Supporting Information

Iron-Catalyzed Intramolecular C–H Amination for the Synthesis of N–H Carbazoles and Indoles

Zheng-Lin Wang,†[a] Yun-Hao Zhang,†[a] Jun-Yu Huang,†[a] Jian Zhou,[a] Ya-Qin Yu,[c] Dexin Feng*[b] and Da-Zhen Xu*[a]

[a]National Engineering Research Center of Pesticide (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China. Fax: +86 22 2350 5948; E-mail: xudazhen@nankai.edu.cn

[b]Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. Fax: +86 532 80662765; E-mail: fengdx@qibebt.ac.cn.

[c]Key Laboratory for Water Environment and Resources, Tianjin Normal University, Tianjin, 300387, China.

† These authors contributed equally to this work.

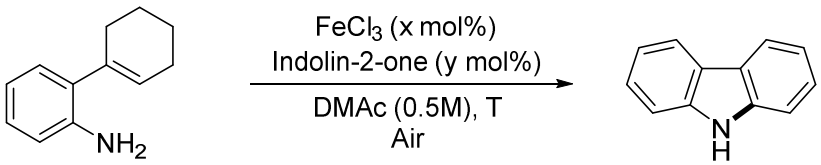
Table of contents

1. General information

All reagents including the starting materials are commercially available (purchased from Sigma-Aldrich, TCI, and Alfa Aesar) and were used without further purification. Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-d_6 or $CDCl_3$ as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource.

2. Optimization details

Table S1. Optimization of the reaction conditions for the synthesis of carbazole.[a]



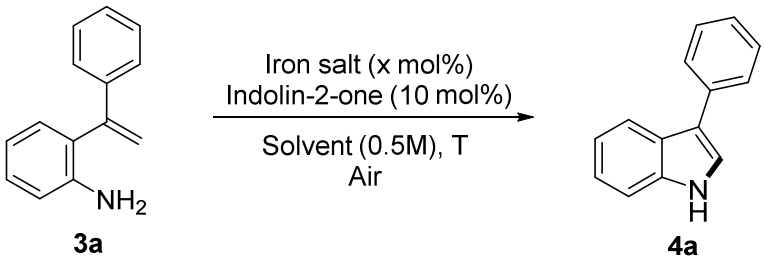
1a **2a**

Entry	$FeCl_3$ (x mol%)	indolin-2-one (y mol%)	T [°C]	Yield[b] [%]
1	10	100	100	83
2	10	50	100	86
3	10	20	100	89
4	**10**	**10**	**100**	**95**
5	10	0	100	–
6	0	10	100	–
7	20	10	100	91
8	50	10	100	92
9	10	10	80	trace
10	10	10	120	84

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), under an air balloon, 12 h.

[b] Yields of isolated products.

Table S2. Optimization of the reaction conditions for the synthesis of indole.[a]



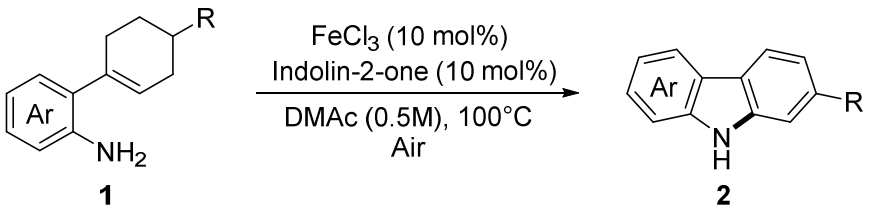
3a **4a**

Entry	Iron salt (x mol%)	Solvent	T [°C]	Time (h)	Yield[b] [%]
1	$FeCl_3$ (10)	DMAc	100	3	82
2	$FeBr_3$ (10)	DMAc	100	2	89
3	$Fe(OTf)_3$ (10)	DMAc	100	6	51
4	$Fe(NO_3)_3 \cdot 9H_2O$ (10)	DMAc	100	2	81
5	$Fe_2(SO_4)_3$ (10)	DMAc	100	6	23
6	$Fe(OAc)_2$(10)	DMAc	100	4	79
7	**$FeBr_3$(20)**	**DMAc**	**100**	**1**	**91**
8	$FeBr_3$(50)	DMAc	100	1	85
9	$FeBr_3$(20)	DMAc	100	1	79
10	$FeBr_3$(20)	DMF	100	2	83
11	$FeBr_3$(20)	DMSO	100	4	62
12	$FeBr_3$(20)	DMAc	50	6	79
13	$FeBr_3$(20)	DMAc	120	4	47

