Palladium-catalyzed Regioselective Intramolecular Direct Arylation of *N*-(*o*-Bromophenyl)-3-Indolecarboxamides: Access to Spiro-Indoline-3,3´-Oxindoles and 5,11-Dihydro-6*H*-indolo[3,2-*c*]quinolin-6-ones

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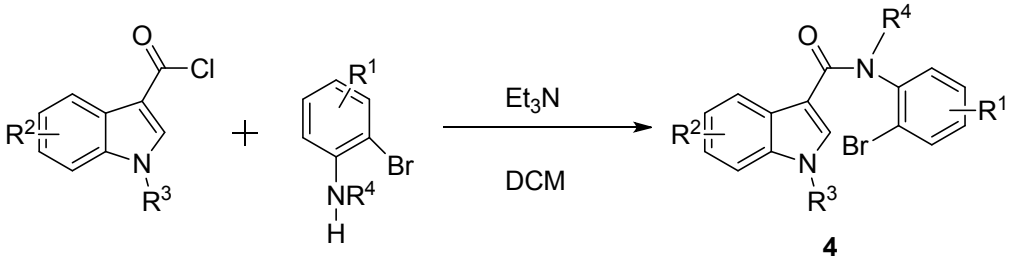
Content **Page**

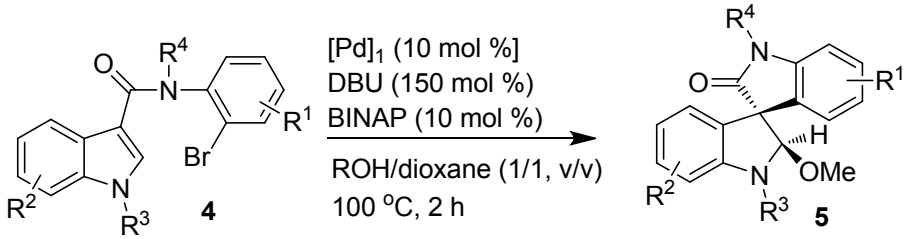
General procedure for the preparation of 4



4

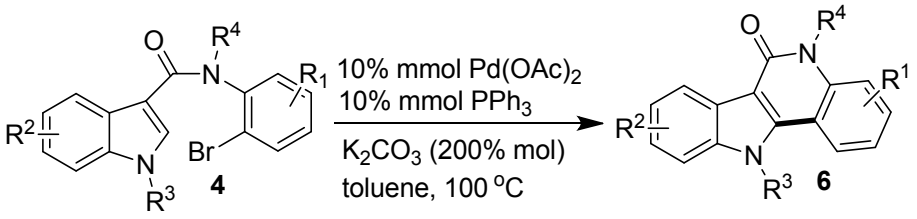
To the mixture of aniline (3 mmol) and Et_3N (6 mmol) in dry CH_2Cl_2 (20 mL) was added indole-3-carbonyl chloride (12 mmol) dropwise at -10 °C. After addition, the mixture was warmed to room temperature and stirred for 12 h. H_2O (30 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL), and the combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel (using petroleum ether : ethyl acetate = 14 : 1 as the eluent) to give product **4**.

General procedure for the preparation of 5



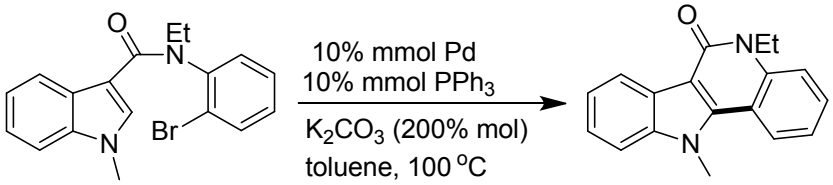
To a dried Schlenk tube were added 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride dichloromethane complex(16.4 mg, 0.02 mmol) and BINAP (12.5 mg 0.02 mmol) under N_2, MeOH (1 mL) and dioxane (1 mL) was then introduced via syringe. The resulting mixture was stirred at room temperature for 1 h, after which **4** (0.2 mmol) and DBU (0.3 mmol) were added and the tube was sealed using Teflon cap. The mixture was stirred at 100 ℃ for 2 h. H_2O (5 mL) was added to the reaction and the resulting mixture was extracted with ethyl acetate (3× 5 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography on silica gel (using petroleum ether/ethyl acetate = 14:1 as the eluent) to give product **5**.

General procedure for the preparation of 6



To a dried Schlenk tube were added $Pd(OAc)_2$ (5.0 mg, 0.02 mmol) and PPh_3 (5.3 mg 0.02 mmol) under N_2, toluene (2 mL) was then introduced via syringe. The resulting mixture was stirred at room temperature for 1 h, after which **4** (0.2 mmol) and K_2CO_3 (0.4mmol) were added and the tube was sealed using Teflon cap. The mixture was stirred at 100 ℃for 3 h. H_2O (5 mL) was added to the reaction and the resulting mixture was extracted with ethyl acetate (3× 5 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography on a silica gel (using petroleum ether/ethyl acetate = 14:1 as the eluent) to give product **6**.

Table S1: Optimization of the catalyst for the formation of **6a**[a]



4a **6a**

Entry	Pd	L	Base	Solvent	Yield(%)[b]
1	$Pd(OAc)_2$	Binap	K_2CO_3	dioxane	42
2	$Pd(TFA)_2$	Binap	K_2CO_3	dioxane	28
3	$PdCl_2$	Binap	K_2CO_3	dioxane	35
4	$Pd(PPh_3)_4$	Binap	K_2CO_3	dioxane	26
5	$Pd_2(dba)_3$	Binap	K_2CO_3	dioxane	27

[a]Reaction conditions, unless otherwise noted: [Pd] (10 mol %), BINAP (10 mol %), K_2CO_3 (200 mol %), and **4a** (0.1 mmol) in dioxane (1 mL) at 100 °C under N_2 for 3 h. [b]Yields were determined by ^1H NMR spectroscopy with CH_2Br_2 as an internal standard.

X-Ray crystal structure of **5ae** (CCDC1552253):

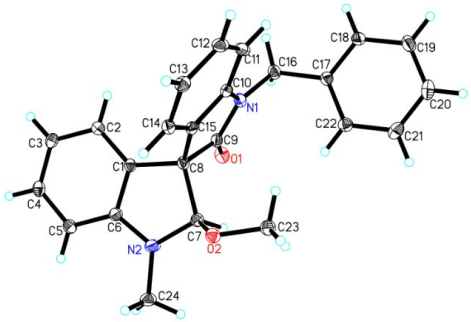
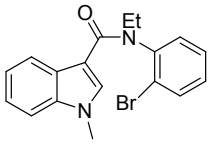


Table 1 Crystal data and structure refinement for 5ae.

Identification code	5ae
Empirical formula	$C_{24}H_{22}N_2O_2$
Formula weight	370.43
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.8659(4)
b/Å	9.3188(3)
c/Å	14.7114(5)
α/°	90
β/°	99.781(3)
γ/°	90
Volume/Å^3	1873.28(10)
Z	4
ρ_{calc}g/cm^3	1.313
μ/mm^{-1}	0.667
F(000)	784.0
Crystal size/mm^3	0.18 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.102 to 147.22
Index ranges	-17 ≤ h ≤ 16, -11 ≤ k ≤ 11, -15 ≤ l ≤ 18
Reflections collected	7326
Independent reflections	3681 [R_{int} = 0.0212, R_{sigma} = 0.0255]
Data/restraints/parameters	3681/0/255
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1104
Largest diff. peak/hole / e Å^{-3}	0.19/-0.24

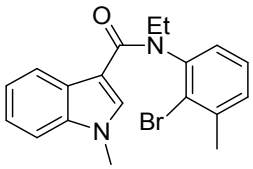
Characterization of 4

N-(2-Bromophenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4a)



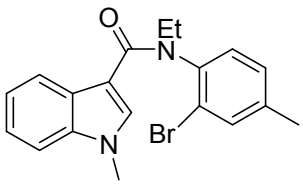
Yellow solid (1.67 g, 65%), mp: 165.3 – 166.1 °C; IR (KBr) 3051, 2973, 2931, 1626, 1468, 1242, 986, 841, 746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 4.9 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.35–7.29 (m, 2H), 7.26 – 7.17 (m, 4H), 6.01 (s, 1H), 4.34 – 4.28 (m, 1H), 3.57 – 3.54 (m, 1H), 3.51 (s, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 142.8, 136.1, 133.9, 131.9, 131.3, 129.2, 128.6, 128.4, 124.6, 122.7, 122.6, 121.3, 109.8, 109.0, 44.0, 33.0, 12.9;HRMS (ESI) m/z calcd for $C_{18}H_{17}BrN_2NaO$ $[M + Na]^+$: 379.0422; found: 379.0419.

N-(2-bromo-3-methylphenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4b)



Yellow solid (739mg, 66%), mp: 152.3 – 153.1 °C; IR (KBr) 3052, 2983, 2921, 1622, 1458, 1240, 956, 840, 756cm^{-1};1H NMR (400 MHz, CDCl3) δ 8.46 – 8.38 (m, 1H), 7.28 – 7.18 (m, 6H), 7.13 (d, J = 7.5 Hz, 1H), 5.99 (s, 1H), 4.39 – 4.34 (m, 1H), 3.52 – 3.42 (m, 4H), 2.46 (d, J = 6.4 Hz, 3H), 1.26 (d, J = 7.1 Hz, 3H);13C NMR (101 MHz, CDCl3) δ 165.1, 142.9, 140.5, 136.1, 131.3, 130.0, 129.2, 128.7, 127.6, 127.1, 122.7, 122.5, 121.2, 109.8, 109.0, 44.0, 33.0, 23.9, 13.0；HRMS (ESI) m/z calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0570.

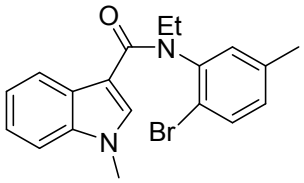
N-(2-Bromo-4-methylphenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4c)



Yellow solid (750 mg, 67%), mp: 110.2 – 111.6 °C; IR (film) 3050, 2973, 2872, 1632, 1466, 1281, 987, 856, 777cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.40 (m, 1H), 7.57 – 7.53 (m, 1H), 7.27 – 7.18 (m, 3H), 7.13 (d, J = 1.6 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.06 (s, 1H), 4.32 – 4.27 (m, 1H),

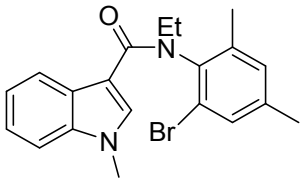
3.61– 3.56 (m, 1H), 3.51 (s, 3H), 2.32 (s, 3H), 1.28 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 134.0, 139.7, 136.1, 134.3, 131.9, 131.4, 129.3, 128.7, 124.1, 122.6, 122.5, 121.2, 109.8, 109.1, 44.0, 33.1, 20.9, 12.9;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0579.

N-(2-Bromo-5-methylphenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4d)



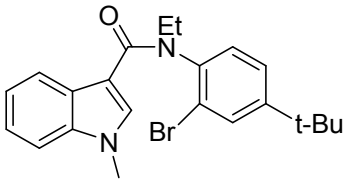
Yellow solid (445 mg, 64%), mp: 108.5 – 109.3 °C; IR (film) 3050, 2970, 2854, 1656, 1453, 1272, 983, 865, 790cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.44 (m, 1H), 7.57 – 7.53 (m, 1H), 7.27 – 7.18 (m, 3H), 7.13 (d, J = 1.6 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.06 (s, 1H), 4.32 – 4.27 (m, 1H), 3.61 – 3.56 (m, 1H), 3.51 (s, 3H), 2.32 (s, 3H), 1.28 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 142.4, 138.8, 136.1, 133.5, 132.3, 131.4, 130.1, 128.7, 122.7, 122.5, 121.3, 121.1, 109.7, 109.1, 44.2, 33.1, 20.9, 13.0;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0574.

N-(2-Bromo-4,6-dimethylphenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4e)



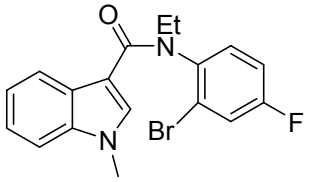
White solid (700 mg, 70%), mp: 135.1 – 136.6 °C; IR (film) 3057, 2926, 2832, 1623, 1443, 1279, 983, 844, 772cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.29 (m, 1H), 7.40 (t, J = 4.6 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.03 (d, J = 0.5 Hz, 1H), 6.00 (s, 1H), 4.11 – 4.01 (m, 1H), 3.88 – 3.65 (m, 1H), 3.53 (s, 3H), 2.38 (s, 3H), 2.19 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 139.4, 139.3, 139.0, 136.2, 132.0, 131.3, 130.6, 128.9, 125.0, 122.8, 122.5, 121.3, 109.7, 109.0, 44.3, 33.1, 20.8, 19.1, 13.1;HRMS (ESI) *m/z*calcd for $C_{20}H_{21}BrN_2NaO$ $[M + Na]^+$: 407.0735; found: 407.0725.

N-(2-Bromo-4-tert-butylphenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4f)



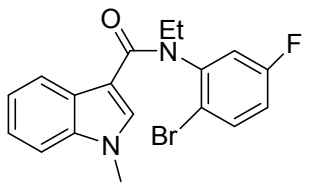
White solid (824 mg, 60%), mp: 155.8 – 156.4 °C; IR (film) 3056, 2963, 2868, 1625, 1466, 1281, 938, 830, 770cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.45 (m, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.38 – 7.36(m, 1H), 7.25 – 7.19 (m, 3H), 7.17 – 7.12 (m, 1H), 5.89 (s, 1H), 4.35 – 4.30 (m, 1H), 3.60 – 3.54 (m, 1H), 3.43 (s, 3H), 1.38 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 153.3, 139.9, 136.1, 131.5, 131.3, 130.8, 128.7, 125.6, 124.3, 122.7, 122.5, 121.2, 109.7, 109.1, 43.9, 34.9, 32.9, 31.3, 13.1;HRMS (ESI) *m/z*calcd for $C_{22}H_{25}BrN_2NaO$ $[M + Na]^+$: 435.1048; found: 435.1042.

N-(2-Bromo-4-fluorophenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4g)



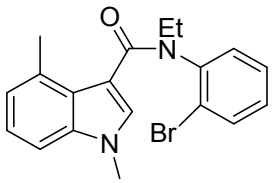
White solid (841 mg, 61%), mp: 150.4 – 151.2 °C; IR (film) 3057, 2930, 2850, 1623, 1444, 1279, 983, 844, 772cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 7.41 – 7.38 (m, 1H), 7.24 – 7.19 (m, 3H), 7.17 – 7.13 (m, 1H), 7.05 – 7.00 (m, 1H), 6.07 (s, 1H), 4.28 – 4.22 (m, 1H), 3.56 – 3.49 (m, 1H), 3.48 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 161.3 (d, $J_{C\text{-}F}$ = 251.2 Hz), 139.1, 136.2, 132.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.1, 128.5, 125.0 (d, $J_{C\text{-}F}$ = 9.9 Hz), 122.7, 122.5, 121.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 120.9, 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 109.6, 109.2, 44.1, 33.1, 12.9;HRMS (ESI) *m/z*calcd for $C_{18}H_{16}BrFN_2NaO$ $[M + Na]^+$: 397.0328; found: 397.0328.

N-(2-Bromo-5-fluorophenyl)-N-ethyl-1-methyl-1H-indole-3-carboxamide(4h)



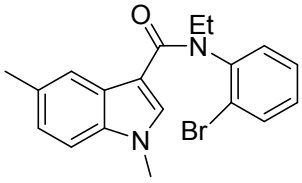
Yellow solid (850 mg, 62%), mp: 145.9 – 146.4 °C; IR (film) 3052, 2926, 2855, 1625, 1435, 1265, 972, 860, 750cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.35 (m, 1H), 7.64 – 7.61 (m, 1H), 7.29 – 7.21 (m, 3H), 7.09 – 7.06 (m, 1H), 7.00 – 6.98 (m, 1H), 6.23 (s, 1H), 4.36 – 4.15 (m, 1H), 3.73 – 3.61 (m, 1H), 3.56 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 161.9 (d, $J_{C\text{-}F}$ = 248.7 Hz), 144.1, 136.2, 134.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.2, 128.3, 122.8, 122.4, 121.4, 119.1 (d, $J_{C\text{-}F}$ = 3.8 Hz), 119.0 (d, $J_{C\text{-}F}$ = 22.1 Hz), 116.5 (d, $J_{C\text{-}F}$ = 22.0 Hz), 109.7, 109.2, 44.2, 33.1, 13.0;HRMS (ESI) *m/z*calcd for $C_{18}H_{16}BrFN_2NaO$ $[M + Na]^+$: 397.0328; found: 397.0327.

N-(2-Bromophenyl)-N-ethyl-1,4-dimethyl-1H-indole-3-carboxamide(4k)



Yellow solid (693 mg, 63%), mp: 148.3 – 150.1°C; IR (film) 3056, 2972, 2874, 1650, 1459, 1268, 1026, 826, 750cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.05 (br, 1H), 7.00 (d, J = 7.0 Hz, 2H), 6.80 (br, 1H), 4.36 (br, 1H), 3.65 – 3.60 (m, 1H), 3.45 (br, 3H), 2.81 (s, 3H), 1.30 (br, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 142.8, 136.8, 133.7, 131.8, 131.6, 129.5, 128.7, 128.3, 126.0, 123.4, 122.5, 122.2, 111.3, 107.1, 43.9, 32.9, 21.0, 12.8;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0577.

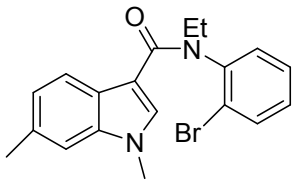
N-(2-Bromophenyl)-N-ethyl-1,5-dimethyl-1H-indole-3-carboxamide(4l)



Yellow solid (760 mg, 69%), mp: 145.2 – 146.9 °C; IR (film) 3057, 2976, 2874, 1684, 1475, 1267, 1022, 826, 740cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.70 – 7.67 (m, 1H), 7.30 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.09 – 7.03 (m, 2H), 5.95 (s, 1H), 4.33 – 4.28 (m, 1H), 3.57 –3.52 (m, 1H), 3.48 (s, 3H), 2.47 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 142.8, 134.6, 134.0, 131.9, 131.4, 130.8, 129.1, 128.8, 128.4, 124.6, 124.2, 122.3, 109.2, 108.7,

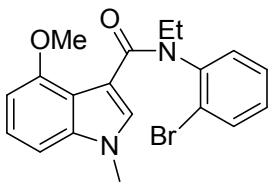
44.0, 33.1, 21.5, 12.9;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0571.

N-(2-Bromophenyl)-N-ethyl-1,6-dimethyl-1H-indole-3-carboxamide(4m)



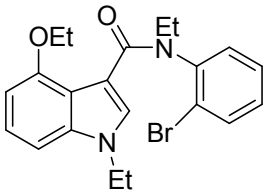
Yellow oil (704 mg, 64%); IR (film) 3054, 2975, 2874, 1657, 1475, 1242, 1032, 852, 763cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.70 – 7.66 (m, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.11 – 7.02 (m, 2H), 5.95 (s, 1H), 4.33 – 4.28 (m, 1H), 3.58 – 3.49 (m, 1H), 3.48 (s, 3H), 2.47 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 142.8, 136.5, 134.0, 132.5, 131.9, 130.9, 129.1, 128.4, 126.4, 124.6, 123.1, 122.3, 109.6, 109.0, 44.0, 32.9, 21.8, 13.0; HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0574.

N-(2-Bromophenyl)-N-ethyl-4-methoxy-1-methyl-1H-indole-3-carboxamide(4n)



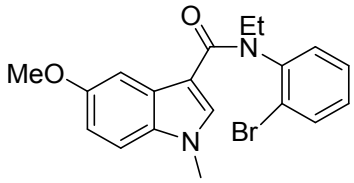
Yellow solid (714 mg, 62%), mp: 125.9 – 126.7 ^{o}C; IR (film) 3057, 2935, 2874, 1652, 1473, 1259, 1058, 830, 739cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (br, 1H), 7.20 (s, 1H), 7.09 (s, 1H), 7.00 – 6.76 (m, 4H), 6.53 (d, J = 7.7 Hz, 1H), 4.46 (br, 1H), 3.98 (s, 3H), 3.53 (br, 3H), 3.37 (br, 1H), 1.28 (br, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 153.7, 137.7, 133.1, 131.4, 128.5, 127.9, 125.3, 125.2, 123.7, 123.0, 116.7, 111.3, 102.5, 100.5, 55.5, 43.0, 33.0, 12.6;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO_2$ $[M + Na]^+$: 409.0528; found: 409.0520.

N-(2-Bromophenyl)-4-ethoxy-N,1-diethyl-1H-indole-3-carboxamide(4o)



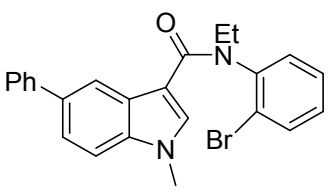
Yellow solid (758 mg, 61%), mp: 127.6 – 129.2°C; IR (film) 3050, 2965, 2870, 1623, 1456, 1236, 1052, 842, 751cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 13.2 Hz, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.03 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 13.4 Hz, 3H), 6.74 (d, J = 6.3 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 4.56 – 4.36 (m, 1H), 4.25 – 4.16 (m, 2H), 3.86 (br, 2H), 3.52 – 3.26 (m, 1H), 1.56 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.1, 3H), 1.22 – 1.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 153.2, 142.2, 136.8, 133.0, 132.0, 128.4, 127.9, 123.6, 122.8, 117.1, 111.5, 102.4, 101.2, 100.0, 63.7, 43.0, 41.0, 15.2, 15.2, 12.6;HRMS (ESI) *m/z*calcd for $C_{21}H_{23}BrN_2NaO_2$ [M + Na]$^+$: 437.0841; found: 437.0836.

N-(2-Bromophenyl)-N-ethyl-5-methoxy-1-methyl-1H-indole-3-carboxamide(4p)



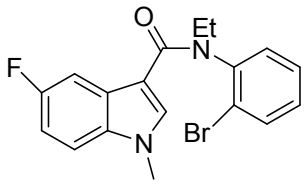
Yellow solid (704 mg, 64%), mp: 168.8 – 170.5 °C; IR (film) 3057, 2932, 2876, 1656, 1470, 1246, 1013, 820, 741cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 2.5 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.40 –7.31(m, 2H), 7.31 – 7.24 (m, 1H), 7.10 (d, J = 8.8 Hz, 1H), 6.91 – 6.89 (m, 1H), 5.92 (s, 1H), 4.37 – 4.32 (m, 1H), 3.94 (s, 3H), 3.59 –3.50 (m, 1H), 3.50 (s, 3H), 1.27 (t, J = 7.1 Hz ,3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 155.5, 142.8, 134.0, 132.0, 131.6, 131.3, 129.4, 129.2, 128.5, 124.7, 113.6, 109.9, 109.2, 103.6, 55.8, 44.0, 33.2, 13.0;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO_2$ [M + Na]$^+$: 409.0528; found: 409.0530.

N-(2-Bromophenyl)-N-ethyl-1-methyl-5-phenyl-1H-indole-3-carboxamide(4q)



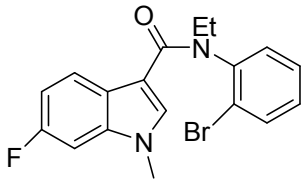
Yellow solid (857 mg, 66%), mp: 188.9 – 190.1 °C; IR (film) 3058, 2956, 2870, 1623, 1473, 1236, 1031, 806, 758cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.73 (t, J = 9.1 Hz, 3H), 7.53 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.28 (d, J = 6.2 Hz, 2H), 6.06 (s, 1H), 4.40 – 4.25 (m, 1H), 3.62 – 3.56 (m, 1H), 3.56 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 142.7, 142.2, 135.7, 134.8, 134.0, 132.2, 131.9, 131.9, 129.1, 128.6, 128.5, 128.5, 128.4, 127.6, 126.5, 124.6, 122.4, 121.2, 110.1, 109.3, 44.1, 33.2, 12.9;HRMS (ESI) *m/z*calcd for $C_{24}H_{21}BrN_2NaO$ $[M + Na]^+$: 455.0735; found: 455.0735.

N-(2-Bromophenyl)-N-ethyl-5-fluoro-1-methyl-1H-indole-3-carboxamide(4r)



Yellow solid (730 mg, 65%), mp: 185.1 – 186.2 °C; IR (film) 3057, 2931, 2855, 1623, 1446, 1279, 973, 846, 762cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.10 (m, 1H), 7.72 – 7.70 (m, 1H), 7.40 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 7.12 – 7.09 (m, 1H), 7.00 – 6.94 (m, 1H), 5.97 (s, 1H), 4.33 – 4.28 (m, 1H), 3.59 – 3.54 (m, 1H), 3.51 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 159.0 (d, $J_{C\text{-}F}$ = 234.5 Hz), 142.6, 134.1, 132.7, 132.5, 131.8, 129.3, 129.3, 128.6, 124.7, 111.1 (d, $J_{C\text{-}F}$ = 26.5 Hz), 109.8, 109.7, 107.9 (d, $J_{C\text{-}F}$ = 25.0 Hz), 44.1, 33.3, 12.9;HRMS (ESI) *m/z*calcd for $C_{18}H_{16}BrFN_2NaO$ $[M + Na]^+$: 397.0328; found: 397.0328.

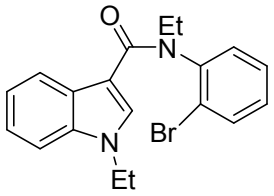
N-(2-Bromophenyl)-N-ethyl-6-fluoro-1-methyl-1H-indole-3-carboxamide(4s)



Yellow solid (696 mg, 62%), mp: 140.6 – 142.4 °C; IR (film) 3052, 2954, 2872 1625, 1452, 1256, 980, 850, 761cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.34 (m, 1H), 7.71 – 7.69 (m, 1H), 7.40 – 7.35 (m, 1H), 7.33 – 7.25 (m, 2H), 7.03 – 6.98 (m, 1H), 6.89 – 6.86 (m, 1H), 5.95 (s, 1H), 4.34 – 4.29 (m, 1H), 3.59 – 3.54 (m, 1H), 3.47 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 160.2 (d, $J_{C\text{-}F}$ = 248.7 Hz), 142.6, 136.2 (d, $J_{C\text{-}F}$ = 11.8 Hz), 134.0, 131.8, 131.6,

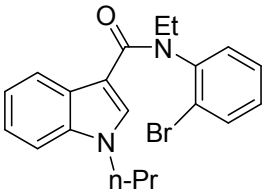
129.31, 128.5, 125.0, 124.6, 123.8 (d, $J_{C\text{-}F}$ = 9.7 Hz), 109.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 95.6, 95.4, 44.1, 33.1, 12.9;HRMS (ESI) *m/z*calcd for $C_{18}H_{16}BrFN_2NaO$ $[M + Na]^+$: 397.0328; found: 397.0325.

N-(2-Bromophenyl)-N,1-diethyl-1H-indole-3-carboxamide(4t)



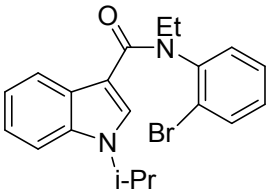
Yellow solid (680 mg, 61%), mp: 122.7 – 123.5 °C; IR (film) 3054, 2976, 2875, 1625, 1460, 1280, 954, 846, 746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.30 (m, 1H), 7.68 – 7.66 (m, 1H), 7.34 – 7.26 (m, 2H), 7.24 – 7.19 (m, 4H), 6.10 (s, 1H), 4.33 – 4.28 (m, 1H), 3.90 – 3.84 (m, 2H), 3.60 – 3.54 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 142.9, 135.2, 133.9, 132.0, 129.6, 129.1, 128.7, 128.4, 124.7, 122.7, 122.4, 121.2, 109.8, 109.1, 43.9, 41.0, 14.9, 12.9;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}BrN_2NaO$ $[M + Na]^+$: 393.0579; found: 393.0573.

N-(2-Bromophenyl)-N-ethyl-1-propyl-1H-indole-3-carboxamide(4u)



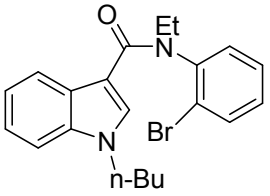
Yellow syrup (720 mg, 63%); IR (film) 3054, 2966, 2874, 1628, 1466, 1280, 984, 841, 746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.41 (m, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.25 – 7.20 (m, 4H), 6.11 (s, 1H), 4.34 – 4.29 (m, 1H), 3.82 – 3.78 (m, 2H), 3.75 – 3.52 (m, 1H), 1.66 – 1.52 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 0.64 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 142.9, 135.4, 133.9, 131.9, 130.7, 129.1, 128.7, 128.5, 124.7, 122.6, 122.4, 121.2, 109.3, 109.2,48.0, 43.9, 22.8, 12.9, 11.2;HRMS (ESI) *m/z*calcd for $C_{20}H_{21}BrN_2NaO$ $[M + Na]^+$: 407.0735; found: 407.0739.

N-(2-Bromophenyl)-N-ethyl-1-isopropyl-1H-indole-3-carboxamide(4v)



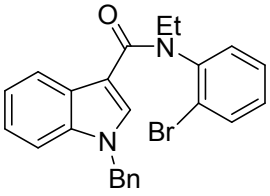
Yellow solid (776 mg, 67%), mp: 122.6 –123.9 °C; IR (film) 3057, 2973, 2883, 1625, 1460, 1278, 1028, 841, 746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.37 (m, 1H), 7.67 – 7.66 (m, 1H), 7.34 – 7.25 (m, 2H), 7.24 – 7.16 (m, 4H), 6.21 (s, 1H), 4.46 – 4.39 (m, 1H), 4.32 – 4.27 (m, 1H), 3.67 – 3.53 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (d, J = 6.6 Hz, 3H), 1.16 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 143.0, 135.0, 133.8, 132.0, 129.1, 128.6, 128.4, 126.9, 124.8, 122.6, 122.3, 121.3, 109.6, 109.2, 47.1, 43.8, 22.4, 22.4, 13.0;HRMS (ESI) *m/z*calcd for $C_{20}H_{21}BrN_2NaO$ $[M + Na]^+$: 407.0735; found: 407.0732.

N-(2-Bromophenyl)-1-butyl-N-ethyl-1H-indole-3-carboxamide(4w)



Yellow solid (816 mg, 68%), mp: 89.3 – 90.4 °C; IR (film) 3057, 2959, 2867, 1625, 1465, 1279, 1014, 841, 745cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.40 (m, 1H), 7.70 – 7.68 (m, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.21 (m, 4H), 6.12 (s, 1H), 4.37 – 4.24 (m, 1H), 3.84 (t, J = 6.7 Hz, 2H), 3.64 – 3.58 (m, 1H), 1.61 – 1.51 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.03 – 0.98 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 143.0, 135.4, 133.9, 131.9, 130.7, 129.0, 128.7, 128.4, 124.7, 122.6, 122.4, 121.2, 109.5, 109.2, 46.0, 43.9, 31.5, 19.7, 13.5, 12.9;HRMS (ESI) *m/z*calcd for $C_{21}H_{23}BrN_2NaO$ $[M + Na]^+$: 421.0891; found: 421.0894.

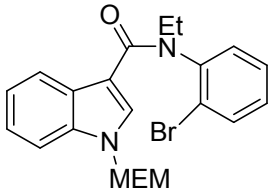
1-Benzyl-N-(2-bromophenyl)-N-ethyl-1H-indole-3-carboxamide(4x)



White solid (842 mg, 65%), mp: 114.8 – 115.1 °C; IR (film) 3058, 2972, 2869, 1626, 1466, 1280, 987, 841, 744cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.41 (m, 1H), 7.62 – 7.52 (m, 1H), 7.29

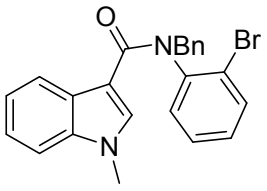
– 7.24 (m, 6H), 7.22 – 7.18 (m, 2H), 7.16 – 7.09 (m, 1H), 6.90 – 6.87 (m, 2H), 6.10 (s, 1H), 5.02 (s, 2H), 4.33 – 4.28 (m, 1H), 3.64 – 3.59 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 142.8, 136.0, 135.6, 133.9, 131.7, 130.7, 129.0, 129.0, 128.8, 128.3, 127.8, 127.8, 127.5, 127.1, 124.5, 122.9, 122.7, 121.5, 110.2, 109.5, 50.1, 43.9, 12.9;HRMS (ESI) *m/z*calcd for $C_{24}H_{21}BrN_2NaO$ $[M + Na]^+$: 455.0735; found: 455.0731.

N-(2-Bromophenyl)-N-ethyl-1-((2-methoxyethoxy)methyl)-1H-indole-3-carboxamide(4y)



Yellow syrup (830 mg, 64%); IR (film) 3057, 2975, 2884, 1632, 1468, 1276, 985, 841, 745cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 7.67 – 7.64 (m, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 2H), 7.24 – 7.29 (m, 1H), 6.23 (s, 1H), 5.29 (s, 2H), 4.31 – 4.26 (m, 1H), 3.66 – 3.61 (m, 1H), 3.34 – 3.33 (m, 2H), 3.32 (s, 3H), 3.18 – 3.07 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 142.7, 135.5, 133.9, 131.7, 130.3, 129.1, 128.9, 128.4, 124.6, 123.2, 122.5, 121.9, 111.2, 109.8, 76.4, 71.5, 67.0, 59.0, 44.0, 12.9;HRMS (ESI) *m/z*calcd for $C_{21}H_{23}BrN_2NaO_3$ $[M + Na]^+$: 453.0790; found: 453.0784.

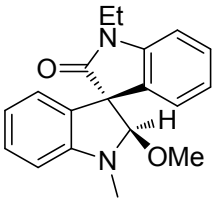
N-Benzyl-N-(2-bromophenyl)-1-methyl-1H-indole-3-carboxamide(4ae)



Yellow solid (880mg, 68%), mp: 147.5 – 149.3^{o}C; IR (film) 3041, 2951, 2876, 1655, 1457, 1280, 1032, 841, 785cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.47 (m, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 7.1 Hz, 2H), 7.29 (dd, J = 11.1, 4.7 Hz, 5H), 7.24 – 7.18 (m, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.04 – 5.88 (m, 2H), 4.29 (d, J = 14.5 Hz, 1H), 3.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 142.3, 137.6, 136.1, 133.9, 132.3, 131.5, 131.5,139.4, 129.4, 129.4, 129.3, 128.7, 128.3, 128.2, 127.3, 124.5, 122.8, 121.4, 109.4, 109.1, 46.3, 33.1;HRMS (ESI) *m/z*calcd for $C_{23}H_{19}N_2NaO$ $[M + Na]^+$: 441.0578; found: 441.0558.

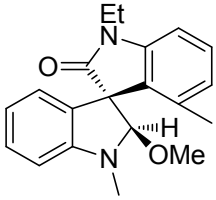
Characterization of 5

Cis-1-Ethyl-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5a)



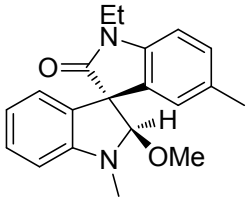
Yellow syrup (49.9 mg, 81%); IR (film) 2961, 2871, 1710, 1680, 1495, 1102, 951,746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.7 Hz, 1H), 7.26 (s, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.62 – 6.53 (m, 3H), 4.92 (s, 1H), 3.91 – 3.79 (m, 2H), 3.02 (s, 3H), 2.96 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 150.7, 142.4, 129.3, 128.5, 128.4, 128.4, 126.7, 123.0, 122.7, 118.7, 108.1, 107.3, 102.9, 61.0, 56.5, 34.9, 32.8, 12.6;HRMS (ESI) *m/z*calcd for $C_{19}H_{20}N_2NaO_2$ [M + Na]$^{+}$: 331.1422; found: 331.1423.

Cis-1-ethyl-2'-methoxy-1',4-dimethyl-3,3'-spirobi[indolin]-2-one (5b)



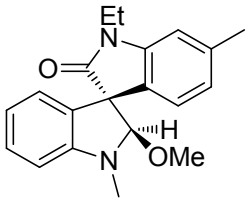
Yellow syrup (42.2 mg, 65%); IR (film) 2930, 2885, 1719, 1690, 1498, 1119, 956,725cm^{-1};1H NMR (400 MHz, CDCl3) δ 7.20 (t, J = 7.8 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.82 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.59 (t, J = 7.4 Hz, 1H), 6.54 (dd, J = 4.6, 3.4 Hz, 2H), 5.00 (s, 1H), 3.94 – 3.72 (m, 2H), 2.99 (s, 3H), 2.95 (s, 3H), 2.02 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H);13C NMR (101 MHz, CDCl3) δ 177.9, 150.7, 142.7, 138.3, 129.3, 128.3, 127.2, 126.5, 125.2, 123.2, 118.5, 106.7, 105.6, 103.9, 61.5, 56.2, 35.0, 32.9, 18.6, 12.6; HRMS (ESI) m/z calcd for $C_{20}H_{22}N_2NaO_2$ [M + Na]+: 345.1579; found: 345.1580.

Cis-1-Ethyl-2'-methoxy-1',5-dimethyl-3,3'-spirobi[indolin]-2-one(5c)



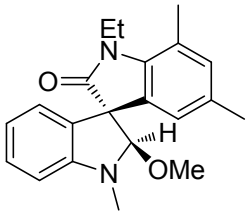
Yellow syrup(45.1 mg, 70%); IR (film) 2929, 2875, 1709, 1680, 1493, 1109, 955,745cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.04 (m, 3H), 6.80 (t, J = 7.7 Hz, 1H), 6.64 – 6.51 (m, 3H), 4.94 (s, 1H), 3.81 – 3.79 (m, 2H), 3.02 (s, 3H), 2.96 (s, 3H), 2.26 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 150.6, 139.9, 132.3, 129.6, 129.3, 128.8, 128.5, 127.3, 123.0, 118.8, 107.8, 107.4, 103.1, 61.0, 56.4, 35.0, 33.0, 21.0, 12.6; HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$: 345.1579; found: 345.1576.

Cis-1-Ethyl-2'-methoxy-1',6-dimethyl-3,3'-spirobi[indolin]-2-one(5d)



Yellow syrup (47.0 mg, 73%); IR (film) 2929, 2873, 1709, 1681, 1445, 1103, 950,748cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 2H), 6.84 (d, J = 7.6 Hz, 1H), 6.77 (s, 1H), 6.64 – 6.52 (m, 3H), 4.92 (s, 1H), 3.86 – 3.83 (m,2H), 3.05 (s, 3H), 2.98 (s, 3H), 2.42 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 150.8, 142.4, 139.4, 128.6, 128.4, 126.7, 126.6, 122.7, 122.6, 119.5, 108.3, 108.0, 103.2, 60.7, 56.5, 34.9, 32.8, 21.9 , 12.6;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$: 345.1579; found: 345.1583.

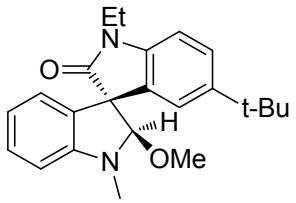
Cis-1-Ethyl-2'-methoxy-1',5,7-trimethyl-3,3'-spirobi[indolin]-2-one(5e)



Yellow syrup (43.0 mg, 64%); IR (film) 3053, 2925, 2892, 1707, 1681, 1484, 1341, 1097, 744cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 6.89 (d, J = 15.8 Hz, 2H), 6.64 – 6.56 (m, 3H), 4.95 (s, 1H), 4.17 – 3.99 (m, 2H), 3.04 (s, 3H), 2.97 (s, 3H), 2.56 (s, 3H), 2.22 (s, 3H), 1.26 (t,

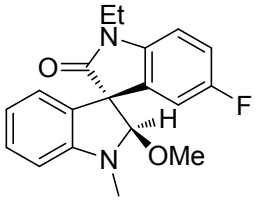
J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 150.6, 137.7, 132.9, 132.1, 130.1, 129.3, 129.2, 125.1, 123.0, 118.8, 118.6, 107.3, 103.3, 60.3, 56.4, 36.8, 33.0, 18.9, 18.4, 14.6;HRMS (ESI) *m/z*calcd for $C_{21}H_{24}N_2NaO_2$ $[M + Na]^+$: 359.1735; found: 359.1735.

Cis-5-Tert-butyl-1-ethyl-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5f)



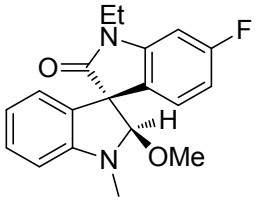
Yellow syrup (53.5 mg, 65%); IR (film) 3053, 2961, 2872, 1710, 1680, 1496, 1342, 1115, 980,769cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.23 – 7.12 (m, 1H), 6.89 – 6.85 (m, 1H), 6.63 – 6.54 (m, 3H), 4.85 (s, 1H), 3.85 – 3.79 (m, 2H), 3.03 (s, 3H), 3.00 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 150.9, 145.9, 140.6, 129.4, 127.7, 124.9, 124.6, 123.1, 118.3, 107.3, 106.8, 102.2, 61.3, 56.6, 34.9, 34.6, 32.4, 31.6, 12.7;HRMS (ESI) *m/z*calcd for $C_{23}H_{28}BrN_2NaO_2$ $[M + Na]^+$: 387.2048; found: 387.2048.

Cis-1-Ethyl-5-fluoro-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5g)



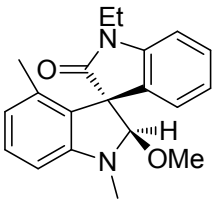
Yellow syrup (46.9 mg, 72%); IR (film) 3046, 2930, 2869, 1710, 1679, 1490, 1131, 959,748cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.7 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.88 – 6.85 (m, 1H), 6.67 – 6.55 (m, 3H), 4.95 (s, 1H), 3.87 – 3.82 (m, 2H), 3.08 (s, 3H), 2.99 (s, 3H), 1.32 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 159.2 (d, $J_{C\text{-}F}$ = 239.3 Hz), 150.6, 138.4, 130.1 (d, $J_{C\text{-}F}$ = 8.7 Hz), 129.6, 128.8, 122.9, 118.8, 114.9 (d, $J_{C\text{-}F}$ = 18.7 Hz), 114.7 (d, $J_{C\text{-}F}$ = 18.7 Hz),108.5 (d, $J_{C\text{-}F}$ = 8.7 Hz),107.5, 102.8, 61.2, 56.7, 35.1, 32.8, 12.5;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}FN_2NaO_2$ $[M + Na]^+$: 349.1328; found: 349.1330.

Cis-1-Ethyl-6-fluoro-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5h)



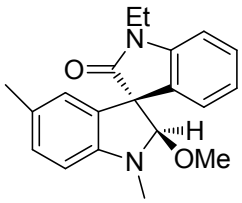
Yellow syrup (48.2 mg, 74%); IR (film) 3061, 2933, 2826, 1718, 1610, 1496, 1348, 1015, 821,746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 6.71 – 6.52 (m, 5H), 4.88 (s, 1H), 3.84 – 3.77 (m, 2H), 3.03 (s, 3H), 2.96 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 163.4 (d, $J_{C\text{-}F}$ = 243.8 Hz), 150.6, 144.0 (d, $J_{C\text{-}F}$ = 11.4 Hz), 129.3, 127.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 123.6 (d, $J_{C\text{-}F}$ = 3.0 Hz),122.9, 118.8, 108.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 107.3, 102.7, 96.9 (d, $J_{C\text{-}F}$ = 27.5 Hz), 60.6, 56.6, 35.2, 32.7, 26.9, 12.6;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}FN_2NaO_2$ [M + Na]$^{+}$: 349.1328; found: 349.1325.

Cis-1-Ethyl-2'-methoxy-1',4'-dimethyl-3,3'-spirobi[indolin]-2-one(5k)



Yellow syrup (42.5 mg, 66%); IR (film) 3053, 2932, 2824, 1711, 1596, 1483, 1352, 1098, 904,751cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 1H), 7.21 – 7.19 (m, 1H), 7.12 – 7.06 (m, 1H), 7.05 – 7.01 (m, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.51 – 6.40 (m, 2H), 4.95 (s, 1H), 3.98 – 3.83 (m, 2H), 3.04 (s, 3H), 2.92 (s, 3H), 2.11 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 151.0, 142.3, 134.4, 129.4, 128.4, 126.9, 126.8, 126.6, 122.8, 121.2, 107.9, 105.2, 104.1, 61.1, 56.5, 35.0, 33.2, 17.1, 12.3;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ [M + Na]$^{+}$: 345.1579; found: 345.1577.

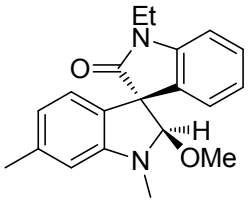
Cis-1-Ethyl-2'-methoxy-1',5'-dimethyl-3,3'-spirobi[indolin]-2-one(5l)



Yellow syrup (43.8 mg, 68%); IR (film) 3053, 2932, 1713, 1611, 1352, 1098, 962,751cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 6.9 Hz, 1H), 7.00 (t, J = 7.3, 1H),

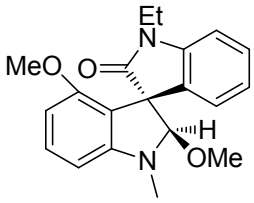
6.94 (t, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 4.90 (s, 1H), 3.91 – 3.78 (m, 2H), 3.01 (d, *J* = 3.9 Hz, 3H), 2.92 (s, 3H), 2.11 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 150.8, 142.4, 139.4, 128.6, 128.4, 126.7, 126.6, 122.7, 122.6, 119.5, 108.3, 108.0, 103.2, 60.7, 56.5, 34.9, 32.8, 21.9, 12.6; HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$: 345.1579; found: 345.1576.

Cis-1-Ethyl-2'-methoxy-1',6'-dimethyl-3,3'-spirobi[indolin]-2-one(5m)



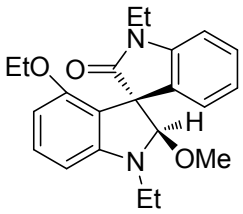
Yellow syrup (41.9 mg, 65%); IR (film) 3052, 2935, 2842, 1710, 1607,1486, 1094, 752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.47 – 6.38 (m, 3H), 4.91 (d, *J* = 5.9 Hz, 1H), 3.90 – 3.79 (m, 2H), 3.01 (s, 3H), 2.94 (s, 3H), 2.28 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 150.8, 142.4, 139.4, 128.6, 128.4, 126.7, 126.6, 122.7, 122.6, 119.5, 108.3, 108.0, 103.2, 60.7, 56.5, 34.9, 32.8, 21.9, 12.6;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$: 345.1579; found: 345.1570.

Cis-1-Ethyl-2',4'-dimethoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5n)



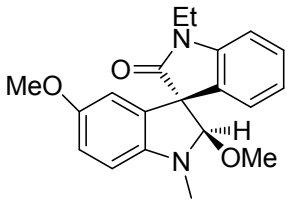
Yellow syrup (48.0 mg, 71%); IR (film) 3055, 2936, 2822, 1712, 1610, 1485, 1356, 1093, 968,737cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.22 – 7.20 (m, 1H), 7.13 (t, *J* = 8.1 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 8.3 Hz, 1H), 5.00 (s, 1H), 4.06 – 3.94 (m, 1H), 3.80 – 3.75 (m, 1H), 3.49 (s, 3H), 3.02 (s, 3H), 2.91 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 155.4, 152.0, 142.4, 130.6, 128.1, 127.4, 125.9, 122.3, 115.8, 107.6, 104.4, 102.7, 101.2, 59.2, 56.1, 55.2, 34.8, 33.5, 12.4;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_3$ $[M + Na]^+$: 361.1528; found: 361.1525.

Cis-4'-Ethoxy-1,1'-diethyl-2'-methoxy-3,3'-spirobi[indolin]-2-one(5o)



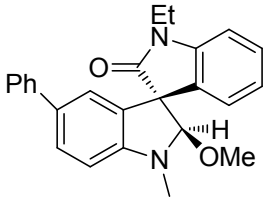
Yellow syrup (52.7 mg, 72%); IR (film) 2977, 1710, 1680, 1467, 1095, 918,749cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.19 – 7.17 (m, 1H), 7.05 (t, J = 8.1 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.21 (d, J = 7.8 Hz, 1H), 6.11 (d, J = 8.2 Hz, 1H), 5.14 (s, 1H), 3.92 – 3.87 (m, 1H), 3.83 – 3.73 (m, 2H), 3.64 – 3.56 (m, 1H), 3.43 – 3.33 (m, 2H),2.91 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 155.0, 150.9, 142.9, 130.5, 127.9, 127.7, 126.1, 122.2, 115.9, 107.4, 102.8, 101.1, 100.6, 63.2, 59.4, 55.7, 40.0, 34.9, 14.5, 12.6, 11.3;HRMS (ESI) *m/z*calcd for $C_{22}H_{26}N_2NaO_3$ $[M + Na]^+$: 389.1841; found: 389.1837.

Cis-1-Ethyl-2',5'-dimethoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5p)



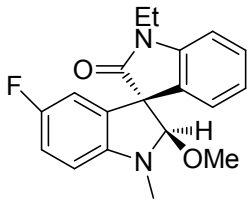
Yellow syrup (43.3 mg, 64%); IR (film) 3055, 2934, 2832, 1710, 1608, 1493, 1351, 1098, 1028,752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.73 – 6.71 (m, 1H), 6.55 – 6.48 (m, 1H), 6.18 (d, J = 2.5 Hz, 1H), 4.88 (s, 1H), 3.90 – 3.82 (m, 2H), 3.62 (s, 3H), 3.03 (s, 3H), 2.91 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 153.5, 145.1, 142.3, 130.5, 128.5, 128.3, 126.7, 122.8, 114.2, 110.3, 108.2, 108.1, 103.8, 61.1, 56.5, 55.9, 35.0, 34.0, 12.6;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_3$ $[M + Na]^+$: 361.1528; found: 361.1528.

Cis-1-Ethyl-2'-methoxy-1'-methyl-5'-phenyl-3,3'-spirobi[indolin]-2-one(5q)



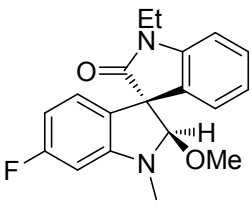
Yellow syrup (53.8 mg, 70%); IR (film) 3054, 2934, 2843, 1710, 1608, 1493, 1351, 1098, 1028, 752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4H), 7.37 – 7.28 (m, 3H), 7.22 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 1.7 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 5.00 (s, 1H), 3.95 – 3.85 (m, 2H), 3.07 (s, 3H), 3.05 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 150.2, 142.6, 141.4, 132.1, 129.9, 128.6, 128.6, 128.5, 128.2, 127.4,126.9, 126.5, 126.2, 122.8, 122.0, 108.2, 107.4, 103.0, 61.0, 56.7, 35.0, 32.7, 27.0, 12.7;HRMS (ESI) *m/z*calcd for $C_{25}H_{24}N_2NaO_2$ $[M + Na]^+$: 407.1735; found: 407.1731.

Cis-1-Ethyl-5'-fluoro-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5r)



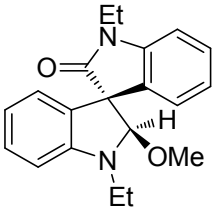
Yellow syrup (47.6 mg, 73%); IR (film) 3057, 2932, 2826, 1711, 1611, 1486, 1354, 1097, 945,755cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 1H), 7.30 – 7.25 (m, 1H), 7.07 – 7.03 (m 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.90 – 6.81 (m, 1H), 6.52 – 6.49 (m, 1H), 6.33 – 6.30 (m, 1H), 4.93 (s, 1H), 3.94 – 3.81 (m, 2H), 3.05 (s, 3H), 2.96 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 156.7 (d, $J_{C\text{-}F}$ = 234.7 Hz), 147.1, 142.4, 130.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.8, 127.8, 126.7, 122.9, 115.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 110.8 (d, $J_{C\text{-}F}$ = 24.6 Hz), 108.3, 107.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 103.3, 60.9, 56.6, 35.0, 33.3, 12.6;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}FN_2NaO_2$ $[M + Na]^+$: 349.1328; found: 349.1322.

