Supporting Information for

Rapid Assembly of cyclopentene spiroisoindolinones via Rhodium-Catalysed Redox–Neutral Cascade Reaction

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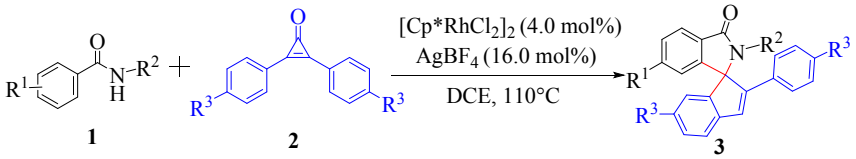
Table of Contents

1. General Methods.

Unless otherwise noted, all of the reagents were used directly without purification. Dichloroethane was distilled from calcium hydride. Melting points were measured on a microscopic apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) spectrometer in deuteraterated chloroform. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J) are reported in hertz (Hz). ^{13}C NMR spectra were recorded at 100 MHz on Bruker DPX-400. The chemical shifts are reported relative to residual $CHCl_3$ (δc = 77.00 ppm) and acetone (δc = 29.84 ppm). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD- Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). X-ray analysis was performed with a single-crystal X-ray diffractometer. Benzamide[1] and cyclopropenone [2,3,4] were prepared according to literatures.

2. General Procedure for the Synthesis of Compound 3.

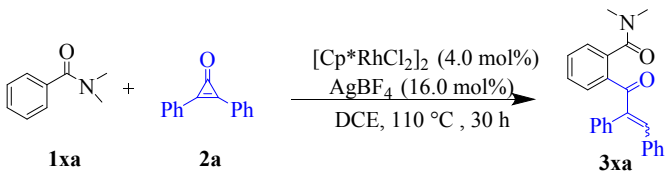


1 **2** **3**

Cyclopropenones (0.15 mmol) were dissolved in 1 mL of anhydrous DCE, the DCE solution of cyclopropenones was added in 10 equal portions over 7.5 h to a stirring solution of benzamides (0.1 mmol), $[Cp^*RhCl_2]_2$ (4 mol%) and $AgBF_4$ (16 mol%) in anhydrous DCE (1.5 mL) under air at 110°C. The resulting mixture was stirred for an additional 2.5 h-24.5 h. When the reaction was completed, the crude mixture was cooled to room temperature. The mixture was purified by column chromatography on silica gel (Elute: DCM/petroleum ether to EtOAc/petroleum ether).

3. Mechanistic Studies

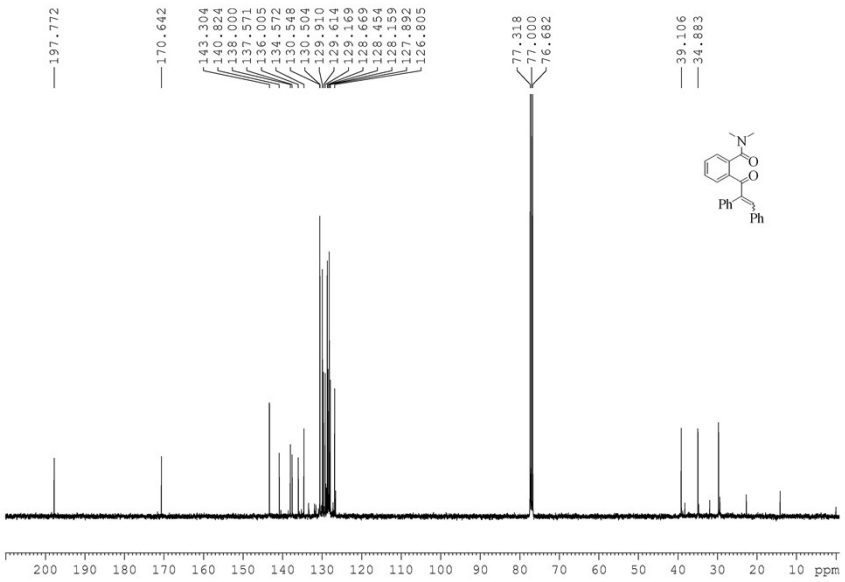
Controlled experiments



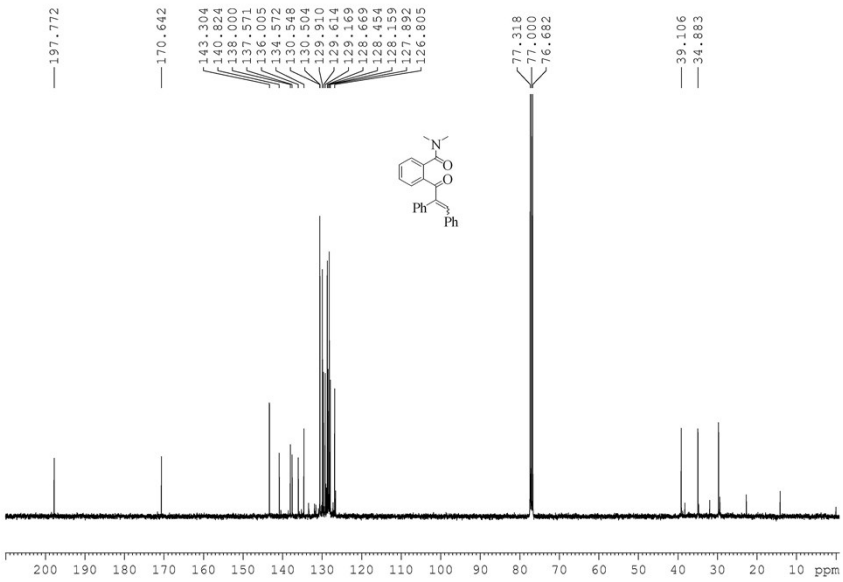
1xa **2a** **3xa**

Cyclopropenones (0.15 mmol) was dissolved in 1 mL of anhydrous DCE, the DCE solution of cyclopropenones was added in 10 equal portions over 7.5 h to a stirring solution of *N*,*N*-dimethylbenzamide (**1xa**) (0.1 mmol), $[Cp^*RhCl_2]_2$ (4 mol%) and $AgBF_4$ (16 mol%) in anhydrous DCE (1.5 mL) under air at

110°C. The resulting mixture was stirred for an additional 22.5 h. When the reaction was completed, the crude mixture was cooled to room temperature. The mixture was purified by column chromatography on silica gel (Elute: petroleum ether - EtOAc). (*Z*/*E*)-2-(2,3-Diphenylacryloyl)-*N*,*N*-dimethylbenzamide (**3xa** and **3xa'**) was obtained in 52% yield, no annulated product was found, which indicated that the N−H group played a key role in this transformation.

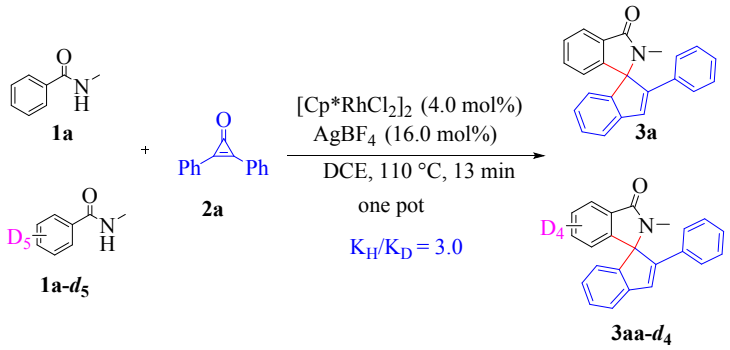


[1]H NMR spectrum of compound 3xa and **3xa'**

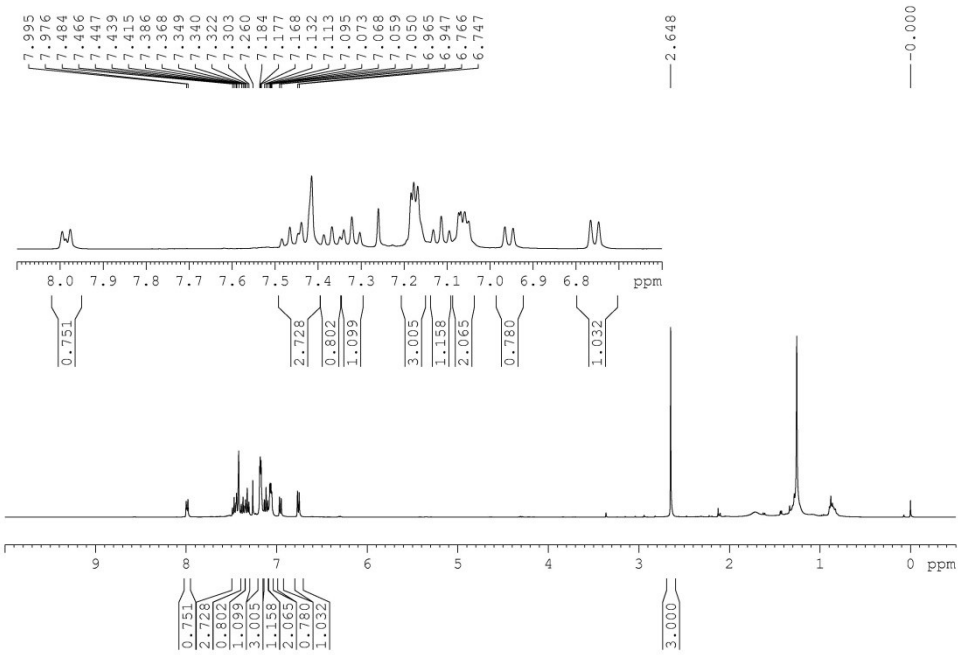


[13]C NMR spectrum of compound 3xa and **3xa'**

One-pot KIE experiment

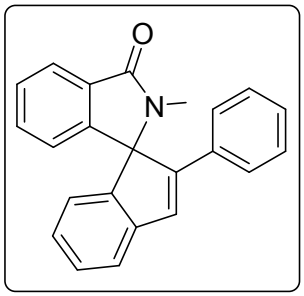


The *N*-(methyl)benzamide **1a** (0.1 mmol), *N*-(methyl)benzamide-d$_5$ **1a-*d*$_5$** (0.1 mmol), diphenylcyclopropenone **2a** (0.1 mmol), [Cp*RhCl$_2$]$_2$ (4 mol%), AgBF$_4$ (16 mol%), anhydrous DCE (2.5 mL) were mixed in a dry reaction tube. The mixture was stirred at 110 °C under air for 13 minutes. Then, the crude mixture was cooled to room temperature, purified by column chromatography on silica gel (Elute: petroleum ether - EtOAc). A KIE value of k_H/k_D = 3.0 was obtained on the basis of ^{1}H NMR analysis (Compared with the standard ^{1}H NMR spectrum of **3aa**, the integration of the peak at 7.99 ppm was 0.75 instead of 1.00).



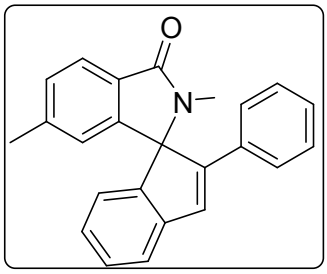
4. Characterization of the Products

2'-Methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3aa)



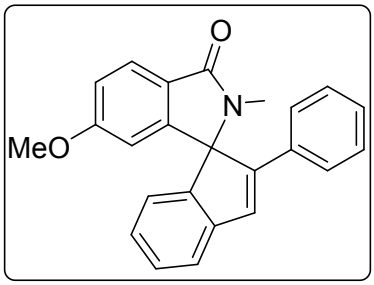
White solid (32 mg, 99% yield); m.p. 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.49-7.42 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.19-7.16 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.08-7.05(m, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 2.65(s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.99, 145.51, 145.07, 144.56, 142.32, 133.07, 132.44, 132.20, 131.27, 129.14, 128.73 (2C), 128.60, 128.27, 126.82, 125.49 (2C), 124.05, 122.11, 121.85, 121.31, 77.95, 25.14 ppm. HRMS (ESI) Calcd. for $C_{23}H_{17}NO$: $[M+H]^+$, 324.1383. Found: m/z 324.1391.

2',6'-Dimethyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ba)



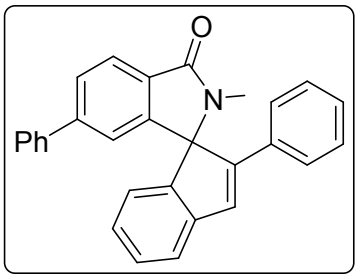
Pale yellow solid (31.4 mg, 93% yield); m.p. 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.34 (t, *J* = 3.7 Hz, 1H), 7.26 (t, *J* = 3.8 Hz, 1H), 7.19-7.18 (m, 3H), 7.13-7.07 (m, 3H), 6.76 (d, *J* = 3.7 Hz, 1H), 6.74 (s, 1H), 2.62 (s, 3H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.08, 145.71, 145.35, 144.88, 142.90, 142.28, 131.10, 133.02, 129.93, 129.67, 129.04, 128.71 (2C), 128.21, 126.76, 125.51 (2C), 123.79, 122.10, 121.79, 121.61, 77.79, 25.05, 21.76 ppm. HRMS (ESI) Calcd. for $C_{24}H_{19}NO$: $[M+H]^+$, 338.1539. Found: m/z 338.1545.

6'-Methoxy-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ca)



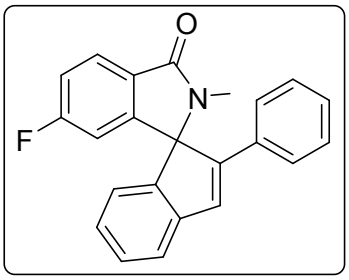
Pale yellow solid (29.6 mg, 84% yield); m.p. 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.43-7.40(m, 2H), 7.32 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 7.20-7.18 (m, 3H), 7.14-7.09 (m, 3H), 6.97 (dd, *J* = 8.4 Hz, 2.2 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H), 2.61 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.86, 163.21, 147.39, 145.77, 144.92, 142.26, 133.11, 131.10, 129.10, 128.76 (2C), 128.27, 126.83, 125.55(2C), 125.36, 125.15, 122.16, 121.83, 115.32, 105.87, 77.71, 55.50, 25.10 ppm. HRMS (ESI) Calcd. for $C_{24}H_{19}NO_2$: $[M+H]^+$, 354.1489. Found: m/z 354.1497.

2'-Methyl-2,6'-diphenylspiro[indene-1,1'-isoindolin]-3'-one (3da)



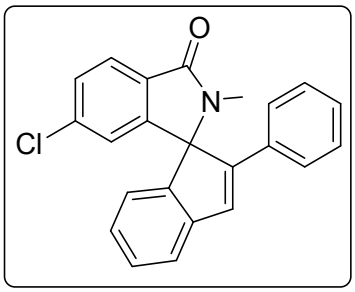
Pale yellow solid (38.0 mg, 95% yield); m.p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.44-7.42 (m, 4H), 7.33-7.24 (m, 5H), 7.18-7.17 (m, 3H), 7.13-7.09 (m, 4H), 6.80 (d, *J* = 7.4 Hz, 1H), 2.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.83, 145.84, 145.65, 145.40, 144.60, 142.34, 139.96, 133.12, 131.34 (2C), 129.17, 128.77 (2C), 128.72 (2C), 128.30, 127.97, 127.81, 127.32 (2C), 126.88, 125.56 (2C), 124.35, 122.20, 121.88, 119.80, 78.05, 25.18 ppm. HRMS (ESI) Calcd. for $C_{29}H_{21}NO$: $[M+H]^+$, 400.1696. Found: m/z 400.1702.

6'-Fluoro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ea)



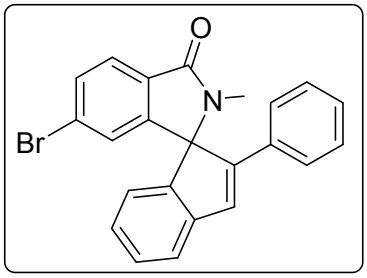
White solid (21.2 mg, 62% yield); m.p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (q, *J* = 4.9 Hz, 1H), 7.44-7.43 (m, 2H), 7.33 (td, *J* = 7.5 Hz, 0.8 Hz, 1H),7.20-7.18 (m, 3H), 7.16-7.08 (m, 4H), 6.77 (d, *J* = 7.4 Hz, 1H), 6.63 (dd, *J* = 7.9 Hz, 2.2 Hz, 1H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.86, 165.31 (d, *J* = 251.0 Hz), 147.72 (d, *J* = 9.7 Hz), 144.95, 143.94, 142.13, 132.76, 131.49, 129.35, 128.76 (2C), 128.37, 126.91, 125.95 (d, *J* = 9.6 Hz), 125.35 (2C), 121.99 (2C), 116.38 (d, *J* = 23.4 Hz), 108.71 (d, *J* = 24.2 Hz), 77.49 (d, *J* = 2.4 Hz), 25.18 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -106.14 (s) ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}FNO$: $[M+H]^+$, 342.1289. Found: m/z 342.1292.

6'-Chloro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3fa)



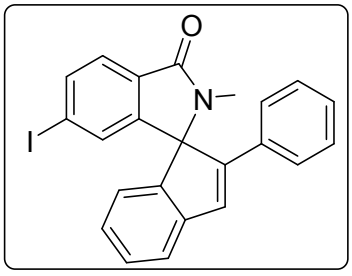
Pale yellow solid (26.8 mg, 75% yield); m.p. 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.44-7.41 (m, 3H), 7.36 (t, *J* = 3.7 Hz , 0.8 Hz, 1H), 7.21-7.19 (m, 3H), 7.14 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 7.09-7.07 (m, 2H), 6.93 (d, *J* = 1.5 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.90, 146.92, 144.97, 143.87, 142.22, 138.47, 132.81, 131.59, 130.90, 129.44, 129.27, 128.84 (2C), 128.46, 127.01, 125.43 (2C), 125.21, 122.10, 122.06, 121.73, 77.58, 25.21 ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}ClNO$: $[M+H]^+$, 358.0993. Found: m/z 358.0996.

6'-Bromo-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ga)



Yellow solid (32.6 mg, 81% yield); m.p. 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 8.1 Hz, 1.7 Hz, 1H), 7.45-7.42 (m, 2H), 7.34 (td, *J* = 7.5 Hz, 0.7 Hz, 1H), 7.21-7.20 (m, 3H), 7.14 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 7.09-7.06 (m, 3H), 6.76 (d, *J* = 7.4 Hz, 1H), 2.63 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.00, 147.08, 144,95 143.22, 132.80, 132.12, 131.12, 131.61, 131.37, 129.45, 128.86 (2C), 128.48, 127.03, 126.85, 125.44 (3C), 124.65, 122.12, 122.07, 77.55, 25.20 ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}BrNO$: $[M+H]^+$, 402.0488. Found: m/z 402.0487.

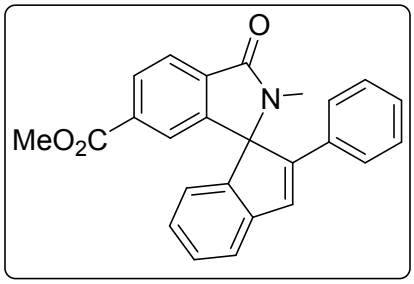
6'-Iodo-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ha)



Pale yellow solid (43.1 mg, 96% yield); m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45-7.42 (m, 2H), 7.35 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.30 (d, *J* = 1.0 Hz, 1H), 7.22-7.19 (m, 3H), 7.14 (td, *J* = 7.5 Hz, 1.00 Hz, 1H), 7.08-7.06 (m, 2H), 6.76 (d, *J* = 7.4 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.21, 147.00, 144.97, 143.85, 142.23, 137.96, 132.82, 131.98, 131.60, 130.45, 129.45, 128.87 (2C), 128.47, 127.04, 125.49, 125.45 (3C), 1224.15, 122.07,

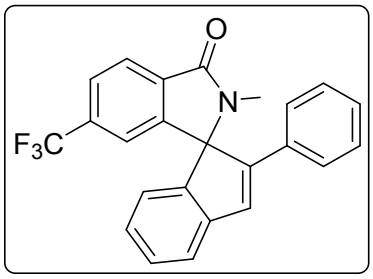
99.12, 77.42, 25.13 ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}INO$: $[M+H]^+$, 450.0349. Found: m/z 450.0348.

Methyl 2'-methyl-3'-oxo-2-phenylspiro[indene-1,1'-isoindoline]-6'-carboxylate (3ia)



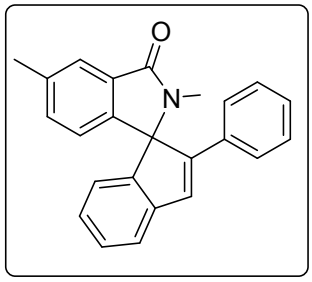
Pale yellow solid (34.7 mg, 91% yield); m.p. 159-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H), δ 8.04 (dd, *J* = 8.0 Hz, 0.5 Hz, 1H), 7.61 (d, *J* = 0.6 Hz, 1H), 7.46-7.45 (m, 2H), 7.34 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.19-7.16 (m, 3H), 7.12 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.06-7.04 (m, 2H), 6.74 (d, *J* = 7.2 Hz, 1H), 3.82(s, 3H), 2.62 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.90, 166.08, 145.36, 144.86, 143.77, 142.40, 136.31, 133.71, 132.91, 131.83, 130.17, 129.43, 128.81 (2C), 128.42, 127.00, 125.44 (2C), 124.06, 122.77, 122.12, 122.06, 77.98, 52.34, 25.33 ppm. HRMS (ESI) Calcd. for Chemical Formula: $C_{25}H_{19}NO_3$: $[M+H]^+$, 382.1438. Found: m/z 382.1442.

2'-Methyl-2-phenyl-6'-(trifluoromethyl)spiro[indene-1,1'-isoindolin]-3'-one (3ja)



Pale yellow solid (28.2 mg, 72% yield); m.p. 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.21-7.19 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06-7.04 (m, 2H), 6.71 (d, *J* = 7.4 Hz,1H), 2.68 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 167.46, 145.85, 144.68, 143.39, 142.26, 135.57, 134.03 (q, *J* = 32.3 Hz), 132.70, 131.96, 129.56, 128.85 (2C), 128.48, 127.10, 126.12 (d, *J* = 271.5 Hz), 125.99 (t, *J* = 3.6 Hz), 125.34 (2C), 124.59, 122.17, 122.05, 118.53 (q, *J* = 3.8 Hz), 77.91, 25.28 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.30 (s) ppm. HRMS (ESI) Calcd. for $C_{24}H_{16}F_3NO$: $[M+H]^+$, 392.1257. Found: m/z 392.1257.

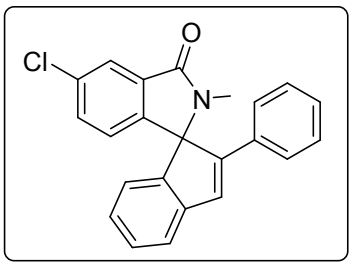
2',5'-Dimethyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ka)



Pale yellow solid (17.9 mg, 53% yield); m.p. 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.42-7.39 (m, 2H), 7.31 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 7.21-71.2 (m, 4H), 7.11-7.06 (m, 3H) 6.83(d, *J* = 7.8 Hz,

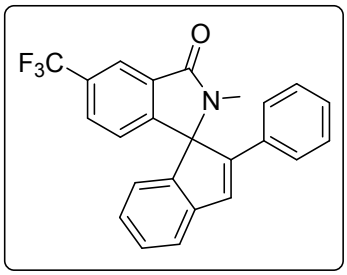
1H), 6.74(d, J = 7.4 Hz, 1H), 2.63 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.08, 145.60, 144.75, 142.25, 142.15, 138.64, 133.17, 133.14, 132.55, 131.06, 128.99, 128.65 (2C), 128.17, 126.72, 125.47 (2C), 124.26, 122.00, 121.75, 120.96, 77.32, 25.07, 21.34 ppm. HRMS (ESI) Calcd. for $C_{24}H_{19}NO$: $[M+H]^+$, 338.1539. Found: m/z 338.1539.

5'-Chloro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3la)



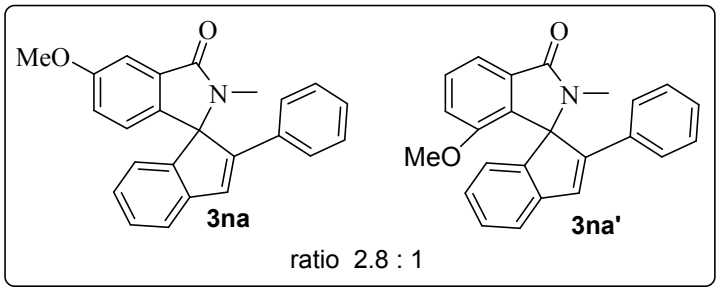
Pale yellow solid (30.1 mg, 84% yield); m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 1.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.21-7.19 (m, 3H), 7.13 (td, J = 7.4 Hz, 0.6 Hz, 1H), 7.08-7.05 (m, 2H), 6.89(d, J = 8.1 Hz, 1H), 6.76 (d, J = 7.4 Hz, 1H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.56, 145.02, 143.93, 143.38, 142.24, 134.80, 134.17, 132.83, 132.38, 131.55, 129.37, 128.83 (2C), 128.45, 126.97, 125.42 (2C), 124.19, 122.66, 122.05, 122.00, 77.67, 25.28 ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}ClNO$: $[M+H]^+$, 358.0993. Found: m/z 358.0998.

