Supporting Information

Empowering boronic acids as hydroxyl synthons for aryne induced three-component coupling reactions

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1. General Information

Unless otherwise mentioned, all reactions were carried out in Schlenk tubes under an atmosphere of nitrogen. Oven-dried glassware with standard vacuum line techniques were used for reaction set-up. All commercial reagents and anhydrous solvents were used as received without further purification unless otherwise noted. Boronic acids were recrystallized from hexane and ethyl acetate. Both potassium fluoride and cesium fluoride were dried at 150°C under vacuum. The 18-crown-6 was recrystallized from acetonitrile. All reactions were monitored by either thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS (Thermo Fisher Trace 1300-ISQ). Visualization was accomplished by UV light (254 nm). Melting point was measured with RY-1 melting point instrument (from NanBei Instrument). The crude products were purified using flash column chromatography with silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). NMR spectra was recorded on a Bruker 400 AVANCE III HD spectrometer at ambient temperature. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.00 ppm or the signal of the residual solvent $CHCl_3$ at δ 7.26 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of the solvent: $CDCl_3$ at δ 77.16 ppm. All the ^{1}H. ^{11}B, ^{13}C and ^{19}F NMR data are reported as follows: (1) chemical shift (δ, ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets and m = multiplet); (3) coupling constants (*J*, Hz). High resolution mass spectrums (HRMS) were recorded on an Agilent Q-TOF 6540 mass spectrometer using electrospray ionization and Agilent 7890B-7250 GC-QTOF mass spectrometer using electron ionization.

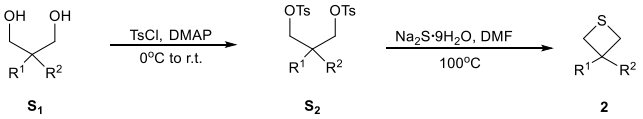
2. Synthesis and Characterization of Starting Material and Reagents

All aryne precursors were prepared following the literature procedures.[1]

2.1 Synthesis and Characterization of Cyclic Thioethers

Cyclic thioether **2a**, **2q-2s** were commercially available. **2b**, **2c**, **2j-2o** and **2t** were prepared following the literature procedures.[2]

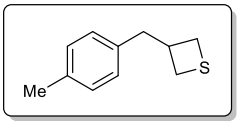
2d-2i and **2p** were synthesized according to the following procedures.



S1 **S2** **2**

General procedure: Step 1: To a solution of diol **S1**[3] (7.5 mmol, 1.0 equiv.) and dimethylaminopyridine (22.5 mmol, 2.75 g, 3.0 equiv.) in DCM (20 mL) was added *p*-toluene sulfonyl chloride (16.5 mmol, 3.14 g, 2.2 equiv.) in DCM (15 mL) at 0°C for 30 minutes. The reaction was kept stirring for 12 hours at room temperature. Then, the reaction was diluted with DCM (3 x 20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography to give **S2**.

Step 2: To a mixture of $Na_2S·9H_2O$ (6 mmol, 1.44 g, 3.0 equiv.) in DMF (10 mL) was added bis(4-methylbenzenesulfonate) (2 mmol, 1.0 equiv.) in DMF (5 mL). The mixture was stirred at 100°C for 12 hours. The reaction was then quenched with water (30 mL) and extracted with EA (3 x 20 mL). The combined organic layer was washed with water (5 x 5 mL) and brine (3 x 5 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography to give cyclic thioether **2**.

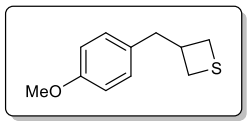


3-(4-methylbenzyl)thietane (2d)

Following the general procedure, the crude product was purified by silica gel chromatography (PE as the eluent) to give **2d** as a yellow oil (0.14 g, 40% yield). R_f = 0.4 (PE:EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.62-3.48 (m, 1H), 3.18 (t, *J* = 8.6 Hz, 2H), 3.11 (t, *J* = 8.3 Hz, 2H), 2.87 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.88, 133.74, 127.26, 126.61, 40.62, 39.76, 29.27, 19.12.

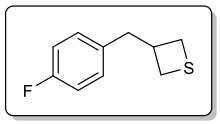


3-(4-methoxybenzyl)thietane (2e)

Following the general procedure, the crude product was purified by silica gel chromatography (PE as the eluent) to give **2e** as a yellow oil (0.19 g, 50% yield). R_f = 0.4 (PE:EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.59-3.44 (m, 1H), 3.16 (t, *J* = 8.8 Hz, 2H), 3.12-3.05 (m, 2H), 2.83 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) 158.12, 130.80, 129.57, 113.90, 55.24, 42.04, 41.77, 31.11.



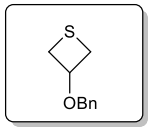
3-(4-fluorobenzyl)thietane (2f)

Following the general procedure, the crude product was purified by silica gel chromatography (PE as the eluent) to give **2f** as a yellow oil (0.33 g, 91% yield). R_f = 0.3 (PE:EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.07 (m, 2H), 7.03-6.95 (m, 2H), 3.57-3.44 (m, 1H), 3.15 (t, *J* = 8.8 Hz, 2H), 3.07 (t, *J* = 8.3 Hz, 2H), 2.86 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.52 (d, *J* = 244.1 Hz), 134.38, 129.97 (d, *J* = 7.8 Hz), 115.27 (d, *J* = 21.1 Hz), 42.01, 41.60, 31.01.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.87.

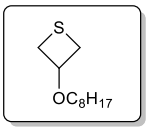


3-(benzyloxy)thietane (2h)

Following the general procedure, the crude product was purified by silica gel chromatography (PE as the eluent) to give **2h** as a pale yellow oil (0.31 g, 87% yield). R_f = 0.5 (PE:EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 4H), 4.74-4.61 (m, 1H), 4.47 (s, 2H), 3.52-3.42 (m, 2H), 3.23-3.13 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.67, 128.53, 127.95, 127.86, 73.25, 69.83, 36.13.

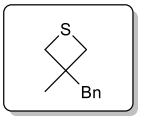


3-(octyloxy)thietane (2i)

Following the general procedure, the crude product was purified by silica gel chromatography (PE:$CHCl_3$ = 1:1 as the eluent) to give **2i** as a pale yellow oil (0.2 g, 50% yield). R_f = 0.4 (PE:EA = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61-4.51 (m, 1H), 3.44-3.32 (m, 4H), 3.23-3.16 (m, 2H), 1.60-1.51 (m, 2H), 1.38-1.21 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 73.60, 67.68, 36.13, 31.80, 29.71, 29.37, 29.23, 26.10, 22.65, 14.09.

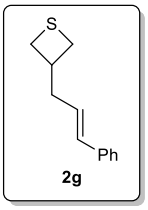


3-benzyl-3-methylthietane (2p)

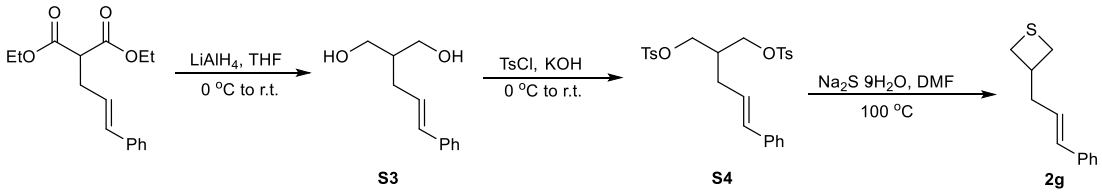
Following the general procedure, the crude product was purified by silica gel chromatography (PE as the eluent) to give **2p** as a pale yellow oil (0.32 g, 90% yield). R_f = 0.4 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.31-7.25 (m, 1H), 7.22-7.18 (m, 2H), 3.29 (d, J = 9.0 Hz, 2H), 2.93 (s, 2H), 2.83 (d, J = 9.0 Hz, 2H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.77, 130.03, 128.19, 126.43, 47.99, 44.82, 36.84, 26.91.



3-cinnamylthietane (2g)



Synthesis of S3: To a suspension of lithium aluminum hydride (60 mmol, 2.28 g, 3.0 equiv.) in anhydrous THF (80 mL) was added diethyl 2-cinnamylmalonate (20 mmol, 5.52 g, 1.0 equiv.) in anhydrous THF (10 mL) at 0ºC. The mixture was kept stirring overnight at room temperature. The reaction mixture was then diluted with ethyl acetate (50 mL) and quenched by sequential addition of water (1 mL), 6 M NaOH (1 mL), and water (3 mL) carefully at 0ºC. After stirring for 30 minutes, the mixture was filtered through Celite and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography (PE:EA = 8:1 as the eluent) to give **S3** as a pale yellow oil (1.12 g, 29% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 7.24-7.19 (m, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.87 (dd, *J* = 10.7, 3.8 Hz, 2H), 3.74 (dd, *J* = 10.0, 7.3 Hz, 2H), 2.25 (td, *J* = 7.2, 1.4 Hz, 2H), 2.00-1.91 (m, 1H).

Synthesis of S4: To a mixture of KOH (46.4 mmol, 2.6 g, 8.0 equiv.) and 2-cinnamylpropane-1,3-diol (5.8 mmol, 1.12 g, 1.0 equiv.) in THF (10 mL) was added *p*-toluene sulfonyl chloride (17.4 mmol, 3.32 g, 3.0 equiv.) in THF (10 mL) dropwise at 0°C. The resulting mixture was stirred at 0°C for 30 minutes and allowed to warm to the room temperature. The mixture was kept stirring overnight. The reaction was quenched with water (30 mL) and extracted with DCM (3 x 20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography (PE:EA = 10:1 as the eluent) to give **S4** as a white solid (2.76 g, 95% yield).

Synthesis of 2g: To a mixture of $Na_2S{\cdot}9H_2O$ (2.25 mmol, 0.54 g, 1.5 equiv.) in DMF (10 mL) was added 2-cinnamylpropane-1,3-diyl bis(4-methylbenzenesulfonate) (1.5 mmol, 0.75 g, 1.0 equiv.) in DMF (5 mL). The mixture was stirred at 100ºC for 12 hours. The reaction was then quenched with water (30 mL) and extracted with EA (3 x 20 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography (PE:EA = 10:1 as the eluent) to give **2g** as a colorless oil (0.13 g, 40% yield). R_f = 0.4 (PE:EA = 10:1).

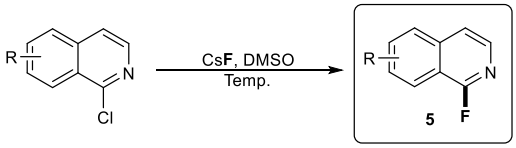
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.26-7.21 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.48-3.34 (m, 1H), 3.25 (t, *J* = 8.7 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H), 2.50 (td, *J* = 7.2, 1.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.33, 131.96, 128.54, 127.21, 126.23, 126.03, 40.22, 39.91, 30.94.

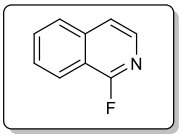
2.2 Synthesis and Characterization of 1-Fluoroisoquinolines.

1-Chloroisoquinolines are all prepared following the literature procedures.[4]

Synthesis of 5a-5c, 5f-5g, 5i-5l, 5n and 5o:



General Procedure: A solution of substituted 1-chloroisoquinolines (8 mmol, 1.0 equiv.) and CsF (24 mmol, 3.6 g, 3.0 equiv.) in DMSO (30 mL) was stirred for 18 hours. The reaction mixture was diluted with water (20 mL), filtrated through celite and extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with water (5 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel chromatography to give substituted 1-fluoroisoquinoline products.



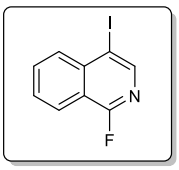
1-fluoroisoquinoline (5a)[5]

Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5a** as a pale yellow oil (0.96 g, 82% yield). R_f = 0.3 (PE:EA = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 5.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77-7.70 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 4.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.96 (d, *J* = 246.6 Hz), 139.61 (d, *J* = 5.6 Hz), 139.18 (d, *J* = 16.2 Hz), 131.48, 127.91, 126.32 (d, *J* = 3.7 Hz), 123.06, 119.33 (d, *J* = 4.8 Hz), 117.66 (d, *J* = 32.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -71.23.



1-fluoro-4-iodoisoquinoline (5b)

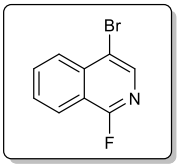
Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5b** as a yellow solid (1.76 g, 81% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.0 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.87 (td, *J* = 8.4, 7.0, 1.2 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.65 (d, *J* = 248.4 Hz), 146.53 (d, *J* = 15.8 Hz), 140.16 (d, *J* = 5.9 Hz), 133.07, 130.74 (d, *J* = 3.1 Hz), 129.02, 123.70, 118.82 (d, *J* = 32.7 Hz), 91.69 (d, *J* = 5.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.22.

HRMS (ESI): Calcd for $C_9H_9FIN^+$ $[M+H]^+$ 273.9523, found 273.9521.



4-bromo-1-fluoroisoquinoline (5c)

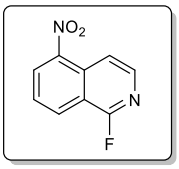
Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5c** as a yellow solid (1.32 g, 73% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.5 Hz, 1H), 8.17-8.11 (m, 2H), 7.90-7.84 (m, 1H), 7.71 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.34 (d, *J* = 247.7 Hz), 140.32 (d, *J* = 16.3 Hz), 137.86, 132.71, 128.87, 126.21, 123.53, 118.65 (d, *J* = 33.3 Hz), 115.89 (d, *J* = 5.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -71.90.

HRMS (ESI): Calcd for $C_9H_6BrFN^+$ $[M+H]^+$ 225.9662, found 225.9661.



1-fluoro-5-nitroisoquinoline (5f)

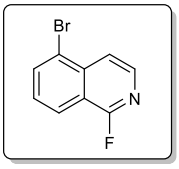
Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **5f** as a white solid (0.8 g, 52% yield). R_f = 0.2 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 6.3 Hz, 1H), 8.31 (d, *J* = 6.3 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.87 (d, *J* = 247.7 Hz), 144.69, 143.06 (d, *J* = 16.3 Hz), 131.82 (d, *J* = 4.9 Hz), 130.01, 129.39, 126.72, 118.71 (d, *J* = 33.1 Hz), 114.86 (d, *J* = 5.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -67.90.

HRMS (ESI): Calcd for $C_9H_6FN_2O^+$ $[M+H]^+$ 193.0408, found 193.0408.



5-bromo-1-fluoroisoquinoline (5g)

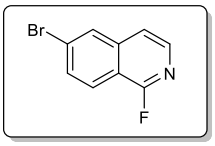
Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5g** as a white solid (1.11 g, 62% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.0 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 5.9 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.85 (d, *J* = 247.0 Hz), 140.49 (d, *J* = 16.4 Hz), 138.60 (d, *J* = 5.6 Hz), 135.15, 128.22, 122.68, 121.27 (d, *J* = 5.4 Hz), 118.75 (d, *J* = 33.1 Hz), 118.44 (d, *J* = 5.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -70.59.

HRMS (ESI): Calcd for $C_9H_6BrFN^+$ $[M+H]^+$ 225.9662, found 225.9661.



6-bromo-1-fluoroisoquinoline (5j)

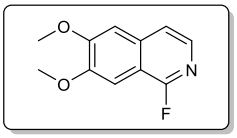
Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5j** as a yellow solid (1.34 g, 75% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 1H), 8.02-7.93 (m, 2H), 7.73-7.65 (m, 1H), 7.45-7.36 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.91 (d, *J* = 246.8 Hz), 140.60 (d, *J* = 16.1 Hz), 140.48, 131.50, 128.60 (d, *J* = 3.5 Hz), 126.55, 124.72, 118.29 (d, *J* = 4.9 Hz), 116.06 (d, *J* = 33.1 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -70.19.

HRMS (ESI): Calcd for $C_9H_6BrFN^+$ $[M+H]^+$ 225.9662, found 225.9662.



1-fluoro-6,7-dimethoxyisoquinoline (5k)

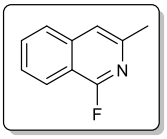
Following the general procedure at 140°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5k** as a white solid (0.79 g, 48% yield). R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.6, 0.9 Hz, 1H), 7.40-7.34 (m, 2H), 7.11 (d, *J* = 1.6 Hz, 1H), 4.04 (d, *J* = 1.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.25 (d, *J* = 241.8 Hz), 153.82, 150.67, 138.11 (d, *J* = 16.3 Hz), 136.56 (d, *J* = 6.4 Hz), 118.10 (d, *J* = 4.2 Hz), 112.66 (d, *J* = 32.3 Hz), 104.88 (d, *J* = 3.7 Hz), 101.15, 56.20, 56.18.

^{19}F NMR (377 MHz, $CDCl_3$) δ -73.99.

HRMS (ESI): Calcd for $C_{11}H_{11}FNO_2^+$ $[M+H]^+$ 208.0768, found 208.0767.



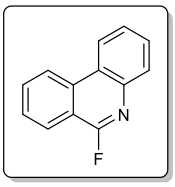
1-fluoro-3-methylisoquinoline (5l)

Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5l** as a pale yellow oil (0.84 g, 65% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.61-7.53 (m, 1H), 7.35 (s, 1H), 2.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.16 (d, *J* = 246.1 Hz), 148.79 (d, *J* = 14.8 Hz), 140.39 (d, *J* = 5.9 Hz), 131.41, 126.84, 125.71 (d, *J* = 4.0 Hz), 123.05, 116.97 (d, *J* = 4.9 Hz), 115.66 (d, *J* = 32.5 Hz), 23.66.

^{19}F NMR (377 MHz, $CDCl_3$) δ -71.55.



6-fluorophenanthridine (5n)

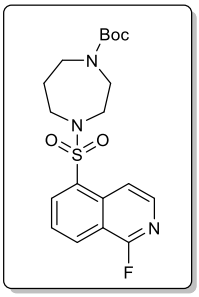
Following the general procedure at 130°C, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5n** as a white solid (0.79 g, 48% yield). R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.7 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.75-7.69 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.12 (d, *J* = 248.5 Hz), 141.56 (d, *J* = 18.3 Hz), 136.49 (d, *J* = 7.0 Hz), 132.05, 129.40, 128.72, 127.90, 126.50, 124.22, 123.95, 122.26, 122.18 (d, *J* = 3.3 Hz), 117.29 (d, *J* = 35.1 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -68.23.

HRMS (ESI): Calcd for $C_9H_6BrFN^+$ $[M+H]^+$ 225.9662, found 225.9662.



Tert-butyl 4-((1-fluoroisoquinolin-5-yl)sulfonyl)-1,4-diazepane-1-carboxylate (5o)

Following the general procedure at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 6:1 as the eluent) to give **5o** as a colorless oil (1.41 g, 43% yield). R_f = 0.2 (PE:EA = 3:1).

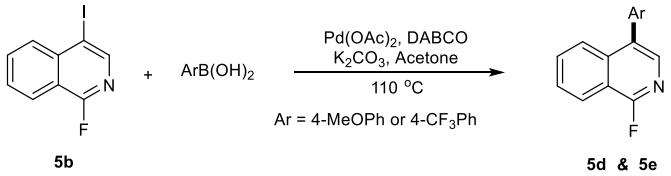
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.27 (m, 2H), 8.24 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 5.9 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 3.54-3.31 (m, 8H), 1.94-1.86 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.05 (d, *J* = 247.5 Hz), 154.99, 154.65, 141.57 (d, *J* = 16.2 Hz), 135.21 (d, *J* = 4.7 Hz), 134.82, 133.63, 133.47, 128.47, 126.66, 118.70 (d, *J* = 32.3 Hz), 116.43 (d, *J* = 5.1 Hz), 79.91, 79.82, 49.91, 49.69, 49.10, 48.99, 47.67, 47.47, 45.91, 45.43, 28.61, 28.31.

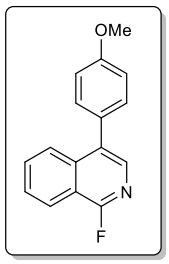
^{19}F NMR (377 MHz, $CDCl_3$) δ -68.54, -68.50.

HRMS (ESI): Calcd for $C_{25}H_{30}N_3O_5S^+$ $[M+H]^+$ 484.1901, found 484.1906.

Synthesis of 5d and 5e



General procedure: A solution of 1-fluoro-4-iodoisoquinoline (2 mmol, 0.54g, 1 equiv.), aryl boronic acid (3 mmol, 0.46 g, 1.5 equiv.), $Pd(OAc)_2$ (0.1 mmol, 23 mg, 0.05 equiv.), DABCO (0.2 mmol, 14 mg, 0.06 equiv.) and K_2CO_3 (6 mmol, 0.83 g, 3 equiv.) in acetone (10 mL) was stirred at 110°C for 24 hours. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution (10 mL), and extracted with DCM (3 x 10 mL). The combined organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography to give 1-fluoro-4-arylisoquinolines.



1-fluoro-4-(4-methoxyphenyl)isoquinolines (5d)

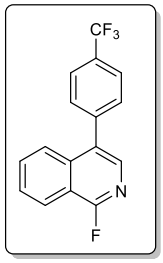
Following the general procedure, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5d** as a white solid (0.44 g, 82% yield). R_f = 0.3 (PE:EA = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 1H), 8.00 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.56, 159.29 (d, *J* = 246.3 Hz), 138.61 (d, *J* = 15.6 Hz), 138.27 (d, *J* = 5.9 Hz), 132.15 (d, *J* = 5.4 Hz), 131.44, 131.19, 128.54, 127.68, 125.20 (d, *J* = 3.3 Hz), 123.26, 117.33 (d, *J* = 32.2 Hz), 114.15, 55.40.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.96.

HRMS (ESI): Calcd for $C_{16}H_{13}FNO^+$ $[M+H]^+$ 254.0976, found 254.0973.



1-fluoro-4-(4-(trifluoromethyl)phenyl)isoquinolines (5e)

Following the general procedure, the crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5e** as a yellow solid (0.44 g, 76% yield). R_f = 0.3 (PE:EA = 20:1).

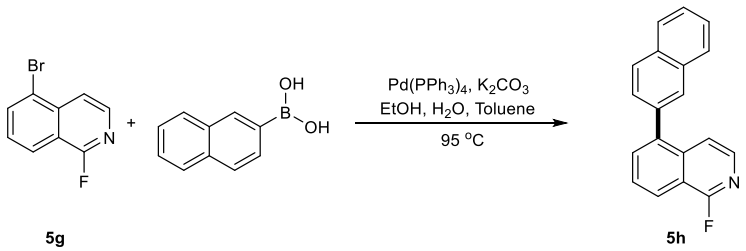
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 8.04 (s, 1H), 7.90-7.68 (m, 6H), 7.64 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.94 (d, *J* = 247.8 Hz), 140.13, 138.94 (d, *J* = 16.3 Hz), 137.78 (d, *J* = 6.0 Hz), 131.98, 131.12 (d, *J* = 5.4 Hz), 130.48, 130.44 (q, *J* = 32.7 Hz), 128.10, 125.67 (q, *J* = 3.4 Hz), 124.65 (d, *J* = 3.0 Hz), 124.11 (dd, *J* = 544.3, 272.0 Hz), 123.54, 117.44 (d, *J* = 32.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.57, -71.19.

HRMS (ESI): Calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$ 292.0744, found 292.0740.

Synthesis of 1-fluoro-5-(naphthalen-2-yl)isoquinoline (5h)



5g **5h**

General procedure: A solution of 5-bromo-1-fluoroisoquinoline (1.5 mmol, 0.34 g, 1.0 equiv.), naphthalen-2-ylboronic acid (2.3 mmol, 0.39 g, 1.5 equiv.), $Pd(PPh_3)_4$ (0.075 mmol, 104 mg, 0.05 equiv.) and K_2CO_3 (6 mmol, 0.83 g, 4.0 equiv.) in ethanol (3 mL)/water (5 mL)/toluene (10 mL) was stirred at 95°C for 36 hours. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution (10 mL), and extracted with DCM (3 x 10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5h** as a yellow solid (0.39 g, 95%). R_f = 0.3 (PE:EA = 20:1).

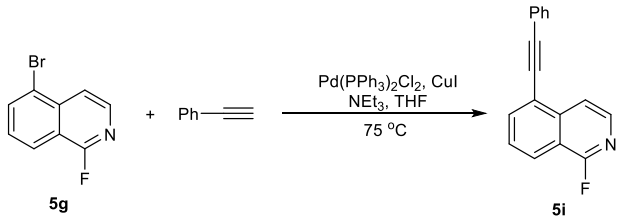
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dt, *J* = 8.2, 1.1 Hz, 1H), 8.07-7.91 (m, 5H), 7.84 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.79-7.73 (m, 1H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.63-7.57 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.42 (d, *J* = 246.4 Hz), 139.43 (d, *J* = 16.1 Hz), 139.40, 138.20 (d, *J* = 5.8 Hz), 136.39, 133.34, 132.80, 132.38, 128.83, 128.23, 128.13, 127.82, 127.72, 127.49, 126.69, 126.57, 122.52, 118.14 (d, *J* = 32.0 Hz), 117.63 (d, *J* = 4.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -70.80.

HRMS (ESI): Calcd for $C_{19}H_{13}FN^+$ $[M+H]^+$ 274.1027, found 274.1025.

Synthesis of 1-fluoro-5-(phenylethynyl)isoquinoline (5i)



General procedure: A solution of 5-bromo-1-fluoroisoquinoline (1.4 mmol, 0.32 g, 1.0 equiv.), ethynylbenzene (1.6 mmol, 0.18 mL, 1.1 equiv.), $Pd(PPh_3)_2Cl_2$ (0.028 mmol, 20.2 mg, 0.02 equiv.) and triethylamine (8.4 mmol, 1.2 mL, 6.0 equiv.) in THF (10 mL) was stirred at 75°C for 24 hours. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl solution (10 mL), and extracted with DCM (3 x 10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (PE:EA = 50:1 as the eluent) to give **5i** as yellow solid (0.25 g, 71%). R_f = 0.4 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.12 (m, 2H), 8.07 (d, *J* = 5.8 Hz, 1H), 8.02-7.97 (m, 1H), 7.71-7.62 (m, 3H), 7.47-7.41 (m, 3H).

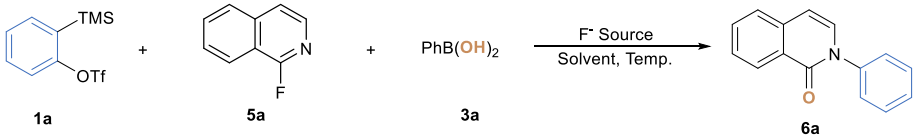
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.24 (d, *J* = 246.6 Hz), 140.11 (d, *J* = 16.2 Hz), 139.92 (d, *J* = 5.7 Hz), 135.02, 131.75, 128.99, 128.57, 127.40, 123.26, 122.60, 120.59 (d, *J* = 4.5 Hz), 117.90 (d, *J* = 4.9 Hz), 117.74 (d, *J* = 32.9 Hz), 95.80, 85.68.

^{19}F NMR (377 MHz, $CDCl_3$) δ -70.82.

HRMS (ESI): Calcd for $C_{17}H_{11}FN^+$ $[M+H]^+$ 248.0870, found 248.0869.

3. Reaction Optimization for Synthesis of Isoquinolin-1(*2H*)ones

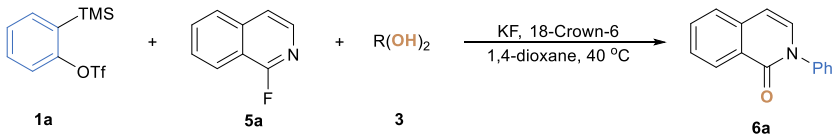
Table S1 Optimization of Reaction Conditions[a]



Entry	Equivalent of **1a** (equiv.)	F^- Source	Solvent	Temp. (°C)	Yield of **6a**[b]
1	1.5	KF/18-Crown-6	THF	40	62%
2	1.5	CsF	CH_3CN	40	43%
3	2	KF/18-Crown-6	THF	40	70%
4	2.5	KF/18-Crown-6	THF	40	72%
5	3	KF/18-Crown-6	THF	40	76%
6	3	KF/18-Crown-6	THF	20	70%
7	3	KF/18-Crown-6	THF	60	65%
8	3	KF/18-Crown-6	CH_3CN	40	52%
9	3	KF/18-Crown-6	1,4-dioxane	40	81% (79%)[c]

[a]Reaction conditions: **1a**, **5a** (0.1 mmol), **3a** (0.15 mmol), F^- source (0.5 mmol), solvent (1 mL) for 24 hours [b]Yields by ^{1}H NMR analysis. [c]Isolated yield.

Table S2 Screening of Boronic Acid[a,b]



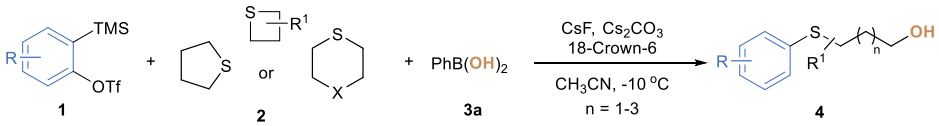
Entry	R	Yield of **6a**	Entry	R	Yield of **6a**
1	Ph	81%	5	4-FPh	75%
2	4-MeOPh	79%	6	2-MePh	85%
3	4-MePh	83%	7	2-FPh	83%
4	4-ClPh	64%	8[c]	*i*-Bu	65%

[a]Reaction conditions: **1a** (0.3 mmol), **5a** (0.1 mmol), **3** (0.15 mmol), KF (0.5 mmol), 18-crown-6 (0.5 mmol), solvent (1 mL) for 24 hours at 40°C. [b]Yields by ^{1}H NMR analysis. [c]48 h.

For the same reason mentioned in the manuscript, we eventually choose $PhB(OH)_2$ for further investigations.

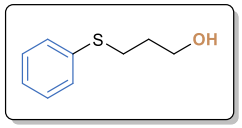
4. General Procedure for Aryne Reaction

4.1 Ring-opening Reaction



General procedure A: To a suspension of CsF (0.6 mmol, 91.1 mg, 3.0 equiv.), Cs_2CO_3 (0.4 mmol, 130.3 mg, 2.0 equiv.), 18-crown-6 (0.4 mmol, 105.6 mg, 2.0 equiv.) and phenylboronic acid (0.3 mmol, 36.6 mg, 1.5 equiv.) in anhydrous CH_3CN (2 mL) was added aryne precursor (0.2 mmol, 1.0 equiv.) and cyclic thioether (0.4 mmol, 2 equiv.) at -10°C. Then the mixture was kept stirring for 12 hours at -10°C. After complete consumption of the aryne precursors indicated by TLC, the reaction was quenched with 1M NaOH (2 mL) and extracted with DCM (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was further purified by silica gel flash chromatography to afford the products.

General procedure B: To a suspension of CsF (0.2 mmol, 30.6 mg, 1.0 equiv.), Cs_2CO_3 (0.8 mmol, 260.6 mg, 4.0 equiv.), 18-crown-6 (0.8 mmol, 211.4 mg, 4.0 equiv.) and phenylboronic acid (0.3 mmol, 36.6 mg, 1.5 equiv.) in anhydrous CH_3CN (2 mL) was added aryne precursor (0.2 mmol, 1.0 equiv.) and cyclic thioether (0.4 mmol, 2.0 equiv.) dropwise at 40°C. Then the mixture was kept stirring for 12 hours at 40°C. After complete consumption of the aryne precursors indicated by TLC, the reaction was quenched with 1M NaOH (2 mL) and extracted with DCM (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was further purified by silica gel flash chromatography to afford the products.



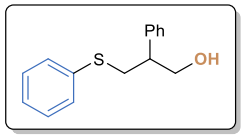
3-(phenylthio)propan-1-ol (4a)[6]

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eulent) to give **4a** as a pale yellow oil (29.0 mg, 85% yield). R_f = 0.4 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.1 Hz, 2H), 1.92-1.84 (m, 2H), 1.70 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.20, 129.16, 128.88, 125.95, 61.33, 31.65, 30.20.

HRMS (EI): Calcd for $C_9H_{12}OS$ $[M]^{\cdot+}$ 168.0603; found 168.0602.



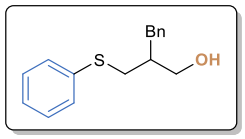
2-phenyl-3-(phenylthio)propan-1-ol (4b)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 8:1 as the eluent) to give **4b** as a yellow oil (23.9 mg, 49% yield). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.27 (td, *J* = 7.3, 1.6 Hz, 3H), 7.24-7.15 (m, 3H), 3.97-3.84 (m, 2H), 3.33 (dd, *J* = 13.0, 7.8 Hz, 1H), 3.22 (dd, *J* = 13.0, 6.9 Hz, 1H), 3.09-3.02 (m, 1H), 1.57 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.89, 136.19, 129.30, 128.93, 128.76, 127.90, 127.27, 126.09, 66.06, 47.42, 36.21.

HRMS (EI): Calcd for $C_{15}H_{16}OS$ $[M]^{\cdot+}$ 244.0916; found 244.0916.



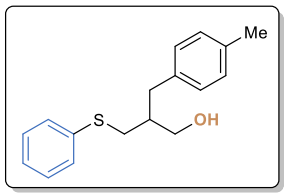
2-benzyl-3-(phenylthio)propan-1-ol (4c)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 6:1 as the eluent) to give **4c** as a yellow oil (44.2 mg, 86% yield). R_f = 0.3 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.26-7.18 (m, 5H), 7.17-7.12 (m, 3H), 3.73 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.63 (dd, *J* = 10.9, 5.4 Hz, 1H), 2.99 (d, *J* = 6.5 Hz, 2H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.14-2.03 (m, 1H), 1.51 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.62, 136.40, 129.15, 128.89, 128.84, 128.40, 126.17, 125.83, 63.84, 42.24, 36.82, 34.59.

HRMS (EI): Calcd for $C_{16}H_{18}OS$ $[M]^{\cdot+}$ 258.1073; found 258.1073.



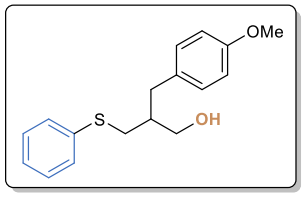
2-(4-methylbenzyl)-3-(phenylthio)propan-1-ol (4d)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **4d** as a yellow oil (38.0 mg, 70% yield). R_f = 0.3 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H), 7.23-7.17 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.76 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.66 (dd, *J* = 10.9, 5.5 Hz, 1H), 3.02 (d, *J* = 6.4 Hz, 2H), 2.77 (d, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.16-2.05 (m, 1H), 1.68 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.59, 136.53, 135.71, 129.16, 129.10, 128.94, 128.90, 125.86, 63.97, 42.37, 36.47, 34.71, 21.07.

HRMS (EI): Calcd for $C_{17}H_{20}OS$ $[M]^{\cdot+}$ 272.1229; found 272.1229.



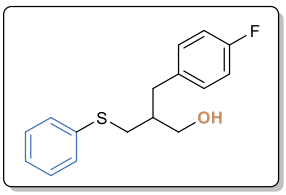
2-(4-methoxybenzyl)-3-(phenylthio)propan-1-ol (4e)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **4e** as a yellow oil (43.7 mg, 76% yield). R_f = 0.3 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 4H), 7.22-7.16 (m, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.75 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.65 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.00 (d, *J* = 6.4 Hz, 2H), 2.74 (d, *J* = 7.3 Hz, 2H), 2.13-2.02 (m, 1H), 1.70 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.06, 136.56, 131.62, 130.13, 128.94, 128.89, 125.86, 113.88, 63.92, 55.30, 42.43, 35.96, 34.63.

HRMS (EI): Calcd for $C_{17}H_{20}O_2S$ $[M]^{\cdot+}$ 288.1179; found 288.1177.



2-(4-fluorobenzyl)-3-(phenylthio)propan-1-ol (4f)

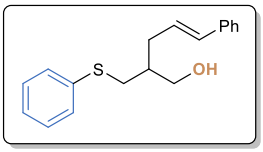
Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 8:1 as the eluent) to give **4f** as a yellow oil (40.0 mg, 73% yield). R_f = 0.3 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3H), 7.23-7.16 (m, 1H), 7.17-7.09 (m, 2H), 7.03-6.95 (m, 2H), 3.74 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.64 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.07-2.93 (m, 2H), 2.77 (d, *J* = 7.2 Hz, 2H), 2.16-1.99 (m, 1H), 1.71 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.48 (d, *J* = 244.1 Hz), 136.36, 135.29, 130.56 (d, *J* = 7.8 Hz), 129.03, 128.99, 126.02, 115.21 (d, *J* = 21.2 Hz), 63.67, 42.37, 35.91, 34.65.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.99.

HRMS (EI): Calcd for $C_{16}H_{18}OS$ $[M]^{\cdot+}$ 276.0979; found 276.0978.



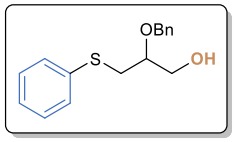
(*E*)-5-phenyl-2-((phenylthio)methyl)pent-4-en-1-ol (4g)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **4g** as a yellow oil (37.6 mg, 67% yield). R_f = 0.3 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.26 (m, 8H), 7.30-7.18 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.3, 7.3 Hz, 1H), 3.81 (dd, *J* = 10.9, 5.0 Hz, 1H), 3.74 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.08 (d, *J* = 6.5 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.06-1.97 (m, 1H), 1.75 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.26, 136.50, 132.21, 129.13, 128.91, 128.47, 127.52, 127.11, 125.98, 125.95, 64.25, 40.60, 35.09, 34.16.

HRMS (EI): Calcd for $C_{18}H_{20}OS$ $[M]^{\cdot+}$ 284.1229; found 284.1229.



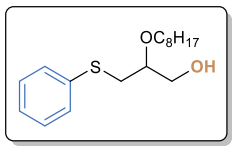
2-(benzyloxy)-3-(phenylthio)propan-1-ol (4h)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 8:1 as the eluent) to give **4h** as a yellow oil (40.2 mg, 74% yield). R_f = 0.4 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 9H), 7.19 (t, *J* = 7.2 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 3.86-3.78 (m, 1H), 3.72-3.61 (m, 2H), 3.19 (dd, *J* = 13.9, 4.6 Hz, 1H), 3.06 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.91 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.83, 135.97, 129.40, 129.01, 128.51, 127.94, 127.93, 126.28, 78.21, 72.08, 63.27, 34.30.

HRMS (EI): Calcd for $C_{16}H_{18}O_2S$ $[M]^{\cdot+}$ 274.1022; found 274.1022.



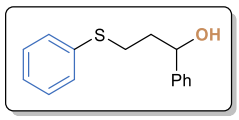
2-(octyloxy)-3-(phenylthio)propan-1-ol (4i)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 8:1 as the eluent) to give **4i** as a yellow oil (30.0 mg, 50% yield). R_f = 0.5 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.34-7.29 (m, 2H), 7.24-7.18 (m, 1H), 3.82 (dd, *J* = 11.6, 3.5 Hz, 1H), 3.69-3.41 (m, 4H), 3.17 (dd, *J* = 13.6, 5.1 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.98 (s, 1H), 1.62-1.50 (m, 2H), 1.38-1.18 (m, 10H), 0.97-0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.23, 129.35, 128.99, 126.22, 78.75, 70.25, 63.32, 34.33, 31.83, 30.00, 29.41, 29.26, 26.10, 22.67, 14.11.

HRMS (EI): Calcd for $C_{17}H_{28}O_2S$ $[M]^{\cdot+}$ 296.1805; found 296.1802.



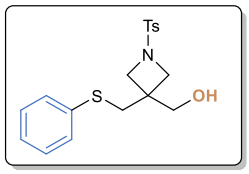
1-phenyl-3-(phenylthio)propan-1-ol (4j)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 15:1 as the eluent) to give **4j** as a yellow oil (31.4 mg, 64% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 6H), 7.32-7.27 (m, 3H), 7.20 (t, *J* = 7.1 Hz, 1H), 4.91 (dd, *J* = 8.1, 4.9 Hz, 1H), 3.05 (t, *J* = 7.3 Hz, 2H), 2.20-2.10 (m, 1H), 2.07-1.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.96, 136.13, 129.20, 128.90, 128.56, 127.75, 125.97, 125.77, 73.08, 38.08, 29.97.

HRMS (EI): Calcd for $C_{15}H_{16}OS$ $[M]^{\cdot+}$ 244.0916; found 244.0915.



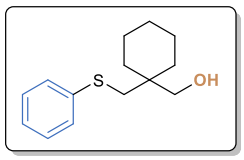
(3-((phenylthio)methyl)-1-tosylazetidin-3-yl)methanol (4k)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 3:1 as the eluent) to give **4k** as a yellow oil (62.2 mg, 86% yield). R_f = 0.2 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32-7.22 (m, 5H), 3.67 (s, 2H), 3.61 (d, *J* = 8.3 Hz, 2H), 3.52 (d, *J* = 8.4 Hz, 2H), 3.06 (s, 2H), 2.48 (s, 3H), 1.61 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.10, 135.62, 131.34, 129.86, 129.76, 129.11, 128.35, 126.78, 64.98, 56.71, 39.13, 38.77, 21.61.

HRMS (ESI): Calcd for $C_{18}H_2NO_3S_2^+$ $[M+H]^+$ 364.1036; found 364.1030.



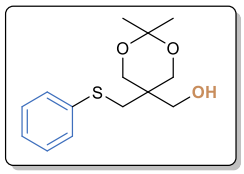
(1-((phenylthio)methyl)cyclohexyl)methanol (4l)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 6:1 as the eluent) to give **4l** as a yellow oil (43.6 mg, 48% yield). R_f = 0.4 (PE:EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 3.60 (s, 2H), 3.10 (s, 2H), 1.55 (s, 1H), 1.53-1.44 (d, *J* = 15.6 Hz, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.59, 129.37, 128.88, 125.90, 67.93, 40.92, 38.99, 32.31, 26.11, 21.47.

HRMS (EI): Calcd for $C_{14}H_{20}OS$ $[M]^{\cdot+}$ 236.1229; found 236.1229.



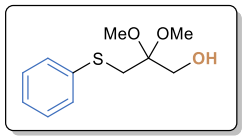
(2,2-dimethyl-5-((phenylthio)methyl)-1,3-dioxan-5-yl)methanol (4m)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4m** as a yellow oil (38.0 mg, 71% yield). R_f = 0.4 (PE:EA = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 3.80-3.73 (m, 6H), 3.10 (s, 2H), 1.71-1.66 (m, 1H), 1.43 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.79, 129.45, 129.02, 126.32, 98.38, 64.34, 63.22, 39.20, 36.43, 24.72, 22.63.

HRMS (EI): Calcd for $C_{14}H_{20}O_3S$ $[M]^{\cdot+}$ 268.1128; found 268.1127.



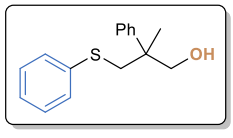
2,2-dimethoxy-3-(phenylthio)propan-1-ol (4n)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4n** as a yellow oil (34.0 mg, 75% yield). R_f = 0.4 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.25-7.19 (m, 1H), 3.78 (d, *J* = 5.8 Hz, 2H), 3.31-3.29 (m, 8H), 1.74 (t, *J* = 6.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.31, 129.53, 128.94, 126.28, 101.61, 61.04, 48.79, 36.18.

HRMS (EI): Calcd for $C_{11}H_{26}O_3S$ $[M]^{\cdot+}$ 228.0815; found 228.0815.



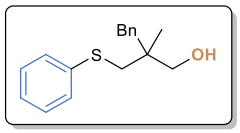
2-methyl-2-phenyl-3-(phenylthio)propan-1-ol (4o)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **4o** as a yellow oil (31.4 mg, 61% yield). R_f = 0.3 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.35-7.30 (m, 4H), 7.27-7.21 (m, 3H), 7.18-7.12 (m, 1H), 3.84 (d, *J* = 11.1 Hz, 1H), 3.78 (d, *J* = 11.1 Hz, 1H), 3.43 (d, *J* = 12.3 Hz, 1H), 3.33 (d, *J* = 12.3 Hz, 1H), 1.55 (s, 1H), 1.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.61, 137.51, 129.40, 128.85, 128.54, 126.79, 126.51, 125.95, 70.54, 44.38, 43.64, 22.37.

HRMS (EI): Calcd for $C_{16}H_{18}OS$ $[M]^{\cdot+}$ 258.1073; found 258.1073.



(5-fluoropentyl)(phenyl)sulfane (4p)

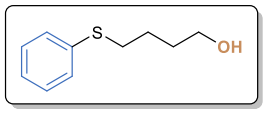
Following the general procedure B, the crude product was purified by silica gel chromatography (PE:EA = 15:1 as the eluent) to give **4p** as a yellow oil (24.1 mg, 45% yield). R_f = 0.3 (PE:EA = 5:1).

Following the general procedure A using 3-MePhB$(OH)_2$, the product **4w** was obtained as a yellow oil (32.2 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.30-7.25 (m, 4H), 7.23-7.20 (m, 3H), 7.20-7.14 (m, 1H), 3.47 (s, 2H), 3.00 (d, *J* = 12.2 Hz, 1H), 2.93 (d, *J* = 12.3 Hz, 1H), 2.72 (s, 2H), 1.50 (s, 1H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.59, 137.38, 130.53, 129.25, 128.95, 128.04, 126.27, 125.97, 67.99, 42.18, 41.73, 40.66, 21.46.

HRMS (EI): Calcd for $C_{17}H_{20}OS$ $[M]^{\cdot+}$ 272.1229; found 272.1232.



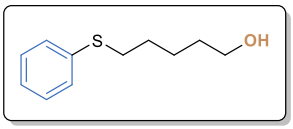
4-(phenylthio)butan-1-ol (4q)[7]

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4q** as a colorless oil (31.3 mg, 86% yield). R_f = 0.4 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 1.79-1.64 (m, 4H), 1.41 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.52, 129.05, 128.83, 125.81, 62.28, 33.41, 31.66, 25.44.

HRMS (EI): Calcd for $C_{10}H_{14}OS$ $[M]^{\cdot+}$ 182.0760; found 182.0761.



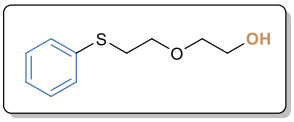
5-(phenylthio)pentan-1-ol (4r)[8]

Following the general procedure A at 40°C, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4r** as a yellow oil (28.8 mg, 74% yield). R_f = 0.4 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.33-7.28 (m, 2H), 7.22-7.17 (m, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.75-1.66 (m, 2H), 1.65-1.48 (m, 4H), 1.42 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.70, 128.93, 128.80, 125.72, 62.64, 33.48, 32.17, 28.85, 24.91.

HRMS (EI): Calcd for $C_{11}H_{16}OS$ $[M]^{\cdot+}$ 196.0916; found 196.0917.



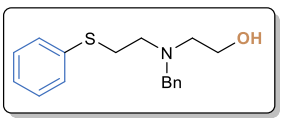
2-(2-(phenylthio)ethoxy)ethan-1-ol (4s)

Following the general procedure A at 40°C, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4s** as a yellow oil (21.0 mg, 53% yield). R_f = 0.4 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.76-3.68 (m, 4H), 3.61-3.57 (t, *J* = 4.2 Hz, 2H), 3.15 (t, *J* = 6.6 Hz, 2H), 2.14 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.74, 129.61, 128.95, 126.33, 71.98, 69.73, 61.73, 33.52.

HRMS (EI): Calcd for $C_{10}H_{14}O_2S$ $[M]^{\cdot+}$ 198.0709; found 198.0707.



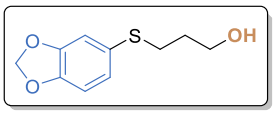
2-(benzyl(2-(phenylthio)ethyl)amino)ethan-1-ol (4t)

Following the general procedure A at 40°C, the crude product was purified by silica gel chromatography (PE:EA = 3:1 as the eluent) to give **4t** as a yellow oil (32.0 mg, 53% yield). R_f = 0.3 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (m, 9H), 7.24-7.15 (m, 1H), 3.69 (s, 2H), 3.57 (t, *J* = 5.2 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.43, 136.01, 129.22, 128.91, 128.88, 128.40, 127.28, 126.00, 58.71, 58.64, 55.54, 52.55, 32.01.

HRMS (ESI): Calcd for $C_{17}H_{21}NOS$ $[M]^{\cdot+}$ 287.1338; found 287.1339.



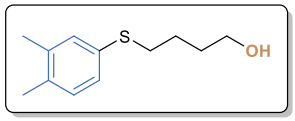
3-(benzo[*d*][1,3]dioxol-5-ylthio)propan-1-ol (4u)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4u** as a yellow oil (36.0 mg, 85% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95-6.93 (m, 1H), 6.93-6.92 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 2H), 3.78 (t, *J* = 6.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 1.91-1.81 (m, 2H), 1.56 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.98, 147.03, 127.76, 125.28, 111.94, 108.70, 101.25, 61.41, 32.41, 31.77.

HRMS (EI): Calcd for $C_{10}H_{12}O_3S$ $[M]^{\cdot+}$ 212.0502; found 212.0500.



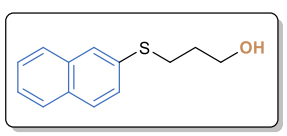
4-((3,4-dimethylphenyl)thio)butan-1-ol (4v)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4v** as a yellow oil (35.5 mg, 85% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.13 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.79 (s, 1H), 1.74-1.70 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.17, 134.70, 132.76, 131.16, 130.06, 127.31, 62.24, 34.10, 31.63, 25.51, 19.64, 19.22.

HRMS (EI): Calcd for $C_{12}H_{18}OS$ $[M]^{\cdot+}$ 210.1073; found 210.1073.



3-(naphthalen-2-ylthio)propan-1-ol (4w)

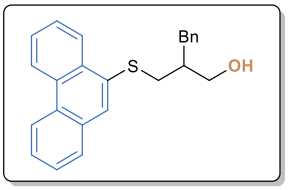
Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 5:1 as the eluent) to give **4w** as a yellow oil (24.0, 55% yield). R_f = 0.3 (PE:EA = 2:1).

Following the general procedure A using 2-MePhB$(OH)_2$, the product **4w** was obtained as a yellow oil (28.8 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 4H), 7.52-7.43 (m, 3H), 3.83 (t, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 7.1 Hz, 2H), 2.03-1.92 (m, 2H), 1.59 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.74, 131.71, 128.39, 127.67, 127.29, 126.99, 126.84, 126.84, 126.53, 125.61, 61.39, 31.66, 30.11.

HRMS (EI): Calcd for $C_{13}H_{14}OS$ $[M]^{\cdot+}$ 218.0760; found 218.0759.



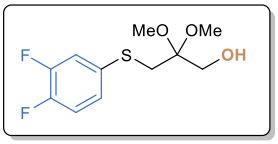
2-benzyl-3-(phenanthren-9-ylthio)propan-1-ol (4x)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4x** as a yellow oil (39.3 mg, 55% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.8 Hz, 1H), 8.65 (d, *J* = 7.9 Hz, 1H), 8.49 (d, *J* = 8.7 Hz, 1H), 7.76-7.66 (m, 4H), 7.65-7.57 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.24 (m, 1H), 7.23-7.19 (m, 2H), 3.83 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.73 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.17 (d, *J* = 6.4 Hz, 2H), 2.88 (dd, *J* = 7.2, 2.1 Hz, 2H), 2.30-2.17 (m, 1H), 1.60 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.63, 132.18, 131.71, 131.08, 130.57, 129.33, 129.15, 128.46, 127.80, 127.04, 126.89, 126.89, 126.83, 126.43, 126.21, 125.39, 123.02, 122.51, 64.06, 42.16, 36.99, 34.53.

HRMS (EI): Calcd for $C_{24}H_{22}OS$ $[M]^{\cdot+}$ 358.1386; found 358.1389.



3-((3,4-difluorophenyl)thio)-2,2-dimethoxypropan-1-ol (4y)

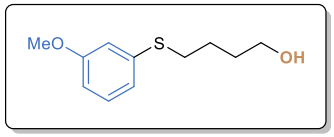
Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4y** as a pale yellow oil (27.5 mg, 52% yield). R_f = 0.4 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 1H), 7.16-7.03 (m, 2H), 3.75 (s, 2H), 3.26 (s, 6H), 3.23 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.16 (dd, J = 250.9, 13.1 Hz), 148.84 (dd, J = 249.5, 13.1 Hz), 132.72 (dd, J = 6.0, 3.9 Hz), 126.12 (dd, J = 6.1, 3.6 Hz), 118.99 (d, J = 18.6 Hz), 117.62 (d, J = 17.9 Hz), 101.52, 60.97, 48.81, 36.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.35 (d, J = 21.0 Hz), -140.05 (d, J = 21.1 Hz).

HRMS (EI): Calcd for $C_{11}H_{14}F_2O_3S$ $[M]^{\cdot+}$ 264.0626; found 264.0626.



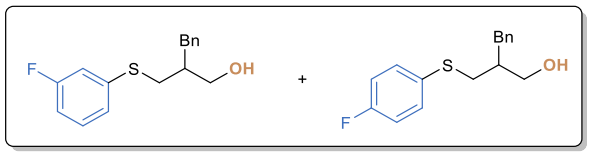
3-((3-methoxyphenyl)thio)propan-1-ole (4z)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4z** as a yellow oil (37.7 mg, 95% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 7.9 Hz, 1H), 6.89 (t, J = 2.1 Hz, 1H), 6.73 (dd, J = 8.2, 2.5 Hz, 1H), 3.81 (s, 3H), 3.67 (t, J = 6.0 Hz, 2H), 2.97 (t, J = 6.9 Hz, 2H), 1.82-1.67 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.74, 137.92, 129.61, 120.94, 114.24, 111.31, 62.21, 55.18, 33.14, 31.65, 25.41.

HRMS (EI): Calcd for $C_{11}H_{16}O_2S$ $[M]^{\cdot+}$ 212.0866; found 212.0865.



3-((3-fluorophenyl)thio)propan-1-ol and 3-((4-fluorophenyl)thio)propan-1-ol (4aa+4aa')

Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 8:1 as the eluent) to give **4aa+4aa'** as a yellow oil (1:2, 36.8 mg, 70% yield). R_f = 0.5 (PE:EA = 5:1).

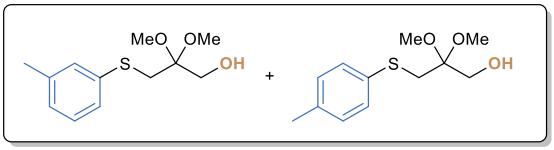
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.14 (m, 21H), 7.03-6.94 (m, 5H), 6.89-6.83 (m, 1H), 3.80-3.72 (m, 3H), 3.70-3.63 (m, 3H), 3.07-2.90 (m, 6H), 2.82-2.76 (m, 6H), 2.18-2.02 (m, 3H), 1.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.84 (d, J = 248.0 Hz), 161.59 (d, J = 246.0 Hz)., 139.56, 139.44, 139.11 (d, J = 7.8 Hz), 131.73 (d, J = 7.9 Hz), 131.24 (d, J = 3.3 Hz), 130.08 (d, J = 8.6 Hz), 129.12,

129.13, 128.48, 128.43, 126.30, 126.21, 123.74 (d, J = 2.9 Hz), 116.00 (d, J = 21.9 Hz), 114.94 (d, J = 23.4 Hz), 112.54 (d, J = 21.2 Hz), 63.82, 63.73, 42.25, 42.24, 36.86, 36.77, 35.98, 34.05.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.24, -115.81.

HRMS (EI): Calcd for $C_{16}H_{17}FOS$ $[M]^{\cdot+}$ 276.0979; found 276.0982.



2,2-dimethoxy-3-(m-tolylthio)propan-1-ol and 2,2-dimethoxy-3-(p-tolylthio)propan-1-ol (4ab+4ab')

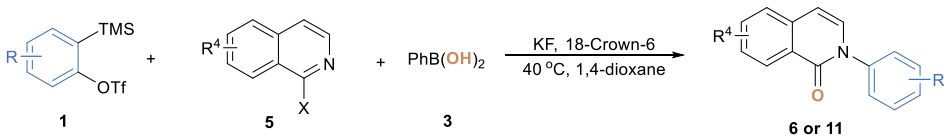
Following the general procedure A, the crude product was purified by silica gel chromatography (PE:EA = 4:1 as the eluent) to give **4ab+4ab'** as a yellow oil (1:1, 39.0 mg, 81% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.24-7.14 (m, 3H), 7.09 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 7.1 Hz, 1H), 3.74 (d, J = 4.5 Hz, 4H), 3.28-3.21 (m, 16H), 2.31 (d, J = 1.7 Hz, 6H), 1.83-1.77 (m, 2H).

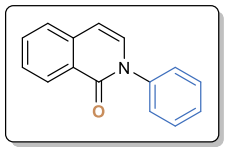
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.77, 136.53, 136.06, 132.56, 130.32, 130.09, 129.76, 128.82, 127.16, 126.48, 101.70, 101.65, 61.04, 61.03, 48.82, 48.79, 36.86, 36.10, 21.27, 20.96.

HRMS (EI): Calcd for $C_{12}H_{18}O_3S$ $[M]^{\cdot+}$ 242.0971; found 242.0973.

4.2 Three-component Reaction of Halo-azaarenes



General procedure C: To a mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.), phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) and 1-fluoroisoquinoline (0.2 mmol, 1.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was added aryne precursor (0.6 mmol, 3.0 equiv.). The mixture was kept stirring at 40°C over 24 hours. After complete consumption of the isoquinoline indicated by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was concentrated *in vacuo*, and the residue was then purified by silica gel flash chromatography to afford the products.



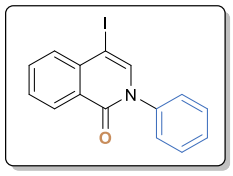
2-phenylisoquinolin-1(*2H*)-one (6a)[9]

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **6a** as a pale yellow solid (34.9 mg, 79% yield). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.1 Hz, 1H), 7.68 (td, *J* = 8.2, 7.7, 1.3 Hz, 1H), 7.58-7.54 (m, 1H), 7.54-7.48 (m, 3H), 7.45-7.39 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.00, 141.36, 137.05, 132.52, 132.13, 129.24, 128.25, 128.05, 127.13, 126.83, 126.55, 125.92, 106.17.

HRMS (ESI): Calcd for $C_{15}H_{12}NO^+$ $[M+H]^+$ 222.0913, found 222.0917.



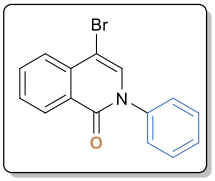
4-iodo-2-phenylisoquinolin-1(*2H*)-one (6b)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **6b** as a yellow solid (63.7 mg, 92% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.82-7.71 (m, 2H), 7.68 (s, 1H), 7.62-7.56 (m, 1H), 7.56-7.50 (m, 2H), 7.48-7.43 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.24, 140.28, 138.05, 137.03, 133.49, 130.40, 129.34, 128.54, 128.39, 128.05, 126.72, 126.65, 72.10.

HRMS (ESI): Calcd for $C_{15}H_{11}INO^+$ $[M+H]^+$ 347.9880, found 347.9871.



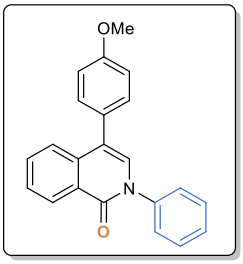
4-bromo-2-phenylisoquinolin-1(*2H*)-one (6c)[9]

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **6c** as a pale yellow solid (57.0 mg, 95% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.91-7.88 (m, 1H), 7.85-7.78 (m, 1H), 7.65-7.59 (m, 1H), 7.56-7.51 (m, 3H), 7.49-7.44 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.04, 140.45, 135.46, 133.27, 132.56, 129.38, 128.66, 128.43, 128.10, 126.69, 126.68, 125.90, 100.19.

HRMS (ESI): Calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$ 300.0019, found 300.0014.



4-(4-methoxyphenyl)-2-phenylisoquinolin-1(*2H*)-one (6d)

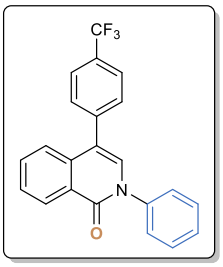
Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **6d** as a yellow oil (60.2 mg, 92% yield). R_f = 0.2 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.9 Hz, 1H), 7.70-7.61 (m, 2H), 7.60-7.55 (m, 1H), 7.54-7.49 (m, 4H), 7.44 (dt, *J* = 4.7, 2.5 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.18 (s, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.48, 159.24, 141.27, 136.74, 132.37, 131.01, 130.86, 129.22, 128.61,

128.30, 128.02, 127.07, 126.82, 126.33, 124.78, 119.22, 114.05, 55.32.

HRMS (ESI): Calcd for $C_{22}H_{18}NO_2^+$ $[M+H]^+$ 328.1332, found 328.1324.



2-phenyl-4-(4-(trifluoromethyl)phenyl)isoquinolin-1(*2H*)-one (6e)

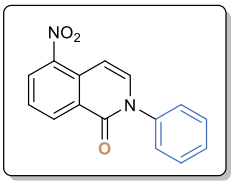
Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **6e** as a yellow solid (51.0 mg, 70% yield). R_f = 0.3 (PE:EA = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.71-7.64 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 3H), 7.56-7.47 (m, 5H), 7.46-7.39 (m, 1H), 7.20 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.50, 141.10, 140.02, 135.88, 132.73, 131.58, 130.30, 130.07 (q, *J* = 32.9 Hz), 129.38, 128.94 128.31, 127.55, 126.84, 126.48, 125.68 (q, *J* = 6.8 Hz), 124.32, 124.12 (q, *J* = 271.9 Hz), 118.35.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51.

HRMS (ESI): Calcd for $C_{22}H_{15}F_3NO^+$ $[M+H]^+$ 366.1100, found 366.1108.



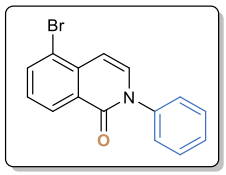
5-nitro-2-phenylisoquinolin-1(*2H*)-one (6f)

Following the general procedure C, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **6f** as a yellow solid (21.0 mg, 40% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.0 Hz, 1H), 8.44 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.50-7.41 (m, 3H), 7.38 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.48, 144.83, 140.42, 135.71, 134.67, 131.00, 129.57, 129.54, 128.71, 128.63, 126.56, 126.11, 100.70.

HRMS (ESI): Calcd for $C_{15}H_{11}N_2O_3^+$ $[M+H]^+$ 267.0764, found 267.0757.



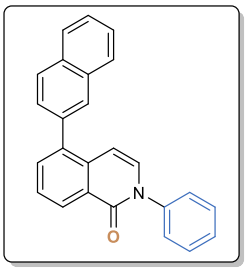
5-bromo-2-phenylisoquinolin-1(*2H*)-one (6g)[10]

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:DCM = 1:1 as the eluent) to give **6g** as a yellow solid (37.0 mg, 62% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.56-7.47 (m, 2H), 7.46-7.40 (m, 3H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.30-7.24 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.24, 140.98, 136.41, 136.28, 133.28, 129.37, 128.33, 128.16, 127.93, 127.67, 126.69, 120.62, 104.78.

HRMS (ESI): Calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$ 300.0019, found 300.0014.



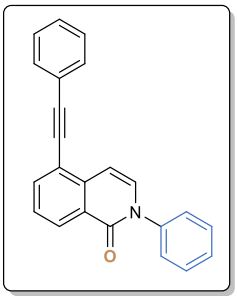
5-(naphthalen-2-yl)-2-phenylisoquinolin-1(*2H*)-one (6h)

Following the general procedure C, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **6h** as a pale yellow solid (62.9 mg, 91% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.98-7.92 (m, 3H), 7.76 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.66-7.57 (m, 4H), 7.57-7.52 (m, 2H), 7.50-7.42 (m, 3H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.02, 141.30, 138.95, 137.05, 135.09, 133.67, 133.29, 132.59, 131.97, 129.28, 128.66, 128.09, 128.04, 128.01, 127.89, 127.81, 127.74, 127.16, 126.79, 126.79,126.52, 126.32, 104.18.

HRMS (ESI): Calcd for $C_{25}H_{18}NO^+$ $[M+H]^+$ 348.1383, found 348.1374.



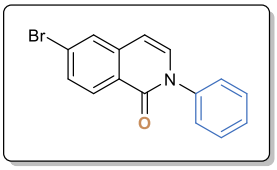
2-phenyl-5-(phenylethynyl)isoquinolin-1(*2H*)-one (6i)

Following the general procedure C, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **6i** as a pink solid (38.6 mg, 60% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.8 Hz, 1H), 7.92 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.67-7.61 (m, 2H), 7.58-7.52 (m, 3H), 7.52-7.46 (m, 3H), 7.45-7.40 (m, 3H), 7.33-7.27 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.76, 141.19, 137.90, 135.98, 132.88, 131.63, 129.33, 128.68, 128.53, 128.47, 128.21, 126.77, 126.77, 126.65, 122.87, 119.84, 104.38, 94.76, 86.32.

HRMS (ESI): Calcd for $C_{23}H_{16}NO^+$ $[M+H]^+$ 322.1226, found 322.1220.



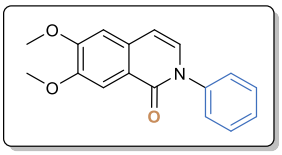
6-bromo-2-phenylisoquinolin-1(*2H*)-one (6j)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **6j** as a yellow solid (46.2 mg, 76% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.57-7.50 (m, 2H), 7.49-7.42 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.53, 141.03, 138.50, 133.51, 130.39, 130.15, 129.33, 128.37, 128.26, 127.68, 126.72, 125.26, 104.98.

HRMS (ESI): Calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$ 300.0019, found 300.0013.



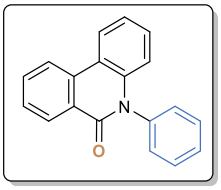
6,7-dimethoxy-2-phenylisoquinolin-1(*2H*)-one (6k)[11]

Following the general procedure C, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **6k** as a yellow solid (46.0 mg, 82% yield). R_f = 0.2 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.49-7.41 (m, 3H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.94 (s, 1H), 6.51 (d, *J* = 7.4 Hz, 1H), 4.04 (s, 3H), 4.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.31, 153.57, 149.42, 141.59, 132.49, 130.88, 129.15, 127.92, 126.85, 120.43, 108.16, 106.07, 105.68, 56.16, 56.10.

HRMS (ESI): Calcd for $C_{17}H_{16}NO_3^+$ $[M+H]^+$ 282.1125, found 282.1117.

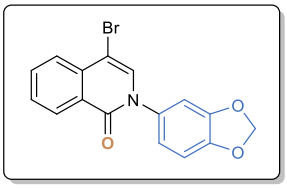


5-phenylphenanthridin-6(*5H*)-one (6n)[12]

Following the general procedure C at 80°C and the reaction time was 48 hours, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **6n** as a yellow solid (20.1 mg, 37% yield, 54% starting material recovered). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63-8.56 (m, 1H), 8.40-8.31 (m, 1H), 7.87-7.81 (m, 1H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.41-7.29 (m, 2H), 6.76-6.68 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.71, 139.21, 138.32, 134.03, 132.84, 130.22, 129.12, 129.11, 129.05, 128.79, 128.15, 125.90, 123.01, 122.66, 121.80, 119.05, 117.04.



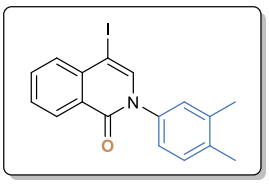
2-(benzo[*d*][1,3]dioxol-5-yl)-4-bromoisoquinolin-1(*2H*)-one (11a)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **11a** as a yellow solid (62.4 mg, 91% yield). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.81 (ddd, *J* = 7.8, 6.9, 1.0 Hz, 1H), 7.64-7.58 (m, 1H), 7.48 (s, 1H), 6.96-6.91 (m, 2H), 6.87 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.07 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 148.15, 147.70, 135.47, 134.34, 133.28, 132.84, 128.68, 128.11, 126.62, 125.91, 120.12, 108.42, 108.20, 101.90, 100.00.

HRMS (ESI): Calcd for $C_{16}H_{11}BrNO_3^+$ $[M+H]^+$ 343.9917, found 343.9921.



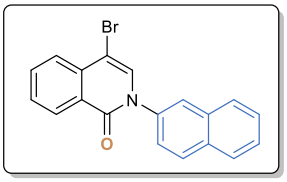
2-(3,4-dimethylphenyl)-4-iodoisoquinolin-1(*2H*)-one (11b)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **11b** as a yellow solid (48.4 mg, 78% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.81-7.72 (m, 2H), 7.67 (s, 1H), 7.58 (ddd, *J* = 8.1, 6.8, 1.5 Hz, 1H), 7.33-7.26 (m, 1H), 7.21 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 7.9, 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.48, 138.47, 138.08, 137.91, 137.18, 137.12, 133.42, 130.45, 130.39, 128.60, 127.98, 127.62, 126.82, 123.83, 71.74, 19.82, 19.47.

HRMS (ESI): Calcd for $C_{17}H_{15}INO^+$ $[M+H]^+$ 376.0193, found 376.0195.



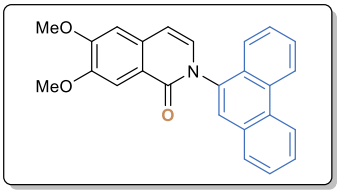
4-bromo-2-(naphthalen-2-yl)isoquinolin-1(*2H*)-one (11c)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **11c** as a yellow solid (44.6 mg, 64% yield). R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.96-7.89 (m, 4H), 7.84 (ddd, *J* = 8.1, 7.6, 1.4 Hz, 1H), 7.68-7.55 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.30, 138.13, 135.55, 133.41, 133.37, 132.75, 132.75, 129.26, 128.70, 128.19, 128.07, 127.80, 126.93, 126.84, 126.76, 125.99, 125.15, 124.66, 100.38.

HRMS (ESI): Calcd for $C_{19}H_{13}BrNO^+$ $[M+H]^+$ 350.0175, found 350.0177.



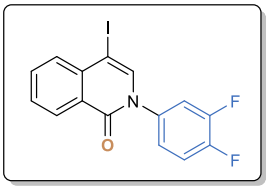
6,7-dimethoxy-2-(phenanthren-9-yl)isoquinolin-1(*2H*)-one (11d)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **11d** as a yellow solid (40.2 mg, 53% yield). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 14.1, 8.4 Hz, 2H), 7.96-7.90 (m, 2H), 7.84 (s, 1H), 7.78-7.70 (m, 2H), 7.67 (t, *J* = 6.9 Hz, 1H), 7.61-7.57 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.03 (s, 1H), 6.61 (d, *J* = 7.3 Hz, 1H), 4.08 (s, 3H), 4.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.86, 153.72, 149.49, 137.18, 132.84, 131.67, 131.36, 131.26, 130.53, 128.91, 128.59, 127.53, 127.39, 127.26, 127.06, 126.28, 123.40, 123.14, 122.72, 120.37, 108.28, 106.23, 105.73, 56.17, 56.15.

HRMS (ESI): Calcd for $C_{25}H_{20}NO_3^+$ $[M+H]^+$ 382.1438, found 382.1441.



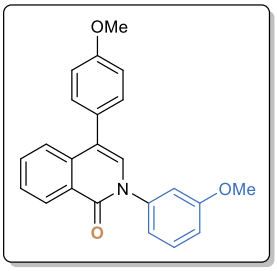
2-(3,4-difluorophenyl)-4-iodoisoquinolin-1(*2H*)-one (11e)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **11e** as a yellow solid (68.0 mg, 87% yield). R_f = 0.2 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.81 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.75 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.64-7.57 (m, 2H), 7.40-7.27 (m, 2H), 7.24-7.18 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.20, 150.26 (dd, *J* = 251.5, 1.0 Hz), 150.20 (d, *J* = 239.4), 137.29, 137.00, 136.26 (dd, *J* = 7.7, 3.8 Hz), 133.89, 130.69, 128.65, 128.46, 126.52, 123.14 (dd, *J* = 6.6, 3.8 Hz), 117.84 (d, *J* = 18.4 Hz), 116.83 (d, *J* = 19.1 Hz), 72.78.

HRMS (ESI): Calcd for $C_{15}H_9F_2INO^+$ $[M+H]^+$ 383.9691, found 383.9694.



