Electronic supplementary information for

Transition-metal-free oxindole synthesis: quinone-K_2CO_3 catalyzed intramolecular radical cyclization

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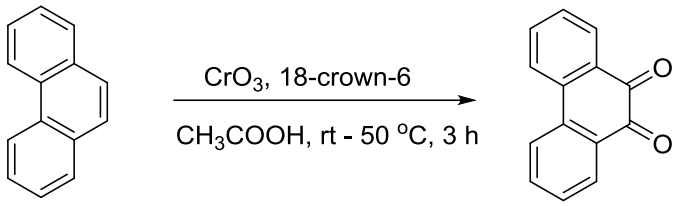
Table of Contents

General Information

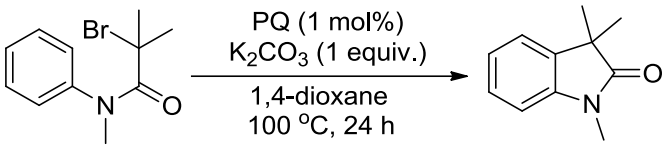
All manipulations were performed under anaerobic and anhydrous conditions by using Schlenk techniques under a dinitrogen atmosphere or in a N_2-filled glovebox, unless otherwise specified. Anhydrous Solvents were obtained with an Innovative Technology PureSolv MD5 solvent purification system or purchased from J&K (1,4-dioxane, SuperDry). The substrates α-bromoanilides (**1**), α-chloroanilide (**1a-Cl**) and α-iodoanilide (**1a-I**) were synthesized according to literature procedures.[S1,S2] ^{1}H, ^{13}C and ^{19}F NMR spectra were collected using Bruker Avance III 300 spectrometers at 298 K, and referenced internally to the residual deuterated solvent resonances. All chemical shifts (δ) were given in parts per million (ppm), and coupling constants (J) were given in hertz (Hz). Multiplicities were described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Thin layer chromatography (TLC) was carried out with glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300–400 mesh silica gel in petroleum ether (b.p. 60–90 ºC). High-resolution ESI mass spectra were obtained using an Agilent 6545 LC/Q-TOF mass spectrometer in positive ion mode, and the data were reported with ion mass-to-charge ratio (m/z) as values in atomic mass units. A single crystal of **2r** was mounted on a glass fiber attached to a copper mounting pin and placed in a low-temperature nitrogen stream.[S3] Crystallographic data were collected on a Rigaku XtaLAB PRO diffractometer with Cu Kα radiation (λ = 1.54178 Å) at 150 K. Empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[S4] All the structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions in the final structure refinement. Structure determination and refinement were carried out using the *SHELXTL* software package.[S5]

Synthesis of 9,10-Phenanthrenequinone (PQ)



A suspension of phenanthrene (1.65 g, 9.25 mmol) in acetic acid (14.3 mL) was added to a solution of CrO_3 (3.70 g, 37 mmol) and 18-crown-6 (367 mg, 1.38 mmol) in acetic acid (27.7 mL) slowly at room temperature. The resulting mixture was stirred for 2.5 hours at 50 ℃. Then, additional amount of CrO_3 (1.35 g, 18.5 mmol) was added. After being stirred for another 30 minutes, the resulting mixture was extracted by CH_2Cl_2. The organic extracts was washed with H_2O and a saturated aqueous solution of $NaHCO_3$. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from hexane to afford 9,10-phenanthrenequinone (1.80 g, 8.64 mmol, 93%) as yellow needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 7.8 Hz), 8.03 (2H, d, J = 8.0 Hz), 7.73 (2H, t, J = 7.8 Hz), 7.48 (2H, t, J = 7.7 Hz). The ^{1}H NMR data was identical with that reported in the literature.[S6]

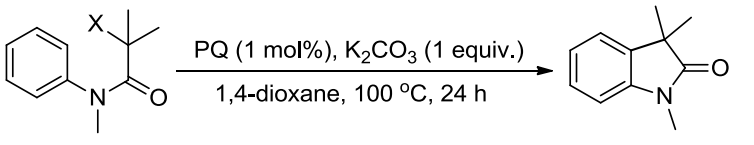
General Procedures for the PQ-Catalyzed Oxindole Synthesis



1 **2**

In a nitrogen-filled glovebox, α-bromoanilide **1** (0.3 mmol, 1.0 equiv.), PQ (1 mol%), K_2CO_3 (0.3 mmol, 1.0 equiv.) and 1,4-dioxane (2 mL) were added to a 25 mL pressure tube equipped with a magnetic stir bar. The tube was sealed, taken out of the glovebox and heated at 100 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure to remove all volatiles. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford the desired compound.

Procedure for the synthesis of **2a** with other α-haloanilides:

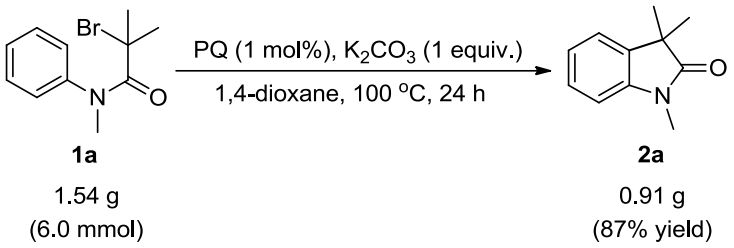


1a-X **2a**

X = Cl (87% yield)
X = I (89% yield)

In a nitrogen-filled glovebox, α-chloroanilide **1a-Cl** or α-iodoanilide **1a-I** (0.3 mmol, 1.0 equiv.), PQ (1 mol%), K_2CO_3 (0.3 mmol, 1.0 equiv.) and 1,4-dioxane (2 mL) were added to a 25 mL pressure tube equipped with a magnetic stir bar. The tube was sealed, taken out of the glovebox and heated at 100 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure to remove all volatiles. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **2a** in 87% or 89% yields, respectively.

Procedure for the gram-scale synthesis of **2a**:

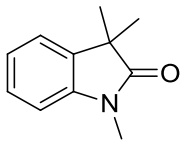


1a
1.54 g
(6.0 mmol)

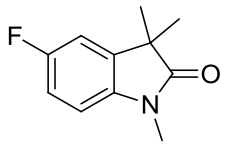
2a
0.91 g
(87% yield)

In a nitrogen-filled glovebox, α-bromoanilide **1a** (1.54 g, 6.0 mmol), PQ (1 mol%), K_2CO_3 (0.82 g, 6.0 mmol) and 1,4-dioxane (30 mL) were added to a 50 mL pressure tube equipped with a magnetic stir bar. The tube was sealed, taken out of the glovebox and heated at 100 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure to remove all volatiles. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford compound **2a** as a yellow oil. Yield: 0.914 g (87%).

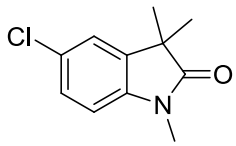
Characterization of Oxindole Products



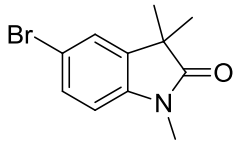
1,3,3-Trimethylindolin-2-one (**2a**):[S7] Colorless oil (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.3 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 142.6, 135.8, 127.7, 122.5, 122.2, 108.0, 44.2, 26.2, 24.4.



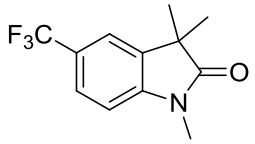
5-Fluoro-1,3,3-trimethylindolin-2-one (**2b**):[S7] Yellow solid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93–6.88 (m, 2H), 6.74–6.70 (m, 1H), 3.16 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.0, 159.4 (d, $^{1}J_{CF}$ = 240.2 Hz), 138.5, 137.5 (d, $^{3}J_{CF}$ = 7.8 Hz), 113.7 (d, $^{2}J_{CF}$ = 23.4 Hz), 110.5 (d, $^{2}J_{CF}$ = 24.5 Hz), 108.5 (d, $^{3}J_{CF}$ = 8.1 Hz), 44.6, 26.3, 24.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –120.9.



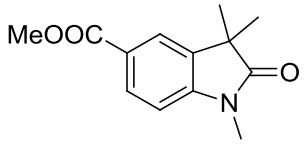
5-Chloro-1,3,3-trimethylindolin-2-one (**2c**):[S8] Yellow solid (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (dd, J = 8.2, 1.8 Hz, 1H), 7.14 (d, J = 1.7 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 3.16 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.8, 141.2, 137.5, 127.8, 127.6, 122.9, 109.0, 44.4, 26.3, 24.3.



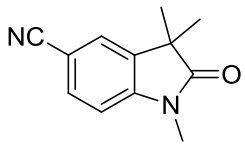
5-Bromo-1,3,3-trimethylindolin-2-one (**2d**):[S8] White solid (98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (dd, J = 8.2, 2.0 Hz, 1H), 7.29 (d, J = 1.9 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 3.18 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.7, 141.7, 137.9, 130.5, 125.7, 115.2, 109.5, 44.4, 26.3, 24.3.



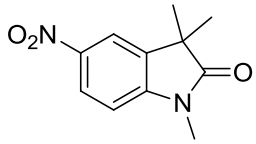
1,3,3-Trimethyl-5-(trifluoromethyl)indolin-2-one (**2e**):[S8] Yellow oil (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, J = 8.1 Hz, 1H), 7.41 (s, 1H), 6.90 (d, J = 8.1 Hz, 1H), 3.23 (s, 3H), 1.37 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.3, 145.8, 136.4, 125.6 (q, $^{3}J_{CF}$ = 4.0 Hz), 124.8 (q, $^{2}J_{CF}$ = 32 Hz), 124.6 (q, $^{1}J_{CF}$ = 270 Hz), 119.4 (q, $^{3}J_{CF}$ = 3.7 Hz), 107.8, 44.3, 26.5, 24.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –61.4.



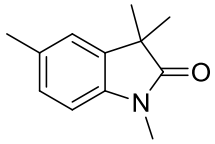
Methyl 1,3,3-trimethyl-2-oxoindoline-5-carboxylate (**2f**):[S8] Yellow solid (88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (dd, J = 8.2, 1.7 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 3.89 (s, 3H), 3.23 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.7, 167.1, 146.9, 135.8, 130.6, 124.5, 123.7, 107.7, 52.1, 44.1, 26.5, 24.3.



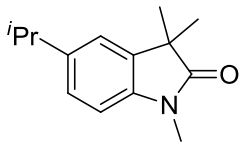
1,3,3-Trimethyl-2-oxoindoline-5-carbonitrile (**2g**):[S8] White solid (98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (dd, J = 8.1, 1.1 Hz, 1H), 7.42 (s, 1H), 6.89 (d, J = 8.1 Hz, 1H), 3.21 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.9, 146.6, 136.7, 133.2, 125.7, 119.3, 108.5, 105.5, 44.0, 26.5, 24.1.



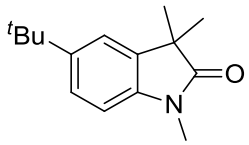
1,3,3-Trimethyl-5-nitroindolin-2-one (**2h**):[S8] Yellow solid (88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (dd, J = 8.6, 2.2 Hz, 1H), 8.06 (d, J = 2.1 Hz, 1H), 6.91 (d, J = 8.6 Hz, 1H), 3.26 (s, 3H), 1.39 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.3, 148.4, 143.5, 136.5, 125.2, 118.3, 107.7, 44.2, 26.7, 24.2.



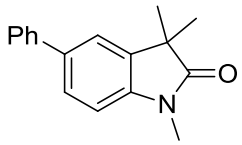
1,3,3,5-Tetramethylindolin-2-one (**2i**):[S7] Yellow oil (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04–7.01 (m, 2H), 6.71 (d, J = 7.7 Hz, 1H), 3.17 (s, 3H), 2.33 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.2, 140.1, 135.7, 131.8, 127.8, 123.0, 107.7, 44.1, 26.1, 24.3, 21.0.



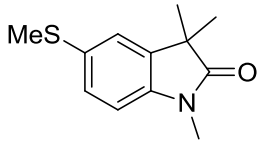
1,3,3-Trimethyl-5-(propan-2-yl)indolin-2-one (**2j**):[S7] White solid (98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 6.76 (d, J = 7.9 Hz, 1H), 3.19 (s, 3H), 2.90 (hept, J = 6.9 Hz, 1H), 1.36 (s, 6H), 1.25 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 143.4, 140.6, 135.9, 125.3, 120.5, 107.8, 44.3, 34.0, 26.2, 24.5, 24.4.



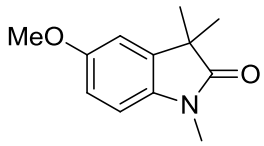
5-(tert-Butyl)-1,3,3-trimethylindolin-2-one (**2k**):[S7] White solid (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J = 8.1 Hz, 1H), 7.25 (s, 1H), 6.78 (d, J = 8.1 Hz, 1H), 3.20 (s, 3H), 1.38 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.5, 145.7, 140.3, 135.5, 124.2, 119.4, 107.4, 44.4, 34.6, 31.7, 26.2, 24.5.



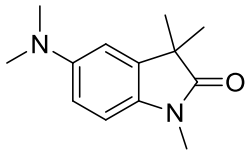
1,3,3-Trimethyl-5-phenylindolin-2-one (**2l**):[S7] Yellow oil (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 7.3 Hz, 2H), 7.52–7.42 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 142.1, 141.1, 136.4, 136.0, 128.8, 127.0, 126.9, 126.6, 121.3, 108.3, 44.4, 26.3, 24.5.



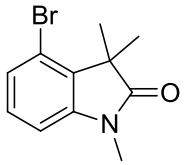
1,3,3-Trimethyl-5-(methylthio)indolin-2-one (**2m**):[S9] Colorless oil (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21–7.16 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H), 3.16 (s, 3H), 2.44 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.9, 141.0, 136.7, 131.3, 127.9, 123.1, 108.5, 44.3, 26.3, 24.3, 17.9.



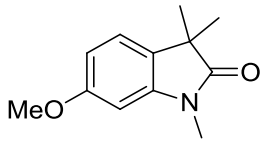
5-Methoxy-1,3,3-trimethylindolin-2-one (**2n**):[S7] Colorless oil (78% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80 (m, 1H), 6.77–6.70 (m, 2H), 3.77 (s, 3H), 3.16 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.0, 156.1, 137.2, 136.2, 111.6, 110.1, 108.3, 55.8, 44.6, 26.3, 24.4.



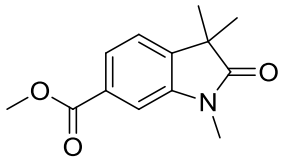
5-(Dimethylamino)-1,3,3-trimethylindolin-2-one (**2o**):[S10] Yellow oil (74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75–6.72 (m, 2H), 6.65 (dd, J = 8.5, 2.4 Hz, 1H), 3.18 (s, 3H), 2.91 (s, 6H), 1.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 147.8, 137.0, 133.9, 112.0, 109.3, 108.4, 44.8, 41.9, 26.3, 24.7.



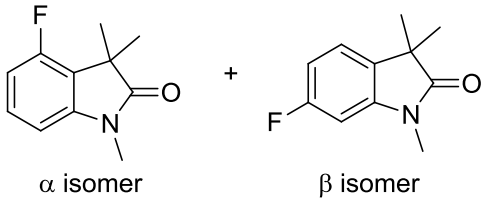
4-Bromo-1,3,3-trimethylindolin-2-one (**2p**):[S9] Colorless oil (77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16–7.08 (m, 2H), 6.77 (d, J = 7.0 Hz, 1H), 3.19 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.8, 144.7, 133.3, 129.2, 126.8, 118.8, 107.1, 46.5, 26.5, 21.4.



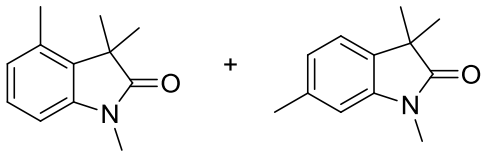
6-Methoxy-1,3,3-trimethylindolin-2-one (**2q**): Colorless oil (47% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (d, J = 8.1 Hz, 1H), 6.55 (dd, J = 8.1, 2.3 Hz, 1H), 6.43 (d, J = 2.3 Hz, 1H), 3.82 (s, 3H), 3.18 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.1, 160.0, 144.0, 128.0, 122.8, 106.2, 96.3, 55.7, 43.8, 26.3, 24.7. HRMS calcd for $C_{12}H_{16}NO_2$: 206.1181 $[M+H]^+$, found: 206.1181.



Methyl 1,3,3-trimethyl-2-oxoindoline-6-carboxylate (**2r**): Colorless oil (41% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (dd, J = 7.7, 1.4 Hz, 1H), 7.49 (d, J = 1.2 Hz, 1H), 7.26 (d, J = 7.7 Hz, 1H), 3.93 (s, 3H), 3.25 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 167.0, 143.1, 141.2, 130.0, 124.6, 122.2, 108.8, 52.4, 44.5, 26.5, 24.3. HRMS calcd for $C_{13}H_{16}NO_3$: 234.1130 $[M+H]^+$, found: 234.1130.

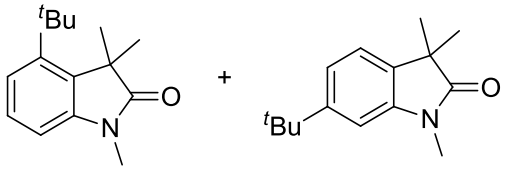


4-Fluoro-1,3,3-trimethylindolin-2-one (**2s**, α isomer) and *6-Fluoro-1,3,3-trimethylindolin-2-one* (**2s**, β isomer):[S11] White solid (95% yield in total, α:β = 1.8:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23–7.16 (m, 1.8H, α), 7.09 (dd, J = 8.1, 5.3 Hz, 1H, β), 6.72–6.66 (m, 2.8H, α + β), 6.62 (d, J = 7.8 Hz, 1.8H, α), 6.55 (dd, J = 8.9, 2.3 Hz, 1H, β), 3.18 (s, 5.5H, α), 3.16 (s, 3H, β), 1.43 (s, 11H, α), 1.32 (s, 6H, β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.6, 180.7, 162.8 (d, $^{1}J_{CF}$ = 243.9 Hz), 159.0 (d, $^{1}J_{CF}$ = 246.9 Hz), 144.8 (d, $^{3}J_{CF}$ = 10.3 Hz), 144.1 (d, $^{3}J_{CF}$ = 11.5 Hz), 131.1 (d, $^{4}J_{CF}$ = 2.9 Hz), 129.3 (d, $^{3}J_{CF}$ = 8.6 Hz), 123.1 (d, $^{3}J_{CF}$ = 9.7 Hz), 120.8 (d, $^{2}J_{CF}$ = 20.0 Hz), 110.2 (d, $^{2}J_{CF}$ = 21.1 Hz), 108.3 (d, $^{2}J_{CF}$ = 22.3 Hz), 104.2 (d, $^{4}J_{CF}$ = 3.1 Hz), 96.9 (d, $^{2}J_{CF}$ = 27.5 Hz), 44.2 (d, $^{3}J_{CF}$ = 2.0 Hz), 43.9, 26.6, 26.3, 24.5, 22.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –113.2, –121.9.



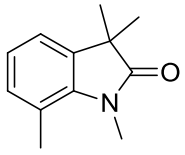
α isomer β isomer

1,3,3,4-Tetramethylindolin-2-one (**2t**, α isomer) and *1,3,3,6-Tetramethylindolin-2-one* (**2t**, β isomer):[S9] Yellow solid (69% yield in total, α:β = 2.3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (t, J = 7.8 Hz, 2.3H, α), 7.07 (d, J = 7.5 Hz, 1H, β), 6.86 (d, J = 7.6 Hz, 1H, β), 6.82 (d, J = 7.8 Hz, 2.3H, α), 6.72–6.65 (m, 3.2H, α + β), 3.19 (s, 10.1H, α + β), 2.39 (s, 6.9H, α), 2.38 (s, 3H, β), 1.44 (s, 13.8H, α), 1.34 (s, 6H, β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.7, 181.4, 142.9, 142.7, 137.7, 134.0, 133.0, 132.6, 127.5, 125.0, 122.9, 122.0, 109.0, 105.8, 45.0, 44.0, 26.3, 26.2, 24.5, 22.4, 21.8, 18.1.

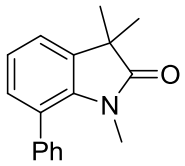


α isomer β isomer

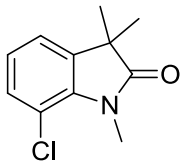
4-(tert-Butyl)-1,3,3-trimethylindolin-2-one (**2u**, α isomer) and *6-(tert-Butyl)-1,3,3-trimethylindolin-2-one* (**2u**, β isomer): Colorless oil (95% yield in total, α:β = 1:2.7). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 4.4 Hz, 2H, α), 7.12 (d, J = 7.7 Hz, 2.8H, α), 7.07 (dd, J = 7.8, 1.6 Hz, 2.7H, β), 6.86 (d, J = 1.3 Hz, 2.7H, β), 6.76 (t, J = 4.4 Hz, 1H, α), 3.22 (s, 8.1H, β), 3.21 (s, 3H, α), 1.58 (s, 6H, α), 1.46 (s, 9H, α), 1.35 (s, 16.8H, β), 1.34 (s, 23.2H, β). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.8, 181.7, 151.3, 148.8, 144.2, 142.6, 133.0, 132.2, 127.7, 122.5, 121.8, 119.3, 106.9, 105.4, 46.8, 44.0, 36.8, 35.0, 33.3, 31.6, 26.7, 26.2, 25.6, 24.5. HRMS calcd for $C_{15}H_{22}NO$: 232.1701 $[M+H]^+$, found: 232.1702.



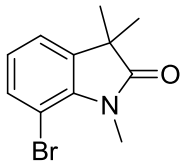
1,3,3,7-Tetramethylindolin-2-one (**2v**):[S1] Colorless oil (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05–7.01 (m, 1H), 6.97–6.90 (m, 2H), 3.48 (s, 3H), 2.56 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.0, 140.3, 136.4, 131.3, 122.4, 120.2, 119.6, 43.4, 29.5, 24.7, 19.0.



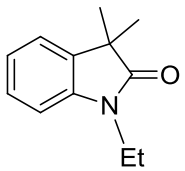
1,3,3-Trimethyl-7-phenylindolin-2-one (**2w**):[S7] Yellow solid (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.34 (m, 5H), 7.21 (dd, J = 6.0, 2.7 Hz, 1H), 7.10–7.03 (m, 2H), 2.75 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.4, 139.6, 139.1, 136.9, 130.7, 130.0, 127.8, 127.6, 125.5, 121.8, 121.4, 43.5, 30.2, 24.9.



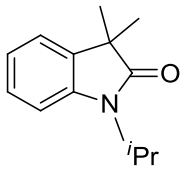
7-Chloro-1,3,3-trimethylindolin-2-one (**2x**):[S1] Colorless oil (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, J = 8.1 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 3.53 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.3, 138.5, 138.4, 129.8, 123.2, 120.7, 115.3, 43.8, 29.4, 24.5.



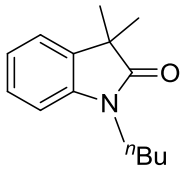
7-Bromo-1,3,3-trimethylindolin-2-one (**2y**):[S1] Colorless oil (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (dd, J = 8.2, 1.1 Hz, 1H), 7.08 (dd, J = 7.3, 1.1 Hz, 1H), 6.88–6.83 (m, 1H), 3.55 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.6, 140.0, 138.9, 133.3, 123.7, 121.4, 102.4, 43.9, 29.8, 24.7.



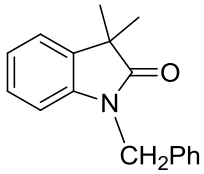
1-Ethyl-3,3-dimethylindolin-2-one (**2z**):[S7] Yellow oil (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.19 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.77 (q, J = 7.2 Hz, 2H), 1.36 (s, 6H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.9, 141.6, 136.0, 127.6, 122.4, 122.2, 108.2, 44.0, 34.5, 24.3, 12.7.



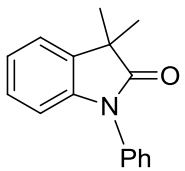
1-Isopropyl-3,3-dimethylindolin-2-one (**2aa**):[S7] Yellow oil (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.19 (m, 2H), 7.05–7.00 (m, 2H), 4.65 (hept, J = 7.0 Hz, 1H), 1.47 (d, J = 7.0 Hz, 6H), 1.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.0, 141.2, 136.4, 127.4, 122.5, 121.9, 109.9, 43.8, 43.5, 24.5, 19.4.



1-Butyl-3,3-dimethylindolin-2-one (**2ab**):[S9] Yellow oil (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23–7.17 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.69 (t, J = 7.2 Hz, 2H), 1.64 (quint, J = 7.4 Hz, 2H), 1.40–1.30 (m, 8H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.0, 141.9, 135.8, 127.4, 122.2, 122.1, 108.2, 43.9, 39.4, 29.4, 24.3, 19.9, 13.6.

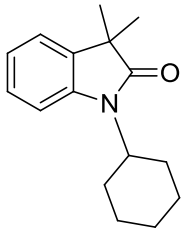


1-Benzyl-3,3-dimethylindolin-2-one (**2ac**):[S7] White solid (77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.19 (m, 6H), 7.12 (t, J = 7.6 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 4.91 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 141.7, 136.1, 135.8, 128.8, 127.6, 127.5, 127.2, 122.5, 122.3, 109.1, 44.2, 43.5, 24.6.

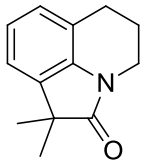


3,3-Dimethyl-1-phenylindolin-2-one (**2ad**):[S7] White solid (89% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.47 (m, 2H), 7.43–7.33 (m, 3H), 7.26 (d, J = 7.0 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 1.48 (s, 6H). ^{13}C

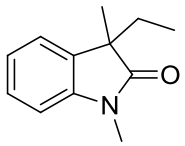
NMR (75 MHz, $CDCl_3$): δ 180.6, 142.4, 135.6, 134.6, 129.5, 127.8, 127.5, 126.5, 122.9, 122.6, 109.3, 44.3, 24.8.



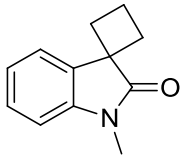
1-Cyclohexyl-3,3-dimethylindolin-2-one (**2ae**):[S9] Yellow solid (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21–7.15 (m, 2H), 7.05–6.95 (m, 2H), 4.21–4.12 (m, 1H), 2.14 (qd, J = 12.5, 3.2 Hz, 2H), 1.86 (d, J = 13.2 Hz, 2H), 1.77–1.70 (m, 2H), 1.46–1.19 (m, 4H), 1.32 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.0, 141.5, 136.2, 127.2, 122.3, 121.7, 109.9, 51.7, 43.6, 29.1, 25.9, 25.3, 24.4.



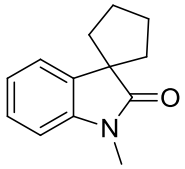
1,1-Dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (**2ag**):[S6] Yellow solid (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04–6.99 (m, 2H), 6.95–6.90 (m, 1H), 3.71 (t, J = 5.7 Hz, 2H), 2.78 (t, J = 5.9 Hz, 2H), 2.00 (quint, J = 5.8 Hz, 2H), 1.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.2, 138.4, 134.3, 126.4, 121.9, 120.1, 120.0, 45.5, 38.8, 24.6, 24.2, 21.2.



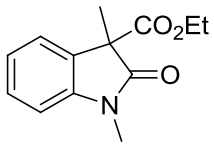
3-Ethyl-1,3-dimethylindolin-2-one (**2ah**):[S9] Yellow oil (89% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 6.5 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 1.99–1.87 (m, 1H), 1.83–1.71 (m, 1H), 1.35 (s, 3H), 0.59 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.7, 143.5, 133.9, 127.6, 122.5, 122.4, 107.8, 48.9, 31.5, 26.0, 23.3, 8.8.



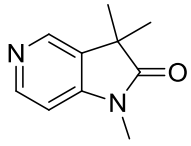
1'-Methylspiro[cyclobutane-1,3'-indolin]-2'-one (**2ai**):[S9] Colorless oil (72% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 1H), 7.25 (td, J = 7.7, 1.3 Hz, 1H), 7.09 (td, J = 7.6, 0.9 Hz, 1H), 6.77 (d, J = 7.7 Hz, 1H), 3.17 (s, 3H), 2.71–2.61 (m, 2H), 2.42–2.19 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.1, 142.9, 134.3, 127.8, 122.5, 122.2, 107.6, 48.1, 31.3, 26.1, 16.8.



1'-Methylspiro[cyclopentane-1,3'-indolin]-2'-one (**2aj**):[S9] Colorless oil (75% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.18 (m, 2H), 7.06–7.01 (m, 1H), 6.81 (d, J = 7.7 Hz, 1H), 3.20 (s, 3H), 2.17–1.94 (m, 6H), 1.86–1.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.9, 142.9, 136.8, 127.3, 122.5, 122.2, 107.7, 53.9, 38.3, 26.6, 26.2.



Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (**2ak**):[S12] Colorless oil (35% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (td, J = 7.7, 1.2 Hz, 1H), 7.28–7.23 (m, 1H), 7.07 (td, J = 7.6, 0.9 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.26 (s, 3H), 1.66 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 169.9, 143.7, 130.4, 129.1, 123.1, 123.0, 108.5, 62.1, 55.2, 26.7, 20.3, 14.0.



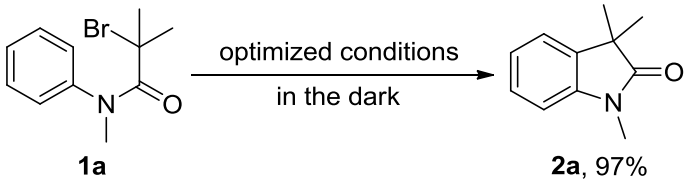
1,3-Dihydro-1,3,3-trimethyl-2H-pyrrolo[3,2-c]pyridin-2-one (**2al**):[S9] Yellow oil (84% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (dd, J = 5.1, 1.4 Hz, 1H), 7.15 (dd, J = 7.9, 5.1 Hz, 1H), 7.06 (dd, J = 7.9, 1.3 Hz, 1H), 3.21 (s, 3H), 1.41 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.0, 156.3, 142.8, 137.7, 122.6, 114.2, 44.7, 26.0, 22.6.

Mechanistic Investigations

Table S1 Isolated yields of **2a** for the PQ-catalyzed intramolecular cyclization with catalysts purchased from various vendors

Vendor	Self made	*Energy Chemical*	*J&K*	*TCI*
Yield (%)	96	90	95	84
purity	–	98%	98%	99.0%
photo				

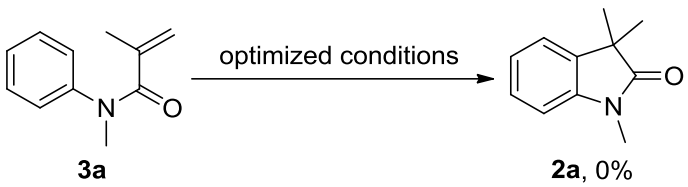
PQ-catalyzed reaction performed in the dark



1a **2a**, 97%

To a solution of **1a** (0.3 mmol, 0.0768 g) and PQ (0.62 mg, 1 mol%) in dry 1,4-dioxane (2 mL) at 100 °C under a nitrogen atmosphere was added K_2CO_3 (0.3 mmol, 0.0415 g) and stirred for 24 h. Upon completion, oxindole **2a** was detected by ^{1}H NMR in a 97% yield with 1,3,5-trimethoxybenzene as an internal standard.