2'-Methyl-2-phenyl-5'-(trifluoromethyl)spiro[indene-1,1'-isoindolin]-3'-one (3ma)



Pale yellow solid (29.4 mg, 75% yield); m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.61 (d, J =8.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.35 (td, J = 7.5 Hz, 0.6 Hz, 1H), 7.21-7.19 (m, 3H), 7.13 (td, J = 7.5 Hz, 0.6 Hz, 1H), 7.08-7.06 (m, 3H), 6.74 (d, J = 7.4 Hz, 1H), 2.68 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.45, 148.87, 144.62, 143.47, 142.23, 133.07, 132.69, 131.86, 131.24 (d, J = 32.8 Hz), 129.53, 129.05 (q, J = 3.6 Hz), 128.86 (2C), 128.50, 127.04, 125.30 (2C), 123.65 (d, J = 271.0 Hz), 122.12, 122.01 (2C), 121.29 (q, J = 3.7 Hz), 77.89, 25.25 ppm.^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.20 (s) ppm. HRMS (ESI) Calcd. for $C_{24}H_{16}F_3NO$: $[M+H]^+$, 392.1257. Found: m/z 392.1258.

5'-Methoxy-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3na) and 7'-Methoxy-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3na')



The products were obtained as pale yellow solid in 70% yield in a 2.8:1 ratio. ^{1}H NMR (400 MHz, CDCl3): δ for **3na**: 7.47 (d, J = 2.3 Hz, 1H), 6.92 (dd, J = 8.4 Hz, 2.4Hz, 1H), 6.83(d, J = 8.3 Hz, 1H), 6.76-6.74(m, 1H), 3.86 (s, 3H), 2.63 (s, 3H).

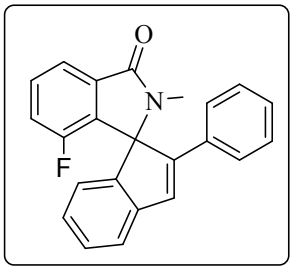
For **3na'**: 7.59 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.76-6.74(m, 1H), 3.34 (s, 3H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, CDCl3): δ for **3na**:168.86, 160.28, 145.47, 144.59, 142.20, 136.71, 133.78, 133.12, 131.05, 129.00, 128.65, 128.18, 126.71, 125.45, 122.20, 121.96, 121.75, 120.33, 106.89, 77.52, 55.58, 25.18 ppm.

For **3na'**: 168.68, 154.20, 144.00, 143.27, 143.07, 134.60, 132.27, 131.51, 130.24, 128.78, 128.56, 127.91, 126.31, 121.64, 121.40, 115.75, 114.37, 76.32, 55.58, 24.42 ppm.

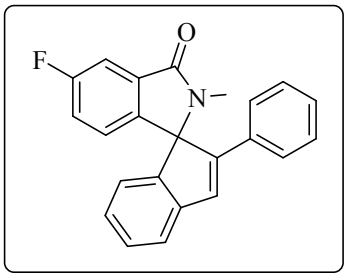
HRMS (ESI) Calcd. for $C_{24}H_{19}NO_2$: $[M+H]^+$, 354.1489. Found: m/z 354.1490.

7'-Fluoro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3oa)



White solid (21.2 mg, 62% yield); m.p. 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.4 Hz, 1H), 7.49-7.42 (m, 3H), 7.35 (td, *J* = 7.5 Hz, 1.00 Hz, 1H), 7.20-7.19 (m, 3H), 7.16-7.10 (m, 3H), 7.05-7.01 (m, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.70 (d, *J* = 2.2 Hz), 1.56.00 (d, *J* = 253.0 Hz), 143.50, 142.75, 142.36, 135.64 (d, *J* = 3.2 Hz), 133.26, 131.98, 131.14 (d, *J* = 14.7 Hz), 130.82 (d, *J* = 6.5 Hz), 129.46, 128.80 (2C), 128.32, 126.85, 125.44 (2C), 122.02, 121.93, 119.80 (d, *J* = 3.8 Hz), 119.16 (d, *J* = 19.2 Hz), 75.67 (d, *J* = 1.9 Hz), 24.73 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -120.18 (s) ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}FNO$: $[M+H]^+$, 342.1289. Found: m/z 342.1291.

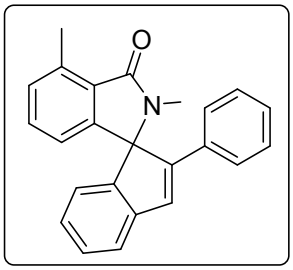
5'-Fluoro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3oa')



White solid (8.2 mg, 24% yield); m.p. 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (q, *J* = 2.3 Hz, 1H),

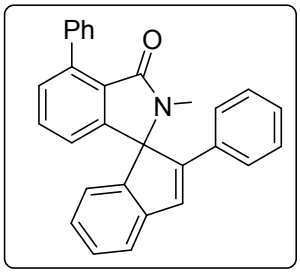
7.44-7.41 (m, 2H), 7.33 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 7.21-7.18 (m, 3H), 7.13 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.09-7.04 (m, 3H), 6.92 (q, *J* = 4.4 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.78, 163.07 (d, *J* = 246.5 Hz), 145.12, 144.10, 142.22, 140.38 (d, *J* = 2.5 Hz), 134.49 (d, *J* = 8.8 Hz), 131.45, 129.31, 128.80 (2C), 128.43 (2C), 126.94, 125.44 (2C), 122.99 (d, *J* = 8.4 Hz), 122.04, 121.97, 119.75 (d, *J* = 23.7 Hz), 110.87 (d, *J* = 23.6 Hz), 77.61, 25.34 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.15 (s) ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}FNO$: $[M+H]^+$, 342.1289. Found: m/z 342.1290.

2',4'-Dimethyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3pa)



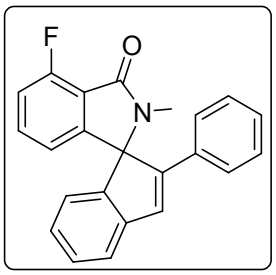
Pale yellow solid (10.1 mg, 30% yield); m.p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* =7.4 Hz, 1H), 7.38 (S, 1H), 7.30 (td, *J* =7.5 Hz, 0.96 Hz, 1H), 7.23-7.17 (m, 5H), 7.12-7.07 (m, 3H), 6.78-6.74 (m, 2H), 2.85 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.83, 145.99, 145.44, 145.14, 142.30, 137.89, 133.28, 131.59, 131.09, 130.66, 129.42, 128.99, 128.71 (2C), 128.19, 126.74, 125.57 (2C), 122.09, 121.78, 118.72, 77.38, 24.95, 17.33 ppm. HRMS (ESI) Calcd. for $C_{24}H_{19}NO$: $[M+H]^+$, 338.1539. Found: m/z 338.1545.

2'-Methyl-2,4'-diphenylspiro[indene-1,1'-isoindolin]-3'-one (3qa)



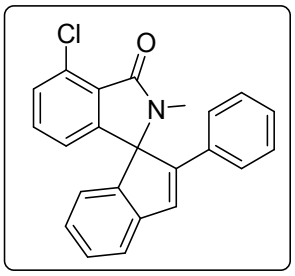
White solid (23.9 mg, 60% yield); m.p. 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.44-7.31 (m, 6H), 7.23-7.12 (m, 6H), 6.93 (q, *J* = 2.7 Hz, 1H), 6.83 (d, *J* = 7.4 Hz,1H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.25, 146.19, 145.86, 144.84, 142.37, 141.21, 137.22, 133.20, 131.75, 131.27, 130.69, 129.87 (2C), 129.09, 128.73 (2C), 128.28, 128.05, 127.85, 127.65 (2C), 126.82, 125.55 (2C), 122.11, 121.87, 120.26, 77.32, 25.11 ppm. HRMS (ESI) Calcd. for $C_{29}H_{21}NO$: $[M+H]^+$, 400.1696. Found: m/z 400.1694.

4'-Fluoro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3ra)



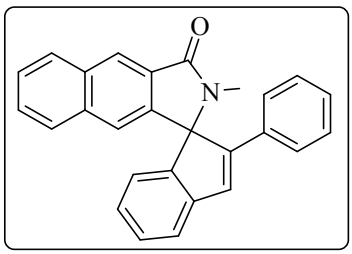
Pale yellow solid (30.7 mg, 90% yield); m.p. 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.35-7.29 (m, 2H), 7.22-7.19 (m, 3H), 7.15-7.06 (m, 4H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.78 (d, *J* = 2.1 Hz), 158.76 (d, *J* = 259.6 Hz), 147.86 (d, *J* = 2.6 Hz), 145.22, 144.19, 142.19, 134.05 (d, *J* = 7.5 Hz), 132.89, 131.49, 129.34, 128.82 (2C), 128.41, 126.96, 125.45 (2C), 122.05, 121.99, 119.58 (d, *J* = 13.6 Hz), 117.35 (d, *J* = 4.0 Hz), 116.01 (d, *J* = 19.5 Hz), 77.68, 25.09 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -117.31 (s) ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}FNO$: $[M+H]^+$, 342.1289. Found: m/z 342.1290.

4'-Chloro-2'-methyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3sa)



White solid (33.6 mg, 94% yield); m.p. 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.42 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24(d, *J* = 7.8 Hz, 1H), 7.21-7.18 (m, 3H), 7.13-7.10 (m, 3H), 6.83(d, *J* = 7.6 Hz,1H), 6.77(d, *J* =7.4 Hz,1H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.43, 147.62, 145.10, 144.15, 142.13, 132.80 (2C), 131.53, 131.44, 130.25 (2C), 129.27, 128.77 (2C), 128.34, 128.19, 126,89, 125.37 (2C), 121.96, 119.82, 76.85, 25.11 ppm. HRMS (ESI) Calcd. for $C_{23}H_{16}ClNO$: $[M+H]^+$, 358.0993. Found: m/z 358.0996.

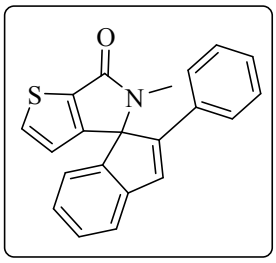
2-Methyl-2'-phenylspiro[benzo[f]isoindole-1,1'-inden]-3(2H)-one (3ta)



Pale yellow solid (14.6 mg, 39% yield); m.p. 247-249 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.50-7.43 (m, 4H), 7.41 (s, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.13-7.06 (m, 6H), 6.77 (d, *J* = 7.44 Hz, 1H), 2.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.66, 146.05, 145.49, 142.17, 139.91, 135.40, 133.18, 132.93, 131.05, 130.06, 129.52, 129.09, 128.69 (2C), 128.19 (2C), 127.59, 126.82, 126.38, 125.52 (2C), 124.38, 122.16, 121.84, 120.20, 77.74, 25.63ppm. HRMS (ESI) Calcd.

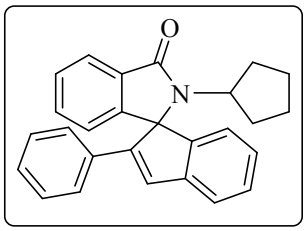
for $C_{27}H_{19}NO$: $[M+H]^+$, 374.1539. Found: m/z 374.1543.

5'-Methyl-2-phenylspiro[indene-1,4'-thieno[2,3-c]pyrrol]-6'(5'H)-one (3ua)



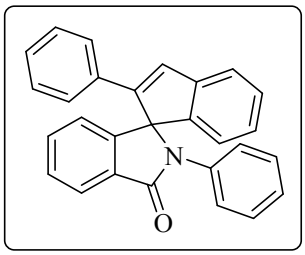
Pale yellow solid (3.0 mg, 9% yield); m.p. 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 4.8 Hz, 1H), 7.41(d, *J* = 7.4 Hz, 1H), 7.36 (s, 1H), 7.32 (td, *J* = 7.5 Hz, 0.88 Hz, 1H), 7.23-7.20 (m, 3H,) 7.16-7.12 (m, 3H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 4.8 Hz, 1H), 2.59 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.71, 154.58, 144.38, 142.74, 142.15, 135.63, 135.22, 133.09, 131.10, 129.23, 128.73 (2C), 128.30, 126.78, 125.37 (2C), 122.02, 121.83, 119.61, 76.46, 25.51 ppm. HRMS (ESI) Calcd. for $C_{21}H_{15}NOS$: $[M+H]^+$, 330.0947. Found: m/z 330.0948.

2'-Cyclopentyl-2-phenylspiro[indene-1,1'-isoindolin]-3'-one (3va)



White solid (26.0 mg, 69% yield); m.p. 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.47-7.41 (m, 3H), 7.36-7.30 (m, 2H), 7.17-7.15 (m, 3H), 7.11 (dd, *J* = 7.5 Hz, 1.04 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.07-7.06 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 3.17-3.08 (m, 1H), 2.19-2.10 (m, 1H), 1.99-1.89 (m, 1H), 1.75-1.68 (m, 2H), 1.46-1.38 (m, 1H), 1.33-1.17(m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.73, 146.62, 145.62, 145.03, 142.21, 133.63, 133.21, 132.07, 130.78, 128.96, 128.53 (2C), 128.52, 128.17, 126.62, 125.75 (2C), 123.68, 122.44, 121.79, 121.11, 78.97, 55.11, 29.24, 28.69, 24.59, 24.53 ppm. HRMS (ESI) Calcd. for $C_{27}H_{23}NO$: $[M+H]^+$, 378.1852. Found: m/z 378.1858.

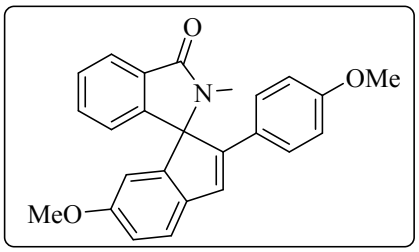
2,2'-Diphenylspiro[indene-1,1'-isoindolin]-3'-one (3wa)



Pale yellow solid (3.9 mg, 10% yield); m.p. 159-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.5 Hz, 1H), 7.35 (td, *J* =7.5 Hz, 0.8 Hz, 1H), 7.42 (td, *J* = 7.6 Hz, 1.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 (s, 1H), 7.28 (td, *J* = 7.4 Hz, 0.92 Hz, 1H), 7.17-7.04 (m, 9H), 7.01-6.99 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.85, 146.47, 145.60, 145.48, 141.79, 136.51, 133.25, 132.97, 131.91, 130.90, 128.98, 128.73, 128.65

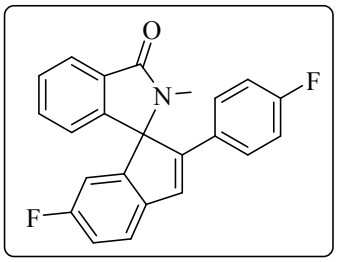
(2C), 128.54 (2C), 128.22, 126.82, 126.42, 125.77 (2C), 124.99 (2C), 124.78, 122.38, 122.04, 121.18, 79.30 ppm. HRMS (ESI) Calcd. for $C_{28}H_{19}NO$: $[M+H]^+$, 386.1539. Found: m/z 386.1541.

6-Methoxy-2-(4-methoxyphenyl)-2'-methylspiro[indene-1,1'-isoindolin]-3'-one(3ab)



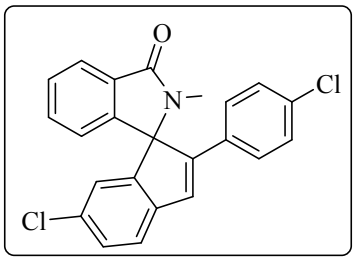
White solid (16.1 mg, 42% yield); m.p. 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ.7.98 (d, *J* =7.5Hz, 1H), 7.46 (td, *J* = 7.4 Hz, 1.0 Hz, 1H), 7.37 (td, *J* =7.5 Hz, 1.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.24 (s, 1H), 6.97 (m, 3H), 6.83(dd, *J*= 8.2 Hz, 2.4 Hz, 1H), 6.69(d, *J* = 9.0 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 1H), 3.71 (s, 3H),3.68 (s, 3H), 2.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.99, 159.21, 159.04, 146.33, 145.57, 143.01, 135.38, 132.32, 132.22, 129.05, 128.55, 126.00, 126.47 (2C), 123.98, 122.05, 121.42, 114.21, 114.11 (2C), 108.59, 77.89, 55.53, 55.16, 25.17 ppm. HRMS (ESI) Calcd. for $C_{25}H_{21}NO_3$: $[M+H]^+$, 384.1594. Found: m/z 384.1598.

6-Fluoro-2-(4-fluorophenyl)-2'-methylspiro[indene-1,1'-isoindolin]-3'-one (3ac)



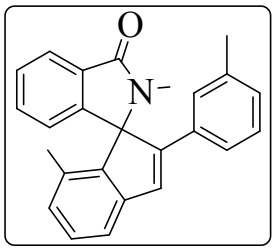
White solid (30.5 mg, 85% yield); m.p. 172-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.7 Hz, 1H), 7.50 (td, *J* = 7.4 Hz, 0.8 Hz, 1H), 7.43-7.35 (m, 2H), 7.30 (s, 1H), 7.05-7.00 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.89-6.84 (m, 2H), 6.49 (dd, *J* = 7.9 Hz, 2.32 Hz, 1H), 266 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.73, 163.58 (d, *J* = 22.81 Hz), 161.11 (d, *J* = 21.50 Hz), 146.80 (d, *J* = 8.7 Hz), 144.54 (d, *J* = 4.4 Hz), 144.26, 137.97 (d, *J* = 2.7 Hz), 132.42, 132.21,130.06, 129.07 (d, *J* = 3.5 Hz), 128.98, 127.13 (d, *J* = 8.0 Hz), 124.23, 122.68 (d, *J* = 8.4 Hz), 121.24, 115.98 (d, *J* = 22.8 Hz), 115.80 (d, *J* = 21.3 Hz), 110.34 (d, *J* = 24.1 Hz), 77.72 (d, *J* = 2.0 Hz), 25.12 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.31 (s), -113.80 (s) ppm. HRMS (ESI) Calcd. for $C_{23}H_{15}F_2NO$: $[M+H]^+$, 360.1194. Found: m/z 360.1194.

6-Chloro-2-(4-chlorophenyl)-2'-methylspiro[indene-1,1'-isoindolin]-3'-one (3ad)



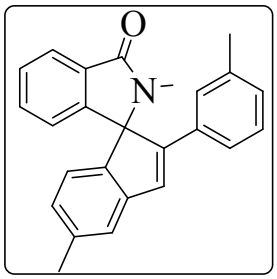
White solid (17.7 mg, 45% yield); m.p. 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.51 (td, *J* = 7.5 Hz, *J* = 0.8 Hz, 1H), 7.41 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.30 (dd, *J* = 8.0 Hz, *J* = 1.9 Hz, 1H), 7.17-7.13 (m, 2H), 6.99-6.95 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 1.8 Hz, 1H), 265 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.68, 146.38, 144.83, 143.96, 140.42, 134.37, 133.06, 132.50, 132.18, 131.10, 130.62, 129.47, 129.08, 129.04 (2C), 126.67 (2C), 124.34, 122.80, 122.74, 121.24, 77.62, 25.17 ppm. HRMS (ESI) Calcd. for $C_{23}H_{15}Cl_2NO$: $[M+H]^+$, 392.0603. Found: m/z 392.0605.

2',7-dimethyl-2-(m-tolyl)spiro[indene-1,1'-isoindolin]-3'-one (3ae)



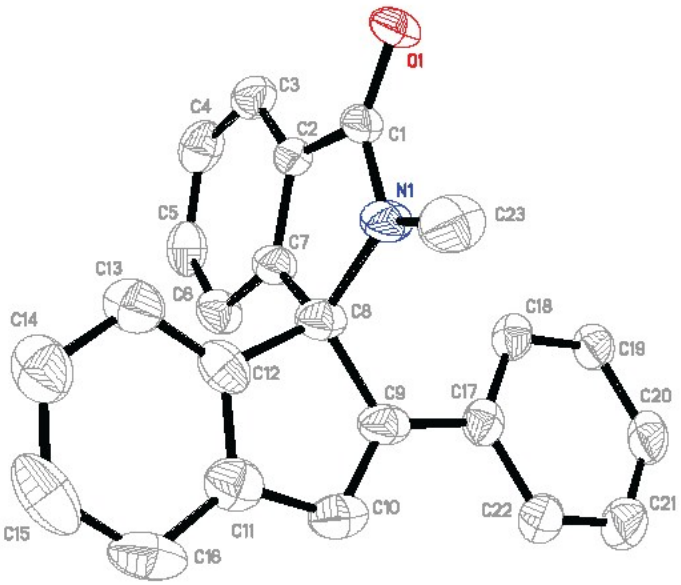
White solid (6.3 mg, 18% yield); m.p. 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.54 (td, *J* = 7.2 Hz, 0.7 Hz, 1H), 7.50-7.46 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.07-7.00 (m, 4H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 2.61 (s, 3H), 2.17 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.84, 147.12, 144.38, 144.20, 141.94, 138.79, 135.07, 134.58, 134.50, 133.08, 132.54, 130.30, 129.96, 129.70, 129.60, 129.29, 127.50, 123.97, 123.44, 122.37, 120.76, 79.37, 25.11, 21.40, 16.17 ppm. HRMS (ESI) Calcd. for $C_{25}H_{21}NO$: $[M+H]^+$, 352.1696. Found: m/z 352.1698.

2',5-dimethyl-2-(m-tolyl)spiro[indene-1,1'-isoindolin]-3'-one (3ae')



White solid (15.7 mg, 45% yield); m.p. 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 7.51 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 7.42 (d, *J* = 7.56 Hz, 1.2Hz, 1H), 7.34 (s, 1H), 7.07-6.93 (m, 5H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 2.56 (s, 3H), 2.36 (s, 3H), 2.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.66, 146.80, 146.55, 143.77, 142.82, 139.87, 138.83, 134.47, 133.63, 132.97, 132.35, 129.74, 129.44, 129.36, 128.23, 127.24, 124.27, 123.67, 123.25, 122.44, 122.23, 78.38, 25.06, 21.47, 21.41 ppm. HRMS (ESI) Calcd. for C25H21NO: [M+H]+, 352.1696. Found: m/z 352.1699.

5. X-Ray Crystallographic Data of 3aa



Single-crystal X-ray Structure of 3aa

The structure of **3aa** was determined by the X-ray diffraction. Recrystallized from CH_2Cl_2/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1543207.