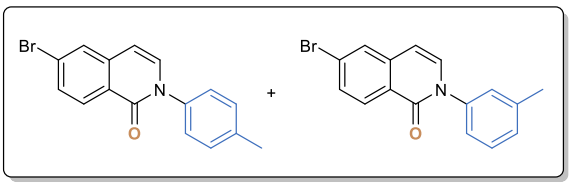
2-(3-methoxyphenyl)-4-(4-methoxyphenyl)isoquinolin-1(*2H*)-one (11f)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **11f** as a yellow solid (61.3 mg, 86% yield). R_f = 0.3 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.9 Hz, 1H), 7.71-7.61 (m, 2H), 7.57 (td, *J* = 7.4, 6.7, 1.6 Hz, 1H), 7.46-7.36 (m, 3H), 7.18 (s, 1H), 7.10-7.06 (m, 2H), 7.05-6.95 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.37, 160.09, 159.17, 142.26, 136.64, 132.33, 130.94, 130.78, 129.89, 128.53, 128.18, 127.01, 126.23, 124.72, 119.12, 118.96, 114.06, 113.99, 112.56, 55.38, 55.26.

HRMS (ESI): Calcd for $C_{23}H_{20}NO_3^+$ $[M+H]^+$ 358.1438, found 358.1438.



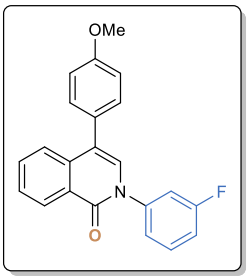
6-bromo-2-(m-tolyl)isoquinolin-1(*2H*)-one and 6-bromo-2-(p-tolyl)isoquinolin-1(*2H*)-one (11g+11g')

Following the general procedure C, the crude product was purified by silica gel chromatography (PE:DCM = 5:1 as the eluent) to give **11g+11g'** as a yellow solid (46.5 mg, 70% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.32 (m, 2H), 7.74-7.72 (m, 2H), 7.64-7.60 (m, 2H), 7.43-7.38 (m, 1H), 7.31 (s, 4H), 7.28-7.19 (m, 5H), 6.48 (d, *J* = 7.5 Hz, 2H), 2.44 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.60, 161.55, 140.88, 139.35, 138.47, 138.47, 138.42, 138.17, 133.65, 133.57, 130.30, 130.26, 130.09, 130.09, 129.86, 129.86, 129.11, 129.04, 128.29, 127.60, 127.56, 127.32, 126.37, 125.15, 125.15, 123.61, 104.87, 104.87, 21.28, 21.10.

HRMS (ESI): Calcd for $C_{16}H_{13}BrNO^+$ $[M+H]^+$ 314.0175, found 314.0177.



2-(3-fluorophenyl)-4-(4-methoxyphenyl)isoquinolin-1(*2H*)-one (11h)

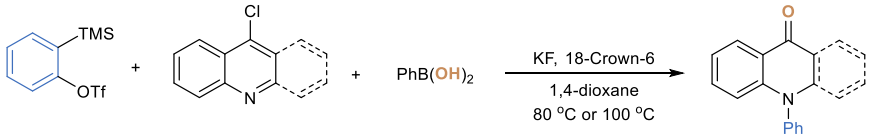
Following the general procedure C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **11h** as a yellow solid (43.9 mg, 62% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.2 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.62-7.51 (m, 2H), 7.50-7.42 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.18 (t, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 5.7 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.93 (d, *J* = 247.9 Hz), 161.62, 159.32, 137.19 (d, *J* = 3.4 Hz), 136.78, 132.53, 131.02, 130.62, 128.70, 128.61, 128.15, 127.25, 126.22, 124.90, 119.51, 116.17 (d, *J* = 22.9 Hz), 114.11, 55.36.

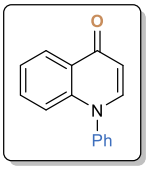
^{19}F NMR (377 MHz, $CDCl_3$) δ -111.18, -113.30.

HRMS (ESI): Calcd for $C_{22}H_{17}FNO_2^+$ $[M+H]^+$ 346.1238, found 346.1237.



1a **7** **3a** **8**

General procedure D: To a mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.), phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) and 4-chloroquinoline and 9-chloroacridine (0.2 mmol, 1.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was added aryne precursor (0.6 mmol, 147 μL, 3.0 equiv.) dropwise. The reaction mixture was kept stirring over 24 hours. After complete consumption of the quinolines indicated by TLC, the mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was concentrated *in vacuo*, and the residue was further purified by silica gel flash chromatography to afford the target products.



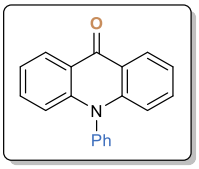
1-phenylquinolin-4(*1H*)-one (8a)[13]

Following the general procedure D at 80°C, the crude product was purified by silica gel chromatography (PE:EA = 2:3 as the eluent) to give **8a** as a yellow solid (34.1 mg, 77% yield). R_f = 0.2 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.64-7.54 (m, 4H), 7.51-7.47 (m, 1H), 7.43-7.34 (m, 3H), 7.01 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.26, 142.67, 141.35, 141.33, 131.81, 130.28, 129.47, 127.54, 126.56, 123.86, 117.24, 110.21.

HRMS (ESI): Calcd for $C_{15}H_{12}NO^+$ $[M+H]^+$ 222.0913, found 222.0913.



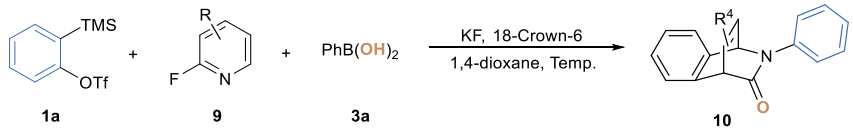
10-phenylacridin-9(*10H*)-one (8b)[14]

Following the general procedure D employing KF (1.2 mmol, 70 mg, 6 equiv.), 18-crown-6 (1.2 mmol, 422.4 mg, 6 equiv.) and aryne precursor (0.8 mmol, 196 μL, 4 equiv.) at 100°C for 48 h, the crude product was purified by silica gel chromatography (PE:EA= 10:1 as the eluent) to give **8b** as a yellow solid (33.0 mg, 61% yield). R_f = 0.4 (PE:EA = 5:1).

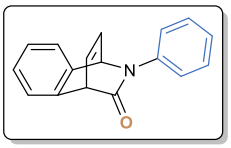
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.78-7.71 (m, 2H), 7.70-7.65 (m, 1H), 7.52 (ddd, *J* = 8.6, 6.9, 1.7 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.16, 143.12, 138.95, 133.24, 131.07, 130.03, 129.57, 127.27, 121.78, 121.51, 116.77.

HRMS (ESI): Calcd for $C_{19}H_{14}NO^+$ $[M+H]^+$ 272.1070, found 272.1068.



General procedure E: To a mixture of KF (1.6 mmol, 93 mg, 8.0 equiv.), 18-crown-6 (1.6 mmol, 422.4 mg, 8.0 equiv.), phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) and substituted 2-fluoropyridines (0.2 mmol, 1.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was added aryne precursor (1 mmol, 245 μL, 5.0 equiv.) dropwise. The mixture was kept stirring over 24 hours at certain temperature. After complete consumption of the pyridines indicated by TLC, the mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was concentrated *in vacuo*, and the residue was further purified by silica gel flash chromatography to afford the target products.



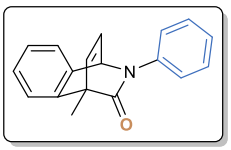
***Cis*-10-phenyl-1,4-dihydro-1,4-(epiminomethano)naphthalen-9-one (10a)**

Following the general procedure E at 40°C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **10a** as a yellow oil (26.0 mg, 53% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.5 Hz, 1H), 7.41-7.35 (m, 3H), 7.30-7.16 (m, 5H), 7.16-7.10 (m, 1H), 7.04 (t, *J* = 6.5 Hz, 1H), 5.65 (d, *J* = 5.0 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.96, 141.51, 140.33, 140.29, 137.25, 136.09, 128.99, 126.20, 126.06, 125.74, 124.49, 122.97, 122.00, 63.26, 56.22.

HRMS (ESI): Calcd for $C_{17}H_{14}NO^+$ $[M+H]^+$ 248.1070, found 248.1069.



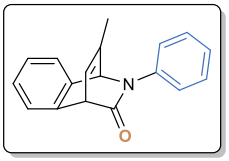
***Cis*-4-methyl-10-phenyl-1,4-dihydro-1,4-(epiminomethano)naphthalen-9-one (10b)**

Following the general procedure E at 40°C, the crude product was purified by silica gel chromatography (PE:EA = 10:1 as the eluent) to give **10b** as a yellow solid (40.0 mg, 77% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4H), 7.26-7.21 (m, 2H), 7.20-7.13 (m, 3H), 7.00 (dd, *J* = 7.1, 5.6 Hz, 1H), 6.68 (dd, *J* = 7.1, 1.8 Hz, 1H), 5.59 (dd, *J* = 5.7, 1.7 Hz, 1H), 1.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.56, 143.34, 142.73, 142.21, 140.71, 136.00, 128.84, 125.94, 125.78, 125.49, 122.81, 121.86, 121.72, 62.42, 55.31, 13.79.

HRMS (ESI): Calcd for $C_{18}H_{16}NO^+$ $[M+H]^+$ 262.1226, found 262.1226.



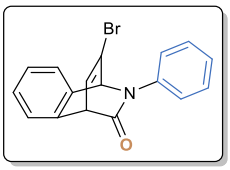
Cis-2-methyl-10-phenyl-1,4-dihydro-1,4-(epiminomethano)naphthalen-9-one (10c)

Following the general procedure E at 60°C, the crude product was purified by silica gel chromatography (PE:EA = 20:1 as the eluent) to give **10c** as a yellow solid (35.0 mg, 67% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.34 (m, 4H), 7.25-7.21 (m, 2H), 7.21-7.15 (m, 3H), 6.60 (dt, *J* = 5.9, 1.9 Hz, 1H), 5.30 (d, *J* = 2.0 Hz, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 2.07 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.27, 146.32, 141.41, 140.93, 140.30, 129.07, 128.91, 126.26, 125.75, 125.56, 124.02, 123.11, 121.82, 68.03, 55.49, 18.35.

HRMS (ESI): Calcd for $C_{18}H_{16}NO^+$ $[M+H]^+$ 262.1226, found 262.1225.



Cis-2-bromo-10-phenyl-1,4-dihydro-1,4-(epiminomethano)naphthalen-9-one (10d)

Following the general procedure E at 100°C, the crude product was purified by silica gel chromatography (DCM as the eluent) to give **10d** as a white solid (46.0 mg, 71% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.36 (m, 4H), 7.32-7.19 (m, 5H), 7.12 (dd, *J* = 6.4, 2.3 Hz, 1H), 5.55 (d, *J* = 2.4 Hz, 1H), 4.77 (d, *J* = 6.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.54, 140.47, 139.54, 138.75, 134.72, 129.11, 127.03, 126.51, 126.39, 126.11, 124.54, 123.31, 122.47, 71.12, 57.25.

HRMS (ESI): Calcd for $C_{17}H_{13}BrNO^+$ $[M+H]^+$ 326.0175, found 326.0177.

4.3 Other Substrates

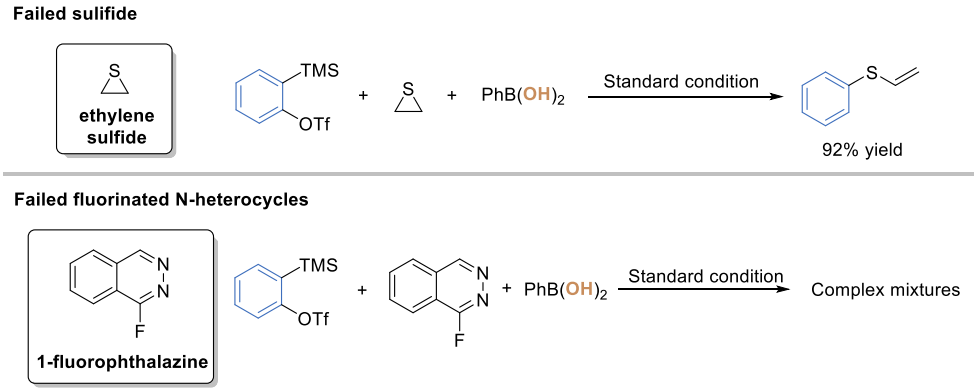
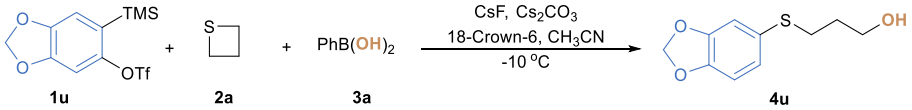


Figure S1. Other substrates.

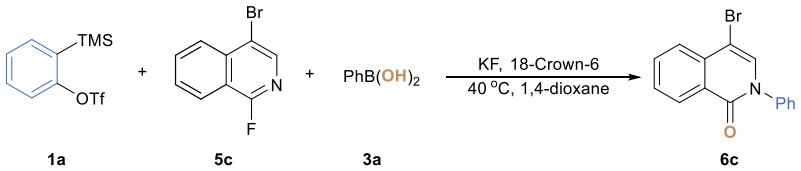
For the ring-opening reaction of ethylene sulfide, the phenyl vinyl sulfide was obtained instead, which might be due to its strong ring strain that led to the fast intramolecular proton transfer and elimination. For the reaction with 1-fluorophthalazine, a complex mixture was obtained instead. Side reaction pathway might contain the previously reported [4+2] cycloaddition and extrusion of nitrogen cascade.

5. Synthetic Application

5.1 Scale-up Reaction

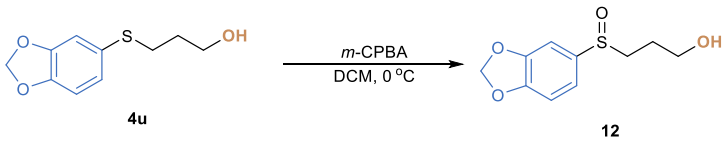


To a suspension of CsF (12 mmol, 1.84 g, 3.0 equiv.), Cs_2CO_3 (8 mmol, 2.61 g, 2.0 equiv.), 18-crown-6 (8 mmol, 2.11g, 3.0 equiv.) and phenylboronic acid (6 mmol, 0.73 g, 1.5 equiv.) in anhydrous CH_3CN (40 mL) was added aryne precursor **1u** (4 mmol, 1.37 g, 1.0 equiv.) and thietane (8 mmol, 0.64 mL, 2.0 equiv.) at -10°C. The mixture was then kept stirring at -10°C for 12 hours. After complete consumption of the aryne precursors indicated by TLC, the reaction mixture was quenched with 1M NaOH (15 mL) and extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was further purified by silica gel flash chromatography (PE:EA = 4:1 as the eluent) to give **4u** as a yellow oil (0.69 g, 81% yield).



To a mixture of KF (12 mmol, 0.7 g, 5.0 equiv.), 18-crown-6 (12 mmol, 3.17 g, 5.0 equiv.), phenylboronic acid (3.6 mmol, 0.44 g, 3.0 equiv.) and 4-bromo-1-fluoroisoquinoline (2.4 mmol, 0.54 g, 1.0 equiv.) in anhydrous 1,4-dioxane (16 mL) was added aryne precursor (7.2 mmol, 1.76 mL, 3.0 equiv.) dropwise. The mixture was kept stirring for 72 hours at 40°C. After complete consumption of isoquinoline indicated by TLC, the mixture was filtrated through a pad of silica gel and washed with DCM. The filtrate was concentrated *in vacuo*, and the residue was further purified by silica gel flash chromatography (PE:EA = 20:1 as the eluent) to give **6c** as a pale yellow solid (0.65 g, 91% yield).

5.2 Downstream Synthesis



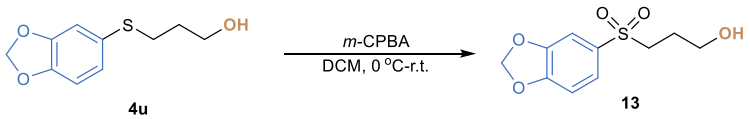
4u 12

To a stirred solution of 3-(benzo[*d*][1,3]dioxol-5-ylthio)propan-1-ol **4u** (0.2 mmol, 42.4 mg, 1.0 equiv.) in DCM (1 mL) was added *m*-CPBA (85%, 0.22 mmol, 44.8 mg, 1.1 equiv.) at 0°C under air. The reaction was kept stirring at 0°C for 30 minutes. The reaction was then quenched with saturated Na_2SO_3 solution (2 mL) and extracted with DCM (3 x 3 mL). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography (EA as the eluent) to give **12** as a pale yellow oil (42.0 mg, 92% yield). R_f = 0.2 (EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.09 (m, 2H), 7.07 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 2H), 3.74-3.61 (m, 2H), 3.52 (br, 1H), 3.01-2.83 (m, 2H), 1.98-1.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.33, 148.73, 135.86, 119.11, 108.76, 104.38, 101.97, 60.77, 54.59, 25.87.

HRMS (ESI): Calcd for $C_{10}H_{13}O_4S^+$ $[M+H]^+$ 229.0529; found 229.0529.



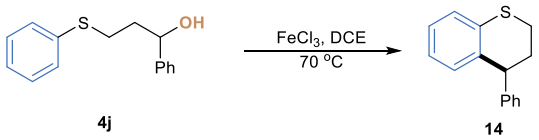
4u 13

To a stirred solution of 3-(benzo[*d*][1,3]dioxol-5-ylthio)propan-1-ol **4u** (0.2 mmol, 42.4 mg, 1.0 equiv.) in DCM (2 mL) was added *m*-CPBA (85%, 0.64 mmol, 130 mg, 3.2 equiv.) at 0°C under air. The reaction was kept stirring at room temperature for 3 hours. The mixture was then quenched with saturated Na_2SO_3 solution (2 mL), extracted with DCM (3 x 3 mL), and washed with 2 M NaOH (1 mL). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was further purified by silica gel flash chromatography (PE:EA = 1:2 as the eluent) to give **13** as a pale yellow oil (47.9 mg, 98% yield). R_f = 0.4 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.11 (s, 2H), 3.70 (t, *J* = 6.0 Hz, 2H), 3.24-3.17 (m, 2H), 2.32 (br, 1H), 2.02-1.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.31, 148.40, 132.17, 124.01, 108.58, 108.00, 102.53, 60.39, 53.54, 25.90.

HRMS (ESI): Calcd for $C_{10}H_{13}O_5S^+$ $[M+H]^+$ 245.0478; found 245.0479.



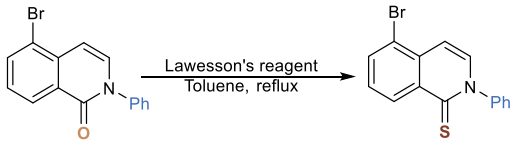
4j 14

To a suspension of $FeCl_3$ (0.1 mmol, 16.2 mg, 1.0 equiv.) in anhydrous DCE (2 mL) was added 1-phenyl-3-(phenylthio)propan-1-ol **4j** (0.1 mmol, 24.4 mg, 1.0 equiv.) in anhydrous DCE (2 mL) dropwise at 0°C. The reaction was kept stirring at 70°C for 12 hours. The reaction was quenched with water (2 mL) and extracted with DCM (3 x 2 mL). The combined organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (pentane as the eluent) to give **14** as a colorless oil (18.3 mg, 81% yield). (Note: The temperature of water bath during solvent evaporation should be controlled under 10°C.) R_f = 0.3 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.17 (m, 4H), 7.16-7.05 (m, 3H), 7.01-6.88 (m, 2H), 4.25 (t, 1H), 2.99-2.84 (m, 2H), 2.39-2.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ145.09, 135.31, 133.49, 131.24, 128.55, 128.43, 126.86, 126.41, 126.36, 123.96, 44.20, 30.66, 23.48.

HRMS (EI): Calcd for $C_{15}H_{14}S$ $[M]^{\cdot+}$ 226.0816; found 226.0812.



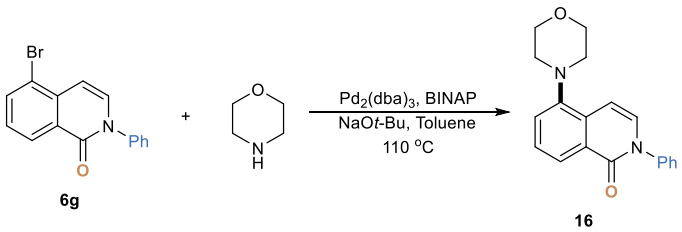
6g 15

To a solution of 5-bromo-2-phenylisoquinolin-1(2*H*)-one (**6g**, 0.2 mmol, 60 mg, 1.0 equiv.) in toluene (6 mL) was added Lawesson's reagent (0.8 mmol, 0.32 g, 4.0 equiv.). The reaction was stirring at 120°C for 16 hours. The reaction mixture was filtered through a pad of celite and washed with DCM. The combined organic layer was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (PE:EA = 20:1 as the eluent) to give **15** as a yellow solid (56.0 mg, 89% yield). R_f = 0.4 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.63-7.56 (m, 2H), 7.56-7.43 (m, 3H), 7.39 (dd, J = 7.3, 1.8 Hz, 2H), 7.34 (d, J = 7.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.72, 146.10, 136.37, 135.86, 134.63, 132.50, 132.01, 129.84, 129.14, 128.99, 126.88, 121.54, 110.07.

HRMS (ESI): Calcd for $C_{15}H_{11}BrNS^+$ $[M+H]^+$ 315.9790; found 315.9793.

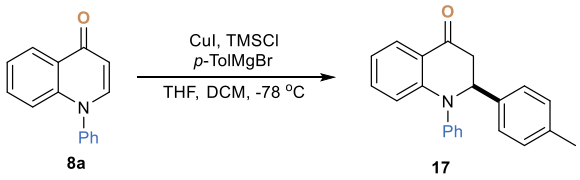


To a solution of 5-bromo-2-phenylisoquinolin-1(2*H*)-one (**6g**, 0.15 mmol, 45 mg, 1.0 equiv.), $Pd_2(dba)_3$ (0.015 mmol, 13.7 mg, 0.1 equiv.), BINAP (0.015 mmol, 9.4 mg, 0.1 equiv.) and *t*-BuOK (0.45 mmol, 43 mg, 3.0 equiv.) in toluene (2 mL) was added morpholine (0.4 mmol, 39 µL, 3.0 equiv.). The reaction was stirring at 110°C for 16 hours. The reaction was filtered through a pad of celite and washed with DCM. The combined organic layer was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (PE:EA = 3:1 as the eluent) to give **16** as a yellow solid (38.0 mg, 83% yield). R_f = 0.3 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.52 (ddd, *J* = 12.9, 7.2, 3.9 Hz, 3H), 7.50-7.39 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.01-3.93 (m, 4H), 3.10-3.07 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.13, 148.45, 141.38, 132.46, 131.57, 129.29, 128.09, 127.98, 127.42, 126.81, 123.42, 121.96, 102.05, 67.31, 53.21.

HRMS (ESI): Calcd for $C_{19}H_{19}N_2O_2^+$ $[M+H]^+$ 307.1441; found 307.1443.



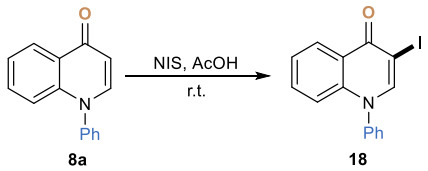
To a solution of CuI (0.4 mmol, 76 mg, 2.0 equiv.) in anhydrous THF (0.5 mL) was added *p*-TolMgBr (1 M in THF, 0.4 mmol, 0.4 mL, 2.0 equiv.) at -78°C, and the mixture was kept stirring at the same temperature for 5 minutes. Chlorotrimethylsilane (0.6 mmol, 65.2 mg, 3.0 equiv.) was then added slowly, and the mixture was kept stirring for another 5 minutes. Next, a solution of 1-phenylquinolin-4(1*H*)-one **8a** (0.2 mmol, 44.2 mg, 1.0 equiv.) in anhydrous THF (0.5 mL)/DCM (0.5 mL) was added dropwise. The reaction was stirred at -78°C for 3 hours, quenched with saturated NH_4Cl solution (2 mL) and extracted with DCM (3 x 2 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (PE:EA = 10:1

as the eluent) to give 1-phenyl-2-(p-tolyl)-2,3-dihydroquinolin-4(1*H*)-one **17** as a yellow solid (51.0 mg, 82% yield). R_f = 0.4 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.39-7.33 (m, 2H), 7.32-7.27 (m, 1H), 7.26-7.20 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.83-6.76 (m, 2H), 5.14 (t, *J* = 5.6 Hz, 1H), 3.37 (dd, *J* = 16.3, 5.7 Hz, 1H), 3.10 (dd, 1H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.41, 150.21, 145.34, 137.24, 136.93, 135.21, 129.67, 129.42, 127.59, 126.89, 125.84, 125.74, 120.82, 118.21, 116.33, 64.09, 44.98, 21.04.

HRMS (ESI): Calcd for $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539; found 314.1539.



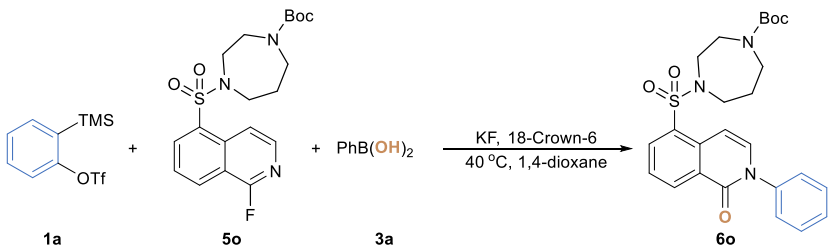
8a **18**

A solution of 1-phenylquinolin-4(1*H*)-one (**8a,** 0.15 mmol, 33.2 mg, 1 equiv.), *N*-iodosuccinimide (0.225 mmol, 51 mg, 1.5 equiv.) in AcOH (2 mL) was kept stirring at room temperature for 3 hours. The reaction was then quenched with water (2 mL) and extracted with DCM (3 x 2 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (PE:EA = 4:1 as the eluent) to give 3-iodo-1-phenylquinolin-4(1*H*)-one **18** as a yellow solid (51.0 mg, 98% yield). R_f = 0.5 (PE:EA = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) 8.46 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.17 (s, 1H), 7.67-7.58 (m, 3H), 7.51 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H), 7.46-7.42 (m, 2H), 7.41-7.35 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.06, 147.31, 140.87, 140.52, 132.03, 130.46, 129.92, 127.51, 127.33, 124.77, 123.04, 117.41, 81.67.

HRMS (ESI): Calcd for $C_{15}H_{11}INO^+$ $[M+H]^+$ 347.9880; found 347.9882.



1a **5o** **3a** **6o**

To a mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.), phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) and *tert*-butyl 4-((1-fluoroisoquinolin-5-

yl)sulfonyl)-1,4-diazepane-1-carboxylate (**5o,** 0.2 mmol, 82 mg, 1.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was added aryne precursor (0.6 mmol, 147 μL, 3.0 equiv.) dropwise. The mixture was kept stirring at 40°C for 3 days. After complete consumption of **5o** indicated by TLC, the mixture was through a pad of silica gel and washed with DCM. The solvent was concentrated *in vacuo*, and the residue was further purified by silica gel flash chromatography (PE:EA = 3:1) to afford **6o** as pale yellow solid (48.0 mg, 50% yield). R_f = 0.3 (PE:EA = 2:1).

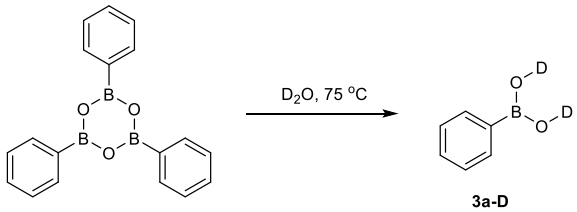
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.0 Hz, 1H), 8.22 (t, *J* = 8.1 Hz, 1H), 7.61-7.50 (m, 3H), 7.47-7.41 (m, 3H), 7.35 (t, *J* = 6.4 Hz, 2H), 3.62-3.50 (m, 4H), 3.48-3.37 (m, 4H), 1.98 (q, *J* = 6.5 Hz, 2H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.94, 155.09, 154.70, 140.49, 134.27, 134.21, 133.69, 133.52, 129.41, 128.55, 128.49, 126.52, 125.93, 102.36, 79.93, 79.85, 50.10, 49.73, 49.19, 47.67, 47.42, 45.91, 45.44, 28.49, 28.35.

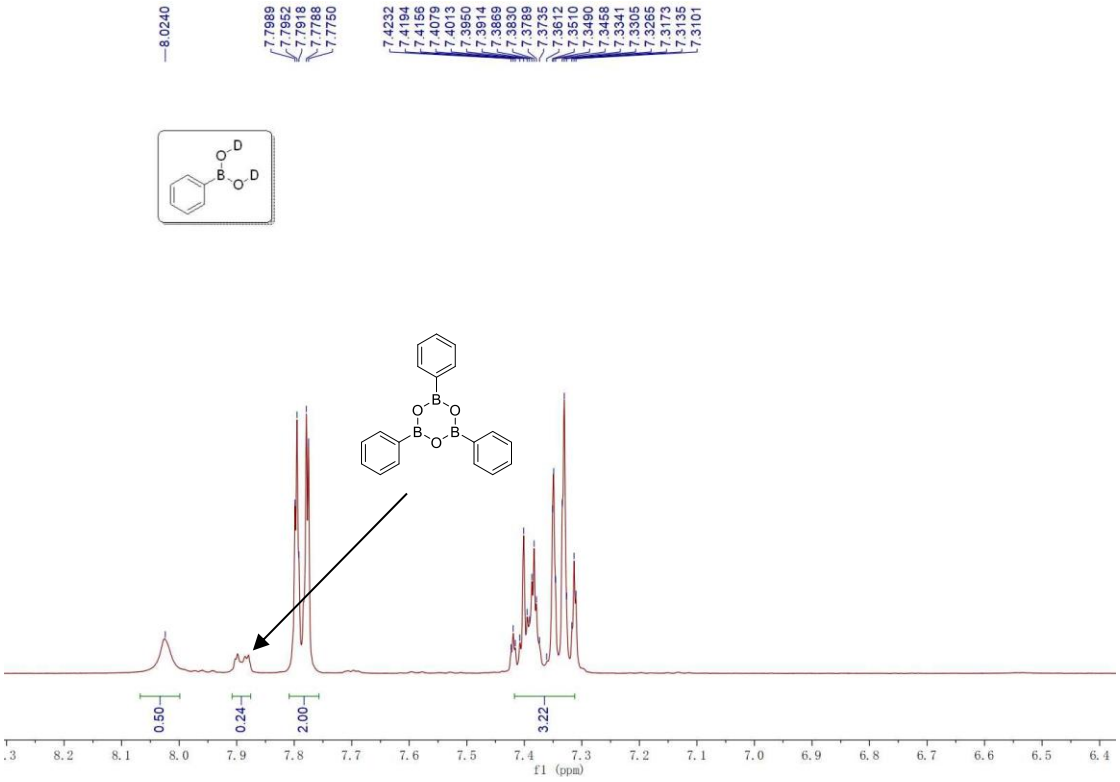
HRMS (ESI): Calcd for $C_{25}H_{30}N_3O_5S^+$ $[M+H]^+$ 484.1901, found 484.1906.

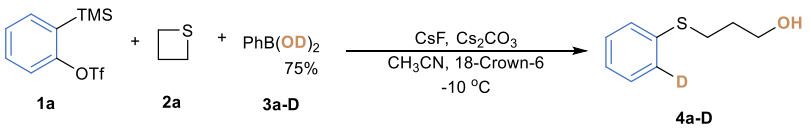
6. Mechanistic Studies

6.1 Deuterium-labeling Study



Synthesis of 3a-D[15]: A flame-dried Schlenk tube equipped with a magnetic bar was added triphenylboroxine (0.50 mmol, 156.0 mg) and D_2O (1.8 mL). The mixture was kept stirring at 75°C for 14 hours. The reaction was then filtered while it was still hot in order to remove excess amount of triphenylboroxines. The filtrate was cooled to room temperature, and a white solid was crashed out of the solution. The obtained solid was dried under vacuum to give **3a-D** (73.0 mg, 40% yield, 75% D) as a white solid, containing with 4% triphenylboroxine. ^{1}H NMR (400 MHz, DMSO-d_6) 8.02 (s, 0.5H), 7.92-7.73 (m, 2H), 7.44-7.24 (m, 3H).





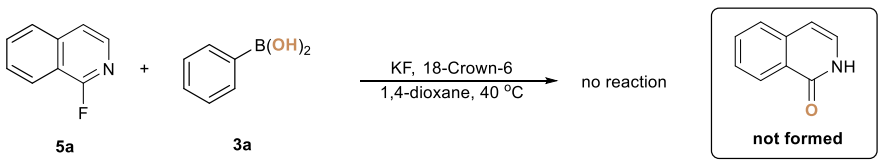
To a suspension of CsF (0.6 mmol, 92 mg, 3.0 equiv.), Cs_2CO_3 (0.4 mmol, 130 mg, 2.0 equiv.), 18-crown-6 (0.4 mmol, 106 mg, 2.0 equiv.) and **3a-D** (0.3 mmol, 36 mg, 1.5 equiv.) in anhydrous CH_3CN (2 mL) was added aryne precursor (0.2 mmol, 49 µL, 1.0 equiv.) and thietane (0.4 mmol, 32 µL, 2.0 equiv.) dropwise at -10°C. The mixture was then kept stirring for 12 hours at -10°C. After complete consumption of aryne precursors indicated by TLC, the reaction was quenched with 1 M NaOH (2 mL) and extracted with DCM (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was further purified by silica gel flash chromatography (PE:EA = 4:1) to afford **4a-D** as a pale yellow oil (29.0 mg, 85% yield, 68% D).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 1.34H), 7.28 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 3.75 (t, J = 7.2 Hz, 2H), 3.03 (t, J = 7.1 Hz, 2H), 1.92-1.84 (m, 2H), 1.70 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.24, 129.23, 128.94, 128.83, 126.02, 61.44, 31.70, 30.27.

HRMS (EI): Calcd for $C_9H_{12}OS$ $[M]^{\cdot+}$ 169.0666; found 169.0671.

6.2 Control Experiment



A mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.), phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) and 1-fluoroisoquinoline in anhydrous 1,4-dioxane (2 mL) was kept stirring at 40°C for 24 hours. The analysis of the reaction mixture suggested that isoquinolin-1(*2H*)-one was not formed.

This experiment indicated the reaction was initiated through the nucleophilic addition of aryne with 1-fluoroisoquinoline.

6.3 Spectroscopic Studies

^{11}B NMR Studies:

a) The ^{11}B NMR of boronic acid was recorded.

b) A mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.) and phenylboronic acid (0.3 mmol, 36.6 mg, 3.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was stirred at 40°C for 24 hours. The reaction mixture was concentrated *in vacuo* and detected by ^{11}B NMR. A new signal was observed at 5.0 ppm.

c) A suspension of CsF (0.6 mmol, 91.1 mg, 3.0 equiv.), Cs_2CO_3 (0.4 mmol, 130.3 mg, 2.0 equiv.), 18-crown-6 (0.4 mmol, 105.6 mg, 2.0 equiv.) and phenylboronic acid (0.3 mmol, 36.6 mg, 1.5 equiv.) in anhydrous CH_3CN (2 mL) was stirred at -10°C for 12 hours. The reaction mixture was concentrated *in vacuo* and detected by ^{11}B NMR. A new signal was observed at 5.0 ppm.

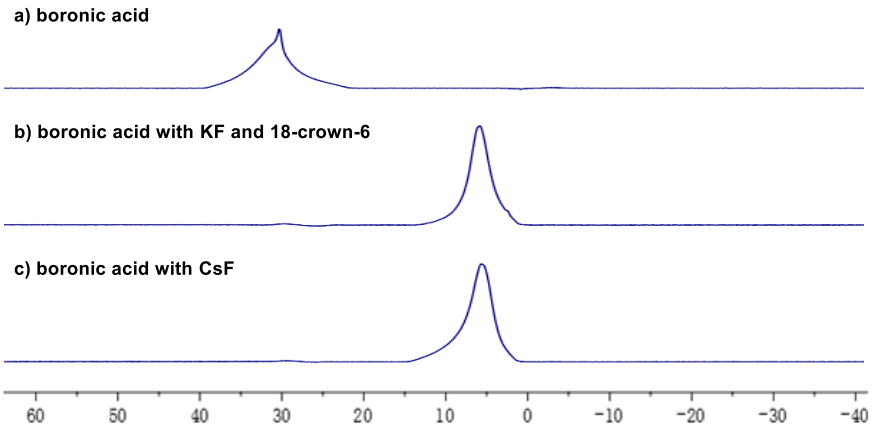
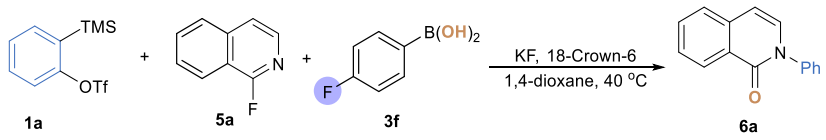


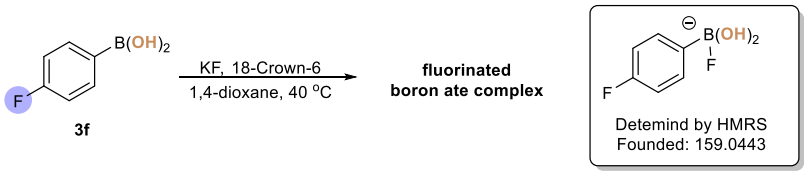
Figure S2. ^{11}B NMR spectrum of boronic acid with fluoride

These new peaks at 5.0 ppm should indicate the formation of fluorinated boronate complex.

^{19}F NMR Studies:



Standard Condition Experiment (I): To a mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.), 4-fluorophenylboronic acid (**3f**, 0.3 mmol, 41.7 mg, 3.0 equiv.) and 1-fluoroisoquinoline (0.2 mmol, 29.4 mg, 1.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was added aryne precursor (0.6 mmol, 147 μL, 3.0 equiv.) dropwise. The reaction mixture was kept stirring at 40°C. A small portion of the mixture was transferred to the NMR tube and detected by ^{19}F NMR at specific time point. The results were shown as follows.



***Control Experiments (II)*:** A mixture of KF (1 mmol, 58.1 mg, 5.0 equiv.), 18-crown-6 (1 mmol, 264.3 mg, 5.0 equiv.) and 4-fluorophenylboronic acid (**3f**, 0.3 mmol, 41.7 mg, 3.0 equiv.) in anhydrous 1,4-dioxane (2 mL) was stirred at 40°C. A small portion of the mixture was transferred to a NMR tube and detected by ^{19}F NMR at specific time point shown as follows.

Specific Time Point:

a) The reaction of *Standard Condition Experiment (I)* was stirred for 24 hours.

b) The reaction of *Standard Condition Experiment (I)* was stirred for 12 hours.

c) The reaction of *Standard Condition Experiment (I)* was stirred for 2 hours.

d) The reaction of *Control Experiments (II)* was stirred for 12 hours.

e) The reaction of *Control Experiments (II)* was stirred for 24 hours.

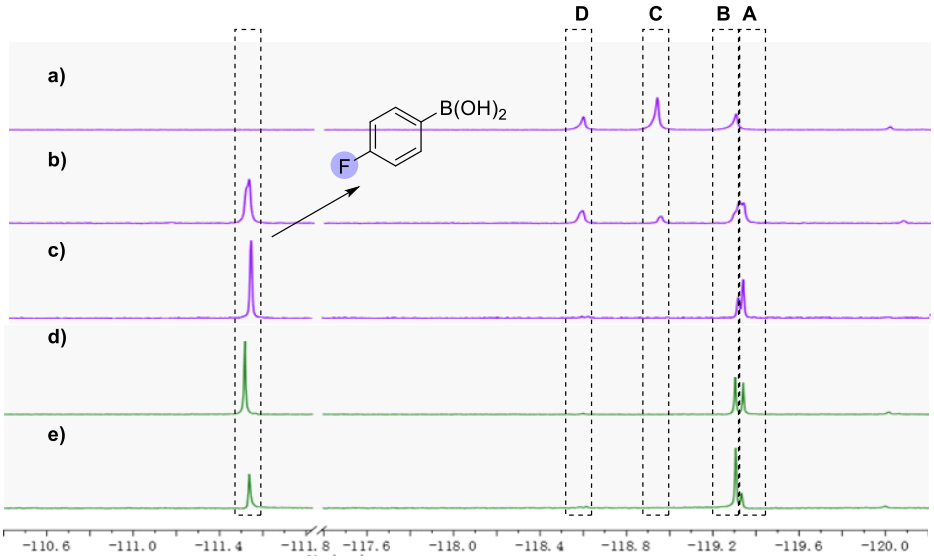


Figure S3. ^{19}F NMR spectrum of 4-fluoroboronic acid under standard condition

^{19}F NMR might indicate the formation of a series of hydroxylated/fluorinated boronate species. The peak of (trihydroxy)phenylborate (δ ≈ -120 ppm) was not observed.

f) To the NMR tube of a) was added 4-fluorophenyltrifluoroborate, and performed ^{19}F NMR experiment

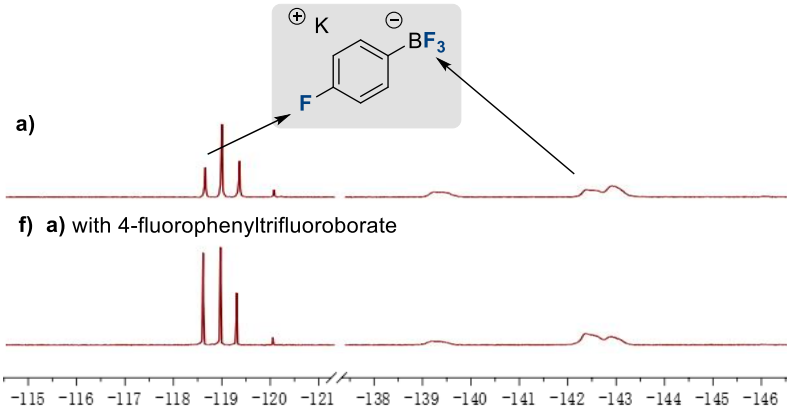


Figure S4. Evidence for the generation of 4-fluorophenyltrifluoroborate by ^{19}F NMR

*The observed intensity increase of peak **D** identified it as 4-fluorophenyl-trifluoroborate.*

6.4 Control Experiments for 4a' Formation

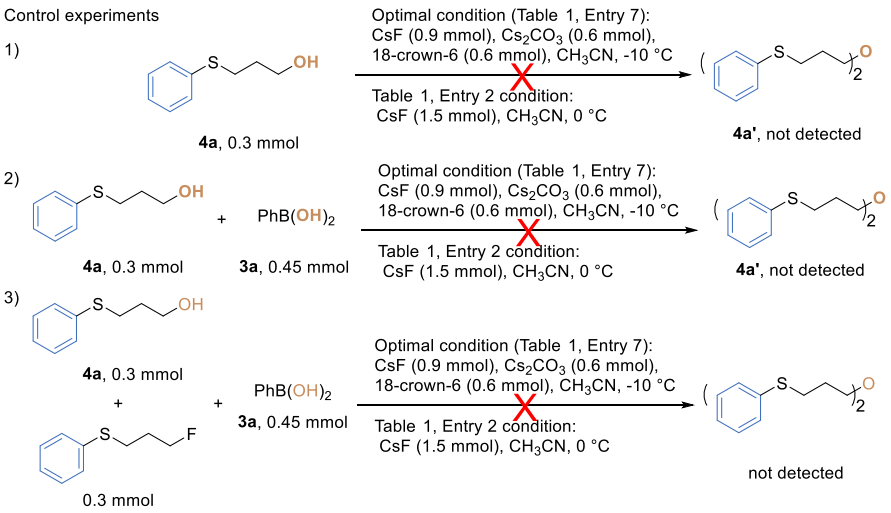


Figure S5. Mechanistic study on the formation of side product **4a'**.

*Control experiments excluded the ether formation between two molecules of **4a** or reaction of **4a** with potential alkyl fluoride. At this stage, we tend to believe that it should be formed via the ring-opening between alkoide of **4a** with cyclic sulfonium ion, which might be generated with moisture.*

7. Density Functional Theory (DFT) Calculations

Computational Methods: All DFT calculations were carried out using Gaussian 09 program.[16] All the geometry optimizations and frequency calculations in this paper were performed with B3LYP functional[17] in implicit 1,4-dioxane or acetonitrile at def2-SVP basis set[18] by using the Solvation Model based on Density (SMD)[19] with keyword in the Gaussian code route section "SCRF = (SMD, Solvent = 1,4-dioxane or acetonitrile)". The vibrational frequencies were computed at the same level of theory as for the geometry optimizations to confirm whether each optimized structure is an energy minimum or a transition state, and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections. Single-point energy calculations were also performed with M06 functional[20] based on optimized geometry using a higher level basis set def2-TZVP[18]. The Gibbs free energies presented in this paper are the M06 calculated single-point energy in 1,4-dioxane or acetonitrile solvent with B3LYP calculated thermodynamic corrections in 1,4-dioxane or acetonitrile solvent.

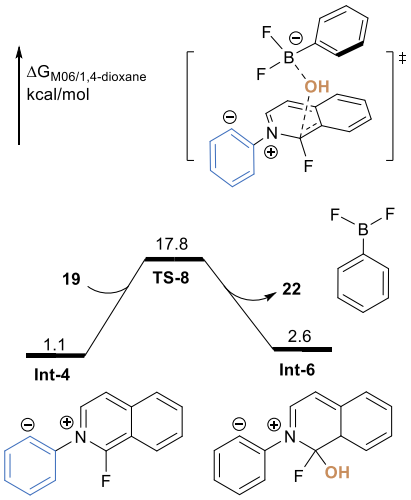


Figure S6. Free energy profiles for the electrophilic substitution of **Int-4** with **19**.

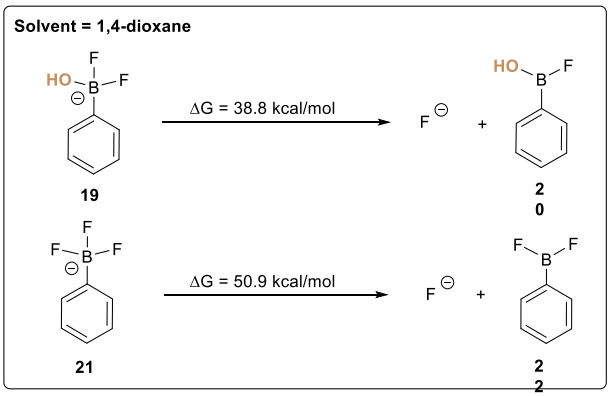


Figure S7. Calculated Gibbs free energy for the fluoride dissociation of difluoro(hydroxy)(phenyl)boronate **19** or trifluoro(phenyl)boronate **21**.

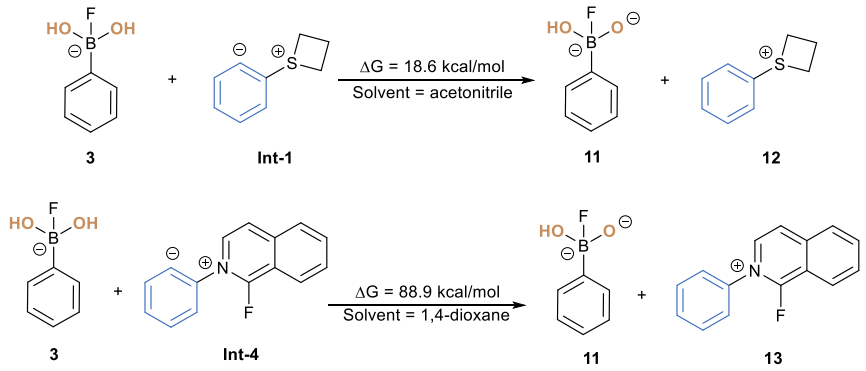


Figure S8. Calculated the relative free energy for the protonation of **Int-1** and **Int-4** using anionic species **3**.

Calculated thermal corrections, and Gibbs free energies of all structures in acetonitrile solvent

Geometry	Thermal Correction to Free Energy	Thermal Correction to Enthalpy	Electronic Energy	Gibbs Free Energy	IF
1	0.047710	0.080522	-230.814975	-230.767265	
2a	0.056092	0.088893	-516.041597	-515.985505	
TS-1	0.116912	0.170435	-746.858053	-746.741141	25.15*i*
Int-1	0.125852	0.171910	-746.887025	-746.761173	
3	0.090195	0.135467	-508.183237	-508.093042	
TS-2	0.237621	0.308624	-1255.051188	-1254.813567	451.24*i*
F-3	0.079771	0.121132	-432.209756	-432.129985	
Int-2	0.138726	0.187000	-822.895246	-822.75652	
TS-3	0.136456	0.183500	-822.894437	-822.757981	521.78*i*
Int-3	0.136918	0.187065	-822.915852	-822.778934	
F-	-0.014159	0.002360	-99.981433	-99.995592	
3a	0.091401	0.133436	-408.171377	-408.079976	
11	0.078300	0.122096	-507.631174	-507.552874	
12	0.142038	0.186528	-747.413472	-747.271434	

Calculated thermal corrections, and Gibbs free energies of all structures in 1,4-dioxane solvent

Geometry	Thermal Correction to Free Energy	Thermal Correction to Enthalpy	Electronic Energy	Gibbs Free Energy	IF
1	0.047960	0.080704	-230.811080	-230.76312	
5a	0.095890	0.136630	-501.026445	-500.930555	
TS-4	0.158718	0.218322	-731.839323	-731.680605	19.00*i*
Int-4	0.168139	0.220416	-731.859972	-731.691833	
3	0.090508	0.135483	-508.140884	-508.050376	
3a	0.091938	0.134067	-408.165835	-408.073897	
TS-5	0.280292	0.356601	-1240.000640	-1239.720348	246.26*i*
F-3	0.080377	0.121530	-432.204048	-432.123671	
Int-5	0.180552	0.235507	-807.816372	-807.63582	
TS-6	0.181064	0.234612	-807.815603	-807.634539	68.04*i*
Int-6	0.181138	0.235993	-807.882918	-807.70178	
F-	-0.014159	0.002360	-99.917634	-99.931793	
Int-7	0.294727	0.373302	-1216.085161	-1215.790434	
TS-7	0.294397	0.371267	-1216.068190	-1215.773793	142.31*i*
6a	0.182127	0.234797	-707.960269	-707.778142	
19	0.079338	0.123490	-532.196764	-532.117426	
TS-8	0.269675	0.344566	-1264.052434	-1263.782759	164.46*i*
22	0.068171	0.109088	-456.239245	-456.171074	
21	0.068218	0.111518	-556.252212	-556.183994	
11	0.077478	0.121321	-507.482222	-507.404744	
13	0.182244	0.235060	-732.378088	-732.195844	

B3LYP geometries for all the optimized compounds and transition states in acetonitrile solvent

1

C	1.46769500	-0.13368300	0.00000200
C	0.62714000	-1.23977600	0.00000200
C	-0.62741600	-1.23973300	-0.00000200
C	-1.46772900	-0.13337800	-0.00000200
C	-0.70491900	1.05887600	0.00000700
C	0.70516800	1.05877500	-0.00000700
H	2.55963000	-0.12994400	0.00000600
H	-2.55966200	-0.12957100	-0.00000600
H	-1.23477800	2.01661600	0.00000700
H	1.23518000	2.01641200	-0.00000700

2a

C	-1.34437800	0.00000200	-0.12682400
C	-0.34803700	1.15401500	0.10622400
C	-0.34803900	-1.15401700	0.10622200
H	-2.22000000	0.00000000	0.54197400
H	-1.70659500	0.00000500	-1.16598100
H	-0.39755900	1.59155900	1.11530000
H	-0.35500400	1.96367000	-0.63815900
H	-0.39755800	-1.59155700	1.11530100
H	-0.35500700	-1.96367700	-0.63815400
S	1.10465300	0.00000000	-0.05275100

TS-1

C	3.14731800	-1.17060800	0.16555600
C	1.78503800	-1.10634400	-0.21249300
C	1.40510100	0.21740700	-0.36119000
C	2.08612000	1.26193200	-0.20833300
C	3.43014700	1.28921800	0.16160600
C	3.93832600	-0.01732800	0.34589900
H	3.59928500	-2.15513200	0.32251100
H	1.16818200	-1.99535700	-0.35450400
H	4.05106100	2.17710700	0.30201200
H	4.98624400	-0.13527400	0.63896600
C	-3.56593200	0.50456800	0.89957100
C	-2.70601900	-0.77422600	0.93716300
C	-2.90870600	1.12376800	-0.34969700
H	-4.62039400	0.25871300	0.70203000
H	-3.52103900	1.12594000	1.80837900
H	-3.23766900	-1.72257600	1.10262500
H	-1.85009800	-0.71331600	1.62638300
H	-3.58653200	1.53978300	-1.10916100
H	-2.12451100	1.86066800	-0.12147900
S	-2.15830600	-0.51318000	-0.82414100

Int-1

C	-2.16694500	1.47377400	0.00007700
C	-0.78596200	1.15067000	-0.00000900
C	-0.57064100	-0.21965700	-0.00005100
C	-1.53315400	-1.24547600	-0.00002200
C	-2.87447600	-0.85848000	0.00004400
C	-3.18709700	0.50965500	0.00009800
H	-2.48283400	2.52788600	0.00008000
H	-1.25804500	-2.30522900	-0.00006900
H	-3.66492500	-1.61391600	0.00005400
H	-4.23776000	0.82046000	0.00014600
C	3.10542400	0.60703700	0.00009000
C	2.14402900	0.22849300	-1.14116700
C	2.14403100	0.22812200	1.14122700
H	4.00307700	-0.02731100	-0.00000900
H	3.41441400	1.66261000	0.00025600
H	2.53432600	-0.30661200	-2.01622200
H	1.46552000	1.04794900	-1.42437700
H	2.53433800	-0.30728800	2.01609100
H	1.46553600	1.04748200	1.42474200
S	1.16094300	-0.86192900	-0.00015100

3

C	2.21995500	-1.19385900	-0.01714200
C	0.81905100	-1.18578800	-0.05817900
C	0.07012100	0.00925300	-0.04389200
C	0.81390100	1.20712400	-0.00249100
C	2.21392300	1.21937900	0.03587400
C	2.92677300	0.01348000	0.03156800
H	2.76371500	-2.14432000	-0.03023500
H	0.28958800	-2.14344900	-0.11217000
H	0.27076400	2.15803900	-0.01234400
H	2.75434300	2.17142700	0.06601500
H	4.02060500	0.01514400	0.06065700
B	-1.57570200	0.02428500	-0.00854300
O	-2.06398900	1.20278500	-0.69499400
H	-2.97506000	1.34748700	-0.40718900
O	-2.11913900	0.00312700	1.35087400

H	-1.85680700	-0.81675900	1.78777200
F	-2.03399500	-1.19709300	-0.69236100

TS-2

C	3.09716800	2.27405400	0.52400000
C	2.45250800	1.23091400	-0.18835700
C	3.19253700	0.04637600	-0.19934800
C	4.44069400	-0.15614700	0.41982600
C	5.01584900	0.90838600	1.11893300
C	4.33757200	2.13411700	1.16774100
H	2.61332500	3.26047900	0.59944000
H	4.96253600	-1.11752100	0.35506900
H	5.98486000	0.78352700	1.61114200
H	4.77976200	2.97824300	1.70910100
C	0.05655200	-1.48563900	-1.73488800
C	0.38887900	-1.79082500	-0.28482300
C	1.33184900	-0.81654000	-2.24731300
H	-0.16215100	-2.41811500	-2.27624100
H	-0.82057700	-0.82703400	-1.81215400
H	0.52460400	-2.80878200	0.07029100
H	0.44739400	-0.98778800	0.44975300
H	1.61707000	-1.04313000	-3.28389300
H	1.32579600	0.27186000	-2.06180000
S	2.56392300	-1.46534600	-1.04441900
C	-4.83510200	1.25141000	-0.68183900
C	-4.24949500	0.24541600	0.09857000
C	-2.87334300	0.23730400	0.40287900
C	-2.10814800	1.30501600	-0.11274200
C	-2.67949400	2.31902400	-0.89177000
C	-4.04939600	2.29547300	-1.18221300
H	-5.90809100	1.22352700	-0.89714100
H	-4.88435100	-0.55571800	0.49100800
H	-1.03523200	1.34844900	0.10131500
H	-2.05485500	3.13298800	-1.27342600
H	-4.49998300	3.08551400	-1.79032800
B	-2.19817800	-0.96153700	1.28259100
O	-1.16641200	-0.44552100	2.14335900
H	-0.78496800	-1.17180800	2.65567100
O	-1.58631300	-2.03745800	0.40269900
H	-2.18168700	-2.29004600	-0.31820100
F	-3.22725800	-1.63751400	2.03863800

F-3

C	-1.94519000	1.20056500	0.00021100
C	-0.54757300	1.20074300	0.00005000
C	0.18015100	-0.00634000	-0.00004400
C	-0.54145000	-1.21751100	-0.00017300
C	-1.93853800	-1.22388300	-0.00017600
C	-2.64238400	-0.01320000	0.00006700
H	-2.49328000	2.14670100	0.00042100
H	-0.01145900	2.15389900	0.00010100
H	0.00060500	-2.16714200	-0.00030200
H	-2.48224300	-2.17256900	-0.00034000
H	-3.73604000	-0.01608200	0.00012700
B	1.74043000	0.00016200	-0.00005300
O	2.45215200	-1.14723900	0.00035000
H	3.41376300	-1.00775000	0.00054600
F	2.39991000	1.17753300	-0.00030000

Int-2

C	-1.91226000	1.60857200	0.17007700
C	-0.70589900	0.90373800	-0.04958200
C	-0.86698200	-0.49558100	-0.14474600
C	-2.11297100	-1.14735000	-0.05436900
C	-3.27760300	-0.39235900	0.12878600
C	-3.17635900	0.99848400	0.24769900
H	-1.88542600	2.70582300	0.26567400
H	-2.17392600	-2.23927600	-0.11600400
H	-4.25015300	-0.89056400	0.19350000
H	-4.07866900	1.60187700	0.39983200
C	2.95479000	-0.16099400	0.31467000
C	2.62245600	1.33597500	0.20909200
C	1.82507900	-1.09341300	0.76749400
H	3.35525300	-0.50978100	-0.65429400
H	3.77409900	-0.27212700	1.05172200
H	2.22089900	1.65824800	1.20222100
H	3.58482400	1.87913900	0.09484200
H	2.25977500	-2.05402400	1.08859400
H	1.29495800	-0.67659800	1.63940900
S	0.54905500	-1.59052600	-0.46961800
O	1.77767300	1.68273100	-0.83309400
H	0.79059000	1.44141200	-0.52157600

TS-3

C	-1.88971000	1.60278600	0.12325800
C	-0.69438000	0.88740700	-0.10608800
C	-0.84510500	-0.51436500	-0.15746300
C	-2.08791000	-1.16186300	-0.01712600

C	-3.24783400	-0.40229200	0.17613700
C	-3.14816600	0.99162100	0.25365800
H	-1.85568300	2.70133200	0.18429900
H	-2.14880600	-2.25476000	-0.04921900
H	-4.21727200	-0.89977000	0.27963600
H	-4.04781200	1.59636900	0.41360200
C	2.93857200	-0.11293200	0.32013900
C	2.53509000	1.37195100	0.23862800
C	1.85150500	-1.10626000	0.74547600
H	3.35895100	-0.42086600	-0.65447500
H	3.75661500	-0.20684200	1.06169500
H	2.09254500	1.63852400	1.23704300
H	3.48220200	1.95921300	0.18877900
H	2.32427800	-2.06529900	1.01362800
H	1.32411700	-0.75093800	1.64618300
S	0.56988600	-1.60294900	-0.48699000
O	1.71133900	1.70035800	-0.81126400
H	0.64960600	1.41103600	-0.49893300

Int-3

C	-2.56015100	1.66234800	0.17757800
C	-1.31874400	1.01483100	0.17278600
C	-1.24948500	-0.37841400	-0.00856600
C	-2.44769100	-1.10165500	-0.18531300
C	-3.67912900	-0.44528000	-0.18145400
C	-3.74512400	0.94249700	0.00107100
H	-2.59381800	2.74626500	0.32088200
H	-2.41153900	-2.18607200	-0.32584700
H	-4.59618600	-1.02474000	-0.32115000
H	-4.71060500	1.45474000	0.00589000
C	2.96233200	-0.69774500	0.19267800
C	4.03990600	0.44841100	0.17916800
C	1.57635400	-0.07572100	0.30221300
H	3.03700800	-1.24124500	-0.76825200
H	3.14893500	-1.42469400	1.00680100
H	4.06981600	0.80100400	1.28668900
H	5.03847300	-0.12949000	0.11573400
H	1.41396000	0.35096800	1.30681300
H	1.54657000	0.74111100	-0.43631700
S	0.26675800	-1.30883200	-0.03807200
O	3.84119400	1.37945800	-0.72378300
H	-0.40989900	1.60218800	0.30720900

3a

C	-1.95259900	-1.21096100	0.00090600
C	-0.55443800	-1.20637900	0.00082100
C	0.17416300	0.00006500	0.00000000
C	-0.55449800	1.20642100	-0.00081900
C	-1.95269000	1.21092100	-0.00090300
C	-2.65515300	-0.00002800	0.00000200
H	-2.49749500	-2.15928400	0.00166700
H	-0.01460800	-2.15736500	0.00147900
H	-0.01476300	2.15746500	-0.00147900
H	-2.49759800	2.15923500	-0.00166400
H	-3.74891700	-0.00008300	0.00000400
B	1.74902400	0.00002800	0.00001000
O	2.39244400	1.20634600	0.00179500
H	3.36058700	1.15212800	0.00165300
O	2.39236200	-1.20639600	-0.00183600
H	3.36050900	-1.15206500	-0.00142200

11

C	2.21868600	-1.18065000	0.02212300
C	0.81723800	-1.19258500	-0.00735000
C	0.02998000	-0.01511900	-0.02449700
C	0.77529200	1.18895300	-0.04750200
C	2.17536600	1.22908500	-0.01816600
C	2.91364500	0.03703900	0.02140600
H	2.77638100	-2.12465300	0.03550900
H	0.30526800	-2.16359100	-0.02671500
H	0.21079400	2.12762500	-0.10671500
H	2.69980700	2.19199900	-0.03819400
H	4.00793700	0.05653800	0.04046400
B	-1.64869500	-0.00064500	0.15027800
O	-2.14186800	1.18453300	-0.67227900
H	-2.78833500	1.54493600	-0.05081500
O	-2.08917200	-0.03971700	1.42117500
F	-2.07792100	-1.24316500	-0.69690800

12

C	2.86727200	-0.88930600	-0.00004900
C	1.52128500	-1.26504000	0.00010600
C	0.54017100	-0.26305200	0.00013200
C	0.87510900	1.09847500	-0.00008500
C	2.22409100	1.45354800	-0.00013200
C	3.21627800	0.46409900	-0.00011900
H	3.64155800	-1.65990000	-0.00002000
H	0.10536200	1.87313000	-0.00005500

H	2.50136000	2.51013200	-0.00019700
H	4.27001500	0.75335300	-0.00020000
C	-3.13710100	0.57246900	-0.00031800
C	-2.18700600	0.20334300	1.15544300
C	-2.18693800	0.20229700	-1.15569400
H	-4.03288700	-0.06326600	-0.00003400
H	-3.44722300	1.62625400	-0.00082000
H	-2.57905700	-0.39995700	1.98416400
H	-1.57191900	1.03112400	1.53210600
H	-2.57888300	-0.40172600	-1.98394000
H	-1.57180000	1.02976400	-1.53298200
S	-1.14864100	-0.83989800	0.00037800
H	1.24276700	-2.32153500	0.00023200

B3LYP geometries for all the optimized compounds and transition states in 1,4-dioxane solvent

1			
C	1.46483200	-0.13375600	0.00000200
C	0.62693600	-1.23981900	0.00000100
C	-0.62705300	-1.23982100	-0.00000100
C	-1.46482900	-0.13364600	-0.00000200
C	-0.70460200	1.05919000	0.00000300
C	0.70468900	1.05914200	-0.00000300
H	2.55683600	-0.13099700	0.00000300
H	-2.55683500	-0.13081200	-0.00000300
H	-1.23401200	2.01707900	0.00000300
H	1.23417000	2.01699100	-0.00000300
5a			
C	1.36255700	-0.74622500	-0.00005000
C	-0.03059200	-0.44103100	-0.00004800
C	-0.36302500	0.95071900	0.00009400
C	0.70783100	1.89080100	0.00021800
C	2.00470400	1.43338700	0.00019700
H	-0.78207600	-2.47949300	-0.00028100
C	-1.05447600	-1.42269800	-0.00017600
C	-1.73642500	1.31651000	0.00010500
H	0.49687800	2.96246500	0.00032500
H	2.84748100	2.13179300	0.00028900
C	-2.71766000	0.34545900	-0.00001600
C	-2.37790000	-1.03078900	-0.00015600
H	-2.00318800	2.37640300	0.00021200
H	-3.77106200	0.63745600	-0.00000400
H	-3.17081400	-1.78270000	-0.00024700
F	1.70205500	-2.04431200	-0.00019600
N	2.32774400	0.11087000	0.00006500
TS-4			
C	-3.18451100	-0.74880500	-0.06795700
C	-3.32044700	0.62725600	-0.02235600
C	-4.35996600	1.32192600	0.07816200
C	-5.65260600	0.81286300	0.16843000
C	-5.64917100	-0.60033400	0.13218000
C	-4.46152100	-1.35189500	0.01846700
H	-2.25544200	-1.31302900	-0.15522100
H	-6.57745100	1.38784000	0.25742900
H	-6.60509200	-1.12973800	0.19551300
H	-4.52548000	-2.44443300	-0.00366400
C	0.90890500	-0.48164300	-0.14204200
C	2.32705800	-0.39999700	-0.03173000
C	2.87034700	0.92344900	0.00991100
C	1.96266900	2.01977400	-0.06127000
C	0.61372000	1.77241500	-0.16478400
H	2.74807700	-2.53072900	0.00167600
C	3.18195000	-1.52997800	0.03523400
C	4.27976600	1.06990000	0.12099100
H	2.33776000	3.04513900	-0.03225400
H	-0.11084100	2.59028700	-0.21887500
C	5.09452900	-0.04257400	0.18577200
C	4.54593500	-1.34919500	0.14261800
H	4.70720700	2.07516200	0.15393300
H	6.17717200	0.08153100	0.27108700
H	5.21020500	-2.21518900	0.19508500
F	0.36734900	-1.71273200	-0.18256600
N	0.09254200	0.51554000	-0.20448200
Int-4			
C	-2.54663200	-0.96949400	0.64377400
C	-1.99500700	0.16438100	0.01989400
C	-2.68042100	1.18553000	-0.63190200
C	-4.07809500	0.96040600	-0.66706400
C	-4.69826700	-0.15069700	-0.08335600
C	-3.93054200	-1.11799000	0.58478600
H	-1.94290200	-1.71065200	1.17364900
H	-4.73147900	1.69078300	-1.16720100
H	-5.78677400	-0.26832500	-0.13261700
H	-4.40783300	-1.97836800	1.06163400
C	0.38056700	-0.61604500	-0.07356800
C	1.78083400	-0.40898200	-0.06196800
C	2.24669200	0.92779600	0.14072400
C	1.26923200	1.95104800	0.30443800
C	-0.06141300	1.65069200	0.26842700
H	2.33018400	-2.48732200	-0.40802800
C	2.70183500	-1.47396200	-0.24951200
C	3.64481600	1.15899400	0.16151100
H	1.57655600	2.98633400	0.46246900
H	-0.88074700	2.36956300	0.31979400
C	4.52649300	0.11018000	-0.01741300
C	4.05574600	-1.21011200	-0.22508000
H	4.01174900	2.17606100	0.31685800

H	5.60279000	0.29862900	-0.00107300
H	4.77172900	-2.02297600	-0.36510600
F	-0.07404200	-1.83344900	-0.28857400
N	-0.51027400	0.35383600	0.09351900

3

C	2.21942800	-1.19354600	-0.01335300
C	0.81974900	-1.18538700	-0.06075300
C	0.07107500	0.00840600	-0.04750200
C	0.81387500	1.20494300	-0.00412400
C	2.21271500	1.21716400	0.03713800
C	2.92685000	0.01271200	0.03736800
H	2.76328700	-2.14495700	-0.02469900
H	0.28654600	-2.14067000	-0.12267400
H	0.26291500	2.15071600	-0.01690300
H	2.75265800	2.17047200	0.06589600
H	4.02127600	0.01460400	0.06989900
B	-1.57645800	0.02311400	-0.01684600
O	-2.05887000	1.24192000	-0.63458200
H	-2.95978600	1.36359600	-0.30990800
O	-2.11153800	-0.05731600	1.35042700
H	-1.94482500	-0.94790500	1.68061200
F	-2.03540700	-1.16044500	-0.74193300

3a

C	-1.96091000	1.19849100	-0.00026600
C	-0.56383400	1.20589900	-0.00036400
C	0.18040100	0.01059000	0.00001300
C	-0.53722000	-1.20230000	0.00008300
C	-1.93369600	-1.22056600	0.00030600
C	-2.64929600	-0.01854200	0.00012600
H	-2.51372900	2.14180400	-0.00050100
H	-0.05432600	2.17623500	-0.00081300
H	0.01509300	-2.14538600	0.00016600
H	-2.46819400	-2.17454800	0.00049200
H	-3.74279500	-0.02982300	0.00020200
B	1.75555300	-0.00255500	0.00001200
O	2.39474600	-1.20797700	-0.00044900
H	3.35691200	-1.10541500	-0.00055400
O	2.52892100	1.12753700	0.00050700
H	2.02726300	1.95199200	0.00109900

TS-5

C	-4.26653700	-0.42108400	0.06048000
C	-2.90972400	-0.76713000	-0.02679700
C	-2.39782200	-2.04073100	-0.32573900
C	-3.29872500	-3.06118400	-0.64180600
C	-4.67186400	-2.78880300	-0.61394900
C	-5.11896200	-1.51109900	-0.24504500
H	-2.92831200	-4.06232900	-0.88301200
H	-5.38871600	-3.58196900	-0.86194200
H	-6.21210000	-1.36878400	-0.20188000
C	-0.92127600	0.63789500	-0.58760900
C	-0.31539100	1.97510000	-0.46011300
C	-0.59620800	2.76075800	0.68568300
C	-1.53288000	2.25349700	1.64534400
C	-2.18222800	1.08924700	1.38784600
H	0.73061600	1.84219300	-2.34777800
C	0.53706200	2.45968500	-1.46884000
C	0.03217200	4.02535400	0.79725700
H	-1.76056300	2.81619600	2.55142900
H	-2.97453000	0.69076800	2.01893600
C	0.88200400	4.48813300	-0.19587900
C	1.13338800	3.70813600	-1.34175400
H	-0.17178700	4.63864600	1.67925600
H	1.35629300	5.46827900	-0.09228300
H	1.79826100	4.08033200	-2.12515900
F	-1.18894500	0.28496000	-1.87294400
N	-1.93900800	0.31794300	0.26767500
C	4.62301200	-2.80997400	0.22099000
C	3.32440900	-2.49171800	0.63455700
C	2.73455700	-1.24924800	0.33741400
C	3.50872400	-0.33714700	-0.40676600
C	4.80876300	-0.64137400	-0.82434500
C	5.37240400	-1.88321700	-0.51072200
H	5.05261300	-3.78573700	0.46939400
H	2.74532800	-3.22417200	1.20468000
H	3.08255000	0.63637800	-0.67367100
H	5.38417200	0.08945600	-1.40151300
H	6.38769100	-2.12745900	-0.83741900
B	1.24431500	-0.88200300	0.87636900
O	0.42566700	-0.43808900	-0.44683800
H	0.25284500	-1.19717600	-1.02696100
O	1.15025200	0.18359600	1.80485100
H	1.88476600	0.79874800	1.71081300
F	0.56302100	-2.01827900	1.34427400
H	-1.33093700	-2.26372000	-0.26578200

F-3

C	-1.94495800	-1.19977800	-0.00001900
C	-0.54837700	-1.20098500	-0.00003800
C	0.17906200	0.00531100	-0.00011700
C	-0.54074700	1.21652400	-0.00004400
C	-1.93678900	1.22341900	0.00005100
C	-2.64057900	0.01381900	0.00005200
H	-2.49393000	-2.14530600	0.00004700
H	-0.01040900	-2.15295400	-0.00002100
H	0.00462900	2.16398200	-0.00003700
H	-2.48014200	2.17221800	0.00010300
H	-3.73420200	0.01738000	0.00014200
B	1.73699600	-0.00236900	-0.00019400
O	2.45052700	1.14694300	0.00003900
H	3.40778600	1.00081700	0.00018600
F	2.40126800	-1.17441100	0.00010300

