Supporting Information

Synthesis of 3-Spirocyclobutyl Oxindoles *via* N-Heterocyclic Carbene-Catalyzed Radical Alkylarylation of Bicyclo[1.1.0]butanes

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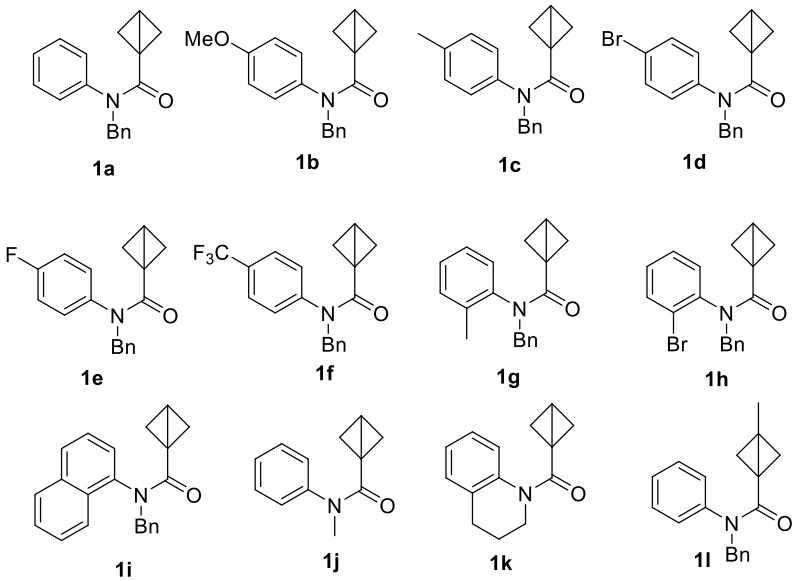
1. General methods and materials

Unless otherwise mentioned, all reactions were carried out under an atmosphere of argon in dry glassware and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). IR spectra were taken on a FT-IR spectrometer in KBr pellets and reported in cm^{-1}. ^{1}H NMR spectra were measured on a 400 MHz spectrometer in $CDCl_3$ (100 MHz, ^{13}C NMR) with chemical shift (δ) given in ppm relative to TMS as internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple), coupling constants (Hz), integration. High-resolution mass spectra (HRMS) were measured with ESI in a positive mode.

The *N*-aryl bicyclobutyl amides **1** were synthesized according to the reported procedure (prepared from 3-oxocyclobutanecarboxylic acid (CAS: 23761-23-1, 5 g/CNY 36) in four steps)[1]. The radical precursors **2** were commercially available.



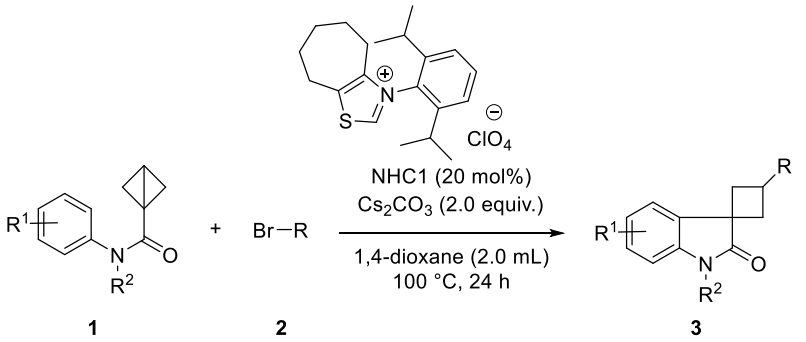
1a **1b** **1c** **1d**

1e **1f** **1g** **1h**

1i **1j** **1k** **1l**

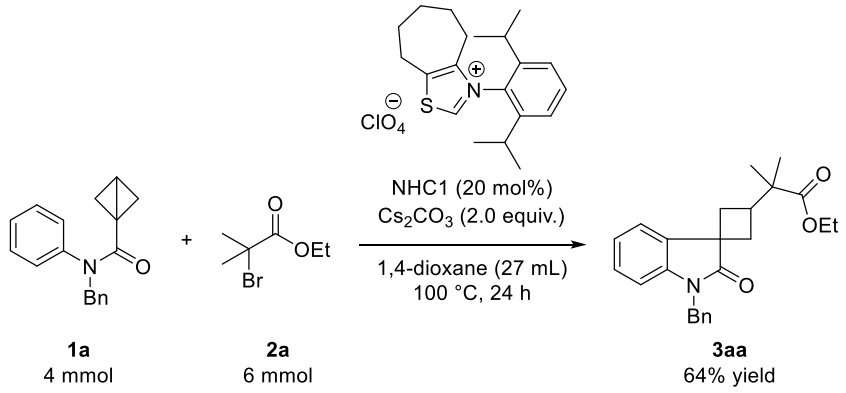
2. General Procedures

2.1 General procedure for the synthesis of product 3



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with bicyclobutyl *N*-aryl amides **1** (0.3 mmol, 1.0 equiv.), alkyl bromides **2** (0.45 mmol, 1.5 equiv.), **NHC1** (24.8 mg, 0.06 mmol, 0.2 equiv.), Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.) and 2 mL of anhydrous 1,4-dioxane under argon. The reaction mixture was stirred at 100 ℃ in heating mantle for 24 h monitored by TLC analysis. After the reaction was complete, water was added and extracted with ethyl acetate. The organic phase was then evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (PE/EA=10/1) to give product **3**. All the products were prepared according to the above procedure.

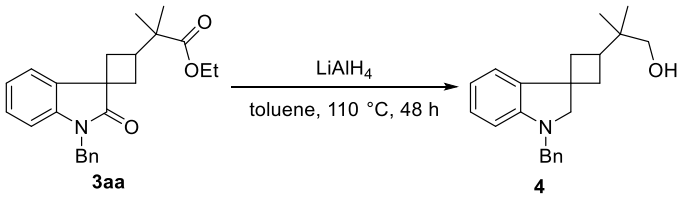
2.2 General procedure for gram-scale reaction



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with bicyclobutyl *N*-aryl amides **1a** (4 mmol, 1.0 equiv.), alkyl bromides **2a** (6 mmol, 1.5 equiv.), **NHC1** (331.1 mg, 0.8 mmol, 0.2 equiv.), Cs_2CO_3 (2.6 g, 8 mmol, 2.0 equiv.) and 27 mL of anhydrous 1,4-dioxane under argon. The reaction mixture was stirred at 100 ℃ in heating mantle for 24 h monitored by TLC analysis. After the reaction was complete, water was added and extracted with ethyl acetate. The organic

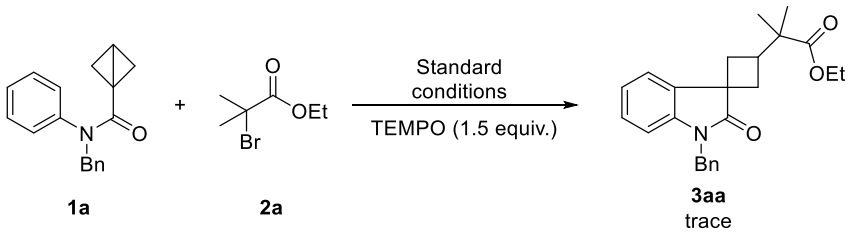
phase was then evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (PE/EA=10/1) to give product **3aa** (0.97 g, 64% yield).

2.3 Procedures for the transformations[2]

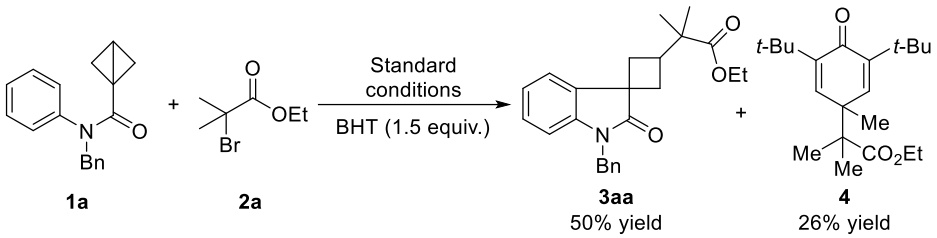


In a flame-dried schlenk tube, **3aa** (0.15 mmol, 56.6 mg) was dissolved in anhydrous toluene (1.5 mL), $LiAlH_4$ (1.5 mmol, 56.9 mg) was then added slowly at 0 ℃ under Ar. The reaction mixture was stirred at 110 ℃ for 48 h. After cooling to room temperature, the reaction was quenched with a saturated solution of NH_4Cl. The reaction was then extracted with ether three times. The combined organic extracts were washed with brine, dried with $MgSO_4$, filtrated and concentrated in vacuo. The product was purified by flash column chromatography (petroleum ether/EtOAc, 20:1) to yield **4aa** (41 mg, 85% yield) as a colorless oil.

2.4 Procedures for the radical trapping experiments.



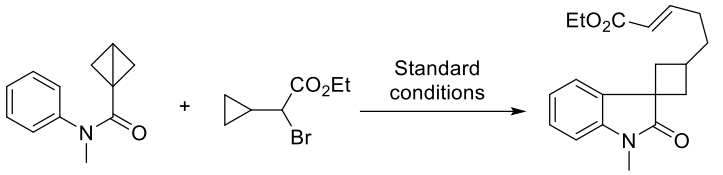
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with bicyclobutyl *N*-aryl amides **1a** (0.3 mmol, 1.0 equiv.), alkyl bromides **2a** (0.45 mmol, 1.5 equiv.), **NHC1** (24.8 mg, 0.06 mmol, 0.2 equiv.), Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.), TEMPO (70.3 mg, 0.45 mmol, 1.5 equiv.) and 2 mL of anhydrous 1,4-dioxane under argon. The reaction mixture was stirred at 100 ℃ in heating mantle for 24 h monitored by TLC analysis, and only trace amount of product **3aa** was detected.



1a **2a** **3aa** 50% yield **4** 26% yield

An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with bicyclobutyl *N*-aryl amides **1a** (0.3 mmol, 1.0 equiv.), alkyl bromides **2a** (0.45 mmol, 1.5 equiv.), **NHC1** (24.8 mg, 0.06 mmol, 0.2 equiv.), Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.), BHT (99.1 mg, 0.45 mmol, 1.5 equiv.) and 2 mL of anhydrous 1,4-dioxane under argon. The reaction mixture was stirred at 100 ℃ in heating mantle for 24 h monitored by TLC analysis. After the reaction was complete, water was added and extracted with ethyl acetate. The organic phase was then evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (PE/EA=10/1) to give product **3aa** (57 mg, 50% yield).

2.5 Procedures for the radical clock reaction[1]

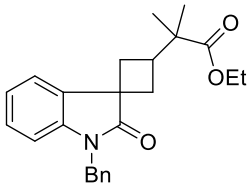


1j **2m** **3jm** 40% yield, 1.5:1 d.r.

An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with bicyclobutyl N-aryl amides **1j** (0.3 mmol, 1.0 equiv.), alkyl bromides **2m** (0.45 mmol, 1.5 equiv.), **NHC1** (24.8 mg, 0.06 mmol, 0.2 equiv.), Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.) and 2 mL of anhydrous 1,4-dioxane under argon. The reaction mixture was stirred at 100 ℃ in heating mantle for 24 h monitored by TLC analysis. After the reaction was complete, water was added and extracted with ethyl acetate. The organic phase was then evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (PE/EA=10/1) to give product **3jm** (38 mg, 40% yield).

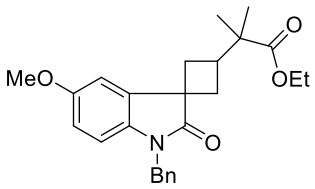
3. Characterization Data of the Products

Ethyl-2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropanoate (3aa)



Yellow oil; 79% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, J = 7.2 Hz, 0.66H, major), 7.27 – 7.15 (m, 5.66H, major+minor), 7.10 – 7.03 (m, 1H, major+minor), 7.00 – 6.95 (m, 1H, major+minor), 6.63 (d, J = 8.0 Hz, 0.65H, major), 6.59 (d, J = 8.0 Hz, 0.33H, minor), 4.82 (s, 0.64H, minor), 4.80 (s, 1.35H, major), 4.14 – 4.07 (m, 2H, major+minor), 3.18 – 3.09 (m, 0.35H, minor), 3.05 – 2.95 (m, 0.70H, major), 2.66 (t, J = 10.4 Hz, 1.35H, major+minor), 2.44 – 2.35 (m, 1.32H, major+minor), 2.12 (t, J = 9.2 Hz, 1.4H, major+minor), 1.23 – 1.16 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.3, 179.0, 176.9, 176.7, 142.2, 142.1, 136.0, 135.9, 134.6, 133.2, 128.6, 127.8, 127.5, 127.4, 127.2, 122.7, 122.5, 121.9, 108.7, 108.5, 60.4, 60.3, 43.7, 43.5(1), 43.4(8), 43.4, 43.2, 43.1, 37.9, 36.9, 33.4, 33.0, 21.7, 21.3, 14.2(1), 14.1(7); **IR** (KBr) (ν, cm^{-1}): 3427, 3063, 1715, 1613, 1488, 1467, 1455, 1274, 1216, 1154, 732; **HRMS** (ESI-TOF) m/z: $C_{24}H_{28}NO_3$ $[M + H]^+$ calcd for 378.2064, found 378.2063.

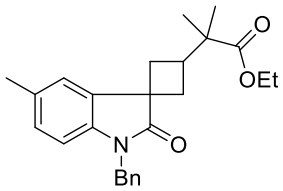
Ethyl-2-(1'-benzyl-5'-methoxy-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropanoate (3ba)



Yellow oil; 65% yield; 1.8:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.19 (m, 5.65H, major+minor), 6.96 (s, 0.35H, minor), 6.67 – 6.63 (m, 1H, major+minor), 6.60 – 6.53 (m, 1H, major+minor), 4.86 (s, 0.70H, minor), 4.85 (s, 1.32H, major), 4.21 – 4.14 (m, 2H, major+minor), 3.79 (s, 2H, major), 3.76 (s, 1H, minor), 3.26 – 3.16 (m, 0.36H, minor), 3.10 – 3.00 (m, 0.66H, major), 2.74 (t, J = 10.4 Hz, 1.3H, major+minor), 2.52 – 2.40 (m, 1.46H, major+minor), 2.18 (t, J = 9.2 Hz, 1.28H, major+minor), 1.31 – 1.22 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.0, 178.8, 177.0, 176.7, 156.0(9), 156.0(6), 136.1, 136.0(2), 136.0(0), 135.7, 135.6, 134.7, 128.6, 127.4, 127.2, 111.6, 111.3, 110.6,

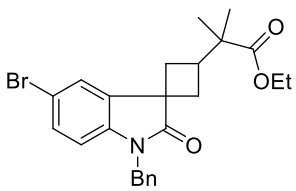
109.9, 108.9, 108.8, 60.4, 60.3, 55.8, 55.7, 43.8, 43.6, 43.5(2), 43.5(0), 43.4(5), 37.9, 36.9, 33.5, 33.0, 21.8, 21.3, 14.3, 14.2; **IR** (KBr) (ν, cm^{-1}): 3423, 1709, 1601, 1494, 1471, 1298. 1272, 1198, 1175, 1152, 864, 802, 735; **HRMS** (ESI-TOF) m/z: $C_{25}H_{30}NO_4$ $[M + H]^+$ calcd for 408.2169, found 408.2167.

Ethyl-2-(1'-benzyl-5'-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoate (3ca)



Yellow oil; 72% yield; 1.8:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 0.64H, major), 7.30 – 7.20 (m, 5H, major+minor), 7.13 (s, 0.35H, minor), 6.93 (t, J = 8 Hz, 1H, major+minor), 6.60 – 6.54 (m, 1H, major+minor), 4.87 (s, 0.68H, minor), 4.85 (s, 1.26H, major), 4.22 – 4.14 (m, 2H, major+minor), 3.26 – 3.17 (m, 0.35H, minor), 3.12 – 3.03 (m, 0.64H, major), 2.73 (t, J = 10.4 Hz, 1.28H, major+minor), 2.51 – 2.40 (m, 1.38H, major+minor), 2.35 (s, 2H, major), 2.32 (s, 1H, minor), 2.18 (t, J = 9.6 Hz, 1.36H, major+minor), 1.31 – 1.23 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm, major+minor) 181.2, 179.0, 177.1, 176.7, 139.8, 139.7, 136.1, 136.0, 134.6, 133.3, 132.1, 132.0, 128.6, 128.0, 127.7, 127.4, 127.2, 123.5, 122.8, 108.4, 108.2, 60.4, 60.3, 43.7, 43.5(1), 43.5(0), 43.4, 43.2(3), 43.1(5), 37.9, 36.9, 33.4, 33.0, 21.8, 21.3, 21.0, 14.2(2) 14.1(9); **IR** (KBr) (ν, cm^{-1}): 3428, 1712, 1622, 1600, 1495, 1455, 1273, 1223, 1190, 1152, 1109, 859, 806, 734; **HRMS** (ESI-TOF) m/z: $C_{25}H_{30}NO_3$ $[M + H]^+$ calcd for 392.2220, found 392.2218.

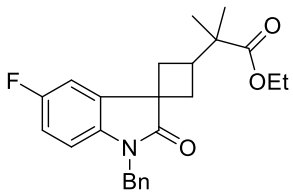
Ethyl-2-(1'-benzyl-5'-bromo-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoate (3da)



Yellow oil; 78% yield; 1.6:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.67 (s, 0.58H, major), 7.42 (s, 0.38H, minor), 7.32 – 7.21 (m, 6H, major+minor), 6.57 – 6.51 (m, 1H, major+minor), 4.86 (s, 0.74H, minor), 4.85 (s, 1.19H, major), 4.22 – 4.15 (m, 2H, major+minor), 3.24 – 3.15 (m, 0.37H, minor), 3.08 – 2.99 (m, 0.61H, major), 2.74 (t, J = 10 Hz, 1.24H, major+minor), 2.52 – 2.41 (m, 1.5H, major+minor), 2.20 (t, J = 10 Hz, 1.25H, major+minor), 1.32 – 1.22 (m, 9H,

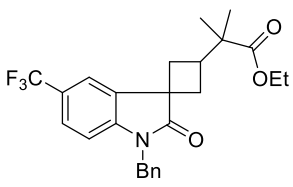
major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 180.6, 178.4, 176.8, 176.5, 141.2, 141.1, 136.6, 135.5, 135.4, 135.2, 130.6, 130.3, 128.7, 127.6, 127.1, 126.1, 125.2, 115.2, 110.2, 110.0, 60.5, 60.4, 43.8, 43.6, 43.4(4), 43.3(9), 43.3(5), 43.2, 37.8, 36.9, 33.4, 32.9, 21.8, 21.1, 14.2(4), 14.2(0); **IR** (KBr) (v, cm^{-1}): 3422, 1720, 1607, 1482, 1455, 1426, 1271, 1213, 1152, 1108, 871, 807, 733; **HRMS** (ESI-TOF) m/z: $C_{24}H_{27}BrNO_3$ $[M + H]^+$ calcd for 456.1169 found 456.1169.

Ethyl-2-(1'-benzyl-5'-fluoro-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoate (3ea)



Yellow oil; 64% yield; 1.8:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm, major+minor) 7.32 – 7.20 (m, 5.64H, major+minor), 7.09 (d, J = 7.6 Hz, 0.36H, minor), 6.85 – 6.78 (m, 1H, major+minor), 6.61 – 6.54 (m, 1H, major+minor), 4.87 (s, 0.70H, minor), 4.86 (s, 1.25H, major), 4.22 – 4.15 (m, 2H, major+minor), 3.24 – 3.15 (m, 0.36H, minor), 3.08 – 2.98 (m, 0.64H, major), 2.75 (t, J = 10.4 Hz, 1.28H, major+minor), 2.53 – 2.41 (m, 1.47H, major+minor), 2.19 (t, J = 9.6 Hz, 1.26H, major+minor), 1.32 – 1.22 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.0, 178.7, 176.8, 176.6, 159.4 (d, J_{CF} = 240 Hz), 159.3 (d, J_{CF} = 240 Hz), 138.0(3) (d, J_{CF} = 3 Hz), 137.9(8) (d, J_{CF} = 2 Hz), 136.2 (d, J_{CF} = 10 Hz), 135.7(3), 135.6(5), 134.9 (d, J_{CF} = 10 Hz), 128.7, 127.6, 127.2, 113.9 (d, J_{CF} = 20 Hz), 113.6 (d, J_{CF} = 30 Hz), 110.9 (d, J_{CF} = 20 Hz), 110.2 (d, J_{CF} = 30 Hz), 109.2 (d, J_{CF} = 20 Hz), 109.0 (d, J_{CF} = 20 Hz), 60.5, 60.4, 43.9, 43.7(0), 43.6(8), 43.4(9), 43.4(7), 43.4(5), 43.4(1), 37.8, 36.9, 33.4, 32.9, 21.8, 21.3, 14.2(4), 14.2(0); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -120.44, -120.63; **IR** (KBr) (v, cm^{-1}): 3424, 1716, 1609, 1490, 1455, 1278, 1229, 1170, 862, 808, 744; **HRMS** (ESI-TOF) m/z: $C_{24}H_{27}FNO_3$ $[M + H]^+$ calcd for 396.1969, found 396.1969.

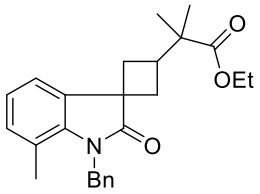
Ethyl-2-(1'-benzyl-2'-oxo-5'-(trifluoromethyl)spiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropanoate (3fa)



Yellow oil; 48% yield; 1.6:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm, major+minor) 7.77 (s, 0.62H, major), 7.54 (s, 0.38H, minor), 7.47 – 7.38 (m, 1H, major+minor), 7.35 – 7.19 (m,

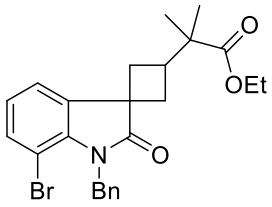
5H, major+minor), 6.77 (d, J = 8.2 Hz, 0.60H, major), 6.73 (d, J = 8.0 Hz, 0.38H, minor), 4.92 (s, 0.73H, minor), 4.90 (s, 1.25H, major), 4.26 – 4.16 (m, 2H, major+minor), 3.30 – 3.15 (m, 0.40H, minor), 3.15 – 3.02 (m, 0.64H, major), 2.82 – 2.72 (m, 1.28H, major+minor), 2.58 – 2.45 (m, 1.59H, major+minor), 2.30 – 2.15 (m, 1.26H, major+minor), 1.38 – 1.20 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.2, 179.0, 176.8, 176.6, 145.2, 145.1, 135.4, 135.3, 135.1, 133.8, 128.9, 127.8, 127.2, 125.7, 125.6(9), 125.6 (q, J_{CF} = 4.2 Hz), 125.4 (q, J_{CF} = 4.1 Hz), 124.8(5) (q, J_{CF} = 32.2 Hz), 124.8(2) (q, J_{CF} = 32.5 Hz), 123.7 (q, J_{CF} = 130.2 Hz), 123.6 (q, J_{CF} = 117.2 Hz), 119.8 (q, J_{CF} = 3.5 Hz), 119.0 (q, J_{CF} = 3.6 Hz), 108.5, 108.3, 60.6, 60.5, 44.0, 43.7, 43.6, 43.5, 43.2, 43.0, 37.8, 37.0, 33.5, 33.0, 21.9, 21.3, 14.3, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -61.24, -61.45; **IR** (KBr) (ν, cm^{-1}): 3432, 2978, 1723, 1362, 1330, 1272, 1218, 1159, 1118, 891, 821, 698, 733; **HRMS** (ESI-TOF) m/z: $C_{25}H_{26}F_3KNO_3$ $[M + K]^+$ calcd for 484.1496, found 484.1495.

Ethyl-2-(1'-benzyl-7'-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoat (3ga)



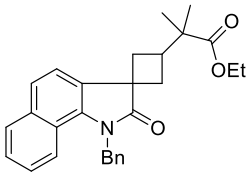
Yellow oil; 51% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.49 (d, J = 7.6 Hz, 0.6H, major), 7.29 – 7.20 (m, 3.4H, major+minor), 7.13 – 7.08 (m, 2H, major+minor), 7.02 – 6.96 (m, 1H, major+minor), 6.93 – 6.89 (m, 1H, major+minor), 5.18 (s, 0.78H, minor), 5.16 (s, 1.20H, major), 4.21 – 4.14 (m, 2H, major+minor), 3.26 – 3.16 (m, 0.4H, minor), 3.14 – 3.05 (m, 0.6H, major), 2.75 (t, J = 10.4 Hz, 1.24H, major+minor), 2.53 – 2.42 (m, 1.6H, major+minor), 2.26 – 2.19 (m, 4H, major+minor), 1.34 – 1.23 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 182.4, 180.3, 177.1, 176.8, 140.3, 140.2, 137.9, 137.8, 135.4, 134.0, 131.7, 131.5, 128.7, 127.0, 125.6(1), 125.5(6), 122.7(0), 122.6(6), 120.8, 119.9, 119.5, 119.3, 60.4, 60.3, 45.0, 44.7, 43.5(3), 43.4(8), 42.6, 42.5, 37.7, 36.8, 34.0, 33.3, 21.8, 21.3, 18.7, 18.6, 14.3, 14.2; **IR** (KBr) (ν, cm^{-1}): 3427, 1713, 1651, 1603, 1496, 1470, 1444, 1416, 1271, 1153, 772, 743; **HRMS** (ESI-TOF) m/z: $C_{25}H_{30}NO_3$ $[M + H]^+$ calcd for 392.2220, found 392.2220.