Table S1 Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{23}H_{17}NO$
Formula weight	323.38
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.92466(18)
b/Å	11.5149(3)
c/Å	19.0209(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1735.69(9)
Z	4

ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.589
F(000)	680.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.978 to 134.116
Index ranges	-3 ≤ h ≤ 9, -13 ≤ k ≤ 13, -22 ≤ l ≤ 18
Reflections collected	6178
Independent reflections	3109 [R_{int} = 0.0229, R_{sigma} = 0.0295]
Data/restraints/parameters	3109/26/222
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0710, wR_2 = 0.1928
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.2066
Largest diff. peak/hole / e Å^{-3}	0.43/-0.18
Flack parameter	-0.3(4)

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C_1	-1436(6)	4918(4)	6643(3)	71.4(12)
C_2	-30(6)	4294(4)	6317(2)	66.6(11)
C_3	-39(9)	3314(5)	5903(3)	90.2(17)
C_4	1469(12)	2919(5)	5653(4)	101.8(19)
C_5	2950(10)	3497(6)	5803(3)	94.1(18)
C_6	2976(7)	4460(5)	6239(3)	85.9(15)
C_7	1442(6)	4847(4)	6489(3)	73.5(12)
C_8	1107(6)	5834(5)	7008(3)	78.1(14)
C_9	1976(6)	6951(5)	6861(3)	84.4(15)
C_{10}	3074(8)	7244(6)	7334(4)	99.1(16)
C_{11}	3001(9)	6381(6)	7908(4)	97.9(16)
C_{12}	1846(7)	5579(6)	7746(3)	84.4(15)
C_{13}	1457(9)	4702(7)	8185(3)	103.8(19)
C_{14}	2291(10)	4616(9)	8814(4)	119(3)
C_{15}	3459(12)	5388(11)	9001(4)	135(4)
C_{16}	3890(9)	6308(8)	8533(5)	123(3)
C_{17}	1671(13)	7617(6)	6161(3)	74(2)
C_{18}	779(8)	7190(4)	5587(4)	75(2)
C_{19}	589(8)	7868(7)	4988(3)	91(3)
C_{20}	1292(10)	8973(7)	4962(4)	112(4)
C_{21}	2184(13)	9400(5)	5535(5)	128(4)

C_{22}	2374(14)	8722(7)	6135(4)	107(3)
C_{17A}	1850(40)	7910(30)	6244(9)	74(2)
C_{18A}	820(30)	7133(17)	5890(11)	75(2)
C_{19A}	330(30)	7360(20)	5202(10)	91(3)
C_{20A}	870(30)	8370(30)	4868(10)	112(4)
C_{21A}	1910(50)	9150(30)	5223(19)	128(4)
C_{22A}	2400(50)	8920(30)	5911(18)	107(3)
C_{23}	-1744(9)	6601(6)	7442(5)	124(3)
N_1	-764(5)	5849(4)	6989(3)	83.5(14)
O_1	-2947(4)	4679(4)	6638(2)	99.9(14)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C_1	52(2)	78(3)	84(3)	23(2)	-7(2)	-11(2)
C_2	64(2)	63(2)	73(3)	11(2)	-12(2)	-7(2)
C_3	109(4)	76(3)	85(3)	5(3)	-24(3)	-20(3)
C_4	137(6)	74(3)	94(4)	-9(3)	1(4)	10(4)
C_5	105(4)	90(4)	87(4)	2(3)	10(3)	35(4)
C_6	61(3)	93(4)	103(4)	-11(3)	4(3)	12(3)
C_7	59(2)	71(3)	91(3)	-9(2)	-3(2)	0(2)
C_8	58(3)	82(3)	94(4)	-11(3)	5(2)	-8(2)
C_9	55(2)	81(3)	117(4)	-27(3)	6(3)	-5(2)
C_{10}	86(4)	92(3)	119(4)	-15(3)	6(3)	-23(3)
C_{11}	92(4)	106(4)	96(4)	-19(2)	2(3)	-1(3)
C_{12}	68(3)	116(4)	70(3)	-6(3)	0(2)	12(3)
C_{13}	88(4)	127(5)	96(4)	1(4)	-3(3)	-13(4)
C_{14}	111(5)	157(7)	90(4)	29(5)	1(4)	-3(5)
C_{15}	111(5)	227(11)	69(3)	-21(5)	-18(4)	47(7)
C_{16}	91(5)	143(6)	136(6)	-63(6)	-5(4)	-24(4)
C_{17}	65(4)	72(5)	86(4)	5(4)	17(3)	12(4)
C_{18}	75(3)	76(3)	75(7)	22(4)	17(4)	3(3)
C_{19}	75(4)	96(7)	102(5)	43(5)	5(4)	-2(4)
C_{20}	76(5)	105(8)	154(8)	70(7)	15(5)	5(5)
C_{21}	99(6)	93(6)	193(12)	48(8)	2(8)	-9(5)
C_{22}	89(4)	79(6)	154(9)	15(6)	-8(6)	2(4)
C_{17A}	65(4)	72(5)	86(4)	5(4)	17(3)	12(4)
C_{18A}	75(3)	76(3)	75(7)	22(4)	17(4)	3(3)
C_{19A}	75(4)	96(7)	102(5)	43(5)	5(4)	-2(4)
C_{20A}	76(5)	105(8)	154(8)	70(7)	15(5)	5(5)
C_{21A}	99(6)	93(6)	193(12)	48(8)	2(8)	-9(5)

C_{22A}	89(4)	79(6)	154(9)	15(6)	-8(6)	2(4)
C_{23}	79(4)	104(4)	190(8)	-28(5)	47(5)	5(3)
N_1	48.6(18)	81(3)	121(4)	-10(3)	13(2)	-4.6(18)
O_1	49.5(17)	115(3)	135(3)	31(3)	-17.6(19)	-18.4(19)

Table S4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C_1	C_2	1.464(7)	C_{11}	C_{16}	1.385(11)
C_1	N_1	1.366(7)	C_{12}	C_{13}	1.345(9)
C_1	O_1	1.229(6)	C_{13}	C_{14}	1.371(10)
C_2	C_3	1.376(8)	C_{14}	C_{15}	1.331(12)
C_2	C_7	1.368(7)	C_{15}	C_{16}	1.425(14)
C_3	C_4	1.365(10)	C_{17}	C_{18}	1.3900
C_4	C_5	1.379(11)	C_{17}	C_{22}	1.3900
C_5	C_6	1.385(9)	C_{18}	C_{19}	1.3900
C_6	C_7	1.379(7)	C_{19}	C_{20}	1.3900
C_7	C_8	1.529(7)	C_{20}	C_{21}	1.3900
C_8	C_9	1.486(8)	C_{21}	C_{22}	1.3900
C_8	C_{12}	1.549(8)	C_{17A}	C_{18A}	1.3900
C_8	N_1	1.483(6)	C_{17A}	C_{22A}	1.3900
C_9	C_{10}	1.296(9)	C_{18A}	C_{19A}	1.3900
C_9	C_{17}	1.555(8)	C_{19A}	C_{20A}	1.3900
C_9	C_{17A}	1.62(2)	C_{20A}	C_{21A}	1.3900
C_{10}	C_{11}	1.477(10)	C_{21A}	C_{22A}	1.3900
C_{11}	C_{12}	1.336(9)	C_{23}	N_1	1.447(8)

Table S5 Bond Angles for 3aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N_1	C_1	C_2	107.0(4)	C_{16}	C_{11}	C_{10}	131.0(7)
O_1	C_1	C_2	128.9(5)	C_{11}	C_{12}	C_8	109.6(6)
O_1	C_1	N_1	124.1(5)	C_{11}	C_{12}	C_{13}	122.2(6)
C_3	C_2	C_1	129.9(5)	C_{13}	C_{12}	C_8	128.1(6)
C_7	C_2	C_1	108.6(4)	C_{12}	C_{13}	C_{14}	119.0(7)
C_7	C_2	C_3	121.5(5)	C_{15}	C_{14}	C_{13}	121.3(8)
C_4	C_3	C_2	117.9(6)	C_{14}	C_{15}	C_{16}	119.8(6)
C_3	C_4	C_5	120.8(6)	C_{11}	C_{16}	C_{15}	117.4(7)
C_4	C_5	C_6	121.6(6)	C_{18}	C_{17}	C_9	125.2(6)
C_7	C_6	C_5	116.9(6)	C_{18}	C_{17}	C_{22}	120.0
C_2	C_7	C_6	121.2(5)	C_{22}	C_{17}	C_9	114.8(6)
C_2	C_7	C_8	110.6(4)	C_{19}	C_{18}	C_{17}	120.0
C_6	C_7	C_8	128.0(5)	C_{18}	C_{19}	C_{20}	120.0

C_7	C_8	C_{12}	112.2(5)	C_{19}	C_{20}	C_{21}	120.0
C_9	C_8	C_7	116.1(4)	C_{20}	C_{21}	C_{22}	120.0
C_9	C_8	C_{12}	99.2(5)	C_{21}	C_{22}	C_{17}	120.0
N_1	C_8	C_7	99.6(4)	C_{18A}	C_{17A}	C_9	86.9(16)
N_1	C_8	C_9	116.7(5)	C_{18A}	C_{17A}	C_{22A}	120.0
N_1	C_8	C_{12}	113.7(5)	C_{22A}	C_{17A}	C_9	152.1(17)
C_8	C_9	C_{17}	121.1(5)	C_{19A}	C_{18A}	C_{17A}	120.0
C_8	C_9	C_{17A}	134.6(10)	C_{20A}	C_{19A}	C_{18A}	120.0
C_{10}	C_9	C_8	113.9(6)	C_{19A}	C_{20A}	C_{21A}	120.0
C_{10}	C_9	C_{17}	124.8(6)	C_{22A}	C_{21A}	C_{20A}	120.0
C_{10}	C_9	C_{17A}	111.5(10)	C_{21A}	C_{22A}	C_{17A}	120.0
C_9	C_{10}	C_{11}	108.2(6)	C_1	N_1	C_8	113.1(4)
C_{12}	C_{11}	C_{10}	108.8(6)	C_1	N_1	C_{23}	123.1(5)
C_{12}	C_{11}	C_{16}	120.2(7)	C_{23}	N_1	C_8	121.9(5)

Table S6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C_1	C_2	C_3	C_4	178.8(6)	C_{10}	C_9	C_{17}	C_{22}	-14.6(8)
C_1	C_2	C_7	C_6	-178.5(5)	C_{10}	C_9	C_{17A}	C_{18A}	172.2(10)
C_1	C_2	C_7	C_8	5.3(6)	C_{10}	C_9	C_{17A}	C_{22A}	7(4)
C_2	C_1	N_1	C_8	-7.9(6)	C_{10}	C_{11}	C_{12}	C_8	2.8(7)
C_2	C_1	N_1	C_{23}	-172.9(6)	C_{10}	C_{11}	C_{12}	C_{13}	-177.6(6)
C_2	C_3	C_4	C_5	-1.0(9)	C_{10}	C_{11}	C_{16}	C_{15}	176.7(7)
C_2	C_7	C_8	C_9	-135.3(5)	C_{11}	C_{12}	C_{13}	C_{14}	-1.0(10)
C_2	C_7	C_8	C_{12}	111.5(5)	C_{12}	C_8	C_9	C_{10}	5.5(6)
C_2	C_7	C_8	N_1	-9.2(6)	C_{12}	C_8	C_9	C_{17}	-179.7(6)
C_3	C_2	C_7	C_6	1.7(8)	C_{12}	C_8	C_9	C_{17A}	-173.4(18)
C_3	C_2	C_7	C_8	-174.6(5)	C_{12}	C_8	N_1	C_1	-109.2(6)
C_3	C_4	C_5	C_6	3.2(10)	C_{12}	C_8	N_1	C_{23}	55.9(8)
C_4	C_5	C_6	C_7	-3.0(9)	C_{12}	C_{11}	C_{16}	C_{15}	-3.1(11)
C_5	C_6	C_7	C_2	0.6(9)	C_{12}	C_{13}	C_{14}	C_{15}	0.7(12)
C_5	C_6	C_7	C_8	176.1(5)	C_{13}	C_{14}	C_{15}	C_{16}	-1.6(13)
C_6	C_7	C_8	C_9	48.8(8)	C_{14}	C_{15}	C_{16}	C_{11}	2.8(12)
C_6	C_7	C_8	C_{12}	-64.4(8)	C_{16}	C_{11}	C_{12}	C_8	-177.3(6)
C_6	C_7	C_8	N_1	174.9(6)	C_{16}	C_{11}	C_{12}	C_{13}	2.3(10)
C_7	C_2	C_3	C_4	-1.4(8)	C_{17}	C_9	C_{10}	C_{11}	-178.8(6)
C_7	C_8	C_9	C_{10}	-115.0(6)	C_{17}	C_{18}	C_{19}	C_{20}	0.0
C_7	C_8	C_9	C_{17}	59.8(8)	C_{18}	C_{17}	C_{22}	C_{21}	0.0
C_7	C_8	C_9	C_{17A}	66.2(19)	C_{18}	C_{19}	C_{20}	C_{21}	0.0
C_7	C_8	C_{12}	C_{11}	118.5(6)	C_{19}	C_{20}	C_{21}	C_{22}	0.0

C_7	C_8	C_{12}	C_{13}	-61.1(7)	C_{20}	C_{21}	C_{22}	C_{17}	0.0
C_7	C_8	N_1	C_1	10.3(6)	C_{22}	C_{17}	C_{18}	C_{19}	0.0
C_7	C_8	N_1	C_{23}	175.5(6)	C_{17A}	C_9	C_{10}	C_{11}	174.9(14)
C_8	C_9	C_{10}	C_{11}	-4.2(7)	C_{17A}	C_{18A}	C_{19A}	C_{20A}	0.0
C_8	C_9	C_{17}	C_{18}	-8.8(10)	C_{18A}	C_{17A}	C_{22A}	C_{21A}	0.0
C_8	C_9	C_{17}	C_{22}	171.3(5)	C_{18A}	C_{19A}	C_{20A}	C_{21A}	0.0
C_8	C_9	C_{17A}	C_{18A}	-9(2)	C_{19A}	C_{20A}	C_{21A}	C_{22A}	0.0
C_8	C_9	C_{17A}	C_{22A}	-174(3)	C_{20A}	C_{21A}	C_{22A}	C_{17A}	0.0
C_8	C_{12}	C_{13}	C_{14}	178.6(7)	C_{22A}	C_{17A}	C_{18A}	C_{19A}	0.0
C_9	C_8	C_{12}	C_{11}	-4.8(6)	N_1	C_1	C_2	C_3	-178.7(5)
C_9	C_8	C_{12}	C_{13}	175.6(6)	N_1	C_1	C_2	C_7	1.4(6)
C_9	C_8	N_1	C_1	136.1(5)	N_1	C_8	C_9	C_{10}	128.0(6)
C_9	C_8	N_1	C_{23}	-58.7(8)	N_1	C_8	C_9	C_{17}	-57.2(8)
C_9	C_{10}	C_{11}	C_{12}	0.7(8)	N_1	C_8	C_9	C_{17A}	-50.9(19)
C_9	C_{10}	C_{11}	C_{16}	-179.1(7)	N_1	C_8	C_{12}	C_{11}	-129.4(6)
C_9	C_{17}	C_{18}	C_{19}	-180.0(8)	N_1	C_8	C_{12}	C_{13}	51.0(8)
C_9	C_{17}	C_{22}	C_{21}	180.0(7)	O_1	C_1	C_2	C_3	2.8(8)
C_9	C_{17A}	C_{18A}	C_{19A}	-172(2)	O_1	C_1	C_2	C_7	-177.1(5)
C_9	C_{17A}	C_{22A}	C_{21A}	163(4)	O_1	C_1	N_1	C_8	170.7(5)
C_{10}	C_9	C_{17}	C_{18}	165.4(6)	O_1	C_1	N_1	C_{23}	5.7(9)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H_3	-1042	2933	5797	108
H_4	1499	2253	5377	122
H_5	3955	3234	5607	113
H_6	3981	4829	6358	103
H_{10}	3785	7885	7315	119
H_{13}	636	4161	8062	125
H_{14}	2035	4007	9117	143
H_{15}	3991	5328	9435	162
H_{16}	4736	6837	8643	148
H_{18}	308	6451	5604	90
H_{19}	-8	7582	4604	109
H_{20}	1165	9427	4561	134
H_{21}	2654	10140	5518	154
H_{22}	2971	9008	6519	129
H_{18A}	452	6460	6113	90
H_{19A}	-367	6840	4965	109
H_{20A}	543	8519	4408	134

H_{21A}	2272	9819	4999	154
H_{22A}	3091	9440	6148	129
H_{23A}	-2416	7114	7159	186
H_{23B}	-998	7048	7733	186
H_{23C}	-2469	6138	7733	186

Table S8 Atomic Occupancy for 3aa.

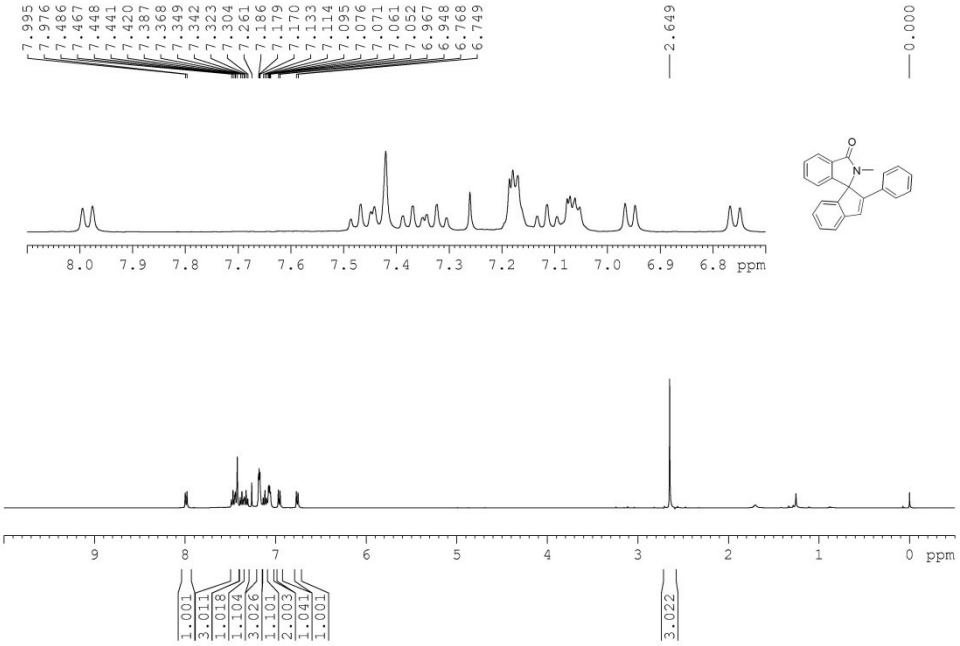
Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C_{17}	0.751(15)	C_{18}	0.751(15)	H_{18}	0.751(15)
C_{19}	0.751(15)	H_{19}	0.751(15)	C_{20}	0.751(15)
H_{20}	0.751(15)	C_{21}	0.751(15)	H_{21}	0.751(15)
C_{22}	0.751(15)	H_{22}	0.751(15)	C_{17A}	0.249(15)
C_{18A}	0.249(15)	H_{18A}	0.249(15)	C_{19A}	0.249(15)
H_{19A}	0.249(15)	C_{20A}	0.249(15)	H_{20A}	0.249(15)
C_{21A}	0.249(15)	H_{21A}	0.249(15)	C_{22A}	0.249(15)
H_{22A}	0.249(15)				

Crystal Data for $C_{23}H_{17}NO$ (*M* =323.38 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 7.92466(18) Å, *b* = 11.5149(3) Å, *c* = 19.0209(6) Å, *V* = 1735.69(9) Å^3, *Z* = 4, *T* = 293(2) K, μ(CuKα) = 0.589 mm^{-1}, *Dcal* = 1.237 g/cm^3, 6178 reflections measured (8.978° ≤ 2Θ ≤ 134.116°), 3109 unique (R_{int} = 0.0229, R_{sigma} = 0.0295) which were used in all calculations. The final R_1 was 0.0710 (I > 2σ(I)) and wR_2 was 0.2066 (all data).

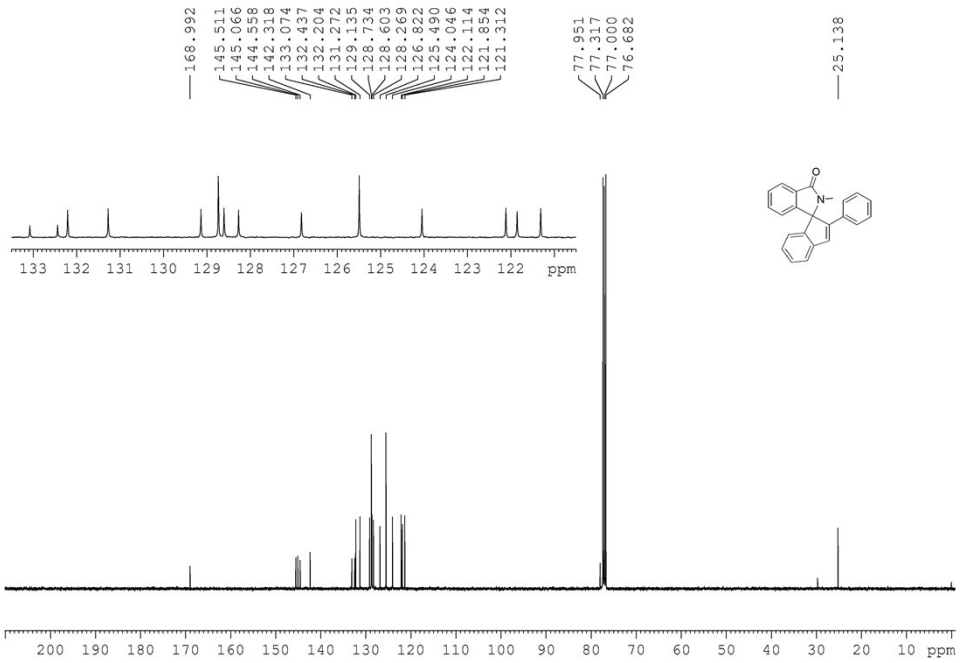
6. References

1. Liu, S.-L.; Li, X.-H.; Shi, T.-H.; Yang, G.-C.; Wang, H.-L.; Gong, J.-F.; Song, M.-P. *Eur. J. Org. Chem.* **2017**, *2017*, 2280.
2. Vanos. C. M.;Lambert. T. H. *Angew. Chem. Int. Ed*. **2011**, *50*, 12222.
3. Nacsa, D. E.; Lambert H. T. *Org. Lett.* **2013**, *15*, 38.
4. W.-T. Zhao, F. Gao, D. Zhao. *Angew. Chem. Int. Ed.* 2018, **57**, 6329.

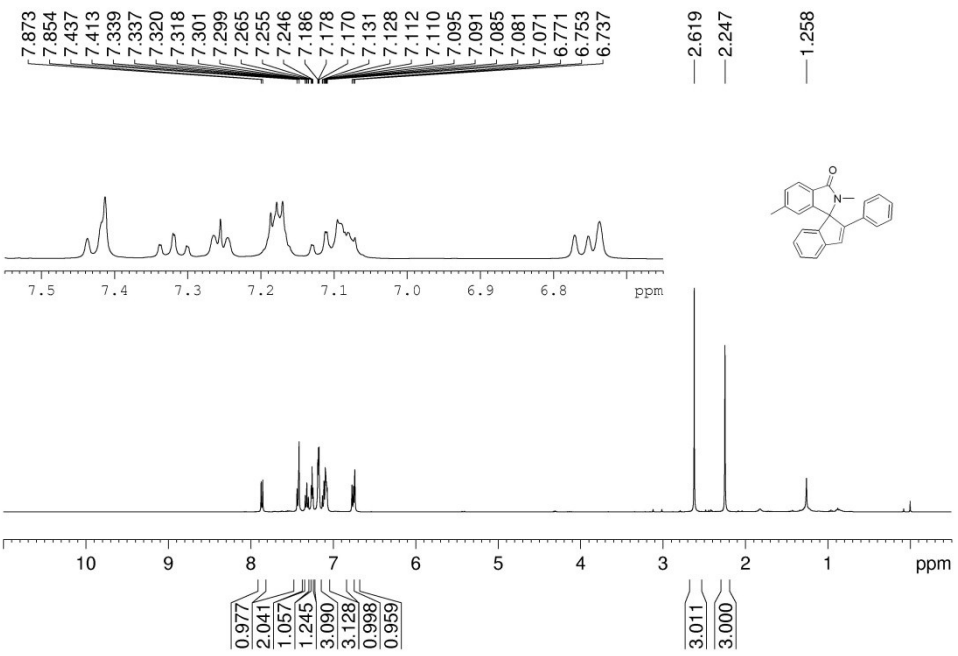
7. Copies of NMR Spectra



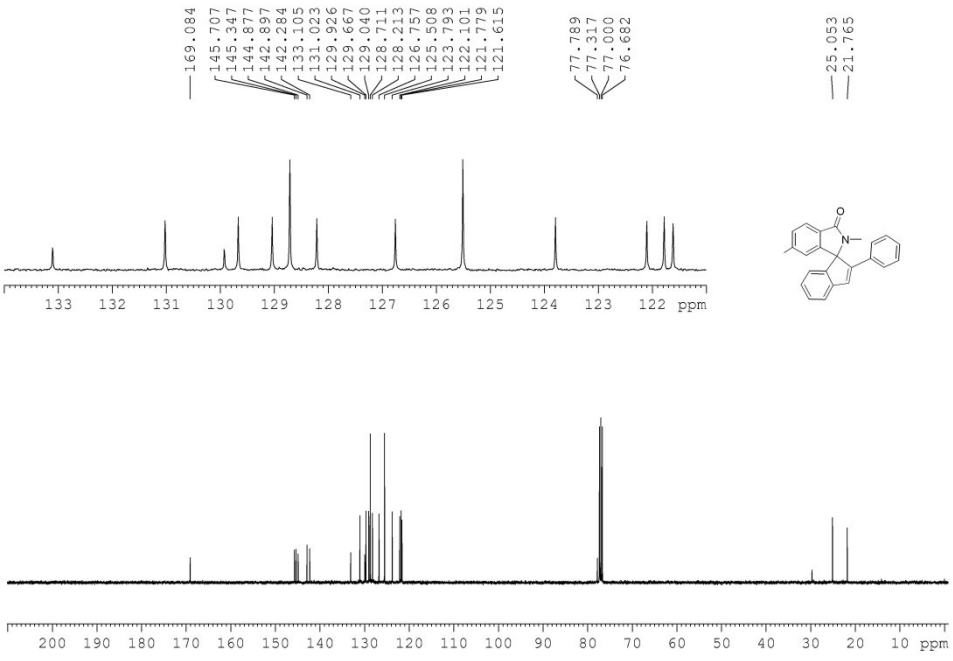
^{1}H NMR spectrum of compound 3aa



^{13}C NMR spectrum of compound 3aa



^{1}H NMR spectrum of compound 3ba



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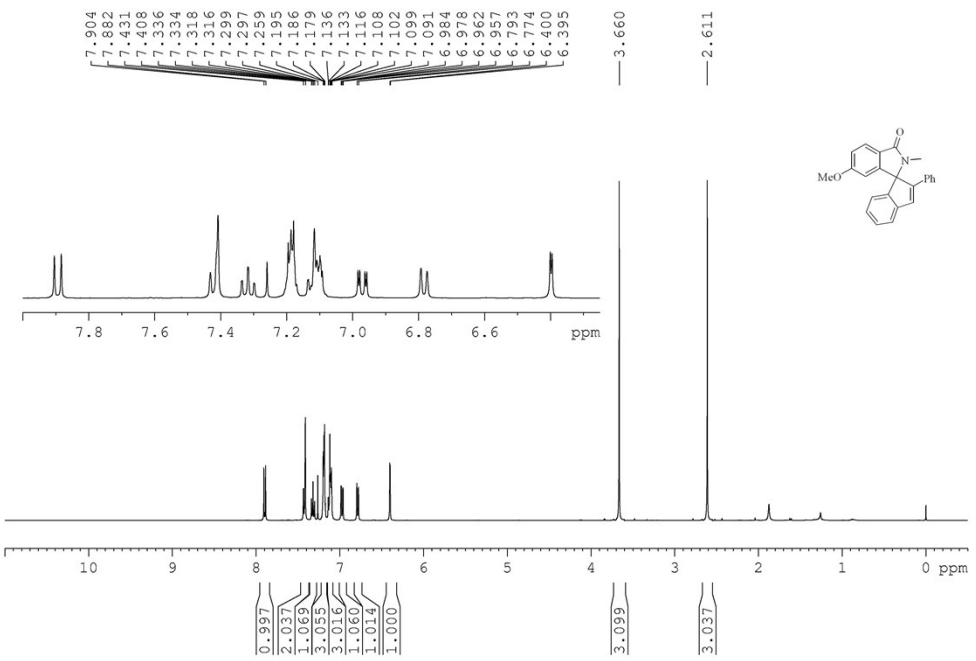

