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Supporting information

for

Internal 2D networking of silver bromide with bidentate N-heterocyclic carbene ligand enables the formation of inherently heterogeneous reusable catalyst for multicomponent A^3–coupling.

Sundaravelu Nallappan[a], Oleksander Kucherak[a], Anita Kiss[a], Ringaile Lapinskaite[a], Ivana Císařová[b], and Lukas Rycek[a]*

[a] Dr. S. Nallappan, Dr. Oleksander Kucherak, Dr. Anita Kiss, Dr. R. Lapinskaite, Dr. L. Rycek

Department of Organic Chemistry, Faculty of Science

Charles University

Hlavova 8, 128 00 Prague

E-mail: rycekl@natur.cuni.cz

[b] Ivana Císařová

Department of Inorganic Chemistry, Faculty of Science

Charles University

Hlavova 8, 128 00 Prague (Czech Republic).

[c] Dr. R. Lapinskaite

Department of Organic Chemistry, Center for Physical Sciences and Technology,

Akademijos g. 7, Vilnius, 08412, Lithuania.

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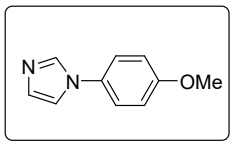
1. General information

All the chemicals were purchased from the common sources Sigma Aldrich, Acros Organics, Alfa Aesar, Strem Chemicals, PENTA Chemicals, Cambridge Isotope Laboratories, Inc. Unless otherwise noted, all of the materials are commercially available and used without further purifications or prepared by known methodologies. All the reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching using an appropriate mixture of ethyl acetate and hexanes. All the reactions were carried out in IKA magnetic stirrers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (100 MHz for ^{13}C and 400 MHz for ^{1}H) instrument. ^{1}H NMR spectra were reported relative to residual $CDCl_3$ (δ 7.26 ppm) and DMSO-d_6 (δ 2.50 ppm). Whenever the residual peak overlaps with the compound, spectra are reported as residual TMS. ^{13}C NMR was reported relative to $CDCl_3$ (δ 77.16 ppm) and DMSO-d_6 (δ 39.52 ppm). All chemical shifts δ are reported in ppm. Mass spectrometry was performed on a Thermo Fisher LTQ Orbitrap XL hybrid FT mass spectrometer with a combination of ion trap MS and the Orbitrap mass analyser. Infrared spectra were measured in KBr with a Thermo Nicolet AVATAR 370 FT-IR spectrometer. Unless otherwise stated, the reaction that requires heating was carried out with the oil bath as the heat source. Solvents used for extraction and column chromatography were laboratory grade and used after the distillation.

2. Experimental spectral data

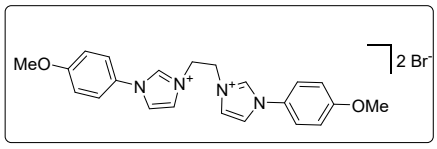
2.1. Preparation of the ligand and complex

1-(4-methoxyphenyl)-1H-imidazole (3): A flame-dried round-bottom flask was charged with



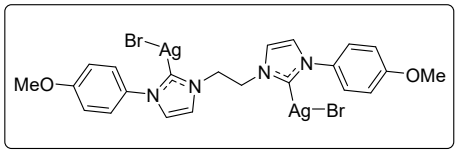
NaH (60% in mineral oil, 1 eq., 1.18 g, 29.4 mmol), (which was previously rinsed with pentane), imidazole (1 eq., 2.00 g, 29.4 mmol) and DMSO (50 mL). The resulting suspension was stirred at room temperature for 30 minutes under argon atmosphere. Subsequently, CuI (0.08 eq., 0.47 g 2.4 mmol) and 1-iodo-4-methoxybenzene (0.8 eq., 5.73 g, 24.5 mmol) were added. The reaction mixture was refluxed at 120 °C for 24 hours. The conversion was checked by TLC (DCM /MeOH = 20:1, visualization with ninhydrin and AMC). The mixture was allowed to cool to room temperature, then water (50 mL) was added. The crude mixture was extracted with EtOAc (3 x 50 mL). Then, the combined organic phase was washed with brine (3 x 40 mL), dried over $MgSO_4$, filtered and evaporated. The product obtained was purified by column chromatography, on silica gel with a mixture of DCM/MeOH = 20:1, yielding a deep orange solid (2.76 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.33 – 7.27 (m, 2H), 7.19 (t, 1H, *J* = 1.2 Hz), 7.17 (t, 1H, *J* = 1.2 Hz), 7.00 – 6.95 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 136.0, 130.9, 130.2, 123.3 (2C), 118.9, 115.0 (2C), 55.7. HRMS (ESI+) m/z: Calcd for $C_{10}H_{11}N_2O$ = 175.0866; Found = 175.0872.

3,3'-(ethane-1,2-diyl)bis(1-(4-methoxyphenyl)-1H-imidazol-3-ium) (4): In a thick-wall tube 1-



(4-methoxyphenyl)-1H-imidazole (**3**) (2 eq., 1.48 g, 3.93 mmol) and dibromoethane (1 eq., 0.37 mL, 1.97 mmol) were mixed. The resulting solution was stirred at 100 °C for 40 min, then it was allowed to cool to room temperature. The formed pale-brown residue was triturated with THF, sonicated for 1 min and crushed into small pieces with a spatula. The precipitate was filtered off, washed with THF (2 x 3 mL) and dried in air to give the ligand B as a white powder (2.08 g, 91%). ^{1}H NMR (400 MHz, DMSO-d^6) δ 9.95 – 9.90 (m, 1H), 8.27 (t, *J* = 1.9 Hz, 1H), 7.96 (t, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 9.1 Hz, 2H), 4.91 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 160.07, 135.94, 127.77, 123.49, 123.29, 121.52, 115.15, 55.79, 48.71. Mp: 269 °C. HRMS (ESI): m/z: Calcd for $C_{22}H_{24}N_4O_2^{++}$ 376.1888; Found ½ $[M]^{++}$:188.0944.

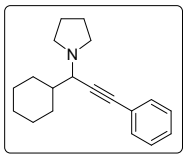
Silver Complex (5): In a solution of ligand **4** (1.0 eq., 500 mg, 1.33 mmol) in acetonitrile (10 mL) was added silver(I) oxide (1.15 eq., 355 mg, 1.53 mmol). After stirring the suspension at 50°C overnight, brown suspension obtained. Then, the mixture was cooled to room temperature and filtered to give a grey powder, which was then treated with DMF (5mL), sonicated for 1 min, heated to 50°C, and filtered again. The treatment with DMF (5 mL) was repeated two times. The combined DMF solutions were concentrated under vacuum to 2 mL, and then diluted with Et_2O (15 mL). The formed precipitate was filtered off, washed with MeOH (4mL), and acetone (4 mL), and dried in vacuo to give the title product as a white powder (115 mg, 21%). M.p. = 217 °C. ^{1}H NMR (600 MHz, DMSO-d^6) δ 7.72 (d, 2H, *J* = 1.9 Hz), 7.62 (d, 2H, *J* = 1.9 Hz), 7.33 (d, 4H, *J* = 8.3 Hz), 6.91 (d, 4H, *J* = 8.3 Hz), 4.67 (s, 4H), 3.78 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d^6) δ 178.9, 159.1, 132.5, 125.1, 123.2, 122.8, 114.5, 55.6, 51.4.



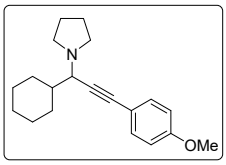
2.2. General procedure for A^3-coupling:

General procedure for the A^3-coupling reaction (Method A): In an oven-dried reaction tube, aldehyde (1.5 equiv, 1.5 mmol), amine (1.0 equiv, 1.0 mmol), terminal alkyne (1.5 equiv, 1.5 mmol) were successively added along with Ag-NHC complex (0.5 mol%). The reaction tube was closed by a teflon screw cap, mixture was flushed with argon before being progressively heated to 80°C under neat conditions and left to stir for 5 h. The reaction was monitored through TLC, and after the completion of the reaction, the compound was purified directly through silica column separation of crude product using hexanes and ethyl acetate mixture afforded the corresponding tertiary propargylamine in good yield.

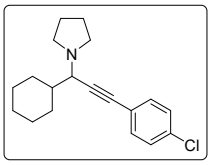
General procedure for the A^3-coupling reaction (Method B): In an oven-dried reaction tube, aldehyde (1.5 equiv, 1.5 mmol), amine (1.0 equiv, 1.0 mmol), terminal alkyne (1.5 equiv, 1.5 mmol) were successively added along with Ag-NHC complex (0.5 mol%). The mixture was flushed with argon and 2ml of $CHCl_3$ were added. The reaction tube was closed by a teflon screw cap and allowed to stir for 5 h successively at room temperature. The reaction was monitored using TLC, and after the completion of the reaction, the compound was purified directly through silica column separation of crude product using hexanes and ethyl acetate mixture affording the corresponding tertiary propargylamine.

1-(1cyclohexyl-3-phenylprop-2-yn-1-yl)pyrrolidine (9a): According to general procedure, 

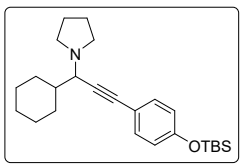
cyclohexane carboxaldehyde (168 mg, 1.5 mmol), pyrrolidine (142 mg, 1.5 mmol), and phenylacetylene (159 mg, 1.5 mmol) afforded compound **9a** (389 mg, 98%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.44 (m, 2H), 7.26 – 7.27 (m, 3H), 3.36 (d, 1H, *J* = 8.4 Hz), 2.73 – 2.67 (m, 4H), 2.12 (d, 1H, *J* = 11.1 Hz), 1.98 (d, 1H, *J* = 11.7 Hz), 1.82 – 1.74 (m, 6H), 1.70 – 1.57 (m, 2H), 1.27 – 1.08 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.8, 123.8, 88.0, 85.9, 61.4, 50.2 (2C), 41.5, 30.8, 30.4, 26.8, 26.4, 26.3, 23.7 (2C). The data is in accordance with the one reported in the literature.[1]

1-(1-cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-yl)pyrrolidine (9b): Following the general 

procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), pyrrolidine (106 mg, 1.5 mmol), and 4-methxoyphenylacetylene (198 mg, 1.5 mmol) were used as starting substrates, yielding compound **9b** (433 mg, 97%) as a yellow oil. Purified by column chromatography using silicagel as stationary phase and a mixture of EtOAc: Hex (10:90) as eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.36 (d, *J* = 8.3 Hz, 1H), 2.87 – 2.60 (m, 4H), 2.14 – 1.94 (m, 2H), 1.83 – 1.55 (m, 8H), 1.32 – 1.08 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 133.2, 115.9, 113.9, 86.3, 85.6, 61.4, 55.4, 50.2, 41.5, 30.8, 30.4, 26.8, 26.4, 26.3, 23.7. The spectroscopic data is in accordance with the one reported in the literature.[2]

1-(3-(4-chlorophenyl)-1-cyclohexylprop-2-yn-1-yl)pyrrolidine (9c): Following the general 

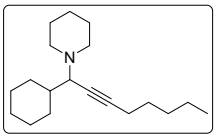
procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), pyrrolidine (106 mg, 1.5 mmol), and 4-chlorophenylacetylene (204 mg, 1.5 mmol) were used as starting substrates, yielding compound **9c** (440 mg, 97%) as a yellow oil. Purified by column chromatography using silicagel as stationary phase and a mixture of EtOAc: Hex (10:90) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.36 (d, *J* = 8.5 Hz, 1H), 2.79 – 2.60 (m, 4H), 2.14 – 1.93 (m, 2H), 1.84 – 1.56 (m, 8H), 1.32 – 1.07 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 133.0, 128.5, 122.2, 89.1, 84.8, 61.3, 50.1, 41.4, 30.7, 30.4, 26.8, 26.3, 26.3, 23.6. The spectroscopic data is in accordance with the one reported in the literature.[2]

1-(3-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1-cyclohexylprop-2-yn-1-yl)pyrrolidine (9d): 

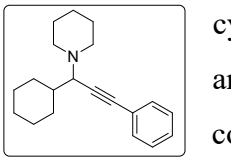
Following the general procedure, cyclohexane carboxaldehyde (168 mg, 1.5

mmol), pyrrolidine (106 mg, 1.5 mmol), and tert-butyl(4-ethynylphenoxy)dimethylsilane (348 mg, 1.5 mmol) were used as starting substrates, yielding compound **9d** (558 mg, 93%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Ethylacetate: Hex as eluent; R_f 0.40 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.35 (d, *J* = 8.5 Hz, 1H), 2.79 – 2.61 (m, 4H), 2.17 – 2.05 (m, 1H), 2.00 – 1.92 (m, 1H), 1.84 – 1.75 (m, 6H), 1.70 – 1.52 (m, 2H), 1.31 – 1.12 (m, 5H), 1.00 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 133.1, 120.2, 116.6, 86.5, 85.7, 61.4, 50.1, 41.5, 30.8, 30.4, 26.8, 26.4, 26.3, 25.8, 23.6, 18.3, -4.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{40}NOSi$: 398.2873; Found: 398.2873.

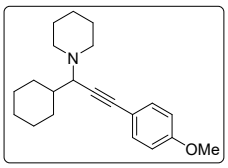
1-(1-cyclohexyloct-2-yn-1-yl)piperidine (9e): According to general procedure, cyclohexane carboxaldehyde (0.168 g, 1.5 mmol), piperidine (0.128 g, 1.5 mmol), and 1-heptyne (0.144 g, 1.5 mmol) afforded compound **9e** (83 mg, 20%) as pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (dt, *J* = 8.0, 2.0 Hz, 1H), 2.63 (dt, *J* = 8.5, 4.1 Hz, 2H), 2.57 – 2.50 (m, 2H), 2.22 – 2.17 (m, 2H), 2.02 – 1.94 (m, 1H), 1.87 – 1.81 (m, 1H), 1.77 – 1.68 (m, 6H), 1.68 – 1.62 (m, 1H), 1.62 – 1.46 (m, 2H), 1.50 – 1.05 (m, 10H), 0.92 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 86.0, 77.8, 64.1 (2C), 50.7, 39.8 (2C), 31.3, 31.2, 30.6, 29.1, 27.0, 26.5 (2C), 26.3, 24.9, 22.3, 18.8 (2C), 14.1. The data is in accordance with the one reported in the literature.[1]



1-(1-cyclohexyl-3-phenylprop-2-yn-1-yl)piperidine (9f): Following the general procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), piperidine (128 mg, 1.5 mmol), and phenylacetylene (153 mg, 1.5 mmol) were used as starting substrates, yielding compound **9f** (329 mg, 78%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Ethylacetate: Hex as eluent (2: 98); R_f 0.60 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.35 – 7.27 (m, 3H), 3.15 (d, *J* = 9.9 Hz, 1H), 2.77 – 2.57 (m, 2H), 2.54 – 2.29 (m, 2H), 2.17 – 2.03 (m, 2H), 1.86 – 1.56 (m, 8H), 1.52 – 1.40 (m, 2H), 1.36 – 1.16 (m, 3H), 1.12 – 0.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.8, 123.9, 87.8, 86.3, 64.5, 50.9, 39.7, 31.5, 30.6, 26.9, 26.4, 26.3, 26.2, 24.8. The spectroscopic data is in accordance with the one reported in the literature.[1]

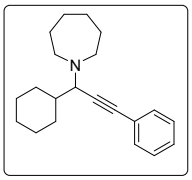


1-(1-cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-yl)piperidine (9g): According to general procedure, cyclohexanecarboxaldehyde (0.168 g, 1.5 mmol), piperidine (0.128



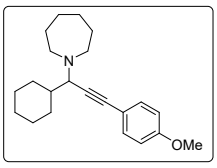
g, 1.5 mmol), and 4-ethynilanisole (0.198 g, 1.5 mmol) afforded compound **9g** (401 mg, 86%) as yellow crystalline solid. Purified by column chromatography using silicagel as stationary phase and Ethylacetate: Hex as eluent (5:95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.10 (d, *J* = 9.9 Hz, 1H), 2.70 – 2.59 (m, 2H), 2.46 – 2.36 (m, 2H), 2.17 – 2.01 (m, 2H), 1.83 – 1.74 (m, 2H), 1.67 – 1.53 (m, 5H), 1.50 – 1.41 (m, 2H), 1.34 – 1.16 (m, 4H), 1.09 – 0.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 133.1, 116.1, 113.9, 86.2, 86.0, 64.5, 55.3, 50.9, 39.7, 31.4, 30.6, 26.9, 26.4 (3C), 26.2, 24.9. The data is in accordance with the one reported in the literature.[4]

1-(1-cyclohexyl-3-phenylprop-2-yn-1-yl)azepane (9h): Following the general procedure,

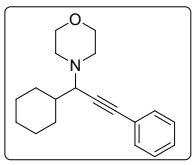


cyclohexane carboxaldehyde (168 mg, 1.5 mmol), azepane (150 mg, 1.5 mmol), and phenylacetylene (153 mg, 1.5 mmol) were used as starting substrates, yielding compound **9h** (365 mg, 82%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Hex as eluent; R_f 0.75 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 3.18 (d, *J* = 10.1 Hz, 1H), 2.88 – 2.76 (m, 2H), 2.65 – 2.54 (m, 2H), 2.25 – 2.06 (m, 2H), 1.83 – 1.57 (m, 11H), 1.58 – 1.46 (m, 1H), 1.35 – 1.15 (m, 3H), 1.07 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.6, 124.1, 89.1, 85.0, 65.4, 52.8, 40.9, 31.3, 30.8, 29.4, 27.3, 27.0, 26.4, 26.2. The spectroscopic data is in accordance with the one reported in the literature.[3]

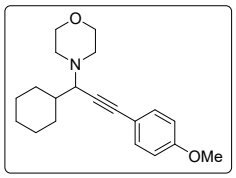
1-(1-cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-yl)azepane (9i): Following the general



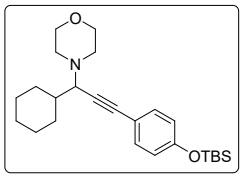
procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), azepane (150 mg, 1.5 mmol), and 4-methoxyphenylacetylene (198 mg, 1.5 mmol) were used as starting substrates, yielding compound **9i** (368 mg, 76%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Hex as eluent; R_f 0.70 (5% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.13 (d, *J* = 10.0 Hz, 1H), 2.83 – 2.72 (m, 2H), 2.60 – 2.50 (m, 2H), 2.20 – 2.04 (m, 2H), 1.77 – 1.56 (m, 11H), 1.54 – 1.44 (m, 1H), 1.31 – 1.12 (m, 3H), 1.04 – 0.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 133.2, 116.3, 113.9, 87.4, 84.7, 65.4, 55.4, 52.8, 41.0, 31.3, 30.8, 29.4, 27.3, 27.0, 26.4, 26.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{32}NO$: 326.2478; Found: 326.2478.