Ethyl-2-(1'-benzyl-7'-bromo-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoate(3ha)



Yellow oil; 51% yield; 1.1:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 6.8 Hz, 0.51H, major), 7.32 – 7.14 (m, 6.5H, major+minor), 6.96 – 6.91 (m, 1H, major+minor), 5.38 (s, 0.9H, minor), 5.37 (s, 0.98H, major), 4.21 – 4.14 (m, 2H, major+minor), 3.23 – 3.13 (m, 0.49H, minor), 3.10 – 3.02 (m, 0.53H, major), 2.75 (t, J = 10.4 Hz,1H, major+minor), 2.52 – 2.42 (m, 2H, major+minor), 2.21 (t, J = 9.6 Hz,1H, major+minor), 1.31 – 1.21 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 182.0, 179.9, 176.9, 176.7, 139.7, 139.6, 138.0, 137.6(4), 137.5(6), 136.6, 133.7, 133.5, 128.5, 127.0, 126.3(2), 126.2(6), 123.9, 123.9, 122.0, 121.1, 102.3, 102.0, 60.5, 60.4, 44.5, 44.2, 43.5, 43.4, 42.8(8), 42.8(5), 37.6, 36.9, 34.1, 33.4, 21.9, 21.2, 14.3, 14.2; **IR** (KBr) (v, cm^{-1}): 3424, 1721, 1608, 1574, 1496, 1450, 1272, 1221, 1146, 1108, 771, 743; **HRMS** (ESI-TOF) m/z: $C_{24}H_{27}BrNO_3$ $[M + H]^+$ calcd for 456.1169 found 456.1169.

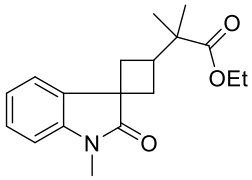
Ethyl-2-(1-benzyl-2-oxo-1,2-dihydrospiro[benzo[g]indole-3,1'-cyclobutan]-3'-yl)-2-methylpro panoate (3ia)



Yellow oil; 31% yield; 1.3:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, J = 7.6 Hz, 0.57H, major), 7.75 – 7.66 (m, 1.43H, major+minor), 7.62 – 7.56 (m, 1H, major+minor), 7.47 – 7.44 (m, 1.43H, major+minor), 7.34 – 7.16 (m, 6H, major+minor), 6.86 – 6.81 (m, 1H, major+minor), 5.39 (s, 0.89H, minor), 5.35 (s, 1.15H, major), 4.21 – 4.12 (m, 2H, major+minor), 3.27 – 3.04 (m, 2H, major+minor), 2.95-2.90 (m, 1H, major+minor), 2.53-2.48 (m, 1H, major+minor), 2.31-2.27 (m, 1H, major+minor), 1.28 – 1.22 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 177.3, 177.0, 173.6, 172.5, 138.3, 137.8, 136.8, 136.7, 136.5, 136.3, 133.5, 133.2, 128.8, 128.7(3), 128.6(6), 127.2, 127.1(0), 127.0(5), 127.0, 126.4(4), 126.3(9), 126.3, 126.2(0), 126.1(6), 126.1, 122.8, 122.2, 122.2, 121.3, 119.3, 119.1, 109.6, 109.5, 60.4(2), 60.3(9), 46.2, 46.1, 43.7, 43.4, 43.1, 43.0, 39.8, 37.0, 36.2, 36.0,

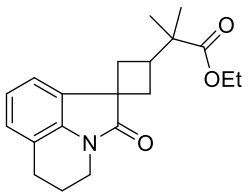
22.1, 21.5, 14.2(4), 14.2(1); **IR** (KBr) (ν, cm^{-1}): 3447, 1723, 1667, 1623, 1586, 1471, 1455, 1440, 1202, 1145, 817, 768, 730; **HRMS** (ESI-TOF) m/z: $C_{28}H_{30}NO_3$ $[M + H]^+$ calcd for 428.2220, found 428.2220.

Ethyl-2-methyl-2-(1'-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)propanoate (3ja)[1]



Yellow oil; 82% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, J = 7.2 Hz, 0.6H, major), 7.33 (d, J = 8.8 Hz, 0.4H, minor), 7.29 – 7.23 (m, 1H, major+minor), 7.12 – 7.06 (m, 1H, major+minor), 6.82 – 6.76 (m, 1H, major+minor), 4.21 – 4.14 (m, 2H, major+minor), 3.35 – 3.00 (m, 4H, major+minor), 2.69 (t, J = 10.8Hz, 1.29H, major+minor), 2.41 (d, J = 9.6 Hz, 1.23H, major+minor), 2.14 (t, J = 10 Hz, 1.29H, major+minor), 1.30 – 1.22 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.1, 178.9, 176.9, 176.7, 143.1, 143.0, 134.6, 133.3, 127.8, 127.6, 122.6, 122.5, 121.8, 107.7, 107.5, 60.4, 60.3, 43.5, 43.4, 43.2, 43.1, 38.0, 36.8, 33.2, 32.9, 26.1, 26.0, 21.7, 21.3, 14.2(1), 14.1(7); **IR** (KBr) (ν, cm^{-1}): 3423, 1716, 1614, 1494, 1471, 1422, 1275, 1249, 1146, 1091, 750; **HRMS** (ESI-TOF) m/z: $C_{18}H_{24}NO_3$ $[M + H]^+$ calcd for 302.1751, found 302.1750.

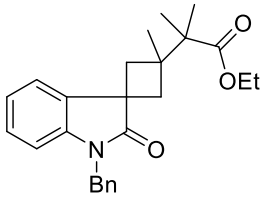
Ethyl-2-methyl-2-(2'-oxo-5',6'-dihydro-2'H,4'H-spiro[cyclobutane-1,1'-pyrrolo[3,2,1-ij]quinolin]-3-yl)propanoate (3ka)



Yellow oil; 73% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, J = 7.6 Hz, 0.66H, major), 7.15 (d, J = 7.2 Hz, 0.34H, minor), 7.03 – 6.94 (m, 2H, major+minor), 4.20 – 4.14 (m, 2H, major+minor), 3.71 – 3.66 (m, 2H, major+minor), 3.20 – 3.10 (m, 0.33H, minor), 3.07 – 2.98 (m, 0.66H, major), 2.78 – 2.73 (m, 2H, major+minor), 2.64 (t, J = 10.4 Hz, 1.35H, major+minor), 2.41 (d, J = 9.6 Hz, 1.28H, major+minor), 2.12 (t, J = 9.6 Hz, 1.33H, major+minor), 2.02 – 1.95 (m, 2H, major+minor), 1.30 – 1.21 (m, 9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 180.0, 177.6, 177.0, 176.7, 138.9, 138.8, 133.0, 131.7, 126.6, 126.4, 121.8(8), 121.8(6), 120.3, 119.8, 119.6, 119.5, 60.4, 60.2, 44.4, 44.2, 43.5, 43.4,

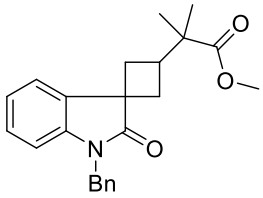
38.7, 38.6, 38.2, 36.9, 32.8, 32.6, 24.5, 24.3, 21.7, 21.3, 21.0(2), 20.9(9), 14.2(1), 14.1(7); **IR** (KBr) (ν, cm^{-1}): 3424, 1709, 1626, 1602, 1482, 1241, 1145, 746; **HRMS** (ESI-TOF) m/z: $C_{20}H_{26}NO_3$ $[M + H]^+$ calcd for 328.1907, found 328.1906.

Ethyl-2-(1'-benzyl-3-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methyl propanoate (3la)



Yellow oil; 32% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.62 (d, J = 8.4 Hz, 0.4H, minor), 7.51 (d, J = 8.4 Hz, 0.6H, major), 7.31 – 7.26 (m, 5H, major+minor), 7.17 – 7.02 (m, 2H, major+minor), 6.71 – 6.66 (m, 1H, major+minor), 4.88 (s, 2H, major+minor), 4.18 – 4.11 (m, 2H, major+minor), 3.17 (d, J = 12 Hz, 0.8H, minor), 2.83 (d, J = 12.4 Hz, 1.2H, major), 2.31 (d, J = 12 Hz, 1.2H, major), 2.01 (d, J = 12 Hz, 0.8H, minor), 1.65 (s, 1.8H, major), 1.58 (s, 1.16H, minor), 1.50 (s, 1.2H, minor), 1.39 (s, 1.91H, major), 1.34 (s, 3H, major+minor), 1.26 – 1.21 (m, 3H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.4, 181.2, 177.5, 177.1, 142.5, 142.2, 136.1, 136.0, 135.1, 134.7, 128.7, 127.7, 127.5, 127.3, 123.4, 122.8, 122.6, 122.5, 108.7, 108.5, 60.3, 60.2, 47.7, 47.5, 43.8, 43.7, 41.2, 41.0, 39.8, 39.3, 37.2, 36.8, 25.5, 22.8, 21.1, 20.9, 14.2; **IR** (KBr) (ν, cm^{-1}): 3433, 1710, 1633, 1466, 1261, 798; **HRMS** (ESI-TOF) m/z: $C_{25}H_{30}NO_3$ $[M + H]^+$ calcd for 392.2220, found 392.2220.

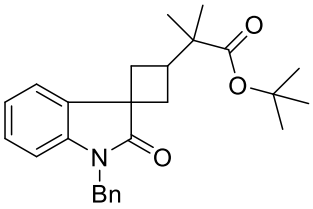
Methyl-2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropano ate (3ab)



Yellow oil; 73% yield; 2:1 d.r.; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, J = 6.8 Hz, 0.65H, major), 7.36 – 7.22 (m, 6H, major+minor), 7.18 – 7.10 (m, 1H, major+minor), 7.07 – 7.02 (m, 1H, major+minor), 6.71 (d, J = 7.6 Hz, 0.65H, major), 6.67 (d, J = 7.6 Hz, 0.35H, minor), 4.89 (s, 0.68H, minor), 4.87 (s, 1.31H, major), 3.72 (s, 3H, major+minor), 3.23 – 3.16 (m, 0.36H, minor), 3.12 – 3.02 (m, 0.73H, major), 2.72 (t, J = 10.4 Hz, 1.36H, major+minor), 3.52 – 3.41 (m, 1.55H, major+minor), 2.19 (t, J = 9.6 Hz, 1.31H, major+minor), 1.27 – 1.24 (m, 6H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.3, 179.0, 177.4, 177..2, 142.2, 142.1,

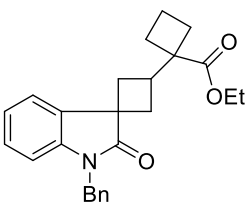
136.0(4), 135.9(6), 134.6, 133.2, 129.4, 128.7, 128.6, 128.3, 127.8, 127.6, 127.5, 127.2, 122.7, 122.5, 121.9, 108.7, 108.5, 51.7, 51.6, 43.8, 43.7, 43.6, 43.5, 43.1(1), 43.0(7), 37.9, 37.0, 33.4, 33.0, 21.9, 21.4; **IR** (KBr) (*v*, cm-1): 3431, 1712, 1650, 1613, 1487, 1466, 1455, 1434, 1274, 1216, 1146, 748; **HRMS** (ESI-TOF) m/z: $C_{23}H_{26}NO_3$ $[M + H]^+$ calcd for 364.1907, found 364.1907.

Tert-butyl-2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropanoate (3ac)



Yellow oil; 90% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.58 (d, J = 8 Hz, 0.7H, major), 7.36 (d, J = 4 Hz, 0.35H, minor), 7.33 – 7.02 (m, 7H, major+minor), 6.71 – 6.66 (m, 1H, major+minor), 4.89 (s, 0.67H, minor), 4.87 (s, 1.36H, minor), 3.26 – 3.17 (m, 0.35H, minor), 3.10 – 3.00 (m, 0.71H, major), 2.76 – 2.71 (m, 1.43H, major+minor), 2.51 – 2.42 (m, 1.21H, major+minor), 2.21 – 2.16 (m, 1.5H, major+minor), 1.47 (s, 9H, major+minor), 1.22 (s, 4H, major), 1.19 (s, 2H, minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.4, 179.1, 176.3, 176.1, 142.3, 142.2, 136.1, 136.0, 134.7, 133.4, 129.5, 128.7, 127.8, 127.6, 127.5, 127.3, 122.8, 122.6, 122.5, 121.9, 108.8, 108.5, 80.2, 80.1, 44.0, 43.8, 43.6, 43.4, 43.3, 38.2, 36.8, 33.5, 33.2, 28.1, 28.0, 21.7, 21.3; **IR** (KBr) (*v*, cm^{-1}): 3432, 1716, 1613, 1487, 1467, 1282, 1254, 1214, 1143, 748; **HRMS** (ESI-TOF) m/z: $C_{26}H_{32}NO_3$ $[M + H]^+$ calcd for 406.2377, found 406.2377.

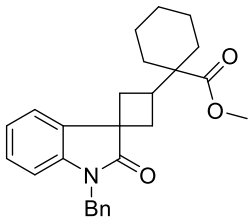
Ethyl-1-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)cyclobutane-1-carboxylate (3ad)



Yellow oil; 72% yield; 2.3:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, J = 4 Hz, 0.67H, major), 7.37 (d, J = 8 Hz, 0.35H, minor), 7.28 – 7.02 (m, 7H, major+minor), 6.73 – 6.67 (m, 1H, major+minor), 4.89 (s, 0.60H, minor), 4.88 (s, 1.40H, major), 4.22 – 4.15 (m, 2H, major+minor), 3.50 – 3.41 (m, 0.31H, minor), 3.23 – 3.14 (m, 0.71H, major), 2.84 – 2.79 (m, 1.40H, major+minor), 2.58 – 1.84 (m, 9H, major+minor), 1.30 – 1.24 (m, 3H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

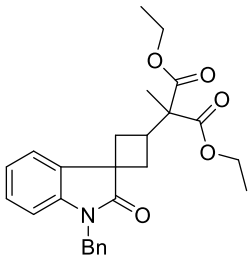
(ppm, major+minor) 181.2, 179.1, 176.8, 176.5, 142.3, 142.1, 136.0, 135.9, 134.6, 133.1, 128.7, 127.9, 127.6, 127.5, 127.2, 122.6(5), 122.5(9), 122.5, 121.9, 108.7, 108.5, 60.4, 60.3, 49.3, 43.8, 43.5(4), 43.5(0), 43.4, 34.8, 33.9, 33.4, 33.0, 26.7, 25.8, 15.5(4), 15.4(6), 14.3, 14.2; **IR** (KBr) (ν, cm^{-1}): 3422, 1716, 1613, 1487, 1466, 1455, 1284, 1213, 1168, 1135, 1113, 748; **HRMS** (ESI-TOF) m/z: $C_{25}H_{28}NO_3$ $[M + H]^+$ calcd for 390.2064, found 390.2062.

Methyl-1-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)cyclohexane-1-carboxylate (3ae)



Yellow oil; 70% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, J = 8 Hz, 0.65H, major), 7.27 – 7.24 (m, 5.38H, major+minor), 7.15 – 7.02 (m, 2H, major+minor), 6.70 – 6.65 (m, 1H, major+minor), 4.87 (s, 0.65H, minor), 4.85 (s, 1.37H, major), 3.79 (s, 3H, major+minor), 3.17 – 3.07 (m, 0.37H, minor), 2.91 – 2.82 (m, 0.73H, major), 2.79 – 2.74 (m, 1.29H, major), 2.47 – 2.38 (m, 1.39H, major), 2.20 – 2.11 (m, 3.39H, major+minor), 1.73 – 1.61 (m, 2H, major+minor), 1.36 – 1.16 (m, 6H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.2, 178.9, 175.7, 142.2, 142.1, 136.0, 135.9, 134.5, 133.1, 128.6, 127.8, 127.6, 127.4, 127.2, 122.6, 122.5(2), 122.4(9), 121.8, 108.7, 108.5, 51.6, 51.3, 49.3, 49.2, 43.7, 43.5, 43.2, 43.1, 39.1, 37.3, 33.1, 32.7, 30.9, 30.5, 25.7(4), 25.6(9), 23.3(3), 23.3(0); **IR** (KBr) (ν, cm^{-1}): 3431, 1717, 1613, 1487, 1466, 1453, 1432, 1221, 1202, 1166, 1136, 1100, 749; **HRMS** (ESI-TOF) m/z: $C_{26}H_{30}NO_3$ $[M + H]^+$ calcd for 404.2220, found 404.2219.

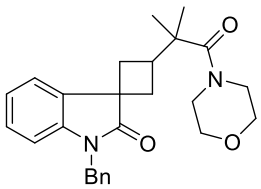
Diethyl-2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylmalonate (3af)[1]



Yellow oil; 73% yield; 2.3:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, J = 7.6 Hz, 0.7H, major), 7.46 (d, J = 7.6 Hz, 0.3H, minor), 7.31 – 7.20 (m, 5H, major+minor), 7.18 – 7.12 (m, 1H, major+minor), 7.09 – 7.04 (m, 1H, major+minor), 6.71 – 6.66 (m, 1H, major+minor), 4.89 (s, 0.59H, minor), 4.87 (s, 1.41H, major), 4.28 – 4.21 (m, 4H, major+minor), 3.52 – 3.42 (m, 1H, major+minor),

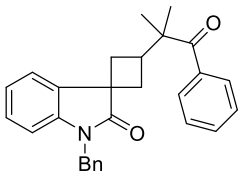
2.79 (t, *J* = 10.4 Hz, 1.4H, major), 2.69 (t, *J* = 10 Hz, 0.6H, minor), 2.58 (t, *J* = 10 Hz, 0.6H, minor), 2.31 (t, *J* = 10 Hz, 1.4H, major), 1.57 (s, 2.1H, major), 1.48 (s, 0.9H, minor), 1.31 – 1.26 (m, 6H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.2, 178.7, 171.7, 171.4, 171.3, 143.6, 142.2, 142.1, 137.6, 136.0, 135.9, 134.3, 133.0, 128.9, 128.6, 128.3, 127.8, 127.7(1), 127.6(7), 127.4, 127.2(3), 127.1(9), 127.1, 126.6, 123.1, 122.6(3), 122.5(8), 108.8, 108.4, 61.3, 61.1, 55.6, 55.2, 53.5, 43.7(3), 43.6(9), 43.6(7), 43.5, 37.1, 34.7, 34.1(2), 34.0(7), 33.4, 18.1, 17.2, 17.0, 14.0, 10.1; **IR** (KBr) (ν, cm^{-1}): 3443, 1727, 1637, 1496, 1488, 1466, 1455, 1267, 1170, 1125, 748; **HRMS** (ESI-TOF) m/z: $C_{26}H_{30}NO_5$ $[M + H]^+$ calcd for 436.2118, found 436.2119.

1'-Benzyl-3-(2-methyl-1-morpholino-1-oxopropan-2-yl)spiro[cyclobutane-1,3'-indolin]-2'-one (3ag)



Yellow oil; 44% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.62 (d, *J* = 7.6 Hz, 0.69H, major), 7.39 (d, *J* = 7.6 Hz, 0.34H, minor), 7.32 – 7.02 (m, 7H, major+minor), 7.32 – 7.02 (m, 1H, major+minor), 4.89 (s, 0.65H, minor), 4.87 (s, 1.34H, minor), 3.69 (d, *J* = 10.4 Hz, 8H, major+minor), 3.52 – 3.47 (m, 0.35H, minor), 3.44 – 3.34 (m, 0.66H, major), 2.68 (t, *J* = 10.8 Hz, 1.37H, major+minor), 2.47 (d, *J* = 9.2 Hz, 1.35H, major+minor), 2.29 (t, *J* = 9.6 Hz, 1.38H, major+minor), 1.36 (d, *J* = 11.6 Hz, 6H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.2, 179.5, 175.9, 174.8, 142.2, 142.0, 136.0, 134.8, 133.0, 128.6, 127.8, 127.5, 127.2(2), 127.1(7), 122.8, 122.6, 122.0, 115.7, 108.6, 108.5, 66.8(5), 66.7(8), 45.7, 45.5, 43.7, 43.5, 43.4, 43.3(4), 43.2(9), 42.9, 38.7, 36.6, 33.6, 33.5, 22.6, 21.0; **IR** (KBr) (*v*, cm^{-1}): 1628, 1487, 1466, 1455, 1417, 1269, 1244, 1219, 1172, 1117, 1067, 1034, 750; HRMS (ESI-TOF) m/z: $C_{26}H_{31}N_2O_3$ $[M + H]^+$ calcd for 419.2329, found 419.2329.

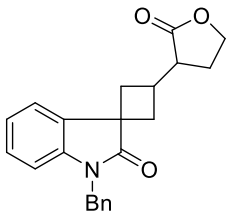
1'-Benzyl-3-(2-methyl-1-oxo-1-phenylpropan-2-yl)spiro[cyclobutane-1,3'-indolin]-2'-one (3ah)



Yellow oil; 68% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.65 – 7.61 (m, 2H, major+minor), 7.56 (d, *J* = 7.2 Hz,

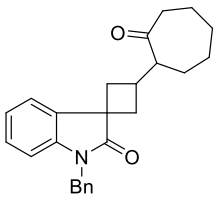
0.7H, minor), 7.48 – 7.39 (m, 3.41H, major+minor), 7.31 – 7.22 (m, 5H, major+minor), 7.17 – 7.11 (m, 1H, major+minor), 7.08 – 7.03 (m, 1H, major+minor), 6.71 (d, *J* = 7.6 Hz, 0.67H, major), 6.67 (d, *J* = 7.6 Hz, 0.35H, minor), 4.87 (s, 2H, major+minor), 3.62 – 3.52 (m, 0.35H, minor), 3.42 – 3.33 (m, 0.7H, major), 2.71 (t, *J* = 10.4 Hz, 1.38H, major+minor), 2.46 (d, *J* = 9.6 Hz, 1.37H, major+minor), 2.19 (t, *J* = 9.6 Hz, 1.35H, major+minor), 1.45 (s, 4H, major), 1.40 (s, 2H, minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 209.2, 208.9, 181.1, 179.2, 142.2, 142.1, 139.5, 139.3, 136.0, 135.9, 134.5, 133.1, 130.7, 128.7, 128.1(5), 128.1(1), 127.9, 127.6, 127.5, 127.3(0), 127.2(6), 127.2, 122.8, 122.6, 122.0, 108.8, 108.6, 49.0, 43.8, 43.6, 43.5, 43.4, 37.5, 36.4, 33.3, 33.1, 22.1, 21.7; **IR** (KBr) (*v*, cm^{-1}): 3449, 1709, 1671, 1613, 1487, 1466, 1455, 1267, 1215, 1171, 1110, 1079, 1029, 750; **HRMS** (ESI-TOF) m/z: $C_{28}H_{28}NO_2$ $[M + H]^+$ calcd for 410.2115, found 410.2115.

1'-Benzyl-3-(2-oxotetrahydrofuran-3-yl)spiro[cyclobutane-1,3'-indolin]-2'-one (3ai)



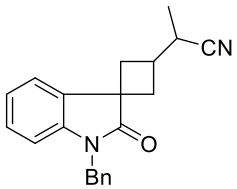
Yellow oil; 25% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.6 Hz, 0.67H, major), 7.48 (d, *J* = 7.6 Hz, 0.33H, minor), 7.32 – 7.23 (m, 5H, major+minor), 7.18 – 7.12 (m, 1H, major+minor), 7.10 – 7.04 (m, 1H, major+minor), 6.72 – 6.67 (m, 1H, major+minor), 4.88 (s, 2H, major+minor), 4.43 – 4.22 (m, 2H, major+minor), 3.32 – 3.21 (m, 0.34H, minor), 3.14 – 2.99 (m, 1.38H, major+minor), 2.81 – 2.70 (m, 1.64H, major+minor), 2.65 – 2.37 (m, 3.74H, major+minor), 2.28 – 2.18 (m, 0.72H, major), 2.07 – 1.97 (m, 0.33H, minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.0, 179.4, 178.2, 177.8, 142.2, 142.1, 136.0, 135.8, 134.0, 132.6, 128.7, 128.0, 127.9, 127.6, 127.5, 127.2, 123.3, 122.8(1), 122.7(7), 122.2, 108.9, 108.5, 66.5, 66.4, 44.9, 44.6, 43.8, 43.6, 43.0, 35.9, 35.5, 34.9, 34.2, 30.2, 29.5, 26.9, 26.0; **IR** (KBr) (*v*, cm^{-1}): 3446, 1768, 1706, 1613, 1488, 1466, 1455, 1212, 1164, 1110, 751, 732; **HRMS** (ESI-TOF) m/z: $C_{22}H_{22}NO_3$ $[M + H]^+$ calcd for 348.1594, found 348.1591.

1'-Benzyl-3-(2-oxocycloheptyl)spiro[cyclobutane-1,3'-indolin]-2'-one (3aj)



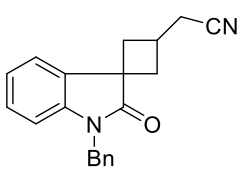
Yellow oil; 40% yield; 1.6:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, J = 7.5 Hz, 0.62H, major), 7.36 (d, J = 7.5 Hz, 0.38H, minor), 7.33 – 7.18 (m, 5H, major+minor), 7.17 – 6.97 (m, 2H, major+minor), 6.75 – 6.61 (m, 1H, major+minor), 4.88 (s, 2H, major+minor), 3.23 – 2.81 (m, 1.78H, major+minor), 2.75 – 2.13 (m, 6.52H, major+minor), 2.02 – 1.72 (m, 3.84H, major+minor), 1.66 – 1.13 (m, 3.97H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 215.1, 214.7, 181.1, 179.6, 142.2, 142.0, 136.0, 135.9, 134.7, 132.9, 128.7, 127.8, 127.6, 127.5, 127.2(5), 127.1(9), 122.7(3), 122.6(9), 122.5, 122.2, 108.7, 108.5, 59.6, 58.1, 44.7, 44.5, 43.7(9), 43.7(6), 43.6, 42.5, 37.0, 36.9, 36.5, 35.3, 31.3, 30.9, 29.9, 29.2, 29.1, 28.5, 28.1, 27.9, 25.0, 23.6.; **IR** (KBr) (ν, cm^{-1}): 3447, 1704, 1612, 1487, 1466, 1454, 1209, 1166, 1078, 1029, 749; **HRMS** (ESI-TOF) m/z: $C_{25}H_{28}NO_2$ $[M + H]^+$ calcd for 374.2115, found 374.2115.