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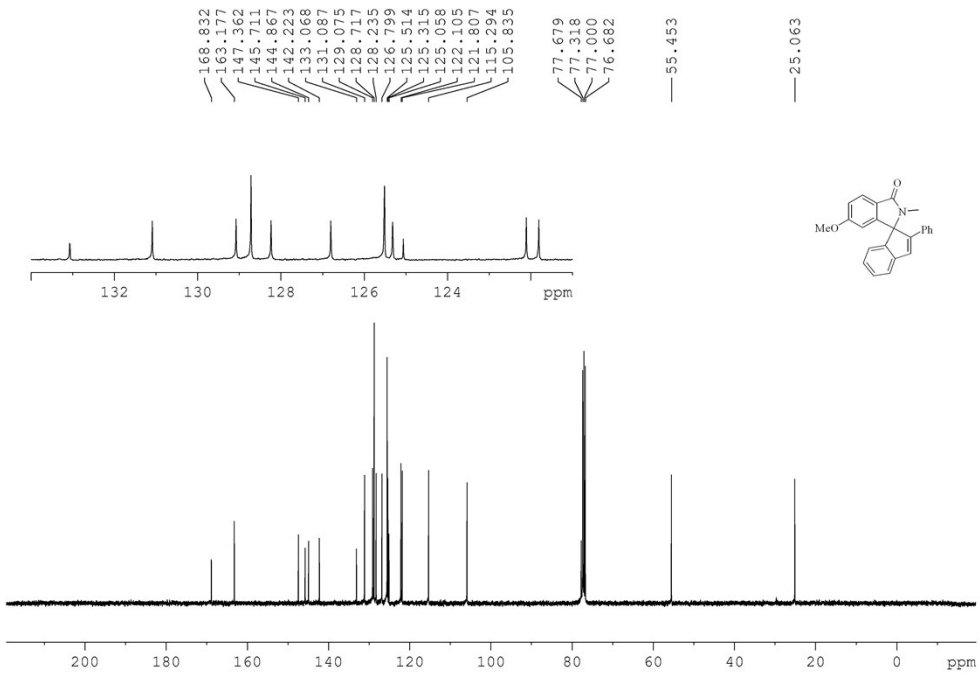

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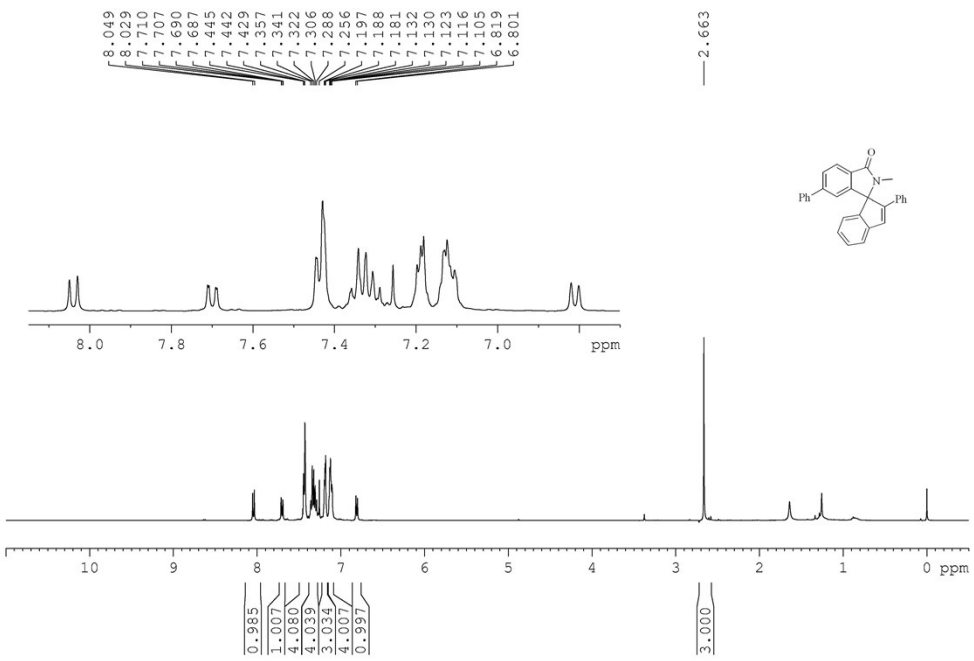

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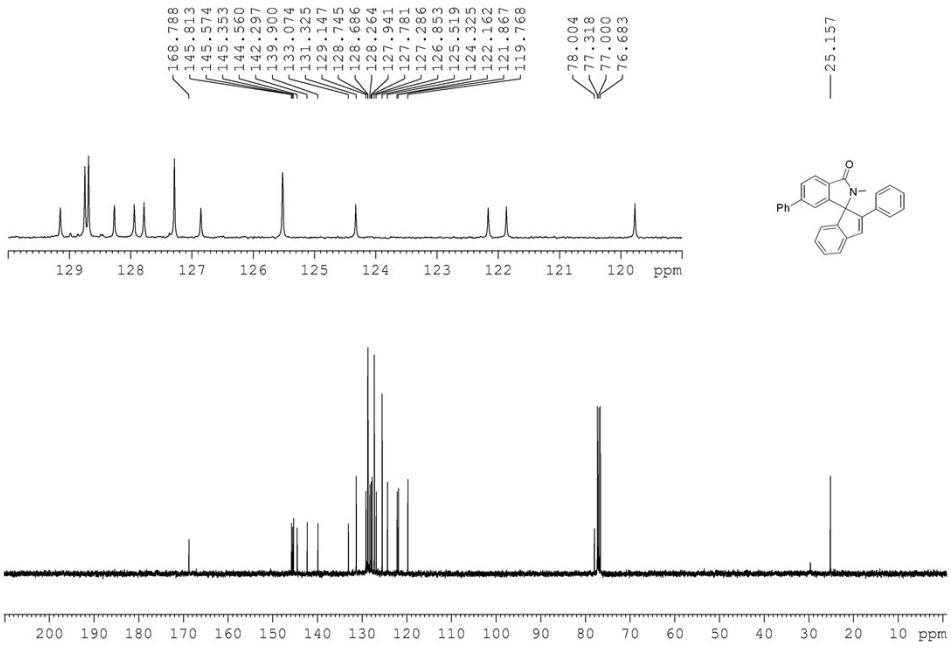

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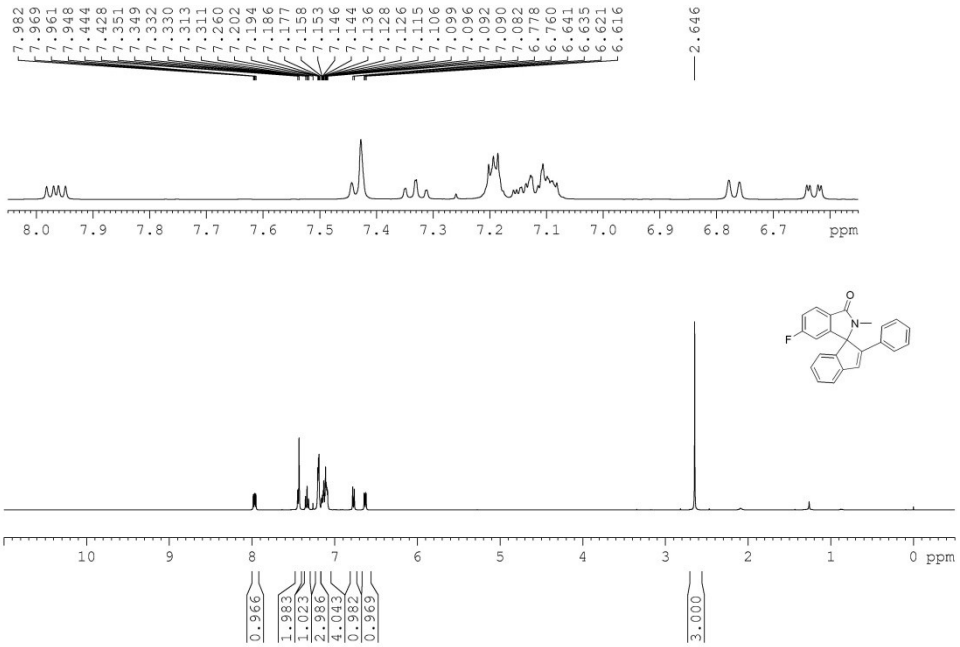

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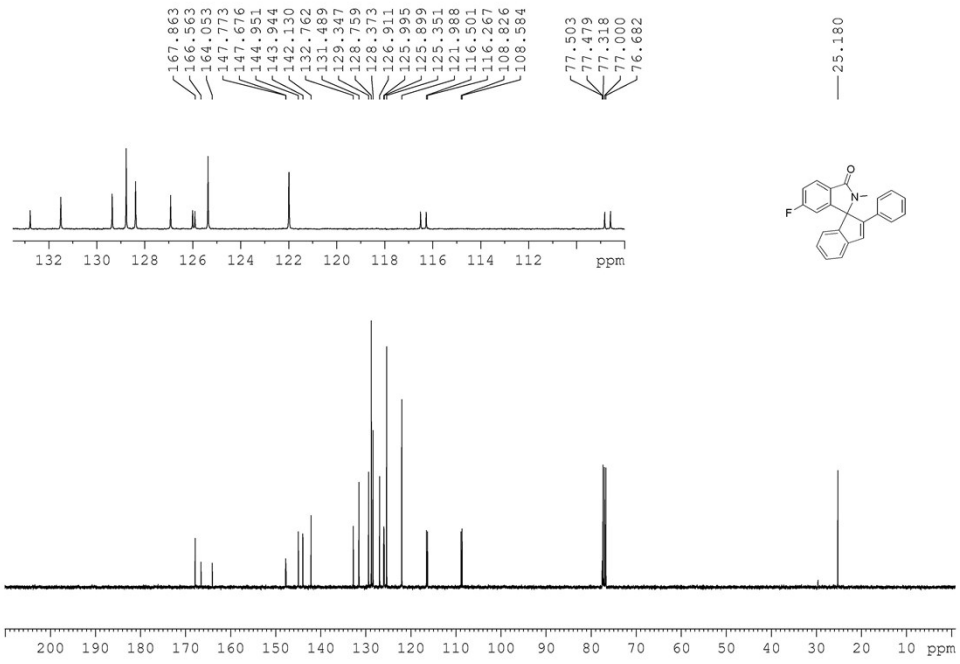

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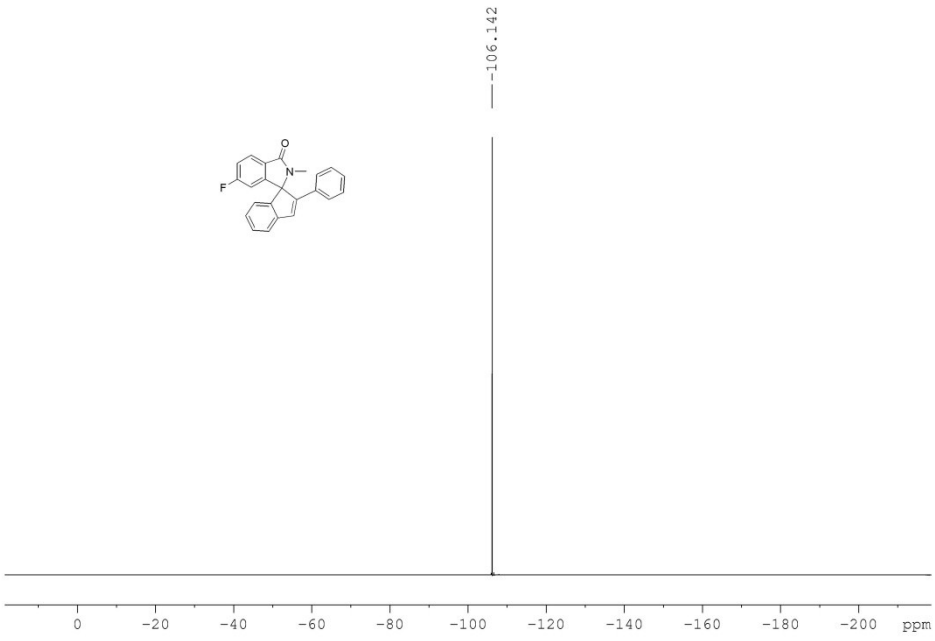
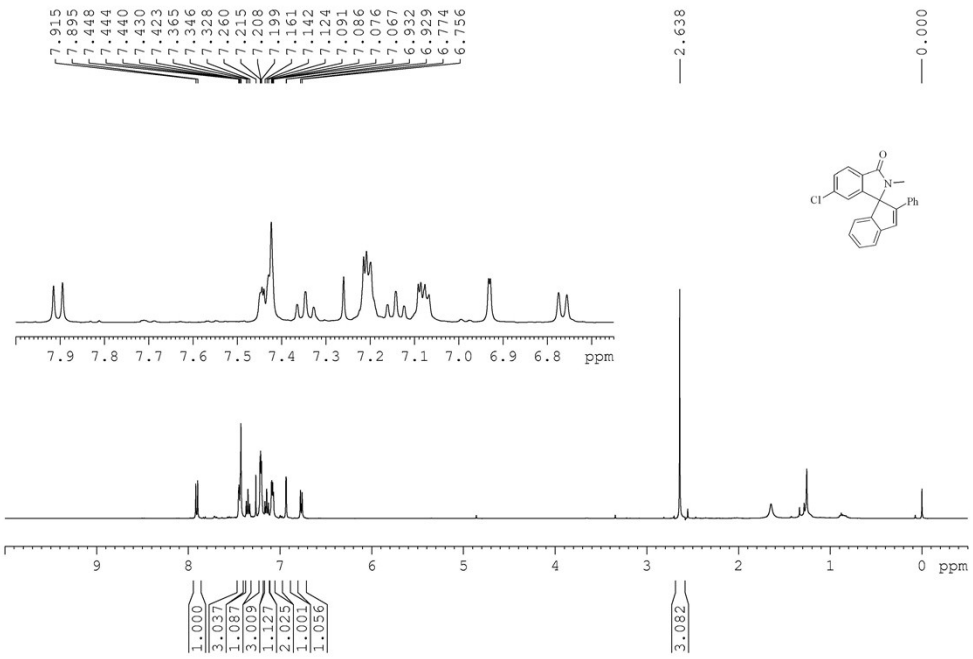
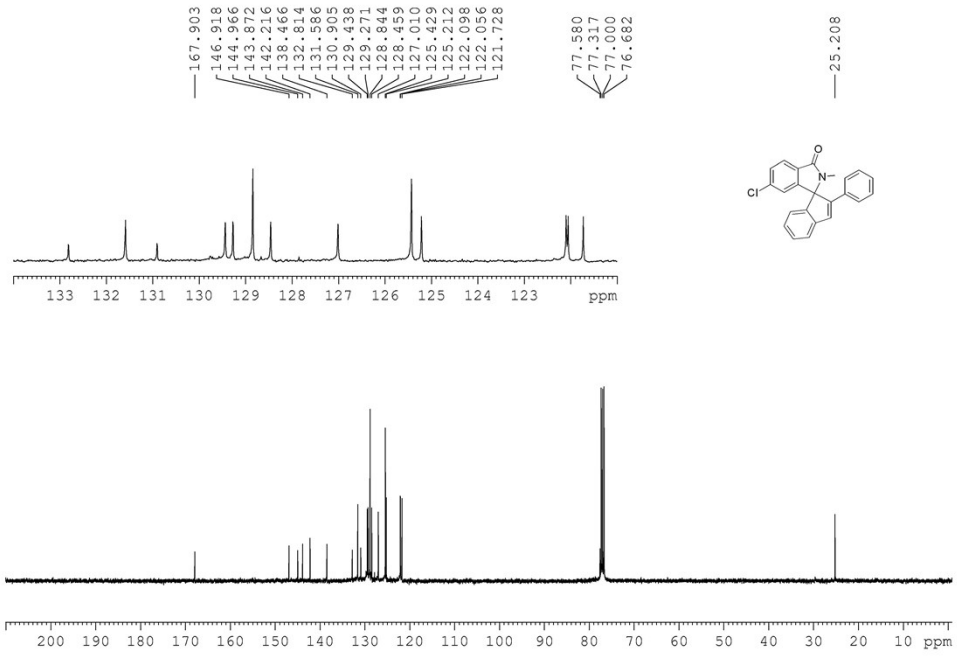


^{19}F NMR spectrum of compound 3ea



^{1}H NMR spectrum of compound 3fa



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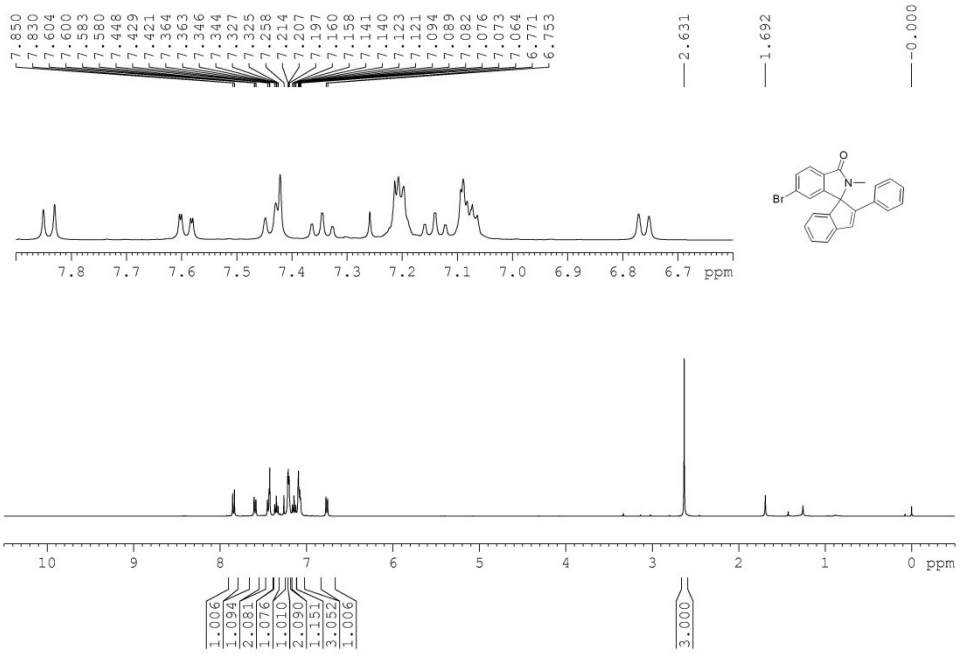
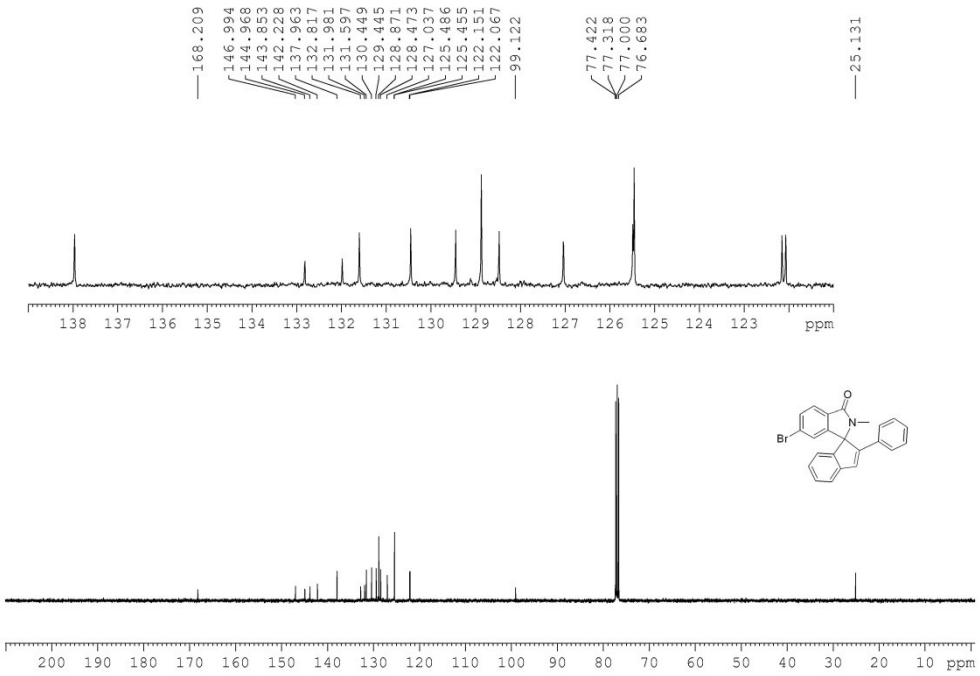
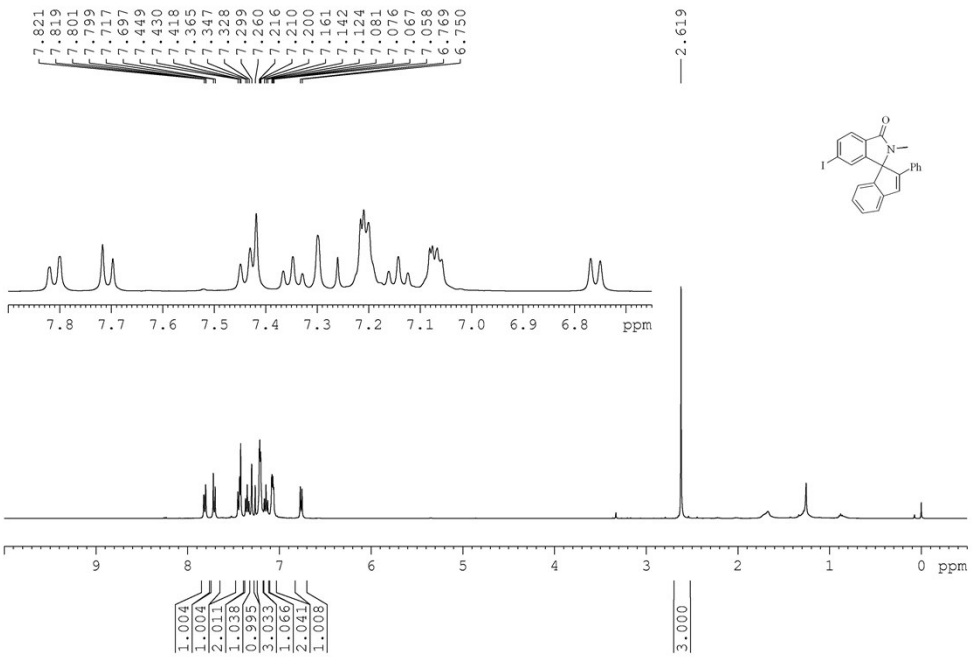


