# SUPPORTING INFORMATION

# Iodide/$H_2O_2$ Catalyzed Intramolecular Oxidative Amination for the Synthesis of 3,2'-Pyrrolidinyl Spirooxindoles

Yu-Ting Gao,[a,b] Xiao-Yang Jin,[a,b] Qi Liu,[a,b] An-Di Liu,[a,b] Liang Cheng,*[a,b] Dong Wang,[a] and Li Liu*[a,b]

**Table of Contents**

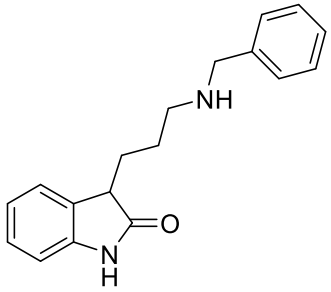
**General**

Unless otherwise noted, all reagents were obtained from commercially suppliers and were used without further purification. All reactions were carried out under argon atmosphere using Schlenk techniques. Oxindoles **1** were obtained from commercially suppliers or prepared according to the literature procedures.[1-3] Alkynes were obtained from commercially suppliers.

TLC analysis was performed on glass-baked silica plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether / ethyl acetate / dichloromethane/methanol. $^{1}H$, $^{13}C$ NMR Spectra were obtained on Bruker 300 MHz, 400 MHz or 500 MHz NMR spectrometer in the deuterated solvents indicated. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or (br). Melting points were measured on Beijing Tech X-4 apparats without correction. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. HRMS were obtained using electrospray ionization (ESI) mass spectrometer.

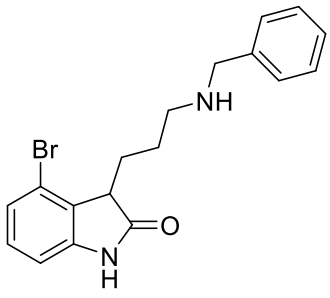
## 2. General procedure for synthesis of 1

To a mixture of indolyl propionic acid[S1] (10.0 mmol, 1.9 g) and triethylamine (20.0 mmol, 2.8 mL) in dichloromethane (70 mL) was added 1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxid hexafluorophosphate (12.0 mmol, 4.6 g) and benzylamine (12.0 mmol, 1.3 mL). The mixture was stirred at room temperature for 1 hour and then diluted with dichloromethane (200 mL). The organic layer was washed by water (200 mL * 2), dried over anhydrous sodium sulfate and evaporated to afford the intermediate *N*-benzyl-3-(1*H*-indol-3-yl)propanamide without further purification. *N*-benzyl-3-(1*H*-indol-3-yl)propanamide (8.0 mmol, 2.3 g) was dissolved in dry tetrahydrofuran (40 mL) under argon, and then a solution of lithium aluminum hydride (32.0 mmol, 12.8 mL, 2.5 M in THF) was added dropwise. The mixture was heated to reflux overnight and then cooled to room temperature. To the vigorously stirring mixture were added $H_2O$ (4 mL), 15% NaOH (4 mL), $H_2O$ (4 mL * 3) at 0 ℃. After being stirred at 0 ℃ for another 10 minutes, the mixture was filtered through celite, the white filter cake was washed with methanol and the filtrate was concentrated *in vacuum*. The crude was purified by silica column chromatography (elute: dichloromethane /methanol 10/1, with 1‰ $NH_4OH$) to afford the intermediate *N*-benzyl-3-(1*H*-indol-3-yl)propan-1-amine[S2] as a yellow oil. To the solution of *N*-benzyl-3-(1*H*-indol-3-yl)propan-1-amine (6.9 mmol,1.8 g) in dimethyl sulfoxide (20.7 mmol, 1.5 mL) and methanol (0.3 mL) was added concentrated hydrochloric acid (20.7 mmol, 1.7 mL) slowly at 0 ℃. The resulting mixture was stirred at 50 ℃ for 5 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (50 mL) and washed with $H_2O$ (50 mL). Aqueous phase was adjust to pH = 7 by ammonium hydroxide and extracted with ethyl acetate (50 mL * 2). The organic was dried over anhydrous sodium sulfate, evaporated and purified by silica column chromatography (elute: dichloromethane /methanol 10/1, with 1‰ $NH_4OH$) to afford the desired product 3-(3-(benzylamino)propyl)indolin-2-one **1a**[S3].



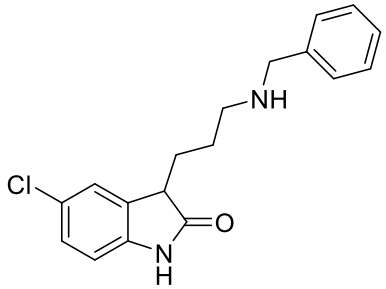

**1a**

**3-(3-(benzylamino)propyl)indolin-2-one 1a**. Yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.47 (br, 1H), 7.31 (s, 1H), 7.30 (s, 2H), 7.24-7.16 (m, 3H), 7.03-6.98 (t, *J* = 7.5, 1H), 6.86-6.84 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 2H), 3.49-3.45 (t, *J* = 6.0 Hz, 1H), 2.68-2.63 (m, 2H), 2.49 (br, 1H), 2.05-1.98 (dd, *J* = 14.1, 8.1 Hz, 2H), 1.66-1.53 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 178.7, 142.7, 136.2, 129.4, 129.0, 128.3, 127.7, 127.6, 124.0, 121.2, 109.2, 51.3, 47.3, 44.7, 27.2, 23.6. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3203, 3061, 2929, 2856, 1683, 1471, 751. HRMS (ESI): calcd for $C_{18}H_{21}ON_2^+$ $[M+H]^+$: 281.1648, found: 281.1647.



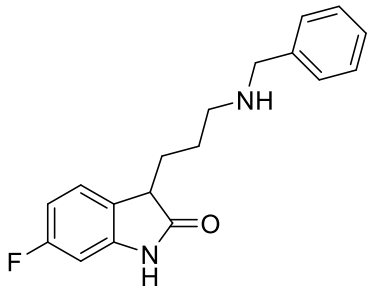

**1b**

**3-(3-(benzylamino)propyl)-4-bromoindolin-2-one 1b**. Pink solid, m. p. 83-85 °C. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.70 (s, 1H), 8.56 (bs, 1H), 7.43-7.38 (m, 6H), 7.16-7.14 (d, $J$ = 5.4 Hz, 2H), 6.86-6.84 (d, $J$ = 3.9 Hz, 1H), 4.01 (s, 2H), 3.60 (s, 1H), 2.84-2.79 (t, $J$ = 7.8 Hz, 2H), 2.21-2.18 (m, 1H), 2.02-1.98 (m, 1H), 1.42-1.37 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 177.3, 144.8, 133.0, 130.0, 129.8, 128.54, 128.49, 127.8, 124.6, 118.4, 108.7, 50.2, 46.5, 46.2, 24.6, 21.4. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3360, 2920, 2848, 1698, 1458, 1019, 699. HRMS (ESI): calcd for $C_{18}H_{20}ON_2Br^+$ $[M+H]^+$: 359.0754, found: 359.0750.




**1c**

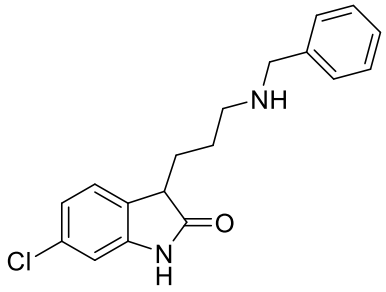
**3-(3-(benzylamino)propyl)-5-chloroindolin-2-one 1c**. Orange solid, m. p. 89-91 °C. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 10.59 (s, 1H), 8.81 (br, 1H), 7.51-7.48 (m, 2H), 7.39-7.36 (m, 4H), 7.24-7.21 (t, $J$ = 8.0 Hz, 1H), 6.85-6.82 (m,1H), 4.02 (s, 2H), 3.53-3.51 (t, $J$ = 5.5 Hz, 1H), 2.83-2.80 (m, 2H), 1.89-1.85 (m, 2H), 1.60-1.58 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 178.2, 141.7, 133.0, 131.5, 129.8, 128.6, 128.5, 127.5, 125.4, 124.3, 110.6, 50.3, 46.5, 44.8, 26.6, 22.2. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3446, 2920, 2849, 1702, 1478, 699. HRMS (ESI): calcd for $C_{18}H_{20}ON_2Cl^+$ $[M+H]^+$: 315.1259, found: 315.1257.




**1d**

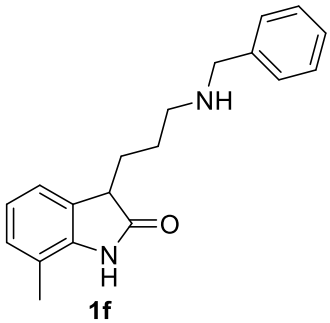
**3-(3-(benzylamino)propyl)-6-fluoroindolin-2-one 1d**. Pink solid, m. p. 81-83 °C. $^{1}$H NMR (500 MHz, DMSO-*d6*) δ 10.62 (s, 1H), 9.05 (br, 1H), 7.52-7.51 (m, 2H), 7.40 (m, 1H), 7.39-7.38 (m, 2H), 7.30-7.26 (m, 1H), 6.77-6.74 (m, 1H), 6.66-6.64 (m, 1H), 4.04 (s, 2H), 3.47-3.45 (t, $J$ = 5.5 Hz, 1H), 2.85-2.82 (t, $J$ = 6.5 Hz, 2H), 1.91-1.82 (m, 2H), 1.64-1.63 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 178.9, 163.0, 161.0, 144.3, 144.2, 132.5, 129.9, 128.7, 128.5, 125.33, 125.26, 125.02, 125.00, 107.3, 107.1, 97.5, 97.3, 50.1, 46.4, 44.0, 26.9, 22.0. $^{19}$F NMR (377 MHz, DMSO-*d6*) -

113.9(s). IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3359, 3195, 2920, 2849, 1702, 1469, 1340. HRMS (ESI): calcd for $C_{18}H_{20}ON_2F^+$ $[M+H]^+$: 299.1554, found: 299.1554.



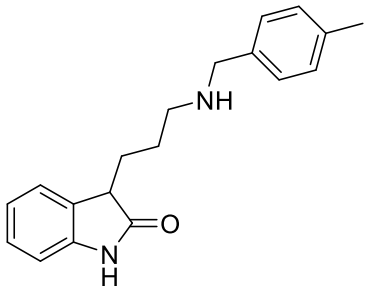

**1e**

**3-(3-(benzylamino)propyl)-6-chloroindolin-2-one 1e**. Orange solid, m. p. 89-91 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 10.64 (s, 1H), 9.07 (br, 1H), 7.53-7.50 (m, 2H), 7.43-7.38(m, 3H), 7.30-7.27 (m, 1H), 7.01-6.87 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.87-6.86 (d, *J* = 1.5 Hz, 1H), 4.04 (s, 2H), 3.50-3.47 (t, *J* = 5.7 Hz, 1H), 2.85-2.80 (t, *J* = 7.8 Hz, 2H), 1.91-1.81 (m, 2H), 1.65-1.63 (m, 2H). $^{13}$C NMR (75 MHz, DMSO) δ 178.4, 144.3, 132.5, 131.9, 129.8, 128.6, 128.5, 128.1, 125.5, 120.8, 109.3, 50.0, 46.3, 44.1, 26.7, 21.9. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3360, 3188, 2920, 2848, 1703, 1486, 749. HRMS (ESI): calcd for $C_{18}H_{20}ON_2Cl^+$ $[M+H]^+$: 315.1259, found: 315.1258.



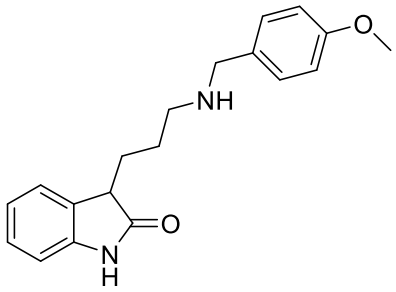

**1f**

**3-(3-(benzylamino)propyl)-7-methylindolin-2-one 1f**. White solid, m. p. 202-204 °C. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 10.45 (s, 1H), 9.00 (br, 1H), 7.51-7.48 (m, 2H), 7.45-7.40(m, 3H), 7.10-7.07 (d, *J* = 7.2 Hz, 1H), 7.01-6.98 (d, *J* = 7.8 Hz, 1H), 6.90-6.85 (t, *J* = 7.5 Hz, 1H), 4.07 (s, 2H), 3.49-3.48 (t, *J* = 5.4 Hz, 1H), 2.90-2.85 (m, 2H), 2.19 (s, 3H), 1.91-1.82 (m, 2H), 1.68-1.61 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 179.0, 141.3, 132.2, 129.9, 129.0, 128.81, 128.78, 128.6, 121.3, 118.5, 50.1, 46.5, 44.8, 26.8, 22.0, 16.5. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3392, 2946, 2838, 1702, 1458, 694. HRMS (ESI): calcd for $C_{19}H_{23}ON_2^+$ $[M+H]^+$: 295.1805, found: 295.1804.



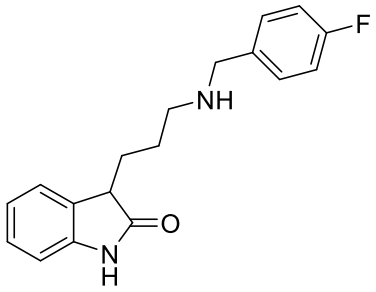

**1g**

**3-(3-((4-methylbenzyl)amino)propyl)indolin-2-one 1g**. Yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.04 (br, 1H), 7.22-7.10 (m, 6H), 7.03-6.98 (t, *J* = 7.2 Hz, 1H), 6.85-6.83 (m, 1H), 3.71 (s, 2H), 3.49-3.46 (t, *J* = 6.0 Hz, 1H), 2.65-2.60 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.02-1.97 (m, 2H), 1.72 (br, 1H), 1.64-1.52 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 180.2, 141.6, 136.9, 136.5, 129.5, 129.1, 128.1, 127.8, 124.1, 122.2, 109.6, 53.5, 48.9, 45.7, 28.1, 26.0, 21.1. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3204, 3022, 2923, 2857, 1706, 1620, 1486, 751. HRMS (ESI): calcd for $C_{19}H_{23}ON_2^+$ $[M+H]^+$: 295.1805, found: 295.1804.



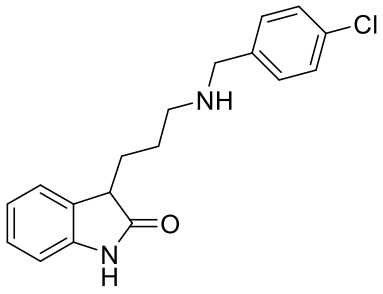

**1h**

**3-(3-((4-methoxybenzyl)amino)propyl)indolin-2-one 1h**. Yellow oil. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.34 (br, 1H), 7.23-7.13 (m, 4H), 6.96-6.91 (t, *J* = 7.5 Hz, 1H), 6.85-6.81 (m, 3H), 3.71 (s, 3H), 3.56 (s, 2H), 3.42-3.38 (t, *J* = 5.7 Hz, 1H), 2.97 (br, 1H), 2.46-2.41(t, *J* = 7.2 Hz, 2H), 1.89-1.79 (m, 2H), 1.43-1.37 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 178.9, 158.0, 142.8, 132.6, 129.7, 129.1, 127.5, 123.9, 121.2, 113.4, 109.1, 54.9, 52.2, 48.3, 45.0, 27.7, 25.5. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3197, 2933, 2835, 1698, 1471, 1177, 751. HRMS (ESI): calcd for $C_{19}H_{23}O_2N_2^+$ $[M+H]^+$: 311.1765, found: 311.1747.



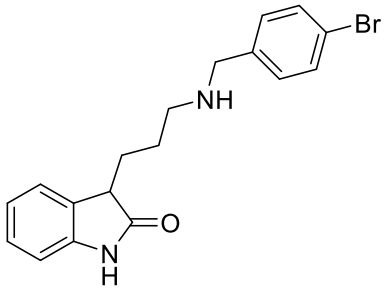

**1i**

**3-(3-((4-fluorobenzyl)amino)propyl)indolin-2-one 1i**. Yellow solid, m. p. 101-103 °C. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.42 (s, 1H), 8.86 (br, 1H), 7.57-7.52 (m, 2H), 7.28-7.15 (m, 4H), 6.98-6.93 (t, *J* = 7.5 Hz, 1H), 6.84-6.82 (d, *J* = 7.8 Hz, 1H), 4.05 (s, 2H), 3.50-3.48 (t, *J* = 5.7 Hz, 1H), 2.87-2.82 (t, *J* = 7.8 Hz, 2H), 1.89-1.82 (m, 2H), 1.67-1.59 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 178.5, 163.4, 161.0, 142.7, 132.3, 132.3, 129.2, 128.6, 127.6, 124.0, 121.2, 115.4, 115.2, 109.2, 49.1, 46.2, 44.5, 26.9, 22.0. $^{19}$F NMR (377 MHz, DMSO-$d_6$) δ -113.9(s). IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3361, 2920, 2849, 1703, 1471, 1226, 751. HRMS (ESI): calcd for $C_{18}H_{20}ON_2F^+$ $[M+H]^+$: 299.1554, found: 299.1553.



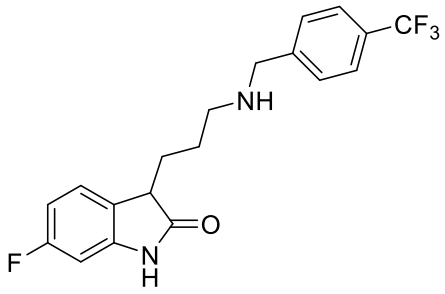

**1j**

**3-(3-((4-chlorobenzyl)amino)propyl)indolin-2-one 1j**. Yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.76 (br, 1H), 7.31-7.28 (m, 1H), 7.25-7.17(m, 5H), 7.03-6.98 (t, *J* = 7.5 Hz, 1H), 6.87-6.84 (d, *J* = 7.8 Hz, 1H), 3.72 (s, 2H), 3.49-3.45 (t, *J* = 5.7 Hz, 1H), 2.64-2.59 (t, *J* = 7.2 Hz, 2H), 2.24-2.19 (m, 1H), 2.04-1.97 (dd, *J* = 14.1, 7.8 Hz, 2H), 1.62-1.51 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 180.2, 141.6, 138.3, 132.7, 129.5, 129.4, 128.5, 127.9, 124.1, 122.3, 109.7, 53.0, 48.7, 45.7, 28.0, 25.9. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3200, 2932, 1714, 1471, 1015, 751. HRMS (ESI): calcd for $C_{18}H_{20}ON_2Cl^+$ $[M+H]^+$: 315.1259, found: 315.1256.




**1k**

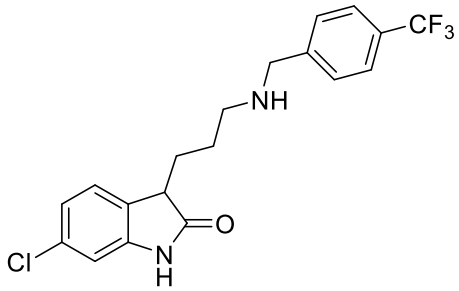
**3-(3-((4-bromobenzyl)amino)propyl)indolin-2-one 1k**. Yellow solid, m. p. 102-104 °C. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.41 (s, 1H), 8.33 (br, 1H), 7.60-7.58 (d, *J* = 8.1 Hz, 2H), 7.44-7.41 (d, *J* = 8.1 Hz, 2H), 7.27-7.24 (d, *J* = 7.2 Hz, 1H), 7.20-7.15 (t, *J* = 7.8 Hz, 1H), 6.97-6.92 (t, *J* = 7.5 Hz, 1H), 6.84-6.81 (d, *J* = 7.8 Hz, 1H), 3.96 (s, 2H), 3.48-3.44 (t, *J* = 5.7 Hz, 1H), 2.80-2.74 (t, *J* = 7.5 Hz, 2H), 1.91-1.80 (m, 2H), 1.64-1.55 (m, 2H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 178.6, 142.7, 131.8, 131.3, 129.3, 127.7, 124.0, 121.6, 121.2, 109.2, 49.8, 46.8, 44.7, 26.9, 22.7. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3366, 3197, 2922, 2850, 1702, 1622, 1471, 753. HRMS (ESI): calcd for $C_{18}H_{20}ON_2Br^+$ $[M+H]^+$: 359.0754, found: 359.0740.




**1l**

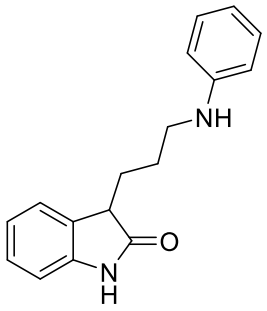
**6-fluoro-3-(3-((4-(trifluoromethyl)benzyl)amino)propyl)indolin-2-one 1l**. Orange oil. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.56 (br, 1H), 7.69-7.66 (d, *J* = 7.8 Hz, 2H), 7.58-7.55 (d, *J* = 7.8 Hz, 2H), 7.30-7.25 (m, 1H), 6.81-6.67 (m, 2H), 3.77 (s, 2H), 3.48-3.44 (t, *J* = 6.3Hz, 1H), 2.56 (s, 1H), 1.95-1.87 (m, 3H), 1.49-1.41 (m, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 179.3, 162.9, 161.0, 146.1, 144.3, 144.2, 129.5, 125.5, 125.13, 125.05, 124.8, 107.2, 107.0, 97.4, 97.2,

52.4, 48.5, 44.5, 27.7, 25.5. $^{19}$F NMR (377 MHz, DMSO-$d_6$) δ -60.86(s), -113.93 (s). IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3633, 2952, 2855, 1717, 1558, 1329, 1020, 849, 737. HRMS (ESI): calcd for $C_{19}H_{19}ON_2F_4^+$ $[M+H]^+$: 367.1428, found: 367.1422.



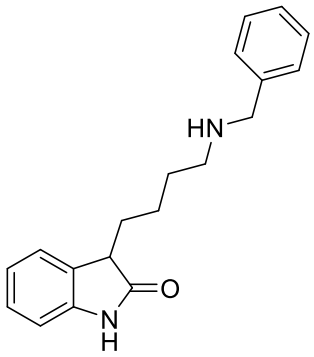

**1m**

**6-chloro-3-(3-((4-(trifluoromethyl)benzyl)amino)propyl)indolin-2-one 1m.** Orange oil. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 10.57 (br, 1H), 7.71-7.68 (d, $J$ = 7.8 Hz, 2H), 7.58-7.56 (d, $J$ = 7.8 Hz, 2H), 7.30-7.28 (m, 1H), 7.05-7.02 (m, 1H), 6.89 (s, 1H), 3.77 (s, 2H), 3.52-3.48 (t, $J$ = 5.7 Hz, 1H), 2.57 (s, 1H), 1.97-1.86 (m, 3H), 1.50-1.38 (m, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 178.9, 146.1, 144.3, 131.8, 128.6, 128.4, 125.3, 124.83, 124.80, 120.8, 109.2, 52.3, 48.5, 44.6, 27.5, 25.5. $^{19}$F NMR (377 MHz, DMSO-$d_6$) δ -60.79 (s). IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3419, 3181, 2952, 2800, 1704, 1619, 1326, 1127, 1068, 737. HRMS (ESI): calcd for $C_{19}H_{19}ON_2ClF_3^+$ $[M+H]^+$: 382.1133, found: 383.1126.



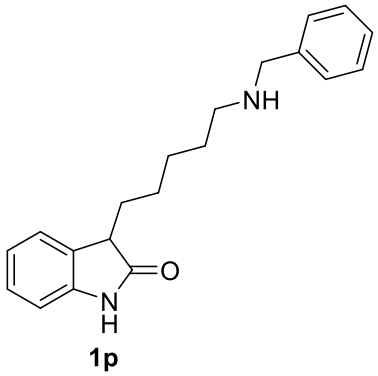

**1n**

**3-(3-(phenylamino)propyl)indolin-2-one 1n**. Pale yellow solid, m. p. 105-107 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.24-7.22 (m, 2H), 7.17-7.14 (t, $J$ = 7.5 Hz, 2H), 7.06-7.03 (t, $J$ = 7.5 Hz, 1H), 6.93-6.91 (d, $J$ = 8.5 Hz, 1H), 6.70-6.67 (m, 1H), 6.57-6.56 (d, $J$ = 8.5 Hz, 2H), 3.67 (br, 1H), 3.56-3.54 (t, $J$ = 5.5 Hz, 2H), 3.14-3.11 (t, $J$ = 7.0 Hz, 2H), 2.13-2.09 (m, 2H), 1.77-1.66 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 180.4, 148.2, 141.6, 129.3, 129.2, 128.0, 124.0, 122.4, 117.2, 112.7, 109.8, 45.7, 43.7, 27.9, 25.7. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3368, 3210, 2925, 2855, 1707, 1602, 1471, 749. HRMS (ESI): calcd for $C_{17}H_{19}ON_2^+$ $[M+H]^+$: 267.1492, found: 267.1494.




**1o**

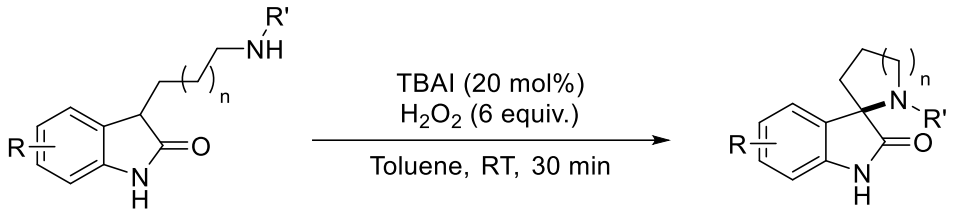
**3-(4-(benzylamino)butyl)indolin-2-one 1o**. Pale yellow solid, m. p. 172-173 ℃. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 10.41 (s, 1H), 8.66 (br, 1H), 7.52-7.50 (m, 2H), 7.38-7.36 (m, 3H), 7.26-7.24 (d, *J* = 7.5 Hz, 1H),7.19-7.14 (t, *J* = 7.5 Hz, 1H), 6.96-6.91 (t, *J* = 7.2 Hz, 1H), 6.84-6.82 (d, *J* = 7.5 Hz, 1H), 3.99 (s, 2H), 3.43-3.39 (m, 1H), 2.77- 2.71 (t, *J* = 7.5 Hz, 2H), 1.85-1.76 (m, 2H), 1.65-1.60 (m, 2H), 1.32-1.24 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 178.7, 142.7, 133.3, 129.7, 129.5, 128.42, 128.38, 127.5, 123.9, 121.1, 109.1, 50.2, 46.4, 44.9, 29.5, 25.8, 22.6. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3359, 2920, 2849, 1702, 1472, 751. HRMS (ESI): calcd for $C_{19}H_{23}ON_2^+$ [M+H]$^+$: 295.1805, found: 295.1802.




**1p**

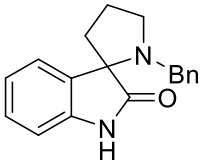
**3-(5-(benzylamino)pentyl)indolin-2-one 1p**. Yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.47 (br, 1H), 7.34-7.28 (m, 5H), 7.24-7.20 (m, 2H), 7.05-7.00 (m, 1H), 6.90-6.88 (d, *J* = 8.1 Hz, 1H), 3.80 (s, 2H), 3.49-3.45 (t, *J* = 6.0 Hz, 1H), 2.65-2.60 (t, *J* = 6.9 Hz, 2H), 2.22 (br, 1H), 2.00-1.95 (m, 2H), 1.55-1.48 (m, 2H), 1.45-1.36 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 180.2, 141.5, 139.7, 129.7, 128.4, 128.2, 127.8, 127.0, 124.1, 122.2, 109.6, 53.8, 49.0, 45.9, 30.4, 29.5, 27.2, 25.5. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3197, 3061, 2830, 2856, 1683, 1506, 1471, 749. HRMS (ESI): calcd for $C_{20}H_{25}ON_2^+$ [M+H]$^+$: 309.1961, found: 309.1959.

**3. General procedure for synthesis of 2**



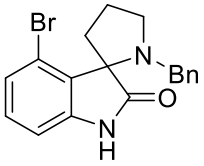

**1a-n** **2a-n**

To the mixture of oxindole **1** (0.10 mmol) and TBAI (20 mol%) in toluene (0.5 mL) was added 35% $H_2O_2$ (6 equiv.), the reaction mixture was stirred at room temperature until completion the reaction. After that time, the mixture was quenched by saturated sodium thiosulfate solution (1 mL) and diluted with dichloromethane (10 mL). The organic layer was washed by water (10 mL * 2), dried over anhydrous sodium sulfate and evaporated to afford the crude product. The crude was purified by silica column chromatography (elute: petroleum ether/ethyl acetate 2/1) to give the pure desired products **2**.



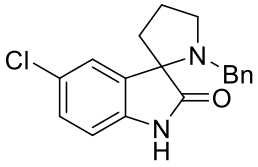

**2a**

**1'-benzylspiro[indoline-3,2'-pyrrolidin]-2-one 2a**. White solid, 21.9 mg (from 0.10 mmol), 79% yield, m. p. 154-156 ℃. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 10.28 (s, 1H), 7.35-7.33 (d, $J$ = 7.5 Hz, 1H), 7.26-7.22 (m, 2H), 7.20-7.18 (m, 4H), 7.03-7.00 (t, $J$ = 7.5 Hz, 1H), 6.80-6.79 (d, $J$ = 7.5 Hz, 1H), 3.31-3.25 (m, 2H), 2.98-2.91 (m, 2H), 2.14-2.06 (m, 2H), 2.04-1.98 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 179.7, 142.4, 139.3, 130.7, 128.7, 128.1, 127.9, 126.8, 123.8, 121.9, 109.4, 70.8, 53.1, 50.4, 35.8, 21.7. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3207, 3061, 3028, 2925, 2852, 1706, 1620, 1470, 749. HRMS (ESI): calcd for $C_{18}H_{17}ON_2^-$ [M-H]$^-$: 277.1364, found: 277.1364.



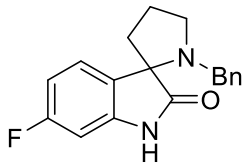

**2b**

**1'-benzyl-4-bromospiro[indoline-3,2'-pyrrolidin]-2-one 2b**. White solid, 17.6 mg (from 0.10 mmol), 49% yield, m. p. 169-171 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.32-7.31 (d, $J$ = 7.5 Hz, 2H), 7.26-7.15 (m, 4H), 7.08-7.05 (m, 1H), 6.81-6.80 (dd, $J$ = 7.5, 1.0 Hz, 1H), 3.59-3.49 (m, 2H), 3.17-3.10 (m, 2H), 2.68-2.63 (m, 1H), 2.25- 2.18 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.3, 143.2, 139.5, 130.1, 128.7, 128.5, 128.0, 127.4, 126.8, 119.9, 108.9, 72.5, 53.4, 51.1, 32.8, 23.1. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3213, 3086, 3027, 2964, 2831, 1717, 1613, 1447, 736. HRMS (ESI): calcd for $C_{18}H_{18}ON_2Br^+$ [M+H]$^+$: 357.0597, found: 354.0594.



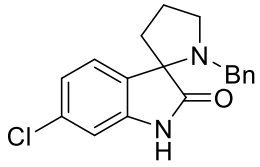

**2c**

**1'-benzyl-5-chlorospiro[indoline-3,2'-pyrrolidin]-2-one 2c**.White solid, 14.3 mg (from 0.10 mmol), 46% yield, m. p. 149-151 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.34 (s, 1H), 7.25-7.19 (m, 6H), 6.79-6.78 (d, *J* = 8.0 Hz, 1H), 3.52-3.45 (m, 2H), 3.18-3.13 (m, 1H), 3.10-3.07 (m, 1H), 2.35-2.31 (m, 1H), 2.24-2.21 (m, 1H), 2.17-2.08 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.2, 139.5, 138.9, 133.4, 128.6, 128.5, 128.2, 128.1, 127.0, 124.6, 110.8, 71.7, 53.9, 51.4, 37.0, 22.3. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3213, 3063, 3029, 2963, 2840, 1717, 1619, 1475, 733. HRMS (ESI): calcd for $C_{18}H_{18}ON_2Br^+$ $[M+H]^+$: 313.1102, found: 313.1102.



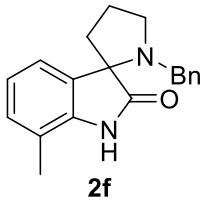

**2d**

**1'-benzyl-6-fluorospiro[indoline-3,2'-pyrrolidin]-2-one 2d**.White solid, 15.3 mg (from 0.10 mmol), 52% yield, m. p. 141-143 ℃. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.33-7.29 (m, 1H), 7.23-7.15 (m, 5H), 6.81-6.74 (m, 1H), 6.65-6.62 (dd, *J* = 14.5, 2.1 Hz, 1H), 3.52-3.41 (m, 2H), 3.22-3.06 (m, 2H), 2.35-2.04 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.1, 164.1, 162.2, 142.5, 142.4, 139.0, 128.5, 128.1, 126.9, 126.7, 126.6, 125.3, 125.2, 109.2, 109.0, 98.7, 98.4, 71.2, 53.8, 51.2, 36.7, 22.1. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -111.7 (s). IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3226, 3063, 3029, 2965, 2836, 1717, 1622, 1456, 733. HRMS (ESI): calcd for $C_{18}H_{18}ON_2F^+$ $[M+H]^+$: 297.1398, found: 297.1400.



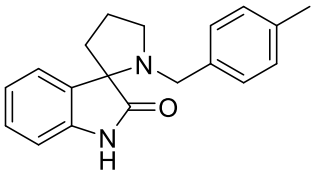

**2e**

**1'-benzyl-6-chlorospiro[indoline-3,2'-pyrrolidin]-2-one 2e**.White solid, 19.0 mg (from 0.10 mmol), 61% yield, m. p. 170-172 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.30-7.28 (m, 1H), 7.25-7.21 (m, 2H), 7.20-7.18 (m, 3H), 7.08-7.05 (m, 1H), 6.89 (s, 1H), 3.50-3.42 (m, 2H), 3.19-3.14 (m, 1H), 3.10-3.06 (m, 1H), 2.35-2.29 (m, 1H), 2.27-2.22 (m, 1H), 2.17-2.07 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.6, 142.2, 139.0, 134.3, 129.8, 128.5, 128.1, 127.0, 125.2, 122.8, 110.5, 71.3, 53.9, 51.2, 36.7, 22.2. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3232, 3064, 3029, 2965, 2834, 1717, 1615, 1455, 732. HRMS (ESI): calcd for $C_{18}H_{18}ON_2Cl^+$ $[M+H]^+$: 313.1102, found: 313.1101.



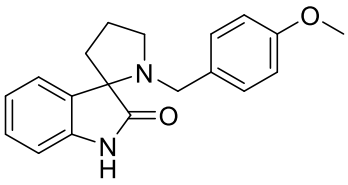

**2f**

**1'-benzyl-7-methylspiro[indoline-3,2'-pyrrolidin]-2-one 2f**.White solid, 20.5 mg (from 0.10 mmol), 70% yield, m. p. 148-150 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.23-7.16 (m, 6H), 7.07-7.05 (m, 1H), 7.03-7.00 (m, 1H), 3.51-3.42 (m, 2H), 3.20-3.15 (m, 1H), 3.10-3.06 (m, 1H), 2.35-2.31 (m, 1H), 2.29 (s, 3H), 2.27-2.21 (m, 1H), 2.19-2.14 (m, 1H), 2.11-2.08 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.0, 139.9, 139.4, 130.9, 130.0, 128.5, 128.0, 126.8, 122.7, 121.5, 119.0, 72.0, 54.0, 51.2, 36.7, 22.2, 16.2. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3280, 3061, 3028, 2964, 2837, 1704, 1627, 1458, 732. HRMS (ESI): calcd for $C_{19}H_{21}ON_2^+$ $[M+H]^+$: 293.1648, found: 293.1648.



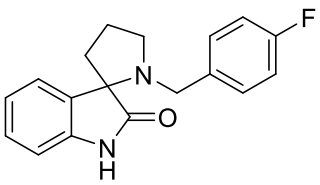
**2g**

**1'-(4-methylbenzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2g**.White solid, 22.7 mg (from 0.10 mmol), 79% yield, m. p. 96-98 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.37-7.36 (d, *J* = 7.0 Hz, 1H), 7.23-7.20 (t, *J* = 8.0 Hz, 1H), 7.09-7.06 (m, 3H), 7.03-7.01 (m, 2H), 6.89-6.87 (d, *J* = 8.0 Hz, 1H), 3.45-3.38 (m, 2H), 3.20-3.15 (m, 1H), 3.09 -3.05 (m, 1H), 2.35-2.30 (m, 1H), 2.26 (s, 3H), 2.22-2.04 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.0, 141.3, 136.3, 136.2, 131.4, 128.7, 128.6, 128.4, 124.1, 122.7, 109.9, 71.7, 53.5, 51.1, 36.6, 22.2, 21.0. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3215, 3025, 2971, 2830, 1706, 1620, 1471, 750. HRMS (ESI): calcd for $C_{19}H_{21}ON_2^+$ $[M+H]^+$: 293.1648, found: 293.1647.