4-(1-cyclohexyl-3-phenylprop-2-yn-1-yl)morpholine (9j): Following the general procedure, 

cyclohexane carboxaldehyde (168 mg, 1.5 mmol), morpholine (130 mg, 1.5 mmol), and phenylacetylene (153 mg, 1.5 mmol) were used as starting substrates, yielding compound **9j** (290 mg, 68%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Hex: EA (97:3) as eluent; R_f 0.65 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.25 – 7.18 (m, 3H), 3.74 – 3.60 (m, 4H), 3.05 (d, *J* = 9.8 Hz, 1H), 2.69 – 2.57 (m, 2H), 2.49 – 2.37 (m, 2H), 2.08 – 1.91 (m, 2H), 1.74 – 1.53 (m, 4H), 1.16 – 0.83 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.9, 123.5, 86.9, 86.7, 67.3, 64.1, 50.0, 39.2, 31.1, 30.5, 26.8, 26.3, 26.1. The spectroscopic data is in accordance with the one reported in the literature.[1]

4-(1-cyclohexyl-3-(4-methoxyphenyl)prop-2-yn-1-yl)morpholine (9k): Following the general 

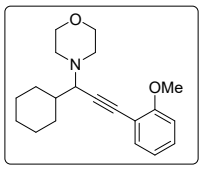
procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), morpholine (130 mg, 1.5 mmol), and 4-methoxyphenylacetylene (198 mg, 1.5 mmol) were used as starting substrates, yielding compound **9k** (278 mg, 59%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Hex: EA (95:5) as eluent; R_f 0.60 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.83 – 3.68 (m, 7H), 3.13 (d, *J* = 9.8 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.57 – 2.46 (m, 2H), 2.17 – 1.99 (m, 2H), 1.83 – 1.55 (m, 4H), 1.30 – 0.93 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 133.1, 115.7, 113.9, 86.6, 85.1, 67.3, 64.1, 55.3, 50.0, 39.2, 31.1, 30.4, 26.8, 26.3, 26.1. The spectroscopic data is in accordance with the one reported in the literature.[5]

4-(3-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1-cyclohexylprop-2-yn-1-yl)morpholine (9l): 

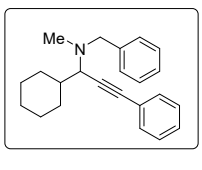
Following the general procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), morpholine (130 mg, 1.5 mmol), and tert-butyl(4-ethynylphenoxy)dimethylsilane (348 mg, 1.5 mmol) were used as starting substrates, yielding compound **9l** (319 mg, 51%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Ethylacetate: Hex as eluent (5:95); R_f 0.50 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.84 – 3.68 (m, 4H), 3.13 (d, *J* = 9.8 Hz, 1H), 2.76 – 2.66 (m, 2H), 2.57 – 2.47 (m, 2H), 2.17 – 2.01 (m, 2H), 1.83 – 1.56 (m, 5H), 1.20-1.10 (s, 4H), 1.05-1.10 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 133.2, 120.2, 116.4, 86.7, 85.3, 67.4,

64.1, 39.3, 31.1, 30.5, 26.9, 26.3, 26.2, 25.8, 18.4, -4.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{40}NO_2Si$: 414.2822; Found: 414.2819.

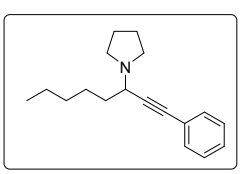
4-(1-cyclohexyl-3-(2-methoxyphenyl)prop-2-yn-1-yl)morpholine (9m): Following the general procedure, cyclohexane carboxaldehyde (168 mg, 1.5 mmol), morpholine (130 mg, 1.5 mmol), and 2-methoxyphenylacetylene (198 mg, 1.5 mmol) were used as starting substrates, yielding compound **9m** (298 mg, 63%) as a colourless oil, Purified by column chromatography using silicagel as stationary phase and Hex as eluent; R_f 0.60 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.32 – 7.23 (m, 1H), 6.96 – 6.84 (m, 2H), 3.89 (s, 3H), 3.84 – 3.61 (m, 4H), 3.21 (d, *J* = 9.8 Hz, 1H), 2.75 (s, 2H), 2.63 – 2.40 (m, 2H), 2.26 – 2.01 (m, 2H), 1.83 – 1.60 (m, 4H), 1.36 – 1.02 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 133.6, 129.3, 120.4, 112.8, 110.8, 91.2, 82.9, 67.4, 64.3, 55.9, 50.0, 39.3, 31.0, 30.5, 26.9, 26.3, 26.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{28}NO_2$: 314.2114; Found: 314.2109.



N-benzyl-1-cyclohexyl-N-methyl-3-phenylprop-2-yn-1-amine (9n): Following the general procedure, cyclohexane carboxaldehyde (56 mg, 0.5 mmol), N-methyl-1-phenylmethanamine (61 mg, 0.5 mmol), and phenylacetylene (51 mg, 0.5 mmol) were used as starting substrates, yielding compound **9n** (136 mg, 85%) as a colourless oil, Purified by column chromatography using silica gel as stationary phase and Hex as eluent; R_f 0.60 (10% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.46 – 7.25 (m, 8H), 3.76 (d, *J* = 13.4 Hz, 1H), 3.59 (d, *J* = 13.4 Hz, 1H), 3.27 (d, *J* = 10.3 Hz, 1H), 2.40 – 2.20 (m, 4H), 2.20 – 2.11 (m, 1H), 1.84 – 1.61 (m, 4H), 1.36 – 1.16 (m, 3H), 1.06 – 0.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.79, 131.80, 128.91, 128.27, 128.21, 127.77, 126.86, 123.74, 86.96, 86.51, 62.03, 59.49, 40.10, 37.79, 31.37, 30.31, 26.76, 26.24, 26.04. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}N$: 318.2216; Found: 318.2216. The spectroscopic data is in accordance with the one reported in the literature.[4]

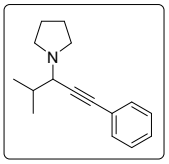


1-(1-phenyloct-1-yn-3-yl)pyrrolidine (9o): Following the general procedure, hexanal (150 mg, 1.5 mmol), pyrrolidine (106 mg, 1.5 mmol), and phenylacetylene (153 mg, 1.5 mmol) were used as starting substrates, yielding compound **9o** (310 mg, 81%) as a pale yellow oil. Purified by column chromatography using silicagel as stationary phase and a mixture of EtOAc: Hex (10:90) as eluent. R_f 0.50 (20% ethyl acetate in



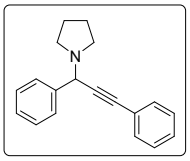
hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.36 – 7.24 (m, 3H), 3.71 (t, *J* = 7.3 Hz, 1H), 2.88 – 2.63 (m, 4H), 1.86 – 1.32 (m, 12H), 0.97 – 0.86 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.9, 123.6, 88.4, 85.4, 55.3, 49.9, 35.2, 31.8, 26.5, 23.6, 22.7, 14.2. The spectroscopic data is in accordance with the one reported in the literature.[4]

1-(4-methyl-1-phenylpent-1-yn-3-yl)pyrrolidine (9p): Following the general procedure,



isobutyraldehyde (108 mg, 1.5 mmol), pyrrolidine (108 mg, 1.5 mmol), and phenylacetylene (153 mg, 1.5 mmol) were used as starting substrates, yielding compound **9p** (306 mg, 90%) as pale yellow oil. Purified by column chromatography using silicagel as stationary phase and a mixture of EtOAc: Hex (10:90) as eluent; colourless oil; R_f 0.70 (20% ethyl acetate in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.38 – 7.25 (m, 3H), 3.36 – 3.21 (m, 1H), 2.84 – 2.59 (m, 4H), 2.01 – 1.77 (m, 5H), 1.19 – 1.04 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.3, 127.9, 123.7, 87.8, 85.8, 62.7, 50.5, 32.0, 23.7(2C), 20.4, 19.6. The spectroscopic data is in accordance with the one reported in the literature.[4]

1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (9q): According to general procedure, benzaldehyde



(0.160 g, 1.5 mmol), pyrrolidine (0.142 g, 1.5 mmol), and phenylacetylene (0.159 g, 1.5 mmol), afforded compound **9q** (74 mg, 19%) as pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.49 (m, 2H), 7.39 – 7.28 (m, 6H), 4.89 (s, 1H), 2.70 (s, 4H), 1.81 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 131.9, 128.4 (3C), 128.4 (4C), 128.2, 127.7, 123.4, 87.0, 59.3, 50.4 (2C), 29.8, 23.6 (2C). The data is in accordance with the one reported in the literature.[2]

3.0. Copies of ^{1}H and ^{13}C spectra

Figure S 1 ^{1}H NMR spectra of metal complex **3** in $CDCl_3$ (400 MHz)

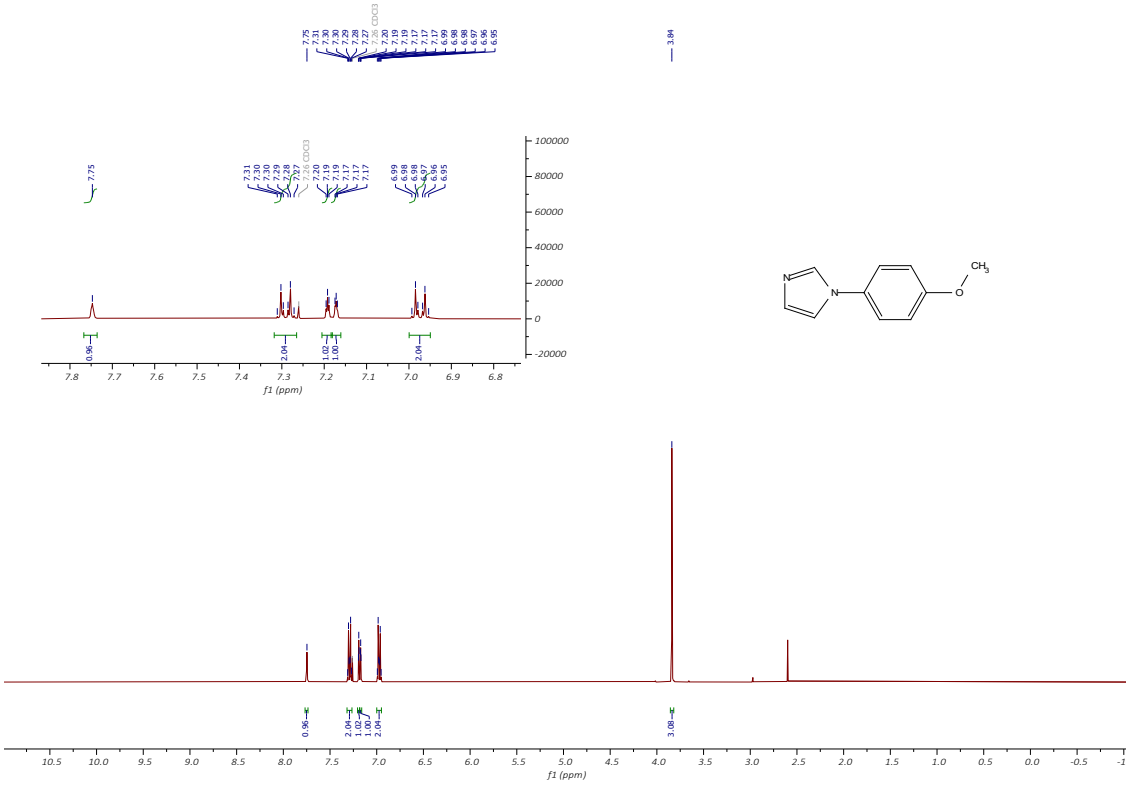


Figure S 2 ^{13}C NMR spectra of compound **3** in $CDCl_3$ (101 MHz)

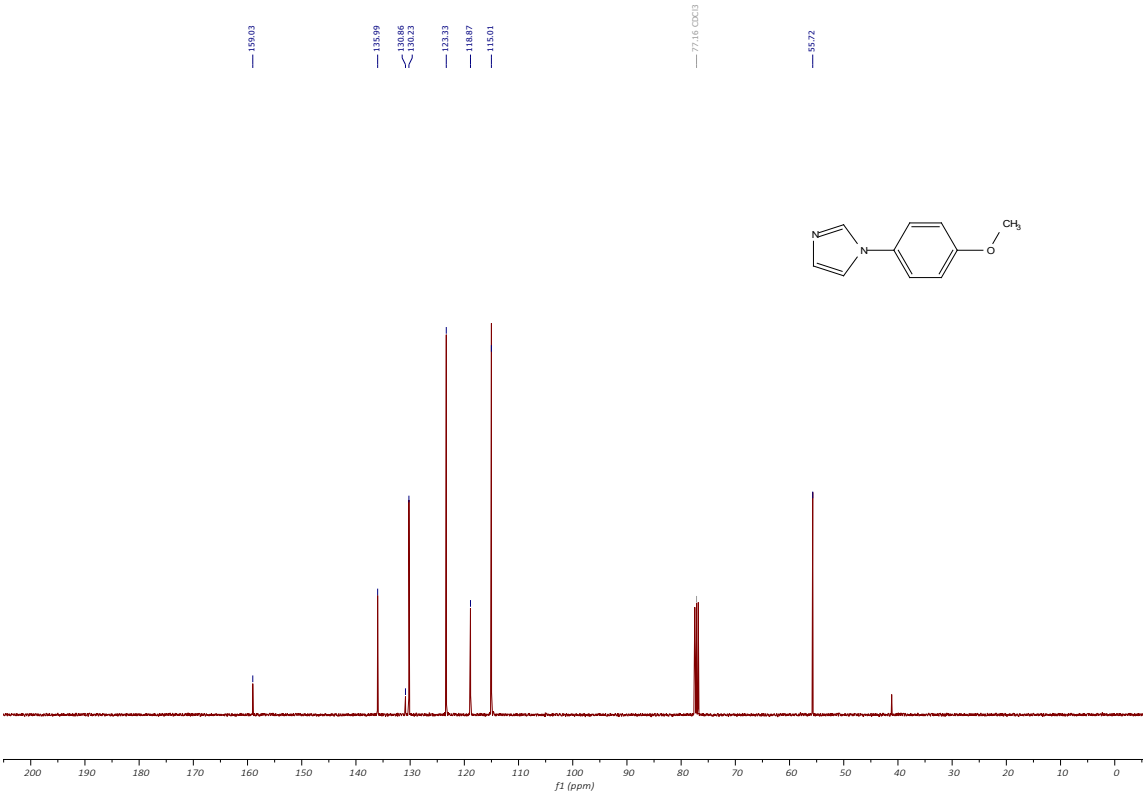


Figure S 3 ^{1}H NMR spectra of ligand **4** in DMSO-d^{6} (400 MHz)

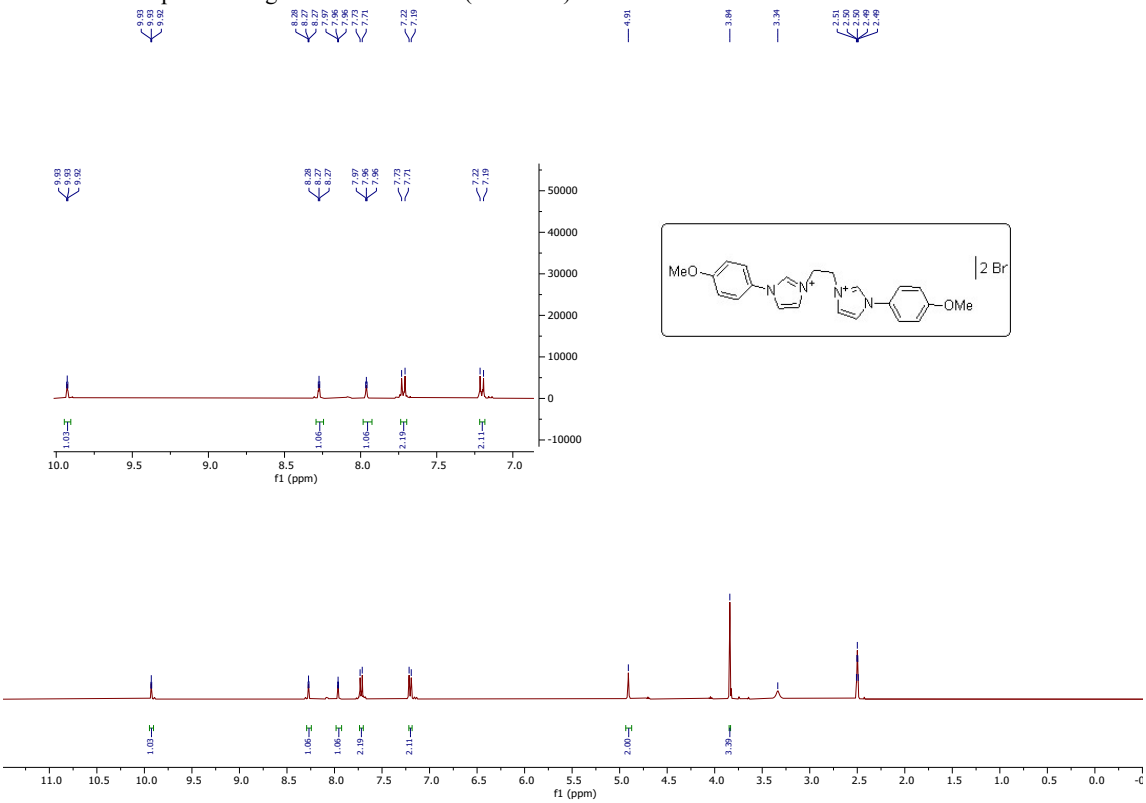


Figure S 4 ^{13}C NMR spectra of ligand **4** in DMSO-d^{6} (101 MHz)

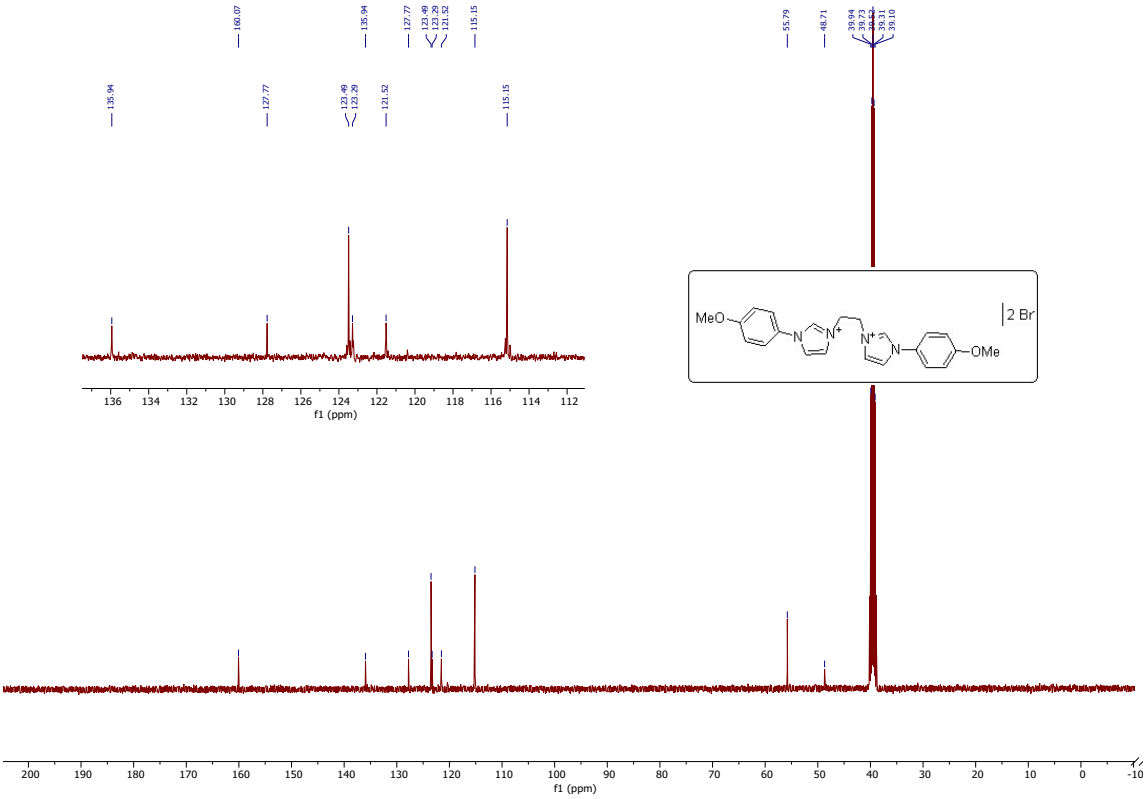


Figure S 5 ^{1}H NMR spectra of silver complex **5** in DMSO-d^{6} (400 MHz)