Int-5

C	2.59857700	-0.82774500	0.56708800
C	1.99260000	0.32481900	0.01838400
C	2.68142300	1.34545100	-0.66788300
C	4.06164000	1.07532400	-0.81007100
C	4.70010700	-0.09586700	-0.36450900
C	3.96389400	-1.04915500	0.34350900
H	2.03396400	-1.52263600	1.19562500
H	4.70478600	1.81676300	-1.31517400
H	5.77013800	-0.25668400	-0.54824400
H	4.44405900	-1.94625000	0.74757500
C	-0.32227100	-0.66821000	0.12954500
C	-1.77552400	-0.32822200	-0.09148300
C	-2.25071700	0.98002700	0.17208800
C	-1.29312900	2.00892200	0.48451200
C	0.03768000	1.72216400	0.43316100
H	-2.26963300	-2.33301200	-0.69834800
C	-2.66308400	-1.33671600	-0.48805500
C	-3.64048200	1.22051600	0.05468400
H	-1.62224300	3.02905700	0.68865400
H	0.81294100	2.48344600	0.53035000
C	-4.51482800	0.20828100	-0.32347900
C	-4.02868400	-1.07863400	-0.60524000
H	-4.01873000	2.22736200	0.25533000
H	-5.58530400	0.41884100	-0.40836600
H	-4.71417100	-1.87461600	-0.90812100
F	-0.26865100	-1.31088500	1.43424500
N	0.54485700	0.47464900	0.19422000
O	0.08822000	-1.61283600	-0.77480500
H	1.05908300	-1.66989700	-0.72209300

TS-6

C	2.65246200	-0.48076500	0.95845000
C	1.98511400	0.32171500	0.00708400
C	2.58615600	0.95907200	-1.09726800
C	3.98255400	0.70223000	-1.16443200
C	4.69344400	-0.09930000	-0.26022900
C	4.02325500	-0.69888000	0.81537700
H	2.10142500	-0.92586400	1.79080200
H	4.57135200	1.15038300	-1.98338400
H	5.77216300	-0.26094300	-0.38544400
H	4.56160500	-1.32066900	1.53783800
C	-0.30644700	-0.65170400	0.03872400
C	-1.77624200	-0.32962400	-0.08553300
C	-2.25836100	0.97415400	0.18810700
C	-1.30761400	2.02136700	0.46504000
C	0.02492400	1.73844000	0.41854800
H	-2.26839600	-2.34714700	-0.65369200
C	-2.66614500	-1.35406000	-0.43357700
C	-3.65558300	1.19393200	0.12427300
H	-1.64376500	3.04198200	0.65313500
H	0.78539800	2.51291900	0.53272300
C	-4.53062300	0.16654800	-0.20819000
C	-4.03878000	-1.11702400	-0.49557900
H	-4.04013400	2.19670400	0.33332700
H	-5.60642000	0.36202200	-0.25163000
H	-4.72488000	-1.92521600	-0.76260700
F	-0.18665300	-1.45267300	1.24077000
N	0.53674500	0.49288000	0.20764700
O	0.11345300	-1.45846000	-0.98964900
H	1.05801100	-1.26920600	-1.13911500

Int-6

C	-2.72623300	1.24971600	-0.56231700
C	-1.93380000	0.25880500	0.05747300
C	-2.56912200	-0.93262000	0.47797500
C	-3.93668000	-1.10813700	0.28427500
C	-4.72147900	-0.11119200	-0.31222200
C	-4.10157300	1.06815500	-0.73185900
H	-2.25437300	2.15720300	-0.94492200
H	-4.40386300	-2.03914300	0.62064400

H	-5.79645800	-0.25589800	-0.45124100
H	-4.68785700	1.85406500	-1.21840700
C	0.38469000	-0.79488900	0.34636800
C	1.81202600	-0.35935200	-0.00693600
C	2.25593700	0.97287000	0.17794500
C	1.27771100	1.98852600	0.50328700
C	-0.05318000	1.69415800	0.49080000
H	2.36636800	-2.36539800	-0.52661200
C	2.73154000	-1.34591900	-0.38206200
C	3.63015600	1.26205300	0.00985100
H	1.59984600	3.00407600	0.74322500
H	-0.79016900	2.47202200	0.71552600
C	4.53432100	0.26790000	-0.35510400
C	4.08348600	-1.04463400	-0.56207400
H	3.97688900	2.28957600	0.16225000
H	5.59336900	0.51288700	-0.48375500
H	4.78701000	-1.82909800	-0.85693800
F	-0.05952700	-1.53327500	-0.89825600
N	-0.55849800	0.44926500	0.24365500
O	0.25003500	-1.48150800	1.37999700
H	-1.95261400	-1.68625900	0.96658400

Int-7

C	-3.05843300	2.71762300	-1.08954500
C	-2.36143500	1.98581900	-0.11202000
C	-1.40921300	2.65270100	0.68249500
C	-1.16583900	4.01212300	0.49302400
C	-1.87106700	4.73994500	-0.47371600
C	-2.82301600	4.08520100	-1.25875600
H	-3.77518400	2.20356900	-1.73430200
H	-0.42176700	4.51253800	1.11929000
H	-1.67685000	5.80686700	-0.61312100
H	-3.37695700	4.63548300	-2.02499100
C	-1.50774800	-0.33297500	0.36337100
C	-1.94715100	-1.77284300	0.08532200
C	-3.31233800	-2.15059900	0.09855600
C	-4.31483100	-1.11421500	0.21364800
C	-3.94502300	0.19211800	0.16130300
H	0.08161200	-2.43441600	-0.14238600
C	-0.96348500	-2.74701900	-0.11304300
C	-3.64292500	-3.51485600	-0.05485300
H	-5.37207200	-1.37389300	0.29239100
H	-4.69365400	0.98854800	0.18515800
C	-2.65116800	-4.47679600	-0.22981700
C	-1.30370200	-4.09305400	-0.26740700
H	-4.69720700	-3.80914800	-0.04451100
H	-2.92662000	-5.52949200	-0.34587100
H	-0.51987100	-4.84158900	-0.41286500
N	-2.64004100	0.61296600	0.08052300
O	-0.38482900	0.04166100	-0.13345500
H	-0.89141800	2.09369100	1.45956000
C	6.33941600	-0.88299700	-0.99591900
C	4.94201500	-0.83976200	-1.01710500
C	4.21582000	-0.07594500	-0.08387800
C	4.94946900	0.64768700	0.87534700
C	6.34678600	0.61310200	0.90483500
C	7.04650600	-0.15469800	-0.03277700
H	6.88113600	-1.48578000	-1.73138300
H	4.39222500	-1.41040000	-1.77085800
H	4.40425300	1.24741100	1.60964000
H	6.89423900	1.18479500	1.66060600
H	8.14017600	-0.18566000	-0.01264900
B	2.62962700	-0.03500900	-0.10424500
O	1.96630900	-0.72304100	-1.08207200
H	0.99201500	-0.58878000	-0.95053900
F	-1.43664200	-0.29153300	1.85859600
O	1.97548400	0.67838400	0.85199500
H	0.99634900	0.57494000	0.70089900

TS-7

C	-4.27124500	-0.99097000	-0.35474600
C	-2.87195900	-0.92792400	-0.25961200
C	-2.13596400	-2.11219700	-0.08445100
C	-2.80521100	-3.33328000	-0.00313700
C	-4.20026000	-3.40049200	-0.10970900
C	-4.92979600	-2.22324000	-0.29161700
H	-4.84627400	-0.06776800	-0.46116200
H	-2.22232200	-4.24823100	0.13783600
H	-4.71387200	-4.36413000	-0.04822600
H	-6.02063000	-2.25641000	-0.36788200
C	-1.11744900	0.62682900	0.54074300
C	-0.68158200	2.06620400	0.47627800
C	-1.08241700	2.91985200	-0.58076300
C	-1.99109300	2.39756800	-1.57483200
C	-2.51397500	1.15504500	-1.42238100
H	0.45495000	1.87818600	2.28314600
C	0.15591700	2.55799500	1.48436300
C	-0.60299400	4.24749600	-0.60459700

H	-2.27128400	3.00031200	-2.44066500
H	-3.21905100	0.74349800	-2.14767800
C	0.24072600	4.71928900	0.39693400
C	0.62037400	3.87290000	1.44965100
H	-0.90800300	4.90718000	-1.42305400
H	0.60537000	5.75045800	0.36267100
H	1.28434700	4.23930800	2.23764200
N	-2.21150500	0.32628600	-0.36513300
O	-1.05758300	-0.01746900	1.60537800
H	-1.04951400	-2.05621400	-0.02759100
C	4.52237100	0.11529200	-1.39497100
C	3.33368100	-0.11316100	-0.69569500
C	3.18054900	-1.24753700	0.12600100
C	4.25973600	-2.14755500	0.20829400
C	5.45718400	-1.91851900	-0.48030400
C	5.59089900	-0.78299200	-1.28484000
H	4.61765600	0.99946200	-2.03311900
H	2.47991100	0.56192100	-0.79577300
H	4.16849000	-3.04453000	0.83101400
H	6.28611500	-2.62782900	-0.39045900
H	6.52288400	-0.60082200	-1.82890400
B	1.81684800	-1.49209300	0.91389800
O	1.47180300	-0.69338500	1.94819900
H	0.48608600	-0.55919200	1.98734000
O	1.10638100	-2.65716600	0.66164200
H	1.41828900	-3.07576800	-0.14997400
F	0.24593000	0.00639900	-0.52268100

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C	-2.53945500	-0.80136500	0.87646200
C	-1.92109000	0.14193100	0.04593500
C	-2.69013200	0.90699700	-0.83954500
C	-4.07712700	0.73966300	-0.88346000
C	-4.69690000	-0.19975500	-0.05612800
C	-3.92368600	-0.96968900	0.81951700
H	-1.93701300	-1.40029200	1.55975300
H	-4.67148400	1.34068300	-1.57635600
H	-5.78065500	-0.33548600	-0.09463500
H	-4.40235200	-1.70716500	1.46883100
C	0.36425200	-0.74764700	-0.12074500
C	1.80735500	-0.42882200	-0.07995500
C	2.27052200	0.89043300	0.16541700
C	1.29701700	1.92857900	0.38316000
C	-0.02441300	1.62794400	0.34932200
H	2.34127700	-2.47302200	-0.48280700
C	2.72977800	-1.47027700	-0.29601600
C	3.66408900	1.12696600	0.18942500
H	1.61315600	2.95197500	0.58993600
H	-0.79544900	2.37796400	0.52914600
C	4.56004400	0.08884200	-0.02502700
C	4.09464300	-1.21707400	-0.26949600
H	4.02808400	2.14022000	0.37908900
H	5.63505200	0.28728800	-0.00425400
H	4.80685200	-2.02863300	-0.43747900
N	-0.49911100	0.34818500	0.10763300
O	-0.07907500	-1.86448700	-0.34200500
H	-2.20046700	1.62473100	-1.50181100

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C	-2.20984000	-1.19982900	-0.02514400
C	-0.80986800	-1.18752400	-0.04579600
C	-0.07070600	0.00967600	-0.02549400
C	-0.81365600	1.20570100	0.00456800
C	-2.21304200	1.21215900	0.02172800
C	-2.92110800	0.00443700	0.00962500
H	-2.75023300	-2.15286300	-0.04053100
H	-0.26381500	-2.13504200	-0.08667600
H	-0.27386500	2.15829300	0.00315500
H	-2.75714700	2.16295300	0.04162700
H	-4.01586100	0.00258200	0.02319000
B	1.56478200	0.00852000	-0.00950600
O	2.06439600	1.05949500	-0.86528400
H	3.02790700	1.04934700	-0.79761000
F	2.04923900	0.18254100	1.33636000
F	2.05334500	-1.27938100	-0.42639000

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C	-1.92511000	-1.21279800	0.00008500
C	-0.52958100	-1.21165200	-0.00009500
C	0.19155000	-0.00060500	-0.00003400
C	-0.52877600	1.21092800	0.00003200
C	-1.92438000	1.21302300	-0.00007500
C	-2.62267100	0.00038000	0.00003000
H	-2.47267200	-2.15885500	0.00011500
H	0.01137200	-2.16178200	-0.00006700
H	0.01286300	2.16063500	-0.00007100
H	-2.47127100	2.15947600	-0.00007100
H	-3.71621200	0.00075300	0.00007800

B	1.73915300	-0.00025000	0.00001600
F	2.44215800	1.12754800	0.00004800
F	2.44383800	-1.12695100	-0.00001700

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C	-2.19947300	-1.20657700	0.00266700
C	-0.80004800	-1.19743400	-0.01757600
C	-0.06049100	0.00010300	-0.02238500
C	-0.80017700	1.19753300	-0.01756100
C	-2.19961900	1.20651500	0.00269400
C	-2.90834500	-0.00007200	0.01451200
H	-2.74171200	-2.15837300	0.00495700
H	-0.25910100	-2.14909800	-0.03901400
H	-0.25934000	2.14926800	-0.03893200
H	-2.74196600	2.15825400	0.00503100
H	-4.00293300	-0.00013900	0.02871400
B	1.57311300	0.00005400	-0.00022100
F	2.08007800	1.15304700	-0.65127200
F	2.07995400	-1.15220900	-0.65273400
F	2.05645700	-0.00090400	1.33358900

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C	-4.29250200	0.31255400	-0.25219000
C	-3.06488600	-0.31717900	0.00489200
C	-2.84240500	-1.70475000	0.07765400
C	-3.90643700	-2.56570100	-0.21004700
C	-5.15645700	-2.01665000	-0.51929200
C	-5.32746800	-0.62378800	-0.50523400
H	-3.76221300	-3.64969400	-0.16636700
H	-5.99946200	-2.68099800	-0.74858600
H	-6.34676200	-0.25559800	-0.71218900
C	-0.82294700	0.59643200	-0.58482300
C	0.08098400	1.76547200	-0.49284200
C	-0.06525200	2.68688800	0.57310000
C	-1.13667800	2.49021600	1.50865000
C	-2.01666600	1.47723200	1.30196800
H	1.16628700	1.23072300	-2.28366900
C	1.07313400	1.95250700	-1.47038200
C	0.82973400	3.78196000	0.63309700
H	-1.27568900	3.17268300	2.34773300
H	-2.90219800	1.32202200	1.91688700
C	1.81159000	3.95359600	-0.33171900
C	1.93553800	3.03944600	-1.39481300
H	0.73030300	4.49874200	1.45273200
H	2.49241500	4.80719600	-0.26701900
H	2.71004000	3.17774200	-2.15302100
F	-1.19241400	0.31748400	-1.87177400
N	-1.90321600	0.56849700	0.27152700
C	4.20578800	-2.96493800	-0.51986800
C	2.90206100	-2.71660100	-0.07778100
C	2.50919800	-1.44923000	0.39006200
C	3.48568900	-0.43605400	0.40498400
C	4.79313400	-0.67331300	-0.03215000
C	5.15783600	-1.94058000	-0.49897500
H	4.48256600	-3.96177800	-0.87694000
H	2.17216200	-3.53219400	-0.08743600
H	3.21790200	0.55885000	0.77203100
H	5.53279500	0.13301400	-0.00701300
H	6.17979700	-2.13002500	-0.84092800
B	1.00145700	-1.17282300	0.88258000
O	0.13423200	-0.72729100	-0.41309100
H	-0.37079700	-1.48698300	-0.75376300
F	0.34563900	-2.32787300	1.31255100
H	-1.88741900	-2.12442600	0.40785200
F	0.86718700	-0.12977200	1.77756700

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C	2.21822900	-1.17418700	0.03164900
C	0.81881800	-1.19645900	-0.00259800
C	0.02390900	-0.02359600	-0.03862100
C	0.76251300	1.18553500	-0.06431600
C	2.16031200	1.23386100	-0.03186100
C	2.91076800	0.04753200	0.02010000
H	2.78282400	-2.11715200	0.05273000
H	0.30048300	-2.16462900	-0.02111600
H	0.17753100	2.11043100	-0.13908900
H	2.67970100	2.20237300	-0.06517600
H	4.00674700	0.07413100	0.03653200
B	-1.65356000	-0.02720700	0.13526500
O	-2.16909500	1.21168600	-0.61678700
H	-2.70306900	1.54692000	0.11689600
O	-2.03176100	-0.07852000	1.42586000
F	-2.08187400	-1.22416500	-0.73509000

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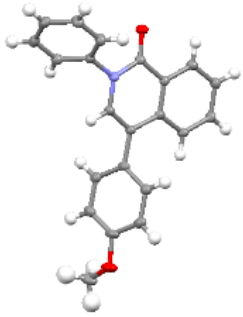
C	2.51354100	-0.63665700	1.01452400
C	1.92114900	0.16966500	0.03967000
C	2.67147300	0.78307000	-0.96664400

C	4.05315000	0.57984500	-0.99191900
C	4.66301800	-0.22640200	-0.02612400
C	3.89516500	-0.83290400	0.97294800
H	1.90753100	-1.09858900	1.79638200
H	4.65193300	1.05059700	-1.77463800
H	5.74365700	-0.38375400	-0.05195800
H	4.37229900	-1.45924800	1.72981500
C	-0.38554900	-0.59585500	-0.10734000
C	-1.78235500	-0.41977600	-0.07855000
C	-2.27508800	0.90644600	0.15773900
C	-1.32520100	1.95283000	0.34621000
C	0.01151700	1.68985800	0.30893000
H	-2.28855200	-2.50536300	-0.46338000
C	-2.67960700	-1.50333100	-0.28114800
C	-3.67466700	1.10859700	0.19117800
H	-1.66030000	2.97494300	0.53040100
H	0.78451100	2.44187300	0.46007600
C	-4.53250400	0.04192700	-0.00504800
C	-4.03681000	-1.26483000	-0.24200300
H	-4.06462800	2.11253000	0.37103800
H	-5.61219000	0.20644800	0.02144500
H	-4.73846700	-2.08750500	-0.39417300
F	0.12495800	-1.77737200	-0.34002500
N	0.48188300	0.40401700	0.08055900
H	2.18301800	1.40139600	-1.72323000

8. Crystal Data

X-ray structure of **6d**

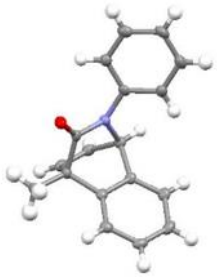


CCDC 2064724

Table S1. Crystal data and structure refinement for **6d**

Identification code	6d
Empirical formula	$C_{22}H_{17}NO_2$
Formula weight	327.37
Temperature / K	109(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	8.9864(4)
b / Å	15.1402(11)
c / Å	24.1044(11)
α/°	90.00
β/°	95.057(4)
γ/°	90.00
Volume / Å^3	3266.8(3)
Z	8
ρ_{calc} / mg mm^{-3}	1.313
μ / mm^{-1}	0.085
F(000)	1376
Crystal size / mm^3	0.30 × 0.25 × 0.23
2Θ range for data collection/°	6.36 to 52
Index ranges	$-11 \le h \le 10$, $-18 \le k \le 18$, $-26 \le l \le 29$
Reflections collected	19832
Independent reflections	6401[R(int) = 0.0420 (inf-0.9Å)]
Data/restraints/parameters	6401/0/453
Goodness-of-fit on F^2	1.042
Final R indexes [I>2σ (I)]	R_1 = 0.0465, wR_2 =0.0920
Final R indexes [all data]	R_1 = 0.0648, wR_2 = 0.1014
Largest diff. peak/hole / e Å^{-3}	0.212/-0.202

X-ray structure of **10b**



CCDC 2087612

Table S2. Crystal data and structure refinement for **10b**

Identification code	10b
Empirical formula	$C_{18}H_{15}NO$
Formula weight	261.31
Temperature / K	112.15(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	14.8247(4)
b / Å	11.5912(3)
c / Å	15.5420(4)
α/°	90.00
β/°	97.987(3)
γ/°	90.00
Volume / $Å^3$	2644.75(11)
Z	8
ρ_{calc} / mg mm^{-3}	1.313
μ / mm^{-1}	0.081
F(000)	1104
Crystal size / mm^3	0.40 × 0.37 × 0.35
2Θ range for data collection/°	6.36 to 52
Index ranges	$-18 \le h \le 18$, $-14 \le k \le 13$, $-19 \le l \le 19$
Reflections collected	14473
Independent reflections	5185[R(int) = 0.0335 (inf-0.9Å)]
Data/restraints/parameters	5185/0/363
Goodness-of-fit on F^2	1.032
Final R indexes [I>2σ (I)]	R_1 = 0.0446, wR_2 =0.0980
Final R indexes [all data]	R_1 = 0.0643, wR_2 = 0.1104
Largest diff. peak/hole / e $Å^{-3}$	0.233/-0.248

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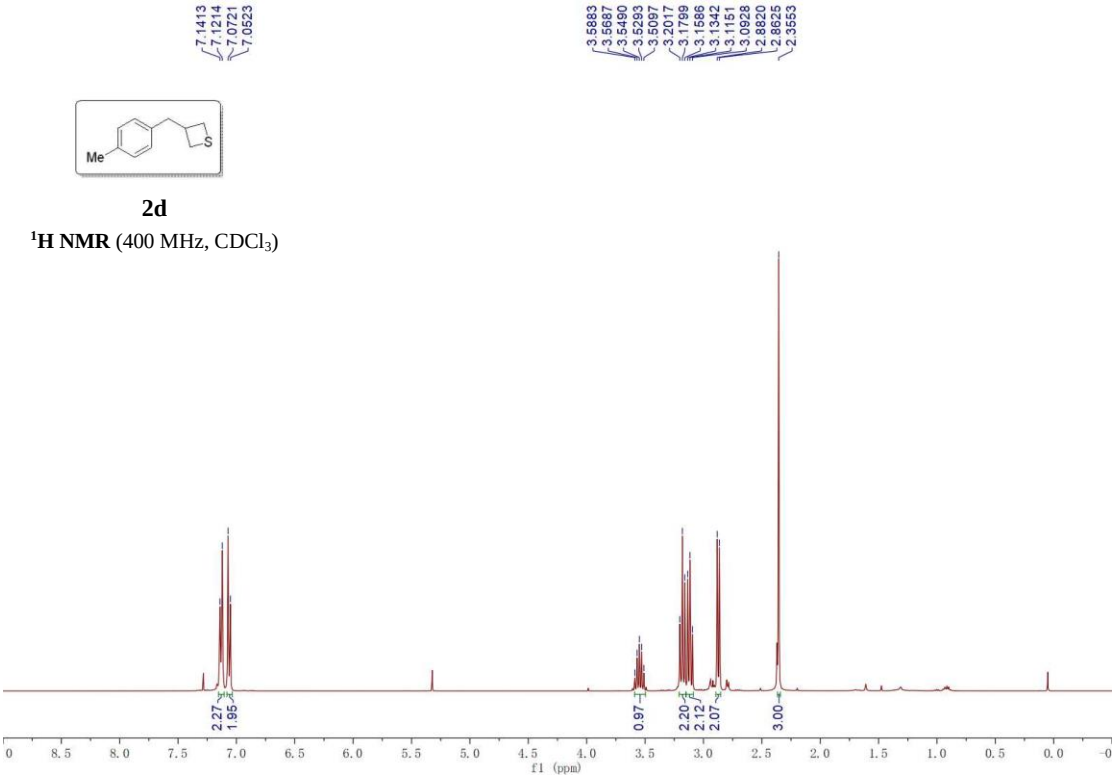
10. Spectra



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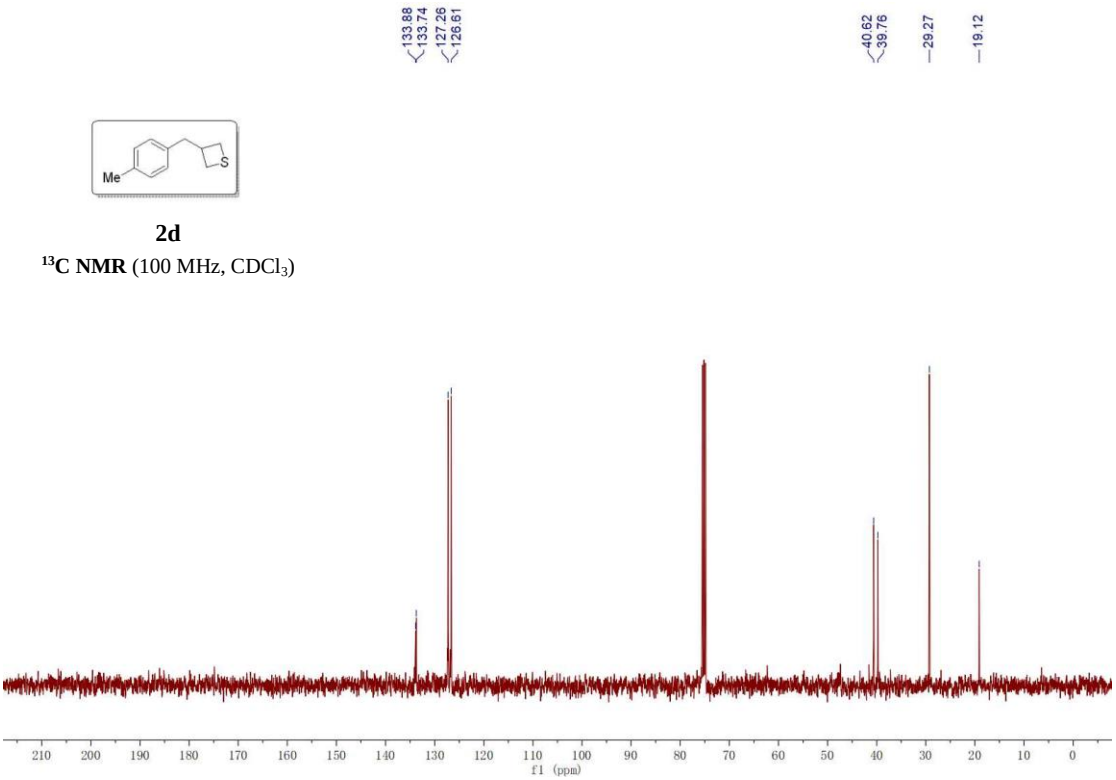

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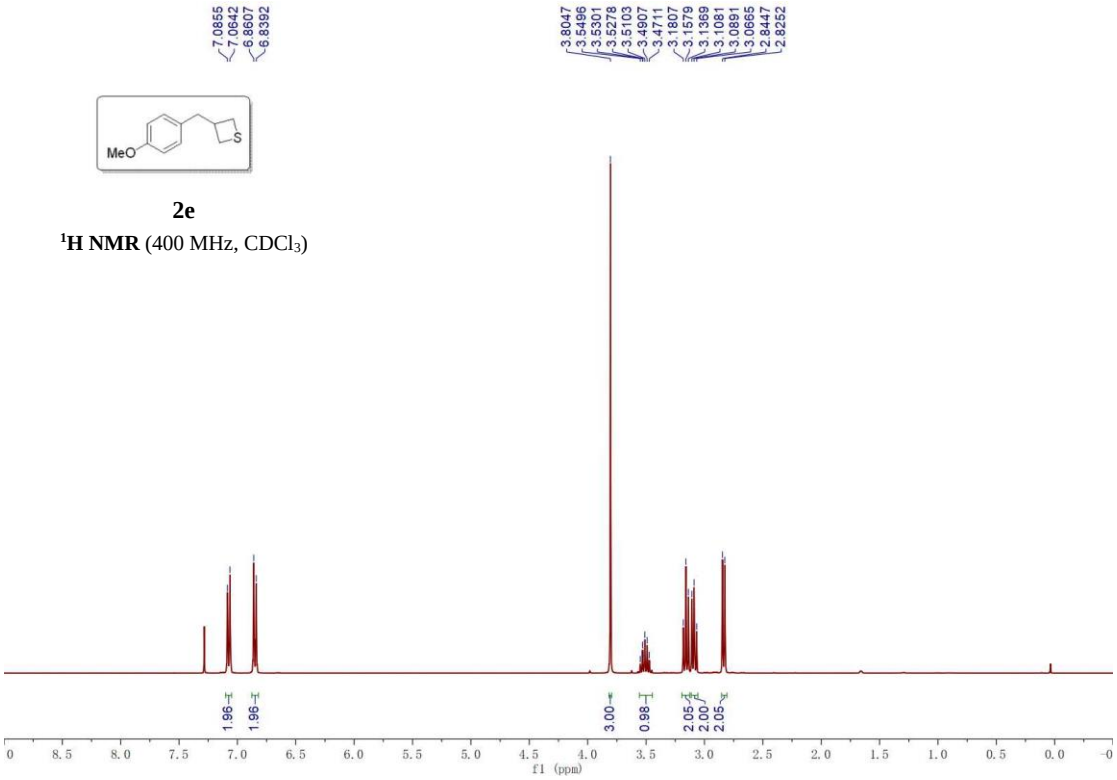

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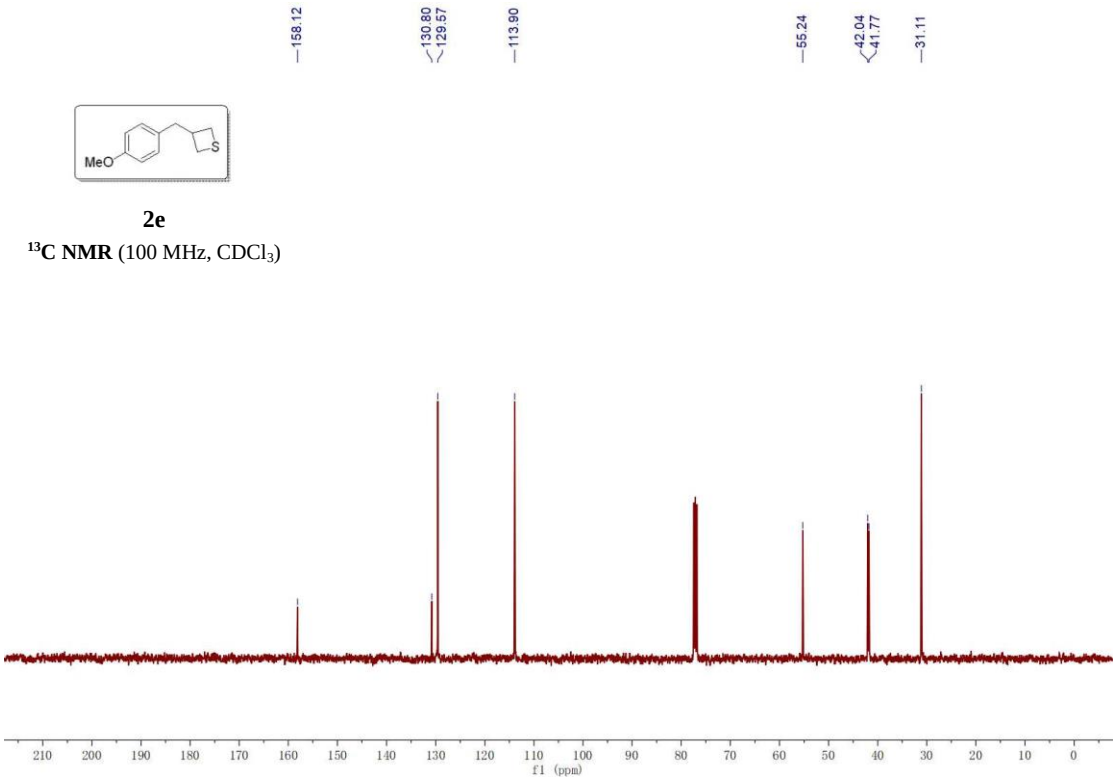

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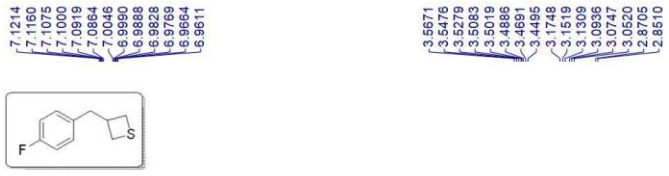

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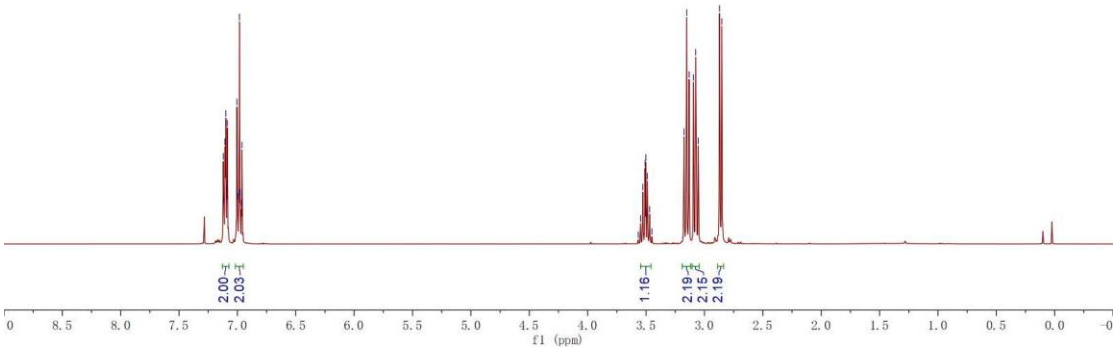

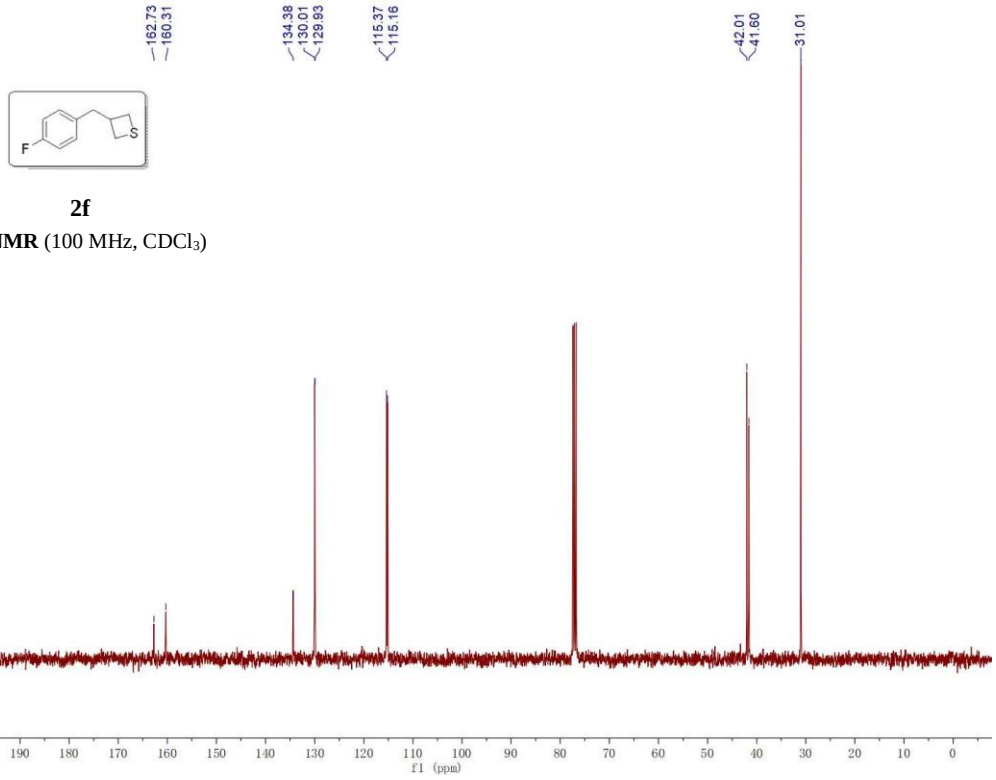

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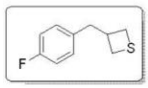

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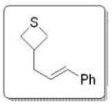

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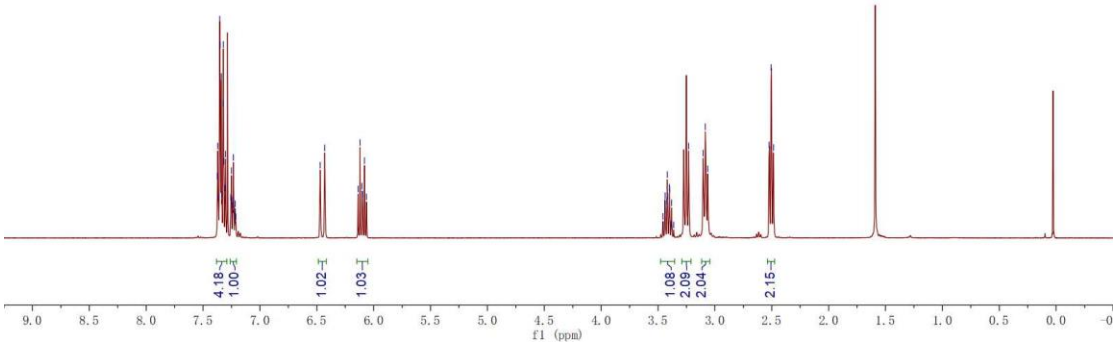

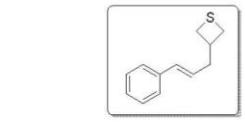

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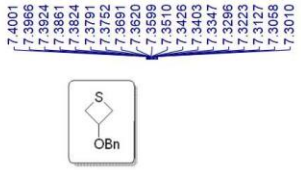

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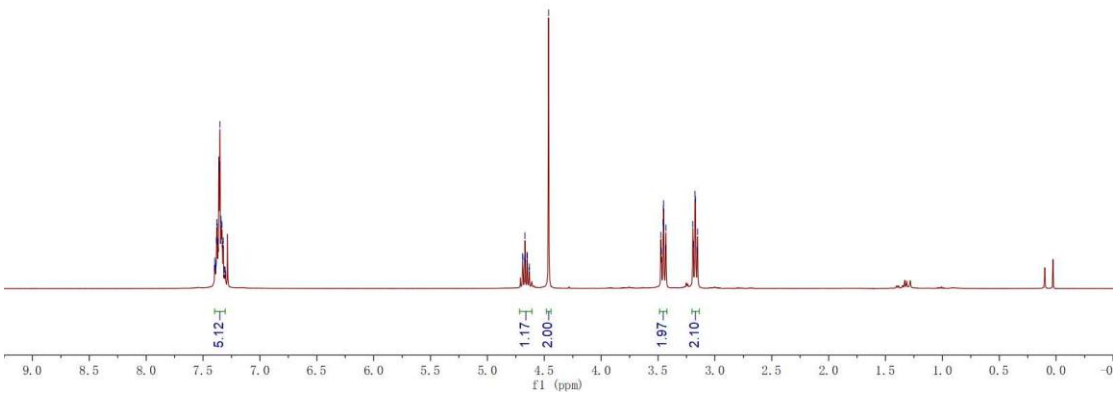

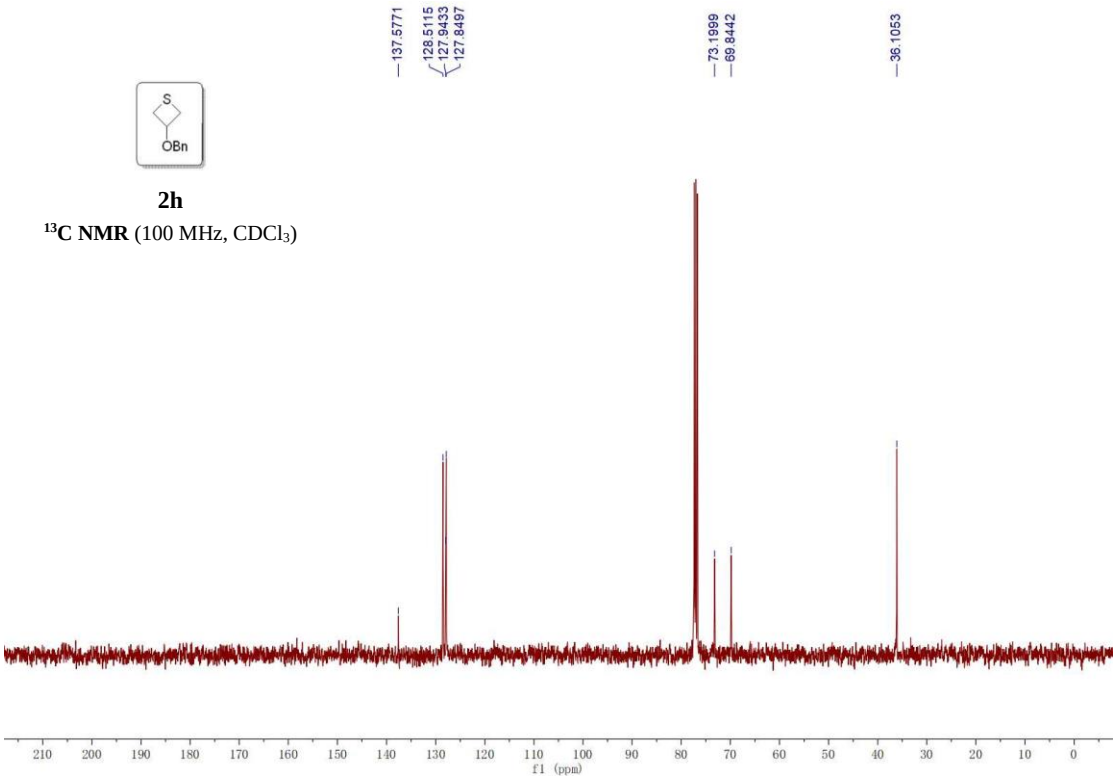

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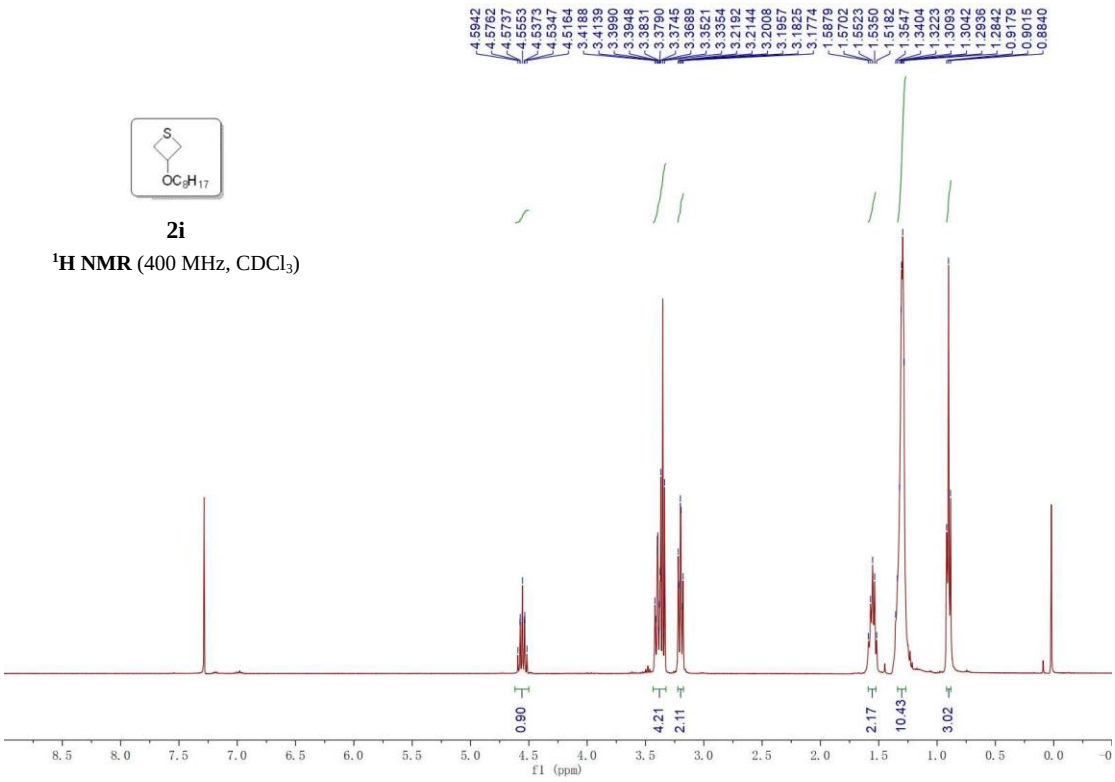

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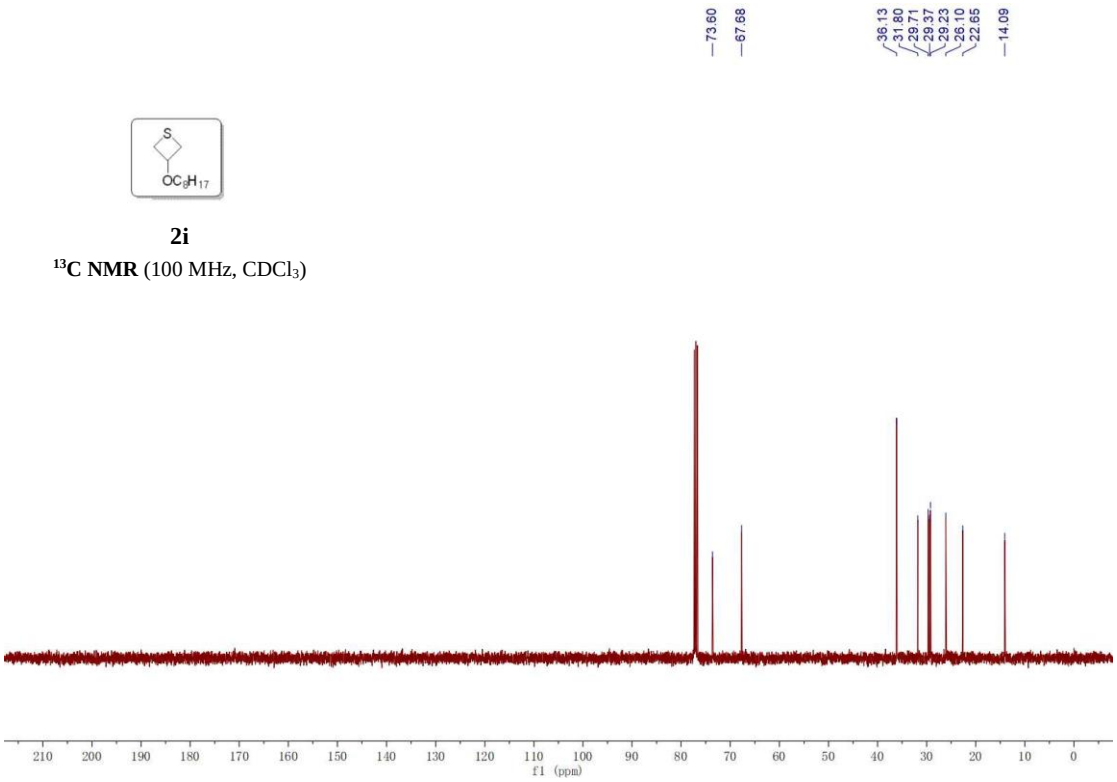

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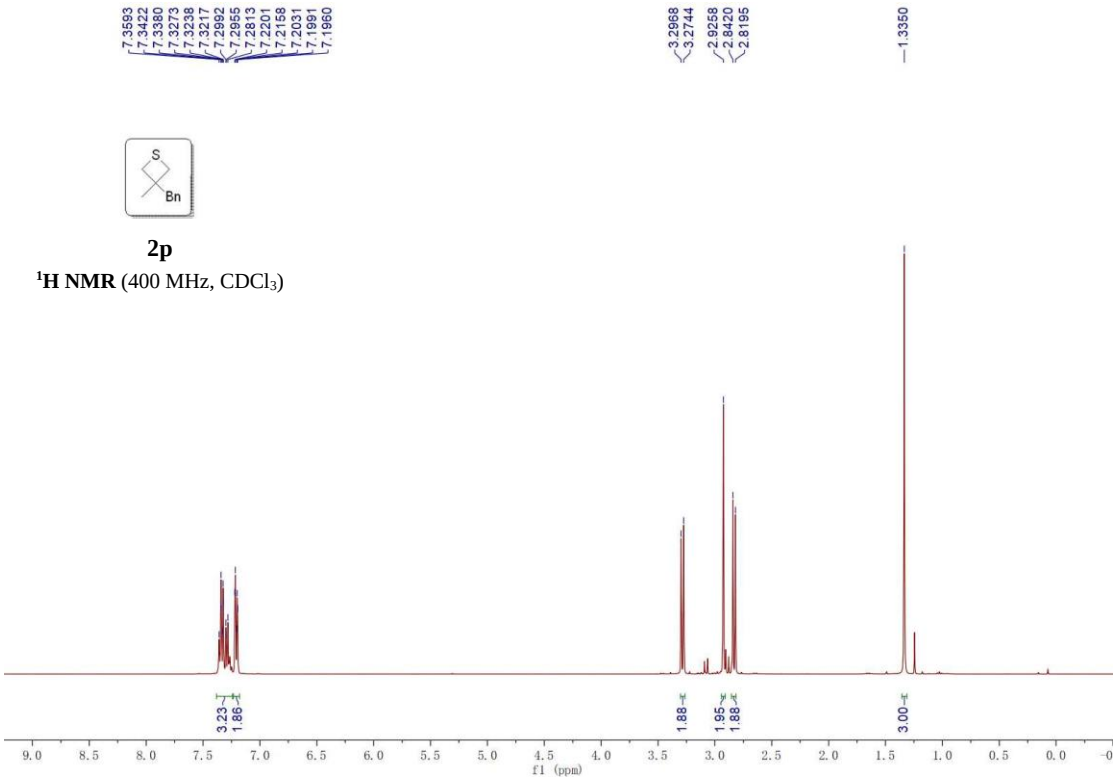

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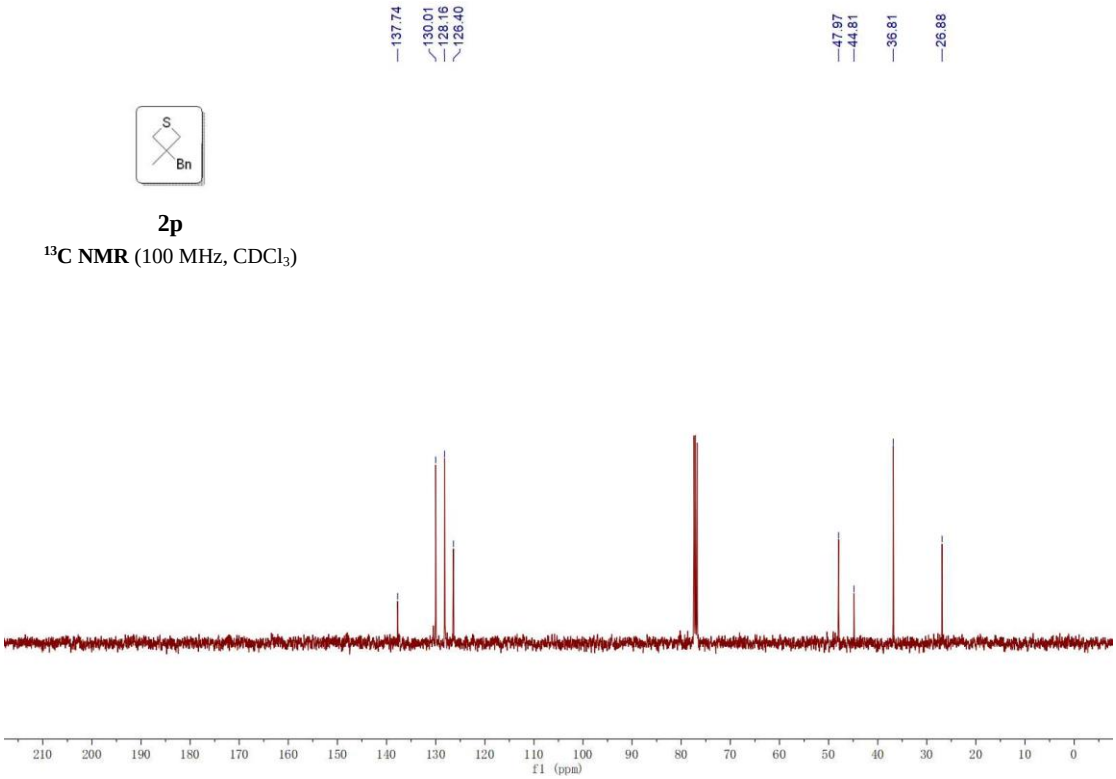

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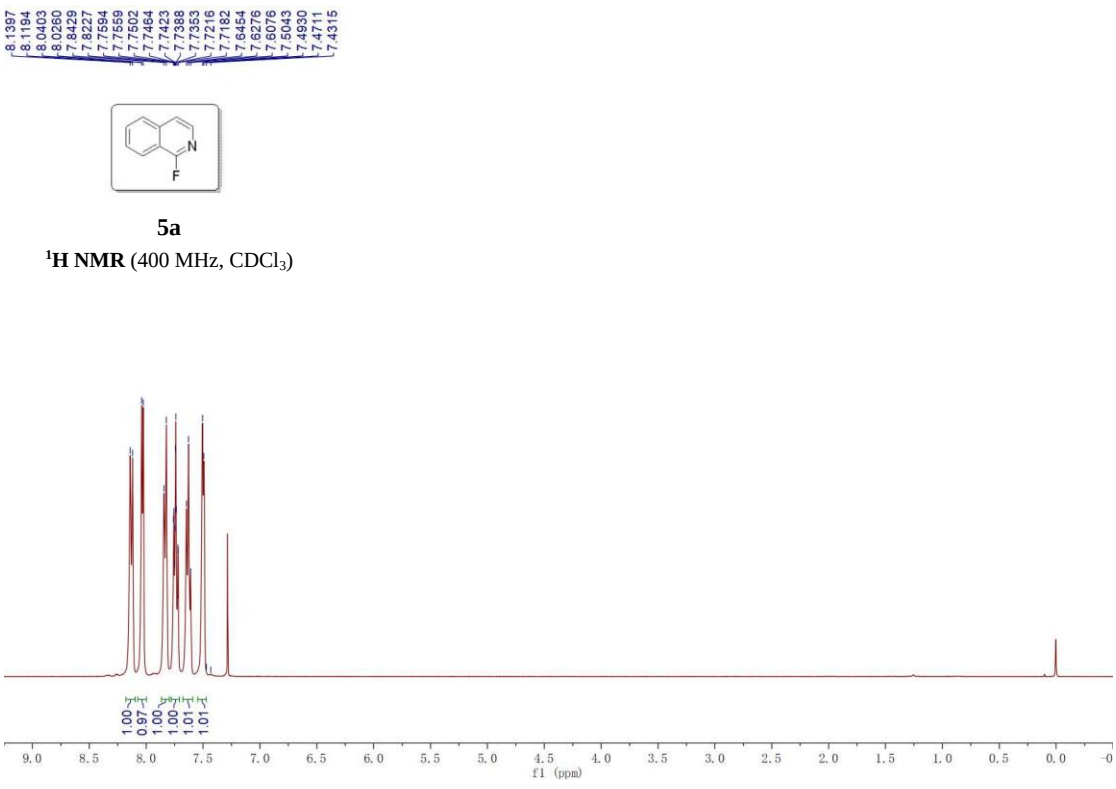

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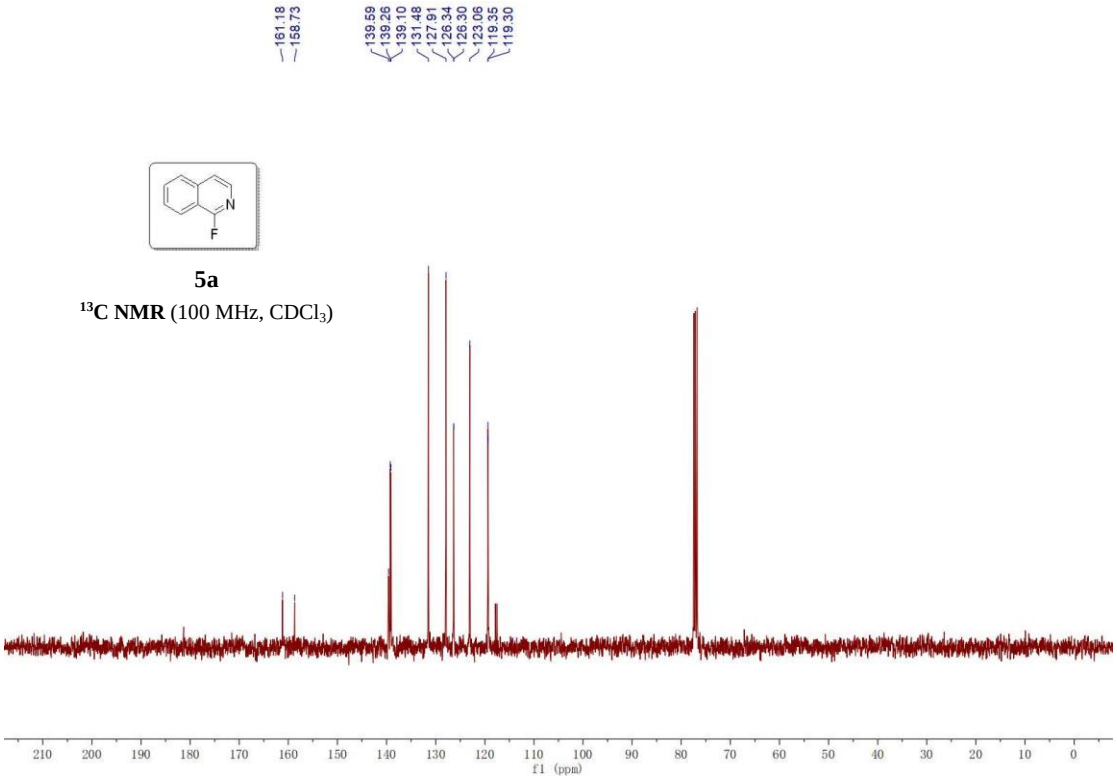

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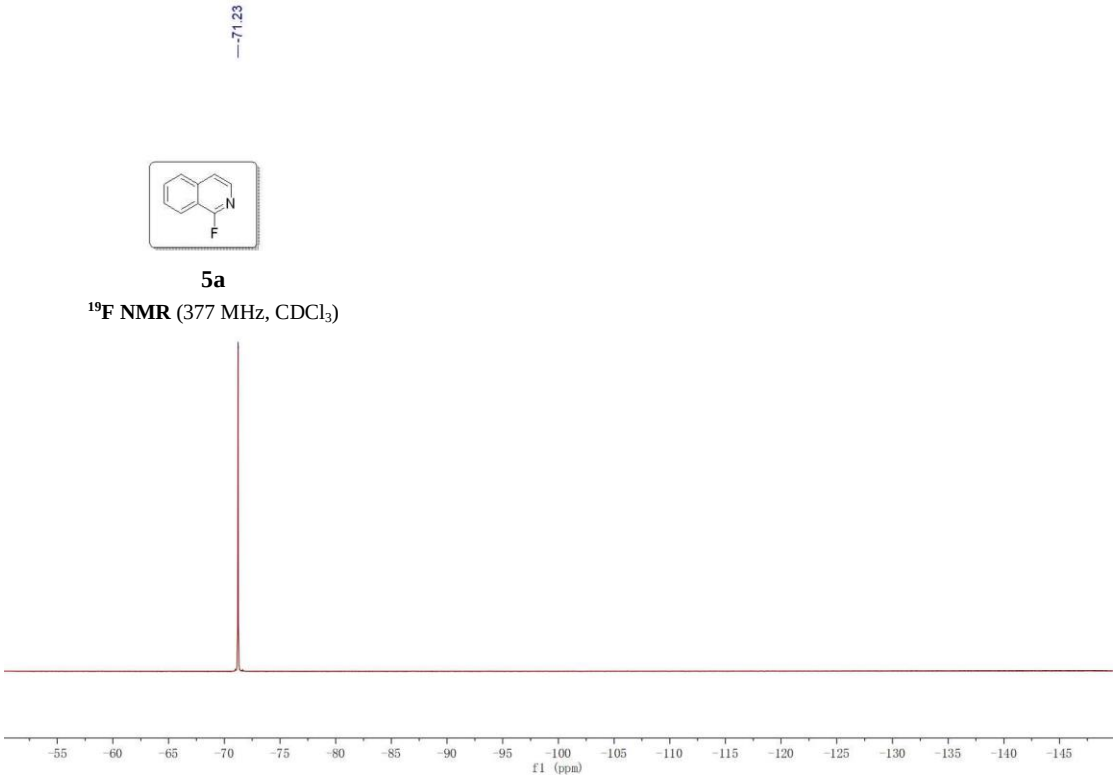

5a

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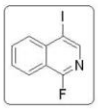

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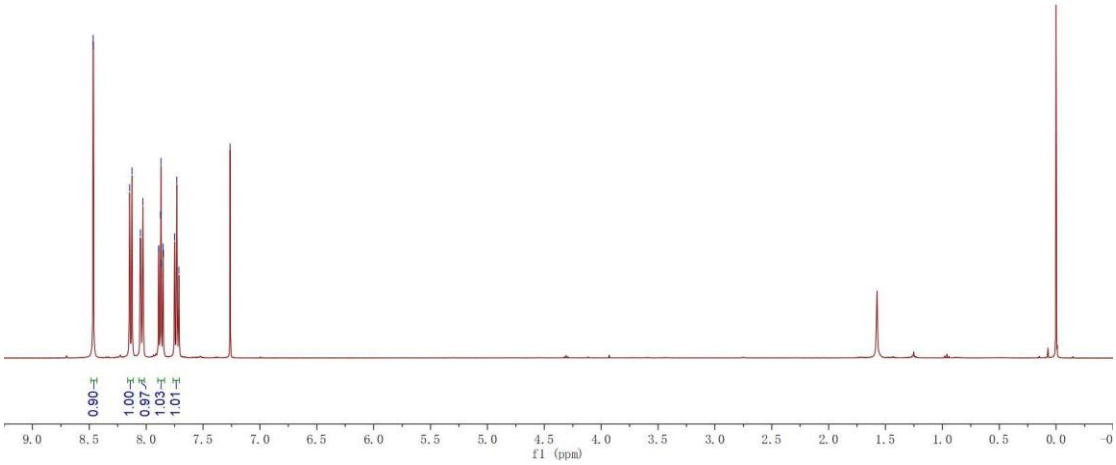

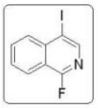

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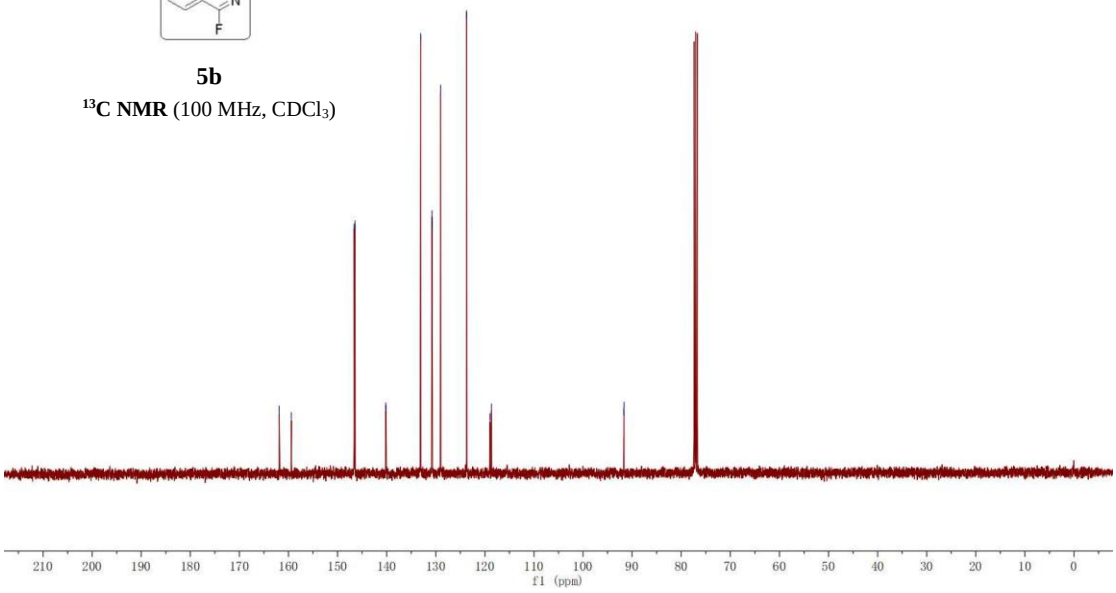

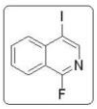

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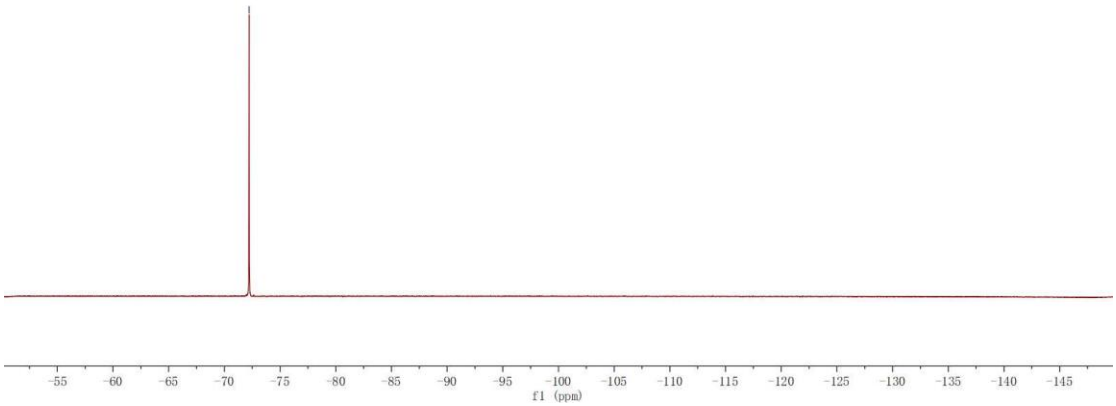

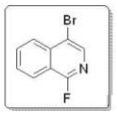

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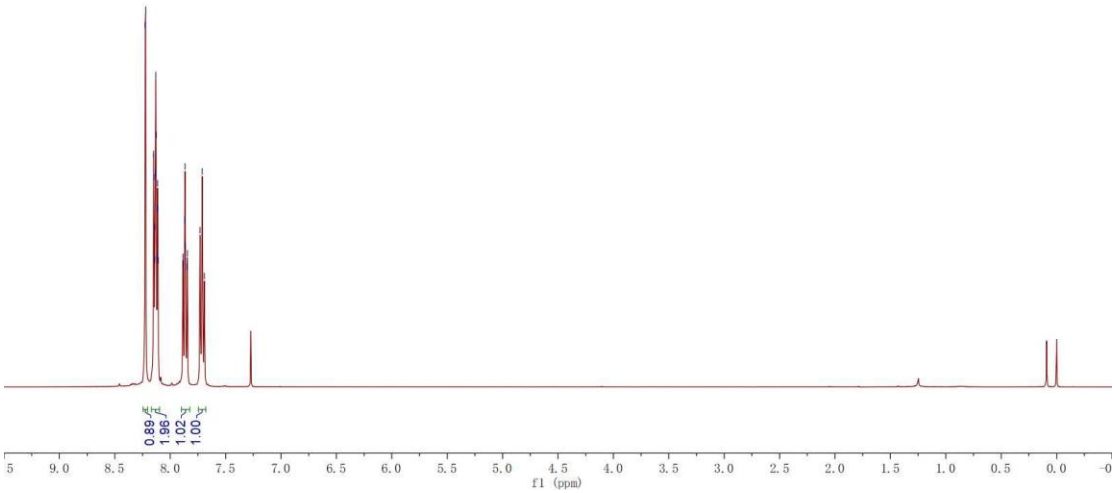

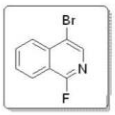

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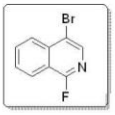

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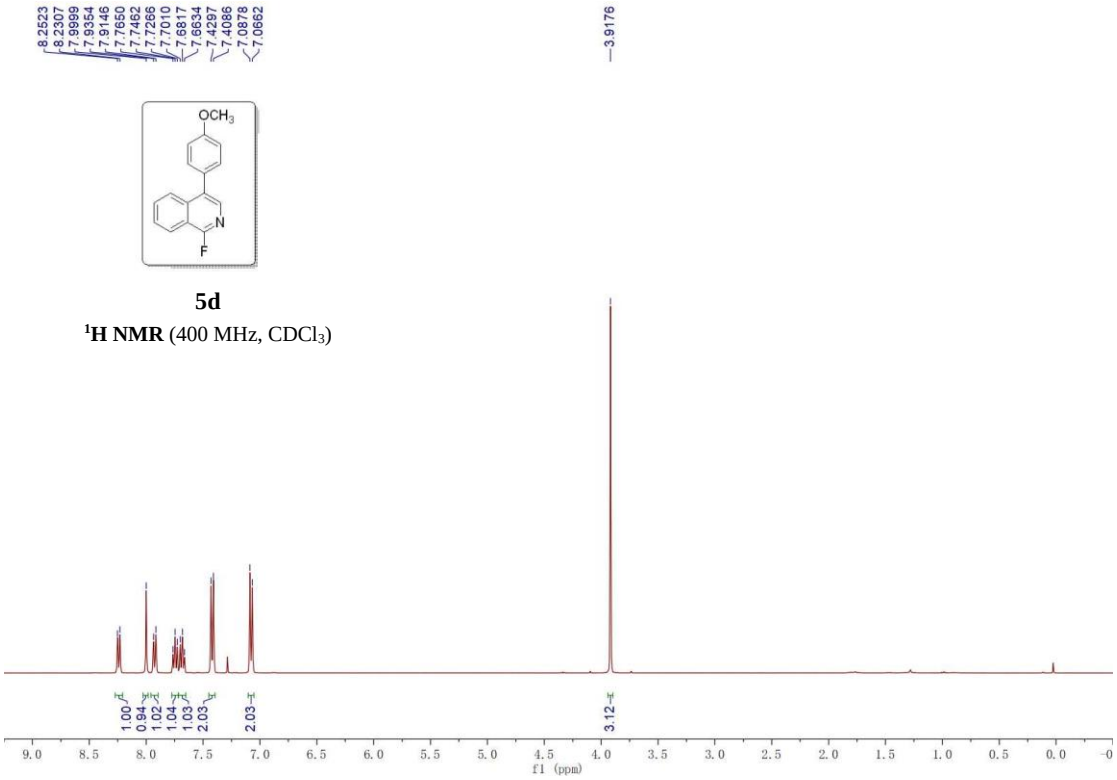

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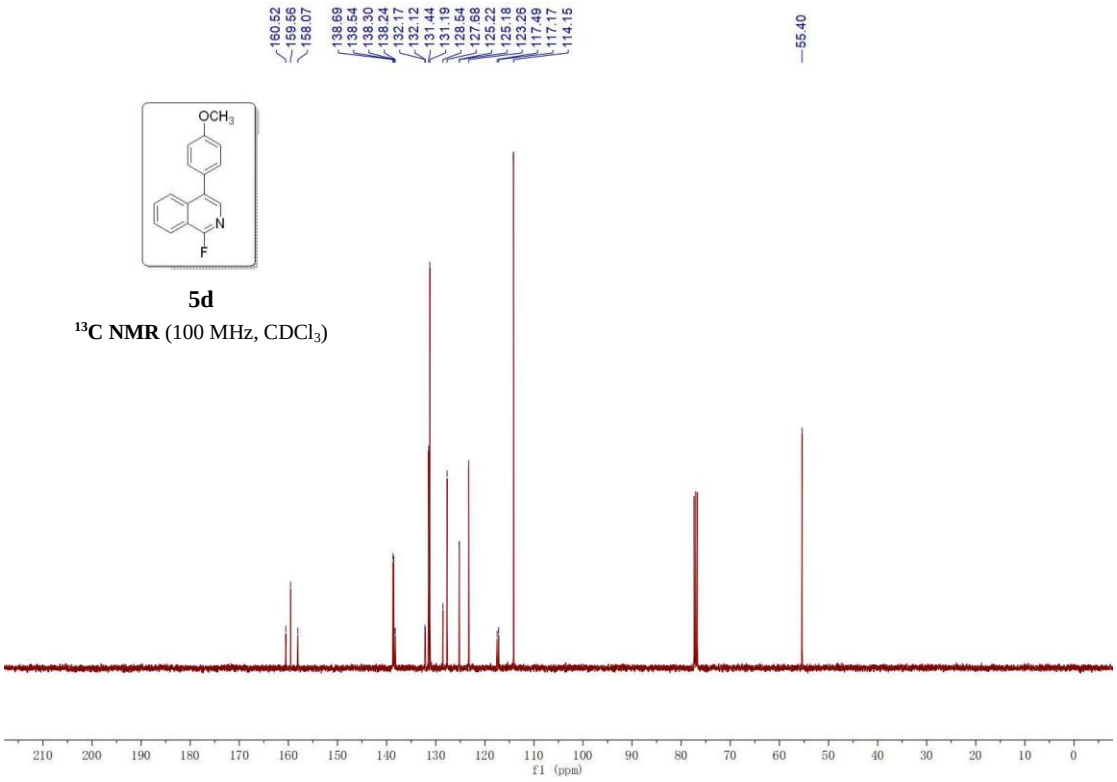