2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)propanenitrile (3ak)



Yellow oil; 71% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.53 (d, J = 7.6 Hz, 0.4H, minor), 7.47 (d, J = 7.2 Hz, 0.6H, major), 7.32 – 7.02 (m, 7H, major+minor), 6.73 – 6.67 (m, 1H, major+minor), 4.89 (s, 0.79H, minor), 4.87 (s, 1.22H, minor), 3.16 – 3.08 (m, 1H, major+minor), 2.88 – 2.75 (m, 1H, major+minor), 2.71 – 2.56 (m, 2H, major+minor), 2.52 – 2.42 (m, 2H, major+minor), 1.33 – 1.28 (m, 3H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 180.7, 179.0, 142.1(5), 142.1(2), 135.8, 135.7, 133.5, 132.2, 128.7, 128.1, 128.0, 127.6, 127.5, 127.2, 123.3, 122.9, 122.8, 122.1, 121.6, 121.2, 108.9, 108.6, 43.9, 43.8(3), 43.7(9), 43.6, 35.7, 35.4, 34.9, 34.4, 33.2, 31.3, 31.1, 30.7, 15.3, 15.0; **IR** (KBr) (ν, cm^{-1}): 2239, 1613, 1488, 1466, 1455, 1435, 751; **HRMS** (ESI-TOF) m/z: $C_{21}H_{21}N_2O$ $[M + H]^+$ calcd for 317.1648, found 317.1646.

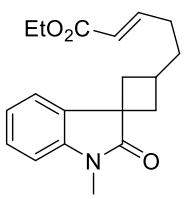
2-(1'-benzyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)acetonitrile (3al)



Yellow oil; 20% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 7.2 Hz, 0.4H, minor), 7.47 (d, J = 7.2 Hz,

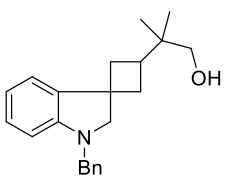
0.6H, major), 7.33 – 7.26 (m, 5H, major+minor), 7.20 – 7.14 (m, 1H, major+minor), 7.10 – 7.06 (m, 1H, major+minor), 6.72 – 6.88 (m, 1H, major+minor), 4.88 (s, 2H, major+minor), 3.38 – 3.31 (m, 0.43H, minor), 3.07 – 2.99 (m, 0.65H, major), 2.88 (d, *J* = 9.6 Hz, 1.22H, major), 2.74 – 2.61 (m, 2.75H, major+minor), 2.53 – 2.44 (m, 2H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 180.6, 179.3, 142.3, 142.2, 135.9, 135.7, 133.4, 132.2, 128.8, 128.3, 128.2, 127.7, 127.6, 127.3, 123.2, 122.9(4), 122.9(1), 122.2, 118.5, 117.9, 109.0, 108.7, 44.5, 44.2, 43.9, 43.7, 36.2, 26.6, 24.8, 23.5, 23.1; **IR** (KBr) (ν, cm^{-1}): 2247, 1613, 1488, 1467, 1455,748; **HRMS** (ESI-TOF) m/z: $C_{20}H_{19}N_2O$ $[M + H]^+$ calcd for 303.1492, found 303.1490.

Ethyl-(E)-5-(1'-methyl-2'-oxospiro[cyclobutane-1,3'-indolin]-3-yl)pent-2-enoate (3im)[1]



Yellow oil; 40% yield; 1.5:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.51 (d, *J* = 7.2 Hz, 0.6H, major), 7.35 (d, *J* = 6.4 Hz, 0.4H, minor), 7.28 – 7.25 (m, 2H, major+minor), 7.12 – 7.08 (m, 1H, major+minor), 7.02 – 6.95 (m, 1H, major+minor), 6.81 – 6.77 (m, 1H, major+minor), 5.84 (d, *J* = 15.6 Hz, 1H, major+minor), 4.22 – 4.17 (m, 2H, major+minor), 3.21 – 3.18 (m, 3H, major+minor), 2.91 – 2.84 (m, 0.4H, minor), 2.75 – 2.69 (m, 0.6H, major), 2.67 – 2.59 (m, 1H, major+minor), 2.39 – 2.30 (m, 2.36H, major+minor), 2.24 – 2.18 (m, 1.82H, major+minor), 2.07 – 2.01 (m, 0.71H, major), 1.84 – 1.78 (m, 1.23H, major+minor), 1.75 – 1.69 (m, 1H, major+minor), 1.31 – 1.28 (m, 3H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 181.2, 179.2, 166.7, 148.7, 148.6, 143.1, 143.0, 134.8, 133.3, 127.9, 127.7, 122.6(1), 122.5(8), 122.5, 121.9, 121.6, 121.5, 107.8, 107.6, 60.2, 44.8, 37.6, 37.0, 35.7, 34.6, 29.8, 29.7, 29.6, 28.8, 26.3, 26.1, 14.3.

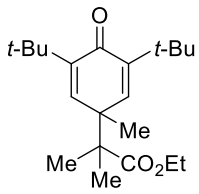
2-(1'-benzylspiro[cyclobutane-1,3'-indolin]-3-yl)-2-methylpropan-1-ol (4)



Yellow oil; 85% yield; 2:1 d.r.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.39 (d, *J* = 7.2 Hz, 0.7H, major), 7.35 – 7.26 (m, 5H, major+minor), 7.16 (d, *J* = 7.2 Hz, 0.35H, minor), 7.10 – 7.05 (m, 1H, major+minor), 6.77 – 6.72 (m, 1H, major+minor), 6.51 (d, *J* =

8 Hz, 2H, major+minor), 4.25 (s, 0.64H, minor), 4.21 (s, 1.36H, major), 3.41 (s, 0.65H, minor), 3.29 (s, 2H, major+minor), 3.21 (s, 1.35H, major), 2.64 – 2.55 (m, 0.7H, major), 2.31 – 2.26 (m, 0.35H, minor), 2.22 – 2.15 (m, 2H, major+minor), 2.09 – 1.97 (m, 2H, major+minor), 1.35 (s, 1H, major+minor), 0.87 (s, 2H, minor), 0.83 (s, 4H, major); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm, major+minor) 151.8, 151.4, 138.4, 138.3, 138.2, 136.8, 128.4(8), 128.4(6), 127.9(1), 127.8(8), 127.7, 127.6, 127.1(0), 127.0(8), 122.5, 121.6, 118.1, 118.0, 107.0, 106.9, 70.9, 70.8, 67.7, 66.8, 53.2(5), 53.2(1), 41.9, 41.1, 36.6, 36.2(4), 36.1(9), 36.0, 35.9, 35.6, 20.4, 20.2; **IR** (KBr) (v, cm^{-1}):2955, 1604, 1485, 1453, 1384, 1043, 737; **HRMS** (ESI-TOF) m/z: $C_{22}H_{28}NO$ $[M + H]^+$ calcd for 322.2165, found 322.2163.

Ethyl-2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (5)[3]



Yellow oil; 26% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 6.56 (s, 2H), 4.17 – 4.11 (m, 2H), 1.30 – 1.21 (m, 24H), 1.07 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 186.2, 175.4, 147.0, 143.7, 60.7, 48.9, 42.9, 34.9, 29.4, 21.9, 21.6, 14.2; **IR** (KBr) (v, cm^{-1}): 3447, 1725, 1660, 1639, 1365, 1254, 1139, 913.

References

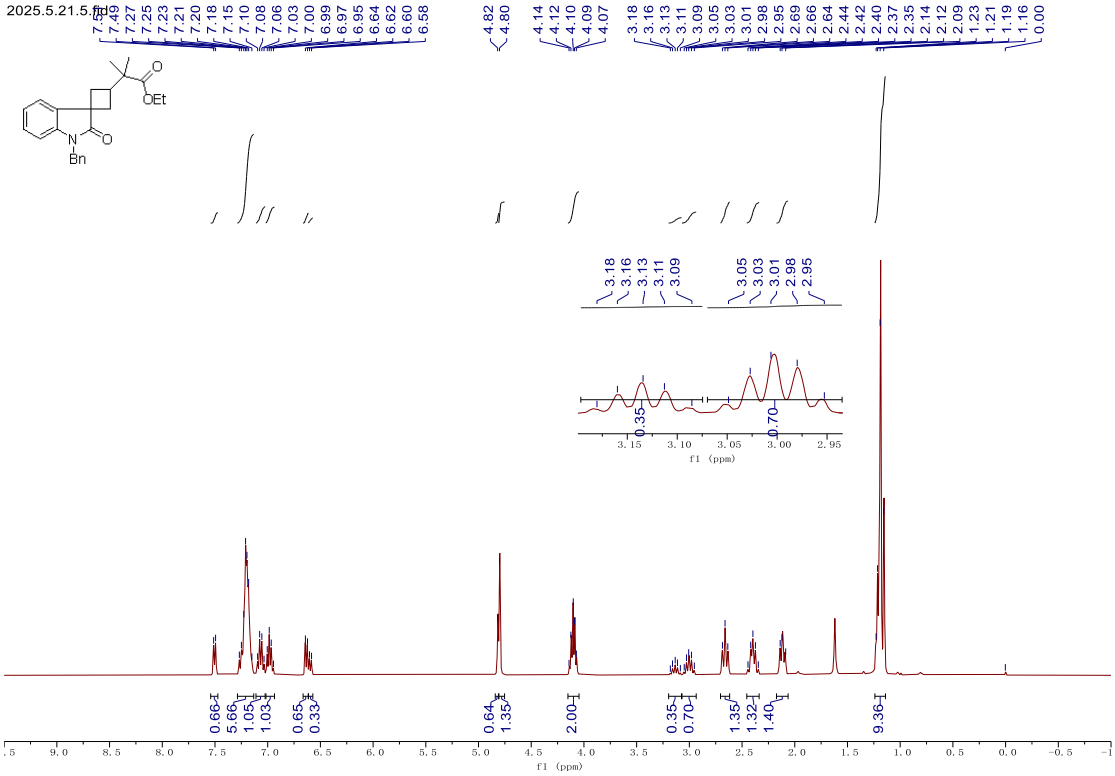
[1] J.-H. Fan, J. Yuan, P.-F. Xia, J. Zhou, L.-J. Zhong, P.-F. Huang, Y. Liu, K.-W. Tang and J.-H. Li, Photoredox-Catalyzed Alkylarylation of N-Aryl Bicyclobutyl Amides with α-Carbonyl Alkyl Bromides: Access to 3-Spirocyclobutyl Oxindoles, *Org. Lett.*, 2024, **26**, 2073–2078.

[2] L. Su, H. Sun, J. Liu and C. Wang, Construction of Quaternary Carbon Center *via* NHC Catalysis Initiated by an Intermolecular Heck-Type Alkyl Radical Addition, *Org. Lett.*, 2021, **23**, 4662–4666.

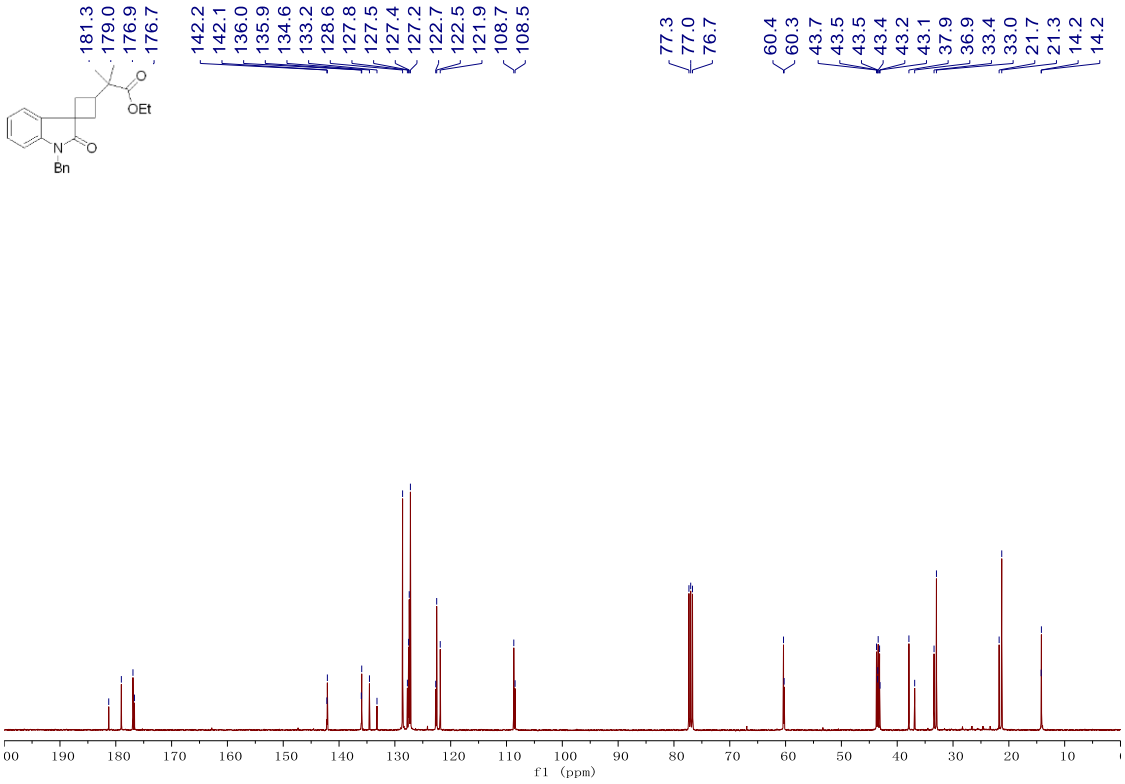
[3] (a) N. Tsuchiya and T. Nishikata, Construction of Vicinal Quaternary Carbons via Cu-catalyzed Dearomative Radical Addition, *Chem. Lett.*, 2019, **48**, 718–721; (b) L.-X. Liu, C.-Y. Zhou and C.-M. Wang, Construction of highly congested quaternary carbon centers by NHC catalysis through dearomatization, *Green Synth. Catal.*, 2023, **4**, 263-267.

4. Copies of NMR Spectrum

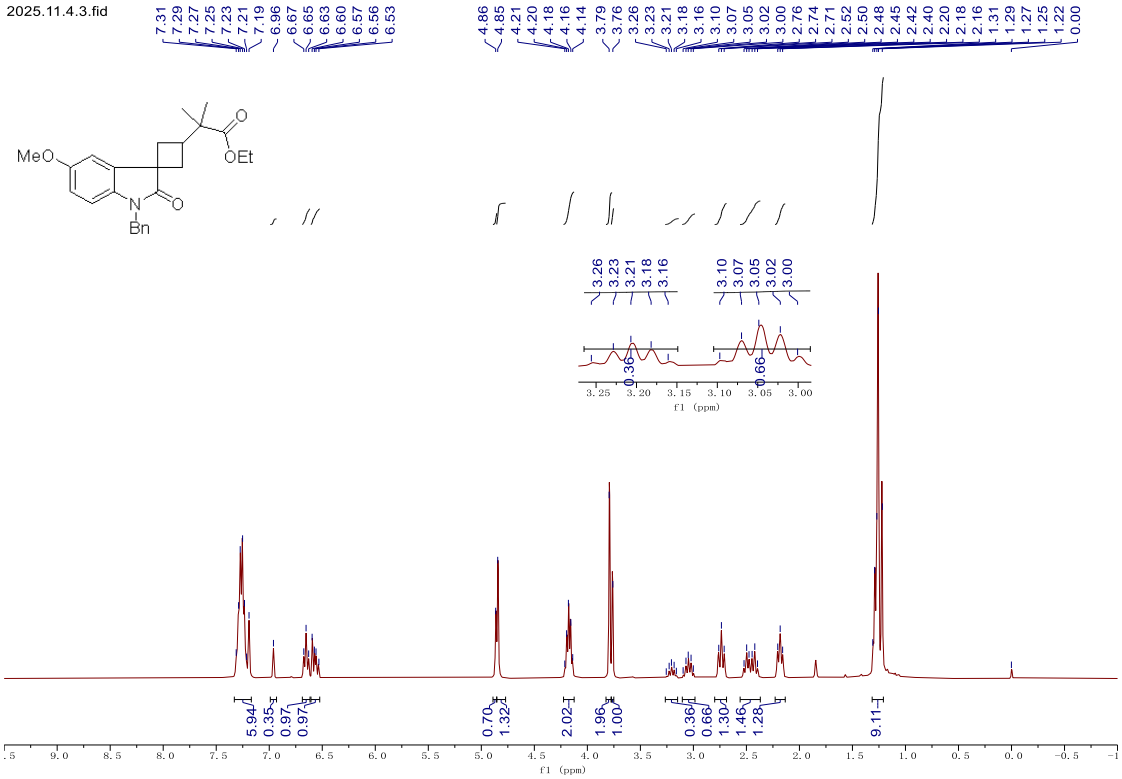
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3aa**)



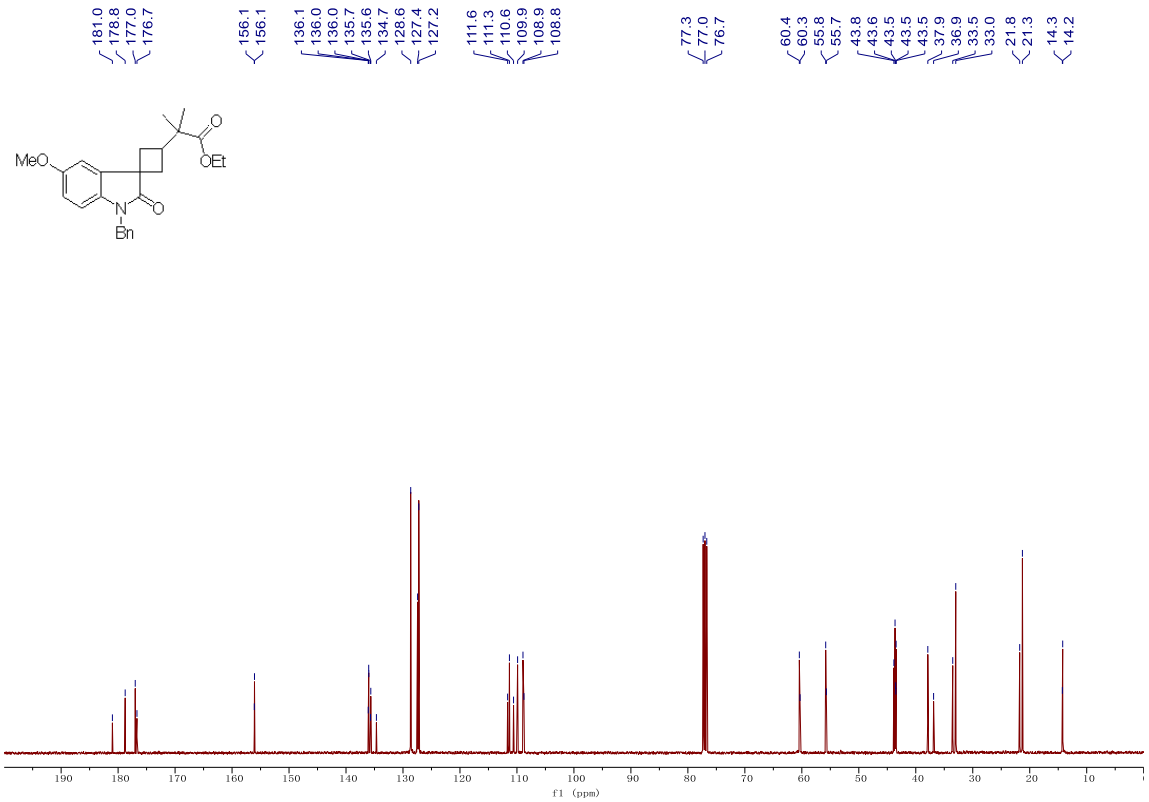
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3aa**)



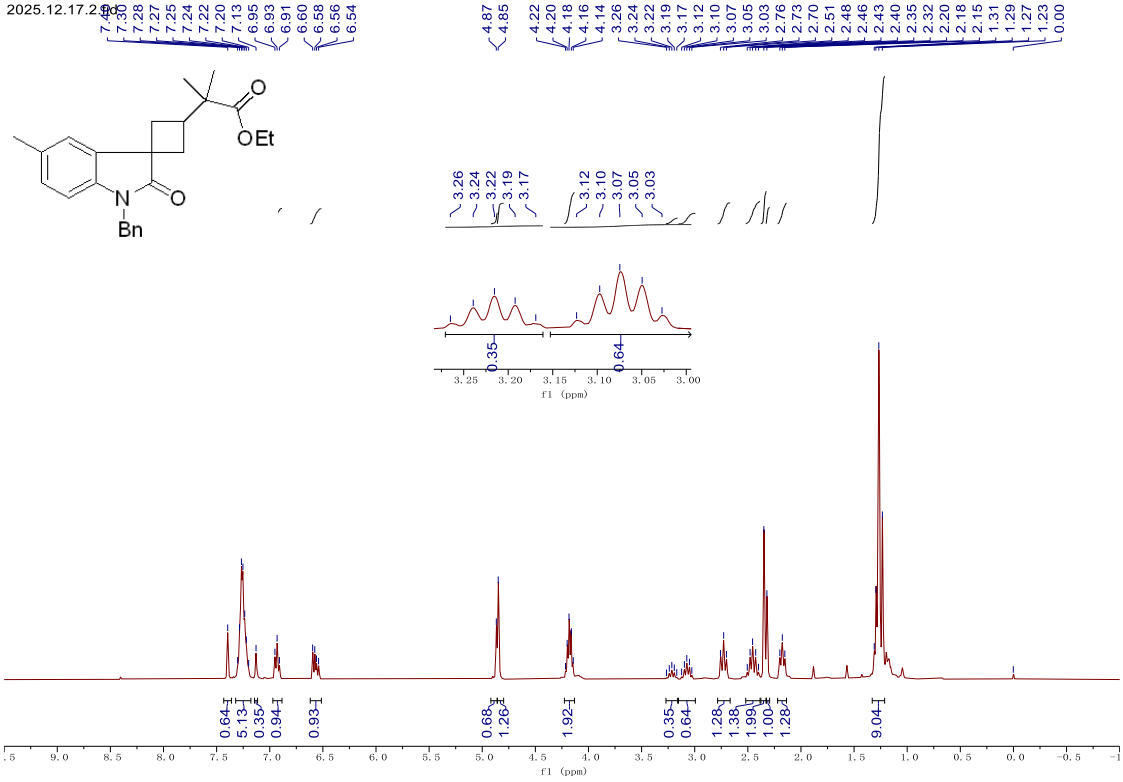
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ba**)



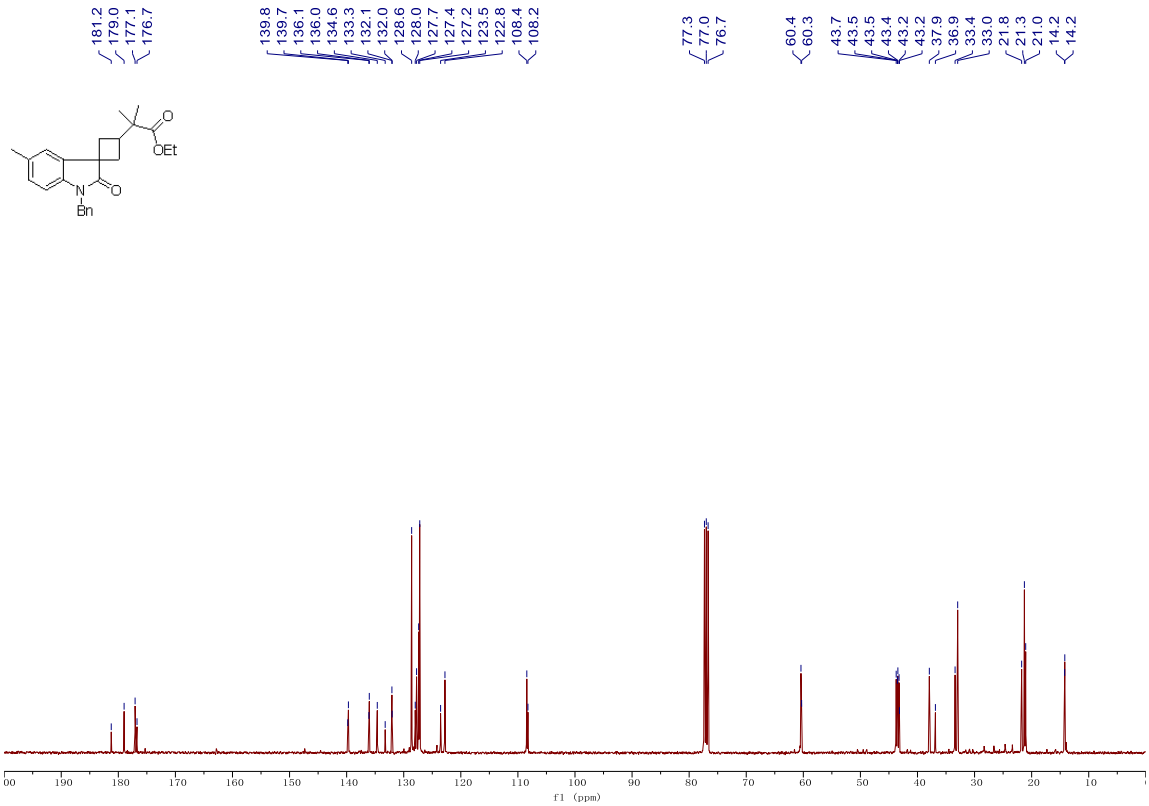
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ba**)