Cis-1-Ethyl-6'-fluoro-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5s)



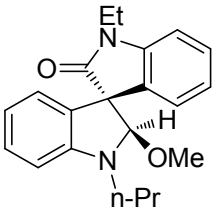
Yellow syrup (45.6 mg, 70%); IR (film) 3058, 2932, 2823, 1712, 1609, 1494, 1352, 1094, 1026,752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.28 – 7.25 (m, 1H), 7.07 – 7.03 (m, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.50 – 6.43 (m, 1H), 6.31 – 6.23 (m, 2H), 4.94 (s, 1H), 3.90 – 3.74 (m, 2H), 3.03 (s, 3H), 2.97 (s, 3H), 1.33(t, J = 7.2 Hz ,3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 164.5 (d, J_{C-F} = 241.9 Hz), 152.3 (d, J_{C-F} = 12.1 Hz), 142.6, 128.7, 128.0, 126.8, 124.6, 123.8 (d, J_{C-F} = 10.8 Hz), 122.8, 108.2, 104.4 (d, J_{C-F} = 23.2 Hz), 102.8, 95.2 (d, J_{C-F} = 27.4 Hz), 60.3, 56.7, 35.0, 32.2, 12.6;HRMS (ESI) *m/z*calcd for $C_{19}H_{19}FN_2NaO_2$ $[M + Na]^+$: 349.1328; found: 349.1331.

Cis-1,1'-Diethyl-2'-methoxy-3,3'-spirobi[indolin]-2-one(5t)



Yellow syrup (46.4 mg, 72%); IR (film) 3054, 2975, 2884, 1710, 1678, 1607,1489, 1353, 1095, 987,747cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2H), 7.17 – 7.13 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.58 (t, J = 7.1 Hz, 2H), 6.54 – 6.52 (m, 1H), 5.07 (s, 1H), 3.95 – 3.72 (m, 2H), 3.52 – 3.39 (m, 2H), 2.98 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 5.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 149.6, 142.6, 129.4, 129.2, 128.5, 128.4, 126.8, 123.1, 122.7, 118.1, 108.0, 107.0, 100.1, 60.9, 56.1, 39.7, 34.9, 12.6, 11.9;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ $[M + Na]^+$: 345.1579; found: 345.1579.

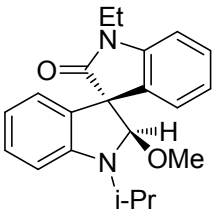
Cis-1-Ethyl-2'-methoxy-1'-propyl-3,3'-spirobi[indolin]-2-one(5u)



Yellow syrup (51.7 mg, 77%); IR (film) 2967, 1710, 1677, 1489, 1355, 1265, 1091,900,742cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.14 – 7.12 (m, 1H), 7.06 – 7.02 (m, 1H), 6.96 (t, J = 7.9 Hz, 1H), 6.60 – 6.48 (m, 3H), 5.03 (s, 1H), 3.93 – 3.81 (m, 2H), 3.38 – 3.27 (m, 2H),

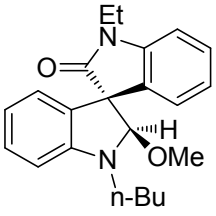
2.97 (s, 3H), 1.83 – 1.70 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 150.1, 142.7, 129.2, 129.1, 128.5,128.4, 126.9, 123.1, 122.7, 117.8, 108.0, 106.6, 100.7, 61.0, 56.2, 47.3, 34.9, 20.7, 12.7, 11.7;HRMS (ESI) *m/z*calcd for $C_{21}H_{24}N_2NaO_2$ [M + Na]$^+$: 359.1735; found: 359.1737.

Cis-1-Ethyl-1'-isopropyl-2'-methoxy-3,3'-spirobi[indolin]-2-one(5v)



Yellow syrup (53.8 mg, 80%); IR (film) 3057, 2972, 1710, 1672, 1489, 1087, 942,752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.21 – 7.09 (m, 1H), 7.07 – 7.03 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.62 (d, J = 7.9 Hz, 1H), 6.56 (t, J = 7.4 Hz, 1H), 6.48 – 6.46 (m, 1H), 5.02 (s, 1H), 3.99 – 3.93 (m, 1H), 3.84 (q, J = 7.2 Hz, 2H), 2.87 (s, 3H), 1.40 (dd, J = 6.7, 4.7 Hz, 6H), 1.33 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 149.5, 143.0, 129.4, 129.1, 128.4, 127.2, 123.2, 122.7, 117.7, 107.9, 107.4, 97.6, 61.0, 55.2, 46.8, 34.8, 21.1, 21.1, 19.4, 12.7;HRMS (ESI) *m/z*calcd for $C_{21}H_{24}N_2NaO_2$ [M + Na]$^+$: 359.1735; found: 359.1730.

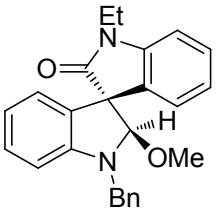
Cis-1'-Butyl-1-ethyl-2'-methoxy-3,3'-spirobi[indolin]-2-one(5w)



Yellow syrup (51.8 mg, 74%); IR (film) 305, 2931, 2870, 1710, 1678, 1490, 1355, 1089, 940,749cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 1H), 7.30 – 7.27 (m, 1H), 7.16 – 7.11 (m, 1H), 7.06 – 7.02 (m, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.59 – 6.53 (m, 2H), 6.52 – 6.50 (m, 1H), 5.04 (s, 1H), 3.86 (q, J = 7.2 Hz, 2H), 3.39 – 3.31 (m, 2H), 2.97 (s, 3H), 1.78 – 1.68 (m, 2H), 1.51 – 1.46 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 150.0, 142.7, 129.2, 129.1, 128.5, 128.4, 126.9, 123.0, 122.7, 117.9, 108.0, 106.6, 100.7, 61.0, 56.2, 45.2, 34.9, 29.4, 20.4, 14.0, 12.7;HRMS (ESI) *m/z*calcd for $C_{22}H_{26}N_2NaO_2$ [M + Na]$^+$:

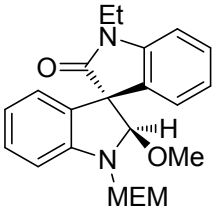
373.1892; found: 373.1893.

Cis-1'-Benzyl-1-ethyl-2'-methoxy-3,3'-spirobi[indolin]-2-one(5x)



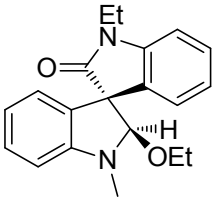
Yellow syrup (53.0 mg, 69%); IR (film) 3057, 2931, 2874, 1711, 1607, 1490, 1353, 1102, 936,743cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.3 Hz, 2H), 7.39 – 7.34 (m, 5H), 7.10 – 7.04 (m, 2H), 6.96 (d, J = 7.9 Hz, 1H), 6.64 – 6.53 (m, 2H), 6.44 (d, J = 7.9 Hz, 1H), 5.04 (s, 1H), 4.67 (d, J = 16.0 Hz, 1H), 4.51 (d, J = 16.0 Hz, 1H), 3.89 – 3.83 (m, 2H), 2.92 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 150.0, 142.9, 137.8, 129.3, 139.3, 129.1, 128.9, 128.6, 128.1, 127.5, 127.5,127.5, 127.1, 123.1, 122.7, 118.3, 108.0, 107.0, 100.7, 61.0, 56.5, 49.2, 34.9, 12.7;HRMS (ESI) *m/z*calcd for $C_{25}H_{24}N_2NaO_2$ $[M + Na]^+$: 407.1735; found: 407.1727.

Cis-1-Ethyl-2'-methoxy-1'-((2-methoxyethoxy)methyl)-3,3'-spirobi[indolin]-2-one(5y)



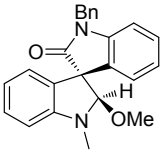
Yellow syrup (48.9 mg, 64%); IR (film) 3055, 2929, 2865, 1712, 1608, 1480, 1092, 938,746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.28 – 7.24 (m, 1H), 7.17 – 7.12 (m, 1H), 7.05 – 7.00 (m, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.66 – 6.61 (m, 1H), 6.52 – 6.50 (m, 1H), 5.12 (s, 1H), 4.97 (s, 2H), 3.85 – 3.73 (m, 4H), 3.61 – 3.58 (m, 2H), 3.40 (s, 3H), 3.01 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 148.7, 142.9, 129.3, 129.2, 128.6, 128.0, 127.1, 123.3, 122.8, 119.4, 108.1, 107.8, 98.7, 76.9, 72.1, 67.1, 61.1, 59.0, 56.6, 34.9, 12.7;HRMS (ESI) *m/z*calcd for $C_{22}H_{26}N_2NaO_4$ $[M + Na]^+$: 405.1790; found: 405.1792.

Cis-2'-Ethoxy-1-ethyl-1'-methyl-3,3'-spirobi[indolin]-2-one(5ab)



Yellow syrup (34.1 mg, 53%); IR (film) 3052, 2926, 1709, 1680, 1489, 1352, 1094, 747cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 1H), 7.26 (s, 1H), 7.19 – 7.15 (m, 1H), 7.05 – 7.00 (m, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.63 – 6.55 (m, 3H), 5.03 (s, 1H), 3.90 – 3.81 (m, 2H), 3.39 – 3.33 (m, 1H), 3.00 – 2.92 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 150.8, 142.5, 129.3, 129.2, 128.8, 128.4, 126.8, 123.0, 122.6, 118.6, 108.0, 107.2, 101.4, 64.5, 61.2, 34.9, 32.5, 14.7, 12.6;HRMS (ESI) *m/z*calcd for $C_{20}H_{22}N_2NaO_2$ [M + Na]$^+$: 345.1579; found: 345.1580.

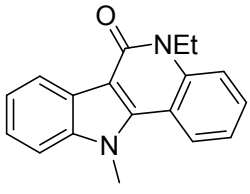
Cis-1-Benzyl-2'-methoxy-1'-methyl-3,3'-spirobi[indolin]-2-one(5ae)



Yellow solid (48.8mg, 66%), mp: 139.5 – 141.7^{o}C; IR (film) 3049, 2963, 2872, 1635, 1425, 1275, 1010, 851, 747cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 6H), 7.26 – 7.17 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.67 – 6.57 (m, 3H), 5.06 (d, J = 15.5 Hz, 1H), 5.00 (d, J = 6.9 Hz, 1H), 4.96 (d, J = 15.5 Hz, 1H), 3.04 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 150.7, 142.6, 136.0, 129.4, 129.4, 129.3, 128.9, 128.5, 128.5, 128.1, 127.8, 127.5, 126.7, 123.1, 118.7, 109.0, 107.3, 102.9, 61.0, 56.8, 44.1, 32.7, 26.9;HRMS (ESI) *m/z*calcd for $C_{24}H_{22}N_2NaO_2$ [M + Na]$^+$: 393.1579; found: 393.1572.

Characterization of 6

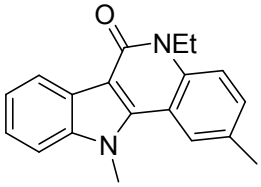
5-Ethyl-11-methyl-5H-indolo[3,2-c]quinolin-6(11H)-one (6a)



White solid (47.5 mg, 86%), mp: 172.5 – 174.3 ^{o}C; IR (film) 3050, 2959,1687, 1465, 1280, 1014, 841, 745cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 7.5 Hz, 1H), 8.37 (d, J = 8.1 Hz, 1H),

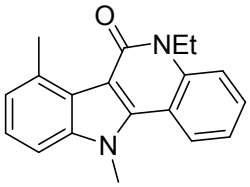
7.55 – 7.40 (m, 4H), 7.40 – 7.31 (m, 2H), 4.51 (q, J = 7.1 Hz, 2H), 4.37 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 140.8, 135.0, 126.3, 126.2, 125.9, 124.0, 122.7, 122.3, 121.8, 121.0, 120.1, 118.6, 114.9, 110.5, 37.2, 31.6, 13.2;HRMS (ESI) *m/z*calcd for $C_{18}H_{16}N_2NaO$ $[M + Na]^+$: 299.1160; found: 299.1151.

5-Ethyl-2,11-dimethyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6b)



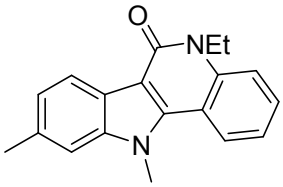
White solid (44.7mg, 77%), mp: 154.3 – 156.7°C; IR (film) 3043, 2931, 1676, 1462, 1243, 1004, 851, 723cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.1 Hz, 1H), 8.21 (s, 1H), 7.51 (d, J = 3.8 Hz, 2H), 7.34 (dd, J = 12.0, 6.3 Hz, 2H), 7.26 (d, J = 7.4 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.36 (s, 3H), 2.53 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 140.7, 133.0, 131.8, 127.3, 126.4, 125.8, 124.0, 122.8, 121.8, 120.8, 120.0, 118.4, 114.8, 110.5,37.2, 31.5, 21.1, 13.2;HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO$ $[M + Na]^+$: 313.1317; found: 313.1316.

5-Ethyl-7,11-dimethyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6d)



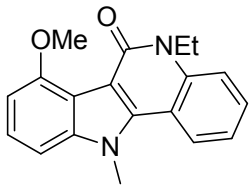
White solid (43.5mg, 75%), mp: 139.5 – 141.8°C; IR (film) 3051, 2986, 1680, 1442, 1305, 1024, 851, 740cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.49 – 7.36 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 6.7 Hz, 1H), 4.57 – 4.47 (m, 2H), 4.40 (s, 3H), 3.05 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 141.7, 134.9, 132.7, 127.2, 126.9, 126.0, 125.9, 124.1, 121.8, 121.4, 120.3, 119.6, 114.8, 108.2, 37.4, 31.8, 26.1, 13.0; HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO$ $[M + Na]^+$: 313.1317; found: 313.1306.

5-Ethyl-9,11-dimethyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6e)



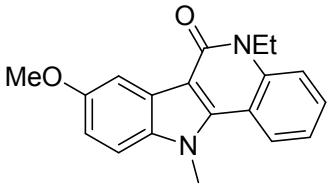
White solid (42.3mg, 73%), mp: 142.1 – 143.9°C; IR (film) 3033, 2956, 1680, 1423, 1313, 1034, 848, 754cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 7.8 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.36 (dd, J = 16.1, 8.9 Hz, 2H), 7.19 (d, J = 8.2 Hz, 1H), 4.52 (q, J = 7.0 Hz, 2H), 4.37 (s, 3H), 2.59 (s, 3H), 1.44 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 141.3, 136.3, 135.1, 126.1, 126.0, 124.0, 122.9, 122.3, 122.3, 120.1, 119.6, 118.8, 114.9, 110.4, 37.2, 31.5, 22.2, 13.2;HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO$ $[M + Na]^+$: 313.1317; found: 313.1302.

5-Ethyl-7-methoxy-11-methyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6f)



Yellow oil (42.8mg, 70%); IR (film) 3033, 2965, 1682, 1453, 1310, 1004, 852, 742cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, J = 8.2 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.37 (s, 3H), 4.09 (s, 3H), 1.43 (dd, J = 8.8, 4.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 155.2, 142.8, 135.0, 128.5, 127.0, 126.2, 125.8, 121.8, 120.5, 119.6, 114.4, 112.6, 103.4, 101.3, 55.5, 46.3, 37.3, 13.1;HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO_2$ $[M + Na]^+$: 329.1266; found: 329.1256.

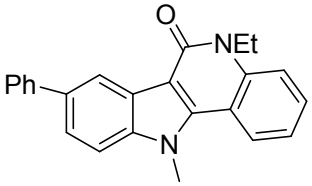
5-Ethyl-8-methoxy-11-methyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6g)



White solid (44.1mg, 72%), mp: 156.4 – 158.5°C; IR (film) 3023, 2934, 1674, 1425, 1350, 1008, 832, 761cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 7.8 Hz, 1H), 7.73 (s, 1H), 7.52 – 7.33 (m, 4H), 7.19 (d, J = 9.0 Hz, 1H), 4.49 (q, J = 7.0 Hz, 2H), 4.34 (s, 3H), 3.98 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 154.9, 136.1, 134.9, 126.6, 125.9, 123.6, 122.2,

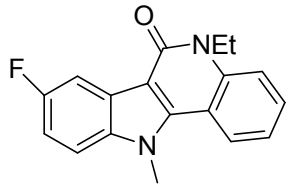
121.8, 120.2, 117.9, 116.4, 114.9, 111.3, 104.1,56.1, 37.2, 31.6, 13.2;HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO_2$ $[M + Na]^+$: 329.1266; found: 329.1256.

5-Ethyl-11-methyl-8-phenyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6h)



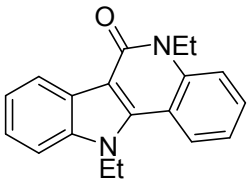
White solid (53.5mg, 76%), mp: 193.9 – 194.8°C; IR (film) 3045, 2954, 1682, 1465, 1296, 1023, 847, 746cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.43 (m, 2H), 7.75 (dd, J = 13.4, 8.3 Hz, 3H), 7.58 (d, J = 8.7 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.38 (t, J = 7.4 Hz, 2H), 4.52 (q, J = 7.0 Hz, 2H), 4.40 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 142.6, 140.2, 135.1, 134.6, 128.9, 127.6, 126.9, 126.9, 126.8, 126.3, 125.8, 124.0, 122.4, 122.4, 122.3, 121.2, 120.0, 118.8, 114.9, 110.8, 37.3, 31.7, 13.2;HRMS (ESI) *m/z*calcd for $C_{24}H_{20}N_2NaO$ $[M + Na]^+$: 375.1473; found: 375.1460.

5-Ethyl-8-fluoro-11-methyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6i)



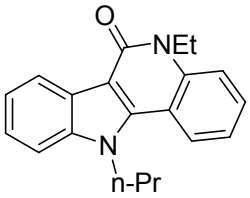
White solid (40.2mg, 69%), mp: 201.7 – 203.2°C; IR (film) 3052, 2956, 1676, 1465, 1300, 1024, 846, 744cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.8 Hz, 1H), 8.06 – 7.95 (m, 1H), 7.52 – 7.45 (m, 3H), 7.41 (q, J = 6.6 Hz, 1H), 7.32 – 7.28 (m, 1H), 4.52 (q, J = 7.1 Hz, 2H), 4.38 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 235.6 Hz), 156.4, 137.3, 134.9, 127.3, 126.3, 123.6, 122.5, 121.6(d, $J_{C\text{-}F}$ = 10.2 Hz), 119.7, 118.2, 114.8 (d, $J_{C\text{-}F}$ = 20.1 Hz), 114.5, 111.4(d, $J_{C\text{-}F}$ = 10.1 Hz), 107.6 (d, $J_{C\text{-}F}$ = 20.3 Hz), 37.3, 31.7, 13.1;HRMS (ESI) *m/z*calcd for $C_{18}H_{15}N_2FNaO$ $[M + Na]^+$: 317.1066; found: 317.1053.

5,11-Diethyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6j)



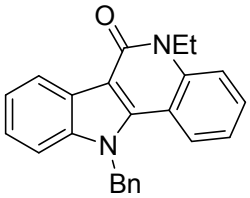
White solid (47.6mg, 82%), mp: 168.3 – 170.2°C; IR (film) 3029, 2963, 1691, 1456, 1301, 1004, 847, 749cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.8 Hz, 1H), 8.44 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.38 (dd, J = 17.4, 7.7 Hz, 2H), 4.98 (q, J = 7.1 Hz, 2H), 4.55 (q, J = 7.1 Hz, 2H), 1.53 – 1.43 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 139.7, 135.1, 126.2, 125.9, 125.8, 124.0, 122.9, 122.3, 122.0, 120.9, 120.0, 118.8, 114.9, 110.6, 39.7, 37.3, 16.0, 13.2;HRMS (ESI) *m/z*calcd for $C_{19}H_{18}N_2NaO$ $[M + Na]^+$: 313.1317; found: 313.1303.

5-Ethyl-11-propyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6k)



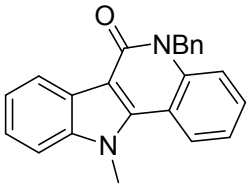
White solid (48.0mg, 79%), mp: 150.3 – 152.7°C; IR (film) 3045, 2953, 1678, 1425, 1296, 1034, 861, 735cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H), 7.57 – 7.43 (m, 4H), 7.35 (dd, J = 18.1, 7.5 Hz, 2H), 4.92 – 4.78 (m, 2H), 4.52 (q, J = 7.1 Hz, 2H), 1.99 – 1.85 (m, 2H), 1.44 (t, J = 7.0 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 140.1, 135.1, 126.2, 126.1, 125.8, 124.0, 122.8, 122.3, 121.9, 120.8, 120.0, 118.7, 114.9, 110.9, 46.3, 37.3, 24.2, 13.2, 11.4;HRMS (ESI) *m/z*calcd for $C_{20}H_{20}N_2NaO$ $[M + Na]^+$: 327.1473; found: 327.1454.

11-Benzyl-5-ethyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6l)



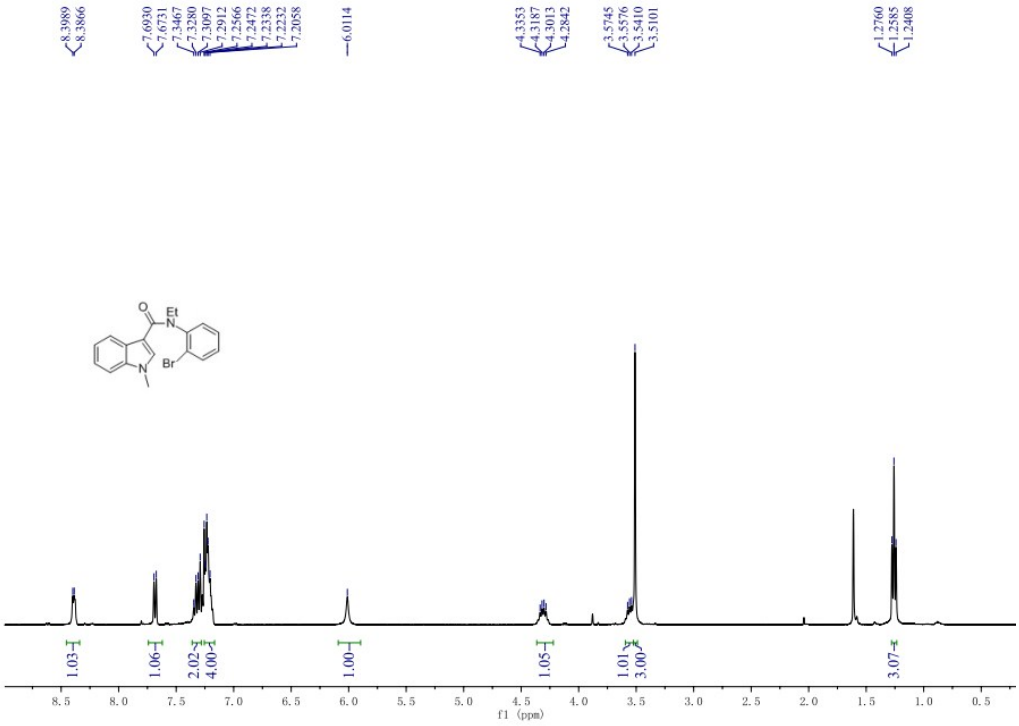
White solid (55.6mg, 79%), mp: 147.5 – 149.3°C; IR (film) 3050, 2951, 1695, 1467, 1289, 1015, 821, 765cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.9 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.46 – 7.36 (m, 2H), 7.29 – 7.24 (m, 2H), 7.22 (t, J = 6.5 Hz, 3H), 6.26 (s, 2H), 4.55 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 140.4, 138.5, 135.2, 128.6, 127.1, 126.7, 126.7, 126.5, 126.1, 126.0, 124.1, 122.8, 122.4, 122.4, 122.2, 121.3, 119.9, 119.2, 114.9, 111.4, 47.9, 37.3, 13.2; HRMS (ESI) *m/z*calcd for $C_{24}H_{20}N_2NaO$ $[M + Na]^+$: 375.1473; found: 375.1461.

5-Benzyl-11-methyl-5H-indolo[3,2-c]quinolin-6(11H)-one(6m)

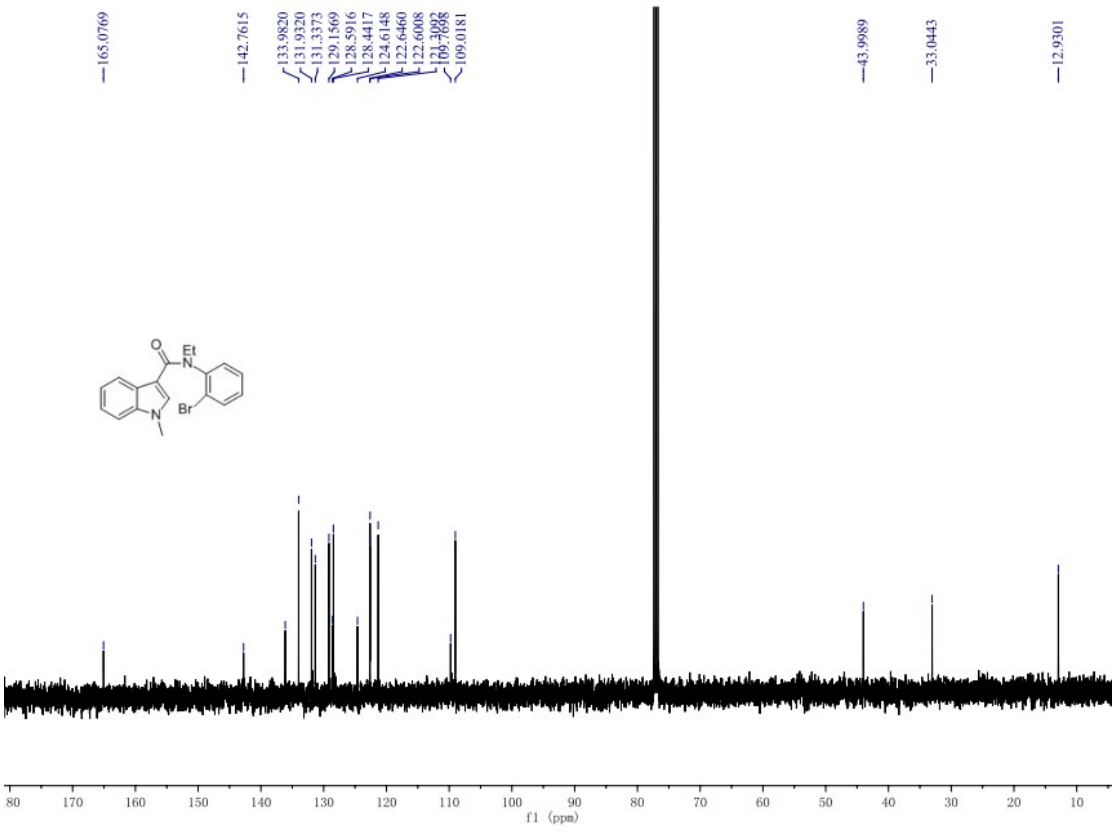


White solid (46.0mg, 68%), mp: 190.5 – 192.3°C; IR (film) 3045, 2963, 1665, 1435, 1278, 1023, 847, 740cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, J = 21.5, 7.9 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.38 – 7.31 (m, 4H), 7.28 (d, J = 7.0 Hz, 2H), 7.23 (d, J = 7.3 Hz, 3H), 5.70 (s, 2H), 4.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 140.9, 136.9, 135.6, 128.8, 127.2, 126.4, 126.3, 126.2, 126.2, 126.1, 123.8, 122.8, 122.8, 122.6, 121.8, 121.1,120.0, 119.1, 115.9, 110.7, 45.9, 31.7;HRMS (ESI) *m/z*calcd for $C_{23}H_{18}N_2NaO$ $[M + Na]^+$:361.1317; found: 361.1302.

