Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Vinyl Cation-Mediated Intramolecular Hydroarylation of Alkynes Using Pyridinium Reagents

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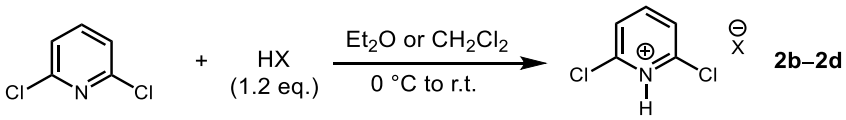
Contents

1. General information

General reagent information: Anhydrous chloroform, 1,2-dichloroethane, tetrahydrofuran, and α,α,α-trifluorotoluene were purchased from Acros (AcroSeal packaging), Sigma Aldrich (Sure/Seal packaging), and Frontier Scientific (J&KSeal packaging), respectively, and were transferred into an argon-filled glovebox and used as received. Other dry solvents were obtained by distillation and storage over 3Å or 4Å molecular sieves. All other reagents were purchased from Oakwood, Acros, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle *SiliaFlash® F60* silica gel, unless otherwise indicated.

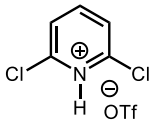
General analytical information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 500 MHz instruments. All ^{19}F NMR spectra are ^{1}H decoupled and reported in δ units, parts per million (ppm). All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 2.50 ppm (DMSO-d_6), 7.26 ppm ($CDCl_3$) or 2.05 ppm ($(CD_3)_2CO$). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 39.52 ppm (DMSO-d_6), 77.16 ppm ($CDCl_3$) or 29.84 ppm ($(CD_3)_2CO$). Thin-layer chromatography (TLC) was performed on Silicycle 250 μm (analytical) or 1000 μm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. High resolution mass spectra were recorded on a Thermo Scientific Q-Exactive mass spectrometer. NMR yields were determined using a known mass of 1,1,2,2-tetrachloroethane as the internal standard for ^{1}H NMR spectroscopy.

2. Synthetic procedures and characterization data for dichloropyridinium salts



2b–2d

2,6-Dichloropyridinium triflate (2b)



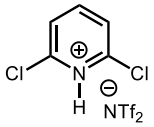
To a solution of 2,6-dichloropyridine (7.39 g, 50 mmol, 1.0 equiv) in dry Et_2O (60 mL) under nitrogen was added trifluoromethanesulfonic acid (5.25 mL, 60 mmol, 1.2 equiv) dropwise by syringe over 5 min at 0 °C to give a white precipitate. Subsequently, the mixture was allowed to reach room temperature and stirring was continued for 1 h. The solid was collected by filtration using a medium-porosity fritted funnel, washed with Et_2O (2 × 30 mL), and dried under vacuum to give a white solid, (11.6 g, 87% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 14.3 – 13.7 (bs, 1H), δ 7.95 (t, J = 7.3 Hz, 1H), 7.59 (d, J = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 149.2, 142.8, 123.7, 120.7 (q, $J_{C\text{-}F}$ = 322 Hz).

^{19}F NMR (471 MHz, DMSO-d_6) δ –77.1.

2,6-Dichloropyridinium bistriflimide (2c)



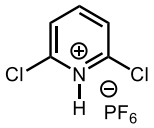
To a solution of 2,6-dichloropyridine (739 mg, 5 mmol, 1.0 equiv) in dry CH_2Cl_2 (8 mL) under nitrogen was added a solution of bistriflimidic acid (1.40 g, 5 mmol, 1.0 equiv) in dry CH_2Cl_2 (2 mL) dropwise by syringe over 5 min at 0 °C. After the mixture was allowed to reach room temperature, the solvent was removed directly from the closed flask under vacuum with the aid of a cold trap cooled to –78 °C to give a grey solid (2.00 g, 93% yield).

^{1}H NMR (500 MHz, DMSO- d_6) δ 14.4 – 14.2 (bs, 1H), δ 7.91 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 7.1 Hz, 2H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 149.4, 142.8, 123.7, 119.8 (q, $J_{C\text{-}F}$ = 333 Hz)

^{19}F NMR (471 MHz, DMSO- d_6) δ –78.1

2,6-Dichloropyridinium hexafluorophosphate (2d)



Under nitrogen, propionic anhydride (11.7 g, 90.0 mmol, 9.0 equiv) was added dropwise by syringe over 5 min to a solution of hexafluorophosphoric acid (55 wt. % in H_2O, 3.2 g, 12.0 mmol, 1.2 equiv) at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 5 min before being cooled to 0 °C once again. The resultant solution was added dropwise by syringe over 5 min to a solution of 2,6-dichloropyridine (1.48 g, 10.0 mmol, 1.0 equiv) in dry dichloromethane (6 mL) under nitrogen to give a white precipitate. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. Subsequently, the reaction mixture was filtered using a Schlenk frit under nitrogen. The collected solid was washed with dry CH_2Cl_2 (5 × 5 mL) and dried under high vacuum overnight to provide a white solid (2.10 g, 71% yield).

^{1}H NMR (500 MHz, DMSO- d_6) δ 13.5 – 12.8 (bs, 1H), δ 7.94 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 2H).

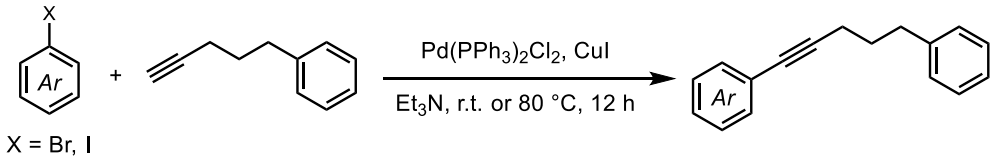
^{13}C NMR (126 MHz, DMSO- d_6) δ 149.2, 142.7, 123.6.

^{19}F NMR (471 MHz, DMSO- d_6) δ –70.1 (d, $J_{P\text{-}F}$ = 710 Hz).

^{31}P NMR (202 MHz, DMSO- d_6) δ –139.4 (sept, $J_{P\text{-}F}$ =710 Hz).

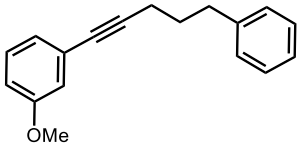
3. Synthetic procedures and characterization data for unreported starting materials

3.1 Method A:



In an argon-filled glovebox, a 50 mL round-bottom flask equipped with a magnetic stir bar was charged with $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol, 1.0 mol %), CuI (29 mg, 0.15 mmol, 3.0 mol %), and aryl iodide or aryl bromide (5.0 mmol, 1.0 equiv). The Flask was sealed and removed from the glovebox, and triethylamine (25 ml) and 5-phenyl-1-pentyne (760 µl, 5.0 mmol, 1.0 equiv) were added by syringe successively. The reaction mixture was then stirred at room temperature (aryl iodide) or 80 °C (aryl bromide) for 12 hours. After the reaction was judged to be complete (as monitored by TLC), the reaction mixture was quenched by addition of water (40 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered through a silica gel pad. The filtrate was concentrated *in vacuo* and the crude residue was purified by silica gel column chromatography to give the corresponding pure alkynes.

1-Methoxy-3-(5-phenylpent-1-yn-1-yl)benzene (1h)



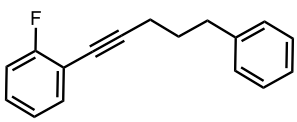
Prepared from the corresponding aryl iodide. Hexanes/EtOAc (39:1) was used as the eluent to give the title product as a yellow oil (925 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.15 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.83 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.78 (s, 3H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.94 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 141.6, 129.2, 128.5, 128.3, 125.9, 124.9, 124.1, 116.4, 114.1, 89.7, 81.0, 55.2, 34.8, 30.2, 18.8.

HRMS (ESI) calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, Found: 251.1430.

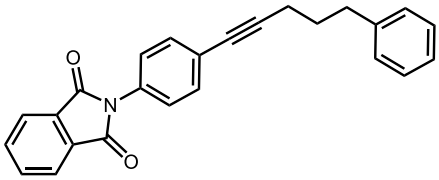
1-Fluoro-2-(5-phenylpent-1-yn-1-yl)benzene (1l)



Prepared from the corresponding aryl iodide. Hexanes was used as the eluent to give the title product as a colorless oil (964 mg, 81% yield).

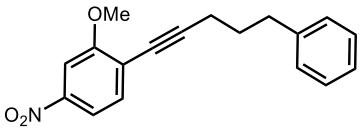
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.6, 1.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.17 – 7.08 (m, 4H), 7.01 – 6.93 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.86 (app. p, *J* = 7.3 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 250.2 Hz), 141.5, 133.5 (d, $J_{C\text{-}F}$ = 1.5 Hz), 129.2 (d, $J_{C\text{-}F}$ = 7.9 Hz), 128.6, 128.4, 125.9, 123.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 112.4 (d, $J_{C\text{-}F}$ = 15.8 Hz), 95.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 74.5, 34.7, 30.2, 19.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ –111.0.
HRMS (ESI) calcd for $C_{17}H_{16}F$ $[M+H]^+$: 239.1231, Found: 239.1231.

2-(4-(5-Phenylpent-1-yn-1-yl)phenyl)isoindoline-1,3-dione (1m)



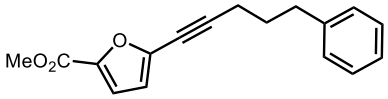
Prepared from the corresponding aryl iodide. Hexanes/EtOAc (4:1) was used as the eluent to give the title product as a yellow solid (1.51 g, 83% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2H), 7.73 – 7.61 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.07 (m, 3H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.84 (app. p, *J* = 7.2 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.5, 134.4, 132.1, 131.6, 130.8, 128.5, 128.3, 126.1, 125.8, 123.7, 123.7, 90.9, 80.4, 34.7, 30.1, 18.8.
HRMS (ESI) calcd for $C_{25}H_{20}O_2N$ $[M+H]^+$: 366.1489, Found: 366.1498.

2-Methoxy-4-nitro-1-(5-phenylpent-1-yn-1-yl)benzene (1n)



Prepared from the corresponding aryl iodide. Hexanes/EtOAc (19:1) was used as the eluent to give the title product as a yellow oil (1.03 g, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.08 (m, 3H), 3.86 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.87 (app. p, *J* = 7.3 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 147.5, 141.3, 133.4, 128.5, 128.3, 125.9, 120.3, 115.6, 105.4, 99.9, 76.1, 56.2, 34.6, 30.0, 19.2.
HRMS (ESI) calcd for $C_{36}H_{35}O_6N_2$ $[2M+H]^+$: 591.2490, Found: 591.2500.

Methyl 5-(5-phenylpent-1-yn-1-yl)furan-2-carboxylate (1o)



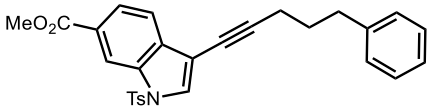
Prepared from the corresponding aryl bromide. Hexanes/EtOAc (9:1) was used as the eluent to give the title product as a yellow oil (992 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.54 (d, *J* = 3.5 Hz, 1H), 3.89 (s, 3H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.93 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.6, 141.0, 140.7, 128.4, 128.3, 125.9, 118.7, 115.3, 96.6, 70.8, 51.9, 34.6, 29.5, 18.7.

HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $[M+H]^+$: 246.1277, Found: 246.1282.

Methyl 3-(5-phenylpent-1-yn-1-yl)-1-tosyl-1*H*-indole-6-carboxylate (1p)



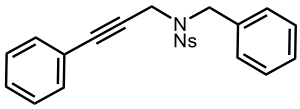
Prepared from the corresponding aryl iodide. Hexanes/EtOAc (9:1) was used as the eluent to give the title product as a yellow solid (1.43 g, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 0.7 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.87 – 7.82 (m, 3H), 7.73 – 7.67 (m, 1H), 7.38 – 7.30 (m, 2H), 7.29 – 7.22 (m, 5H), 4.00 (d, *J* = 2.2 Hz, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 2.00 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.5, 141.3, 134.7, 134.6, 133.6, 130.7, 130.0, 128.4, 128.3, 127.1, 126.9, 125.9, 124.6, 120.2, 115.2, 105.7, 94.7, 71.1, 52.2, 34.8, 30.1, 21.5, 18.9.

HRMS (ESI) calcd for $C_{28}H_{24}O_4NS$ $[M+H]^+$: 472.1577, Found: 472.1564.

***N*-Benzyl-4-nitro-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1s)**



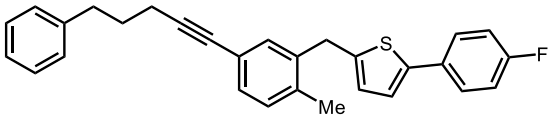
Prepared using iodobenzene and with *N*-benzyl-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.66 g, 5.00 mmol) used in place of 5-phenyl-1-pentyne. Hexanes/EtOAc (9:1) was used as the eluent to give the title product as a yellow oil (1.24 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.20 (m, 8H), 7.04 (d, *J* = 7.0 Hz, 2H), 4.46 (s, 2H), 4.20 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 145.0, 134.3, 131.4, 129.2, 129.1, 129.1, 129.0, 128.7, 128.6, 124.3, 86.8, 80.9, 50.6, 36.8.

HRMS (ESI) calcd for $C_{22}H_{19}O_2N_2S$ $[M+H]^+$: 407.1060, Found: 407.1071.

2-(4-Fluorophenyl)-5-(2-methyl-5-(5-phenylpent-1-yn-1-yl)benzyl)thiophene (1u)



Prepared from the corresponding aryl iodide. Hexanes/EtOAc (39:1) was used as the eluent to give the title product as a yellow oil (1.80 g, 85% yield).

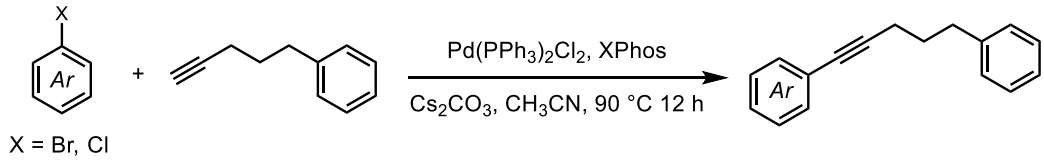
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.33 – 7.18 (m, 7H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.00 (m, 3H), 6.68 (d, *J* = 3.6 Hz, 1H), 4.09 (s, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 1.93 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 103.5 Hz), 143.1, 141.8, 141.7, 132.7, 131.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.6, 130.3, 128.7, 128.5, 127.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.1 (d, $J_{C\text{-}F}$ = 17.5 Hz), 122.8, 121.9, 116.0, 115.7, 89.5, 81.2, 35.0, 34.1, 30.5, 19.5, 19.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –115.1.

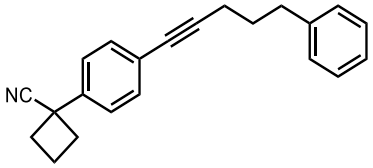
HRMS (ESI) calcd for $C_{29}H_{26}FS$ $[M+H]^+$: 425.1734, Found: 425.1737.

3.2 Method B:



In an argon-filled glovebox, a reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was charged with $Pd(PPh_3)_2Cl_2$ (0.03 mmol, 1.0 mol %), XPhos (0.09 mmol, 3.0 mol %), Cs_2CO_3 (7.8 mmol, 2.6 equiv), aryl halide (3.0 mmol, 1.0 equiv), and CH_3CN (6 mL). The mixture was stirred at room temperature for 30 min. Then, the corresponding terminal alkyne (3.6 mmol, 1.2 equiv) was added. The reaction mixture was then stirred at 90 °C for 12 h. After the reaction was judged to be complete (as monitored by TLC), the reaction mixture was quenched by addition of water (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered through a silica gel pad. The filtrate was concentrated *in vacuo* and the crude residue was purified by silica gel column chromatography to give the corresponding pure alkynes.

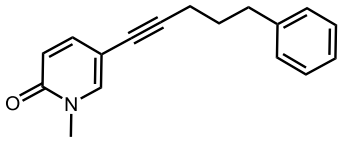
1-(4-(5-Phenylpent-1-yn-1-yl)phenyl)cyclobutane-1-carbonitrile (1q)



Prepared from the corresponding aryl chloride. Hexanes/EtOAc (19:1) was used as the eluent to give the title product as a yellow oil (621 mg, 69% yield).

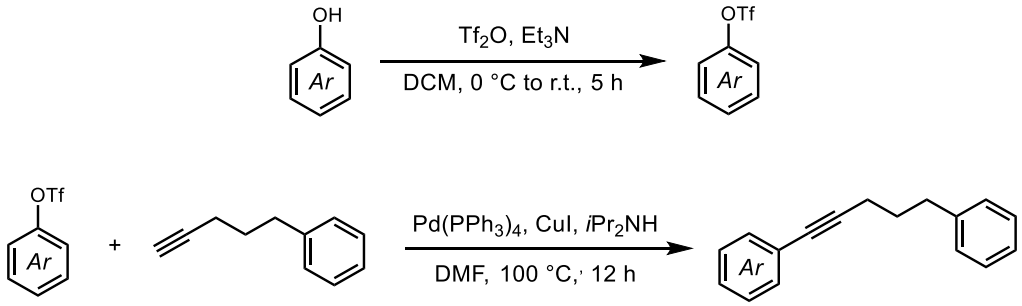
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.29 – 7.22 (m, 3H), 2.90 – 2.78 (m, 4H), 2.69 – 2.58 (m, 2H), 2.52 – 2.41 (m, 3H), 2.16 – 2.05 (m, 1H), 1.98 (app. p, *J* = 7.3 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 138.9, 132.0, 128.5, 128.3, 125.9, 125.4, 124.1, 123.6, 90.7, 80.4, 40.0, 34.8, 34.6, 30.2, 18.8, 17.0.
HRMS (ESI) calcd for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747, Found: 300.1749.

1-Methyl-5-(5-phenylpent-1-yn-1-yl)pyridin-2(1*H*)-one (1r)



Prepared from the corresponding aryl bromide. Hexanes/EtOAc (1:1) was used as the eluent to give the title product as a yellow oil (218 mg, 29% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.3 Hz, 1H), 7.30 (m, 3H), 7.23 – 7.17 (m, 3H), 6.50 (d, *J* = 9.4 Hz, 1H), 3.52 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.89 (m, *J* = 7.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 142.2, 141.4, 141.2, 128.5, 128.4, 126.0, 120.3, 103.1, 90.2, 76.3, 37.8, 34.9, 30.2, 18.8.
HRMS (ESI) calcd for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383, Found: 252.1383.

3.3 Method C:

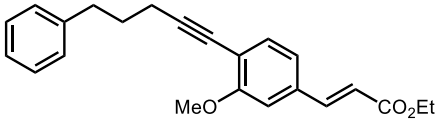


Preparation of aryl trifluoromethanesulfonate: To a solution of phenol (7.4 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) at 0 °C was added triethylamine (14.8 mmol, 2.0 equiv) and trifluoromethanesulfonic anhydride (8.2 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 5 hours, followed by the addition of aqueous sat. $NaHCO_3$ (40 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with brine (80 mL) and dried over Na_2SO_4. After filtration and concentration *in vacuo*, the crude product was purified by silica gel column chromatography to afford the corresponding aryl trifluoromethanesulfonate.

Coupling step: In an argon-filled glovebox, a 50 mL round-bottom flask equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (0.33 mmol, 10 mol %), CuI (0.33 mmol, 10 mol %), the corresponding aryl trifluoromethanesulfonate (3.3 mmol, 1.0 equiv), *i*Pr_2NH

(10.0 mmol, 3.0 equiv), and DMF (15 ml). Then, the corresponding terminal alkyne (4.0 mmol, 1.2 equiv) was added. The reaction mixture was then stirred at 100 °C for 12 h. After the reaction was judged to be complete (as monitored by TLC), the mixture was quenched with water (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered through a silica gel pad. The filtrate was concentrated *in* vacuo, and the crude residue was purified by silica gel column chromatography to give the corresponding pure alkynes.

Ethyl (*E*)-3-(3-methoxy-4-(5-phenylpent-1-yn-1-yl)phenyl)acrylate (1t)



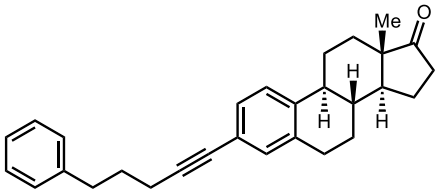
Hexanes/EtOAc (9:1) was used as the eluent to give the title product as a yellow oil (876 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.07 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.00 (bs, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.95 (app. p, *J* = 7.4 Hz , 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 160.2, 144.1, 141.8, 135.2, 133.9, 128.7, 128.5, 126.0, 120.7, 118.8, 115.5, 109.6, 96.6, 60.7, 55.9, 34.9, 30.4, 19.4, 14.4.

HRMS (ESI) calcd for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1798, Found: 349.1799.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(5-phenylpent-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (1v)



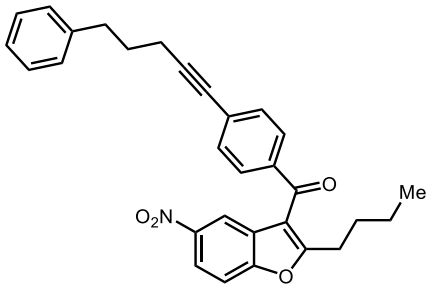
Hexanes/EtOAc (9:1) was used as the eluent to give the title product as a yellow oil (875 mg, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.06 (m, 6H), 2.78 (dd, *J* = 8.9, 4.1 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.40 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.35 – 2.26 (m, 3H), 2.18 (td, *J* = 10.8, 4.0 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.98 – 1.79 (m, 5H), 1.57 – 1.30 (m, 6H), 0.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.78, 141.9, 139.6, 136.6, 132.2, 129.1, 128.7, 128.5, 126.0, 125.4, 121.5, 89.2, 81.3, 50.7, 48.1, 44.6, 38.2, 36.0, 35.0, 31.8, 30.5, 29.3, 26.6, 25.8, 21.7, 19.0, 14.0.

HRMS (ESI) calcd for $C_{29}H_{33}O$ $[M+H]^+$: 397.2526, Found: 397.2529.

(2-Butyl-5-nitrobenzofuran-3-yl)(4-(5-phenylpent-1-yn-1-yl)phenyl)methanone (1w)



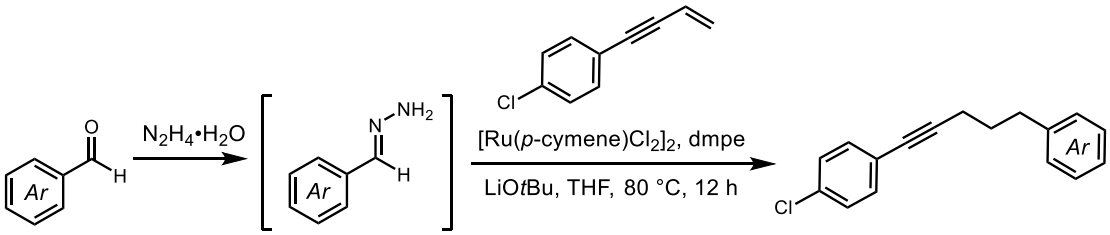
Hexanes/EtOAc (4:1) was used as the eluent to give the title product as a yellow oil (1.08 g, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.3 Hz, 1H), 8.19 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 8.6 Hz, 3H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.94 (app. p, *J* = 7.1 Hz, 2H), 1.73 (app. p, *J* = 7.6 Hz, 2H), 1.31 (app. sex, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 167.9, 156.2, 144.6, 141.3, 136.9, 131.8, 129.4, 129.0, 128.4, 128.3, 127.5, 125.9, 120.3, 117.7, 116.9, 111.3, 94.2, 80.5, 34.8, 30.0, 29.8, 28.0, 22.2, 18.9, 13.5.

HRMS (ESI) calcd for $C_{30}H_{28}NO_4$ $[M+H]^+$: 466.2013, Found: 466.2015.

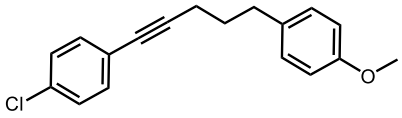
3.4 Method D:



Preparation of hydrazone: A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was charged with substituted benzaldehyde (6 mmol, 2 equiv) before ethanol (1.7 mL) and hydrazine monohydrate (18 mmol, 0.87 mL, 6 equiv) were added. The reaction mixture was stirred at room temperature for 1 h and concentrated *in vacuo*. The crude material was dissolved in Et_2O (20 mL) and washed with water (3 × 20 mL). The organic layer was dried over sodium sulfate and concentrated *in vacuo* to give the aryl hydrazone which was used immediately without further purification.

Coupling step: A flame dried pressure vessel (150 mL, Chemglass, part# CG-1880-06) equipped with a magnetic stir bar was transferred to an argon-filled glovebox and charged with [Ru(p-cymene)Cl_2]$_2$ (92 mg, 0.15 mmol, 5 mol %), THF (10mL) and DMPE (50 µL, 0.3 mmol, 10 mol %) and stirred at room temperature for 30 min. THF (5 mL) was used to dissolve and add the hydrazone and enyne (3.0 mmol, 1 equiv) before sealing the vessel and transferring from glovebox to an oil bath. The mixture was stirred at 80 °C for 12 h. After the reaction was complete the mixture was filtered through a plug of celite which was rinsed with ethyl acetate. The filtrate was concentrated *in vacuo* and purified by silica gel column chromatography.[1]

1-Chloro-4-(5-(4-methoxyphenyl)pent-1-yn-1-yl)benzene (1x)



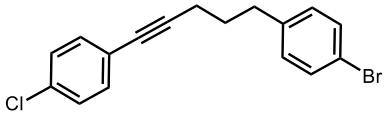
Hexanes/Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (482 mg, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.89 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 133.7, 133.5, 132.9, 129.6, 128.7, 122.7, 91.2, 80.2, 55.4, 34.1, 30.6, 18.9.

HRMS (ESI) calcd for $C_{18}H_{18}ClO$ $[M+H]^+$: 285.1041, Found: 285.1027.

1-Bromo-4-(5-(4-chlorophenyl)pent-4-yn-1-yl)benzene (1y)



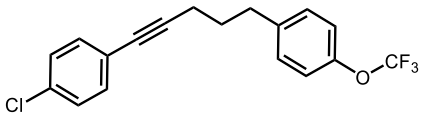
Hexanes/Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (404 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.89 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 133.7, 132.9, 131.6, 130.5, 128.7, 122.5, 119.9, 90.7, 80.4, 34.4, 30.1, 18.9.

HRMS (APCI) calcd for $C_{17}H_{14}BrCl$ $[M\cdot]^+$: 331.9962, Found: 331.9973.

1-Chloro-4-(5-(4-(trifluoromethoxy)phenyl)pent-1-yn-1-yl)benzene (1z)



Hexanes was used as the eluent to give the title product as a yellow oil (508 mg, 50% yield).

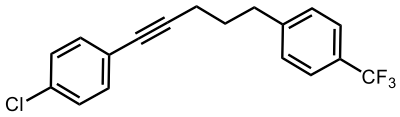
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.78 (t, *J* = 7.5, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.91 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 140.4, 133.8, 132.9, 129.9, 128.7, 121.7, 120.7 (q, $J_{C\text{-}F}$ = 256.6 Hz), 121.1, 90.7, 80.5, 34.3, 30.2, 18.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ –57.9.

EA Calcd. for $C_{18}H_{14}ClF_3O$ C, 63.82; H, 4.17. Found: C, 64.05; H, 4.14.

1-chloro-4-(5-(4-(trifluoromethyl)phenyl)pent-1-yn-1-yl)benzene (1aa)



Hexanes/Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (233 mg, 24% yield).

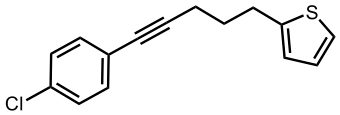
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.25 (d, *J* = 8.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.92 (app. p, *J* = 7.3 Hz 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 133.7, 132.8, 128.9, 128.6, 128.4 (q, *J* = 32.2 Hz), 125.3 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.7 Hz), 122.3, 90.4, 80.4, 34.6, 29.8, 18.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.2.

HRMS (ESI) calcd for $C_{18}H_{14}ClF_3$ $[M^{\cdot}]^+$: 322.0731, Found: 322.0737.

2-(5-(4-chlorophenyl)pent-4-yn-1-yl)thiophene (1ab)



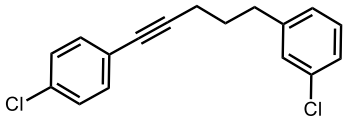
Hexanes/Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (476 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.14 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.85 – 6.81 (m, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.97 (app. p, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 133.6, 132.8, 128.5, 126.8, 124.5, 123.2, 122.4, 90.5, 80.3, 30.4, 28.9, 18.7.

HRMS (ESI) calcd for $C_{15}H_{14}ClS$ $[M+H]^+$: 261.0499, Found: 261.0501.

1-chloro-3-(5-(4-chlorophenyl)pent-4-yn-1-yl)benzene (1ac)



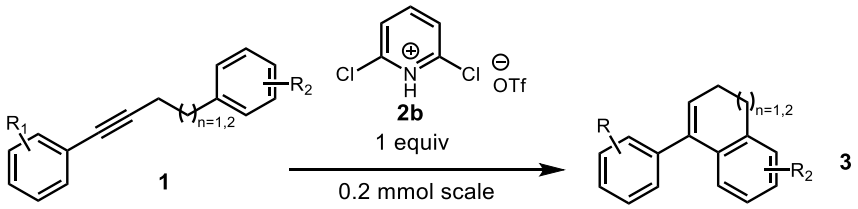
Hexanes/Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (348 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.10 (d, *J* = 7.3 Hz, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.91 (app. p, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 134.3, 133.7, 132.9, 129.8, 128.8, 128.7, 126.9, 126.3, 122.5, 90.7, 80.5, 34.6, 30.0, 18.9.

HRMS (ESI) calcd for $C_{17}H_{13}Cl_2$ $[M-H]^+$: 287.0389, Found: 287.0400.

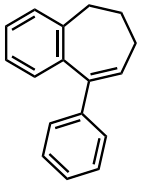
4. General procedure for intramolecular hydroarylation of alkynes



A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was flame dried under vacuum. The reaction tube was cooled under argon and transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv), dry $CHCl_3$ or DCE (1.0 mL) and alkyne (**1**) (0.2 mmol, 1.0 equiv) were added in succession. The reaction tube was sealed and removed from the glovebox. After stirring at 70 °C or 90 °C for the indicated time, the reaction mixture was cooled to room temperature and passed through a pad of silica gel with the aid of suction using CH_2Cl_2 as eluent The filtrate was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product.

5. Characterization data for products

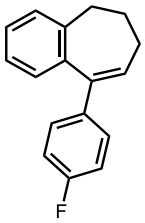
9-Phenyl-6,7-dihydro-5*H*-benzo[7]annulene (3a)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and pent-1-yne-1,5-diyldibenzene (**1a**) (0.2 mmol, 44 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3a** as a colorless oil (32 mg, 73% yield) with spectral properties identical to those reported in the literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 6H), 7.24 – 7.17 (m, 2H), 7.05 – 6.97 (m, 1H), 6.46 (t, *J* = 7.4 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.19 (app. p, *J* = 7.1 Hz, 2H), 1.99 (app. q, *J* = 7.2 Hz, 2H).

9-(4-Fluorophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3b)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-fluoro-4-(5-phenylpent-1-yn-1-yl)benzene (**1b**) (0.2 mmol, 48 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3b** as a colorless oil (36 mg, 75% yield).

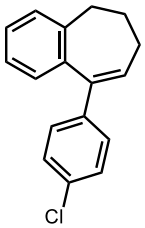
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 7.02 – 6.94 (m, 3H), 6.39 (t, *J* = 7.3 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.18 (app. p, *J* = 7.1 Hz, 2H), 1.96 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, $J_{C\text{-}F}$ = 245.9 Hz), 142.2, 142.0, 140.1, 138.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.4 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.1, 128.6, 128.2 (d, $J_{C\text{-}F}$ = 1.1 Hz), 127.1, 125.9, 114.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 35.2, 32.3, 25.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –115.9.

HRMS (ESI) calcd for $C_{17}H_{16}F$ $[M+H]^+$: 249.1231, Found: 239.1237.

9-(4-Chlorophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3c)



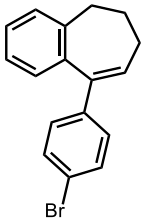
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-chloro-4-(5-phenylpent-1-yn-1-yl)benzene (**1c**) (0.2 mmol, 51 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3c** as a colorless oil (37 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 3H), 6.97 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.43 (t, *J* = 7.4 Hz, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.18 (app. p, *J* = 7.1 Hz, 2H), 1.97 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 141.9, 140.8, 139.8, 132.8, 129.2, 129.1, 128.9, 128.6, 128.3, 127.2, 125.9, 35.2, 32.3, 25.4.

HRMS (ESI) calcd for $C_{17}H_{16}Cl$ $[M+H]^+$: 255.0935, Found 255.0937.

9-(4-Bromophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3d)



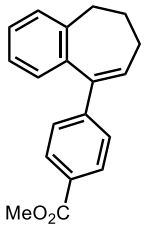
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-bromo-4-(5-phenylpent-1-yn-1-yl)benzene (**1d**) (0.2 mmol, 60 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3d** as a colorless oil (44 mg, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.46 (t, *J* = 7.4 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 1.99 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 142.1, 141.4, 139.9, 131.4, 129.7, 129.2, 129.1, 128.8, 127.4, 126.1, 121.1, 35.3, 32.5, 25.5.

HRMS (ESI) calcd for $C_{17}H_{16}Br$ $[M+H]^+$: 299.0430, Found 299.0429.

Methyl 4-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)benzoate (3e)



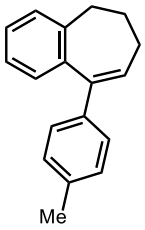
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and methyl 4-(5-phenylpent-1-yn-1-yl)benzoate (**1e**) (0.2 mmol, 56 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes/EtOAc 39:1) afforded **3e** as a colorless oil (18 mg, 32% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.24 (td, *J* = 7.4, 1.5 Hz, 1H), 7.20 (td, *J* = 7.4, 1.6 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.59 – 6.53 (m, 1H), 3.92 (s, 3H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 2.01 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 146.8, 142.3, 142.1, 139.5, 130.5, 129.5, 129.1, 128.7, 128.5, 127.8, 127.3, 126.0, 52.0, 35.0, 32.3, 25.5.

HRMS (ESI) calcd for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, Found 279.1378.

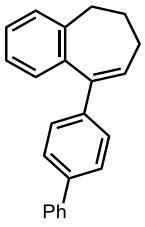
9-(*p*-Tolyl)-6,7-dihydro-5*H*-benzo[7]annulene (3f)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-methyl-4-(5-phenylpent-1-yn-1-yl)benzene (**1f**) (0.2 mmol, 46 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3f** as a colorless oil (33 mg, 72% yield) with spectral properties identical to those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.23 – 7.14 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.41 (t, *J* = 7.4 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 2.17 (app. p, *J* = 7.1 Hz, 2H), 1.96 (app. q, *J* = 7.2 Hz, 2H).

9-([1,1'-Biphenyl]-4-yl)-6,7-dihydro-5*H*-benzo[7]annulene (3g)



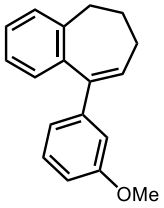
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-methyl-4-(5-phenylpent-1-yn-1-yl)benzene (**1g**) (0.2 mmol, 59 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3g** as a colorless oil (40 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.21 (m, 6H), 7.11 (d, *J* = 6.6 Hz, 1H), 6.55 (t, *J* = 7.4 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.22 (app. p, *J*=6.7 Hz, 2H), 2.03 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 142.2, 141.3, 140.9, 140.2, 139.8, 129.3, 128.7, 128.6, 128.5, 128.3, 127.2, 127.1, 127.0, 126.9, 125.9, 35.2, 32.3, 25.4.

HRMS (ESI) calcd for $C_{23}H_{21}$ $[M+H]^+$: 297.1638, Found 297.1635.

9-(3-Methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3h)



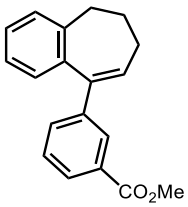
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1h** (0.2 mmol, 50 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 39:1) afforded **3h** as a colorless oil (25 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 4H), 7.03 (dd, *J* = 7.3, 1.7 Hz, 1H), 6.89 – 6.77 (m, 3H), 6.46 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.18 (app. p, *J* = 7.1 Hz, 2H), 1.97 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 143.8, 142.8, 142.1, 140.1, 129.3, 129.0, 128.6, 128.5, 127.0, 125.8, 120.6, 113.6, 112.4, 55.2, 35.2, 32.3, 25.3.

HRMS (ESI) calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, Found 251.1430.

Methyl 3-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)benzoate (3i)

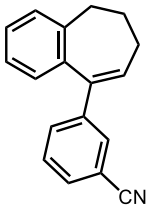


The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and methyl 3-(5-phenylpent-1-yn-1-yl)benzoate (**1i**) (0.2 mmol, 56 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes/EtOAc 39:1) followed by heating under vacuum at 70 °C for 24h to remove residual 2,6-dichloropyridine afforded **3h** as a colorless oil (38 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.6 Hz, 1H), 7.95 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.17 (m, 2H), 6.96 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 3H), 2.68 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 2.01 (app. q, *J* = 7.2 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 142.7, 142.2, 139.8, 132.5, 130.1, 129.6, 129.0, 128.9, 128.7, 128.2, 128.1, 127.2, 126.0, 122.8, 52.1, 35.2, 32.3, 25.4.
HRMS (ESI) calcd for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, Found 279.1377.

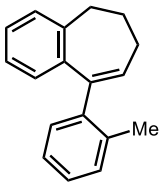
Reaction conducted on 5 mmol:
A flame dried pressure vessel (150 mL, Chemglass, part# CG-1880-06) equipped with a magnetic stir bar was transferred to an argon-filled glovebox and charged with 2,6-dichloropyridinium trifluoromethanesulfonate (5 mmol, 1.49 g, 1.0 equiv), dry DCE (25 mL) and **1i** (5 mmol, 1.39 g, 1.0 equiv) in succession. The reaction tube was sealed and removed from the glovebox. After stirring at 90 °C for 24 h, the reaction mixture was cooled to room temperature and passed through a pad of silica gel with the aid of suction using CH_2Cl_2 as eluent. The filtrate was concentrated *in vacuo* and purified by flash column chromatography to give the desired product, still slightly contaminated with 2,6-dichloropyridine. Subsequent heating of this material under vacuum at 70 °C for 24 h to remove residual 2,6-dichloropyridine afforded pure **3i** as a colorless oil (893 mg, 64% yield).

3-(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)benzonitrile (3j)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 3-(5-phenylpent-1-yn-1-yl)benzonitrile (**1j**) (0.2 mmol, 49 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes/EtOAc 19:1) afforded **3j** as a colorless oil (10 mg, 20% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.47 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.18 (m, 3H), 6.95 – 6.88 (m, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 2.01 (app. q, *J* = 7.2 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.2, 141.2, 139.0, 132.2, 131.4, 130.7, 130.4, 128.9, 128.84, 128.83, 127.6, 126.1, 118.9, 112.3, 35.0, 32.2, 25.4.
HRMS (ESI) calcd for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277, Found 246.1268.

9-(*o*-Tolyl)-6,7-dihydro-5*H*-benzo[7]annulene (3k)



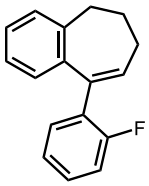
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-methyl-2-(5-phenylpent-1-yn-1-yl)benzene (**1k)** (0.2 mmol, 49 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3k** as a colorless oil (34 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.17 – 7.06 (m, 3H), 6.77 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.16 (t, *J* = 7.0 Hz, 1H), 2.77 (t, *J* = 6.9 Hz, 2H), 2.22 (app. p, *J* = 7.1 Hz, 2H), 2.05 (app. q, *J* = 7.1 Hz, 2H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.0, 141.3, 140.9, 136.2, 130.5, 130.2, 130.1, 128.8, 128.0, 127.1, 126.6, 125.9, 125.6, 34.9, 32.9, 25.6, 20.2.

HRMS (ESI) calcd for $C_{18}H_{19}$ $[M+H]^+$: 235.1481, Found 235.1480.

9-(2-Fluorophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3l)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-fluoro-2-(5-phenylpent-1-yn-1-yl)benzene (**1l**) (0.2 mmol, 46 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3l** as a colorless oil (34 mg, 74% yield).

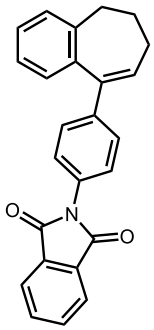
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.04 (m, 6H), 7.00 (t, *J* = 9.3 Hz, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.38 (t, *J* = 7.1 Hz, 1H), 2.73 (t, *J* = 6.9 Hz, 2H), 2.20 (app. p, *J* = 7.0 Hz, 2H), 2.03 (app. q, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (d, $J_{C\text{-}F}$ = 248.1 Hz), 141.4, 140.4, 137.5, 131.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 131.4 (d, $J_{C\text{-}F}$ = 3.7 Hz), 130.4 (d, $J_{C\text{-}F}$ = 13.6 Hz), 128.6, 128.6, 128.0, 126.9, 125.8, 123.7 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.4 Hz), 35.0, 32.4, 25.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –114.8.

HRMS (ESI) calcd for $C_{17}H_{16}F$ $[M+H]^+$: 239.1234, Found 239.1231.

2-(4-(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)phenyl)isoindoline-1,3-dione (3m)



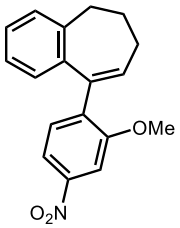
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1m** (0.2 mmol, 73 mg, 1.0 equiv) in DCE at 70 °C for 12 h. Purification by flash column chromatography (hexanes/EtOAc 4:1) afforded **3m** as a yellow solid (42 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.45 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 7.11 – 7.05 (m, 1H), 6.52 (t, *J* = 7.4 Hz, 1H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 2.00 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 142.2, 142.1, 139.8, 134.4, 131.8, 130.3, 129.4, 129.3, 128.6, 128.5, 127.2, 126.2, 125.9, 123.7, 35.1, 32.3, 25.4.

HRMS (ESI) calcd for $C_{25}H_{20}O_2N$ $[M-H]^-$ 364.1332, Found 364.1330.

9-(2-Methoxy-4-nitrophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3n)



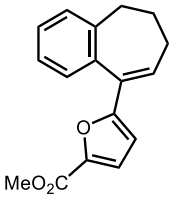
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1n** (0.2 mmol, 59 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 19:1) afforded **3n** as a colorless oil (29 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.18 (td, *J* = 7.4, 1.4 Hz, 1H), 7.10 (td, *J* = 7.5, 1.4 Hz, 1H), 6.75 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.35 (t, *J* = 7.1 Hz, 1H), 3.66 (s, 3H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.21 (app. p, *J* = 7.1 Hz, 2H), 2.05 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 147.9, 141.3, 140.1, 139.2, 138.9, 132.4, 131.1, 128.6, 127.2, 126.9, 125.7, 115.8, 106.1, 56.0, 34.7, 32.2, 25.5.

HRMS (ESI) calcd for $C_{18}H_{18}O_3N$ $[M+H]^+$: 296.1281, Found 296.1285.

Methyl 5-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)furan-2-carboxylate (3o)



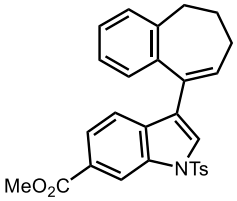
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1o** (0.2 mmol, 54 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 9:1) afforded **3o** as a colorless oil (33 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 1H), 7.26 (d, *J* = 3.1 Hz, 3H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 3.5 Hz, 1H), 3.90 (s, 3H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.17 (app. p, *J* = 7.1 Hz, 2H), 2.00 (app. q, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 157.7, 143.0, 141.8, 136.5, 131.4, 130.1, 128.9, 128.2, 127.8, 126.0, 119.6, 109.0, 51.8, 34.6, 31.9, 24.6.

HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $[M+H]^+$: 269.1172, Found 269.1176.

Methyl 3-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)-1-tosyl-1*H*-indole-6-carboxylate (3p)



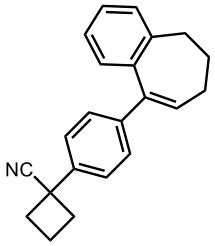
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1p** (0.2 mmol, 94 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 9:1) afforded **3p** as a yellow solid (61 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.79 (t, *J* = 8.6 Hz, 3H), 7.61 (s, 1H), 7.29 – 7.22 (m, 4H), 7.18 – 7.09 (m, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.55 (t, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 2.71 (t, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 2.20 (app. p, *J* = 7.0 Hz, 2H), 2.03 (app. q, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 145.2, 141.6, 139.2, 134.89, 134.86, 133.9, 133.4, 130.0, 128.9, 128.5, 127.4, 126.9, 126.4, 126.0, 124.7, 124.3, 122.8, 120.8, 115.3, 52.2, 35.2, 32.3, 25.2, 21.6.

HRMS (ESI) calcd for $C_{28}H_{24}O_4NS$ $[M+H]^+$: 472.1577, Found: 472.1581.

1-(4-(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)phenyl)cyclobutane-1-carbonitrile (3q)



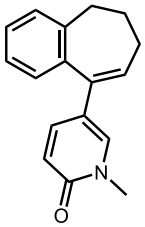
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1q** (0.2 mmol, 60 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 19:1) afforded **3q** as a colorless oil (42 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 7.30 – 7.21 (m, 2H), 7.04 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.51 (t, *J* = 7.4 Hz, 1H), 2.92 – 2.82 (m, 2H), 2.74 – 2.62 (m, 4H), 2.53 – 2.41 (m, 1H), 2.23 (app. p, *J* = 7.1 Hz, 2H), 2.17 – 2.07 (m, 1H), 2.03 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 142.1, 141.9, 139.8, 138.3, 129.1, 129.0, 128.6, 128.3, 127.2, 125.8, 125.4, 124.4, 39.9, 35.1, 34.6, 32.3, 25.3, 17.0.

HRMS (ESI) calcd for $C_{22}H_2N$ $[M+H]^+$: 300.1747, Found 300.1749.

5-(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)-1-methylpyridin-2(1*H*)-one (3r)



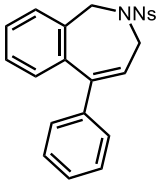
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1r** (0.2 mmol, 50 mg, 1.0 equiv) in DCE at 100 °C for 48 h. Purification by flash column chromatography (EtOAc) afforded **3r** as a brown solid (45 mg, 90% yield).

^{1}H NMR (500 MHz, $(CD_3)_2O$) δ 7.24 (d, *J* = 2.0 Hz, 1H), 7.09 (m, 2H), 7.04 – 6.94 (m, 2H), 6.83 (m, 1H), 6.16 (d, *J* = 9.5 Hz, 1H), 6.12 (t, *J* = 7.5 Hz, 1H), 3.26 (s, 3H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.90 (app. p, *J* = 7.0 Hz, 2H), 1.63 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (126 MHz, $(CD_3)_2O$) δ 162.6, 142.9, 140.5, 139.7, 139.2, 138.1, 129.6, 129.2, 128.2, 126.8, 126.7, 121.0, 119.9, 37.4, 35.8, 32.6, 25.6.

HRMS (ESI) calcd for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383, Found: 252.1393.

2-((4-nitrophenyl)sulfonyl)-5-phenyl-2,3-dihydro-1H-benzo[c]azepine (3s)



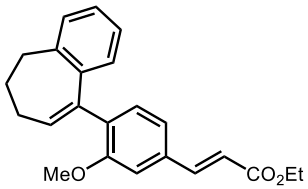
The title compound was prepared following a modified general procedure by reacting 2,6-dichloropyridinium bistriflimide (0.04 mmol, 17 mg, 0.2 equiv) and N-benzyl-4-nitro-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1s**) (0.2 mmol, 41 mg, 1.0 equiv) in DCE at 90 °C for 1.5 h. Purification by preparative-scale thin-layer chromatography (9:1 hexanes/EtOAc) afforded **3s** as a colorless oil (14 mg, 17% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.23 (m, 6H), 7.22 – 7.13 (m, 2H), 7.04 – 6.96 (m, 1H), 6.13 (t, *J* = 7.2 Hz, 1H), 4.35 (s, 2H), 3.77 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.1, 145.3, 140.2, 139.4, 134.0, 129.7, 129.6, 128.7, 128.5, 128.5, 128.5, 128.4, 124.3, 120.2, 49.9, 44.1.

HRMS (ESI) calcd for $C_{22}H_{19}O_2N_2S$ $[M+H]^+$: 407.1060, Found: 407.1070.

Ethyl (*E*)-3-(4-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)-3-methoxyphenyl)acrylate (3t)



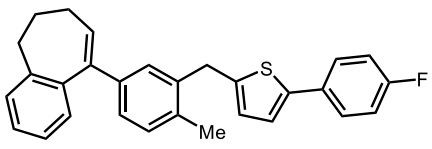
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1t** (0.2 mmol, 70 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 9:1) afforded **3t** as a yellow solid (47 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 3H), 7.02 (s, 1H), 6.89 – 6.83 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.35 (t, *J* = 7.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 2.79 (t, *J* = 6.9 Hz, 2H), 2.23 (app. p, *J* = 7.0 Hz, 2H), 2.05 (app. q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 157.5, 144.5, 141.2, 141.0, 139.8, 134.7, 134.6, 131.4, 130.7, 128.3, 127.3, 126.4, 125.5, 120.8, 117.8, 110.2, 60.4, 55.5, 34.8, 32.2, 25.3, 14.3.

HRMS (ESI) calcd for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1798, Found 349.1797.

2-(5-(6,7-Dihydro-5*H*-benzo[7]annulen-9-yl)-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (3u)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1u** (0.2 mmol, 85 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes/Et_2O 39:1) afforded **3u** as a colorless oil (57 mg, 66% yield).

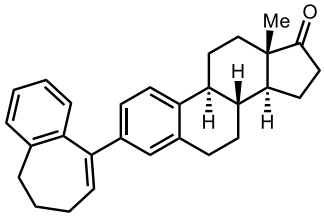
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.28 – 7.15 (m, 4H), 7.12 – 6.97 (m, 6H), 6.64 (d, *J* = 3.6 Hz, 1H), 6.43 (t, *J* = 7.3 Hz, 1H), 4.08 (s, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.31 (s, 3H), 2.17 (app. p, *J* = 7.0 Hz, 2H), 1.95 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 246.6 Hz), 143.9, 142.8, 142.4, 141.5, 140.5, 140.5, 138.0, 135.4, 131.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.5, 129.4, 129.3, 128.7, 128.0, 127.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.1, 126.8, 125.9, 125.9, 122.8, 115.8 (d, $J_{C\text{-}F}$ = 21.7 Hz), 35.4, 34.4, 32.5, 25.5, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ –115.2.

HRMS (ESI) calcd for $C_{29}H_{26}FS$ $[M+H]^+$: 425.1734, Found 425.1731.

(8*R*,9*S*,13*S*,14*S*)-3-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3v)



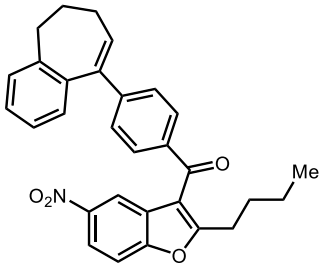
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1v** (0.2 mmol, 79 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes/EtOAc 9:1) afforded **3v** as a colorless oil (42 mg, 53% yield).

^{1}H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.25 – 7.14 (m, *J* = 13.4 Hz, 6H), 2.88 (dd, *J* = 8.8, 4.0 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.45 – 2.35 (m, *J* = 6.9 Hz, 3H), 2.34 – 2.25 (m, 1H), 2.20 – 1.87 (m, 7H), 1.62 (d, *J* = 15.2 Hz, 2H), 1.53 – 1.37 (m, 4H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 142.5, 142.1 140.2, 139.8, 138.6, 136.1, 129.2, 128.4, 128.3, 127.8, 126.9, 125.7, 125.3, 125.1, 50.4, 47.9, 44.4, 38.1, 35.8, 35.2, 32.3, 31.5, 29.4, 26.5, 25.7, 25.2, 21.5, 13.8.

HRMS (ESI) calcd for $C_{29}H_{33}O$ $[M+H]^+$: 397.2526, Found: 397.2526.