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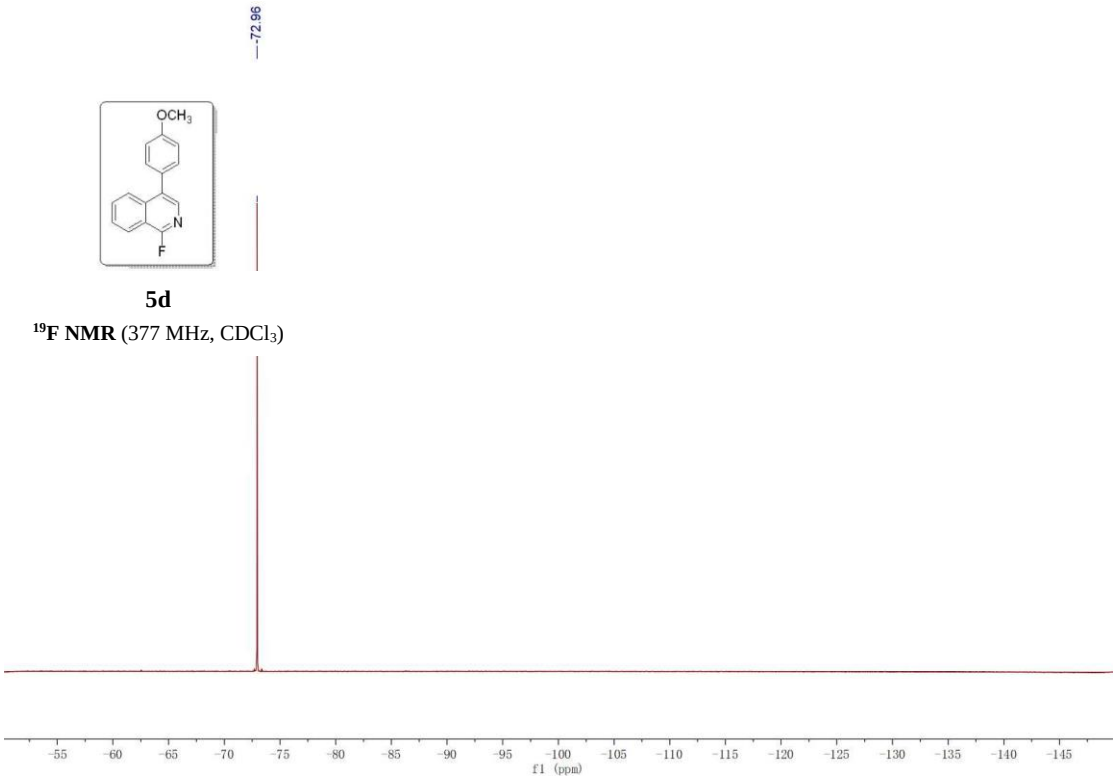

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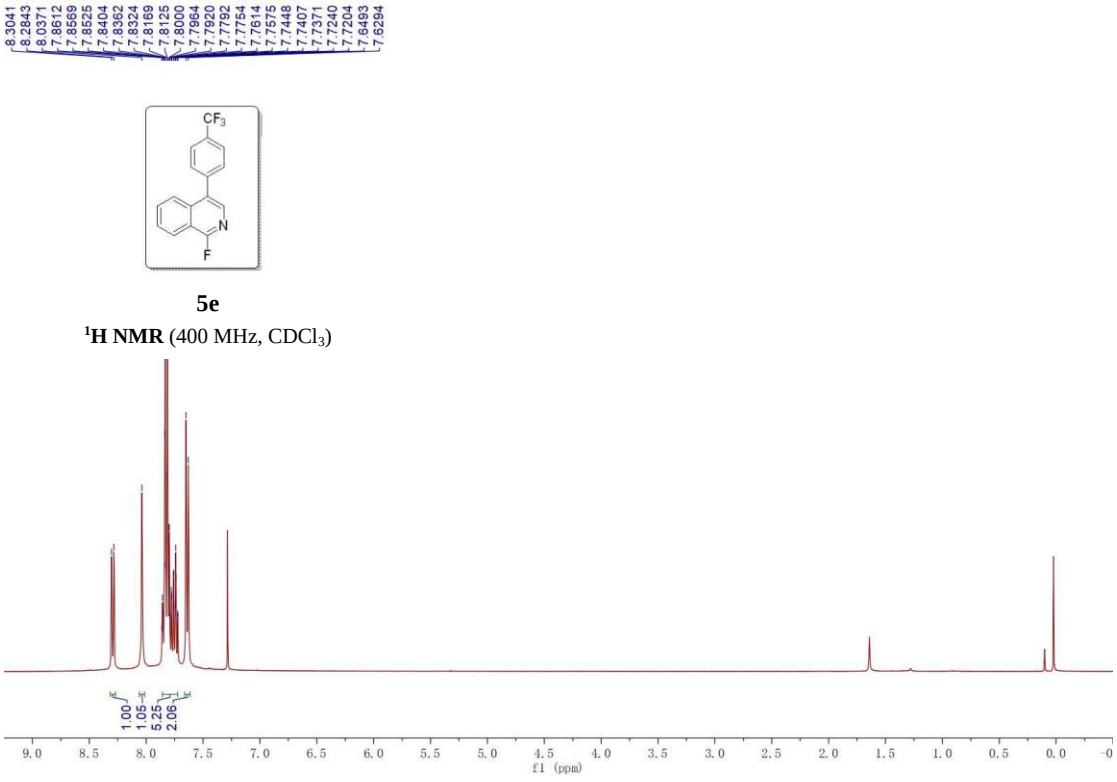

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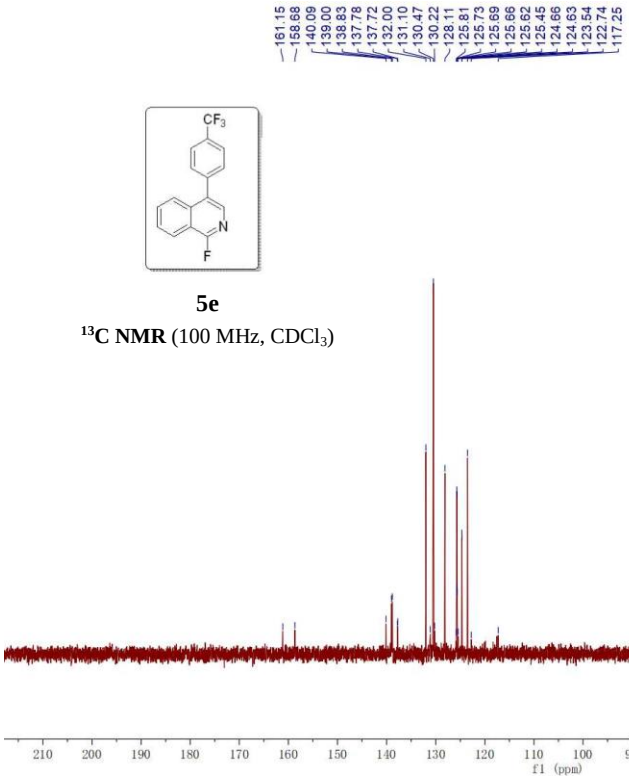

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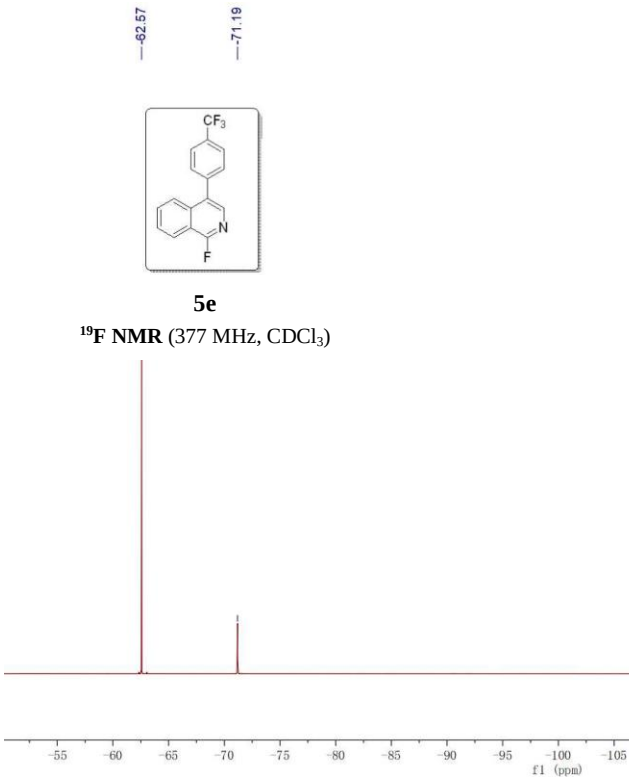

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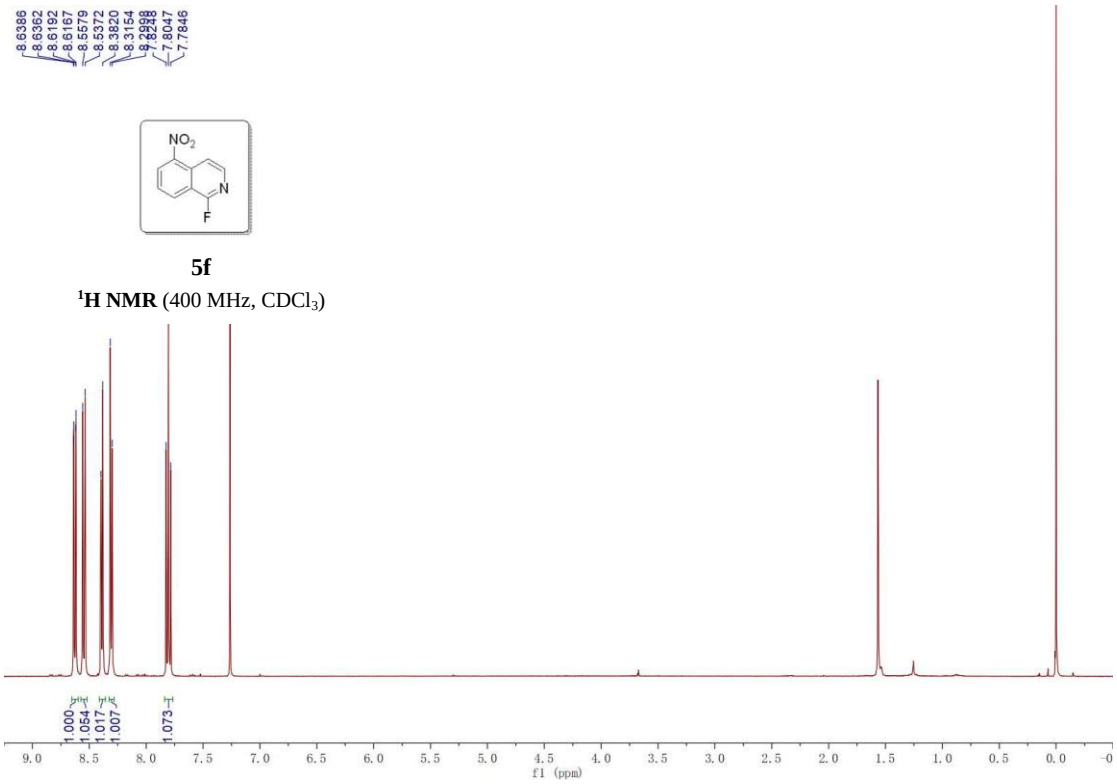

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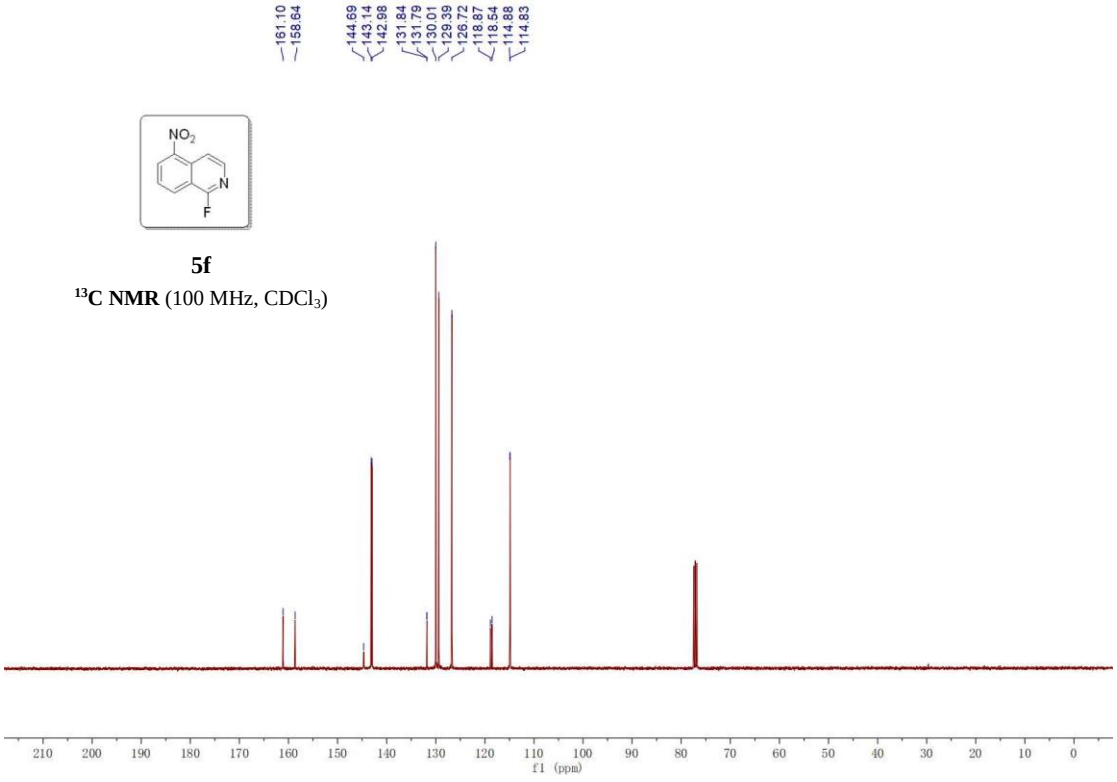

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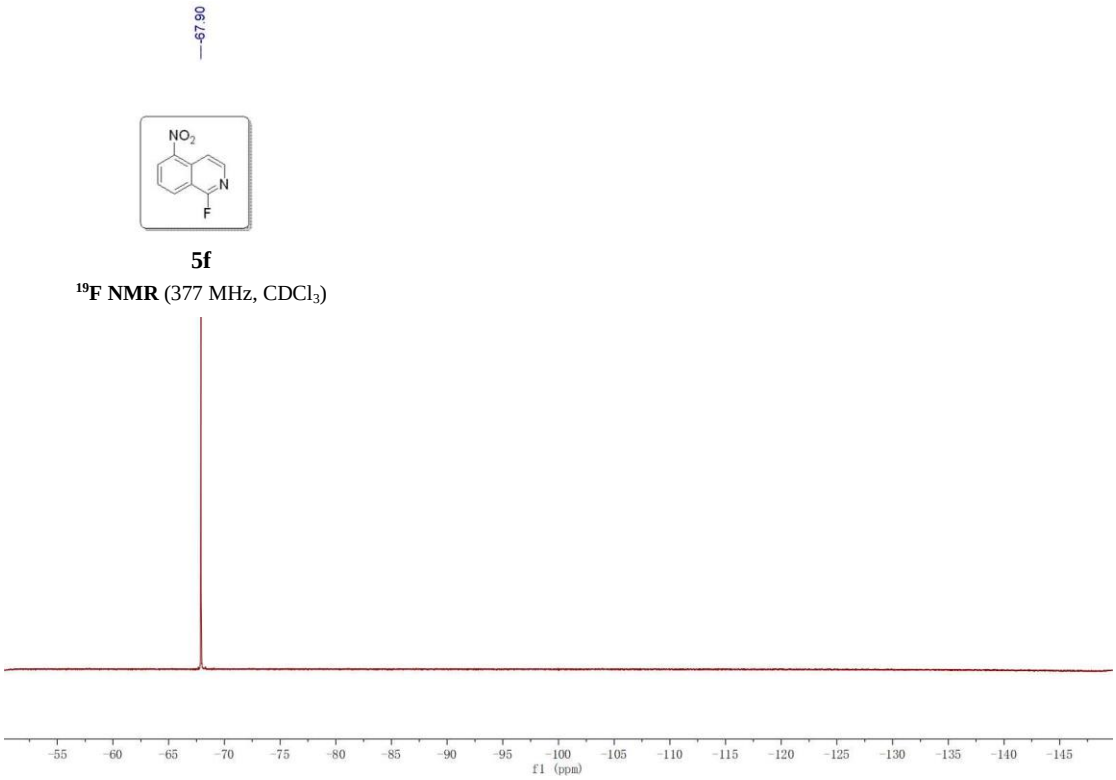

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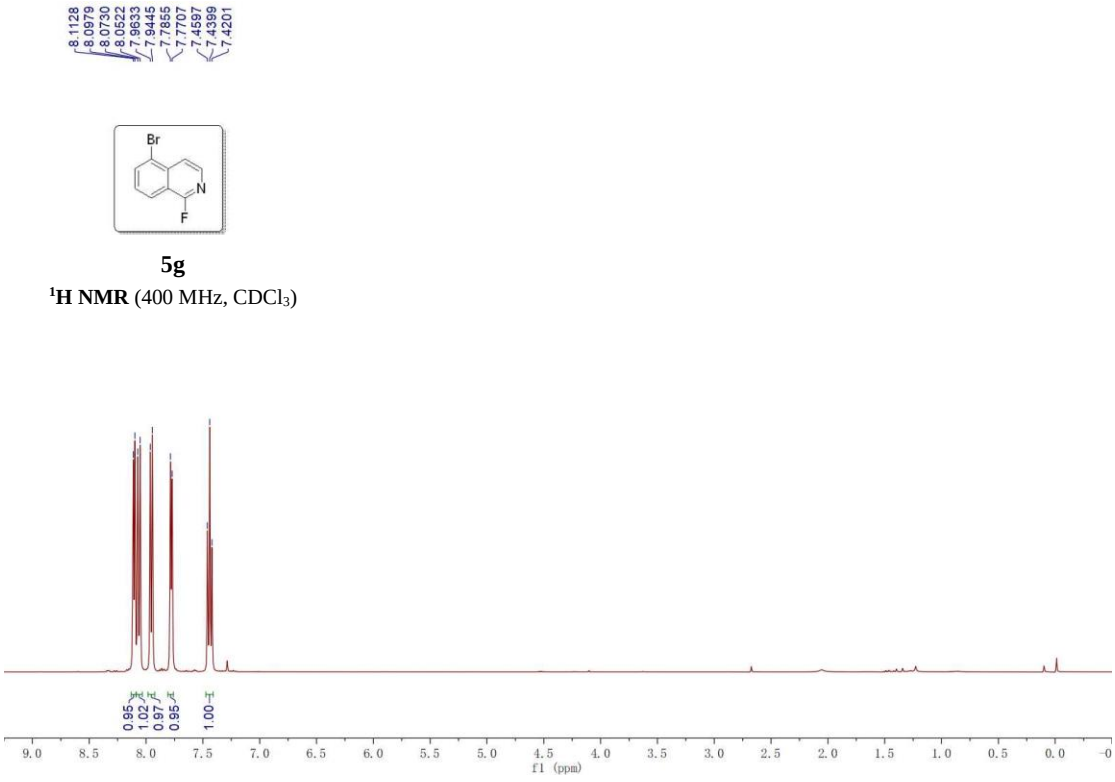
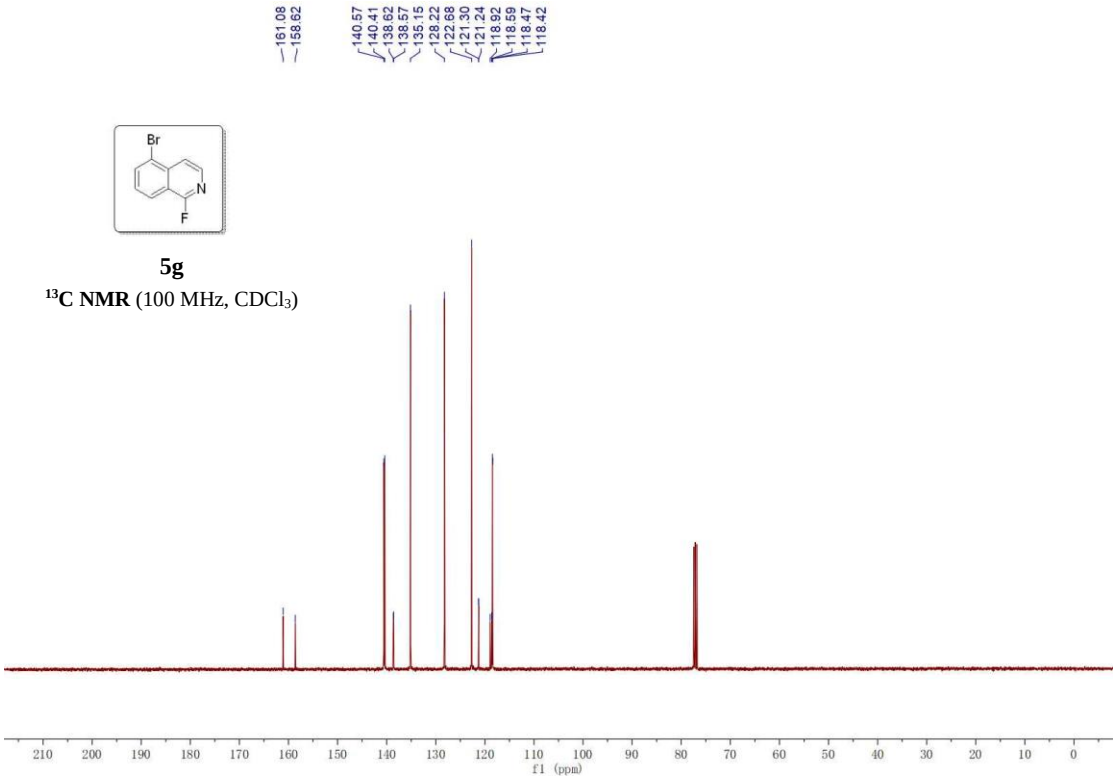


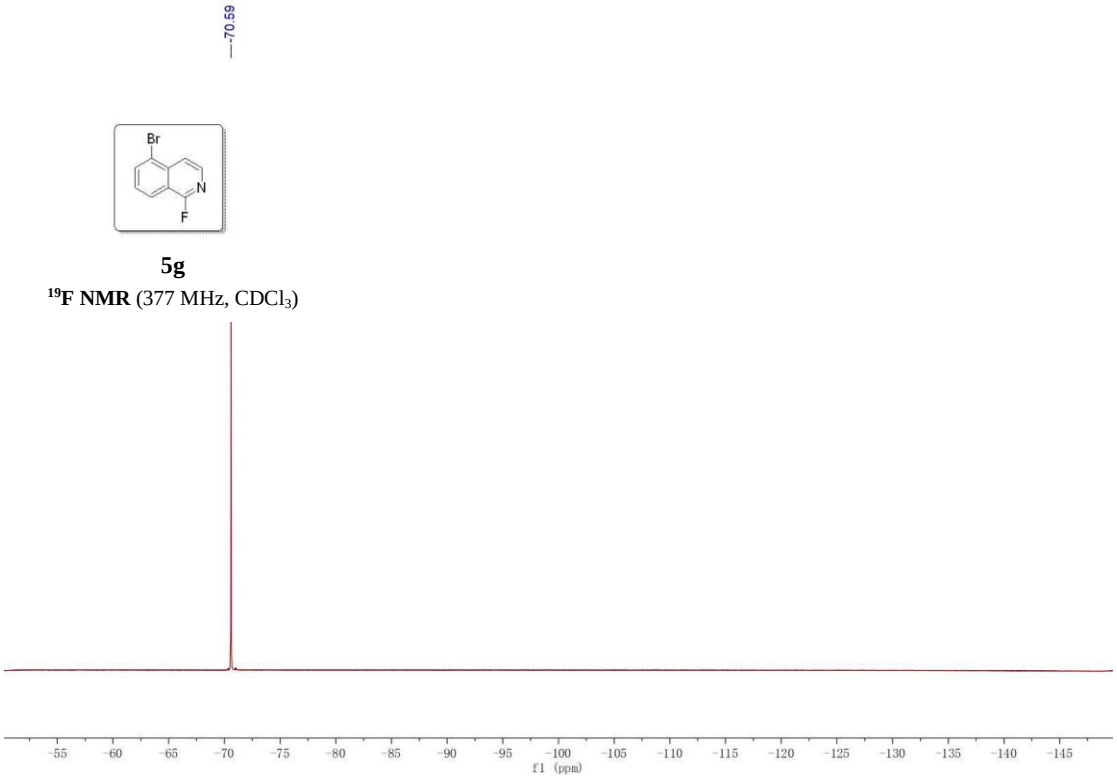
5g

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



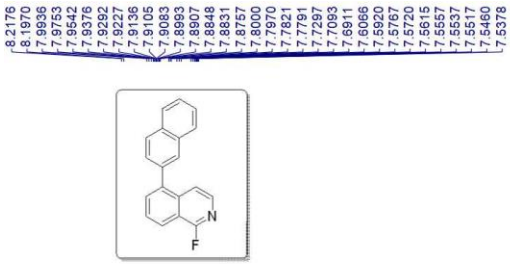
5g

^{13}C NMR (100 MHz, $CDCl_3$)



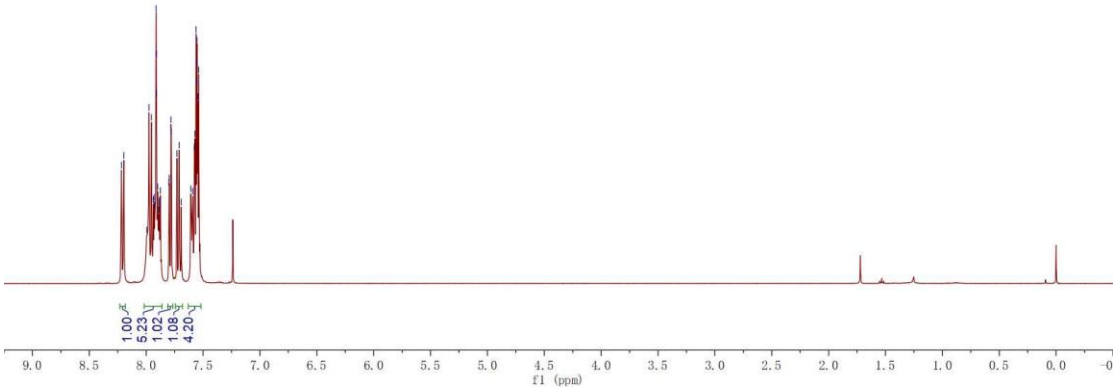
5g

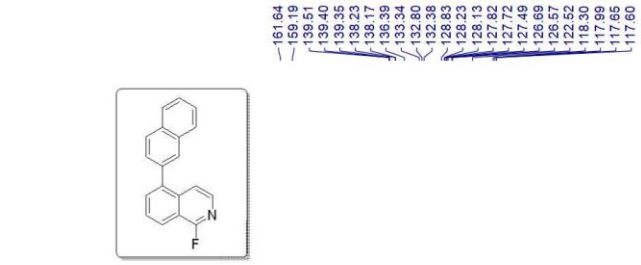
^{19}F NMR (377 MHz, $CDCl_3$)



5h

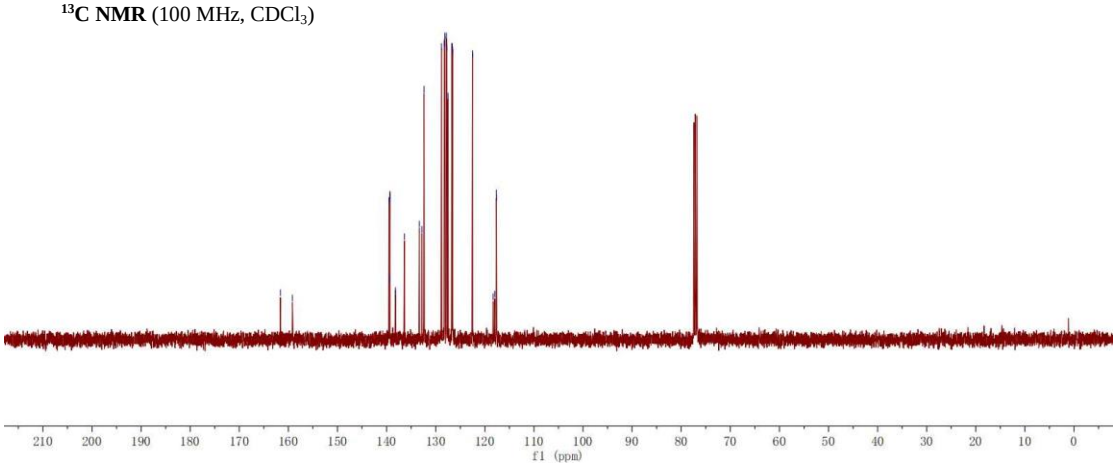
^{1}H NMR (400 MHz, $CDCl_3$)

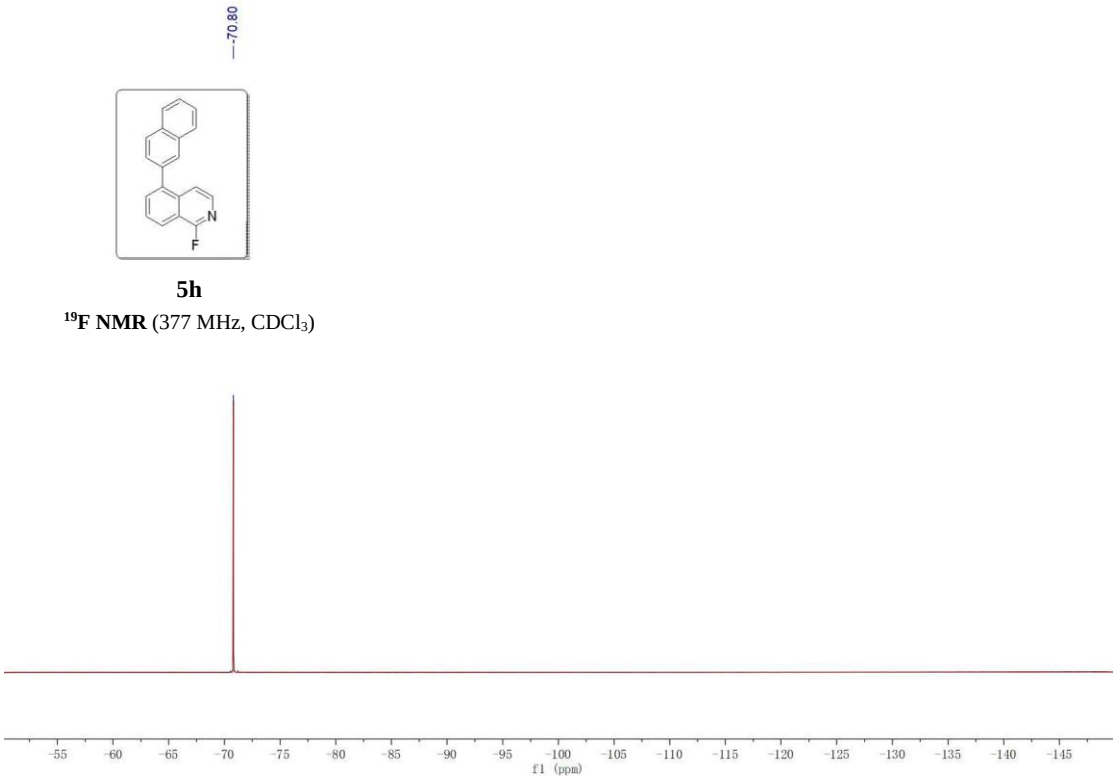




5h

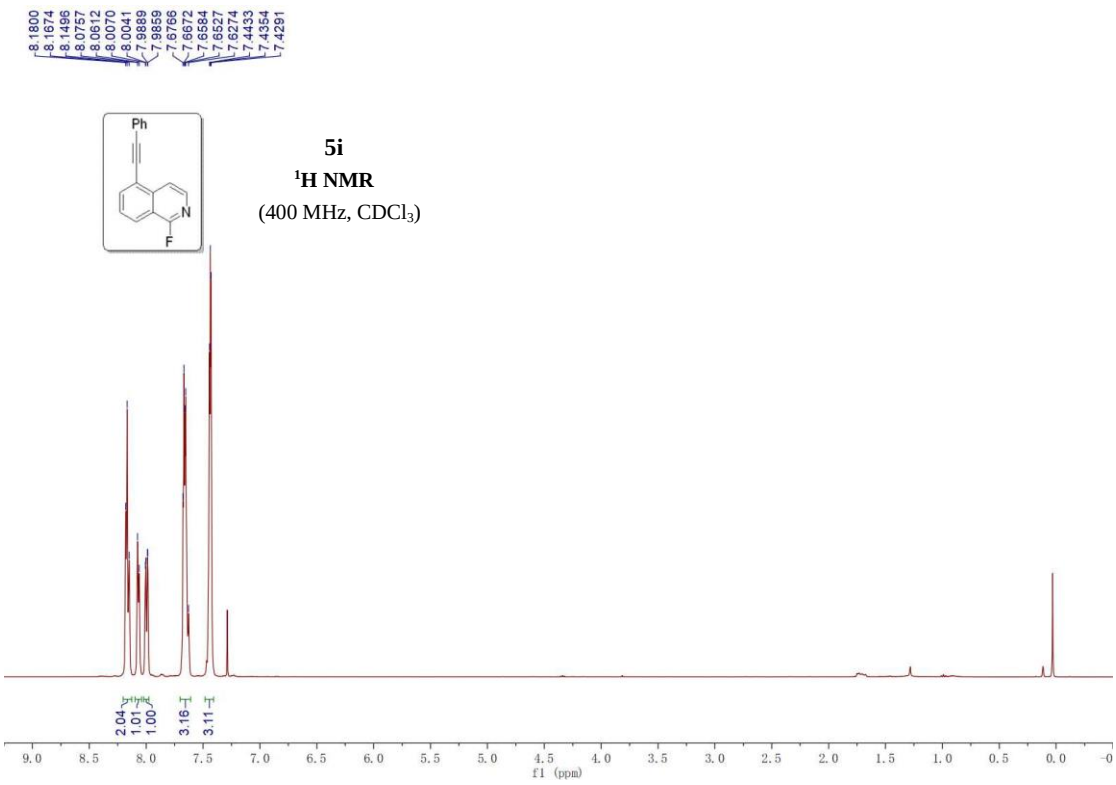
^{13}C NMR (100 MHz, $CDCl_3$)





5h

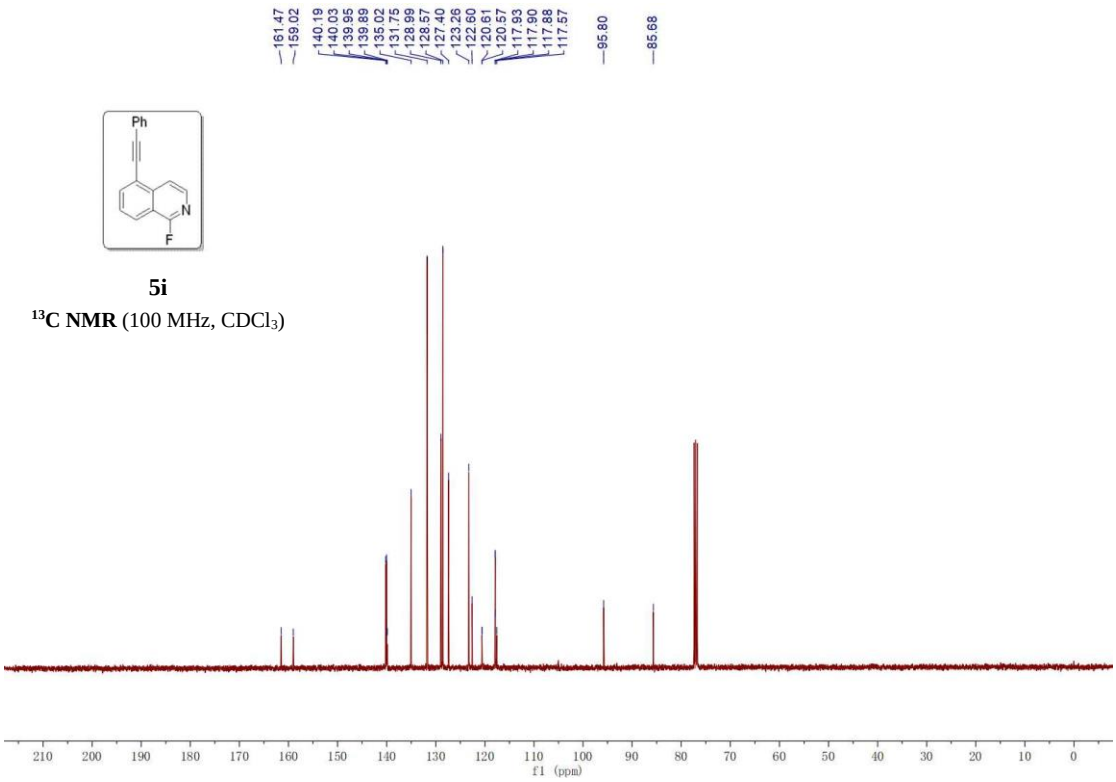
^{19}F NMR (377 MHz, $CDCl_3$)



5i

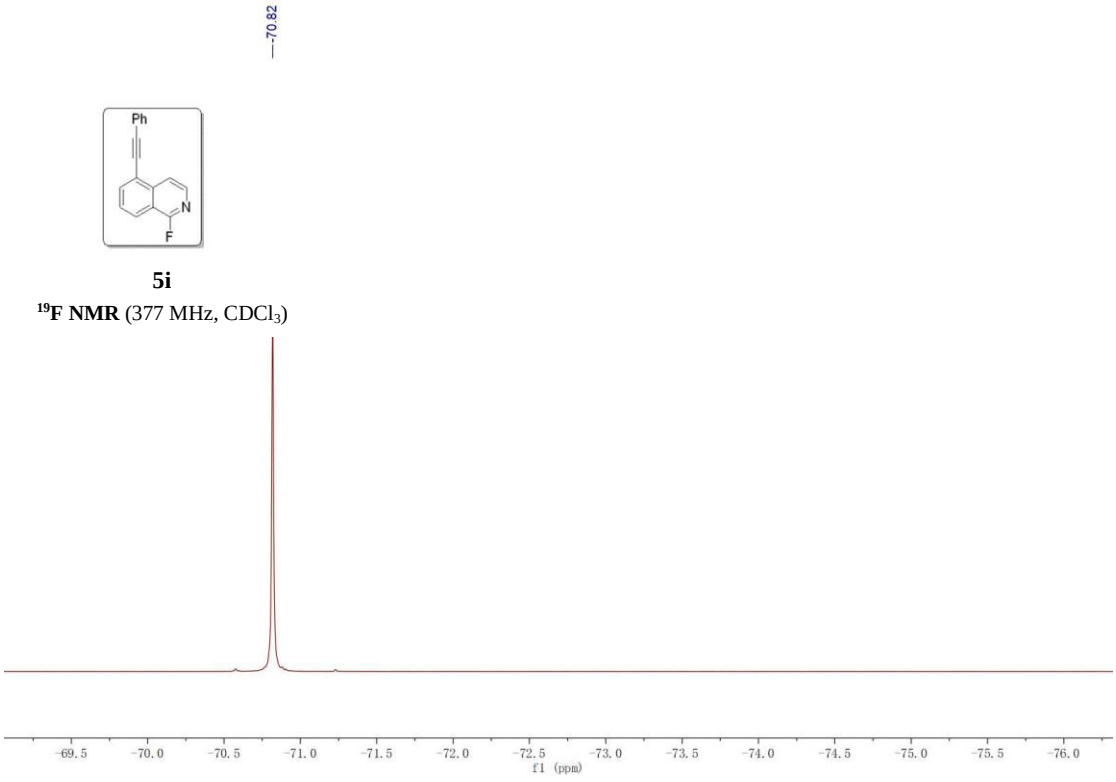
^{1}H NMR

(400 MHz, $CDCl_3$)



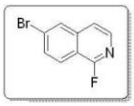
5i

^{13}C NMR (100 MHz, $CDCl_3$)



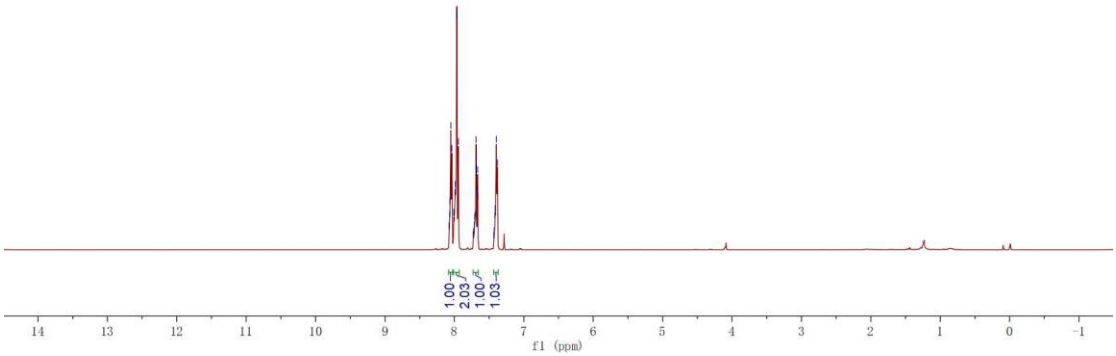
5i

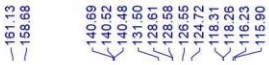
^{19}F NMR (377 MHz, $CDCl_3$)

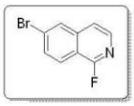


5j

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

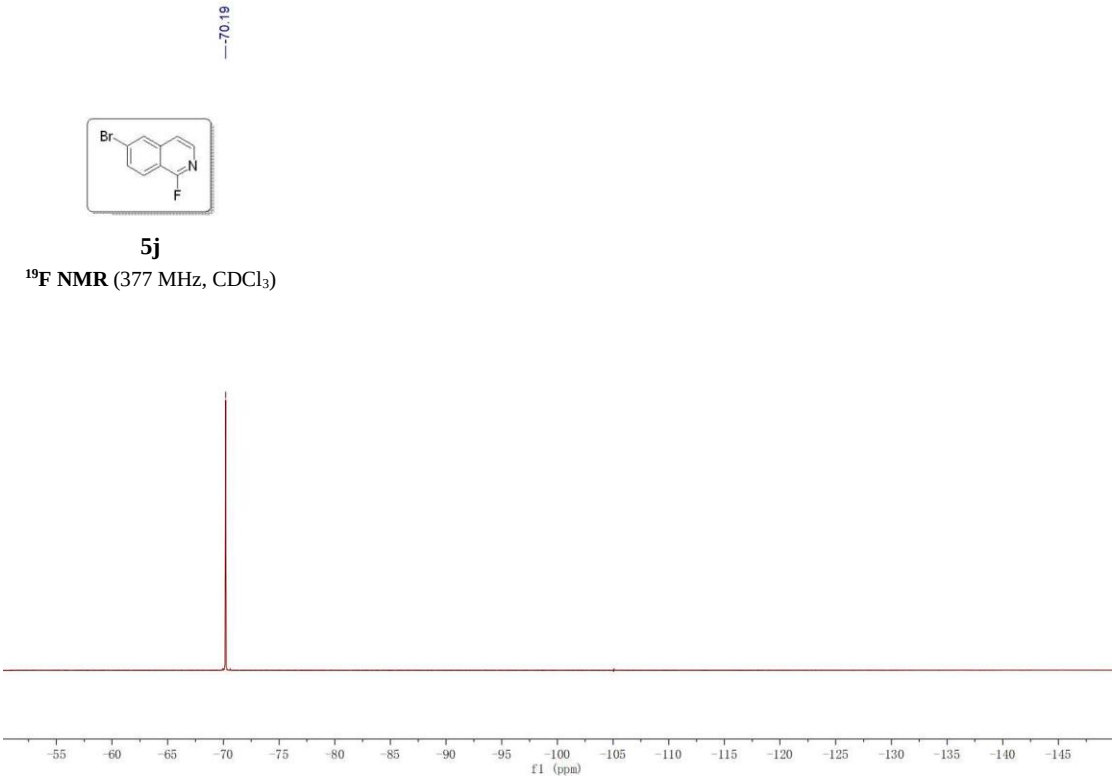






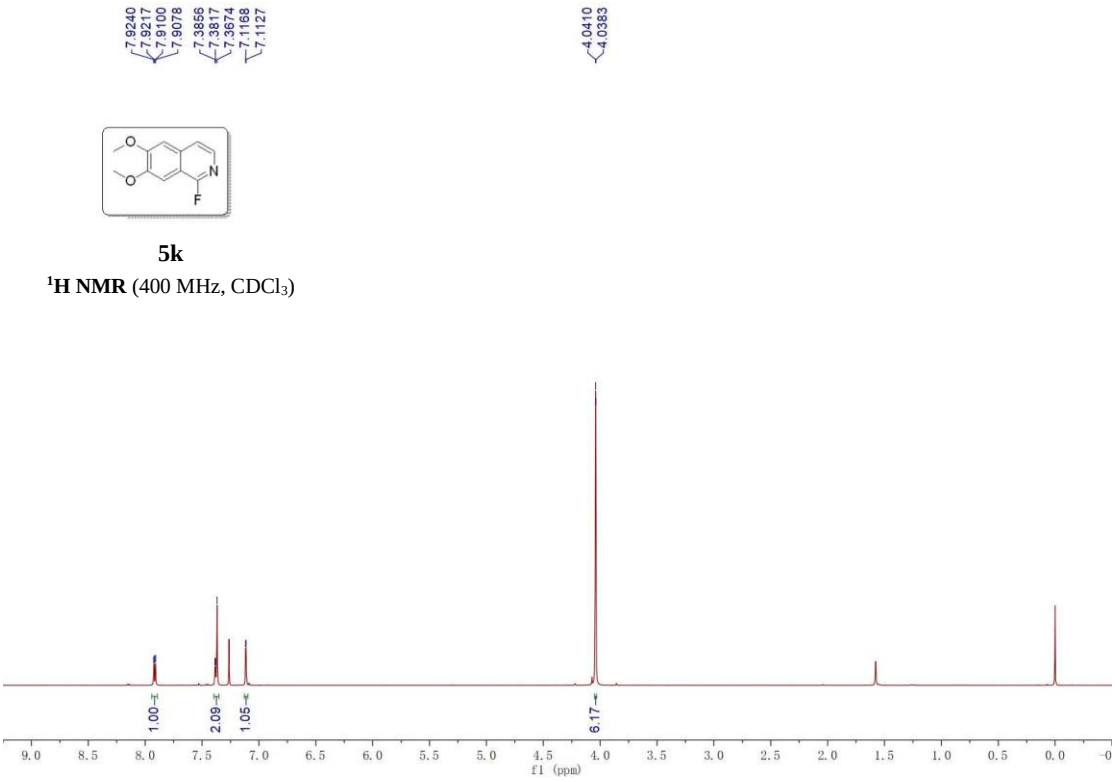
5j

^{13}C NMR (100 MHz, $CDCl_3$)



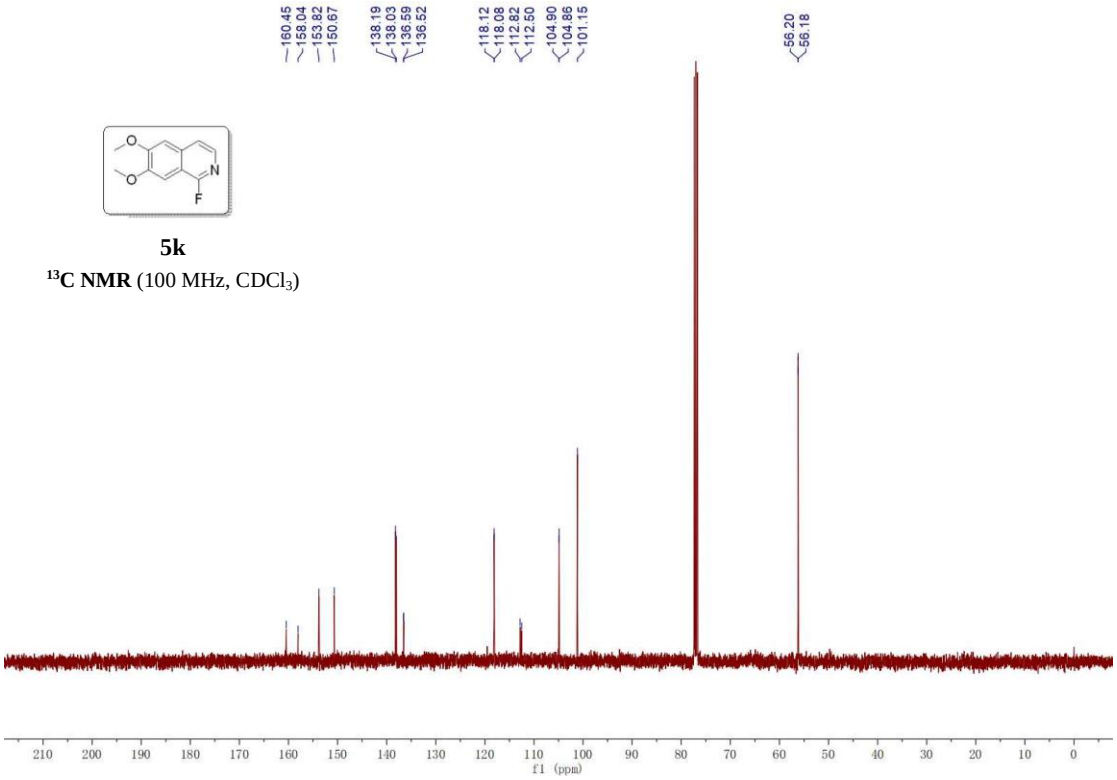
5j

^{19}F NMR (377 MHz, $CDCl_3$)



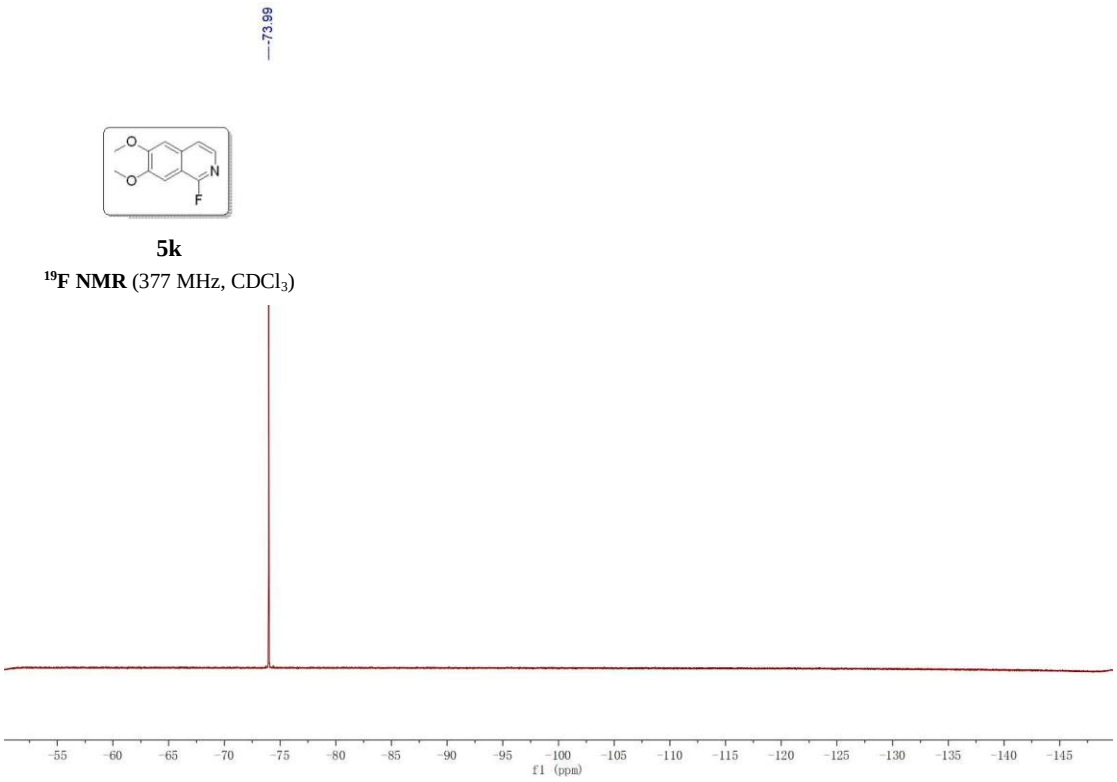
5k

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



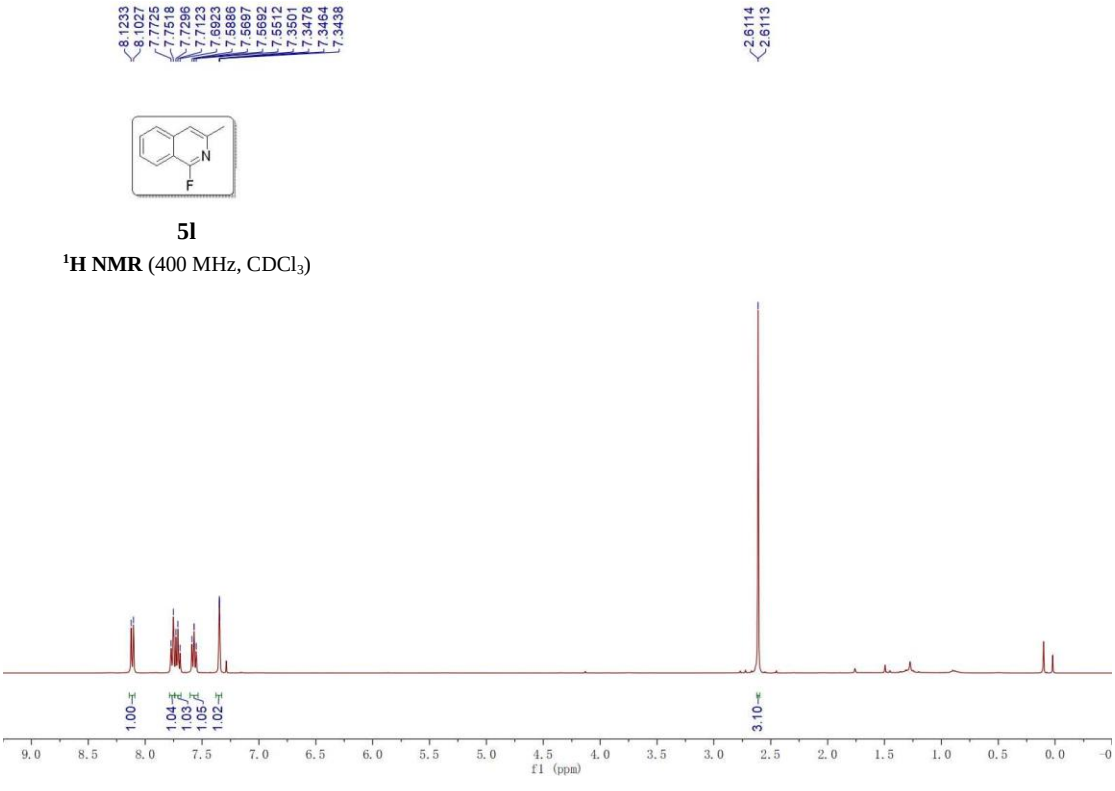
5k

^{13}C NMR (100 MHz, $CDCl_3$)



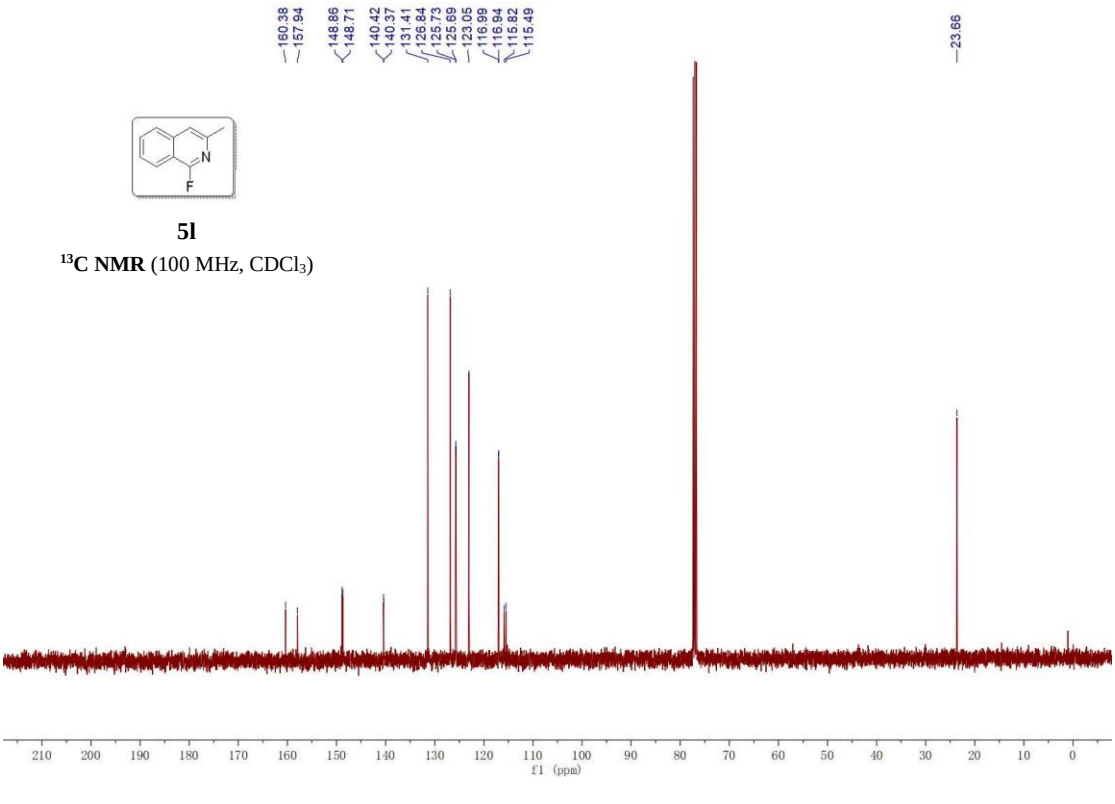
5k

^{19}F NMR (377 MHz, $CDCl_3$)



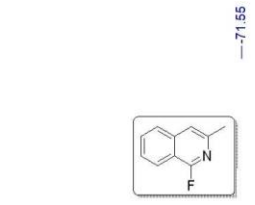
5l

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



5l

^{13}C NMR (100 MHz, $CDCl_3$)



5l

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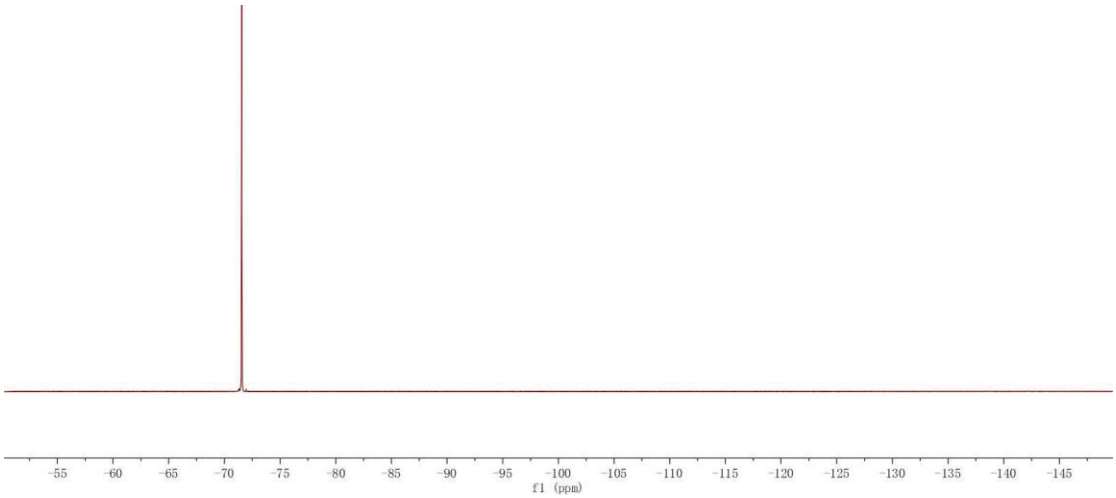
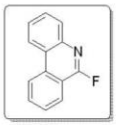
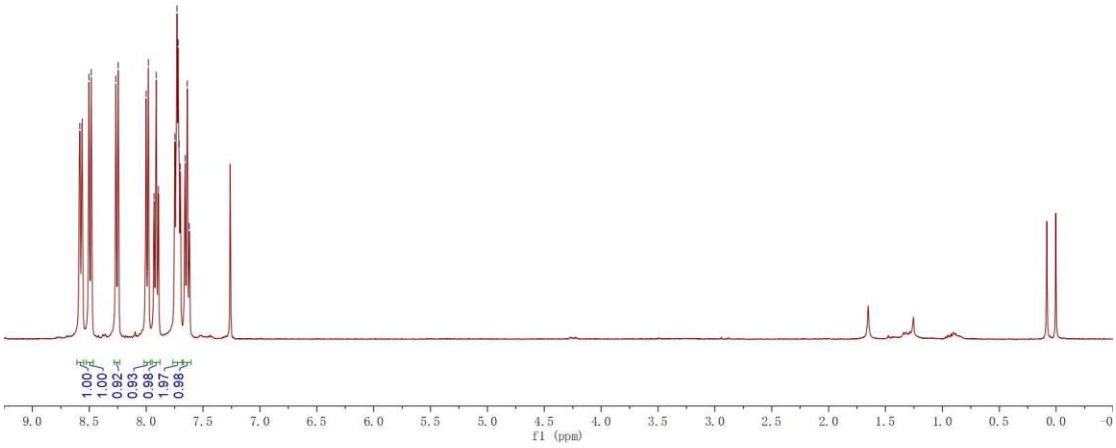
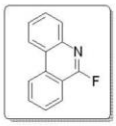




5n

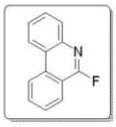
^{1}H NMR (400 MHz, $CDCl_3$)





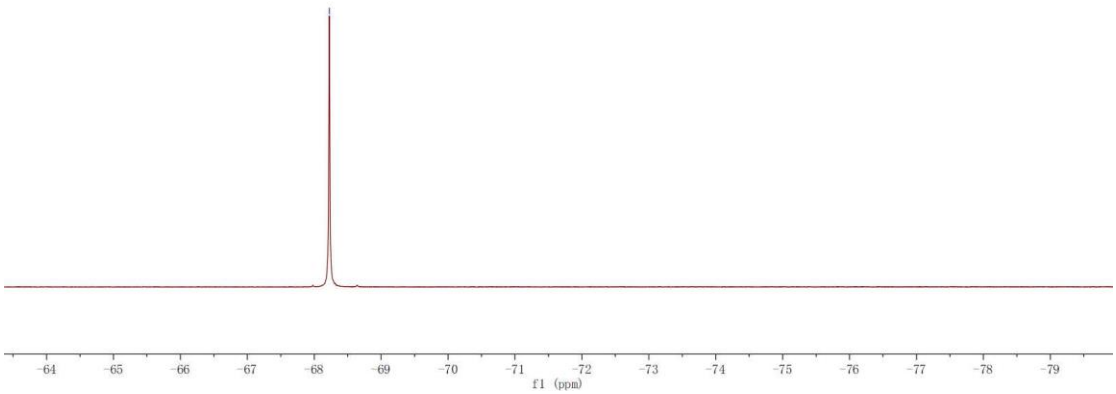
5n

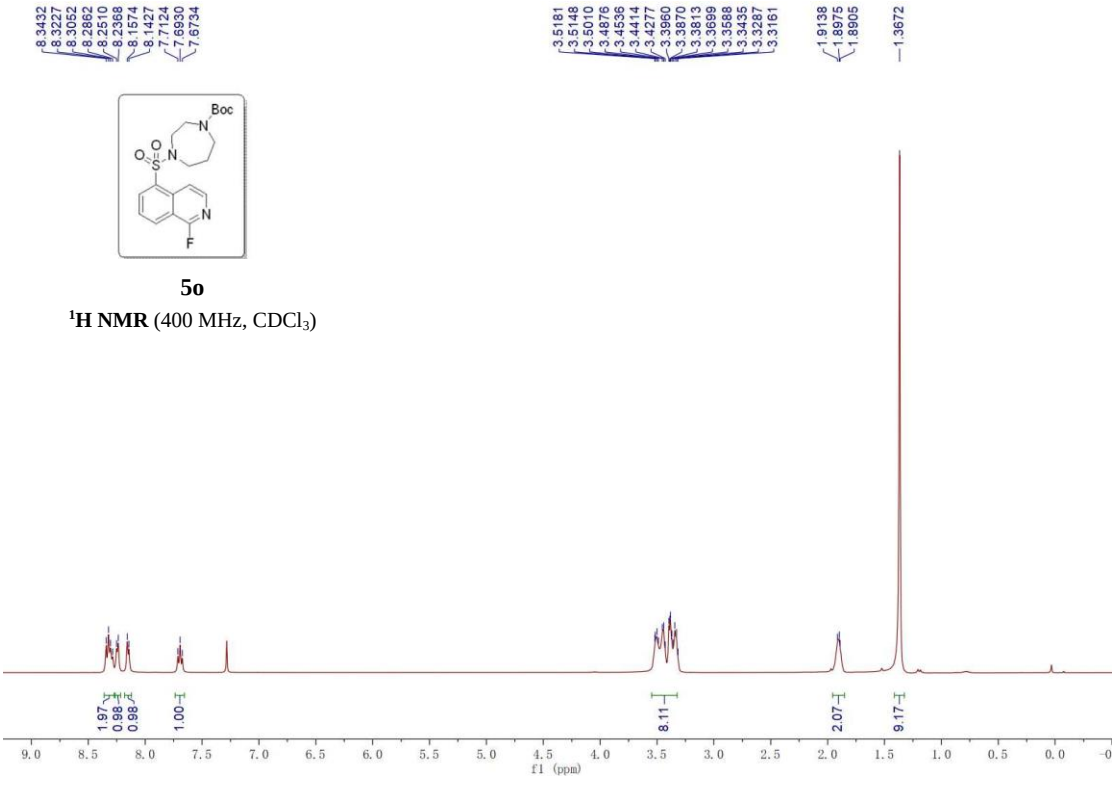
^{13}C NMR (100 MHz, $CDCl_3$)



5n

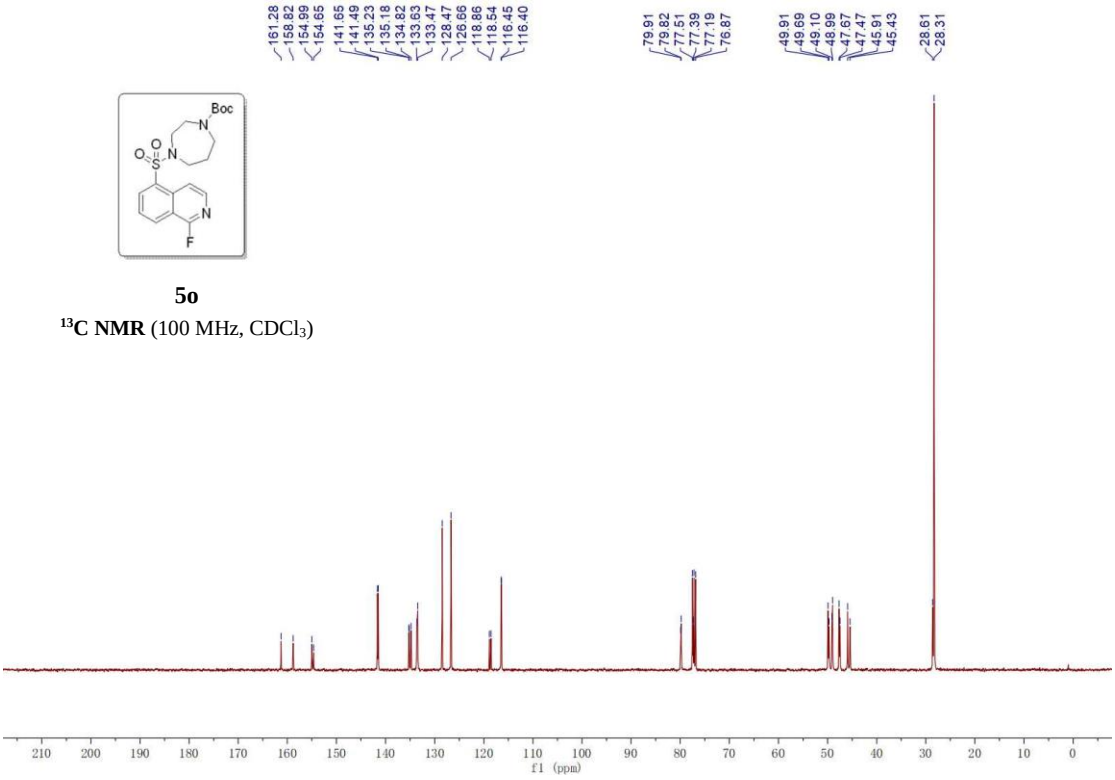
^{19}F NMR (377 MHz, $CDCl_3$)





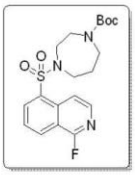
5o

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



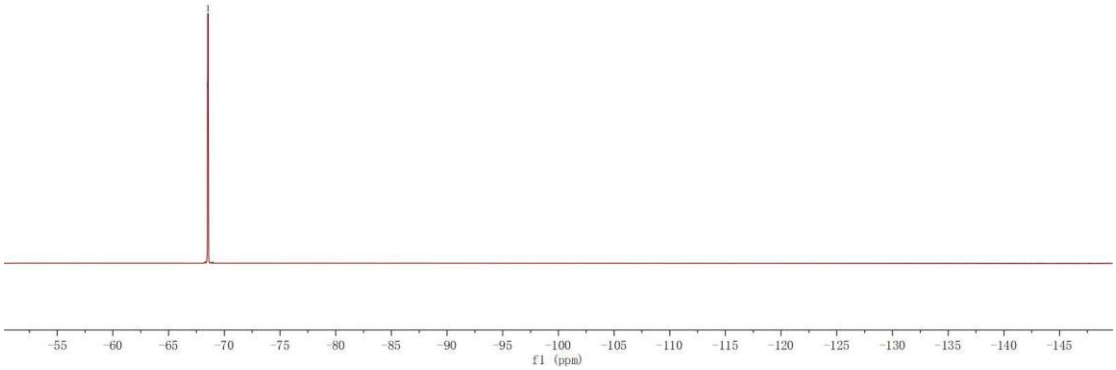
5o

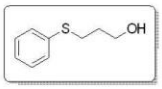
^{13}C NMR (100 MHz, $CDCl_3$)