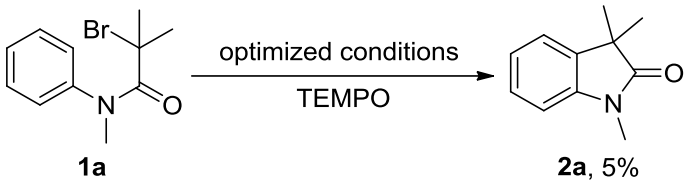
Heck-type cyclization reaction



3a **2a**, 0%

To a solution of **3a**[S7] (0.3 mmol, 0.0526 g) and PQ (0.62 mg, 1 mol%) in dry 1,4-dioxane (2 mL) at 100 °C under a nitrogen atmosphere was added K_2CO_3 (0.3 mmol, 0.0415 g) and stirred for 24 h. Upon completion, no desired product of **2a** was detected by ^{1}H NMR.

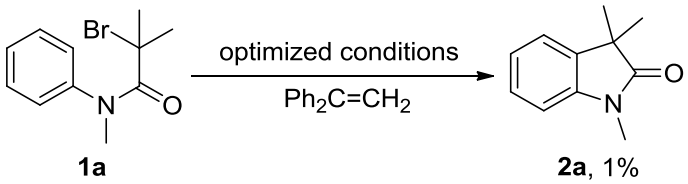
Radical trapping experiment with TEMPO



1a **2a**, 5%

To a solution of **1a** (0.3 mmol, 0.0768 g), TEMPO (46.9 mg, 1 equiv) and PQ (0.62 mg, 1 mol%) in dry 1,4-dioxane (2 mL) at 100 °C under a nitrogen atmosphere was added K_2CO_3 (0.3 mmol, 0.0415 g) and stirred for 24 h. Upon completion, only a minimal amount of oxindole **2a** (5%) was detected by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

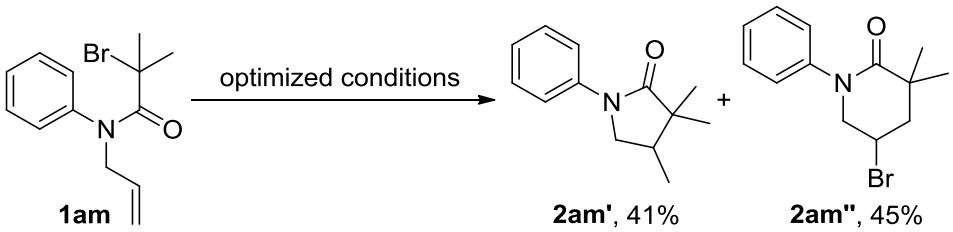
Radical trapping experiment with 1,1-diphenylethylene



1a **2a**, 1%

To a solution of **1a** (0.3 mmol, 0.0768 g), 1,1-diphenylethylene (54.1 mg, 1 equiv) and PQ (0.62 mg, 1 mol%) in dry 1,4-dioxane (2 mL) at 100 °C under a nitrogen atmosphere was added K_2CO_3 (0.3 mmol, 0.0415 g) and stirred for 24 h. Upon completion, only trace amount of oxindole **2a** (1%) was detected by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

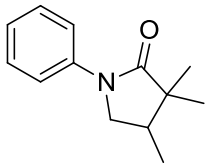
Using *N*-allyl substrate 1ag for PQ-catalyzed cyclization



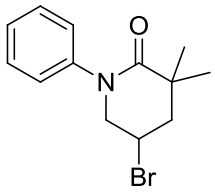
1am **2am'**, 41% **2am''**, 45%

To a solution of α-bromoanilide **1am** (0.3 mmol, 0.0847 g) and PQ (0.62 mg, 1 mol%) in dry 1,4-dioxane (2 mL) at 100 °C under a nitrogen atmosphere was added K_2CO_3 (0.3 mmol, 0.0415 g) and stirred for 24 h. Upon completion, the residue was

purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20:1 as the eluent) to afford the products **2am'** and **2am''** in 41% and 45% yield, respectively.



3,3,4-Trimethyl-1-phenyl-2-pyrrolidinone (**2ag**):[S9] white solid (41% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 3.78 (dd, J = 9.4, 7.6 Hz, 1H), 3.38 (t, J = 9.3 Hz, 1H), 2.25–2.16 (m, 1H), 1.22 (s, 3H), 1.09 (d, J = 6.9 Hz, 3H), 1.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 179.4, 139.9, 128.9, 124.3, 119.7, 52.4, 44.8, 37.8, 23.8, 18.5, 12.5.



5-Bromo-3,3-dimethyl-1-phenyl-2-piperidinone (**2ag'**):[S9] white solid (45% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 3.99 (dd, J = 9.9, 7.6 Hz, 1H), 3.60–3.53 (m, 2H), 3.39 (t, J = 10.5 Hz, 1H), 2.62–2.54 (m, 1H), 1.32 (s, 3H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.7, 139.4, 129.0, 124.7, 119.8, 50.6, 45.5, 45.3, 31.3, 24.5, 18.6.

NMR Spectra of Oxindole Products

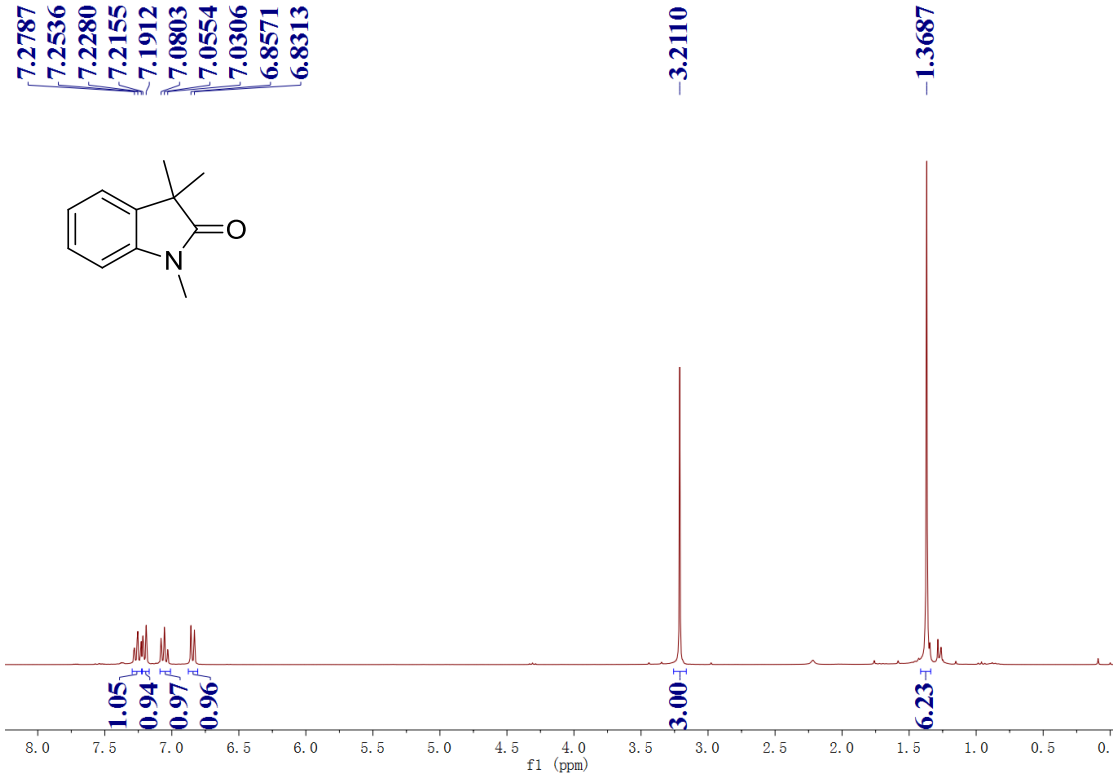


Fig. S1 ^{1}H NMR spectrum of **2a** in $CDCl_3$.

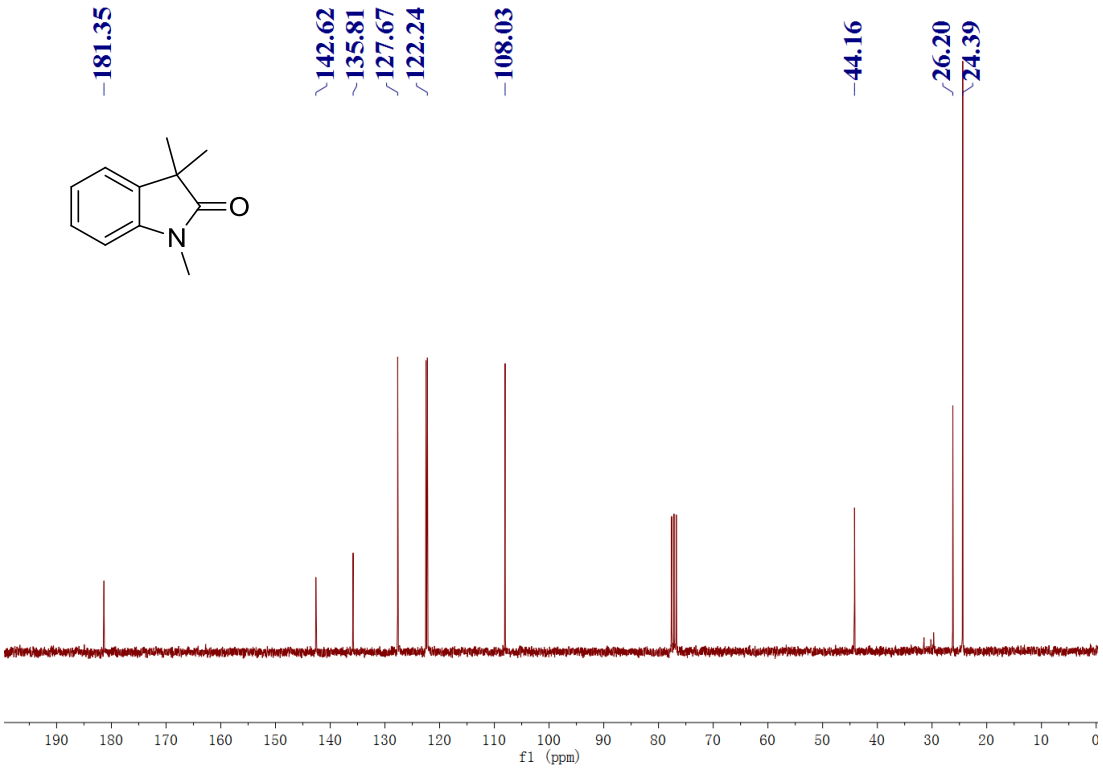


Fig. S2 ^{13}C NMR spectrum of **2a** in $CDCl_3$.

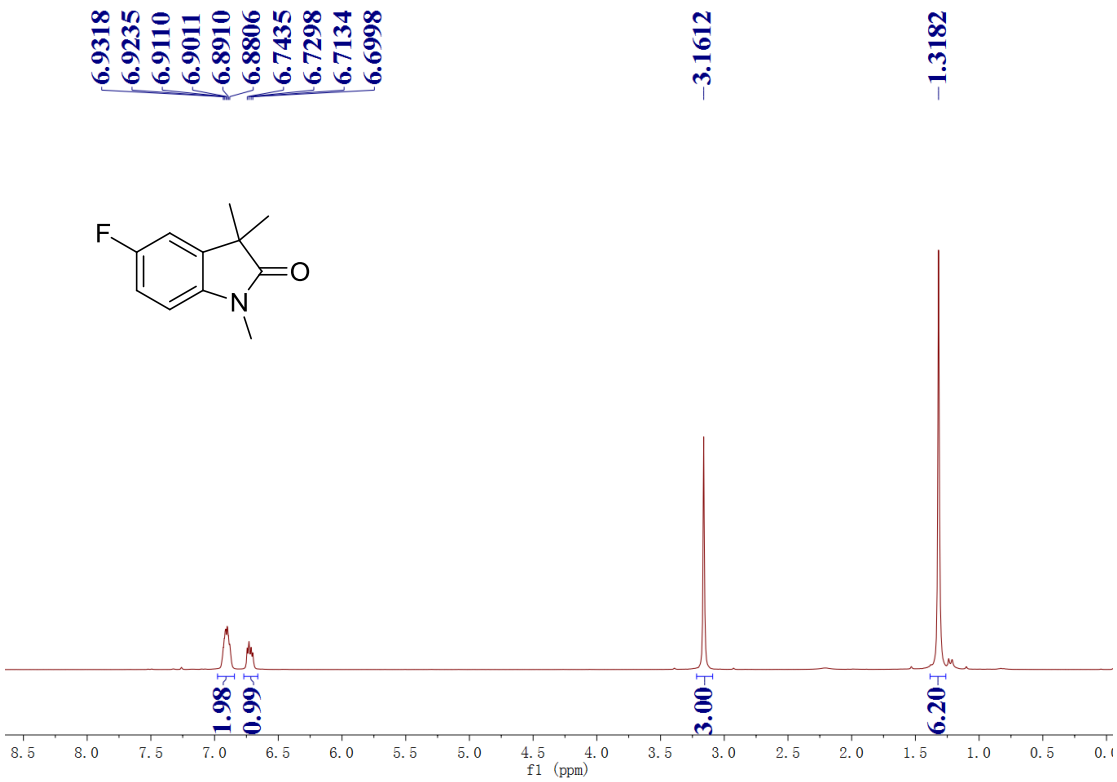


Fig. S3 ^{1}H NMR spectrum of **2b** in $CDCl_3$.

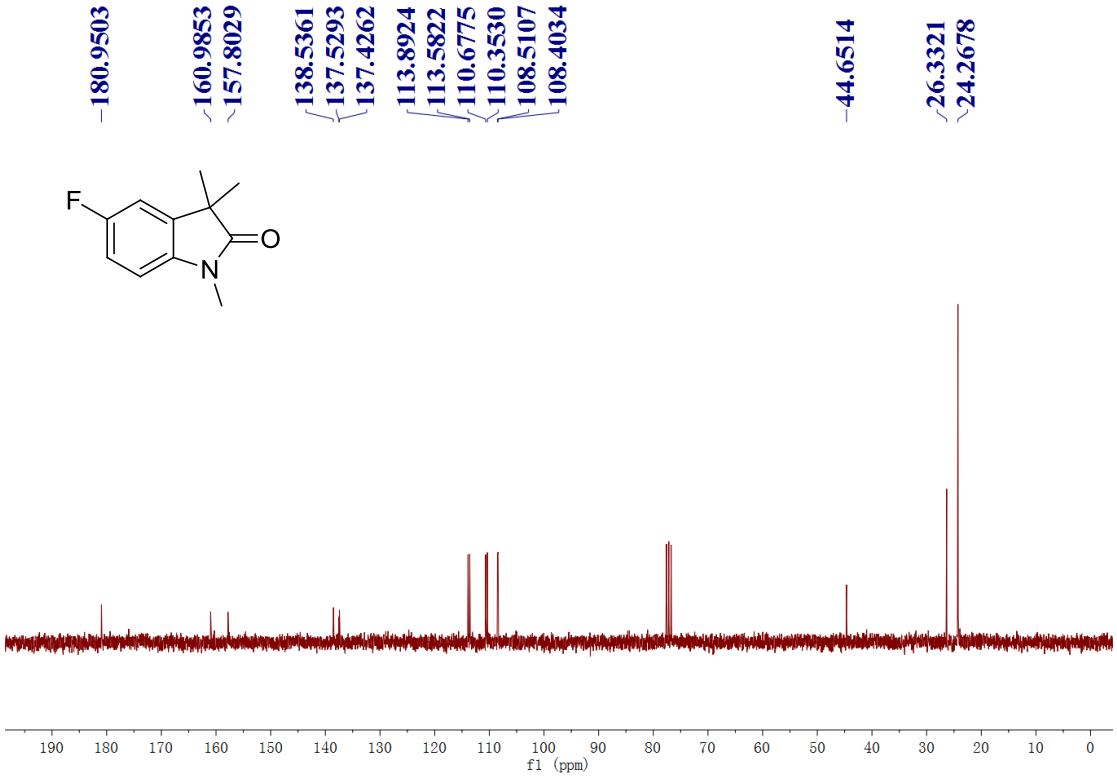


Fig. S4 ^{13}C NMR spectrum of **2b** in $CDCl_3$.

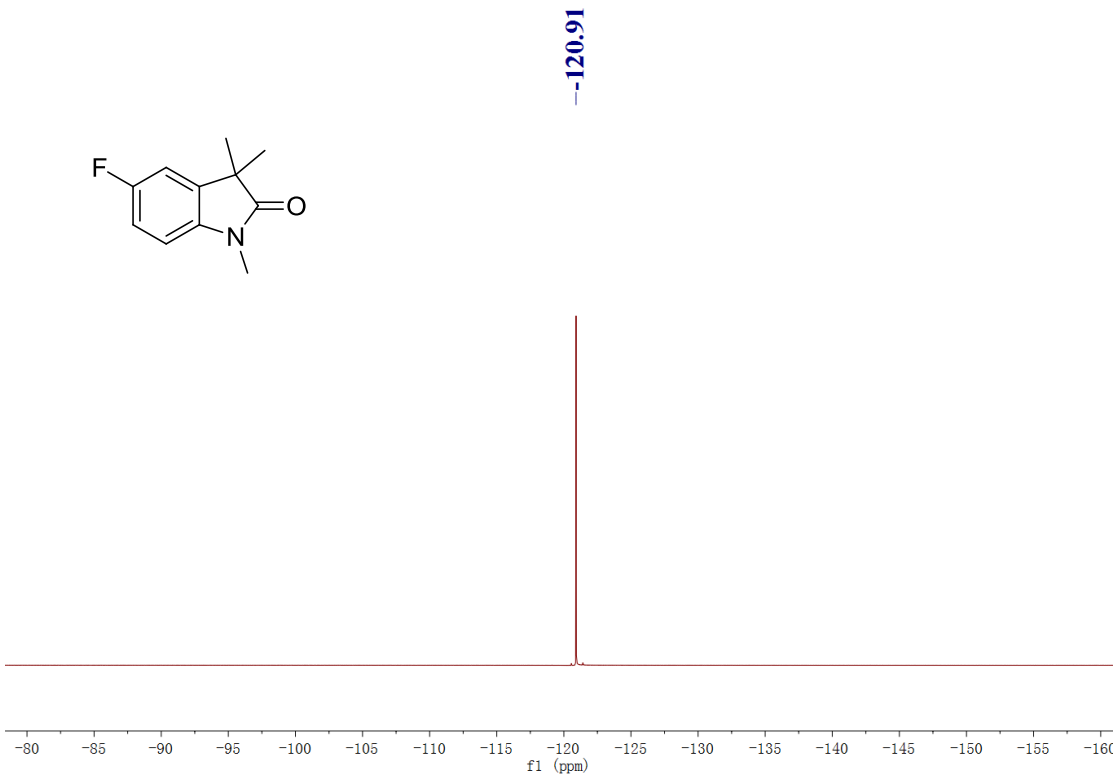


Fig. S5 ^{19}F NMR spectrum of **2b** in $CDCl_3$.

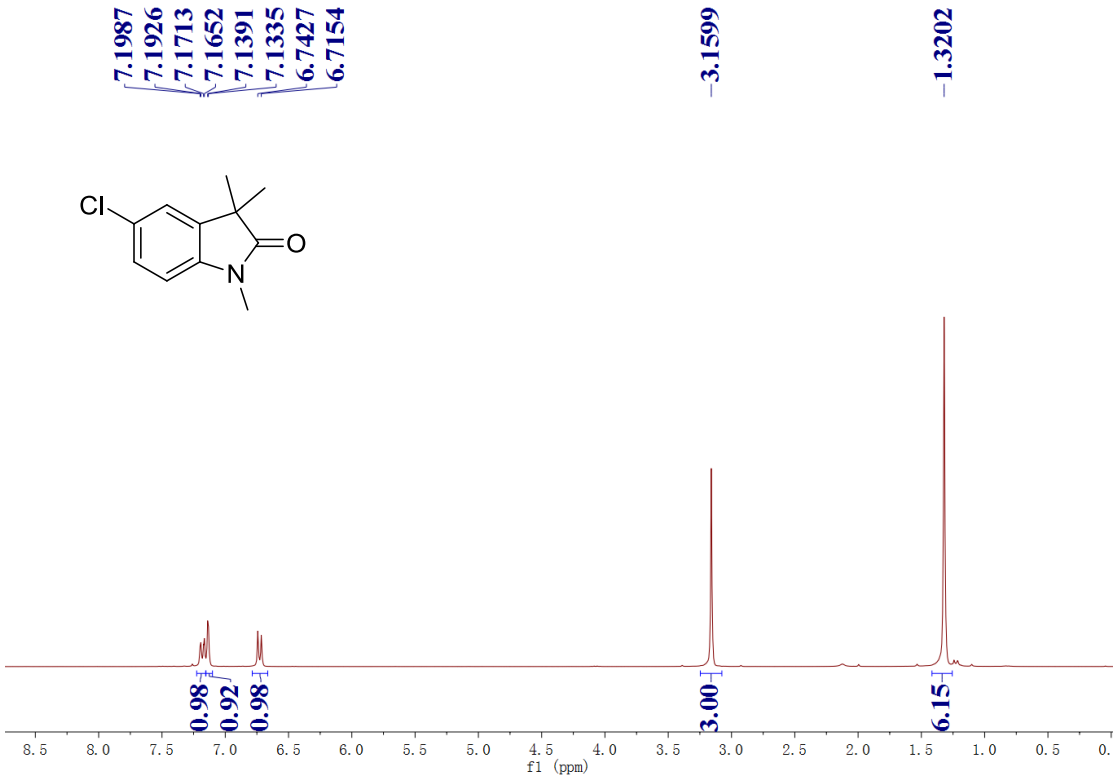


Fig. S6 ^{1}H NMR spectrum of **2c** in $CDCl_3$.

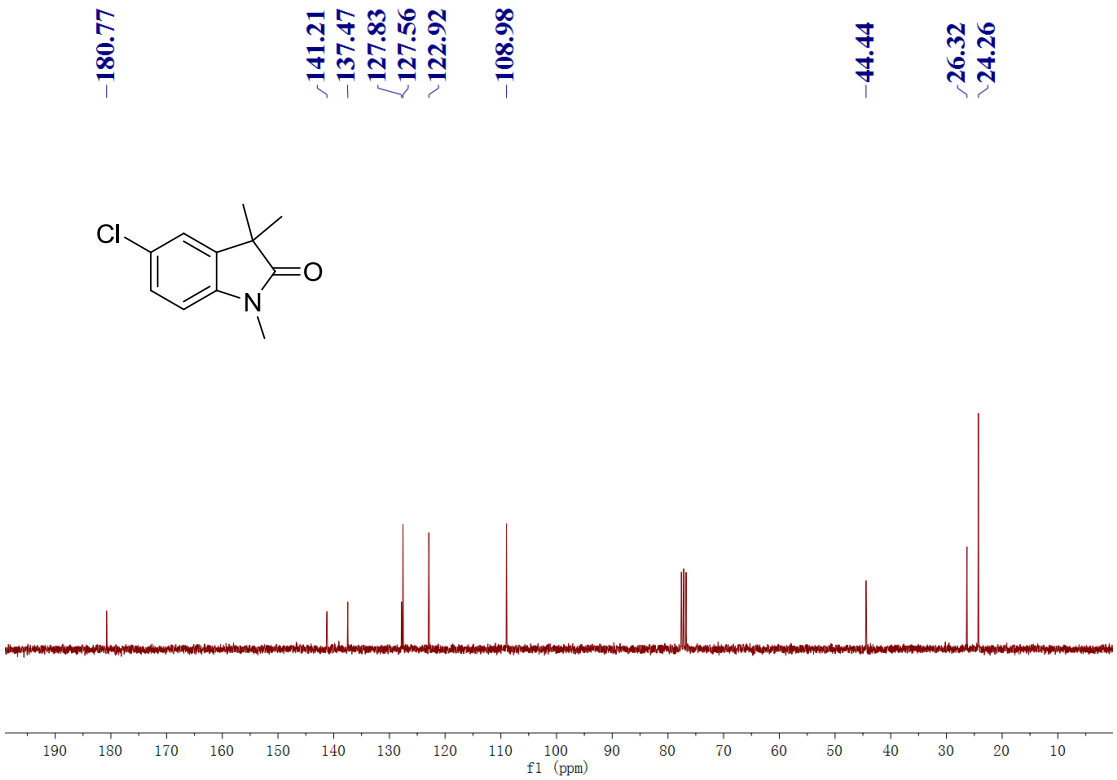


Fig. S7 ^{13}C NMR spectrum of **2c** in $CDCl_3$.

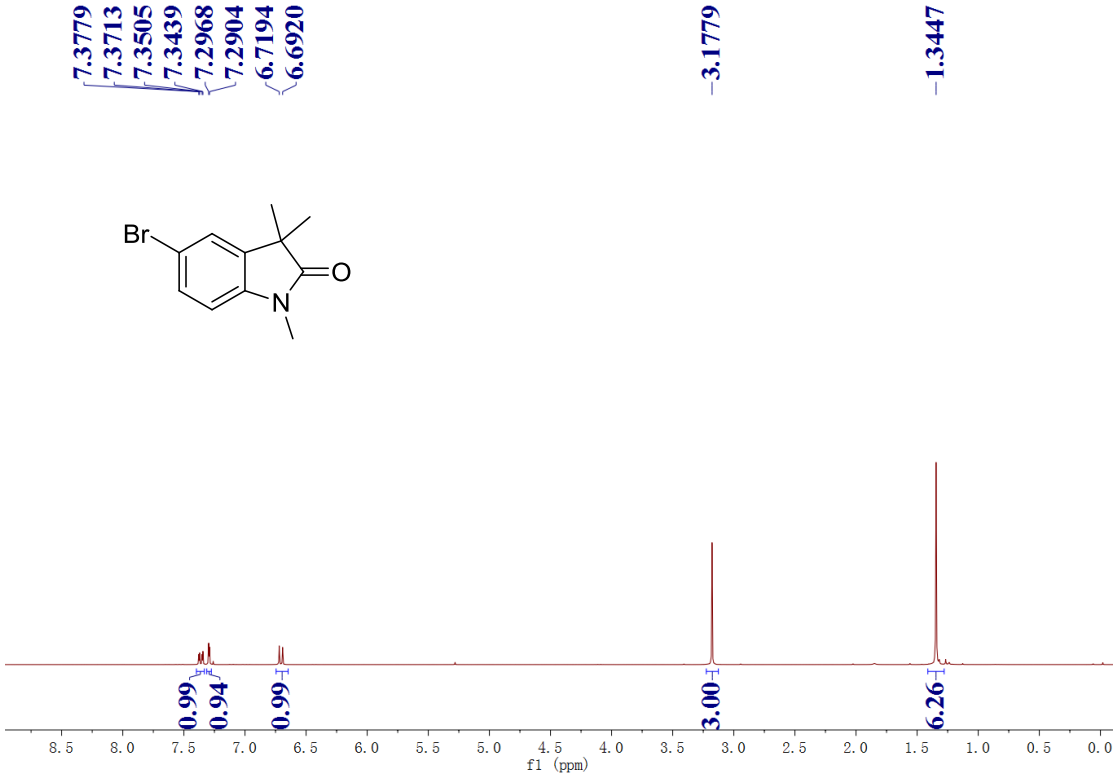


Fig. S8 ^{1}H NMR spectrum of **2d** in $CDCl_3$.

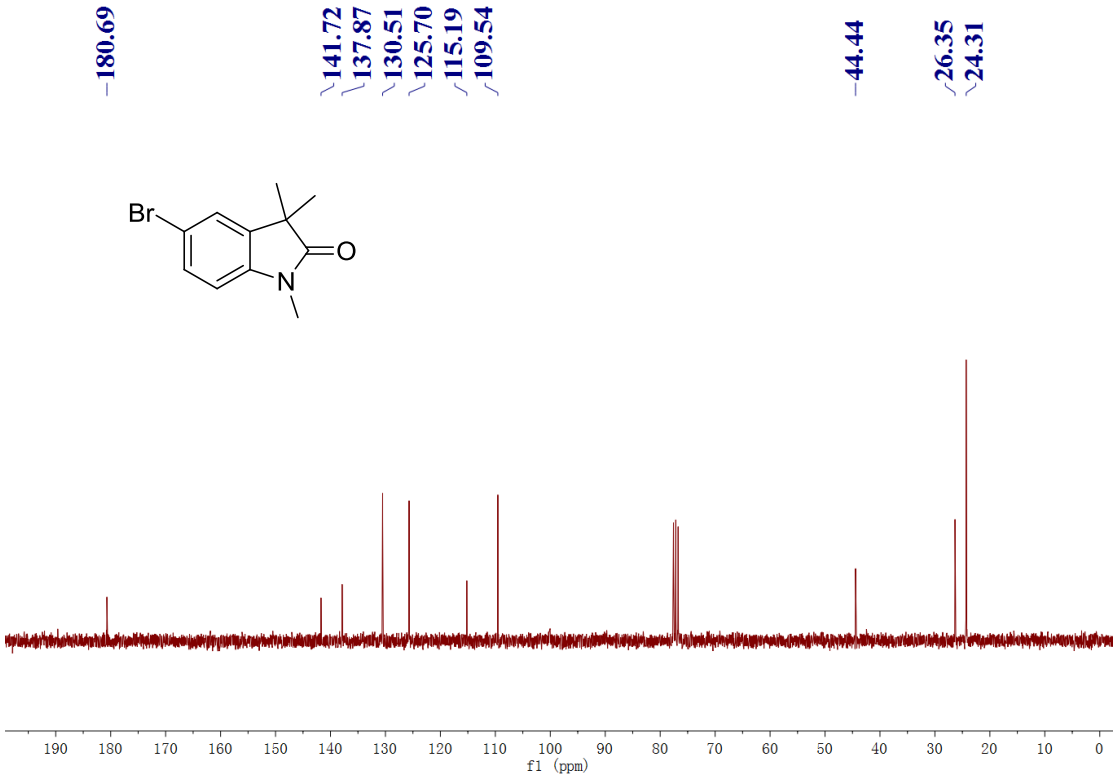


Fig. S9 ^{13}C NMR spectrum of **2d** in $CDCl_3$.

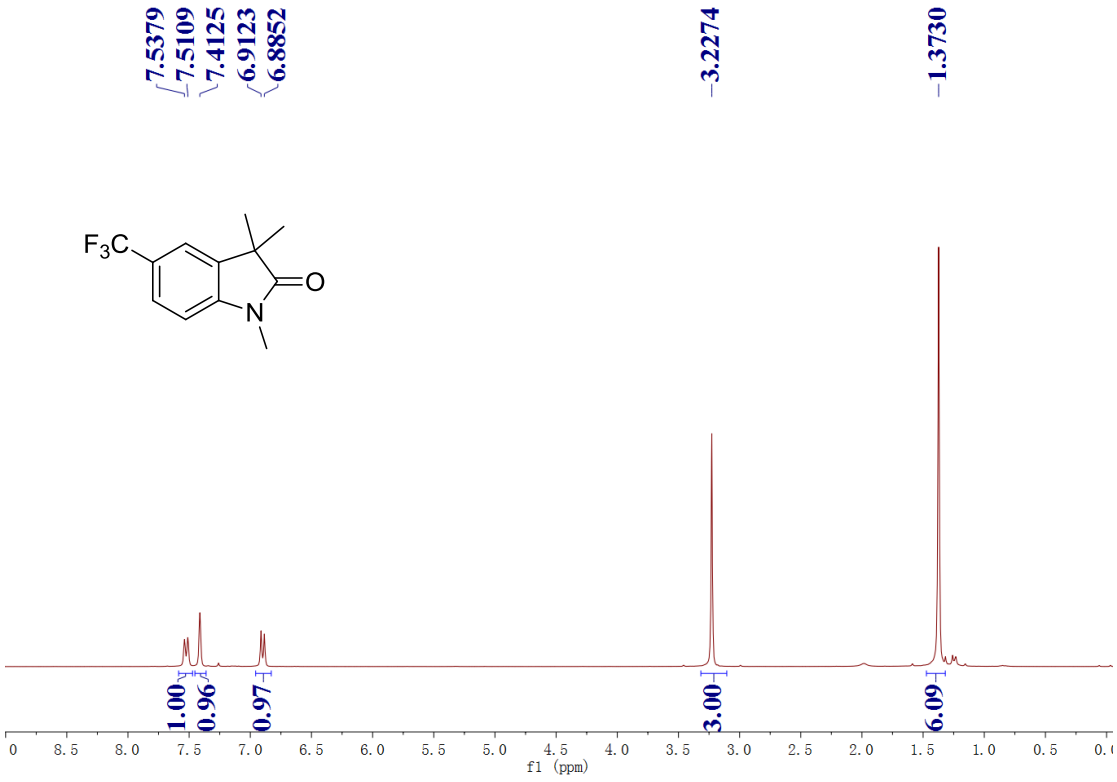


Fig. S10 ^{1}H NMR spectrum of **2e** in $CDCl_3$.

