Temperature-mediated Heterolytic Cleavage of 3-Halooxindoles: Rapid Access to 3-Functionalized-2-oxindoles

Xiong-Li Liu,[a,b,*] Jing Yue,[b] Shuang Chen,[b] Huan-Huan Liu,[b] Kai-Mo Yang,[b] Ting-Ting Feng,[a] and Ying Zhou[a,*]

[a] College of Pharmaceutical Sciences, Guizhou University of Chinese Medicine, Guiyang, 550025

[b] Guizhou Engineering Center for Innovative Traditional Chinese Medicine and Ethnic Medicine, Guizhou University, Guiyang, 550025

** Corresponding Author: Xiong-Li Liu and Ying Zhou*

** E-mail address: xlliu1@gzu.edu.cn (X.-L. Liu) and zhouy@gzu.edu.cn (Y. Zhou)*

Supporting Information

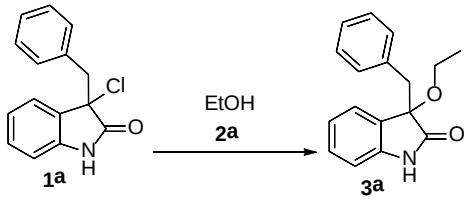
Table of Contents

1. General Experimental Information

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DMX 400 or 500 MHz NMR spectrometers in $CDCl_3$ or DMSO-d_6 using TMS as internal standard. Chemical shifts were reported as δ values (ppm). High-resolution mass spectra (HRMS-ESI) were obtained on a Micro^{TM} Q-TOF Mass Spectrometer. Melting points were uncorrected and recorded on an Electothermal 9100 digital melting point apparatus.

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel GF_{254} plates. Column chromatography was performed on silica gel (300-400 mesh).

2. Table S1: Optimization of Reaction Conditions for Synthesis of Compound 3a.[a]



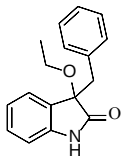
Entry[a]	Temp. (°C)	Time (h)	Yield (%)
1	25	48	-
2	80	12	83
3	80	24	92
4	80	48	87
5	70	24	75

[a] The reactions were carried out with 0.4 mmol of **1a**, in EtOH (3.0 mL) for the specified temperture and time.

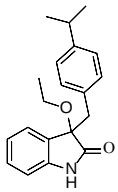
3. Procedure for the Synthesis of Compounds 3

In a sealed Schlenk tube equipped with a magnetic stirring bar was added 3-chloroxindole **1** (0.4 mmol) in 3.0 mL of alcohol **2**. The reaction mixture was stirred at 80 °C in oil bath for 24 h. After completion of the reaction, as indicated by TLC, purification by flash column chromatography (hexane/EtOAc) was carried out to furnish the corresponding product **3**.

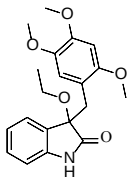
4. Characterization Data of Compounds 3:



3a: White soild, m.p. 122.8-128.6 °C; Yield 92%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.15-1.18 (m, 3H), 3.10-3.17 (m, 2H), 3.21-3.28 (m, 1H), 3.32 (d, J = 16.0 Hz, 1H), 6.78 (d, J = 9.0 Hz, 1H), 6.93-6.95 (m, 2H), 7.01-7.11 (m, 5H), 7.20-7.24 (m, 1H), 8.95 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 15.3, 43.8, 61.2, 83.6, 110.3, 122.5, 125.1, 126.6, 127.1, 127.5, 129.6, 130.5, 134.0, 141.0, 179.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{17}NNaO_2$ $[M+Na]^+$: 290.1151; Found: 290.1154.

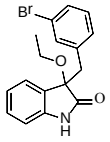


3b: White soild, m.p. 129.9-132.8 °C; Yield 89%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.13-1.17 (m, 9H), 2.73-2.80 (m, 1H), 3.06 (d, J = 16.5 Hz, 1H), 3.11-3.14 (m, 1H), 3.21-3.27 (m, 1H), 3.30 (d, J = 16.0 Hz, 1H), 6.81 (d, J = 9.5 Hz, 1H), 6.87-6.90 (m, 2H), 6.92-6.94 (m, 2H), 7.01 (d, J = 5.0 Hz, 2H), 7.19-7.25 (m, 1H), 9.29 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 15.5, 24.0, 33.7, 43.5, 61.3, 83.7, 110.5, 122.6, 125.3, 125.8, 127.4, 129.7, 130.7, 131.4, 141.2, 147.3, 179.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{23}NNaO_2$ $[M+Na]^+$: 332.1621; Found: 332.1626.

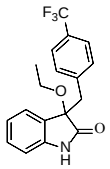


3c: White soild, m.p. 118.5-123.3 °C; Yield 91%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.09-1.13 (m, 3H), 3.03-3.07 (m, 1H), 3.15-3.25 (m, 3H), 3.38 (s, 3H), 3.64 (s, 3H), 3.76 (s, 3H), 6.26 (s, 1H), 6.72 (s, 1H), 6.74 (d, J = 9.5 Hz, 1H), 6.89 (d, J = 5.5 Hz, 2H), 7.10-7.14 (m, 1H), 9.14 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 15.5, 35.9, 55.9, 56.1, 56.2, 61.1, 83.5, 96.9, 110.2, 114.2, 115.4, 122.1, 125.4, 127.7, 129.3, 141.1, 142.1, 148.3, 152.1, 178.6, 179.6; HRMS (ESI-TOF) m/z:

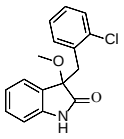
Calcd. for $C_{20}H_{23}NNaO_5$ $[M+Na]^+$: 380.1468; Found: 380.1471.



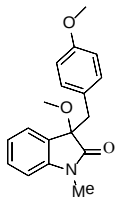
3d: White soild, m.p. 119.8-124.6 °C; Yield 89%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.14-1.18 (m, 3H), 3.03 (d, J = 16.0 Hz, 1H), 3.08-3.16 (m, 1H), 3.21-3.29 (m, 2H), 6.79 (d, J = 9.5 Hz, 1H), 6.88-7.05 (m, 4H), 7.09-7.10 (m, 1H), 7.21-7.26 (m, 2H), 8.70 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 15.4, 43.5, 61.4, 83.3, 110.5, 121.7, 122.8, 125.3, 126.9, 129.2, 129.4, 130.0, 133.7, 136.6, 140.9, 178.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{16}BrNNaO_2$ $[M+Na]^+$: 368.0257; Found: 368.0255.



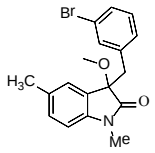
3e: White soild, m.p. 70.6-75.7 °C; Yield 84%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.15-1.18 (m, 3H), 3.10-3.16 (m, 2H), 3.22-3.28 (m, 1H), 3.37 (d, J = 13.0 Hz, 1H), 6.82 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.0 Hz, 1H), 7.03-7.06 (m, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.24-7.27 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 8.94 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 15.2, 43.5, 61.3, 83.1, 110.5, 122.8 (q, J = 270.8 Hz), 124.5, 125.1, 126.7(q, J = 3.3 Hz), 129.9 (q, J = 33.1 Hz), 131.0, 138.3, 140.8, 178.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{18}H_{16}F_3NNaO_2$ $[M+Na]^+$: 358.1025; Found: 358.1032.



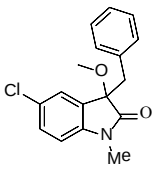
3f: White soild, m.p. 165.7-169.0 °C; Yield 89%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.13 (s, 3H), 3.39 (d, J = 13.5 Hz, 1H), 3.50 (d, J = 13.5 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.97-7.01 (m, 1H), 7.15-7.19 (m, 2H), 7.23-7.31 (m, 2H), 7.46-7.48 (m, 1H), 9.59 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.4, 53.2, 83.3, 110.5, 122.5, 125.4, 125.9, 126.1, 128.2, 129.0, 129.8, 132.5, 132.7, 135.2, 141.0, 179.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{14}ClNNaO_2$ $[M+Na]^+$: 310.0605; Found: 310.0603.



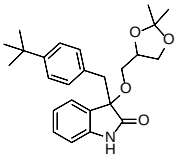
3g: White soild, m.p. 101.4-102.9 ºC; Yield 77%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.97 (s, 3H), 3.02 (s, 3H), 3.03 (d, J = 16.0 Hz, 1H), 3.18 (d, J = 16.0 Hz, 1H), 3.68 (s, 3H), 6.57-6.62 (m, 3H), 6.76 (d, J = 11.0 Hz, 2H), 7.00-7.07 (m, 2H), 7.21-7.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 25.9, 43.1, 53.4, 55.2, 84.2, 108.2, 113.0, 122.7, 124.9, 126.1, 126.2, 129.8, 131.5, 144.0, 158.4, 175.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{18}H_{19}NNaO_3$ $[M+Na]^+$: 320.1257; Found: 320.1261.



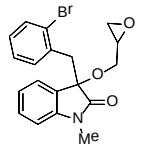
3h: White soild, m.p. 125.3-127.1 ºC; Yield 61%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.22 (m, 3H), 2.89 (d, J = 13.0 Hz, 1H), 2.92 (s, 3H), 2.94 (s, 3H), 3.12 (d, J = 13.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 6.72 (s, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.85-6.88 (m, 1H), 6.94 (s, 1H), 6.98 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.8, 25.7, 43.1, 53.0, 83.4, 107.8, 121.1, 125.3, 125.4, 128.8, 129.0, 129.5, 129.9, 132.0, 133.1, 136.3, 141.1, 175.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{18}H_{18}BrNNaO_2$ $[M+Na]^+$: 382.0413; Found: 382.0417.



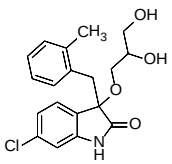
3i: Light yellow oil; Yield 67%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.00 (s, 3H), 3.11 (s, 3H), 3.16 (d, J = 12.5 Hz, 1H), 3.28 (d, J = 12.5 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 6.5 Hz, 2H), 7.09 (d, J = 2.0 Hz, 1H), 7.12-7.16 (m, 3H), 7.26-7.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 25.9, 43.9, 53.5, 83.9, 109.0, 125.1, 126.9, 127.7, 128.0, 129.6, 130.3, 133.5, 142.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{16}ClNNaO_2$ $[M+Na]^+$: 324.0762; Found: 324.0764.



3j: White soild, m.p. 62.3-63.1 ^{o}C; Yield 76%; 17:10 *dr*; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (major + minor): 1.23 (s, 8.0 H), 1.25 (s, 14.3H), 1.32 (s, 13.7H), 2.99-3.09 (m, 2.8 H), 3.12-3.22 (m, 2.0H), 3.29-3.35 (m, 3.4H), 3.75-3.80 (m, 2.1H), 4.04-4.13 (m, 2.5H), 4.22-4.28 (m, 2.2H), 6.72-6.79 (m, 2.1H), 6.85-6.92 (m, 5.8H), 6.99-7.06 (m, 3.0H), 7.09-7.16 (m, 4.2H), 7.19-7.25 (m, 2.6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (major + minor): 25.2, 25.3, 26.6, 26.7, 31.3, 31.4, 34.3, 34.4, 42.9, 43.1, 66.2, 67.0, 67.1, 67.2, 74.1, 74.3, 83.2, 83.5, 109.2, 109.4, 110.2, 122.6, 124.5, 124.6, 125.6, 129.8, 130.2, 130.4, 140.8, 149.5, 149.6, 177.8, 177.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{25}H_{31}NNaO_4$ $[M+Na]^+$: 432.2145; Found: 432.2148.

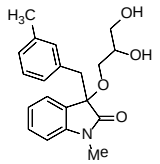


3k: White soild, m.p. 88.9-91.3 ^{o}C; Yield 72%; 6:5 *dr*; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (major + minor): 2.42-2.44 (m, 1.0H), 2.54-2.56 (m, 1.2H), 2.70-2.74 (m, 2.3H), 2.93-2.97 (m, 1.0H), 3.05-3.09 (m, 1.3H), 3.14-3.19 (m, 8.3H), 3.21-3.24 (m, 2.2H), 3.26-3.28 (m, 1.3H), 3.30-3.34 (m, 2.4H), 3.52 (d, J = 5.5 Hz, 1.3H), 3.56 (d, J = 5.0 Hz, 1.0H), 6.71-6.76 (m, 4.6H), 6.91-6.95 (m, 2.4H), 7.03-7.07 (m, 2.3H), 7.19-7.24 (m, 2.4H), 7.26-7.30 (m, 2.4H), 7.37-7.39 (m, 2.3H), 7.45-7.49 (m, 2.4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (major + minor): 26.1, 26.2, 41.9, 42.0, 44.6, 44.7, 50.3, 50.4, 65.8, 67.0, 82.3, 82.4, 108.0, 108.1, 122.6, 125.4, 126.7, 128.5, 129.9, 130.0, 132.4, 132.6, 143.3, 143.5, 175.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{18}BrNNaO_3$ $[M+Na]^+$: 410.0362; Found: 410.0364.

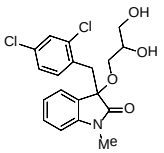


3l: White soild, m.p. 94.5-105.5 ^{o}C; Yield 79%; 10:9 *dr*; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (major + minor): 1.87-1.88 (m, 6.5H), 2.87-2.91 (m, 2.4H), 3.01-3.14 (m, 4.8H), 3.21-3.28 (m, 4.6H), 3.36-3.43 (m, 3.1H), 3.54-3.78 (m, 7.5H), 6.41 (d, J = 8.0 Hz, 1.9H), 6.79-6.83 (m, 4.3H),

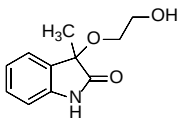
6.93-7.10 (m, 9.5H), 9.18 (br s, 2.0H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (major + minor): 19.8, 39.4, 63.3, 63.5, 66.5, 67.7, 70.5, 70.8, 83.0, 83.1, 111.4, 122.6, 124.6, 125.4, 126.6, 127.3, 127.4, 130.2, 131.6, 131.7, 132.4, 135.7, 137.6, 141.9, 179.6, 179.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{20}ClNNaO_4$ $[M+Na]^+$: 384.0973; Found: 384.0977.



3m: Light yellow oil; Yield 54%; 10:9 *dr*; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (major + minor): 2.08-2.09 (m, 5.7H), 2.37-2.39 (m, 1.6H), 2.90-2.91 (m, 5.9H), 2.91-3.06 (m, 5.6H), 3.12-3.22 (m, 4.8H), 3.43-3.46 (m, 1.9H), 3.55-3.66 (m, 2.8H), 3.73-3.77 (m, 1.8H), 6.55-6.60 (m, 5.6H), 6.84-6.92 (m, 3.6H), 6.96-7.02 (m, 3.8H), 7.16-7.21 (m, 2.0H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (major + minor): 21.2, 26.0, 43.9, 44.0, 63.5, 63.6, 66.7, 67.7, 70.5, 70.7, 83.7, 83.8, 108.4, 122.8, 124.9, 126.1, 127.4, 127.5, 129.9, 131.1, 133.5, 133.6, 137.1, 143.4, 176.4, 176.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{23}NNaO_4$ $[M+Na]^+$: 364.1519; Found: 364.1525.

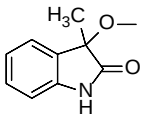


3n: Light yellow oil; Yield 71%; 10:9 *dr*; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (major + minor): 2.98-3.06 (m, 3.7H), 3.14-3.22 (m, 11.6H), 3.41-3.50 (m, 4.3H), 3.61-3.73 (m, 3.1H), 3.72-3.83 (m, 1.8H), 6.80 (d, J = 9.5 Hz, 2.0H), 6.83-6.86 (m, 2.0H), 6.98-7.02 (m, 2.0H), 7.13-7.16 (m, 1.9H), 7.23-7.25 (m, 1.8H), 7.27-7.34 (m, 4.3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (major + minor): 26.3, 39.2, 39.3, 63.4, 63.5, 66.3, 67.5, 70.4, 70.6, 82.3, 82.4, 108.5, 108.6, 122.9, 123.0, 124.9, 126.4, 128.9, 130.1, 130.9, 133.3, 143.0, 176.3, 176.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{19}Cl_2NNaO_4$ $[M+Na]^+$: 418.0583; Found: 418.0587.

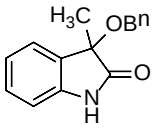


3o: Light yellow oil; Yield 79%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.50 (s, 3H), 3.15-3.23 (m, 3H), 3.56-3.63 (m, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.97-7.00 (m, 1H), 7.15-7.20 (m, 1H), 7.23 (d, J = 7.0

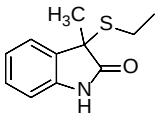
Hz, 1H), 9.60 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 24.0, 61.6, 67.3, 79.8, 111.0, 123.2, 124.0, 129.1, 129.8, 140.7, 179.9, 222.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{11}H_{13}NNaO_3$ $[M+Na]^+$: 230.0788; Found: 230.0785.



3p: White soild, m.p. 109.7-114.4 ^{o}C; Yield 93%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.63 (s, 3H), 3.13 (s, 3H), 7.03 (d, J = 7.5 Hz, 1H), 7.12-7.15 (m, 1H), 7.31-7.36 (m, 2H), 9.76 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.8, 53.2, 80.2, 110.8, 123.0, 124.0, 128.8, 129.7, 140.8, 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{10}H_{11}NNaO_2$ $[M+Na]^+$: 200.0682; Found: 200.0683.



3q: White soild, m.p. 127.0-129.7 ^{o}C; Yield 90%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.71 (s, 3H), 4.16 (d, J = 9.0 Hz, 1H), 4.33 (d, J = 9.0 Hz, 1H), 7.05 (d, J = 6.5 Hz, 1H), 7.14-7.17 (m, 1H), 7.26-7.28 (m, 1H), 7.31-7.33 (m, 5H), 7.42 (d, J = 6.0 Hz, 1H), 9.58 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 24.2, 68.0, 80.0, 110.9, 123.3, 124.2, 127.8, 128.1, 128.3, 129.9, 137.6, 140.8, 179.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{15}NNaO_2$ $[M+Na]^+$: 276.0995; Found: 276.0991.



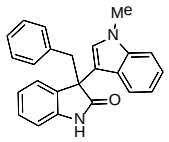
3r: Light yellow soid, m.p. 220.3-224.5 ^{o}C; Yield 87%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.07-1.10 (m, 3H), 1.69 (s, 3H), 2.27-2.33 (m, 1H), 2.43-2.49 (m, 1H), 7.00 (d, J = 6.0 Hz, 1H), 7.09-7.12 (m, 1H), 7.23-7.26 (m, 1H), 7.35 (d, J = 6.0 Hz, 1H), 9.59 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.7, 22.5, 23.4, 51.4, 110.3, 123.0, 123.9, 128.8, 132.3, 140.0, 181.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{11}H_{13}NNaOS$ $[M+Na]^+$: 230.0610; Found: 230.0617.

5. General Experimental Procedures for Synthesis of Compounds 5 and 7

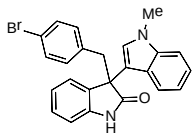
In a sealed tube equipped with a magnetic stirring bar was added 3-chloroxindole **1** (0.2 mmol), 0.5 mmol of indole **4** or 0.4 mmol of pyrrole **6** and 0.3 mL or 0.5 mL of toluene. The reaction

mixture was constantly stirred in an oil bath at 80 °C in N_2 for 16 h or 8 h. After a considerable amount of starting material had been consumed with no further improvement in the product formation (TLC monitoring), the resulting mixture was cooled to room temperature, and was purified by chromatography on silica gel (petroleum ether/EtOAc 10:1 to 15:1) to afford the desired 3-indolyloxindole **5** or 3-pyrroliyloxindole **7**.

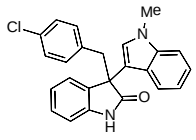
6. Characterization Data of Compounds 5 and 7



5a: Light yellow soid, m.p. 222.2-223.4 °C; Yield 67%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.48 (d, J = 10.4Hz, 1H), 3.68 (s, 3H), 3.78 (d, J = 10.4Hz, 1H), 6.58 (d, J = 6.4Hz, 1H), 6.82-6.86 (m, 3H), 6.90-7.00 (m, 4H), 7.04-7.11 (m, 4H), 7.17-7.20 (m, 1H), 8.01 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 32.9, 42.4, 54.5, 109.4, 109.6, 113.6, 119.3, 120.5, 121.8, 122.2, 125.1, 125.9, 126.5, 127.5, 127.6, 128.0, 130.2, 132.5, 135.3, 137.5, 140.7, 180.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{20}N_2NaO$ $[M+Na]^+$: 375.1468; Found: 375.1473.

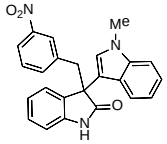


5b: Light yellow soid, m.p. 276.7-278.1 °C; Yield 70%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.42 (d, J = 12.8Hz, 1H), 3.67 (s, 3H), 3.71 (d, J = 12.8Hz, 1H), 6.59 (d, J = 7.6Hz, 1H), 6.71 (d, J = 8.4Hz, 2H), 6.84-6.88 (m, 1H), 6.90-6.94 (m, 1H), 7.02 (s, 1H), 7.05-7.11 (m, 6H), 7.18-7.21 (m, 1H), 8.05 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 32.9, 41.7, 54.3, 109.4, 109.8, 113.2, 119.3, 120.4, 120.7, 121.9, 122.3, 124.9, 125.8, 127.5, 128.2, 130.6, 131.9, 132.0, 134.4, 137.5, 140.6, 179.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}BrN_2NaO$ $[M+Na]^+$: 453.0573; Found: 453.0569.

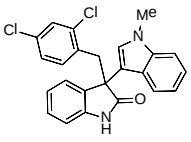


5c: Light yellow soid, m.p. 256.0-257.4 °C; Yield 68%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.43 (d,

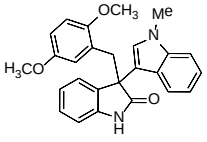
J = 10.0Hz, 1H), 3.67 (s, 3H), 3.74 (d, *J* = 10.0Hz, 1H), 6.59-6.61 (m, 1H), 6.77 (d, *J* = 6.8Hz, 2H), 6.84-6.87 (m, 1H), 6.90-6.94 (m, 3H), 7.02 (s, 1H), 7.06-7.11 (m, 4H), 7.18-7.21 (m, 1H), 7.99 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 32.9, 41.7, 54.4, 109.4, 109.8, 113.3, 119.4, 120.4, 121.9, 122.3, 125.0, 125.8, 127.5, 127.7, 128.2, 131.5, 132.1, 132.5, 133.9, 137.6, 140.7, 179.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}ClN_2NaO$ $[M+Na]^+$: 409.1078; Found: 409.1085.



5d: Light yellow soid, m.p. 202.7-205.3 °C; Yield 69%; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 3.62 (d, *J* = 12.8Hz, 1H), 3.77 (s, 3H), 3.96 (d, *J* = 12.8Hz, 1H), 6.68 (d, *J* = 7.6Hz, 1H), 6.94-6.98 (m, 1H), 7.03-7.07 (m, 1H), 7.09 (s, 1H), 7.14-7.25 (m, 5H), 7.28-7.33 (m, 2H), 7.69 (s, 1H), 7.90-7.92 (m, 1H), 8.18 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 32.9, 41.8, 54.3, 109.5, 109.9, 112.7, 119.5, 120.4, 121.8, 122.0, 125.0, 127.5, 128.5, 128.6, 147.4, 179.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}N_3NaO_3$ $[M+Na]^+$: 420.1319; Found: 420.1325.

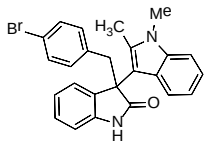


5e: Light yellow soid, m.p. 259.1-260.5 °C; Yield 64%; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 3.74 (s, 3H), 3.90 (d, *J* = 13.2Hz, 1H), 3.97 (d, *J* = 13.2Hz, 1H), 6.73 (d, *J* = 7.6Hz, 1H), 6.89-7.00 (m, 3H), 7.02-7.05 (m, 2H), 7.13-7.20 (m, 4H), 7.28 (d, *J* = 8.0Hz, 1H), 7.35 (d, *J* = 8.0Hz, 1H), 8.29 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 32.9, 37.2, 54.2, 109.5, 113.1, 119.4, 120.7, 121.9, 122.1, 125.7, 126.0, 126.5, 127.7, 128.3, 129.0, 131.2, 131.7, 132.6, 132.9, 135.5, 137.6, 140.3, 180.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{18}Cl_2N_2NaO$ $[M+Na]^+$: 443.0688; Found: 443.0690.

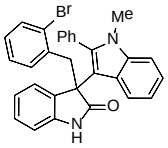


5f: Light yellow soid, m.p. 219.2-220.9 °C; Yield 60%; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 3.39 (s, 3H), 3.46 (s, 3H), 3.70 (s, 3H), 3.76 (d, *J* = 12.8Hz, 1H), 3.87 (d, *J* = 13.2Hz, 1H), 6.48 (d, *J* = 8.8Hz, 1H), 6.53-6.56 (m, 1H), 6.61-6.65 (m, 2H), 6.84-6.93 (m, 2H), 7.01-7.5 (m, 1H), 7.11-7.19

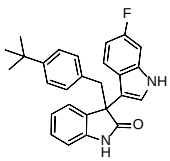
(m, 4H), 7.22-7.25 (m, 1H), 9.08 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 32.7, 34.7, 54.4, 55.2, 55.3, 109.2, 109.3, 110.8, 113.3, 114.0, 115.9, 119.1, 120.6, 121.4, 121.6, 125.2, 125.7, 125.9, 127.5, 127.6, 132.4, 137.5, 140.8, 151.6, 152.6, 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{26}H_{24}N_2NaO_3$ $[M+Na]^+$: 435.1679; Found: 435.1687.



5g: Light yellow soid, m.p. 270.0-271.3 ^{o}C; Yield 57%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.25 (s, 3H), 3.61 (s, 3H), 3.80 (d, J = 9.6Hz, 1H), 3.93 (d, J = 9.6Hz, 1H), 6.61 (d, J = 6.0Hz, 1H), 6.75 (d, J = 6.8Hz, 2H), 6.85-6.92 (m, 2H), 7.01-7.05 (m, 1H), 7.07-7.10 (m, 1H), 7.19-7.23 (m, 3H), 7.37 (d, J = 6.8Hz, 2H), 10.2 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 11.7, 29.3, 40.0, 55.3, 108.9, 109.0, 109.4, 118.8, 119.5, 119.7, 120.1, 121.5, 124.6, 126.5, 127.9, 130.1, 132.3, 133.6, 134.2, 135.3, 136.1, 141.5, 179.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{25}H_{21}BrN_2NaO$ $[M+Na]^+$: 467.0729; Found: 467.0734.

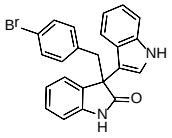


5h: Light yellow soid, m.p. 274.4-275.2 ^{o}C; Yield 45%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.16 (d, J = 10.4Hz, 1H), 3.46 (d, J = 10.8Hz, 1H), 6.58 (d, J = 6.4Hz, 1H), 6.70 (d, J = 6.4Hz, 1H), 6.74-6.81 (m, 2H), 6.88-6.92 (m, 2H), 7.00-7.03 (m, 2H), 7.07-7.11 (m, 1H), 7.21 (d, J = 6.4Hz, 2H), 7.41 (d, J = 6.4Hz, 1H), 7.49-7.60 (m, 4H), 7.66 (d, J = 6.0Hz, 1H), 10.5 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 30.6, 40.5, 55.2, 109.2, 110.3, 111.2, 119.6, 125.6, 126.1, 127.2, 128.5, 128.6, 128.7, 128.8, 129.4, 130.9, 131.8, 131.9, 132.7, 132.9, 133.9, 136.0, 136.5, 139.5, 142.0, 180.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{30}H_{23}BrN_2NaO$ $[M+Na]^+$: 529.0886; Found: 529.0891.

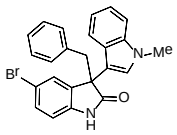


5i: Light yellow soid, m.p. 287.7-289.6 ^{o}C; Yield 40%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.20

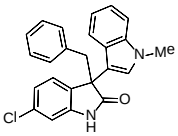
(s, 9H), 3.55 (d, J = 10.4 Hz, 1H), 3.66 (d, J = 10.0 Hz, 1H), 6.73 (d, J = 6.0 Hz, 2H), 6.84 (d, J = 6.4 Hz, 2H), 6.94-7.01 (m, 2H), 7.10 (d, J = 6.8 Hz, 2H), 7.14-7.17 (m, 2H), 7.20 (d, J = 6.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 10.3 (br s, 1H), 11.2 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 31.6, 34.4, 41.2, 54.1, 97.9 (d, J_{CF} = 26.3 Hz), 107.5 (d, J_{CF} = 23.8 Hz), 109.6, 115.6, 120.8, 120.9, 121.8, 122.5, 124.6, 124.8, 125.2, 128.4, 130.2, 133.0, 133.4, 137.1, 142.4, 148.8, 159.2 (d, J_{CF} = 233.8 Hz), 179.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{27}H_{25}FN_2NaO$ [M+Na]$^+$: 435.1843; Found: 435.1840.



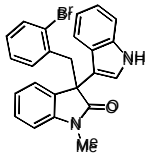
5j: Light yellow soid, m.p. 103.7-105.8 ^{o}C; Yield 56%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.56 (d, J = 10.4 Hz, 1H), 3.65-3.69 (m, 1H), 6.69-6.71 (m, 1H), 6.75-6.79 (m, 1H), 6.82-6.84 (m, 2H), 6.89-6.93 (m, 2H), 6.99-7.02 (m, 1H), 7.10-7.13 (m, 1H), 7.17 (d, J = 5.6 Hz, 1H), 7.24-7.26 (m, 2H), 7.34-7.36 (m, 1H), 7.48 (s, 1H), 10.3 (br s, 1H), 11.1 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 40.6, 53.7, 109.2, 111.6, 114.5, 118.5, 119.2, 119.7, 121.1, 121.4, 123.7, 124.8, 125.1, 128.0, 130.3, 132.2, 132.4, 135.5, 136.7, 141.9, 179.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{17}BrN_2NaO$ [M+Na]$^+$: 439.0416; Found: 439.0422.



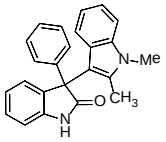
5k: Light yellow soid, m.p. >300.0 ^{o}C; Yield 70%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.61-3.67 (m, 2H), 3.78 (s, 3H), 6.63 (d, J = 8.0 Hz, 1H), 6.83-6.92 (m, 4H), 7.07-7.11 (m, 4H), 7.27 (d, J = 8.5 Hz, 1H), 7.36 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.52 (s, 1H), 10.47 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 32.5, 41.0, 54.0, 110.0, 111.0, 113.2, 118.9, 119.0, 121.3, 125.3, 126.5, 127.6, 128.2, 130.0, 130.7, 135.3, 135.6, 137.0, 141.3, 178.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}BrN_2NaO$ [M+Na]$^+$: 453.0573; Found: 453.0577.



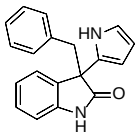
5l: Light yellow soid, m.p. 159.6-161.1 °C; Yield 71%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.55 (d, J = 12.5 Hz, 1H), 3.68 (d, J = 12.5 Hz, 1H), 3.77 (s, 3H), 6.67 (s, 1H), 6.84-6.95 (m, 5H), 7.08-7.10 (m, 4H), 7.19 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.48 (s, 1H), 10.5 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 32.5, 41.1, 53.6, 109.1, 109.9, 113.3, 118.8, 119.3, 121.1, 121.3, 125.4, 126.3, 126.5, 127.6, 128.2, 130.0, 131.5, 132.0, 135.7, 137.1, 143.4, 179.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}ClN_2NaO$ $[M+Na]^+$: 409.1078; Found: 409.1085.



5m: White soild, m.p. 173.1-174.9 °C; Yield 62%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.06 (s, 3H), 3.79 (d, J = 13.6 Hz, 1H), 3.99 (d, J = 13.6 Hz, 1H), 6.75-6.79 (m, 1H), 6.85-6.91 (m, 3H), 6.95-7.02 (m, 3H), 7.07-7.11 (m, 1H), 7.14-7.19 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 2.0 Hz, 1H), 11.13 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 26.5, 53.6, 57.5, 108.4, 112.1, 112.2, 114.3, 119.0, 119.7, 121.6, 122.1, 124.3, 124.4, 125.4, 125.6, 127.4, 128.7, 129.0, 130.6, 131.1, 132.8, 132.9, 136.0, 137.2, 143.5, 178.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{19}BrN_2NaO$ $[M+Na]^+$: 453.0573; Found: 453.0579.

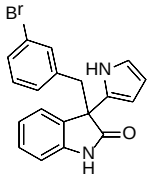


5n: Light yellow soid, m.p. 161.7-163.2 °C; Yield 73%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.96 (s, 3H), 3.55 (s, 3H), 6.48 (d, J = 7.5 Hz, 1H), 6.70-6.73 (m, 1H), 6.92-7.03 (m, 3H), 7.15 (d, J = 7.5 Hz, 1H), 7.22-7.33 (m, 7H), 10.76 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 11.7, 29.2, 57.6, 109.2, 109.9, 110.7, 118.5, 120.1, 126.4, 127.1, 128.1, 128.3, 134.1, 135.0, 136.3, 141.2, 141.9, 178.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{20}N_2NaO$ $[M+Na]^+$: 375.1468; Found: 375.1467.

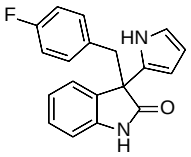


7a: Light yellow soid, m.p. 73.7-75.5 °C; Yield 85%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.45 (d,

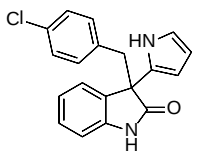
J = 13.2 Hz, 1H), 3.51 (d, *J* = 10.4 Hz, 1H), 5.66 (s, 1H), 5.93 (s, 1H), 6.68 (d, *J* = 6.0 Hz, 1H), 6.77 (s, 1H), 6.87-6.89 (m, 2H), 6.98-7.01 (m, 1H), 7.07-7.15 (m, 4H), 7.32 (d, *J* = 6.0 Hz, 1H), 10.3 (br s, 1H), 10.9 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 42.3, 54.1, 105.9, 106.8, 109.3, 118.6, 121.2, 125.2, 126.4, 127.5, 128.0, 129.8, 129.9, 131.1, 136.2, 141.8, 178.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{16}N_2NaO$ $[M+Na]^+$: 311.1155; Found: 311.1154.



7b: Light yellow soid, m.p. 187.5-191.0 ^{o}C; Yield 84%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.32 (d, *J* = 10.4 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 5.99 (s, 1H), 6.12 (s, 1H), 6.70 (d, *J* = 6.0 Hz, 1H), 6.78 (d, *J* = 6.0 Hz, 1H), 6.83 (s, 1H), 6.89-6.93 (m, 2H), 7.08-7.11 (m, 1H), 7.20-7.25 (m, 3H), 8.30 (br s, 1H), 9.21 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 45.0, 53.6, 107.7, 108.1, 110.2, 118.7, 121.6, 122.5, 125.5, 127.9, 128.6, 128.8, 129.1, 129.9, 133.1, 137.5, 140.4, 179.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{15}BrN_2NaO$ $[M+Na]^+$: 389.0260; Found: 389.0266.

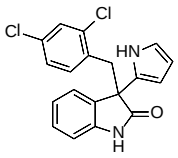


7c: Light yellow soid, m.p. 191.2-193.9 ^{o}C; Yield 86%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.35 (s, 2H), 5.99 (s, 1H), 6.12 (s, 1H), 6.74-6.77 (m, 4H), 6.83 (s, 1H), 7.07-7.10 (m, 1H), 7.19-7.26 (m, 2H), 7.91 (br s, 1H), 9.16 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 44.7, 53.9, 107.6, 108.1, 110.2, 114.5 (d, J_{CF} = 21.3 Hz), 118.7, 122.5, 125.6, 128.1, 128.5, 130.1, 130.9, 131.0, 131.6, 131.7, 140.5, 161.9 (d, J_{CF} = 243.8 Hz), 179.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{15}FN_2NaO$ $[M+Na]^+$: 329.1061; Found: 329.1065.

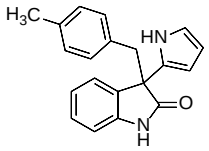


7d: Light yellow soid, m.p. 136.0-137.7 ^{o}C; Yield 86%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.31 (d, *J* = 10.4 Hz, 1H), 3.36 (d, *J* = 10.4 Hz, 1H), 5.97 (s, 1H), 6.11 (s, 1H), 6.69 (d, *J* = 6.4 Hz, 2H),

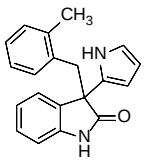
6.75 (d, *J* = 6.4 Hz, 1H), 6.82 (s, 1H), 7.01 (d, *J* = 6.8 Hz, 2H), 7.06-7.09 (m, 1H), 7.18-7.21 (m, 2H), 8.55 (br s, 1H), 9.24 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 44.6, 53.7, 107.6, 108.1, 110.2, 118.7, 122.4, 125.5, 127.8, 128.5, 131.5, 133.7, 140.4, 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{15}ClN_2NaO$ [M+Na]$^+$: 345.0765; Found: 345.0770.



7e: Light yellow soid, m.p. 99.8-103.6 ^{o}C; Yield 84%; ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) *δ*: 3.51 (d, *J* = 14.0Hz, 1H), 3.64 (d, *J* = 14.0Hz, 1H), 5.61 (s, 1H), 5.90 (s, 1H), 6.74 (d, *J* = 8.4Hz, 2H), 6.85-6.91 (m, 2H), 7.05 (d, *J* = 7.2Hz, 1H), 7.11-7.19 (m, 2H), 7.37 (s, 1H), 10.50 (br s, 1H), 10.93 (br s, 1H); ^{13}C NMR (DMSO-*d*$_6$, 100 MHz) *δ*: 38.2, 53.6, 107.0, 107.3, 109.9, 119.4, 121.6, 127.2, 128.9, 129.1, 132.4, 133.6, 142.0, 178.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{14}Cl_2N_2NaO$ [M+Na]$^+$: 379.0375; Found: 379.0381.

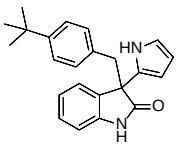


7f: Light yellow soid, m.p. 156.5-158.9 ^{o}C; Yield 84%; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 2.17 (s, 3H), 3.34 (d, *J* = 10.8 Hz, 1H), 3.37 (d, *J* = 10.8 Hz, 1H), 5.97 (s, 1H), 6.10 (s, 1H), 6.65-6.70 (m, 3H), 6.80-6.84 (m, 3H), 7.04-7.07 (m, 1H), 7.14-7.17 (m, 1H), 7.21 (s, 1H), 8.62 (br s, 1H), 9.27 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 21.0, 44.9, 54.0, 107.4, 107.9, 110.1, 118.6, 122.2, 125.6, 128.2, 128.3, 128.5, 130.0, 130.4, 132.1, 136.2, 140.6, 180.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_2NaO$ [M+Na]$^+$: 325.1311; Found: 325.1315.

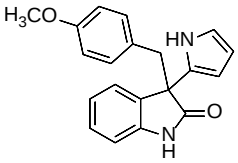


7g: Light yellow soid, m.p. 148.7-150.6 ^{o}C; Yield 83%; ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) *δ*: 1.98 (s, 3H), 3.35 (d, *J* = 13.6Hz, 1H), 3.48 (d, *J* = 14.0Hz, 1H), 5.60 (s, 1H), 5.89 (s, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.73-6.77 (m, 2H), 6.81-6.90 (m, 2H), 6.96 (d, *J* = 4.0Hz, 3H), 7.12-7.16 (m, 1H), 10.4 (br s, 1H), 10.9 (br s, 1H); ^{13}C NMR (DMSO-*d*$_6$, 100 MHz) *δ*: 20.1, 38.9, 53.9, 106.9, 107.2,

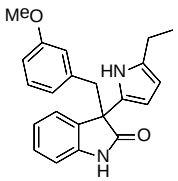
109.8, 119.1, 121.4, 125.4, 125.7, 126.8, 128.5, 129.7, 130.1, 130.3, 131.3, 135.0, 137.4, 142.3, 178.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$: 325.1311; Found: 325.1313.



7h: Light yellow soid, m.p. 168.7-170.6 °C; Yield 85%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.20 (s, 9H), 3.33 (d, J = 10.8 Hz, 1H), 3.40 (d, J = 10.8 Hz, 1H), 5.97 (s, 1H), 6.11 (s, 1H), 6.70 (d, J = 6.0 Hz, 3H), 6.81 (s, 1H), 7.04-7.08 (m, 3H), 7.16-7.24 (m, 2H), 8.40 (br s, 1H), 9.25 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 31.2, 34.3, 44.8, 53.8, 107.4, 107.9, 110.1, 118.5, 122.2, 124.5, 125.6, 128.3, 129.8, 132.2, 140.5, 149.5, 180.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{24}N_2NaO$ $[M+Na]^+$: 367.1781; Found: 367.1786.

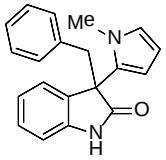


7i: Light yellow soid, m.p. 214.1-215.0 °C; Yield 81%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.31 (d, J = 10.8 Hz, 1H), 3.35 (d, J = 10.8 Hz, 1H), 3.71 (s, 3H), 5.99 (s, 1H), 6.12 (s, 1H), 6.60 (d, J = 6.8 Hz, 2H), 6.70 (d, J = 6.8 Hz, 2H), 6.74 (d, J = 6.4 Hz, 1H), 6.82 (s, 1H), 7.07-7.10 (m, 1H), 7.19-7.22 (m, 1H), 7.25 (s, 1H), 7.54 (br s, 1H), 9.14 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 44.8, 53.9, 55.0, 107.3, 108.0, 110.0, 113.0, 118.5, 122.3, 125.7, 127.3, 128.3, 128.4, 130.4, 131.2, 140.4, 158.3, 179.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_2NaO_2$ $[M+Na]^+$: 341.1260; Found: 341.1266.

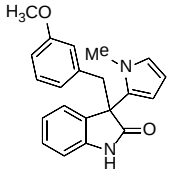


7j: Light yellow soid, m.p. 256.7-258.4 °C; Yield 76%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.17-1.20 (m, 3H), 2.53-2.61 (m, 2H), 3.41 (d, J = 6.4 Hz, 1H), 3.48 (d, J = 7.2 Hz, 1H), 3.55 (s, 3H), 5.45 (s, 1H), 5.60 (s, 1H), 6.40 (s, 1H), 6.48 (d, J = 6.0 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 6.0 Hz, 1H), 6.97-7.01 (m, 2H), 7.12-7.15 (m, 1H), 7.30 (d, J = 6.0 Hz, 1H), 10.2 (br s,

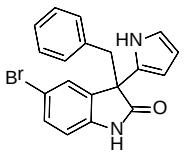
1H), 10.6 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 14.0, 20.4, 42.0, 54.1, 54.6, 102.8, 105.6, 109.3, 112.0, 115.2, 121.0, 122.3, 125.2, 127.8, 128.1, 128.4, 131.3, 134.8, 137.8, 141.9, 158.3, 178.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{22}N_2NaO_2$ $[M+Na]^+$: 369.1573; Found: 369.1577.



7k: Light yellow soid, m.p. 296.8-297.3 ^{o}C; Yield 77%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.94 (s, 3H), 3.46 (d, J = 10.0 Hz, 1H), 3.50 (d, J = 10.0 Hz, 1H), 5.97-5.98 (m, 1H), 6.36-6.37 (m, 1H), 6.55 (d, J = 6.4 Hz, 1H), 6.62 (s, 1H), 6.73 (d, J = 5.6 Hz, 2H), 6.95-7.11 (m, 6H), 10.32 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 33.7, 42.8, 54.4, 106.4, 109.2, 109.7, 122.2, 124.4, 124.6, 127.7, 128.7, 130.4, 131.5, 135.3, 142.3, 178.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$: 325.1311; Found: 325.1315.

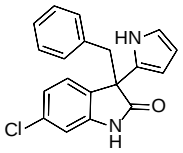


7l: Light yellow soid, m.p. 247.8-248.5 ^{o}C; Yield 76%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.49-3.51 (m, 5H), 6.01-6.02 (m, 1H), 6.26 (s, 1H), 6.39-6.41 (m, 2H), 6.62-6.67 (m, 3H), 6.96-7.03 (m, 2H), 7.09 (d, J = 5.6 Hz, 1H), 7.14-7.17 (m, 1H), 10.4 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 33.7, 42.8, 54.3, 55.0, 106.4, 109.1, 109.7, 112.8, 115.6, 122.1, 122.9, 124.4, 124.6, 128.7, 131.2, 131.6, 136.8, 142.4, 158.6, 178.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{21}H_{20}N_2NaO_2$ $[M+Na]^+$: 355.1417; Found: 355.1419.

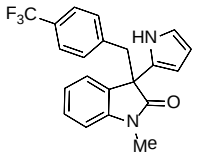


7m: Light yellow soid, m.p. 202.1-203.8 ^{o}C; Yield 90%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.43-3.52 (m, 2H), 5.67 (s, 1H), 5.91 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H), 6.87 (s, 2H), 7.07 (s, 3H), 7.26 (d, J = 7.5 Hz, 1H), 7.48 (s, 1H), 10.4 (br s, 1H), 10.9 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 41.8, 54.5, 105.9, 106.9, 111.2, 123.0, 118.7, 126.5, 127.6, 128.0, 129.2,

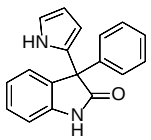
129.8, 130.7, 133.7, 135.8, 141.1, 177.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{15}BrN_2NaO$ $[M+Na]^+$: 389.0260; Found: 389.0265.



7n: Light yellow soid, m.p. 203.1-204.5 °C; Yield 91%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.43-3.51 (m, 2H), 5.66 (s, 1H), 5.90 (s, 1H), 6.66 (s, 1H), 6.74 (s, 1H), 6.87 (d, J = 3.0 Hz, 2H), 6.99-7.01 (m, 1H), 7.07 (s, 3H), 7.28 (d, J = 8.0 Hz, 1H), 10.4 (br s, 1H), 10.9 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 41.9, 54.0, 106.0, 106.9, 109.4, 118.7, 120.9, 127.6, 129.2, 129.9, 130.0, 132.2, 135.9, 143.4, 178.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{15}ClN_2NaO$ $[M+Na]^+$: 345.0765; Found: 345.0771.



7o: White soild, m.p. 121.7-124.1 °C; Yield 81%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.27-3.35 (m, 3H), 5.87 (s, 1H), 6.00 (s, 1H), 6.58 (d, J = 5.6 Hz, 1H), 6.71-6.75 (m, 3H), 6.97-7.00 (m, 1H), 7.11-7.14 (m, 2H), 7.20 (d, J = 5.6 Hz, 2H), 9.35 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 26.2, 45.6, 53.2, 107.7, 108.1, 108.6, 118.9, 122.6, 123.5 (q, J = 270.9 Hz), 124.4, 124.5, 125.3, 128.7, 130.5, 132.7 (q, J = 32.9 Hz), 139.7, 143.3, 177.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{21}H_{17}F_3N_2NaO$ $[M+Na]^+$: 393.1185; Found: 393.1181.

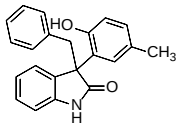


7p: Light yellow soid, m.p. 283.1-285.4 °C; Yield 91%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 5.91 (s, 1H), 5.99 (s, 1H), 6.76 (s, 1H), 6.99 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 7.5 Hz, 3H), 7.27-7.35 (m, 4H), 7.42 (d, J = 7.0 Hz, 1H), 10.66 (br s, 1H), 10.74 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 57.6, 106.5, 107.7, 109.9, 119.4, 121.9, 125.5, 127.1, 127.3, 128.2, 128.4, 128.7, 133.3, 141.4, 141.6, 177.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{18}H_{14}N_2NaO$ $[M+Na]^+$: 297.0998; Found: 297.1004.

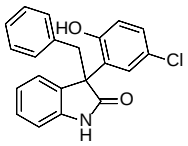
7. General Experimental Procedures for Synthesis of Compounds 9

In a sealed tube equipped with a magnetic stirring bar was added 3-chloroxindole **1** (0.2 mmol), 0.4 mmol of phenol **8** and 1.0 mL of toluene. The reaction mixture was constantly stirred in an oil bath at 80 °C for 8 h. After a considerable amount of starting material had been consumed with no further improvement in the product formation (TLC monitoring), the resulting mixture was cooled to room temperature, and was purified by chromatography on silica gel (petroleum ether/EtOAc 8:1 to 10:1) to afford the desired *o*/*p*-hydroxyaryl 2-oxindole **9**.

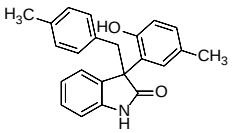
8. Characterization Data of Compounds 9:



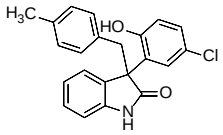
9a: Light yellow soid, m.p. 42.5-44.3 °C; Yield 90%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 2.30 (s, 3H), 3.33 (d, J = 10.0 Hz, 1H), 3.62 (d, J = 10.5 Hz, 1H), 6.46 (d, J = 6.5 Hz, 1H), 6.59 (d, J = 6.5 Hz, 1H), 6.71-6.73 (m, 2H), 6.85-6.88 (m, 1H), 6.92-6.94 (m, 1H), 6.98-7.02 (m, 3H), 7.04-7.07 (m, 2H), 7.40 (s, 1H), 9.18 (br s, 1H), 9.94 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 21.0, 41.9, 55.9, 108.8, 115.9, 121.1, 123.8, 126.7, 127.6, 128.6, 128.8, 130.5, 136.1, 143.4, 153.2, 180.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{19}NNaO_2$ [M+Na]$^+$: 352.1308; Found: 352.1315.



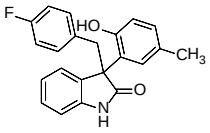
9b: Light yellow soid, m.p. 121.6-123.0 °C; Yield 89%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 3.29 (d, J = 10.0 Hz, 1H), 3.63 (d, J = 10.0 Hz, 1H), 6.47 (d, J = 6.0 Hz, 1H), 6.68-6.72 (m, 3H), 6.86-6.89 (m, 1H), 6.99-7.02 (m, 3H), 7.05-7.08 (m, 2H), 7.18-7.20 (m, 1H), 7.62 (d, J = 2.0 Hz, 1H), 9.74 (br s, 1H), 9.99 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 41.7, 55.7, 108.8, 117.4, 121.3, 123.8, 127.6, 127.9, 128.1, 128.2, 130.5, 132.9, 143.5, 154.5, 179.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{21}H_{16}ClNNaO_2$ [M+Na]$^+$: 372.0762; Found: 372.0762.



9c: Light yellow soid, m.p. 89.8-92.3 ^{o}C; Yield 90%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.22 (s, 6H), 3.46 (d, J = 11.5 Hz, 1H), 3.96 (d, J = 11.0 Hz, 1H), 6.73 (d, J = 6.5 Hz, 2H), 6.82 (d, J = 6.0 Hz, 1H), 6.86 (d, J = 6.5 Hz, 2H), 6.96 (s, 1H), 6.99 (d, J = 6.5 Hz, 1H), 7.05-7.07 (m, 1H), 7.21-7.24 (m, 1H), 7.27-7.30 (m, 2H), 8.56 (br s, 1H), 10.10 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.7, 21.0, 40.7, 59.7, 110.7, 119.9, 122.6, 123.9, 127.2, 128.5, 129.2, 129.4, 130.1, 130.4, 132.2, 154.2, 183.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{21}NNaO_2$ $[M+Na]^+$: 366.1465; Found: 366.1470.

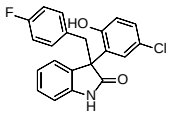


9d: Light yellow soid, m.p. 88.2-90.5 ^{o}C; Yield 85%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.22 (s, 3H), 3.45 (d, J = 11.0 Hz, 1H), 3.85 (d, J = 11.0 Hz, 1H), 7.00 (d, J = 6.5 Hz, 2H), 6.82 (d, J = 6.5 Hz, 1H), 6.87 (d, J = 6.5 Hz, 2H), 7.00 (d, J = 7.0 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H), 7.18-7.20 (m, 1H), 7.22-7.31 (m, 3H), 8.48 (br s, 1H), 10.43 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.0, 40.5, 59.4, 110.9, 121.3, 123.0, 127.1, 128.5, 128.9, 129.4, 129.7, 130.1, 131.7, 136.5, 140.2, 155.3, 182.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{18}ClNNaO_2$ $[M+Na]^+$: 386.0918; Found: 386.0914.

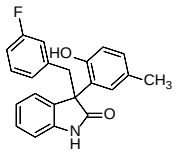


9e: Light yellow soid, m.p. 45.3-47.9 ^{o}C; Yield 75%; ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 2.30 (s, 3H), 3.32 (d, J = 10.0 Hz, 1H), 3.62 (d, J = 10.0 Hz, 1H), 6.49 (d, J = 6.0 Hz, 1H), 6.58 (d, J = 6.5 Hz, 1H), 6.71-6.74 (m, 2H), 6.82-6.88 (m, 3H), 6.92-6.94 (m, 1H), 7.01-7.06 (m, 2H), 7.40 (s, 1H), 9.16 (br s, 1H), 9.97 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 21.0, 41.0, 55.8, 108.8, 114.3 (d, J_{CF} = 21.5 Hz), 115.8, 121.2, 123.8, 127.5, 127.7 (d, J_{CF} = 21.5 Hz), 128.7 (d, J_{CF} = 22.5 Hz), 132.2, 133.4, 143.4, 153.2, 161.4 (d, J_{CF} = 241.4 Hz), 180.0; HRMS (ESI-TOF) m/z: Calcd. for

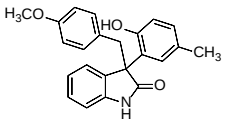
$C_{22}H_{18}FNNaO_2$ [M+Na]$^+$: 370.1214; Found: 370.1219.



9f: Light yellow soid, m.p. 76.8-79.6 ^{o}C; Yield 77%; ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.28 (d, J = 10.5 Hz, 1H), 3.64 (d, J = 10.0 Hz, 1H), 6.49 (d, J = 6.5 Hz, 1H), 6.68 (d, J = 7.0 Hz, 1H), 6.68-6.73 (m, 2H), 6.82-6.89 (m, 3H), 7.02-7.05 (m, 1H), 7.07 (d, J = 6.0 Hz, 1H), 7.17-7.20 (m, 1H), 7.61 (d, J = 2.0 Hz, 1H), 9.71 (br s, 1H), 10.01 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 40.8, 55.6, 108.9, 114.3 (d, J_{CF} = 21.0 Hz), 117.3, 121.4, 122.9, 123.8, 128.0 (d, J_{CF} = 15.5 Hz), 128.3, 130.3, 131.8, 132.2, 132.6, 143.5, 154.4, 161.4 (d, J_{CF} = 240.3 Hz), 179.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{21}H_{15}ClFNNaO_2$ [M+Na]$^+$: 390.0668; Found: 390.0673.

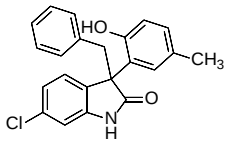


9g: Light yellow soid, m.p. 37.3-38.5 ^{o}C; Yield 82%; ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 2.30 (s, 3H), 3.33 (d, J = 10.5 Hz, 1H), 3.66 (d, J = 10.5 Hz, 1H), 6.44 (d, J = 8.5 Hz, 1H), 6.49 (d, J = 6.0 Hz, 1H), 6.66 (d, J = 6.5 Hz, 2H), 6.86-6.90 (m, 2H), 6.92-6.94 (m, 1H), 7.01-7.07 (m, 3H), 7.39 (s, 1H), 9.15 (br s, 1H), 10.0 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 21.0, 41.5, 55.8, 108.8, 113.6 (d, J_{CF} = 20.1 Hz), 115.8, 117.0 (d, J_{CF} = 21.5 Hz), 121.2, 123.8, 126.7, 127.5, 127.7, 128.6, 128.8, 129.3, 133.3, 139.0, 143.4, 153.1, 161.5(d, J_{CF} = 240.1 Hz), 179.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{18}FNNaO_2$ [M+Na]$^+$: 370.1214; Found: 370.1217.

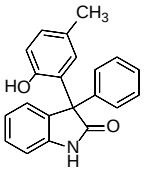


9h: Light yellow soid, m.p. 46.0-49.5 ^{o}C; Yield 87%; ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 2.30 (s, 3H), 3.30 (d, J = 10.0 Hz, 1H), 3.48 (s, 3H), 3.60 (d, J = 10.0 Hz, 1H), 6.19 (s, 1H), 6.37 (d, J = 6.0 Hz, 1H), 6.49 (d, J = 6.5 Hz, 1H), 6.57 (d, J = 6.5 Hz, 1H), 6.61-6.63 (m, 1H), 6.86-6.89 (m, 1H), 6.91-6.95 (m, 2H), 7.01-7.06 (m, 2H), 7.38 (s, 1H), 9.16 (br s, 1H), 9.95 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 21.0, 41.9, 55.0, 55.8, 108.8, 112.6, 115.5, 115.9, 121.1, 123.0, 123.8, 127.5, 127.6, 127.9, 128.5, 128.6, 128.7, 133.7, 137.6, 143.6, 153.2, 158.5, 180.0; HRMS

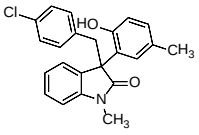
(ESI-TOF) m/z: Calcd. for $C_{23}H_{21}NNaO_3$ $[M+Na]^+$: 382.1414; Found: 382.1413.



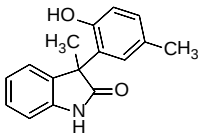
9i: Light yellow soid, m.p. 241.9-243.0 ºC; Yield 88%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 2.31 (s, 3H), 3.32 (d, J = 10.0 Hz, 1H), 3.63 (d, J = 10.5 Hz, 1H), 6.45 (s, 3H), 6.57 (d, J = 7.0 Hz, 1H), 6.76 (d, J = 6.0 Hz, 2H), 6.87-6.89 (m, 1H), 6.94 (d, J = 7.0 Hz, 1H), 7.02-7.09 (m, 4H), 7.43 (s, 1H), 9.16 (br s, 1H), 10.09 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 21.0, 41.6, 55.4, 108.6, 120.8, 125.1, 126.8, 127.5, 127.7, 128.6, 128.9, 130.5, 132.7, 135.8, 145.0, 153.0, 180.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{18}ClNNaO_2$ $[M+Na]^+$: 386.0918; Found: 386.0924.



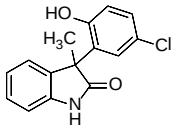
9j: Light yellow soid, m.p. 267.9-271.0 ºC; Yield 89%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 2.09 (s, 3H), 6.57 (s, 1H), 6.63 (d, J = 6.5 Hz, 1H), 6.89-6.92 (m, 2H), 6.94-6.96 (m, 1H), 7.10 (d, J = 6.0 Hz, 1H), 7.19-7.22 (m, 1H), 7.28-7.32 (m, 5H), 9.29 (br s, 1H), 10.44 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 20.9, 60.4, 109.8, 116.1, 121.6, 126.1, 127.3, 127.6, 128.2, 128.5, 128.8, 129.1, 129.3, 130.6, 133.3, 140.1, 142.9, 153.5, 179.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{21}H_{17}NNaO_2$ $[M+Na]^+$: 338.1151; Found: 338.1155.



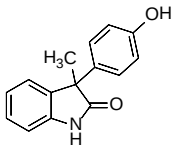
9k: Light yellow soid, m.p. 85.8-86.3 ºC; Yield 83%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.20 (s, 3H), 3.02 (s, 3H), 3.40 (d, J = 11.0 Hz, 1H), 4.04 (d, J = 11.5 Hz, 1H), 6.75-6.78 (m, 3H), 6.92 (s, 1H), 7.02-7.08 (m, 4H), 7.26-7.29 (m, 1H), 7.34-7.38 (m, 2H), 10.58 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 20.7, 26.3, 40.4, 59.3, 109.2, 120.3, 122.9, 127.0, 127.7, 128.8, 129.0, 130.3, 131.5, 134.1, 143.1, 154.6, 180.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{20}ClNNaO_2$ $[M+Na]^+$: 400.1075; Found: 400.1076.



9l: Light yellow soid, m.p. 53.7-56.3 ^{o}C; Yield 86%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.55 (s, 3H), 2.29 (s, 3H), 6.54 (d, J = 7.0 Hz, 1H), 6.78-6.85 (m, 3H), 6.89-6.91 (m, 1H), 7.08-7.11 (m, 1H), 7.27 (d, J = 1.5 Hz, 1H), 9.05 (br s, 1H), 10.32 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 21.0, 24.1, 50.2, 109.3, 115.4, 121.4, 122.7, 127.3, 127.7, 128.7, 128.8, 136.8, 142.6, 153.1, 182.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{15}NNaO_2$ [M+Na]$^{+}$: 276.0995; Found: 276.0991.



9m: Light yellow soid, m.p. 38.5-40.3 ^{o}C; Yield 84%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.55 (s, 3H), 6.64 (d, J = 7.0 Hz, 1H), 6.81-6.85 (m, 3H), 7.09-7.15 (m, 2H), 7.44 (s. 1H), 9.64 (br s, 1H), 10.37 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 23.9, 50.2, 109.4, 117.0, 121.5, 122.7, 122.8, 127.6, 128.0, 128.3, 130.2, 135.9, 142.6, 154.3, 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{12}ClNNaO_2$ [M+Na]$^{+}$: 296.0449; Found: 296.0453.



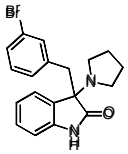
9n: Light yellow soid, m.p. 61.6-62.0 ^{o}C; Yield 90%; ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.53 (s, 3H), 6.62-6.64 (m, 2H), 6.85 (d, J = 9.5 Hz, 1H), 6.89-6.93 (m, 1H), 6.96 (d, J = 10.5 Hz, 2H), 7.06 (d, J = 9.0 Hz, 1H), 7.12-7.16 (m, 1H), 9.32 (br s, 1H), 10.38 (br s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 23.6, 51.6, 110.0, 115.5, 122.1, 124.4, 127.8, 128.2, 131.9, 136.2, 141.7, 156.6, 181.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{13}NNaO_2$ [M+Na]$^{+}$: 262.0838; Found: 262.0833.

9. General Experimental Procedures for Synthesis of Compounds 11

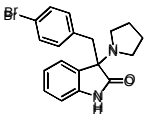
In a sealed tube equipped with a magnetic stirring bar was added 3-chloroxindole **1** (0.2 mmol), 0.4 mmol of amine **10** and 1.0 mL of toluene. The reaction mixture was constantly stirred in an oil

bath at 80 °C for 5 h. After a considerable amount of starting material had been consumed with no further improvement in the product formation (TLC monitoring), the resulting mixture was cooled to room temperature, and was purified by chromatography on silica gel (petroleum ether/EtOAc 8:1 to 10:1) to afford the desired 3-amino-2-oxindole **11**.

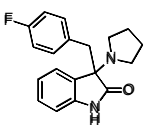
10. Characterization Data of Compounds 11:



11a: Light yellow soid, m.p. 158.7-160.5 ^{o}C; Yield 87%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.75 (s, 4H), 2.74-2.77 (m, 2H), 2.92-2.94 (m, 2H), 3.27 (d, J = 12.5 Hz, 1H), 3.44 (d, J = 12.5 Hz, 1H), 6.64 (d, J = 7.5 Hz, 1H), 6.80-6.88 (m, 2H), 6.97 (s, 1 H), 7.03-7.07 (m, 1H), 7.13-7.18 (m, 2H), 7.35 (d, J = 7.5 Hz, 1H), 8.10 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.2, 42.0, 46.9, 69.9, 109.7, 121.5, 122.3, 124.9, 128.7, 128.9, 129.0, 129.4, 129.5, 133.1, 137.3, 140.4, 179.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{19}BrN_2NaO$ $[M+Na]^+$: 393.0573; Found: 393.0575.

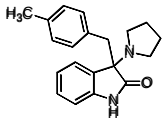


11b: Light yellow soid, m.p. 172.1-173.4 ^{o}C; Yield 90%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.73-2.76 (m, 2H), 2.89-2.93 (m, 2H), 3.24 (d, J = 12.5 Hz, 1H), 3.44 (d, J = 12.5 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 2H), 7.02-7.06 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.12-7.17 (m, 1H), 7.37 (d, J = 7.5 Hz, 1H), 8.54 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.3, 41.8, 47.0, 70.1, 109.9, 120.6, 122.3, 124.9, 128.8, 129.4, 130.6, 132.1, 133.9, 140.5, 179.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{19}BrN_2NaO$ $[M+Na]^+$: 393.0573; Found: 393.0578.

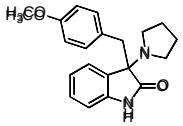


11c: Light yellow soid, m.p. 156.9-157.4 ^{o}C; Yield 85%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.73 (s, 4H), 2.72-2.76 (m, 2H), 2.88-2.90 (m, 2H), 3.29 (d, J = 12.5 Hz, 1H), 3.46 (d, J = 12.5 Hz, 1H), 6.60-6.66 (m, 3H), 6.76-6.81 (m, 2H), 7.02-7.06 (m, 1H), 7.12-7.17 (m, 1H), 7.37 (d, J = 7.0 Hz, 1H), 8.90 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.2, 41.6, 46.9, 70.2, 109.8, 114.3 (d, J_{CF} =

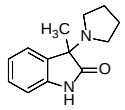
21.4 Hz), 122.1, 124.8, 128.6, 129.4, 130.5, 131.6, 140.7, 161.5 (d, J_{CF} = 243.8 Hz), 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{19}FN_2NaO$ [M+Na]$^+$: 333.1374; Found: 333.1369.