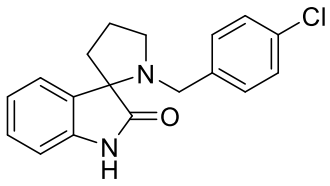
**2h**

**1'-(4-methoxybenzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2h**.White solid, 17.1 mg (from 0.10 mmol), 56% yield, m. p. 135-137 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.37-7.36 (d, *J* = 7.0 Hz, 1H), 7.24-7.21 (t, *J* = 7.5 Hz, 1H), 7.10-7.07 (m, 3H), 6.87-6.85 (d, *J* = 8.0 Hz, 1H), 6.77-6.75 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 3.44-3.36 (m, 2H), 3.20-3.15 (m, 1H), 3.09-3.05 (m, 1H), 2.35-2.30 (m, 1H), 2.24-2.21 (m, 1H), 2.18-2.07 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.6, 158.5, 141.2, 131.5, 131.4, 129.7, 128.6, 124.2, 122.7, 113.4, 109.8, 71.5, 55.1, 53.3, 51.2, 36.7, 22.2. IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3251, 2962, 2834, 1700, 1622, 1471, 751. HRMS (ESI): calcd for $C_{19}H_{19}ON_2^-$ $[M-H]^-$: 307.1452, found: 307.1454.



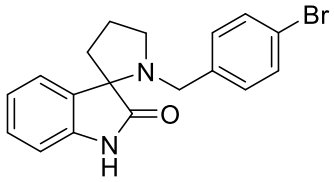
**2i**

**1'-(4-fluorobenzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2i**.White solid, 10.9 mg (from 0.10 mmol), 37% yield, m. p. 126-127 ℃. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.36-7.35 (d, *J* = 7.0 Hz, 1H), 7.24-7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.16-7.13 (m, 2H), 7.10-7.07 (t, *J* = 7.5 Hz, 1H), 6.92-6.88 (m, 2H), 6.84-6.82 (d, *J* = 7.5 Hz, 1H), 3.46-3.39 (m, 2H), 3.17-3.13 (m, 1H), 3.07-3.03 (m, 1H), 2.35-2.30 (m, 1H), 2.28-2.20 (m, 1H), 2.18-2.13 (m, 1H), 2.11-2.06 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.6, 162.8, 160.9, 141.1, 134.9, 131.3, 130.1, 130.0, 128.7, 124.1, 122.8, 114.8, 114.7, 109.9, 71.5, 53.2, 51.3, 36.7, 22.2. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -116.1 (s). IR $\nu_{max}$ (KBr, film, $cm^{-1}$): 3213, 3086, 2964, 2836, 1717, 1622, 1471, 750. HRMS (ESI): calcd for $C_{18}H_{18}ON_2F^+$ $[M+H]^+$: 297.1398, found: 297.1395.



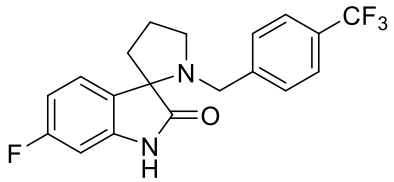

**2j**

**1'-(4-chlorobenzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2j**. White solid, 23.3 mg (from 0.10 mmol), 74% yield, m. p. 140-142 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.36-7.34 (d, *J* = 7.5 Hz, 1H), 7.25-7.21 (m, 1H), 7.19-7.18 (m, 2H), 7.13-7.12 (m, 2H), 7.10-7.07 (td, *J* = 7.5, 0.5 Hz, 1H), 6.88-6.86 (d, *J* = 7.5 Hz, 1H), 3.46-3.39 (m, 2H), 3.17-3.13 (m, 1H), 3.07-3.04 (m, 1H), 2.36-2.31 (m, 1H), 2.28-2.21 (m, 1H), 2.19-2.13 (m, 1H), 2.12-2.04 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.5, 141.1, 137.8, 132.5, 131.2, 129.8, 128.7, 128.1, 124.1, 122.7, 109.9, 71.5, 53.2, 51.3, 36.7, 22.2. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3212, 2925, 2849, 1705, 1622, 1471, 750. HRMS (ESI): calcd for $C_{18}H_{18}ON_2Cl^+$ $[M+H]^+$: 313.1102, found: 313.1099.



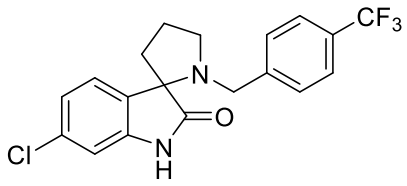

**2k**

**1'-(4-bromobenzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2k**. White solid, 19.6 mg (from 0.10 mmol), 55% yield, m. p. 140-142 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.35-7.33 (m, 3H), 7.24-7.21 (t, *J* = 7.5 Hz, 1H), 7.09-7.07 (m, 3H), 6.86-6.85 (d, *J* = 8.0 Hz, 1H), 3.43-3.38 (m, 2H), 3.17-3.12 (q, *J* = 7.5 Hz, 1H), 3.07-3.03 (m, 1H), 2.35-2.30 (m, 1H), 2.28-2.20 (m, 1H), 2.19-2.13 (m, 1H), 2.12-2.08 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.3, 141.1, 138.3, 131.2, 131.1, 130.2, 128.7, 124.2, 122.9, 120.6, 109.8, 71.5, 53.3, 51.3, 36.7, 22.3. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3216, 3090, 2925, 2851, 1706, 1621, 1470, 750. HRMS (ESI): calcd for $C_{18}H_{18}ON_2Br^+$ $[M+H]^+$: 357.0597, found: 357.0594.



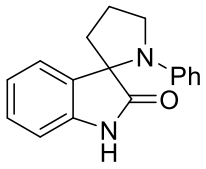

**2l**

**6-fluoro-1'-(4-(trifluoromethyl)benzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2l**. Syrup, 20.5 mg (from 0.10 mmol), 56% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.84 (br, 1H), 7.50-7.47 (d, J = 7.8 Hz, 2H), 7.33-7.27 (m, 3H), 6.79-6.74 (m, 1H), 6.65-6.62 (mz, 1H), 3.51 (s, 2H), 3.19-3.04 (m, 2H), 2.35-2.10 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.9, 164.2, 162.23, 143.2, 142.5, 142.4, 129.4, 129.1, 128.8, 128.6, 126.38, 126.36, 125.5, 125.3, 125.2, 125.1, 125.03, 125.00, 124.97, 109.4, 109.2, 98.7, 98.5, 713, 53.4, 51.3, 36.7, 22.2. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -62.4 (s), -111.3 (s). IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3235, 2964, 2842, 1717, 1619, 1458, 1326, 1125, 1067, 1019, 810. HRMS (ESI): calcd for $C_{19}H_{17}ON_2F_4^+$ $[M+H]^+$: 365.1272, found: 365.1266.



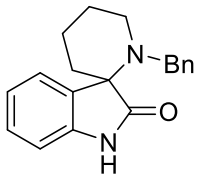
**2m**

**6-chloro-1'-(4-(trifluoromethyl)benzyl)spiro[indoline-3,2'-pyrrolidin]-2-one 2m**. Syrup, 19.7 mg (from 0.10 mmol), 52% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.75 (br, 1H), 7.51-7.47 (m, 2H), 7.33-7.27 (m, 3H), 7.09-7.06 (m, 1H), 6.91-6.90 (m, 1H), 3.51 (s, 2H), 3.17-3.07 (m, 2H), 2.33-2.13 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.5, 143.2, 142.2, 134.5, 129.5, 128.6, 125.09, 125.05, 125.0, 123.0, 110.6, 71.3, 53.5, 51.3, 36.7, 22.3. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -62.4 (s). IR $\nu_{max}$ (KBr, film, cm$^{-1}$):3232, 2963, 2938, 1713, 1616, 1486, 1325, 1124, 1066, 812. HRMS (ESI): calcd for $C_{19}H_{17}ON_2ClF_3^+$ $[M+H]^+$: 381.0976, found: 381.0971.



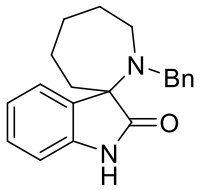
**2n**

**1'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one 2n**. White solid, 19.0 mg (from 0.10 mmol), 72% yield, m. p. 140-142 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.22-7.18 (td, *J* = 7.6, 0.8 Hz, 1H), 7.13-7.11 (d, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 2H), 7.00-6.96 (m, 1H), 6.89-6.86 (d, *J* = 8.0 Hz, 1H), 6.63-6.59 (t, *J* = 7.2 Hz, 1H), 6.28-6.26 (d, *J* = 8.0 Hz, 2H), 3.85-3.82 (m, 2H), 2.57-2.52 (m, 1H), 2.46-2.37 (m, 1H), 2.33-2.18 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 181.5, 145.3, 139.2, 132.1, 129.0, 128.6, 123.02, 122.99, 117.0, 112.7, 110.8, 69.7, 50.5, 41.8, 23.0. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3202, 3092, 3059, 2922, 2851, 1717, 1505, 1469, 746. HRMS (ESI): calcd for $C_{17}H_{15}ON_2^-$ $[M-H]^-$: 263.1190, found: 263.1191.



**2o**

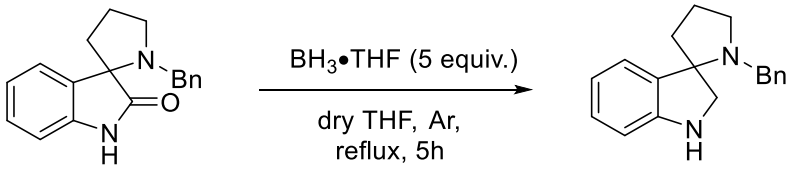
**1'-benzylspiro[indoline-3,2'-piperidin]-2-one 2o**. White solid, 9.8 mg (from 0.10 mmol), 34% yield, m. p. 167-169 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.50 (br, 1H), 7.48-7.46 (d, *J* = 7.5 Hz, 1H), 7.26-7.25 (m, 4H), 7.23-7.18 (m, 2H), 7.09-7.06 (t, *J* = 7.5 Hz, 1H), 6.83-6.82 (d, *J* = 7.5 Hz, 1H), 3.38-3.36 (d, *J* = 13.0 Hz, 1H), 3.20-3.19 (d, *J* = 13.0 Hz, 1H), 3.16-3.11 (m, 1H), 2.71-2.67 (m, 1H), 2.11-2.04 (m, 1H), 1.96-1.88 (m, 2H), 1.76-1.72 (m, 1H), 1.69-1.62 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 180.7, 140.2, 139.4, 133.1, 128.5, 128.4, 128.0, 126.8, 124.1, 122.7, 109.7, 66.3, 56.3, 46.1, 35.3, 25.6, 19.1. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3210, 3061, 3028, 2929, 2851, 1702, 1619, 1472, 754. HRMS (ESI): calcd for $C_{19}H_{19}ON_2^-$ $[M-H]^-$: 291.1503, found: 291.1504.




**2p**

**1-benzylspiro[azepane-2,3'-indolin]-2'-one 2p**. White solid, 4.7 mg (from 0.10 mmol), 15% yield, m. p. 177-179 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.62-7.61 (d, *J* = 7.5 Hz, 1H), 7.32-7.30 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.24-7.17 (m, 2H), 7.08-7.05 (t, *J* = 7.5 Hz, 1H), 6.85-6.83 (d, *J* = 7.5 Hz, 1H), 3.55-3.50 (dd, *J* = 15.0, 10.5 Hz, 1H), 3.44-3.42 (d, *J* = 13.5 Hz, 1H), 3.24-3.21 (d, *J* = 13.0 Hz, 1H), 2.68-2.64 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.19-2.05 (m, 2H), 1.92-1.84 (m, 3H), 1.60 (m, 1H) 1.47-1.40 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.4, 140.3, 139.8, 134.8, 128.5, 128.2, 128.0, 126.8, 124.0, 122.7, 109.7, 69.6, 56.5, 47.2, 38.3, 32.4, 30.1, 22.7. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3207, 3028, 2925, 2853, 1704, 1651, 1469, 747. HRMS (ESI): calcd for $C_{20}H_{23}ON_2^+$ $[M+H]^+$: 307.1805, found: 307.1808.

**4. Reduction of 2a**

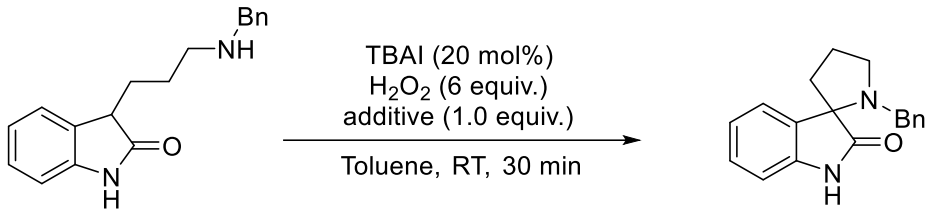



**2a** **3**

1'-benzylspiro[indoline-3,2'-pyrrolidin]-2-one **2a** (0.5 mmol, 139.0 mg) was dissolved in dry THF (10 mL), $B_2H_6$ (2.5 mmol, 2.5 mL, 1M in THF) was added slowly under the Ar. The mixture was heated to reflux for 5 hours. And then to the vigorously stirring mixture were added methanol (5 ml) at 0 ℃. After being stirred at 0 ℃ 10 minutes, the mixture was warmed to room temperature and reflux for another 30 minutes. After this time, the solvent was removed under vacuum and residue was purified by silica column chromatography (elute: dichloromethane /methanol 10/1, with 1‰ $NH_4OH$) to afford the desired product 1'-benzylspiro[indoline-3,2'-pyrrolidine] **3** as an orange solid.

**1'-benzylspiro[indoline-3,2'-pyrrolidine] 3**. Orange solid, 70.0 mg (from 0.50 mmol), 53% yield, m. p. 79-81 ℃. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.59-7.58 (d, *J* = 7.5 Hz, 1H), 7.31-7.30 (m, 4H), 7.25-7.23 (m, 1H), 7.18-7.15 (t, *J* = 7.5 Hz, 1H), 7.11-7.09 (t, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 3.77 (s, 2H), 2.81-2.78 (t, *J* = 7.5 Hz, 4H), 2.73 (m, 2H), 2.06 (s, 1H), 1.95-1.92 (t, *J* = 7.5 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.2, 136.3, 128.4, 128.2, 127.4, 126.9, 121.8, 121.2, 119.0, 118.8, 116.1, 111.0, 62.5, 53.9, 49.1, 30.2, 30.0, 22.8. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 3414, 3241, 3057, 2926, 2849, 1456, 1098, 741, 697. HRMS (ESI): calcd for $C_{18}H_{21}N_2^+$ $[M+H]^+$: 265.1699, found: 265.1695.

**5. Control experiment**




**1a** **2a**

| entry | additive | yield |
|---|---|---|
| 1 | TEMOP | 52% |
| 2 | BHT | 72% |
| 3 | HQ | 51% |

3-(3-(benzylamino)propyl)indolin-2-one **1a** (0.10 mmol, 28.0 mg), TBAI (0.02 mmol, 7.4 mg) and additive (0.1 mmol) was dissolved in toluene (0.5 mL). 35% of $H_2O_2$ (0.6 mmol, 52.0 μL) was added and the reaction mixture was stirred at room temperature for 0.5 h. After that time, the mixture was quenched by saturated sodium thiosulfate solution (1 mL) and diluted with dichloromethane (10 mL). The organic layer was washed by water (10 mL * 2), dried over anhydrous sodium sulfate and evaporated to afford the crude product. The crude was purified by silica column chromatography (elute: petroleum ether/ethyl acetate 2/1) to give the pure products **2a**.

## 6. X-ray crystallographic data

### X-ray crystallography of compound 2k (CCDC 1847718)

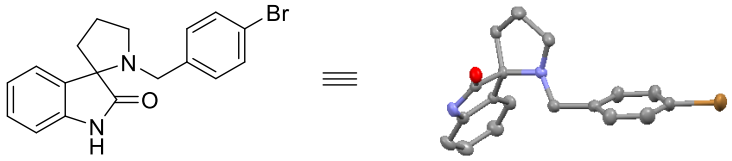



Table 1. Crystal data and structure refinement for mx6777.

| | | |
|---|---|---|
| Identification code | mx6777 | |
| Empirical formula | C18 H17 Br N2 O | |
| Formula weight | 357.24 | |
| Temperature | 173.15 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 9.7607(14) Å | α= 90°. |
| | b = 17.628(3) Å | β= 90.749(3)°. |
| | c = 18.635(4) Å | γ = 90°. |

| | |
|---|---|
| Volume | 3206.1(10) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.480 $Mg/m^3$ |
| Absorption coefficient | 2.567 $mm^{-1}$ |
| F(000) | 1456 |
| Crystal size | 0.224 x 0.172 x 0.131 $mm^3$ |
| Theta range for data collection | 1.590 to 27.507°. |
| Index ranges | -12<=h<=12, -22<=k<=22, -24<=l<=24 |
| Reflections collected | 23623 |
| Independent reflections | 7302 [R(int) = 0.0895] |
| Completeness to theta = 25.242° | 99.4 % |
| Absorption correction | None |
| Max. and min. transmission | 1.0000 and 0.7611 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7302 / 0 / 397 |
| Goodness-of-fit on $F^2$ | 1.123 |
| Final R indices [I>2sigma(I)] | R1 = 0.0737, wR2 = 0.1523 |
| R indices (all data) | R1 = 0.0920, wR2 = 0.1642 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.427 and -0.918 $e.Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for mx6777. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br1 | 5295(1) | 10162(1) | 6385(1) | 49(1) |
| N1 | 1974(3) | 6772(2) | 6451(2) | 25(1) |
| O1 | 1417(3) | 5564(2) | 5288(1) | 26(1) |
| C1 | 1101(4) | 6111(2) | 6502(2) | 22(1) |
| N2 | -703(3) | 5576(2) | 5810(2) | 26(1) |
| C2 | 658(4) | 5727(2) | 5787(2) | 21(1) |
| C3 | -1294(4) | 5879(2) | 6432(2) | 23(1) |
| C4 | -2649(4) | 5853(2) | 6647(2) | 29(1) |
| C5 | -2966(4) | 6204(2) | 7290(2) | 32(1) |
| C6 | -1963(4) | 6569(2) | 7704(2) | 27(1) |
| C7 | -616(4) | 6583(2) | 7478(2) | 24(1) |
| C8 | -276(4) | 6235(2) | 6842(2) | 21(1) |
| C9 | 3404(4) | 6520(2) | 6352(2) | 32(1) |
| C10 | 3435(4) | 5689(2) | 6595(2) | 31(1) |
| C11 | 2025(4) | 5551(2) | 6919(2) | 24(1) |
| C12 | 1523(4) | 7374(2) | 5971(2) | 30(1) |
| C13 | 2385(4) | 8076(2) | 6066(2) | 28(1) |
| C14 | 2887(5) | 8469(2) | 5487(2) | 34(1) |
| C15 | 3743(5) | 9097(3) | 5580(2) | 39(1) |
| C16 | 4082(5) | 9332(2) | 6262(2) | 32(1) |
| C17 | 3575(6) | 8962(3) | 6850(2) | 44(1) |
| C18 | 2714(6) | 8336(3) | 6755(2) | 44(1) |
| Br1A | -74(1) | -88(1) | 3548(1) | 56(1) |
| C1A | 3969(4) | 3266(2) | 5857(2) | 21(1) |
| O1A | 3564(3) | 4384(2) | 5069(1) | 28(1) |
| N1A | 3084(3) | 2720(2) | 5490(2) | 24(1) |
| C2A | 4359(4) | 3982(2) | 5413(2) | 24(1) |

| | | | | |
|---|---|---|---|---|
| N2A | 5735(3) | 4088(2) | 5482(2) | 25(1) |
| C3A | 6356(4) | 3480(2) | 5850(2) | 22(1) |
| C4A | 7733(4) | 3354(3) | 5982(2) | 32(1) |
| C5A | 8092(4) | 2676(3) | 6323(2) | 35(1) |
| C6A | 7103(5) | 2151(3) | 6528(2) | 36(1) |
| C7A | 5719(4) | 2301(2) | 6403(2) | 27(1) |
| C8A | 5361(4) | 2965(2) | 6058(2) | 21(1) |
| C9A | 1660(4) | 2993(2) | 5527(2) | 30(1) |
| C10A | 1641(4) | 3535(3) | 6167(2) | 37(1) |
| C11A | 3076(4) | 3513(2) | 6490(2) | 27(1) |
| C12A | 3533(4) | 2500(2) | 4775(2) | 27(1) |
| C13A | 2683(4) | 1859(2) | 4472(2) | 27(1) |
| C14A | 2184(5) | 1890(3) | 3775(2) | 35(1) |
| C15A | 1365(5) | 1308(3) | 3499(2) | 41(1) |
| C16A | 1062(5) | 701(3) | 3925(2) | 37(1) |
| C17A | 1553(5) | 646(3) | 4616(2) | 40(1) |
| C18A | 2369(5) | 1223(2) | 4889(2) | 36(1) |

Table 3. Bond lengths [Å] and angles [°] for mx6777.

| | |
|---|---|
| Br1-C16 | 1.894(4) |
| N1-C1 | 1.448(5) |
| N1-C9 | 1.478(5) |
| N1-C12 | 1.453(5) |
| O1-C2 | 1.231(4) |
| C1-C2 | 1.551(5) |
| C1-C8 | 1.509(5) |
| C1-C11 | 1.540(5) |
| N2-H2 | 0.8800 |
| N2-C2 | 1.355(5) |
| N2-C3 | 1.408(5) |
| C3-C4 | 1.387(5) |
| C3-C8 | 1.394(5) |
| C4-H4 | 0.9500 |
| C4-C5 | 1.388(6) |
| C5-H5 | 0.9500 |
| C5-C6 | 1.396(6) |
| C6-H6 | 0.9500 |
| C6-C7 | 1.386(6) |
| C7-H7 | 0.9500 |
| C7-C8 | 1.380(5) |
| C9-H9A | 0.9900 |
| C9-H9B | 0.9900 |
| C9-C10 | 1.534(6) |
| C10-H10A | 0.9900 |
| C10-H10B | 0.9900 |
| C10-C11 | 1.529(6) |
| C11-H11A | 0.9900 |
| C11-H11B | 0.9900 |
| C12-H12A | 0.9900 |

| | |
|---|---|
| C12-H12B | 0.9900 |
| C12-C13 | 1.505(6) |
| C13-C14 | 1.379(6) |
| C13-C18 | 1.395(6) |
| C14-H14 | 0.9500 |
| C14-C15 | 1.397(6) |
| C15-H15 | 0.9500 |
| C15-C16 | 1.372(6) |
| C16-C17 | 1.373(6) |
| C17-H17 | 0.9500 |
| C17-C18 | 1.397(6) |
| C18-H18 | 0.9500 |
| Br1A-C16A | 1.907(4) |
| C1A-N1A | 1.457(5) |
| C1A-C2A | 1.559(5) |
| C1A-C8A | 1.502(5) |
| C1A-C11A | 1.539(5) |
| O1A-C2A | 1.226(4) |
| N1A-C9A | 1.473(5) |
| N1A-C12A | 1.461(5) |
| C2A-N2A | 1.360(5) |
| N2A-H2A | 0.8800 |
| N2A-C3A | 1.406(5) |
| C3A-C4A | 1.381(5) |
| C3A-C8A | 1.388(5) |
| C4A-H4A | 0.9500 |
| C4A-C5A | 1.398(6) |
| C5A-H5A | 0.9500 |
| C5A-C6A | 1.394(6) |
| C6A-H6A | 0.9500 |
| C6A-C7A | 1.393(6) |
| C7A-H7A | 0.9500 |

| | |
|---|---|
| C7A-C8A | 1.378(5) |
| C9A-H9AA | 0.9900 |
| C9A-H9AB | 0.9900 |
| C9A-C10A | 1.529(6) |
| C10A-H10C | 0.9900 |
| C10A-H10D | 0.9900 |
| C10A-C11A | 1.517(6) |
| C11A-H11C | 0.9900 |
| C11A-H11D | 0.9900 |
| C12A-H12C | 0.9900 |
| C12A-H12D | 0.9900 |
| C12A-C13A | 1.507(5) |
| C13A-C14A | 1.384(6) |
| C13A-C18A | 1.399(6) |
| C14A-H14A | 0.9500 |
| C14A-C15A | 1.394(6) |
| C15A-H15A | 0.9500 |
| C15A-C16A | 1.367(7) |
| C16A-C17A | 1.373(6) |
| C17A-H17A | 0.9500 |
| C17A-C18A | 1.384(6) |
| C18A-H18A | 0.9500 |

| | |
|---|---|
| C1-N1-C9 | 108.9(3) |
| C1-N1-C12 | 117.0(3) |
| C12-N1-C9 | 115.0(3) |
| N1-C1-C2 | 117.0(3) |
| N1-C1-C8 | 116.0(3) |
| N1-C1-C11 | 101.9(3) |
| C8-C1-C2 | 100.6(3) |
| C8-C1-C11 | 113.6(3) |
| C11-C1-C2 | 107.9(3) |

| | |
|---|---|
| C2-N2-H2 | 124.3 |
| C2-N2-C3 | 111.4(3) |
| C3-N2-H2 | 124.3 |
| O1-C2-C1 | 125.9(3) |
| O1-C2-N2 | 125.3(3) |
| N2-C2-C1 | 108.7(3) |
| C4-C3-N2 | 128.8(3) |
| C4-C3-C8 | 122.2(3) |
| C8-C3-N2 | 108.9(3) |
| C3-C4-H4 | 121.4 |
| C3-C4-C5 | 117.3(4) |
| C5-C4-H4 | 121.4 |
| C4-C5-H5 | 119.3 |
| C4-C5-C6 | 121.4(4) |
| C6-C5-H5 | 119.3 |
| C5-C6-H6 | 119.9 |
| C7-C6-C5 | 120.1(4) |
| C7-C6-H6 | 119.9 |
| C6-C7-H7 | 120.2 |
| C8-C7-C6 | 119.5(3) |
| C8-C7-H7 | 120.2 |
| C3-C8-C1 | 109.7(3) |
| C7-C8-C1 | 130.6(3) |
| C7-C8-C3 | 119.5(4) |
| N1-C9-H9A | 110.7 |
| N1-C9-H9B | 110.7 |
| N1-C9-C10 | 105.4(3) |
| H9A-C9-H9B | 108.8 |
| C10-C9-H9A | 110.7 |
| C10-C9-H9B | 110.7 |
| C9-C10-H10A | 110.8 |
| C9-C10-H10B | 110.8 |

| | |
|---|---|
| H10A-C10-H10B | 108.9 |
| C11-C10-C9 | 104.7(3) |
| C11-C10-H10A | 110.8 |
| C11-C10-H10B | 110.8 |
| C1-C11-H11A | 111.2 |
| C1-C11-H11B | 111.2 |
| C10-C11-C1 | 102.9(3) |
| C10-C11-H11A | 111.2 |
| C10-C11-H11B | 111.2 |
| H11A-C11-H11B | 109.1 |
| N1-C12-H12A | 109.4 |
| N1-C12-H12B | 109.4 |
| N1-C12-C13 | 111.3(3) |
| H12A-C12-H12B | 108.0 |
| C13-C12-H12A | 109.4 |
| C13-C12-H12B | 109.4 |
| C14-C13-C12 | 121.6(4) |
| C14-C13-C18 | 118.3(4) |
| C18-C13-C12 | 120.0(4) |
| C13-C14-H14 | 119.4 |
| C13-C14-C15 | 121.3(4) |
| C15-C14-H14 | 119.4 |
| C14-C15-H15 | 120.3 |
| C16-C15-C14 | 119.4(4) |
| C16-C15-H15 | 120.3 |
| C15-C16-Br1 | 119.2(3) |
| C15-C16-C17 | 120.7(4) |
| C17-C16-Br1 | 120.1(3) |
| C16-C17-H17 | 120.1 |
| C16-C17-C18 | 119.7(4) |
| C18-C17-H17 | 120.1 |
| C13-C18-C17 | 120.5(4) |

| | |
|---|---|
| C13-C18-H18 | 119.7 |
| C17-C18-H18 | 119.7 |
| N1A-C1A-C2A | 115.7(3) |
| N1A-C1A-C8A | 114.4(3) |
| N1A-C1A-C11A | 102.0(3) |
| C8A-C1A-C2A | 101.1(3) |
| C8A-C1A-C11A | 115.4(3) |
| C11A-C1A-C2A | 108.8(3) |
| C1A-N1A-C9A | 108.5(3) |
| C1A-N1A-C12A | 114.8(3) |
| C12A-N1A-C9A | 115.0(3) |
| O1A-C2A-C1A | 126.0(4) |
| O1A-C2A-N2A | 126.0(4) |
| N2A-C2A-C1A | 108.0(3) |
| C2A-N2A-H2A | 124.5 |
| C2A-N2A-C3A | 111.1(3) |
| C3A-N2A-H2A | 124.5 |
| C4A-C3A-N2A | 128.4(4) |
| C4A-C3A-C8A | 121.9(4) |
| C8A-C3A-N2A | 109.7(3) |
| C3A-C4A-H4A | 121.4 |
| C3A-C4A-C5A | 117.1(4) |
| C5A-C4A-H4A | 121.4 |
| C4A-C5A-H5A | 119.3 |
| C6A-C5A-C4A | 121.5(4) |
| C6A-C5A-H5A | 119.3 |
| C5A-C6A-H6A | 120.0 |
| C7A-C6A-C5A | 120.1(4) |
| C7A-C6A-H6A | 120.0 |
| C6A-C7A-H7A | 120.7 |
| C8A-C7A-C6A | 118.6(4) |
| C8A-C7A-H7A | 120.7 |

| | |
|---|---|
| C3A-C8A-C1A | 109.5(3) |
| C7A-C8A-C1A | 129.8(3) |
| C7A-C8A-C3A | 120.8(4) |
| N1A-C9A-H9AA | 110.7 |
| N1A-C9A-H9AB | 110.7 |
| N1A-C9A-C10A | 105.1(3) |
| H9AA-C9A-H9AB | 108.8 |
| C10A-C9A-H9AA | 110.7 |
| C10A-C9A-H9AB | 110.7 |
| C9A-C10A-H10C | 110.6 |
| C9A-C10A-H10D | 110.6 |
| H10C-C10A-H10D | 108.7 |
| C11A-C10A-C9A | 105.8(3) |
| C11A-C10A-H10C | 110.6 |
| C11A-C10A-H10D | 110.6 |
| C1A-C11A-H11C | 111.1 |
| C1A-C11A-H11D | 111.1 |
| C10A-C11A-C1A | 103.5(3) |
| C10A-C11A-H11C | 111.1 |
| C10A-C11A-H11D | 111.1 |
| H11C-C11A-H11D | 109.0 |
| N1A-C12A-H12C | 109.3 |
| N1A-C12A-H12D | 109.3 |
| N1A-C12A-C13A | 111.7(3) |
| H12C-C12A-H12D | 107.9 |
| C13A-C12A-H12C | 109.3 |
| C13A-C12A-H12D | 109.3 |
| C14A-C13A-C12A | 120.5(4) |
| C14A-C13A-C18A | 118.4(4) |
| C18A-C13A-C12A | 121.1(4) |
| C13A-C14A-H14A | 119.7 |
| C13A-C14A-C15A | 120.7(4) |

| | |
|---|---|
| C15A-C14A-H14A | 119.7 |
| C14A-C15A-H15A | 120.3 |
| C16A-C15A-C14A | 119.3(4) |
| C16A-C15A-H15A | 120.3 |
| C15A-C16A-Br1A | 119.1(3) |
| C15A-C16A-C17A | 121.6(4) |
| C17A-C16A-Br1A | 119.2(4) |
| C16A-C17A-H17A | 120.5 |
| C16A-C17A-C18A | 119.0(4) |
| C18A-C17A-H17A | 120.5 |
| C13A-C18A-H18A | 119.5 |
| C17A-C18A-C13A | 121.0(4) |
| C17A-C18A-H18A | 119.5 |

---

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mx6777. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br1 | 57(1) | 36(1) | 53(1) | -12(1) | 17(1) | -20(1) |
| N1 | 24(2) | 22(2) | 29(2) | -2(1) | 1(1) | -4(1) |
| O1 | 29(2) | 25(1) | 24(1) | -5(1) | 2(1) | -2(1) |
| C1 | 23(2) | 20(2) | 22(2) | -3(1) | -1(1) | -1(2) |
| N2 | 25(2) | 33(2) | 19(2) | -4(1) | -3(1) | -7(2) |
| C2 | 26(2) | 19(2) | 19(2) | 0(1) | -1(1) | 2(2) |
| C3 | 27(2) | 26(2) | 16(2) | 0(1) | 3(1) | -4(2) |
| C4 | 24(2) | 38(2) | 25(2) | -2(2) | -1(2) | -9(2) |
| C5 | 29(2) | 37(2) | 30(2) | -2(2) | 5(2) | -4(2) |
| C6 | 33(2) | 27(2) | 23(2) | -2(2) | 3(2) | 4(2) |
| C7 | 27(2) | 23(2) | 22(2) | -1(1) | -4(2) | -1(2) |
| C8 | 25(2) | 18(2) | 20(2) | 0(1) | 1(1) | -1(2) |
| C9 | 24(2) | 34(2) | 38(2) | -3(2) | 4(2) | -6(2) |
| C10 | 26(2) | 33(2) | 34(2) | 1(2) | -1(2) | -1(2) |
| C11 | 26(2) | 23(2) | 23(2) | -2(1) | -5(2) | -1(2) |
| C12 | 34(2) | 29(2) | 26(2) | 3(2) | -1(2) | -3(2) |
| C13 | 33(2) | 24(2) | 25(2) | -3(2) | 2(2) | 2(2) |
| C14 | 45(3) | 31(2) | 25(2) | -1(2) | 2(2) | -4(2) |
| C15 | 50(3) | 36(2) | 30(2) | 5(2) | 11(2) | -8(2) |
| C16 | 38(2) | 20(2) | 39(2) | -3(2) | 5(2) | -6(2) |
| C17 | 70(4) | 35(3) | 28(2) | -1(2) | 4(2) | -14(2) |
| C18 | 68(4) | 33(2) | 30(2) | 2(2) | 7(2) | -21(2) |
| Br1A | 57(1) | 59(1) | 51(1) | -28(1) | 12(1) | -28(1) |
| C1A | 22(2) | 18(2) | 24(2) | 0(1) | -2(1) | -3(2) |
| O1A | 30(2) | 23(1) | 32(2) | 6(1) | -7(1) | -1(1) |
| N1A | 21(2) | 25(2) | 27(2) | -1(1) | 2(1) | -1(1) |
| C2A | 26(2) | 23(2) | 23(2) | -4(2) | -4(2) | 2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2A | 27(2) | 22(2) | 27(2) | 6(1) | 0(1) | -8(1) |
| C3A | 25(2) | 25(2) | 16(2) | 2(1) | -2(1) | -2(2) |
| C4A | 21(2) | 43(2) | 30(2) | 10(2) | -1(2) | -5(2) |
| C5A | 24(2) | 50(3) | 31(2) | 11(2) | -6(2) | 4(2) |
| C6A | 34(2) | 36(2) | 36(2) | 12(2) | -1(2) | 2(2) |
| C7A | 29(2) | 25(2) | 26(2) | 7(2) | 0(2) | -2(2) |
| C8A | 20(2) | 21(2) | 21(2) | 0(1) | -1(1) | -3(2) |
| C9A | 22(2) | 31(2) | 38(2) | -4(2) | -2(2) | -2(2) |
| C10A | 23(2) | 41(3) | 46(3) | -8(2) | 2(2) | 2(2) |
| C11A | 25(2) | 25(2) | 31(2) | -2(2) | 0(2) | -5(2) |
| C12A | 26(2) | 27(2) | 29(2) | -1(2) | 3(2) | -3(2) |
| C13A | 25(2) | 26(2) | 29(2) | -3(2) | 5(2) | 1(2) |
| C14A | 43(3) | 32(2) | 30(2) | 3(2) | -4(2) | -3(2) |
| C15A | 46(3) | 50(3) | 26(2) | -5(2) | -4(2) | -7(2) |
| C16A | 35(2) | 38(2) | 37(2) | -14(2) | 6(2) | -11(2) |
| C17A | 48(3) | 32(2) | 40(2) | -5(2) | 3(2) | -12(2) |
| C18A | 44(3) | 34(2) | 29(2) | -3(2) | -1(2) | -8(2) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for mx6777.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H2 | -1158 | 5322 | 5478 | 31 |
| H4 | -3331 | 5604 | 6365 | 35 |
| H5 | -3885 | 6195 | 7452 | 38 |
| H6 | -2204 | 6808 | 8141 | 33 |
| H7 | 68 | 6830 | 7760 | 29 |
| H9A | 4042 | 6830 | 6647 | 38 |
| H9B | 3666 | 6563 | 5842 | 38 |
| H10A | 3589 | 5347 | 6183 | 37 |
| H10B | 4170 | 5605 | 6958 | 37 |
| H11A | 2030 | 5664 | 7439 | 29 |
| H11B | 1723 | 5021 | 6842 | 29 |
| H12A | 553 | 7498 | 6068 | 36 |
| H12B | 1581 | 7197 | 5468 | 36 |
| H14 | 2647 | 8309 | 5015 | 41 |
| H15 | 4088 | 9360 | 5176 | 46 |
| H17 | 3809 | 9131 | 7320 | 53 |
| H18 | 2351 | 8085 | 7161 | 53 |
| H2A | 6178 | 4485 | 5317 | 30 |
| H4A | 8406 | 3714 | 5846 | 38 |
| H5A | 9031 | 2569 | 6417 | 42 |
| H6A | 7374 | 1690 | 6753 | 43 |
| H7A | 5037 | 1953 | 6553 | 32 |
| H9AA | 1021 | 2565 | 5601 | 36 |
| H9AB | 1394 | 3260 | 5079 | 36 |
| H10C | 1406 | 4056 | 6008 | 44 |
| H10D | 960 | 3368 | 6523 | 44 |

| | | | | |
|---|---|---|---|---|
| H11C | 3136 | 3142 | 6888 | 33 |
| H11D | 3355 | 4018 | 6670 | 33 |
| H12C | 4506 | 2342 | 4800 | 33 |
| H12D | 3464 | 2943 | 4450 | 33 |
| H14A | 2401 | 2312 | 3480 | 42 |
| H15A | 1022 | 1333 | 3021 | 49 |
| H17A | 1336 | 218 | 4904 | 48 |
| H18A | 2720 | 1187 | 5365 | 43 |