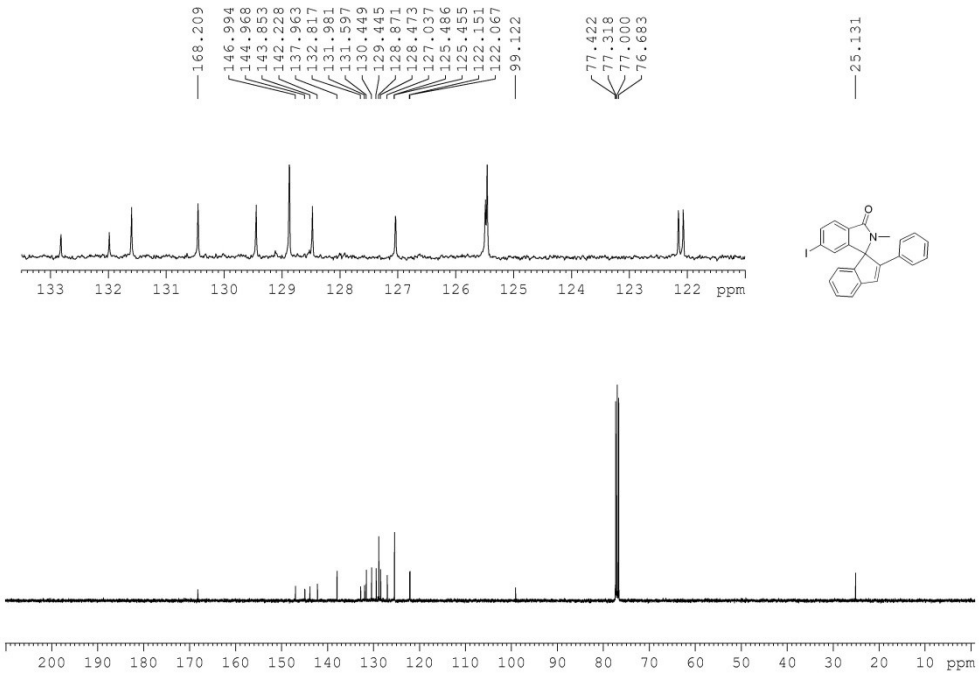
^{1}H NMR spectrum of compound 3ga



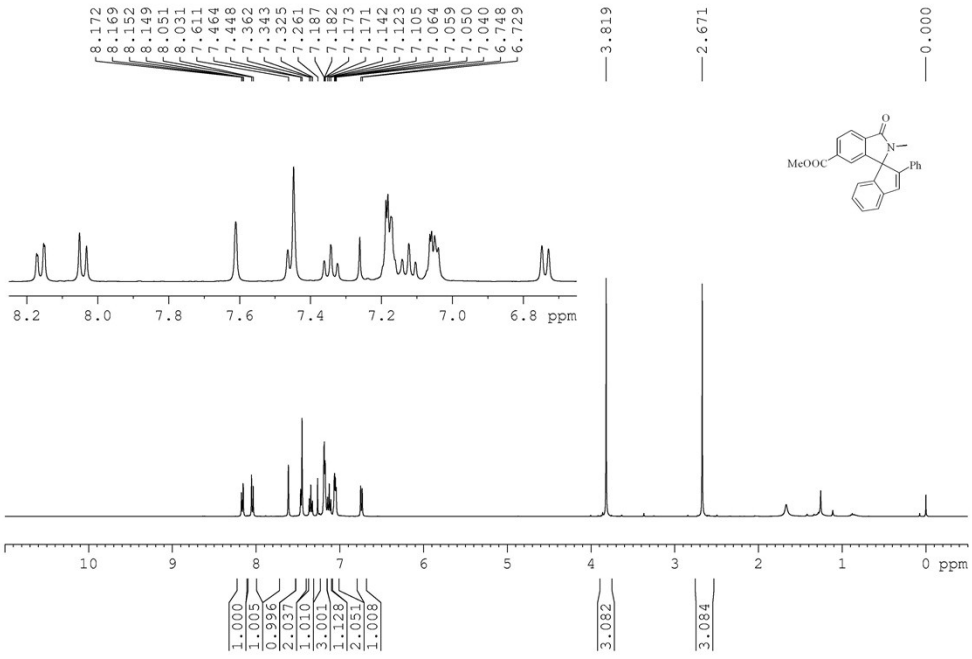
^{13}C NMR spectrum of compound 3ga



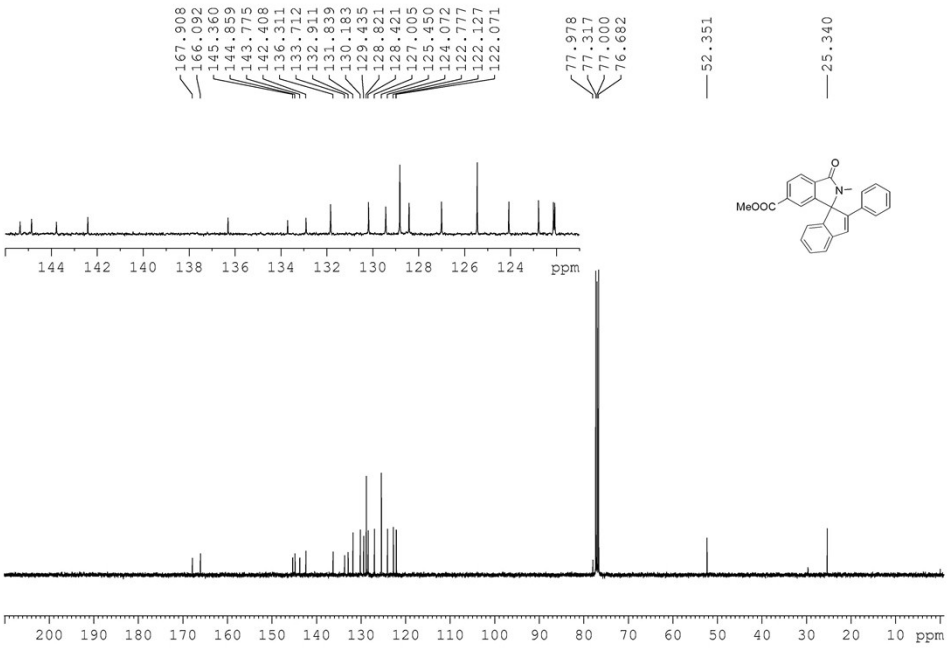
^{1}H NMR spectrum of compound 3ha



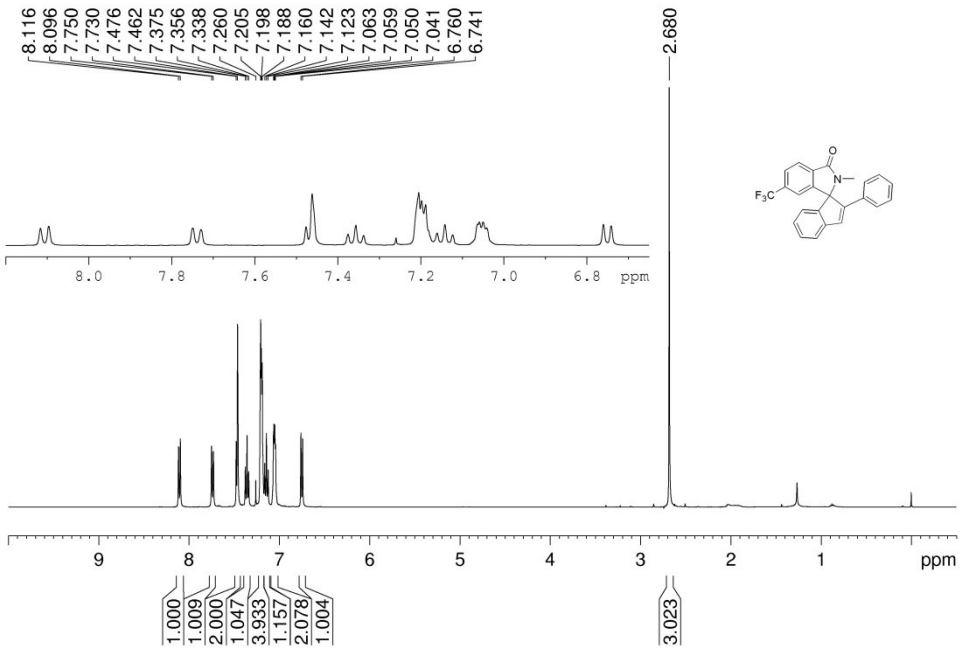
^{13}C NMR spectrum of compound 3ha



^{1}H NMR spectrum of compound 3ia



^{13}C NMR spectrum of compound 3ia



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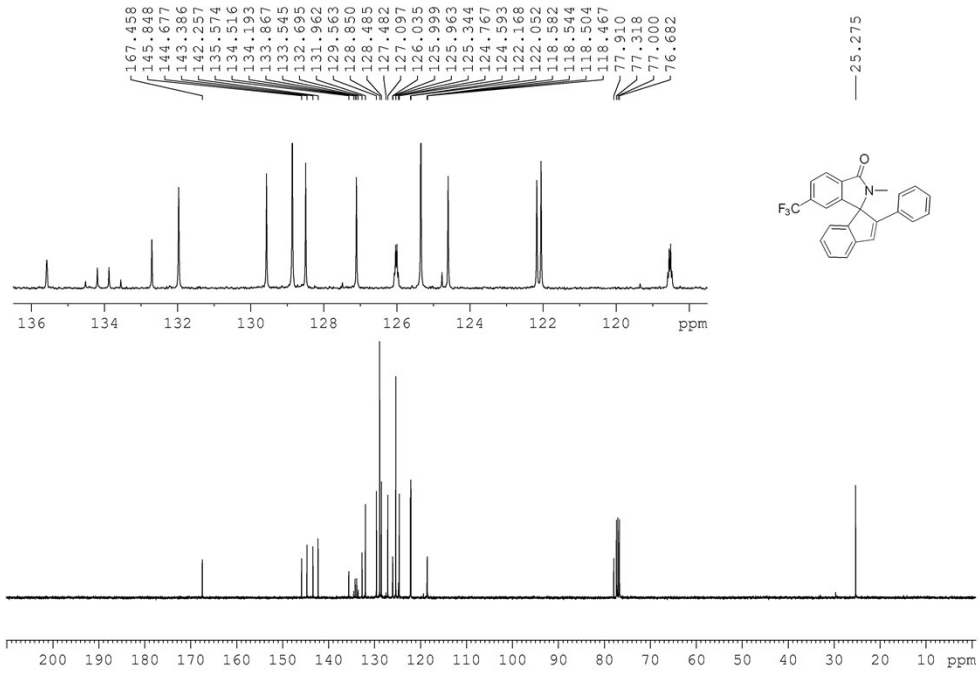

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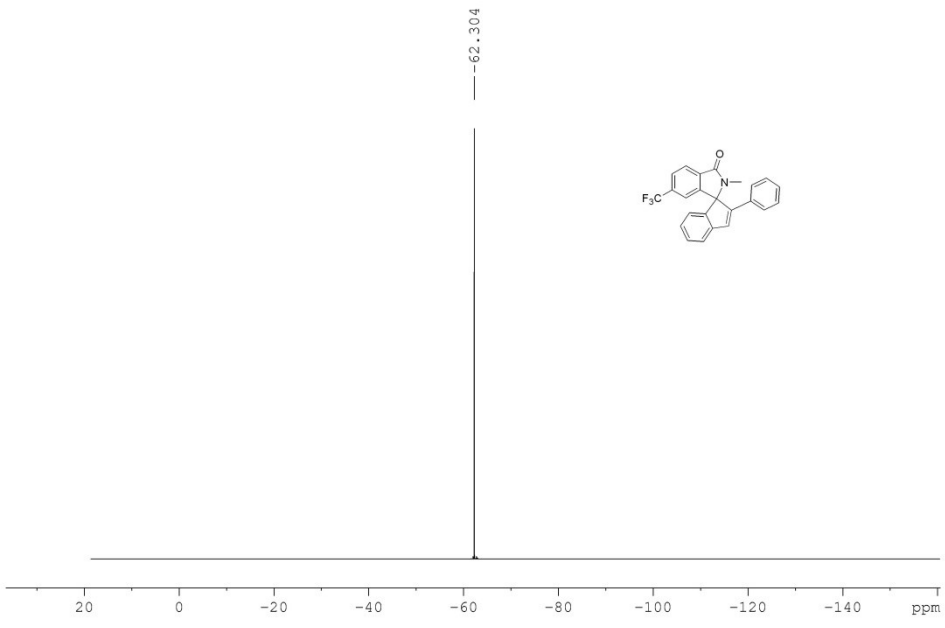
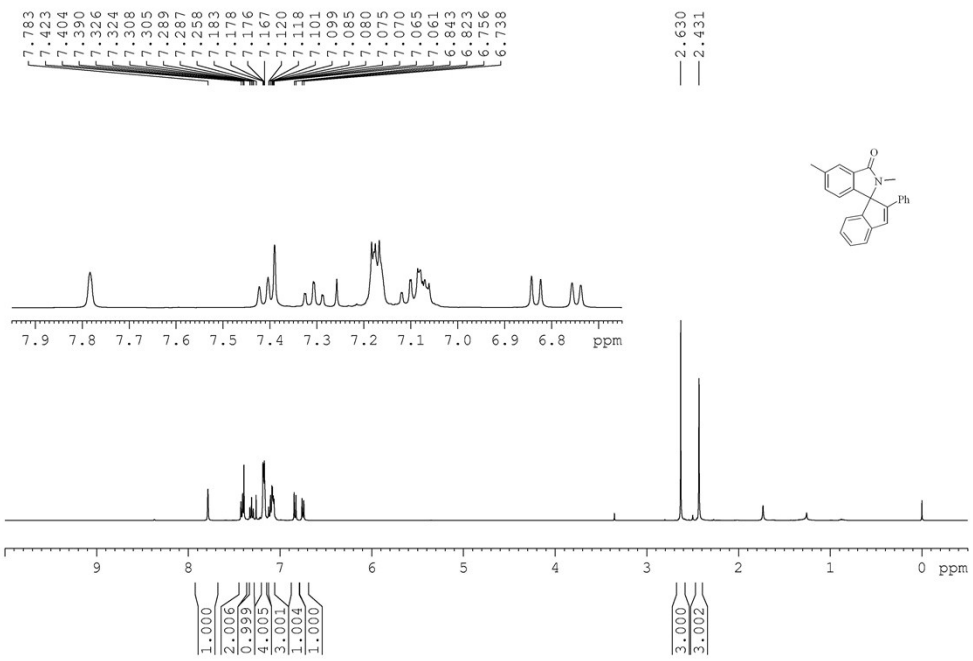
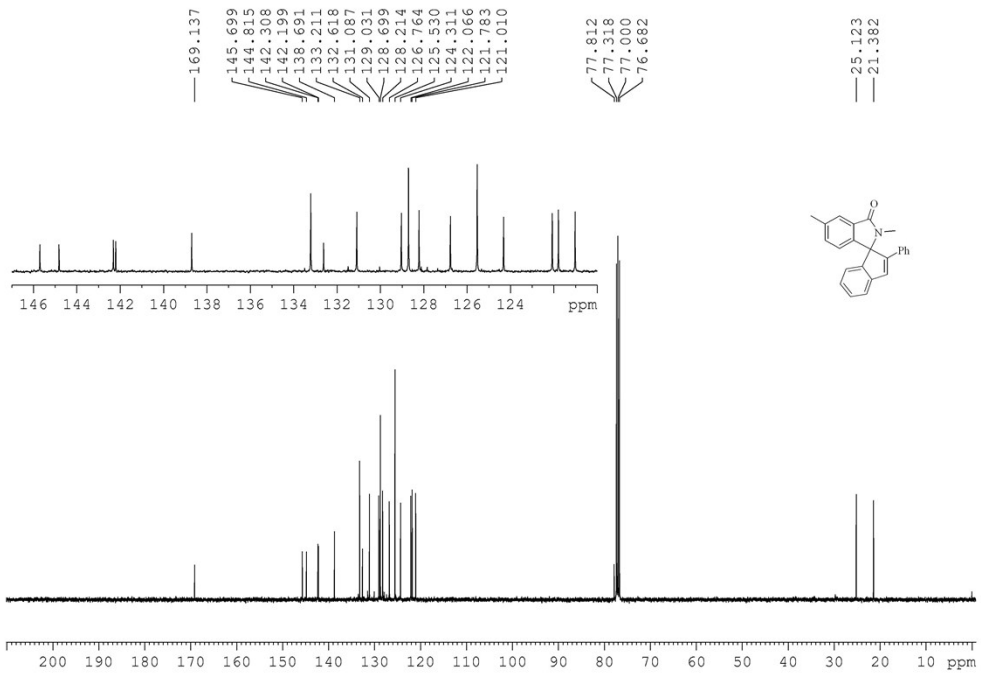


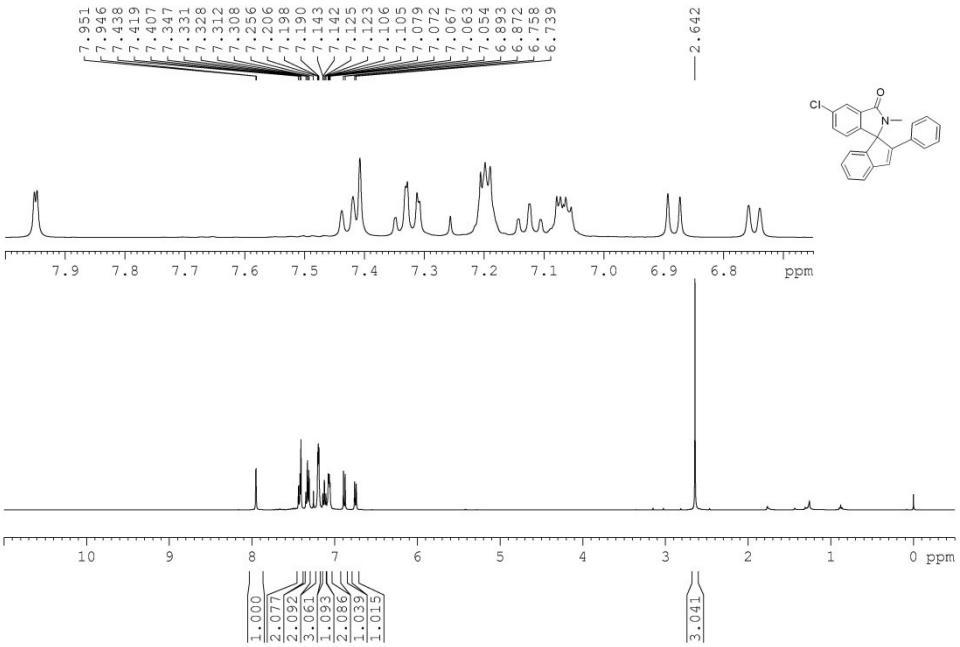
^{19}F NMR spectrum of compound 3ja



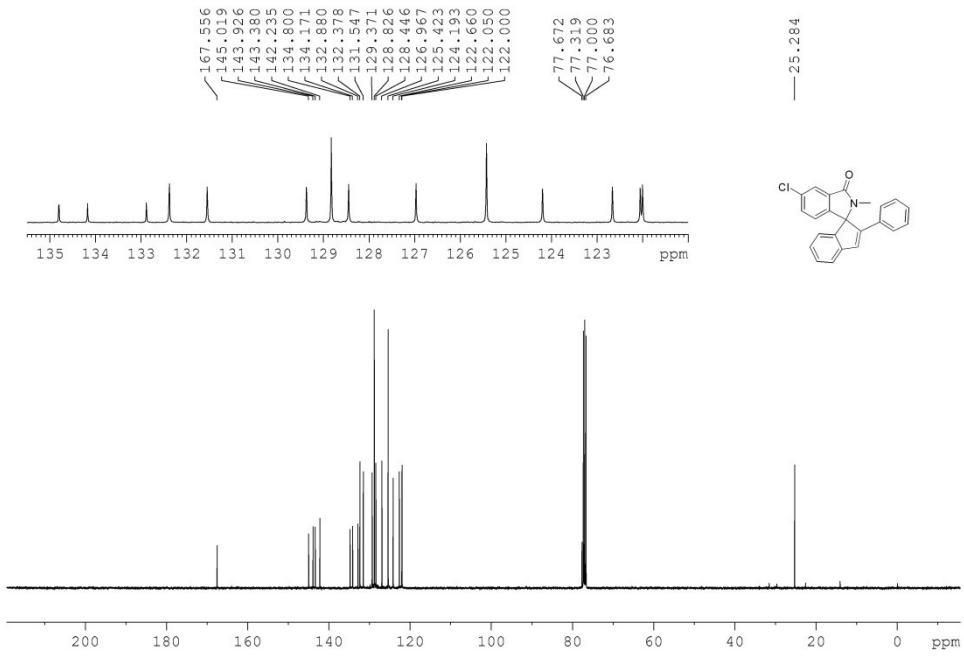
^{1}H NMR spectrum of compound 3ka



^{13}C NMR spectrum of compound 3ka



[1]H NMR spectrum of compound 3la



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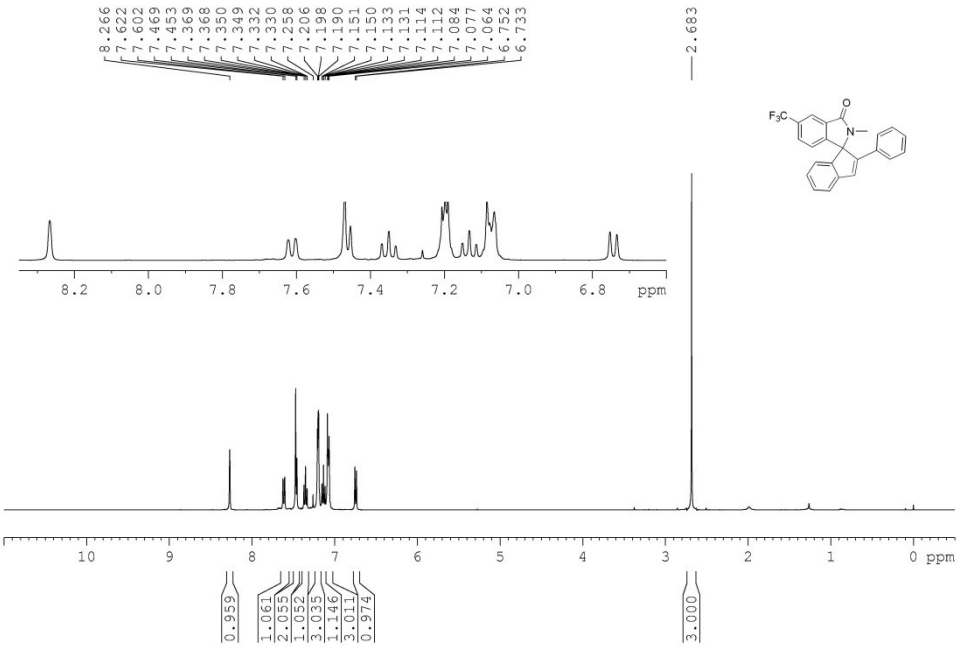
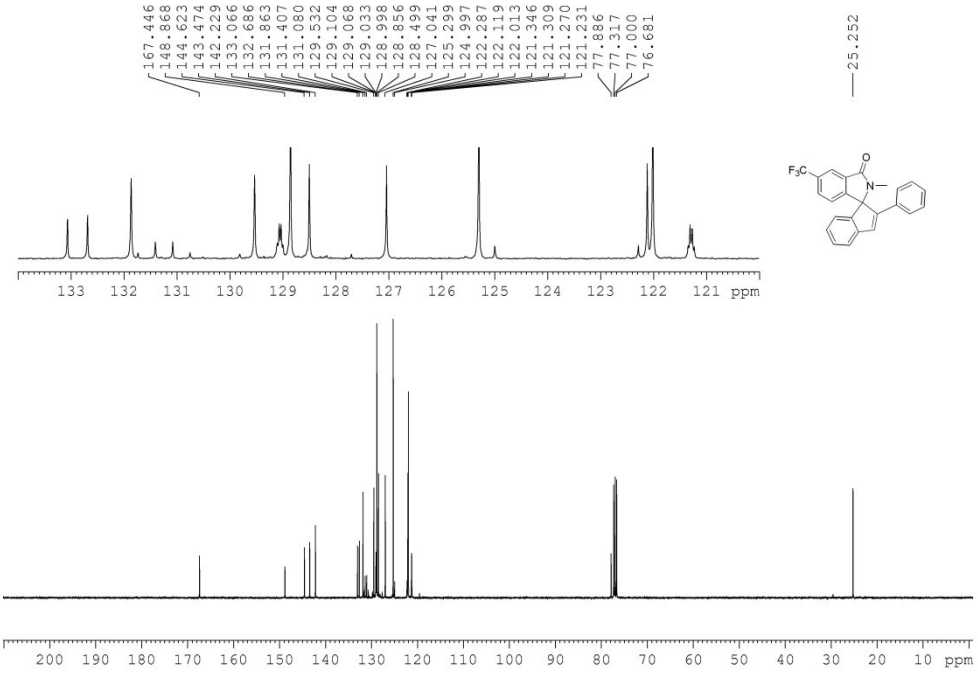
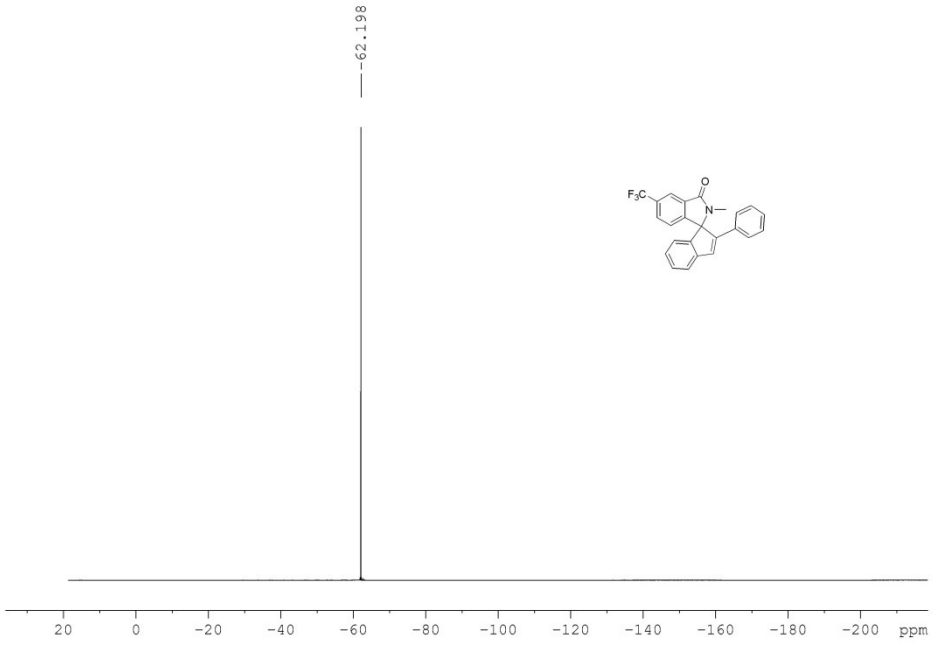