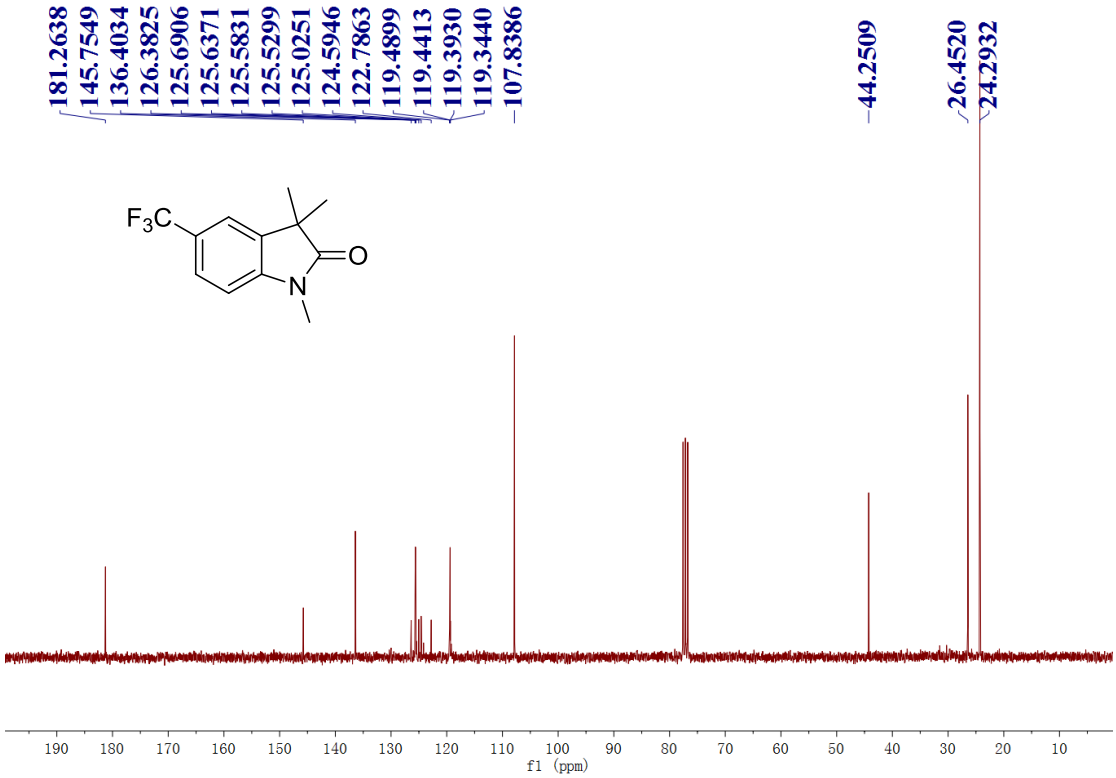


Fig. S11 ^{13}C NMR spectrum of **2e** in $CDCl_3$.

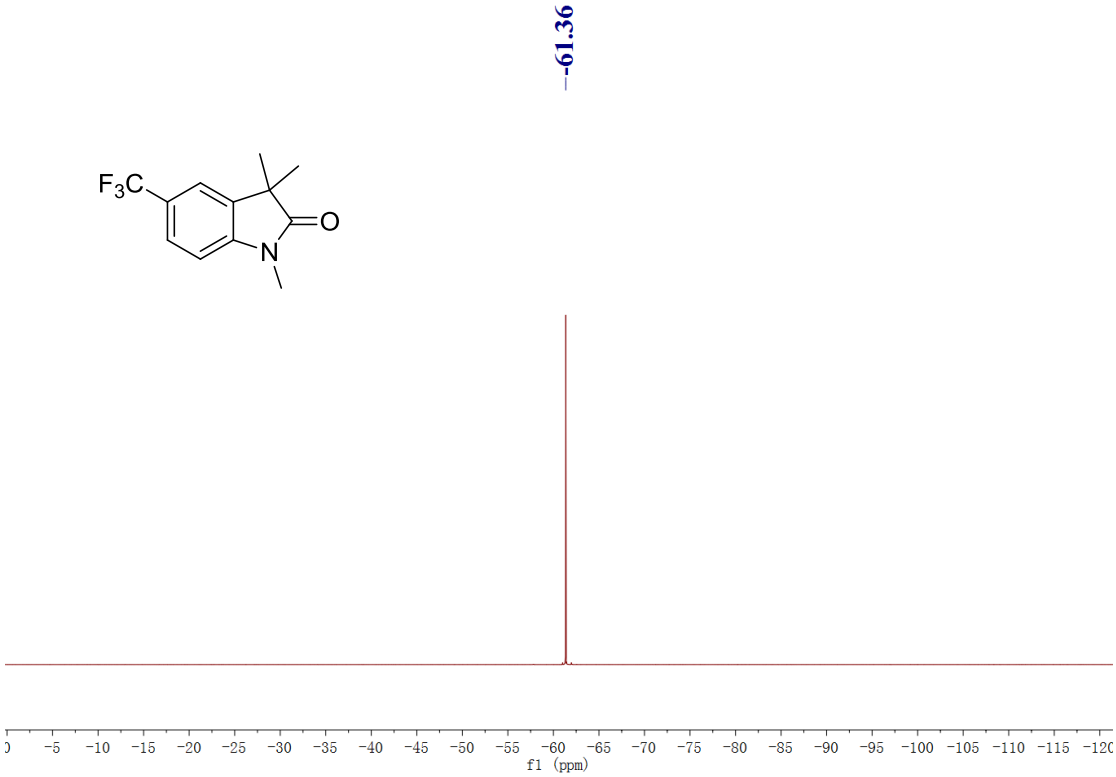


Fig. S12 ^{19}F NMR spectrum of **2e** in $CDCl_3$.

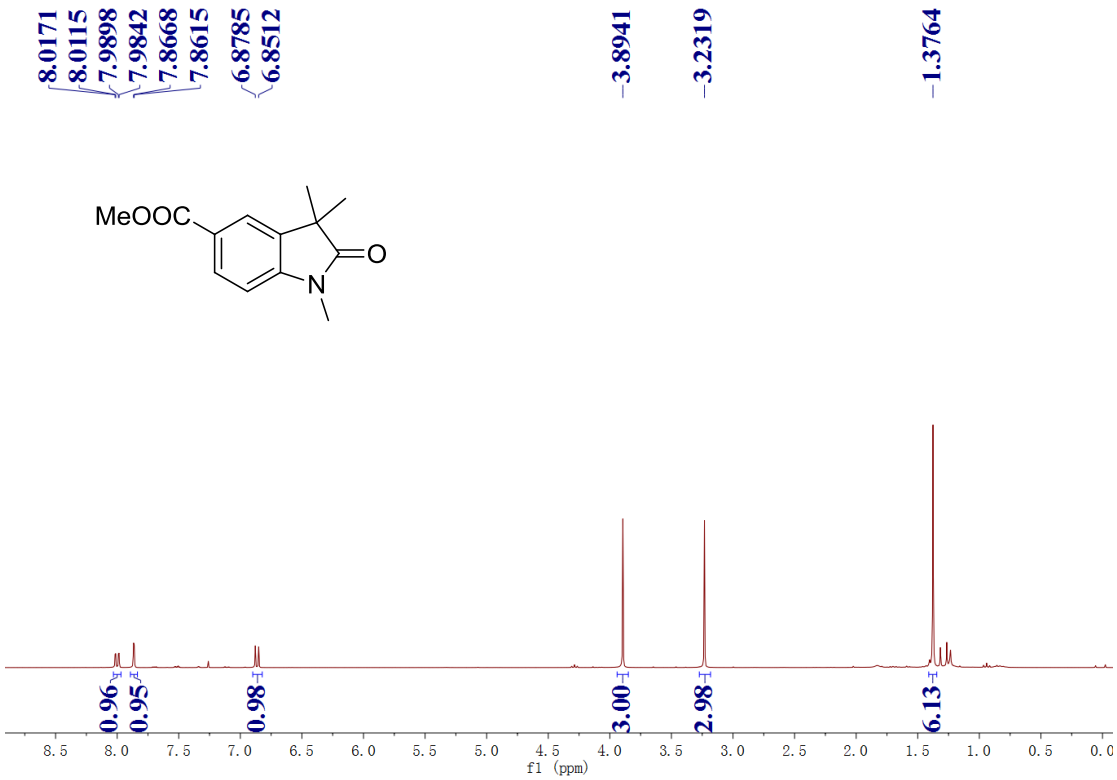


Fig. S13 ^{1}H NMR spectrum of **2f** in $CDCl_3$.

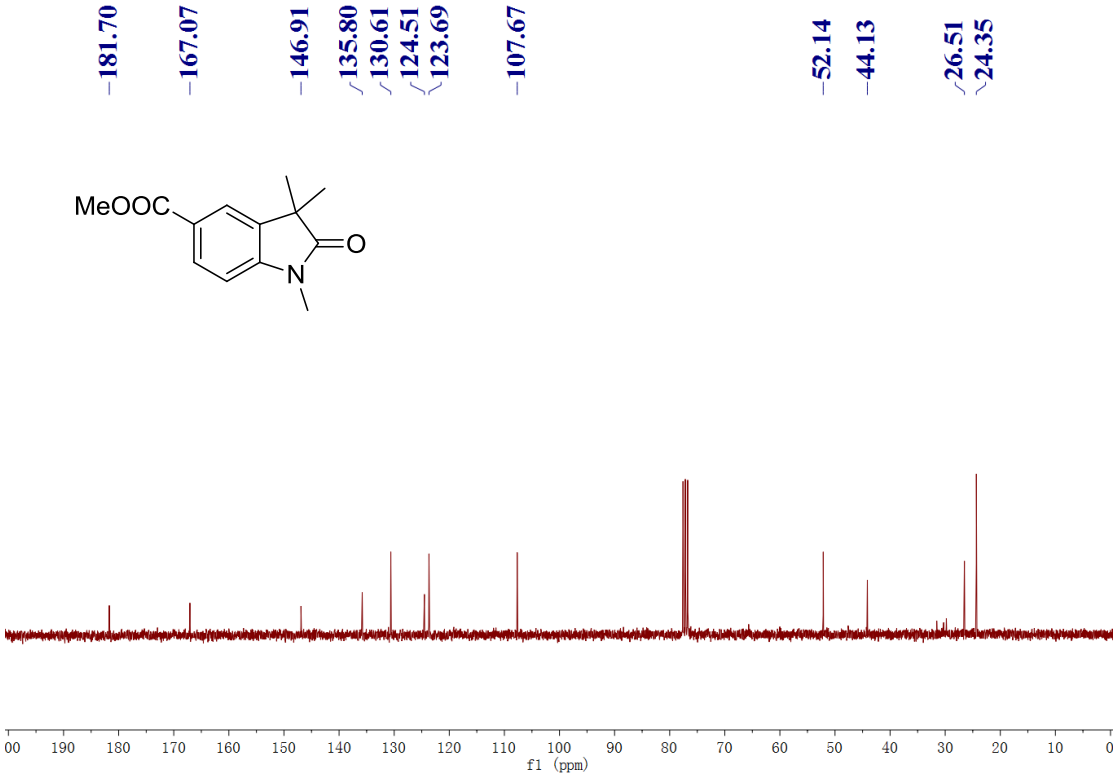


Fig. S14 ^{13}C NMR spectrum of **2f** in $CDCl_3$.

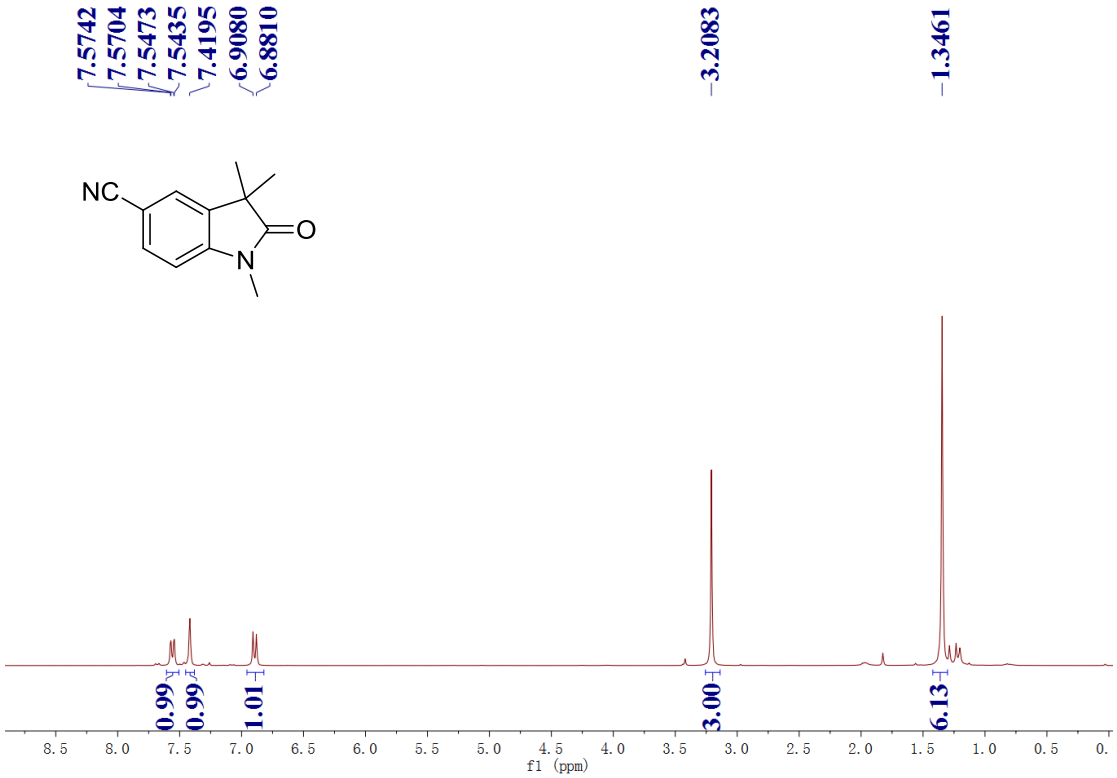


Fig. S15 ^{1}H NMR spectrum of **2g** in $CDCl_3$.

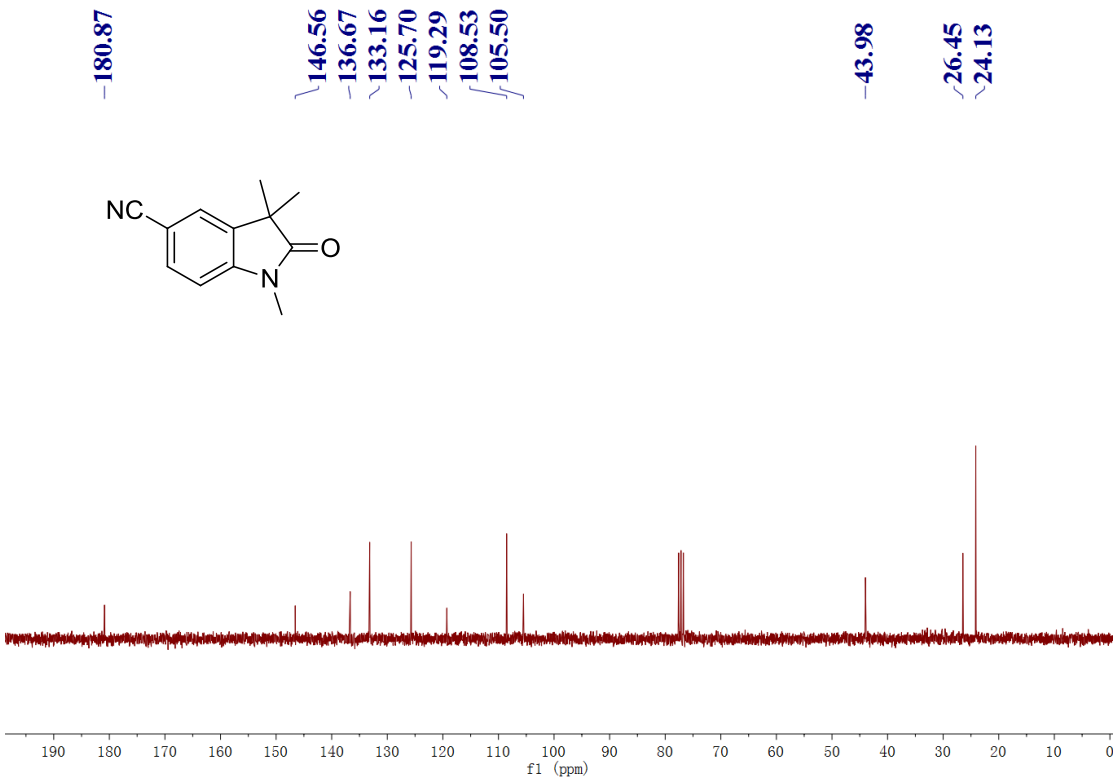


Fig. S16 ^{13}C NMR spectrum of **2g** in $CDCl_3$.

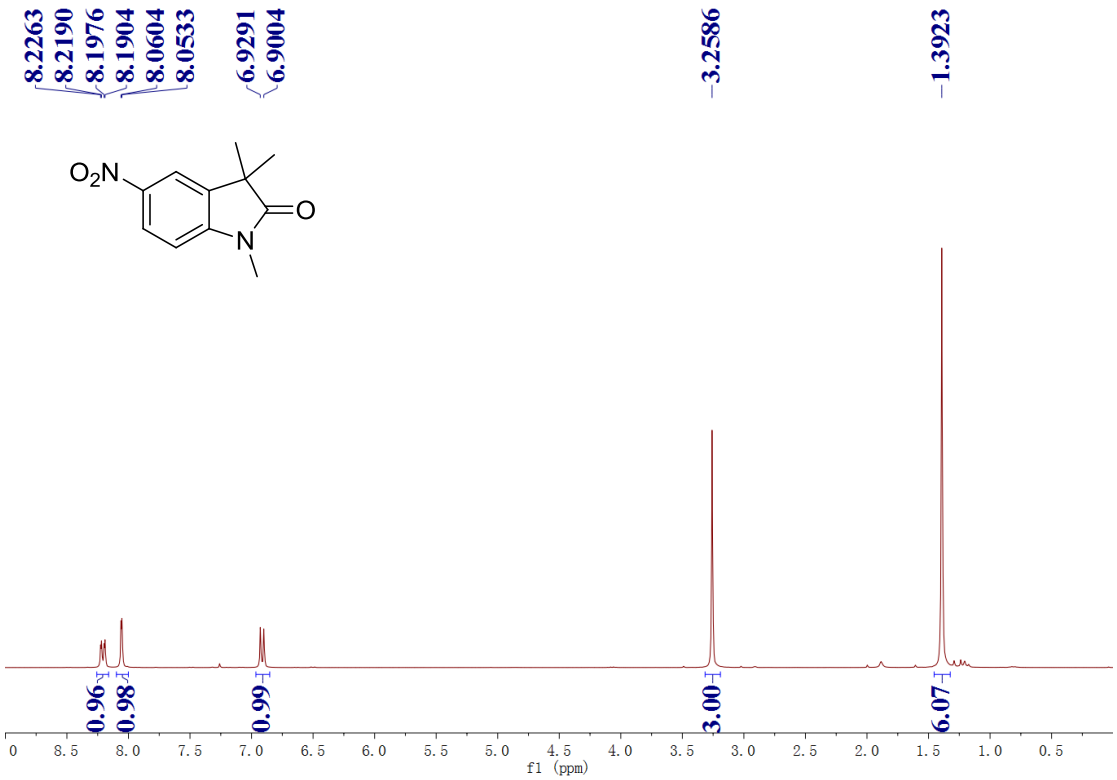


Fig. S17 ^{1}H NMR spectrum of **2h** in $CDCl_3$.

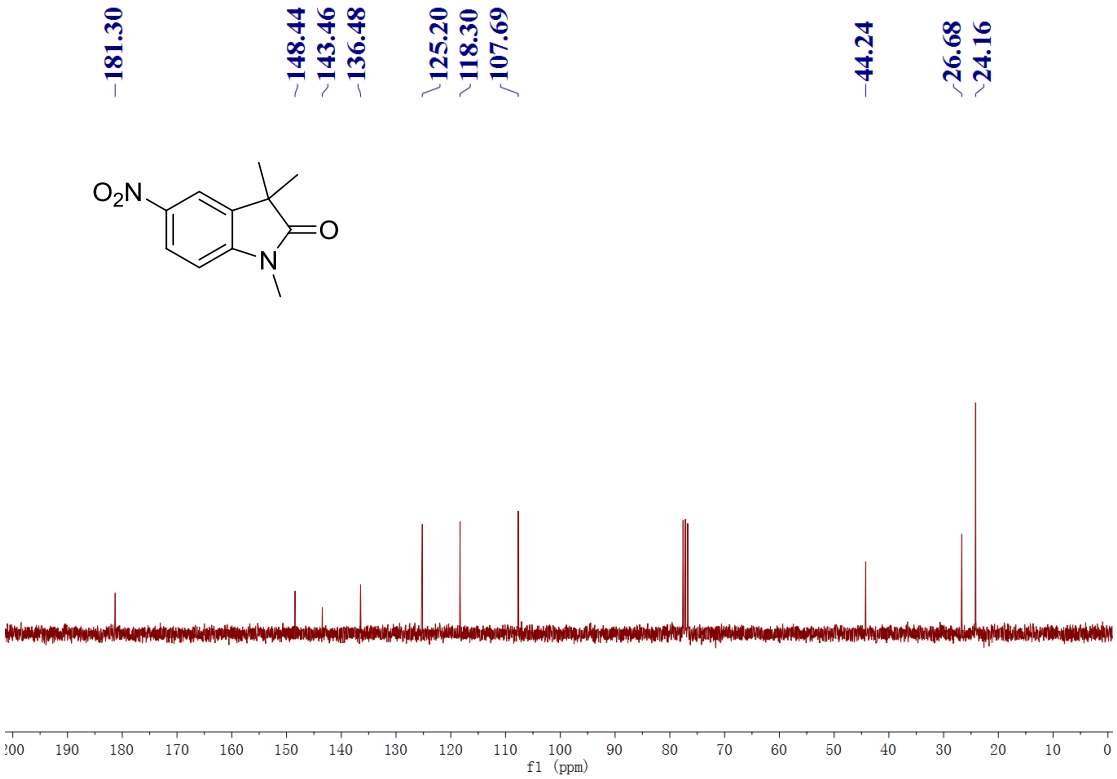


Fig. S18 ^{13}C NMR spectrum of **2h** in $CDCl_3$.

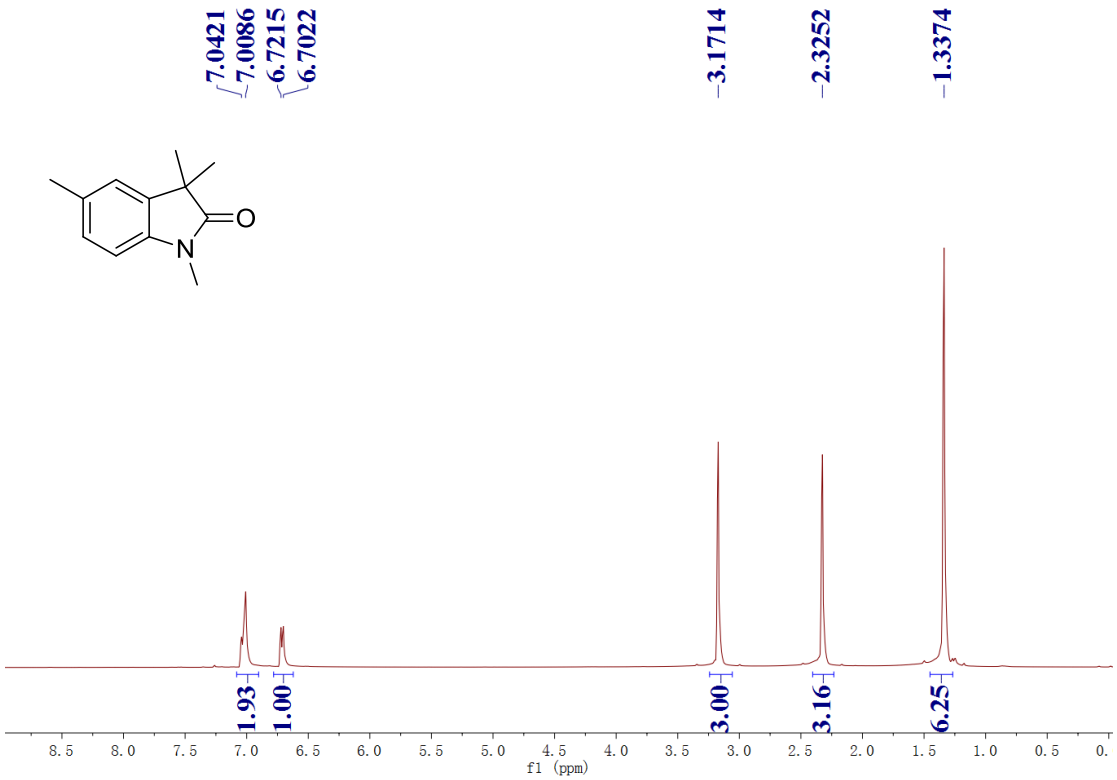


Fig. S19 ^{1}H NMR spectrum of **2i** in $CDCl_3$.

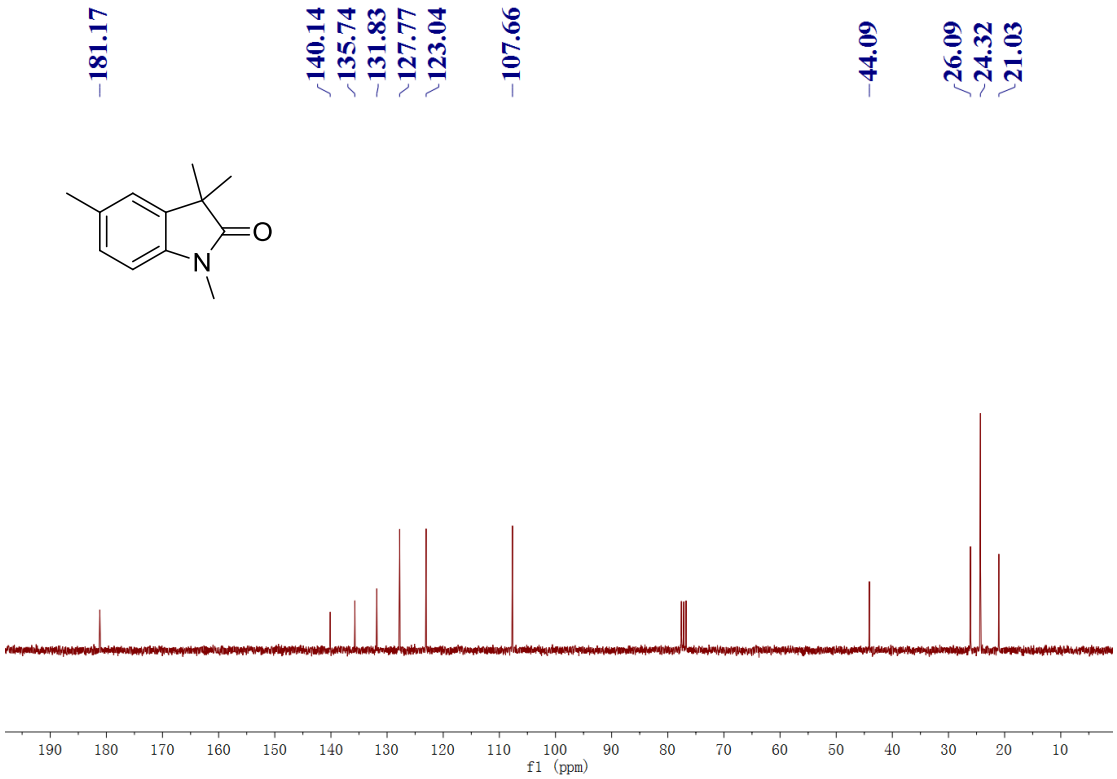


Fig. S20 ^{13}C NMR spectrum of **2i** in $CDCl_3$.

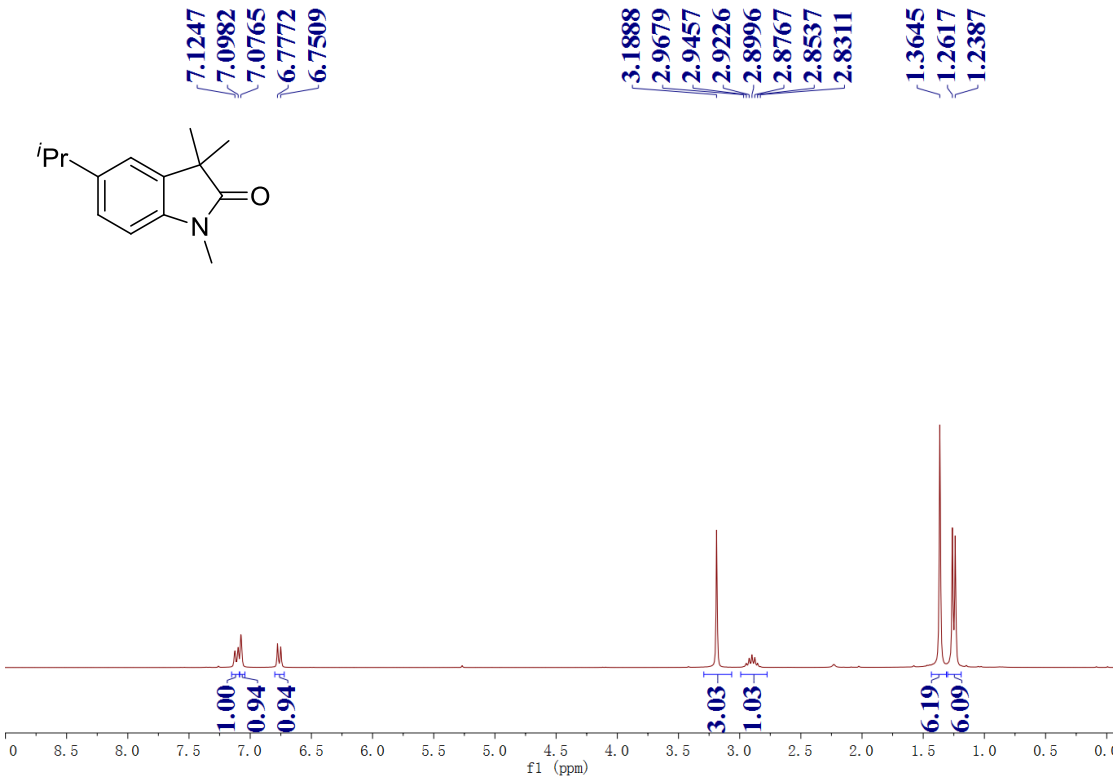


Fig. S21 ^{1}H NMR spectrum of **2j** in $CDCl_3$.