Table 6. Torsion angles [°] for mx6777.

| | |
|---|---|
| Br1-C16-C17-C18 | -178.1(4) |
| N1-C1-C2-O1 | 47.3(5) |
| N1-C1-C2-N2 | -134.5(3) |
| N1-C1-C8-C3 | 134.7(3) |
| N1-C1-C8-C7 | -49.9(5) |
| N1-C1-C11-C10 | -39.7(3) |
| N1-C9-C10-C11 | -7.4(4) |
| N1-C12-C13-C14 | 134.0(4) |
| N1-C12-C13-C18 | -44.8(5) |
| C1-N1-C9-C10 | -18.6(4) |
| C1-N1-C12-C13 | 170.1(3) |
| N2-C3-C4-C5 | -179.7(4) |
| N2-C3-C8-C1 | -4.6(4) |
| N2-C3-C8-C7 | 179.4(3) |
| C2-C1-C8-C3 | 7.4(4) |
| C2-C1-C8-C7 | -177.2(4) |
| C2-C1-C11-C10 | 84.1(3) |
| C2-N2-C3-C4 | 179.4(4) |
| C2-N2-C3-C8 | -0.9(4) |
| C3-N2-C2-O1 | -176.0(4) |
| C3-N2-C2-C1 | 5.8(4) |
| C3-C4-C5-C6 | 0.0(6) |
| C4-C3-C8-C1 | 175.2(3) |
| C4-C3-C8-C7 | -0.8(6) |
| C4-C5-C6-C7 | -0.4(6) |
| C5-C6-C7-C8 | 0.2(6) |
| C6-C7-C8-C1 | -174.6(4) |
| C6-C7-C8-C3 | 0.4(6) |
| C8-C1-C2-O1 | 173.9(4) |
| C8-C1-C2-N2 | -7.9(4) |

| | |
|---|---|
| C8-C1-C11-C10 | -165.3(3) |
| C8-C3-C4-C5 | 0.6(6) |
| C9-N1-C1-C2 | -80.9(4) |
| C9-N1-C1-C8 | 160.4(3) |
| C9-N1-C1-C11 | 36.5(4) |
| C9-N1-C12-C13 | -60.3(4) |
| C9-C10-C11-C1 | 28.7(4) |
| C11-C1-C2-O1 | -66.8(5) |
| C11-C1-C2-N2 | 111.3(3) |
| C11-C1-C8-C3 | -107.6(4) |
| C11-C1-C8-C7 | 67.7(5) |
| C12-N1-C1-C2 | 51.5(4) |
| C12-N1-C1-C8 | -67.1(4) |
| C12-N1-C1-C11 | 168.9(3) |
| C12-N1-C9-C10 | -152.1(3) |
| C12-C13-C14-C15 | -176.8(4) |
| C12-C13-C18-C17 | 176.5(4) |
| C13-C14-C15-C16 | -0.5(7) |
| C14-C13-C18-C17 | -2.4(7) |
| C14-C15-C16-Br1 | 177.8(4) |
| C14-C15-C16-C17 | -0.8(7) |
| C15-C16-C17-C18 | 0.5(8) |
| C16-C17-C18-C13 | 1.1(8) |
| C18-C13-C14-C15 | 2.1(7) |
| Br1A-C16A-C17A-C18A | -179.5(4) |
| C1A-N1A-C9A-C10A | -22.2(4) |
| C1A-N1A-C12A-C13A | 172.2(3) |
| C1A-C2A-N2A-C3A | 6.9(4) |
| O1A-C2A-N2A-C3A | -173.8(4) |
| N1A-C1A-C2A-O1A | 48.2(5) |
| N1A-C1A-C2A-N2A | -132.5(3) |
| N1A-C1A-C8A-C3A | 132.1(3) |

| | |
|---|---|
| N1A-C1A-C8A-C7A | -48.8(5) |
| N1A-C1A-C11A-C10A | -37.5(4) |
| N1A-C9A-C10A-C11A | -2.6(5) |
| N1A-C12A-C13A-C14A | 133.7(4) |
| N1A-C12A-C13A-C18A | -45.7(5) |
| C2A-C1A-N1A-C9A | -80.5(4) |
| C2A-C1A-N1A-C12A | 49.7(4) |
| C2A-C1A-C8A-C3A | 7.1(4) |
| C2A-C1A-C8A-C7A | -173.8(4) |
| C2A-C1A-C11A-C10A | 85.3(4) |
| C2A-N2A-C3A-C4A | 175.2(4) |
| C2A-N2A-C3A-C8A | -2.3(4) |
| N2A-C3A-C4A-C5A | -176.0(4) |
| N2A-C3A-C8A-C1A | -3.5(4) |
| N2A-C3A-C8A-C7A | 177.3(3) |
| C3A-C4A-C5A-C6A | -0.6(7) |
| C4A-C3A-C8A-C1A | 178.7(4) |
| C4A-C3A-C8A-C7A | -0.5(6) |
| C4A-C5A-C6A-C7A | -0.9(7) |
| C5A-C6A-C7A-C8A | 1.7(6) |
| C6A-C7A-C8A-C1A | 179.9(4) |
| C6A-C7A-C8A-C3A | -1.0(6) |
| C8A-C1A-N1A-C9A | 162.6(3) |
| C8A-C1A-N1A-C12A | -67.2(4) |
| C8A-C1A-C2A-O1A | 172.4(4) |
| C8A-C1A-C2A-N2A | -8.4(4) |
| C8A-C1A-C11A-C10A | -162.0(3) |
| C8A-C3A-C4A-C5A | 1.3(6) |
| C9A-N1A-C12A-C13A | -60.9(4) |
| C9A-C10A-C11A-C1A | 24.6(4) |
| C11A-C1A-N1A-C9A | 37.4(4) |
| C11A-C1A-N1A-C12A | 167.6(3) |

| | |
|---|---|
| C11A-C1A-C2A-O1A | -65.8(5) |
| C11A-C1A-C2A-N2A | 113.4(3) |
| C11A-C1A-C8A-C3A | -110.1(4) |
| C11A-C1A-C8A-C7A | 69.0(5) |
| C12A-N1A-C9A-C10A | -152.2(3) |
| C12A-C13A-C14A-C15A | -178.2(4) |
| C12A-C13A-C18A-C17A | 178.0(4) |
| C13A-C14A-C15A-C16A | -0.3(7) |
| C14A-C13A-C18A-C17A | -1.4(7) |
| C14A-C15A-C16A-Br1A | 179.4(4) |
| C14A-C15A-C16A-C17A | -0.6(8) |
| C15A-C16A-C17A-C18A | 0.4(7) |
| C16A-C17A-C18A-C13A | 0.6(7) |
| C18A-C13A-C14A-C15A | 1.2(7) |

Symmetry transformations used to generate equivalent atoms:

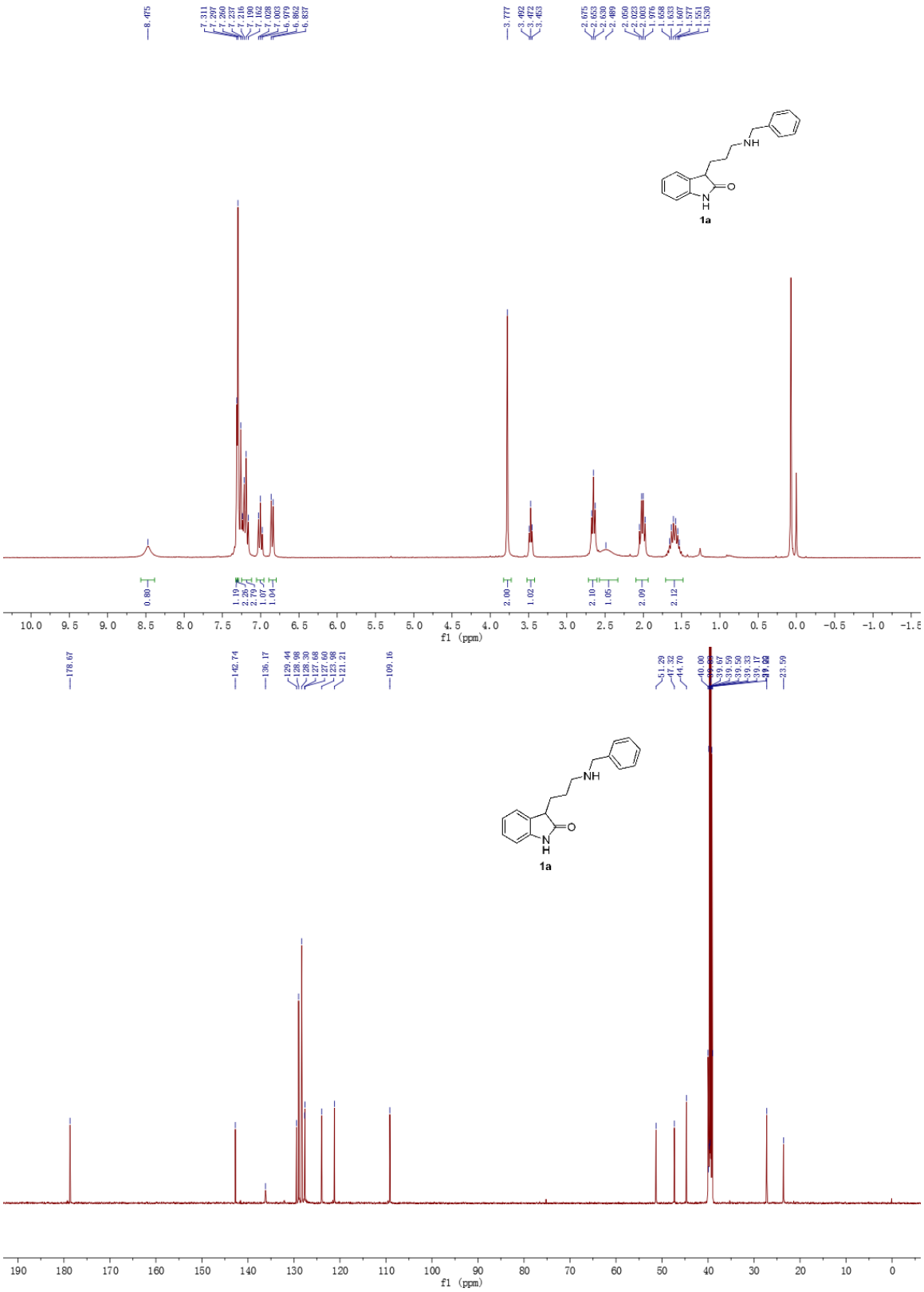
Table 7. Hydrogen bonds for mx6777 [Å and °].

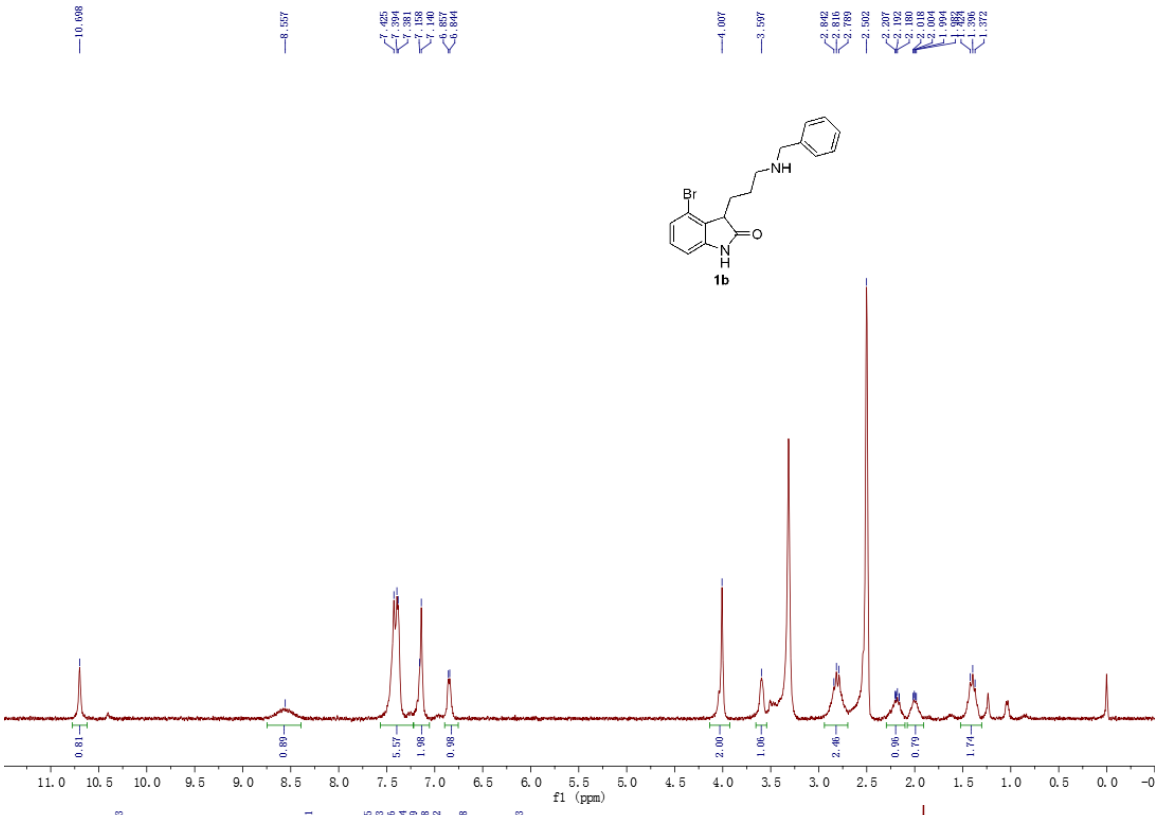
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N2-H2...O1#1 | 0.88 | 2.13 | 2.946(4) | 154.1 |
| N2-H2...O1A#1 | 0.88 | 2.60 | 3.220(4) | 128.3 |
| N2A-H2A...O1#2 | 0.88 | 2.62 | 3.203(4) | 124.8 |
| N2A-H2A...O1A#2 | 0.88 | 2.13 | 2.965(4) | 157.0 |

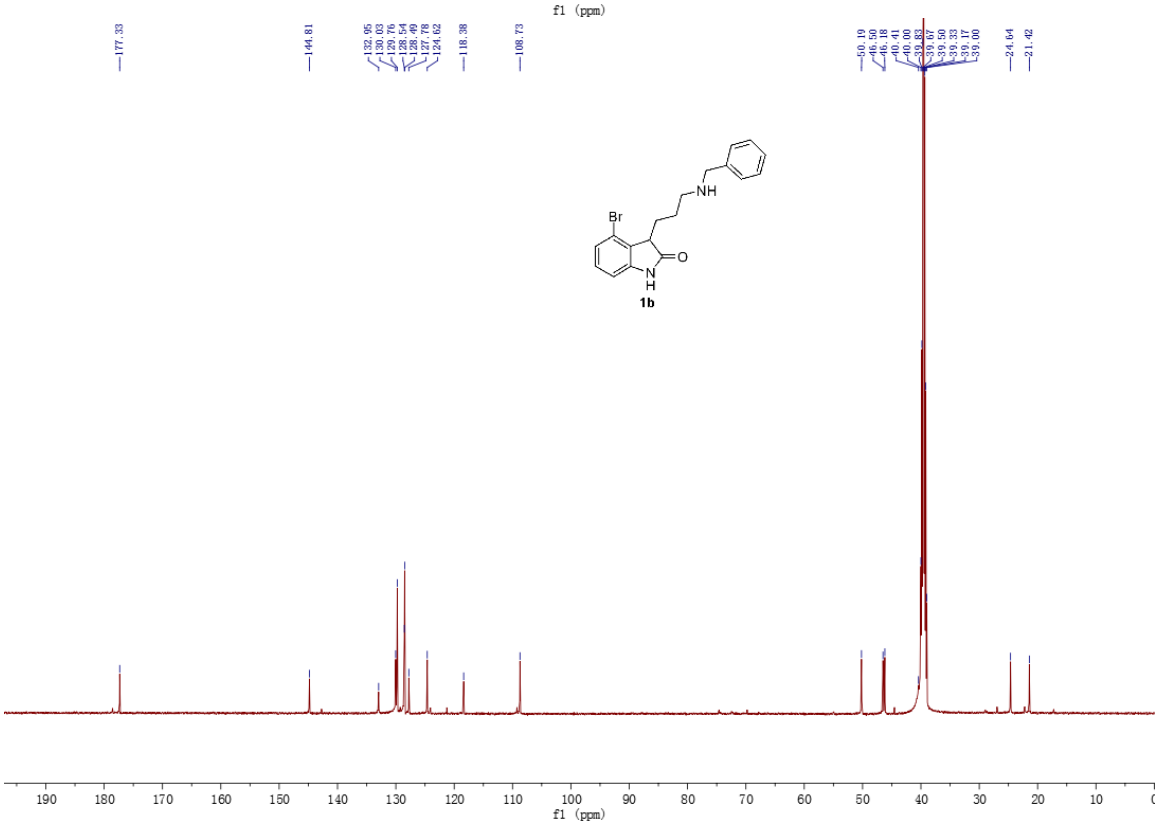
Symmetry transformations used to generate equivalent atoms:

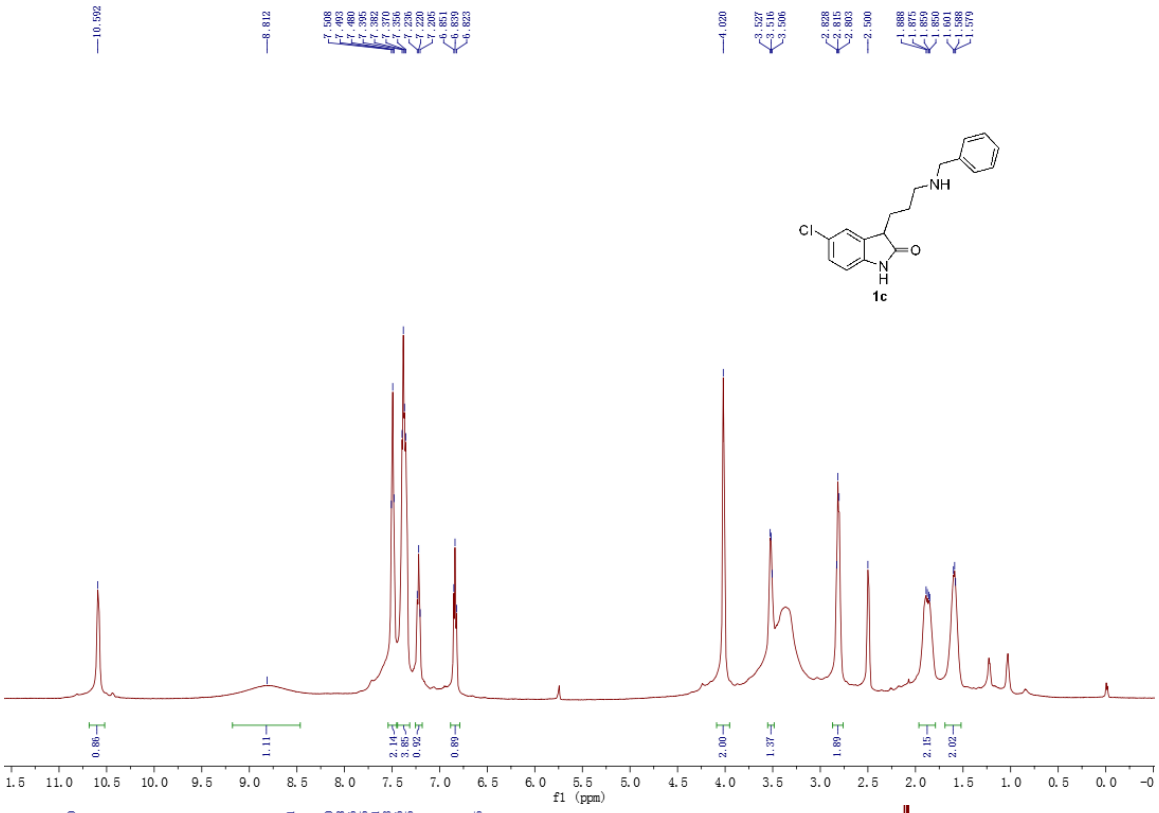
#1 -x,-y+1,-z+1  #2 -x+1,-y+1,-z+1

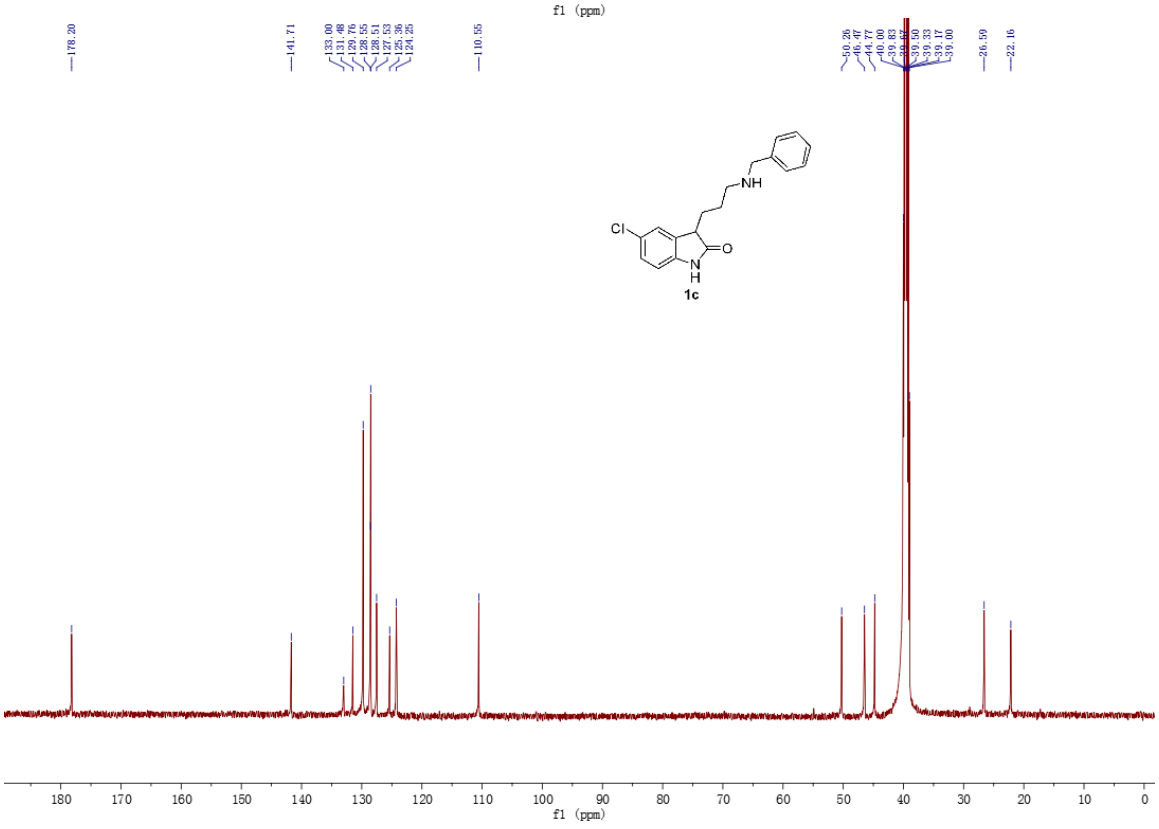
7. NMR spectra

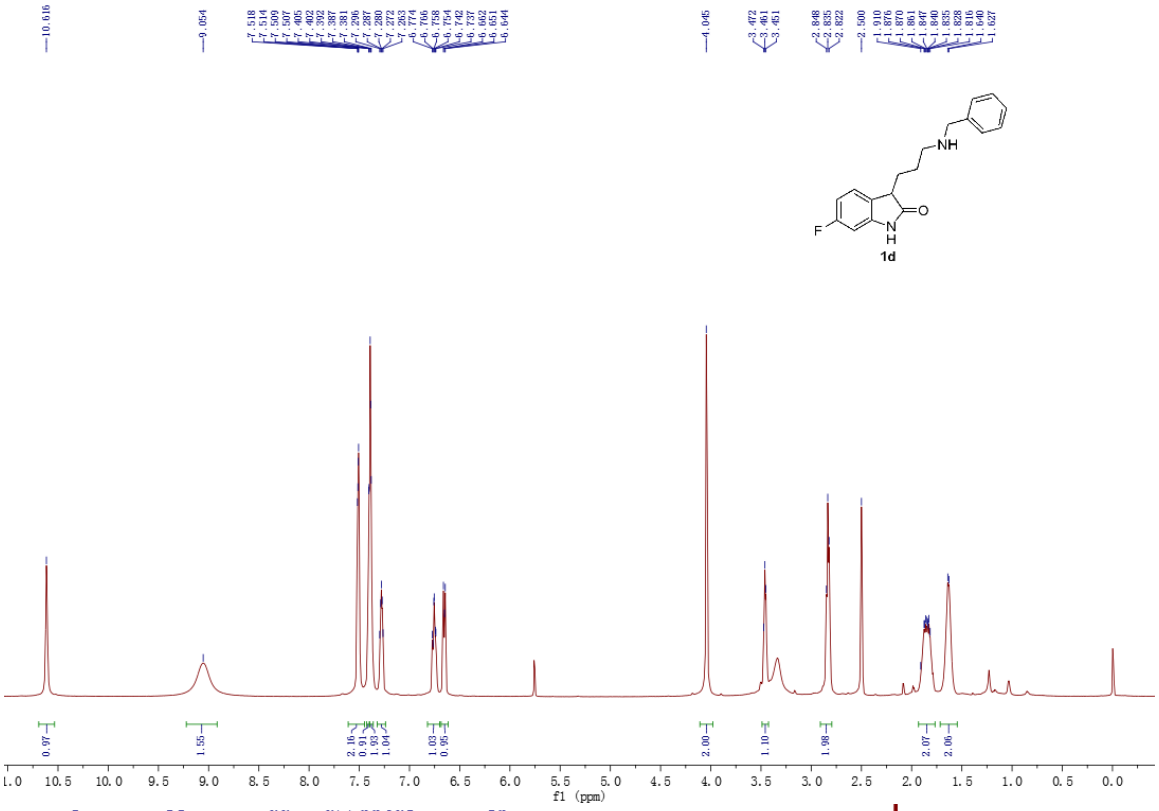


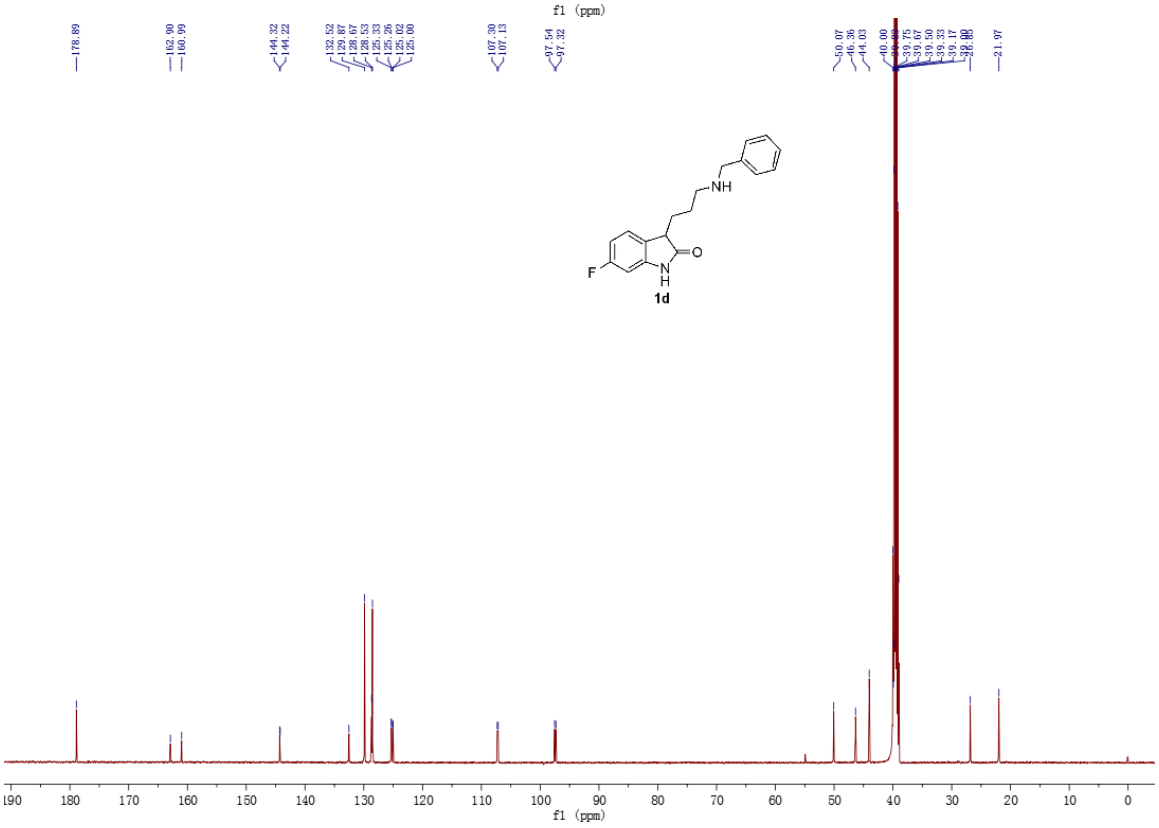

10.698
8.557
7.425
7.394
7.381
7.158
7.140
6.857
6.844
4.007
3.597
2.842
2.816
2.789
2.502
2.207
2.192
2.180
2.018
2.004
1.994
1.396
1.372
NH
Br
O
N
H
1b
0.81
0.89
5.57
1.98
0.98
2.00
1.06
2.46
0.96
0.79
1.74
f1 (ppm)

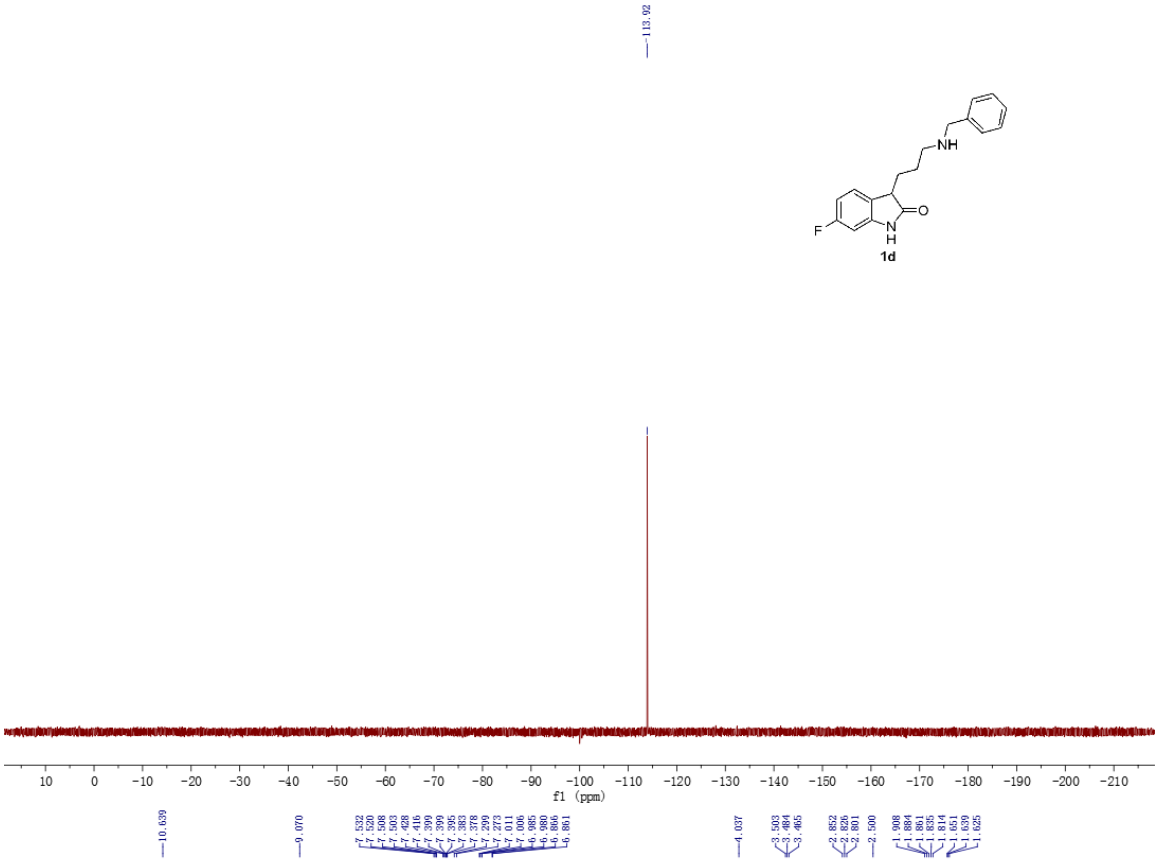

177.33
144.81
132.96
130.65
129.76
128.54
128.49
127.78
124.62
118.38
108.73
50.19
46.50
46.38
40.41
40.00
39.83
39.67
39.50
39.33
39.17
39.00
24.64
21.42
NH
Br
O
N
H
1b
f1 (ppm)

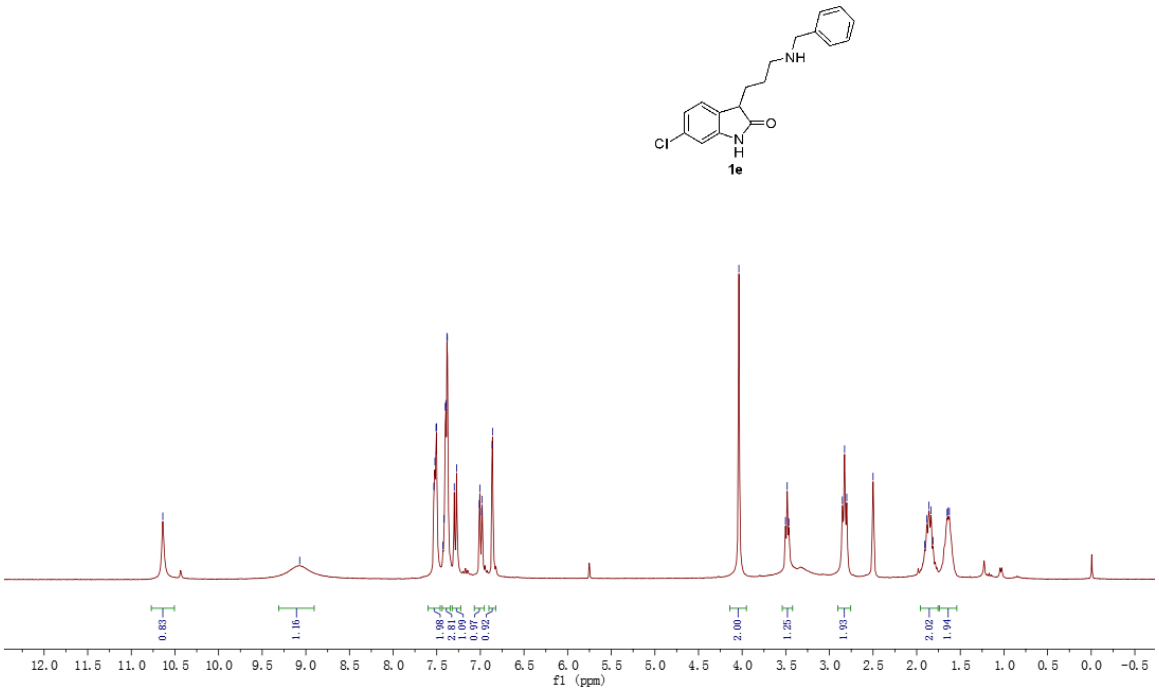

10.592
8.812
7.508
7.493
7.490
7.395
7.382
7.370
7.356
7.235
7.220
7.205
6.851
6.839
6.823
4.020
3.527
3.516
3.506
2.828
2.815
2.803
2.500
1.888
1.875
1.859
1.850
1.601
1.588
1.570
NH
Cl
O
N
H
1c
0.86
1.11
2.14
3.85
0.92
0.89
2.00
1.37
1.89
2.15
2.02
f1 (ppm)