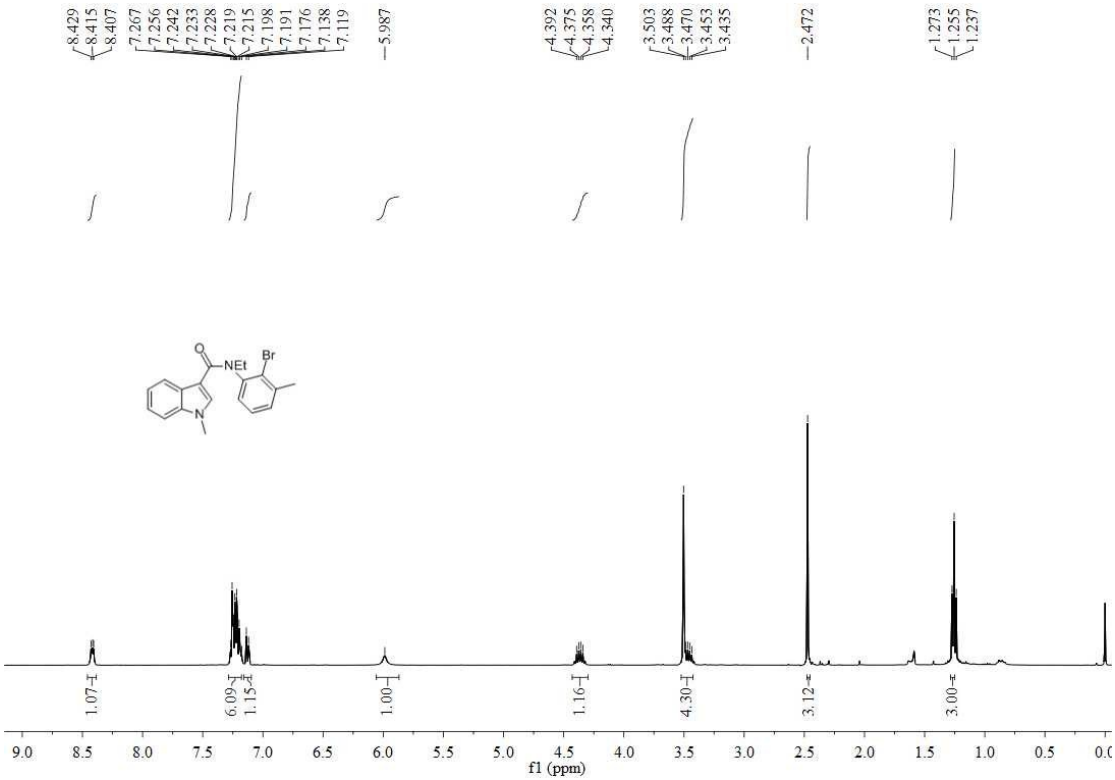
Spectra of all the new compounds



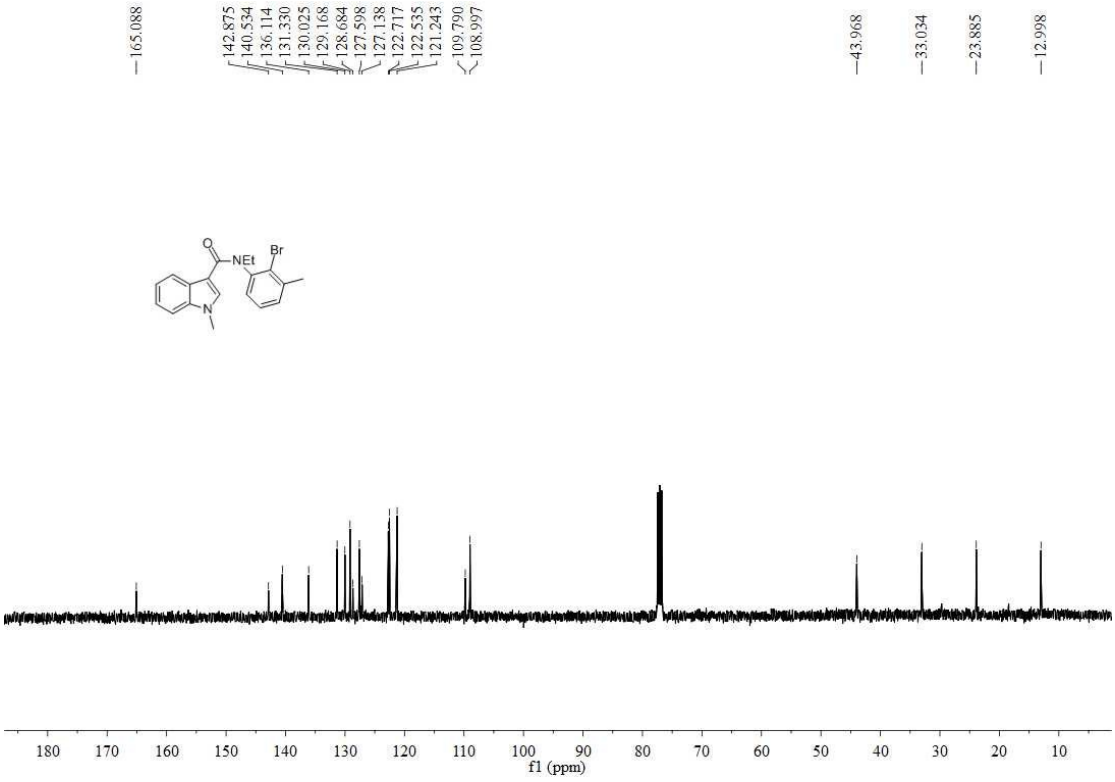
^{1}H NMR spectrum of **4a**



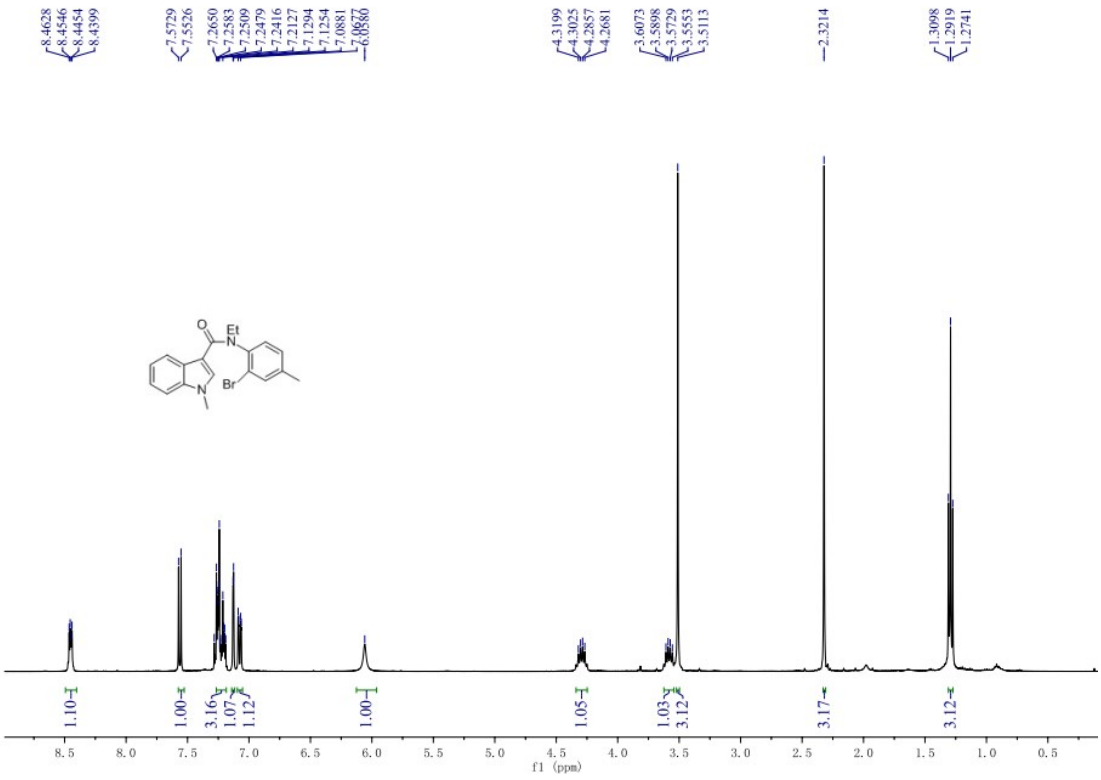
^{13}C NMR spectrum of **4a**



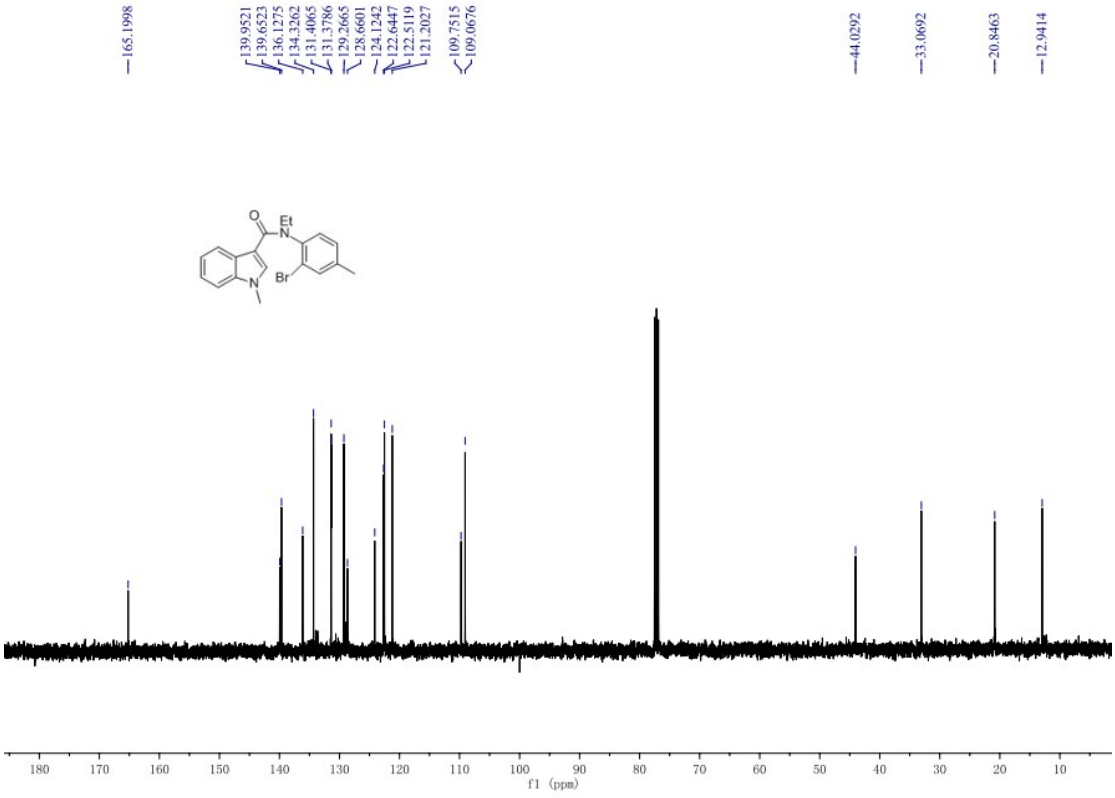
^{1}H NMR spectrum of **4b**



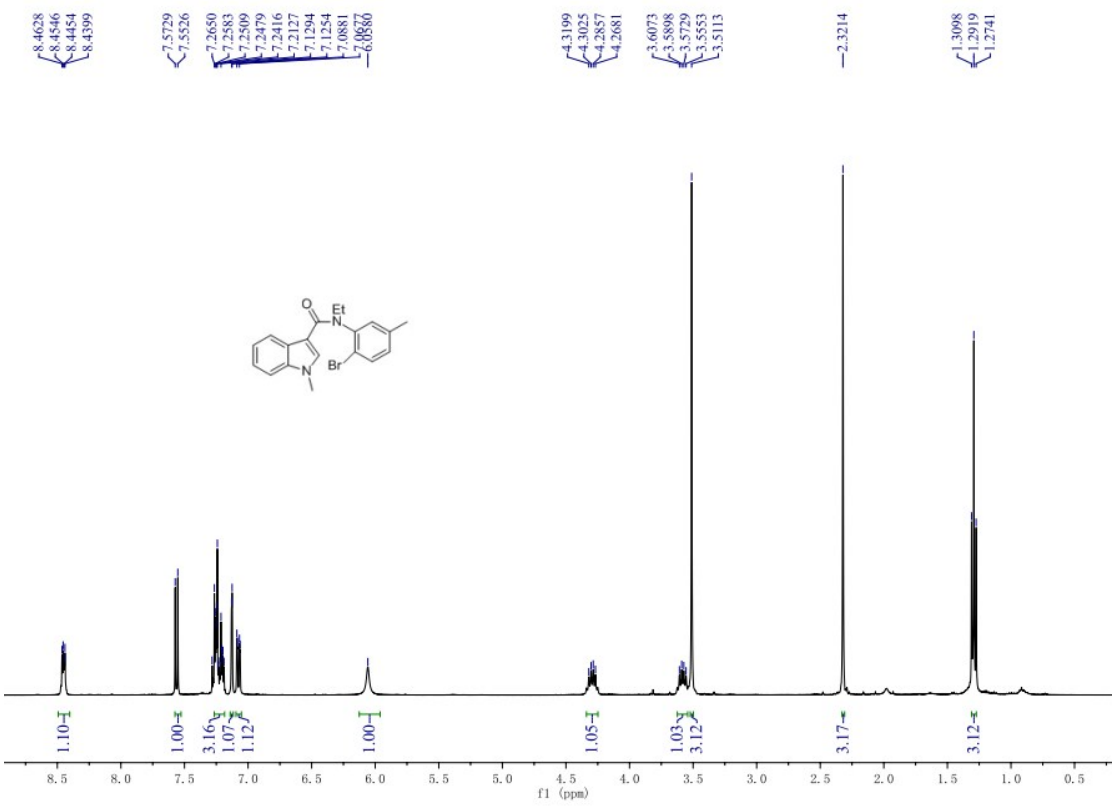
^{13}C NMR spectrum of **4b**



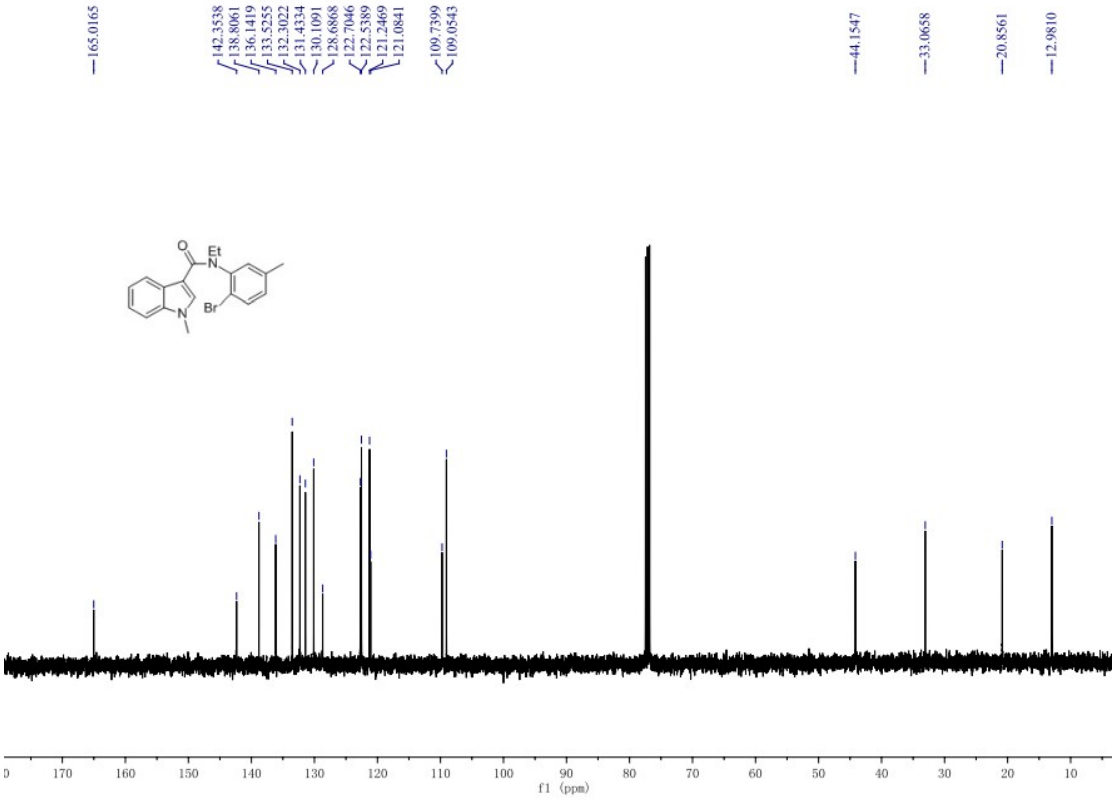
^{1}H NMR spectrum of **4c**



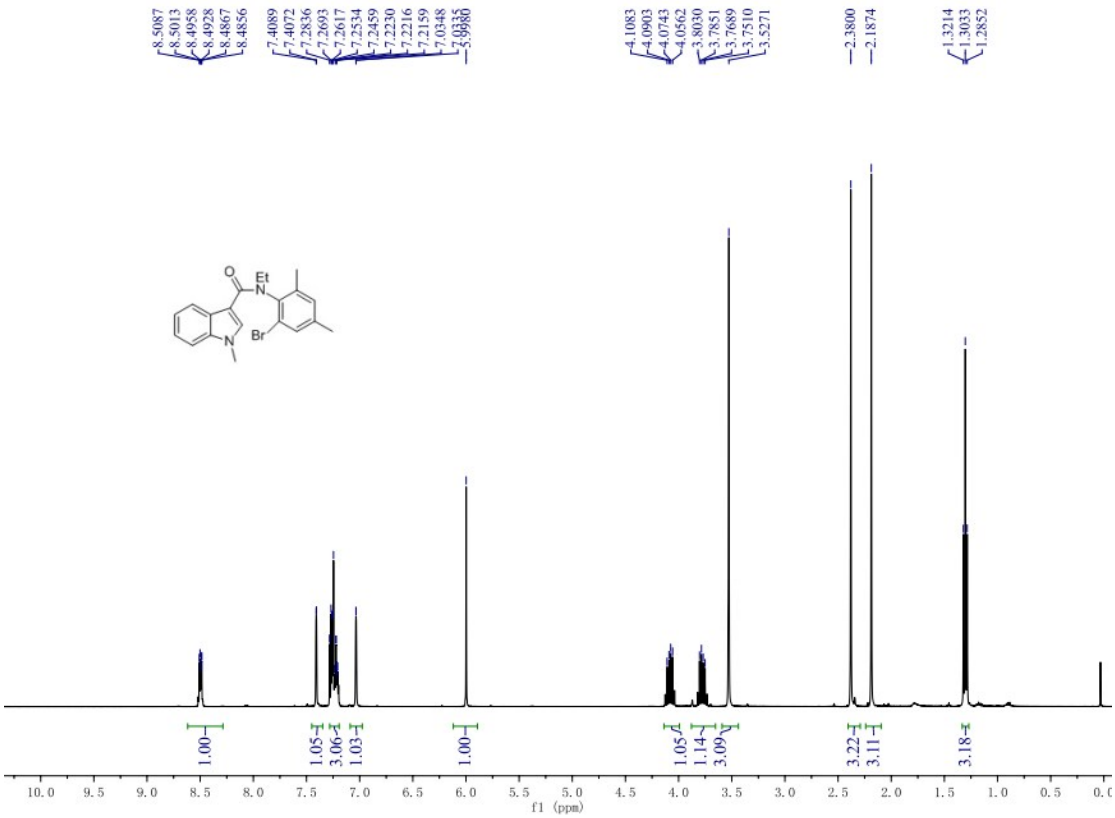
^{13}C NMR spectrum of **4c**



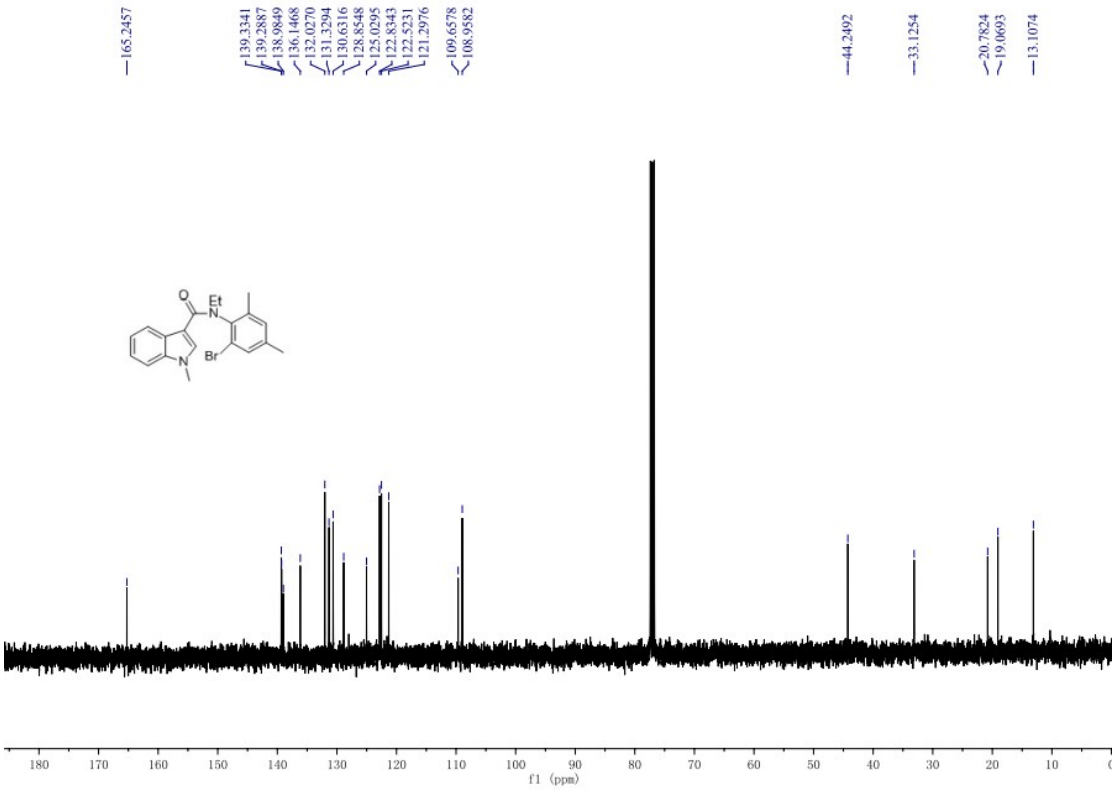
^{1}H NMR spectrum of **4d**



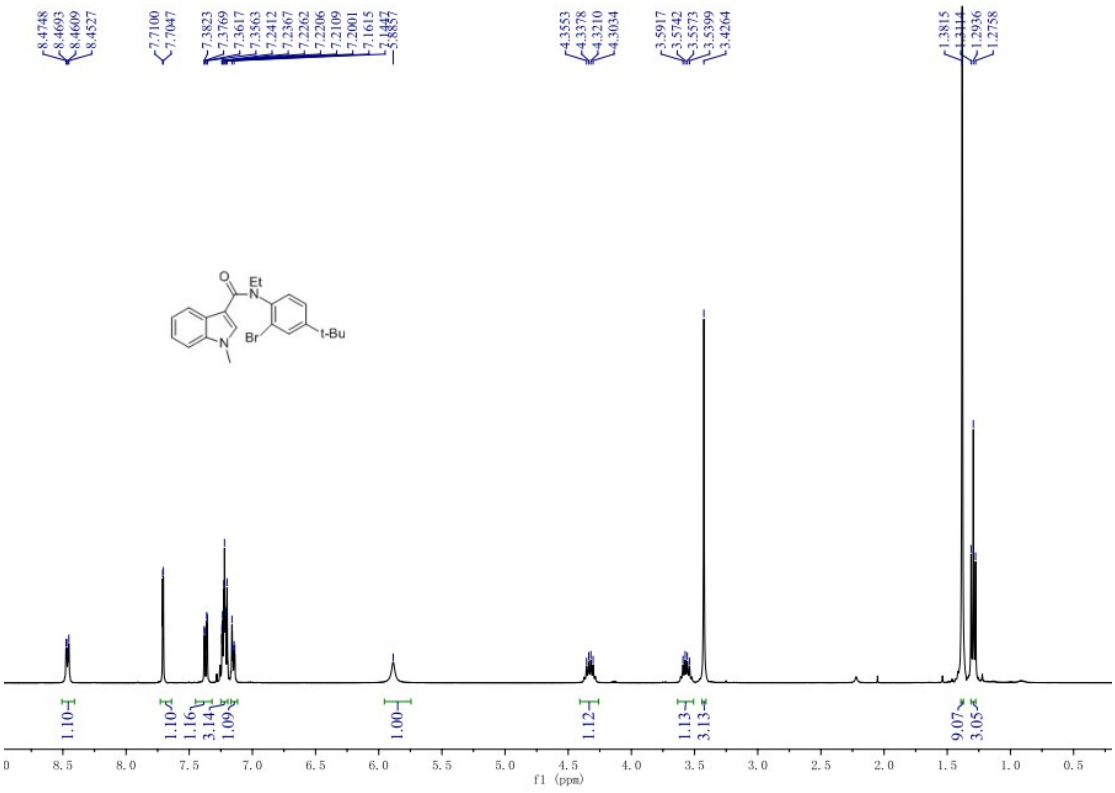
^{13}C NMR spectrum of **4d**



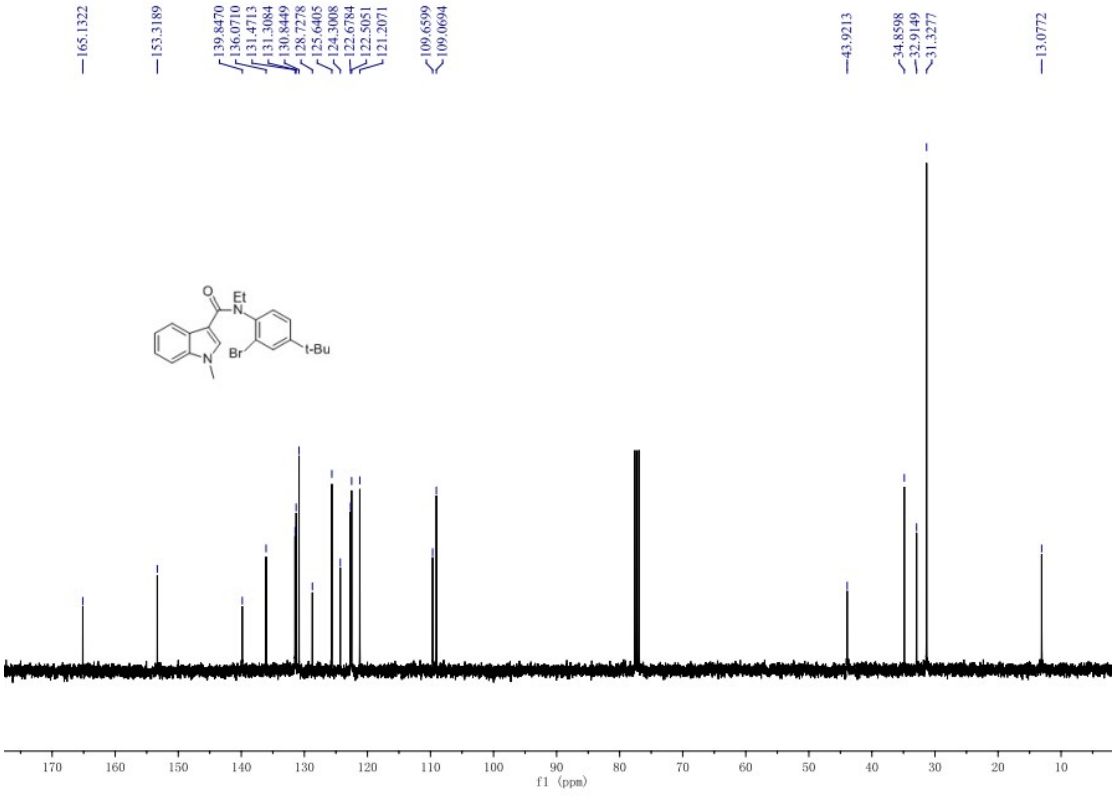
^{1}H NMR spectrum of **4e**



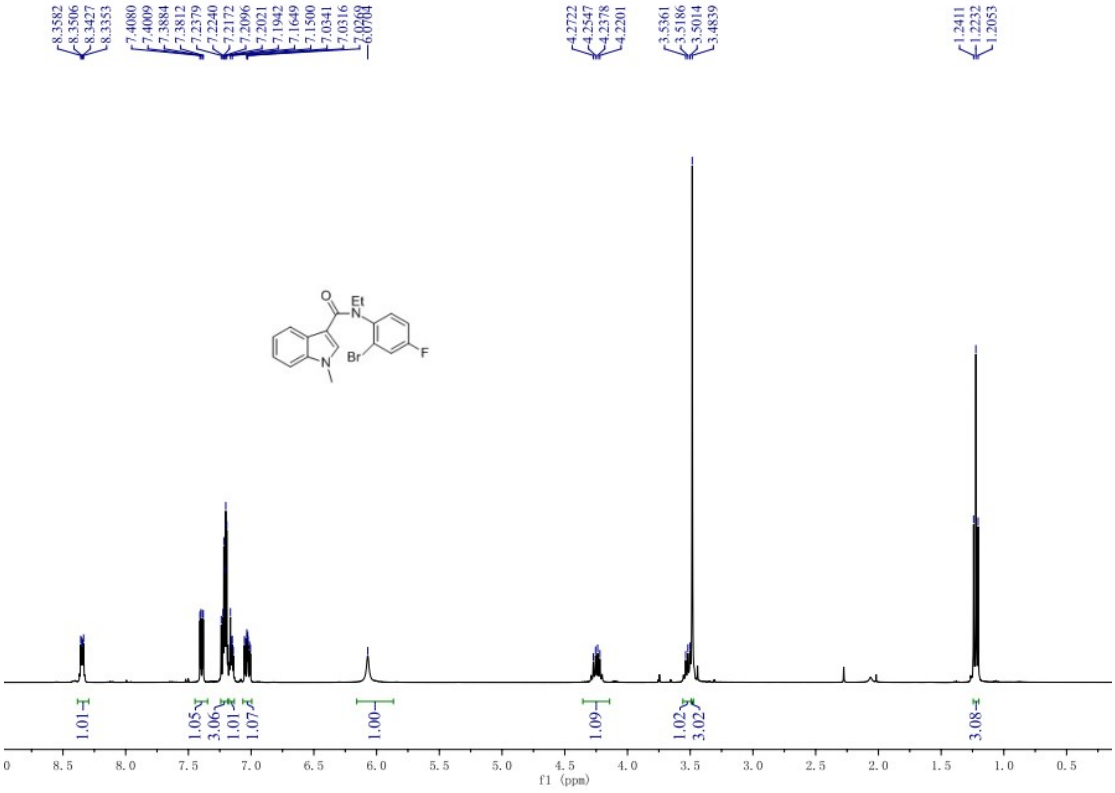
^{13}C NMR spectrum of **4e**



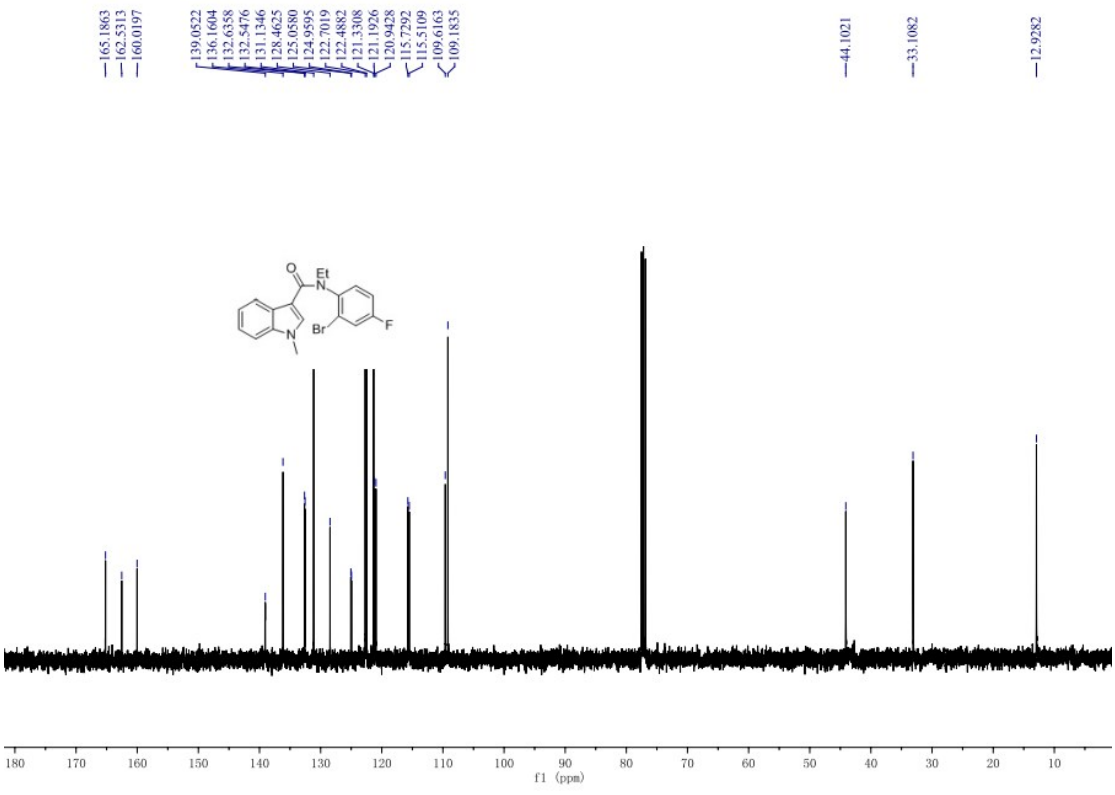
^{1}H NMR spectrum of **4f**



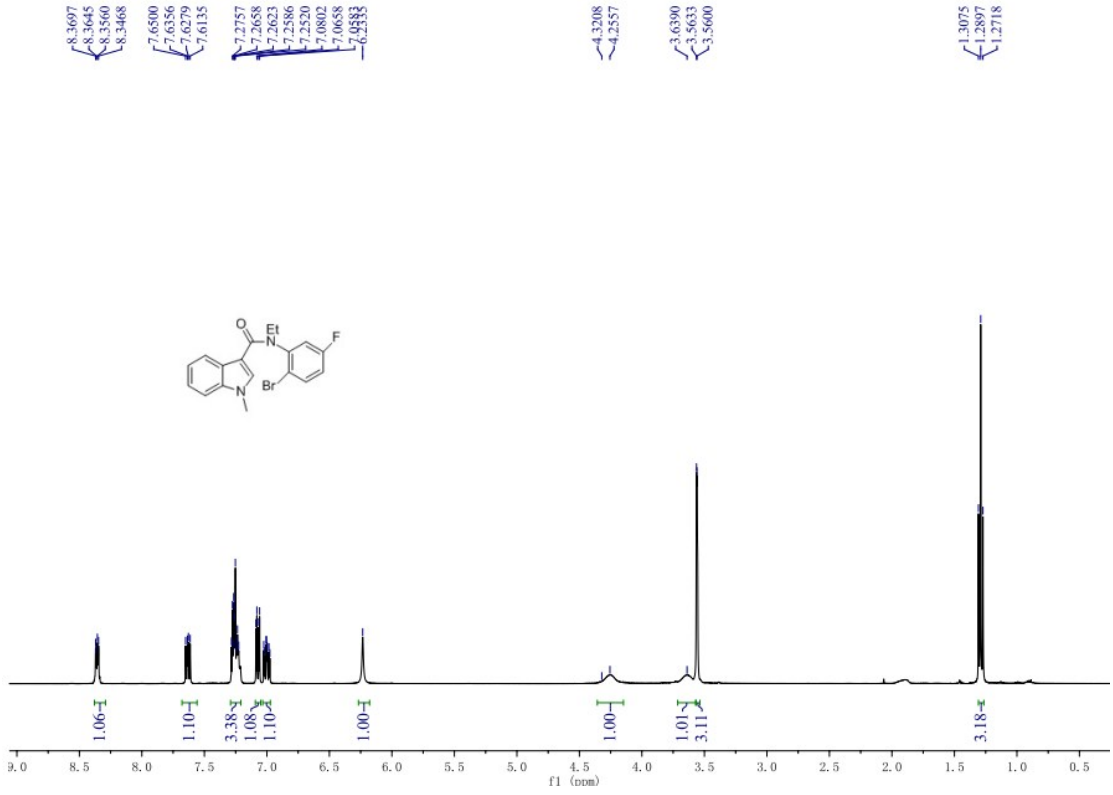
^{13}C NMR spectrum of **4f**



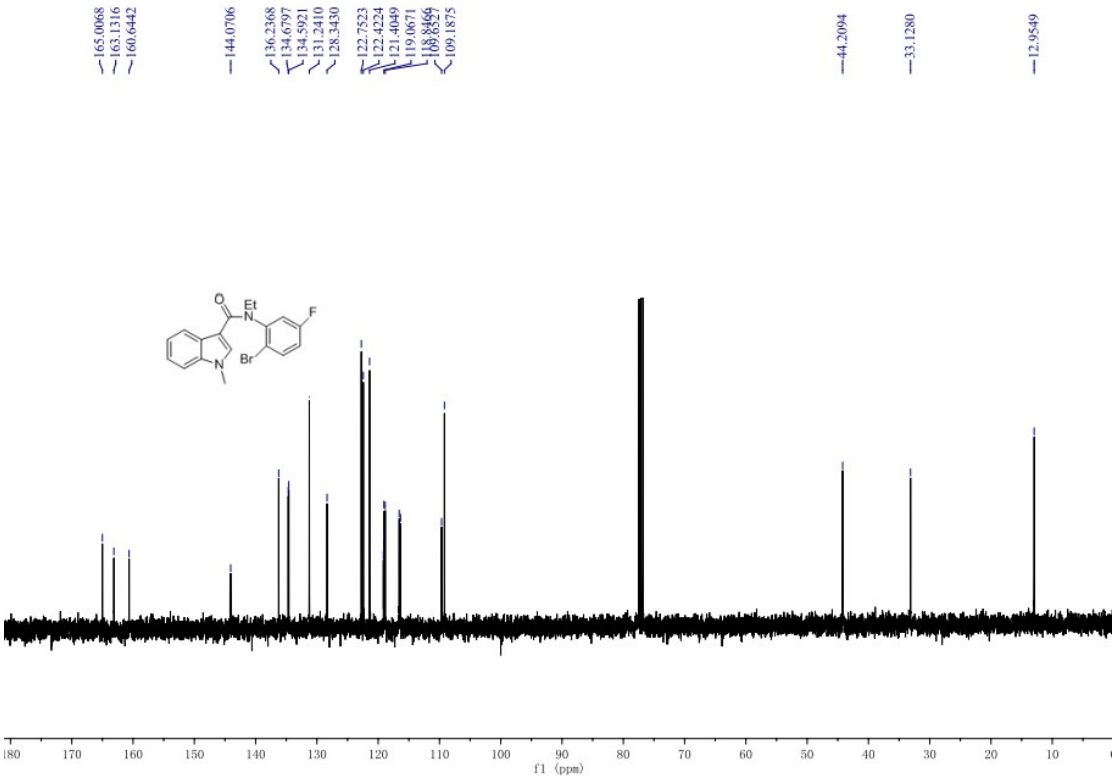
^{1}H NMR spectrum of **4g**



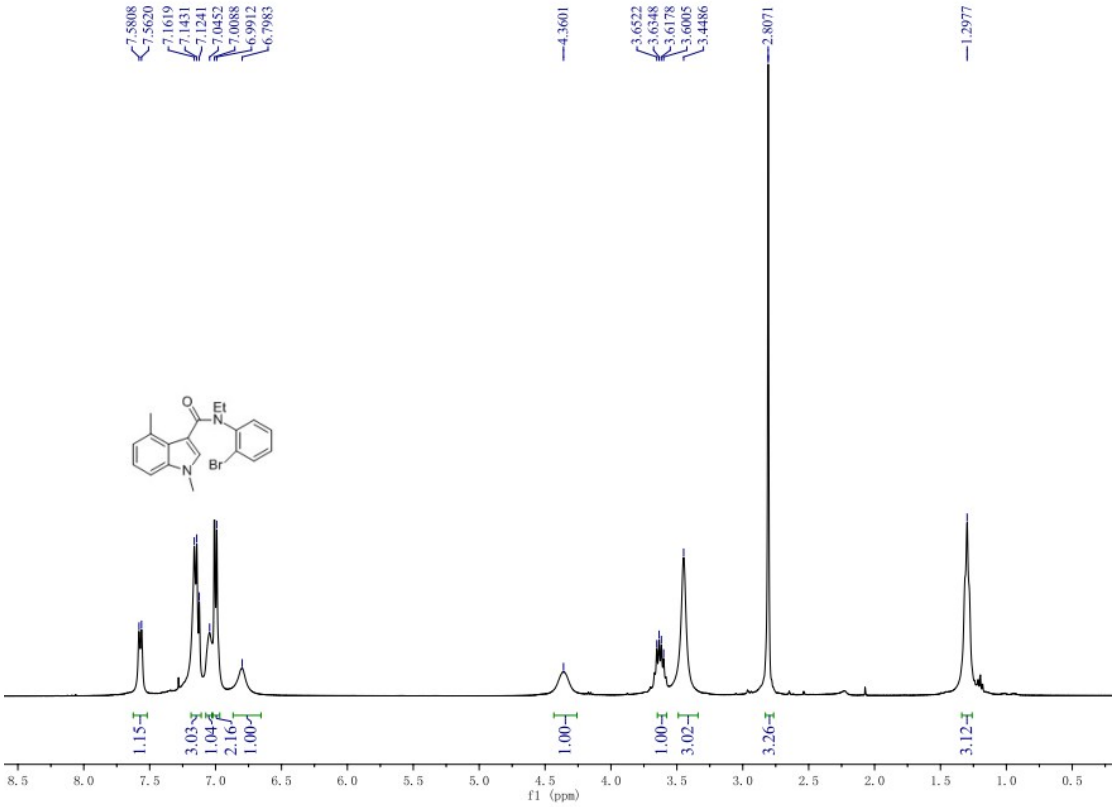
^{13}C NMR spectrum of **4g**



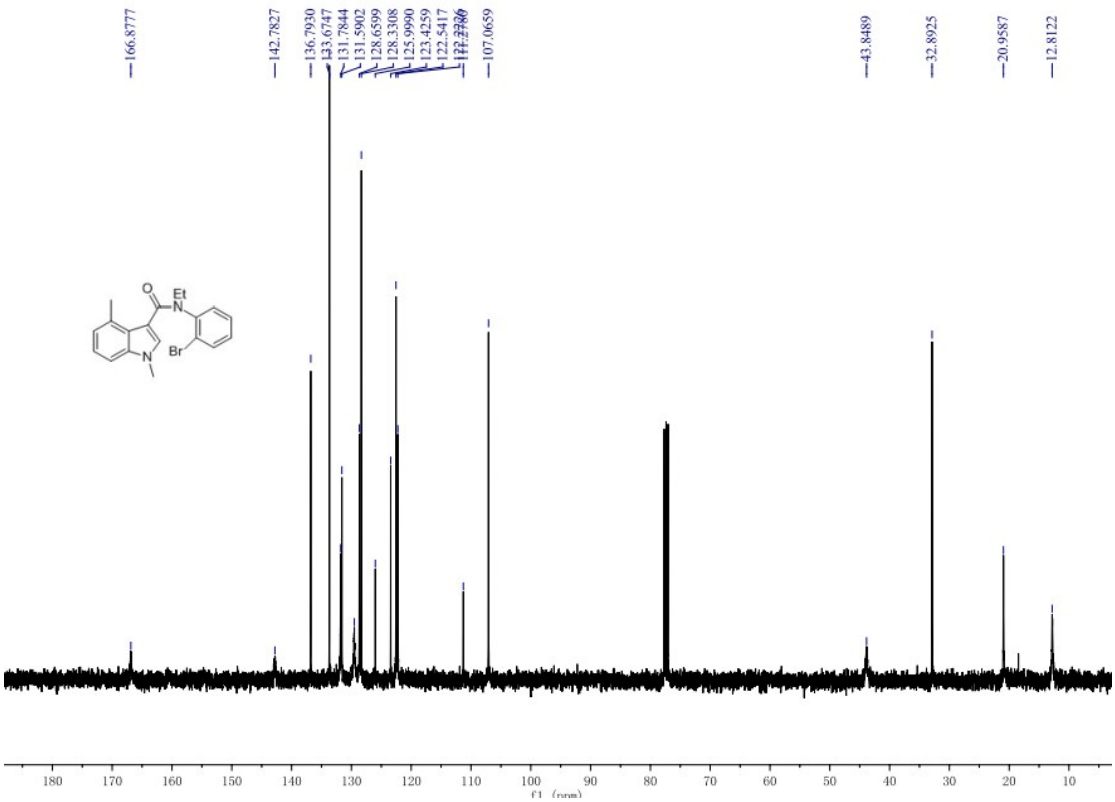
^{1}H NMR spectrum of **4h**



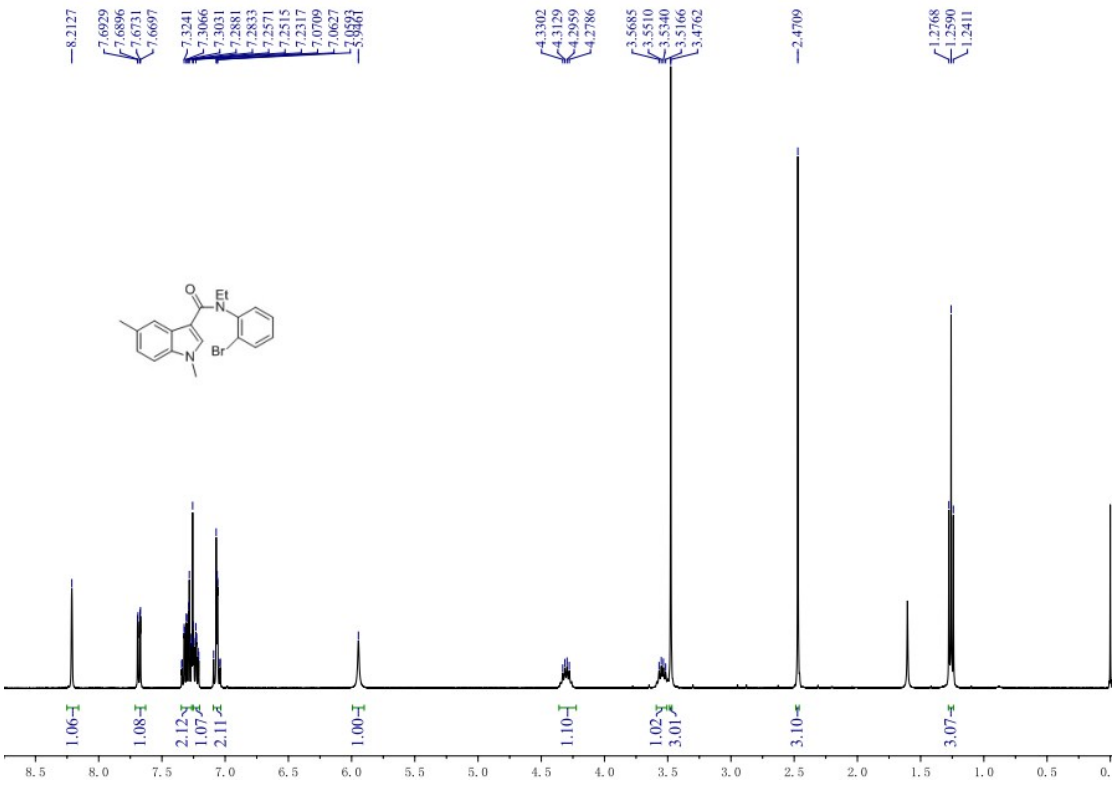
^{13}C NMR spectrum of **4h**



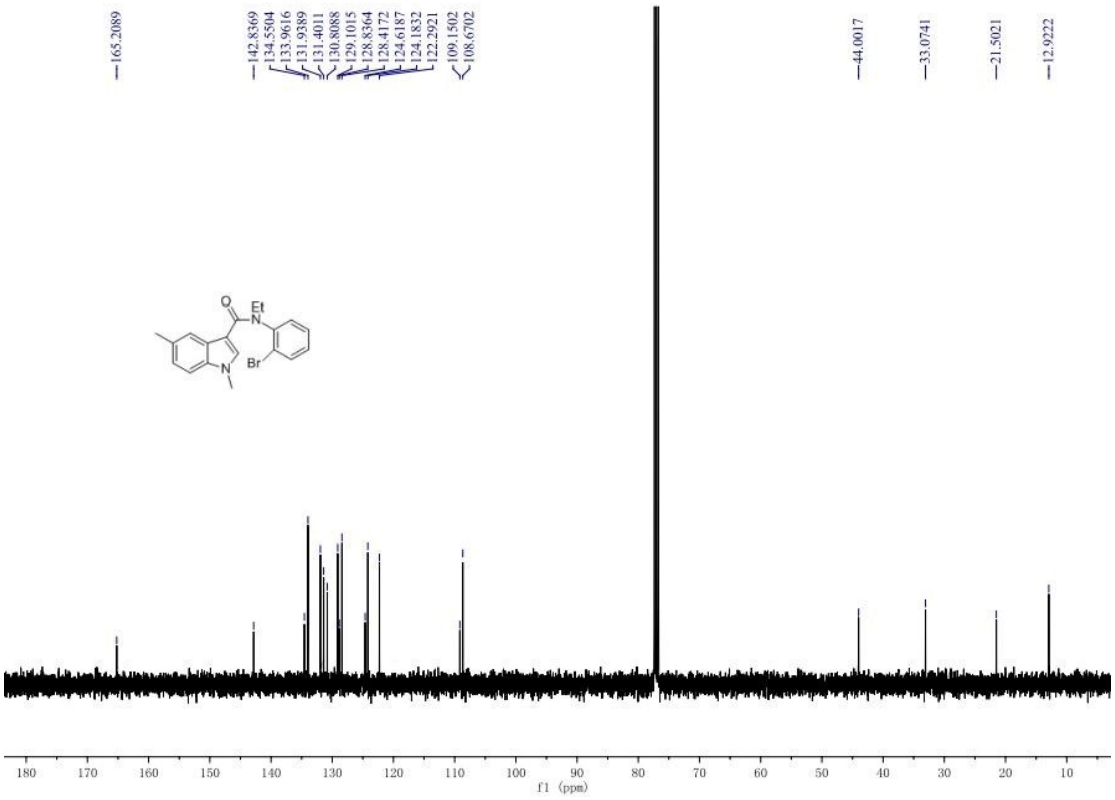
^{1}H NMR spectrum of **4k**



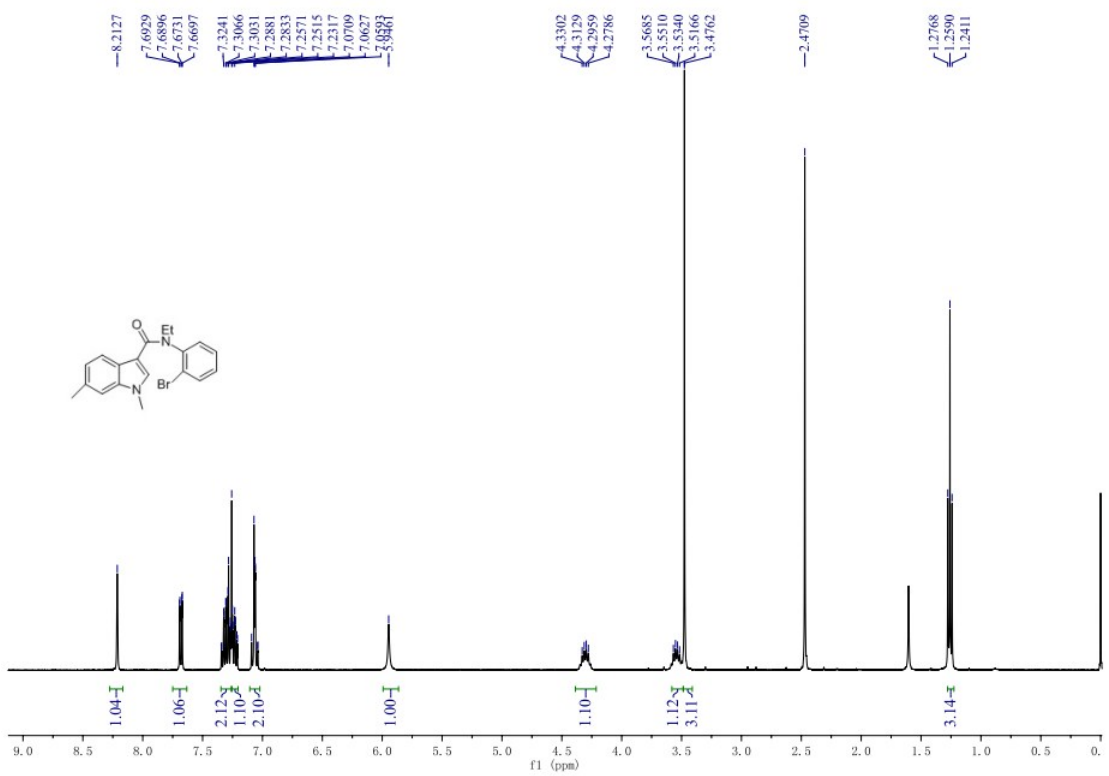
^{13}C NMR spectrum of **4k**



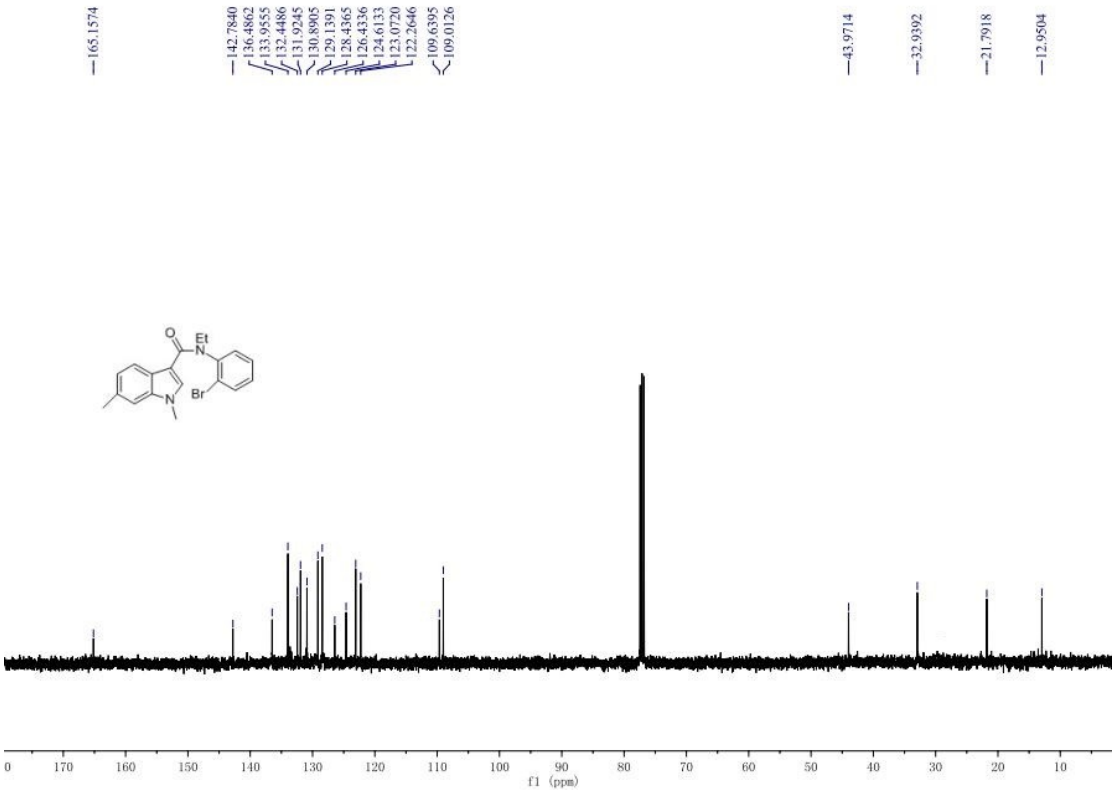
^{1}H NMR spectrum of **4l**