[a] Reaction conditions: **3a** (1.0 mmol, 1.0 equiv), indolin-2-one (0.1 mmol, 0.1 equiv), under an air balloon.

[b] Yields of isolated products.

3. General procedure for the synthesis of carbazoles 2

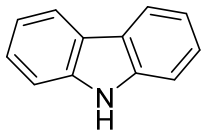


1 **2**

In a 10-mL reaction vial, equipped with a magnetic stirring bar, alkenylaniline **1** (1.0 mmol), indolin-2-one (13.3 mg, 10 mol%) and $FeCl_3$ (16.2 mg, 10 mol%,) were added to DMAc (2.0 mL). Then the vial was placed in a pre-heated metal block at 100 ºC under an air balloon. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled and quenched with cold water (20 mL) and extracted with ethyl acetate (2×15 mL). The combined

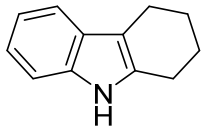
organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (60/1−20/1, v/v) as eluent to afford the pure products.

4. Characterization data of carbazoles 2



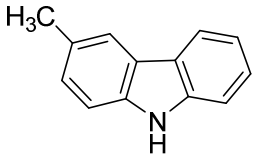
9H-Carbazole (2a)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a brown solid in 95% yield (158.7 mg). Mp 242-244°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.25 (s. 1H, NH), 8.11 (d, 2H, ArH, J = 7.6 Hz), 7.50 (d, 2H, ArH, J = 8.0 Hz), 7.39 (t, 2H, ArH, J = 8.0 Hz), 7.16 (t, 2H, ArH, J = 7.6 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.2, 125.9, 122.8, 120.6, 118.9, 111.4.



2,3,4,9-Tetrahydro-1H-carbazole (2a′)[2]

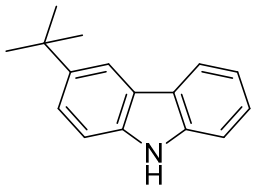
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid. Mp 118-120°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H, NH), 7.45 (d, 1H, ArH, J = 7.6 Hz), 7.24 (d, 1H, ArH, J = 8.4 Hz), 7.11-7.04 (m, 2H, ArH), 2.71-2.68 (m, 4H, CH_2), 1.91-1.84 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 134.1, 127.8, 121.0, 119.1, 117.7, 110.4, 110.1, 23.3 (2), 23.2, 20.9.



3-Methyl-9H-carbazole (2b)[1]

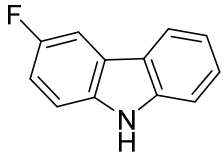
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 91% yield (164.8 mg). Mp 206-208°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, 1H, ArH, J = 7.6 Hz), 7.93 (s, 1H, NH), 7.87 (s, 1H, ArH), 7.39-7.38 (m, 2H, ArH), 7.31 (d, 1H, ArH, J = 8.4 Hz), 7.24 (t, 1H, ArH, J = 1.6 Hz), 7.22-7.18 (m, 1H, ArH), 2.53 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 137.7, 128.7, 127.2, 125.6, 123.5, 123.2, 120.2, 119.2, 110.6, 110.2, 21.4.