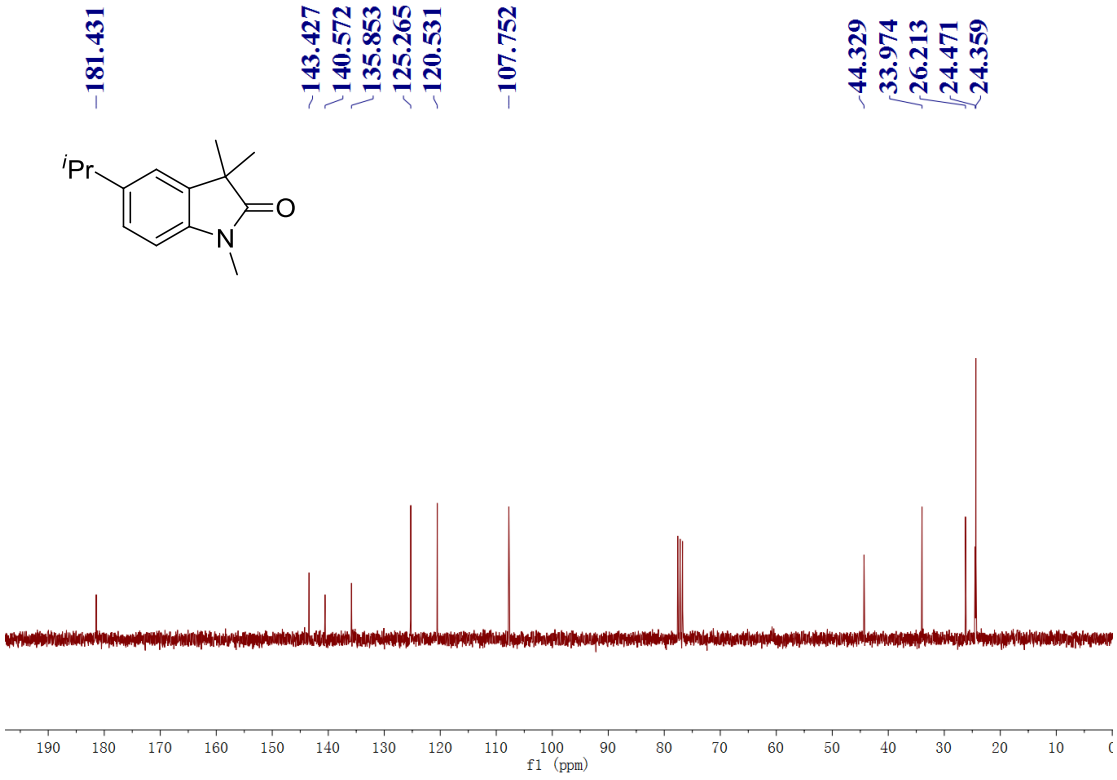


Fig. S22 ^{13}C NMR spectrum of **2j** in $CDCl_3$.

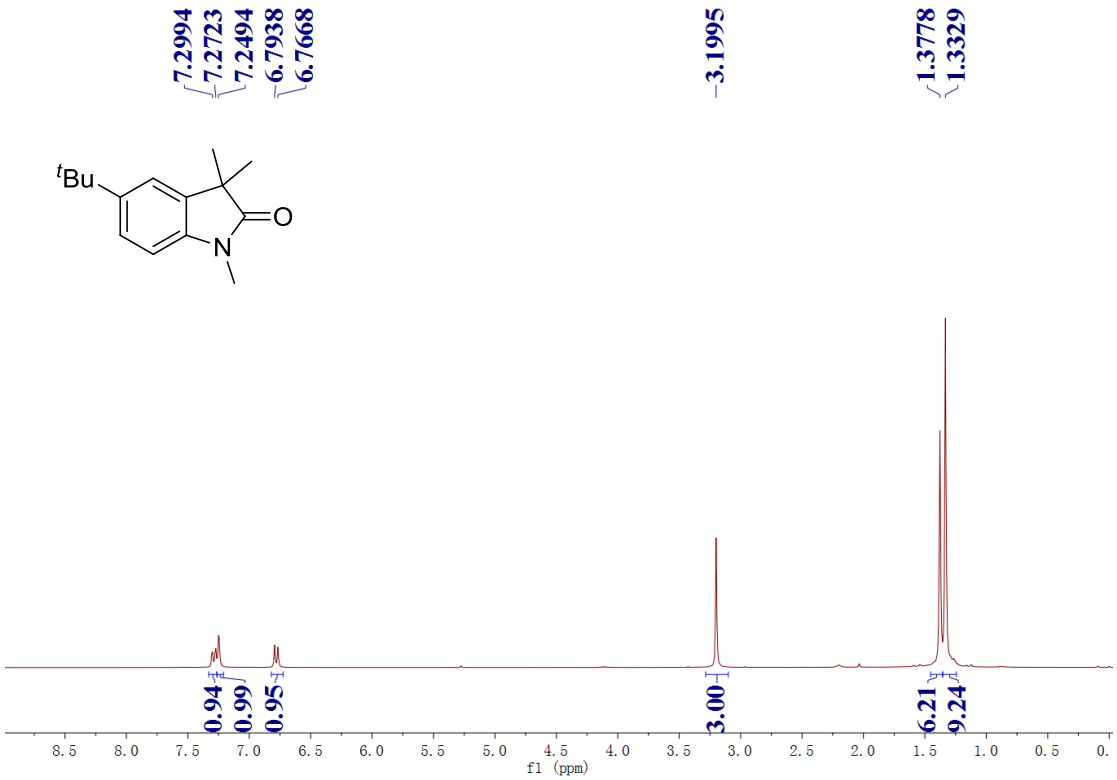


Fig. S23 ^{1}H NMR spectrum of **2k** in $CDCl_3$.

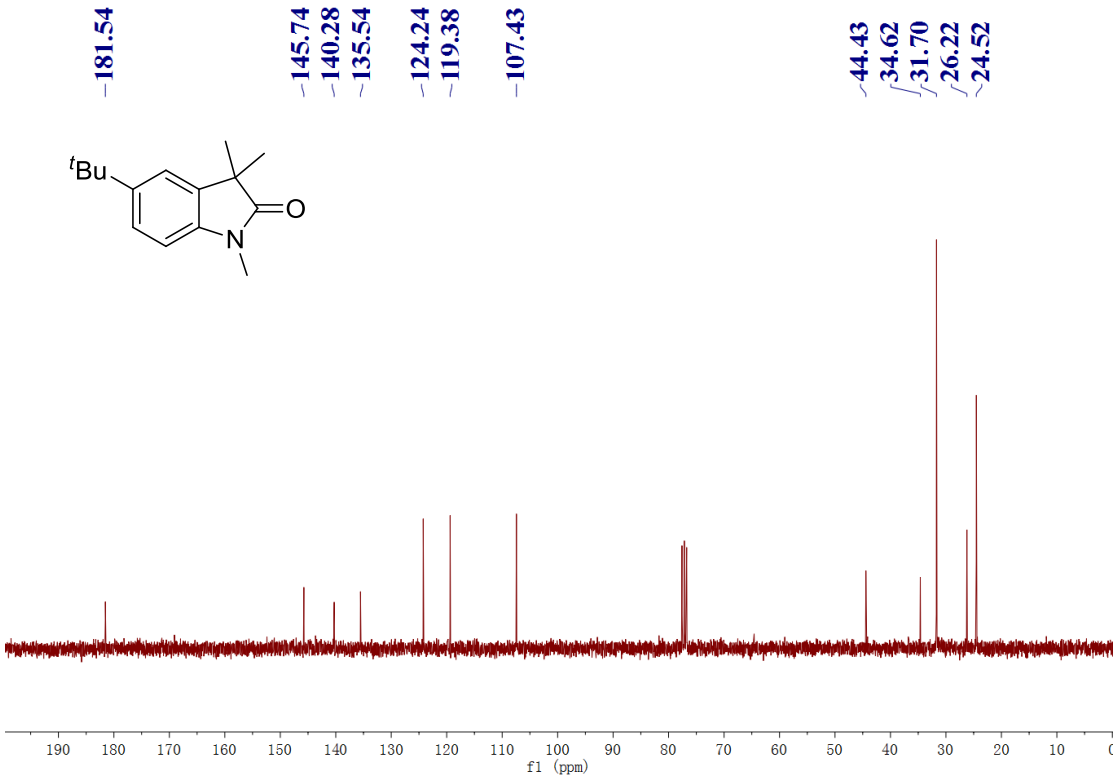


Fig. S24 ^{13}C NMR spectrum of **2k** in $CDCl_3$.

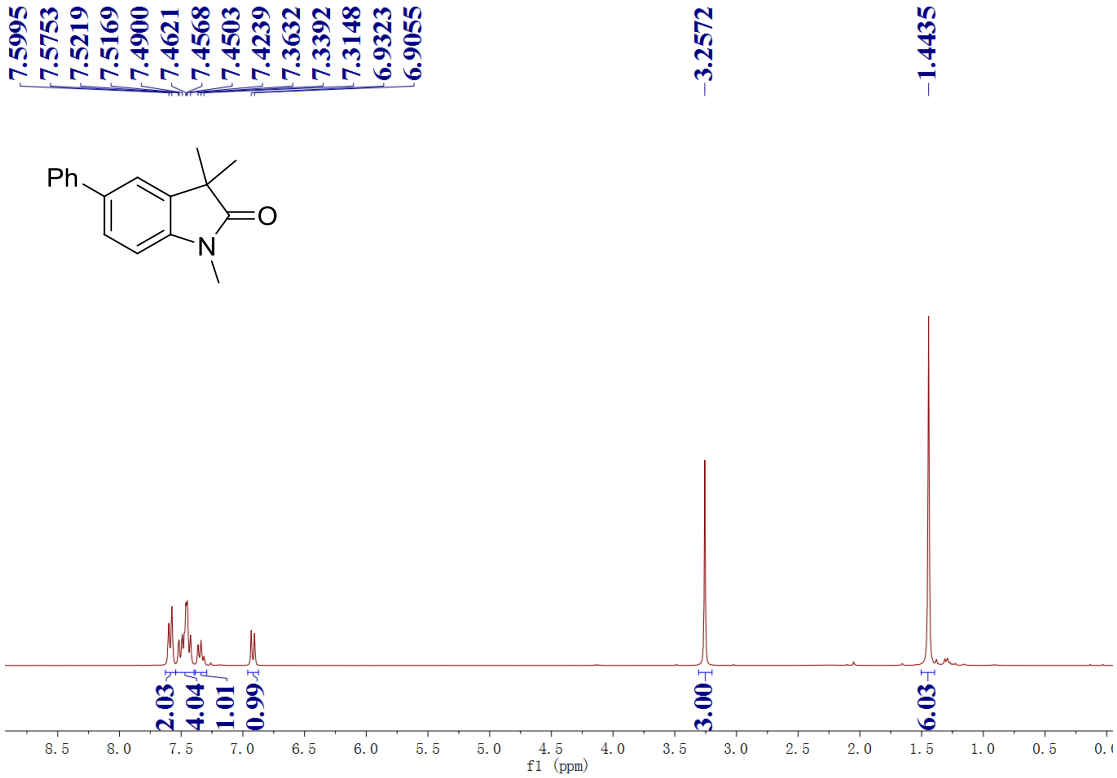


Fig. S25 ^{1}H NMR spectrum of **2l** in $CDCl_3$.

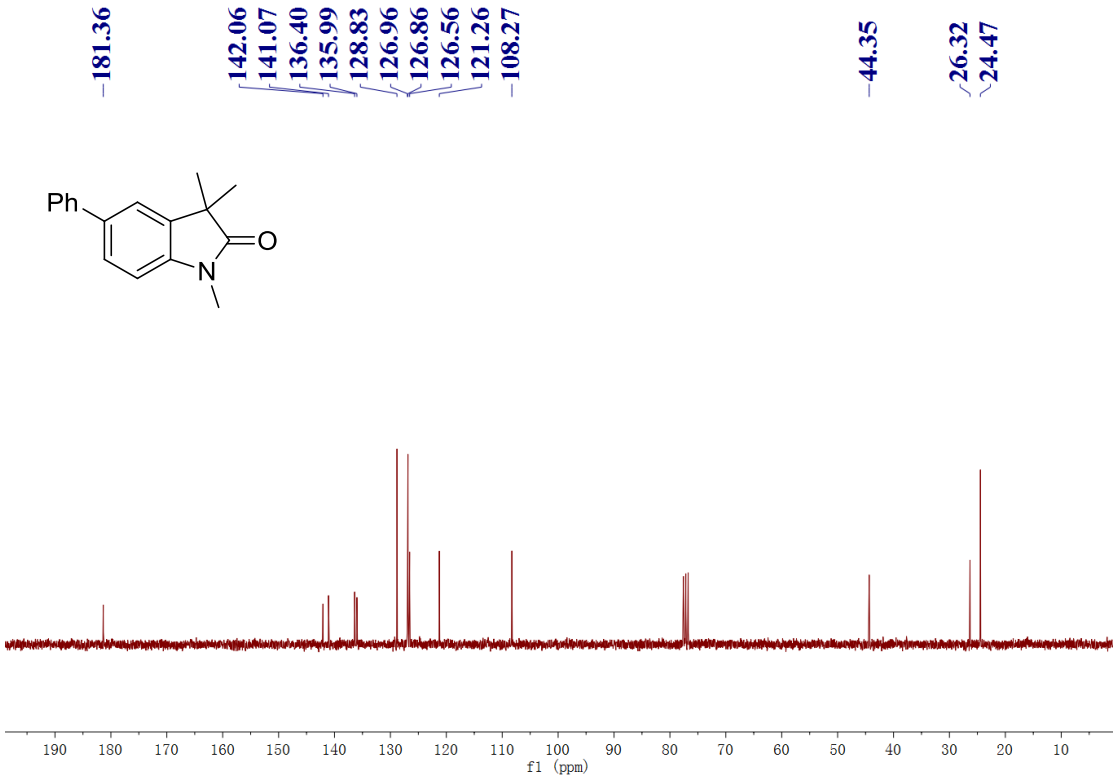


Fig. S26 ^{13}C NMR spectrum of **2l** in $CDCl_3$.

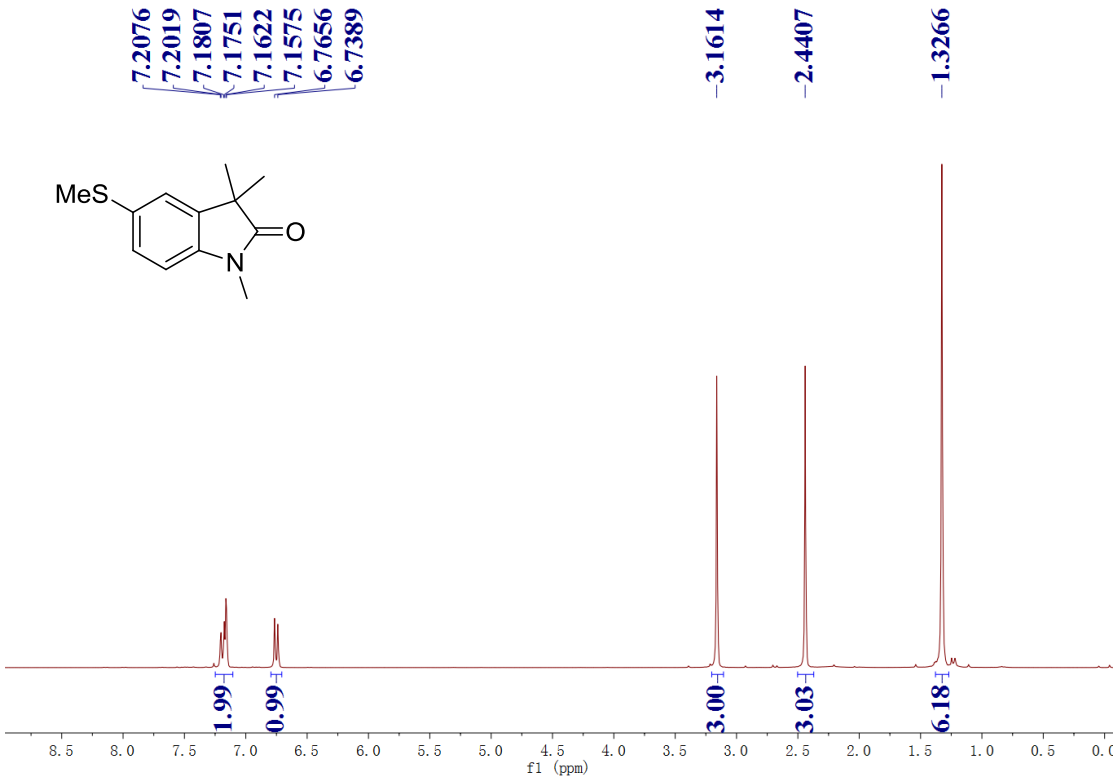


Fig. S27 ^{1}H NMR spectrum of **2m** in $CDCl_3$.

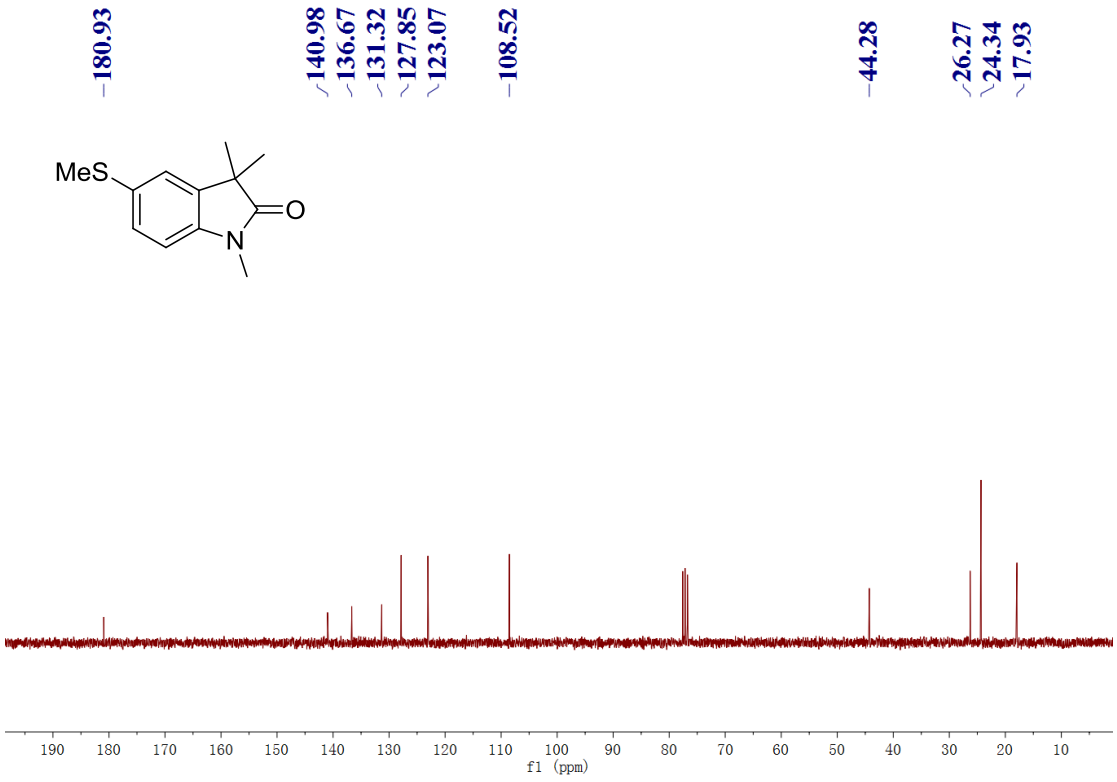


Fig. S28 ^{13}C NMR spectrum of **2m** in $CDCl_3$.

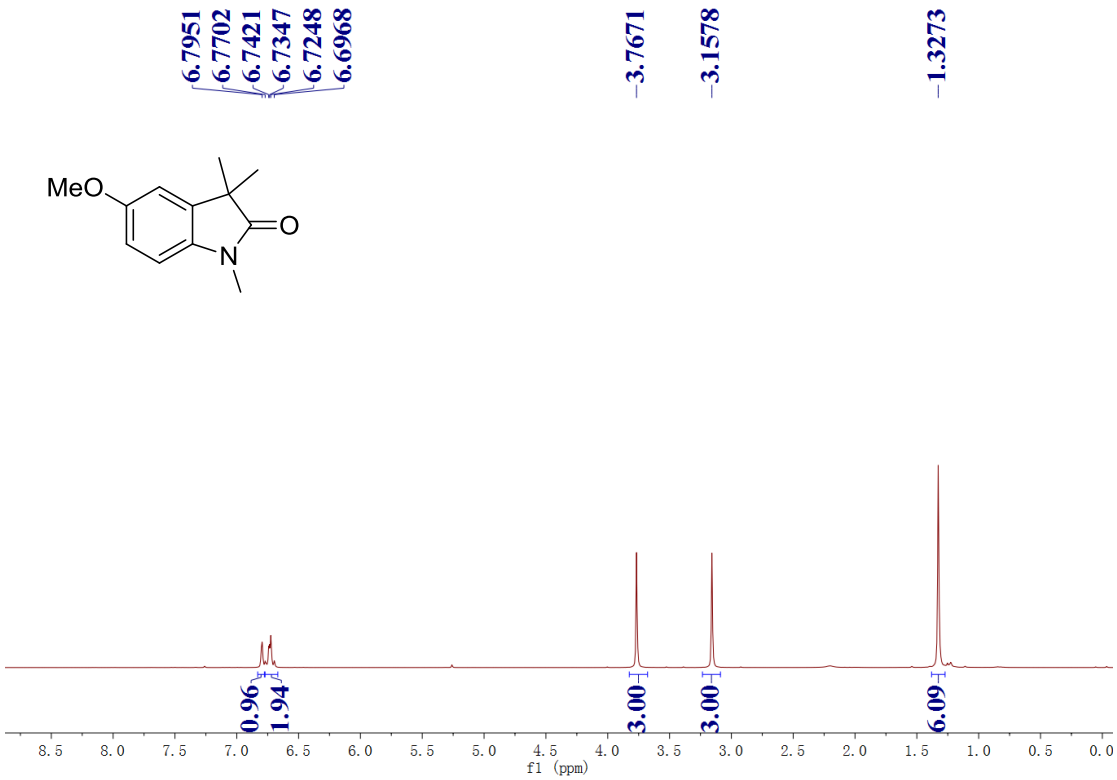


Fig. S29 ^{1}H NMR spectrum of **2n** in $CDCl_3$.

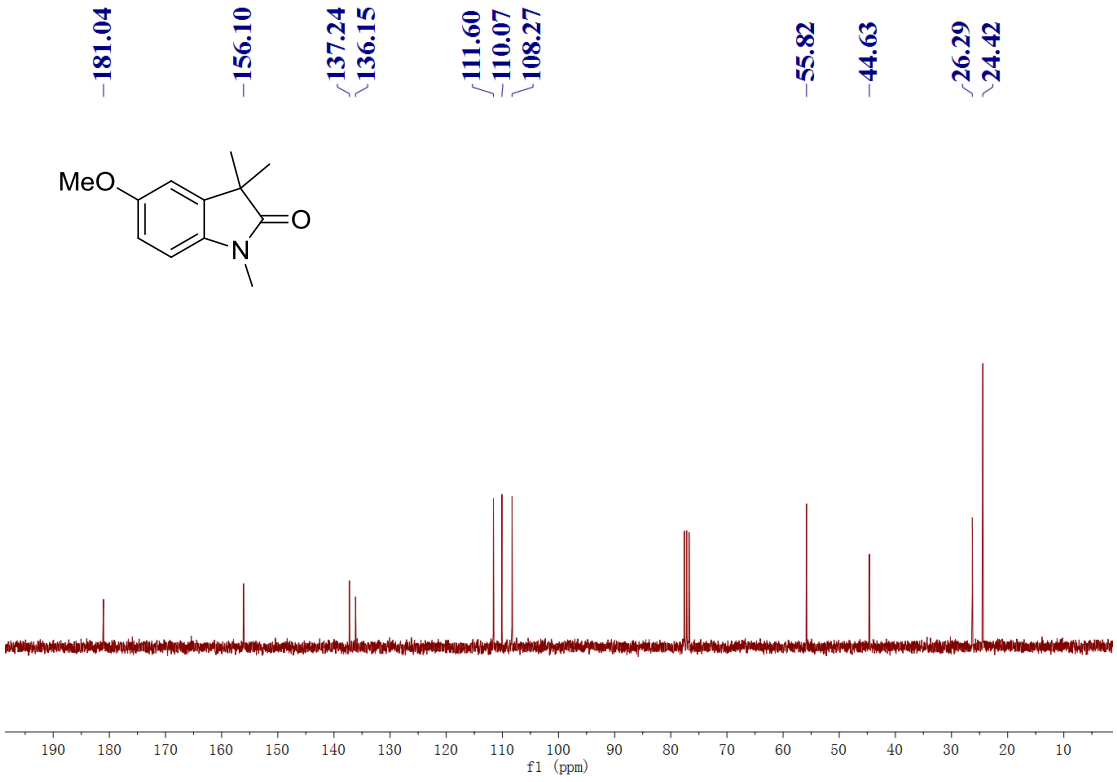


Fig. S30 ^{13}C NMR spectrum of **2n** in $CDCl_3$.

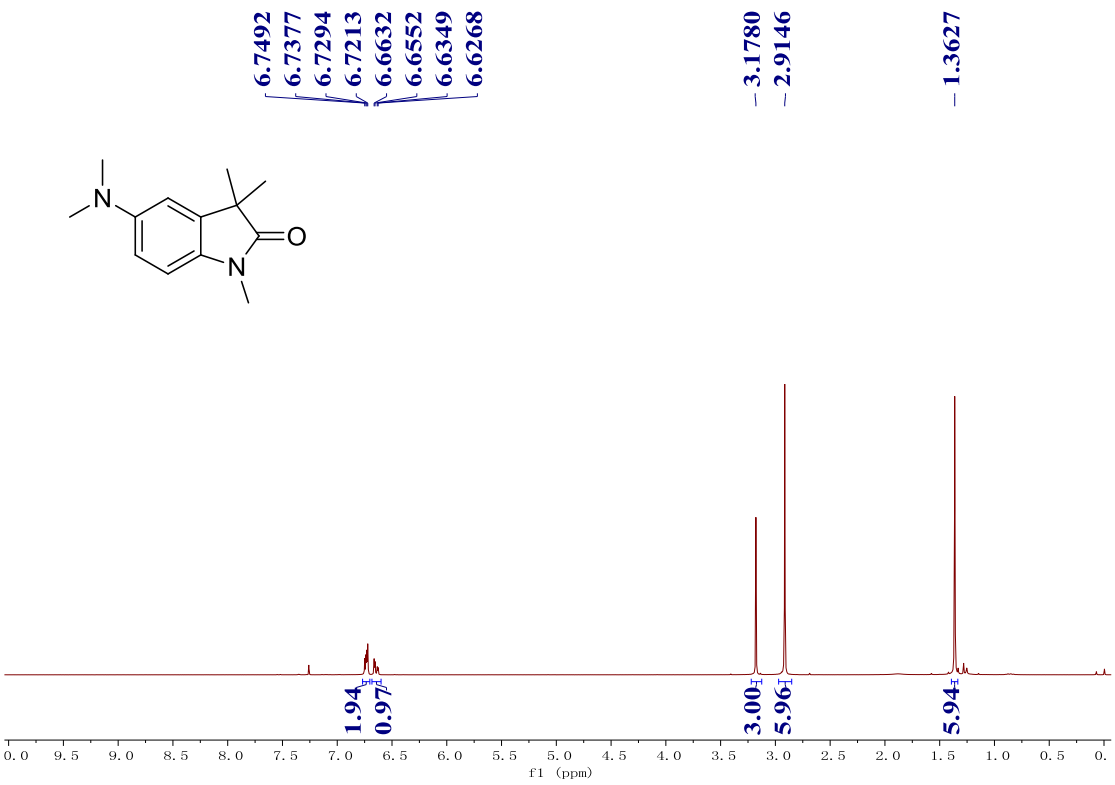


Fig. S31 ^{1}H NMR spectrum of **2o** in $CDCl_3$.

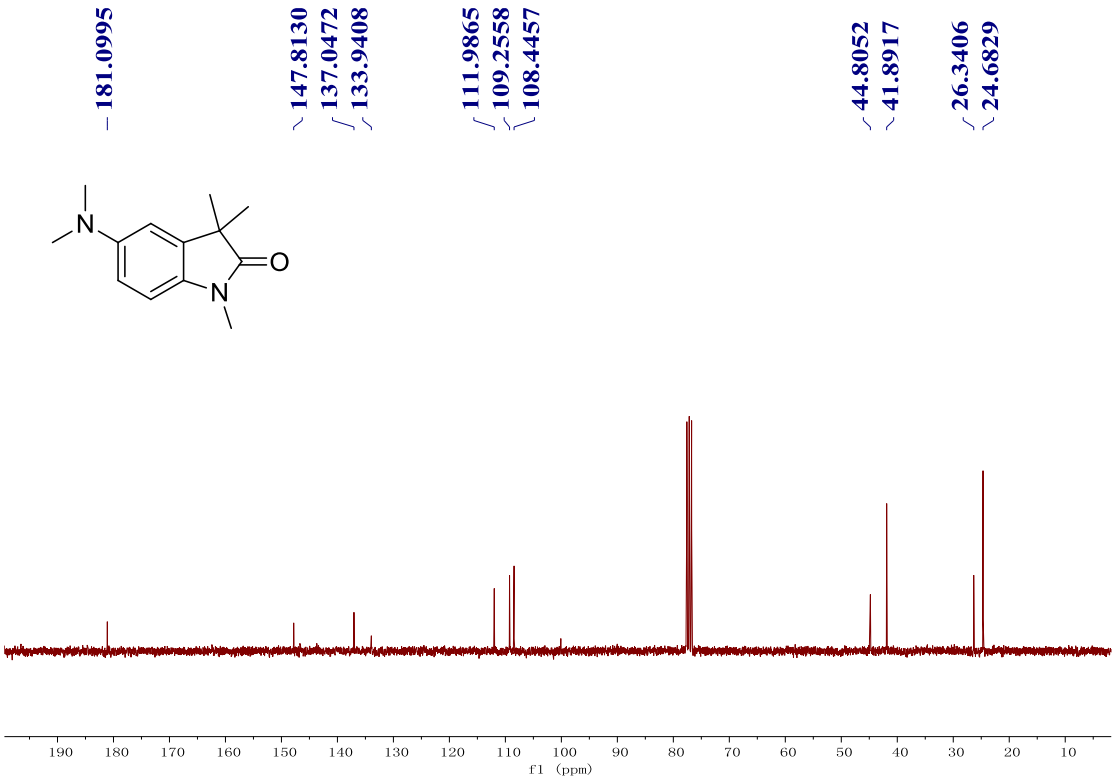


Fig. S32 ^{13}C NMR spectrum of **2o** in $CDCl_3$.

