

Supporting Information

Pd-Catalyzed Domino Larock Annulation/Dearomative Heck Reaction

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1. General information

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under oven for two hours prior to use. ^1H and ^{13}C spectra were recorded on 500 MHz using CDCl_3 solvent with TMS as internal standard. Anhydrous DMF and NMP were freshly distilled under vacuum over CaH_2 . Anhydrous toluene were freshly distilled over Na and benzophenone. Melting points were measured on a microscopic apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on TOF LC/MS mass spectrometer. Column chromatography was carried out using silica gel (200-300 mesh).

2. Substrate synthesis

(1) Synthesis of *N*-benzoyl *o*-iodoaniline derivatives

N-benzoyl *o*-iodoaniline derivatives **1** were synthesized according to the known method¹ by using *o*-iodoaniline and acid chloride (freshly prepared by treating arylcarboxylic acid with oxalyl chloride) as the substrates.

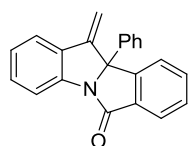
(2) Synthesis of alkynes

Phenylpropyne, 2-butyne, 4-octyne, and 2-butyne-1-ol were purchased from commercial suppliers and used without further purification. Other alkynes **2** were synthesized according to the known method² by using iodobenzene derivatives and propyne (ca. 4% in *N,N*-Dimethylformamide, ca. 1.0 mol/L) as the substrates.

3. General procedure for the domino reaction

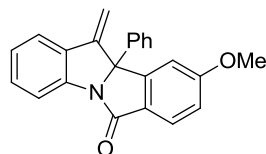
To a Schlenk tube was charged with $\text{Pd}(\text{OAc})_2$ (5 mol%), dppf (6 mol%), LiCl (0.2 mol), **1** (0.2 mmol), alkyne **2** (0.3 mmol, 1.5 equiv), NEt_3 (0.8 mmol, 4.0 equiv) under N_2 , and DMF (2.0 mL). The reaction mixture was then stirred at 120 °C for 2-48 h. When the reaction was completed, the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 50:1 to 10:1) to afford the products **3-5**, and **7**.

11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3a)^{2,3}



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3a** as a white solid (50.7 mg, 82%), m.p. 168-170 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.63 (dd, J = 5.6, 3.6 Hz, 2H), 7.60-7.57 (m, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.51-7.47 (m, 2H), 7.38 (td, J = 7.8, 0.9 Hz, 1H), 7.33-7.29 (m, 2H), 7.28-7.24 (m, 1H), 7.16-7.11 (m, 1H), 5.88 (s, 1H), 5.61 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.5, 149.5, 146.0, 141.3, 140.9, 133.9, 133.6, 132.0, 130.3, 128.9, 128.6, 128.1, 125.7, 125.2, 125.0, 123.1, 121.5, 117.7, 107.8, 78.8.

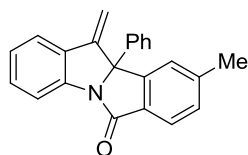
9-methoxy-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3b)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3b** as a white solid (63.3 mg, 93%), m.p. 139-141 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.60 (dd, J = 7.1, 2.0 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.33-7.24 (m, 3H), 7.12 (t, J = 7.6 Hz, 1H), 7.01-6.96 (m, 2H),

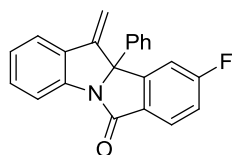
5.87 (s, 1H), 5.59 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 164.3, 151.9, 146.1, 141.8, 141.0, 133.7, 130.3, 128.6, 128.1, 126.8, 125.8, 124.8, 124.4, 121.4, 117.7, 114.9, 108.5, 107.4, 78.3, 55.7; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{28}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 340.1332, Found 340.1348.

9-methyl-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3c)



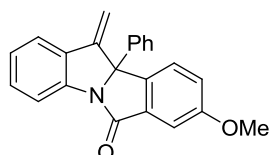
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3c** as a yellow solid (59.0 mg, 91%), m.p. 205-207 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 7.7, 2.2 Hz, 2H), 7.48 (d, J = 9.9 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.33-7.26 (m, 5H), 7.13 (t, J = 7.7 Hz, 1H), 5.87 (s, 1H), 5.61 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 150.0, 146.2, 144.7, 141.6, 141.2, 133.8, 130.3, 130.0, 129.5, 128.6, 128.0, 125.8, 125.0, 124.9, 123.6, 121.4, 117.8, 107.6, 78.7, 22.2; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$): 324.1383, Found 324.1396.

9-fluoro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3d)



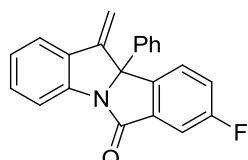
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3d** as a yellow solid (47.9 mg, 73%), m.p. 165-167 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (dd, J = 8.3, 5.0 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.61-7.59 (m, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.34-7.28 (m, 3H), 7.21-7.13 (m, 3H), 5.89 (s, 1H), 5.57 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.6, 166.3 (d, J = 252.5 Hz), 152.0 (d, J = 10 Hz), 145.6, 141.4, 140.3, 133.7, 130.5, 128.8, 128.4, 128.1, 127.4 (d, J = 10 Hz), 125.7, 125.2, 121.5, 117.8, 116.8 (d, J = 23.8 Hz), 110.7 (d, J = 25 Hz), 107.9, 78.4; HRMS m/z (ESI+): Calculated for $\text{C}_{22}\text{H}_{15}\text{FNO}$ ($[\text{M}+\text{H}]^+$): 328.1132, Found 328.1144.

8-methoxy-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3e)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3e** as a white solid (62.0 mg, 91%), m.p. 125-127 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.76-7.74 (m, 1H), 7.59-7.57 (m, 2H), 7.49 (dd, J = 7.6, 1.1 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.39-7.36 (m, 2H), 7.31-7.29 (m, 2H), 7.28-7.23 (m, 1H), 7.17-7.12 (m, 2H), 5.85 (s, 1H), 5.55 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 160.5, 146.2, 142.1, 141.3, 141.2, 134.0, 133.5, 130.3, 128.5, 128.0, 125.7, 125.0, 123.9, 122.0, 121.5, 117.7, 107.6, 107.5, 78.5, 55.7; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{18}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 340.1332, Found 340.1346.

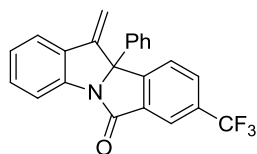
8-fluoro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3f)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3f** as a light yellow solid (56.5 mg, 86%), m.p. 144-146 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, J = 7.9 Hz, 1H), 7.60-7.57 (m, 3H), 7.51-7.48 (m, 2H), 7.37 (td, J = 7.8, 1.2 Hz, 1H), 7.33-7.26 (m, 4H), 7.15 (t, J = 7.6 Hz, 1H), 5.88 (s, 1H), 5.56 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.2, 163.1 (d, J = 247.5 Hz), 145.7, 145.1, 141.0, 140.5, 134.2 (d, J = 7.5 Hz), 133.8, 130.4, 128.6, 128.2, 125.6, 125.3, 124.7 (d, J = 7.5 Hz), 121.6, 121.1 (d, J = 23.8 Hz), 117.7, 111.7 (d, J = 23.8 Hz), 108.0, 78.6; HRMS m/z (ESI+): Calculated for $\text{C}_{22}\text{H}_{15}\text{FNO}$

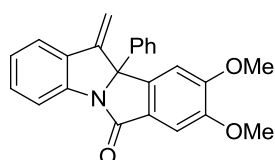
$[\text{M}+\text{H}]^+$: 328.1132, Found 328.1123.

11-methylene-10b-phenyl-8-(trifluoromethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3g)



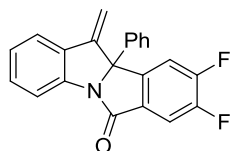
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **3g** as a yellow solid (41.7 mg, 56%), m.p. 142-144 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, J = 1.5 Hz, 1H), 7.86 (dd, J = 8.2, 1.8 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.62-7.60 (m, 2H), 7.51 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.35-7.28 (m, 3H), 7.17 (t, J = 7.5 Hz, 1H), 5.92 (s, 1H), 5.60 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.9, 152.5, 145.4, 141.0, 139.9, 133.7, 133.0, 131.7 (q, J = 33.8 Hz), 130.6, 130.4 (q, J = 3.8 Hz), 128.8, 128.5, 125.7, 125.5, 124.6, 123.9, 122.5 (q, J = 3.8 Hz), 121.6, 117.9, 108.2, 79.0; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{15}\text{F}_3\text{NO}$ ($[\text{M}+\text{H}]^+$): 378.1100, Found 378.1114.

8,9-dimethoxy-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3h)



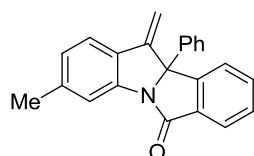
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3h** as a white solid (68.6 mg, 93%), m.p. 170-172 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, J = 7.6 Hz, 1H), 7.56-7.54 (m, 2H), 7.49 (dd, J = 7.5, 1.1 Hz, 1H), 7.38-7.33 (m, 2H), 7.31-7.25 (m, 3H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 6.88 (s, 1H), 5.88 (s, 1H), 5.55 (s, 1H), 3.94 (s, 4H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.2, 154.4, 150.4, 146.1, 144.0, 141.7, 141.1, 133.9, 130.3, 128.5, 128.0, 126.0, 124.7, 124.1, 121.3, 117.7, 107.2, 106.1, 104.9, 78.4, 56.3, 56.2; HRMS m/z (ESI+): Calculated for $\text{C}_{24}\text{H}_{20}\text{NO}_3$ ($[\text{M}+\text{H}]^+$): 370.1438, Found 370.1450.

8,9-difluoro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3i)



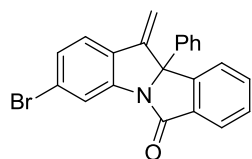
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3i** as a white solid (43.1 mg, 63%), m.p. 190-192 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.73-7.69 (m, 2H), 7.59-7.56 (m, 2H), 7.50 (dd, J = 7.8, 1.1 Hz, 1H), 7.39-7.37 (m, 1H), 7.34-7.28 (m, 4H), 7.18-7.16 (m, 1H), 5.90 (d, J = 1.3 Hz, 1H), 5.53 (d, J = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.7, 153.9 (dd, J = 361.9, 14.0 Hz), 151.9 (dd, J = 357.5, 14.0 Hz), 146.0 (dd, J = 7.5, 3.1 Hz), 145.3, 141.0, 139.9, 133.7, 130.6, 128.8, 128.5, 128.4 (dd, J = 6.3, 2.8 Hz), 125.6, 125.4, 121.6, 117.8, 113.9 (dd, J = 18.9, 1.5 Hz), 112.4 (d, J = 20.0 Hz), 108.1, 78.3; HRMS m/z (ESI+): Calculated for $\text{C}_{22}\text{H}_{14}\text{F}_2\text{NO}$ ($[\text{M}+\text{H}]^+$): 346.1038, Found 346.1054.

3-methyl-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3j)



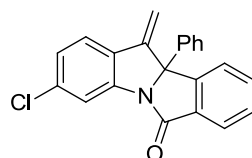
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3j** as a white solid (42.5 mg, 65%), m.p. 156-158 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 7.7 Hz, 1H), 7.62-7.58 (m, 4H), 7.54 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.32-7.23 (m, 3H), 6.95 (d, J = 8.4 Hz, 1H), 5.80 (s, 1H), 5.54 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.5, 149.6, 145.9, 141.5, 141.1, 141.0, 133.5, 132.2, 131.3, 128.8, 128.5, 128.0, 125.9, 125.7, 125.2, 123.1, 121.2, 118.3, 106.6, 79.1, 21.8; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$): 324.1383, Found 324.1393.

3-bromo-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3k)



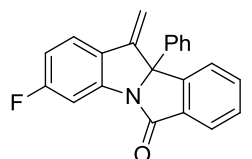
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3k** as a yellow solid (42.9 mg, 55%), m.p. 178-180 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93-7.91 (m, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.56-7.50 (m, 4H), 7.34-7.31 (m, 3H), 7.29-7.25 (m, 2H), 5.87 (s, 1H), 5.62 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 149.4, 145.2, 142.4, 140.6, 133.9, 131.7, 129.1, 128.7, 128.3, 128.2, 125.7, 125.5, 124.0, 123.2, 122.5, 121.1, 108.4, 79.1; HRMS *m/z* (ESI+): Calculated for C₂₂H₁₅BrNO ([M+H]⁺): 388.0332, Found 388.0348.

3-chloro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3l)



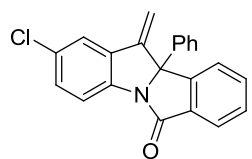
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3l** as a yellow solid (31.6 mg, 46%), m.p. 168-170 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.58-7.49 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33-7.25 (m, 3H), 7.10 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.85 (s, 1H), 5.61 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 149.4, 145.1, 142.2, 140.7, 136.0, 133.9, 132.4, 131.7, 129.1, 128.7, 128.3, 125.7, 125.4, 125.3, 123.1, 122.2, 118.2, 108.3, 79.2; HRMS *m/z* (ESI+): Calculated for C₂₂H₁₅ClNO ([M+H]⁺): 344.0837, Found 344.0853.

3-fluoro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3m)



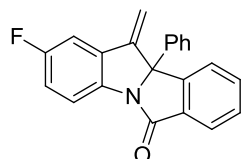
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3m** as a white solid (42.9 mg, 66%), m.p. 176-178 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.63-7.57 (m, 3H), 7.54-7.47 (m, 3H), 7.42 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.33-7.26 (m, 3H), 6.83 (td, *J* = 8.7, 2.4 Hz, 1H), 5.80 (s, 1H), 5.56 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 164.2 (d, *J* = 247.5 Hz), 149.5, 145.1, 142.7 (d, *J* = 11.3 Hz), 140.8, 133.9, 131.7, 129.8 (d, *J* = 2.7 Hz), 129.0, 128.7, 128.2, 125.7, 125.4, 123.1, 122.5 (d, *J* = 10.0 Hz), 112.1 (d, *J* = 23.8 Hz), 107.3 (d, *J* = 2.2 Hz), 105.8 (d, *J* = 26.7 Hz), 79.4; HRMS *m/z* (ESI+): Calculated for C₂₂H₁₅FNO ([M+H]⁺): 328.1132, Found 328.1145.

2-chloro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3n)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3n** as a yellow solid (39.1 mg, 57%), m.p. 150-152 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.57 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.53-7.49 (m, 2H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.34-7.26 (m, 4H), 5.87 (s, 1H), 5.64 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 149.3, 145.1, 140.5, 139.9, 135.5, 133.8, 131.8, 130.6, 130.2, 129.1, 128.7, 128.3, 125.7, 125.4, 123.1, 121.7, 118.7, 109.2, 79.2; HRMS *m/z* (ESI+): Calculated for C₂₂H₁₅ClNO ([M+H]⁺): 344.0837, Found 344.0850.

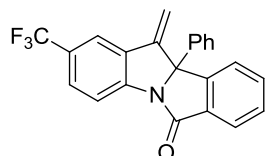
2-fluoro-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3o)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3o** as a yellow solid (45.2 mg, 69%), m.p. 157-159 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93-7.91 (m, 1H), 7.70 (dd, *J* = 8.6, 4.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.53-7.49 (m, 2H), 7.34-7.26 (m, 3H), 7.17 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.07 (td, *J* = 8.8, 2.6 Hz, 1H), 5.87 (d, *J* = 1.1 Hz, 1H),

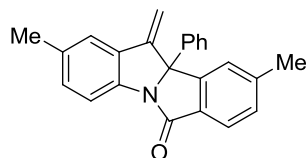
5.64 (d, $J = 1.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 160.6 (d, $J = 241.3$ Hz), 149.3, 145.5 (d, $J = 1.25$ Hz), 140.6, 137.5, 135.6 (d, $J = 8.75$ Hz), 133.7, 131.8, 129.0, 128.7, 128.2, 125.7, 125.3, 123.1, 118.7 (d, $J = 8.8$ Hz), 117.0 (d, $J = 22.5$ Hz), 109.2, 108.6 (d, $J = 23.8$ Hz), 79.4; HRMS m/z (ESI+): Calculated for $\text{C}_{22}\text{H}_{15}\text{FNO}$ ($[\text{M}+\text{H}]^+$): 328.1132, Found 328.1146.

11-methylene-10b-phenyl-2-(trifluoromethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3p)



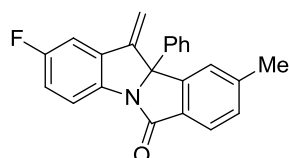
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3p** as a yellow solid (38.8 mg, 51%), m.p. 61-63 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 1.7$ Hz, 1H), 7.65-7.62 (m, 2H), 7.59-7.51 (m, 4H), 7.35-7.27 (m, 3H), 5.98 (s, 1H), 5.72 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.4, 149.4, 144.9, 144.0, 140.4, 134.4, 134.1, 131.5, 129.2, 128.8, 128.4, 127.6 (q, $J = 3.8$ Hz), 125.7, 125.5, 125.2, 123.2, 118.7, 118.7, 117.7, 109.6, 79.1; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{15}\text{F}_3\text{NO}$ ($[\text{M}+\text{Na}]^+$): 378.1100, Found 378.1113.

2,9-dimethyl-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3q)



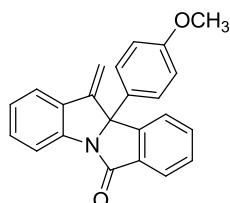
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3q** as a white solid (62.1 mg, 92%), m.p. 128-130 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.70 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.59-7.57 (m, 2H), 7.41-7.38 (m, 2H), 7.30-7.26 (m, 3H), 7.25-7.22 (m, 1H), 7.17 (dd, $J = 8.0, 0.6$ Hz, 1H), 5.81 (s, 1H), 5.53 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 147.0, 146.5, 141.3, 139.3, 139.1, 134.7, 134.5, 134.0, 132.4, 131.0, 128.5, 128.0, 125.7, 125.3, 122.8, 121.9, 117.5, 107.2, 79.0, 21.3, 21.2; HRMS m/z (ESI+): Calculated for $\text{C}_{24}\text{H}_{20}\text{NO}$ ($[\text{M}+\text{H}]^+$): 338.1539, Found 338.1542.

2-fluoro-9-methyl-11-methylene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3r)



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3r** as a white solid (57.6 mg, 84%), m.p. 216-218 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.72 (s, 1H), 7.69 (dd, $J = 8.6, 4.6$ Hz, 1H), 7.58-7.55 (m, 2H), 7.43-7.39 (m, 2H), 7.32-7.25 (m, 3H), 7.16 (dd, $J = 8.2, 2.5$ Hz, 1H), 7.06 (td, $J = 8.8, 2.6$ Hz, 1H), 5.84 (s, 1H), 5.62 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.8, 160.6 (d, $J = 243.5$ Hz), 146.8, 145.8 (d, $J = 3.0$ Hz), 140.9, 139.3, 137.6 (d, $J = 1.8$ Hz), 135.6 (d, $J = 8.7$ Hz), 134.8, 132.0, 128.6, 128.1, 125.7, 125.4, 122.8, 118.7 (d, $J = 8.7$ Hz), 117.0 (d, $J = 24.0$ Hz), 109.0, 108.6 (d, $J = 24.5$ Hz), 79.3, 21.2; HRMS m/z (ESI+): Calculated for $\text{C}_{23}\text{H}_{17}\text{FNO}$ ($[\text{M}+\text{H}]^+$): 342.1289, Found 342.1297.

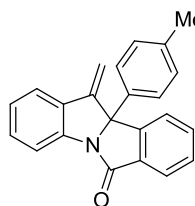
10b-(4-methoxyphenyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3s)^{2,3}



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3s** as a white solid (66.6 mg, 98%), m.p. 142-144 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.52-7.48 (m, 5H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 6.83-6.81 (m, 2H), 5.86 (s, 1H), 5.56 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.6, 159.4, 149.9, 146.2, 141.4, 134.0, 133.6, 133.0, 132.1, 130.4, 128.8, 127.2, 125.2, 125.0, 123.1, 121.4, 117.8,

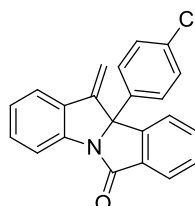
113.9, 107.5, 78.6, 55.2.

11-methylene-10b-(p-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3t)^{2,3}



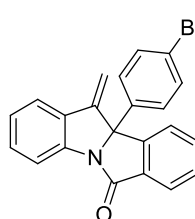
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3t** as a white solid (50.9 mg, 79%), m.p. 154-156 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.77 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.53-7.47 (m, 4H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.15-7.11 (m, 3H), 5.86 (s, 1H), 5.59 (s, 1H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 149.7, 146.1, 141.3, 138.0, 137.9, 133.9, 133.6, 132.1, 130.3, 129.2, 128.8, 125.7, 125.2, 125.0, 123.1, 121.4, 117.7, 107.6, 78.7, 20.9.

10b-(4-chlorophenyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3u)^{2,3}



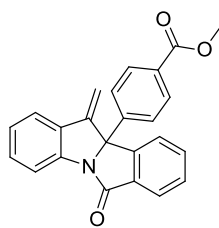
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3u** as a white solid (52.8 mg, 77%), m.p. 145-147 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.93-7.92 (m, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54-7.48 (m, 5H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.27-7.26 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.88 (s, 1H), 5.58 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 149.1, 145.8, 141.2, 139.6, 134.0, 133.7, 133.6, 132.0, 130.5, 129.1, 128.7, 127.3, 125.4, 125.2, 123.0, 121.5, 117.8, 108.0, 78.3.

10b-(4-bromophenyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3v)^{2,3}



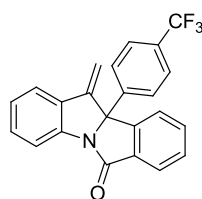
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3v** as a white solid (23.2 mg, 30%), m.p. 162-164 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.60-7.47 (m, 5H), 7.43-7.37 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 5.88 (s, 1H), 5.58 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 169.5, 149.0, 145.7, 141.2, 140.1, 133.8, 132.0, 131.7, 130.6, 129.1, 128.6, 127.7, 125.4, 125.2, 123.0, 122.3, 121.5, 117.9, 108.0, 78.4.

Methyl 4-(11-methylene-6-oxo-6H-isoindolo[2,1-a]indol-10b(11H)-yl)benzoate (3w)



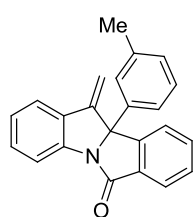
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3w** as a yellow oil (27.2 mg, 37%), m.p. 168-170 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.70-7.69 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 5.63 (s, 1H), 3.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 166.5, 148.8, 146.0, 145.7, 141.3, 133.8, 133.6, 132.1, 130.6, 130.0, 129.9, 129.2, 125.8, 125.5, 125.2, 123.1, 121.6, 117.8, 108.2, 78.6, 52.2; HRMS *m/z* (ESI⁺): Calculated for C₂₄H₁₈NO₃ ([M+H]⁺): 368.1281, Found 368.1298.

11-methylene-10b-(4-(trifluoromethyl)phenyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3x)



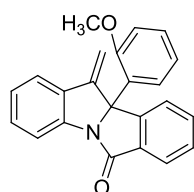
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3x** as a white solid (33.1 mg, 44%), m.p. 127-129 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.95-7.93 (m, 1H), 7.78-7.74 (m, 3H), 7.63 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.57-7.49 (m, 5H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 5.63 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 148.7, 145.7, 145.0, 141.2, 133.9, 133.5, 132.0, 130.7, 130.5, 130.1 (q, *J* = 31.3 Hz), 126.3, 125.6 (q, *J* = 3.8 Hz), 125.5, 125.3, 124.9, 123.0, 121.6, 117.8, 108.3, 78.4; HRMS *m/z* (ESI⁺): Calculated for C₂₃H₁₅F₃NO ([M+H]⁺): 378.1100, Found 378.1116.

11-methylene-10b-(*m*-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3y)



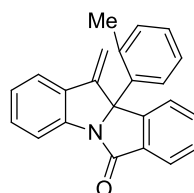
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3y** as a white solid (47.3 mg, 73%), m.p. 199-201 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50-7.47 (m, 2H), 7.45-7.44 (m, 1H), 7.39-7.36 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 5.87 (s, 1H), 5.60 (s, 1H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 149.7, 146.0, 141.4, 140.8, 138.3, 134.0, 133.6, 132.1, 130.3, 128.9, 128.8, 128.4, 126.3, 125.2, 125.0, 123.1, 122.9, 121.5, 117.8, 107.8, 78.9, 21.6; HRMS *m/z* (ESI⁺): Calculated for C₂₃H₁₈NO ([M+H]⁺): 324.1383, Found 324.1396.

10b-(2-methoxyphenyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3z)



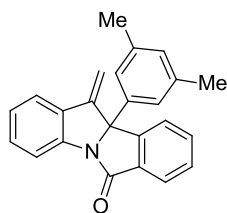
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3z** as a white solid (42.6 mg, 63%), m.p. 140-142 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.73-7.70 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.26 (td, *J* = 8.3, 7.7, 2.1 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.89 (s, 1H), 5.58 (s, 1H), 3.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 158.4, 149.7, 145.5, 141.7, 134.2, 133.4, 132.9, 130.1, 129.8, 128.5, 128.4, 128.3, 124.7, 124.4, 122.9, 121.3, 120.4, 117.5, 112.8, 109.4, 78.7, 55.3; HRMS *m/z* (ESI⁺): Calculated for C₂₃H₁₈NO₂ ([M+H]⁺): 340.1332, Found 340.1345.

11-methylene-10b-(*o*-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3aa)



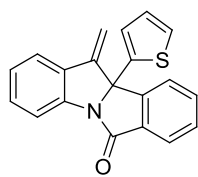
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3aa** as a yellow solid (19.0 mg, 30%), m.p. 188-190 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.94 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.65-7.60 (m, 2H), 7.53 (dd, *J* = 9.5, 7.7 Hz, 2H), 7.37-7.33 (m, 2H), 7.23-7.17 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 6.9, 2.3 Hz, 1H), 5.94 (s, 1H), 5.38 (s, 1H), 1.94 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.8, 148.6, 146.9, 141.7, 138.0, 136.4, 135.1, 133.7, 133.3, 133.2, 130.2, 129.0, 128.8, 128.5, 125.8, 125.2, 124.9, 123.4, 121.5, 118.6, 110.4, 81.0, 20.8; HRMS *m/z* (ESI⁺): Calculated for C₂₃H₁₈NO ([M+H]⁺): 324.1383, Found 324.1398.

10b-(3,5-dimethylphenyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ab)



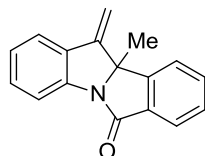
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3ab** as a white solid (32.8 mg, 49%), m.p. 232-234 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.50-7.47 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.20 (s, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 5.85 (s, 1H), 5.59 (s, 1H), 2.26 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 149.8, 146.1, 141.4, 140.7, 138.2, 134.0, 133.6, 132.1, 130.3, 129.9, 128.8, 125.2, 125.0, 123.4, 123.1, 121.5, 117.8, 107.8, 78.9, 21.4; HRMS *m/z* (ESI⁺): Calculated for C₂₄H₂₀NO ([M+H]⁺): 338.1539, Found 338.1550.

11-methylene-10b-(thiophen-2-yl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ac)



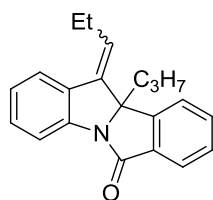
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3ac** as a brown solid (44.4 mg, 71%), m.p. 175-177 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.68-7.64 (m, 2H), 7.54-7.51 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.18-7.15 (m, 3H), 6.90-6.88 (m, 1H), 5.82 (s, 1H), 5.63 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.4, 149.0, 146.9, 146.6, 141.5, 133.7, 133.1, 131.5, 130.5, 129.3, 126.7, 125.5, 125.3, 125.3, 125.1, 123.2, 121.5, 117.9, 106.9, 76.4; HRMS *m/z* (ESI⁺): Calculated for C₂₀H₁₄NOS ([M+H]⁺): 316.0791, Found 316.0806.

10b-methyl-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ad)^{2,3}



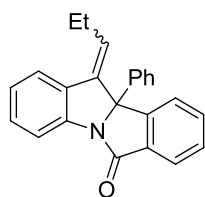
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3ad** as a white solid (36.3 mg, 74%), m.p. 151-153 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.67-7.66 (m, 2H), 7.51-7.48 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.60 (s, 1H), 5.35 (s, 1H), 1.78 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.5, 150.2, 148.1, 141.6, 133.4, 132.7, 132.1, 130.3, 128.8, 125.2, 124.7, 121.8, 121.6, 117.5, 103.8, 73.8, 30.4.