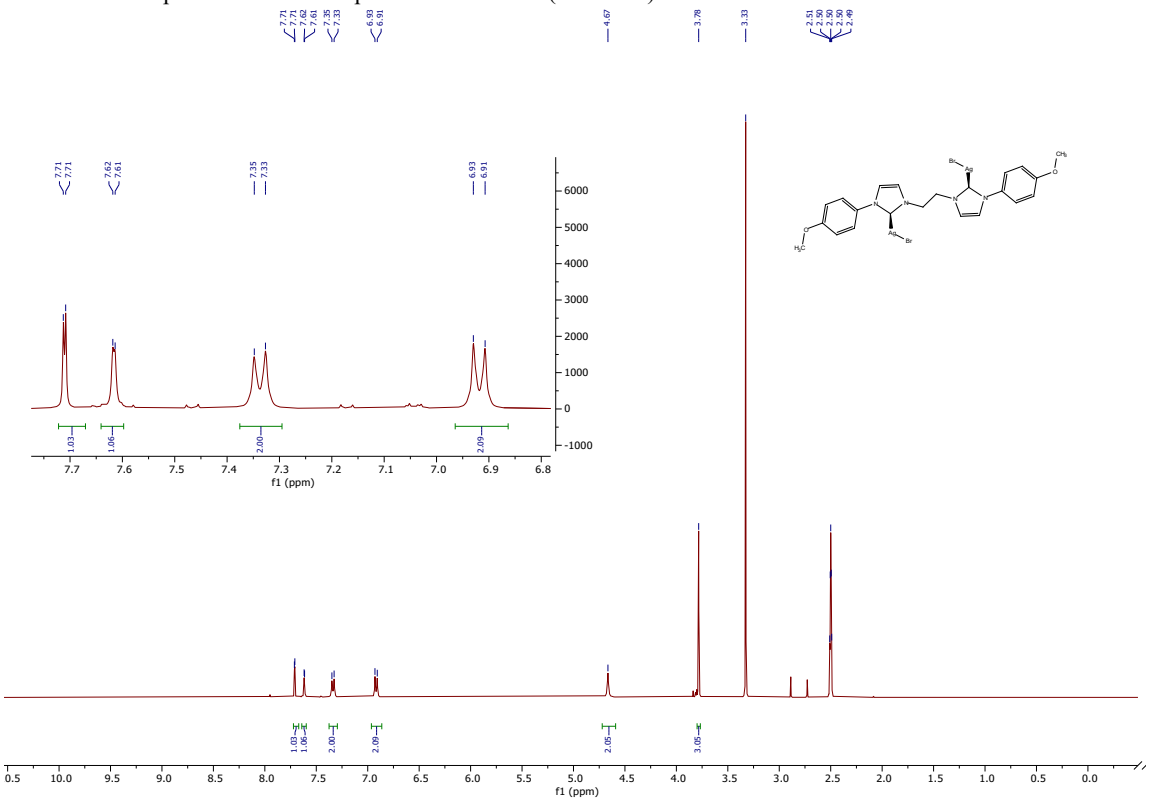


Figure S 6 ^{13}C NMR spectra of ligand **5** in DMSO-d^{6} (101 MHz)

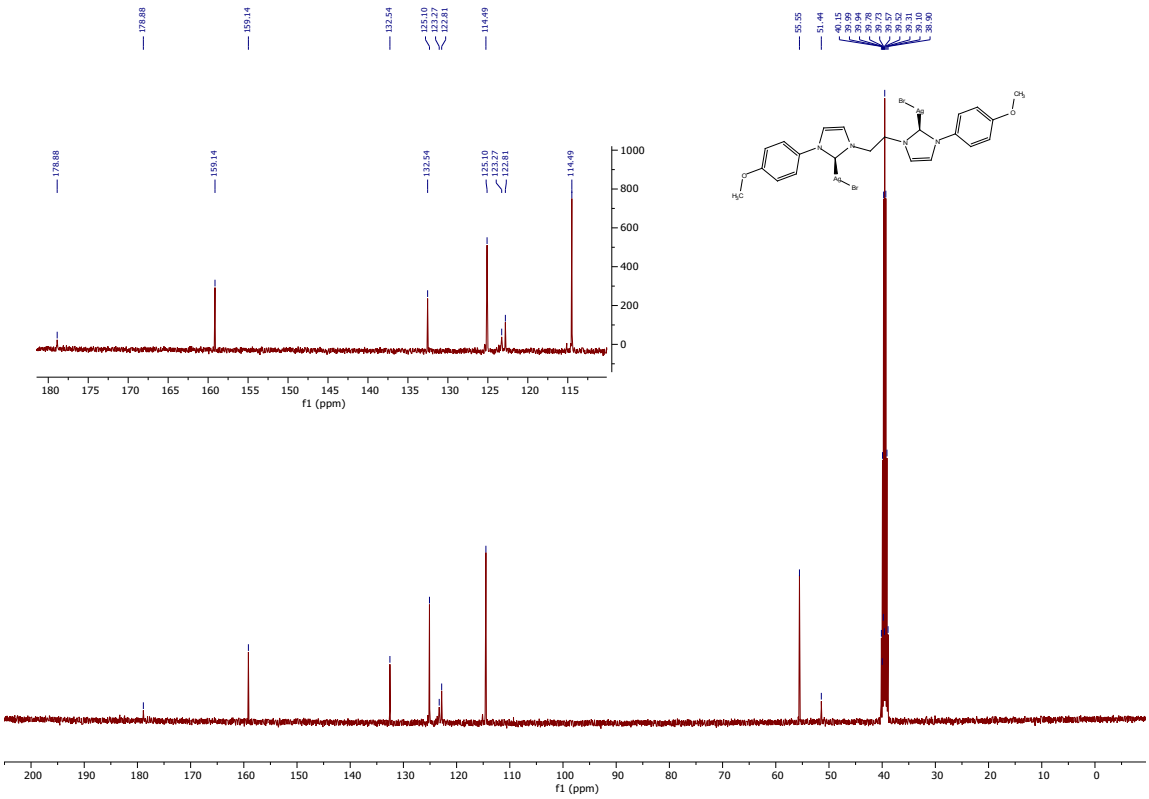


Figure S7 ^{1}H NMR spectra of compound **9a** in $CDCl_3$ (400 MHz)

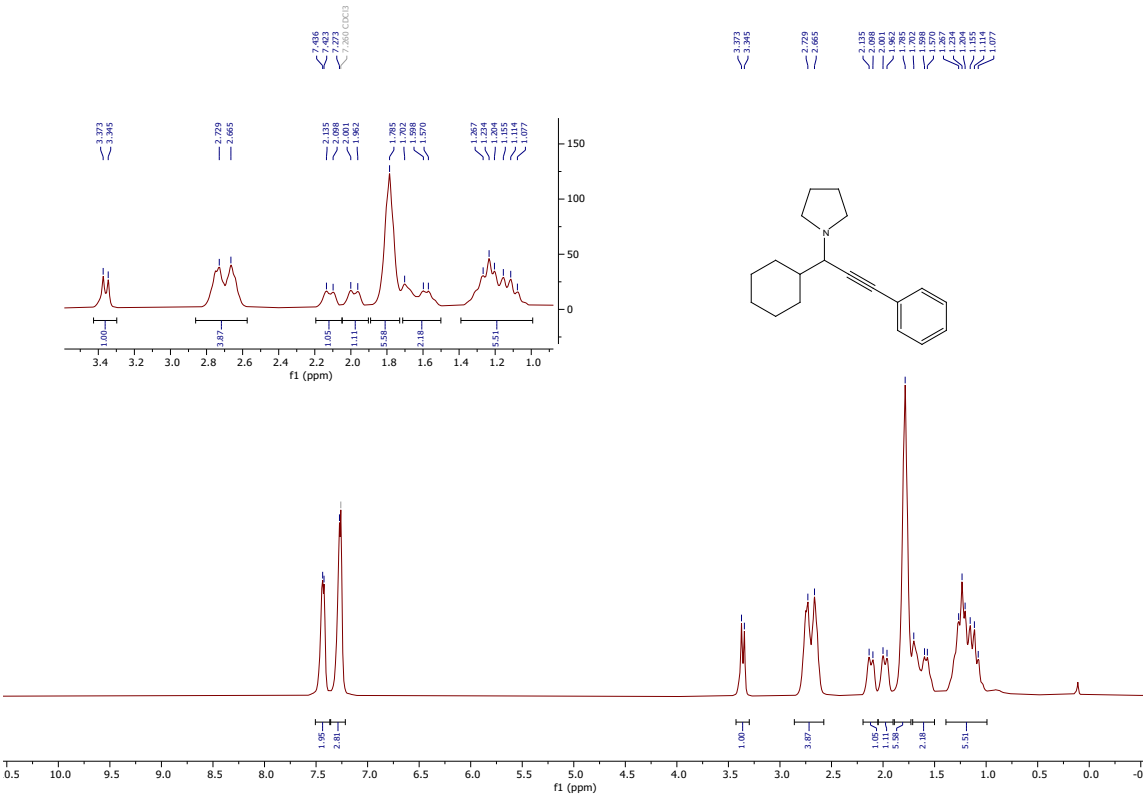


Figure S8 ^{13}C NMR spectra of compound **9a** in $CDCl_3$ (101 MHz)

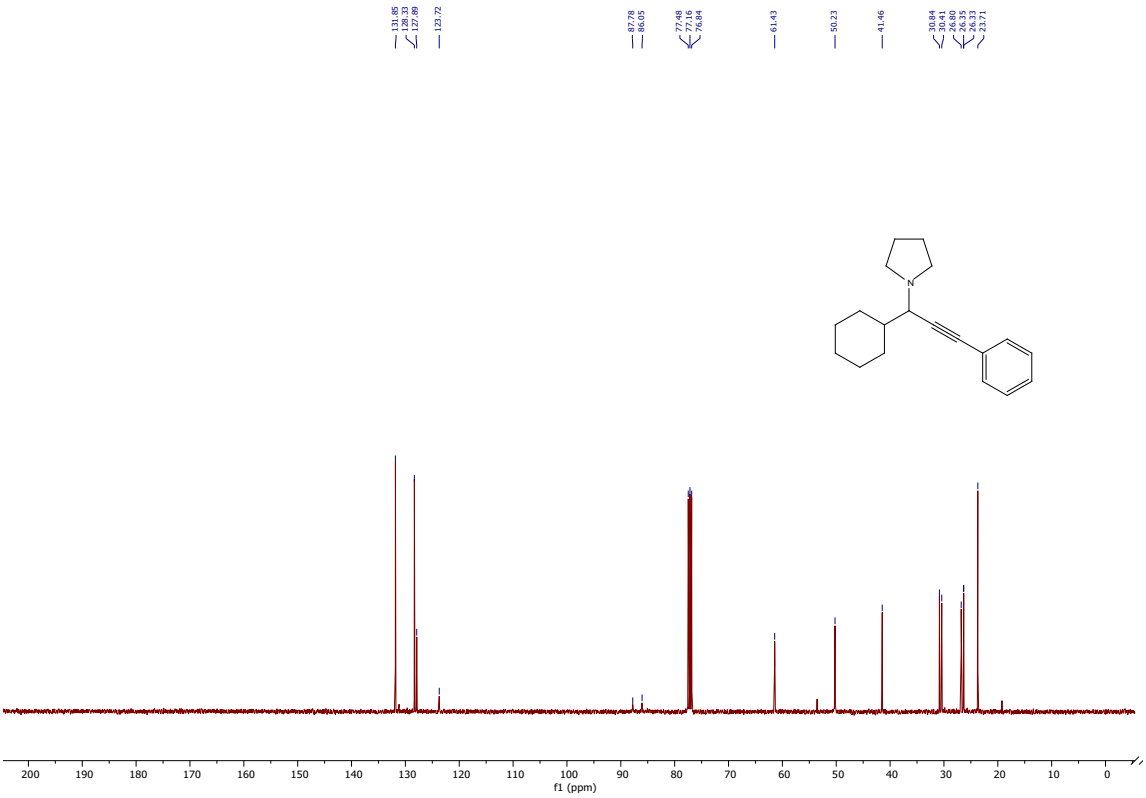


Figure S9 ^{1}H NMR spectra of compound **9b** in $CDCl_3$ (400 MHz)

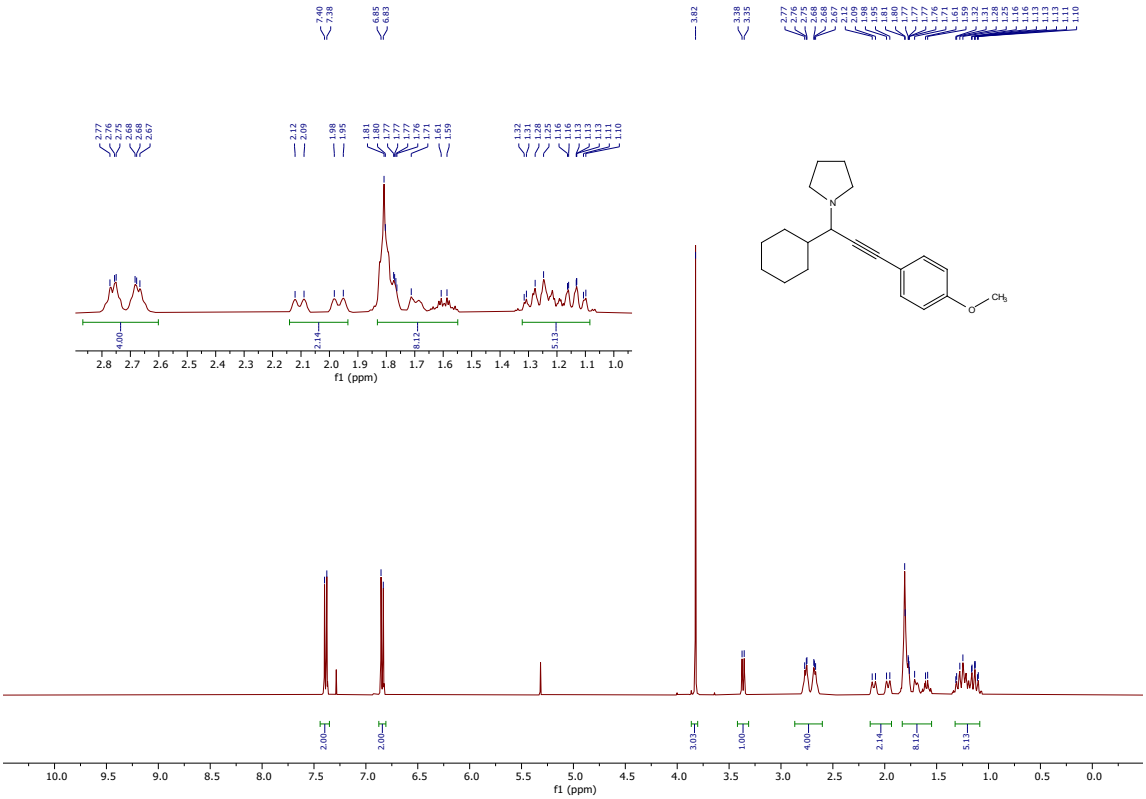


Figure S10 ^{13}C NMR spectra of compound **9b** in $CDCl_3$ (101 MHz)

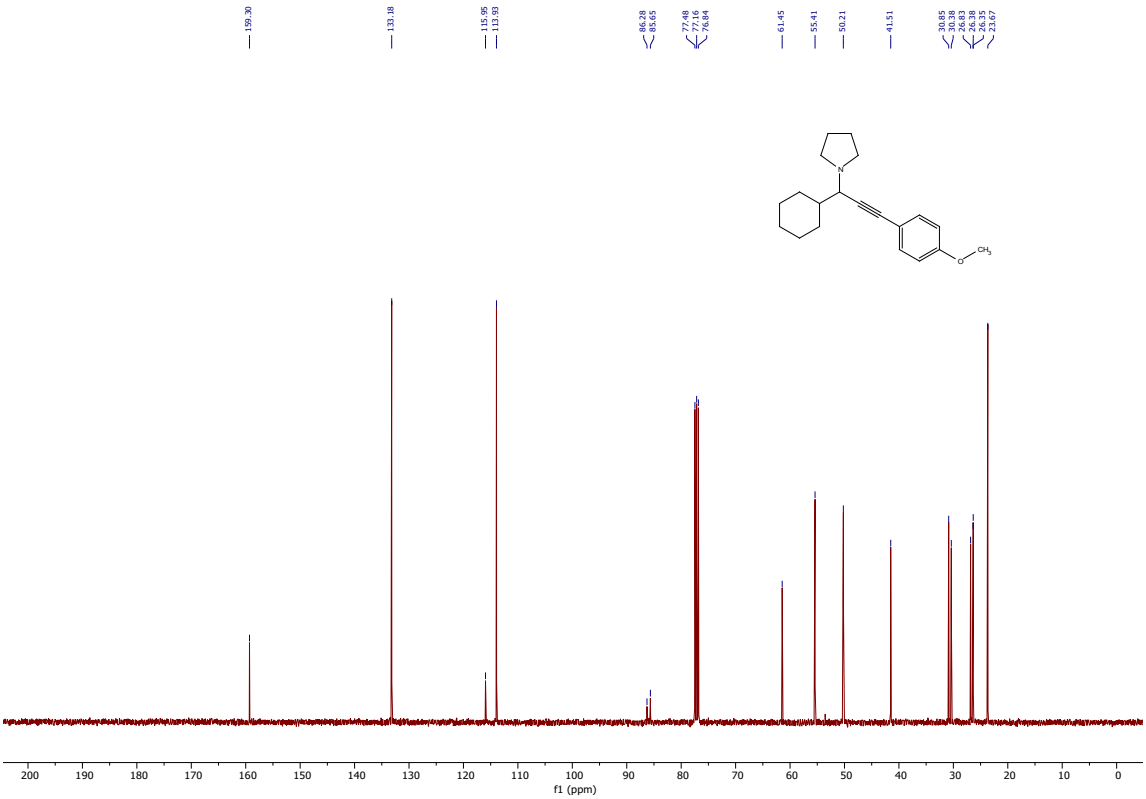


Figure S11 ^{1}H NMR spectra of compound **9c** in $CDCl_3$ (400 MHz)

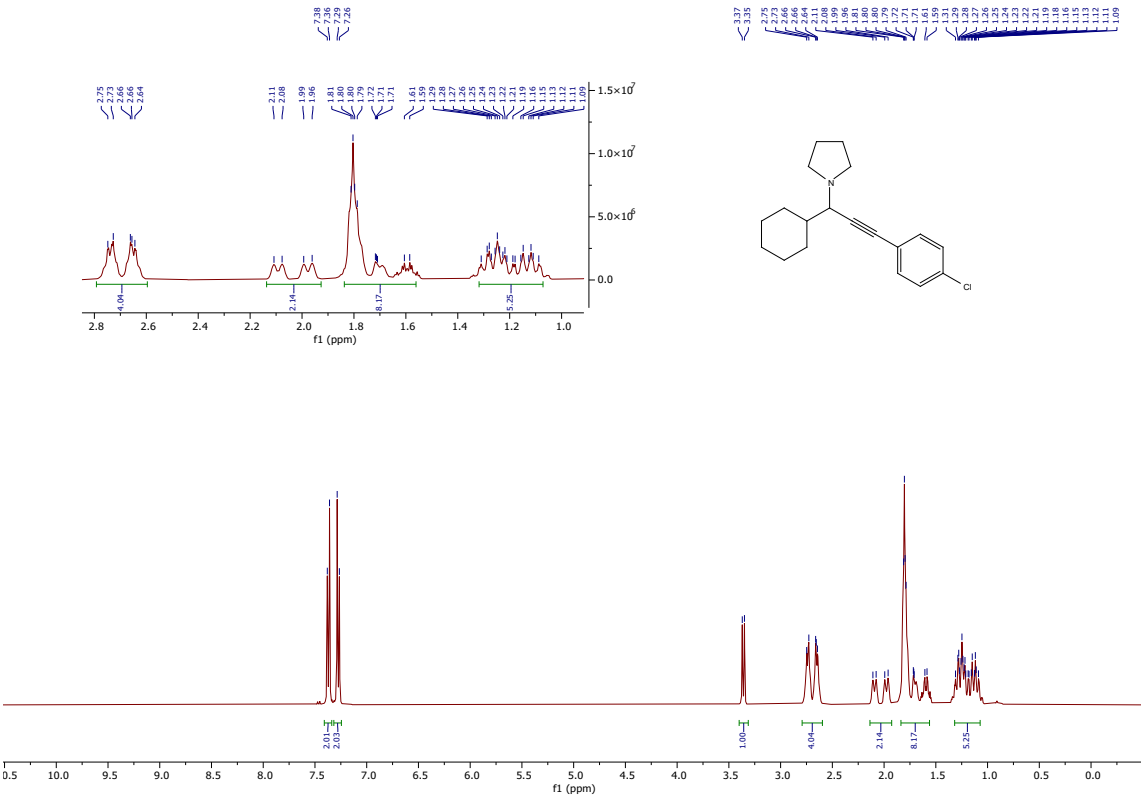


Figure S12 ^{13}C NMR spectra of compound **9c** in $CDCl_3$ (101 MHz)