5o

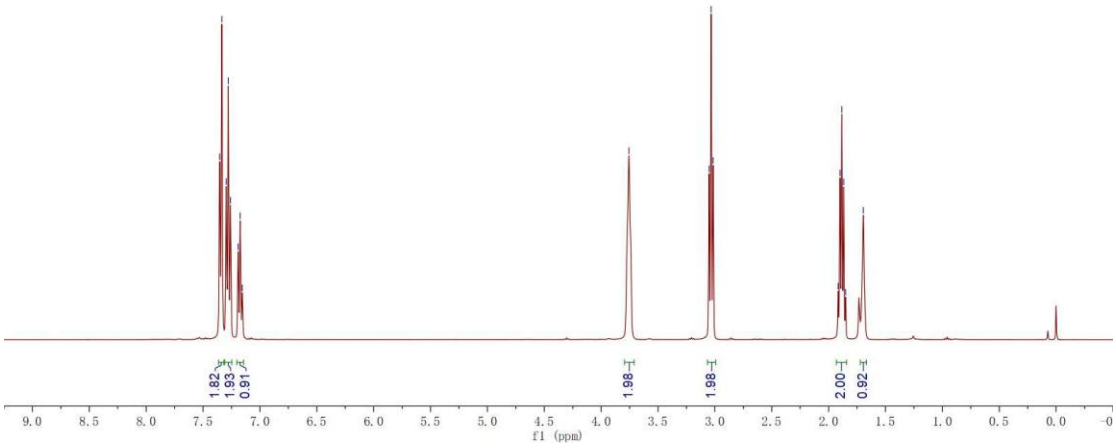
^{19}F NMR (377 MHz, $CDCl_3$)

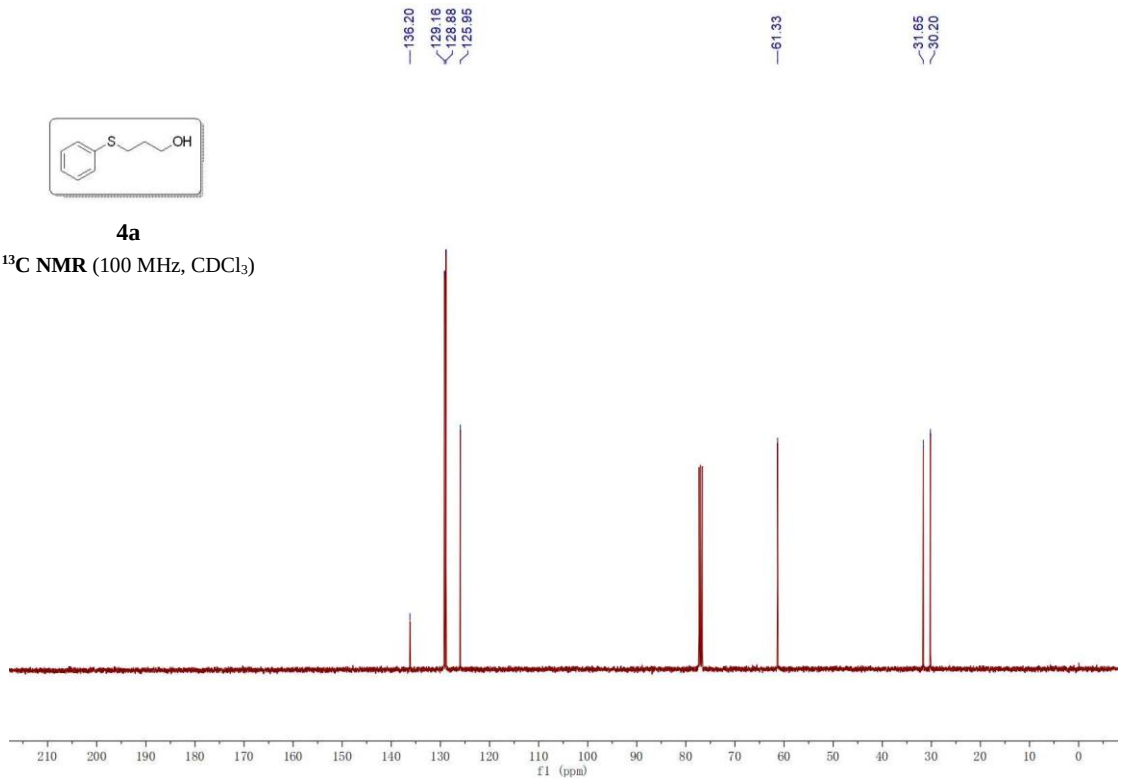




4a

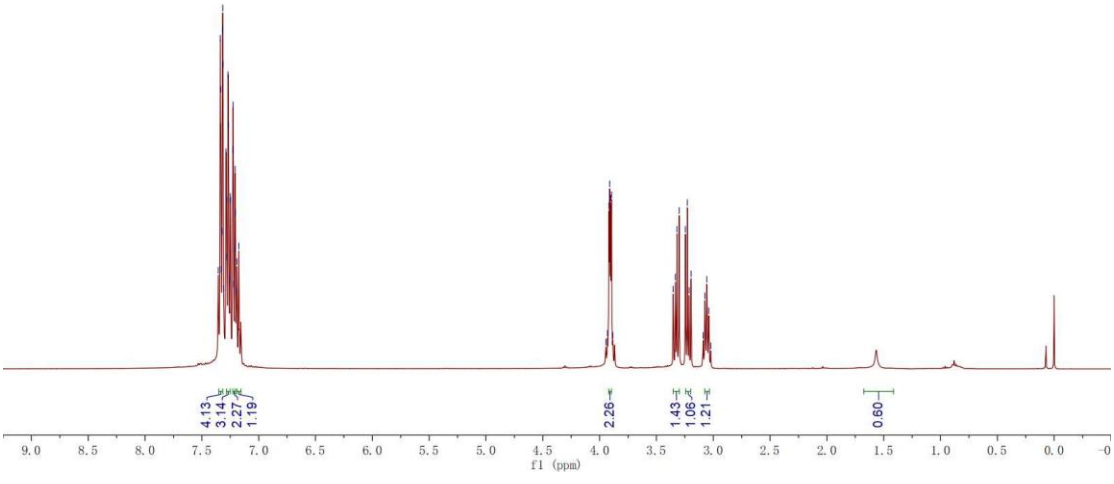
^{1}H NMR (400 MHz, $CDCl_3$)





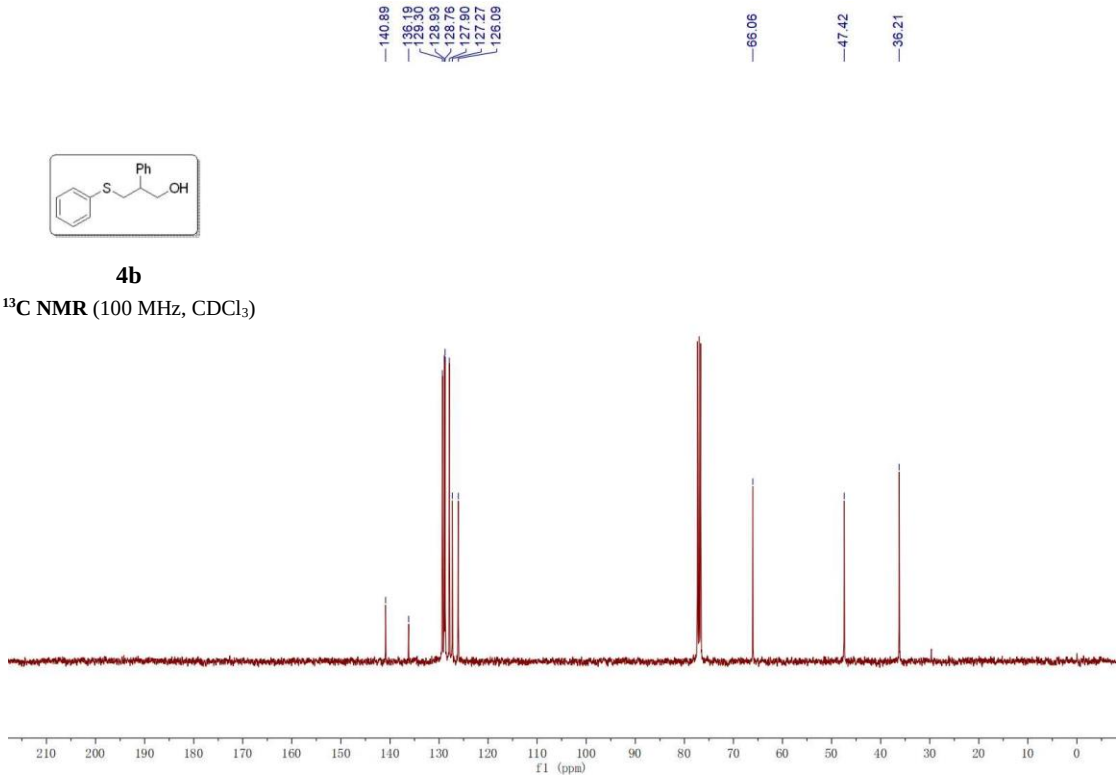
4a

^{13}C NMR (100 MHz, $CDCl_3$)



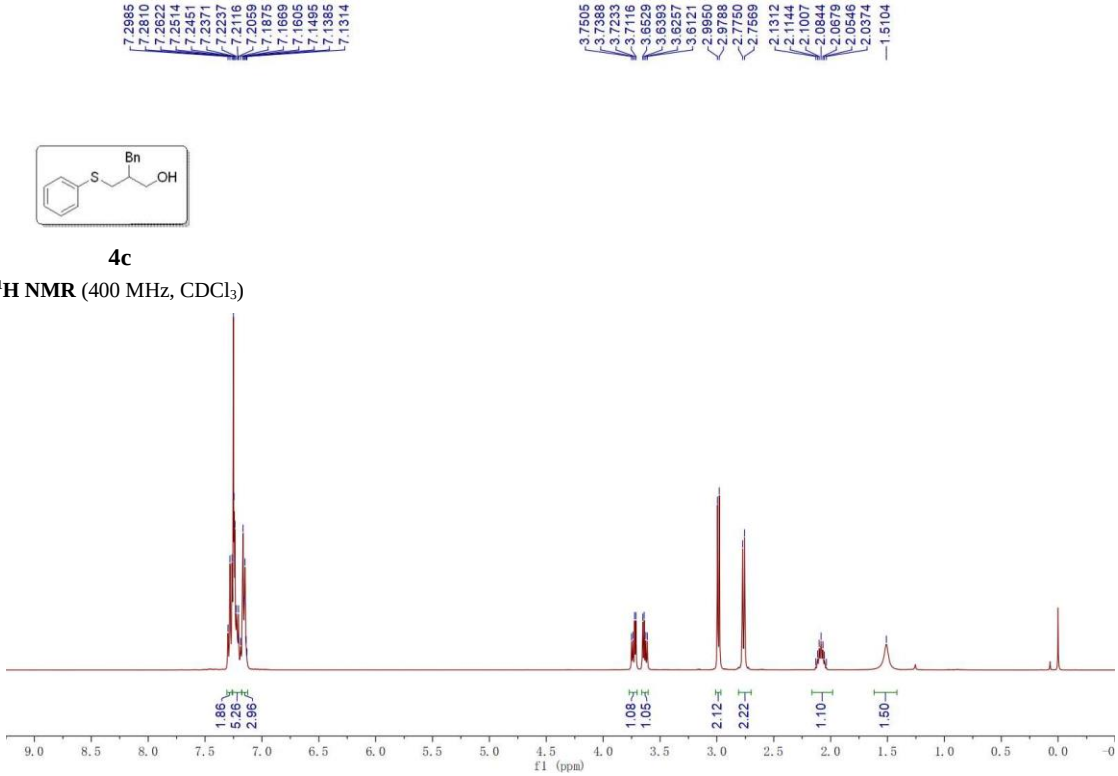
4b

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



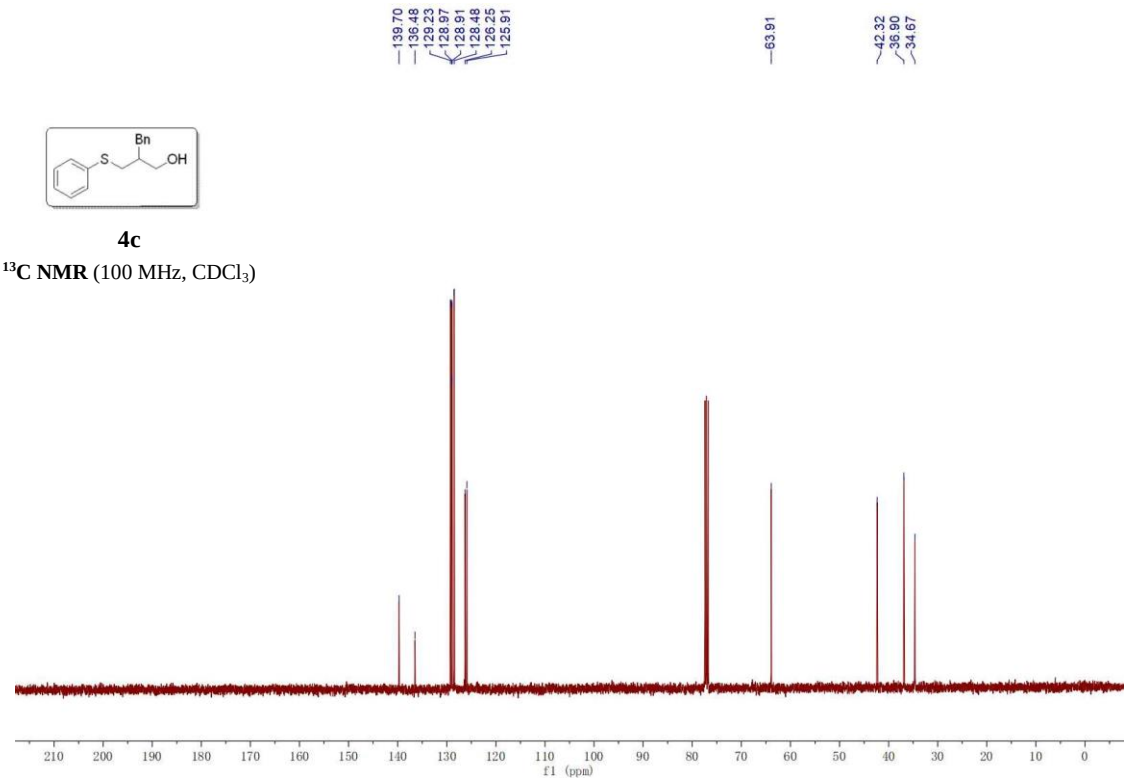
4b

^{13}C NMR (100 MHz, $CDCl_3$)



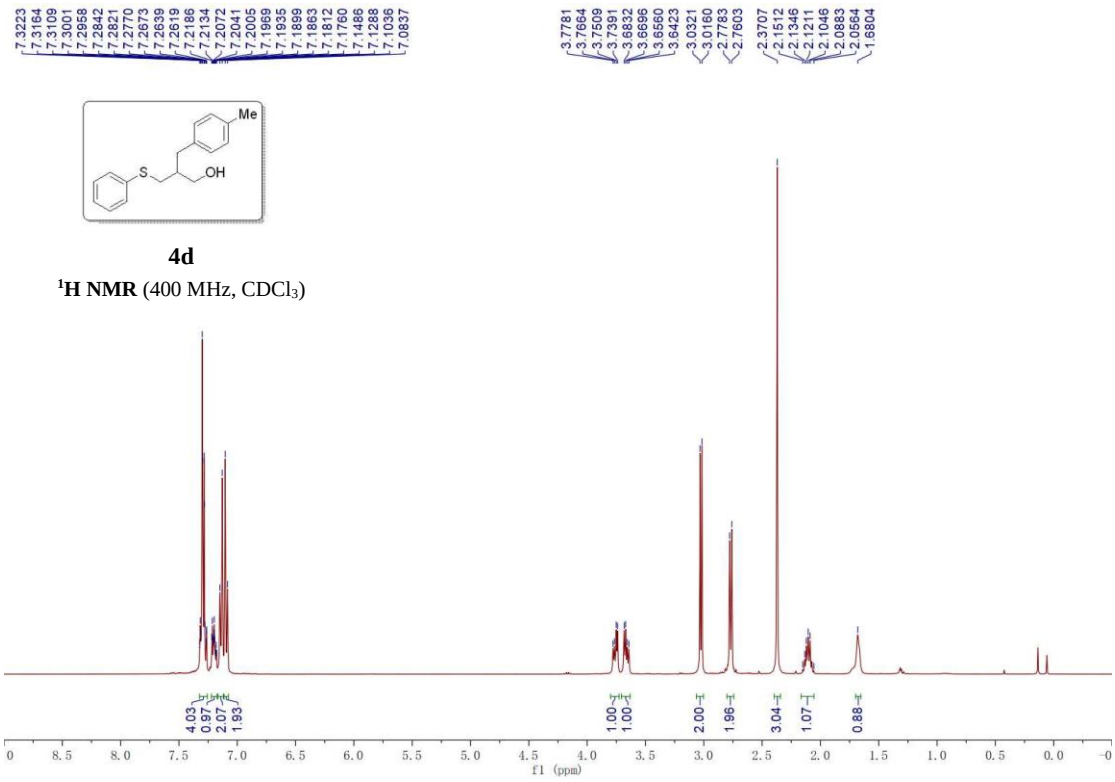
4c

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



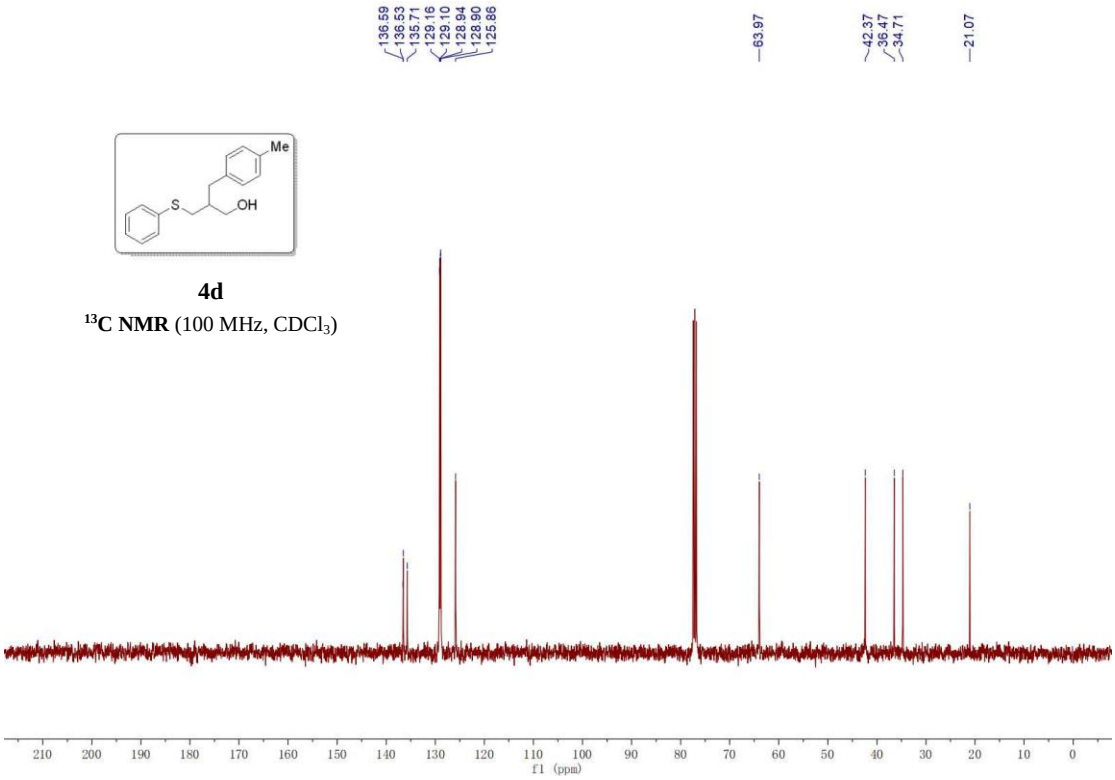
4c

^{13}C NMR (100 MHz, $CDCl_3$)



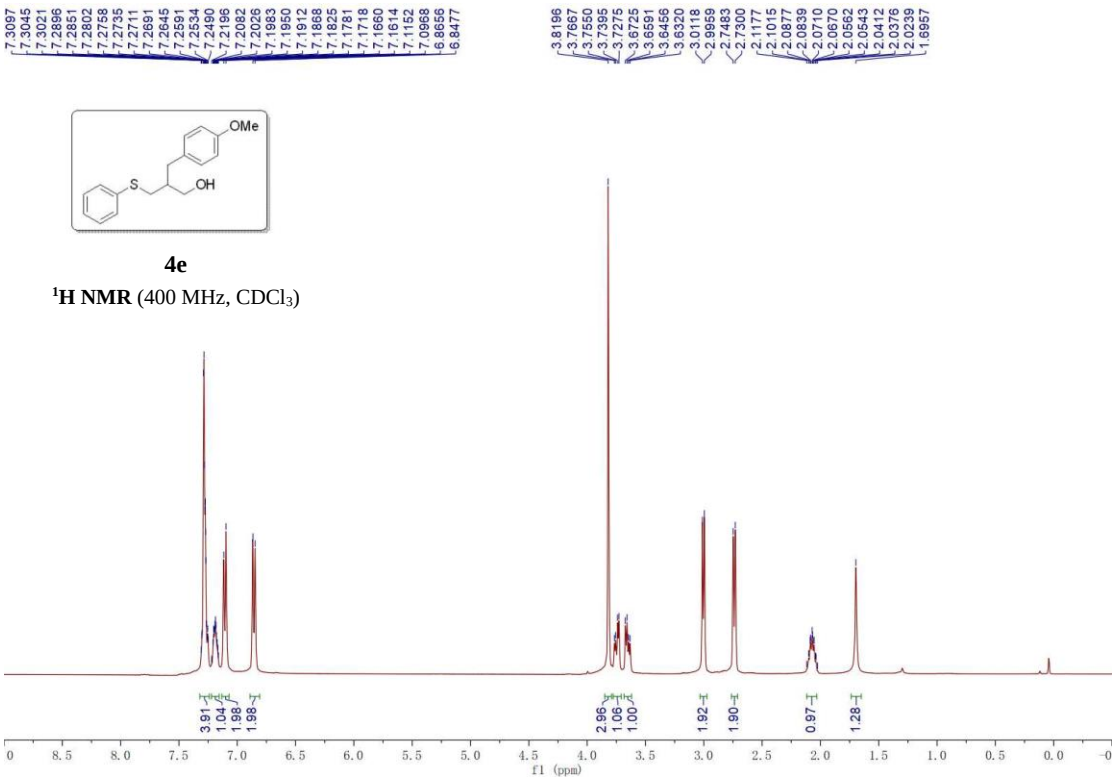
4d

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



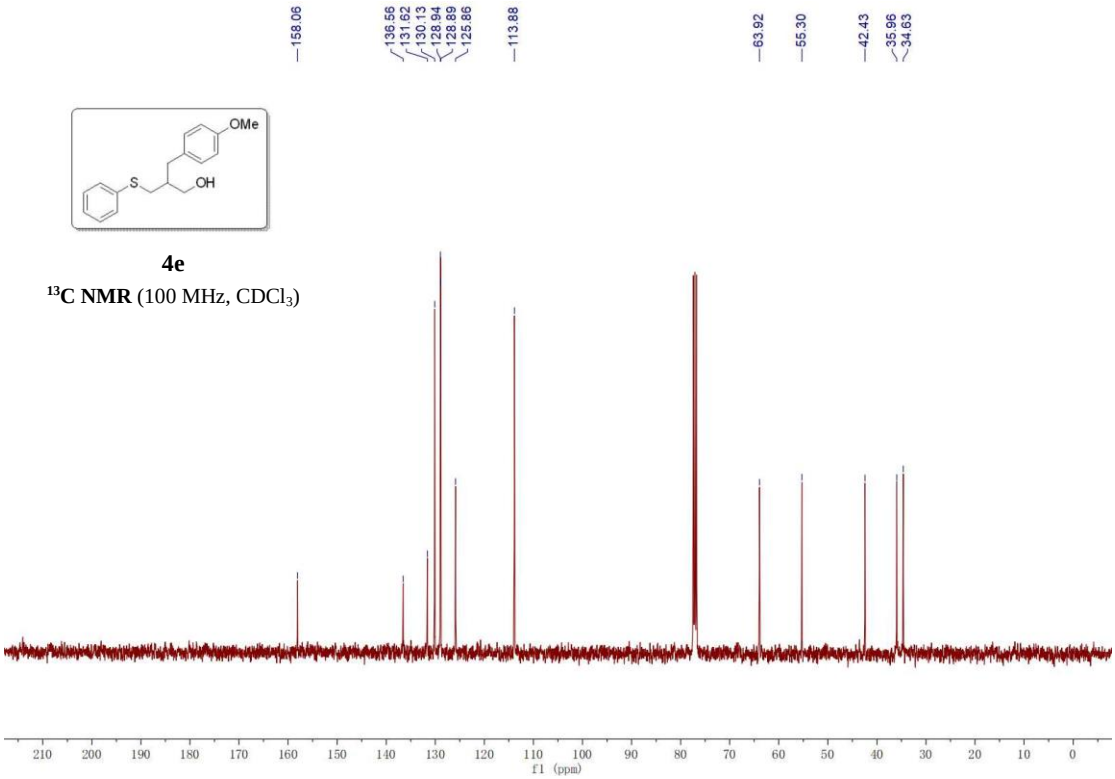
4d

^{13}C NMR (100 MHz, $CDCl_3$)



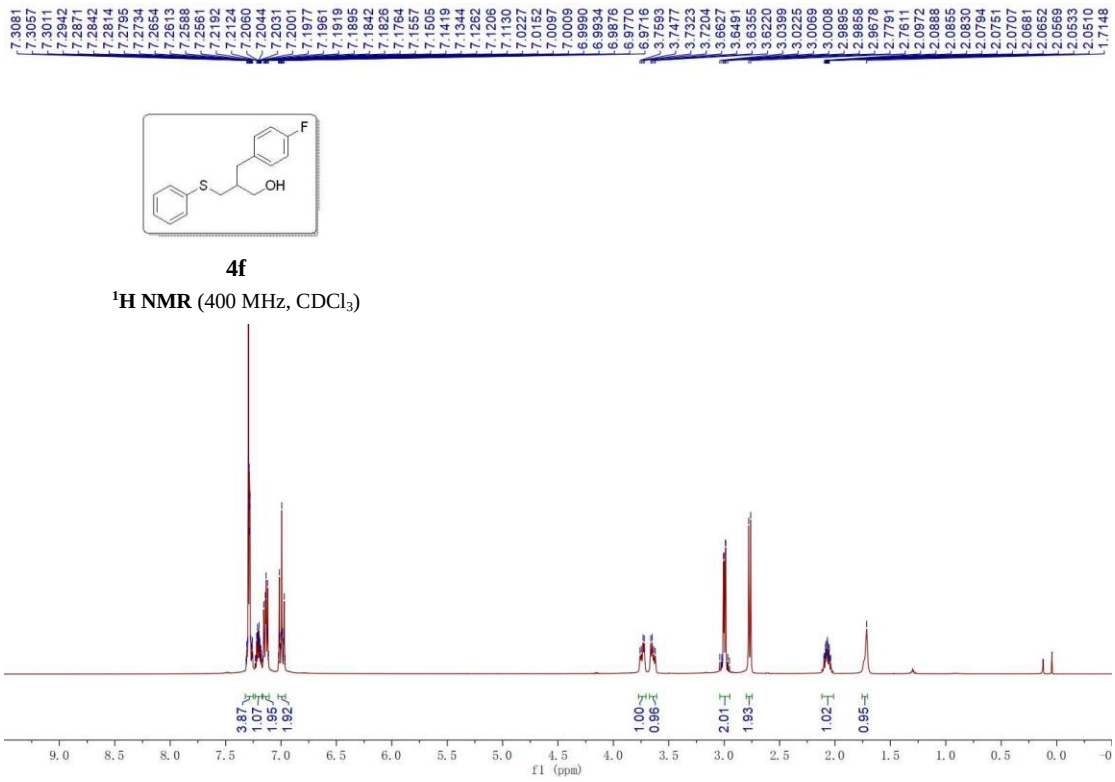
4e

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



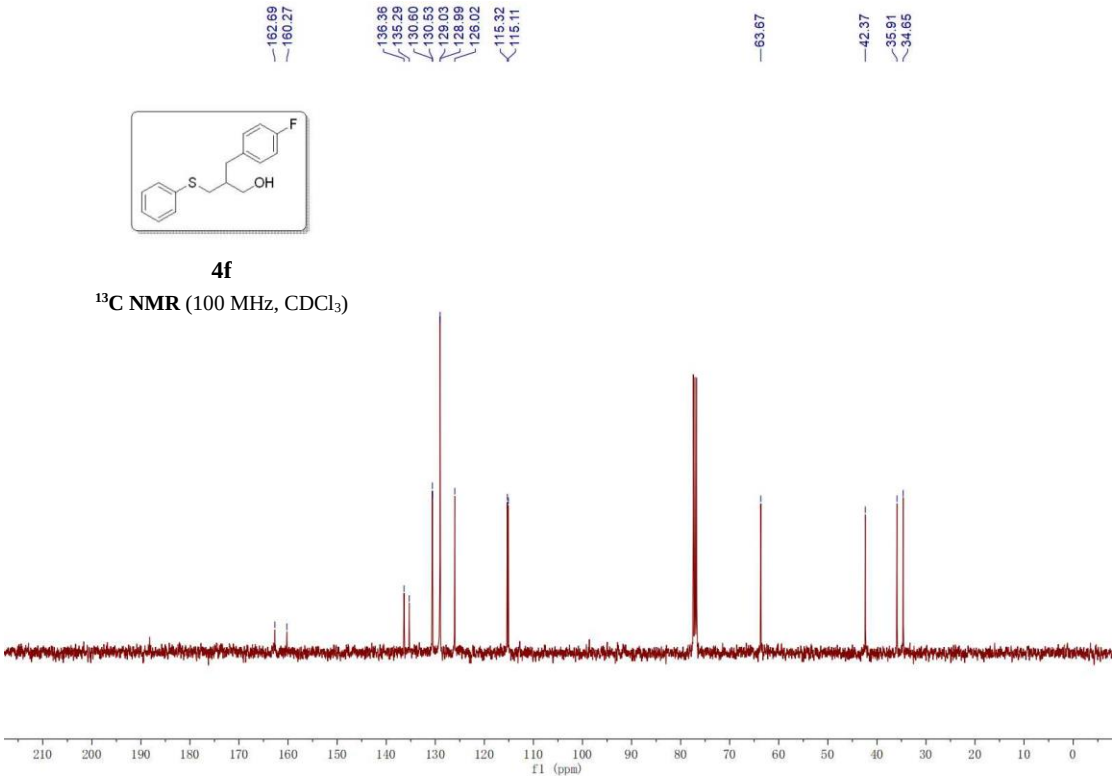
4e

^{13}C NMR (100 MHz, $CDCl_3$)



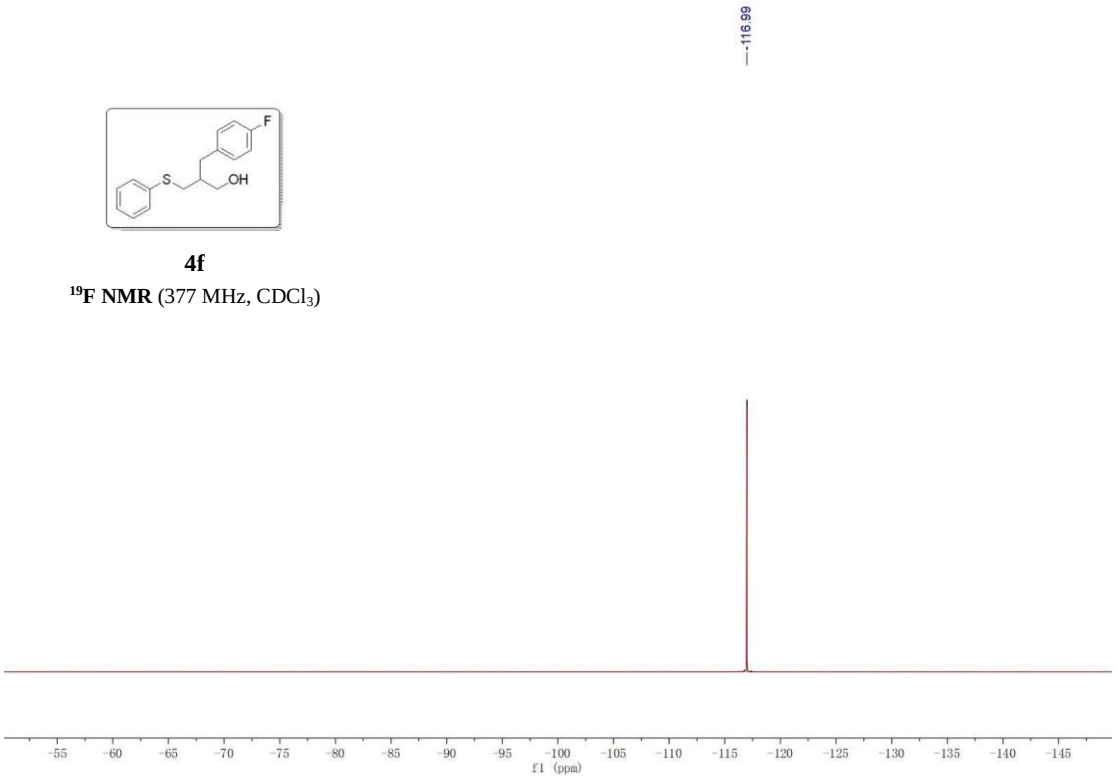
4f

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



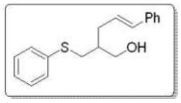
4f

^{13}C NMR (100 MHz, $CDCl_3$)



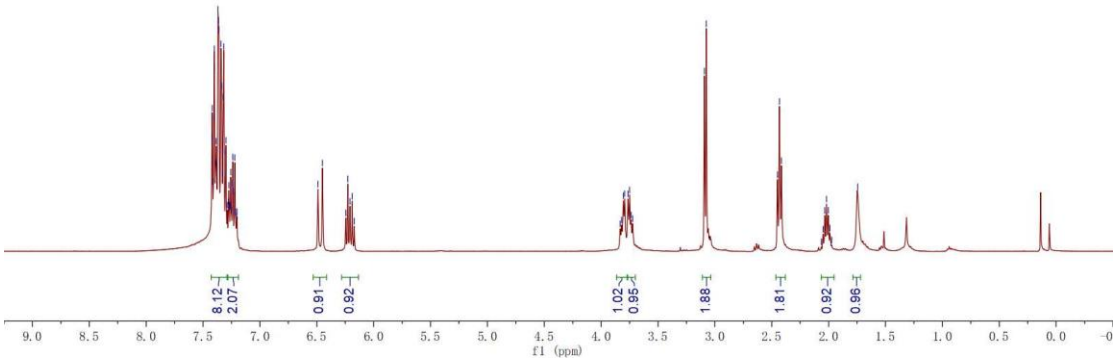
4f

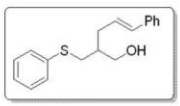
^{19}F NMR (377 MHz, $CDCl_3$)



4g

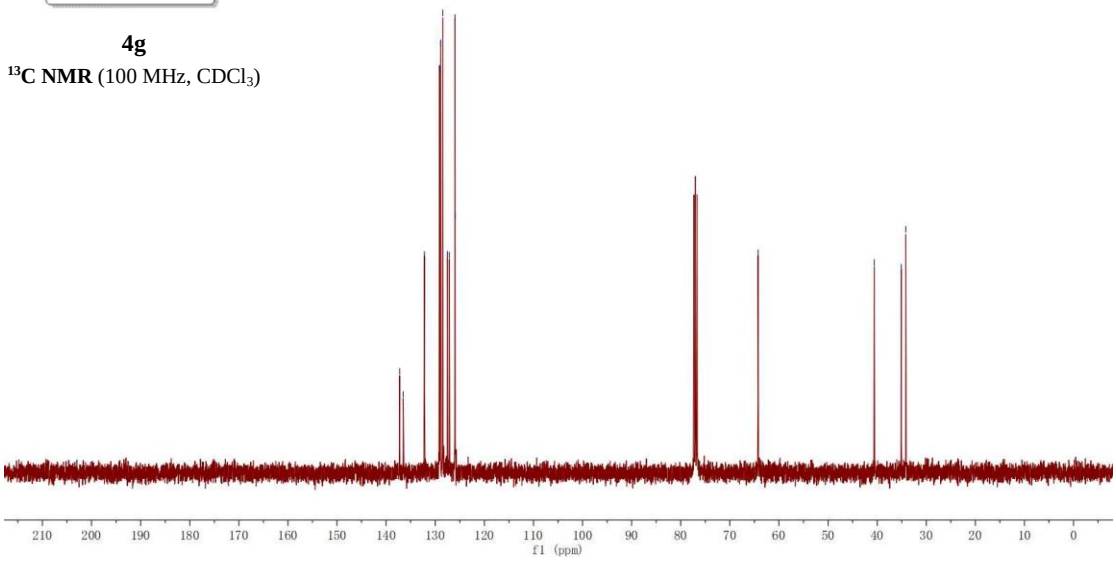
^{1}H NMR (400 MHz, $CDCl_3$)

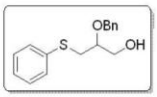




4g

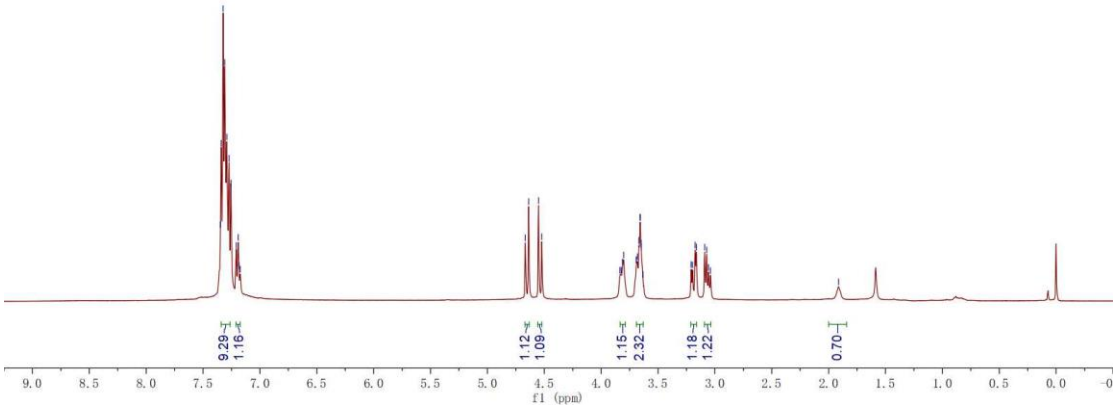
^{13}C NMR (100 MHz, $CDCl_3$)

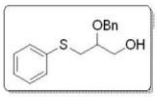




4h

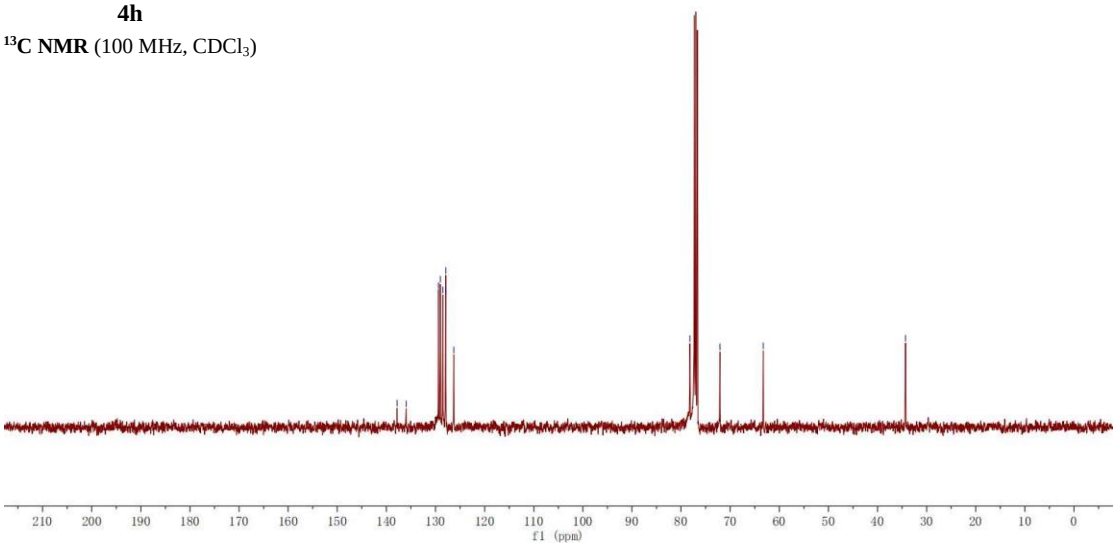
^{1}H NMR (400 MHz, $CDCl_3$)

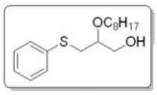




4h

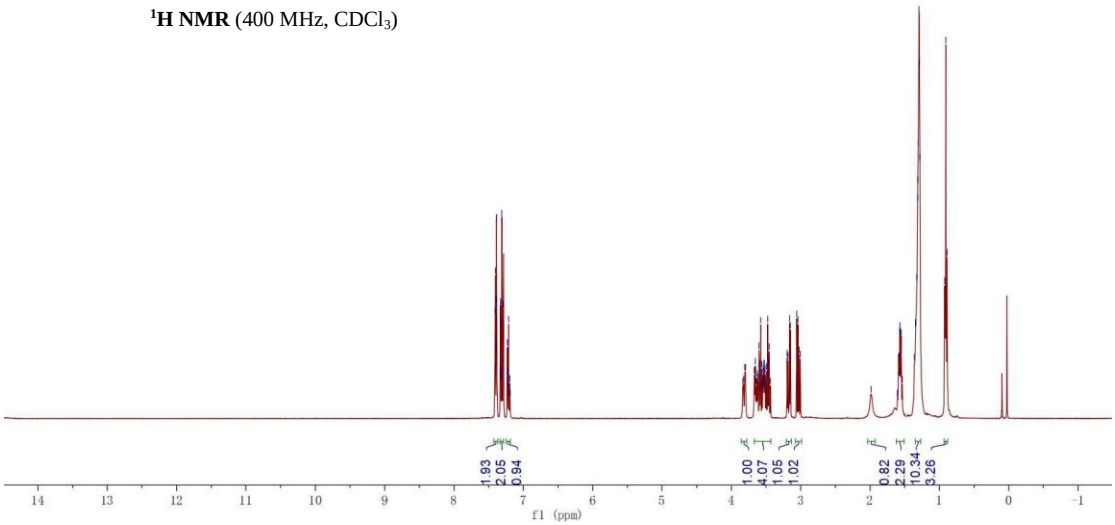
^{13}C NMR (100 MHz, $CDCl_3$)

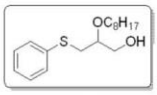




4i

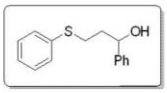
^{1}H NMR (400 MHz, $CDCl_3$)





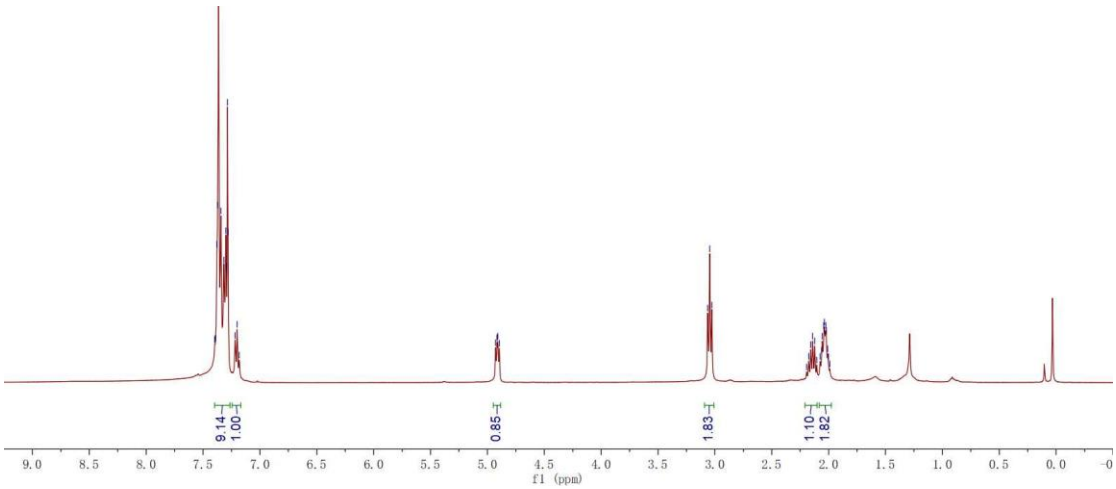
4i

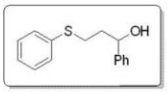
^{13}C NMR (100 MHz, $CDCl_3$)



4j

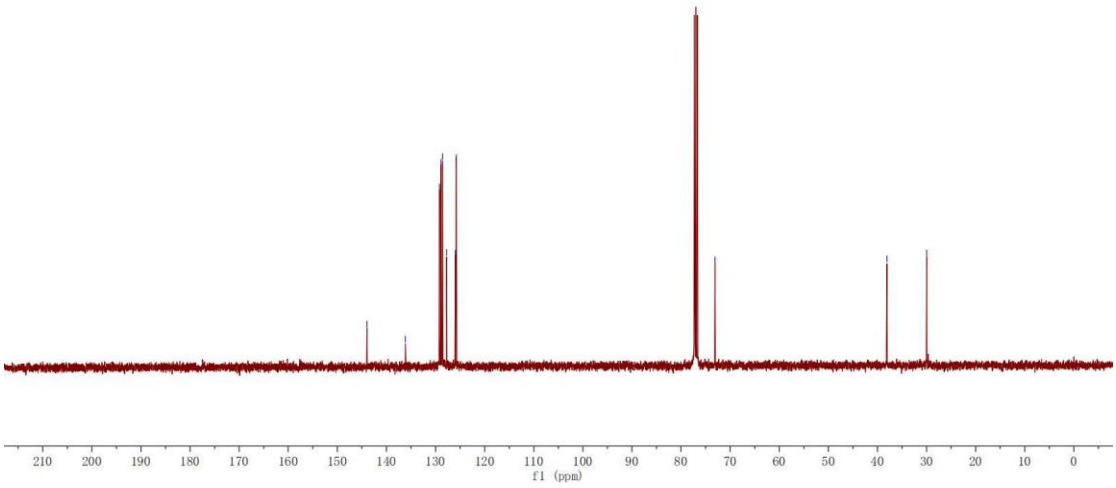
^{1}H NMR (400 MHz, $CDCl_3$)

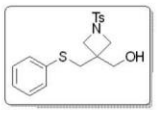




4j

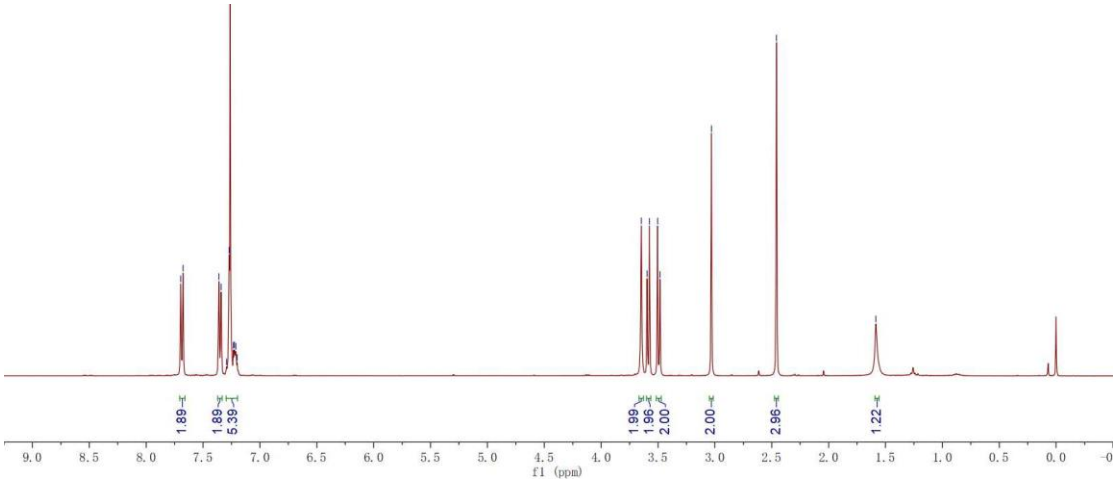
^{13}C NMR (100 MHz, $CDCl_3$)

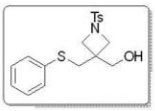




4k

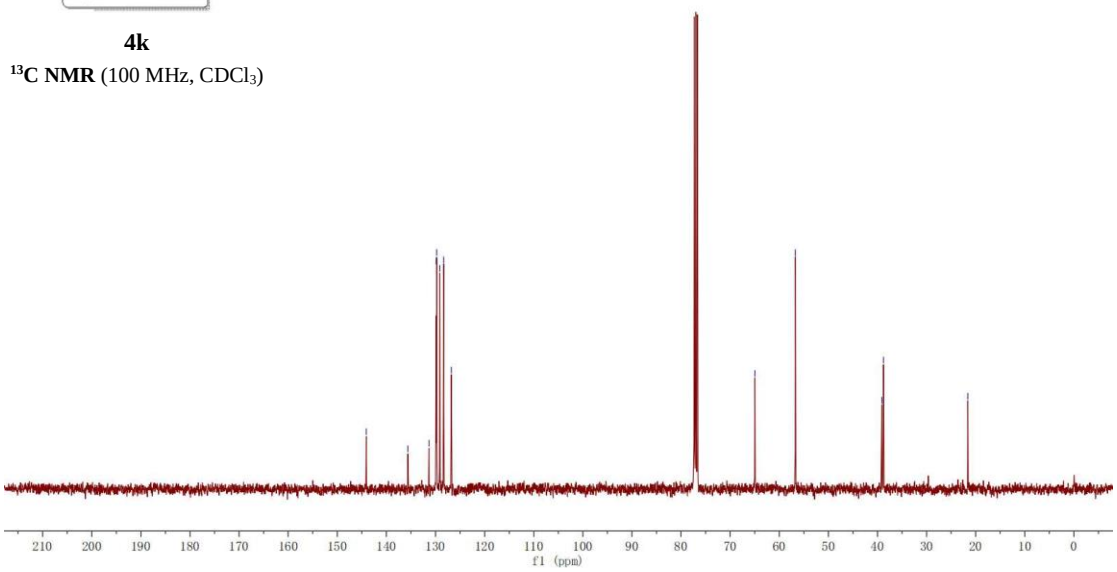
[1]H NMR (400 MHz, $CDCl_3$)

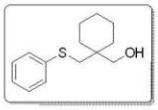




4k

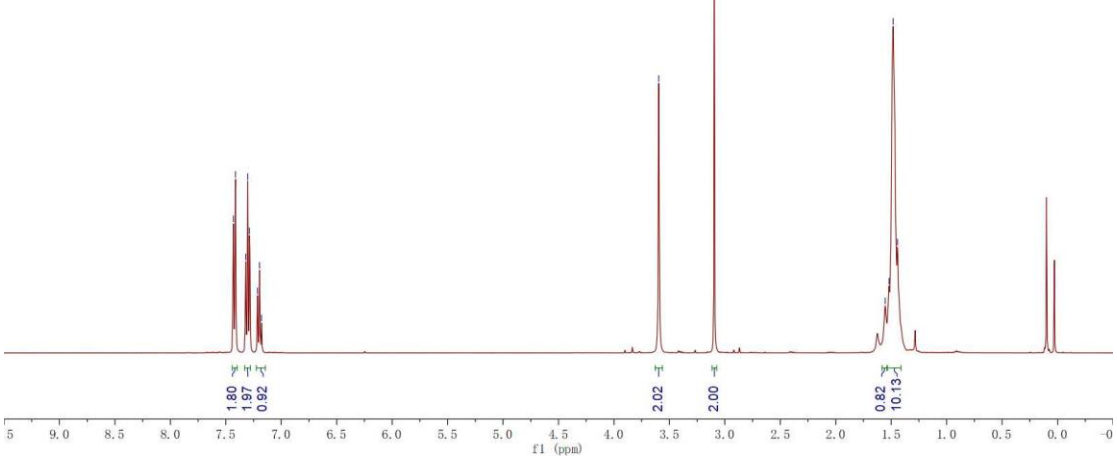
[13]C NMR (100 MHz, $CDCl_3$)

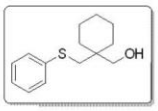




4l

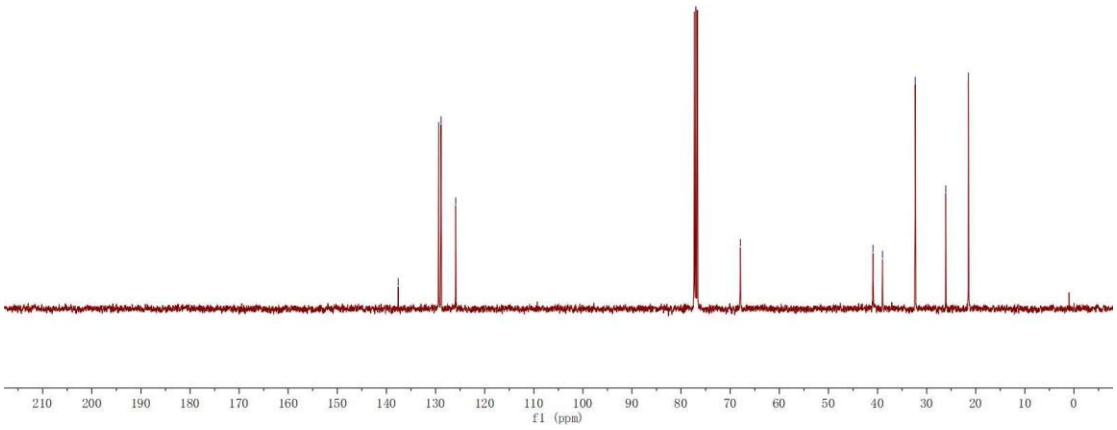
^{1}H NMR (400 MHz, $CDCl_3$)

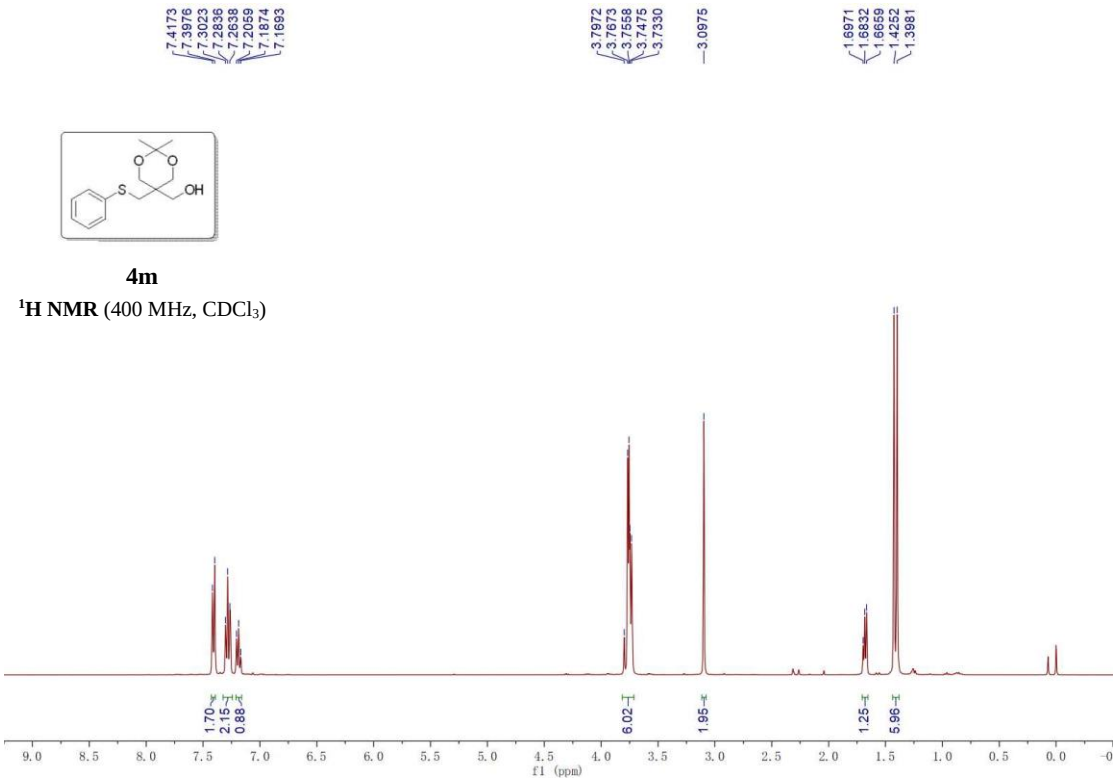




4l

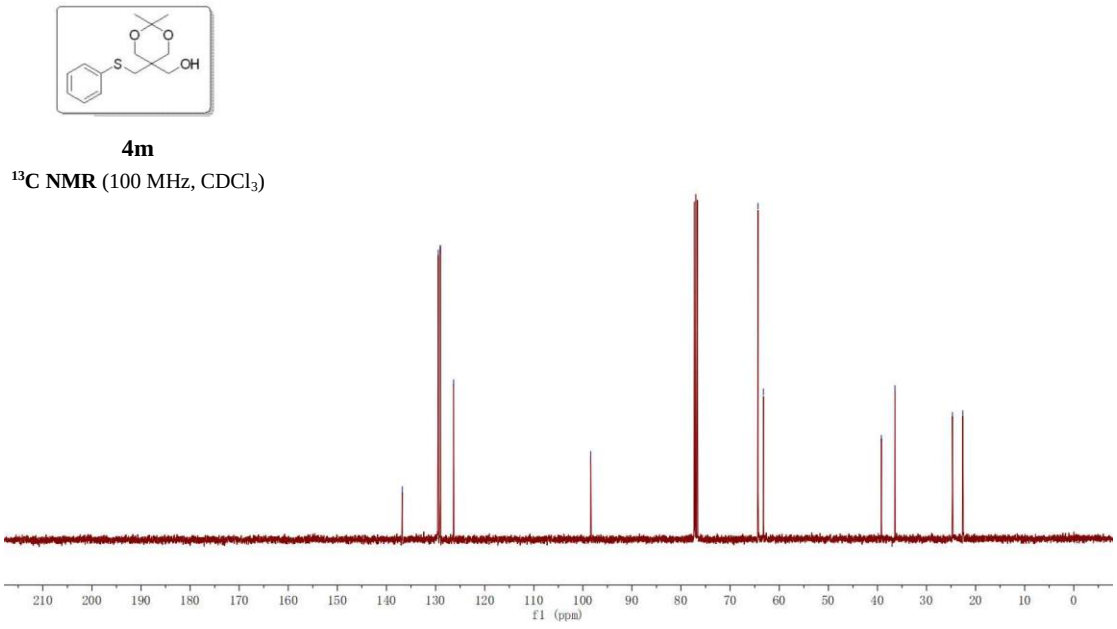
^{13}C NMR (100 MHz, $CDCl_3$)





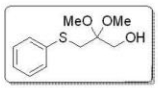
4m

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



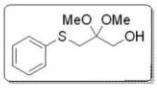
4m

^{13}C NMR (100 MHz, $CDCl_3$)



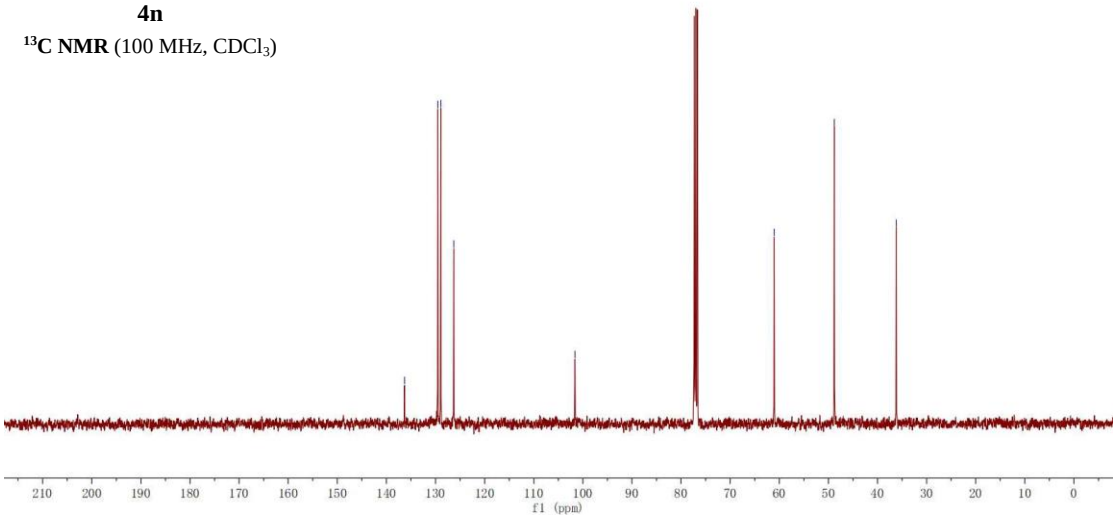
4n

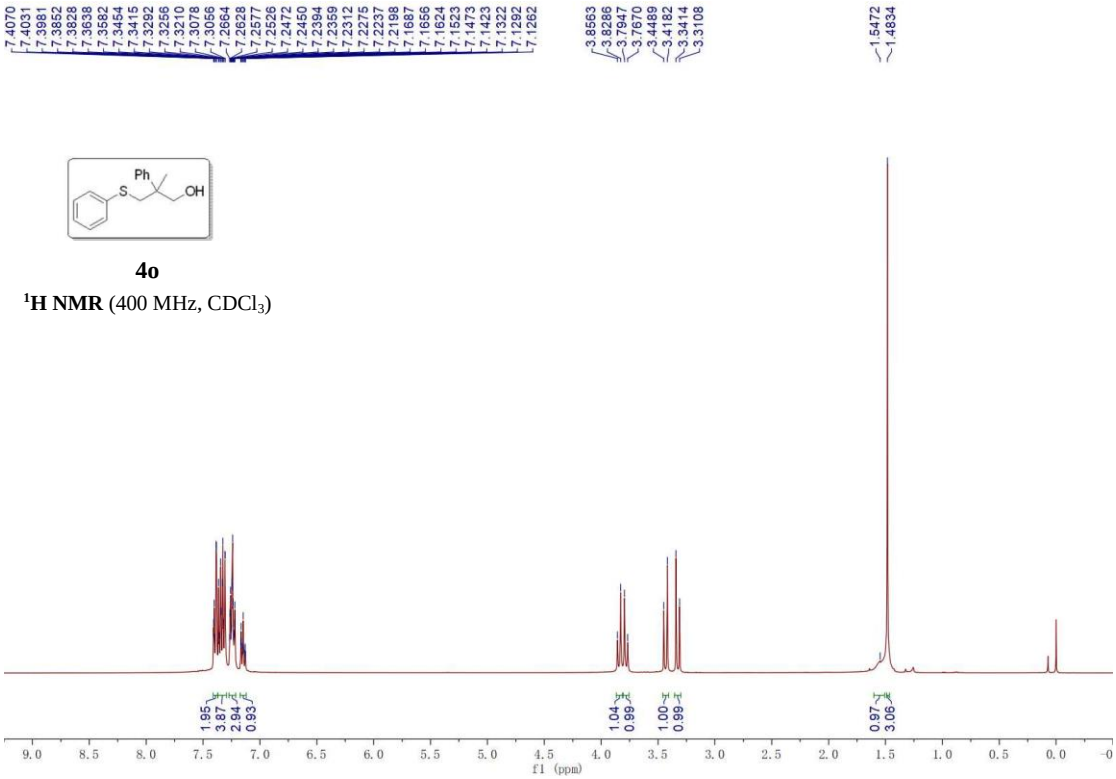
^{1}H NMR (400 MHz, $CDCl_3$)



4n

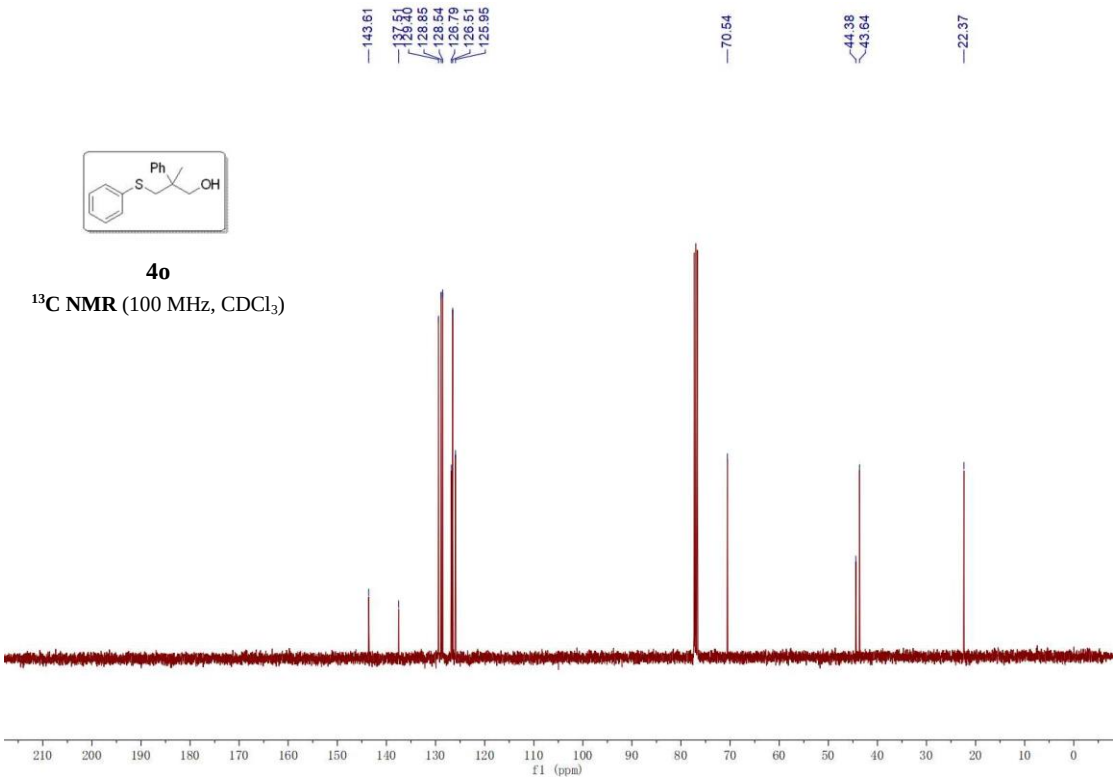
^{13}C NMR (100 MHz, $CDCl_3$)





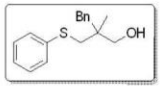
4o

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



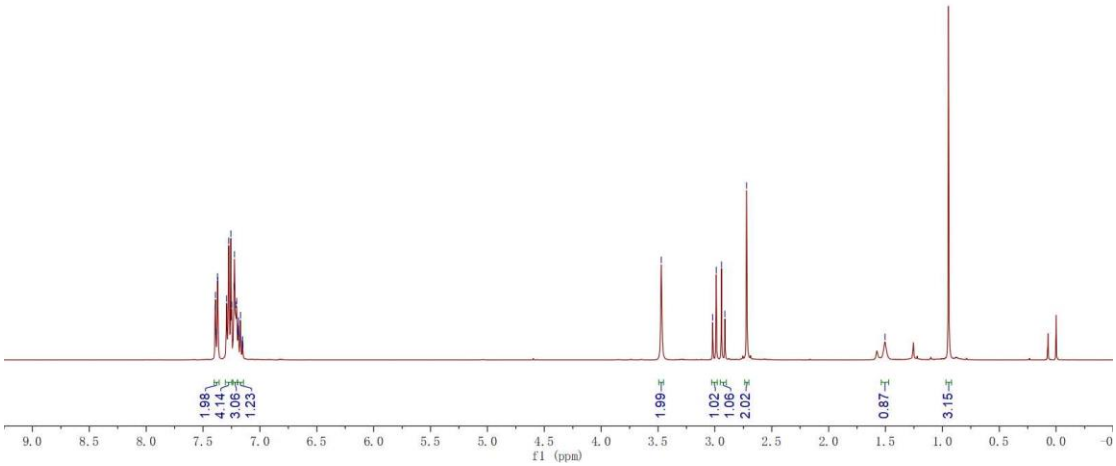
4o

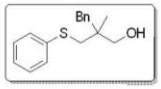
^{13}C NMR (100 MHz, $CDCl_3$)



4p

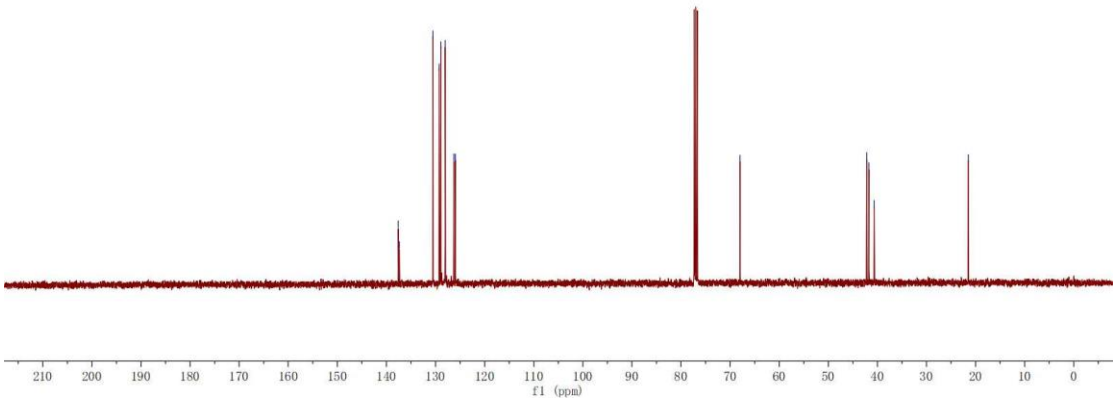
^{1}H NMR (400 MHz, $CDCl_3$)

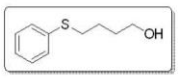




4p

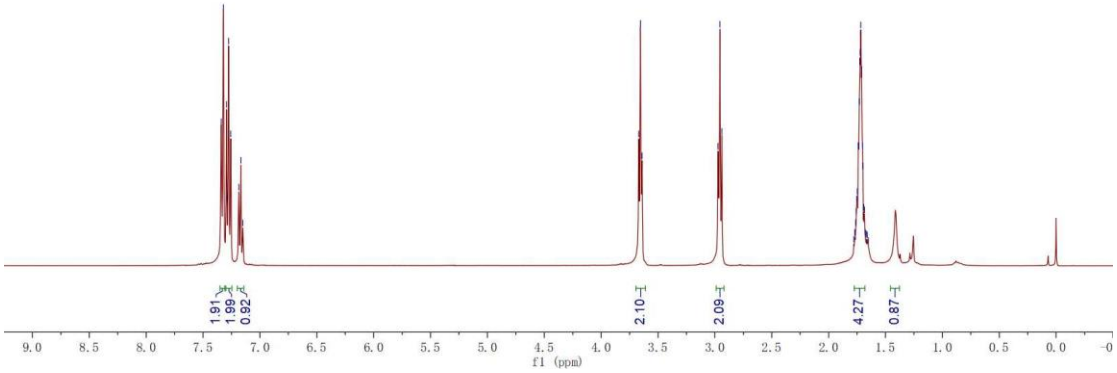
^{13}C NMR (100 MHz, $CDCl_3$)

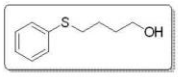




4q

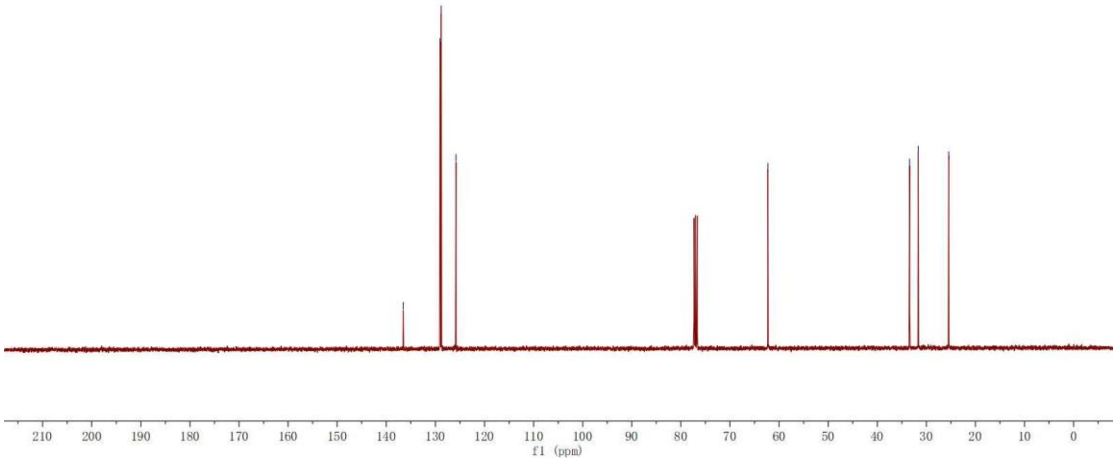
^{1}H NMR (400 MHz, $CDCl_3$)