10b-propyl-11-propylidene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ae)



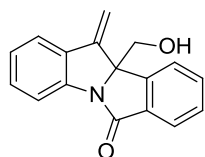
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3ae** as a light yellow oil (46.1 mg, 76%), inseparable mixture (d.r. = 5:1); For major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51-7.46 (m, 1H), 7.36-7.33 (m, 1H), 7.16-7.12 (m, 1H), 5.83 (t, *J* = 7.1 Hz, 1H), 2.57-2.43 (m, 2H), 2.11-2.05 (m, 1H), 1.94-1.88 (m, 1H), 1.32-1.23 (m, 1H), 1.16 (t, *J* = 7.5 Hz, 4H), 0.94-0.88 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 149.8, 142.3, 138.3, 133.5, 133.1, 129.1, 128.6, 127.1, 125.1, 125.1, 124.5, 122.0, 117.3, 76.9, 45.6, 21.7, 17.2, 14.0, 14.0; HRMS *m/z* (ESI⁺): Calculated for C₂₁H₂₂NO ([M+H]⁺): 304.1696, Found 304.1705.

10b-phenyl-11-propylidene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3af)



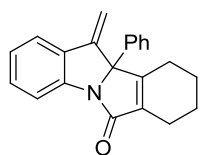
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3af** as a light green oil (44.0 mg, 65%); inseparable mixture (d.r. = 3.3:1); For major isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.58-7.53 (m, 3H), 7.48-7.46 (m, 2H), 7.33 (td, $J = 7.8, 1.0$ Hz, 1H), 7.29-7.27 (m, 3H), 7.25-7.23 (m, 1H), 7.13 (td, $J = 7.6, 1.0$ Hz, 1H), 6.04 (t, $J = 7.5$ Hz, 1H), 2.58-2.47 (m, 2H), 1.22 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.1, 149.9, 141.6, 141.3, 136.7, 133.8, 133.3, 130.7, 129.3, 128.7, 128.5, 127.9, 126.5, 125.9, 125.2, 124.8, 123.5, 118.0, 79.1, 21.6, 14.1; HRMS m/z (ESI+): Calculated for $\text{C}_{24}\text{H}_{19}\text{NONa}$ ($[\text{M} + \text{Na}]^+$): 360.1359, Found 360.1372.

10b-(hydroxymethyl)-11-methylene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (3ag)



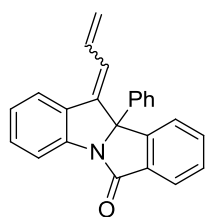
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3ag** as a brown solid (13.1 mg, 25%), m.p. 110-112 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 7.6$ Hz, 1H), 7.75-7.67 (m, 3H), 7.54-7.48 (m, 2H), 7.41-7.37 (m, 1H), 7.16 (td, $J = 7.6, 1.0$ Hz, 1H), 5.72 (s, 1H), 5.44 (s, 1H), 3.92 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 146.8, 144.1, 142.2, 133.7, 133.1, 132.8, 130.5, 129.3, 125.3, 124.9, 122.2, 121.5, 117.4, 105.3, 77.4, 69.2; HRMS m/z (ESI+): Calculated for $\text{C}_{17}\text{H}_{14}\text{NO}_2$ ($[\text{M} + \text{H}]^+$): 264.1019, Found 264.1032.

11-methylene-10b-phenyl-7,8,9,10,10b,11-hexahydro-6H-isoindolo[2,1-a]indol-6-one (3ah)



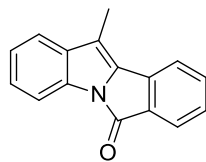
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **3ah** as a white solid (40.0 mg, 64%), m.p. 108-110 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 10$ Hz, 1H), 7.54-7.51 (m, 2H), 7.48 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.36-7.27 (m, 4H), 7.10 (td, $J = 7.6, 1.1$ Hz, 1H), 5.84 (s, 1H), 5.38 (s, 1H), 2.43-2.32 (m, 3H), 2.10-2.06 (m, 1H), 1.82-1.76 (m, 2H), 1.66-1.60 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 161.2, 144.7, 142.1, 138.9, 134.0, 132.1, 130.3, 128.5, 128.1, 126.2, 124.4, 121.0, 117.5, 106.0, 80.6, 23.3, 22.1, 21.5, 20.5; HRMS m/z (ESI+): Calculated for $\text{C}_{22}\text{H}_{20}\text{NO}$ ($[\text{M} + \text{H}]^+$): 314.1539, Found 314.1555.

11-allylidene-10b-phenyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (4)



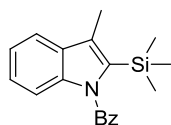
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **4** as a light yellow solid (23.4 mg, 35%), m.p. 286-288 $^{\circ}\text{C}$; inseparable mixture (d.r. = 7.7:1); For major isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 7.7$ Hz, 1H), 7.61 (td, $J = 7.8, 1.1$ Hz, 1H), 7.55-7.49 (m, 4H), 7.36 (td, $J = 7.7, 0.9$ Hz, 1H), 7.31-7.25 (m, 3H), 7.20-7.13 (m, 2H), 6.61 (d, $J = 11.3$ Hz, 1H), 5.55 (d, $J = 16.9$ Hz, 1H), 5.43 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 149.4, 141.7, 141.3, 138.3, 133.5, 133.4, 132.4, 131.5, 129.9, 128.9, 128.6, 128.1, 127.1, 125.9, 125.4, 125.3, 125.1, 123.6, 121.4, 118.22, 79.5; HRMS m/z (ESI+): Calculated for $\text{C}_{24}\text{H}_{17}\text{NONa}$ ($[\text{M} + \text{Na}]^+$): 358.1202, Found 358.1211.

11-methyl-6H-isoindolo[2,1-a]indol-6-one (5)^{2,3}



Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **5** as a white solid (24.7 mg, 53%, with 1-(trimethylsilyl)-1-propyne), m.p. 176-178 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.30-7.26 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.2, 135.8, 135.0, 134.6, 133.9, 133.5, 133.4, 128.0, 126.5, 125.2, 123.6, 121.1, 120.1, 115.3, 113.3, 9.4.

(3-methyl-2-(trimethylsilyl)-1H-indol-1-yl)(phenyl)methanone (7)



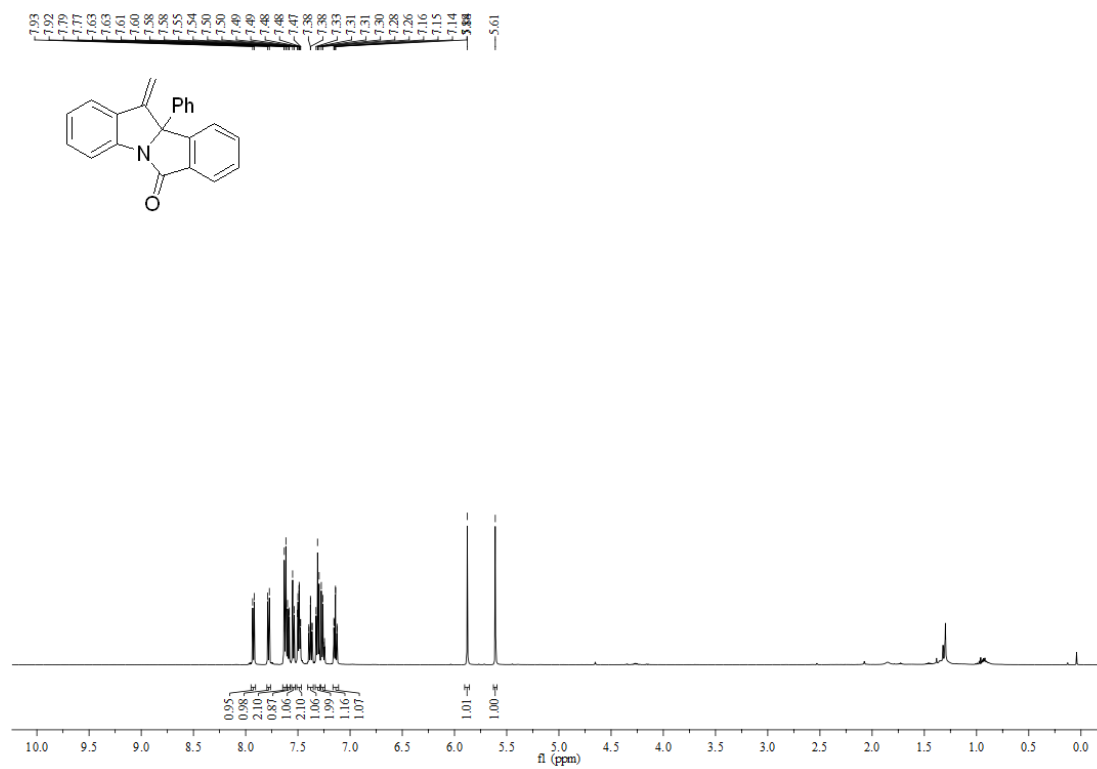
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **7** as a light yellow oil (47.9 mg, 78%); ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.81 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.57-7.54 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.01-6.98 (m, 1H), 6.48 (d, *J* = 8.5 Hz, 1H), 2.47 (s, 3H), 0.46 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 170.5, 138.2, 137.6, 135.7, 132.8, 132.7, 129.6, 128.9, 128.8, 123.8, 122.1, 118.9, 113.8, 11.3, 1.6; HRMS *m/z* (ESI+): Calculated for C₁₉H₂₂NOSi ([M+H]⁺): 308.1465, Found 308.1480.

References:

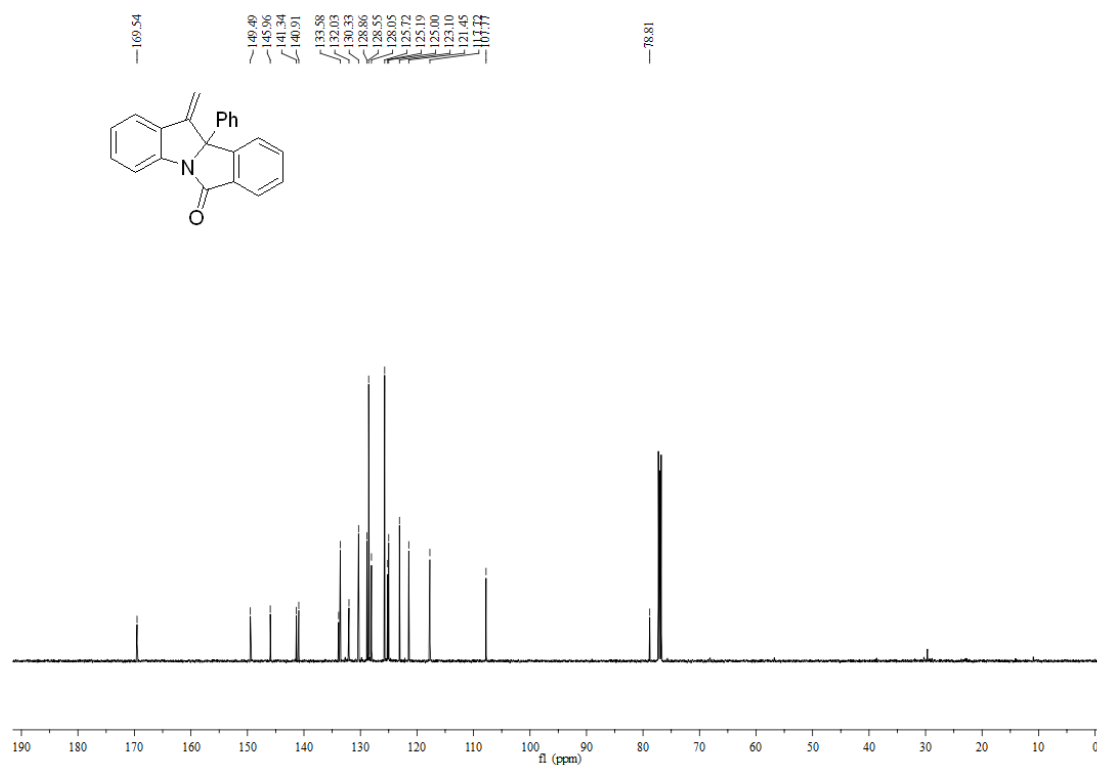
- (1) S. Sasmal, I. Sen, R. G. Hall and S. Pal, *Tetrahedron Lett.*, 2015, **56**, 1374-1377.
- (2) L. Zhao, Z. Li, L. Chang, J. Xu, H. Yao and X. Wu, *Org. Lett.*, 2012, **14**, 2066-2069.
- (3) X. Li, B. Zhou, R.-Z. Yang, F.-M. Yang, R.-X. Liang, R.-R. Liu and Y.-X. Jia, *J. Am. Chem. Soc.*, 2018, **140**, 13945-13951.

4. Copies of ^1H and ^{13}C NMR Spectra

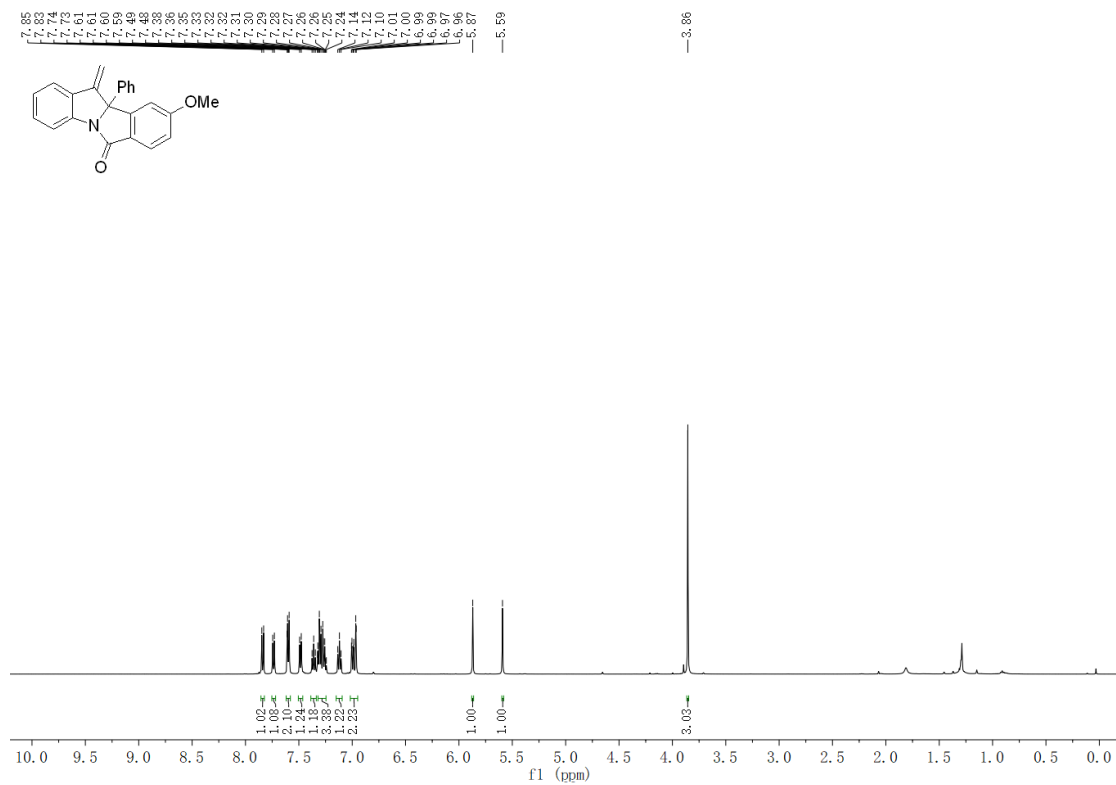
^1H NMR of **3a** (500 MHz, CDCl_3)



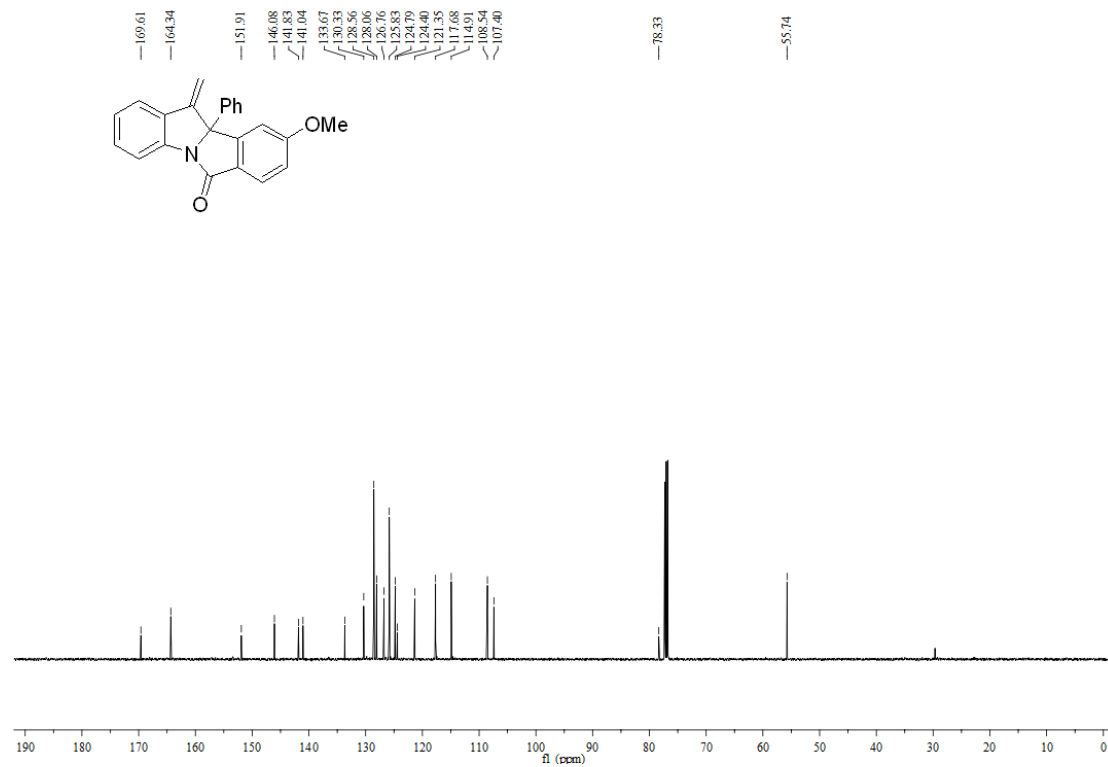
^{13}C NMR of **3a** (125 MHz, CDCl_3)



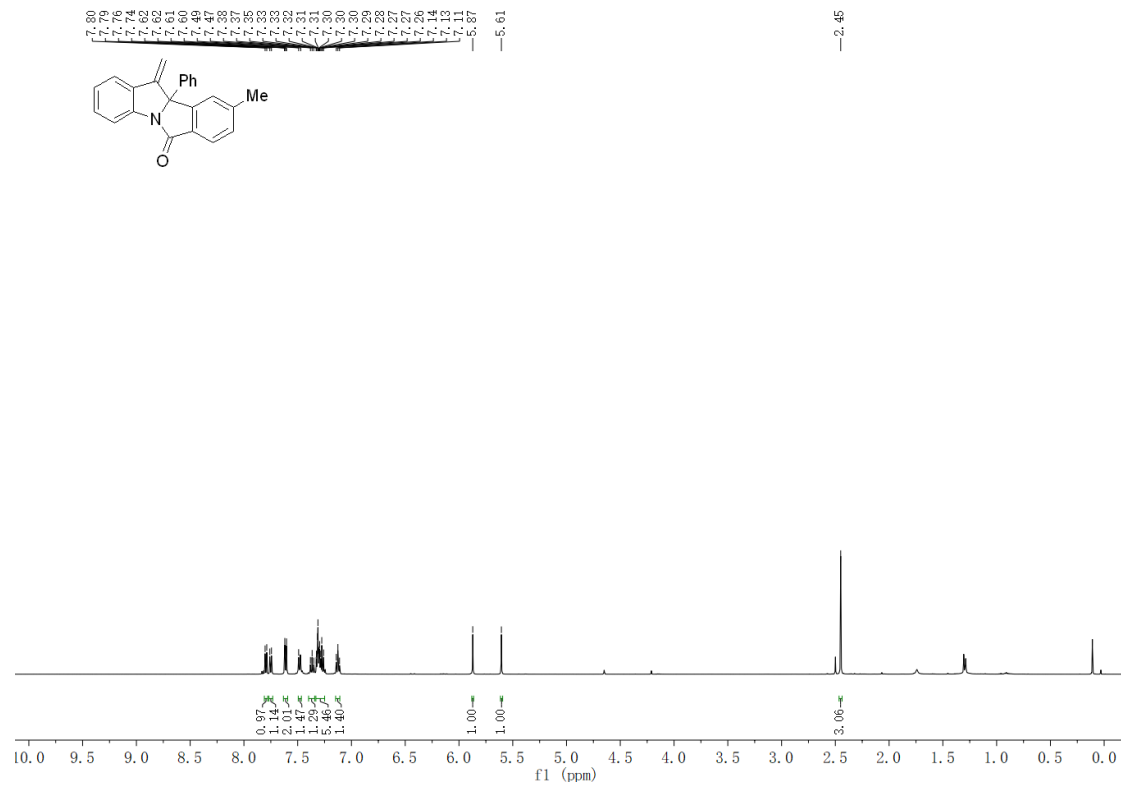
¹H NMR of **3b** (500 MHz, CDCl₃)



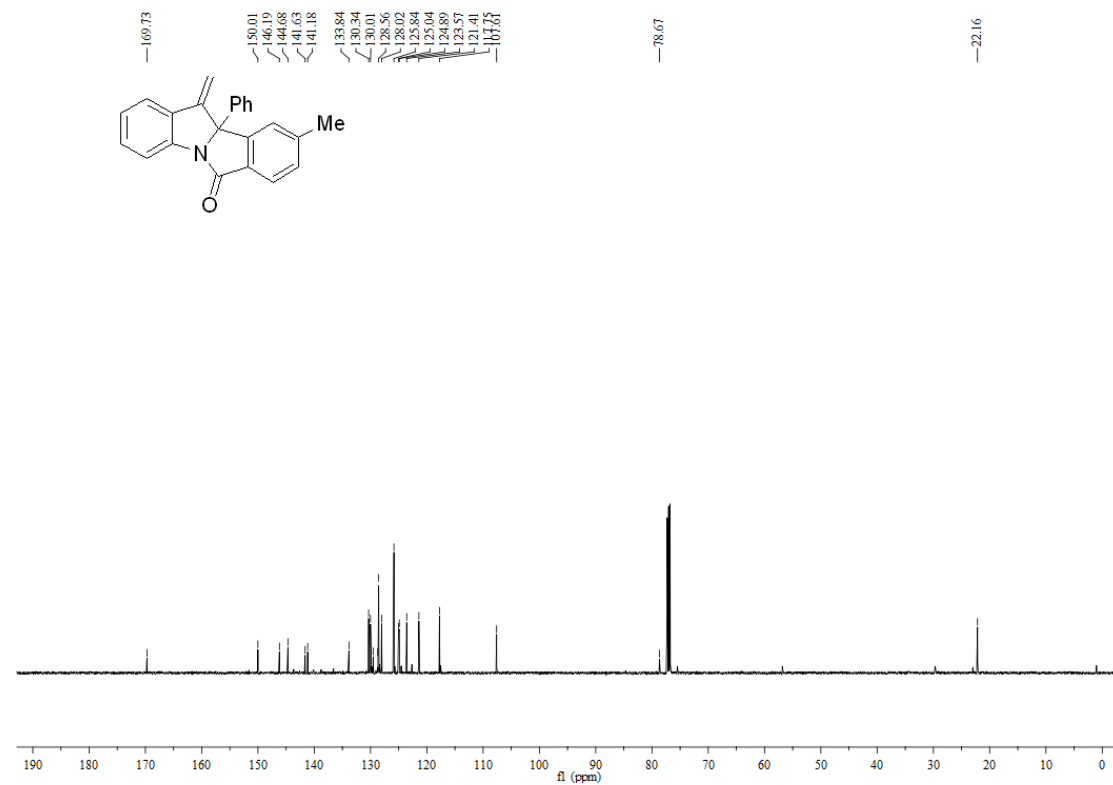
¹³C NMR of **3b** (125 MHz, CDCl₃)



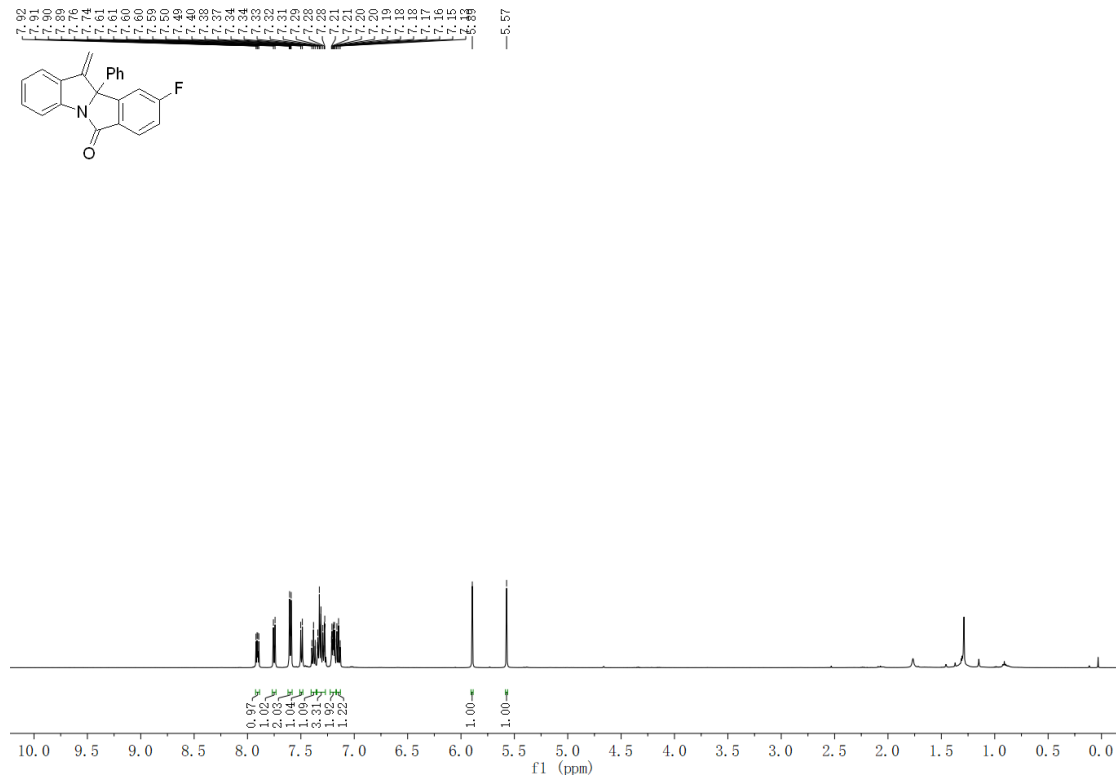
¹H NMR of **3c** (500 MHz, CDCl₃)



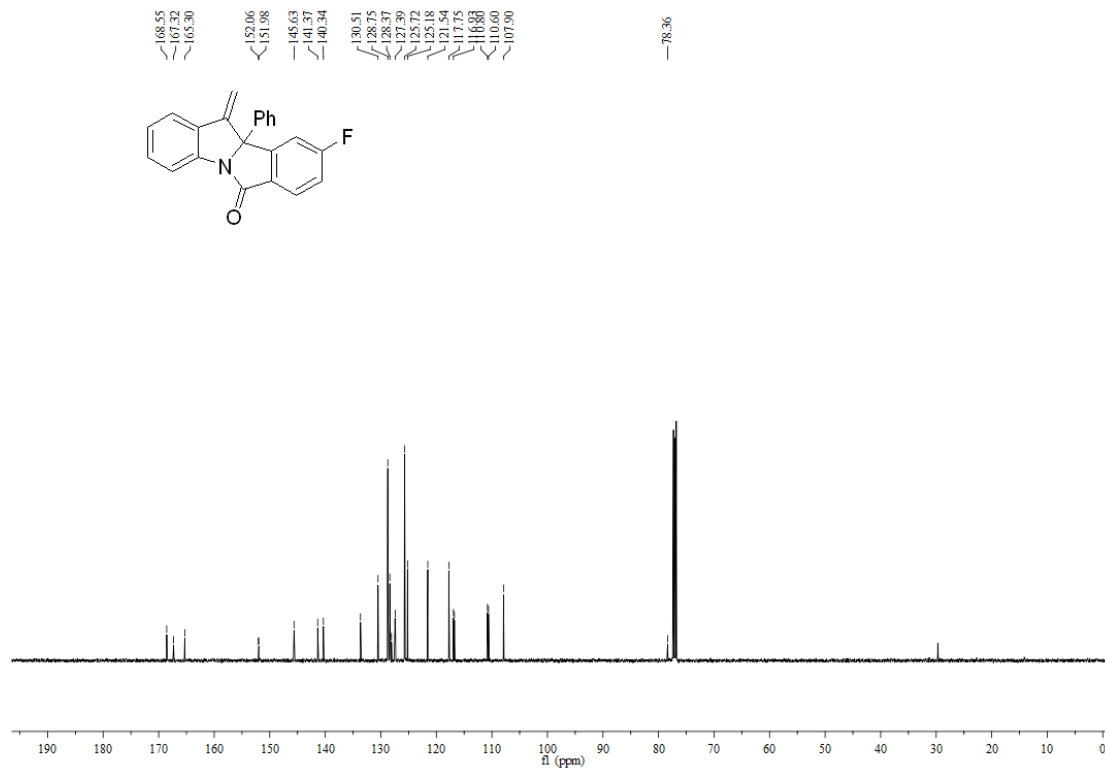
¹³C NMR of **3c** (125 MHz, CDCl₃)