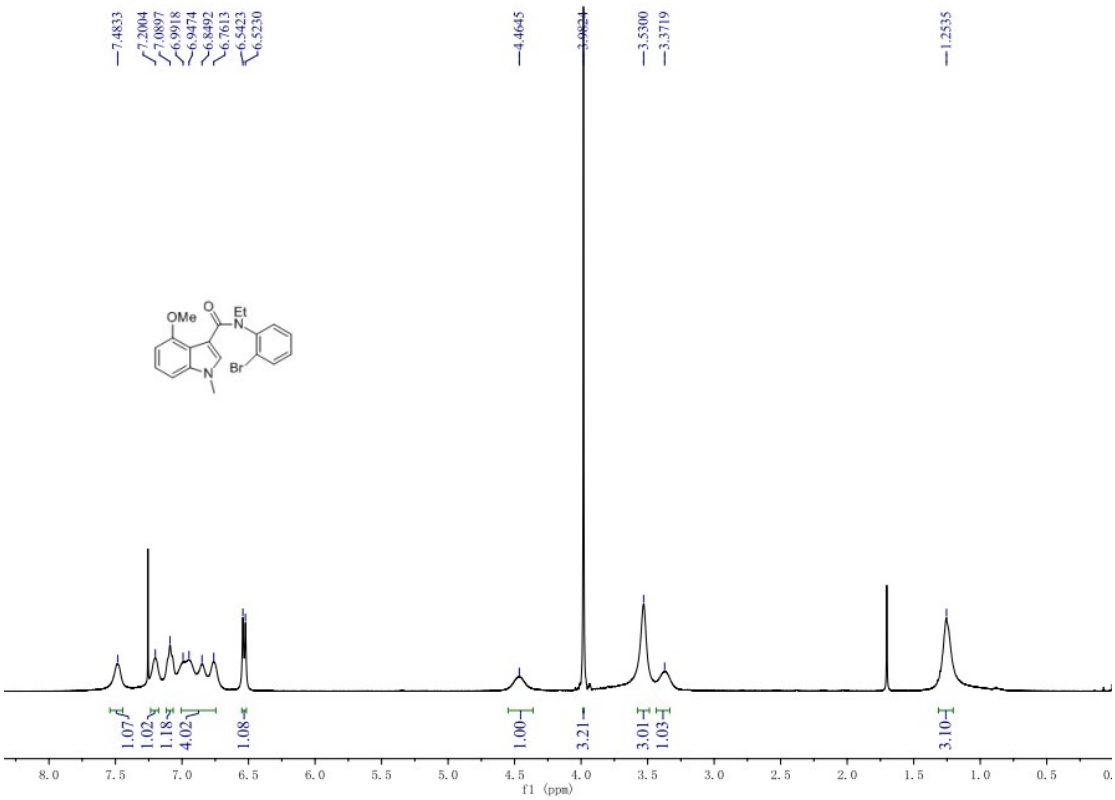
^{13}C NMR spectrum of **4l**



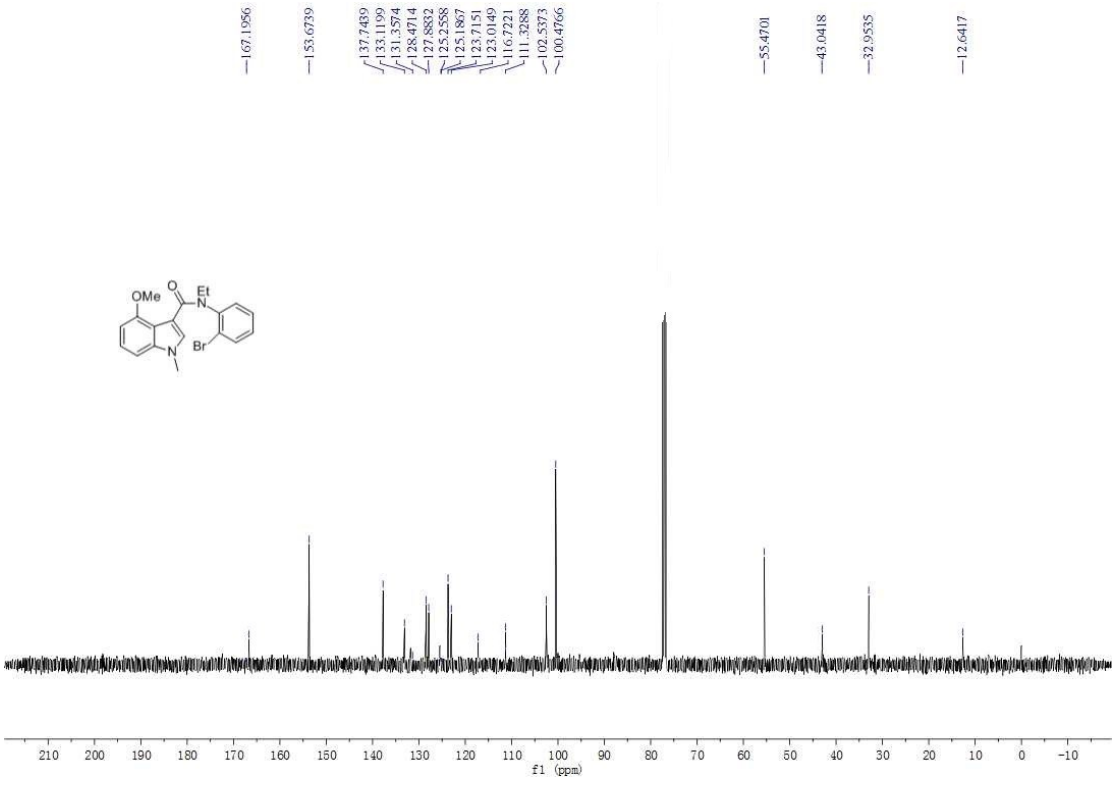
^{1}H NMR spectrum of **4m**



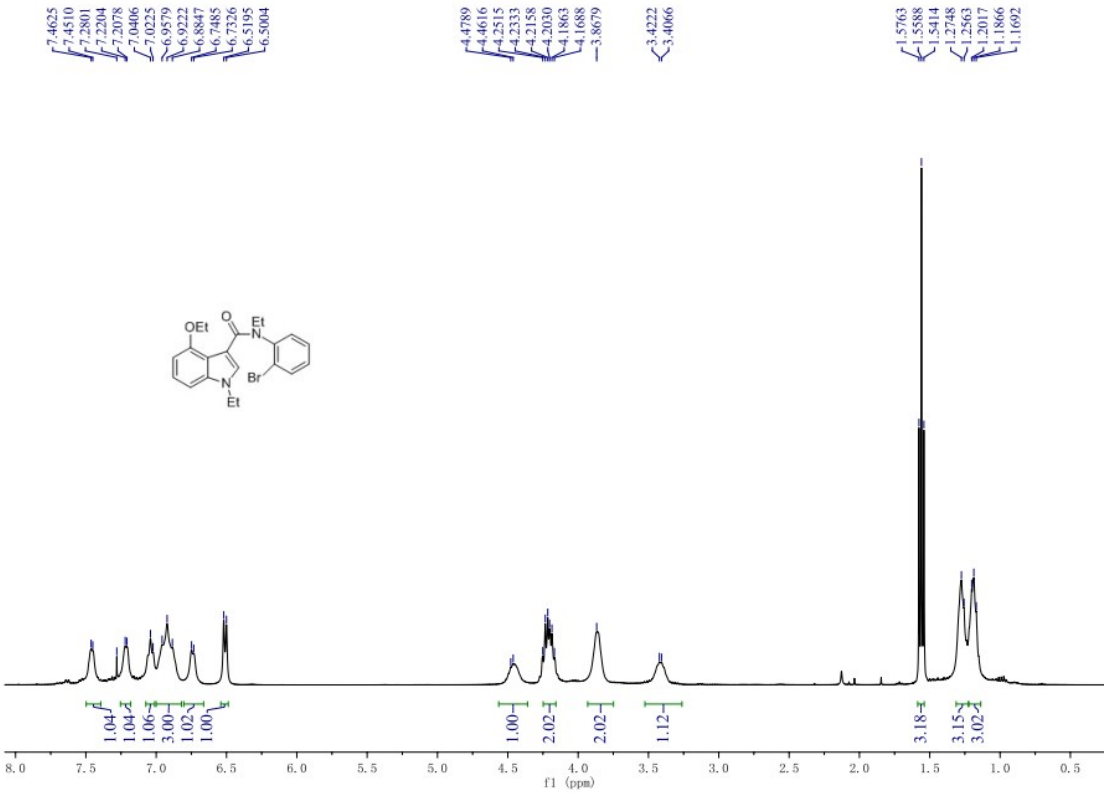
^{13}C NMR spectrum of **4m**



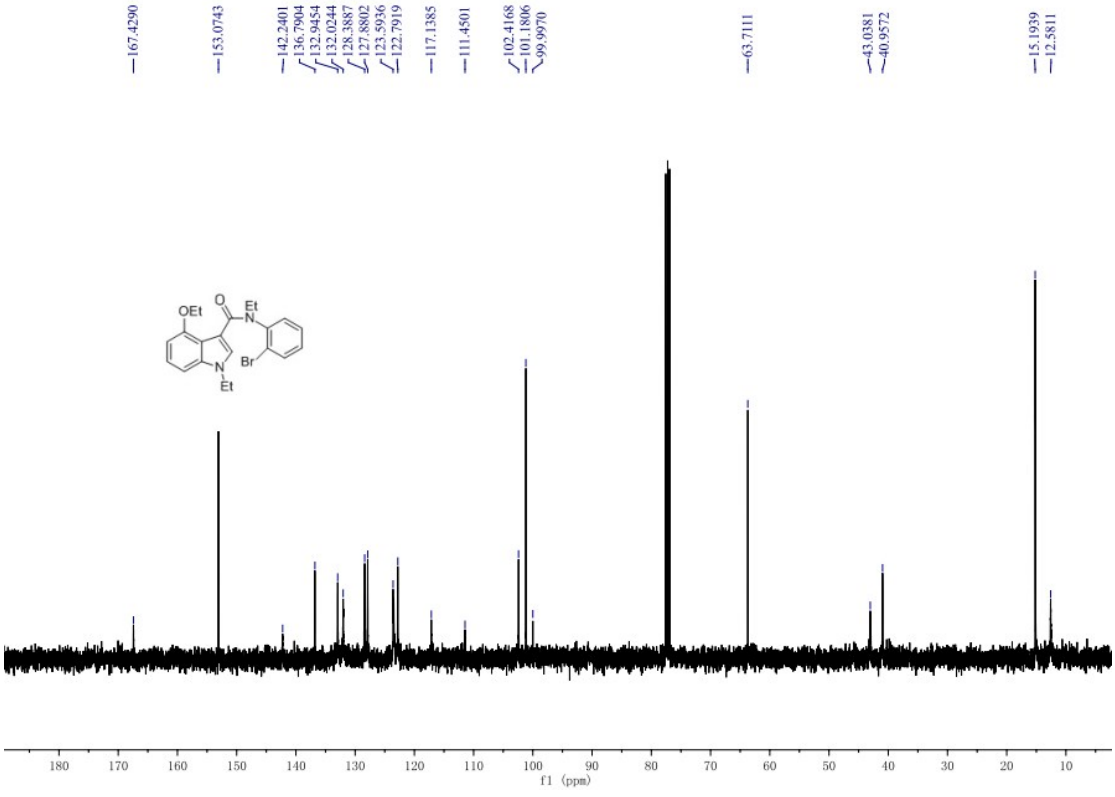
^{1}H NMR spectrum of **4n**



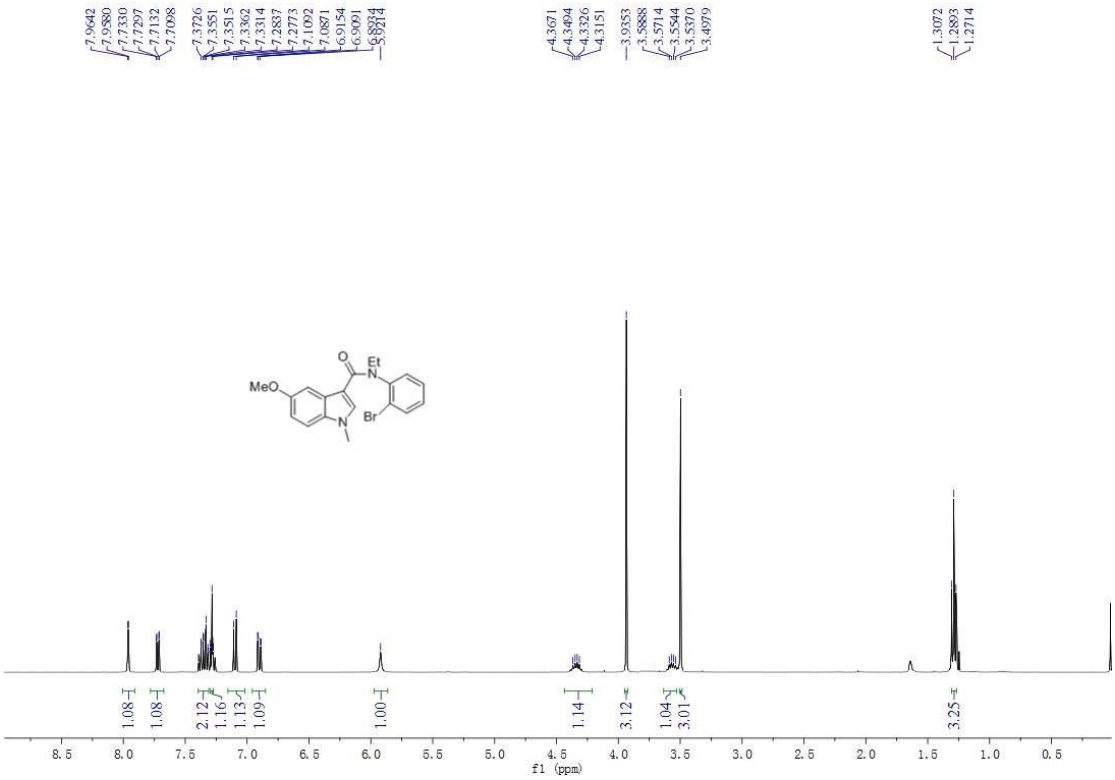
^{13}C NMR spectrum of **4n**



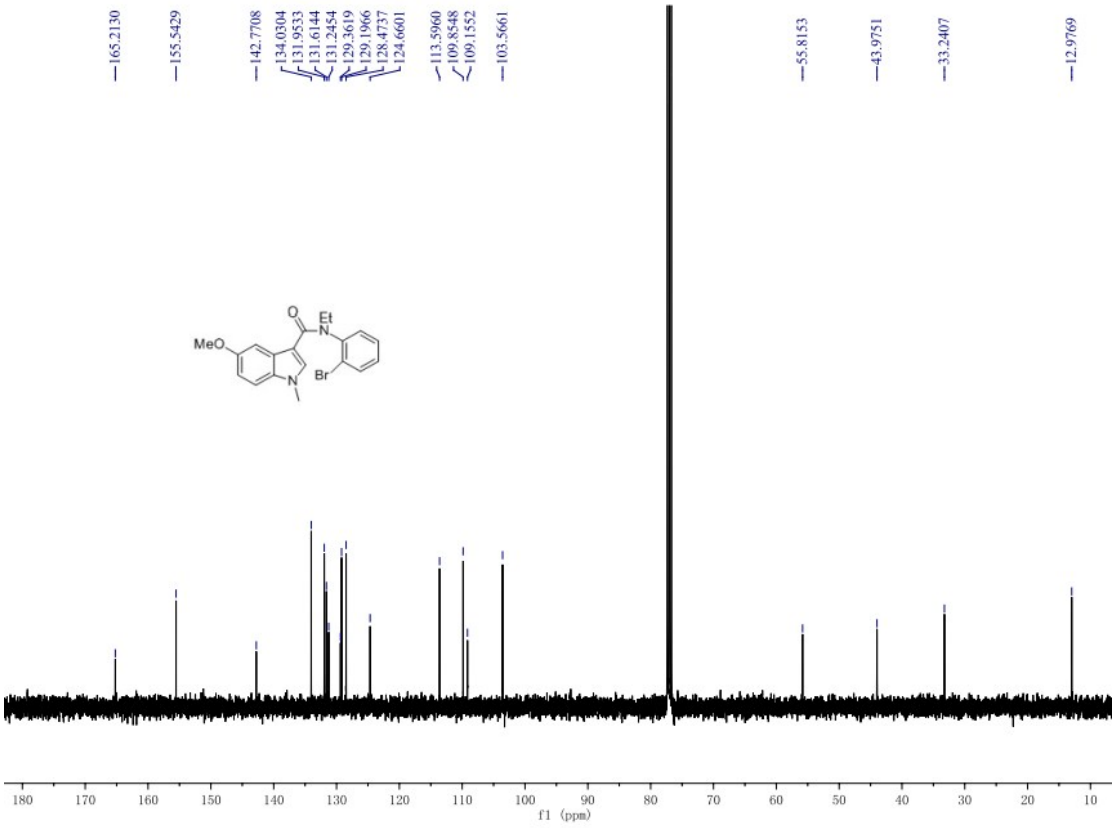
^{1}H NMR spectrum of **4o**



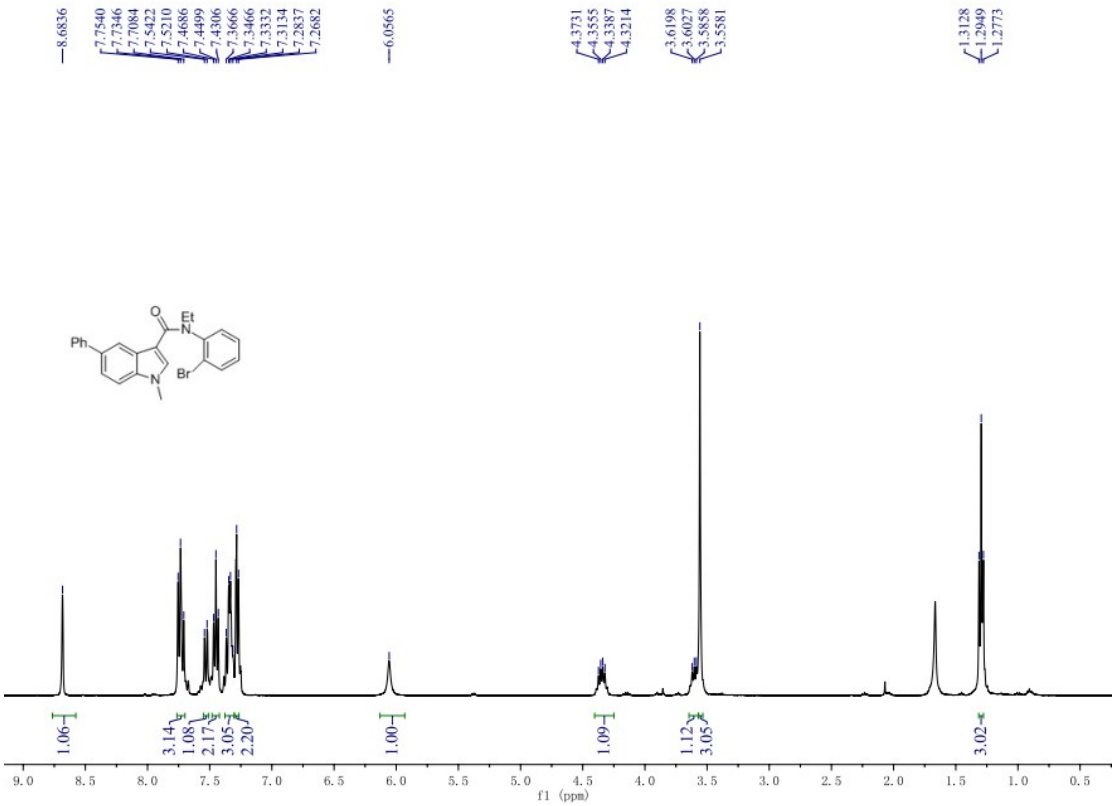
^{13}C NMR spectrum of **4o**



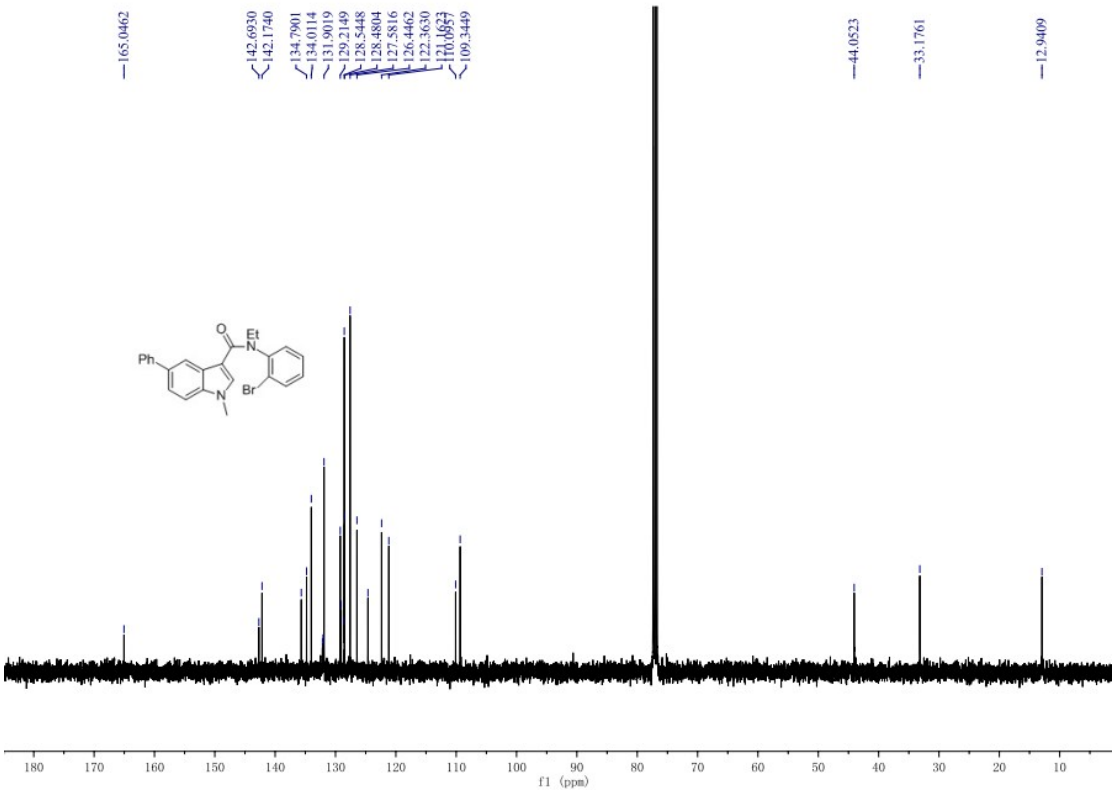
^{1}H NMR spectrum of **4p**



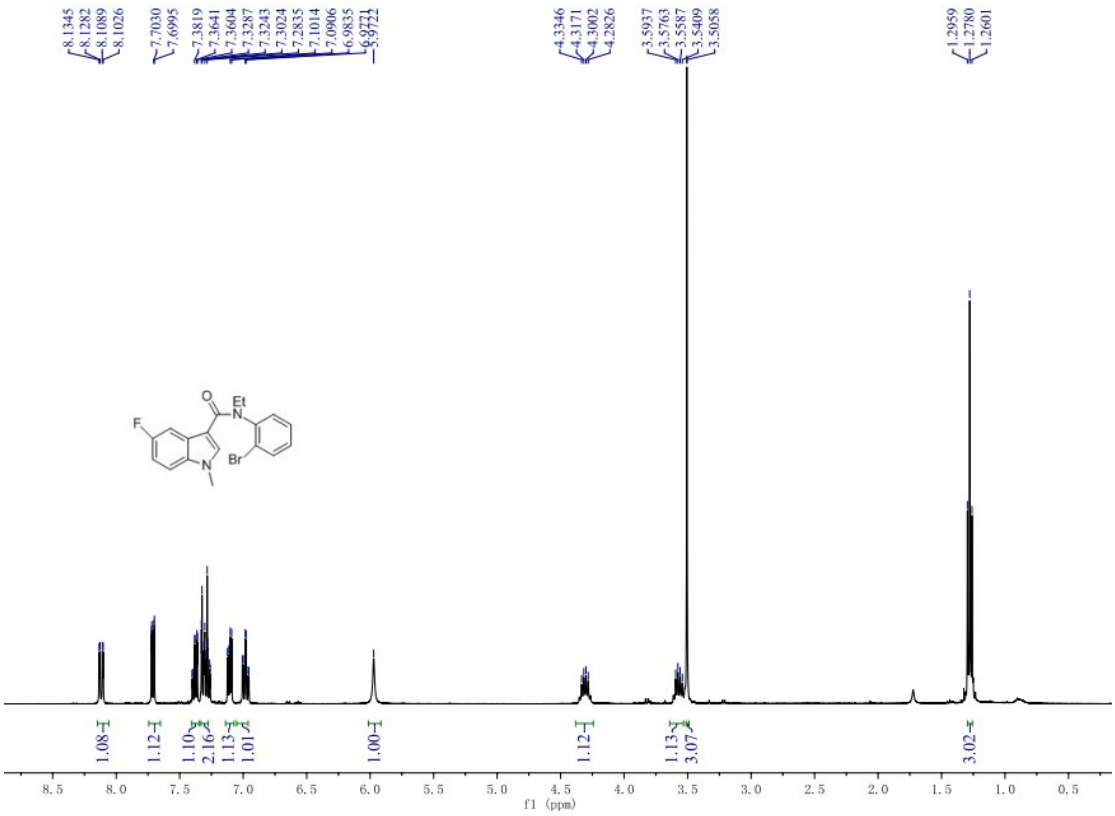
^{13}C NMR spectrum of **4p**



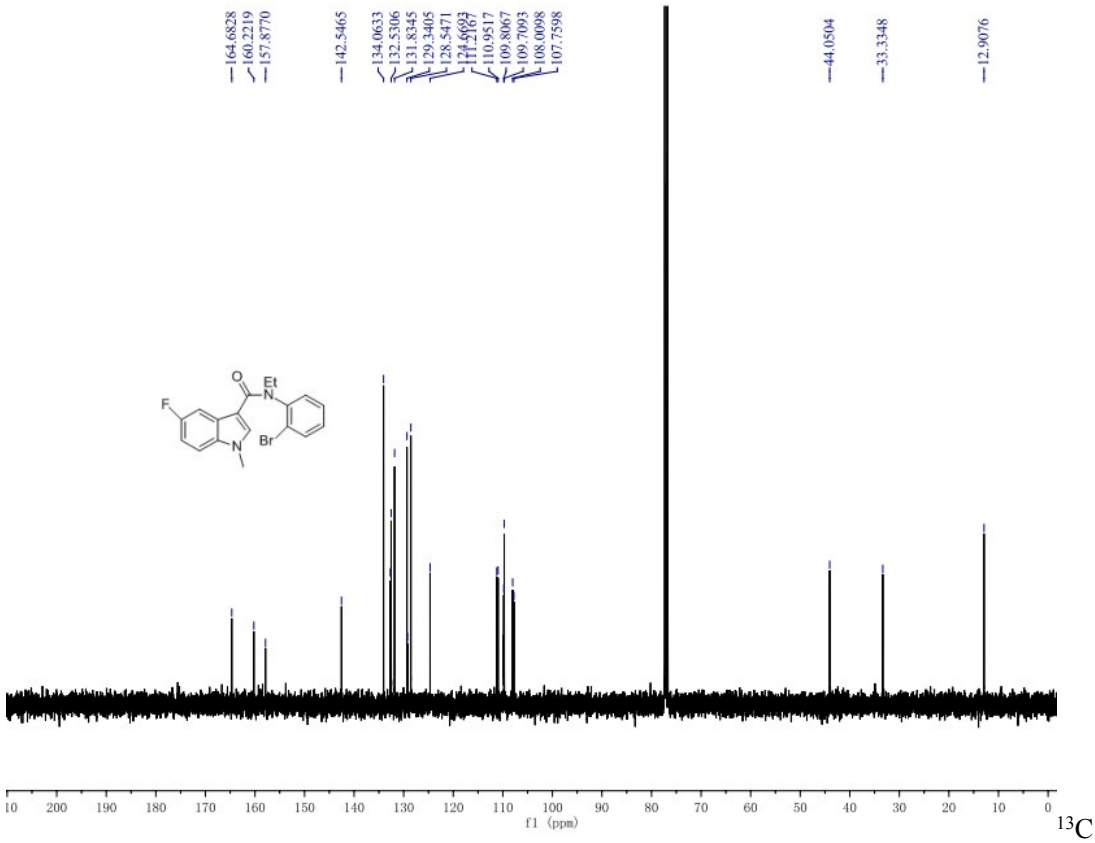
^{1}H NMR spectrum of **4q**



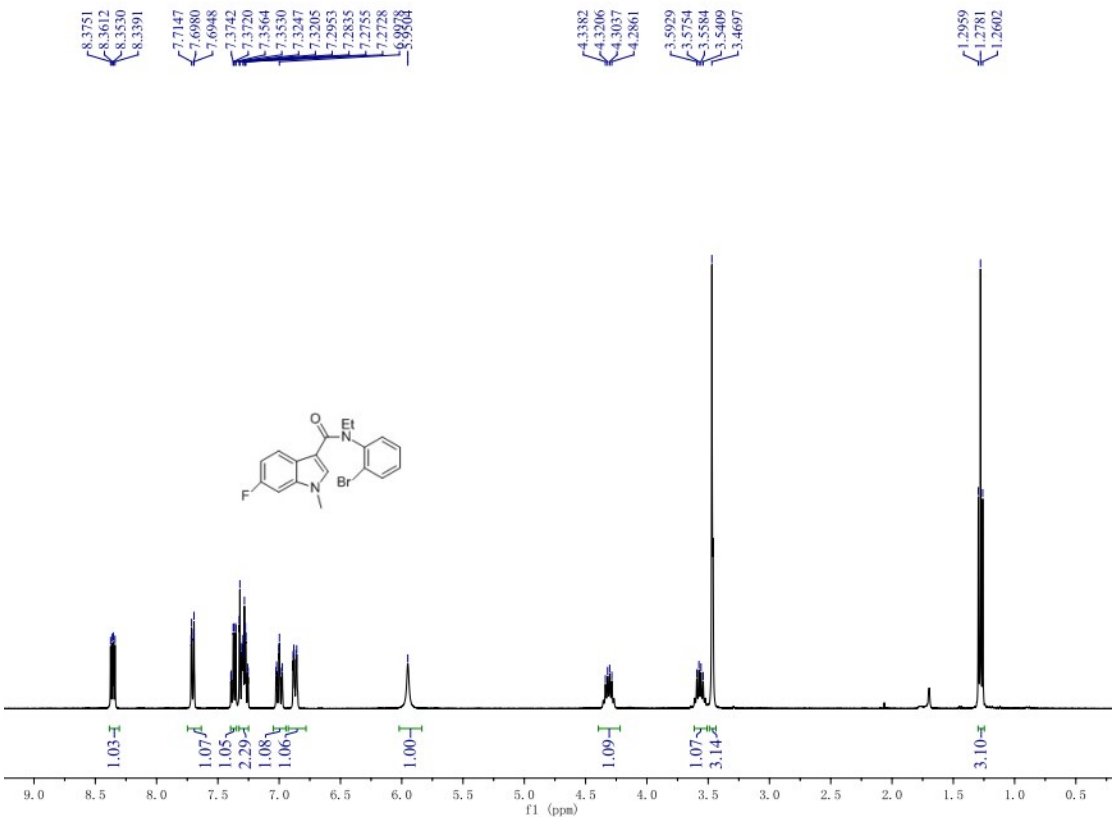
^{13}C NMR spectrum of **4q**



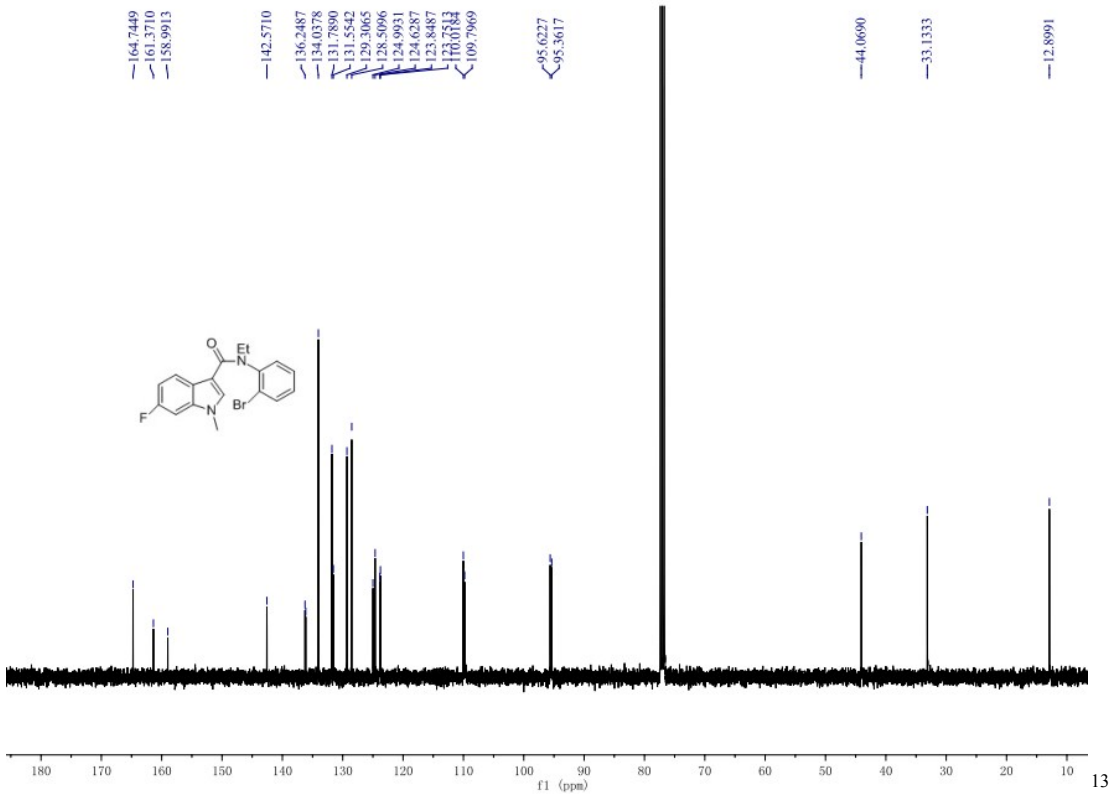
^{1}H NMR spectrum of **4r**



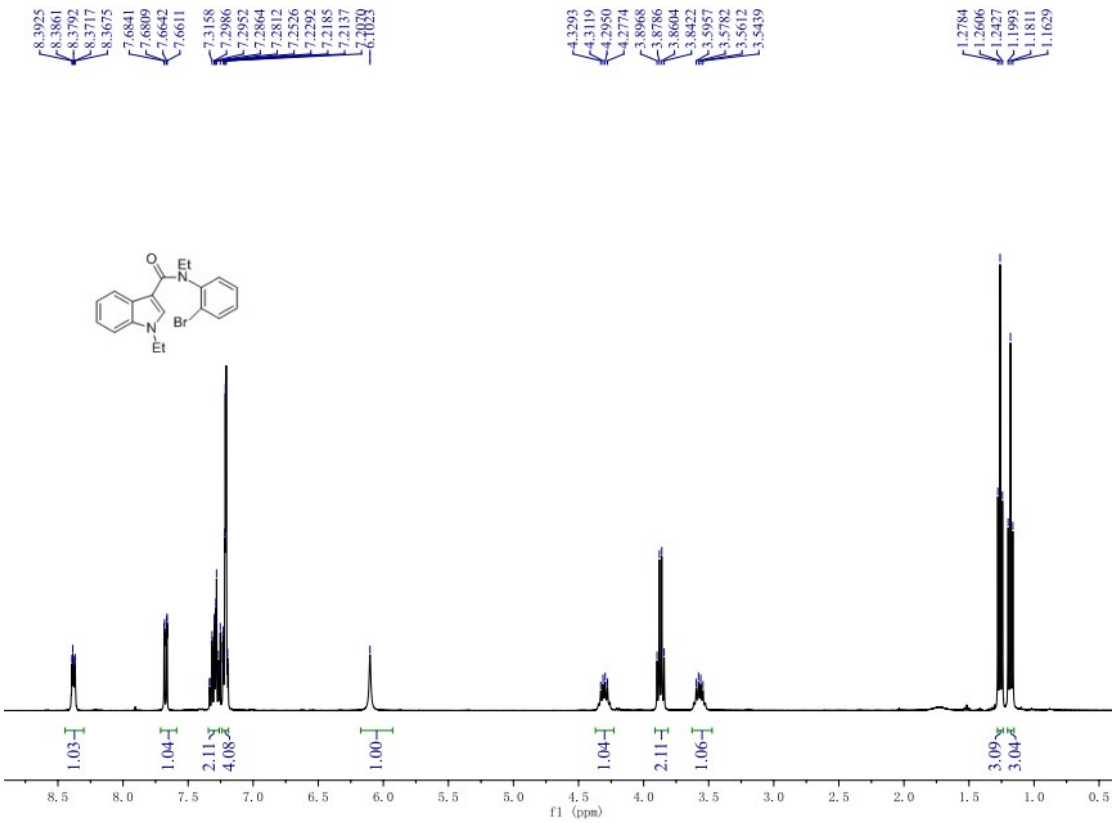
^{13}C NMR spectrum of **4r**



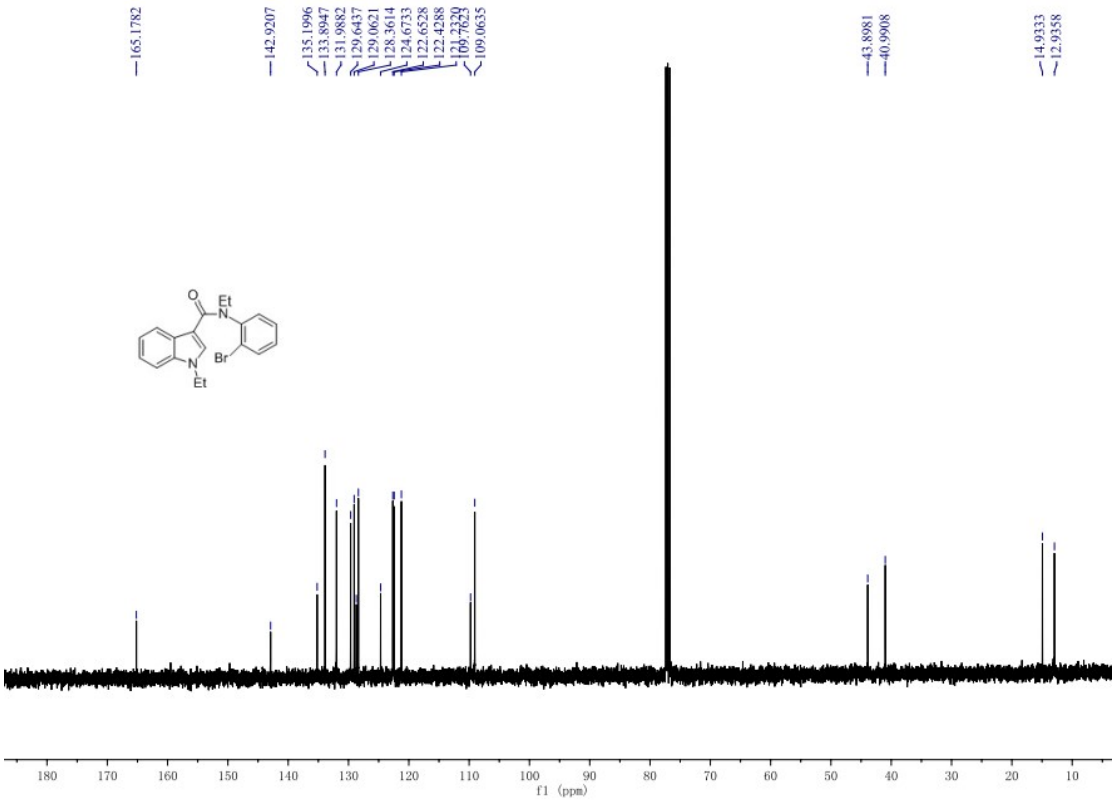
^{1}H NMR spectrum of **4s**



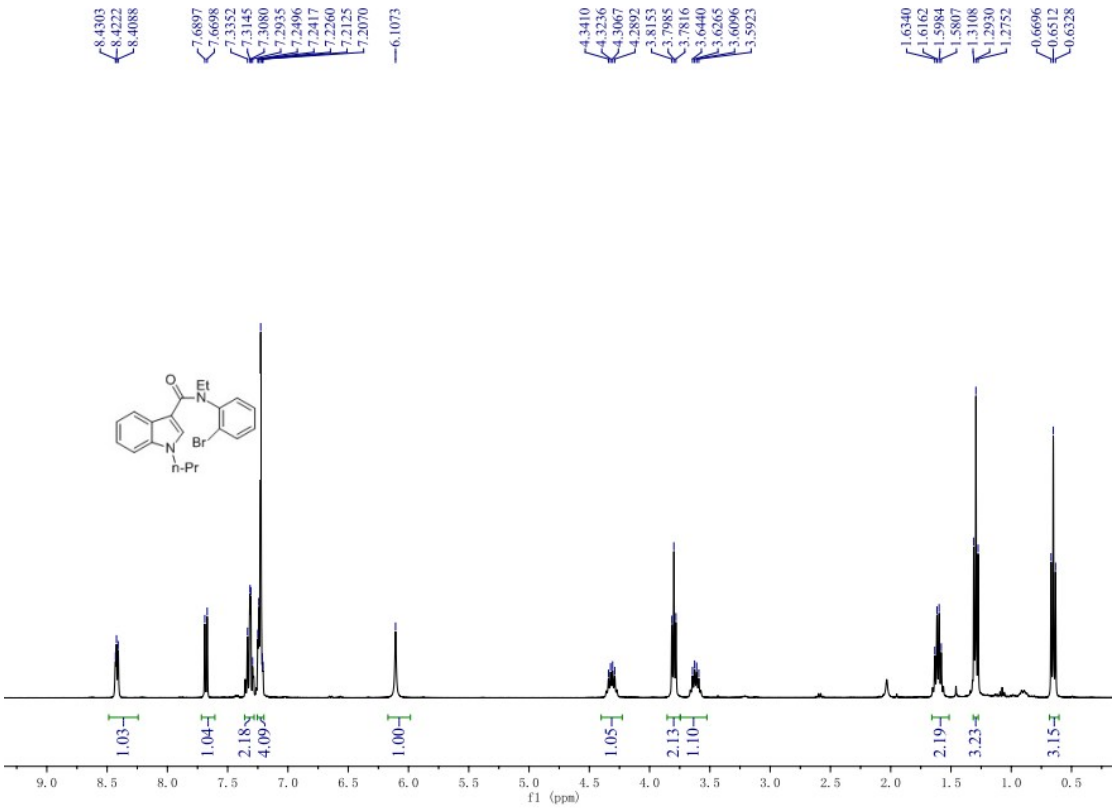
C NMR spectrum of **4s**



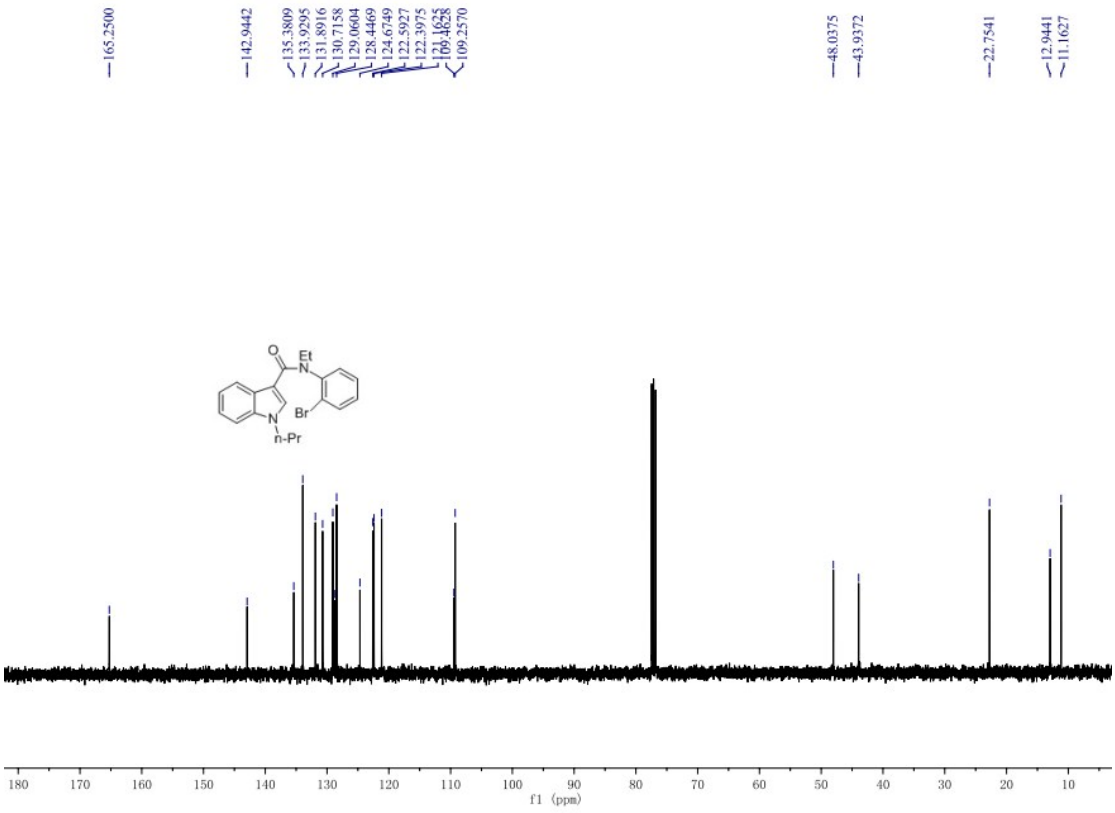
^{1}H NMR spectrum of **4t**



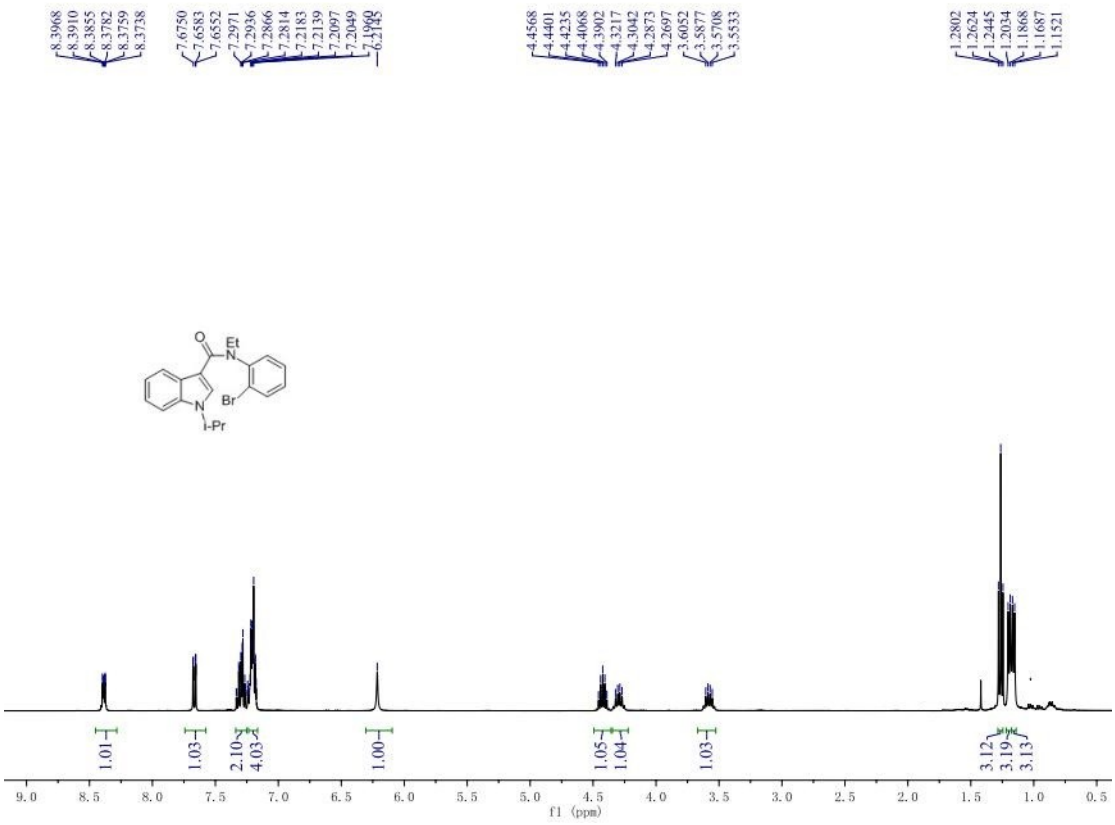
^{13}C NMR spectrum of **4t**



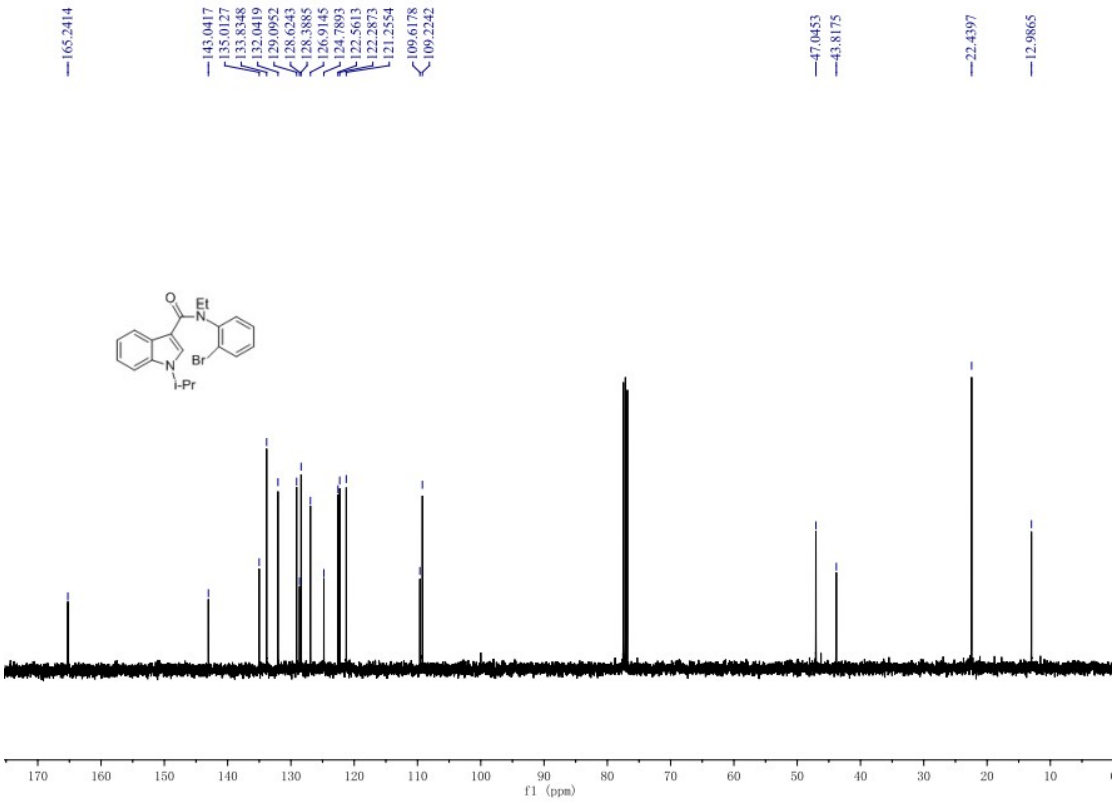
^{1}H NMR spectrum of **4u**



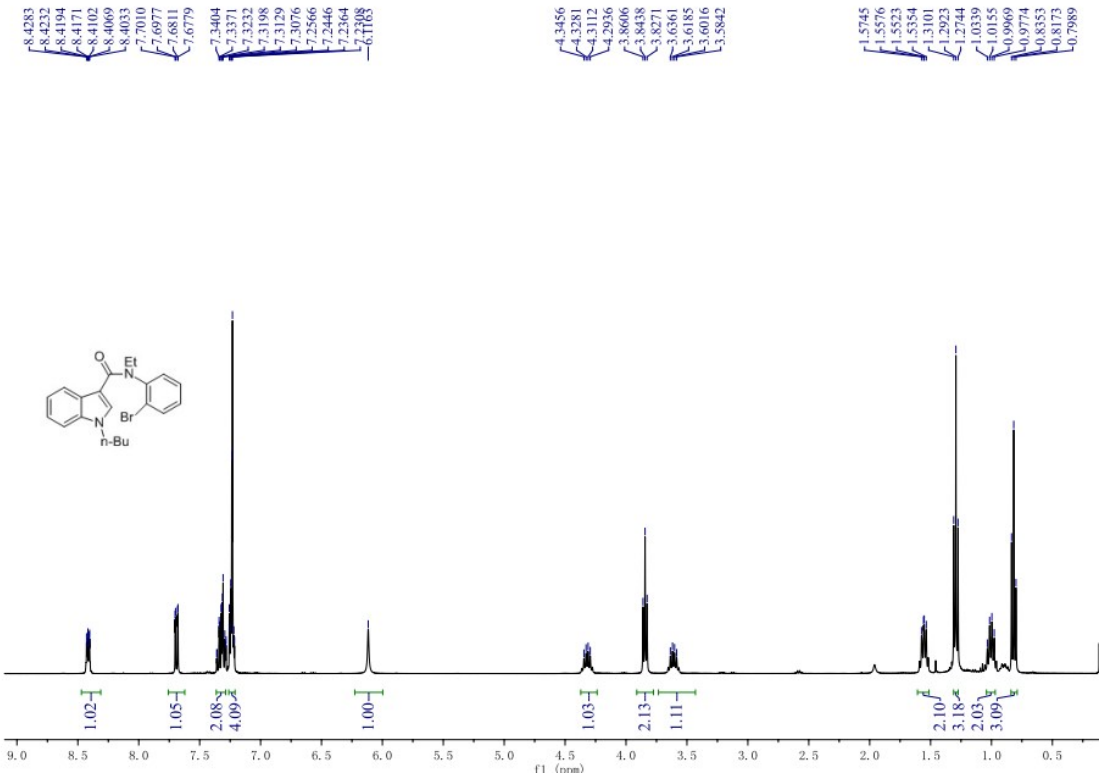
^{13}C NMR spectrum of **4u**



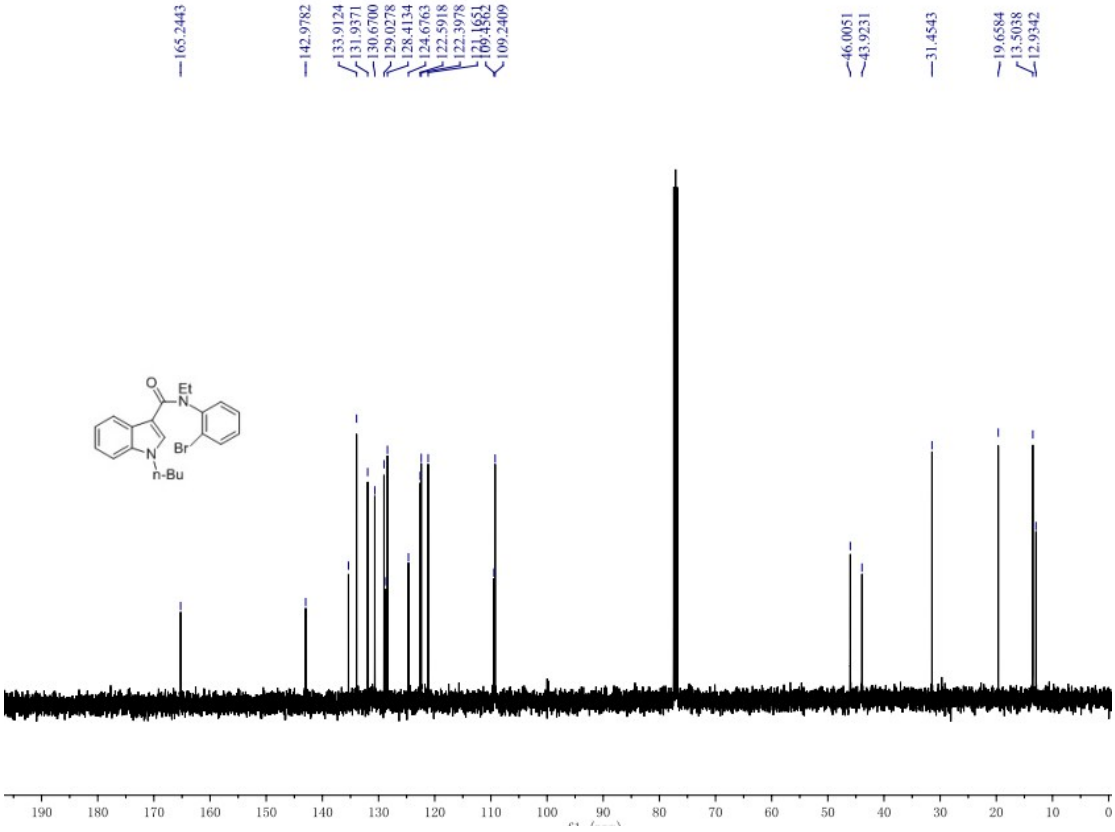
^{1}H NMR spectrum of **4v**



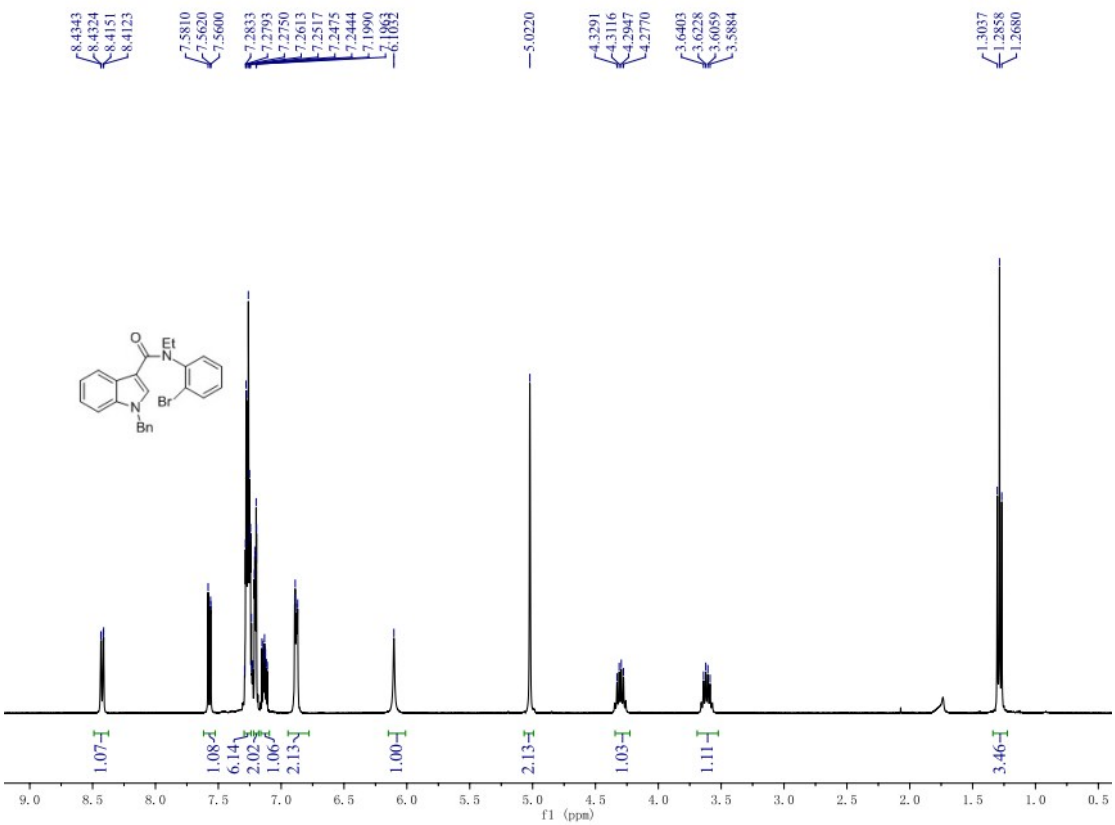