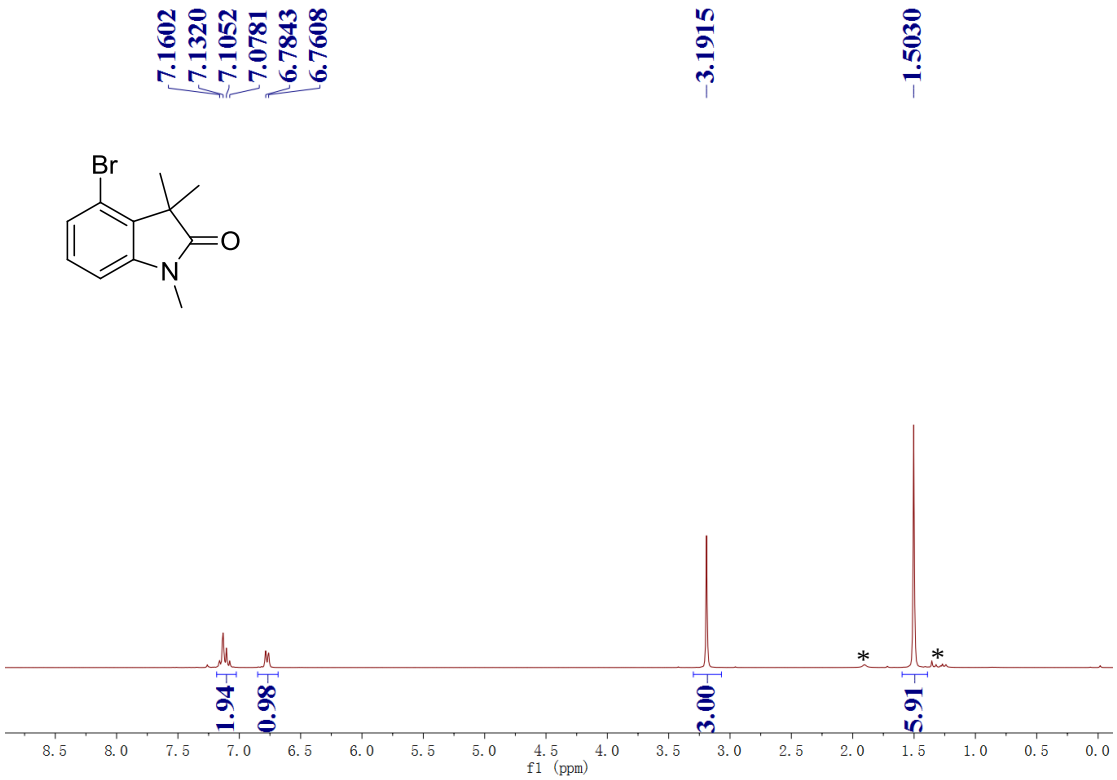


Fig. S33 ^{1}H NMR spectrum of **2p** in $CDCl_3$ (asterisk denotes impurity).

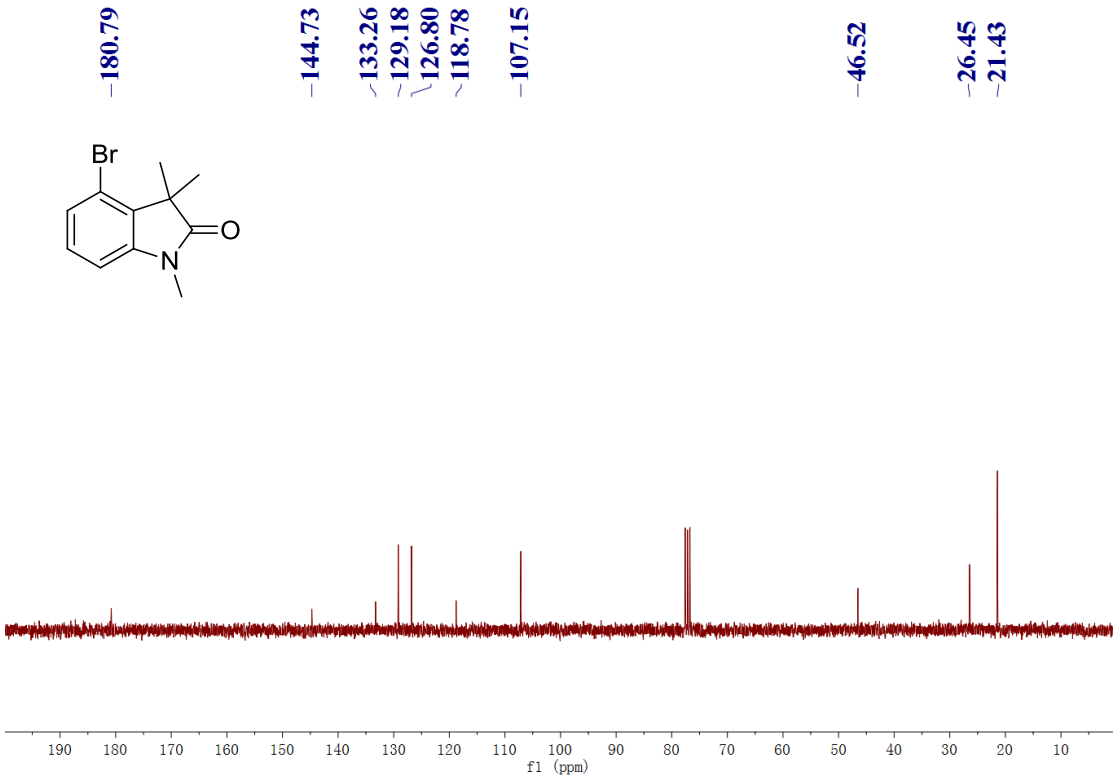


Fig. S34 ^{13}C NMR spectrum of **2p** in $CDCl_3$.

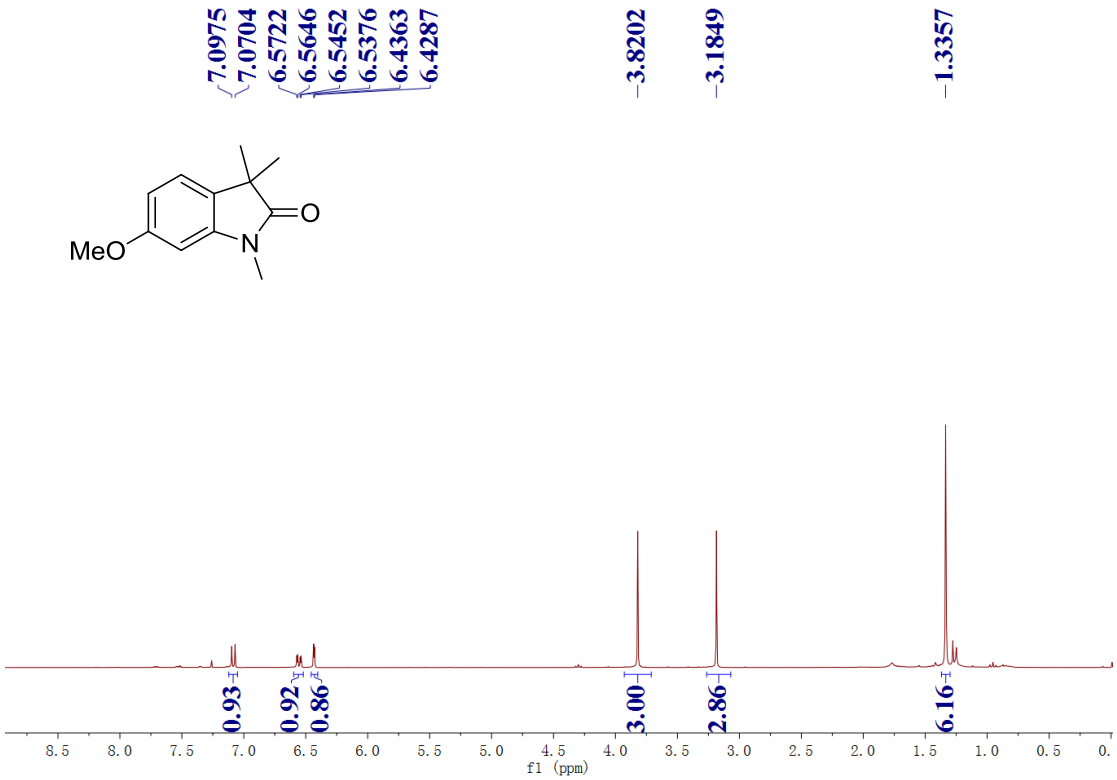


Fig. S35 ^{1}H NMR spectrum of **2q** in $CDCl_3$.

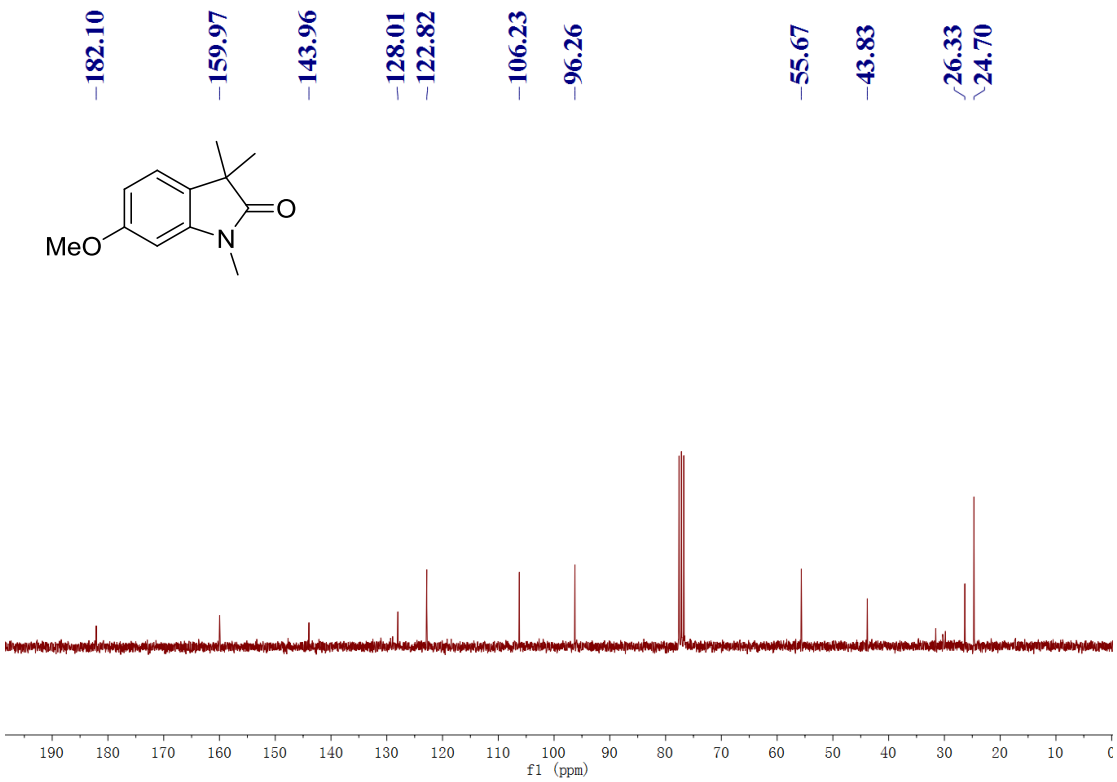


Fig. S36 ^{13}C NMR spectrum of **2q** in $CDCl_3$.

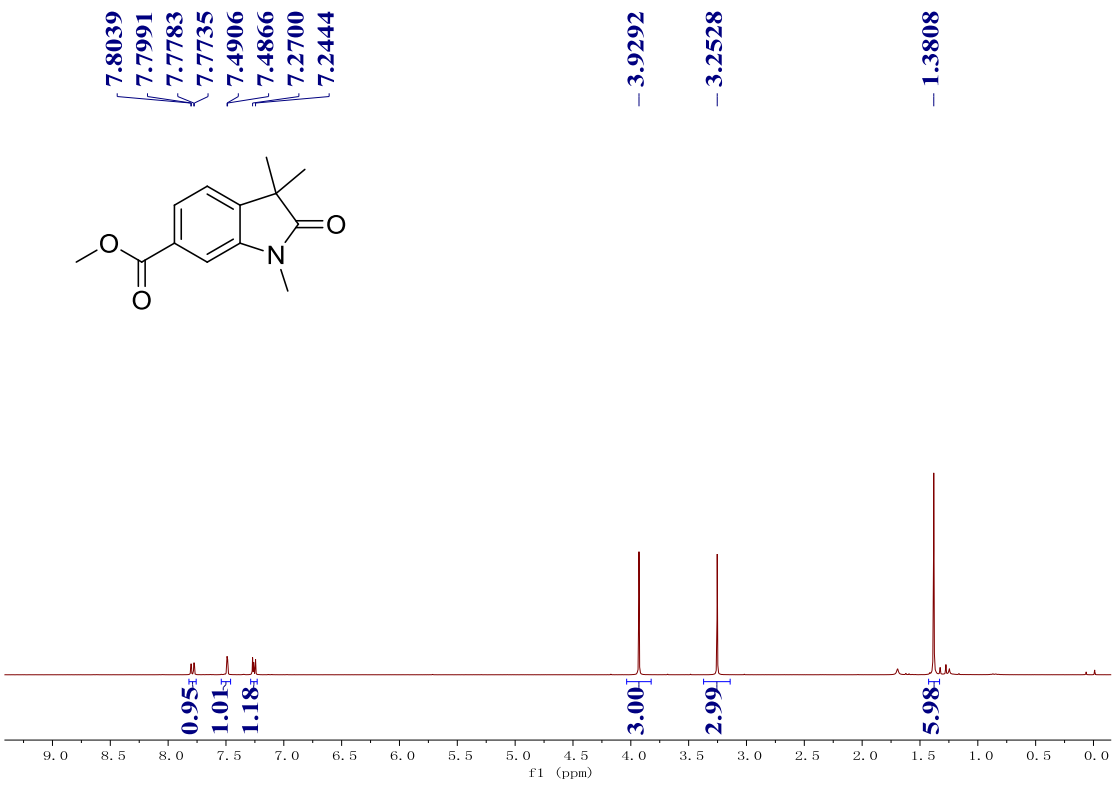


Fig. S37 ^{1}H NMR spectrum of **2r** in $CDCl_3$.

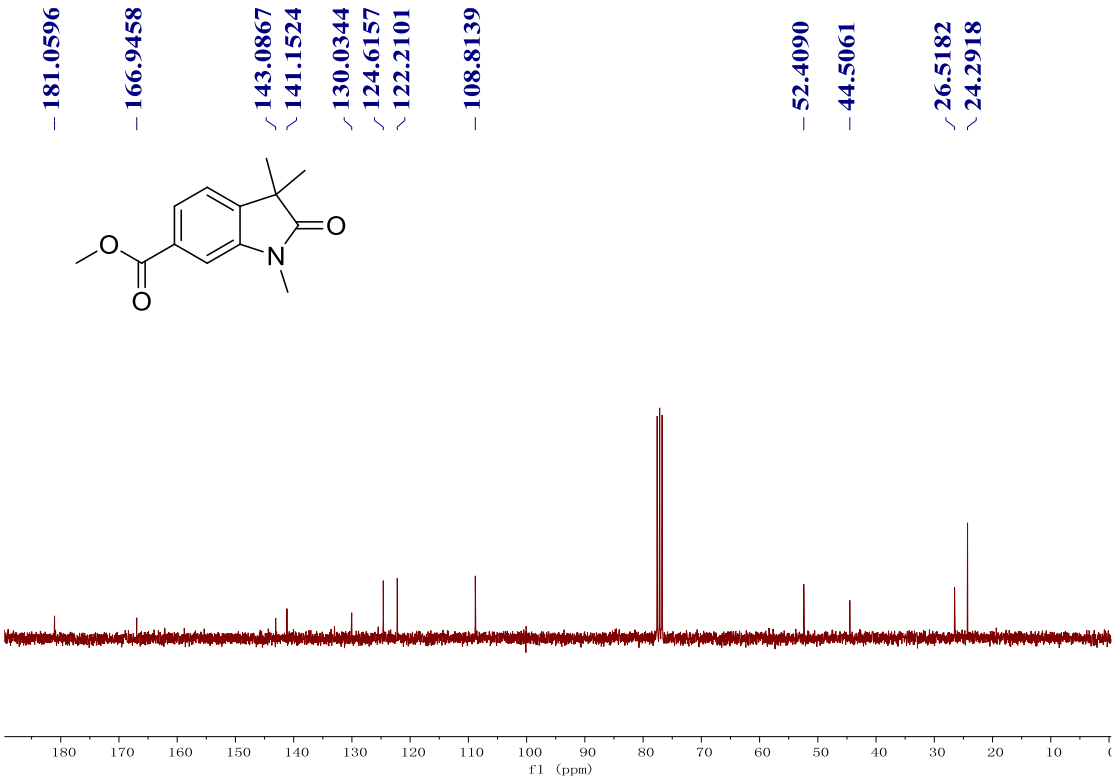


Fig. S38 ^{13}C NMR spectrum of **2r** in $CDCl_3$.

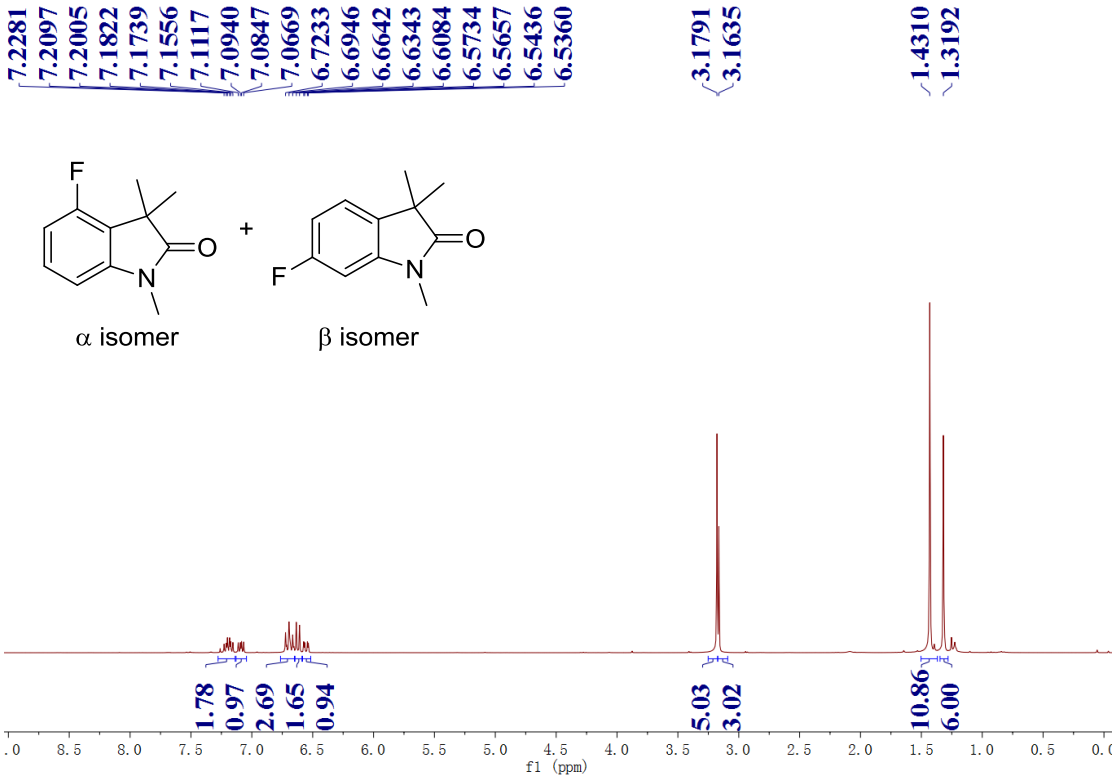


Fig. S39 ^{1}H NMR spectrum of **2s** in $CDCl_3$.

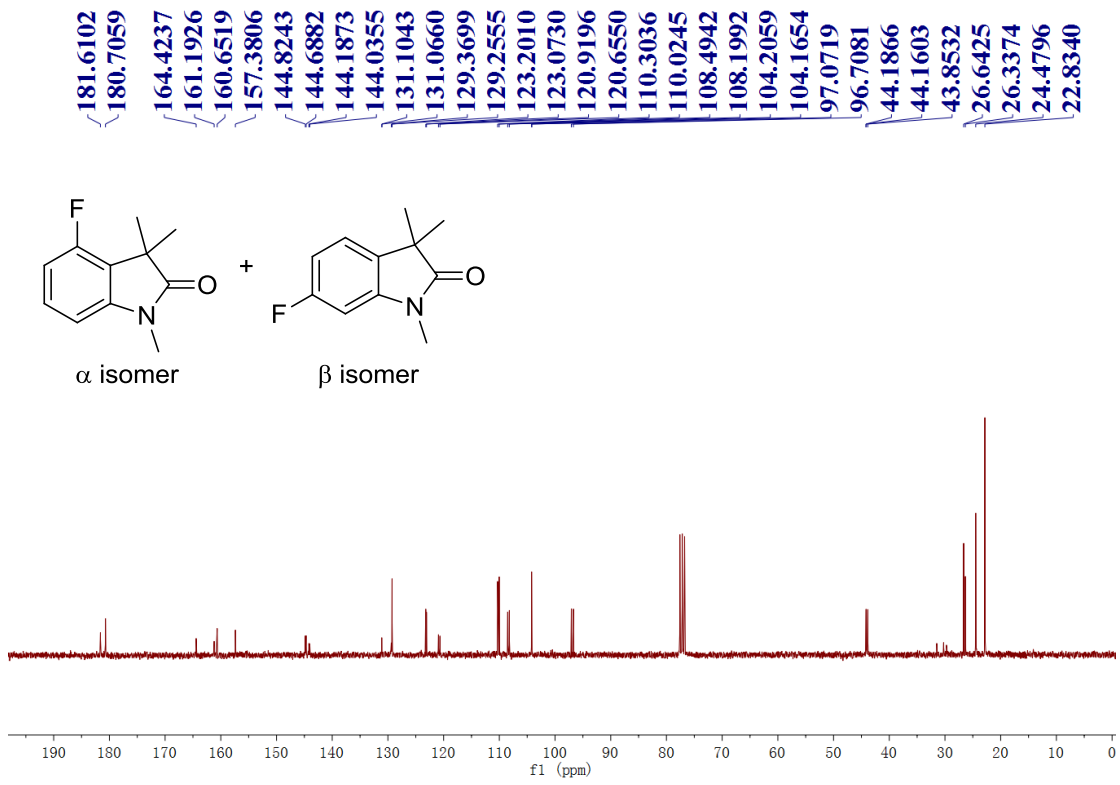


Fig. S40 ^{13}C NMR spectrum of **2s** in $CDCl_3$.

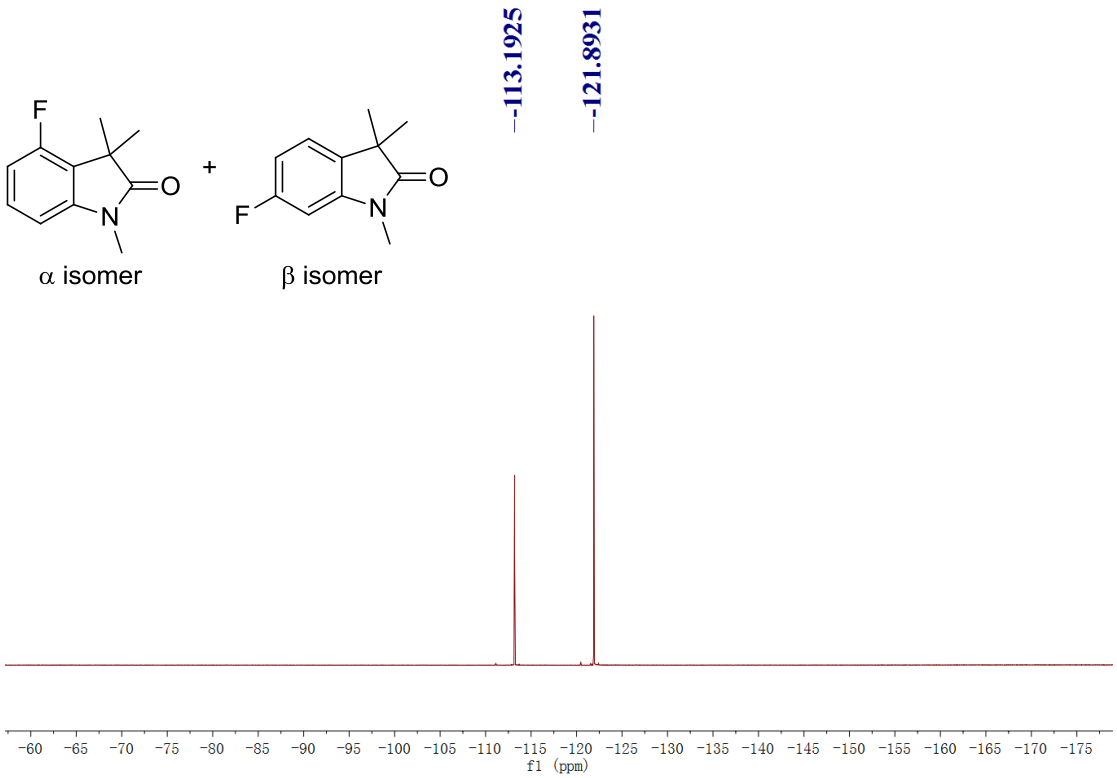


Fig. S41 ^{19}F NMR spectrum of **2s** in $CDCl_3$.

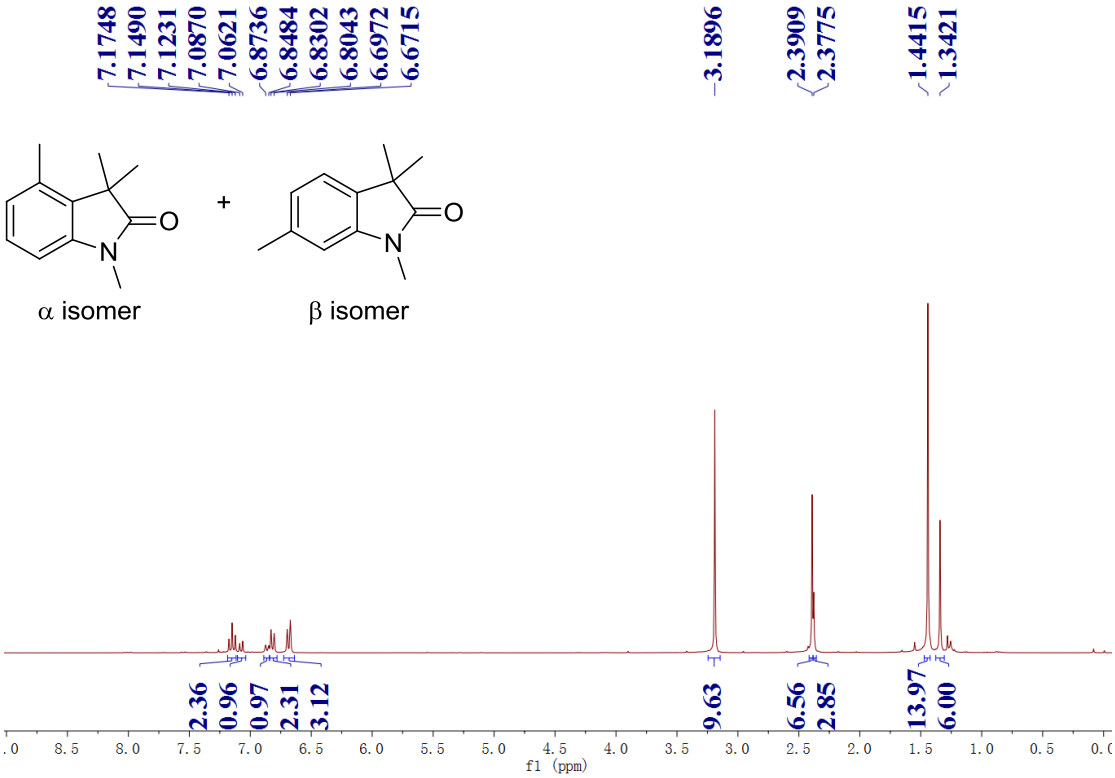


Fig. S42 ^{1}H NMR spectrum of **2t** in $CDCl_3$.

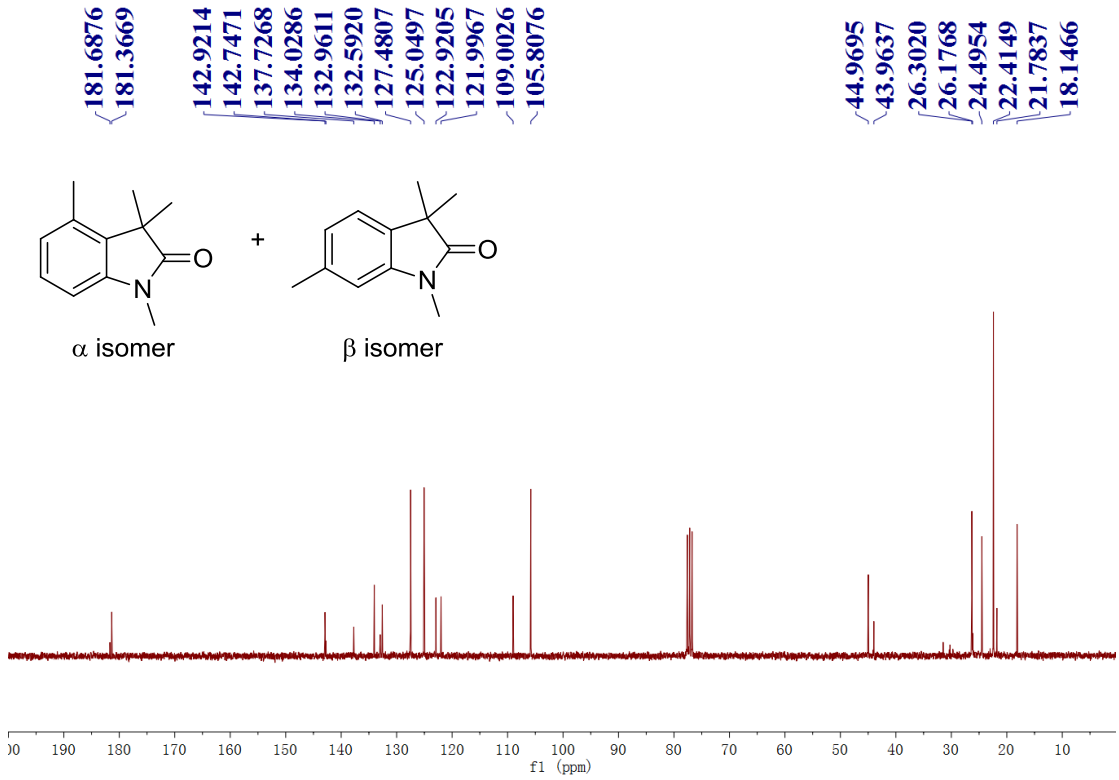


Fig. S43 ^{13}C NMR spectrum of **2t** in $CDCl_3$.