(2-Butyl-5-nitrobenzofuran-3-yl)(4-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)phenyl)methanone (3w)



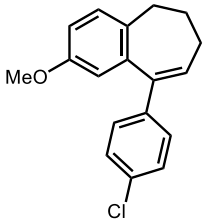
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1w** (0.2 mmol, 93 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes/EtOAc 4:1) afforded **3w** as a yellow oil (50 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.3 Hz, 1H), 8.22 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.32 – 7.27 (m, 1H), 7.27 – 7.19 (m, 2H), 7.06 – 6.96 (m, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.22 (app. p, *J* = 7.1 Hz, 2H), 2.04 (app. q, *J* = 7.4 Hz, 2H), 1.77 (app. p, *J* = 7.6 Hz, 2H), 1.36 (app. sex, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 167.9, 156.3, 147.4, 144.6, 142.1, 139.3, 136.8, 131.1, 129.2, 129.1, 128.7, 128.2, 127.7, 127.4, 126.0, 120.3, 117.8, 117.2, 111.4, 35.0, 32.3, 29.9, 28.0, 25.6, 22.3, 13.6.

HRMS (ESI) calcd for $C_{30}H_{28}NO_4$ $[M+H]^+$: 466.2013, Found: 466.1999.

9-(4-Methoxyphenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3x)



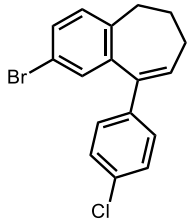
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1x** (0.2 mmol, 57 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes/acetone 199:1), followed by heating under vacuum at 70 °C for 24 h to remove residual dichloropyridine afforded **3x** as a yellow oil (46 mg, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.52 (d, *J* = 2.6 Hz, 1H), 6.42 (t, *J* = 7.4 Hz, 1H), 3.70 (s, 3H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.13 (app. p, *J* = 7.0 Hz, 2H), 1.97 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 142.1, 141.0, 140.7, 133.0, 129.6, 129.3, 128.4, 114.5, 113.2, 55.4, 35.1, 31.5, 25.5.

HRMS (ESI) calcd for $C_{18}H_{18}ClO$ $[M+H]^+$: 285.1041, Found 285.1041.

9-(4-Bromophenyl)-6,7-dihydro-5*H*-benzo[7]annulene (3y)



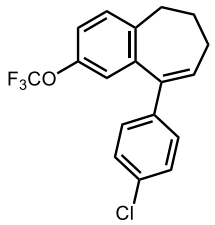
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1y** (0.2 mmol, 67 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes/Et_2O 39:1) afforded **3y** as a yellow oil (47 mg, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 6.46 (t, *J* = 7.4 Hz, 1H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.17 (app. p, *J* = 7.1 Hz, 2H), 1.97 (app. q, *J* = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 141.2, 141.1, 140.2, 133.3, 131.9, 130.5, 130.3, 130.1, 129.3, 128.6, 119.9, 35.0, 31.9, 25.4.

EA Calcd. for $C_{17}H_{14}BrCl$: C, 61.20; H, 4.23. Found: C, 61.23; H, 4.38.

9-(4-(Trifluoromethoxy)phenyl)-6,7-dihydro-5H-benzo[7]annulene (3z)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and **1z** (0.2 mmol, 68 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes) afforded **3z** as a yellow oil (32 mg, 47% yield).

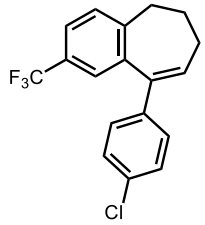
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 3H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.09 (bd, *J* = 8.3 Hz, 1H), 6.85 (bs, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.20 (app. p, *J* = 7.1 Hz, 2H), 1.99 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 141.7, 141.2, 141.1, 140.1, 133.4, 130.2, 130.0, 129.2, 128.6, 121.8, 120.6 (q, $J_{C\text{-}F}$ = 256.7 Hz), 119.9, 35.1, 31.9, 25.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ –58.0.

HRMS (ESI) calcd for $C_{18}H_{15}ClF_3O$ $[M+H]^+$: 339.0758, Found 339.0753.

9-(4-chlorophenyl)-2-(trifluoromethyl)-6,7-dihydro-5H-benzo[7]annulene (3aa)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-chloro-4-(5-(4-(trifluoromethyl)phenyl)pent-1-yn-1-yl)benzene (**1aa)** (0.2 mmol, 60 mg, 1.0 equiv) in DCE at 90 °C for 12 h. Purification by flash column chromatography (hexanes) afforded **3aa** as a colorless oil (7 mg, 12% yield).

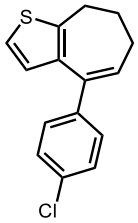
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.22 (s, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.51 (t, *J* = 7.4 Hz, 1H), 6.51 (t, *J* = 7.4 Hz, 1H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.22 (app. p, *J* = 7.1, 2H), 1.97 (app. q, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 141.2, 140.7, 140.1, 133.5, 130.3, 129.3, 129.2, 128.7, 125.9 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 272.1 Hz), 124.1 (q, *J* = 3.5 Hz), 35.2, 32.4, 25.4.
(signal *ipso* to CF_3 group not observed)

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.3.

HRMS (ESI) calcd for $C_{18}H_{14}ClF_3$ $[M\cdot]^+$: 322.0731, Found: 322.0740.

4-(4-chlorophenyl)-7,8-dihydro-6H-cyclohepta[b]thiophene (3ab)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 2-(5-(4-chlorophenyl)pent-4-yn-1-yl)thiophene (**1ab**) (0.2 mmol, 52 mg, 1.0 equiv) in chloroform at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3ab** as a colorless oil (21 mg, 40% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 5.2 Hz, 1H), 6.67 (d, *J* = 5.2 Hz, 1H), 6.30 – 6.25 (m, 1H), 2.91 – 2.85 (m, 2H), 2.26 – 2.18 (m, 4H).

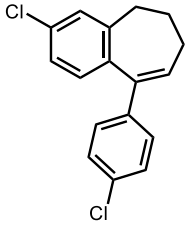
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 140.9, 138.2, 137.0, 132.9, 130.0, 129.0, 128.8, 128.2, 120.7, 34.1, 27.9, 27.2.

HRMS (ESI) calcd for $C_{15}H_{14}ClS$ $[M+H]^+$: 261.0499, Found: 261.0499.

3-chloro-9-(4-chlorophenyl)-6,7-dihydro-5H-benzo[7]annulene (3ac(1)) and 1-chloro-9-(4-chlorophenyl)-6,7-dihydro-5H-benzo[7]annulene (3ac(2))

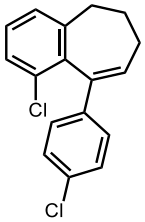
The title compounds were prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-chloro-3-(5-(4-chlorophenyl)pent-4-yn-1-yl)benzene **1ac** (0.2 mmol, 58 mg, 1.0 equiv) in DCE at 90 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3ac(1)** (19 mg, 33% yield) and **3ac(2)** (13 mg, 22% yield) as colorless oils.

3-chloro-9-(4-chlorophenyl)-6,7-dihydro-5H-benzo[7]annulene (3ac(1))



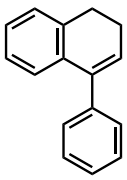
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 3H), 7.20 – 7.14 (m, 3H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.44 (t, *J* = 7.4 Hz, 1H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.19 (app. p, *J* = 7.1 Hz, 2H), 1.98 (app. q, *J* = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 141.2, 140.4, 138.3, 133.1, 132.7, 130.4, 129.5, 129.4, 129.1, 128.7, 128.4, 126.1, 34.9, 32.3, 25.3.
HRMS (ESI) calcd for $C_{17}H_{15}Cl_2$ $[M+H]^+$: 289.0545, Found: 289.0556.

1-chloro-9-(4-chlorophenyl)-6,7-dihydro-5H-benzo[7]annulene (3ac(2))



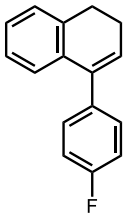
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.55 (t, *J* = 7.4 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.19 – 2.00 (m, 3H), 1.86 – 1.75 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 140.0, 139.9, 137.0, 133.6, 132.6, 131.4, 128.8, 128.6, 128.4, 127.5, 127.0, 33.9, 32.5, 24.9.
HRMS (ESI) calcd for $C_{17}H_{15}Cl_2$ $[M+H]^+$: 289.0545, Found: 289.0554.

4-Phenyl-1,2-dihydronaphthalene (3ad)



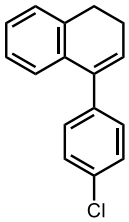
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and but-1-yne-1,4-diyldibenzene (**1ad**) (0.2 mmol, 41 mg, 1.0 equiv) in $CHCl_3$ at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3ad** as a colorless oil (26 mg, 63% yield) with spectral properties identical to those reported in the literature.[3]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.21 – 7.08 (m, 3H), 7.04 – 6.97 (m, 1H), 6.10 (t, *J* = 4.7 Hz, 1H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.48 – 2.36 (m, 2H).

4-(4-Fluorophenyl)-1,2-dihydronaphthalene (3ae)



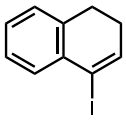
The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-fluoro-4-(4-phenylbut-1-yn-1-yl)benzene (**1ae**) (0.2 mmol, 45 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3ae** as a colorless oil (32 mg, 71% yield) with spectral properties identical to those reported in the literature.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.00 (m, 8H), 6.05 (t, *J* = 4.7 Hz, 1H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.45 – 2.34 (m, 2H).

4-(4-Chlorophenyl)-1,2-dihydronaphthalene (3af)



The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and 1-chloro-4-(4-phenylbut-1-yn-1-yl)benzene (**1af**) (0.2 mmol, 48 mg, 1.0 equiv) in DCE at 70 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3af** as a colorless oil (33 mg, 69% yield) with spectral properties identical to those reported in the literature.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.04 (m, 7H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.04 (t, *J* = 4.7 Hz, 1H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.41 – 2.32 (m, 2H).

4-Iodo-1,2-dihydronaphthalene (3ag)

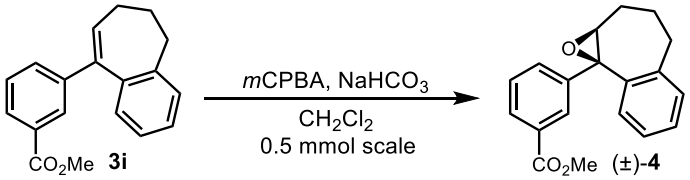


The title compound was prepared following the general procedure by reacting 2,6-dichloropyridinium trifluoromethanesulfonate (0.2 mmol, 60 mg, 1.0 equiv) and (4-iodobut-3-yn-1-yl)benzene (**1ag**) (0.2 mmol, 51 mg, 1.0 equiv) in DCE at 90 °C for 6 h. Purification by flash column chromatography (hexanes) afforded **3ag** as a colorless oil with spectral properties identical to those reported in the literature[5] (23 mg, 45% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 11.0, 4.5 Hz, 1H), 7.16 (td, *J* = 7.4, 1.2 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.38 – 2.30 (m, 2H).

6. Product derivatizations

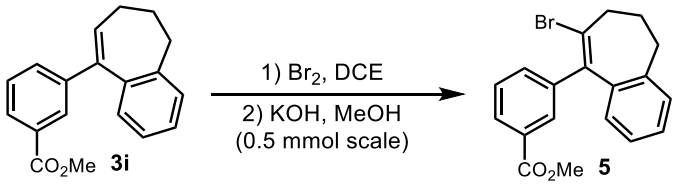
Epoxidation:



To a 50 mL round-bottom flask equipped with a magnetic stir bar and charged with **3i** (0.5 mmol, 139 mg, 1 equiv) and CH_2Cl_2 (20 mL) was added *m*-CPBA (0.6 mmol, 142 mg, 1.2 equiv), and $NaHCO_3$ (2 mmol, 168 mg, 2 equiv) sequentially at 0 °C. The reaction mixture was stirred at that temperature for 1 h, allowed to warm to room temperature, and then stirred for an additional 6 h. The reaction mixture was quenched with saturated aqueous Na_2SO_3 (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography (hexanes/EtOAc 9:1) to afford **4** as a white solid.[6]

Methyl 3-(1a,2,3,4-tetrahydro-8b*H*-benzo[3,4]cyclohepta[1,2-b]oxiren-8b-yl)benzoate (4)
White solid (108 mg, 73% yield)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (bd, *J* = 8.8 Hz, 1H), 7.85 (bs, 1H), 7.38 – 7.27 (m, 5H), 7.19 (bd, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 3.21 (dd, *J* = 9.0, 4.9 Hz, 1H), 3.03 (td, *J* = 12.9, 7.7 Hz, 1H), 2.73 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.33 – 2.24 (m, 1H), 1.99 – 1.88 (m, 1H), 1.78 – 1.70 (m, 1H), 1.12 – 1.03 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 141.7, 137.7, 136.8, 130.7, 130.7, 129.6, 129.0, 128.9, 128.8, 128.5, 127.7, 126.9, 64.7, 61.9, 52.2, 30.9, 28.0, 21.4.
HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, Found 295.1327.

Dibromination/elimination to give vinyl bromide:



To a reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was added **3i** (0.5 mmol, 139 mg, 1 equiv), followed by a solution of Br_2 (0.55 mmol, 88 mg, 1.2 equiv) in DCE (1 mL) dropwise by Pasteur pipette. The reaction mixture was stirred at room temperature for 5 min. At this point no further color change was observed, and the solution remained a pale orange color. A solution of KOH (1.8 mmol, 100 mg, 3.6 equiv) in MeOH (2 mL) was then added by Pasteur pipette. The reaction mixture was stirred at room temperature for 10 min. Passage of the crude reaction mixture through a pad of silica gel using CH_2Cl_2 as an eluent and removal of volatile material *in vacuo* afforded pure **5** without further purification.[7]

Methyl 3-(8-bromo-6,7-dihydro-5*H*-benzo[7]annulen-9-yl)benzoate (5)

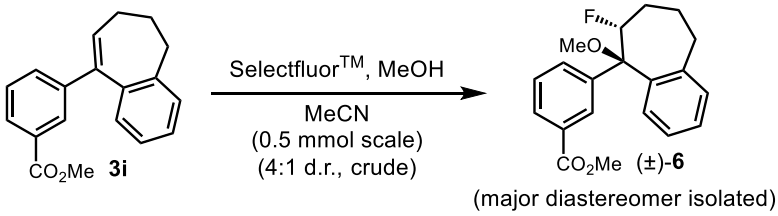
Yellow oil (174 mg, 97% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 1H), 7.92 (s, 1H), 7.46 (bd, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.20 (td, *J* = 7.4, 0.9 Hz, 1H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.33 (app. p, *J* = 7.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 142.5, 140.8, 140.7, 140.2, 134.5, 131.0, 130.1, 129.2, 129.0, 128.6, 128.1, 127.7, 126.3, 123.6, 52.1, 37.9, 34.1, 31.9.

HRMS (ESI) calcd for $C_{19}H_{18}O_2Br$ $[M+H]^+$: 357.0485, Found 357.0481.

Fluoromethoxylation:



A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar and charged with Selectfluor™ (6 mmol, 212 mg, 1.2 equiv) was added a solution of **3i** (0.5 mmol, 139 mg, 1 equiv) in MeCN (5 mL) and MeOH (0.5 mL). The reaction mixture was stirred at room temperature for 8 h and then quenched with saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the crude material as a mixture of diastereomers (4:1 d.r.). Purification by silica gel column chromatography (hexanes/Et_2O 19:1) afforded **6** as a single diastereomer.[8]

Methyl 3-(6-fluoro-5-methoxy-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)benzoate (6)

Colorless oil (125 mg, 76% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.17 (m, *J* = 15.5, 6.9 Hz, 1H), 5.09 (ddd, *J* = 46.2, 8.8, 3.2 Hz, 1H), 3.90 (s, 3H), 3.20 (s, 3H), 3.01 (dd, *J* = 13.5, 10.6 Hz, 1H), 2.61 (dd, *J* = 13.1, 8.9 Hz, 1H), 2.42 – 2.26 (m, 1H), 2.07 – 1.93 (m, *J* = 13.3 Hz, 1H), 1.87 – 1.68 (m, *J* = 20.1, 15.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 142.9, 141.7, 137.8 (d, $J_{C\text{-}F}$ = 4.7 Hz), 133.9 (d, $J_{C\text{-}F}$ = 4.2 Hz), 131.2, 130.5, 130.3 (d, $J_{C\text{-}F}$ = 4.3 Hz), 130.2, 129.2, 128.5, 128.2, 126.4, 94.4 (d, $J_{C\text{-}F}$ = 181.2 Hz), 86.7 (d, $J_{C\text{-}F}$ = 19.6 Hz), 52.6 (d, $J_{C\text{-}F}$ = 1.5 Hz), 52.2, 35.9, 31.9, 31.7, 23.2 (d, $J_{C\text{-}F}$ = 8.9 Hz).

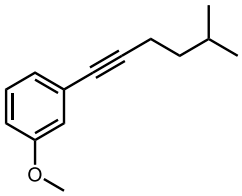
^{19}F NMR (376 MHz, $CDCl_3$) δ –180.8 (bs).

HRMS (ESI) calcd for $C_{20}H_{21}O_3F$ $[M^{+\cdot}]$: 328.1469, Found 328.1457.

7. Cyclization through C−H insertion

Substrate synthesis:

1-Methoxy-3-(5-methylhex-1-yn-1-yl)benzene (7)



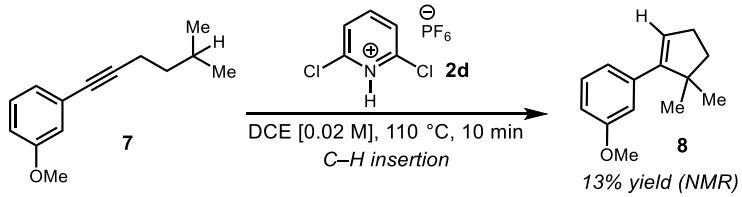
Prepared using Method A from 5-methyl-1-hexyne and 3-iodoanisole. Hexanes:Et_2O (39:1) was used as the eluent to give the title product as a yellow oil (786 mg, 78% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.94 – 6.91 (m, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.79 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.84 – 1.68 (m, *J* = 13.3, 6.7 Hz, 1H), 1.51 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 129.4, 125.3, 124.3, 116.6, 114.2, 90.5, 80.5, 55.4, 37.8, 27.5, 22.4, 17.6.

HRMS (ESI) calcd for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, Found 203.1425.

Formal C−H insertion to give cyclopentene derivative:



A 15 mL plastic tube (VWR part # 76211-284) equipped with a magnetic stir bar was transferred into an argon-filled glovebox. In the glovebox, 2,6-dichloropyridinium hexafluorophosphate (0.2 mmol, 59 mg, 1.0 equiv), DCE (10 mL) and **7** (0.2 mmol, 40 mg, 1.0 equiv) were added in succession. The tube was sealed and removed from the glovebox. After stirring at 110°C for 10 min, the reaction mixture was cooled to room temperature and passed through a pad of silica gel with the aid of suction using CH_2Cl_2 as eluent. The filtrate was concentrated *in vacuo* and an NMR yield (13%) was assessed using a known mass of 1,1,2,2-tetrachloroethane as an internal standard. The crude product was purified twice successively by preparative-scale thin-layer chromatography (hexanes/toluene 49:1) to afford a small sample of **8** as a colorless oil.

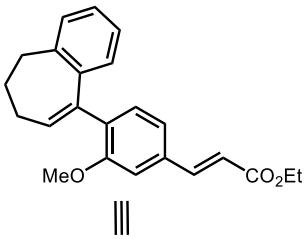
1-(5,5-Dimethylcyclopent-1-en-1-yl)-3-methoxybenzene (8)

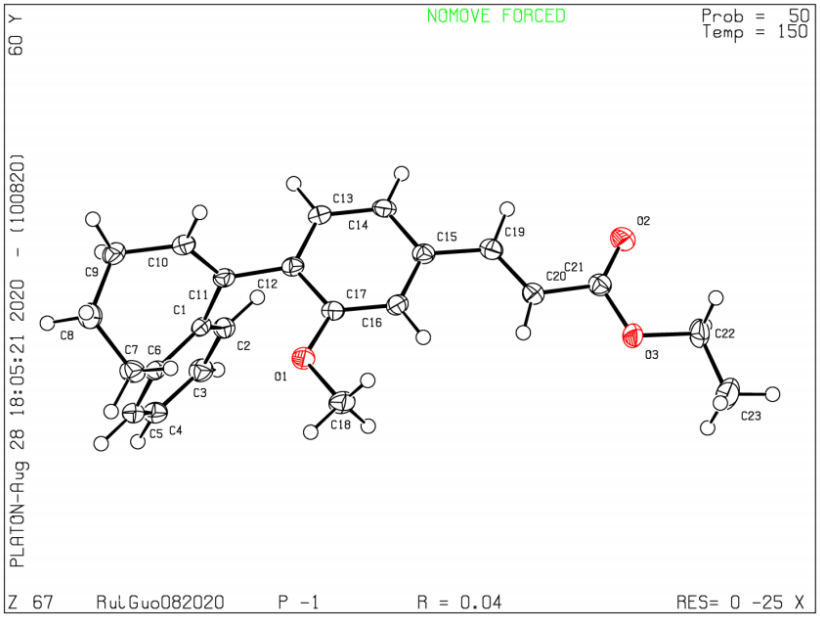
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 1H), 6.92 (bd, *J* = 7.7 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.79 (ddd, *J* = 8.3, 2.5, 0.6 Hz, 1H), 5.74 (t, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 2.36 (td, *J* = 7.0, 2.5 Hz, 2H), 1.85 (t, *J* = 7.0 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 152.1, 139.6, 129.0, 127.8, 120.3, 113.6, 112.0, 55.3, 46.8, 42.6, 29.5, 27.6.

HRMS (ESI) calcd for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, Found 203.1424.

8. X-ray crystallographic data for product 3t





Datablock: RuiGuo082020

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Bond precision:  C-C = 0.0019 A          Wavelength=1.54178

Cell:          a=8.3486(2)       b=10.8563(2)      c=11.6441(2)
               alpha=62.4089(9)  beta=80.6019(9)   gamma=88.2485(10)
Temperature:   150 K

                 Calculated                Reported
Volume           921.56(3)                 921.56(3)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C23 H24 O3                ?
Sum formula      C23 H24 O3                C23 H24 O3
Mr               348.42                    348.42
Dx,g cm-3        1.256                     1.256
Z                2                         2
Mu (mm-1)        0.650                     0.650
F000             372.0                     372.0
F000'            373.09
h,k,lmax         10,13,14                  10,12,14
Nref             3368                      3290
Tmin,Tmax        0.890,0.984               0.890,0.980
Tmin'            0.884

Correction method= # Reported T Limits: Tmin=0.890 Tmax=0.980
AbsCorr = MULTI-SCAN

Data completeness= 0.977          Theta(max)= 68.290

R(reflections)= 0.0445( 3010)     wR2(reflections)= 0.1221( 3290)

S = 1.089                  Npar= 335
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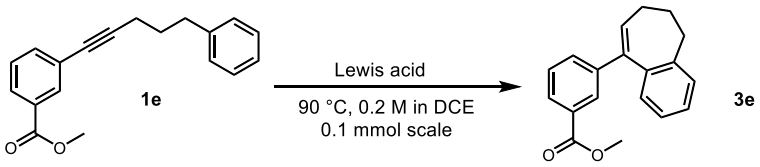
9. Experiments using Lewis acids

Table S1. Comparison with other Lewis acidic promoters



Entry	Acid (1.0 equiv)	Time [h]	NMR yield [%]
1	$Zn(OTf)_2$	12	0
2	$Cu(OTf)_2$	12	<5
3	$In(OTf)_3$	12	16
4	$Bi(OTf)_3$	12	57

10. References

[1] Lv, L.; Yu, L.; Qiu, Z.; Li, C.-J. Switch in Selectivity for Formal Hydroalkylation of 1,3-Dienes and Enynes with Simple Hydrazones. *Angew. Chem. Int. Ed.* **2020**, *59*, 6466.

[2] Stavber, G.; Zupan, M.; Stavber, S. Iodine Induced Transformations of Alcohols under Solvent-Free Conditions. *Tetrahedron Lett.* **2006**, *47*, 8463.

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[4] Wilson, K. L.; Murray, J.; Jamieson, C.; Watson, A. J. B. Cyrene as a Bio-Based Solvent for the Suzuki–Miyaura Cross-Coupling. *Synlett* **2018**, 650.

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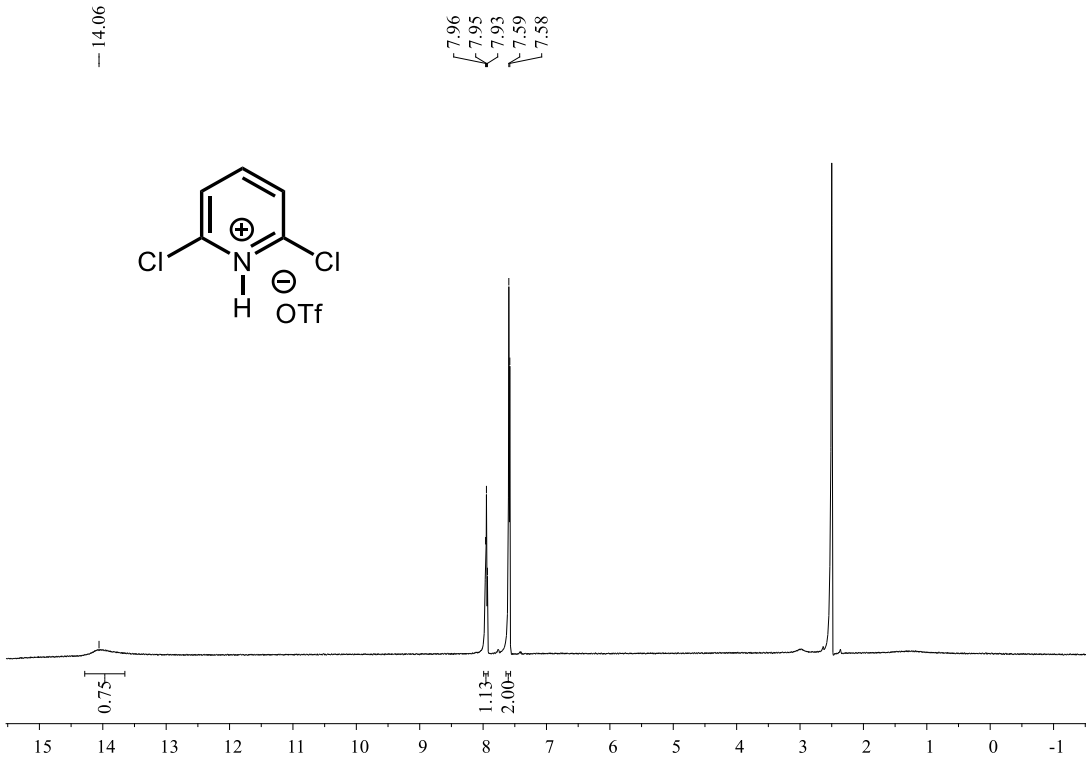
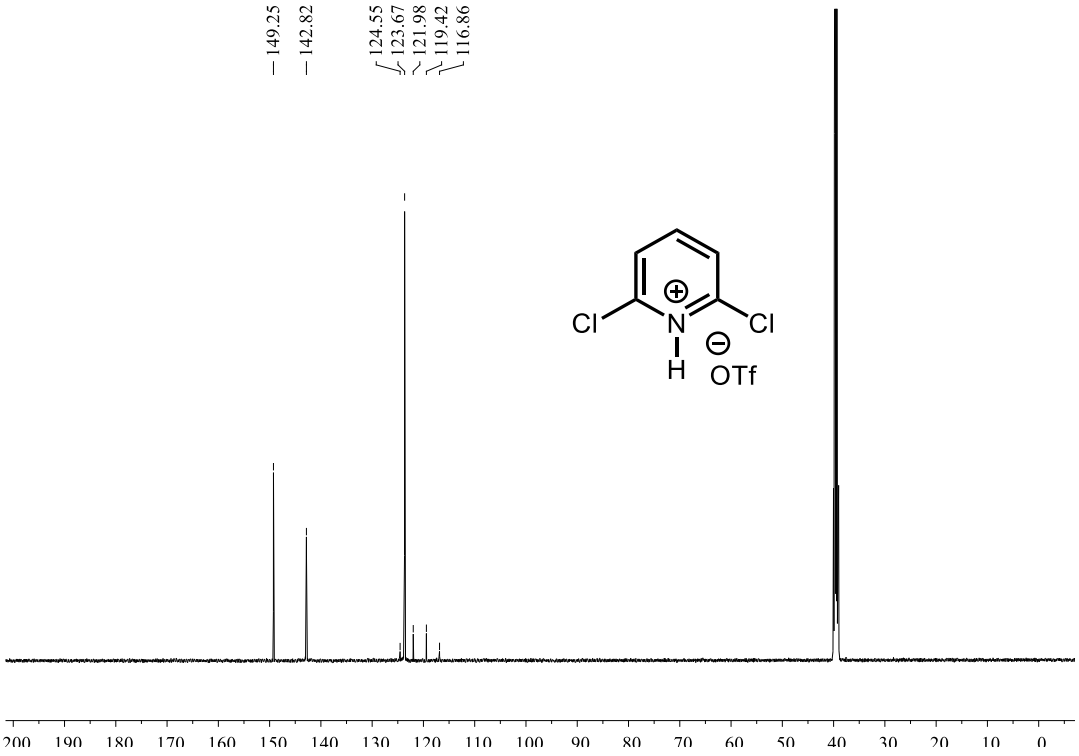
11. Copies of NMR spectra

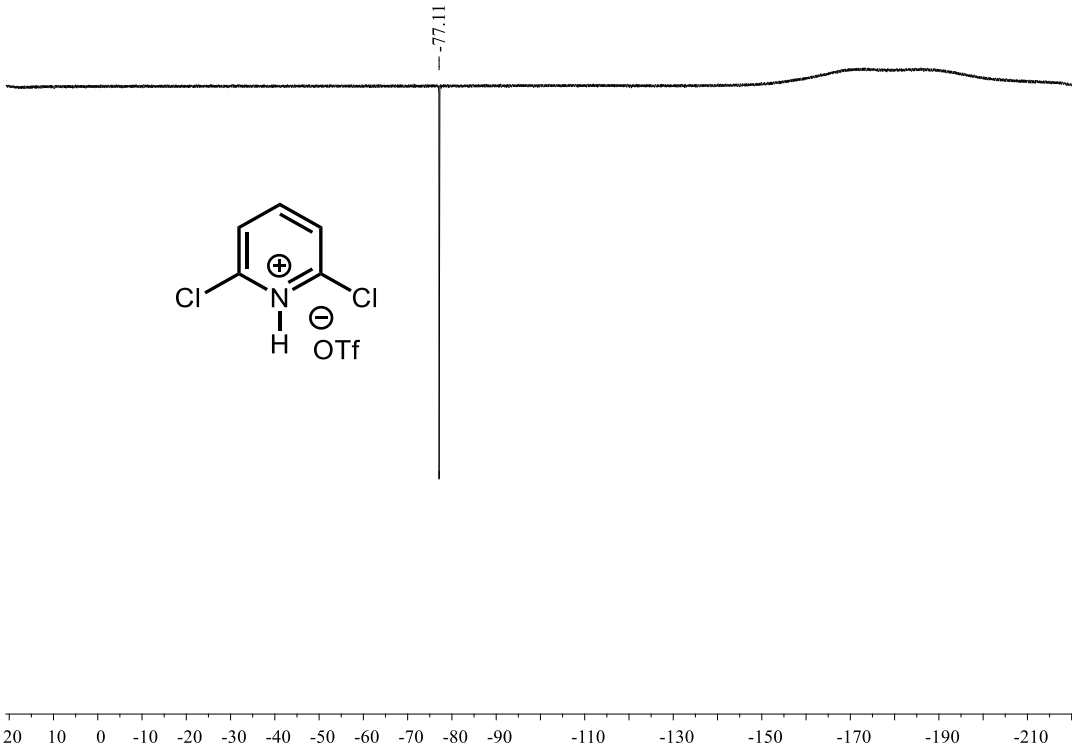
^{1}H NMR (500 MHz, DMSO-d_6) **(2b)**



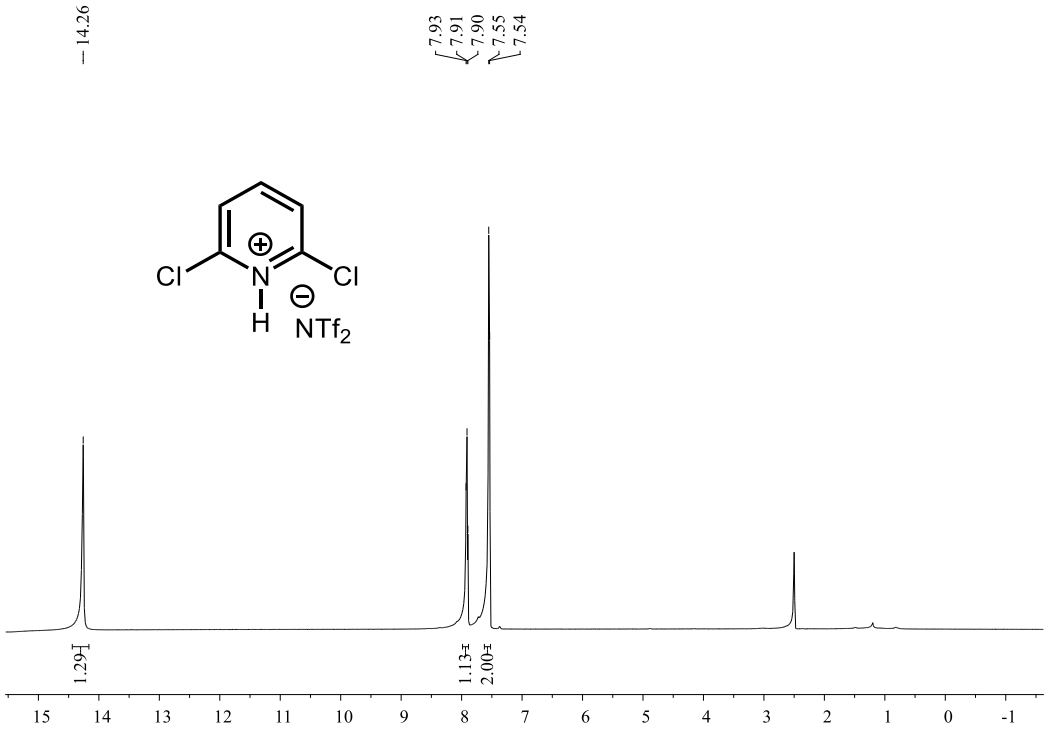
^{13}C NMR (126 MHz, $CDCl_3$ DMSO-d_6) **(2b)**



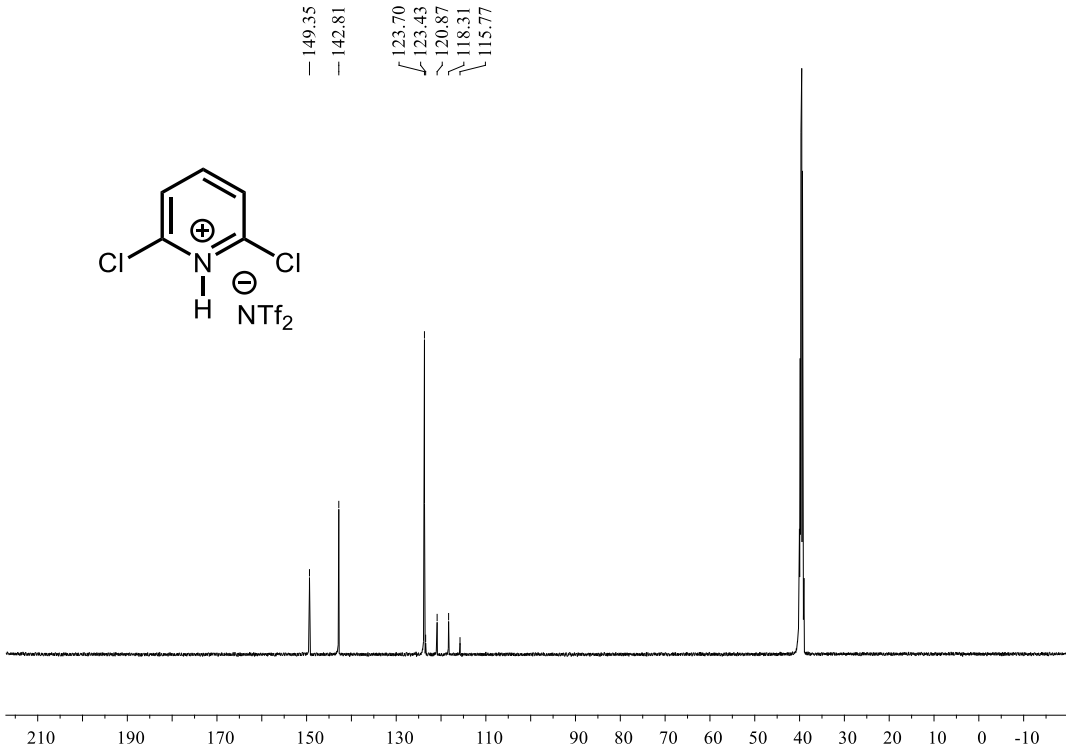
^{19}F NMR (471 MHz, DMSO-d_6) **(2b)**



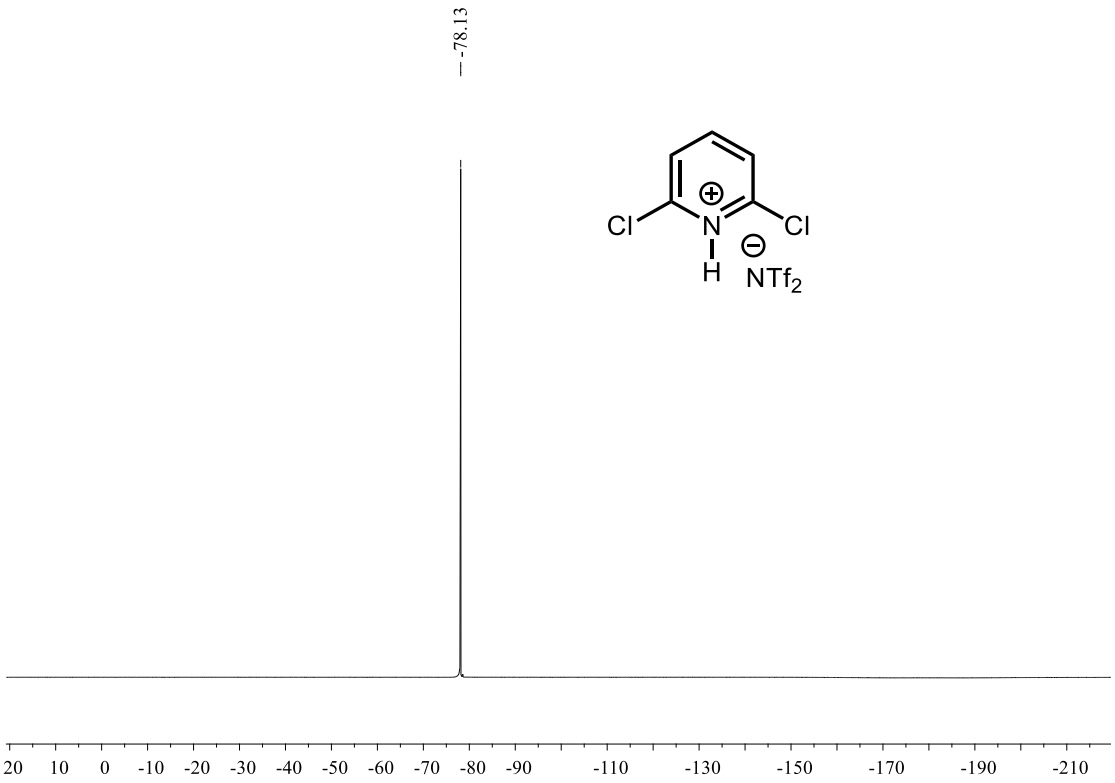
^{1}H NMR (500 MHz, DMSO-d_6) **(2c)**



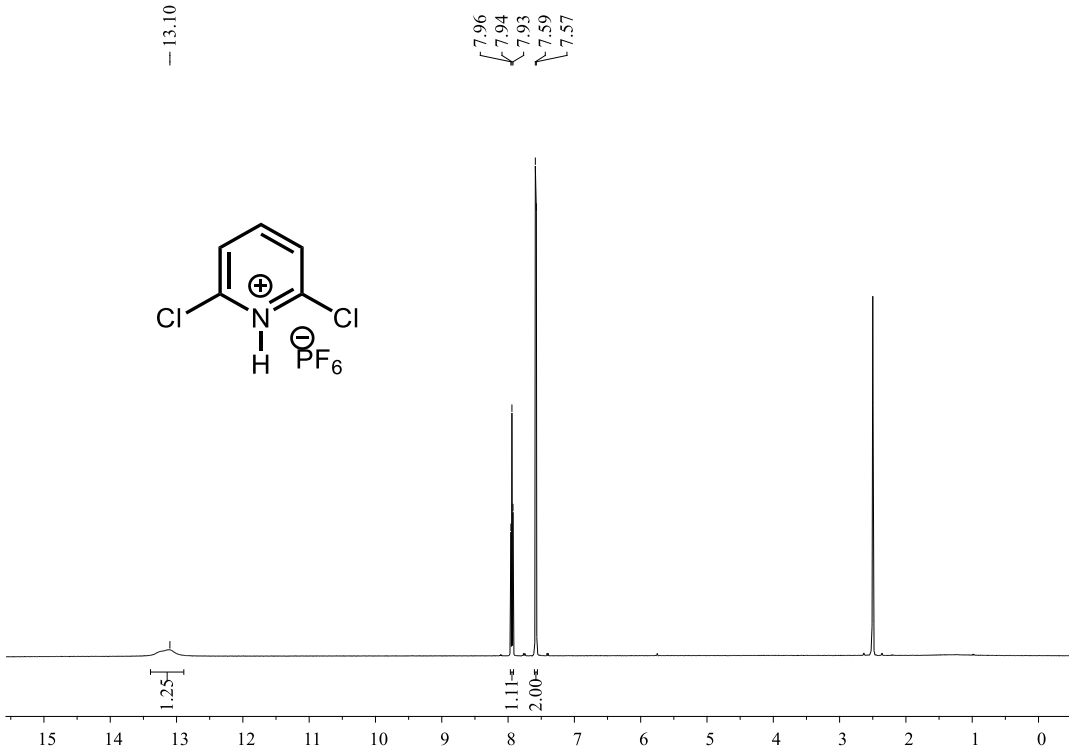
^{13}C NMR (126 MHz, DMSO-d_6) **(2c)**



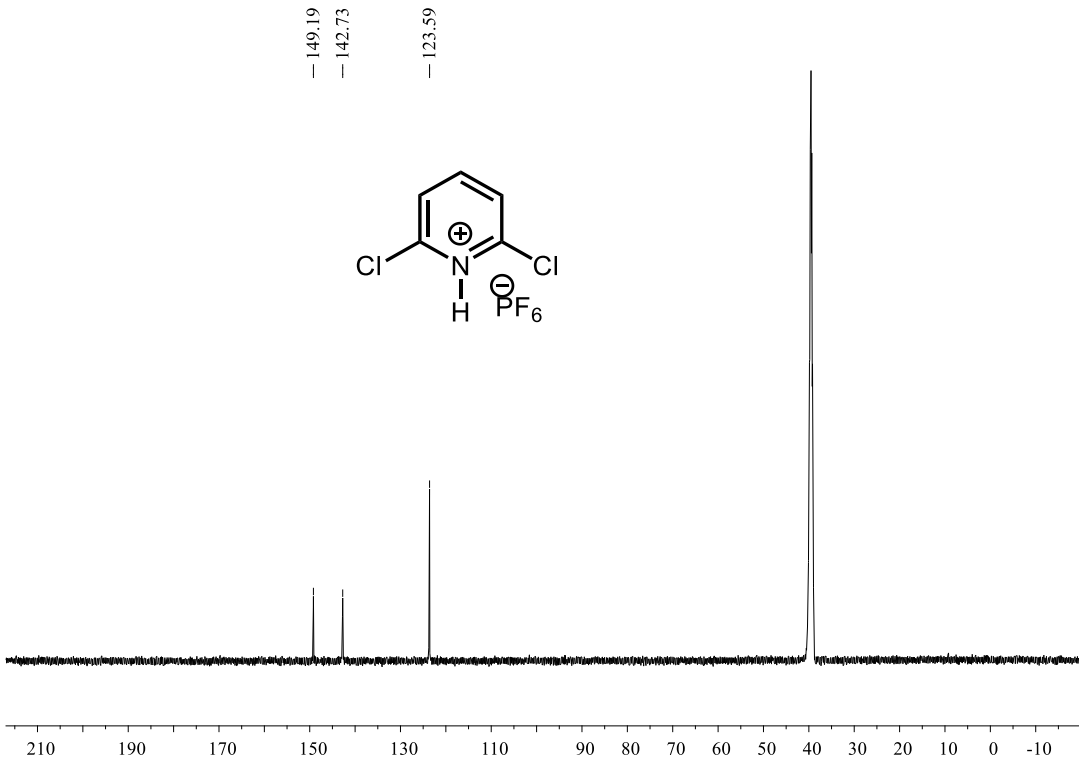
^{19}F NMR (471 MHz, DMSO-d_6) **(2c)**



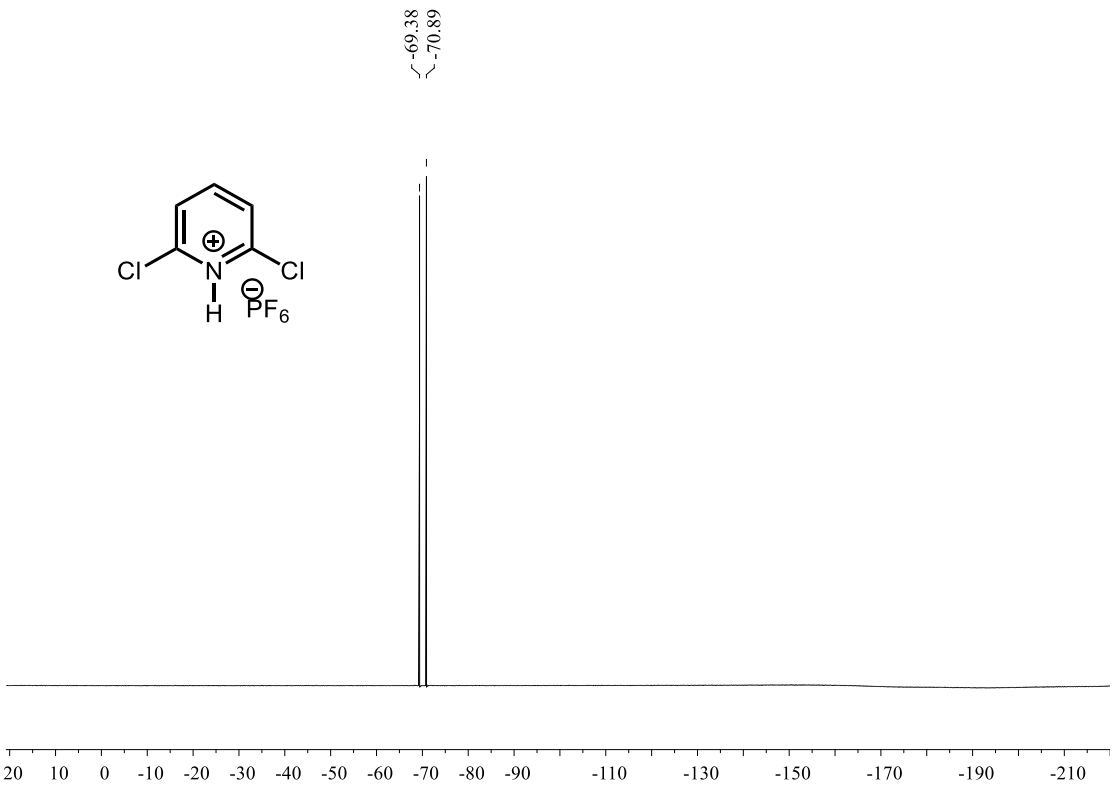
^{1}H NMR (500 MHz, DMSO-d_6) **(2d)**



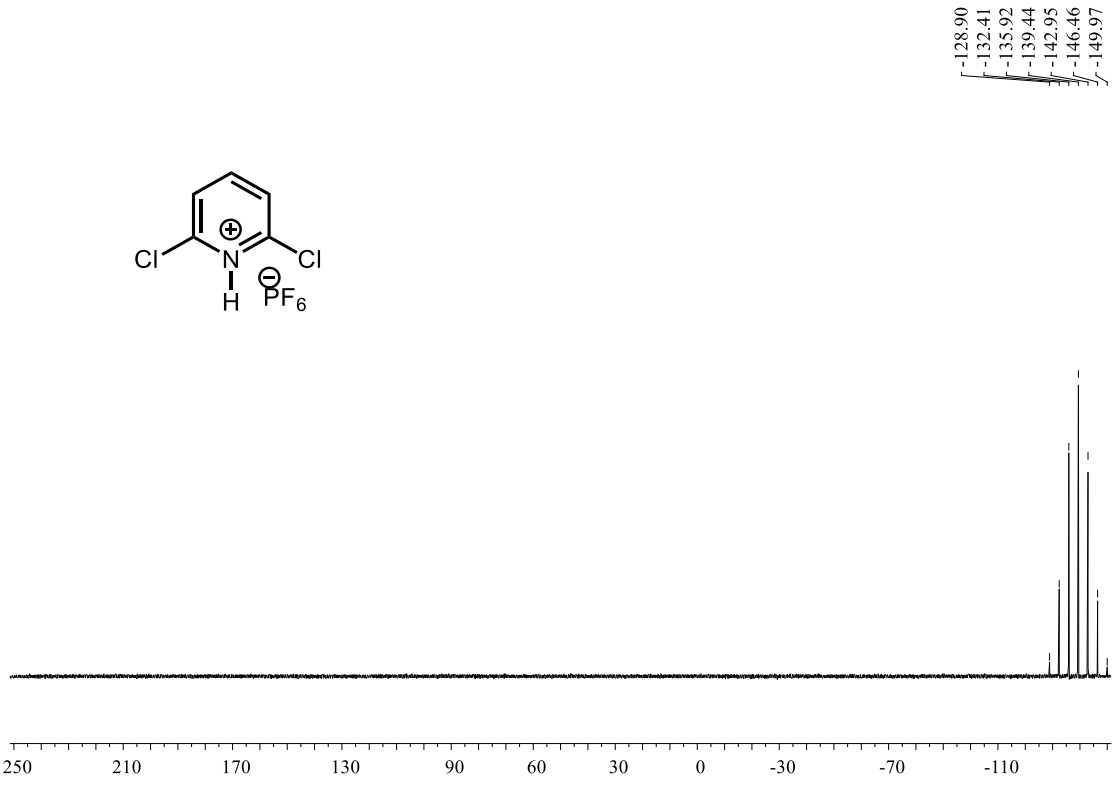
^{13}C NMR (126 MHz, DMSO-d_6)