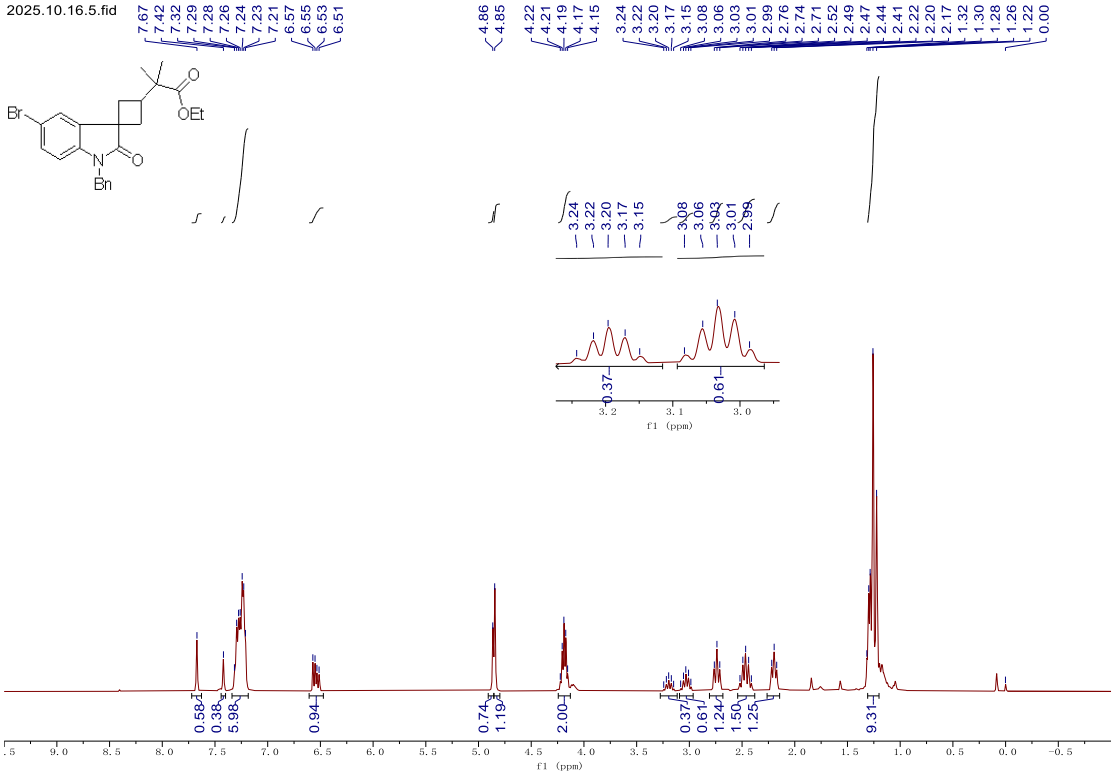
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ca**)



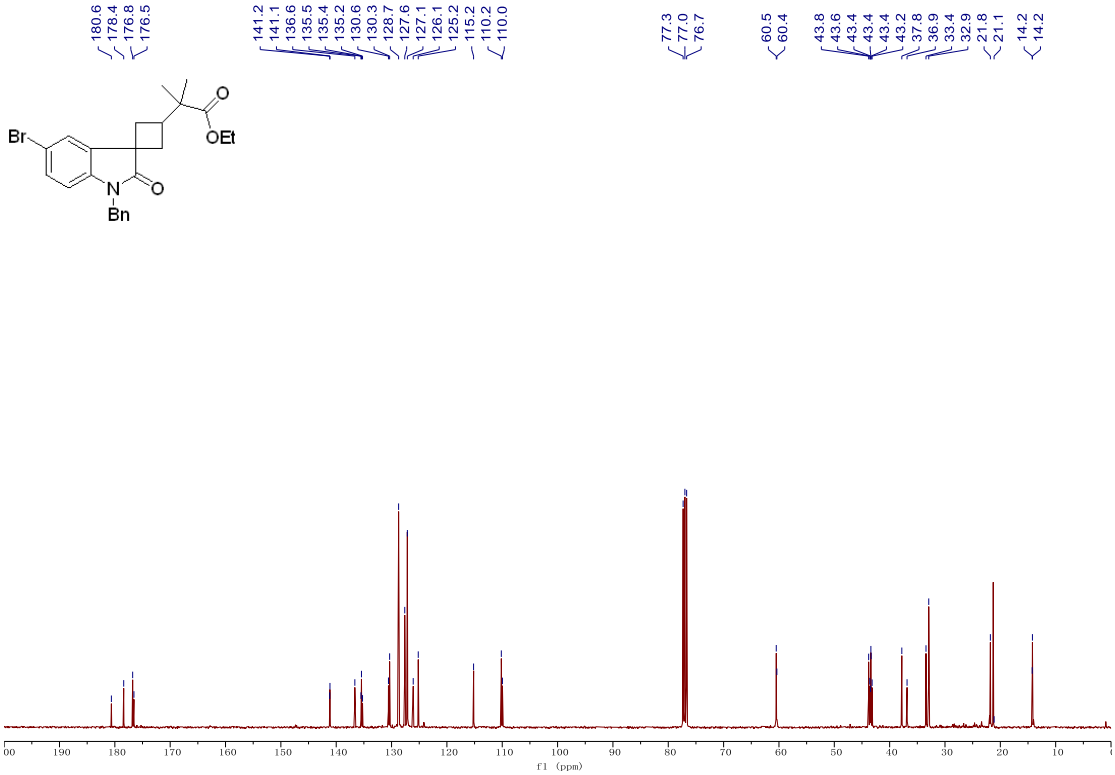
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ca**)



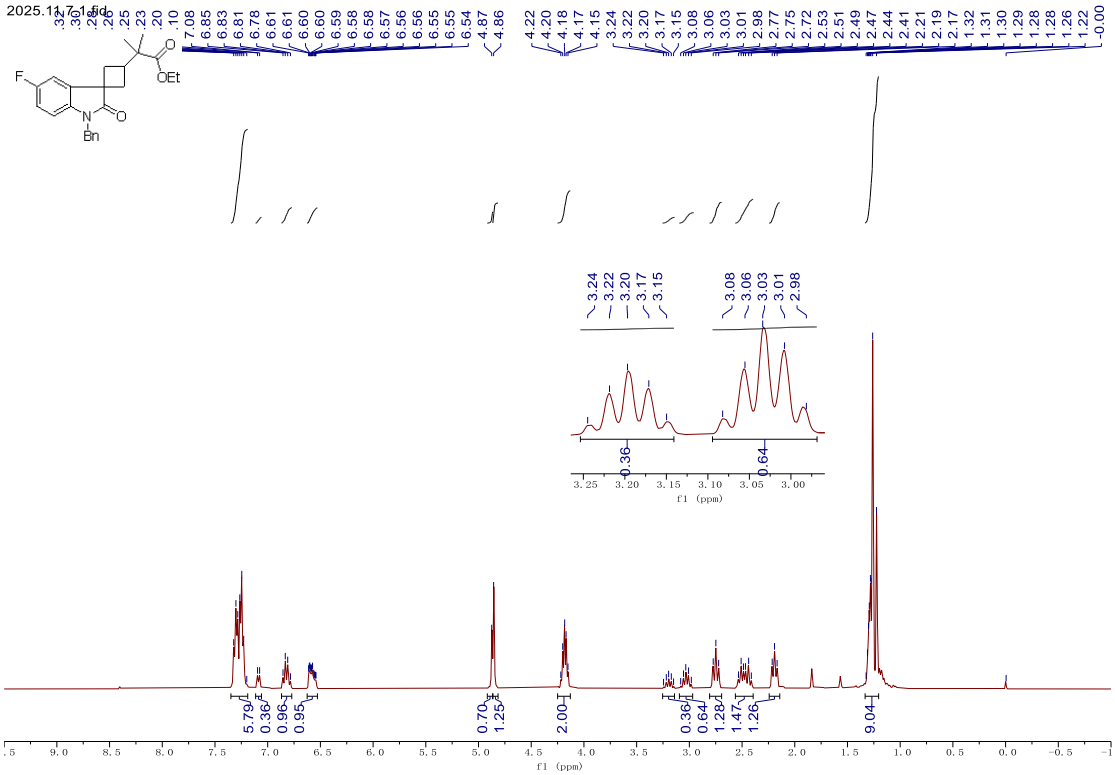
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3da**)



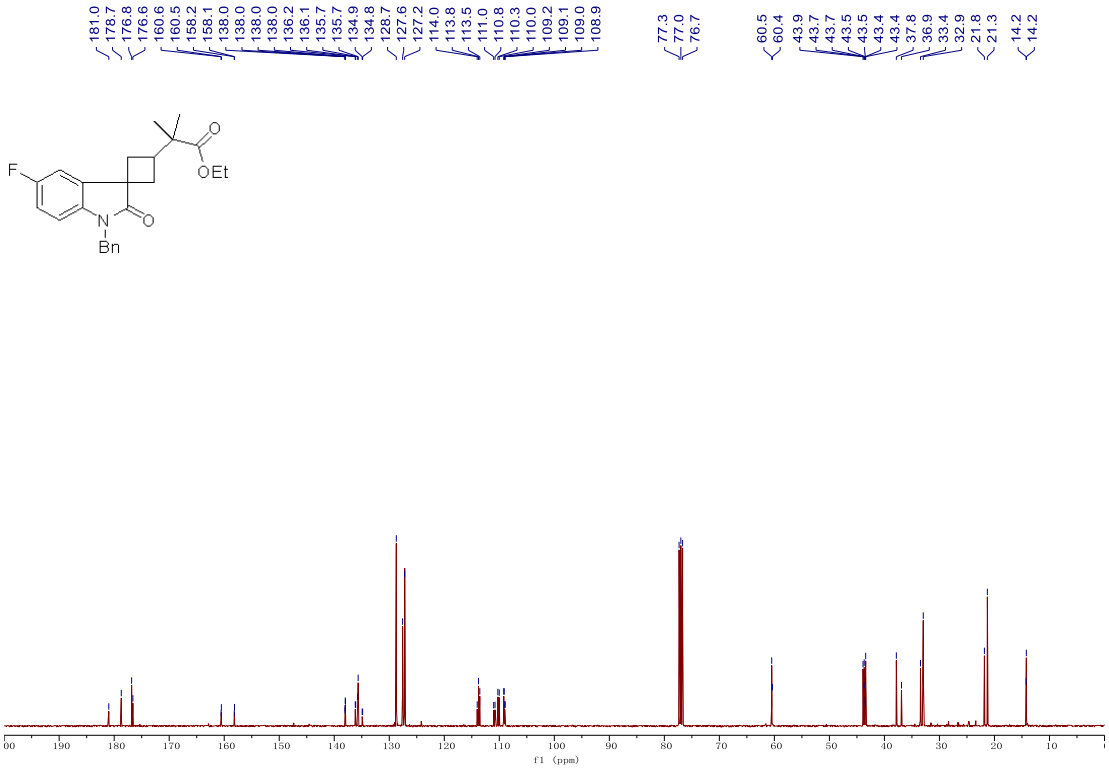
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3da**)



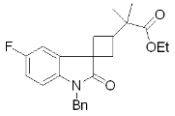
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ea**)



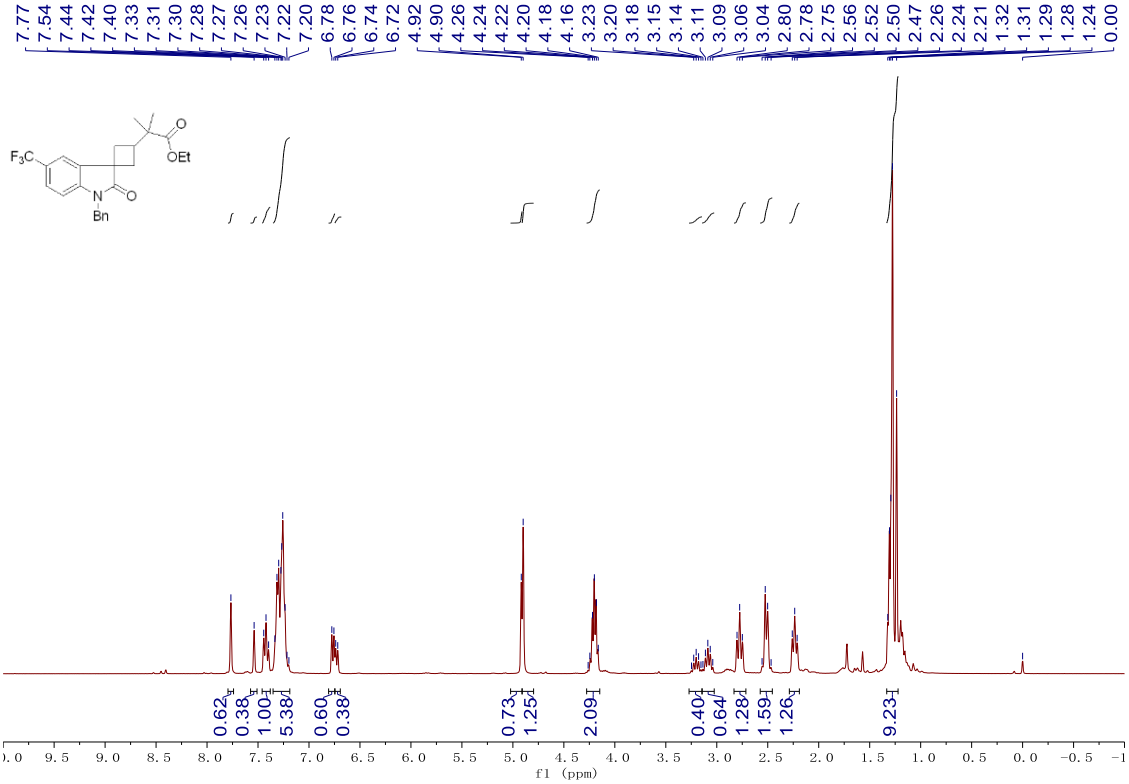
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ea**)



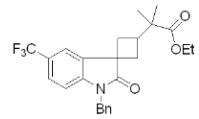
^{19}F NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ea**)

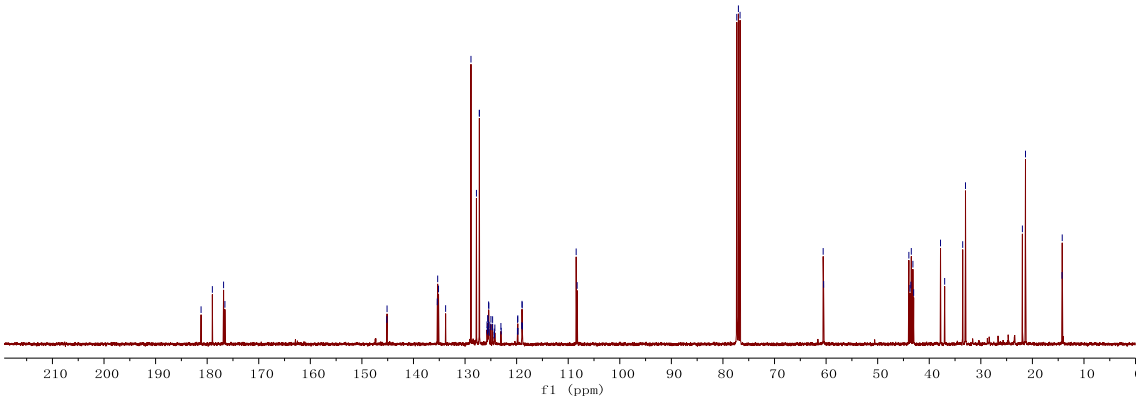


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3fa**)

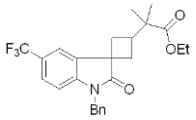


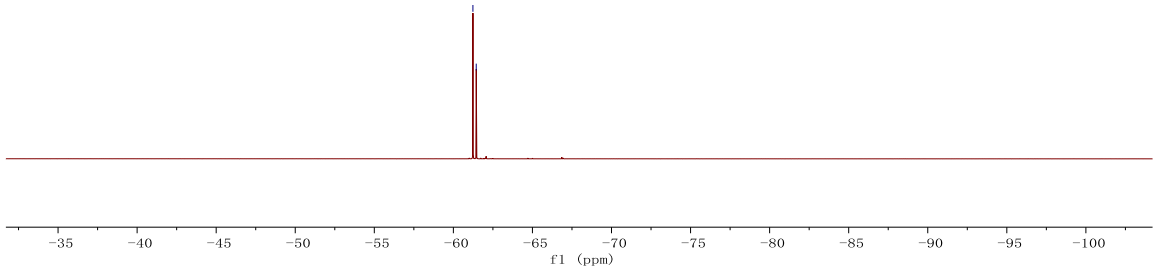
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3fa**)



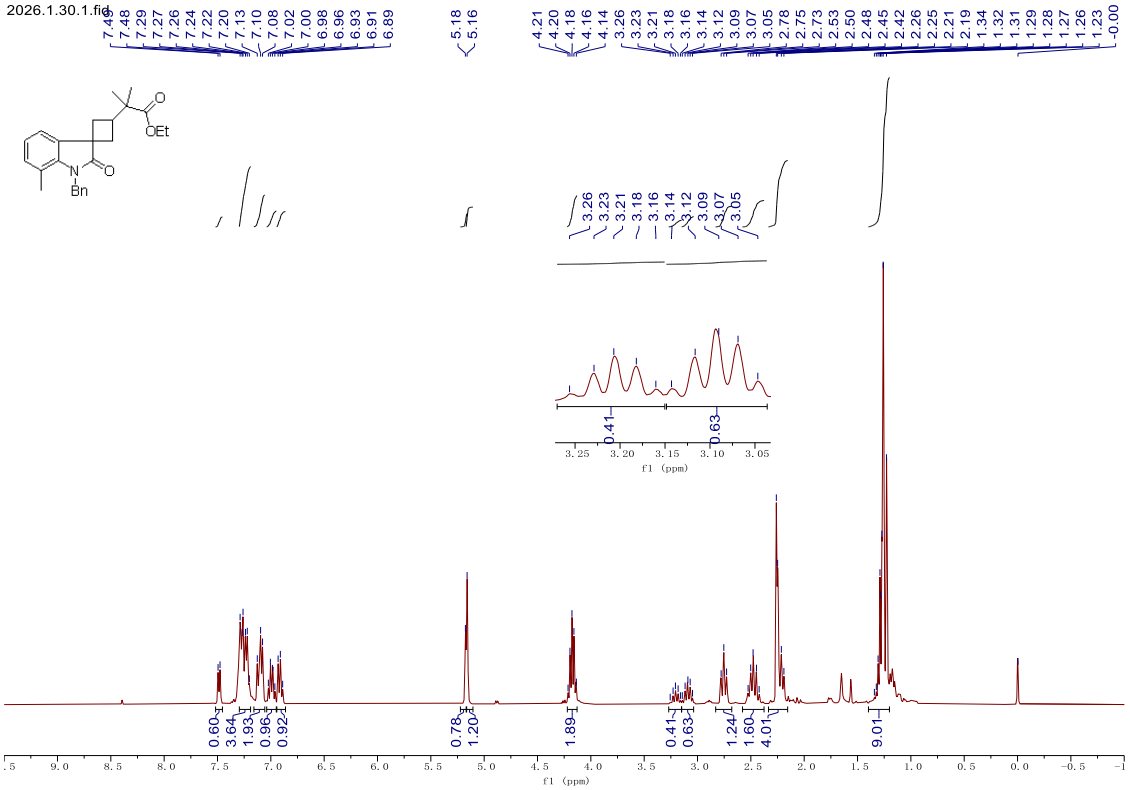


^{19}F NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3fa**)

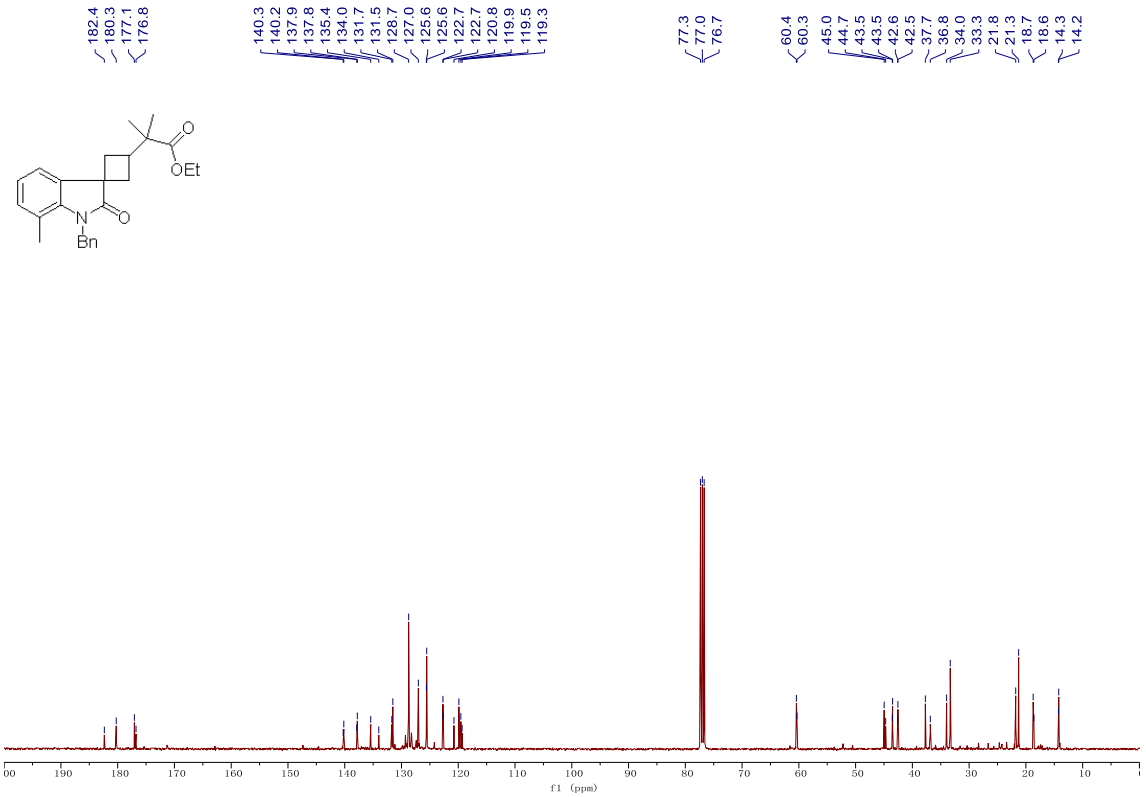




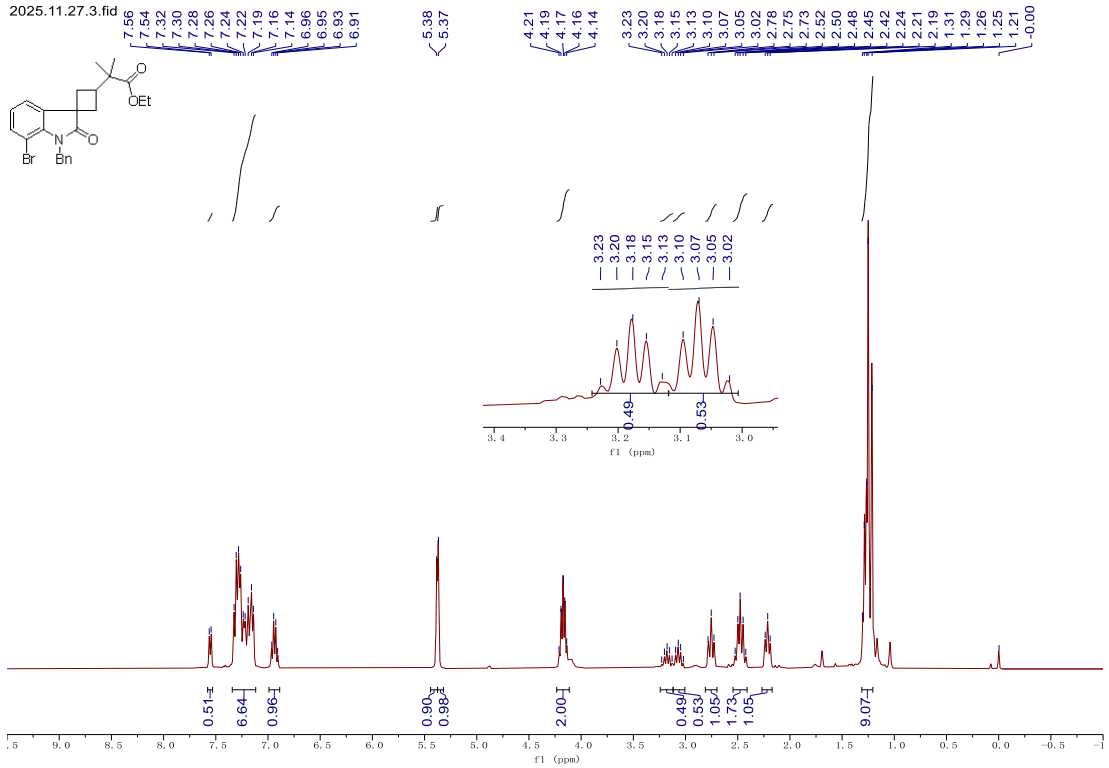
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ga**)