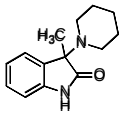
11d: Light yellow soid, m.p. 145.9-146.7 ^{o}C; Yield 88%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.73 (s, 4H), 2.12 (s, 3H), 2.73-2.76 (m, 2H), 2.89-2.92 (m, 2H), 3.27 (d, J = 12.5 Hz, 1H), 3.44 (d, J = 12.5 Hz, 1H), 6.61 (d, J = 7.5 Hz, 1H), 6.71-6.76 (m, 4H), 6.99-7.04 (m, 1H), 7.09-7.13 (m, 1H), 7.36 (d, J = 7.0 Hz, 1H), 8.83 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.8, 23.1, 41.9, 46.8, 70.2, 109.6, 121.9, 124.9, 128.2, 128.4, 129.9, 130.0, 131.7, 135.6, 140.7, 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{22}N_2NaO$ [M+Na]$^+$: 329.1624; Found: 329.1621.



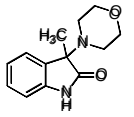
11e: Light yellow soid, m.p. 149.9-152.5 ^{o}C; Yield 81%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.77 (s, 4H), 2.76-2.79 (m, 2H), 2.92-2.95 (m, 2H), 3.29 (d, J = 12.5 Hz, 1H), 3.47 (d, J = 13.0 Hz, 1H), 3.66 (s, 3H), 6.53 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 7.5 Hz, 1H), 6.79 (d, J = 9.0 Hz, 2H), 7.05-7.08 (m, 1H), 7.16-7.19 (m, 1H), 7.42 (d, J = 7.0 Hz, 1H), 8.58 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 23.3, 41.6, 46.9, 54.9, 70.3, 109.7, 112.8, 122.1, 124.9, 126.9, 128.5, 129.9, 131.2, 140.7, 157.9, 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{22}N_2NaO_2$ [M+Na]$^+$: 345.1573; Found: 345.1578.



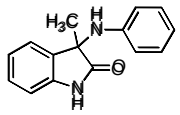
11f: Light yellow soid, m.p. 56.5-59.8 ^{o}C; Yield 88%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.63 (s, 3H), 1.72-1.77 (m, 4H), 2.72-2.76 (m, 2H), 2.82-2.85 (m, 2H), 6.93 (d, J = 6.5 Hz, 1H), 7.02-7.05 (m, 1H), 7.20-7.23 (m, 1H), 7.34 (d, J = 6.0 Hz, 1H), 9.55 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.1, 23.4, 46.9, 64.7, 110.2, 122.5, 124.1, 128.4, 132.4, 140.3, 181.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{13}H_{16}N_2NaO$ [M+Na]$^+$: 239.1155; Found: 239.1161.



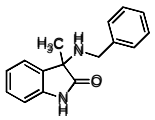
11g: Light yellow soid, m.p. 149.8-150.2 °C; Yield 92%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29-1.34 (m, 2H), 1.45 (7H), 2.54-2.56 (m, 4H), 6.85 (d, J = 8.0 Hz, 1H), 6.91-6.95 (m, 1H), 7.09-7.13 (m, 1H), 7.19-7.21 (m, 1H), 9.82 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.2, 24.5, 26.3, 47.7, 67.4, 110.3, 122.3, 124.0, 128.2, 132.4, 140.5, 181.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{14}H_{18}N_2NaO$ $[M+Na]^+$: 253.1311; Found: 253.1317.



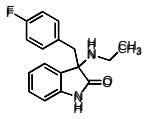
11h: Light yellow soid, m.p. 171.3-173.0 °C; Yield 91%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.45 (s, 3H), 2.59-2.66 (m, 4H), 3.59-3.61 (m, 4H), 6.83-6.86 (m, 1H), 6.93-6.97 (m, 1H), 7.11-7.15 (m, 1H), 7.20 (d, J = 6.0 Hz, 1H), 9.73 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.5, 47.0, 66.7, 67.3, 110.3, 122.6, 124.0, 128.6, 131.5, 140.5, 181.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{13}H_{16}N_2NaO_2$ $[M+Na]^+$: 255.1104; Found: 255.1107.



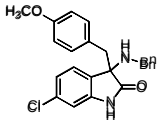
11i: Light yellow soid, m.p. 193.4-193.7 °C; Yield 91%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.40 (s, 3H), 6.08-6.10 (m, 2H), 6.34-6.40 (m, 2H), 6.80-6.89 (m, 4H), 7.08-7.17 (m, 2H), 10.58 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 27.5, 60.7, 110.5, 113.3, 116.9, 122.4, 123.1, 128.9, 129.0, 132.8, 140.9, 146.9, 180.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{14}N_2NaO$ $[M+Na]^+$: 261.0998; Found: 261.0991.



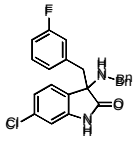
11j: Light yellow soid, m.p. 166.2-166.7 °C; Yield 84%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.51 (s, 3H), 2.24 (br s, 1H), 3.25 (d, J = 12.4 Hz, 1H), 3.50 (d, J = 12.4 Hz, 1H), 6.94-6.96 (m, 1H), 7.08-7.12 (m, 1H), 7.16-7.21 (m, 1H), 7.23-7.26 (m, 5H), 7.40-7.42 (m, 1H), 9.16 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.4, 48.9, 63.9, 110.4, 123.1, 124.2, 127.2, 128.4, 129.0, 131.6, 139.8, 140.6, 182.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{16}N_2NaO$ $[M+Na]^+$: 275.1155; Found: 275.1158.



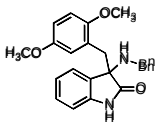
11k: Light yellow soid, m.p. 184.4-185.8 ºC; Yield 93%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 0.83-0.86 (m, 3H), 1.87-1.95 (m, 1H), 2.12-2.20 (m, 1H), 2.88 (d, J = 12.4 Hz, 1H), 2.99 (d, J = 12.8 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.74-6.83 (m, 4H), 6.88-6.92 (m, 1H), 7.02-7.06 (m, 1H), 7.16 (d, J = 7.2 Hz, 1H), 10.08 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 15.7, 38.3, 43.1, 68.5, 109.6, 114.5 (d, J_{CF} = 21.5 Hz), 121.7, 124.9, 128.9, 129.8, 131.8, 132.1, 132.2, 142.5, 161.4 (d, J_{CF} = 240.1 Hz), 162.5, 180.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{17}FN_2NaO$ $[M+Na]^+$: 307.1217; Found: 307.1217.



11l: Light yellow soid, m.p. 205.9-206.7 ºC; Yield 85%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.97 (d, J = 16.0 Hz, 1H), 3.12 (d, J = 16.5 Hz, 1H), 3.24 (d, J = 15.0 Hz, 1H), 3.43 (d, J = 15.0 Hz, 1H), 3.66 (s, 3H), 6.58-6.63 (m, 2H), 6.71 (d, J = 2.5 Hz, 1H), 6.77-6.79 (m, 2H), 7.05-7.07 (m, 1H), 7.20-7.26 (m, 6H), 8.05 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 44.2, 48.7, 55.1, 68.8, 110.7, 113.3, 122.8, 126.0, 127.3, 127.7, 128.3, 128.4, 128.5, 131.3, 134.6, 139.6, 142.1, 158.5, 181.0; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{21}ClN_2NaO_2$ $[M+Na]^+$: 415.1184; Found: 415.1187.

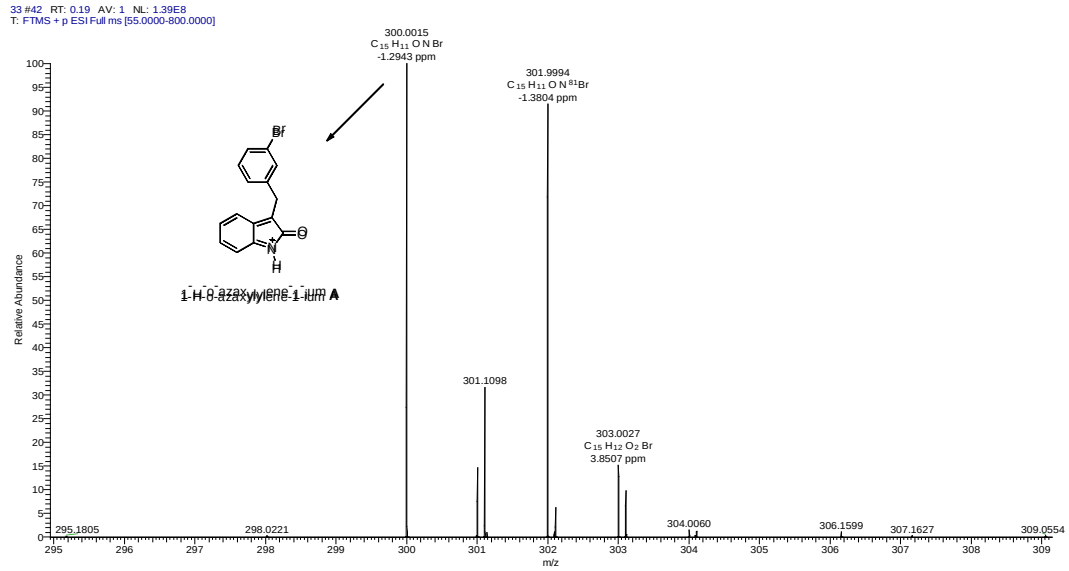


11m: Light yellow soid, m.p. 200.6-202.0 ºC; Yield 90%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.02 (d, J = 16.0 Hz, 1H), 3.14-3.19 (m, 1H), 3.23-3.29 (m, 1H), 3.42-3.47 (m, 1H), 6.60-6.66 (m, 2H), 6.73 (d, J = 2.0 Hz, 1H), 6.78-6.82 (m, 1H), 7.00-7.08 (m, 2H), 7.19-7.28 (m, 6H), 8.31 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 44.5, 48.6, 68.5, 110.9, 114.0 (d, J_{CF} = 22.3 Hz), 117.2 (d, J_{CF} = 23.5 Hz), 123.0, 126.0, 126.1, 127.1, 127.4, 127.5, 128.3, 128.4, 128.5, 129.3, 134.9, 136.6, 139.4, 142.0, 162.3 (d, J_{CF} = 245.1 Hz), 180.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{18}ClFN_2NaO$ $[M+Na]^+$: 403.0984; Found: 403.0989.

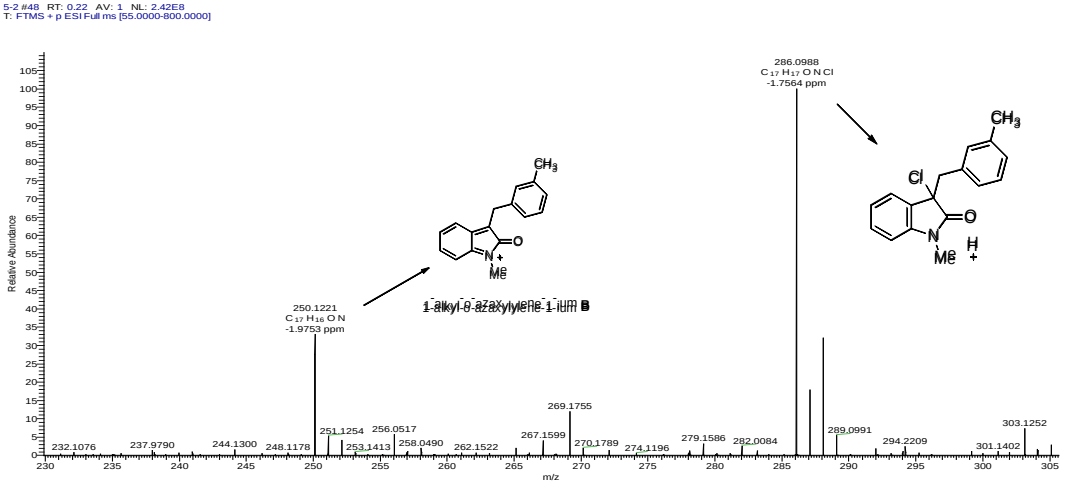


11n: Light yellow soid, m.p. 100.4-101.9 ^{o}C; Yield 88%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.99 (d, J = 12.8 Hz, 1H), 3.25 (d, J = 12.4 Hz, 1H), 3.41 (d, J = 12.8 Hz, 1H), 3.48-3.51 (m, 4H), 3.59 (s, 3H), 6.58-6.67 (m, 3H), 6.78 (d, J = 8.0 Hz, 1H), 6.97-7.01 (m, 1H), 7.14-7.25 (m, 7H), 8.98 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 37.9, 48.5, 55.6, 55.7, 68.6, 109.9, 111.2, 113.3, 117.4, 122.1, 124.4, 125.7, 127.0, 128.2, 128.3, 128.8, 129.5, 140.2, 141.1, 141.2, 152.3, 152.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{24}N_2NaO_3$ $[M+Na]^+$: 411.1679; Found: 403. 411.1672.

11. Figure S1: New Species Detected by ESI-MS Analysis in Different Experimental Program.

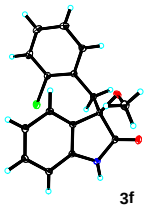


(1) program 1: temperature-mediated heterolytic cleavage for substrate **1e** in toluene at 80 ^{o}C for 1 h



(2) program 2: temperature-mediated heterolytic cleavage for substrate **1o** in toluene at 80 ^{o}C for 1 h

12. X-Ray Crystal Data for Compounds **3f**, **3n**, **5b**, **5c**, **7a, 7j** and **9a**.



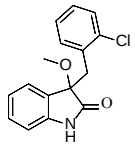


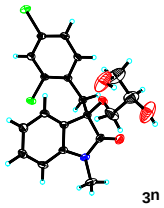
Table S2 Crystal data and structure refinement for 3f

Identification code	**3f**
Empirical formula	$C_{16}H_{14}ClNO_2$
Formula weight	287.73
Temperature/K	100(2)
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å, b/Å, c/Å	9.5976(9), 10.3316(9), 13.9249(13)
α/°, β/°, γ/°	90, 90, 90.
Volume/Å^3	1380.8(2)
Z	4
Density (calculated)	1.384 Mg/m^3
Absorption coefficient	0.277 mm^{-1}
F(000)	600
Crystal size/mm^3	0.740 x 0.650 x 0.580
Theta range for data collection	2.455 to 31.018°.
Index ranges	-13<=h<=13, -14<=k<=14, -19<=l<=20
Reflections collected	15337
Independent reflections	4126 [R(int) = 0.0196]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4126 / 0 / 182
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0251, wR2 = 0.0706
R indices (all data)	R1 = 0.0261, wR2 = 0.0713
Absolute structure parameter	0.055(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.342 and -0.227 e.Å^{-3}

Crystal structure determination of 3f

Crystal data for $C_{16}H_{14}ClNO_2$, M = 287.73, a = 9.5976(9) Å, b = 10.3316(9) Å, c = 13.9249(13) Å, α = 90°, β = 90°, γ = 90°, V = 1380.8(2) Å^3, T = 100(2) K, space group $P212121$, Z = 4, μ(MoKα) = 0.277 mm^{-1}, 15337 reflections measured, 4126 independent reflections (R_{int} = 0.0196). The final R_1 values were 0.0251 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0706 ($I > 2\sigma(I)$). The final R_1 values were 0.0261 (all data). The final $wR(F^2)$ values were 0.0713 (all data). The goodness of fit

on F^2 was 1.064. Flack parameter = 0.055(11).



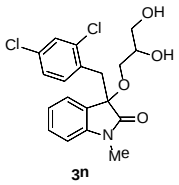


Table S3 Crystal data and structure refinement for 3n

Identification code	**3n**
Empirical formula	$C_{19}H_{19}Cl_2NO_4$
Formula weight	396.25
Temperature/K	100(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
a/Å, b/Å, c/Å	33.580(5), 13.960(2), 8.0737(13)
α/°, β/°, γ/°	90, 100.506(3), 90.
Volume/Å^3	3721.4(10)
Z	8
Density (calculated)	1.414 Mg/m^3
Absorption coefficient	0.373 mm^{-1}
F(000)	1648
Crystal size/mm^3	0.700 x 0.360 x 0.270
Theta range for data collection	1.233 to 28.569°.
Index ranges	-45<=h<=44, -18<=k<=18, -10<=l<=10
Reflections collected	19010
Independent reflections	4742 [R(int) = 0.1026]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4742 / 0 / 236
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0945, wR2 = 0.2570
R indices (all data)	R1 = 0.1178, wR2 = 0.2749
Extinction coefficient	n/a
Largest diff. peak and hole	1.801 and -0.894 e.Å^{-3}

Crystal structure determination of 3n

Crystal data for $C_{19}H_{19}Cl_2NO_4$, M = 396.25, a = 33.580(5) Å, b = 13.960(2) Å, c = 8.0737(13) Å, α = 90°, β = 100.506(3)°, γ = 90°, V = 3721.4(10) Å^3, T = 100(2) K, space group $C2/c$, Z = 8, μ(MoKα) = 0.373 mm^{-1}, 19010 reflections measured, 4742 independent reflections (R_{int} = 0.1026). The final R_1 values were 0.0945 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2570 ($I > 2\sigma(I)$). The final R_1 values were 0.1178 (all data). The final $wR(F^2)$ values were 0.2749 (all data). The

goodness of fit on F^2 was 1.047.

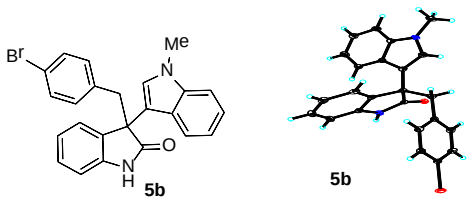
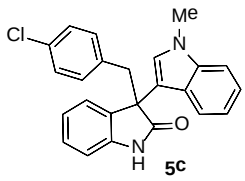


Table S4 Crystal data and structure refinement for 5b

Identification code	**5b**
Empirical formula	$C_{24}H_{19}BrN_2O$
Formula weight	431.32
Temperature/K	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å, b/Å, c/Å	13.0718(11), 15.5471(13), 10.5005(9)
α/°, β/°, γ/°	90, 113.1810(10), 90.
Volume/Å^3	1961.7(3)
Z	4
Density (calculated)	1.460 Mg/m^3
Absorption coefficient	2.112 mm^{-1}
F(000)	880
Crystal size/mm^3	0.360 x 0.320 x 0.060
Theta range for data collection	1.695 to 31.093°
Index ranges	-18<=h<=18, -21<=k<=22, -15<=l<=15
Reflections collected	21919
Independent reflections	5867 [R(int) = 0.0513]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5867 / 0 / 254
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.0855
R indices (all data)	R1 = 0.0703, wR2 = 0.0951

Crystal structure determination of 5b

Crystal data for $C_{24}H_{19}BrN_2O$, M = 431.32, a = 13.0718(11) Å, b = 15.5471(13) Å, c = 10.5005(9) Å, α = 90°, β = 113.1810(10)°, γ = 90°, V = 1961.7(3) Å^3, T = 100(2) K, space group $P21/c$, Z = 4, μ(MoKα) = 2.112 mm^{-1}, 21919 reflections measured, 5867 independent reflections (R_{int} = 0.0513). The final R_1 values were 0.0430 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0855 ($I > 2\sigma(I)$). The final R_1 values were 0.0703 (all data). The final $wR(F^2)$ values were 0.0951 (all data). The goodness of fit on F^2 was 1.005.



5c

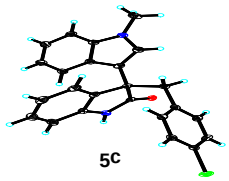
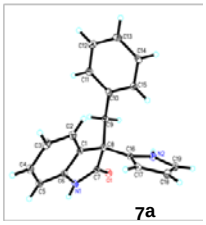

5c

Table S5 Crystal data and structure refinement for 5c

Identification code	**5c**
Empirical formula	$C_{24}H_{19}ClN_2O$
Formula weight	386.86
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å, b/Å, c/Å	12.9966(15), 15.5319(17), 10.5220(12)
α/°, β/°, γ/°	90, 113.397(2), 90.
Volume	1949.3(4) $Å^3$
Z	4
Density (calculated)	1.318 Mg/m^3
Absorption coefficient	0.213 mm^{-1}
F(000)	808
Crystal size	0.310 x 0.250 x 0.050 mm^3
Theta range for data collection	2.153 to 28.268°.
Index ranges	-17<=h<=17, -19<=k<=20, -13<=l<=14
Reflections collected	15650
Independent reflections	4173 [R(int) = 0.1013]
Completeness to theta = 25.242°	82.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4173 / 0 / 254
Goodness-of-fit on F^2	0.835
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1392
R indices (all data)	R1 = 0.1316, wR2 = 0.1615
Extinction coefficient	n/a
Largest diff. peak and hole	0.413 and -0.247 $e.Å^{-3}$

Crystal structure determination of 5c

Crystal data for $C_{24}H_{19}ClN_2O$, M = 386.86, a = 12.9966(15) Å, b = 15.5319(17) Å, c = 10.5220(12) Å, α = 90°, β = 113.397(2)°, γ = 90°, V = 1949.3(4) $Å^3$, T = 100(2) K, space group $P21/c$, Z = 4, μ(MoKα) = 0.213 mm^{-1}, 15650 reflections measured, 4173 independent reflections (R_{int} = 0.1013). The final R_1 values were 0.0594 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1392 ($I > 2\sigma(I)$). The final R_1 values were 0.1316 (all data). The final $wR(F^2)$ values were 0.1615 (all data). The goodness of fit on F^2 was 0.835.



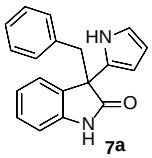
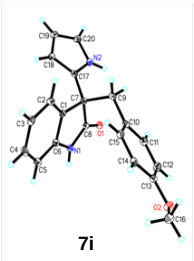


Table S6 Crystal data and structure refinement for 7a

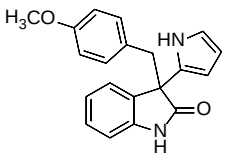
Identification code	**7a**
Empirical formula	$C_{19}H_{16}N_2O$
Formula weight	288.34
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å, b/Å, c/Å	8.8020(5), 9.9463(7), 10.2130(8)
α/°, β/°, γ/°	116.522(7), 100.853(6), 103.243(5).
Volume/Å^3	734.13(10)
Z	2
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.082
F(000)	304.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.728 to 58.976
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -11 ≤ l ≤ 13
Reflections collected	7205
Independent reflections	3407 [R_{int} = 0.0272, R_{sigma} = 0.0451]
Data/restraints/parameters	3407/0/199
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1137
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.1230
Largest diff. peak/hole / e Å^{-3}	0.28/-0.24

Crystal structure determination of 7a

Crystal data for $C_{19}H_{16}N_2O$ (M =288.34 g/mol): triclinic, space group P-1 (no. 2), a = 8.8020(5) Å, b = 9.9463(7) Å, c = 10.2130(8) Å, α = 116.522(7)°, β = 100.853(6)°, γ = 103.243(5)°, V = 734.13(10) Å^3, Z = 2, T = 100.00(10) K, μ(MoKα) = 0.082 mm^{-1},*Dcalc* = 1.304 g/cm^3, 7205 reflections measured (4.728° ≤ 2Θ ≤ 58.976°), 3407 unique (R_{int} = 0.0272, R_{sigma} = 0.0451) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1230 (all data).



7i



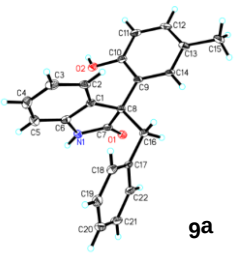
7i

Table S7 Crystal data and structure refinement for 7i

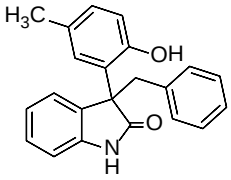
Identification code	**7i**
Empirical formula	$C_{20}H_{18}N_2O_2$
Formula weight	318.36
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å, b/Å, c/Å	8.9263(9), 10.1967(8), 10.2243(10)
α/°, β/°, γ/°	66.159(9), 69.066(9), 79.502(7).
Volume/Å^3	794.23(15)
Z	2
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.087
F(000)	336.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.372 to 59.028
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 14, -12 ≤ l ≤ 13
Reflections collected	14068
Independent reflections	3877 [R_{int} = 0.0417, R_{sigma} = 0.0465]
Data/restraints/parameters	3877/0/218
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1174
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1297
Largest diff. peak/hole / e Å^{-3}	0.37/-0.25

Crystal structure determination of 7i

Crystal data for $C_{20}H_{18}N_2O_2$ (M =318.36 g/mol): triclinic, space group P-1 (no. 2), a = 8.9263(9) Å, b = 10.1967(8) Å, c = 10.2243(10) Å, α = 66.159(9)°, β = 69.066(9)°, γ = 79.502(7)°, V = 794.23(15) Å^3, Z = 2, T = 100.01(10) K, μ(MoKα) = 0.087 mm^{-1}, $Dcalc$ = 1.331 g/cm^3, 14068 reflections measured (4.372° ≤ 2Θ ≤ 59.028°), 3877 unique (R_{int} = 0.0417, R_{sigma} = 0.0465) which were used in all calculations. The final R_1 was 0.0499 (I > 2σ(I)) and wR_2 was 0.1297 (all data).



9a



9a

Table S8 Crystal data and structure refinement for 9a

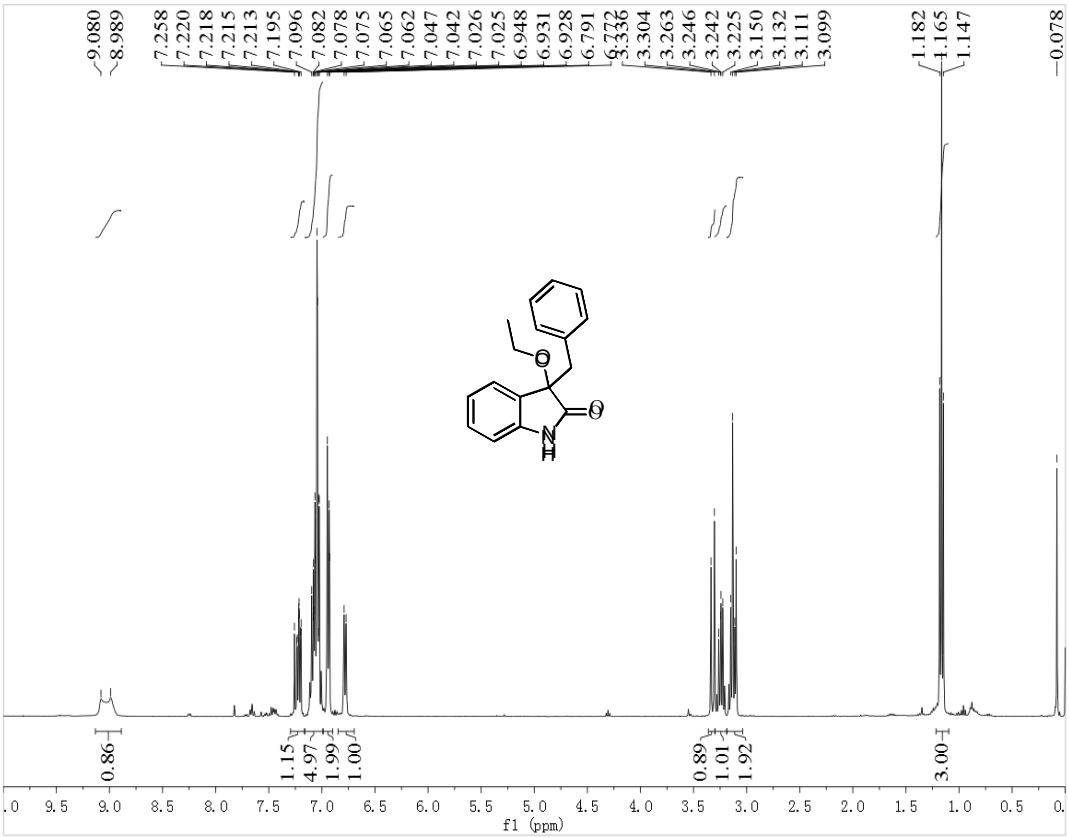
Identification code	**9a**
Empirical formula	$C_{22}H_{19}NO_2$
Formula weight	329.38
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å, b/Å, c/Å	17.598(4), 10.1274(14), 9.5969(14)
α/°, β/°, γ/°	90, 97.306(18), 90.
Volume/Å^3	1696.5(5)
Z	4
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	0.082
F(000)	696.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.65 to 59.186
Index ranges	-23 ≤ h ≤ 22, -13 ≤ k ≤ 9, -9 ≤ l ≤ 12
Reflections collected	8698
Independent reflections	4029 [R_{int} = 0.0720, R_{sigma} = 0.1187]
Data/restraints/parameters	4029/0/228
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0834, wR_2 = 0.1912
Final R indexes [all data]	R_1 = 0.1174, wR_2 = 0.2369
Largest diff. peak/hole / e Å^{-3}	0.47/-0.37

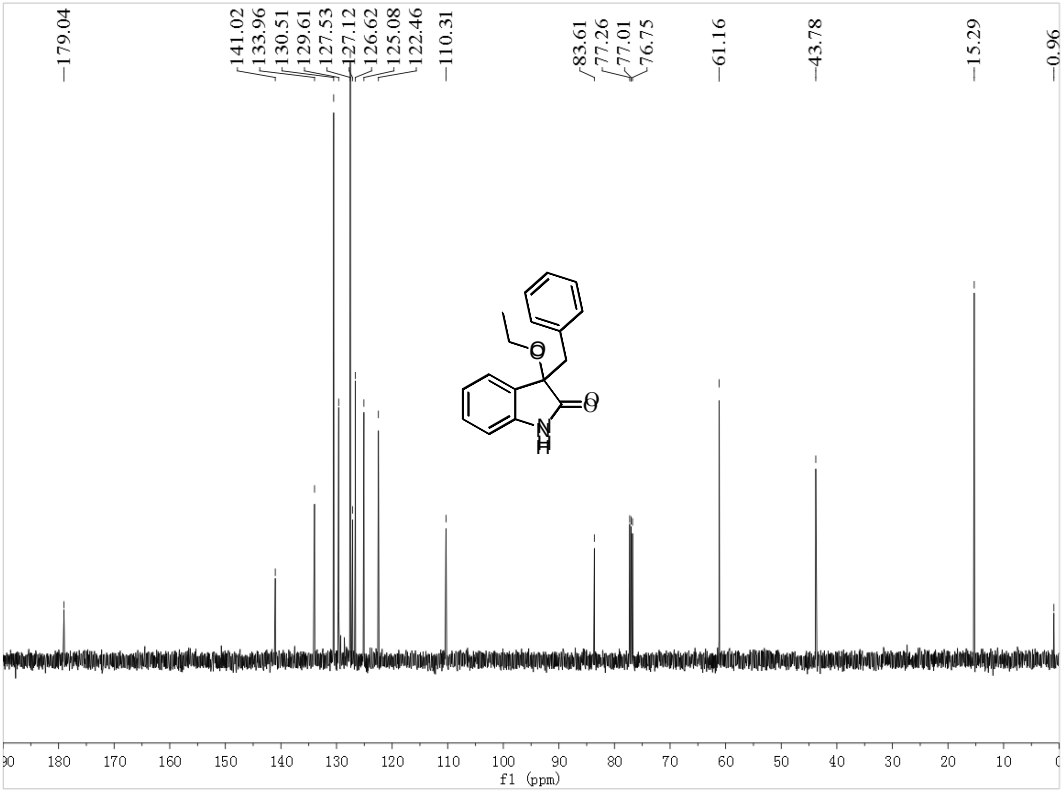
Crystal structure determination of 9a

Crystal Data for $C_{22}H_{19}NO_2$ (*M* =329.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 17.598(4) Å, *b* = 10.1274(14) Å, *c* = 9.5969(14) Å, *β* = 97.306(18)°, *V* = 1696.5(5) Å^3, *Z* = 4, *T* = 100.00(10) K, μ(MoKα) = 0.082 mm^{-1}, *Dcalc* = 1.290 g/cm^3, 8698 reflections measured (4.65° ≤ 2Θ ≤ 59.186°), 4029 unique (R_{int} = 0.0720, R_{sigma} = 0.1187) which were used in all calculations. The final R_1 was 0.0834 (I > 2σ(I)) and wR_2 was 0.2369 (all data).

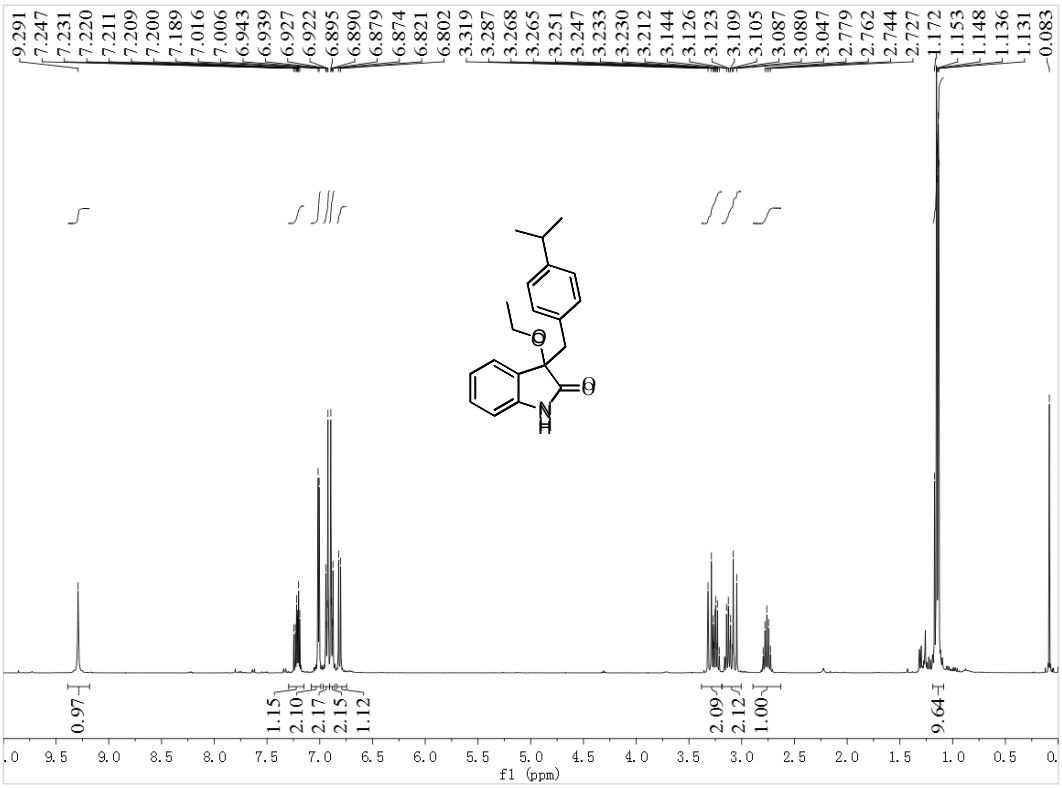
13. The Copies of ^{1}H NMR and ^{13}C NMR Spectra for Compounds **3**, **5, 7, 9** and **11**.