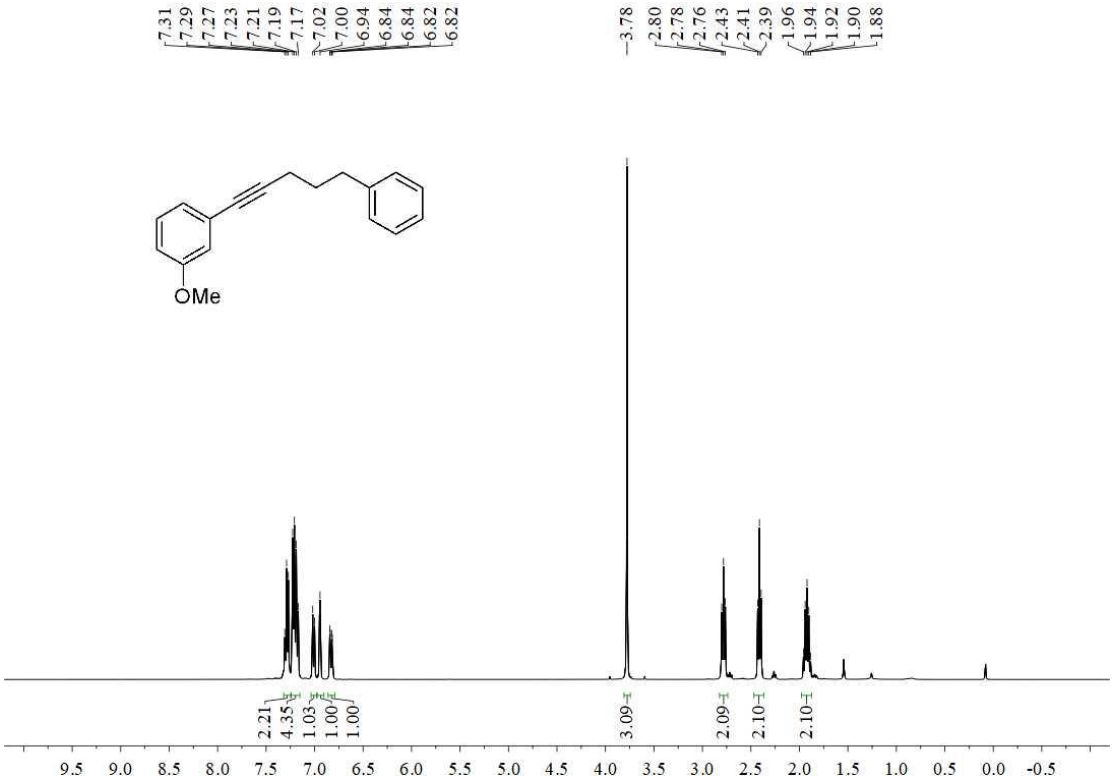
^{19}F NMR (471 MHz, DMSO-d_6) **(2d)**



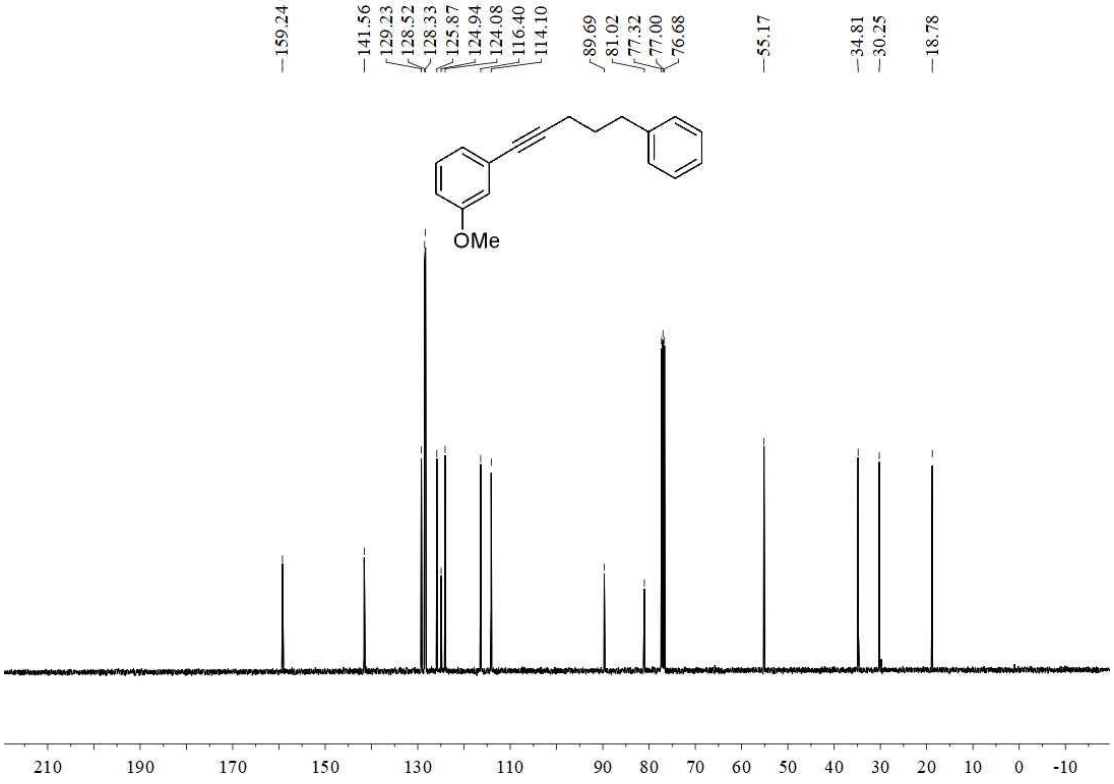
^{31}P NMR (202 MHz, DMSO-d_6) **(2d)**



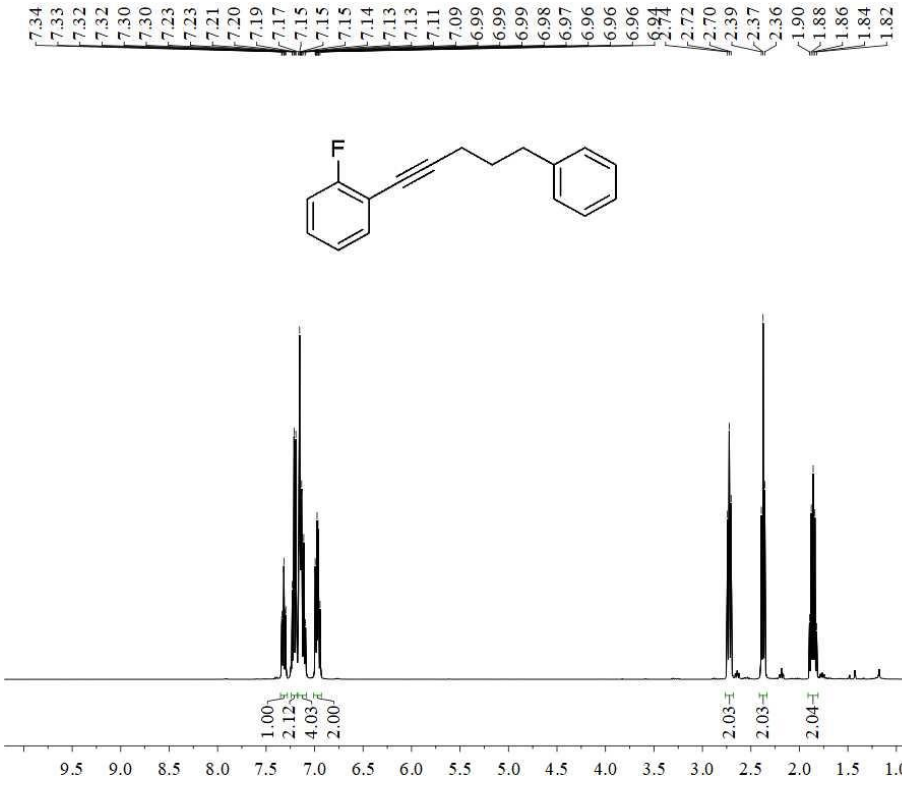
^{1}H NMR (400 MHz, $CDCl_3$) **(1h)**



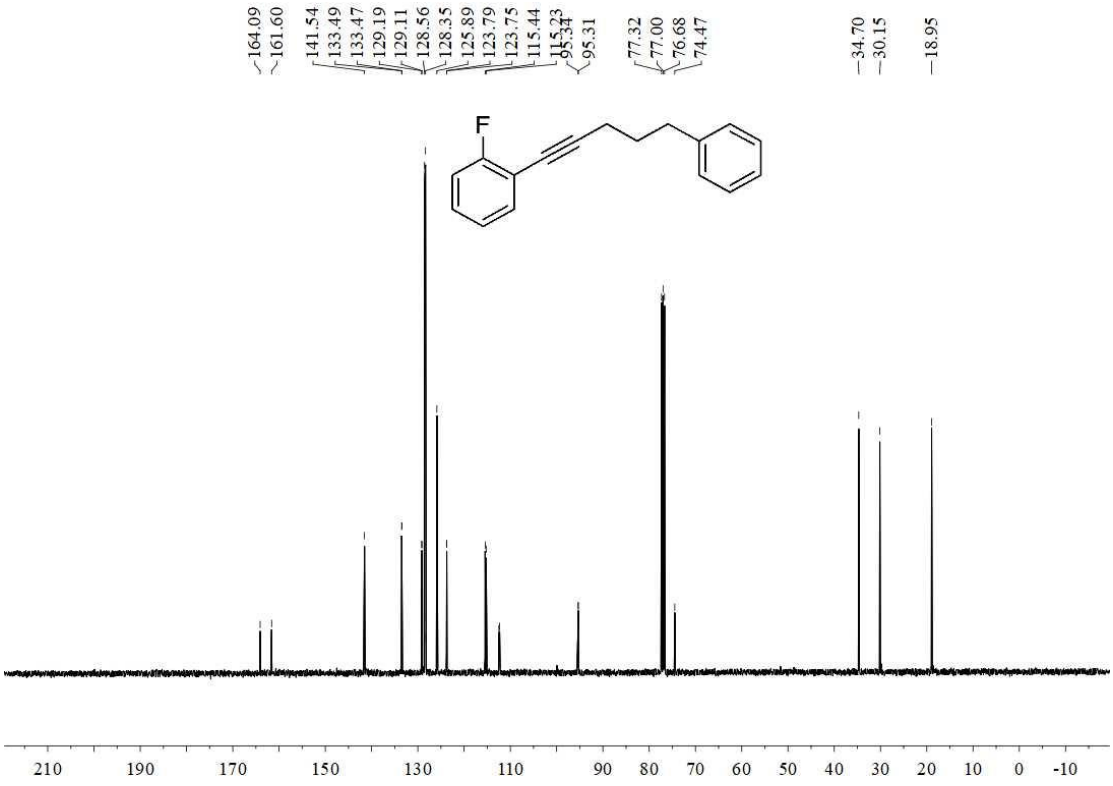
^{13}C NMR (101 MHz, $CDCl_3$) **(1h)**



^{1}H NMR (400 MHz, $CDCl_3$) **(1l)**

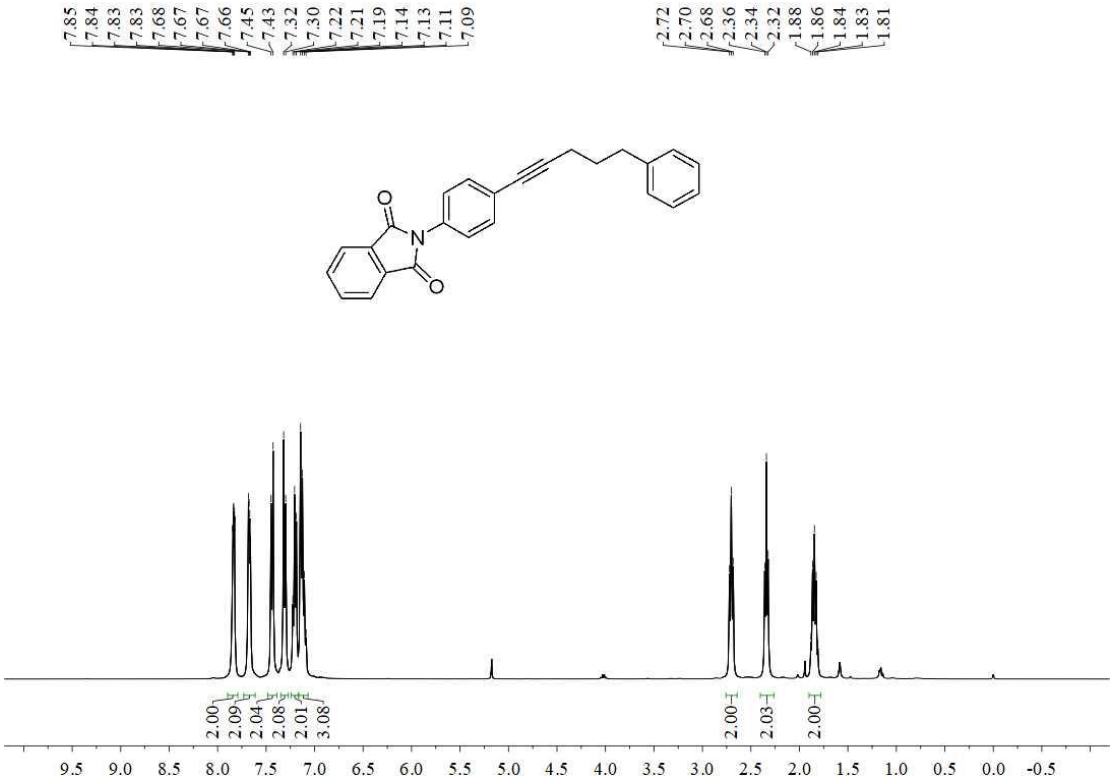


^{13}C NMR (101 MHz, $CDCl_3$) **(1l)**

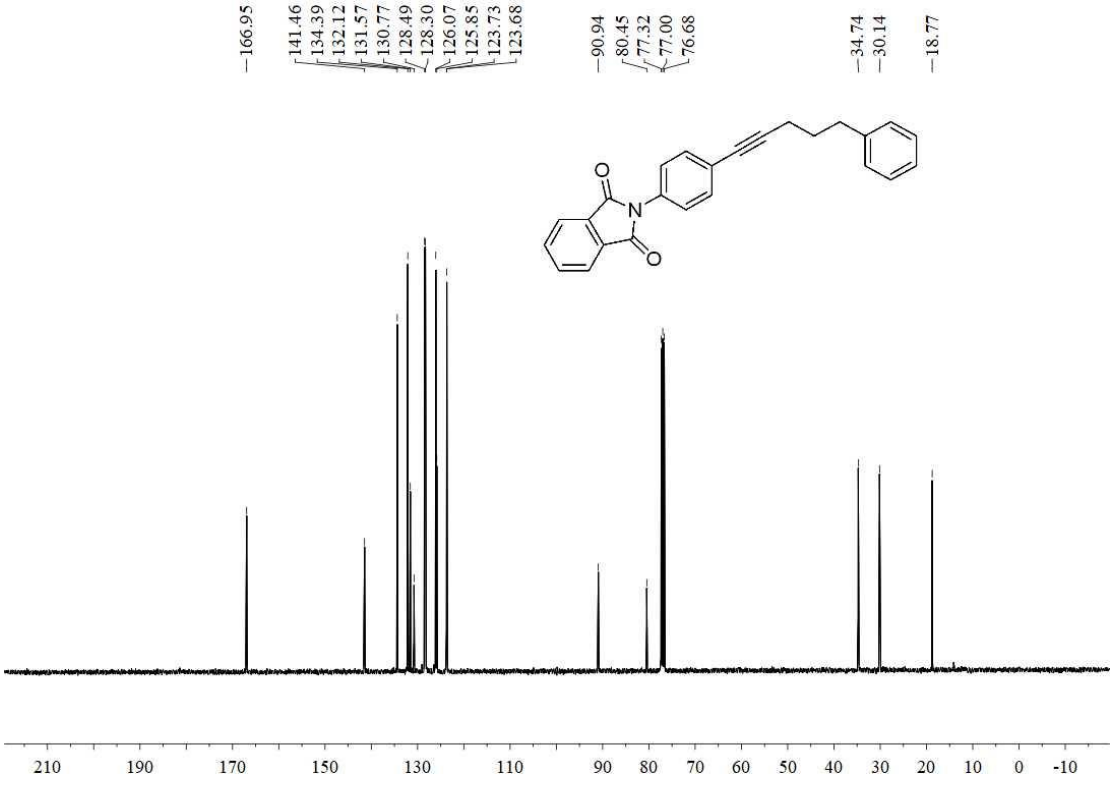


^{19}F NMR (282 MHz, $CDCl_3$) **(1l)**

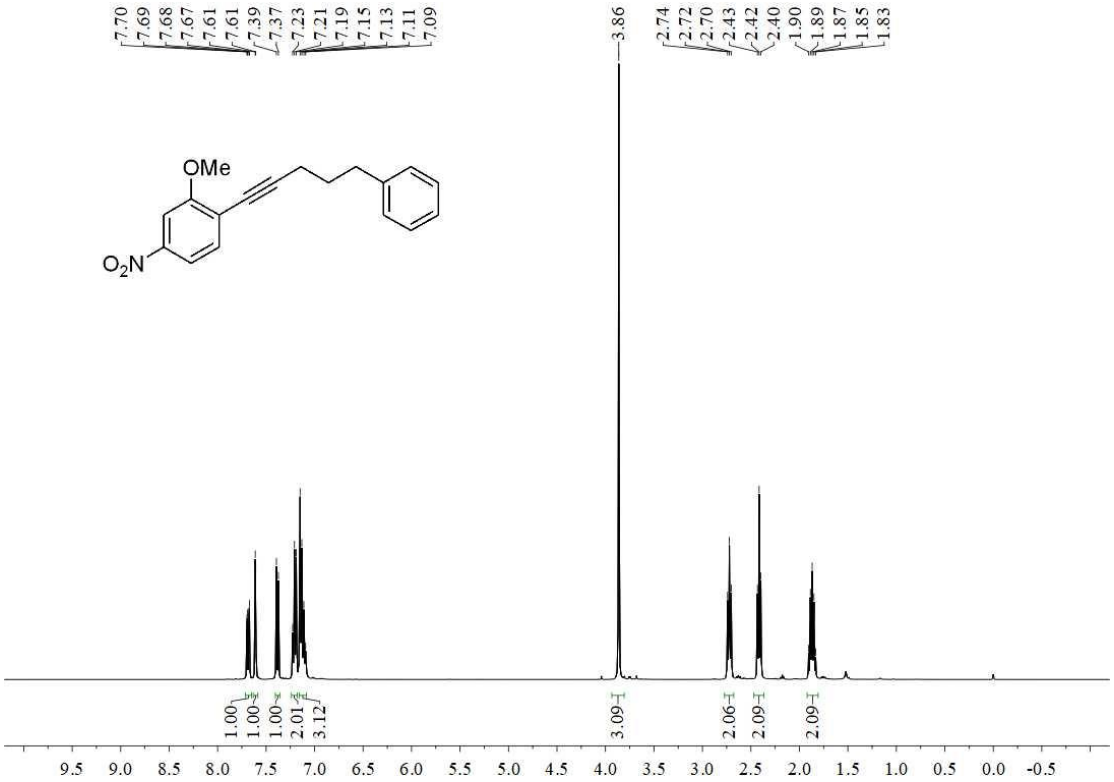
^{1}H NMR (400 MHz, $CDCl_3$) **(1m)**



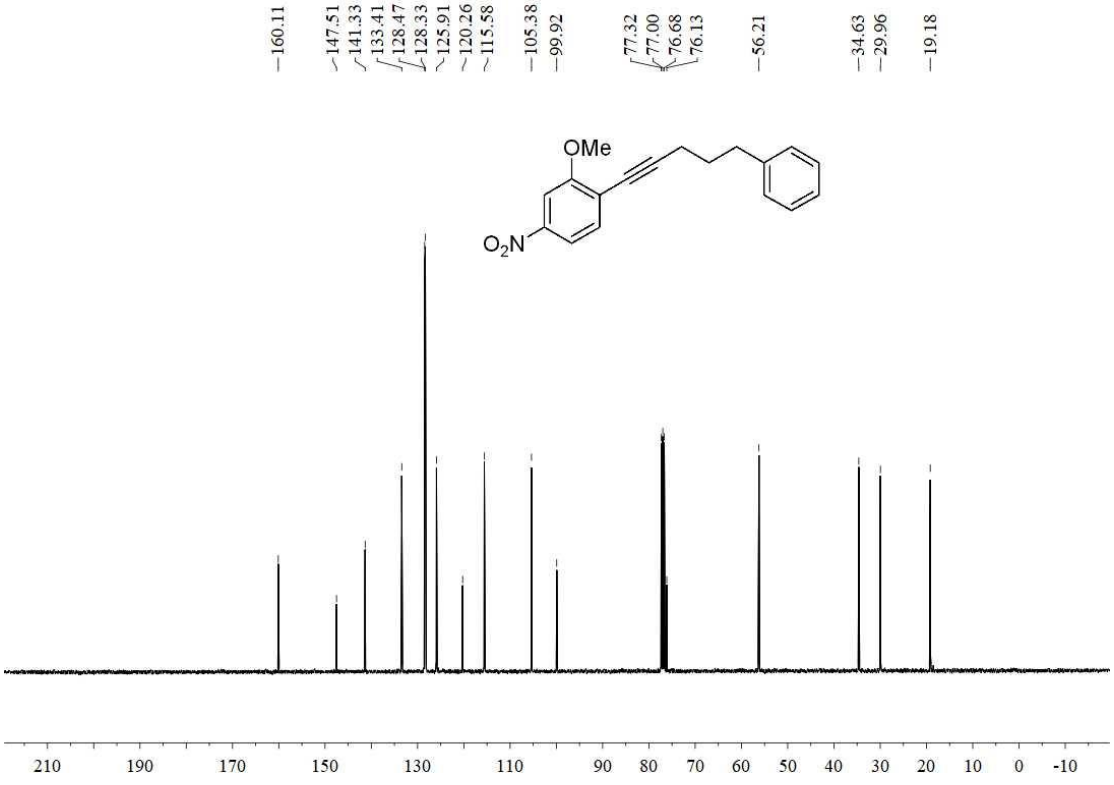
^{13}C NMR (101 MHz, $CDCl_3$) **(1m)**



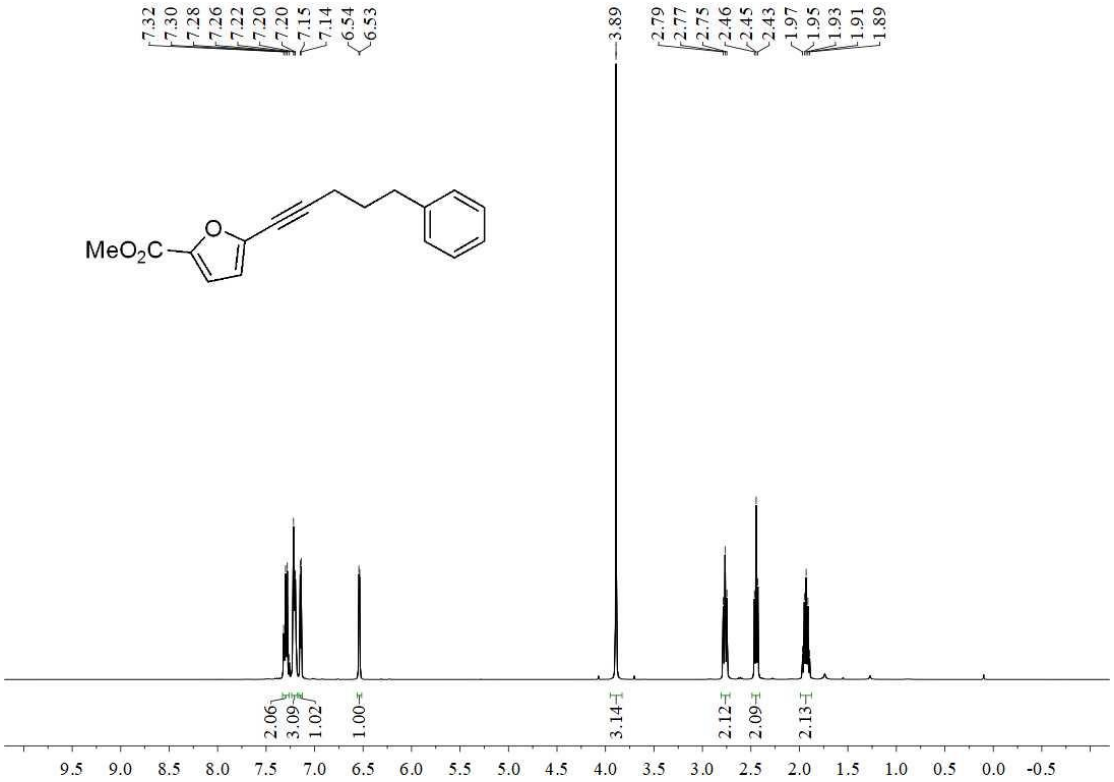
^{1}H NMR (400 MHz, $CDCl_3$) **(1n)**



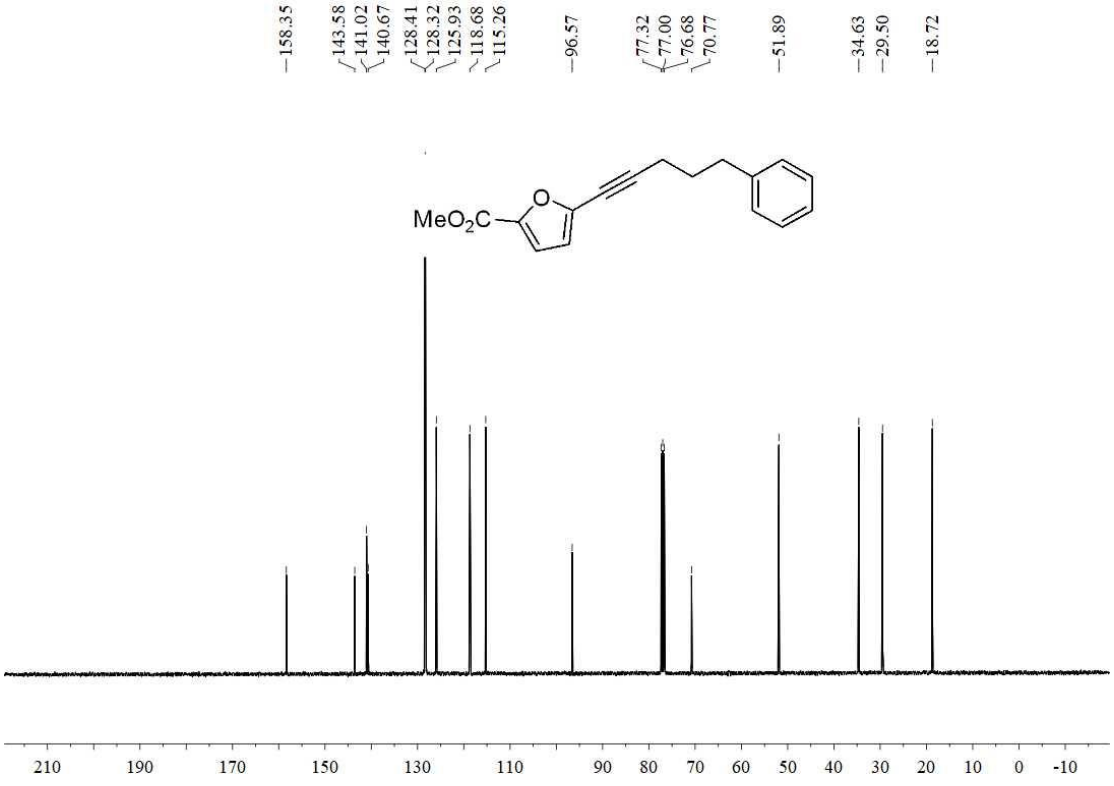
^{13}C NMR (101 MHz, $CDCl_3$) **(1n)**



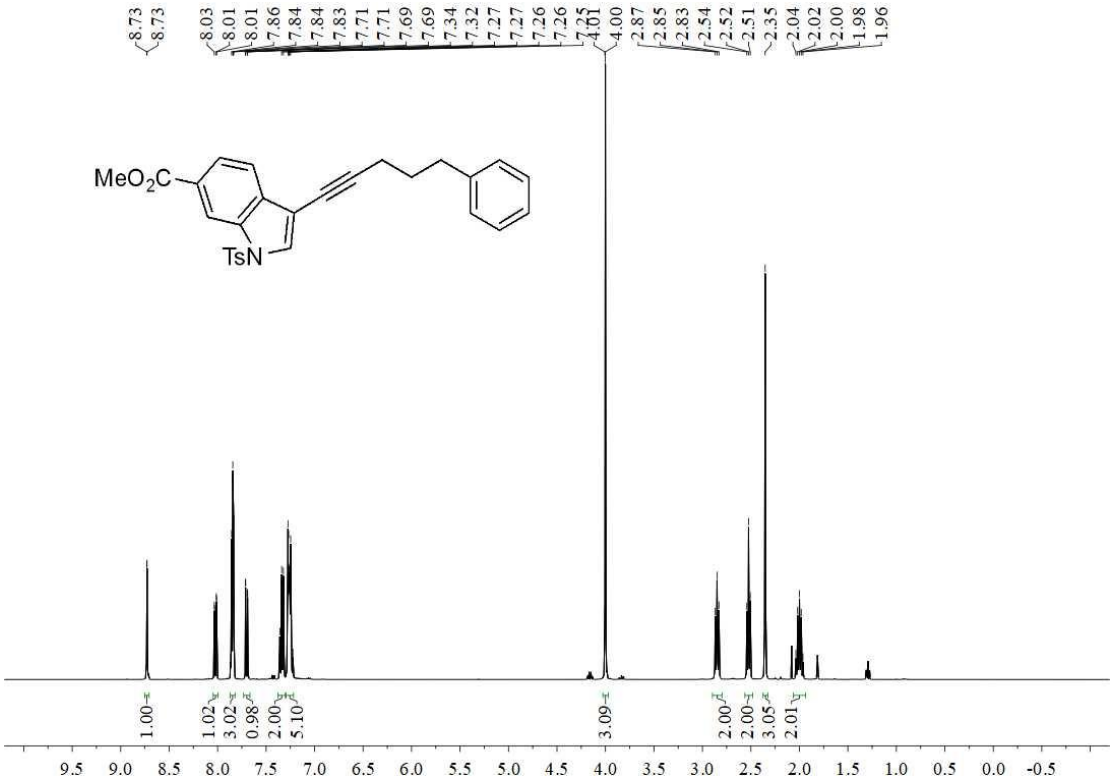
^{1}H NMR (400 MHz, $CDCl_3$) **(1o)**



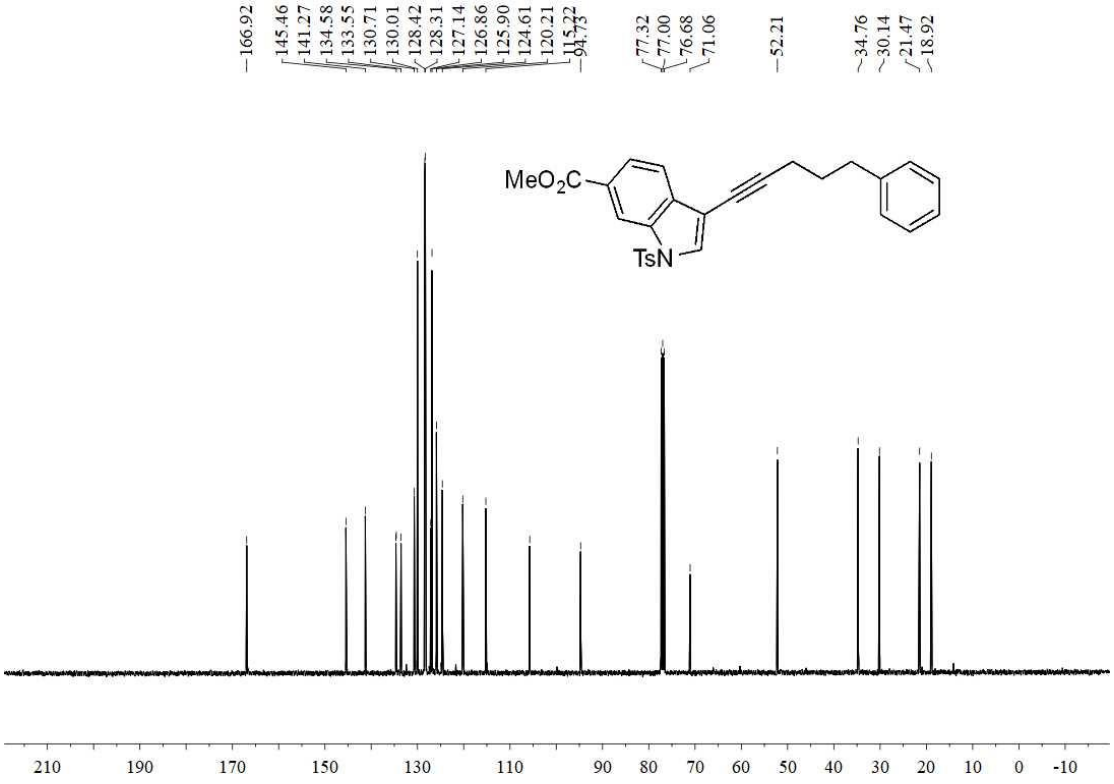
^{13}C NMR (101 MHz, $CDCl_3$) **(1o)**



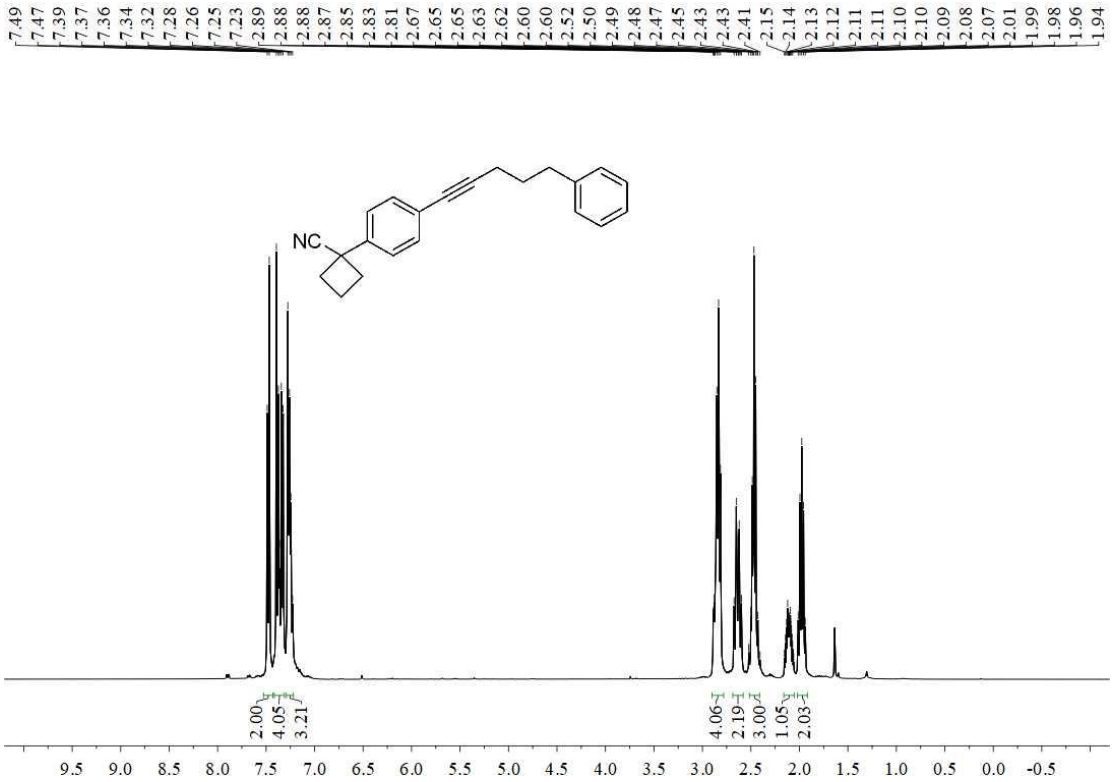
^{1}H NMR (400 MHz, $CDCl_3$) **(1p)**



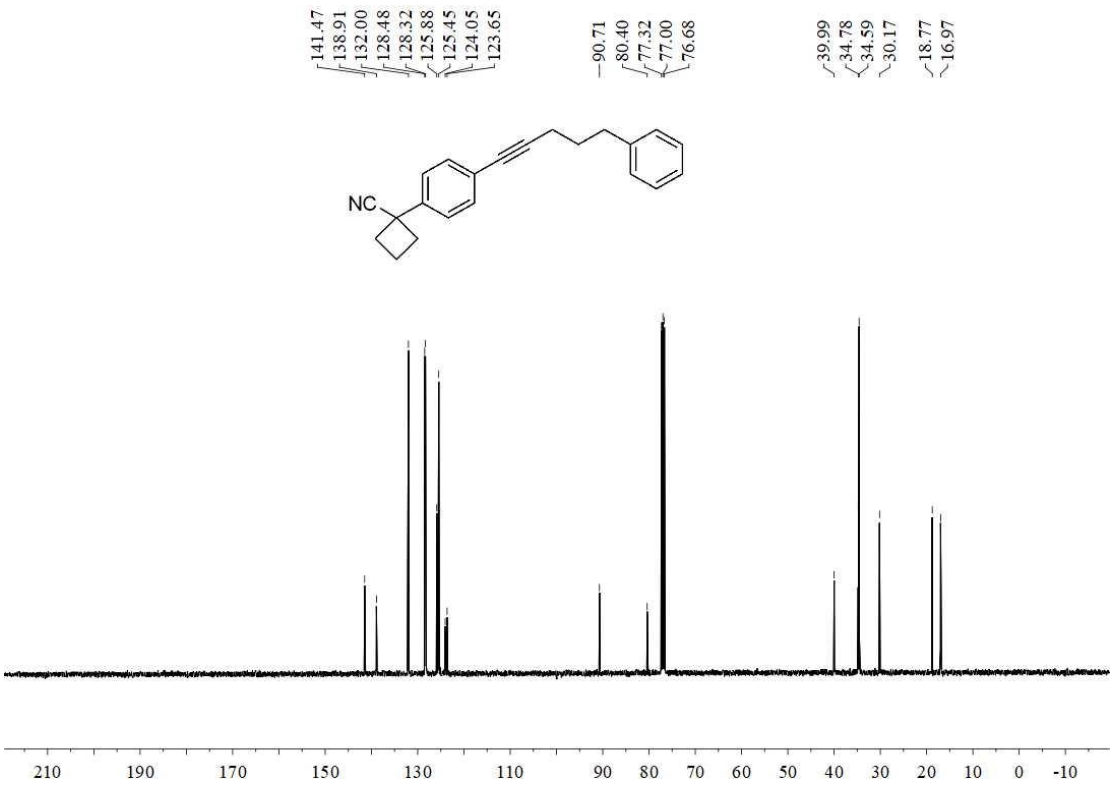
^{13}C NMR (101 MHz, $CDCl_3$) **(1p)**



^{1}H NMR (400 MHz, $CDCl_3$) **(1q)**

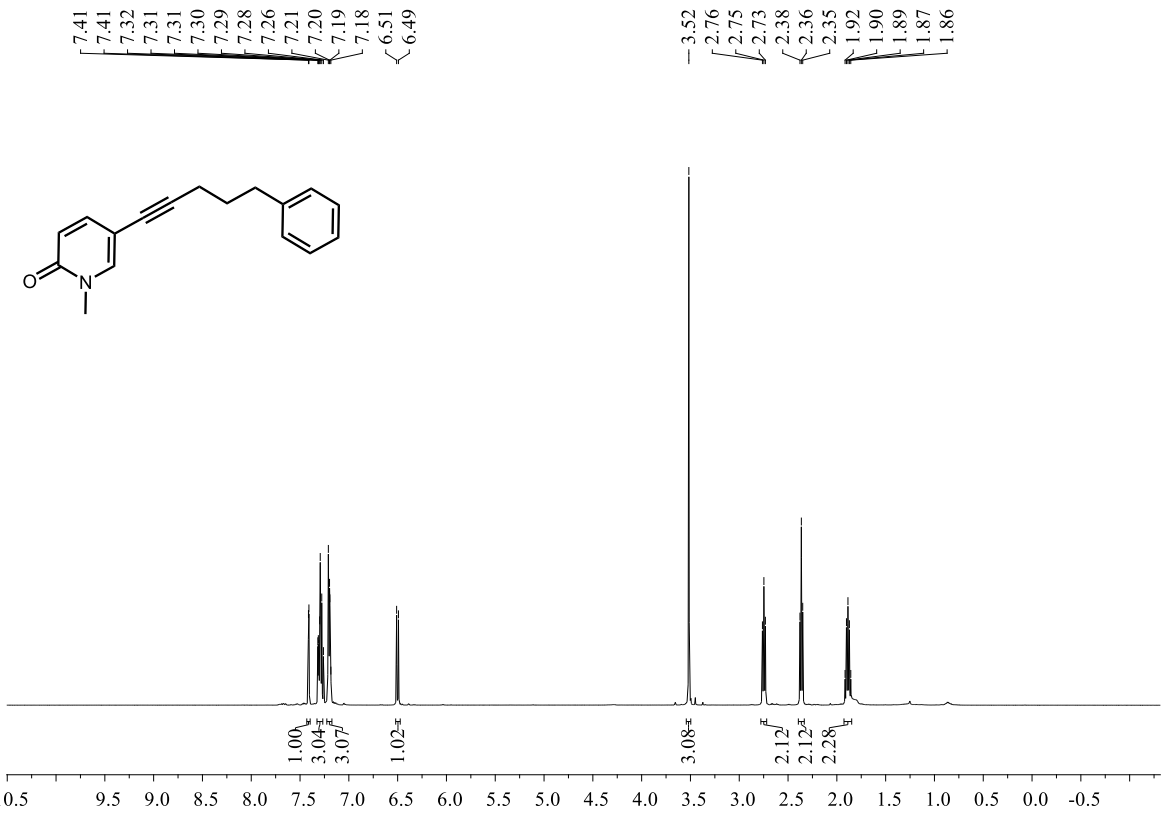


^{13}C NMR (101 MHz, $CDCl_3$) **(1q)**

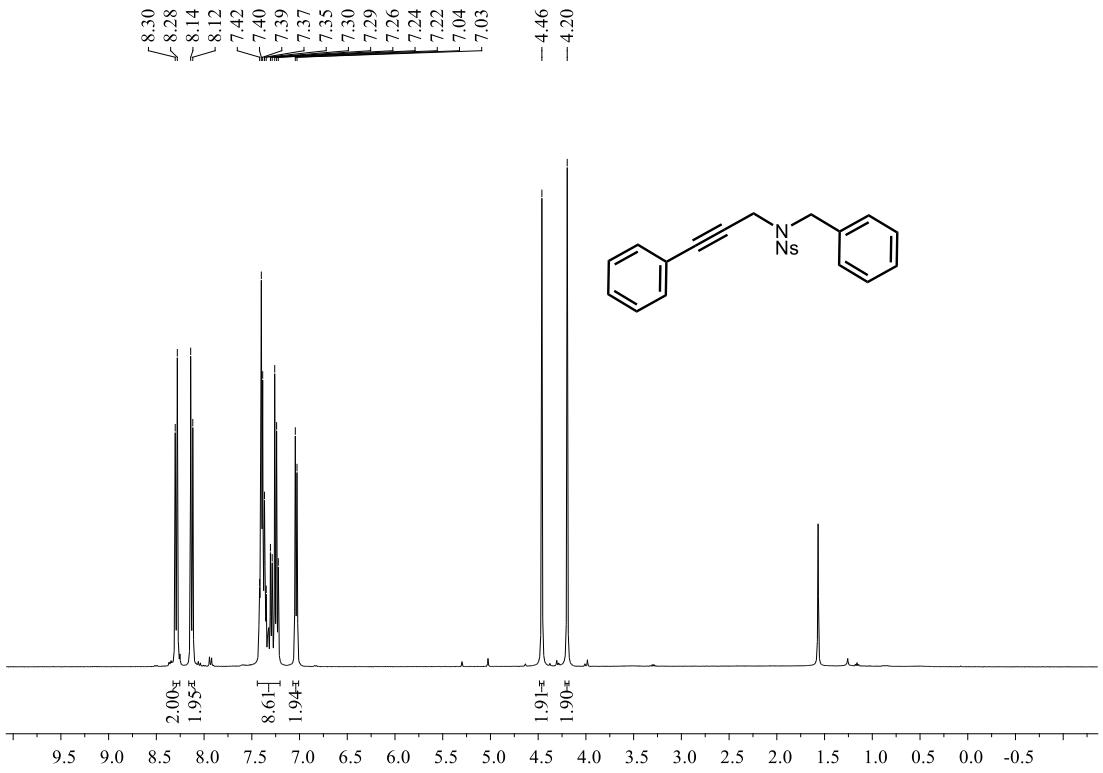


^{1}H NMR (500 MHz, $CDCl_3$) **(1r)**

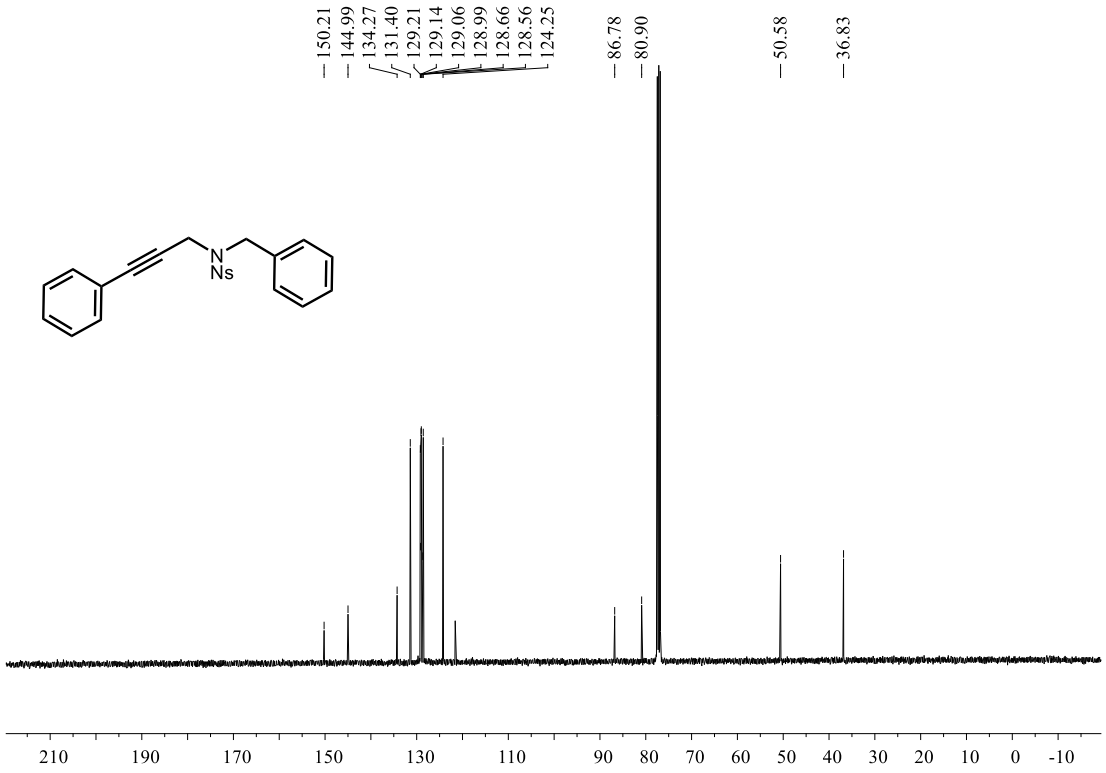
^{13}C NMR (101 MHz, $CDCl_3$) **(1r)**



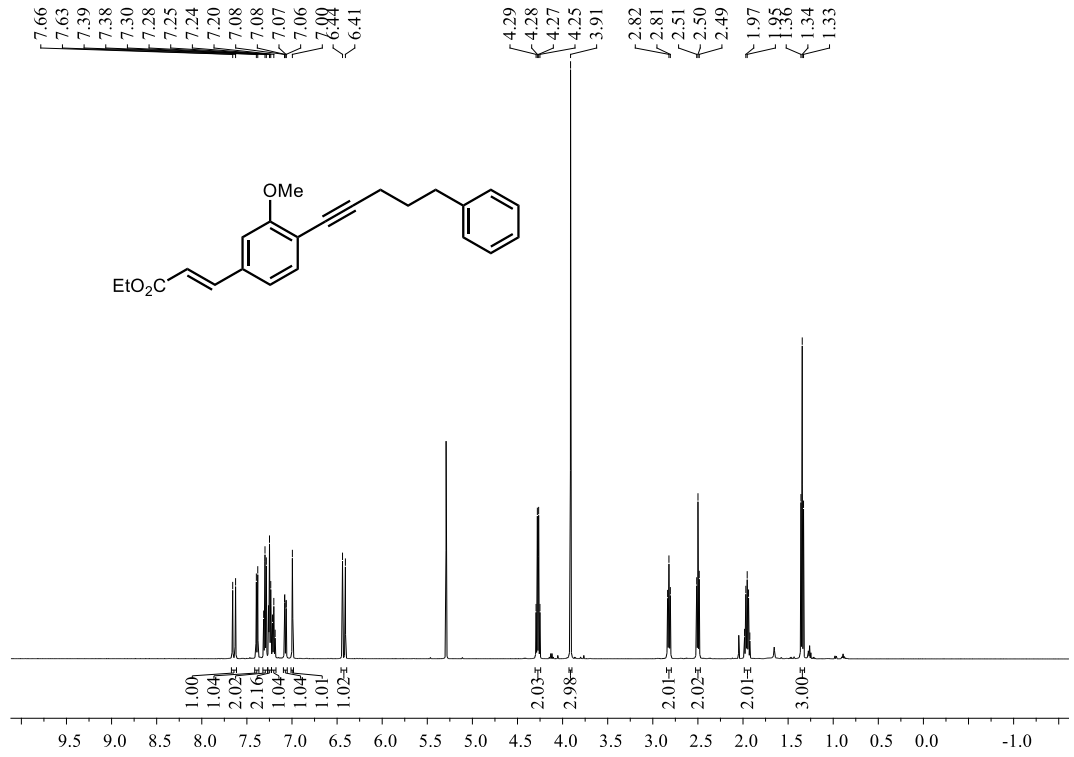
^{1}H NMR (400 MHz, $CDCl_3$) **(1s)**



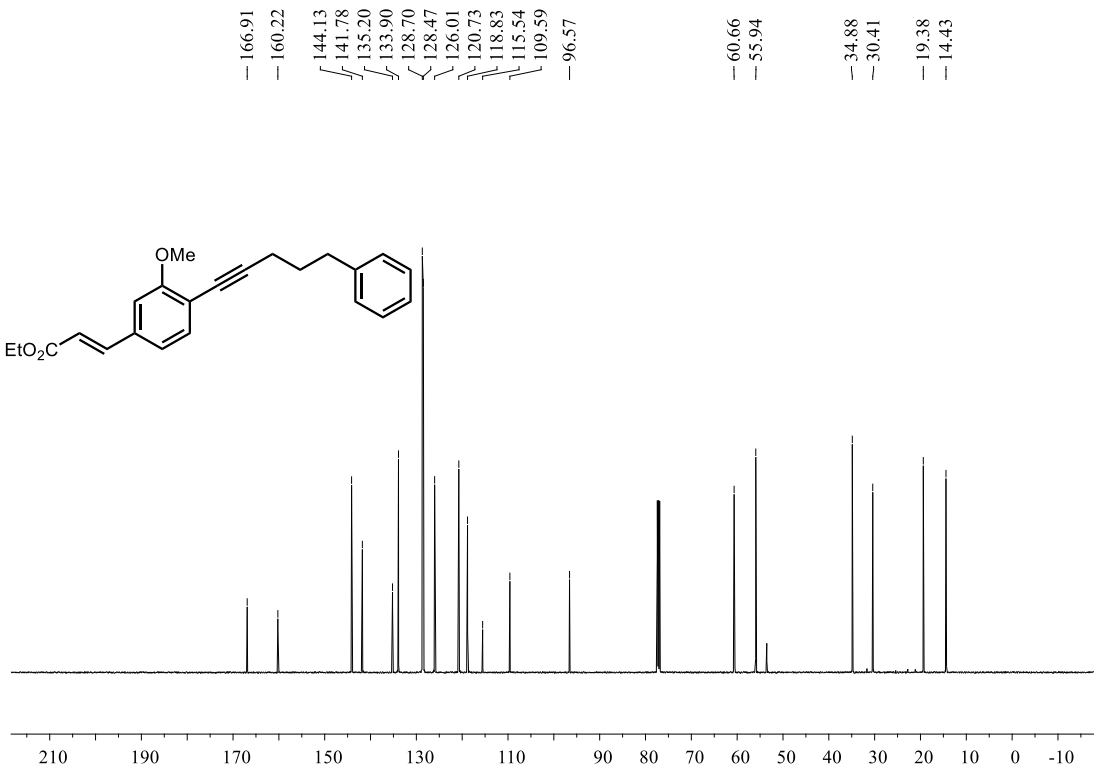
