ESI *for*

Oxidative C-C bond formation and C-N bond cleavage catalyzed by complexes of copper(I) with acridine based (E N E) pincers (E = S/Se), recyclable as a catalyst

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EXPERIMENTAL SECTION

General Remarks

All reactions were carried out in oven-dried round bottom flasks. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on a 0.25 mm silica gel plates (60F−254) and visualized under UV illumination at 254 nm and iodine chamber. Further visualization was achieved by iodine vapour adsorbed on silica gel depending on the product type. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Column chromatography was performed on silica gel 100–200 mesh using a mixture of hexane and ethyl acetate as eluent, and isolated compounds were characterized by ^{1}H NMR, ^{13}C{1H} NMR, and HRMS data. NMR spectra for all the samples were taken in deuterochloroform ($CDCl_3$) as the solvent. ^{1}H and ^{13}C-NMR spectra were recorded at ambient temperature on 300 MHz and 75 MHz spectrometer using tetramethylsilane (TMS) as internal reference. The chemical shifts are quoted in δ units, parts per million (ppm) up field from the signal of internal TMS. ^{1}H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, td = triplet of doublets), integration and coupling constant(s) *J* in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflectron experiments.

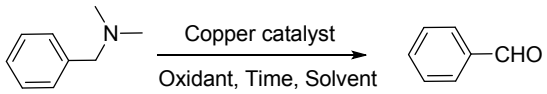
S1.1 Chemicals

$CuBr.SMe_2$, thiophenol, sodium hydroxide, diphenyldiselenide, sodium borohydride were procured from Sigma-Aldrich (USA). *N*,*N*-dimethylbenzylamine (Acros organics), Phenylacetylene (Spectrochem) were used as received. All the solvents of AR grade *i.e.*, acetone, tetrahydrofuran, ethanol were dried and distilled before use by known standard procedures.[1]

S1.2 Solubility and Stability of Complex

Both the complexes show good solubility in CH_2Cl_2, $CHCl_3$, CH_3CN, and DMF and DMSO and were found to be insoluble in hexane. The solutions of **1** and **2** in $CHCl_3$ were found stable under ambient conditions for several months (as evidenced by ^{1}H NMR of the solution).

Table S1. Optimization of the reaction conditions.[h]



1 6

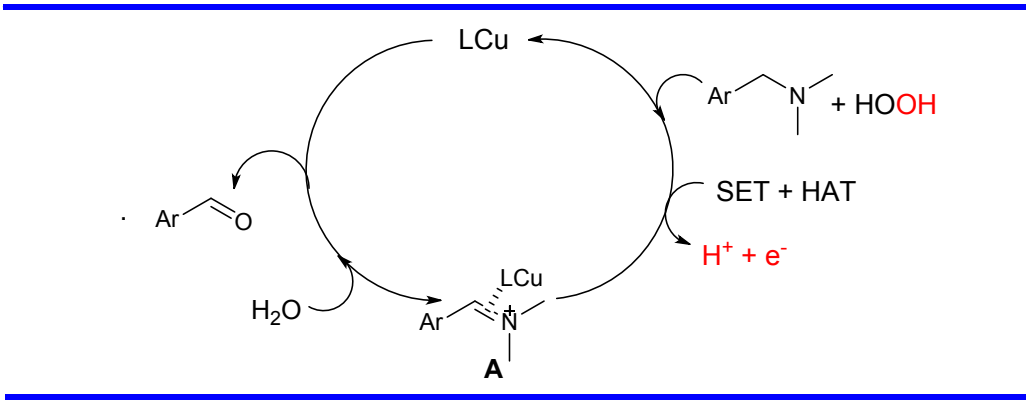
Entry no	Catalyst (mol%)	Oxidant (equiv.)	Solvent	Temp. (°C)	Yield[i] (%)
1	**C2** (5)	TBHP(1)	DMSO	100	34
2	CuCl (5, 10)	TBHP(1)	DMSO	100	17, 22
3	CuI (5, 10)	TBHP(1)	DMSO	100	7, 11
4	CuBr (5, 10)	TBHP(1)	DMSO	100	26, 33
5	$Cu(OAc)_2$ (5, 10)	TBHP(1)	DMSO	100	16, 18
6	**C2** (5)	TBHP(1)	Dioxane	100	**23**
7[c]	**C2** (5)	TBHP(1)	PhCl	100	19
8	**C2** (5)	TBHP(1)	DCE	100	27
9	**C2** (5)	TBHP(1)	none	100	38
10	**C2** (5)	TBHP(2)	none	100	32
11	**C2** (5)	TBHP(4)	none	100	14
12	**C2** (5)	H_2O_2(4)	none	100	51
13	**C2** (5)	H_2O_2(2)	none	100	79
14	**C2** (0.5, **1**)	**H_2O_2(2)**	**none**	**100**	43, **82**, 70[j], 21[k]
15	**C2** (1)	H_2O_2(1)	none	100	40
16	**C2** (1)	H_2O_2(2)	none	80	15
17	**C2** (1)	NBS	none	100	nd
18[d]	**C2** (1)	O_2 Balloon	none	100	nd
19	**C2** (1)	$K_2S_2O_8$	none	100	nd
20	**C2** (1)	Benzoquinone	none	100	nd
21	**C2** (1)	Atm. O_2	none	100	nd
22	**C2** (1)	none	none	100	nd
23	none	H_2O_2(2)	none	100	nd

[h]Reaction conditions. **1** (1 mmol), copper catalyst **C2**, H_2O_2 (30% aq. sol. in water, 2.2 equiv, 0.25 mL), 100 °C, 12 h, [i]Isolated Yield, [j]Complex **C1** as catalyst, [k]CuBr as catalyst.

Using the prepared Cu(I) catalyst **C2**, we investigated the oxidative benzylic bond cleavage (C-N) of **1a** (1 mmol) in the presence of TBHP (70% aq. Solution) and DMSO under nitrogen at 100 °C. After several optimizations (Table S1) the best conditions were found using **C2** (1 mol%), H_2O_2 (2 equiv.) at 100 °C for 12 h in air. After 12 h of reaction time, complete conversion was observed though the oxidized product benzaldehyde (**6a**) was isolated only in 34% yield. To improve the yield of product **6a**, optimization of reaction conditions was carried out (Table S1). With conventional copper salts such as CuCl, CuI, CuBr, and $Cu(OAc)_2$, **6a** was isolated in lower yields even on increasing the catalyst loading up to 10 mol% (Table S1, entries 2−5). Changing to solvents such as dioxane, chlorobenzene, and DCE did not gave encouraging results either (Table S1, entries 6−8). The yield increase under solvent-free condition but decreases on increasing amount of TBHP (Table S1, entries 9−11). Further we found that the reaction was much cleaner with H_2O_2 as the oxidant and 79% yield was (Table S1, entry 13) obtained. On lowering the catalytic loading to 1 mol % similar product yield was obtained but reducing it further led to a reduction in yield. Other oxidants such as NBS, oxygen, $K_2S_2O_8$ and benzoquinone and atmospheric oxygen were screened, and all were found to be ineffective in enabling the C-N bond cleavage (Table S1, entries 17-21). Control reaction in the absence of oxidant or copper catalyst did not give any product (Table S1, entry 22-23). To check the potential of the pincer catalyst we put the reaction with CuBr under optimized conditions, and got only 21% yield of the coupled product (Table S1, entry 14).

Mechanism

A plausible mechanism for the reaction is proposed in Scheme S1.



Scheme S1 Proposed Mechanism

A hydroxy radical is believed to be generated by copper-catalyzed decomposition of H_2O_2, which assists a single electron transfer (SET) from amine to generate a radical cation. This is followed by abstraction of the hydrogen with breaking a benzylic C–H bond of the radical cation to generate an iminium type intermediate and formation of complex **A** takes place which is followed by hydrolysis to afford the final product **6** along with regeneration of the copper catalyst. The time profile for C-N cleavage of **1a** (Figure S1(a)) shows that the yield increases continuously till 12 h of reaction time after which a 100% conversion is observed.

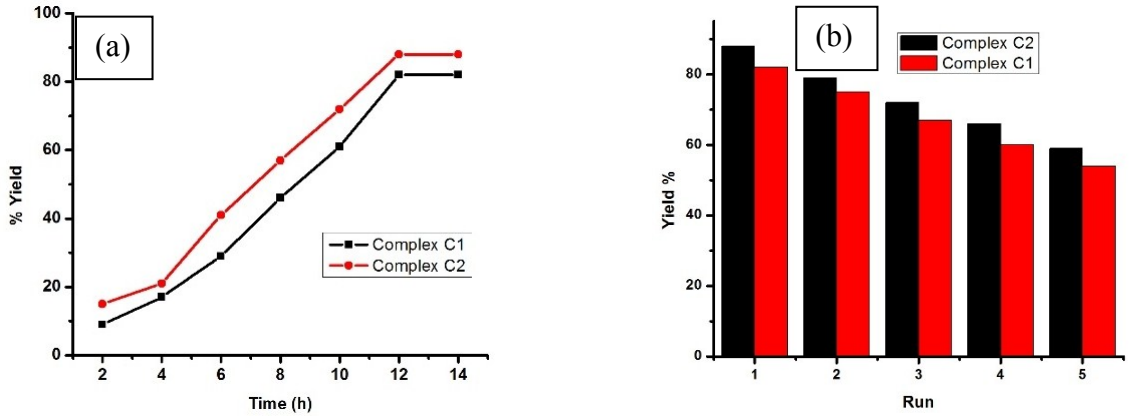


Figure S1(a). Time Profiles of C-N cleavage with Complexes **C1** and **C2. (b)** Reusability of **C1** and **C2** as a catalyst in C-N Cleavage

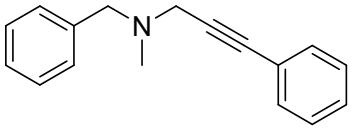
To test the reusability & recyclability of the catalyst, a fresh lot of reactants, **1a** (1 mmol), H_2O_2 (0.25 mL) were added on completion of the first reaction cycle and the reaction was carried out under optimized conditions for 12 h. The process was repeated for 5 cycles and the results are shown in Figure S1(b). The data indicated that a significant amount of catalyst remains alive even after five cycles.

General procedure for the preparation of *N, N*-dimethyl benzylamines:

In a beaker containing 30 mL aq. solution of KOH (73.1 mmol), dimethylamine hydrochloride (38.5 mmol) was added, and the contents were stirred for 5 min. This solution was then added to a 100 mL round bottom flask containing benzyl bromide or chloride (5.0 mmol) in 30 mL DCM. The reaction mixture was stirred for 5h at room temperature. After completion of the reaction, the mixture was washed with brine (1 x 10 mL), subsequently with distilled water (2 x 10 mL) and then dried over anhydrous Na_2SO_4. Solvent was evaporated.

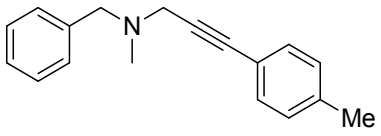
Spectral Data:

N-benzyl-N-methyl-3-phenylprop-2-yn-1-amine (3a)[2]:



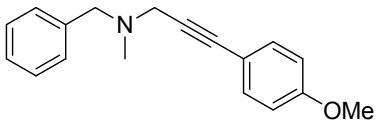
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.52-7.49 (m, 2H), 7.42-7.39 (m, 3H), 7.37-7.28 (m, 5H), 3.68 (s, 2H), 3.55 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.5, 131.8, 129.3, 128.4, 128.3, 128.0, 127.2, 123.3, 85.7, 84.4, 60.3, 45.8, 42.0.

N-benzyl-N-methyl-3-(p-tolyl)prop-2-yn-1-amine (3b)[2]:



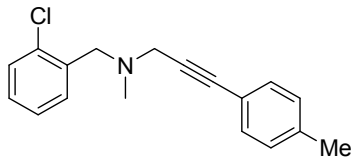
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.39-7.37 (m, 5H), 7.33-7.27 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 3.66 (s, 2H), 3.52 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.4, 138.0, 131.6, 129.2, 129.0, 128.3, 127.1, 120.2, 85.7, 83.6, 60.2, 45.7, 41.9, 21.4.

N-benzyl-3-(4-methoxyphenyl)-N-methylprop-2-yn-1-amine (3c)[2]:



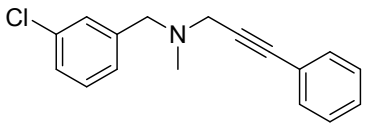
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.43-7.40 (m, 5H), 7.37-7.34 (m, 3H), 7.31-7.26 (m, 1H), 6.85 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 3.65 (s, 2H), 3.51 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 159.4, 138.5, 133.3, 129.2, 128.3, 127.2, 115.5, 113.9, 85.5, 82.9, 60.3, 55.3, 45.8, 42.0.

N-(2-chlorobenzyl)-N-methyl-3-(p-tolyl)prop-2-yn-1-amine (3d)[2]:



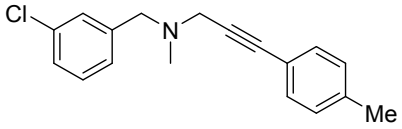
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.37 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 7.15 (s, 1H), 7.11 (td, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 3.66 (s, 2H), 3.47 (s, 2H), 2.33 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.2, 136.3, 134.7, 131.7, 131.2, 129.7, 129.1, 128.5, 126.7, 120.3, 85.9, 83.7, 57.1, 46.3, 42.1, 21.5.

N-(3-chlorobenzyl)-N-methyl-3-phenylprop-2-yn-1-amine (3e)[2]:



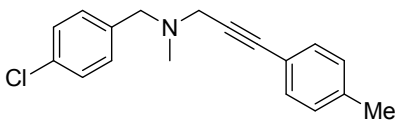
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.51 (m, 2H), 7.44 (s, 1H), 7.37 (s, 3H), 7.30 (s, 3H), 3.66 (s, 2H), 3.57 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 140.8, 134.3, 131.8, 129.6, 129.2, 128.3, 128.1, 127.4, 127.3, 123.2, 85.9, 84.2, 59.7, 45.9, 42.0.

N-(3-chlorobenzyl)-N-methyl-3-(p-tolyl)prop-2-yn-1-amine (3f)[2]:



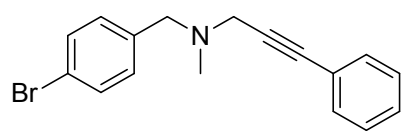
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.30 (d, J_1 = 3.3 Hz, 2H), 7.26 (s, 1H), 7.16 (s, 3H), 7.04 (d, J_1 = 8.1 Hz, 2H), 3.53 (s, 2H), 3.43 (s, 2H), 2.31 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 138.2, 134.2, 131.6, 129.5, 129.0, 127.4, 127.2, 120.1, 85.9, 83.3, 59.6, 45.9, 41.9, 21.4.

N-(4-chlorobenzyl)-N-methyl-3-(p-tolyl)prop-2-yn-1-amine (3g)[2]:



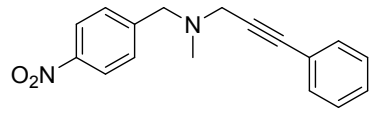
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.28 (d, J = 7.5 Hz, 2H), 7.23 (s, 4H), 7.05 (d, J = 7.5 Hz, 2H), 3.53 (s, 2H), 3.42 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.1, 137.0, 132.9, 131.6, 130.5, 129.0, 128.4, 120.0, 85.9, 83.3, 59.4, 45.7, 41.9, 21.4.

N-(4-bromobenzyl)-N-methyl-3-phenylprop-2-yn-1-amine (3h)[2]:



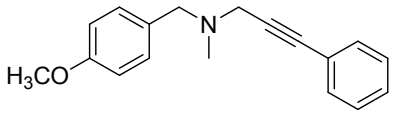
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.46-7.43 (m, 4H), 7.31-7.29 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 8.7 Hz, 1H), 3.58 (s, 2H), 3.49 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 137.5, 131.7, 131.4, 130.8, 128.3, 128.1, 123.9, 121.0, 85.8, 84.1, 59.5, 45.6, 41.9.

N-methyl-N-(4-nitrobenzyl)-3-phenylprop-2-yn-1-amine (3i)[2]:



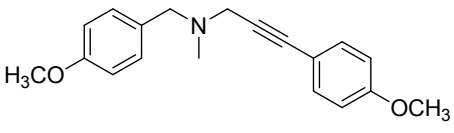
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.48-7.45 (m, 2H), 7.33-7.31 (m, 3H), 3.75 (s, 2H), 3.55 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 146.4, 131.6, 129.6, 128.3, 128.2, 123.5, 122.9, 86.0, 83.7, 59.4, 46.0, 41.9.

N-(4-methoxybenzyl)-N-methyl-3-phenylprop-2-yn-1-amine (3j)[2]:



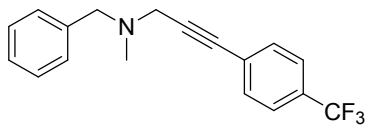
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.50-7.46 (m, 2H), 7.33-7.31 (m, 4H), 7.28 (s, 1H), 6.88 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.60 (s, 2H), 3.51 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 131.7, 130.4, 128.3, 128.0, 123.0, 113.9, 85.7, 84.4, 59.5, 55.2, 45.5, 41.9.

N-(4-methoxybenzyl)-3-(4-methoxyphenyl)-N-methylprop-2-yn-1-amine (3k)[2]:



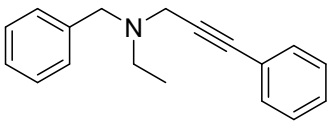
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.41 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.87 (t, J = 7.5 Hz, 4H), 3.82 (s, 3H), 3.81 (s, 3H), 3.58 (s, 2H), 3.49 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 158.8, 133.1, 130.5, 130.5, 115.5, 113.9, 113.7, 85.5, 82.9, 59.6, 55.3, 55.3, 45.6, 41.9.

N-benzyl-N-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (3l)[2]:



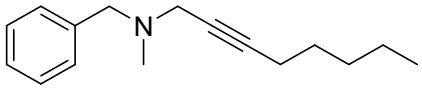
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.61-7.55 (m, 4H), 7.39-7.31 (m, 3H), 7.28 (s, 2H), 3.66 (s, 2H), 3.55 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.2, 132.0, 129.3, 129.6, 128.4, 127.4, 125.3, 125.2, 125.2, 87.3, 84.5, 60.4, 45.7, 42.0.

N-benzyl-N-ethyl-3-phenylprop-2-yn-1-amine (3m)[2]:



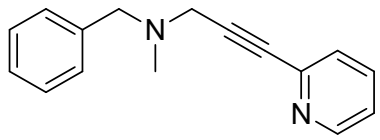
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.49-7.47 (m, 2H), 7.43-7.37 (m, 3H), 7.35-7.30 (m, 5H), 3.70 (s, 2H), 3.54 (s, 2H), 2.67 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 138.9, 131.8, 129.3, 129.0, 128.3, 128.0, 127.1, 123.5.

N-benzyl-N-methyloct-2-yn-1-amine (3n)[2]:



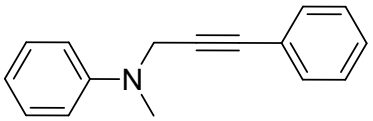
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.27-7.17 (m, 5H), 3.45 (s, 2H), 3.20 (s, 2H), 2.25 (s, 3H), 2.17 (t, J = 6.6 Hz, 2H), 1.53-1.44 (m, 2H), 1.40-1.19 (m, 4H), 0.85 (t, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6, 129.3, 128.3, 127.1, 85.9, 74.6, 60.2, 45.5, 41.9, 31.1, 28.7, 22.2, 18.7, 14.0.

N-benzyl-N-methyl-3-(pyridin-2-yl)prop-2-yn-1-amine (3o)[2]:



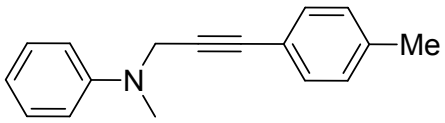
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 8.51 (d, J = 4.5 Hz, 1H), 7.58 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.32-7.23 (m, 3H), 7.22-7.14 (m, 3H), 3.60 (s, 2H), 3.50 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 138.2, 136.1, 129.2, 128.3, 127.2, 127.1, 122.7, 85.3, 84.9, 60.2, 45.6, 41.9, 29.7.

N-methyl-N-(3-phenylprop-2-yn-1-yl)aniline (5a)[2]:



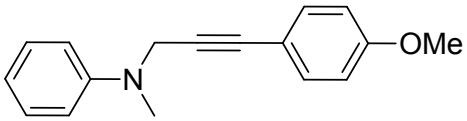
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.36-7.34 (m, 2H), 7.29-7.24 (m, 5H), 6.90 (d, J = 7.8 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 4.25 (s, 2H), 3.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 149.3, 131.7, 129.1, 128.2, 128.1, 123.0, 118.2, 114.4, 85.0, 84.2, 43.3, 38.7.