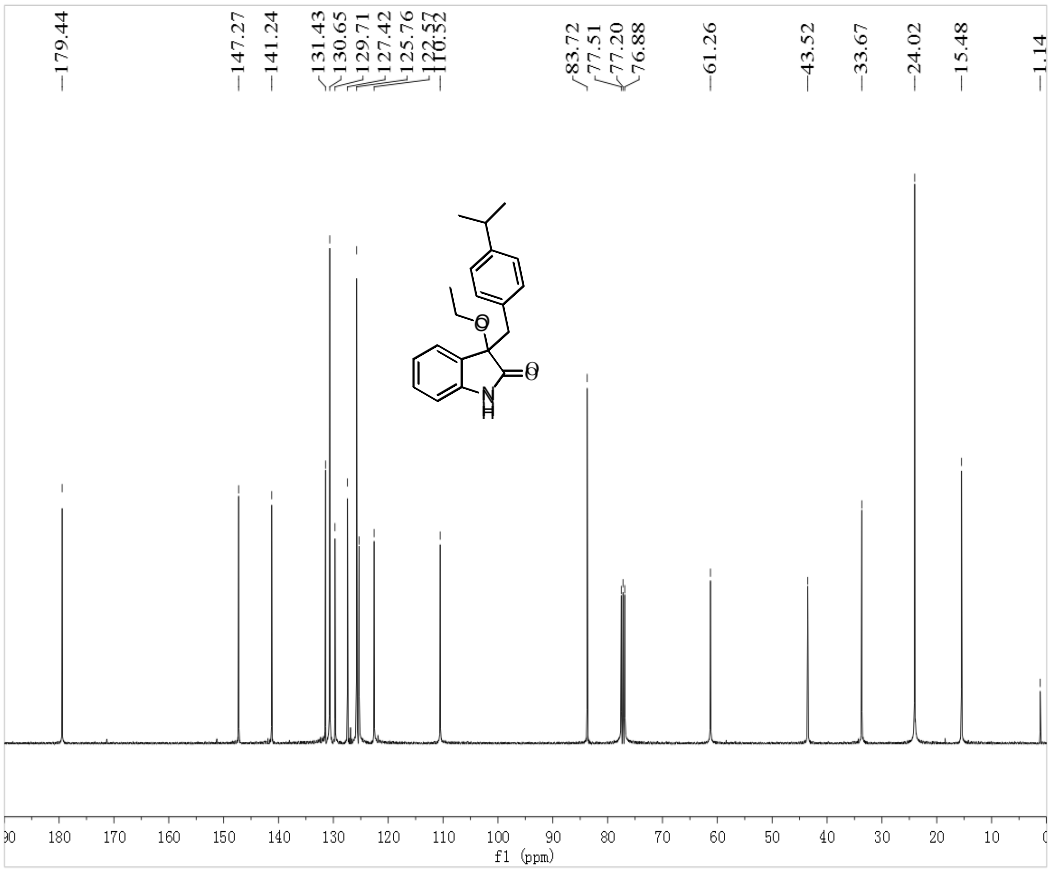
^{1}H and ^{13}C NMR of 3a



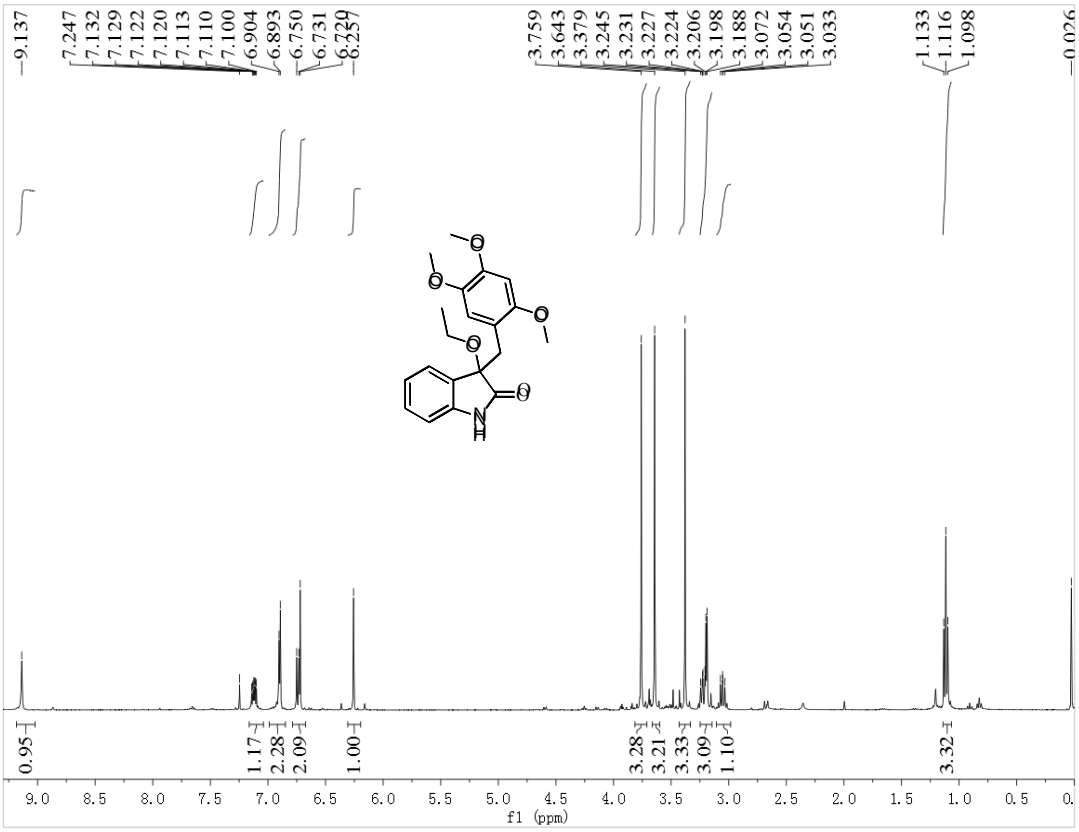


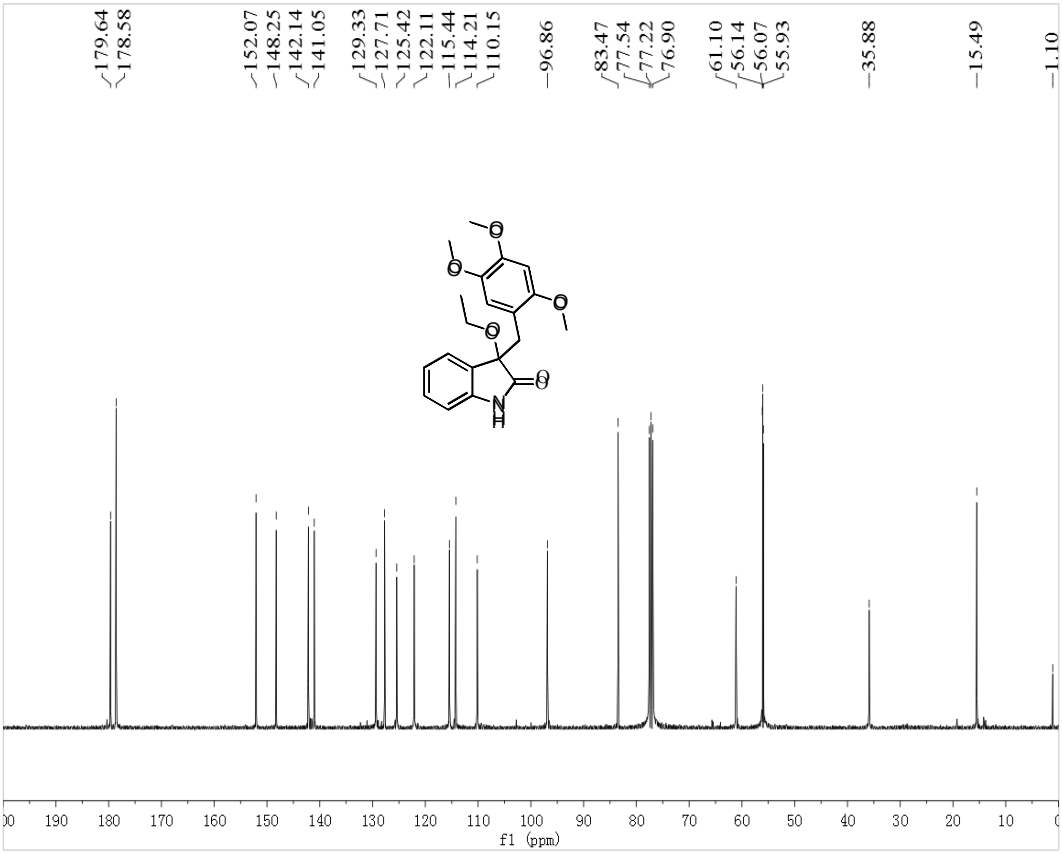
^{1}H and ^{13}C NMR of 3b



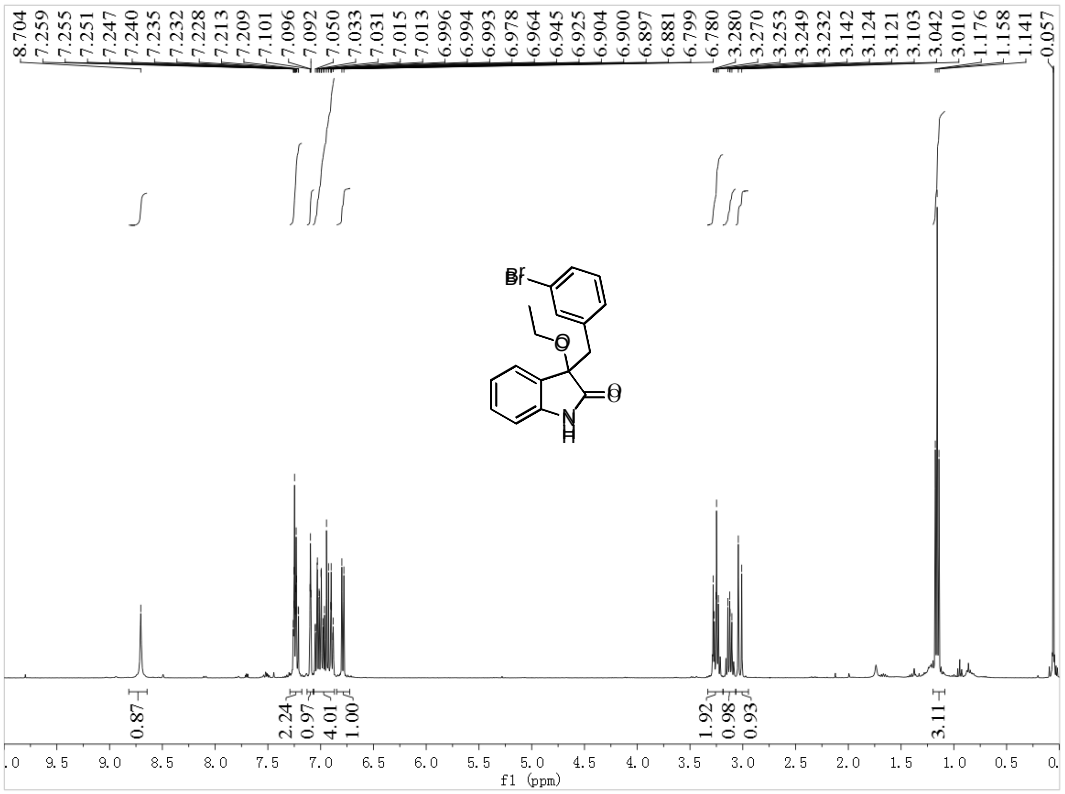


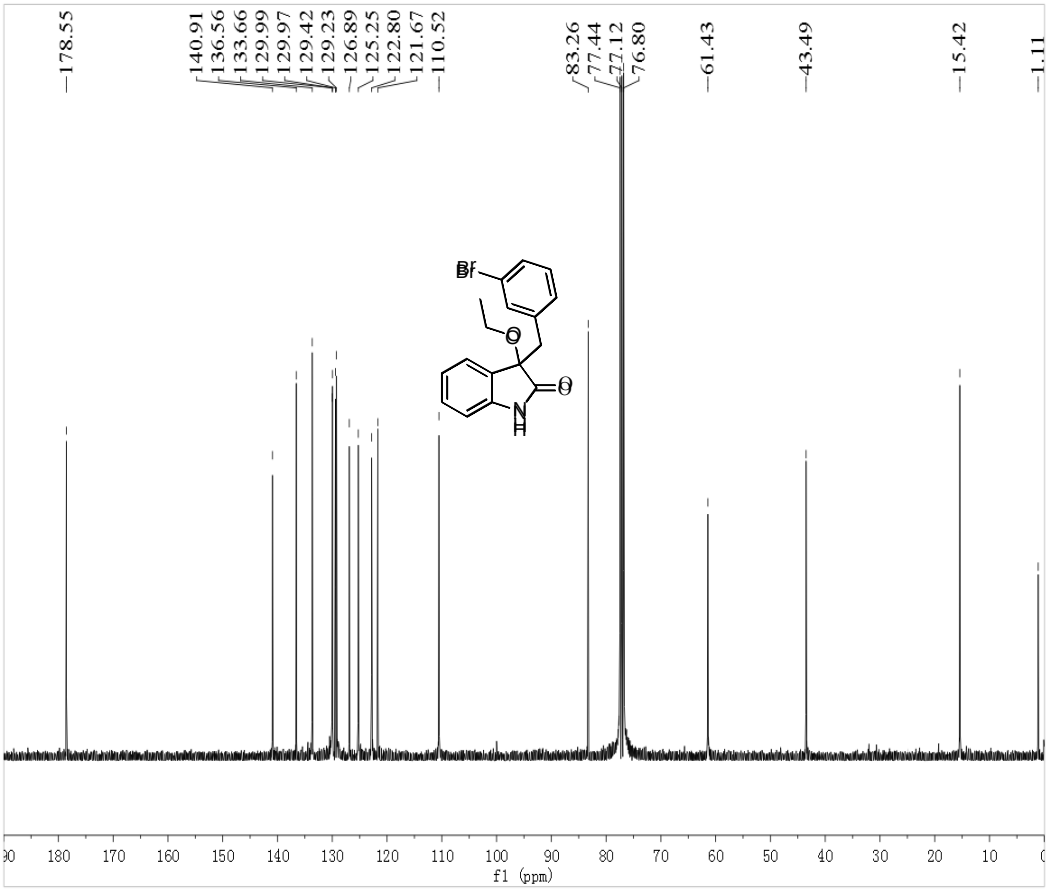
^{1}H and ^{13}C NMR of 3c



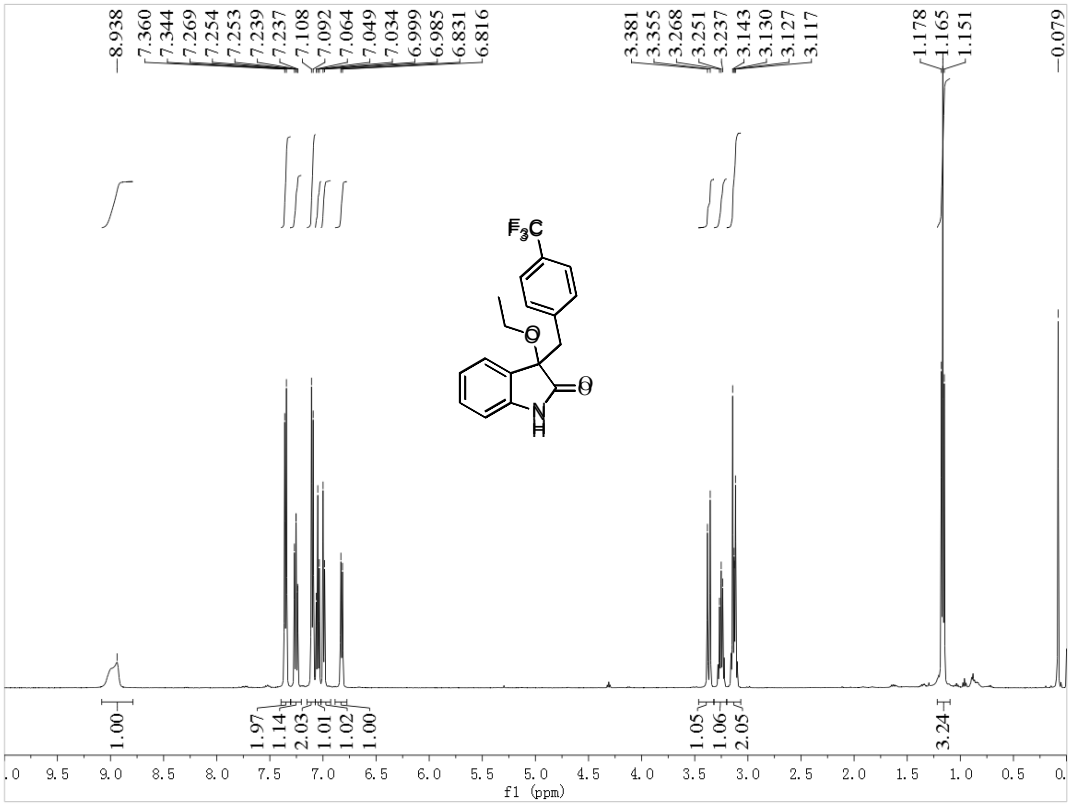


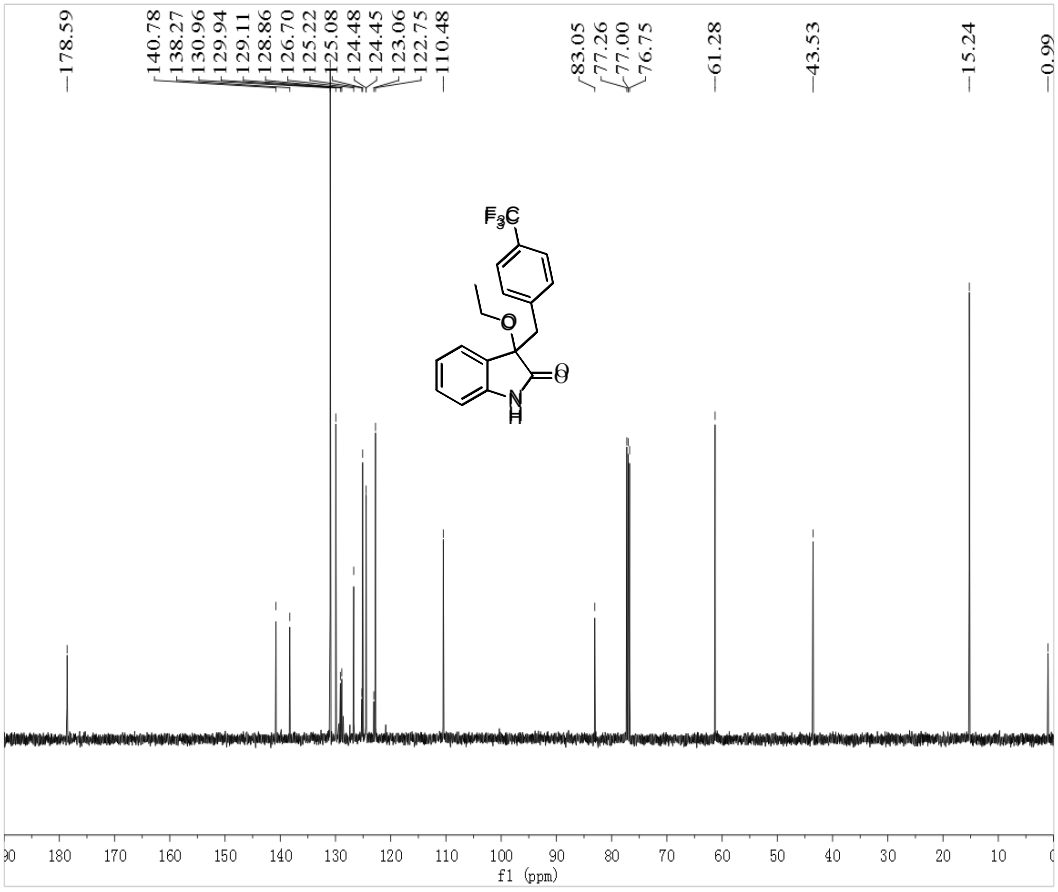
^{1}H and ^{13}C NMR of 3d



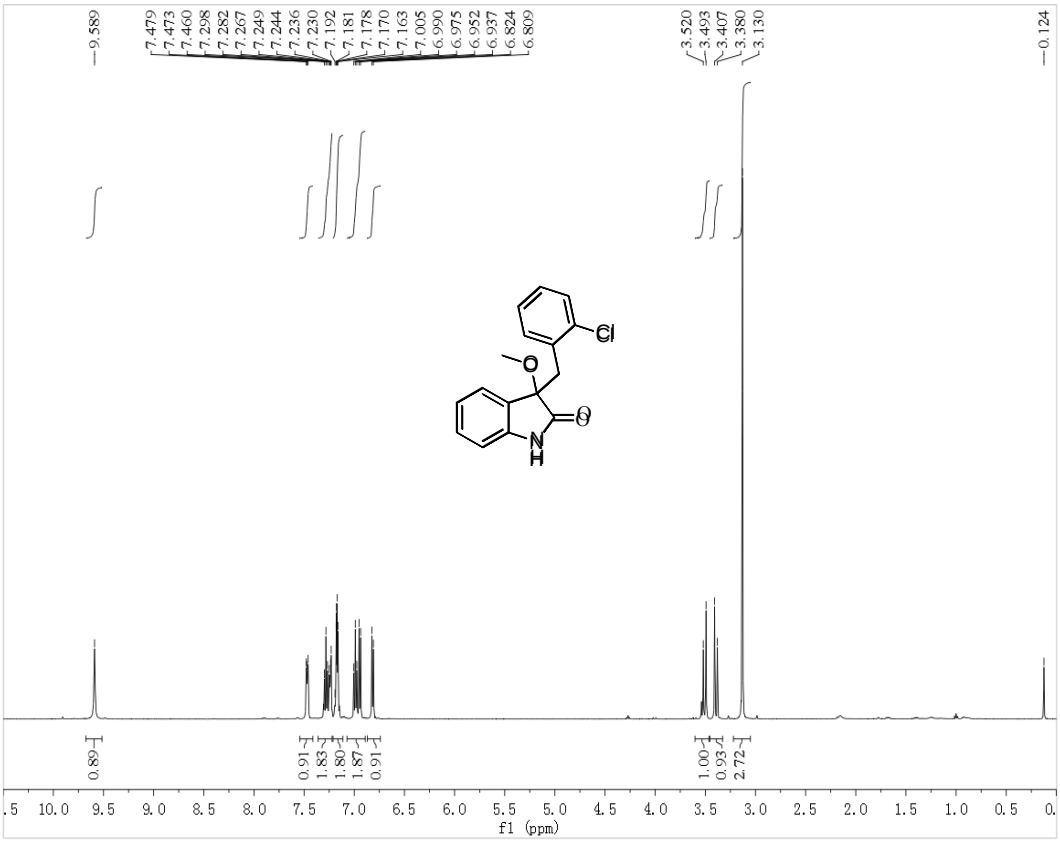


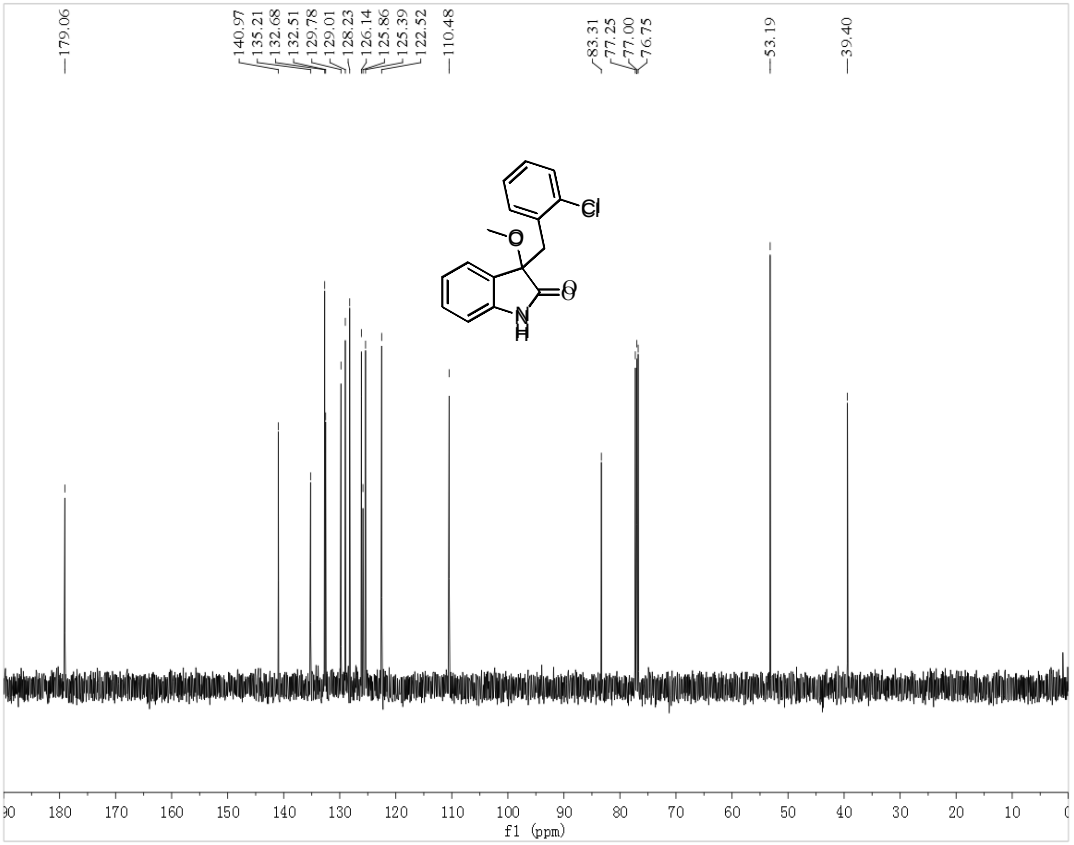
^{1}H and ^{13}C NMR of 3e



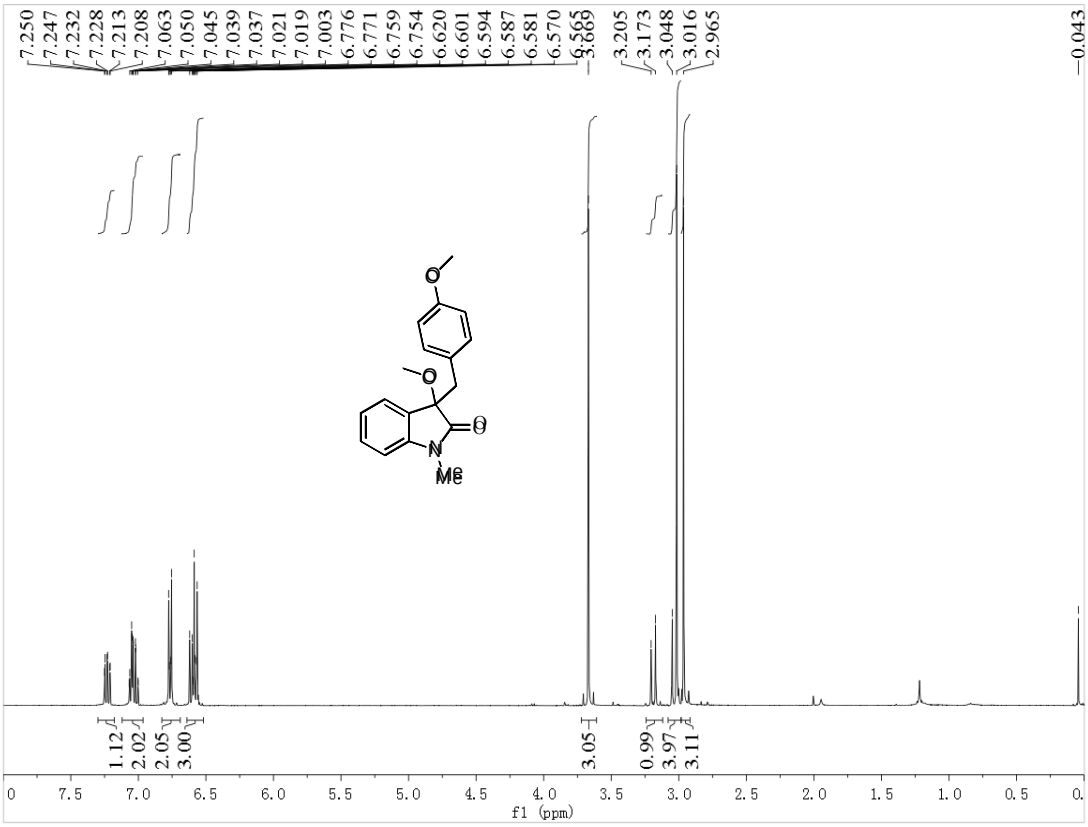


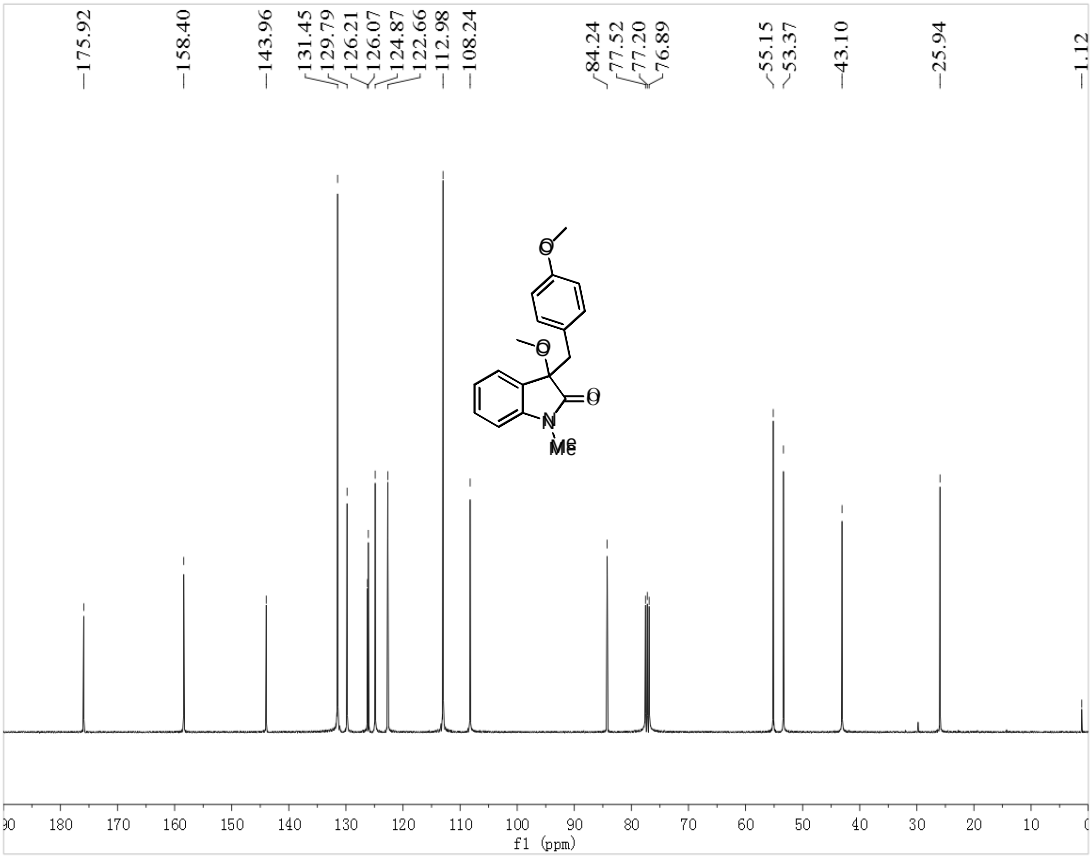
^{1}H and ^{13}C NMR of 3f



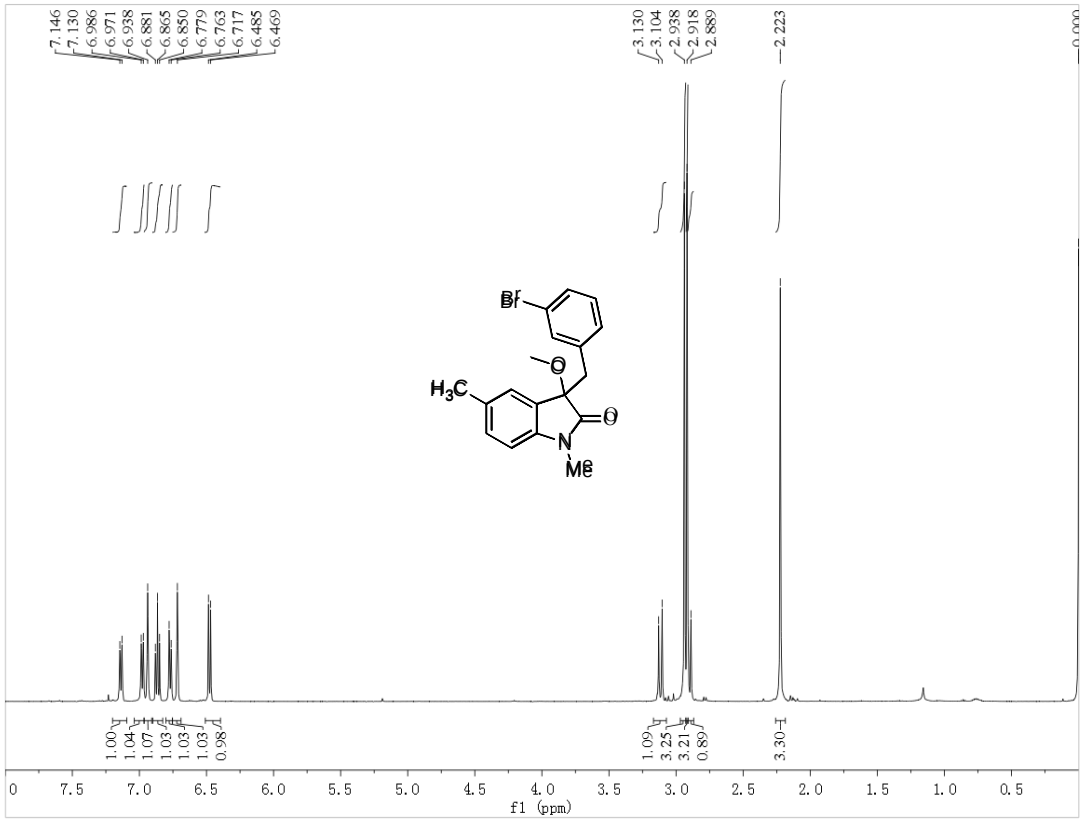


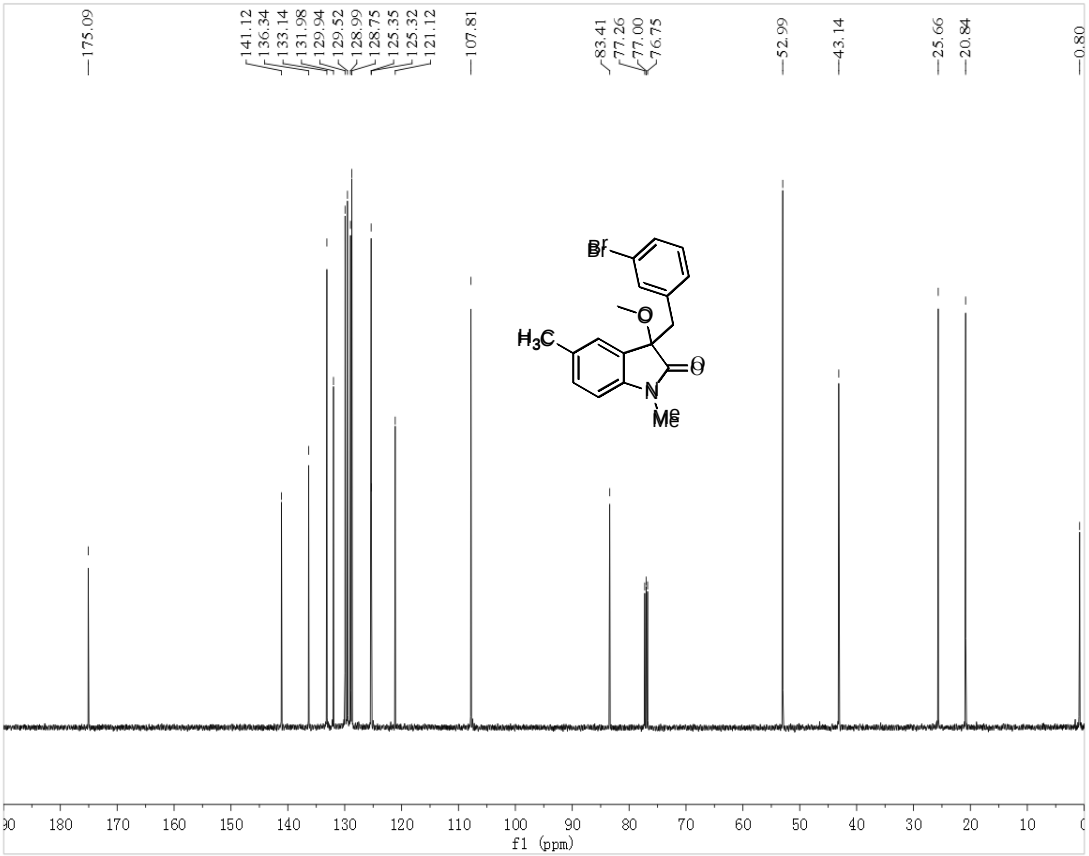
^{1}H and ^{13}C NMR of 3g



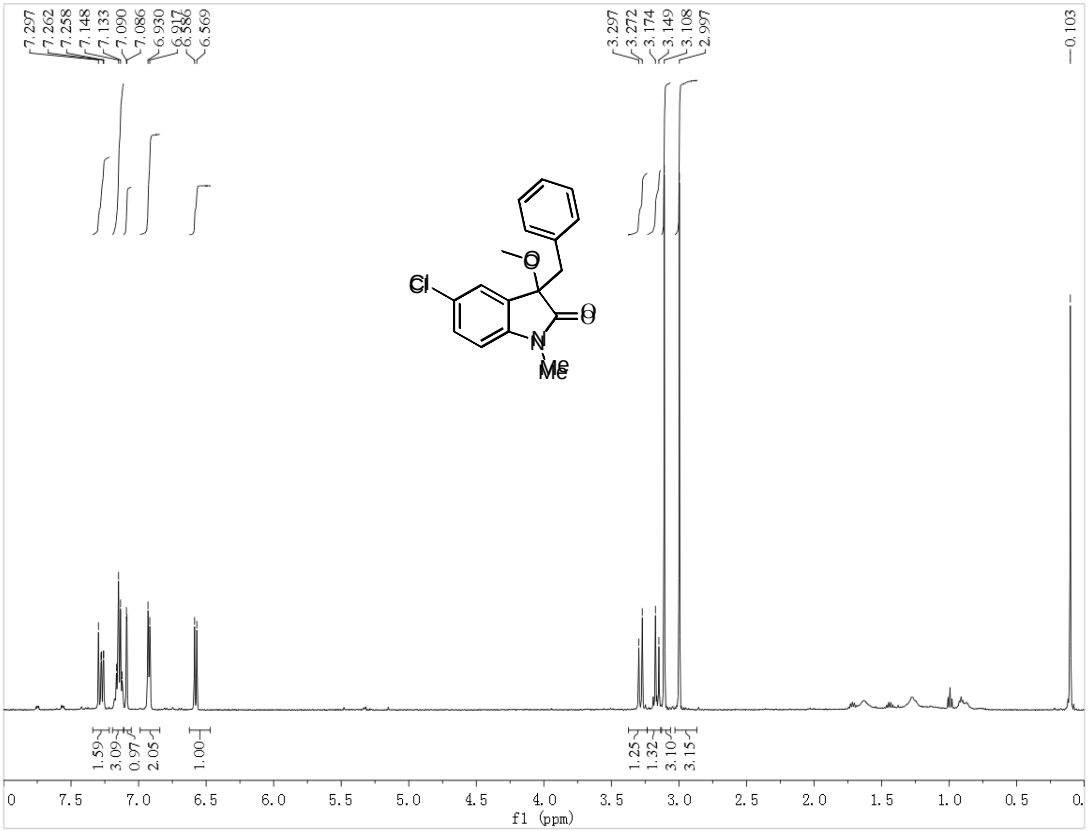


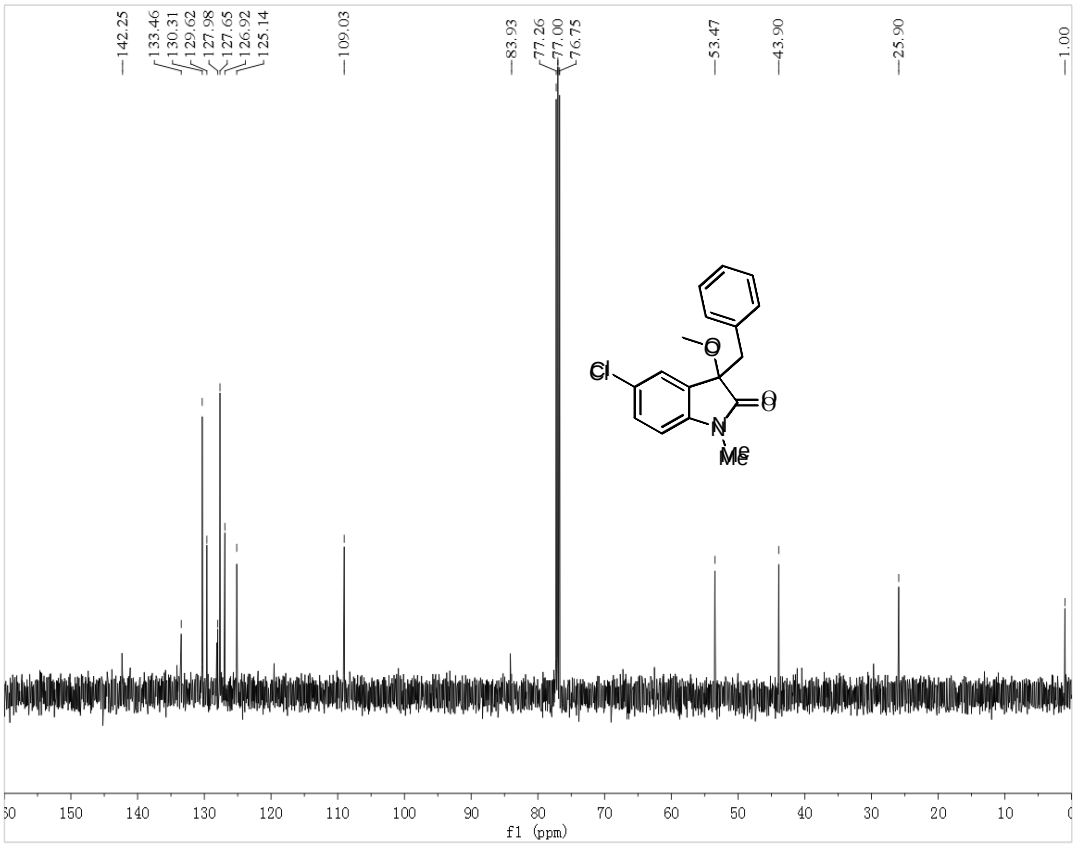
^{1}H and ^{13}C NMR of 3h



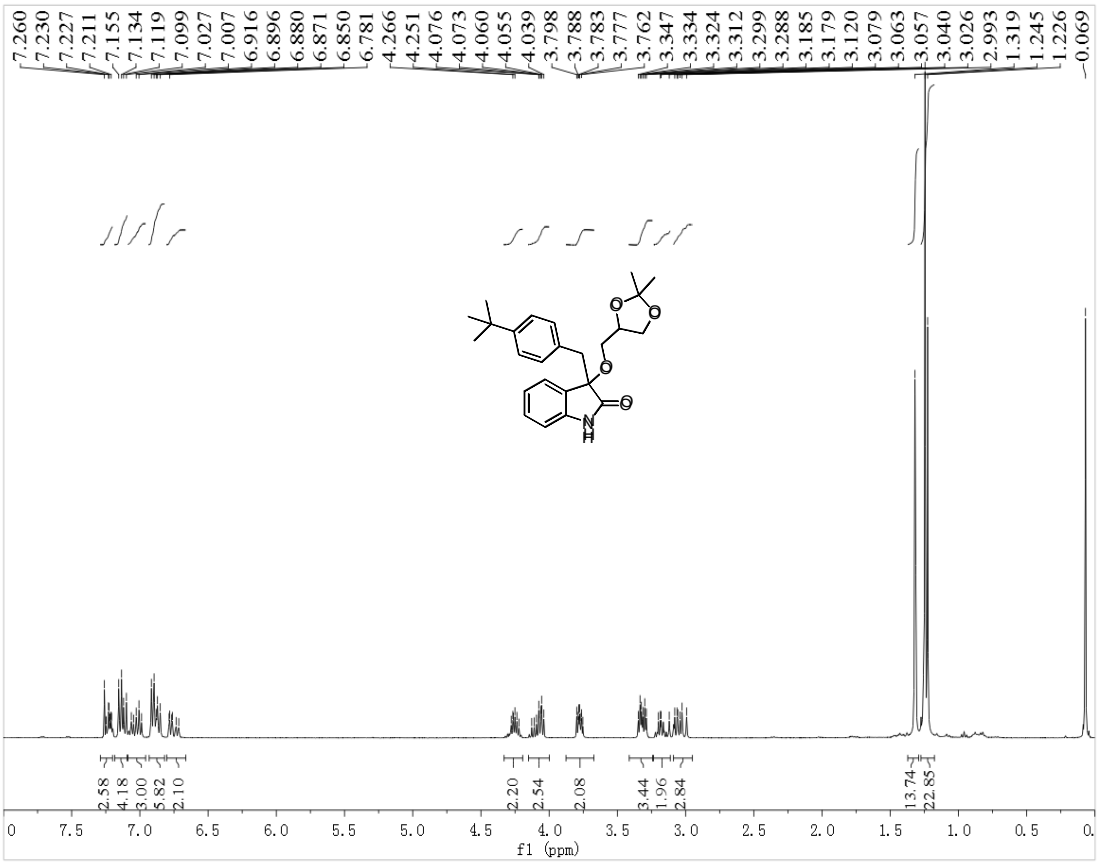


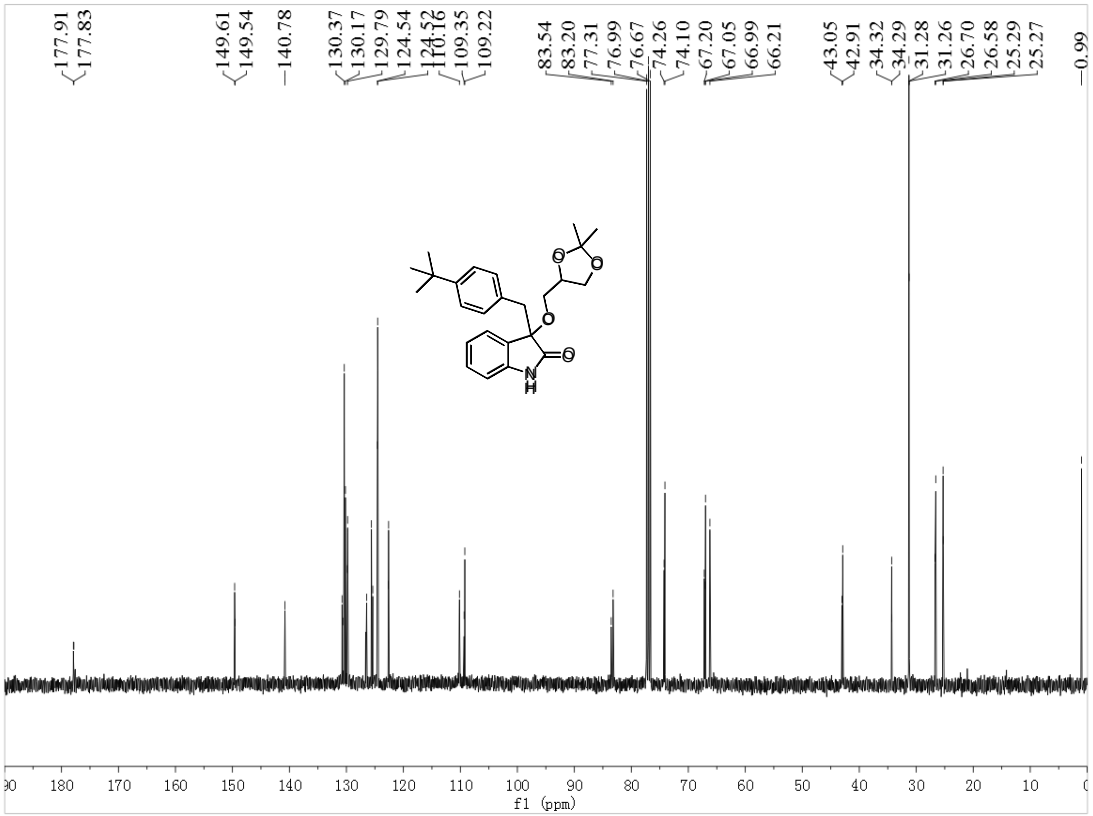
^{1}H and ^{13}C NMR of 3i



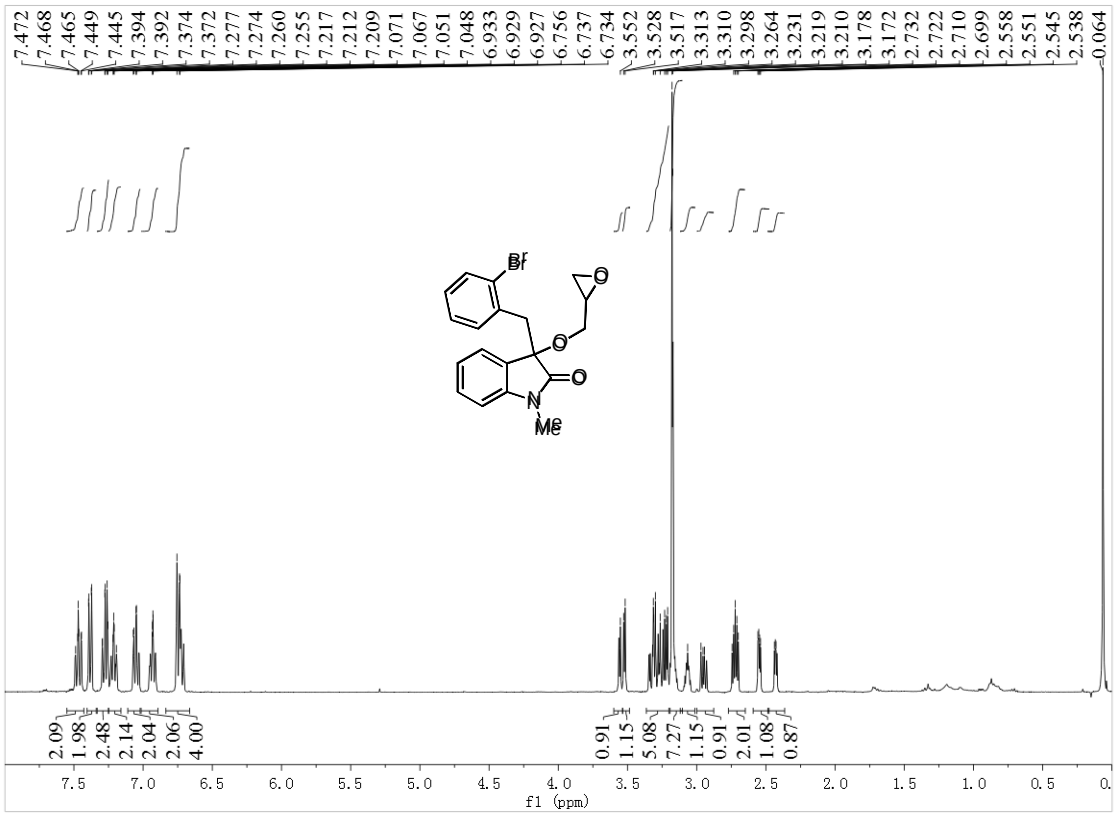


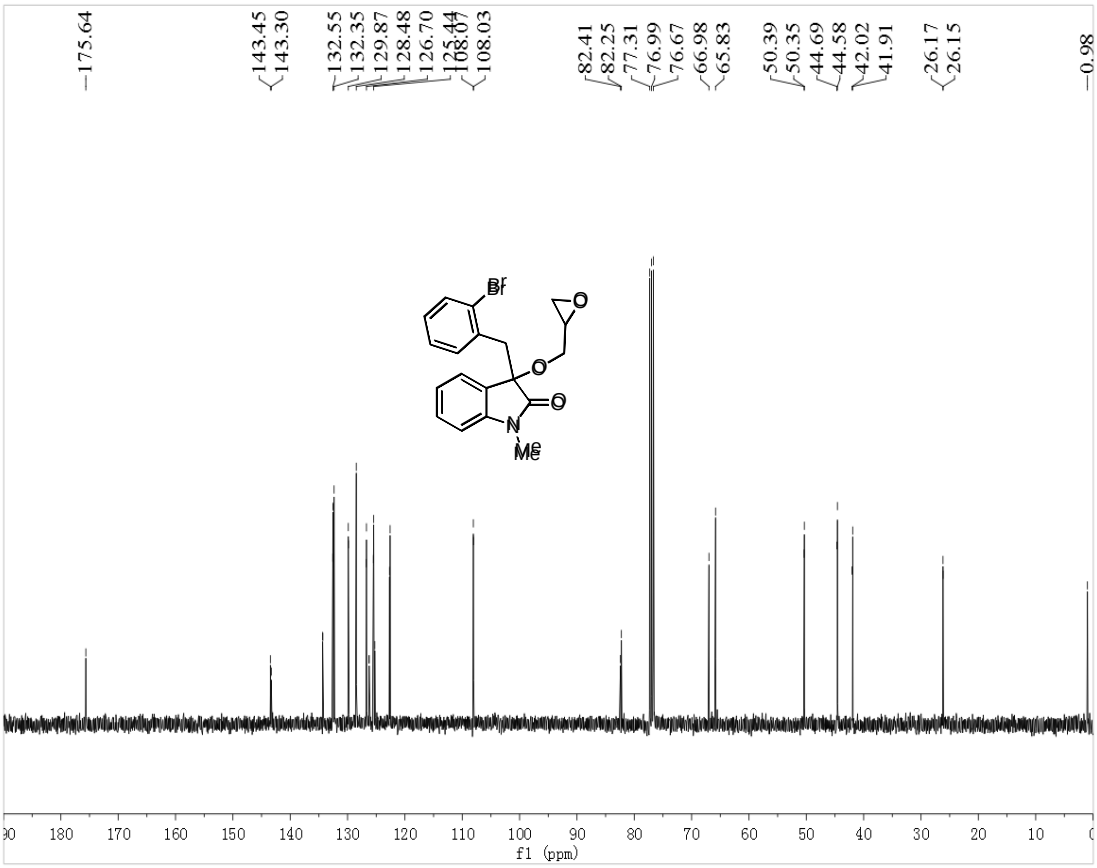
^{1}H and ^{13}C NMR of 3j



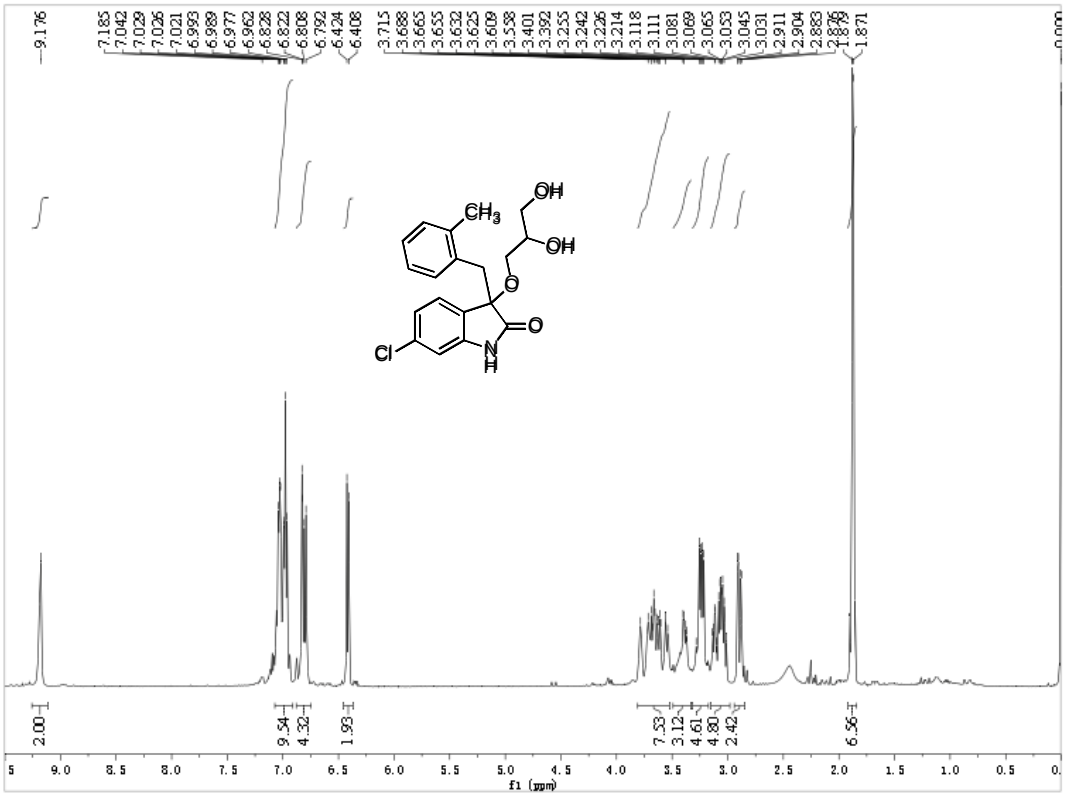


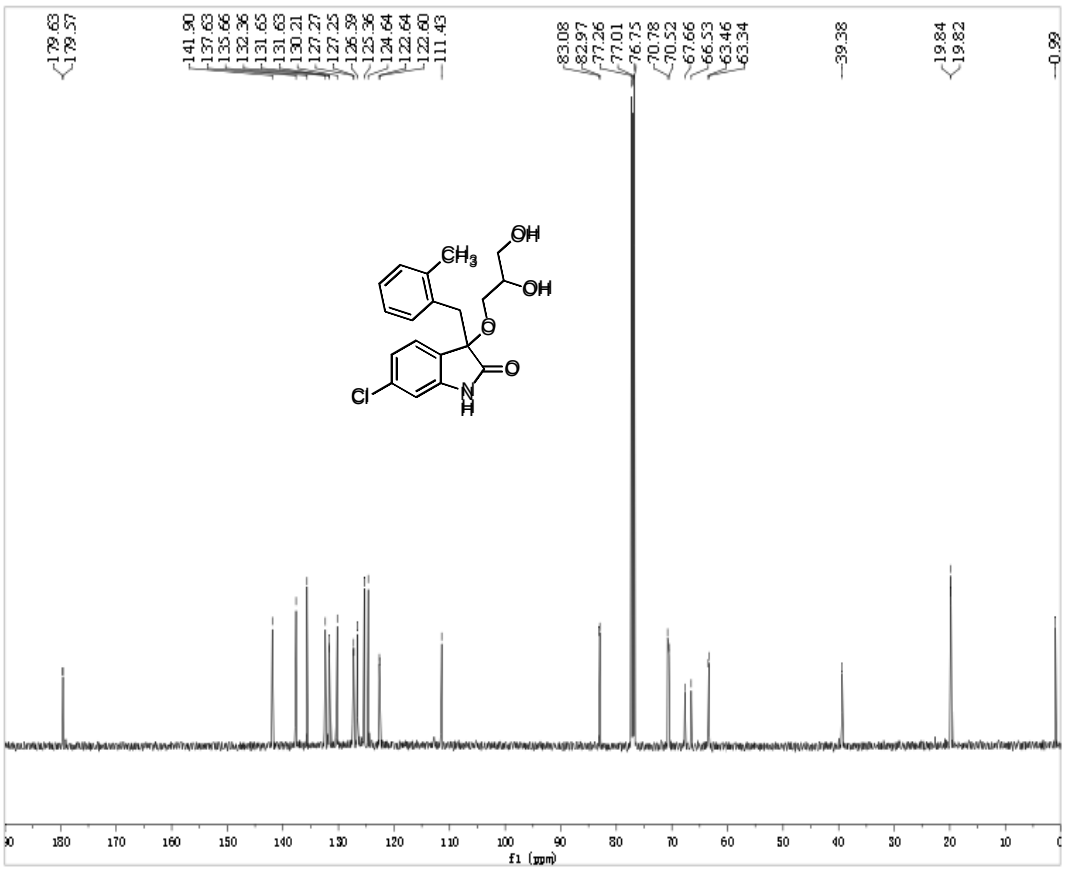
^{1}H and ^{13}C NMR of 3k



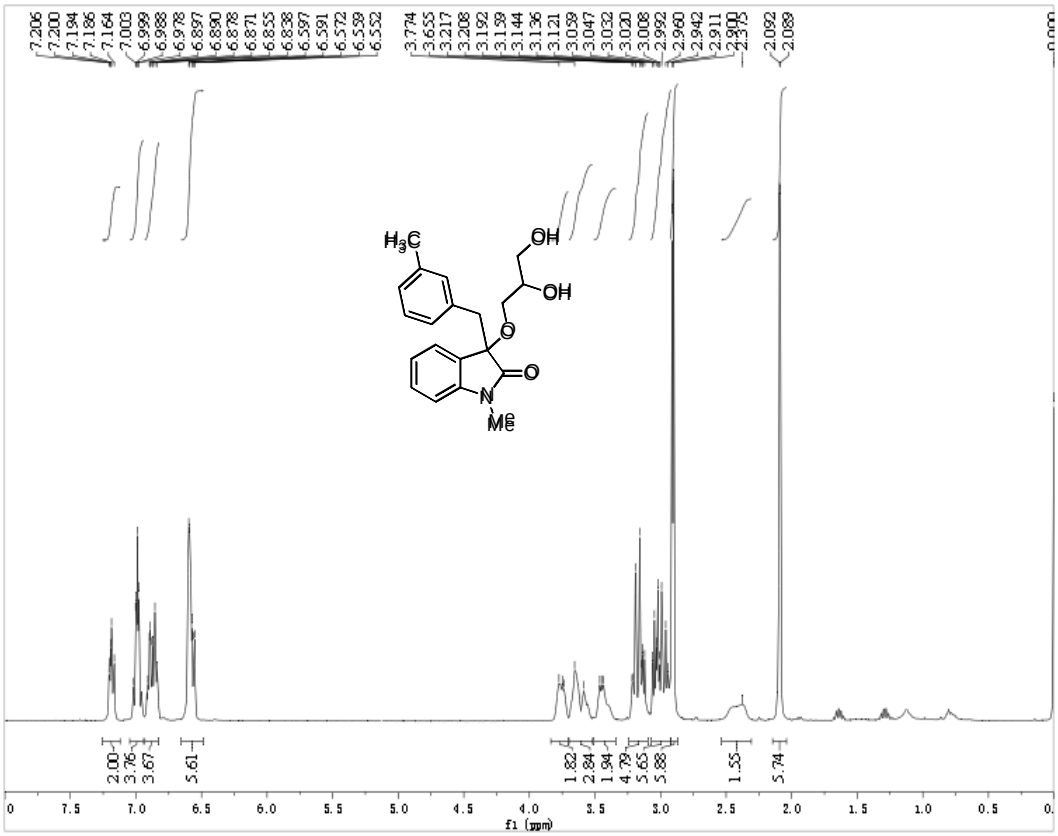


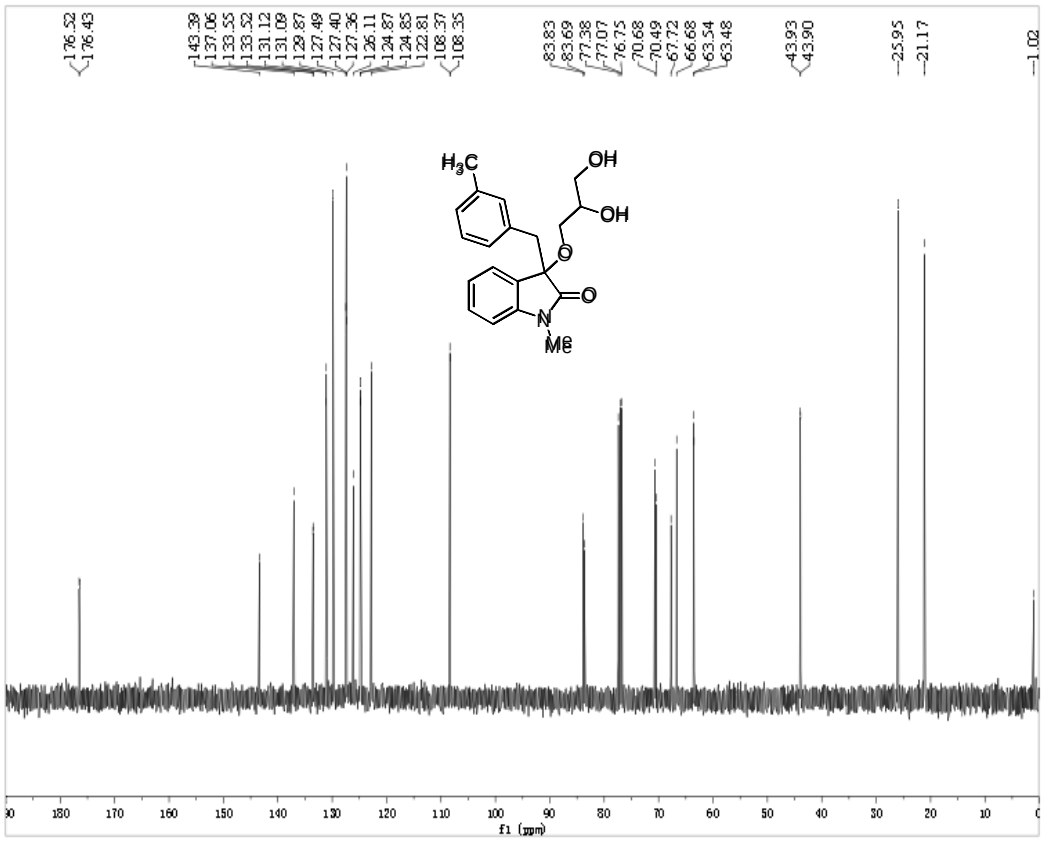
^{1}H and ^{13}C NMR of 3l



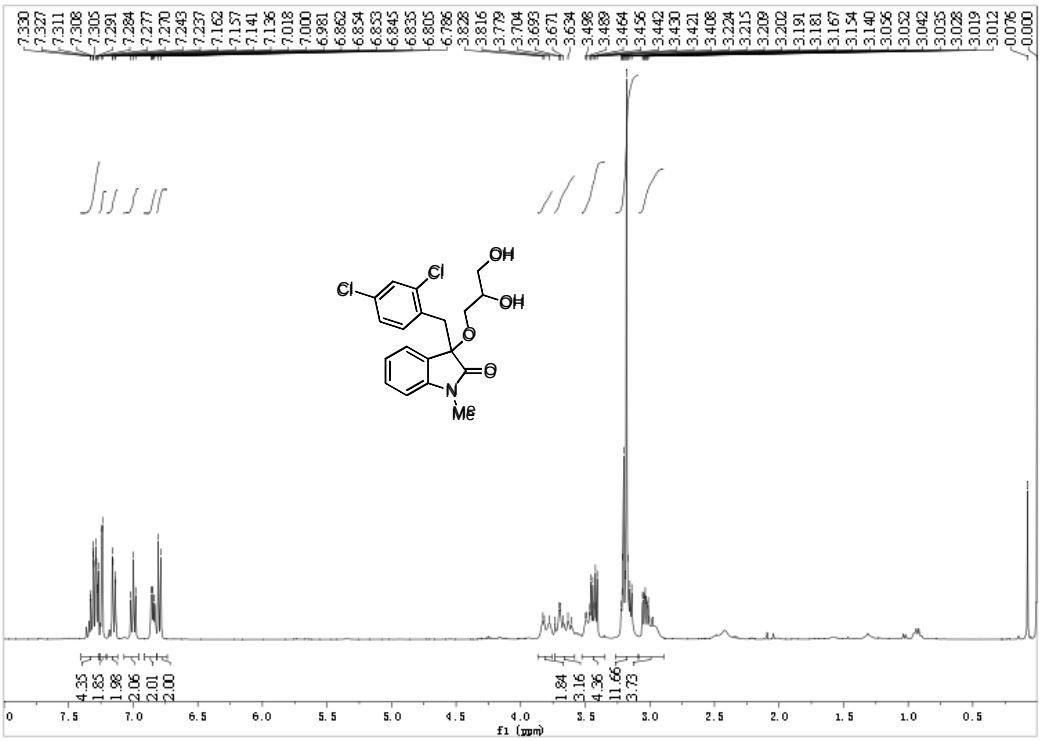


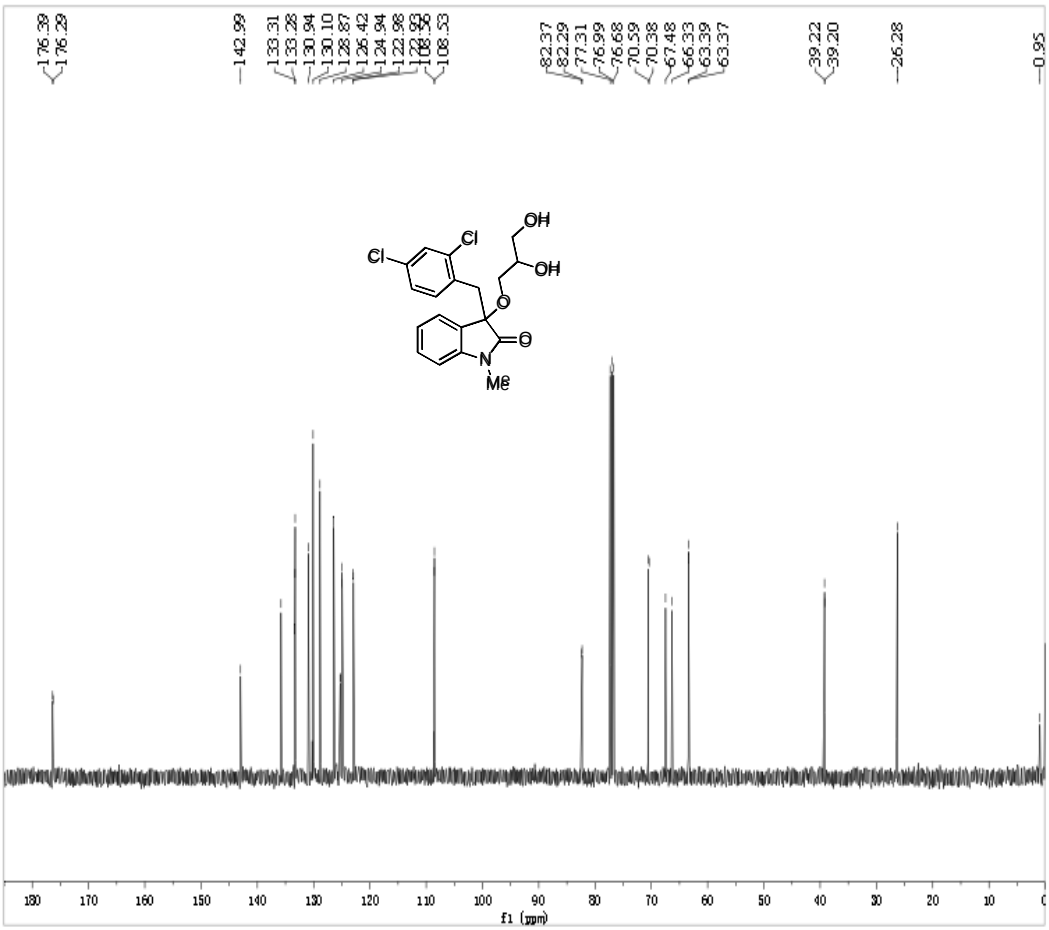