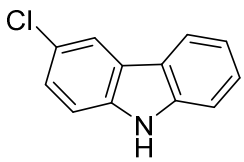
3-(Tert-butyl)-9H-carbazole (2c)[3]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid in 84% yield (187.4 mg). Mp 148-151°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (m, 2H, ArH), 7.89 (s, 1H, NH), 7.49 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.4 Hz), 7.41-7.35 (m, 2H, ArH), 7.33 (d, 1H, ArH, J = 8.8 Hz), 7.23-7.19 (m, 1H, ArH), 1.44 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 139.9, 137.6, 125.6, 123.9, 123.6, 123.0, 120.1, 119.2, 116.3, 110.6, 110.1, 34.7, 32.0.



3-Fluoro-9H-carbazole (2d)[4]

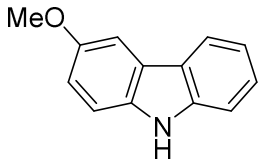
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 90% yield (166.6 mg). Mp 210-213°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H, NH), 8.01 (s, 1H, ArH), 7.72 (dd, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.8 Hz), 7.46-7.40 (m, 2H, ArH), 7.34 (dd, 1H, ArH, J_1 = 4.0 Hz, J_2 = 8.4 Hz), 7.24-7.21 (m, 1H, ArH), 7.15 (dt, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 156.3, 140.5, 135.7, 126.4, 123.8, 123.1, 120.5, 119.5, 113.7, 113.5, 111.1, 111.1, 110.9, 106.1, 105.9. ^{19}F NMR (376MHz, $CDCl_3$): δ -124.5.



3-Chloro-9H-carbazole (2e)[1]

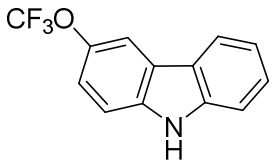
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a white solid in 93% yield (187.4 mg). Mp 200-202°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.42 (s. 1H, NH), 8.22 (s. 1H, ArH), 8.16 (d, 1H, ArH, J = 7.6 Hz), 7.50 (d, 2H, ArH, J = 8.0 Hz),

7.44-7.38 (m, 2H, ArH), 7.18 (t, 1H, ArH, J = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.3, 138.1, 126.3, 125.2, 123.7, 122.8, 121.5, 120.6, 119.7, 118.8, 112.3, 111.2.



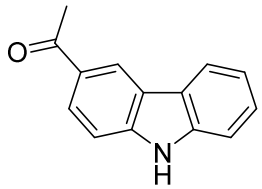
3-Methoxy-9H-carbazole (2f)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 44% yield (86.8 mg). Mp 136-138°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 1H, ArH, J = 8.0 Hz), 7.92 (s, 1H, NH), 7.56 (d, 1H, ArH, J = 2.4 Hz), 7.41-7.37 (m, 2H, ArH), 7.33 (d, 1H, ArH, J = 8.8 Hz), 7.23-7.19 (m, 1H, ArH), 7.07 (dd, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.8 Hz), 3.93 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 134.4, 125.8, 123.8, 123.4, 120.2, 119.1, 115.1, 111.3, 110.7, 103.2, 56.1.



3-(Trifluoromethoxy)-9H-carbazole (2g)[5]

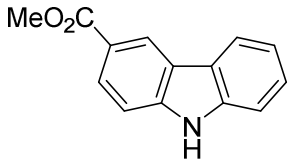
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 73% yield (183.3 mg). Mp 156-159°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H, NH), 8.04 (d, 1H, ArH, J = 7.6 Hz), 7.91 (s, 1H, ArH), 7.47-7.41 (m, 2H, ArH), 7.37 (d, 1H, ArH, J = 8.8 Hz), 7.29-7.23 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.3, 137.7, 126.7, 123.8, 122.9, 122.1, 120.6, 119.9, 119.5, 113.2, 111.1, 110.9. ^{19}F NMR (376MHz, $CDCl_3$): δ -58.1.