N-methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)aniline (5b)[2]:



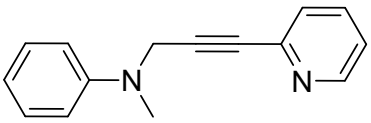
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.31-7.25 (m, 4H), 7.07 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 6.81 (t, J = 7.5 Hz, 1H), 4.25 (s, 2H), 3.03 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 149.4, 138.1, 131.6, 129.1, 128.9, 120.0, 118.1, 114.4, 84.26, 84.23, 43.3, 38.7, 21.4.

N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-N-methylaniline (5c)[2]:



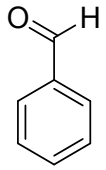
White solid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.32-7.24 (m, 4H), 6.91 (d, J = 8.4 Hz, 2H), 6.83-6.78 (m, 3H), 4.24 (s, 2H), 3.78 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 159.4, 149.4, 133.1, 129.1, 118.1, 115.2, 114.4, 113.8, 84.0, 83.5, 55.2, 43.3, 38.6.

N-methyl-N-(3-(pyridin-2-yl)prop-2-yn-1-yl)aniline (5d)[2]:



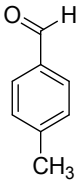
Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 8.52 (d, J = 4.8 Hz, 1H), 7.57 (td, J_1 = 7.8 Hz, J_2= 1.8 Hz 1H), 7.33-7.24 (m, 3H), 7.19-7.15 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.79 (t, J = 8.4 Hz, 1H), 4.28 (s, 2H), 3.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 149.9, 149.1, 143.3, 136.1, 129.1, 127.3, 122.8, 118.2, 114.3, 85.4, 83.6, 43.1, 38.8.

Benzaldehyde (6a)[3]:



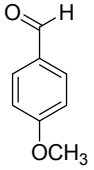
Colourless liquid (^{1}H NMR (300 MHz, $CDCl_3$): 10.02 (s, 1H), 7.88 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55-7.51 (m, 2H).

4-methylbenzaldehyde (6b)[3]:



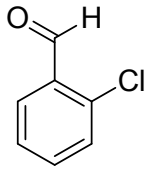
Colourless liquid ^{1}H NMR (300 MHz, $CDCl_3$): 9.94 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H).

4-methoxybenzaldehyde (6c)[3]:



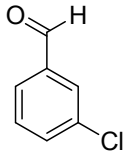
Colourless liquid ^{1}H NMR (300 MHz, $CDCl_3$): 9.87 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).

2-chlorobenzaldehyde (6d)[3]:



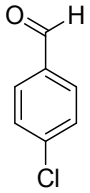
Colourless liquid ^{1}H NMR (300 MHz, $CDCl_3$): 10.45 (s, 1H), 7.89 (dd, *J* = 8.1 Hz, 2.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.42 (dd, *J* = 8.4Hz, 1.2 Hz, 1H), 7.38-7.33 (m, 1H).

3-chlorobenzaldehyde (6e)[3]:



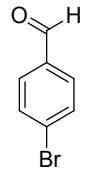
Colourless liquid ^{1}H NMR (300 MHz, $CDCl_3$): 9.98 (s, 1H), 7.86 (t, *J* = 1.8 Hz, 2H), 7.85-7.82 (m, 1H), 7.62-7.59 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 1H).

4-chlorobenzaldehyde (6f)[3]:



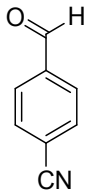
Colourless Solid ^{1}H NMR (300 MHz, $CDCl_3$): 9.99 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H).

4-bromobenzaldehyde (6g)[3]:



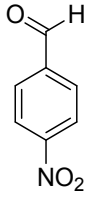
White solid. ^{1}H NMR (300 MHz, $CDCl_3$): 10.1 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H).

4-formylbenzonitrile (6h)[3]:



White solid. ^{1}H NMR (300 MHz, $CDCl_3$): 10.1 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H).

4-nitrobenzaldehyde (6i)[3]:



White Yellow Solid. ^{1}H NMR (300 MHz, $CDCl_3$): 10.2 (s, 1H), 8.41 (d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H).

Crystallographic Description:

The diffraction data on single crystals of **C1** and **C2** were collected on Bruker AXS SMART Apex CCD diffractometer at 298(2) K using Mo Kα radiations (λ = 0.71073 Å) radiations. Frames were collected by ω, φ, and 2θ-rotations with full-quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. All data were processed using the programs SAINT routine in APEX3. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-2014/7 program.[4] Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Further information on the crystal structure determination has been given as table S2 and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications numbers, 1891552 and 1891554. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

References

1. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry,* 5th Eds. ELBS, Longman Group U K Ltd., 1989.
2. S. Gupta, H. Joshi, N. Jain, Ajai K. Singh, *J. Mol. Cat. A: Chem*, 2016, **423**, 135.
3. S. Pan, S. Yan, T. Osako, Y. Uozumi, *Synlett,* 2018, **29**, 1152.
4. (a) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, **46**, 467−473; (b) G. M. Sheldrick, SHELXLNT, version 6.12; University of Gottingen: Germany, 2000; (c) APEX3 and SAINT; Bruker−Nonius AXS Inc.: Madison, WI, 2015; (d) G. M. Sheldrick, SHELXTL, version 2014/7; Universität Göttingen: Germany, 2014. http://shelx.uni-ac.gwdg.de/SHELX/index.php.

(Table S2) Crystallographic description and parameters of C1 and C2:

Identification code	**C1**	**C2**
Empirical formula	C_{27} H_{21} Br Cu N S_2	C_{27} H_{21} Br Cu N Se_2
Formula weight	567.02	660.82
Temperature	100(2) K	297(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions	a = 13.3598(11) Å, α= 90°.	a = 13.5796(15) Å, α= 90°.
	b = 10.9050(9) Å, β= 95.426(2)°.	b = 11.0678(12) Å, β= 95.350(3)°.
	c = 15.8704 (14) Å, γ= 90°.	c = 16.1740(19) Å, γ= 90°.
Volume	2301.8(3) $Å^3$	2420.3(5) $Å^3$
Z	4	4
Density (calculated)	1.636 Mg/m^3	1.814 Mg/m^3
Absorption coefficient	2.882 mm^{-1}	5.577 mm^{-1}
F(000)	1144.0	1288.0
Crystal size	0.18 x 0.16 x 0.15 mm^3	0.20 x 0.18 x 0.16 mm^3
Theta range for data collection	2.269 to 28.346°.	2.233 to 28.341°.
Index ranges	-17<=h<=17, -14<=k<=14, -21<=l<=21	-18<=h<=16, -14<=k<=14, -21<=l<=21
Reflections collected	50632	21003
Independent reflections	5741 [R(int) = 0.2331]	6039 [R(int) = 0.1137]
Completeness to theta = 25.00°	100.0 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5741 / 0 / 289	6039 / 0 / 289
Goodness-of-fit on F^2	1.054	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1512	R1 = 0.0794, wR2 = 0.1674

R indices (all data)	R1 = 0.1432, wR2 = 0.1889	R1 = 0.1816, wR2 = 0.2097
Largest diff. peak and hole	1.503 and -0.631 e.A^{-3}	1.174 and -0.648 e.A^{-3}
CCDC	1891552	1891554

Table S3. Selected bond lengths [Å] and bond angles [^{o}]

	Bond length [Å]	Bond angle [o]
1	Br(1)—Cu(1) 2.3771(9) Cu(1)—N(1) 2.196(5) Cu(1)—S(2) 2.2482(17) Cu(1)—S(1) 2.2979(16) S(2)—C(22) 1.777(6) S(2)—C(21) 1.844(6) S(1)—C(6) 1.774(6) S(1)—C(7) 1.845(7) N(1)—C(16) 1.345(8) N(1)—C(13) 1.361(7)	N(1)—Cu(1)—S(2) 96.69(13) N(1)—Cu(1)—S(1) 97.18(13) S(2)—Cu(1)—S(1) 115.86(6) N(1)—Cu(1)—Br(1) 105.15(13) S(2)— Cu(1)—Br(1) 128.57(5) S(1)— Cu(1)—Br(1) 106.94(5) C(22)— S(2)—C(21) 101.8(3) C(22)— S(2)— Cu(1) 112.2(2) C(21)— S(2)— Cu(1) 99.3(2) C(6)—S(1)—C(7) 101.9(3) C(6)—S(1)— Cu(1) 109.0(2) C(7)—S(1)— Cu(1) 97.4(2) C(16)—N(1)—C(13) 118.2(5) C(16)—N(1)— Cu(1) 109.4(4) C(13)—N(1)— Cu(1) 108.1(4) N(1)—C(13)—C(12) 122.6(5) N(1)—C(13)—C(8) 117.4(5) C(12)—C(13)—C(8) 120.0(6) C(27)—C(22)—C(23) 119.7(6) C(27)—C(22)— S(2) 119.9(5) C(23)—C(22)— S(2) 120.4(5)

		N(1)—C(16)—C(15) 122.8(6) N(1)—C(16)—C(20) 118.5(6)
2	Se(1)—C(6) 1.924(9) Se(1)—C(7) 1.959(9) Se(1)—Cu(1) 2.4177(13) Se(2)—C(22) 1.907(9) Se(2)—C(21) 1.981(9) Se(2)—Cu(1) 2.3603(14) Br(1)—Cu(1) 2.3627(13) Cu(1)—N(1) 2.288(6) N(1)—C(16) 1.323(10) N(1)—C(13) 1.378(10)	C(6)—Se(1)—C(7) 99.5(4) C(6)—Se(1)—Cu(1) 109.5(2) C(7)—Se(1)—Cu(1) 93.2(3) C(22)—Se(2)—C(21) 100.8(4) C(22)—Se(2)—Cu(1) 109.2(3) C(21)—Se(2)—Cu(1) 96.3(2) N(1)—Cu(1)—Se(2) 95.41(17) N(1)—Cu(1)—Br(1) 106.17(16) Se(2)—Cu(1)—Br(1) 131.90(6) N(1)—Cu(1)—Se(1) 97.32(17) Se(2)—Cu(1)—Se(1) 112.86(5) Br(1)—Cu(1)—Se(1) 106.45(5) C(16)—N(1)—C(13) 118.3(7) C(16)—N(1)—Cu(1) 106.9(5) C(13)—N(1)—Cu(1) 105.7(5) N(1)—C(13)—C(12) 122.3(8) N(1)—C(13)—C(8) 117.8(8) C(5)—C(6)—Se(1) 117.9(7) C(1)—C(6)—Se(1) 121.7(7) N(1)—C(16 —C(15) 123.6(8) N(1)—C(16)—C(20) 118.7(8)