^{1}H and ^{13}C NMR of 3m



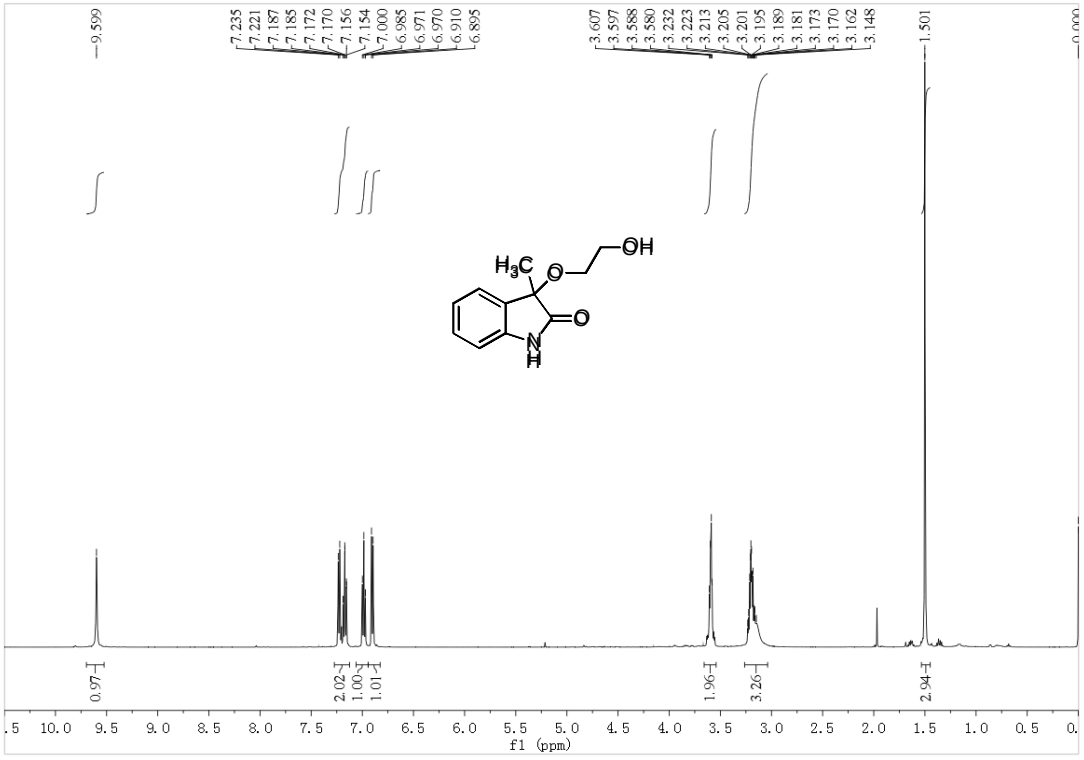


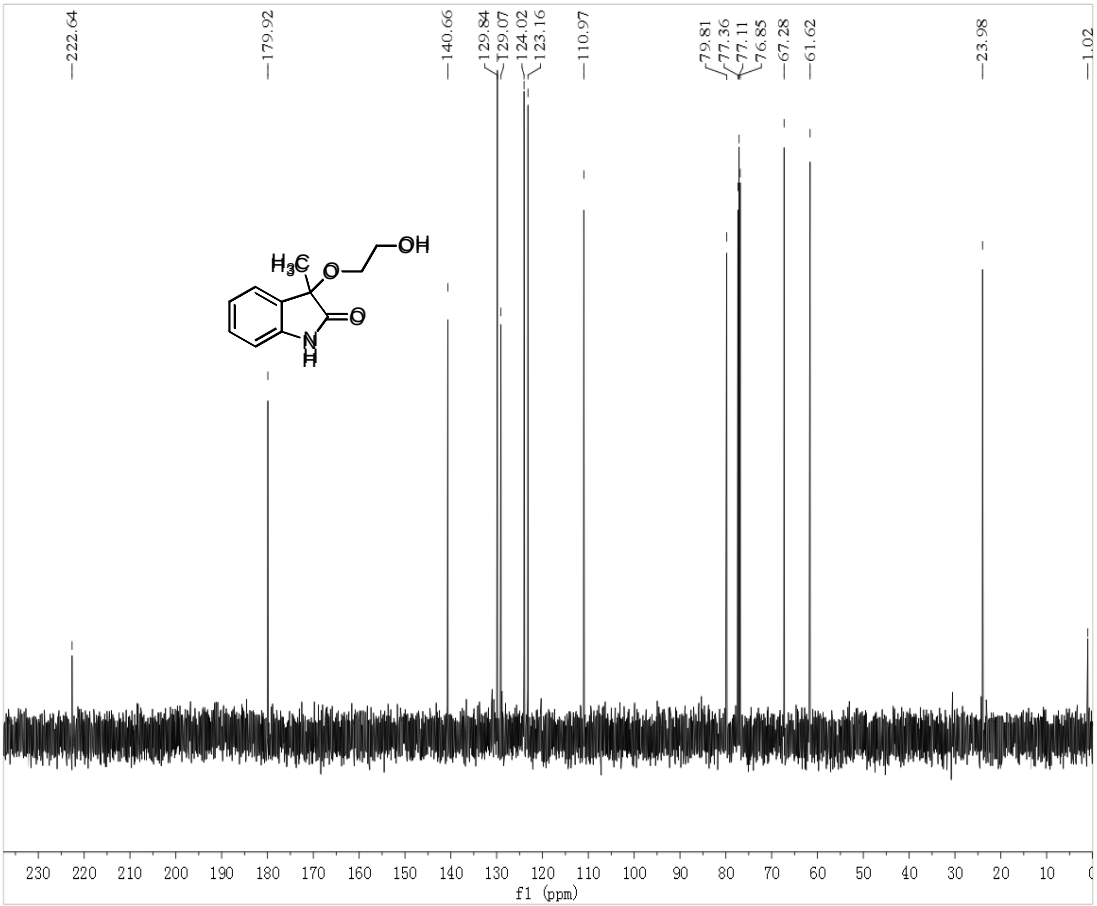
^{1}H and ^{13}C NMR of 3n



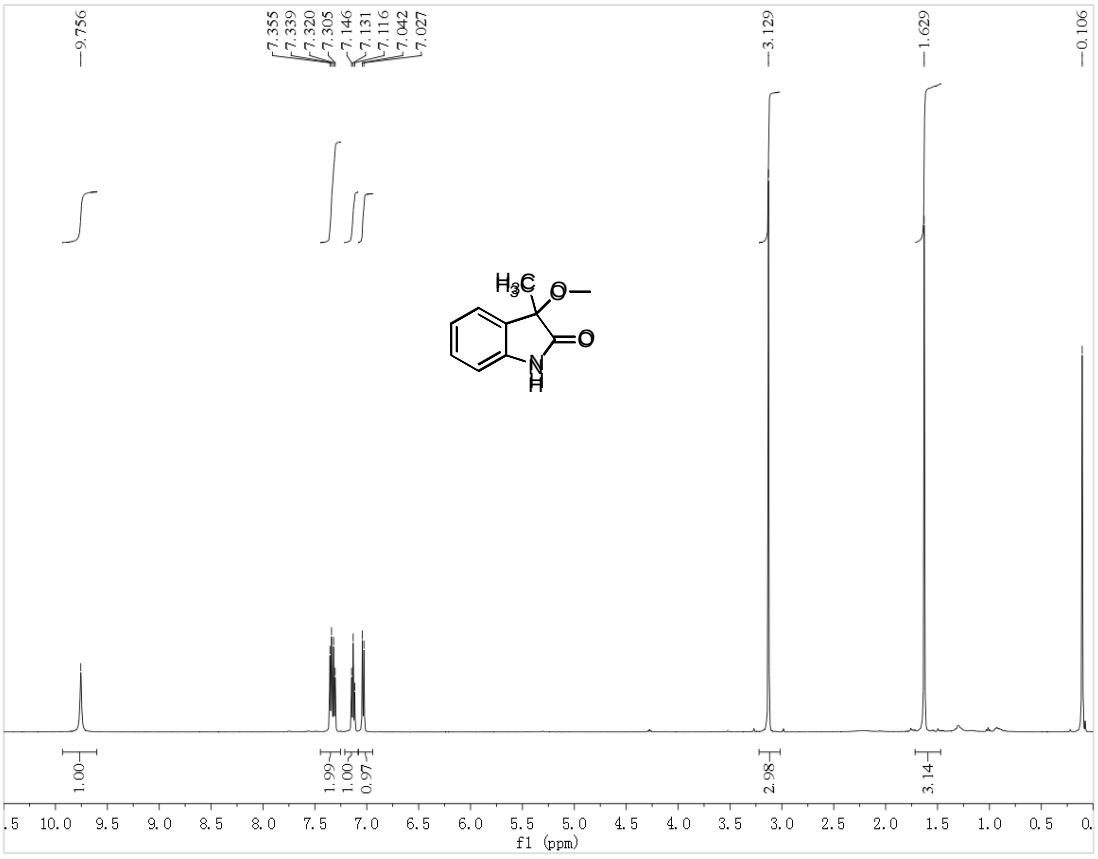


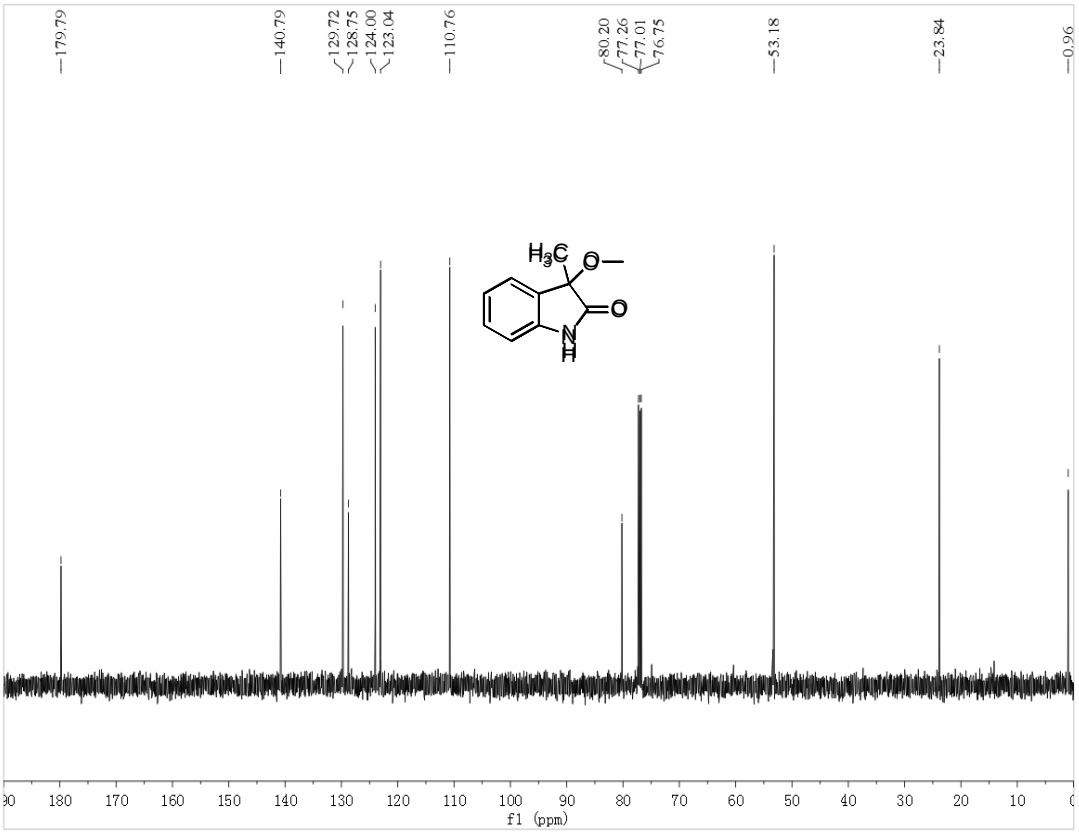
^{1}H and ^{13}C NMR of 3o



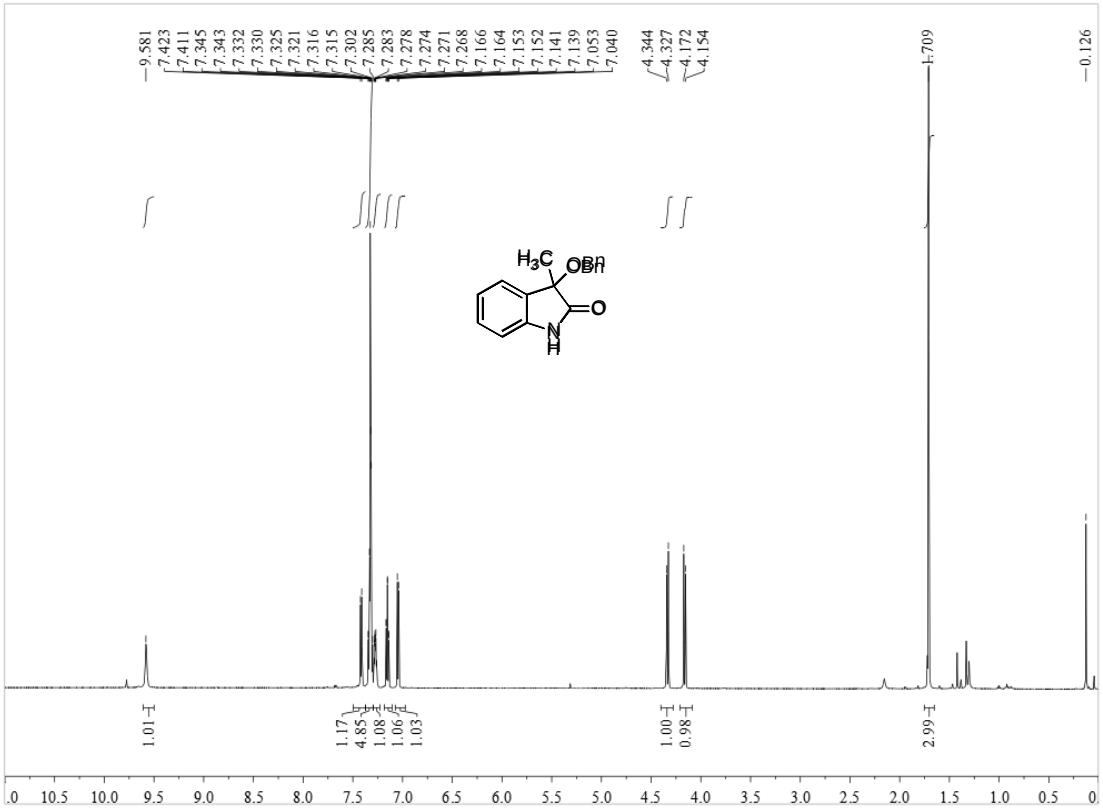


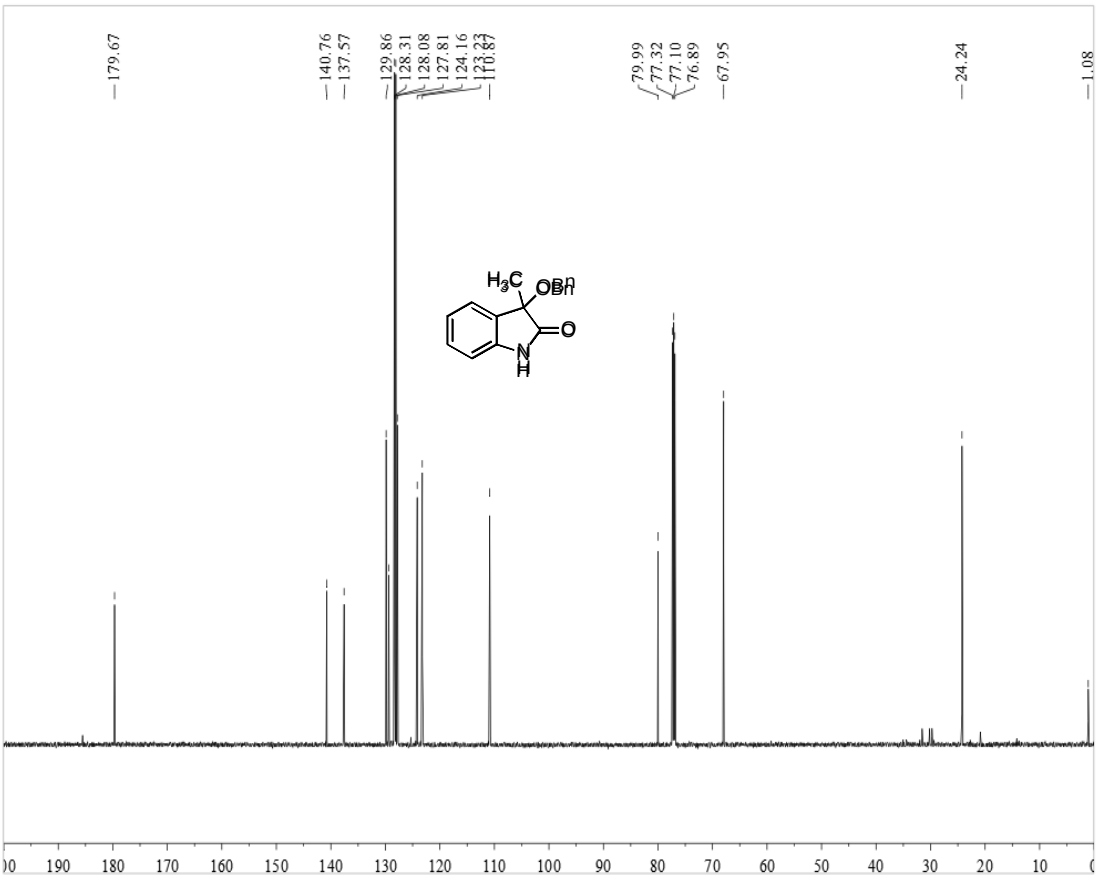
^{1}H and ^{13}C NMR of 3p



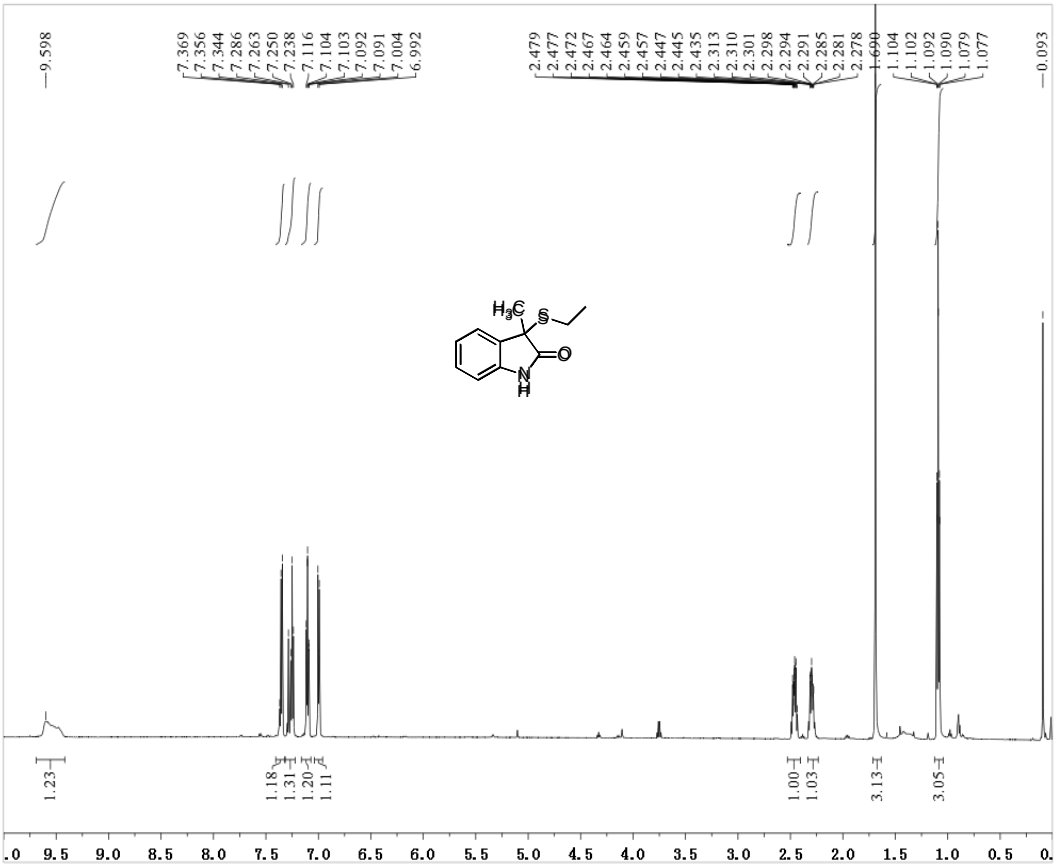


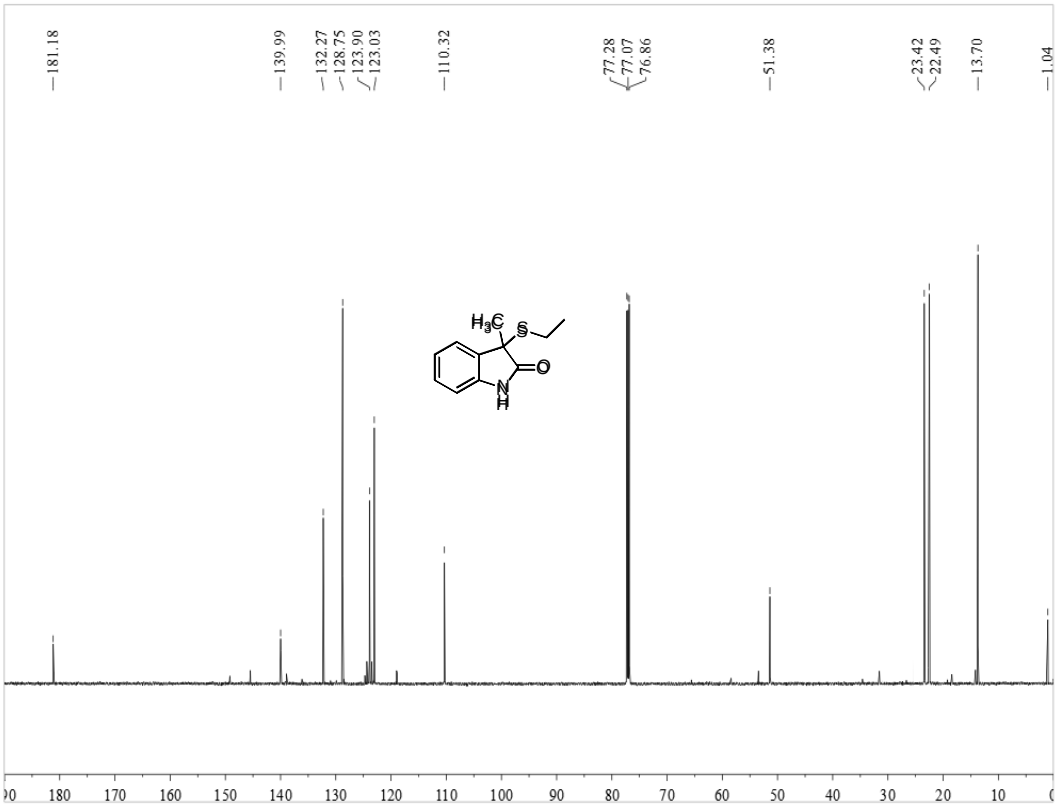
^{1}H and ^{13}C NMR of 3q



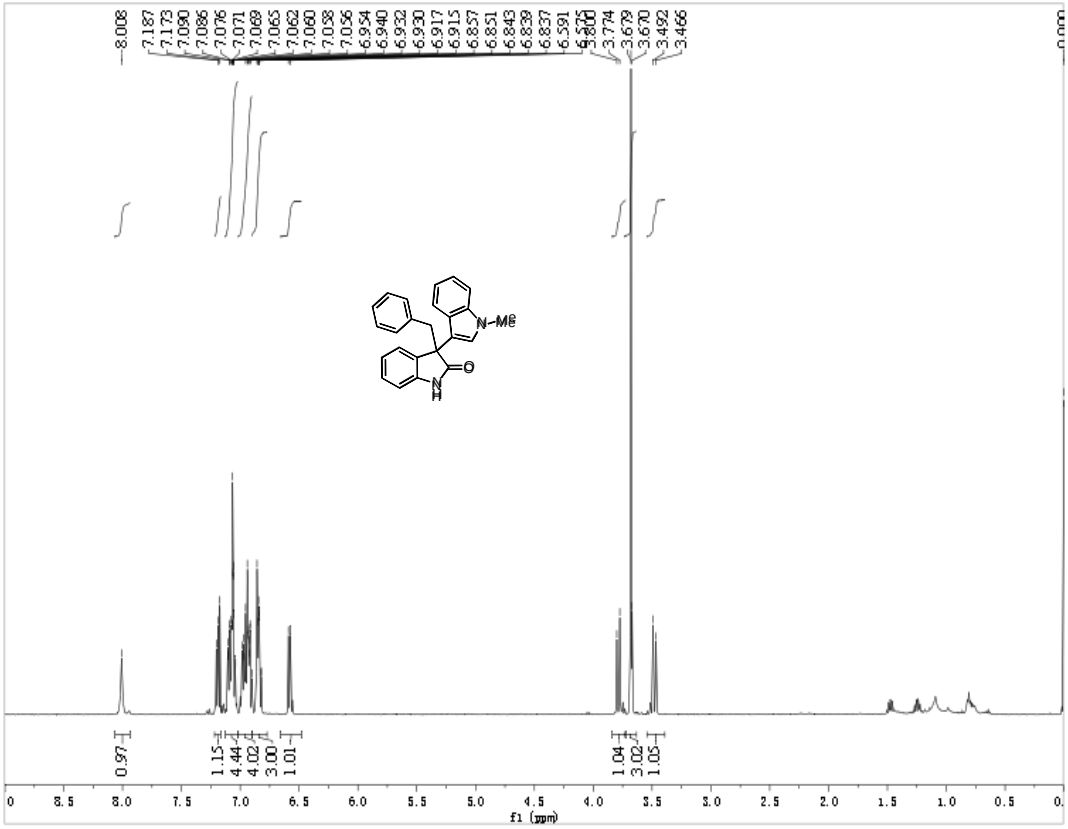


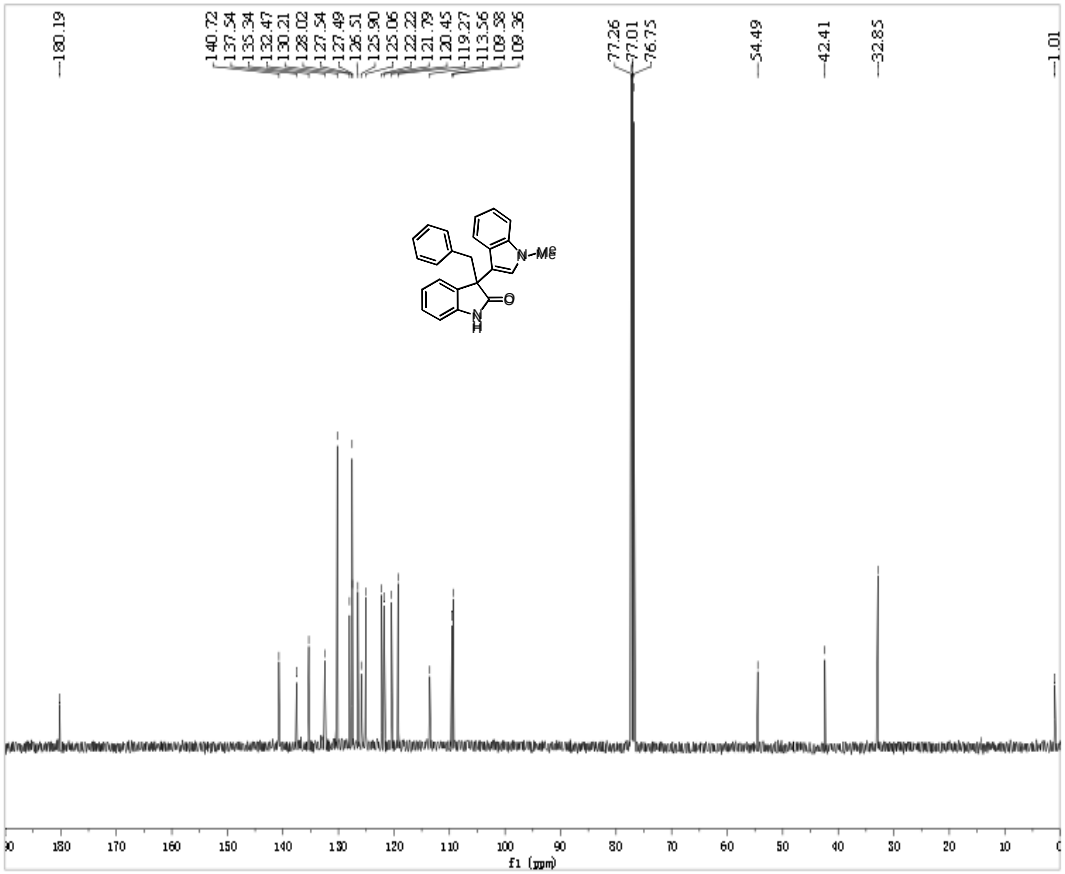
^{1}H and ^{13}C NMR of 3r



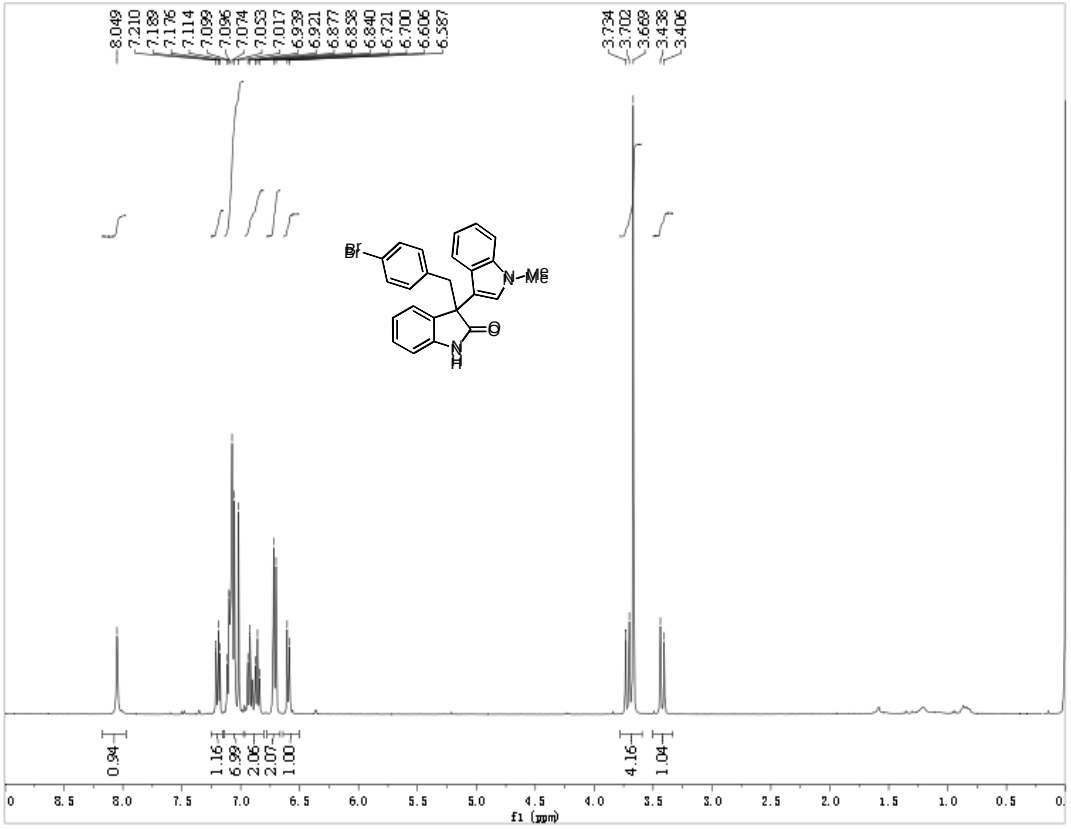


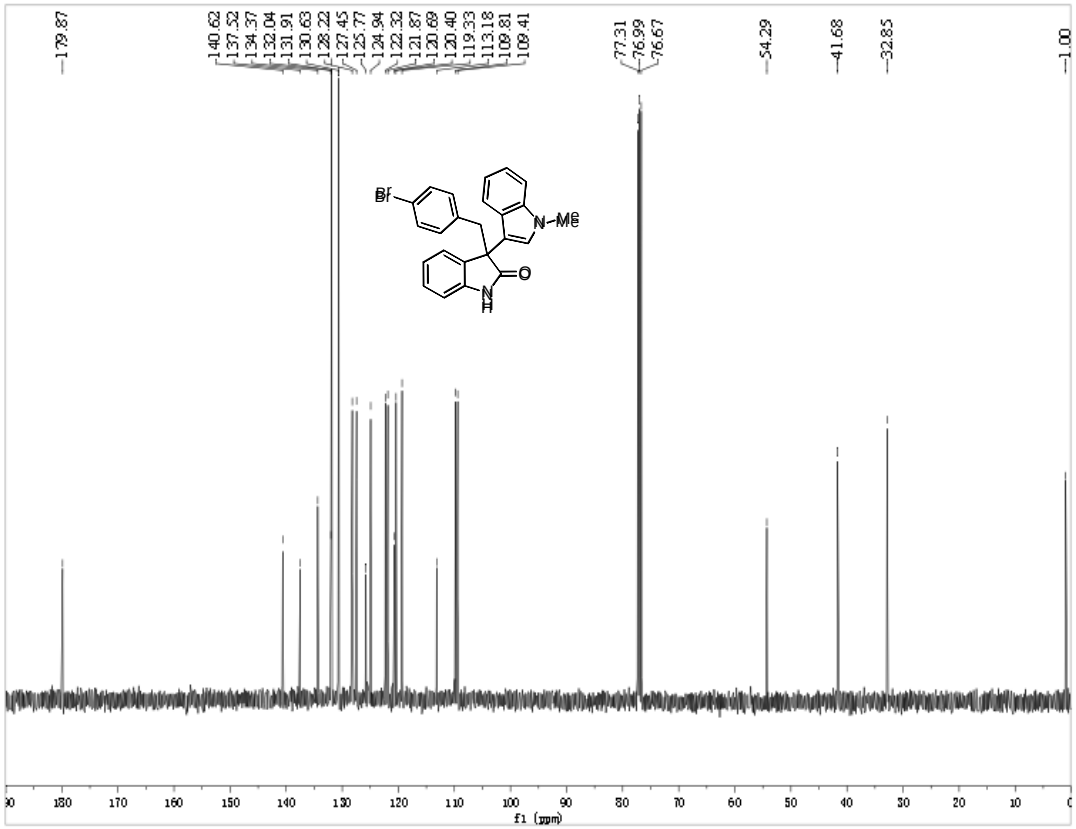
^{1}H and ^{13}C NMR of 5a



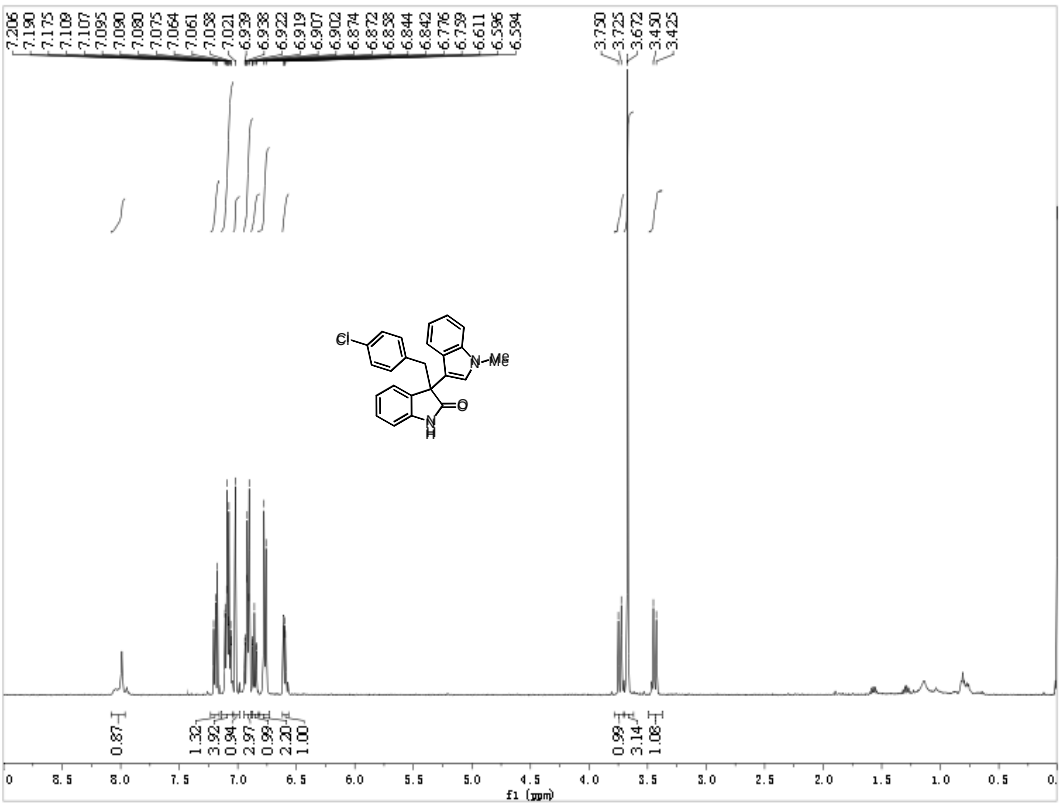


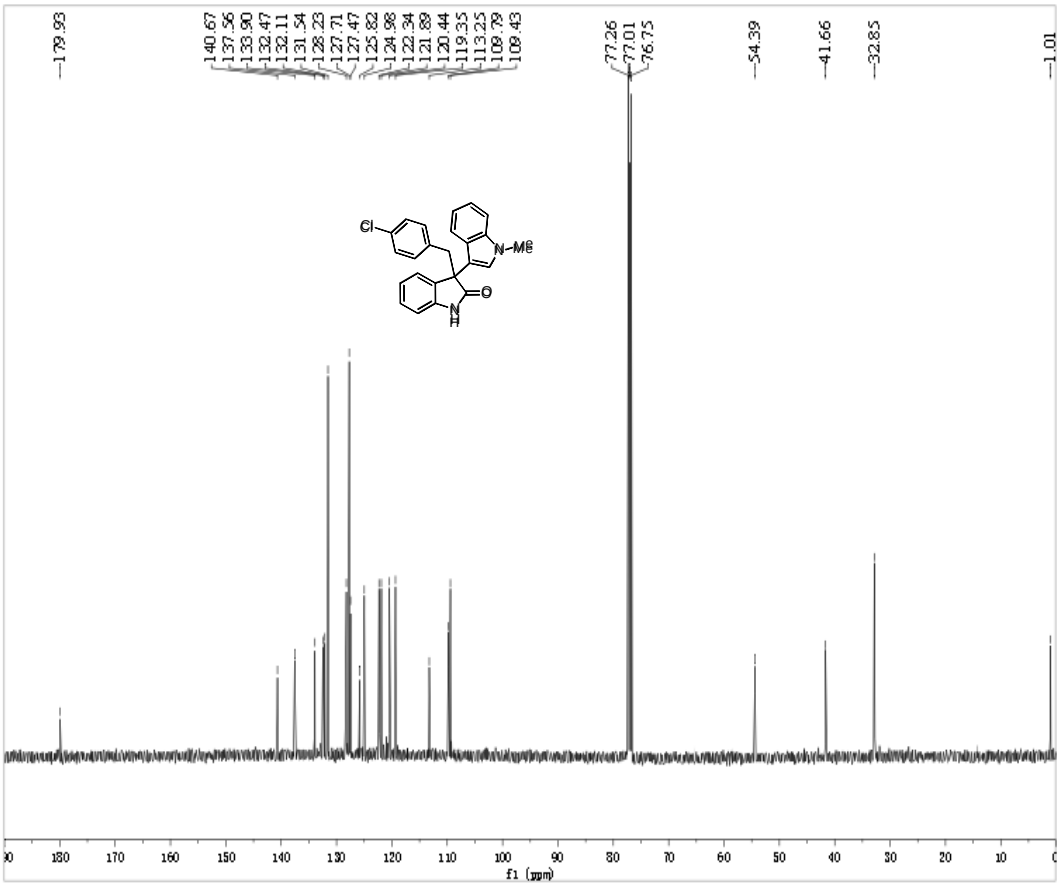
^{1}H and ^{13}C NMR of 5b



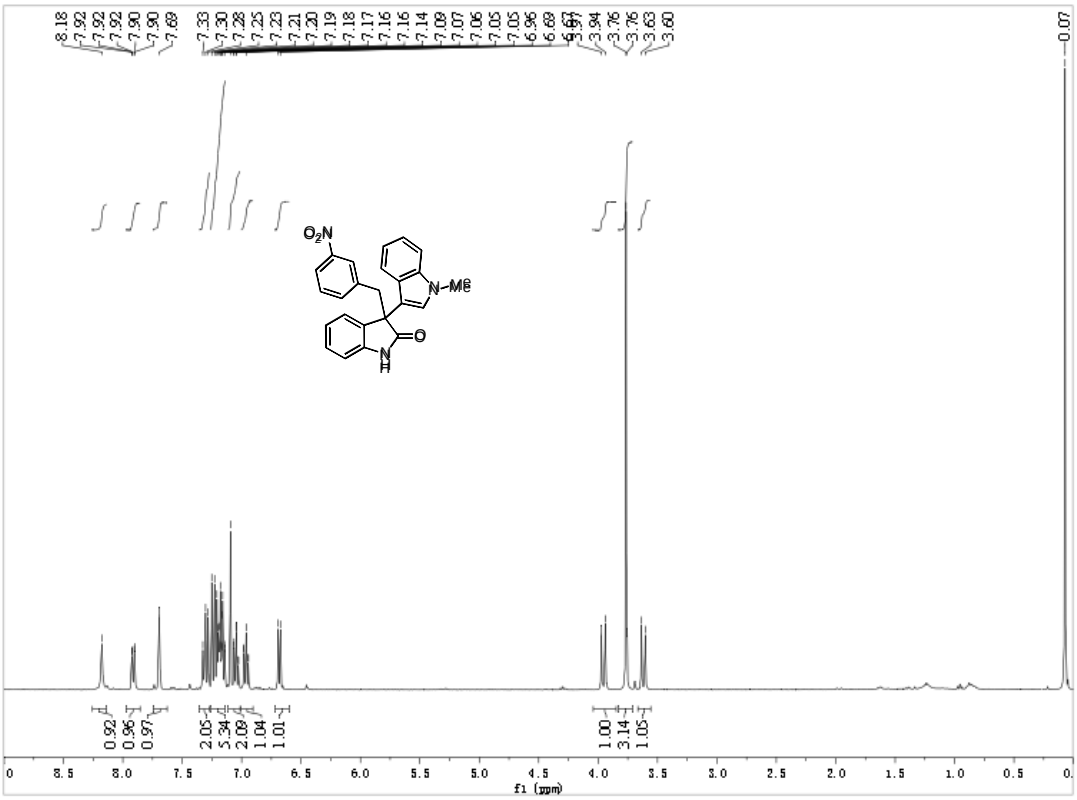


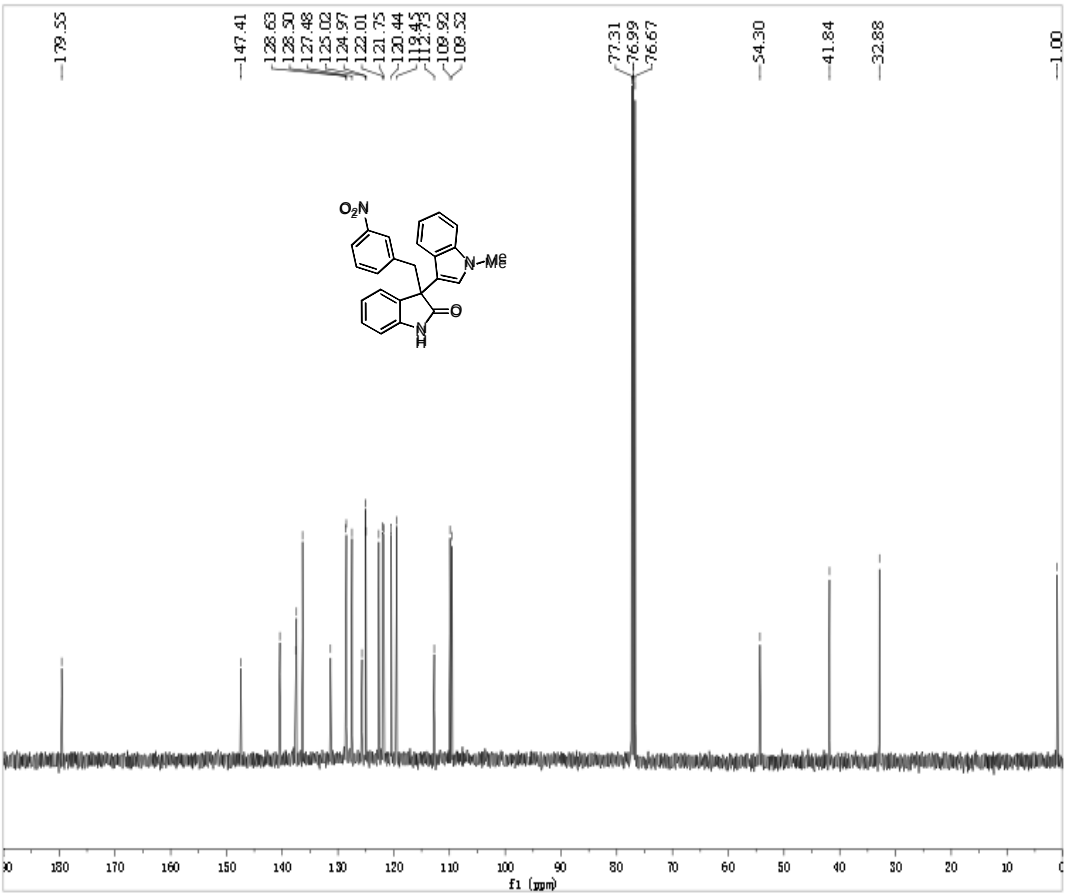
^{1}H and ^{13}C NMR of 5c



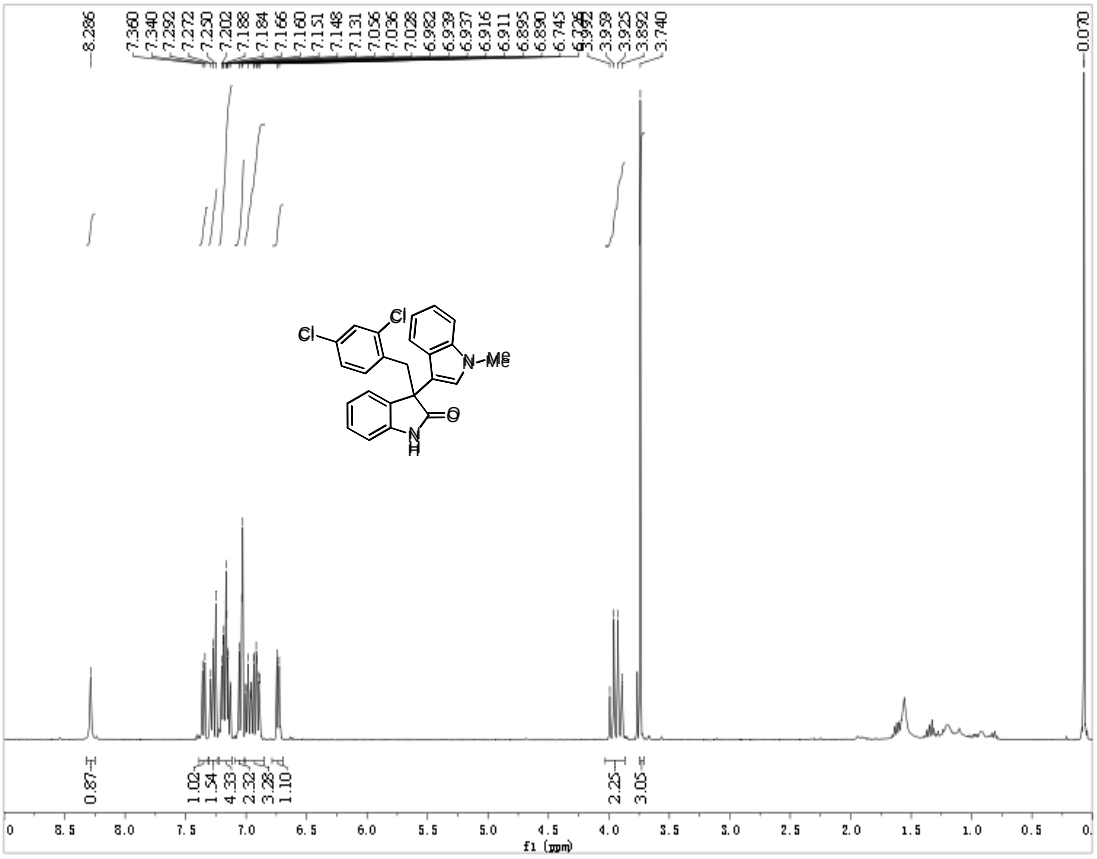


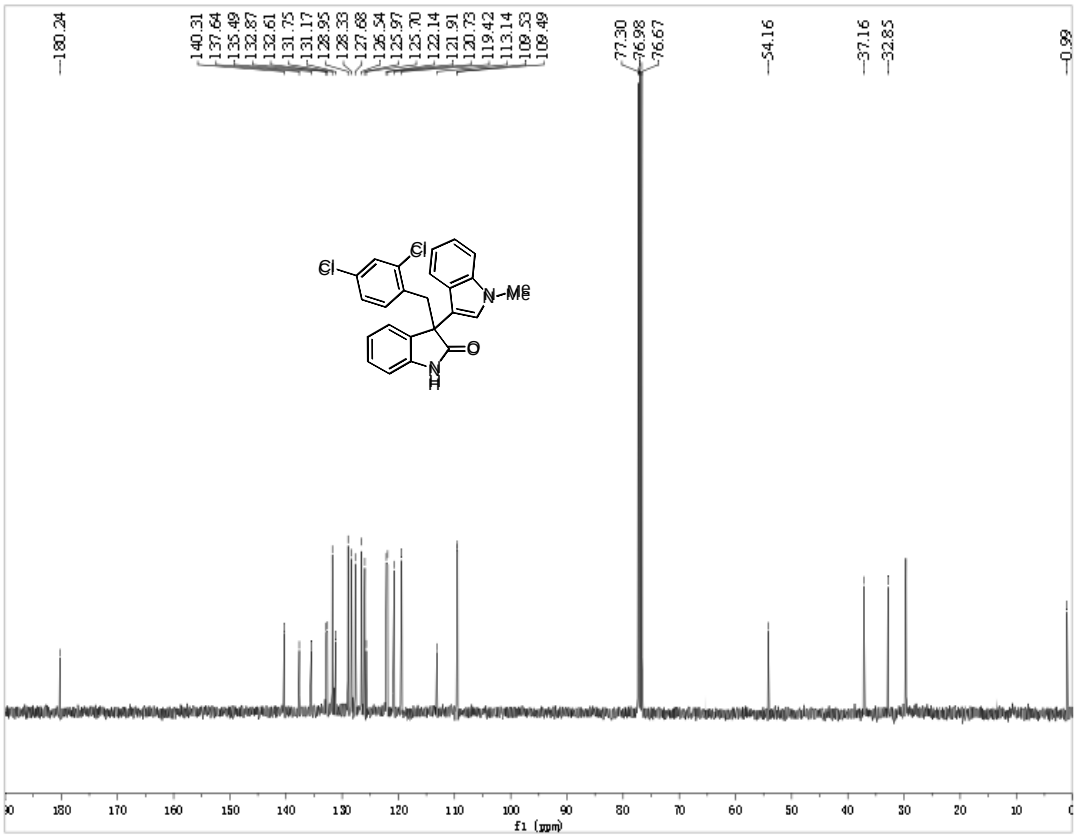
^{1}H and ^{13}C NMR of 5d



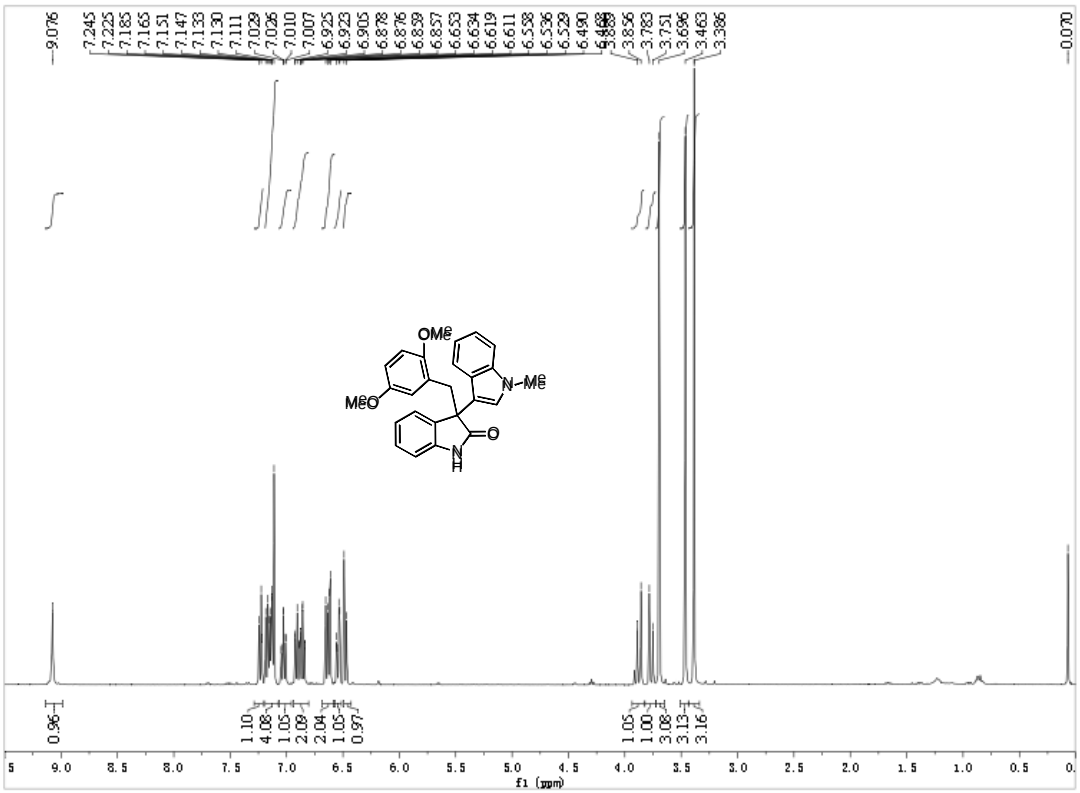


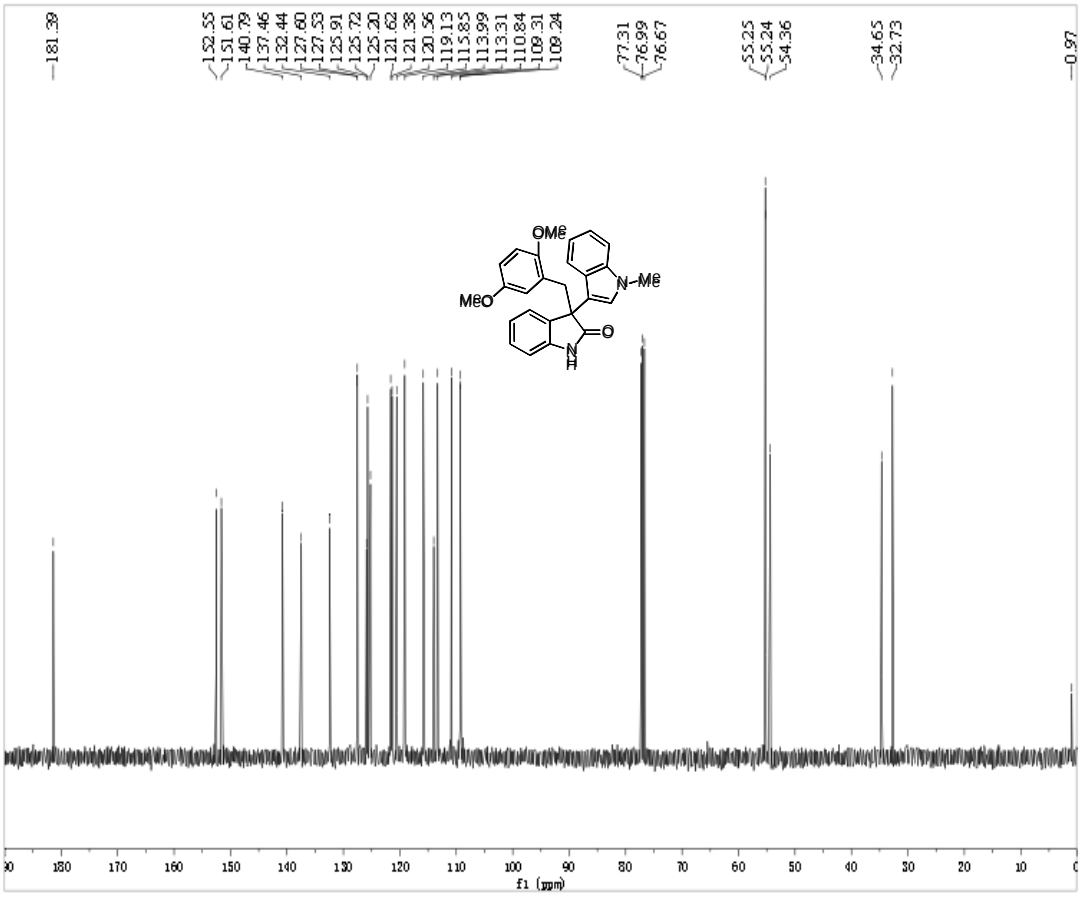
^{1}H and ^{13}C NMR of 5e



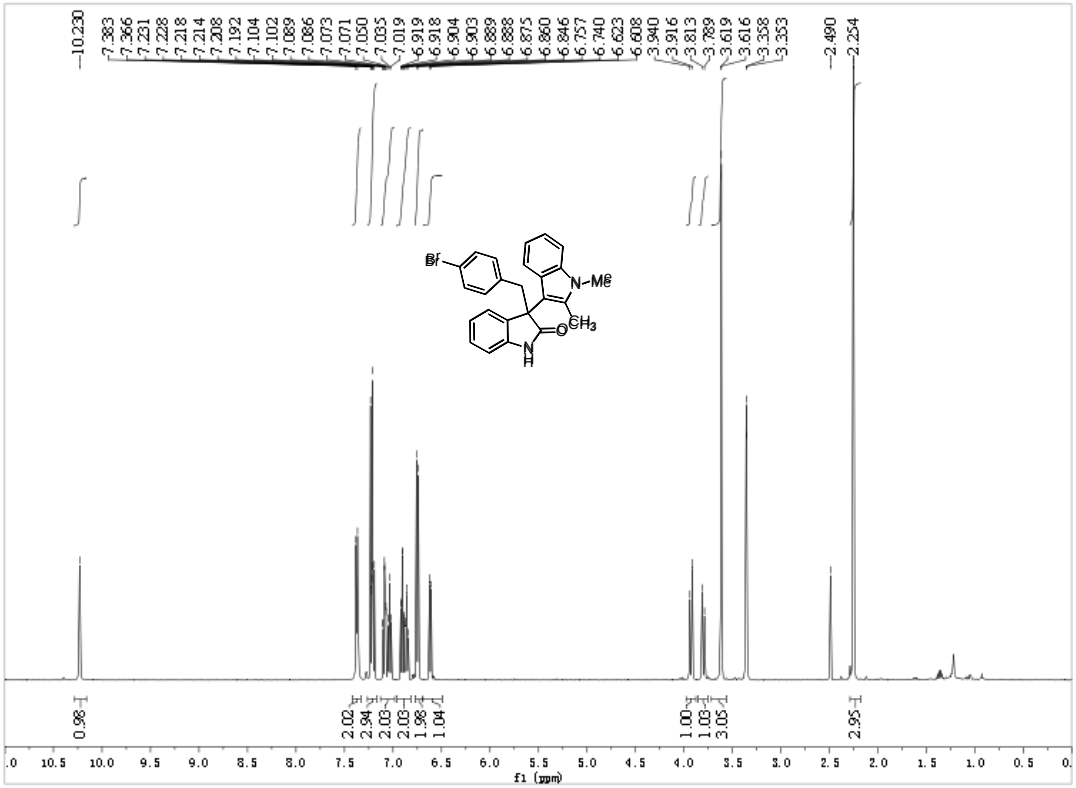


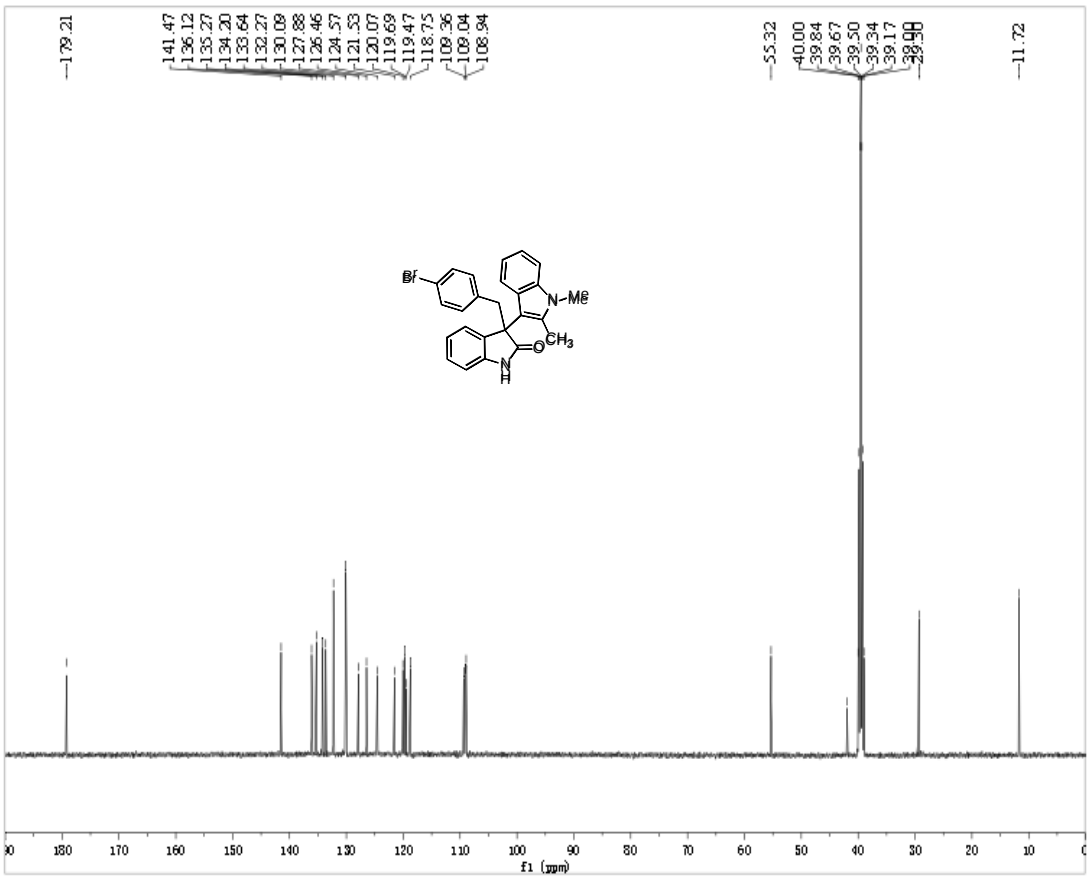
^{1}H and ^{13}C NMR of 5f



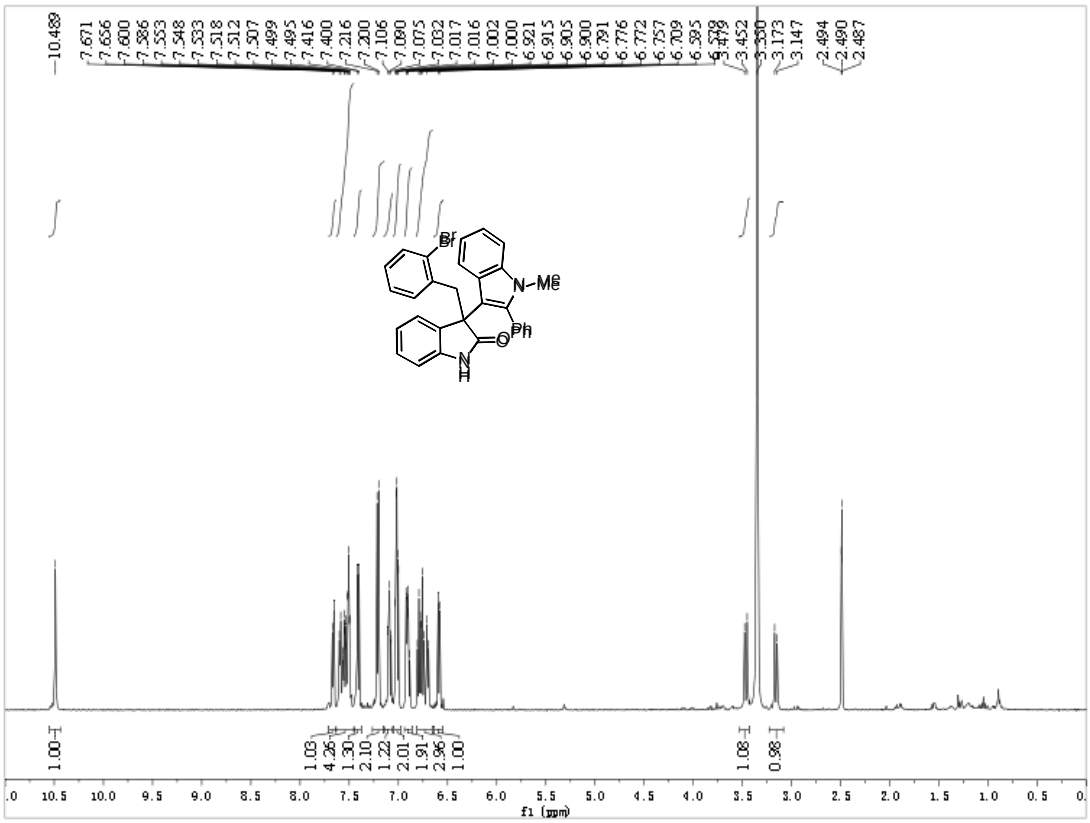


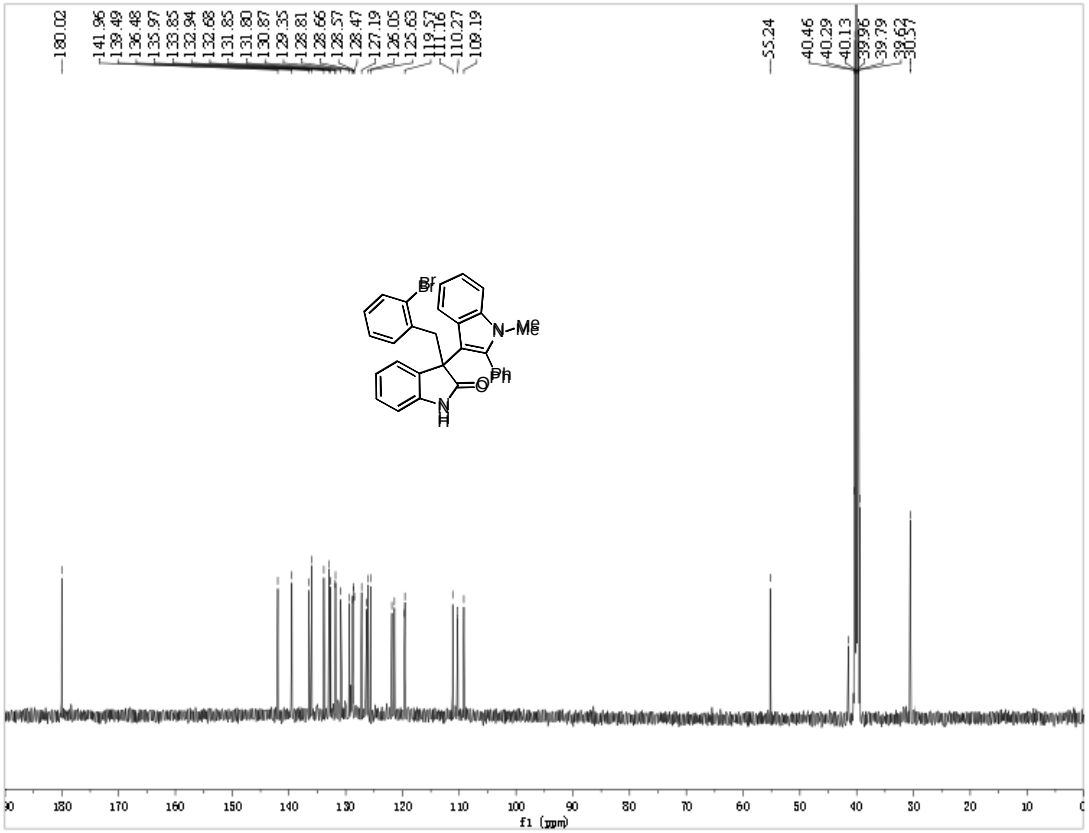
^{1}H and ^{13}C NMR of 5g