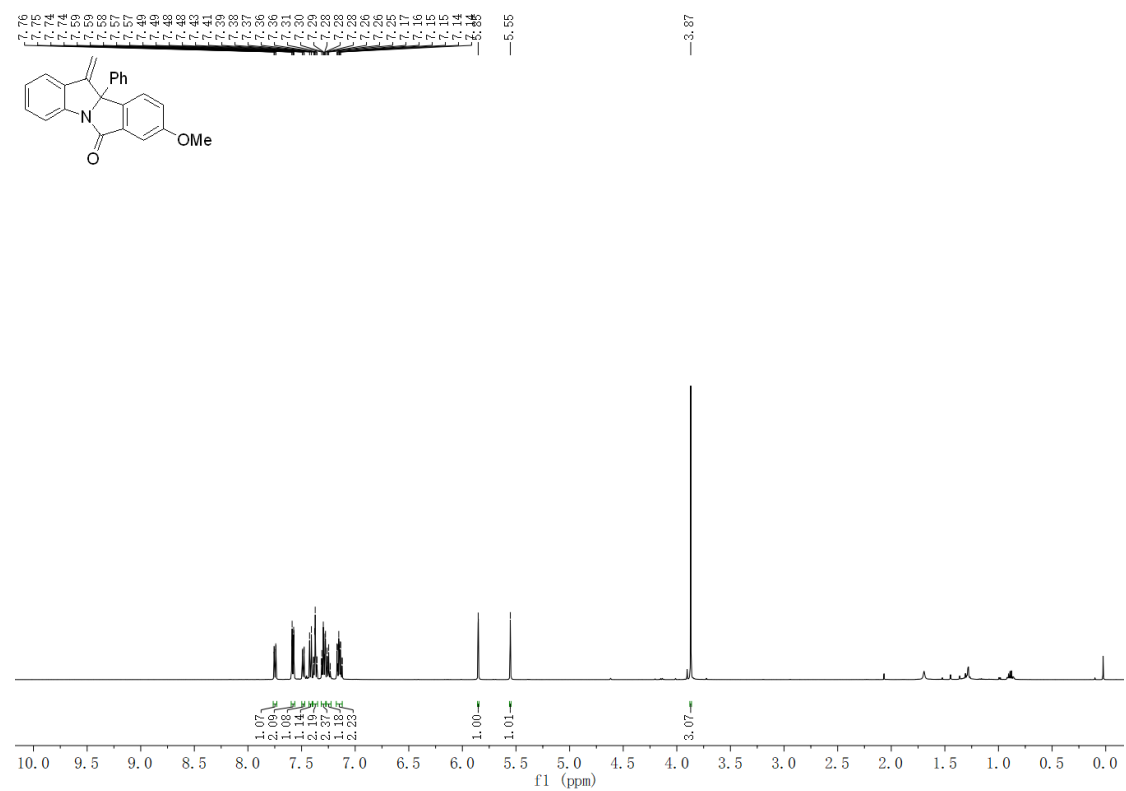
¹H NMR of **3d** (500 MHz, CDCl₃)



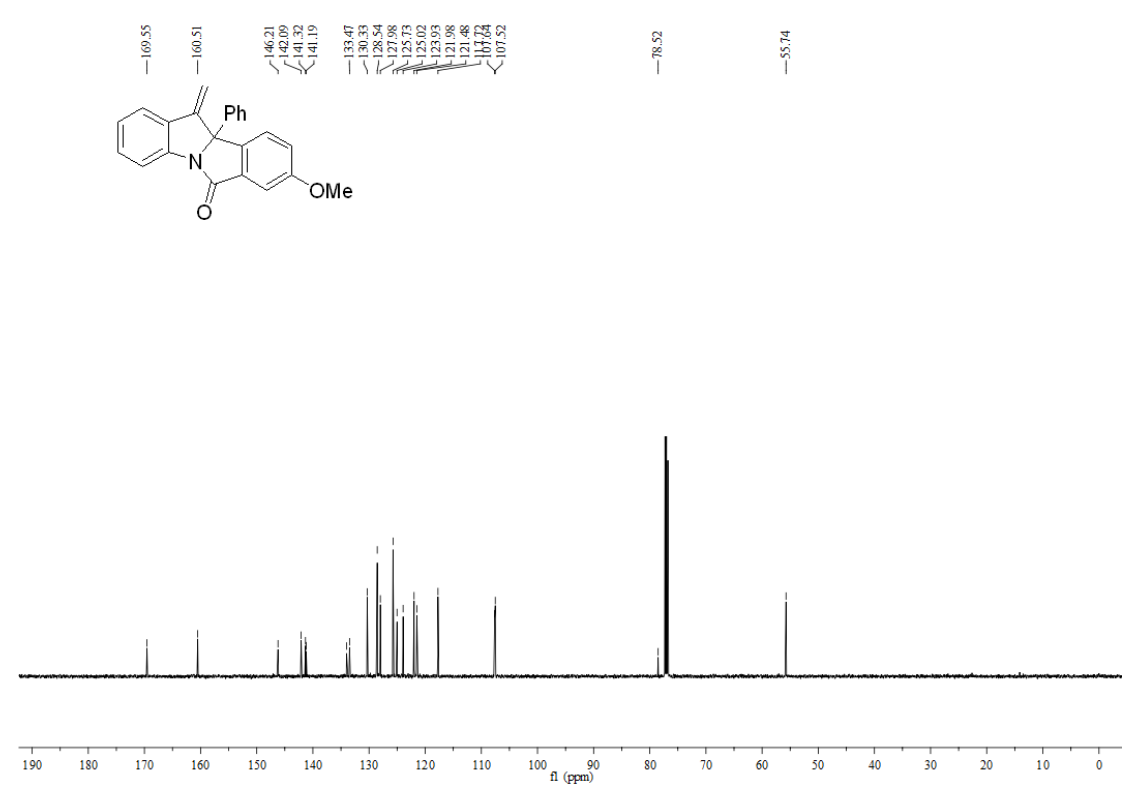
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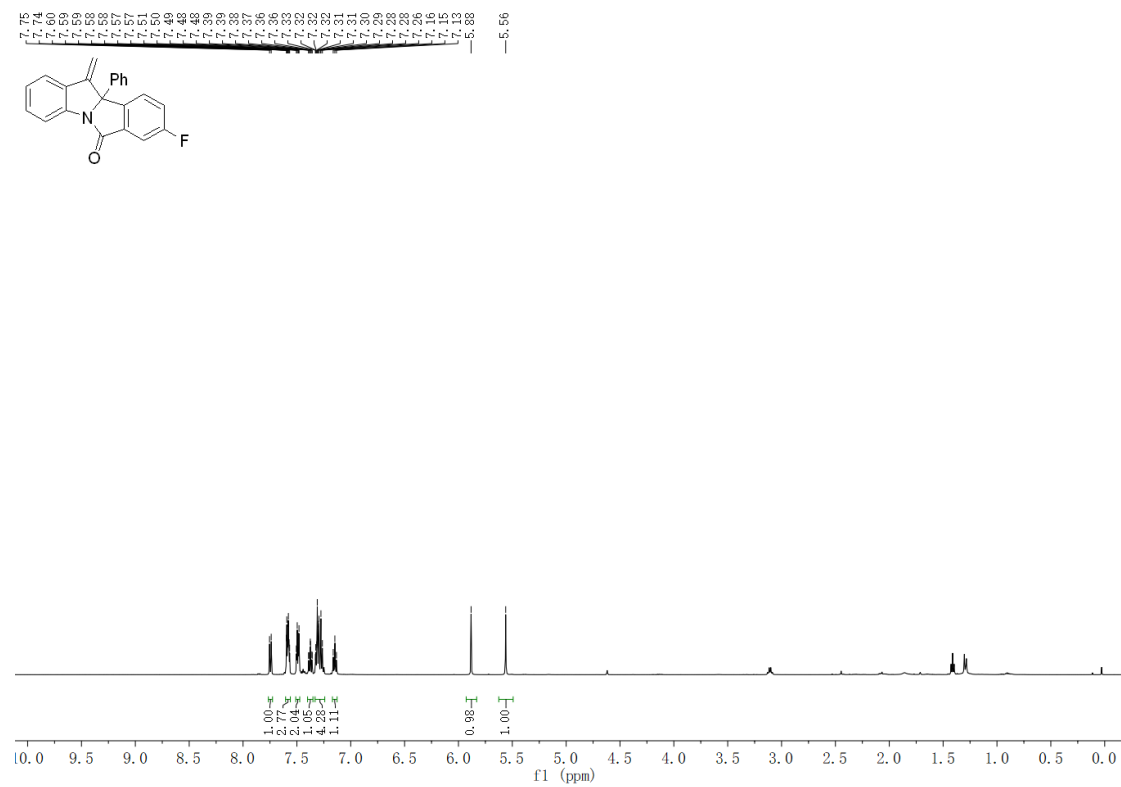
¹H NMR of **3e** (500 MHz, CDCl₃)



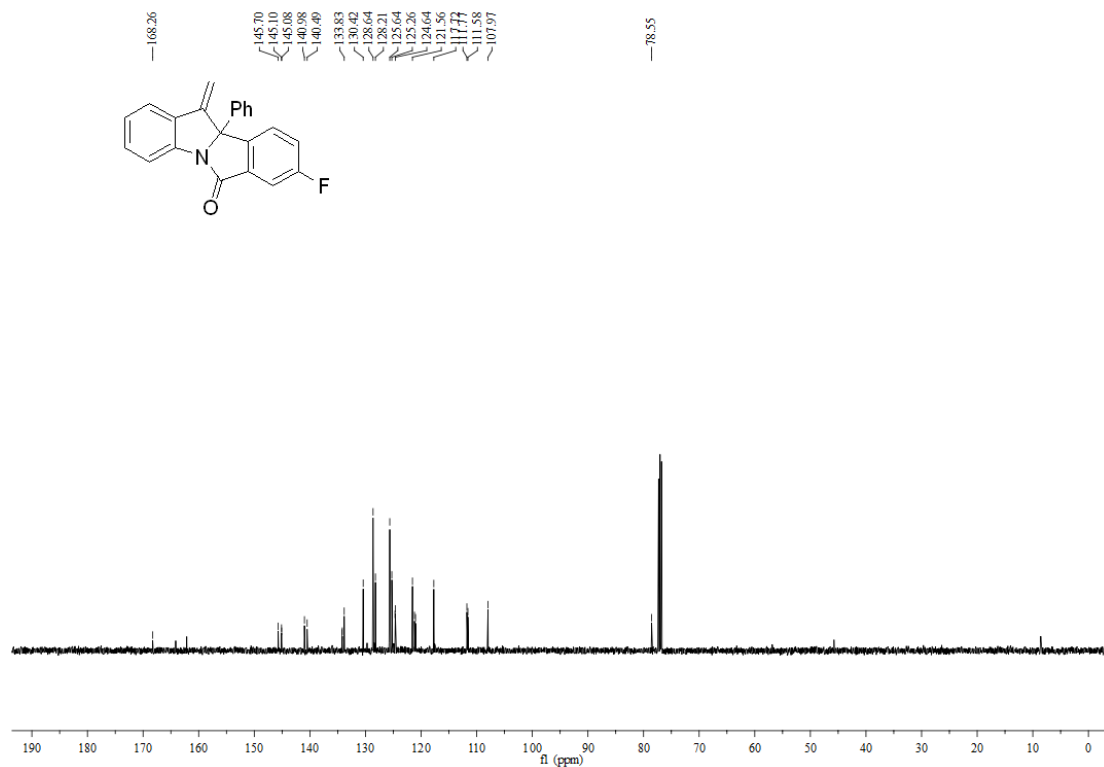
¹³C NMR of **3e** (125 MHz, CDCl₃)



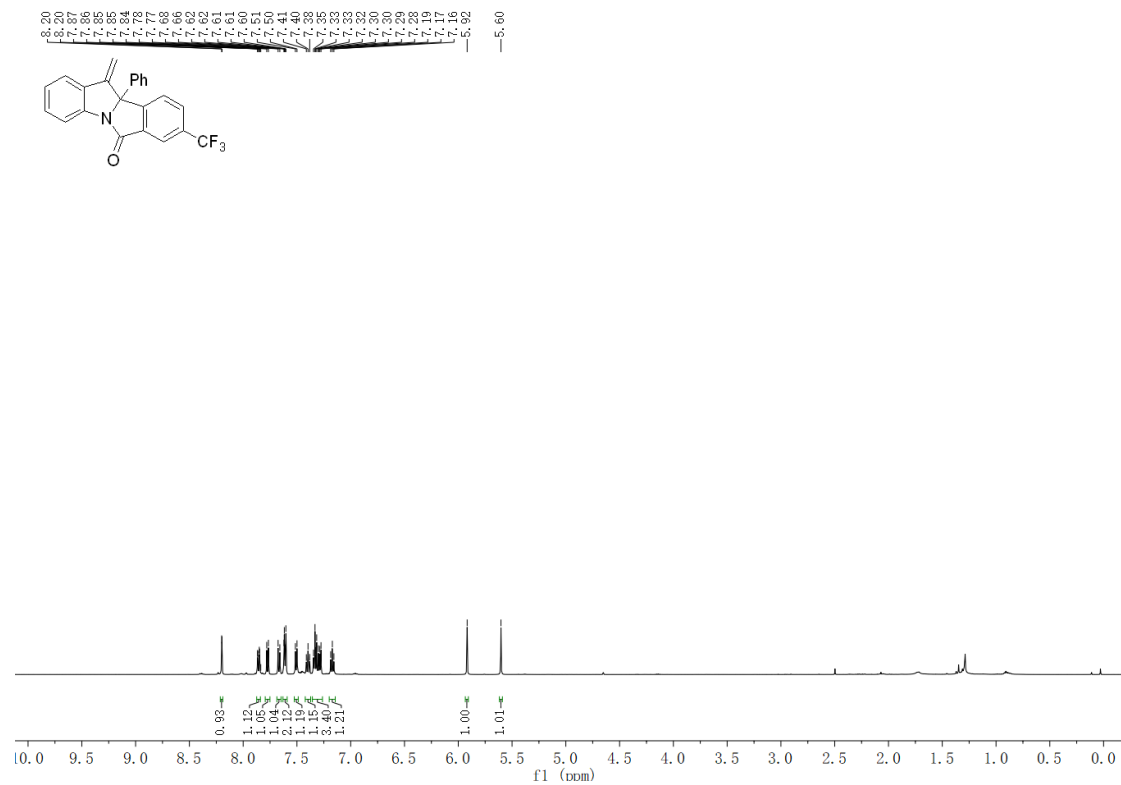
^1H NMR of **3f** (500 MHz, CDCl_3)



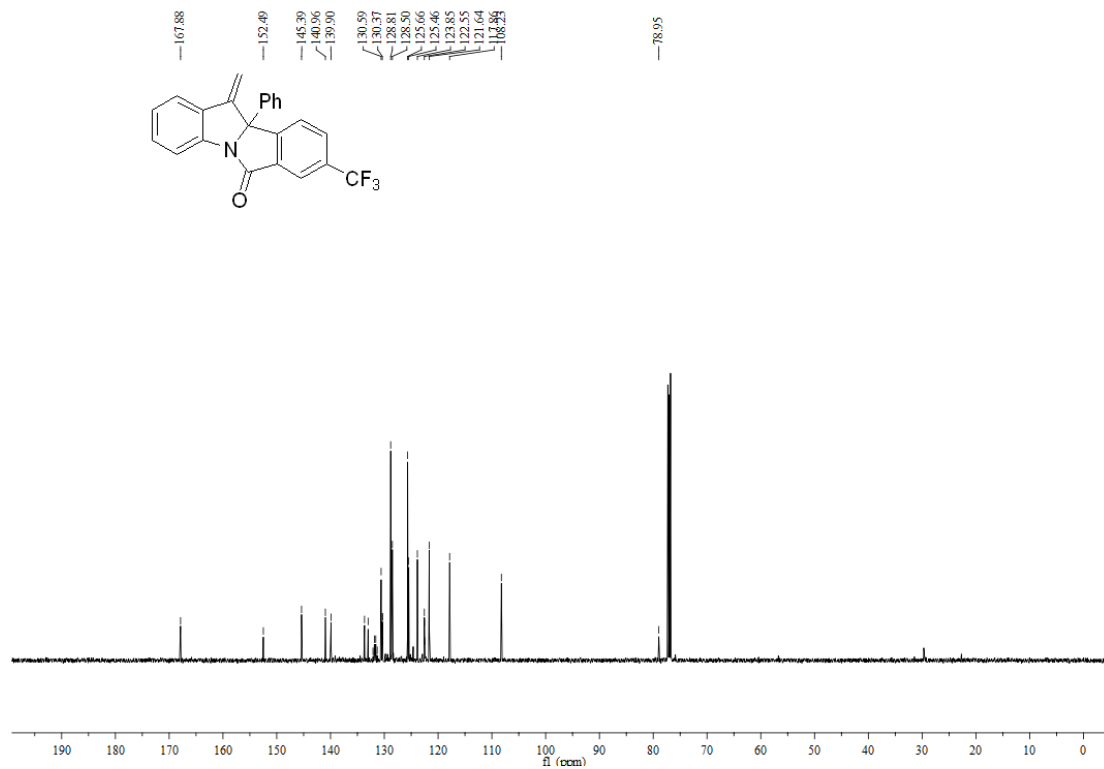
^{13}C NMR of **3f** (125 MHz, CDCl_3)



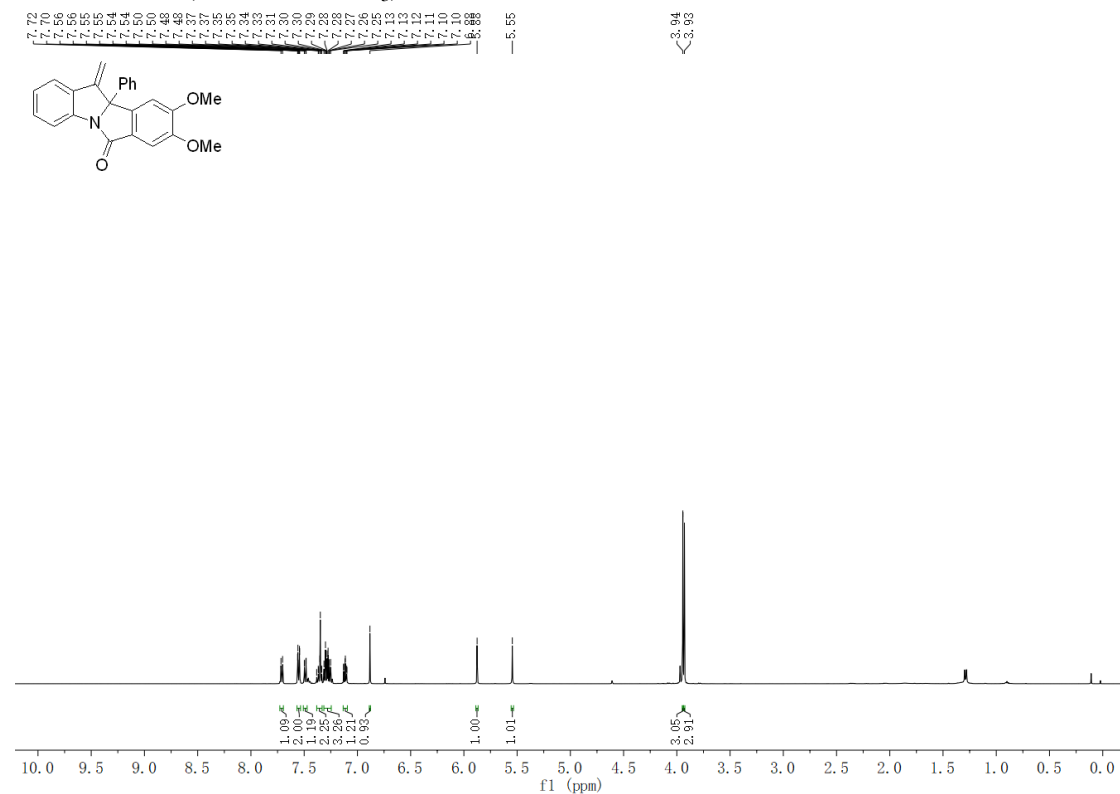
¹H NMR of **3g** (500 MHz, CDCl₃)



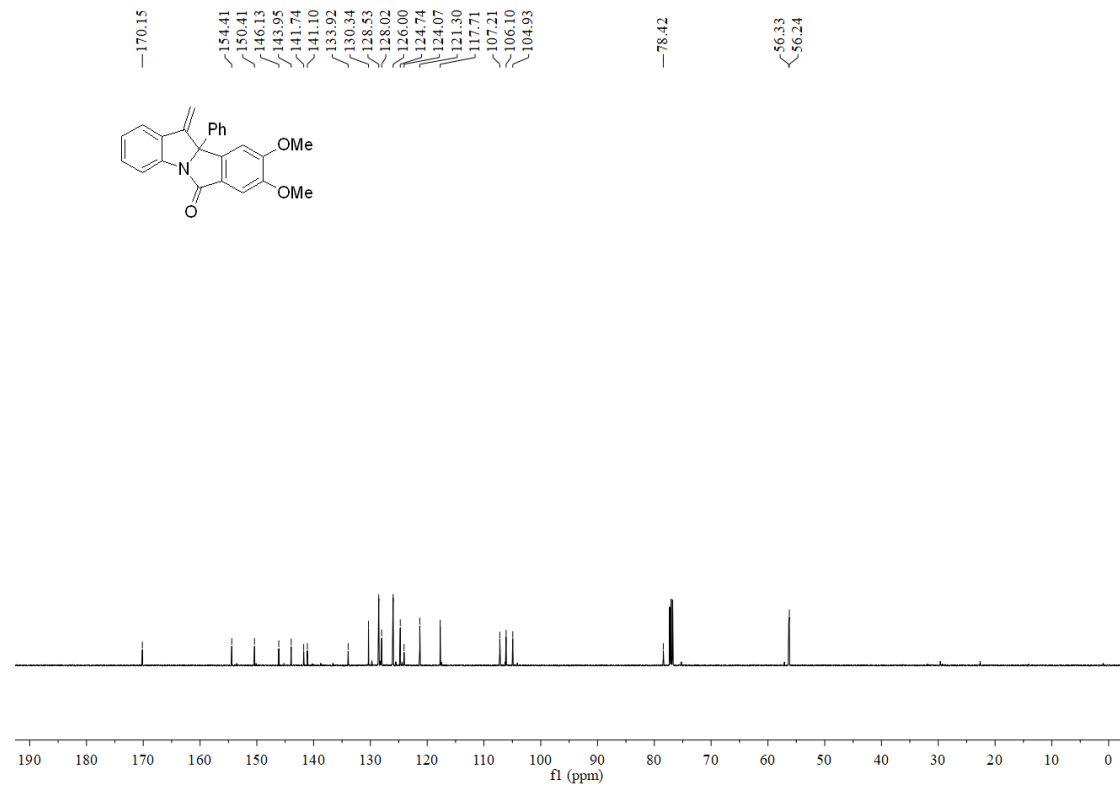
¹³C NMR of **3g** (125 MHz, CDCl₃)



¹H NMR of **3h** (500 MHz, CDCl₃)

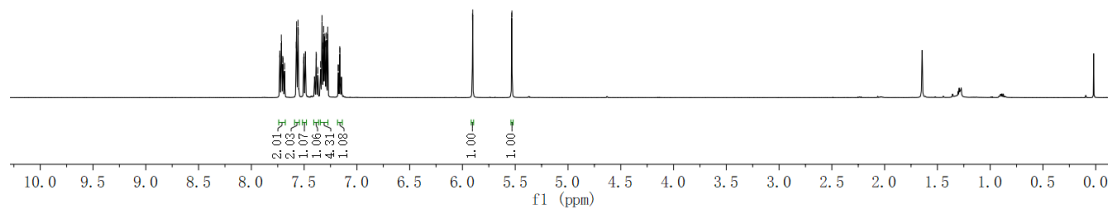
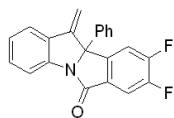


¹³C NMR of **3h** (125 MHz, CDCl₃)



^1H NMR of **3i** (500 MHz, CDCl_3)

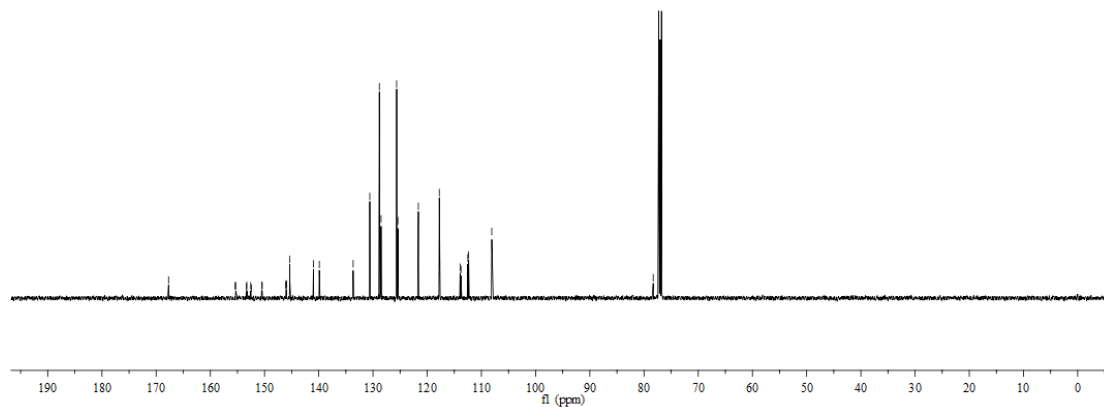
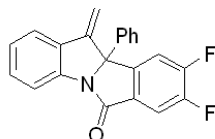
7.73
7.72
7.71
7.70
7.69
7.57
7.56
7.50
7.49
7.39
7.37
7.34
7.33
7.32
7.31
7.30
7.28
7.18
7.16
6.90
6.53



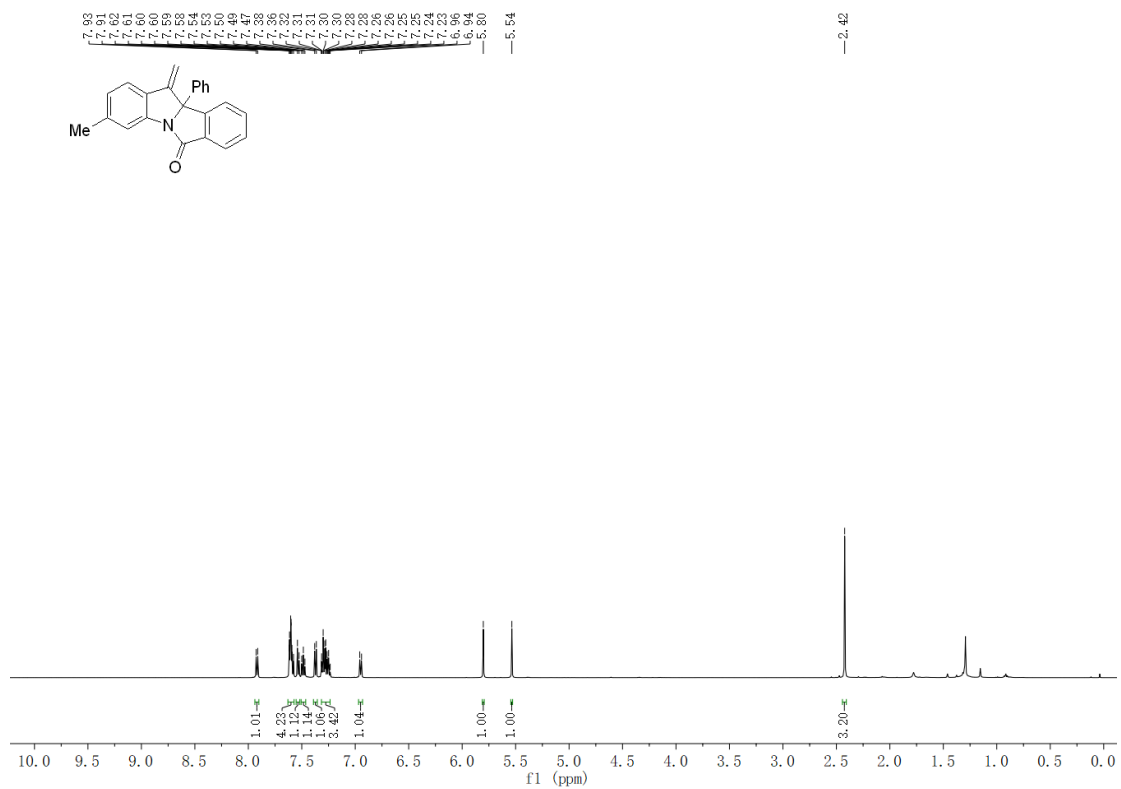
^{13}C NMR of **3i** (125 MHz, CDCl_3)