Copies of ^{1}HNMR, ^{13}CNMR and HRMS data of synthesized compounds

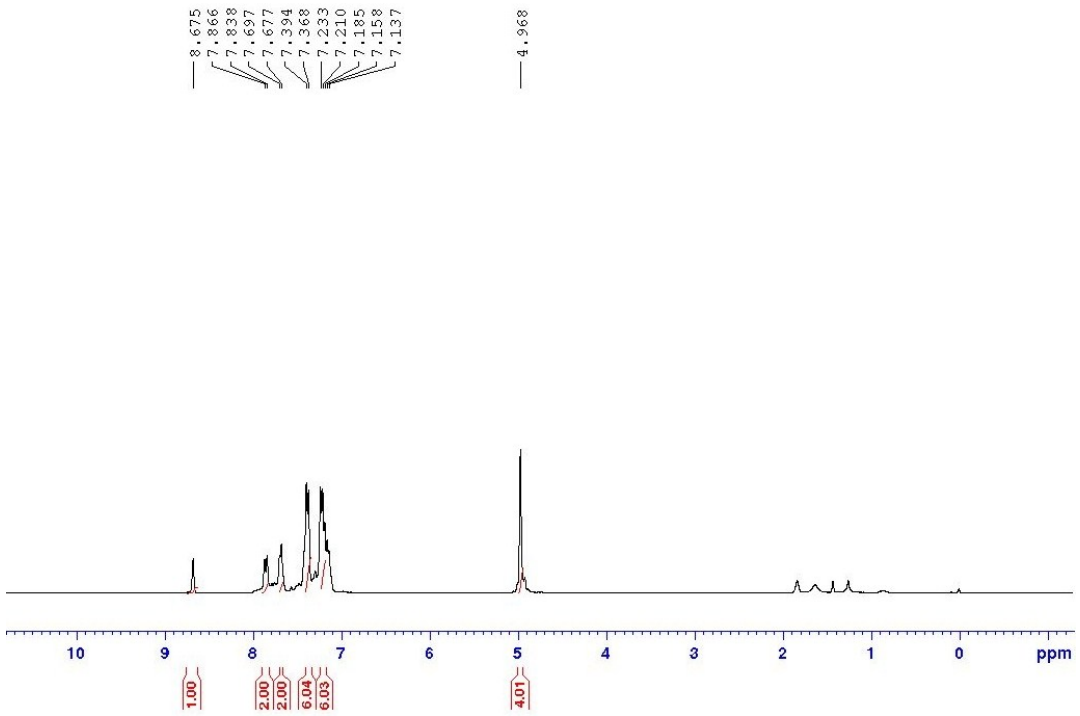


Figure S2: ^{1}H NMR of L1

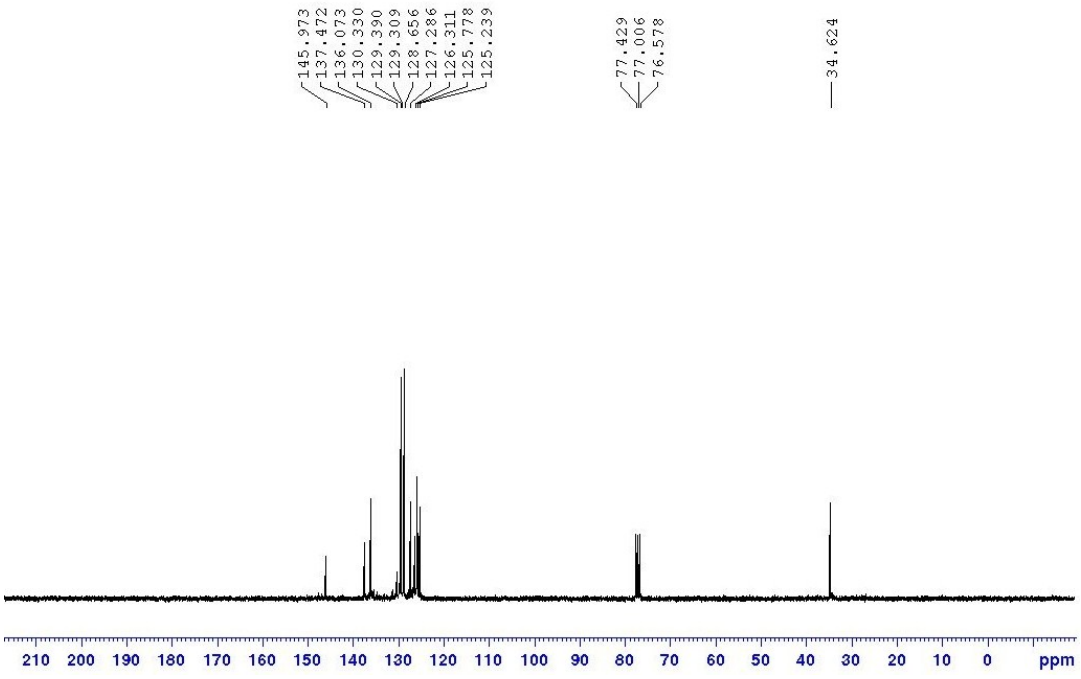


Figure S3: ^{13}C{^{1}H} NMR of L1

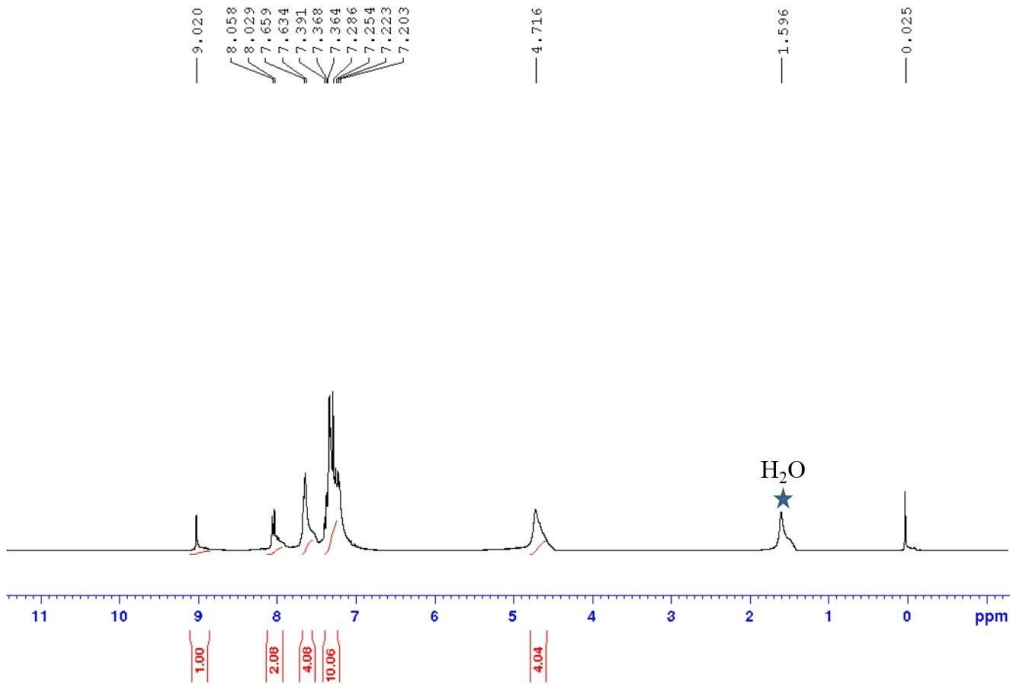


Figure S4: ^{1}H NMR of C1

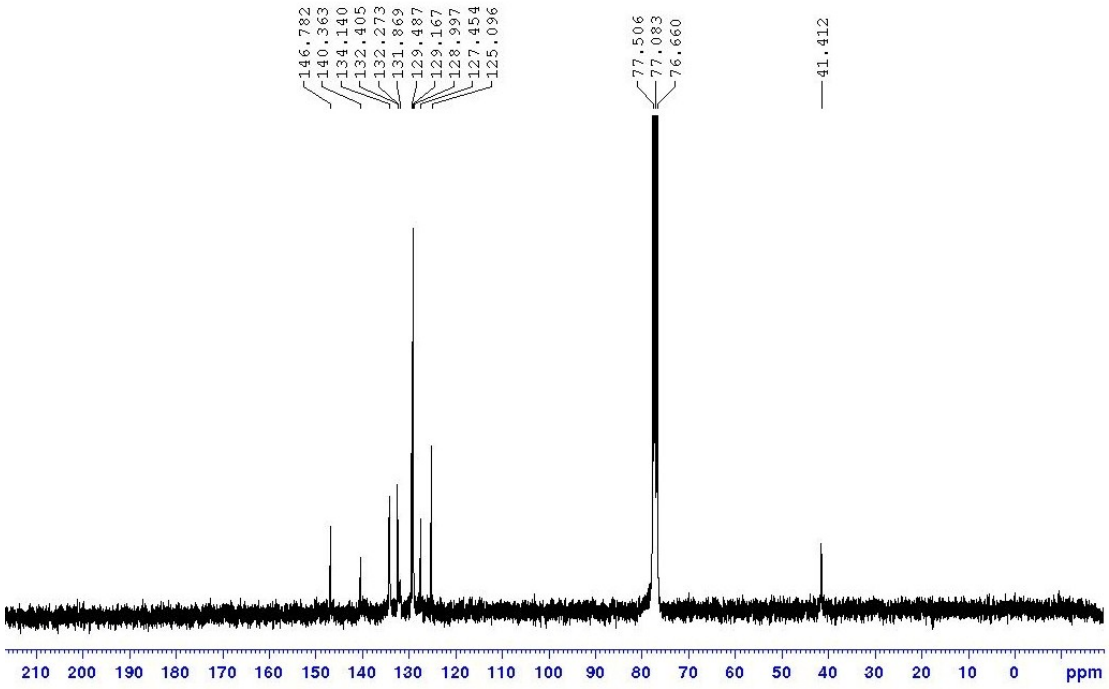


Figure S5: ^{13}C{^{1}H} NMR of C1

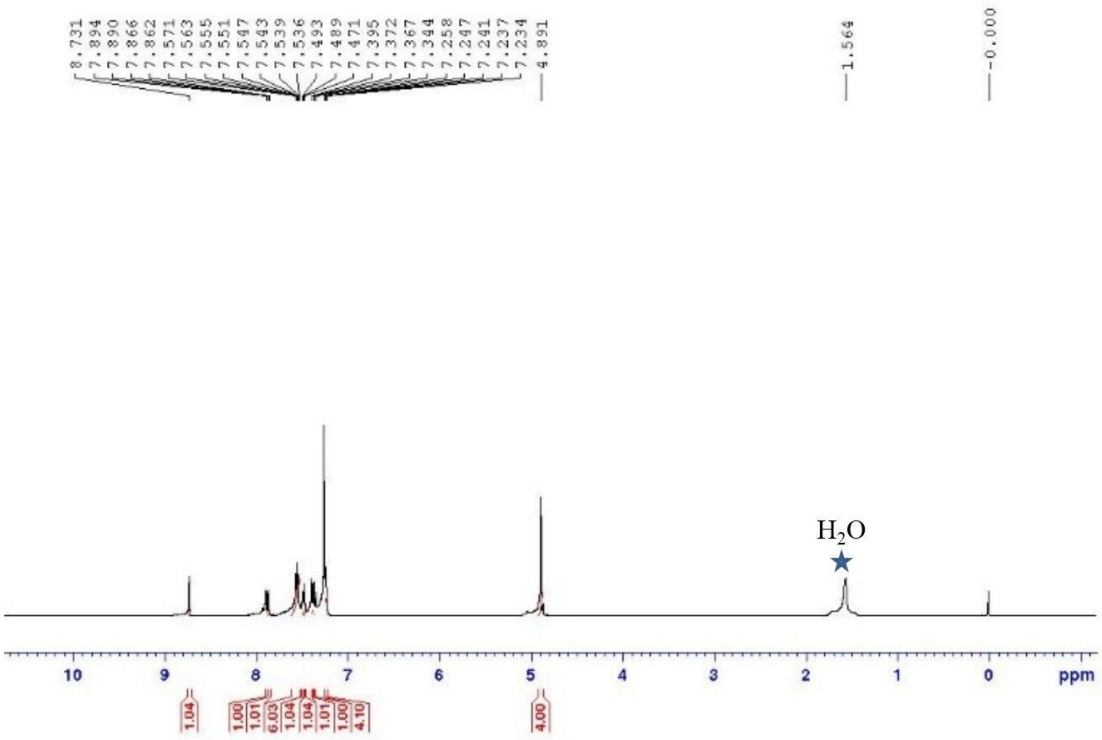


Figure S6: ^{1}H NMR of L2

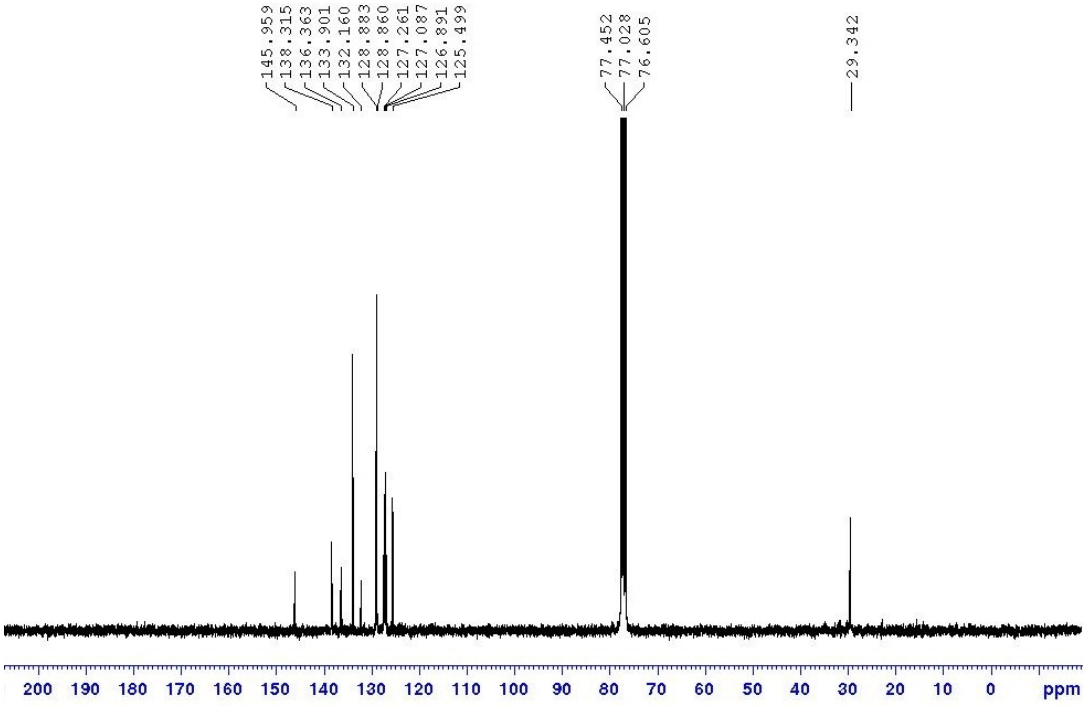


Figure S7: ^{13}C{^{1}H} NMR of L2

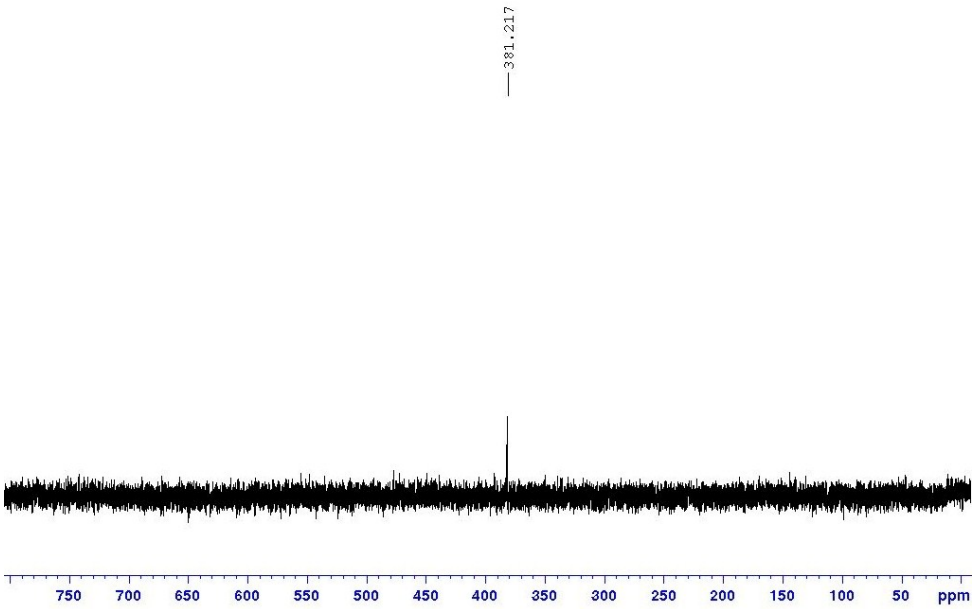


Figure S8: $^{77}Se\{^{1}H\}$ NMR of L2

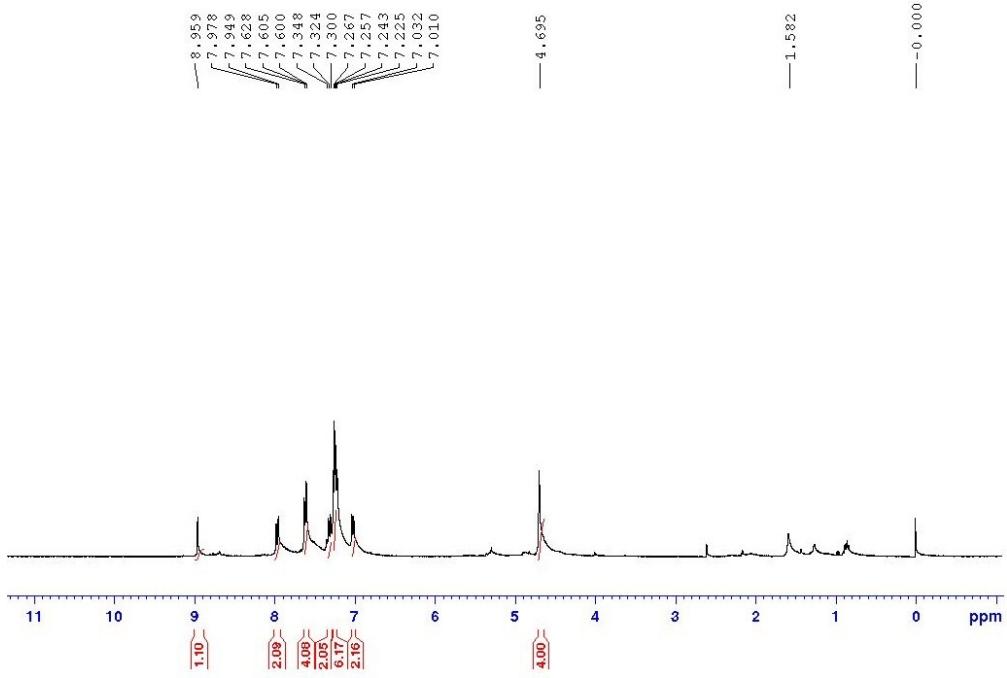


Figure S9: ^{1}H NMR of C2

