**Electronic Supplementary Information**

# Exploring Amine-rich Supramolecular Silver(I)-Metallogels for Autonomous Self-healing and as Catalysts for Three Component Coupling Reaction

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Figures: 21 (Figure S1 – S21)

Schemes: 3 (Scheme S1 – S3)

Tables: 2 (Table S1, S2)

Pages: 50 (S1 – S50)

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**Experimental details**

All the commercially available solvents and reagents were used as received without further purification. N, N-Dimethylformamide (DMF) was purchased from Finar Chemicals. Silver Nitrate ($AgNO_3$), hydrochloric acid (HCl), sodium hydroxide pellets, liq. ammonia, glacial acetic acid, ethylenediaminetetraacetic acid (EDTA), lithium fluoride (LiF), sodium chloride (NaCl), sodium bromide (NaBr), potassium iodide (KI), sodium nitrate ($NaNO_3$), sodium acetate (NaOAc), sodium sulfate ($Na_2SO_4$), triphenylphosphine ($PPh_3$), tetrabutylammonium bromide (TBABr), *p*-toluenesulfonic acid (*p*TsOH), 2,6-diaminopyridine (2,6-DAP) were procured from local Indian suppliers. Silver(I) trifluoromethanesulfonate (AgOTf) and 3,5-diamino-1,2,4-traizole were procured from Sigma Aldrich and used as received.

The synthesized metallogels and corresponding xerogels were characterized using several techniques such as PXRD, FT-IR, TEM, FESEM and dynamic rheological studies. Powder X-ray diffraction (PXRD) analysis was done using Philips X'pert MPD system (PANalytical diffractometer) with Cu $K\alpha_1$ radiation ($\lambda$ = 0.154 nm). The diffraction pattern was measured in the 2θ range from 5-90° at an operating voltage of 40 kV, 30 mA current, with a scan speed of 3º $min^{-1}$ and a step size of 0.013º in $2\theta$ at RT with a scan step time 58.395 sec. Anode material was Cu and the value of $K_{\alpha1}$, $K_{\alpha2}$ and $K_{\beta}$ were 1.54060 [Å], 1.54443 [Å] and 1.39225 [Å] respectively. Fourier transform Infrared Spectra analysis (FT-IR) was recorded on Perkin Elmer-Spectrum G-FTIR spectrometer (Germany) from 400-4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ using KBr pellets. The surface morphology of prepared gel material was analyzed by Field Emission-Scanning Electron Microscope (FESEM) (JEOL JSM 7100F) with an accelerating voltage of 5–15 kV with 10 $\mu$A of emission current. The transition electron microscope (TEM) analysis was done with JEOL, JEM 2100 TEM instrument. The rheological properties of samples were measured by the Anton Paar Rheometer. For the amplitude sweep experiment (Dynamic strain sweep, DSS) and thixotropic loop test, the operating frequency was kept constant at 1 rad $s^{-1}$. For the dynamic frequency sweep measurements, the operating strain was kept constant at 0.1% over the entire frequency range. The xerogels (lyophilized powder derived from the corresponding metallogels) were prepared by freeze drying (lyophilizing) method using a VirTis freezemobile 25EL lyophilizer. NMR spectra were recorded on Bruker AvanceII 500 spectrometer (500 MHz for $^1$H NMR, 126 MHz for $^{13}$C NMR). Chemical shifts were reported in ppm on the δ scale relative to $Me_4Si$ (δ = 0.00 for $^1$H-NMR), $CDCl_3$ (δ = 77.160 for $^{13}$C NMR). Peaks at δ = 1.56–1.61 ppm in $^1$H-NMR spectra of compounds recorded in $CDCl_3$ correspond to water present, if any. Additional peaks at δ =

0.86–0.88 ppm and δ = 1.25–1.28 ppm in $^{1}$H-NMR spectra and δ = 29.7–29. 8 ppm in $^{13}$C-NMR spectra of compounds recorded in $CDCl_3$ correspond to grease present, if any. Multiplicities are indicated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). $^{19}$F NMR spectra were recorded in ppm on the δ scale relative to $CF_3CO_2D$ as an external standard (δ = -76.55 in $CDCl_3$). Melting Points of solid compounds were measured by Thermo Scientific MEL TEMP instrument. All reactions that required heating were conducted in oil bath under continuous stirring by a magnetic stirrer equipped with a hot plate and temperature controller. All low temperature reactions were performed in a Siskin Profichill RFC-90 immersion cooler instrument. For centrifuge, Kubota 6500 instrument was used. For thin-layer chromatography (TLC) analysis throughout this work, Macherey-Nagel pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used. Solvents e.g. DMAc, DMF, DMSO, toluene, THF, dioxan, acetonitrile and DCM were dried by standard drying techniques.[1] All other solvents and commercially available compounds were used without further purification.

**Evaluation of the critical gelator concentration for the metallogels**

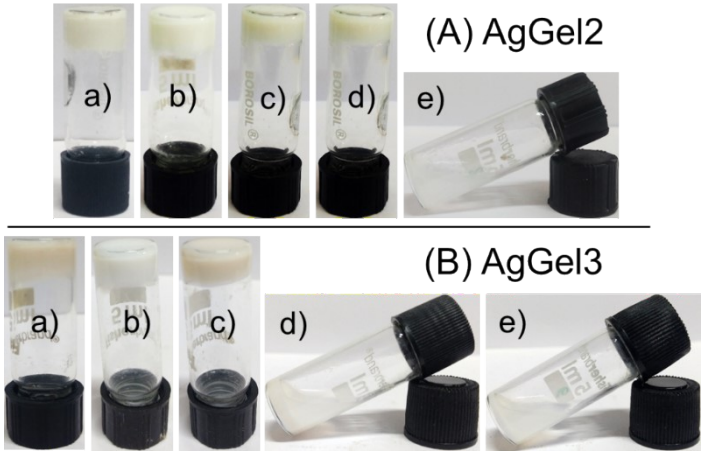



**Figure S1.** Evaluation of critical gelator concentration (CGC) for the gels: A) **AgGel2**, and B) **AgGel3** respectively. In all the cases, the evaluation was performed for a) 0.5 mmol, b) 0.4 mmol, c) 0.3 mmol, d) 0.2 mmol and e) 0.1 mmol for both metal and DATr concentrations.

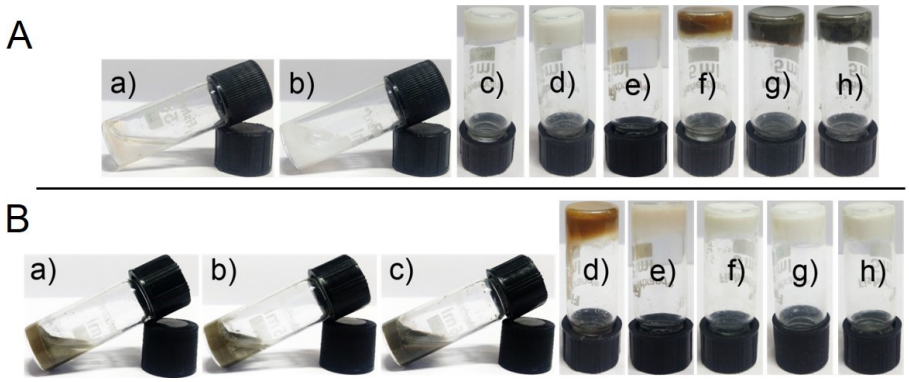



**Figure S2.** A) Effect of Ag(I) concentration on gelation in **AgGel3**. In each case DATr concentration was kept constant at 0.5 mmol and Ag(I) concentrations were varied from a) 0.1 mmol, b) 0.2 mmol, c) 0.3 mmol, d) 0.4 mmol, e) 0.5 mmol, f) 0.6 mmol, g) 0.8 mmol and h) 1 mmol respectively. B) Effect of DATr concentration on gelation in **AgGel3**. In each case Ag(I) concentration was kept constant at 0.5 mmol and DATr concentrations were varied from a) 0.1 mmol, b) 0.2 mmol, c) 0.3 mmol, d) 0.4 mmol, e) 0.5 mmol, f) 0.6 mmol, g) 0.8 mmol and h) 1 mmol respectively.

**FTIR spectra of the AgGels and corresponding xerogels**

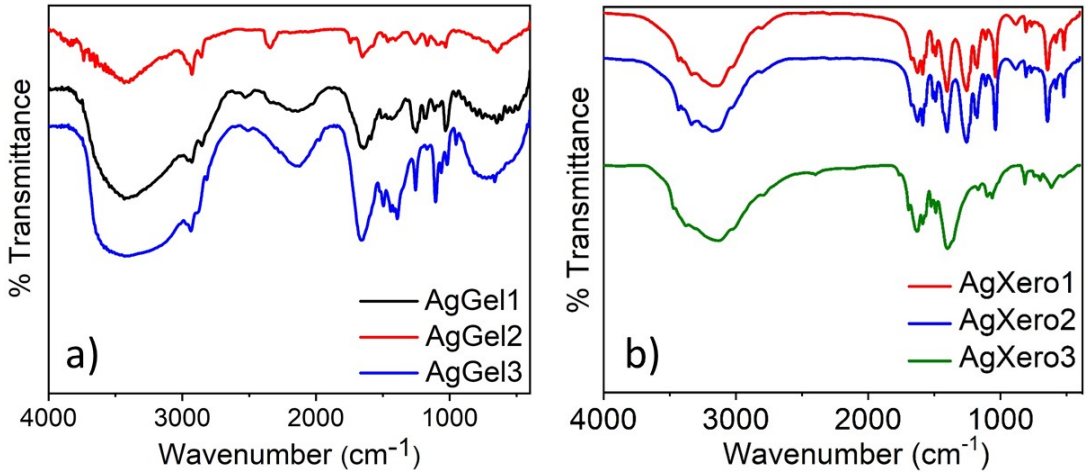



**Figure S3.** FTIR spectra of a) AgGels and b) gel-derived Ag xerogels respectively.

## Mass spectral analysis of AgGels

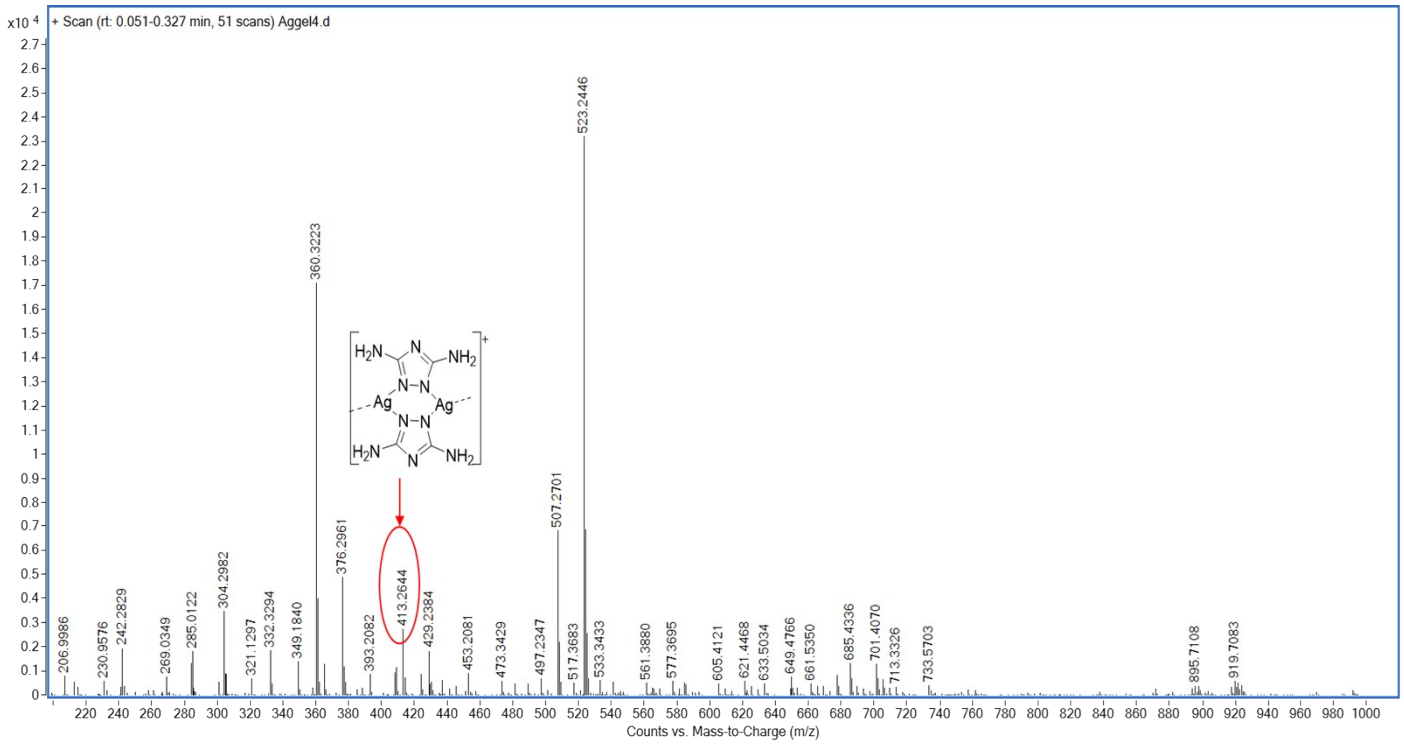



**Figure S4**. Mass spectral pattern of **AgGel2**.

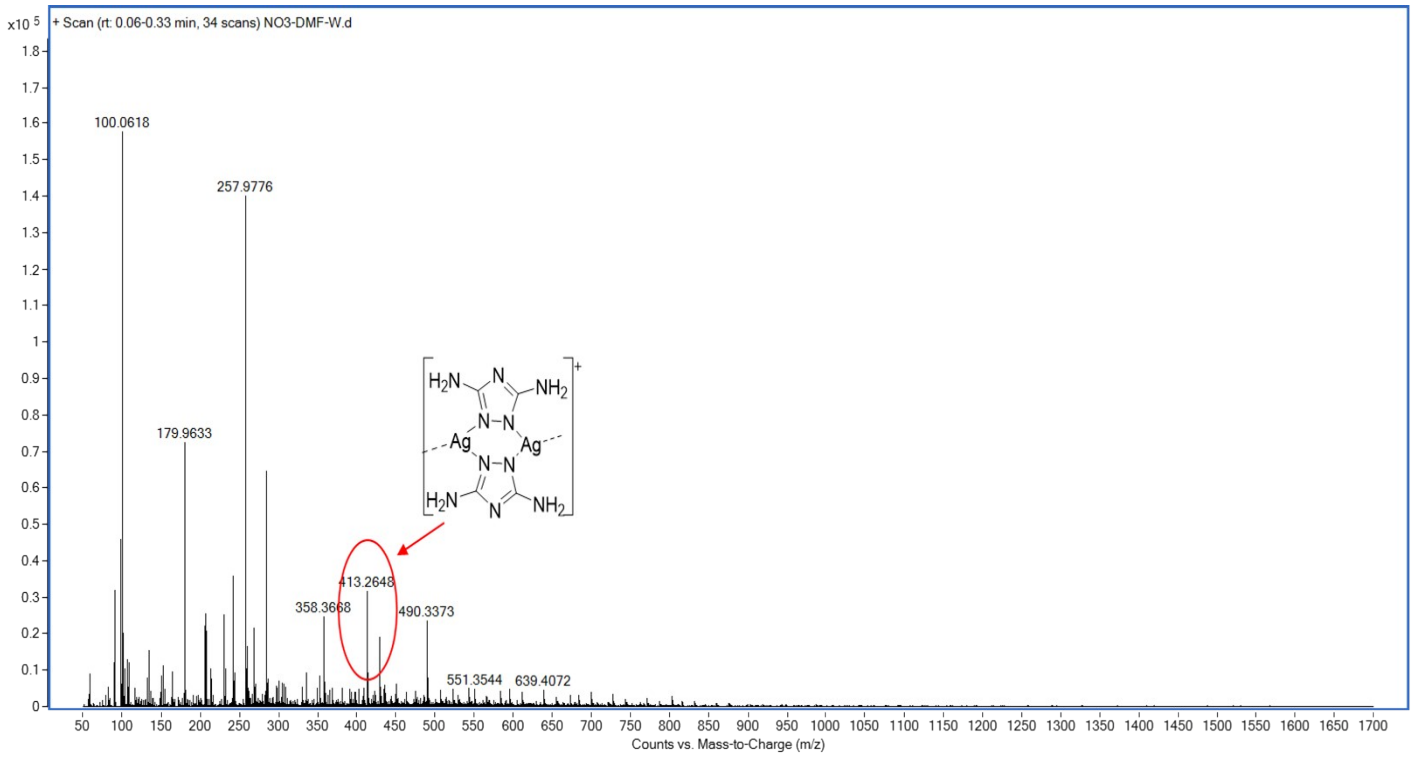



**Figure S5**. Mass spectral pattern of **AgGel3**.

**Effect of Ag(I) concentration on the morphological transformation of metallogel AgGel3**

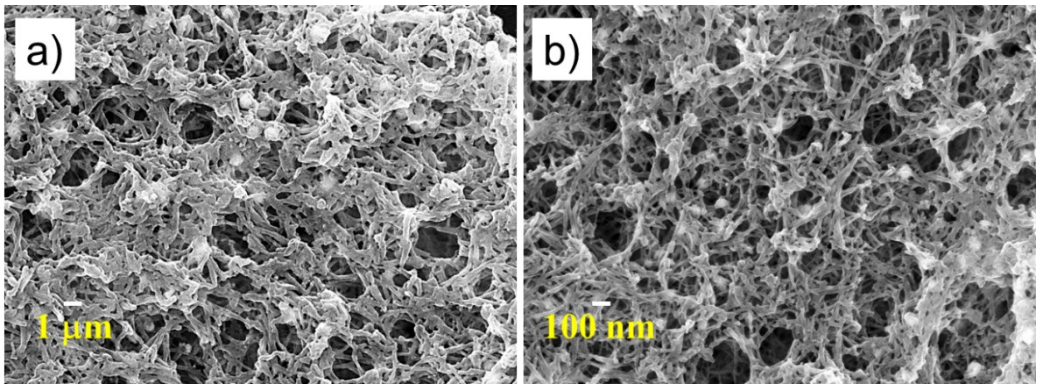



**Figure S6.** FE-SEM images of **AgGel3** having Ag(I): DATr ratio = 0.5:0.4 (mmol) showing entangled network morphology.

**Effect of DATr concentration on the morphological transformation of metallogel AgGel3**

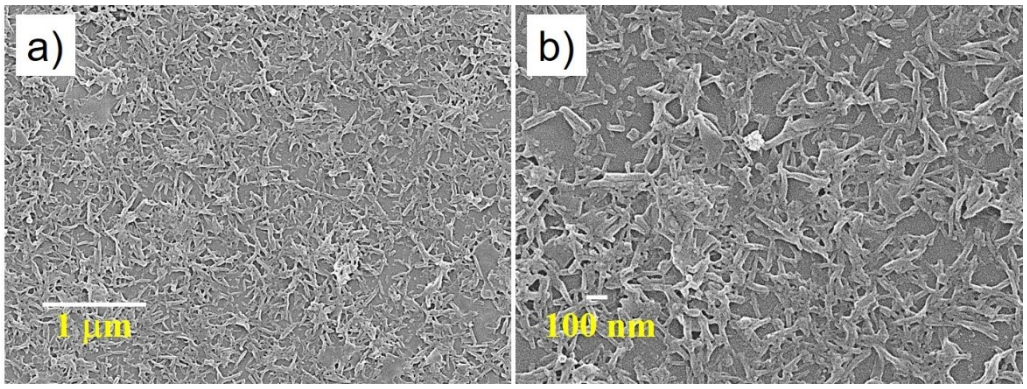



**Figure S7.** FE-SEM images of the metallogel **AgGel3** (both a and b) having Ag(I): DATr ratio = 0.6:0.5 (mmol) showing entangled network morphology.

**FE-SEM images of the metallogel derived xerogels**

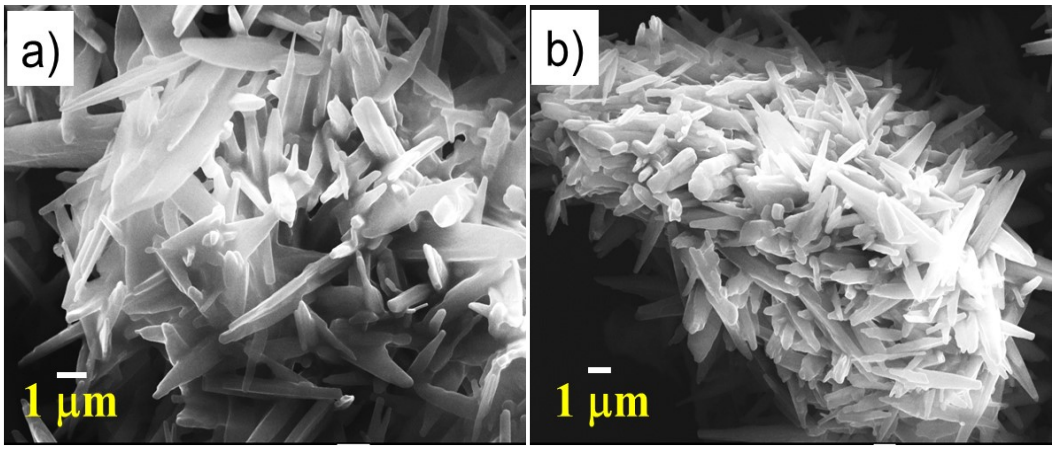



**Figure S8.** a), b) FE-SEM images of **AgXero1** showing rod-like morphology.

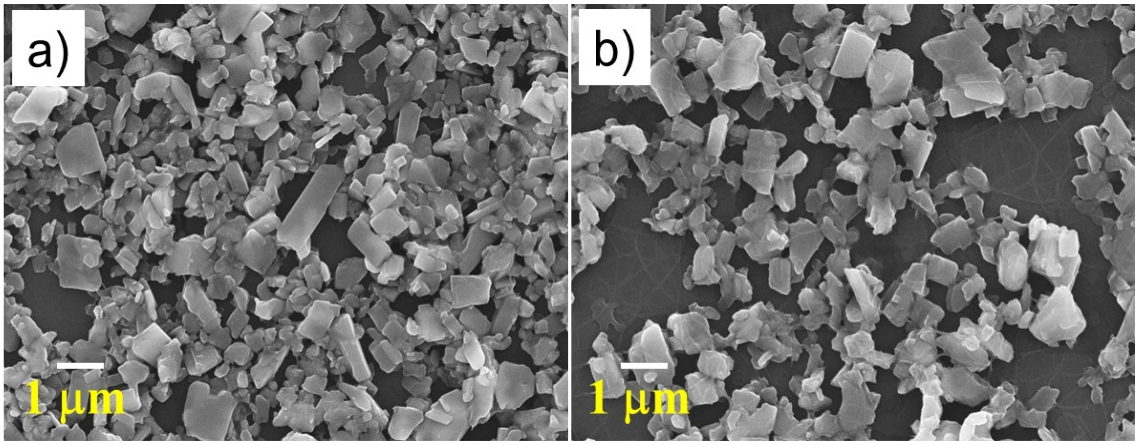



**Figure S9.** a), b) FE-SEM images of **AgXero2** showing rod-like morphology.

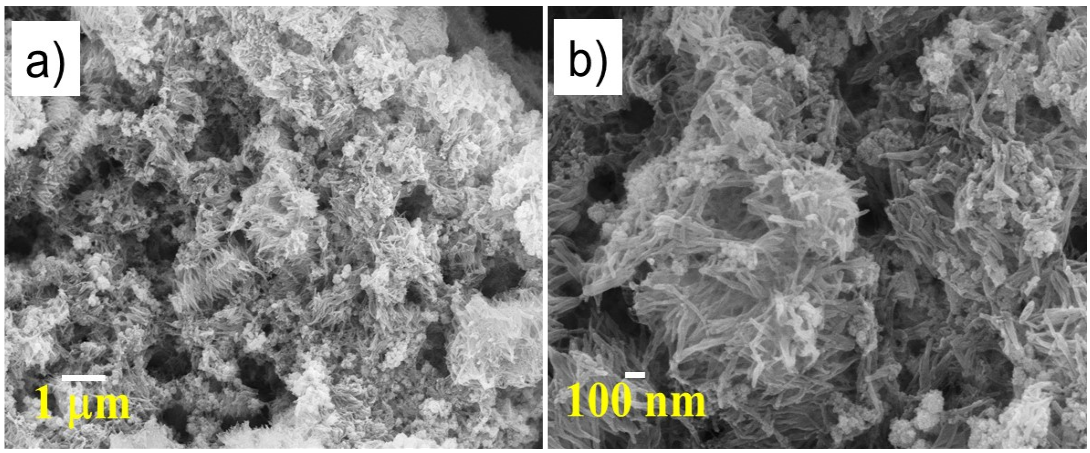



**Figure S10.** a), b) FE-SEM images of **AgXero3** showing entangled lamellae-like morphology.

**TEM images of the metallogel derived xerogels**

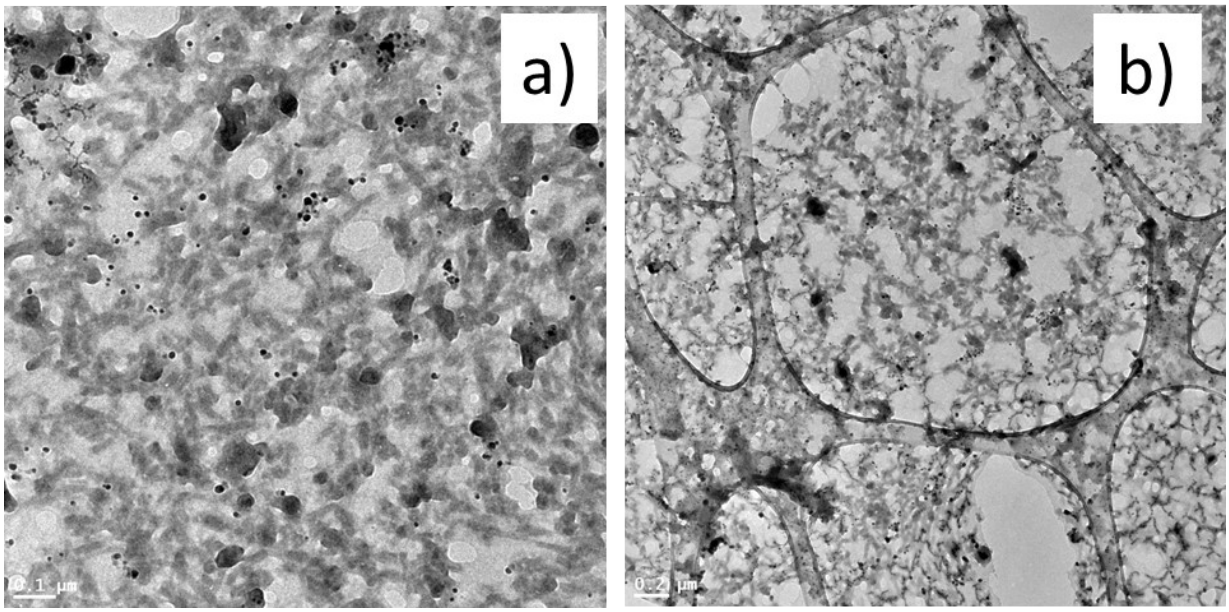



**Figure S11.** TEM images of the **AgGel1** derived xerogel **AgXero1** showing rod/tube-like morphology.

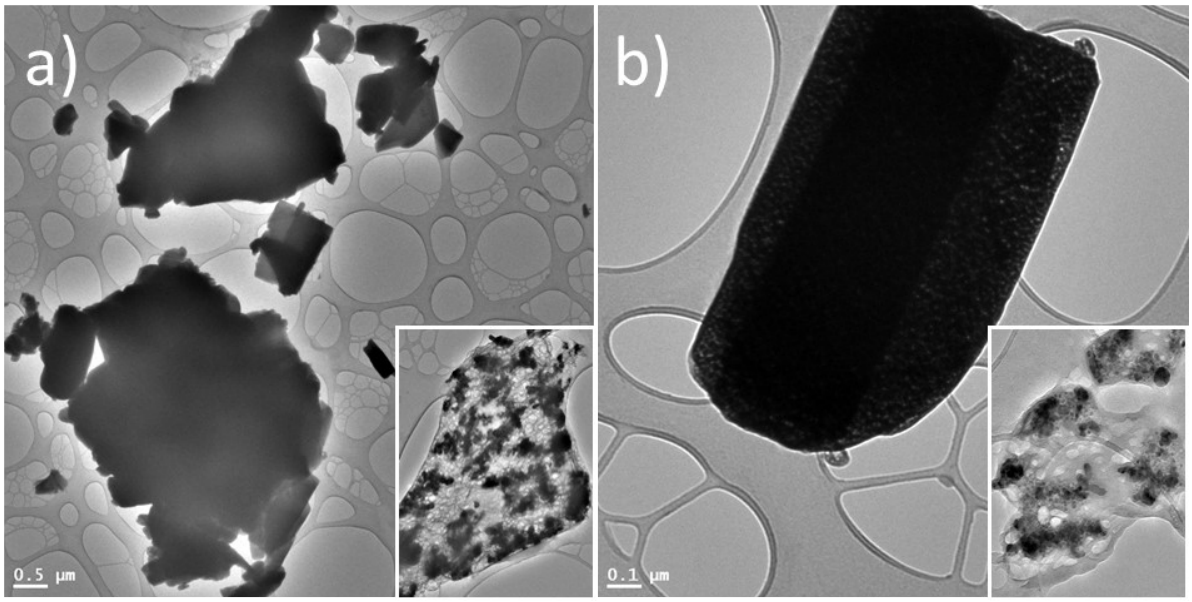



**Figure S12.** TEM images of the **AgGel2** derived xerogel **AgXero2** showing rod/tube-like morphology. The inset images show the corresponding high-resolution images, where the fibrous microstructure of the thick (flat)-belt like superstructure is clearly visible; however, with high resolution the electron beam induced generation of silver nanoparticles over the rod/belt could not be avoided even after using the lowest possible electron beam intensity during TEM analysis.