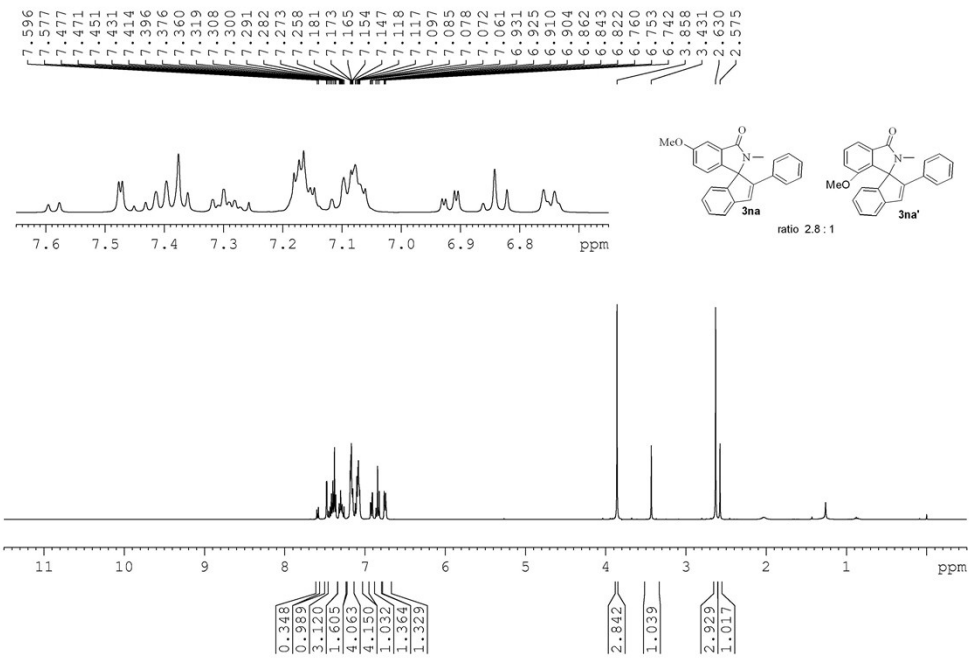
[1]H NMR spectrum of compound 3ma



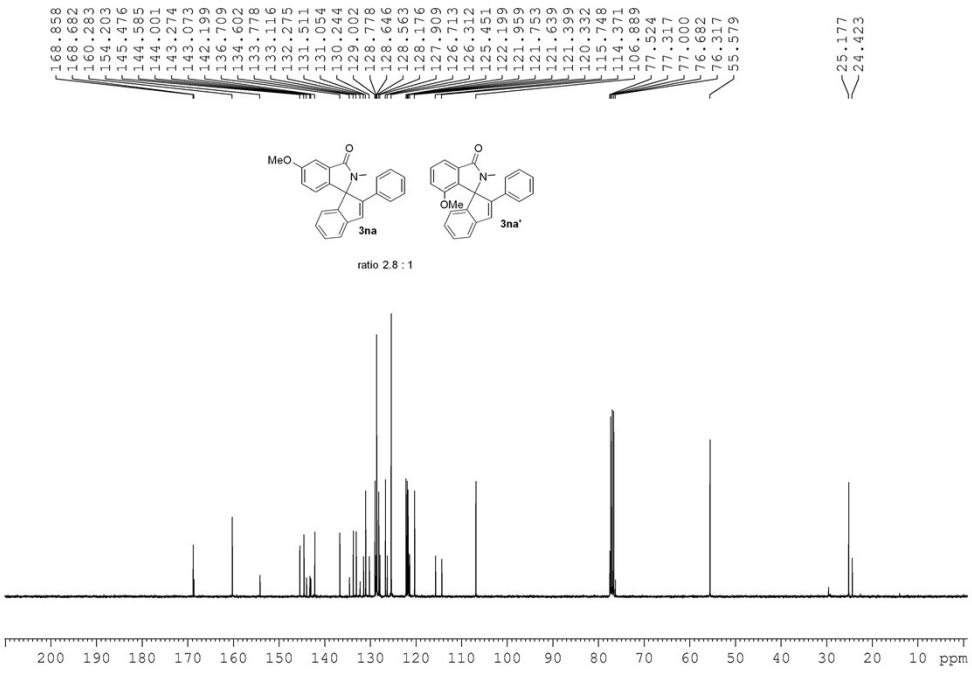
[13]C NMR spectrum of compound 3ma



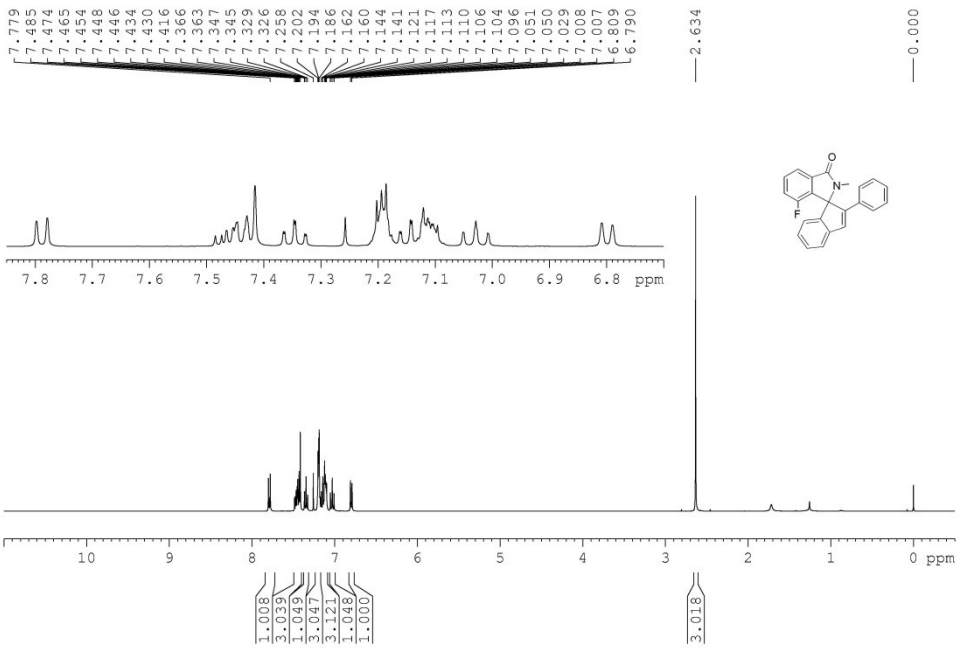
^{19}F NMR spectrum of compound 3ma



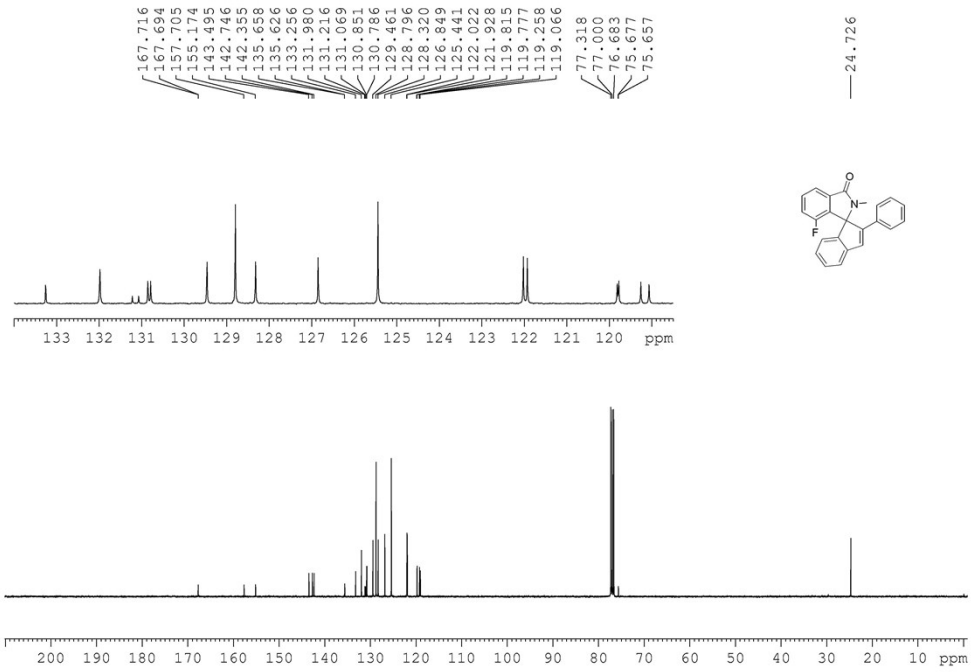
^{1}H NMR spectrum of compound 3na and3na'



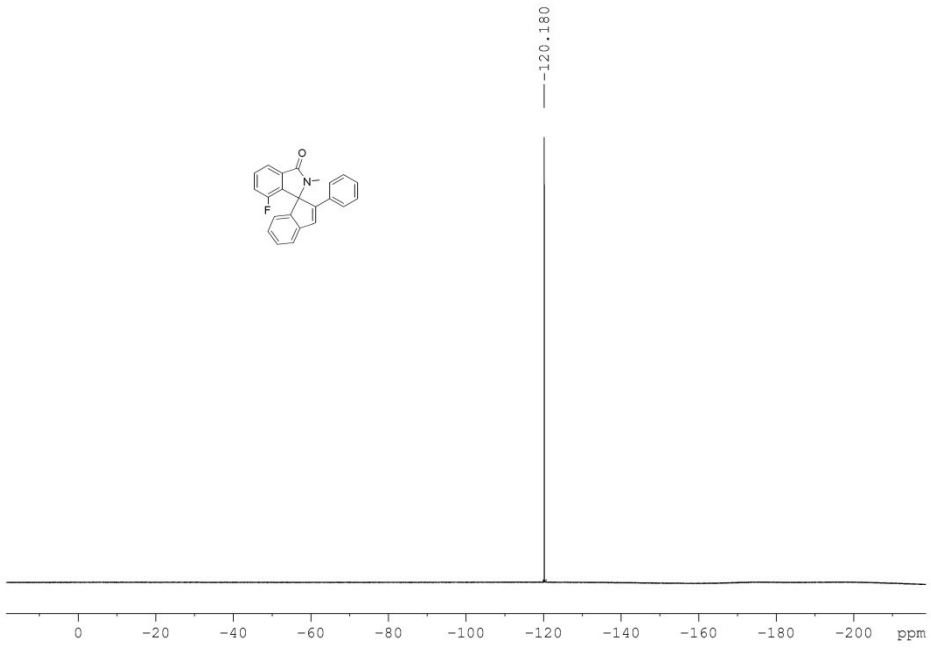
^{13}C NMR spectrum of compound 3na and 3na'



^{1}H NMR spectrum of compound 3oa



^{13}C NMR spectrum of compound 3oa



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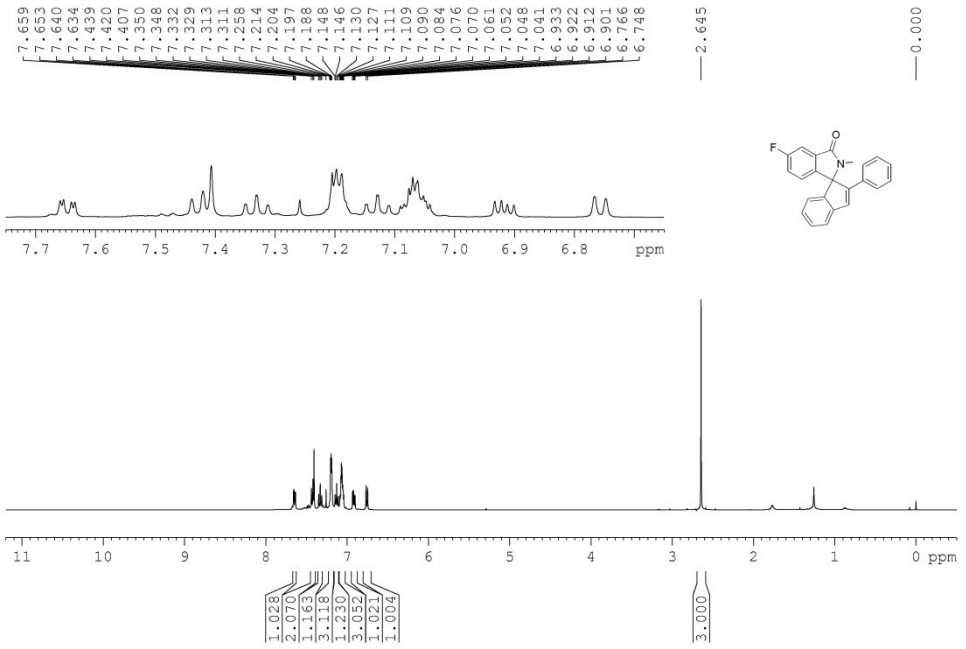
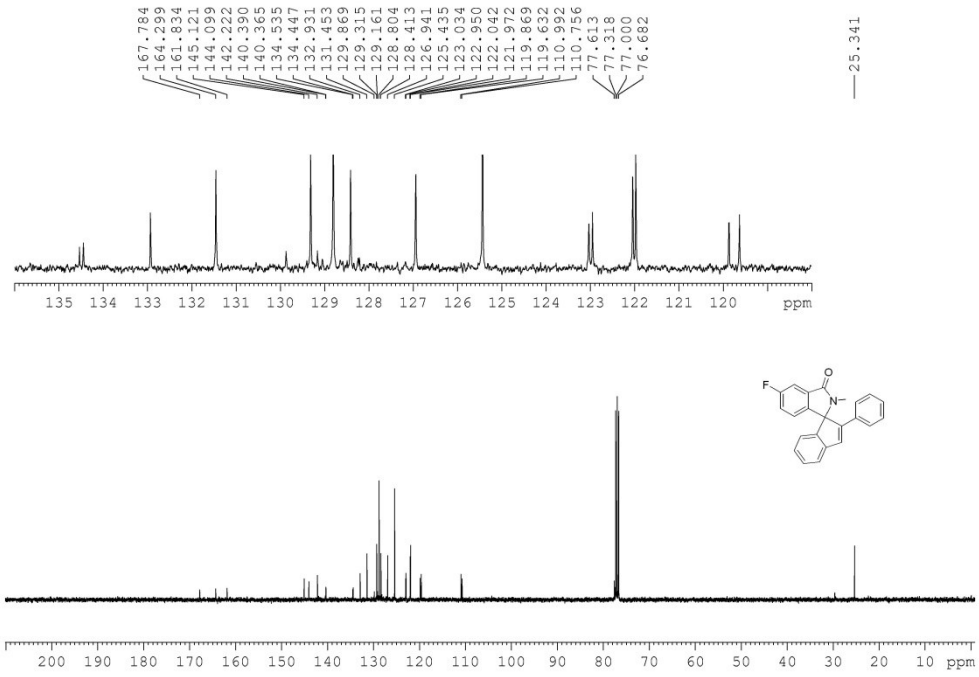


^{1}H NMR spectrum of compound 3oa'



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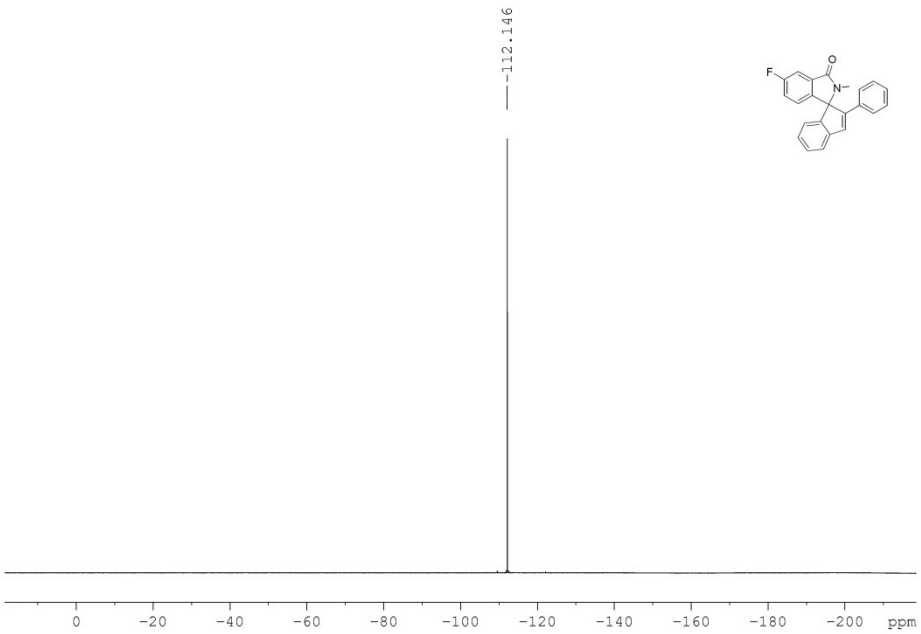

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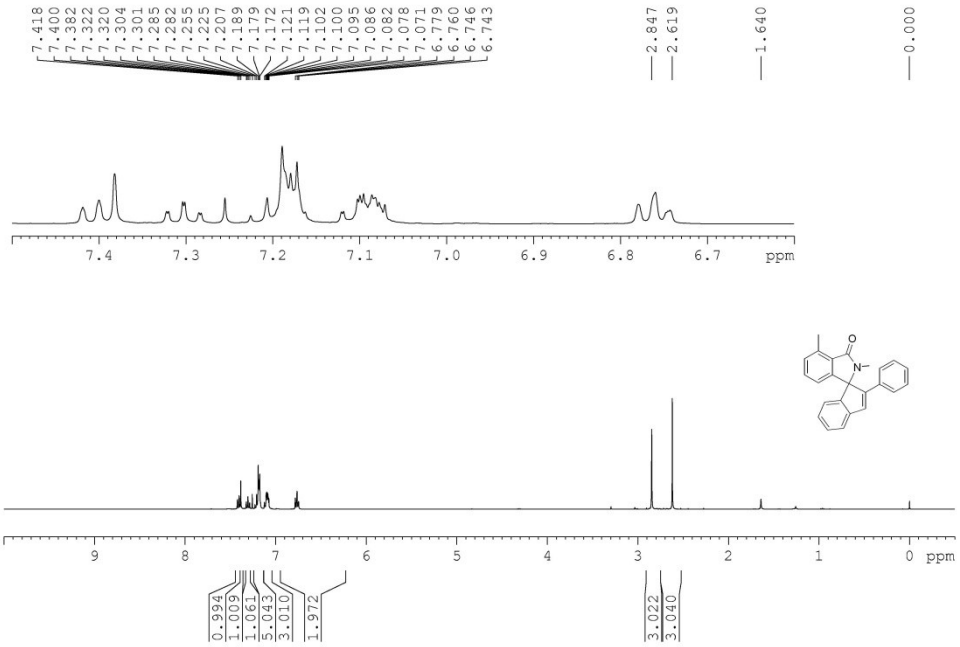

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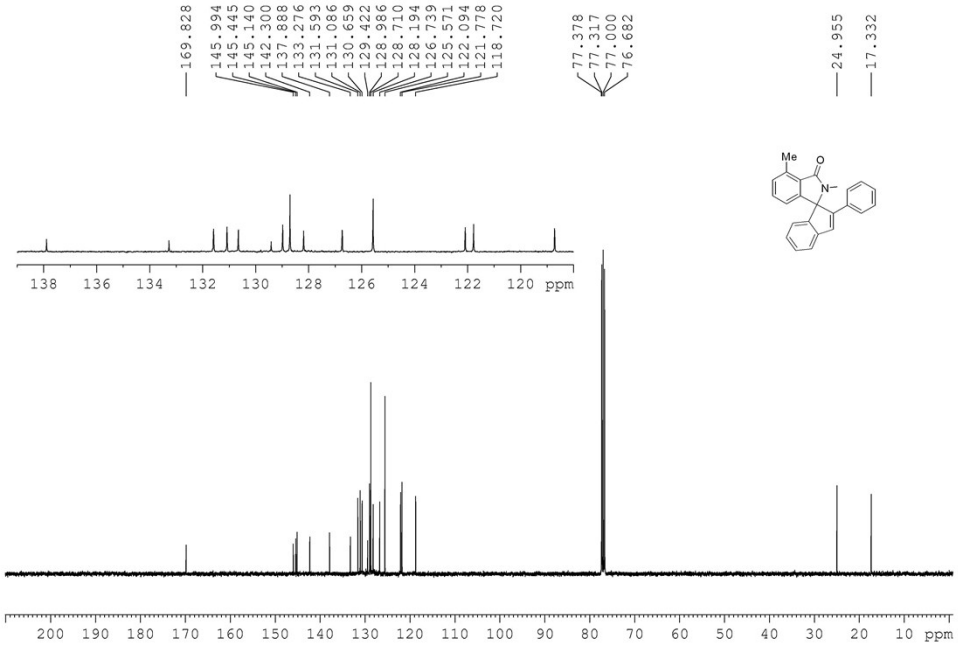

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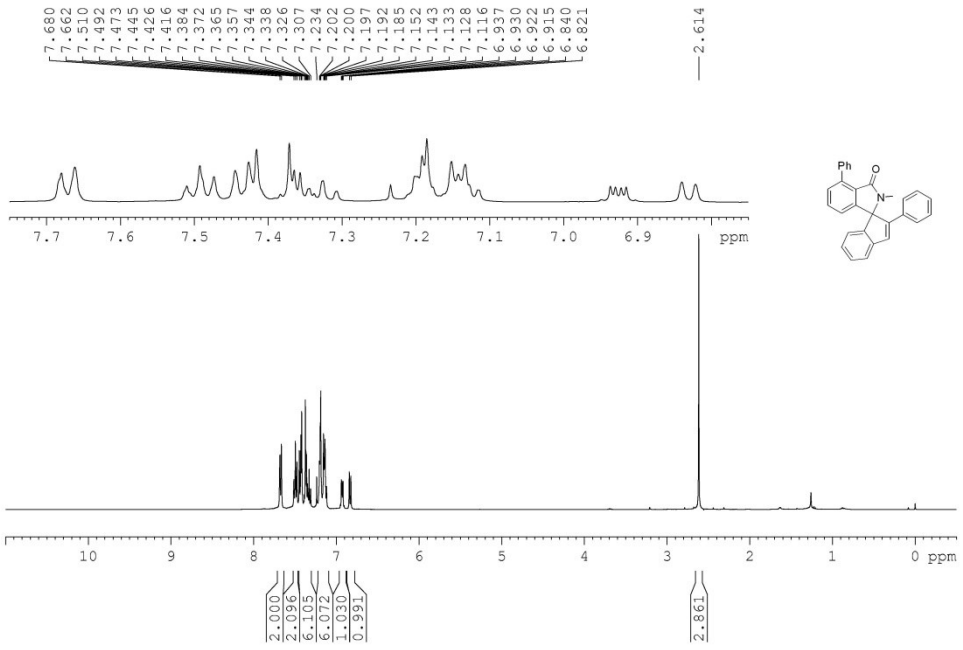
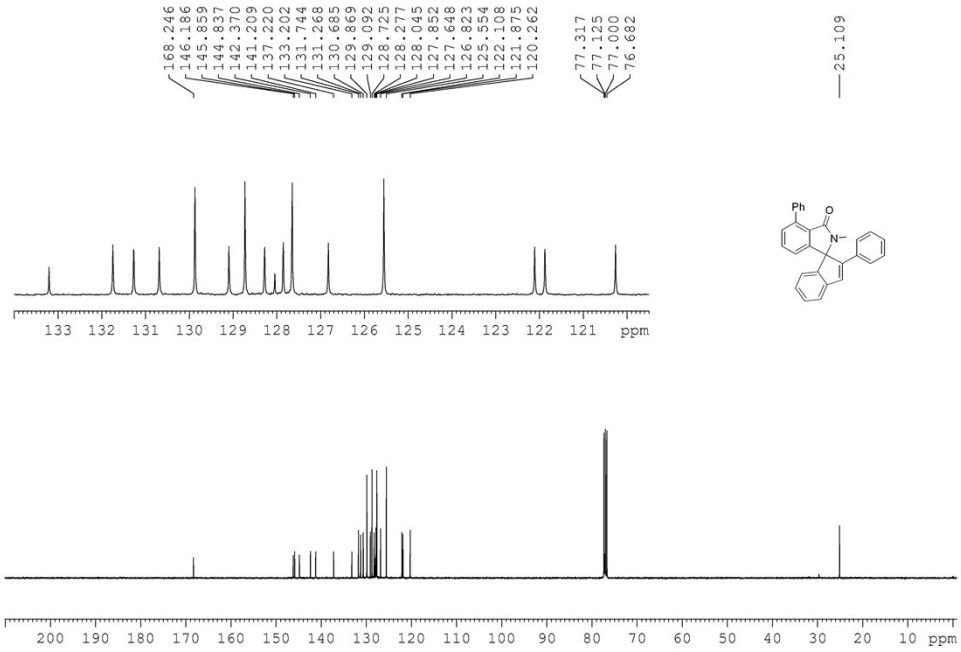
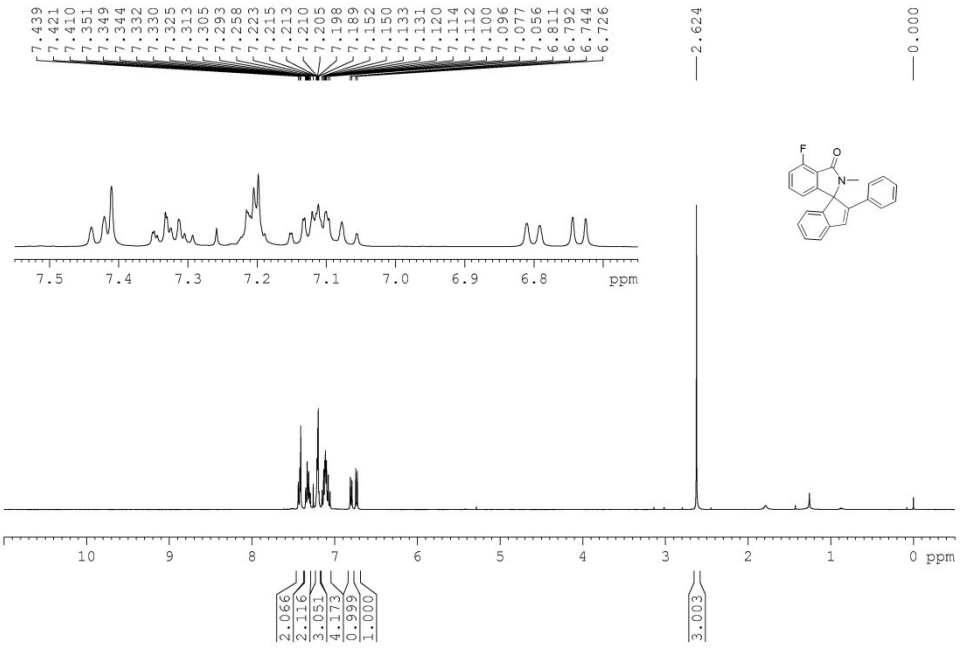