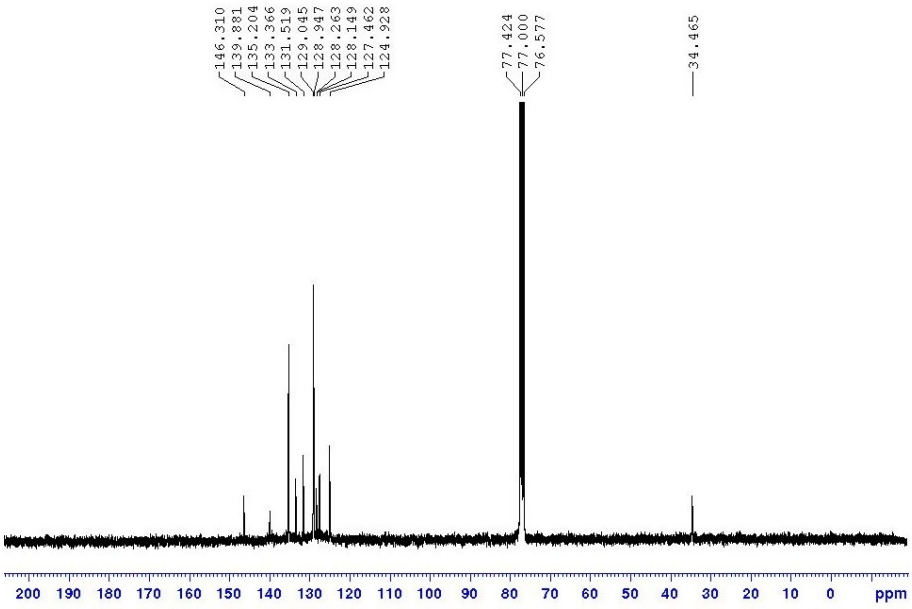


Figure S10: $^{13}C\{^{1}H\}$ NMR of C2

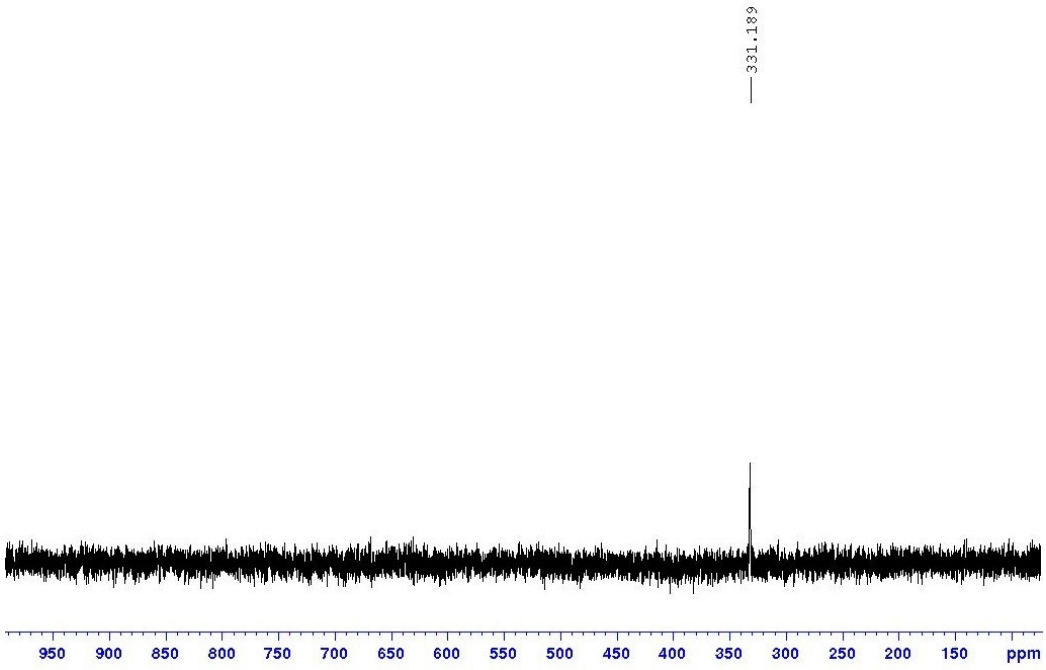


Figure S11: $^{77}Se\{^{1}H\}$ NMR of C2

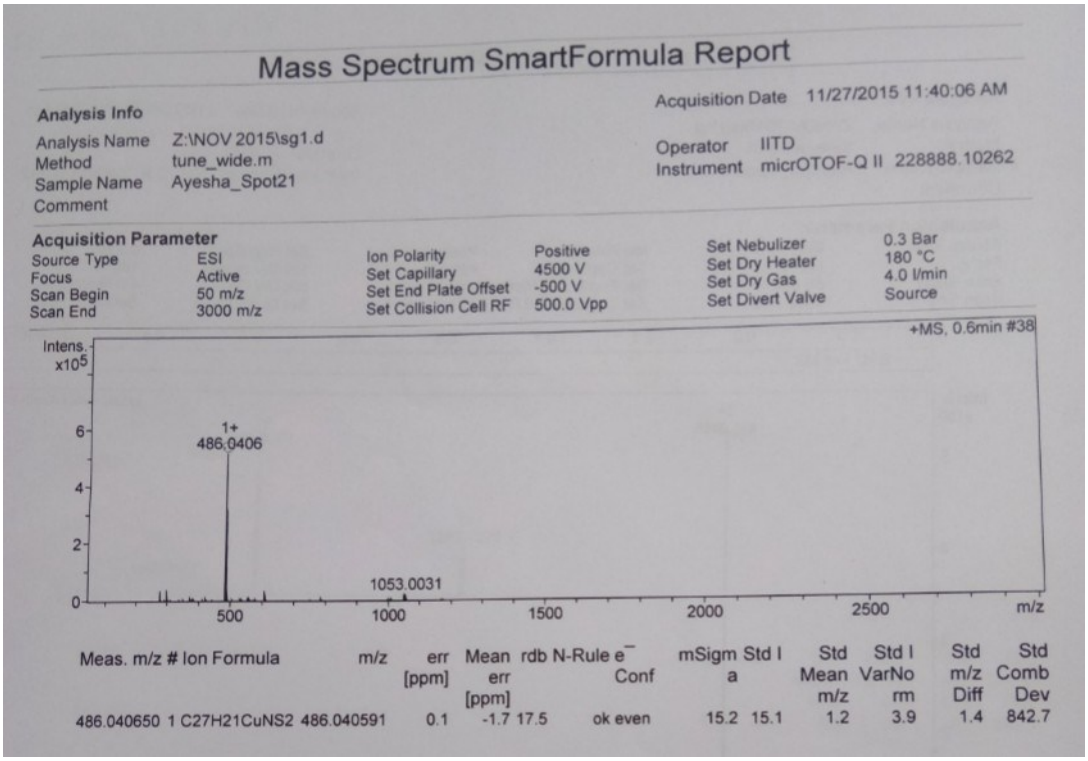


Figure S12: Mass Spectrum of C1

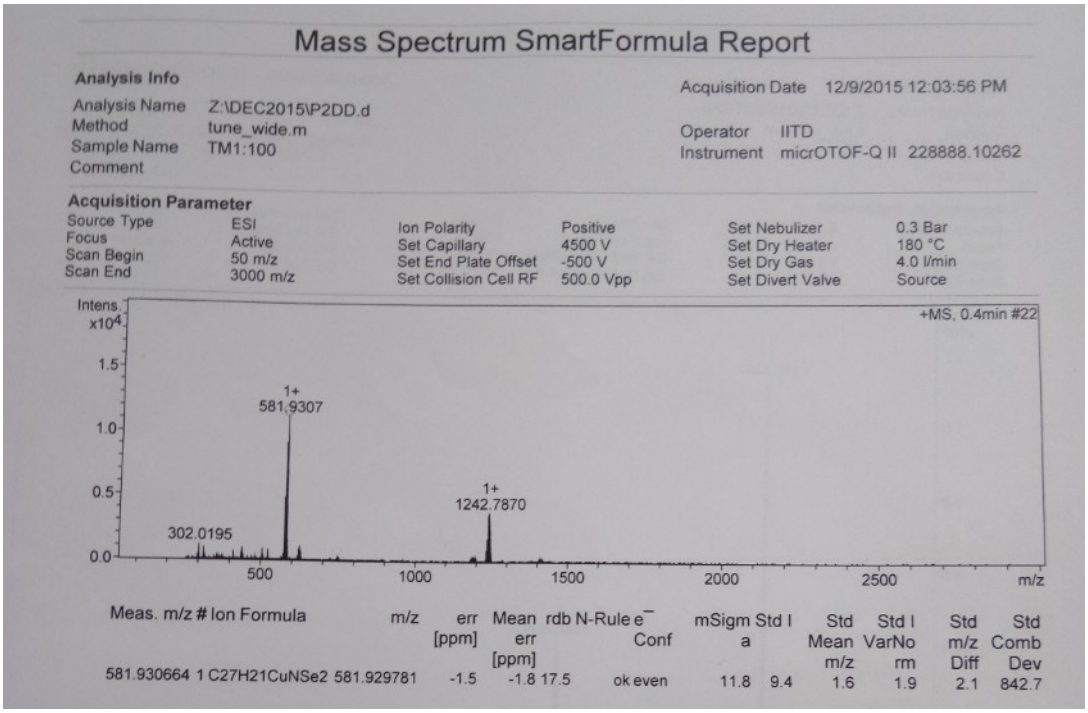


Figure S13: Mass Spectrum of C2

Spectra: ^{1}HNMR and ^{13}CNMR

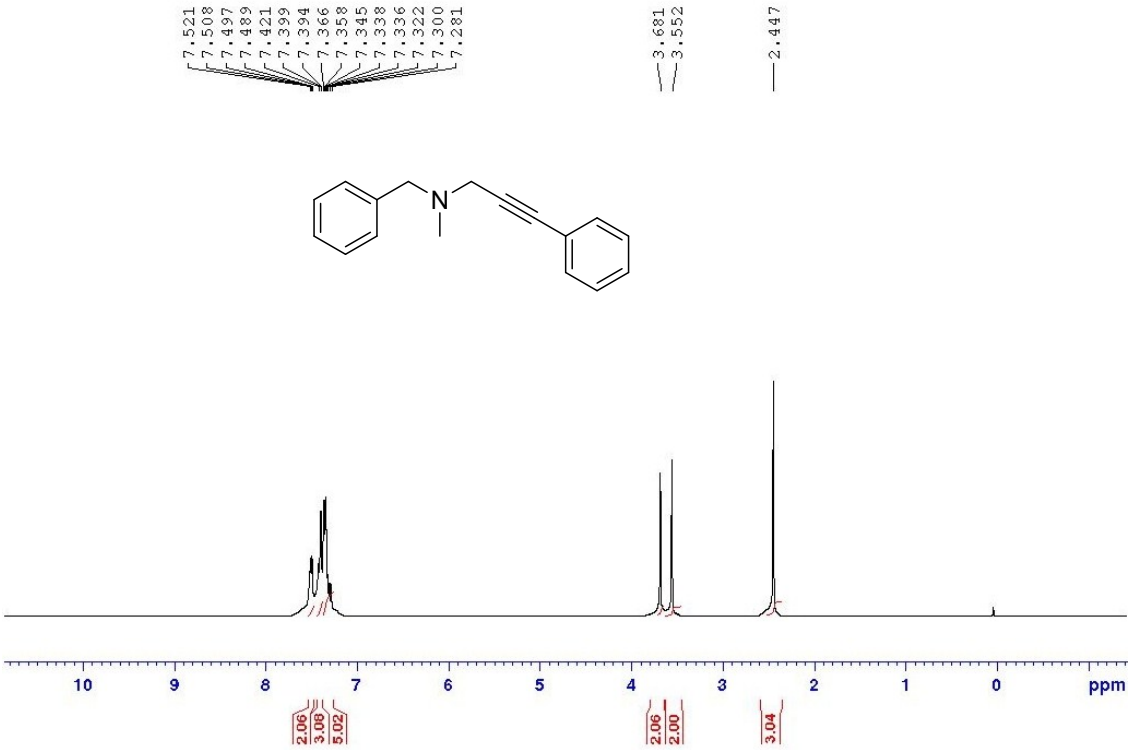


Figure S14: ^{1}H NMR of 3a

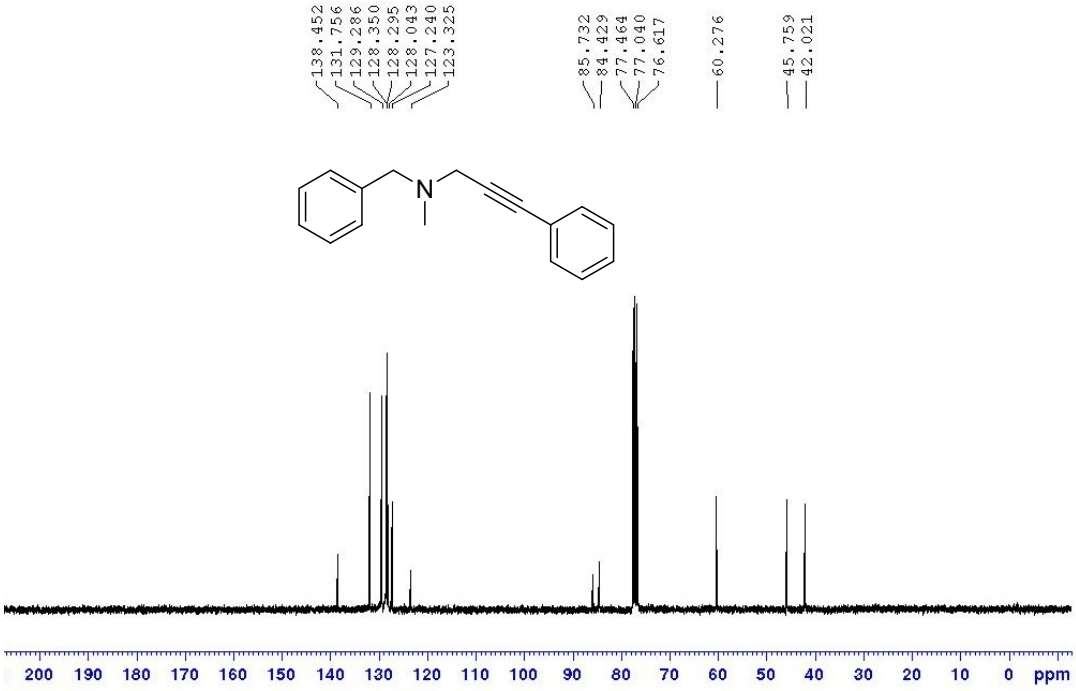


Figure S15: ^{13}C{^{1}H} NMR of 3a

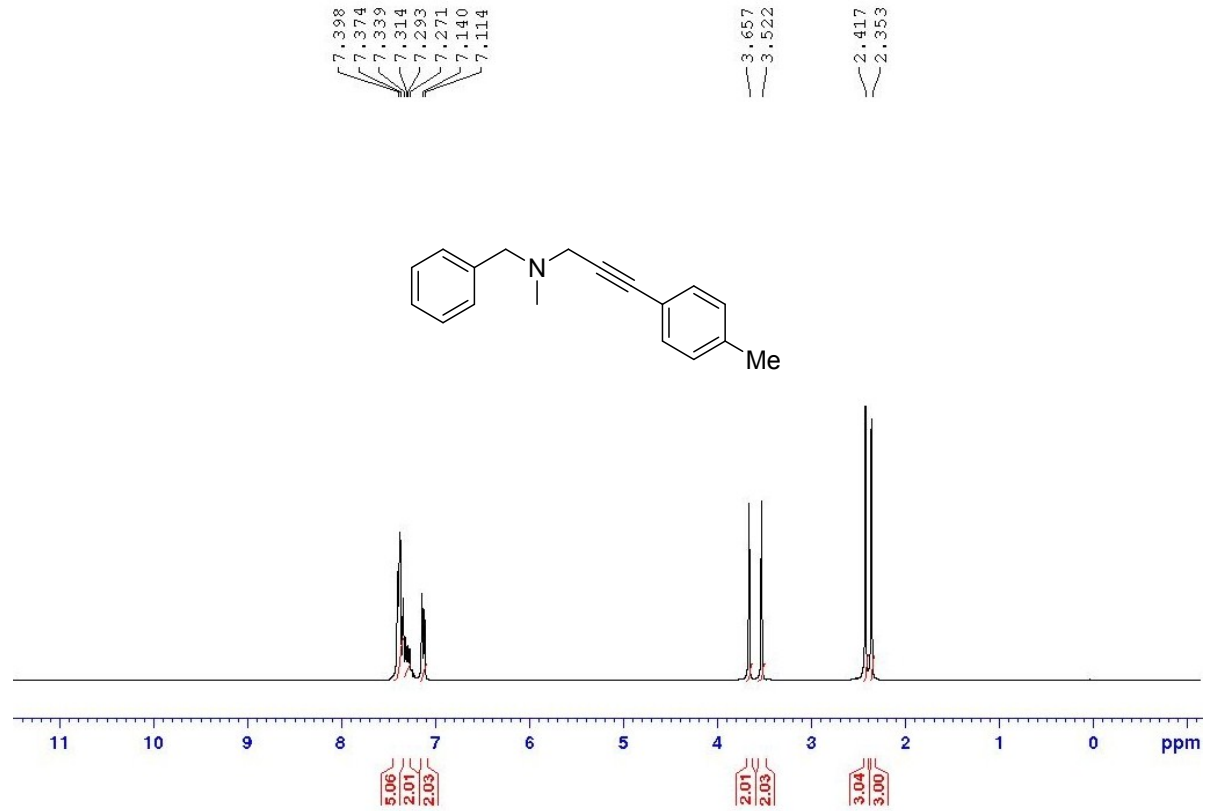


Figure S16: ^{1}H **NMR of 3b**

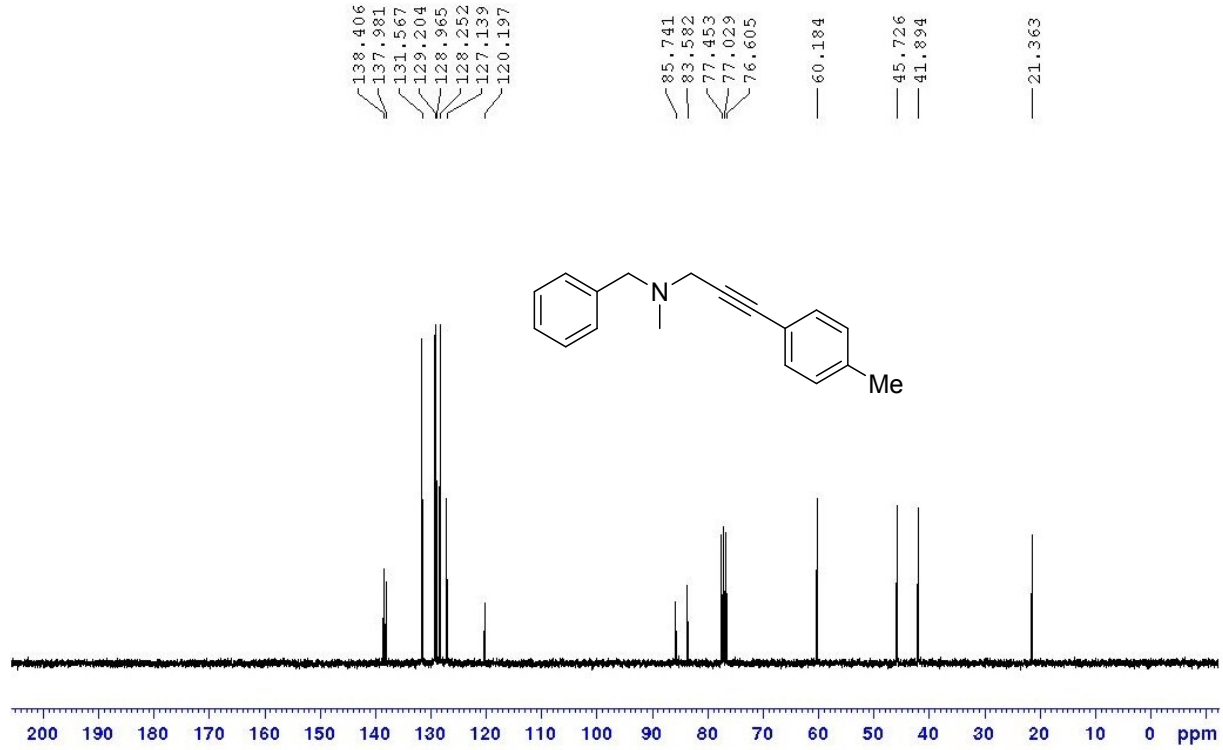


Figure S17: ^{13}C{^{1}H} **NMR of 3b**

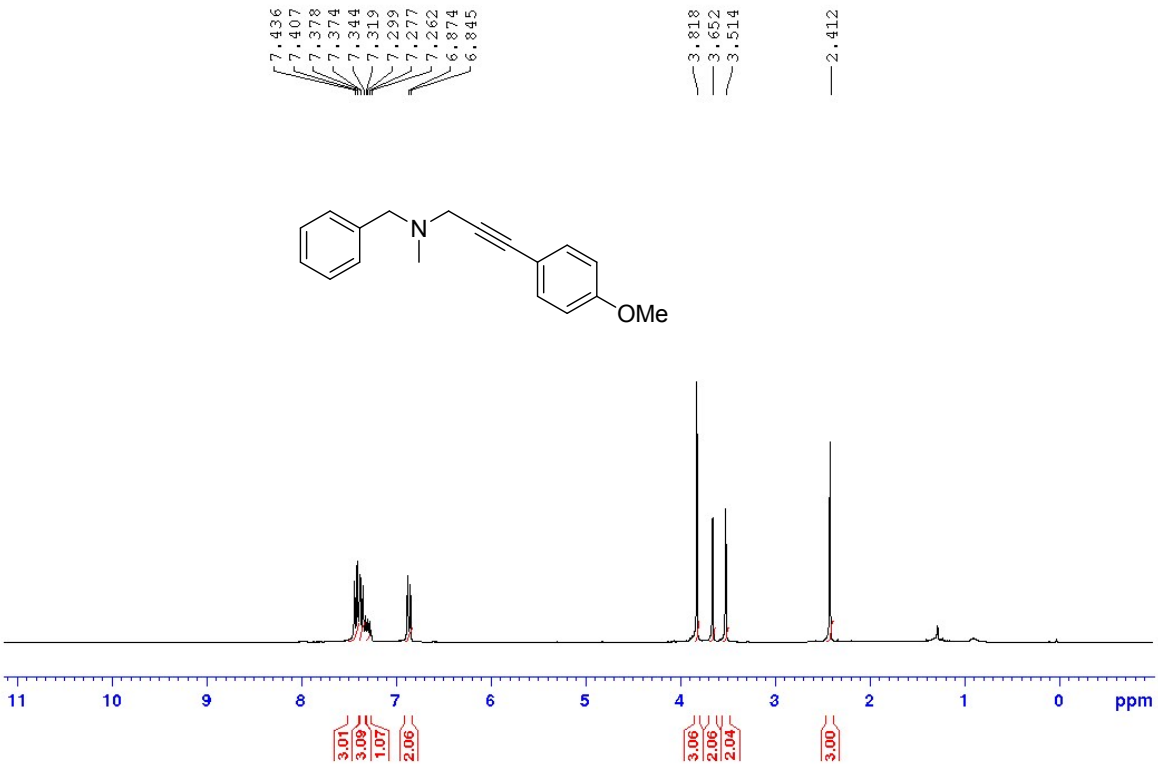