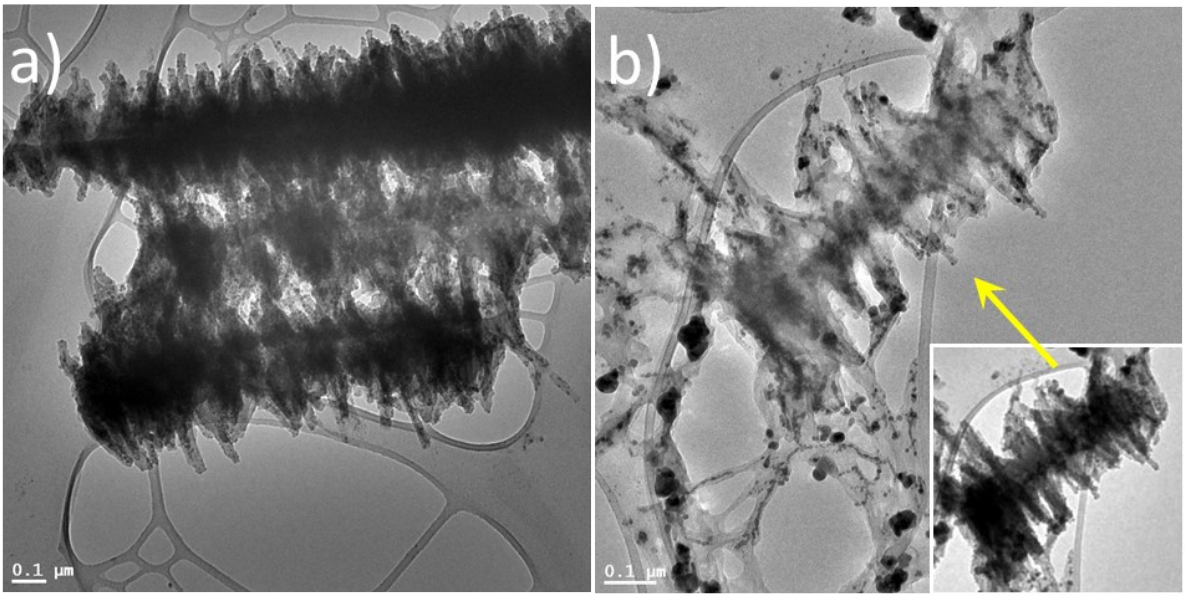



**Figure S13.** TEM images of the **AgGel3** derived xerogel **AgXero3** showing rod/tube-like morphology.

**Rheological experiments (frequency sweep) for the metallogels**

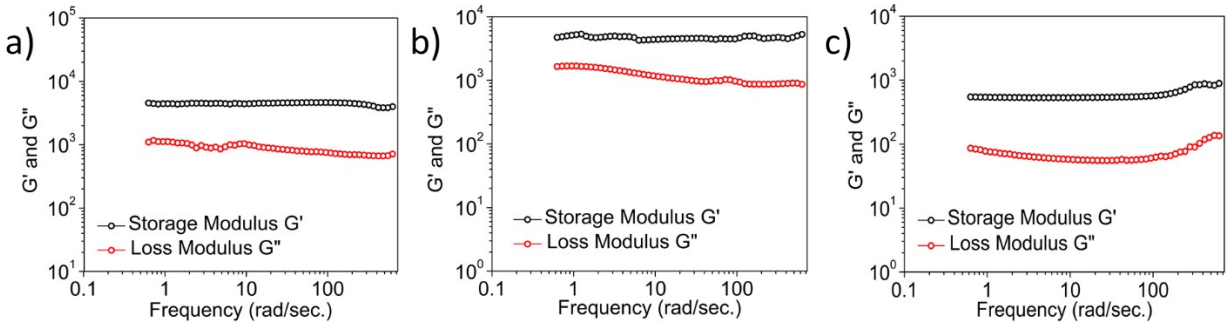



**Figure S14.** Frequency sweep measurements of a) **AgGel1**, b) **AgGel2** and c) **AgGel3** respectively.

**Stimuli-responsive nature of AgGel3**

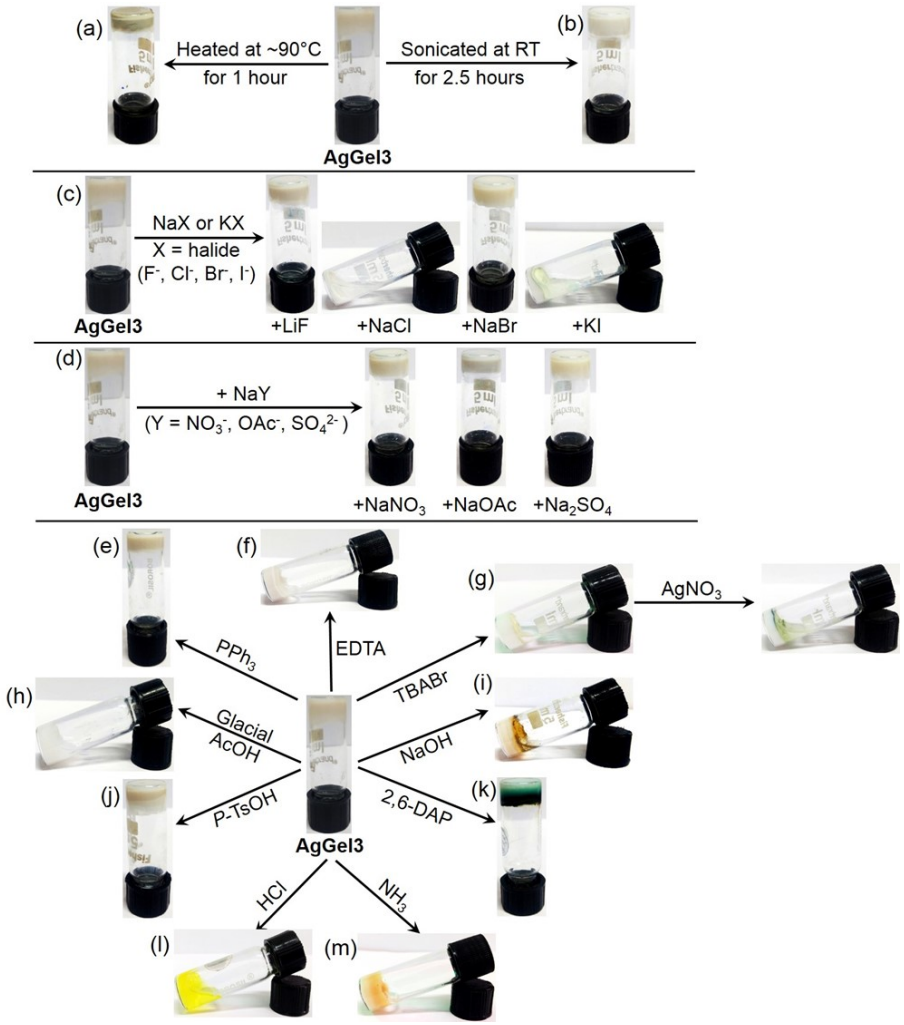



**Figure S15**. Multistimuli-responsive nature of **AgGel3**.

**XPS analysis of the metallogel derived xerogels**

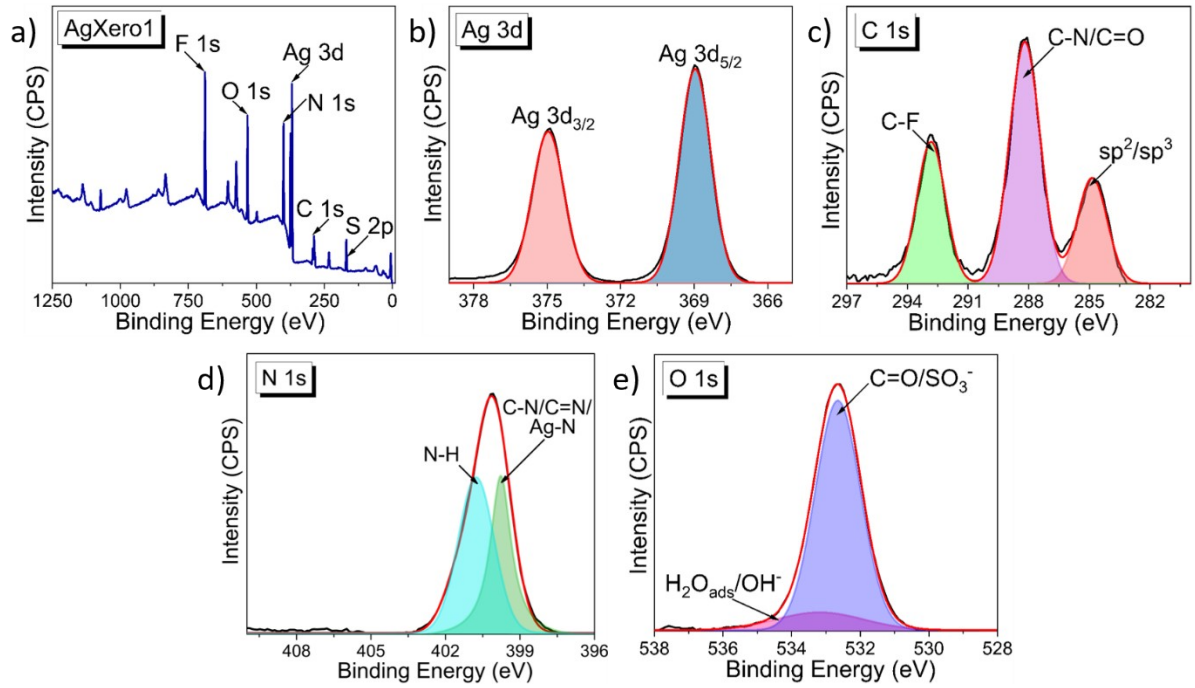



**Figure S16.** XPS Analysis of **AgGel1** derived xerogel **AgXero1**. a) XPS survey spectra; b) Ag 3d; c) C 1s; d) N 1s and e) O 1s spectra respectively.

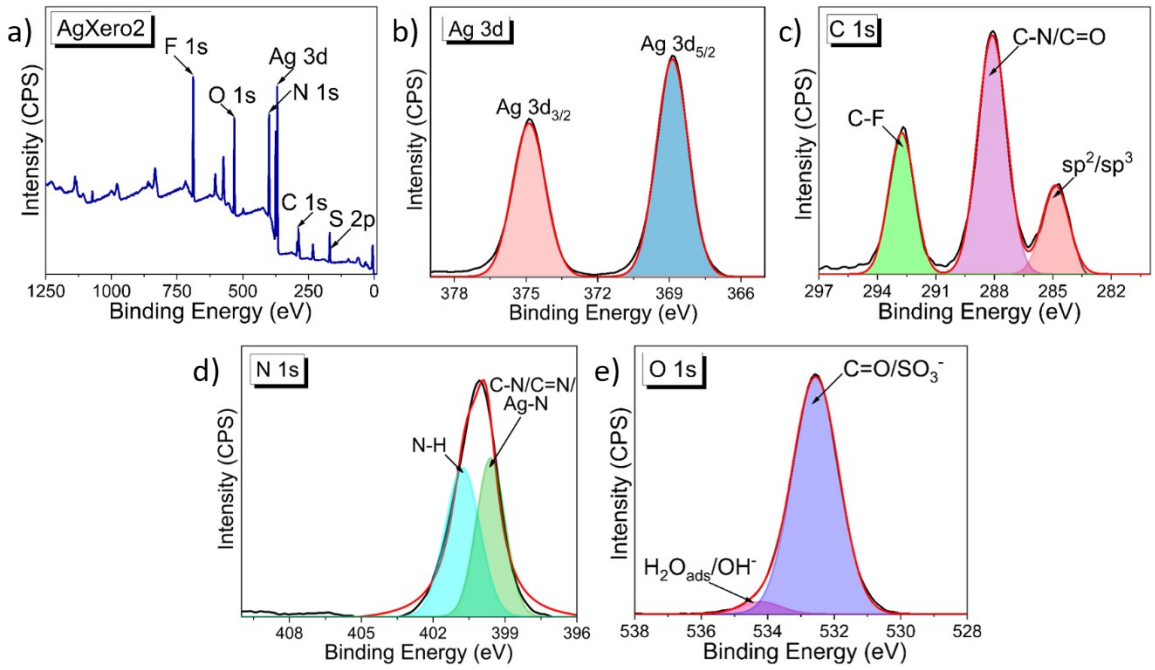



**Figure S17.** XPS Analysis of **AgGel2** derived xerogel **AgXero2**. a) XPS survey spectra; b) Ag 3d; c) C 1s; d) N 1s and e) O 1s spectra respectively.

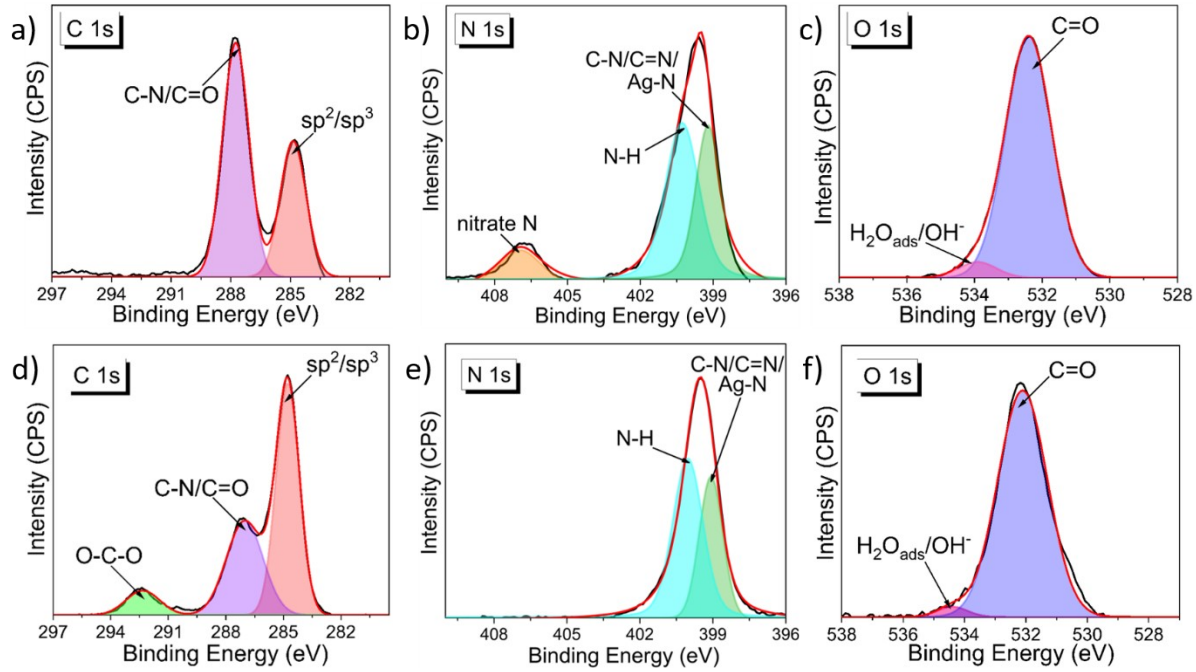



**Figure S18.** XPS Analysis of **AgGel3** derived xerogel **AgXero3**. a), b) and c) represent C 1s, N 1s and O 1s spectra of pristine (fresh) **AgXero3** respectively; whereas d), e) and f) represent C 1s, N 1s and O 1s spectra of recovered (used or spent) **AgXero3** respectively. Change O-C-O to C-O-C

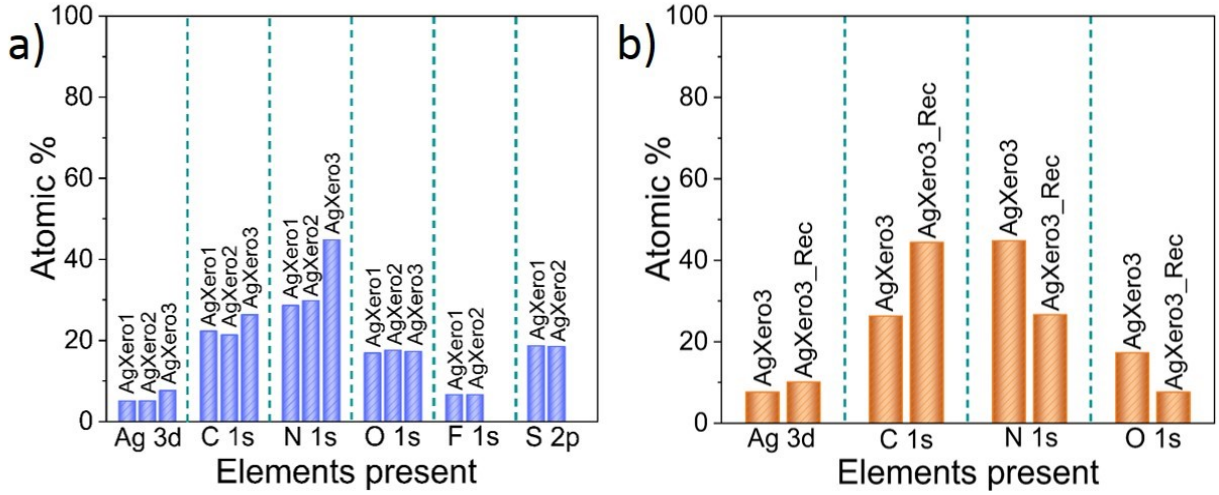


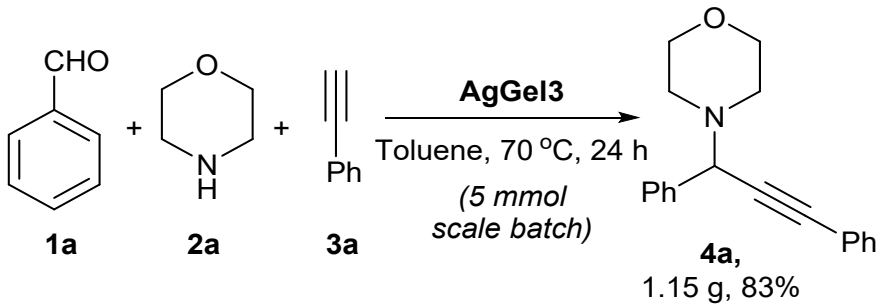

**Figure S19**. The relative composition obtained from the atomic% vs types of elements present plot in case of all the three xerogels (a) and in case of fresh (**AgXero3**) and recovered **AgXero3** (**AgXero3_Rec**) catalyst respectively.

**ICP-MS analysis for the measurement of $Ag^+$ content in xerogels**

**Table S1. ICP-OES Analysis of the gel-derived xerogels**

| Sr. No. | Name of the compounds | Presence of Ag(I) content in 10 mg of samples |
|---|---|---|
| 1 | AgXero1 | 2.334 mg |
| 2. | AgXero2 | 3.738 mg |
| 3. | AgXero3 | 2.5807 mg |
| 4. | AgXero3_Rec (6th cycle) | 3.11 mg |

**Gram scale synthesis of propargylamine via the AgGel3 catalyzed three component coupling reaction**




**Scheme S1.** Gram scale synthesis of propargylamine **4a.**

## Mechanistic Studies for the AgGel3 catalyzed three-component reaction

### Radical scavenging experiment in the presence of TEMPO

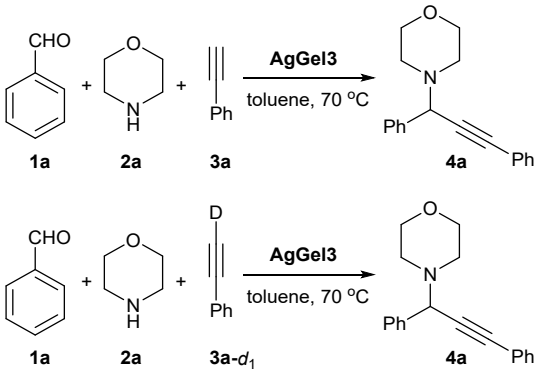
A 15 mL reaction tube was charged with benzaldehyde **1a** (53 mg, 0.5 mmol, 1.0 eq), morpholine **2a** (52 mg, 0.6 mmol, 1.2 eq), phenyl acetylene **3a** (77 mg, 0.75 mmol, 1.5 eq), TEMPO (156 mg, 1.0 mmol, 2.0 eq) and **AgGel3** (36 mg). The vessel was evacuated and back-filled with nitrogen (×3). To it, toluene (3 mL) was added and the reaction mixture was stirred at 70 ºC for 14 h. After cooling, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica-gel to provide 4-(1,3-diphenylprop-2-yn-1-yl)morpholine (**4a**). Yellow oil (118 mg, 85%).

### Radical scavenging experiment in the presence of BHT

A 15 mL reaction tube was charged with benzaldehyde **1a** (53 mg, 0.5 mmol, 1.0 eq), morpholine **2a** (52 mg, 0.6 mmol, 1.2 eq), phenyl acetylene **3a** (77 mg, 0.75 mmol, 1.5 eq), BHT (220 mg, 1.0 mmol, 2.0 eq) and **AgGel3** (36 mg). The vessel was evacuated and back-filled with nitrogen (× 3). To it, toluene (3 mL) was added and the reaction mixture was stirred at 70 ºC for 14 h. After cooling, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica-gel to provide 4-(1,3-diphenylprop-2-yn-1-yl)morpholine (**4a**). Yellow oil (115 mg, 83%).

### Determination of KIE by independent parallel experiment

Two independent reactions with **3a** and **3a**-$d_1$ under the optimal reaction conditions were conducted: Two 15 mL Schlenk tubes were charged with **3a** (51 mg, 0.5 mmol, 1.0 eq) and **3a**-$d_1$ (52 mg, 0.5 mmol, 1.0 eq) separately. To each of them, benzaldehyde **1a** (53 mg, 0.5 mmol, 1.0 eq), morpholine **2a** (44 mg, 0.5 mmol, 1.0 eq) and **AgGel3** (36 mg) were added. Then, the vessels were evacuated and back-filled with nitrogen (× 3) and the reaction mixtures were stirred at 70 ºC for the required time as indicated in the following table. An aliquot of 0.1 mL was withdrawn periodically and passed through a small bed of silica-gel and monitored by GC analysis (Figure S20). Comparison of the two individual reactions showed a kinetic isotope effect of 1.20, precluding the possibility of C–H bond cleavage in the rate determining step.




**Scheme S2.** KIE study by parallel independent experiments.

**Table S2.** KIE study by parallel independent experiments: Experimental parameters

| **Time** (min) | 20 | 40 | 60 | 80 | 100 | 120 |
|---|---|---|---|---|---|---|
| **4a** (from **3a**) (%) | 4.25 | 5.09 | 6.81 | 9.49 | 11.06 | 15.57 |
| **4a** (from **3a**-$d_1$) (%) | 2.11 | 3.57 | 5.57 | 5.95 | 9.83 | 11.16 |

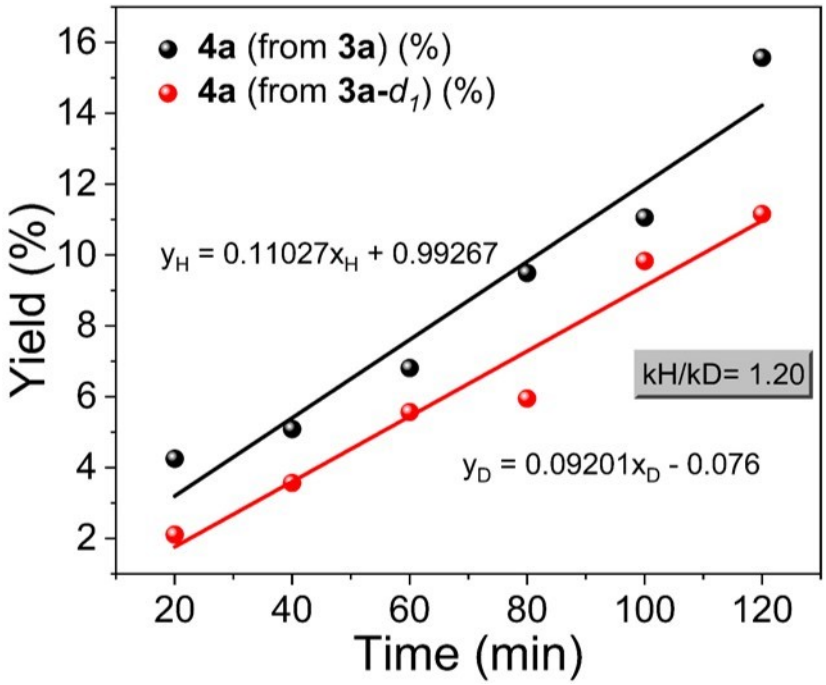
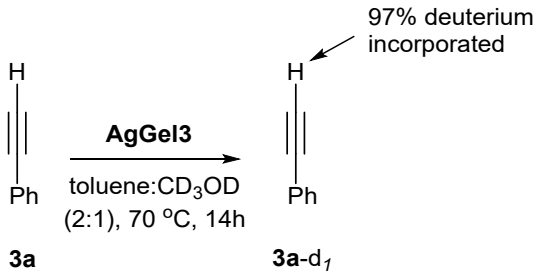



**Figure S20**. Determination of KIE by independent parallel experiments with **3a** and **3a**-$d_1$

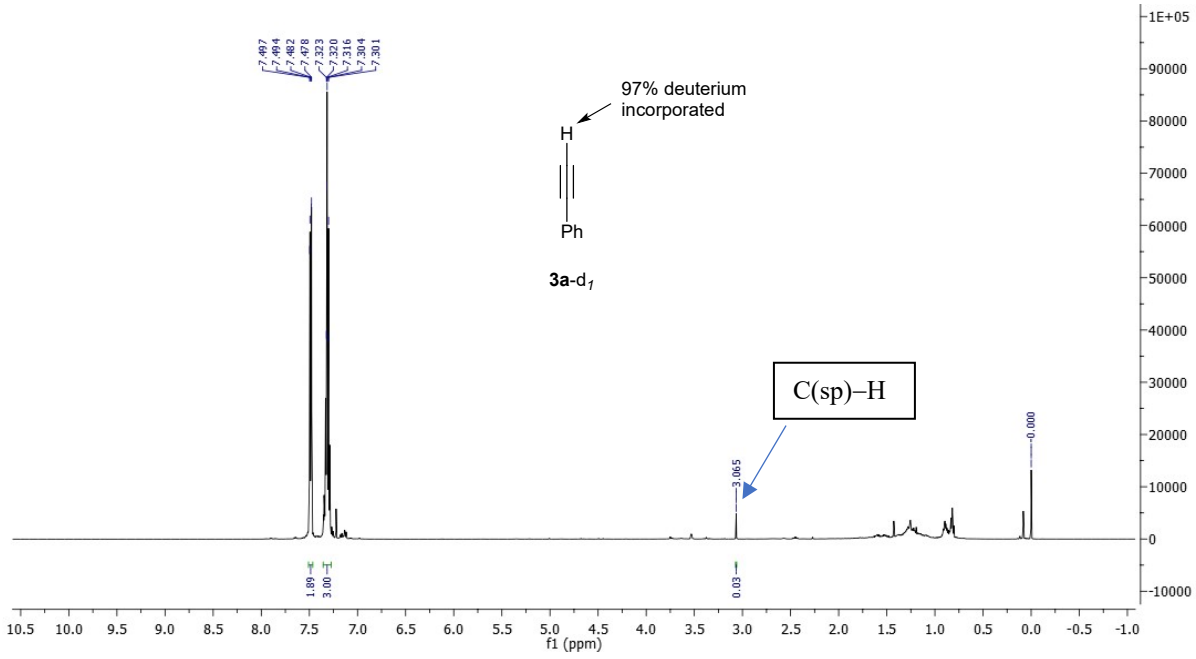
**H/D scrambling experiment:**




**Scheme S3**. H/D scrambling in **3a** by using $CD_3OD$

A 15 mL reaction tube was charged with phenylacetylene **3a** (77 mg, 0.5 mmol, 1.0 eq) and **AgGel3** (36 mg). The vessel was evacuated and back-filled with nitrogen (× 3) and to it, anhydrous toluene (2.0 mL) and methanol-$d_4$ (1.0 mL) were added. Subsequently, the reaction mixture was stirred at 70 ºC for 14 h. After cooling, the solvent was evaporated and the residue was directly subjected to column chromatography on silica-gel to provide the deuterated compound **3a**-$d_1$. $^1$H NMR indicates that there is a scrambling of H/D in the starting material (**3a**) in the presence of **AgGel3** and methanol-$d_4$, suggesting the reversibility of the C–H abstraction step.

**$^1$H NMR (500 MHz, $CDCl_3$):**



**Recyclability studies**

A 100 mL reaction tube was charged with **1a** (212 mg, 2.0 mmol, 1.0 eq), **2a** (209 mg, 2.4 mmol, 1.2 eq), **3a** (306 mg, 3.0 mmol, 1.5 eq) and **AgGel3** (144 mg). The vessel was evacuated and back-filled with nitrogen (× 3). To it, toluene (12 mL) was added and the reaction mixture was stirred at 70 ºC till completion (monitored by TLC). After cooling, the reaction mixture was diluted with diethyl ether (20 mL) and the tube was centrifuged for 3 minutes at 3000 rpm. The supernatant liquid was collected in a round bottom flask. This process was repeated for another two times and the combined organic layer was concentrated in vacuum. The residue was purified by flash column chromatography on silica-gel to provide 4-(1,3-diphenylprop-2-yn-1-yl)morpholine (**4a**) in 85% yield.