^{13}C NMR (101 MHz, $CDCl_3$) **(1s)**



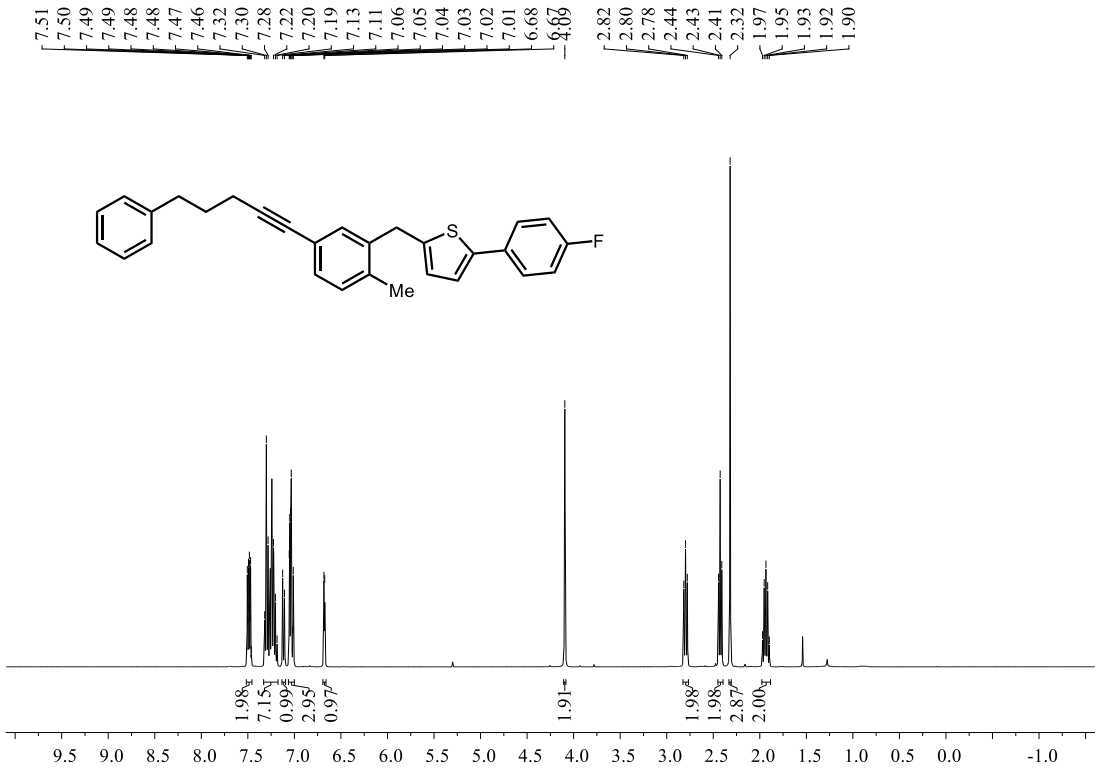
^{1}H NMR (500 MHz, $CDCl_3$) **(1t)**



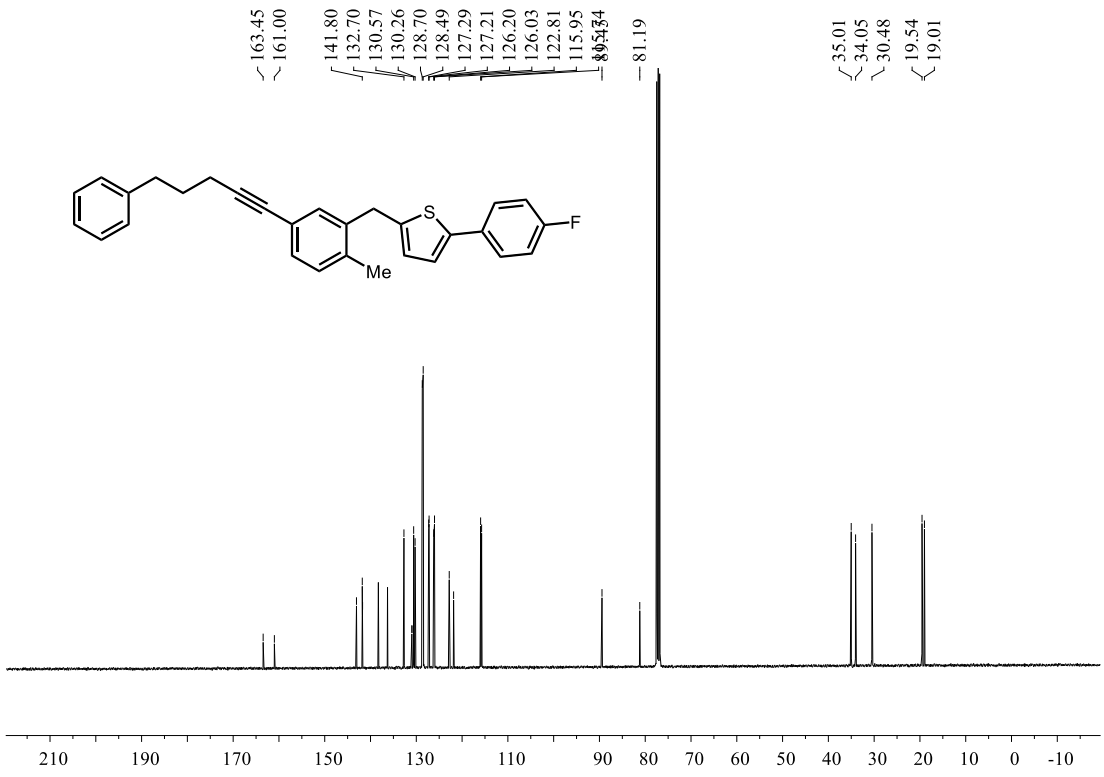
^{13}C NMR (126 MHz, $CDCl_3$) **(1t)**



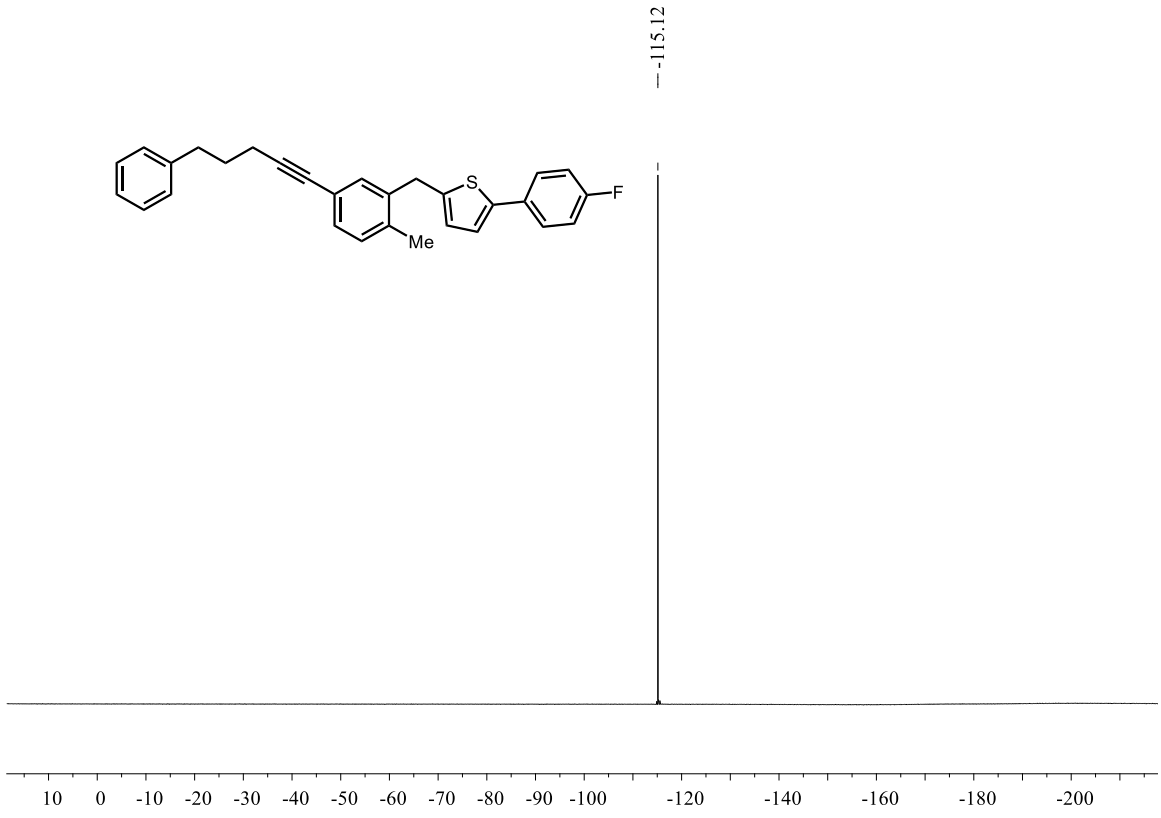
^{1}H NMR (400 MHz, $CDCl_3$) **(1u)**



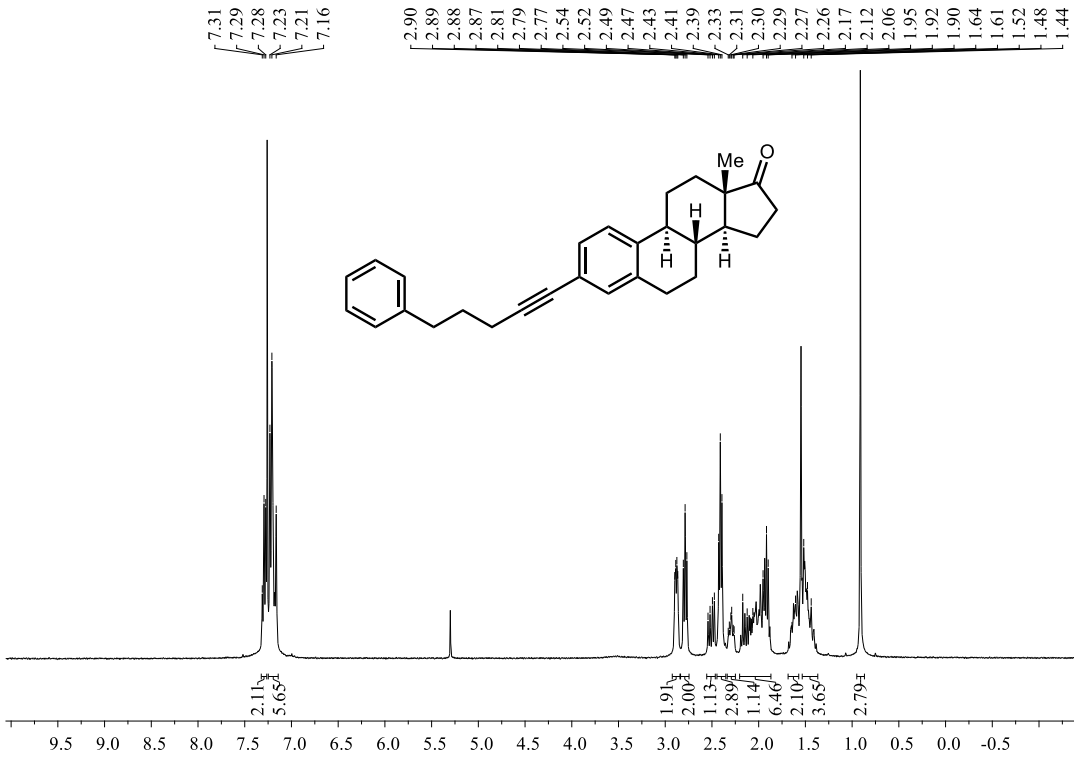
^{13}C NMR (101 MHz, $CDCl_3$) **(1u)**



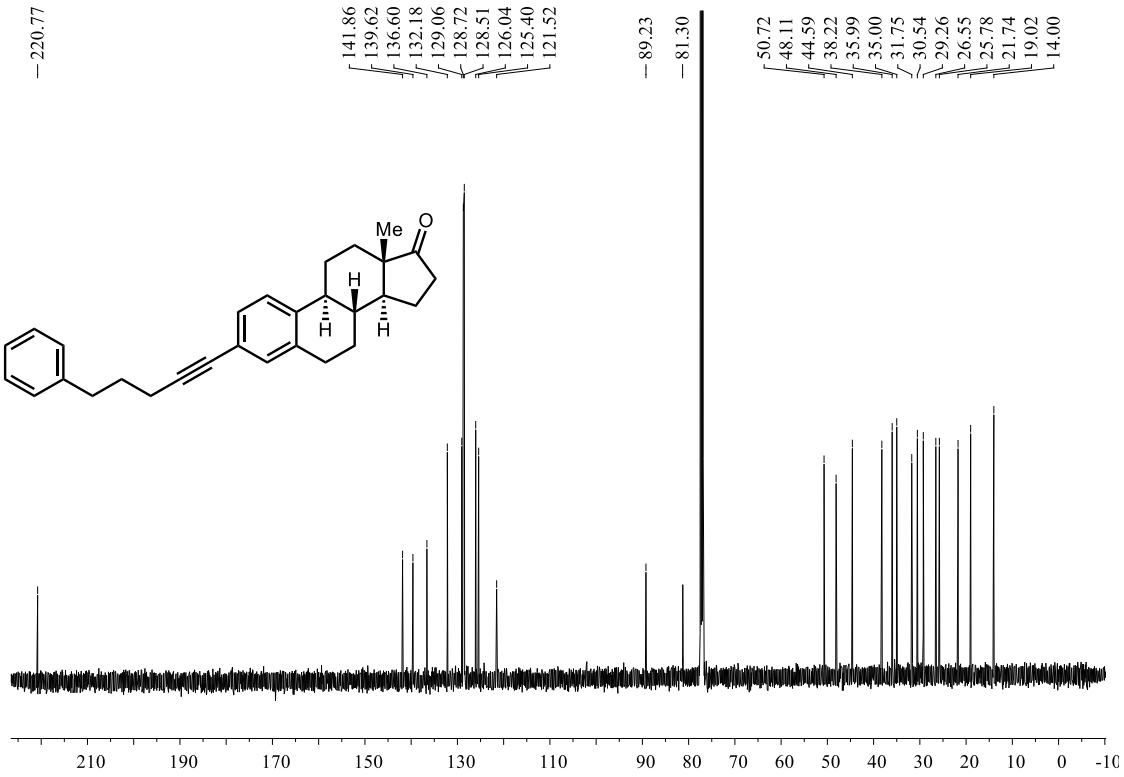
^{19}F NMR (376 MHz, $CDCl_3$) **(1u)**



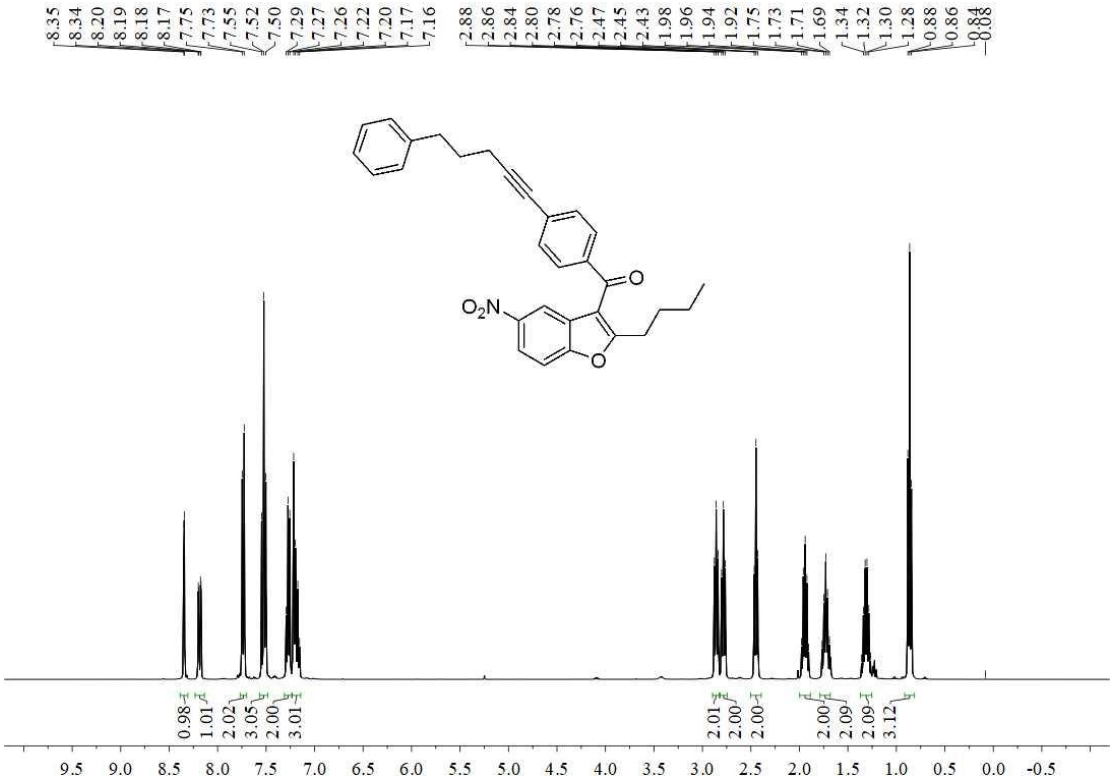
^{1}H NMR (400 MHz, $CDCl_3$) (**1v**)



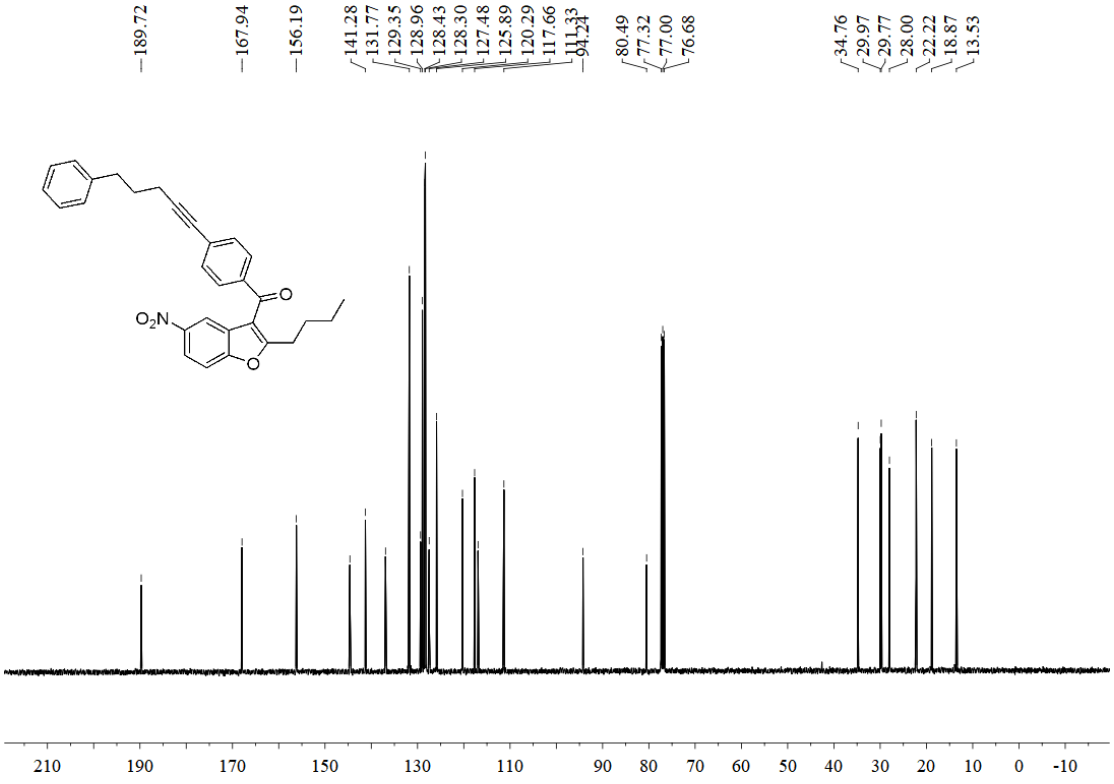
^{13}C NMR (101 MHz, $CDCl_3$) **(1v)**



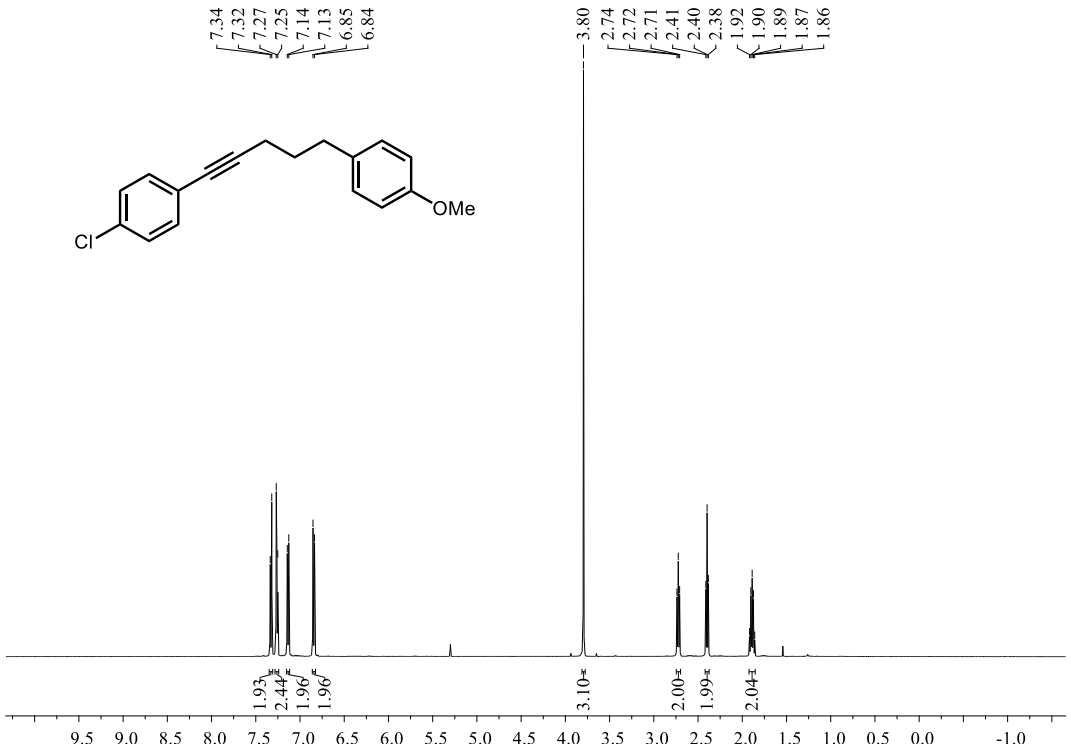
^{1}H NMR (400 MHz, $CDCl_3$) **(1w)**



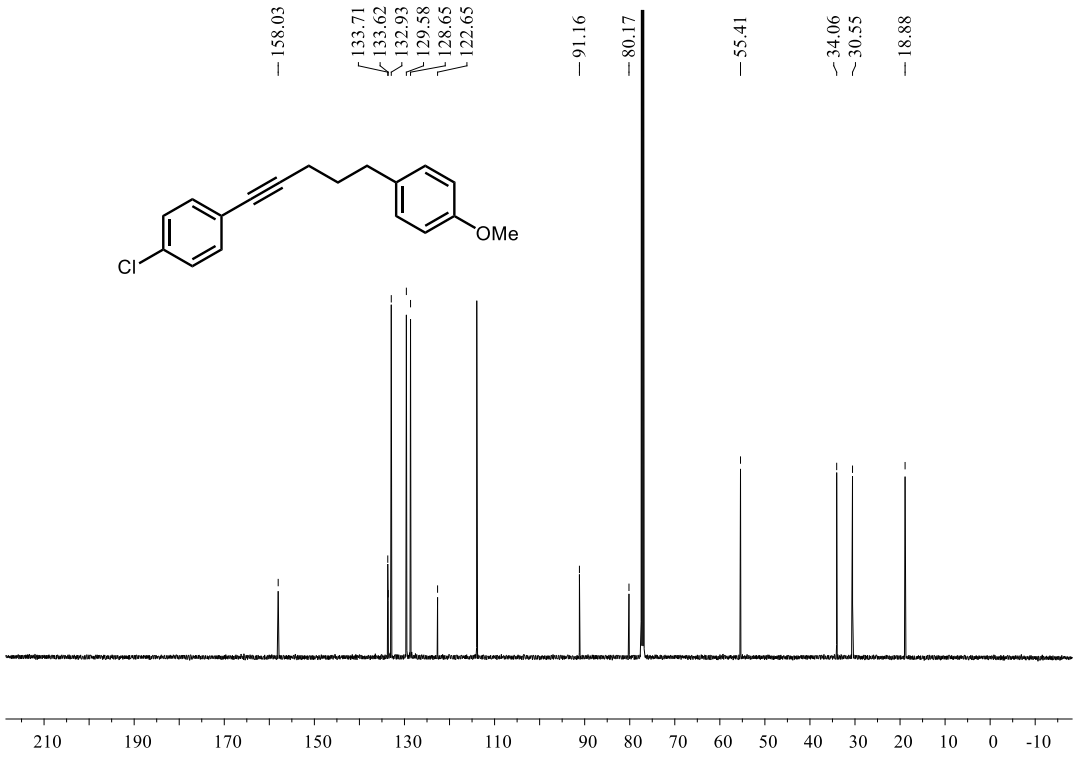
^{13}C NMR (101 MHz, $CDCl_3$) **(1w)**



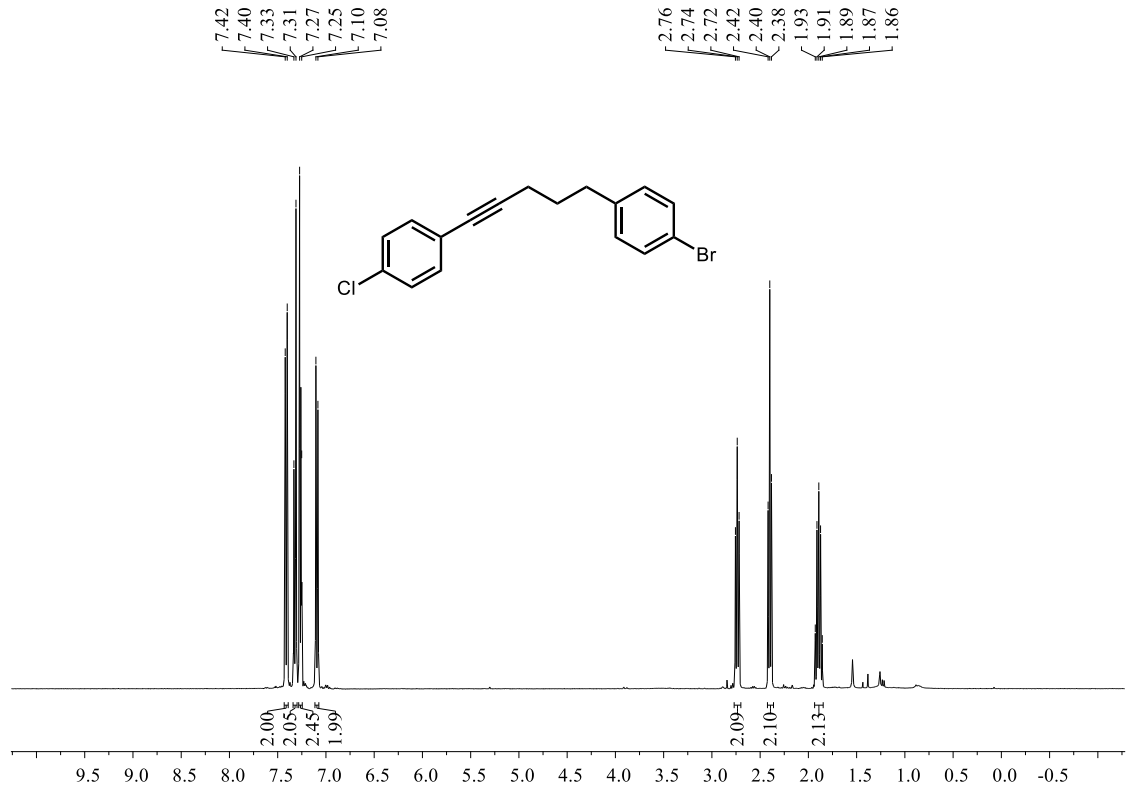
^{1}H NMR (500 MHz, $CDCl_3$) **(1x)**



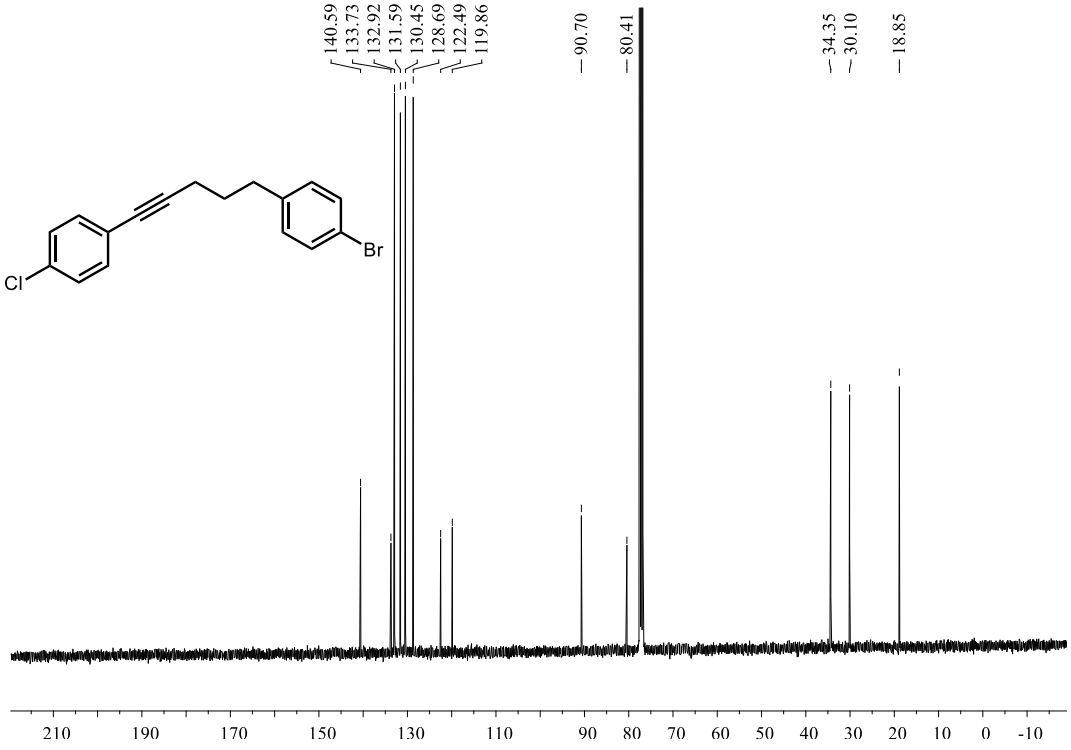
^{13}C NMR (126 MHz, $CDCl_3$) **(1x)**



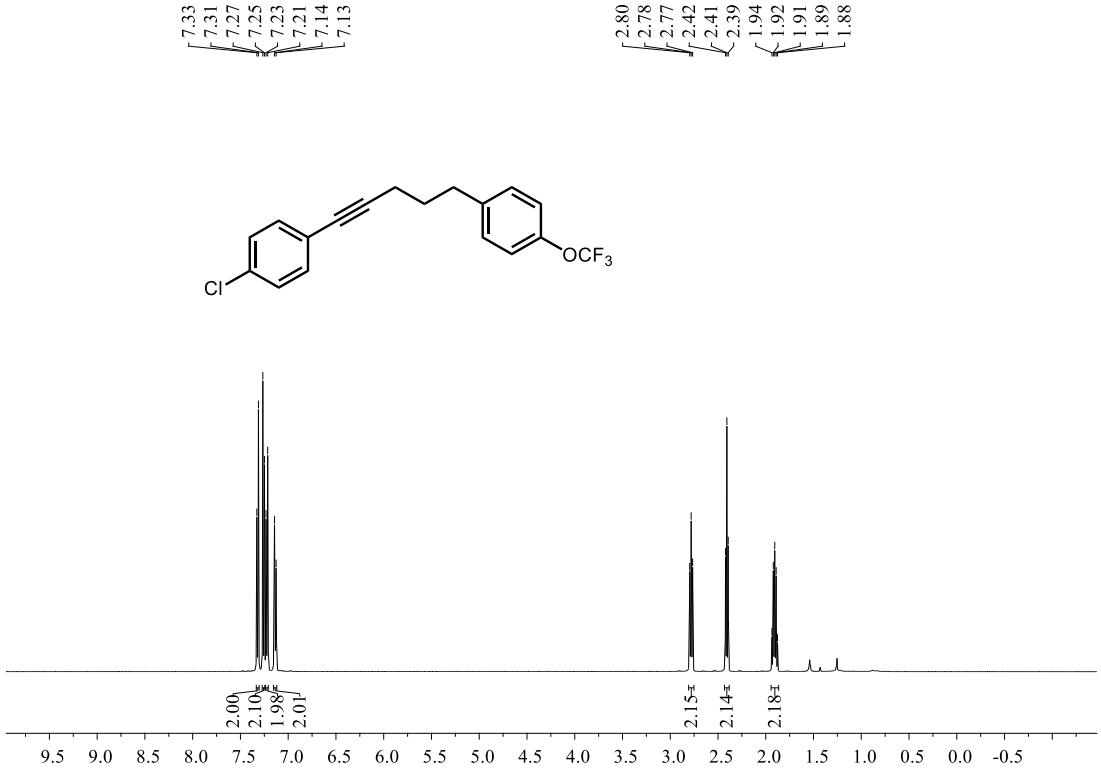
^{1}H NMR (400 MHz, $CDCl_3$) **(1y)**



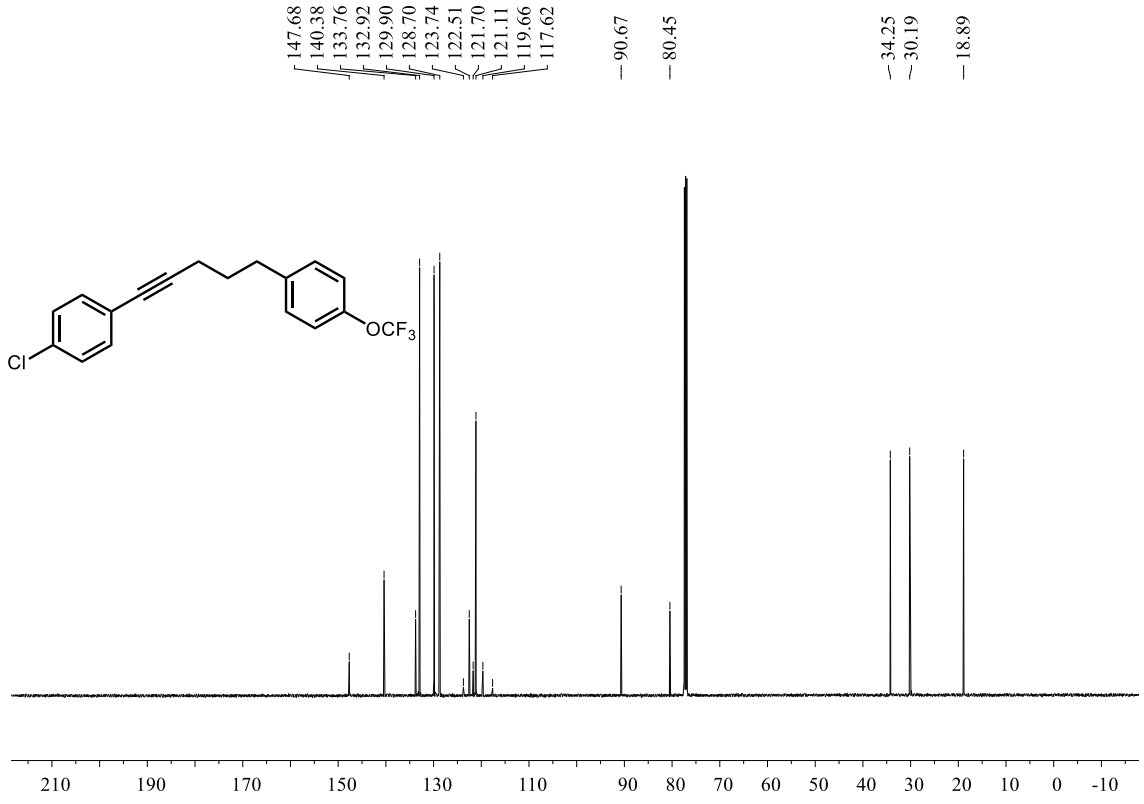
^{13}C NMR (101 MHz, $CDCl_3$) **(1y)**



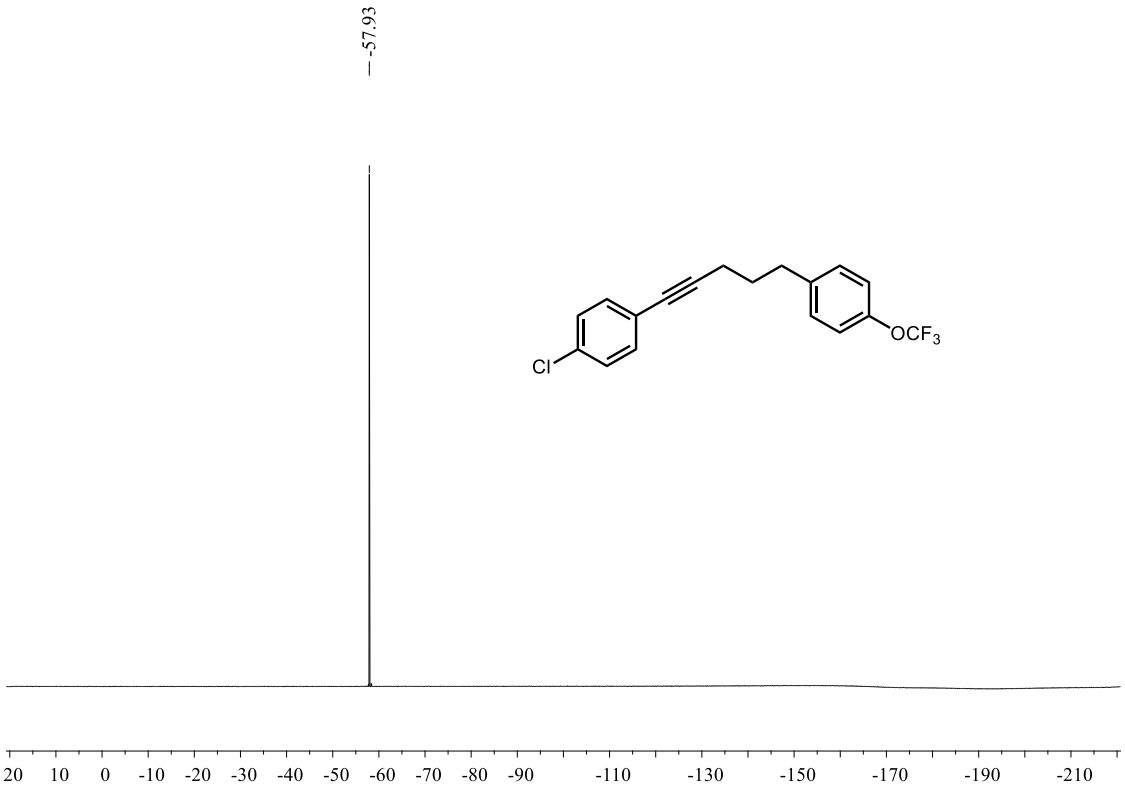
^{1}H NMR (500 MHz, $CDCl_3$) **(1z)**



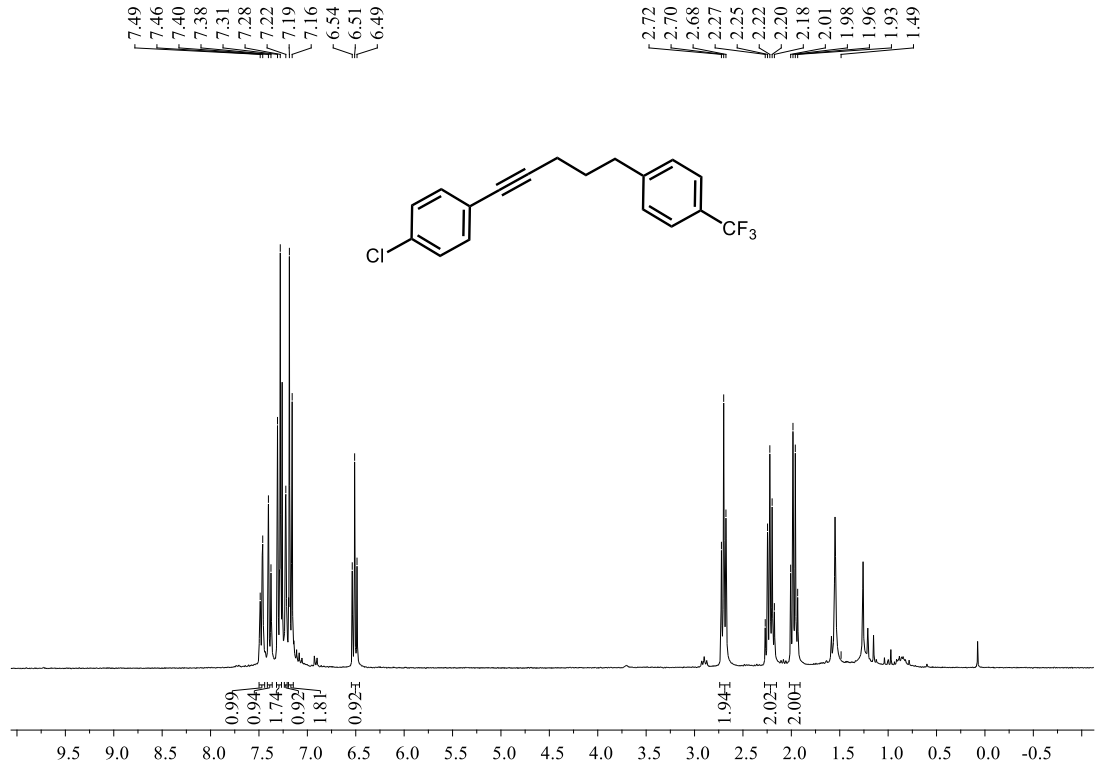
^{13}C NMR (126 MHz, $CDCl_3$) **(1z)**



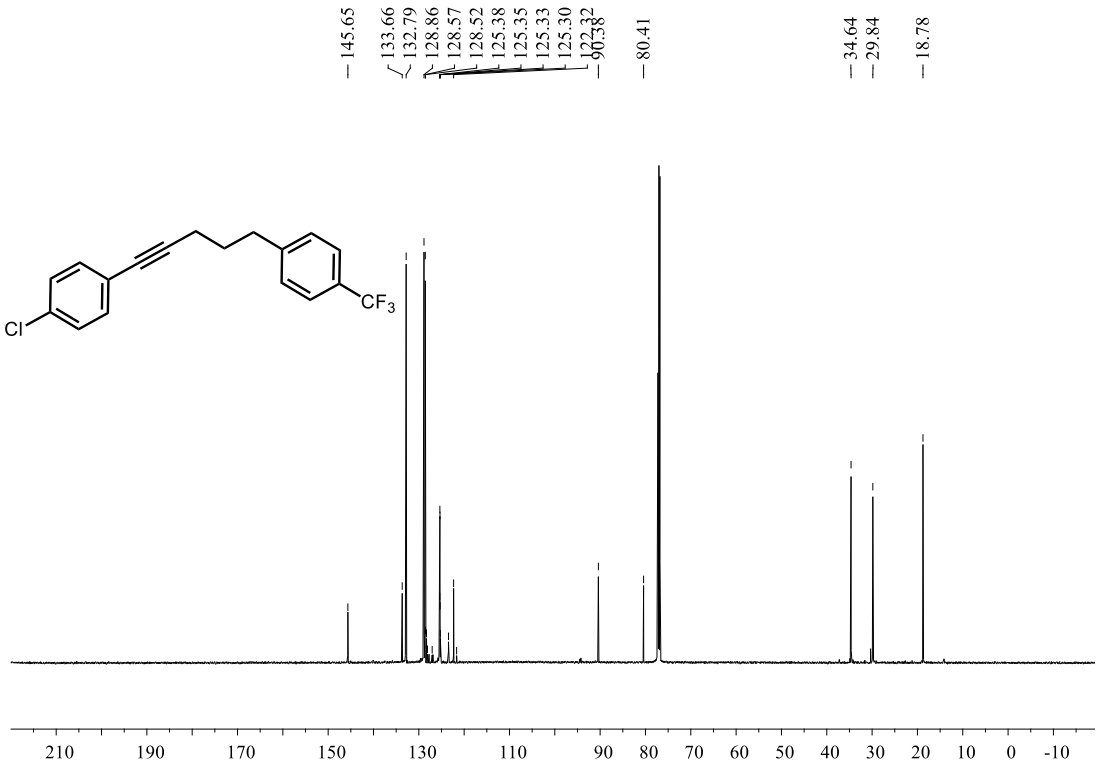
^{19}F NMR (471 MHz, $CDCl_3$) **(1z)**



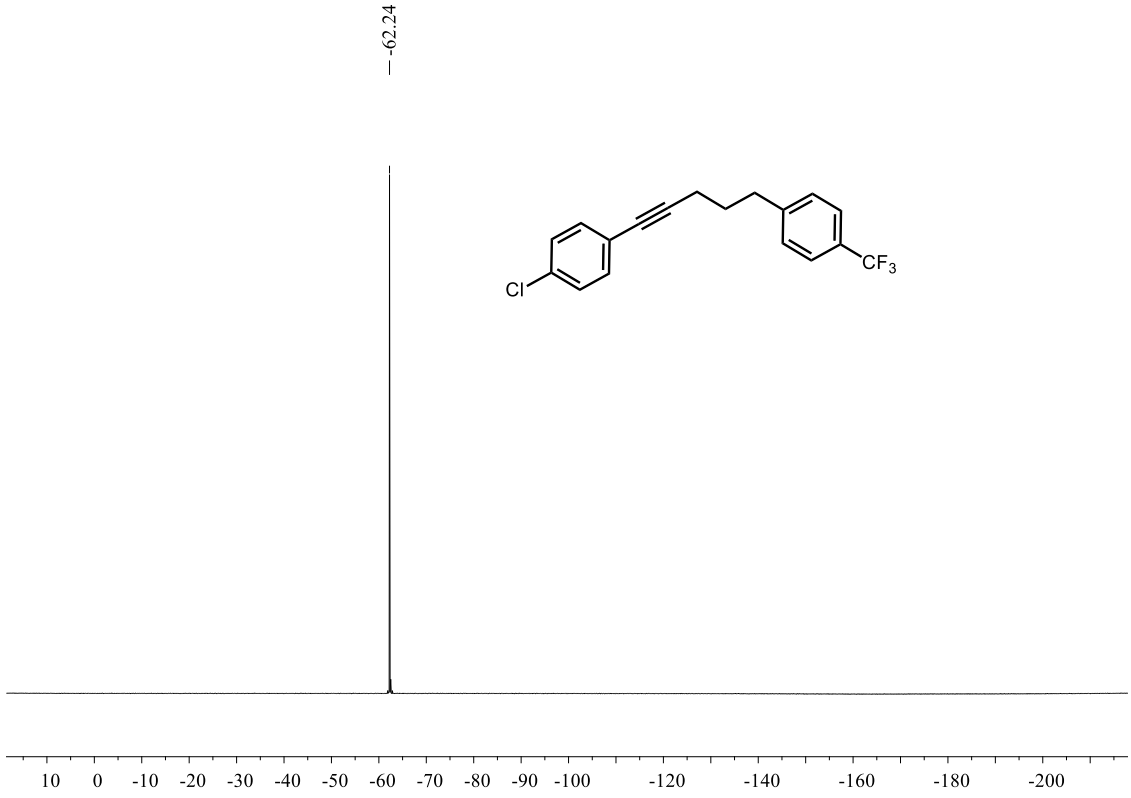
^{1}H NMR (500 MHz, $CDCl_3$) **(1aa)**



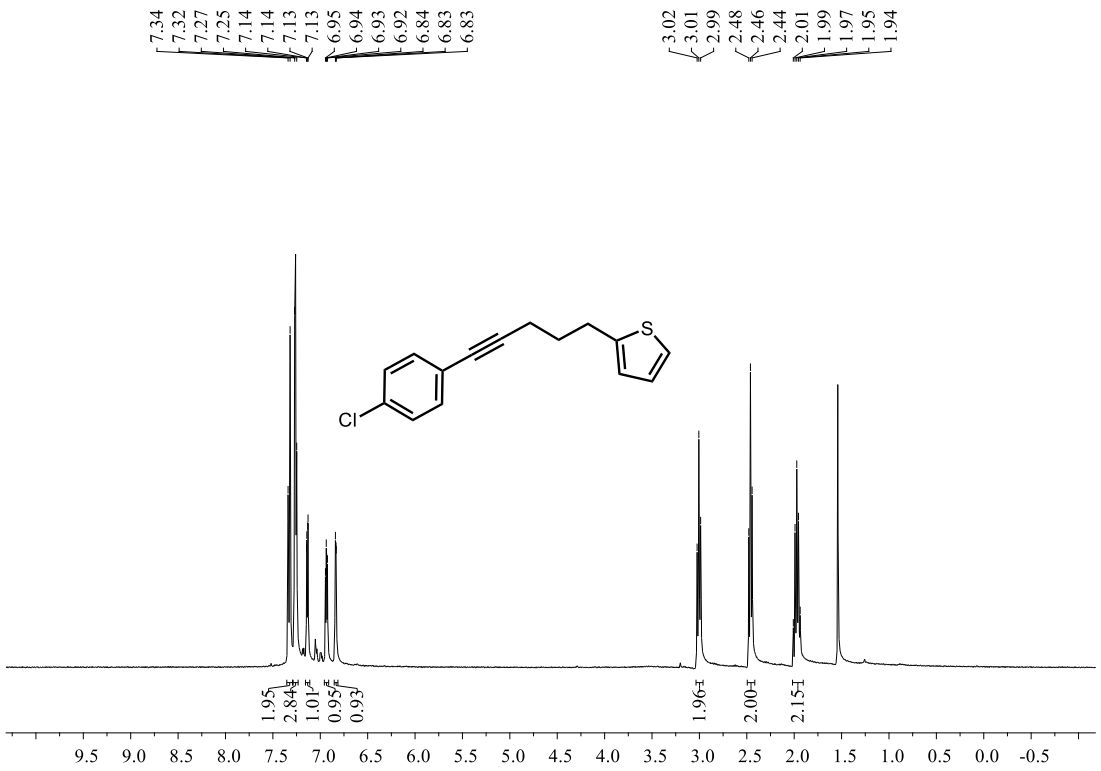
^{13}C NMR (151 MHz, $CDCl_3$) **(1aa)**



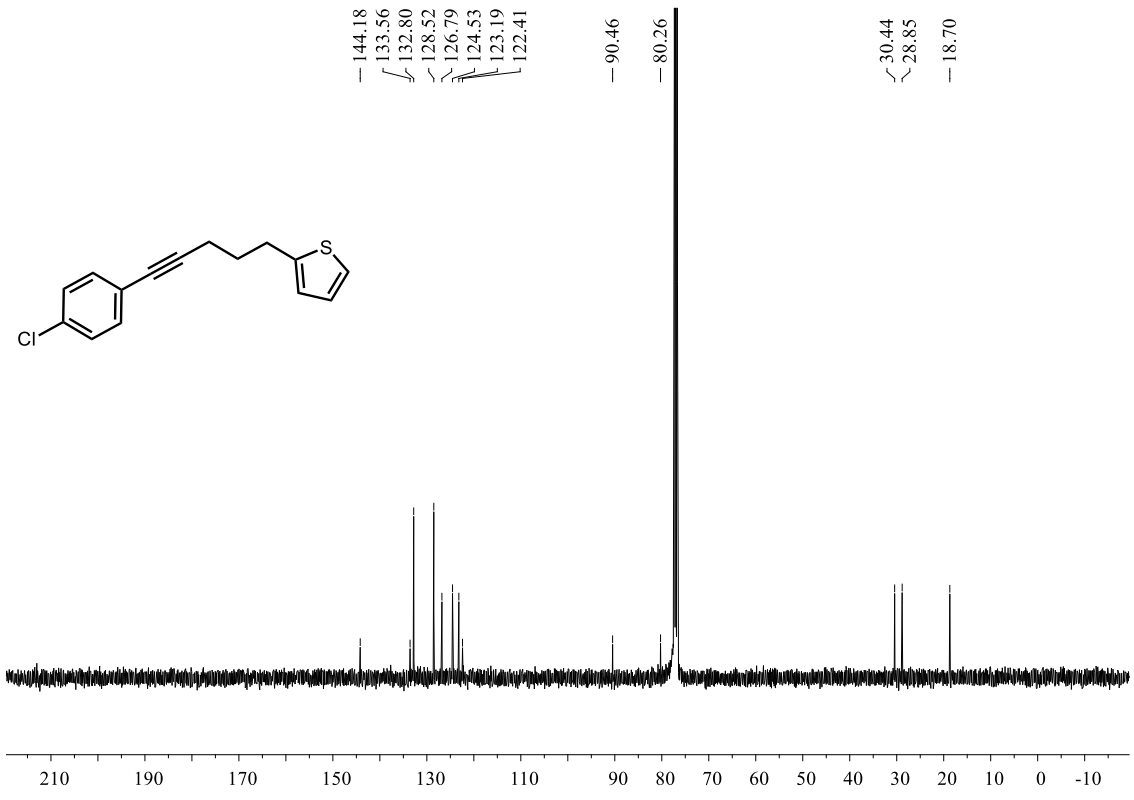
^{19}F NMR (282 MHz, $CDCl_3$) **(1aa)**