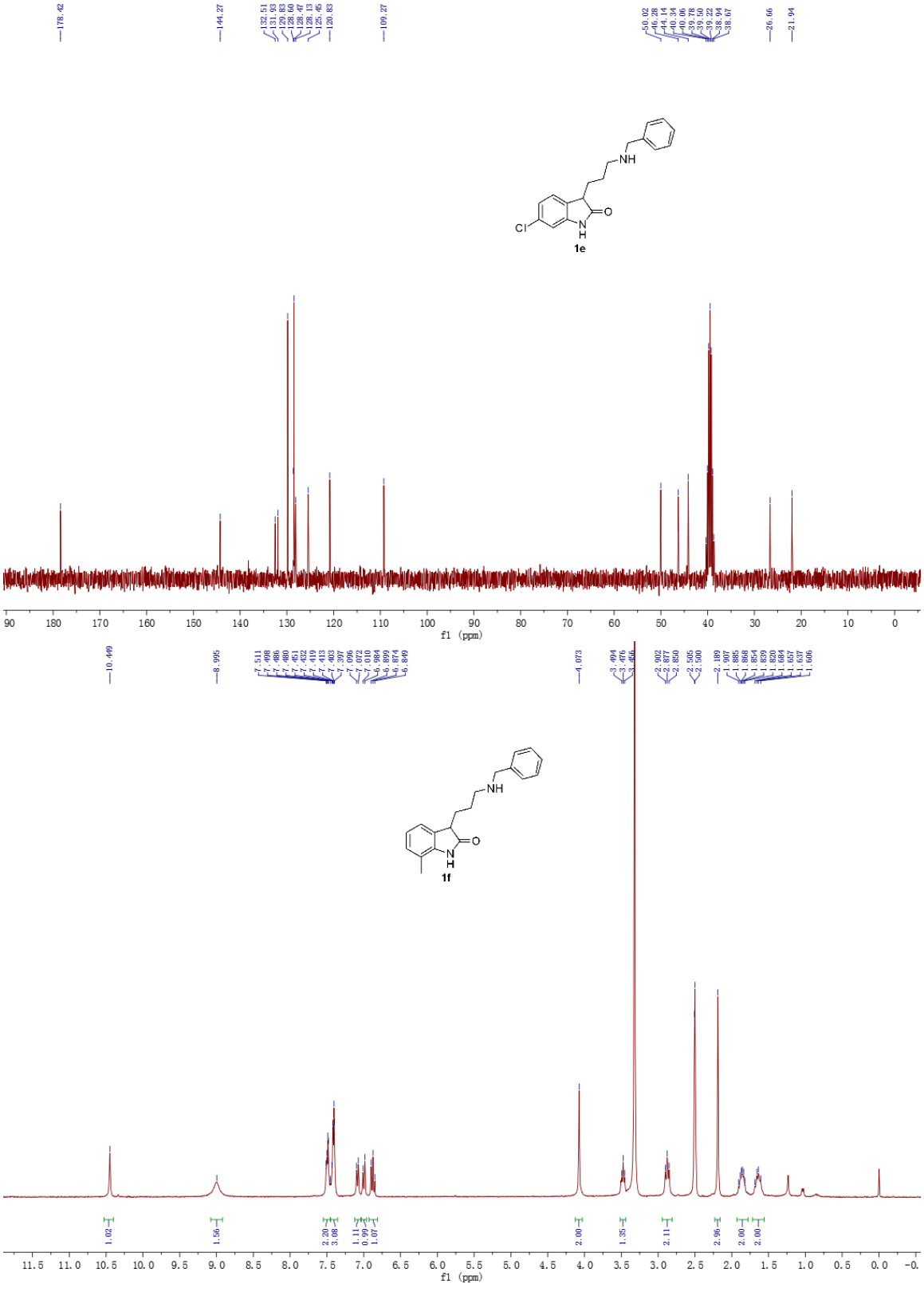

178.20
141.71
133.00
131.46
129.76
128.55
128.51
127.53
125.36
124.25
110.55
50.26
46.47
44.77
40.00
39.83
39.50
39.33
39.17
39.00
26.59
22.16
NH
Cl
O
N
H
1c
f1 (ppm)

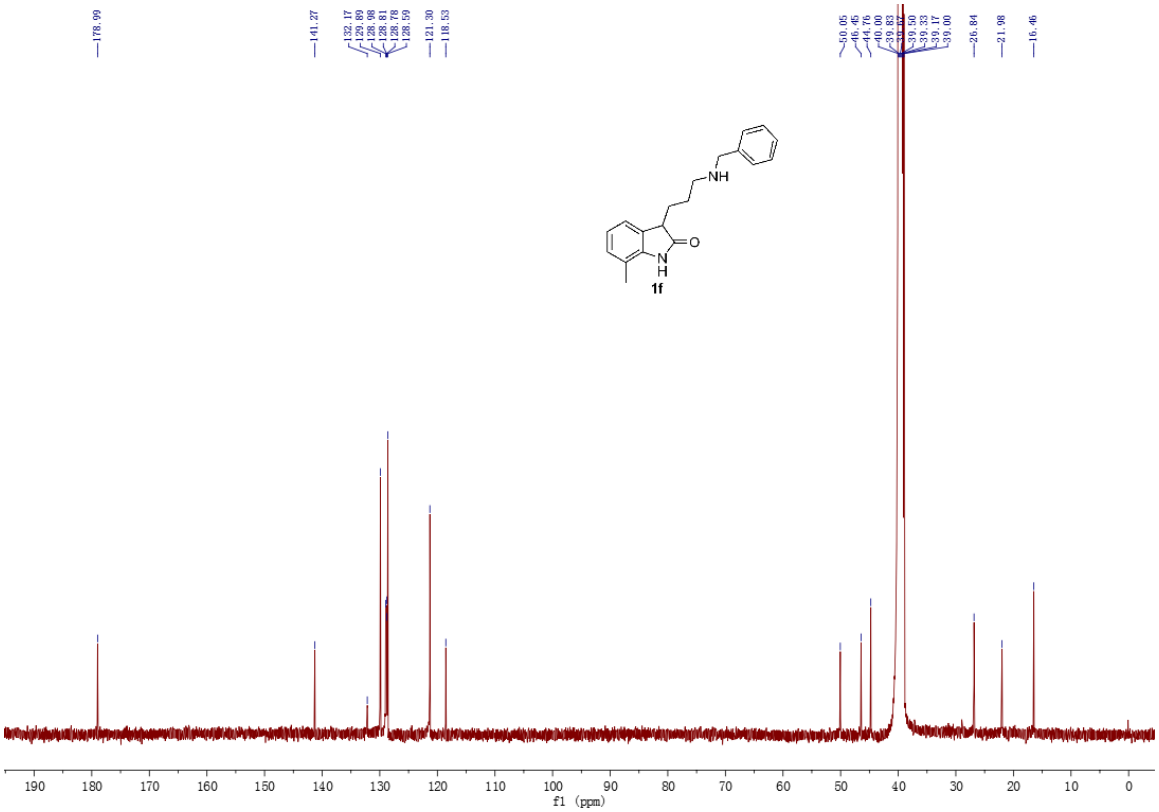

10.616
9.054
7.518
7.514
7.509
7.507
7.405
7.402
7.392
7.387
7.381
7.296
7.287
7.280
7.272
7.263
6.774
6.766
6.758
6.754
6.742
6.737
6.662
6.651
6.644
4.045
3.472
3.461
3.451
2.848
2.835
2.822
2.500
1.910
1.876
1.870
1.861
1.847
1.840
1.835
1.828
1.816
1.640
1.627
NH
O
F
N
H
1d
0.97
1.55
2.16
0.91
1.93
1.04
1.03
0.95
2.00
1.10
1.98
2.07
2.06
f1 (ppm)

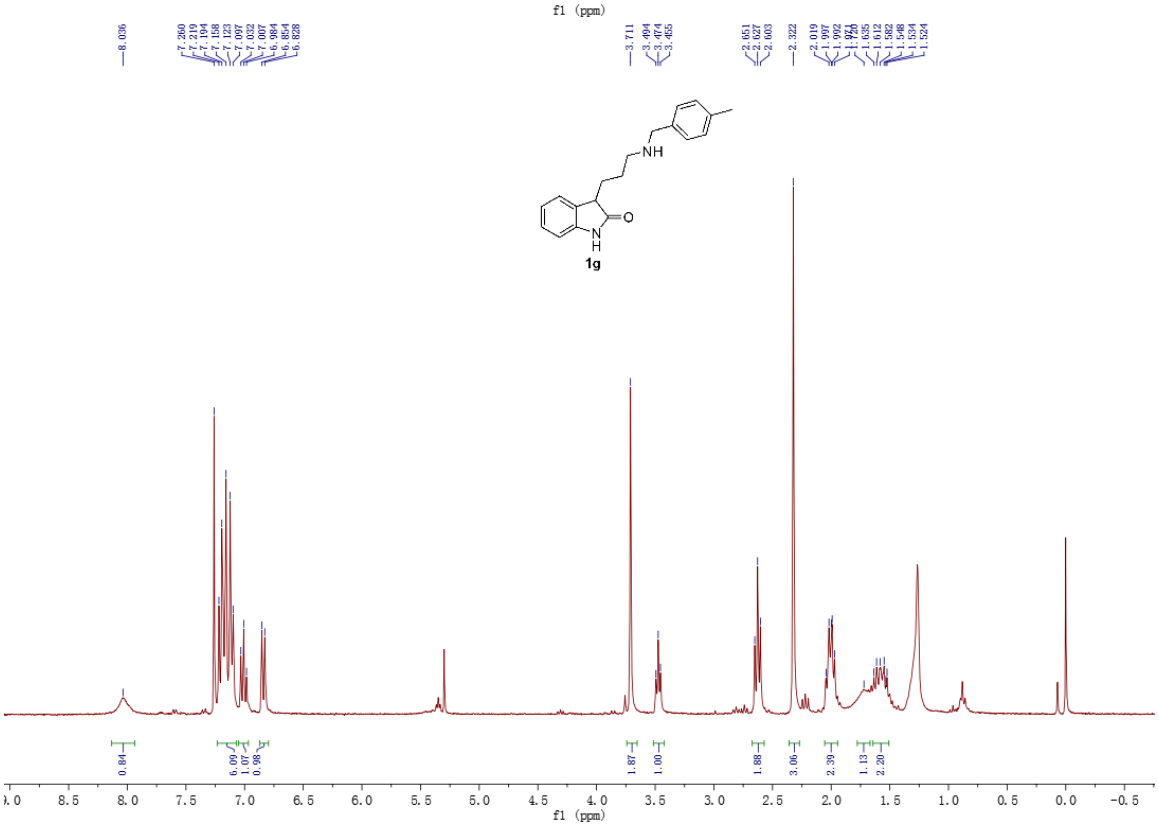

178.89
162.90
160.99
144.32
144.22
132.52
129.67
128.67
128.53
125.33
125.26
125.02
125.00
107.30
107.13
97.54
97.32
50.07
46.36
44.03
40.00
39.75
39.67
39.50
39.33
39.17
32.80
32.68
21.97
NH
O
F
N
H
1d
f1 (ppm)

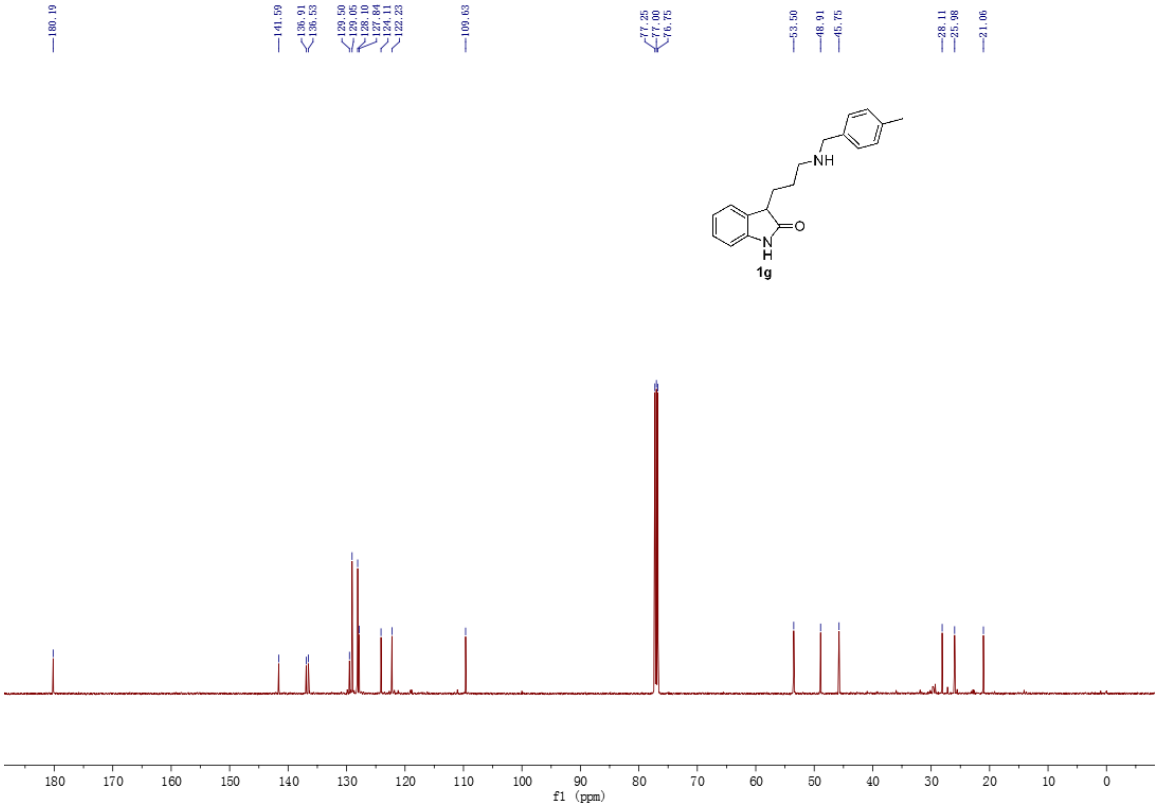

113.92
NH
F
O
N
H
1d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
10.639
9.070
7.532 7.520 7.508 7.503 7.428 7.416 7.399 7.399 7.395 7.388 7.378 7.299 7.273 7.011 7.006 6.985 6.980 6.866 6.861
4.037
3.503 3.484 3.465
2.852 2.826 2.801
2.500
1.908 1.884 1.861 1.835 1.814 1.651 1.639 1.625

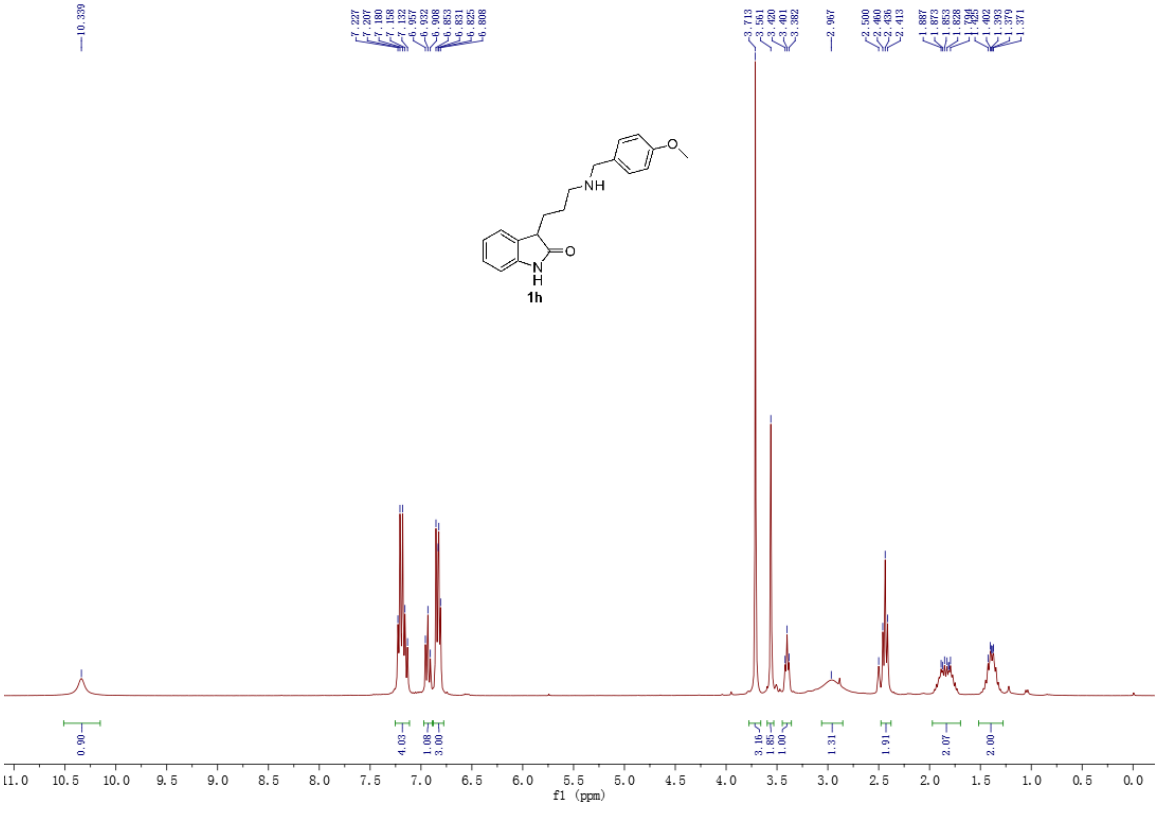

NH
Cl
O
N
H
1e
0.83 1.16 1.98 2.81 1.07 0.97 0.92 2.00 1.25 1.93 2.02 1.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

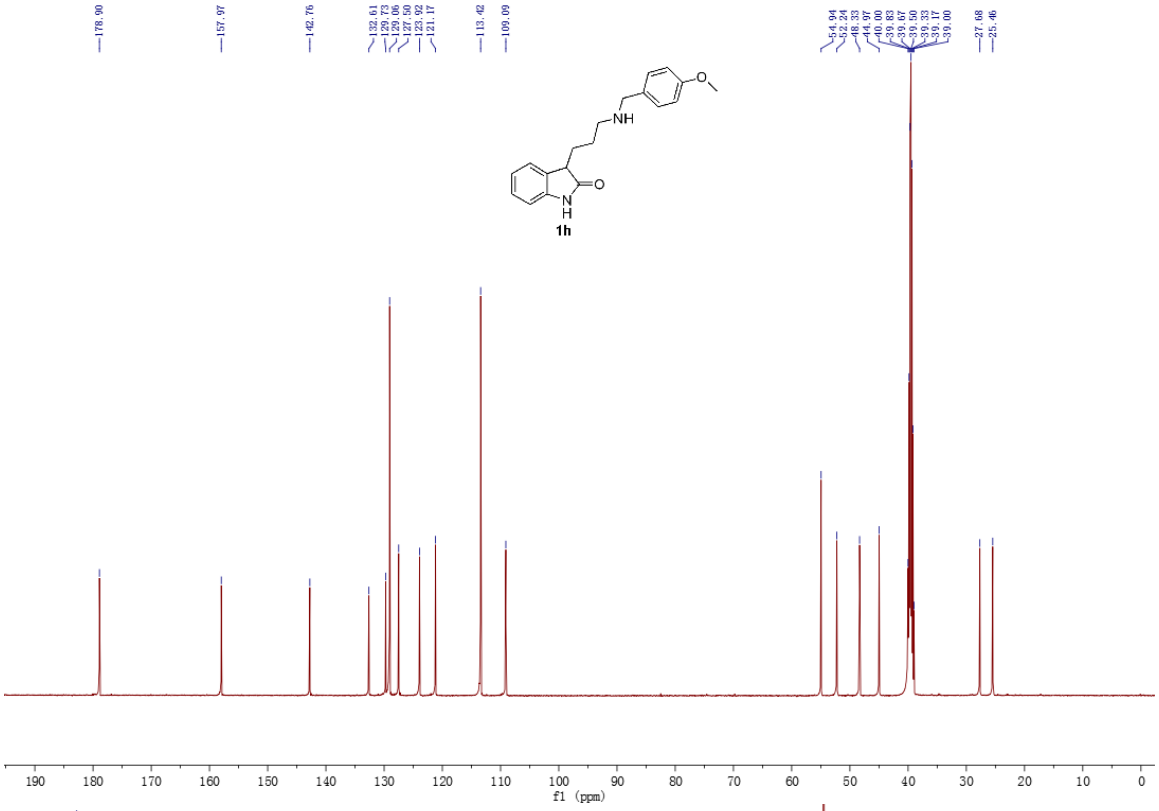

178.42
144.27
132.51
131.93
129.83
128.69
128.47
128.13
125.45
120.83
109.27
50.02
46.28
44.14
40.34
40.05
39.78
39.50
39.22
38.94
38.67
26.66
21.94
NH
O
N
H
Cl
1e
f1 (ppm)
10.449
8.995
7.511
7.498
7.486
7.480
7.451
7.432
7.413
7.403
7.397
7.096
7.072
7.010
6.984
6.899
6.874
6.849
4.073
3.494
3.476
3.458
2.902
2.877
2.850
2.505
2.500
2.189
1.907
1.885
1.868
1.854
1.839
1.820
1.657
1.637
1.606
NH
O
N
H
1f
1.02
1.56
2.20
3.08
1.11
0.99
1.07
2.00
1.35
2.11
2.96
2.00
2.00
f1 (ppm)

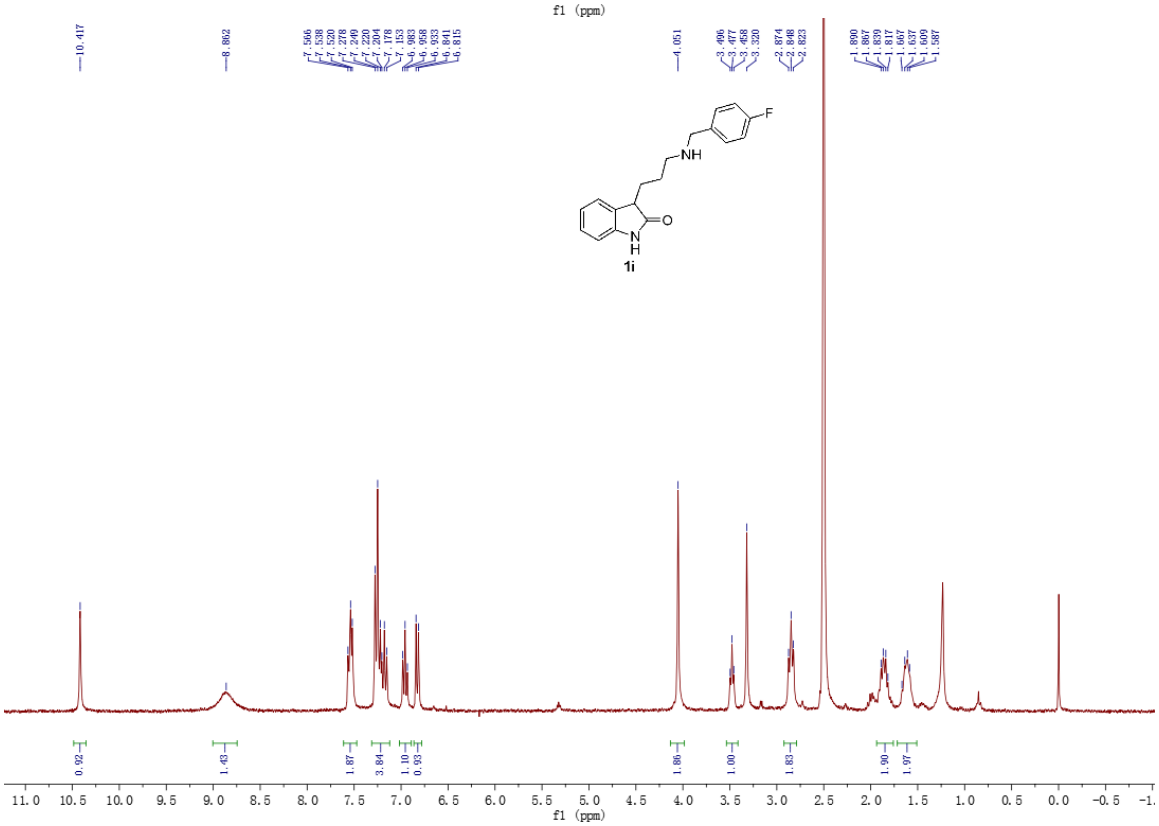

178.99
141.27
132.17
129.89
128.98
128.81
128.78
128.09
121.30
118.53
50.05
46.45
44.76
40.00
39.83
39.67
39.50
39.33
39.17
39.00
26.84
21.98
16.46
NH
O
N
H
1f
f1 (ppm)

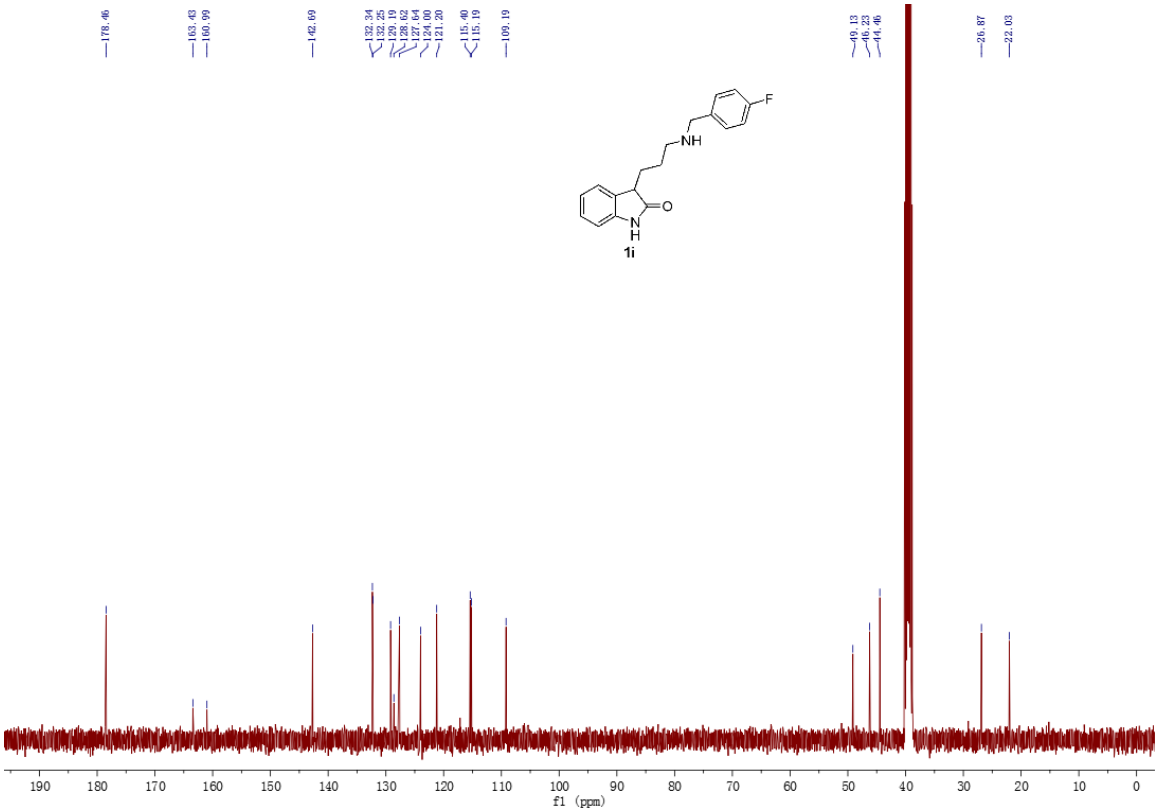

8.036
7.260
7.219
7.194
7.158
7.123
7.097
7.032
7.007
6.984
6.854
6.828
3.711
3.494
3.474
3.455
2.651
2.627
2.603
2.322
2.019
1.997
1.992
1.635
1.612
1.582
1.548
1.534
1.524
NH
O
N
H
1g
0.84
6.09
1.07
0.98
1.87
1.00
1.88
3.06
2.39
1.13
2.20
f1 (ppm)

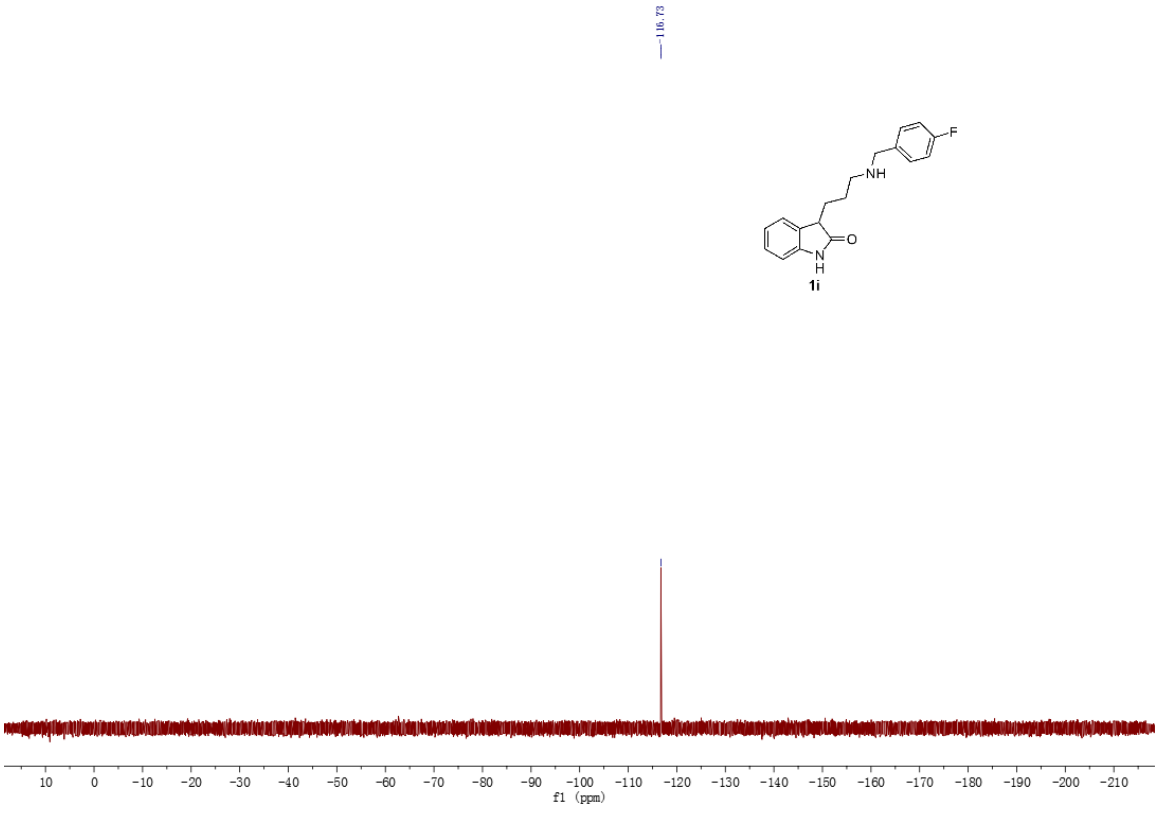

180.19
141.59
136.91
136.53
129.50
129.05
128.10
127.84
124.11
122.23
109.63
77.25
77.00
76.75
53.50
48.91
45.75
28.11
25.98
21.06
NH
O
N
H
1g
f1 (ppm)

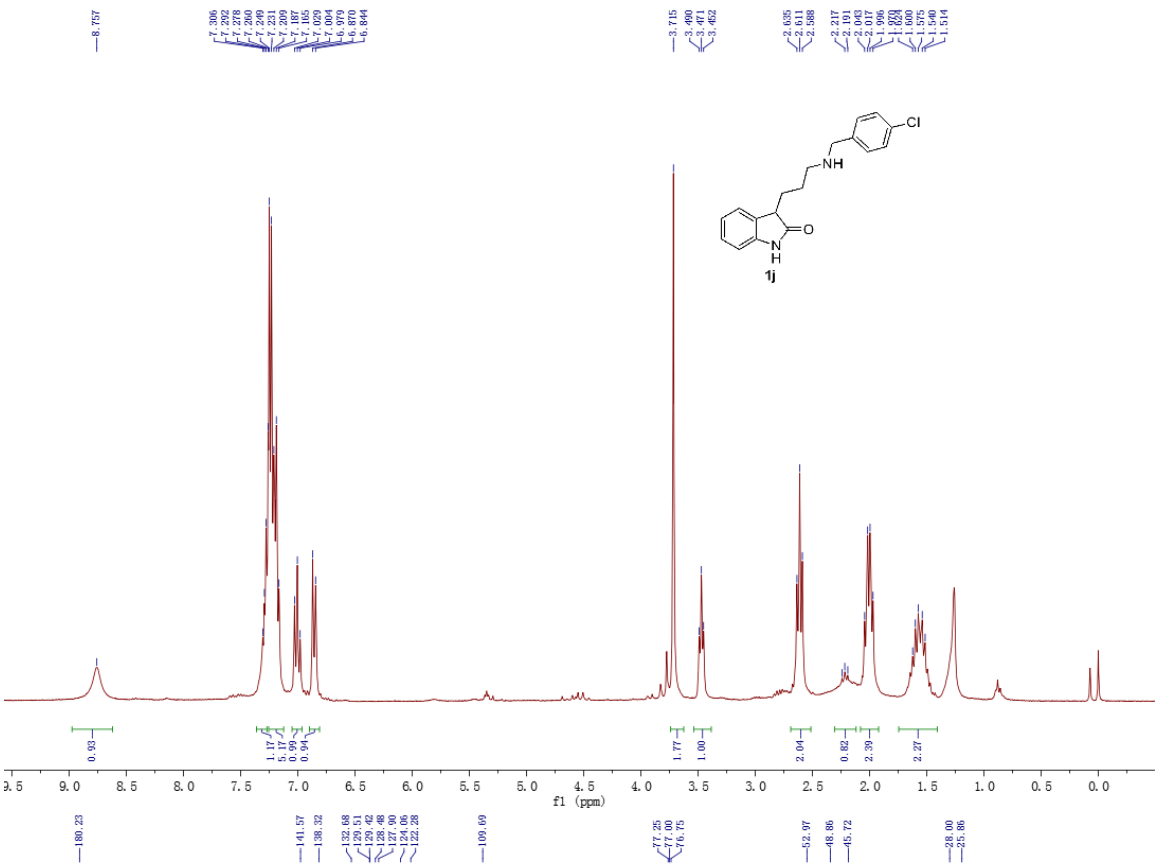

10.339
7.227
7.207
7.188
7.158
7.132
6.957
6.932
6.908
6.853
6.831
6.825
6.808
3.713
3.561
3.460
3.401
3.382
2.967
2.500
2.460
2.436
2.413
1.887
1.873
1.853
1.828
1.402
1.393
1.373
1.371
NH
O
O
N
H
1h
0.90
4.03
1.08
3.00
3.16
1.85
1.00
1.31
1.91
2.07
2.00
f1 (ppm)