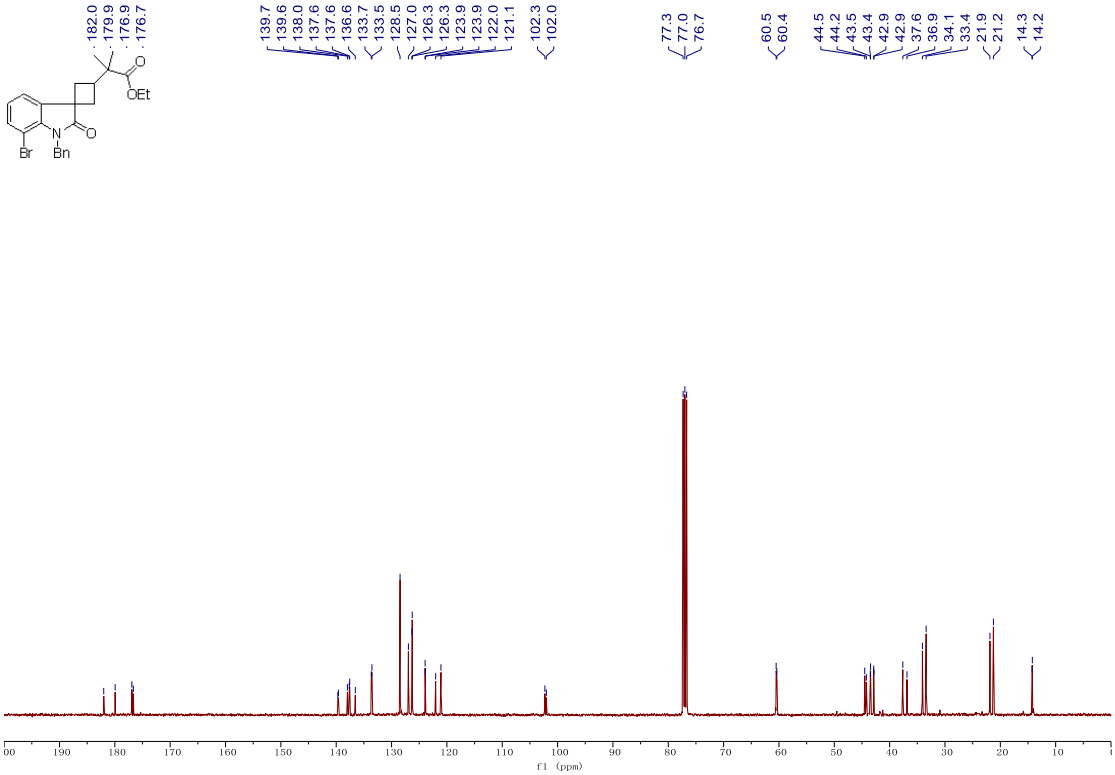
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ga**)



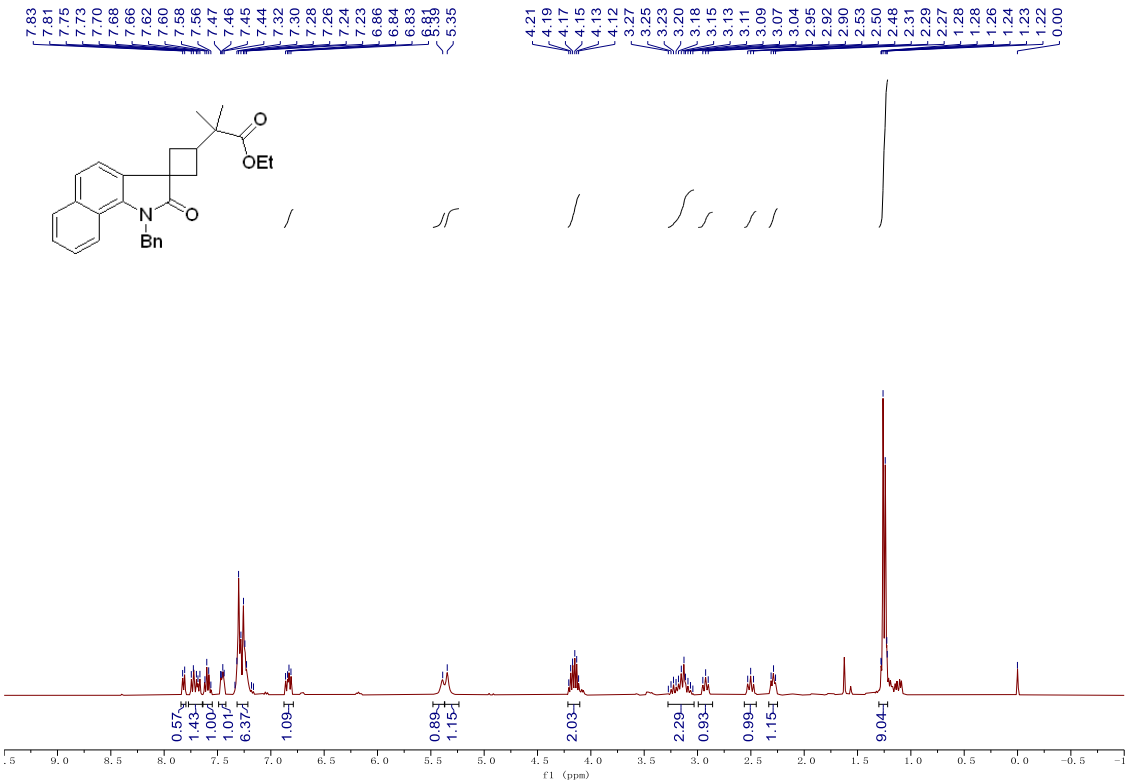
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ha**)



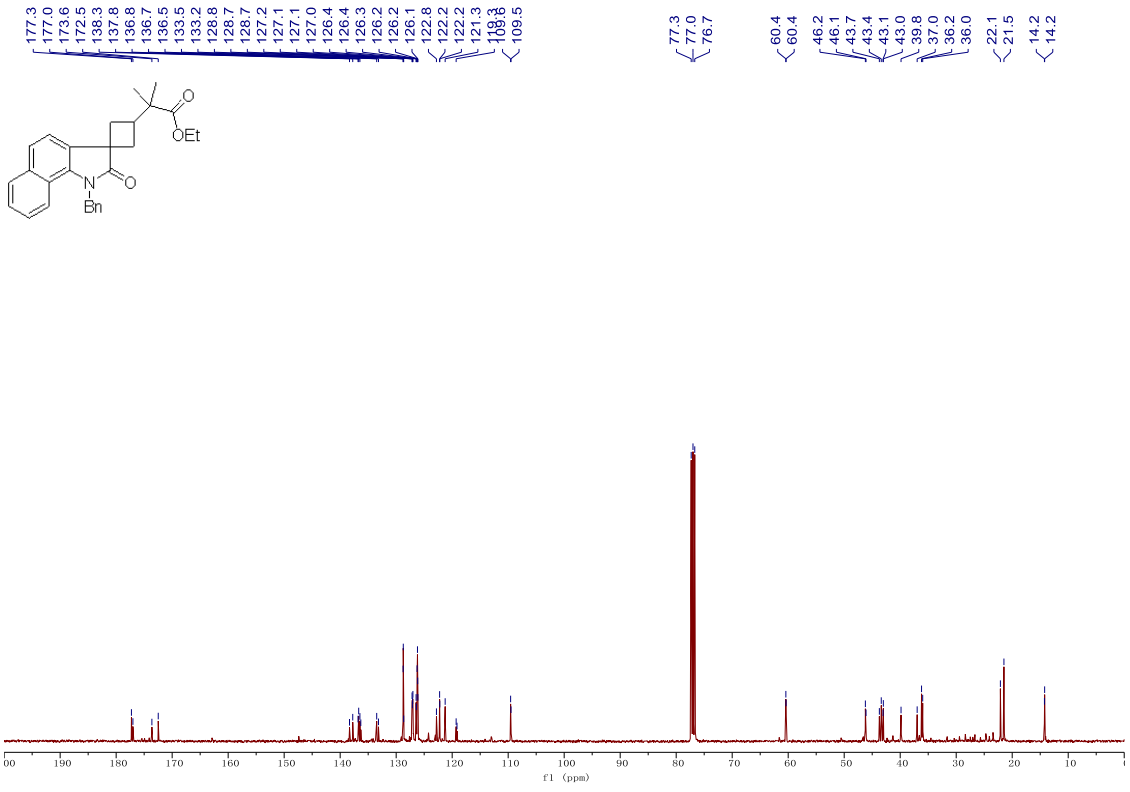
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ha**)



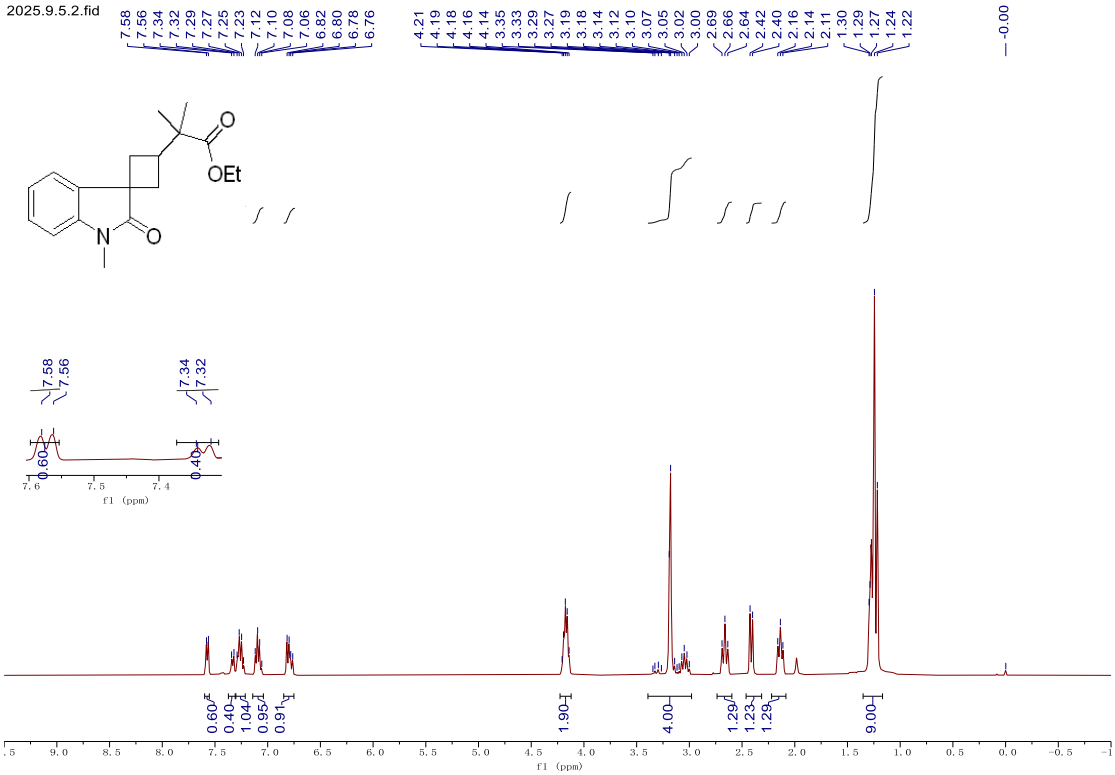
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ia**)



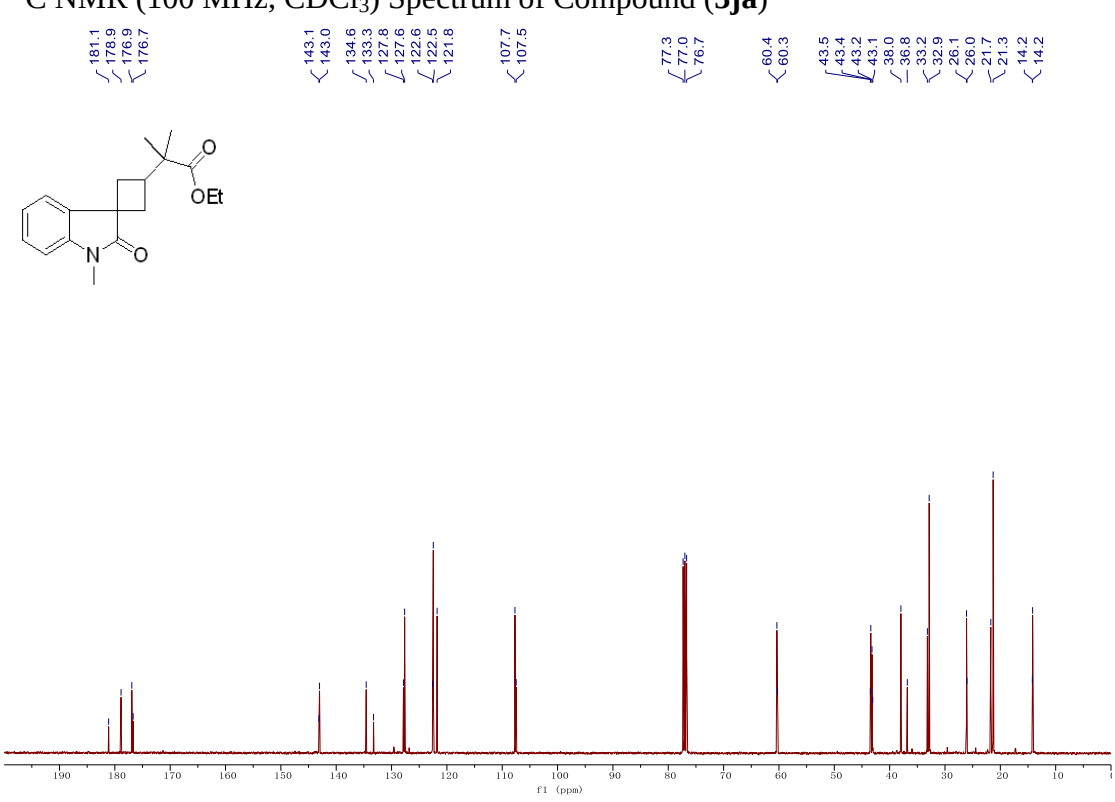
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ia**)



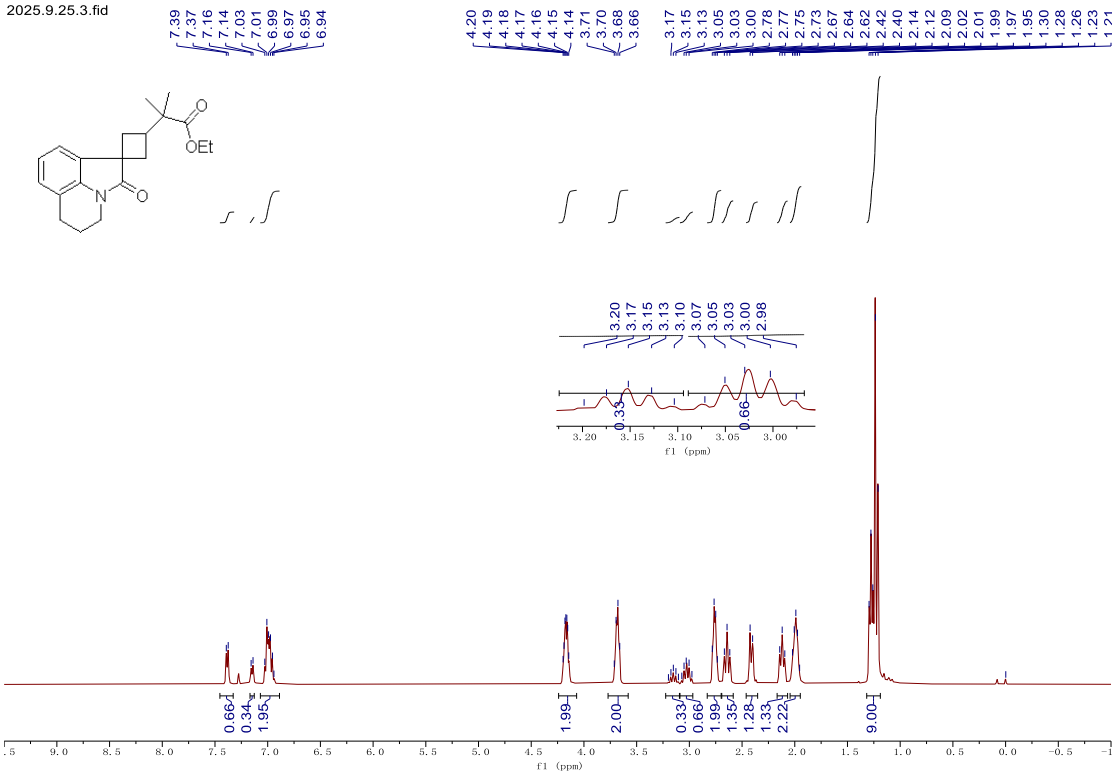
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ja**)



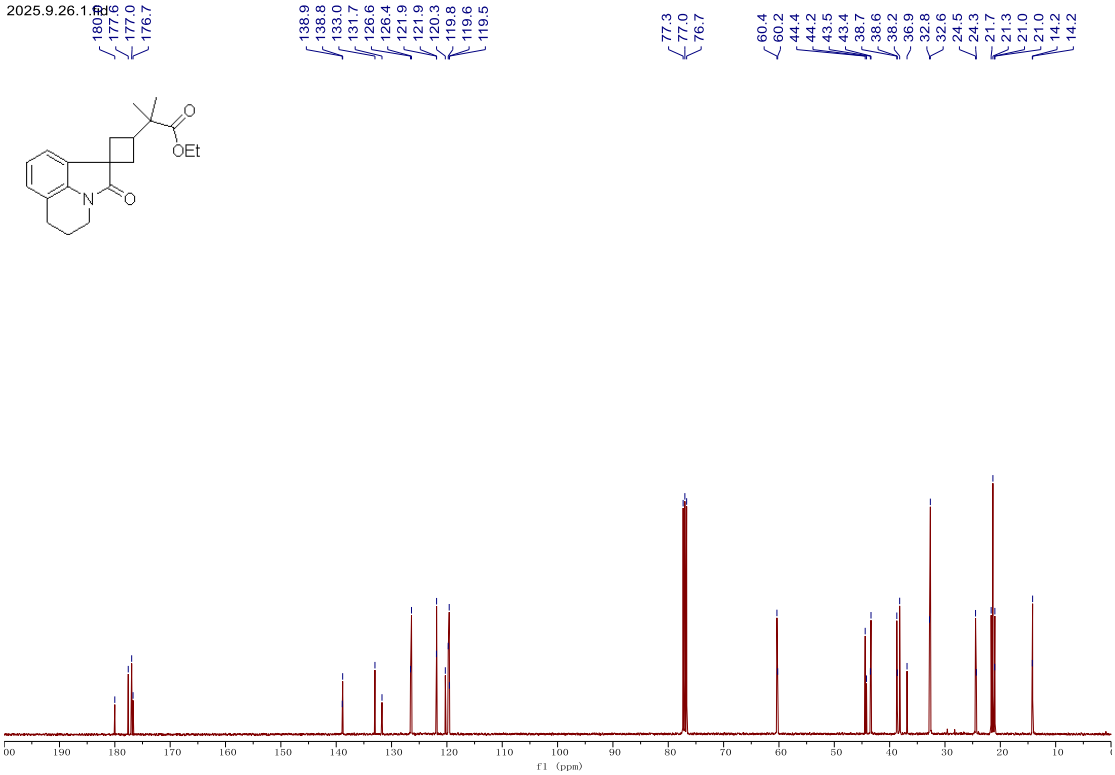
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ja**)



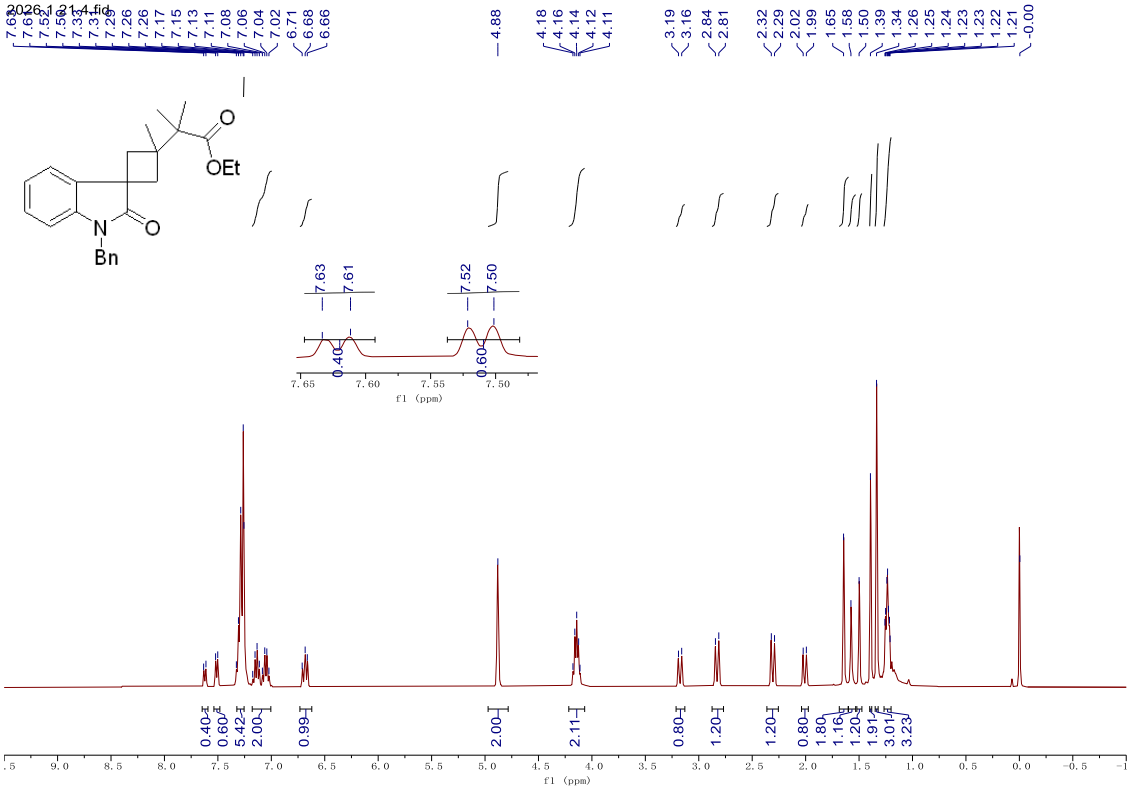
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ka**)



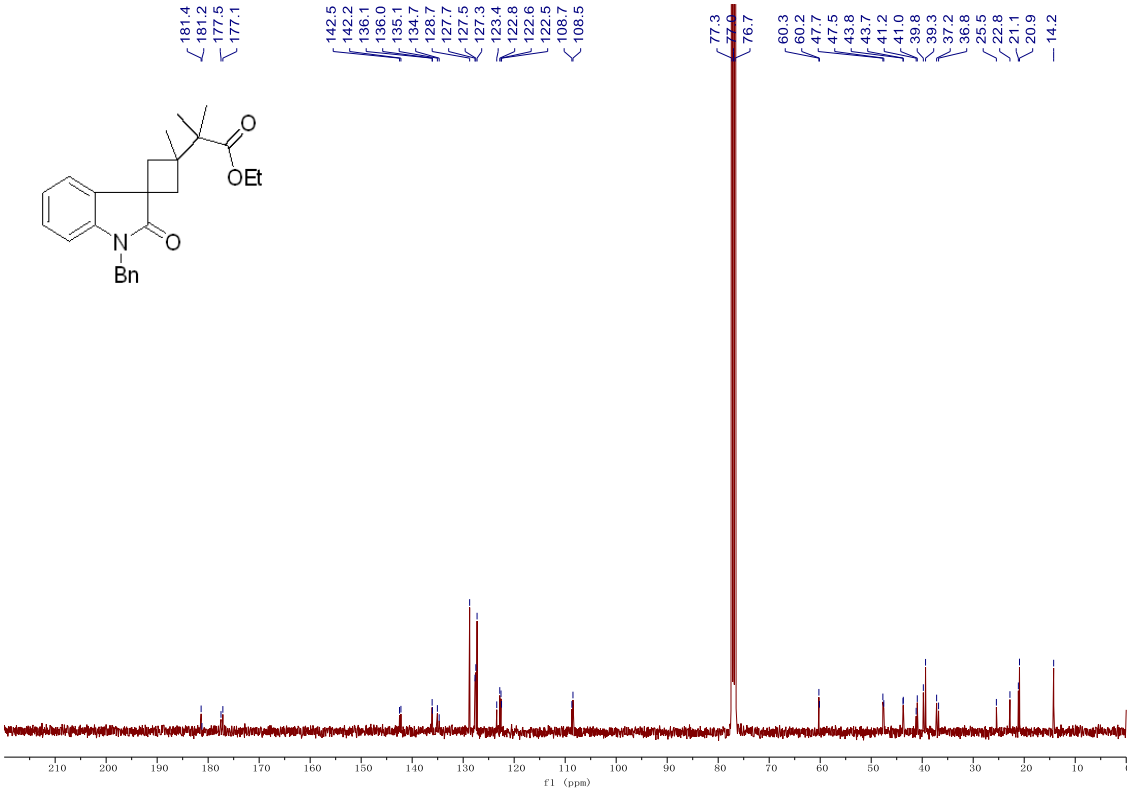
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ka**)