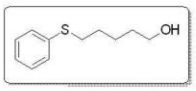




4q

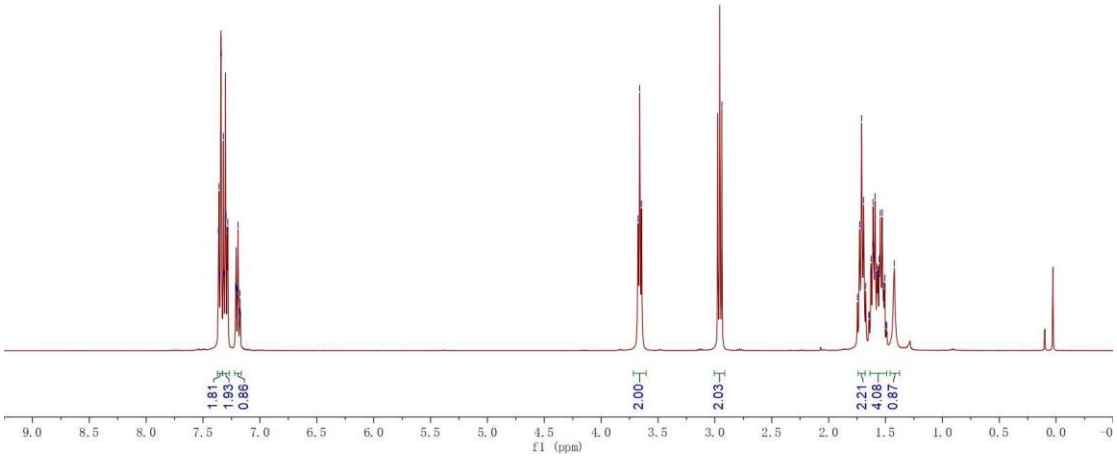
^{13}C NMR (100 MHz, $CDCl_3$)

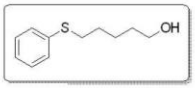




4r

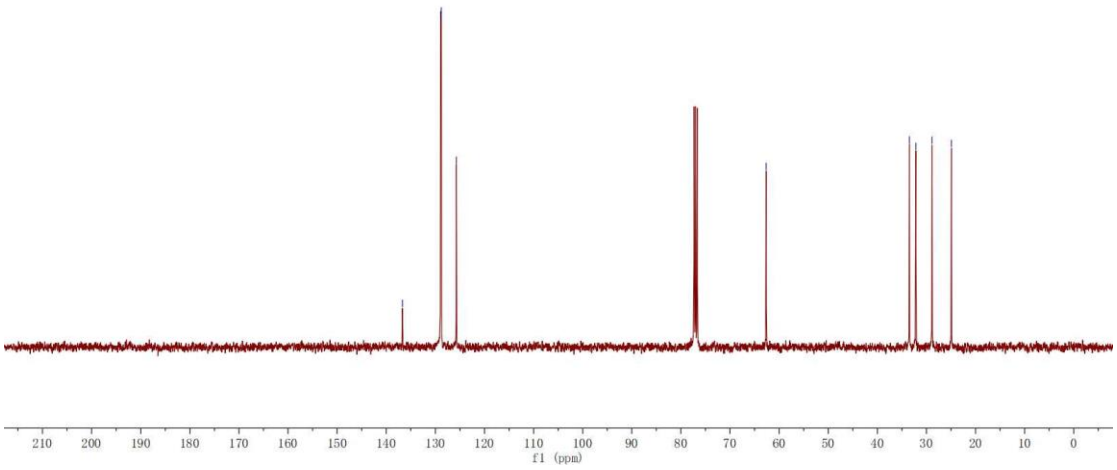
^{1}H NMR (400 MHz, $CDCl_3$)

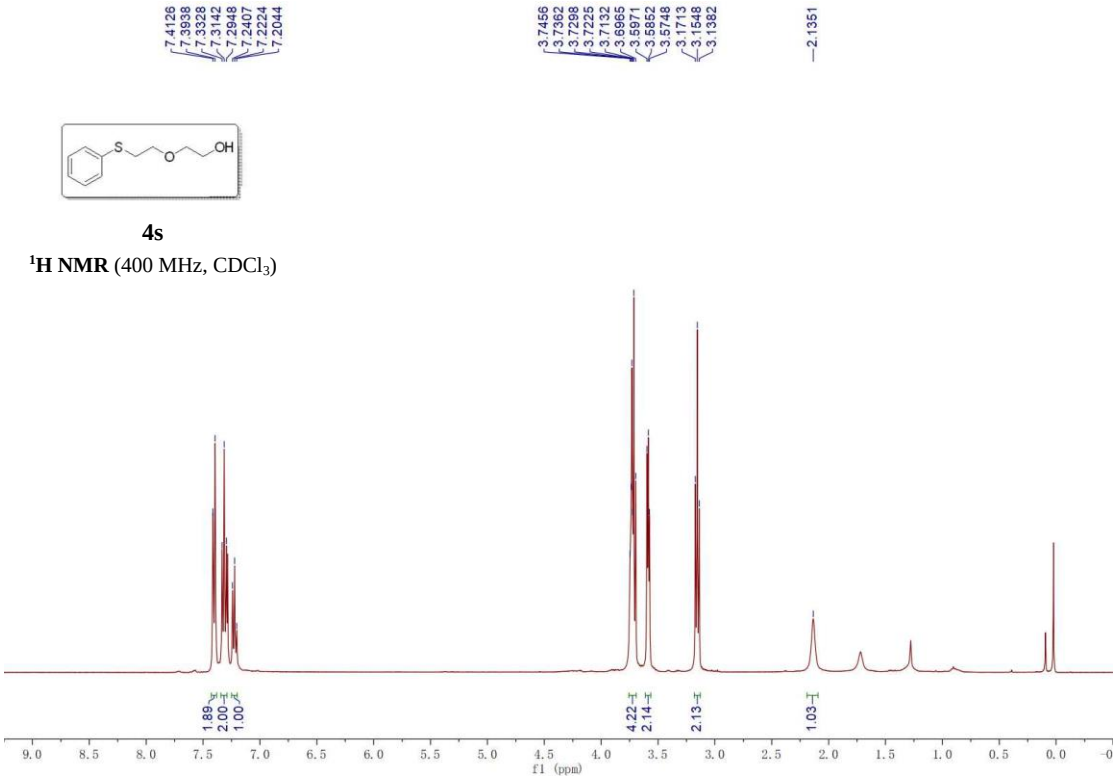




4r

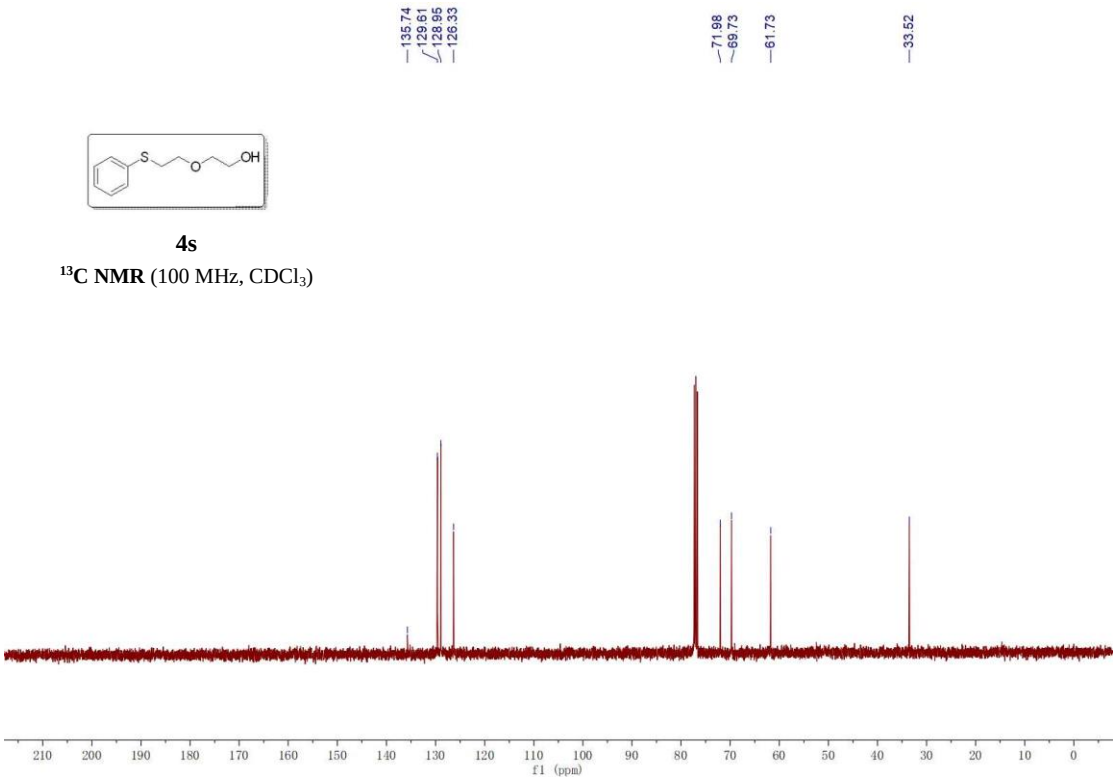
^{13}C NMR (100 MHz, $CDCl_3$)





4s

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

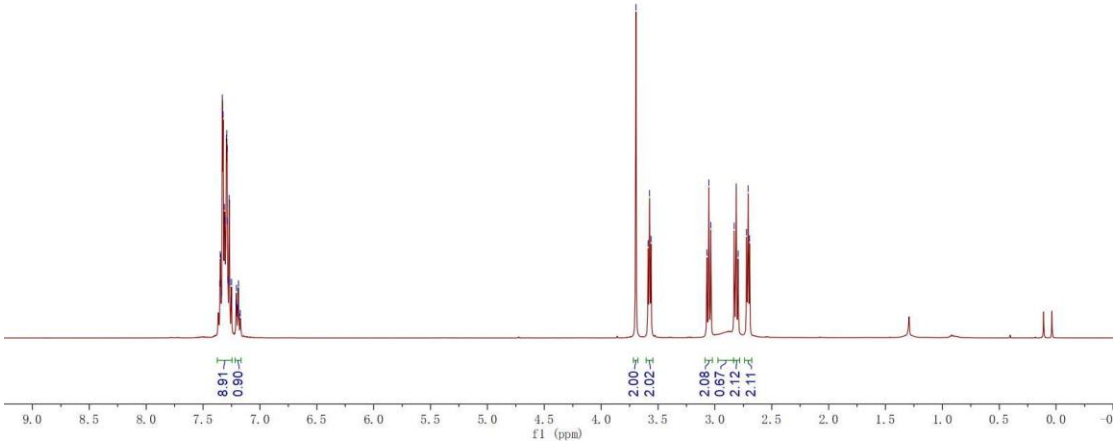


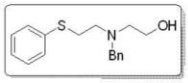
4s

^{13}C NMR (100 MHz, $CDCl_3$)

4t

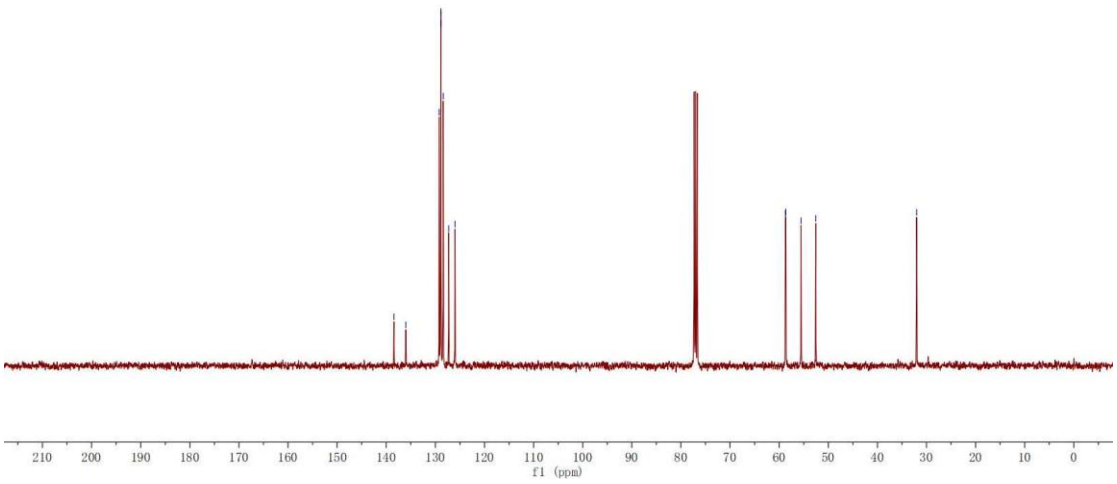
^{1}H NMR (400 MHz, $CDCl_3$)

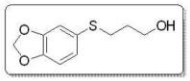




4t

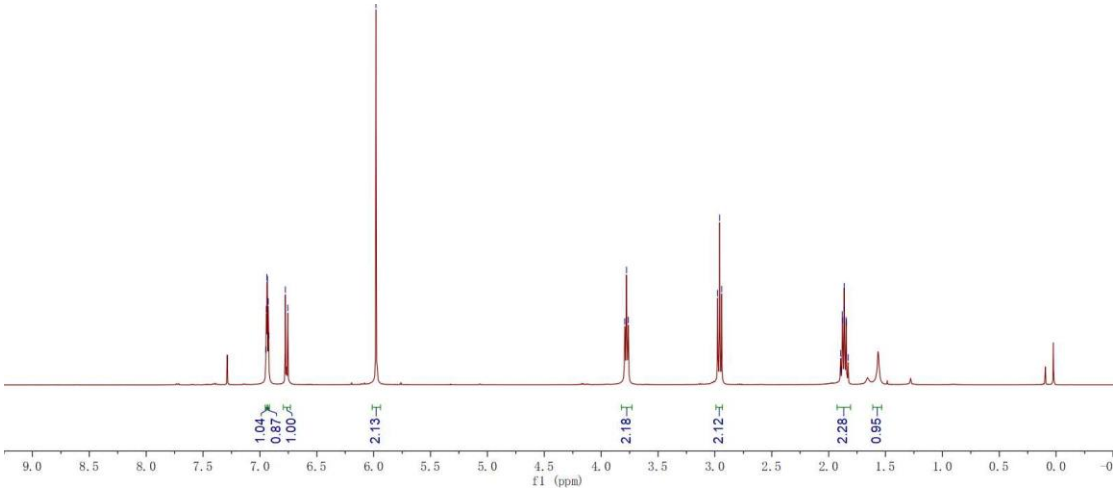
^{13}C NMR (100 MHz, $CDCl_3$)

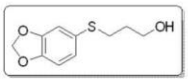




4u

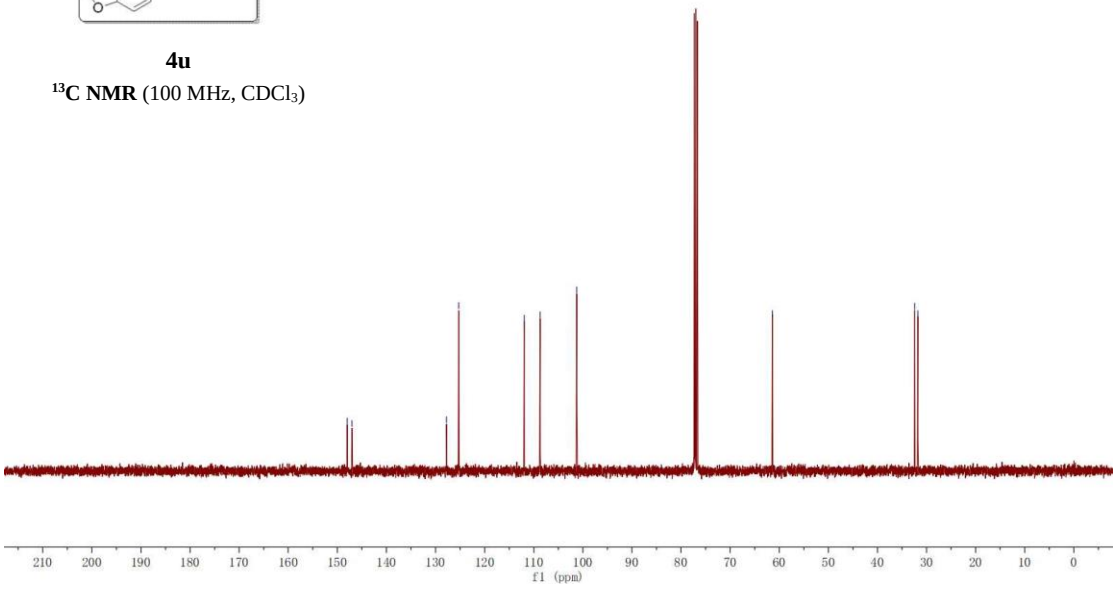
^{1}H NMR (400 MHz, $CDCl_3$)

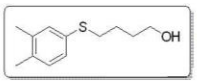




4u

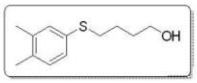
^{13}C NMR (100 MHz, $CDCl_3$)





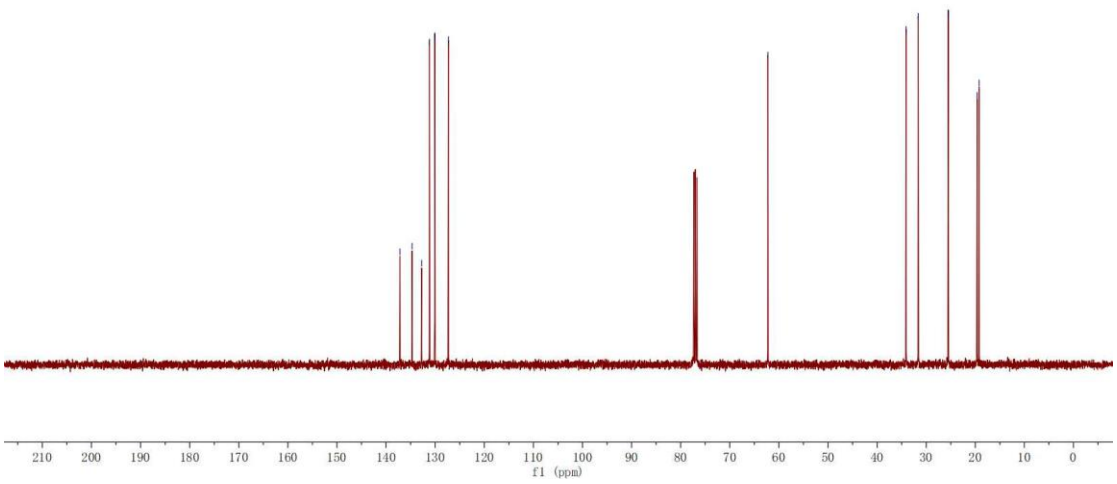
4v

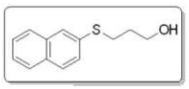
^{1}H NMR (400 MHz, $CDCl_3$)



4v

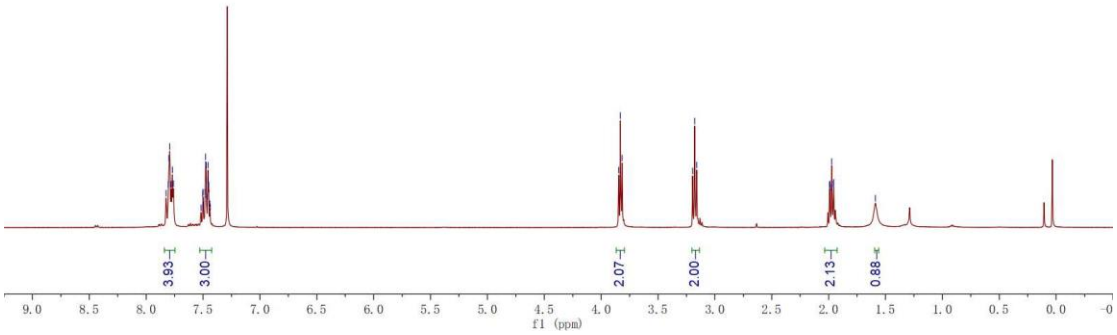
^{13}C NMR (100 MHz, $CDCl_3$)

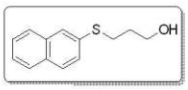




4w

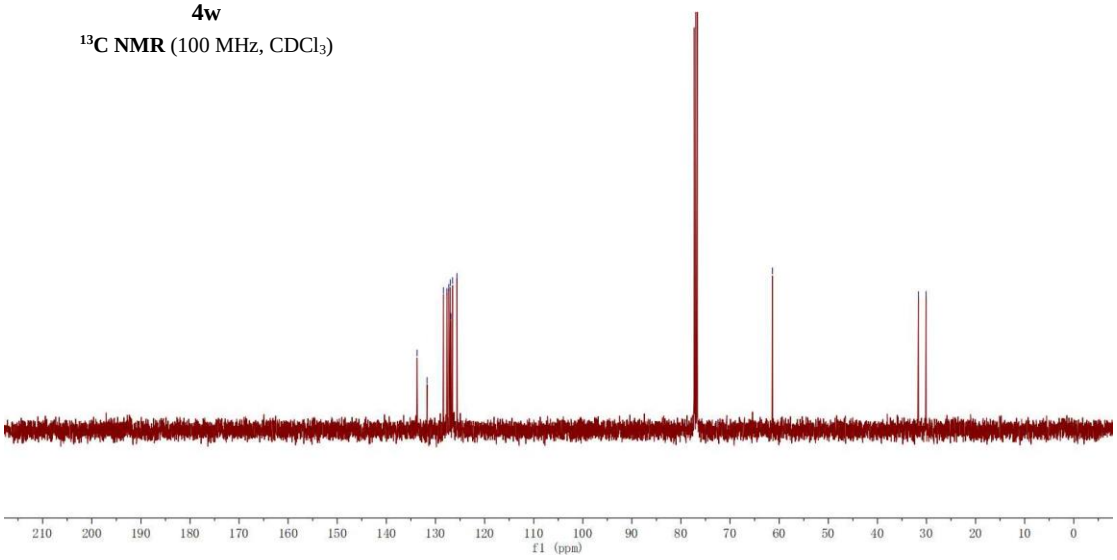
^{1}H NMR (400 MHz, $CDCl_3$)

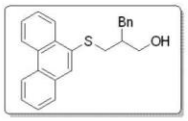




4w

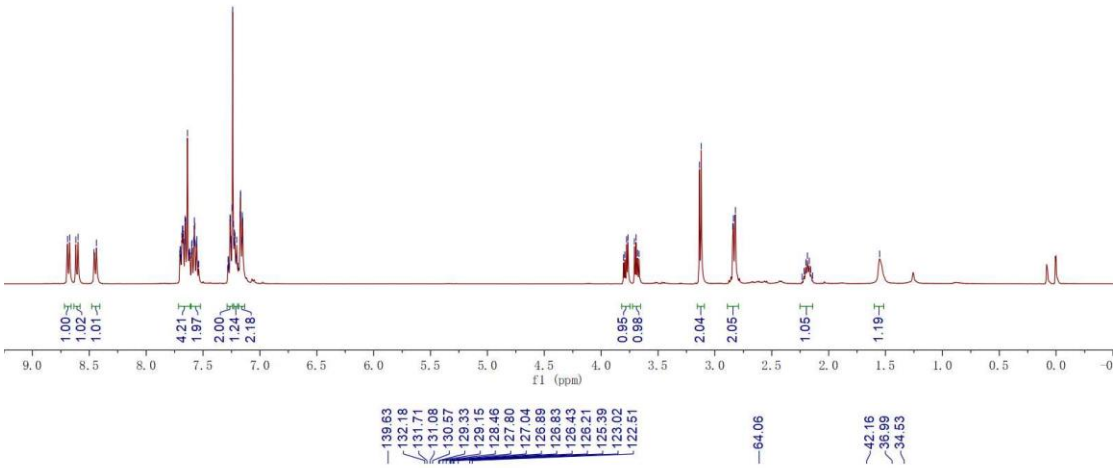
^{13}C NMR (100 MHz, $CDCl_3$)





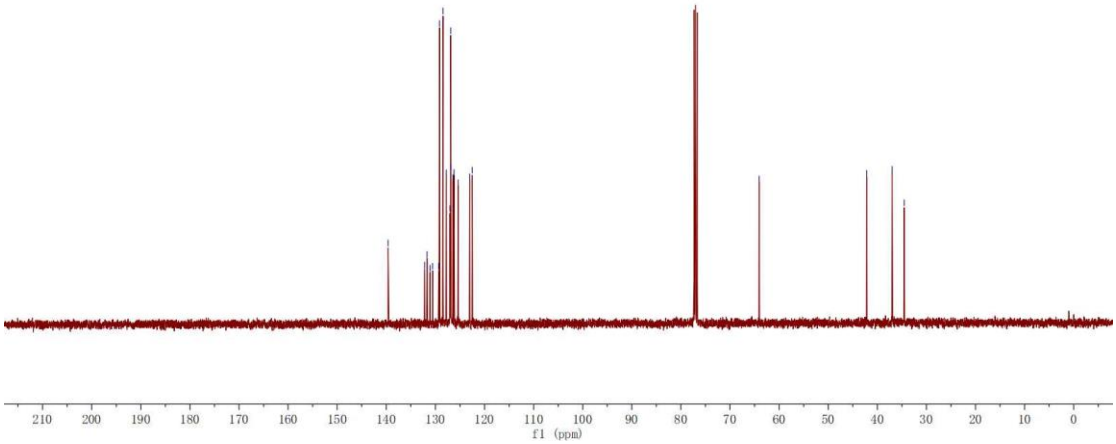
4x

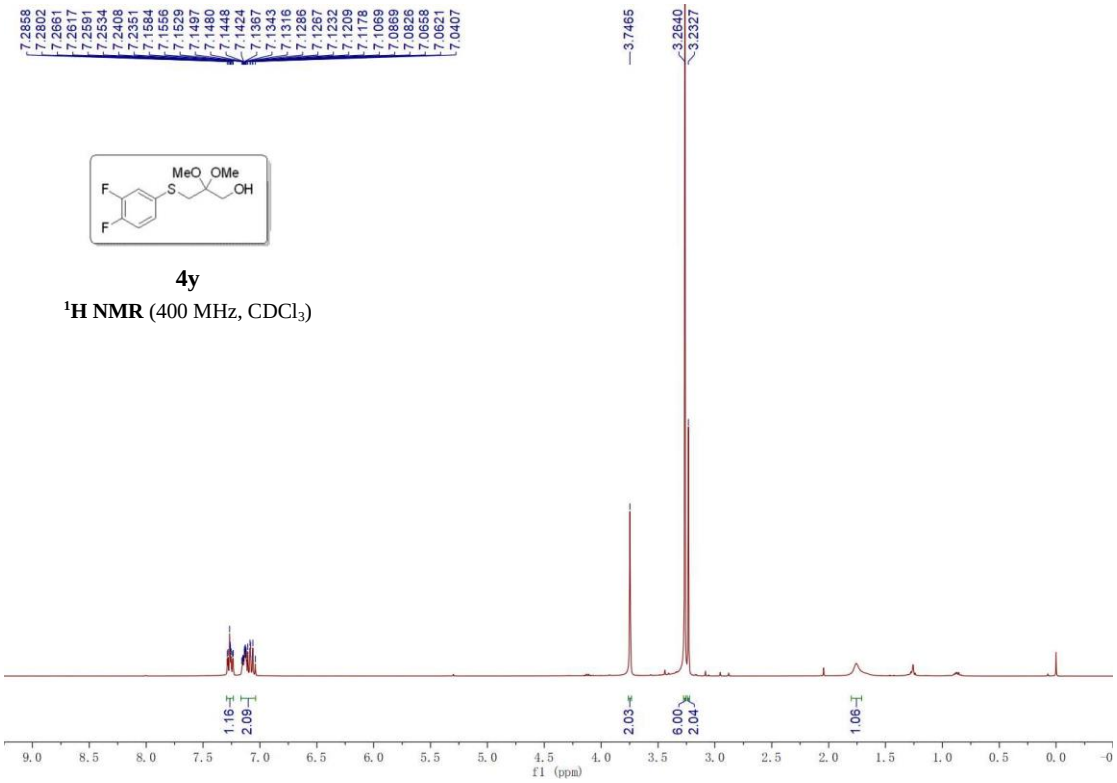
^{1}H NMR (400 MHz, $CDCl_3$)



4x

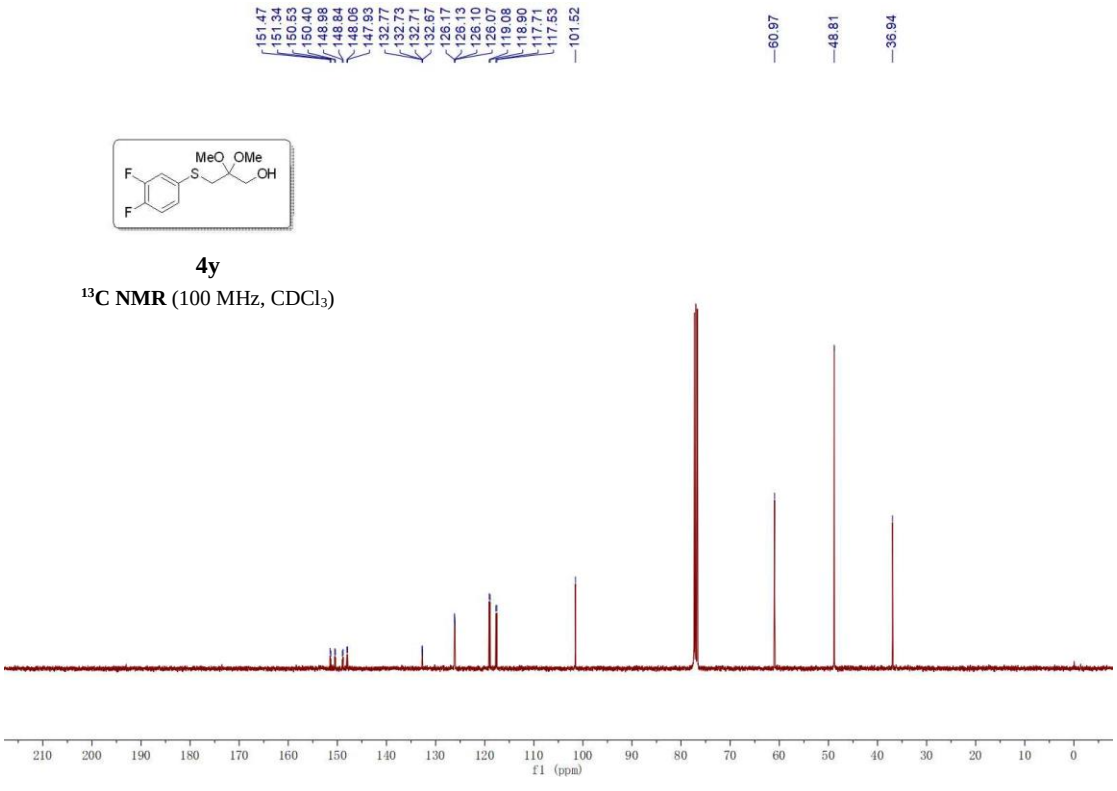
^{13}C NMR (100 MHz, $CDCl_3$)





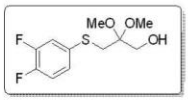
4y

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



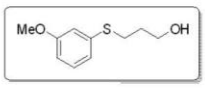
4y

^{13}C NMR (100 MHz, $CDCl_3$)



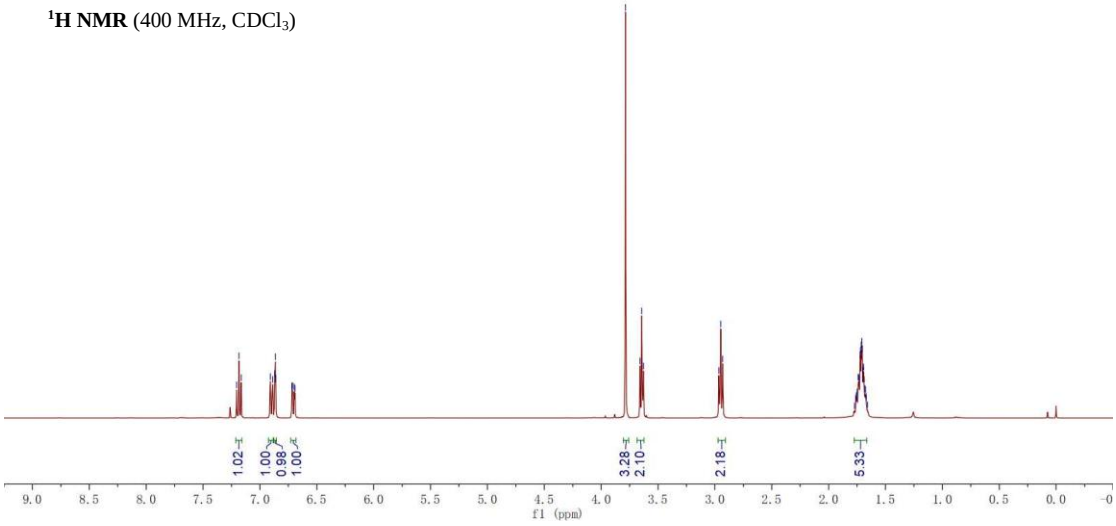
4y

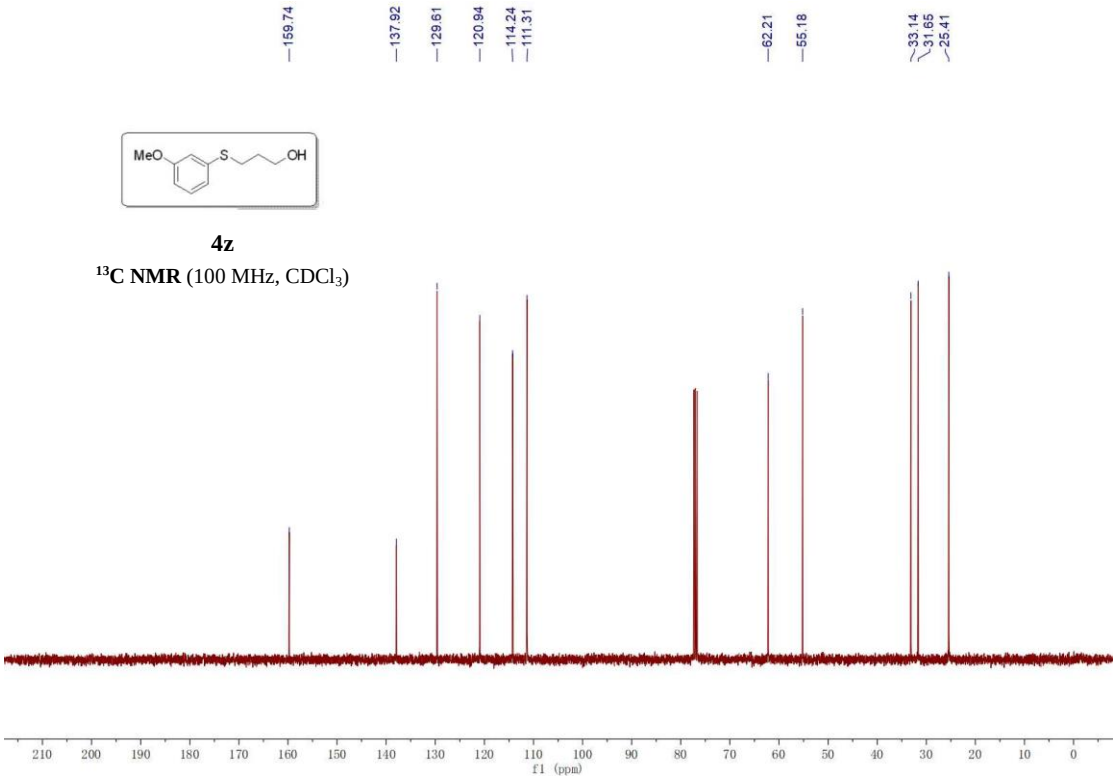
^{19}F NMR (377 MHz, $CDCl_3$)



4z

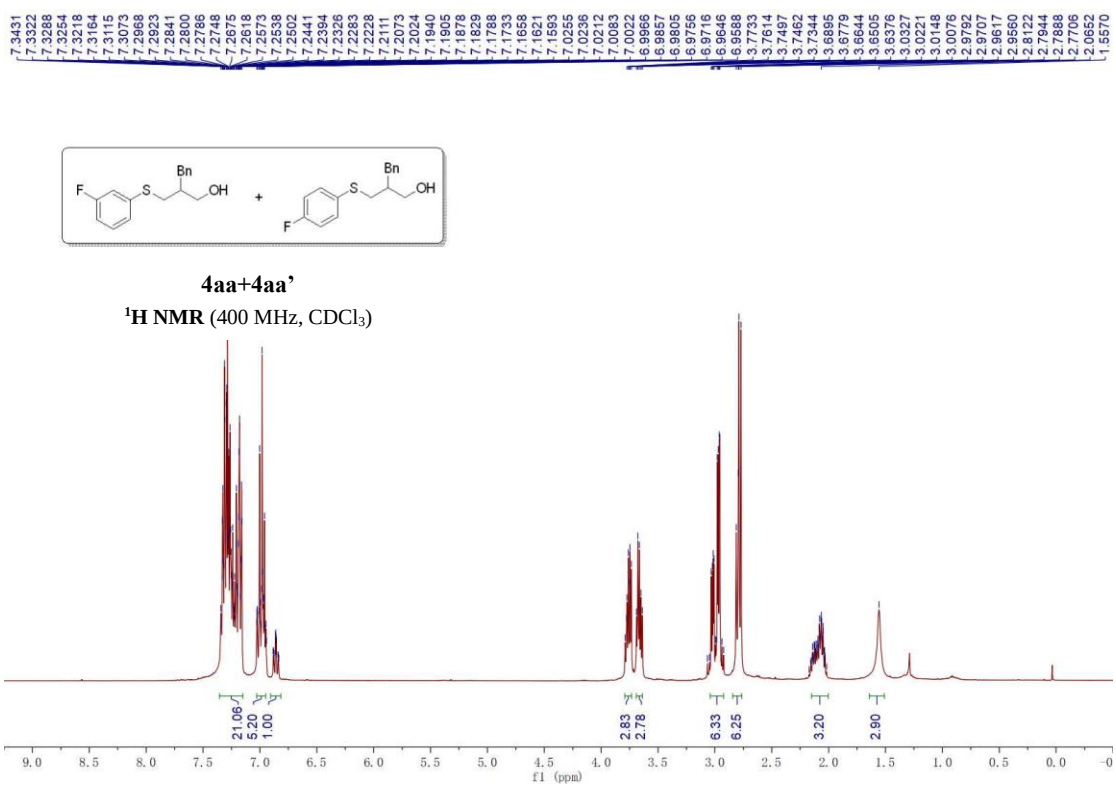
^{1}H NMR (400 MHz, $CDCl_3$)





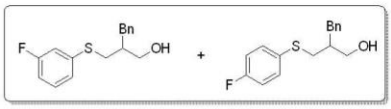
4z

^{13}C NMR (100 MHz, $CDCl_3$)



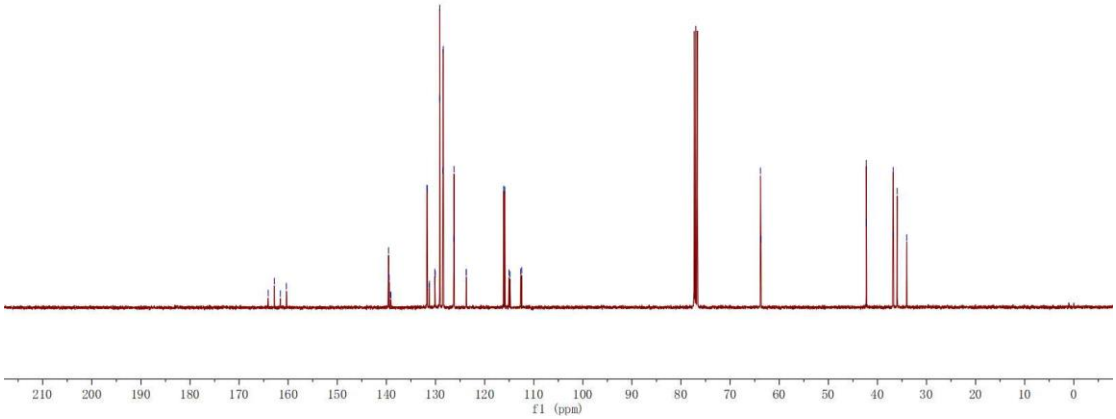
4aa+4aa'

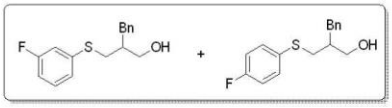
^{1}H NMR (400 MHz, $CDCl_3$)



4aa+4aa'

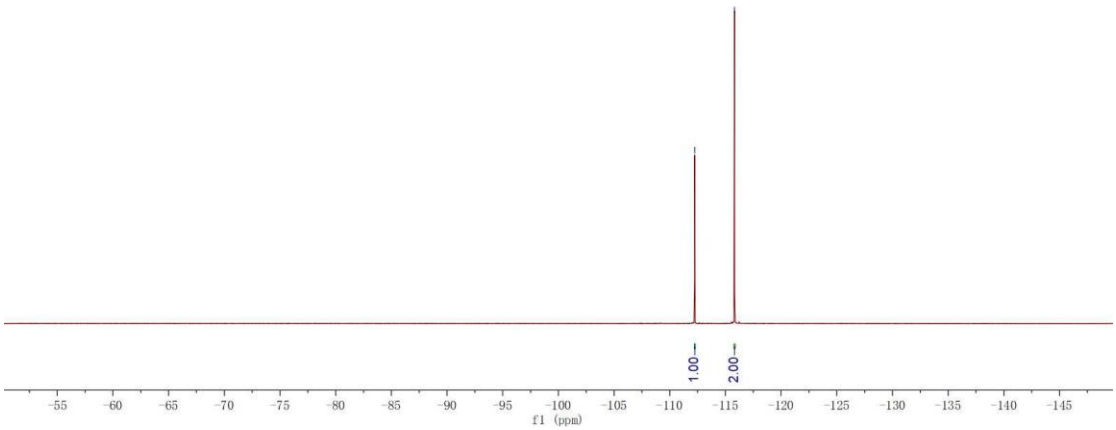
^{13}C NMR (100 MHz, $CDCl_3$)

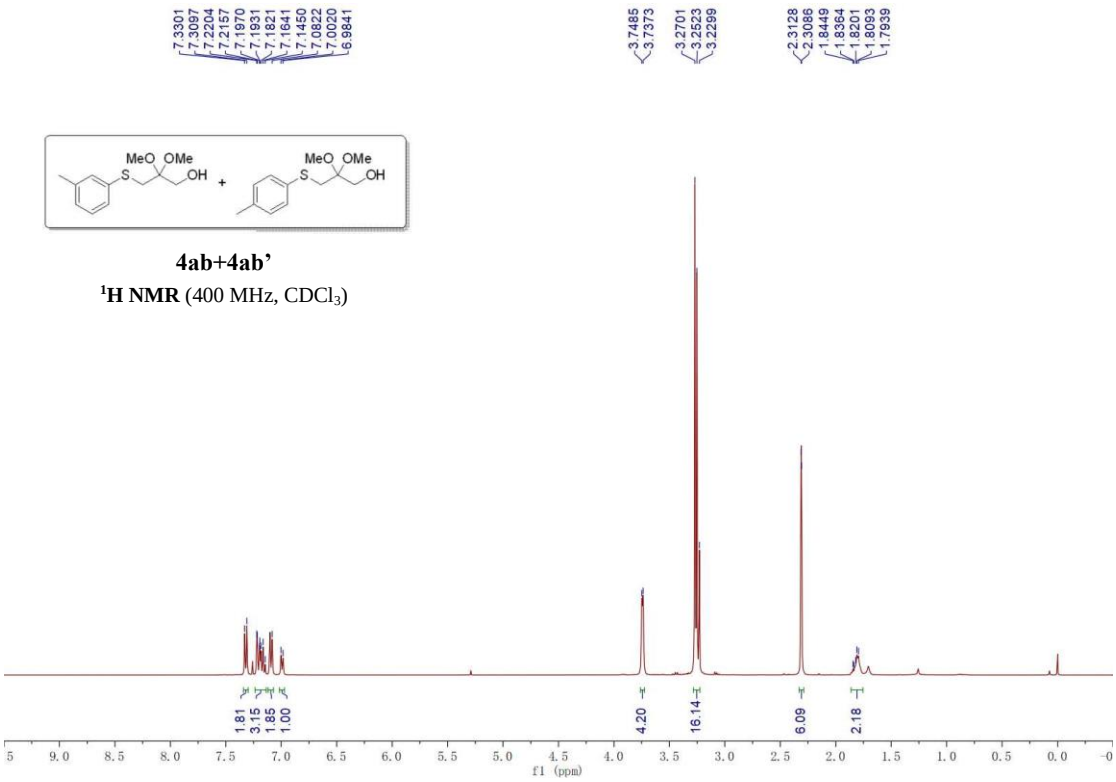




4aa+4aa'

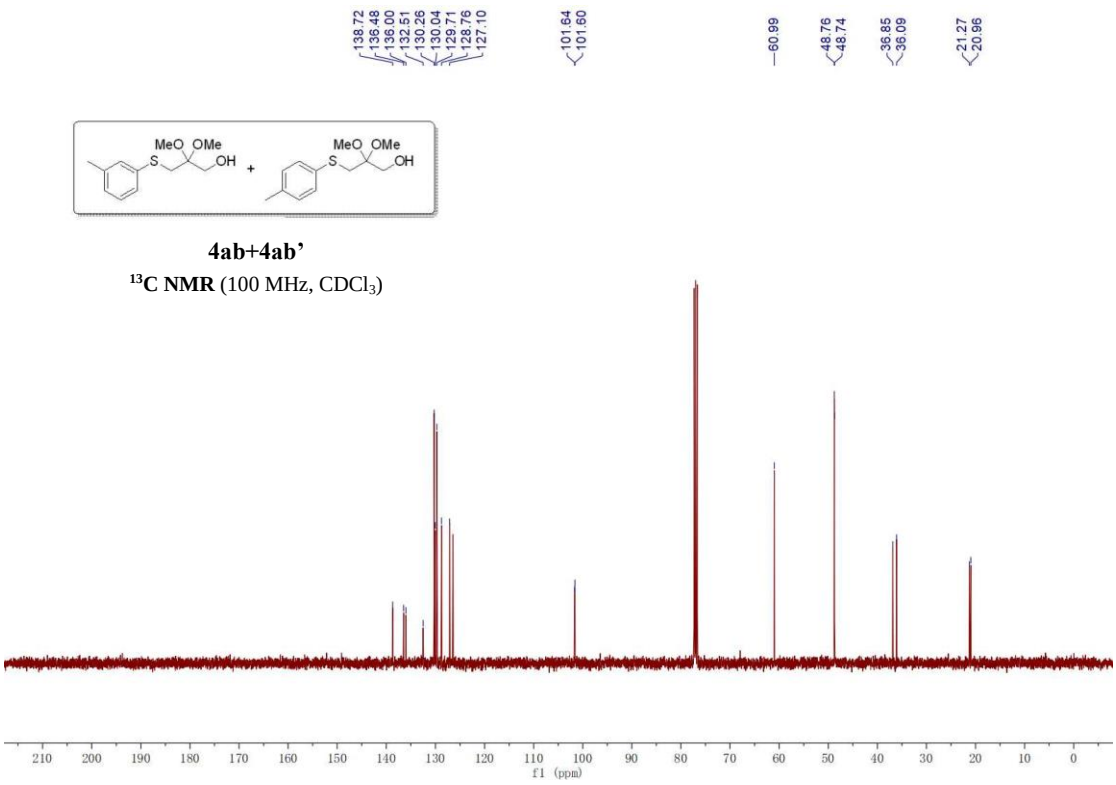
^{19}F NMR (377 MHz, $CDCl_3$)





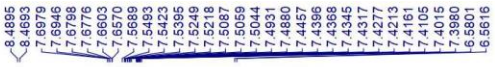
4ab+4ab'

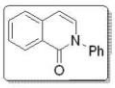
^{1}H NMR (400 MHz, $CDCl_3$)



4ab+4ab'

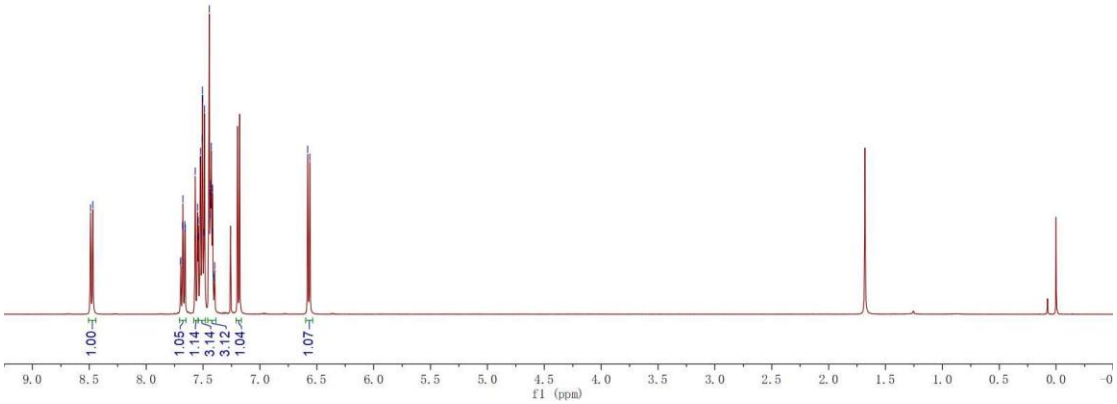
^{13}C NMR (100 MHz, $CDCl_3$)

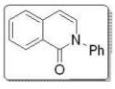




6a

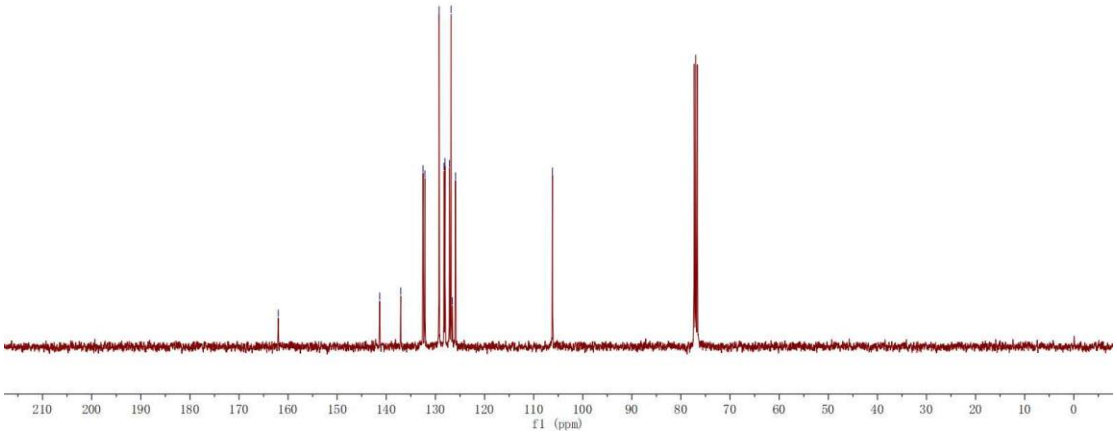
^{1}H NMR (400 MHz, $CDCl_3$)

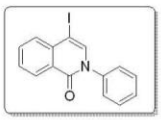




6a

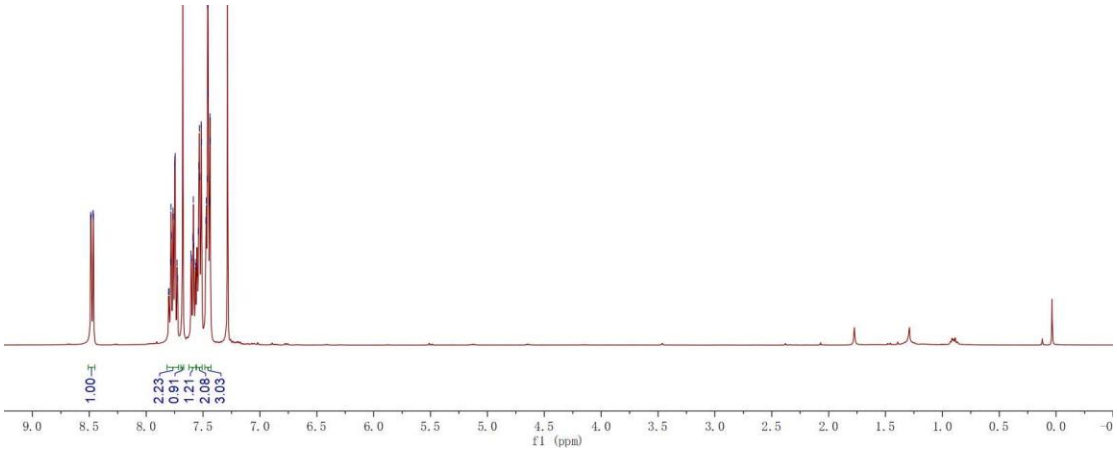
^{13}C NMR (100 MHz, $CDCl_3$)

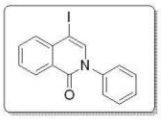




6b

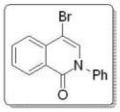
^{1}H NMR (400 MHz, $CDCl_3$)





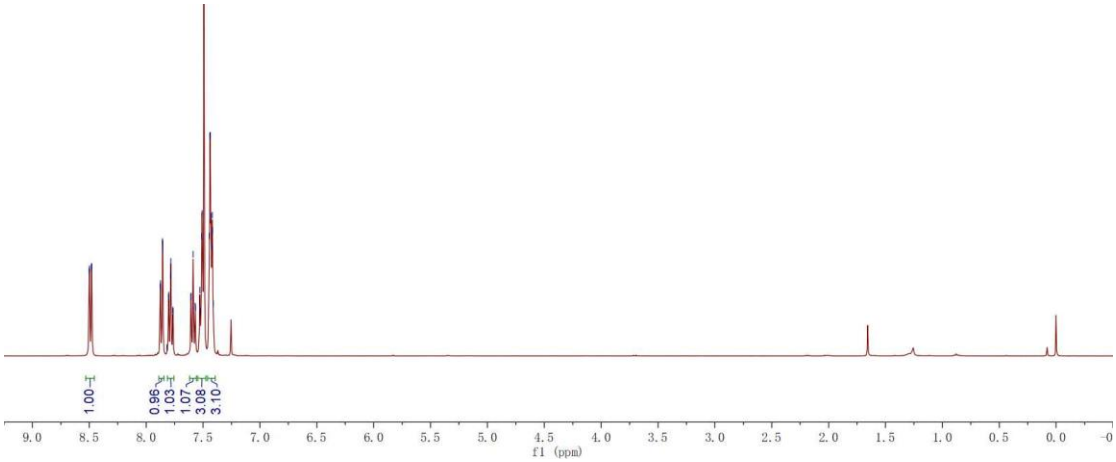
6b

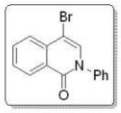
^{13}C NMR (100 MHz, $CDCl_3$)



6c

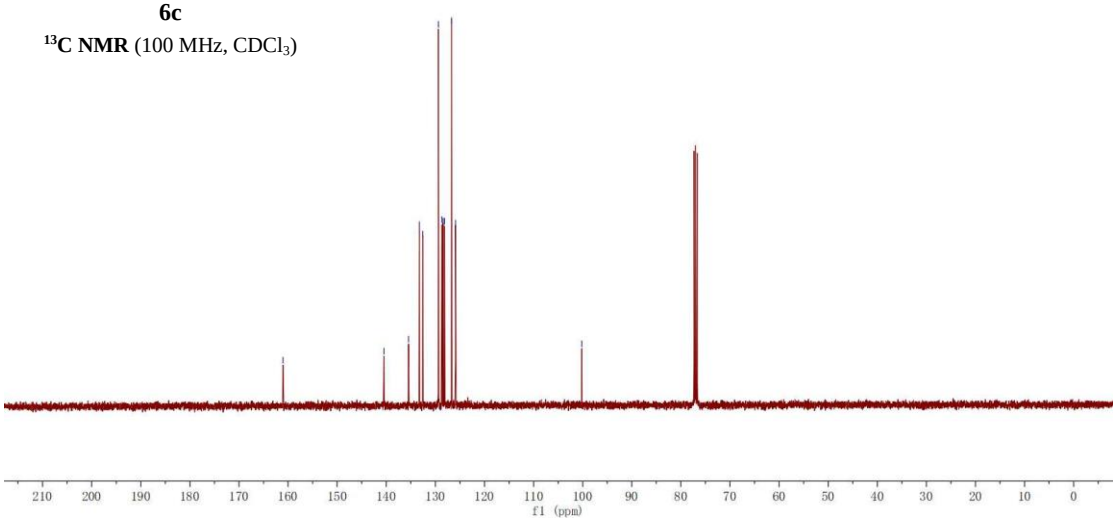
^{1}H NMR (400 MHz, $CDCl_3$)

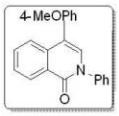




6c

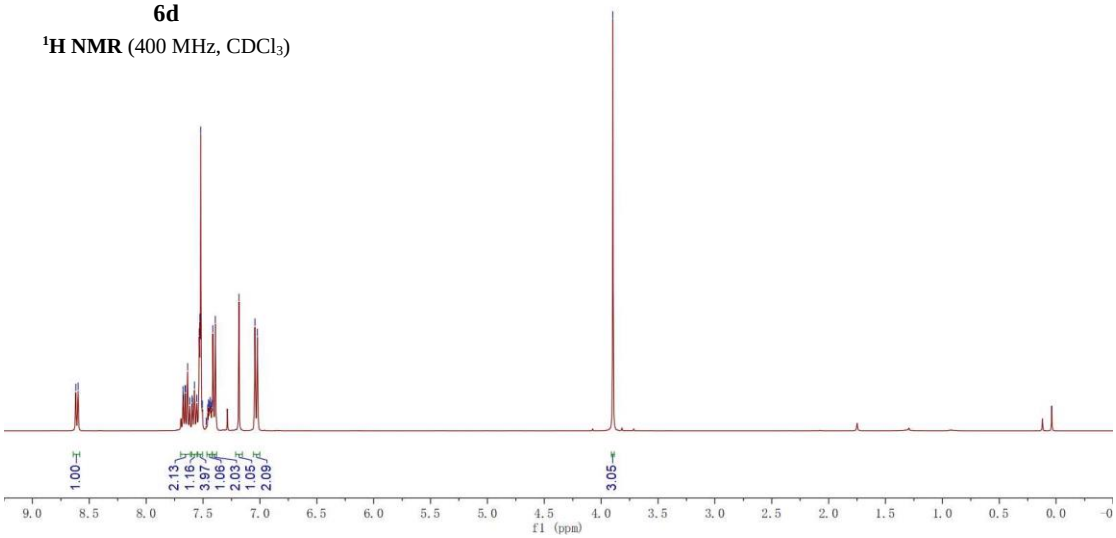
^{13}C NMR (100 MHz, $CDCl_3$)

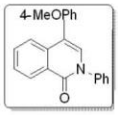




6d

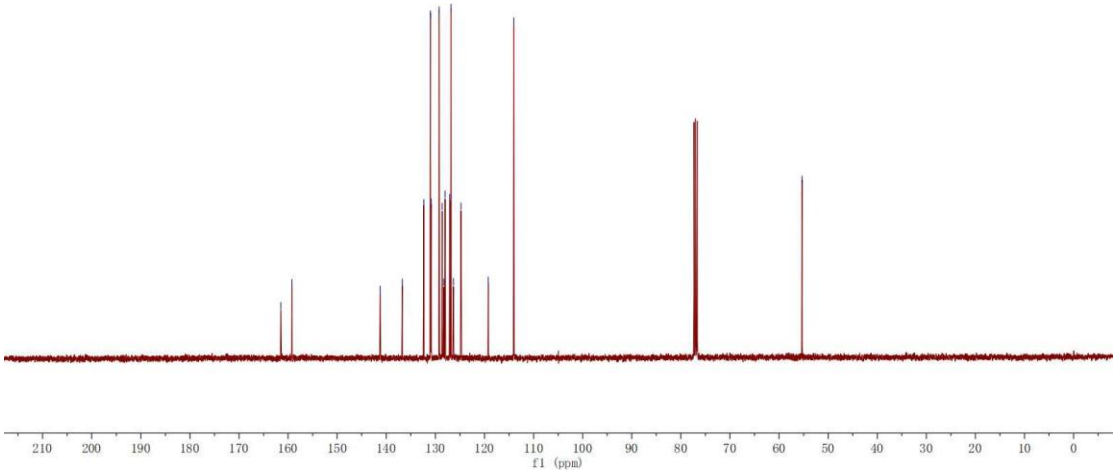
^{1}H NMR (400 MHz, $CDCl_3$)

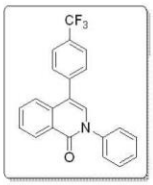




6d

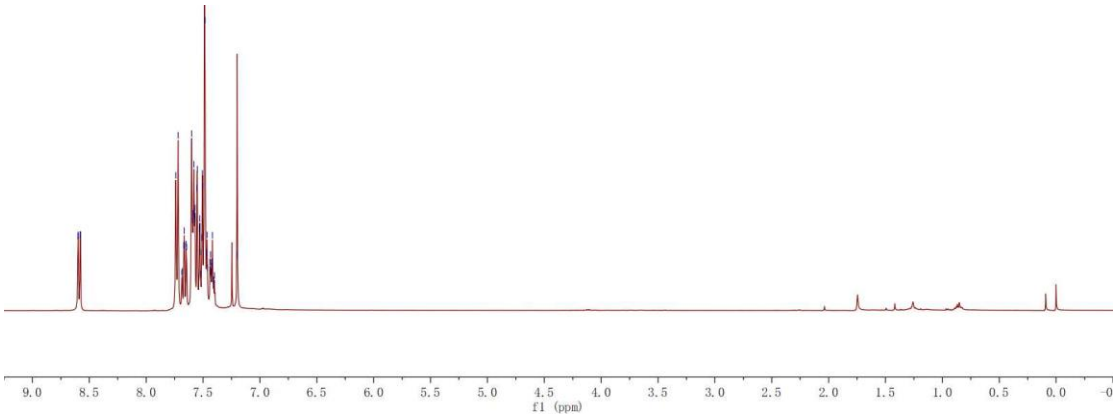
^{13}C NMR (100 MHz, $CDCl_3$)

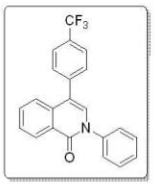




6e

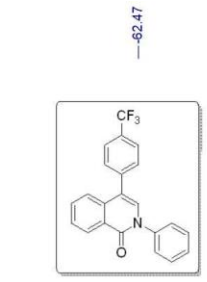
^{1}H NMR (400 MHz, $CDCl_3$)





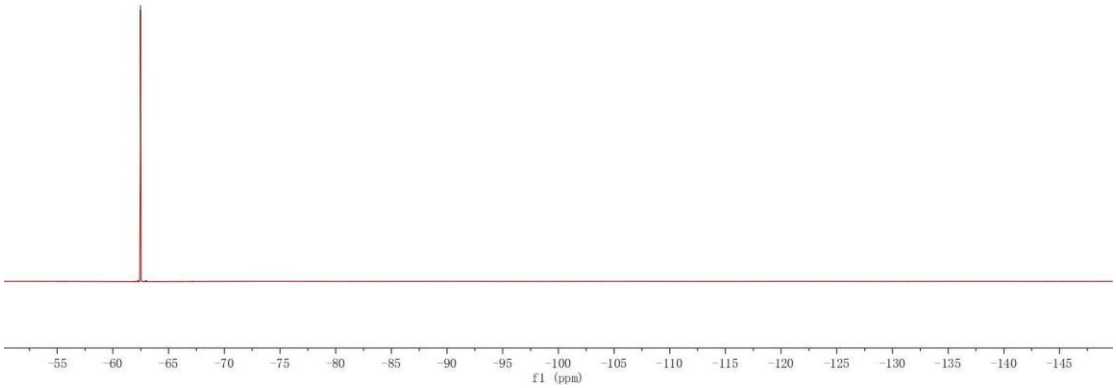
6e

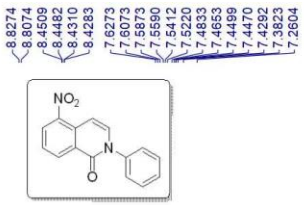
^{13}C NMR (100 MHz, $CDCl_3$)



6e

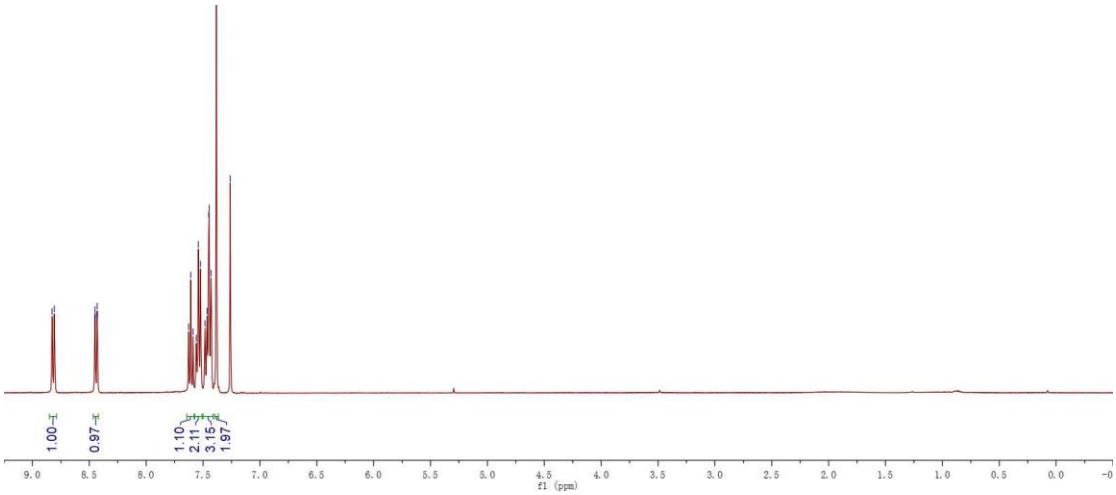
^{19}F NMR (377 MHz, $CDCl_3$)

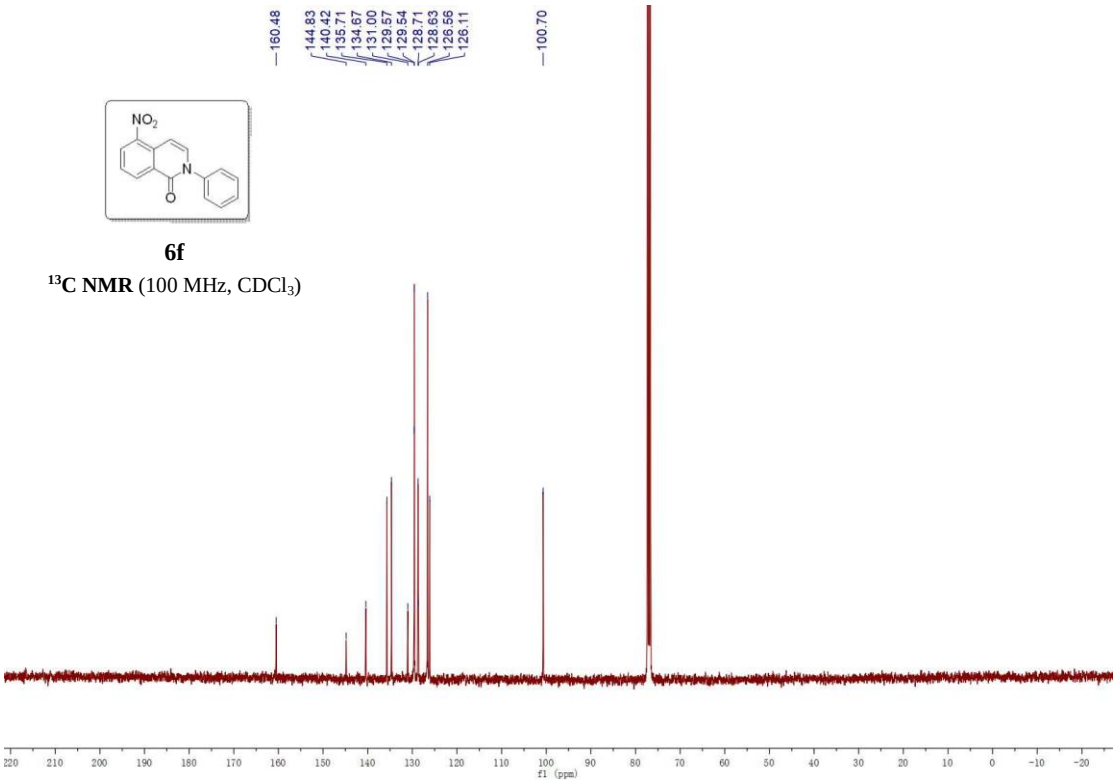




6f

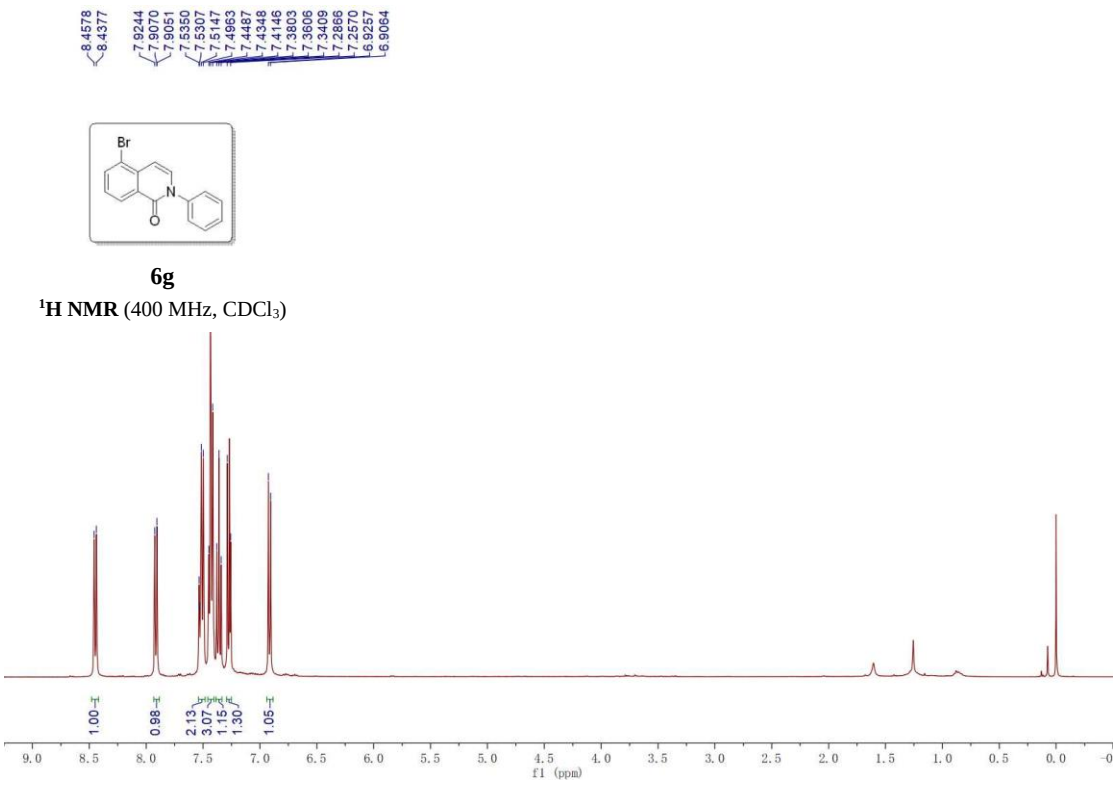
^{1}H NMR (400 MHz, $CDCl_3$)