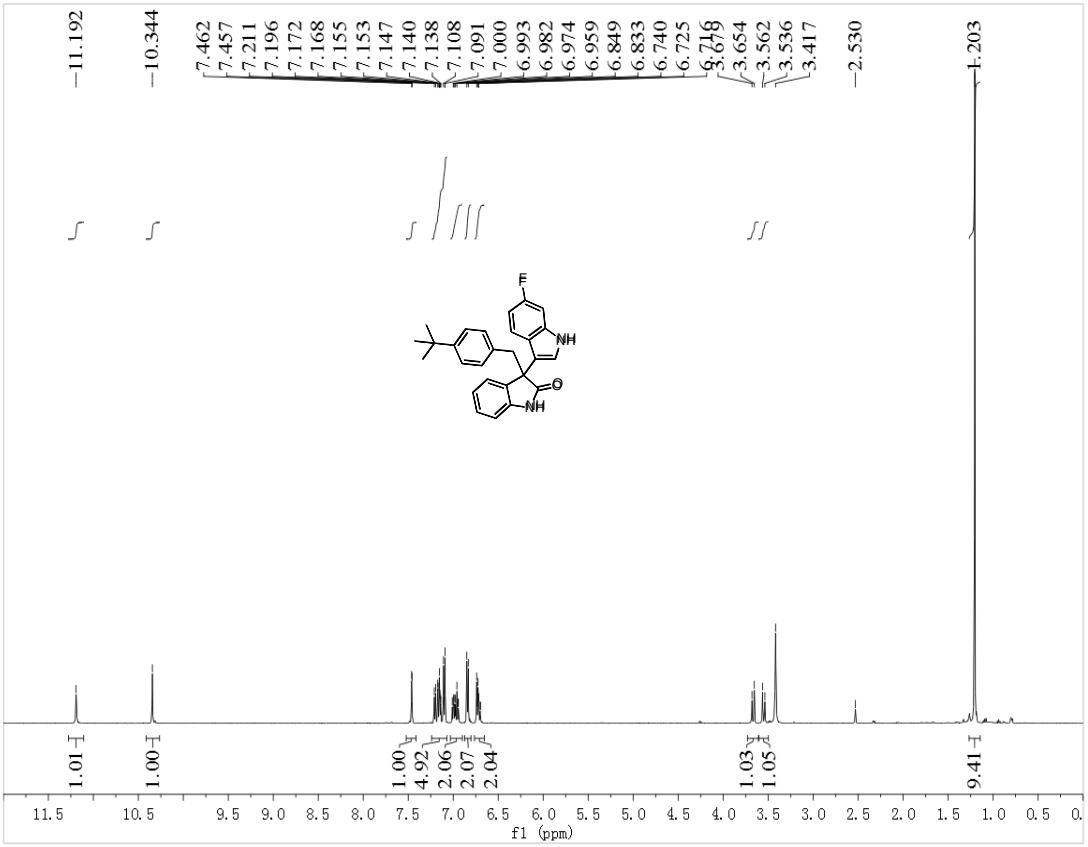


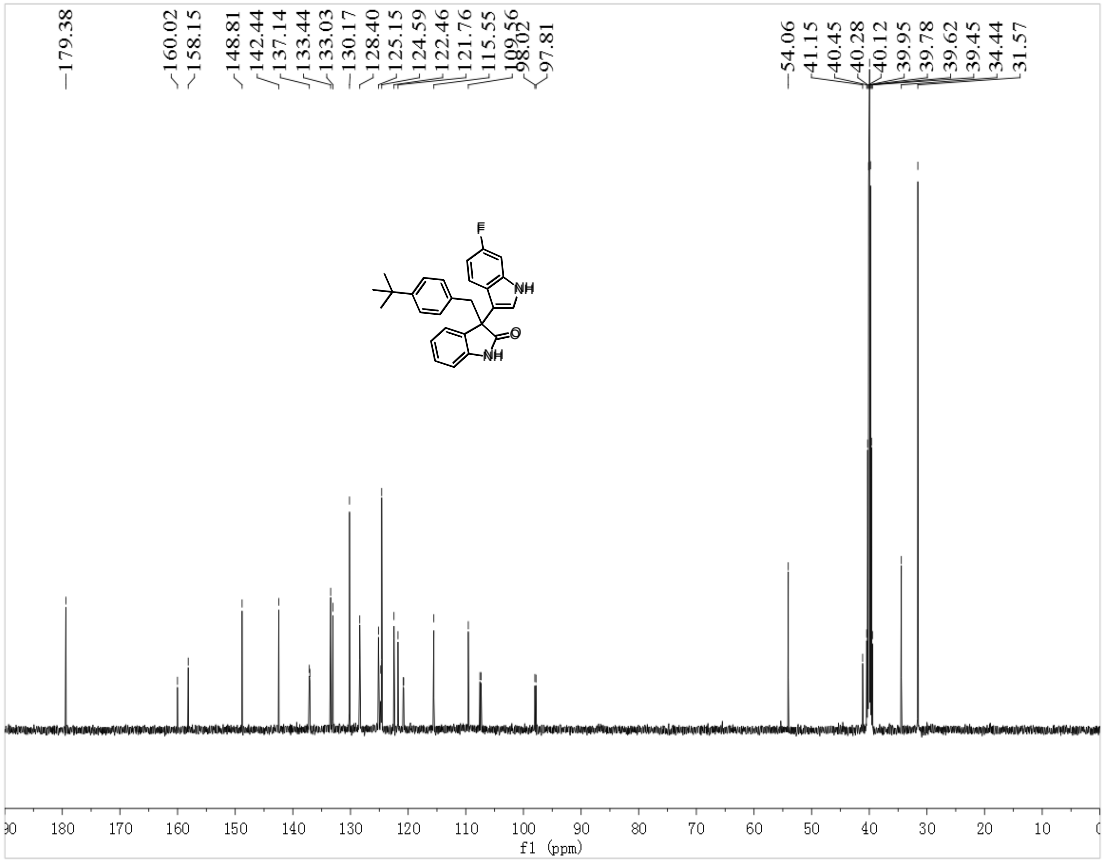
^{1}H and ^{13}C NMR of 5h



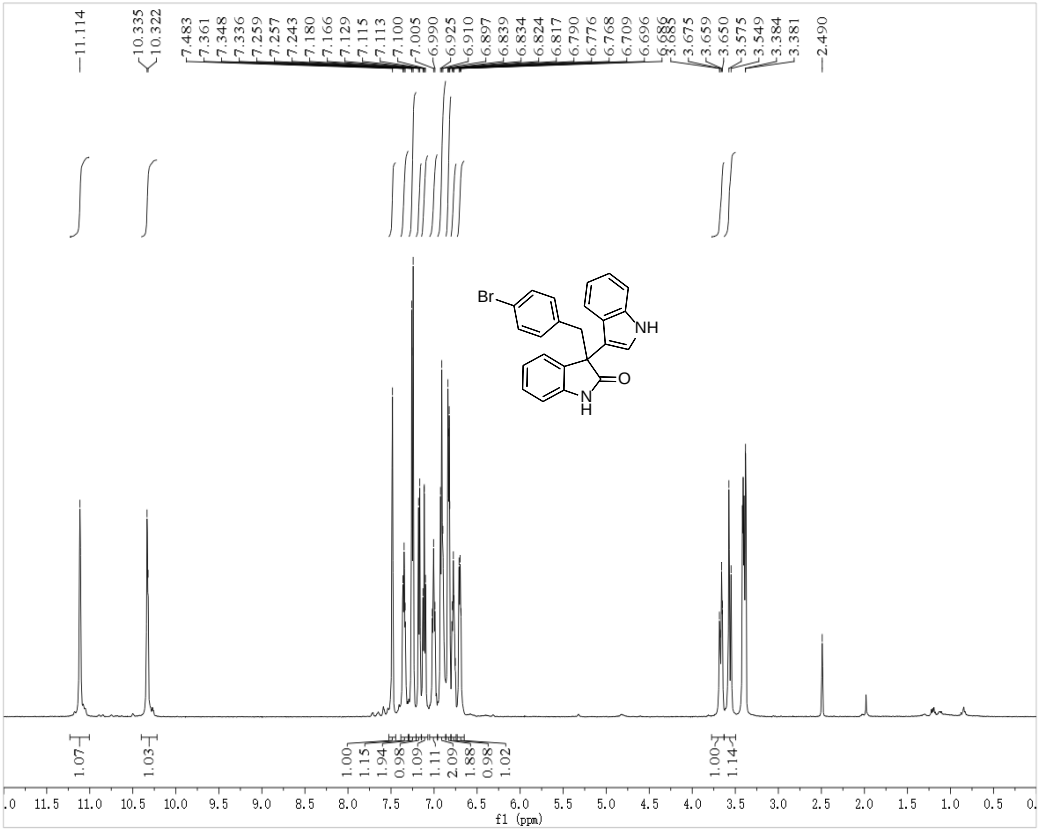


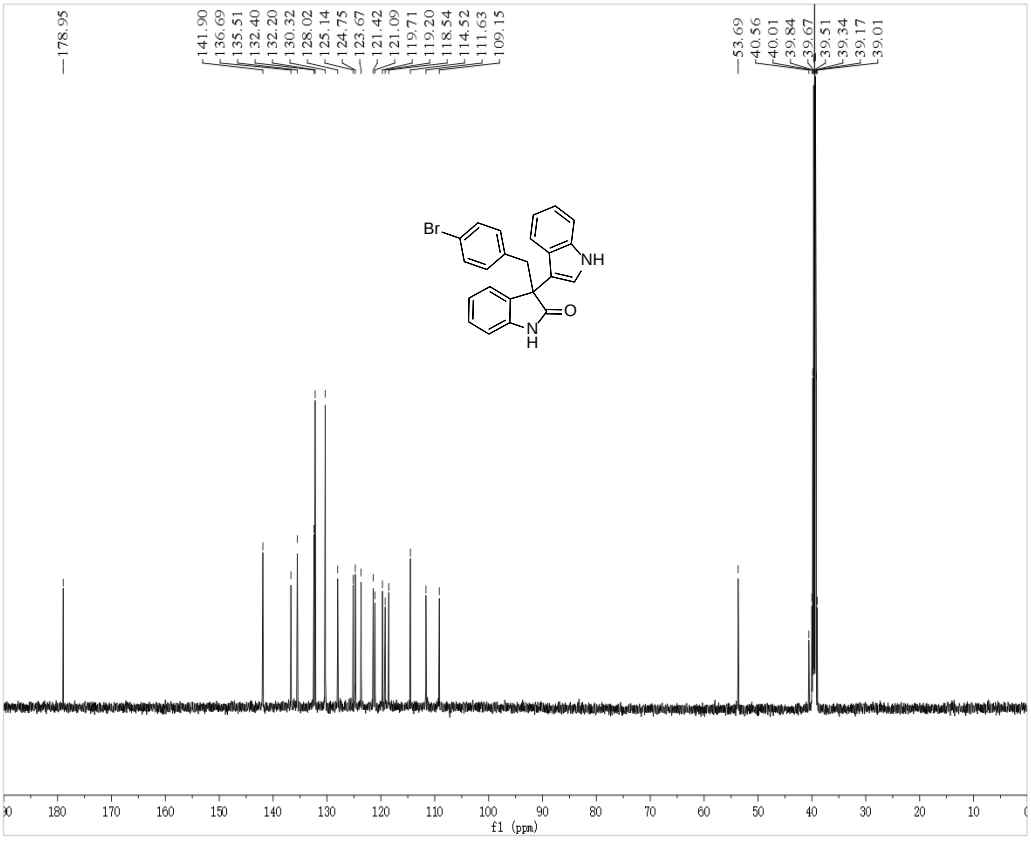
^{1}H and ^{13}C NMR of 5i



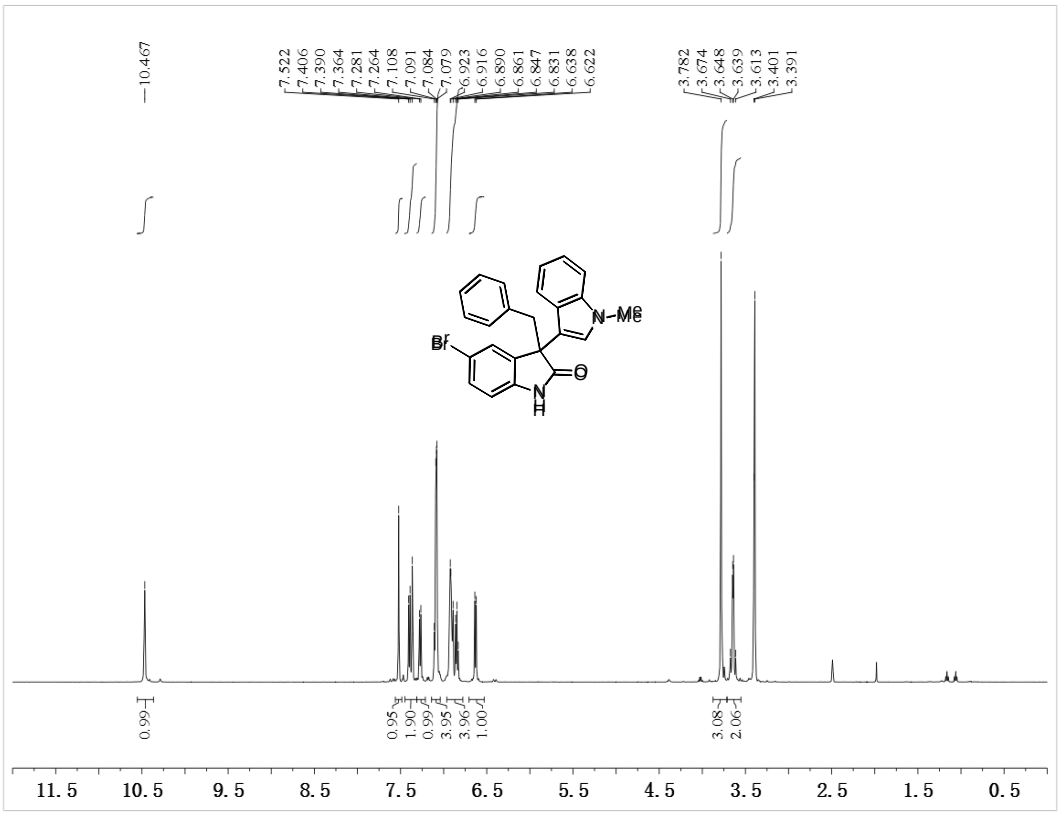


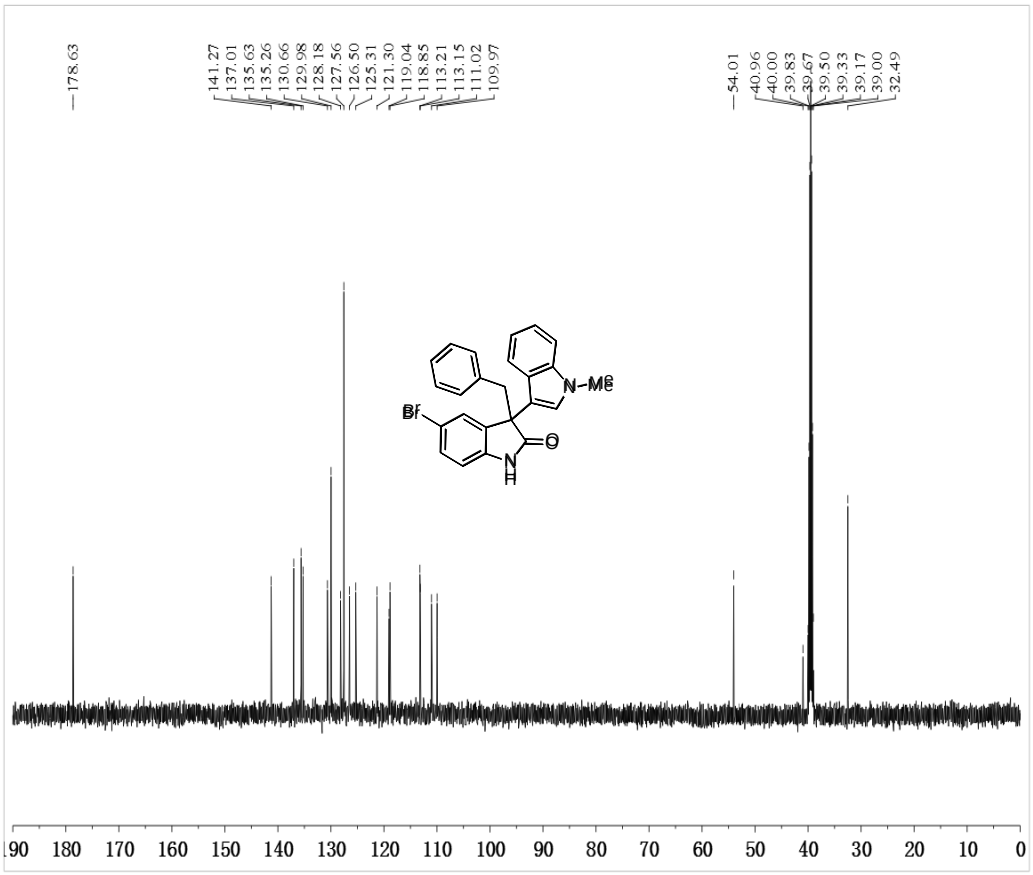
^{1}H and ^{13}C NMR of 5j



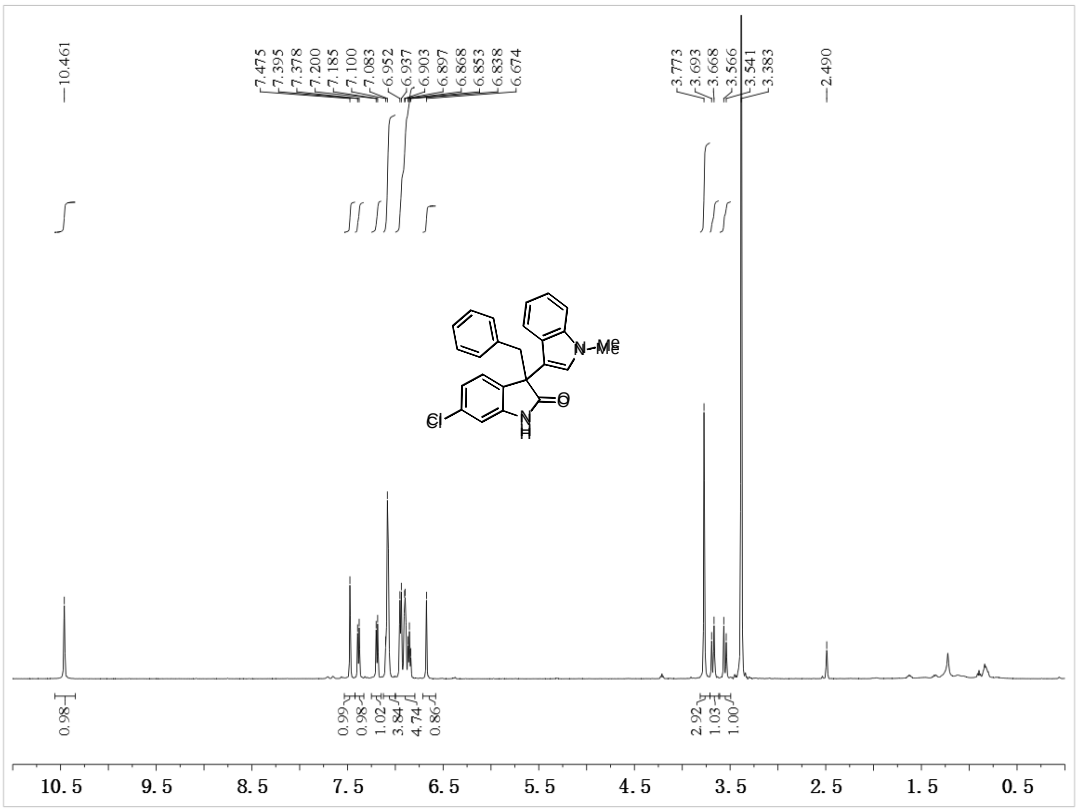


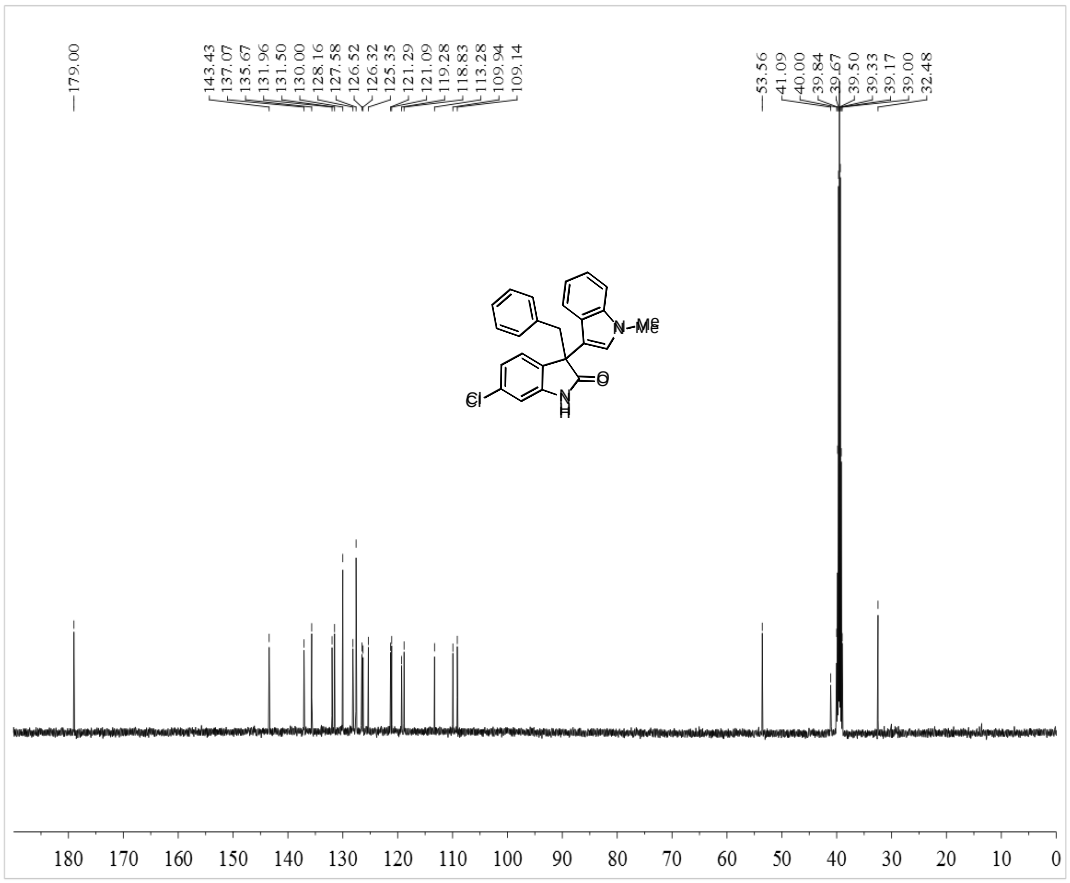
^{1}H and ^{13}C NMR of 5k



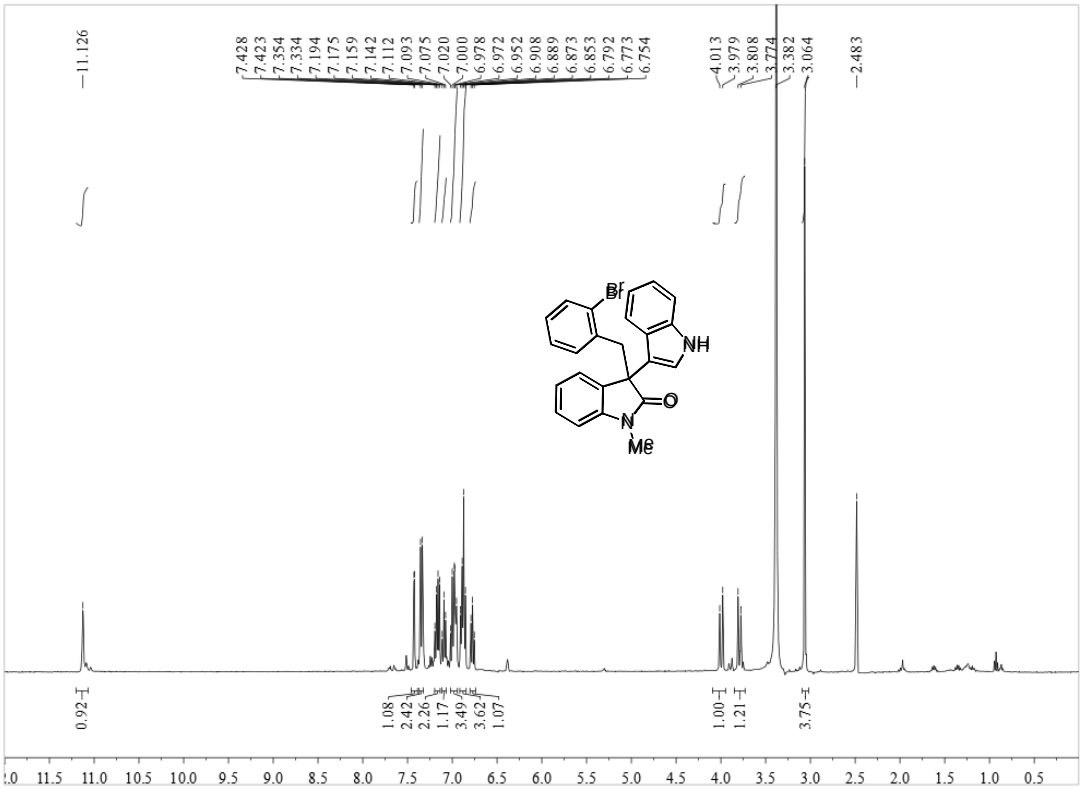


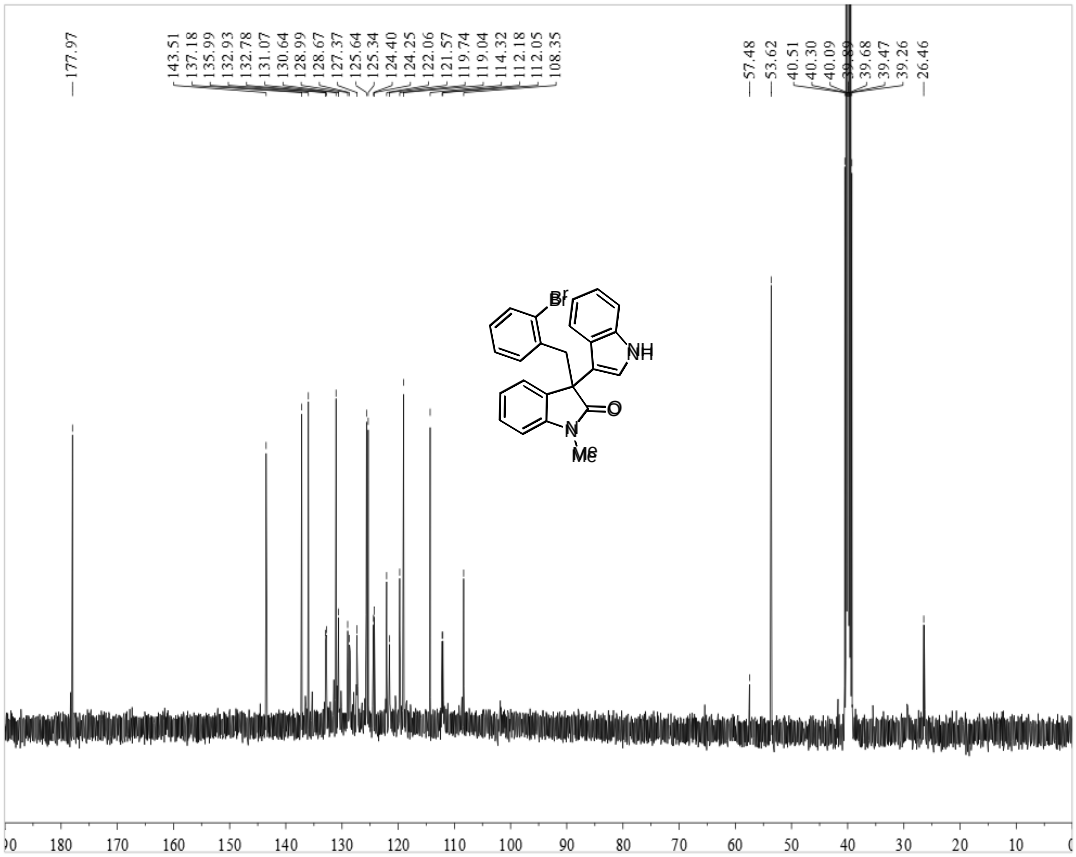
^{1}H and ^{13}C NMR of 5l



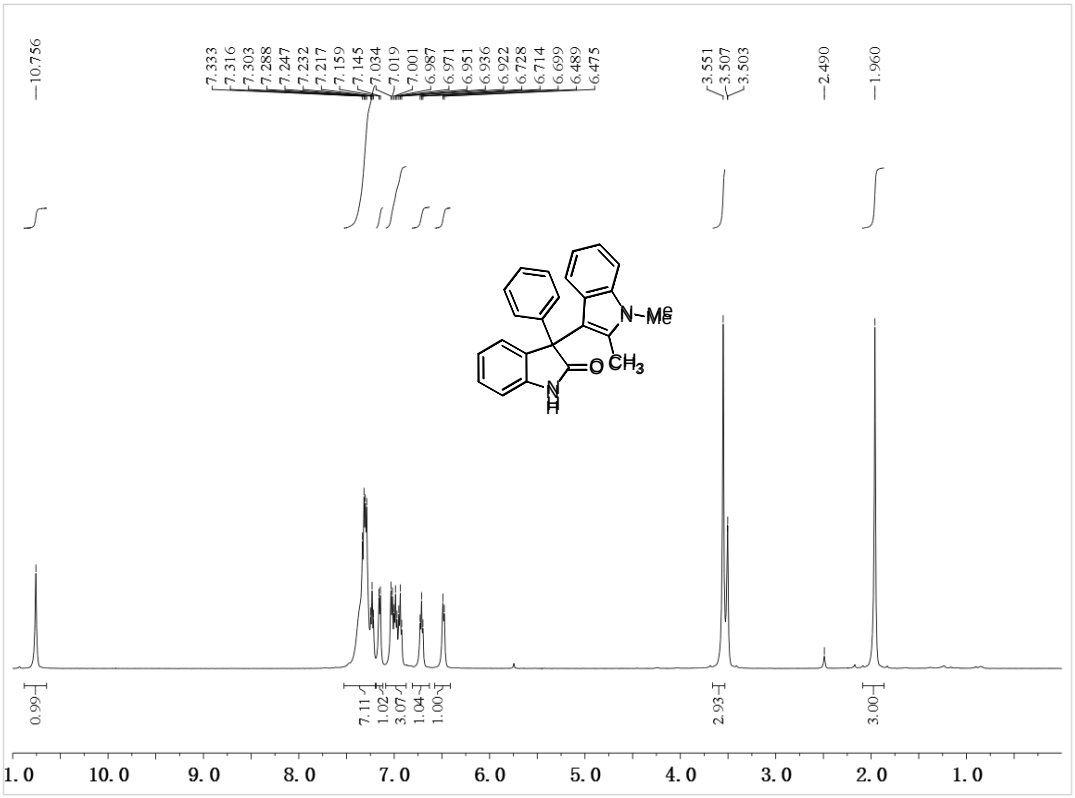


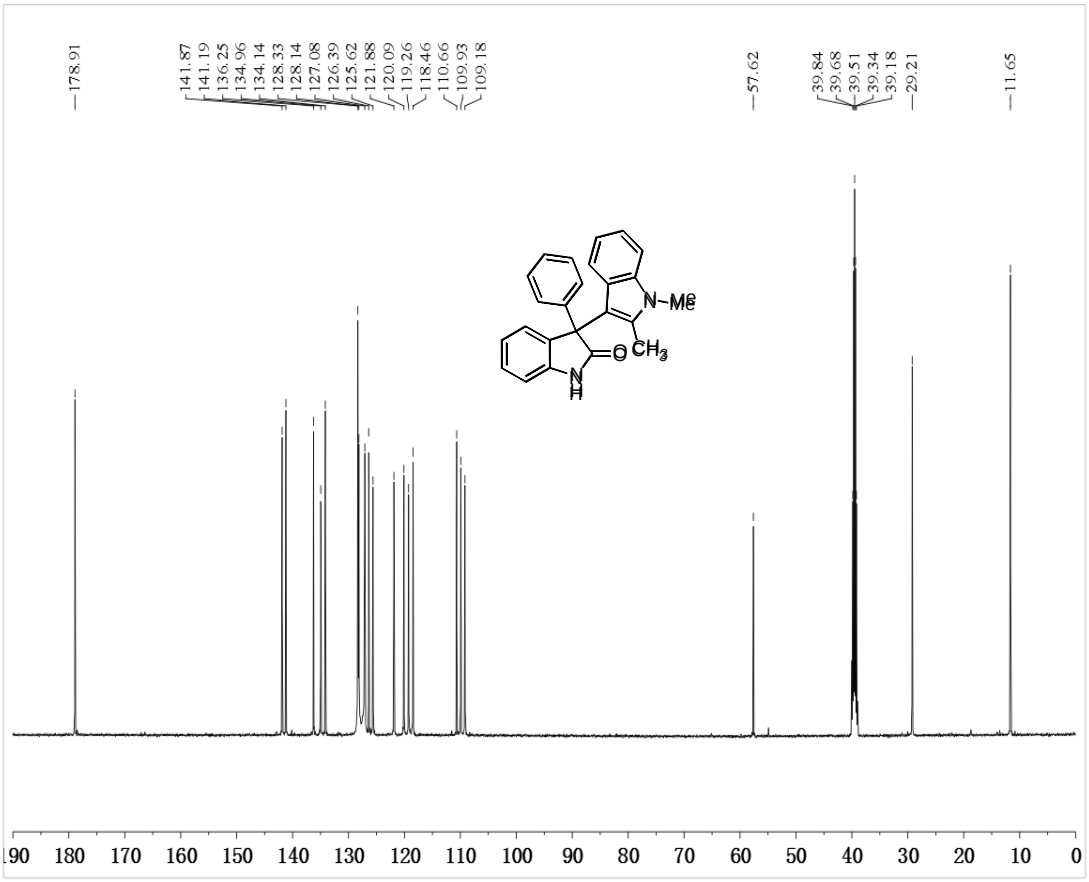
^{1}H and ^{13}C NMR of 5m



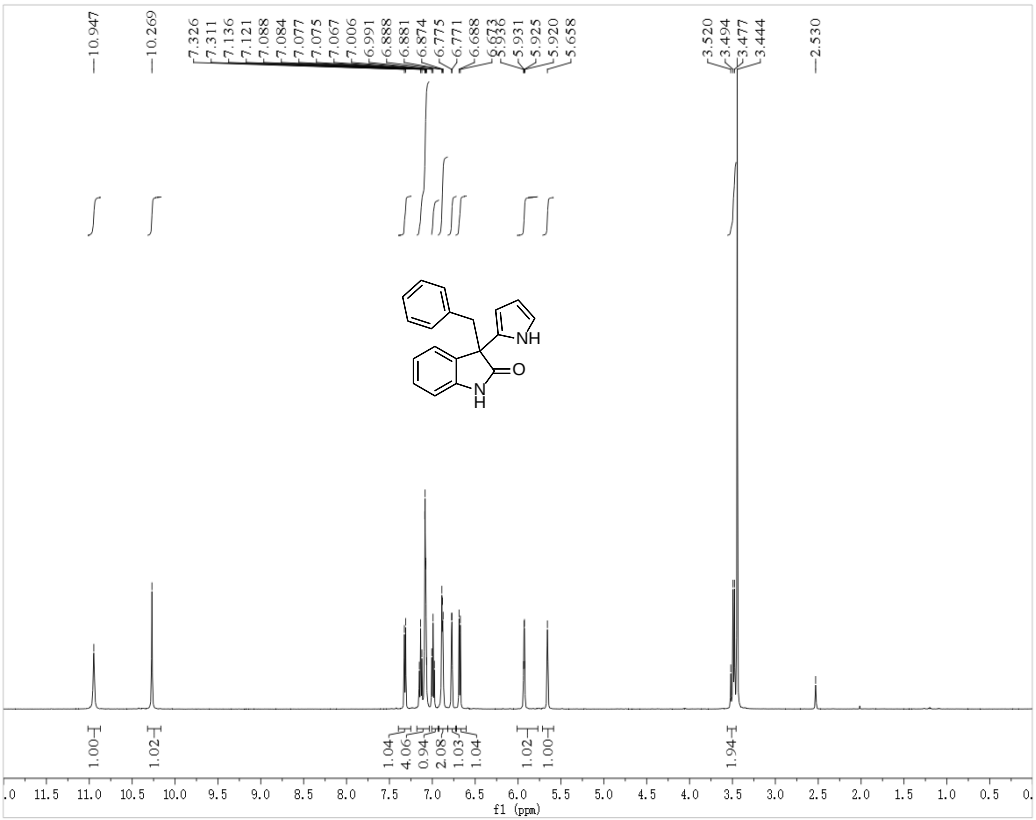


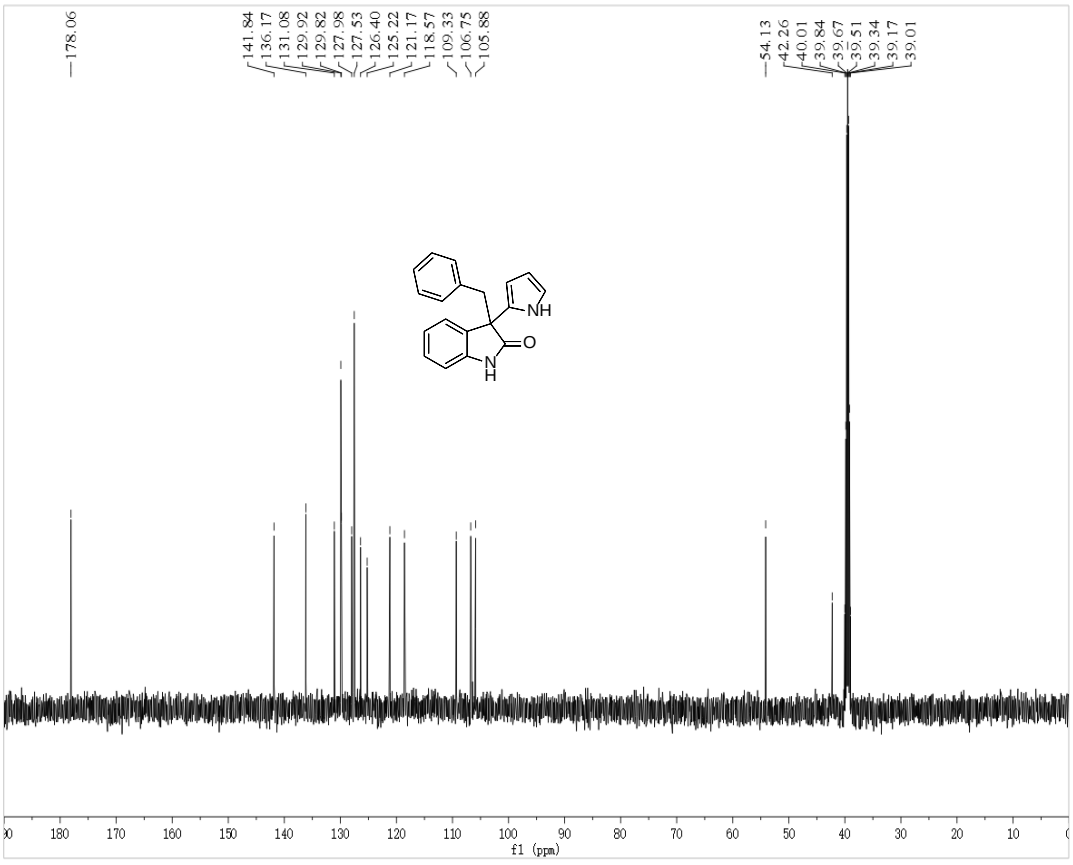
^{1}H and ^{13}C NMR of 5n



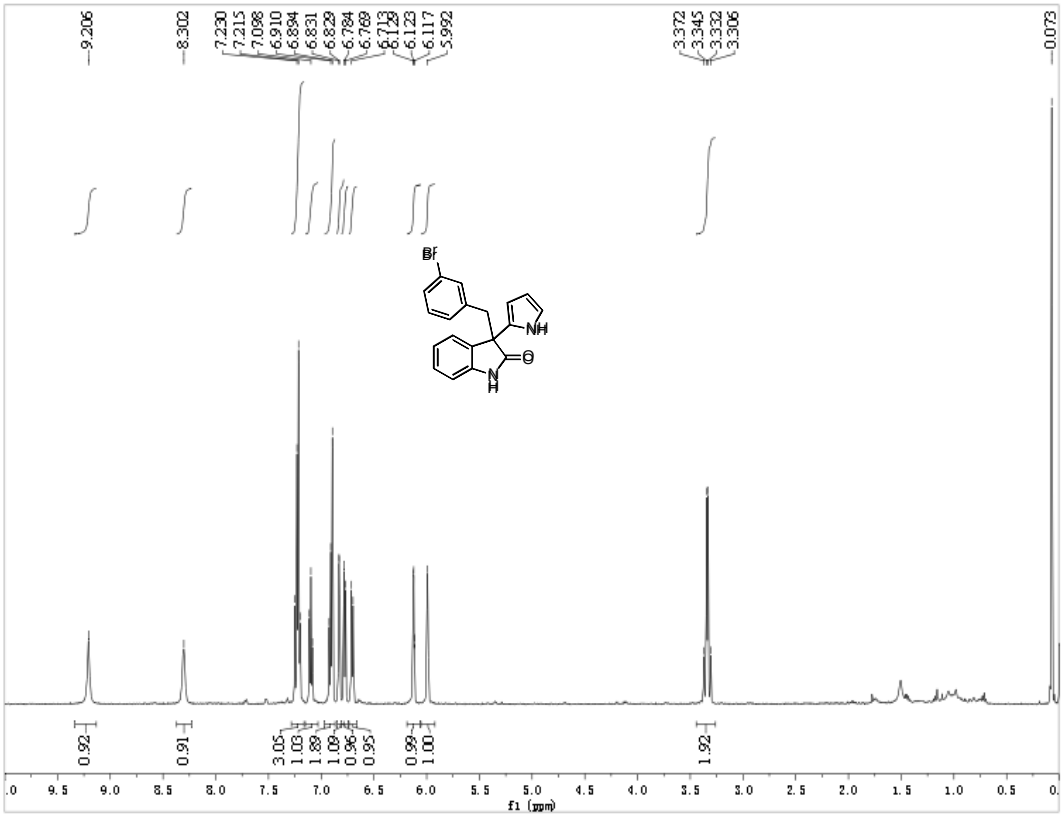


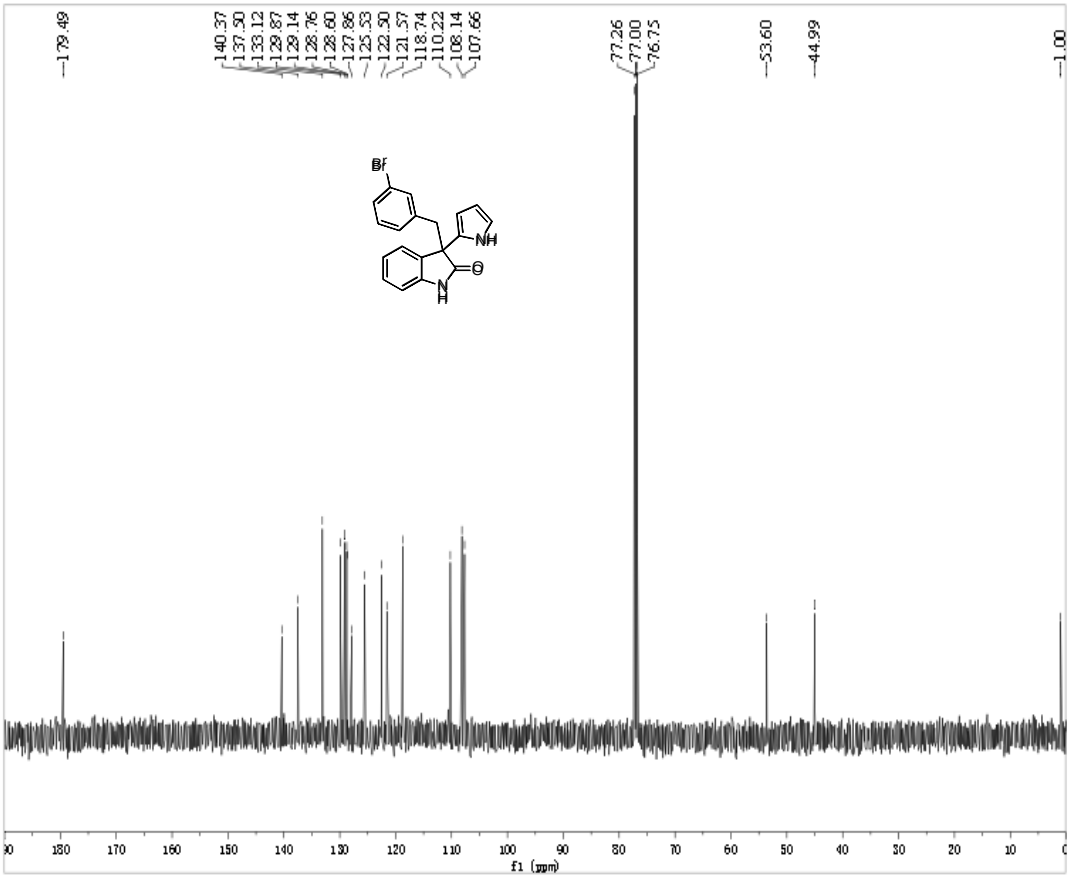
^{1}H and ^{13}C NMR of 7a



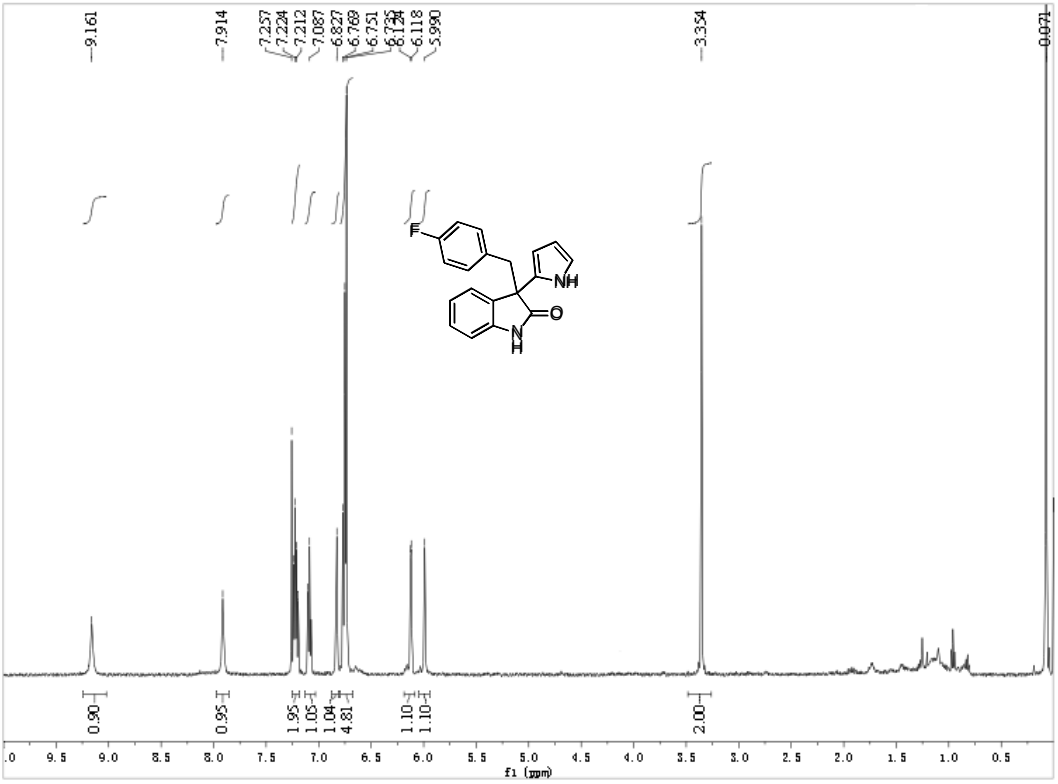


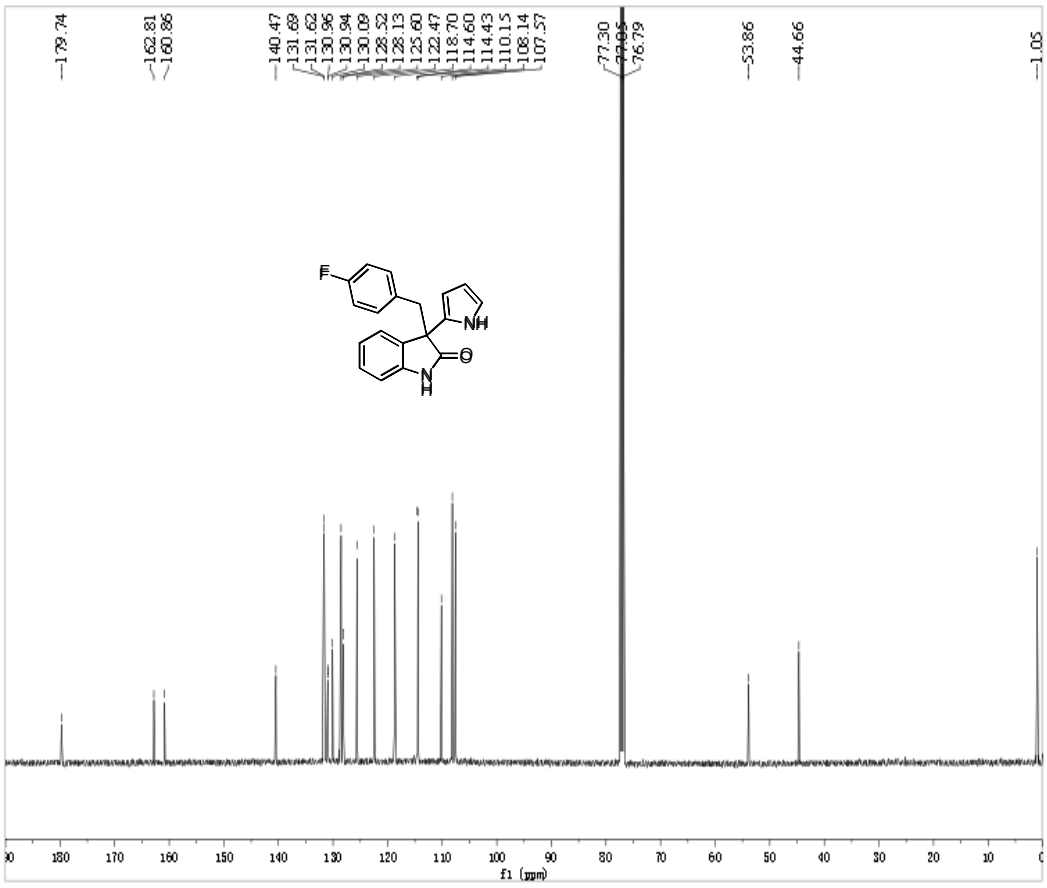
^{1}H and ^{13}C NMR of 7b



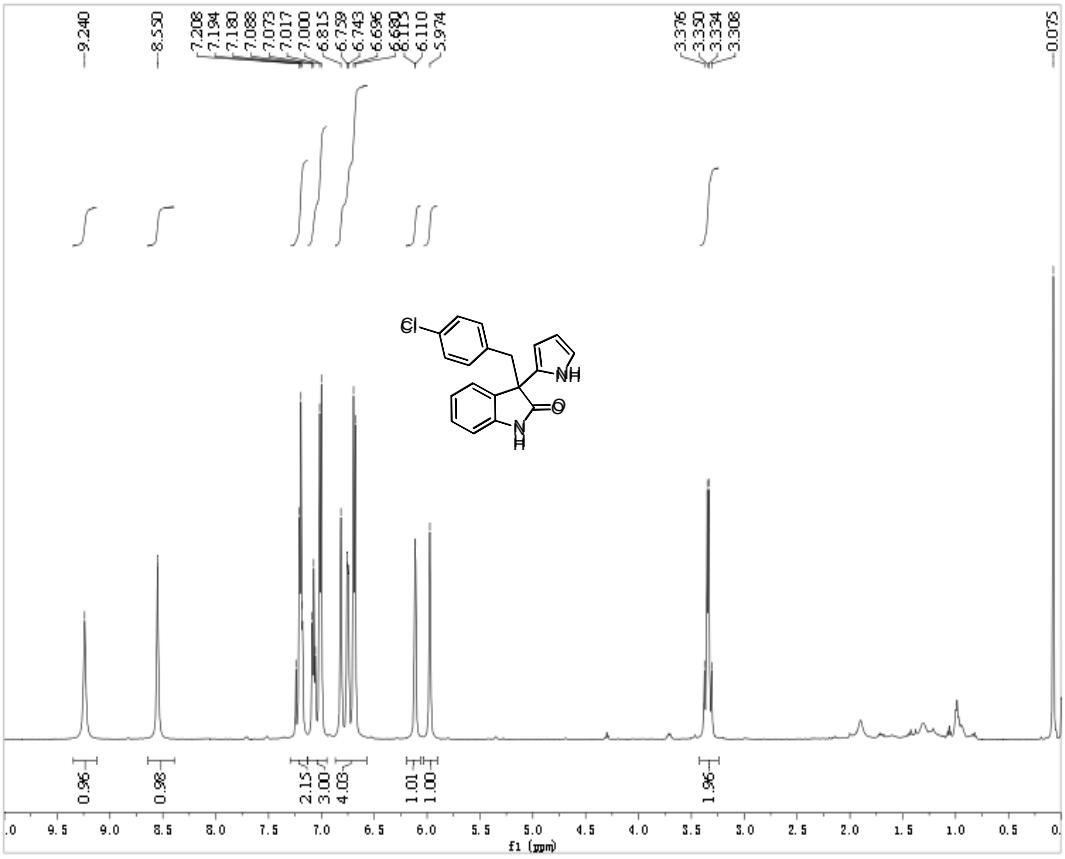


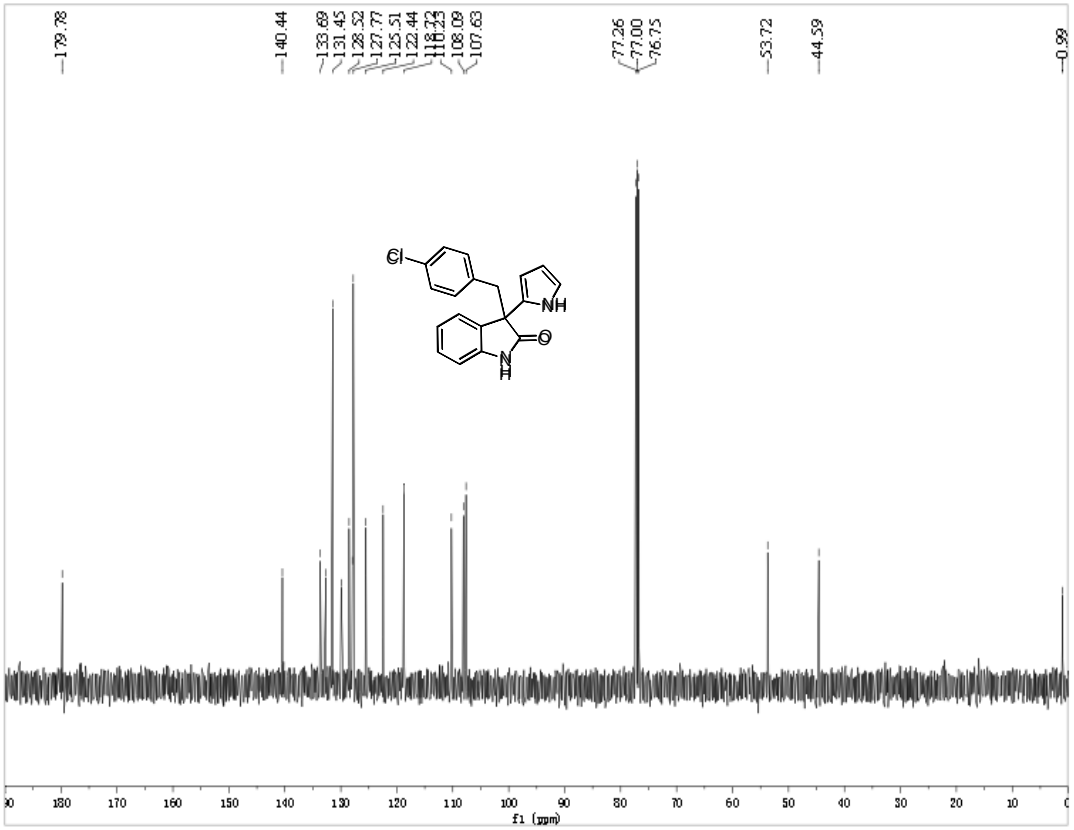
^{1}H and ^{13}C NMR of 7c



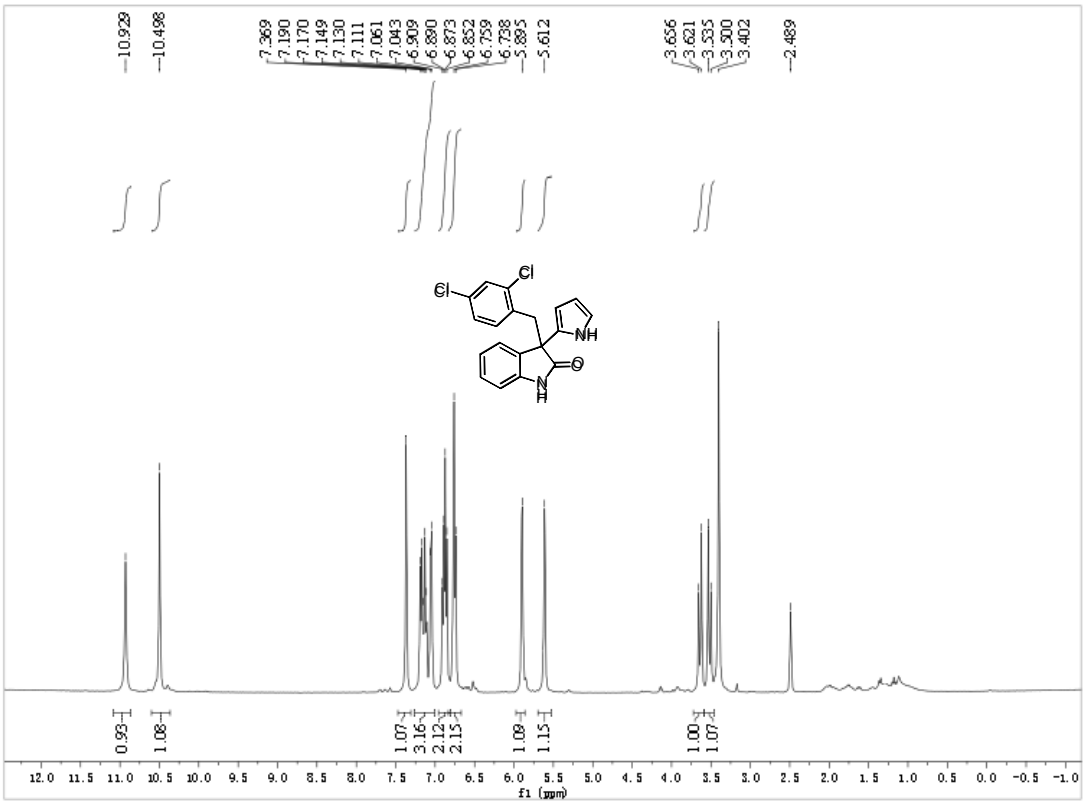


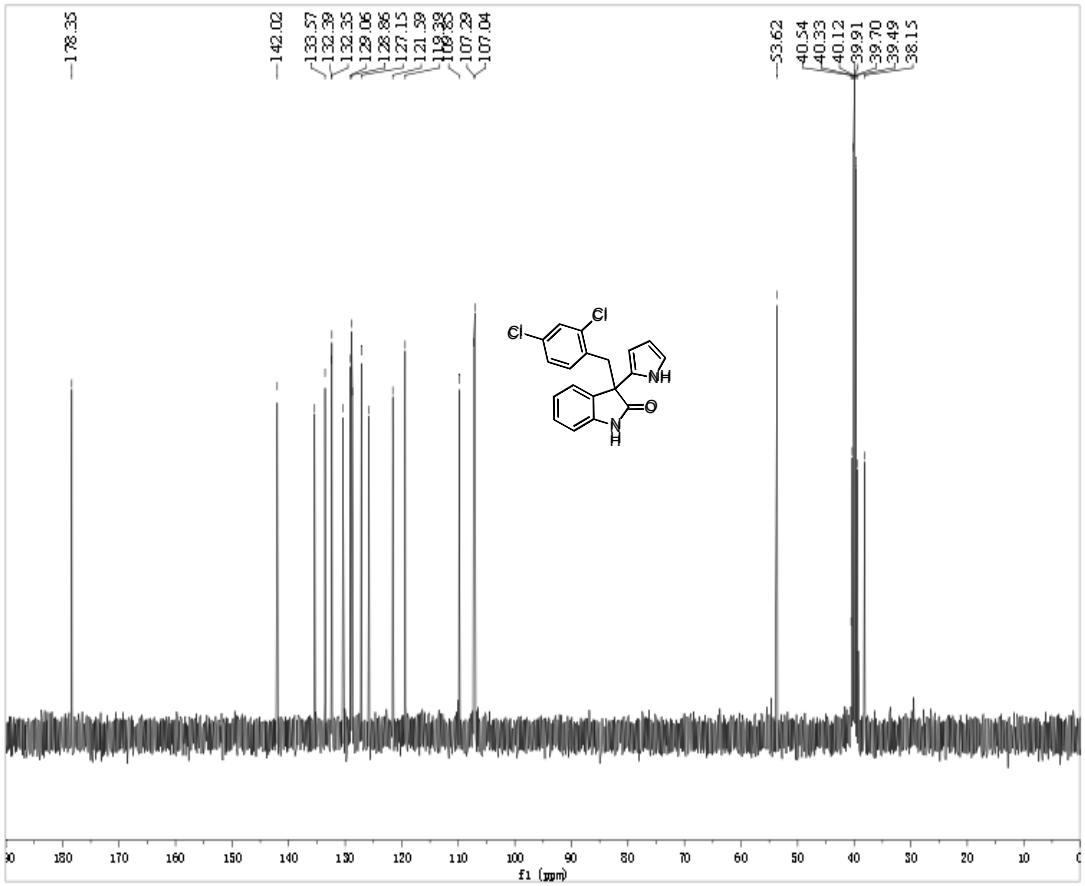
^{1}H and ^{13}C NMR of 7d



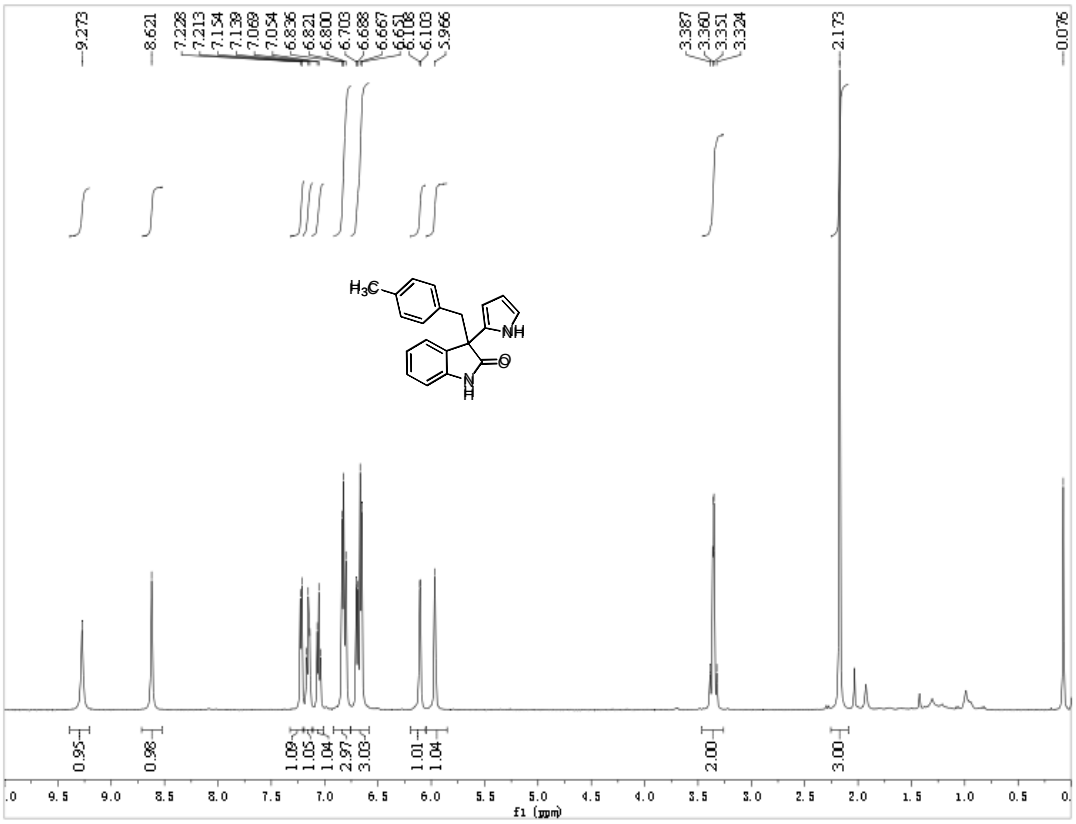


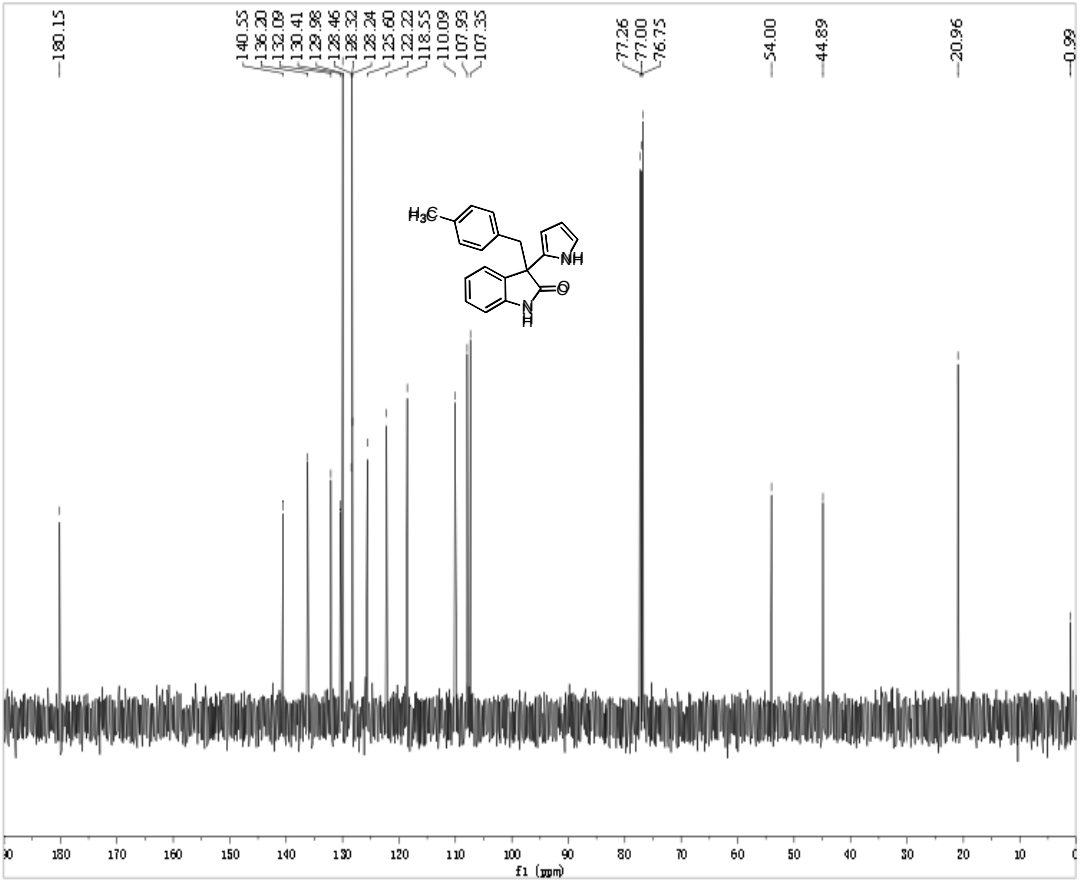
^{1}H and ^{13}C NMR of 7e



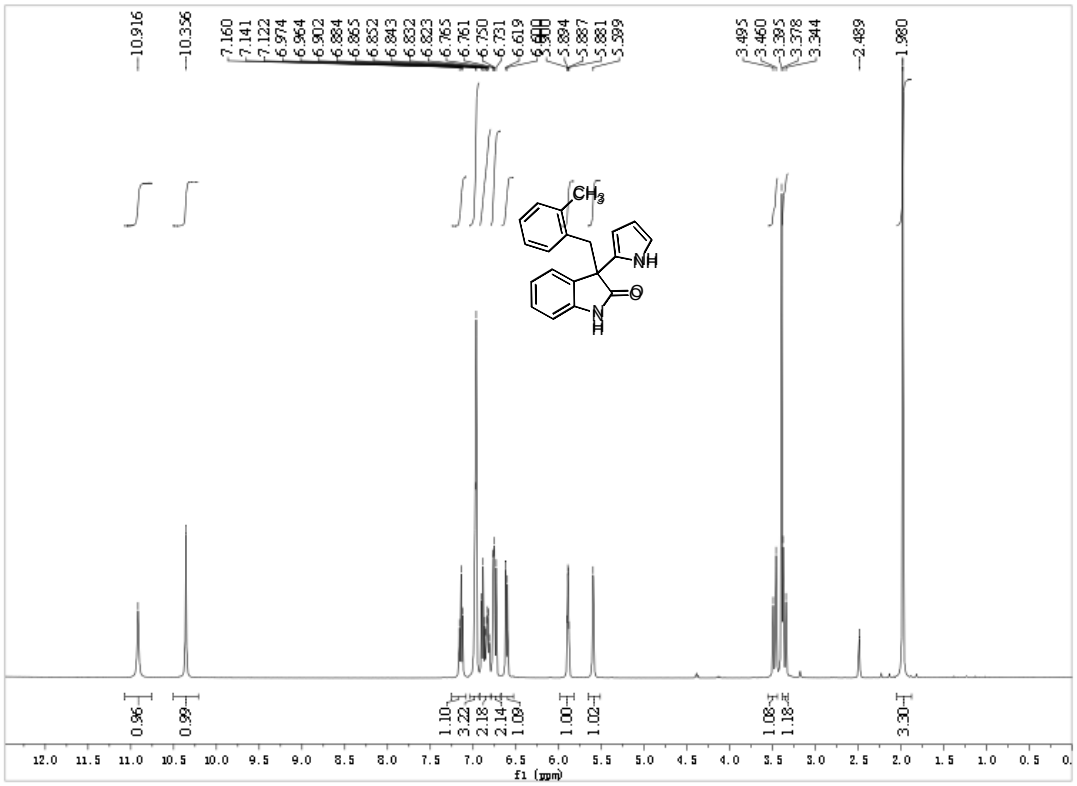