1-(9H-Carbazol-3-yl)ethan-1-one (2h)[4]

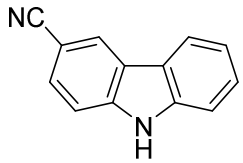
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid in 88% yield (184.1 mg). Mp 164-166°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H, ArH), 8.37 (s, 1H, NH), 8.14 (d, 1H, ArH, J = 8.0 Hz), 8.10 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.4 Hz), 7.48-7.44 (m, 3H, ArH), 7.23-7.29 (m, 1H, ArH), 2.73 (s, 3H, CH_3). ^{13}C NMR (100

MHz, $CDCl_3$): δ 197.8, 142.4, 140.0, 129.5, 126.7, 126.6, 123.5, 123.2, 121.9, 120.6, 120.5, 111.0, 110.3, 26.7.



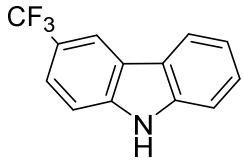
Methyl 9H-carbazole-3-carboxylate (2i)[5]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 41% yield (92.3 mg). Mp 183-185°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H, ArH), 8.36 (s, 1H, NH), 8.15-8.11 (m, 2H, ArH), 7.46-7.42 (m, 3H, ArH), 7.31-7.27 (m, 1H, ArH), 3.98 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 142.3, 139.9, 127.6, 127.4, 123.3, 123.1, 122.9, 121.4, 120.8, 120.6, 111.1, 110.3, 110.1, 52.0.



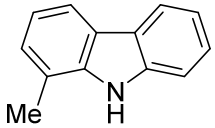
9H-Carbazole-3-carbonitrile (2j)[4]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid in 77% yield (147.8 mg). Mp 181-184°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H, ArH), 8.39 (s, 1H, NH), 8.10 (d, 1H, ArH, J = 7.6 Hz), 7.67 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.4 Hz), 7.54-7.48 (m, 3H, ArH), 7.35-7.31 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.1, 140.7, 129.0, 127.4, 126.0, 123.1, 122.0, 121.4, 121.0, 120.3, 112.5, 112.0, 100.6.



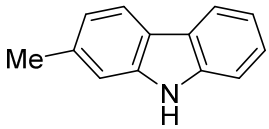
3-(Trifluoromethyl)-9H-carbazole (2k)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 69% yield (162.2 mg). Mp 165-168°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H, ArH), 8.21 (s, 1H, NH), 8.10 (d, 1H, ArH, J = 7.6 Hz), 7.65 (dd, 1H, ArH, J_1 = 1.2 Hz, J_2 = 8.4 Hz), 7.50-7.44 (m, 3H, ArH), 7.31-7.27 (m, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 139.9, 126.8, 126.6, 123.9, 123.0, 122.9, 122.7, 122.7, 122.0, 121.6, 120.6, 120.3, 118.0, 117.9, 117.9, 117.9, 111.0, 110.6. ^{19}F NMR (376MHz, $CDCl_3$): δ -60.1.



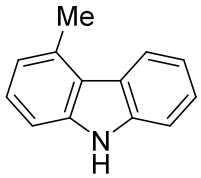
1-Methyl-9H-carbazole (2l)[6]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as an orange solid in 92% yield (166.6 mg). Mp 115-117°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, 1H, ArH, *J* = 8.0 Hz), 8.00 (s, 1H, NH),7.93 (d, 1H, ArH, *J* = 8.0 Hz), 7.47 (d, 1H, ArH, *J* = 8.4 Hz), 7.41 (t, 1H, ArH, *J* = 8.0 Hz), 7.24-7.21 (m, 2H, ArH), 7.16 (t, 1H, ArH, *J* = 7.6 Hz), 2.57 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 138.8, 126.4, 125.7, 123.8, 122.8, 120.5, 119.7, 119.6, 119.5, 117.9, 110.7, 16.9.



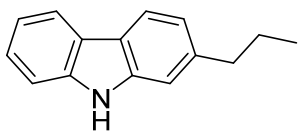
2-Methyl-9H-carbazole (2m)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 67% yield (121.4 mg). Mp 255-257°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 1H, ArH, *J* = 8.0 Hz), 7.94 (d, 1H, ArH, *J* = 8.0 Hz), 7.89 (s, 1H, NH), 7.39-7.35 (m, 2H, ArH), 7.23-7.19 (m, 2H, ArH), 7.06 (d, 1H, ArH, *J* = 7.2 Hz), 2.52 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 139.5, 136.0, 125.3, 123.4, 121.0 (2), 120.0 (2), 119.3, 110.8, 110.5, 22.1.