The catalyst was obtained as the residue upon centrifugation and filtration. The residue was thoroughly washed with water (3 × 15 mL) and acetone (3 × 7 mL) followed by drying under vacuum before further use. The catalyst was recycled for five times (first batch with fresh catalyst + four successive batches with the used catalyst from the previous batch). However, the reaction by employing the reused catalyst required longer time (20 h, 24 h, 30 h and 36 h for 2$^{nd}$, 3$^{rd}$, 4$^{th}$ and 5$^{th}$ run respectively) compared to that of the fresh catalyst (14 h). Ag content in fresh catalyst: 2.58 mg/10 mg, Ag content in recovered catalyst: 3.11 mg/10 mg as detected by ICP-MS (Figure S21).

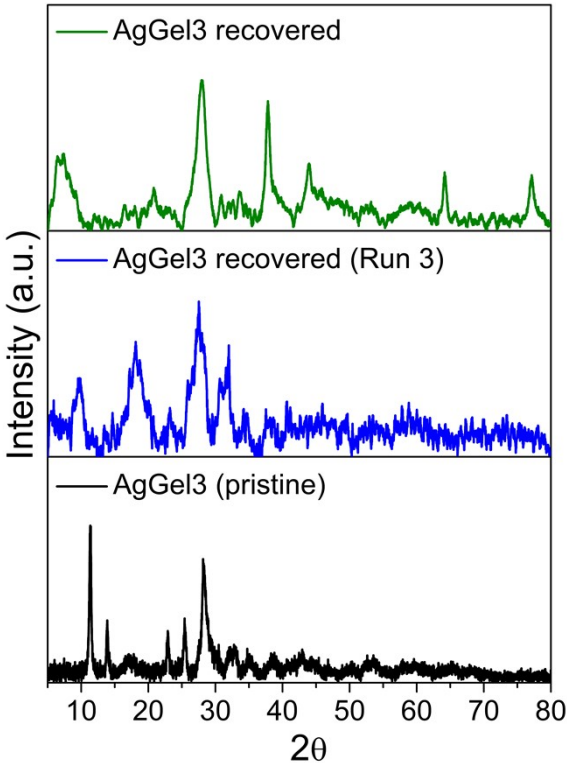



**Figure S21**. PXRD profiles of the **AgGel3** (pristine) catalyst and the recovered **AgGel3** catalyst.

**Preparative Procedures for the AgGel3 catalyzed three-component reaction**

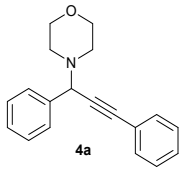
**Preparation of substrates:**

Aryl acetylenes substrates **3b** and **3c** were prepared by reported methods and were characterized by matching their $^{1}H$ and $^{13}C$ NMR spectral data with that of the reported compounds.[2]

**Three-component coupling of aldehyde, alkyne and amines**

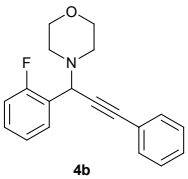
**General procedure.** A 15 mL reaction tube was charged with **1** (0.5 mmol, 1.0 eq), **2** (0.6 mmol, 1.2 eq), **3** (0.75 mmol, 1.5 eq) and **AgGel3** (36 mg). The vessel was evacuated and back-filled with nitrogen (× 3). To it, toluene (3 mL) was added and the reaction mixture was stirred at 70 ºC till completion (monitored by TLC). After cooling, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 25 mL), the combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica-gel to provide the corresponding amide product (**4**).

**Characterization of products**



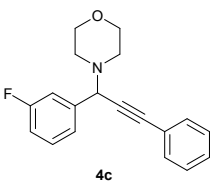
4a

**4-(1,3-diphenylprop-2-yn-1-yl)morpholine (4a**) was prepared according to the general procedure using benzaldehyde (**1a**) (53 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow oil [118 mg, 85%]. $R_f$ = 0.5 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3390, 2928, 1607, 1087, 755 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.63–7.64 (m, 2H), 7.50–7.52 (m, 2H), 7.29–7.38 (m, 6H), 4.79 (s, 1H), 3.69–3.77 (m, 4H), 2.62–2.64 (m, 4H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 137.9, 131.9 (2C), 128.7 (2C), 128.4 (2C), 128.4 (3C), 127.9, 123.1, 88.6, 85.2, 67.3 (2C), 62.2, 50.0 (2C) ppm.



4b

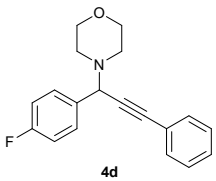
**4-(1-(2-fluorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (4b**) was prepared according to the general procedure using 2-fluorobenzaldehyde (**1b**) (62 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Reddish liquid [106 mg, 72%]. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3400, 2957, 2854, 1455, 1117, 756 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.59–7.62 (m, 1H), 7.41–7.43 (m, 2H), 7.23–7.27 (m, 4H), 7.08–7.11 (m, 1H), 6.99–7.03 (m, 1H), 5.02 (s, 1H), 3.64–3.67 (m, 4H), 2.59–2.61(m, 4H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 131.9 (2C), 130.8 (2C), 130.0, 128.5, 128.4 (2C), 123.8, 122.8, 115.8, 115.6, 87.7, 84.8, 67.1 (2C), 55.5 (2C), 50.0 ppm. $^{19}F$ NMR (564 MHz, $CDCl_3$) δ −117.48 ppm.



4c

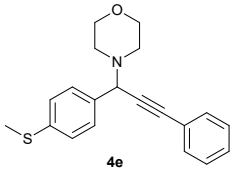
**4-(1-(3-fluorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (4c**) was prepared according to the general procedure using 3-fluorobenzaldehyde (**1c**) (62 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Yellow solid [103 mg, 70%]. Melting point = 68 ºC. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (KBr): ν = 2961, 2825, 1589, 1484, 1115, 755 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.43–7.46 (m, 2H), 7.36–7.37 (m, 1H), 7.23–7.32 (m, 5H), 6.91–

6.95 (m, 1H), 4.72 (s, 1H), 3.64–3.71 (m, 4H), 2.56 (s, 4H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.8, 140.7, 132.0 (2C), 129.8, 128.6, 128.5 (2C), 124.2, 122.8, 115.6, 114.9, 89.0, 84.3, 67.3 (2C), 61.6 (2C), 49.9 ppm. $^{19}$F NMR (564 MHz, $CDCl_3$) δ −113.47 (d, $J$ = 3.948 Hz, 1F) ppm.



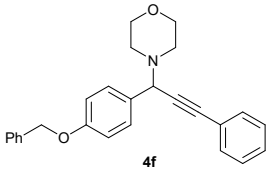
4d

**4-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (4d**) was prepared according to the general procedure using 4-fluorobenzaldehyde (**1d**) (62 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow oil [111 mg, 75%]. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 33968, 2922, 2850, 2337, 1511, 1248, 1170, 691 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52–7.55 (m, 2H), 7.43–7.45 (m, 2H), 7.26–7.27 (m, 3H), 6.96–6.99 (m, 2H), 4.69 (s, 1H), 3.66–3.69 (m, 4H), 2.54 (s, 4H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.5, 161.5, 133.7, 131.9 (2C), 130.3, 130.2, 128.5 (2C), 122.9, 115.3, 115.1, 88.9, 84.8, 67.3 (2C), 61.4 (2C), 49.9 ppm. $^{19}$F NMR (564 MHz, $CDCl_3$) δ −114.77 ppm.



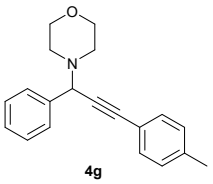
4e

**4-(1-(4-(methylthio)phenyl)-3-phenylprop-2-yn-1-yl)morpholine (4e**) was prepared according to the general procedure using 4-(methylthio)benzaldehyde (**1e**) (76 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow solid [105 mg, 65%]. Melting point = 55 °C. $R_f$ = 0.3 ($Et_2O$:Hexane = 1:4). IR (KBr): ν = 2932, 2816, 1491, 1315, 1116, 757 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.46–7.48 (m, 2H), 7.42–7.44 (m, 2H), 7.25–7.26 (m, 3H), 7.17–7.19 (m, 2H), 4.67 (s, 1H), 3.65–3.69 (m, 4H), 2.54 (s, 4H), 2.42 (s, 3H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.1, 134.8, 131.9 (2C), 129.2 (2C), 128.4 (2C), 126.4 (2C), 123.0, 88.6, 85.0, 67.3 (2C), 61.7, 49.9 (2C), 15.9 ppm.



4f

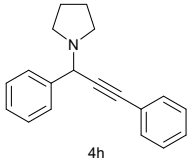
**4-(1-(4-(benzyloxy)phenyl)-3-phenylprop-2-yn-1-yl)morpholine (4f)** was prepared according to the general procedure using 4-(benzyloxy)benzaldehyde (**1f**) (106 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Brown solid [119 mg, 62%]. Melting point = 85 °C. $R_f$ = 0.4 ($Et_2O$:Hexane = 3:7). IR (KBr): ν = 3388, 2857, 2820, 1608, 1248, 1111, 691 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.50–7.54 (m, 4H), 7.43–7.45 (m, 2H), 7.37–7.40 (m, 2H), 7.31–7.34 (m, 4H), 6.96–6.98 (m, 2H), 5.07 (s, 2H), 4.73 (s, 1H), 3.73–3.74 (m, 4H), 2.61–2.62 (m, 4H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 158.5, 137.1, 131.9 (2C), 130.2, 129.9 (2C), 128.7 (2C), 128.4 (2C), 128.3, 128.1, 127.6 (2C), 123.1, 114.6 (2C), 88.4, 85.4, 70.2, 67.3 (2C), 61.6, 49.9 (2C) ppm.



4g

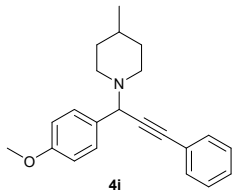
**4-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)morpholine (4g**) was prepared according to the general procedure using benzaldehyde (**1a**) (53 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and 1-ethynyl-4-methylbenzene (**3b**) (87 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Brown oil [89 mg, 61%]. $R_f$ = 0.3 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3398, 2933, 1514, 1118, 757 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.55–7.56 (m, 2H), 7.32–

7.34 (m, 2H), 7.28–7.31 (m, 2H), 7.23–7.24 (m, 1H), 7.06–7.07 (m, 2H), 4.70 (s, 1H), 3.64–3.67 (m, 4H), 2.55–2.56 (m, 4H) 2.29 (s, 3H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.0, 131.8 (2C), 129.2 (2C), 128.8 (2C), 128.3 (2C), 127.9, 120.0, 88.7, 84.4, 67.3 (2C), 62.2 (2C), 50.0, 21.6 ppm.



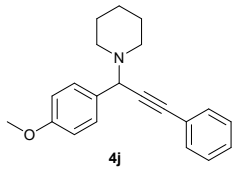
4h

**1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (4h**) was prepared according to the general procedure using benzaldehyde (**1a**) (53 mg, 0.5 mmol), pyrrolidine (**2b**) (43 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Brown oil [93 mg, 71%]. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3365, 2922, 1600, 1071, 755 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.60–7.61 (m, 2H), 7.48–7.49 (m, 2H), 7.34–7.37 (m, 2H), 7.28–7.32 (m, 4H), 4.88 (s, 1H), 2.67–2.70 (m, 4H), 1.77–1.82 (m, 4H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.6, 131.9 (2C), 128.4 (4C), 128.2, 127.7, 123.4, 87.0, 86.8, 56.3, 50.4 (2C), 23.6 (2C) ppm.



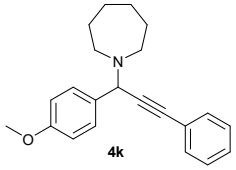
4i

**1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)-4-methylpiperidine (4i**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), 4-methylpiperidine (**2c**) (60 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow liquid [117 mg, 73%]. $R_f$ = 0.6 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3390, 2921, 1607, 1245, 1074, 755 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.49–7.54 (m, 4H), 7.30–7.32 (m, 3H), 6.88–6.89 (m, 2H), 4.75 (s, 1H), 3.80 (s, 3H), 2.91–2.84 (m, 1H), 2.65–2.67 (m, 1H), 2.44–2.49 (m, 1H), 2.13–2.18 (m, 1H), 1.66–1.68 (m, 1H), 1.54–1.57 (m, 1H), 1.26–1.43 (m, 2H), 1.10–1.18 (m, 1H), 0.90–0.91 (m, 3H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 159.1, 131.9 (2C), 130.9, 129.8 (2C), 128.4 (2C), 128.1, 123.5, 113.5 (2C), 87.7, 86.5, 61.6, 55.4, 52.6, 47.6, 34.8, 34.4, 30.9, 22.0 ppm.



4j

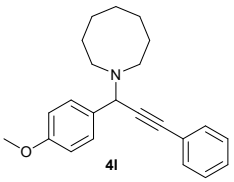
**1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine (4j**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), piperidine (**2d**) (51 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 24 h. Yellow solid [131 mg, 86%]. Melting point = 48 °C. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (KBr): ν = 2820, 1449, 1319, 1115, 756 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.50–7.54 (m, 4H), 7.31–7.33 (m, 3H), 6.88–6.90 (m, 2H), 4.73 (s, 1H), 3.81 (s, 3H), 2.53–2.55 (m, 4H), 1.52–1.64 (m, 4H), 1.43–1.44 (m, 2H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 159.1, 131.9 (2C), 130.9, 129.8 (2C), 128.4 (2C), 128.1, 123.5, 113.5 (2C), 87.7, 86.6, 61.9, 55.4, 50.7 (2C), 26.3 (2C), 24.6 ppm.



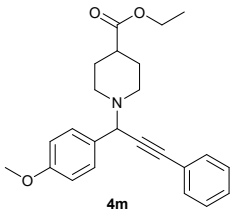
4k

**1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)azepane (4k**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), azepane (**2e**) (60 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow oil [144 mg, 90%]. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3418, 2920, 1650, 1165, 635 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.59–7.61 (m, 2H), 7.50–7.51 (m, 2H), 7.30–7.33 (m, 3H), 4.85 (s, 1H), 3.80 (s, 3H), 2.70–2.72 (m, 4H), 1.58–1.67 (m, 8H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$) δ 158.9, 132.0, 131.9

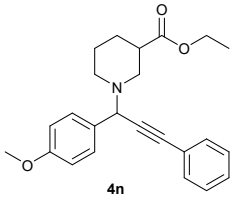
(2C), 129.5 (2C), 128.4 (2C), 128.1, 123.6, 113.4 (2C), 87.2, 87.0, 62.2, 52.6 (2C), 29.1 (2C), 27.1 (2C) ppm.



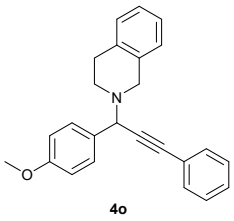
**1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)azocane (4l**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), azocane (**2f**) (68 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow oil [157 mg, 94%]. $R_f$ = 0.8 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3400, 2918, 1609, 1510, 1248, 691 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.0 Hz, 2H), 7.41–7.43 (m, 2H), 7.19–7.24 (m, 3H), 6.79–6.80 (m, 2H), 4.76 (s, 1H), 3.71 (s, 3H), 2.52–2.62 (m, 4H), 1.57–1.60 (m, 2H), 1.44–1.51 (m, 6H), 1.30–1.38 (m, 2H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 158.9, 132.2, 131.9 (2C), 129.8 (2C), 128.4 (2C), 128.0, 123.6, 113.3 (2C), 87.3, 87.1, 62.0, 55.3, 51.3 (2C), 28.1 (2C), 28.0, 26.0 (2C) ppm.



**Ethyl 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine-4-carboxylate (4m**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), ethyl piperidine-4-carboxylate (**2g**) (94 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow oil [155 mg, 82%]. $R_f$ = 0.3 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3366, 2923, 1648, 1461, 1030, 798 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.49–7.54 (m, 4H), 7.32–7.34 (m, 3H), 6.88–6.90 (m, 2H), 4.78 (s, 1H), 4.10–4.17 (m, 2H), 3.81 (s, 3H), 2.96–2.98 (m, 1H), 2.68–2.70 (m, 1H), 2.51–2.56 (m, 1H), 2.19–2.31 (m, 2H), 1.94–1.97 (m, 1H), 1.82–1.89 (m, 2H), 1.64–1.68 (m, 1H), 1.22–1.24 (m, 3H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 175.4, 159.1, 131.9 (2C), 130.5, 129.6 (2C), 128.4 (2C), 128.2, 123.3, 113.6 (2C), 88.1, 85.8, 61.4, 60.4, 55.4, 51.6, 46.8, 41.5, 28.8, 28.4, 14.3 ppm.

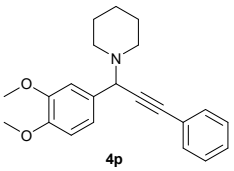


**Ethyl 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine-3-carboxylate (4n**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), ethyl piperidine-3-carboxylate (**2h**) (94 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow liquid [132 mg, 70%]. $R_f$ = 0.4 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3390, 2923, 2115, 1605, 1464, 1030, 756 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.50–7.54 (m, 4H), 7.32–7.34 (m, 3H), 6.88–6.90 (m, 2H), 4.81 (s, 1H), 4.05–4.17 (m, 2H), 3.81 (s, 3H), 2.82–2.83 (m, 1H), 2.59–2.67 (m, 2H), 2.46–2.51 (m, 1H), 1.89–1.92 (m, 1H), 1.61–1.79 (m, 2H), 1.43–1.51 (m, 2H), 1.20–1.26 (m, 3H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 174.4, 159.1, 131.9 (2C), 130.5, 129.6 (2C), 128.4 (2C), 128.2, 123.3, 113.5 (2C), 88.1, 85.6, 61.5, 60.4, 55.4, 42.2, 27.2, 26.9, 24.2, 24.6, 14.3 ppm.



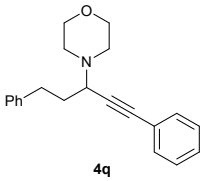
**2-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (4o**) was prepared according to the general procedure using 4-methoxybenzaldehyde (**1g**) (68 mg, 0.5 mmol), 1,2,3,4-tetrahydroisoquinoline (**2i**) (80 mg, 0.6 mmol) and phenylacetylene (**3a**)

(77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow solid [113 mg, 64%]. Melting point = 126 °C. $R_f$ = 0.5 ($Et_2O$:Hexane = 1:4). IR (KBr): ν = 3401, 2822, 1603, 1510, 1245, 738 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.36–7.38 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.21–7.22 (m, 3H), 7.16–7.18 (m, 1H), 7.03–7.11 (m, 3H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.68 (s, 1H), 3.78–3.82 (m, 2H), 3.73 (s, 3H), 2.91–3.01 (m, 2H), 2.70–2.77 (m, 2H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 158.9, 135.6, 134.2, 131.9 (2C), 130.6 (2C), 130.4, 129.1, 128.3 (2C), 128.2, 127.9, 127.0, 125.9, 123.4, 113.8 (2C), 87.7, 86.9, 59.1, 55.4, 54.2, 45.8, 29.2 ppm.



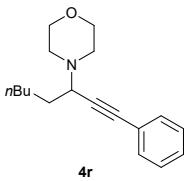
4p

**1-(1-(3,4-dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine (4p)** was prepared according to the general procedure using 3,4-dimethoxybenzaldehyde (**1h**) (83 mg, 0.5 mmol), piperidine (**2d**) (51 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Brown oil [106 mg, 63%]. $R_f$ = 0.5 ($Et_2O$:Hexane = 2:3). IR (Neat): ν = 2932, 2854, 1454, 1118, 757 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.42–7.44 (m, 2H), 7.24–7.26 (m, 3H), 7.09–7.12 (m, 2H), 6.77–6.78 (m, 1H), 4.65 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.48–2.52 (m, 4H), 1.49–1.56 (m, 4H), 1.37–1.38 (m, 2H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 148.8, 148.5, 131.9 (2C), 131.4, 128.4 (2C), 128.2, 123.5, 120.8, 111.7, 110.6, 87.8, 86.5, 62.2, 56.0, 50.9 (2C), 26.3 (2C), 24.6 ppm.



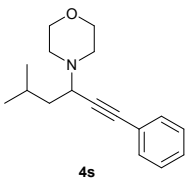
4q

**4-(1,5-diphenylpent-1-yn-3-yl)morpholine (4q)** was prepared according to the general procedure using 3-phenylpropanal (**1i**) (67 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Yellow oil [130 mg, 85%]. $R_f$ = 0.3 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3027, 2953, 2855, 1452, 1117, 756 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.36–7.38 (m, 2H), 7.19–7.23 (m, 5H), 7.14–7.16 (m, 2H), 7.09–7.12 (m, 1H), 3.64–3.72 (m, 4H), 3.40 (t, *J* = 8.5 Hz, 1H), 2.78–2.83 (m, 1H), 2.65–2.73 (m, 3H), 2.46–2.50 (m, 2H), 1.93–1.99 (m, 2H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 141.6, 131.8 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.2, 126.1, 123.1, 86.8, 86.7, 67.2 (2C), 57.2, 49.7 (2C), 34.5, 32.7 ppm.



4r

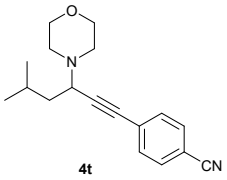
**4-(1-phenyloct-1-yn-3-yl)morpholine (4r)** was prepared according to the general procedure using hexanal (**1j**) (50 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Yellow oil [129 mg, 95%]. $R_f$ = 0.2 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3369, 2956, 1454, 1118, 757 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.42–7.44 (m, 2H), 7.29–7.30 (m, 3H), 3.72–3.80 (m, 4H), 3.48–3.51 (m, 1H), 2.73–2.77 (m, 2H), 2.55–2.59 (m, 2H), 1.66–1.76 (m, 2H), 1.53–1.61 (m, 1H), 1.44–1.49 (m, 1H), 1.32–1.37 (m, 4H), 0.89–0.92 (m, 3H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 131.8 (2C), 128.3 (2C), 128.0, 123.3, 87.3, 86.2, 67.2 (2C), 58.2, 49.8 (2C), 33.0, 31.7, 26.4, 22.7, 14.2 ppm.



4s

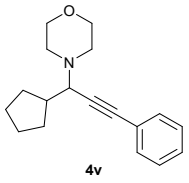
**4-(5-methyl-1-phenylhex-1-yn-3-yl)morpholine (4s)** was prepared according to the general procedure using 3-methylbutanal (**1k**) (43 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg,

0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Yellow oil [122 mg, 95%]. $R_f$ = 0.3 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3399, 2958, 1454, 1118, 756 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.34–7.37 (m, 2H), 7.21–7.23 (m, 3H), 3.66–3.73 (m, 4H), 3.50–3.54 (m, 1H), 2.66–2.70 (m, 2H), 2.49–2.53 (m, 2H), 1.79–1.87 (m, 1H), 1.55–1.61 (m, 1H), 1.45–1.51 (m, 1H), 0.88–0.91 (m, 6H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 131.8 (2C), 128.4 (2C), 128.1, 123.3, 87.1, 86.4, 67.2 (2C), 56.3, 49.8 (2C), 41.8, 25.3, 23.1, 22.2 ppm.



4t

**4-(5-methyl-3-morpholinohex-1-yn-1-yl)benzonitrile (4t**) was prepared according to the general procedure using 3-methylbutanal (**1k**) (43 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and 4-(prop-1-yn-1-yl)benzonitrile (**3c**) (95 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 14 h. Yellow solid [136 mg, 96%]. Melting point = 62 ºC. $R_f$ = 0.4 ($Et_2O$:Hexane = 2:3). IR (KBr): ν = 3405, 2959, 2226, 1601, 1452, 1117, 837, 557 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.59–7.61 (m, 2H), 7.50–7.52 (m, 2H), 3.72–3.80 (m, 4H), 3.60–3.63 (m, 1H), 2.72–2.75 (m, 2H), 2.54–2.58 (m, 2H), 1.85–1.91 (m, 1H) 1.55–1.67 (m, 2H) 0.96–0.99 (m, 6H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 132.3 (2C), 132.0 (2C), 128.2, 118.6, 111.4, 92.3, 84.9, 67.1 (2C), 56.3, 49.8 (2C), 41.5, 25.2, 22.9, 22.2 ppm.



4v

**4-(1-cyclopentyl-3-phenylprop-2-yn-1-yl)morpholine (4v**) was prepared according to the general procedure using cyclopentanecarbaldehyde (**1l**) (49 mg, 0.5 mmol), morpholine (**2a**) (52 mg, 0.6 mmol) and phenylacetylene (**3a**) (77 mg, 0.75 mmol) as the starting materials with **AgGel3** (36 mg) for 16 h. Yellow oil [113 mg, 84%]. $R_f$ = 0.5 ($Et_2O$:Hexane = 1:4). IR (Neat): ν = 3399, 2958, 1490, 1118, 757 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.35–7.37 (m, 2H), 7.21–7.24 (m, 3H), 3.62–3.71 (m, 4H), 3.15 (d, *J* = 9.5 Hz, 1H), 2.64–2.69 (m, 2H), 2.44–2.48 (m, 2H), 2.11–2.19 (m, 1H), 1.81–1.84 (m, 1H), 1.68–1.71 (m, 1H), 1.38–1.59 (m, 6H) ppm. $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 131.8 (2C), 128.3 (2C), 128.0, 123.5, 87.2, 86.2, 67.3 (2C), 63.5, 50.0 (2C), 42.1, 30.8, 30.3, 25.5, 25.4 ppm.

**Representative procedure for the gram-scale synthesis of 4a**

A 100 mL reaction tube was charged with **1a** (530 mg, 5.0 mmol, 1.0 eq), **2a** (520 mg, 6.0 mmol, 1.2 eq), **3a** (770 mg, 7.5 mmol, 1.5 eq) and **AgGel3** (360 mg). The vessel was evacuated and back-filled with nitrogen (× 3). To it, toluene (30 mL) was added and the reaction mixture was stirred at 70 ºC for 24 h (monitored by TLC). After cooling, the reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL), the combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica-gel to provide 4-(1,3-diphenylprop-2-yn-1-yl)morpholine (**4a**) as a yellow oil (1.15 g, 83%).

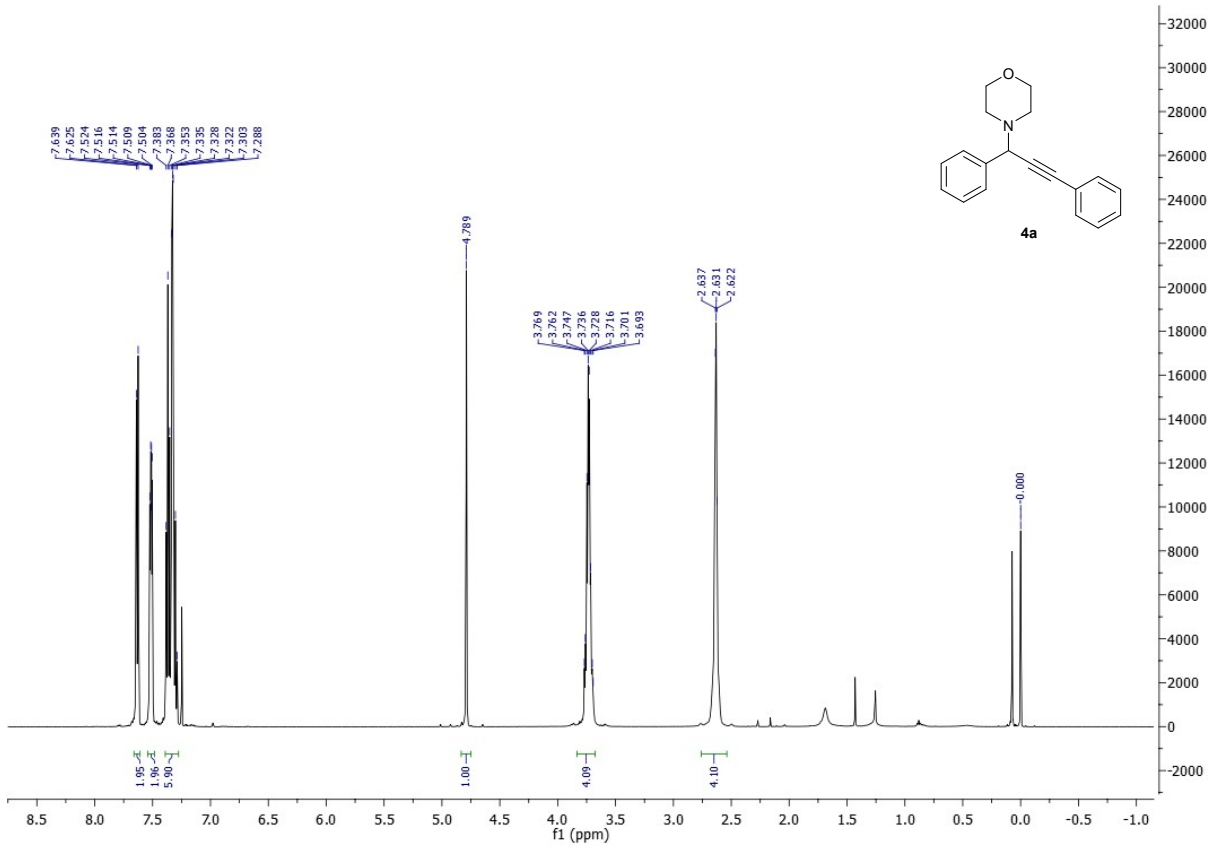
**References**

[1] L. F. Armarego, D. D. Perrin, Butterworth-Heinemann, Oxford: USA, 2000.