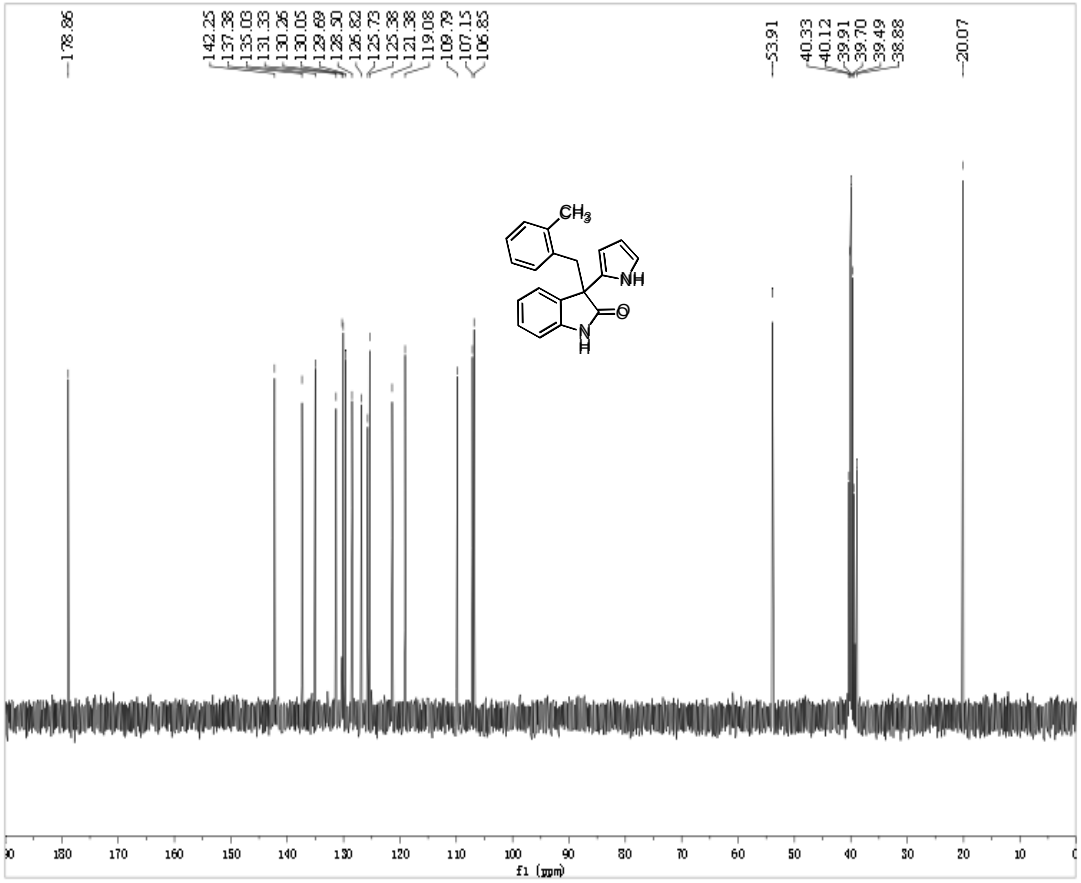
^{1}H and ^{13}C NMR of 7f



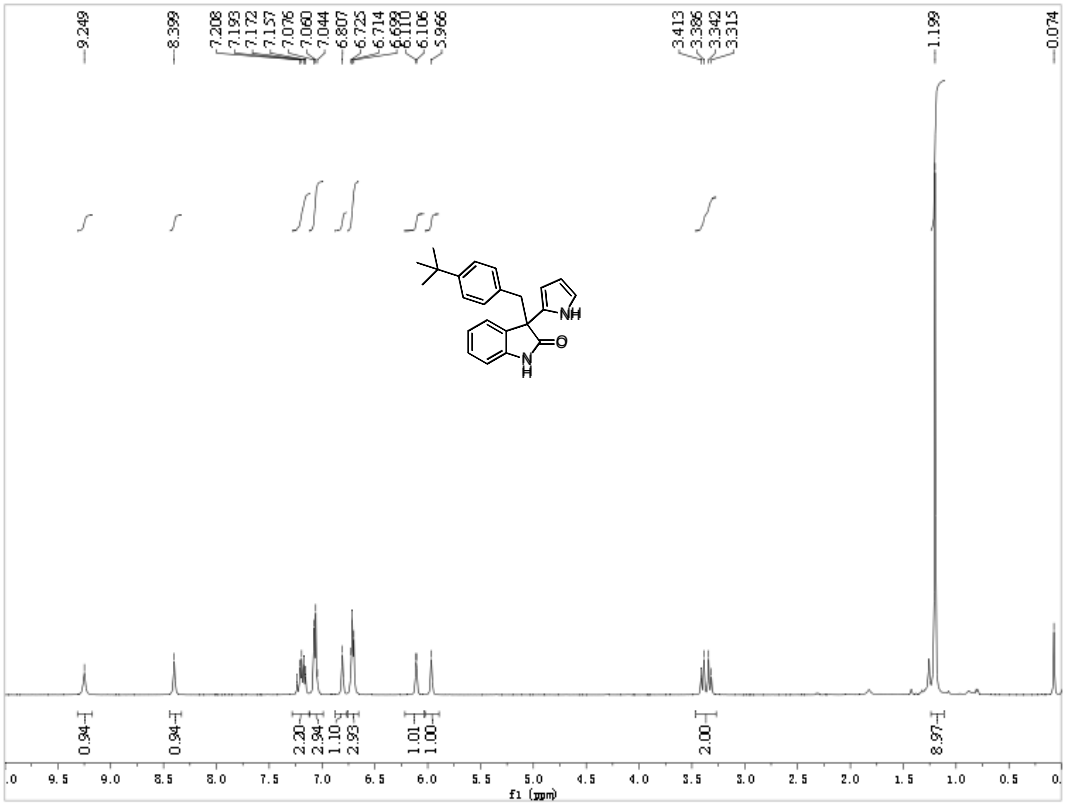


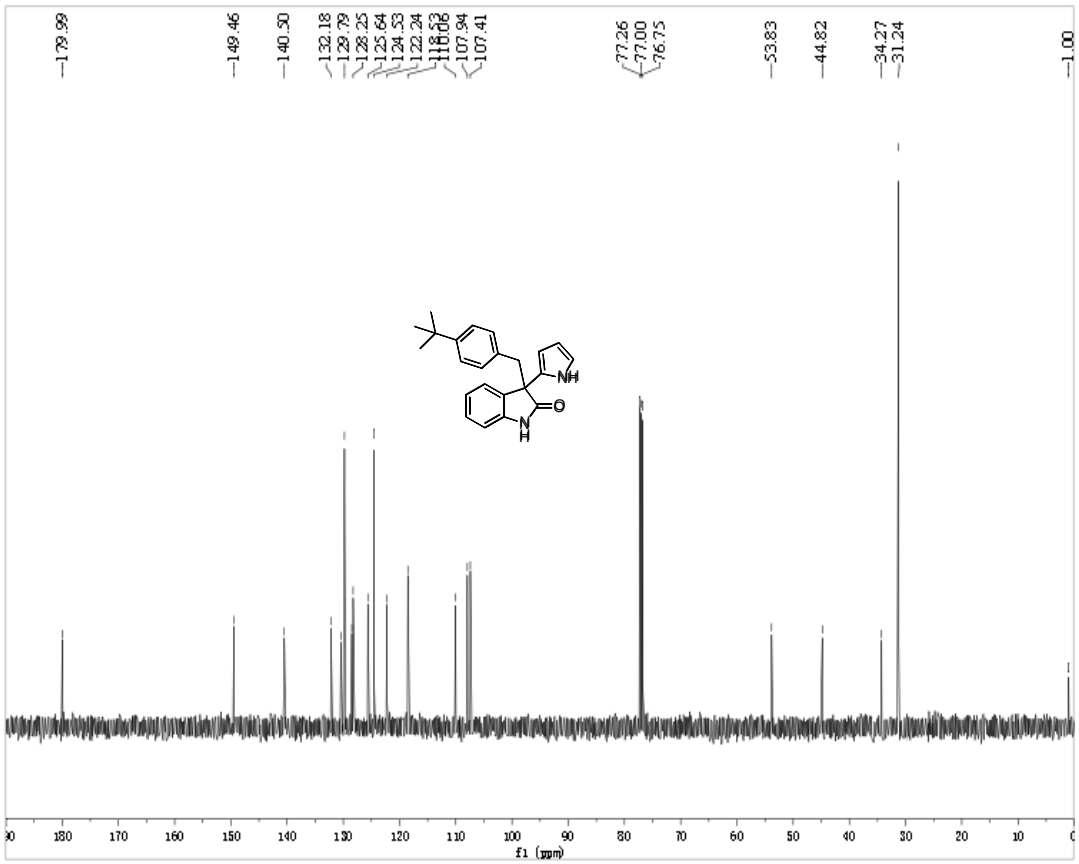
^{1}H and ^{13}C NMR of 7g



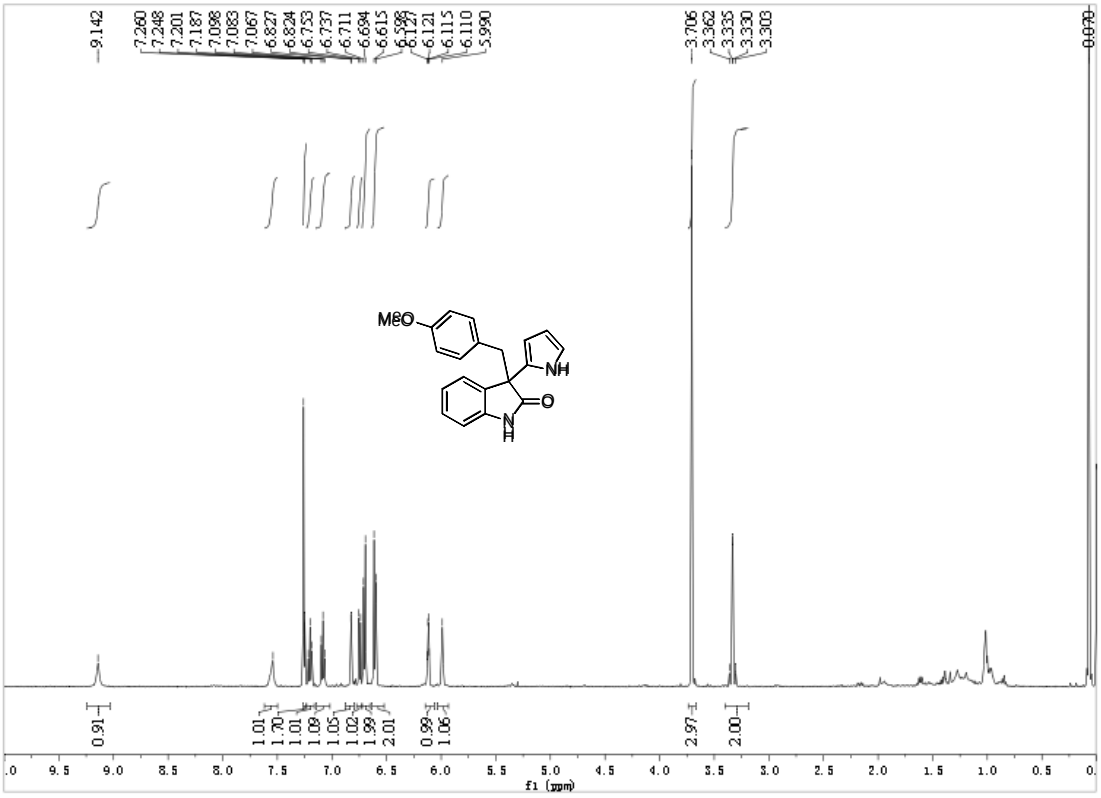


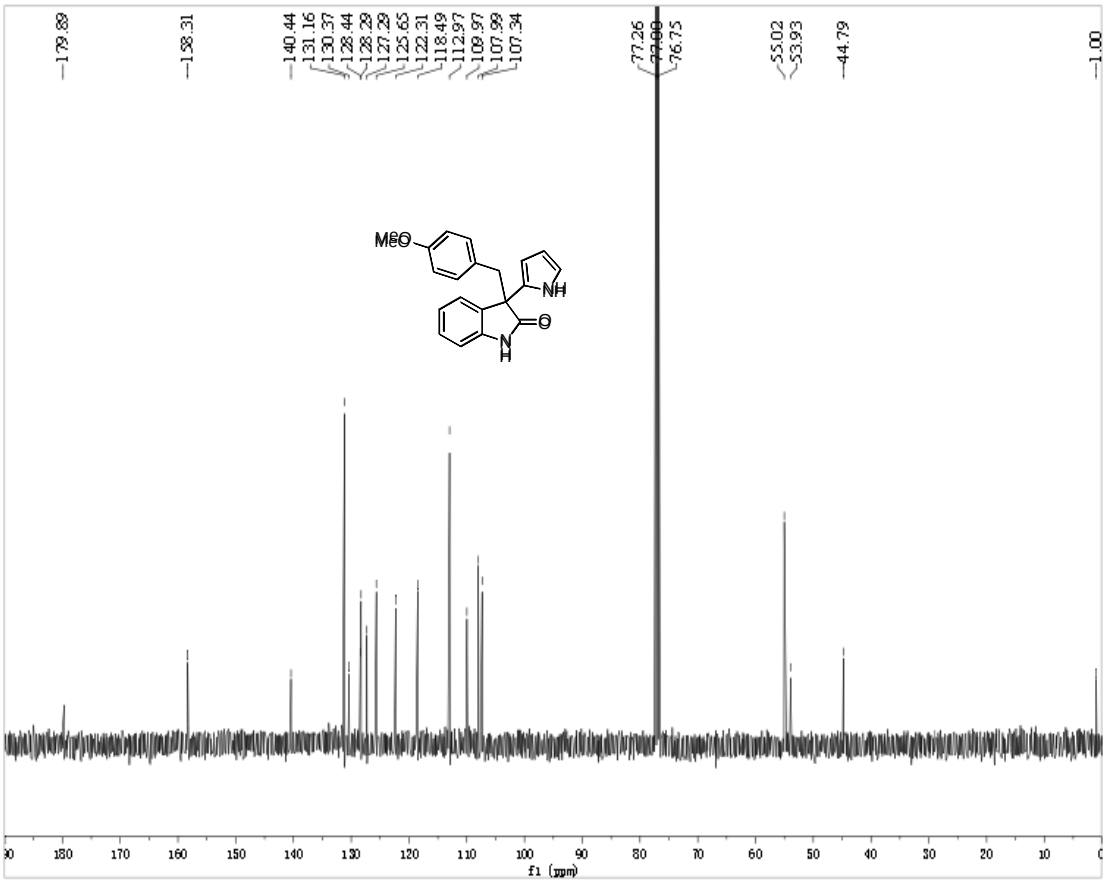
^{1}H and ^{13}C NMR of 7h



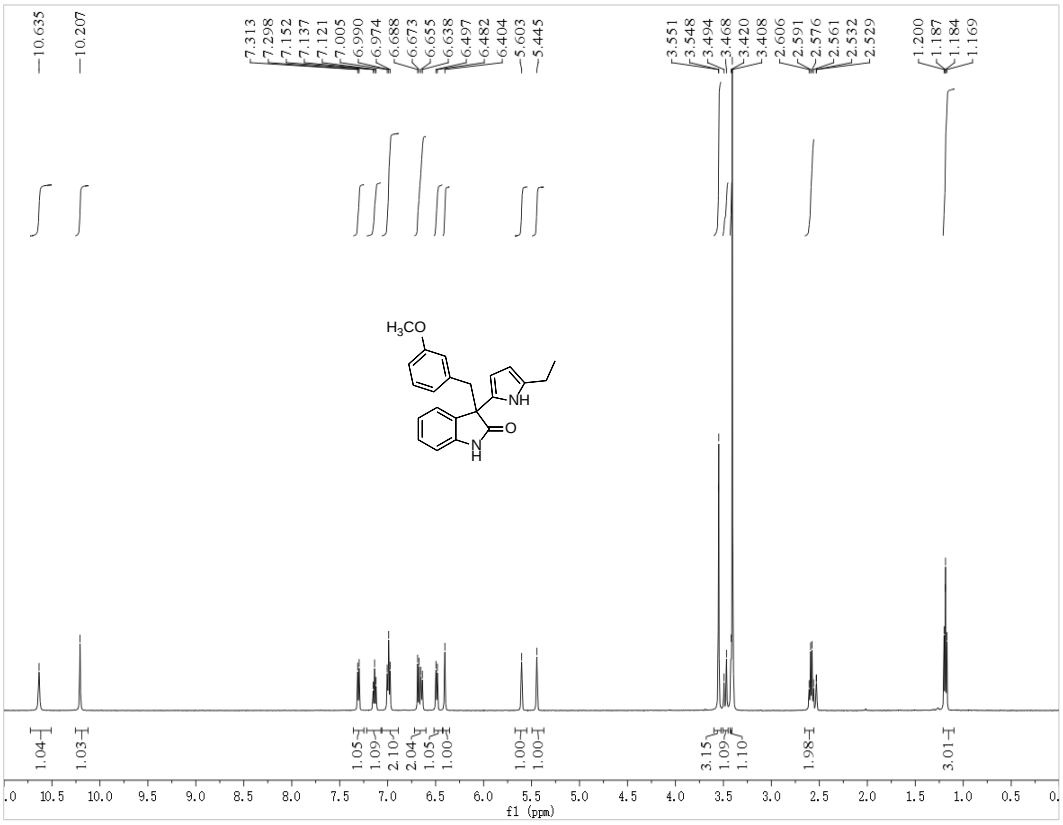


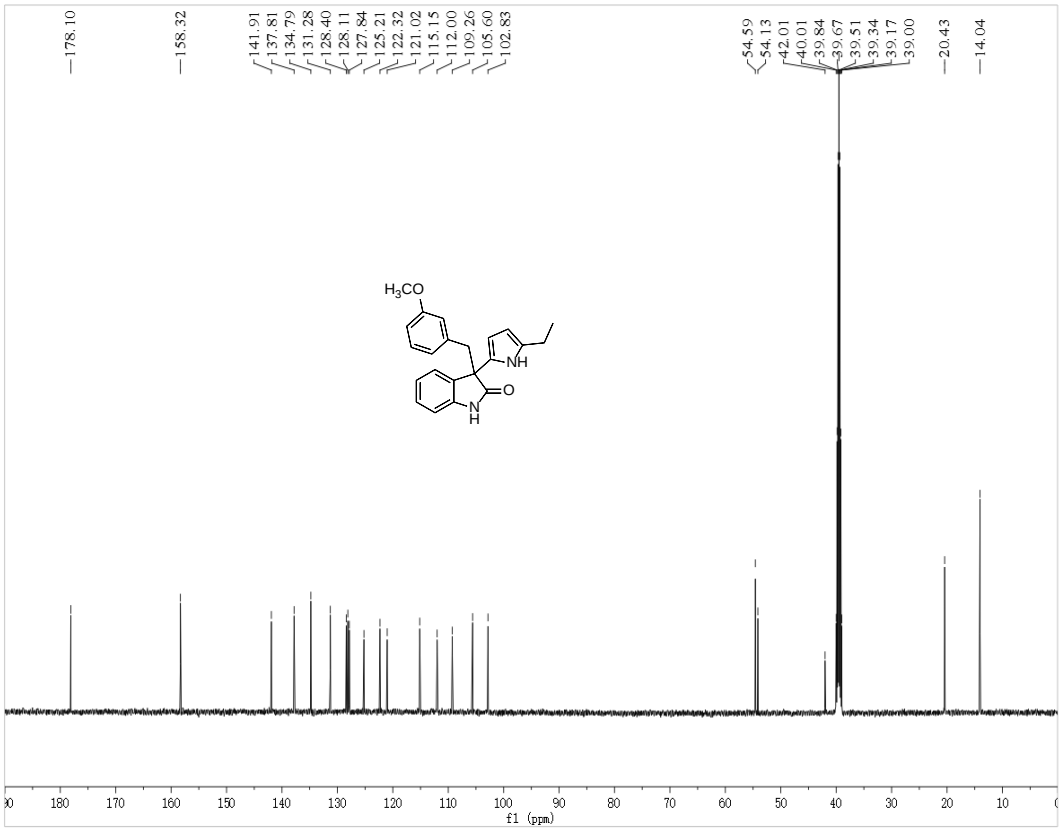
^{1}H and ^{13}C NMR of 7i



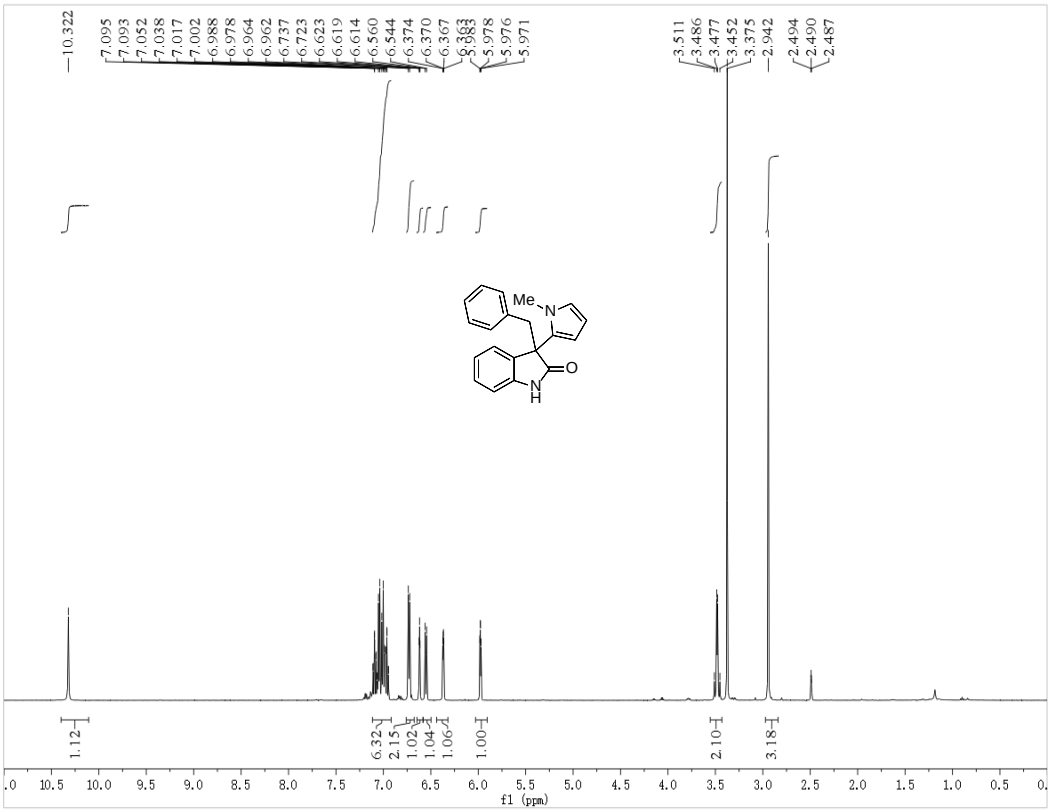


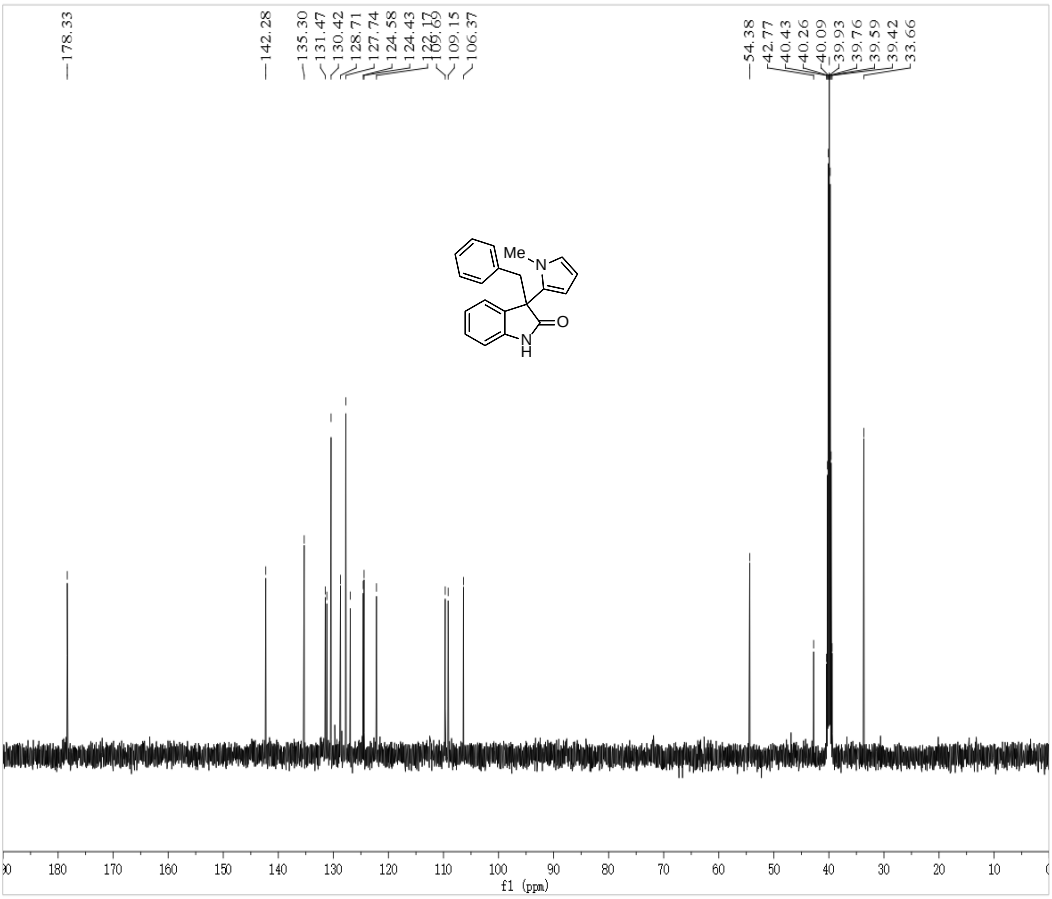
^{1}H and ^{13}C NMR of 7j



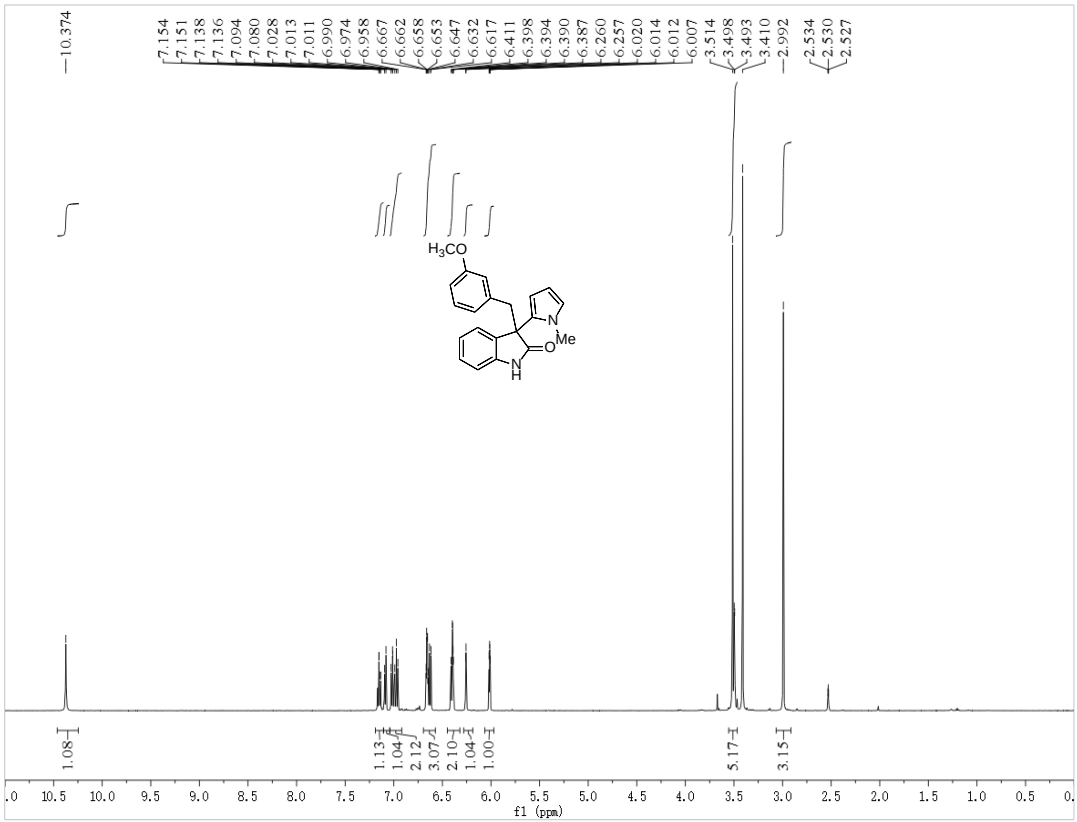


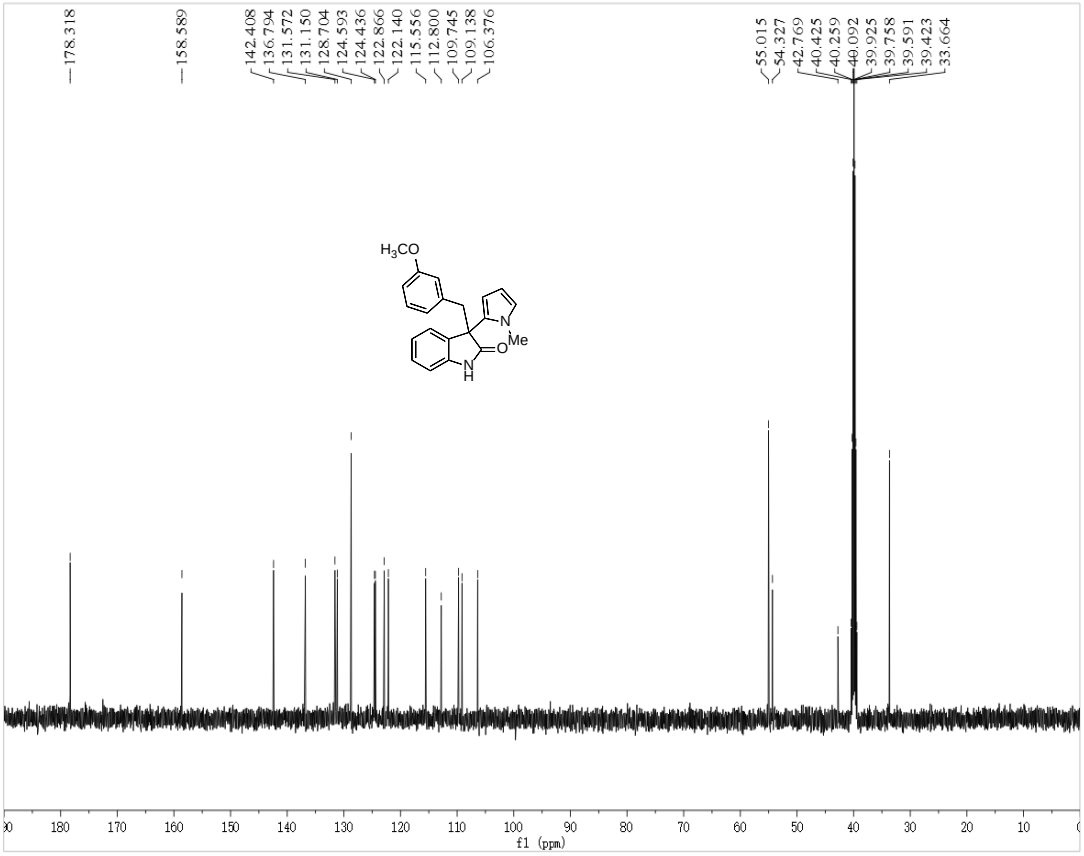
^{1}H and ^{13}C NMR of 7k



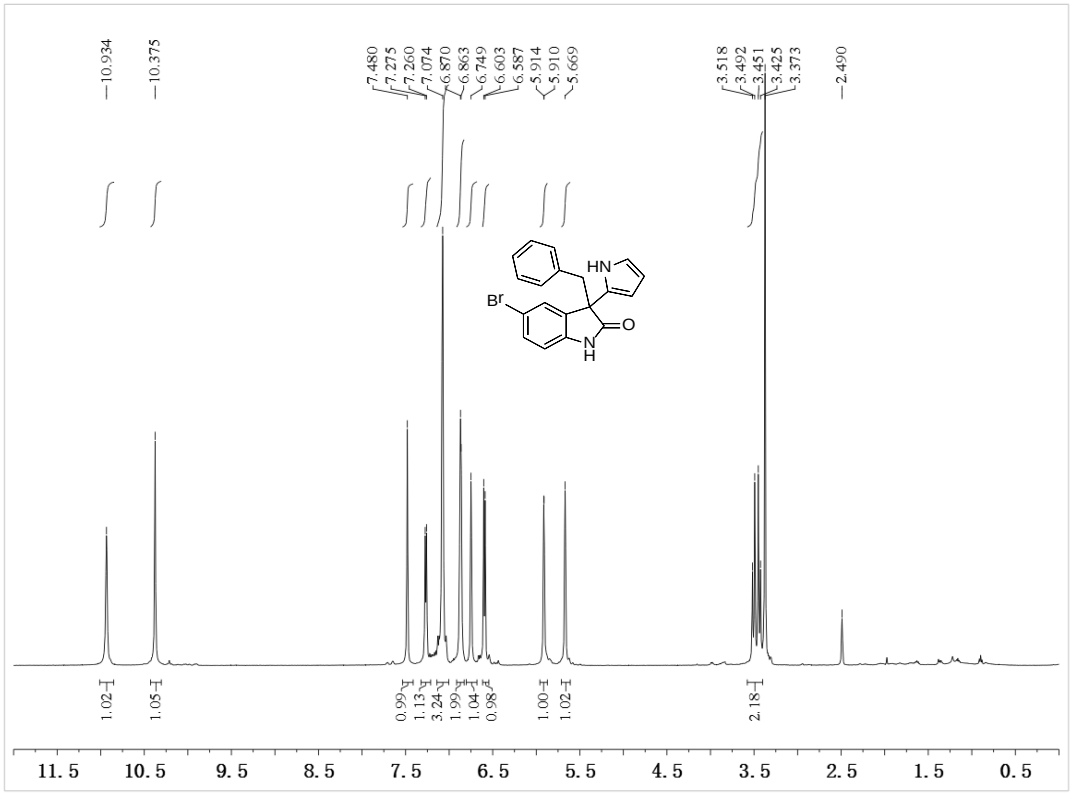


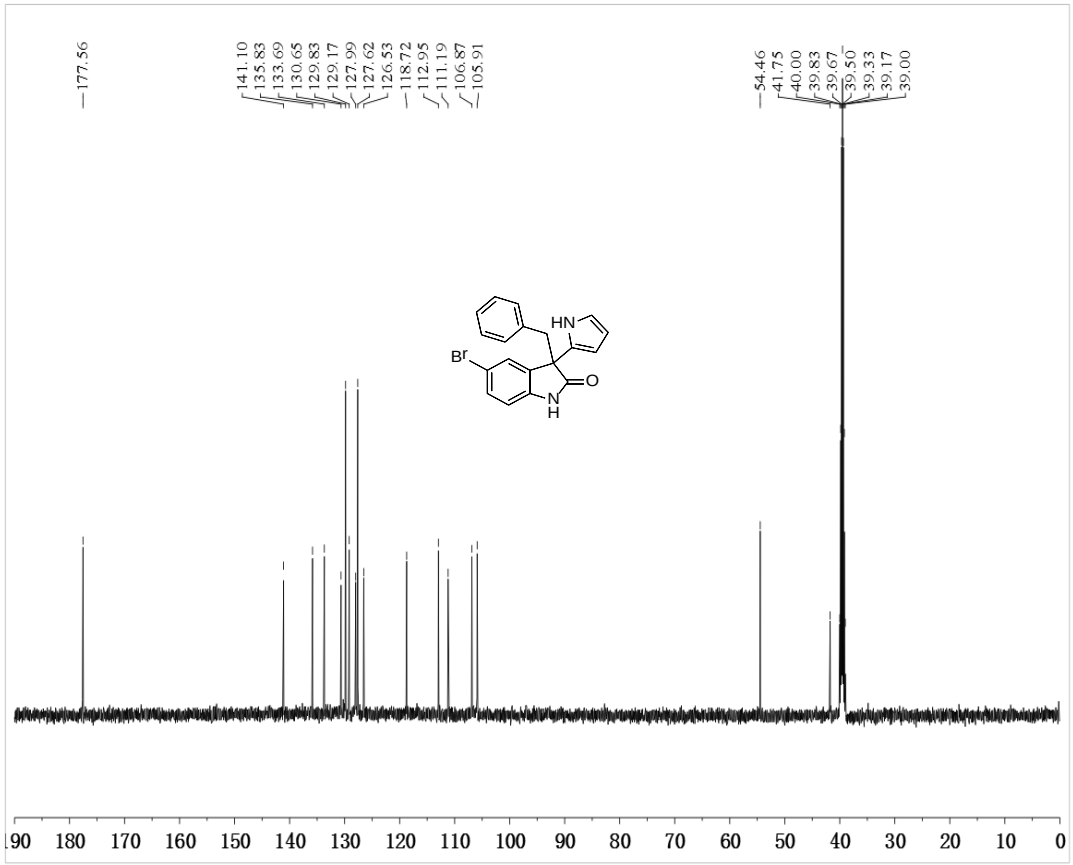
^{1}H and ^{13}C NMR of 7l



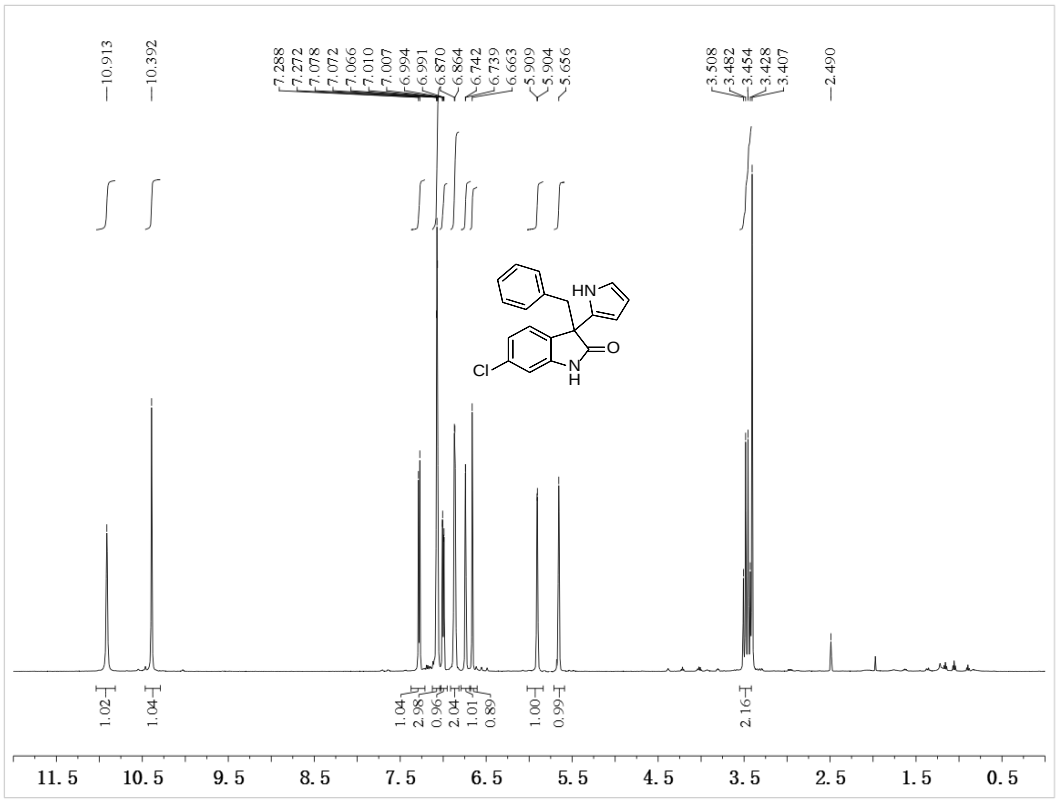


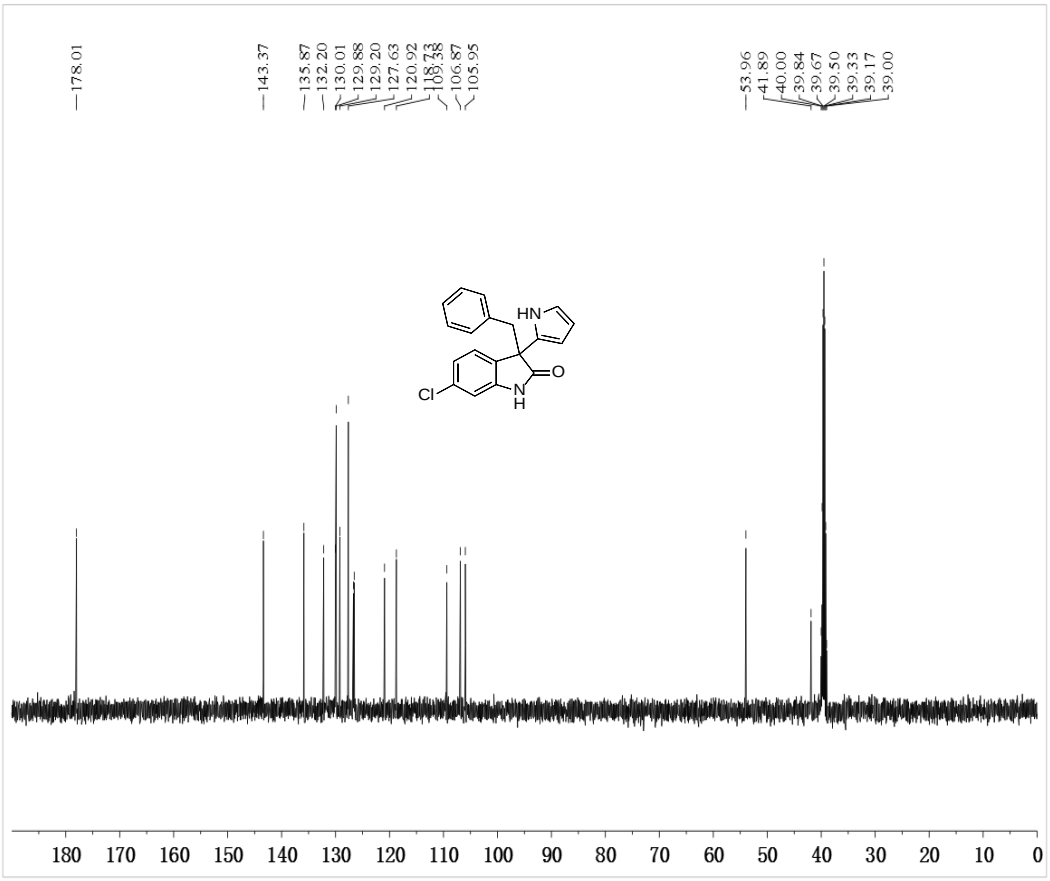
^{1}H and ^{13}C NMR of 7m



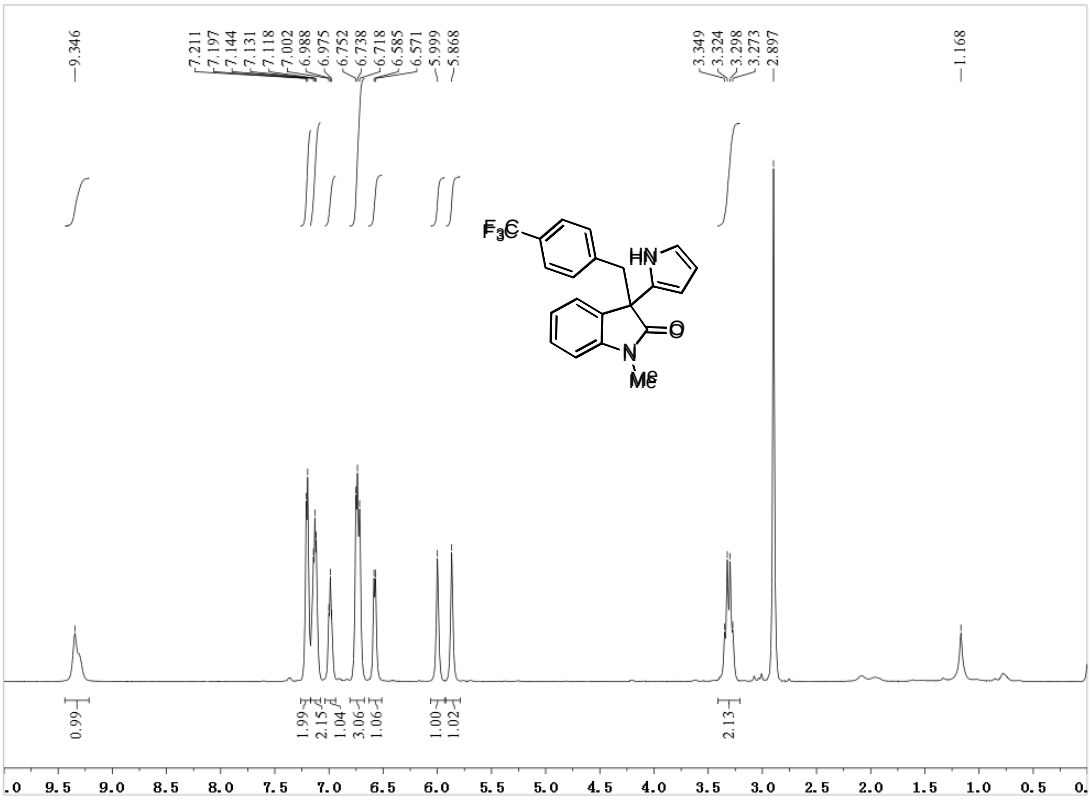


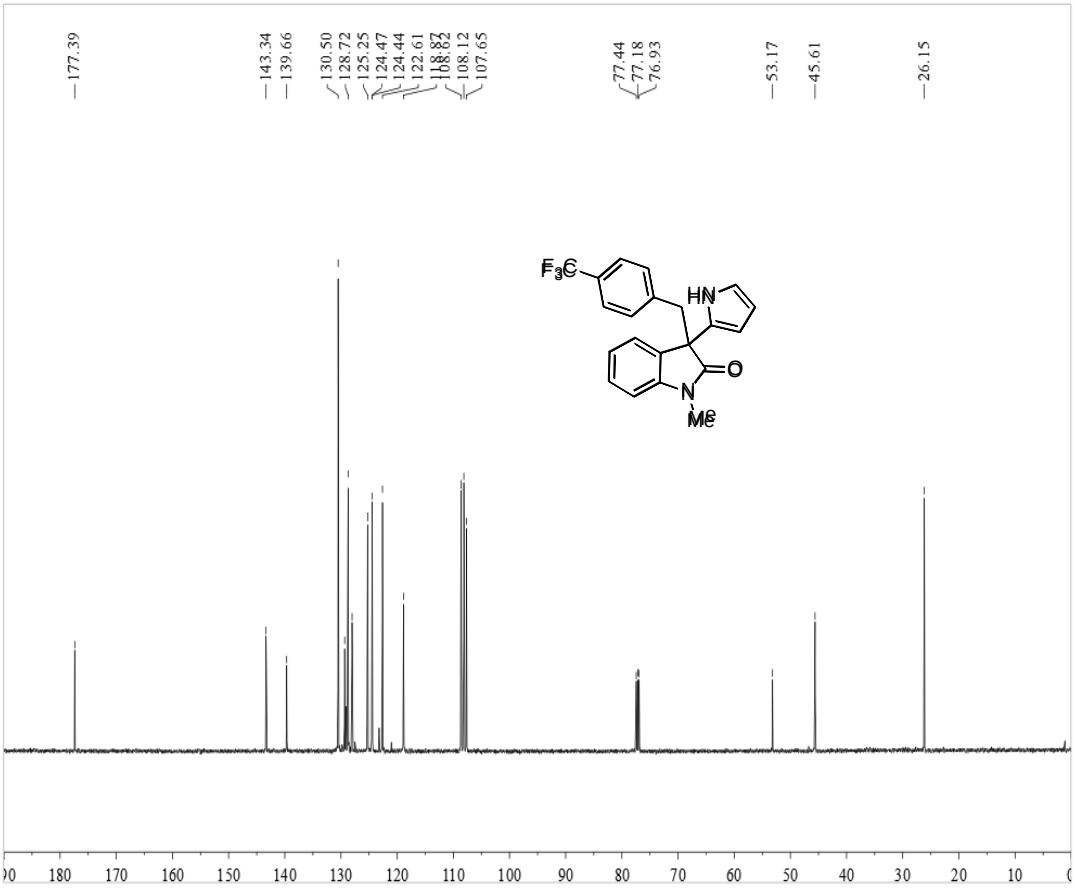
^{1}H and ^{13}C NMR of 7n



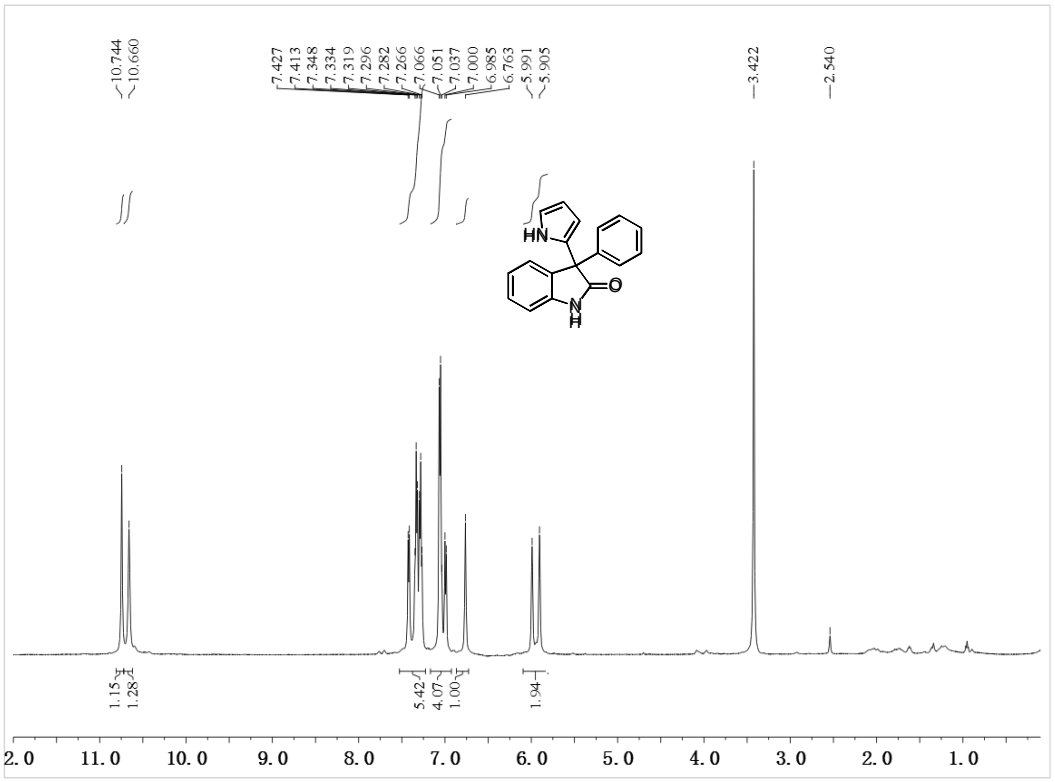


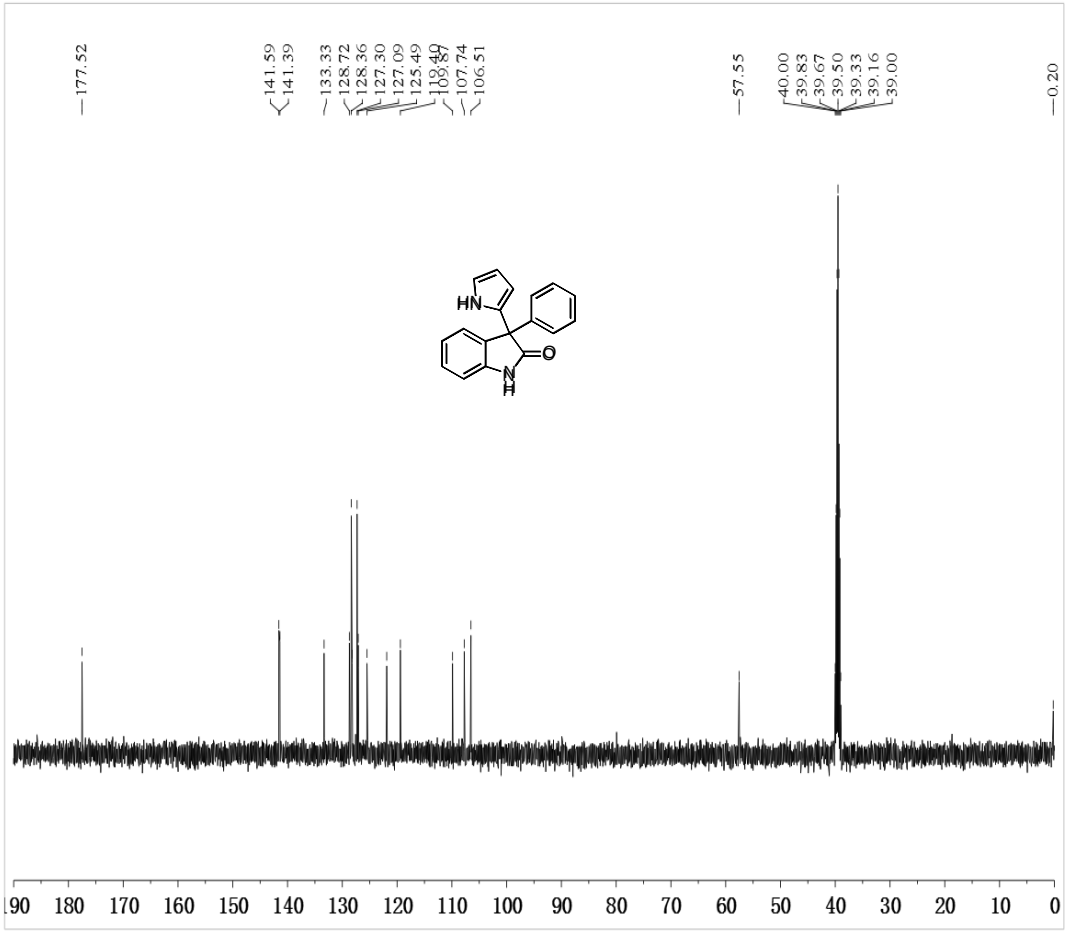
^{1}H and ^{13}C NMR of 7o



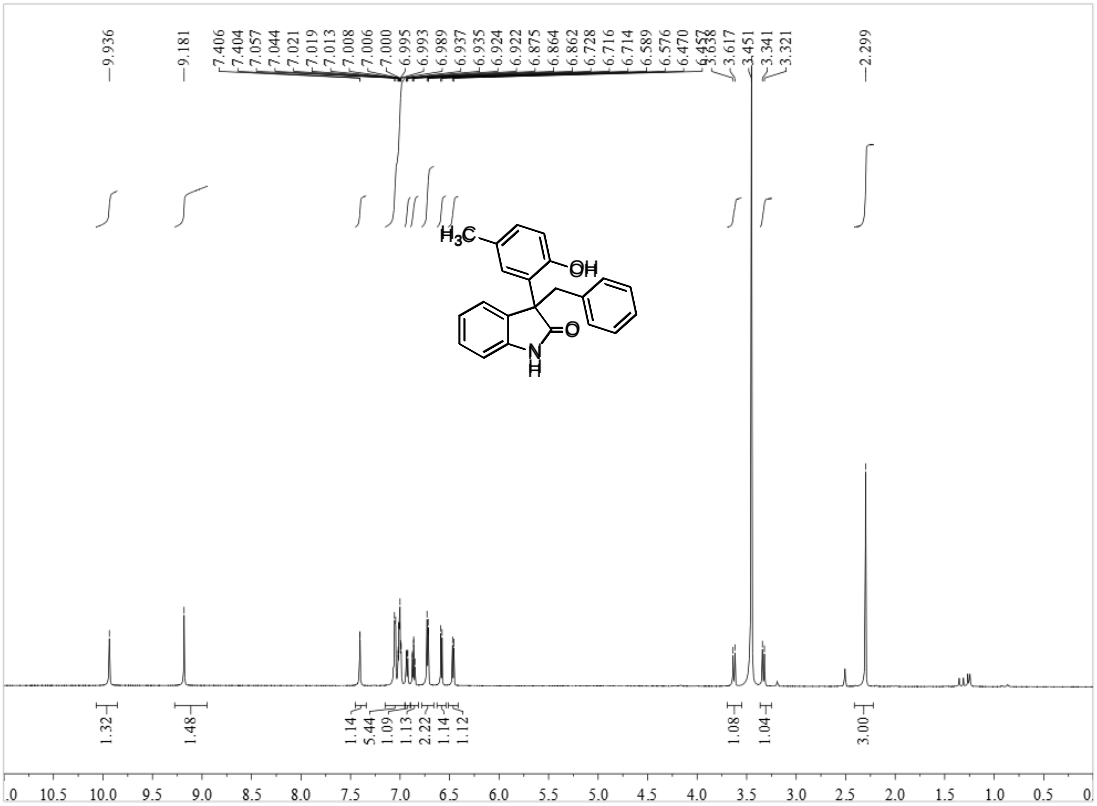


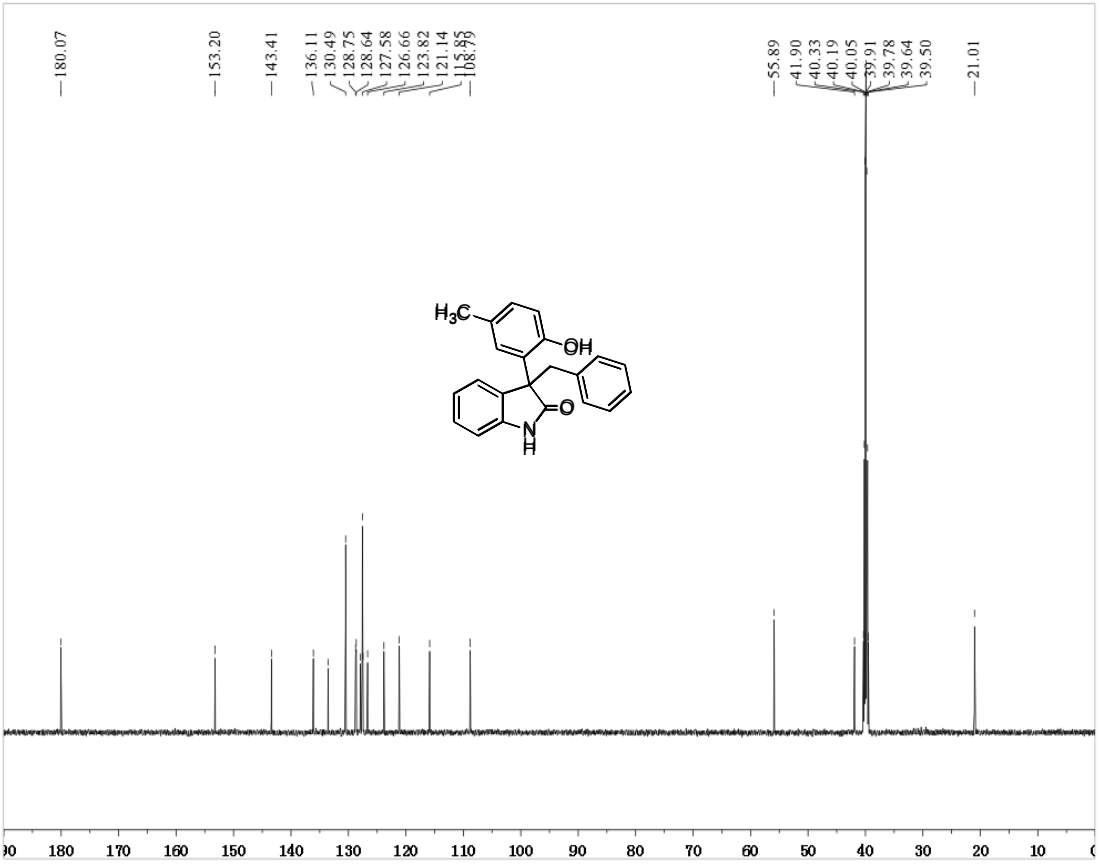
^{1}H and ^{13}C NMR of 7p



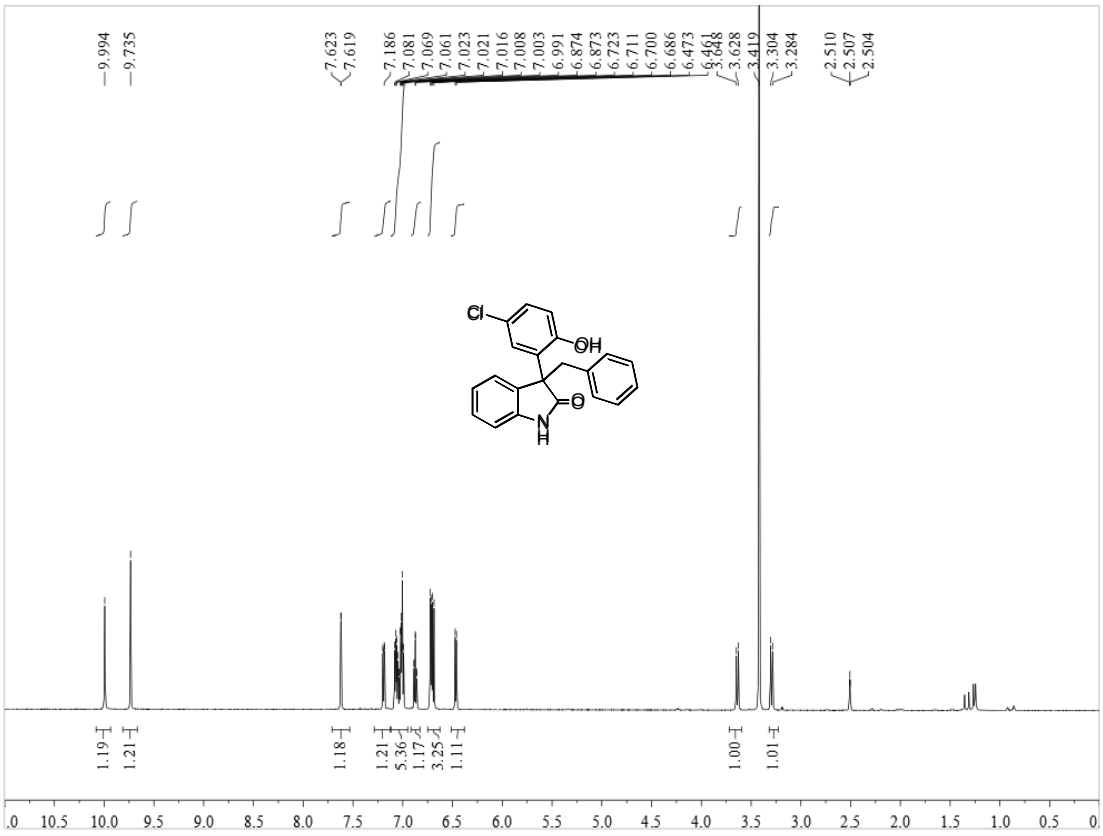


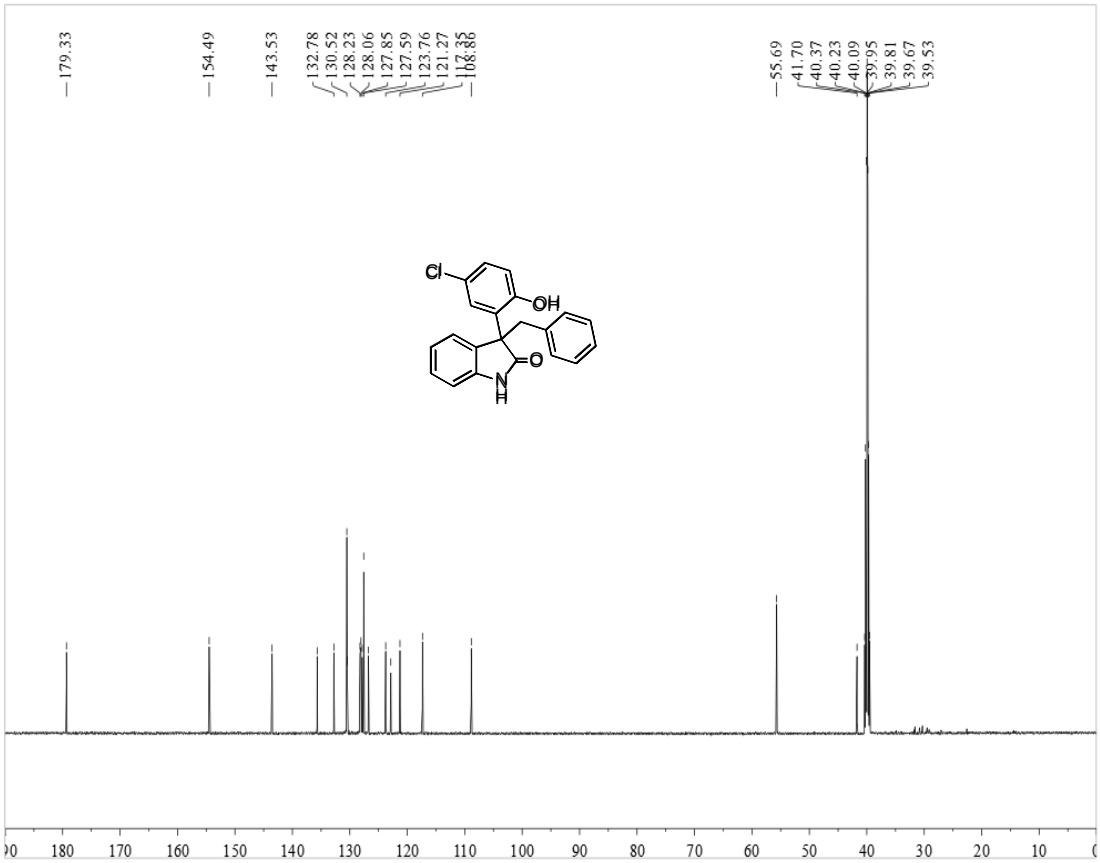
^{1}H and ^{13}C NMR of 9a



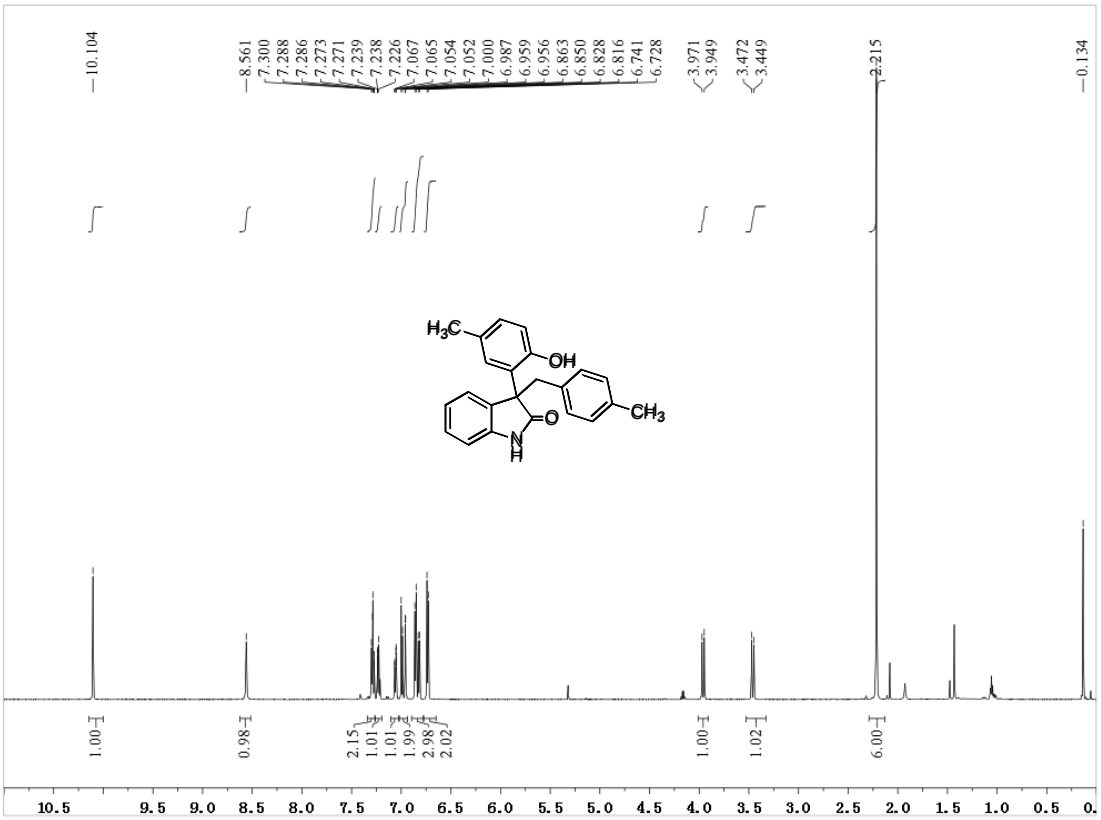


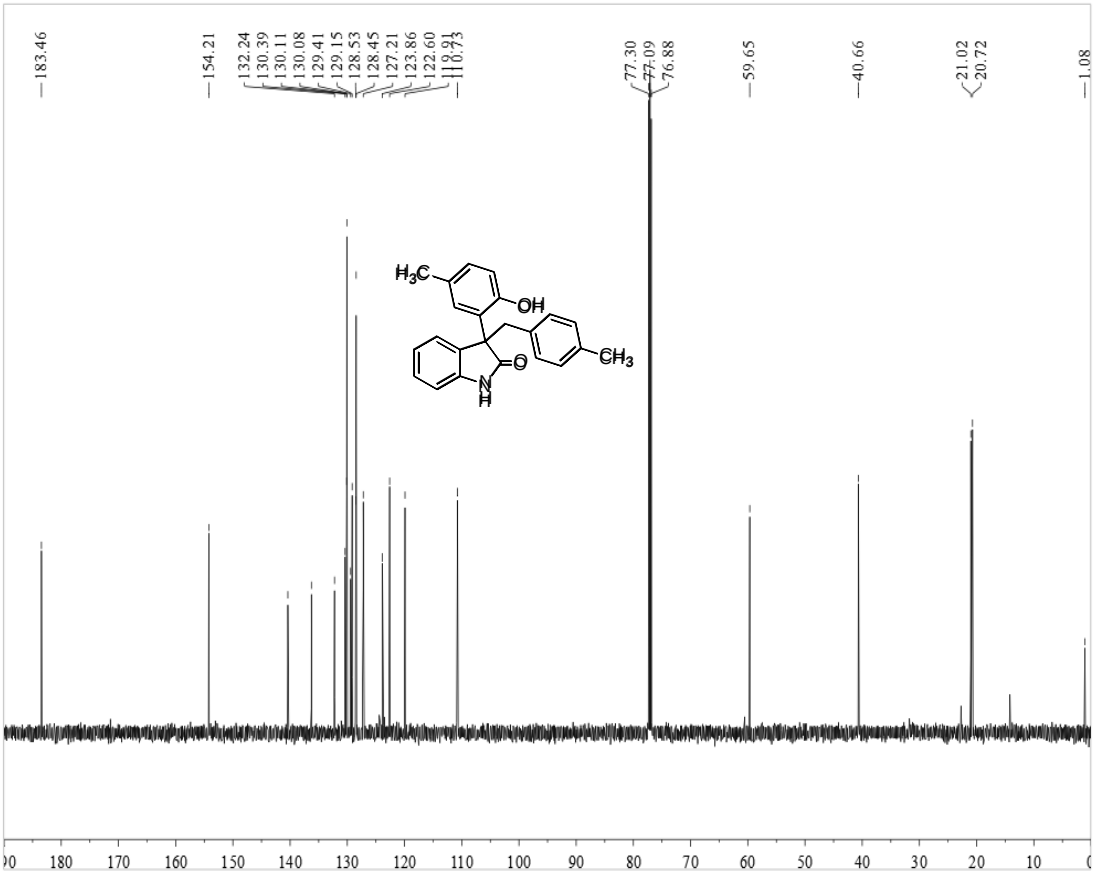
^{1}H and ^{13}C NMR of 9b