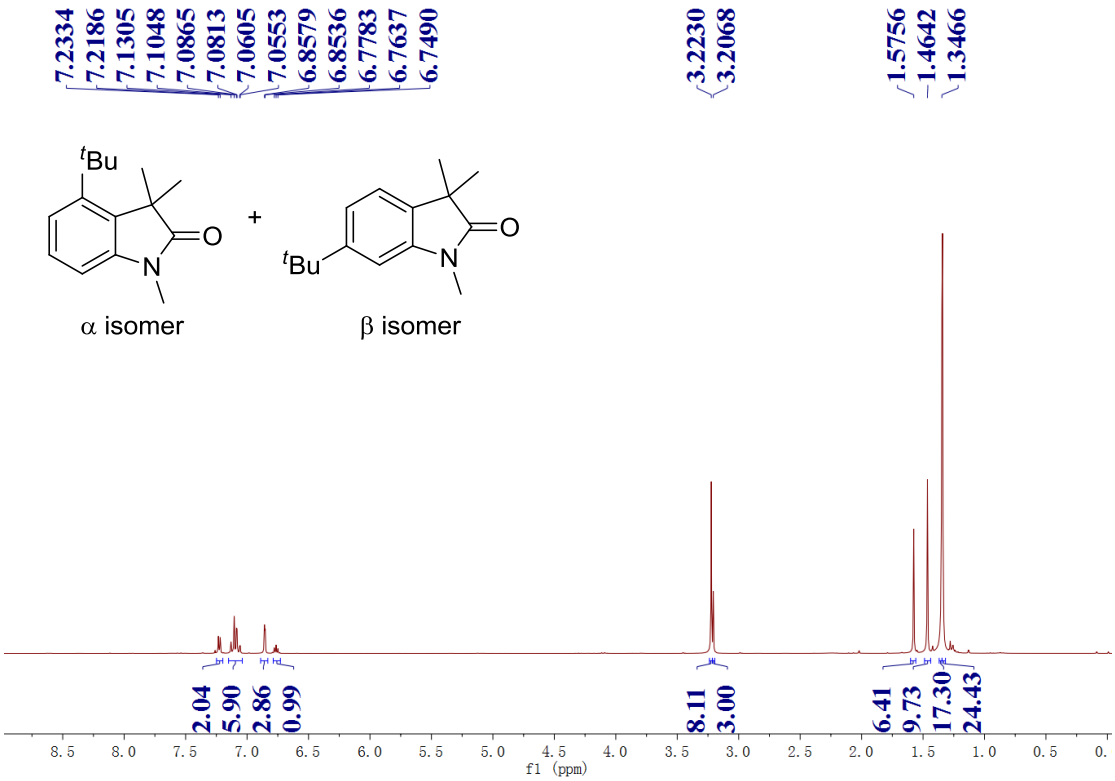


Fig. S44 ^{1}H NMR spectrum of **2u** in $CDCl_3$.

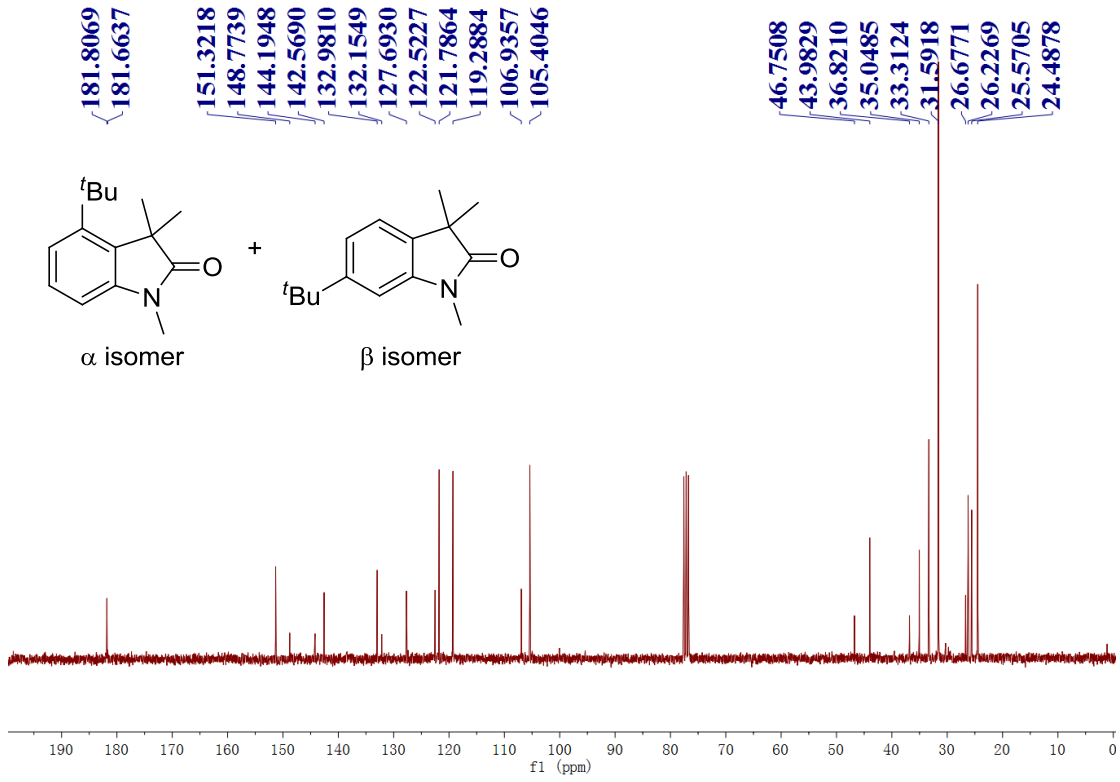


Fig. S45 ^{13}C NMR spectrum of **2u** in $CDCl_3$.

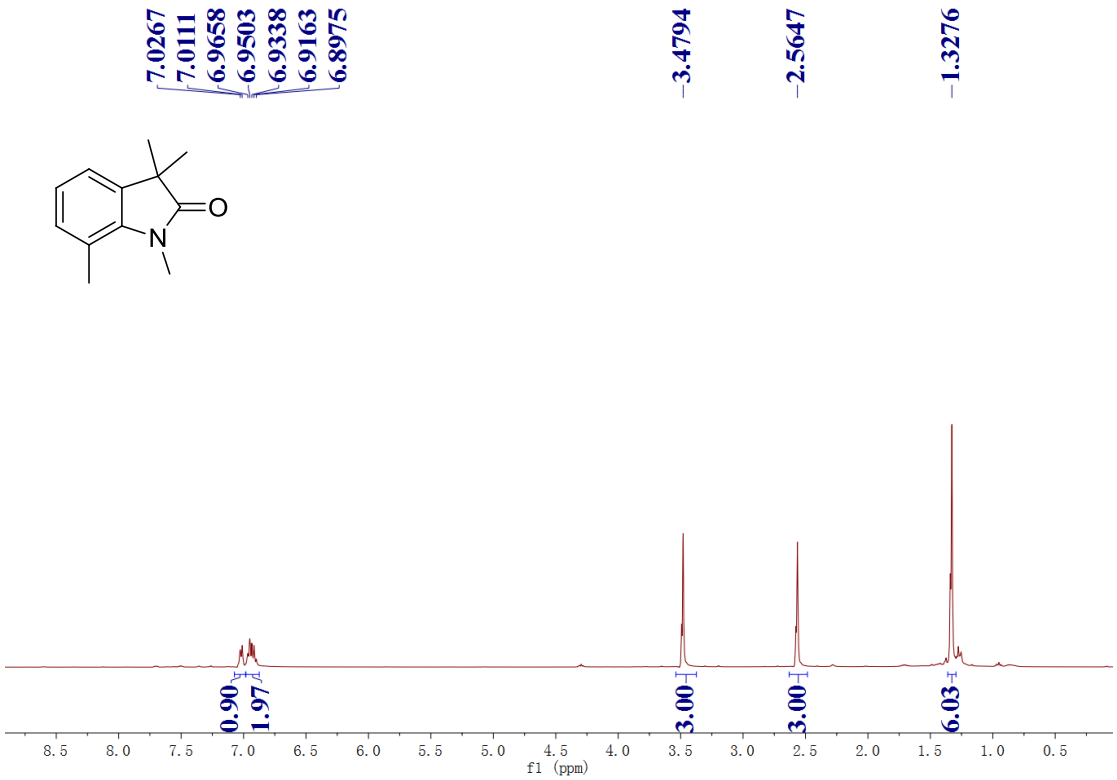


Fig. S46 ^{1}H NMR spectrum of **2v** in $CDCl_3$.

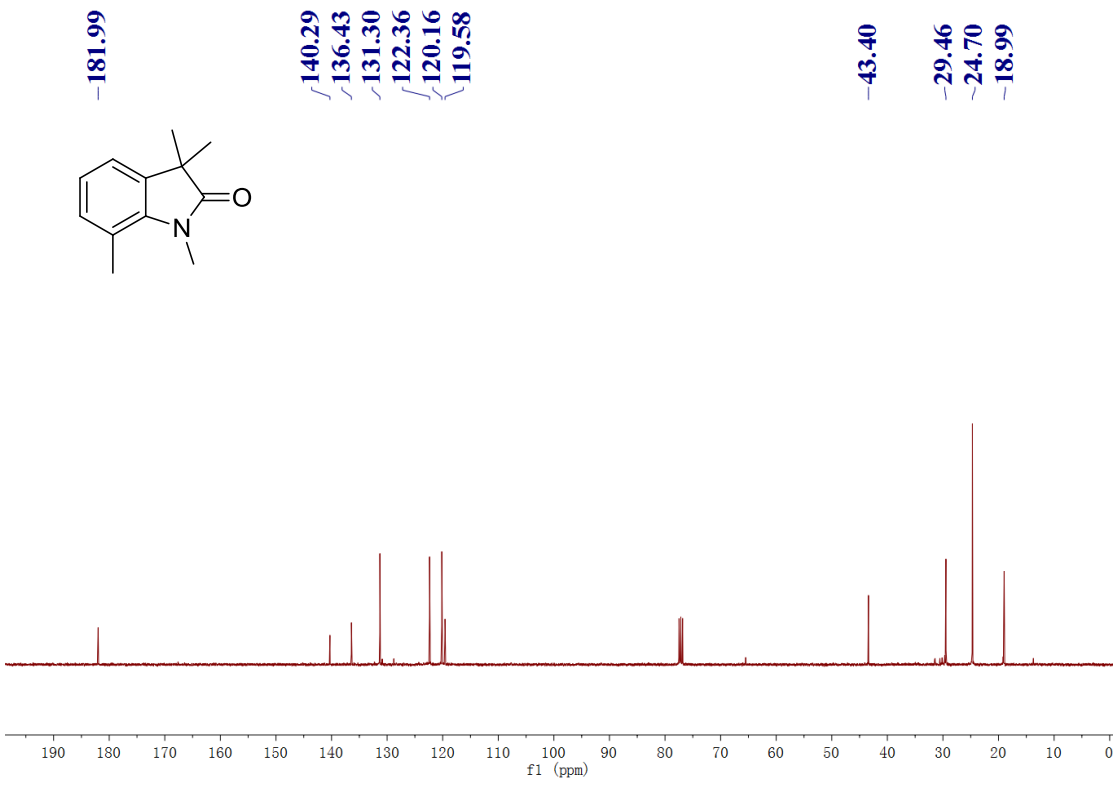


Fig. S47 ^{13}C NMR spectrum of **2v** in $CDCl_3$.

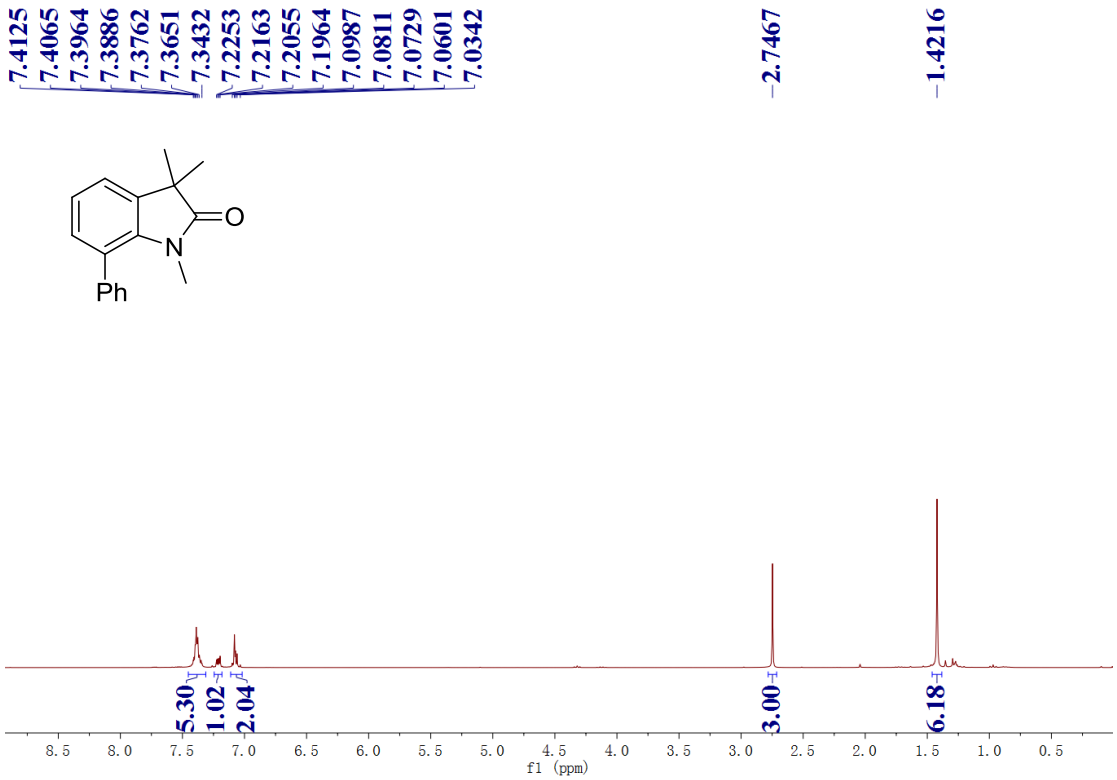


Fig. S48 ^{1}H NMR spectrum of **2w** in $CDCl_3$.

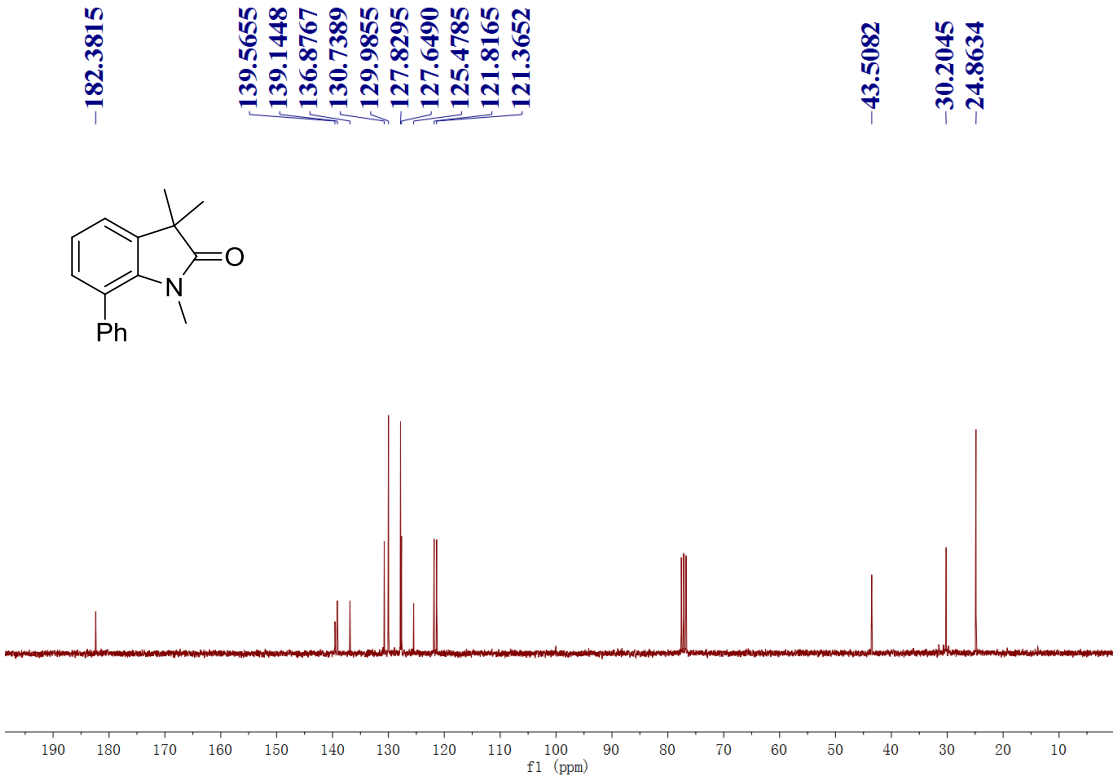


Fig. S49 ^{13}C NMR spectrum of **2w** in $CDCl_3$.

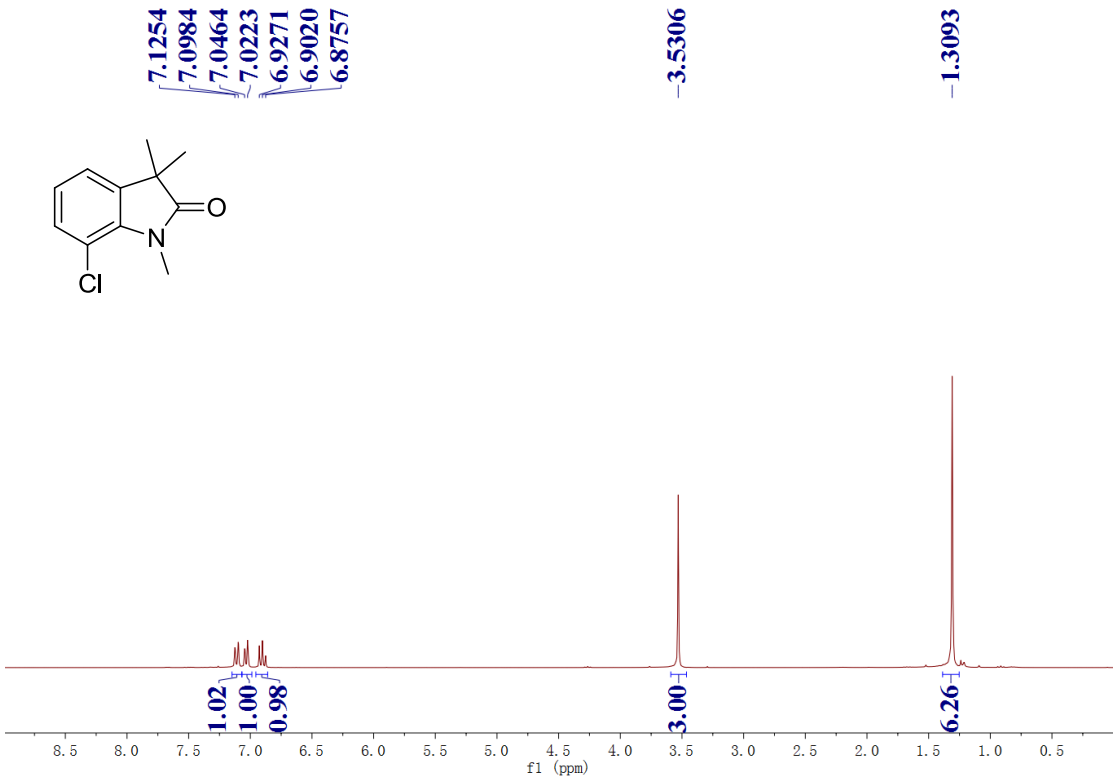


Fig. S50 ^{1}H NMR spectrum of **2x** in $CDCl_3$.

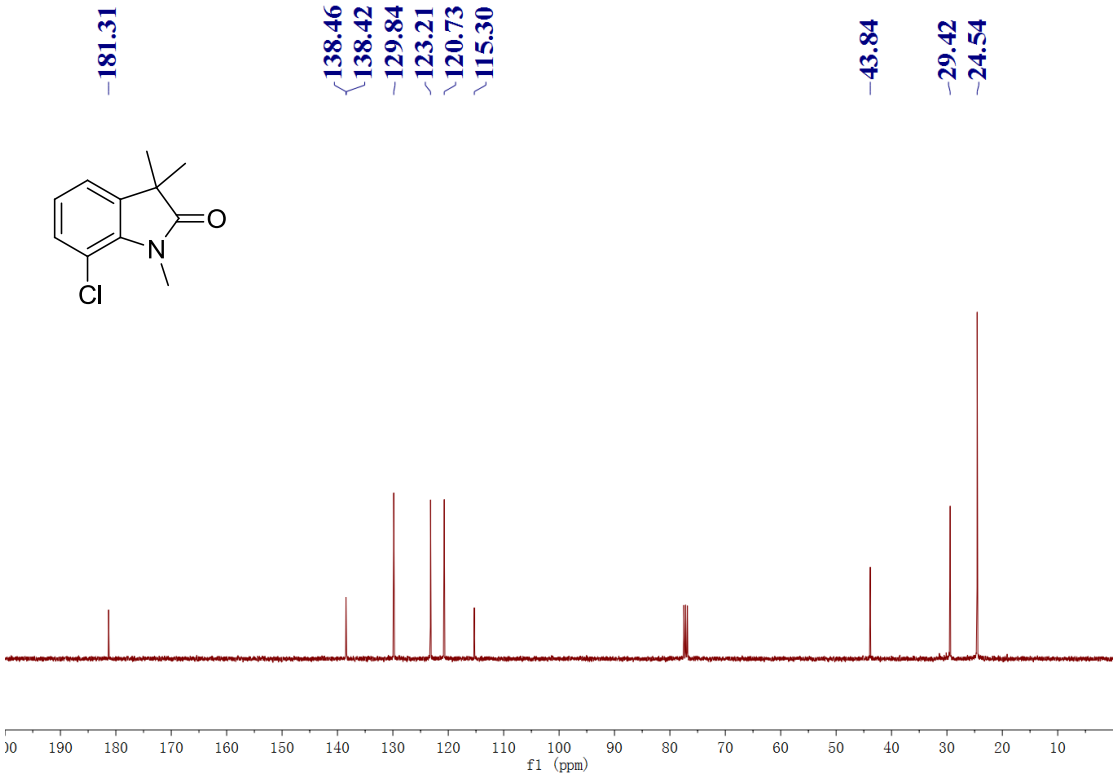


Fig. S51 ^{13}C NMR spectrum of **2x** in $CDCl_3$.

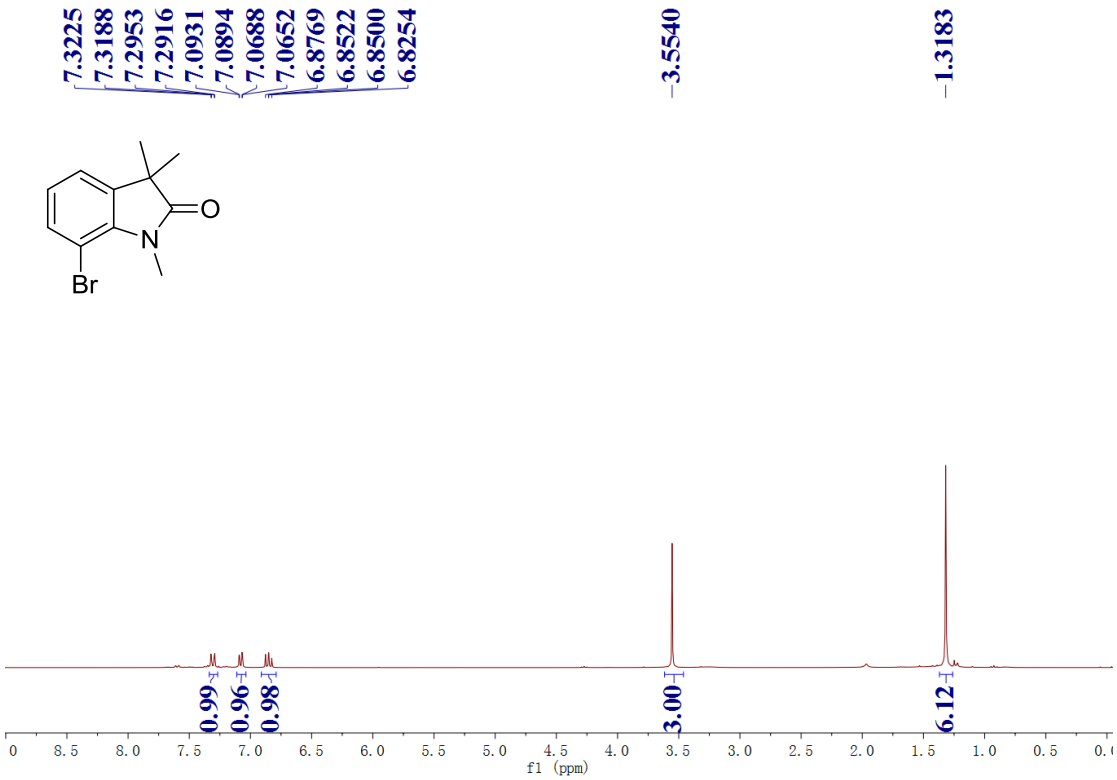


Fig. S52 ^{1}H NMR spectrum of **2y** in $CDCl_3$.

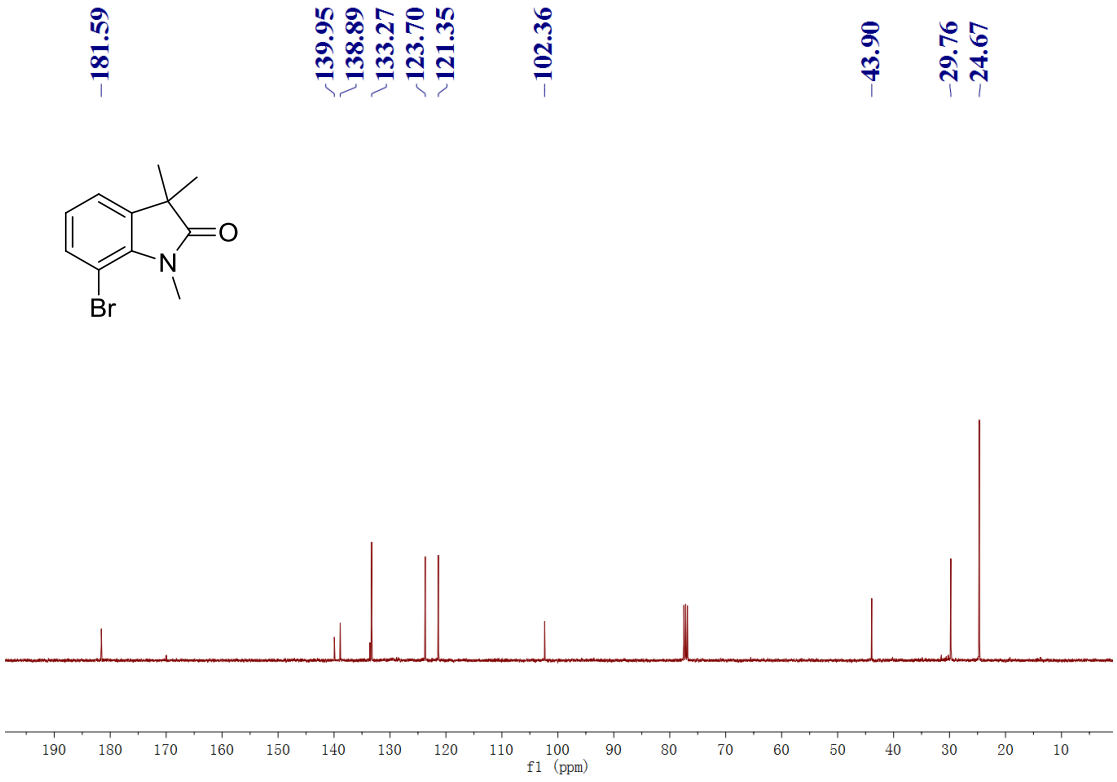


Fig. S53 ^{13}C NMR spectrum of **2y** in $CDCl_3$.

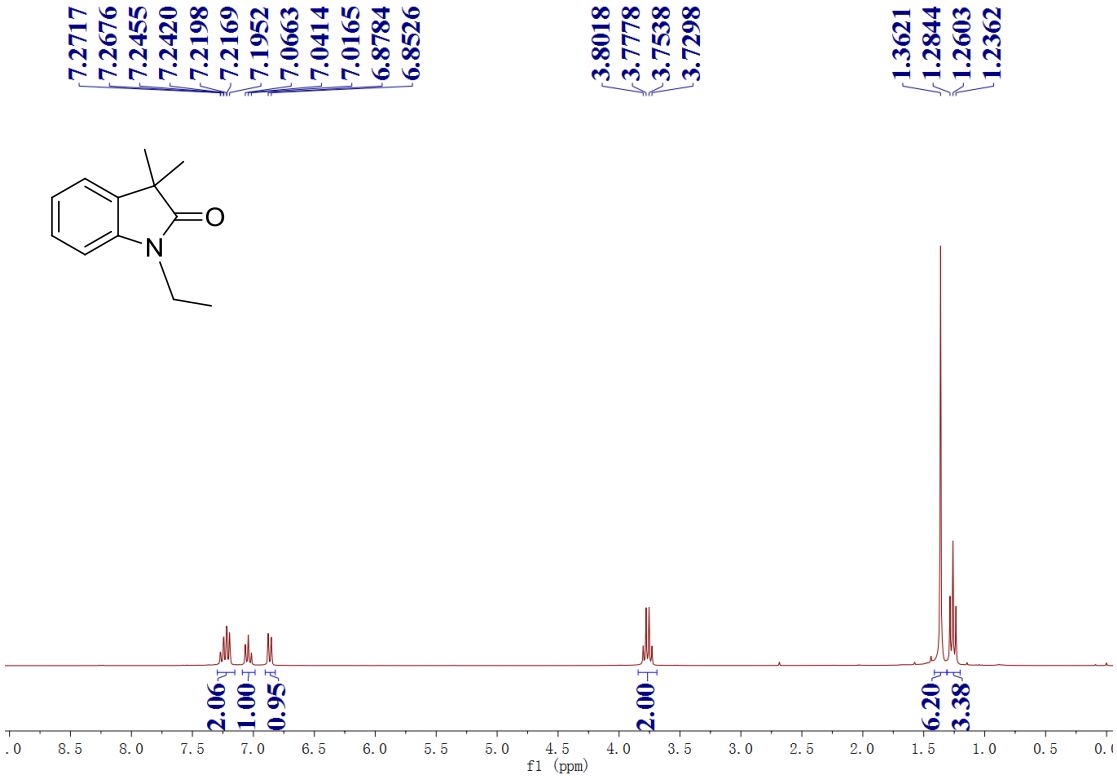


Fig. S54 ^{1}H NMR spectrum of **2z** in $CDCl_3$.

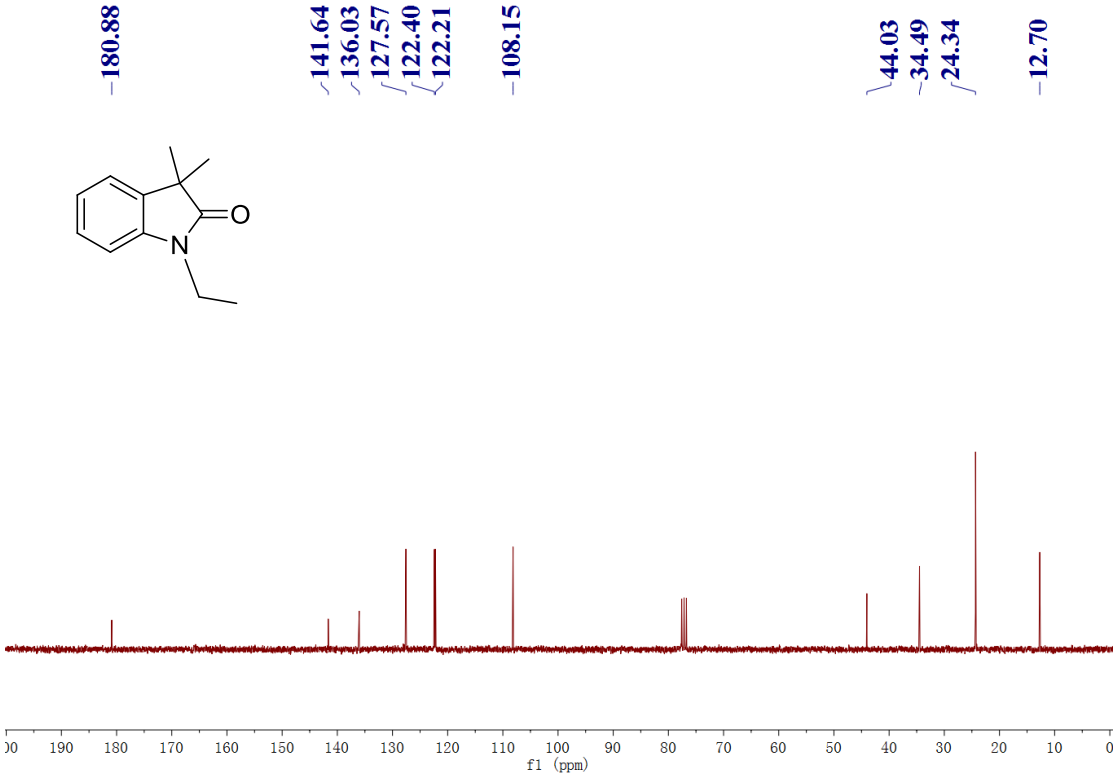


Fig. S55 ^{13}C NMR spectrum of **2z** in $CDCl_3$.