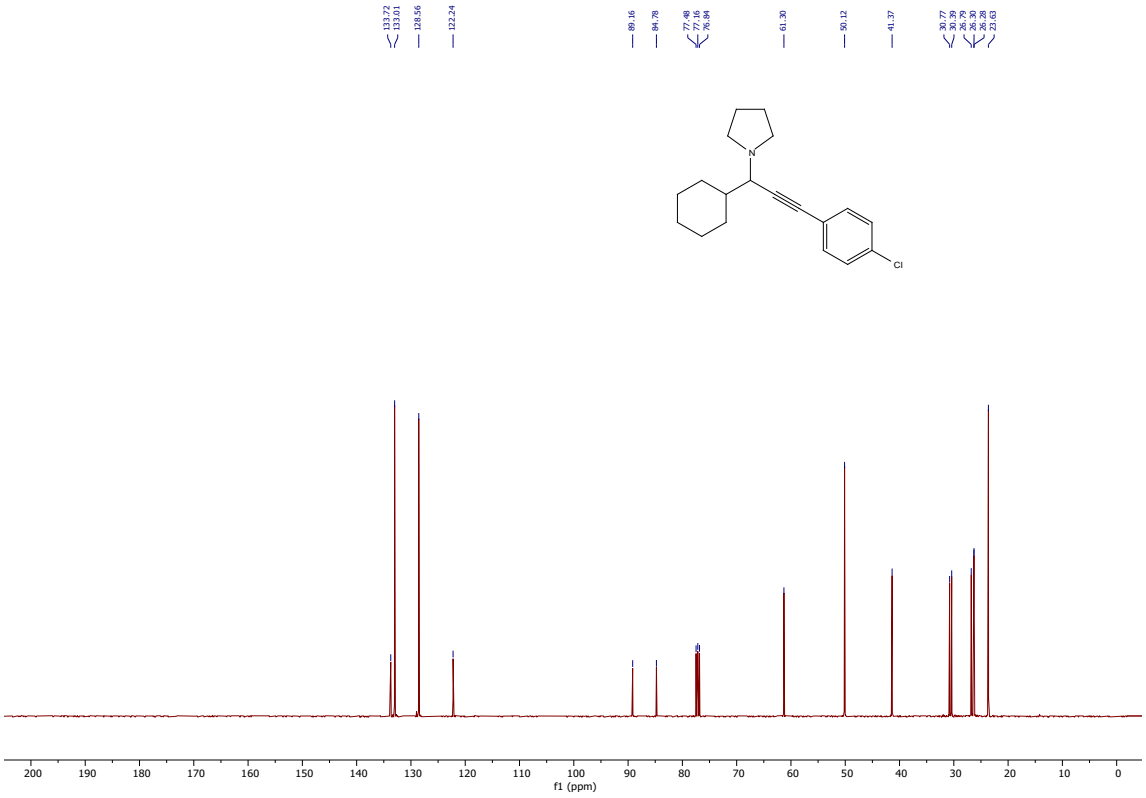


Figure S13 ^{1}H NMR spectra of compound **9d** in $CDCl_3$ (400 MHz)

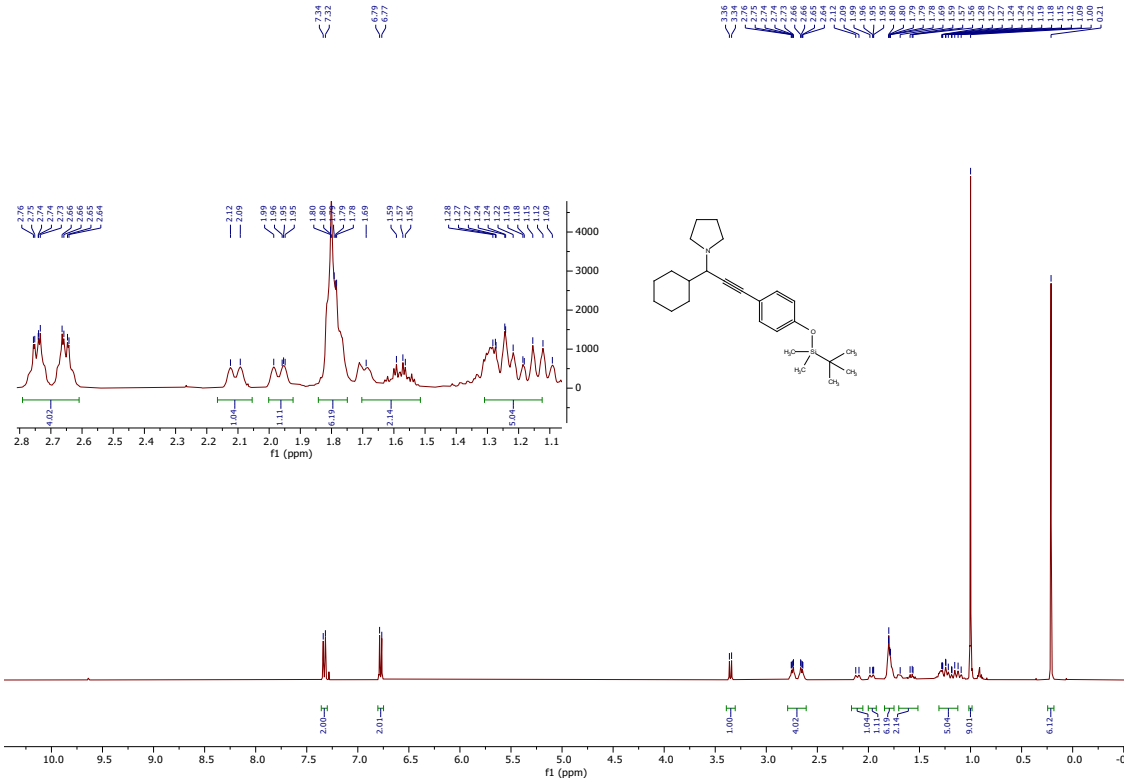


Figure S14 ^{13}C NMR spectra of compound **9d** in $CDCl_3$ (101 MHz)

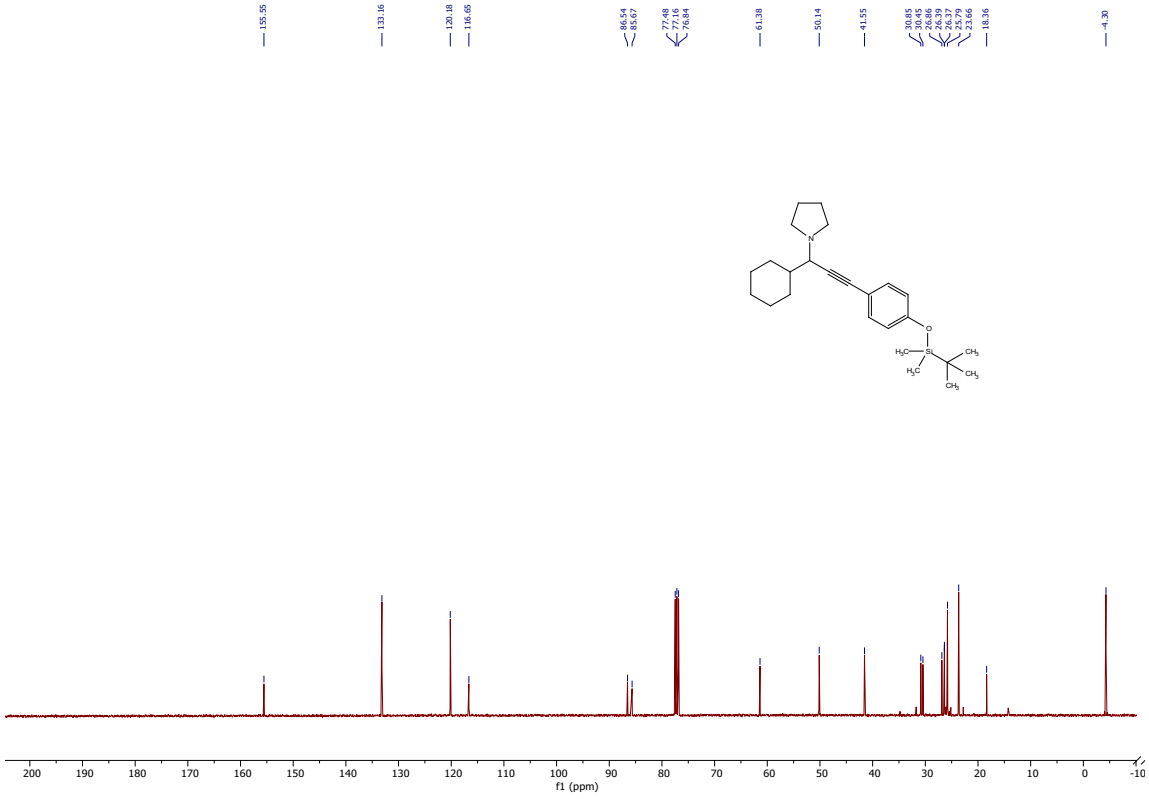


Figure S15 ^{1}H NMR spectra of compound **9e** in $CDCl_3$ (400 MHz)

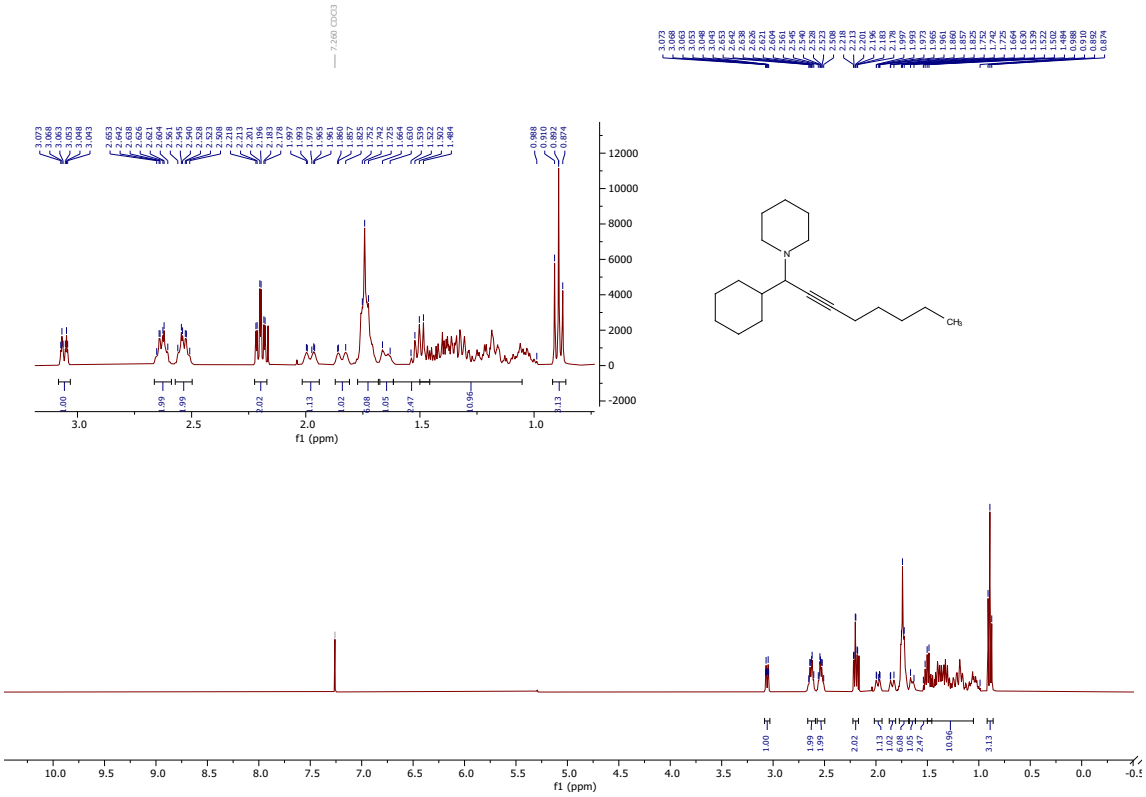


Figure S16 ^{13}C NMR spectra of compound **9e** in $CDCl_3$ (101 MHz)

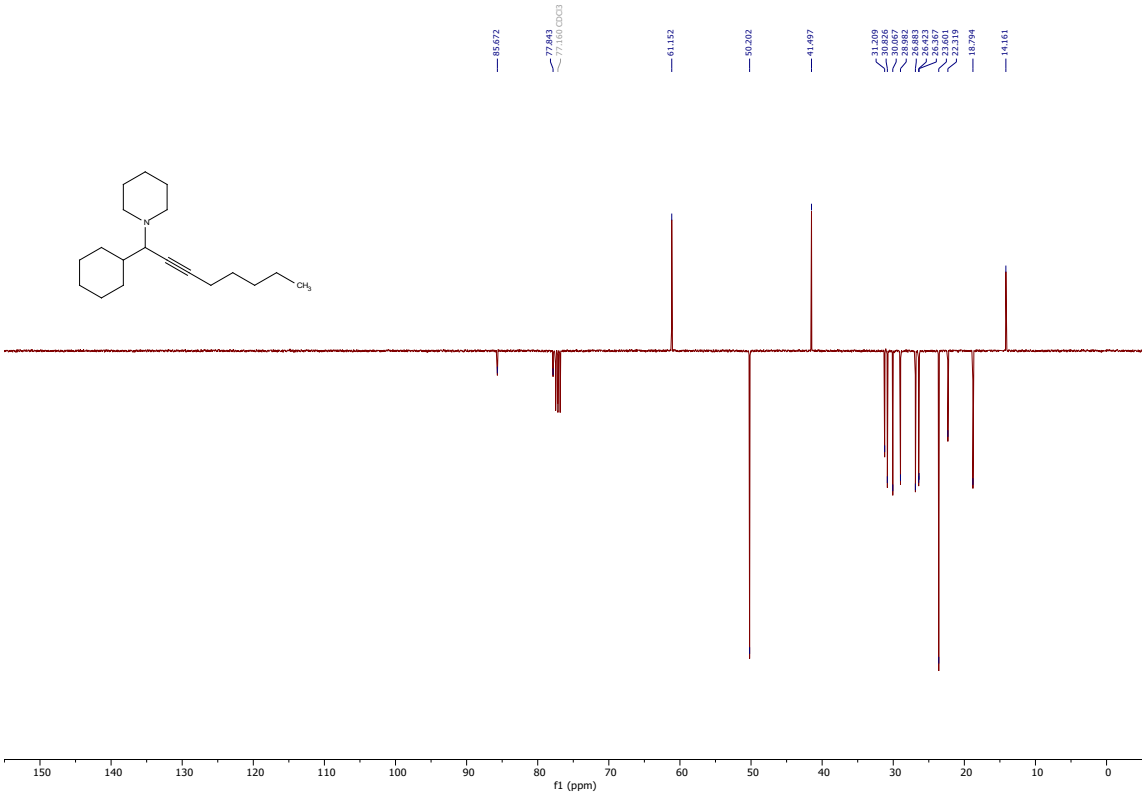


Figure S17 ^{1}H NMR spectra of compound **9f** in $CDCl_3$ (400 MHz)

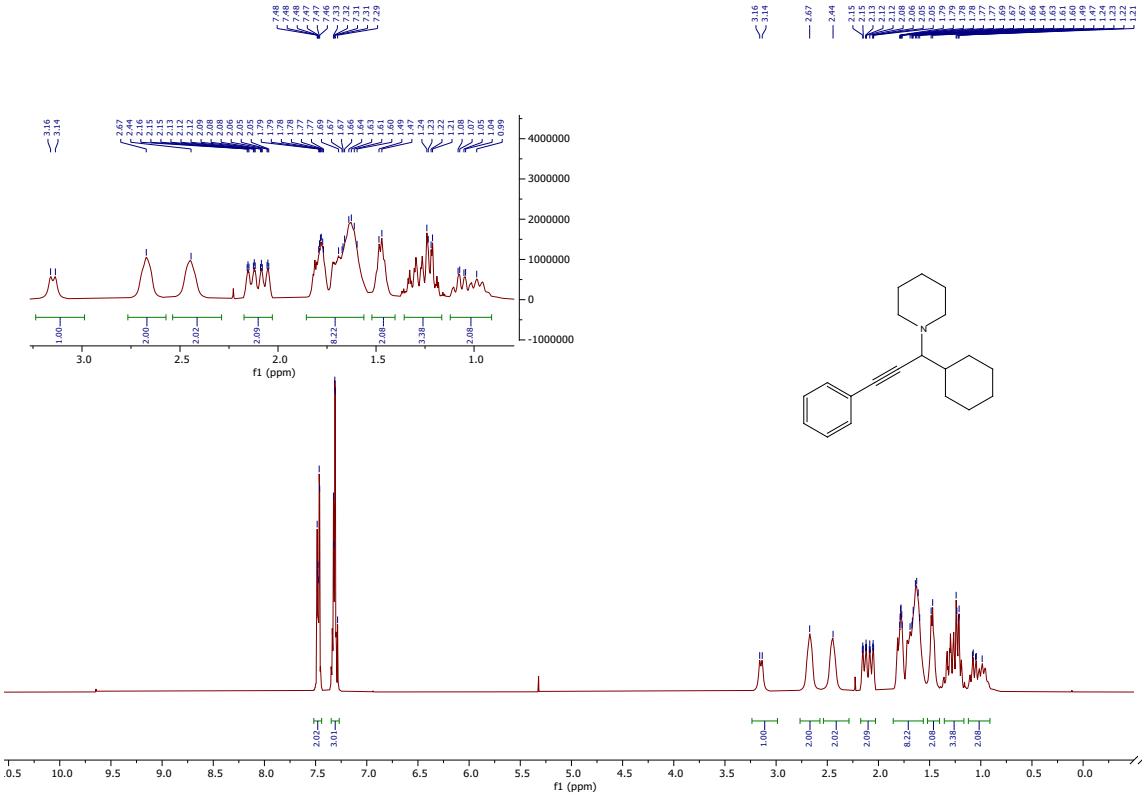


Figure S18 ^{13}C NMR spectra of compound **9f** in $CDCl_3$ (101 MHz)