^{13}C NMR spectrum of **4v**



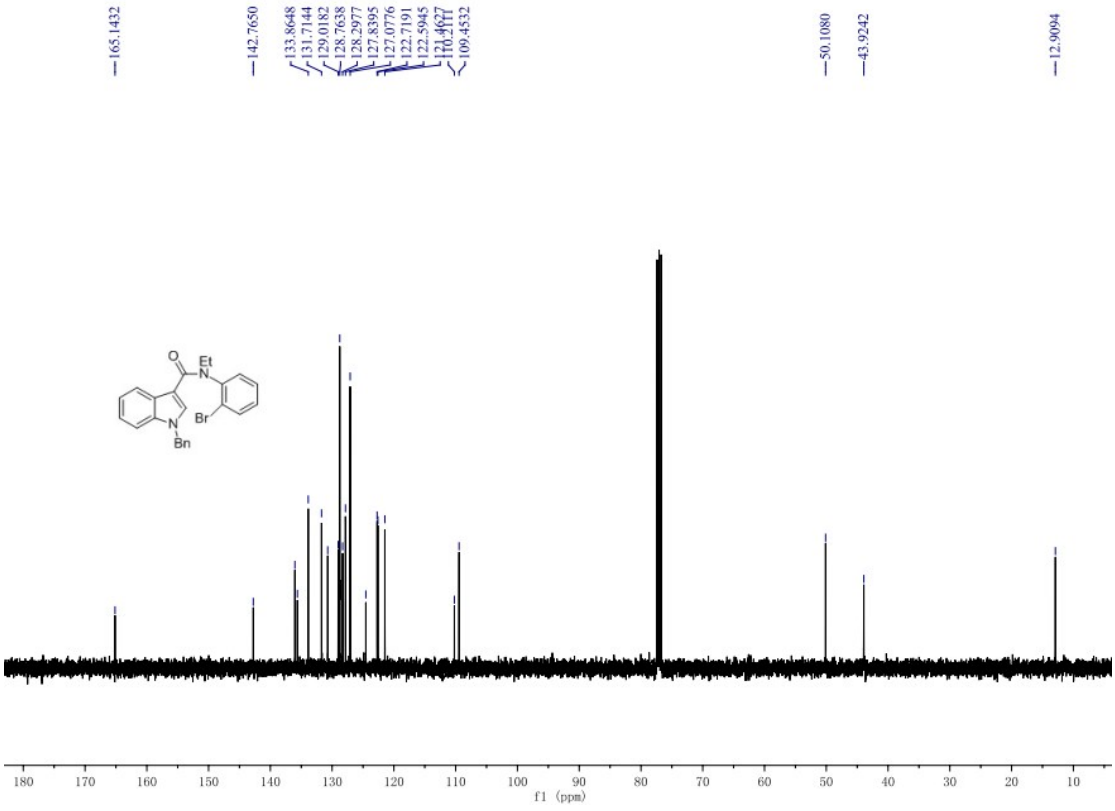
^{1}H NMR spectrum of **4w**



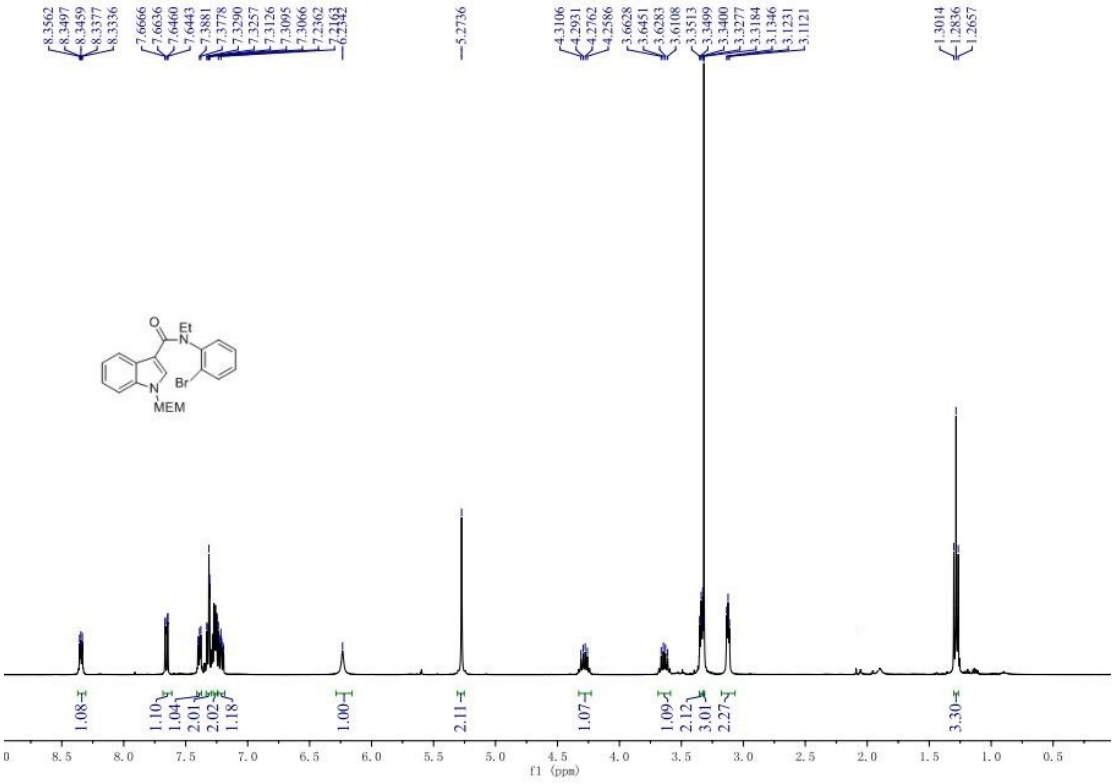
^{13}C NMR spectrum of **4w**



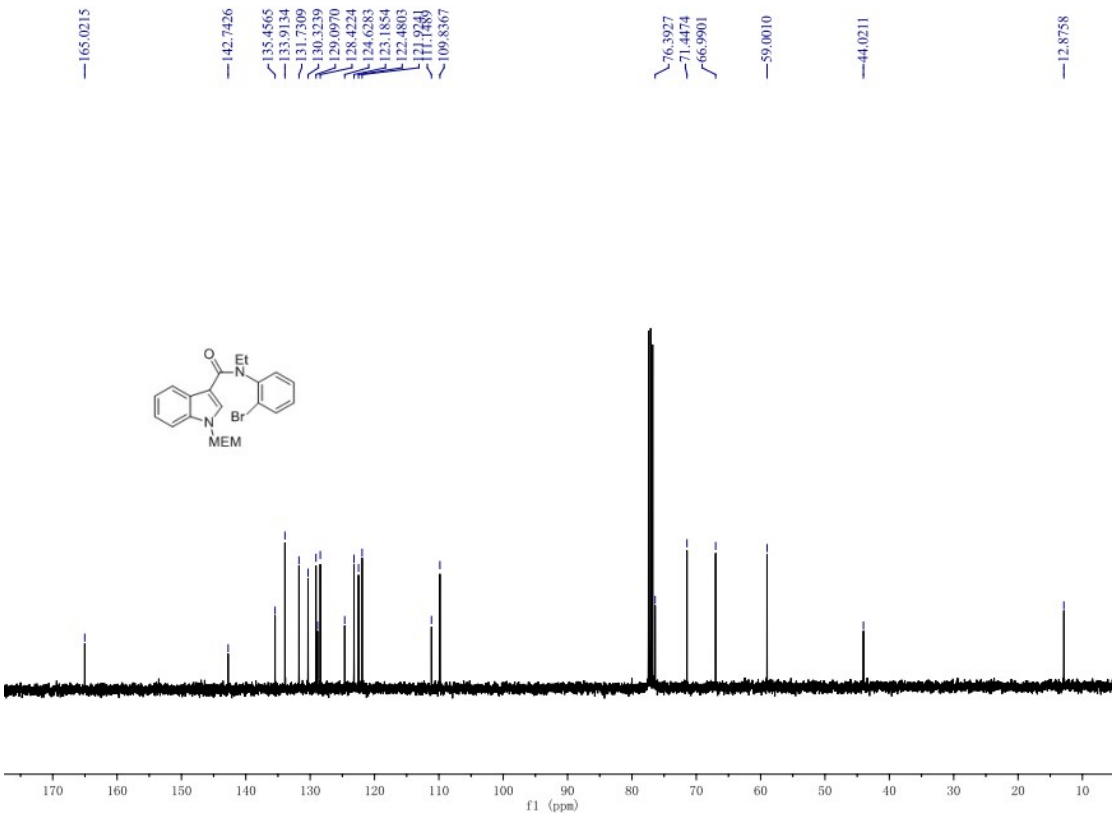
^{1}H NMR spectrum of **4x**



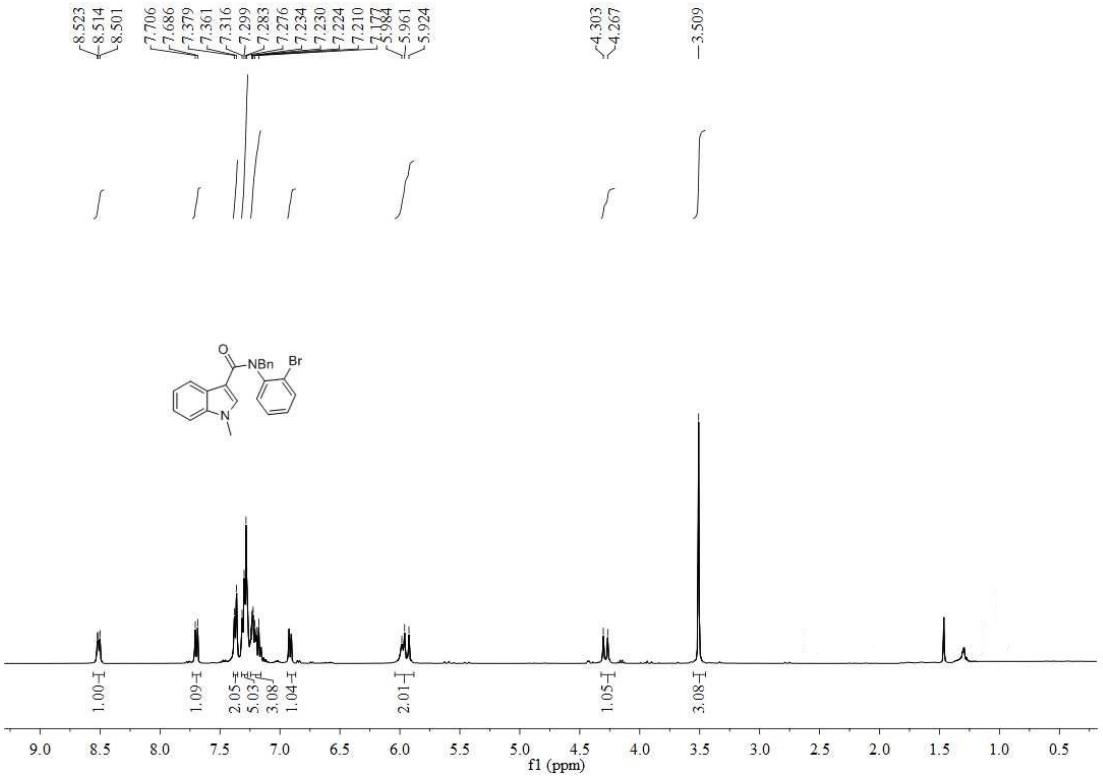
^{13}C NMR spectrum of **4x**



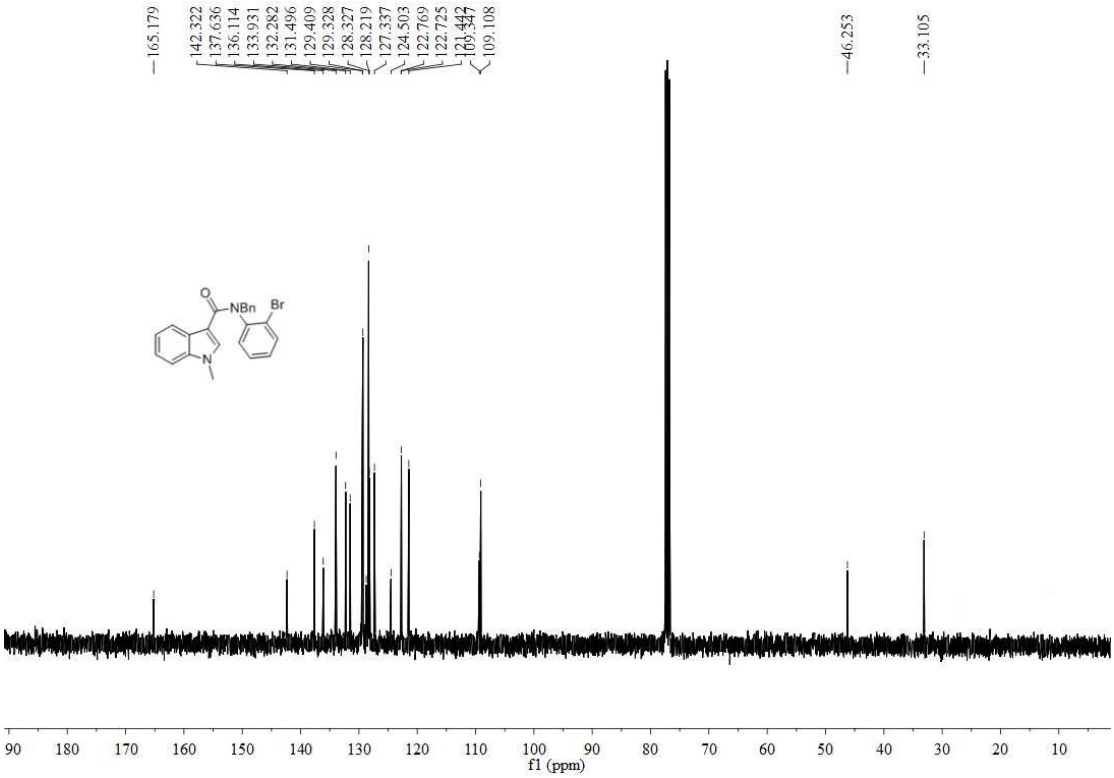
^{1}H NMR spectrum of **4y**



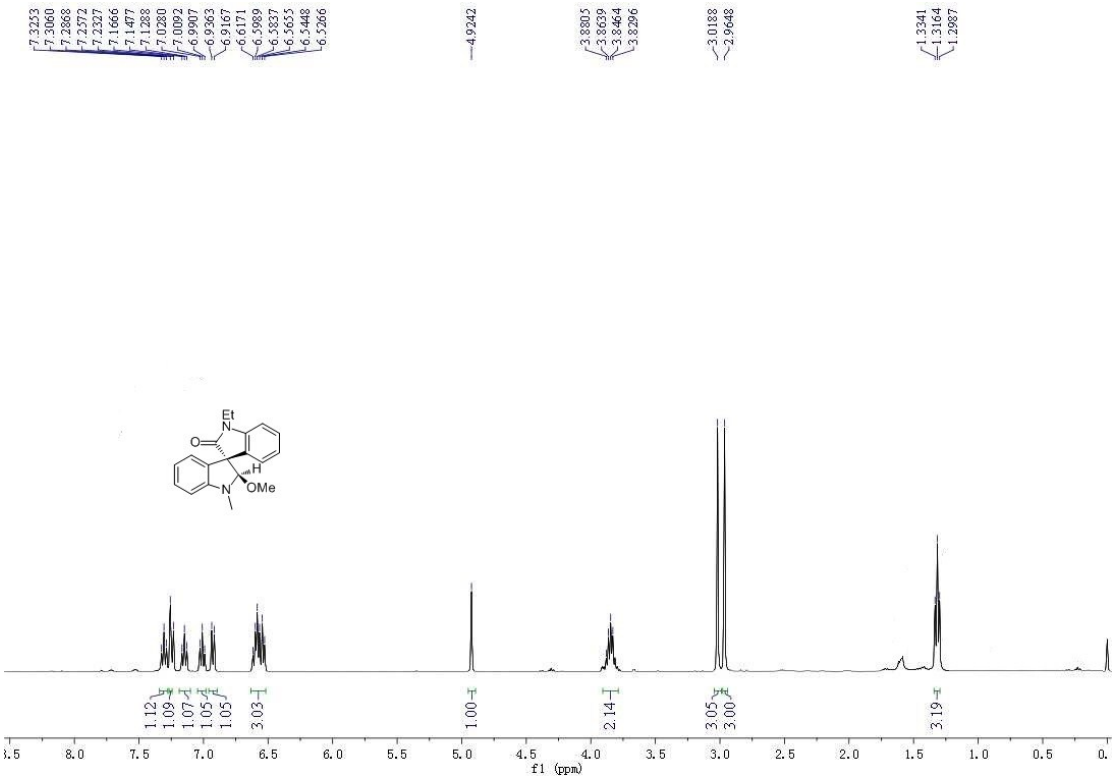
^{13}C NMR spectrum of **4y**



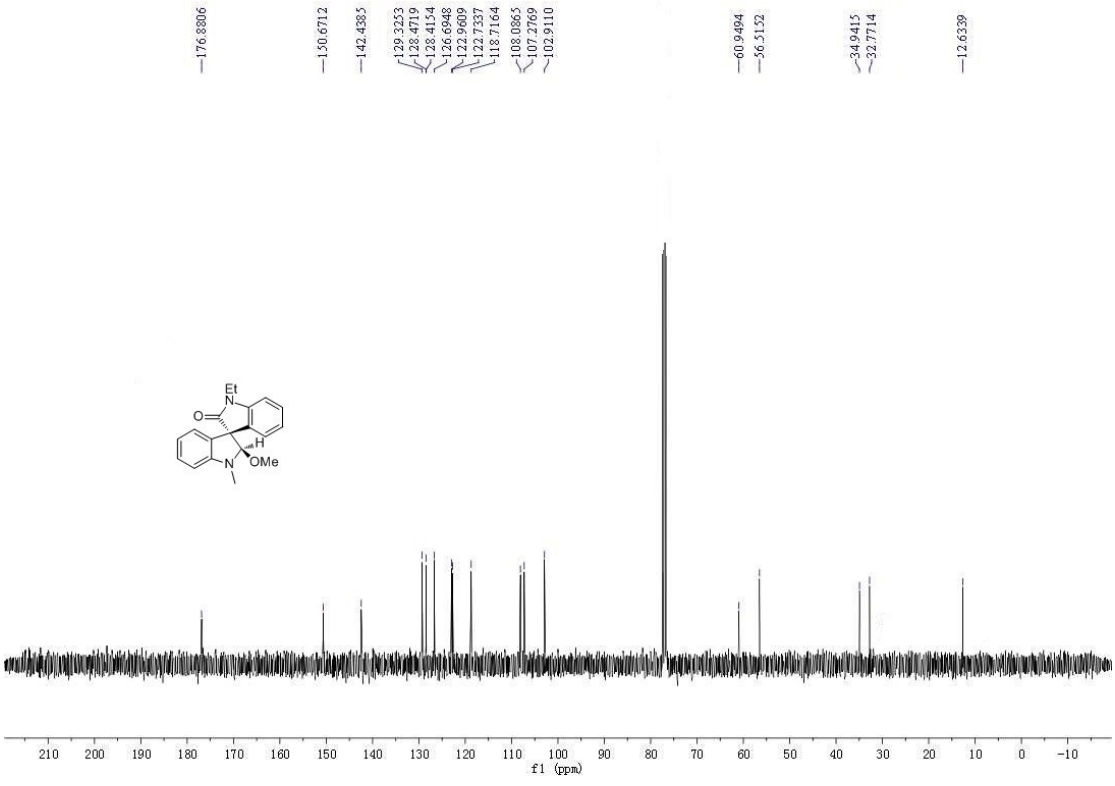
^{1}H NMR spectrum of **4ae**



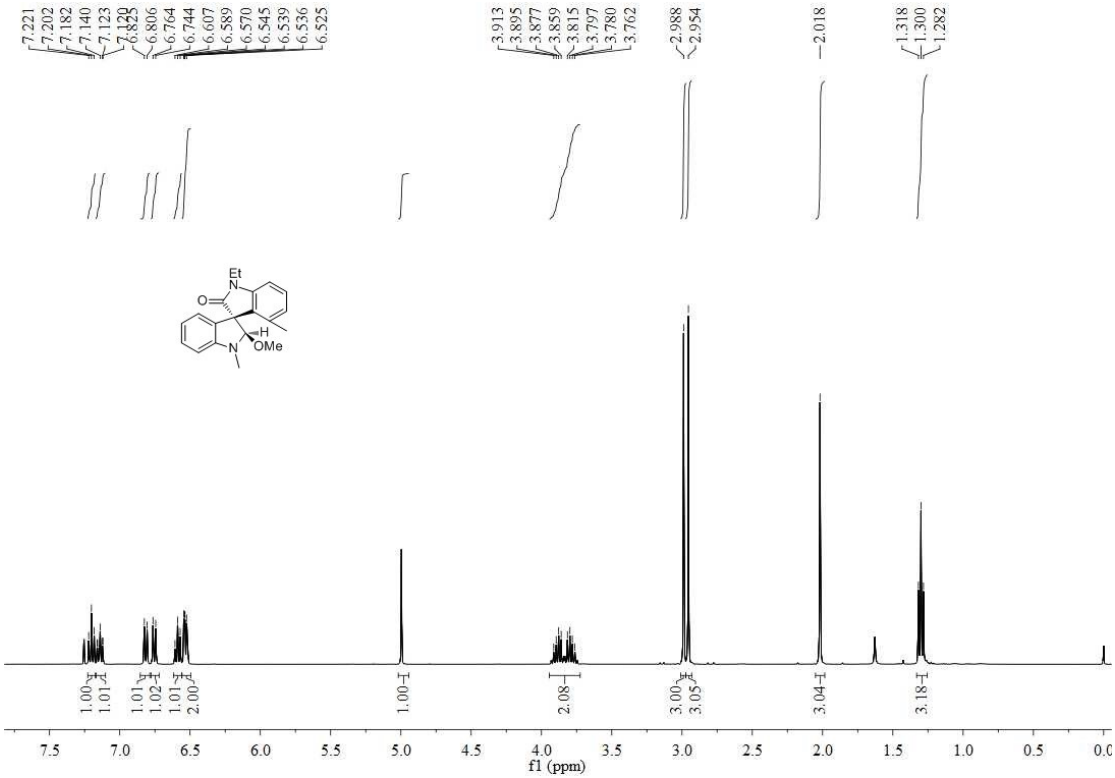
^{13}C NMR spectrum of **4ae**



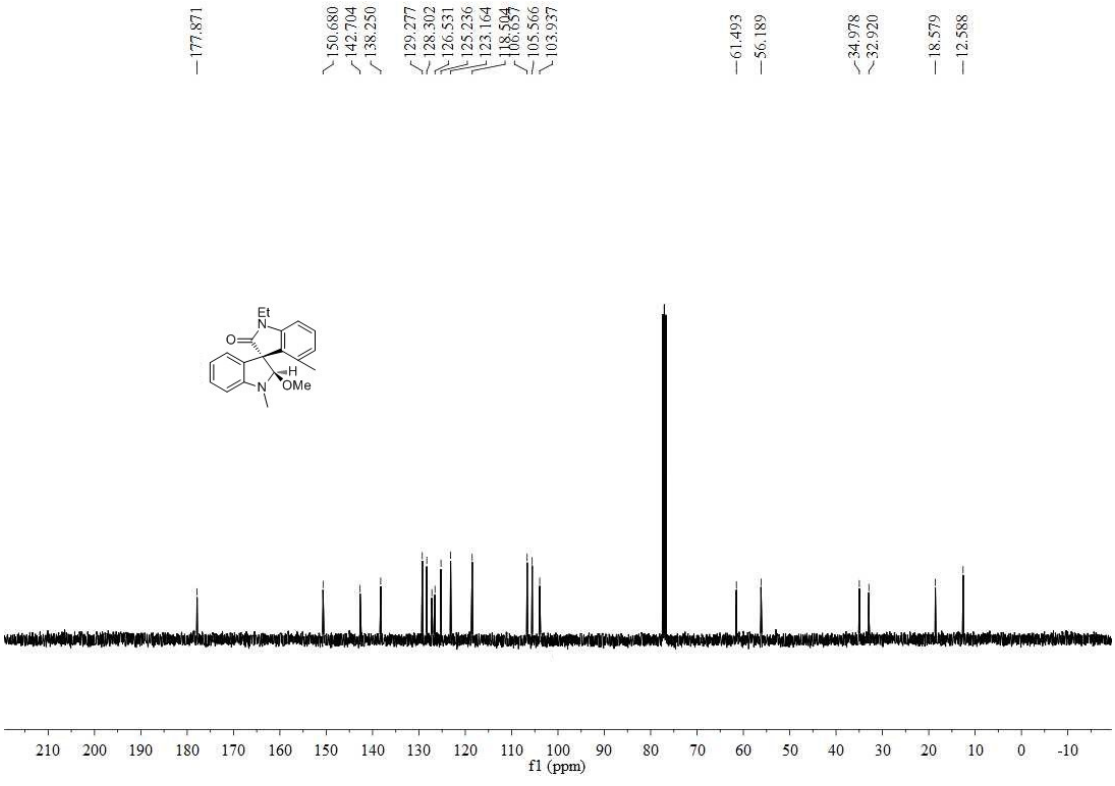
^{1}H NMR spectrum of **5a**



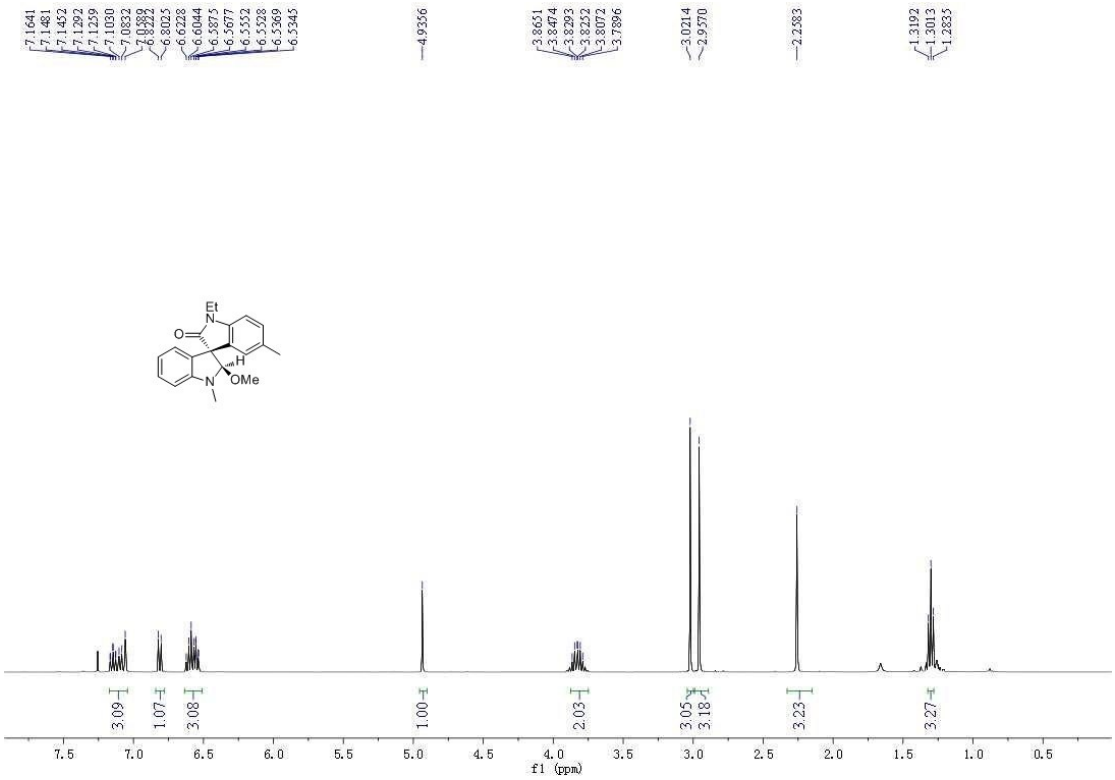
^{13}C NMR spectrum of**5a**



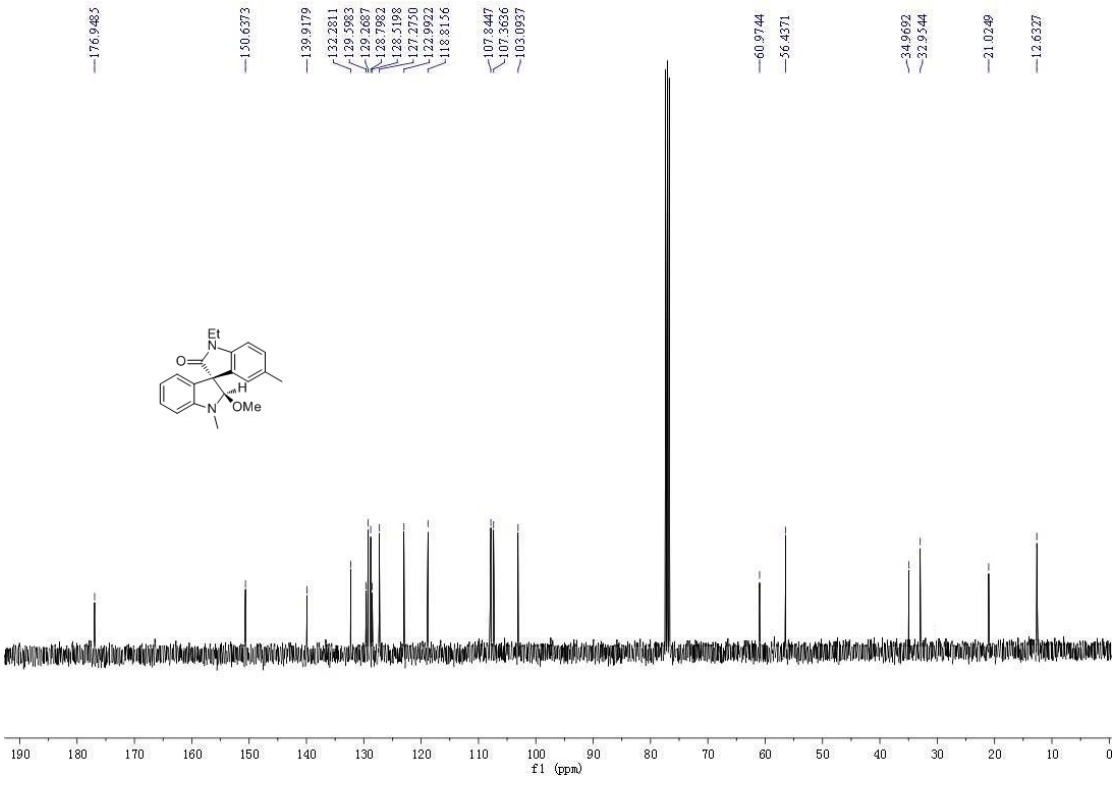
^{1}H NMR spectrum of **5b**



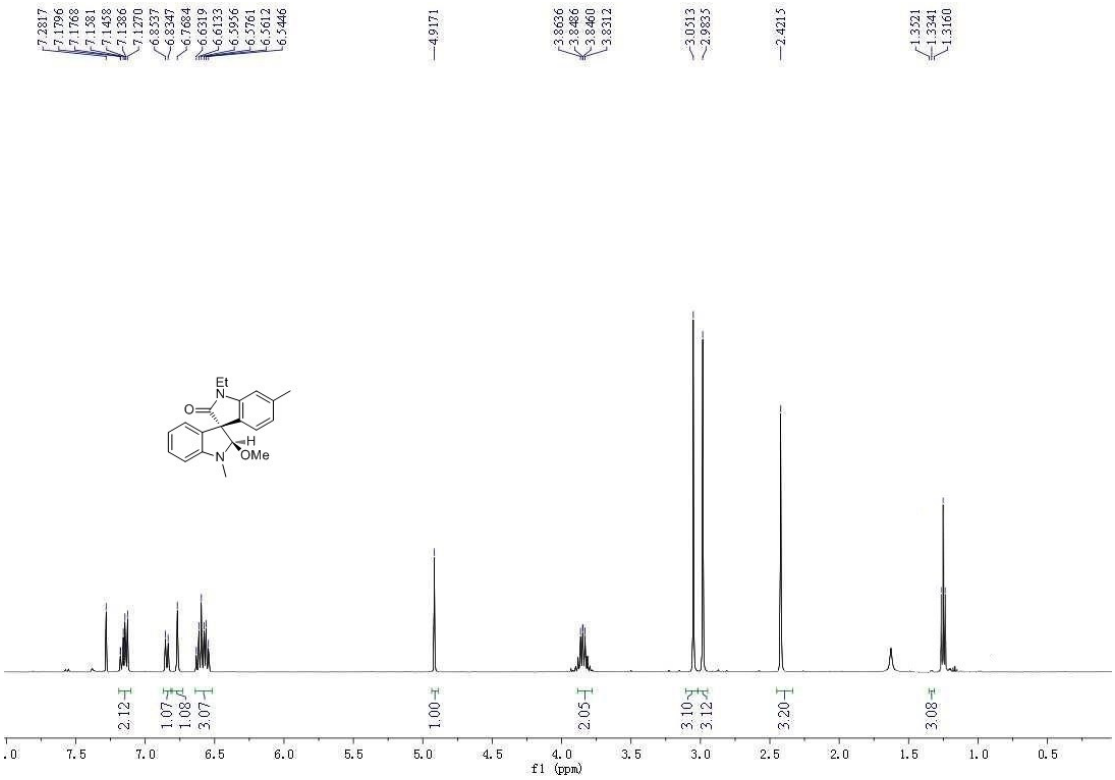
^{13}C NMR spectrum of**5b**



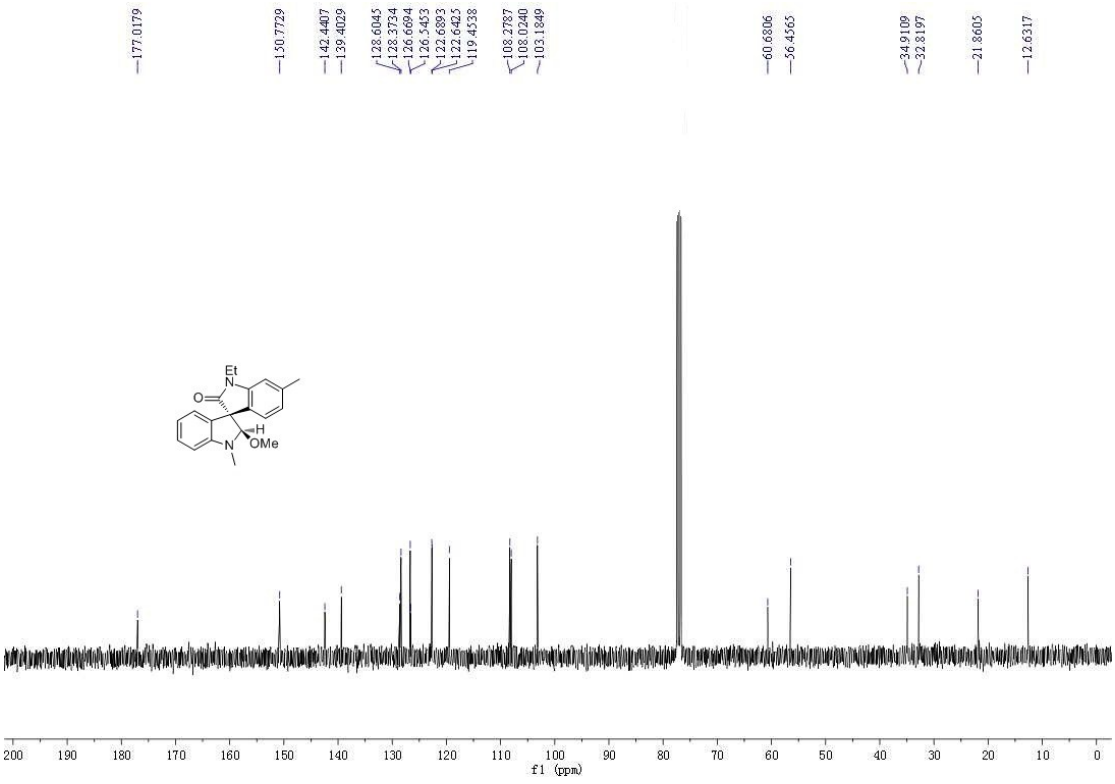
^{1}H NMR spectrum of **5c**



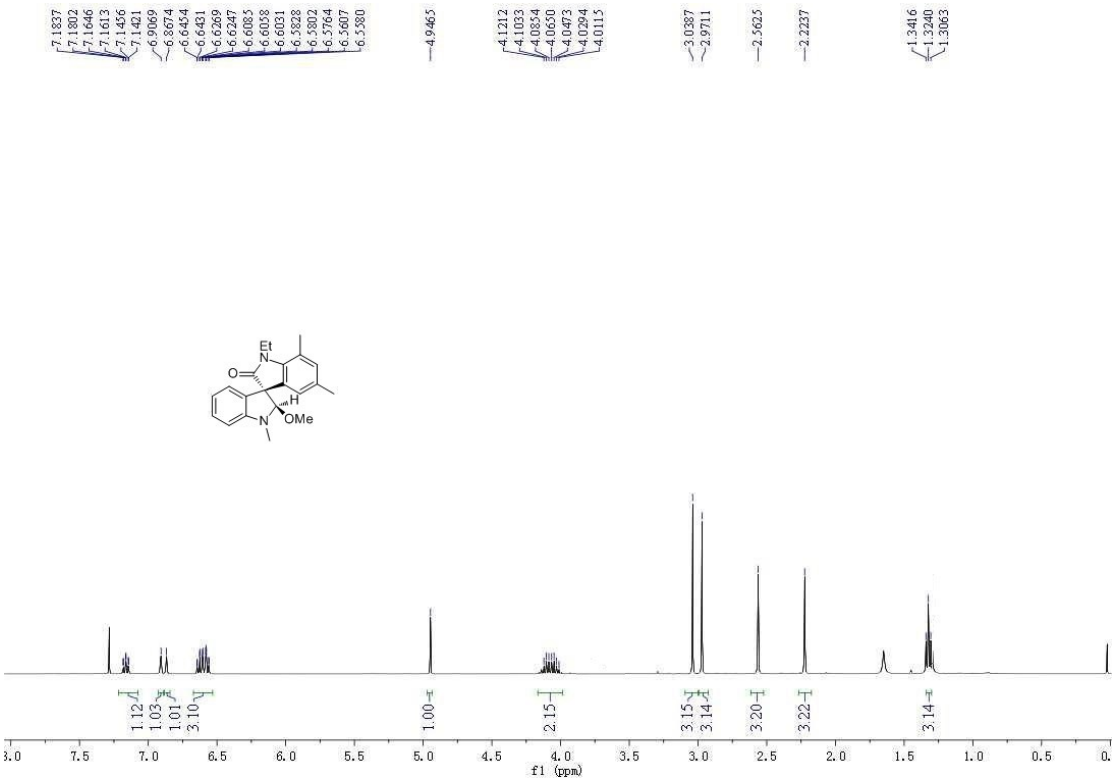
^{13}C NMR spectrum of **5c**



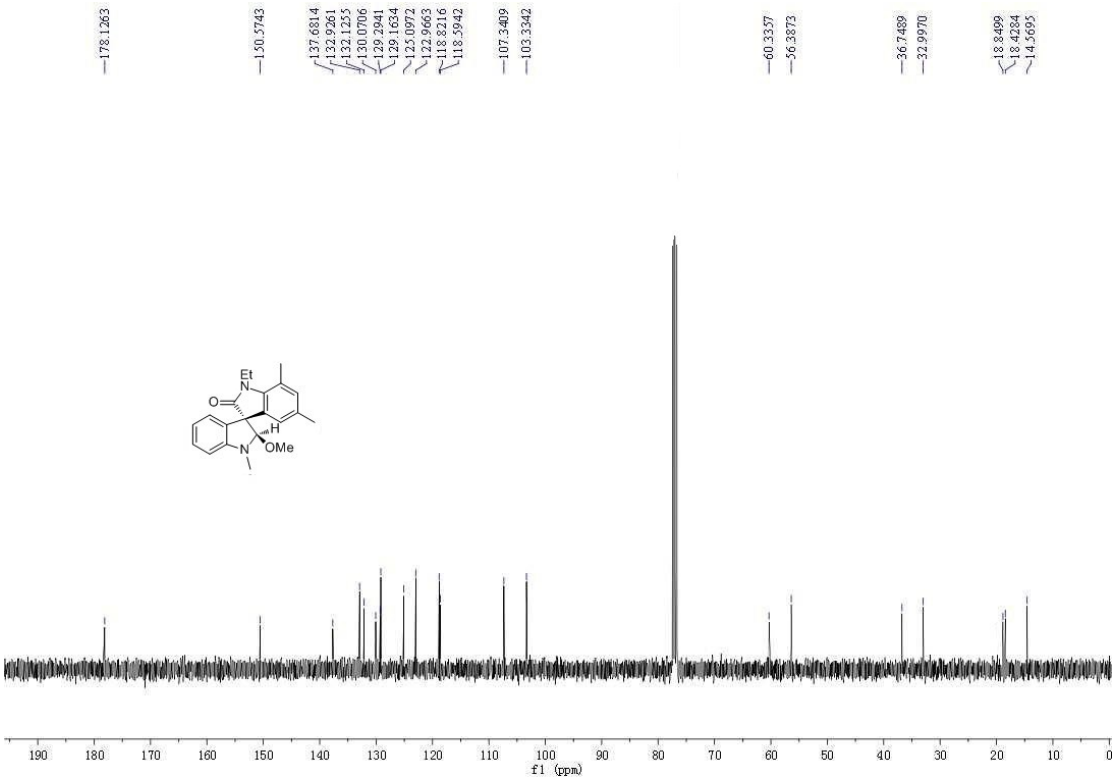
^{1}H NMR spectrum of **5d**



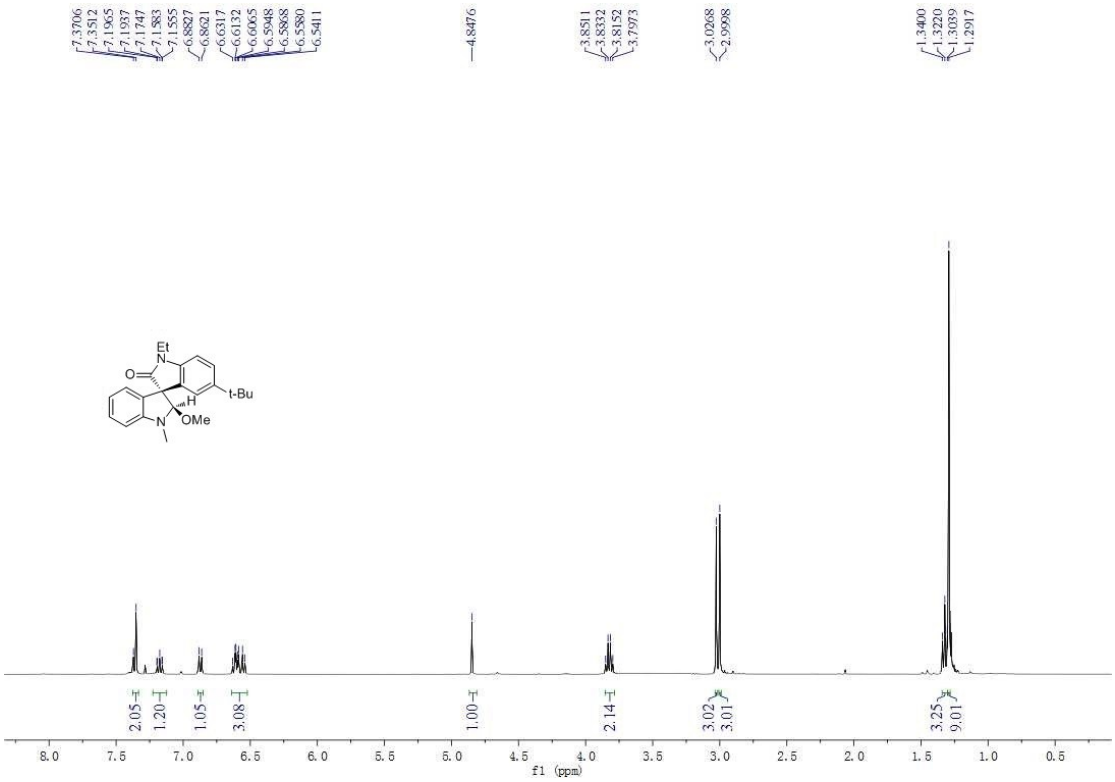
^{13}C NMR spectrum of**5d**



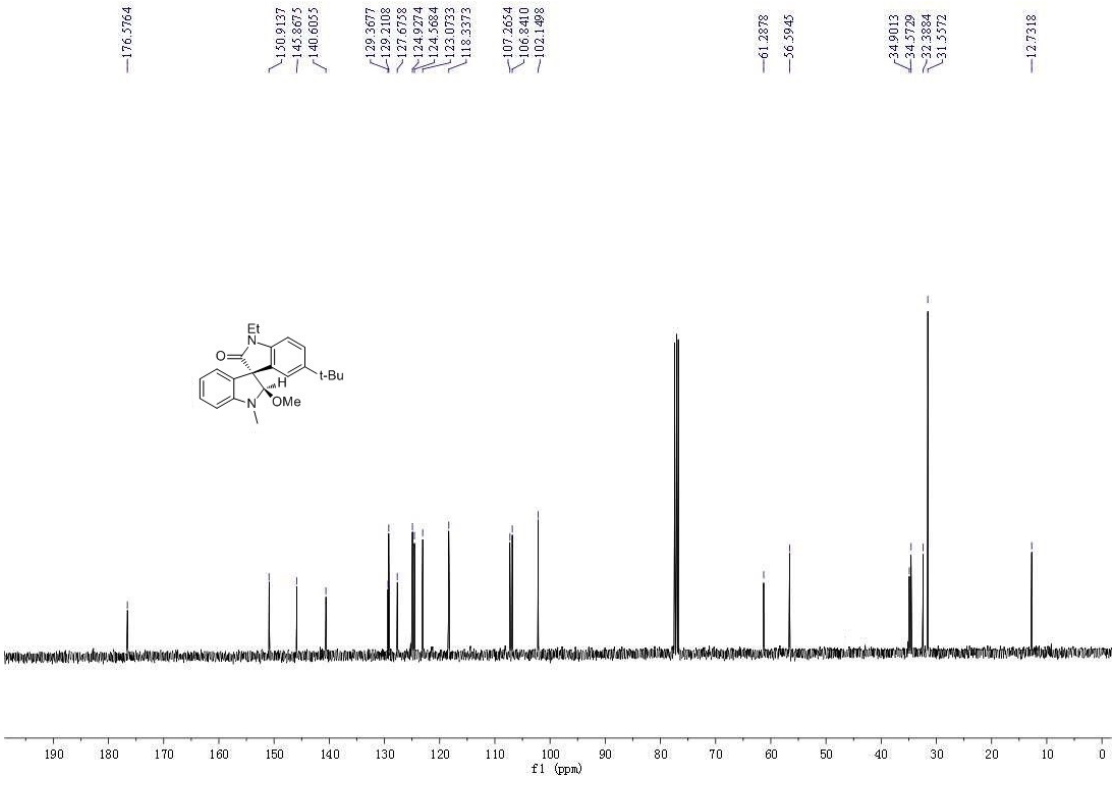
^{1}H NMR spectrum of **5e**



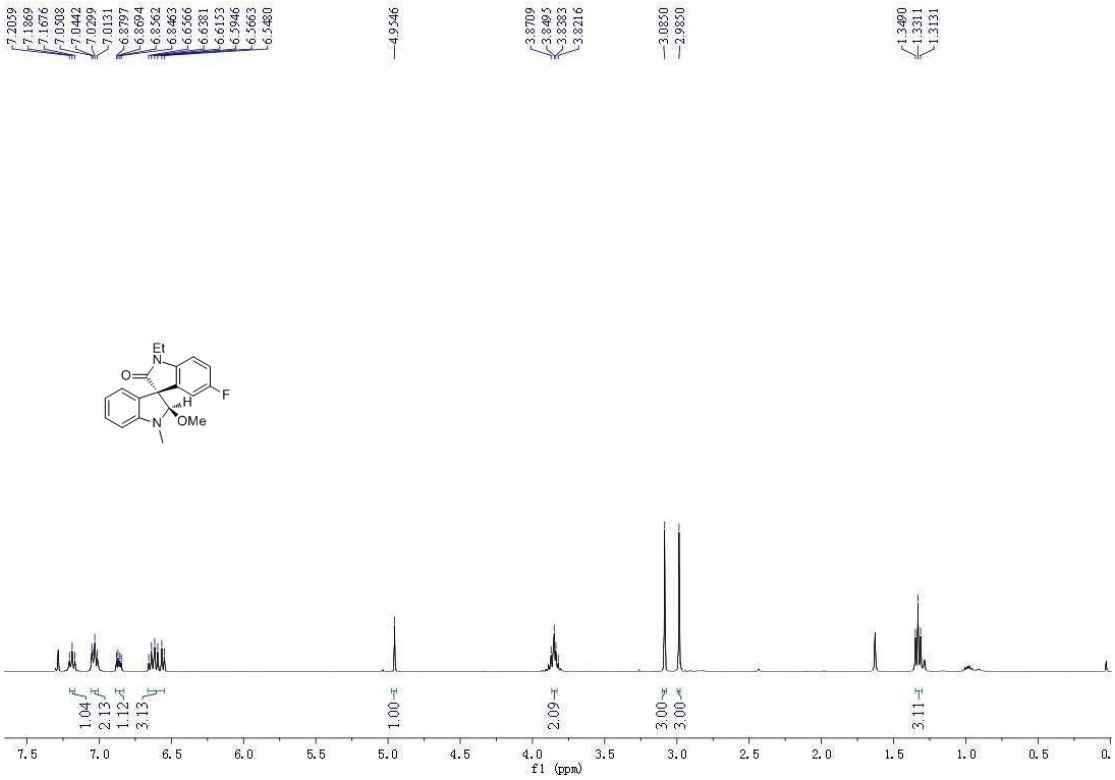
^{13}C NMR spectrum of**5e**



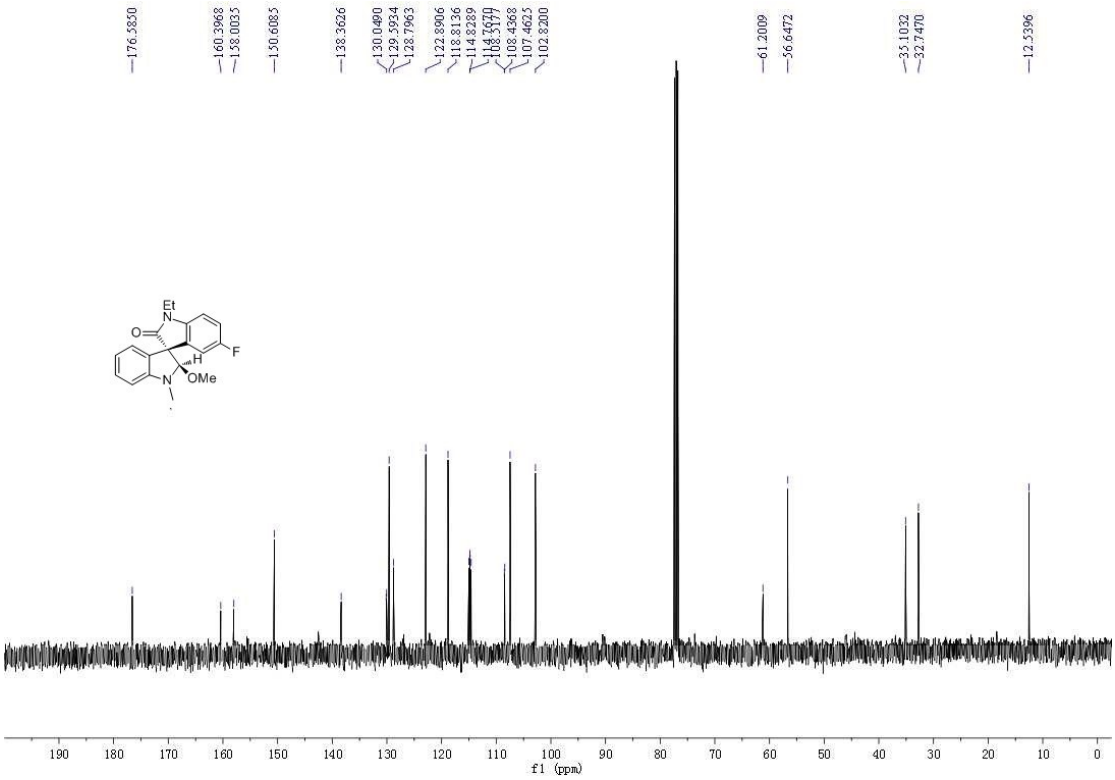
^{1}H NMR spectrum of **5f**



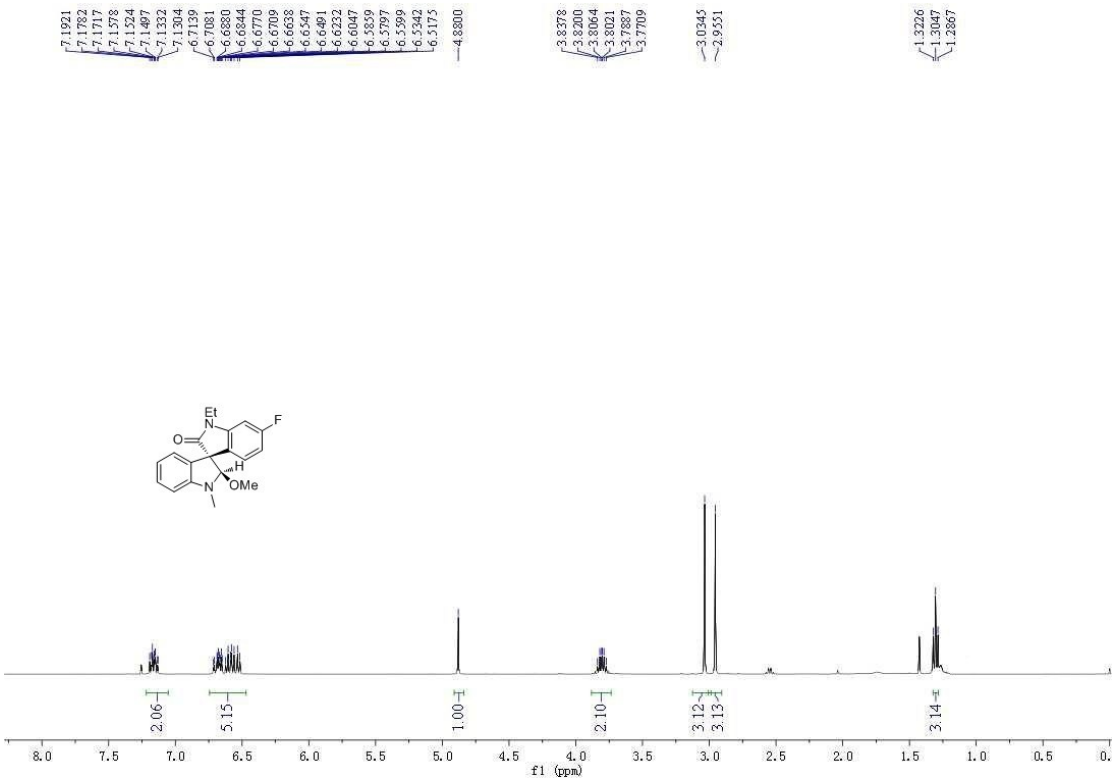