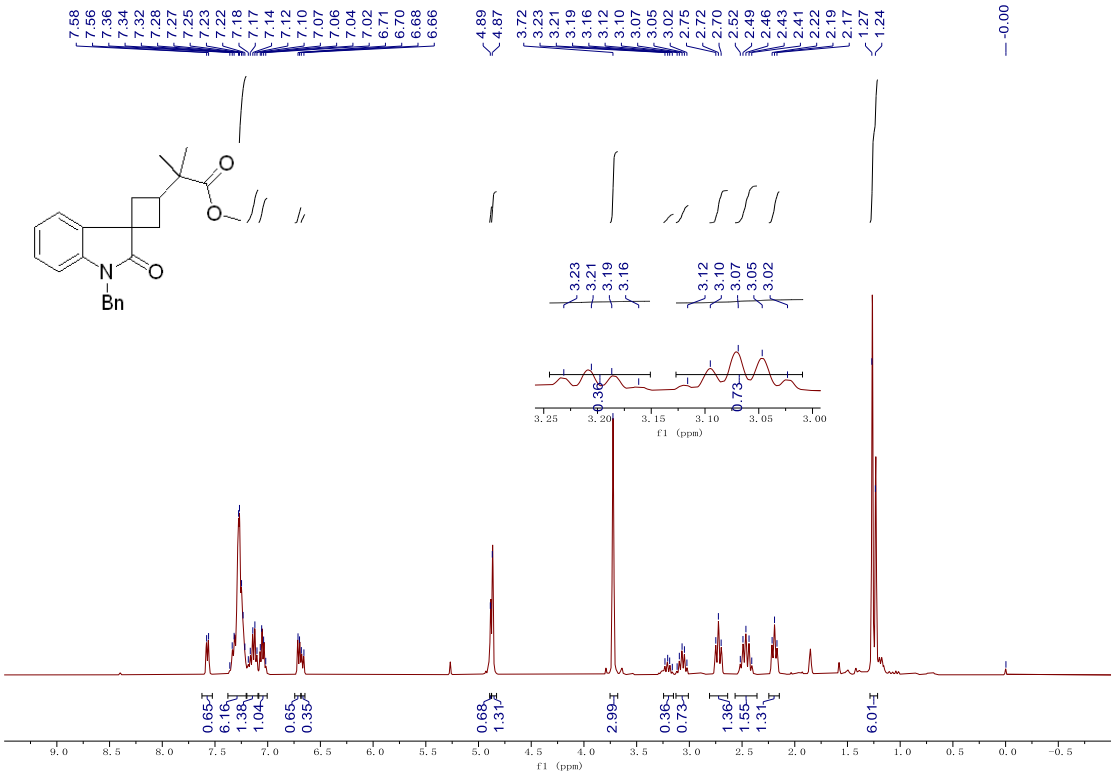
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3la**)



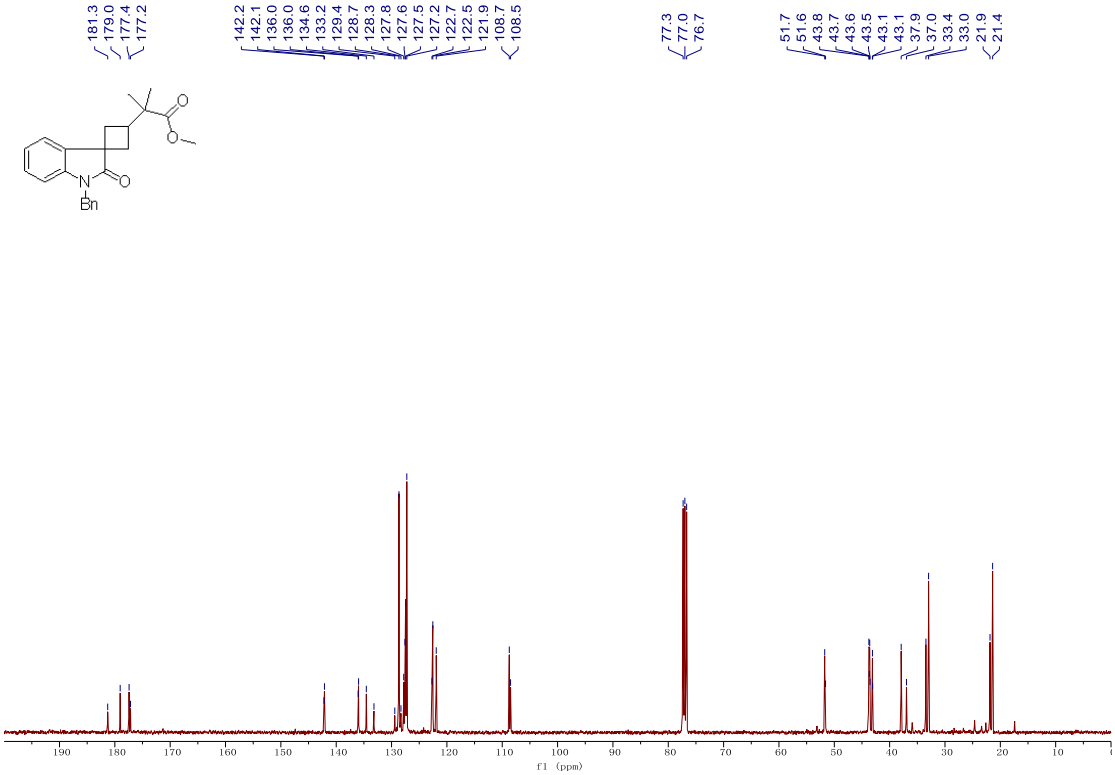
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3la**)



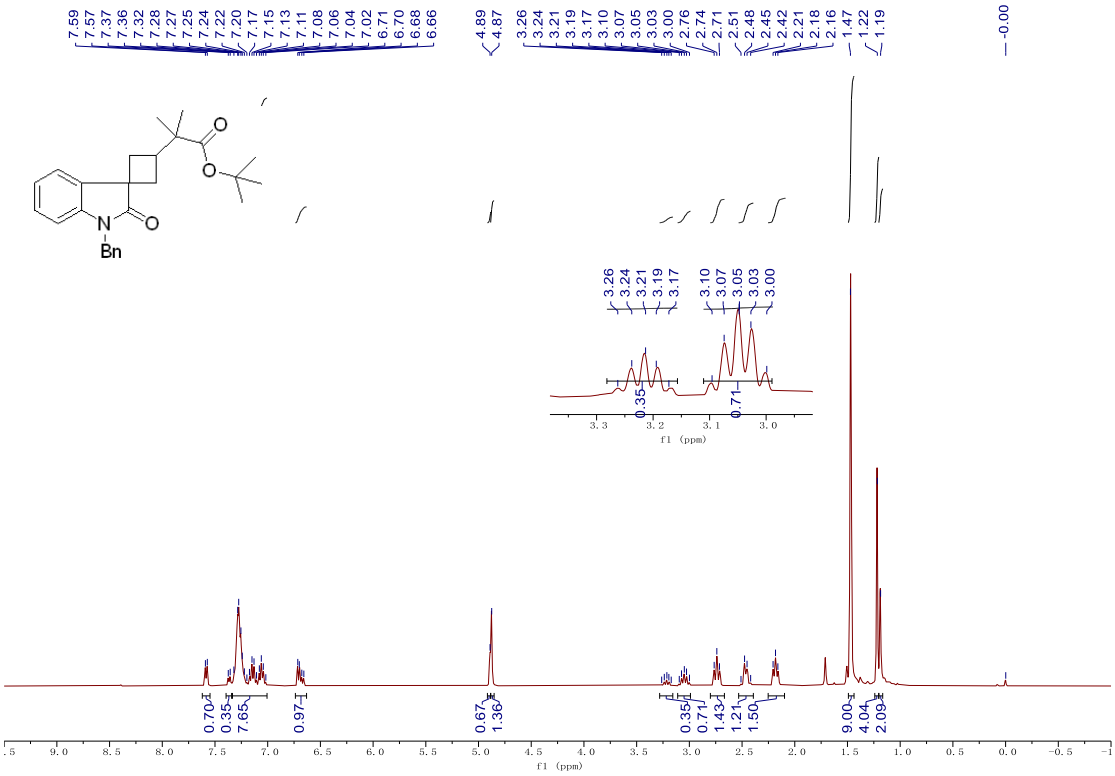
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ab**)



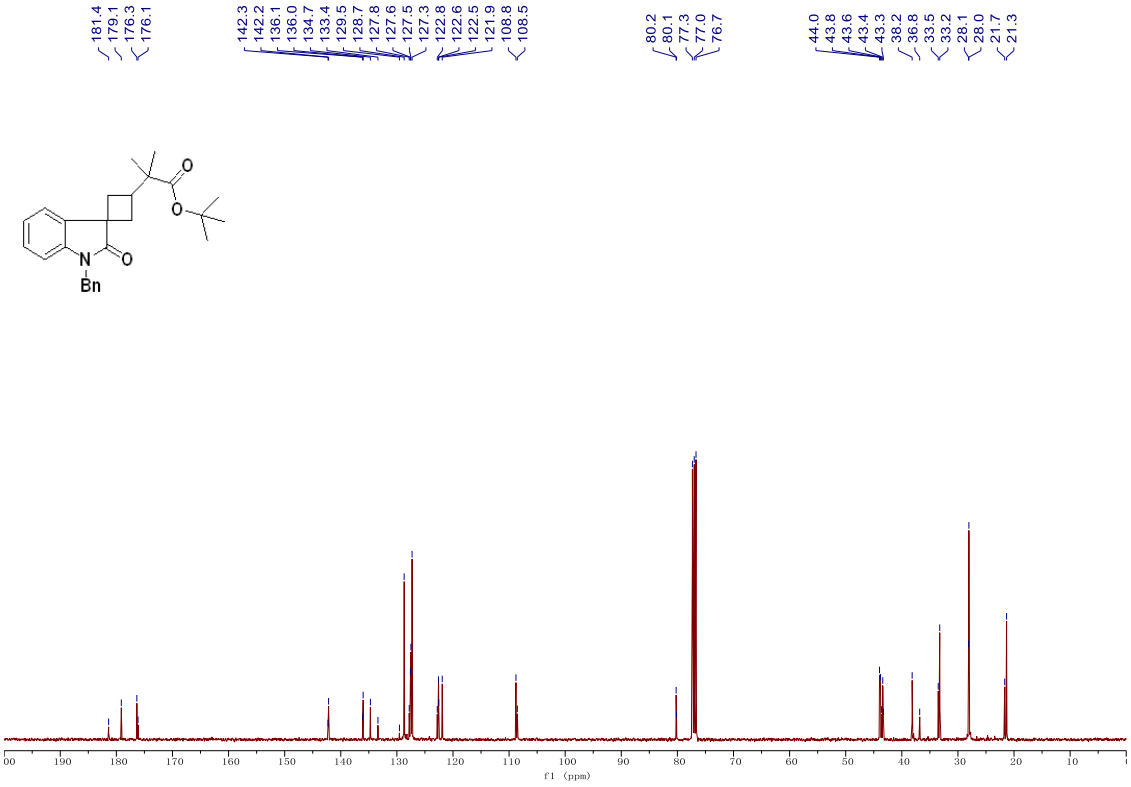
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ab**)



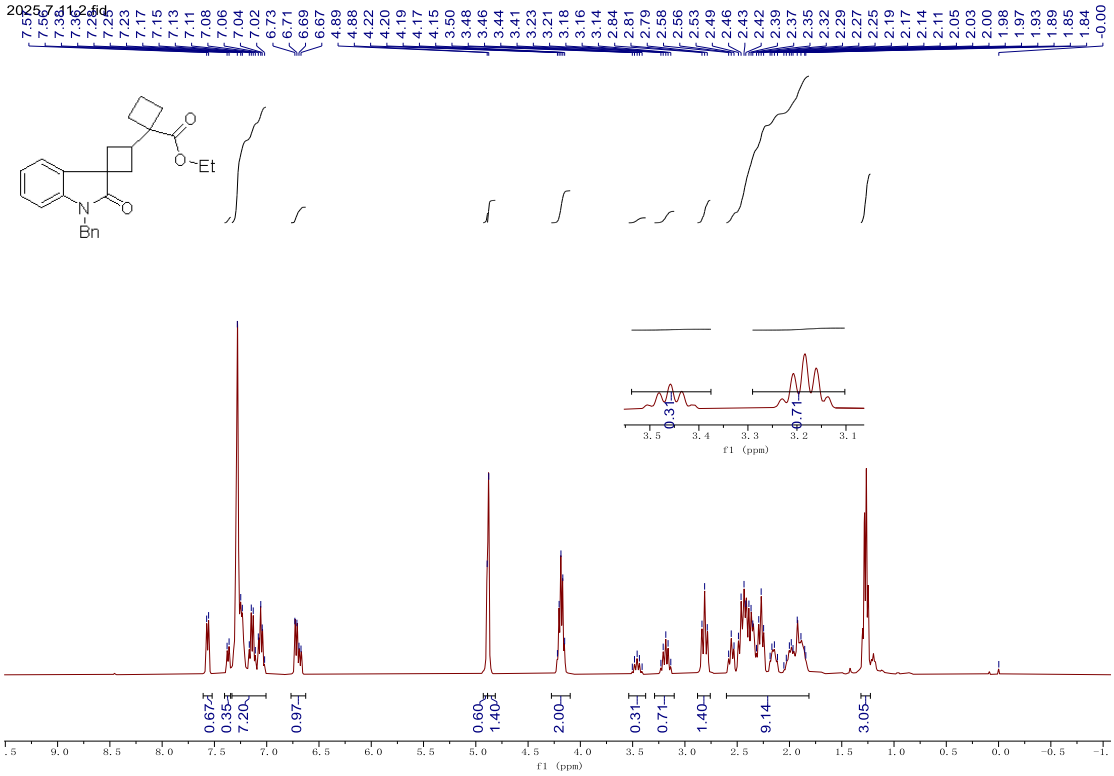
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ac**)



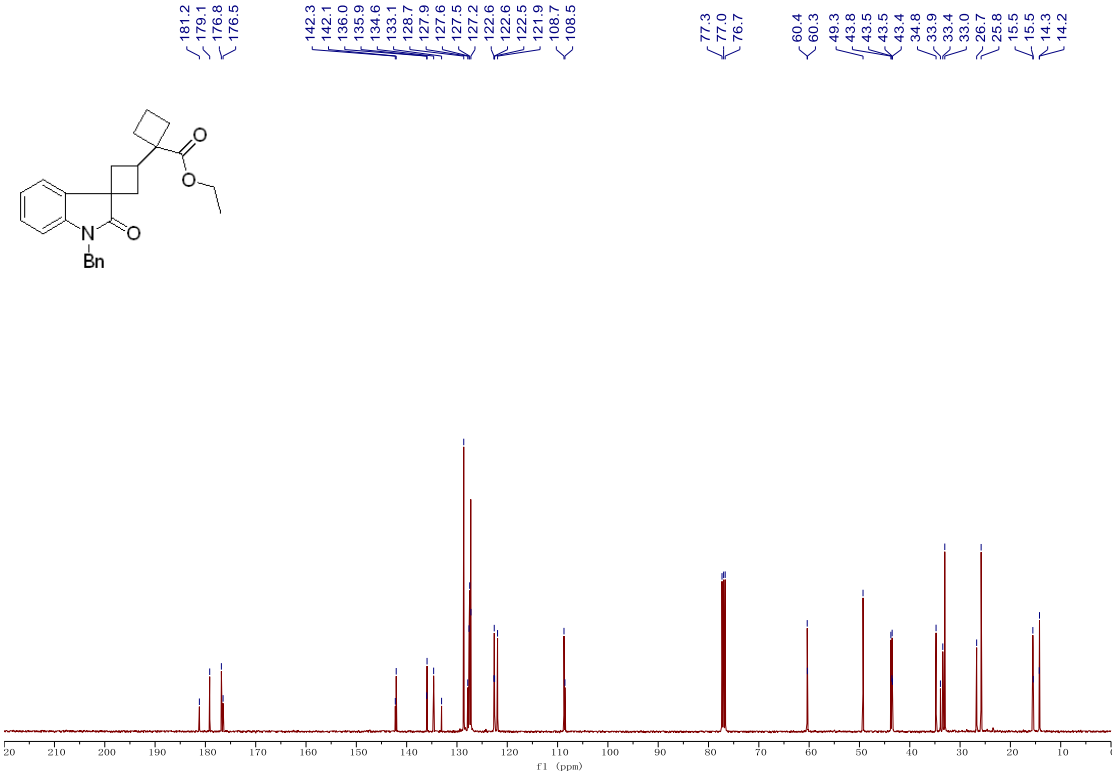
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ac**)



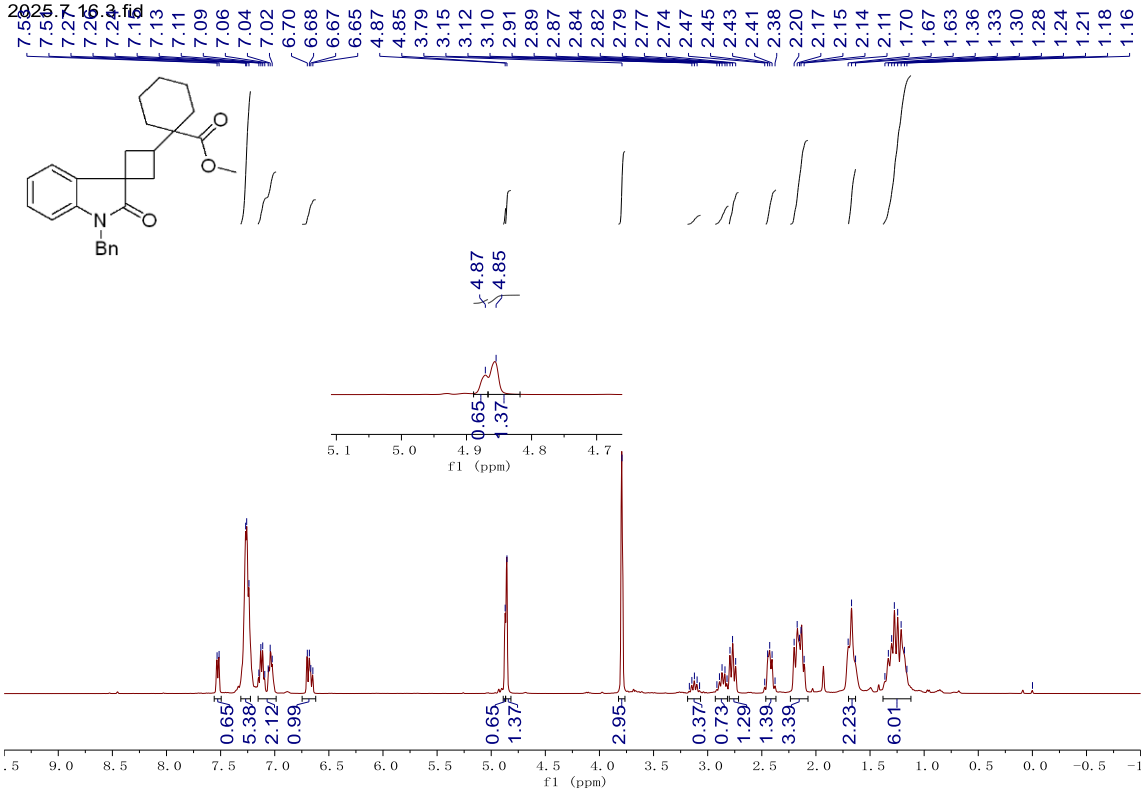
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ad**)



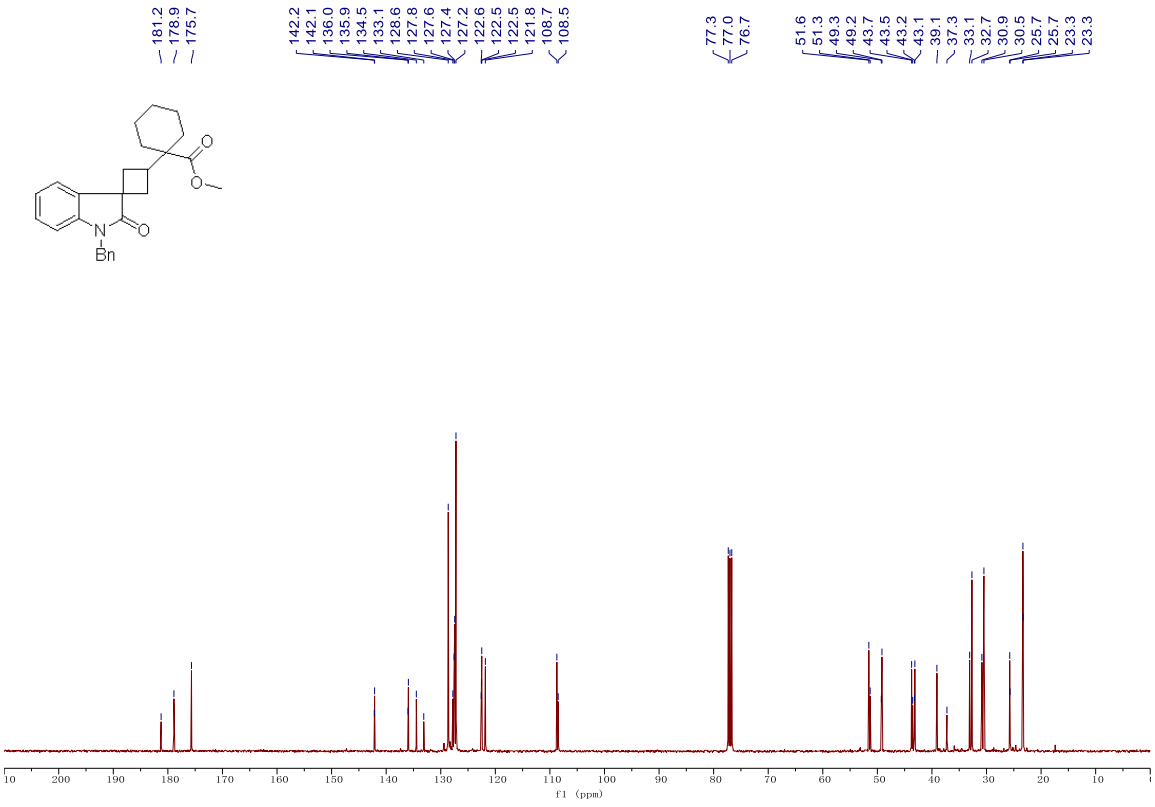
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ad**)



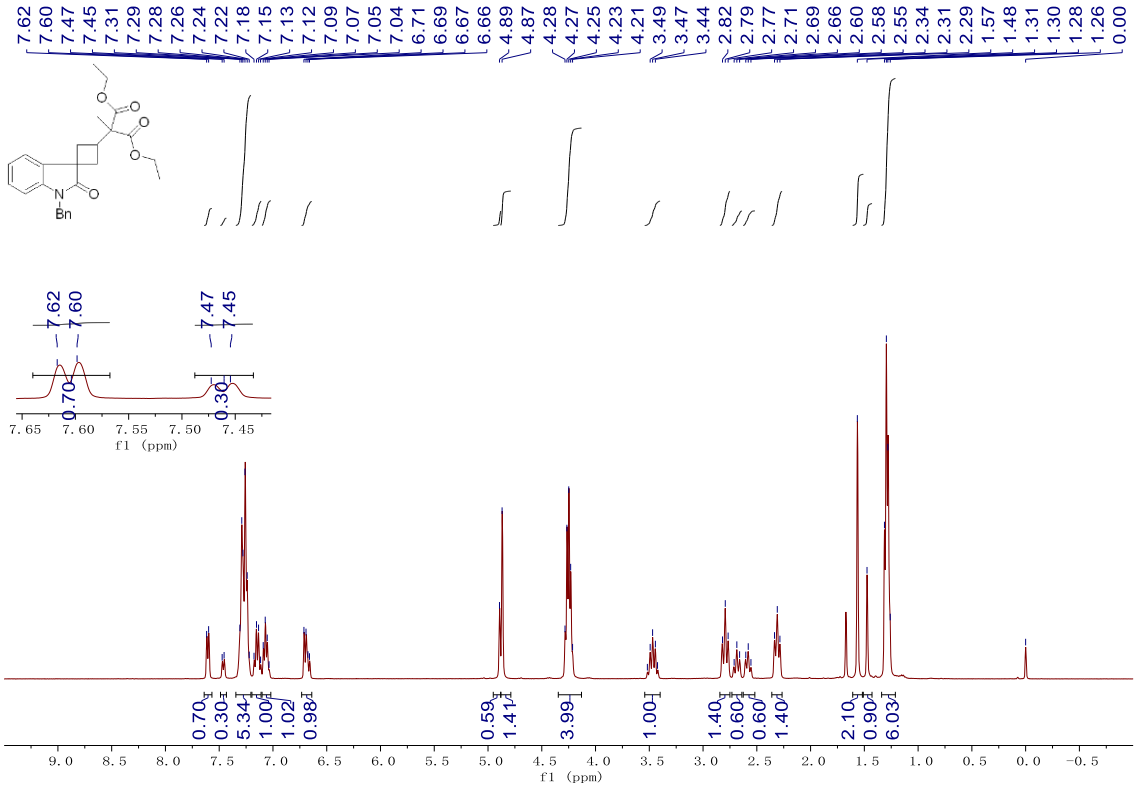
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ae**)