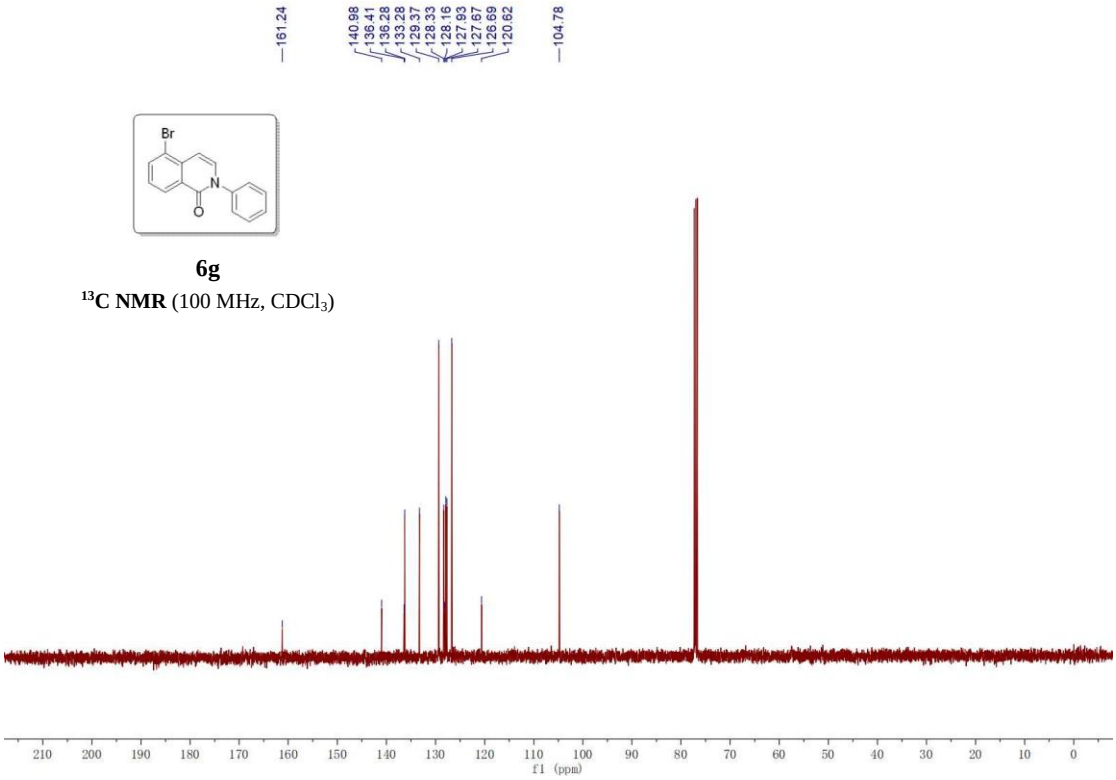
6f

^{13}C NMR (100 MHz, $CDCl_3$)



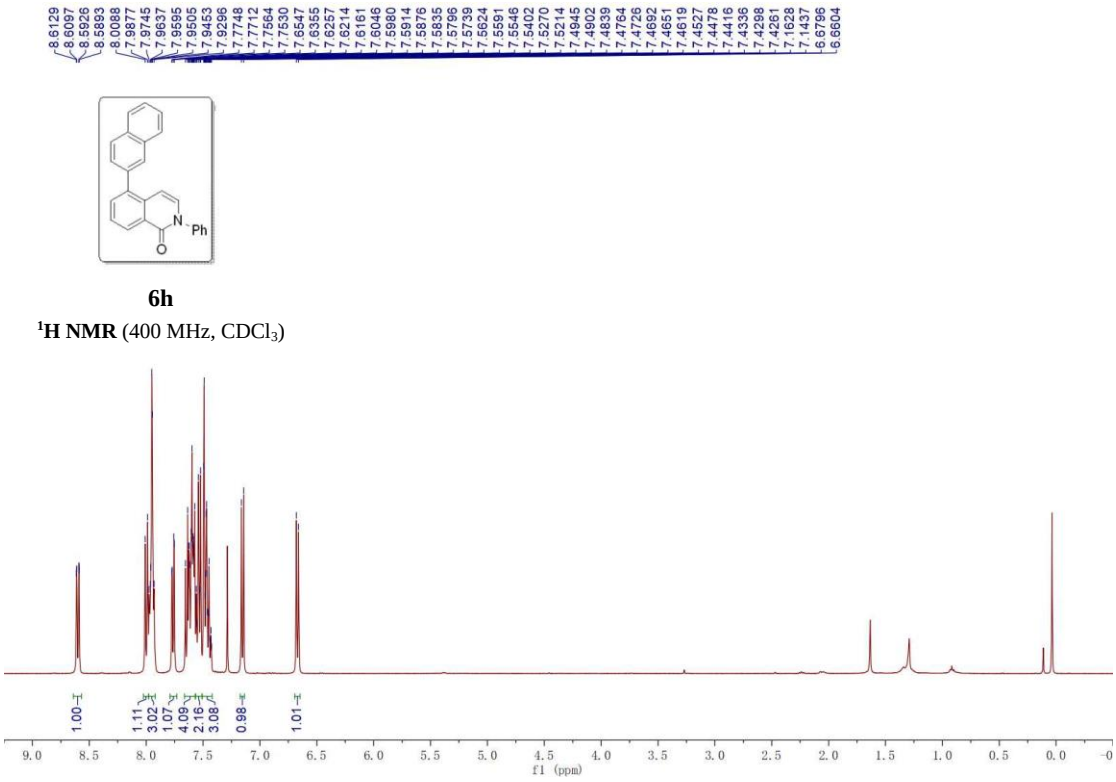
6g

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



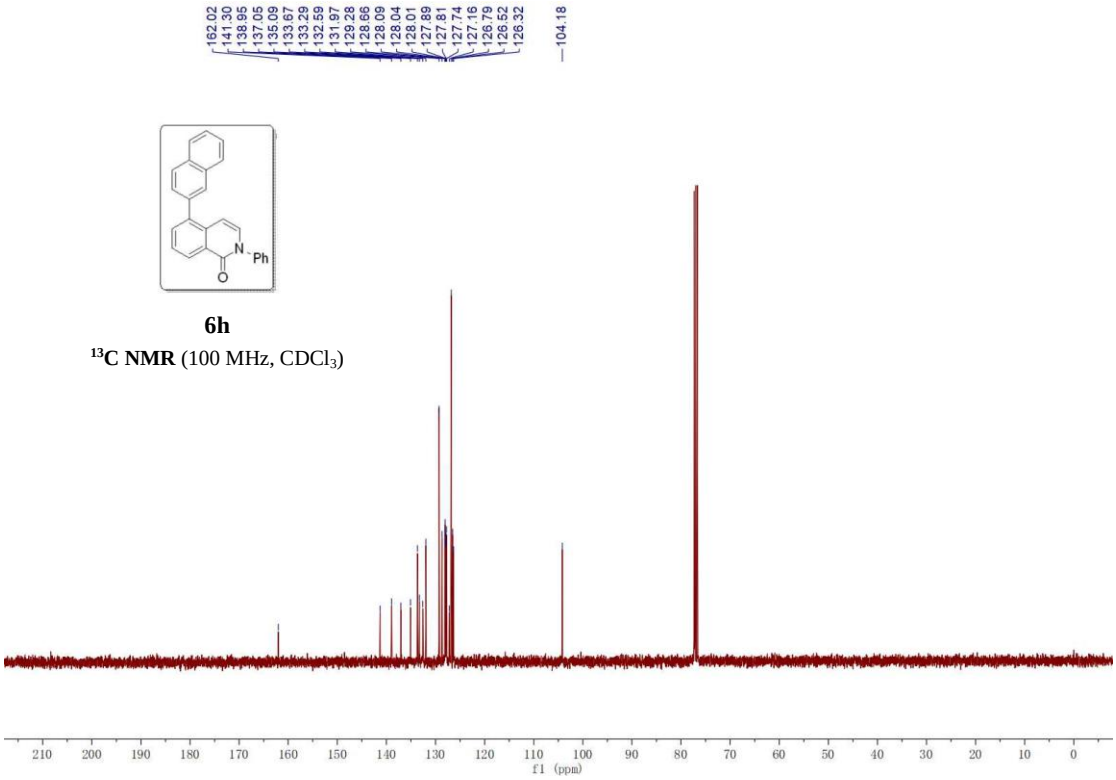
6g

^{13}C NMR (100 MHz, $CDCl_3$)



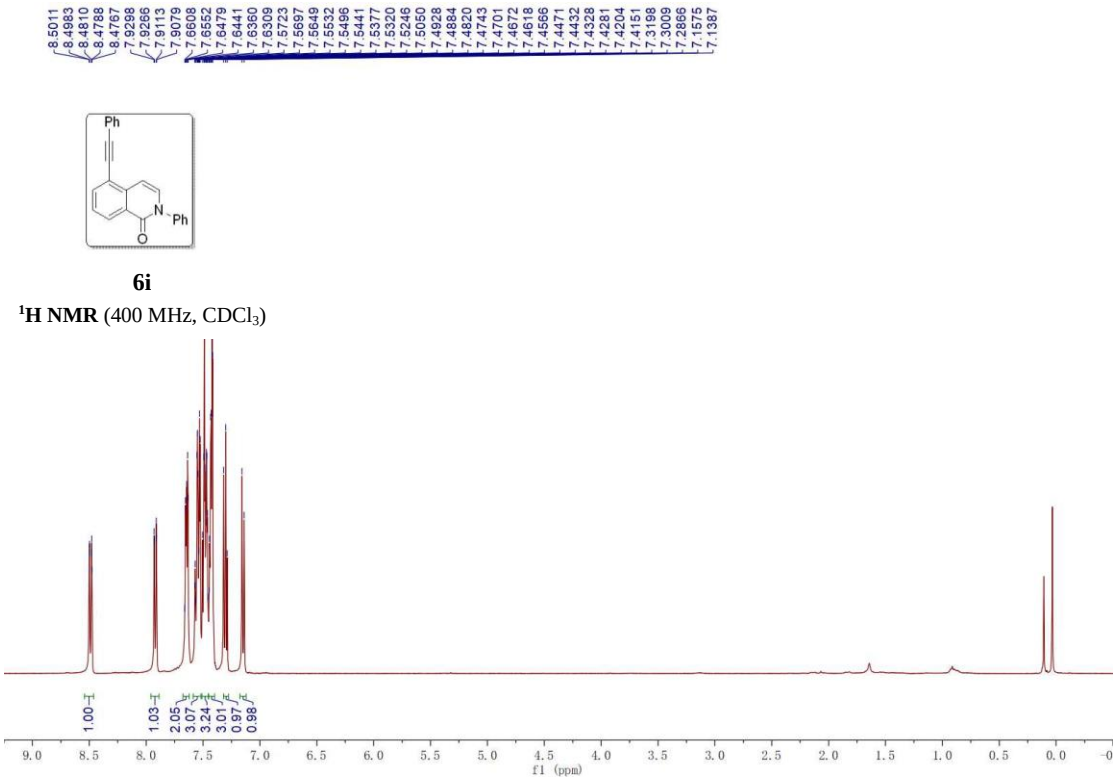
6h

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



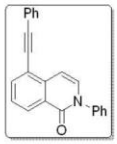
6h

^{13}C NMR (100 MHz, $CDCl_3$)



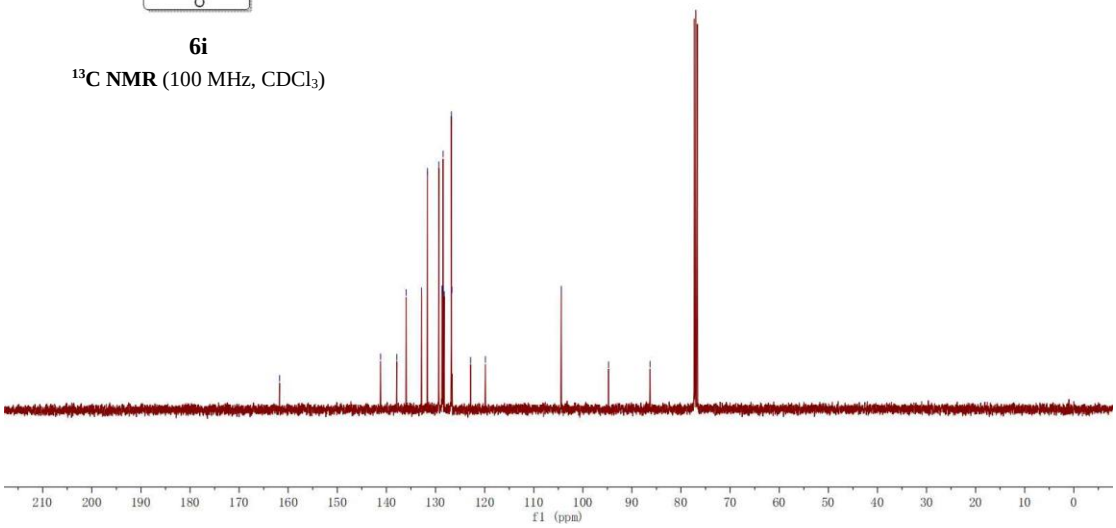
6i

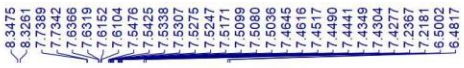
^{1}H NMR (400 MHz, $CDCl_3$)

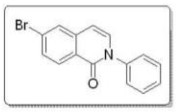


6i

^{13}C NMR (100 MHz, $CDCl_3$)

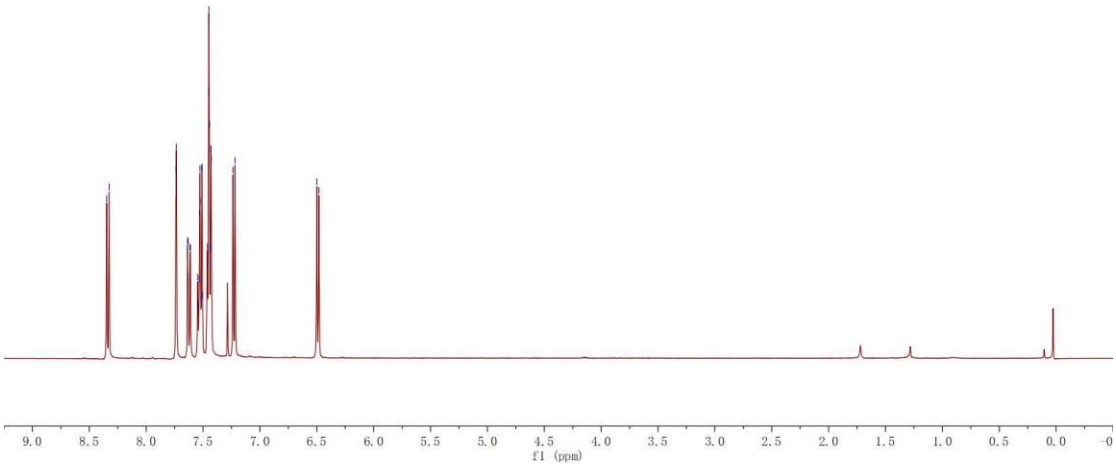


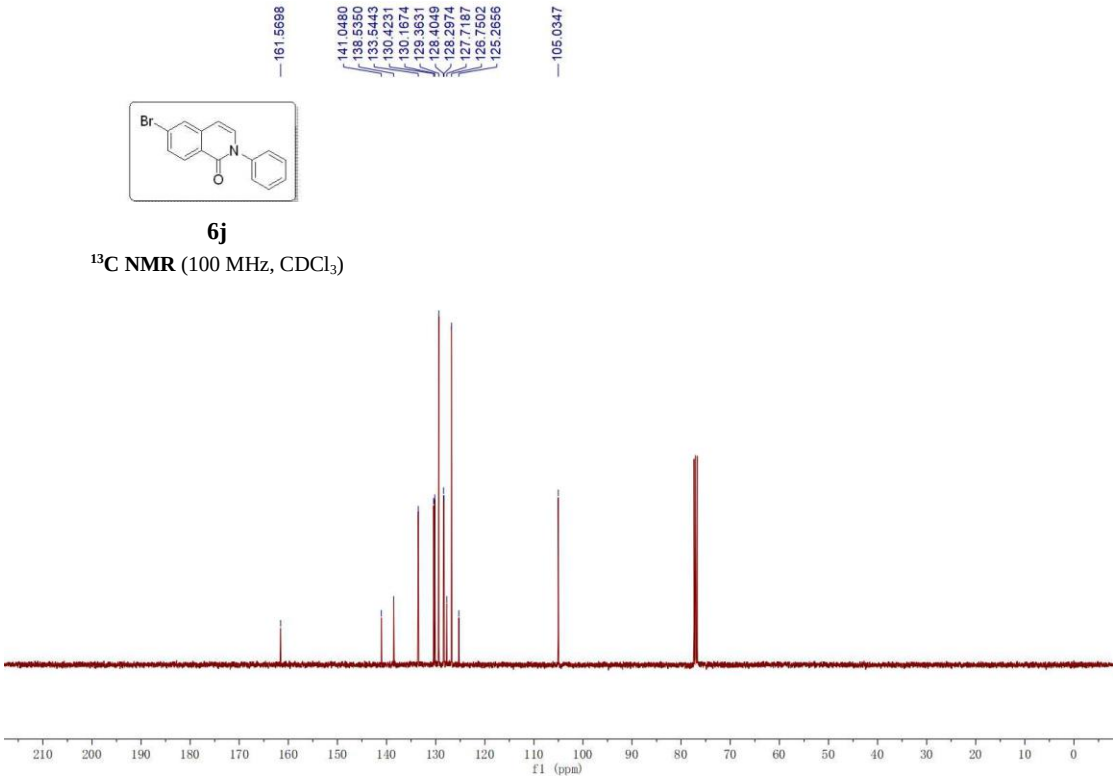




6j

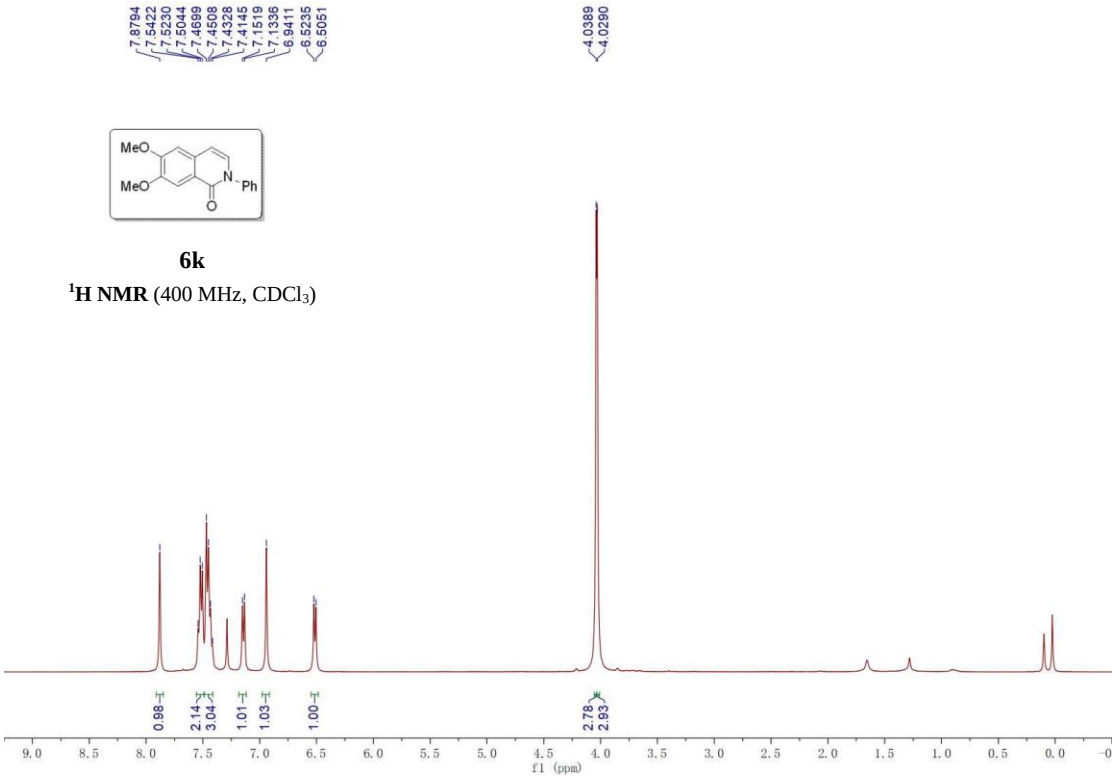
^{1}H NMR (400 MHz, $CDCl_3$)





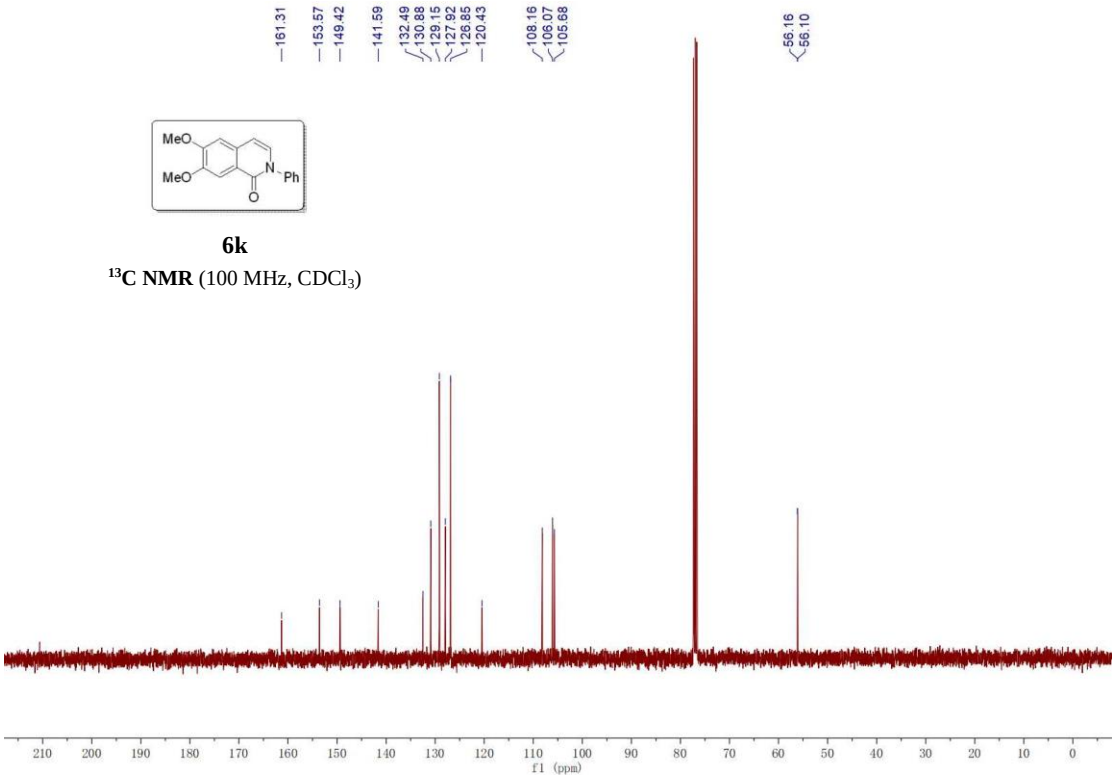
6j

^{13}C NMR (100 MHz, $CDCl_3$)



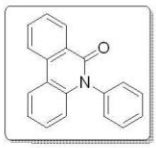
6k

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



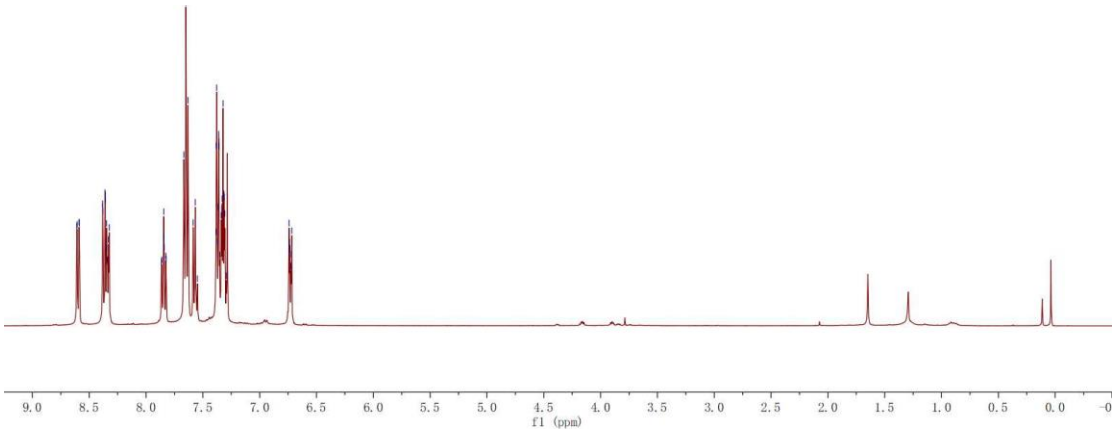
6k

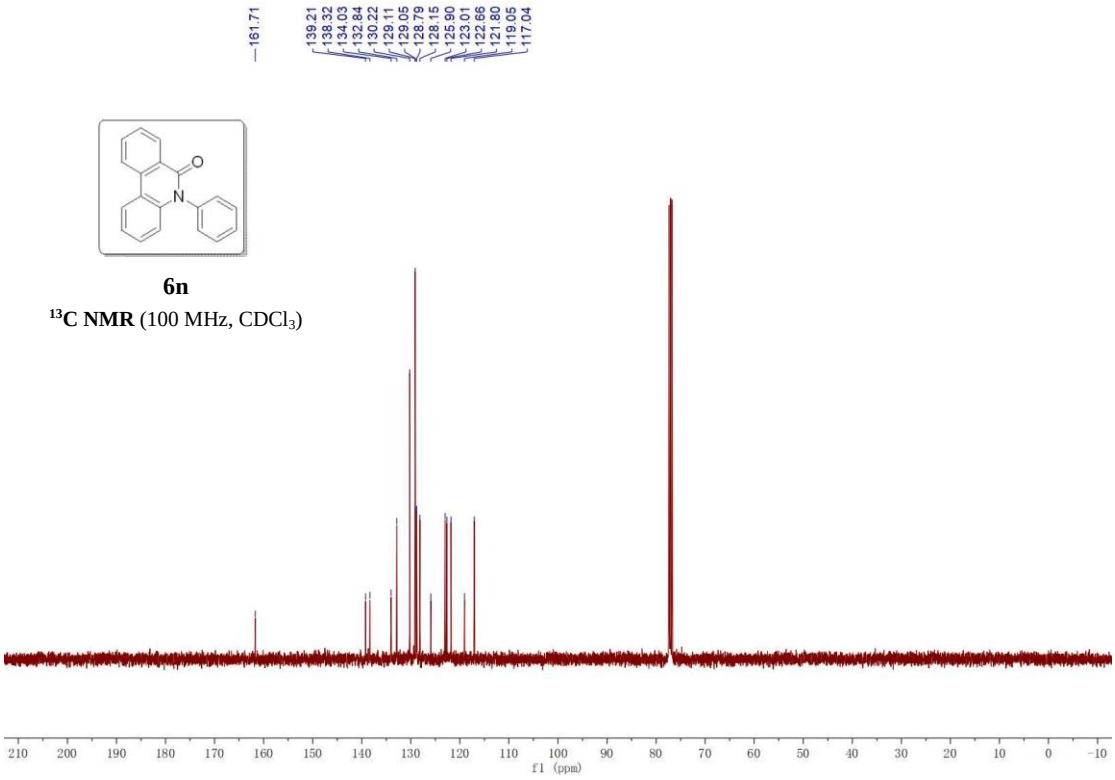
^{13}C NMR (100 MHz, $CDCl_3$)



6n

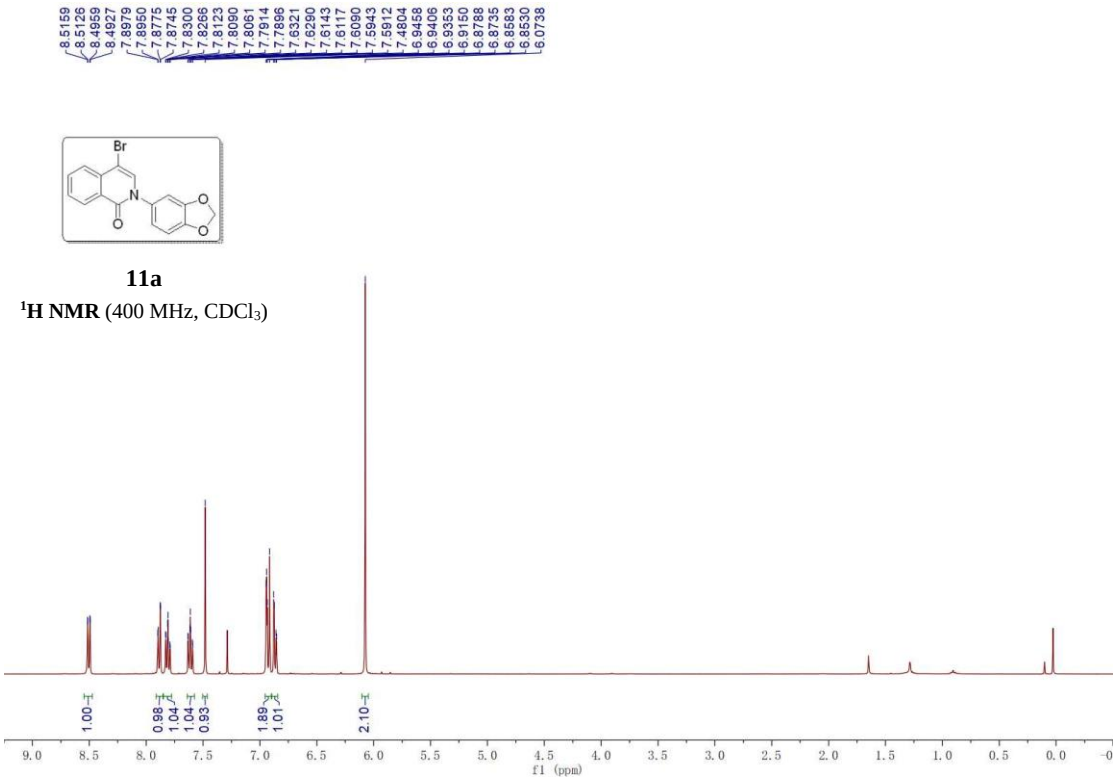
^{1}H NMR (400 MHz, $CDCl_3$)





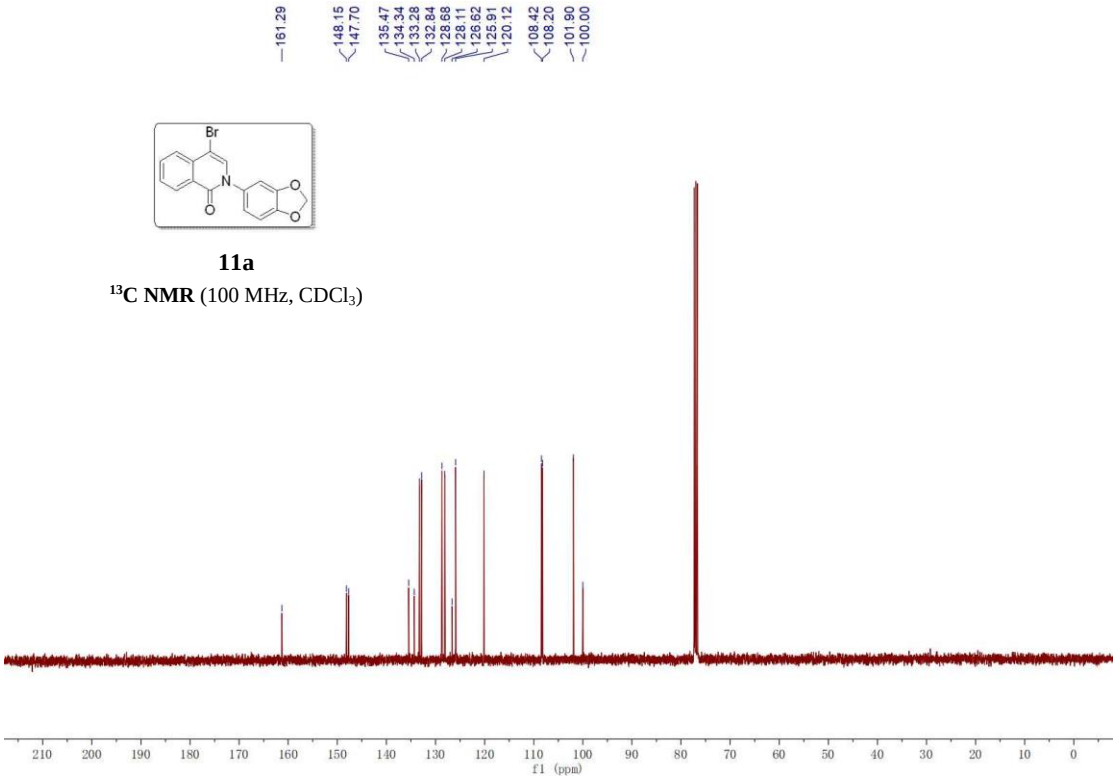
6n

^{13}C NMR (100 MHz, $CDCl_3$)



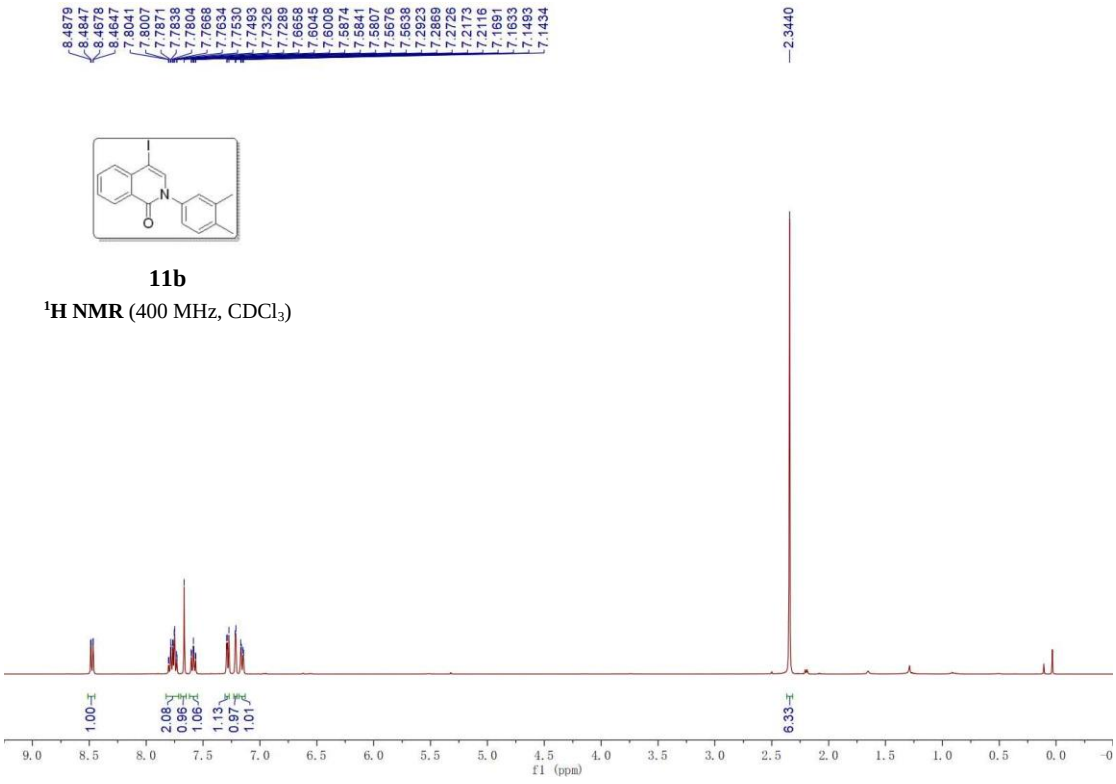
11a

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



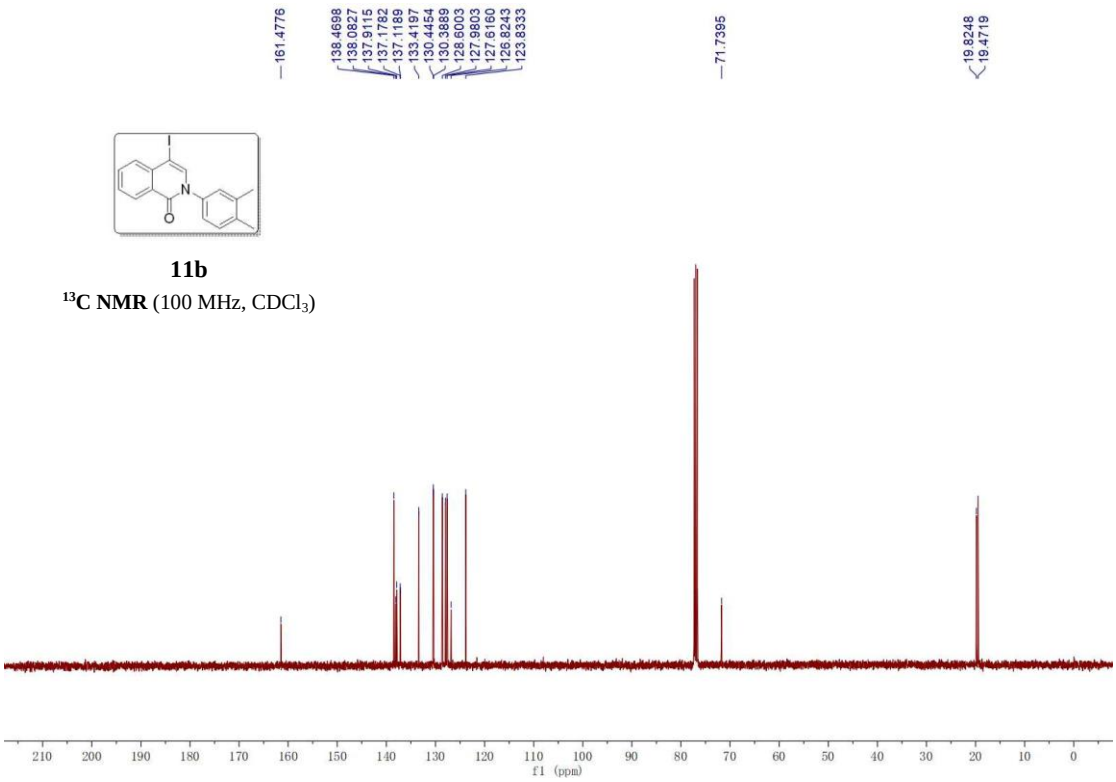
11a

^{13}C NMR (100 MHz, $CDCl_3$)



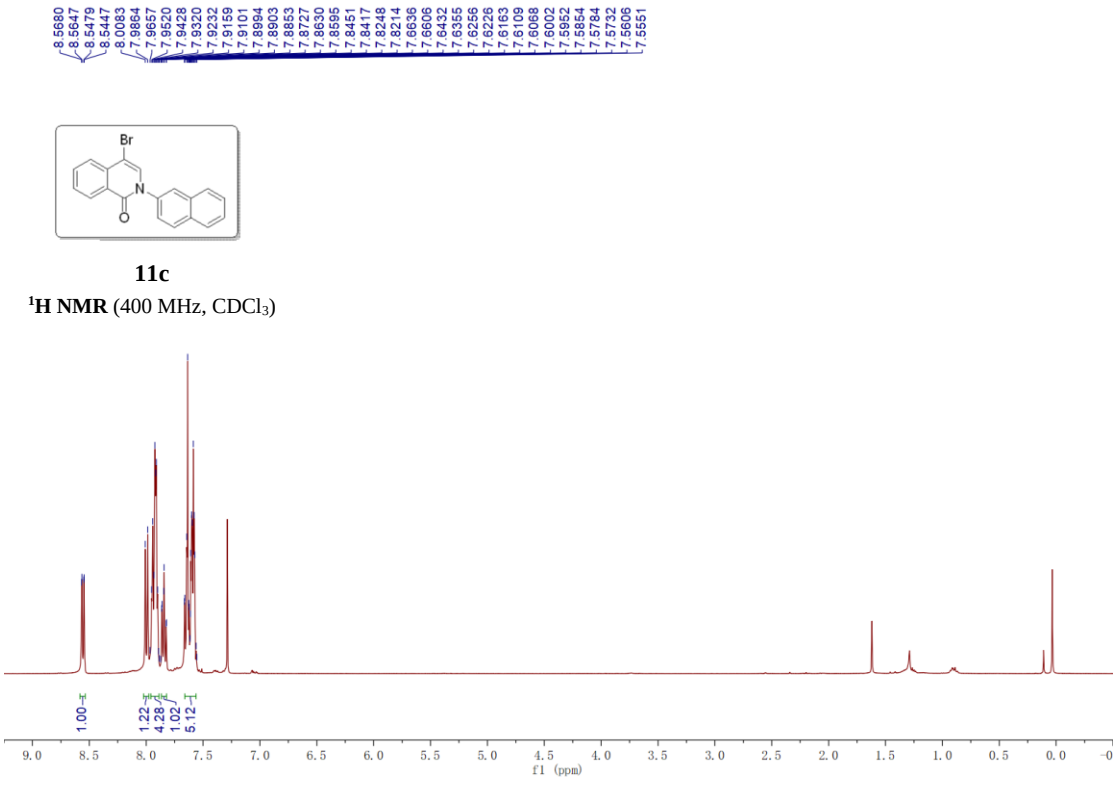
11b

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



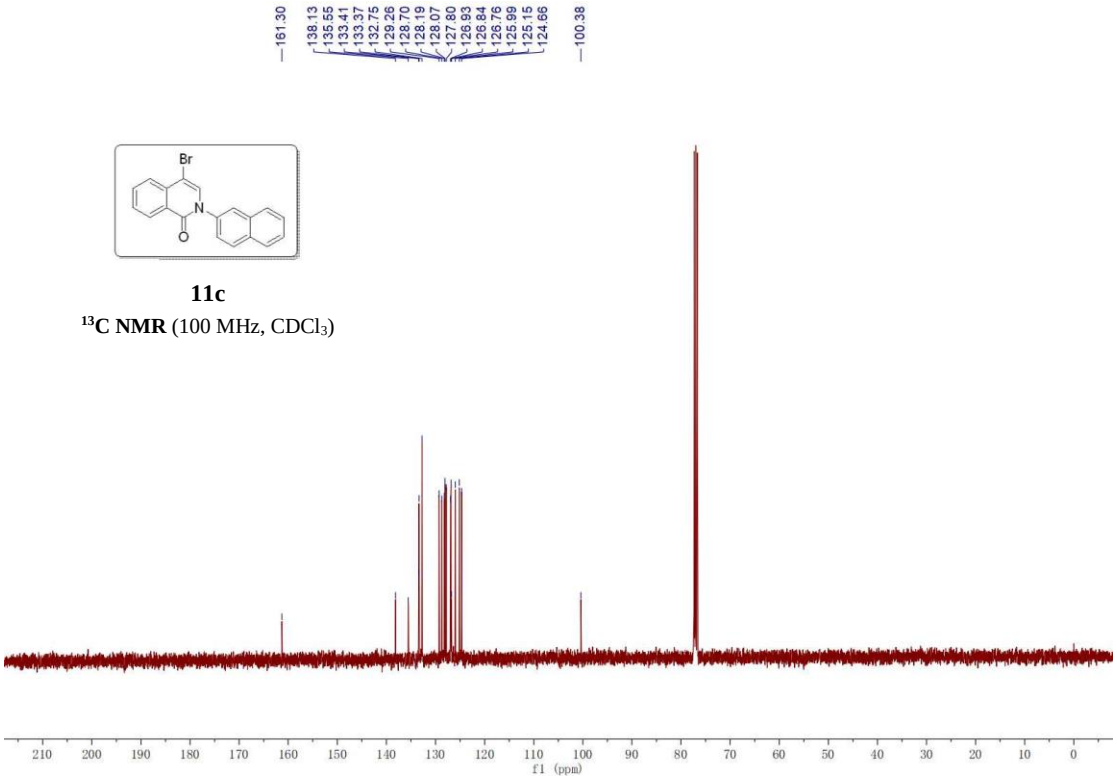
11b

^{13}C NMR (100 MHz, $CDCl_3$)



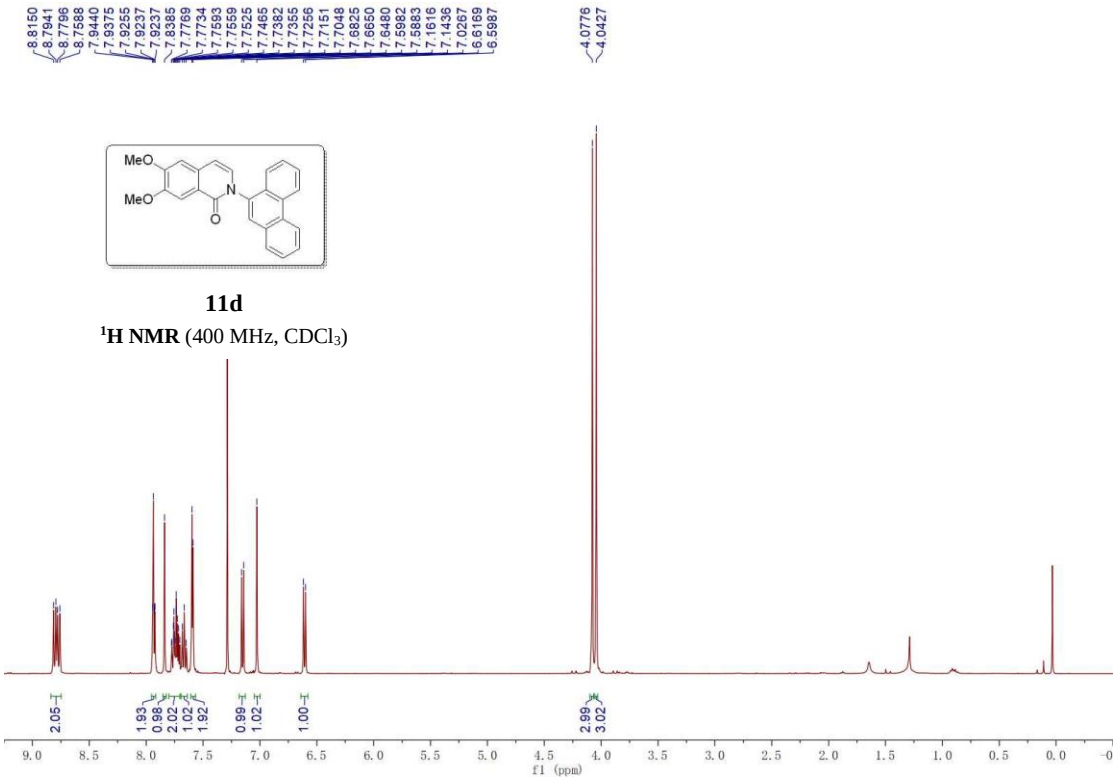
11c

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



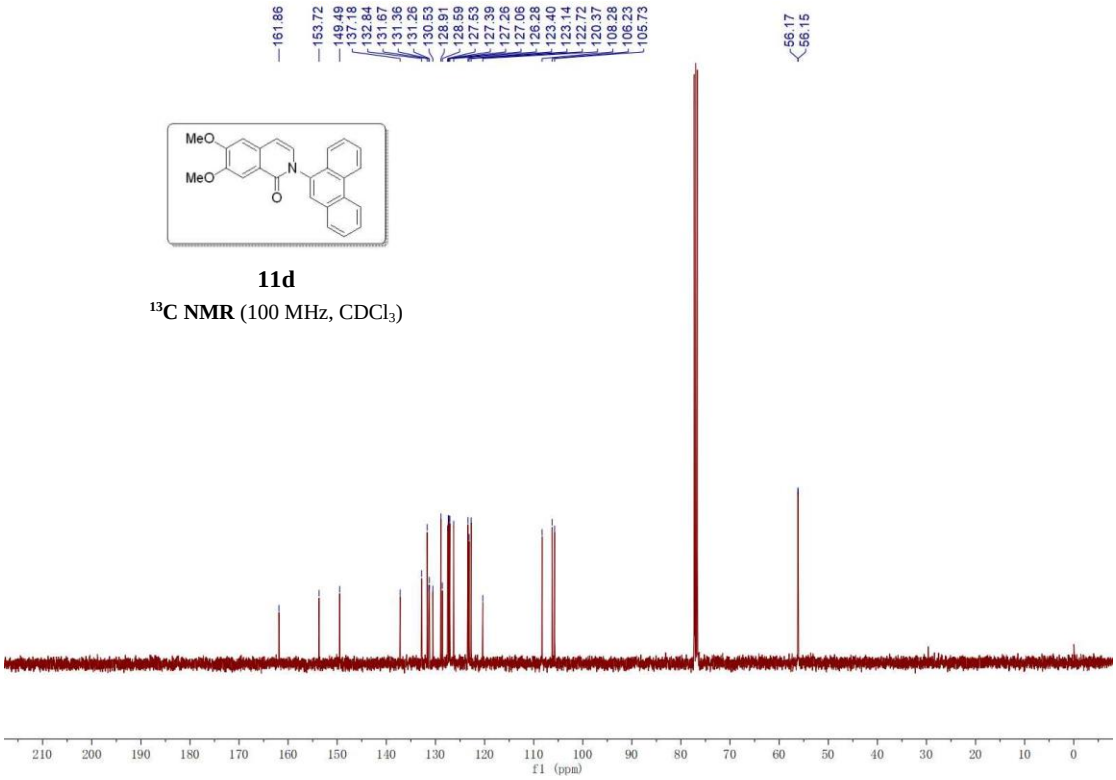
11c

^{13}C NMR (100 MHz, $CDCl_3$)



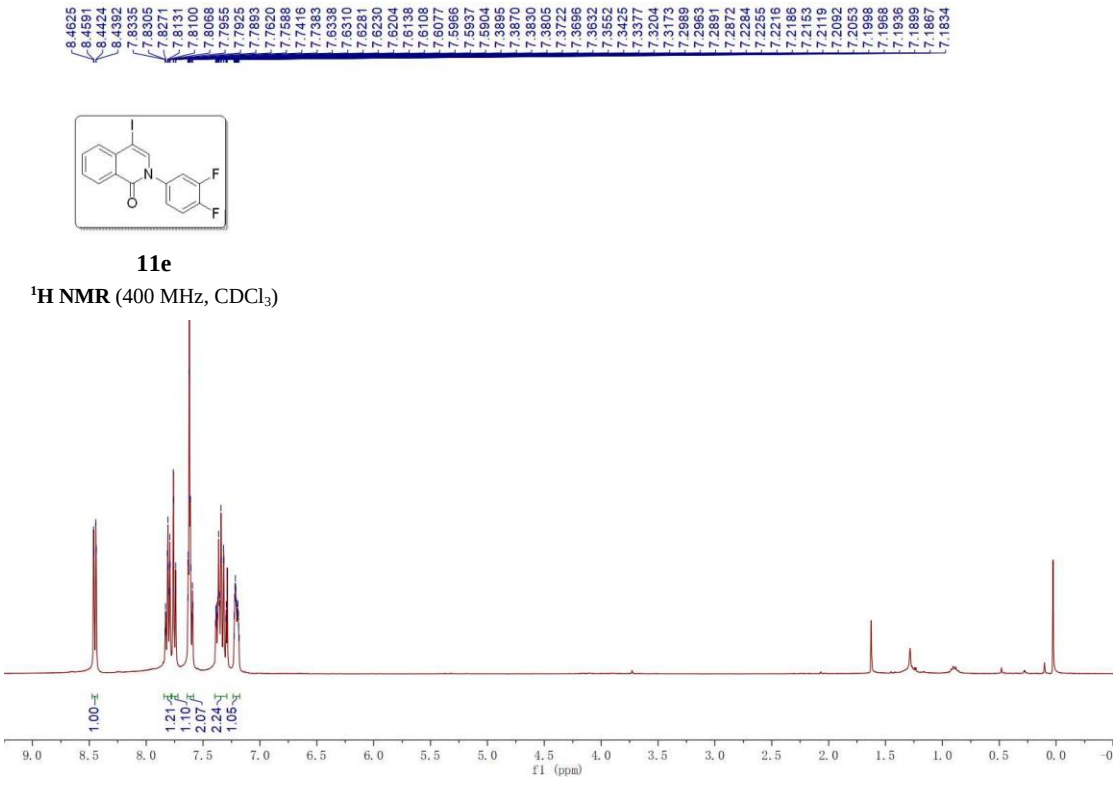
11d

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



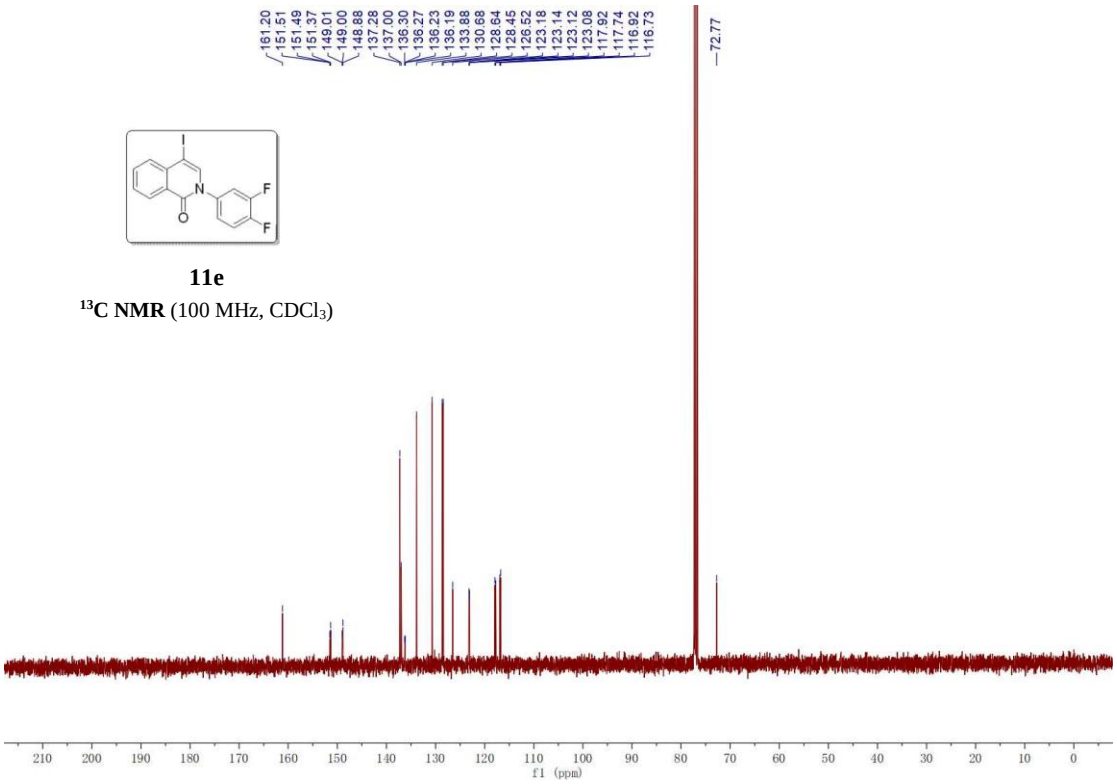
11d

^{13}C NMR (100 MHz, $CDCl_3$)



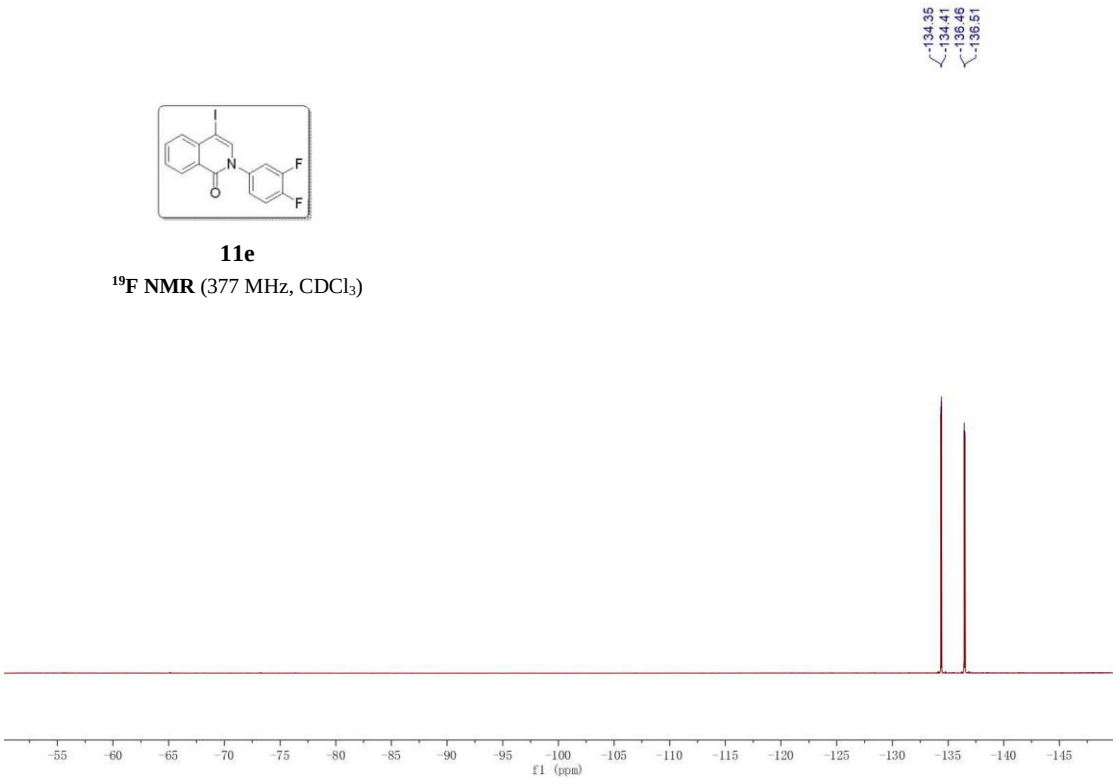
11e

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



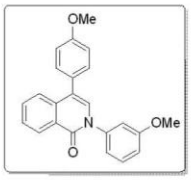
11e

^{13}C NMR (100 MHz, $CDCl_3$)



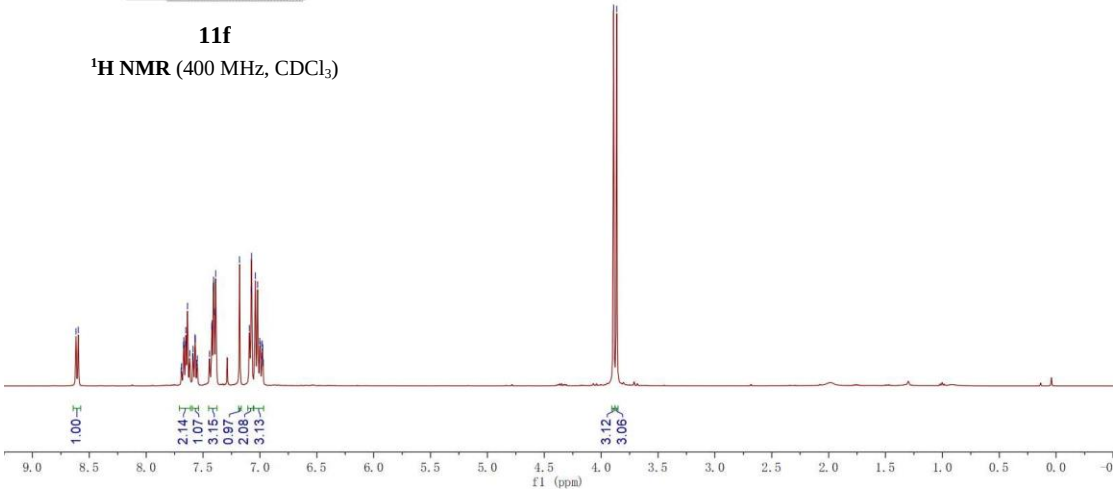
11e

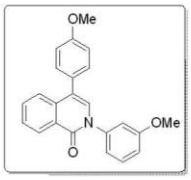
^{19}F NMR (377 MHz, $CDCl_3$)



11f

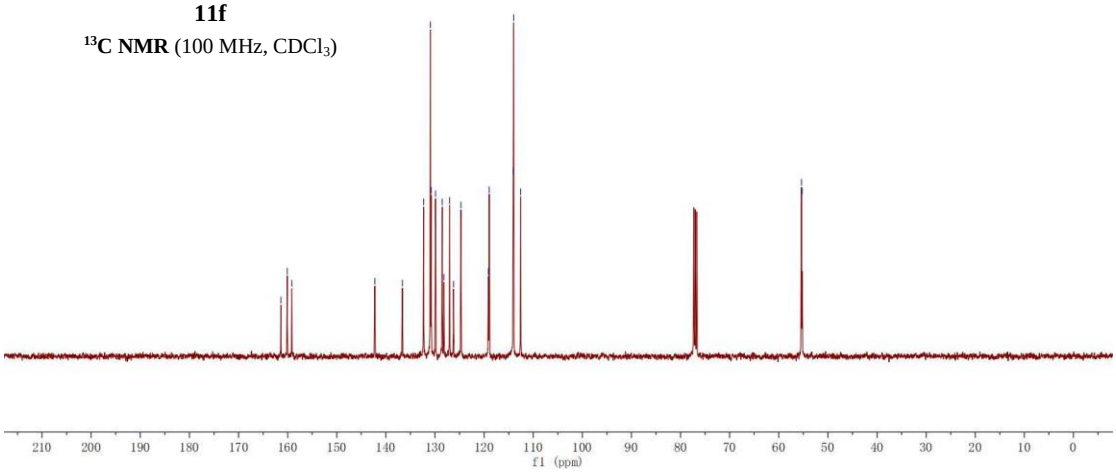
^{1}H NMR (400 MHz, $CDCl_3$)

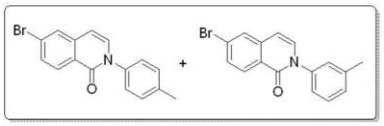




11f

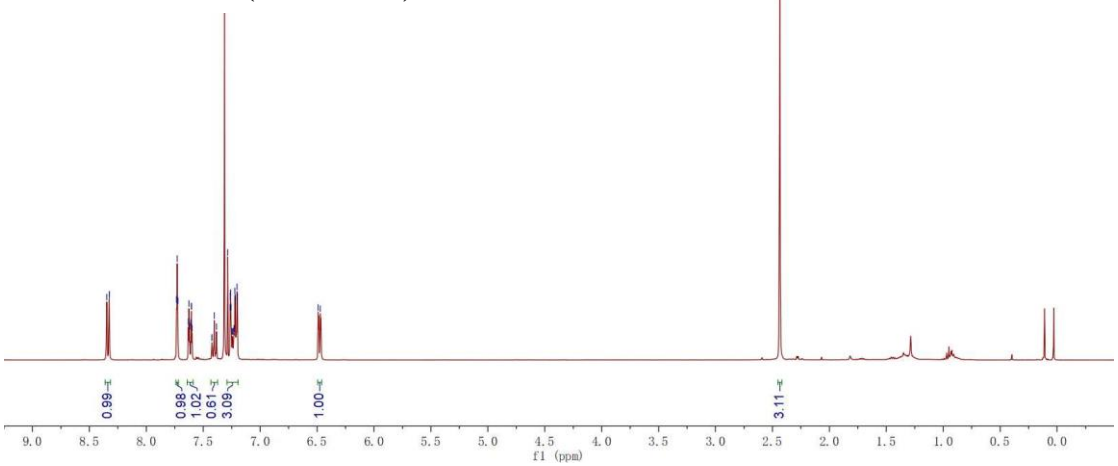
^{13}C NMR (100 MHz, $CDCl_3$)

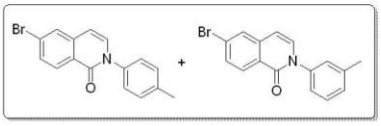




11g+11g'

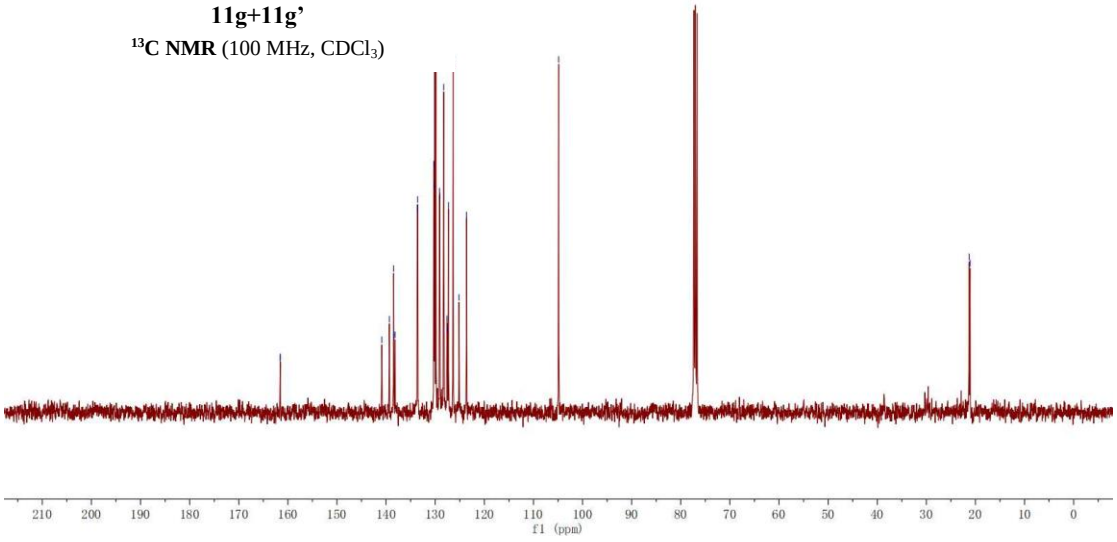
^{1}H NMR (400 MHz, $CDCl_3$)

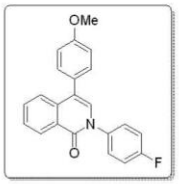




11g+11g'

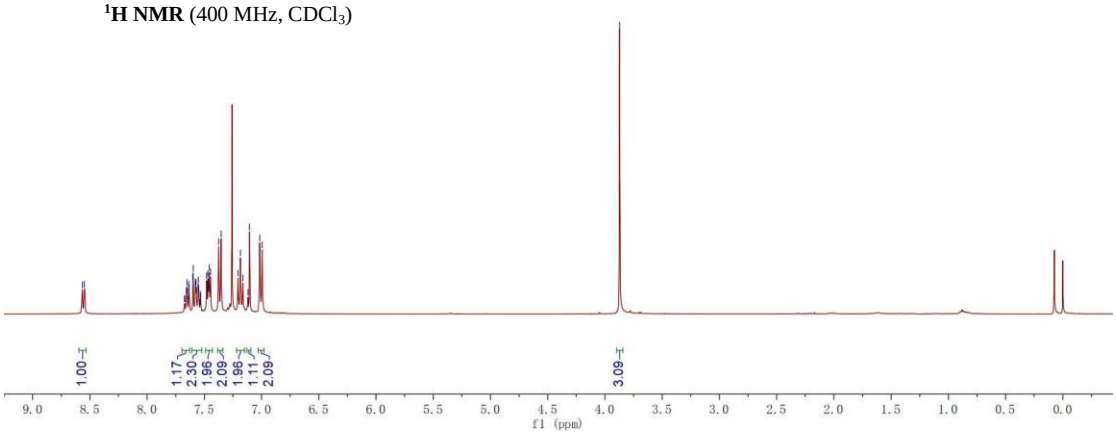
^{13}C NMR (100 MHz, $CDCl_3$)

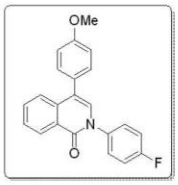




11h

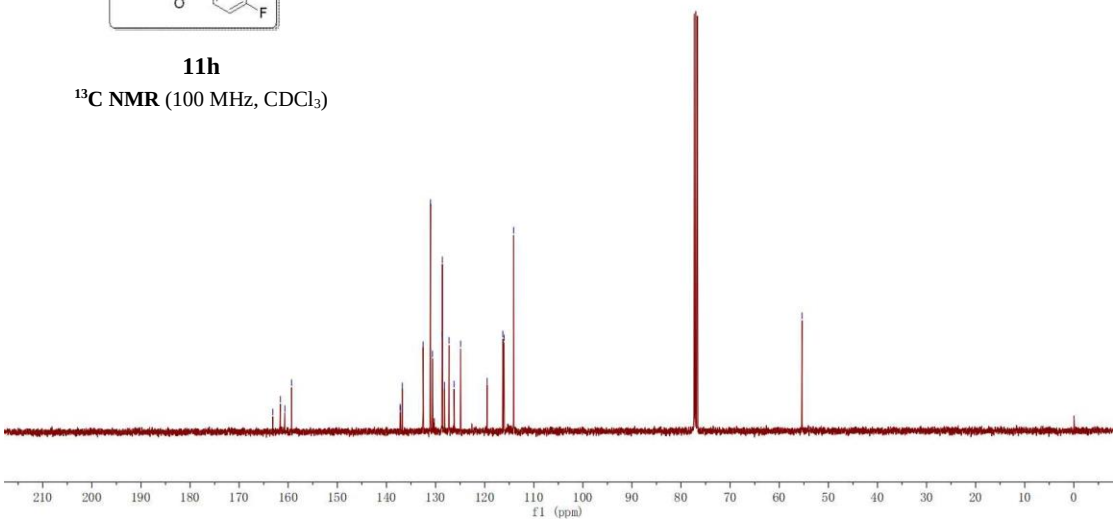
^{1}H NMR (400 MHz, $CDCl_3$)

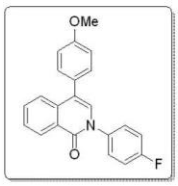




11h

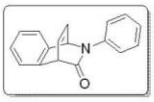
^{13}C NMR (100 MHz, $CDCl_3$)





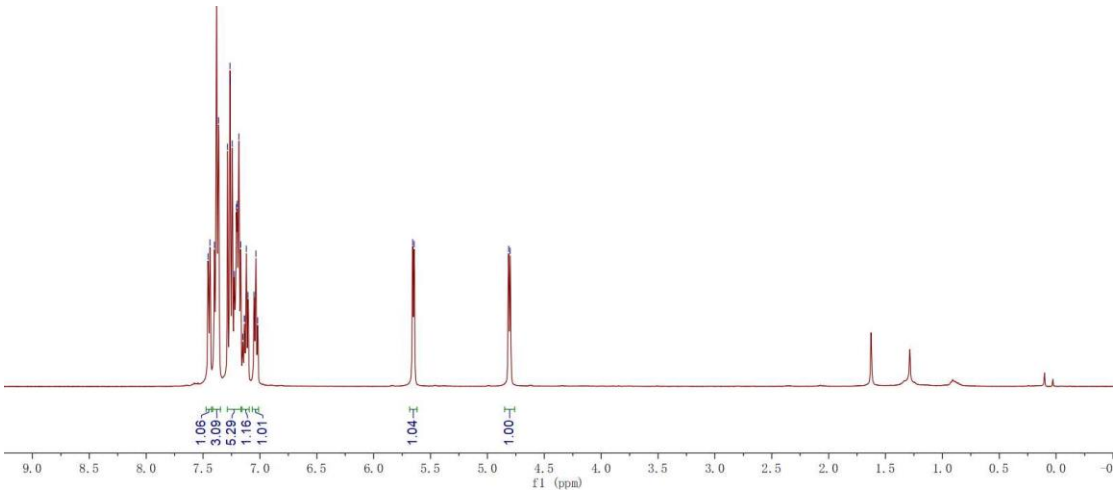
11h

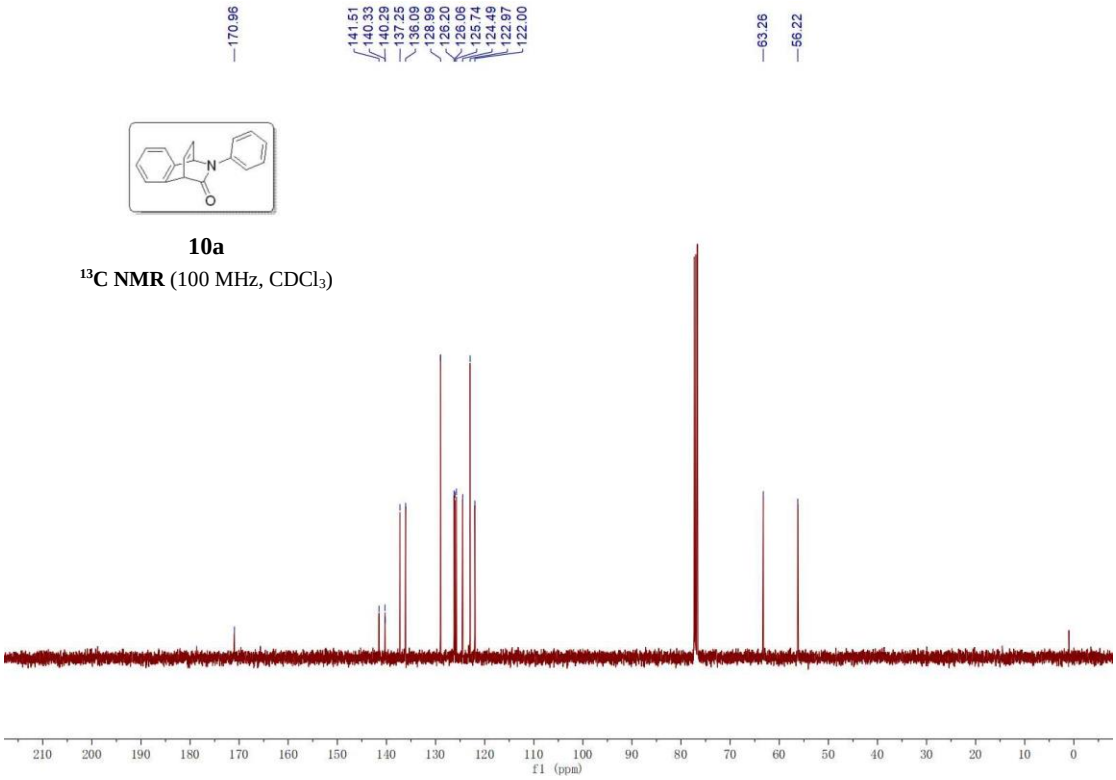
^{19}F NMR (377 MHz, $CDCl_3$)