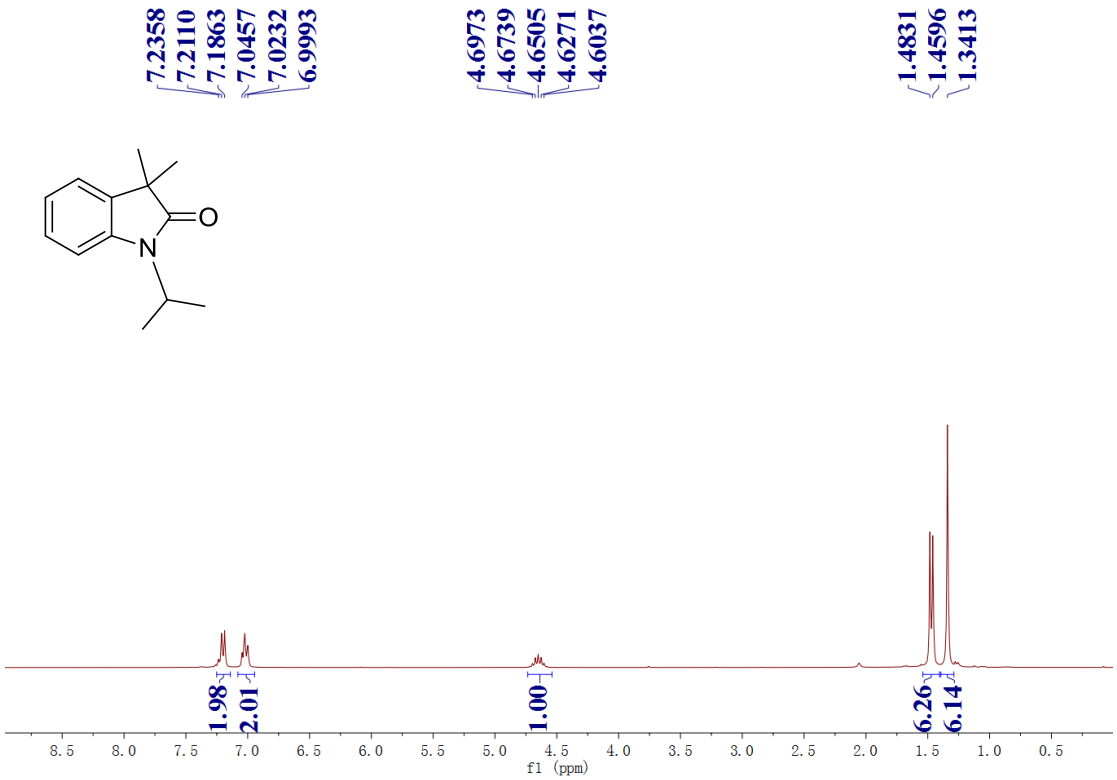


Fig. S56 ^{1}H NMR spectrum of **2aa** in $CDCl_3$.

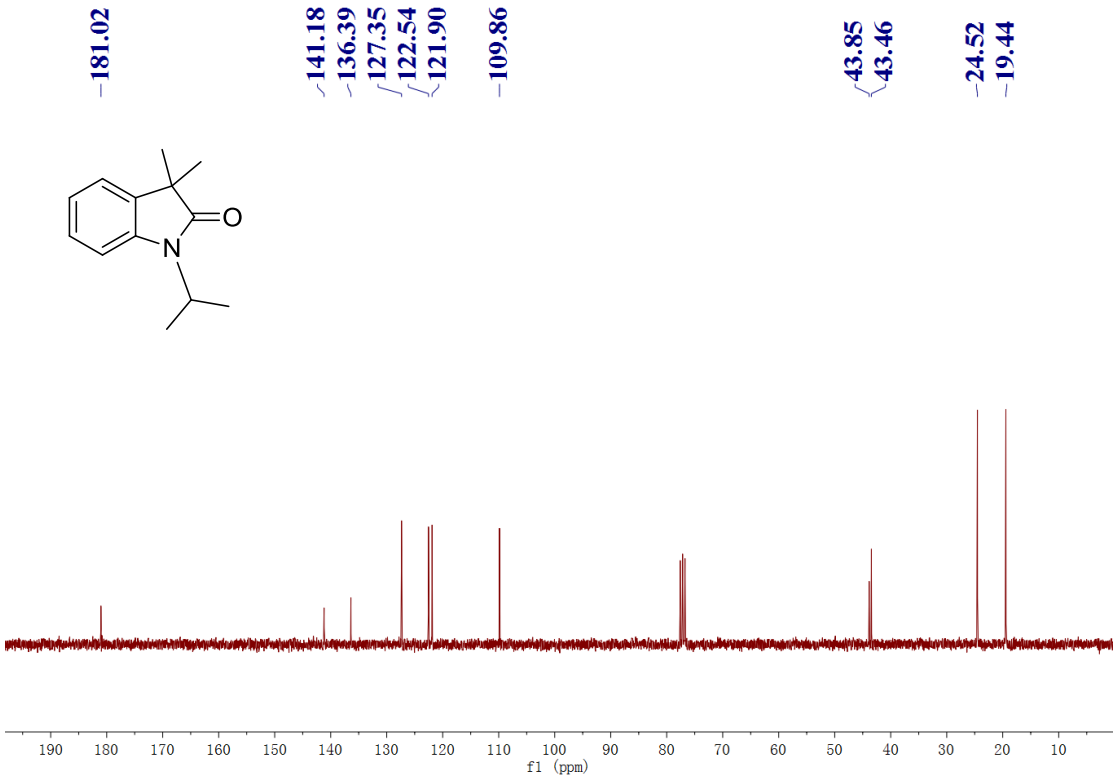


Fig. S57 ^{13}C NMR spectrum of **2aa** in $CDCl_3$.

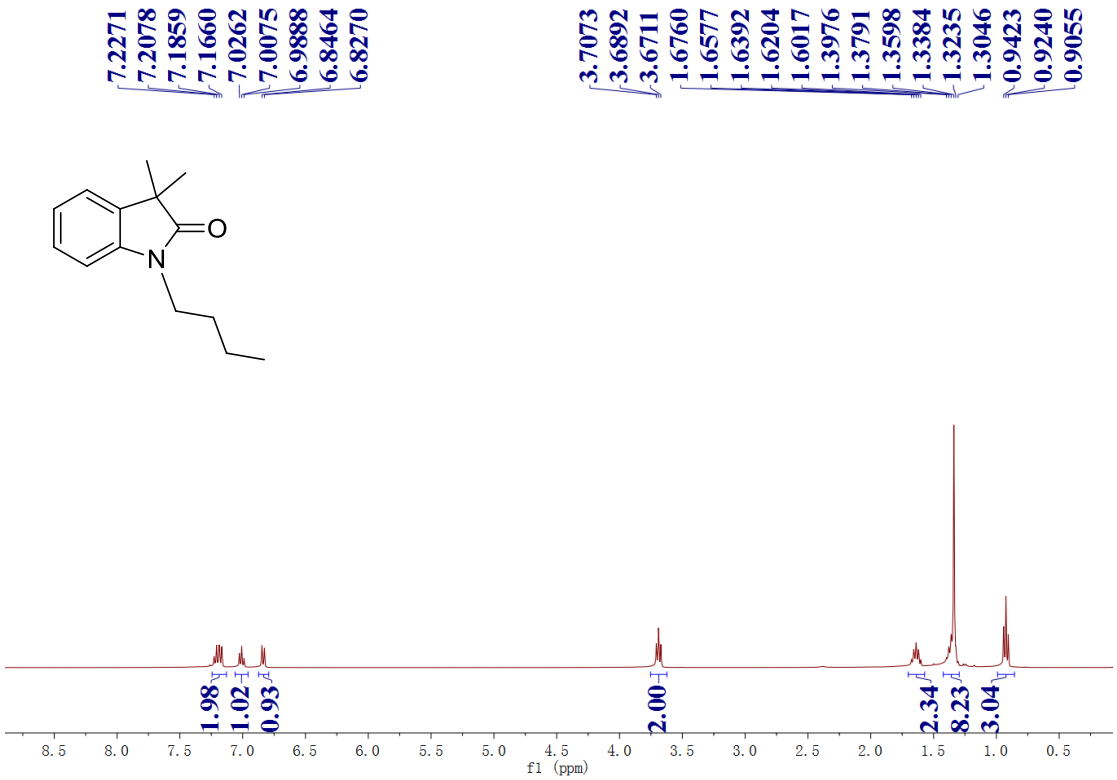


Fig. S58 ^{1}H NMR spectrum of **2ab** in $CDCl_3$.

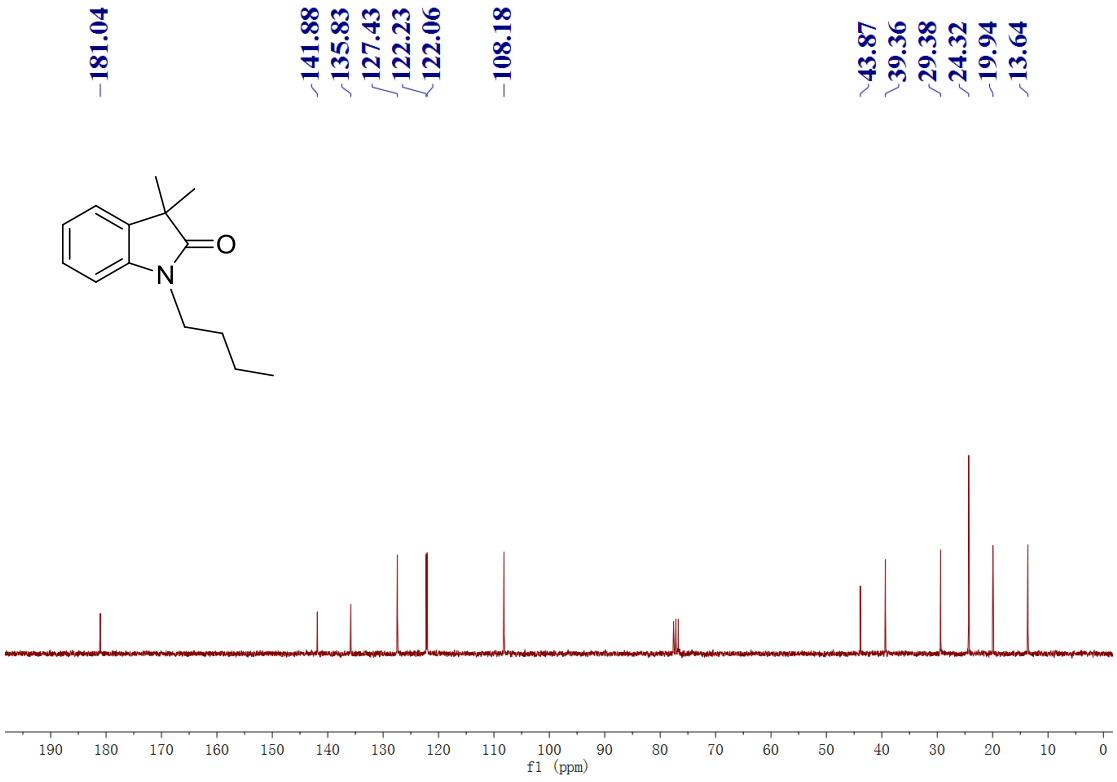


Fig. S59 ^{13}C NMR spectrum of **2ab** in $CDCl_3$.

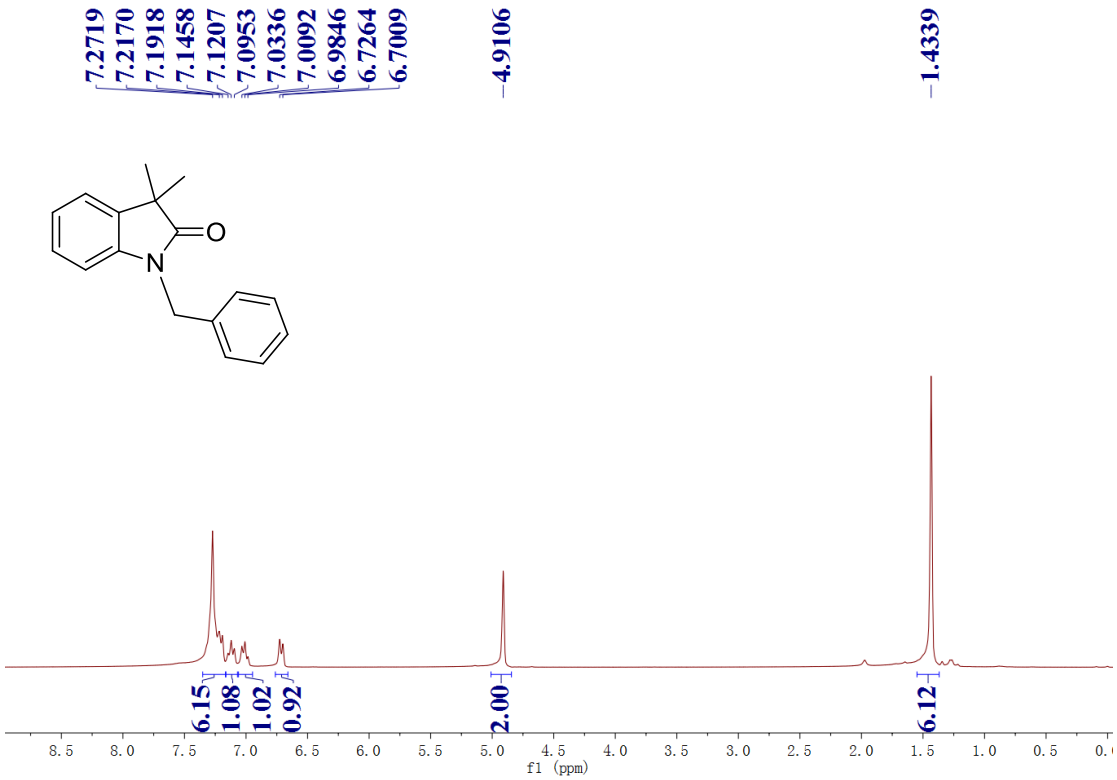


Fig. S60 ^{1}H NMR spectrum of **2ac** in $CDCl_3$.

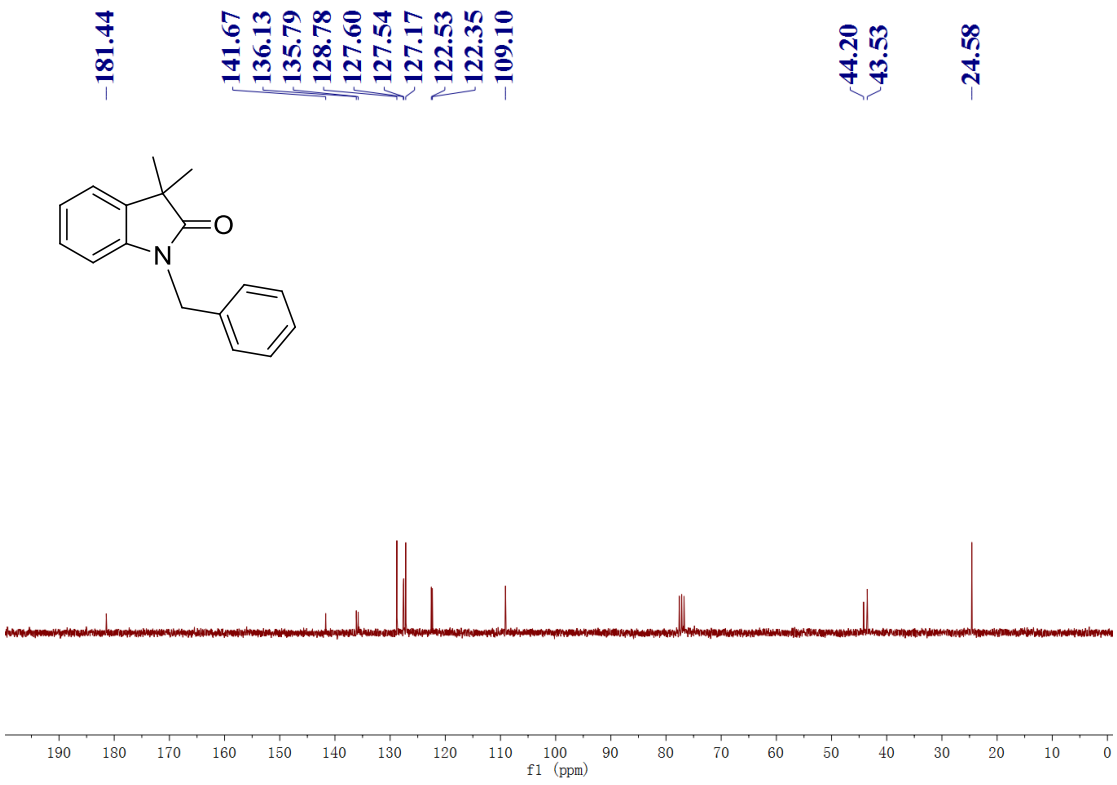


Fig. S61 ^{13}C NMR spectrum of **2ac** in $CDCl_3$.

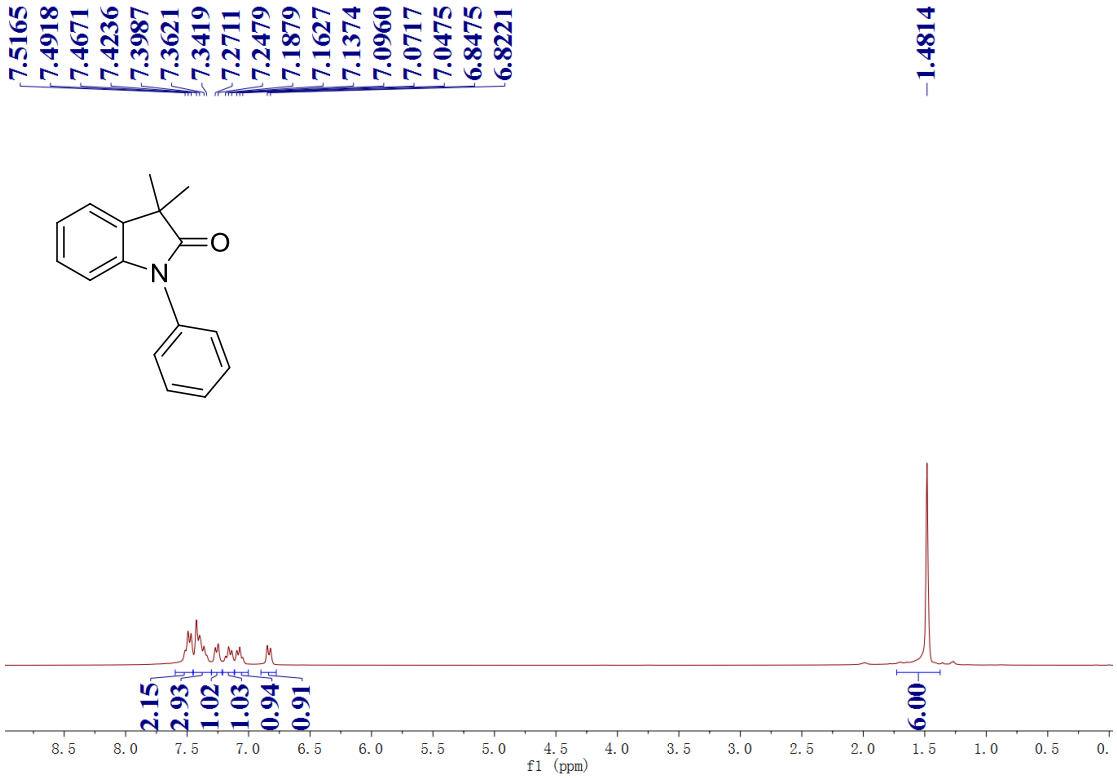


Fig. S62 ^{1}H NMR spectrum of **2ad** in $CDCl_3$.

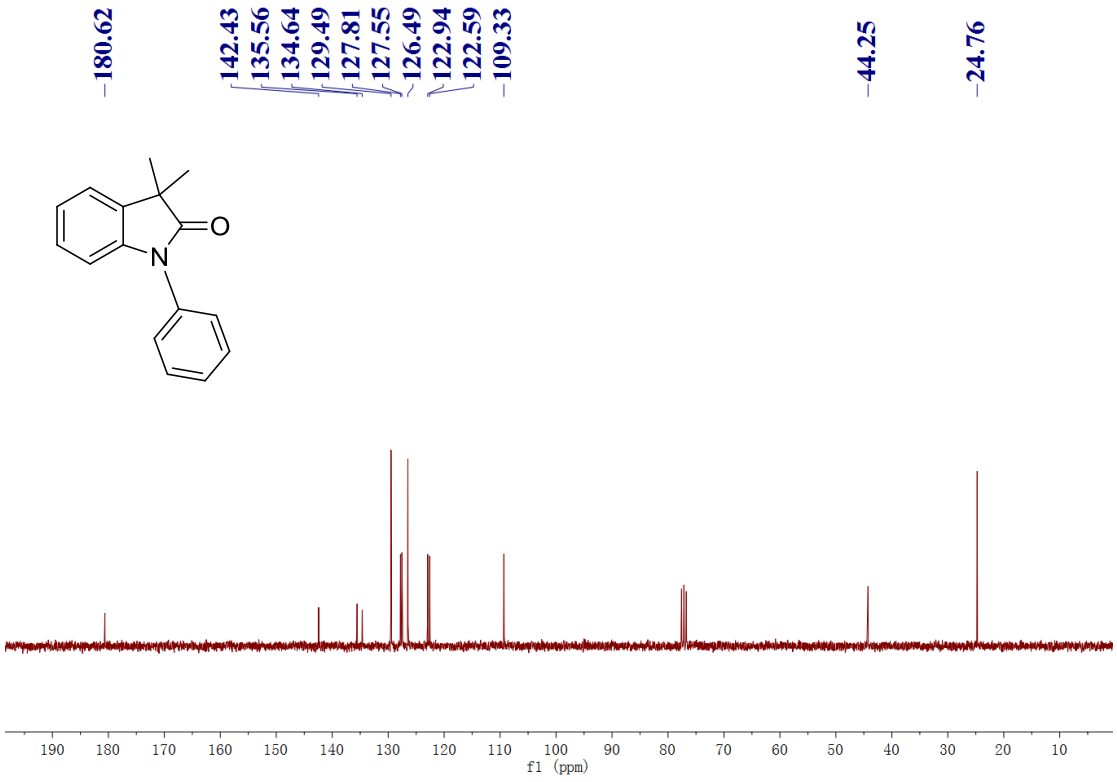


Fig. S63 ^{13}C NMR spectrum of **2ad** in $CDCl_3$.

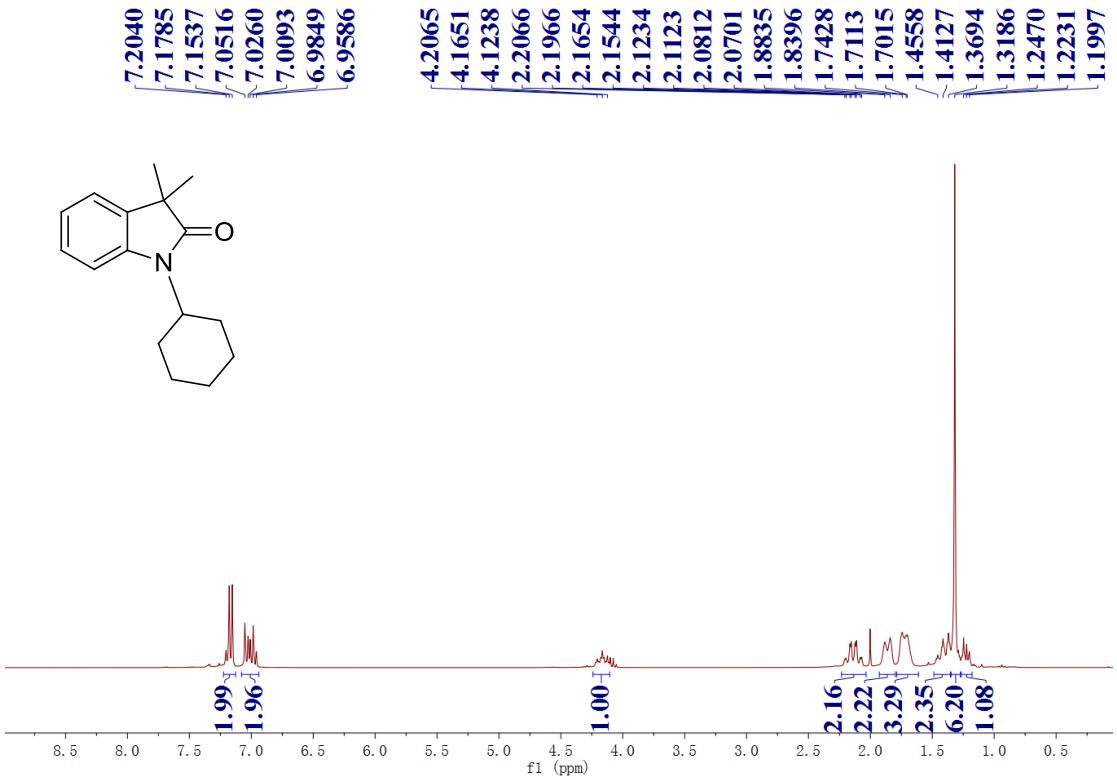


Fig. S64 ^{1}H NMR spectrum of **2ae** in $CDCl_3$.

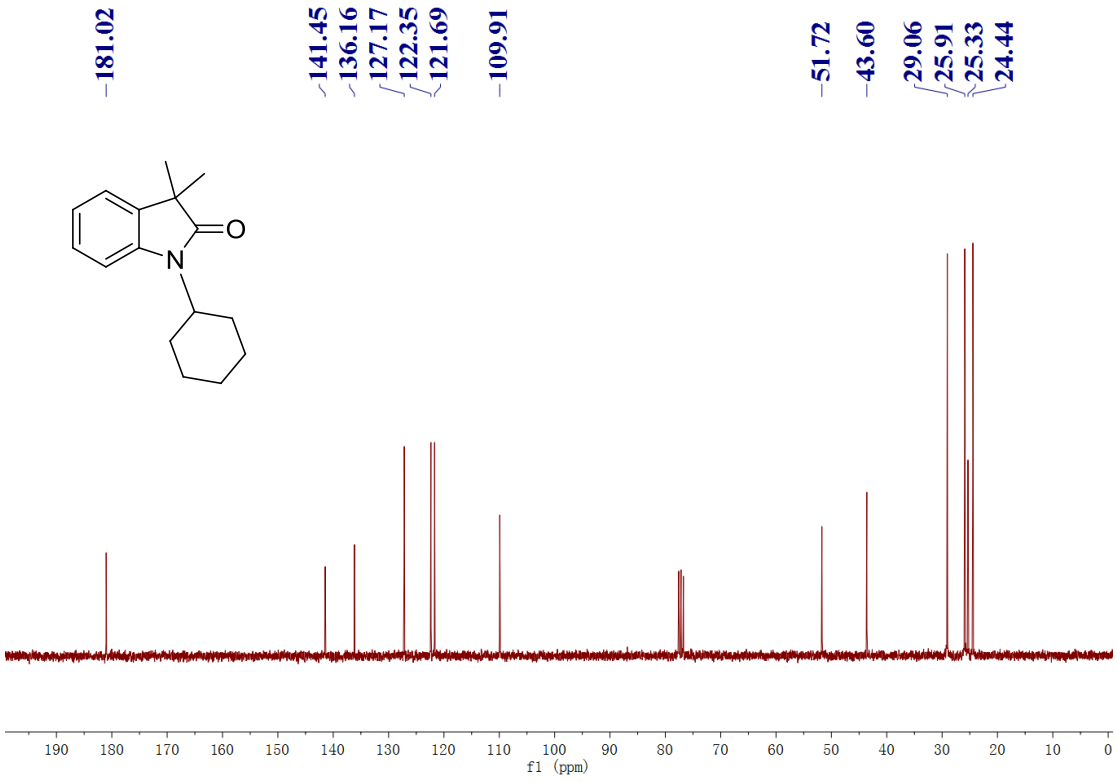


Fig. S65 ^{13}C NMR spectrum of **2ae** in $CDCl_3$.

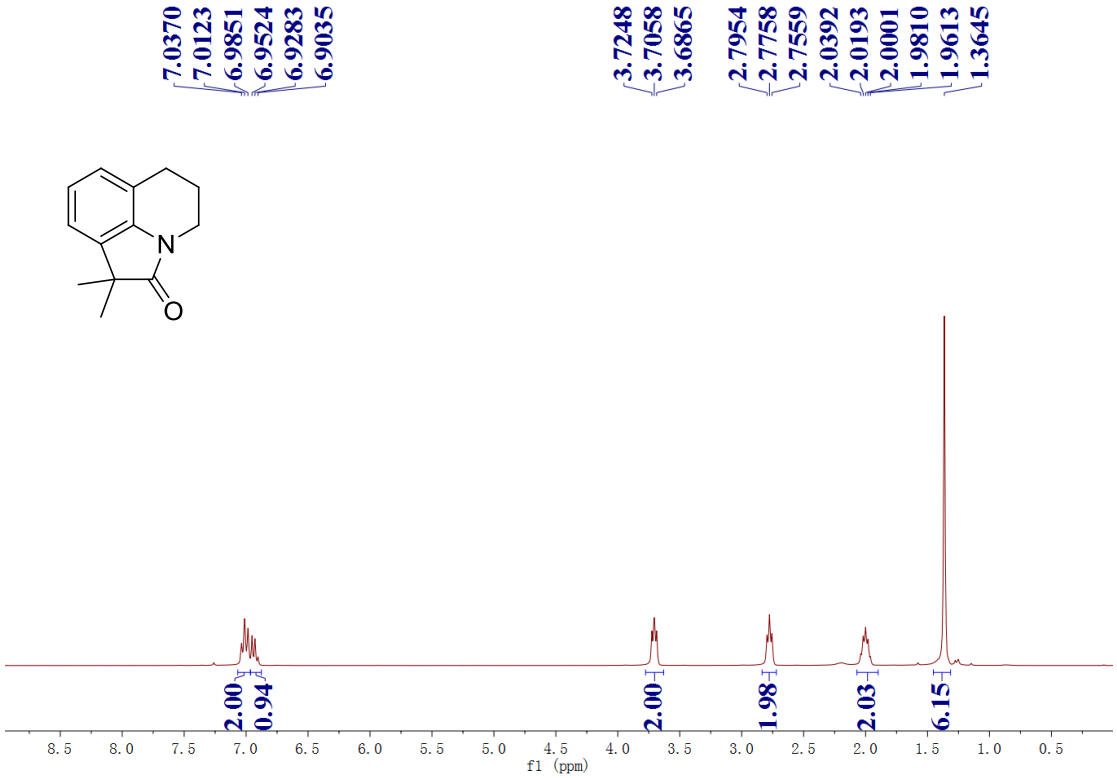


Fig. S66 ^{1}H NMR spectrum of **2ag** in $CDCl_3$.