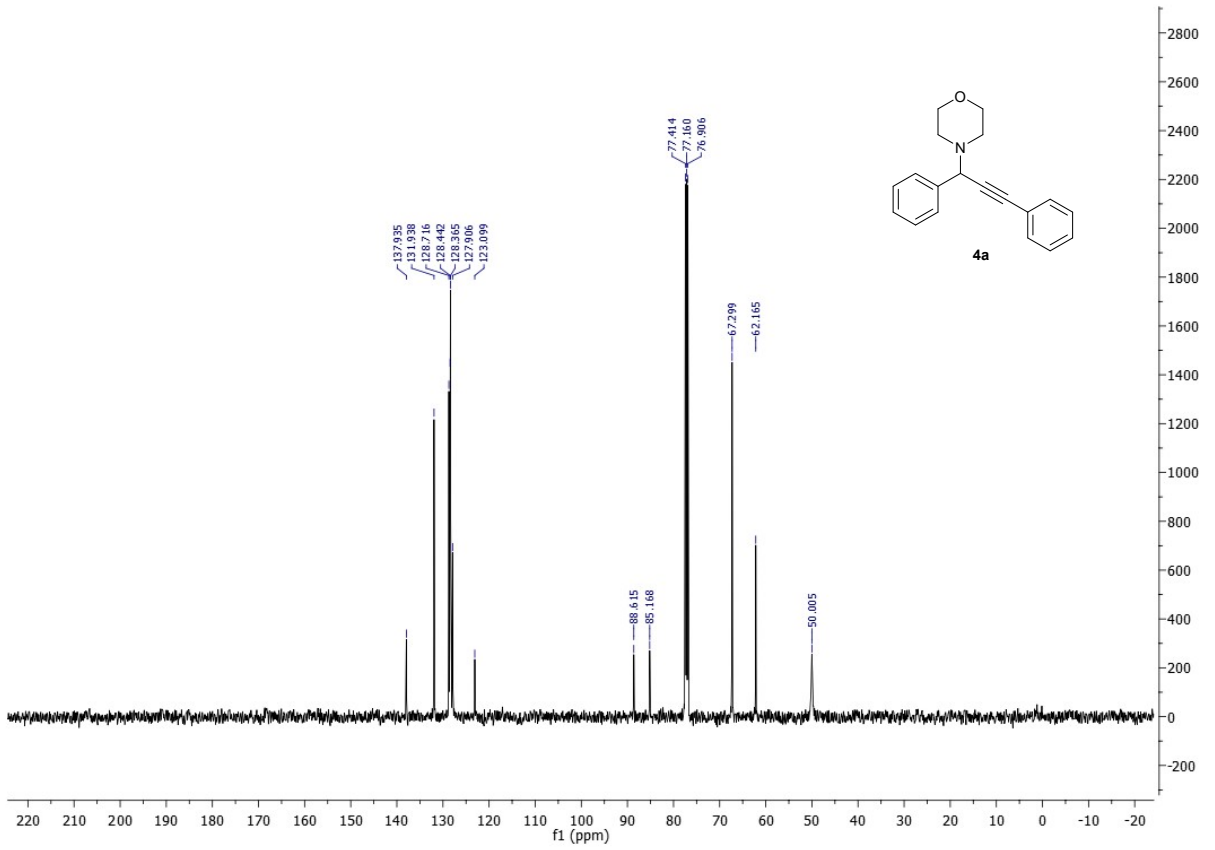
[2] Y. Thummala, G. V. Karunakar, V. R. Doddi, Adv. Synth. Catal. **2019**, *361*, 611–616.

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

$^{1}$H NMR (500 MHz, $CDCl_3$):




$^{13}$C NMR (126 MHz, $CDCl_3$):



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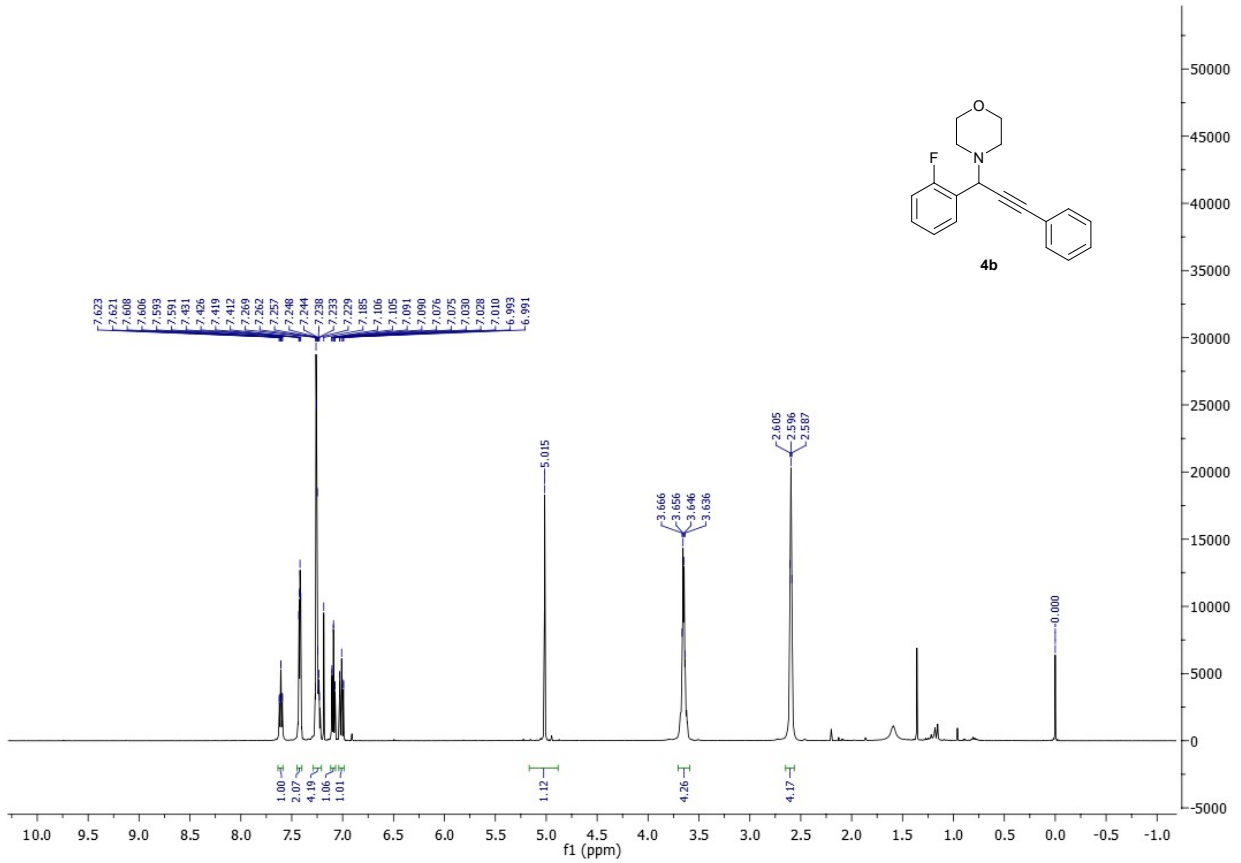


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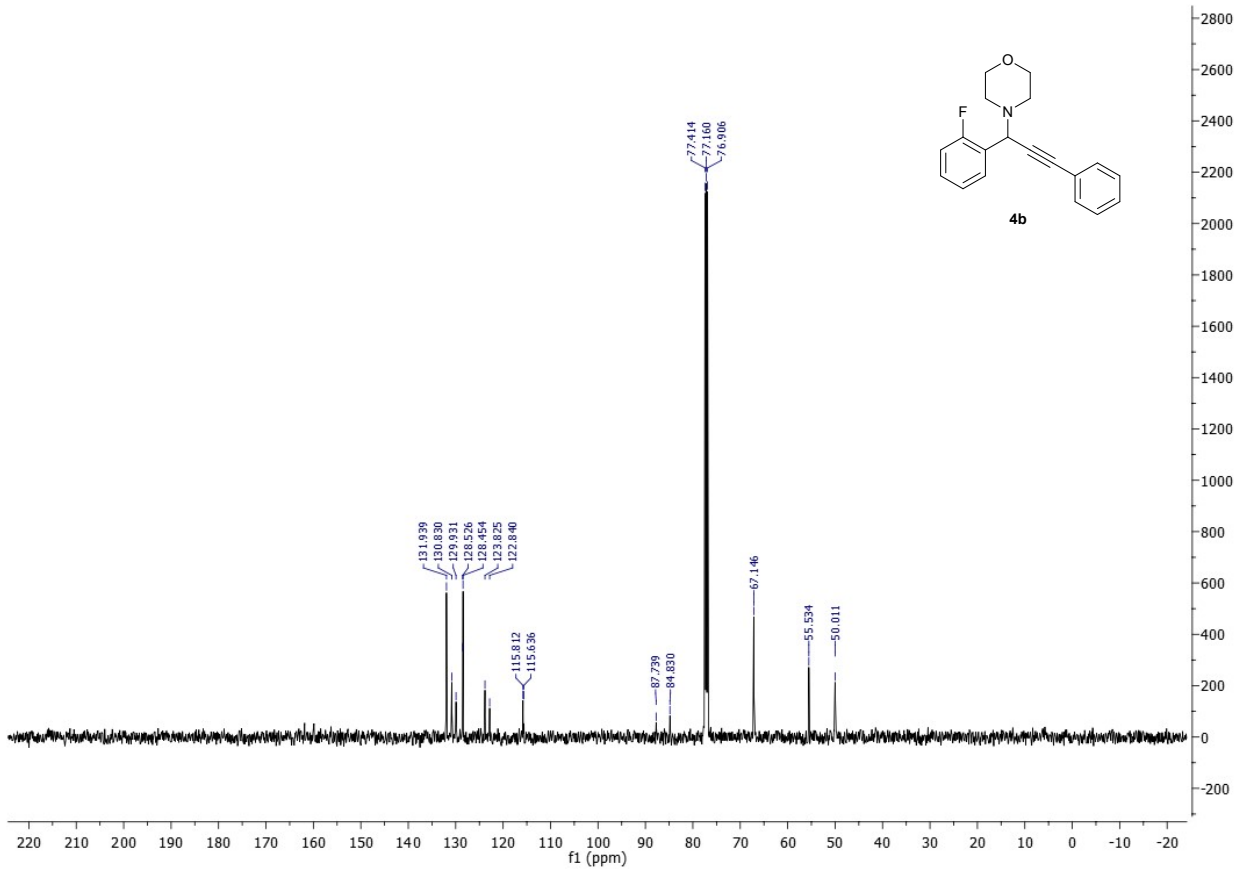
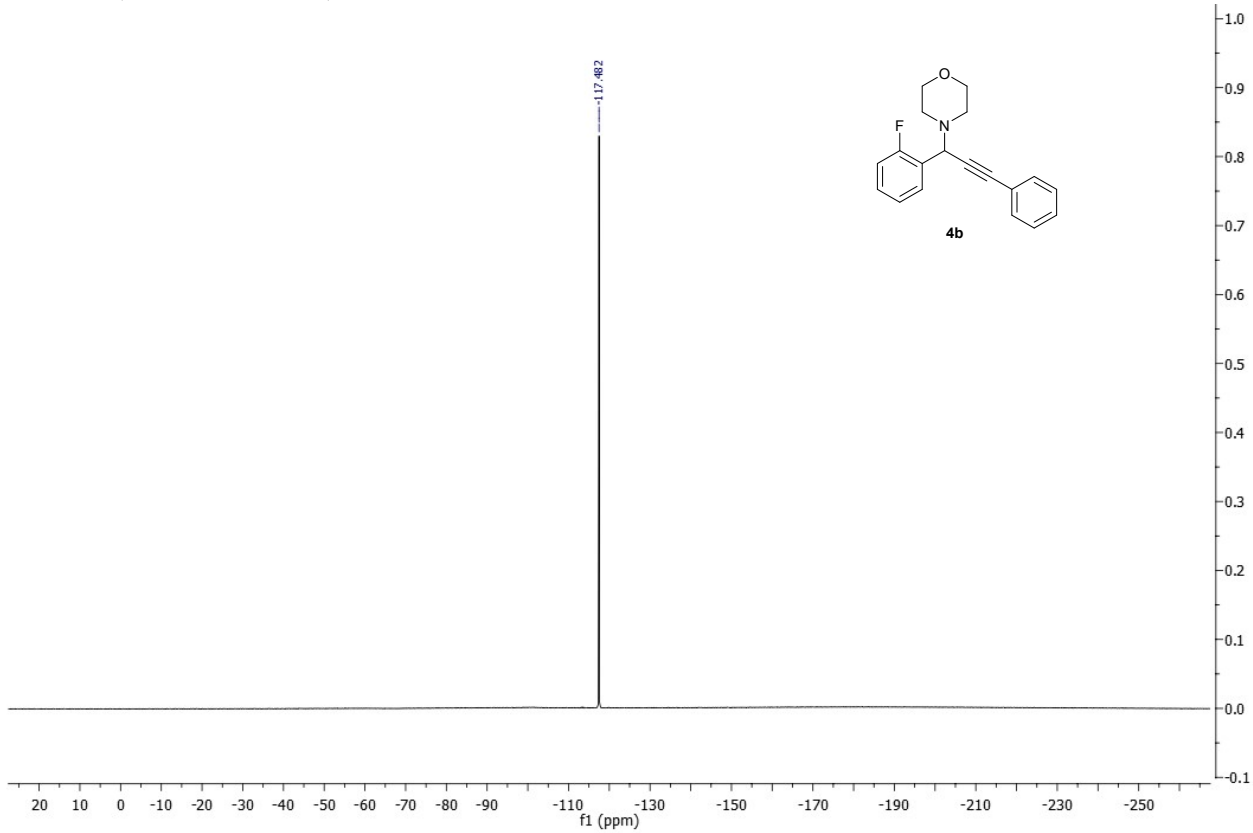



$^{19}F$ NMR (564 MHz, $CDCl_3$):



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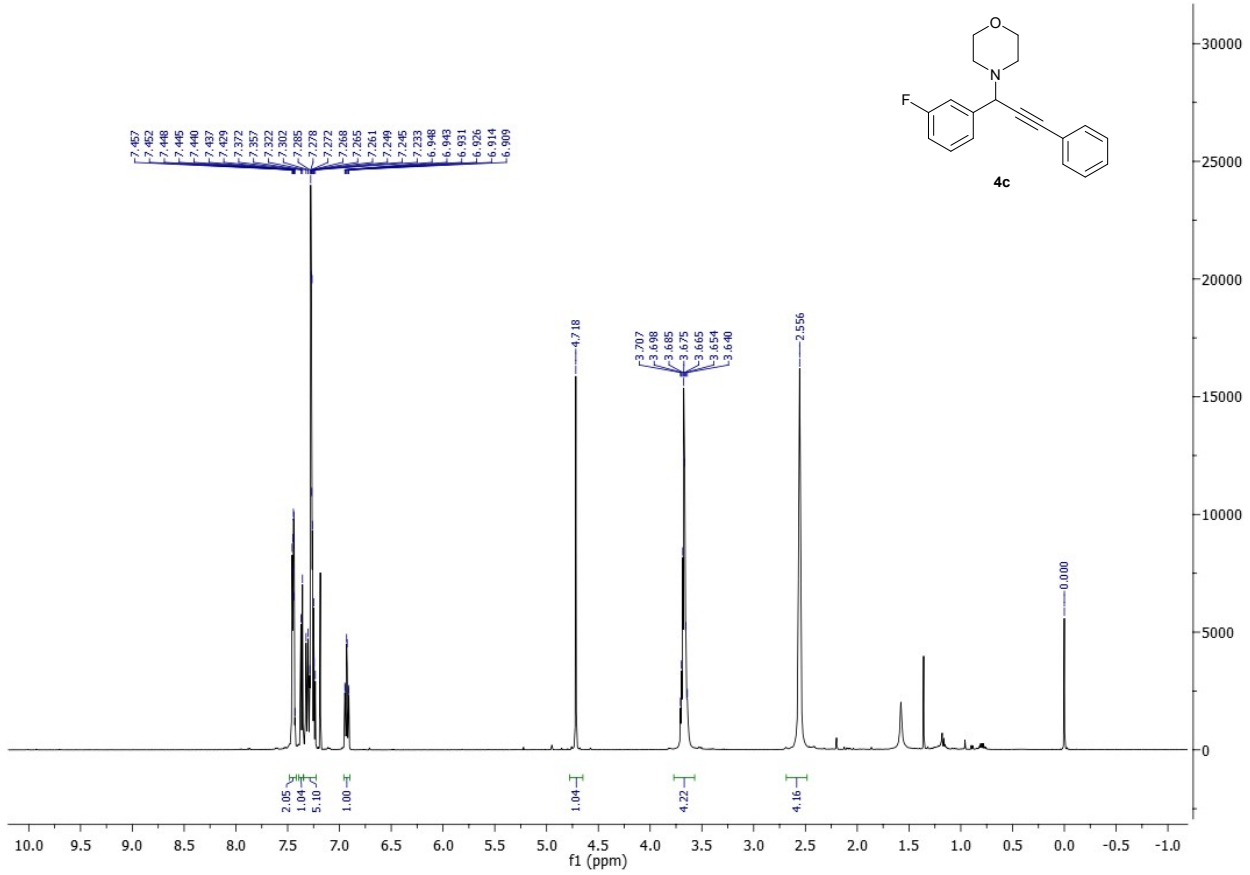


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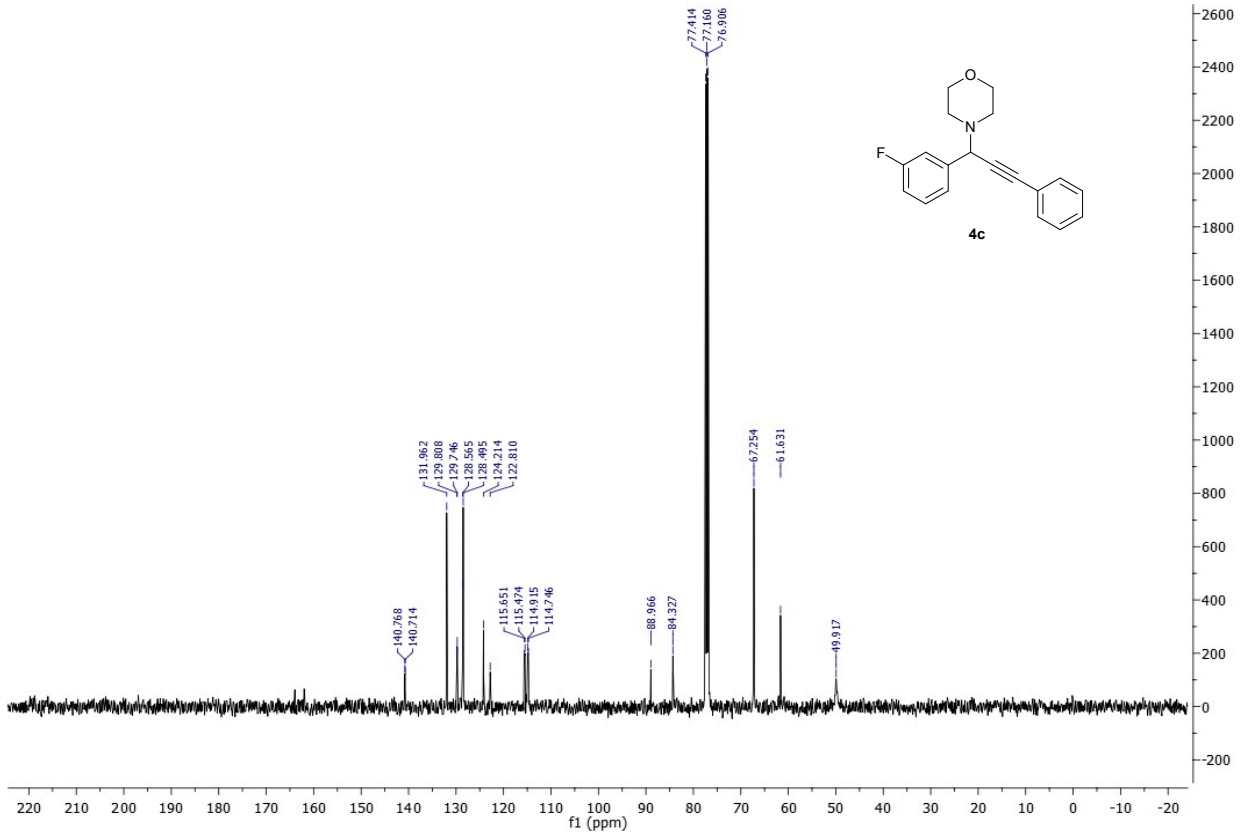
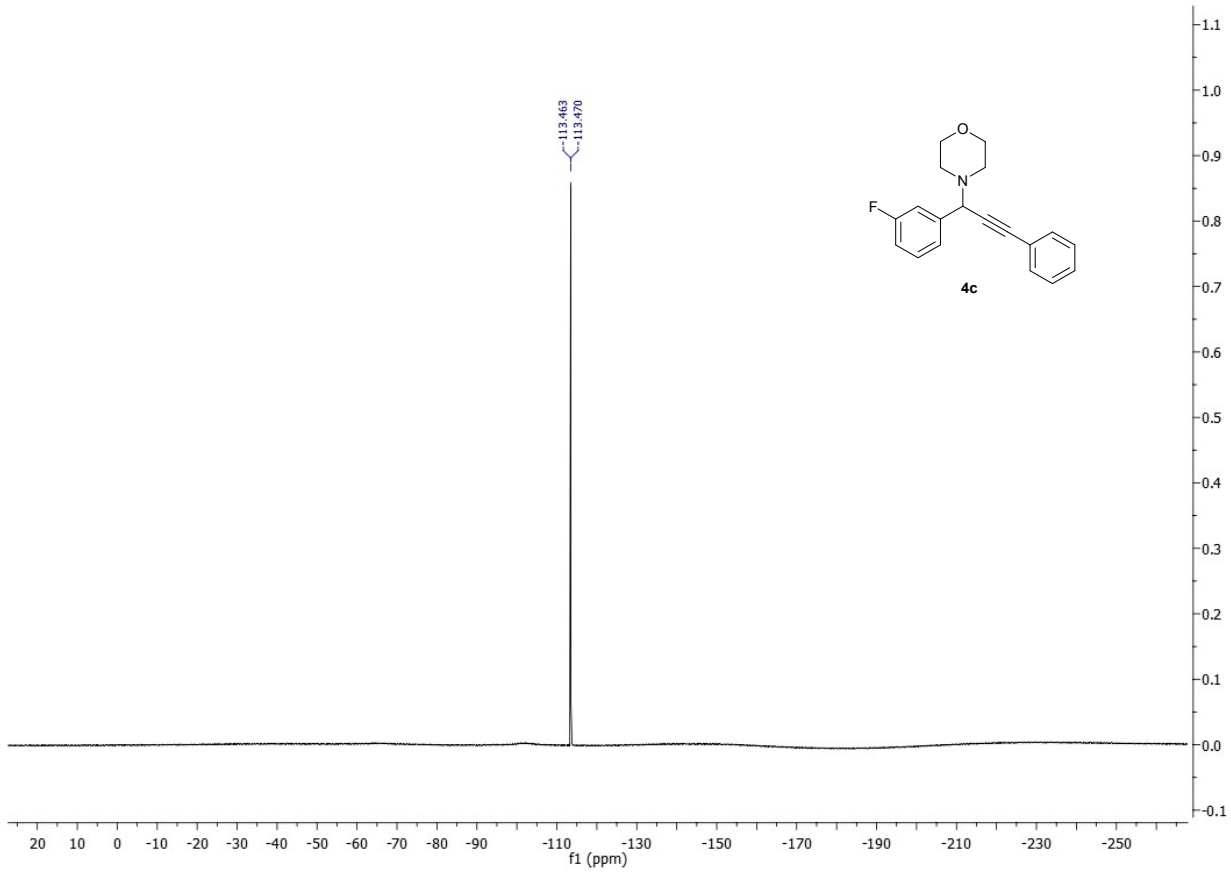


$^{19}F$ NMR (564 MHz, $CDCl_3$):



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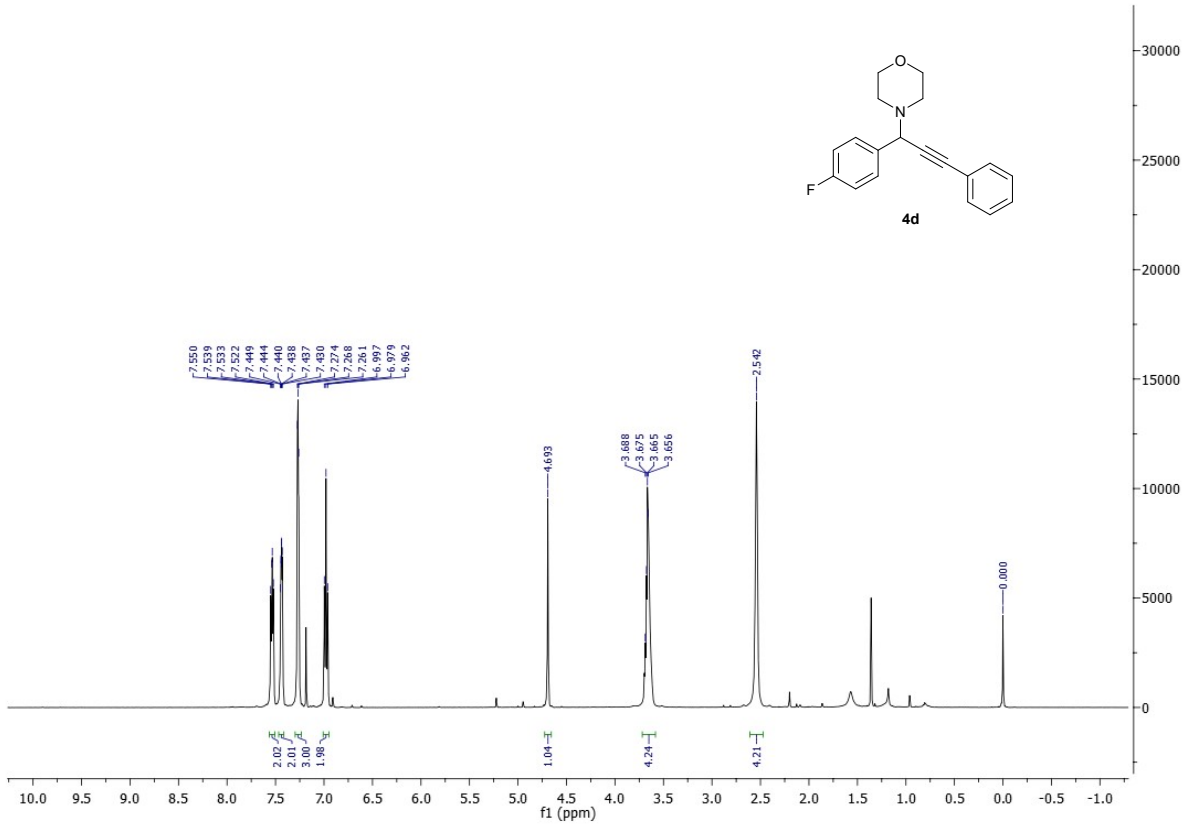