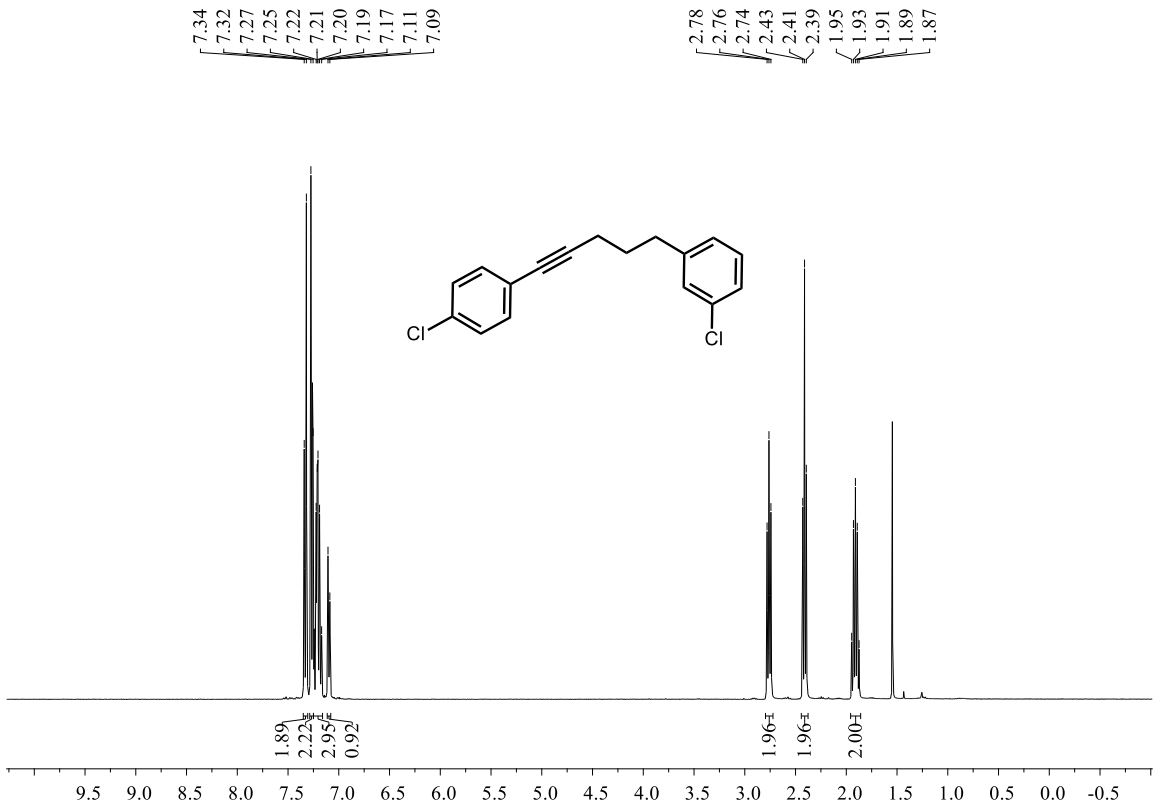
^{1}H NMR (400 MHz, $CDCl_3$) **(1ab)**



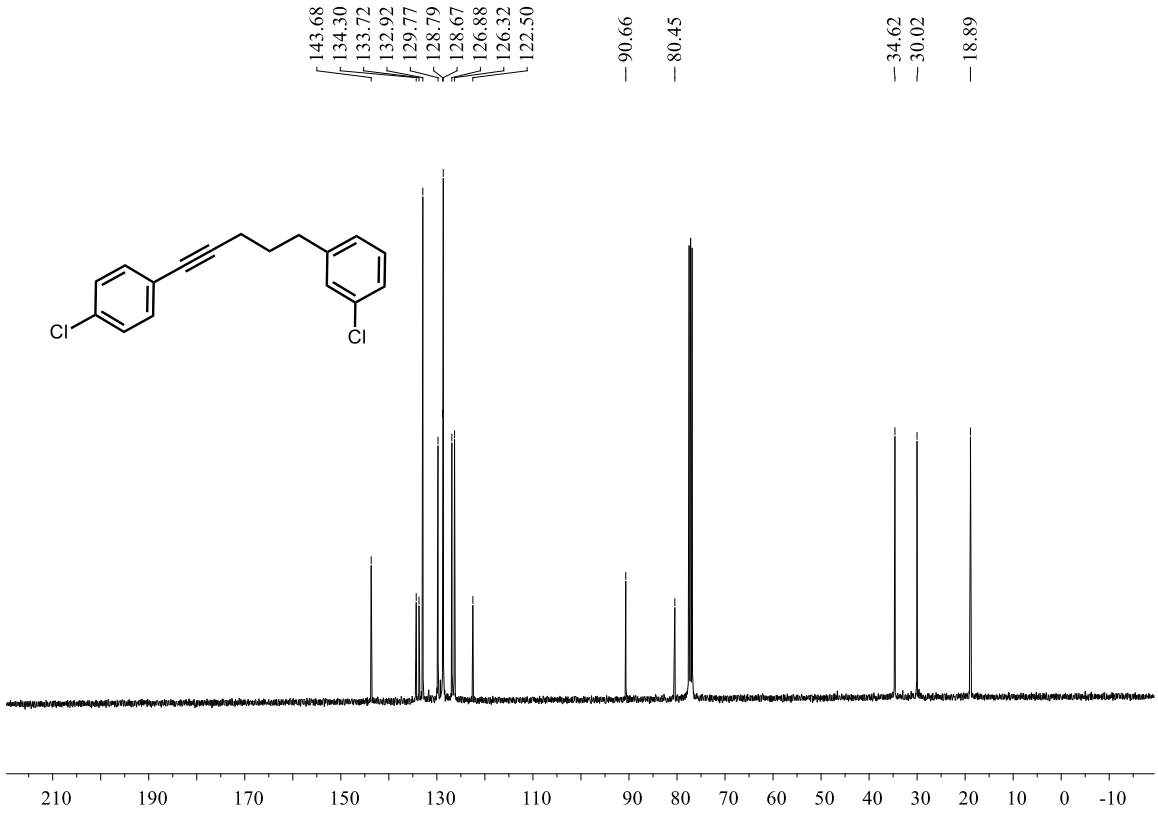
^{13}C NMR (101 MHz, $CDCl_3$) **(1ab)**



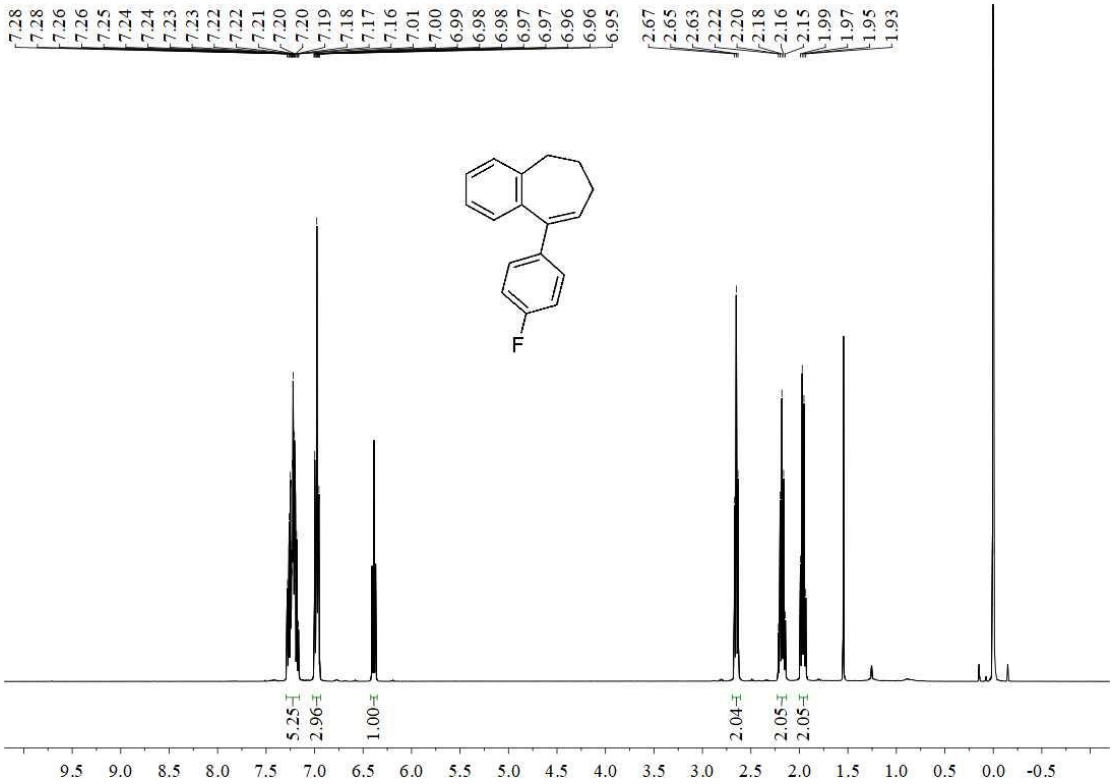
^{1}H NMR (400 MHz, $CDCl_3$) **(1ac)**



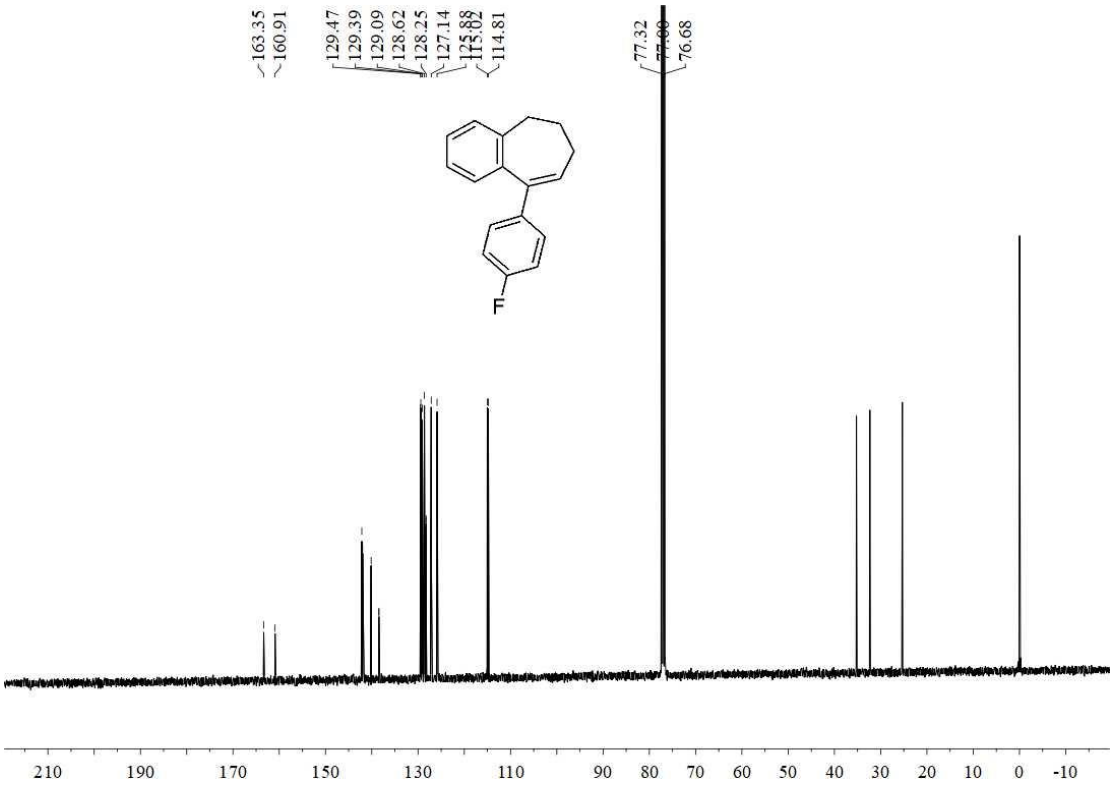
^{13}C NMR (101 MHz, $CDCl_3$) **(1ac)**