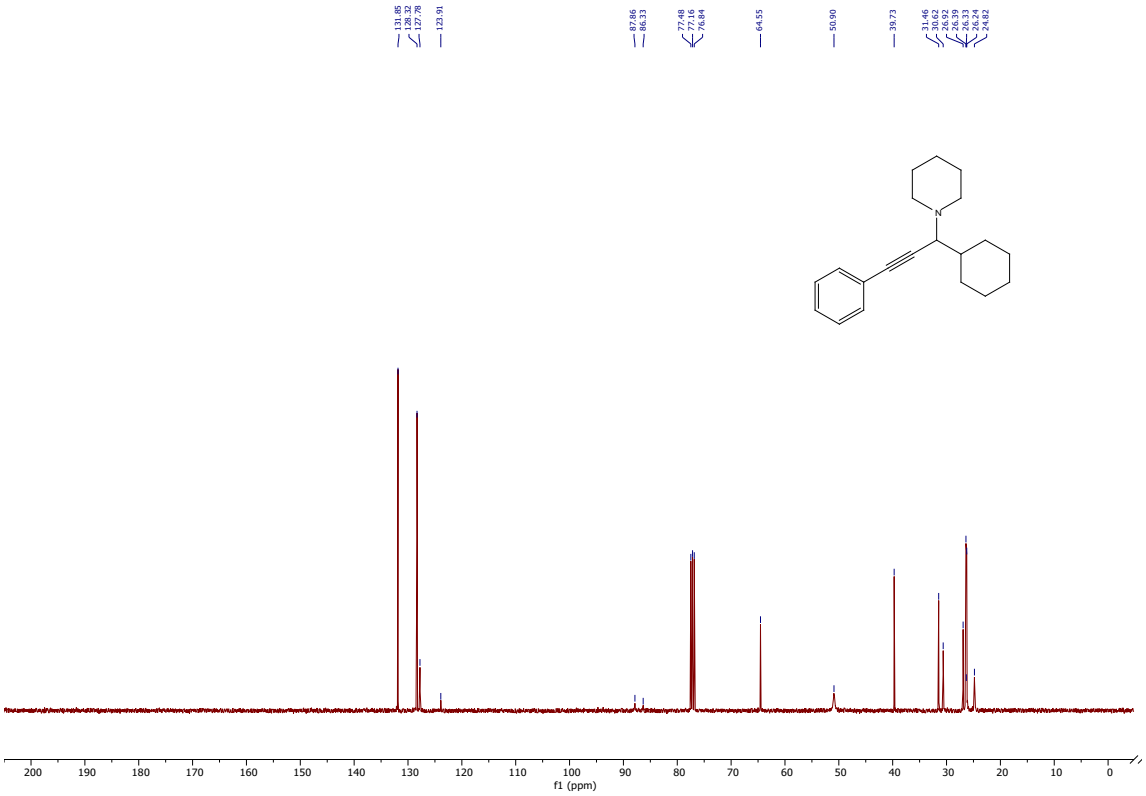


Figure S19 ^{1}H NMR spectra of compound **9g** in $CDCl_3$ (400 MHz)

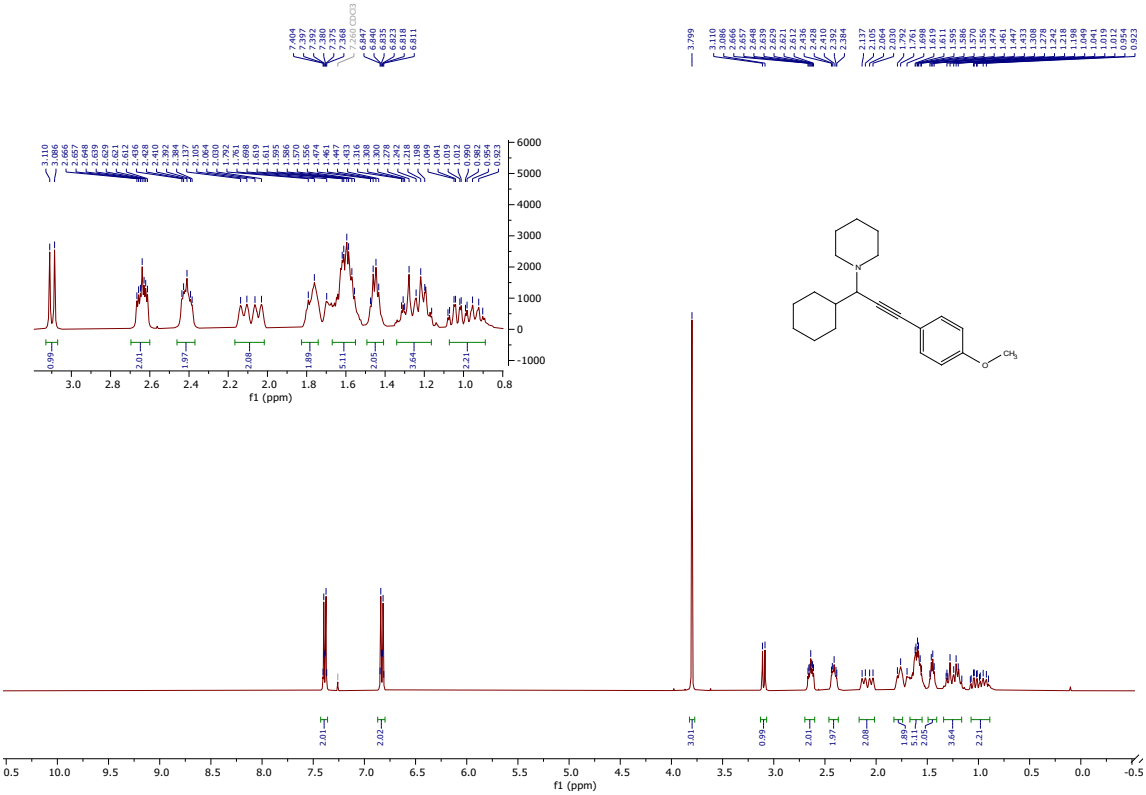


Figure S20 ^{13}C NMR spectra of compound **9g** in $CDCl_3$ (101 MHz)

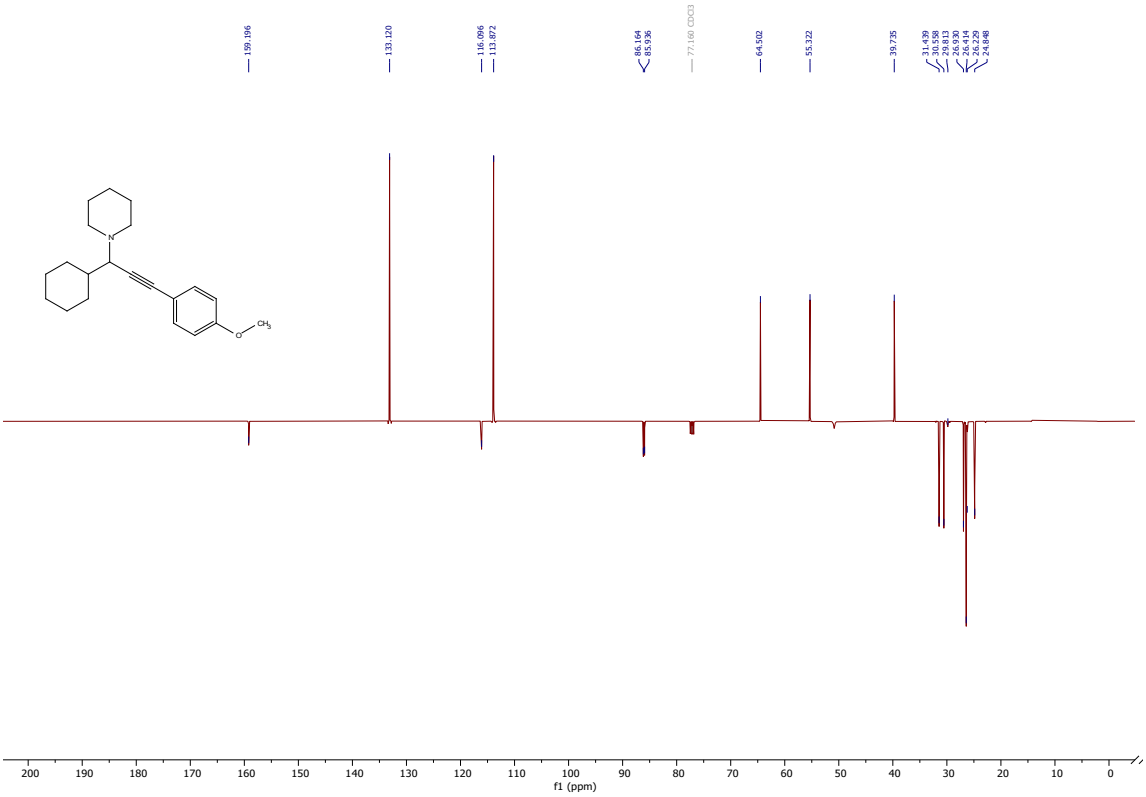


Figure S21 ^{1}H NMR spectra of compound **9h** in $CDCl_3$ (400 MHz)

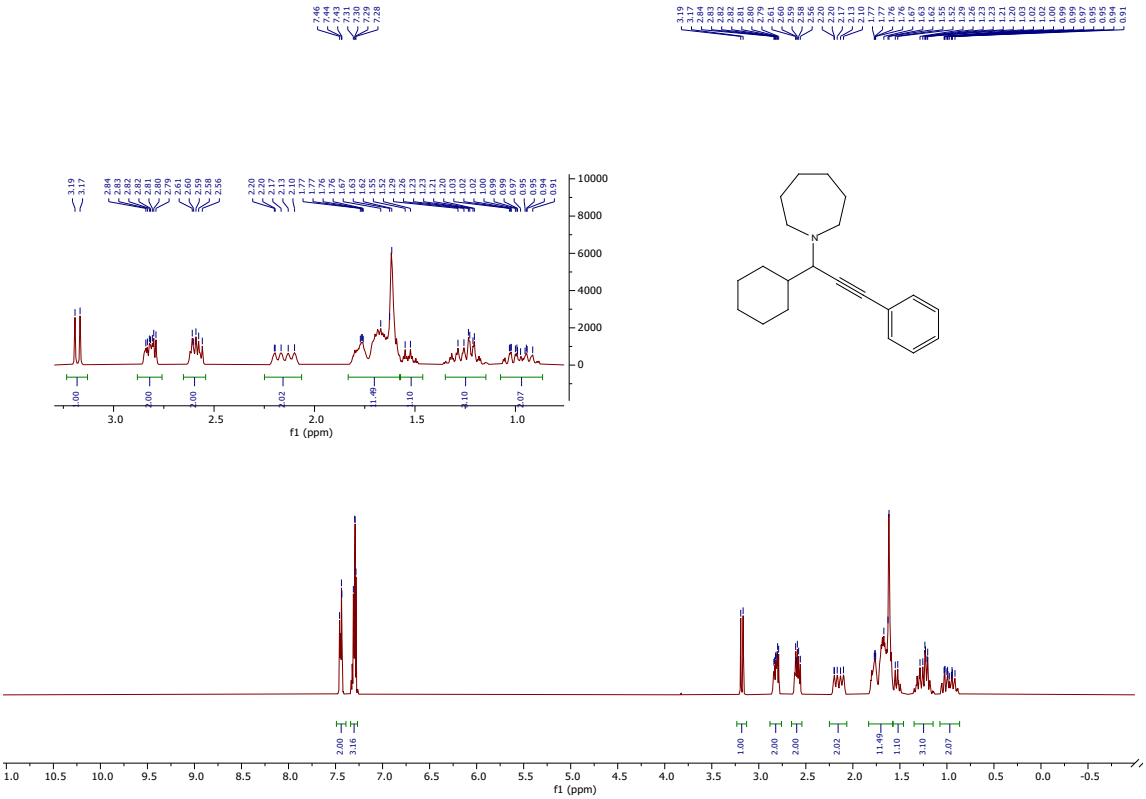


Figure S22 ^{13}C NMR spectra of compound **9h** in $CDCl_3$ (101 MHz)

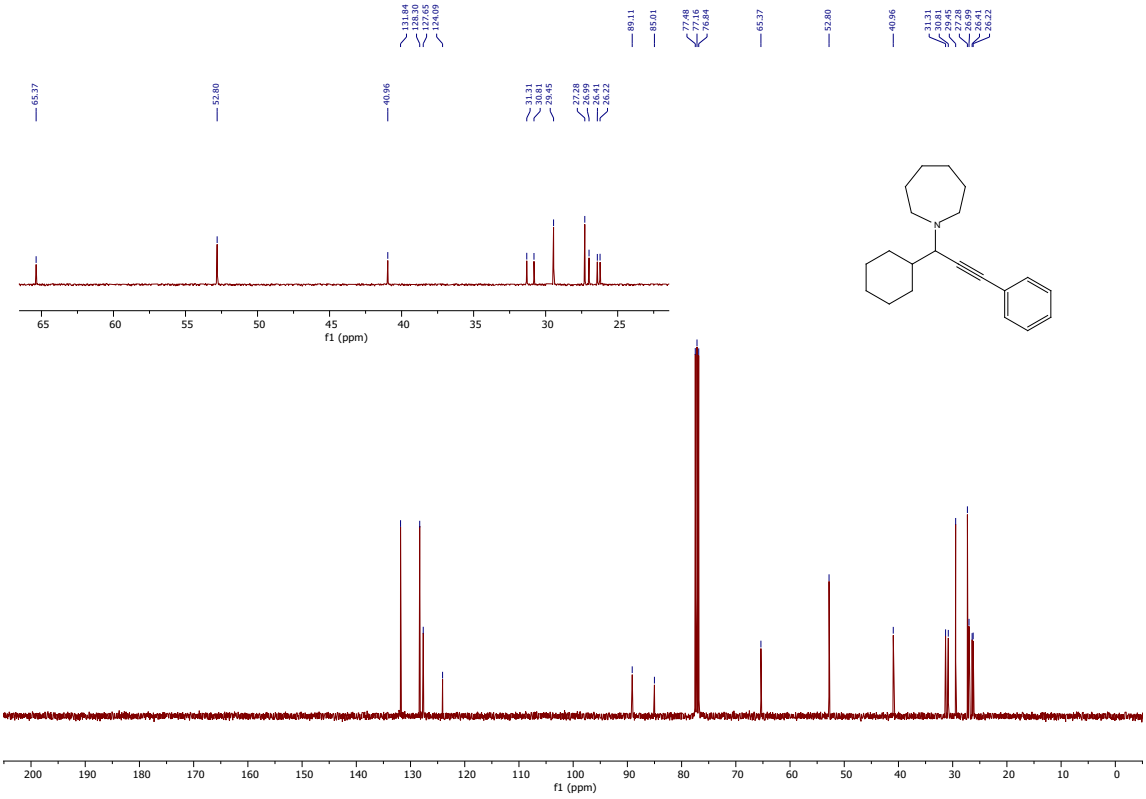


Figure S23 ^{1}H NMR spectra of compound **9i** in $CDCl_3$ (400 MHz)

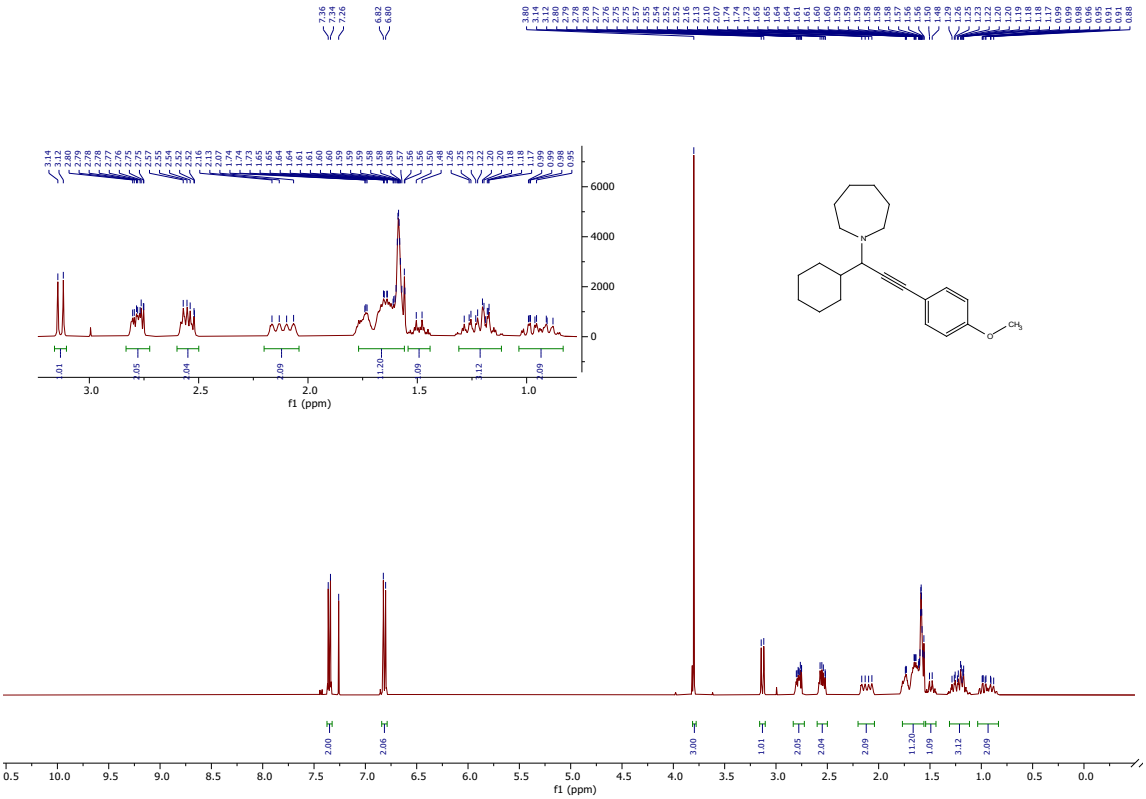


Figure S24 ^{13}C NMR spectra of compound **9i** in $CDCl_3$ (101 MHz)

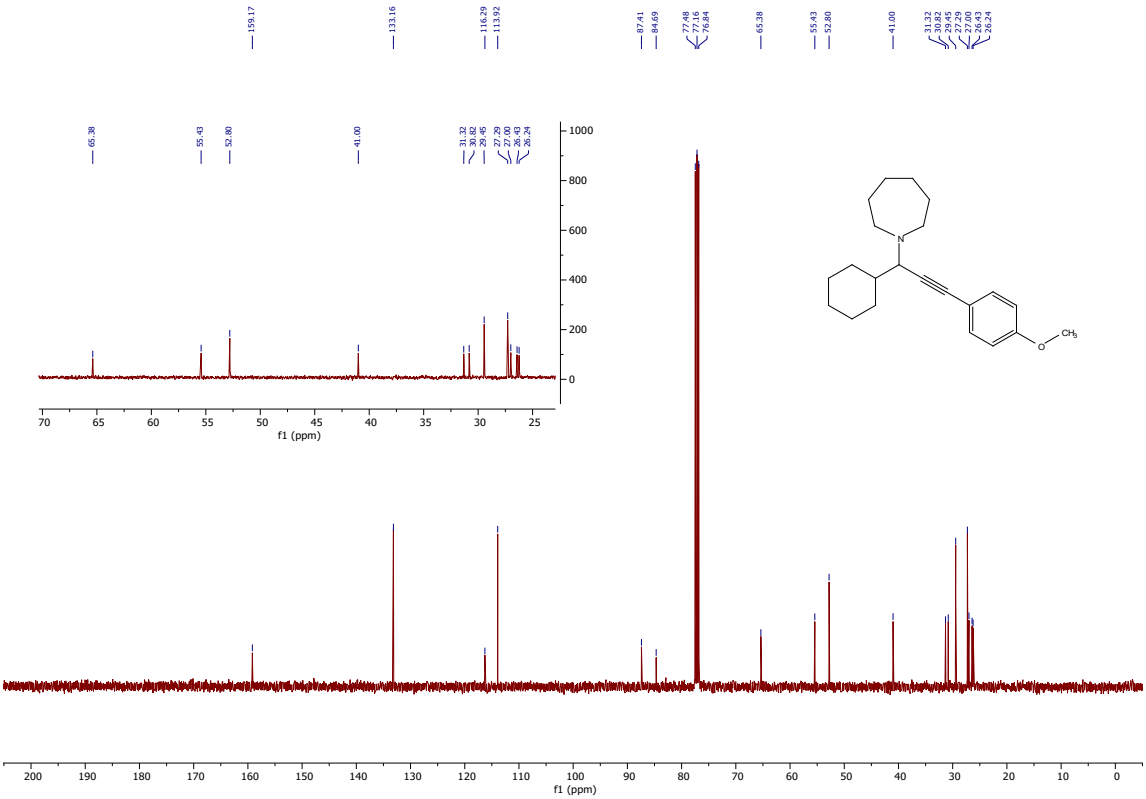


Figure S25 ^{1}H NMR spectra of compound **9j** in $CDCl_3$ (400 MHz)