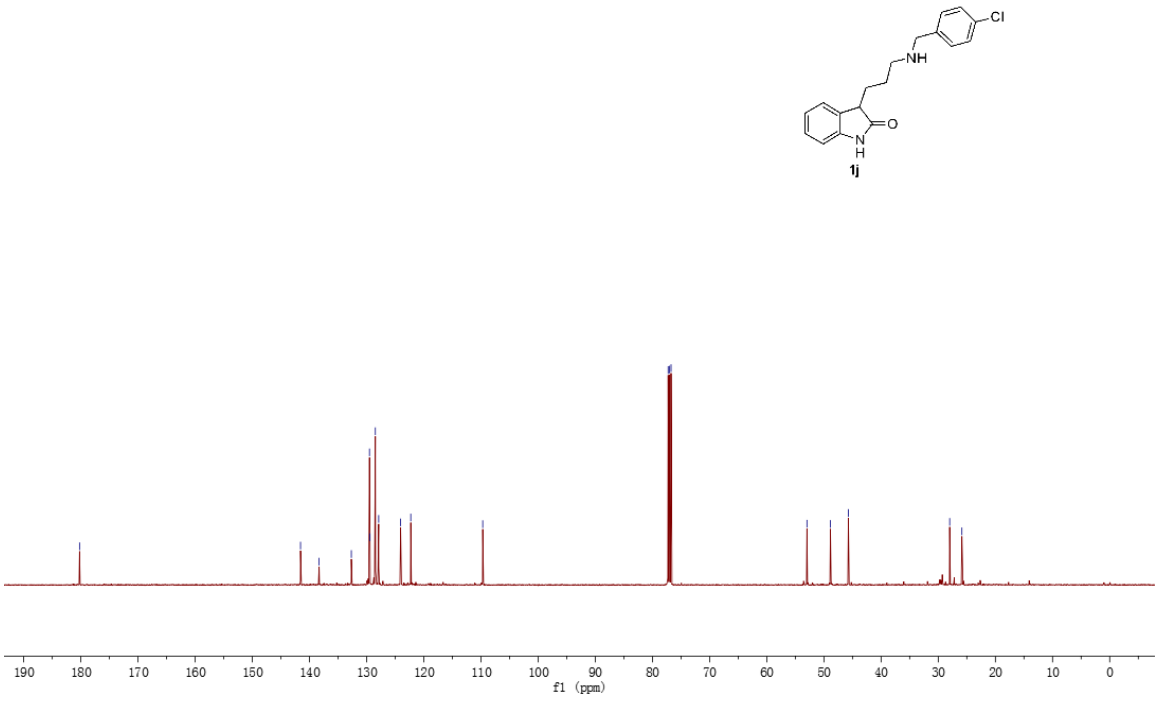

178.90
157.97
142.76
132.61
129.73
129.06
127.89
123.92
121.17
113.42
109.09
54.94
52.24
48.33
44.97
40.00
39.83
39.67
39.50
39.33
39.17
39.00
27.68
25.46
NH
O
N
H
O
1h
f1 (ppm)

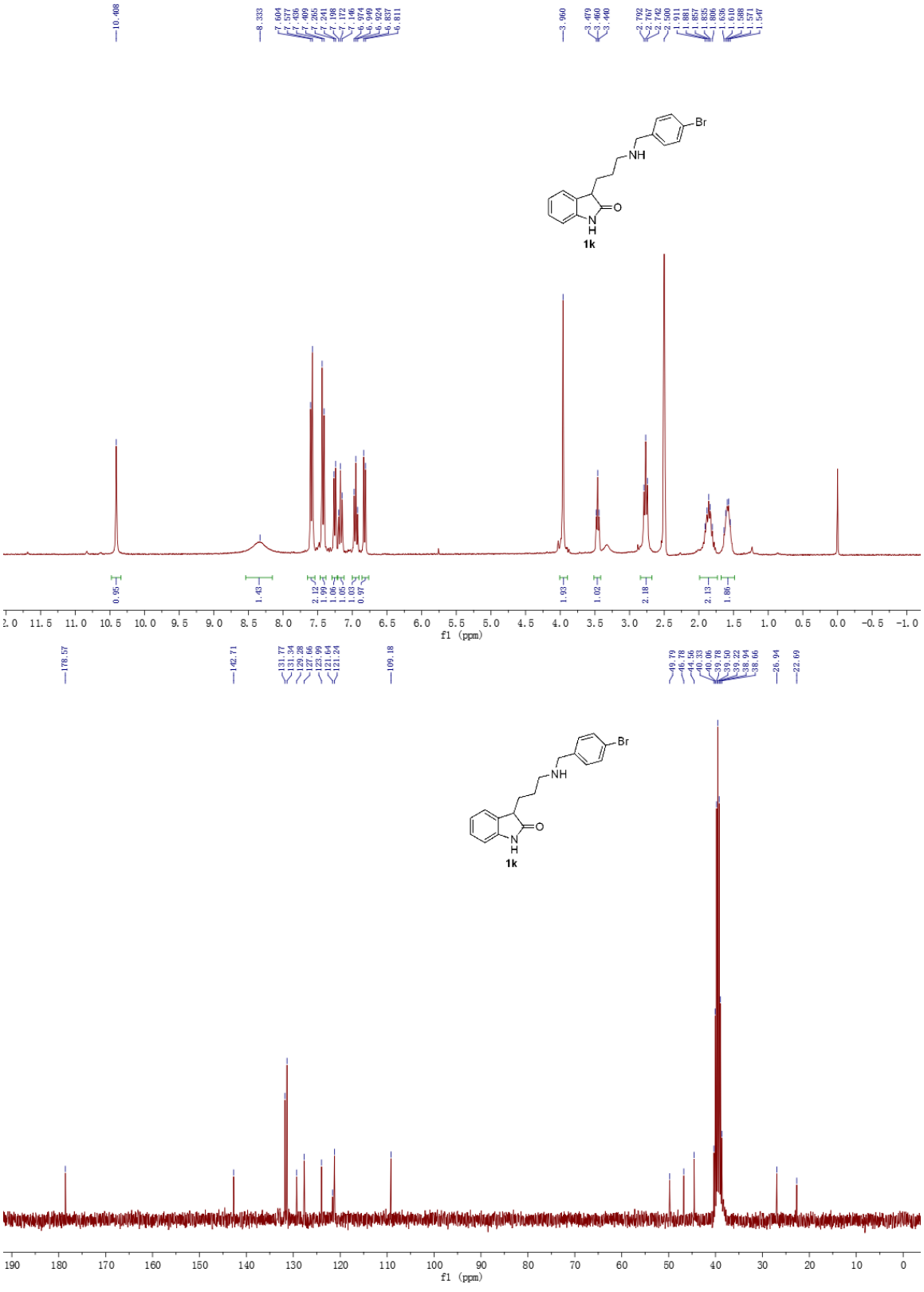

10.417
8.862
7.566
7.538
7.520
7.278
7.260
7.204
7.178
7.153
6.983
6.958
6.855
6.841
6.815
4.051
3.496
3.477
3.466
3.320
2.874
2.848
2.823
1.890
1.867
1.839
1.817
1.697
1.677
1.649
1.587
F
NH
O
N
H
1i
0.92
1.43
1.87
3.84
1.10
0.93
1.86
1.00
1.83
1.90
1.97
f1 (ppm)

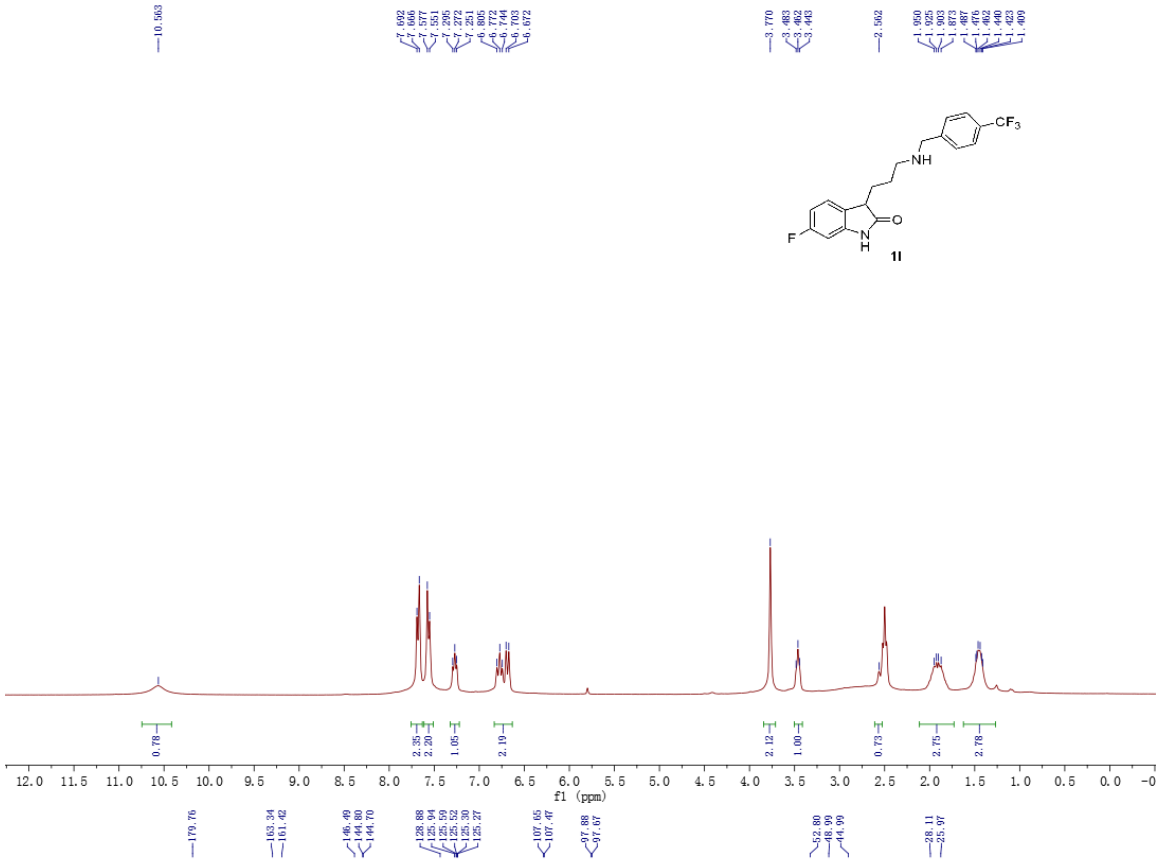

178.46
163.43
160.99
142.69
132.34
132.25
129.19
128.62
127.64
124.00
121.20
115.40
115.19
109.19
49.13
46.23
44.46
26.87
22.03
F
NH
O
N
H
1i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


116.73
F
NH
O
N
H
1i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

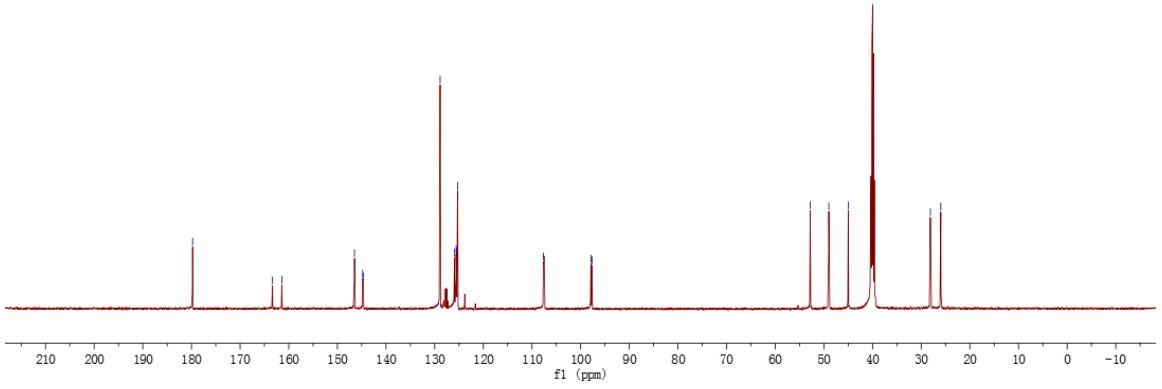

8.757
7.306
7.292
7.278
7.260
7.249
7.231
7.209
7.187
7.165
7.029
7.004
6.979
6.970
6.844
3.715
3.490
3.471
3.452
2.635
2.611
2.588
2.217
2.191
2.045
2.017
1.996
1.628
1.604
1.575
1.540
1.514
Cl
NH
O
N
H
1j
0.93
1.17
1.77
5.99
0.94
1.77
1.00
2.04
0.82
2.39
2.27
f1 (ppm)

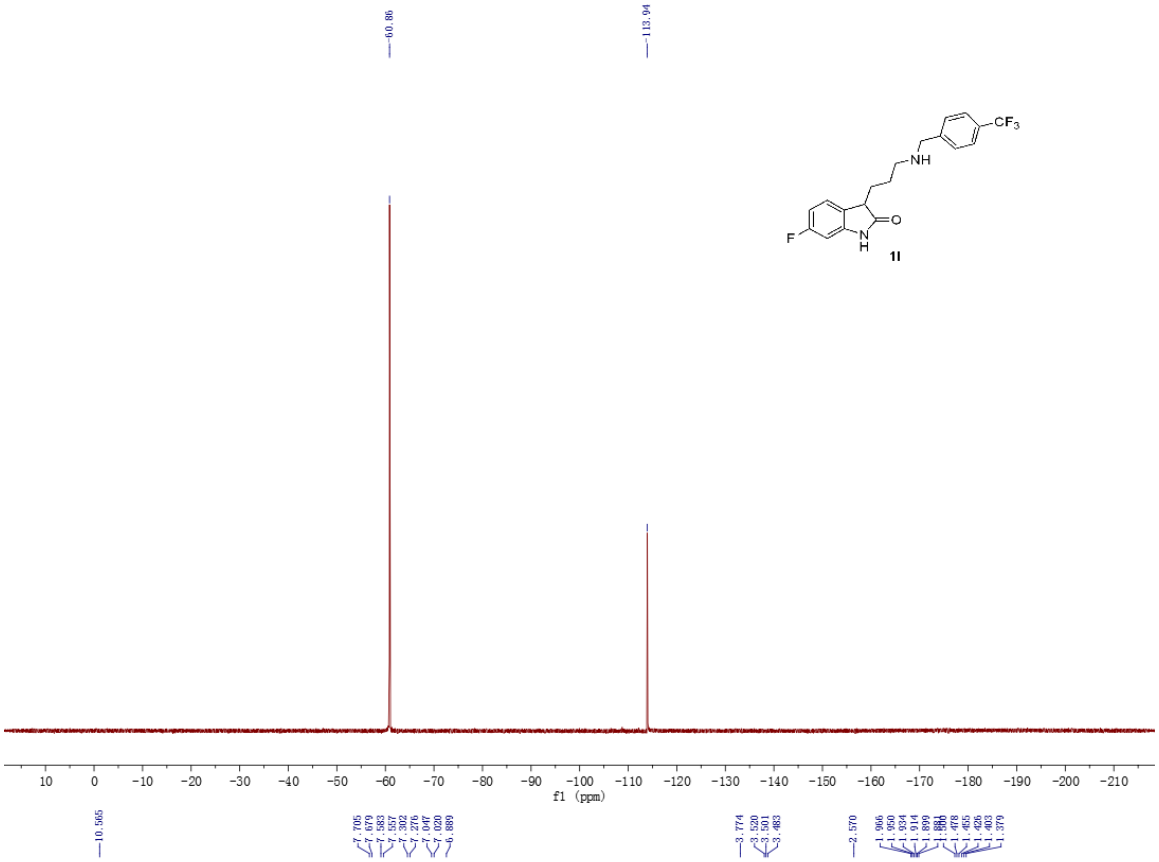

180.23
141.57
138.32
132.68
129.51
129.42
128.98
127.09
124.06
122.28
109.69
77.25
77.00
76.75
52.97
48.86
45.72
28.00
25.86
Cl
NH
O
N
H
1j
f1 (ppm)

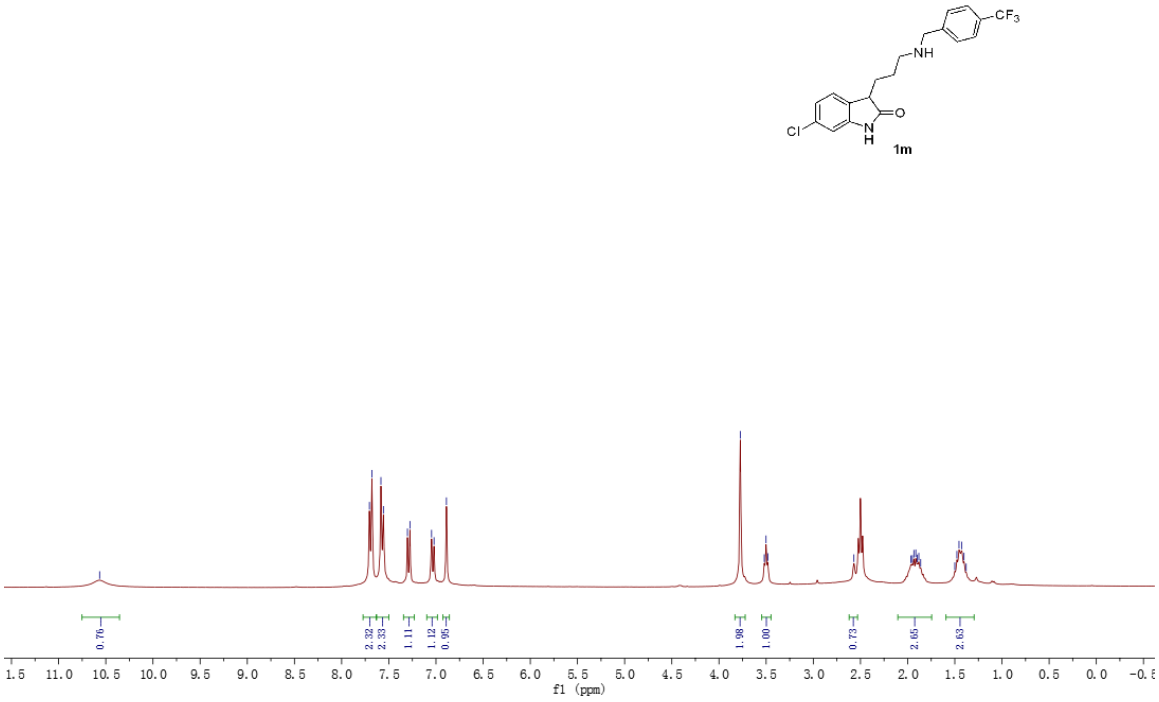

Br
NH
O
N
H
1k
f1 (ppm)

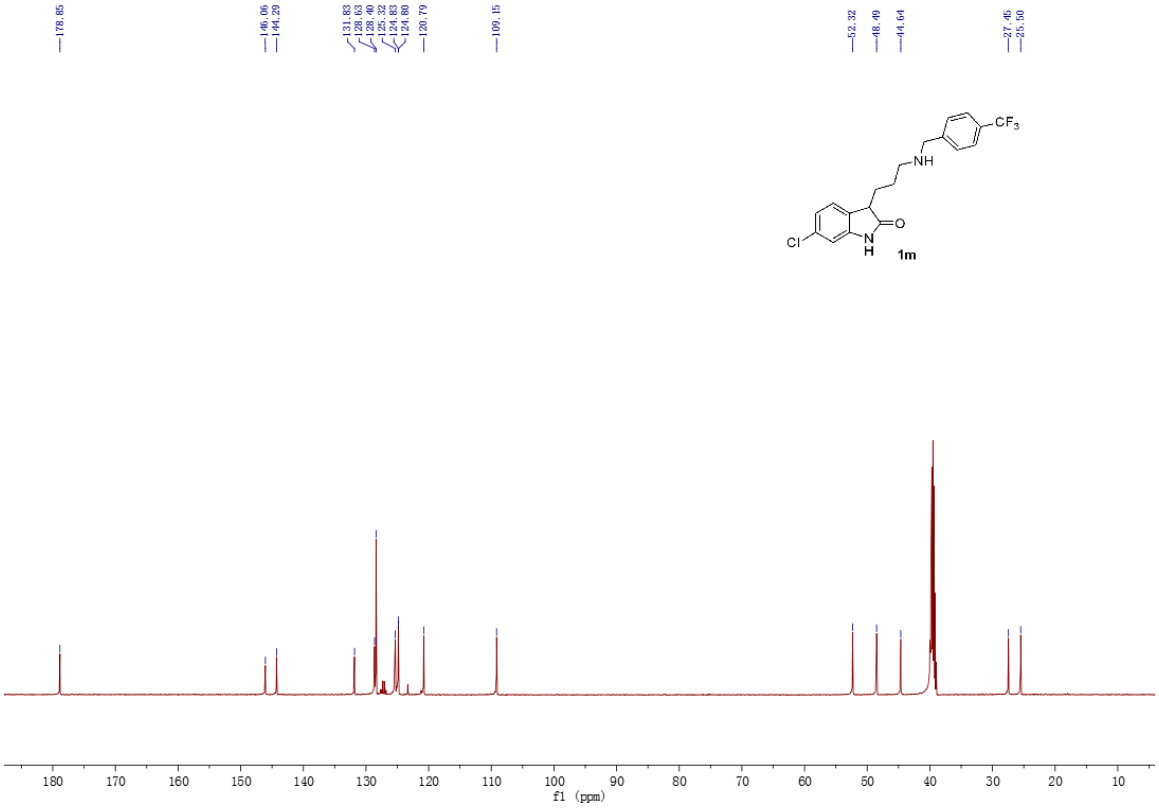

10.563
7.692
7.666
7.577
7.551
7.295
7.272
7.251
6.805
6.772
6.744
6.703
6.672
3.770
3.483
3.462
3.443
2.562
1.950
1.925
1.903
1.873
1.487
1.476
1.462
1.440
1.423
1.409
CF3
NH
O
N
H
F
1l
0.78
2.35
2.20
1.05
2.19
2.12
1.00
0.73
2.75
2.78
f1 (ppm)

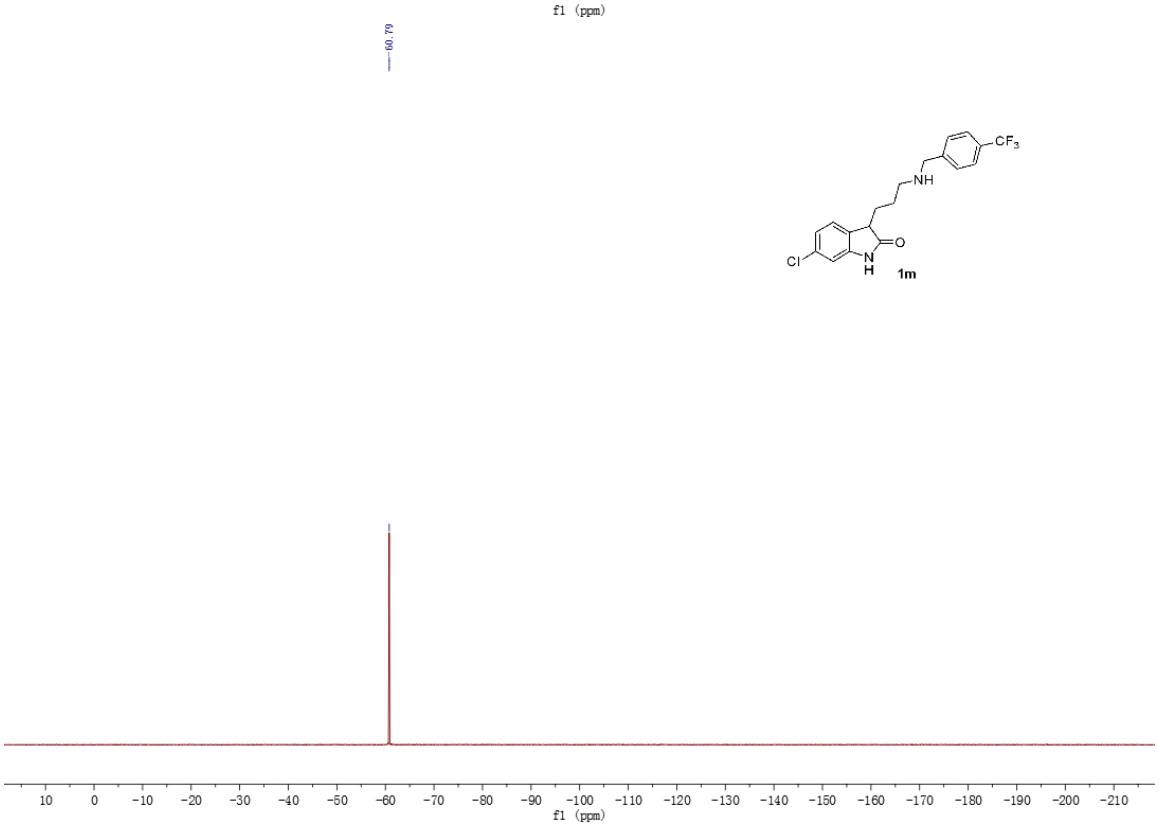

179.76
163.34
161.42
146.49
144.80
144.70
128.88
125.94
125.59
125.52
125.30
125.27
107.65
107.47
97.88
97.67
52.80
48.99
44.99
28.11
25.97
f1 (ppm)

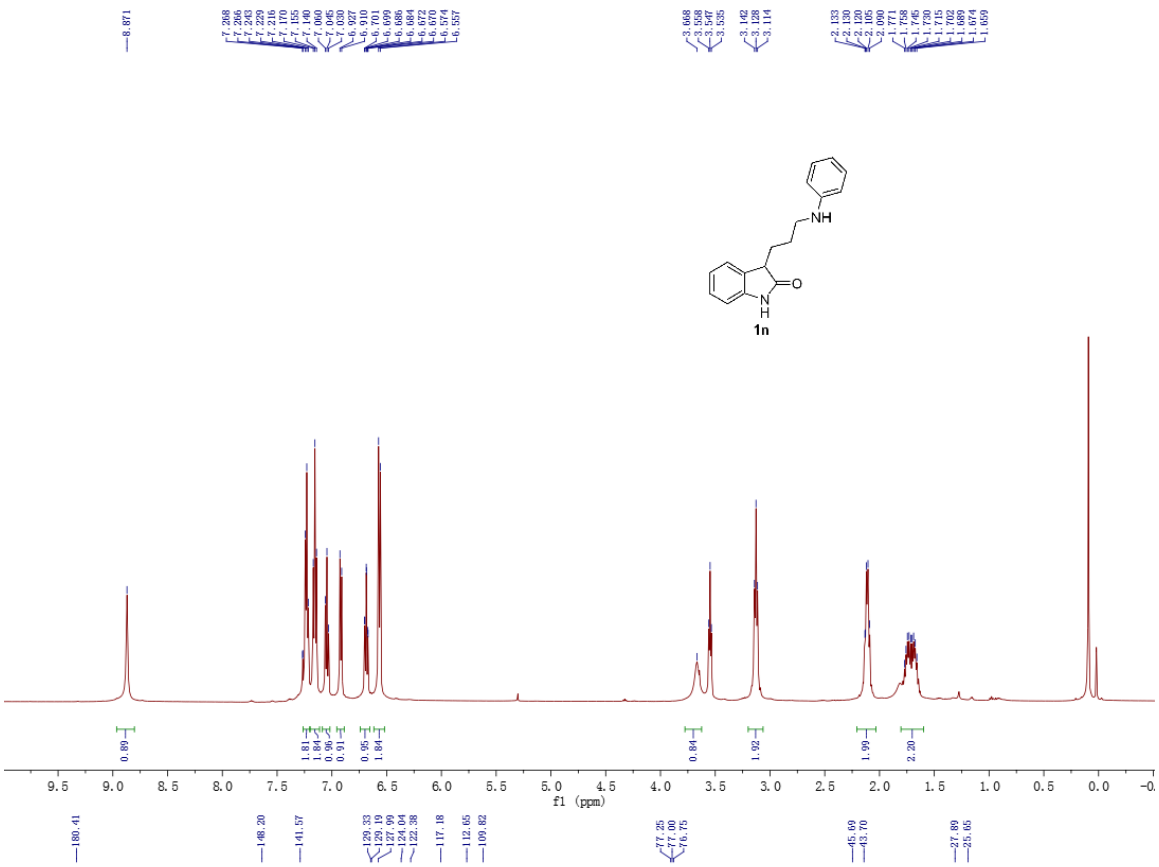

f1 (ppm)

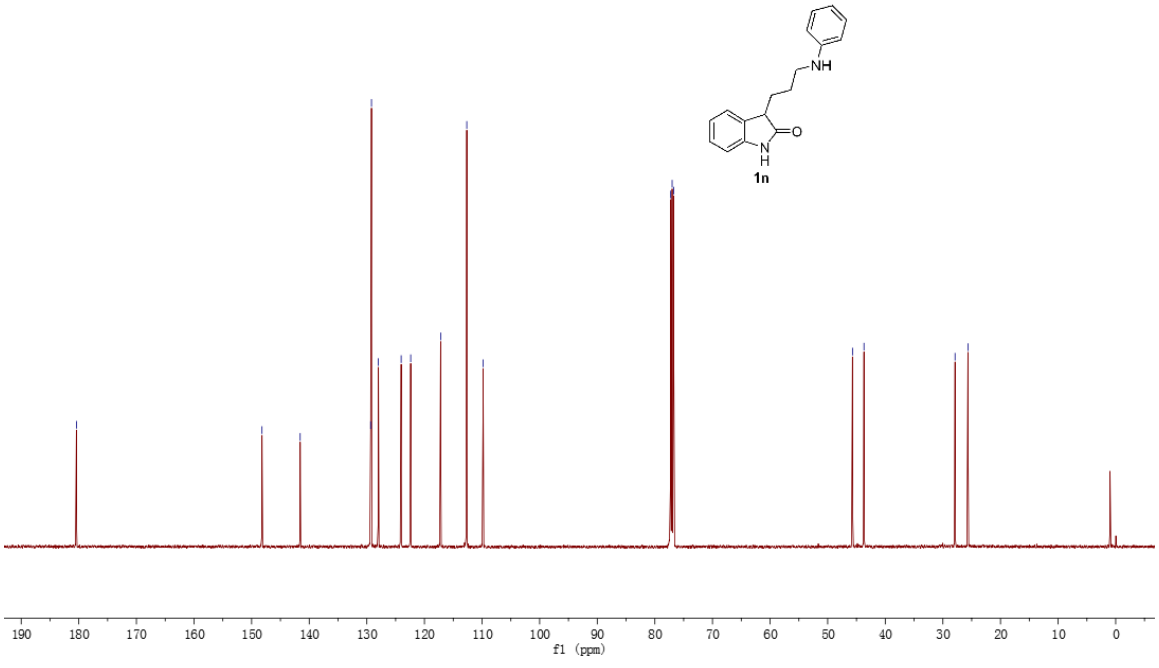

60.86
113.94
CF3
NH
O
N
H
F
1l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
10.565
7.706
7.679
7.583
7.557
7.302
7.276
7.047
7.020
6.889
3.774
3.520
3.501
3.483
2.570
1.966
1.950
1.934
1.914
1.899
1.881
1.865
1.496
1.476
1.465
1.426
1.403
1.379

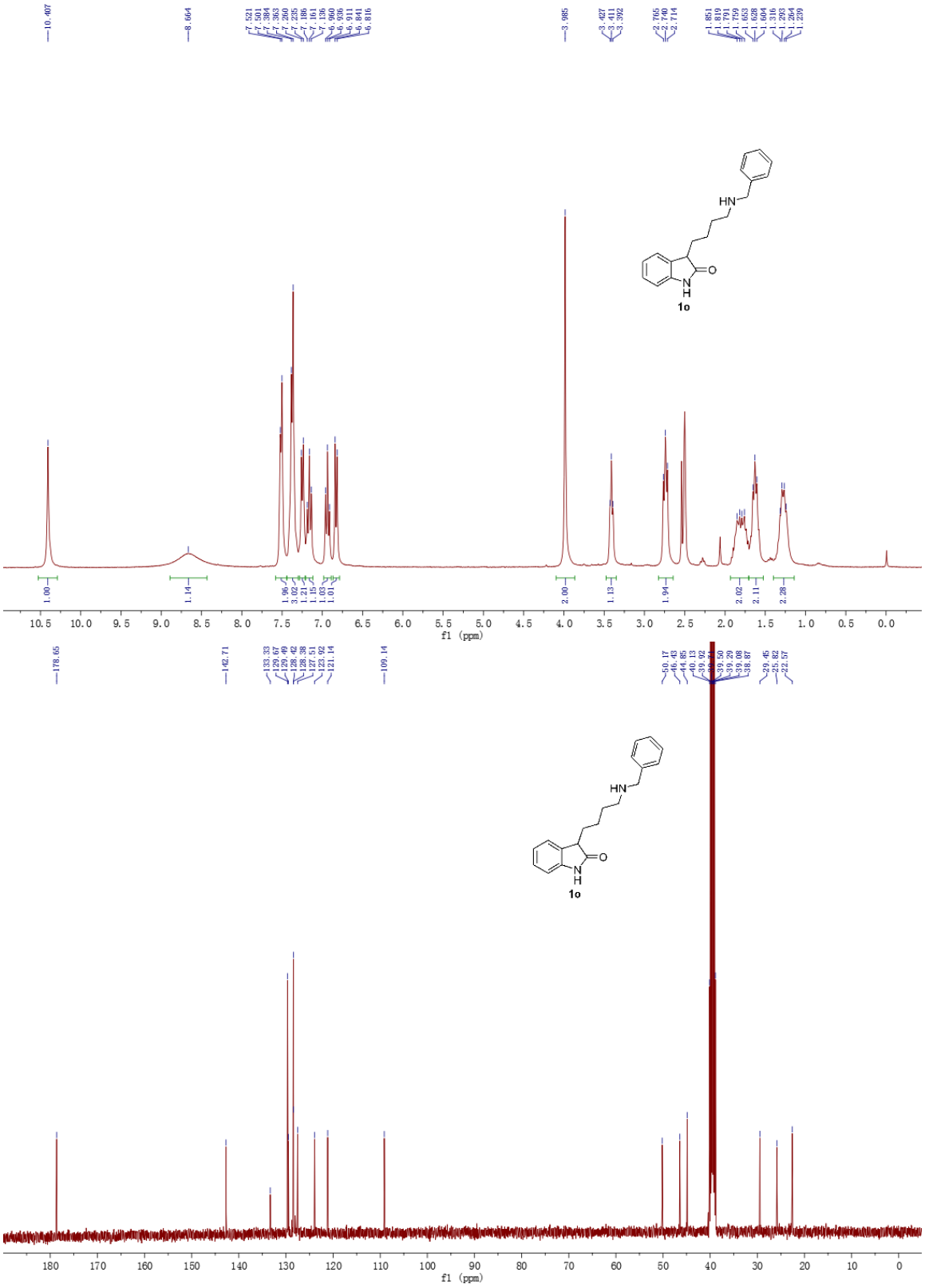

CF3
NH
O
N
H
Cl
1m
0.76
2.32
2.33
1.11
1.12
0.95
1.98
1.00
0.73
2.65
2.63
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

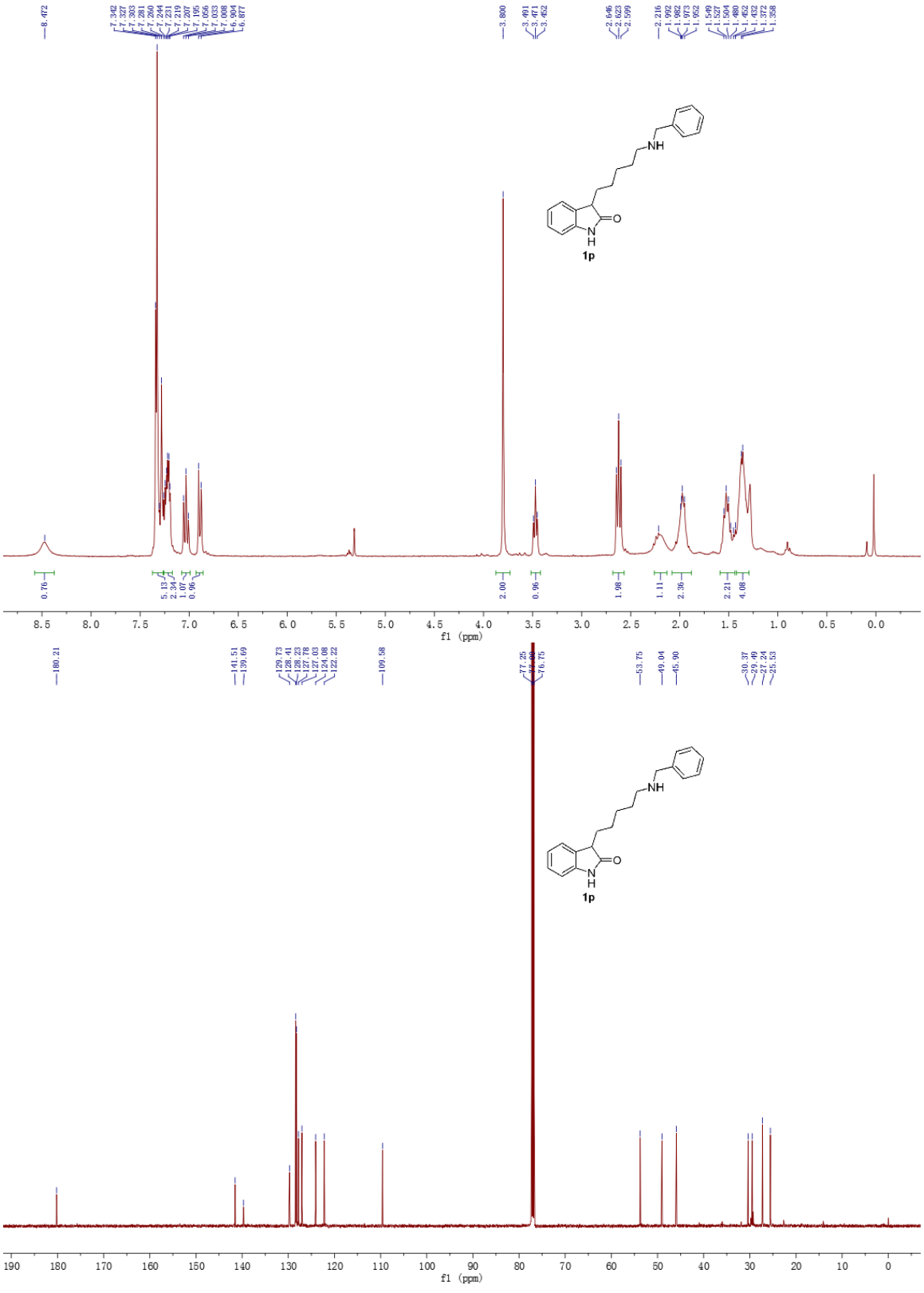

178.85
146.06
144.29
131.83
128.63
128.40
125.32
124.85
124.80
120.79
109.15
52.32
48.49
44.64
27.45
25.50
CF3
NH
O
N
H
Cl
1m
f1 (ppm)