167.71
155.32
153.27
152.55
150.54
146.06
146.03
146.00
145.98
145.34
139.80
130.59
128.82
128.50
125.63
125.41
121.75
115.93
113.77
112.51
112.35
108.09

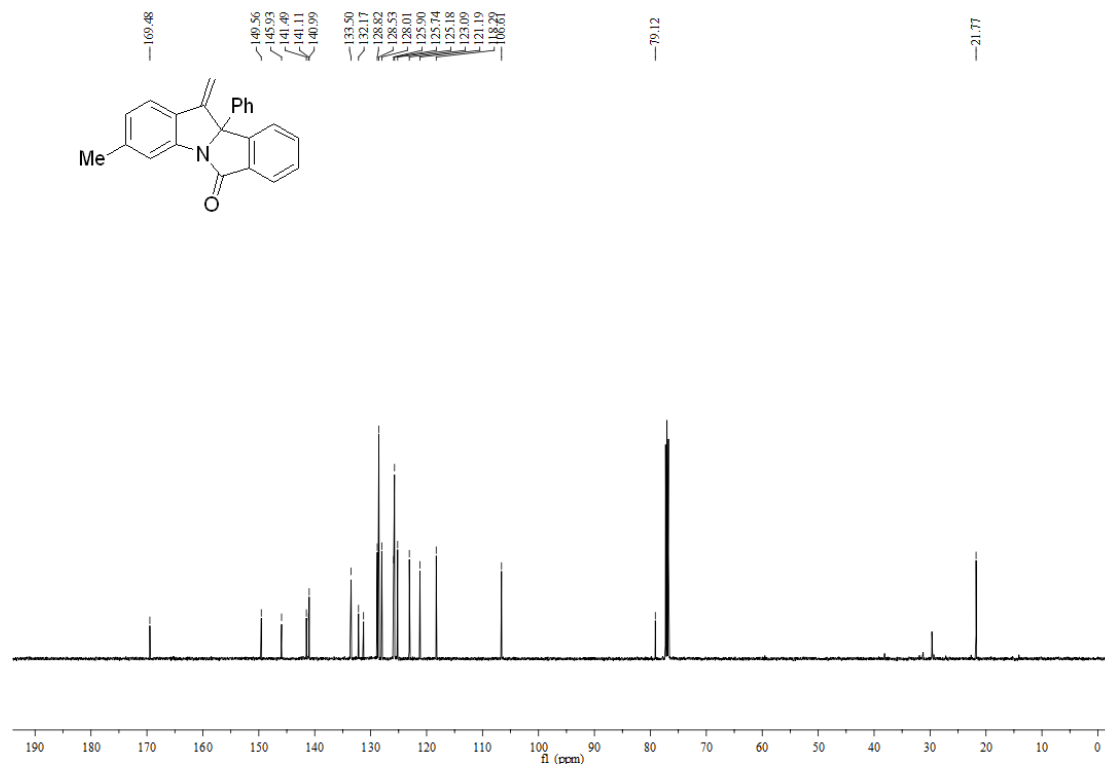
78.30



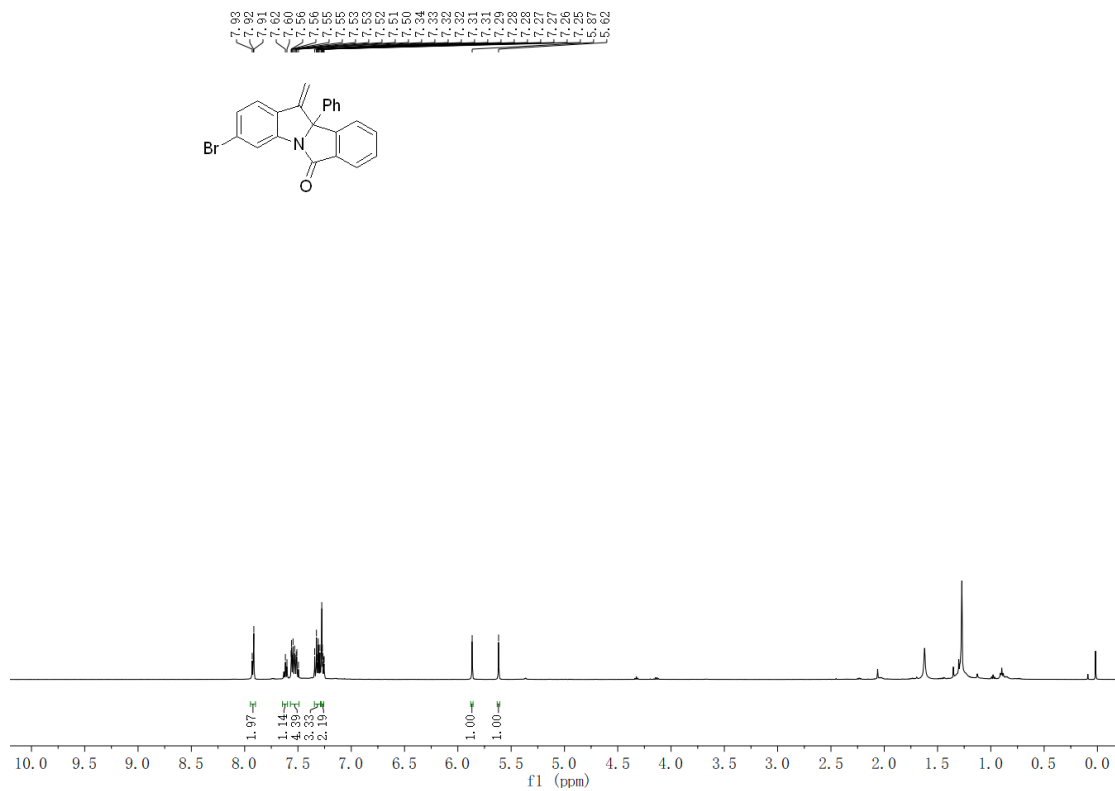
^1H NMR of **3j** (500 MHz, CDCl_3)



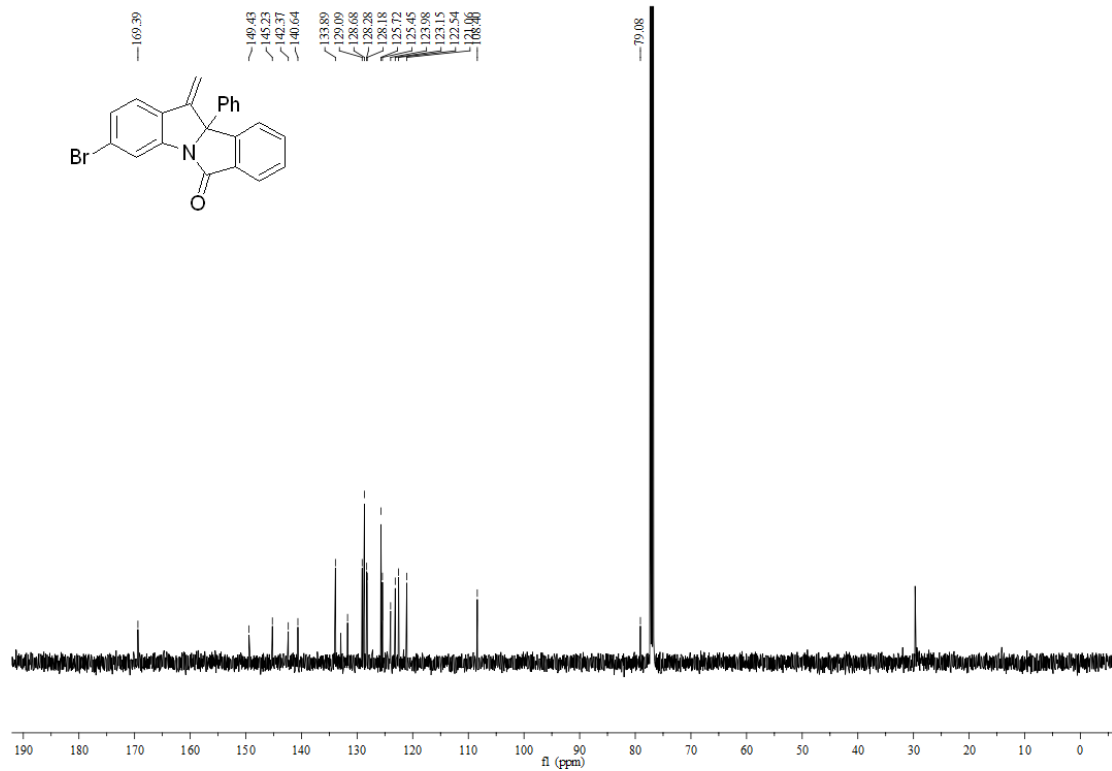
^{13}C NMR of **3j** (125 MHz, CDCl_3)



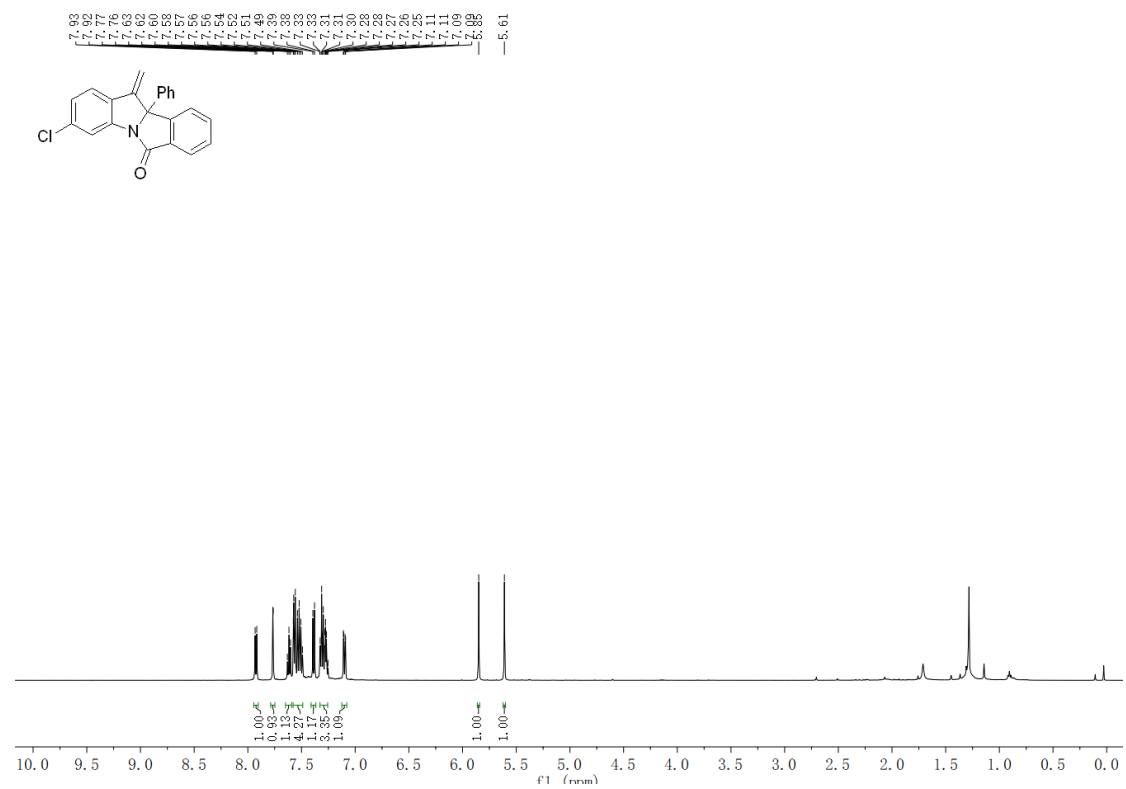
^1H NMR of **3k** (500 MHz, CDCl_3)



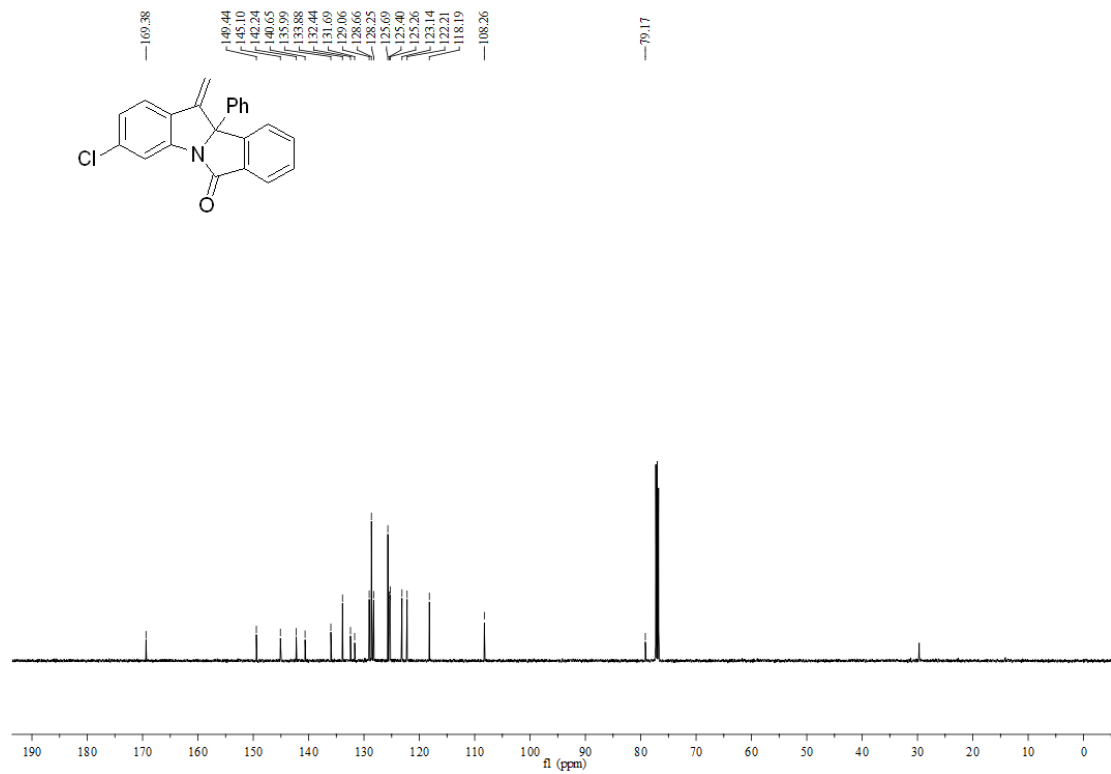
^{13}C NMR of **3k** (125 MHz, CDCl_3)



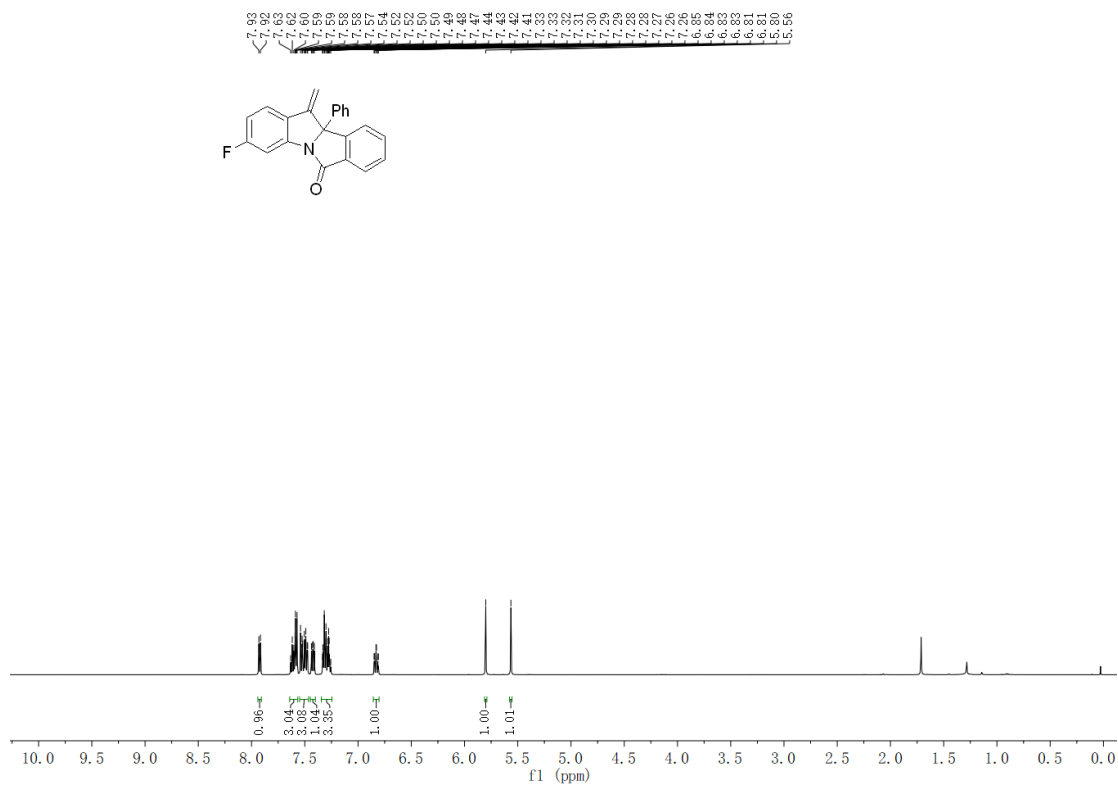
¹H NMR of **31** (500 MHz, CDCl₃)



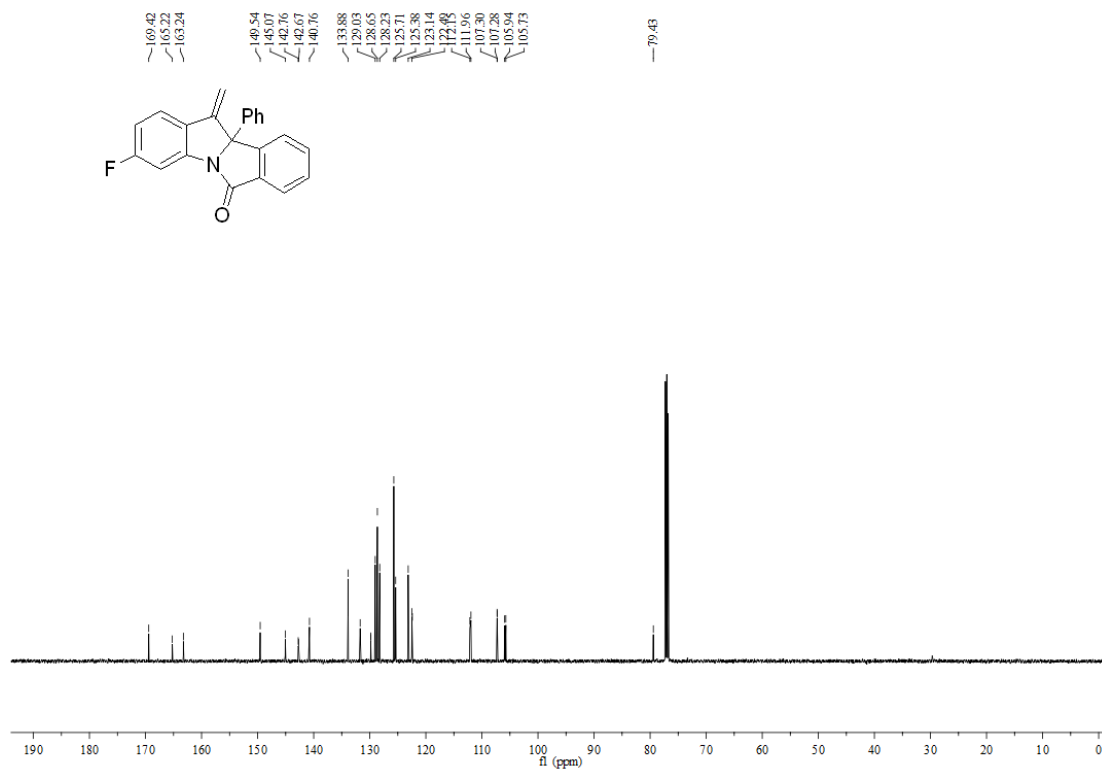
¹³C NMR of **31** (125 MHz, CDCl₃)



¹H NMR of **3m** (500 MHz, CDCl₃)

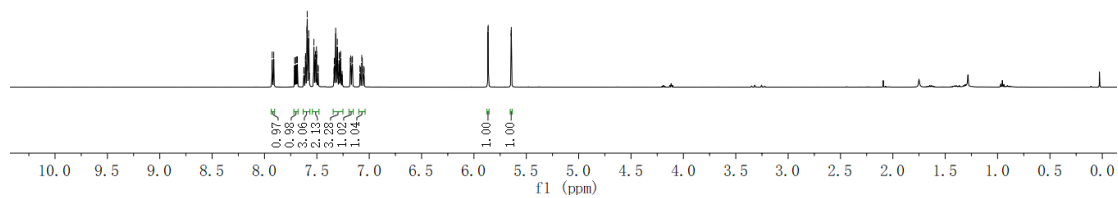
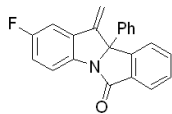


¹³C NMR of **3m** (125 MHz, CDCl₃)



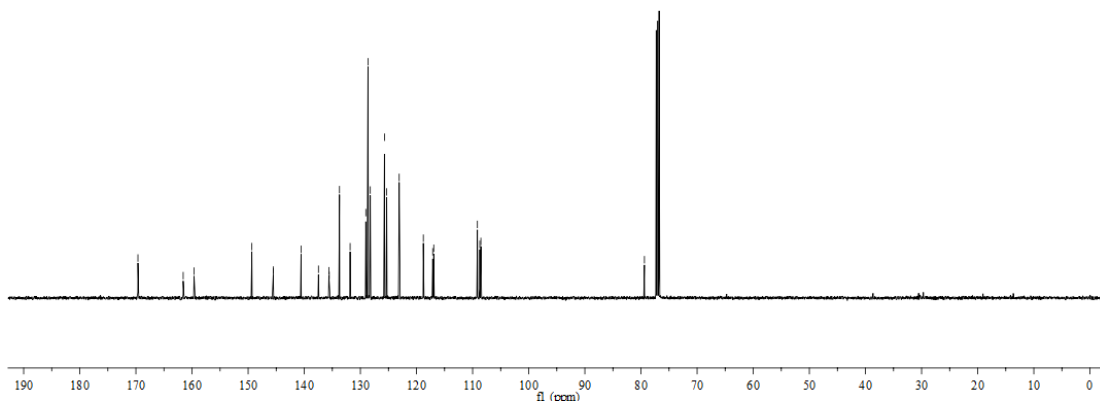
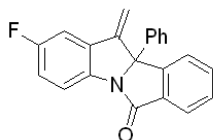
¹H NMR of **3o** (500 MHz, CDCl₃)

7.93, 7.91, 7.71, 7.70, 7.69, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.55, 7.51, 7.50, 7.49, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.29, 7.28, 7.28, 7.27, 7.26, 7.26, 7.26, 7.18, 7.16, 7.09, 7.07, 7.05, 6.87, 6.64, 6.64

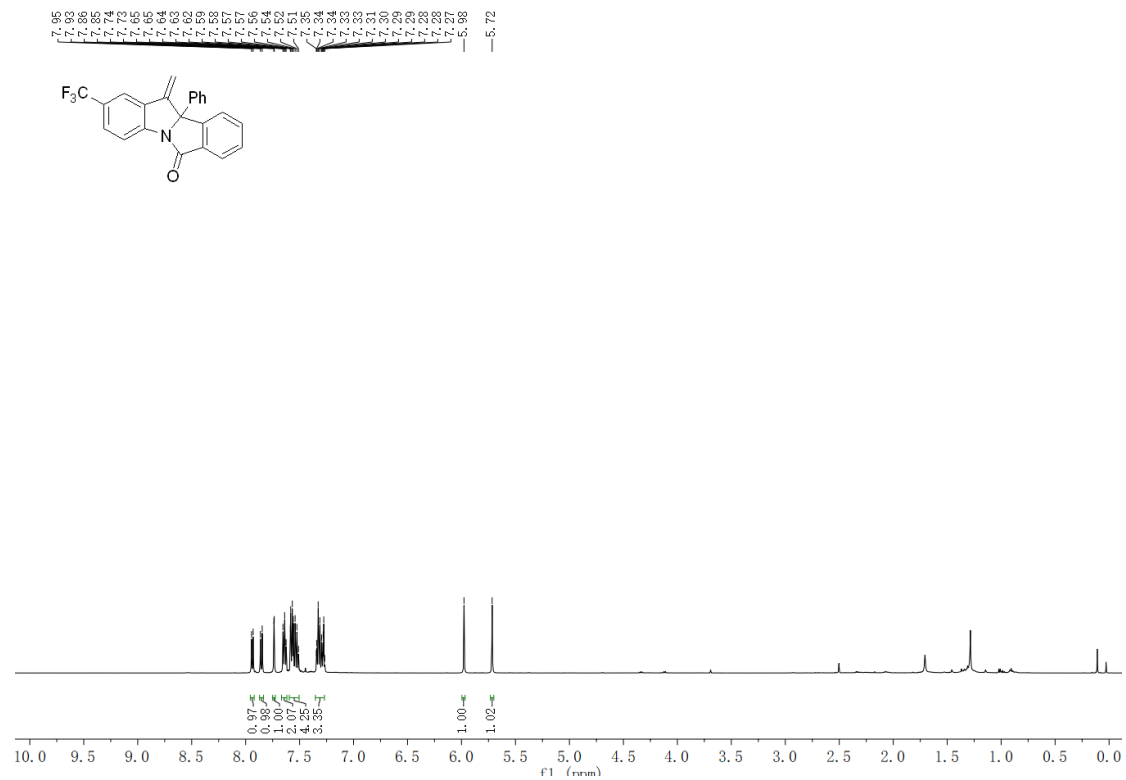


¹³C NMR of **3o** (125 MHz, CDCl₃)

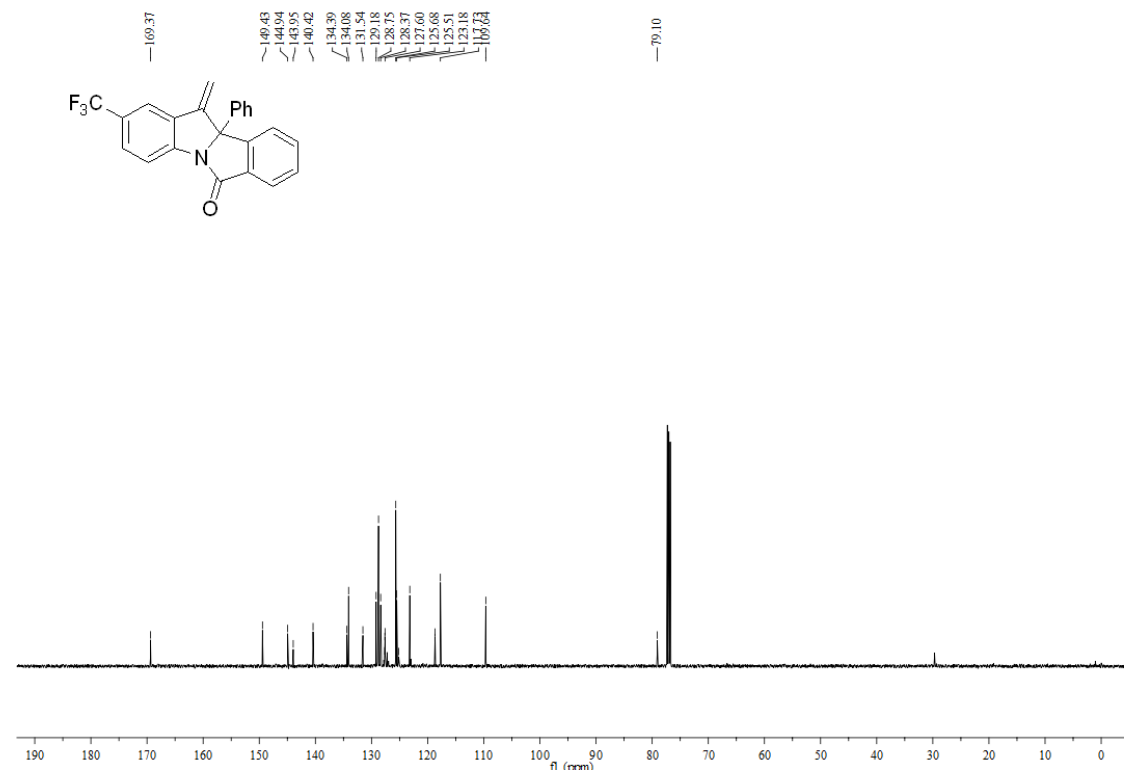
169.64, 161.57, 159.64, 149.34, 145.52, 140.57, 137.47, 136.62, 133.72, 131.83, 129.03, 128.65, 128.24, 125.71, 125.31, 123.09, 118.78, 118.71, 117.01, 109.93, 108.72, 108.53, 79.39



