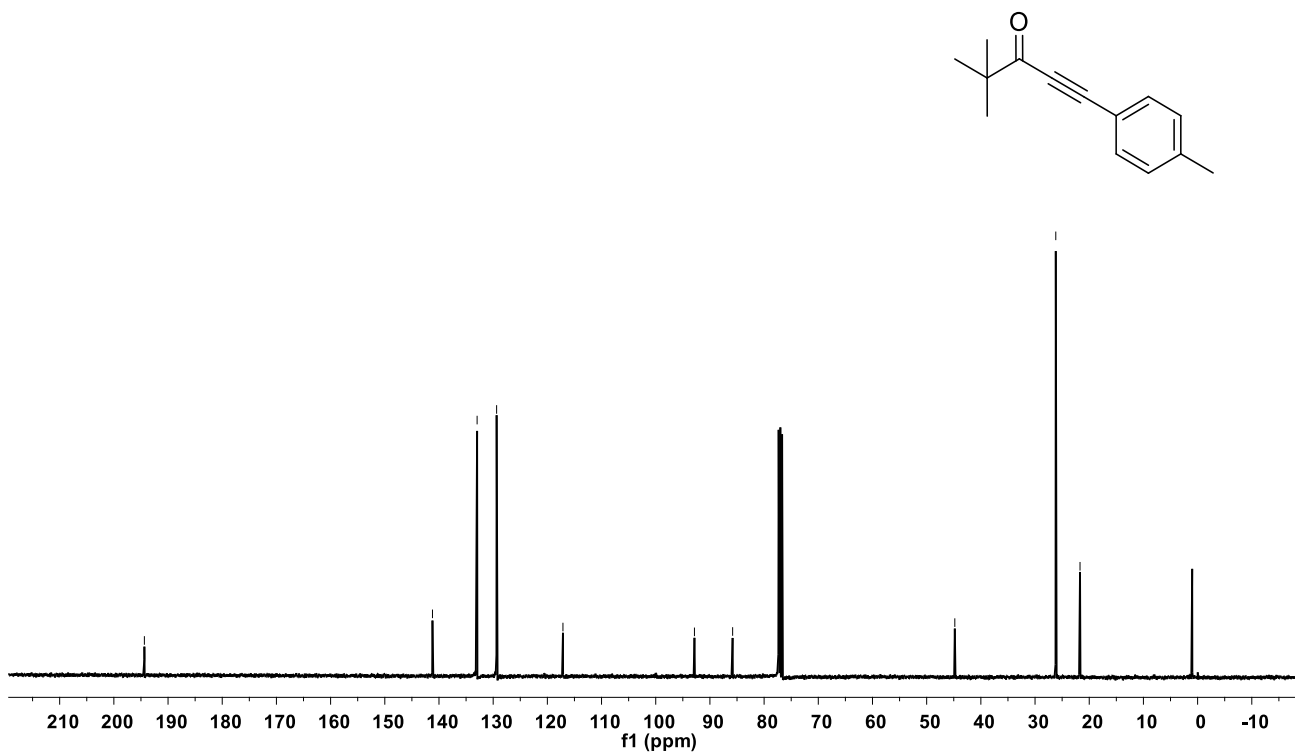
92.855

85.807

44.806

26.170

21.699



## Reference

- (1) G. Mosel, Th. Hübert, M. Nofz, R. Brenneis, P. Köcher, G. J. Kley, *Mater. Sci.* **2001**, *36*, 5017-5025
- (2) Chieh Chung, M. A. White, *Zeitschrift für Kristallographie* **1984**, *166*, 189-197
- (3) B. Ravel, M. J. Newville, *Synchrotron Radiat.* **2005**, *12*, 537
- (4) T. J. Ressler, *Synchrotron Radiat.* **1998**, *5*, 118
- (5) S. S. Palimkar, P. H. Kumar, N. R. Jogdand, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron Lett.* **2006**, *47*, 5527-5530.
- (6) M. Joshi, M. Patel, R. Tiwari, A. K. Verma, *J. Org. Chem.* **2012**, *77*, 5633-5645.
- (7) P. Gandeepan, K. Parthasarathy, T.-H. Su, C.-H. Cheng, *Adv. Synth. Catal.* **2012**, *354*, 457-468.
- (8) T. Toda, E. Hasegawa, T. Mukai, H. Tsuruta, T. Hagiwara,; T. Yoshida, *Chem. Lett.* **1982**, *11*, 1551-1554.
- (9) W. Kim, K. Park, A. Park,; J. Choe, S. Lee, *Org. Lett.* **2013**, *15*, 1654-1657.