10a

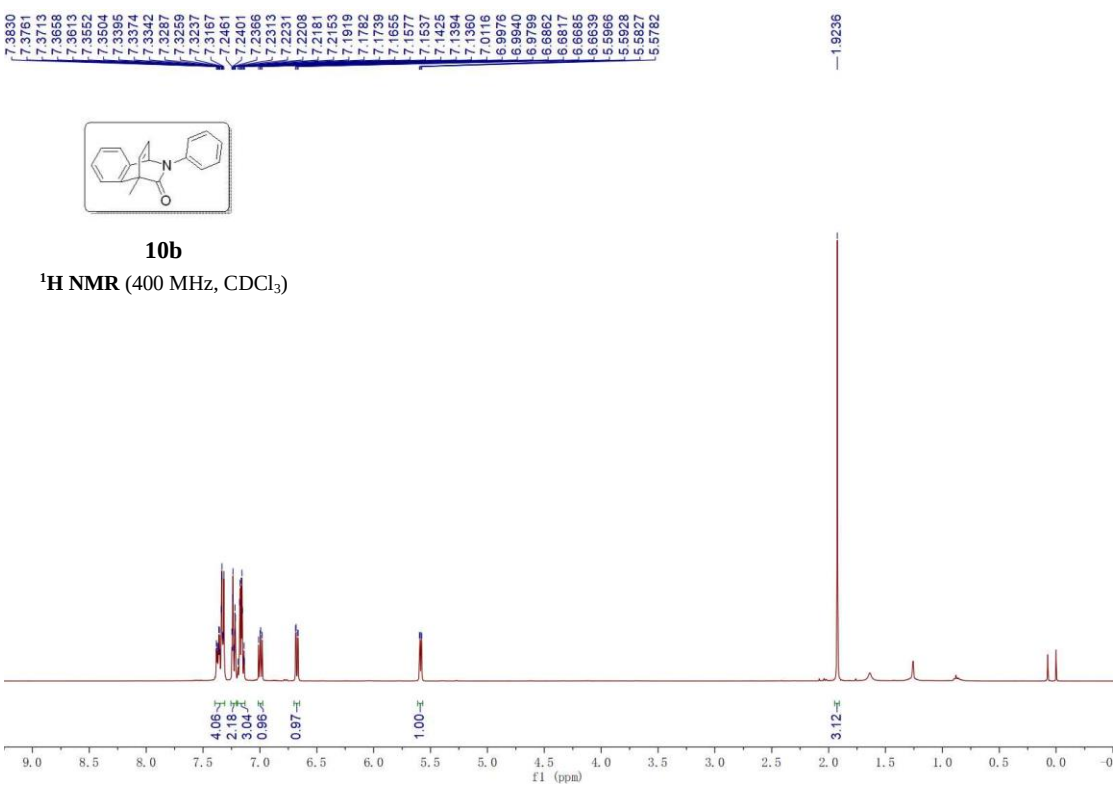
^{1}H NMR (400 MHz, $CDCl_3$)





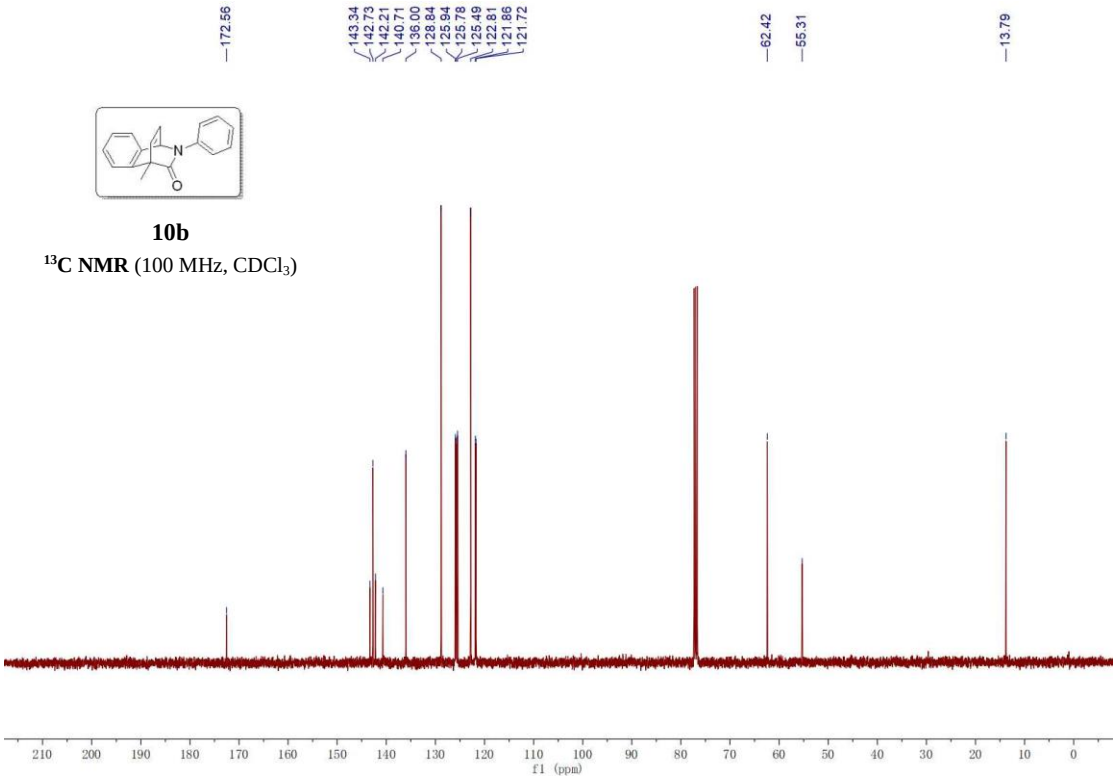
10a

^{13}C NMR (100 MHz, $CDCl_3$)



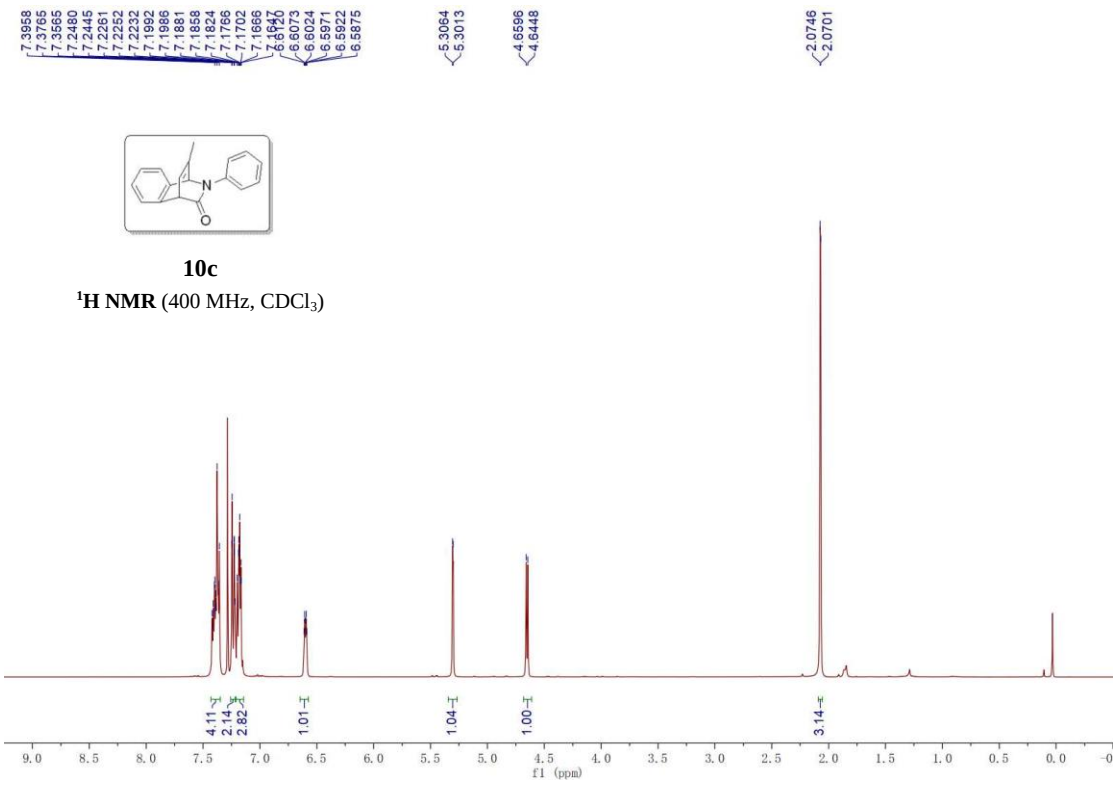
10b

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



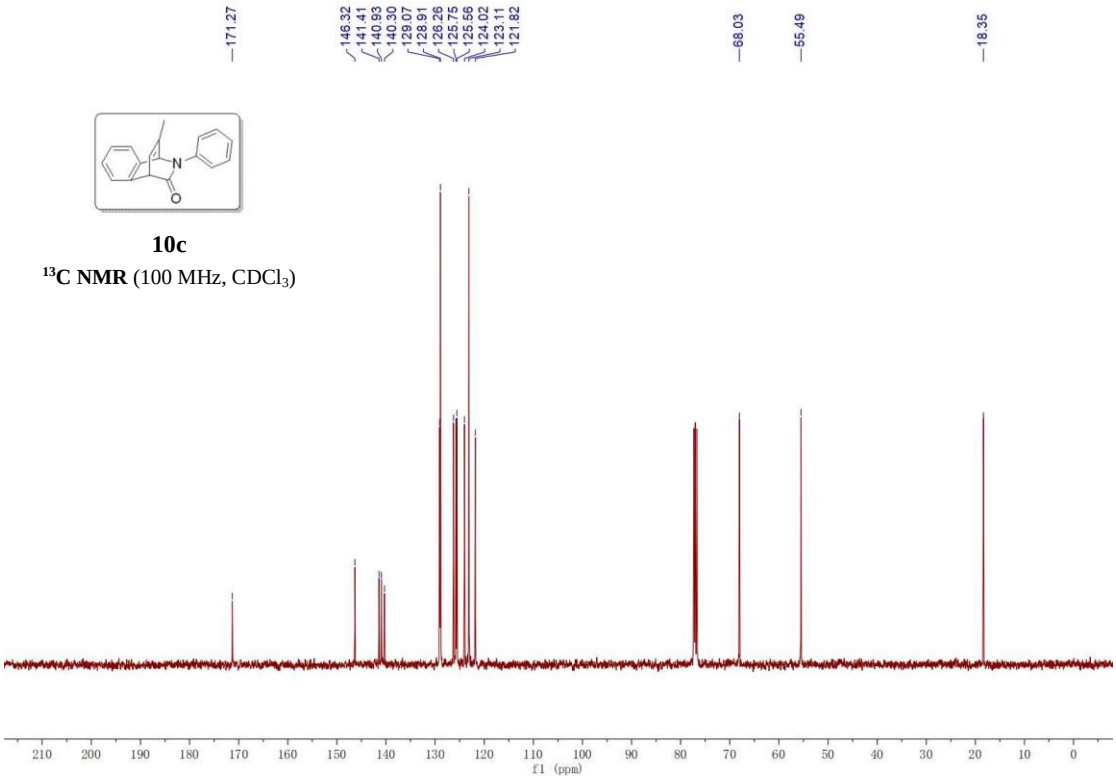
10b

^{13}C NMR (100 MHz, $CDCl_3$)



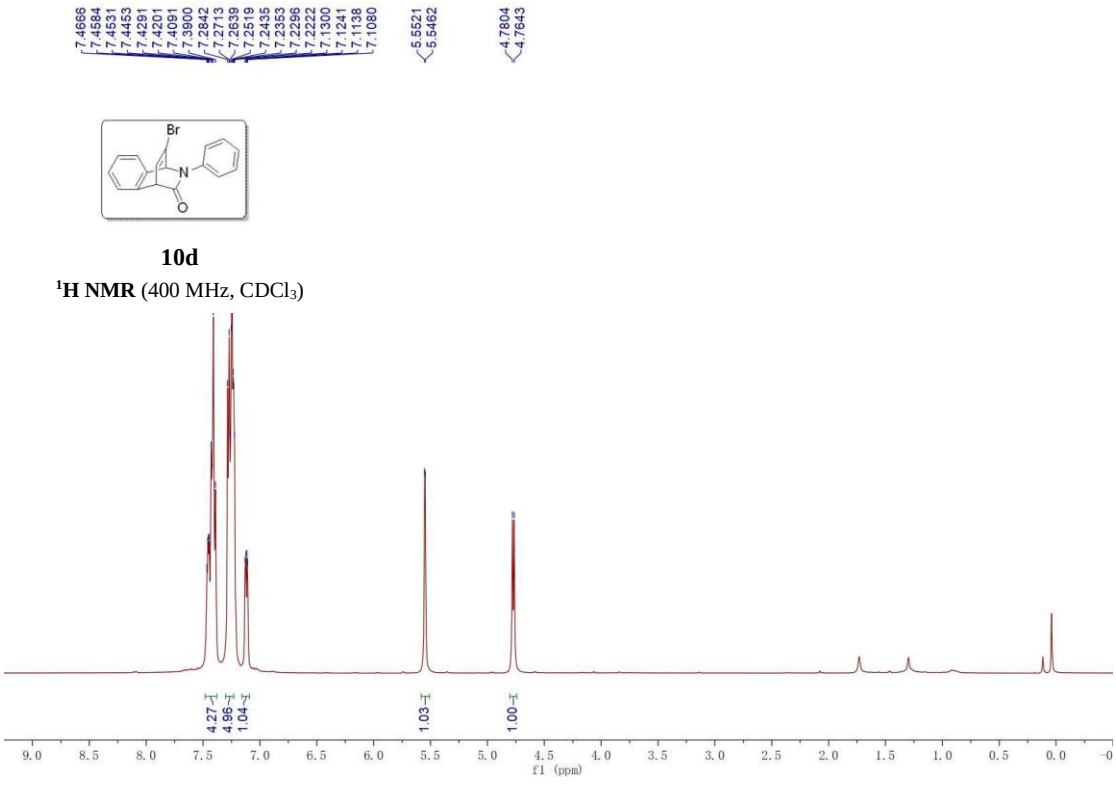
10c

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



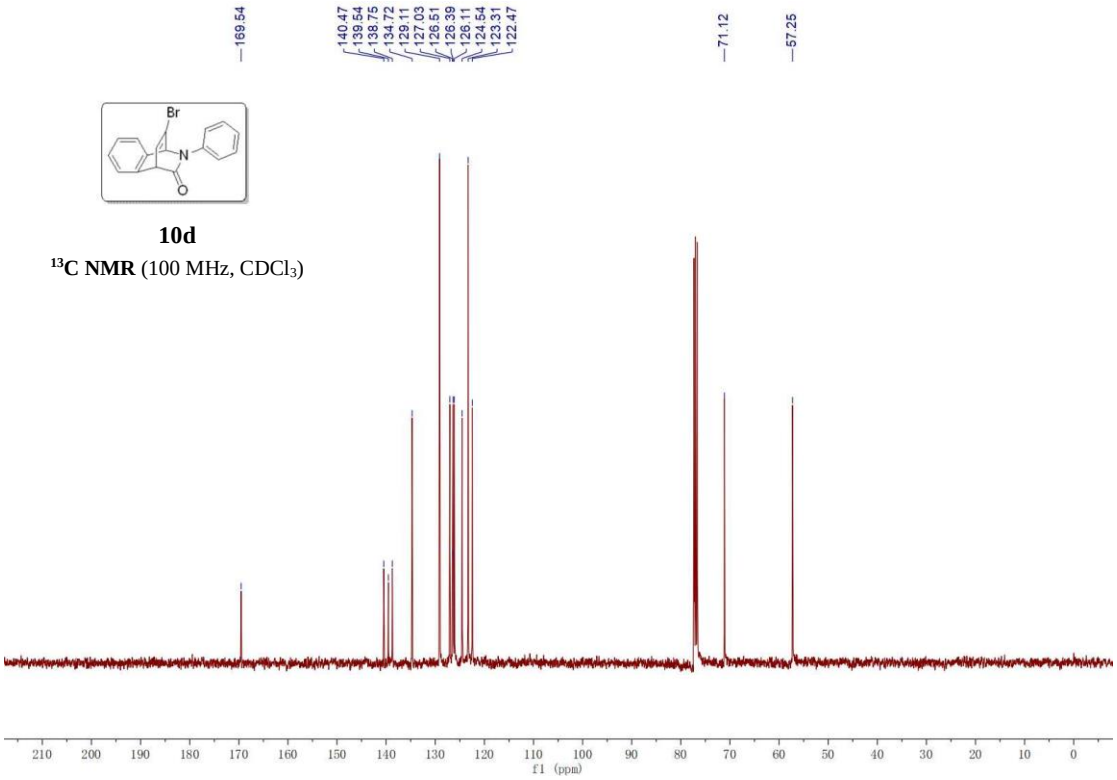
10c

^{13}C NMR (100 MHz, $CDCl_3$)



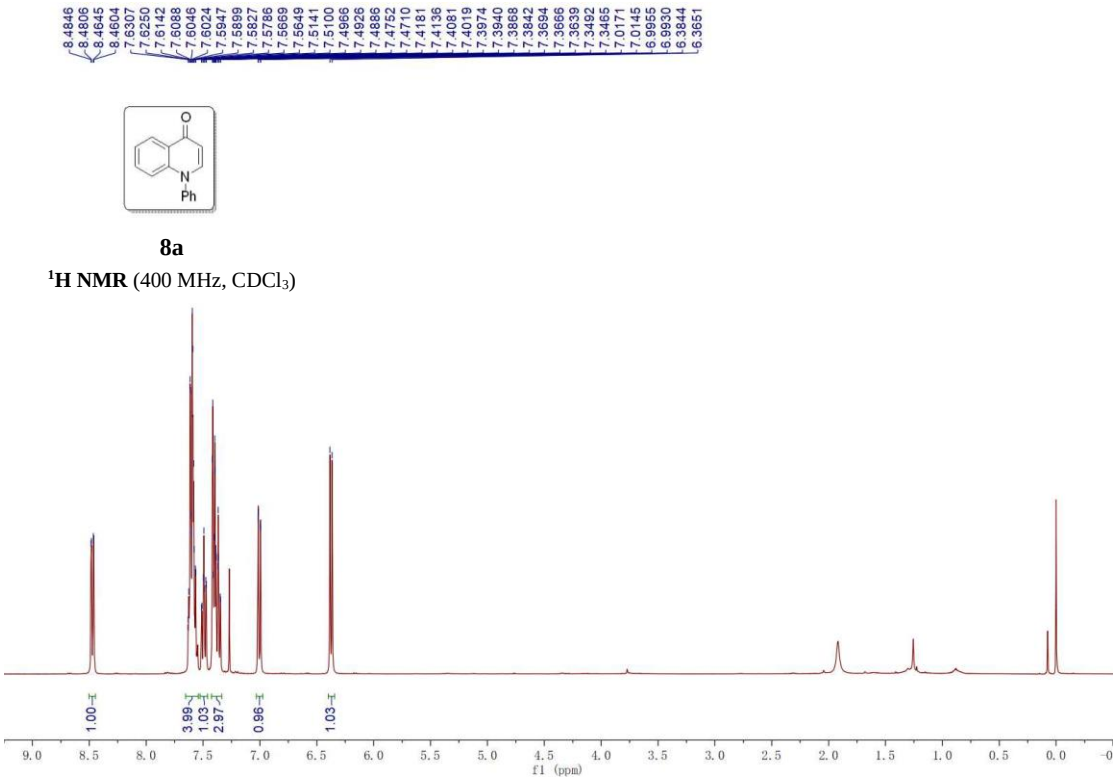
10d

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



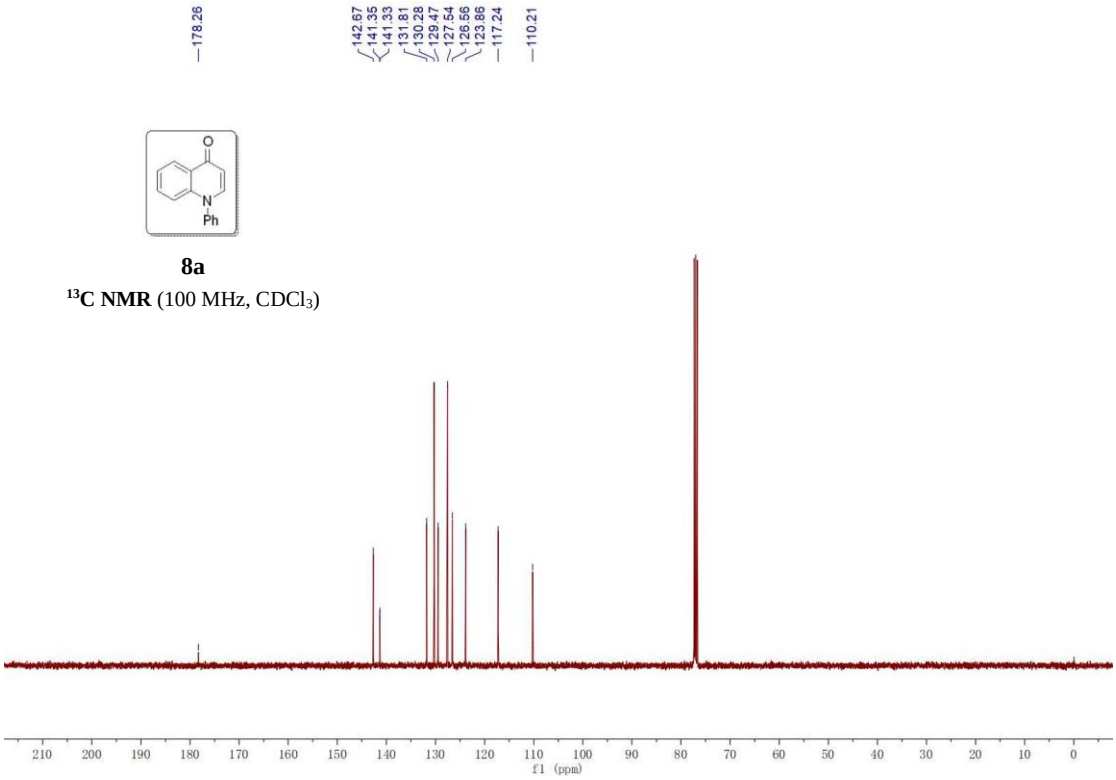
10d

^{13}C NMR (100 MHz, $CDCl_3$)



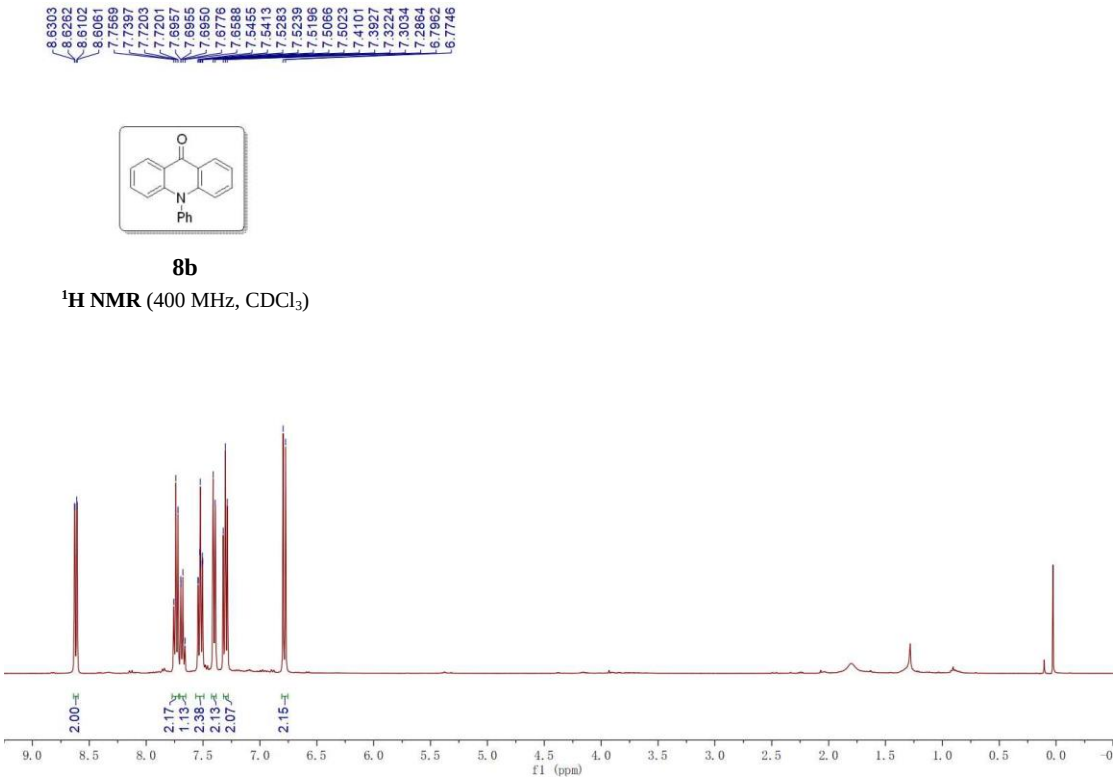
8a

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



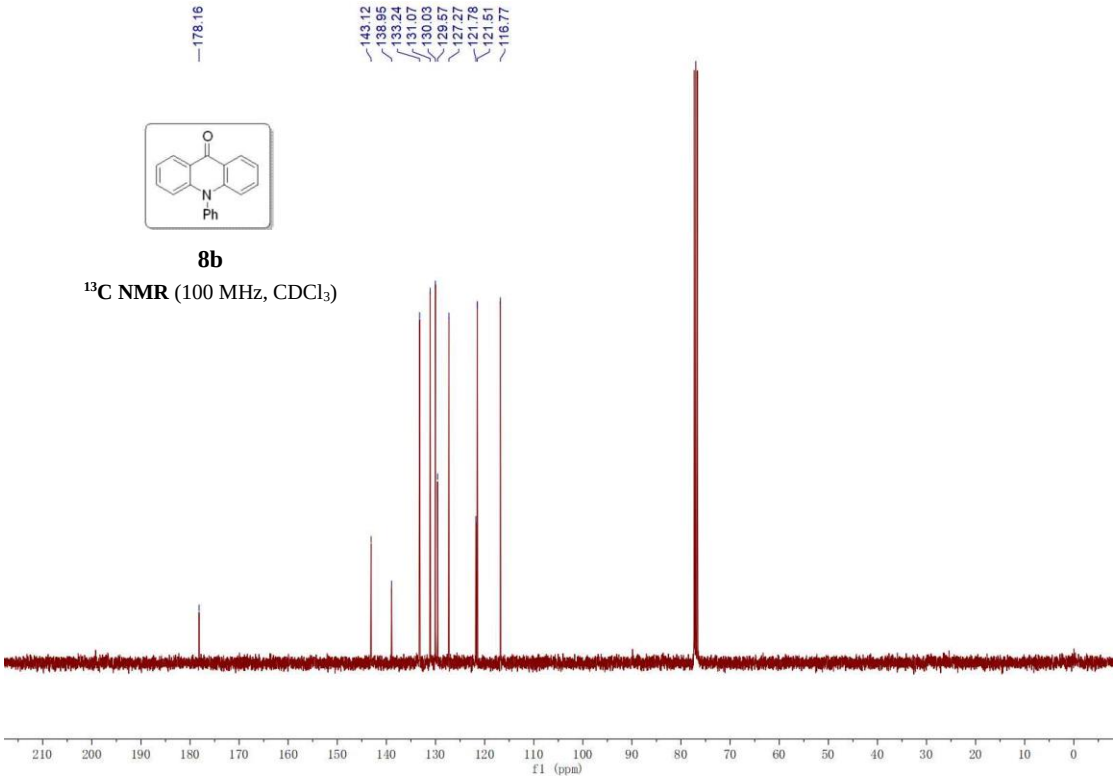
8a

^{13}C NMR (100 MHz, $CDCl_3$)



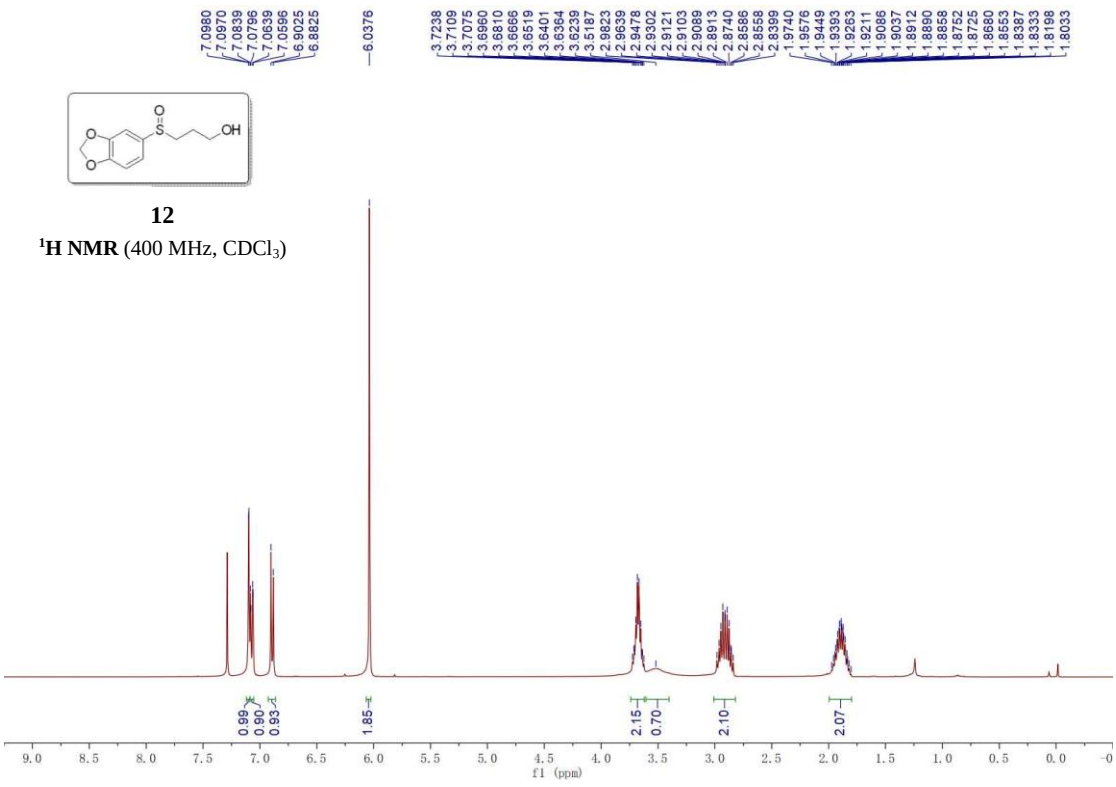
8b

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



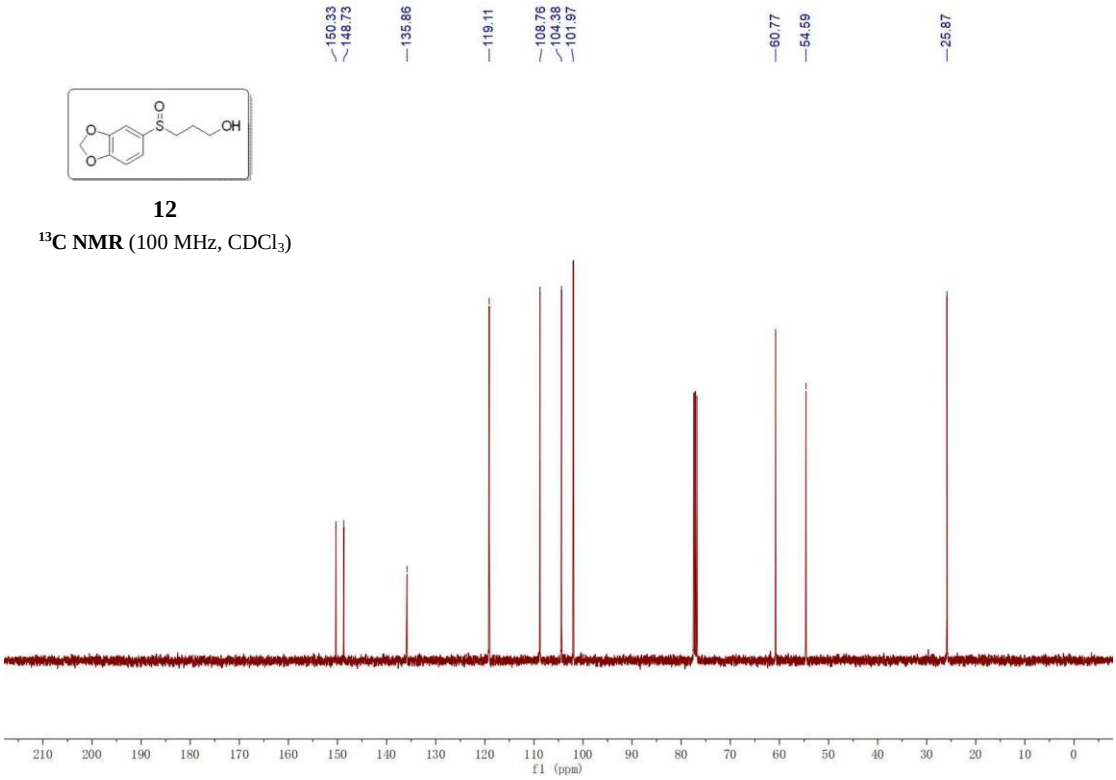
8b

^{13}C NMR (100 MHz, $CDCl_3$)



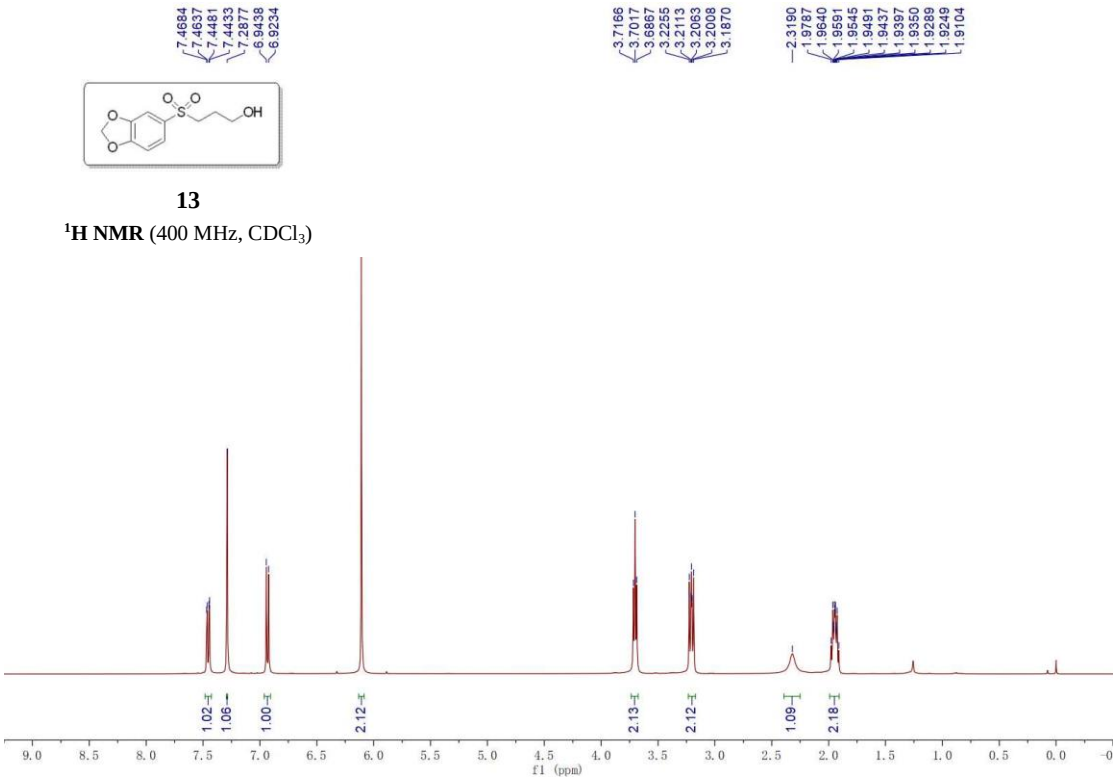
12

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



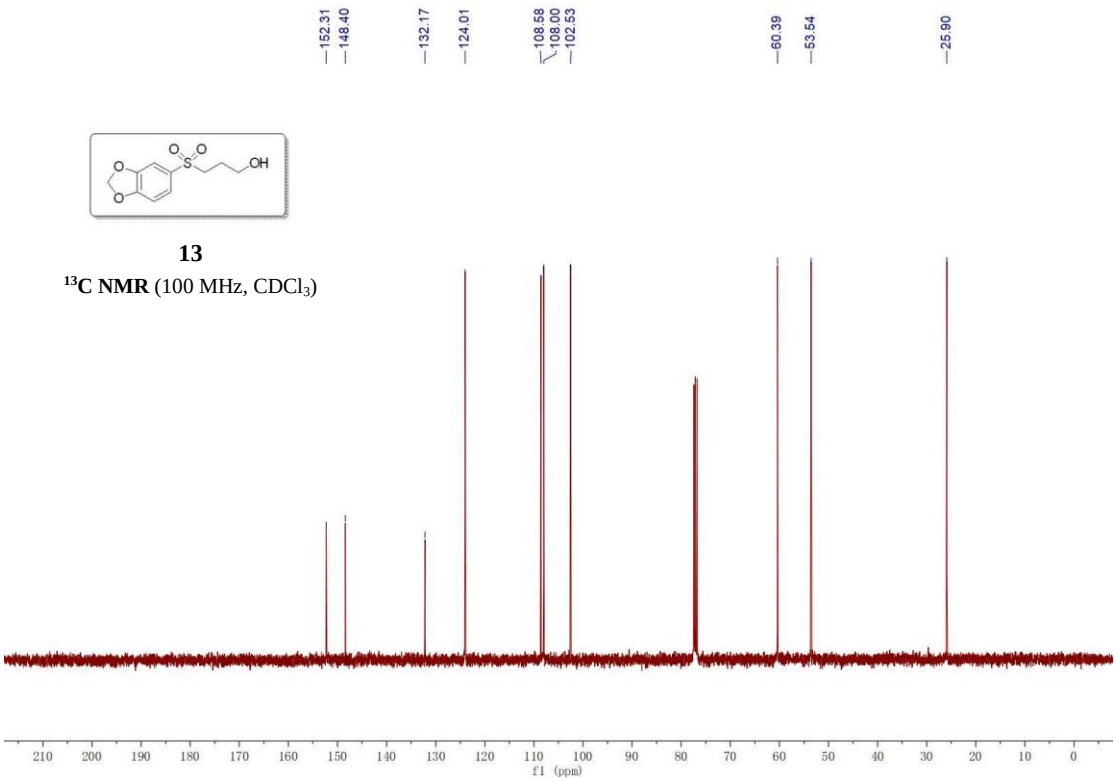
12

^{13}C NMR (100 MHz, $CDCl_3$)



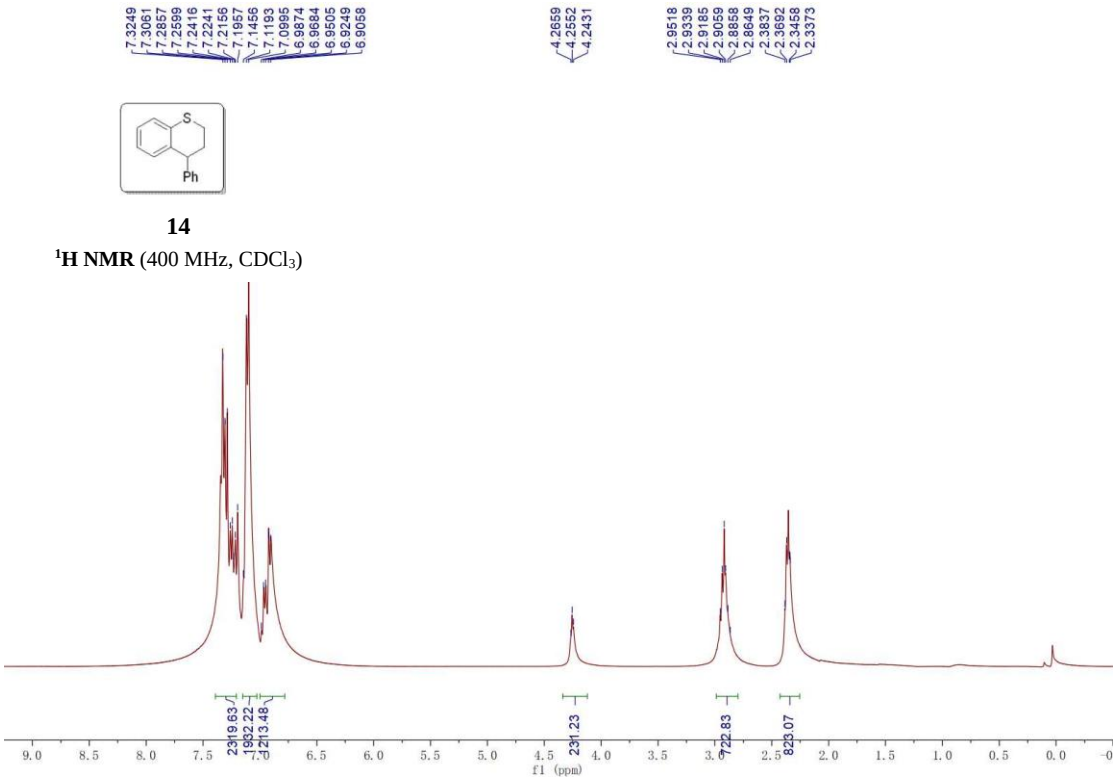
13

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



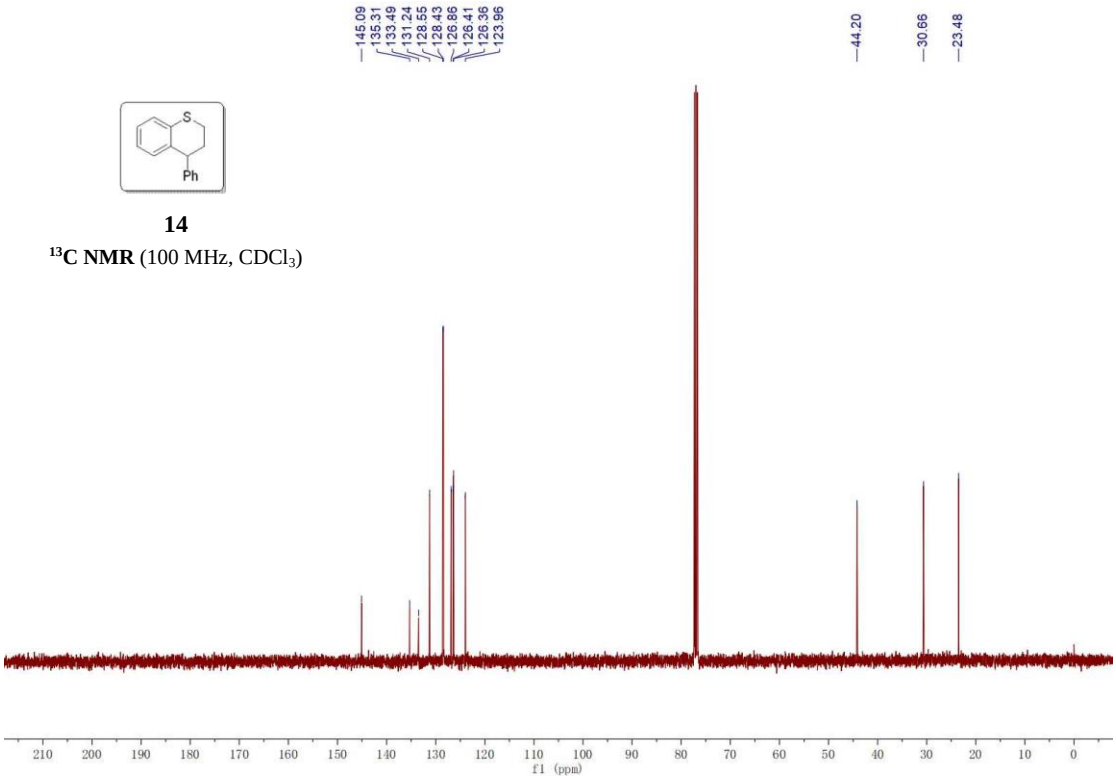
13

^{13}C NMR (100 MHz, $CDCl_3$)



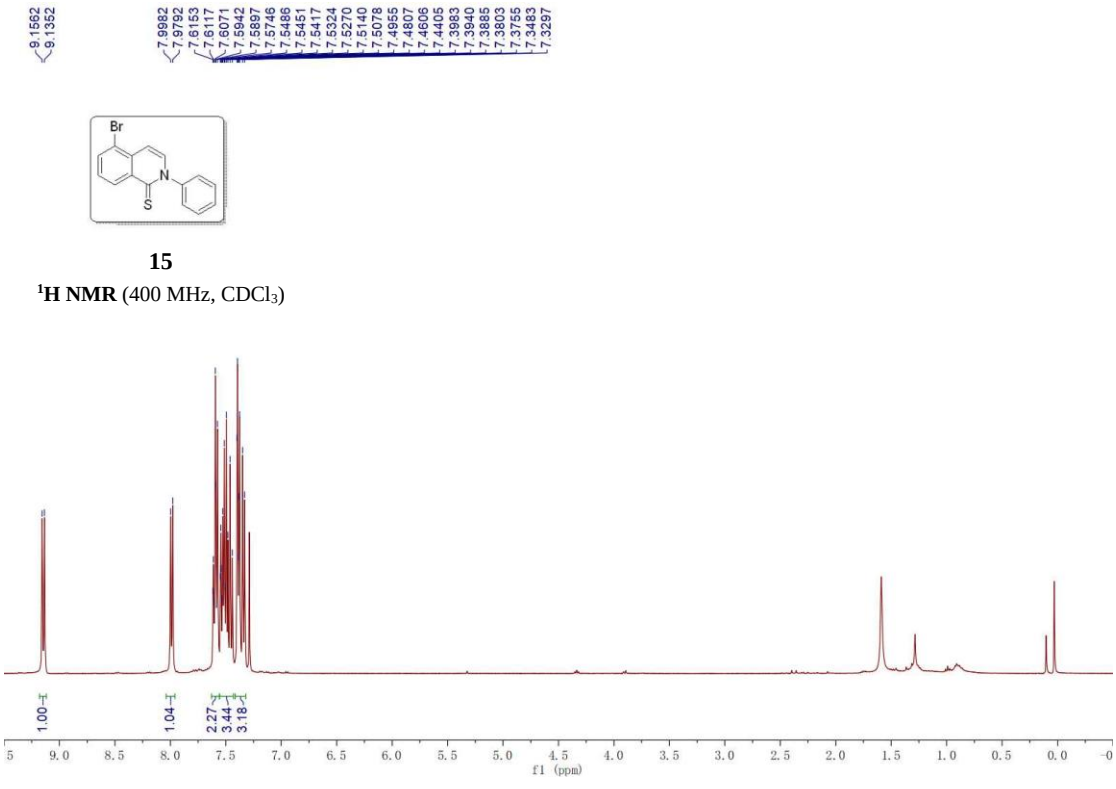
14

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



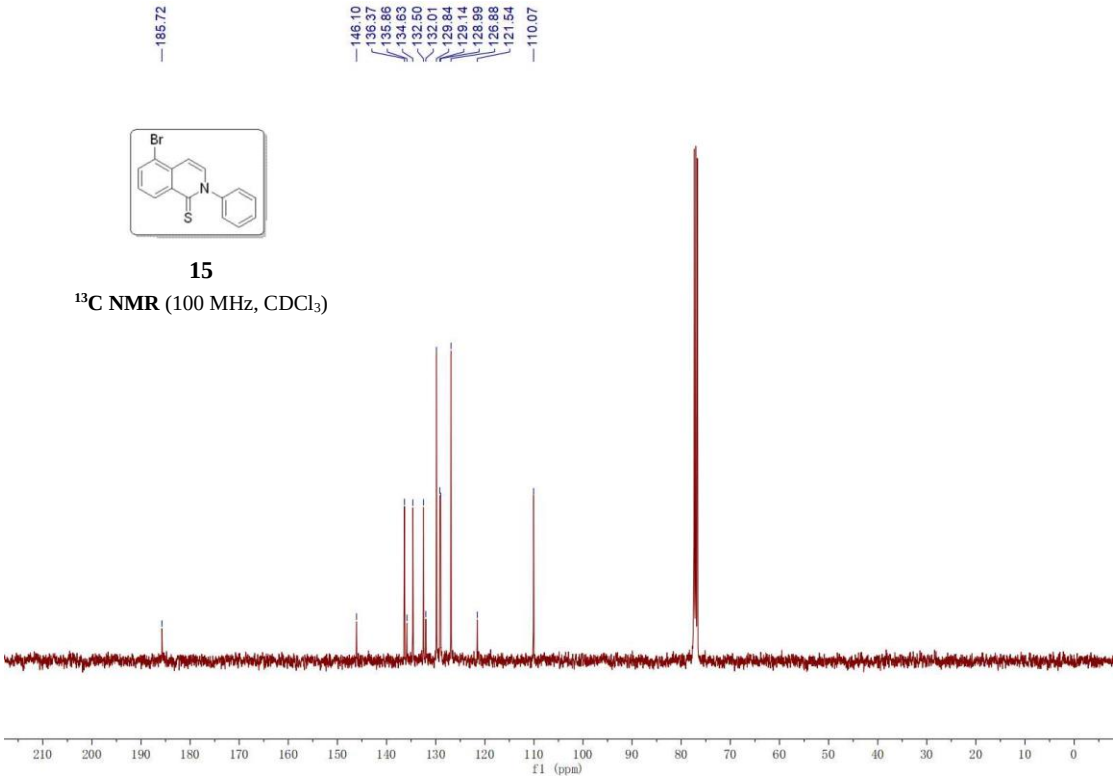
14

^{13}C NMR (100 MHz, $CDCl_3$)



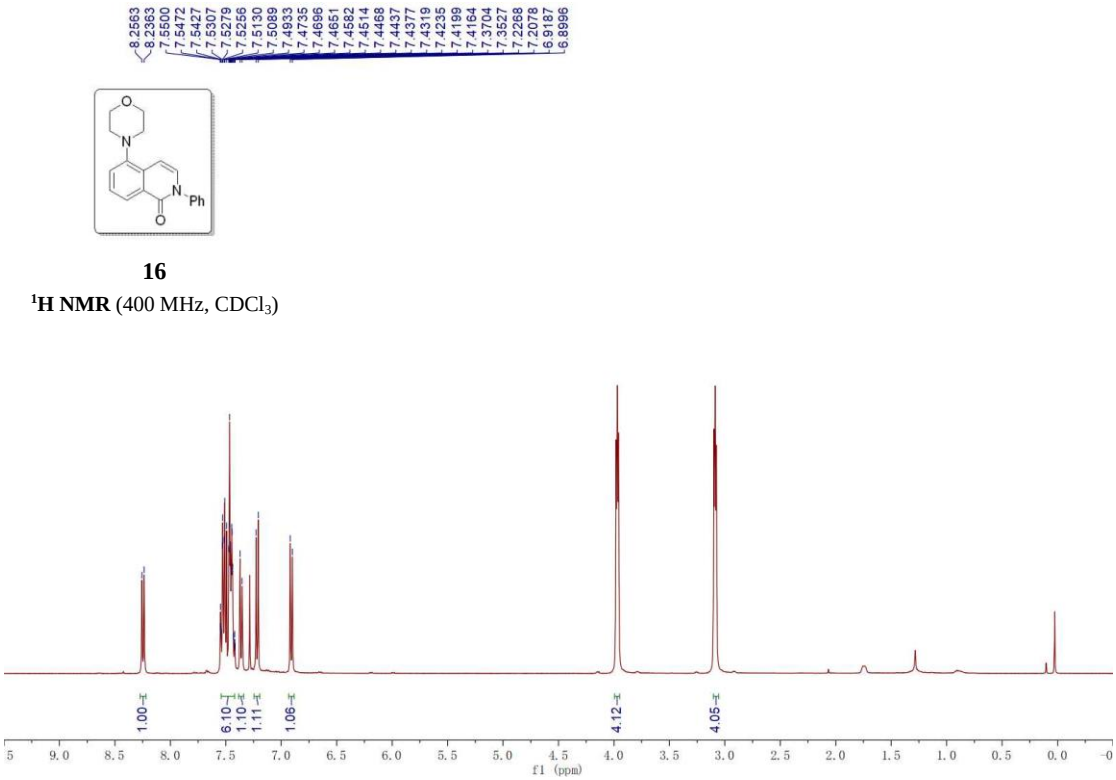
15

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



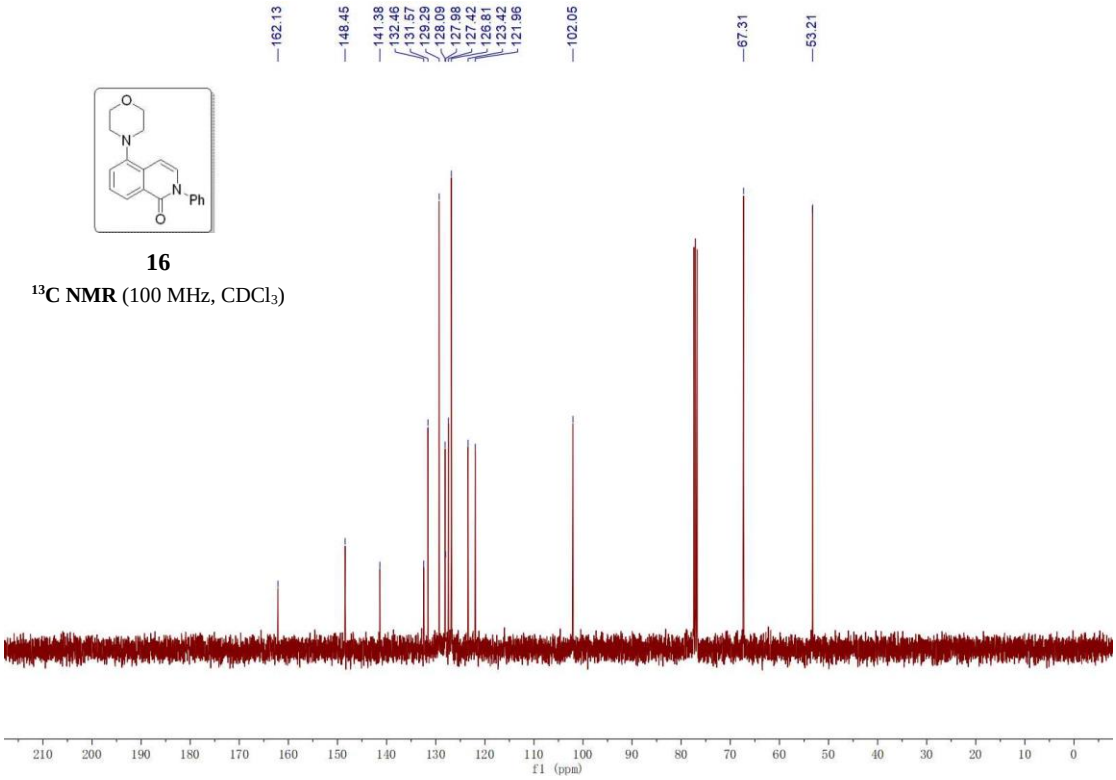
15

^{13}C NMR (100 MHz, $CDCl_3$)



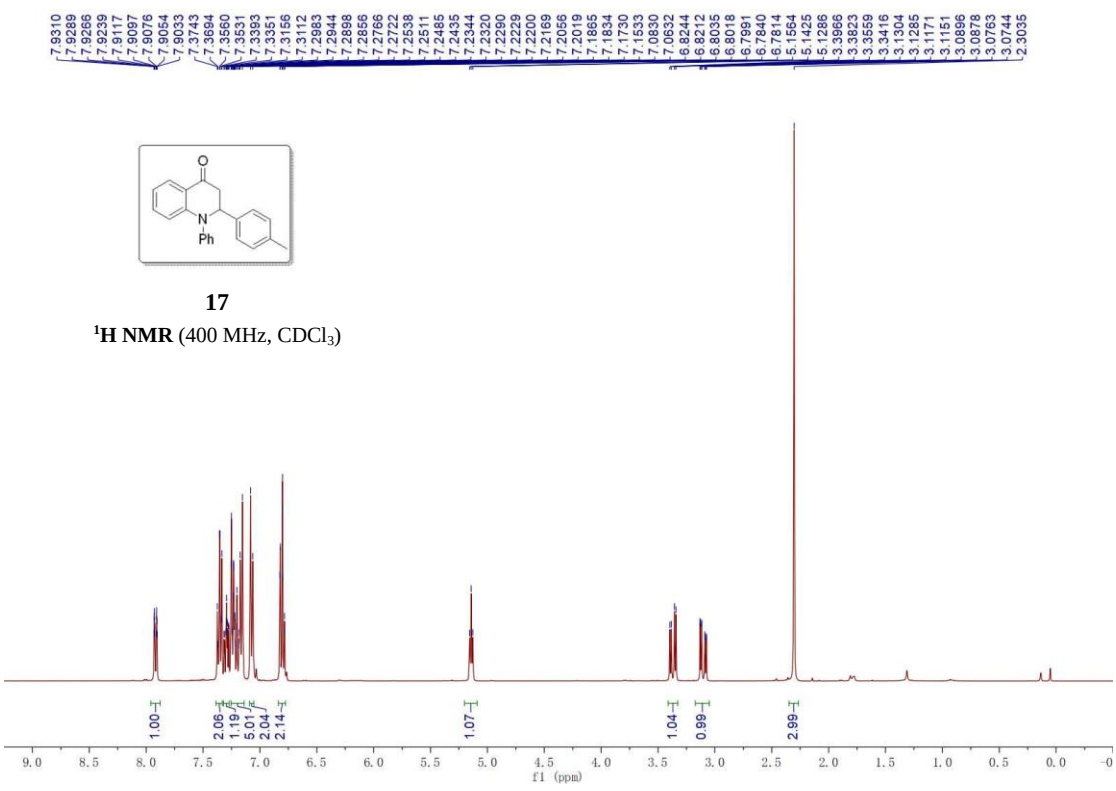
16

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



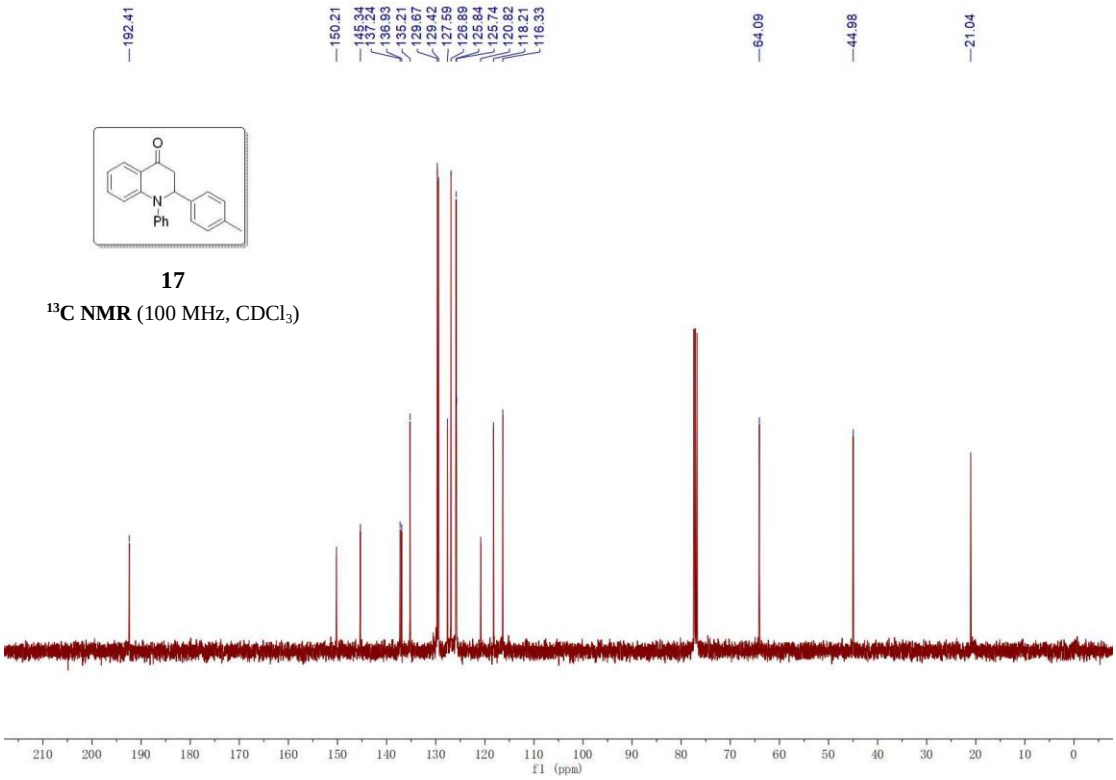
16

^{13}C NMR (100 MHz, $CDCl_3$)



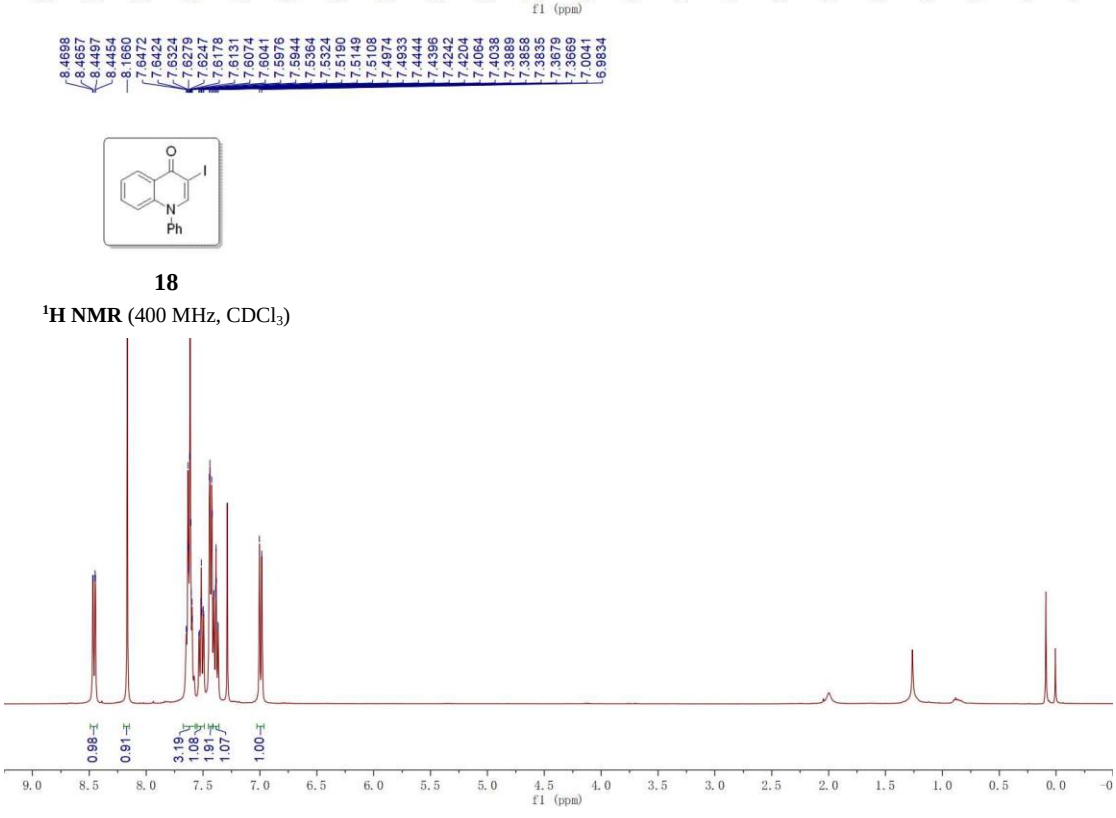
17

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



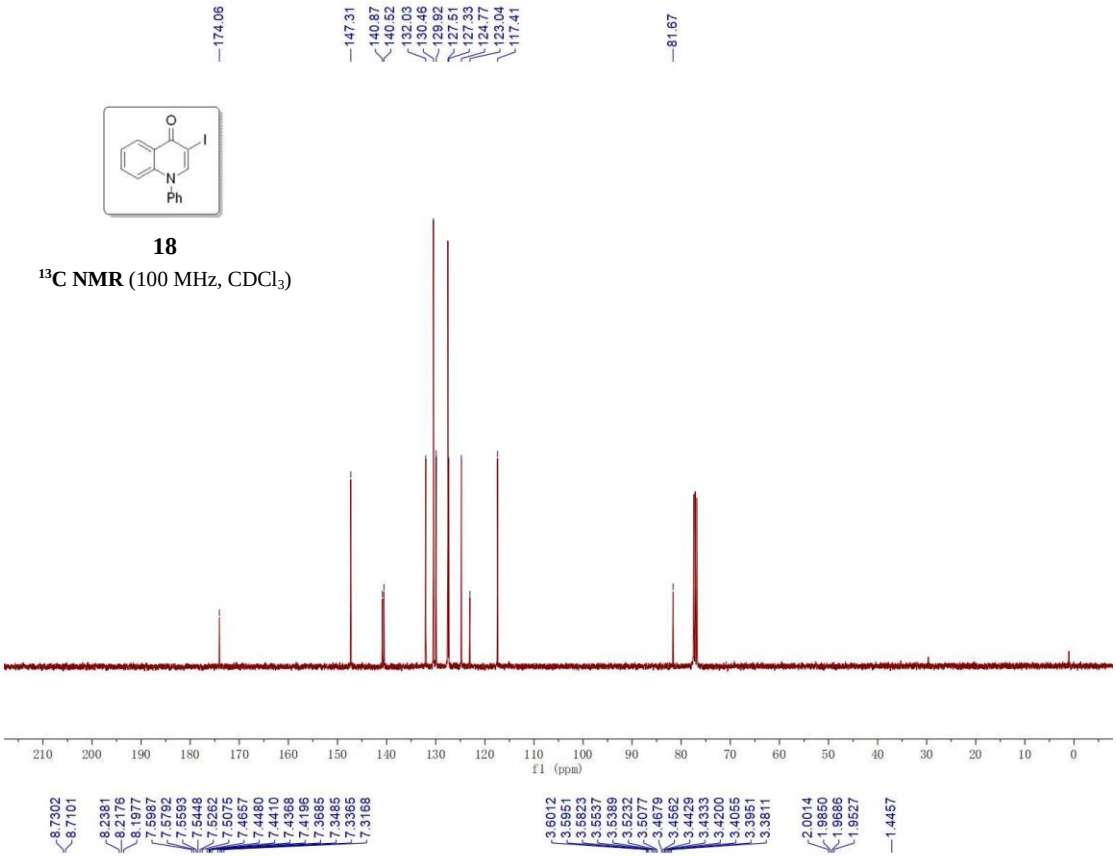
17

^{13}C NMR (100 MHz, $CDCl_3$)



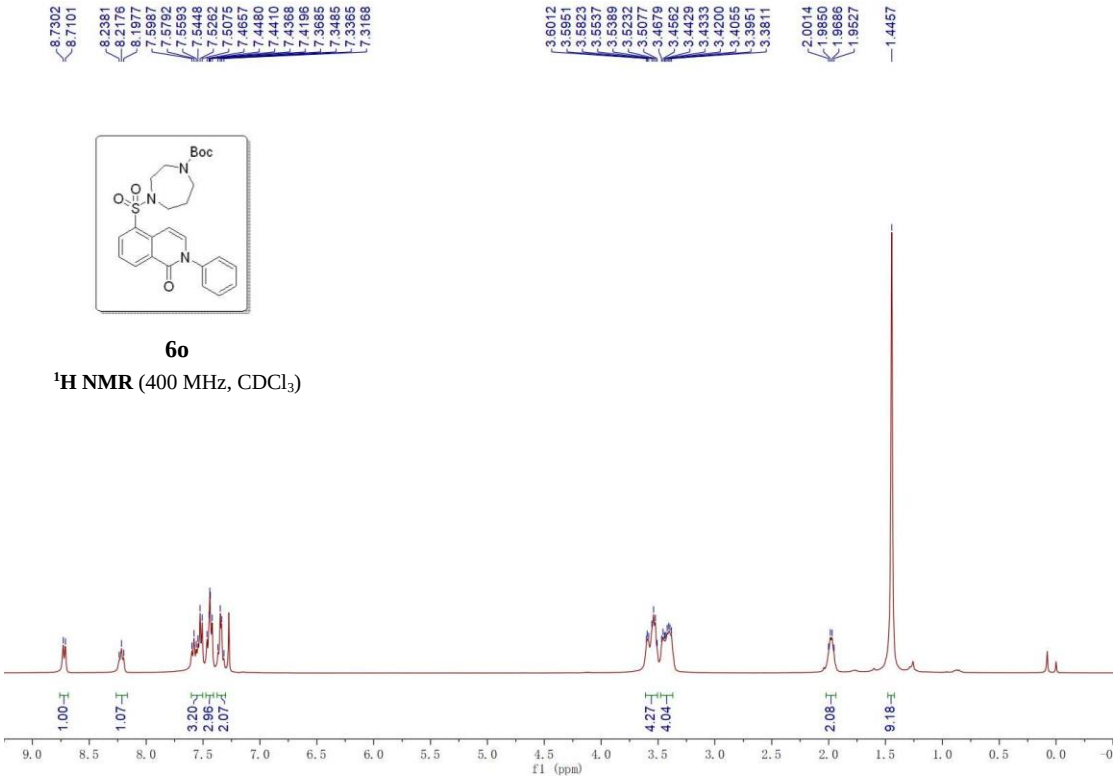
18

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



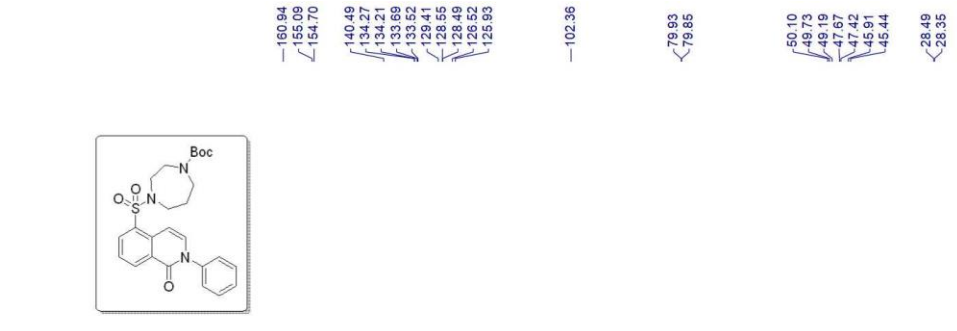
18

^{13}C NMR (100 MHz, $CDCl_3$)



6o

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



6o

^{13}C NMR (100 MHz, $CDCl_3$)