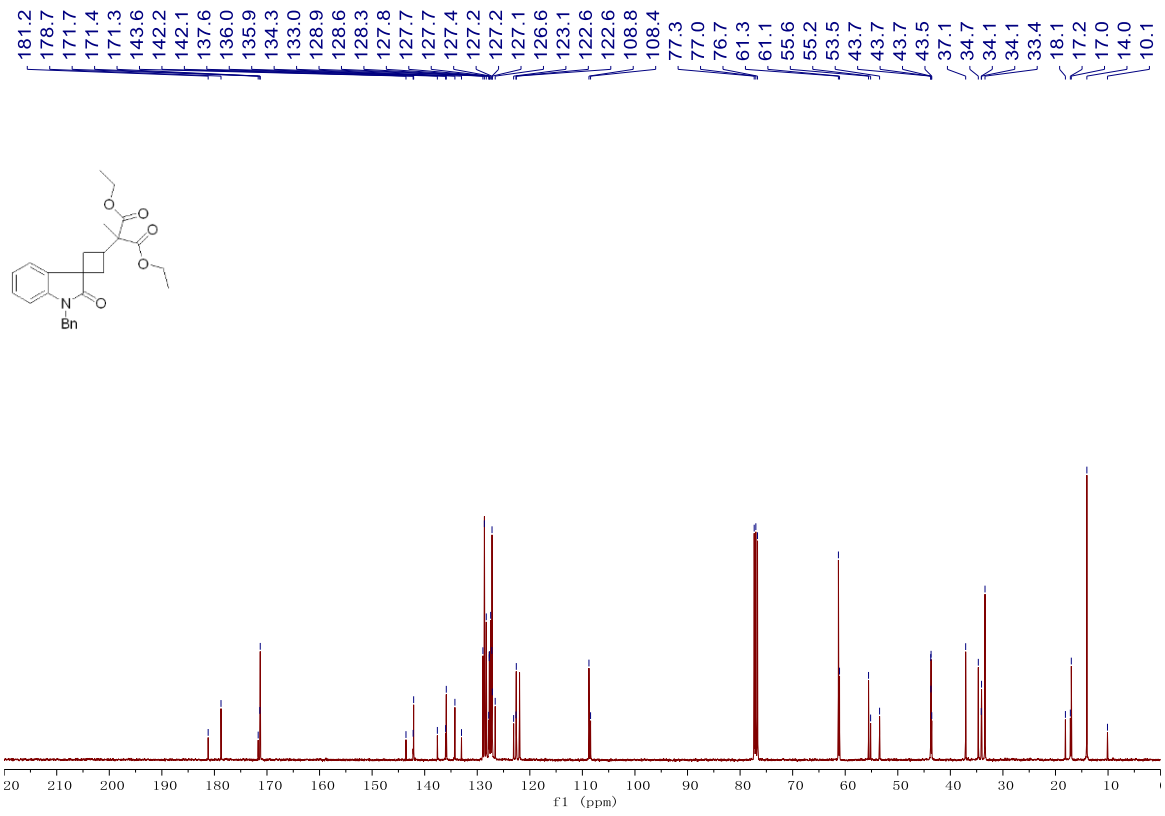
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ae**)



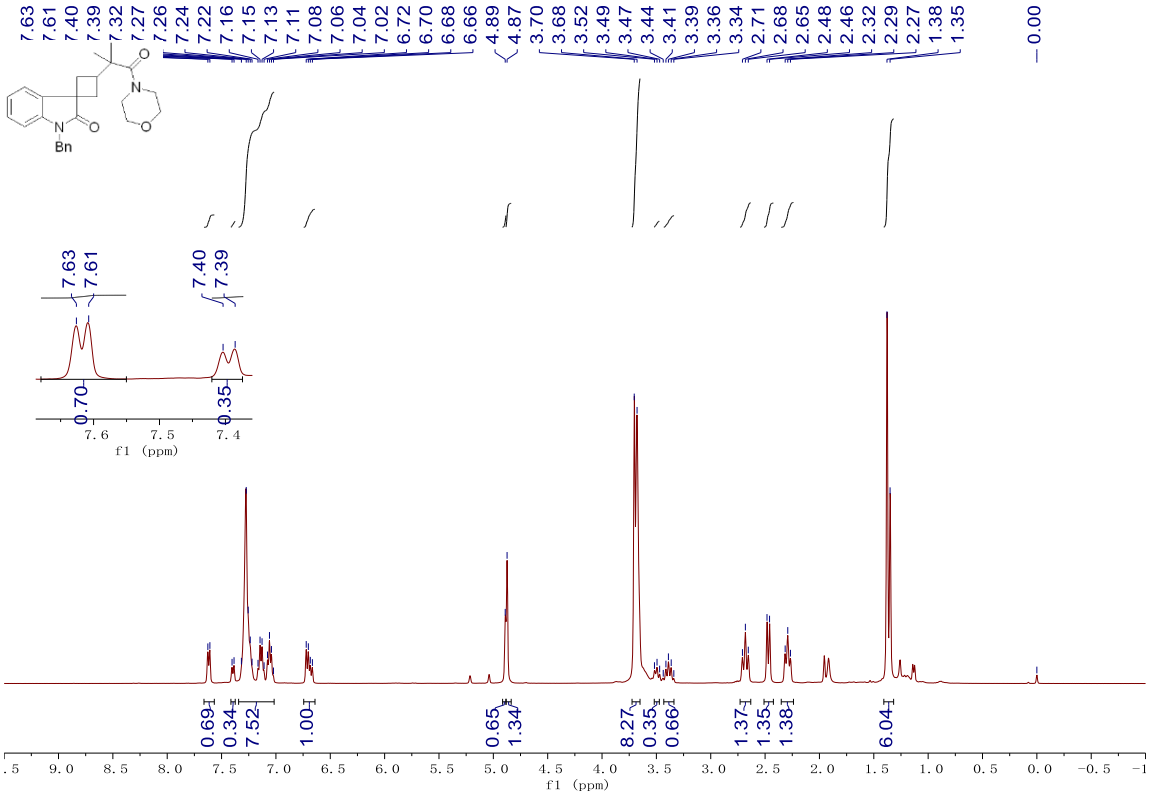
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3af**)



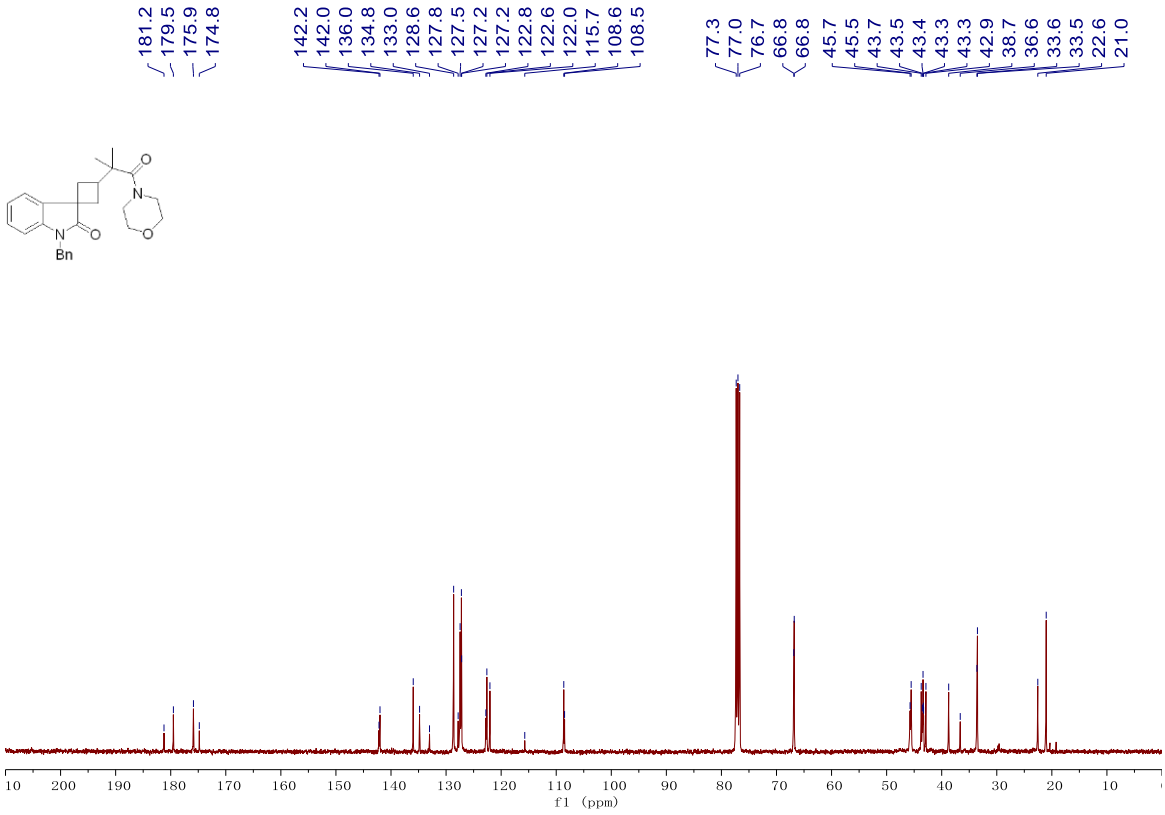
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3af**)



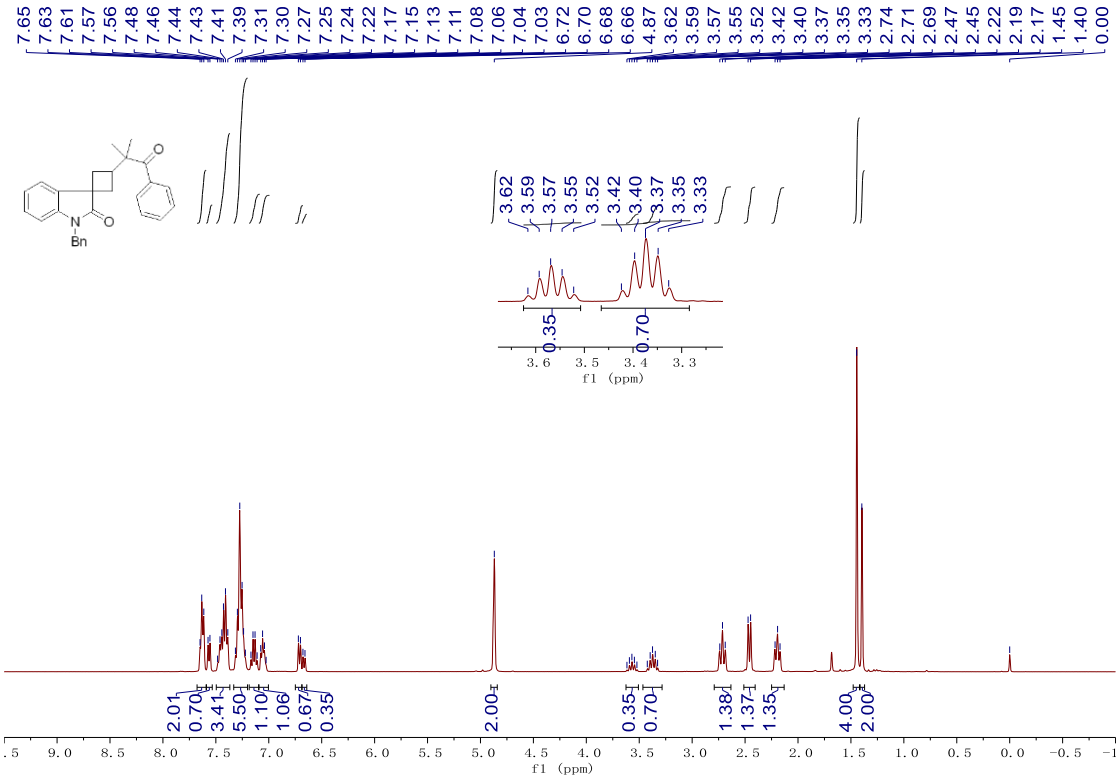
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ag**)



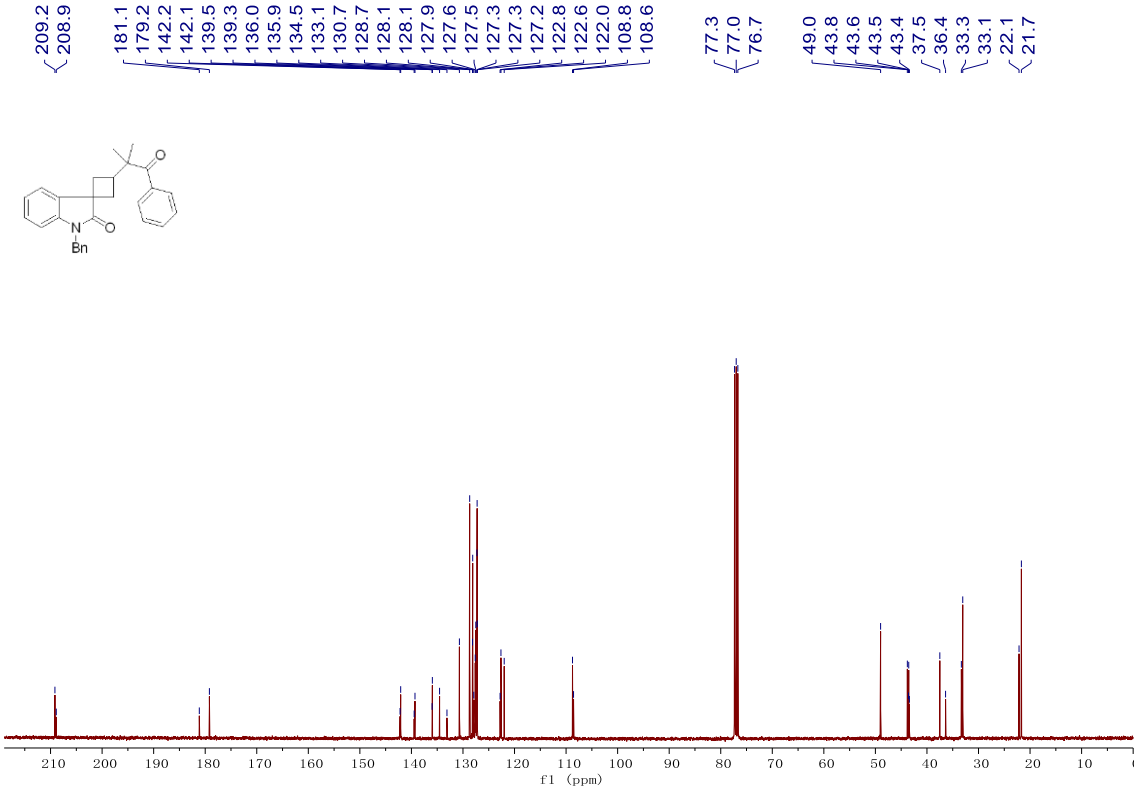
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ag**)



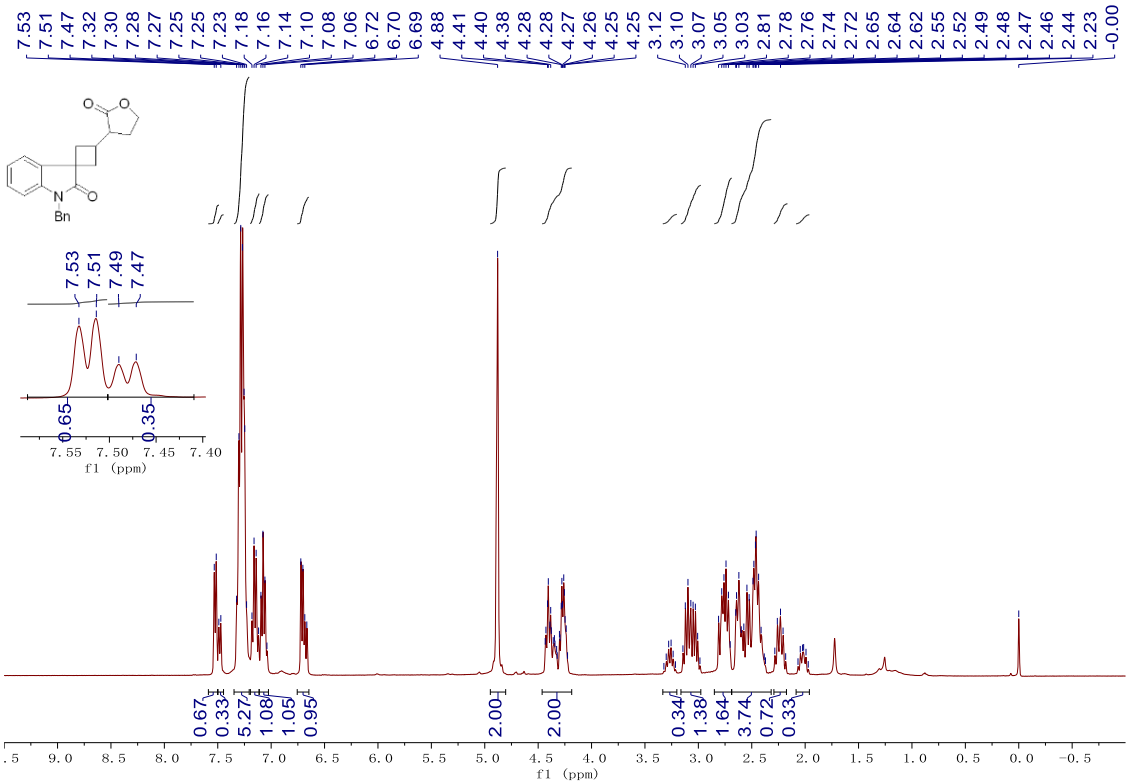
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ah**)



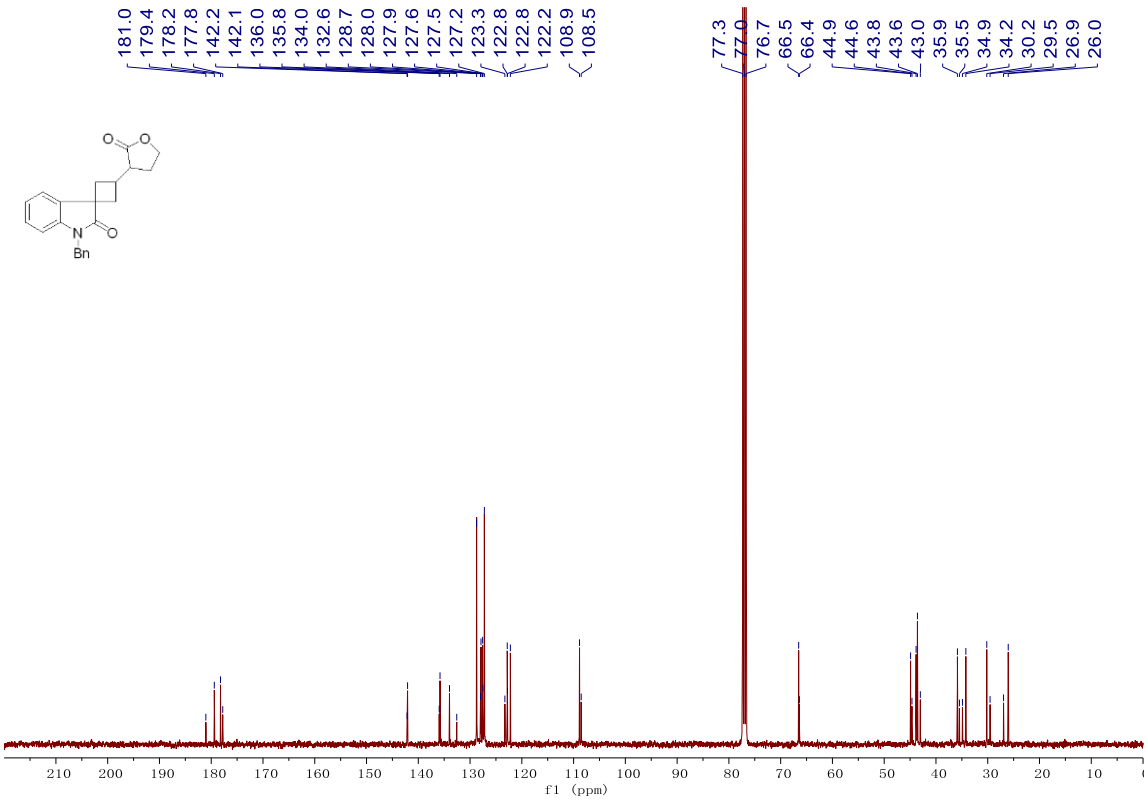
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ah**)



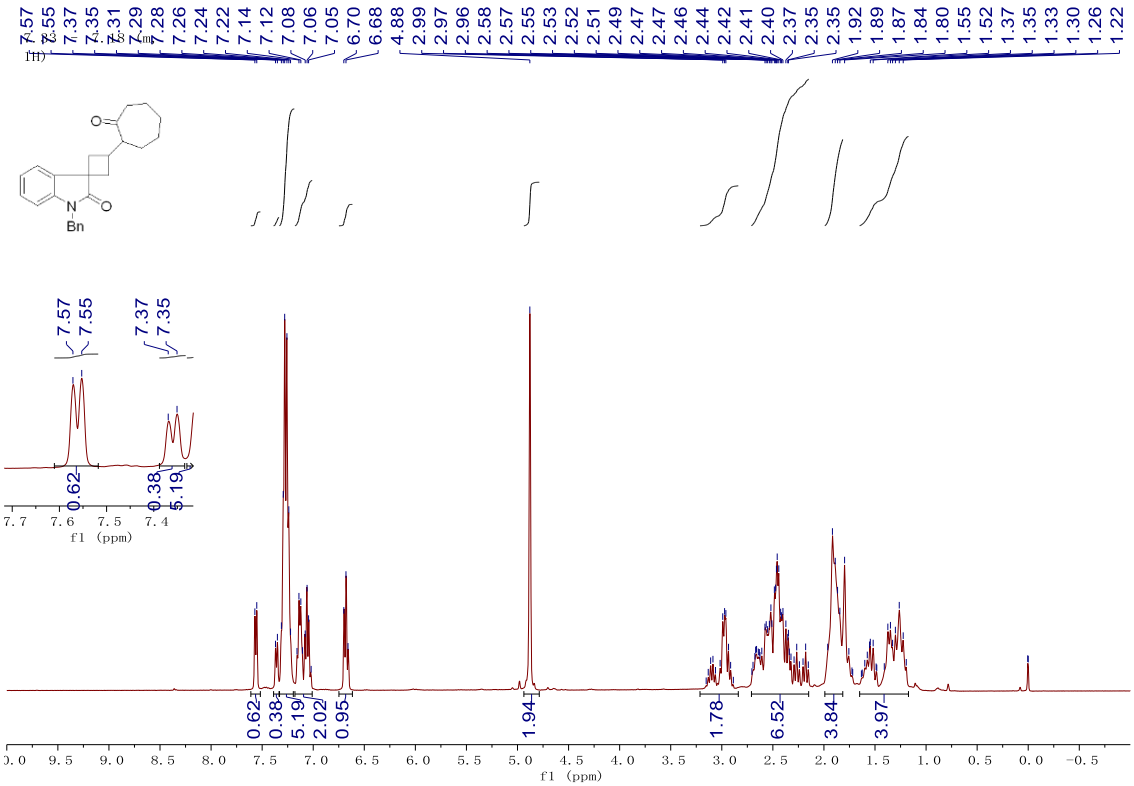
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ai**)



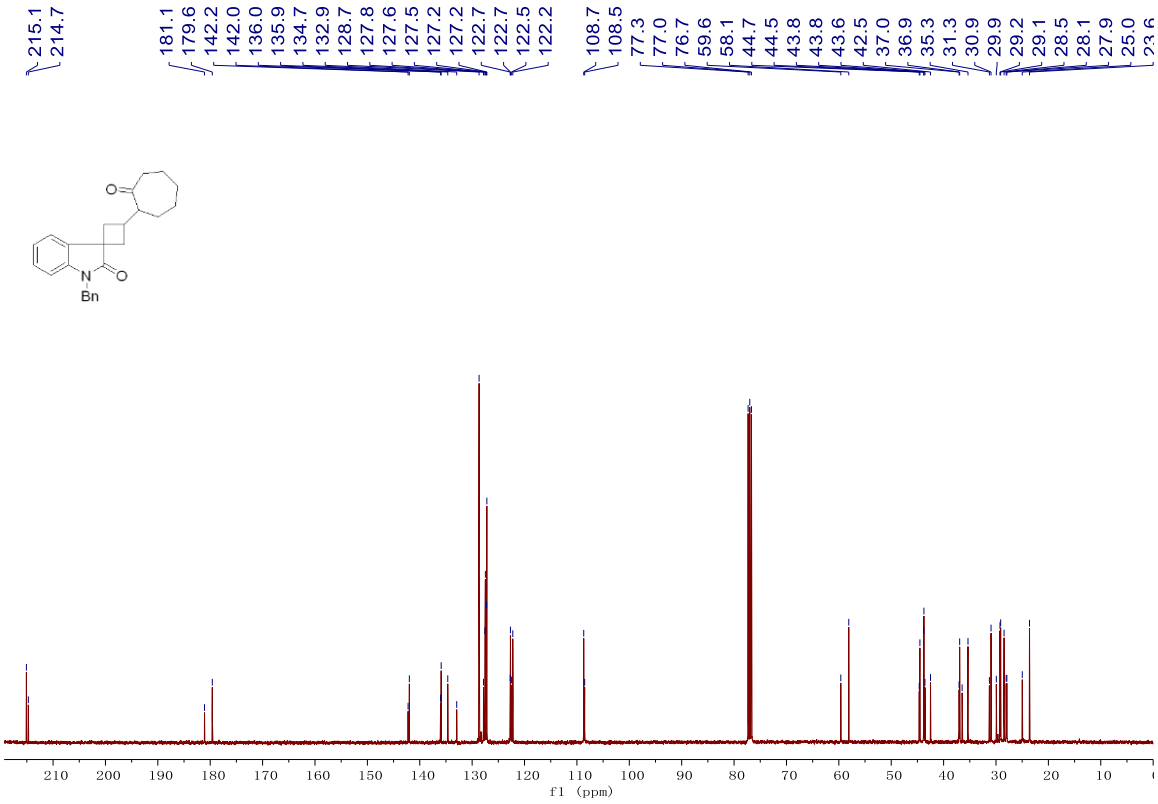
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ai**)