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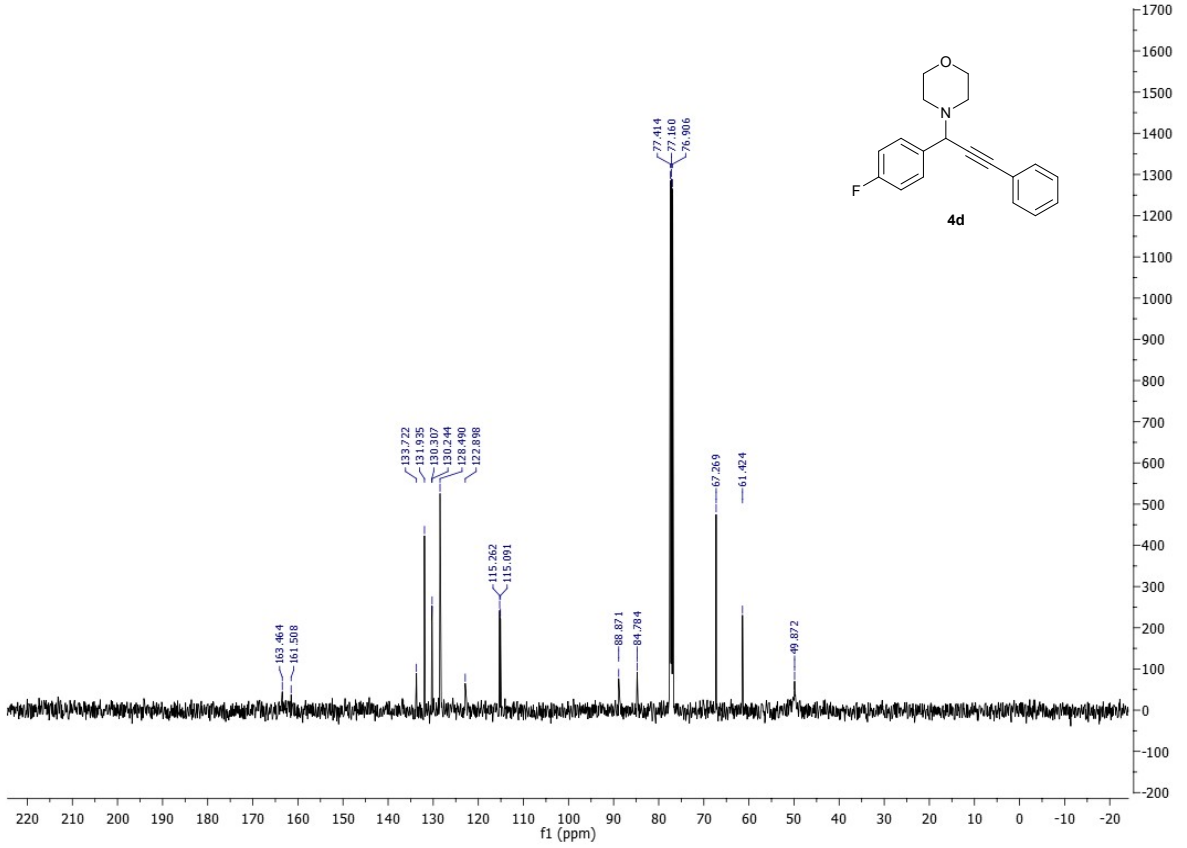
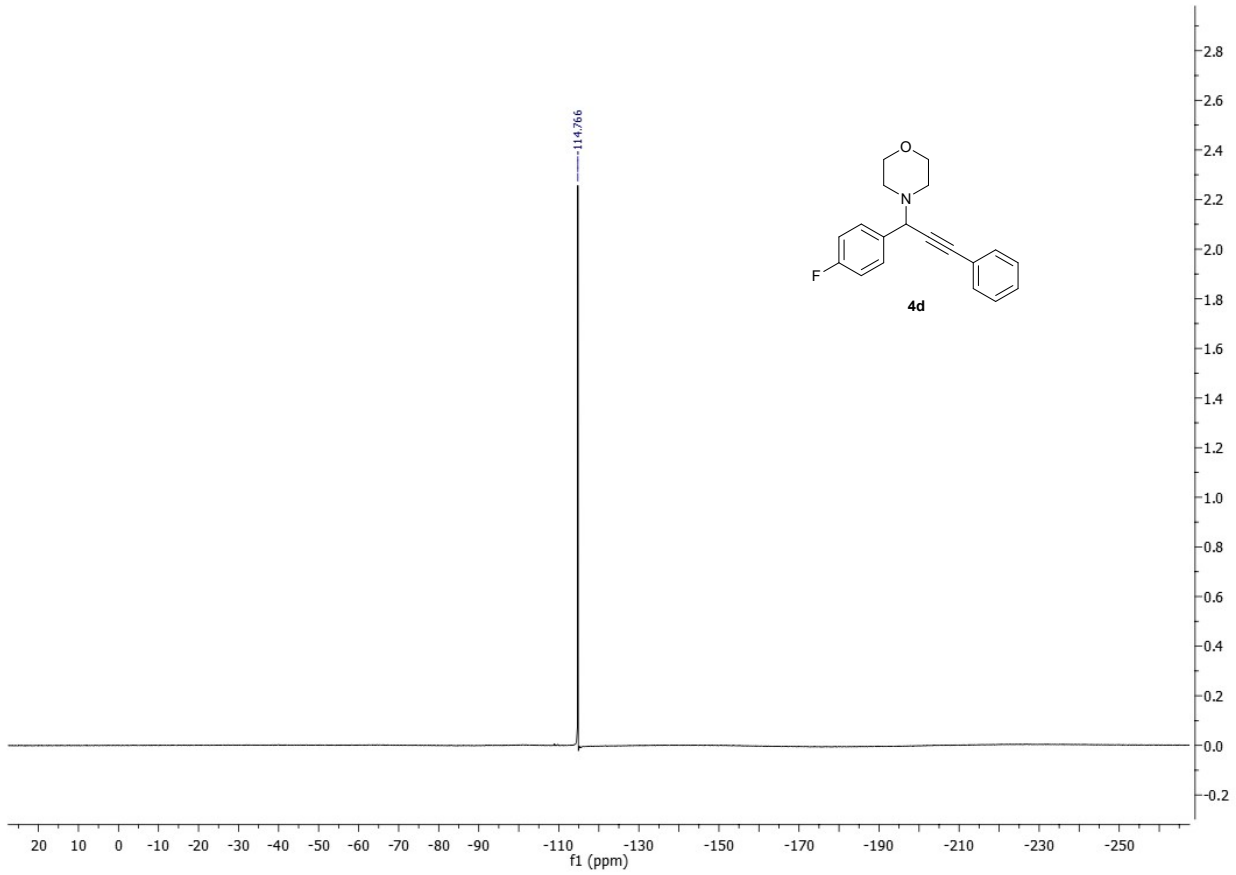
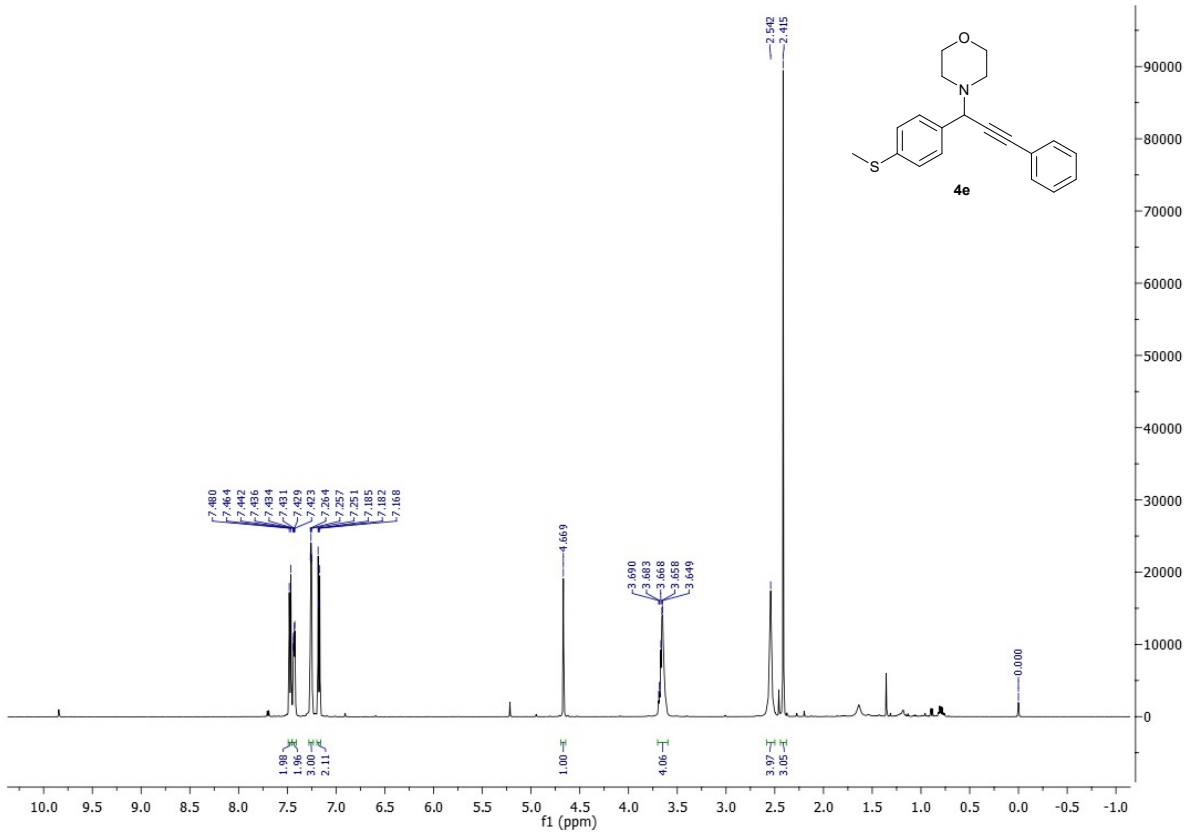


$^{19}F$ NMR (564 MHz, $CDCl_3$):



$^{1}$H NMR (500 MHz, $CDCl_3$

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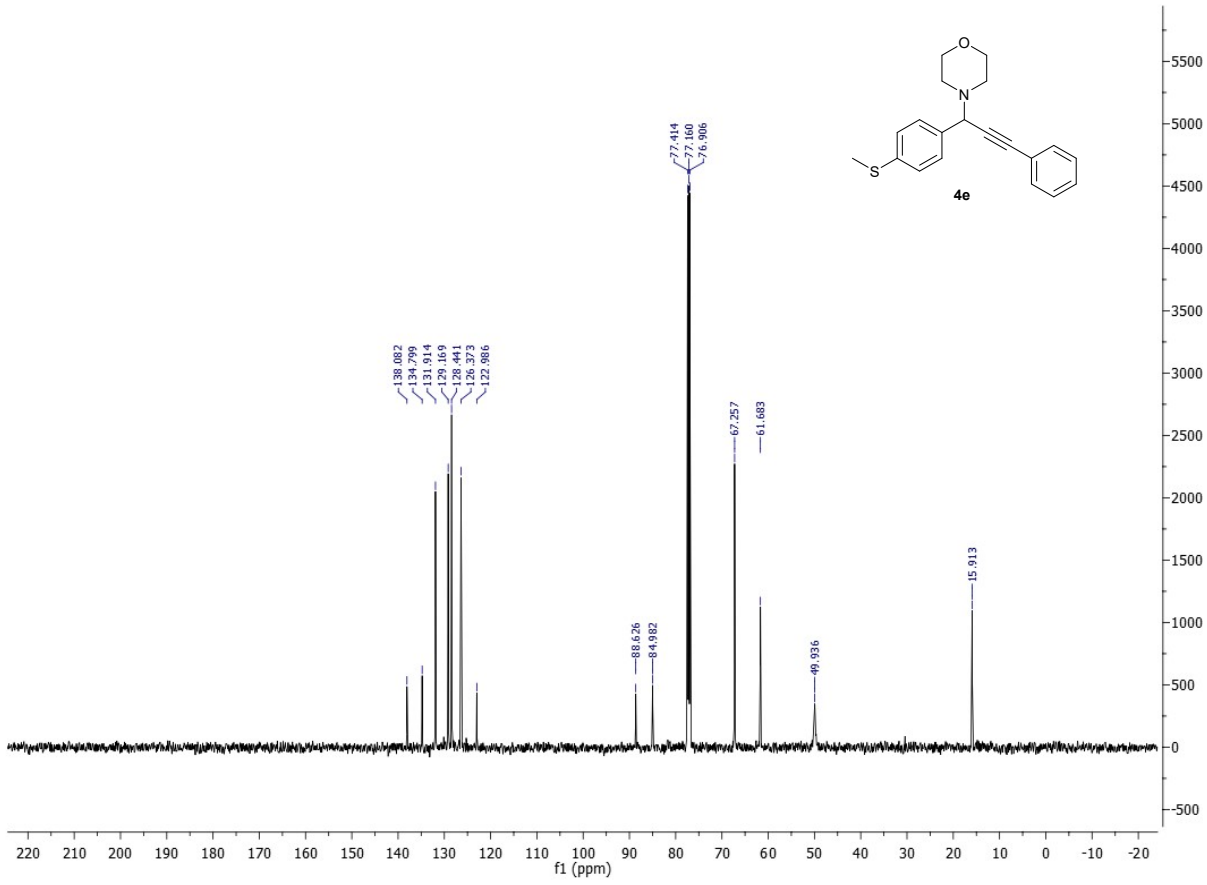

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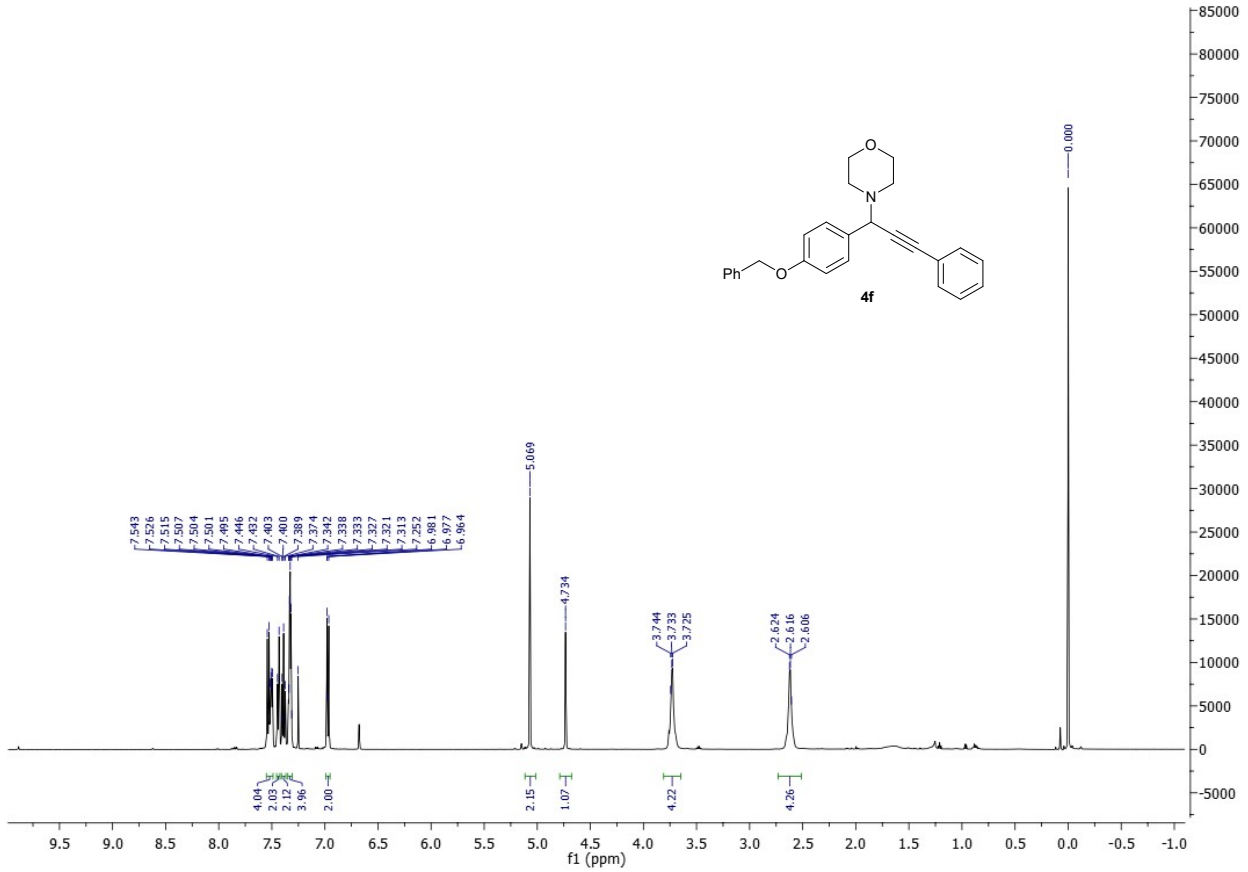


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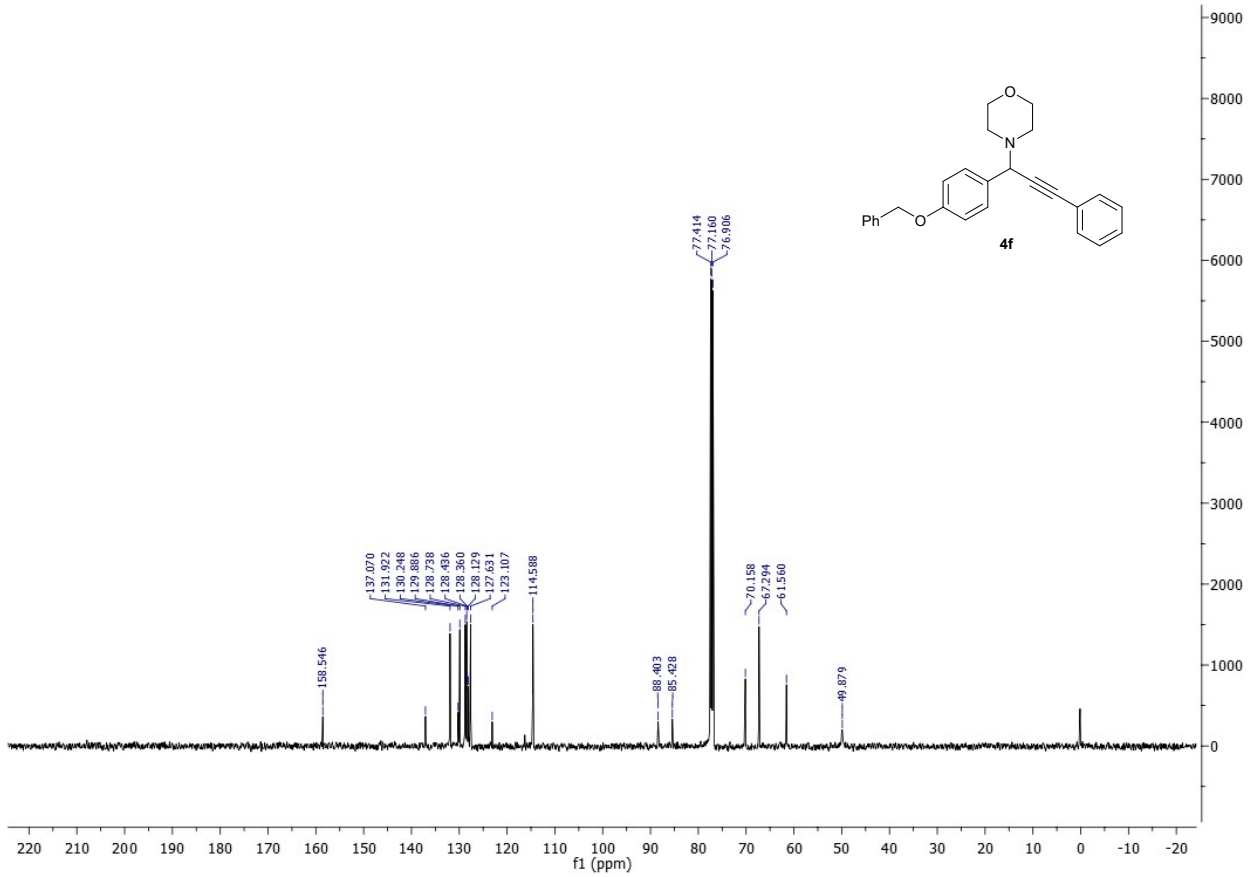

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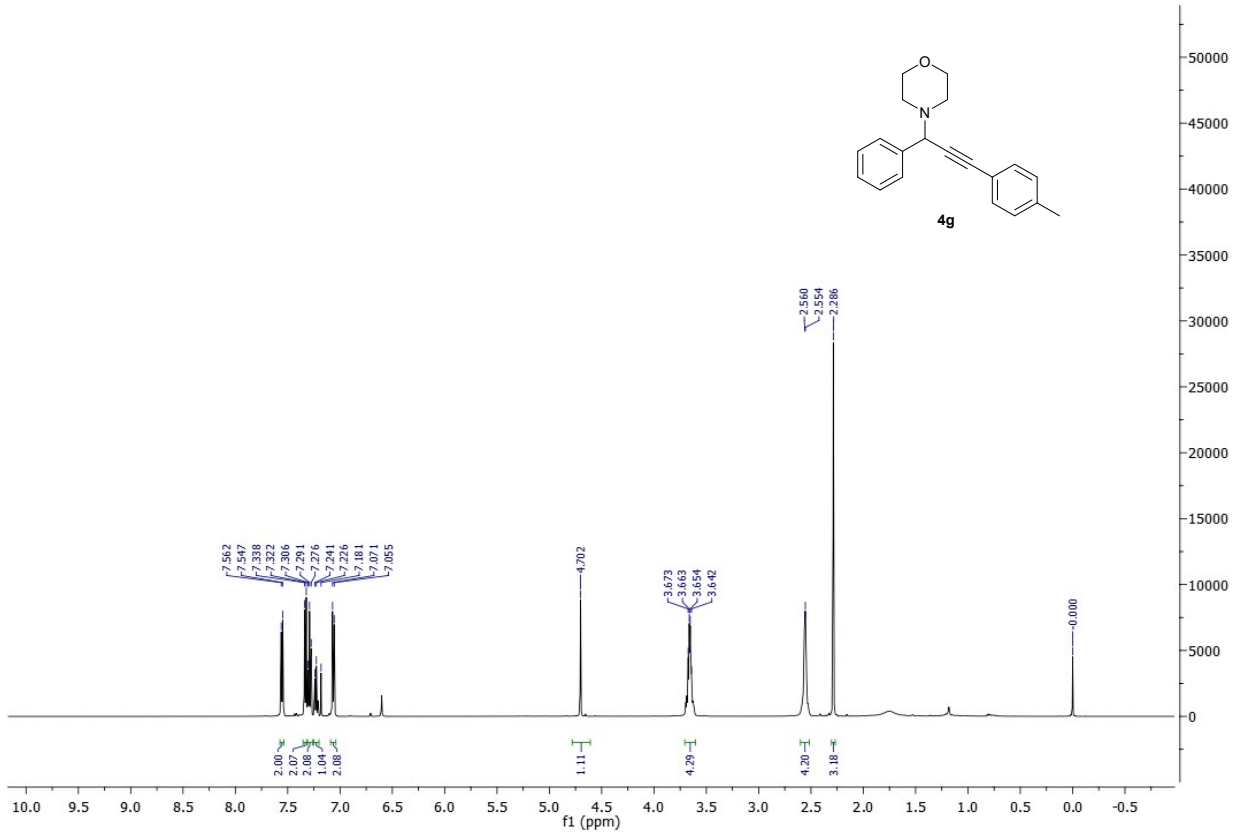


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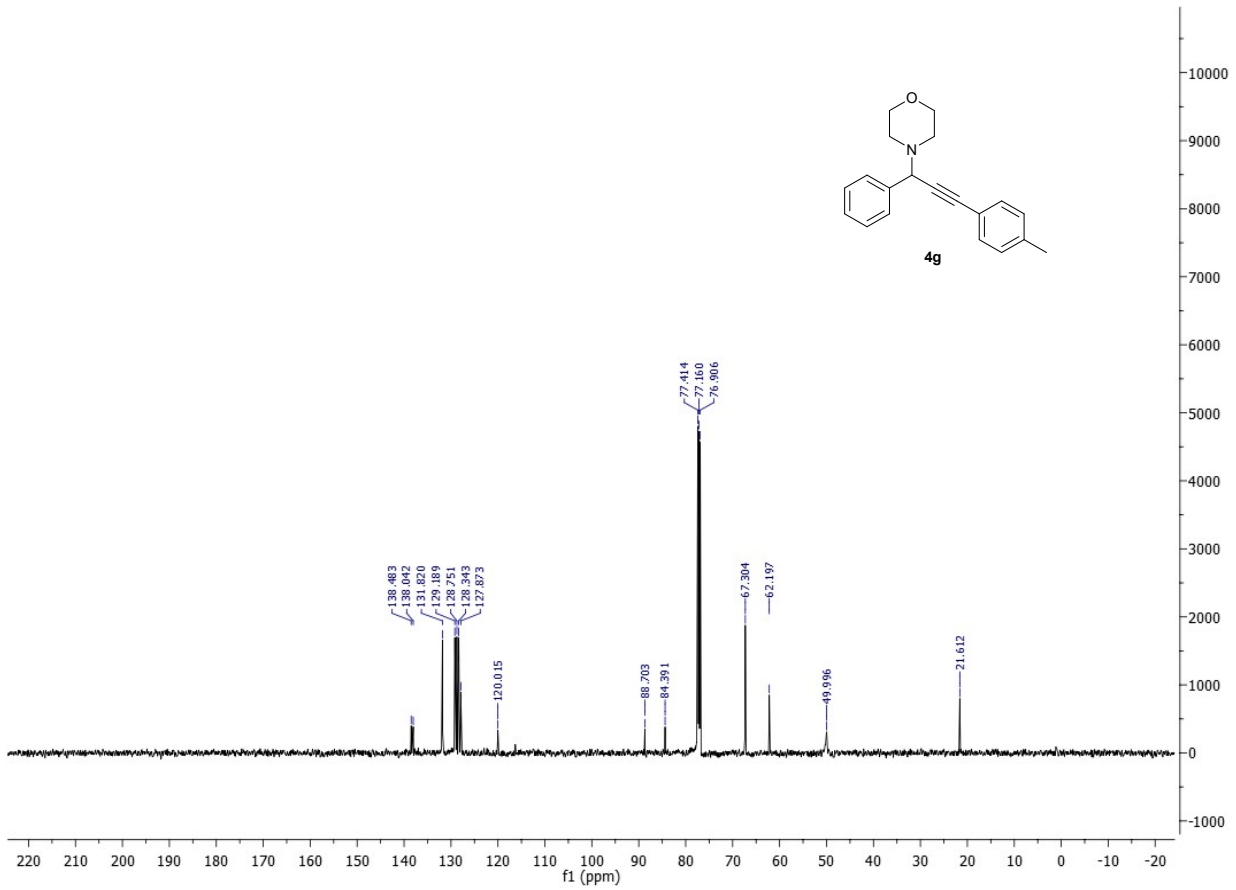

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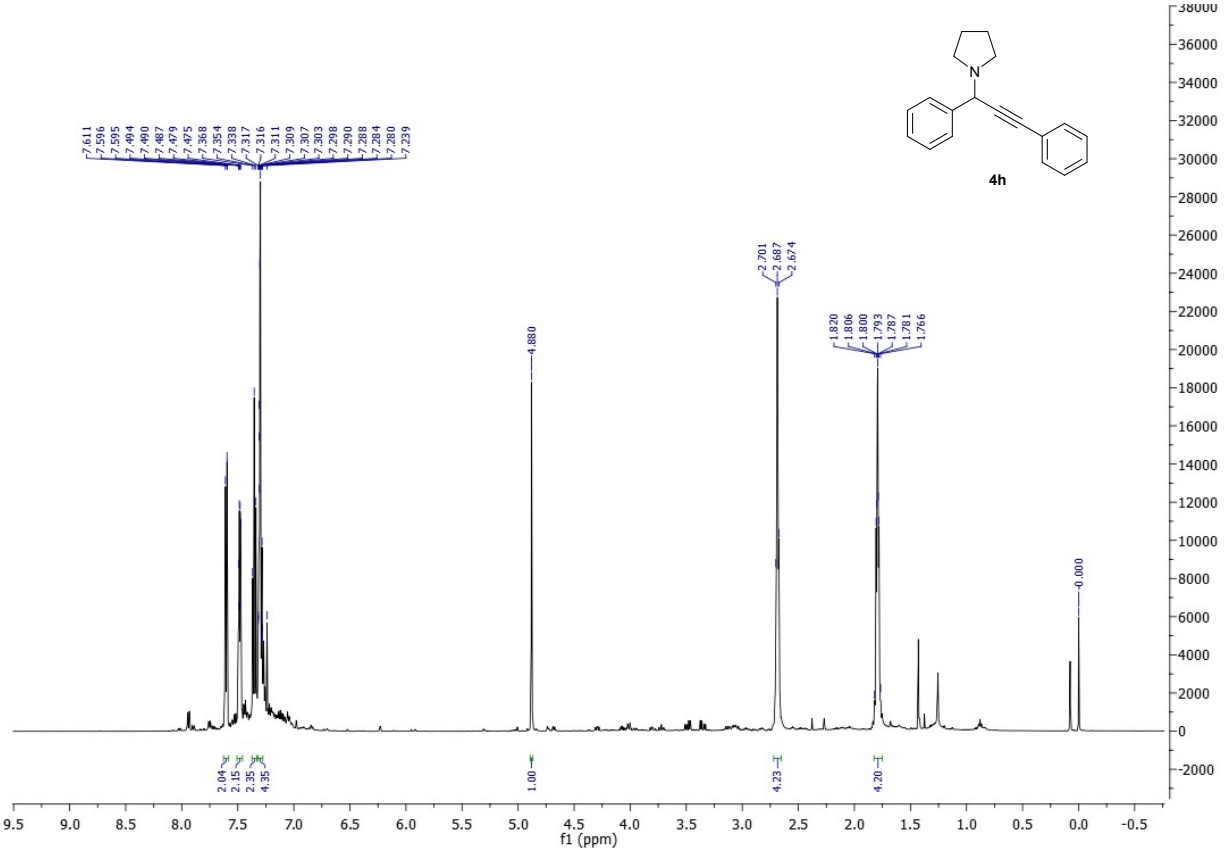