^{13}C NMR spectrum of**5f**



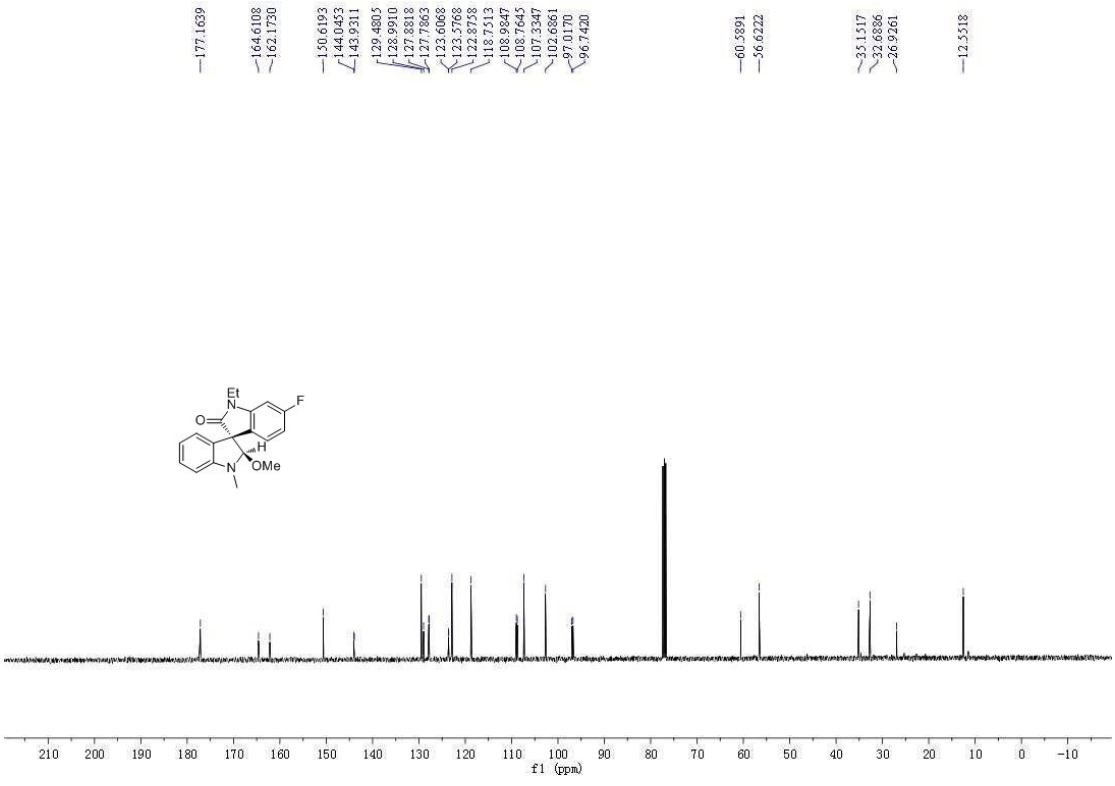
^{1}H NMR spectrum of **5g**



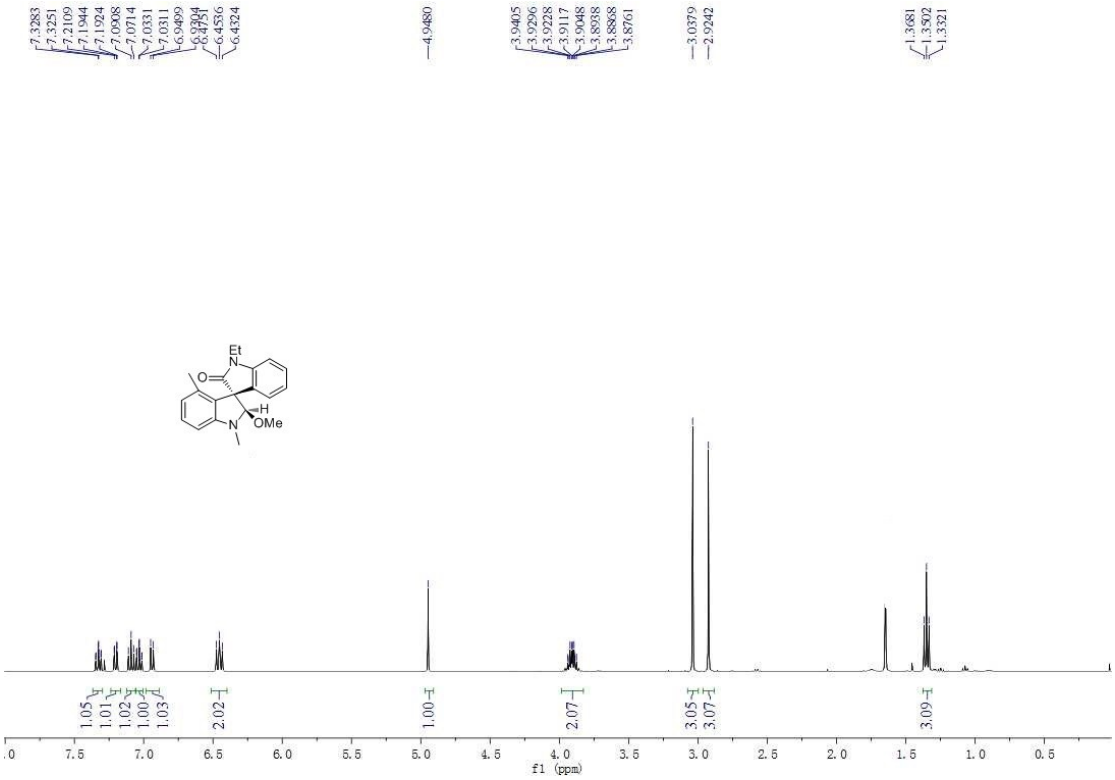
^{13}C NMR spectrum of**5g**



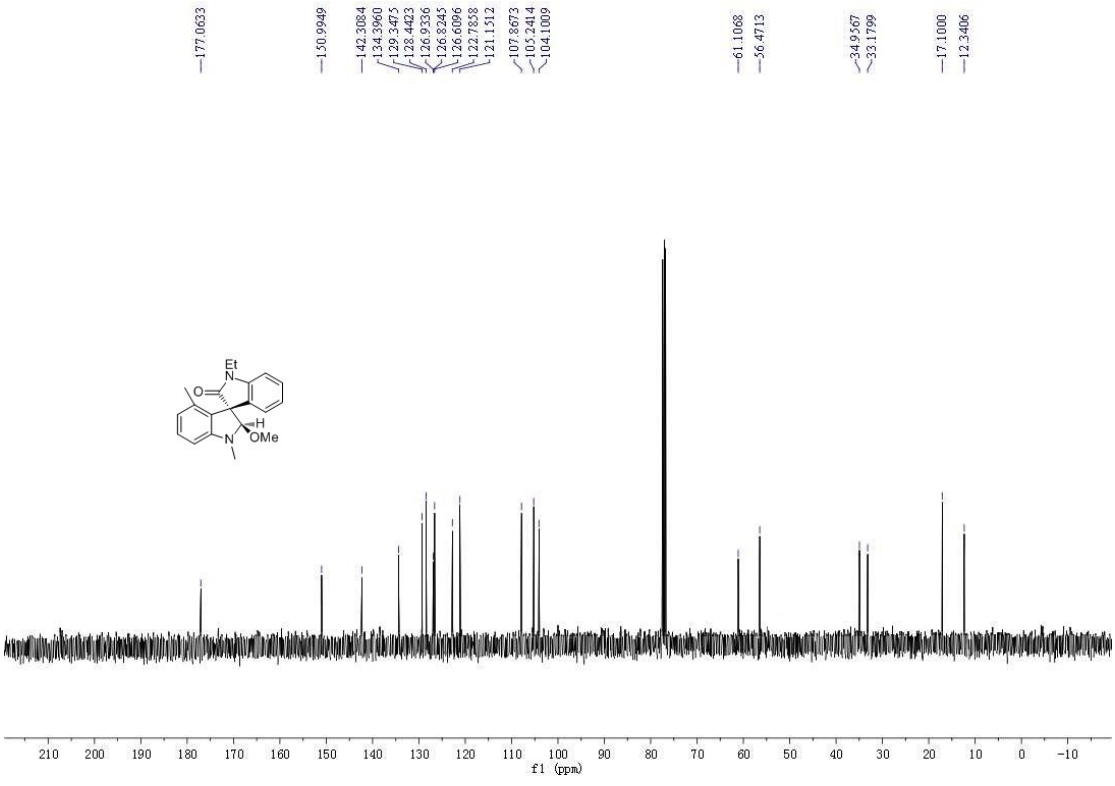
^{1}H NMR spectrum of **5h**



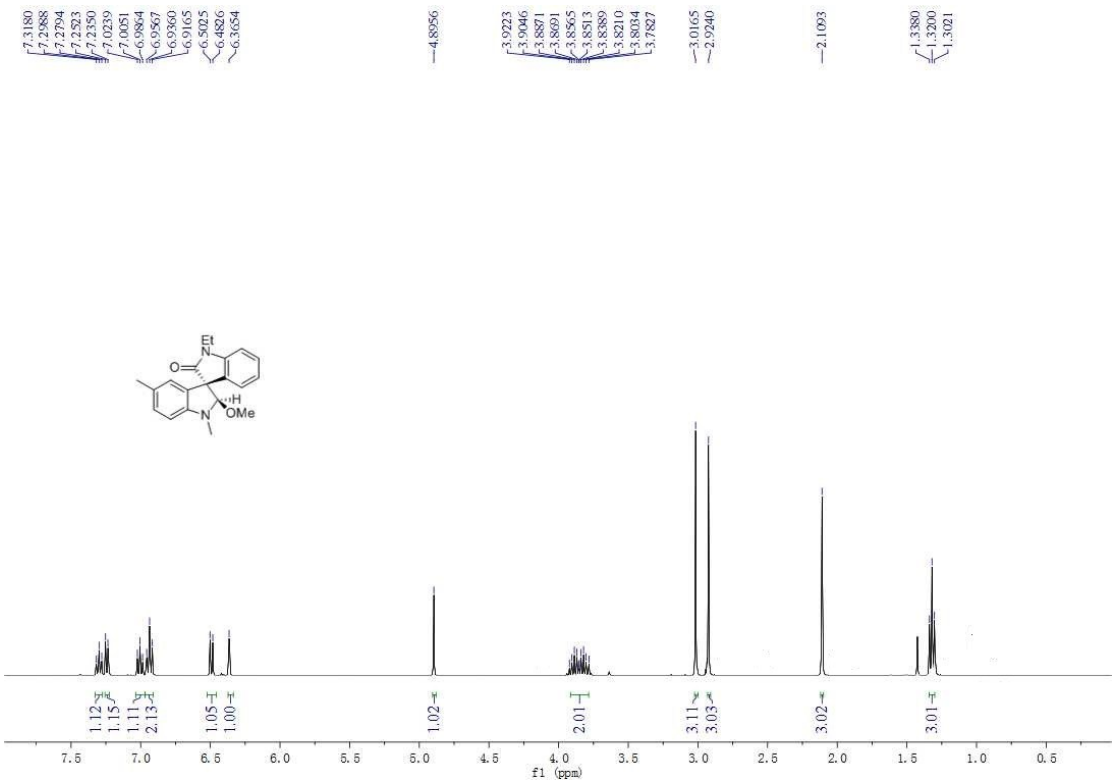
^{13}C NMR spectrum of**5h**



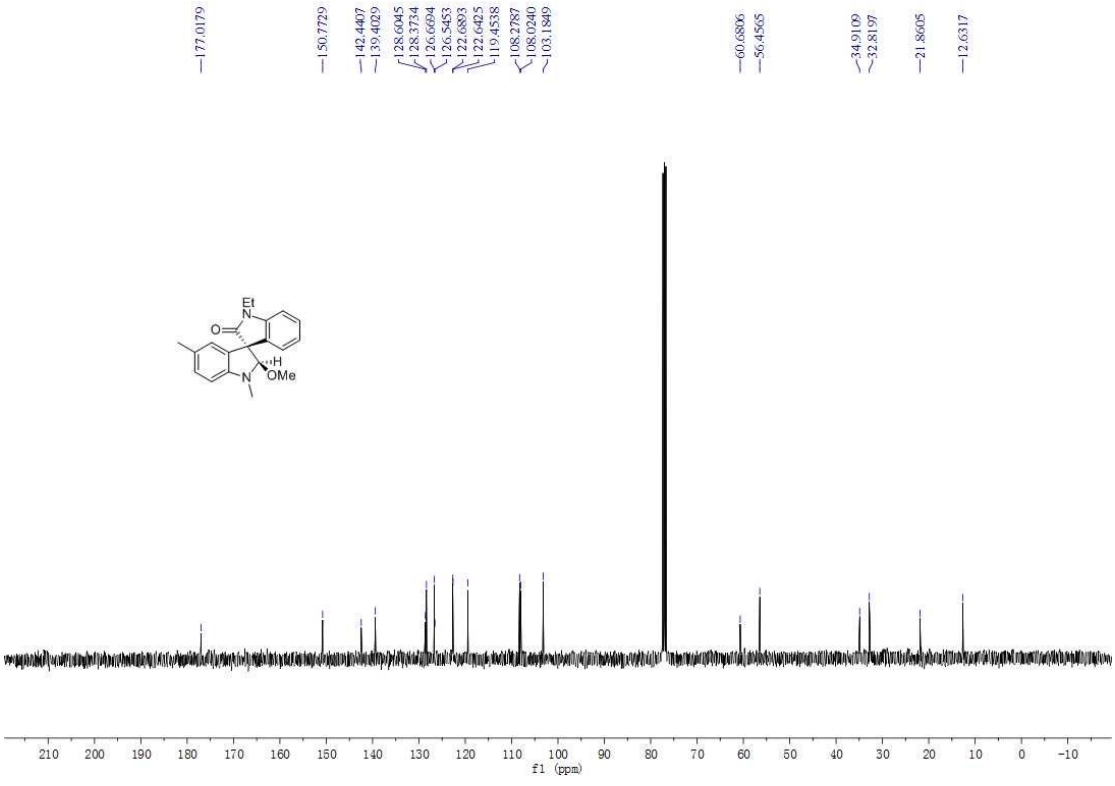
^{1}H NMR spectrum of **5k**



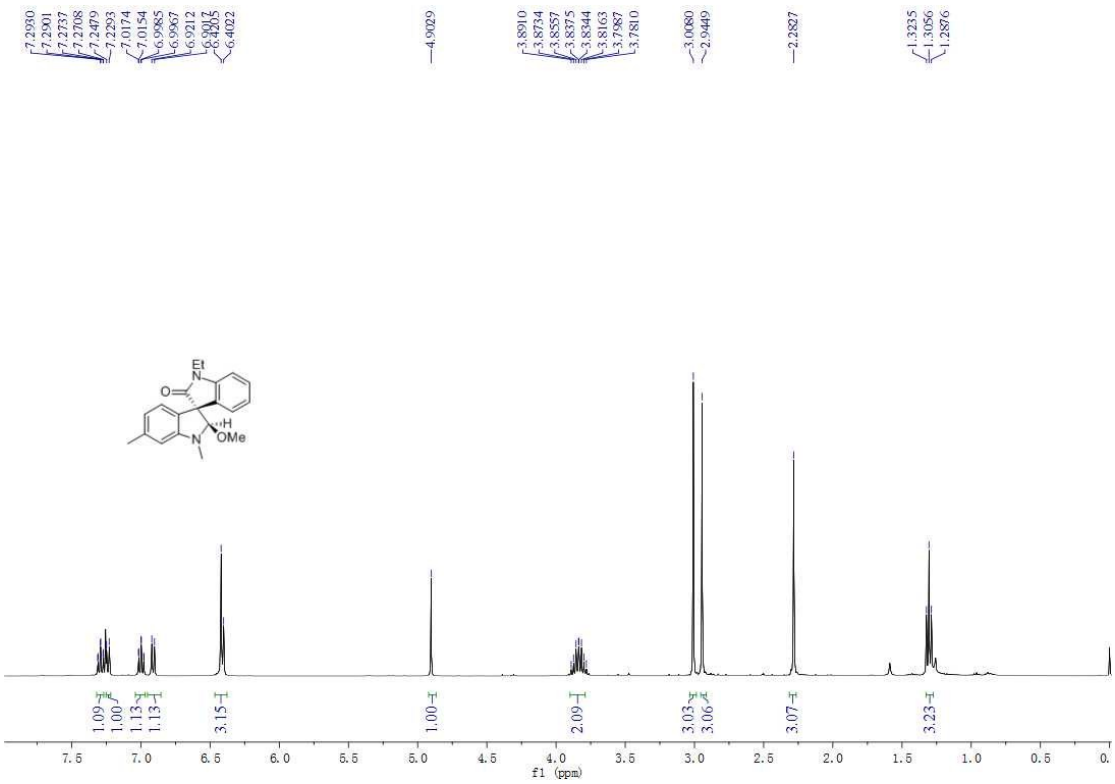
^{13}C NMR spectrum of**5k**



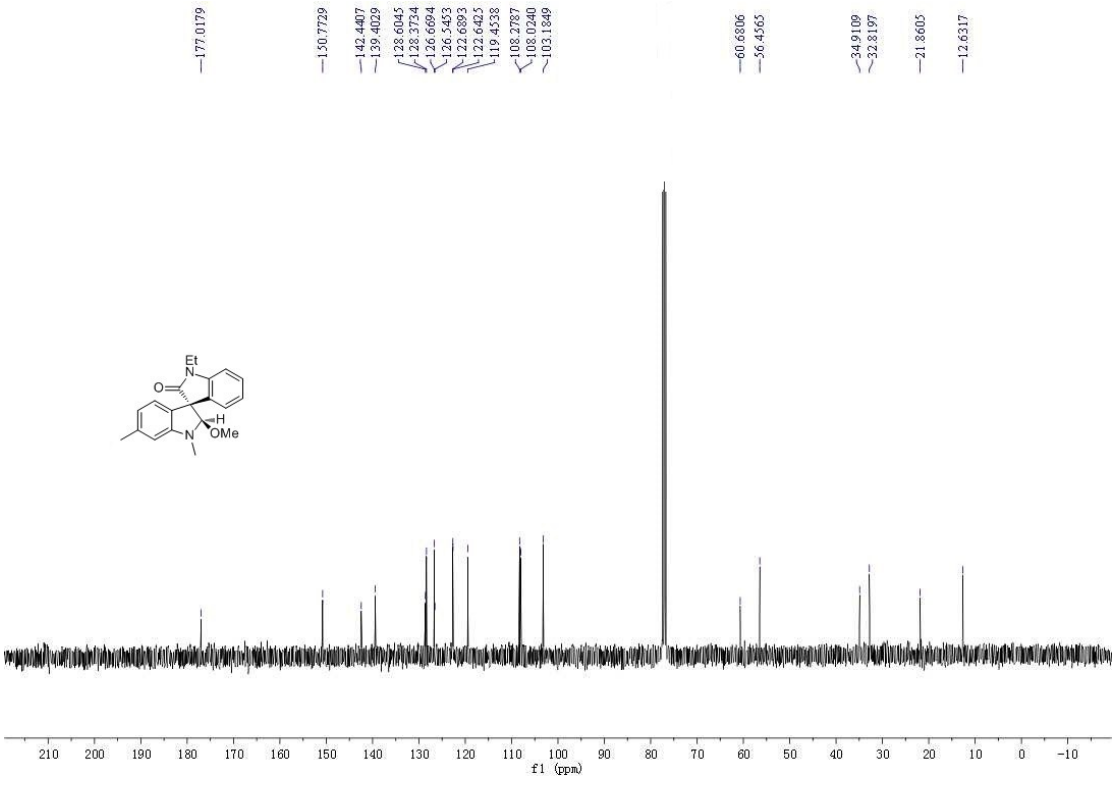
^{1}H NMR spectrum of **5l**



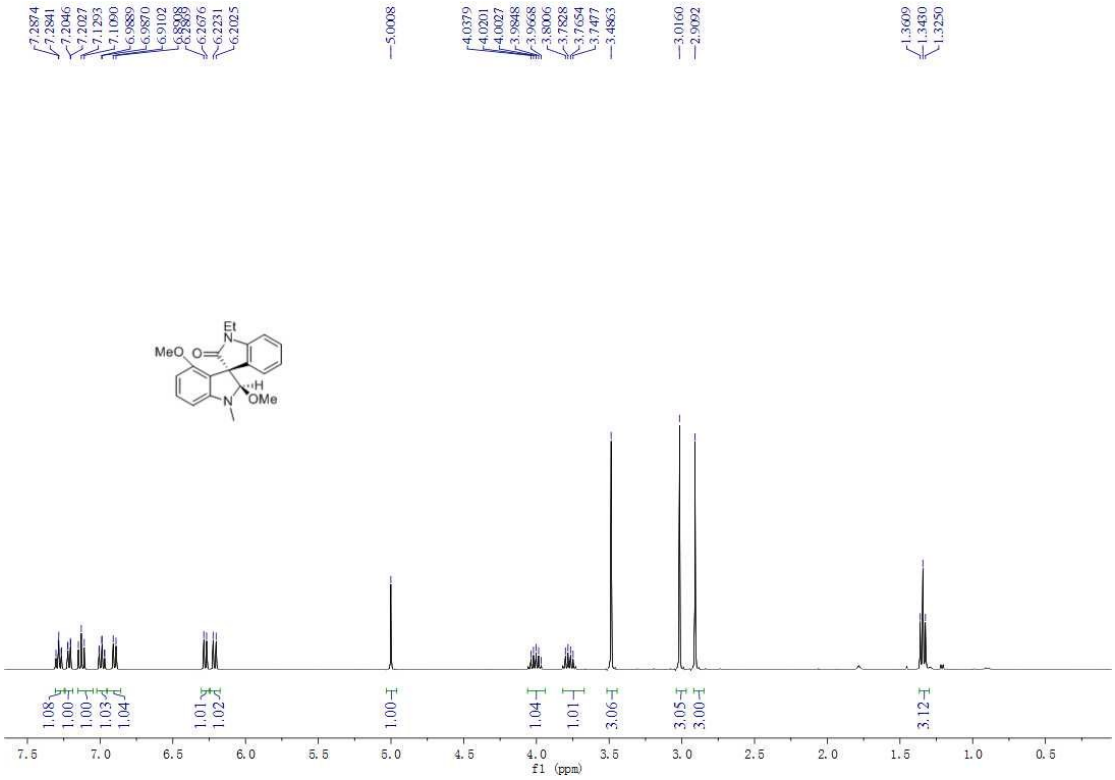
^{13}C NMR spectrum of**5l**



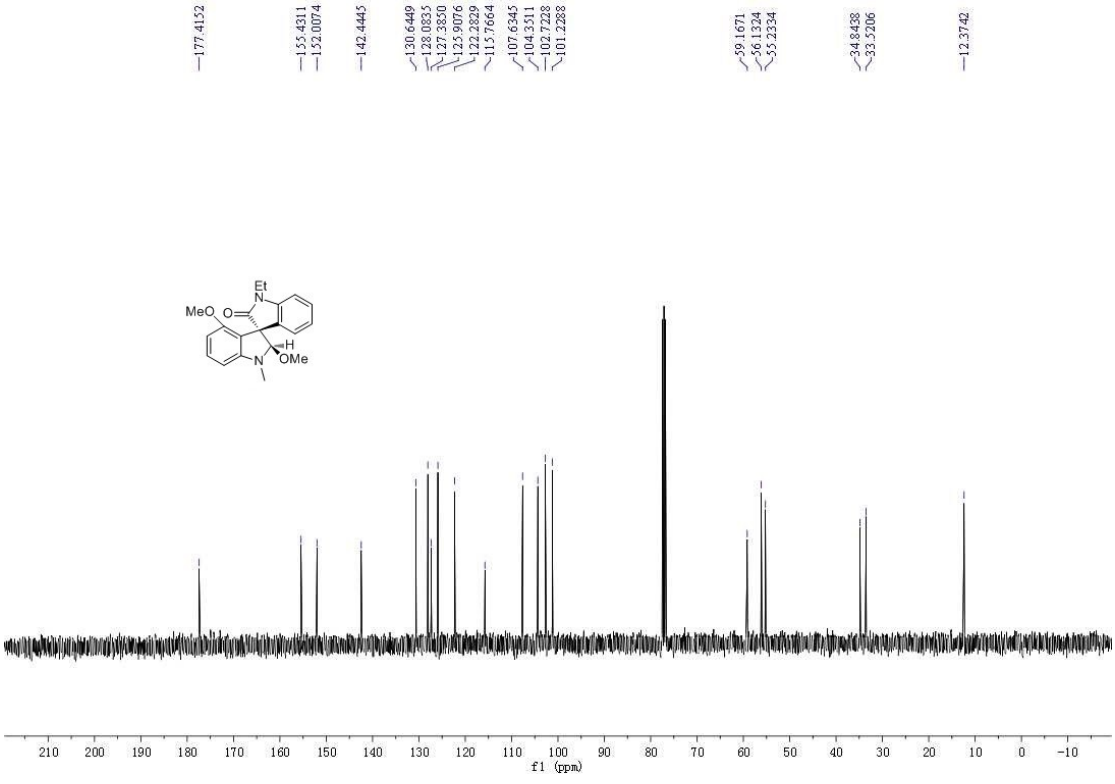
^{1}H NMR spectrum of **5m**



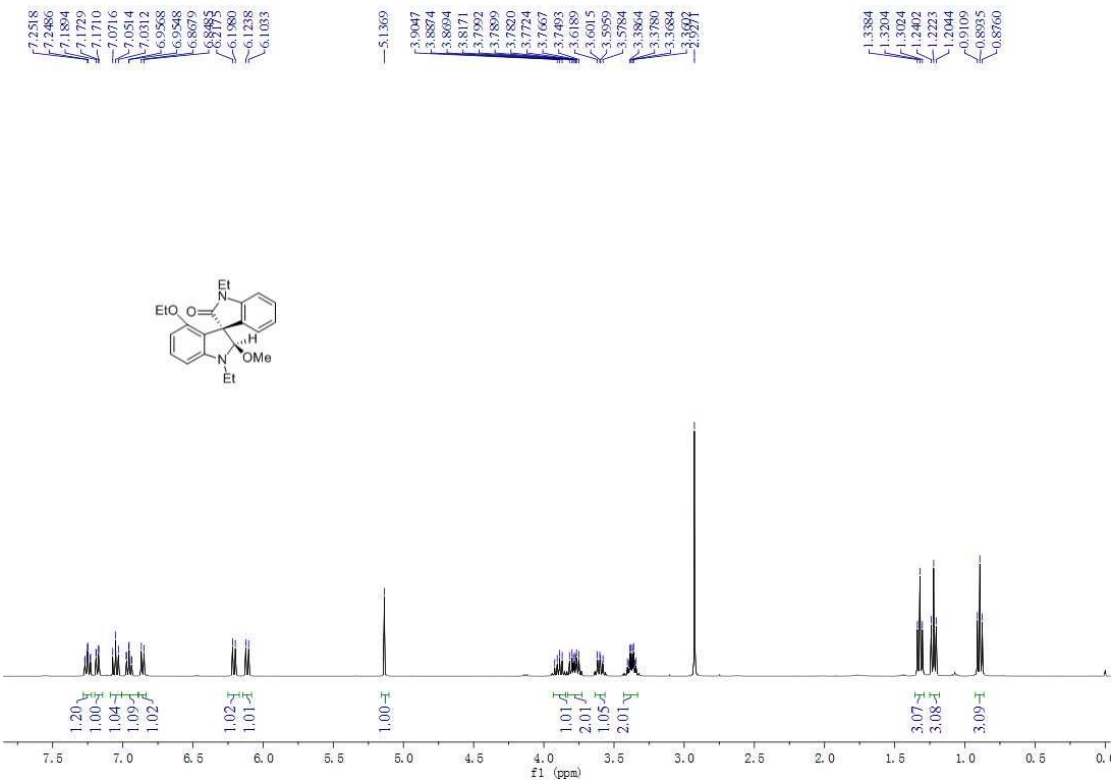
^{13}C NMR spectrum of**5m**



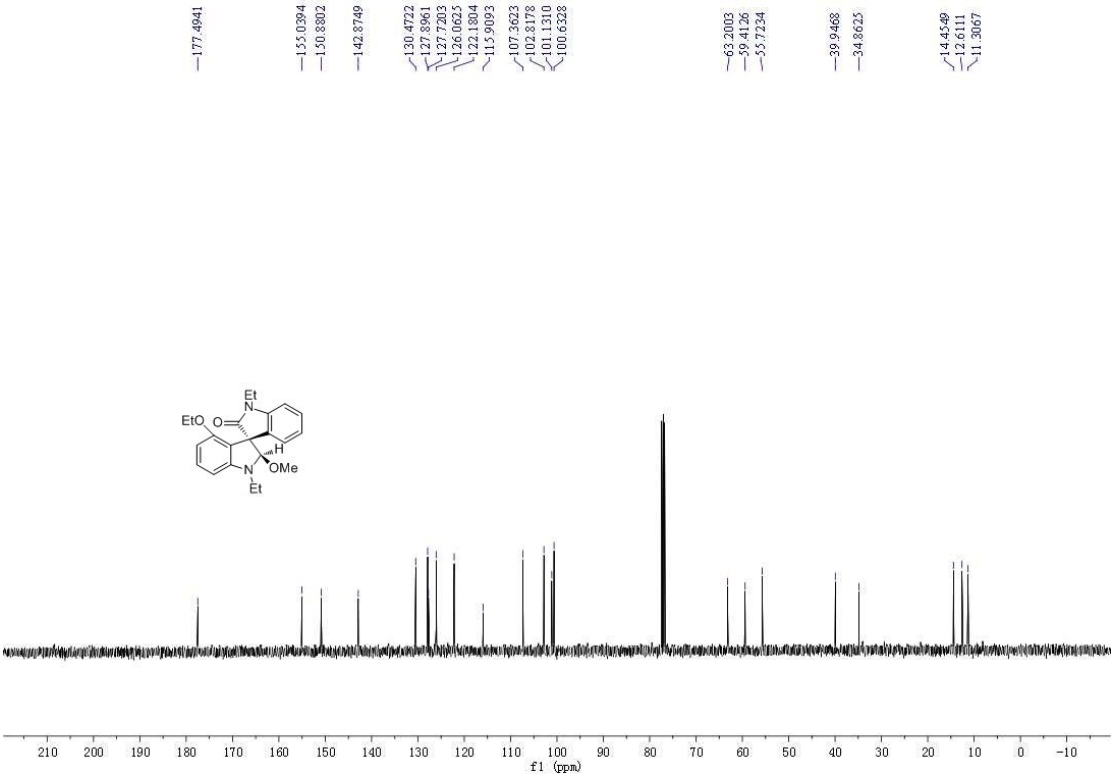
^{1}H NMR spectrum of **5n**



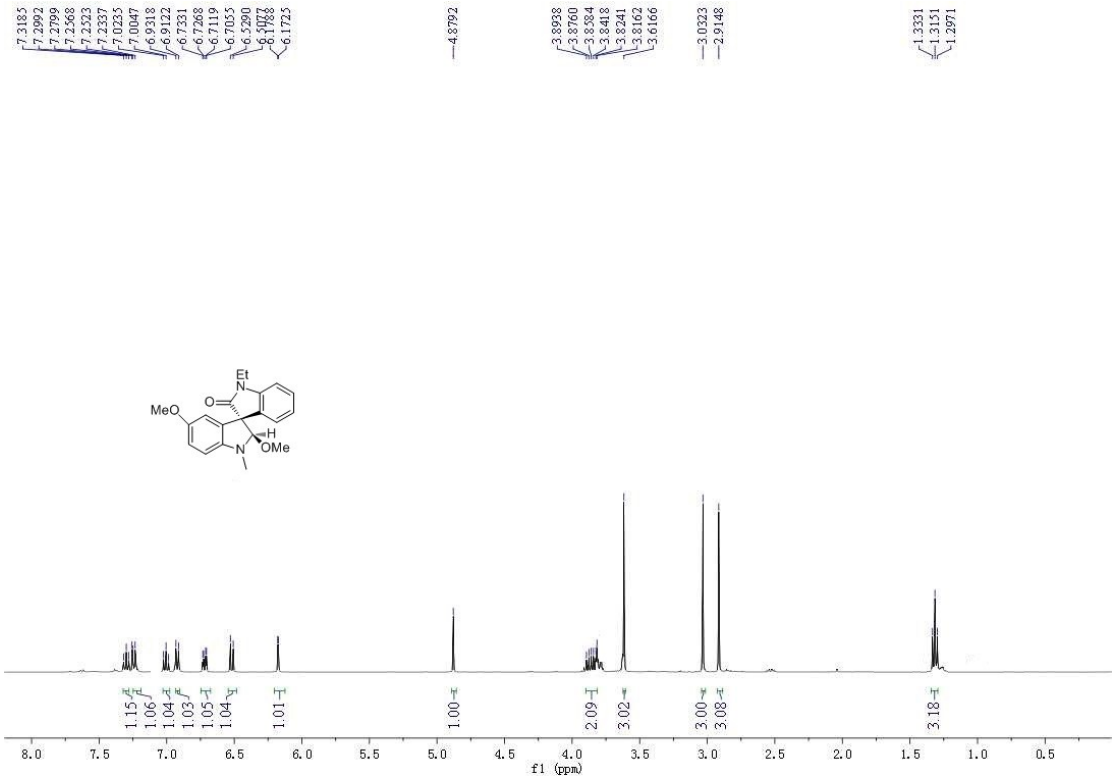
^{13}C NMR spectrum of**5n**



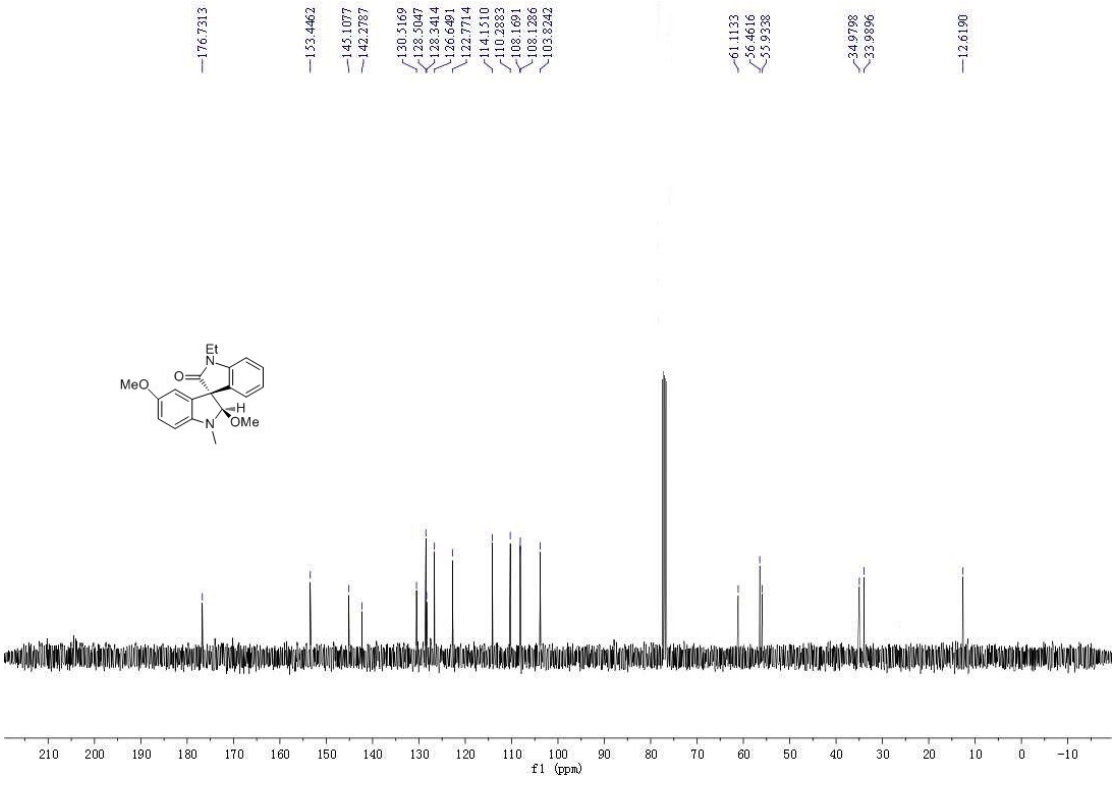
^{1}H NMR spectrum of **5o**



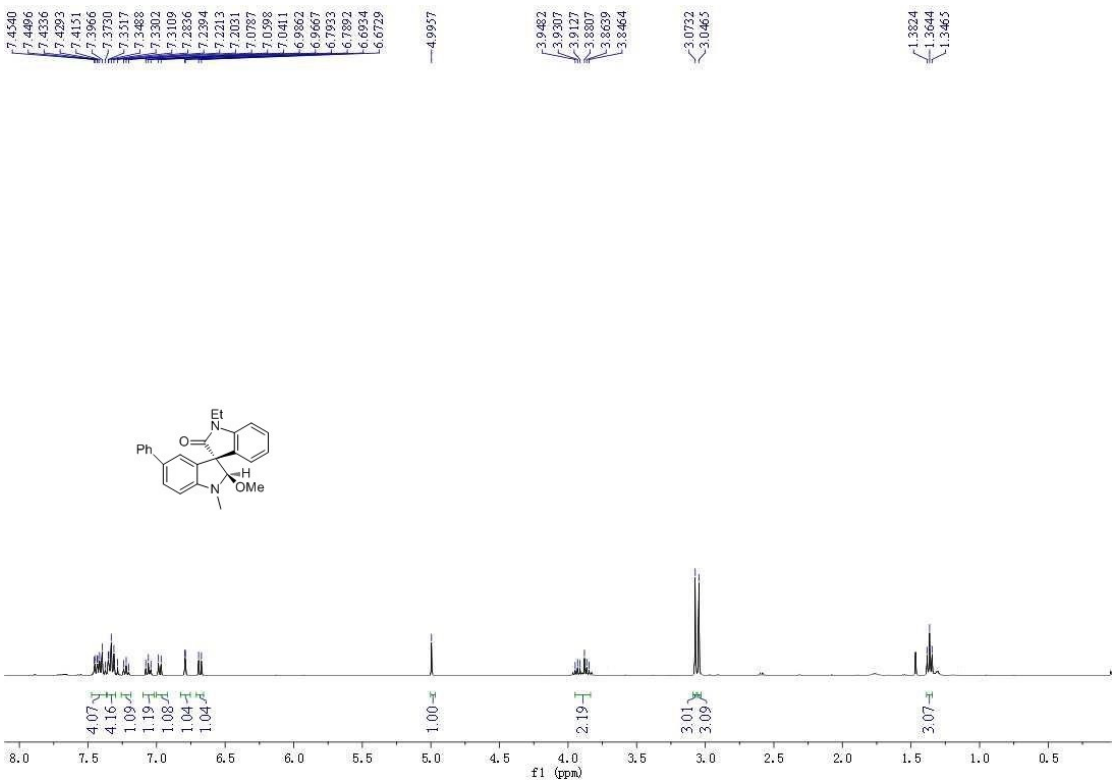
^{13}C NMR spectrum of**5o**



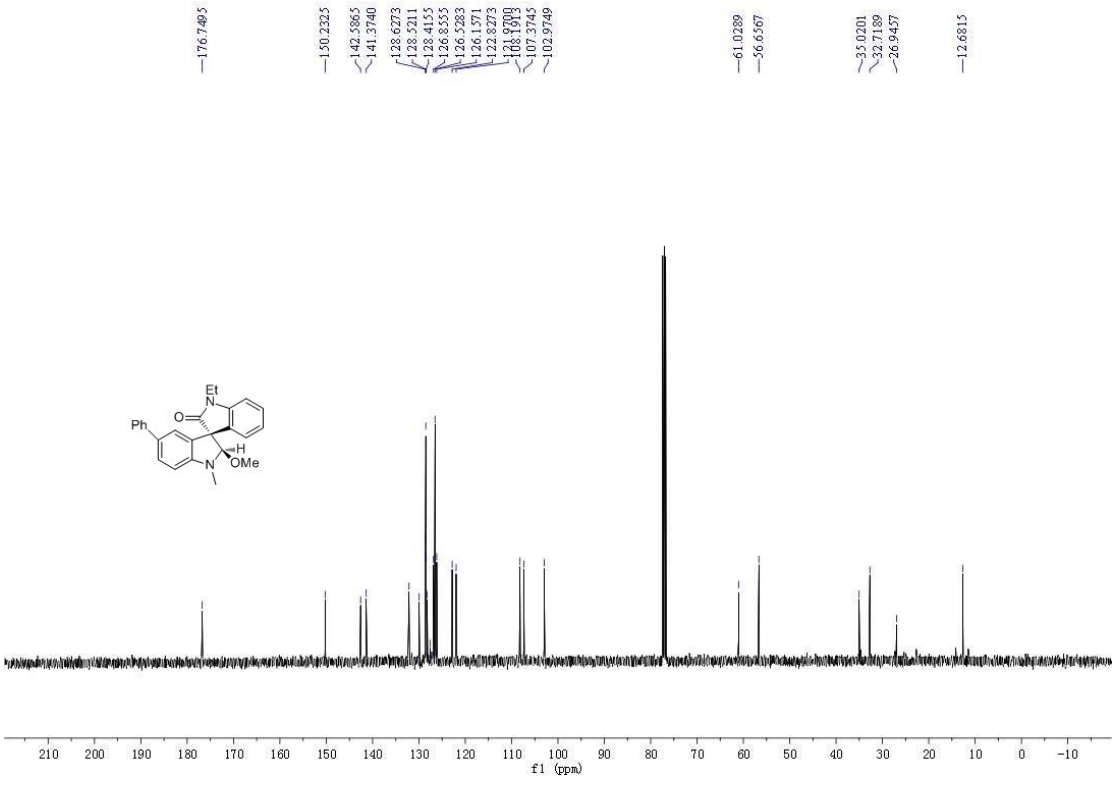
^{1}H NMR spectrum of **5p**



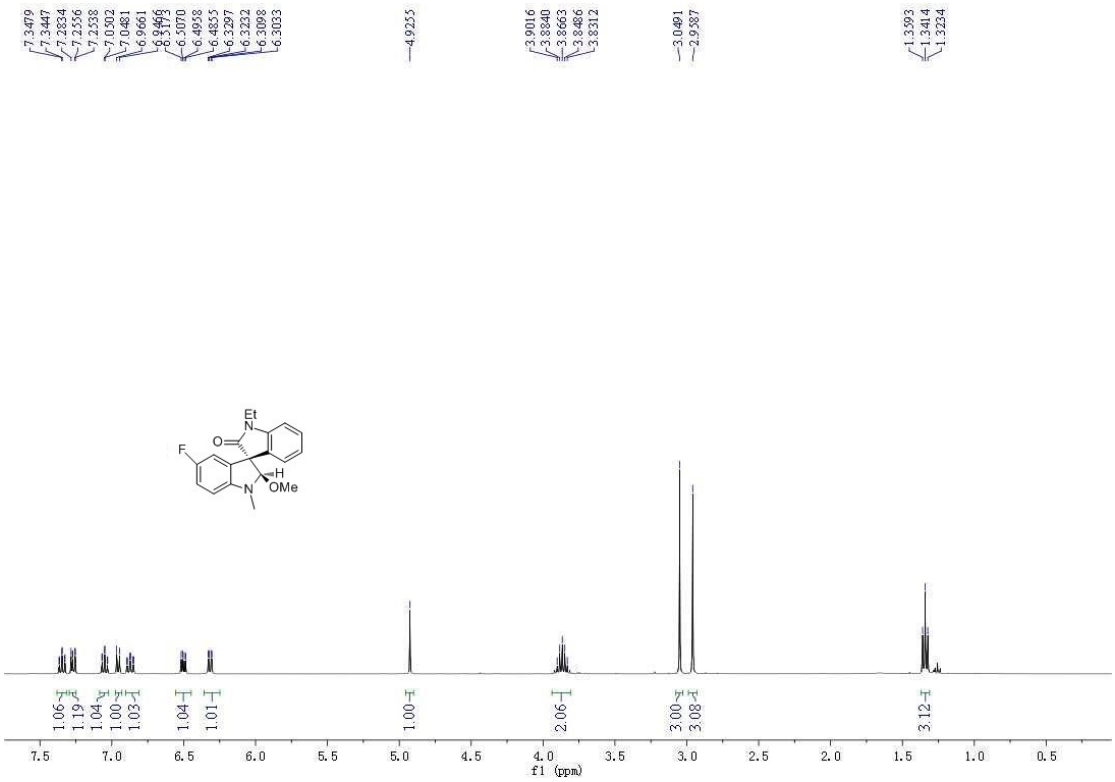
^{13}C NMR spectrum of**5p**



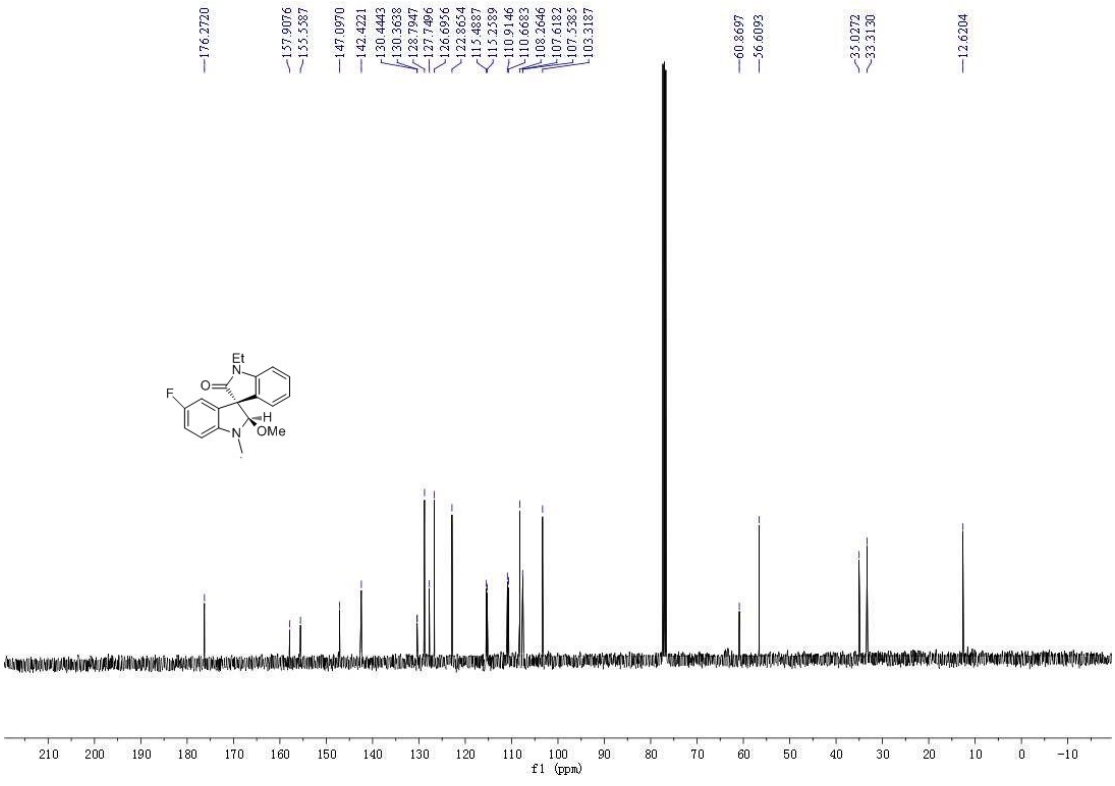
^{1}H NMR spectrum of **5q**



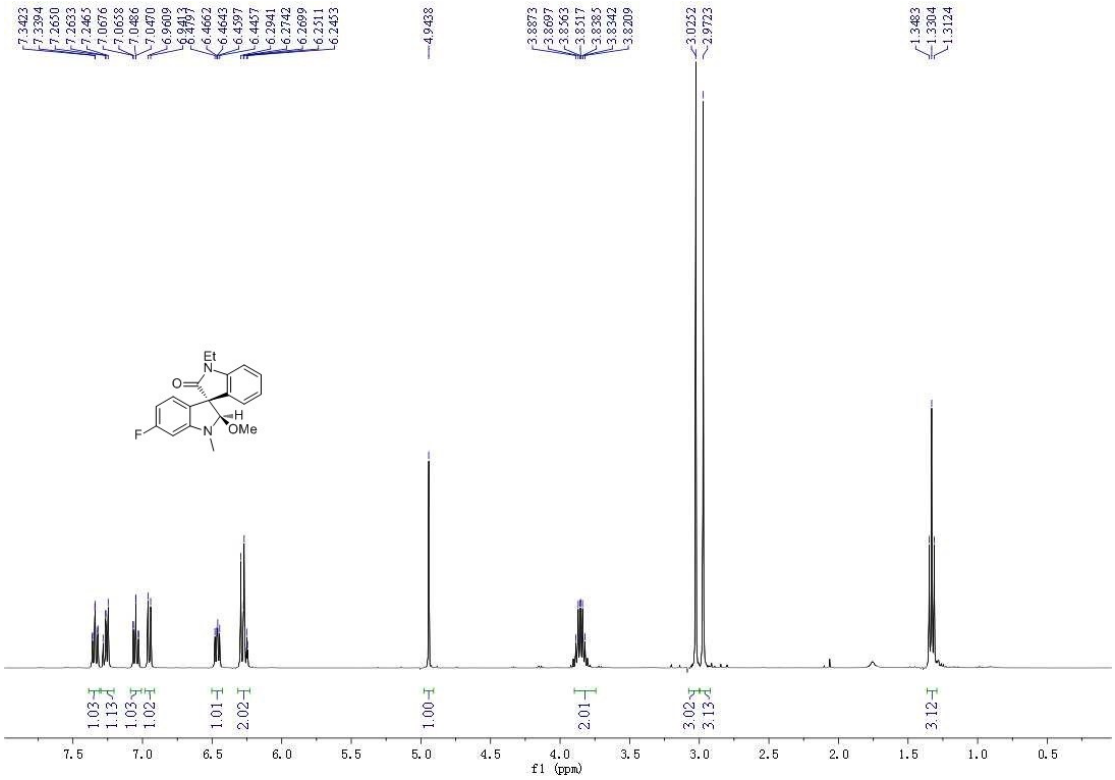
^{13}C NMR spectrum of**5q**



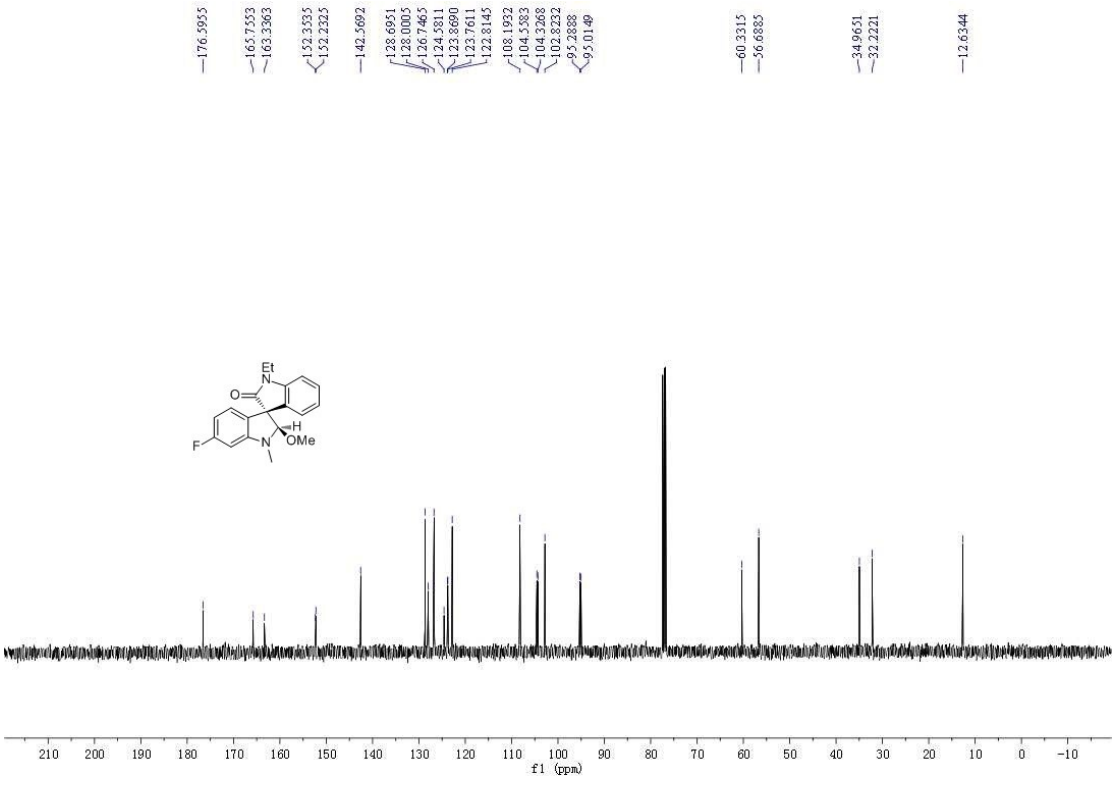
^{1}H NMR spectrum of **5r**



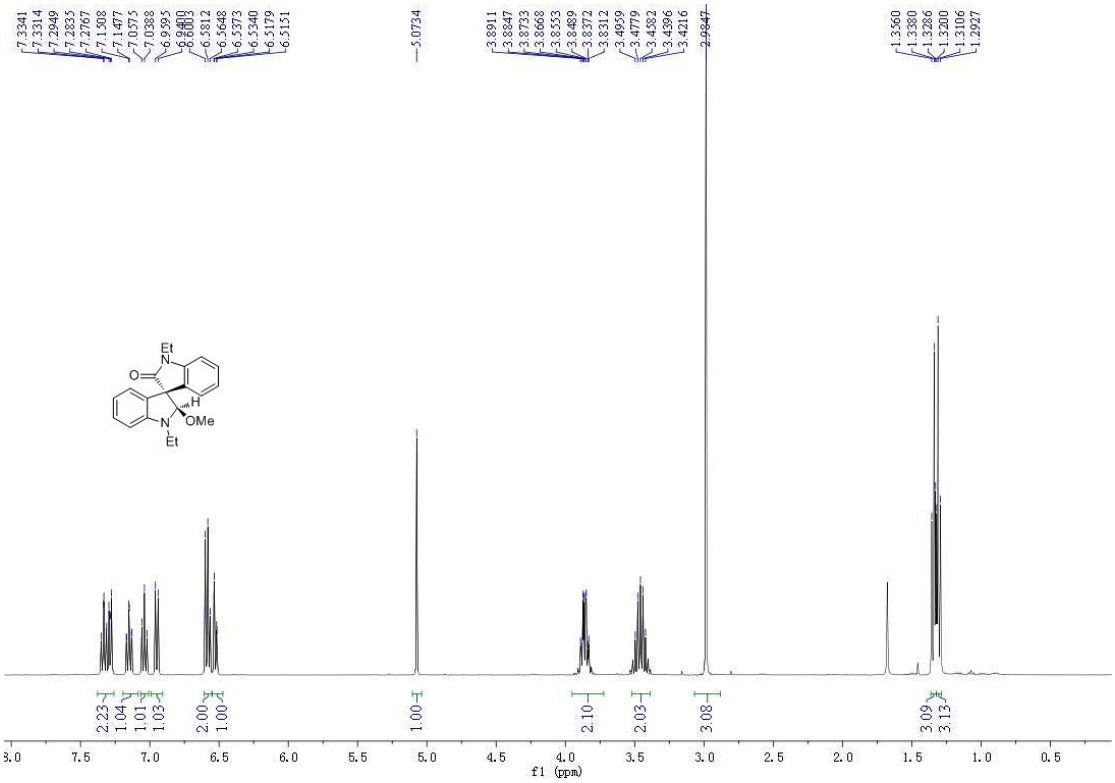
^{13}C NMR spectrum of**5r**