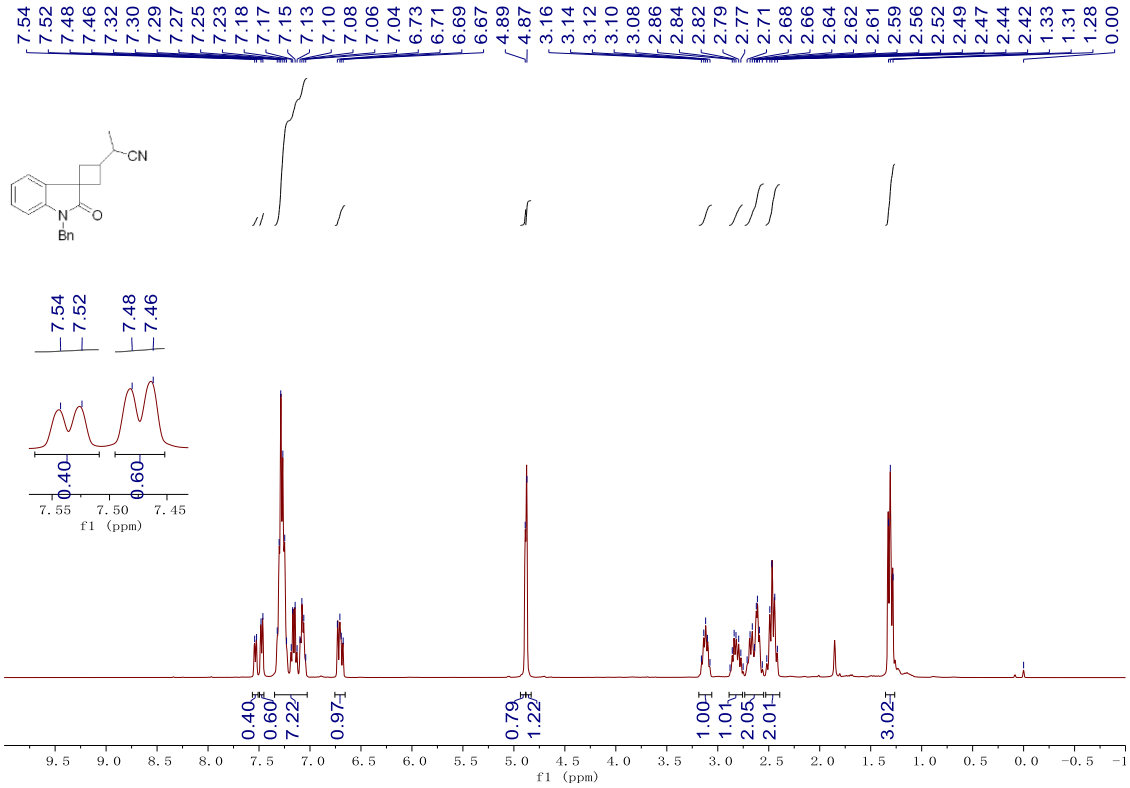
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3aj**)



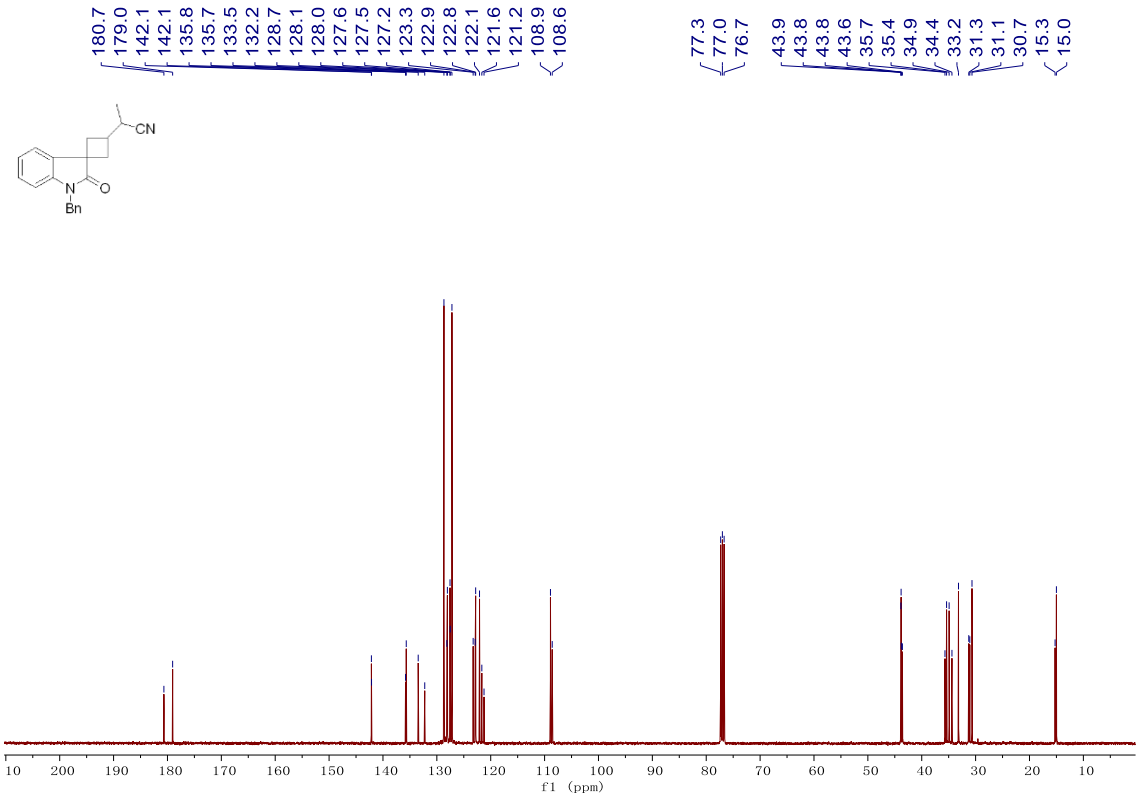
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3aj**)



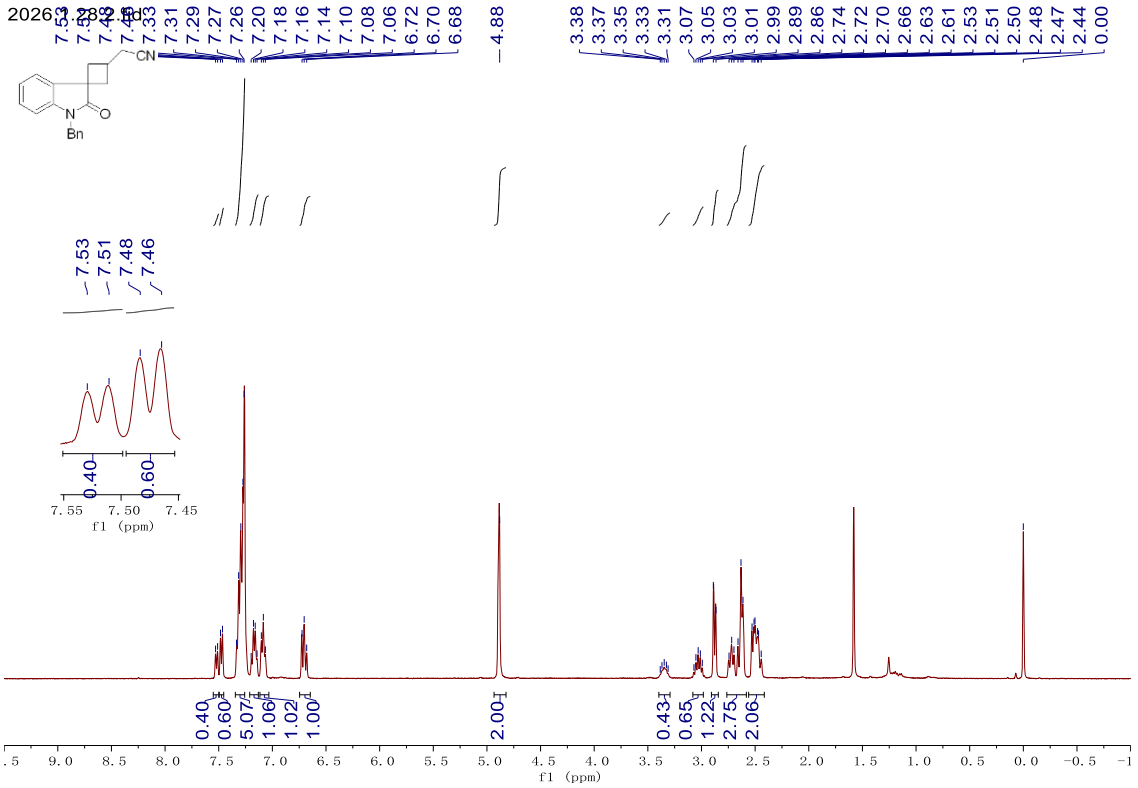
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ak**)



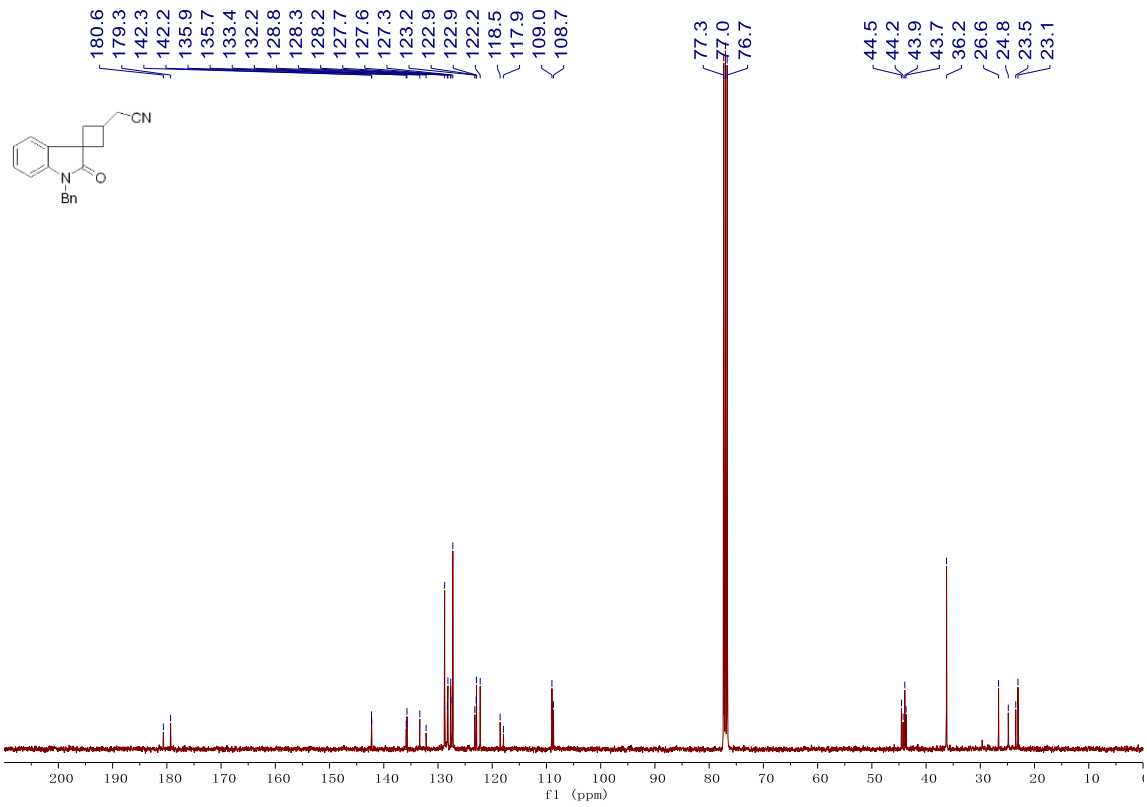
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ak**)



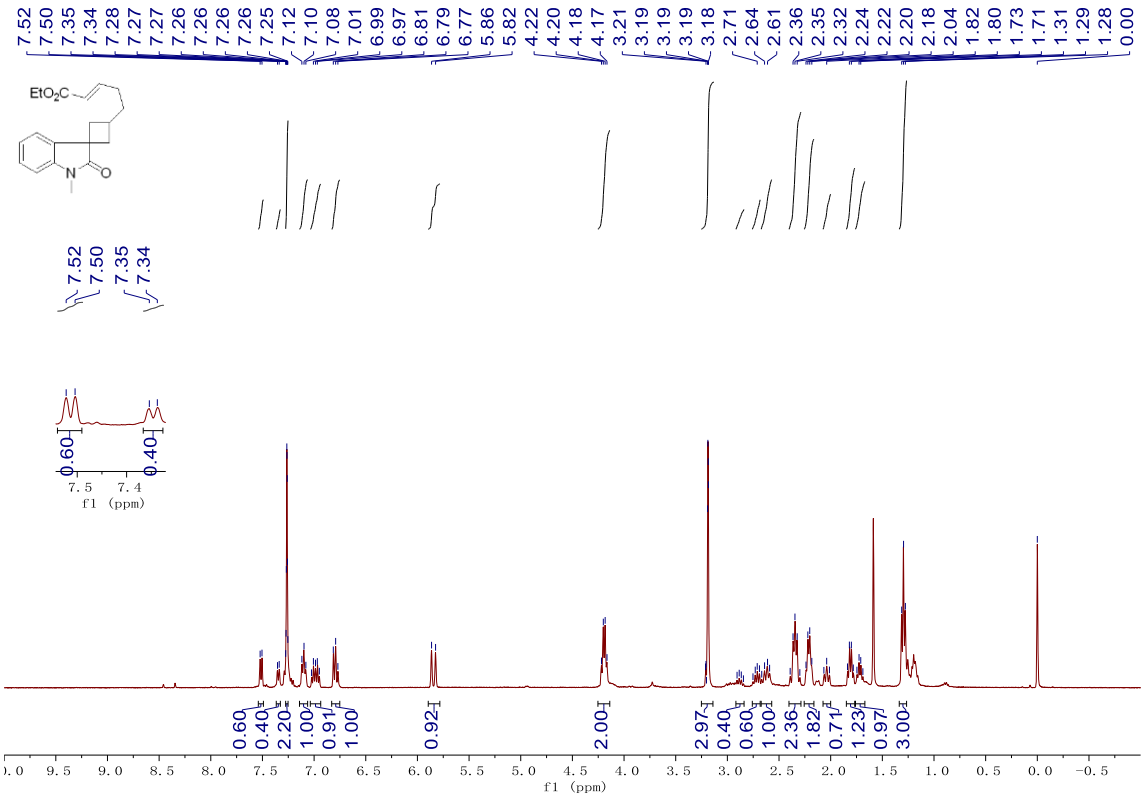
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3al**)



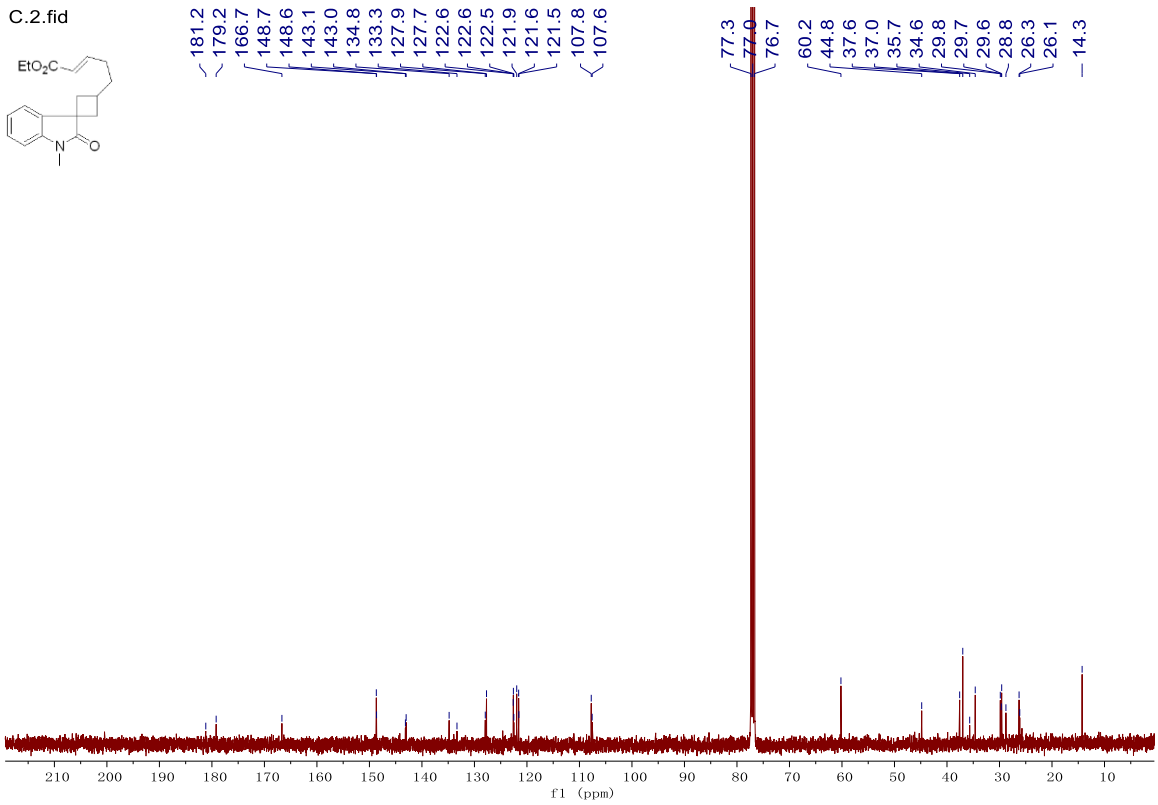
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3al**)



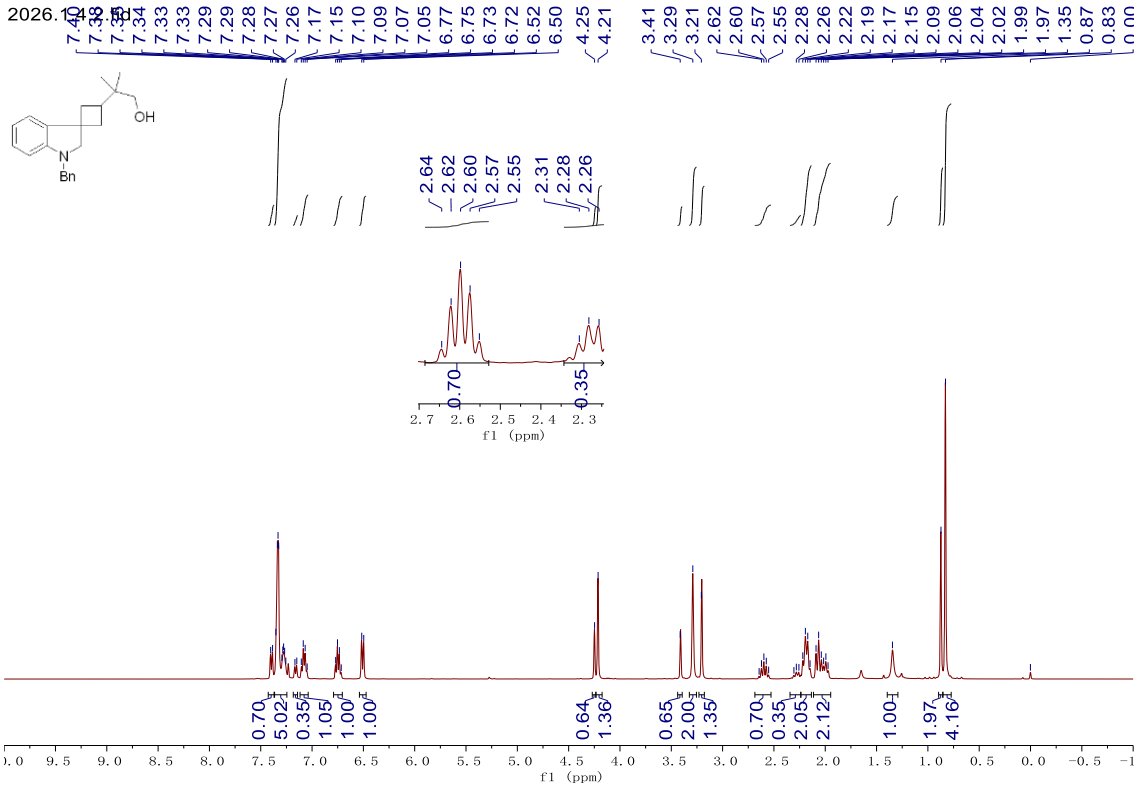
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3jm**)



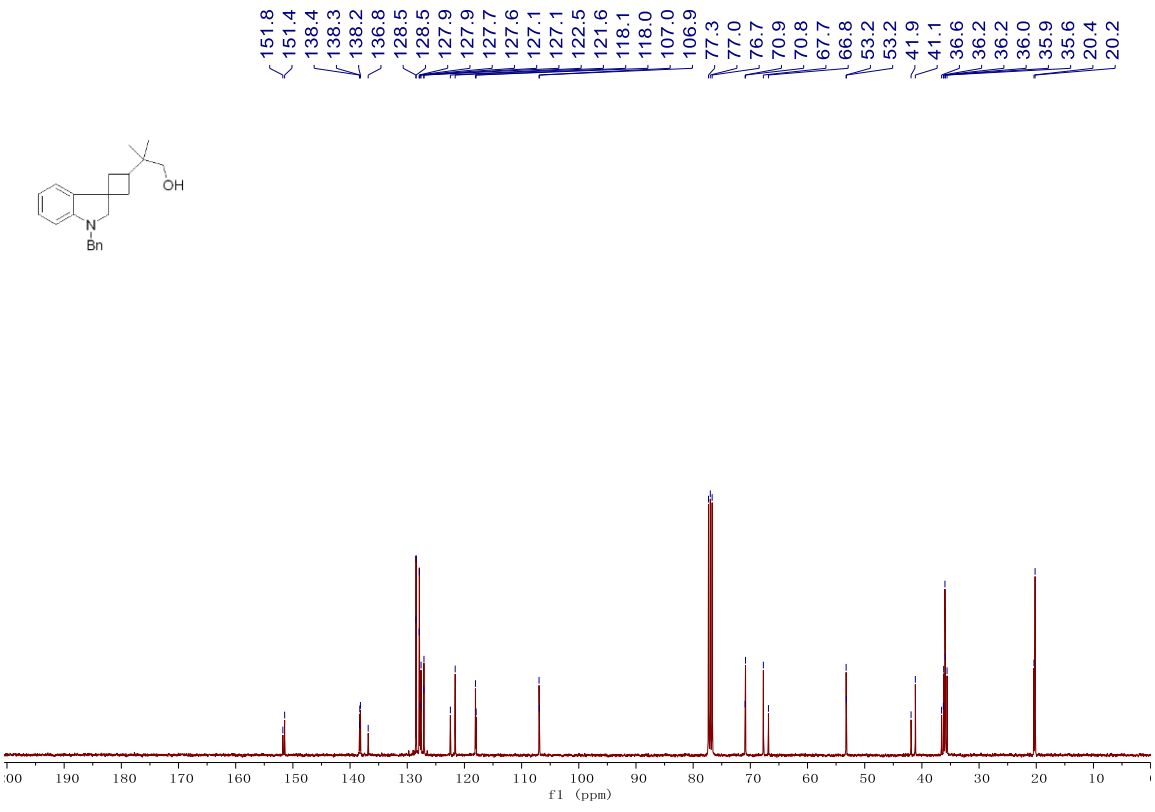
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3jm**)



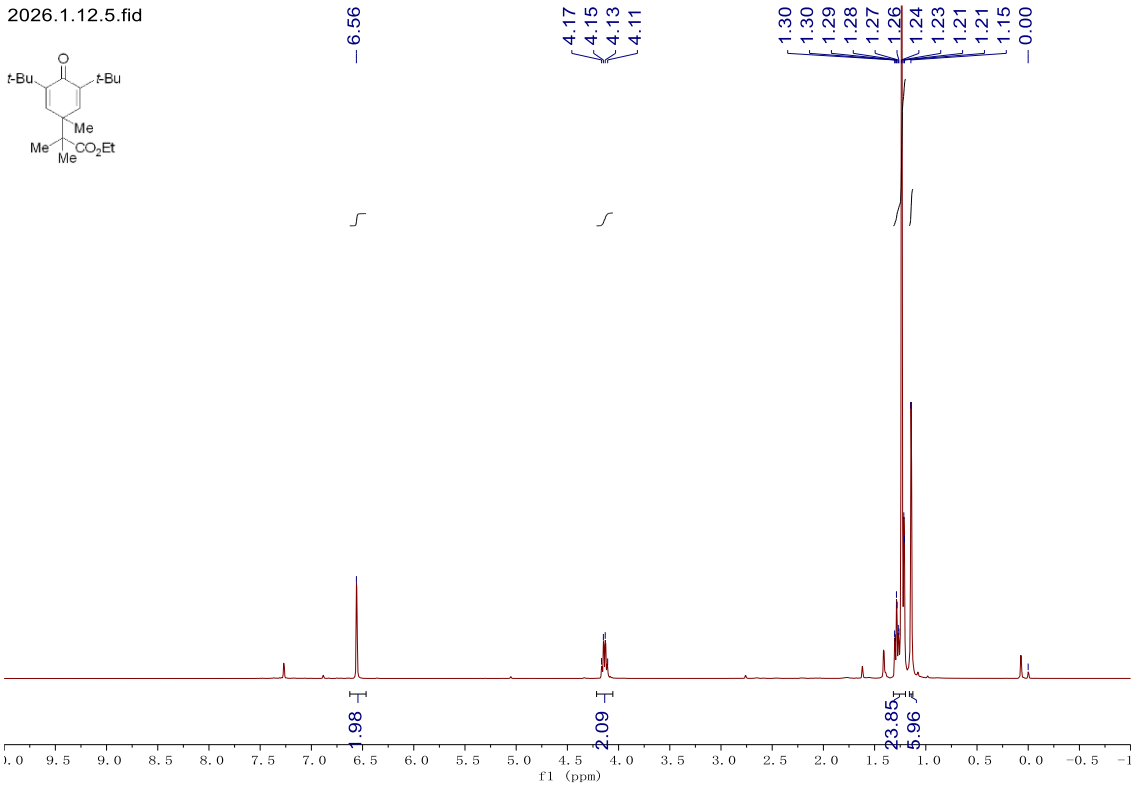
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**4**)



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**4**)



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**5**)



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**5**)