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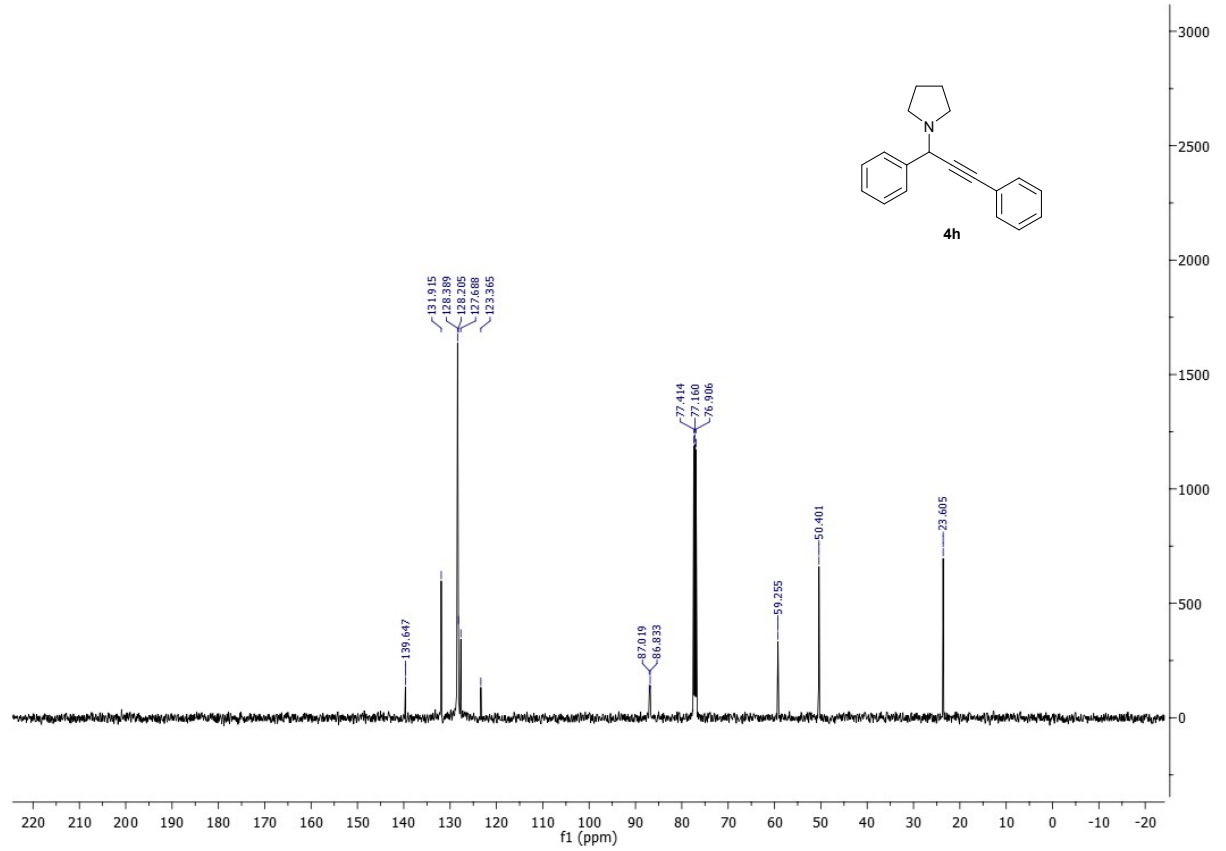

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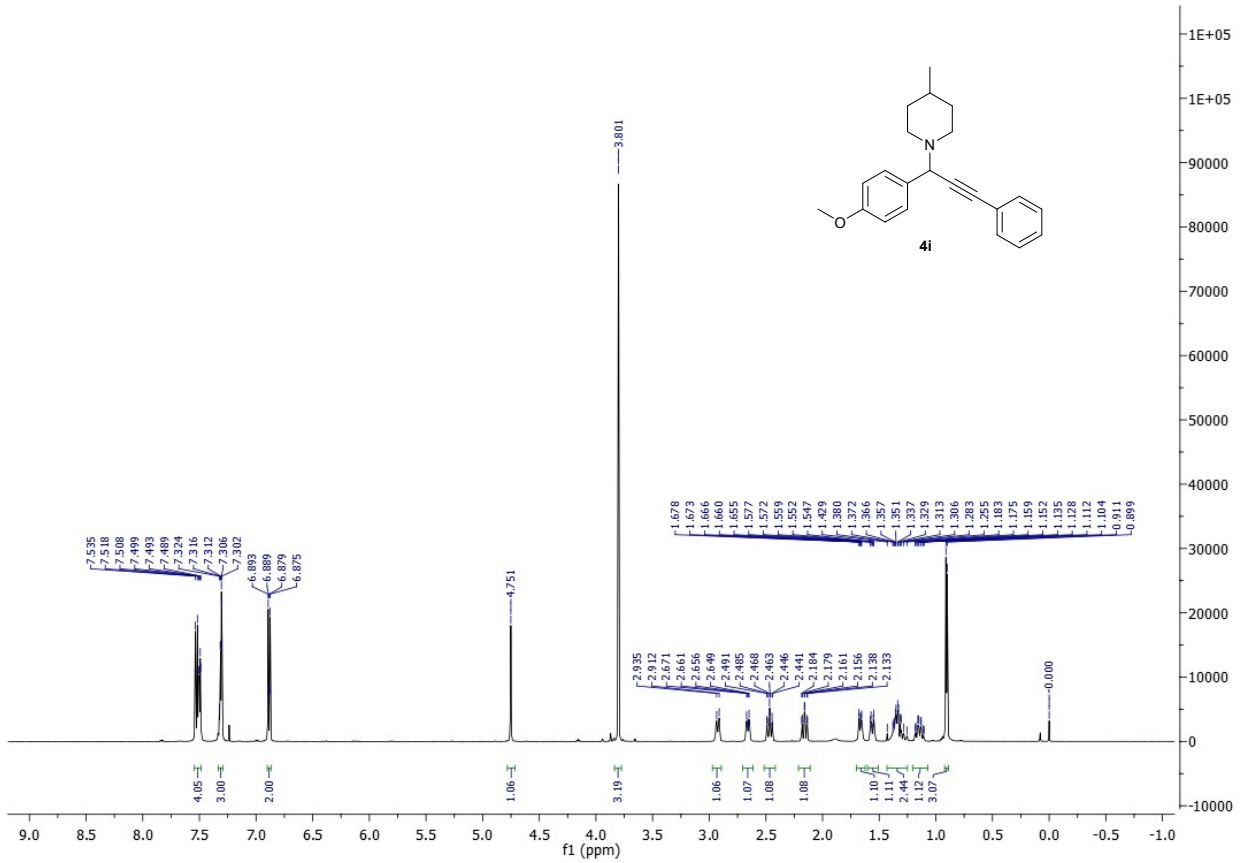
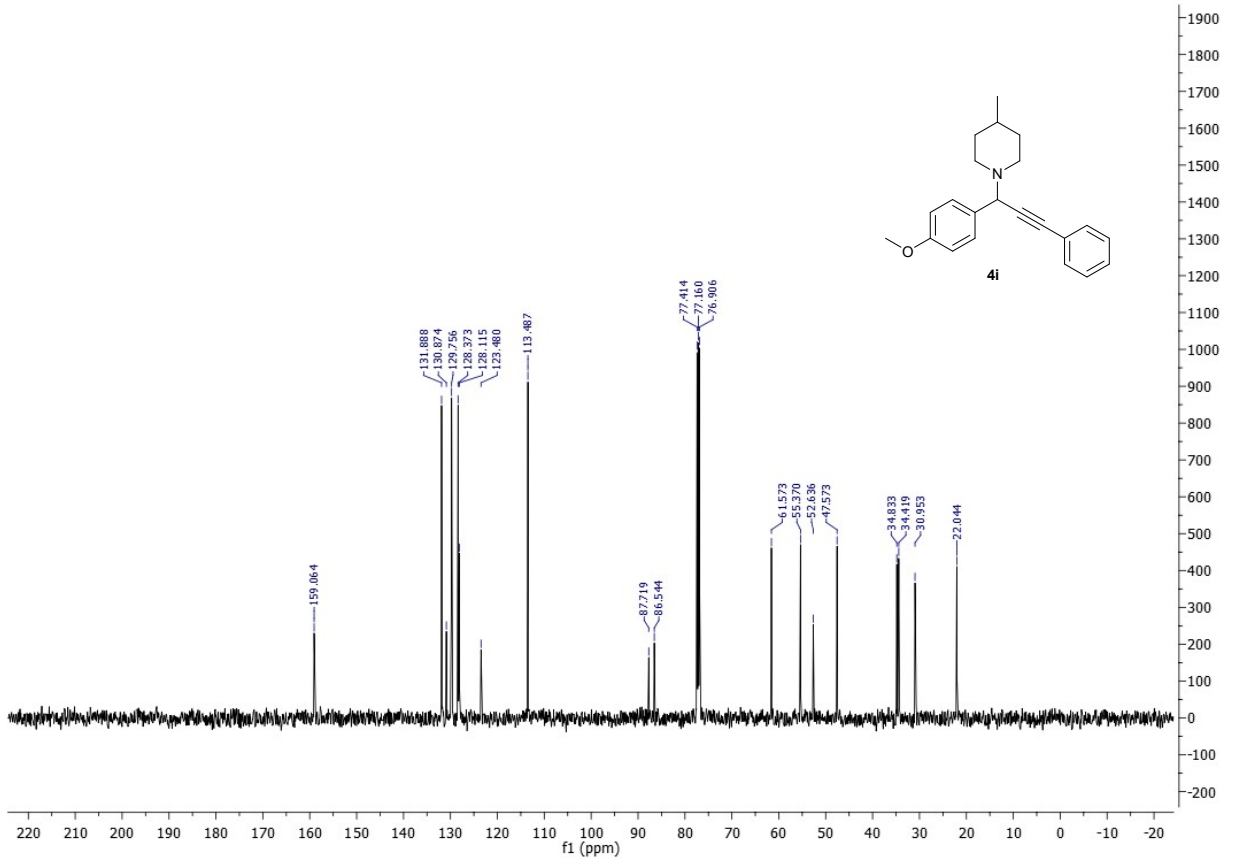
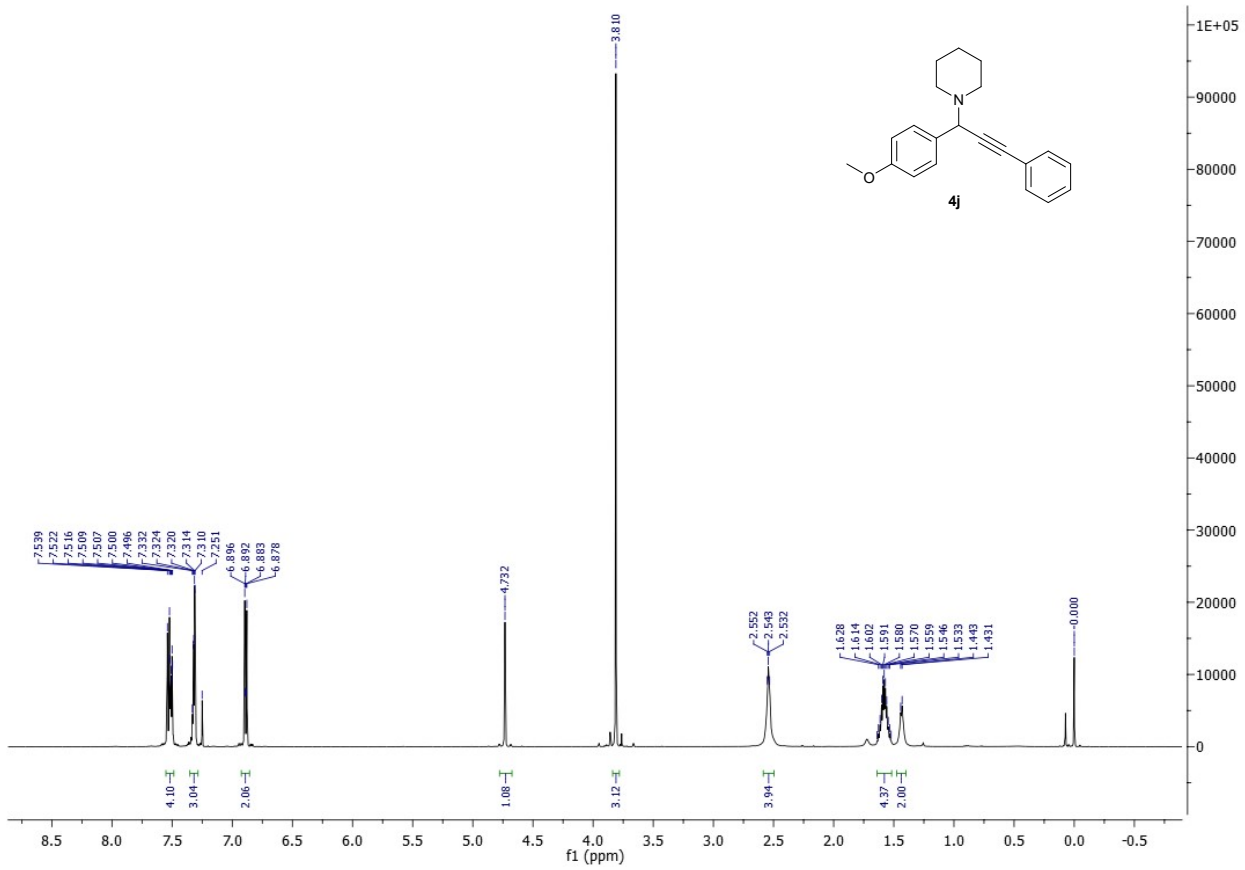


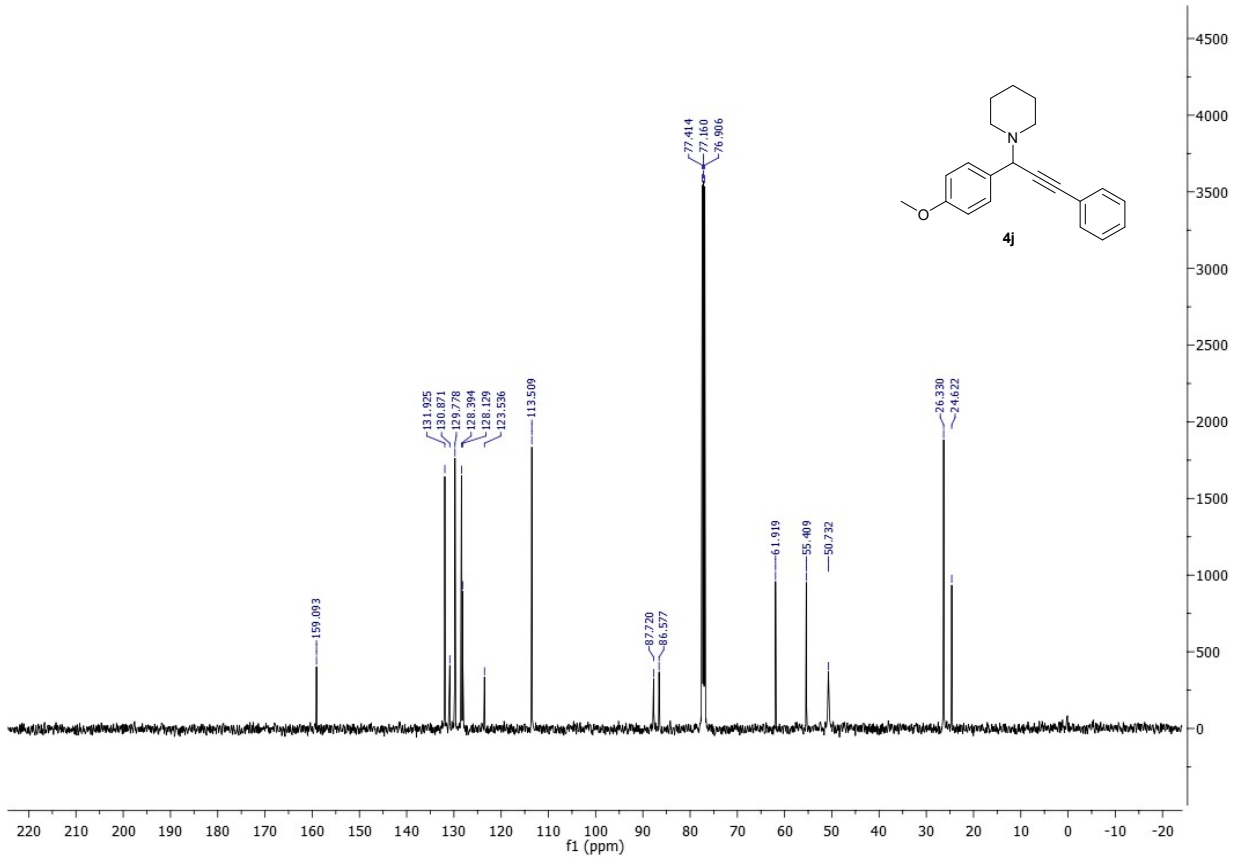

$^{13}$C NMR (126 MHz, $CDCl_3$):



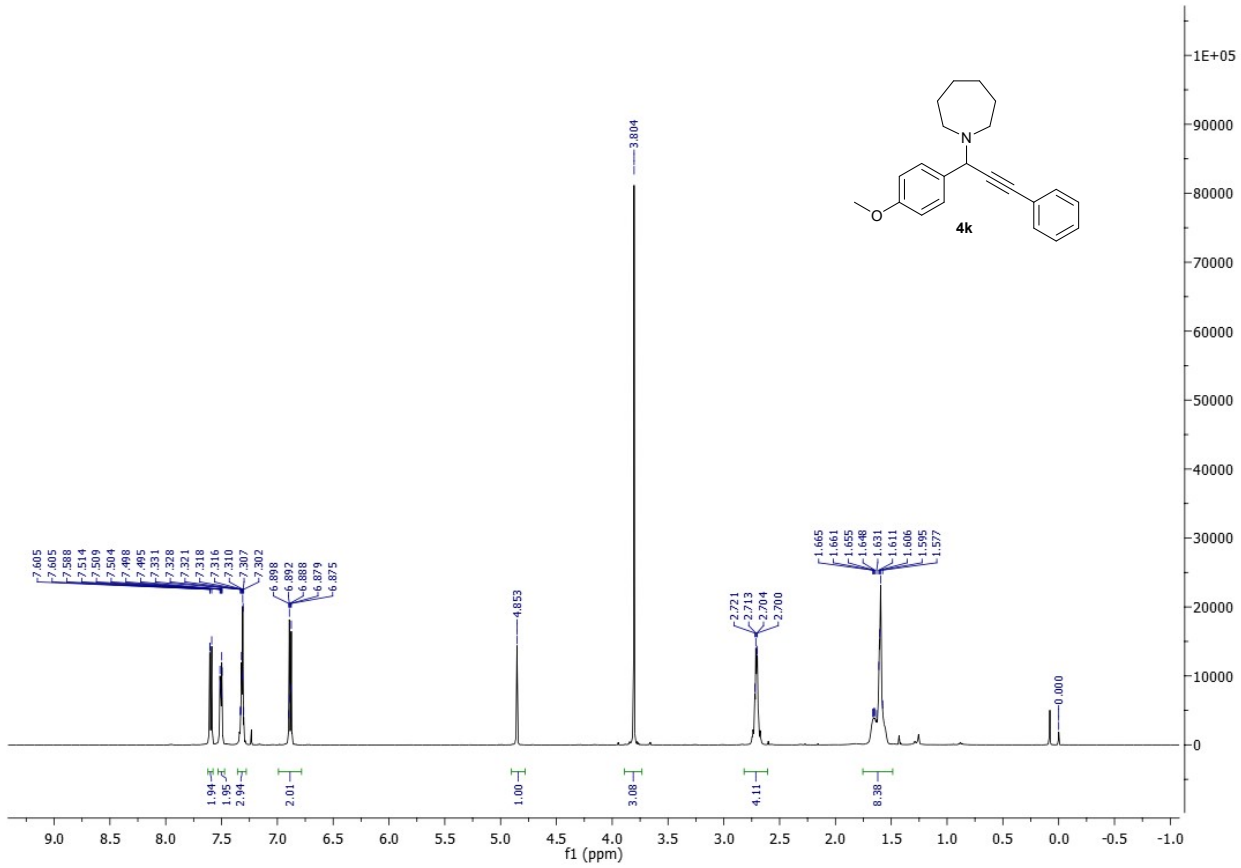
$^{1}$H NMR (500 MHz, $CDCl_3$):



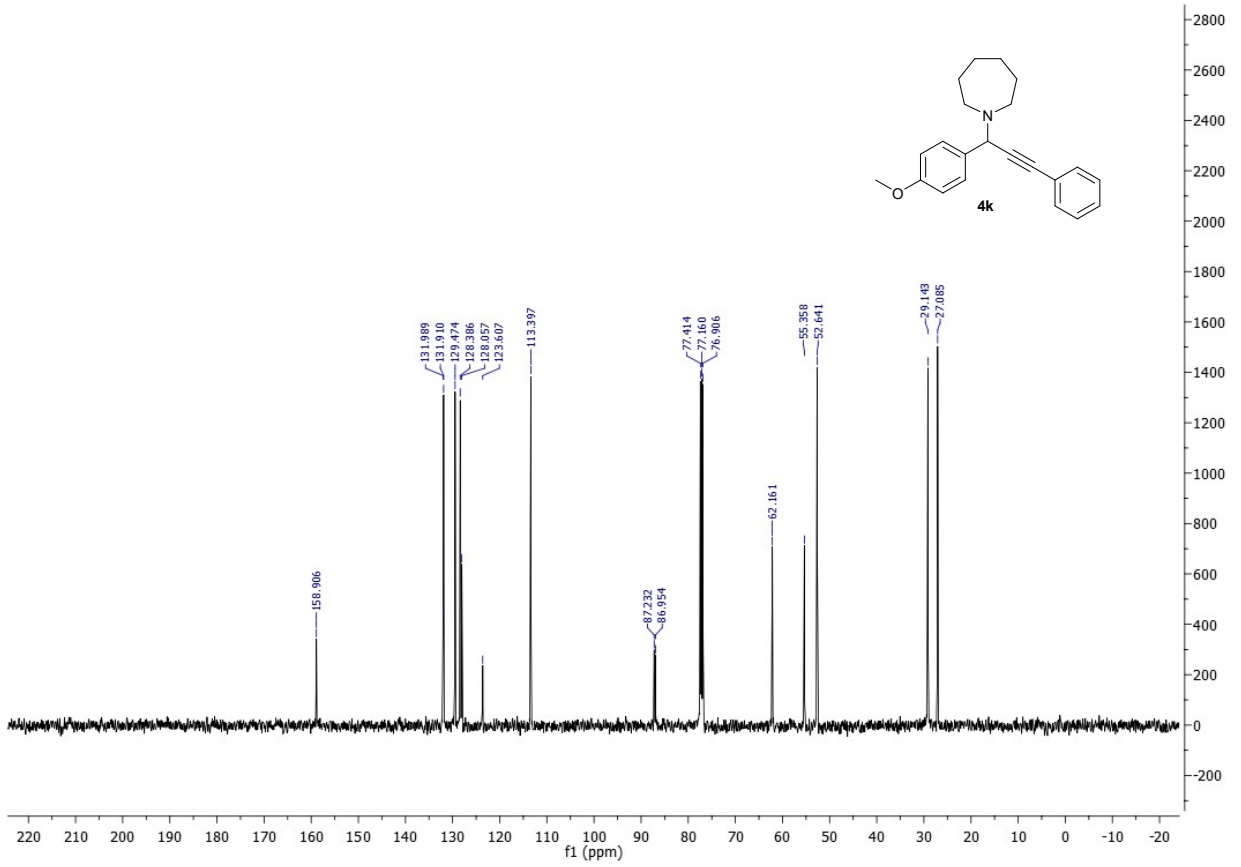

$^{13}$C NMR (126 MHz, $CDCl_3$)



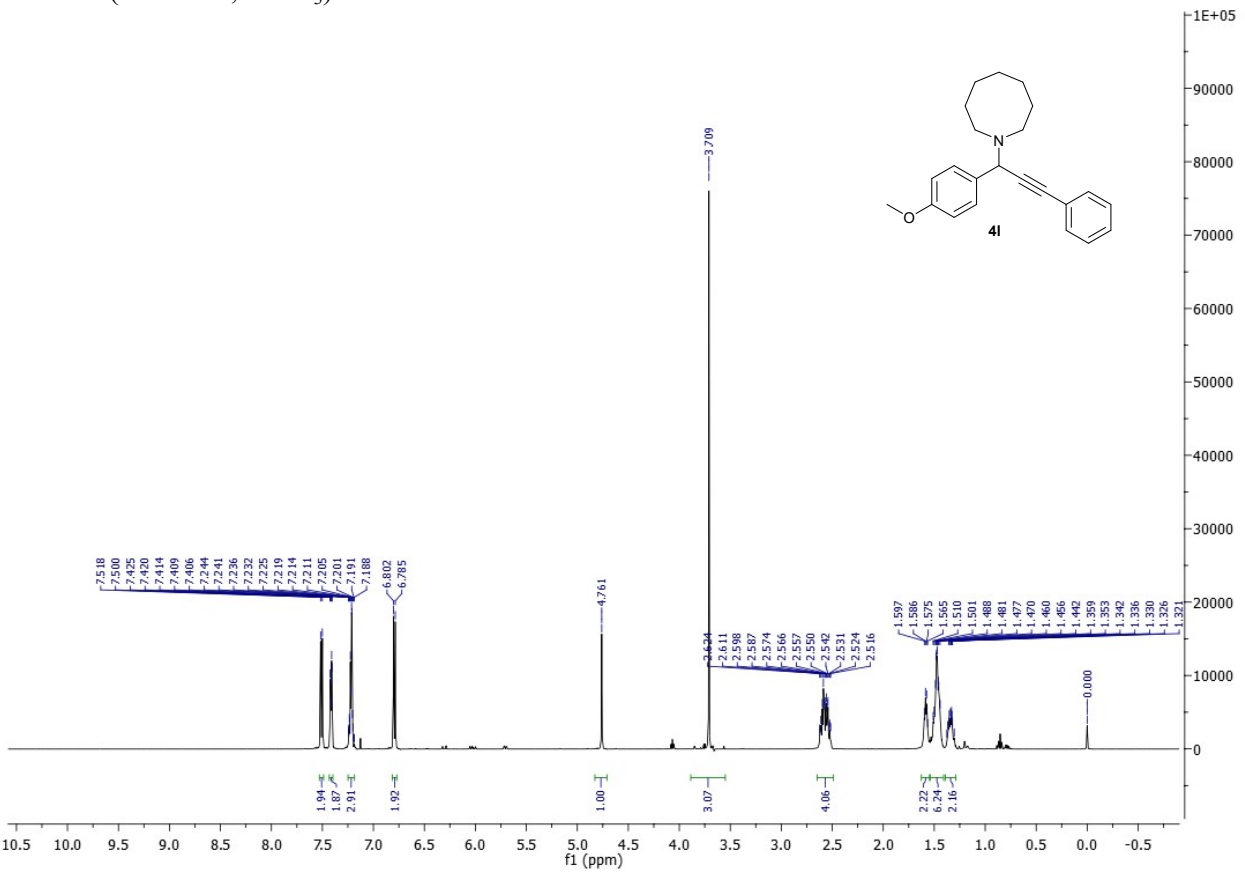
$^{1}$H NMR (500 MHz, $CDCl_3$):



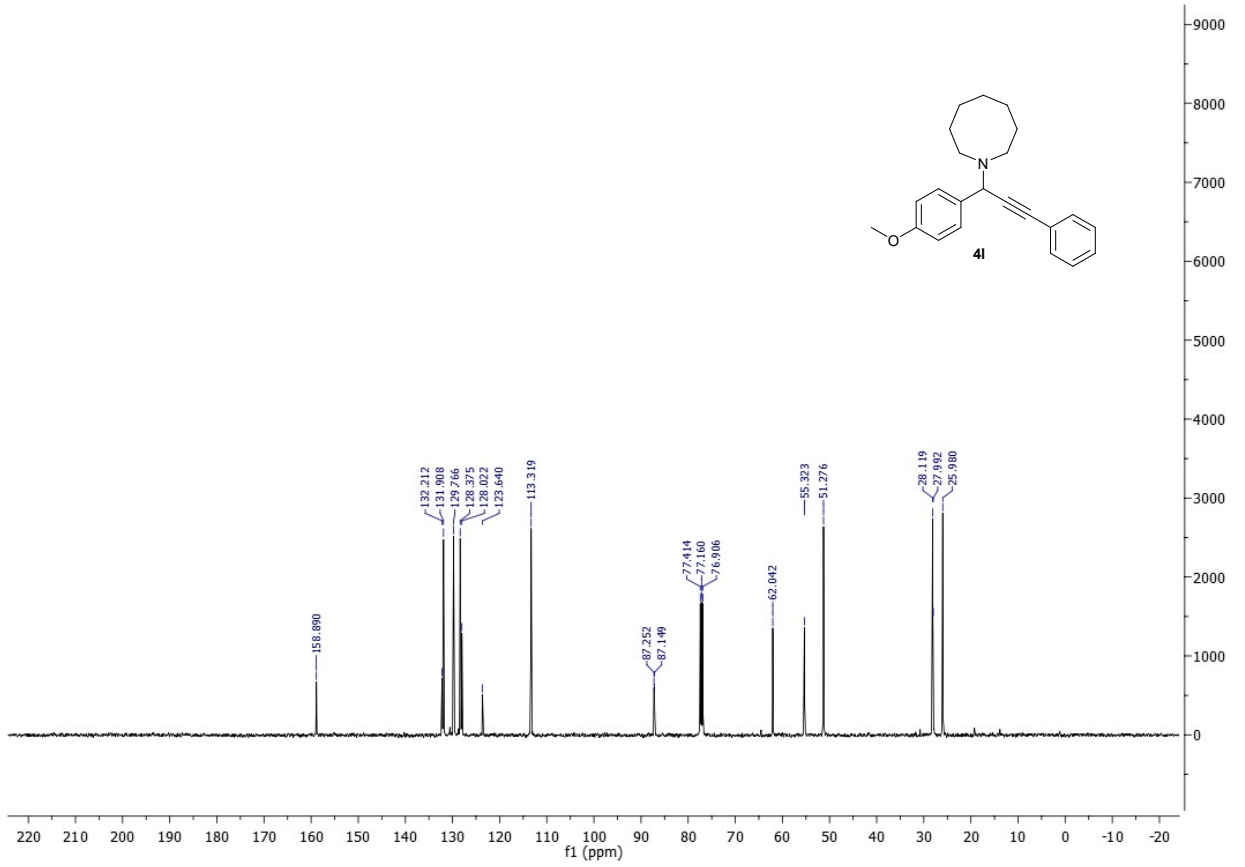

$^{13}$C NMR (126 MHz, $CDCl_3$):