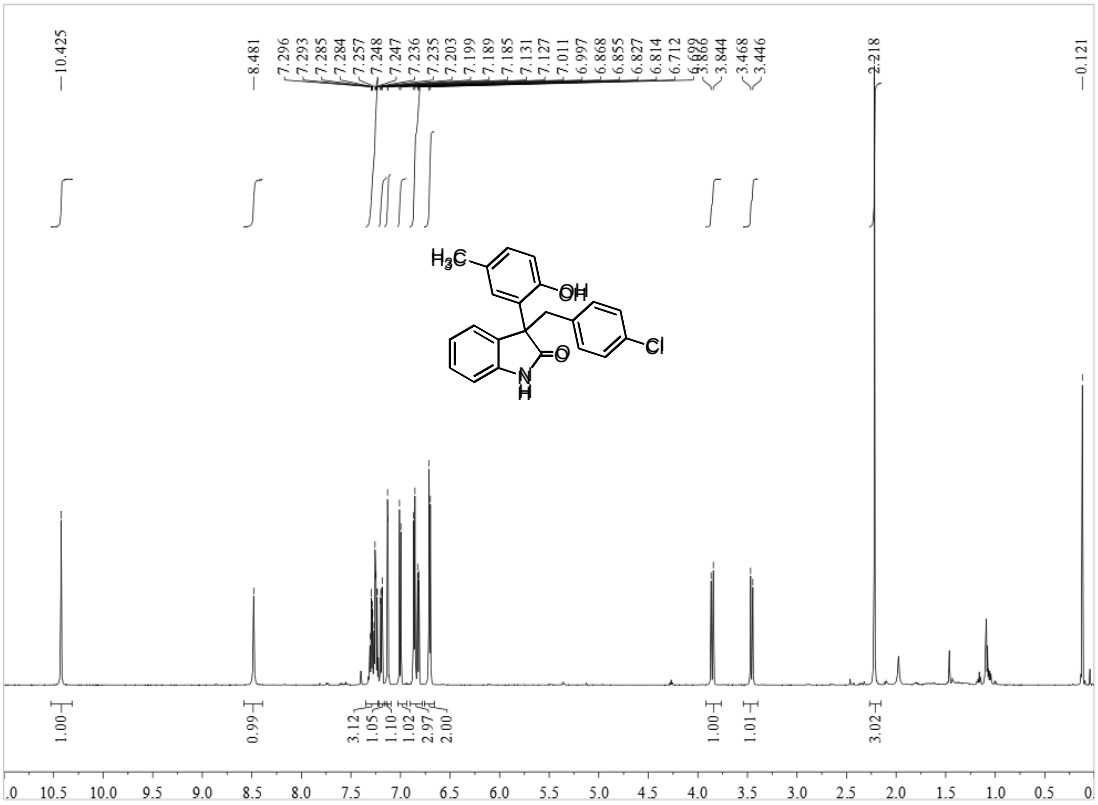


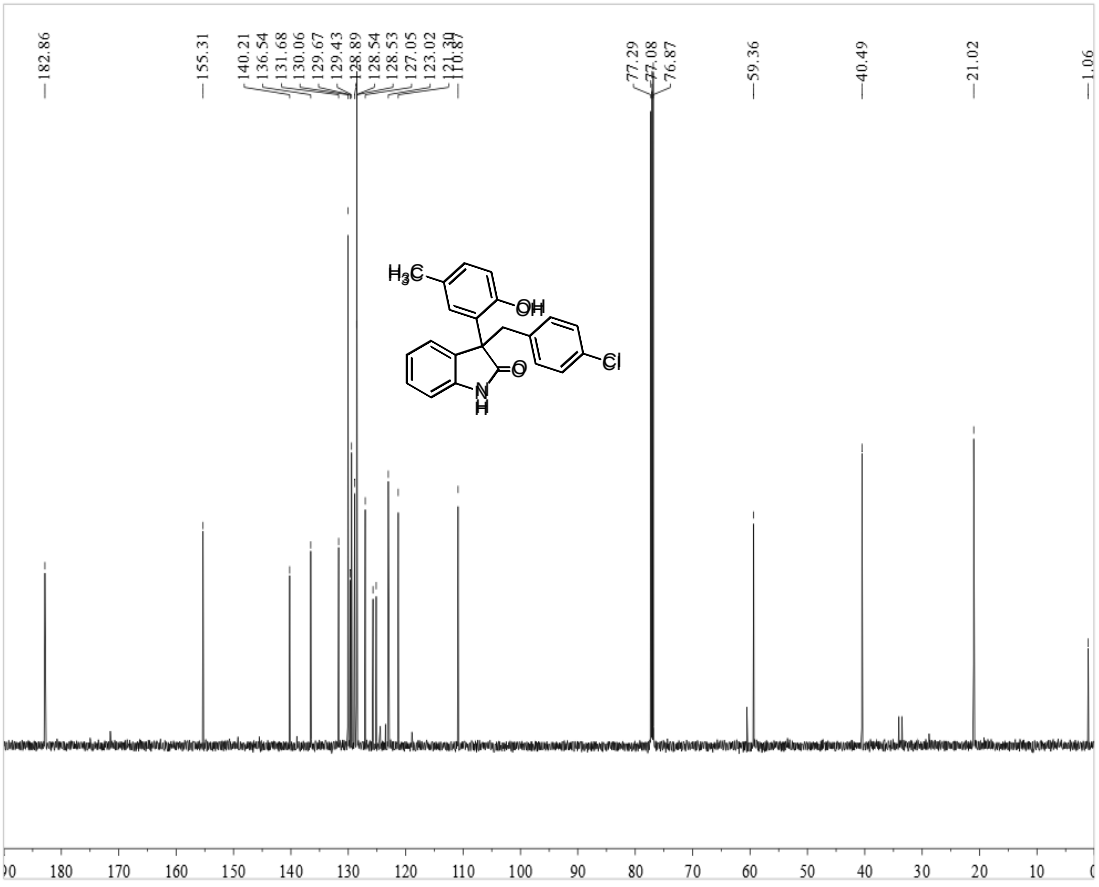
^{1}H and ^{13}C NMR of 9c



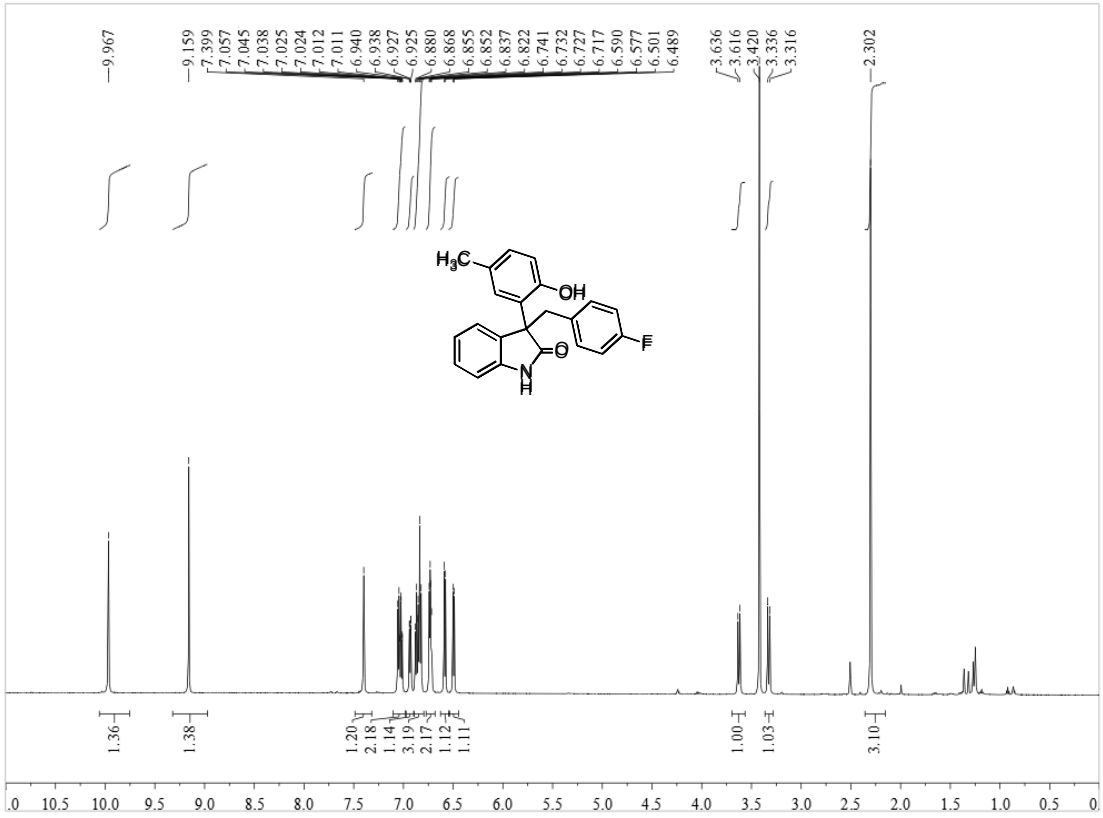


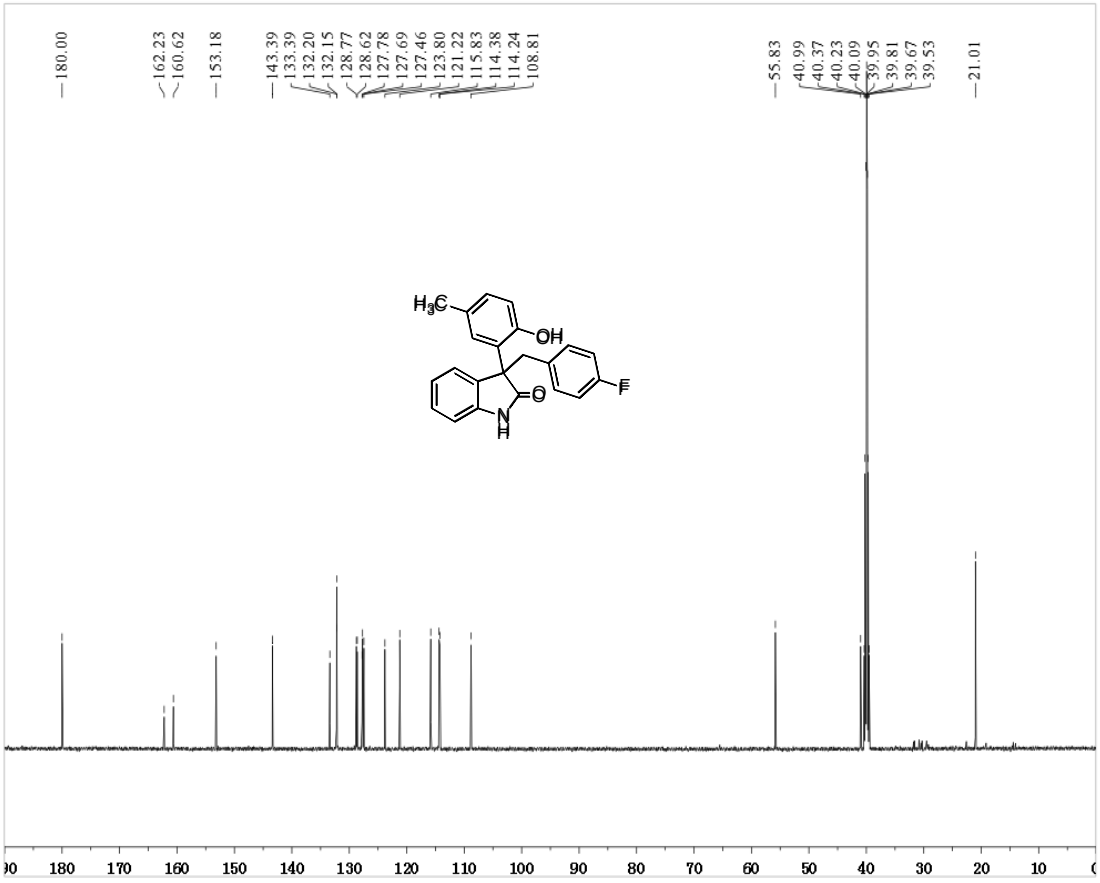
^{1}H and ^{13}C NMR of 9d



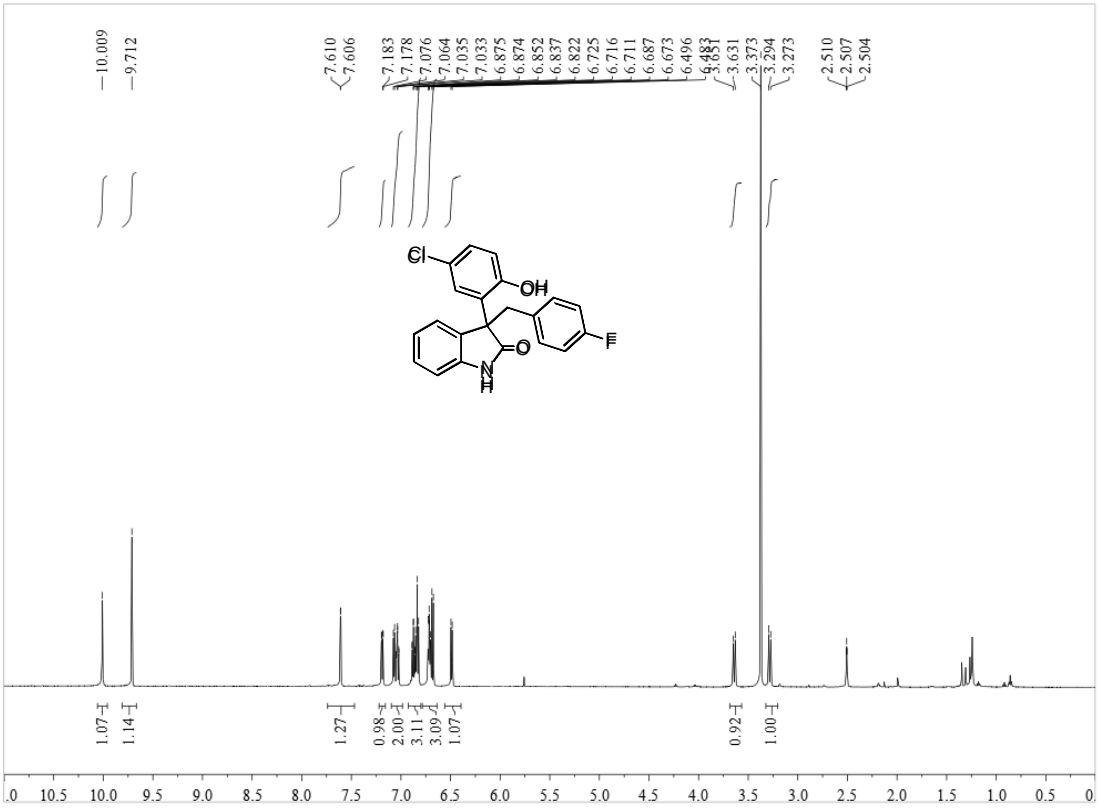


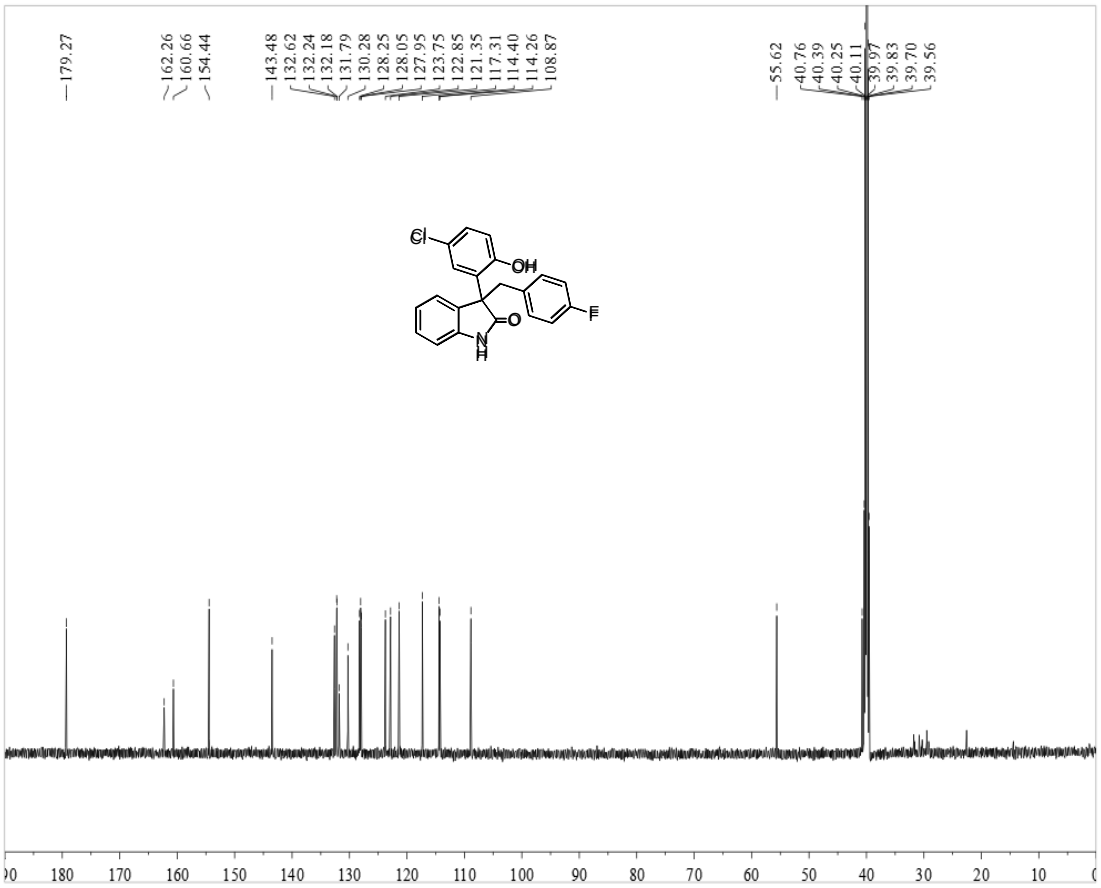
^{1}H and ^{13}C NMR of 9e



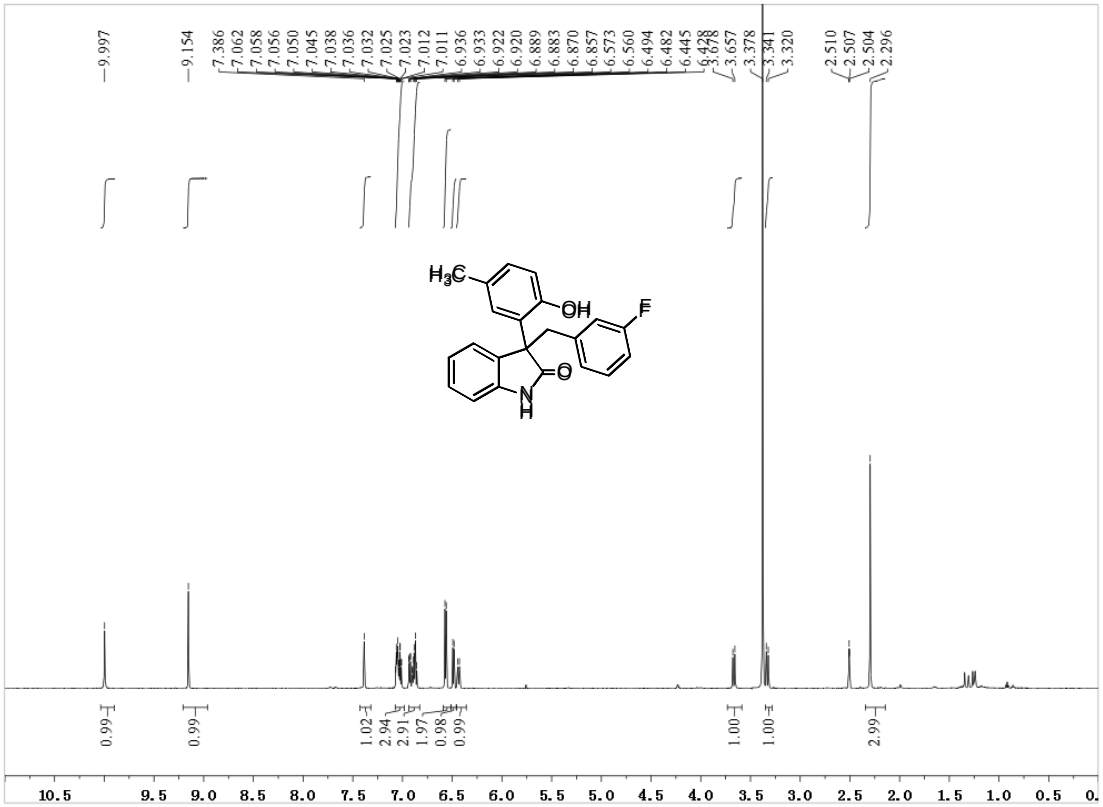


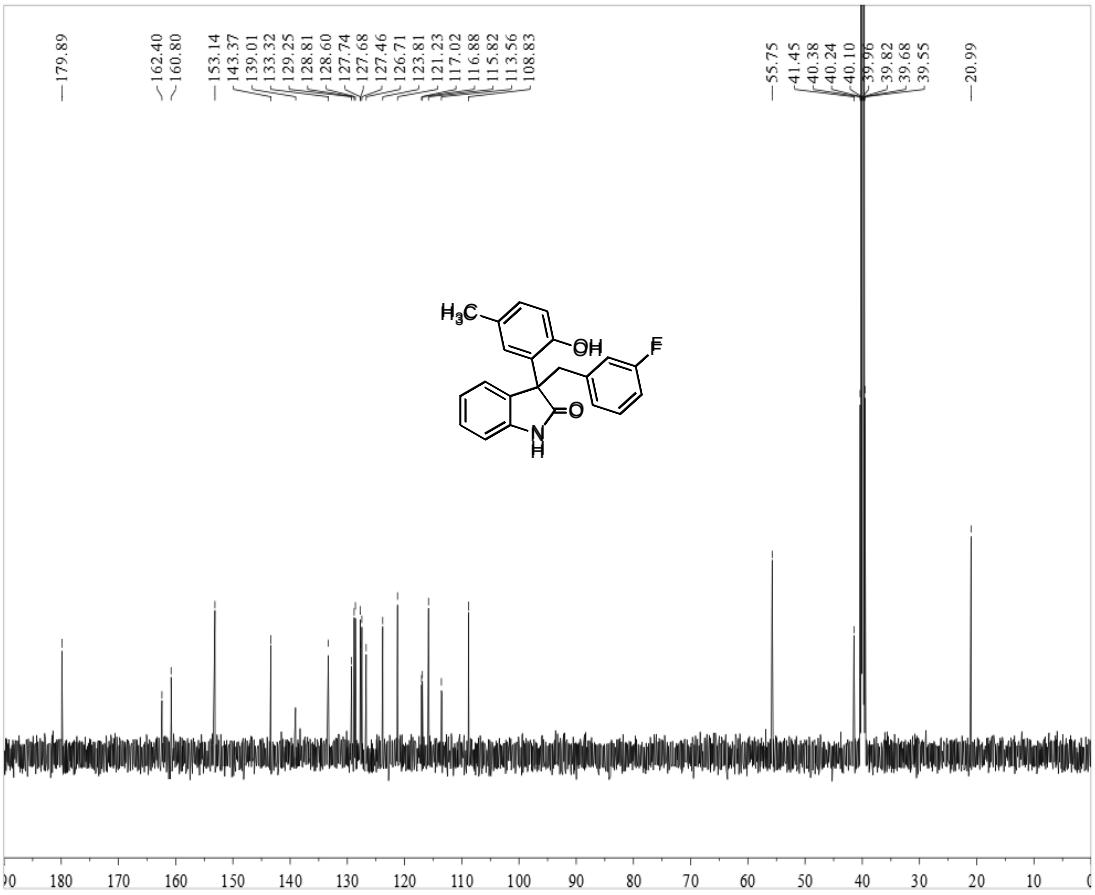
^{1}H and ^{13}C NMR of 9f



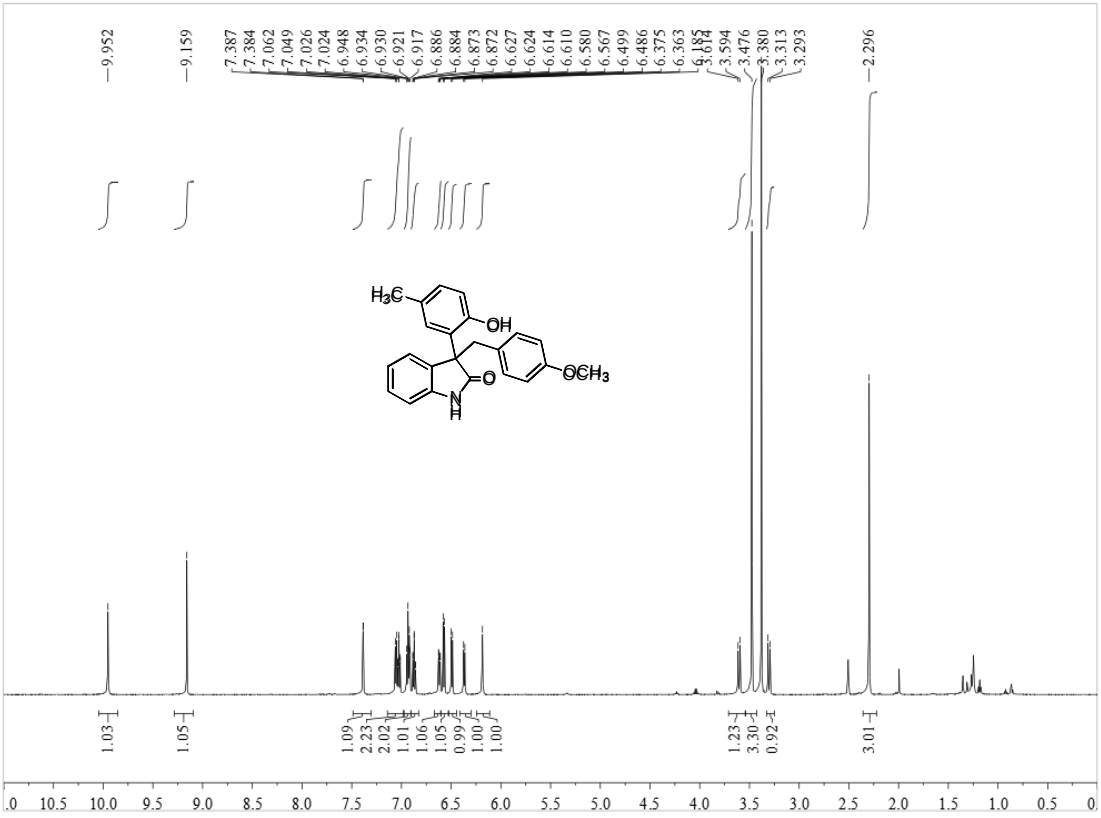


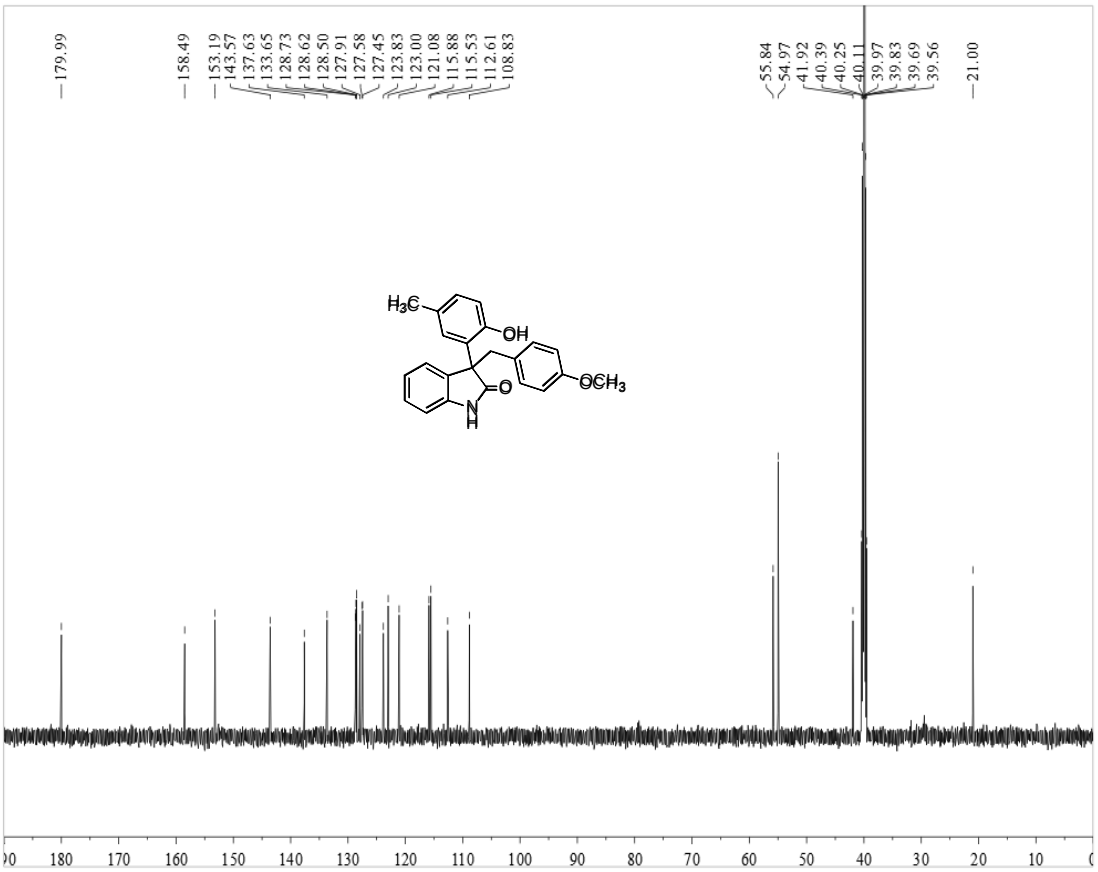
^{1}H and ^{13}C NMR of 9g



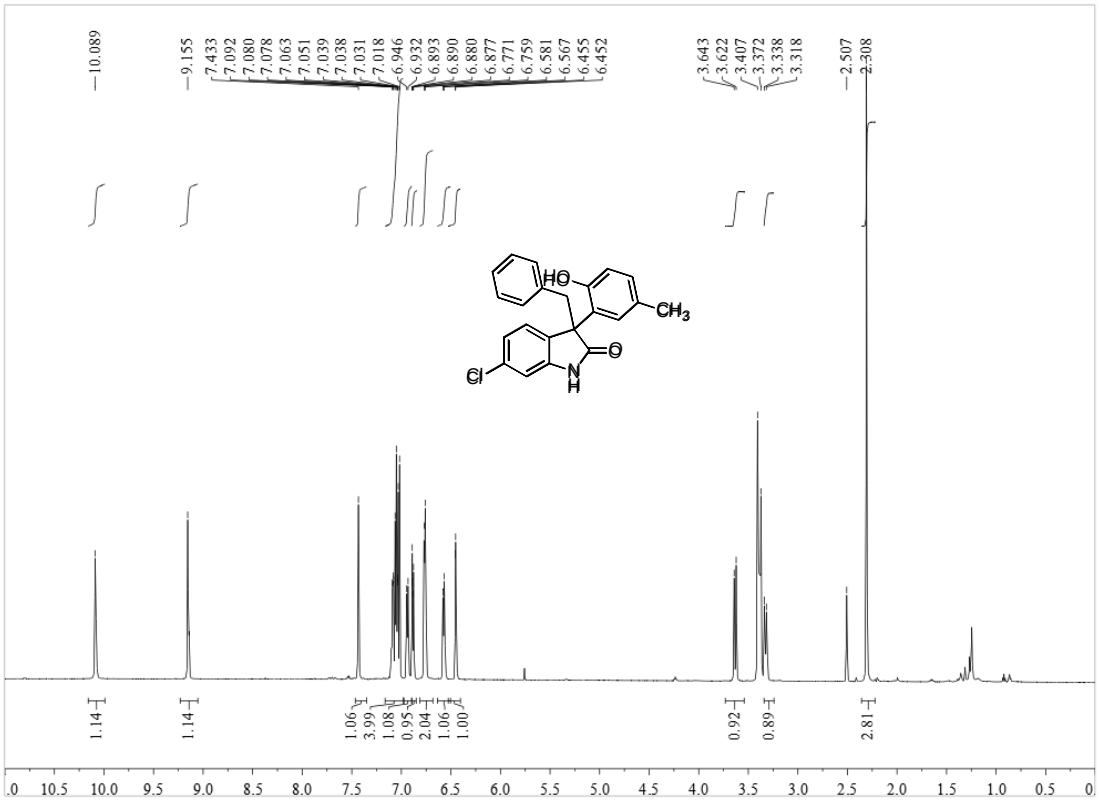


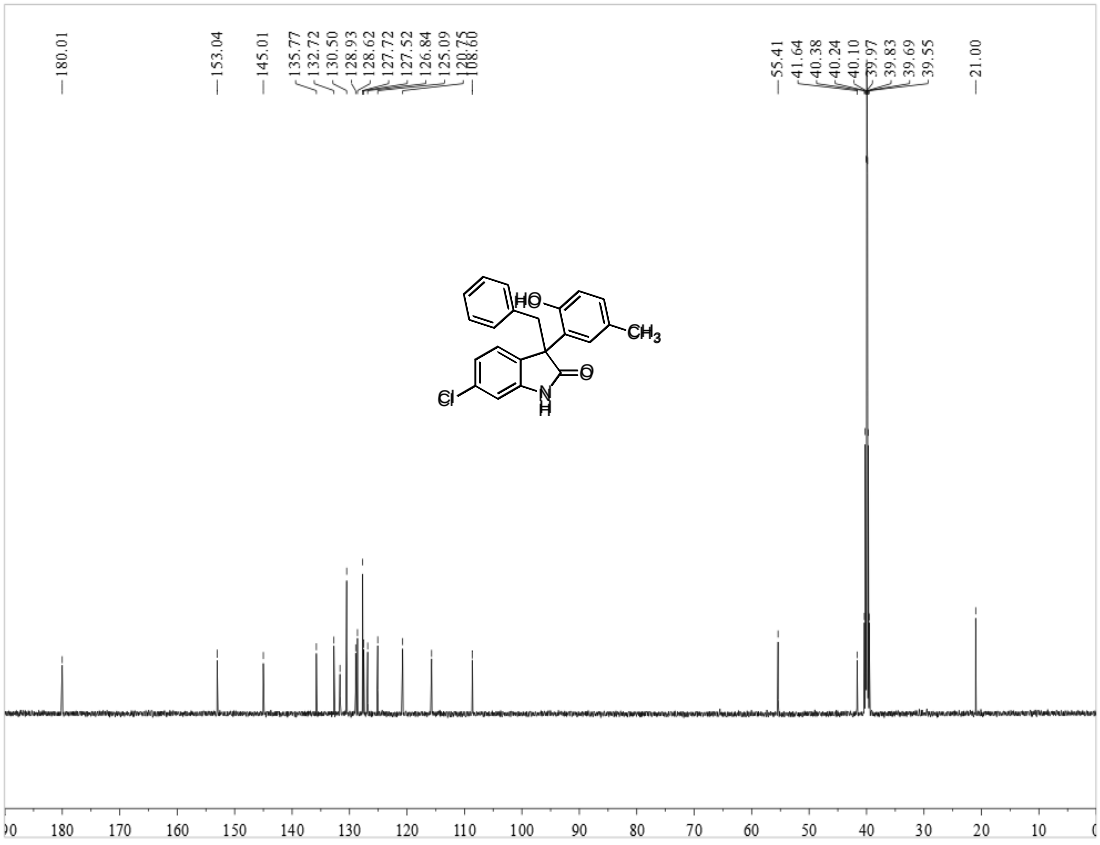
^{1}H and ^{13}C NMR of 9h



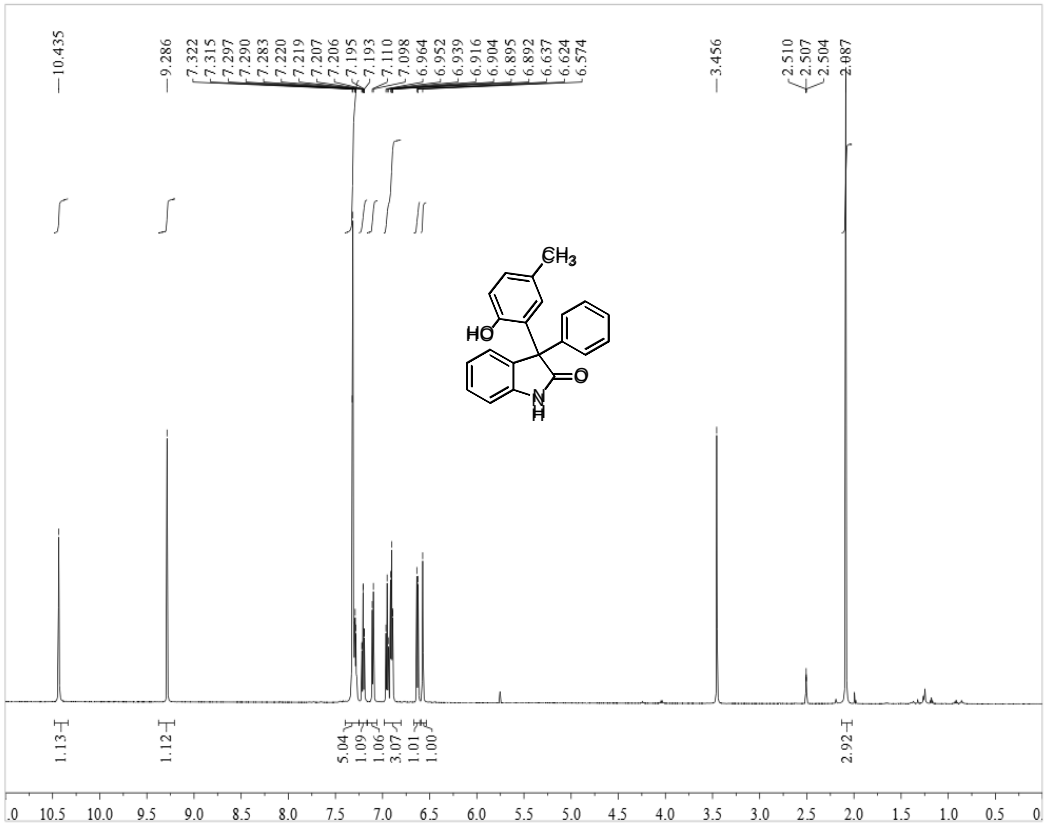


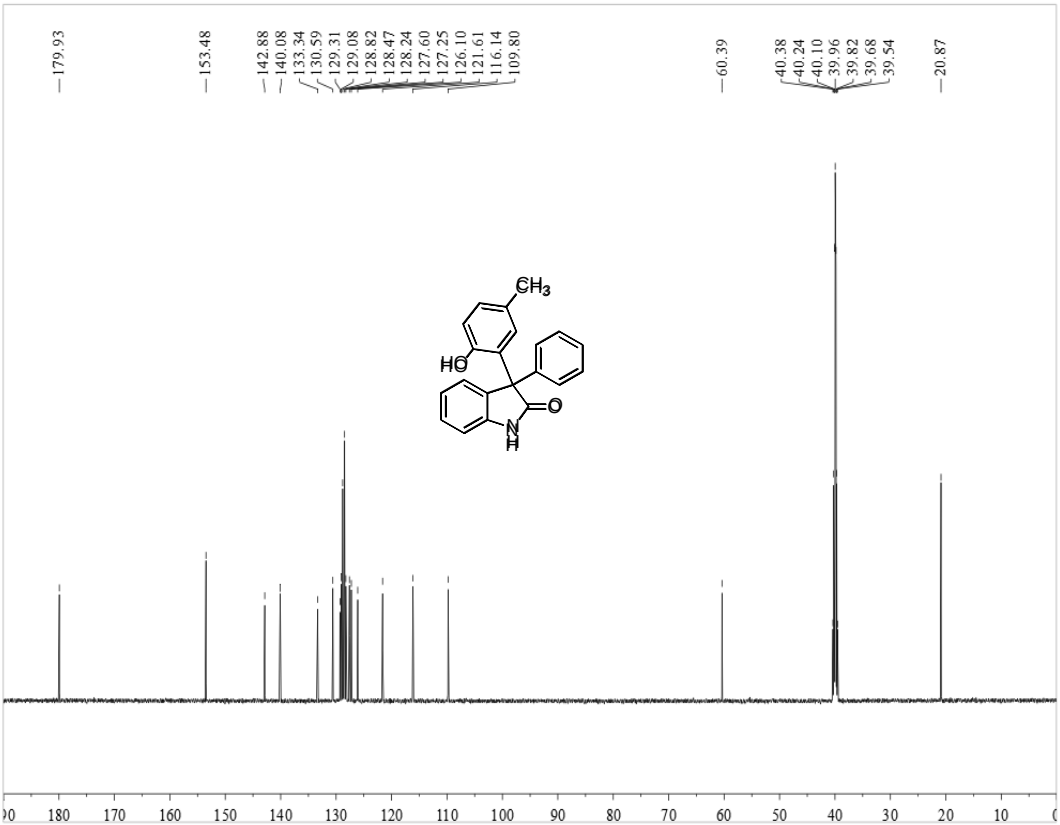
^{1}H and ^{13}C NMR of 9i



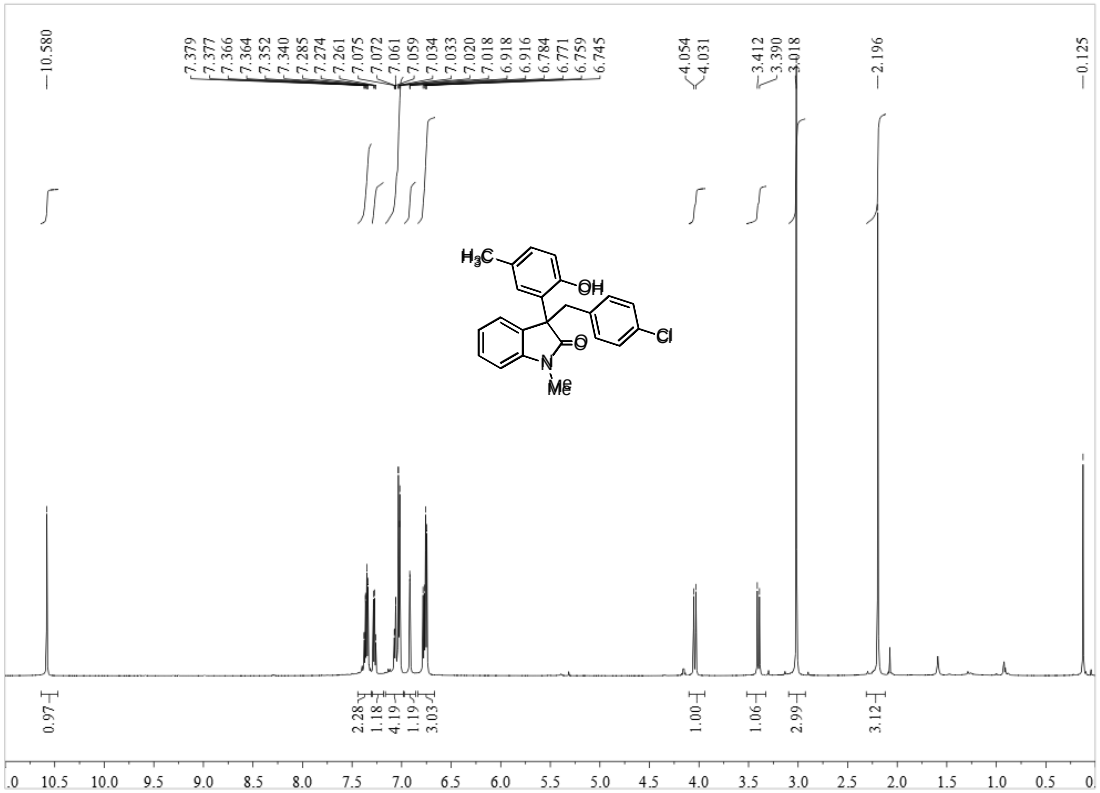


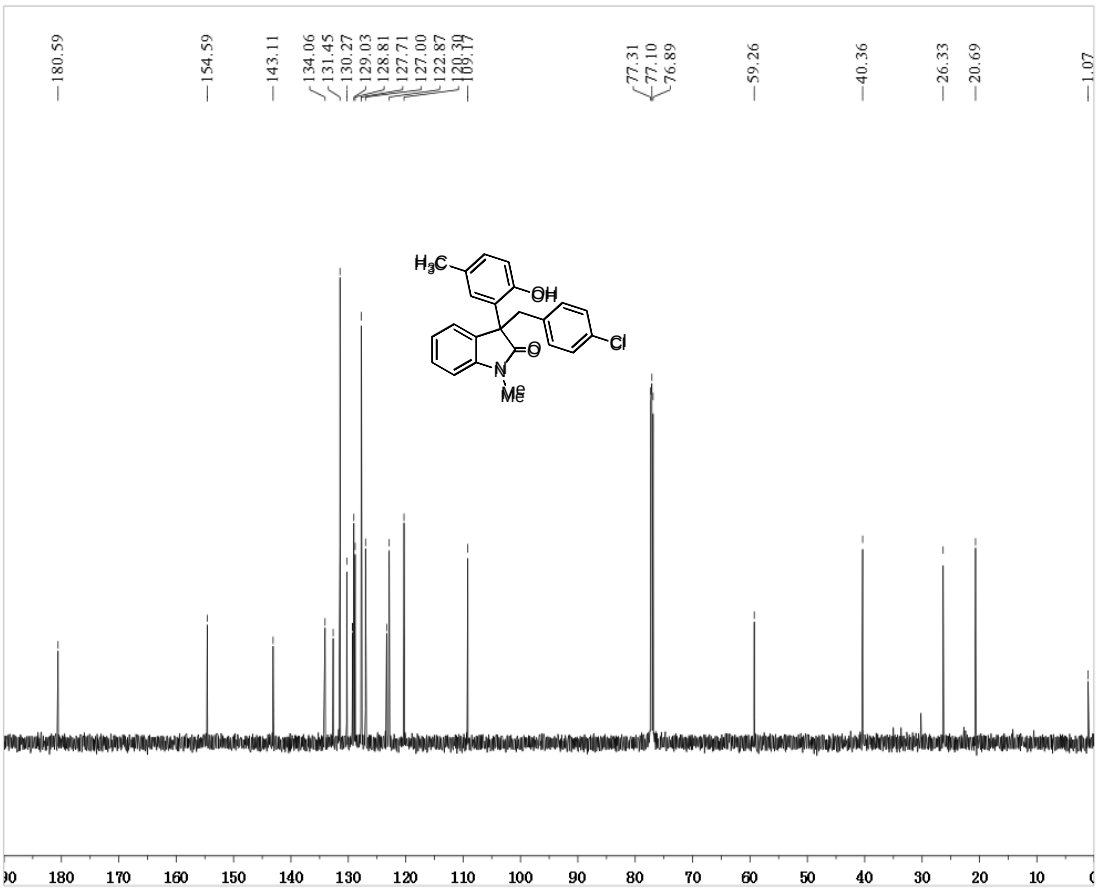
^{1}H and ^{13}C NMR of 9j



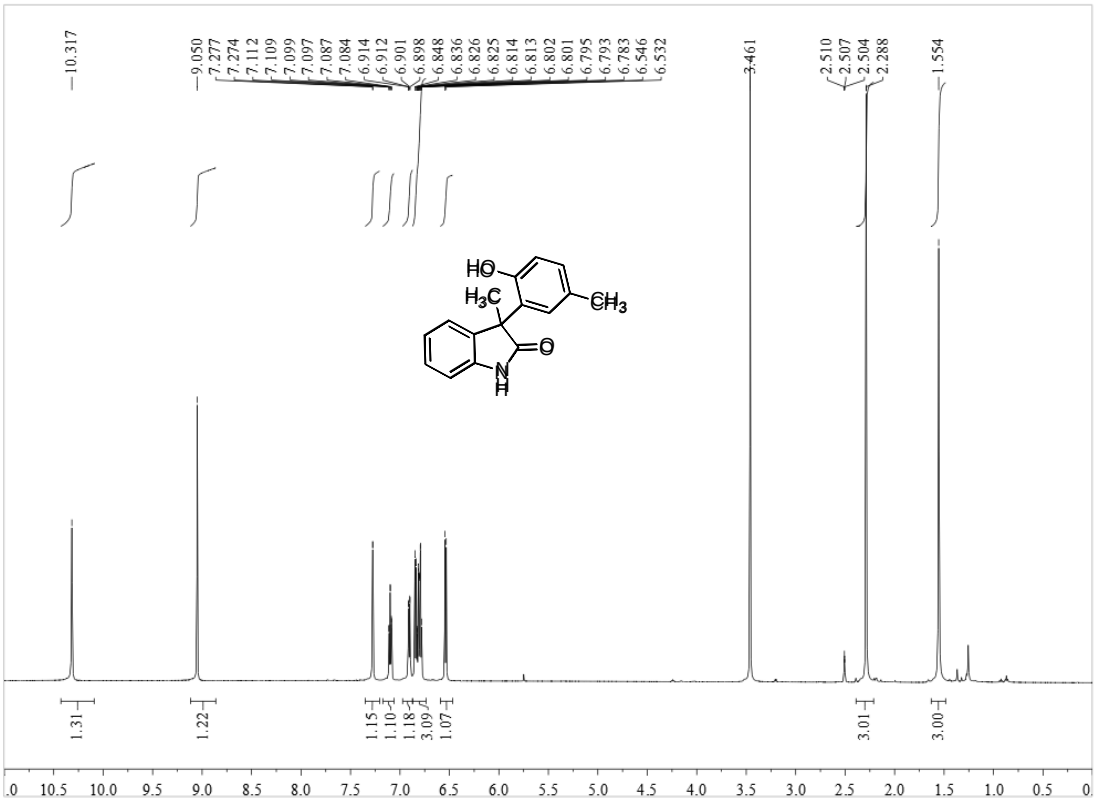


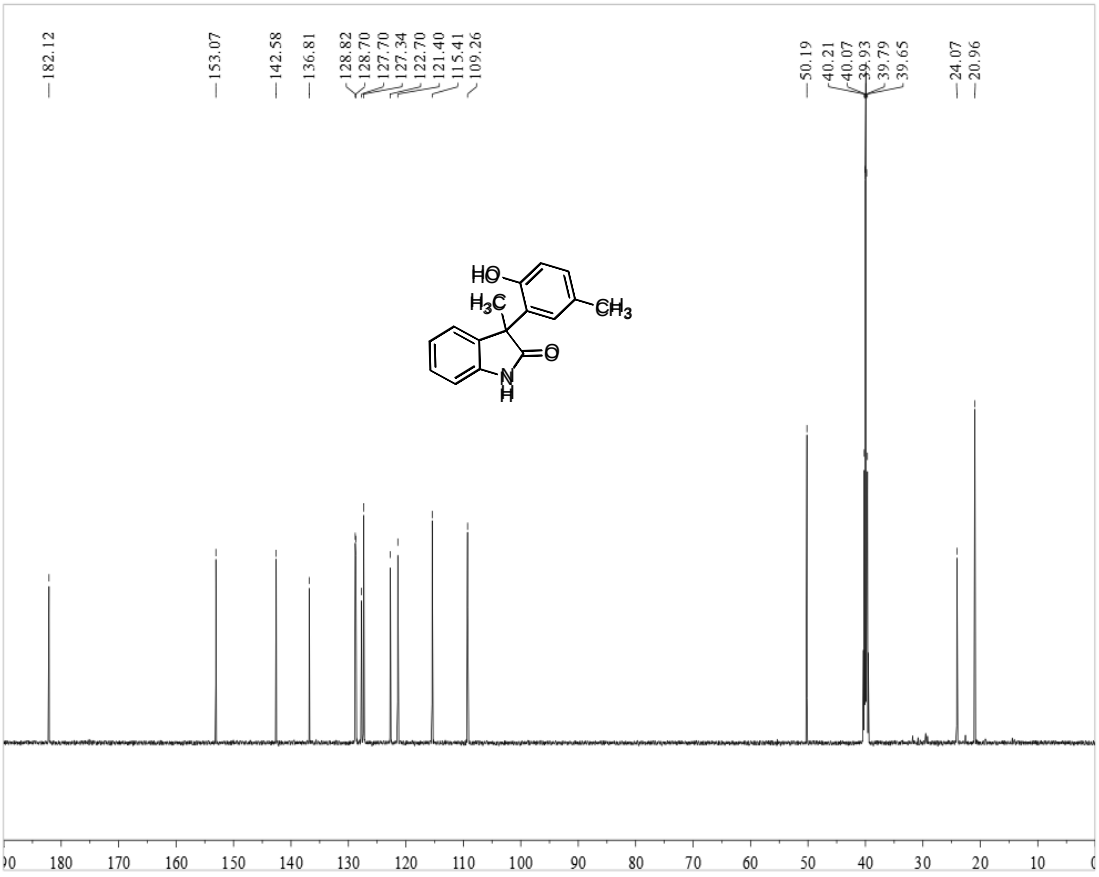
^{1}H and ^{13}C NMR of 9k



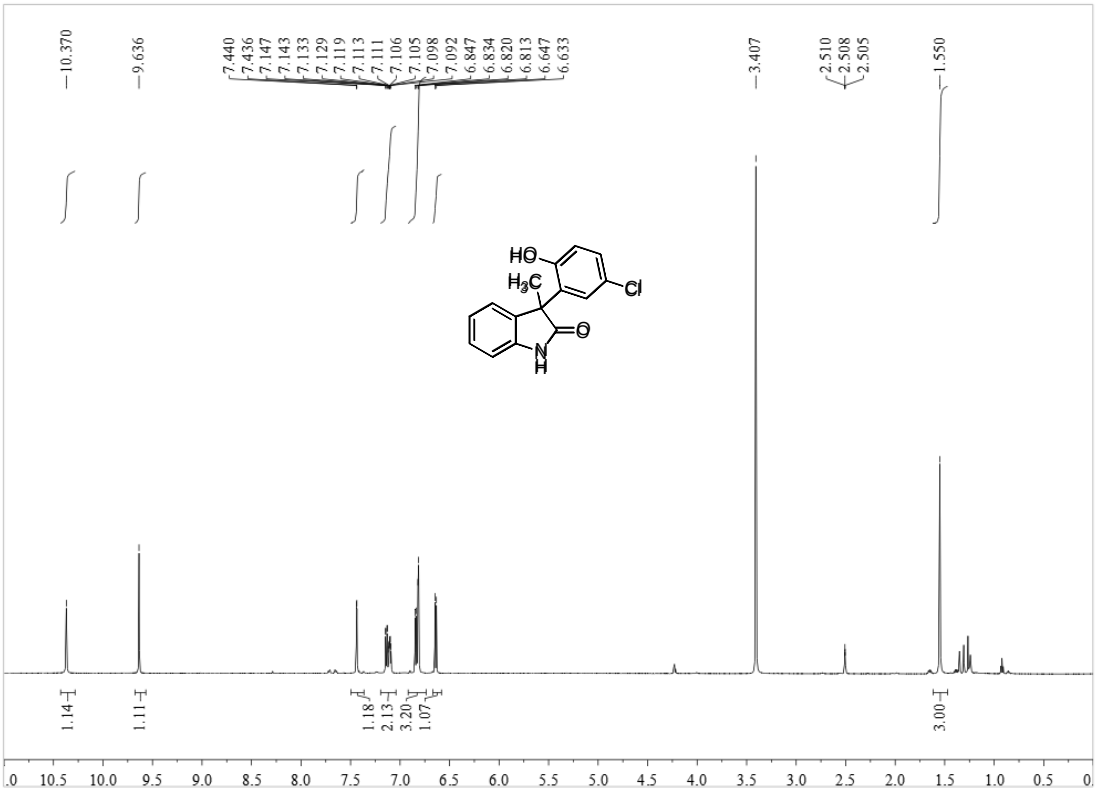


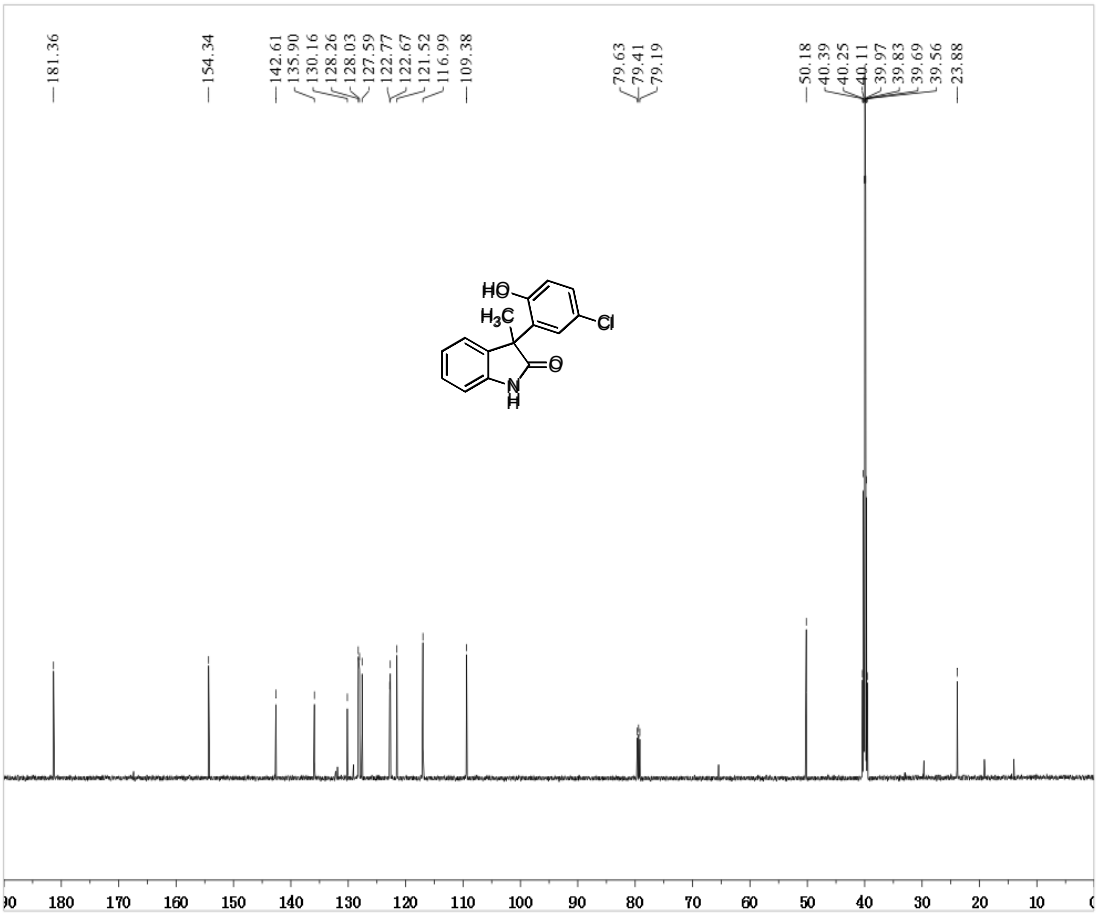
^{1}H and ^{13}C NMR of 9l



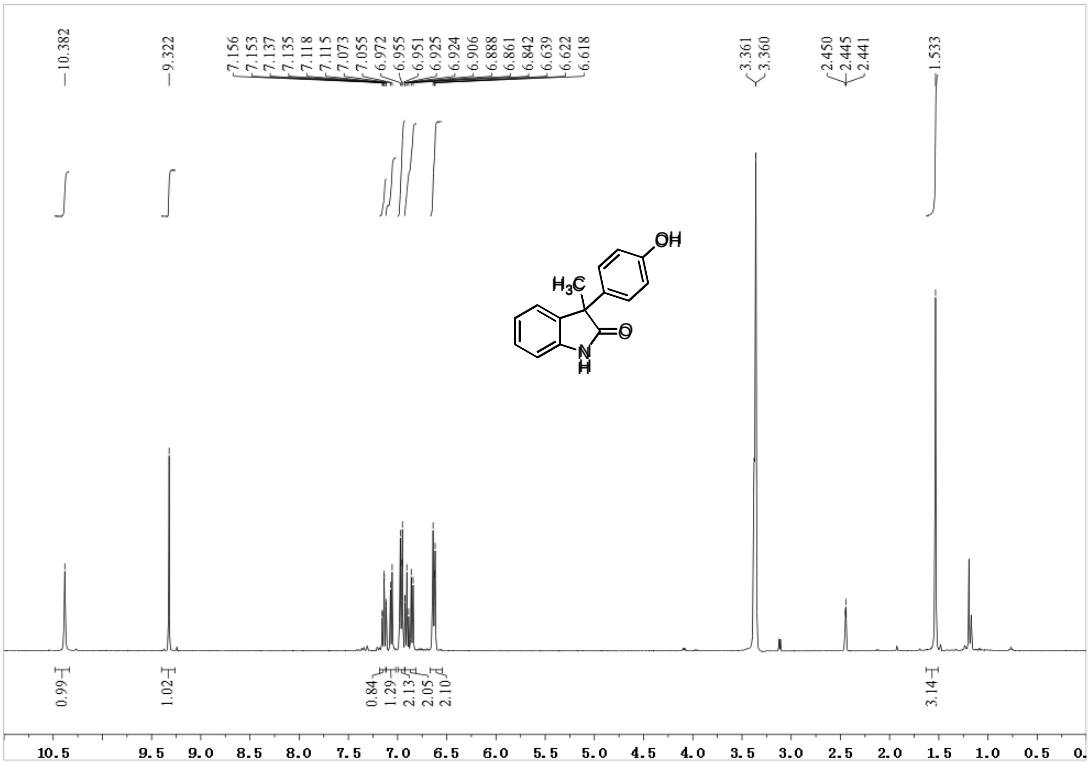


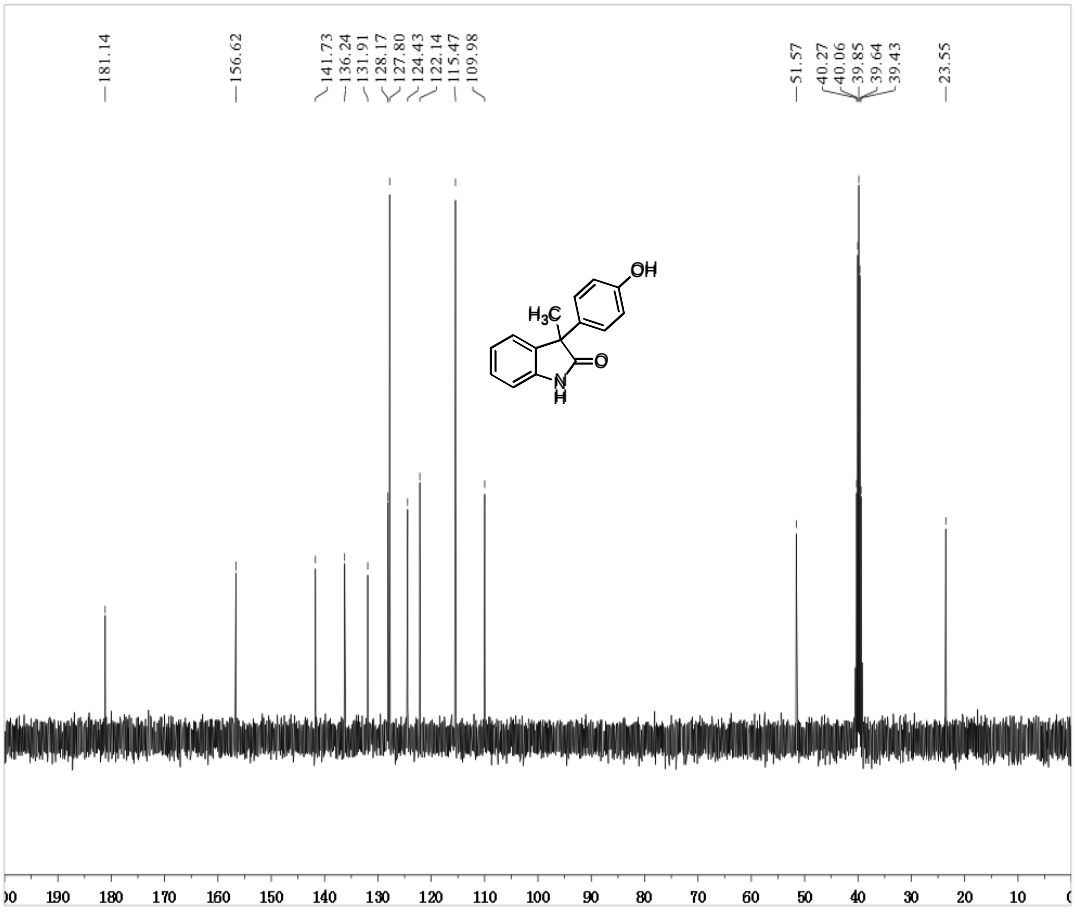
^{1}H and ^{13}C NMR of 9m



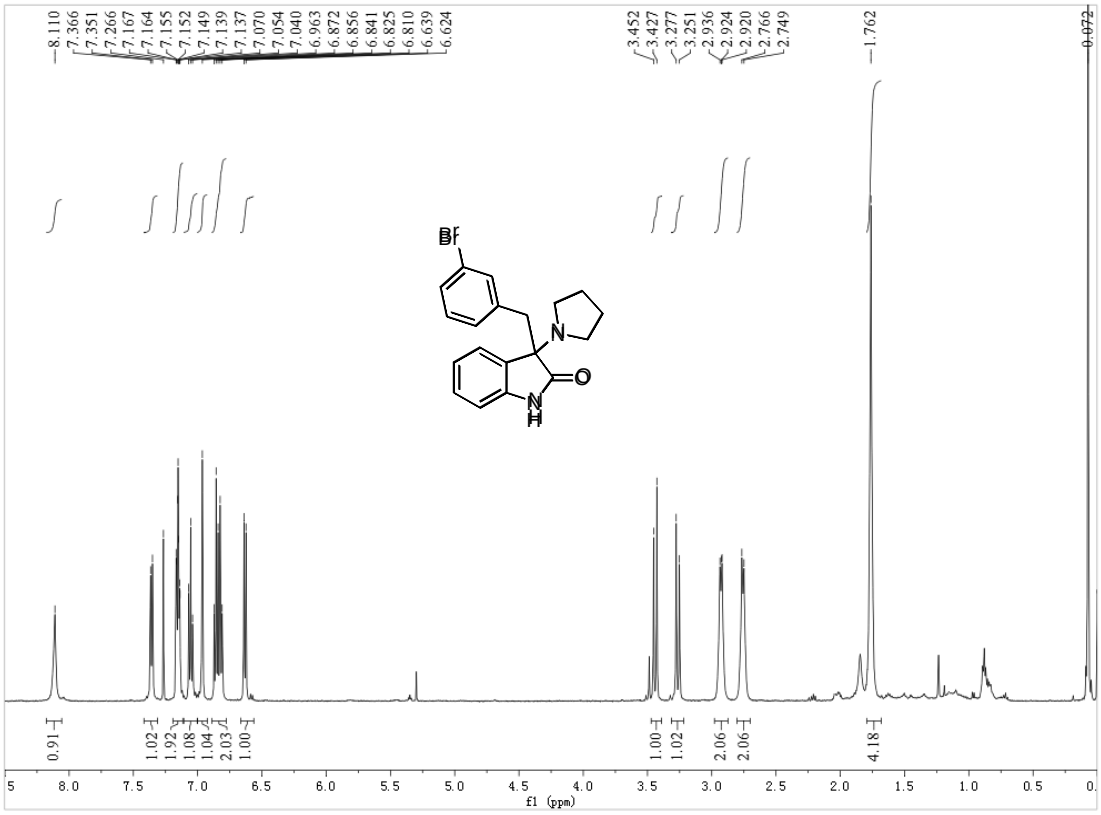


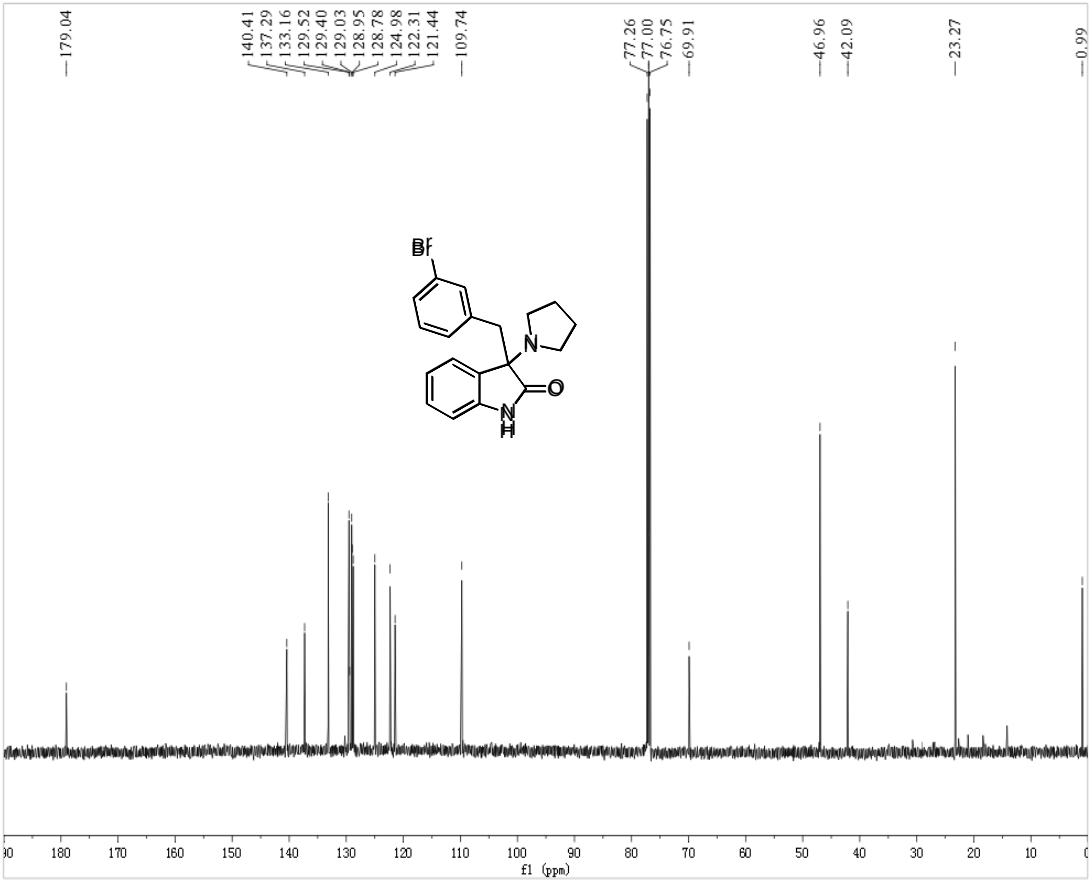
^{1}H and ^{13}C NMR of 9n



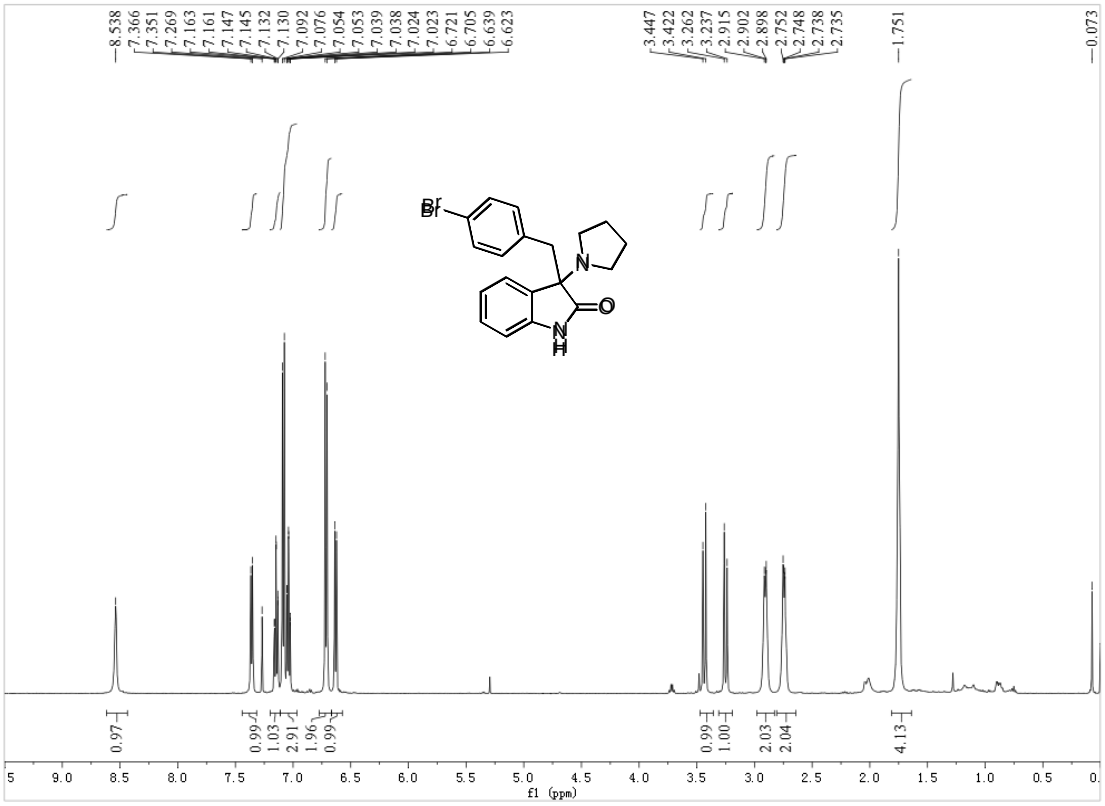