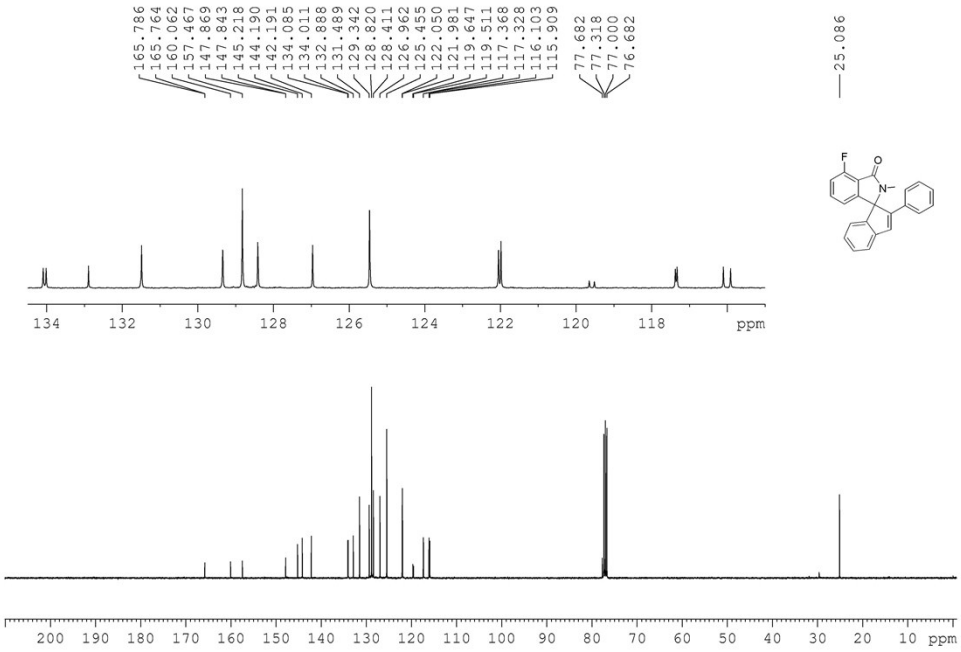
^{1}H NMR spectrum of compound 3qa



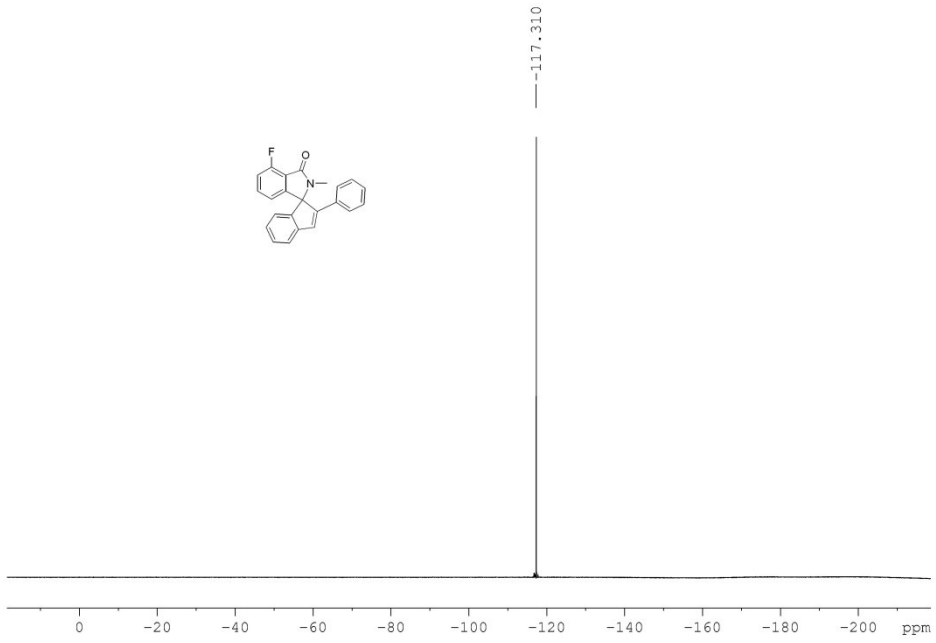
^{13}C NMR spectrum of compound 3qa



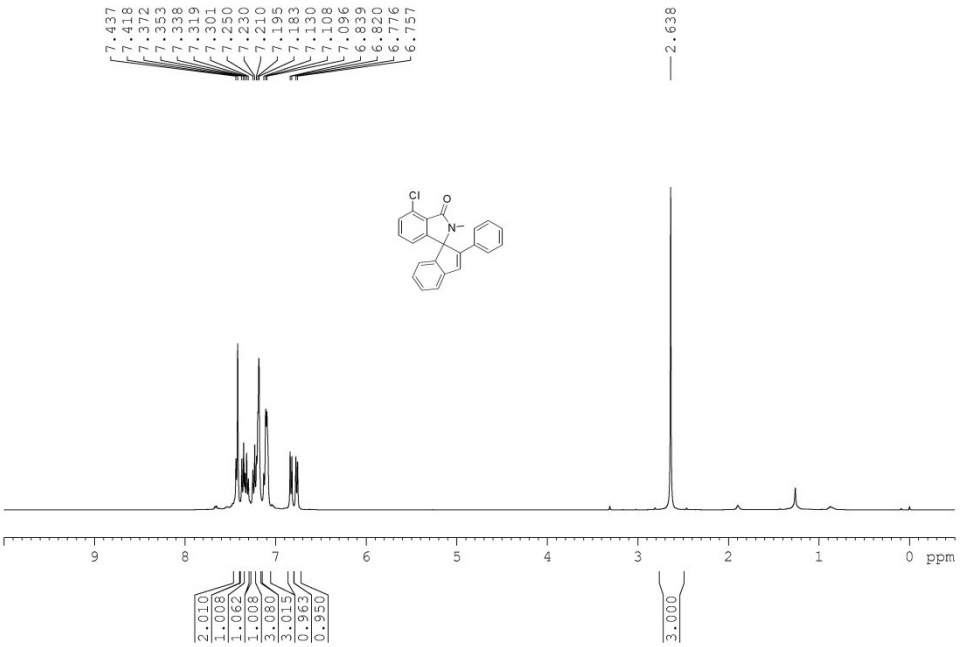
^{1}H NMR spectrum of compound 3ra



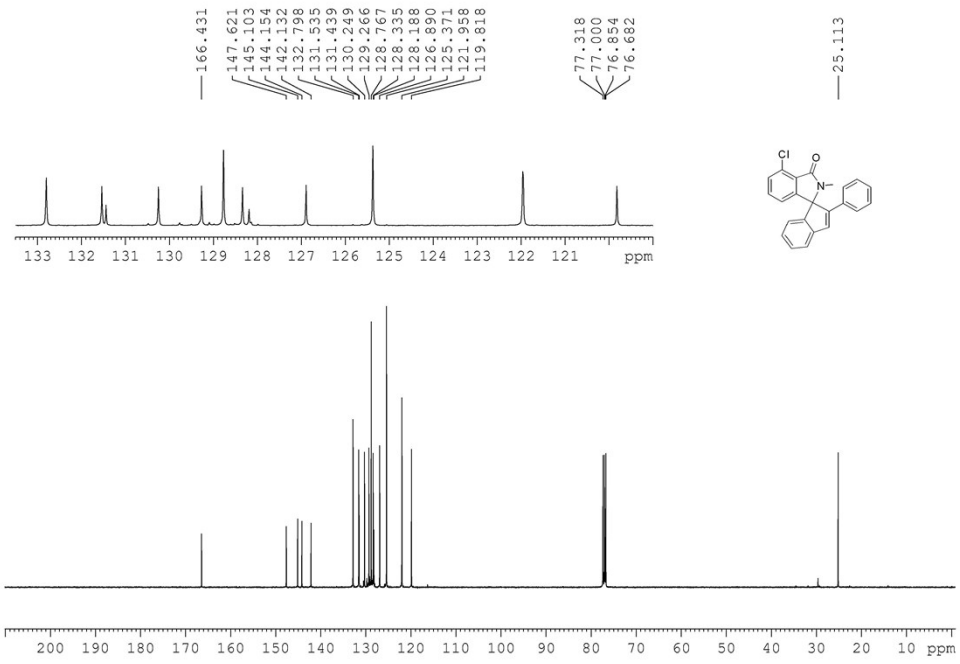
^{13}C NMR spectrum of compound 3ra



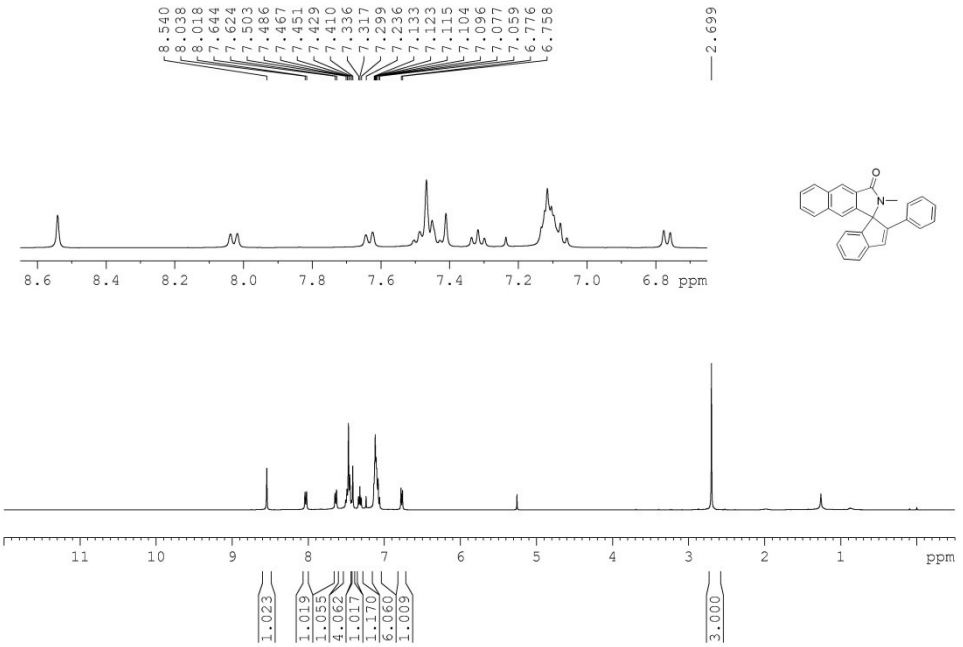
^{19}F NMR spectrum of compound 3ra



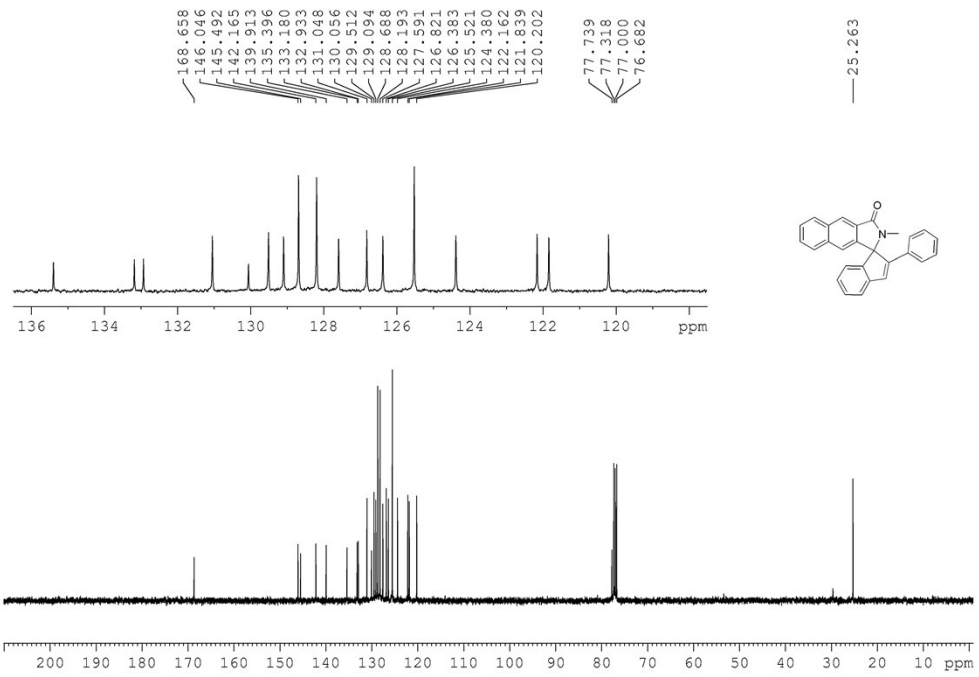
^{1}H NMR spectrum of compound 3sa



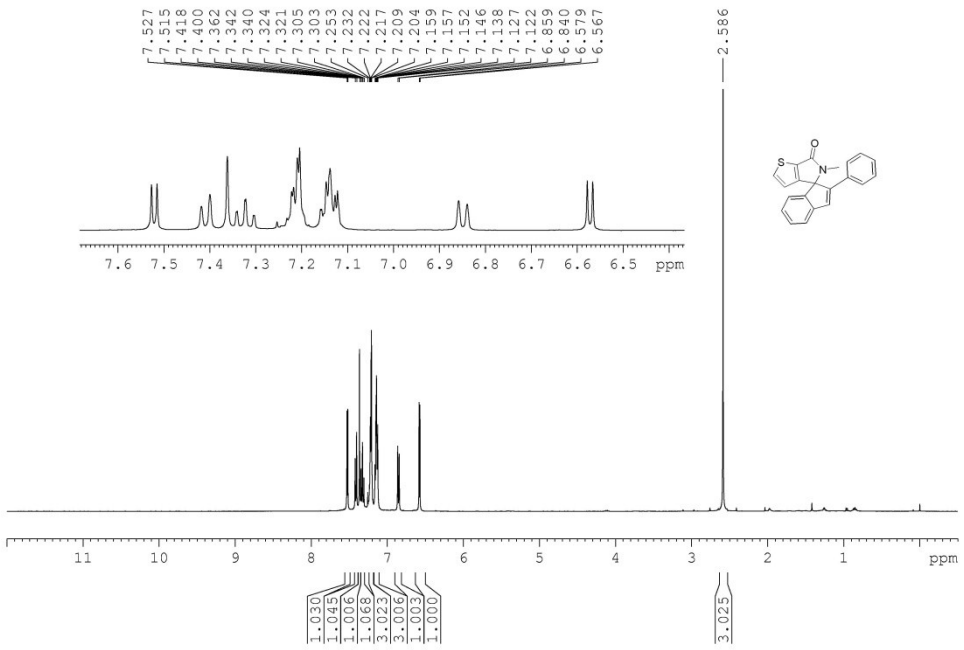
^{13}C NMR spectrum of compound 3sa



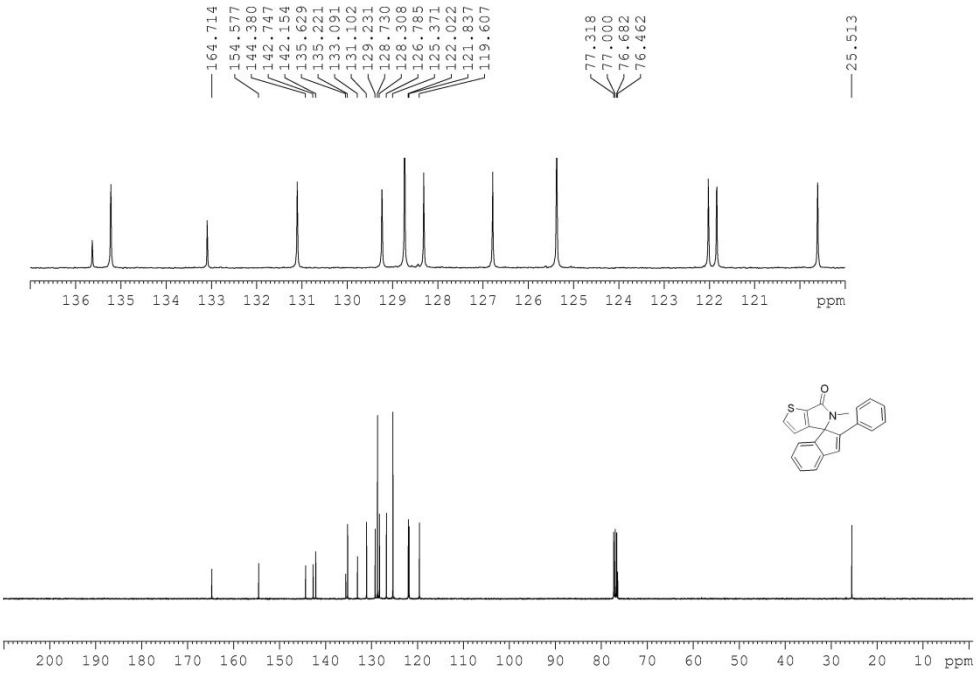
[1]H NMR spectrum of compound 3ta



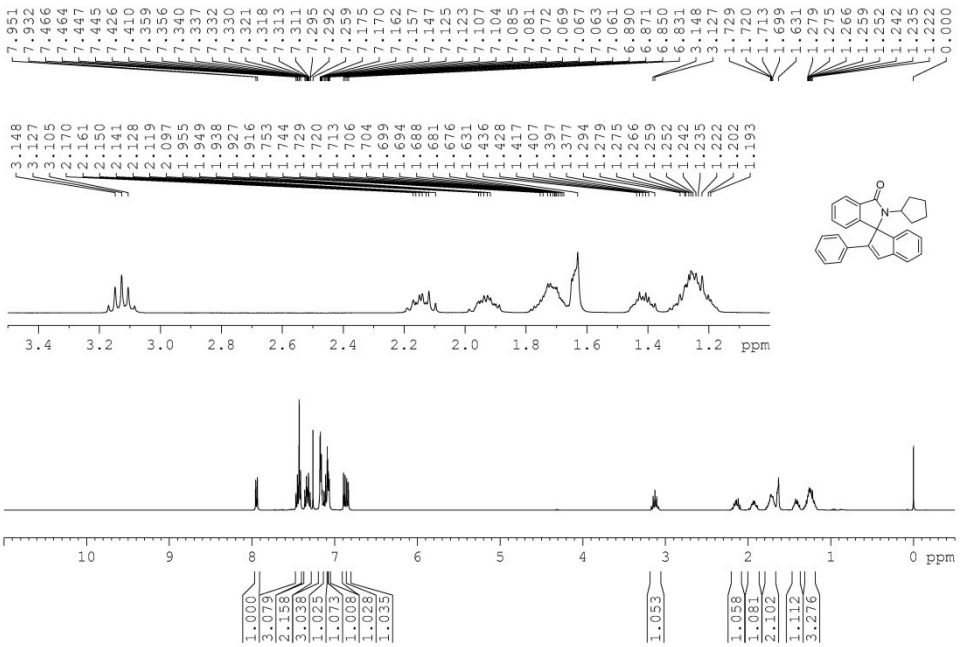
[13]C NMR spectrum of compound 3ta



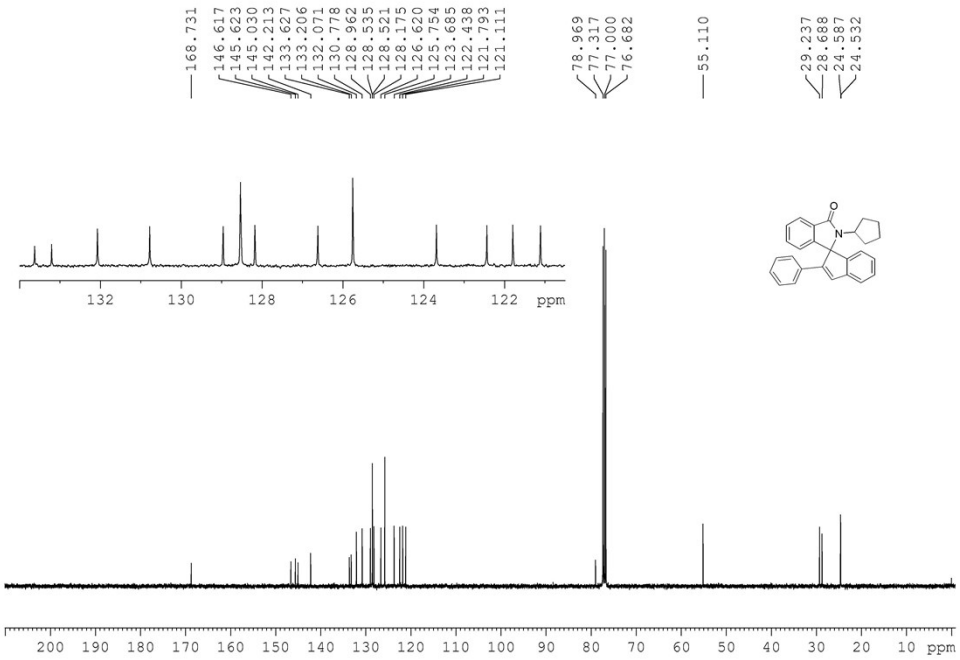
[1]H NMR spectrum of compound 3ua



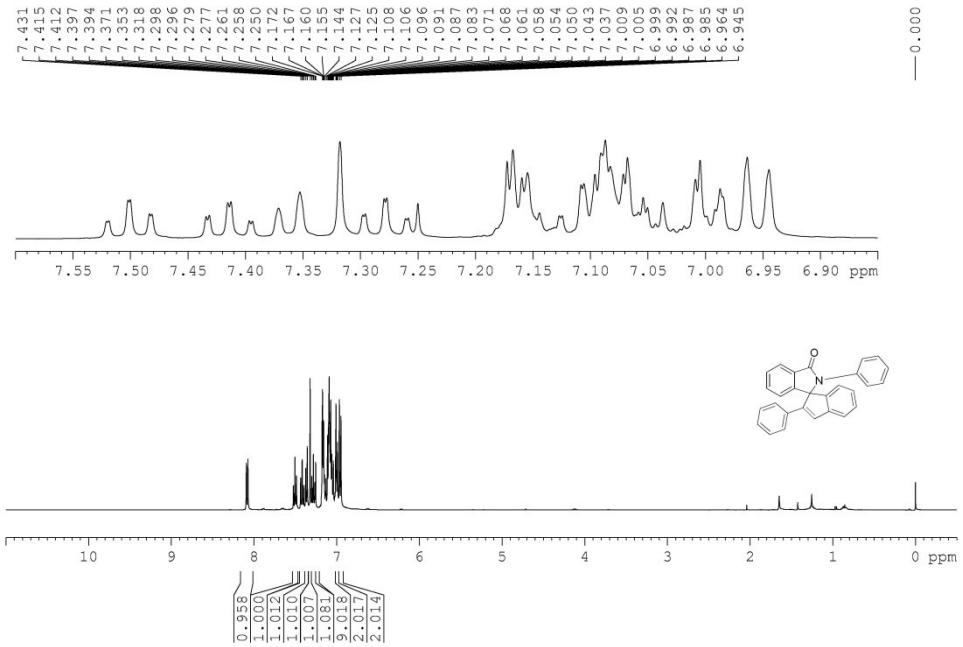
[13]C NMR spectrum of compound 3ua



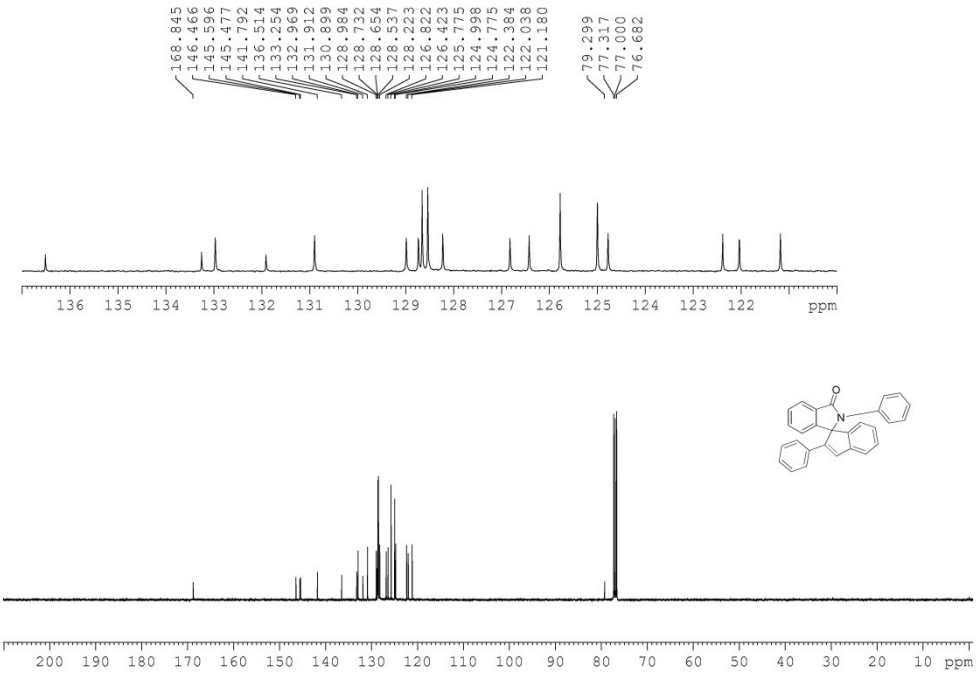
[1] H NMR spectrum of compound 3va



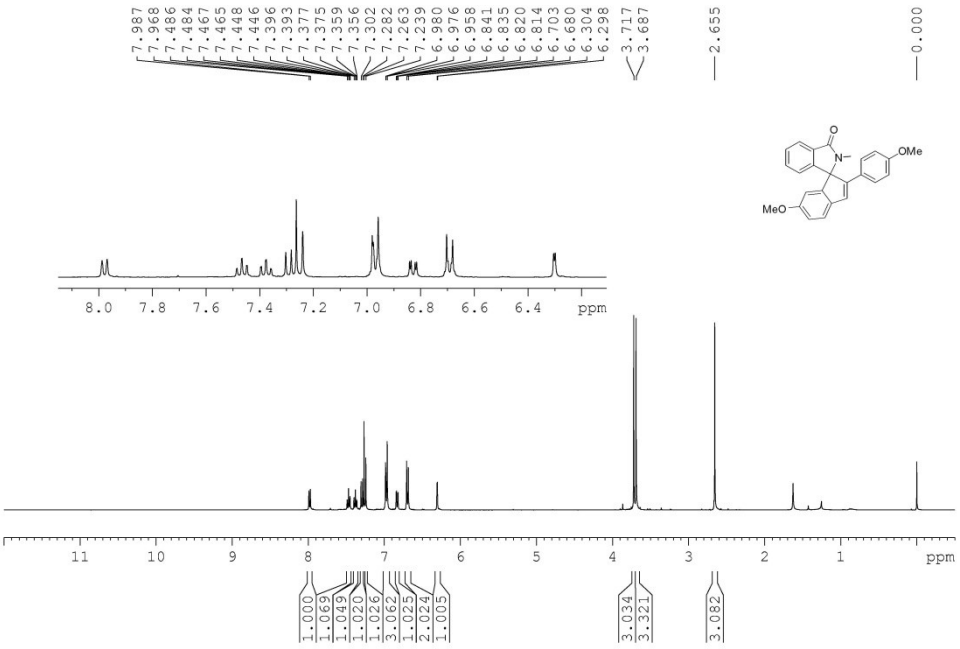