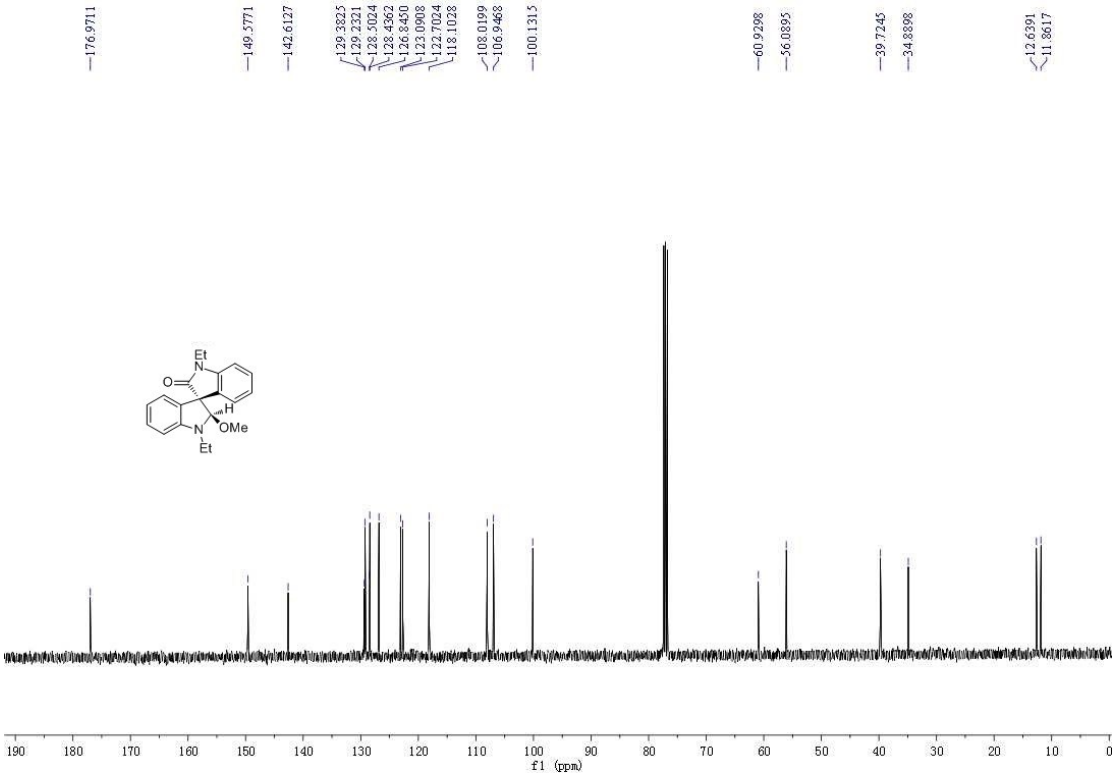
^{1}H NMR spectrum of **5s**



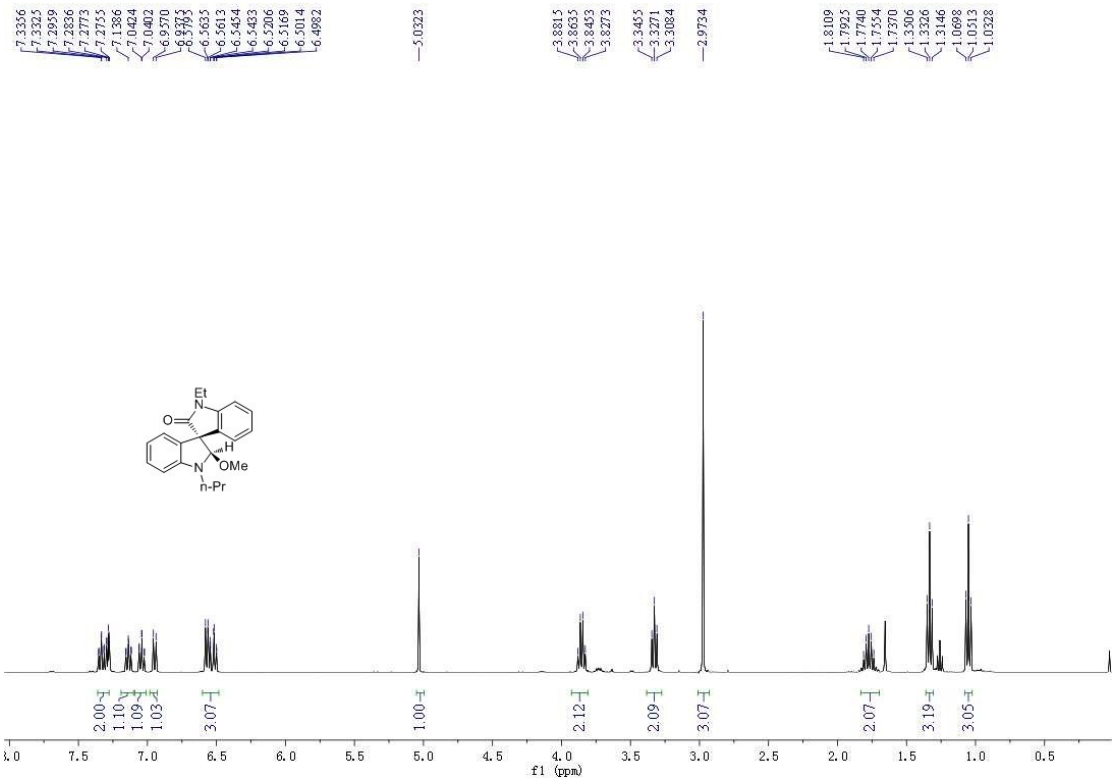
^{13}C NMR spectrum of**5s**



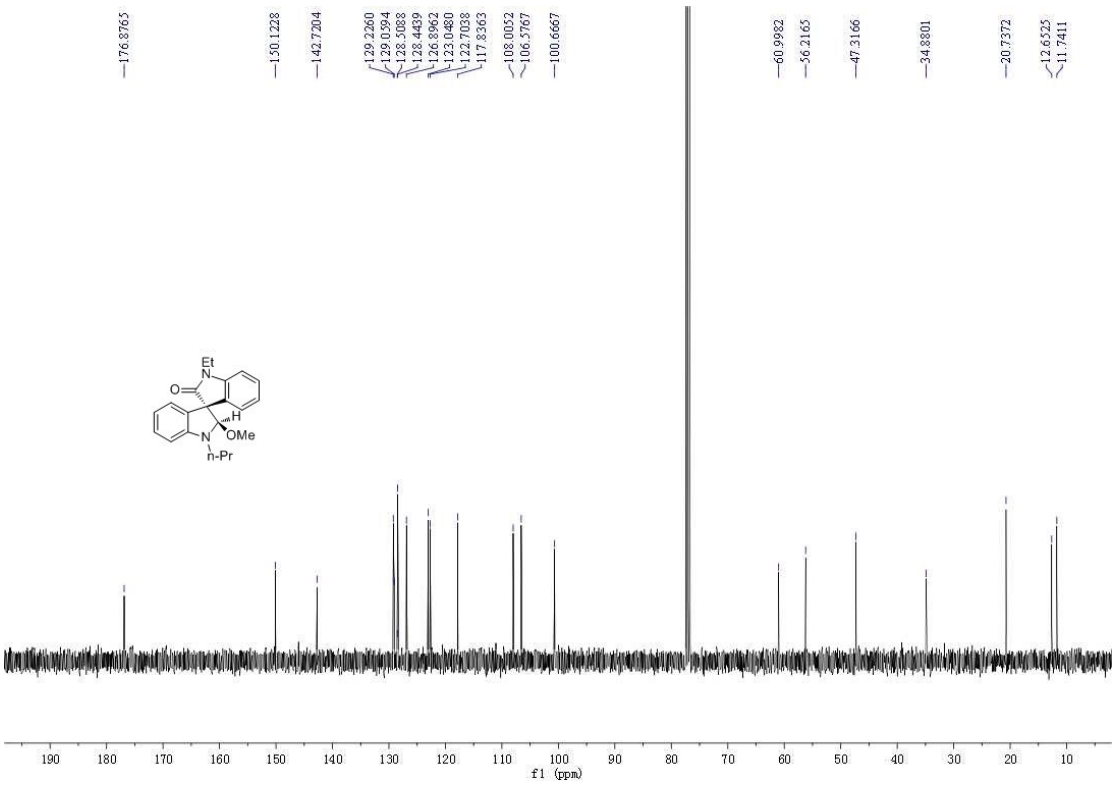
^{1}H NMR spectrum of **5t**



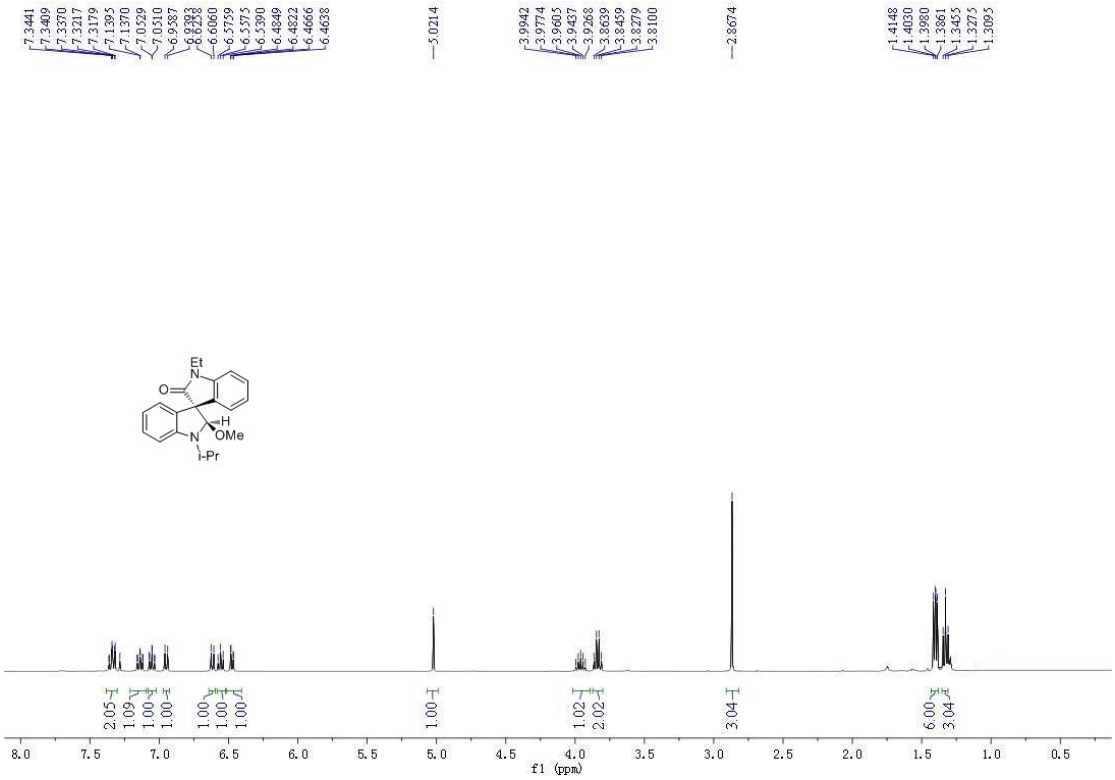
^{13}C NMR spectrum of**5t**



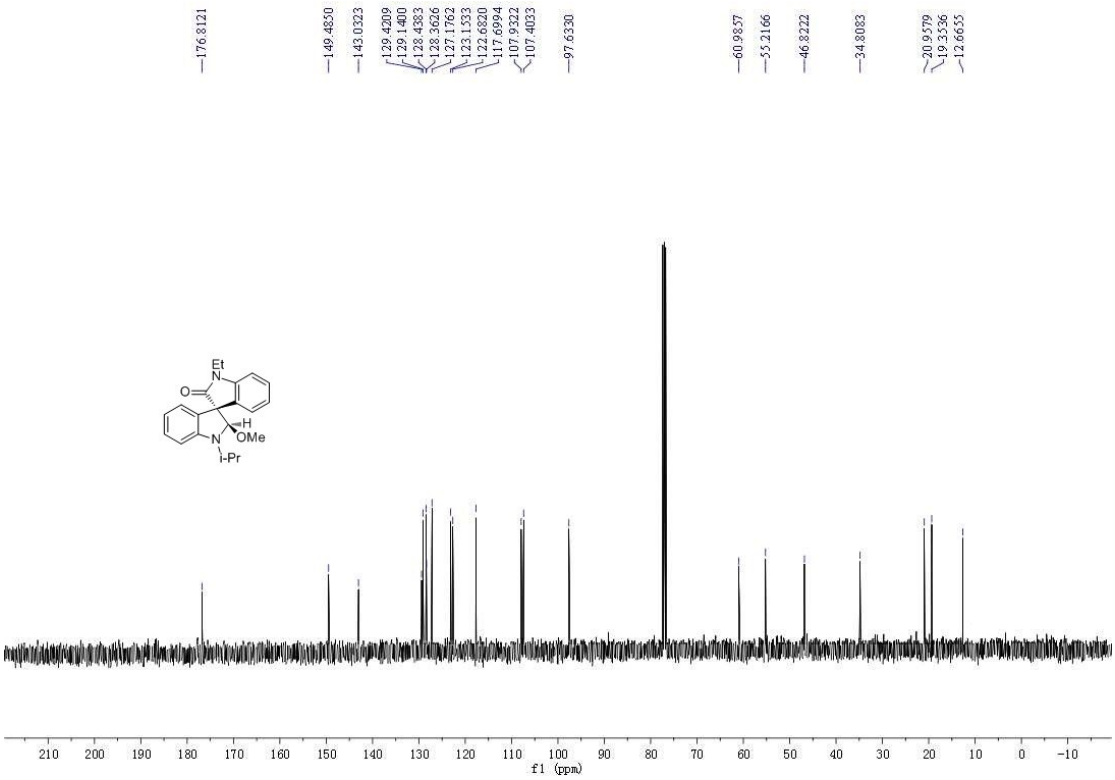
^{1}H NMR spectrum of **5u**



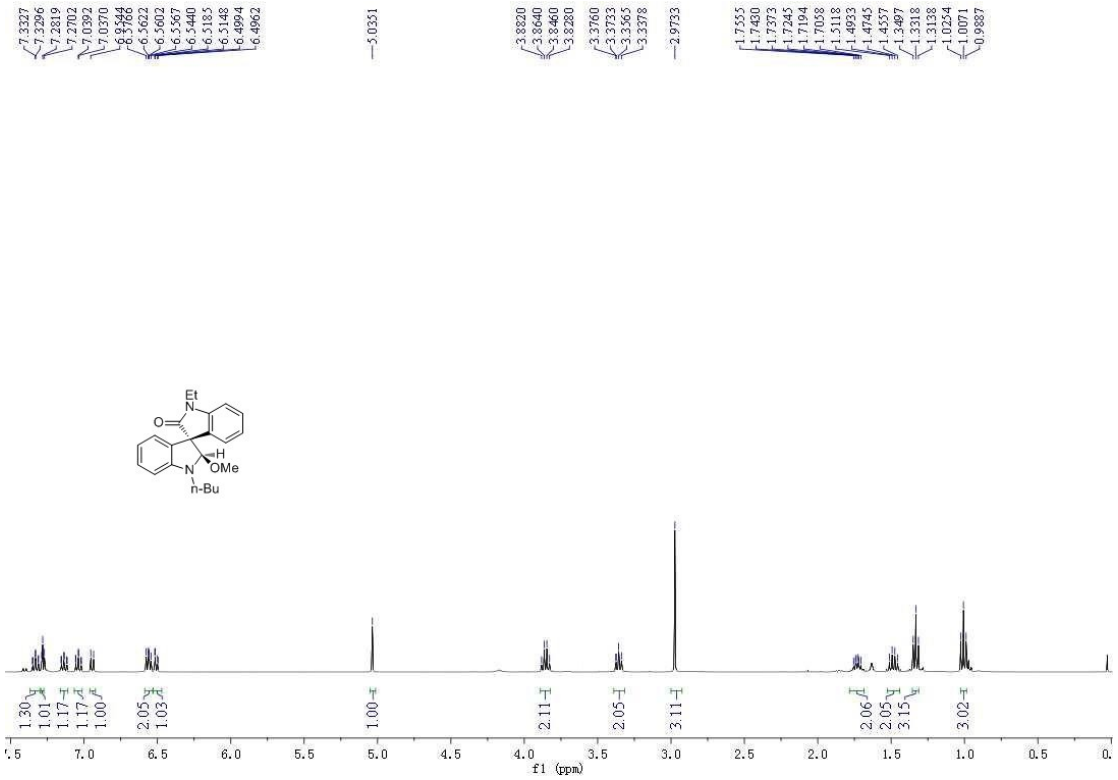
^{13}C NMR spectrum of**5u**



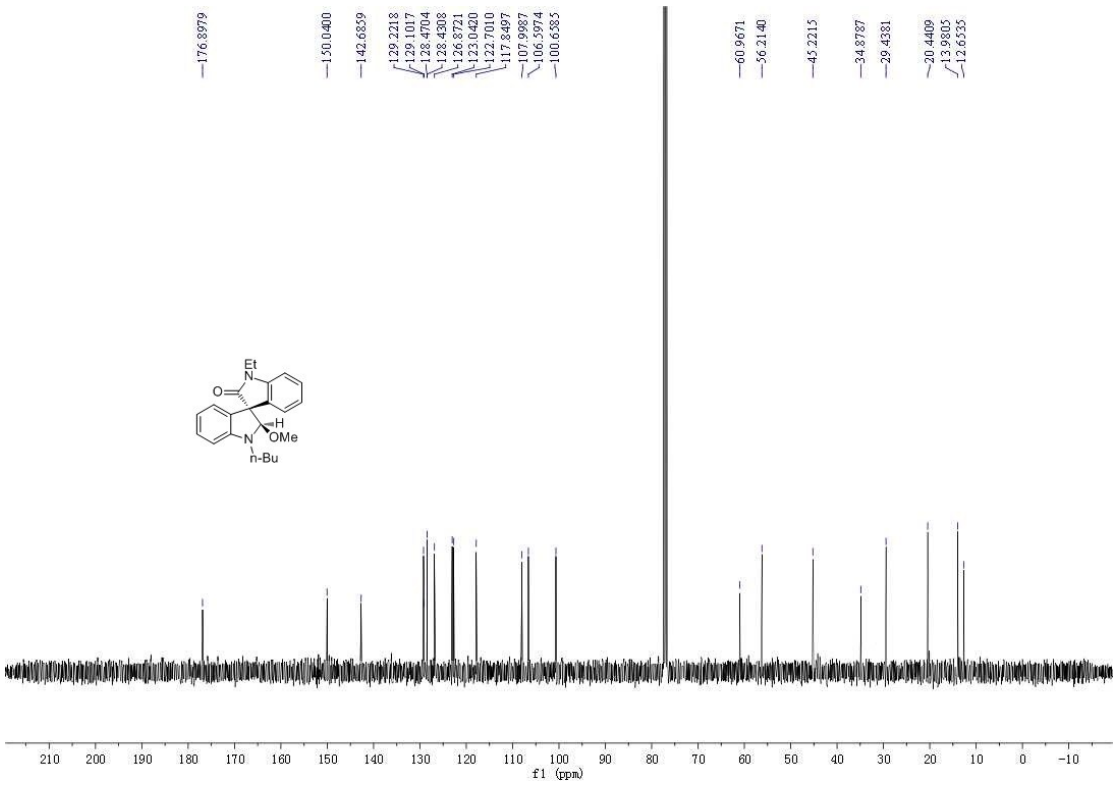
^{1}H NMR spectrum of **5v**



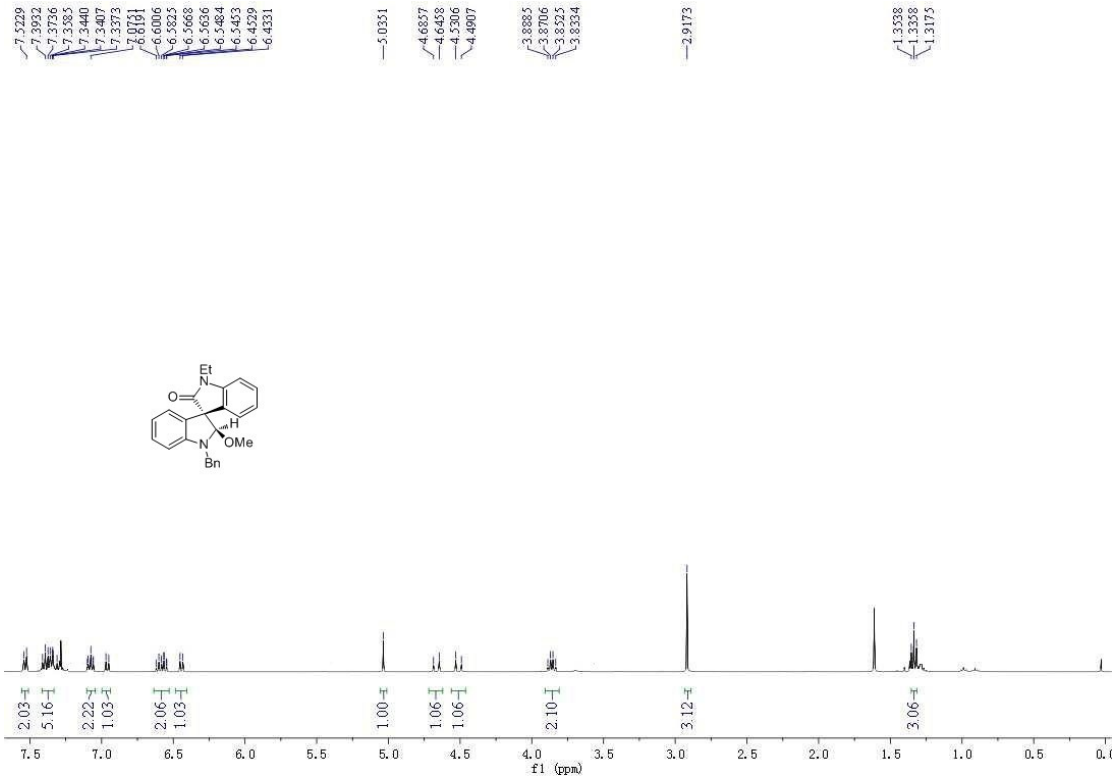
^{13}C NMR spectrum of**5v**



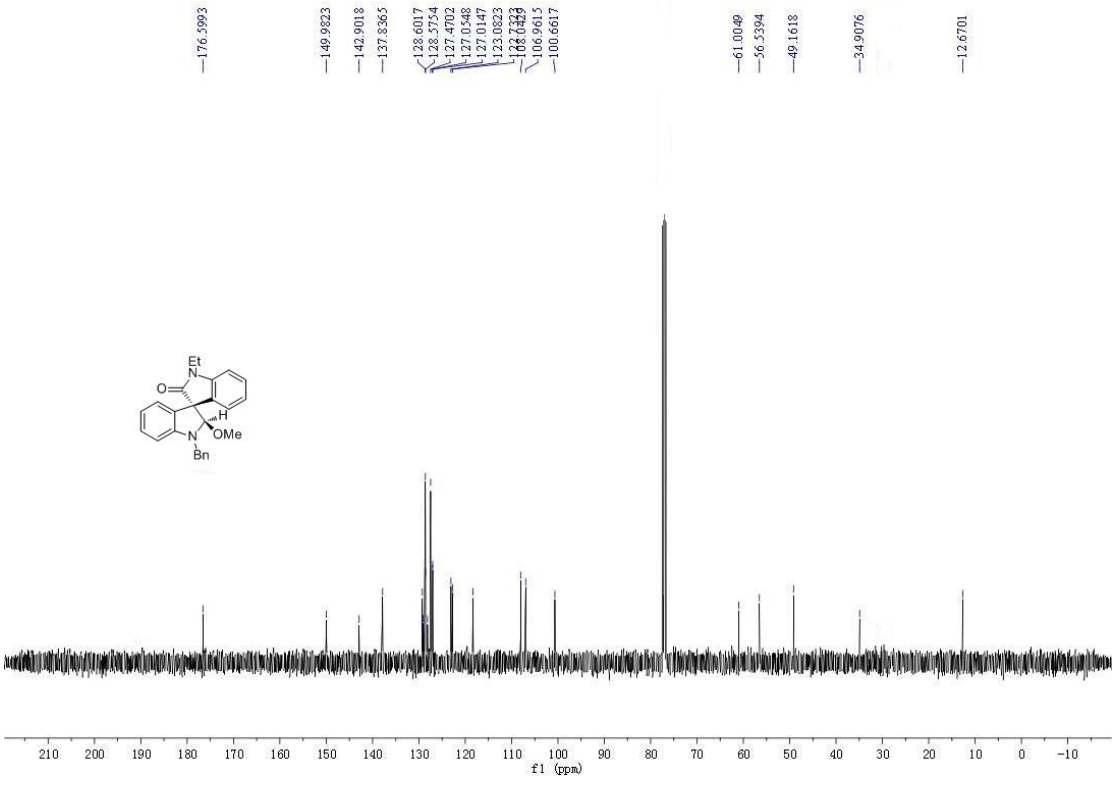
^{1}H NMR spectrum of **5w**



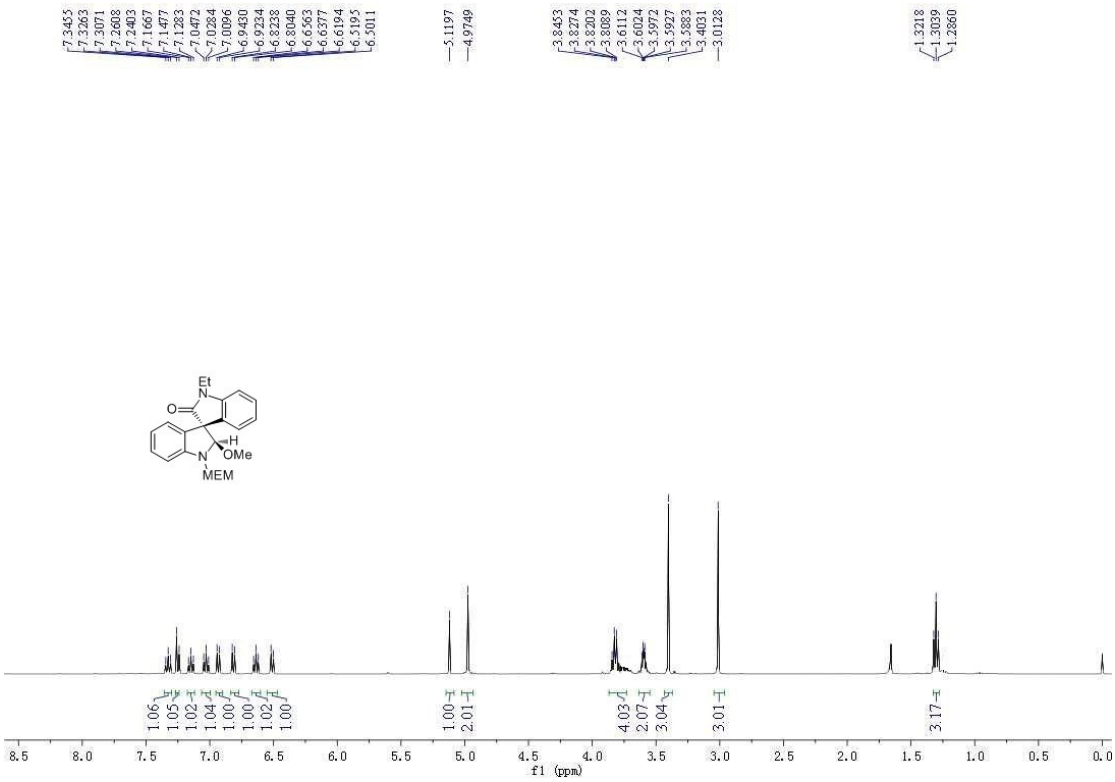
^{13}C NMR spectrum of**5w**



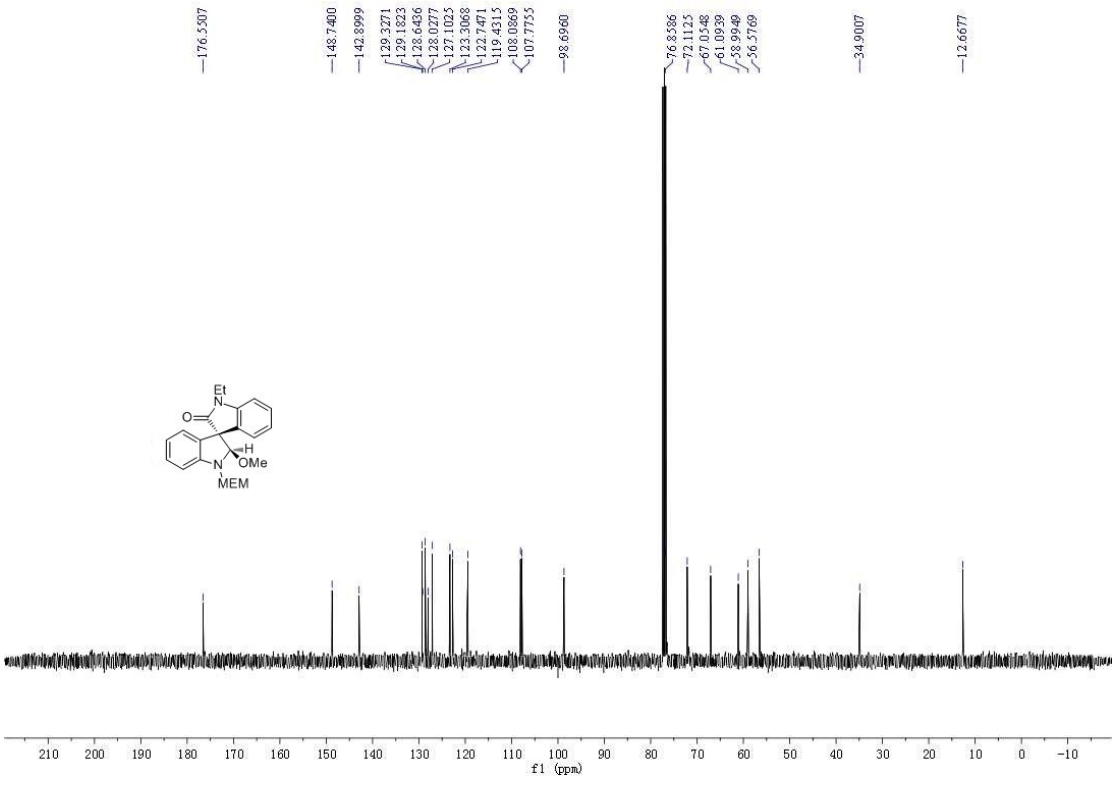
^{1}H NMR spectrum of **5x**



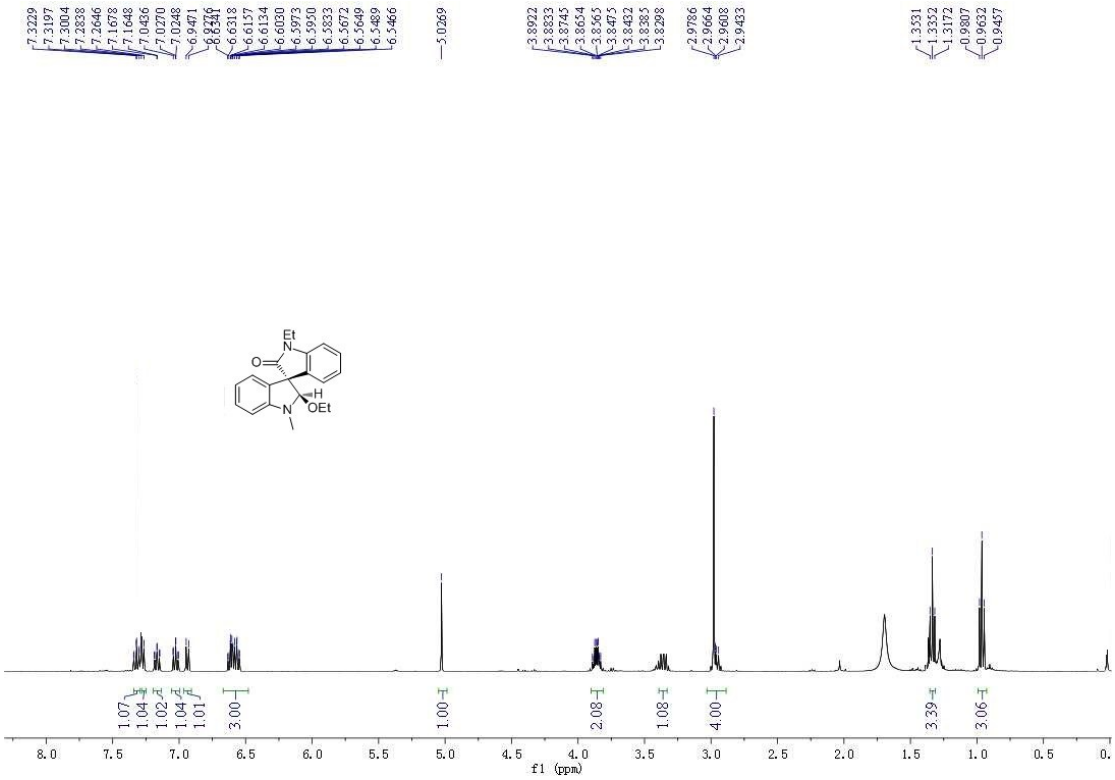
^{13}C NMR spectrum of**5x**



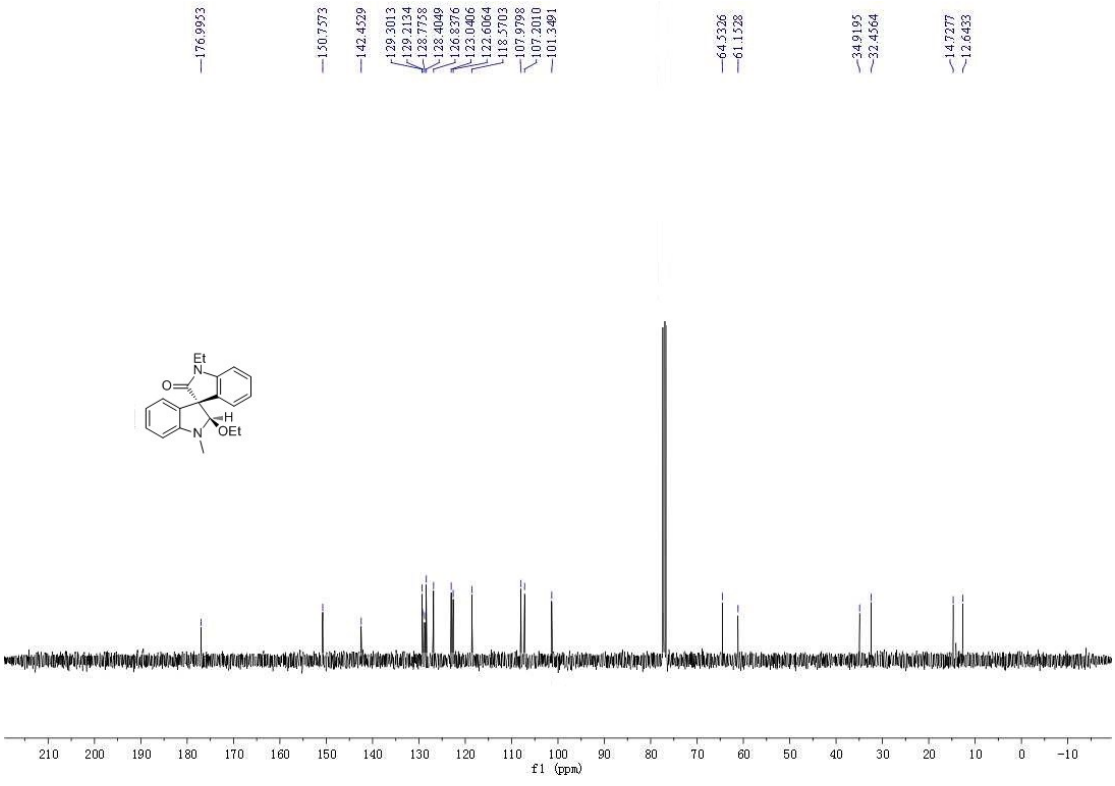
^{1}H NMR spectrum of **5y**



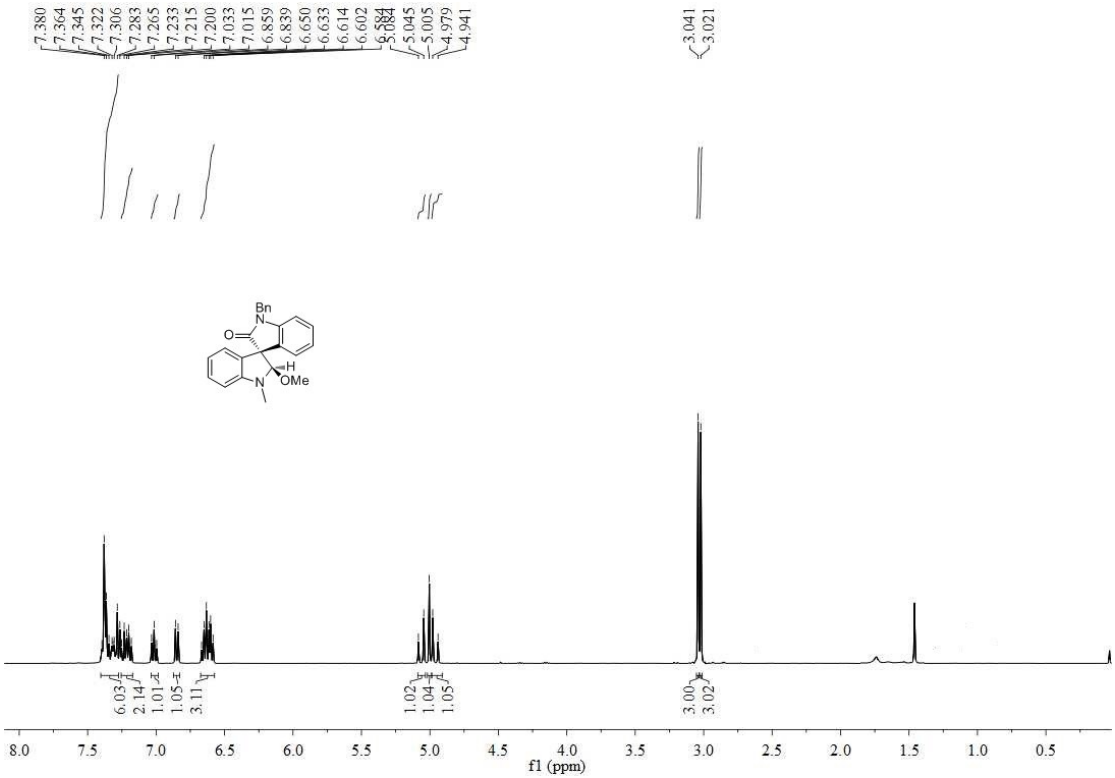
^{13}C NMR spectrum of**5y**



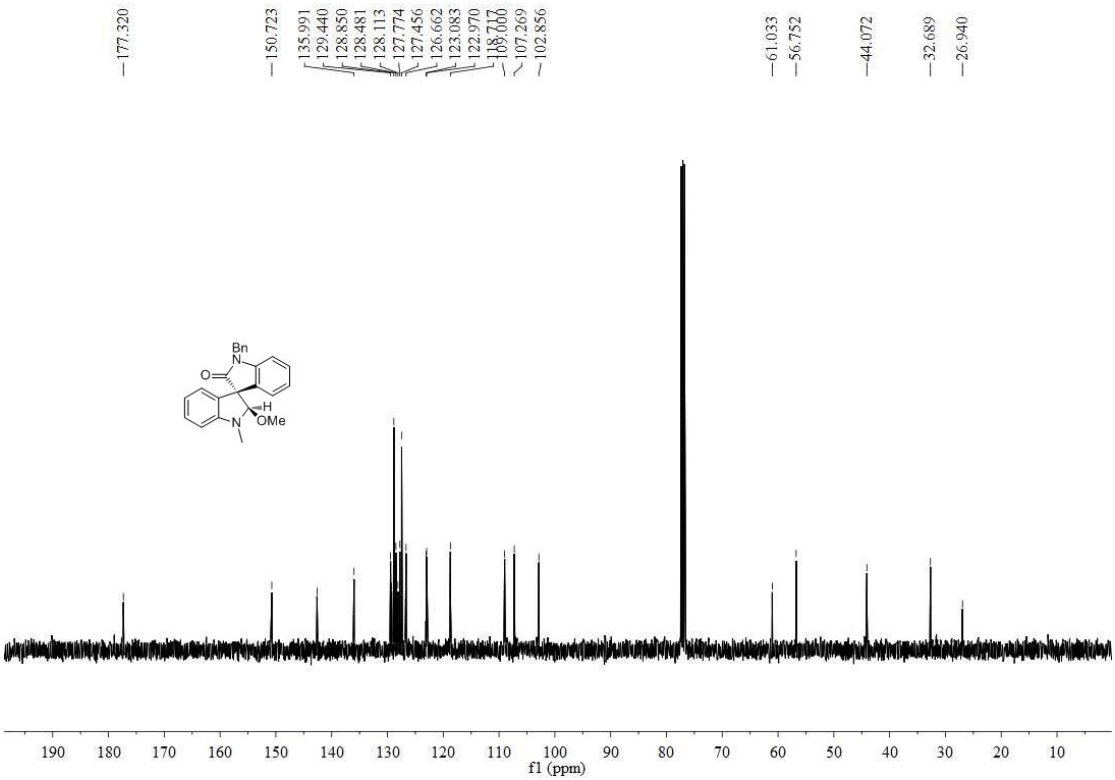
^{1}H NMR spectrum of **5ab**



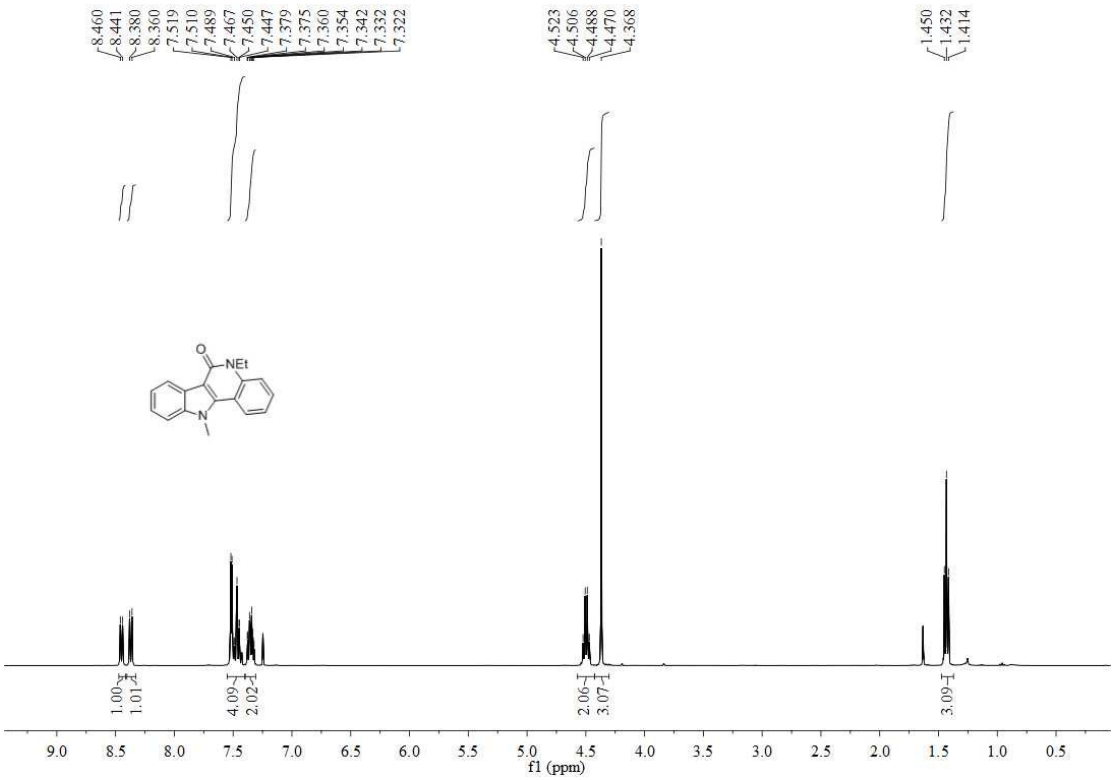
^{13}C NMR spectrum of **5ab**



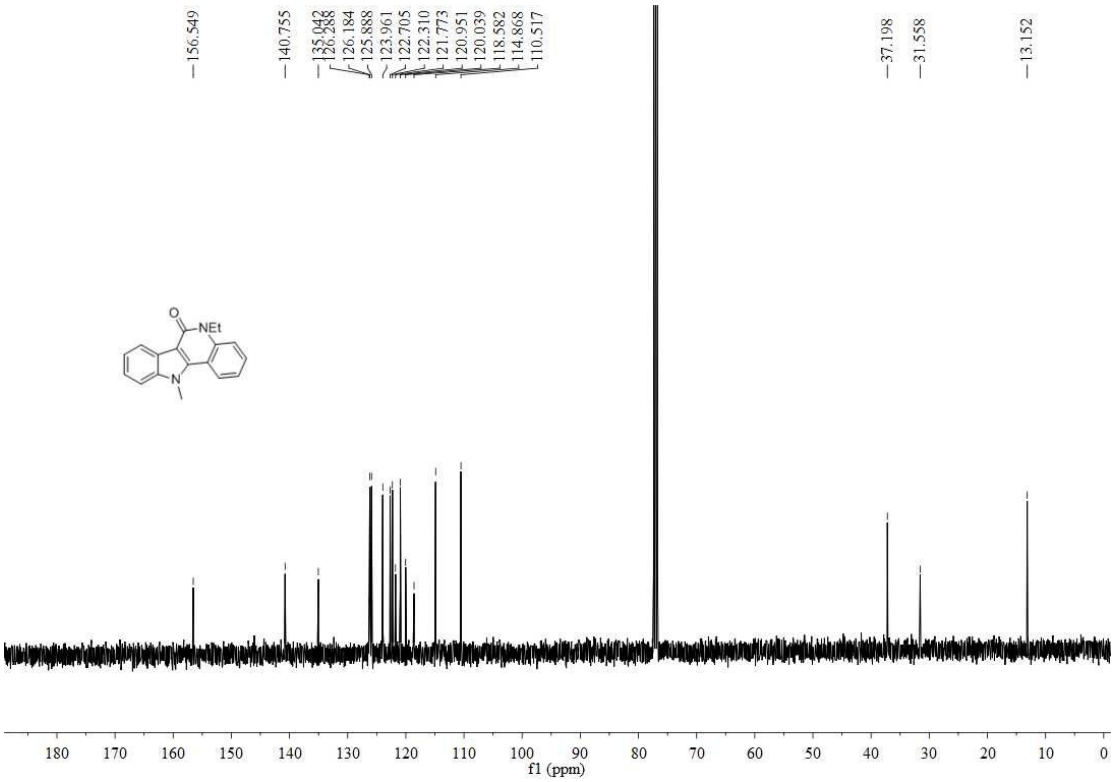
^{1}H NMR spectrum of **5ae**



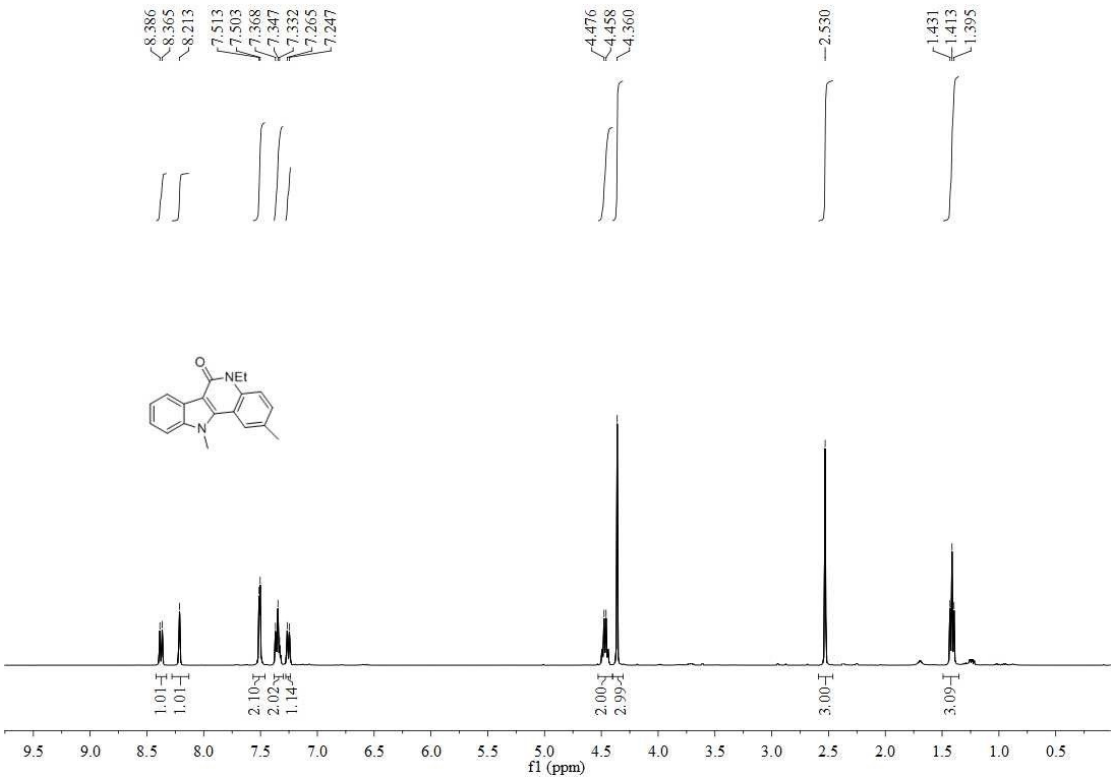
^{13}C NMR spectrum of **5ae**



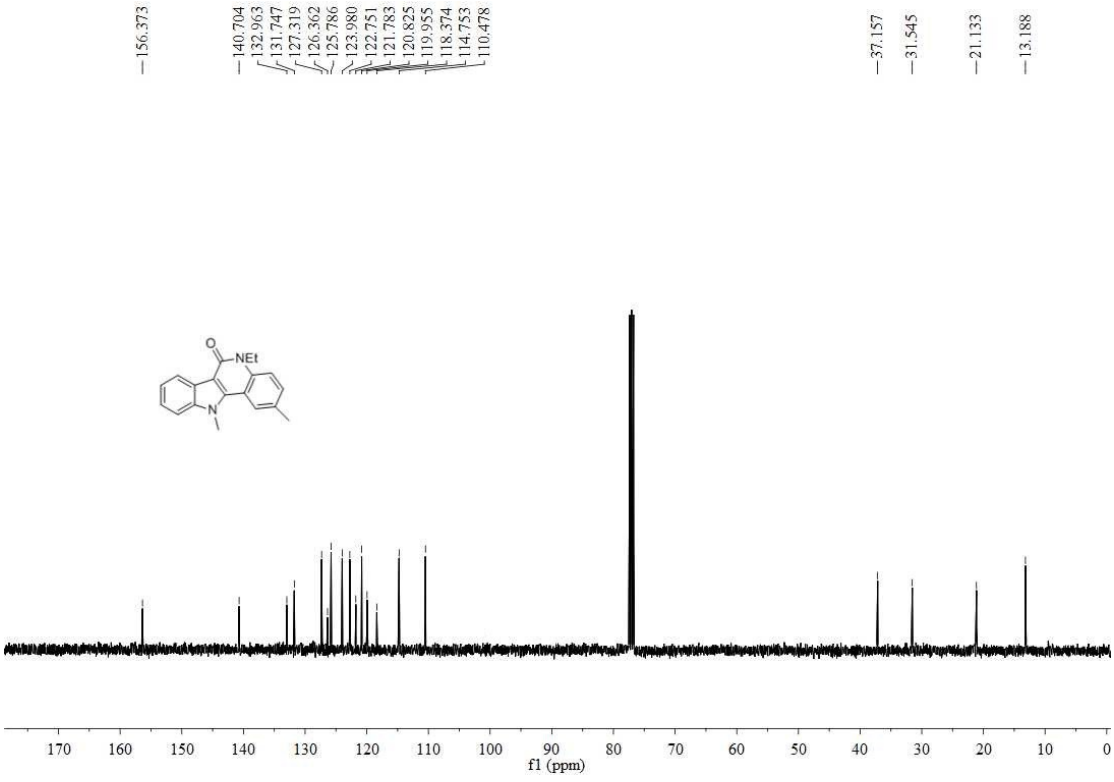
^{1}H NMR spectrum of **6a**



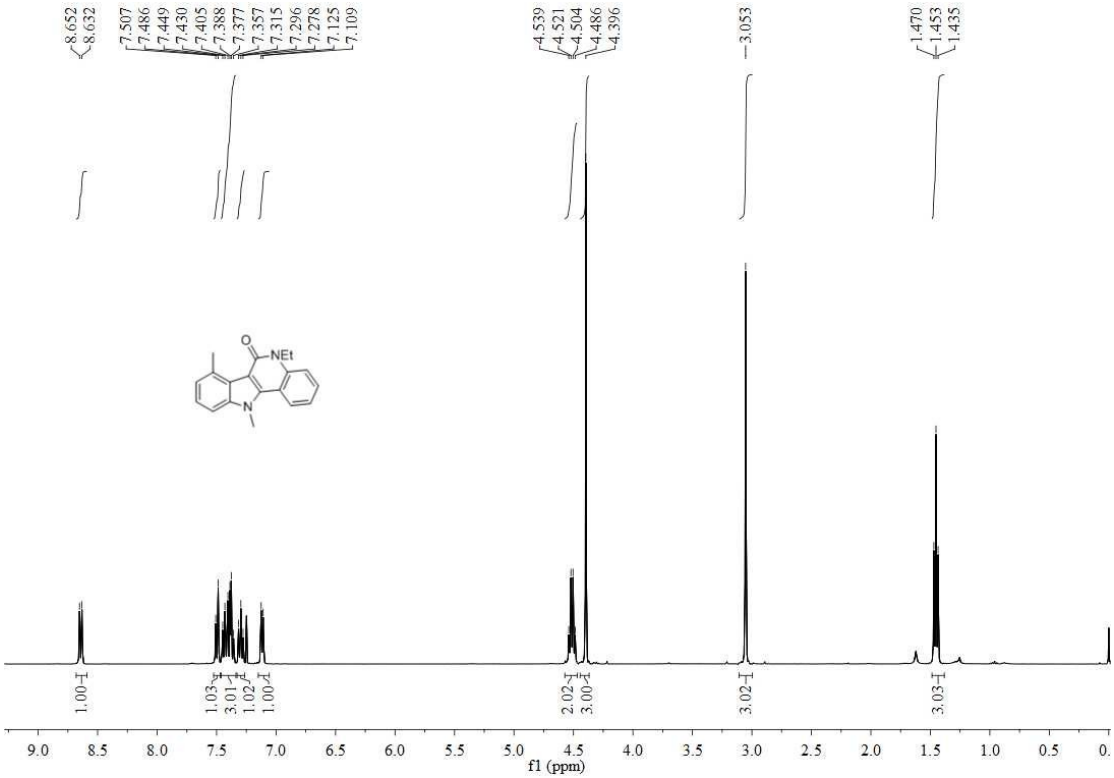
^{13}C NMR spectrum of **6a**