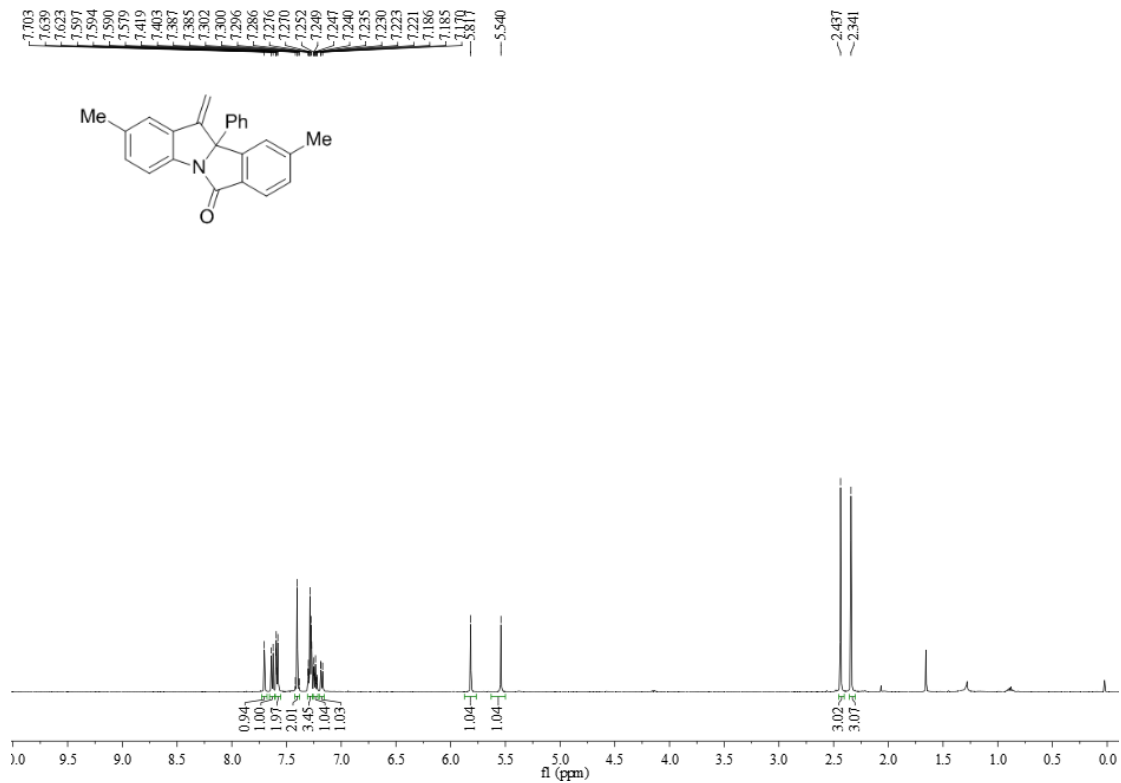
¹H NMR of **3p** (500 MHz, CDCl₃)



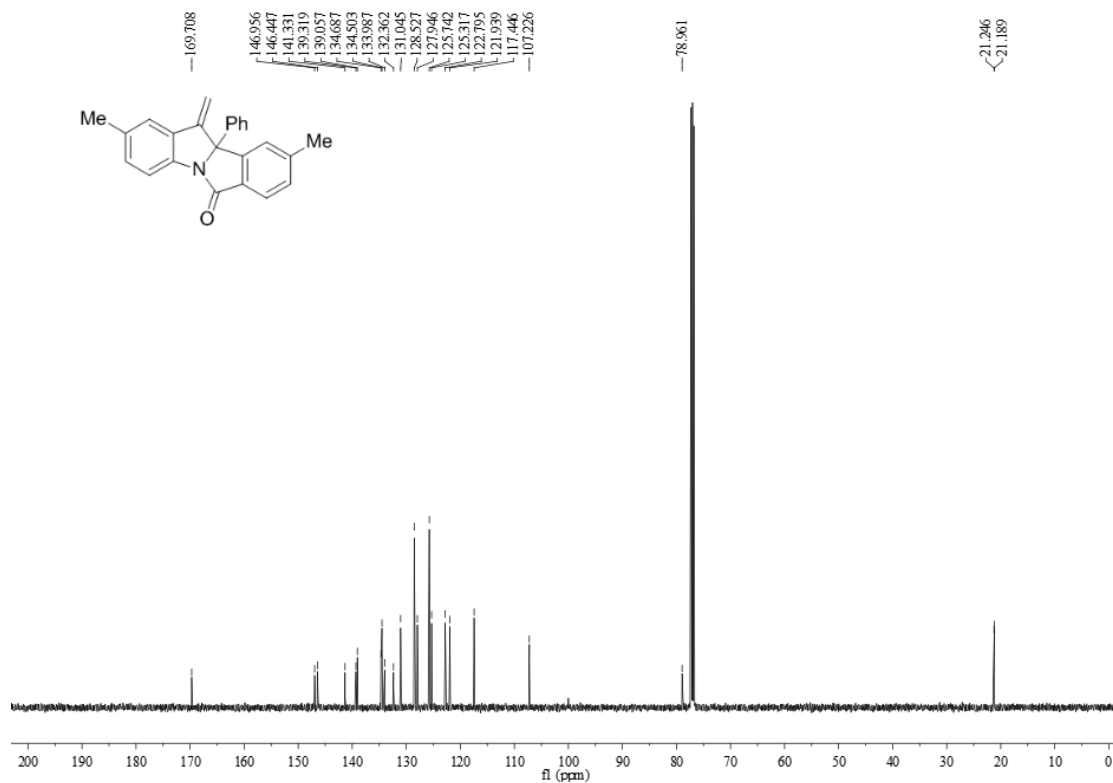
¹³C NMR of **3p** (125 MHz, CDCl₃)



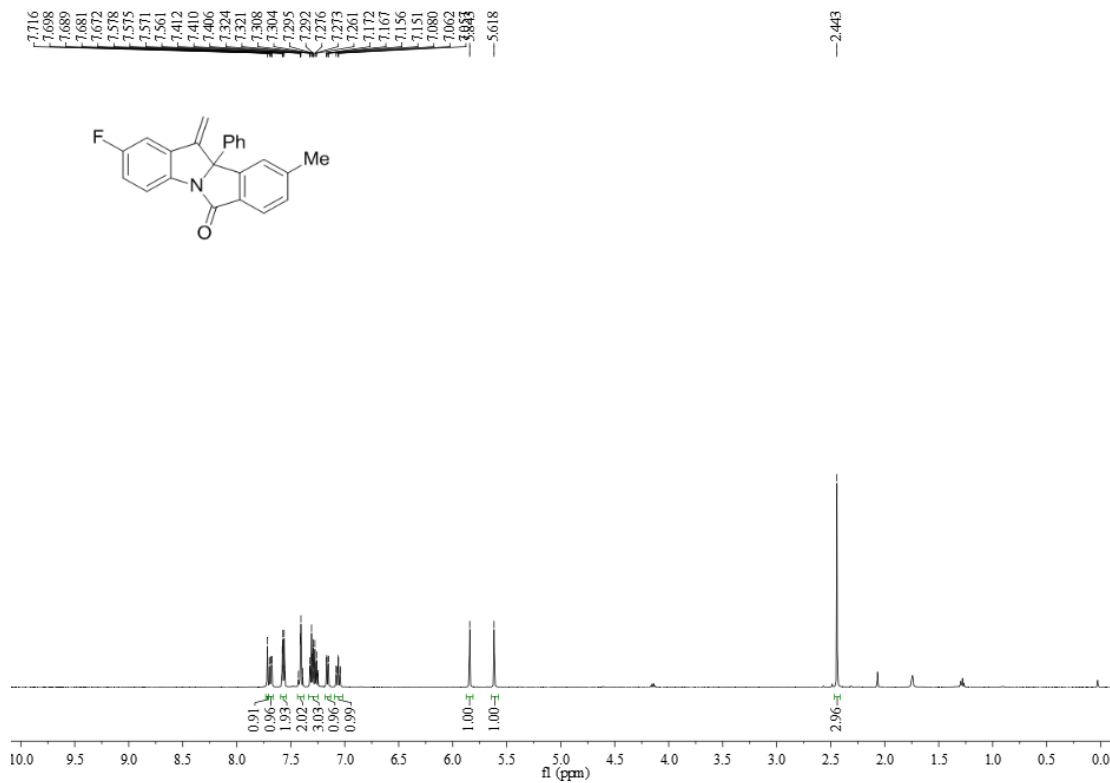
^1H NMR of **3q** (500 MHz, CDCl_3)



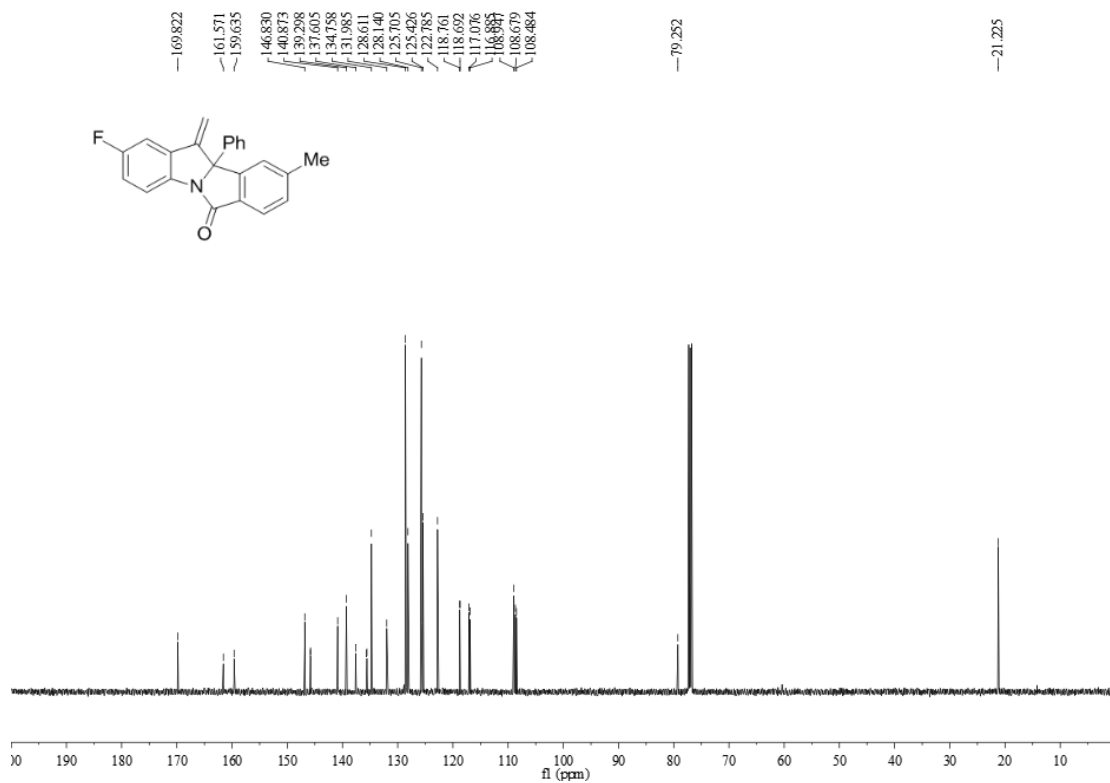
^{13}C NMR of **3q** (125 MHz, CDCl_3)



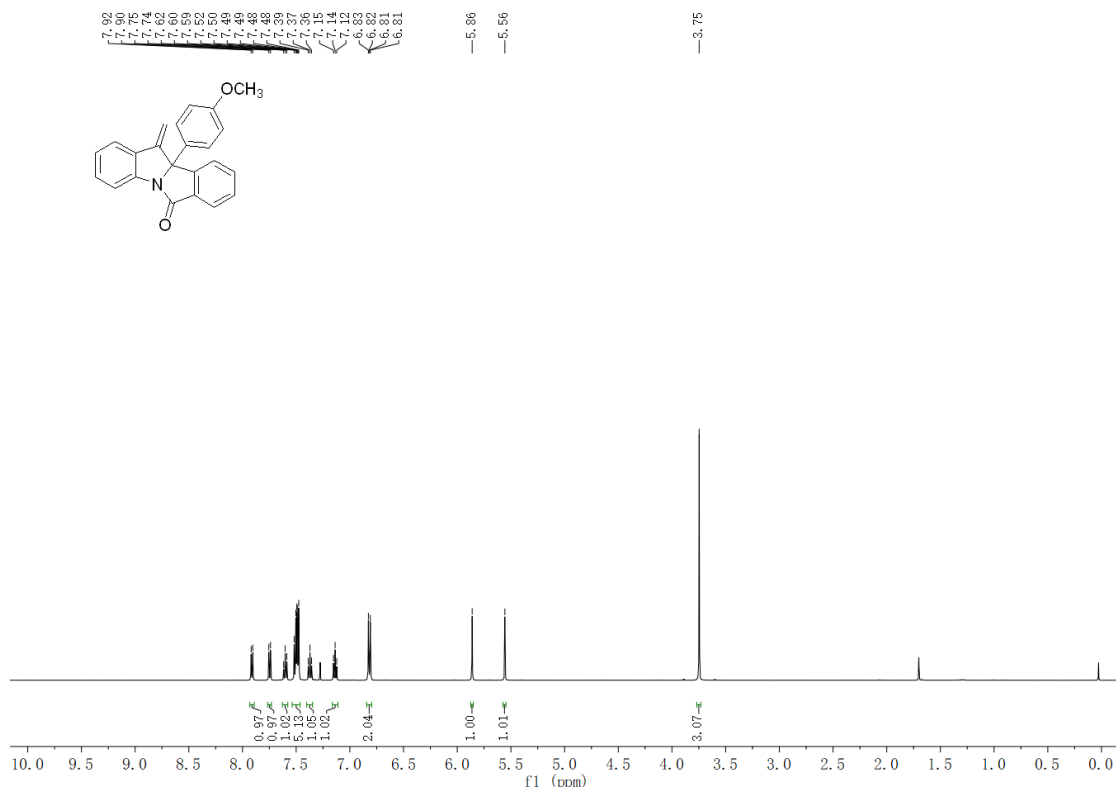
¹H NMR of **3r** (500 MHz, CDCl₃)



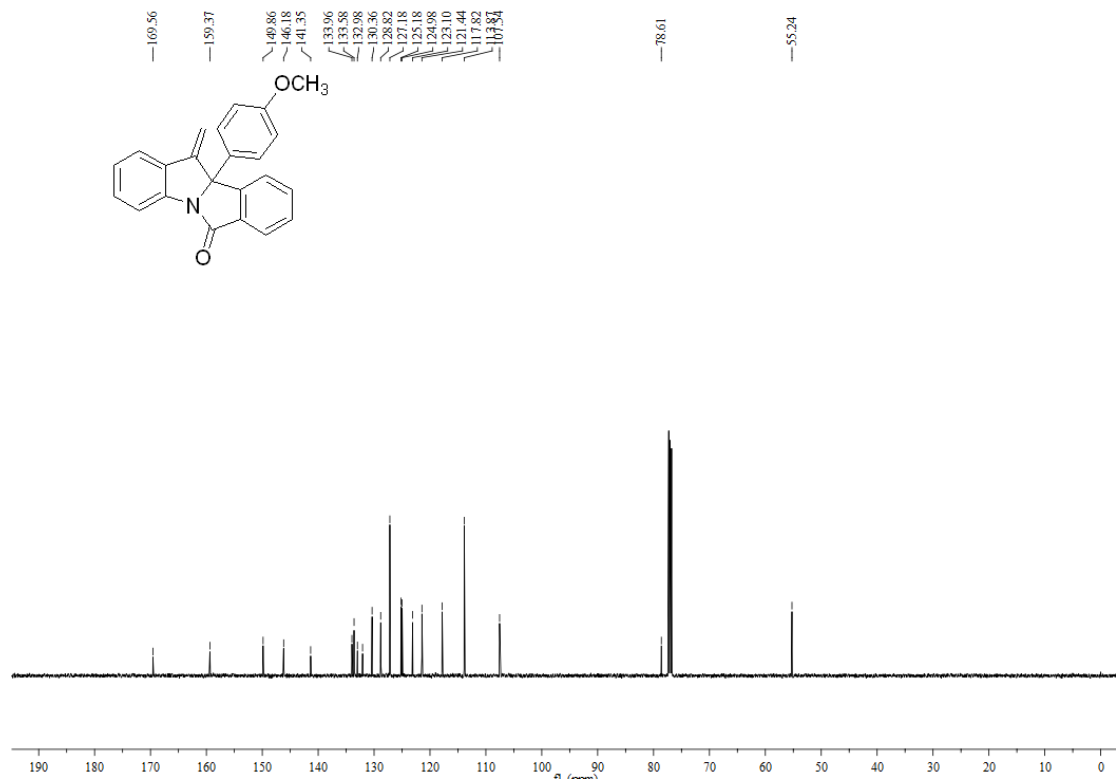
¹³C NMR of **3r** (125 MHz, CDCl₃)



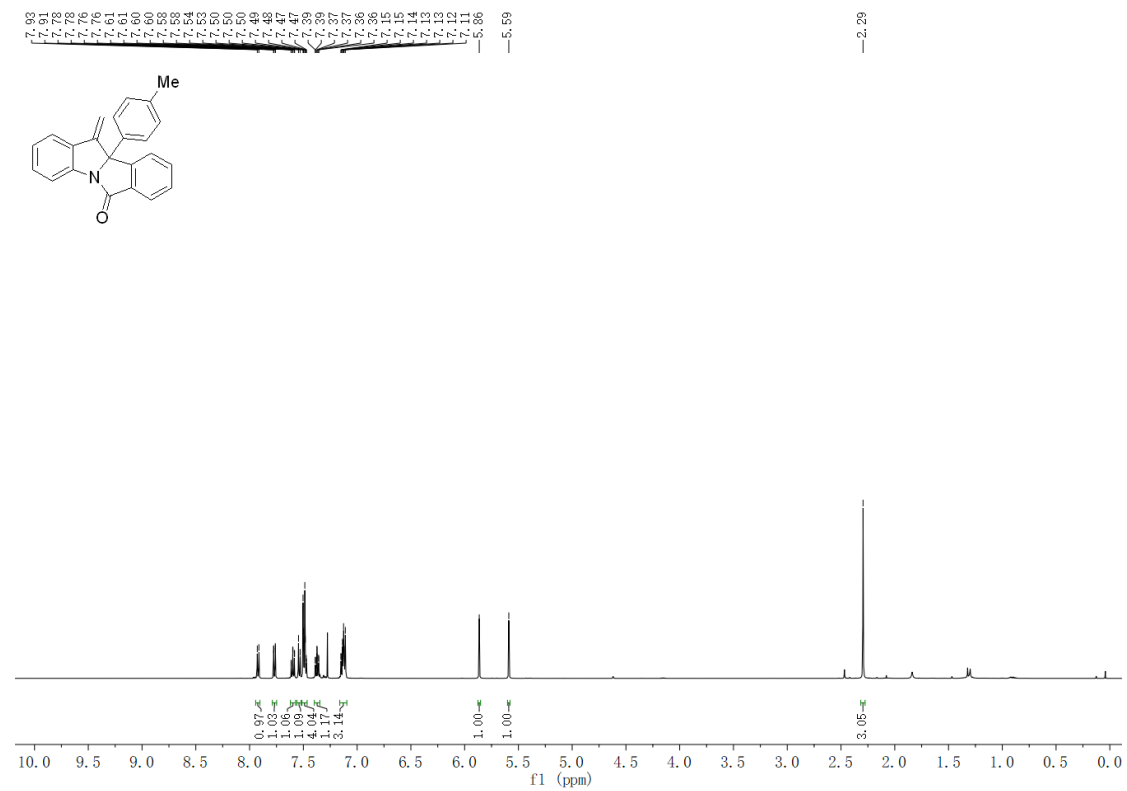
¹H NMR of **3s** (500 MHz, CDCl₃)



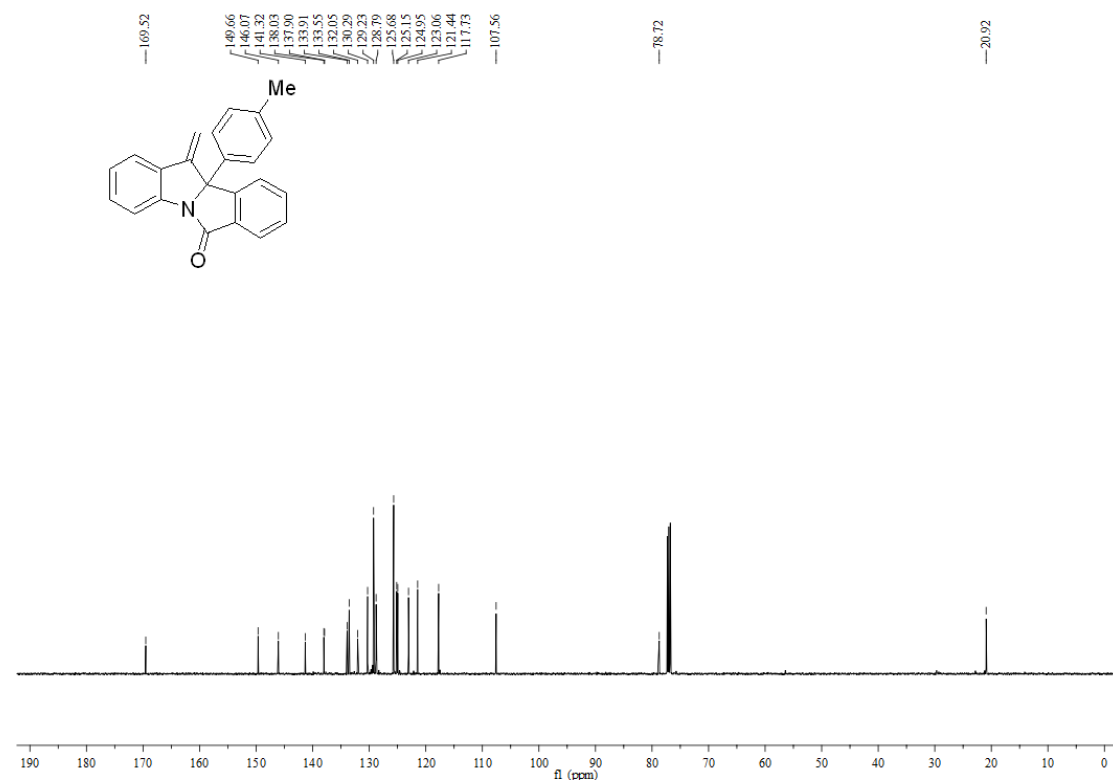
¹³C NMR of **3s** (125 MHz, CDCl₃)



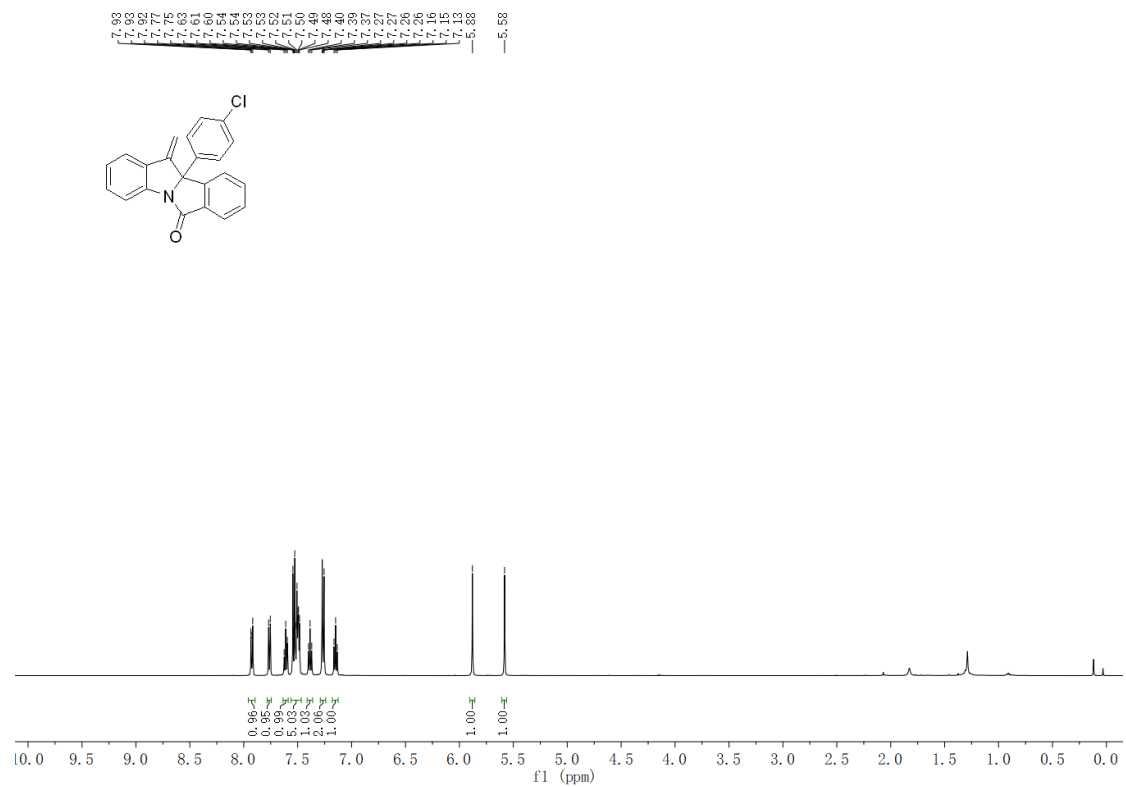
¹H NMR of **3t** (500 MHz, CDCl₃)



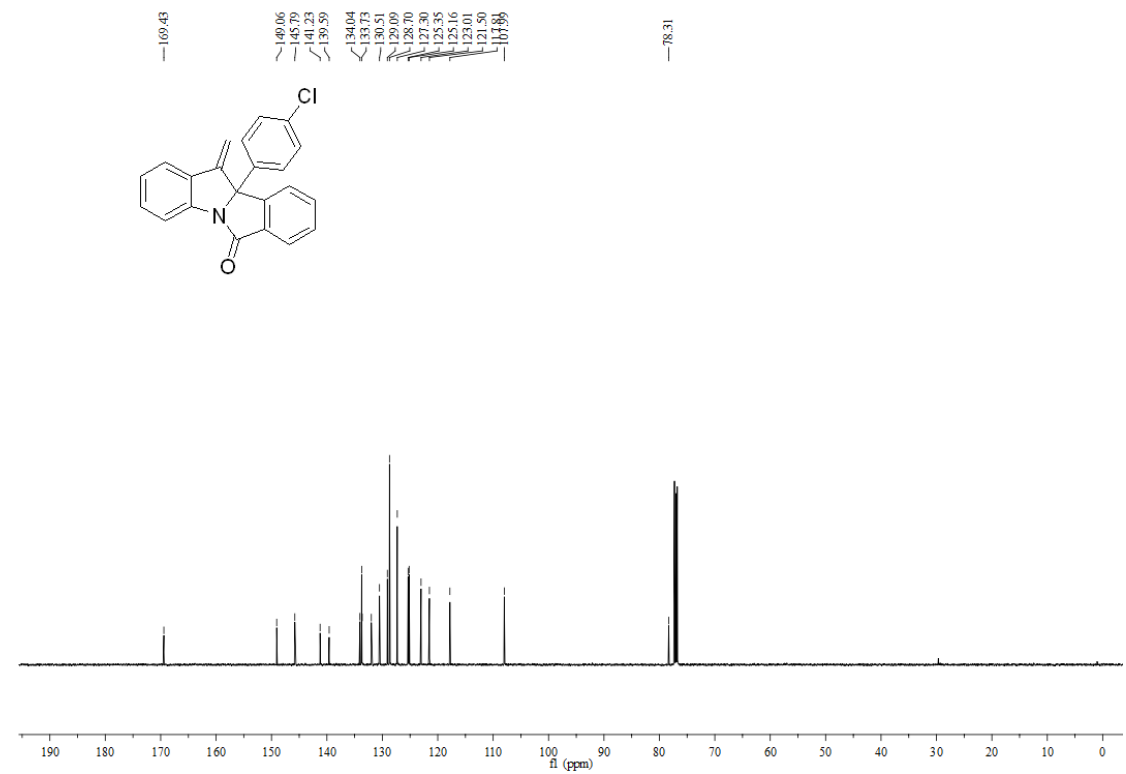
¹³C NMR of **3t** (125 MHz, CDCl₃)