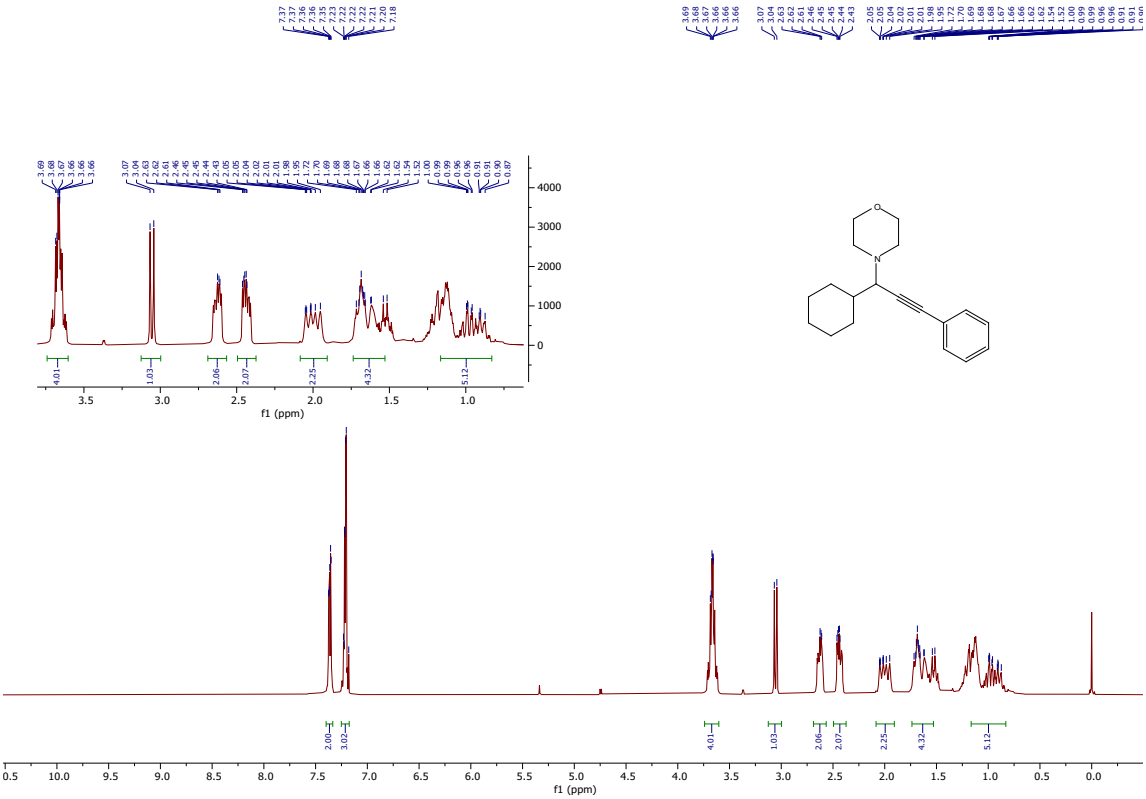


Figure S26 ^{13}C NMR spectra of compound **9j** in $CDCl_3$ (101 MHz)

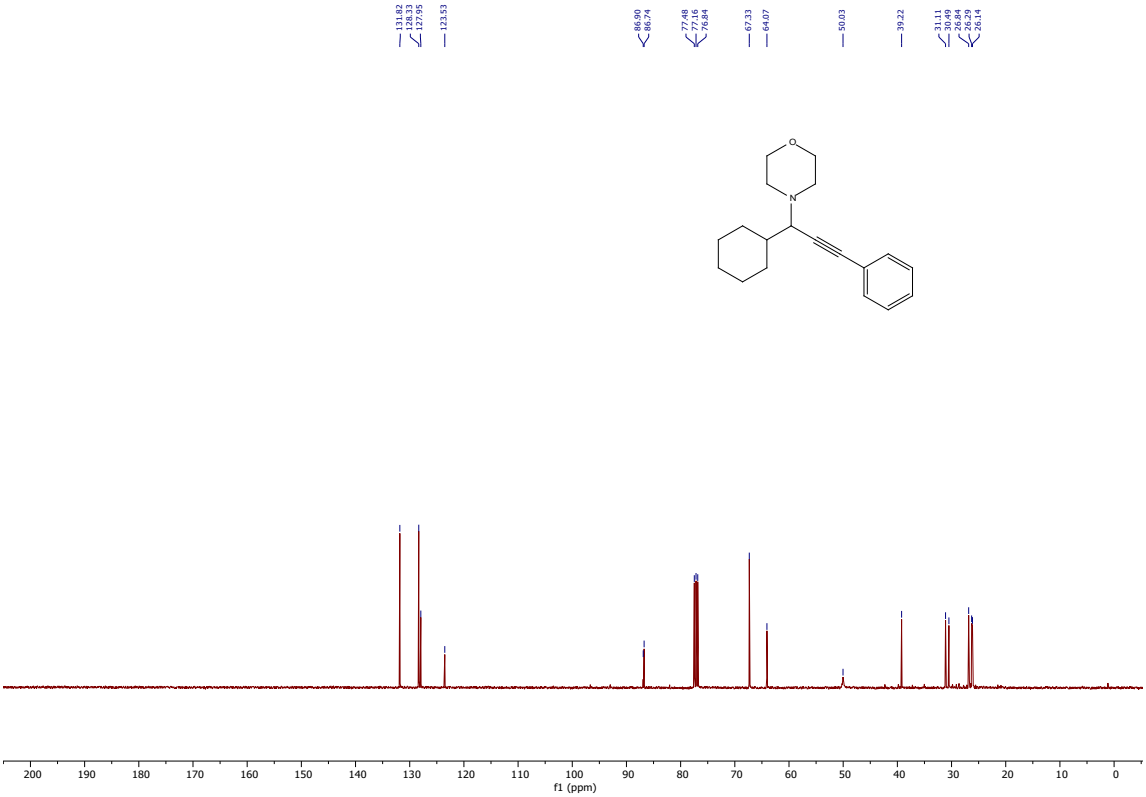


Figure S27 ^{1}H NMR spectra of compound **9k** in $CDCl_3$ (400 MHz)

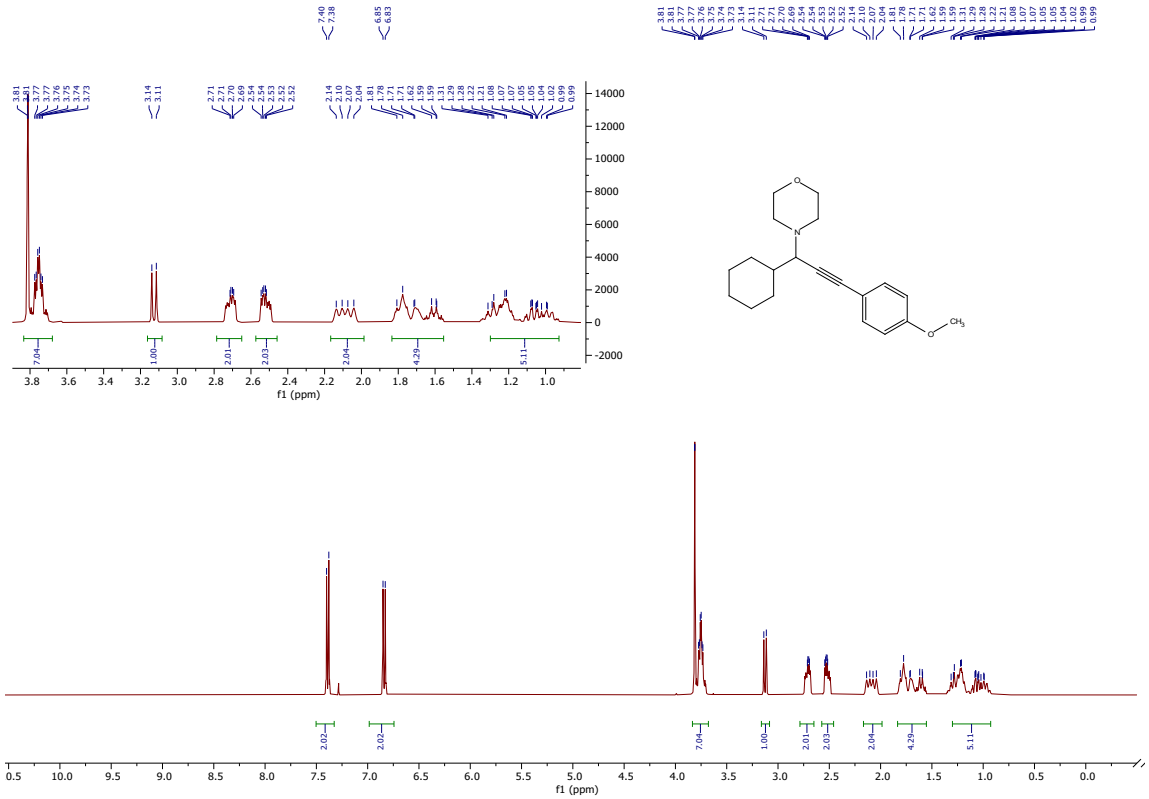


Figure S28 ^{13}C NMR spectra of compound **9k** in $CDCl_3$ (101 MHz)

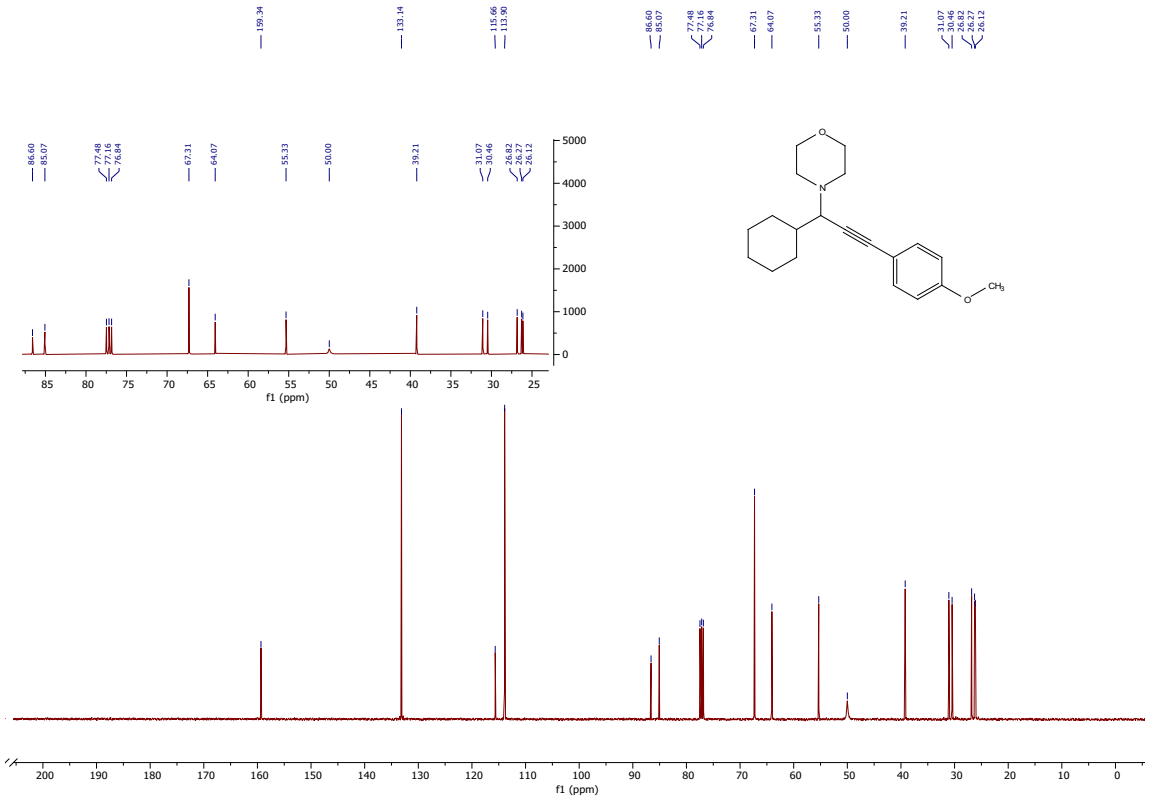


Figure **S29** 1H NMR spectra of compound **9l** in $CDCl_3$ (400 MHz)

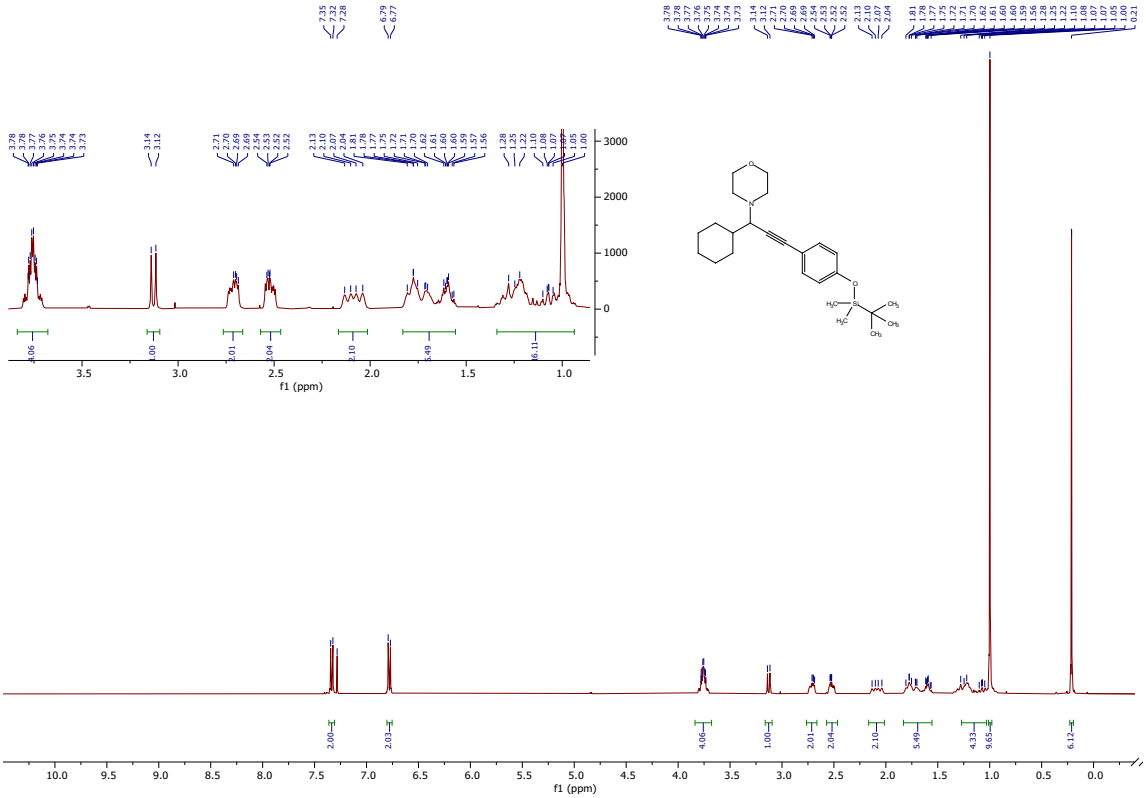


Figure S30 ^{13}C NMR spectra of compound **9l** in $CDCl_3$ (101 MHz)

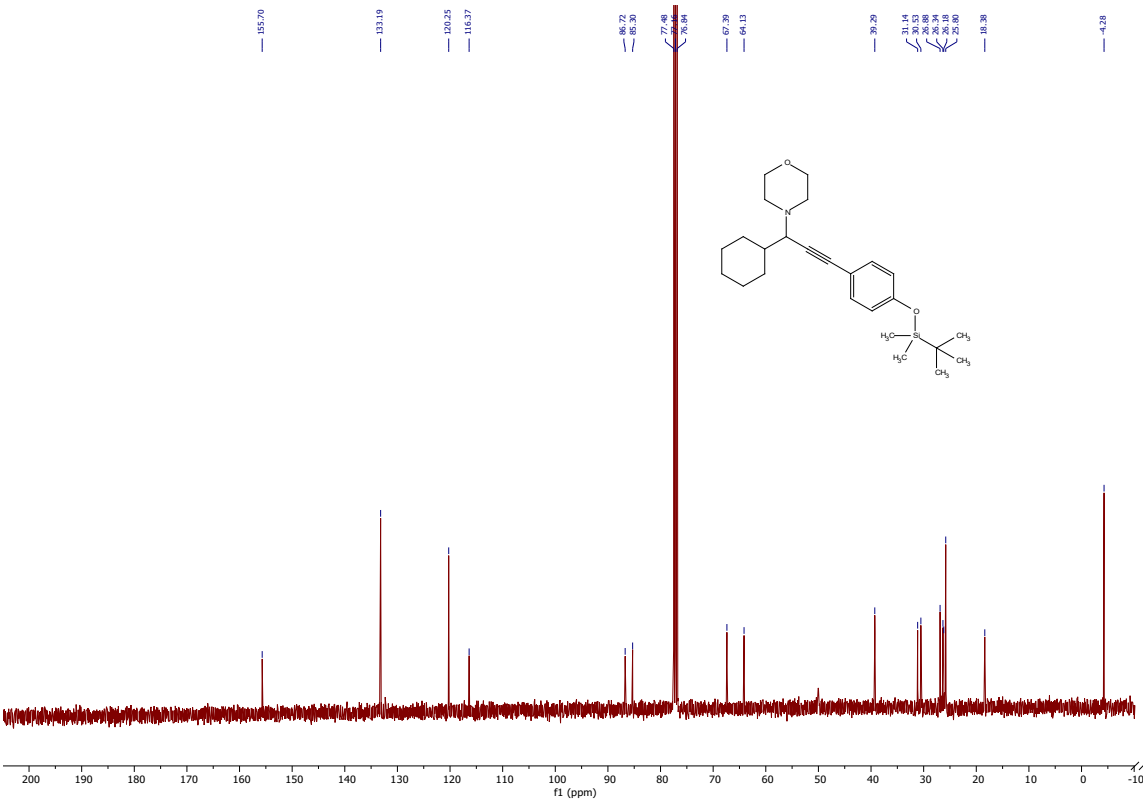


Figure S31 ^{1}H NMR spectra of compound **9m** in $CDCl_3$ (400 MHz)