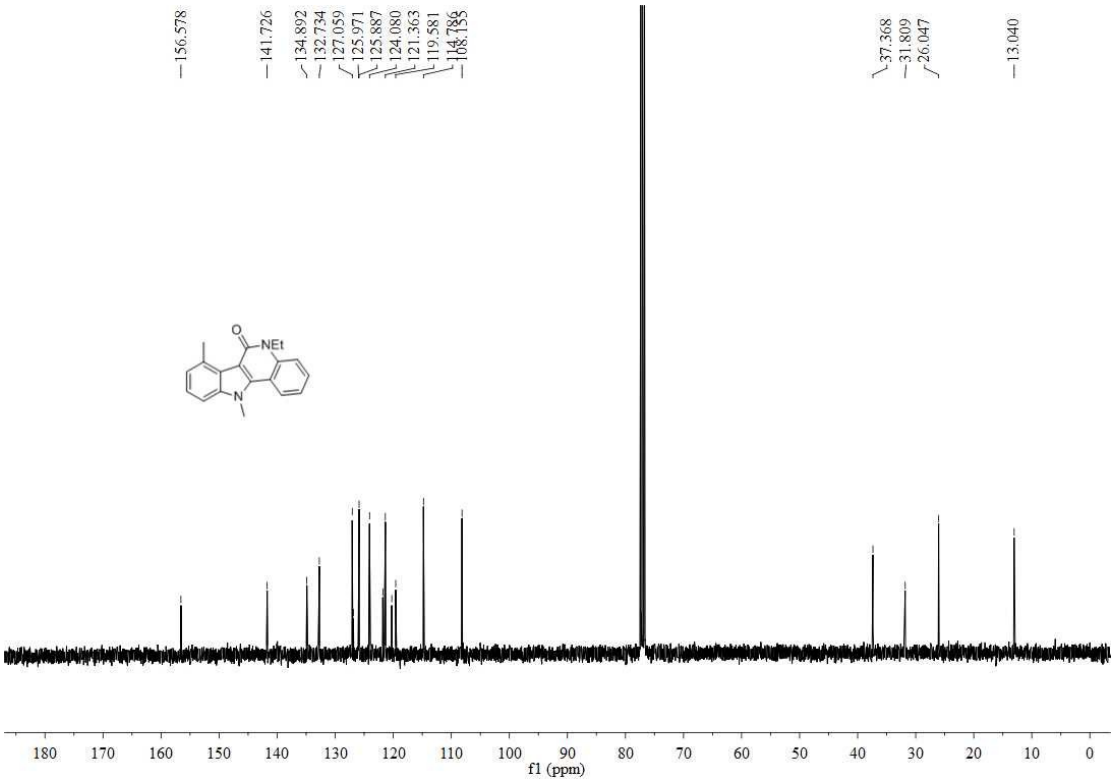
^{1}H NMR spectrum of **6b**



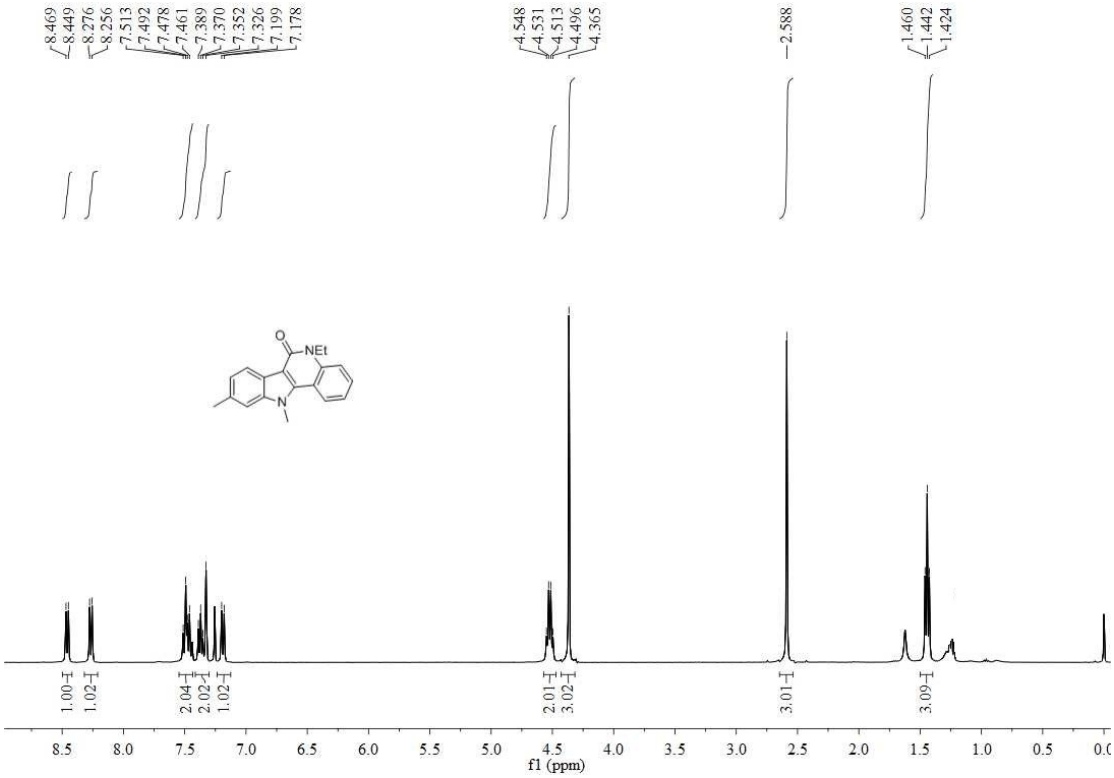
^{13}C NMR spectrum of **6b**



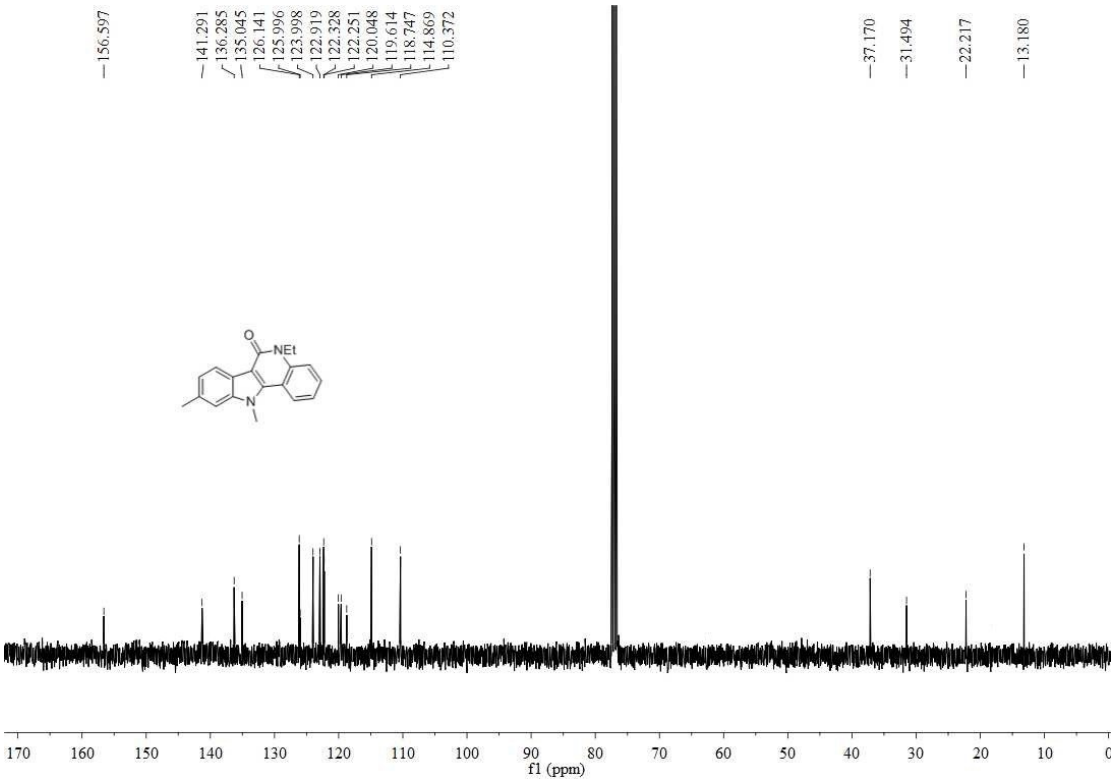
^{1}H NMR spectrum of **6d**



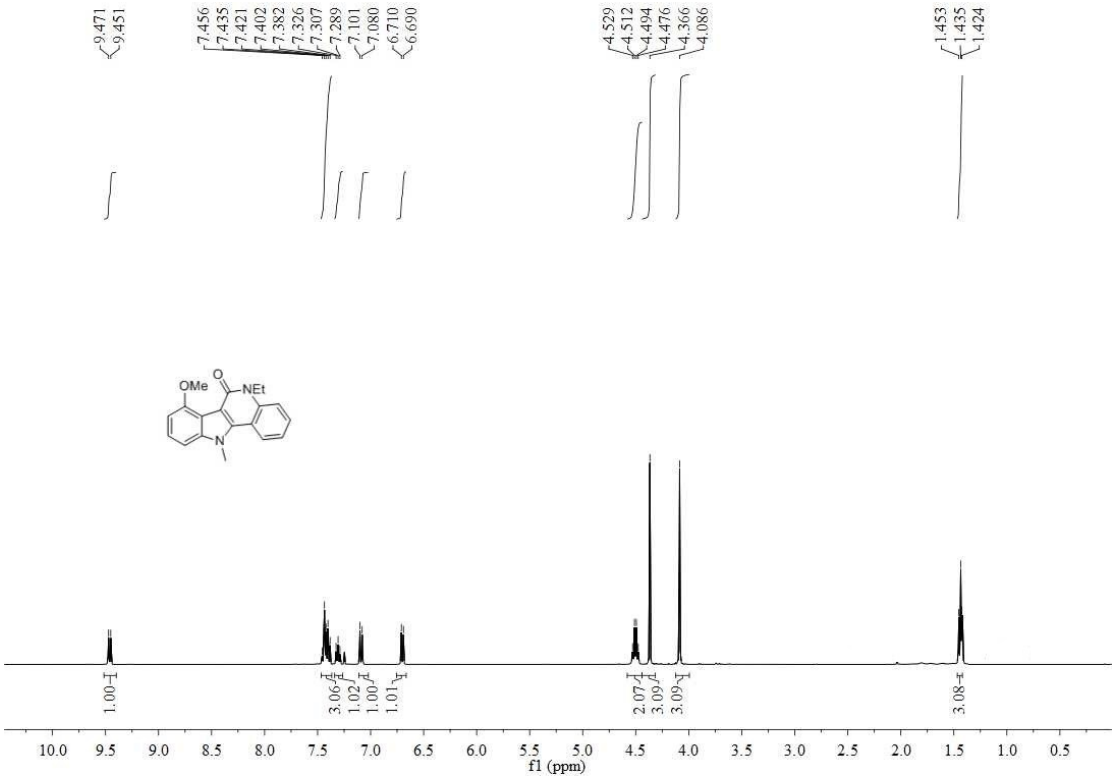
^{13}C NMR spectrum of **6d**



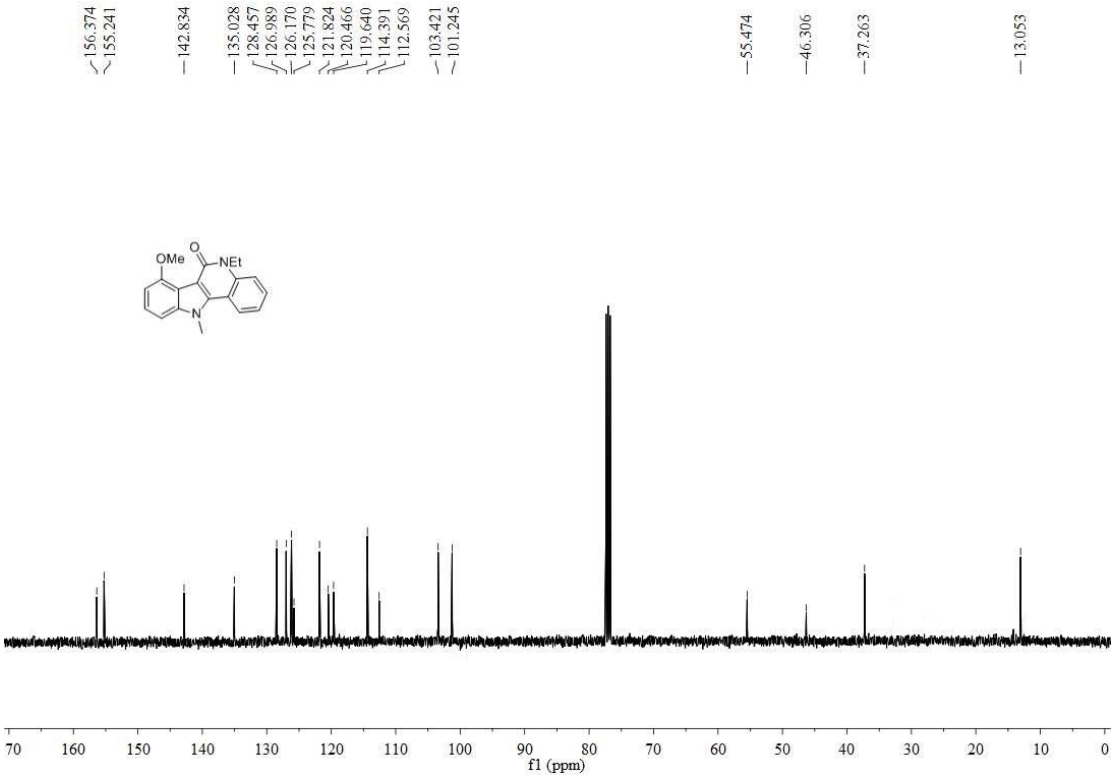
^{1}H NMR spectrum of **6e**



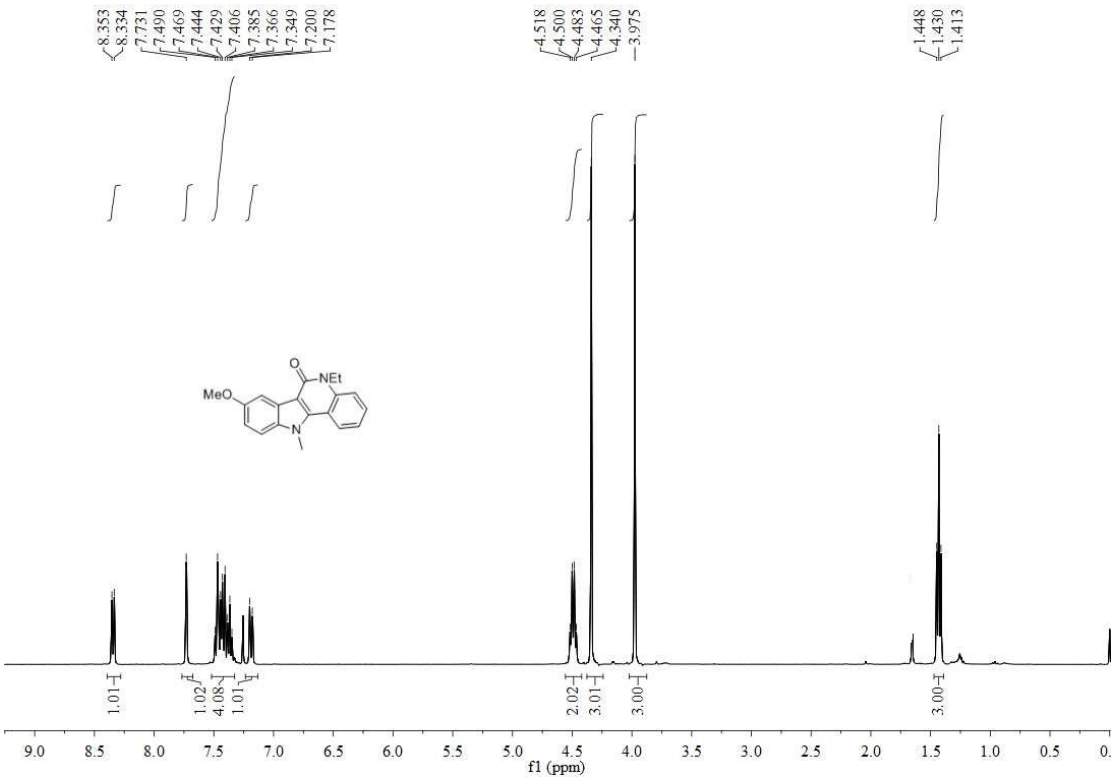
^{13}C NMR spectrum of **6e**



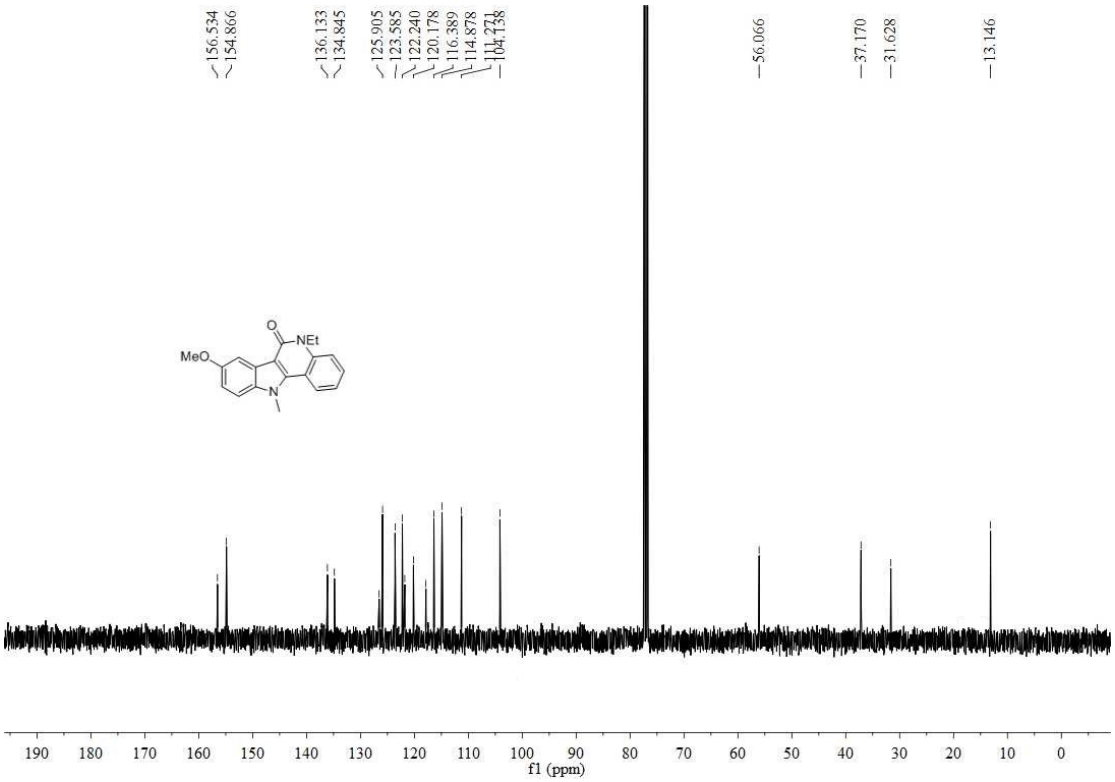
^{1}H NMR spectrum of **6f**



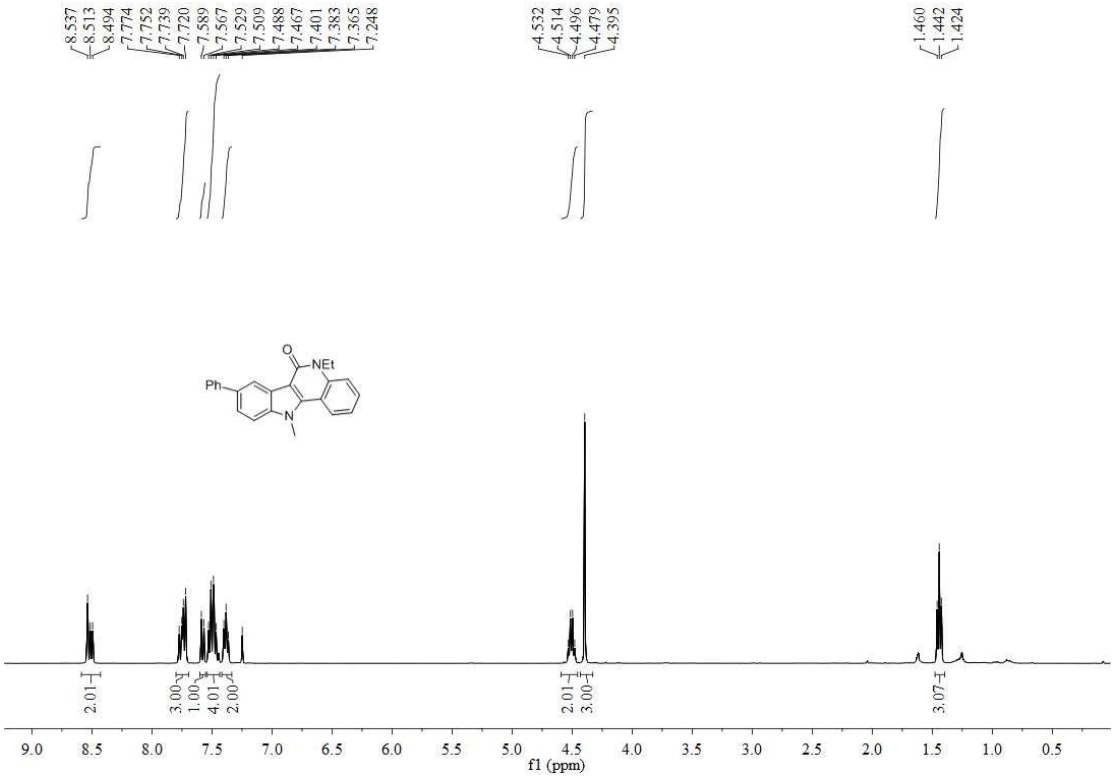
^{13}C NMR spectrum of **6f**



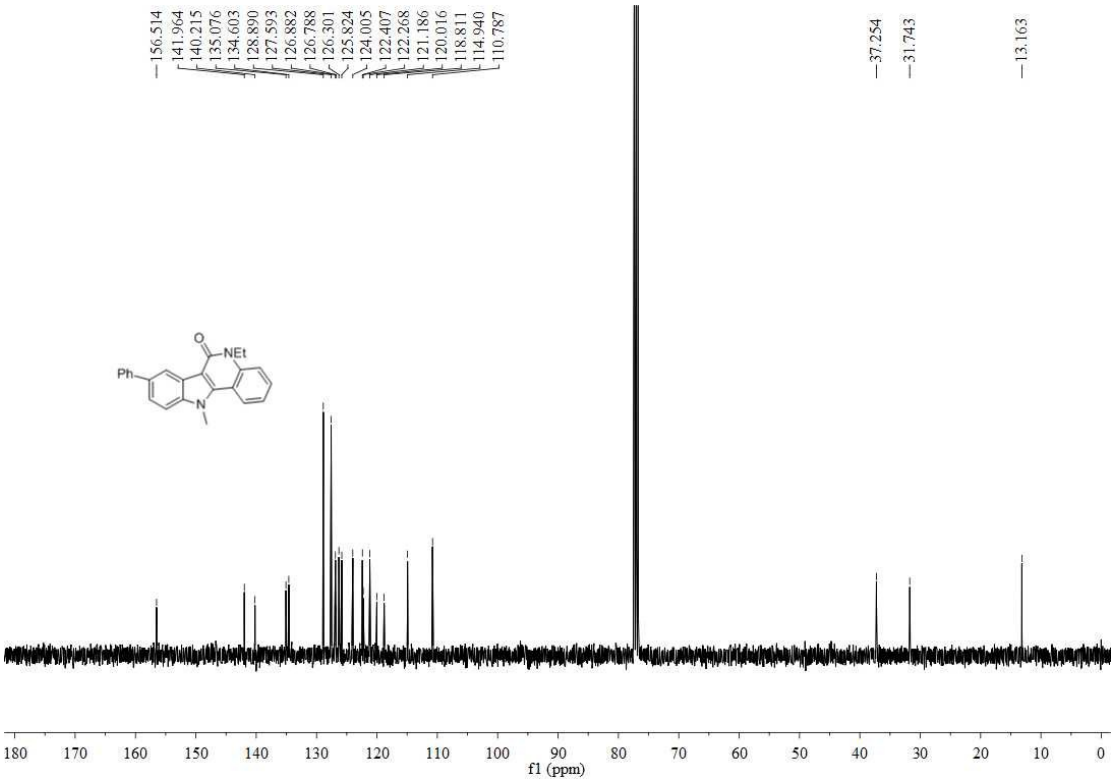
^{1}H NMR spectrum of **6g**



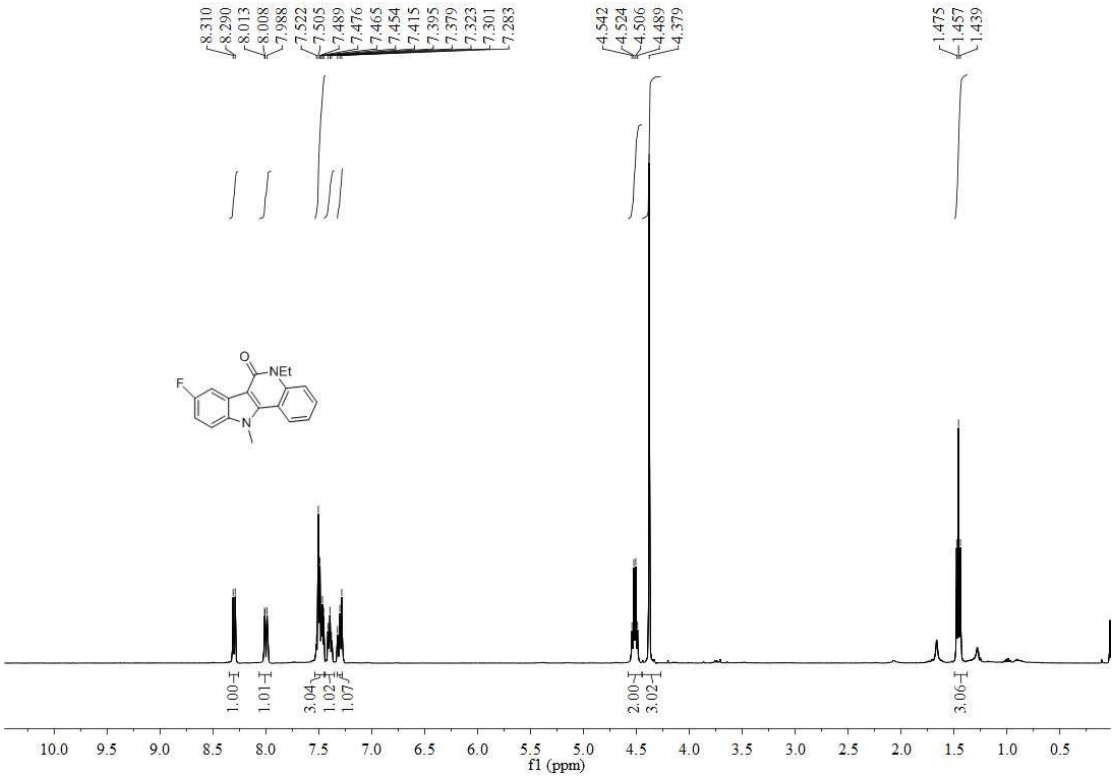
^{13}C NMR spectrum of **6g**



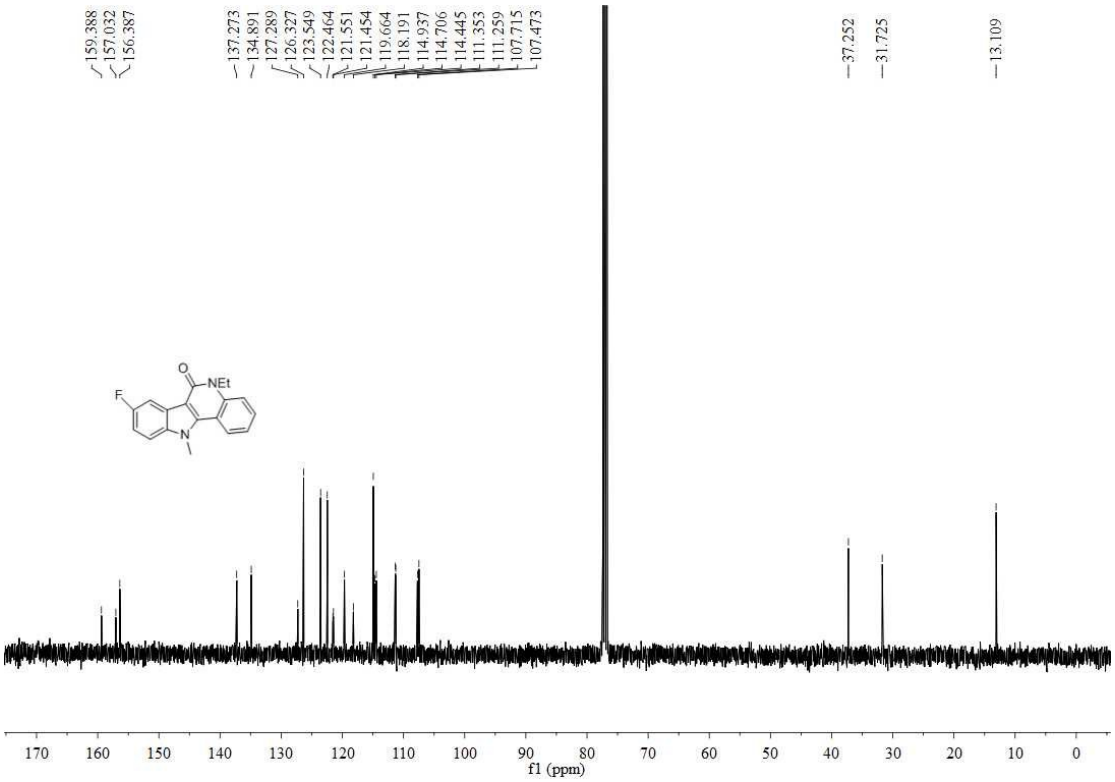
^{1}H NMR spectrum of **6h**



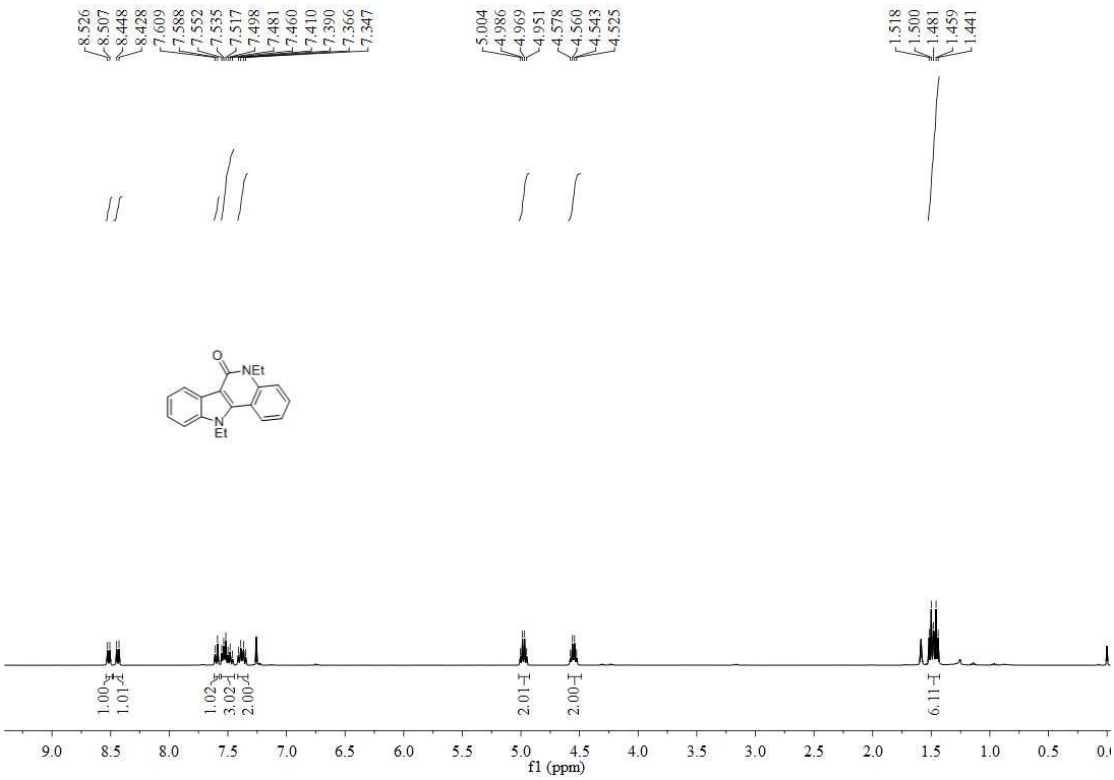
^{13}C NMR spectrum of **6h**



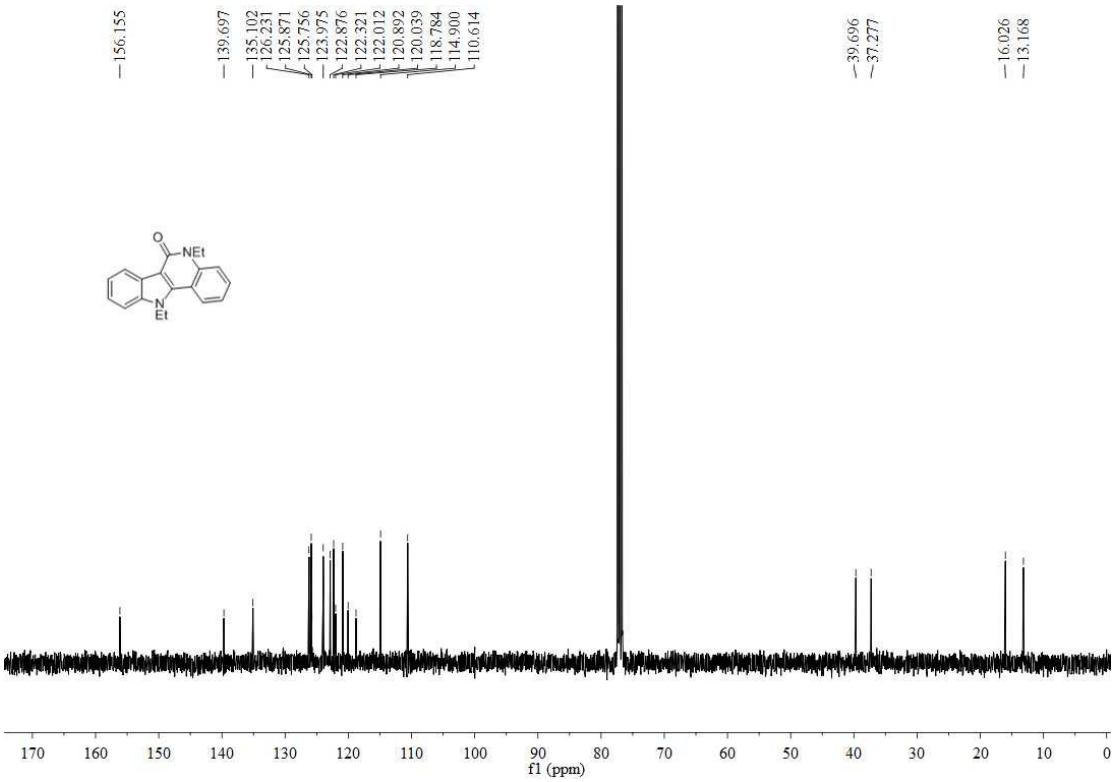
^{1}H NMR spectrum of **6i**



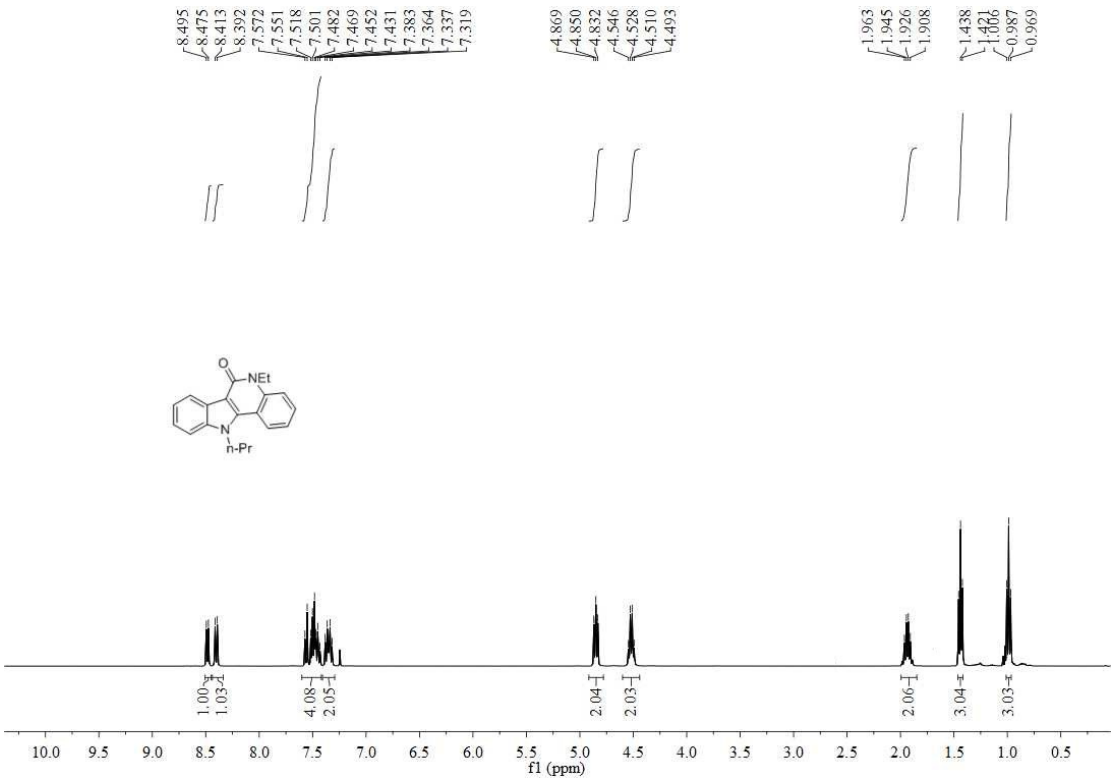
^{13}C NMR spectrum of **6i**



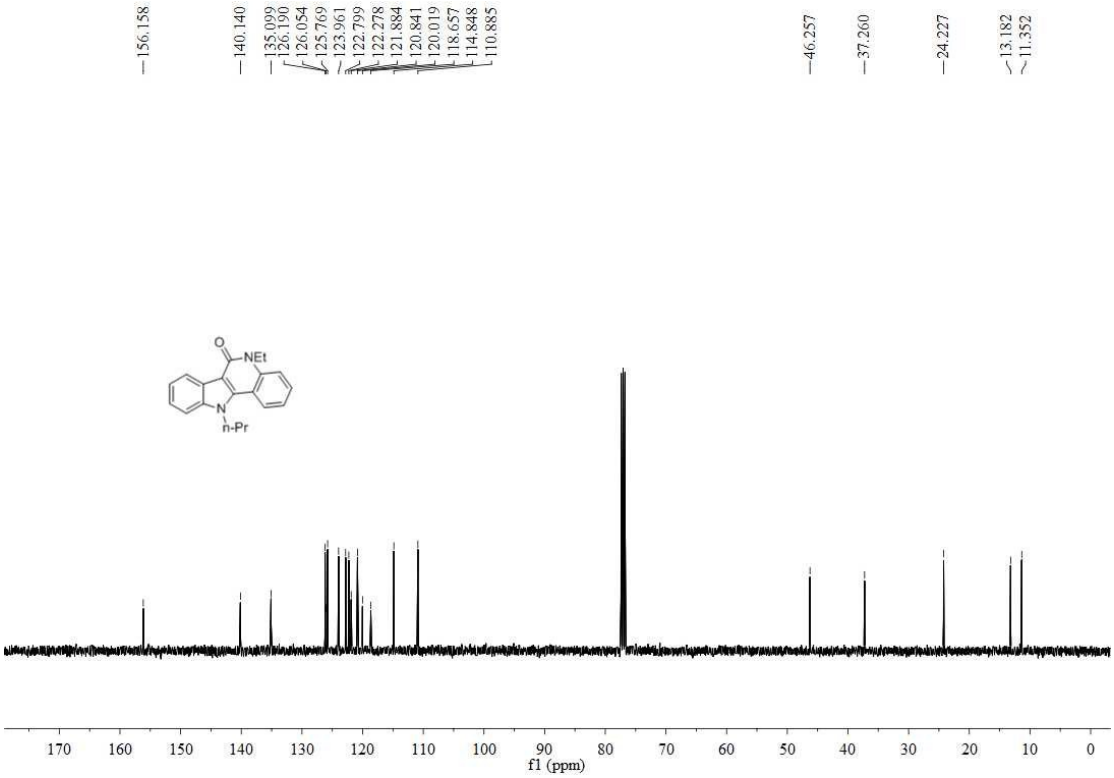
^{1}H NMR spectrum of **6j**



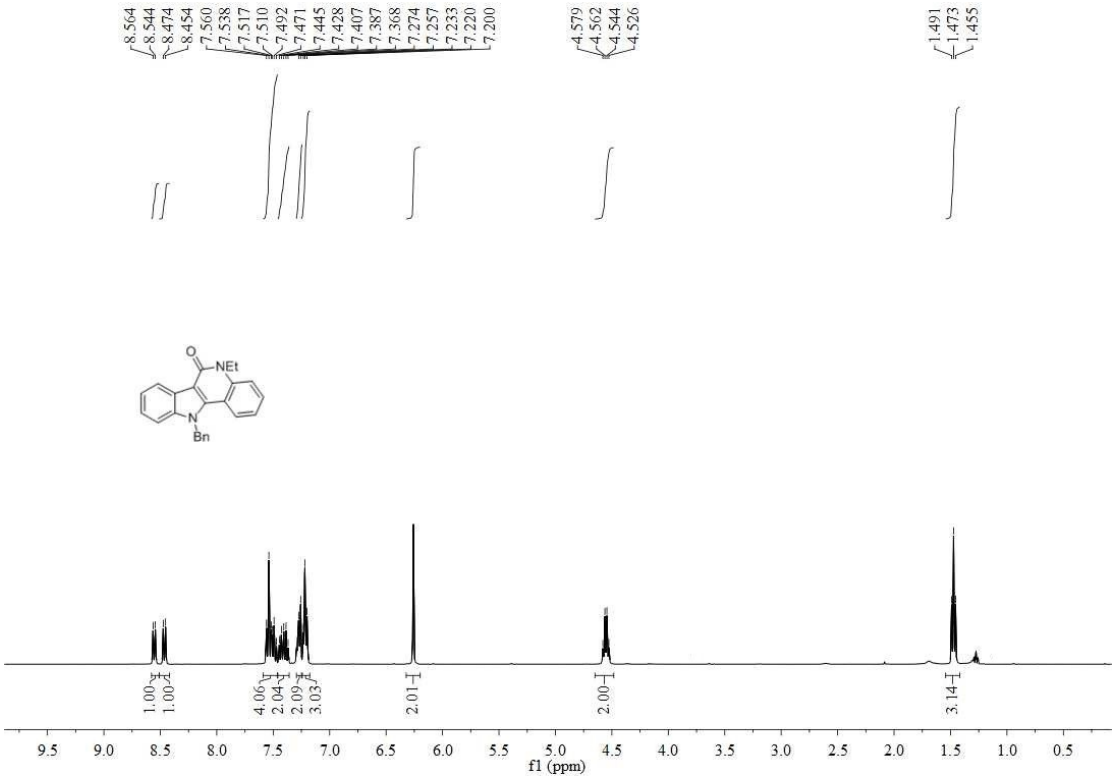
^{13}C NMR spectrum of **6j**



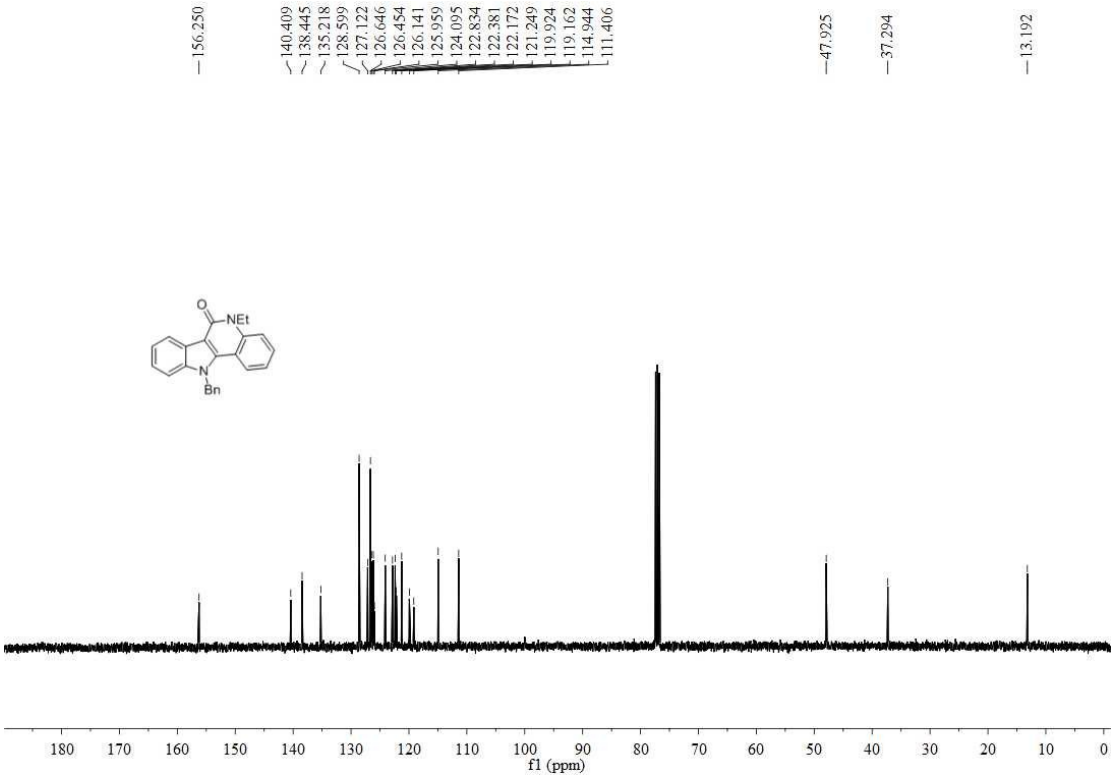
^{1}H NMR spectrum of **6k**



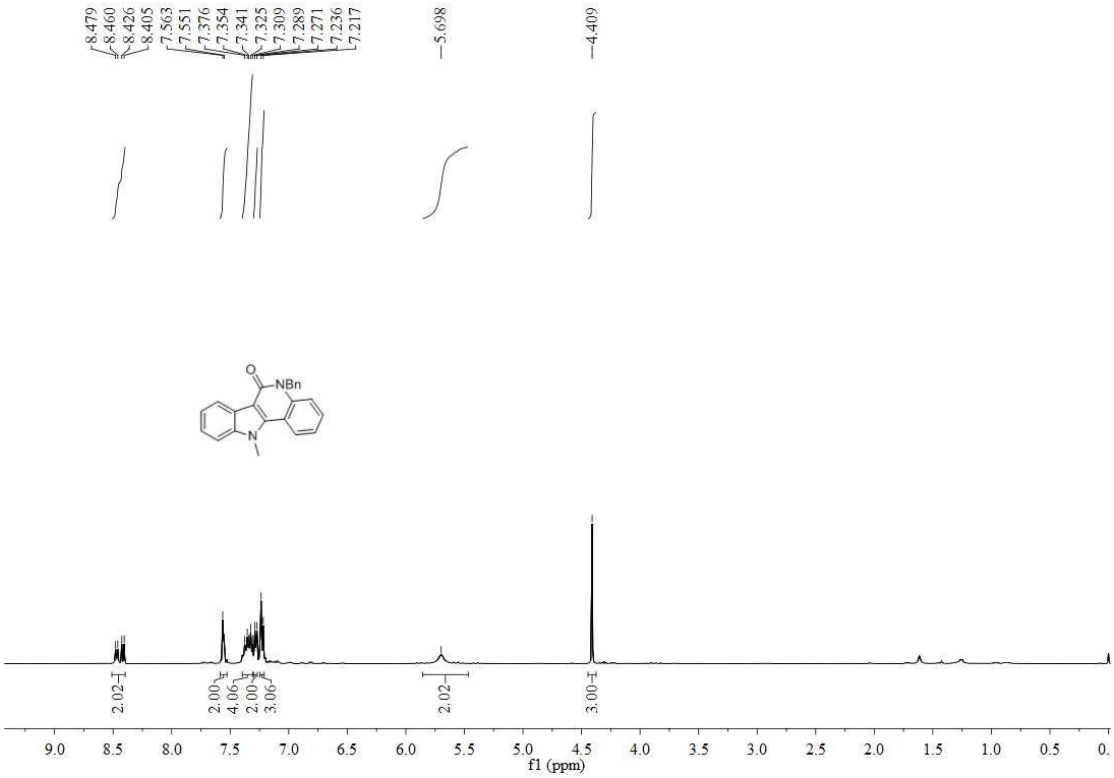
^{13}C NMR spectrum of **6k**



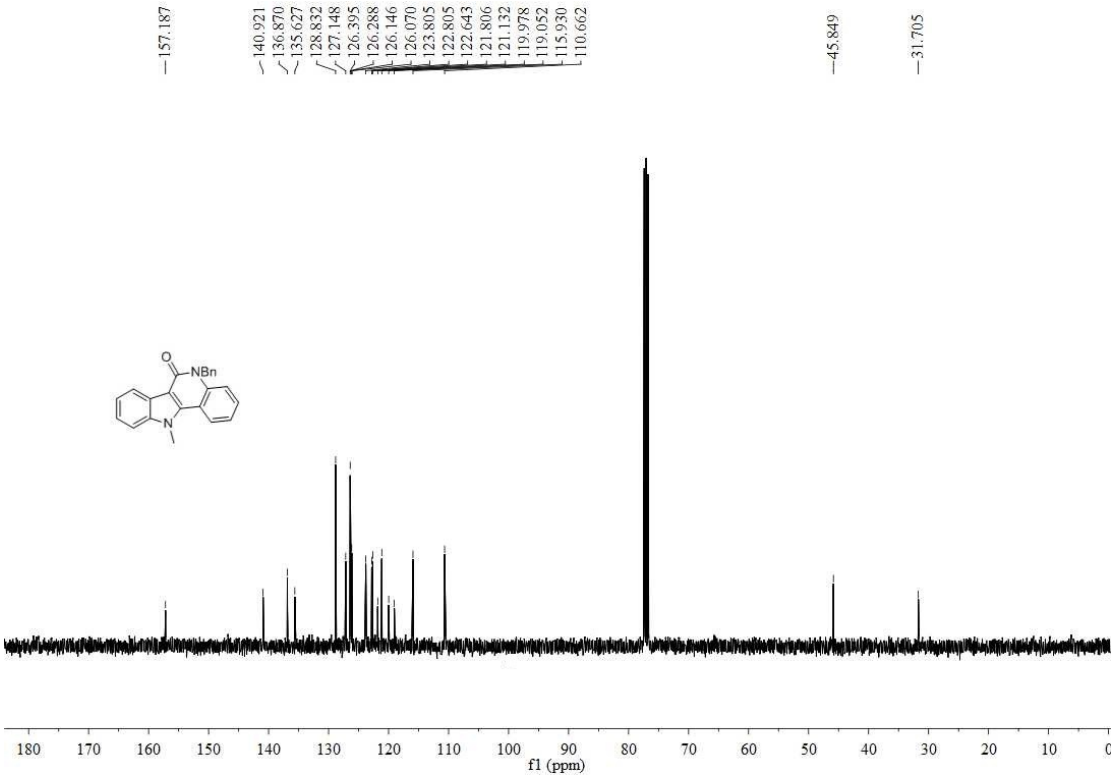
^{1}H NMR spectrum of **6l**



^{13}C NMR spectrum of **6l**



^{1}H NMR spectrum of **6m**



^{13}C NMR spectrum of **6m**