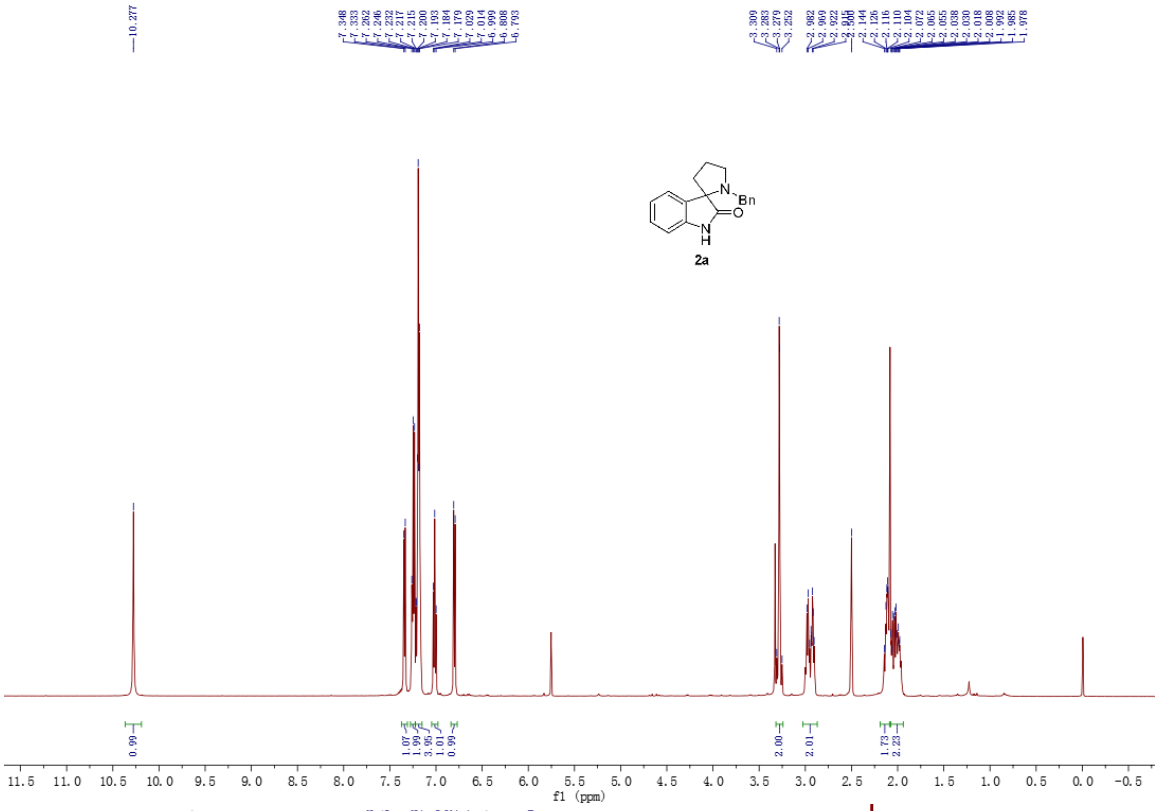

60.79
CF3
NH
O
N
H
Cl
1m
f1 (ppm)

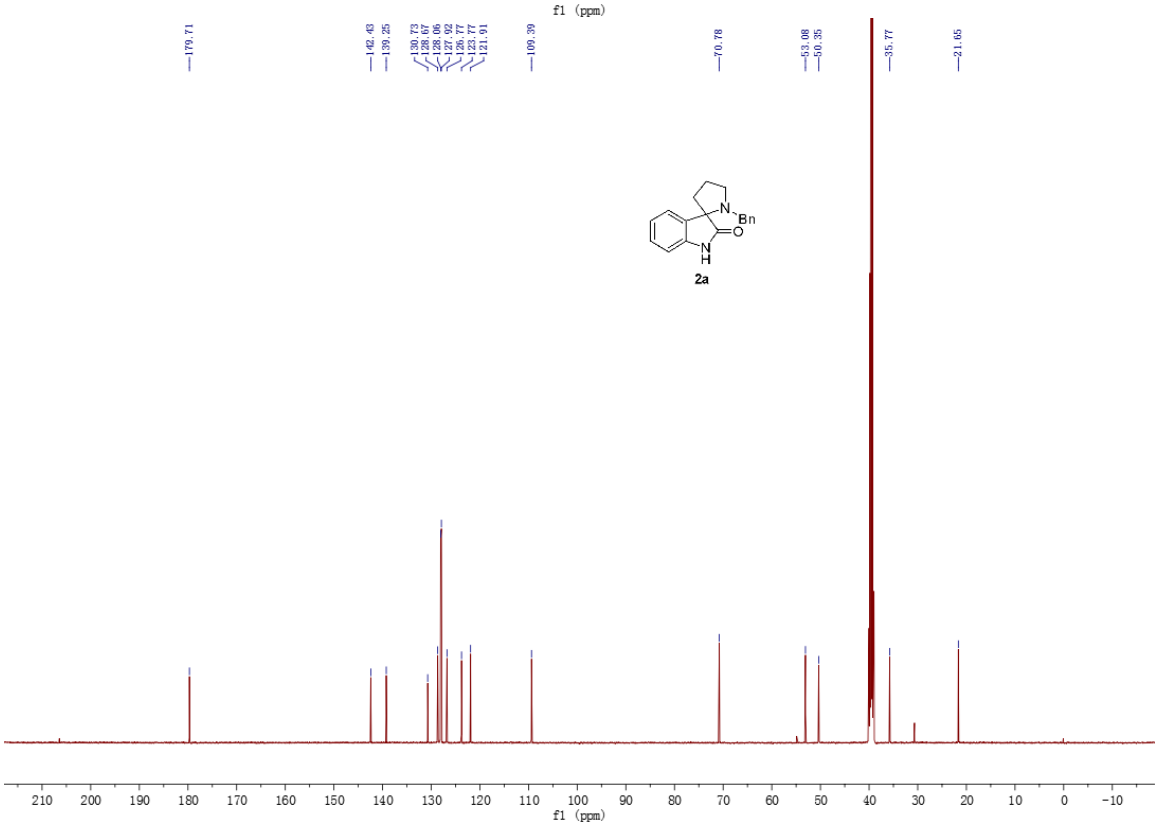

8.871
7.268
7.266
7.243
7.229
7.216
7.170
7.155
7.140
7.060
7.045
7.030
6.977
6.910
6.701
6.699
6.686
6.684
6.672
6.670
6.574
6.557
3.668
3.558
3.547
3.535
3.142
3.128
3.114
2.133
2.130
2.120
2.105
2.090
1.771
1.758
1.745
1.730
1.715
1.702
1.689
1.674
1.659
NH
O
N
H
1n
0.89
1.81
1.84
0.96
0.91
0.95
1.84
0.84
1.92
1.99
2.20
f1 (ppm)


180.41
148.20
141.57
129.33
129.19
127.99
124.04
122.38
117.18
112.65
109.82
77.25
77.00
76.75
45.69
43.70
27.89
25.65
NH
O
N
H
1n
f1 (ppm)


10.407
8.664
7.521
7.511
7.384
7.363
7.260
7.235
7.186
7.101
7.136
6.960
6.936
6.911
6.864
6.816
3.985
3.427
3.411
3.392
2.765
2.740
2.714
1.851
1.819
1.791
1.759
1.653
1.628
1.604
1.316
1.295
1.264
1.239
HN
O
N
H
1o
1.00
1.14
1.96
3.02
1.21
1.15
1.03
1.01
2.00
1.13
1.94
2.02
2.11
2.28
f1 (ppm)
178.65
142.71
133.33
129.67
129.49
128.42
128.38
127.53
123.92
121.14
109.14
50.17
46.45
44.65
40.13
39.92
39.71
39.50
39.29
39.08
38.87
29.45
25.82
22.57
HN
O
N
H
1o
f1 (ppm)


8.472
7.342
7.327
7.303
7.281
7.260
7.244
7.231
7.219
7.207
7.195
7.056
7.033
7.008
6.904
6.877
3.800
3.491
3.471
3.452
2.646
2.623
2.599
2.216
1.992
1.982
1.973
1.952
1.549
1.527
1.504
1.480
1.452
1.432
1.372
1.358
NH
O
N
H
1p
0.70
5.13
2.34
1.07
0.98
2.00
0.96
1.98
1.11
2.38
2.21
4.08
f1 (ppm)
180.21
141.51
139.69
129.73
128.41
128.23
127.78
127.03
125.08
122.22
109.58
77.25
77.00
76.75
53.75
49.04
45.90
30.37
29.49
27.24
25.53
NH
O
N
H
1p
f1 (ppm)

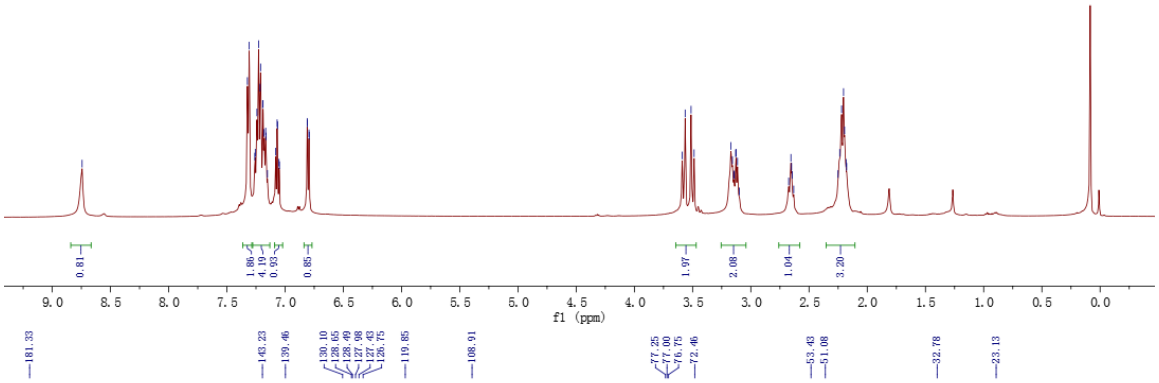

10.277
7.348
7.333
7.282
7.246
7.232
7.217
7.215
7.200
7.193
7.184
7.179
7.029
7.014
6.998
6.808
6.793
3.309
3.283
3.279
3.252
2.982
2.969
2.922
2.905
2.144
2.126
2.116
2.110
2.104
2.072
2.065
2.055
2.038
2.030
2.018
2.008
1.992
1.985
1.978
Bn
N
O
H
2a
0.99
1.07
1.99
3.95
1.01
0.99
2.00
2.01
1.73
2.23
f1 (ppm)


179.71
142.43
139.25
130.73
128.67
128.06
127.92
126.77
123.77
121.91
109.39
70.78
53.08
50.35
35.77
21.65
Bn
N
O
H
2a
f1 (ppm)




Br
N
Bn
O
N
H

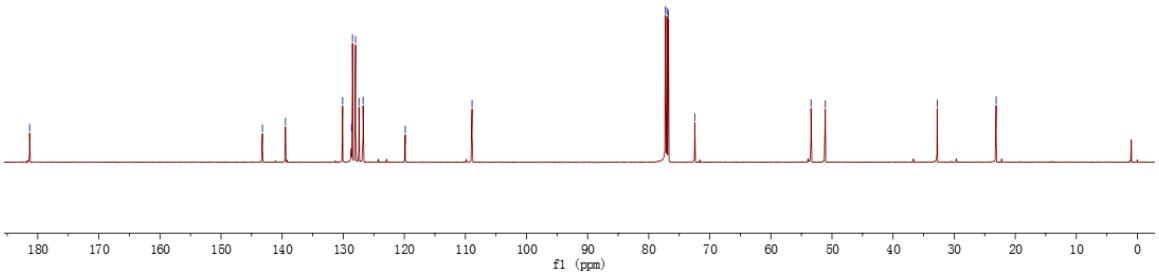
2b

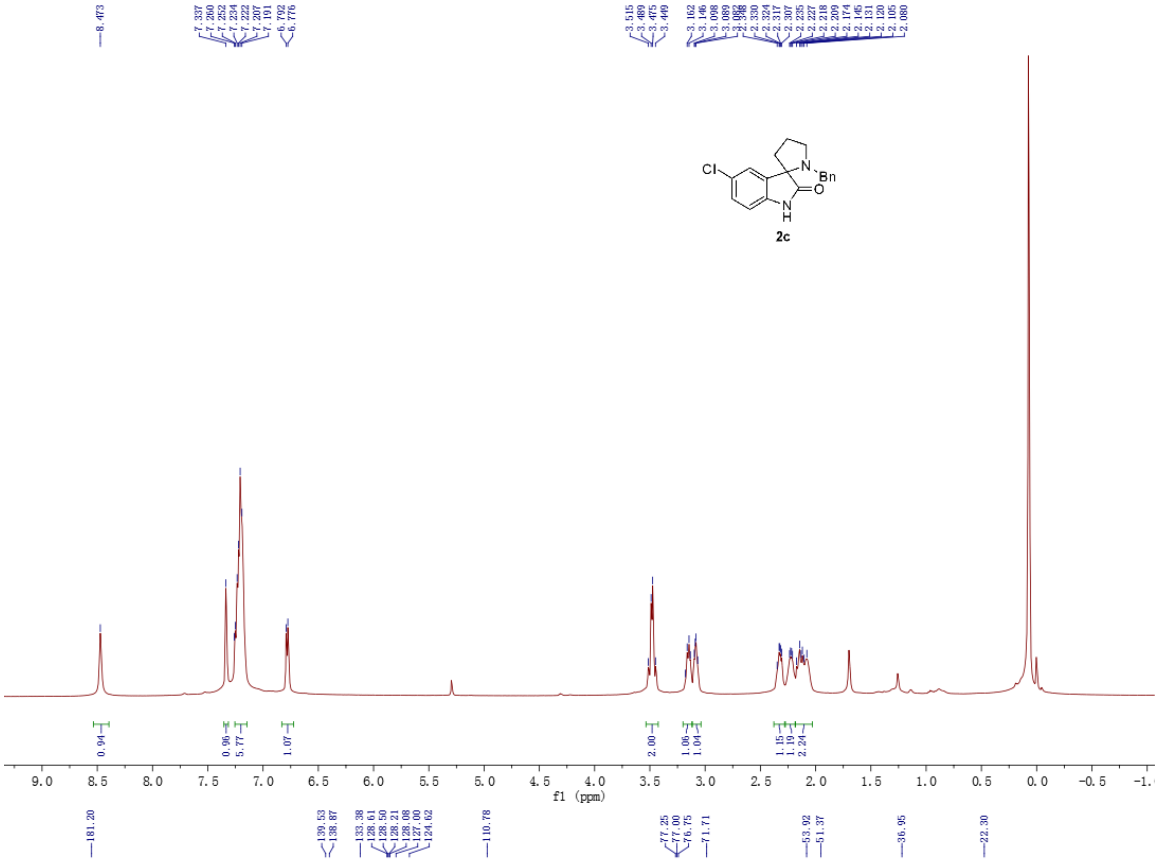

0.81
1.86
4.19
0.93
0.85
1.97
2.08
1.04
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

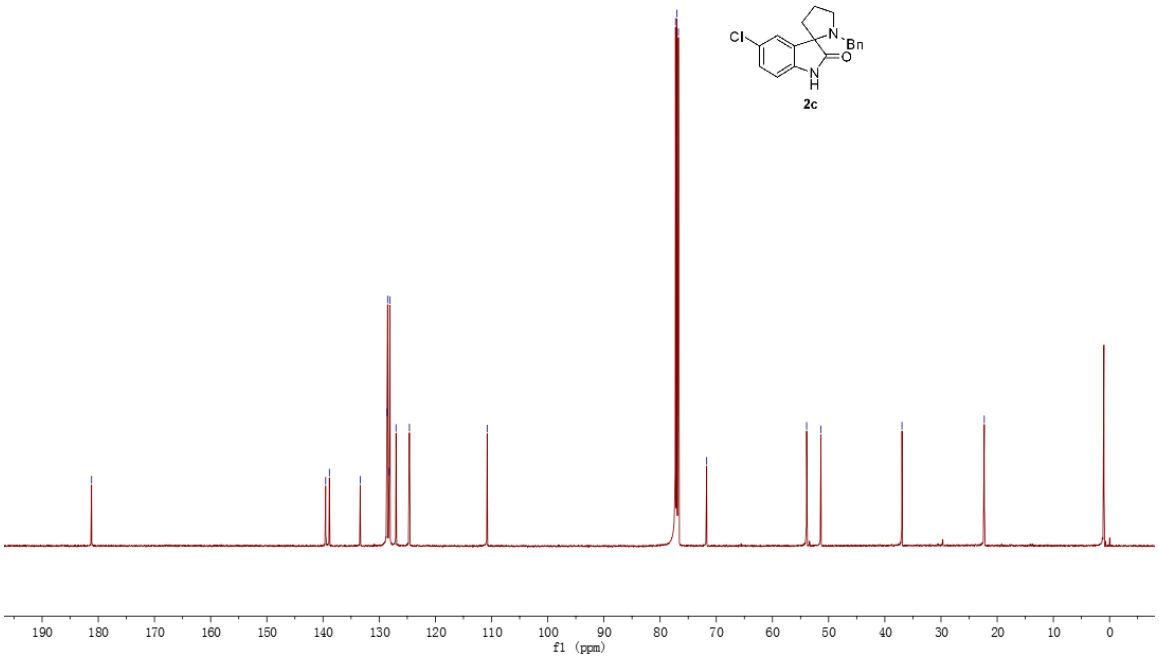


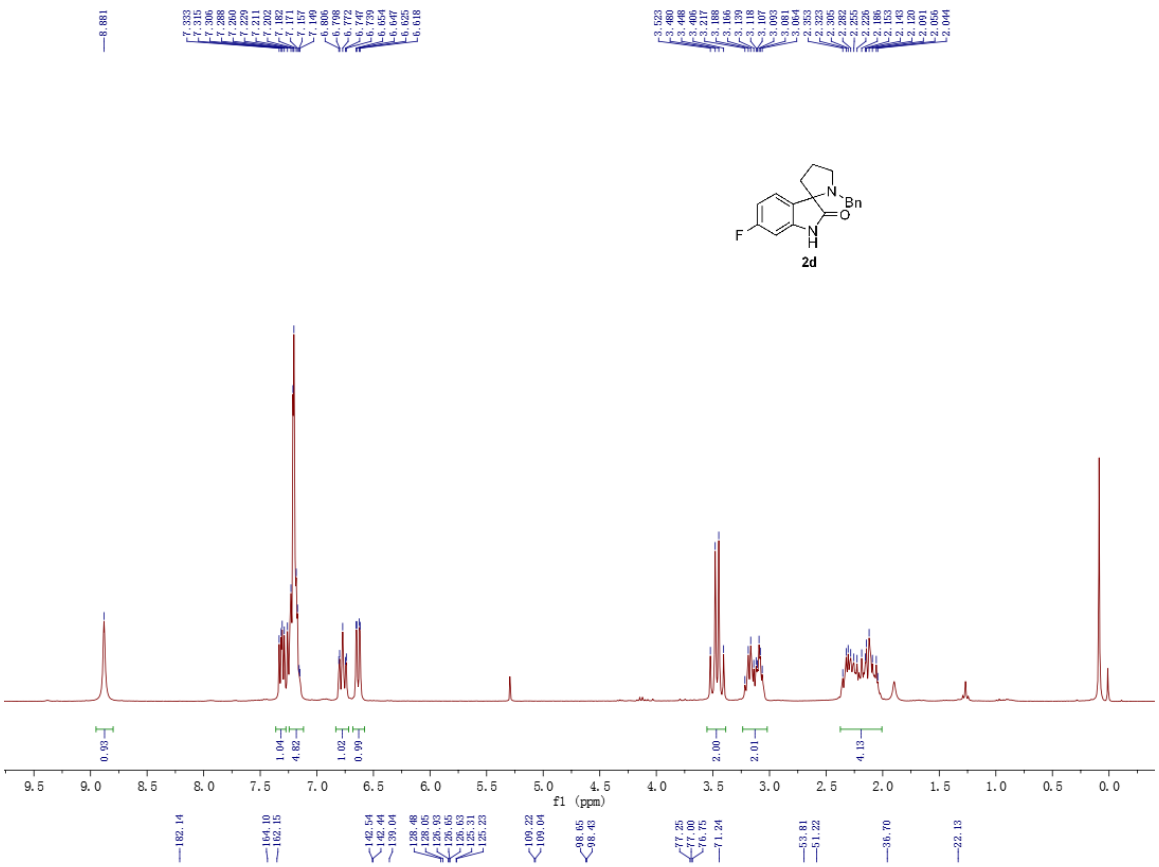

Br
N
Bn
O
N
H

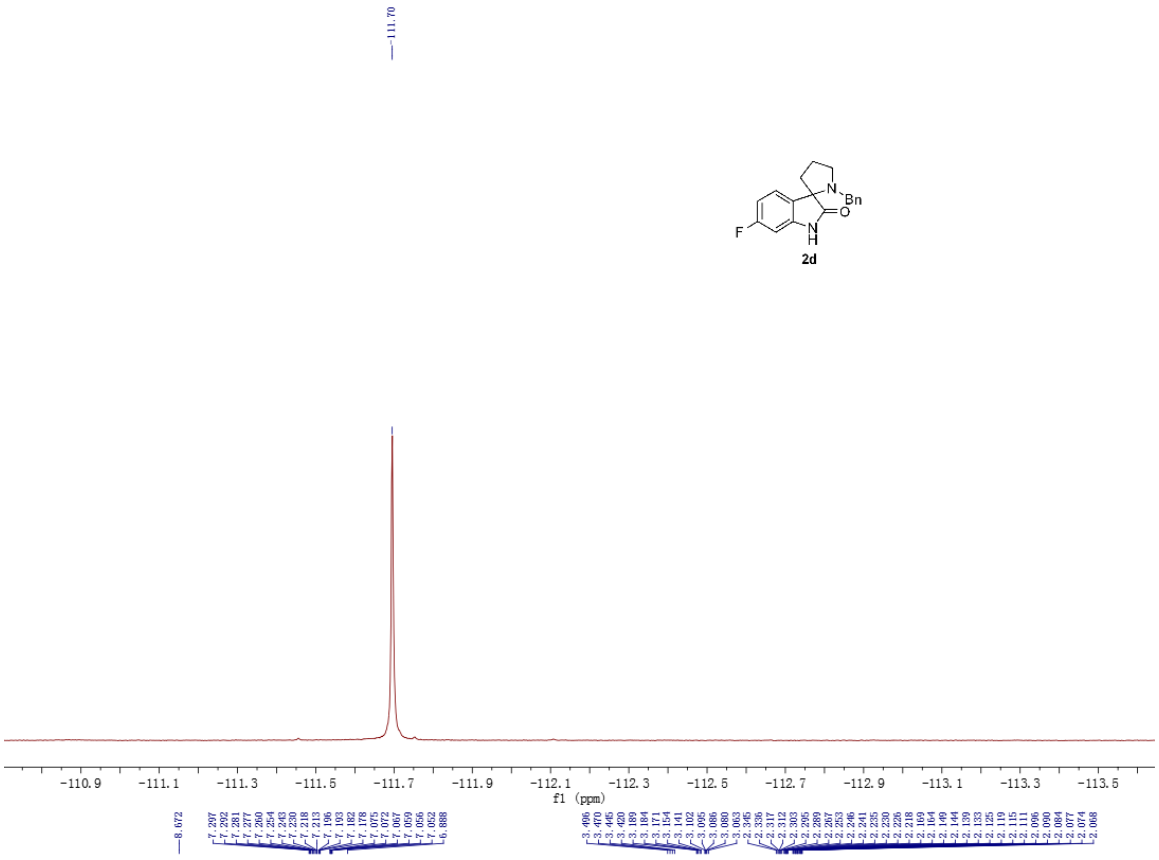
2b

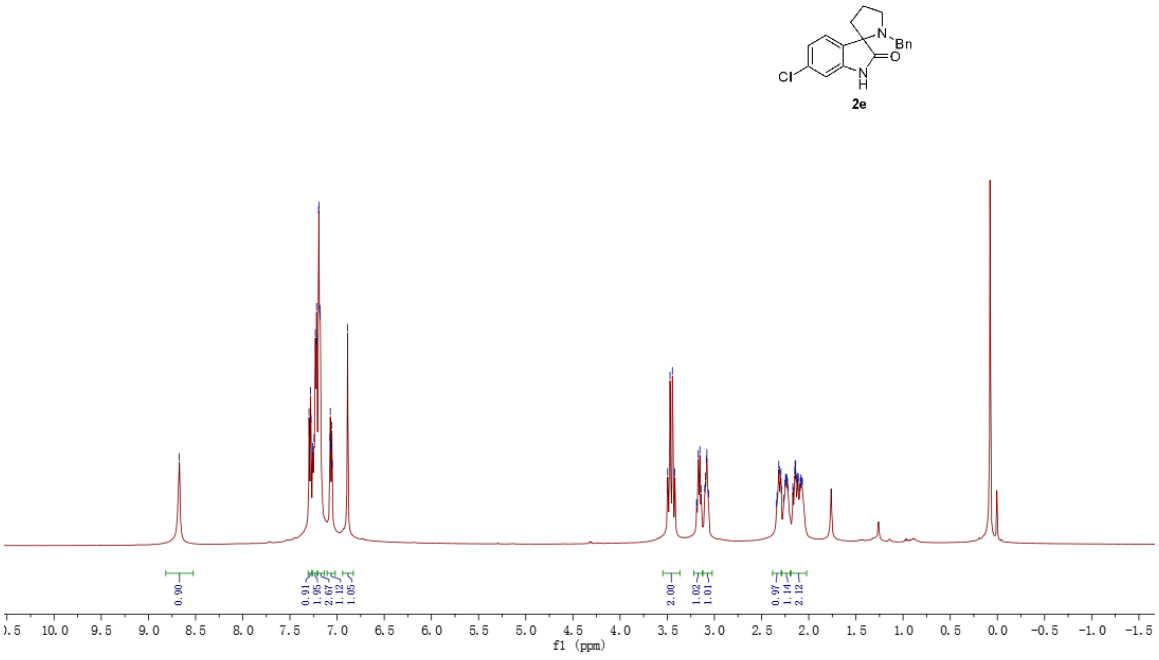

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

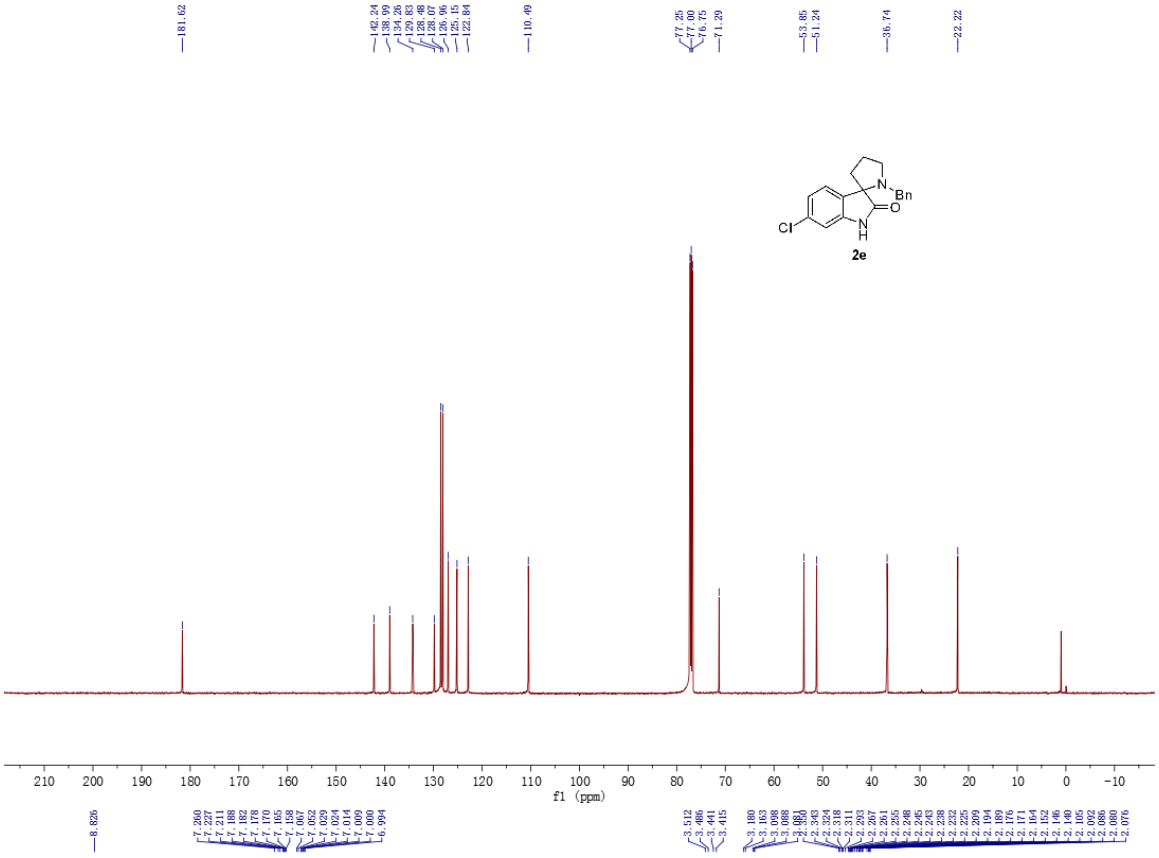

8.473
7.337
7.260
7.252
7.234
7.222
7.207
7.191
6.792
6.776
3.515
3.489
3.475
3.449
3.162
3.146
3.098
3.089
3.082
3.073
3.066
2.330
2.324
2.317
2.307
2.295
2.227
2.218
2.209
2.174
2.145
2.131
2.120
2.105
2.080
Cl
N
Bn
O
N
H
2c
0.94
0.96
5.77
1.07
2.00
1.06
1.04
1.15
1.19
2.24
f1 (ppm)
181.20
139.53
138.87
133.38
128.61
128.50
128.21
128.08
127.00
124.62
110.78
77.25
77.00
76.75
71.71
53.92
51.37
36.95
22.30

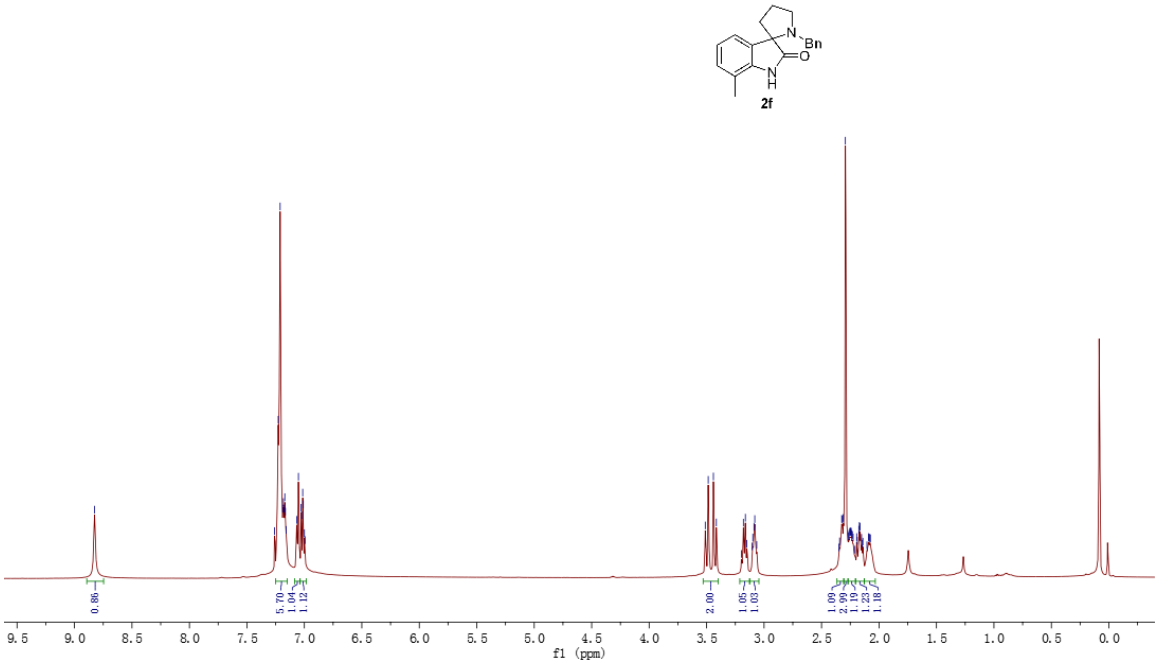

Cl
N
Bn
O
N
H
2c
f1 (ppm)

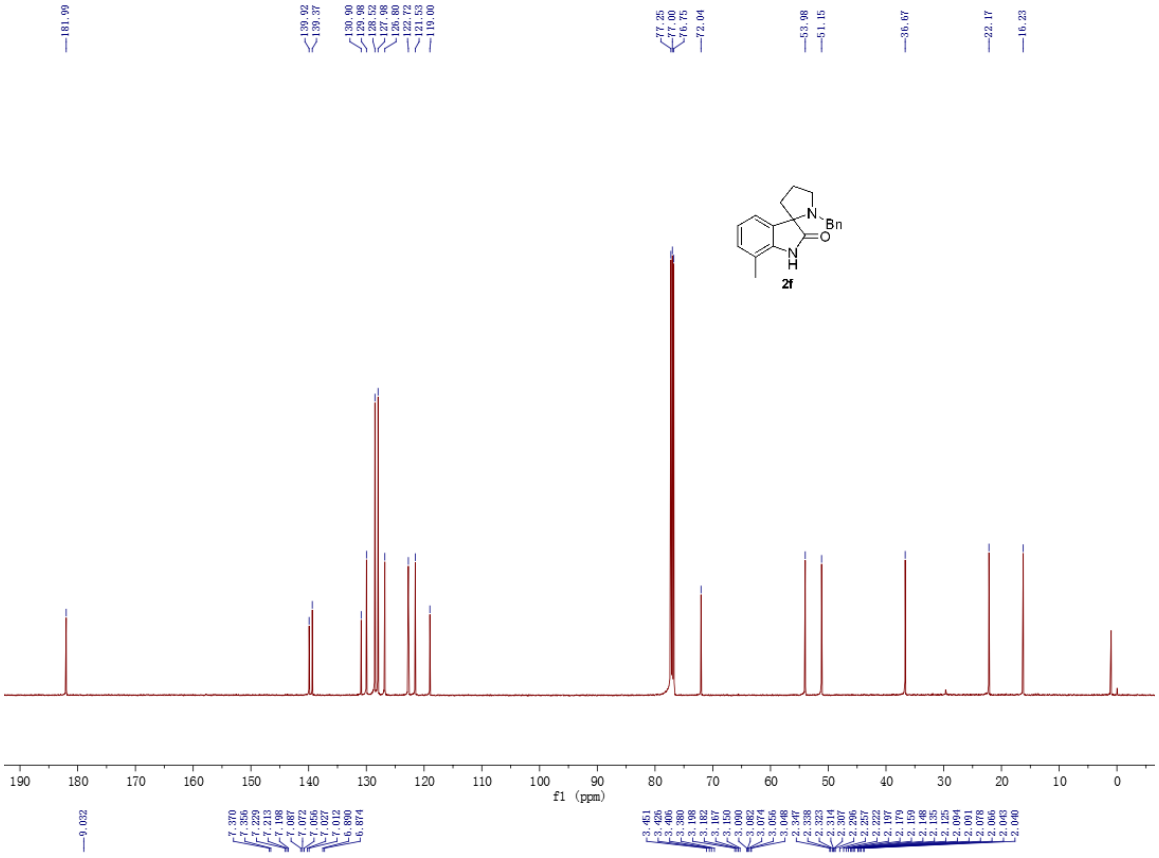

8.881
7.333
7.315
7.306
7.288
7.260
7.229
7.211
7.202
7.182
7.171
7.157
7.149
6.998
6.988
6.772
6.747
6.739
6.654
6.647
6.625
6.618
3.523
3.480
3.448
3.406
3.217
3.188
3.166
3.139
3.118
3.107
3.093
3.081
3.064
2.353
2.323
2.305
2.282
2.255
2.226
2.186
2.153
2.143
2.109
2.091
2.056
2.044
N
Bn
O
F
H
2d
0.93
1.04
4.82
1.02
0.99
2.00
2.01
4.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
182.14
164.10
162.15
142.54
142.44
139.04
128.48
128.05
126.93
126.86
126.63
125.31
125.23
109.22
109.04
98.65
98.43
77.25
77.00
76.75
71.24
53.81
51.22
36.70
22.13
N
Bn
O
F
H
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