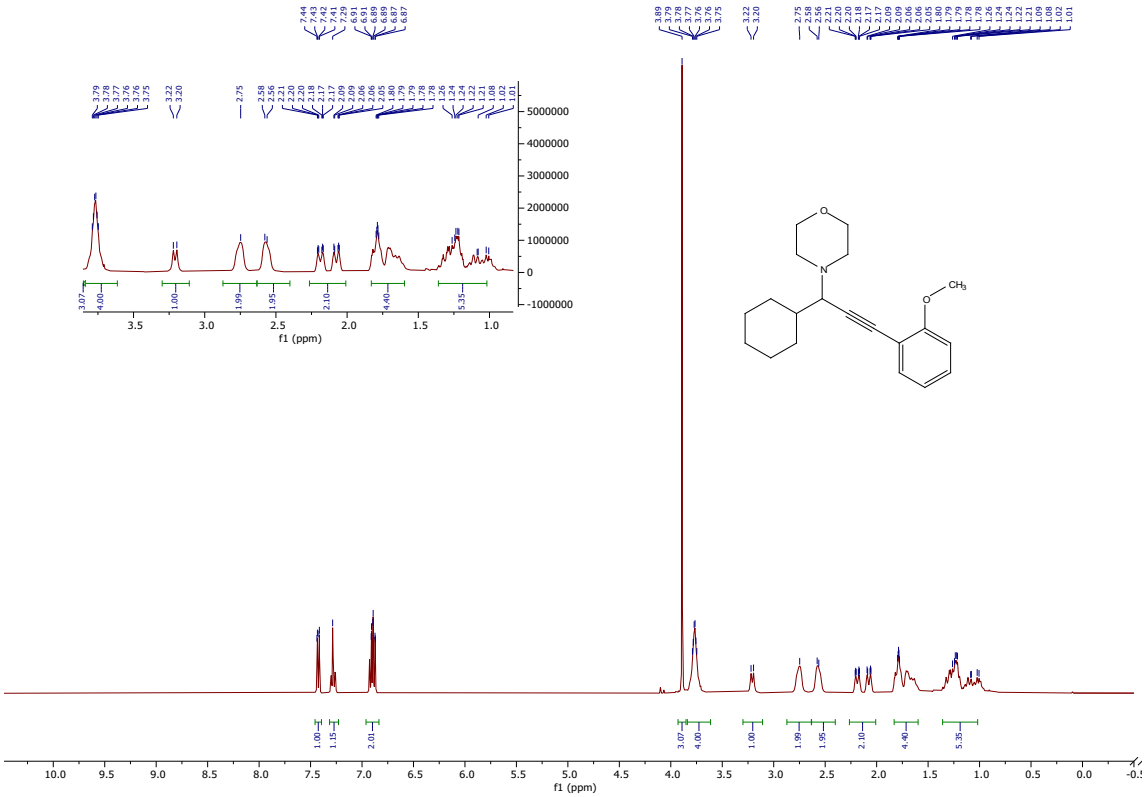


Figure S32 ^{13}C NMR spectra of compound **9m** in $CDCl_3$ (101 MHz)

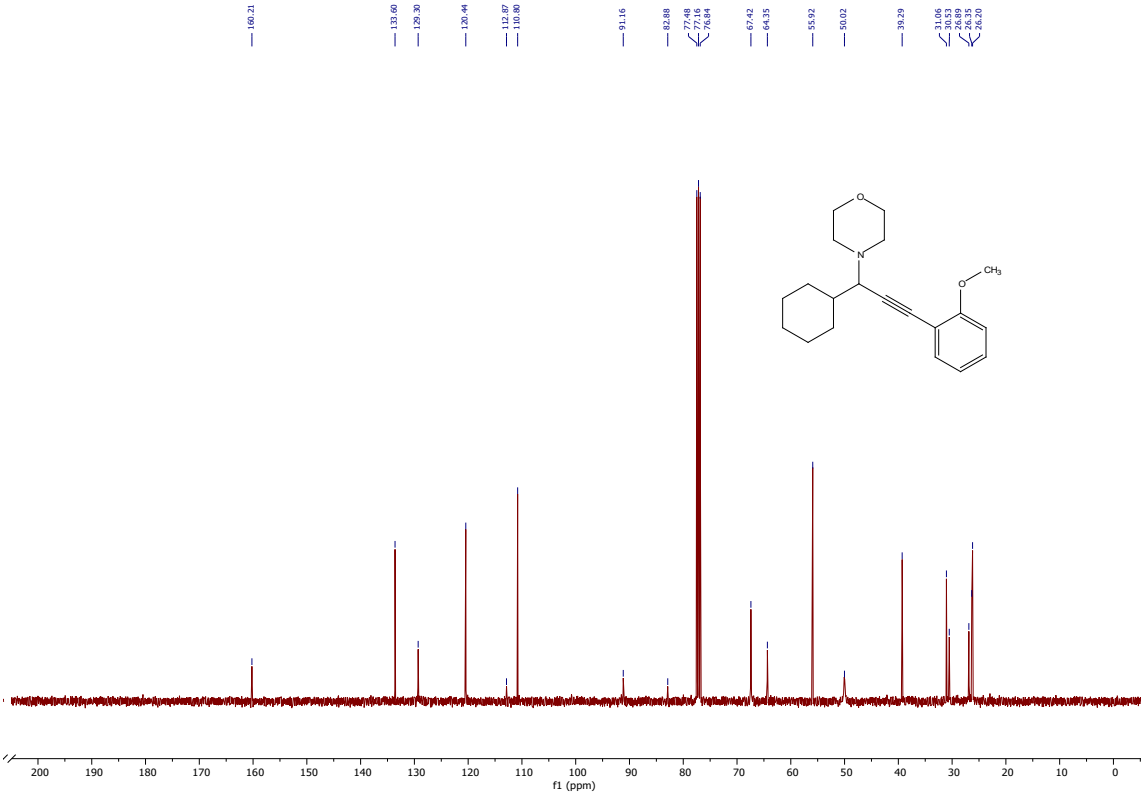


Figure S33 ^{1}H NMR spectra of compound **9n** in $CDCl_3$ (400 MHz)

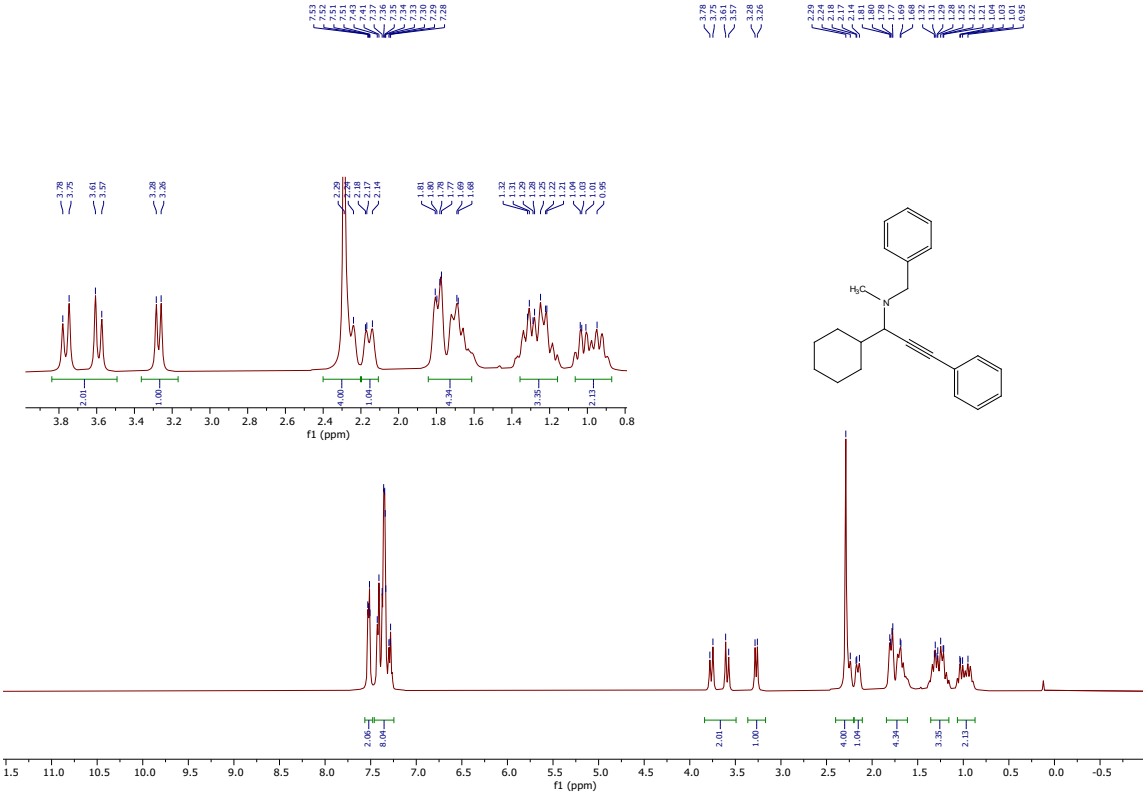


Figure S34 ^{13}C NMR spectra of compound **9n** in $CDCl_3$ (101 MHz)

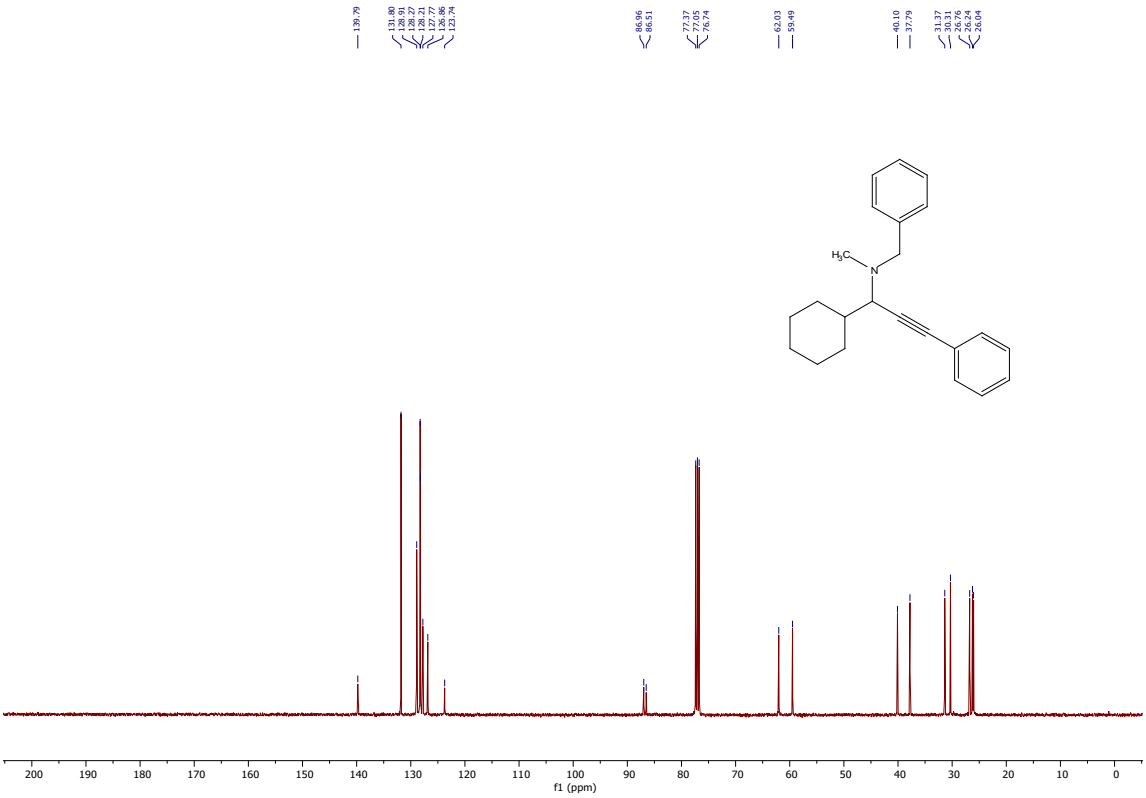


Figure S35 ^{1}H NMR spectra of compound **9o** in $CDCl_3$ (400 MHz)

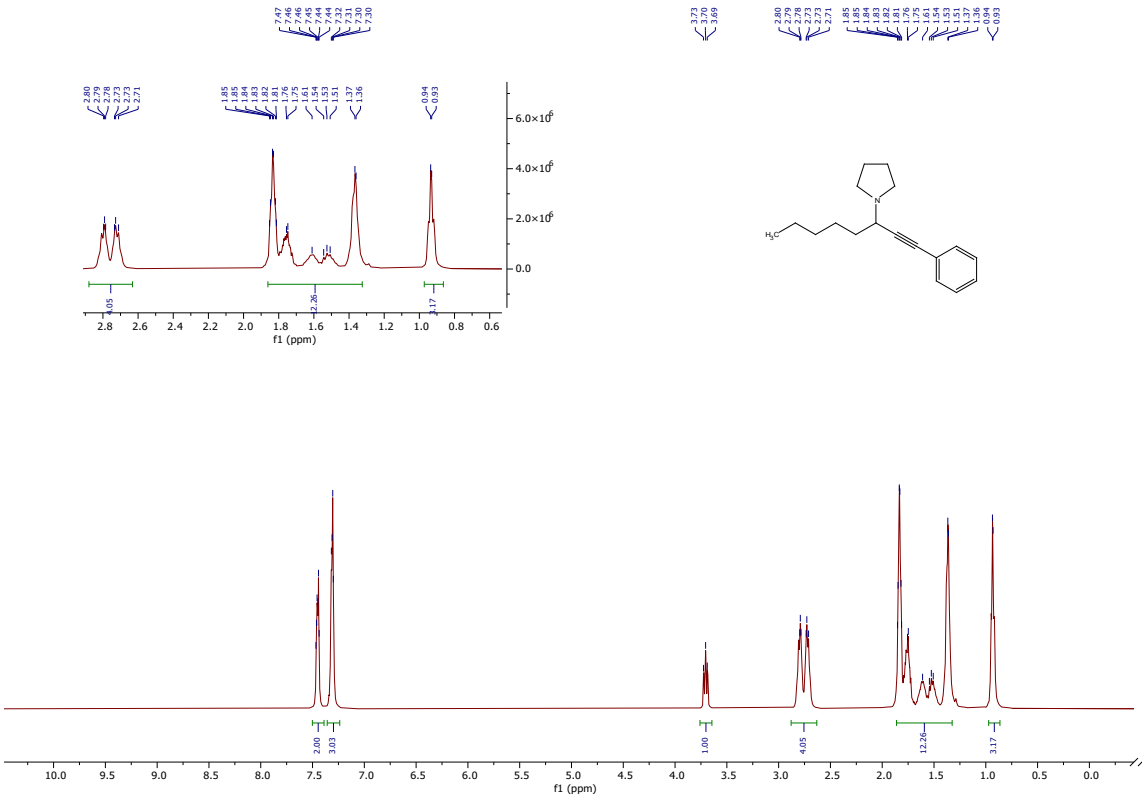


Figure S36 ^{13}C NMR spectra of compound **9o** in $CDCl_3$ (101 MHz)

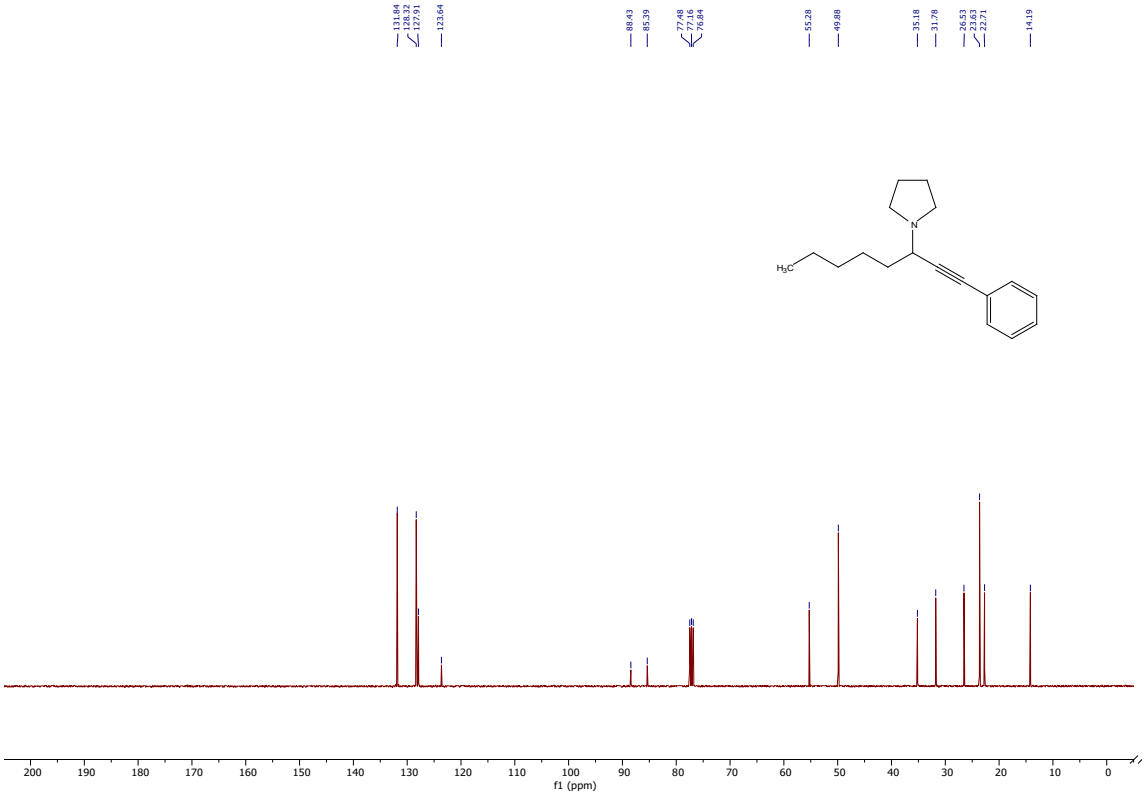


Figure S37 1H NMR spectra of compound **9p** in $CDCl_3$ (400 MHz)

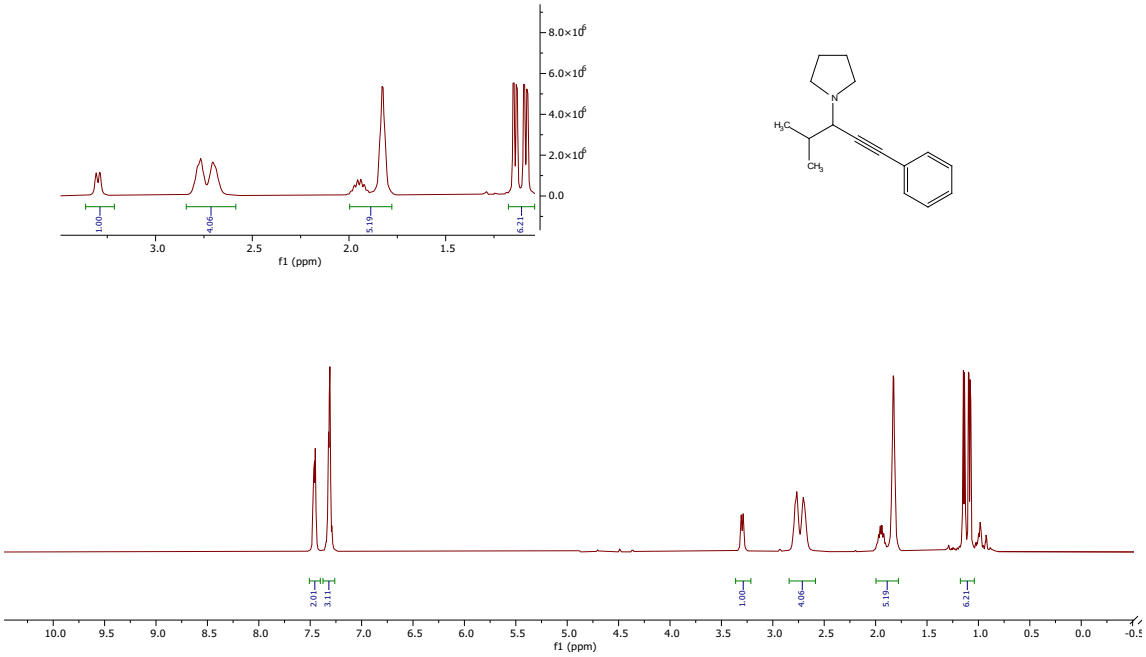


Figure S38 ^{13}C NMR spectra of compound **9p** in $CDCl_3$ (101 MHz)