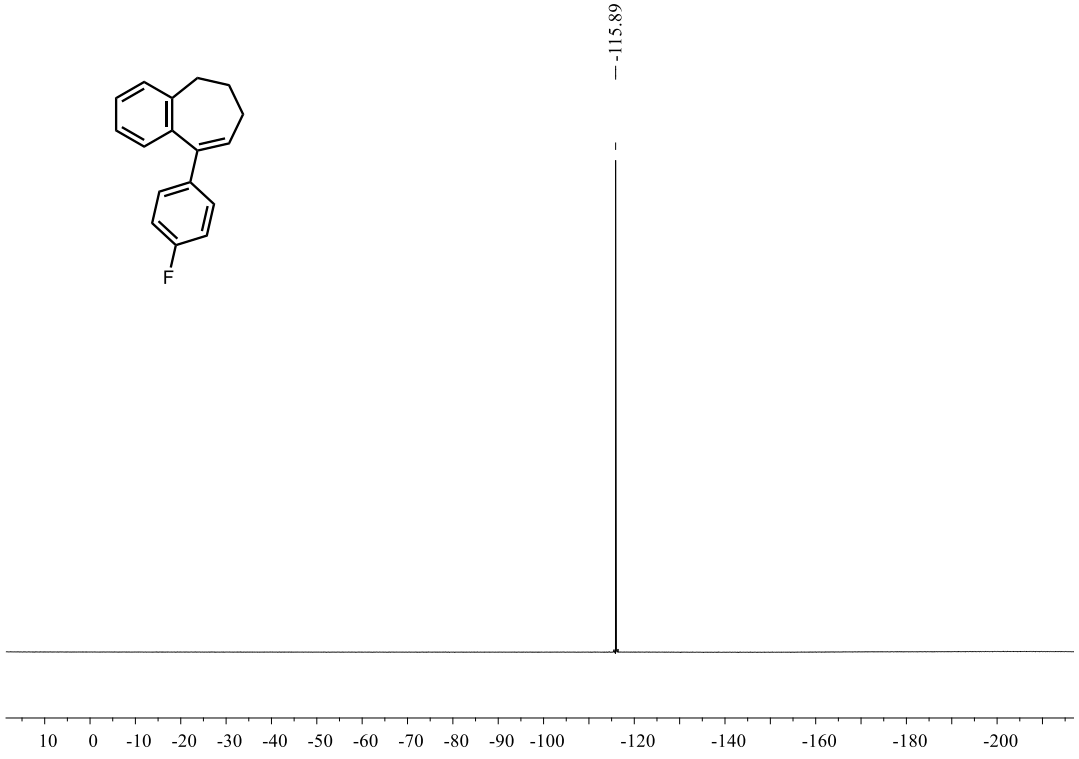
^{1}H NMR (400 MHz, $CDCl_3$) **(3b)**



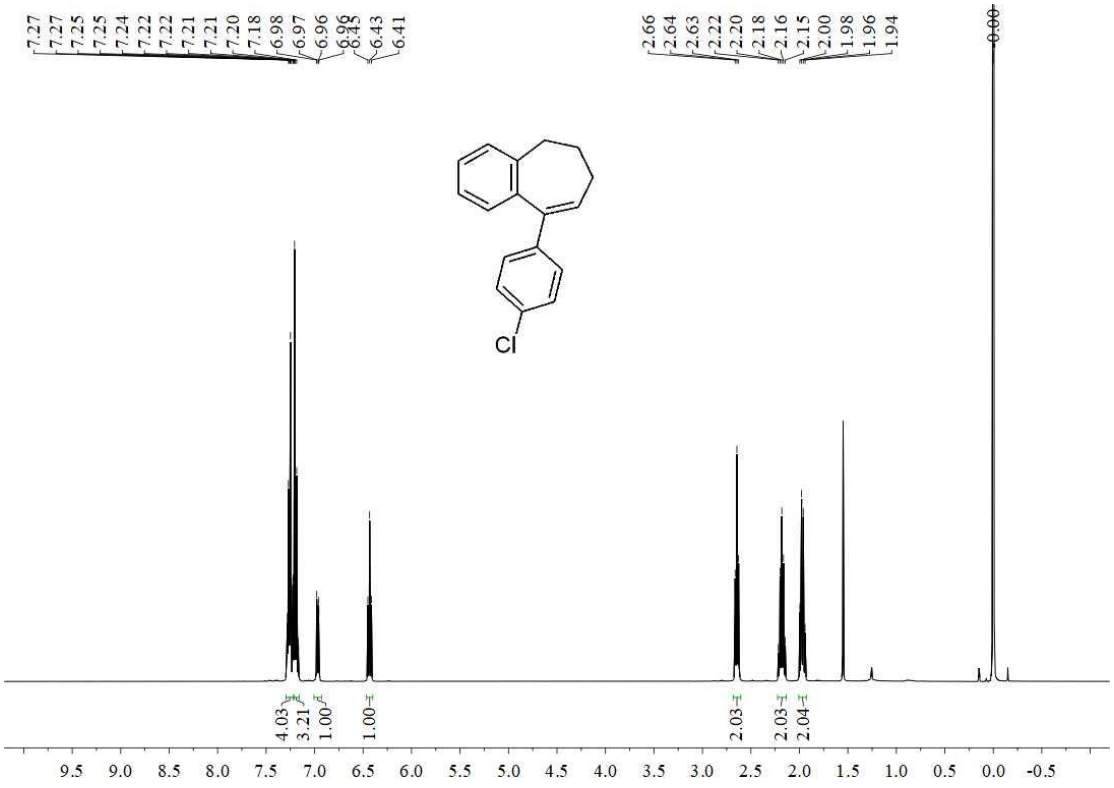
^{13}C NMR (101 MHz, $CDCl_3$) **(3b)**



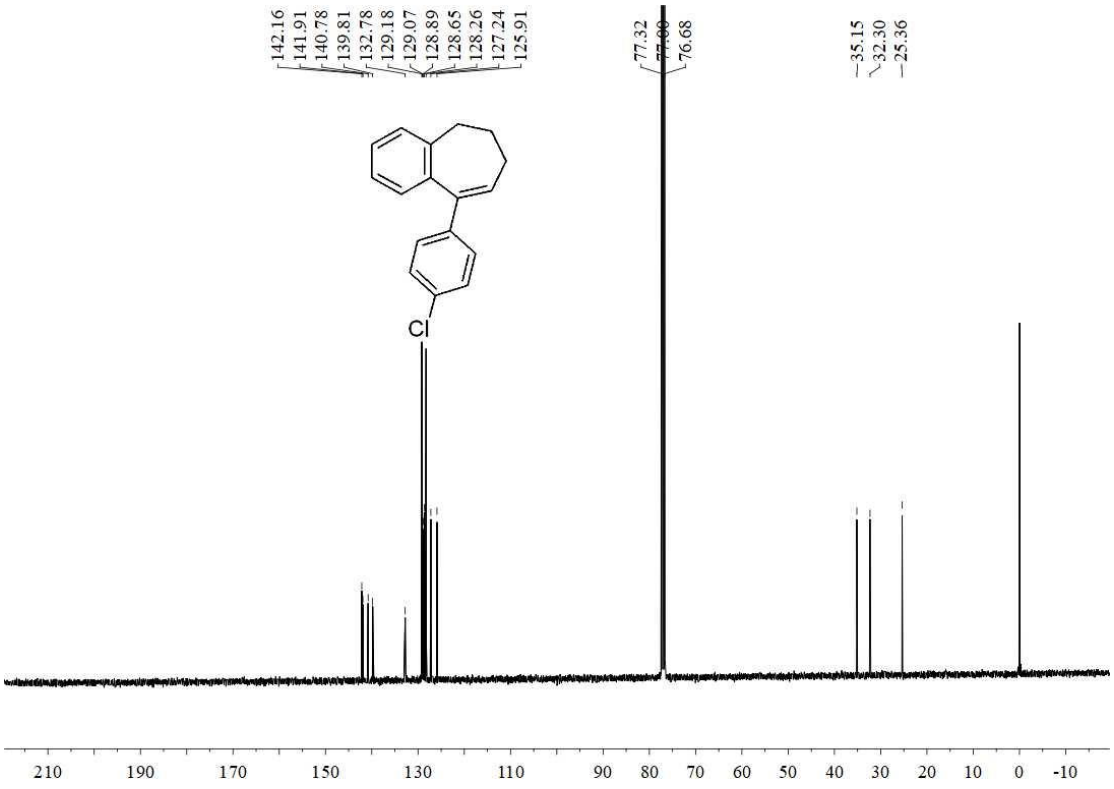
^{19}F NMR (282 MHz, $CDCl_3$) **(3b)**



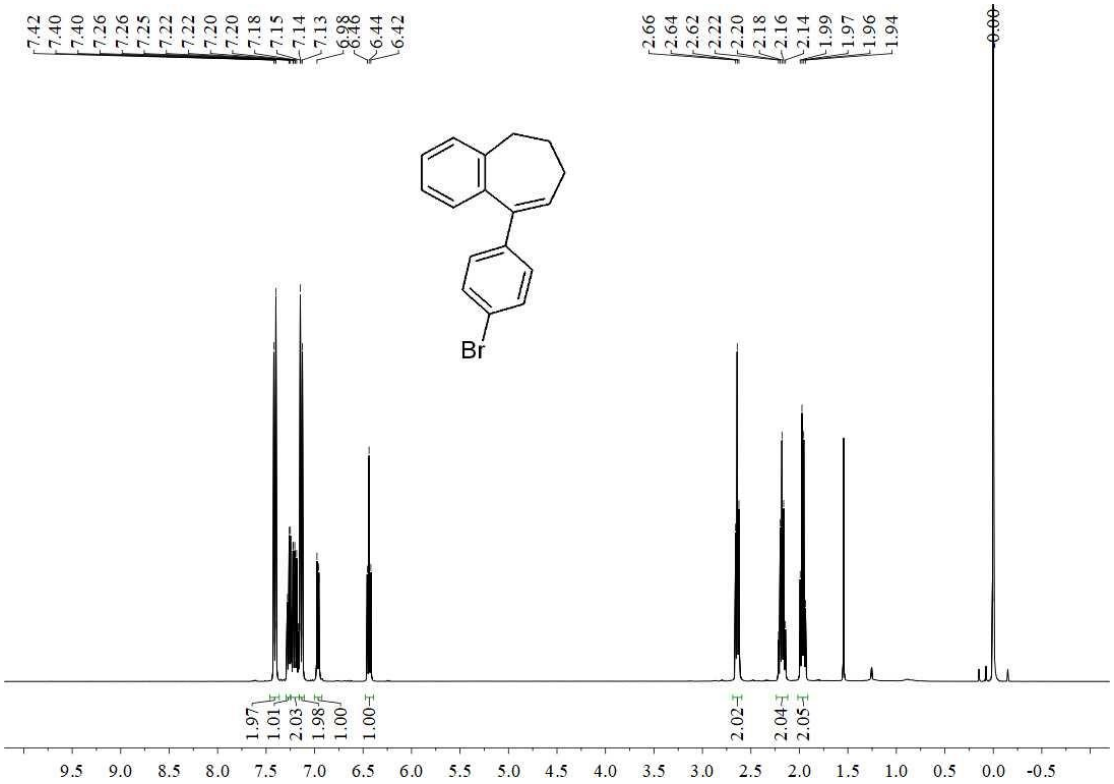
^{1}H NMR (400 MHz, $CDCl_3$) **(3c)**



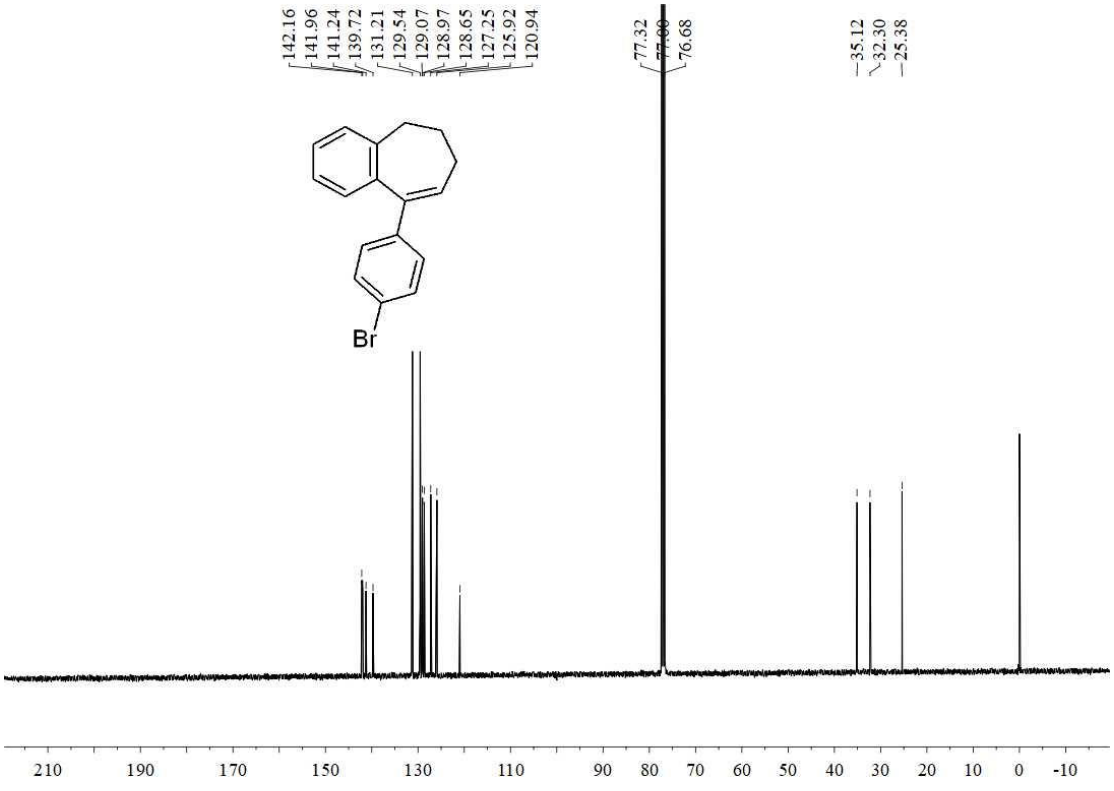
^{13}C NMR (101 MHz, $CDCl_3$) **(3c)**



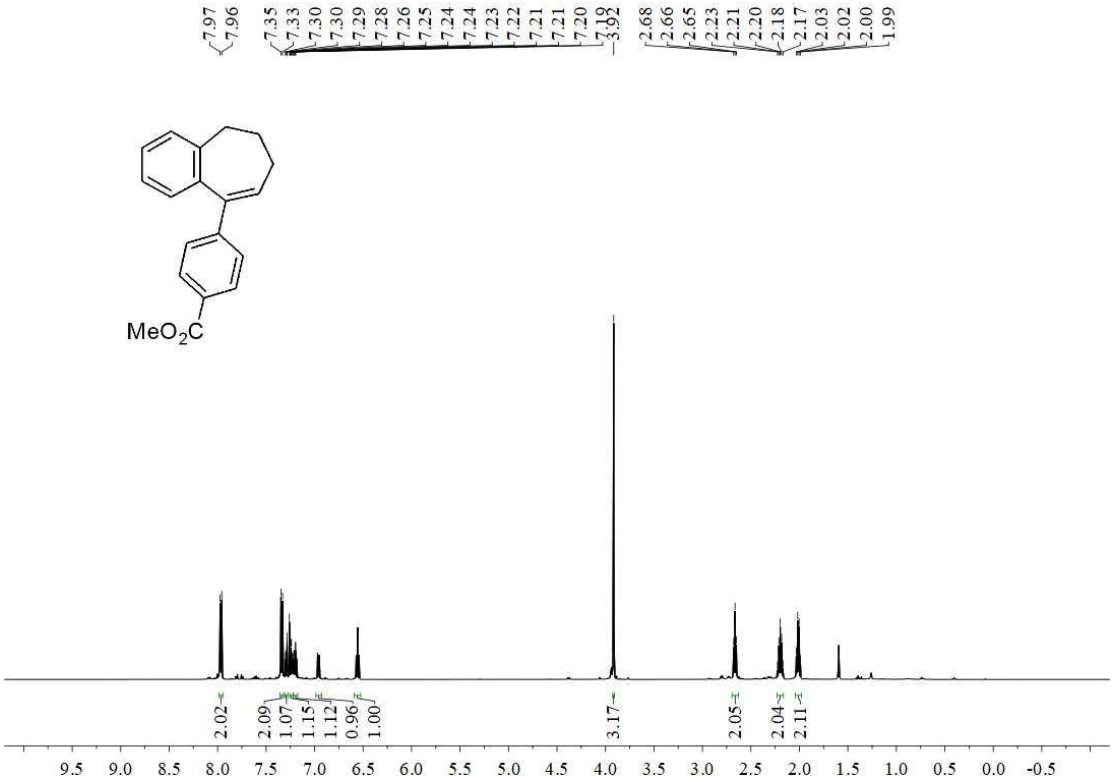
^{1}H NMR (500 MHz, $CDCl_3$) **(3d)**



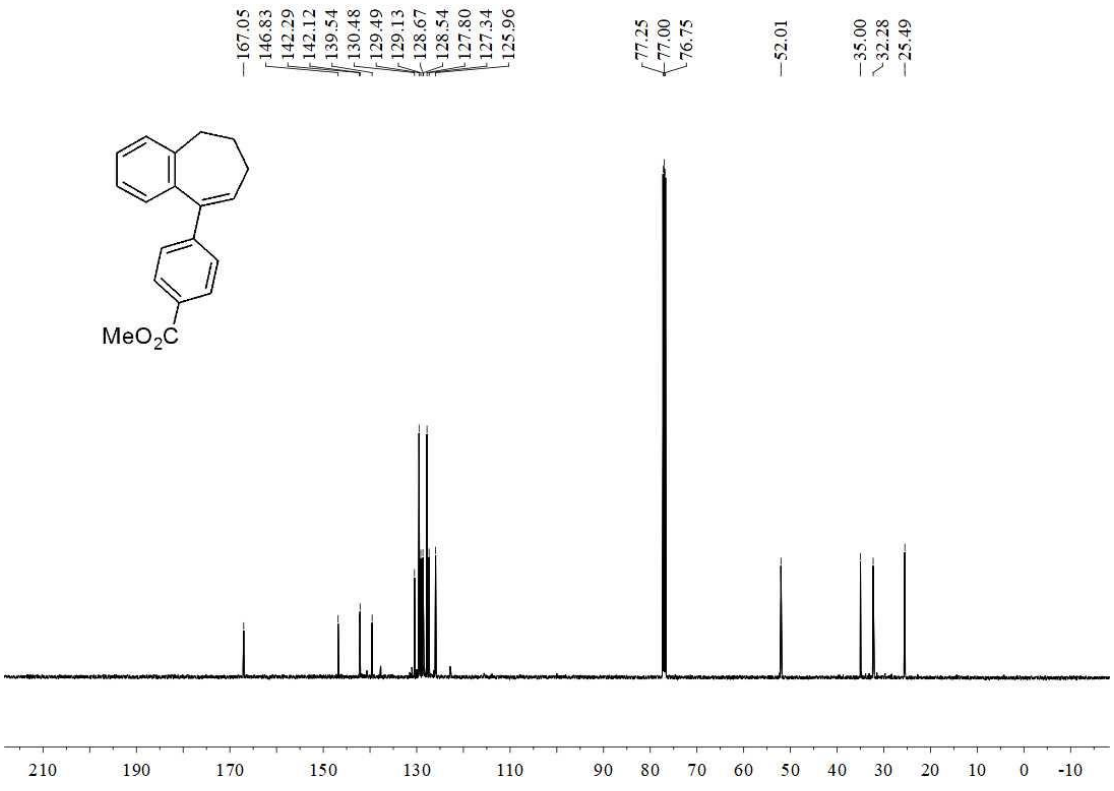
^{13}C NMR (101 MHz, $CDCl_3$) **(3d)**



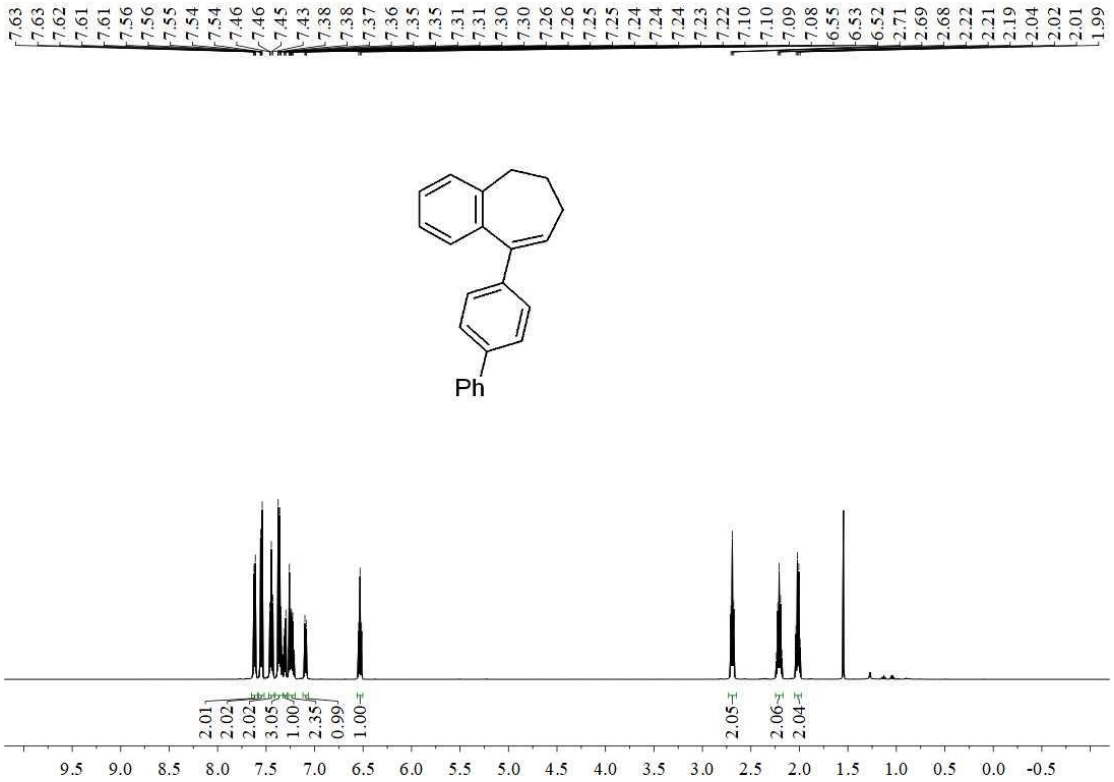
^{1}H NMR (400 MHz, $CDCl_3$) **(3e)**



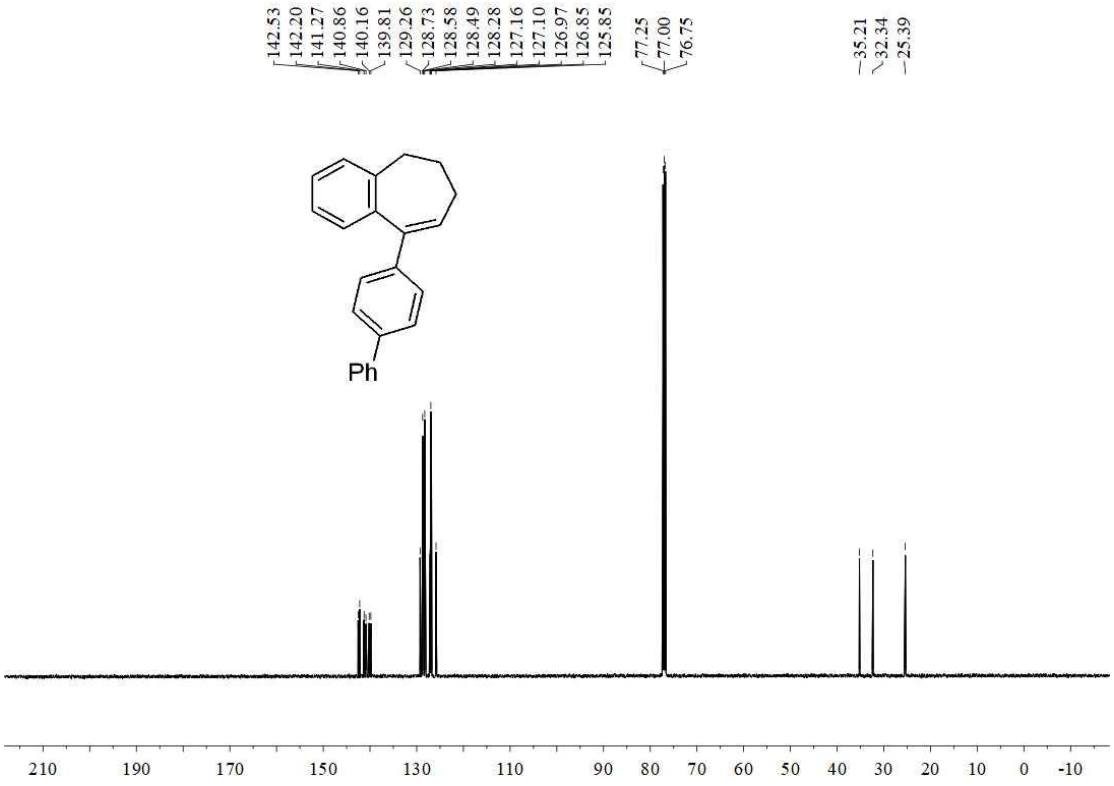
^{13}C NMR (101 MHz, $CDCl_3$) **(3e)**



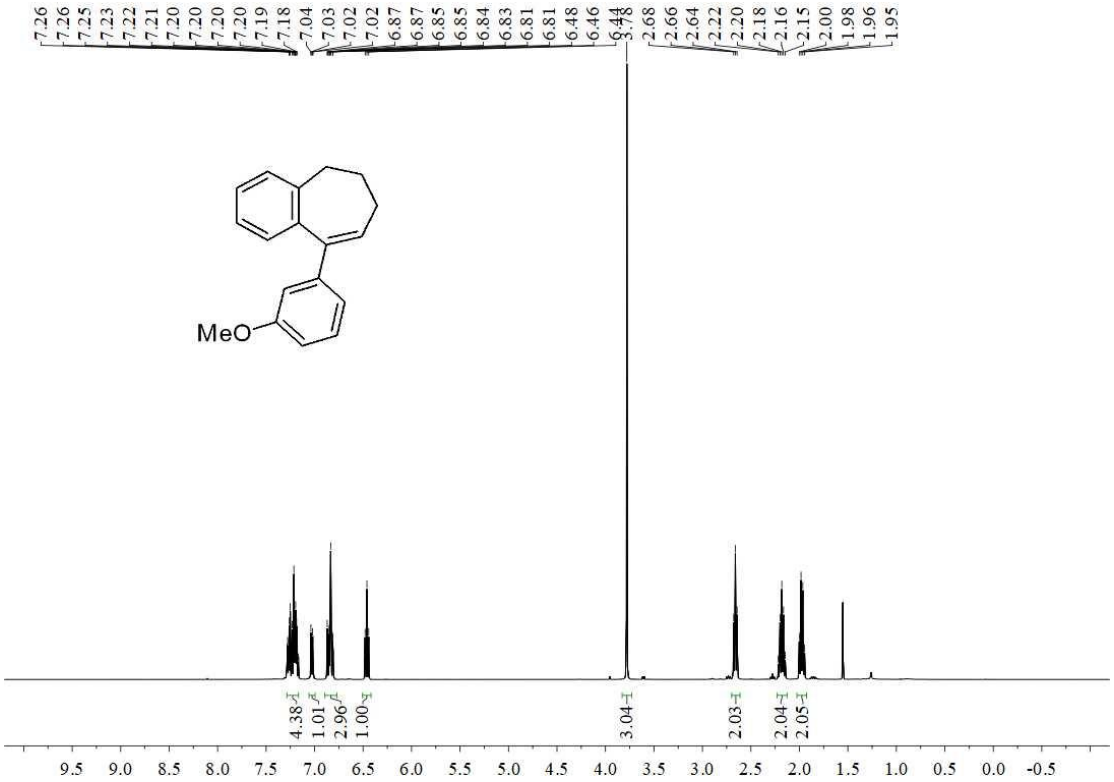
^{1}H NMR (400 MHz, $CDCl_3$) **(3g)**



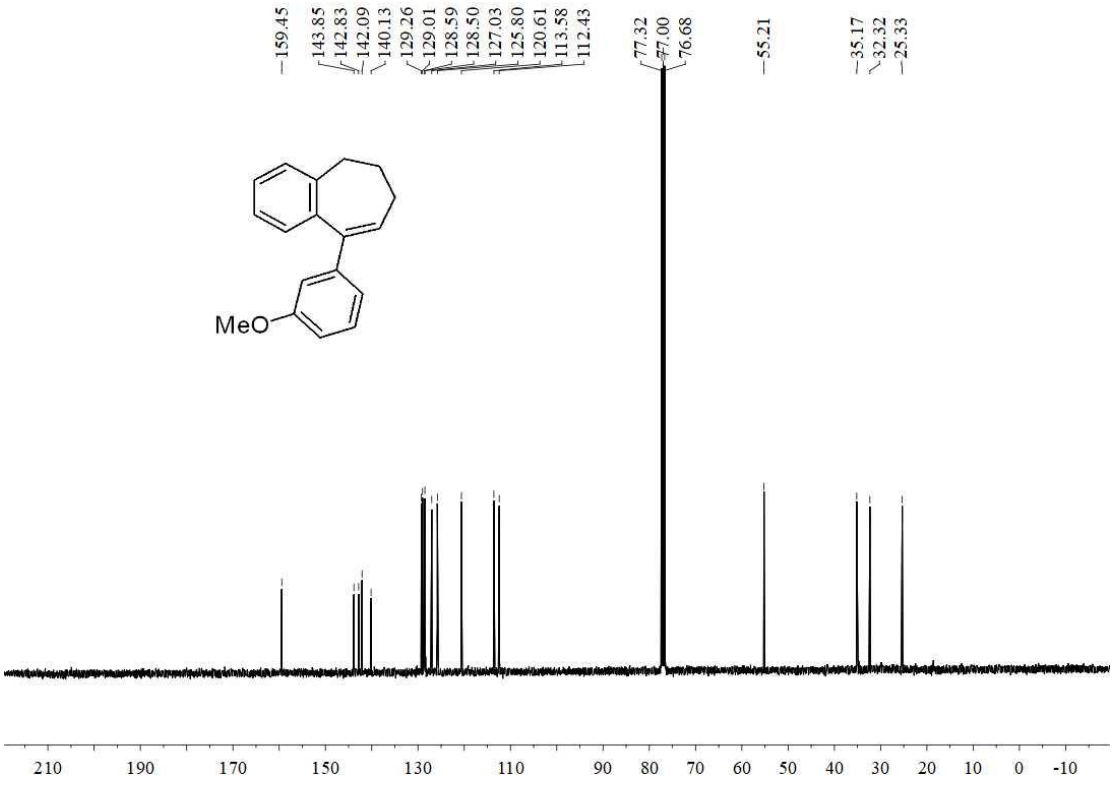
^{13}C NMR (101 MHz, $CDCl_3$) **(3g)**



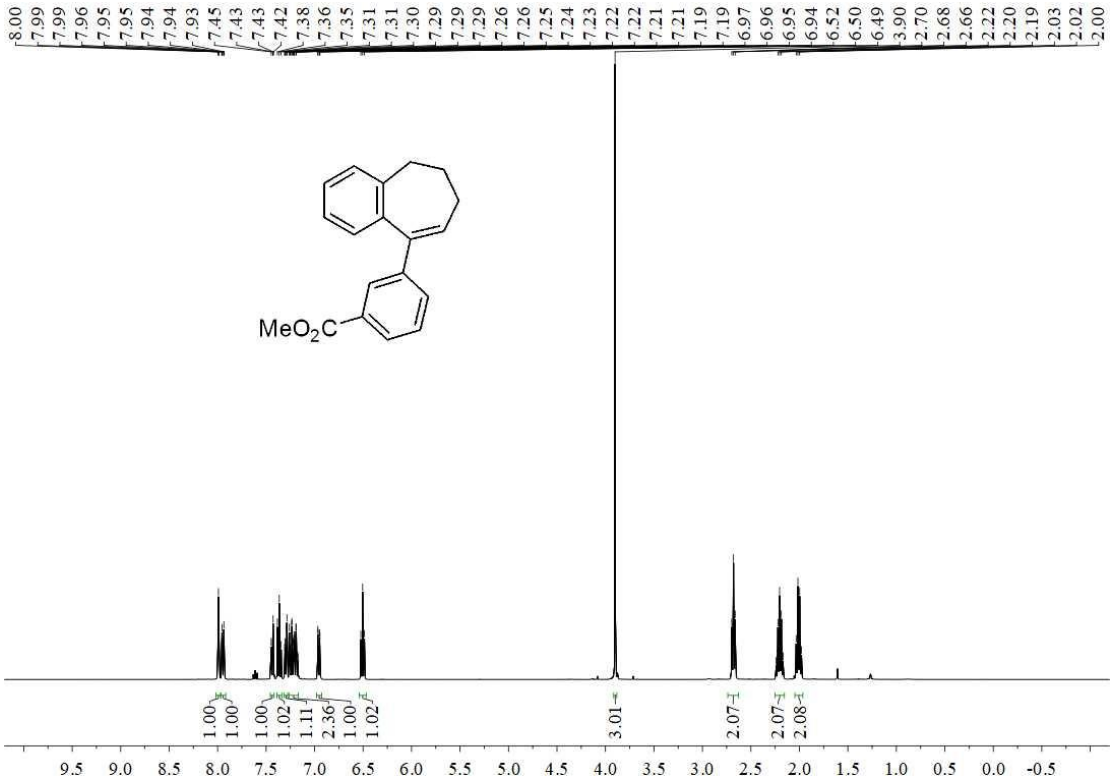
^{1}H NMR (400 MHz, $CDCl_3$) **(3h)**



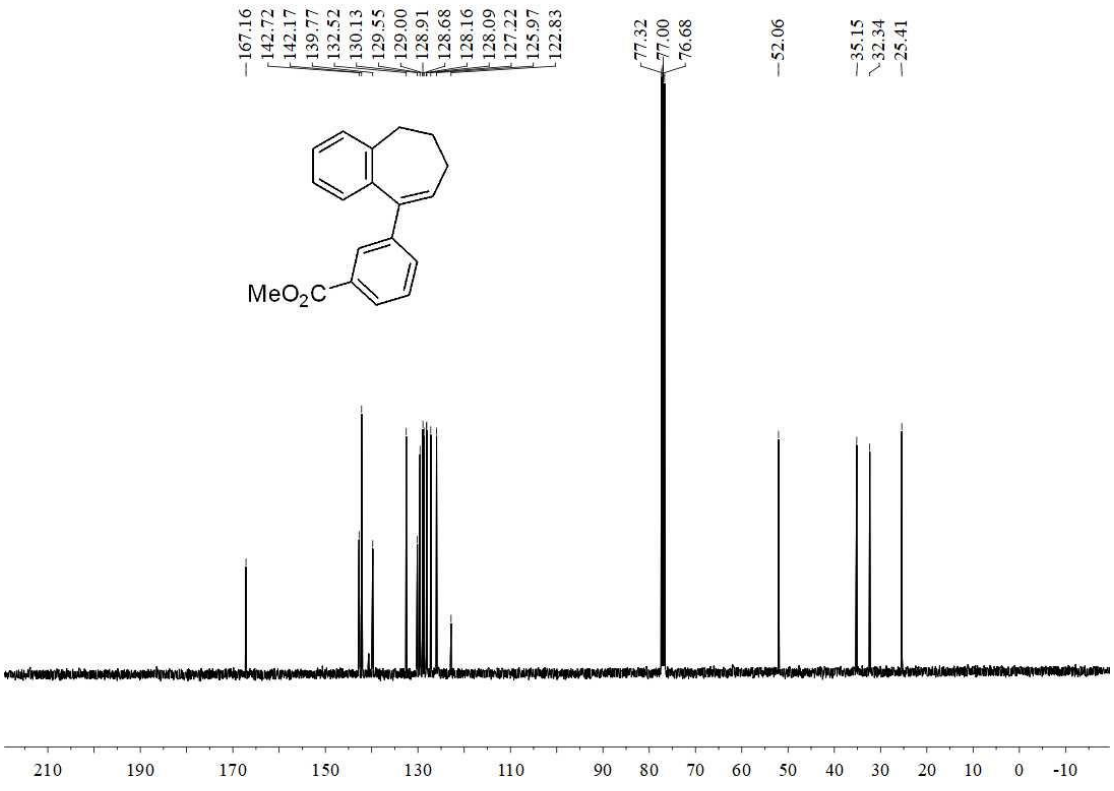
^{13}C NMR (101 MHz, $CDCl_3$) **(3h)**



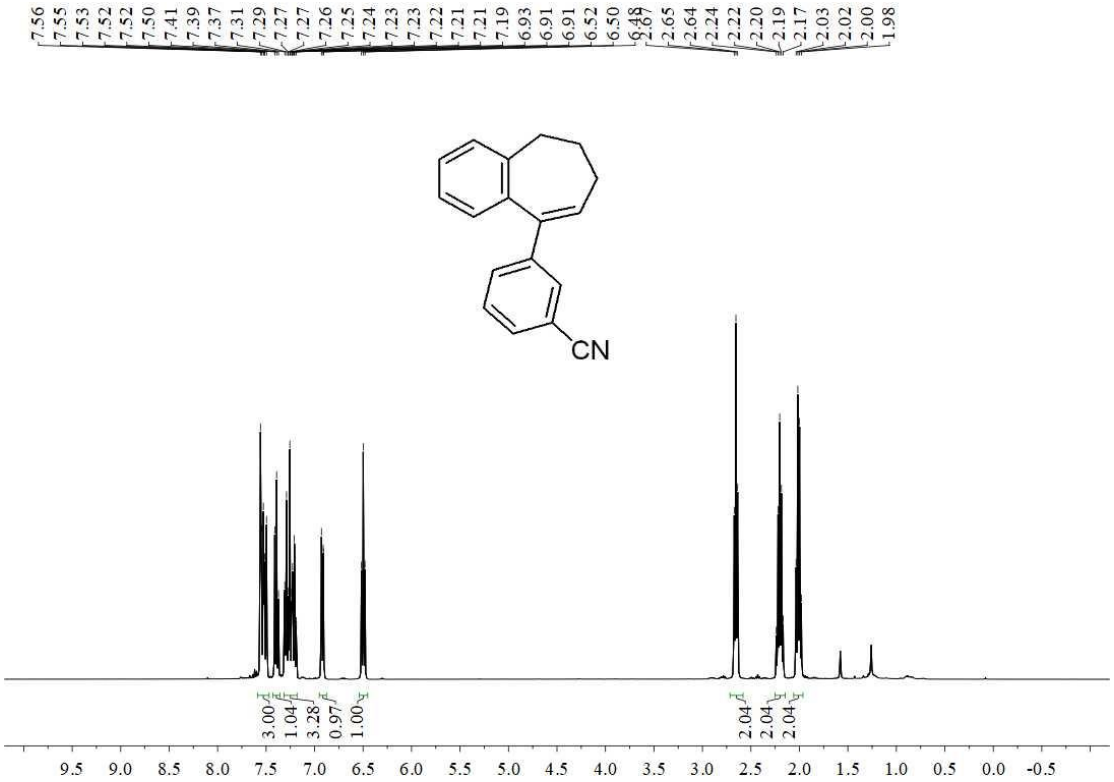
^{1}H NMR (400 MHz, $CDCl_3$) **(3i)**



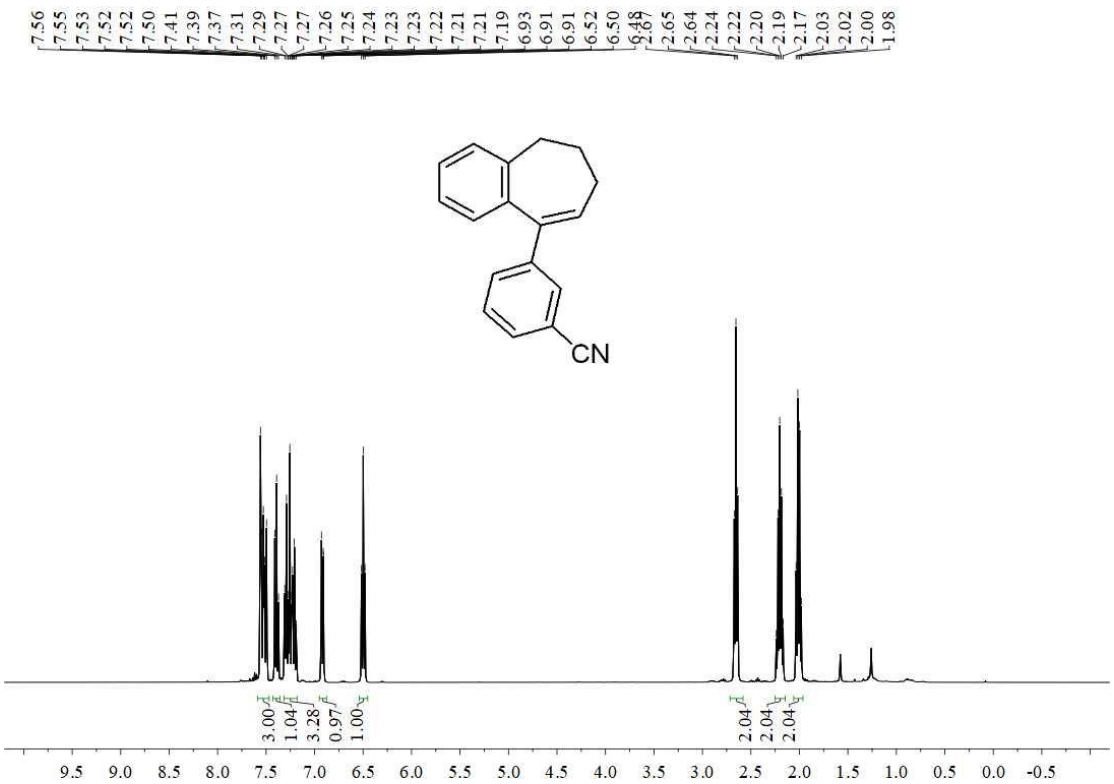
^{13}C NMR (101 MHz, $CDCl_3$) **(3i)**



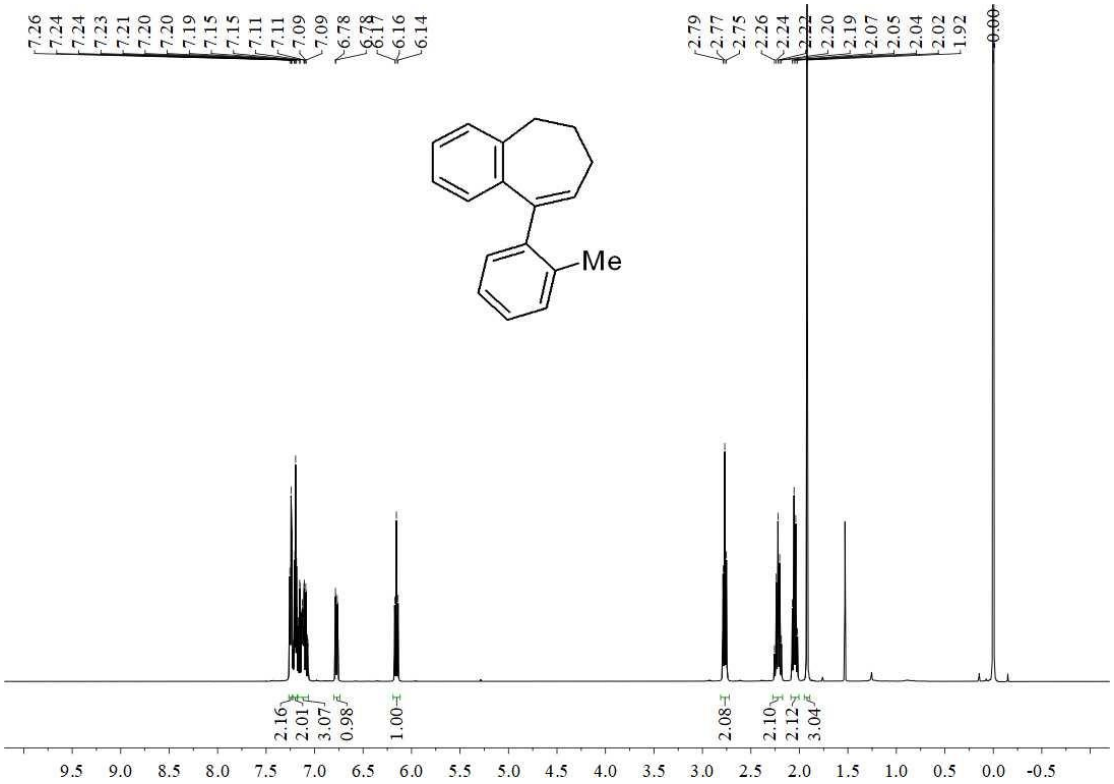
^{1}H NMR (400 MHz, $CDCl_3$) **(3j)**



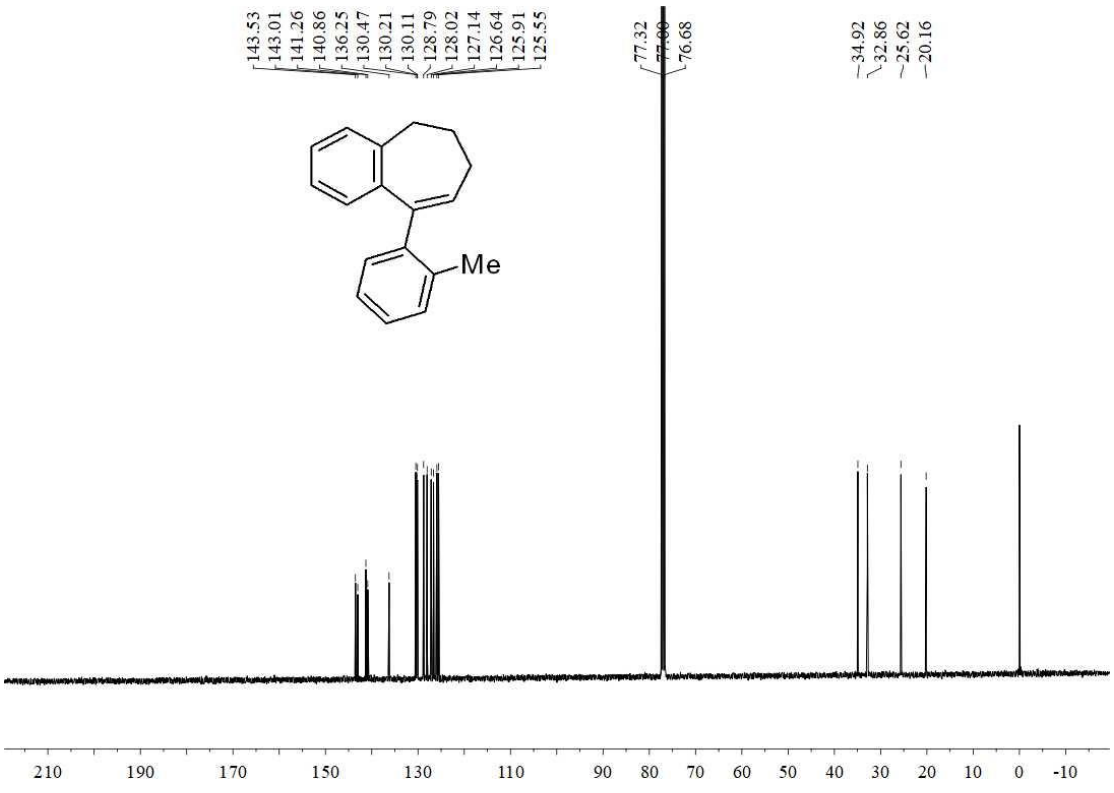
^{13}C NMR (101 MHz, $CDCl_3$) **(3j)**



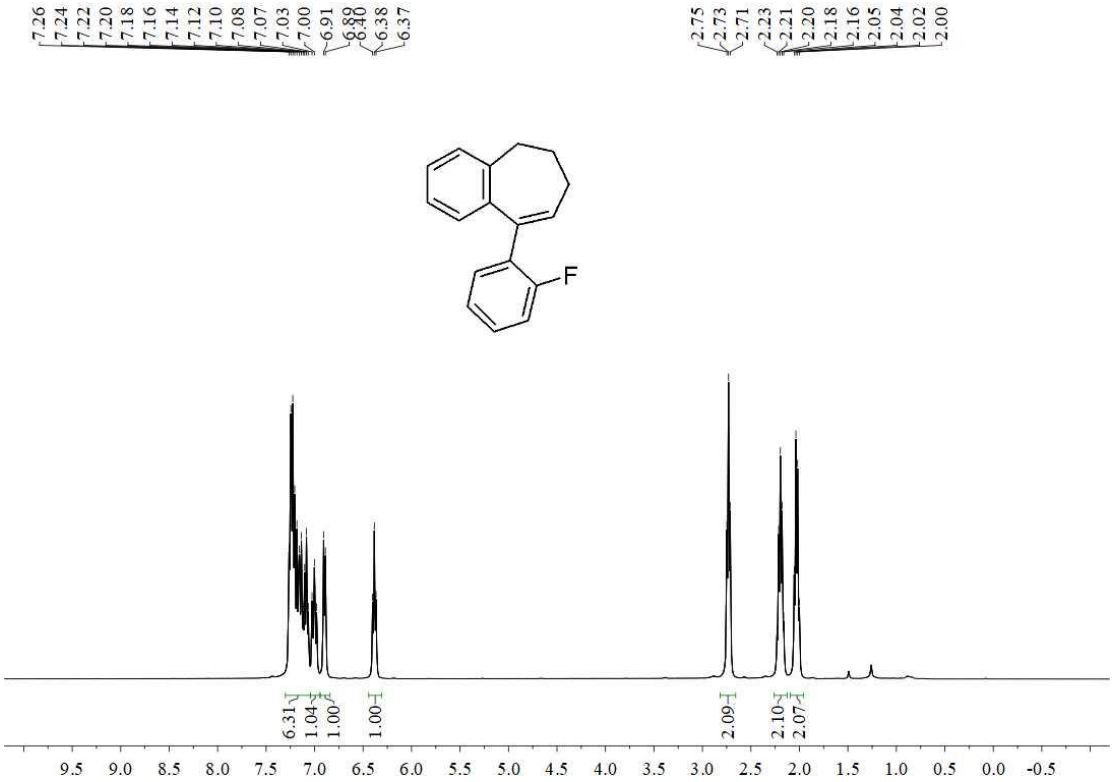
^{1}H NMR (400 MHz, $CDCl_3$) **(3k)**



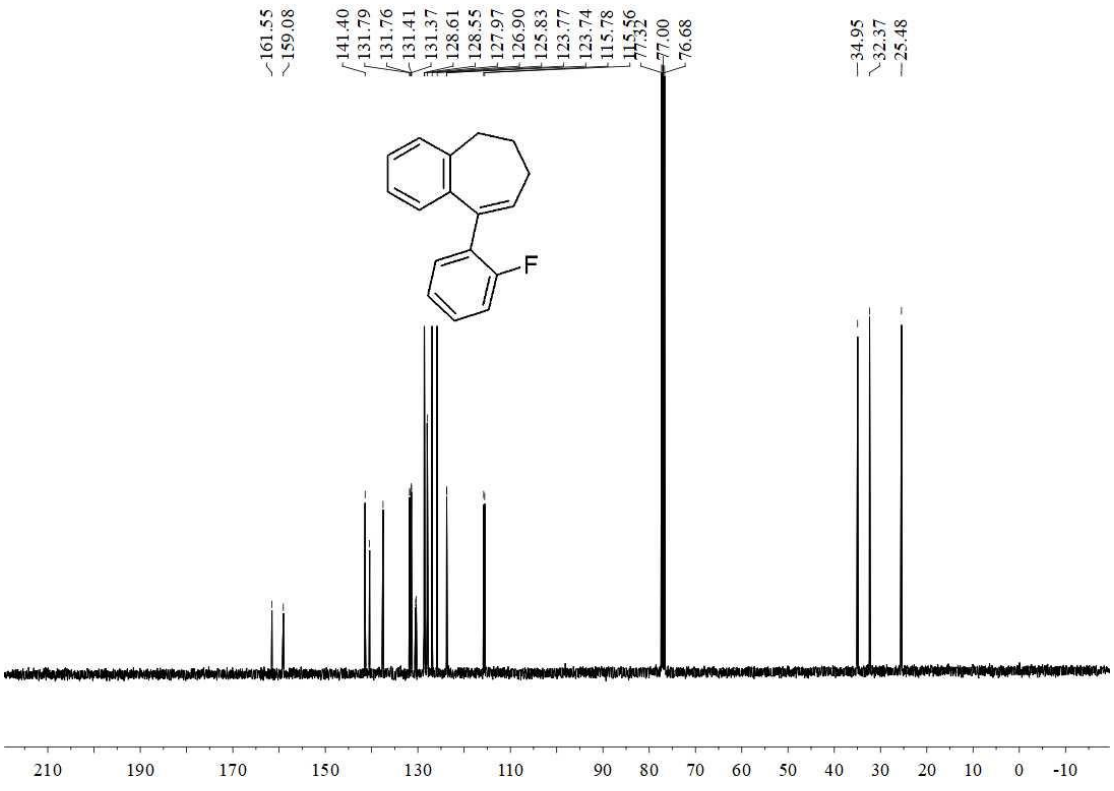
^{13}C NMR (101 MHz, $CDCl_3$) **(3k)**



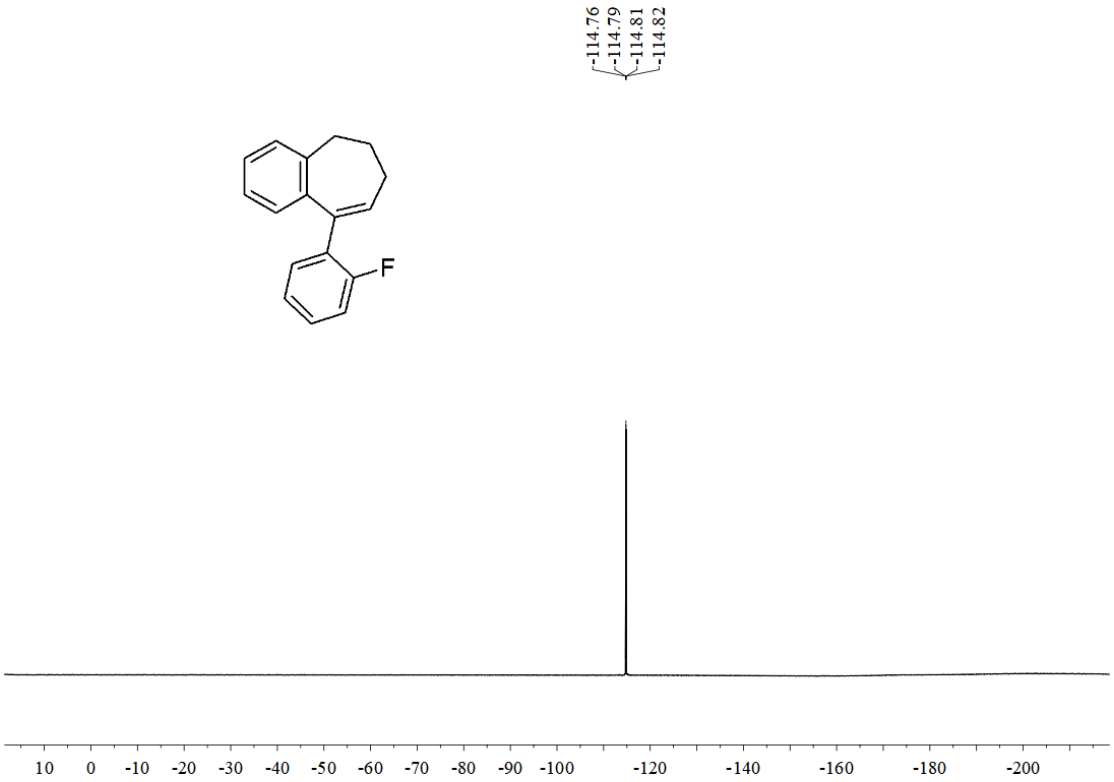
^{1}H NMR (400 MHz, $CDCl_3$) **(3l)**



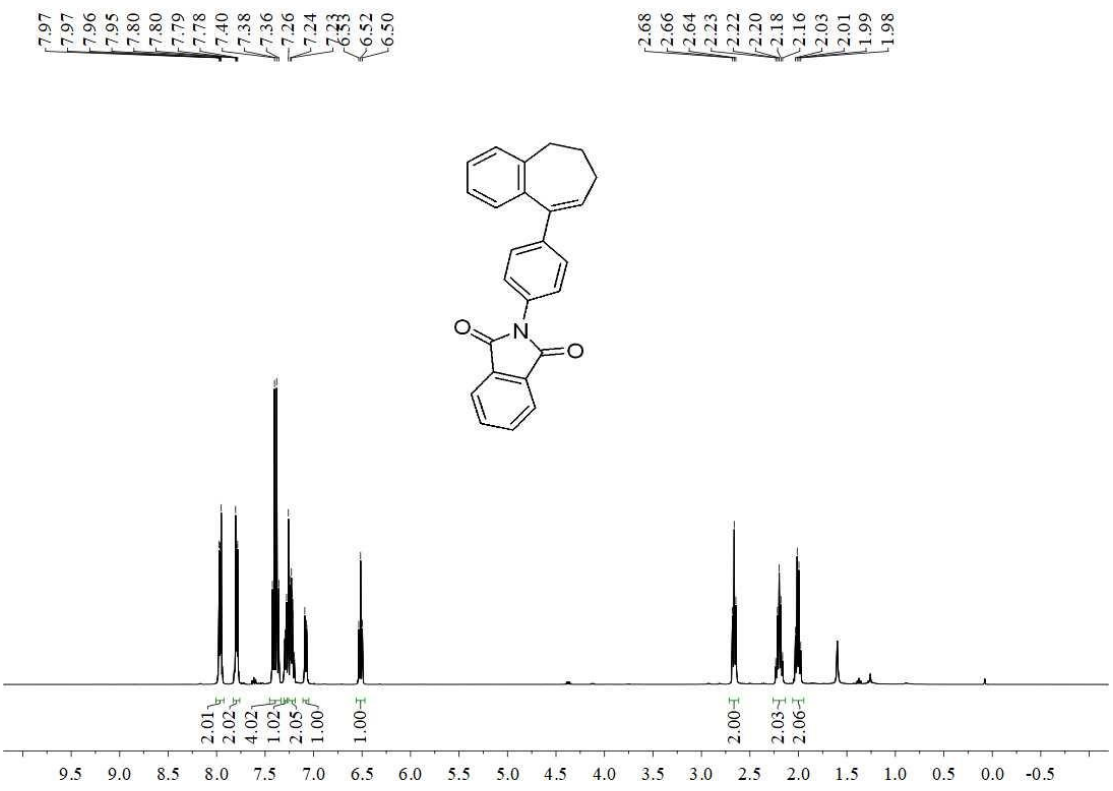
^{13}C NMR (101 MHz, $CDCl_3$) **(3l)**



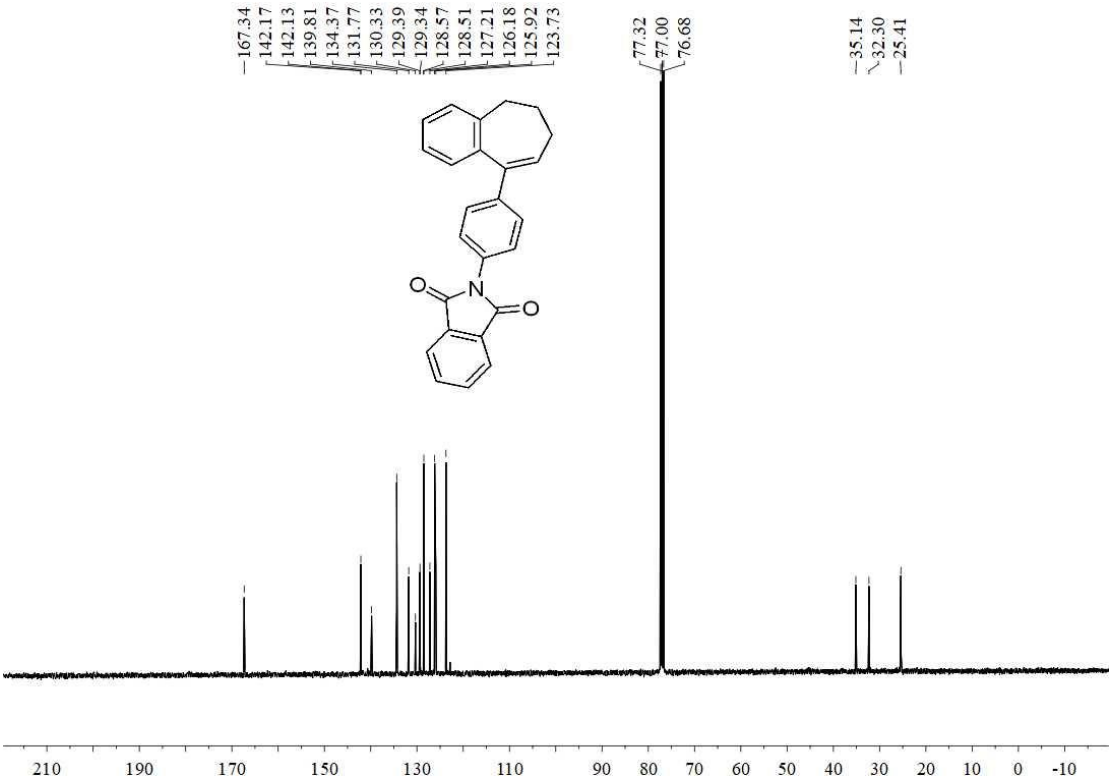
^{19}F NMR (376 MHz, $CDCl_3$) **(3l)**



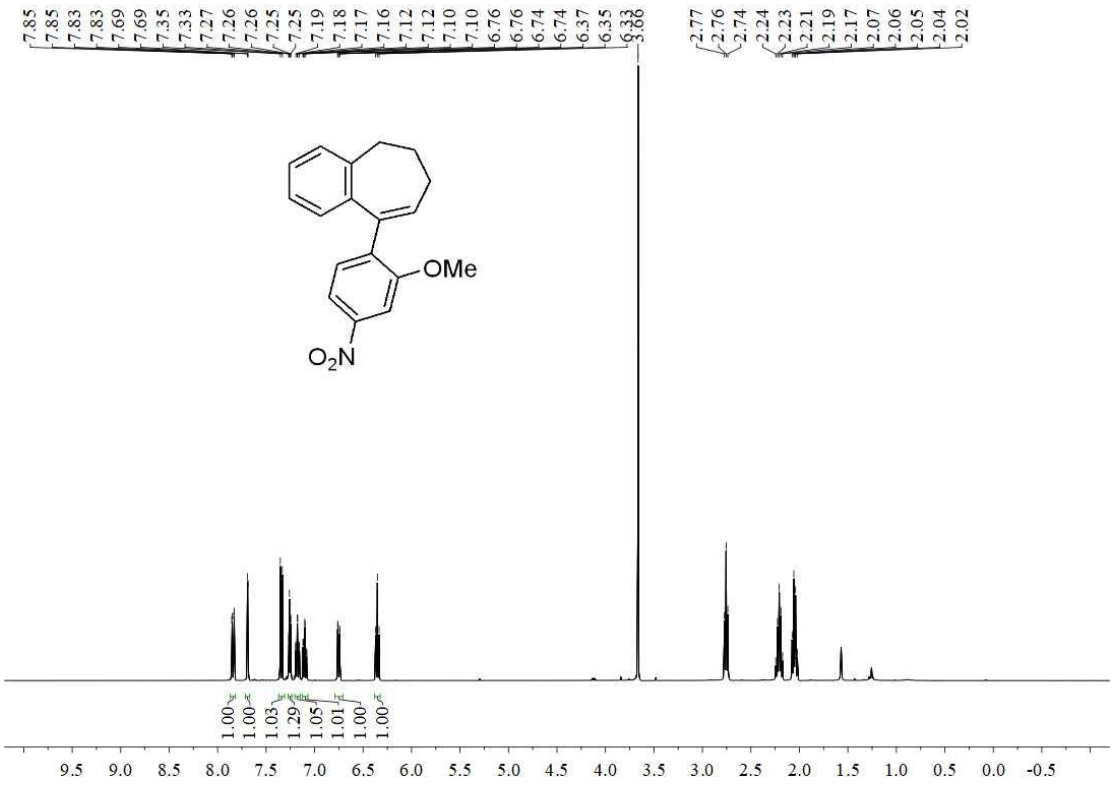
^{1}H NMR (400 MHz, $CDCl_3$) **(3m)**



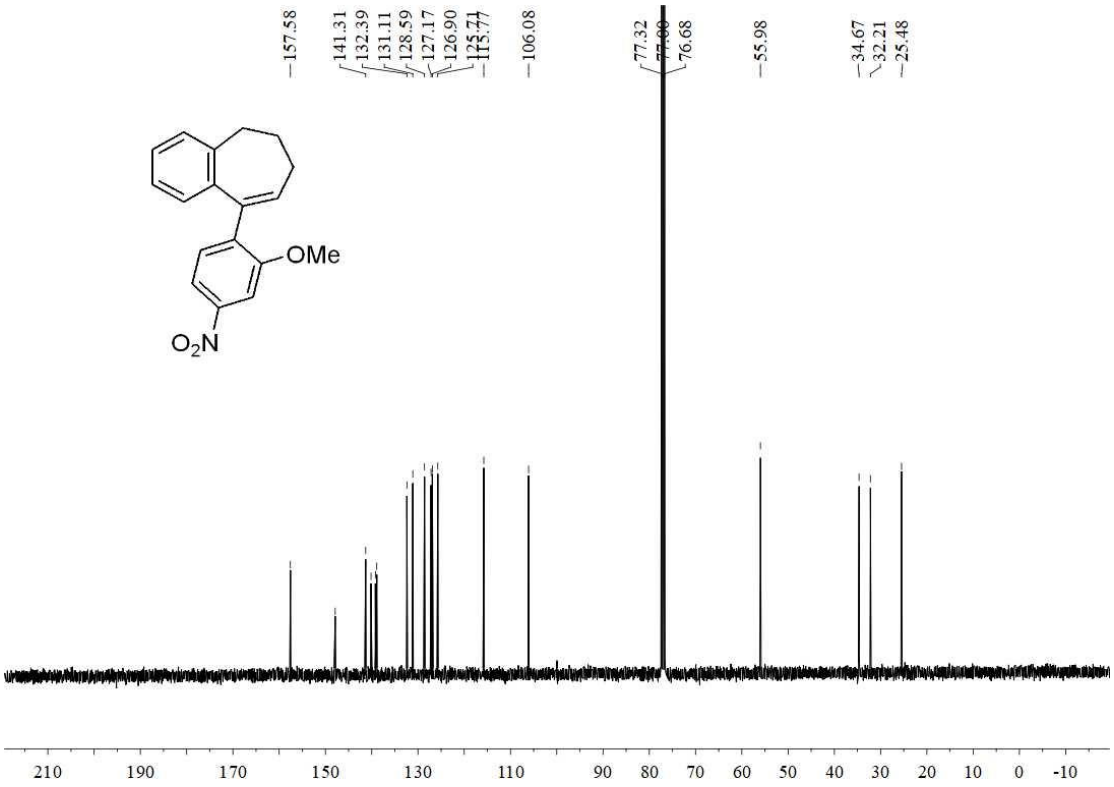
^{13}C NMR (101 MHz, $CDCl_3$) **(3m)**



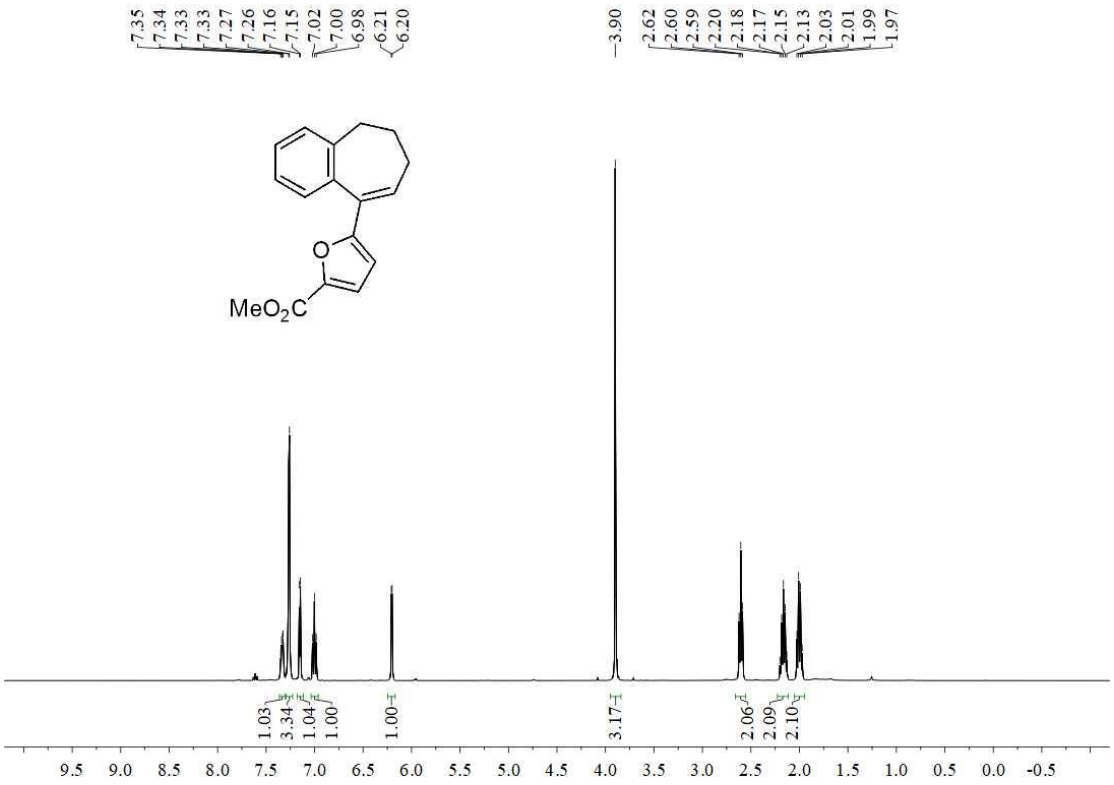
^{1}H NMR (400 MHz, $CDCl_3$) **(3n)**



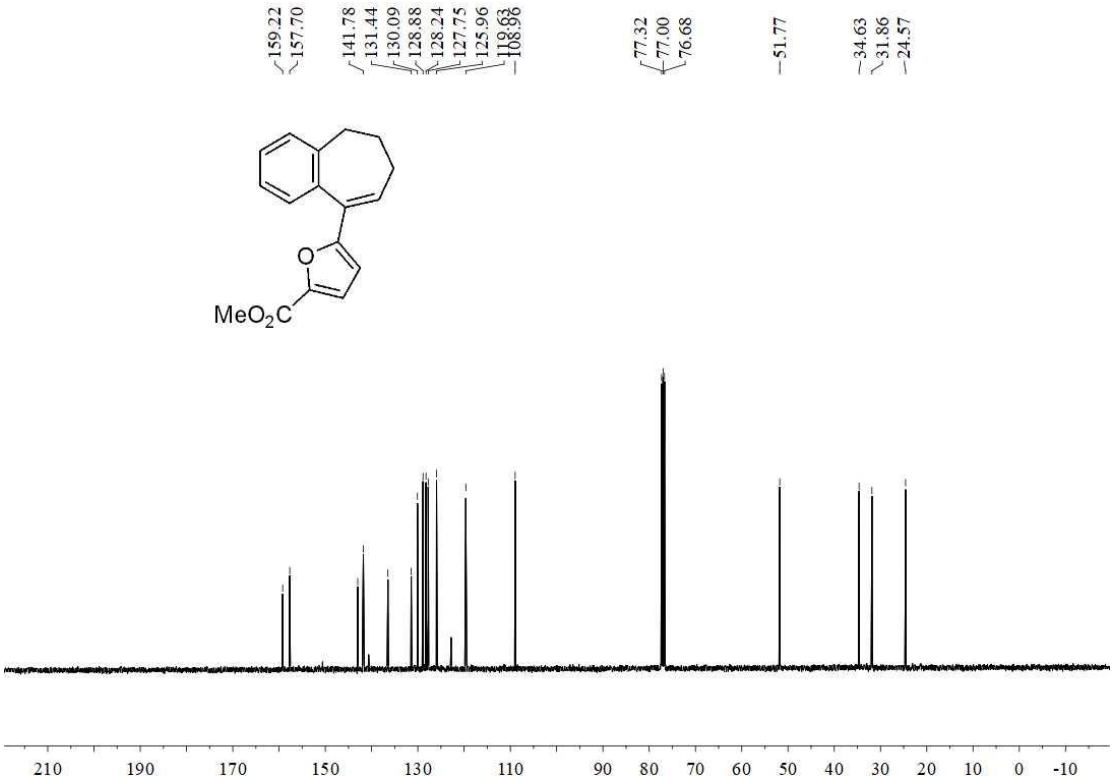
^{13}C NMR (101 MHz, $CDCl_3$) **(3n)**



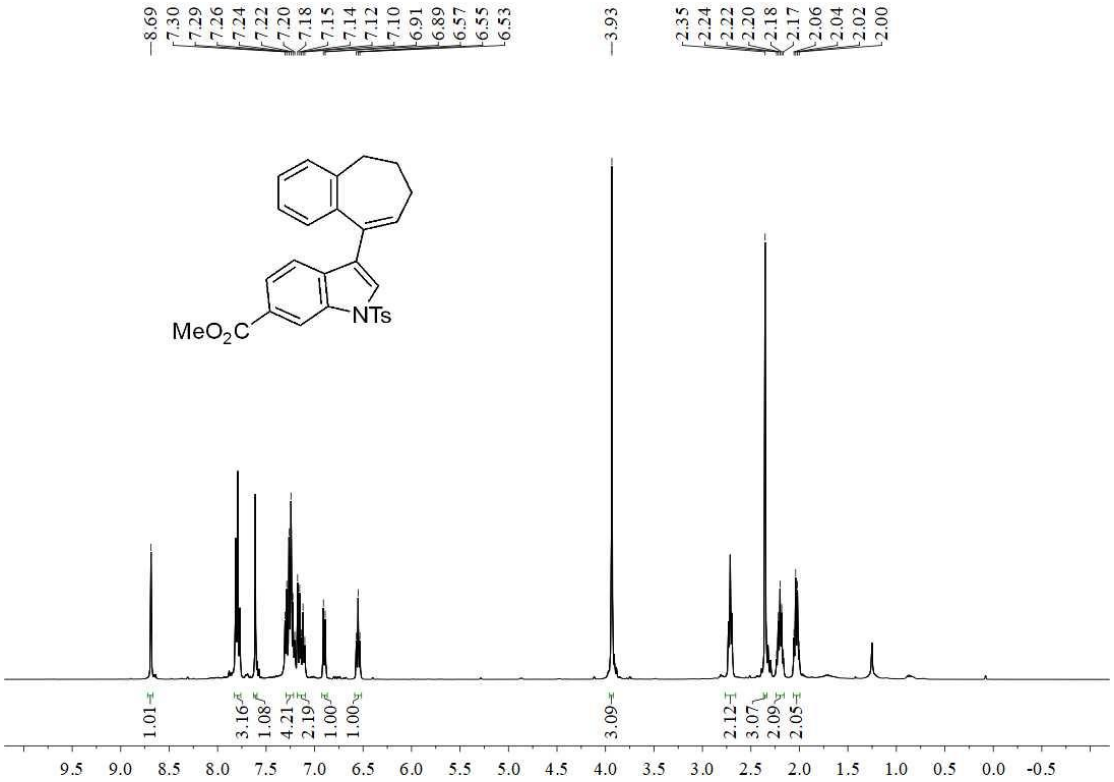
^{1}H NMR (400 MHz, $CDCl_3$) **(3o)**



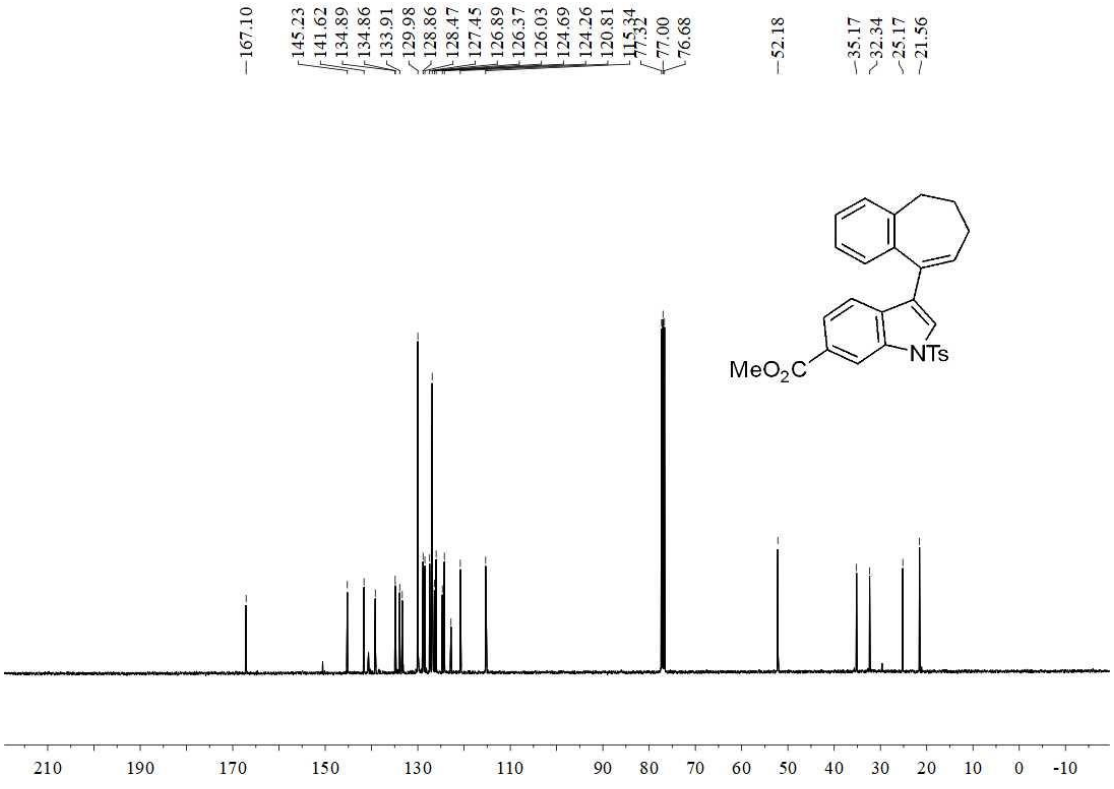
^{13}C NMR (101 MHz, $CDCl_3$) **(3o)**



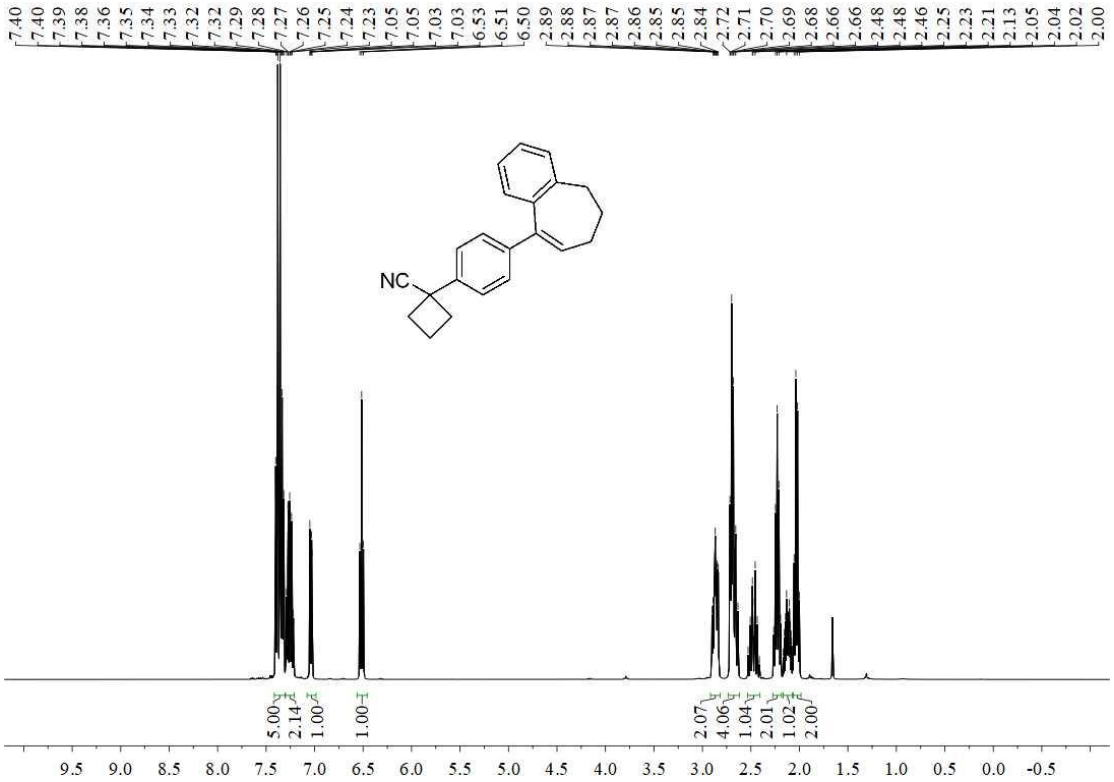
^{1}H NMR (400 MHz, $CDCl_3$) **(3p)**



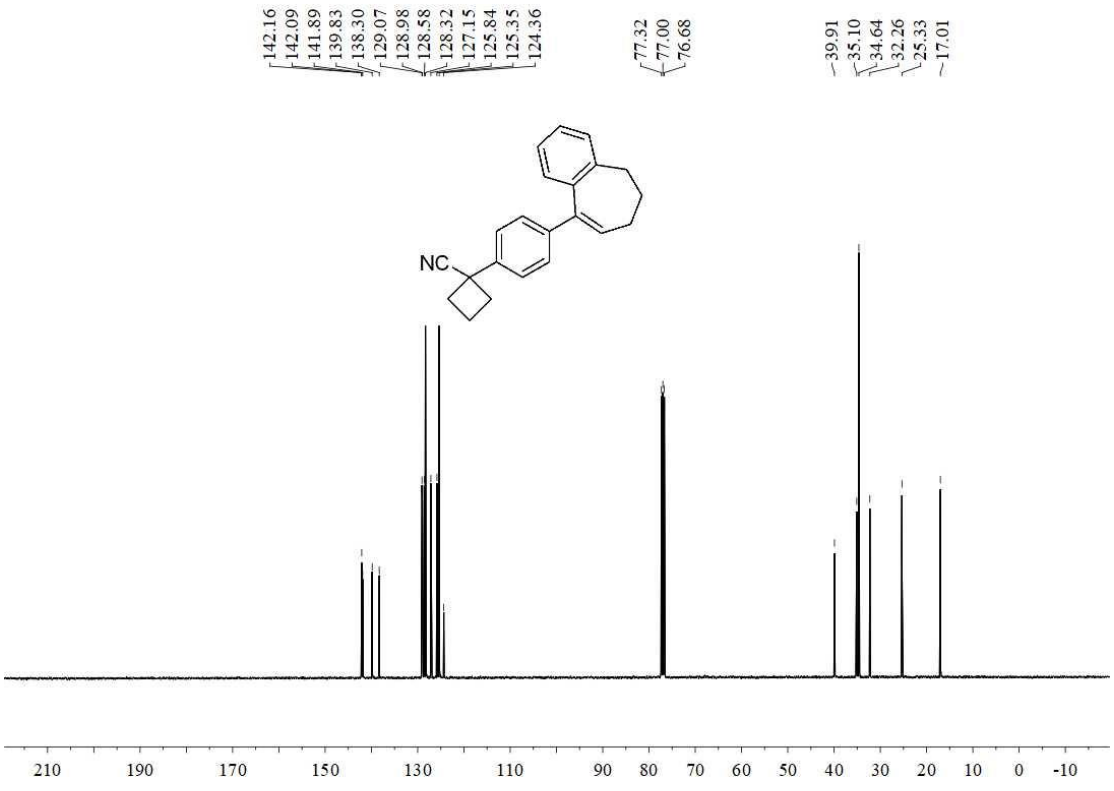
^{13}C NMR (101 MHz, $CDCl_3$) **(3p)**



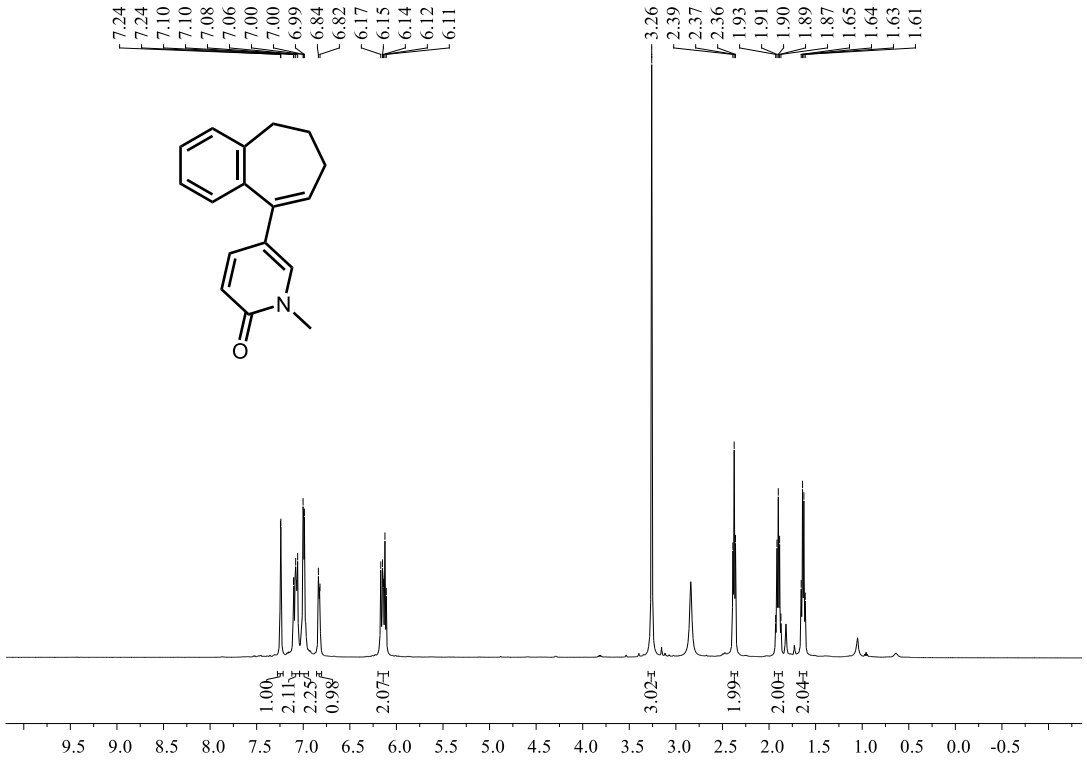
^{1}H NMR (400 MHz, $CDCl_3$) **(3q)**



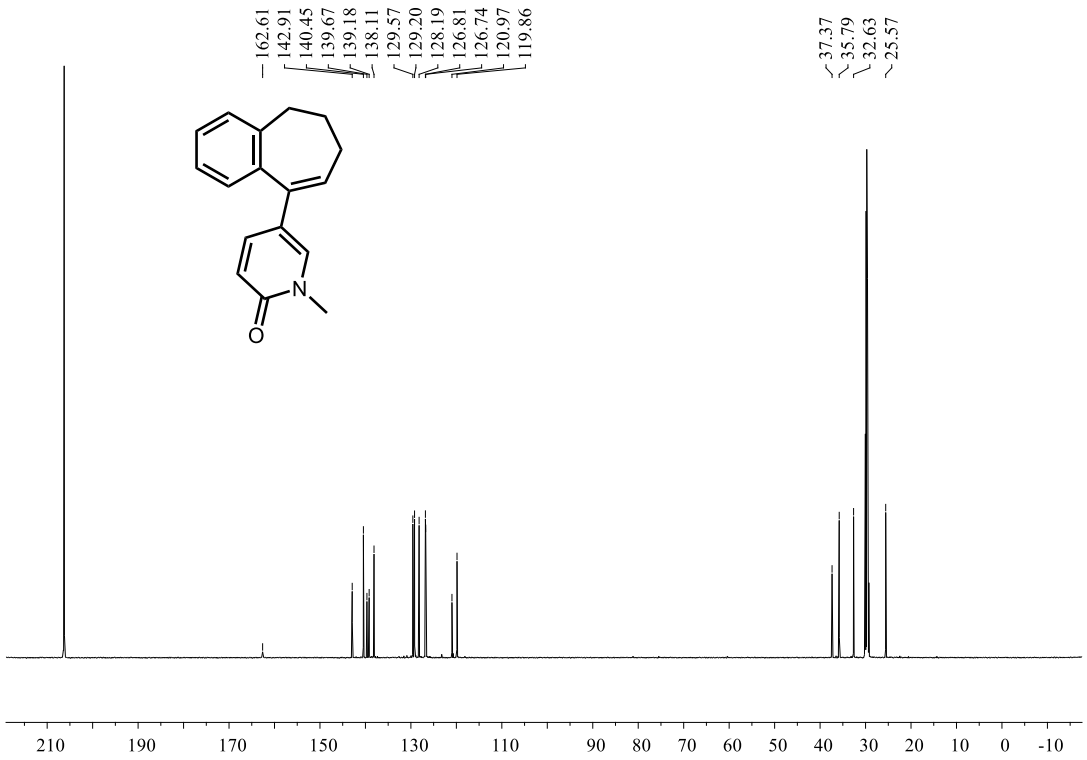
^{13}C NMR (101 MHz, $CDCl_3$) **(3q)**



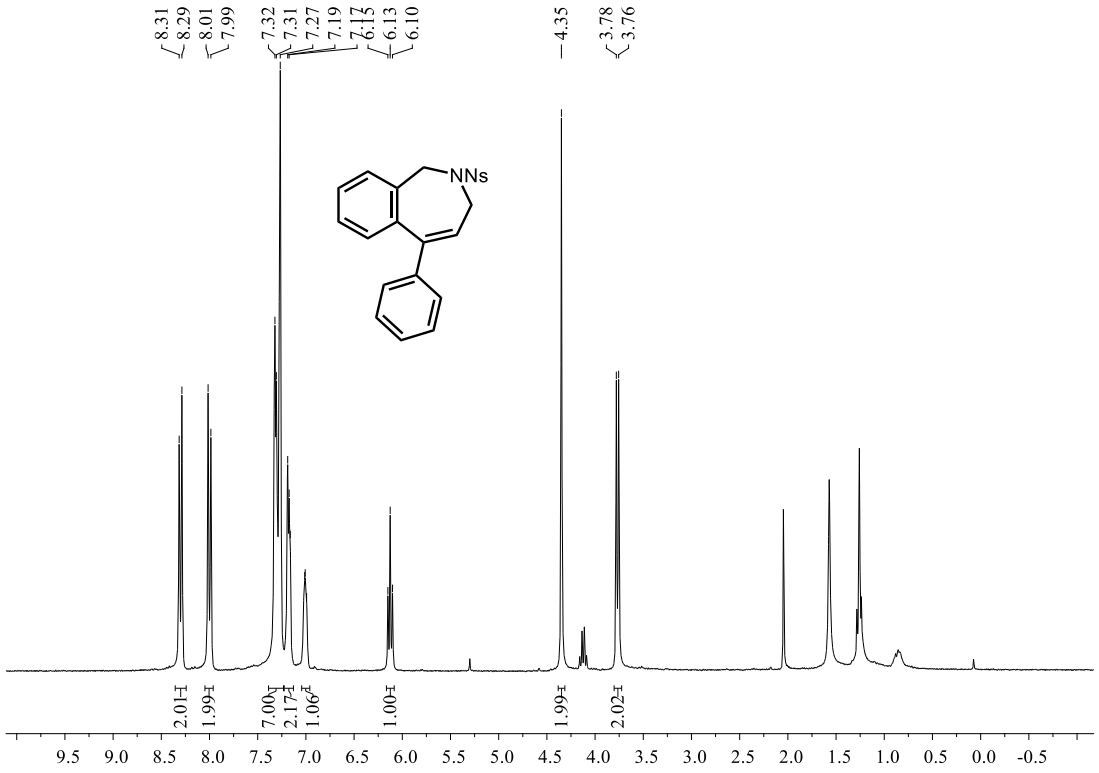
^{1}H NMR (500 MHz, $(CD_3)_2O$) **(3r)**