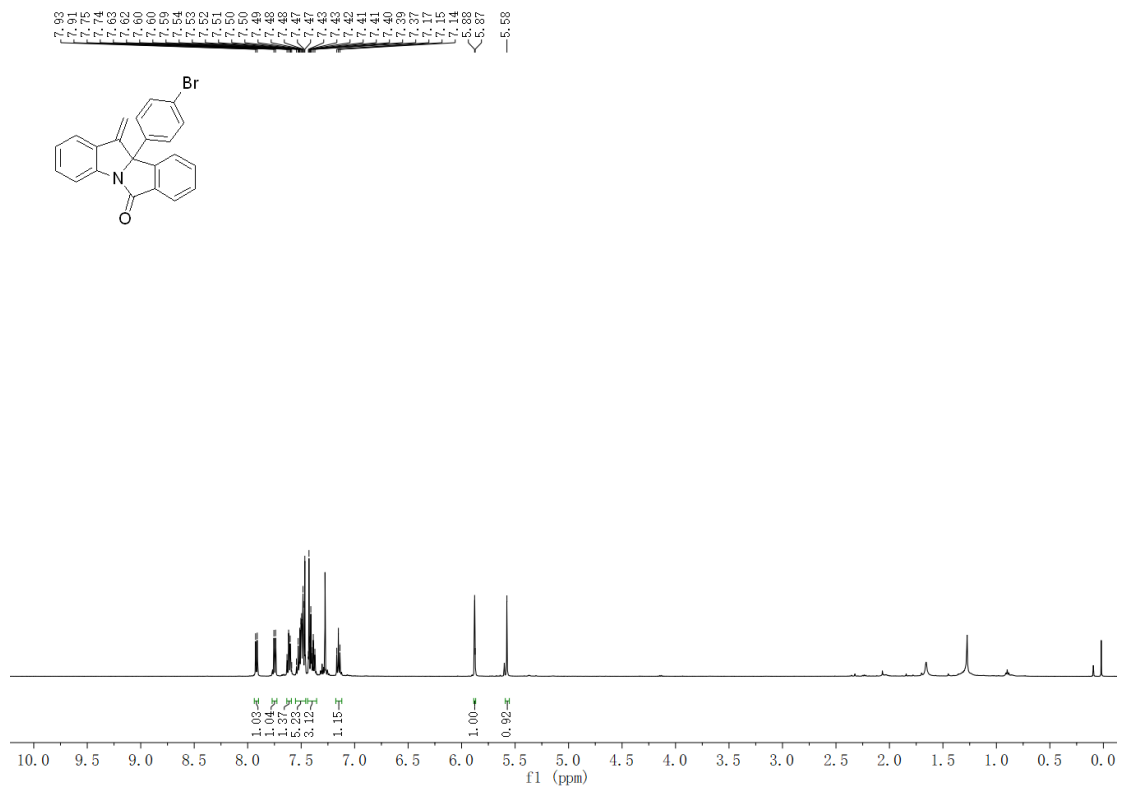
¹H NMR of **3u** (500 MHz, CDCl₃)



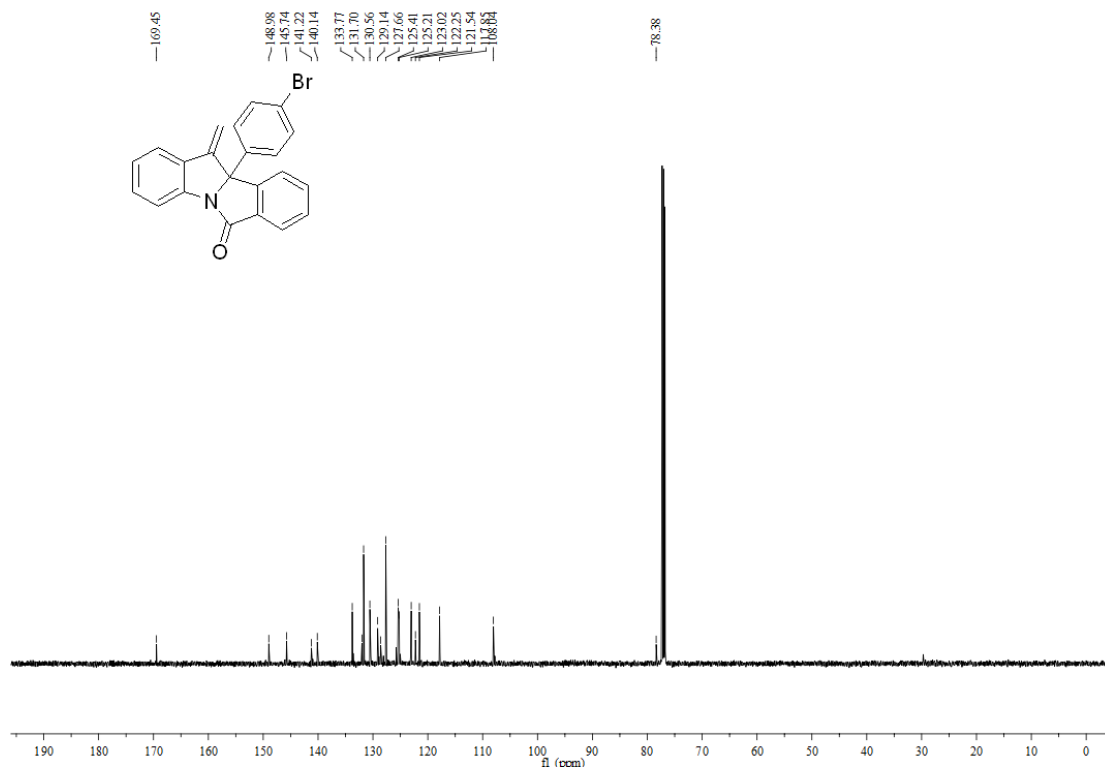
¹³C NMR of **3u** (125 MHz, CDCl₃)



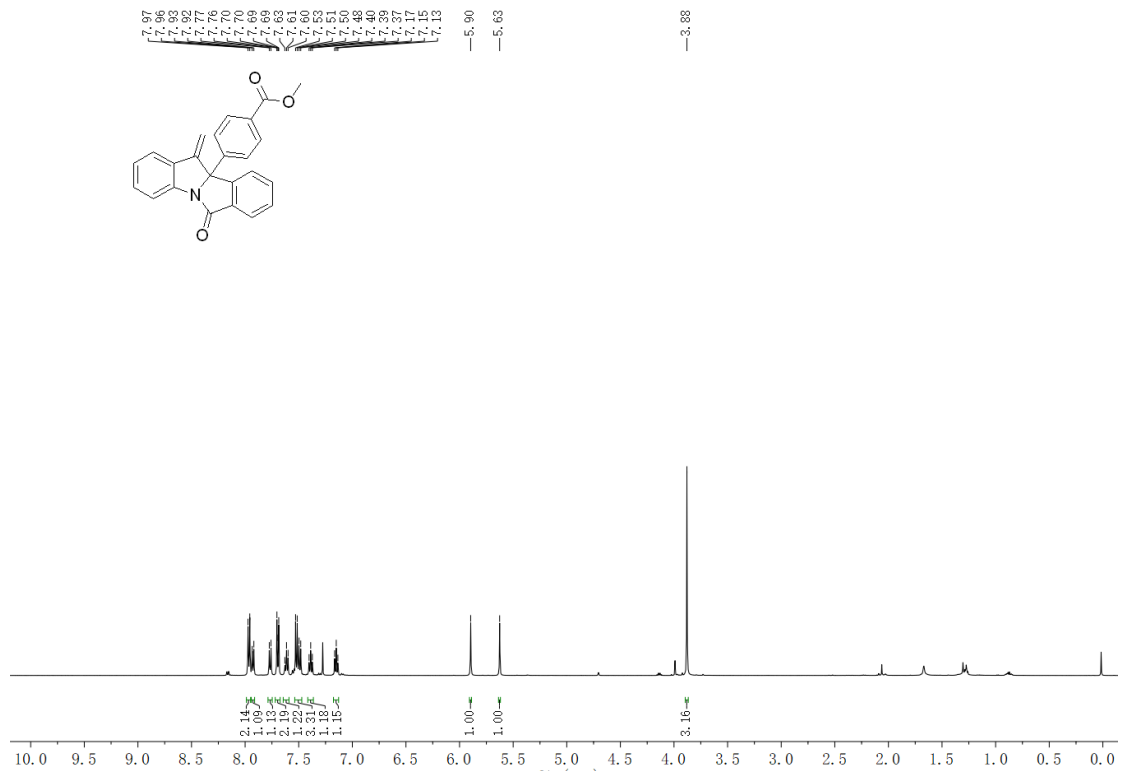
^1H NMR of **3v** (500 MHz, CDCl_3)



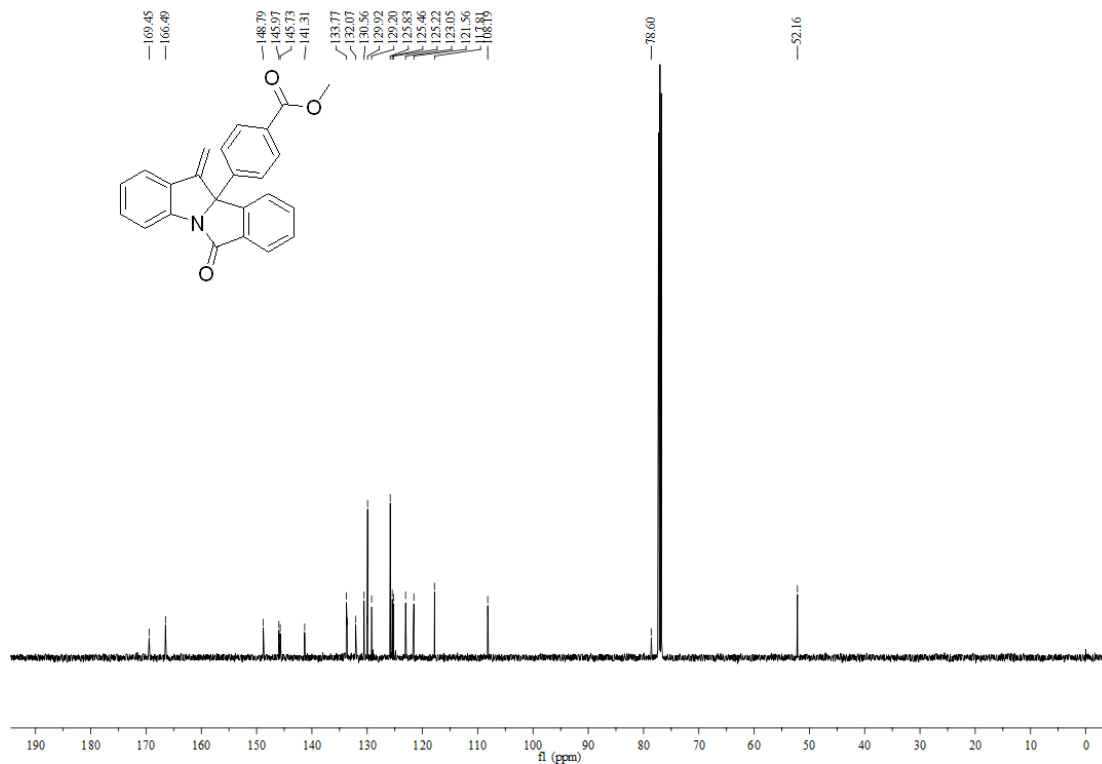
^{13}C NMR of **3v** (125 MHz, CDCl_3)



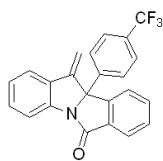
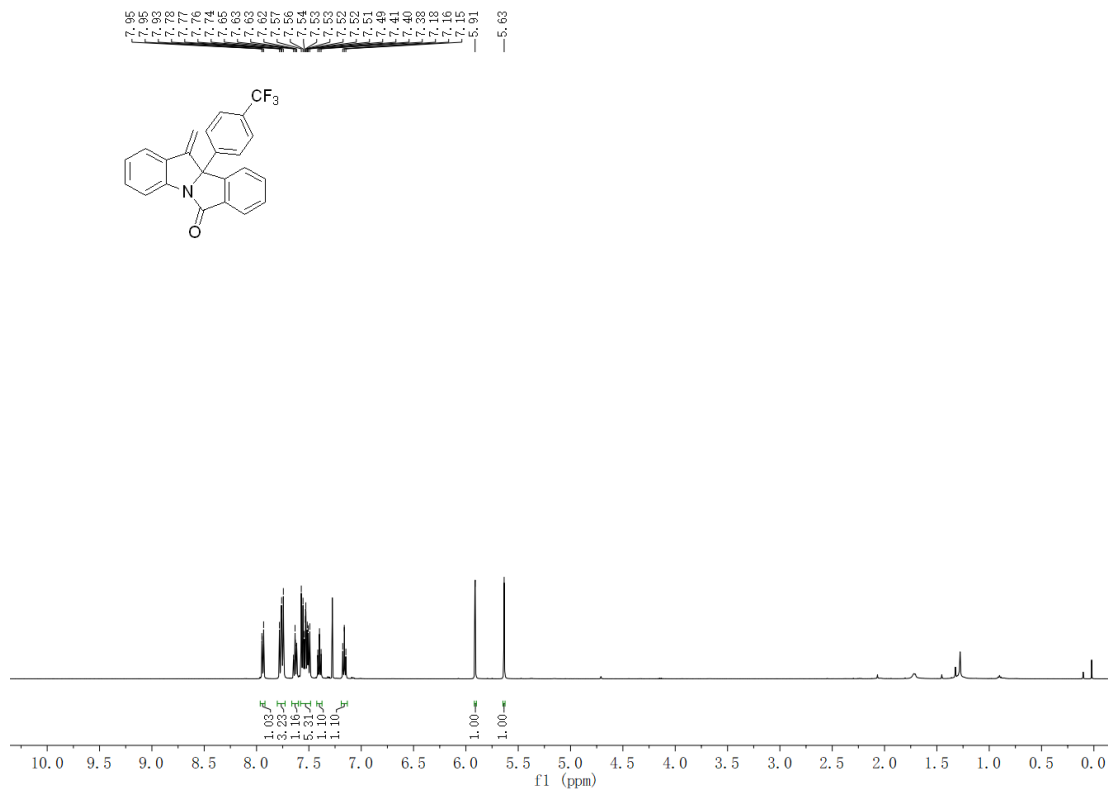
^1H NMR of **3w** (500 MHz, CDCl_3)



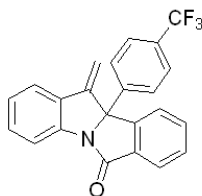
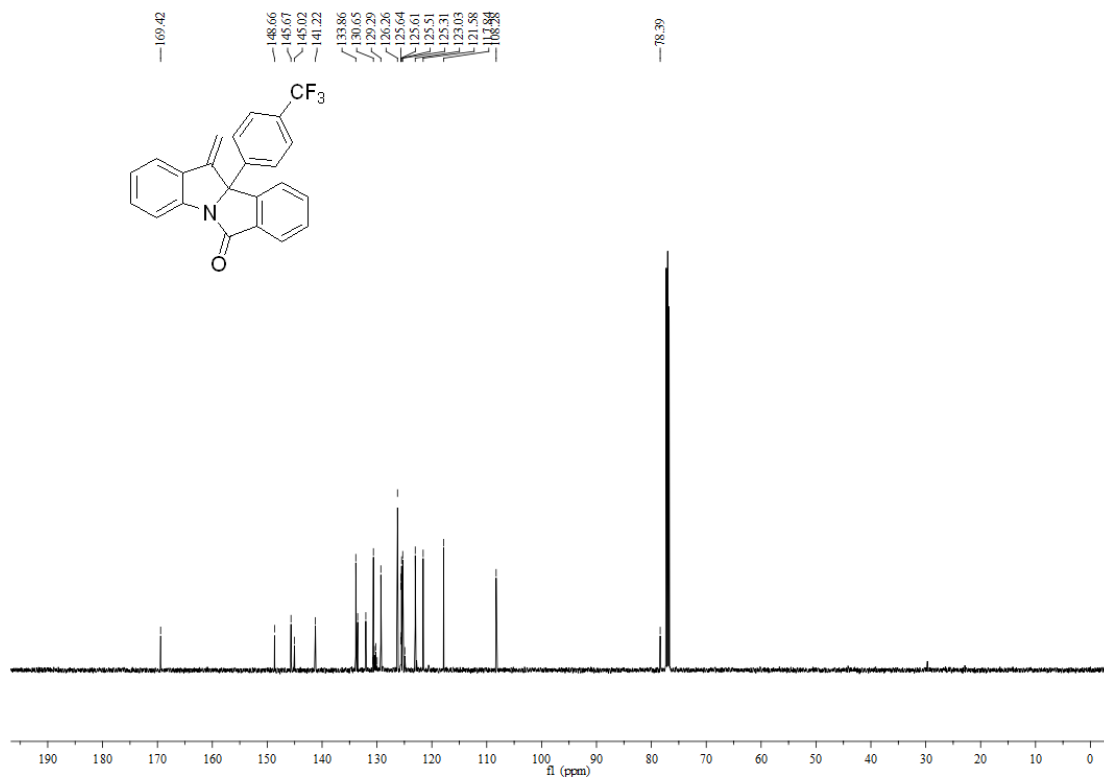
^{13}C NMR of **3w** (125 MHz, CDCl_3)



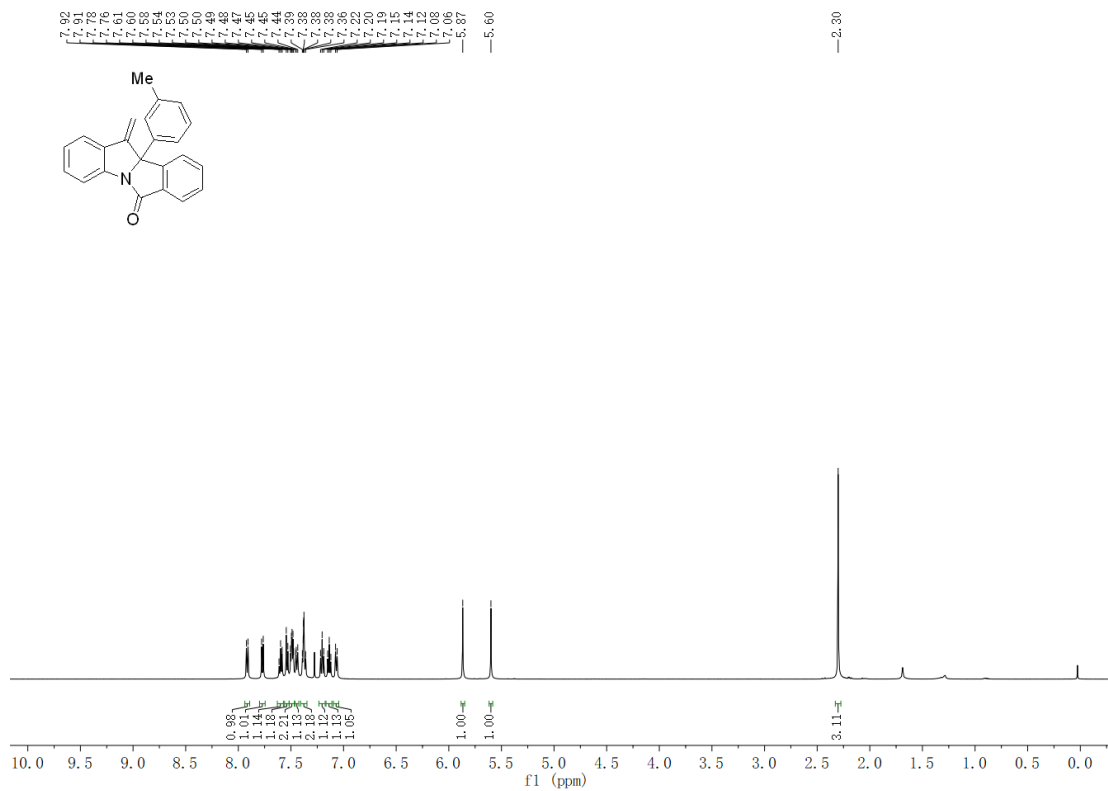
¹H NMR of **3x** (500 MHz, CDCl₃)



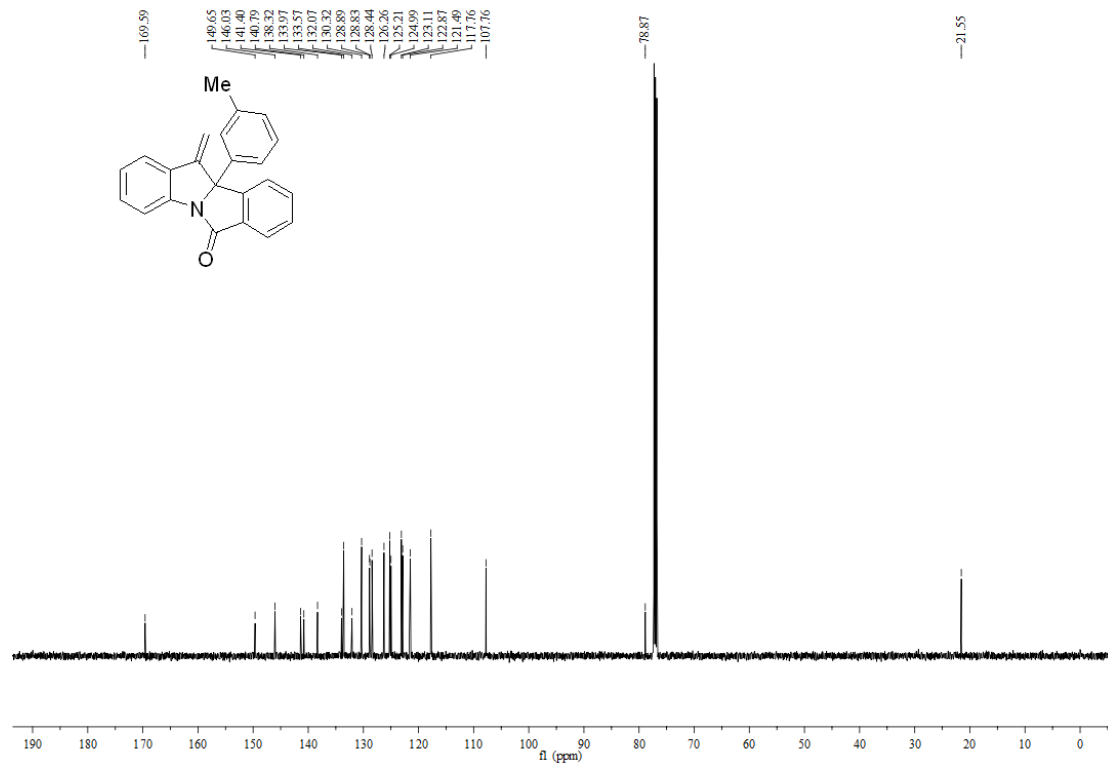
¹³C NMR of **3x** (125 MHz, CDCl₃)



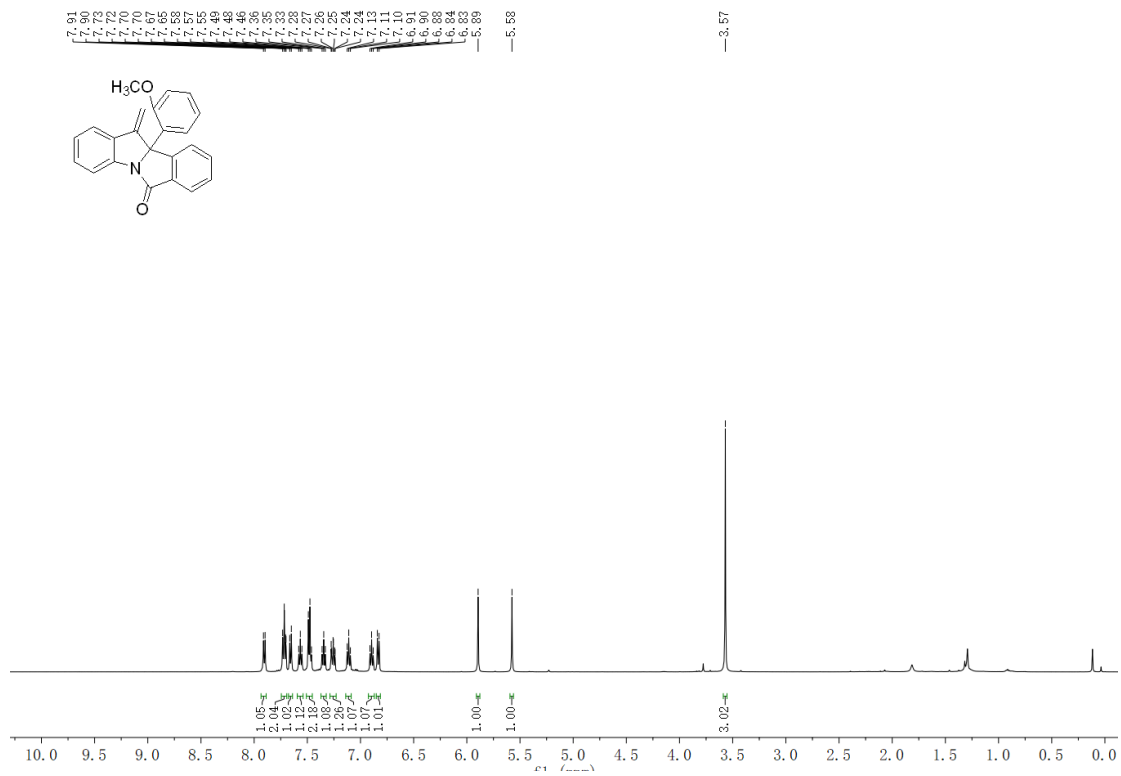
^1H NMR of **3y** (500 MHz, CDCl_3)



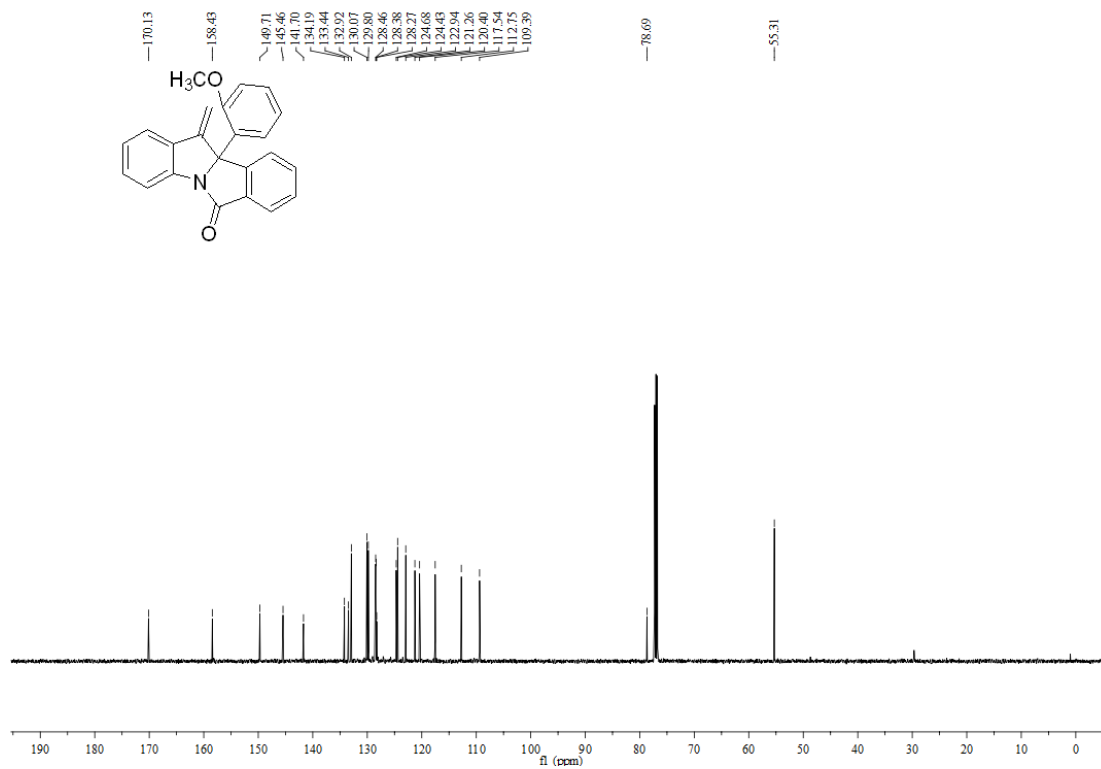
^{13}C NMR of **3y** (125 MHz, CDCl_3)