[13] C NMR spectrum of compound 3va



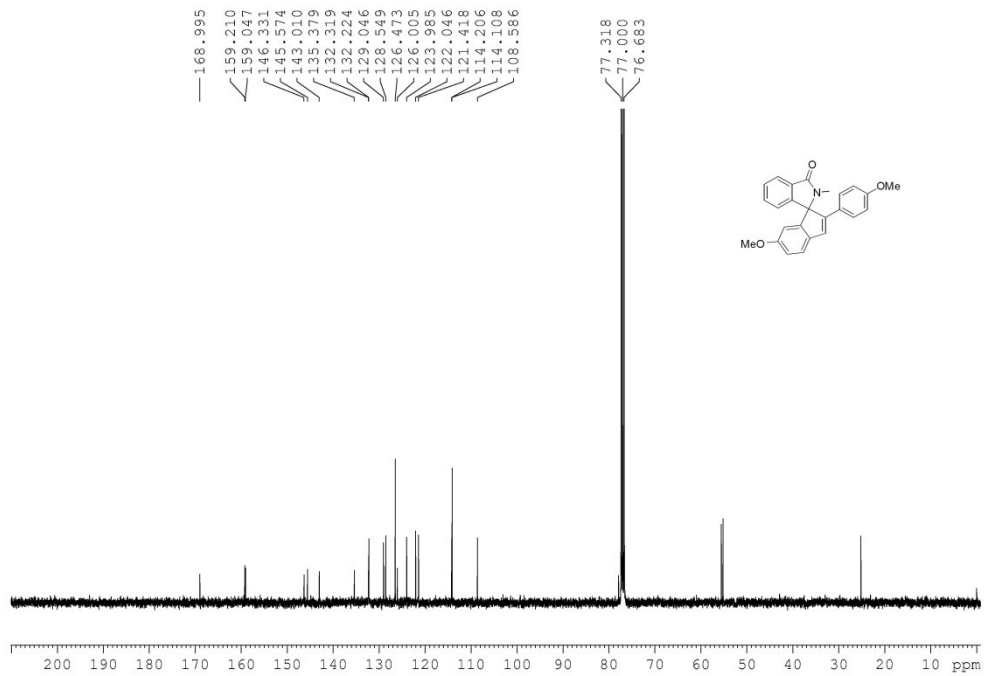
[1] H NMR spectrum of compound 3wa



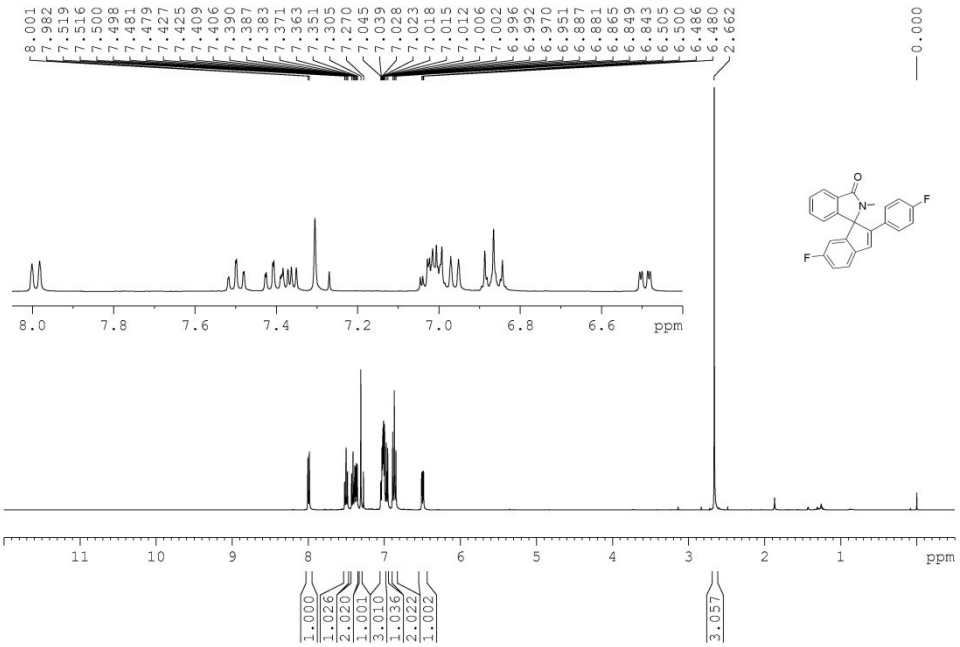
[13] C NMR spectrum of compound 3wa



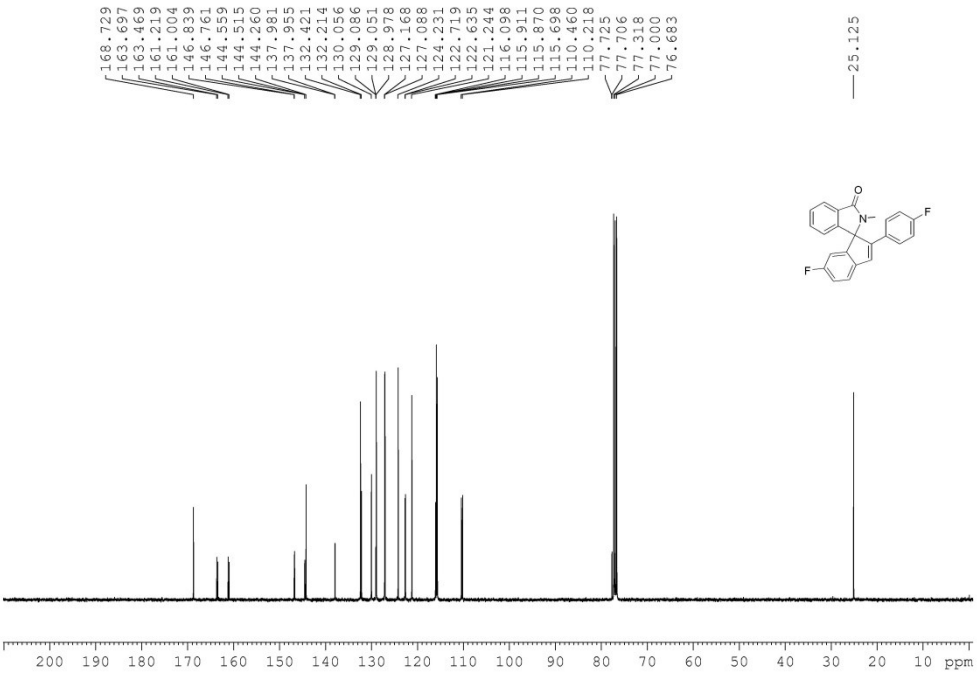
[1] H NMR spectrum of compound 3ab



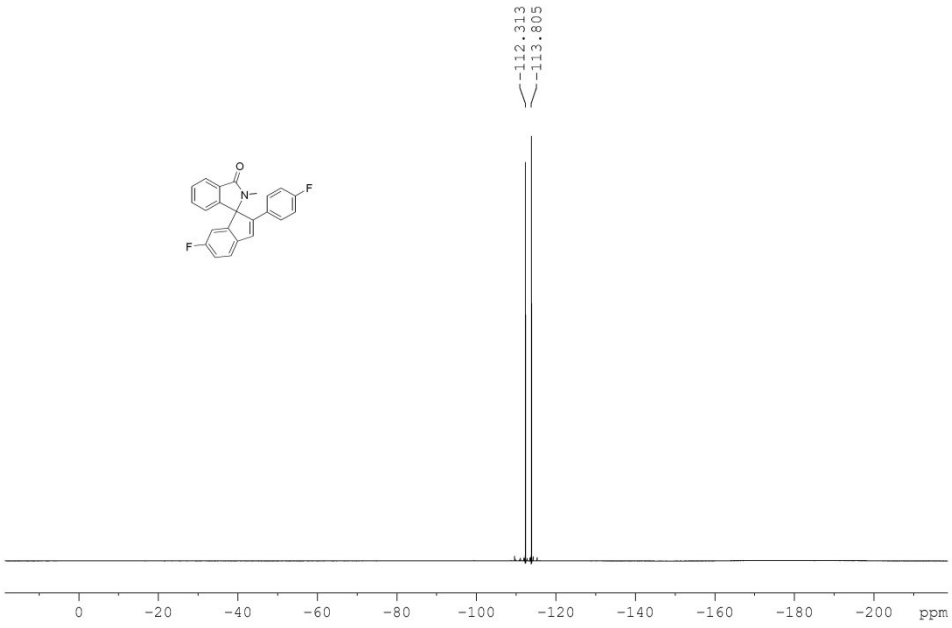
[13] C NMR spectrum of compound 3ab



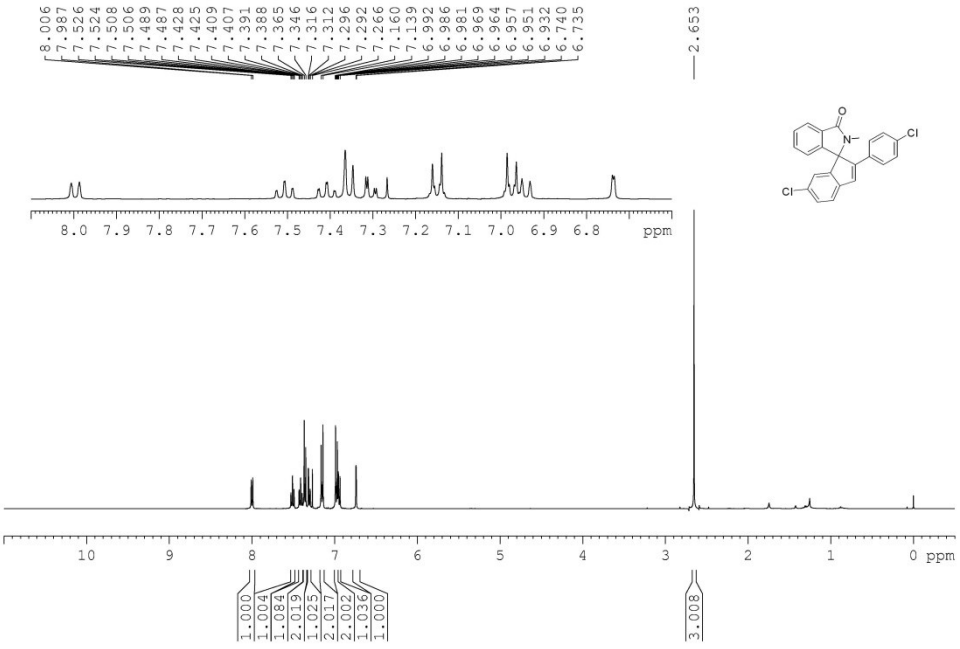
[1] H NMR spectrum of compound 3ac



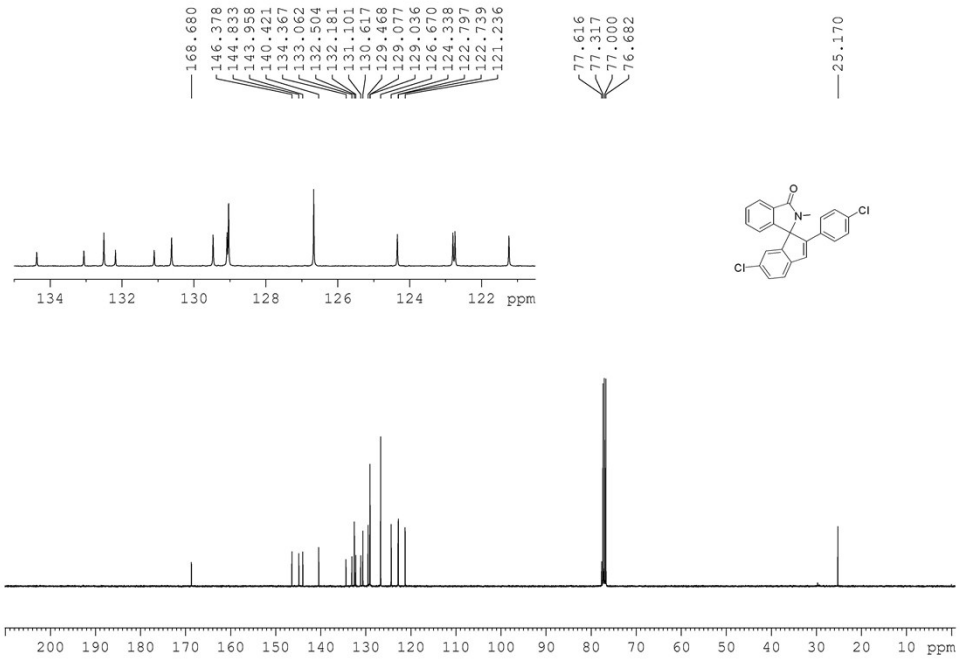
[13] C NMR spectrum of compound 3ac



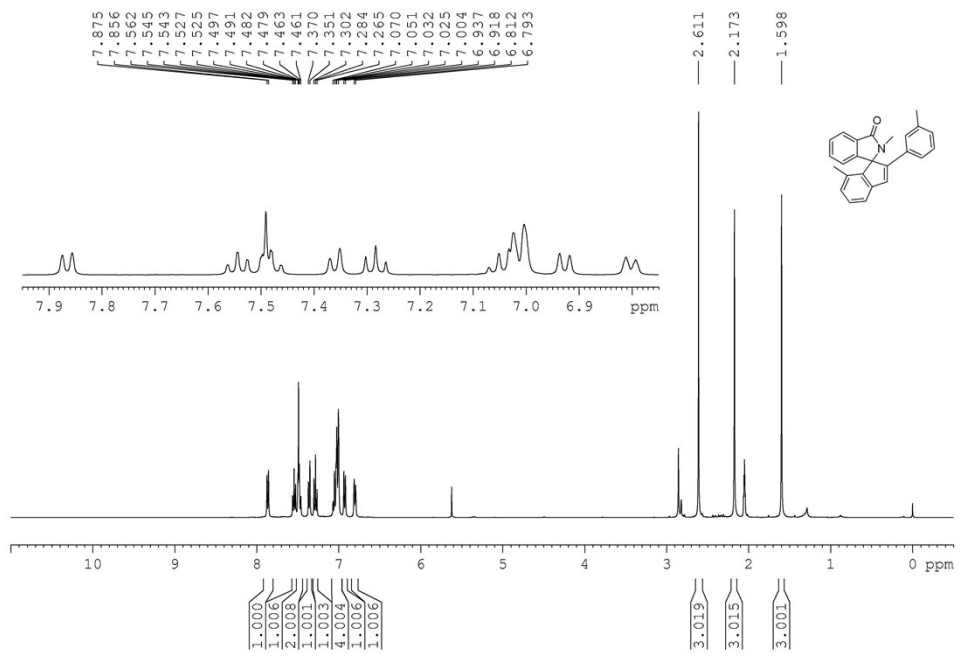
[19] F NMR spectrum of compound 3ac



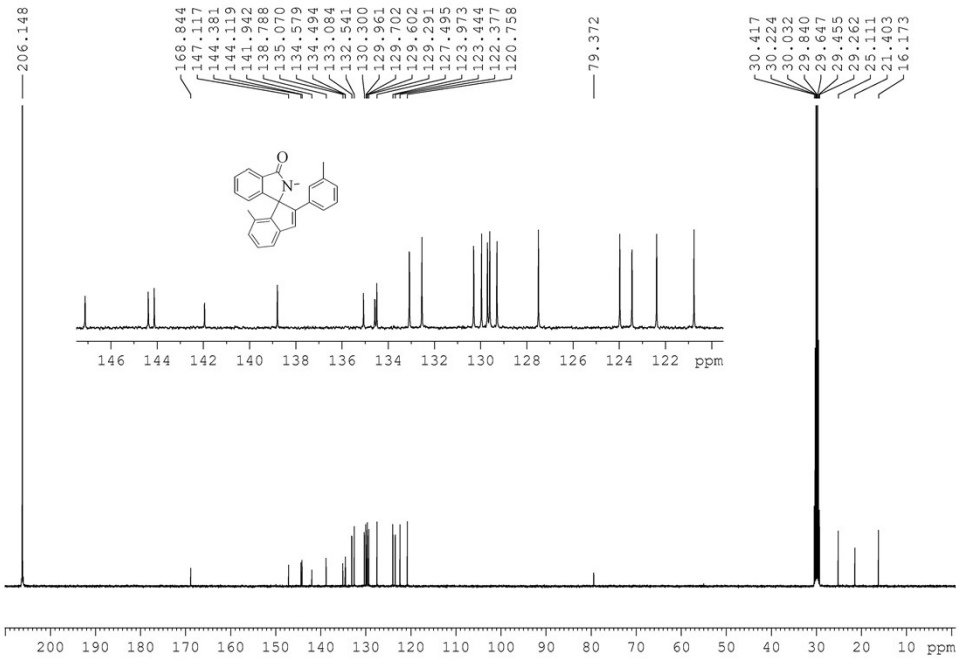
[1] H NMR spectrum of compound 3ad



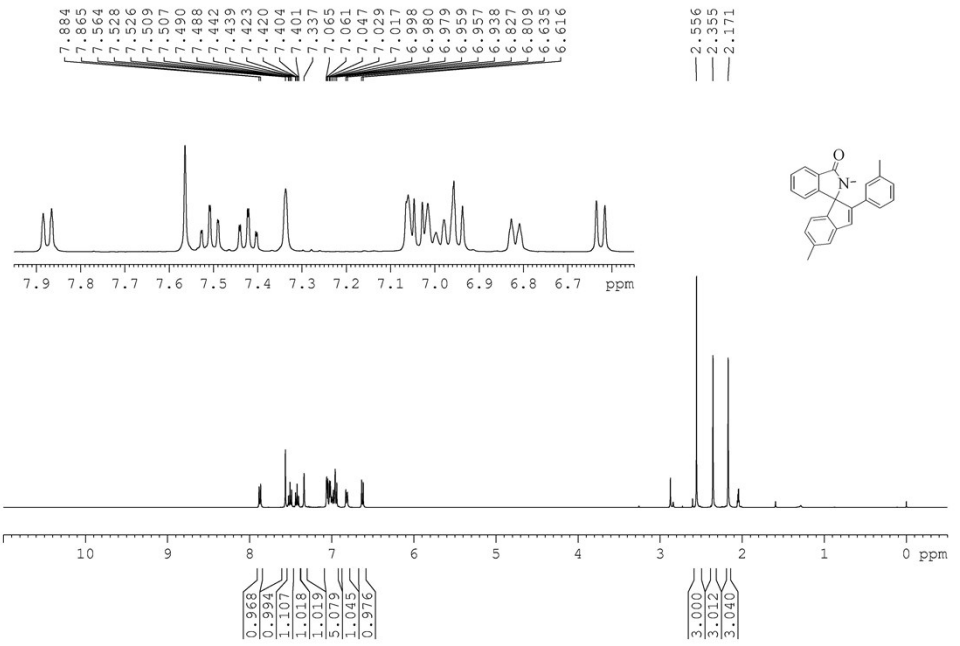
^{13} C NMR spectrum of compound 3ad



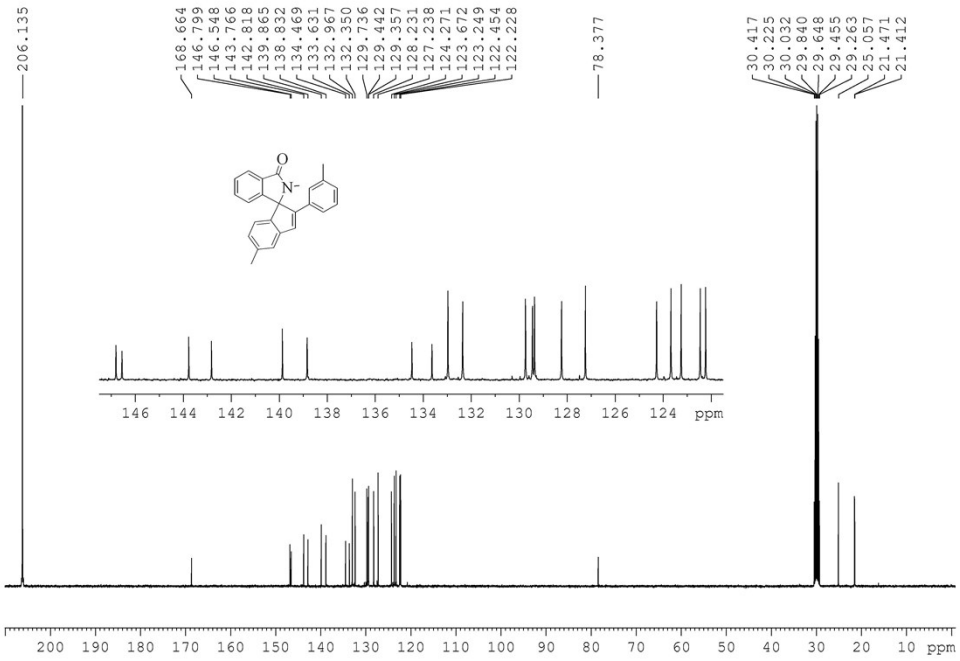
^{1} H NMR spectrum of compound 3ae



[13] C NMR spectrum of compound 3ae



[1] H NMR spectrum of compound 3ae'



^{13} C NMR spectrum of compound 3ae'