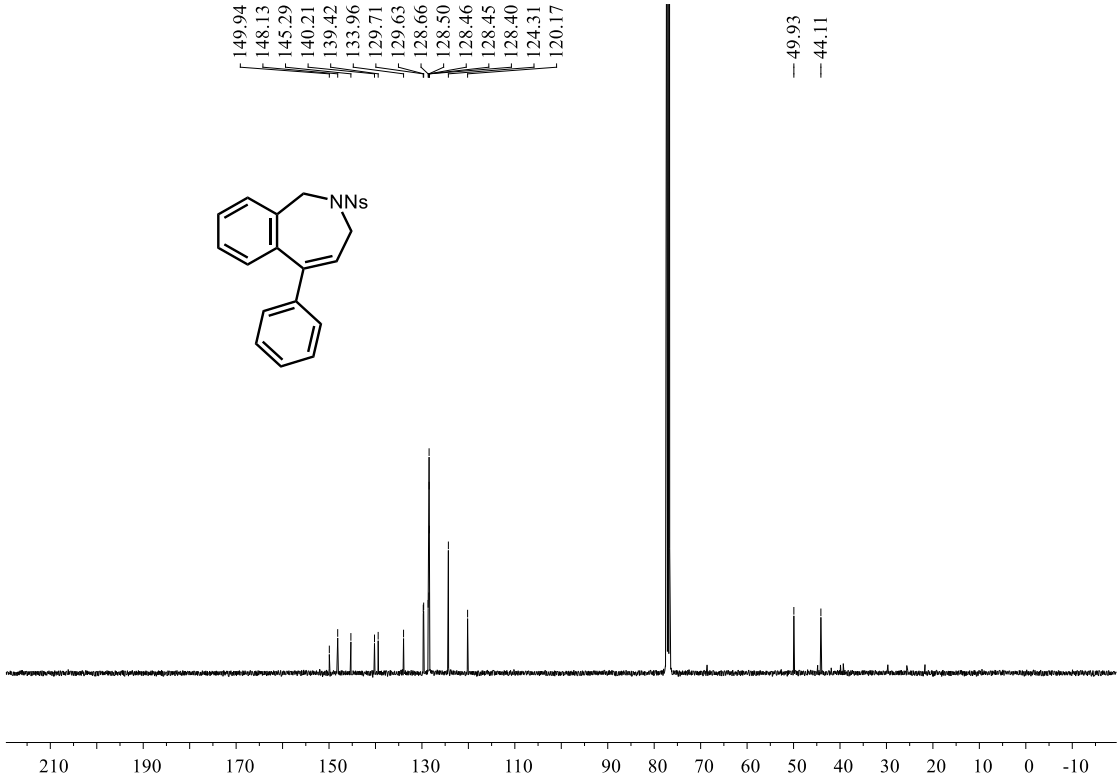
^{13}C NMR (126 MHz, $(CD_3)_2O$) **(3r)**



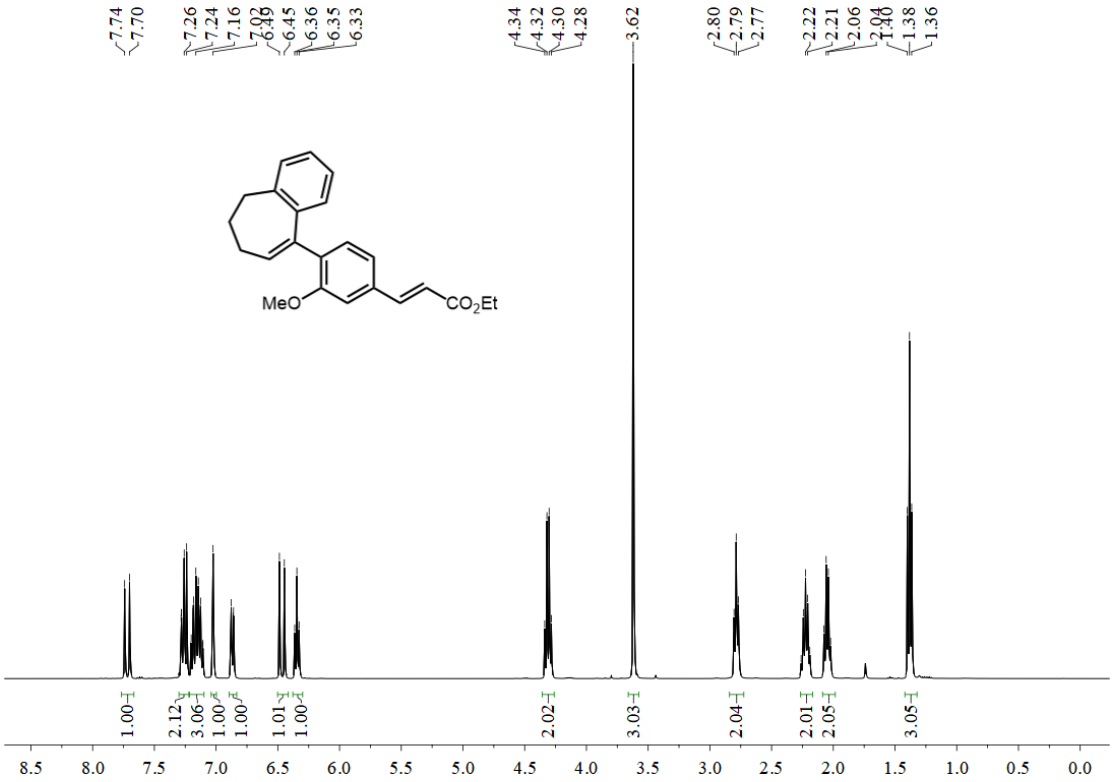
^{1}H NMR (300 MHz, $CDCl_3$) **(3s)**



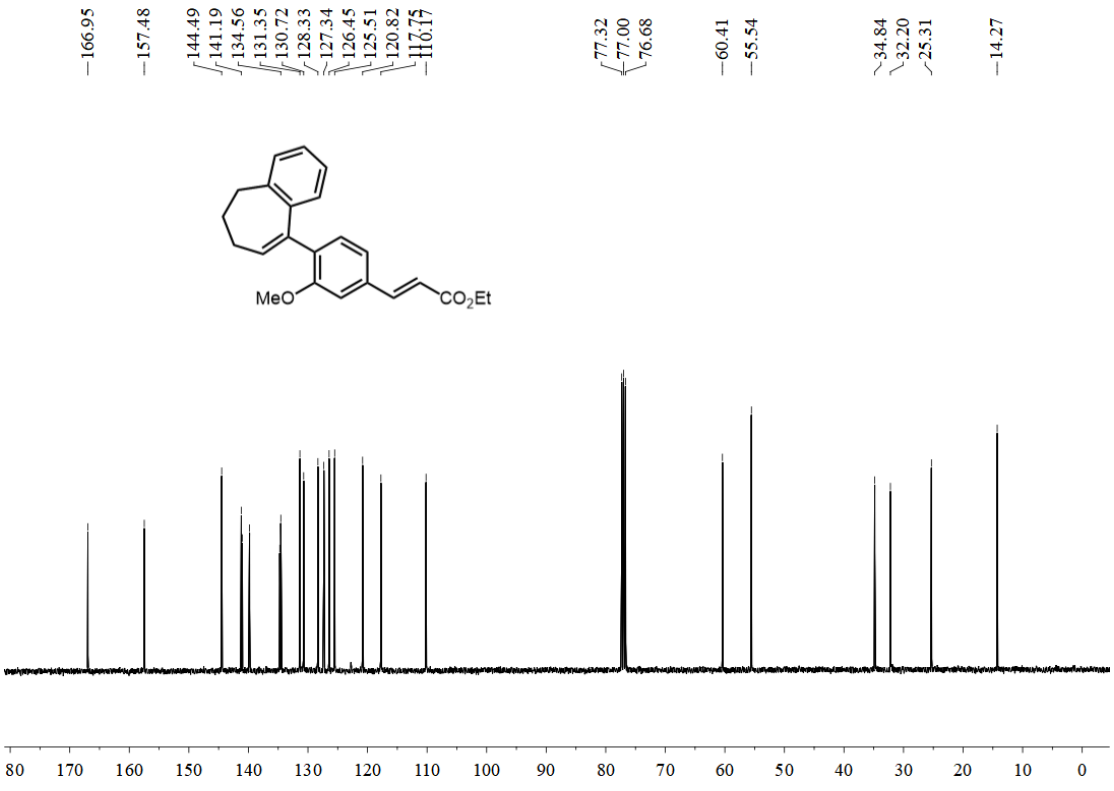
^{13}C NMR (101 MHz, $CDCl_3$) **(3s)**



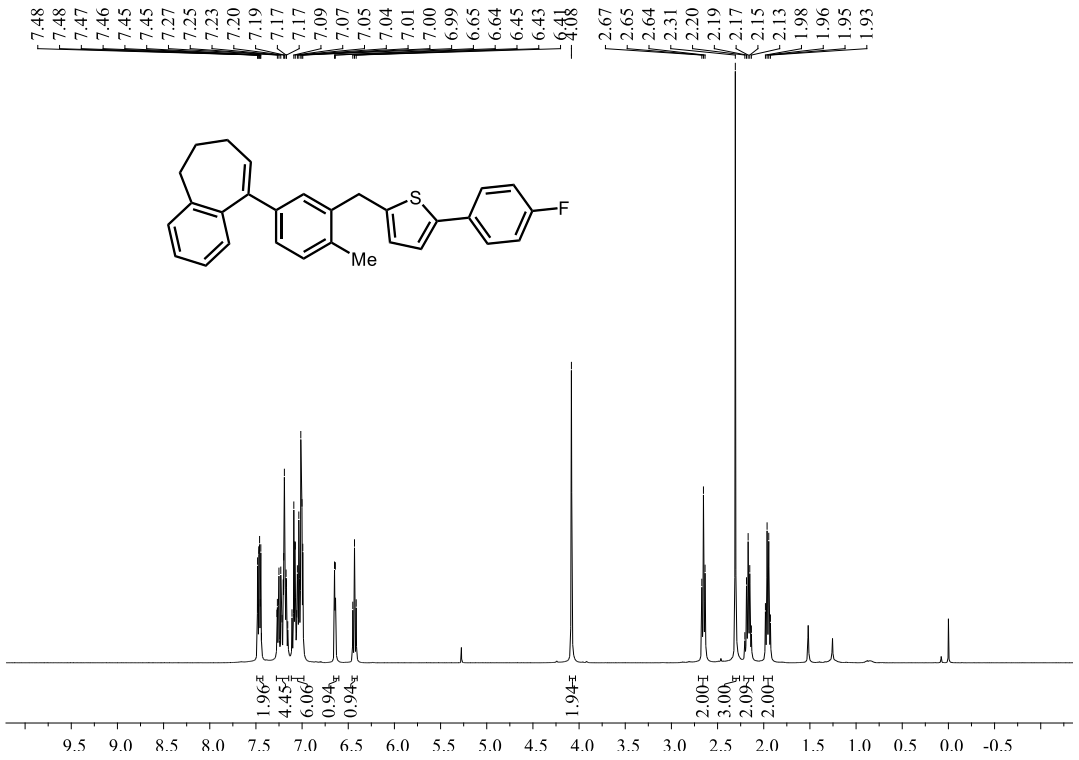
^{1}H NMR (400 MHz, $CDCl_3$) **(3t)**



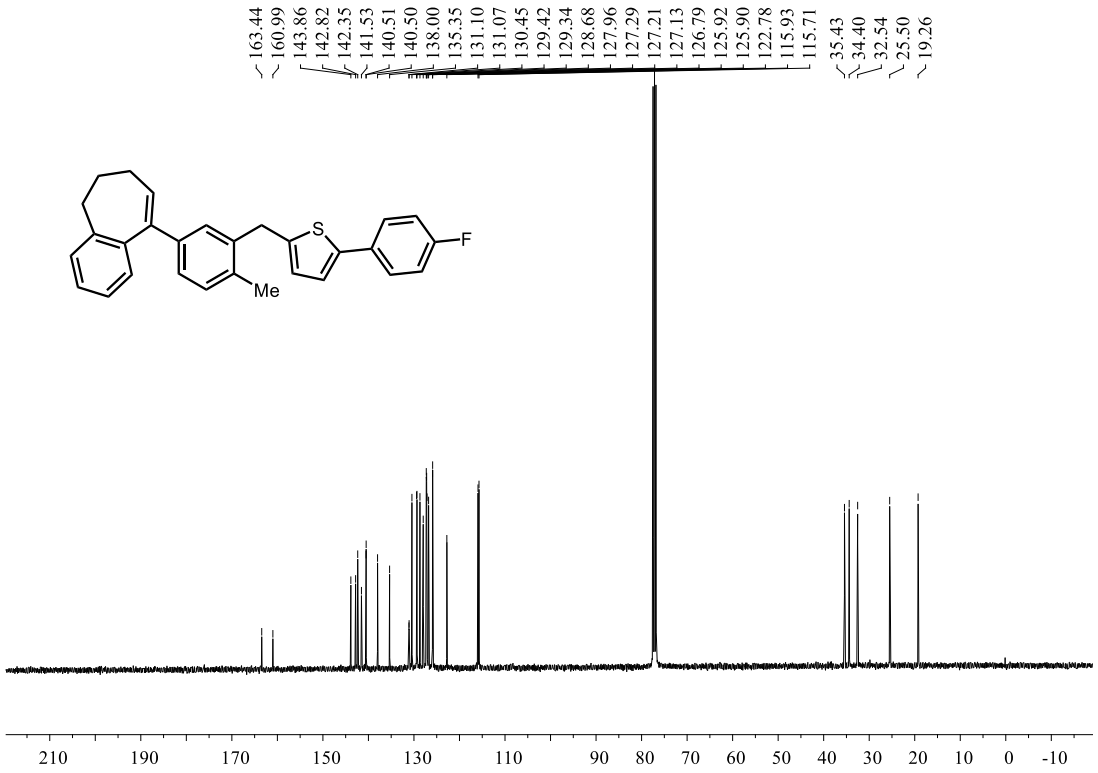
^{13}C NMR (101 MHz, $CDCl_3$) **(3t)**



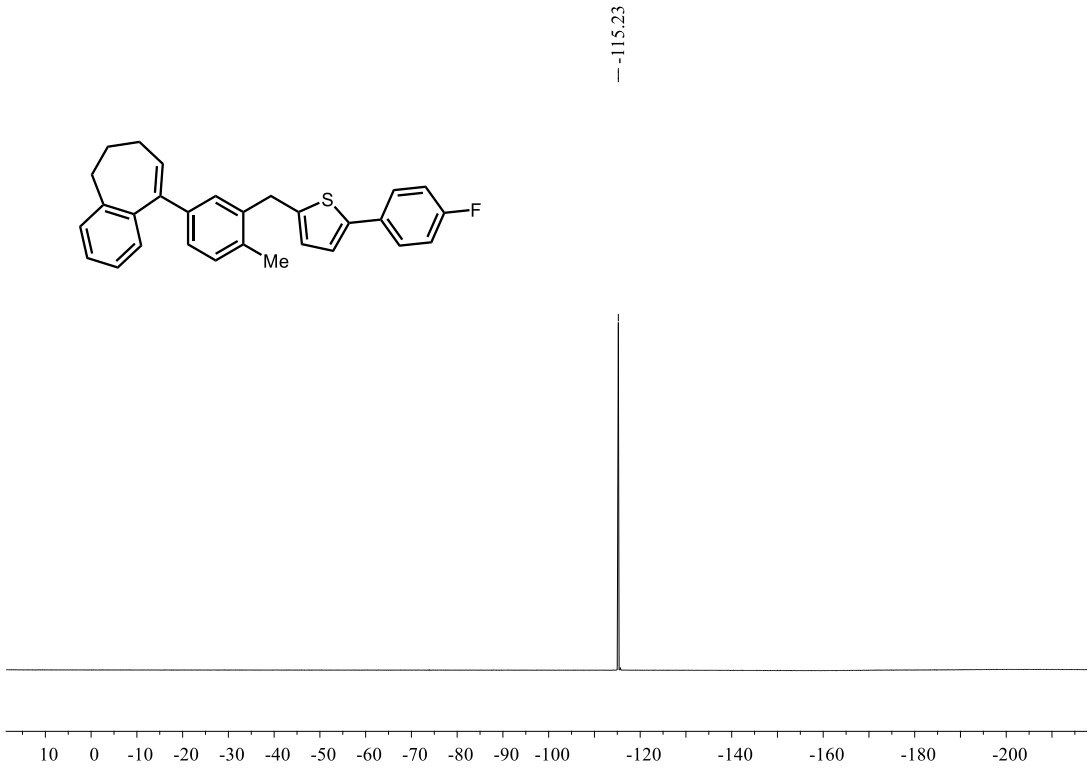
^{1}H NMR (400 MHz, $CDCl_3$) **(3u)**



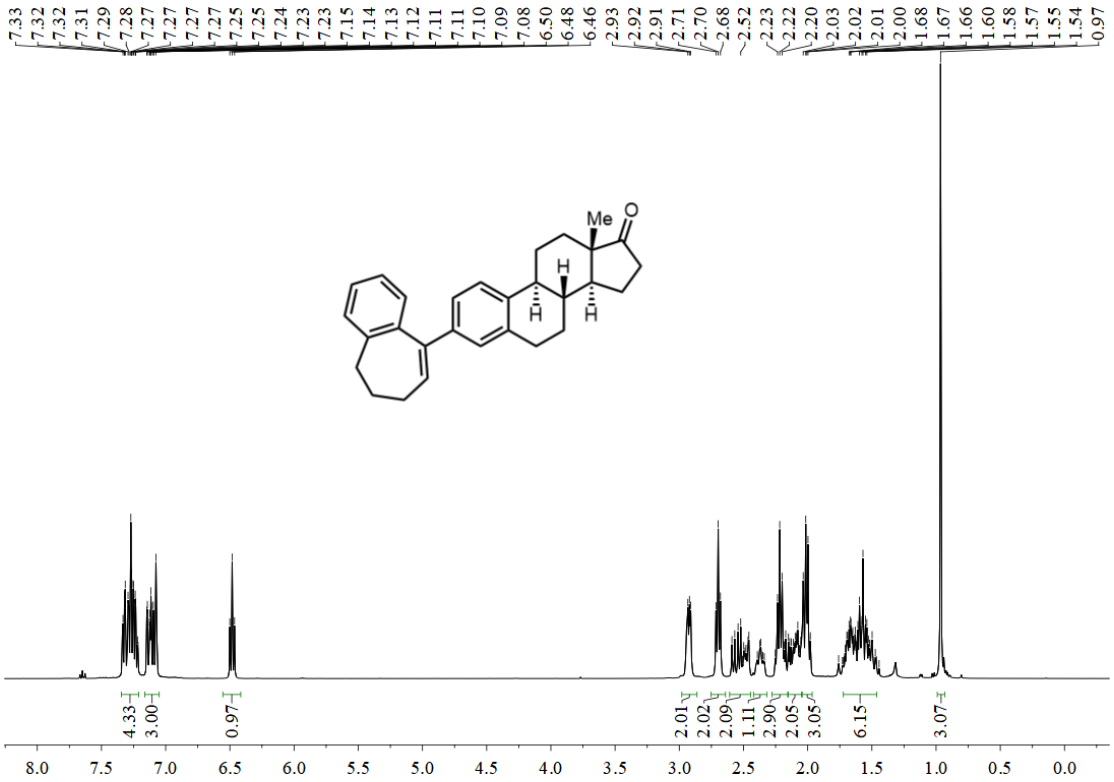
^{13}C NMR (101 MHz, $CDCl_3$) **(3u)**



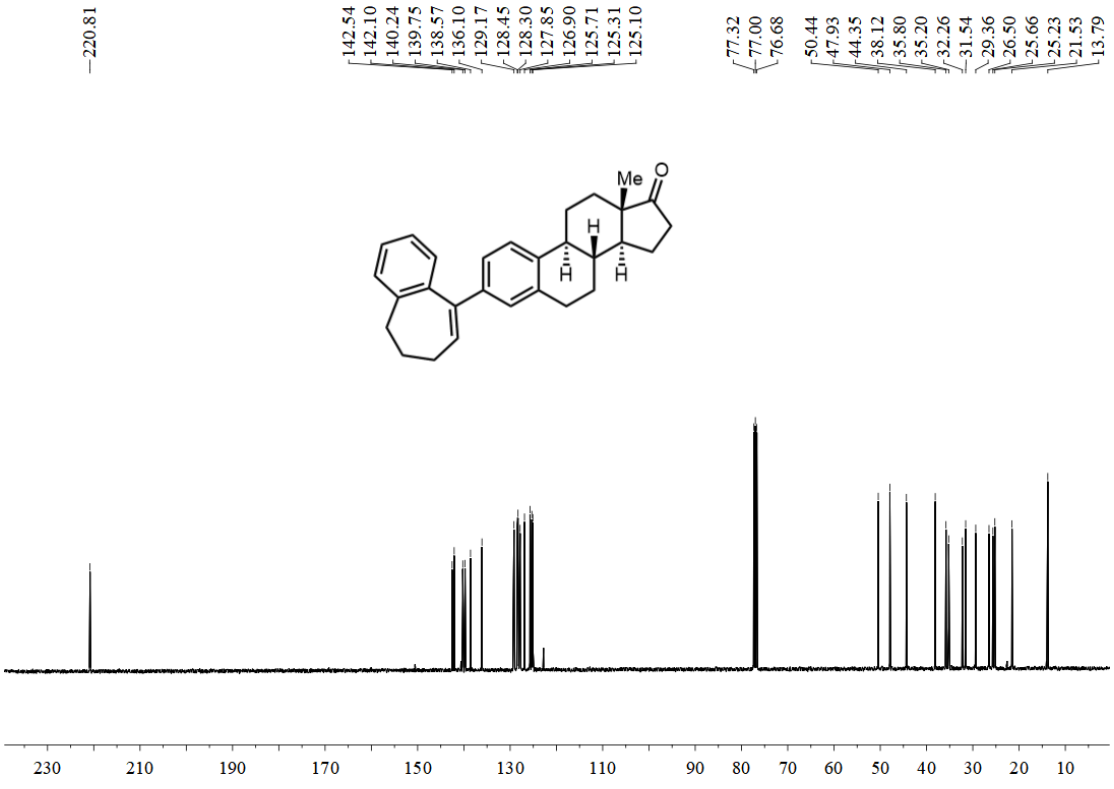
^{19}F NMR (376 MHz, $CDCl_3$) **(3u)**



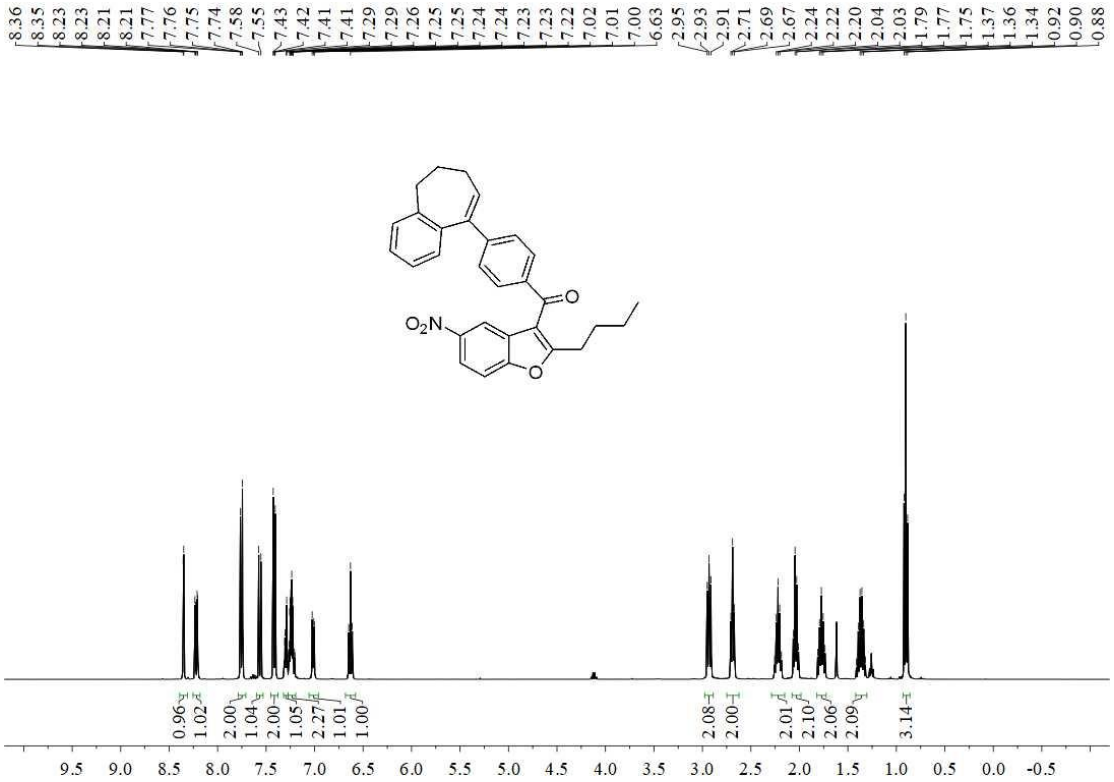
^{1}H NMR (400 MHz, $CDCl_3$) **(3v)**



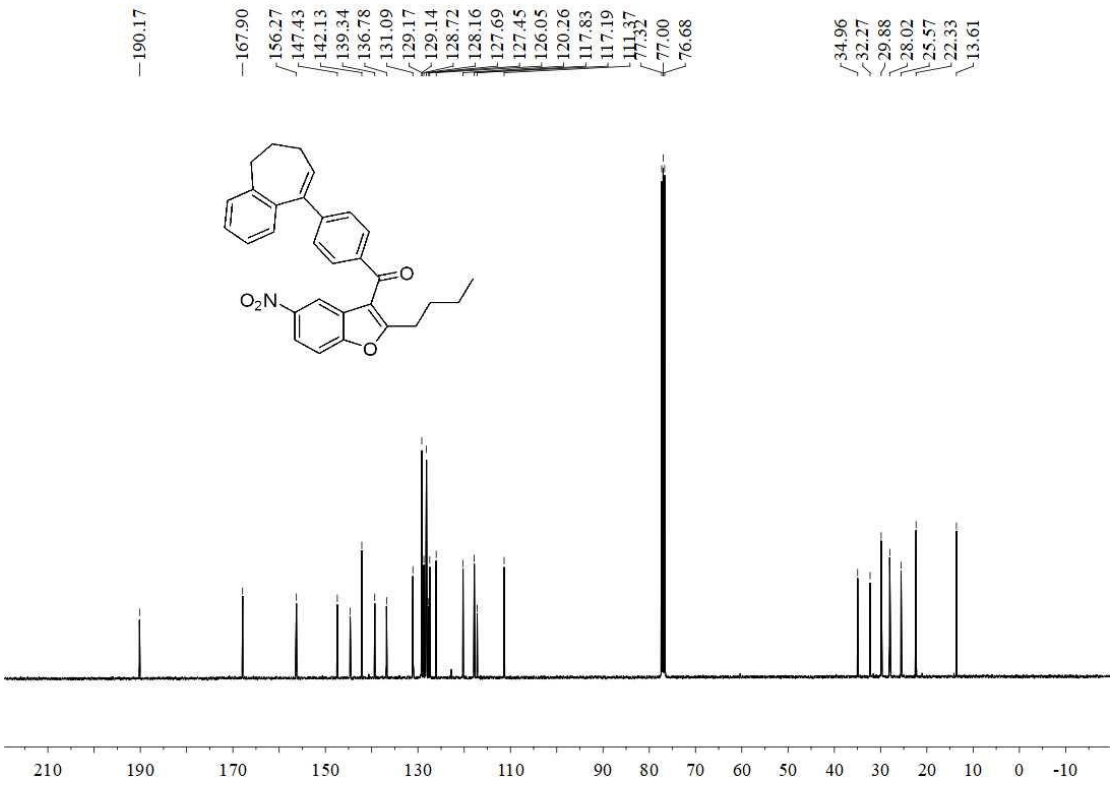
^{13}C NMR (101 MHz, $CDCl_3$) **(3v)**



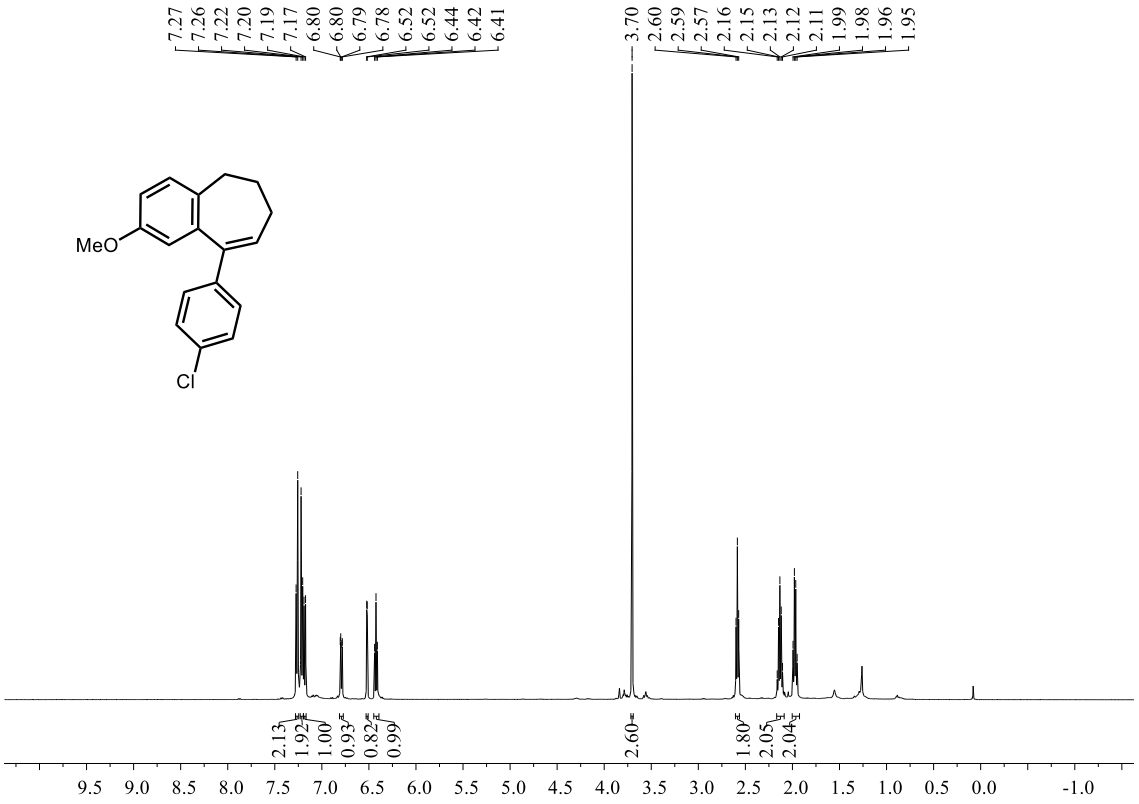
^{1}H NMR (400 MHz, $CDCl_3$) **(3w)**



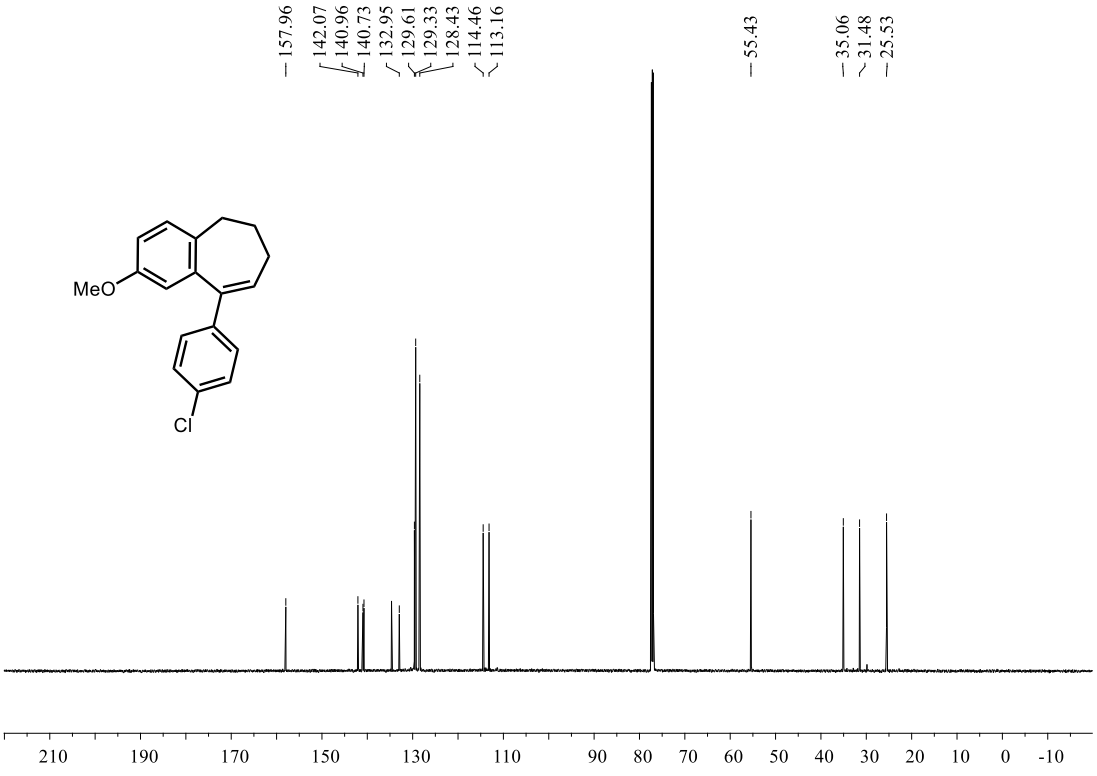
^{13}C NMR (101 MHz, $CDCl_3$) **(3w)**



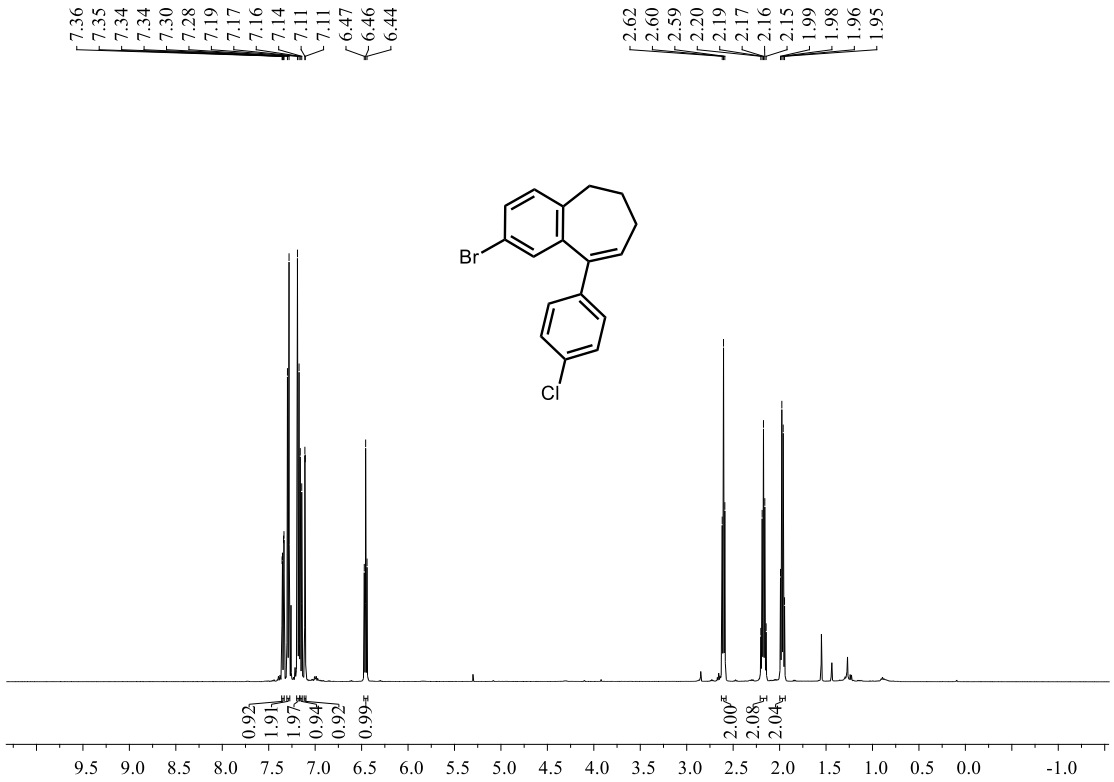
^{1}H NMR (500 MHz, $CDCl_3$) **(3x)**



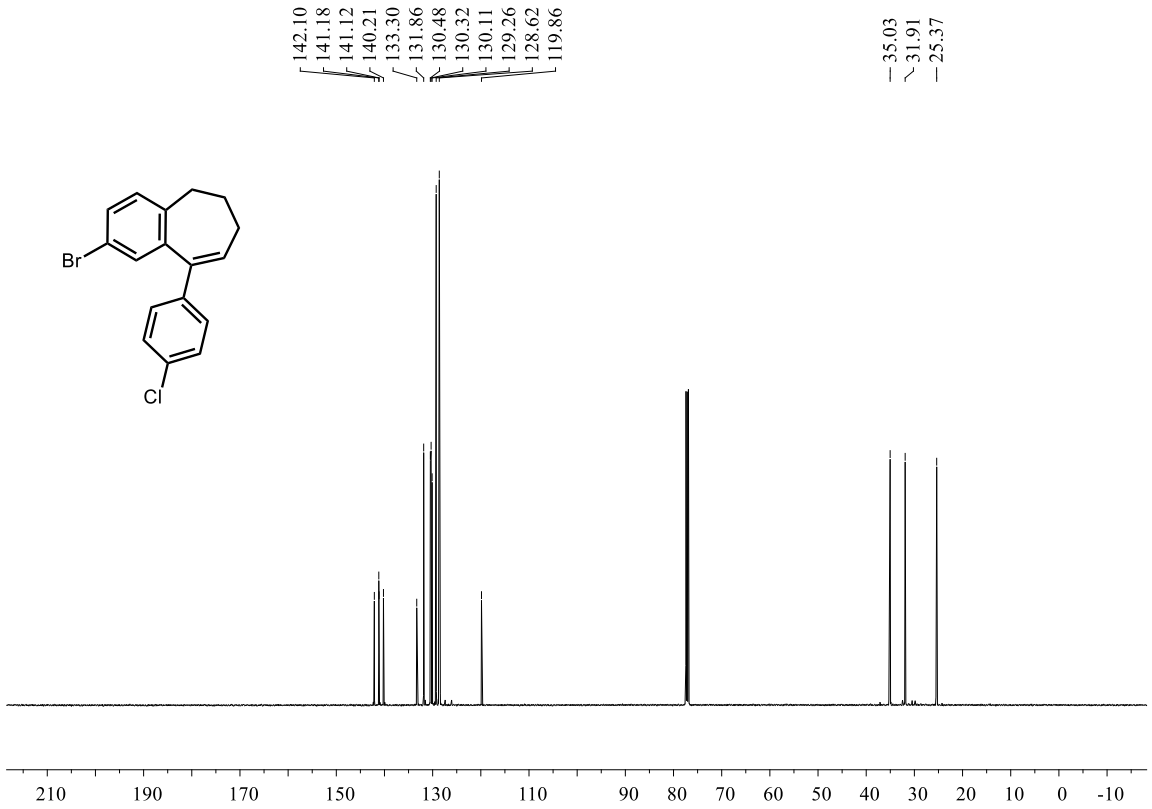
^{13}C NMR (151 MHz, $CDCl_3$) **(3x)**



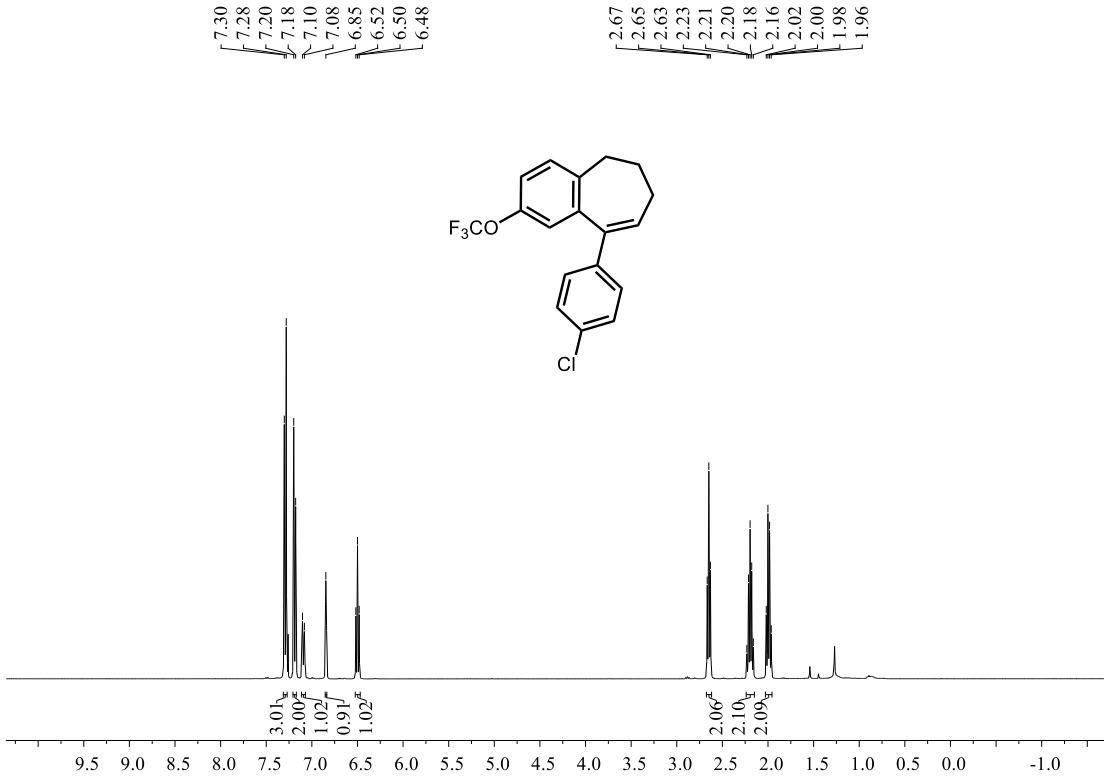
^{1}H NMR (500 MHz, $CDCl_3$) **(3y)**



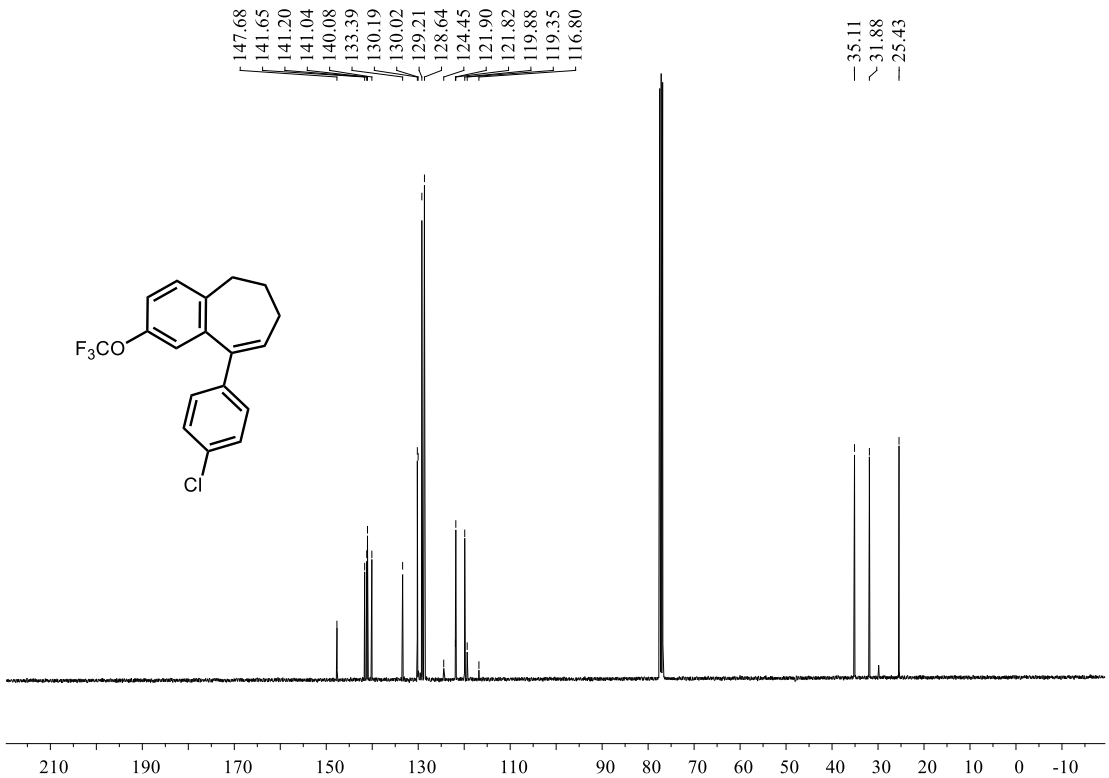
^{13}C NMR (126 MHz, $CDCl_3$) (**3y**)



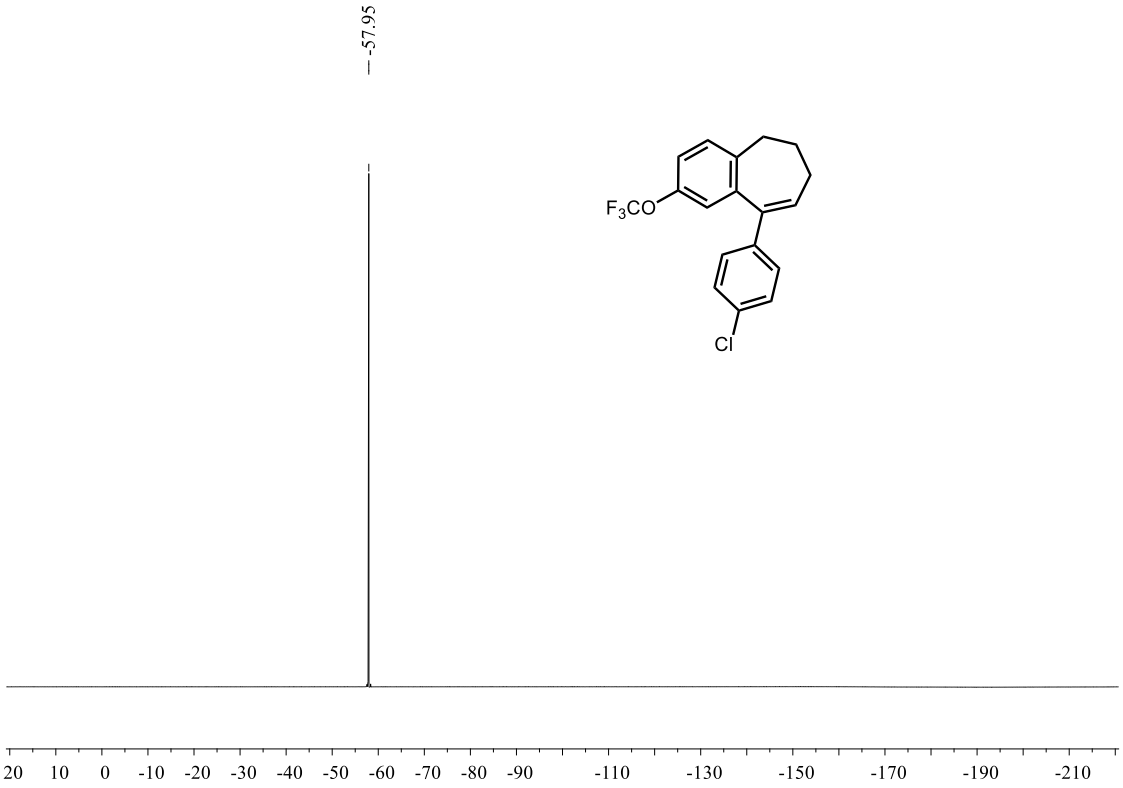
^{1}H NMR (400 MHz, $CDCl_3$) **(3z)**



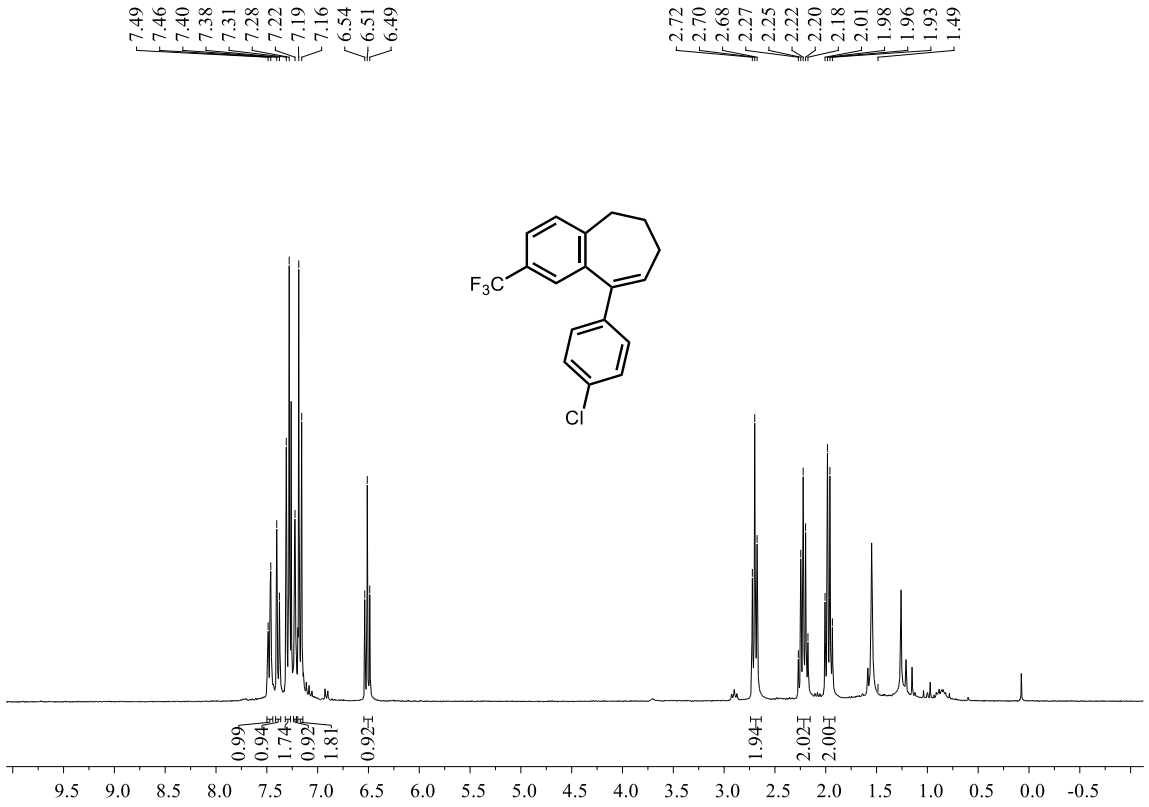
^{13}C NMR (101 MHz, $CDCl_3$) (**3z**)