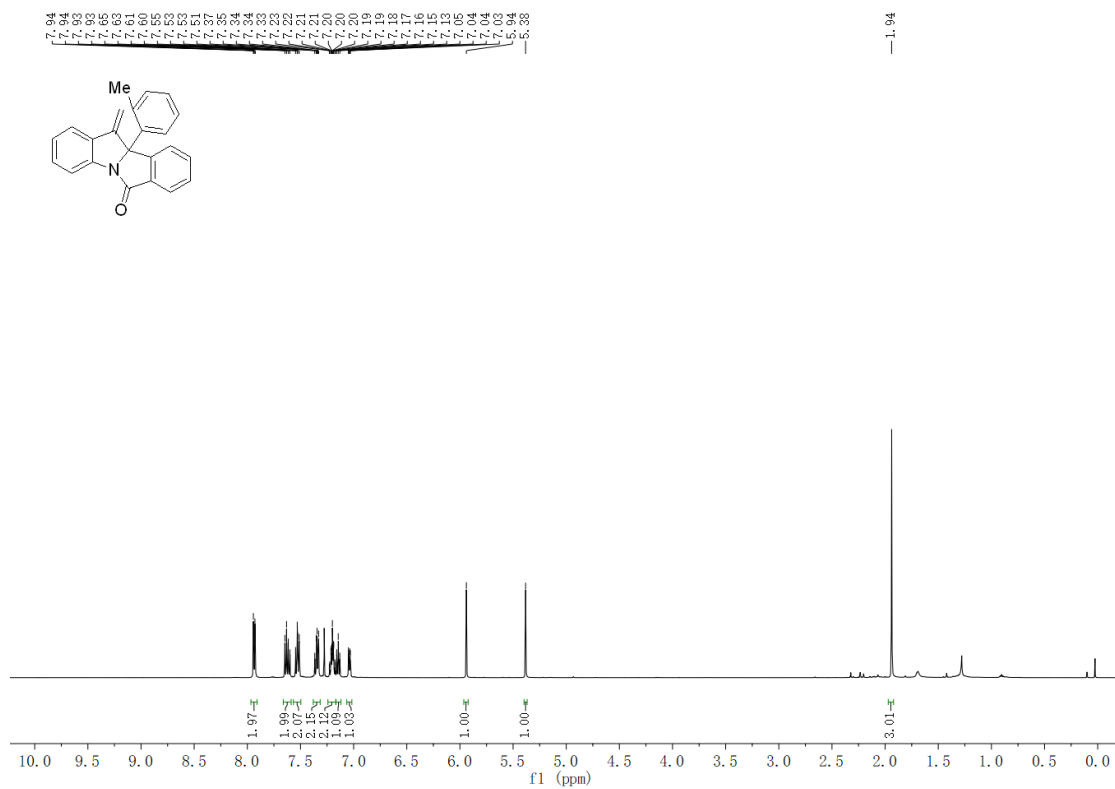
^1H NMR of **3z** (500 MHz, CDCl_3)



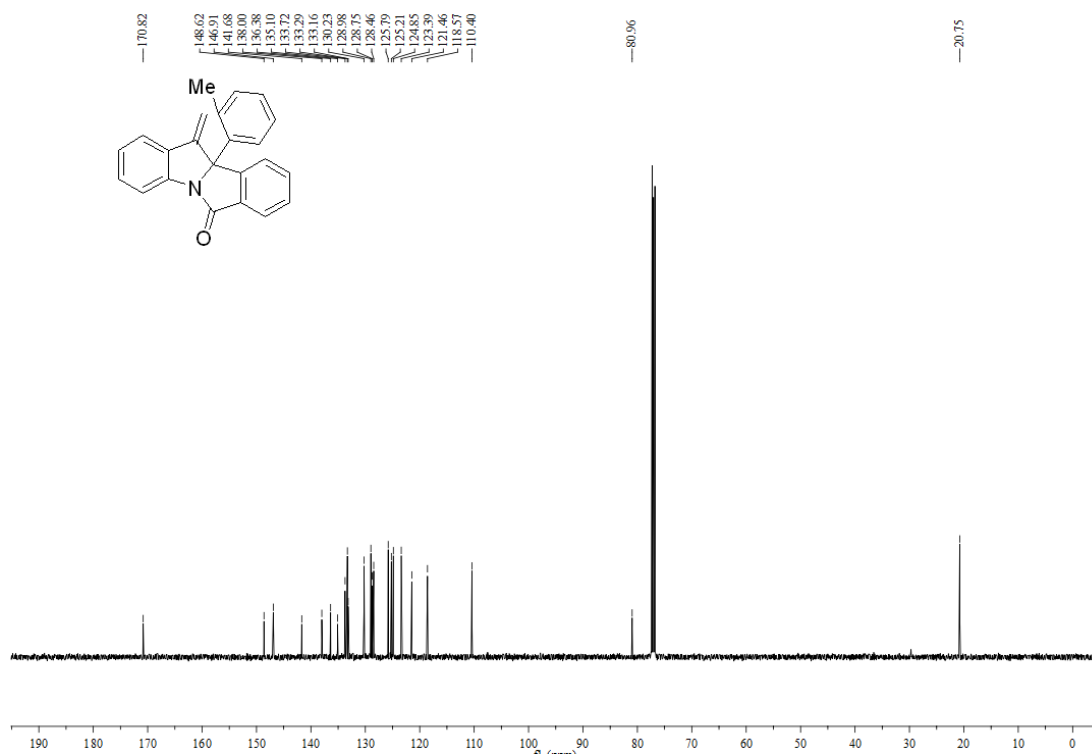
^{13}C NMR of **3z** (125 MHz, CDCl_3)



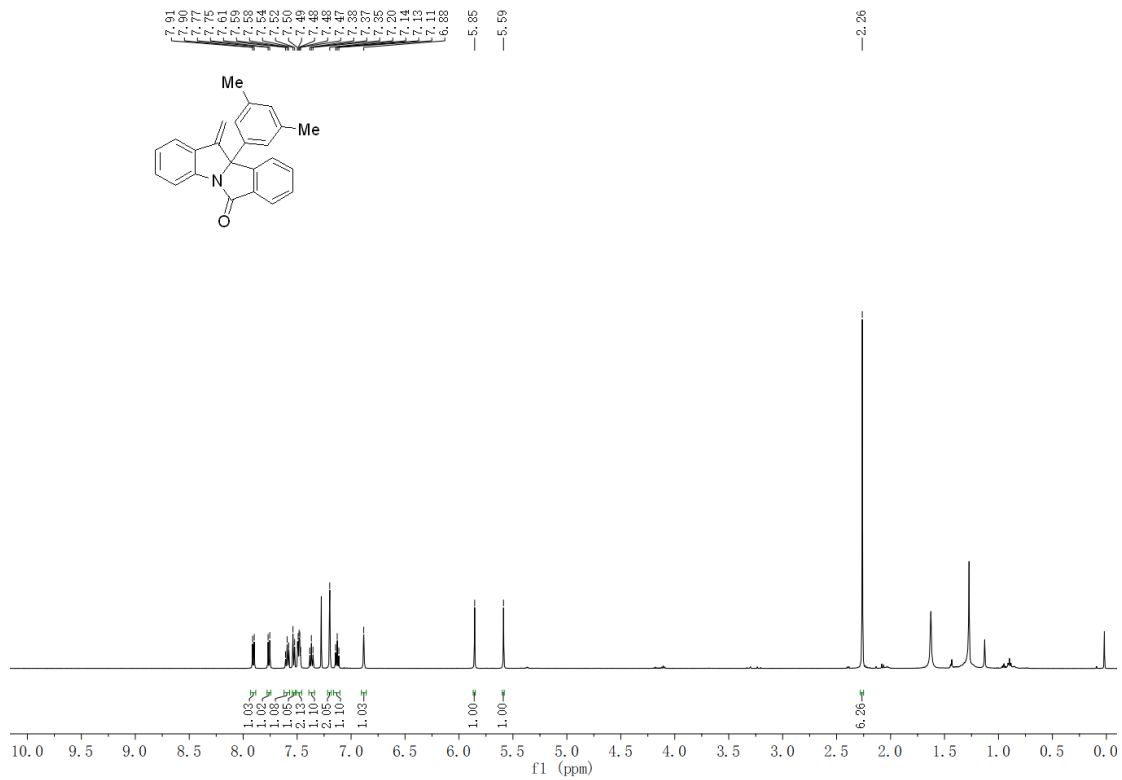
¹H NMR of **3aa** (500 MHz, CDCl₃)



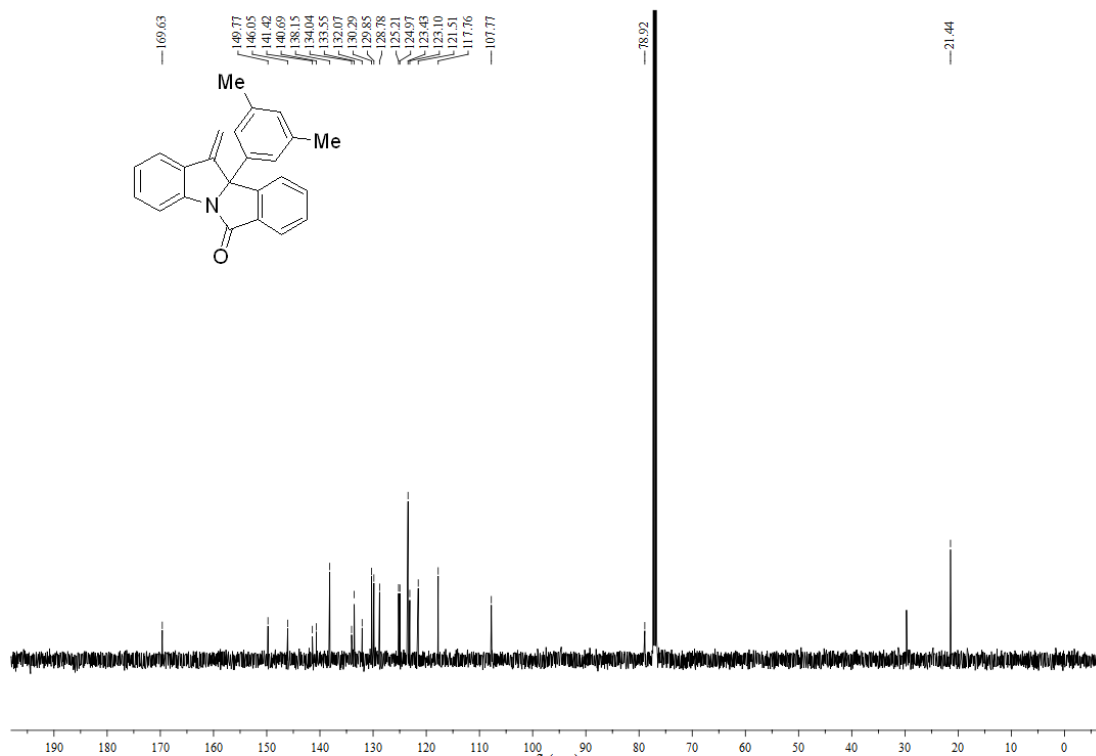
¹³C NMR of **3aa** (125 MHz, CDCl₃)



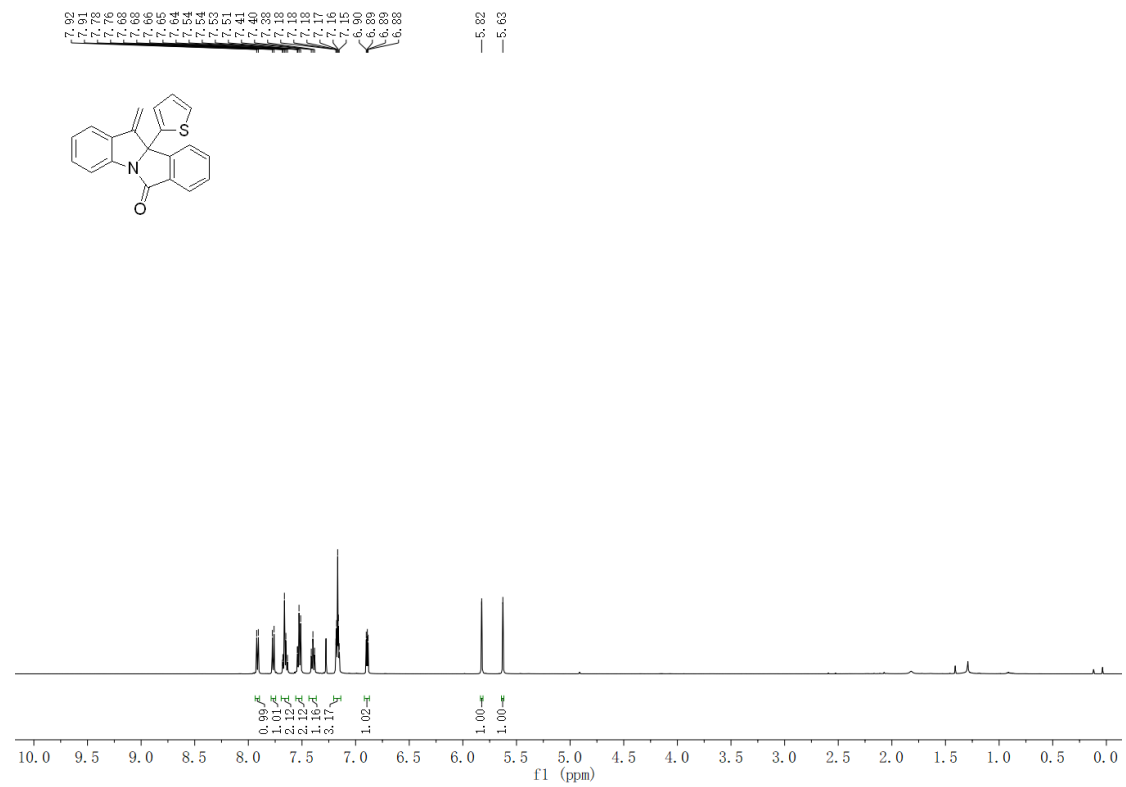
¹H NMR of **3ab** (500 MHz, CDCl₃)



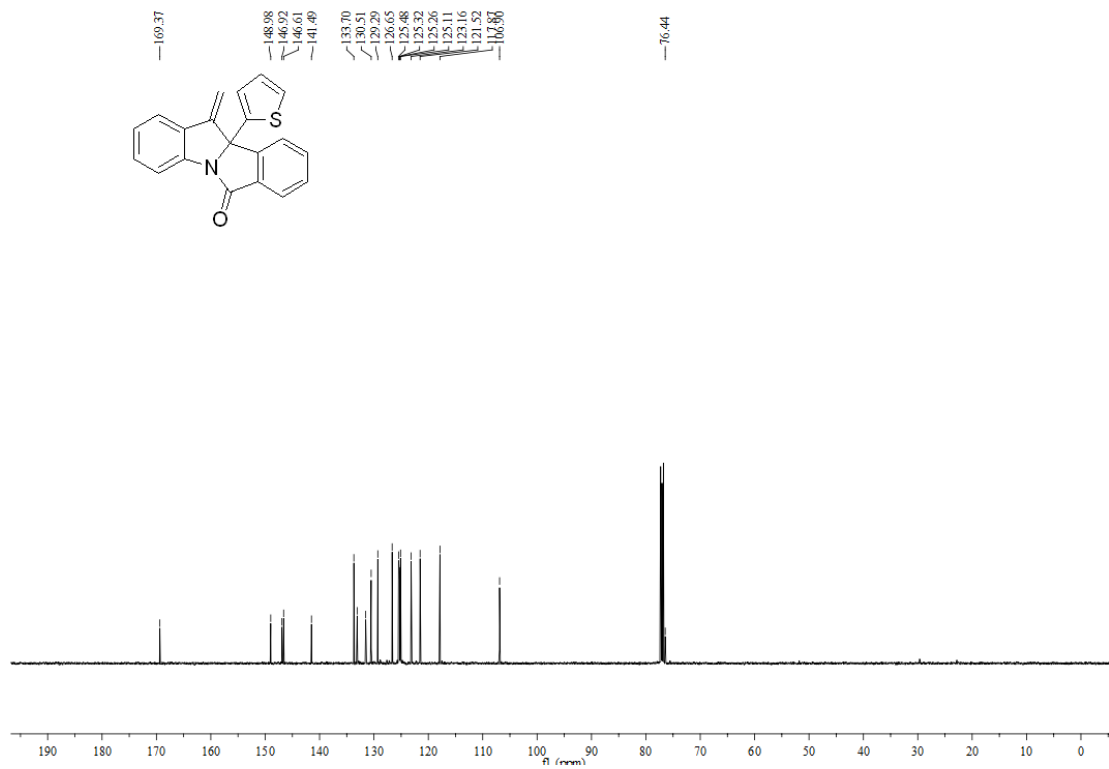
¹³C NMR of **3ab** (125 MHz, CDCl₃)



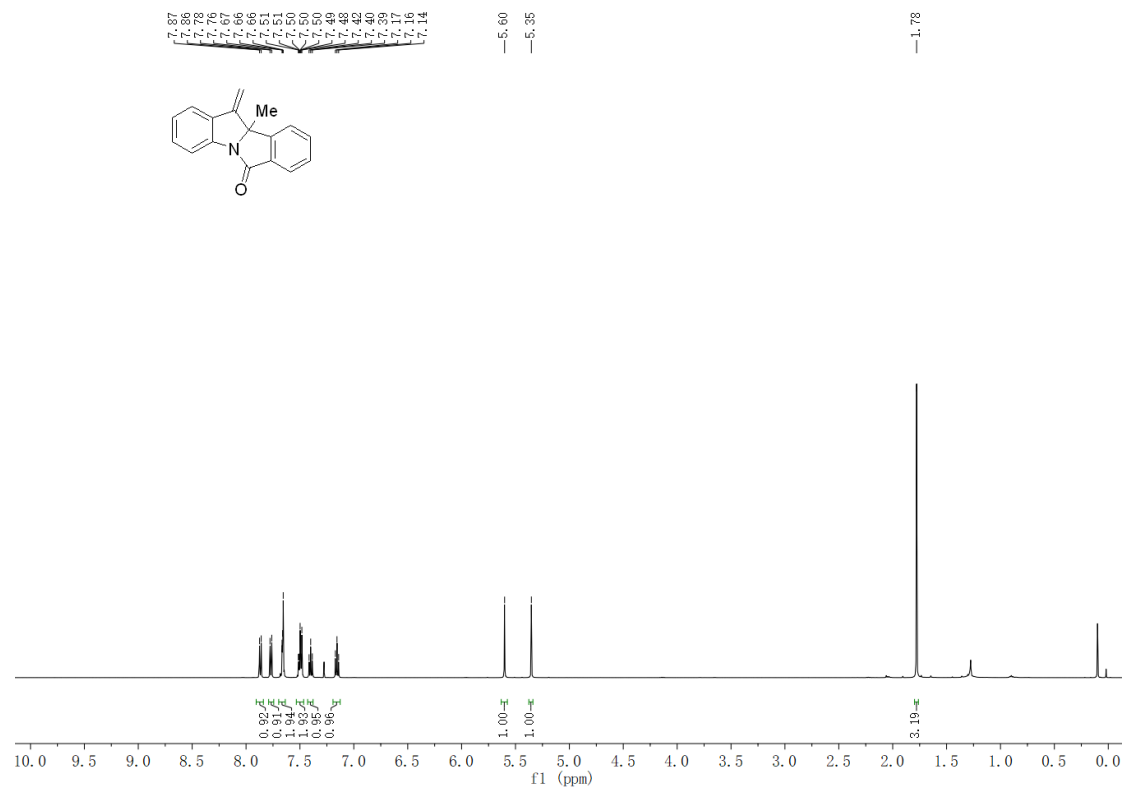
¹H NMR of **3ac** (500 MHz, CDCl₃)



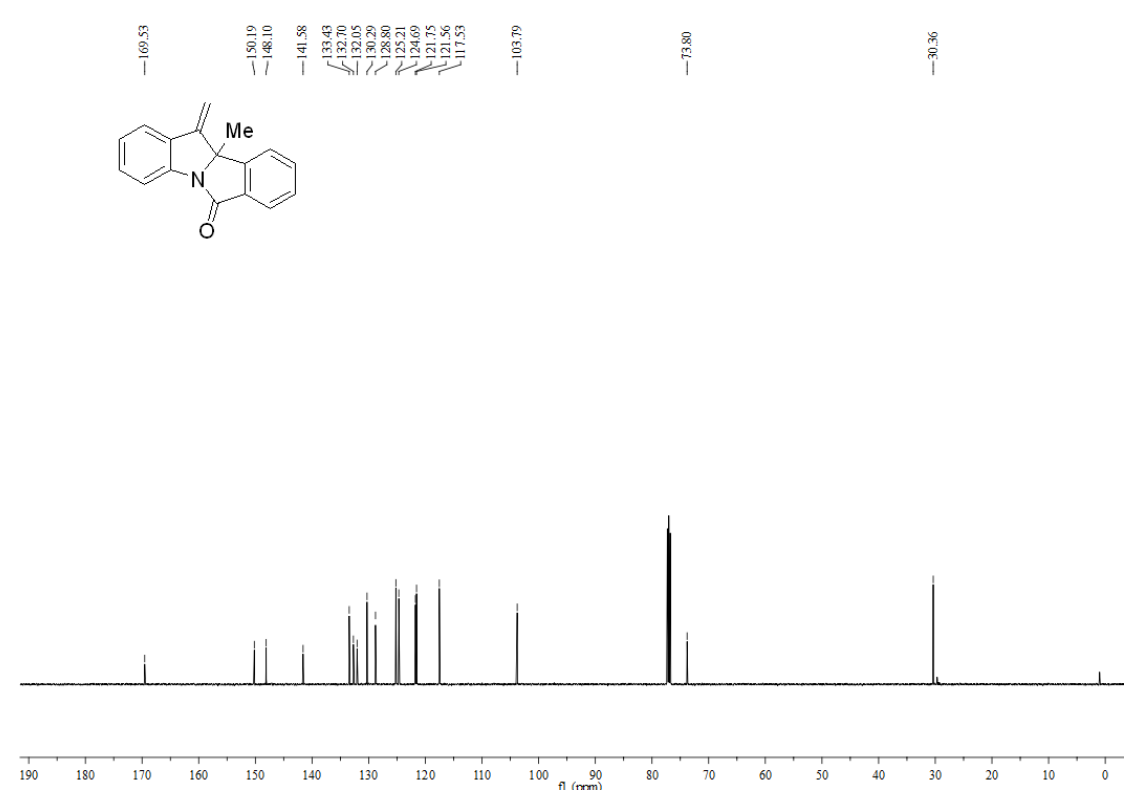
¹³C NMR of **3ac** (125 MHz, CDCl₃)



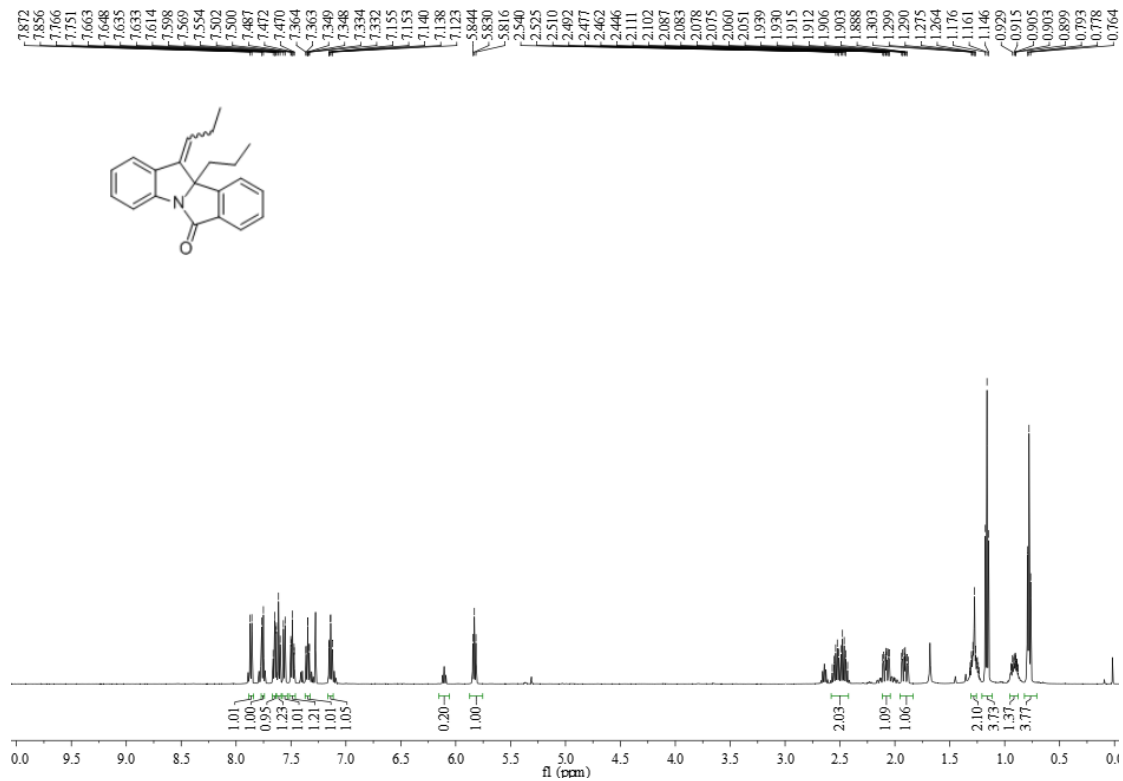
¹H NMR of **3ad** (500 MHz, CDCl₃)



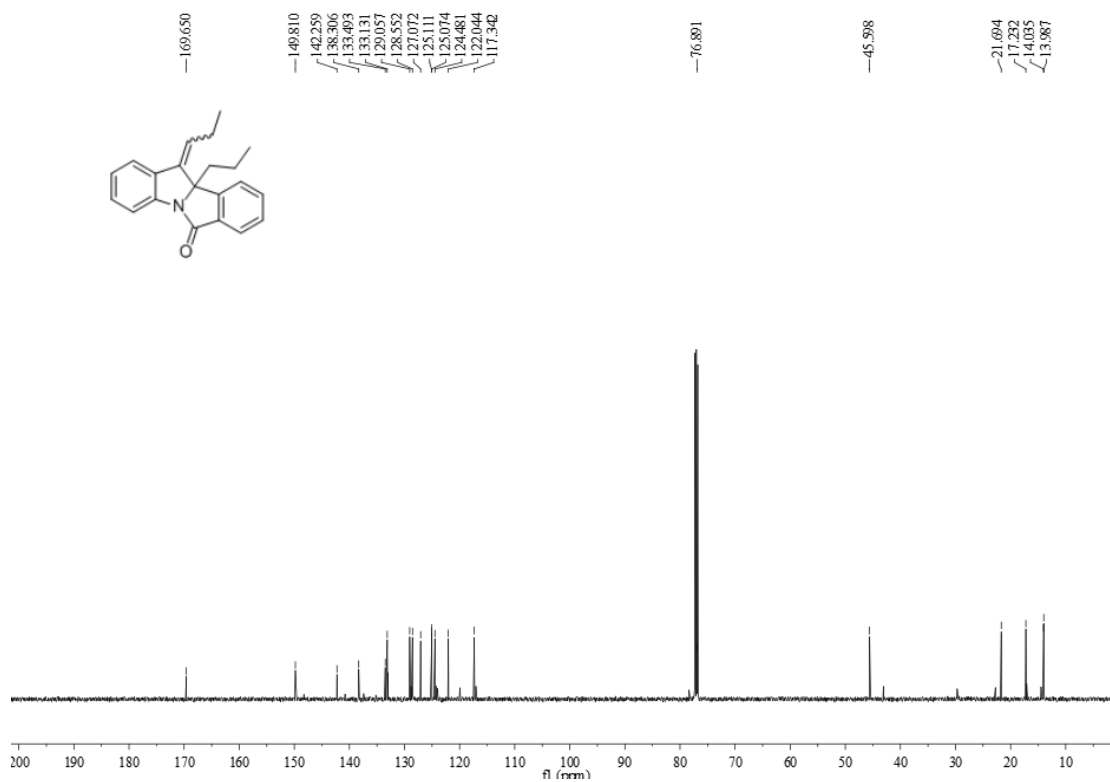
¹³C NMR of **3ad** (125 MHz, CDCl₃)



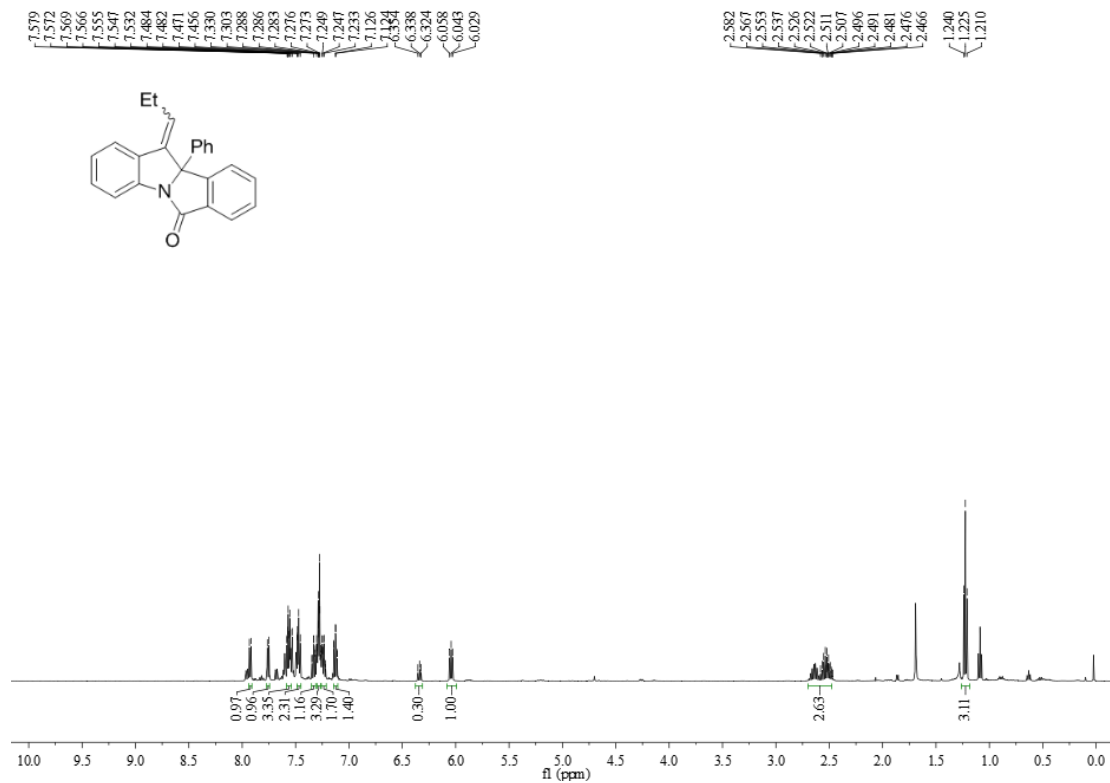
¹H NMR of **3ae** (d.r. = 5:1, 500 MHz, CDCl₃)