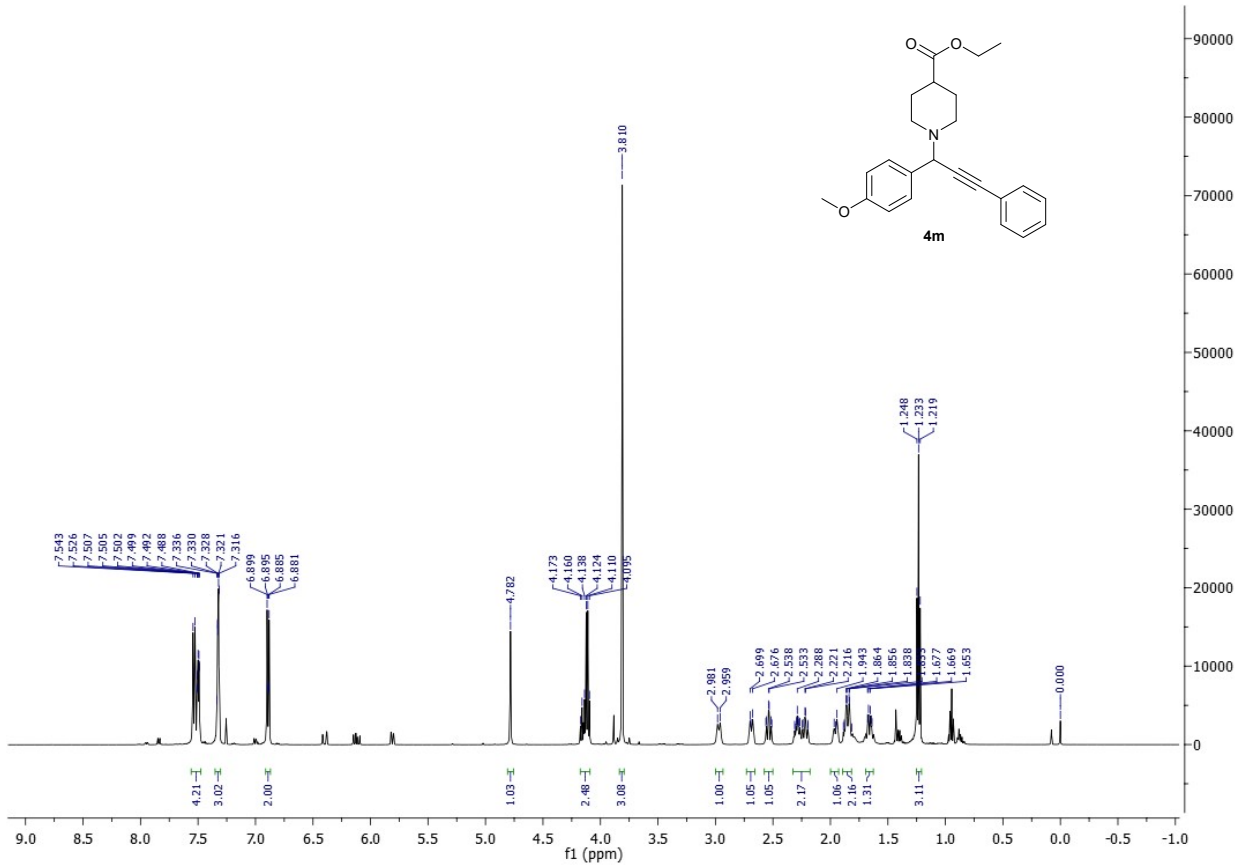
$^{1}$H NMR (500 MHz, $CDCl_3$):



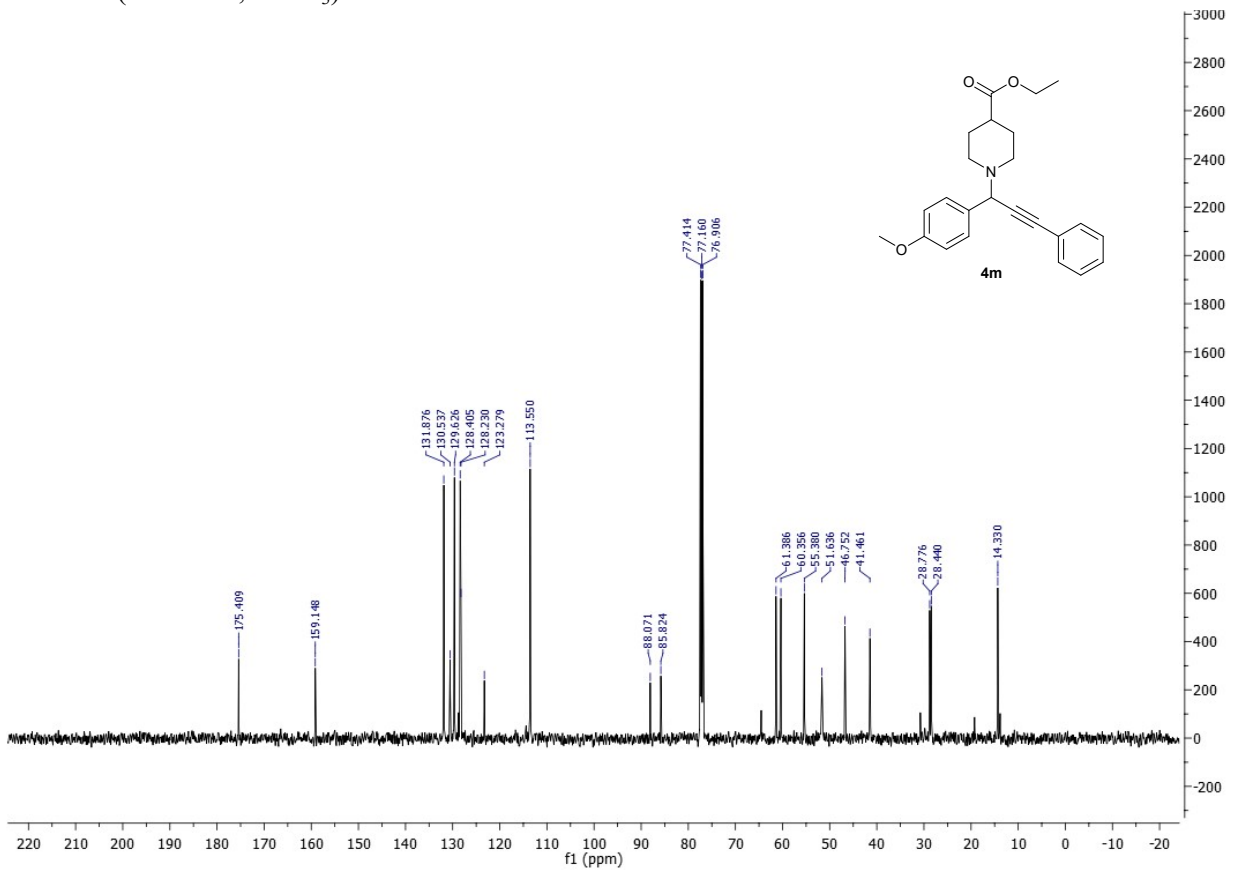

$^{13}$C NMR (126 MHz, $CDCl_3$):



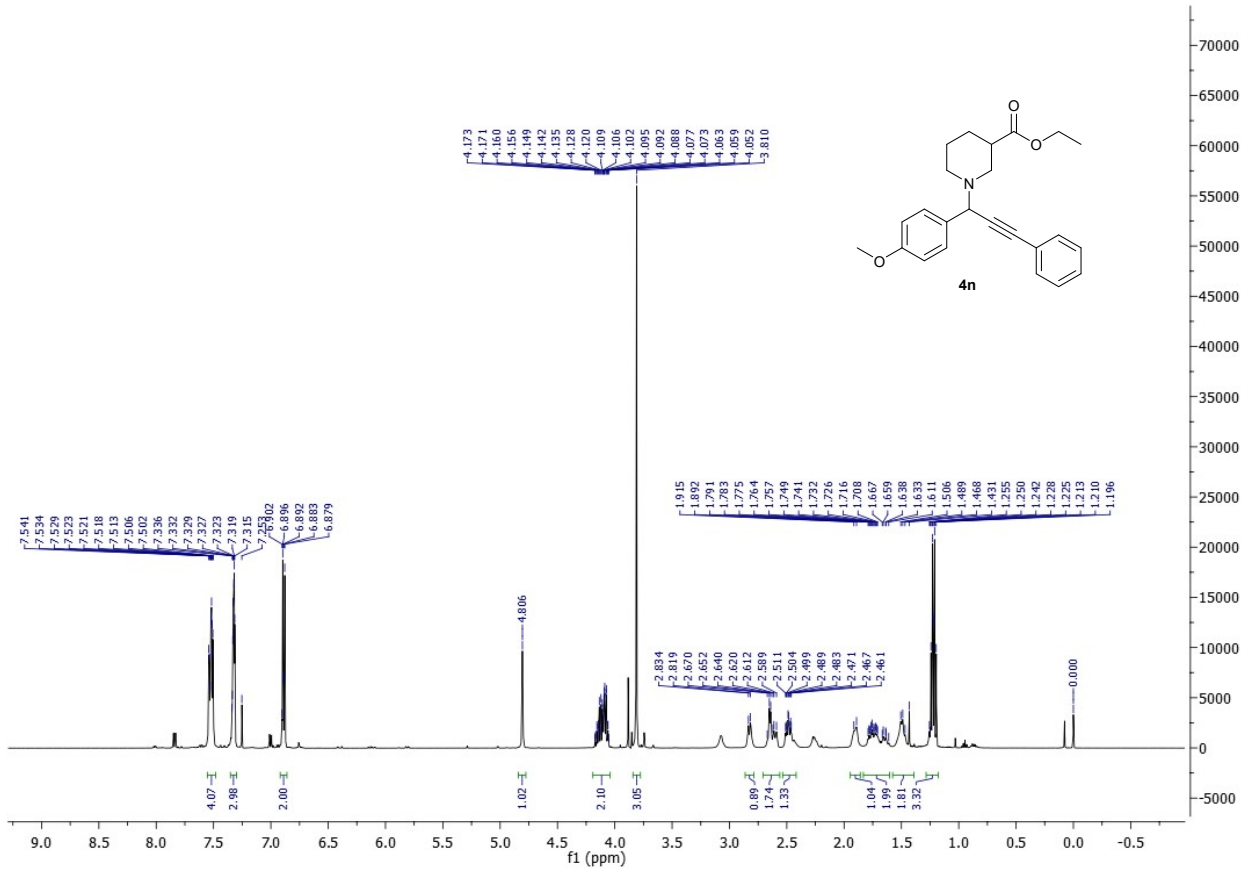
$^{1}$H NMR (500 MHz, $CDCl_3$):



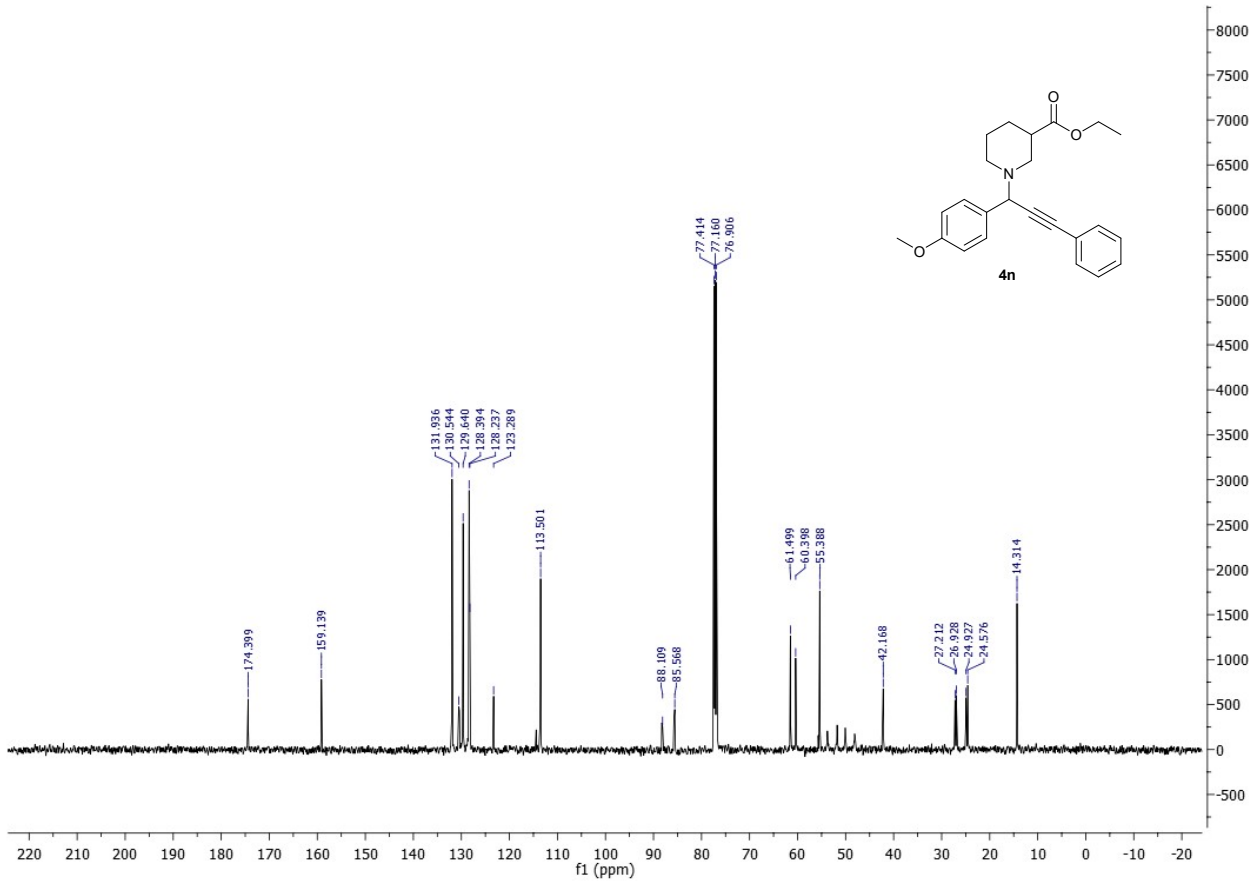

$^{13}$C NMR (126 MHz, $CDCl_3$):



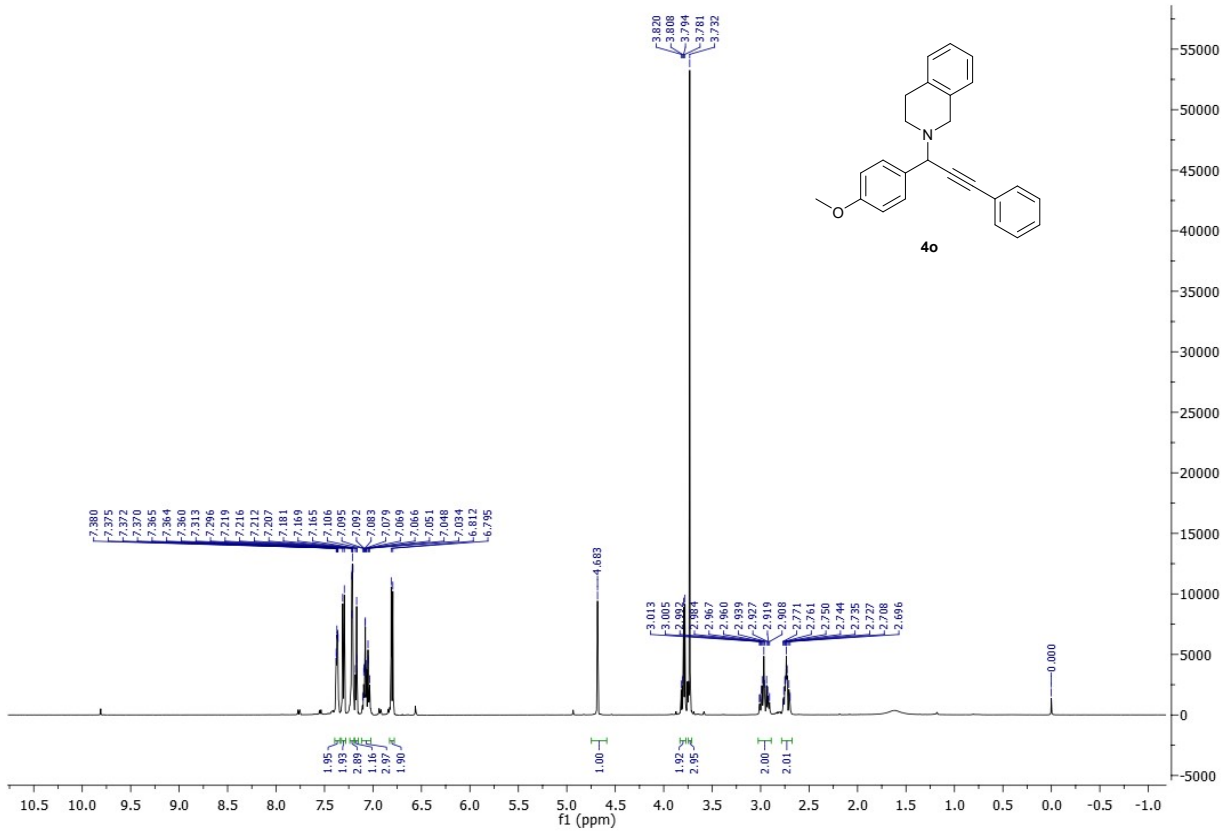
$^{1}$H NMR (500 MHz, $CDCl_3$):



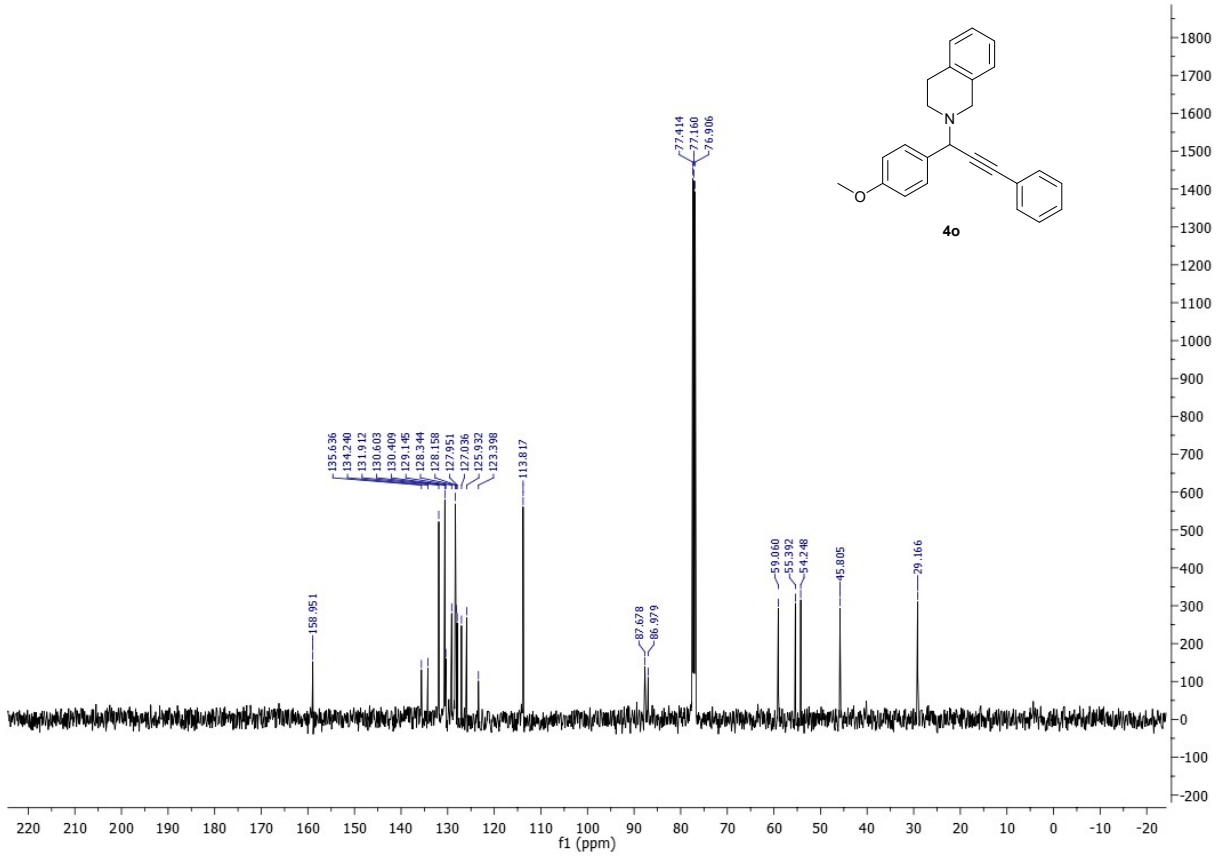

$^{13}$C NMR (126 MHz, $CDCl_3$):



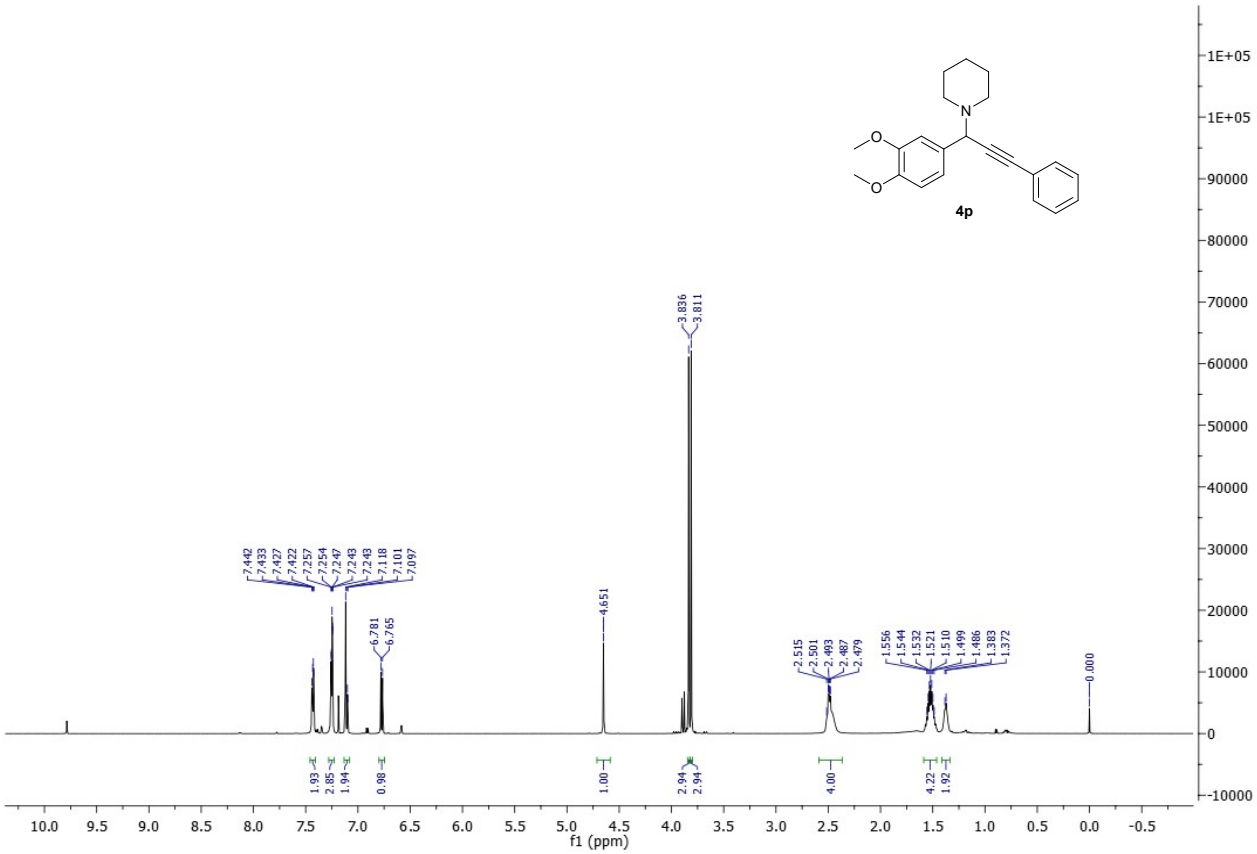
$^{1}$H NMR (500 MHz, $CDCl_3$):



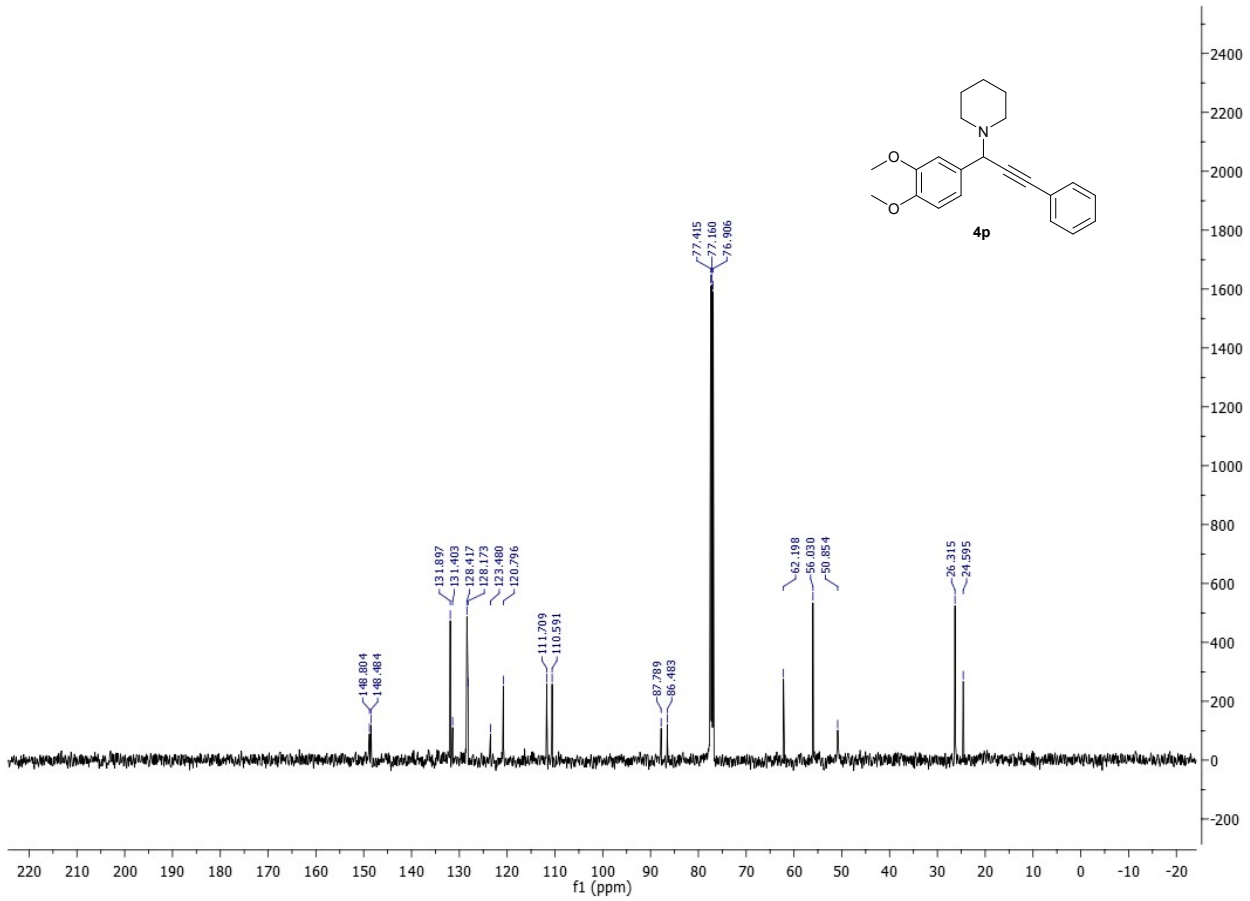

$^{13}$C NMR (126 MHz, $CDCl_3$):