Figure S18: ^{1}H NMR of 3c

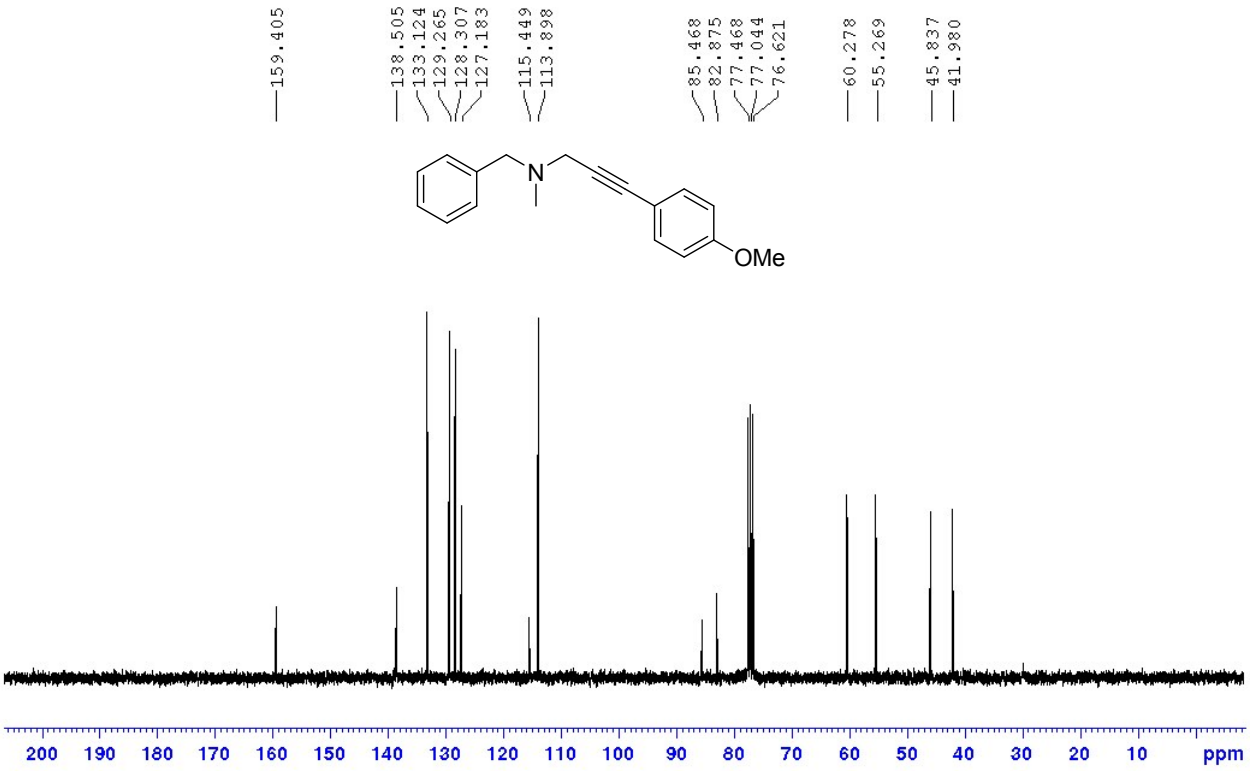


Figure S19: ^{13}C{^{1}H} NMR of 3c

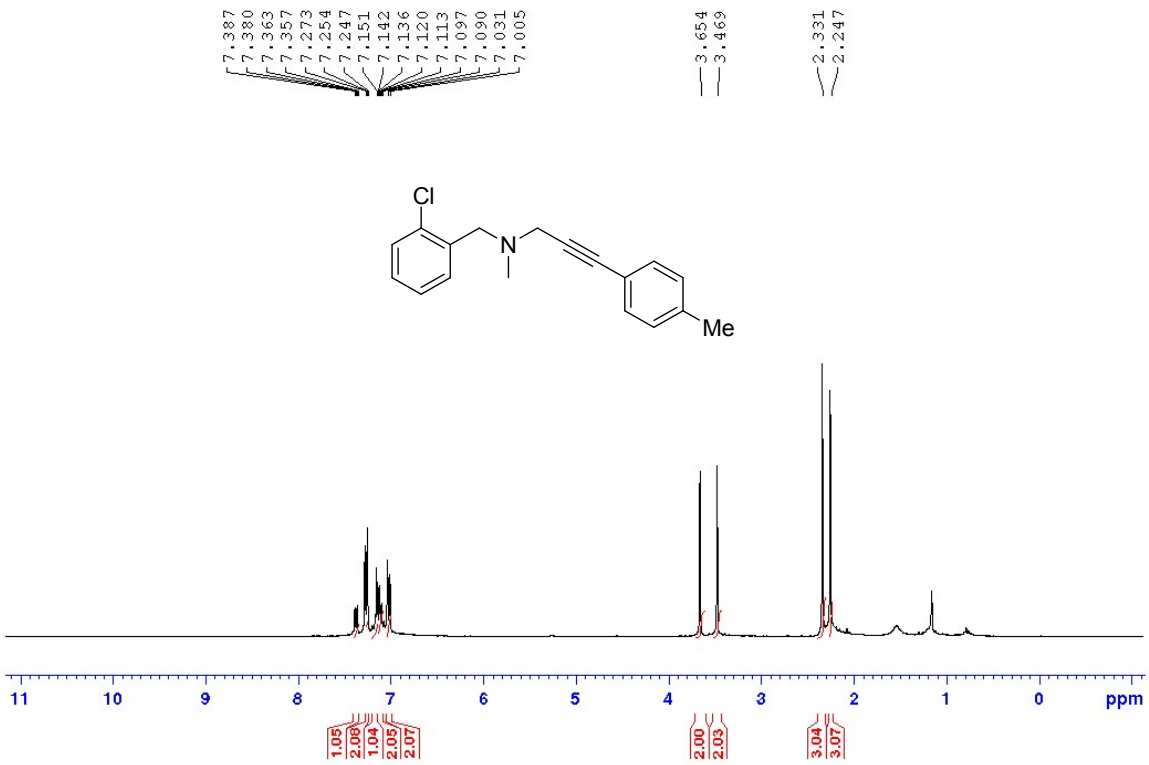


Figure S20: ^{1}H **NMR of 3d**

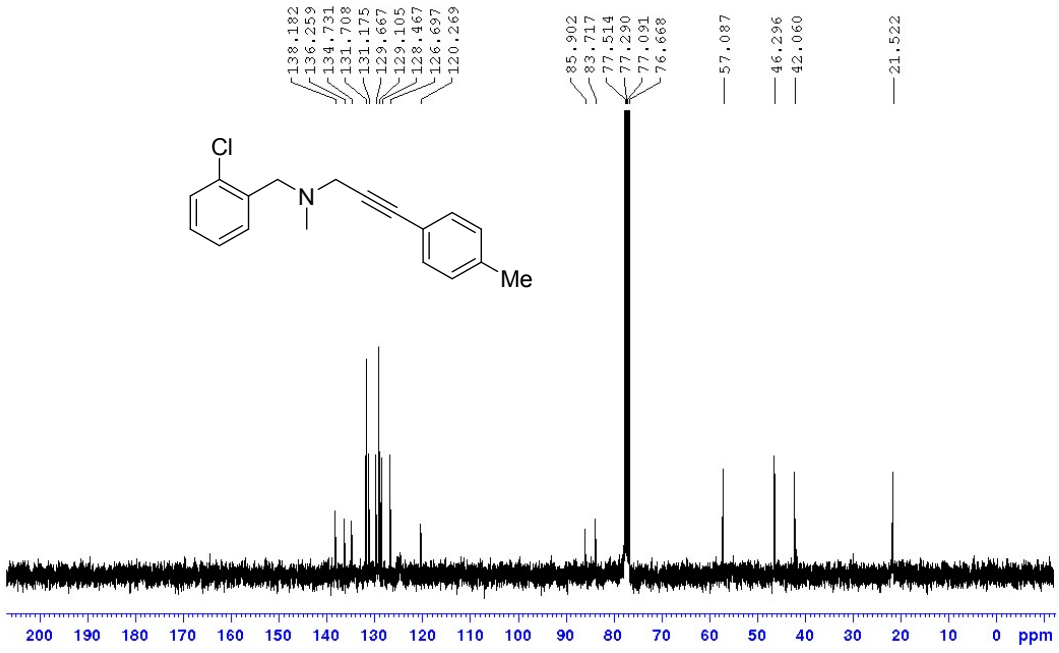


Figure S21: ^{13}C{^{1}H} **NMR of 3d**

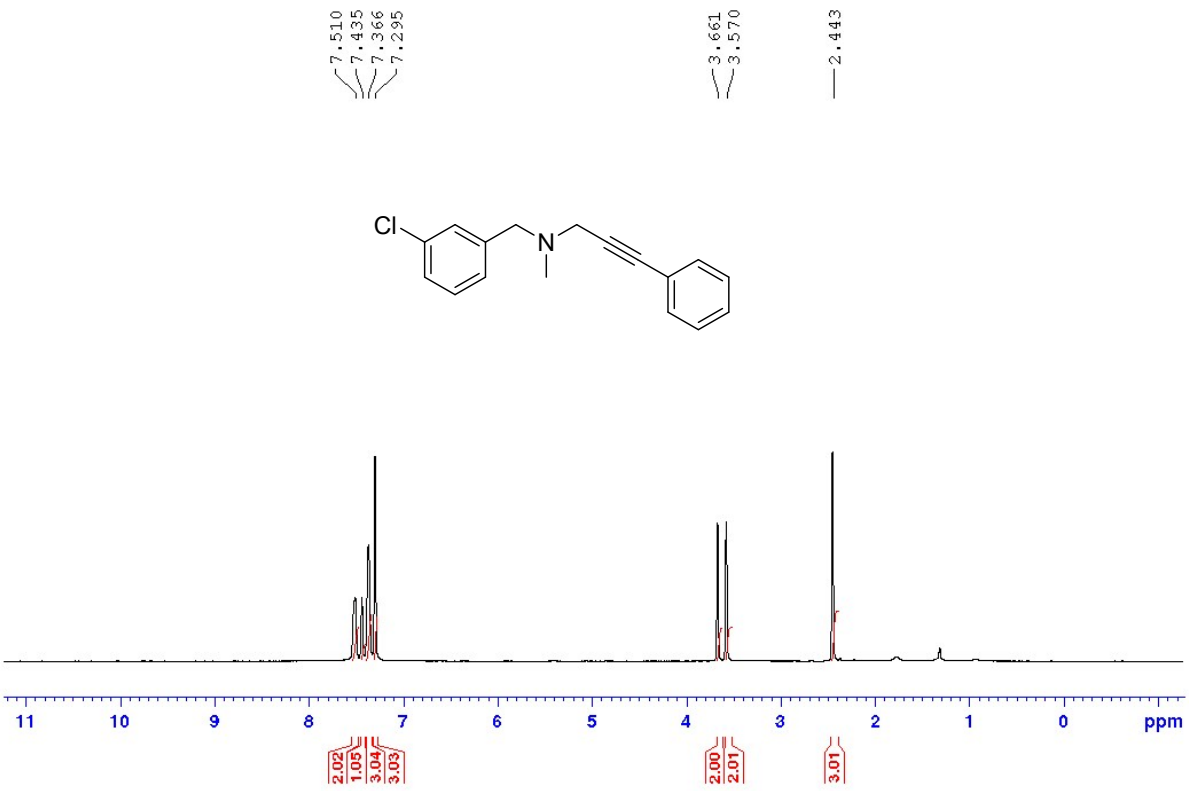


Figure S22: ^{1}H **NMR of 3e**

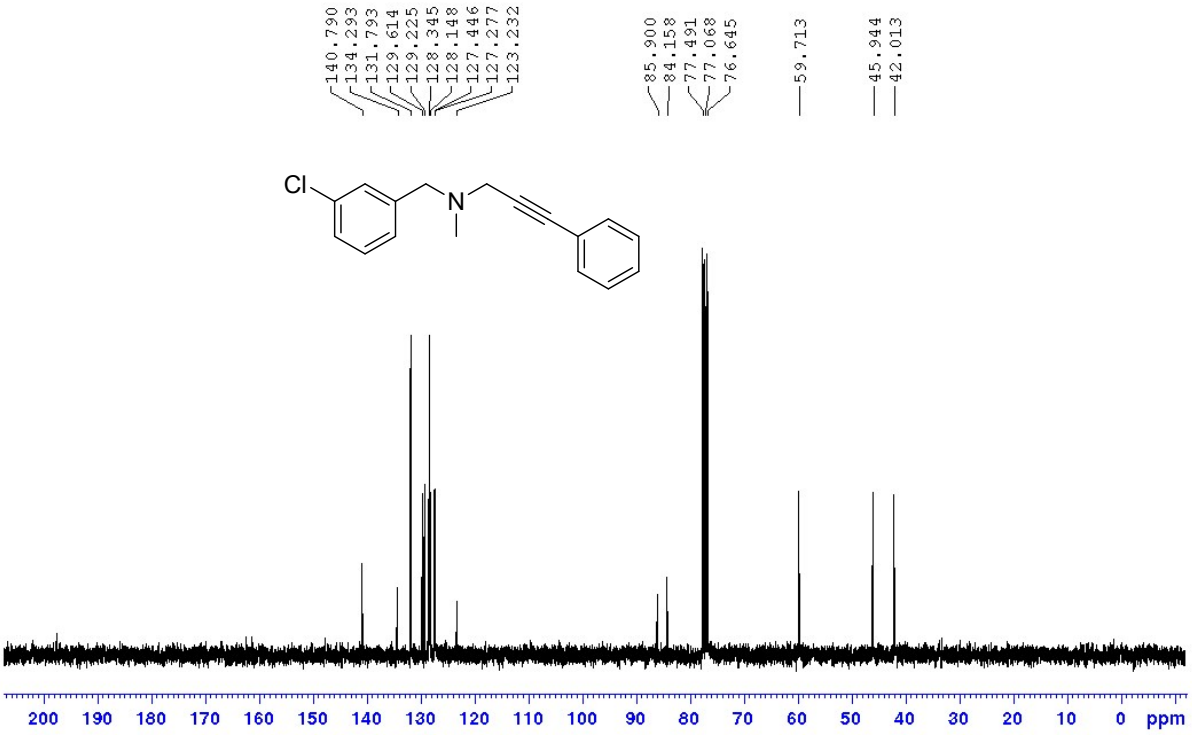


Figure S23: ^{13}C{^{1}H} **NMR of 3e**

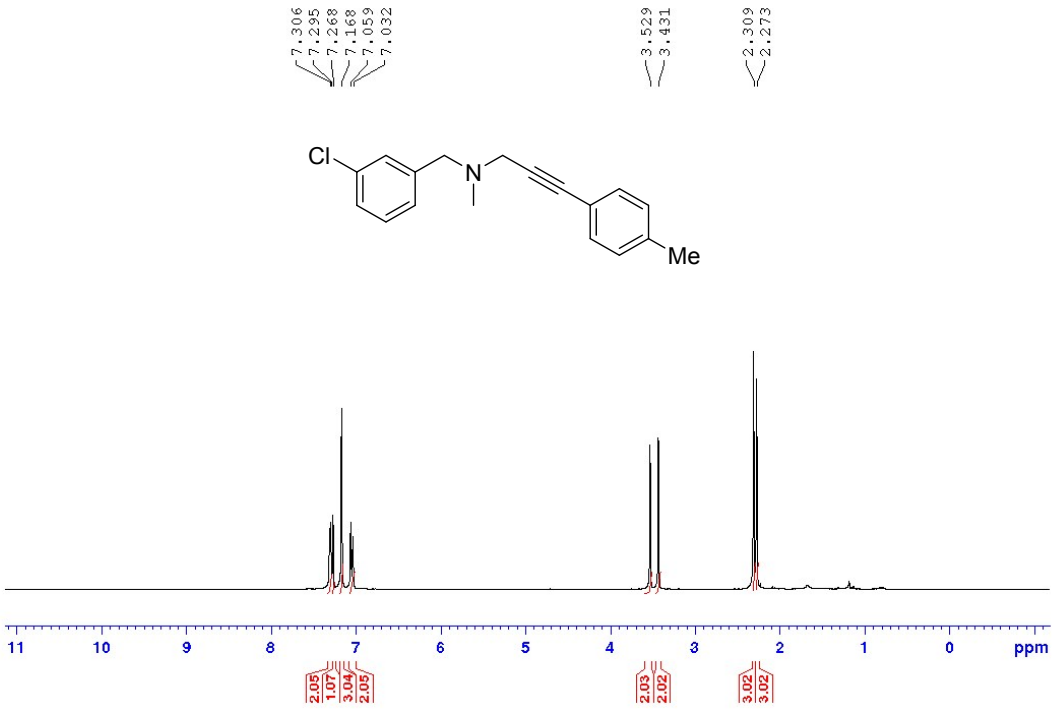


Figure S24: ^{1}H **NMR of 3f**

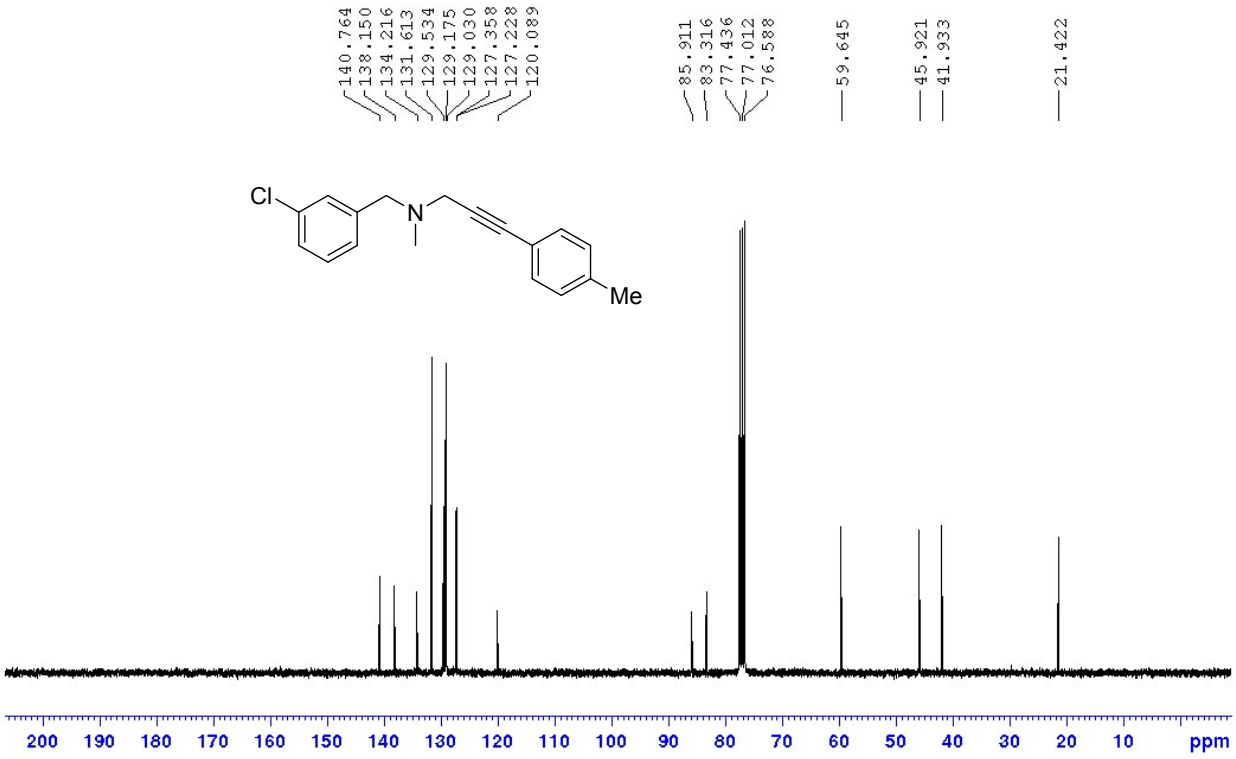


Figure S25: ^{13}C{^{1}H} **NMR of 3f**

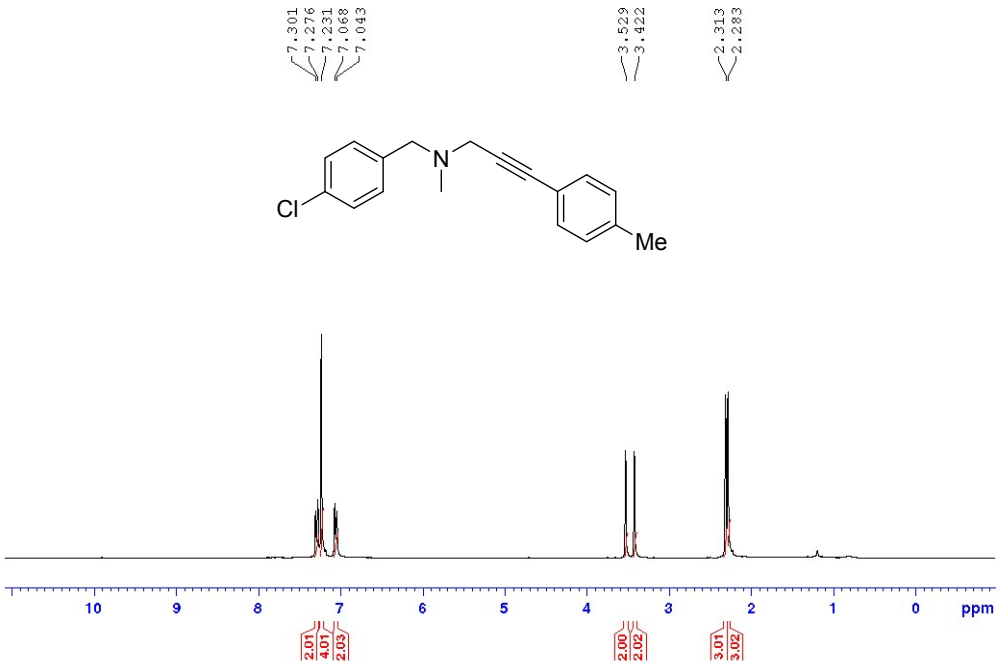


Figure S26: ^{1}H **NMR of 3g**