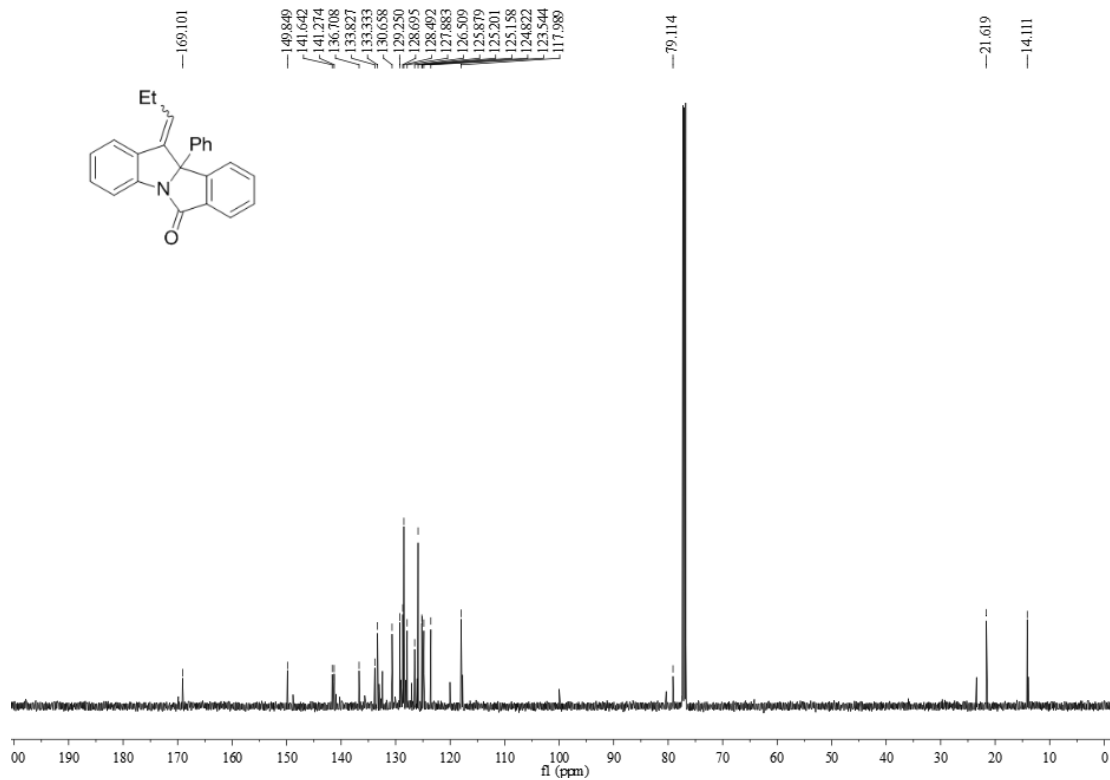
¹³C NMR of **3ae** (d.r. = 5:1, 125 MHz, CDCl₃)



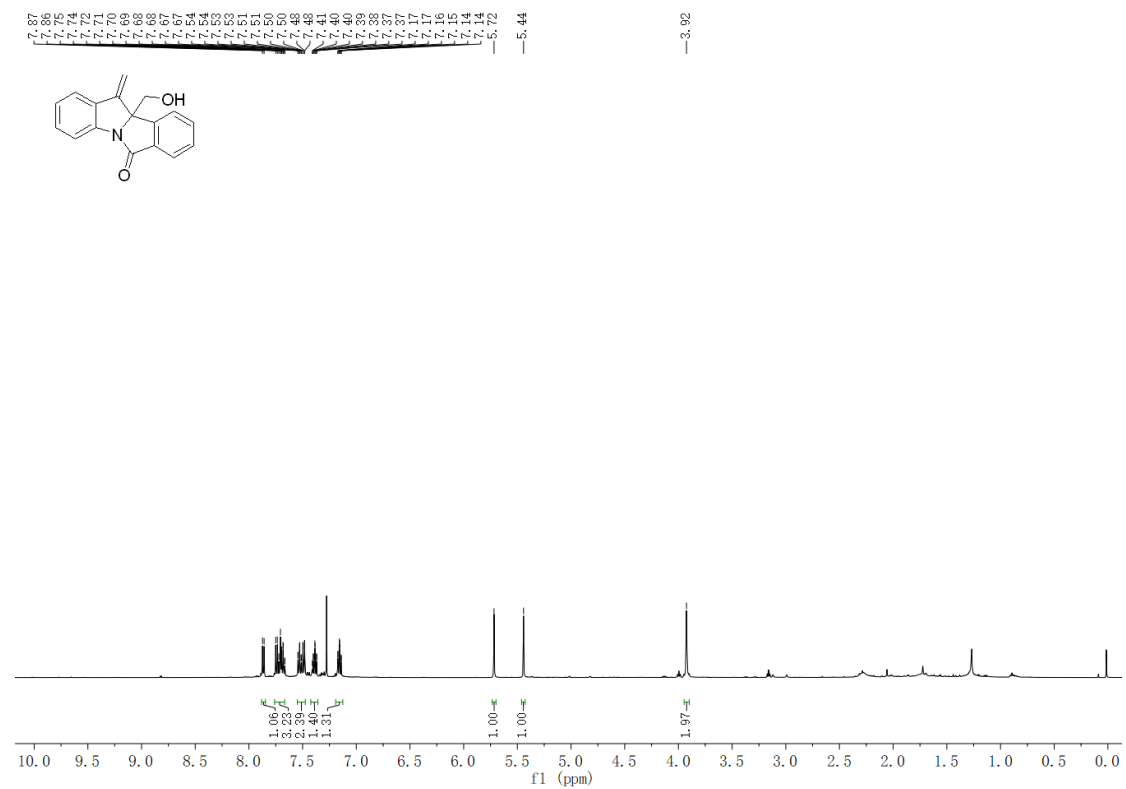
^1H NMR of **3af** (d.r. = 3.3:1, 500 MHz, CDCl_3)



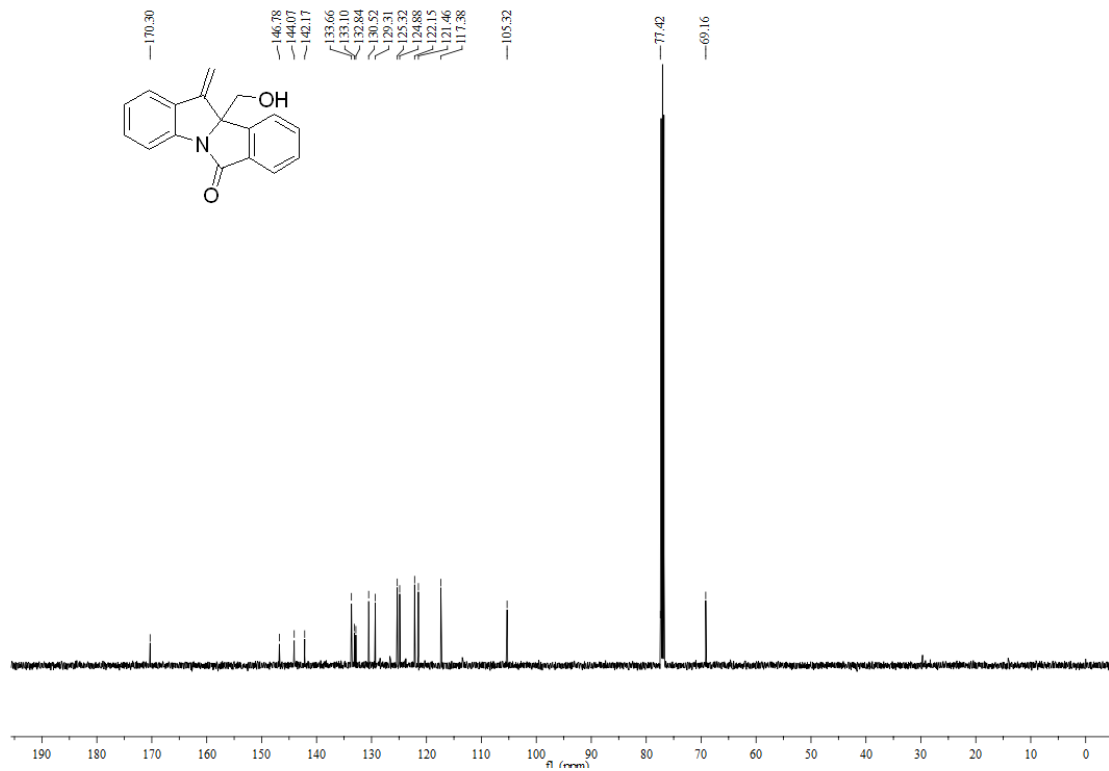
^{13}C NMR of **3af** (d.r. = 3.3:1, 125 MHz, CDCl_3)



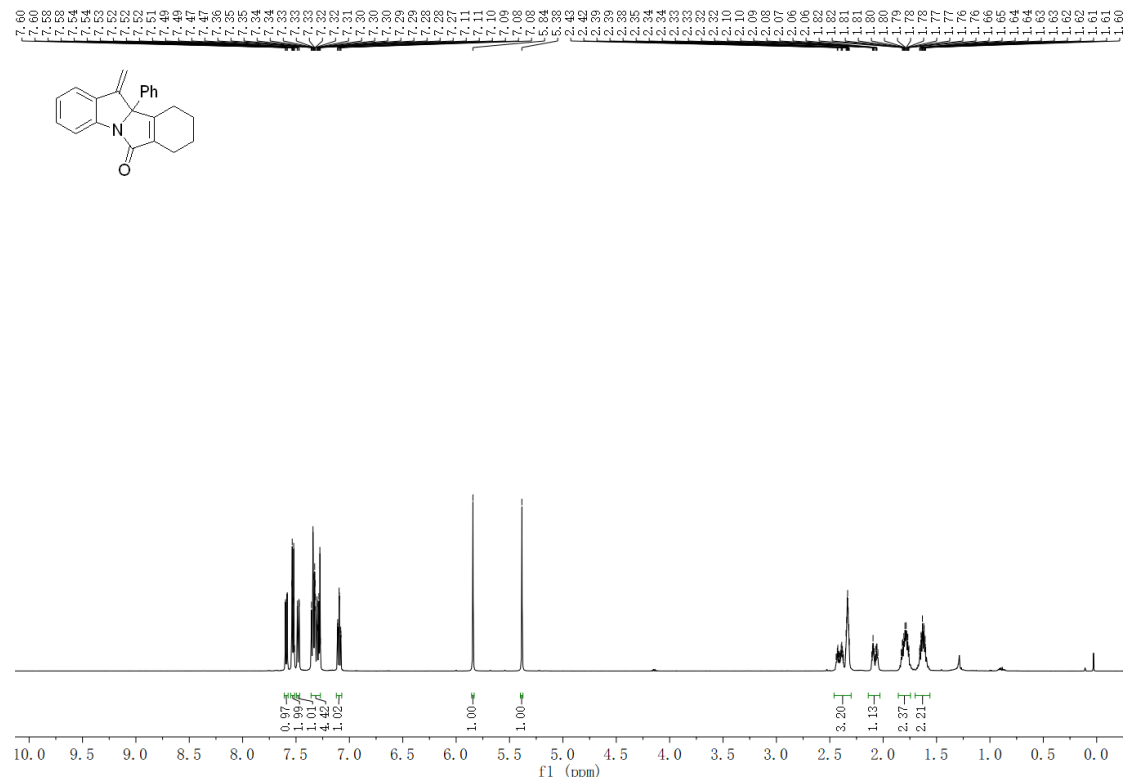
¹H NMR of **3ag** (500 MHz, CDCl₃)



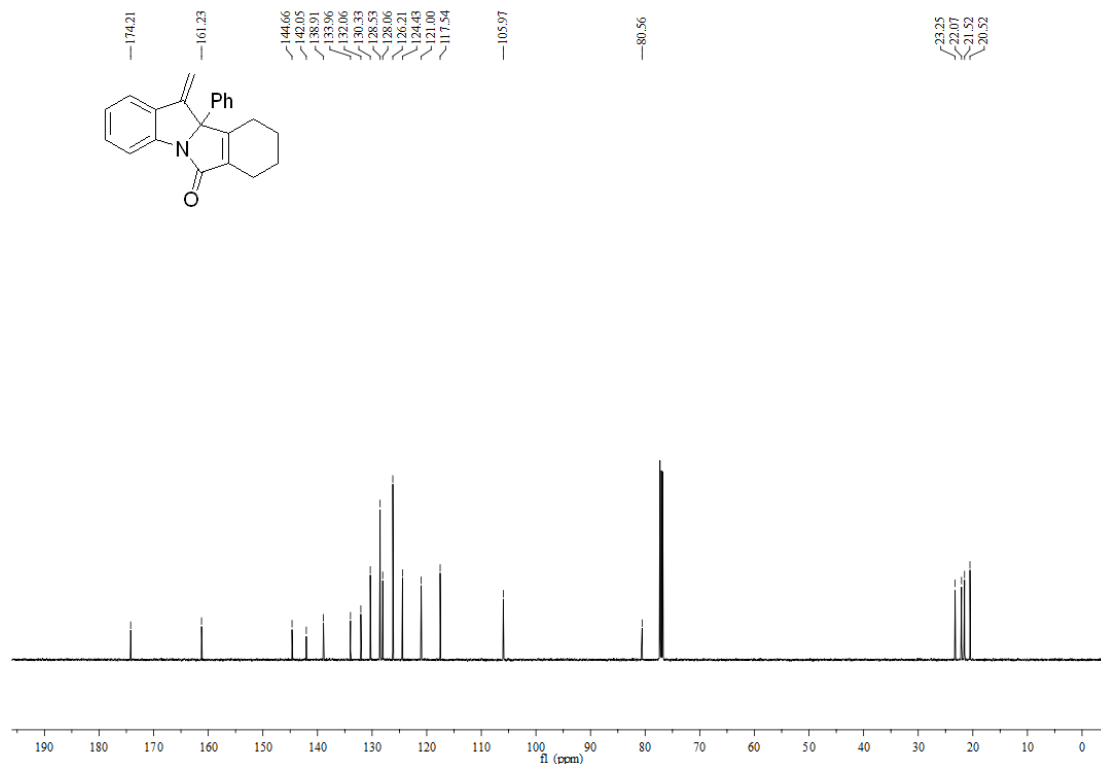
¹³C NMR of **3ag** (125 MHz, CDCl₃)



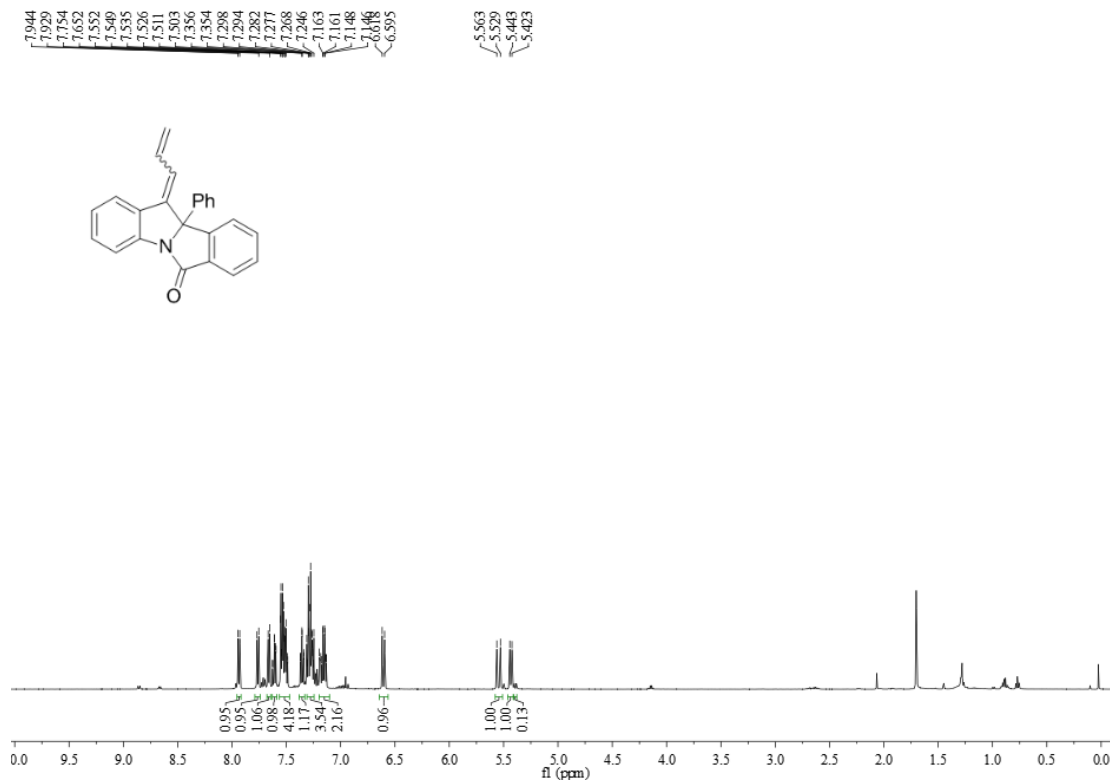
¹H NMR of **3ah** (500 MHz, CDCl₃)



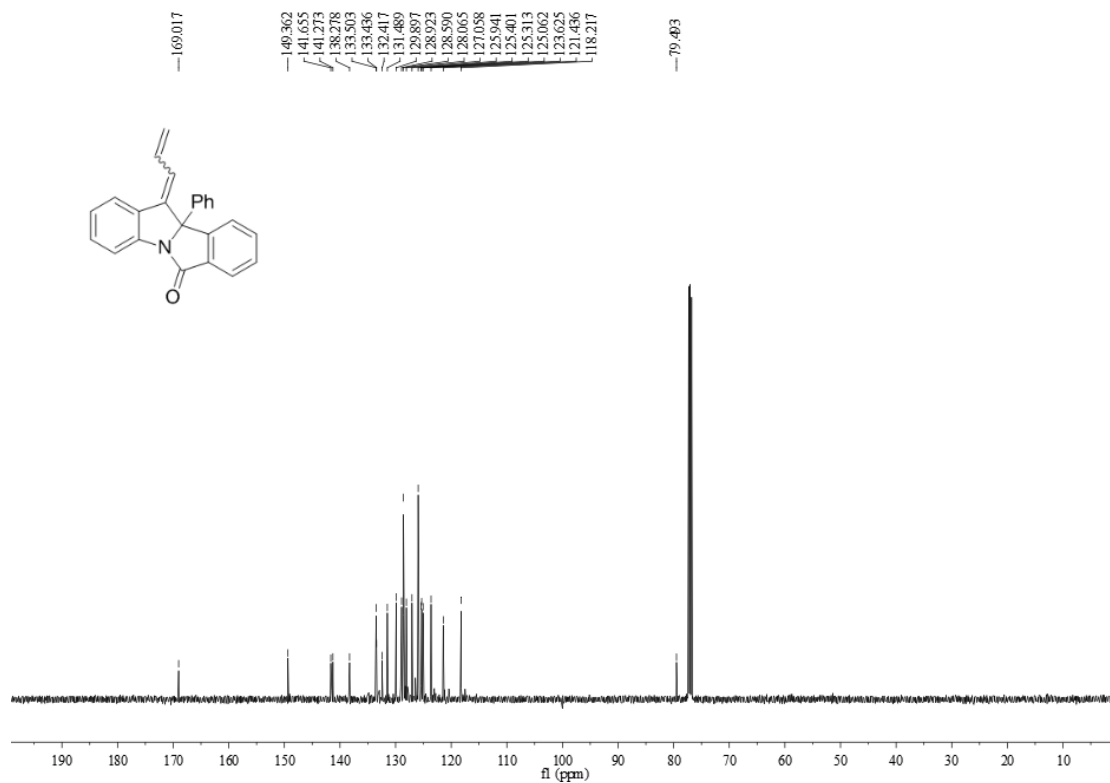
¹³C NMR of **3ah** (125 MHz, CDCl₃)



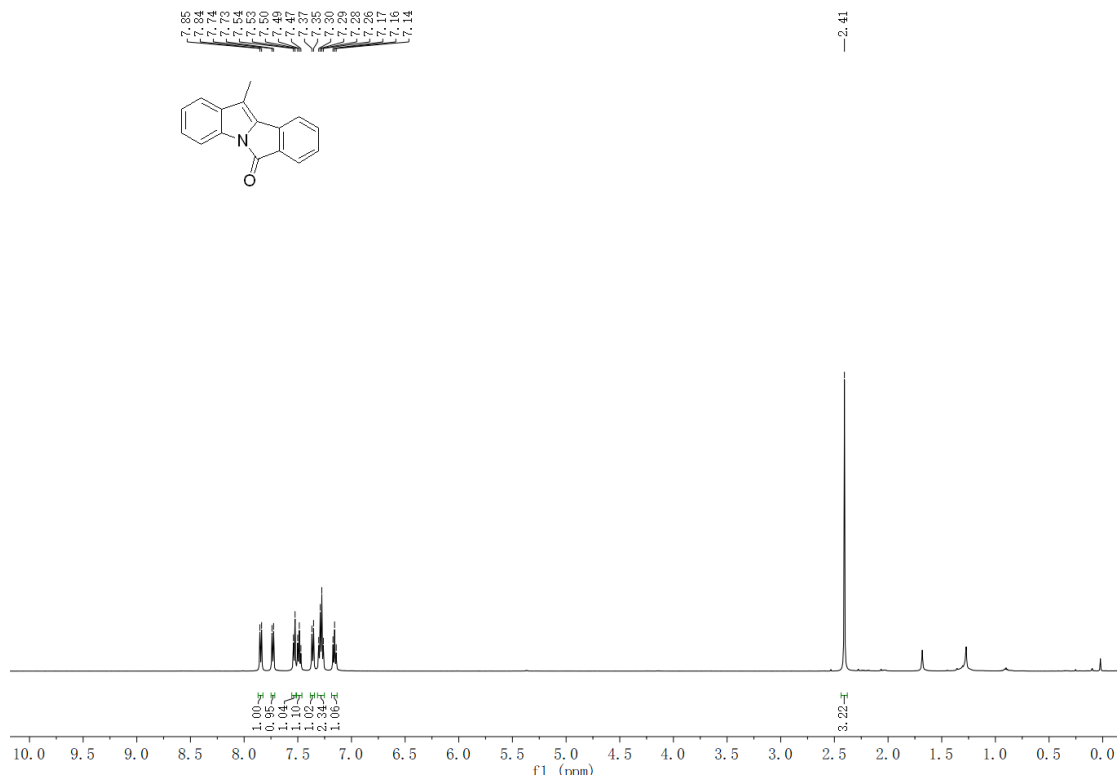
^1H NMR of **4** (d.r. = 7.7:1, 500 MHz, CDCl_3)



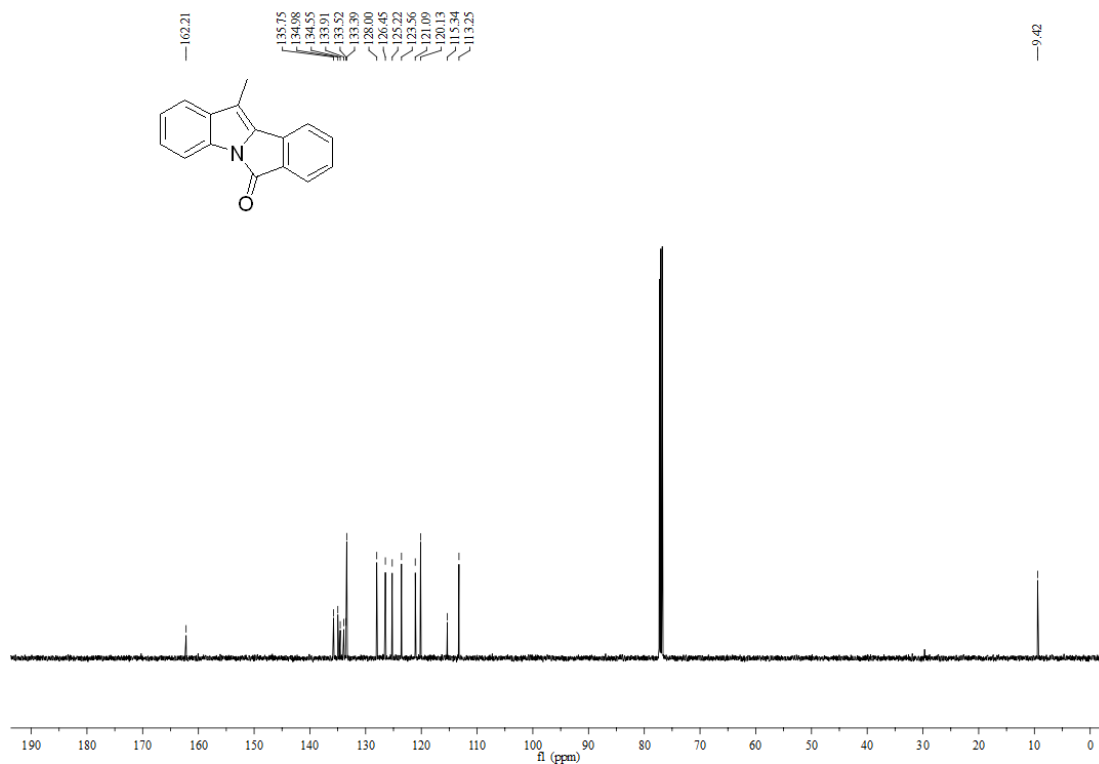
^{13}C NMR of **4** (d.r. = 7.7:1, 125 MHz, CDCl_3)



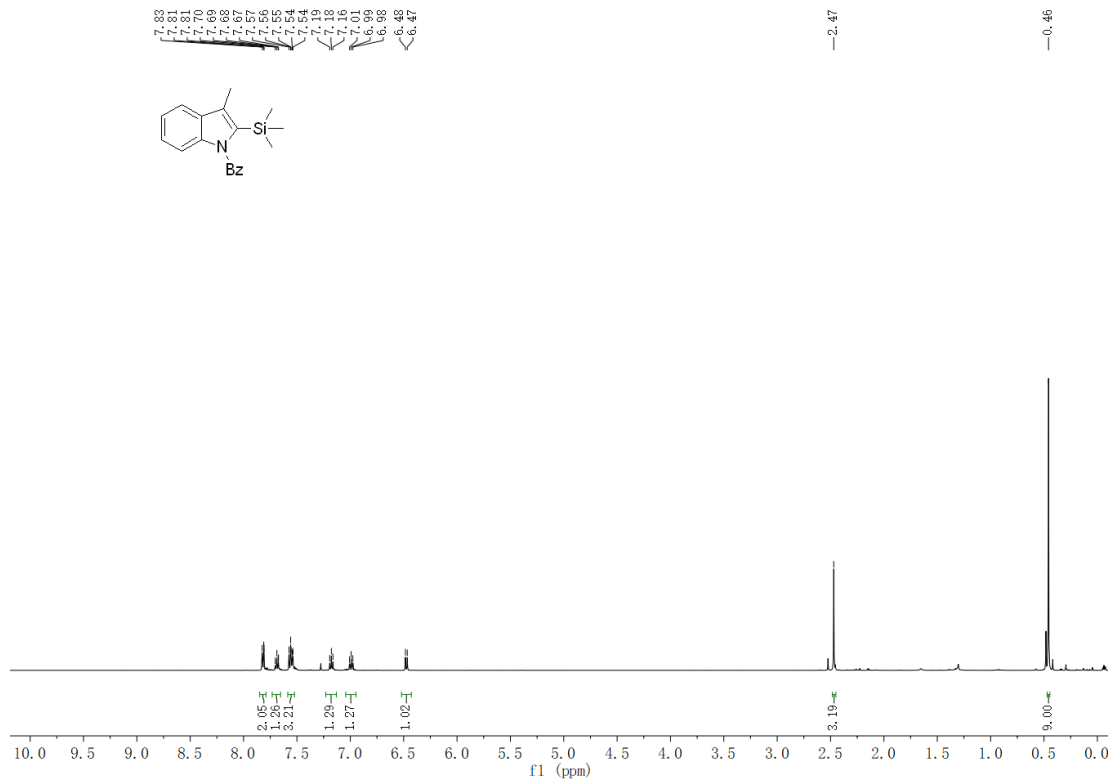
^1H NMR of **5** (500 MHz, CDCl_3)



^{13}C NMR of **5** (125 MHz, CDCl_3)



¹H NMR of **7** (500 MHz, CDCl₃)



¹³C NMR of **7** (125 MHz, CDCl₃)