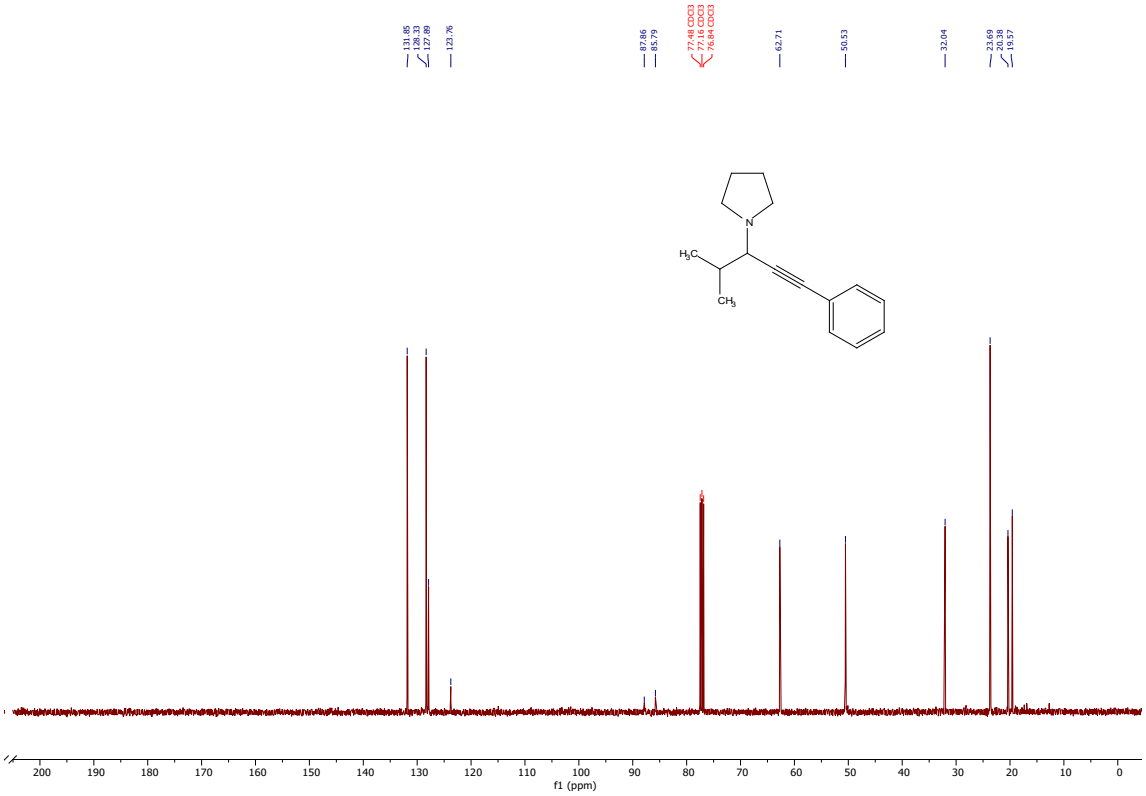


Figure S39 1H NMR spectra of compound **9q** in $CDCl_3$ (400 MHz)

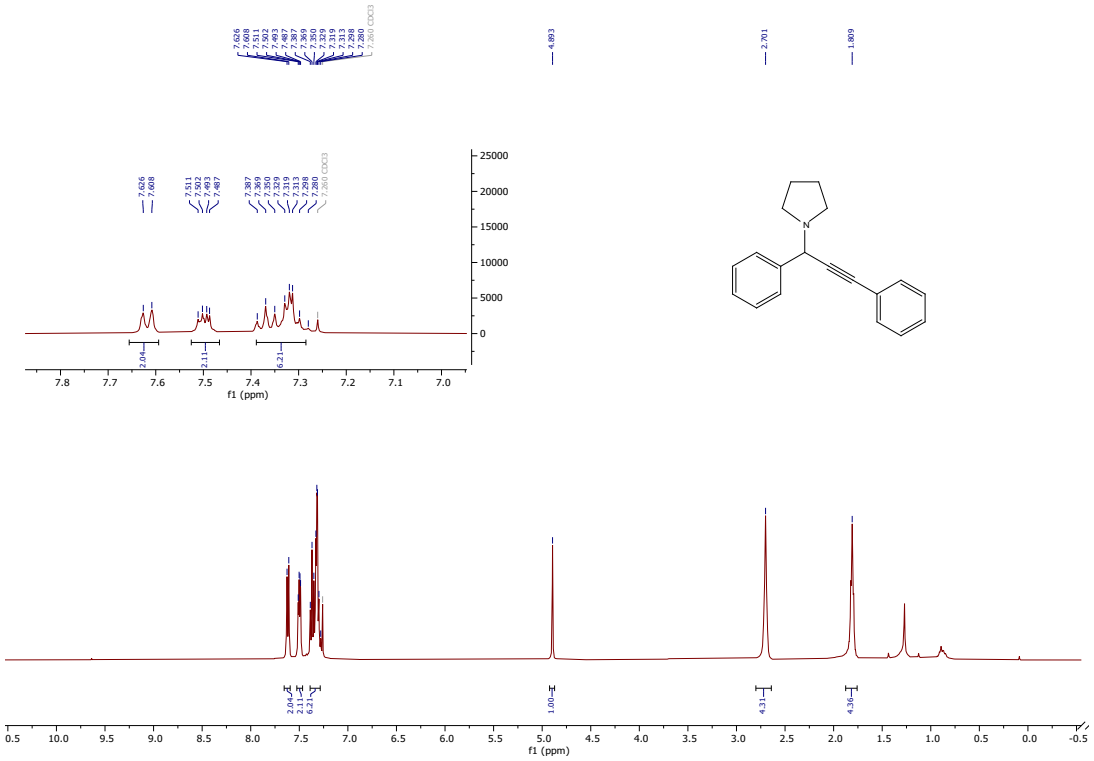


Figure S40 ^{13}C NMR spectra of compound **9q** in $CDCl_3$ (101 MHz)

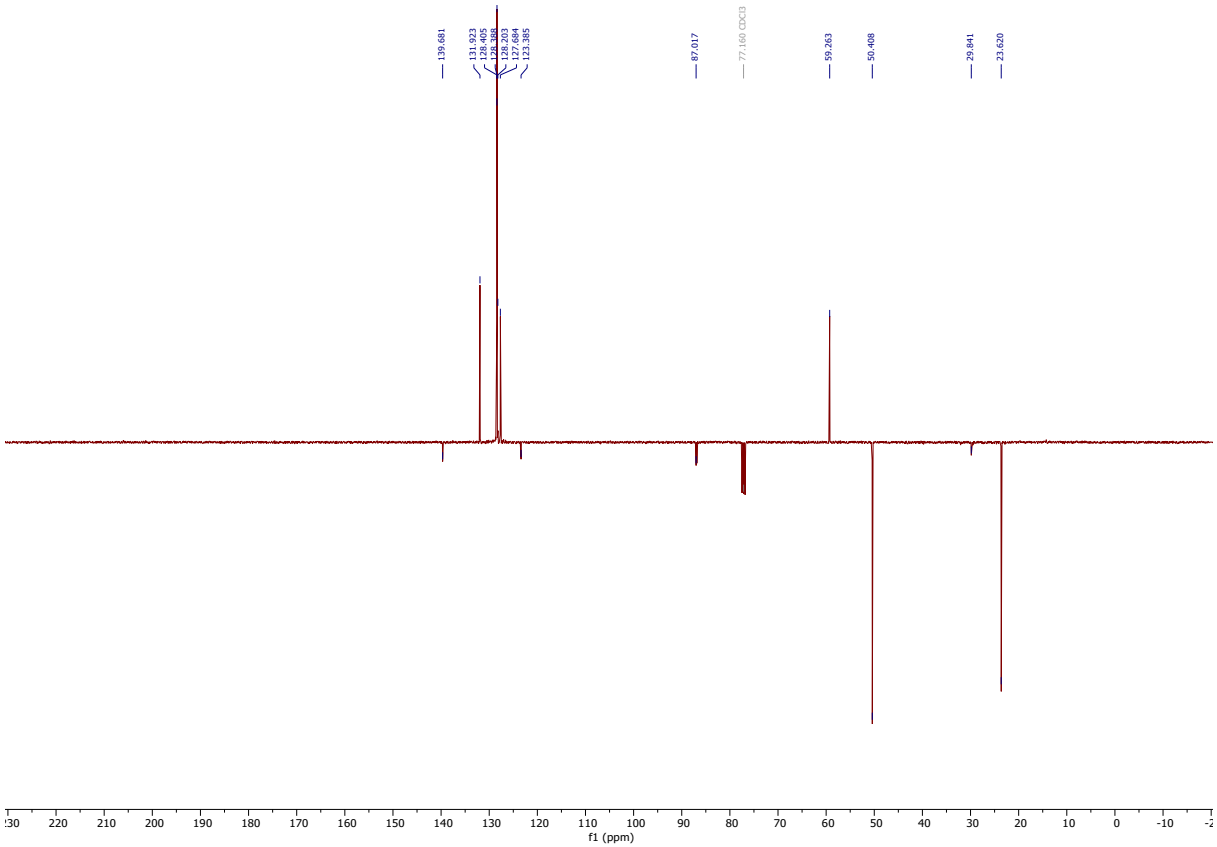


Figure S41 ^{1}H NMR spectra of complex **5** with NH_4PF_6 in DMSO-d^{6} (300 MHz)

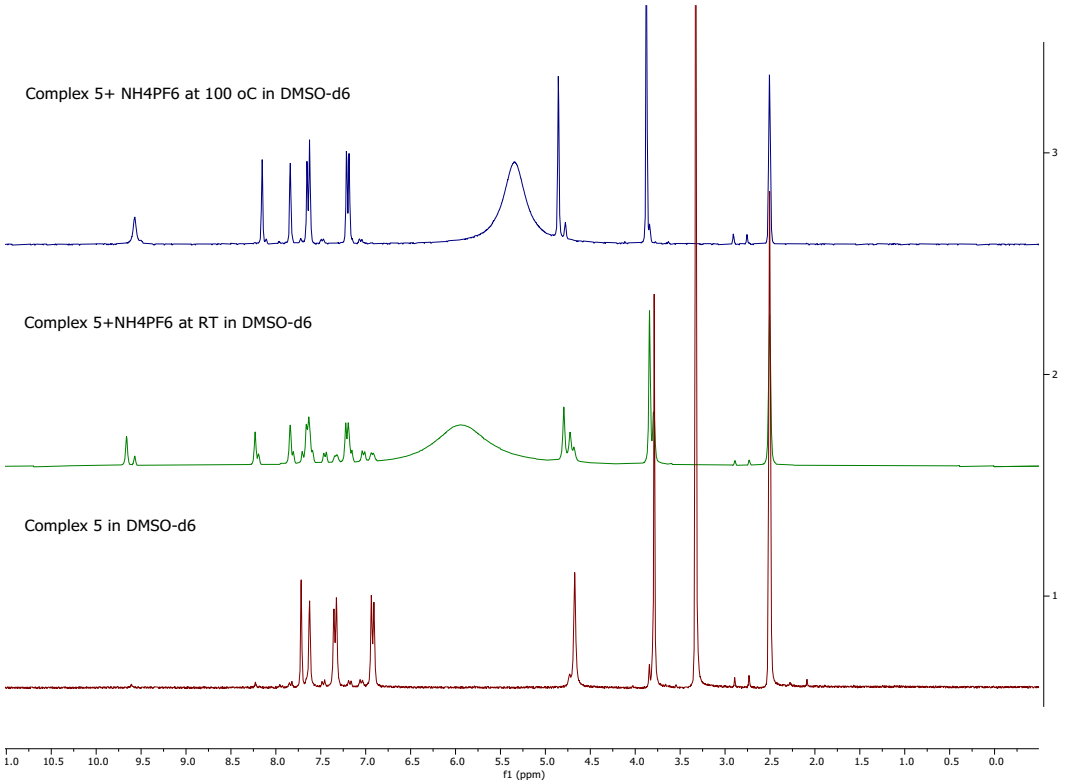
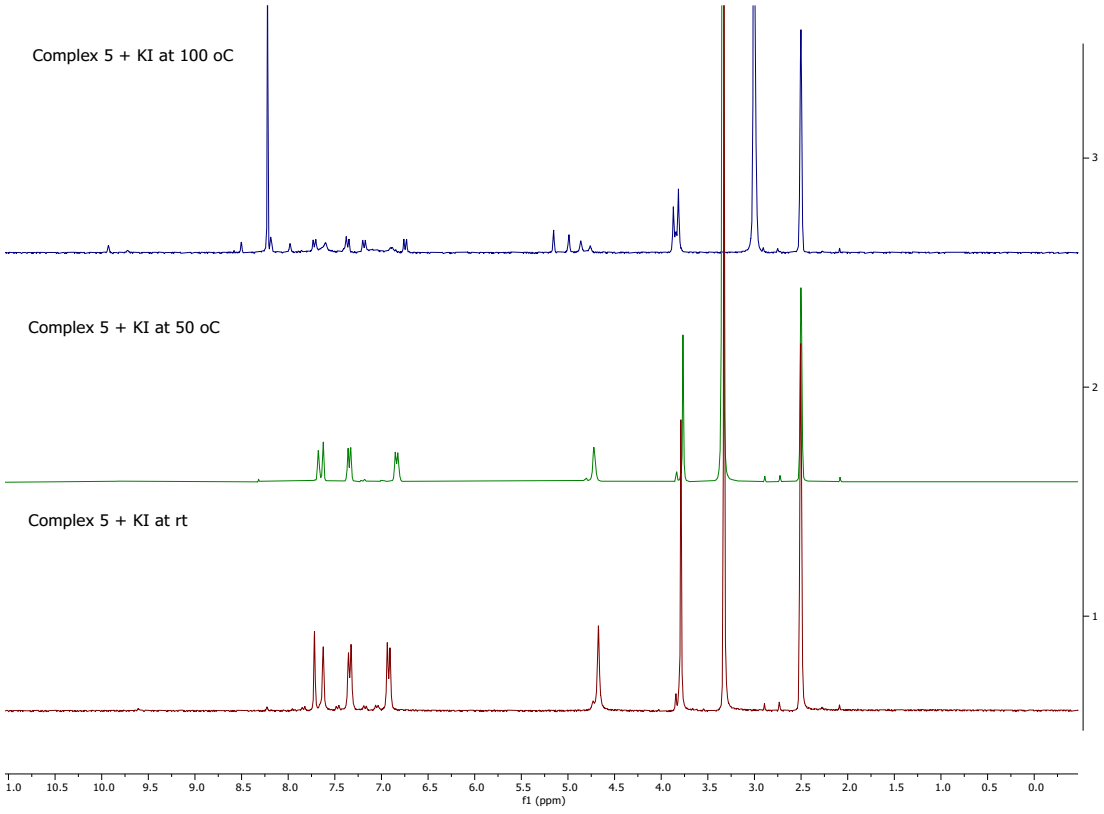


Figure S41 ^{1}H NMR spectra of complex **5** with KI in DMSO-d^{6} (300 MHz)



4.0. X-Ray data

The diffraction data for structure determination of **5** were collected on Bruker D8 VENTURE Kappa Duo PHOTONIII by IμS micro-focus sealed tube CuKα (λ= 1.54178 Å) at low temperature. The position of atoms was determined by direct methods (XT)[6] and refined by full-matrix least squares based on F^2 (SHELXL2019[7]). The hydrogen atoms on carbon were calculated into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety.

Crystal data for **5,** $C_{11}H_{11}AgBrN_2O$, M_r = 375.00; Monoclinic, $P2_1/c$ (No 14), a = 15.3550 (11) Å, b = 4.2932 (3) Å, c = 18.938 (1) Å, β = 111.204 (5)°, V = 1163.91 (14) Å^3, Z = 4, D_x = 2.140 Mg m^{-3}, temperature of sample 120(2) K, colorless needle of dimensions 0.28 × 0.02 × 0.02 mm, multi-scan absorption correction (μ = 17.75 mm^{-1}) T_{min} = 0.54, T_{max} = 0.78; a total of 7588 measured reflections (θ_{max}= 66.9˚), from which 2045 were unique (R_{int} = 0.093) and 1339 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged (Δ/σ_{max}= 0.001) to R = 0.063 for observed reflections and w$R(F^2)$ = 0.148, GOF = 1.01 for 146 parameters and all 2045 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 1.64, $\Delta\rho_{min}$ -1.61 e.Å^{-3}.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number 2348298 for **5** and can be obtained free of charge from the Centre via its website (https://www.ccdc.cam.ac.uk/structures/).

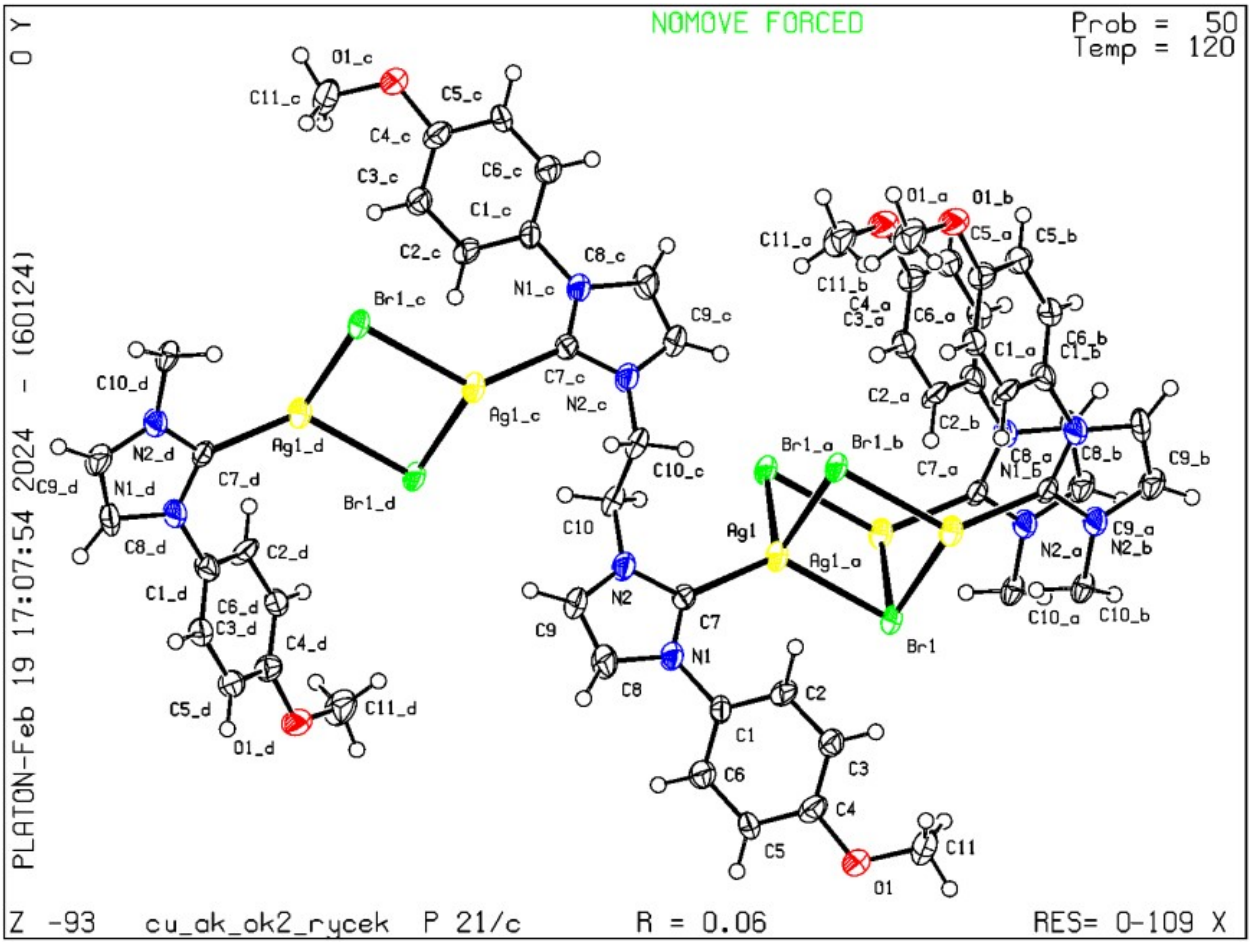


Figure S 37 View on part of the infinite chain of **5.** The displacement ellipsoids at 50% probability level.

5.0. References

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