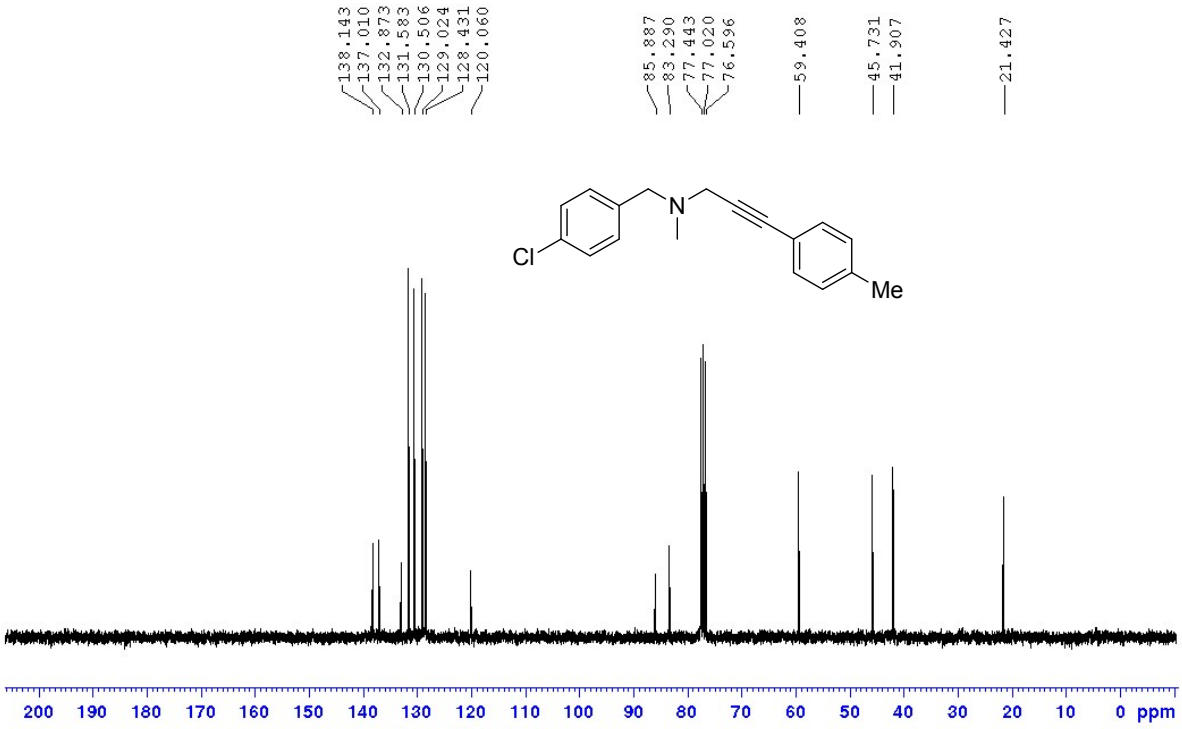


Figure S27: ^{13}C{^{1}H} **NMR of 3g**

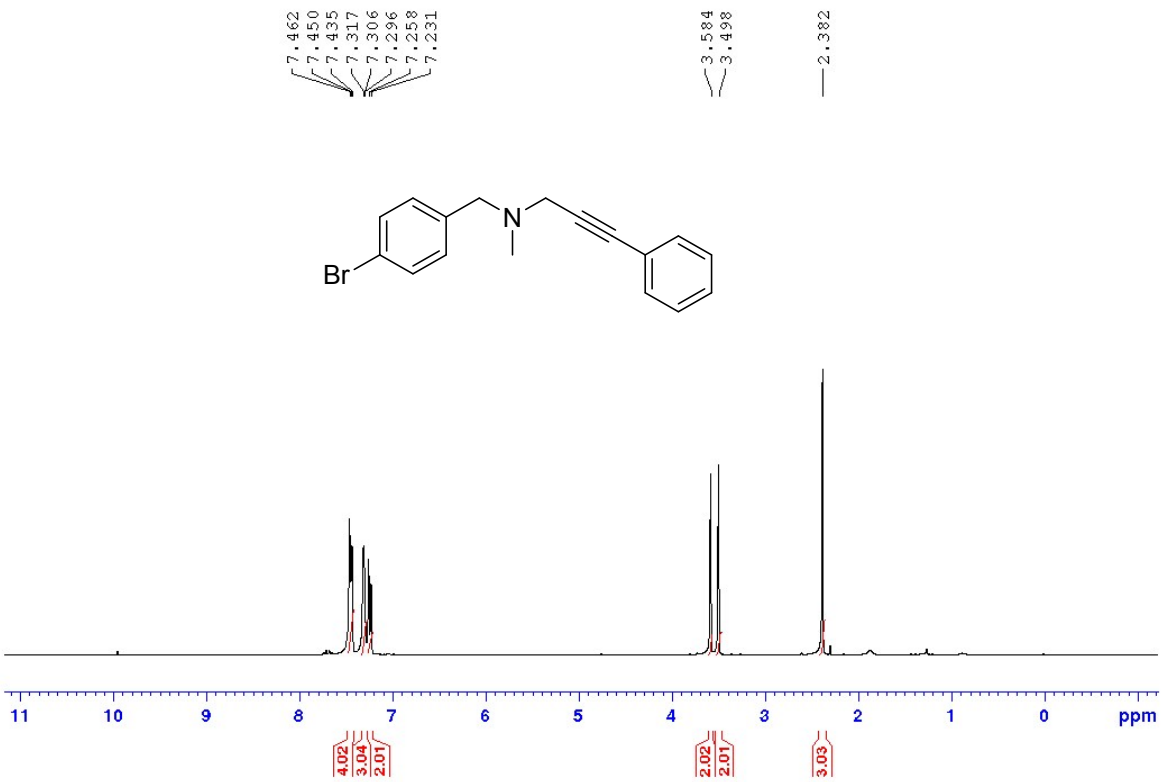


Figure S28: ^{1}H **NMR of 3h**

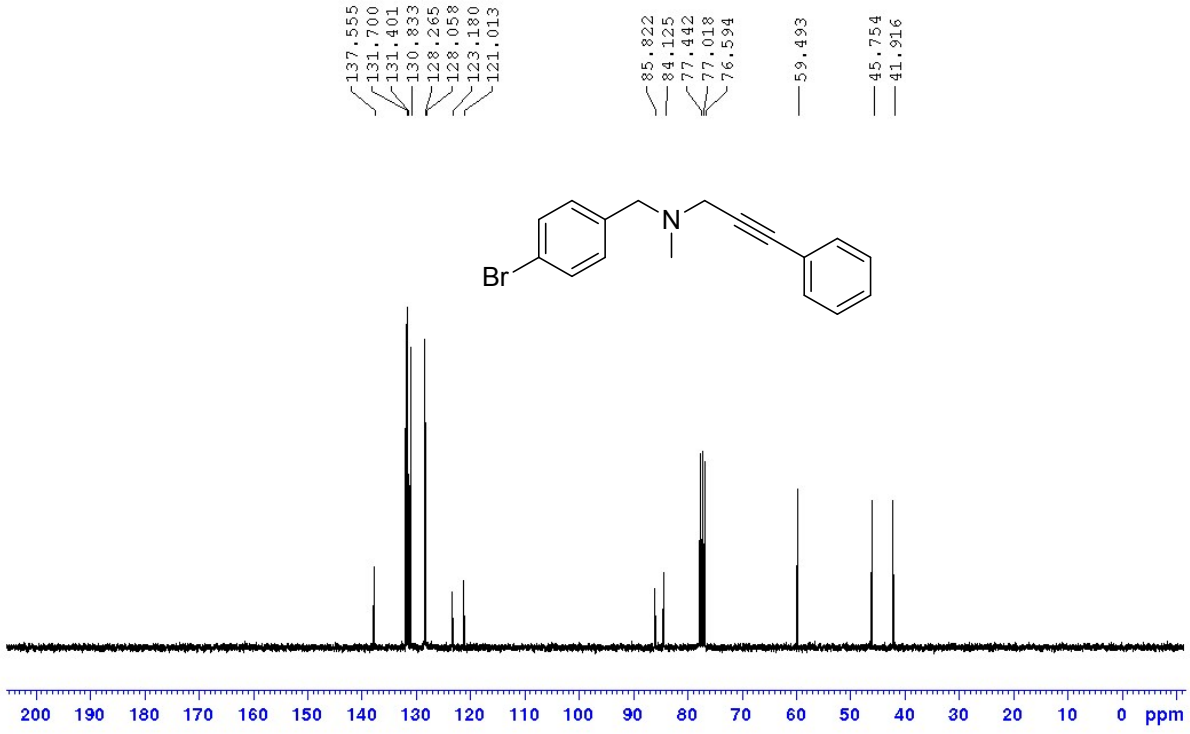


Figure S29: ^{13}C{^{1}H} **NMR of 3h**

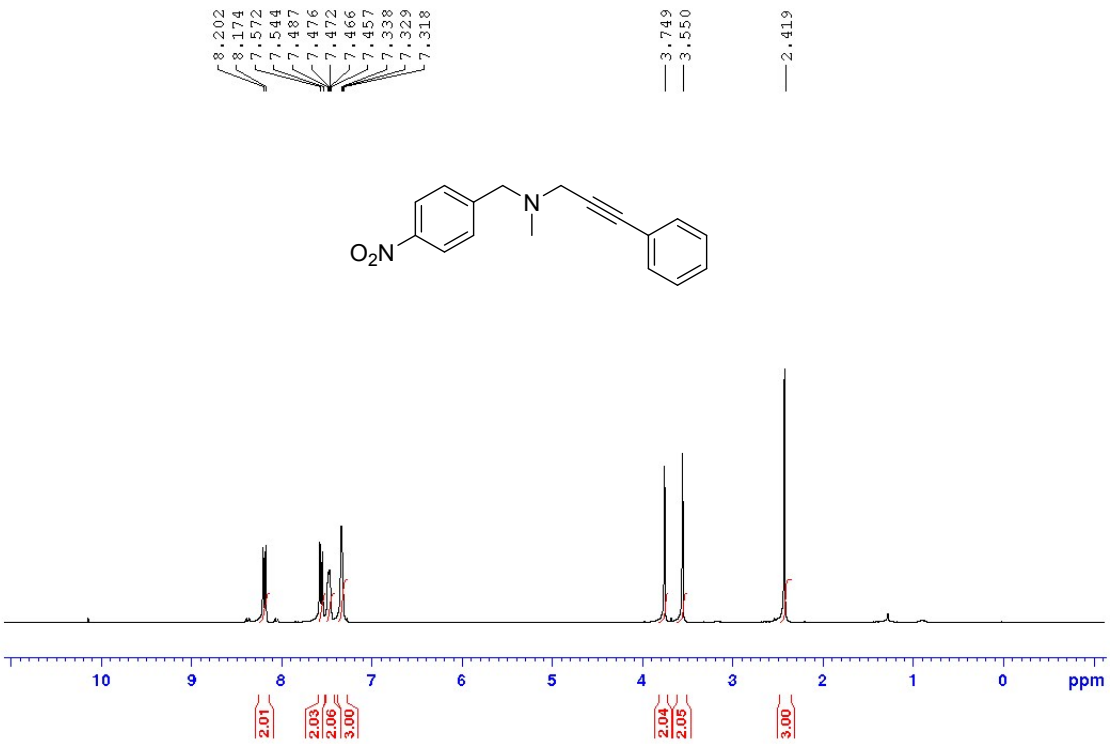


Figure S30: ^{1}H **NMR of 3i**

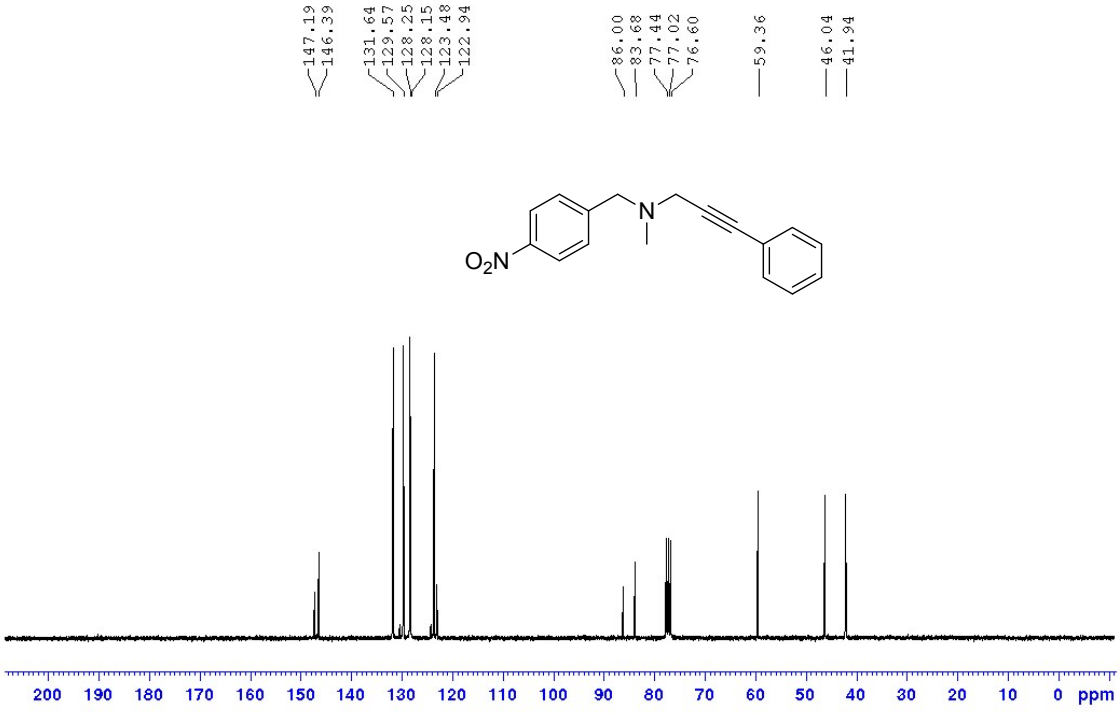


Figure S31: ^{13}C{^{1}H} **NMR of 3i**

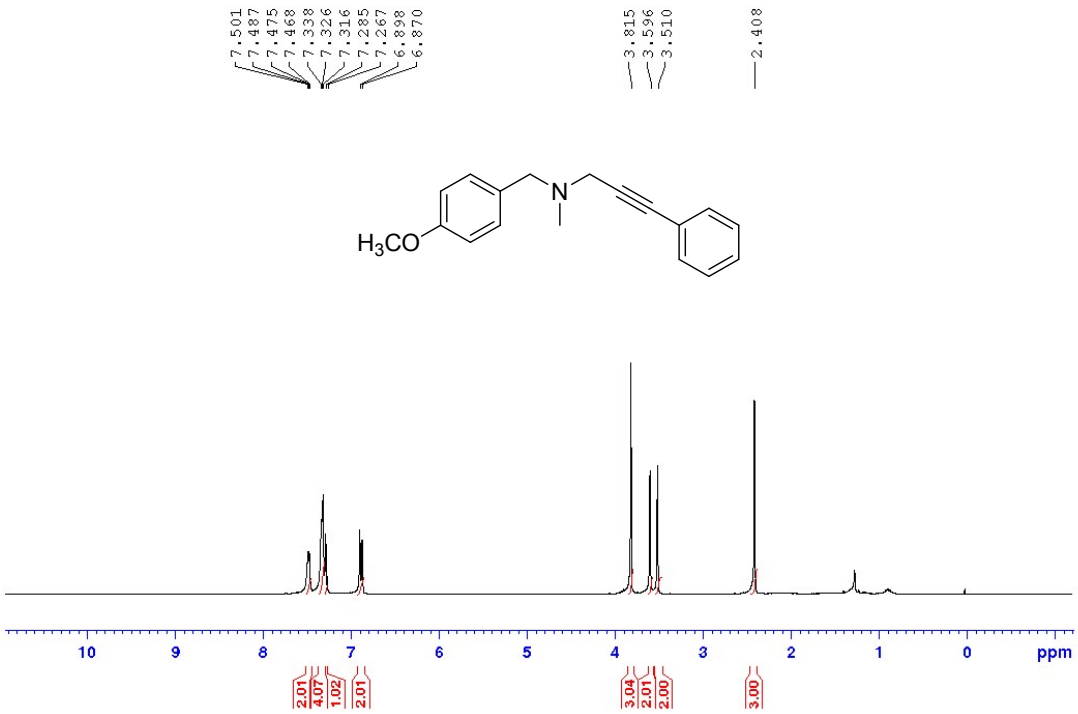


Figure S32: ^{1}H **NMR of 3j**

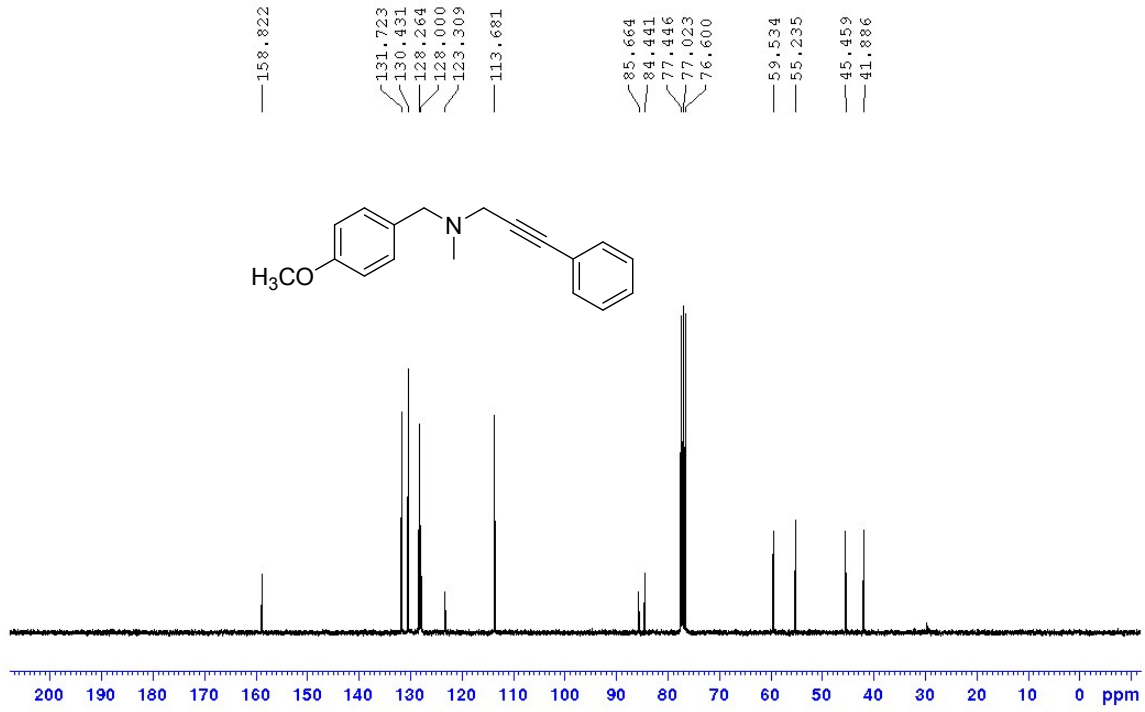


Figure S33: ^{13}C{^{1}H} **NMR of 3j**

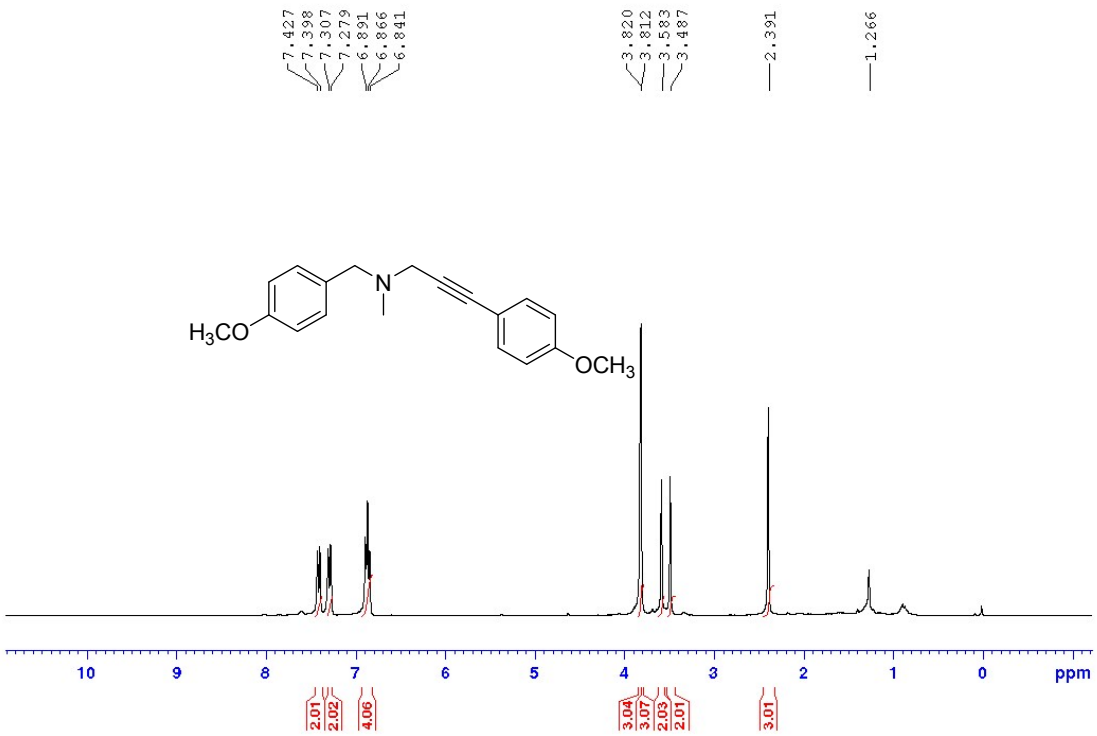


Figure S34: ^{1}H **NMR of 3k**

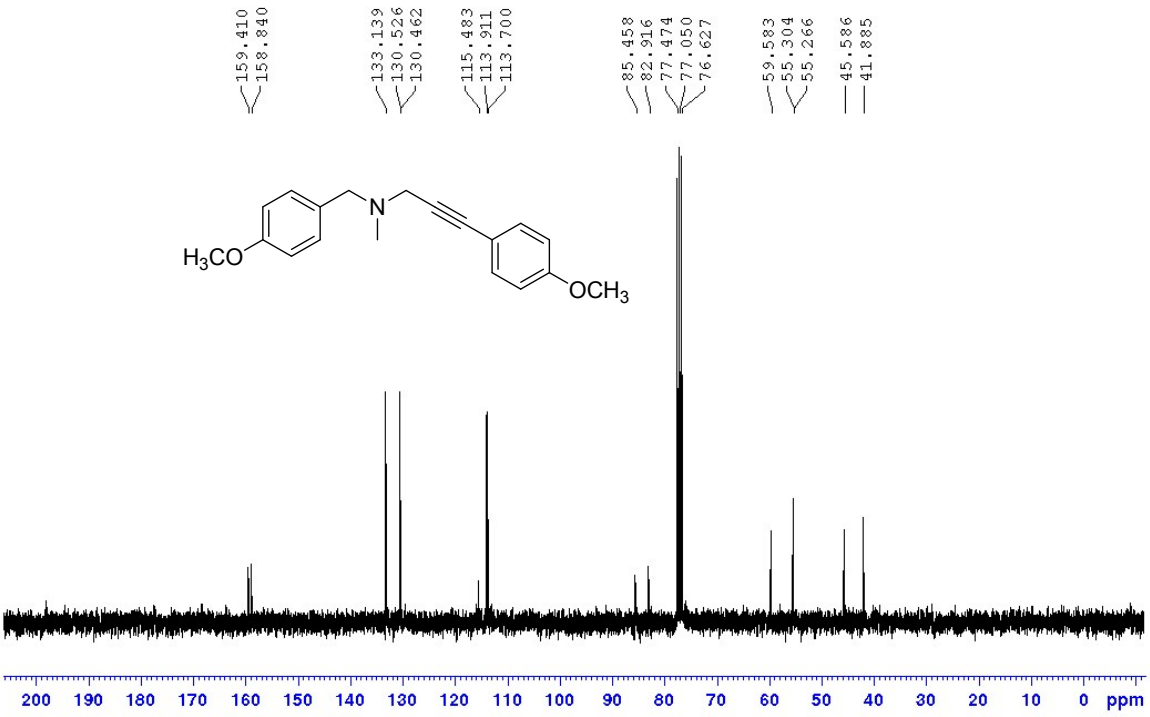


Figure S35: ^{13}C{^{1}H} **NMR of 3k**