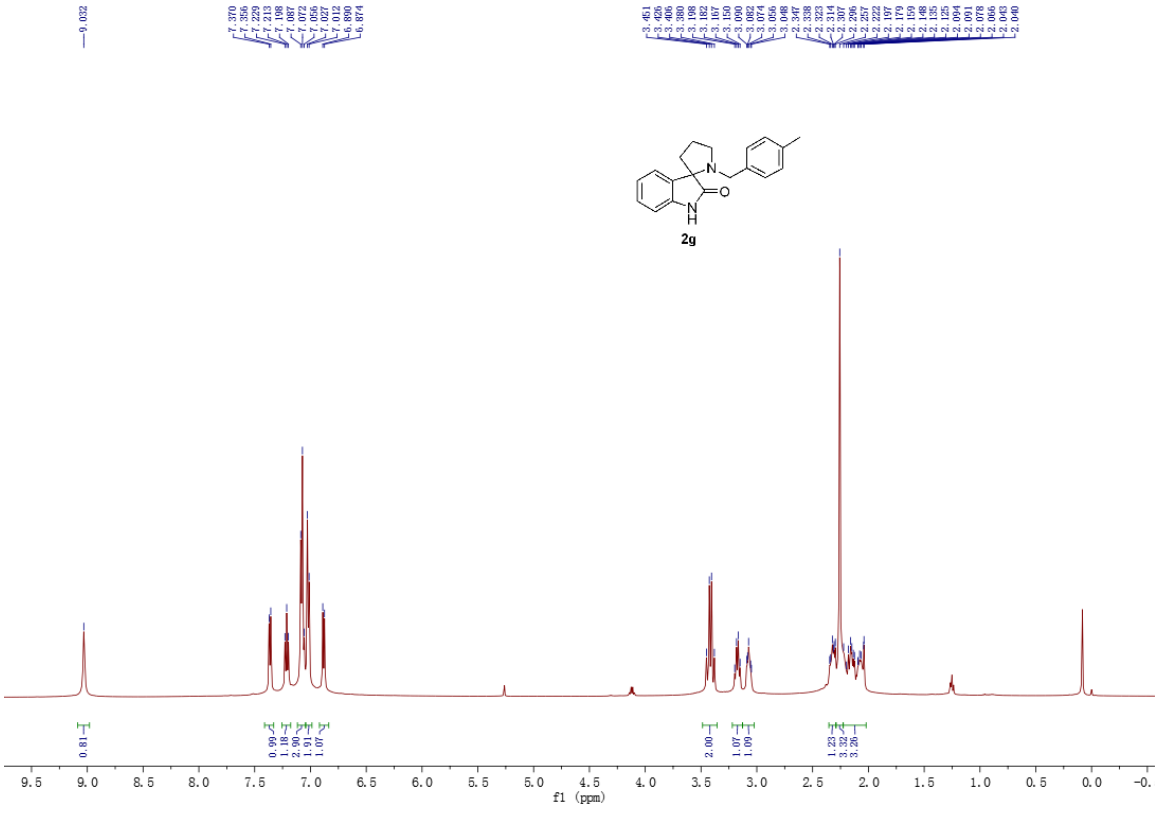

111.70
F
N
Bn
O
H
2d
-110.9
-111.1
-111.3
-111.5
-111.7
-111.9
-112.1
-112.3
-112.5
-112.7
-112.9
-113.1
-113.3
-113.5
f1 (ppm)

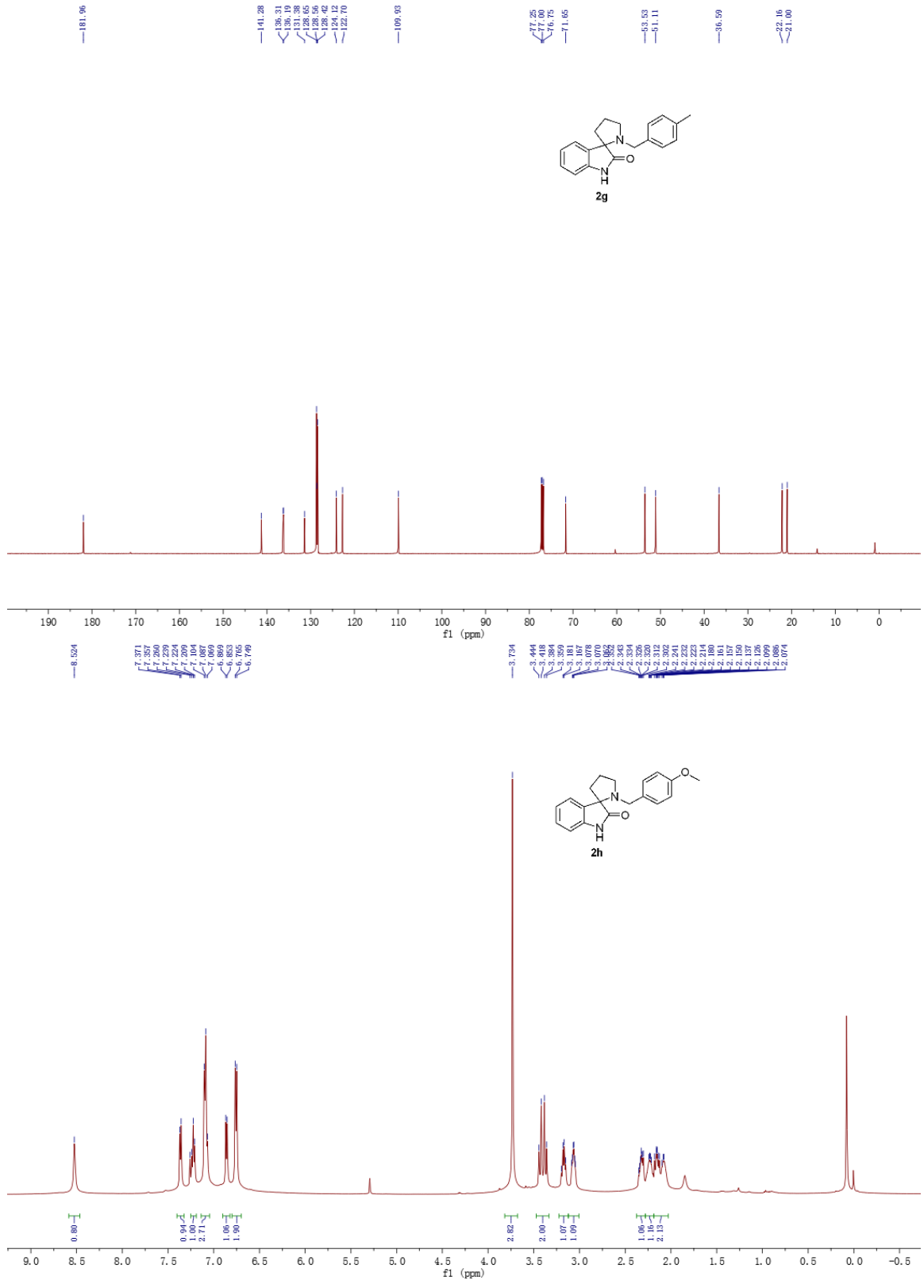

Cl
N
Bn
O
H
2e
f1 (ppm)

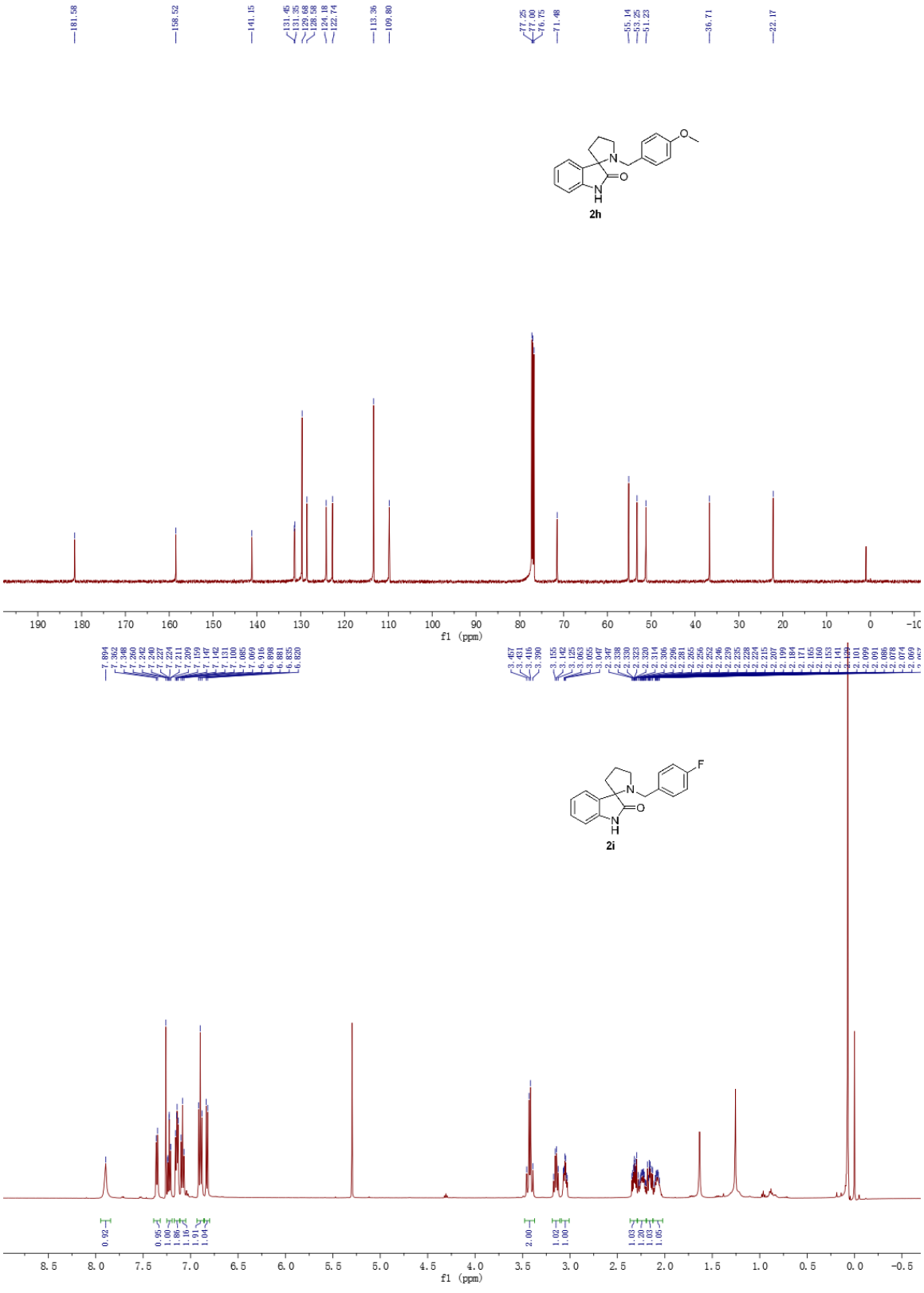

181.62
142.24
138.99
134.26
129.83
128.88
128.07
126.96
125.15
122.84
110.49
77.25
77.00
76.75
71.29
53.85
51.24
36.74
22.22
Cl
N
Bn
O
N
H
2e
f1 (ppm)
8.826
7.260
7.227
7.211
7.188
7.182
7.178
7.170
7.165
7.158
7.067
7.052
7.034
7.024
7.014
7.009
7.000
6.994
3.512
3.486
3.441
3.415
3.180
3.163
3.098
3.088
2.350
2.343
2.334
2.318
2.311
2.293
2.267
2.261
2.255
2.248
2.245
2.243
2.238
2.232
2.225
2.209
2.194
2.189
2.176
2.171
2.164
2.152
2.146
2.140
2.105
2.092
2.086
2.080
2.076

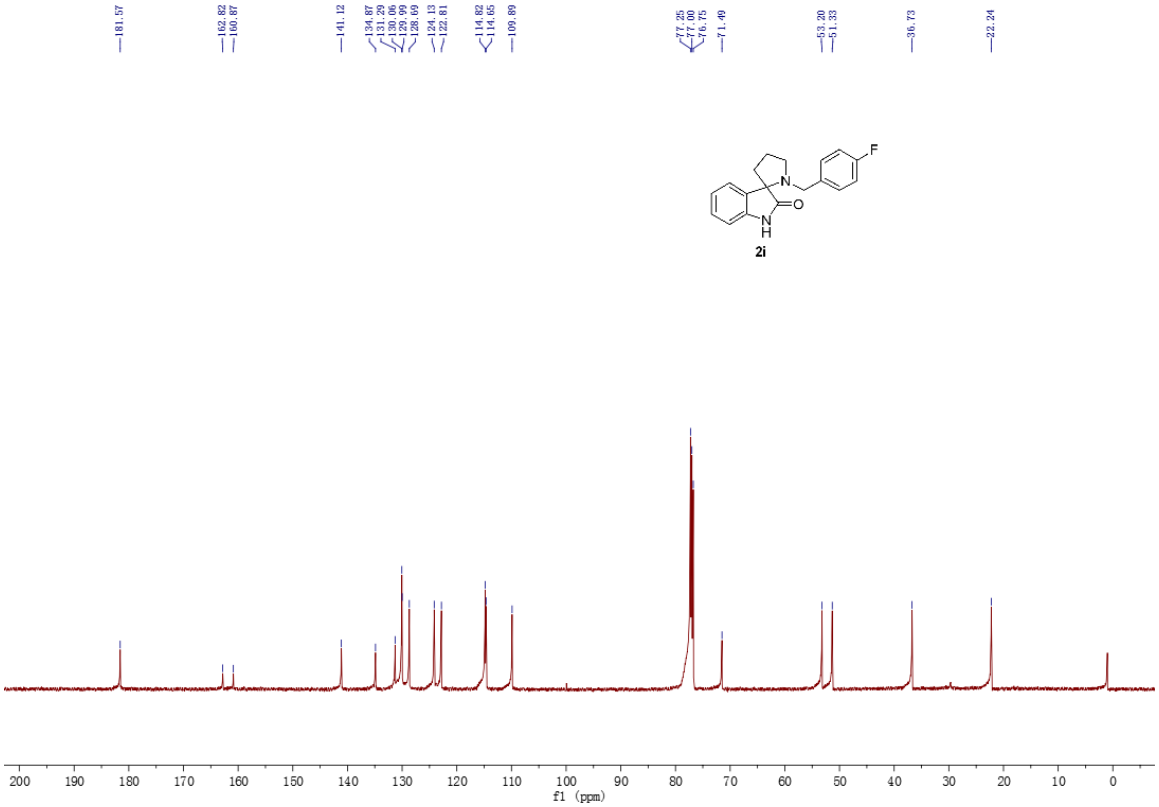

N
Bn
O
N
H
2f
0.86
5.70
1.04
1.12
2.00
1.05
1.03
1.09
2.89
1.23
1.18
f1 (ppm)

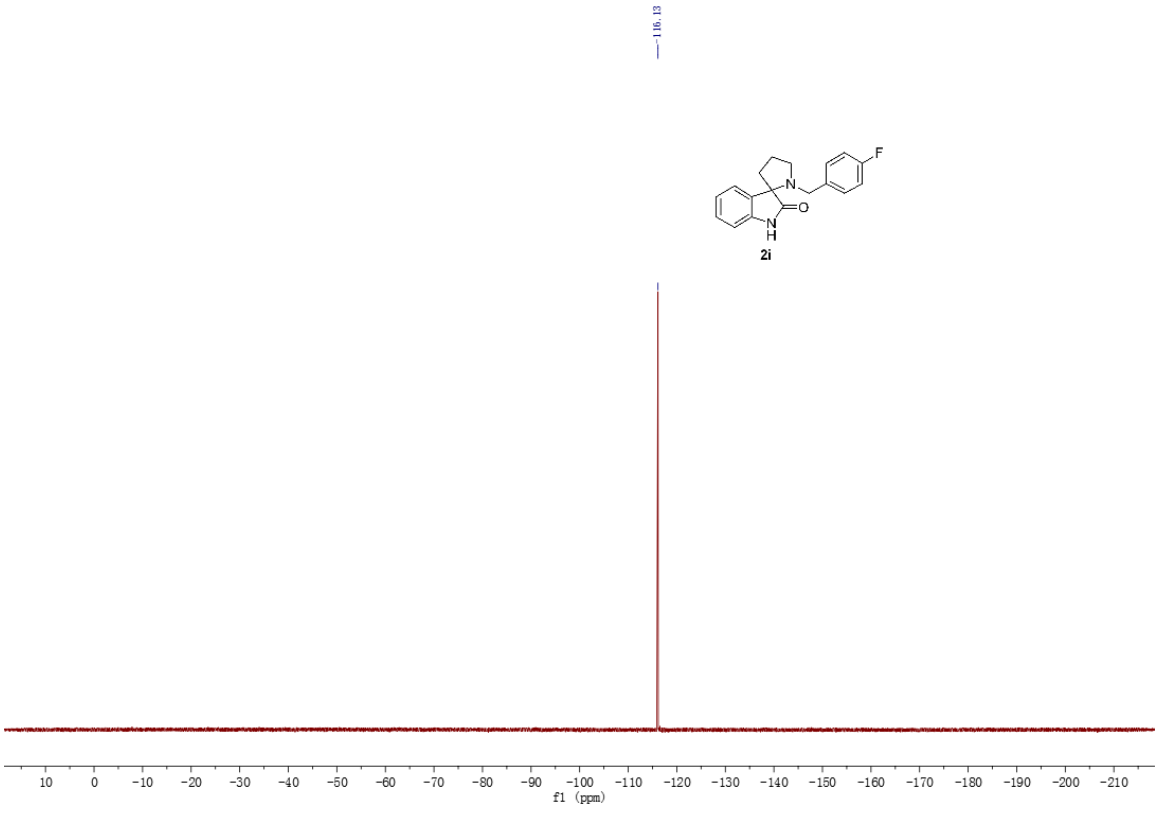

181.99
139.92
139.37
130.90
129.98
128.52
127.98
126.80
122.72
121.53
119.00
77.25
77.00
76.75
72.04
53.98
51.15
36.67
22.17
16.23
Bn
N
O
H
2f
f1 (ppm)

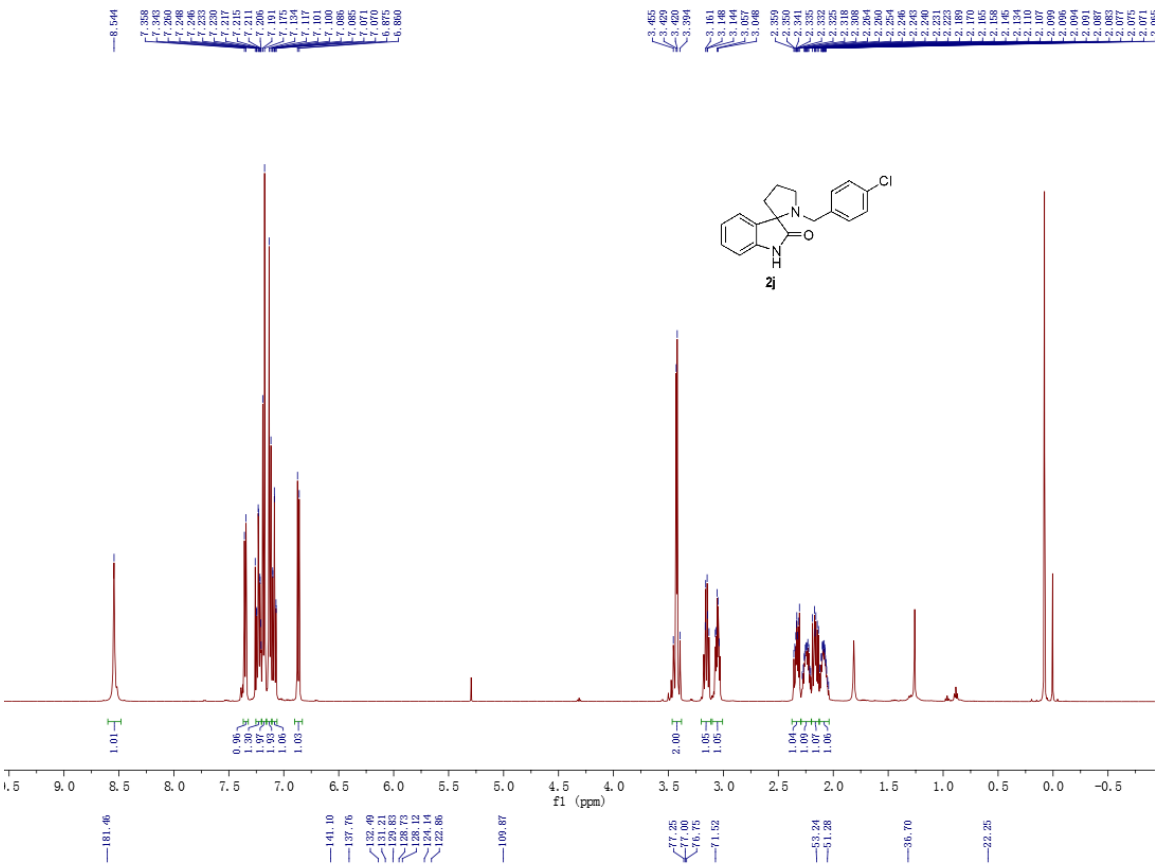

9.032
7.370
7.356
7.229
7.213
7.198
7.087
7.072
7.056
7.027
7.013
6.890
6.874
3.451
3.425
3.406
3.380
3.198
3.182
3.167
3.150
3.090
3.082
3.074
3.056
3.048
2.347
2.338
2.323
2.314
2.307
2.296
2.257
2.222
2.197
2.179
2.159
2.148
2.135
2.125
2.094
2.091
2.078
2.066
2.043
2.040
N
O
H
2g
f1 (ppm)

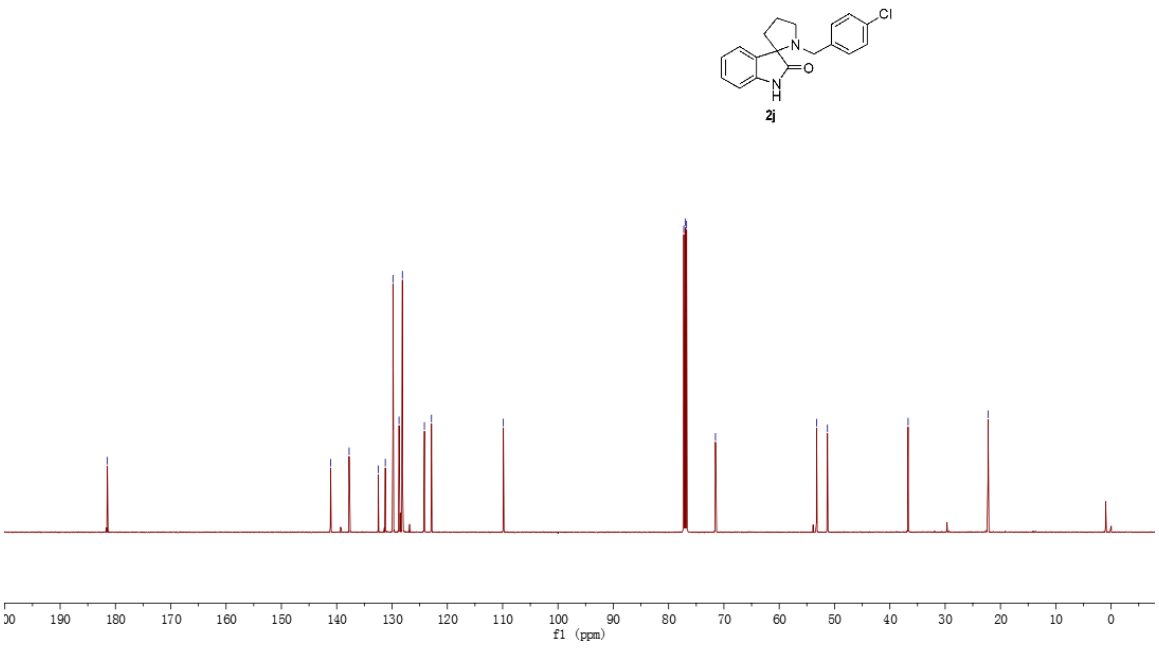

181.96
141.28
136.31
136.19
131.38
128.65
128.36
128.42
124.12
122.70
109.93
77.25
77.00
76.75
71.65
53.53
51.11
36.59
22.16
21.00
2g
f1 (ppm)
8.524
7.371
7.357
7.260
7.239
7.224
7.209
7.104
7.087
7.069
6.869
6.853
6.795
6.749
3.734
3.444
3.418
3.384
3.369
3.181
3.167
3.078
3.070
2.343
2.334
2.326
2.320
2.312
2.302
2.241
2.232
2.223
2.214
2.180
2.161
2.157
2.150
2.135
2.126
2.099
2.086
2.074
2h
f1 (ppm)
0.80
0.94
1.00
2.71
1.06
1.90
2.82
2.00
1.07
1.09
1.06
1.15
2.10

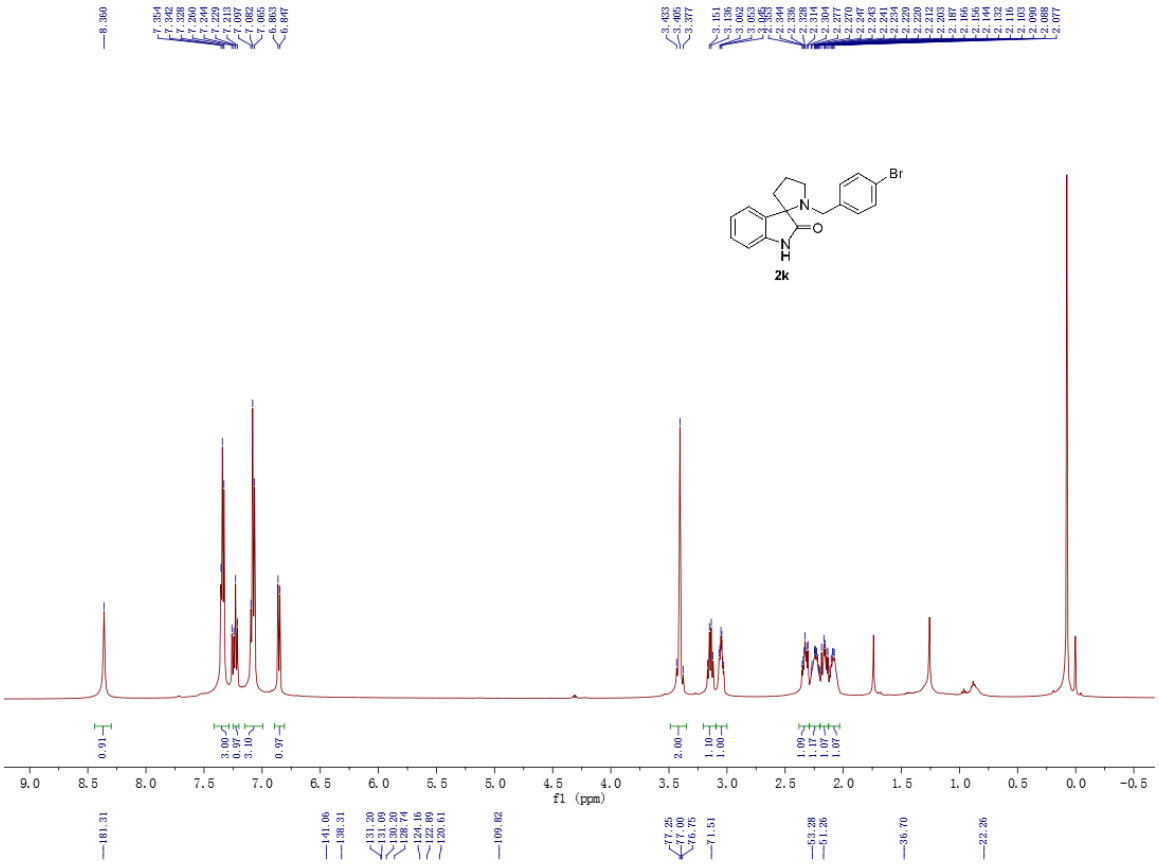

181.58
158.52
141.15
131.45
131.35
129.68
128.98
124.18
122.74
113.36
109.80
77.25
77.00
76.75
71.48
55.14
53.35
51.23
36.71
22.17
2h
f1 (ppm)
2i
f1 (ppm)

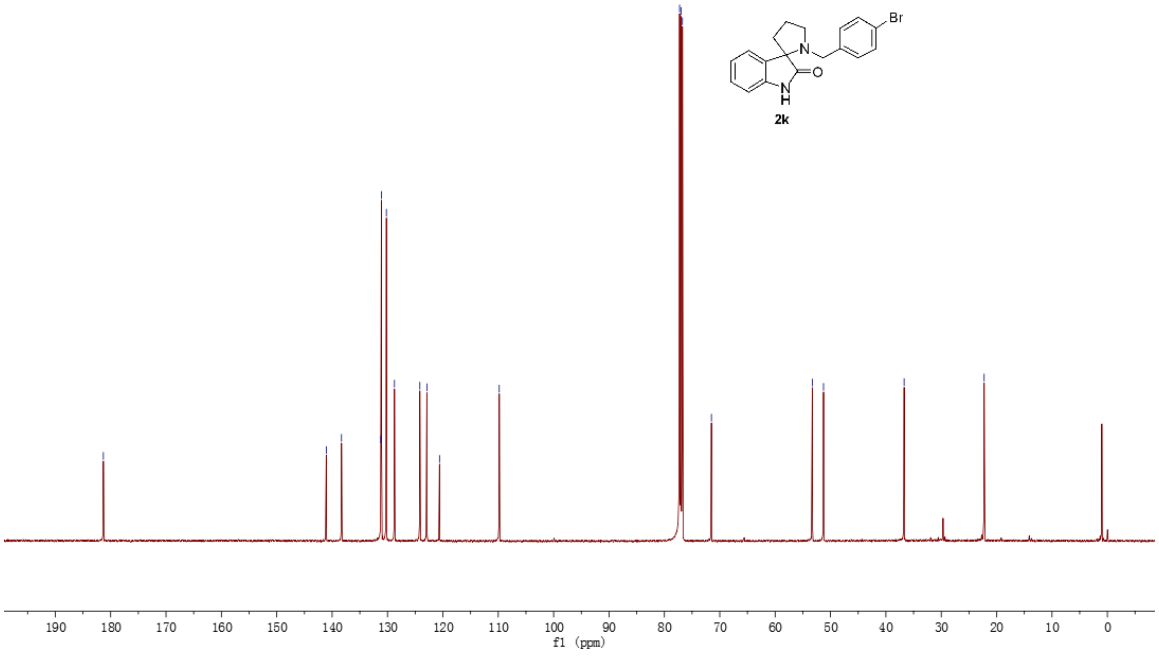

181.57
162.82
160.87
141.12
134.87
131.29
130.06
129.99
128.69
124.13
122.81
114.82
114.65
109.89
77.25
77.00
76.75
71.49
53.20
51.33
36.73
22.24
F
N
O
N
H
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

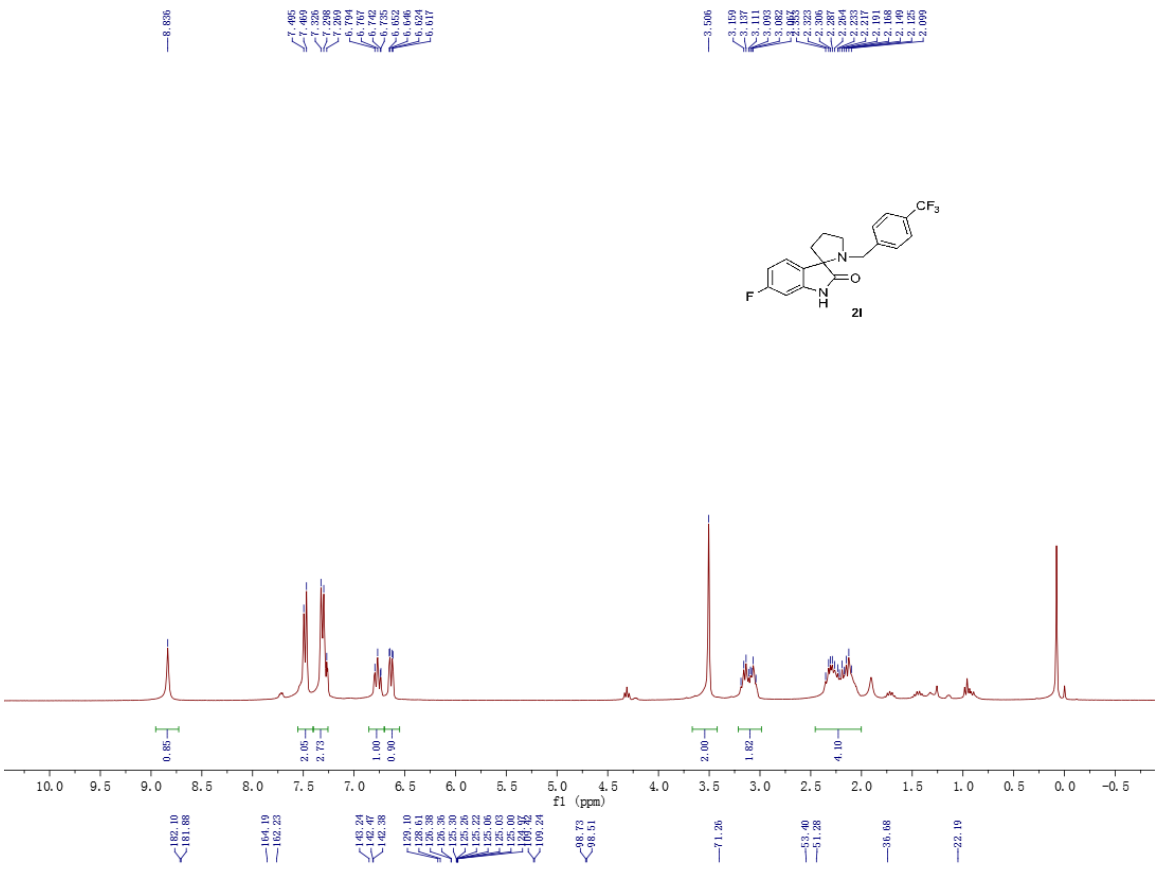

-116.13
F
N
O
N
H
2i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

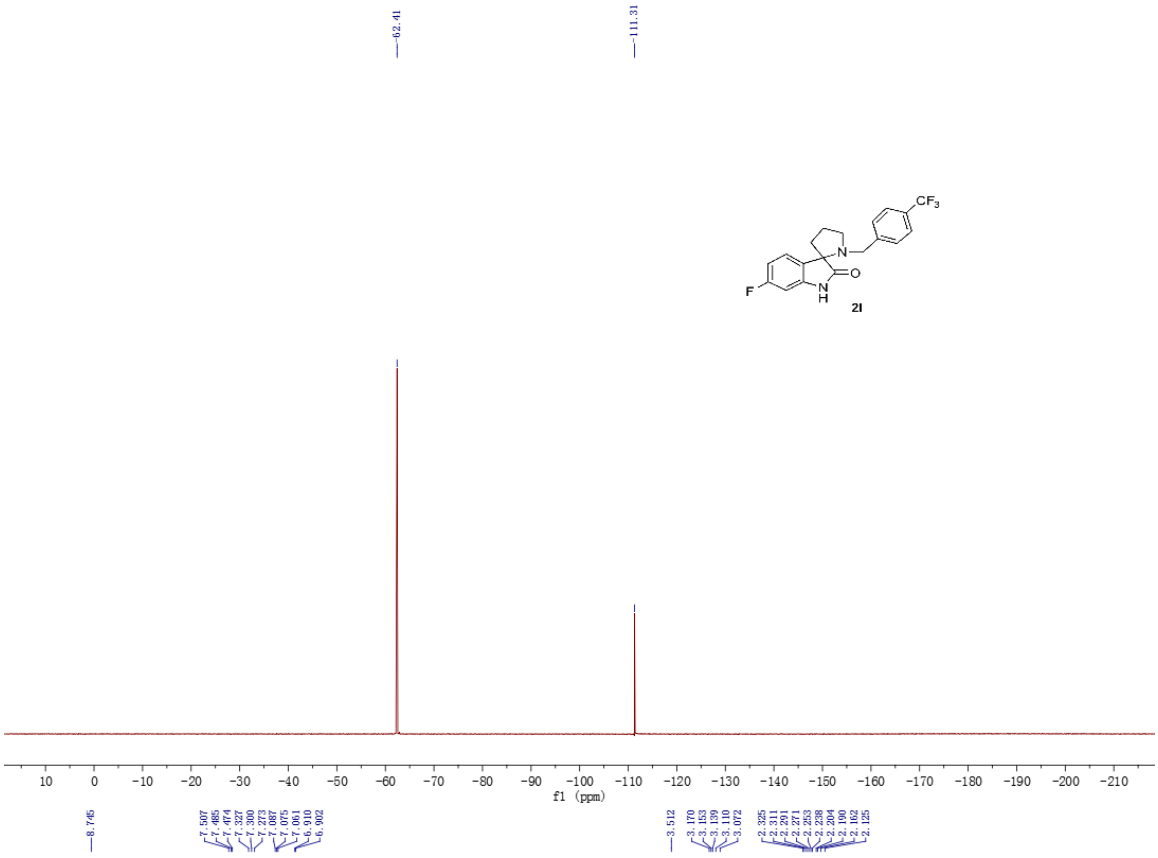

Cl
N
O
N
H
2j
f1 (ppm)