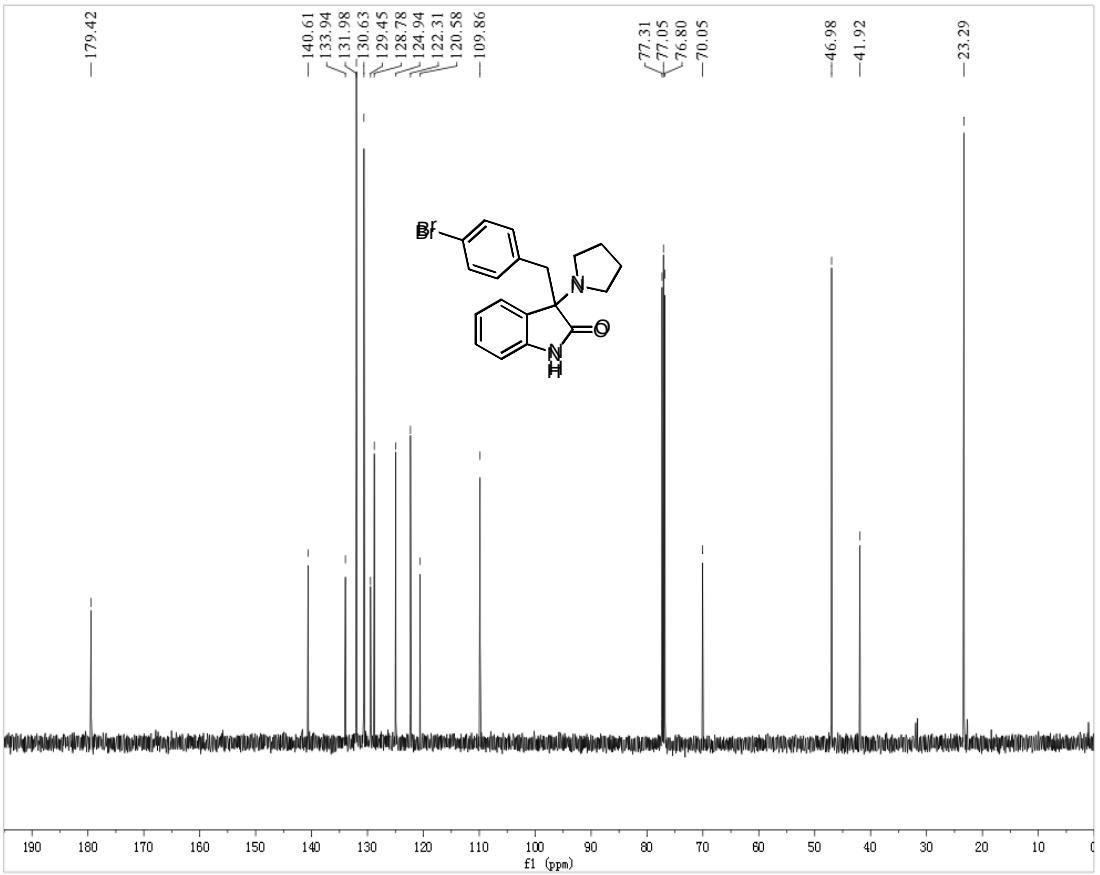
^{1}H and ^{13}C NMR of 11a



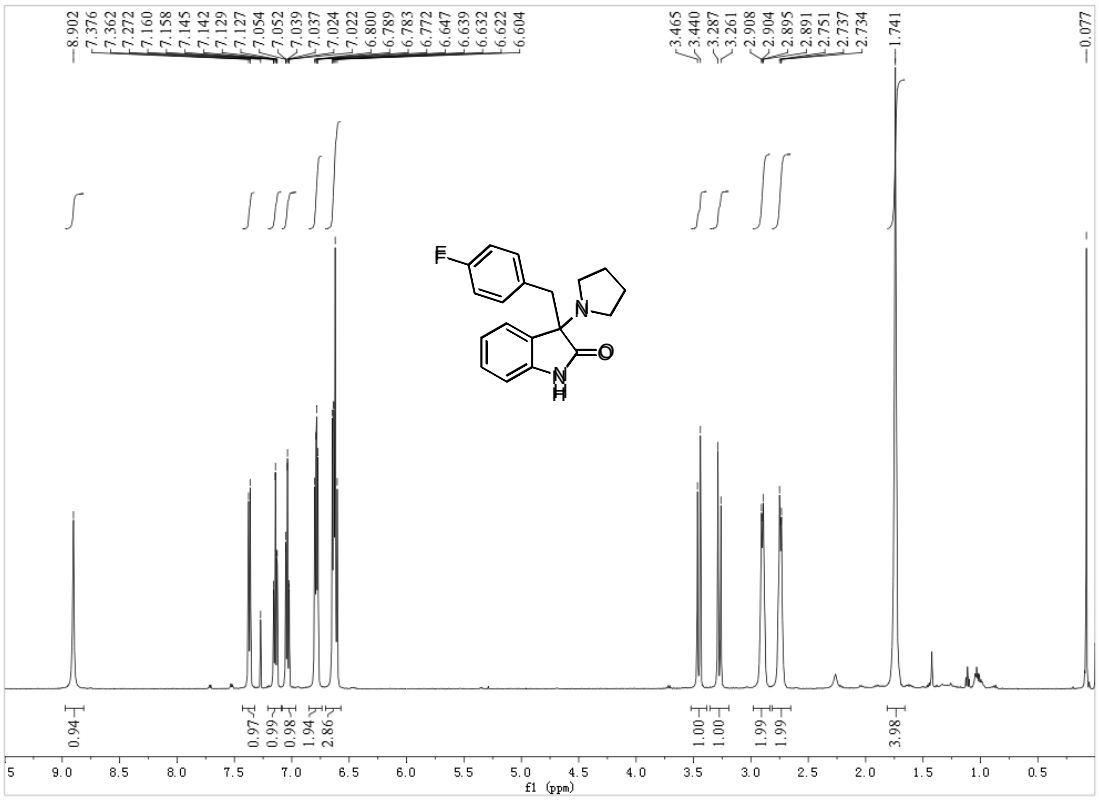


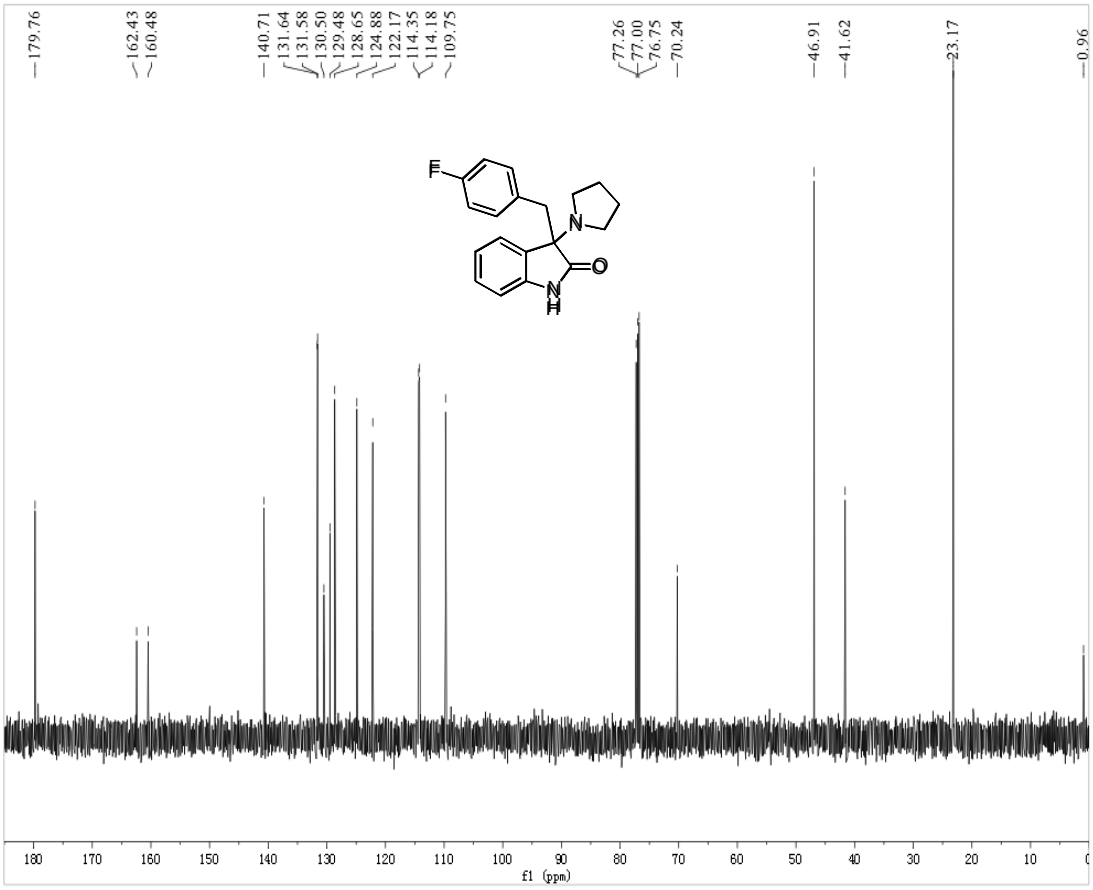
^{1}H and ^{13}C NMR of 11b



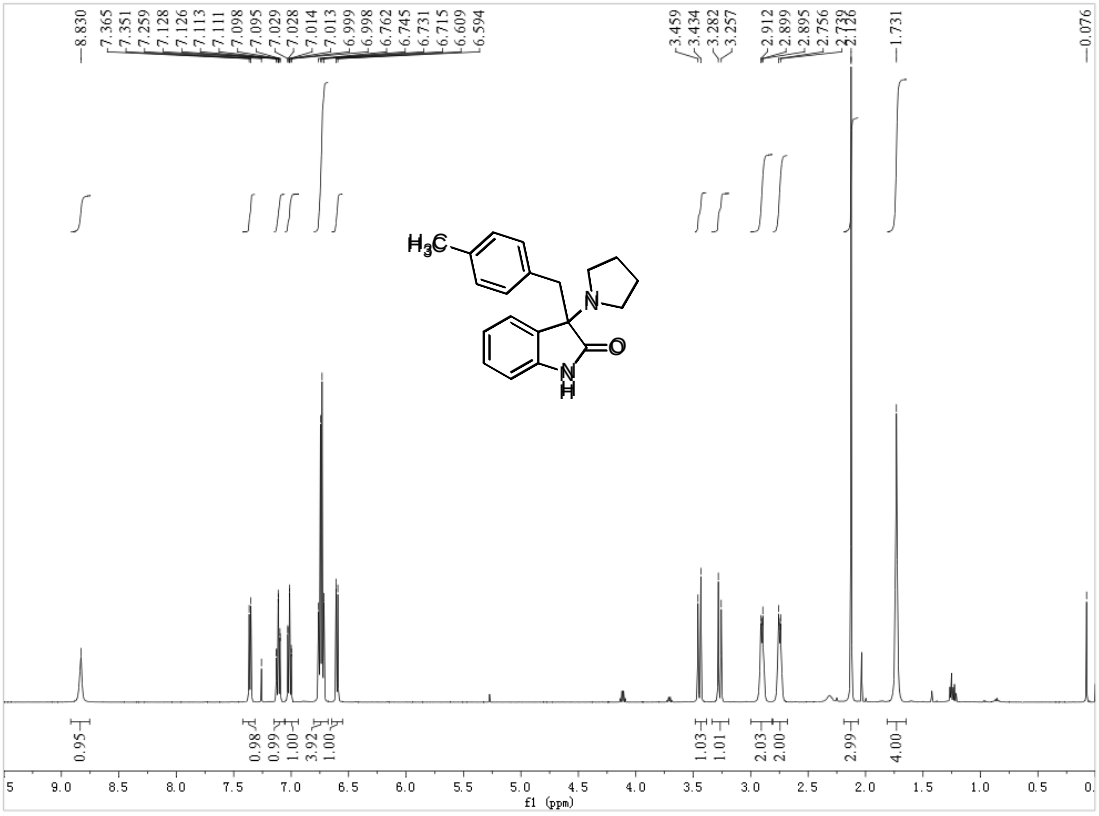


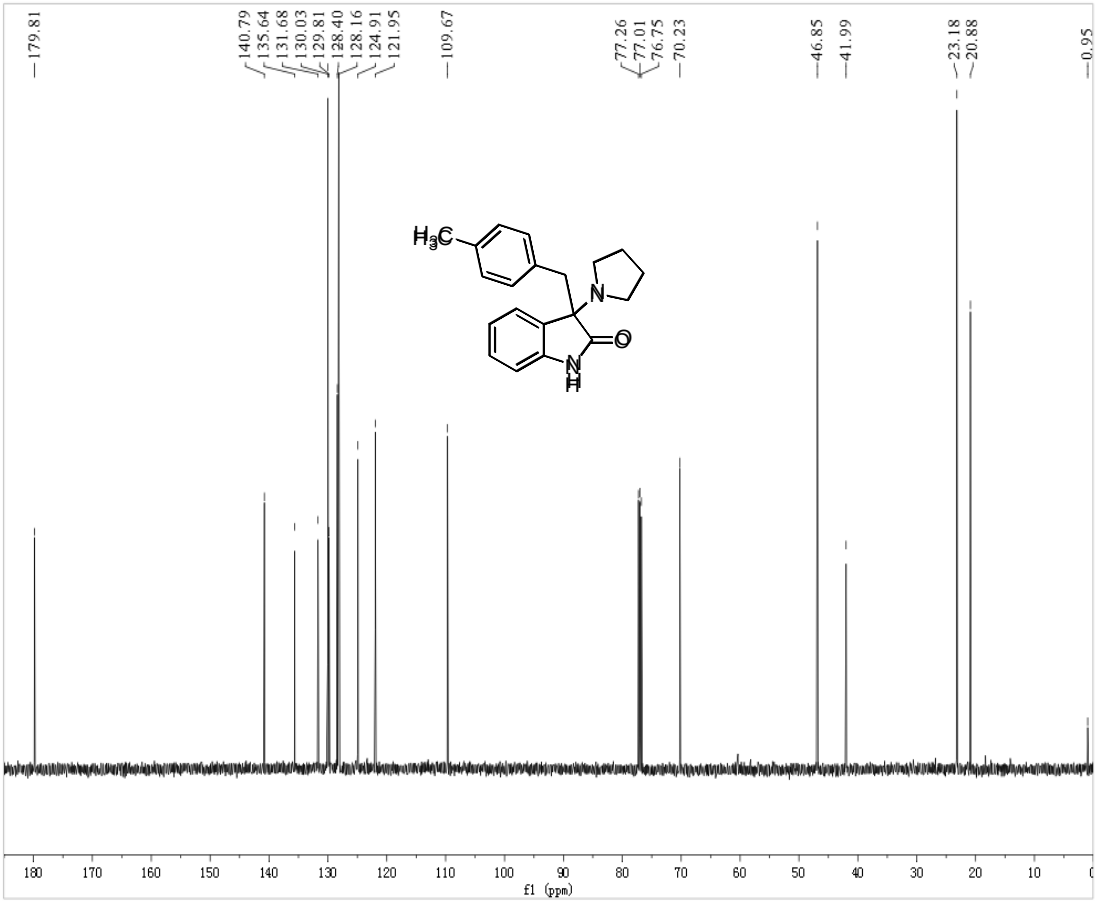
^{1}H and ^{13}C NMR of 11c



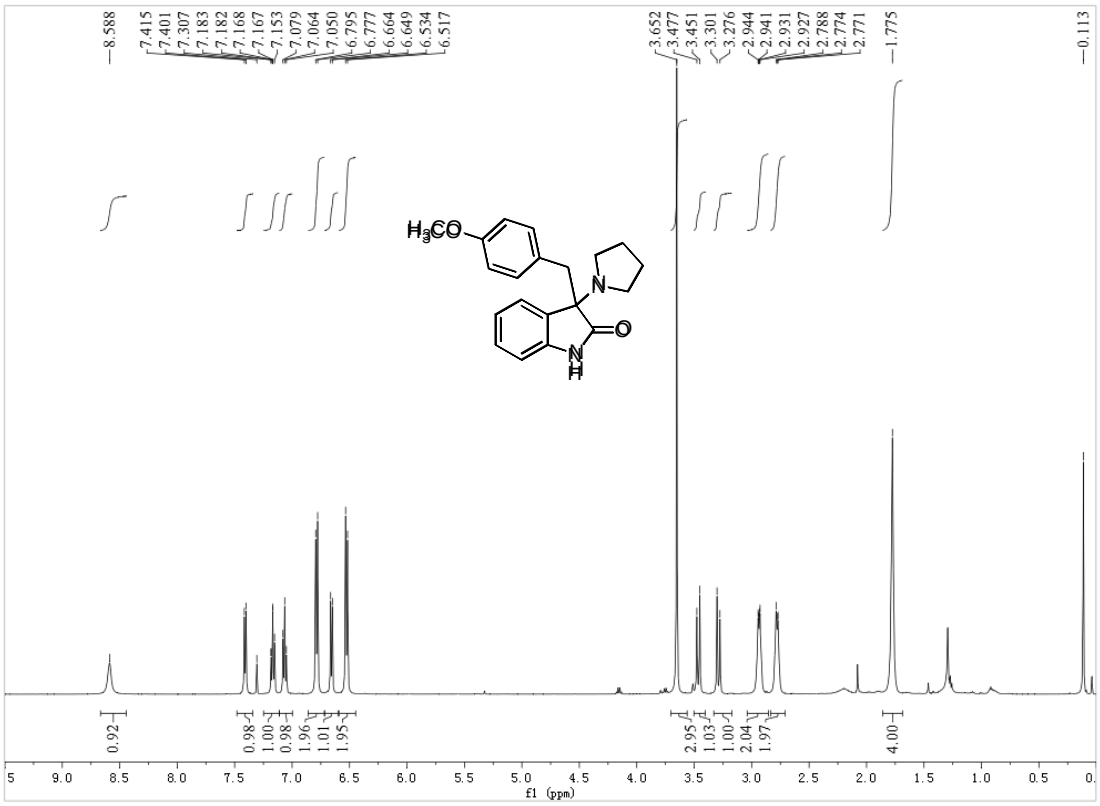


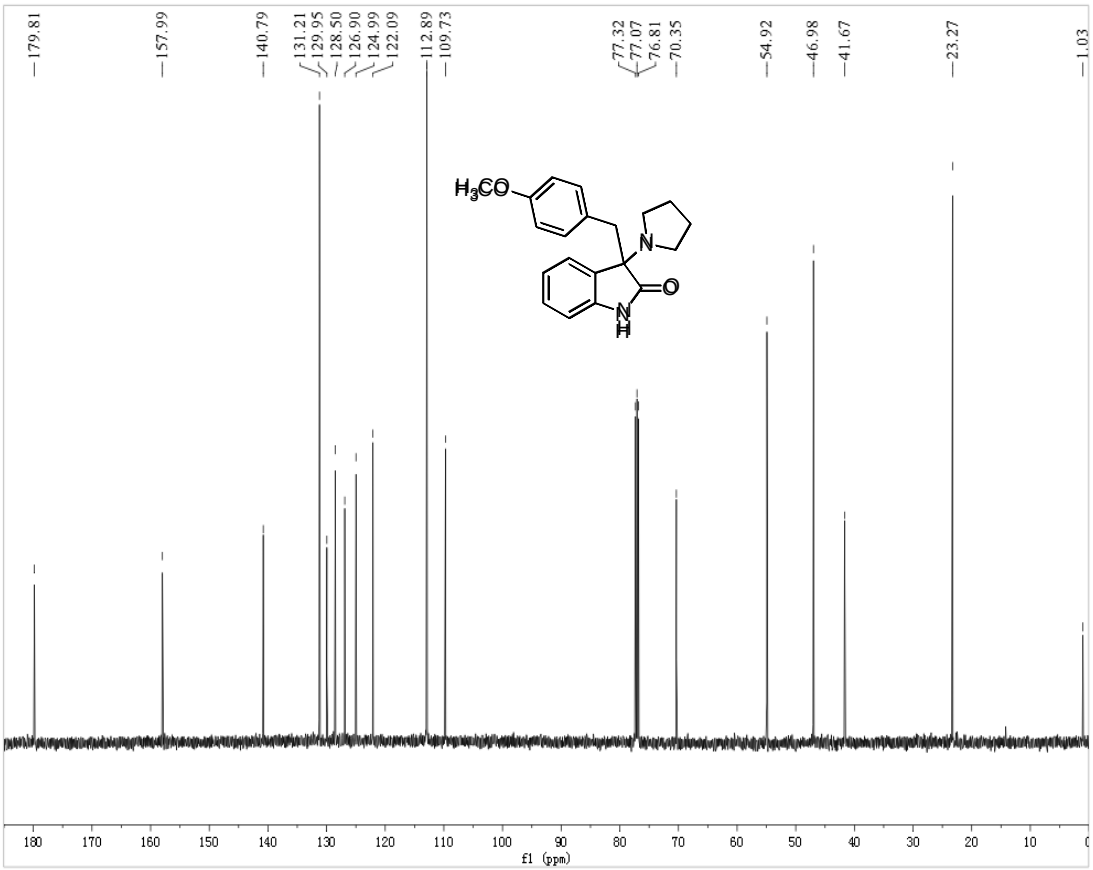
^{1}H and ^{13}C NMR of 11d



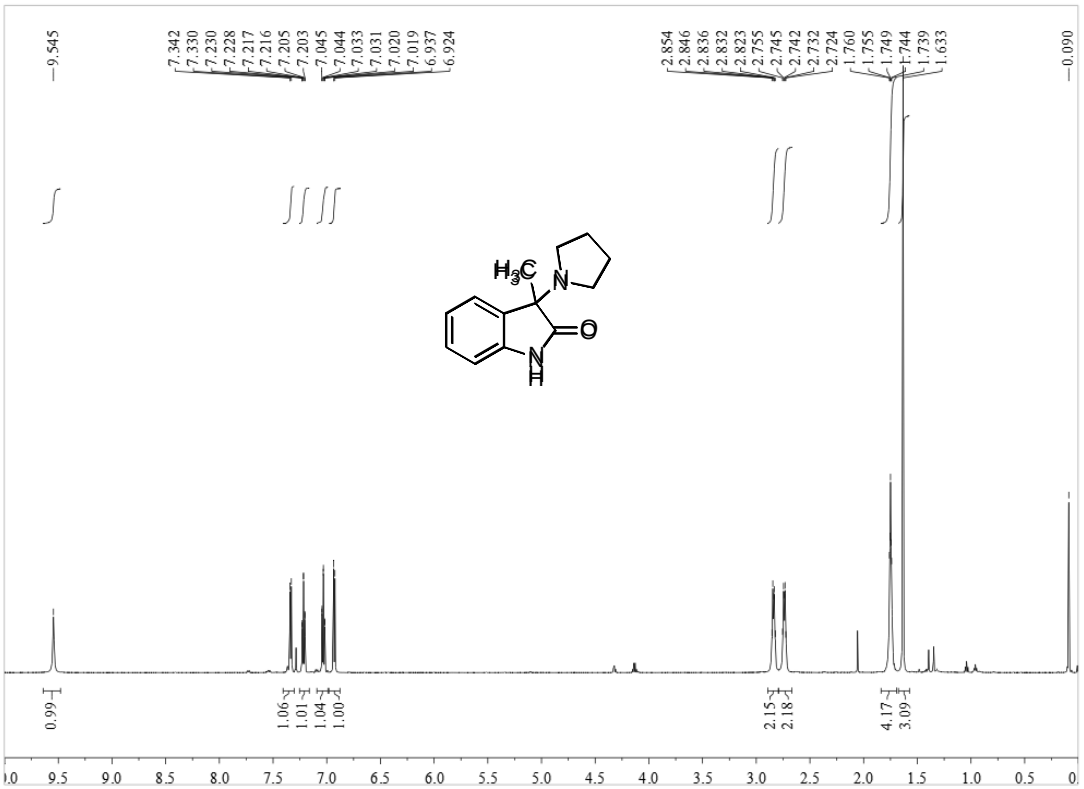


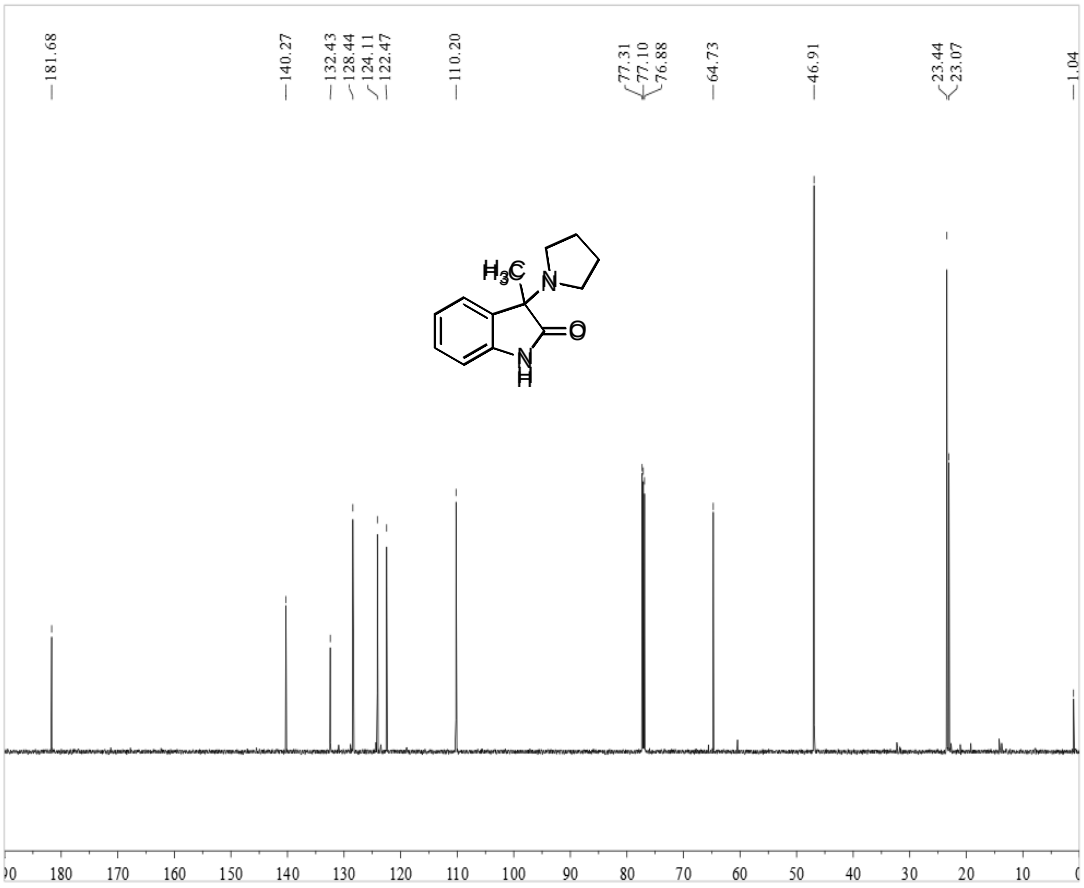
^{1}H and ^{13}C NMR of 11e



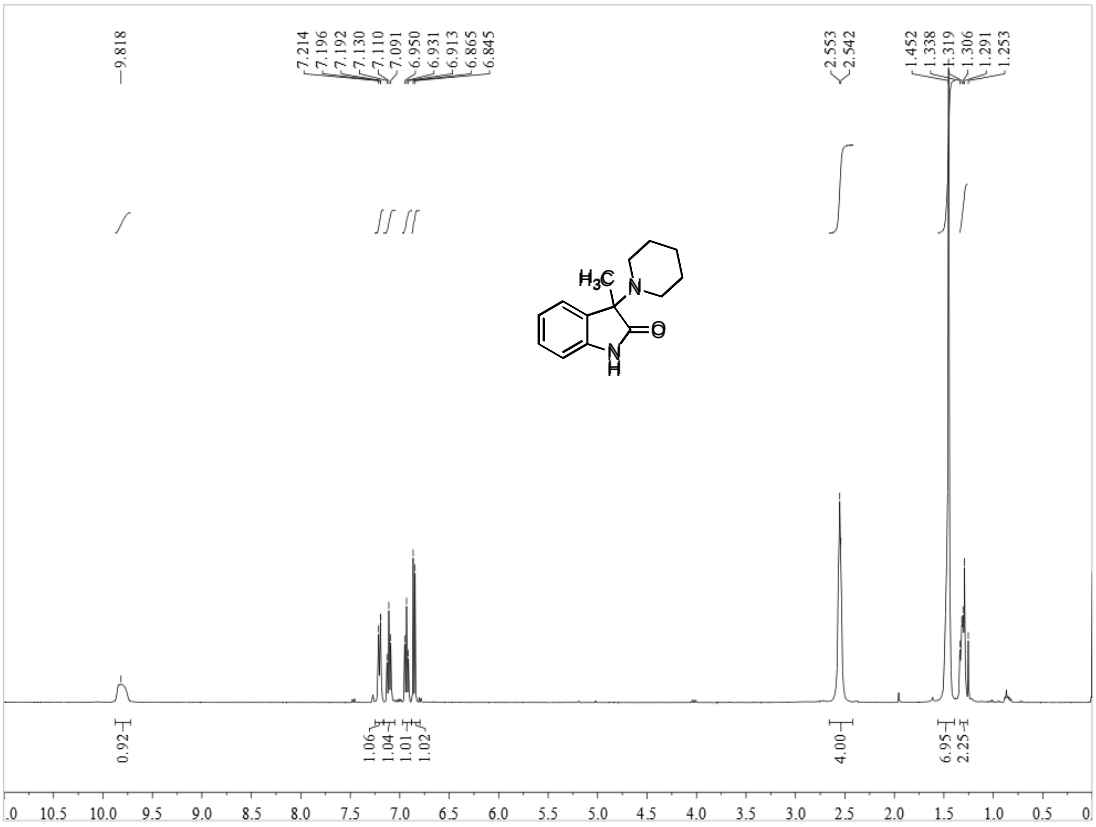


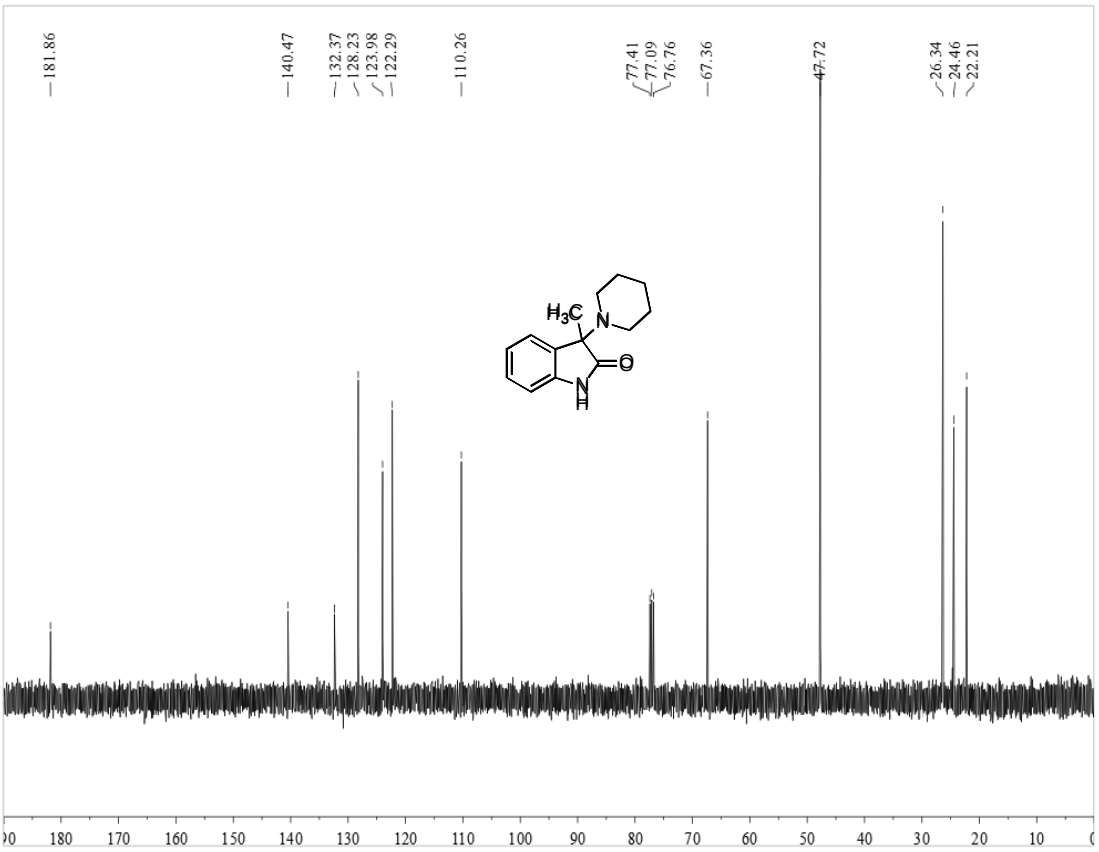
^{1}H and ^{13}C NMR of 11f



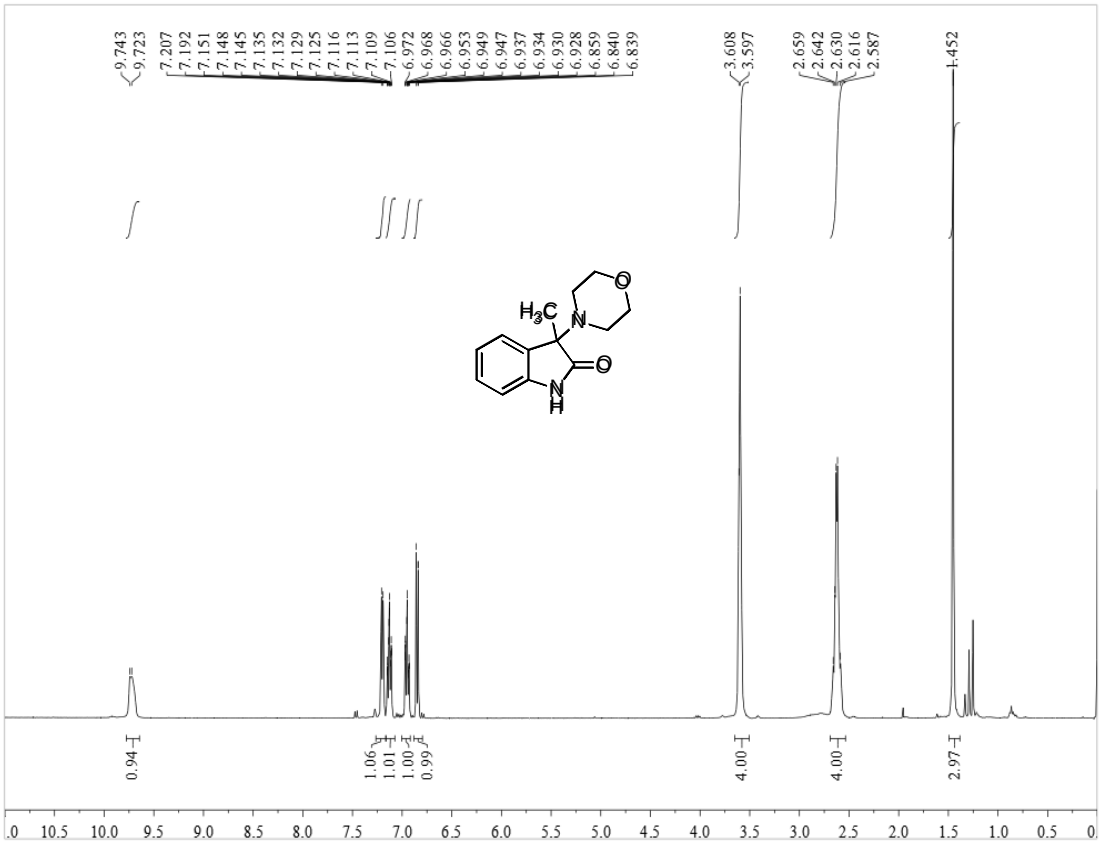


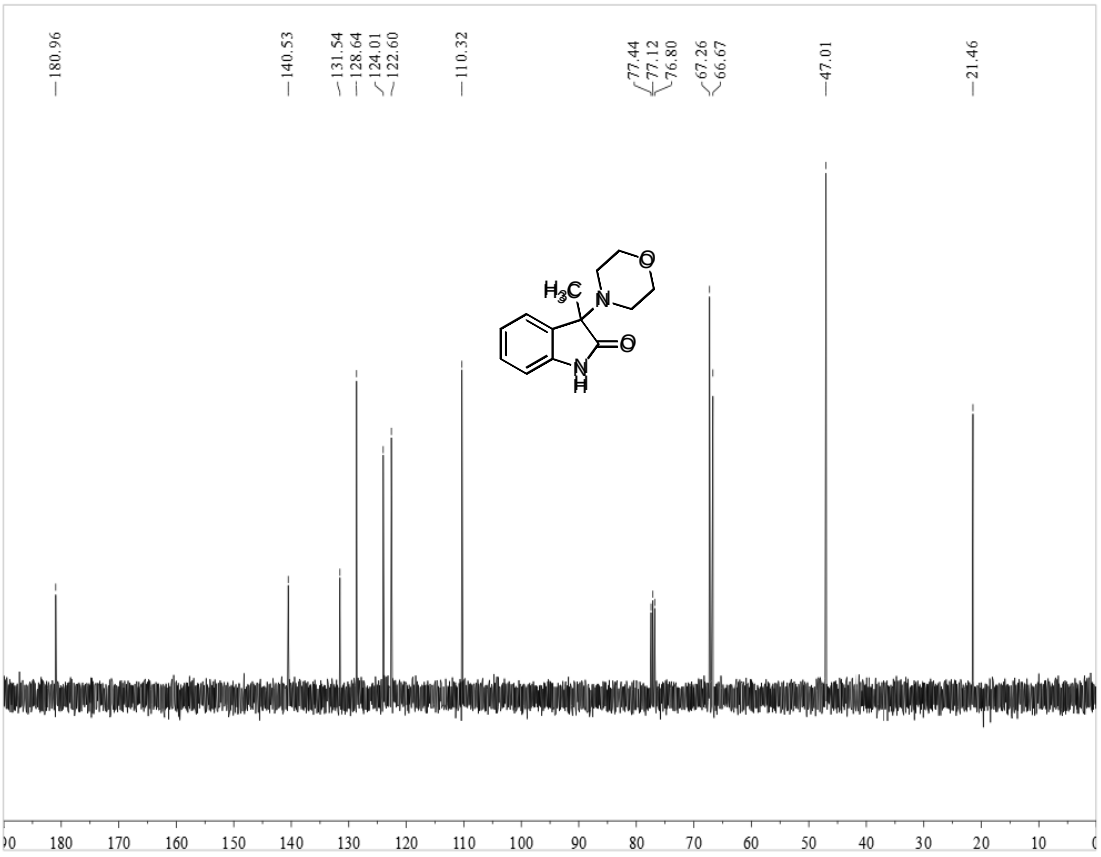
^{1}H and ^{13}C NMR of 11g



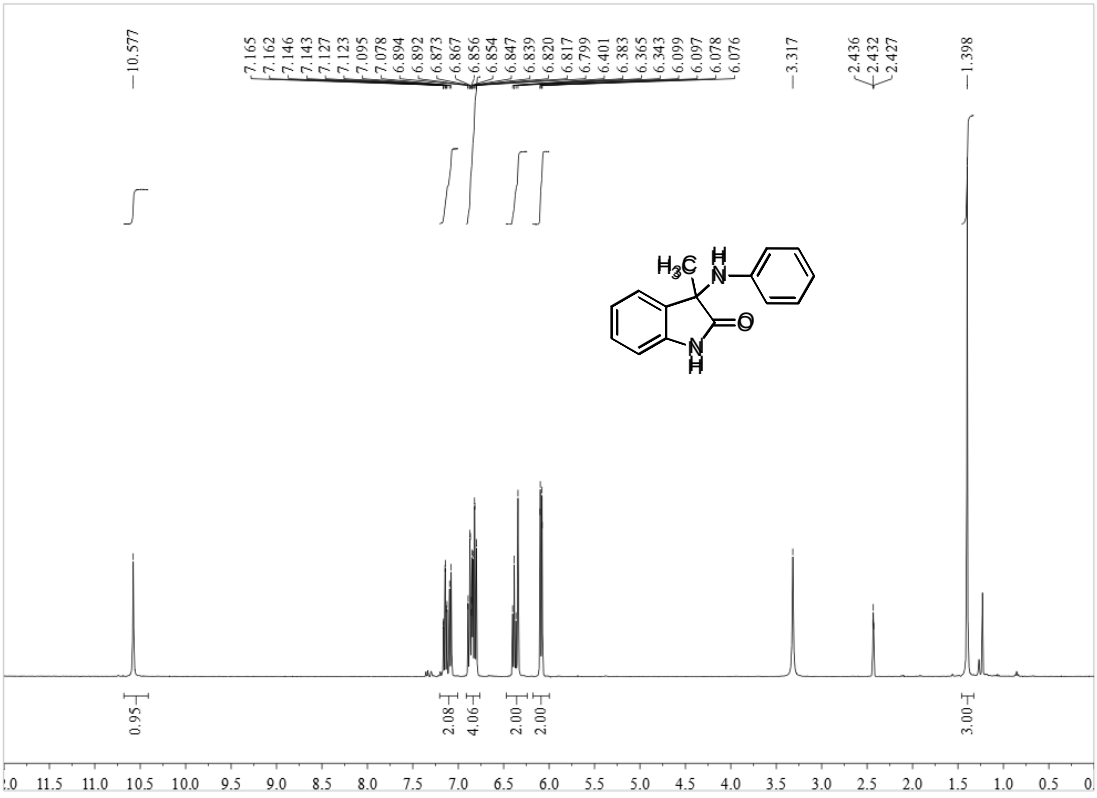


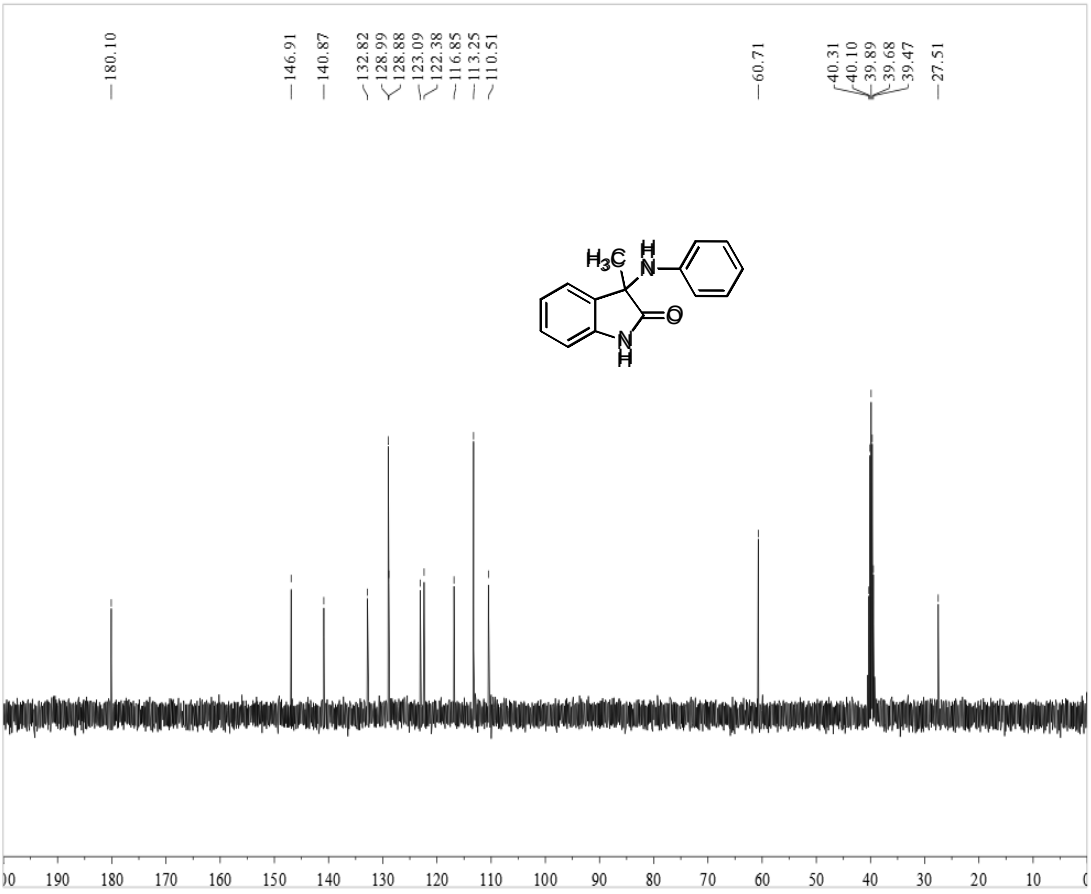
^{1}H and ^{13}C NMR of 11h



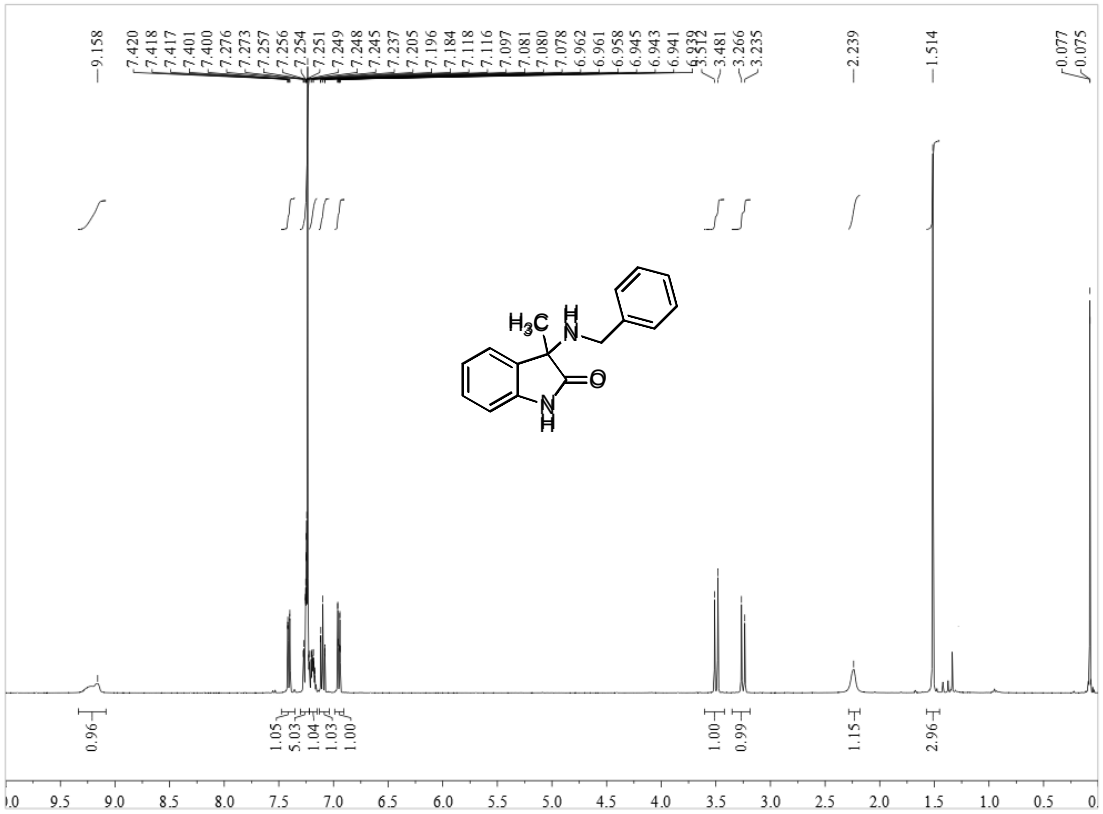


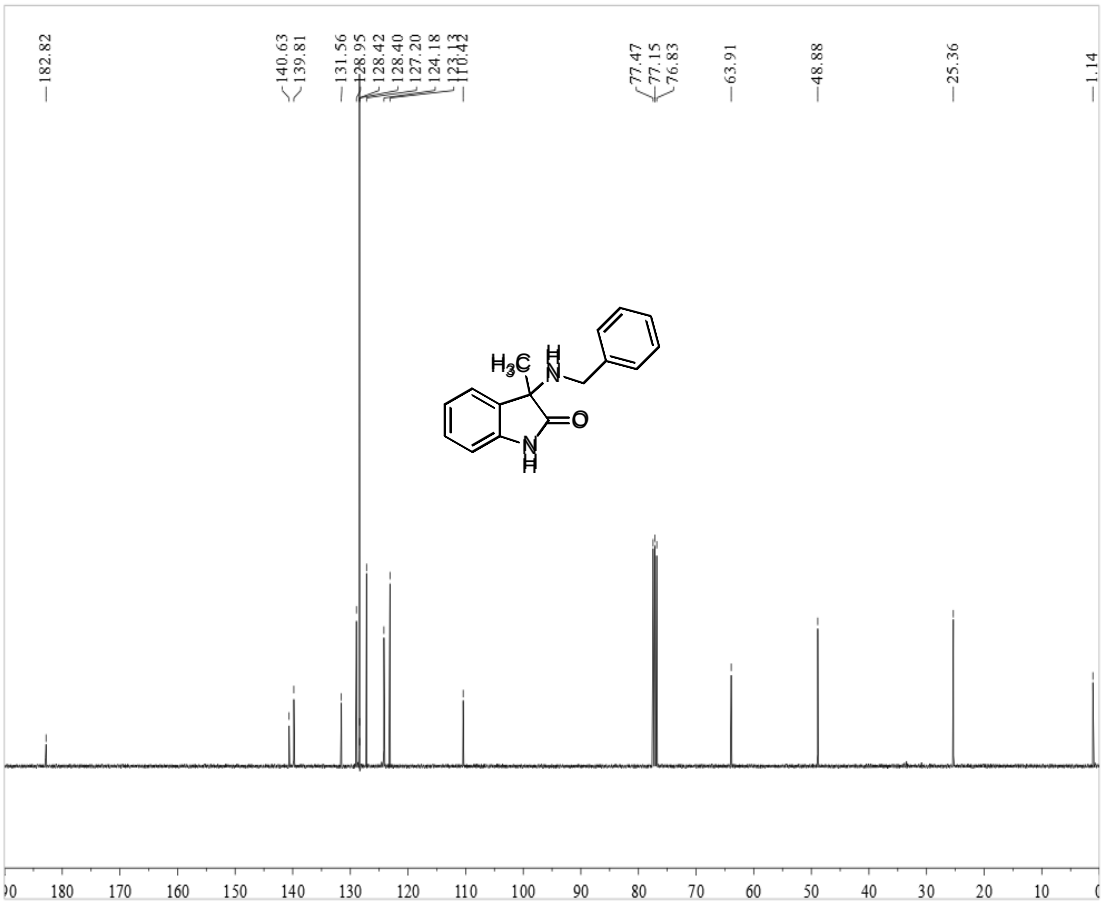
^{1}H and ^{13}C NMR of 11i



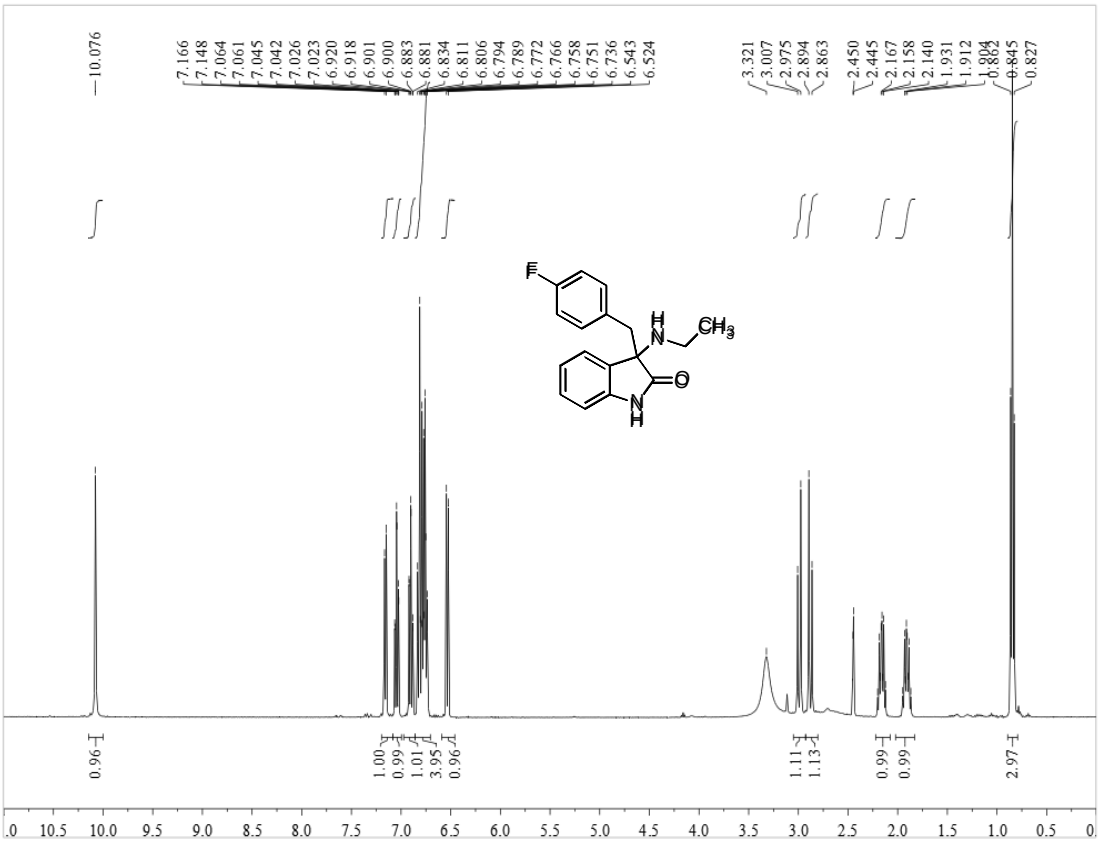


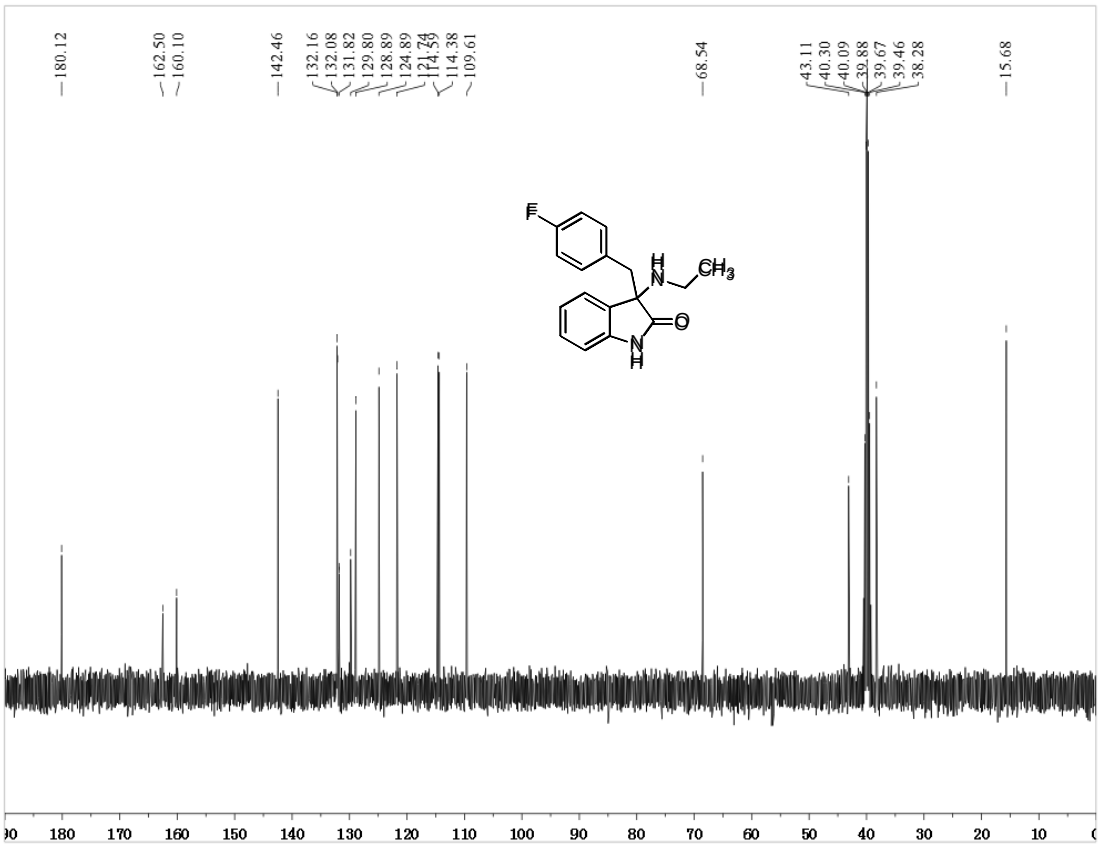
^{1}H and ^{13}C NMR of 11j



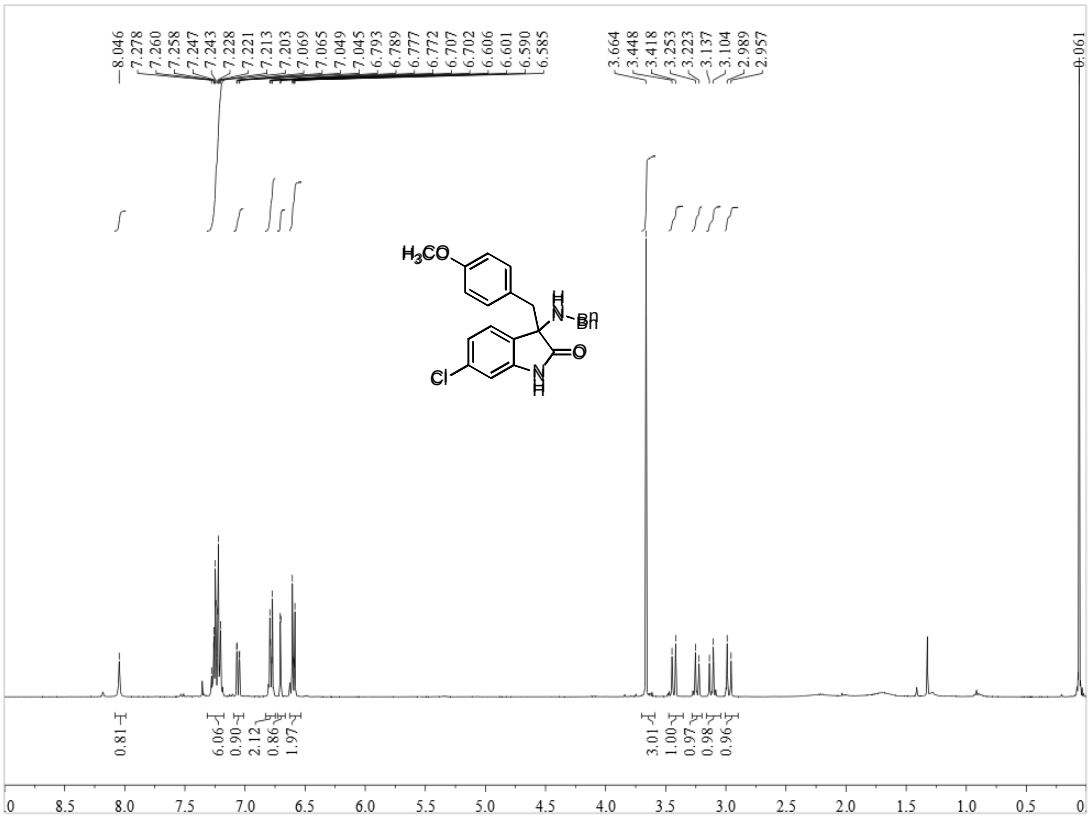


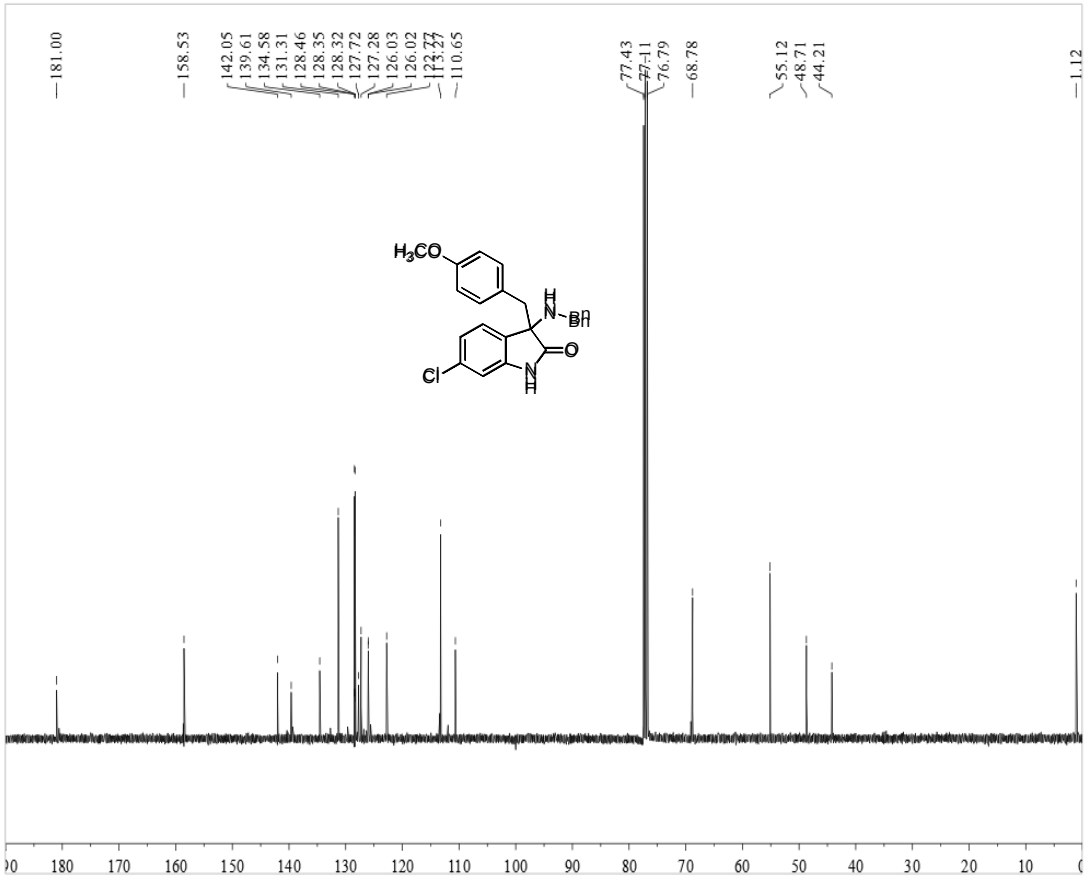
^{1}H and ^{13}C NMR of 11k



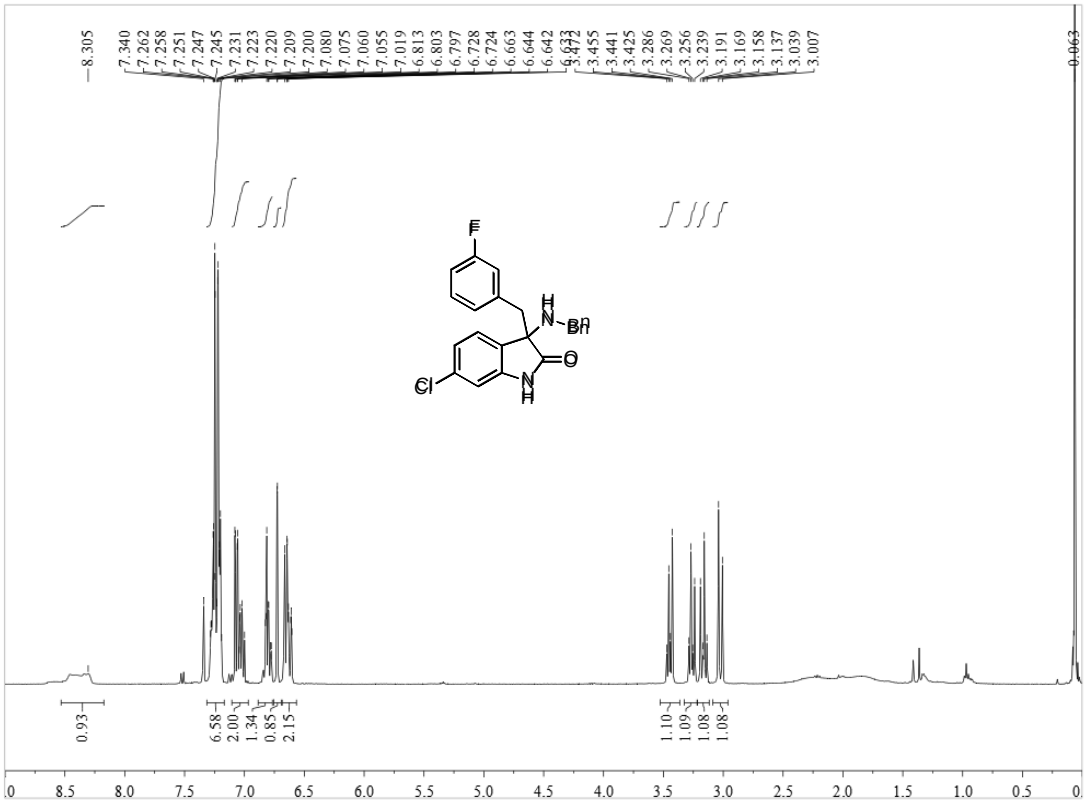


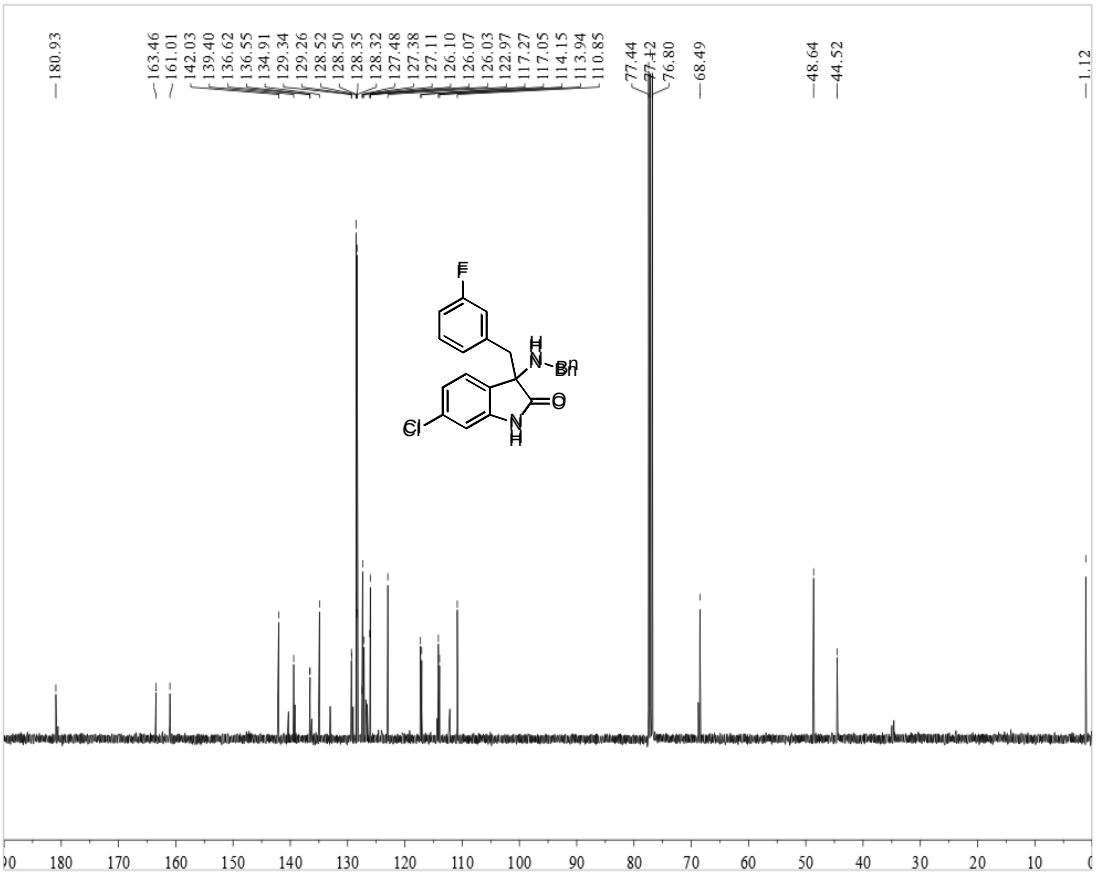
^{1}H and ^{13}C NMR of 11l





^{1}H and ^{13}C NMR of 11m





^{1}H and ^{13}C NMR of 11n