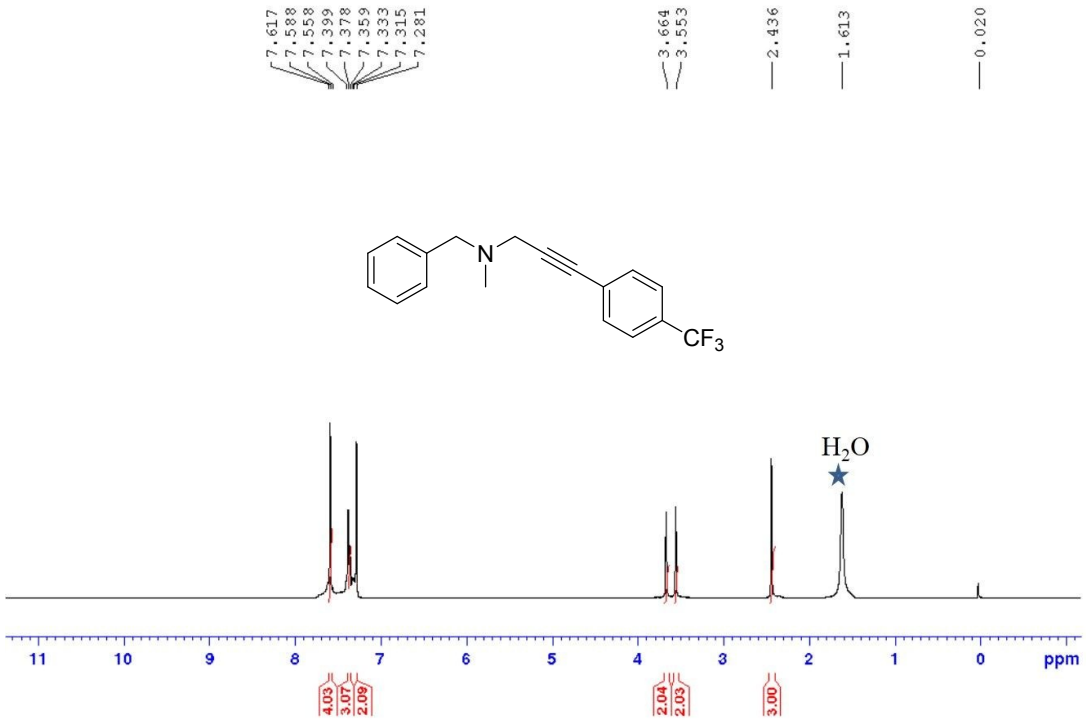


Figure S36: ^{1}H **NMR of 3l**

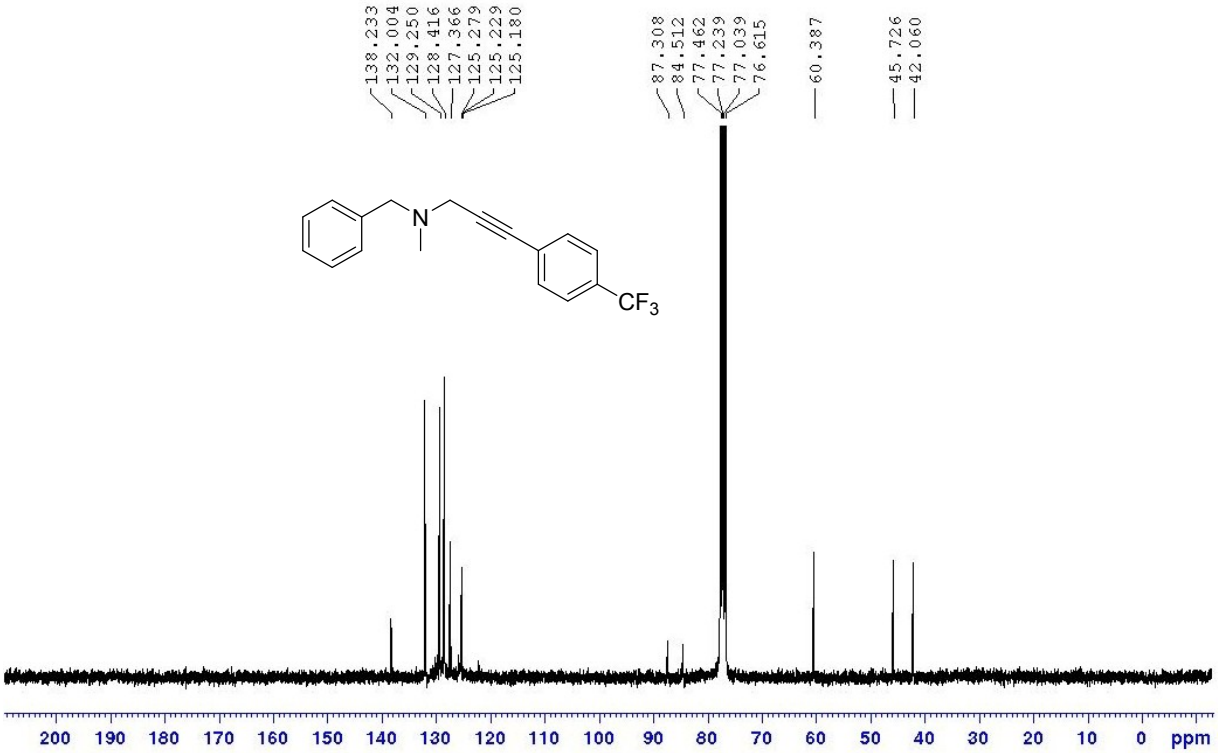


Figure S37: ^{13}C{^{1}H} **NMR of 3l**

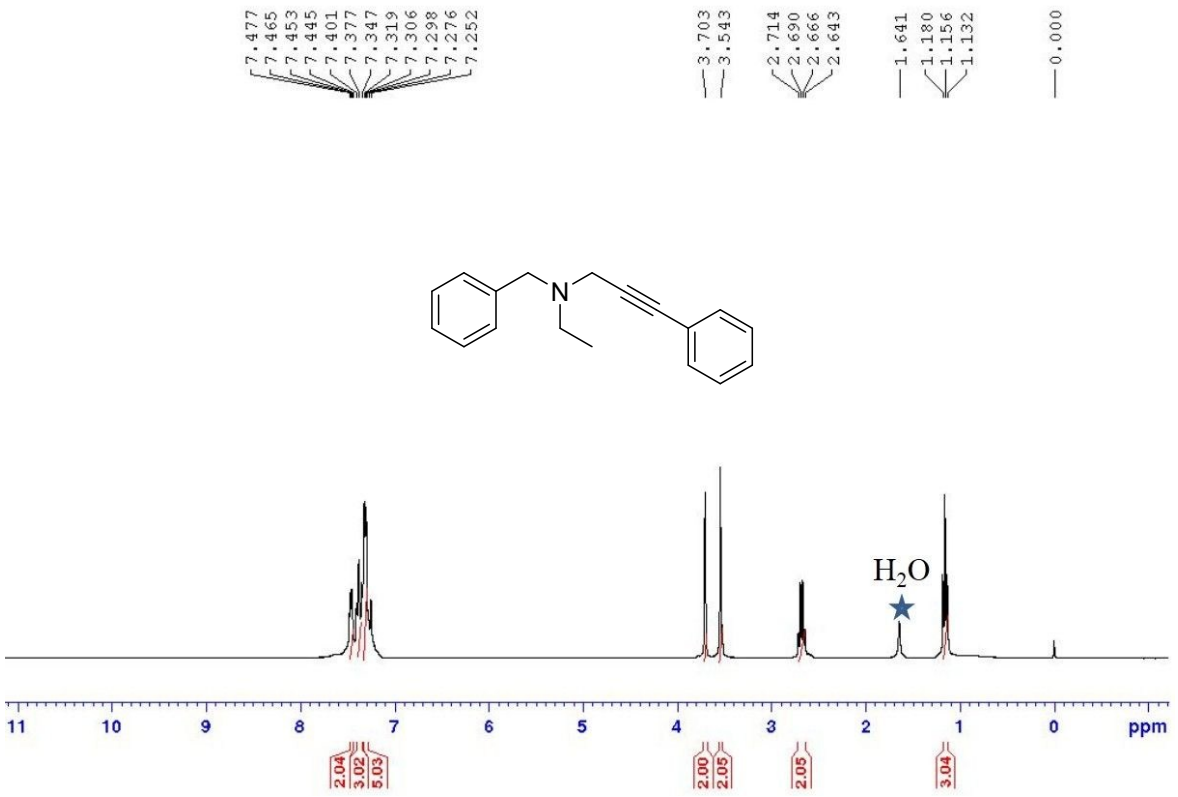


Figure S38: ^{1}H **NMR of 3m**

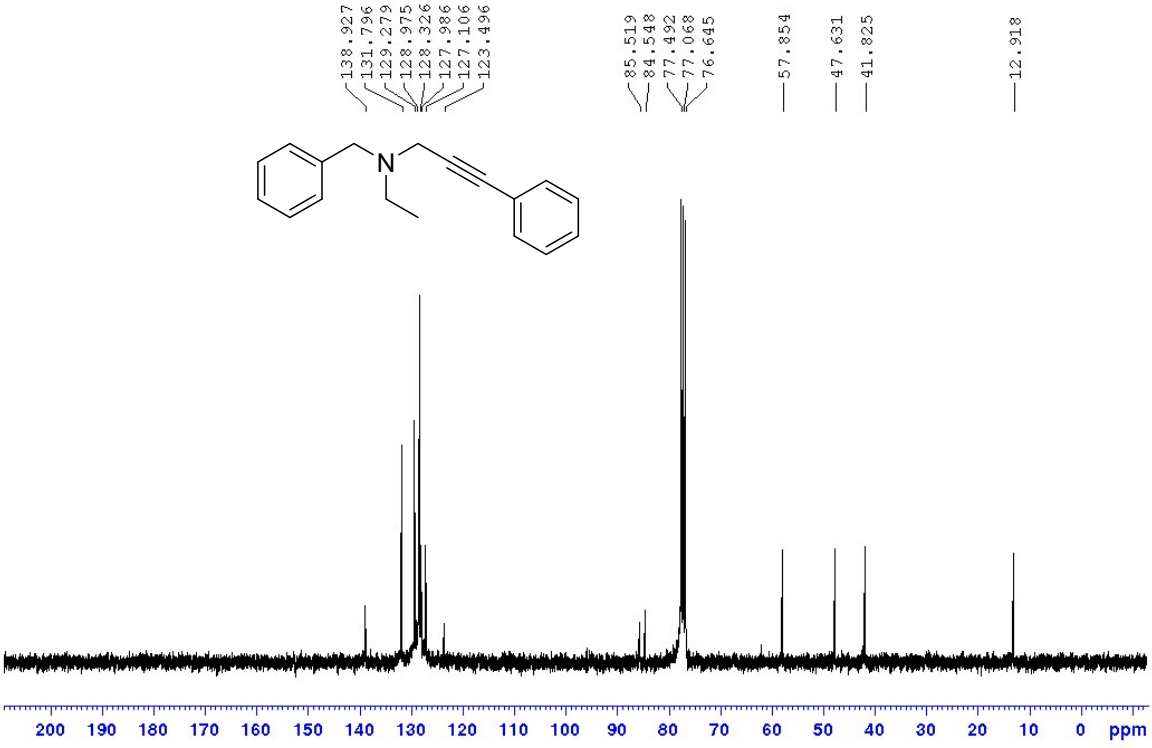


Figure S39: ^{13}C{^{1}H} **NMR of 3m**

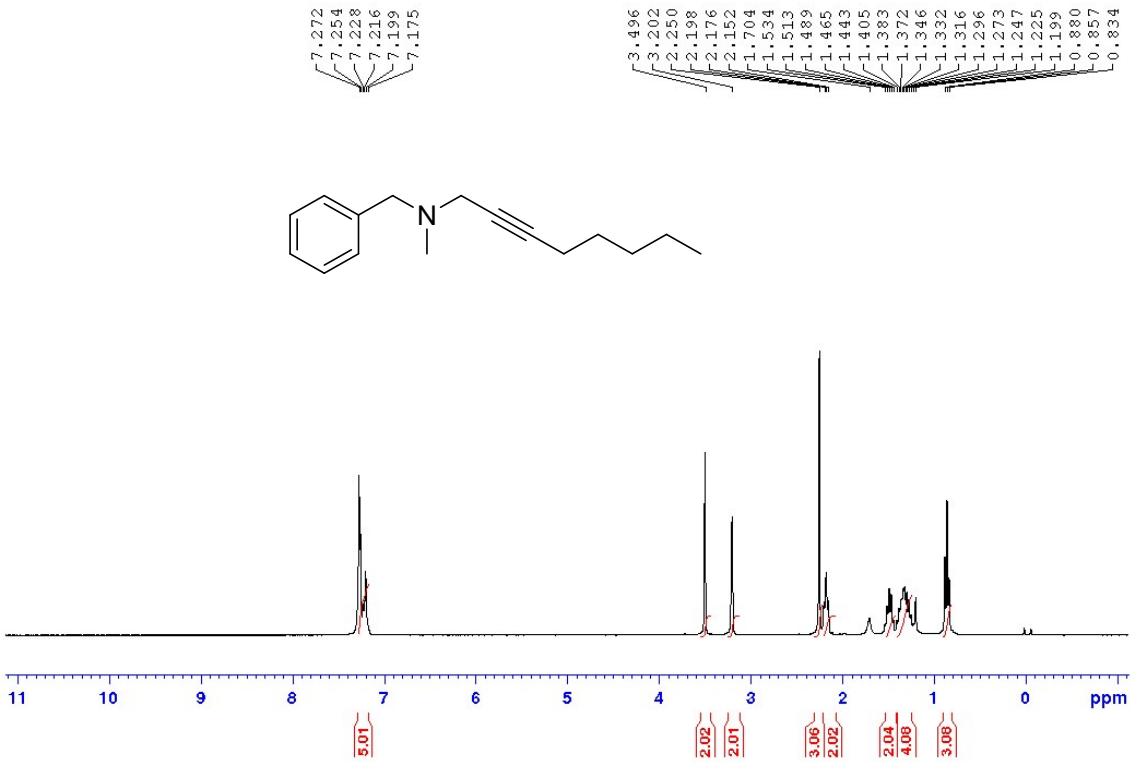


Figure S40: ^{1}H **NMR of 3n**

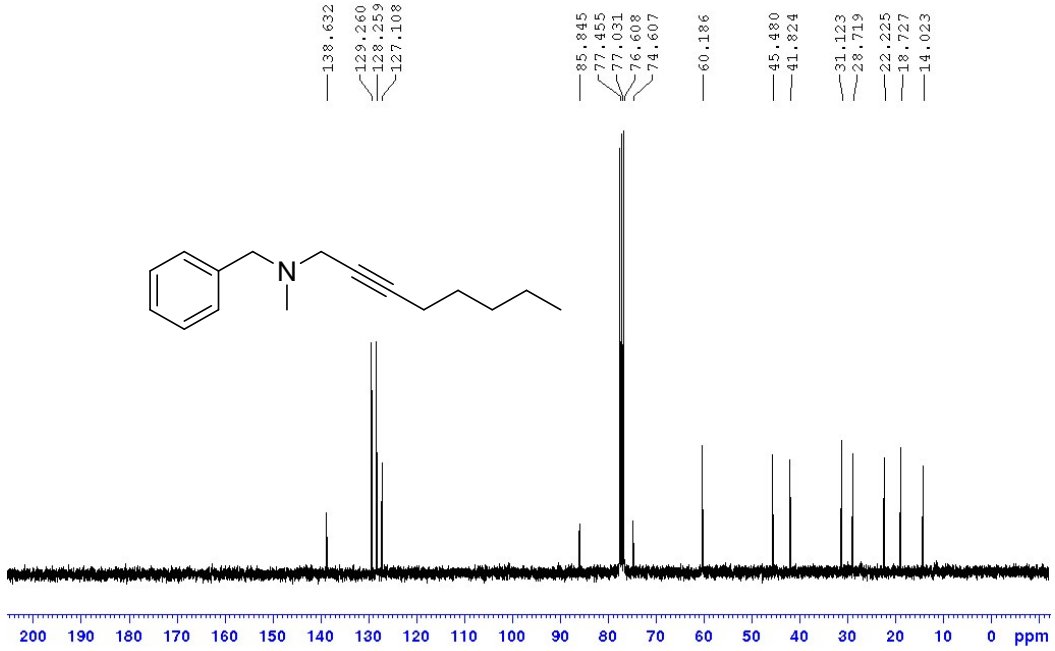


Figure S41: ^{13}C{^{1}H} **NMR of 3n**

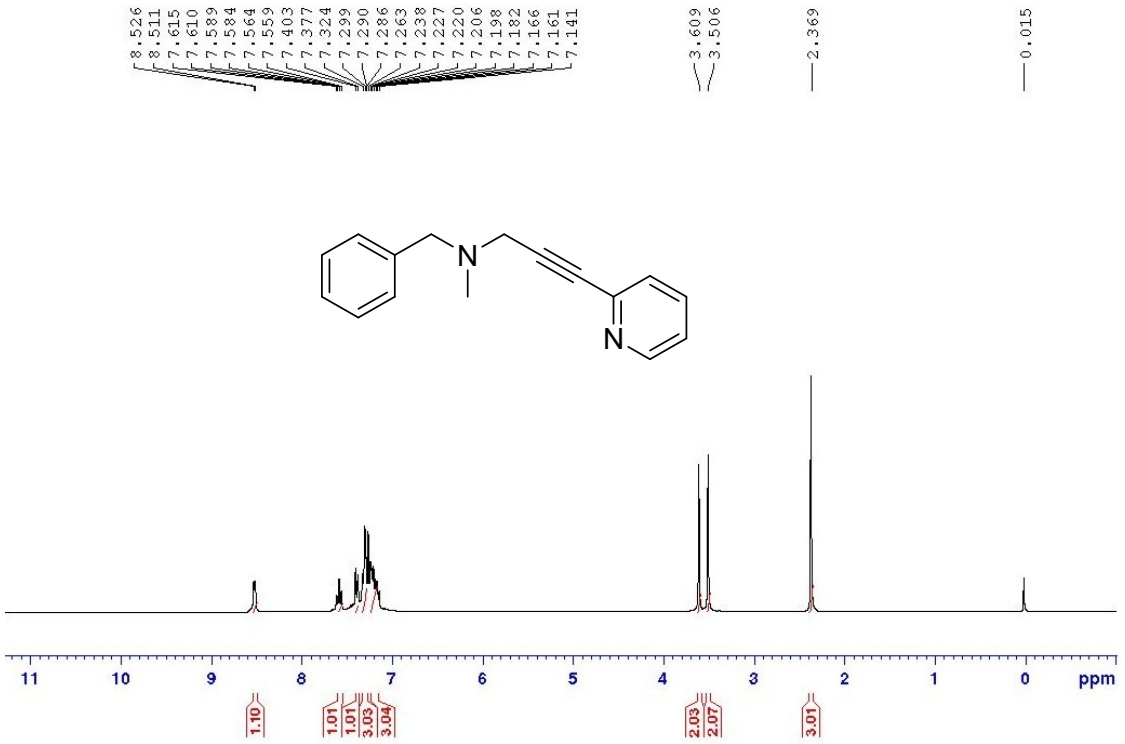


Figure S42: ^{1}H **NMR of 3o**

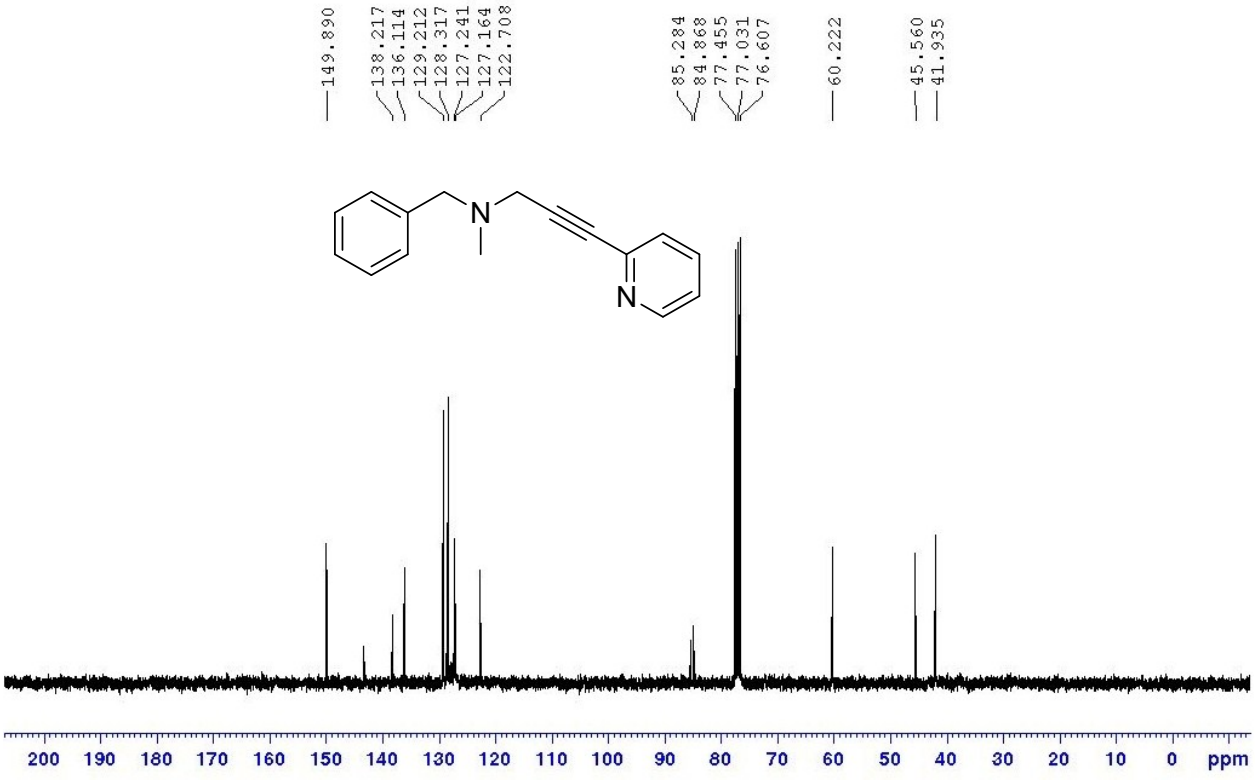


Figure S43: ^{13}C{^{1}H} **NMR of 3o**

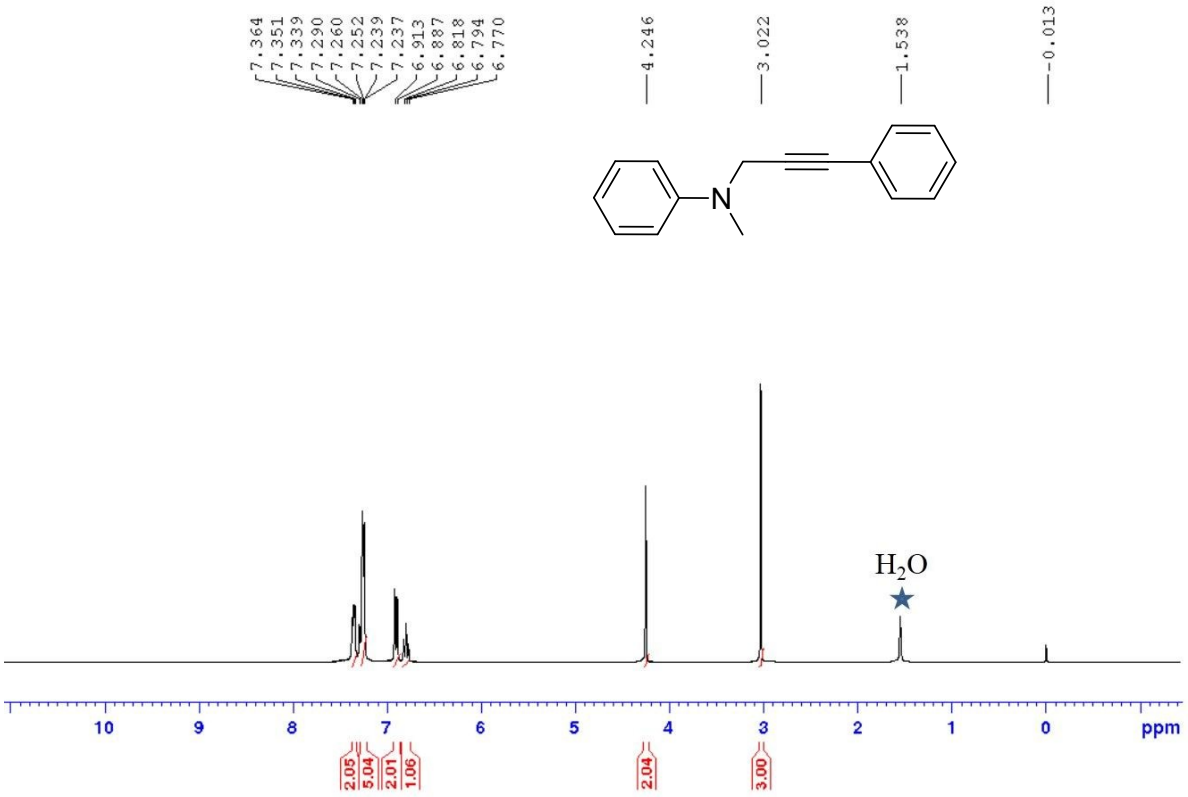