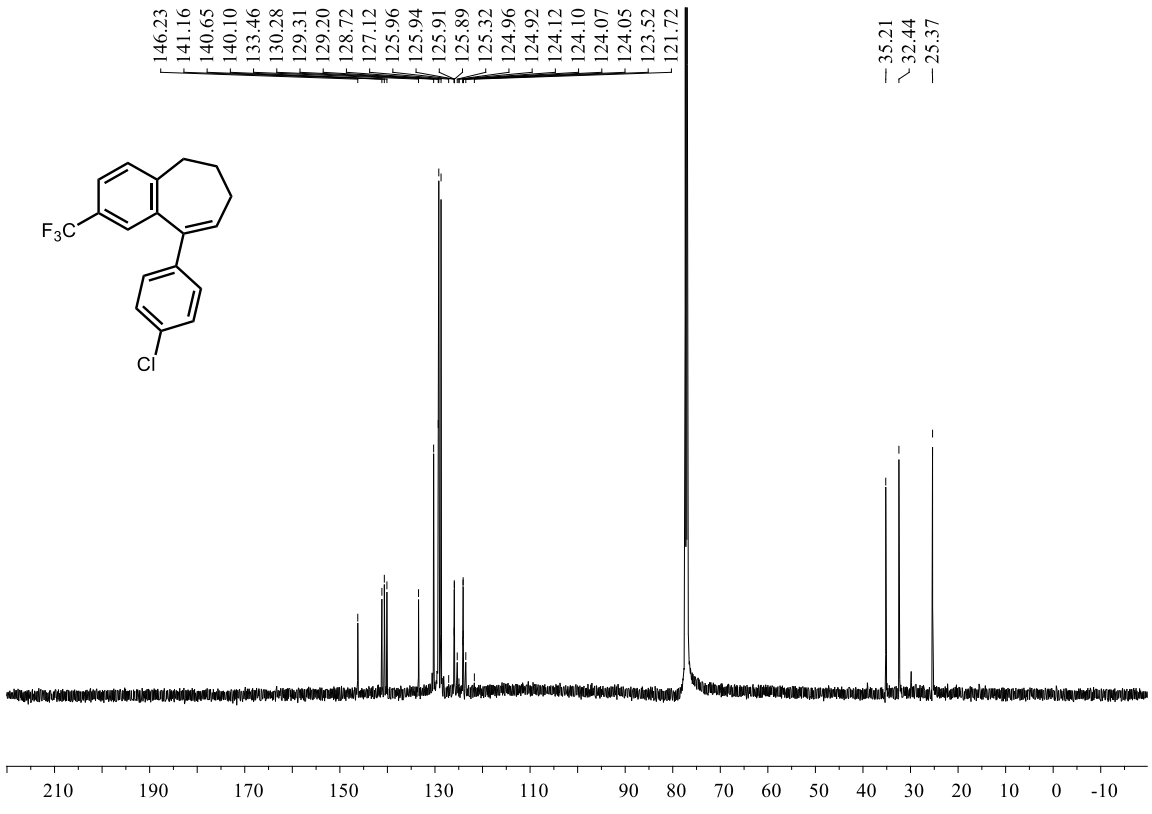
^{19}F NMR (471 MHz, $CDCl_3$) **(3z)**



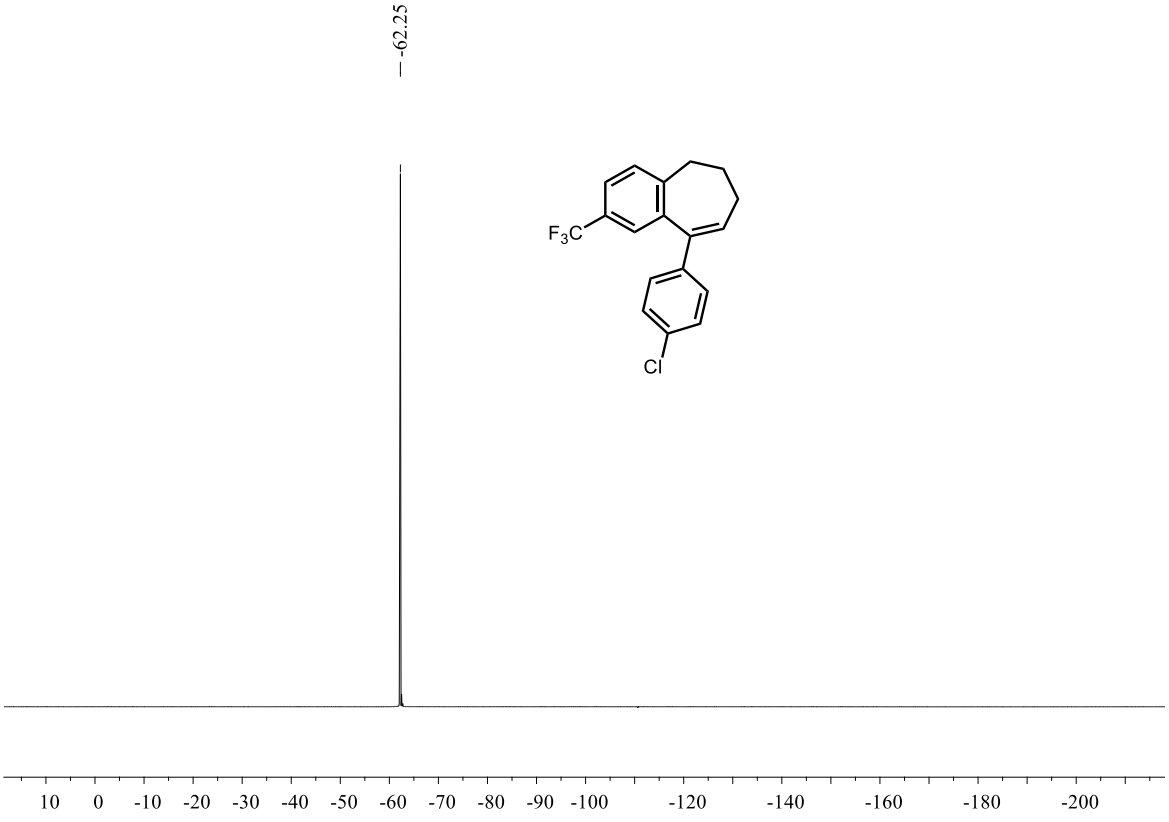
^{1}H NMR (300 MHz, $CDCl_3$) **(3aa)**



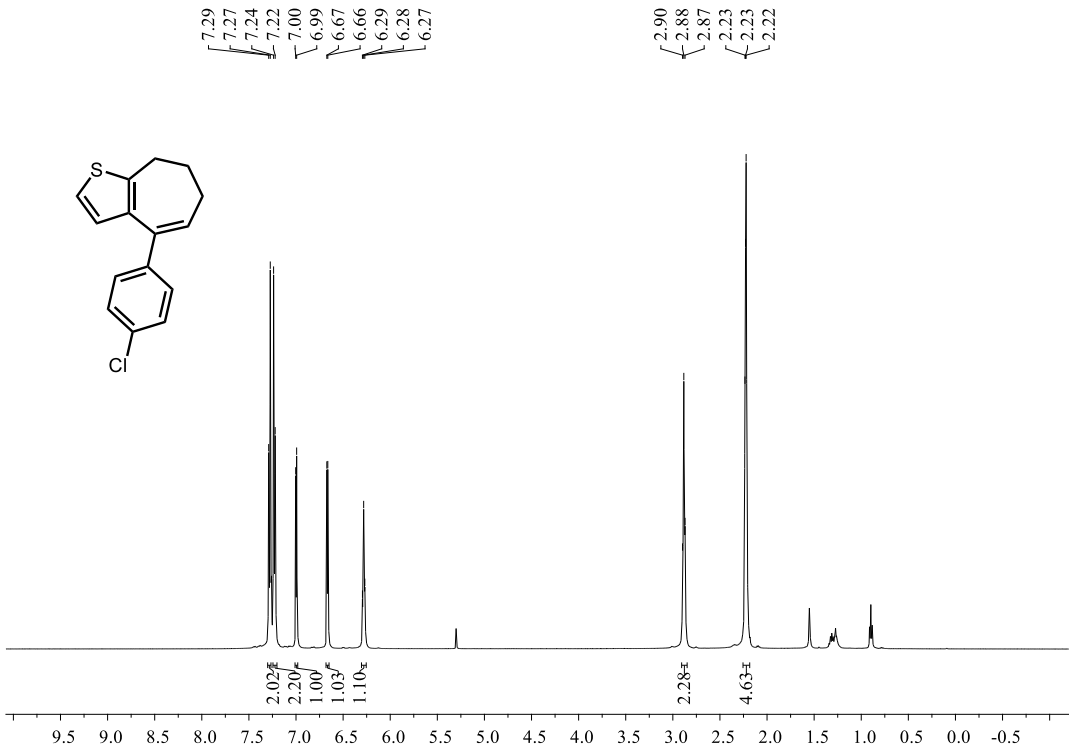
^{13}C NMR (151 MHz, $CDCl_3$) **(3aa)**



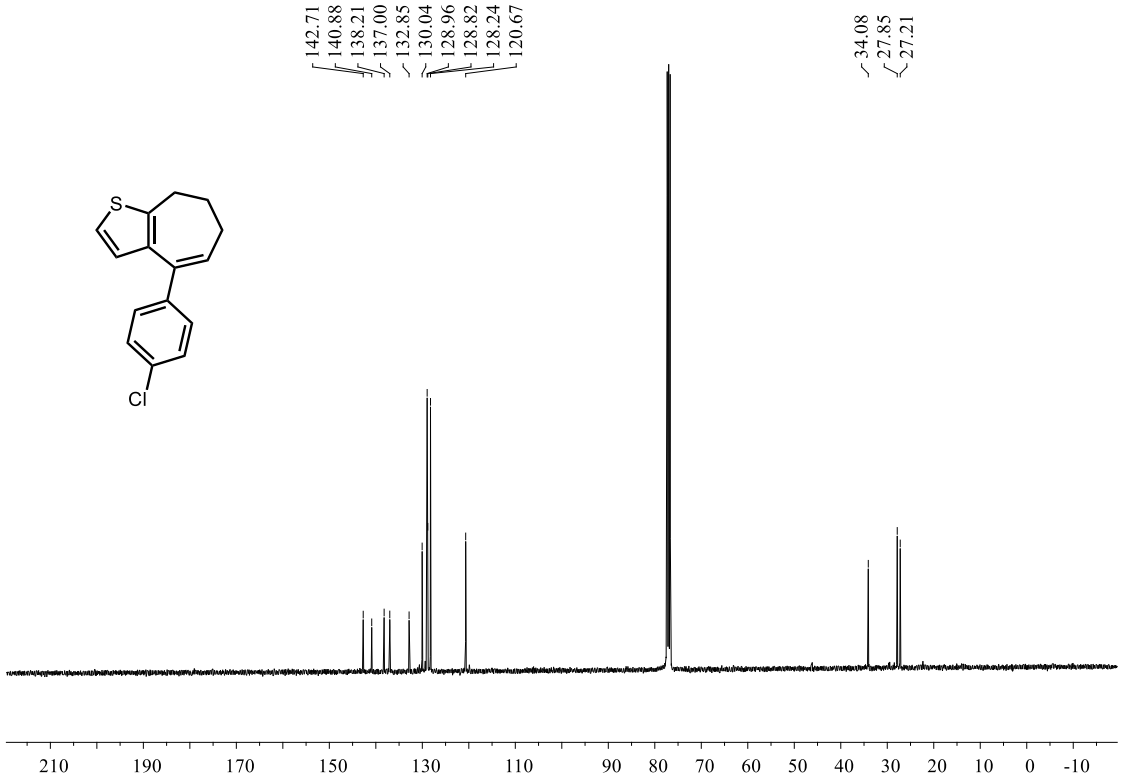
^{19}F NMR (376 MHz, $CDCl_3$) **(3aa)**



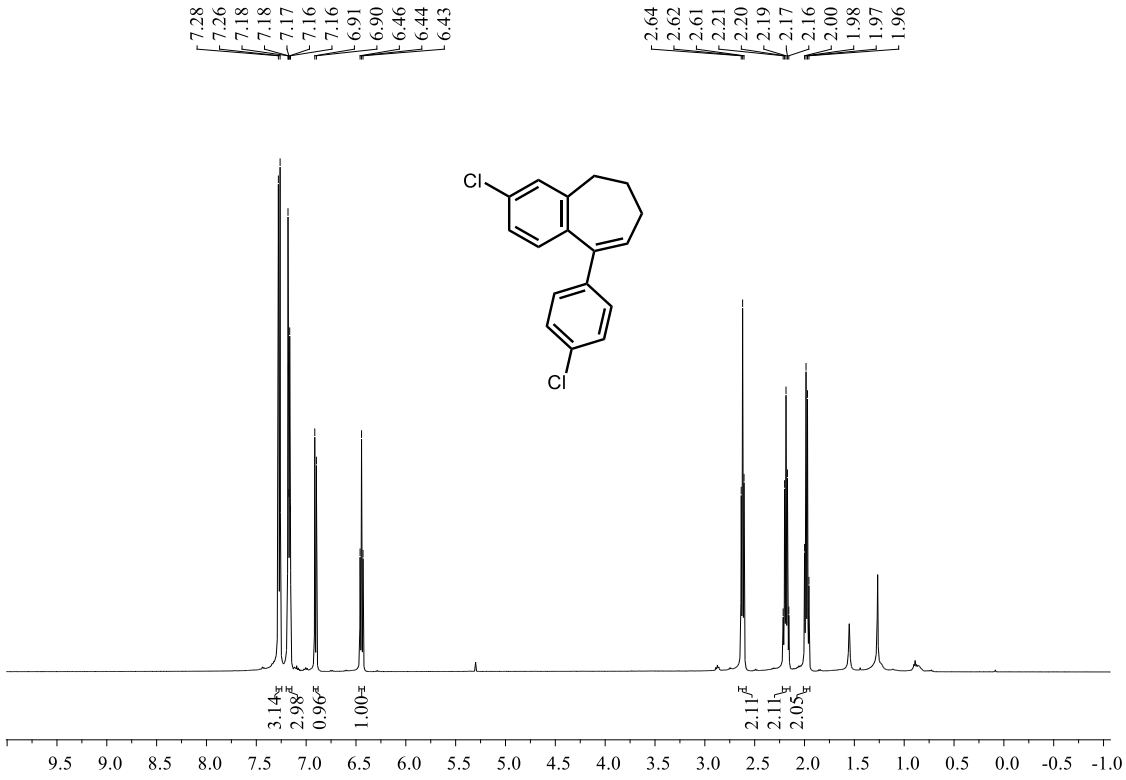
^{1}H NMR (500 MHz, $CDCl_3$) **(3ab)**



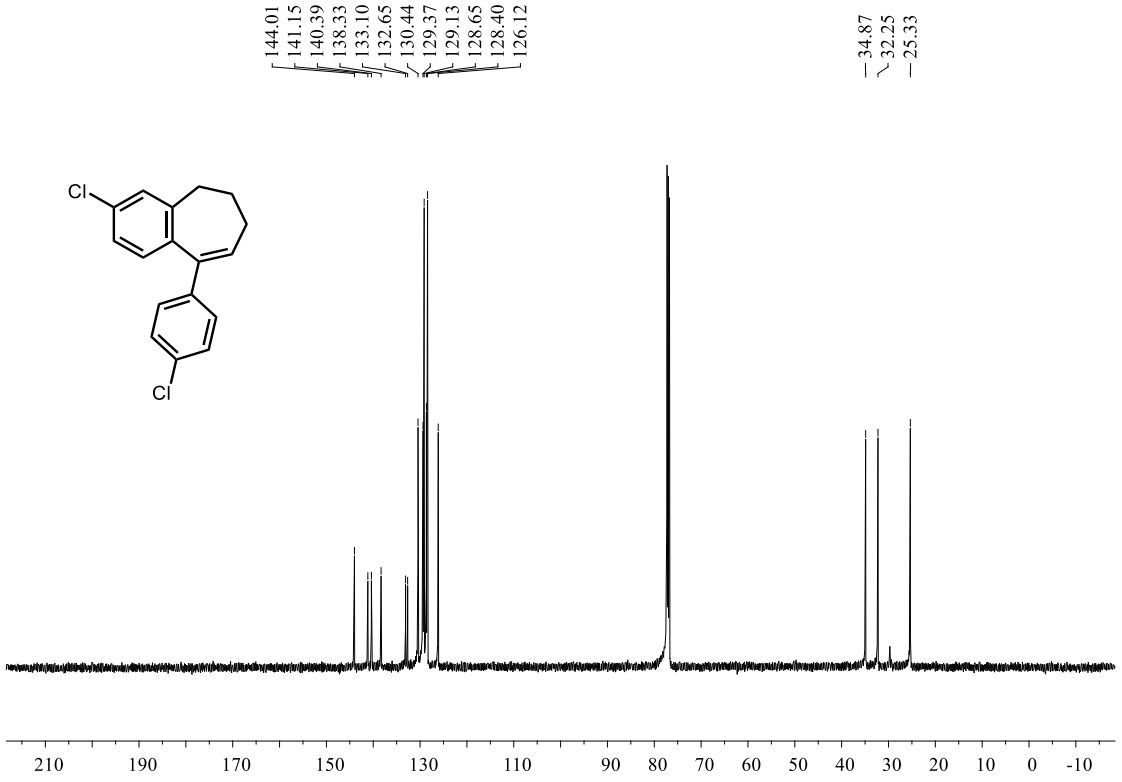
^{13}C NMR (101 MHz, $CDCl_3$) **(3ab)**



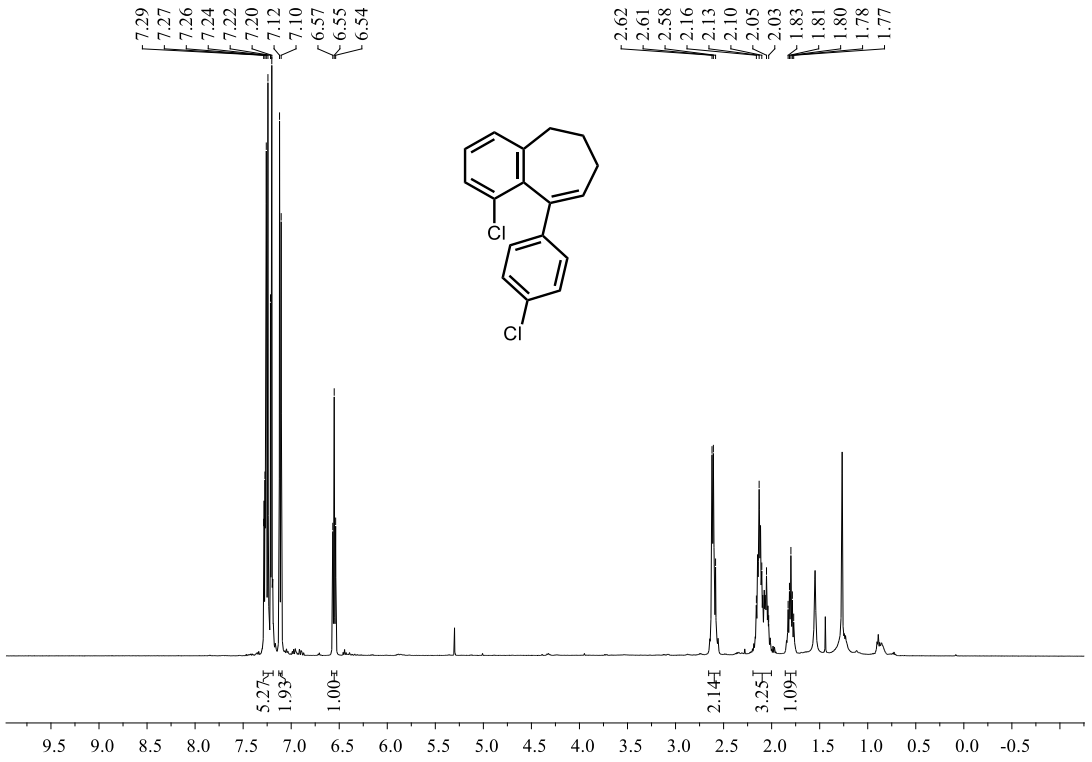
^{1}H NMR (500 MHz, $CDCl_3$) **(3ac(1))**



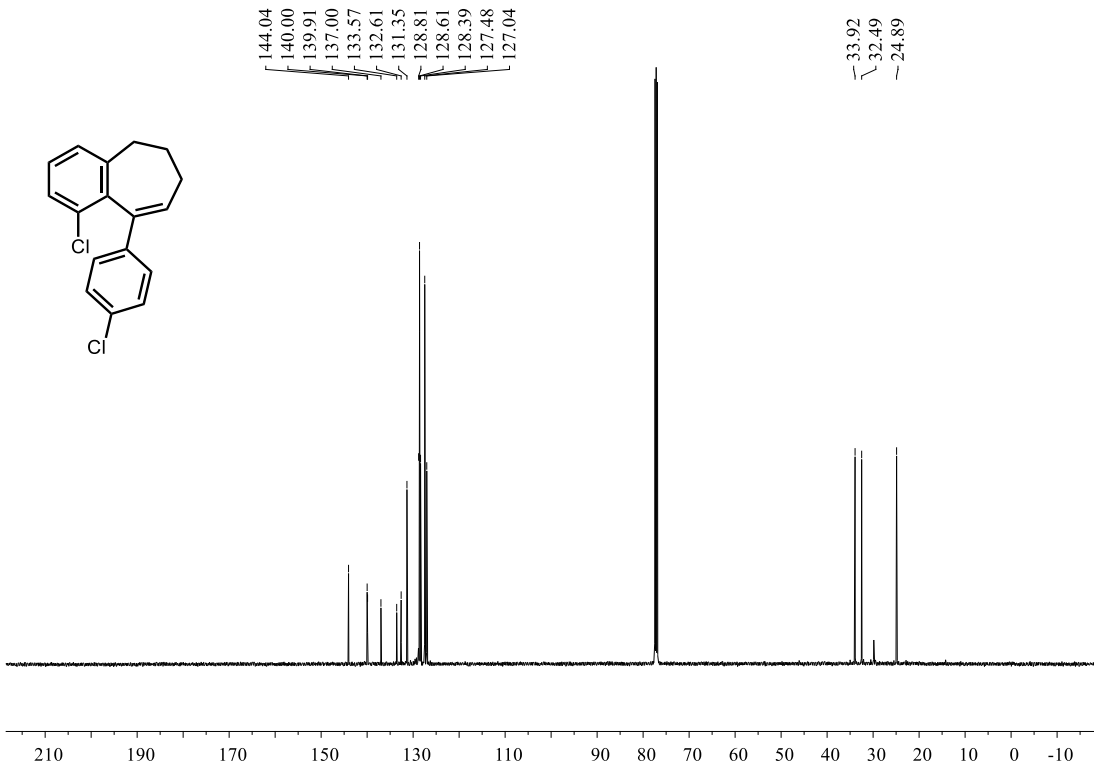
^{13}C NMR (126 MHz, $CDCl_3$) **(3ac(1))**



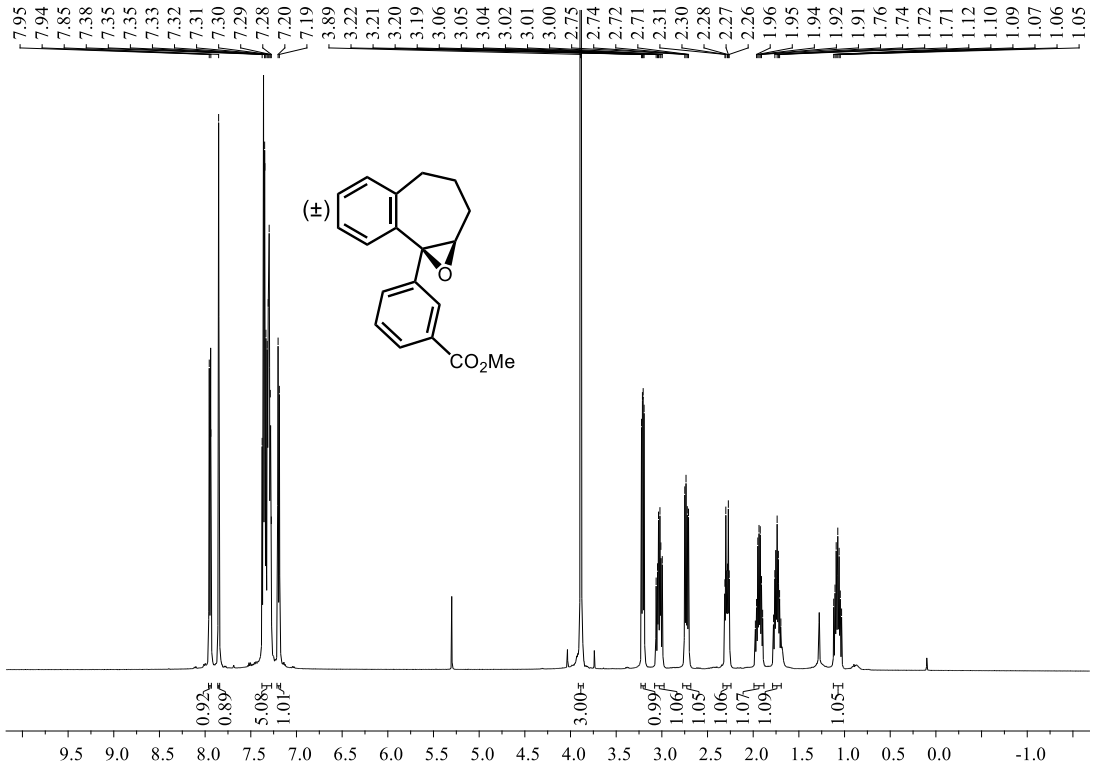
^{1}H NMR (500 MHz, $CDCl_3$) **(3ac(2))**



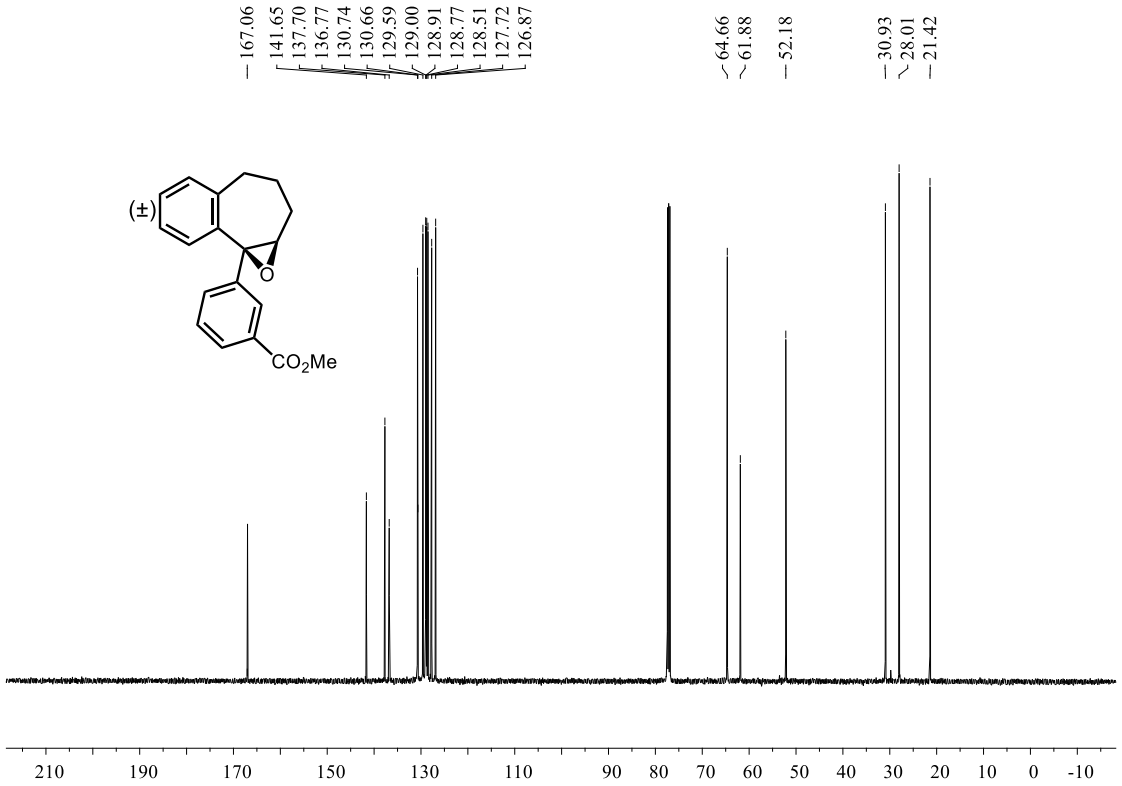
^{13}C NMR (126 MHz, $CDCl_3$) **(3ac(2))**



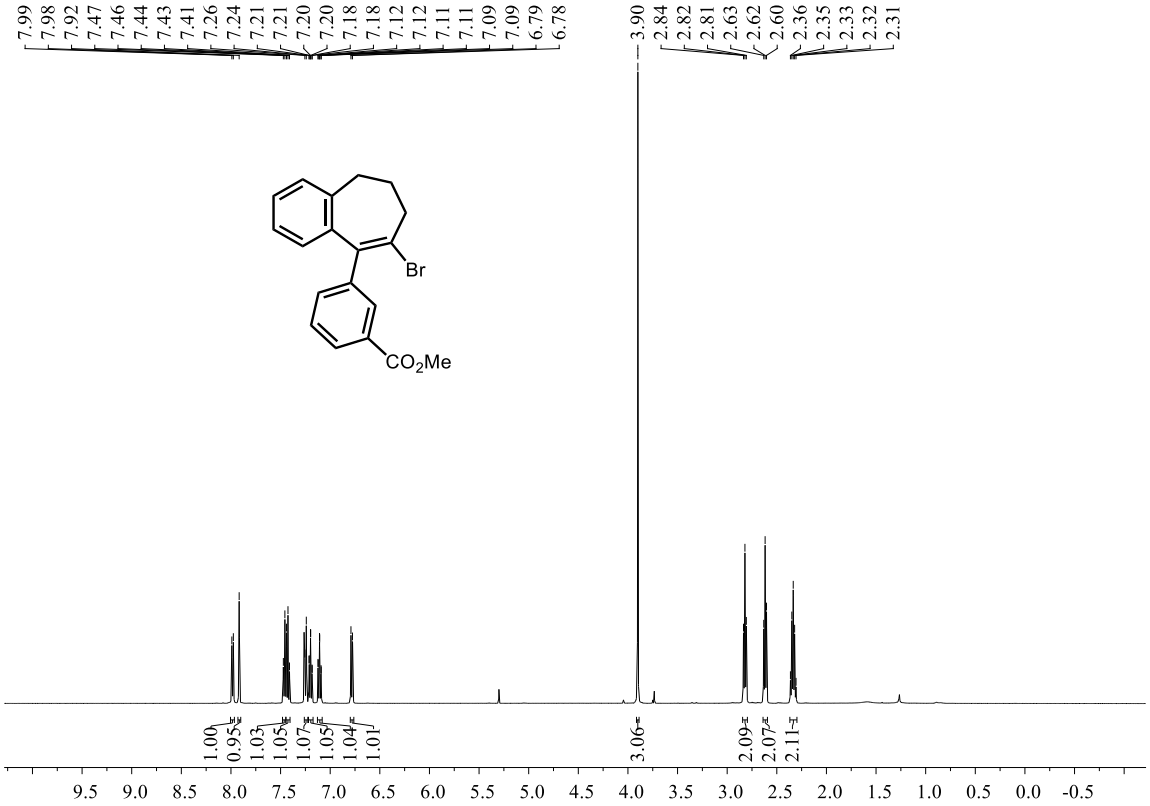
^{1}H NMR (500 MHz, $CDCl_3$) **(4)**



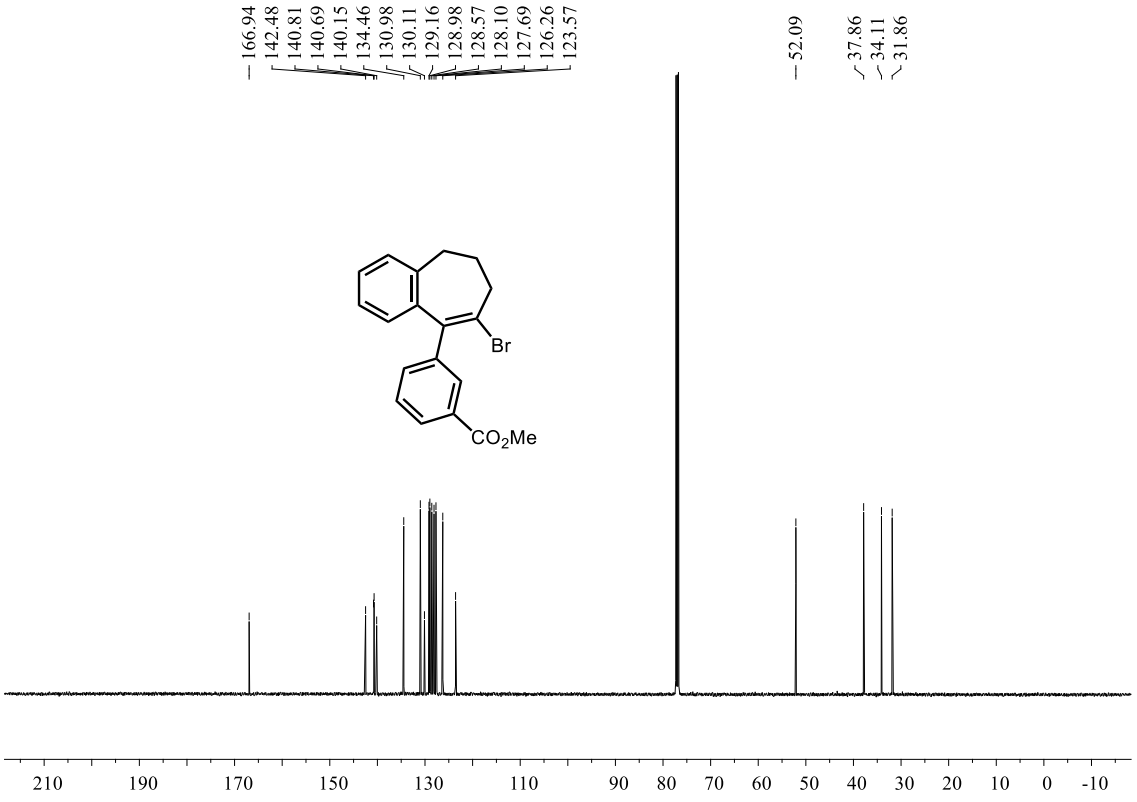
^{13}C NMR (126 MHz, $CDCl_3$) (**4**)



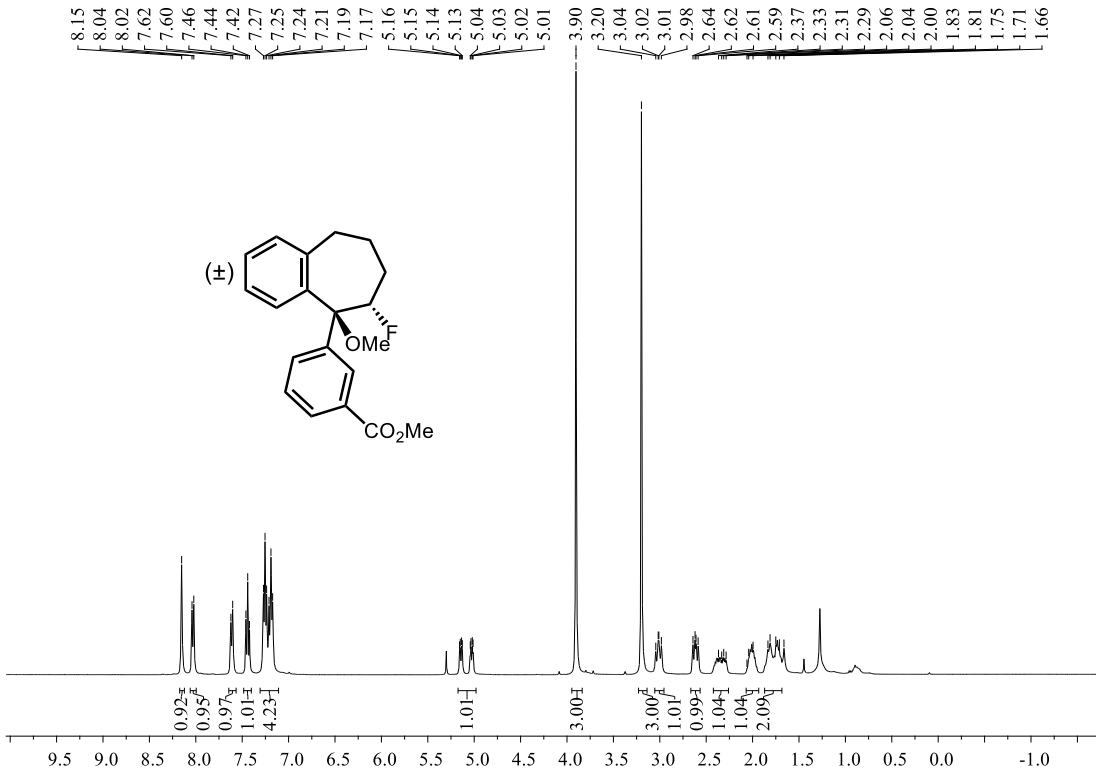
^{1}H NMR (500 MHz, $CDCl_3$) (**5**)



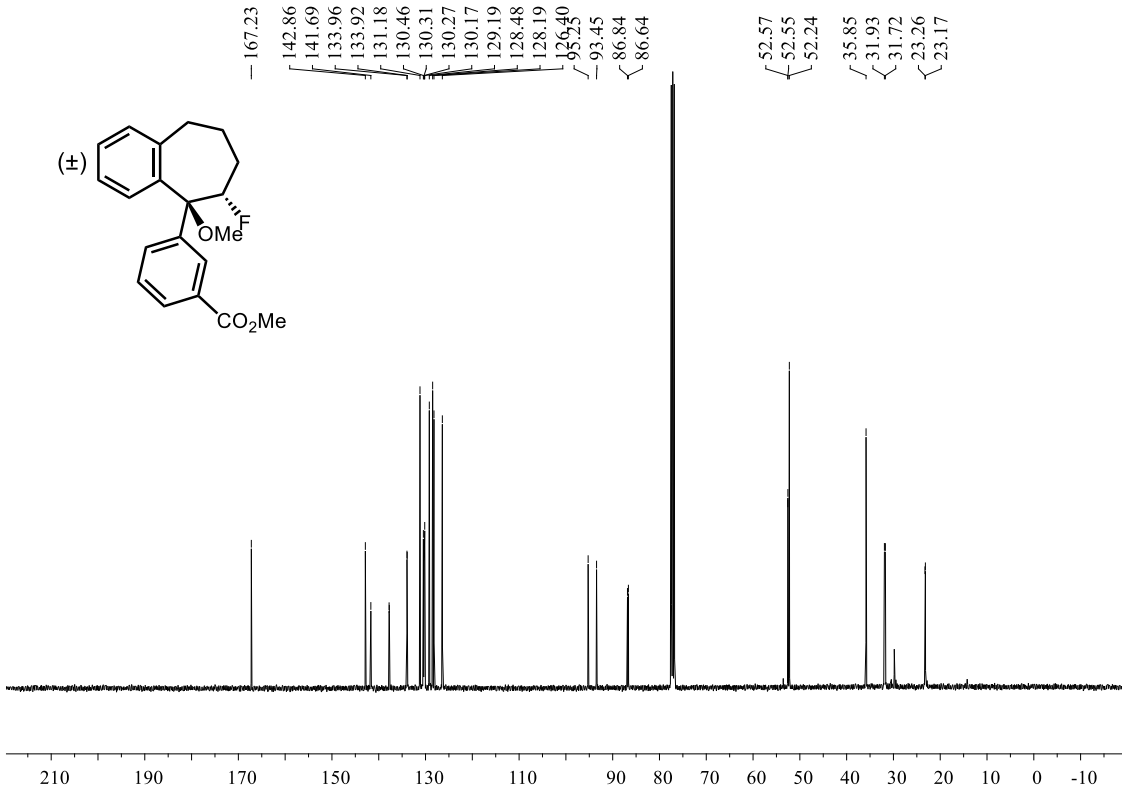
^{13}C NMR (126 MHz, $CDCl_3$) (**5**)



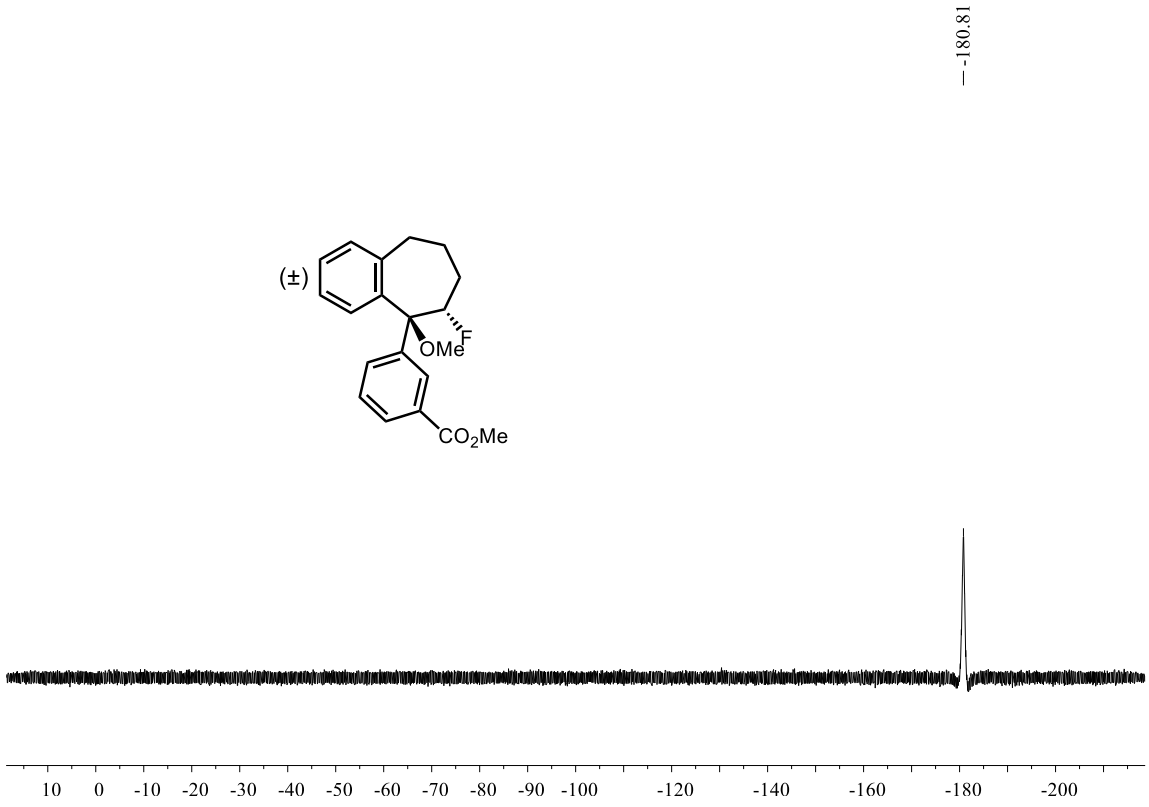
^{1}H NMR (400 MHz, $CDCl_3$) (**6**)



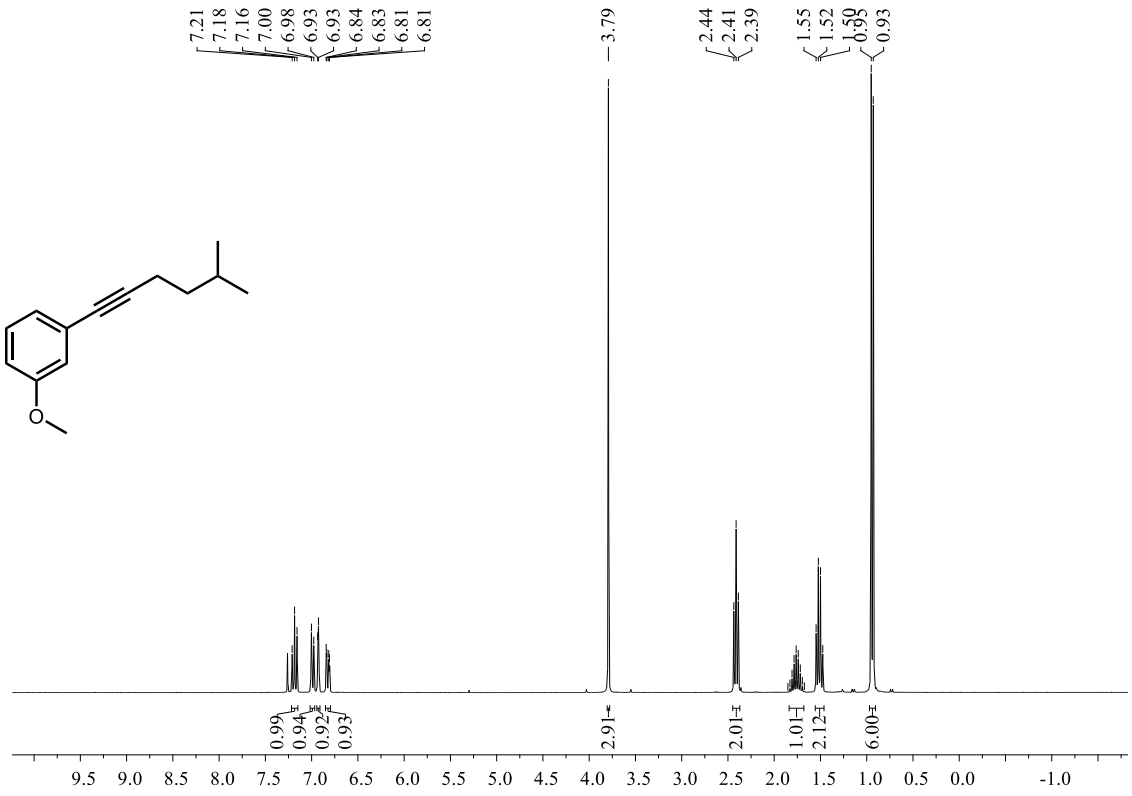
^{13}C NMR (101 MHz, $CDCl_3$) (**6**)



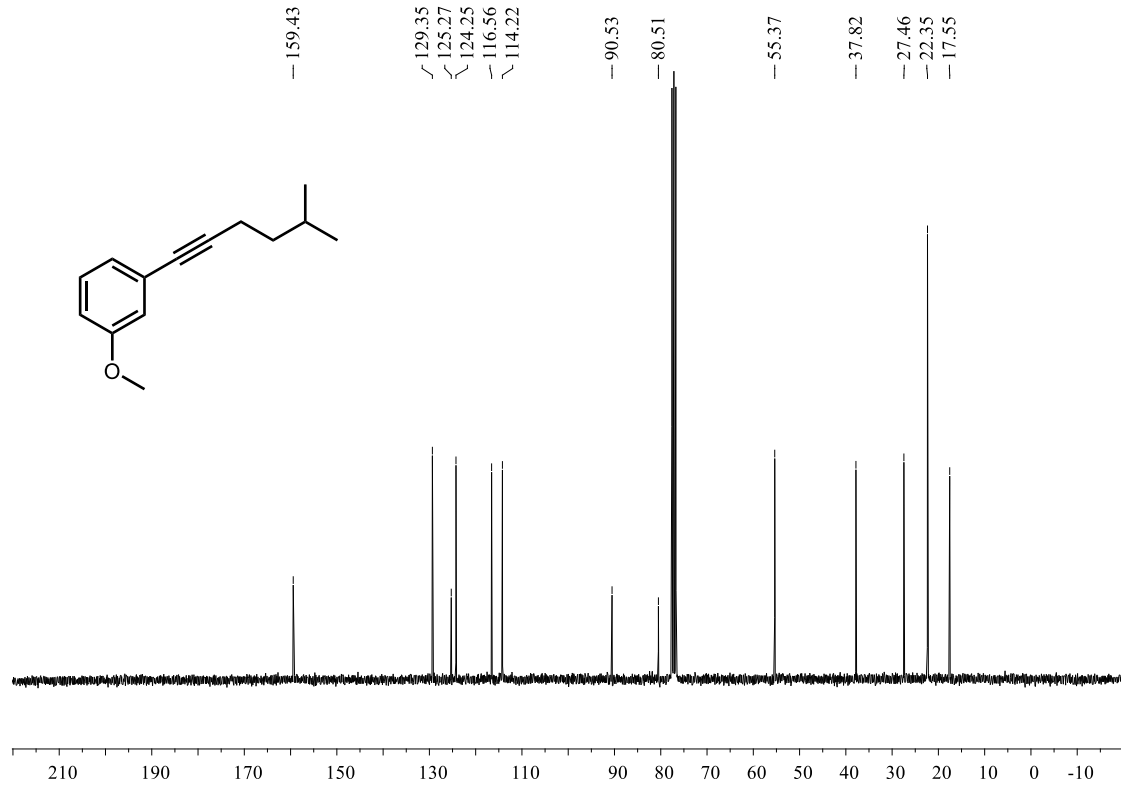
^{19}F NMR (376 MHz, $CDCl_3$) (**6**)



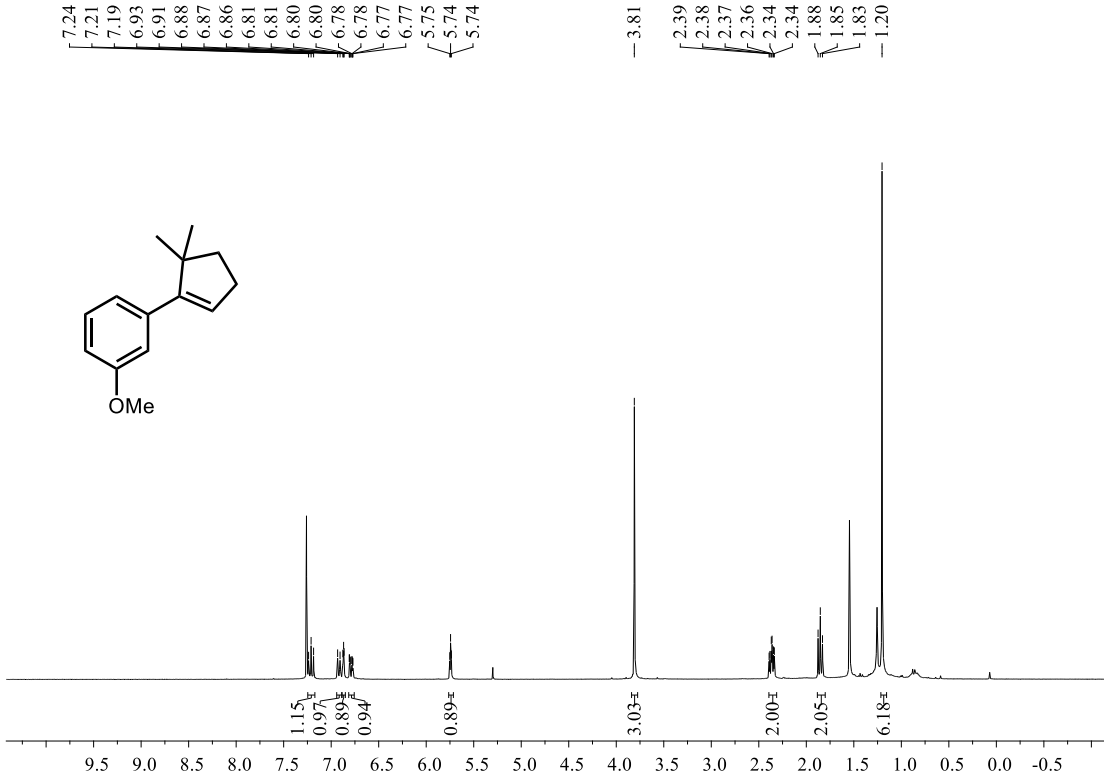
^{1}H NMR (300 MHz, $CDCl_3$) (**7**)



^{13}C NMR (75 MHz, $CDCl_3$) (**7**)



^{1}H NMR (300 MHz, $CDCl_3$) (**8**)



^{13}C NMR (151 MHz, $CDCl_3$) (**8**)