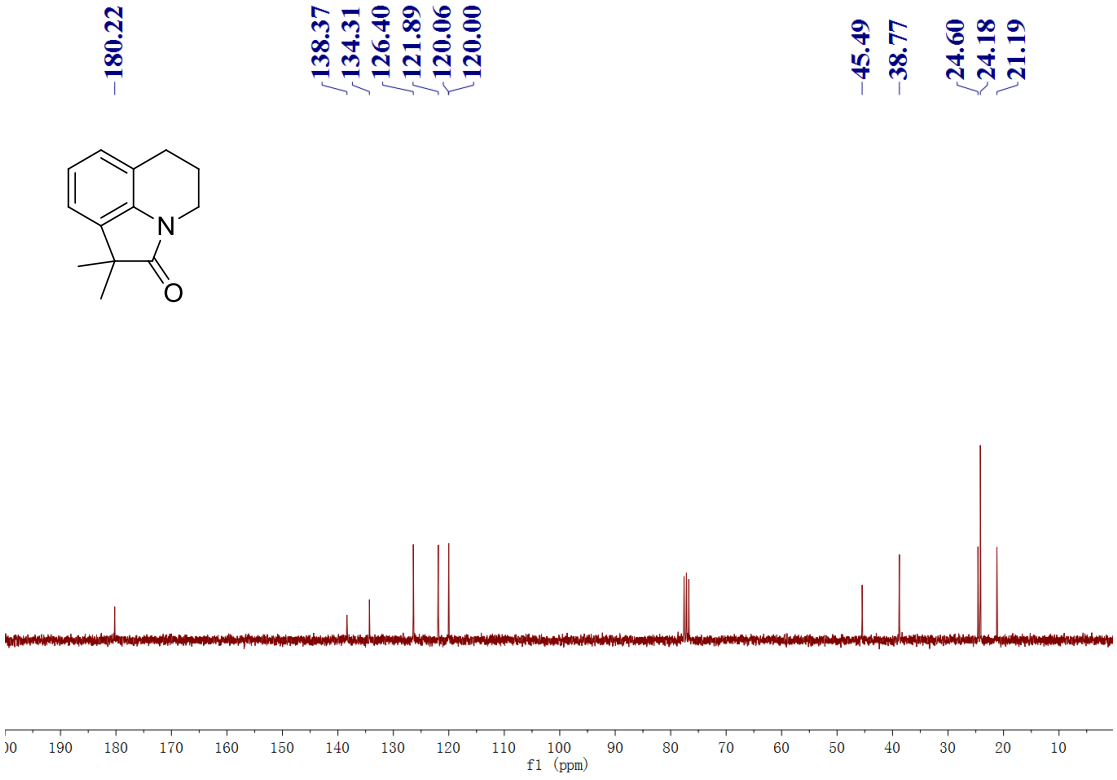


Fig. S67 ^{13}C NMR spectrum of **2ag** in $CDCl_3$.

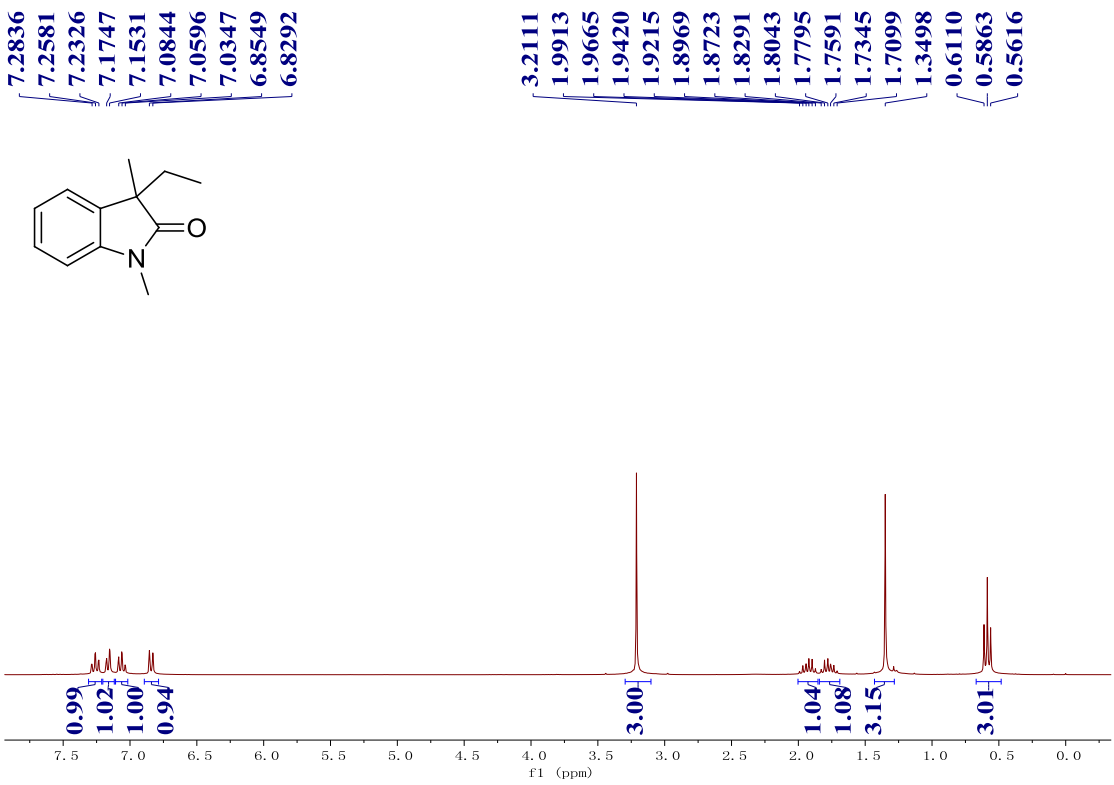


Fig. S68 ^{1}H NMR spectrum of **2ah** in $CDCl_3$.

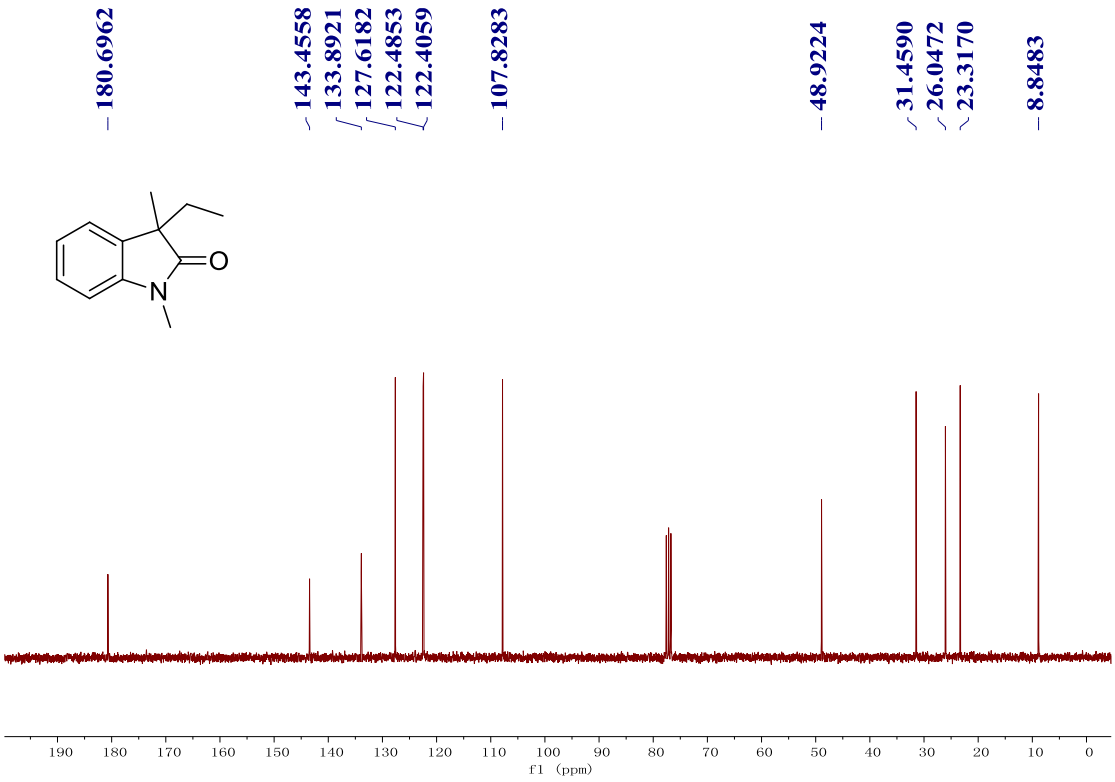


Fig. S69 ^{13}C NMR spectrum of **2ah** in $CDCl_3$.

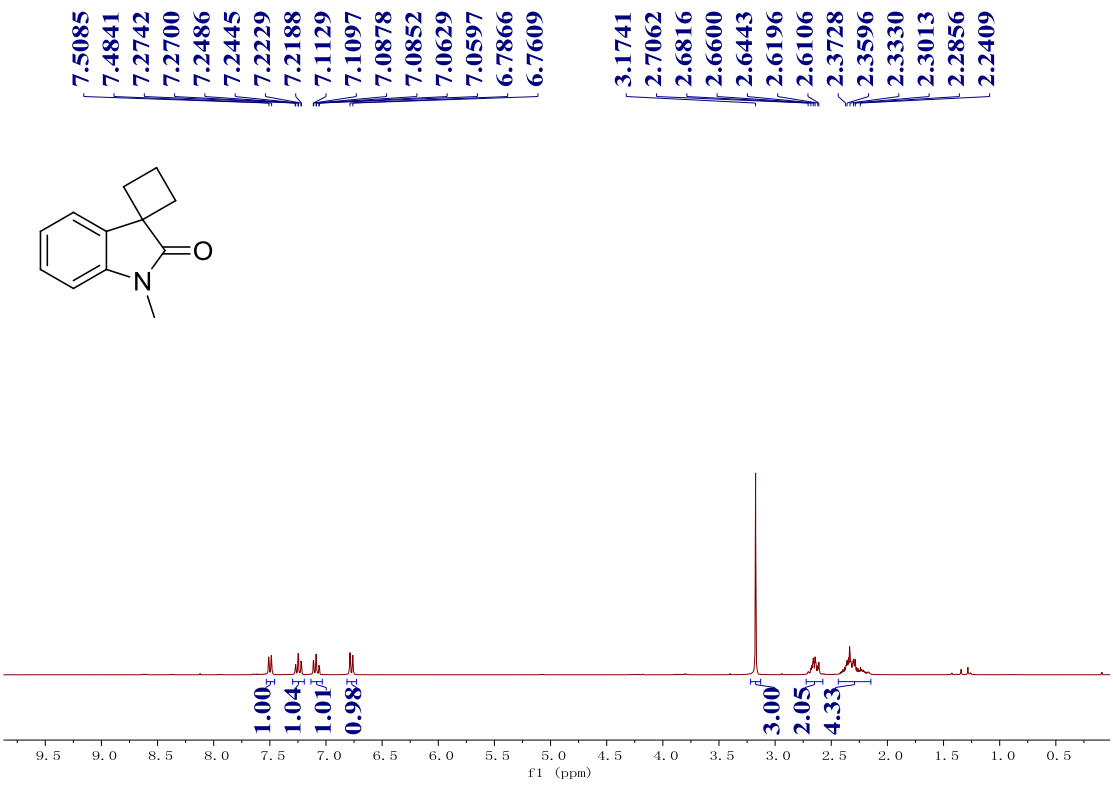


Fig. S70 ^{1}H NMR spectrum of **2ai** in $CDCl_3$.

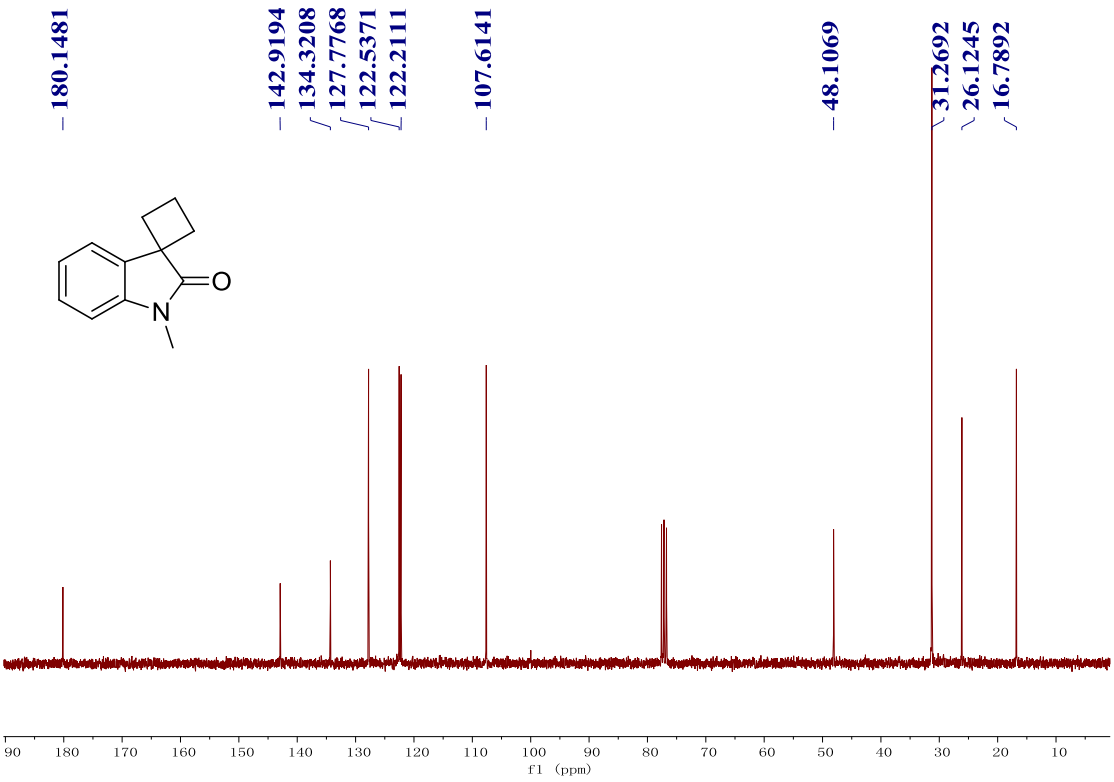


Fig. S71 ^{13}C NMR spectrum of **2ai** in $CDCl_3$.

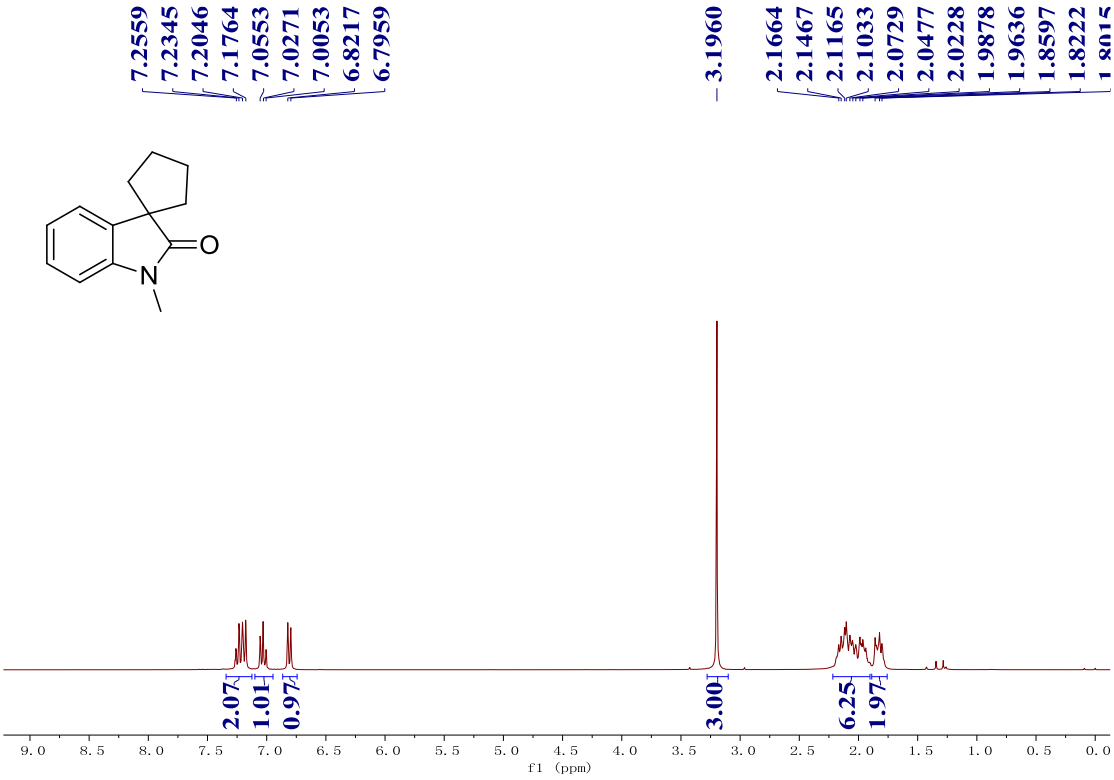


Fig. S72 ^{1}H NMR spectrum of **2aj** in $CDCl_3$.

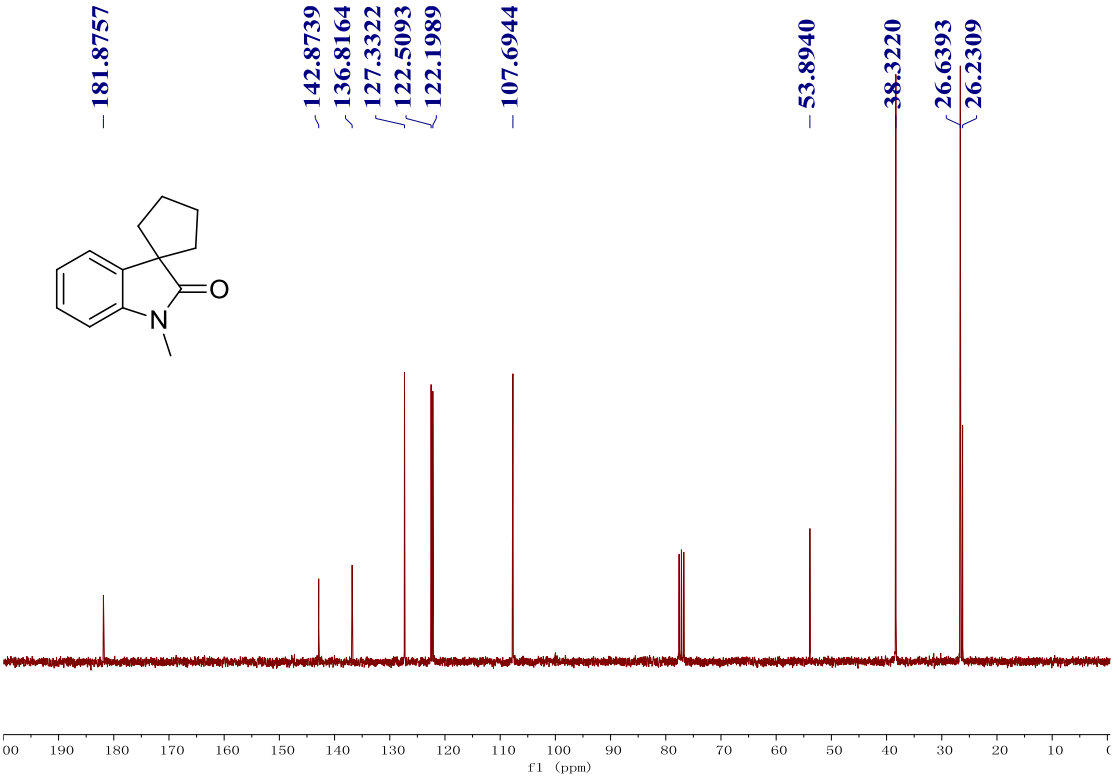


Fig. S73 ^{13}C NMR spectrum of **2aj** in $CDCl_3$.

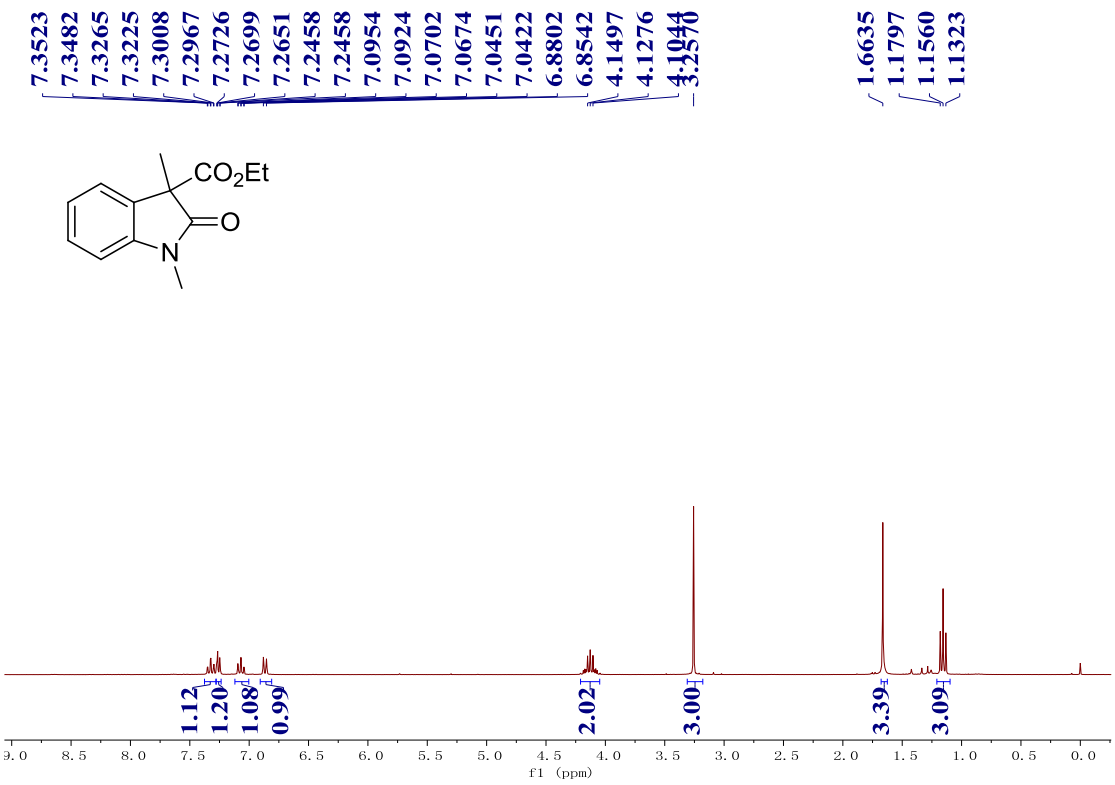


Fig. S74 ^{1}H NMR spectrum of **2ak** in $CDCl_3$.

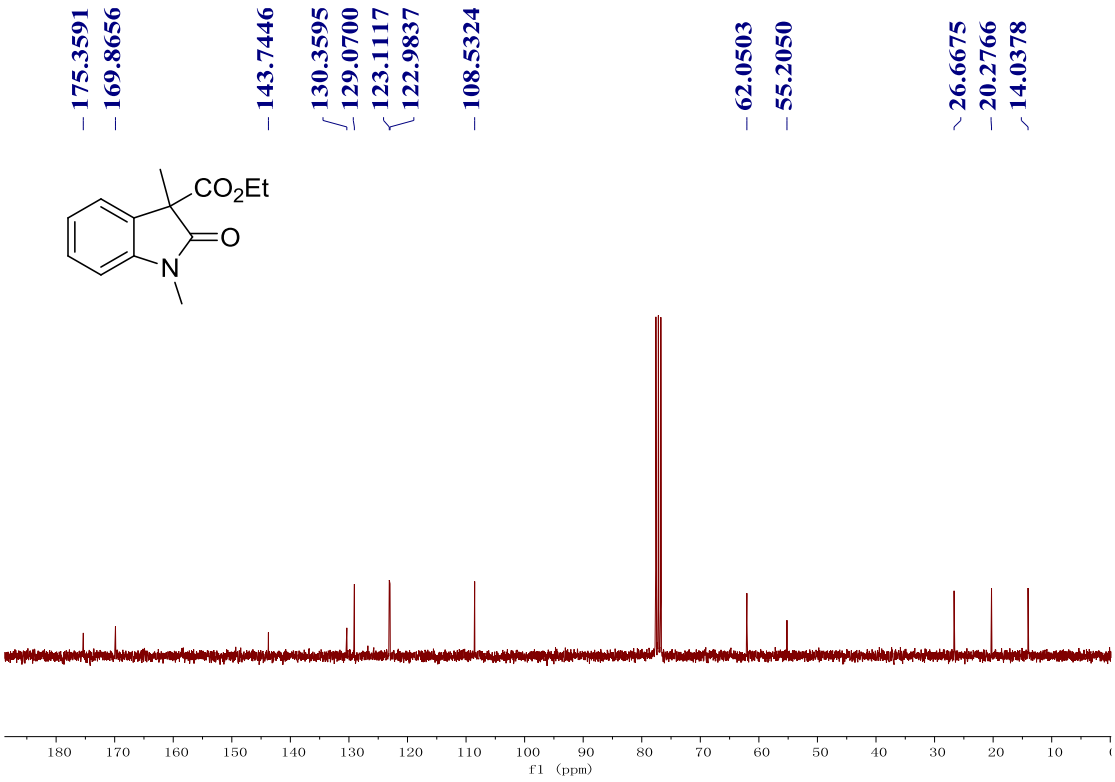


Fig. S75 ^{13}C NMR spectrum of **2ak** in $CDCl_3$.

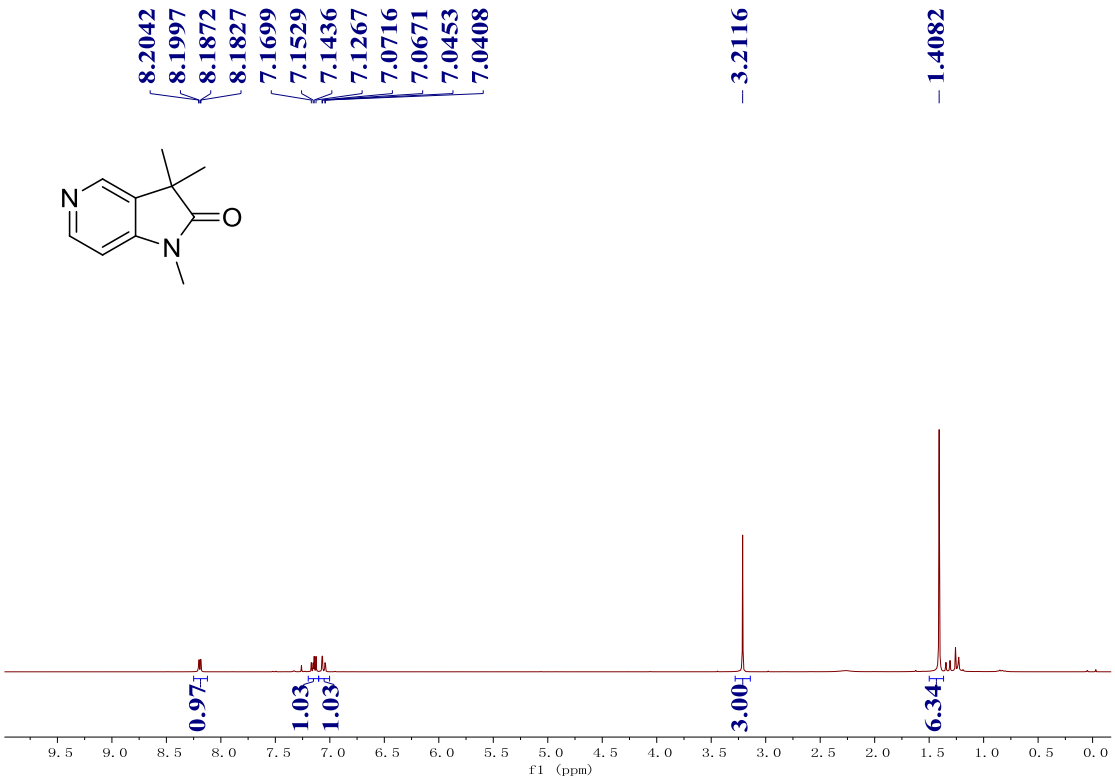


Fig. S76 ^{1}H NMR spectrum of **2al** in $CDCl_3$.

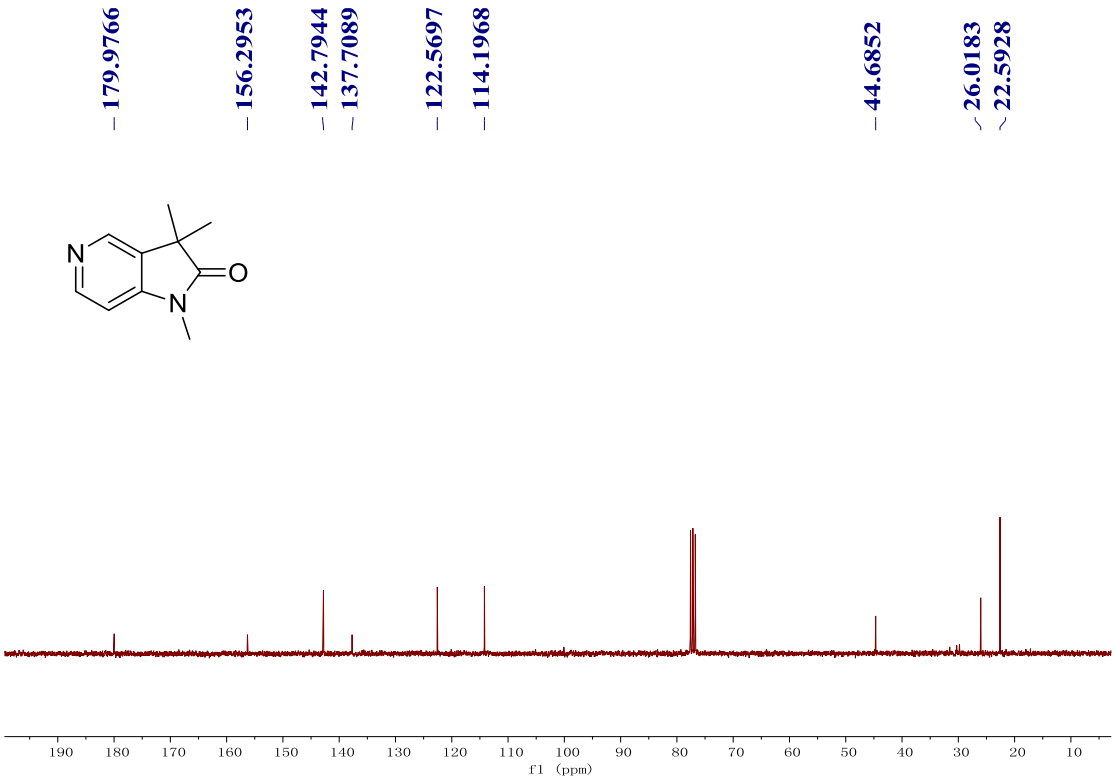


Fig. S77 ^{13}C NMR spectrum of **2al** in $CDCl_3$.

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