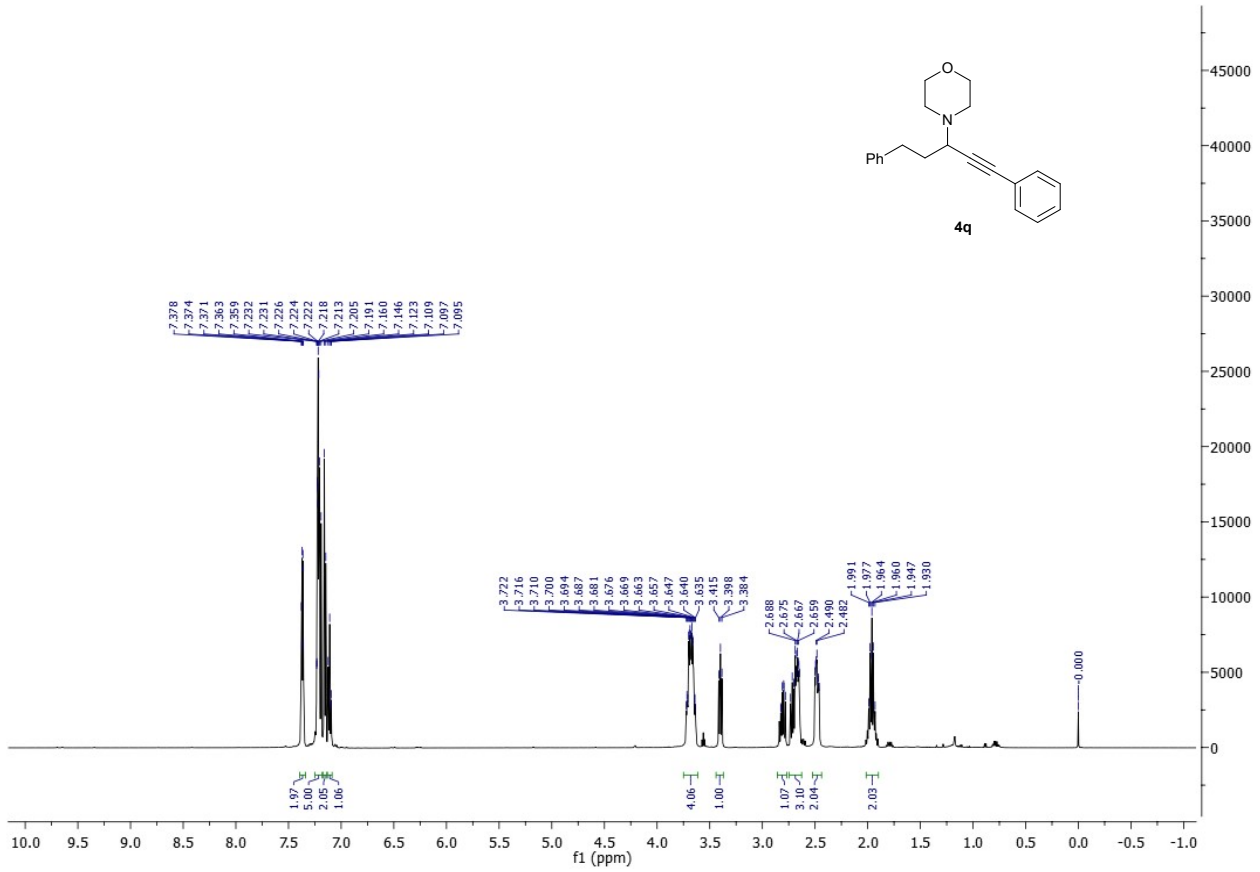
$^1$H NMR (500 MHz, $CDCl_3$):



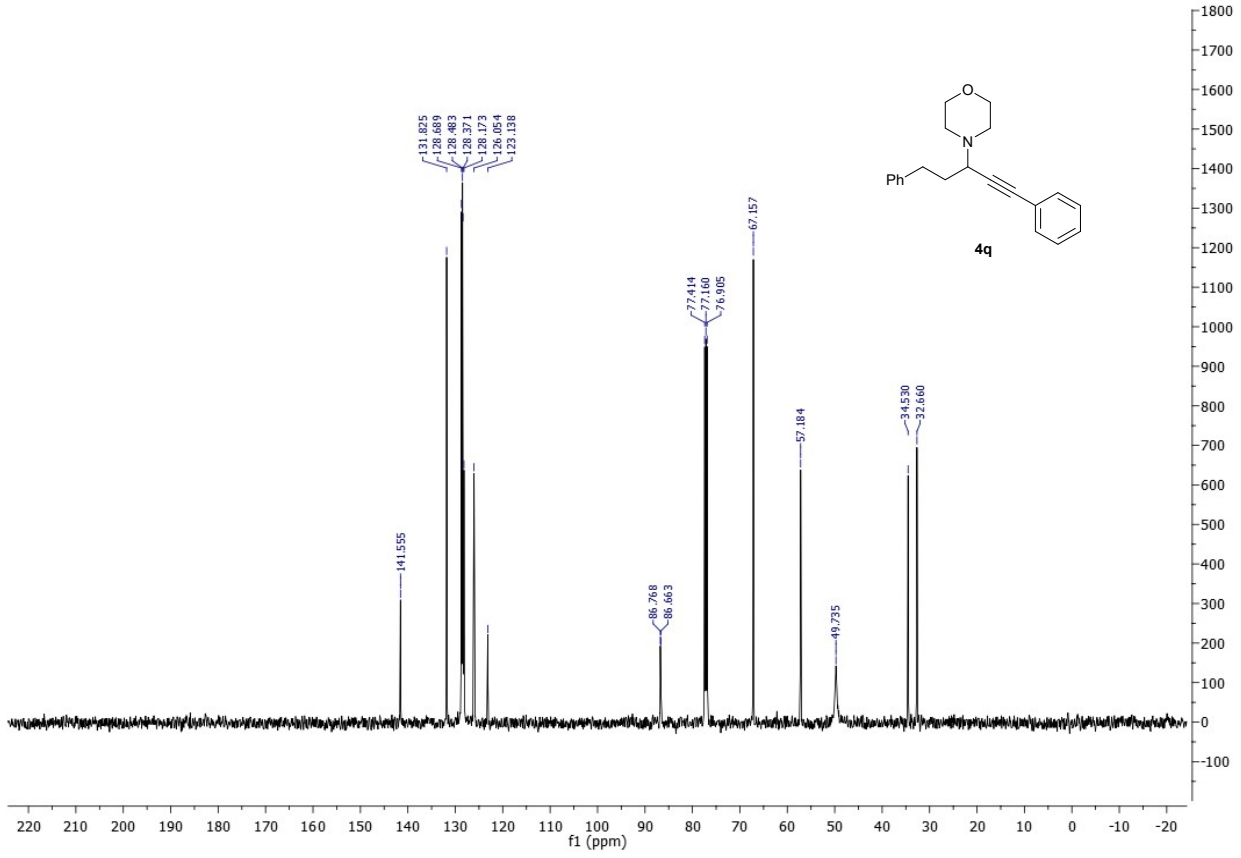
$^{13}C$ NMR (126 MHz, $CDCl_3$):



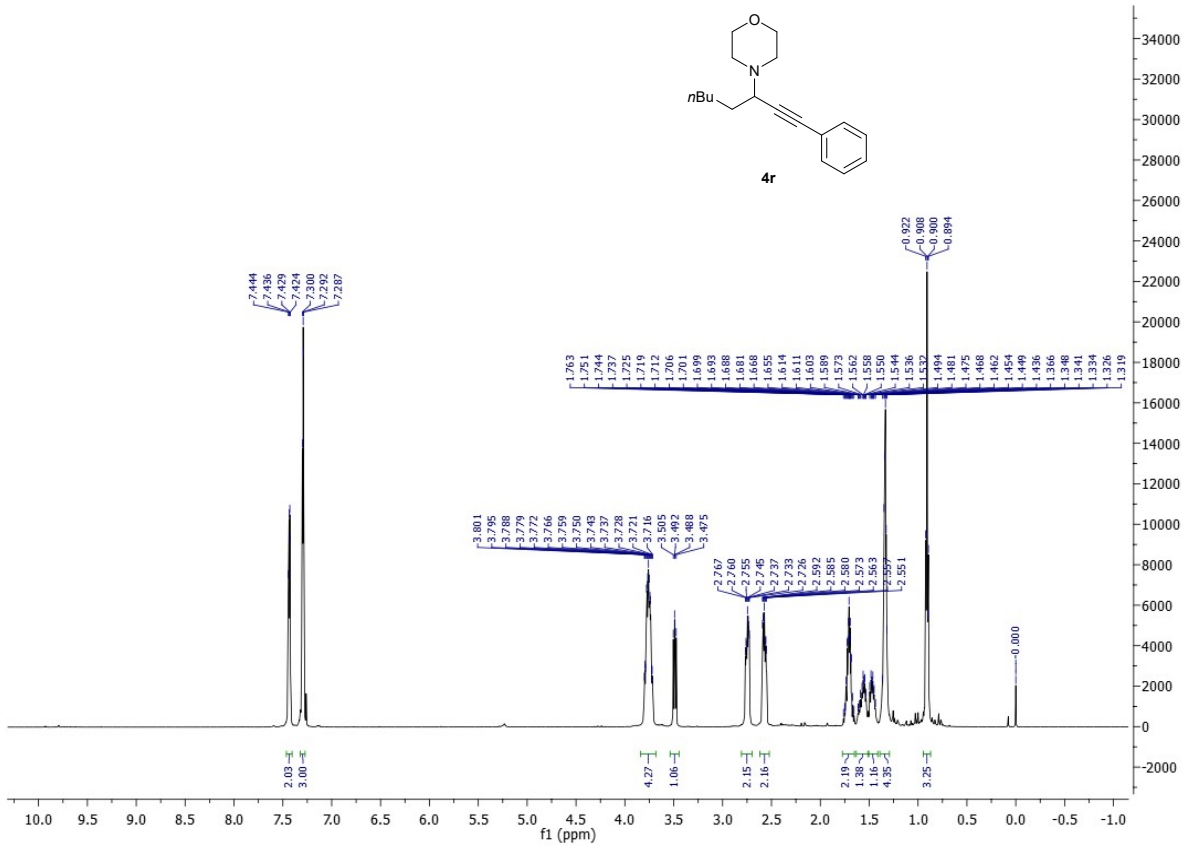

$^{1}H$ NMR (500 MHz, $CDCl_3$):



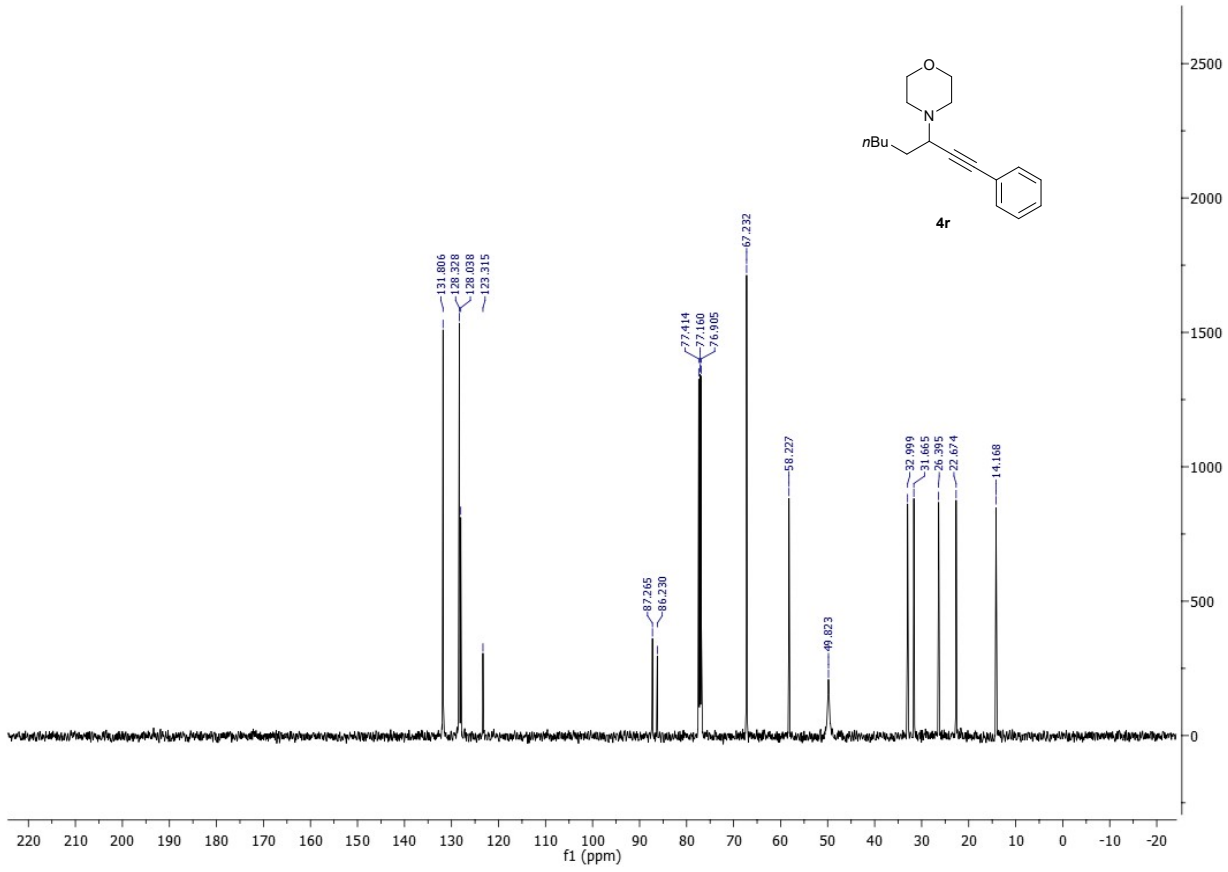

$^{13}$CNMR (126 MHz, $CDCl_3$):



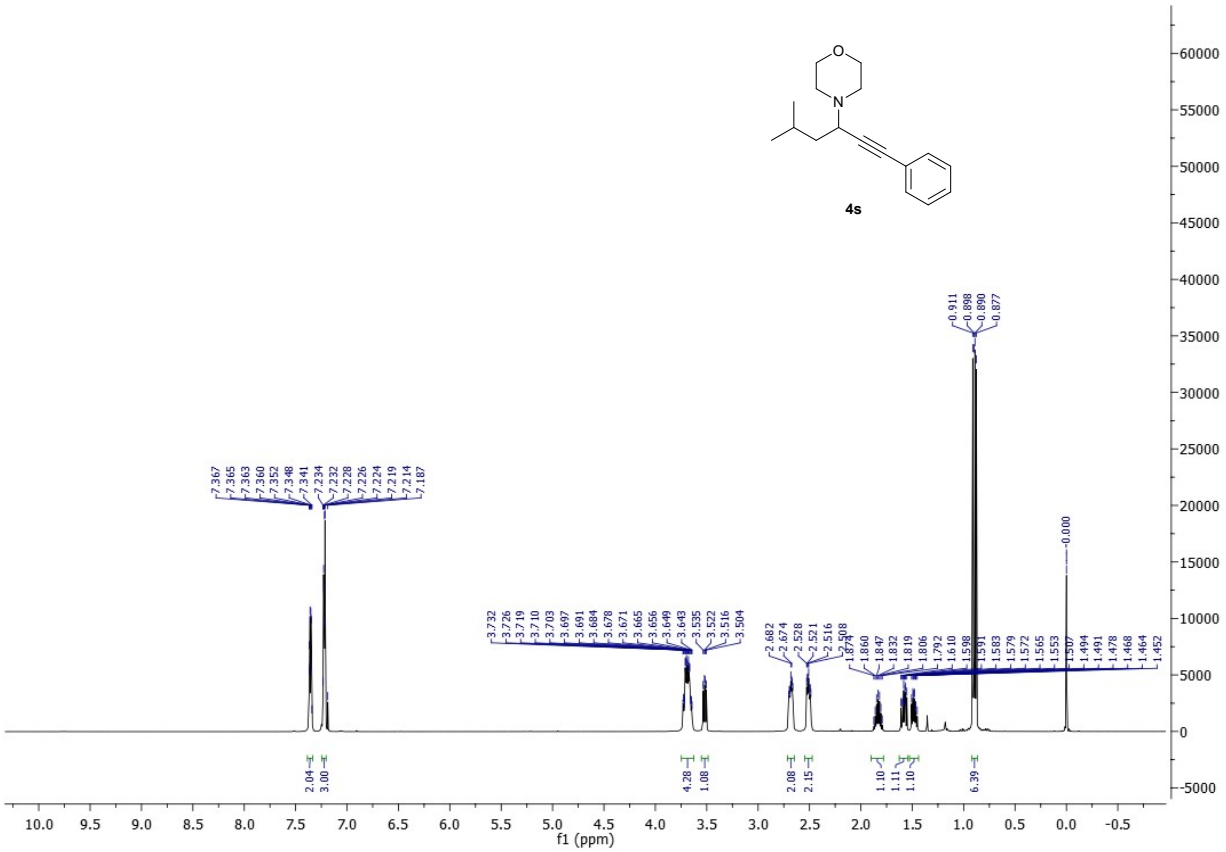
$^{1}$H NMR (500 MHz, $CDCl_3$):



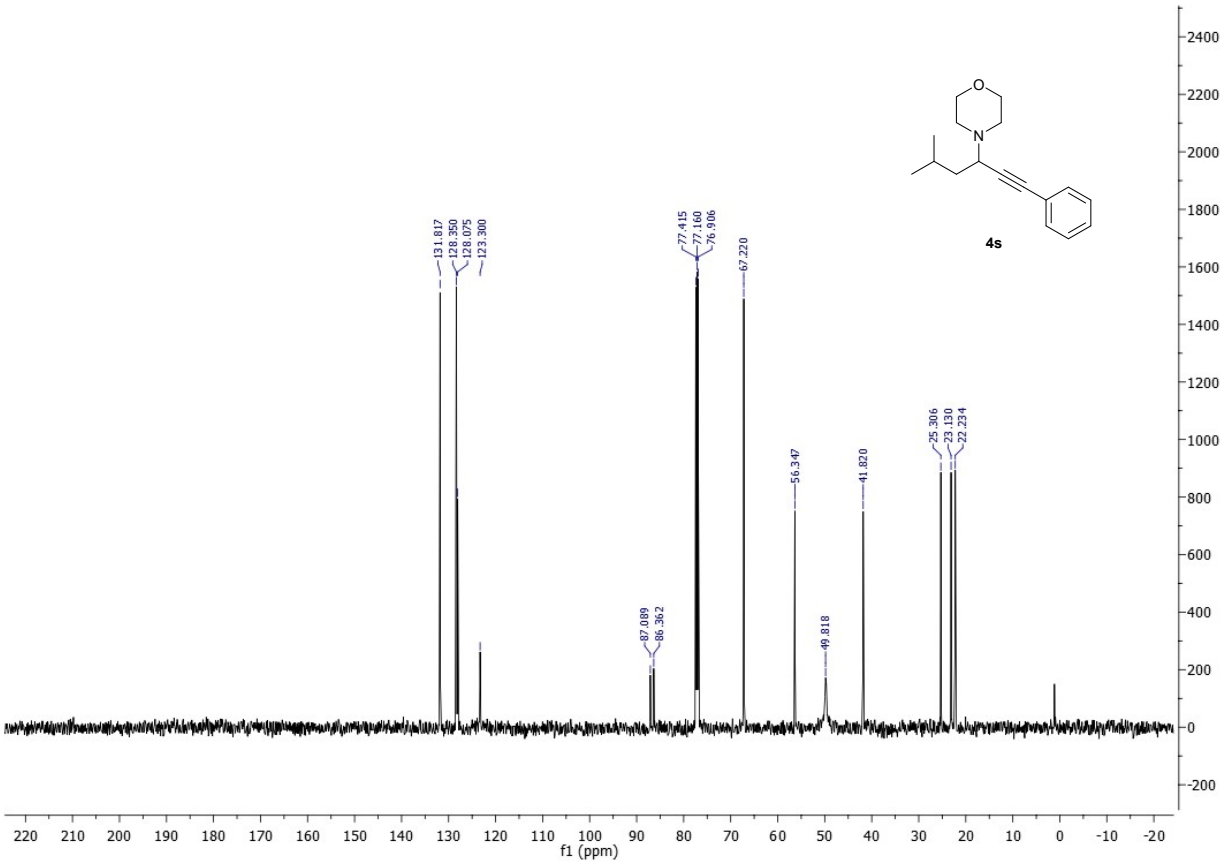

$^{13}$C NMR (126 MHz, $CDCl_3$):



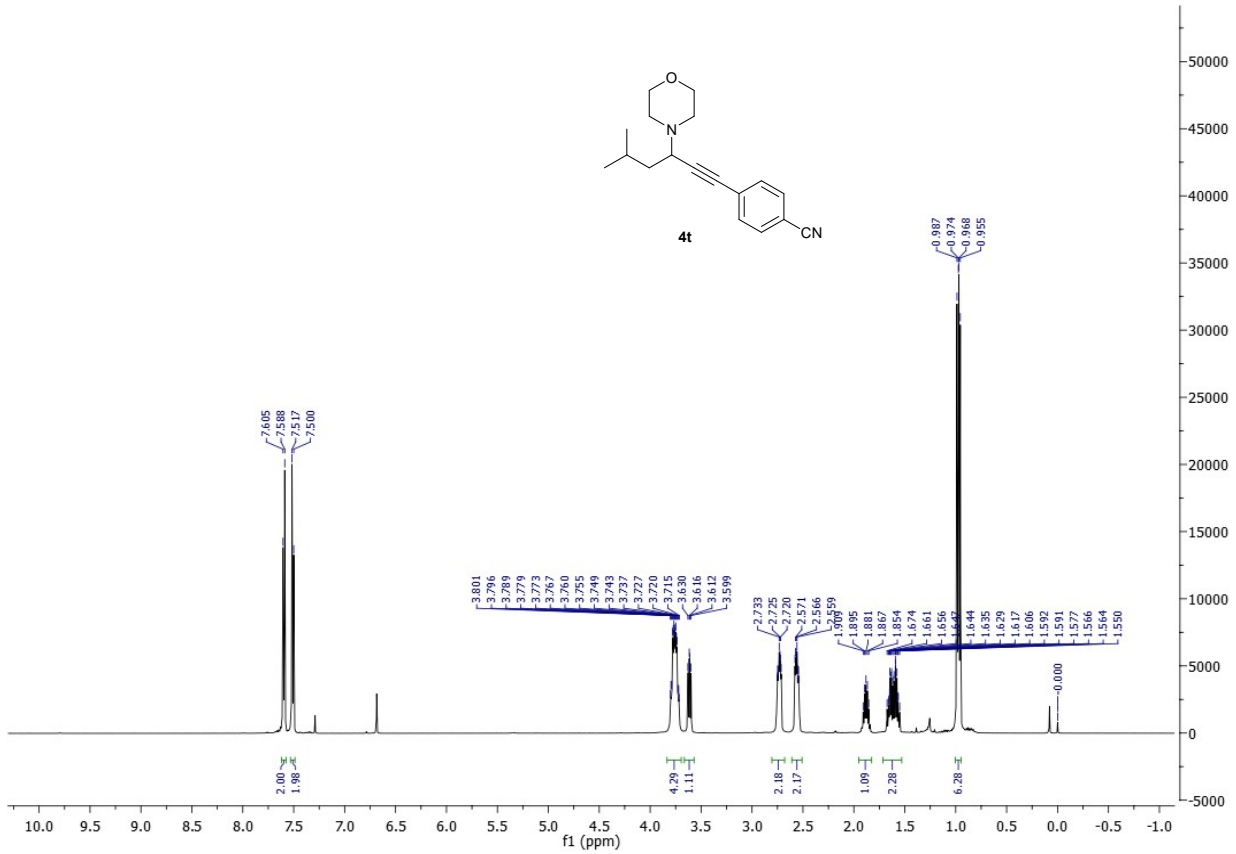
$^{1}$H NMR (500 MHz, $CDCl_3$):



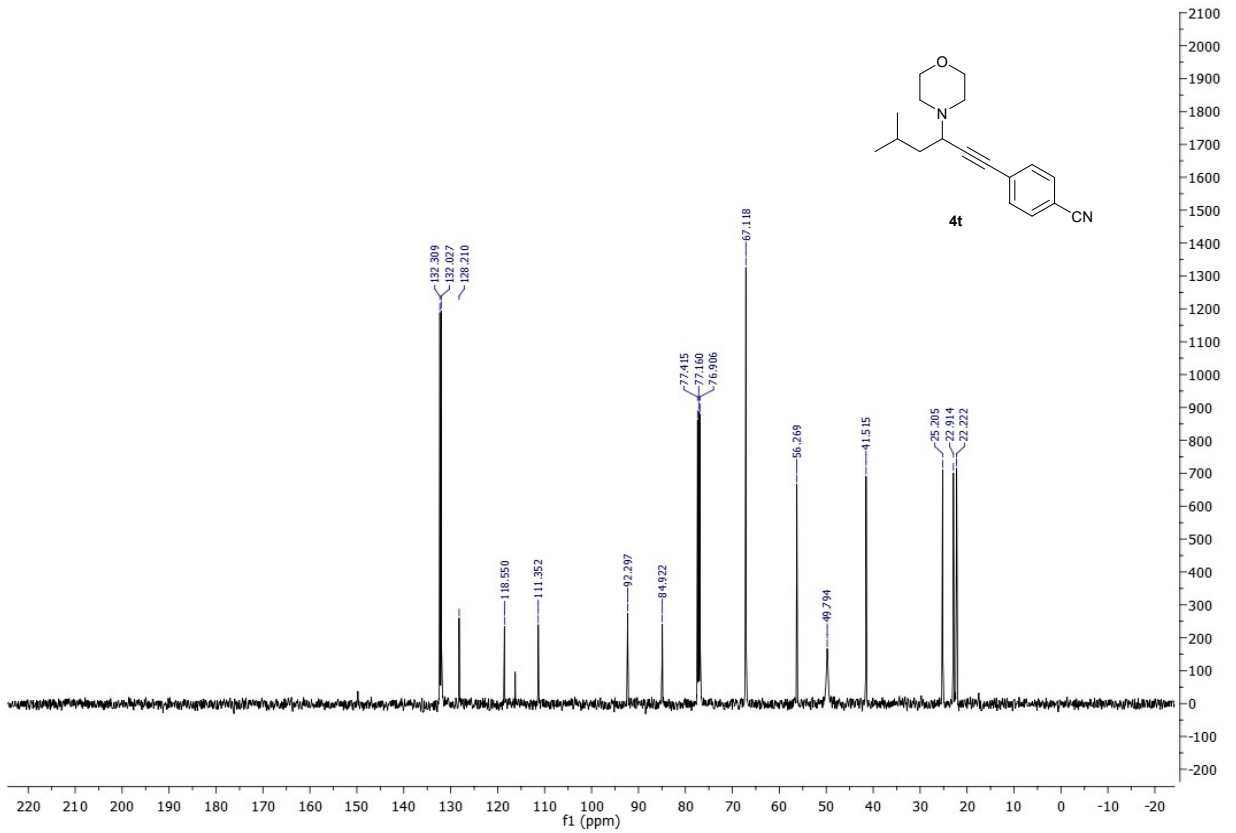

$^{13}$C NMR (126 MHz, $CDCl_3$):



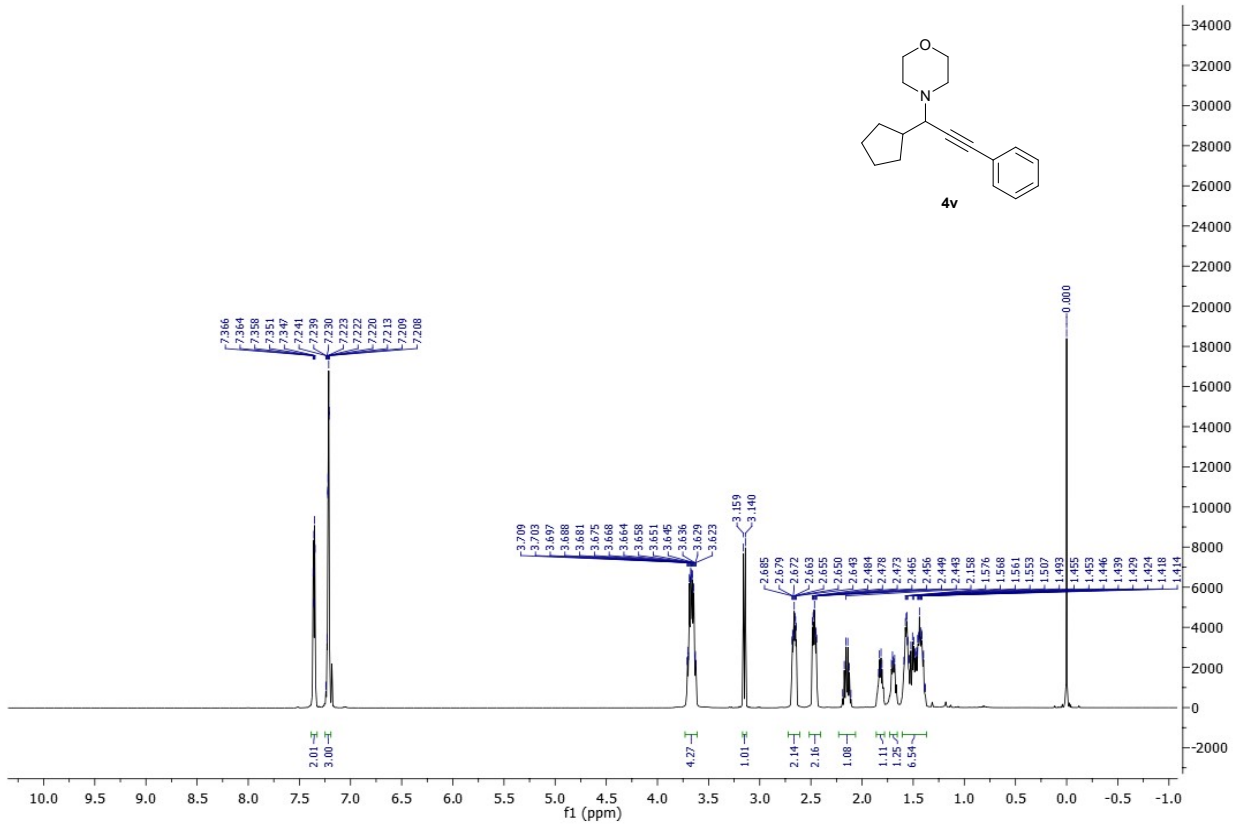
$^{1}$H NMR (500 MHz, $CDCl_3$):




$^{13}$C NMR (126 MHz, $CDCl_3$):



$^{1}$H NMR (500 MHz, $CDCl_3$):




$^{13}$C NMR (126 MHz, $CDCl_3$):