Figure S44: ^{1}H **NMR of 5a**

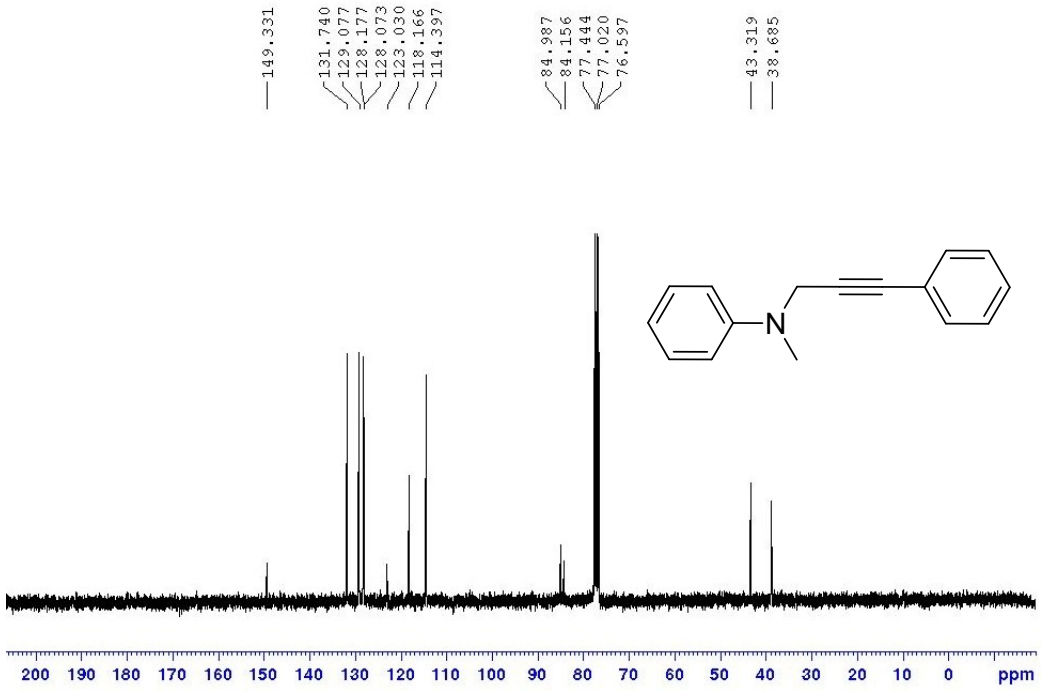


Figure S45: ^{13}C{^{1}H} **NMR of 5a**

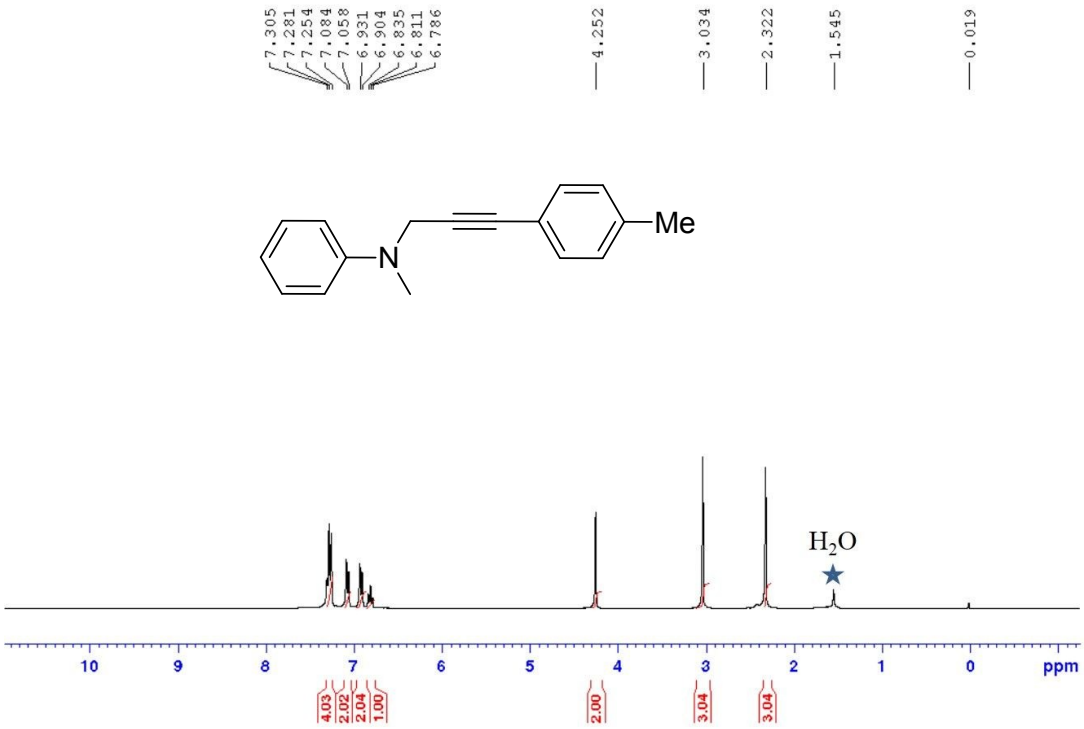


Figure S46: ^{1}H **NMR of 5b**

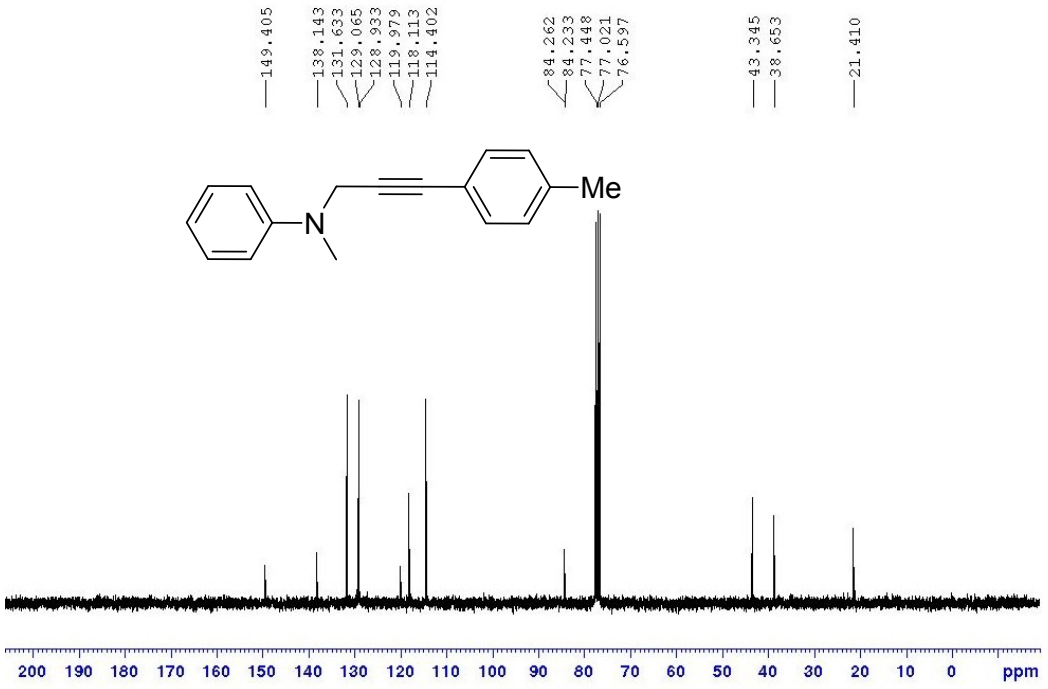


Figure S47: ^{13}C{^{1}H} **NMR of 5b**

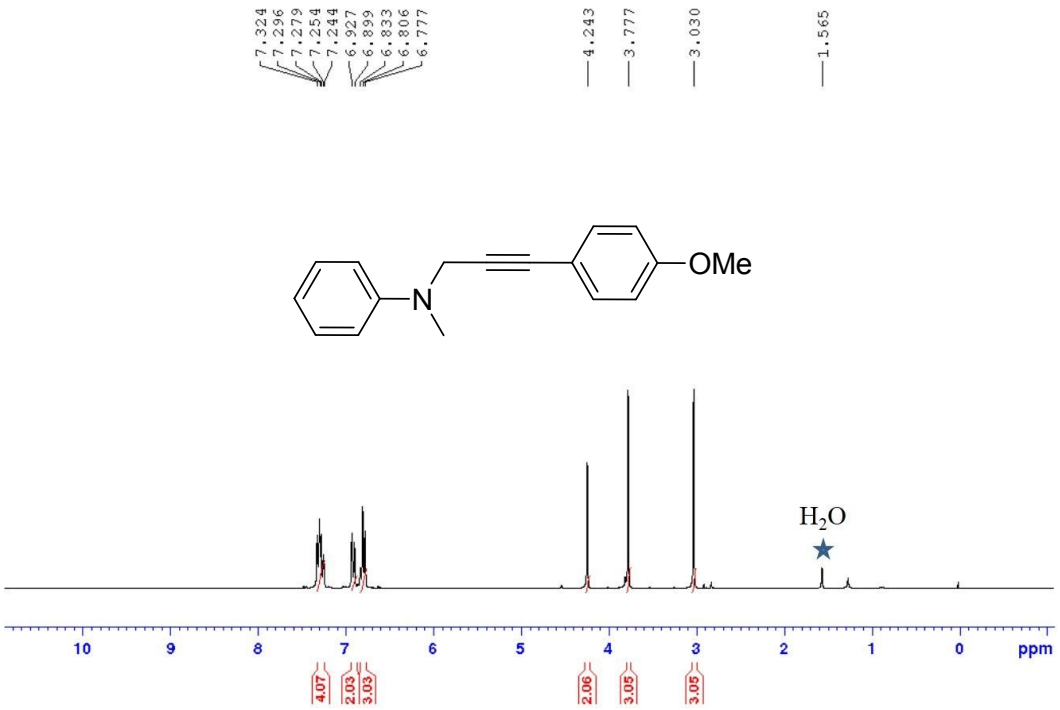


Figure S48: ^{1}H **NMR of 5c**

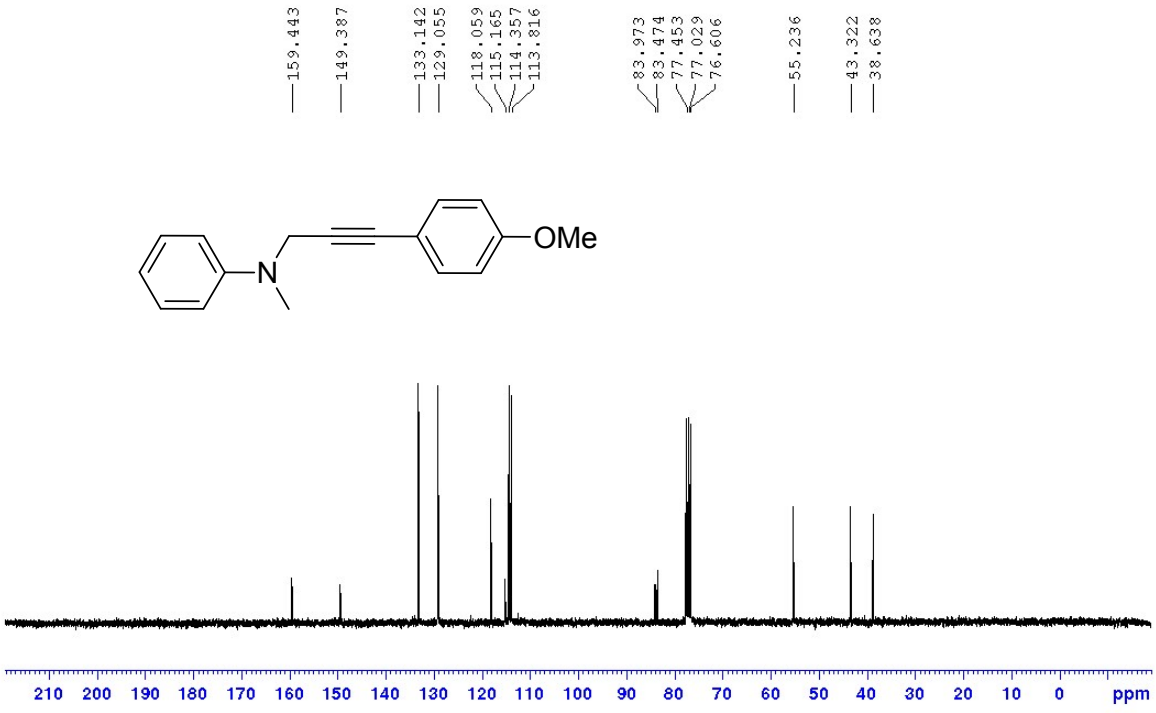


Figure S49: ^{13}C{^{1}H} **NMR of 5c**

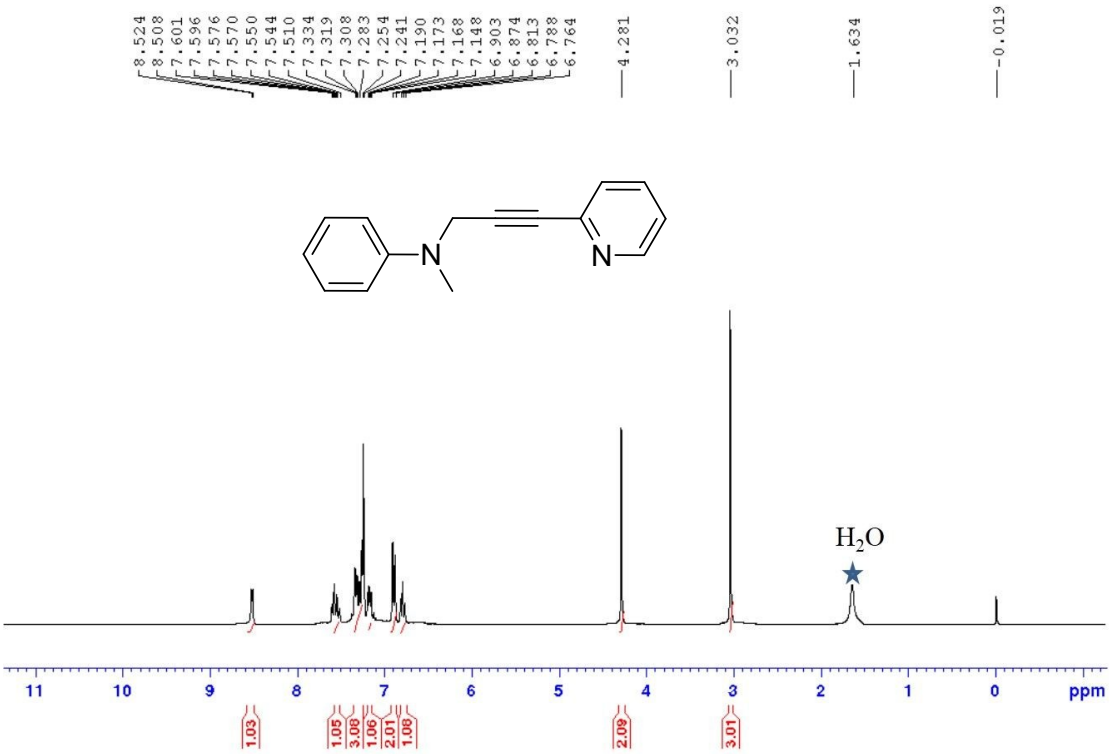


Figure S50: ^{1}H **NMR of 5d**

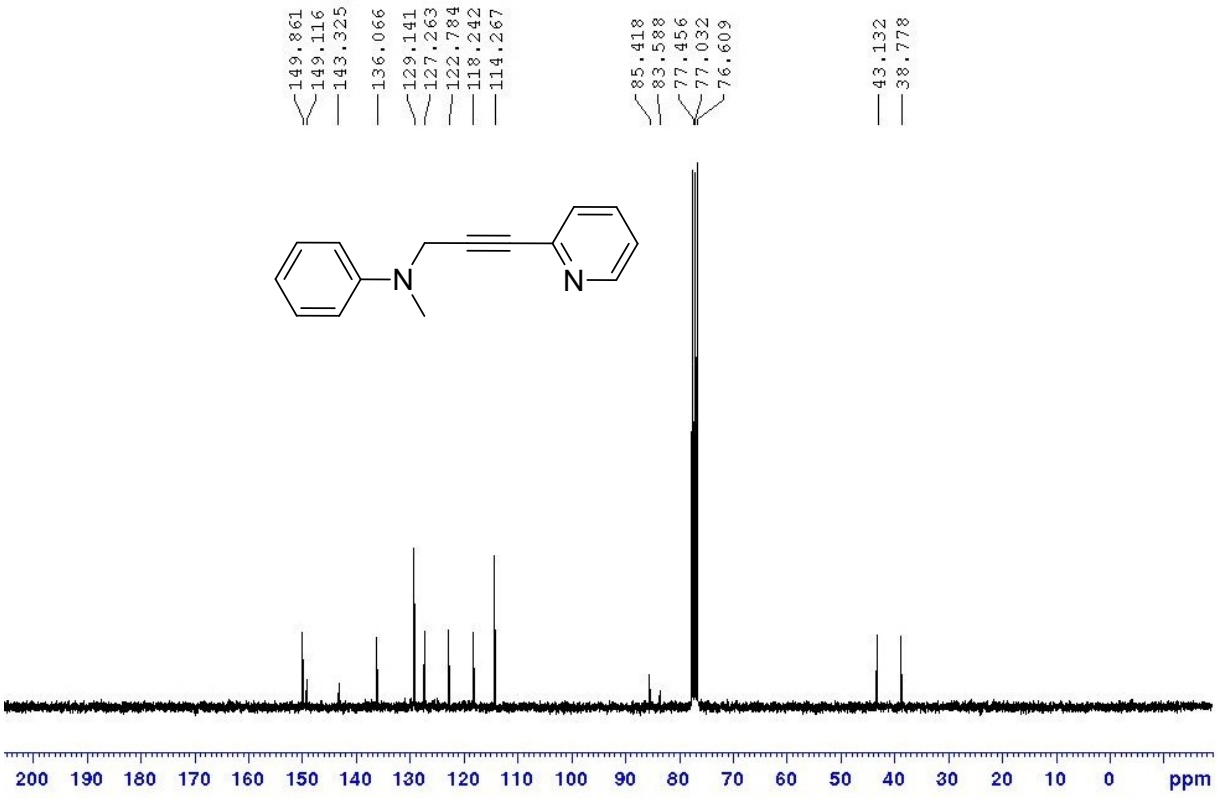


Figure S51: ^{13}C{^{1}H} **NMR of 5d**

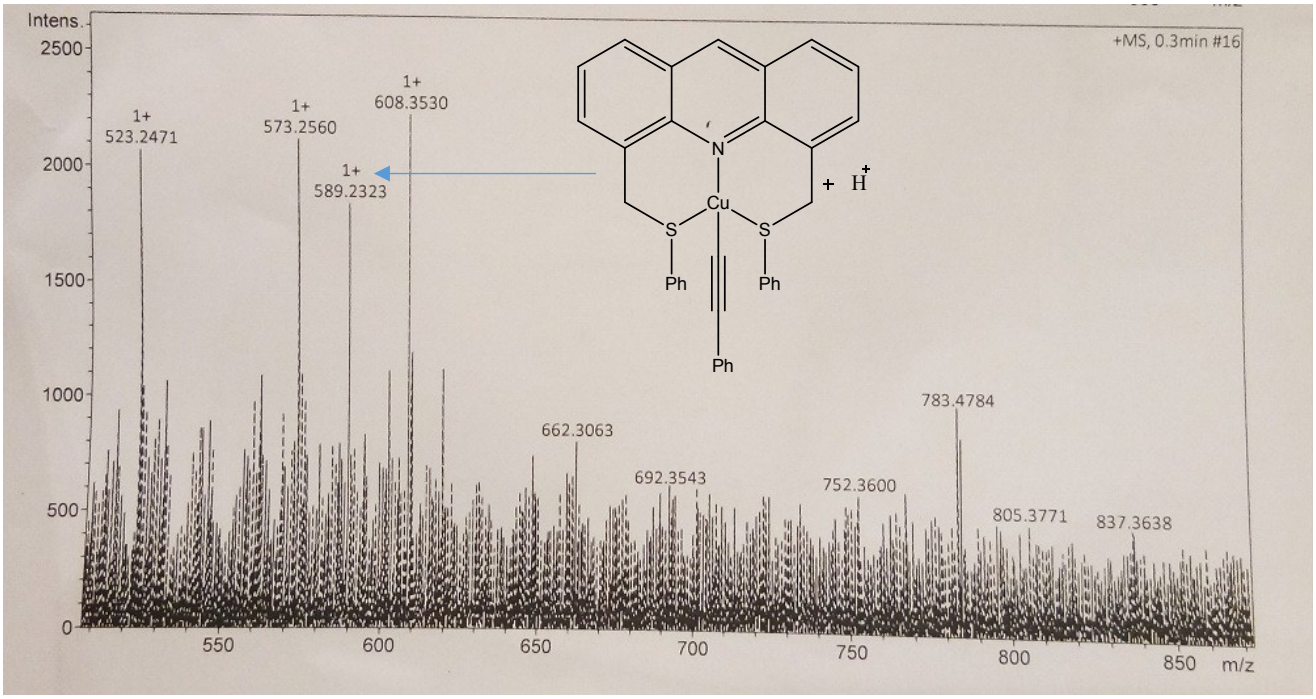


Figure S52: Mass Spectrum of Intermediate A