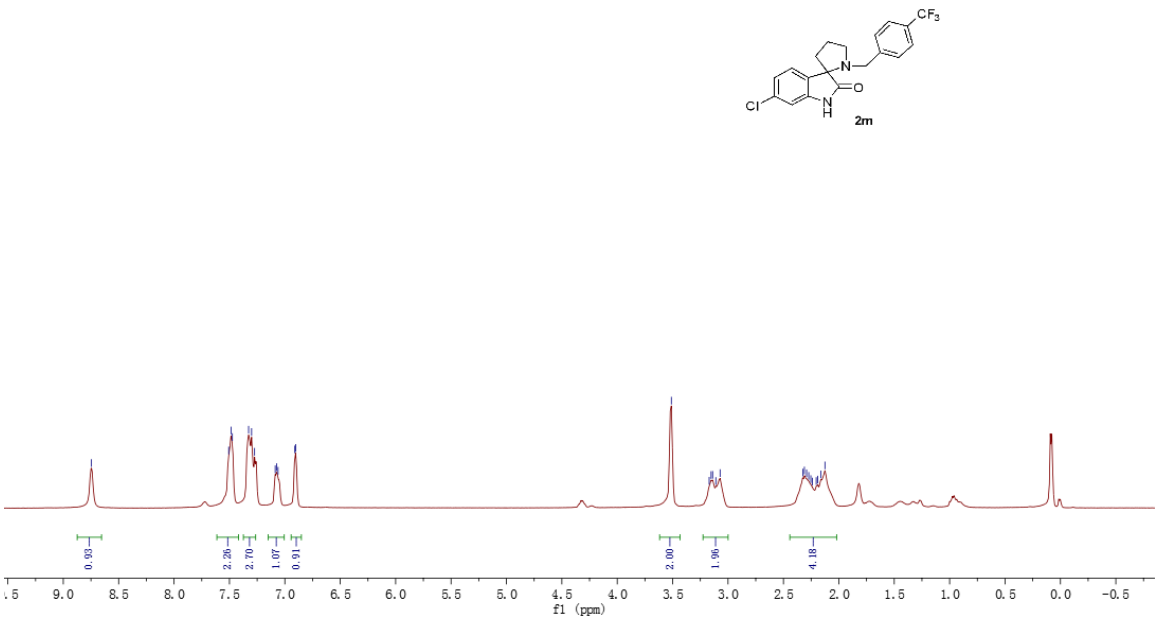

Cl
N
O
N
H
2j
f1 (ppm)

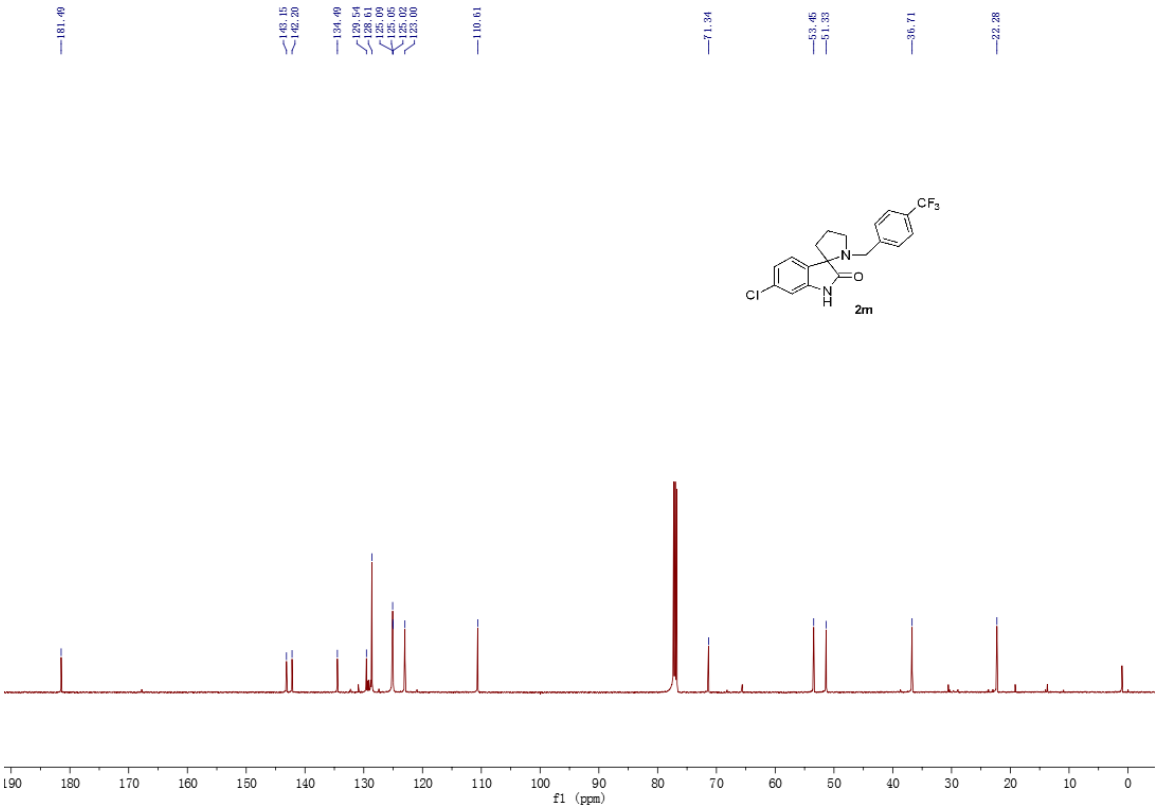

8.360
7.354
7.342
7.328
7.260
7.244
7.229
7.213
7.097
7.082
7.065
6.863
6.847
3.433
3.405
3.377
3.151
3.136
3.062
3.053
3.045
3.035
2.344
2.336
2.328
2.314
2.304
2.277
2.270
2.247
2.243
2.241
2.234
2.229
2.220
2.212
2.203
2.197
2.166
2.156
2.144
2.132
2.116
2.103
2.090
2.088
2.077
Br
N
O
N
H
2k
0.91
3.00
0.97
3.10
0.97
2.00
1.10
1.00
1.09
1.17
1.07
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

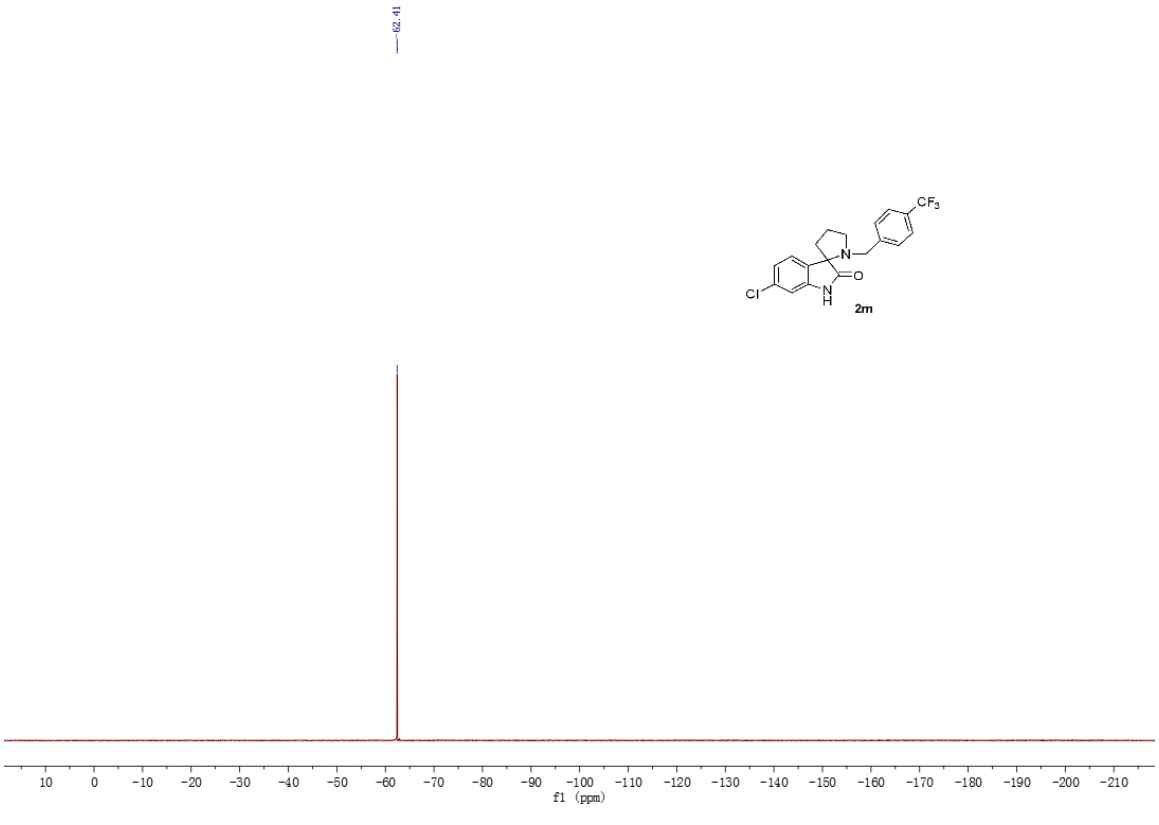

181.31
141.06
138.31
131.20
131.09
130.20
128.74
124.16
122.89
120.61
109.82
77.25
77.00
76.75
71.51
53.28
51.26
36.70
22.26
Br
N
O
N
H
2k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

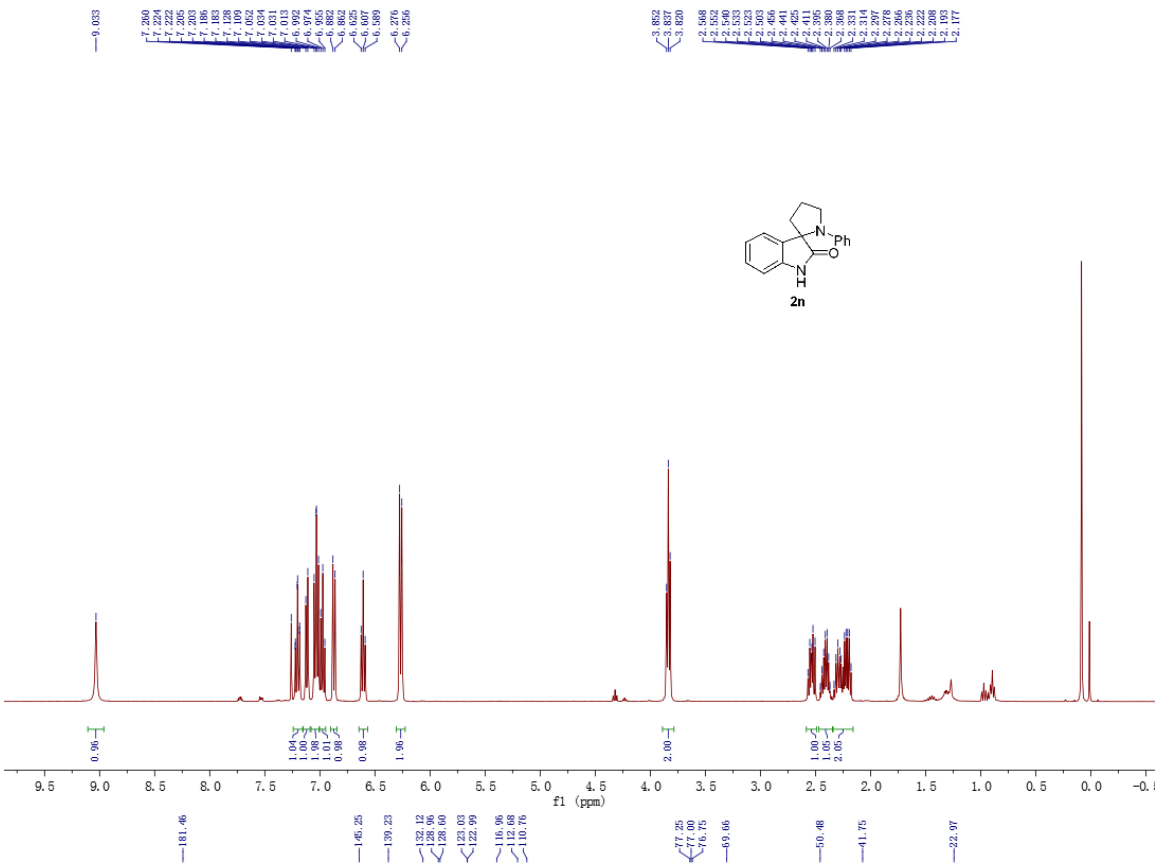

8.836
7.495
7.469
7.326
7.298
7.269
6.794
6.767
6.742
6.735
6.652
6.646
6.624
6.617
3.506
3.159
3.137
3.111
3.093
3.082
2.323
2.306
2.287
2.264
2.233
2.217
2.191
2.168
2.149
2.125
2.099
CF3
N
O
N
H
F
2l
0.85
2.05
2.73
1.00
0.90
2.00
1.82
4.10
f1 (ppm)
182.10
181.88
164.19
162.23
143.24
142.47
142.38
129.10
128.51
126.38
126.36
125.30
125.25
125.22
125.06
125.03
125.00
109.24
98.73
96.51
71.26
53.40
51.28
36.68
22.19
CF3
N
O
N
H
F
2l
f1 (ppm)

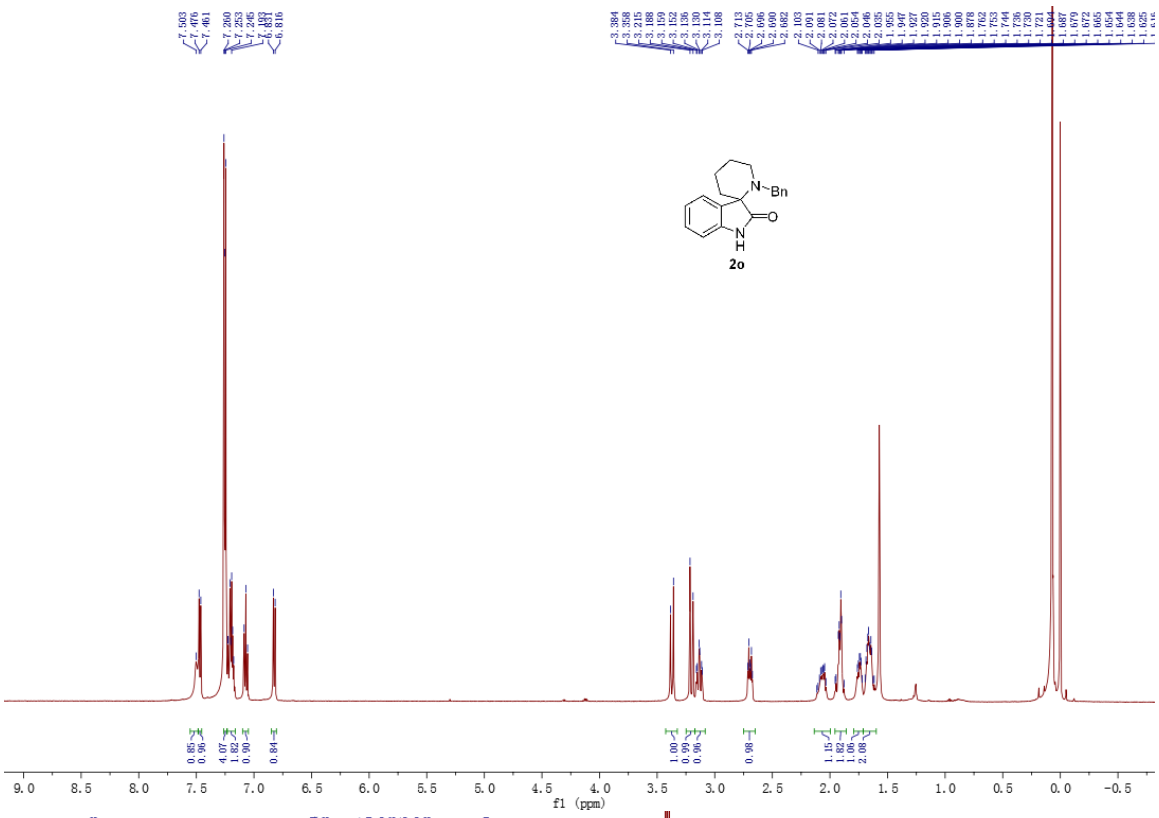

-62.41
-111.31
F
2l
f1 (ppm)
8.745
7.507
7.485
7.474
7.337
7.300
7.273
7.087
7.075
7.061
6.910
6.902
3.512
3.170
3.153
3.139
3.110
3.072
2.325
2.311
2.291
2.271
2.253
2.238
2.204
2.169
2.160
2.125

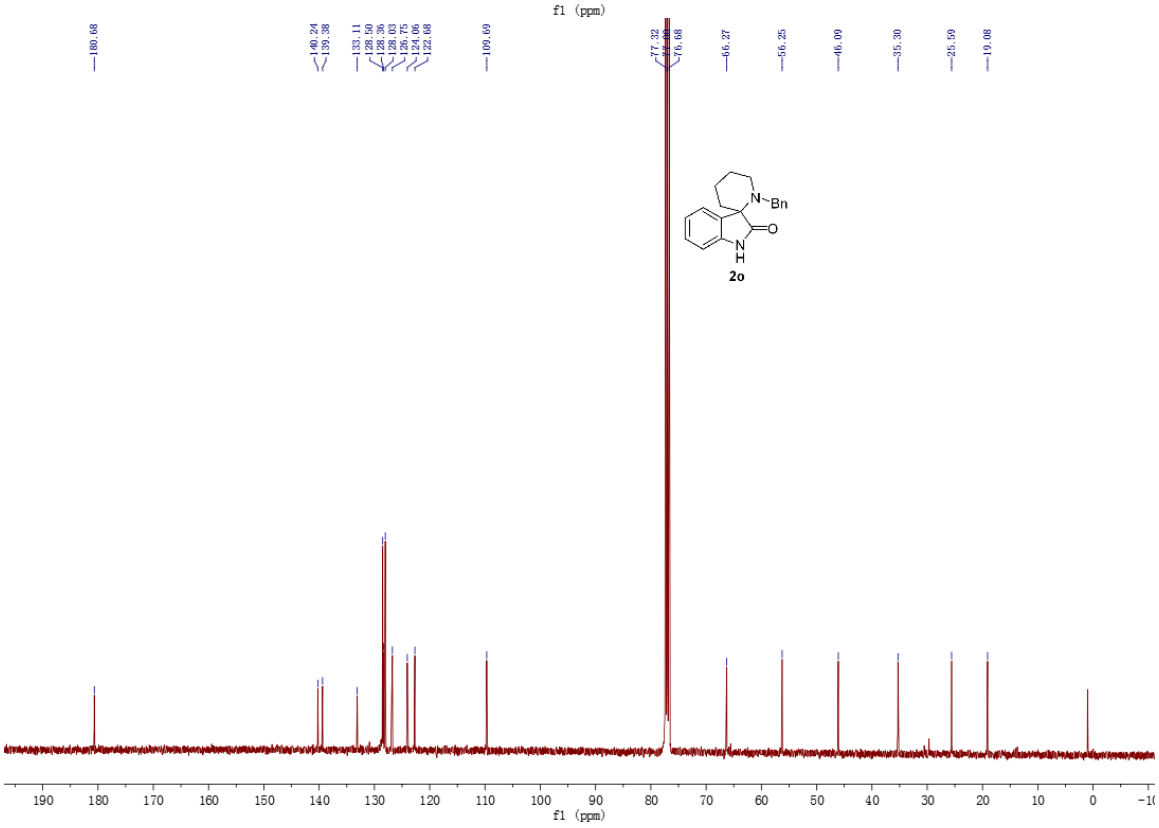

Cl
2m
f1 (ppm)
0.93
2.26
2.70
1.07
0.91
2.00
1.90
4.18

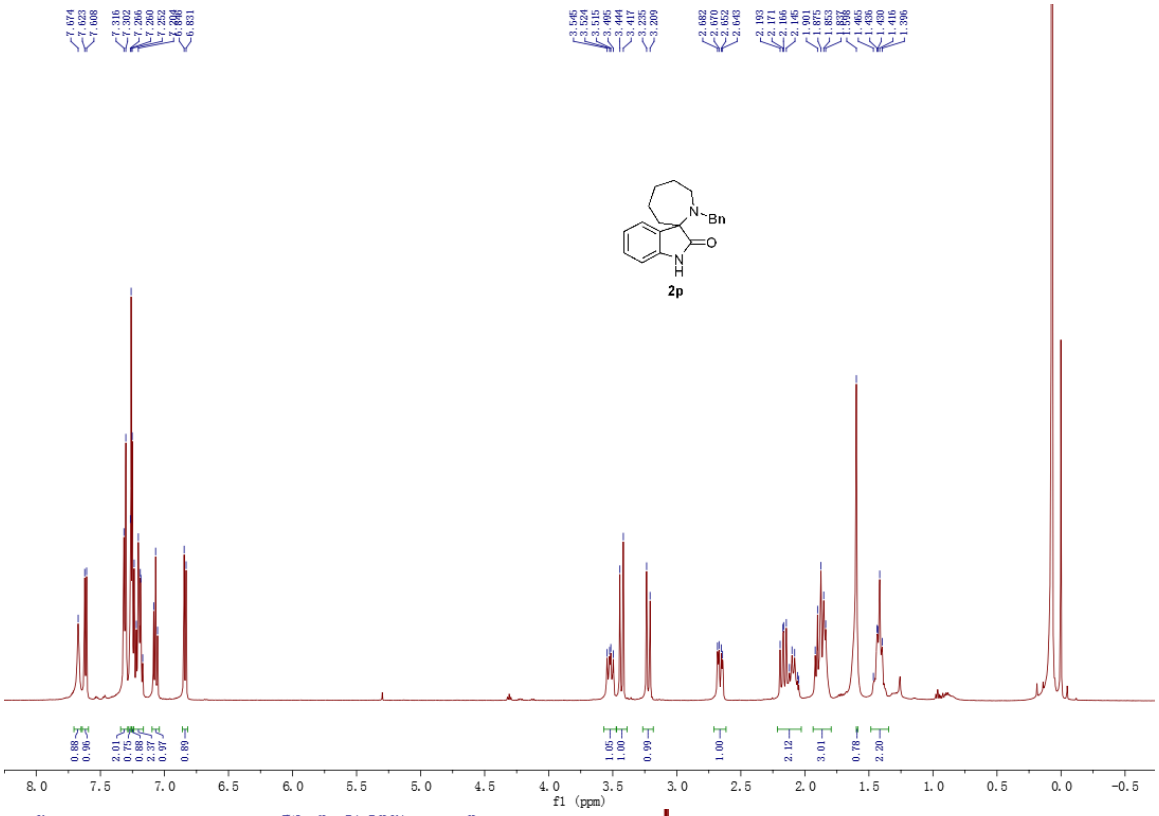

181.49
143.15
142.20
134.49
129.54
128.61
125.89
125.05
125.02
123.00
110.61
71.34
53.45
51.33
36.71
22.28
CF3
N
O
N
H
Cl
2m
f1 (ppm)

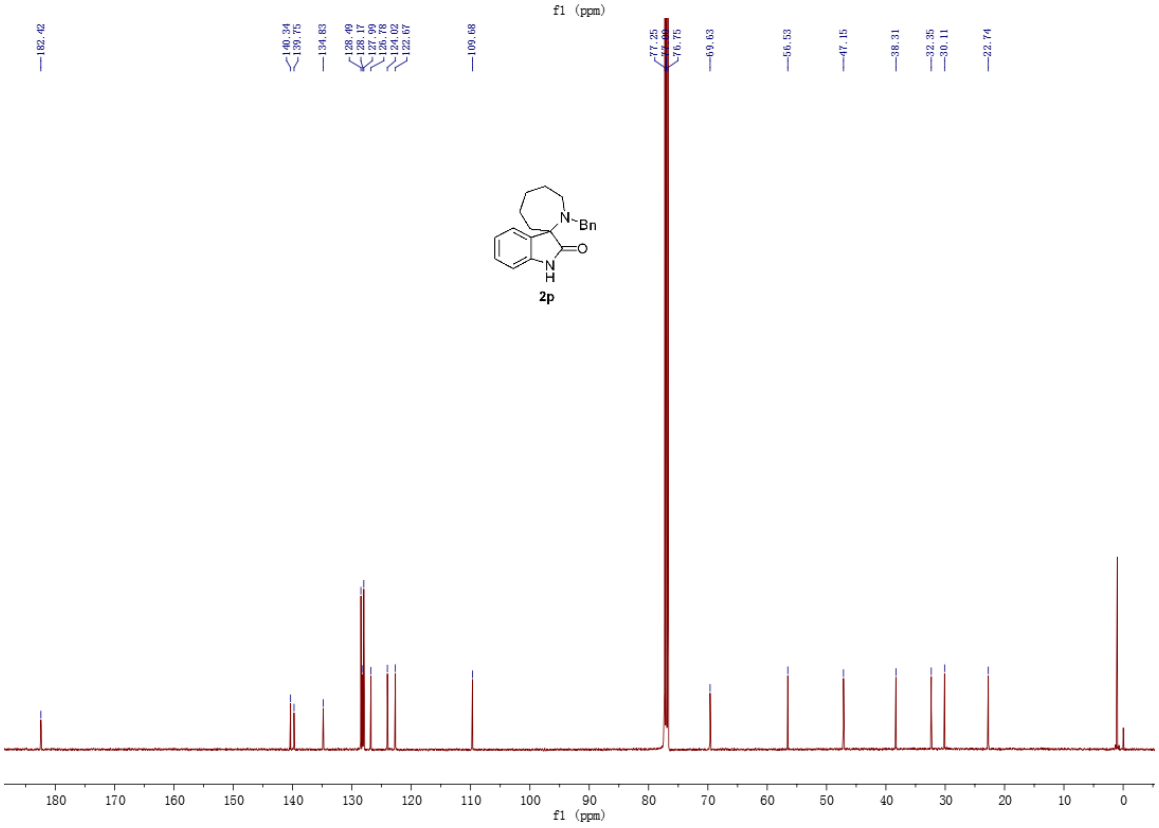

62.41
CF3
N
O
N
H
Cl
2m
f1 (ppm)

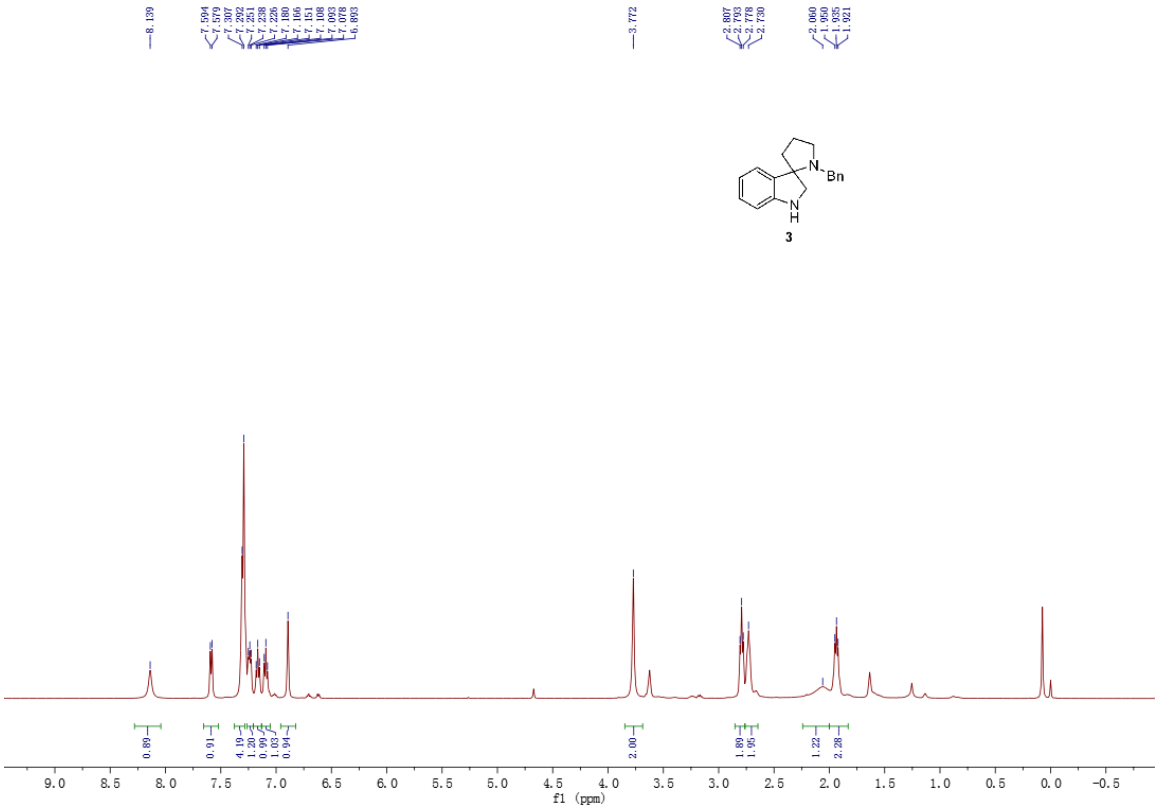

9.033
7.260
7.224
7.222
7.205
7.203
7.186
7.183
7.108
7.100
7.052
7.034
7.031
7.013
6.992
6.974
6.955
6.882
6.862
6.625
6.607
6.589
6.276
6.256
3.852
3.837
3.820
2.568
2.552
2.540
2.533
2.523
2.503
2.486
2.441
2.425
2.411
2.395
2.388
2.368
2.331
2.314
2.297
2.278
2.256
2.236
2.222
2.208
2.193
2.177
Ph
N
O
H
2n
0.96
1.04
1.00
1.98
1.01
0.98
0.98
1.96
2.00
1.09
1.05
2.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
181.46
145.25
139.23
132.12
128.96
128.60
123.03
122.99
116.96
112.68
110.76
77.25
77.00
76.75
69.66
50.48
41.75
22.97
Ph
N
O
H
2n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

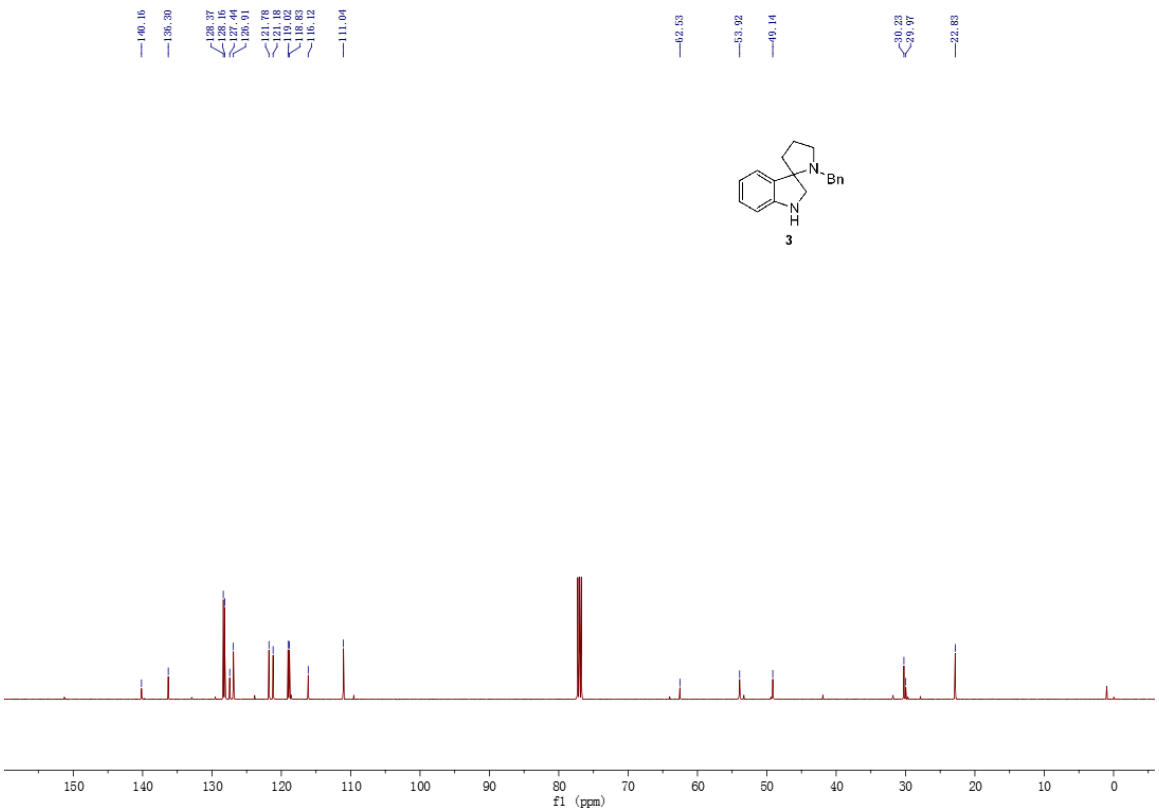

N
Bn
O
N
H
2o
f1 (ppm)


N
Bn
O
N
H
2o
f1 (ppm)


7.674
7.623
7.608
7.316
7.302
7.286
7.260
7.252
6.831
3.545
3.524
3.515
3.495
3.444
3.417
3.235
3.209
2.682
2.670
2.652
2.643
2.193
2.171
2.166
2.145
1.901
1.875
1.853
1.498
1.465
1.436
1.430
1.416
1.396
N
Bn
O
N
H
2p
0.88
0.96
2.01
0.75
0.88
2.37
0.97
0.89
1.05
1.00
0.99
1.00
2.12
3.01
0.78
2.20
f1 (ppm)


182.42
140.34
139.75
134.83
128.49
128.17
127.99
126.78
125.02
122.67
109.68
77.25
77.00
76.75
69.63
56.53
47.15
38.31
32.35
30.11
22.74
N
Bn
O
N
H
2p
f1 (ppm)


8.139
7.594
7.579
7.307
7.292
7.251
7.238
7.226
7.180
7.166
7.151
7.108
7.093
7.078
6.893
3.772
2.807
2.793
2.778
2.730
2.060
1.990
1.935
1.921
N
Bn
N
H
3
0.89
0.91
4.19
1.20
0.99
1.03
0.94
2.00
1.89
1.95
1.22
2.28
f1 (ppm)


140.16
136.30
128.37
128.16
127.44
126.91
121.78
121.18
119.02
118.83
116.12
111.04
62.53
53.92
49.14
30.23
29.97
22.83
N
Bn
N
H
3
f1 (ppm)

**References**

[S1] Li, G.; Huang, L.; Xu, J.; Sun, W.; Xie, J.; Hong, L.; Wang, R. *Adv. Synth. Catal.* **2016**, *358*, 2873.

[S2] Martin, D. B. C.; Nguyen, L. Q.; Vanderwal, C. D. *J. Org. Chem.* **2012**, *77*, 17 .

[S3] Cashion, D.; Mortensen, D; Huang, D.-H.; Torres, E.; Parens, J.; Sapienza, J.; Hansen, J.; Leftheris, K.; Correa, M.; Delgado, M. M.; Raheja, R.; Papa, P.; Bahmanyar, S.; Hesge, S.; Norris, S.; Plantevin-Krentiskysky, V.; Calabrese, A. A.; Cathers, B. E.; Whitefield, B. W.; Bennett, B. "Substituted Diaminopyrimidyl Compouns, Compositions Thereof, and Methods of Treatment Therewith." WO 095679 A1, June 25, 2015.