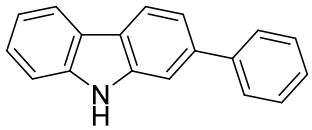
4-Methyl-9H-carbazole (2n)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid in 79% yield (143.1 mg). Mp 115-116°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, 1H, ArH, *J* = 8.0 Hz), 8.05 (s, 1H, NH), 7.44-7.41 (m, 2H, ArH), 7.34-7.23 (m, 3H, ArH), 7.02 (d, 1H, ArH, *J* = 6.8 Hz), 2.88 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 139.5, 133.4, 125.7, 125.2, 124.0, 122.6, 121.9, 120.9, 119.4, 110.4, 108.1, 20.8.



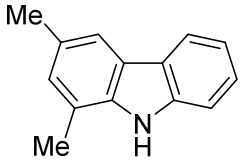
2-Propyl-9H-carbazole (2o)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 84% yield (175.6 mg). Mp 226-228°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 1H, ArH, *J* = 8.0 Hz), 7.96 (d, 1H, ArH, *J* = 8.0 Hz), 7.87 (s, 1H, NH), 7.36 (d, 2H, ArH, *J* = 3.6 Hz) 7.22-7.18 (m, 2H, ArH), 7.06 (d, 1H, ArH, *J* = 8.0 Hz), 2.74 (t, 2H, CH_2, *J* = 8.0 Hz), 1.77-1.68 (m, 2H, CH_2), 0.98 (t, 3H, CH_3, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 139.9, 139.5, 125.3, 123.5, 121.3, 120.5, 120.0(2), 119.3, 110.5, 110.2, 38.7, 25.0, 13.9. HRMS (ESI) m/z: calcd for $C_{15}H_{16}N^+$ ($[M+H]^+$), 210.1277; found, 210.1277.



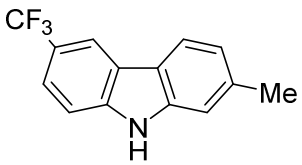
2-Phenyl-9H-carbazole (2p)[1]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a pink solid in 72% yield (175.2 mg). Mp 287-289°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.34 (s. 1H, NH), 8.18 (d, 1H, ArH, *J* = 8.4 Hz), 8.13 (d, 1H, ArH, *J* = 8.0 Hz), 7.76 (d, 2H, ArH, *J* = 7.2 Hz), 7.72 (s. 1H, ArH), 7.52-7.45 (m, 4H, ArH), 7.42-7.36 (m, 2H, ArH), 7.17 (t, 1H, ArH, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.7, 140.8, 140.7, 138.3, 129.4, 127.5(2), 126.1, 122.6, 122.3, 121.1, 120.7, 119.2, 118.3, 111.5, 109.3.



1,3-Dimethyl-9H-carbazole (2q)[1]

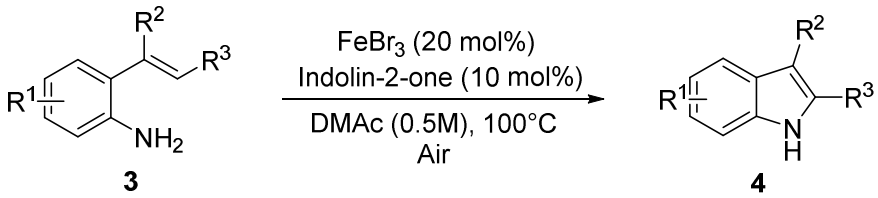
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a yellow solid in 76% yield (148.3 mg). Mp 93-95°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 1H, ArH, *J* = 7.6 Hz), 7.85 (s, 1H, NH), 7.72 (s, 1H, ArH),7.43 (d, 1H, ArH, *J* = 8.0 Hz), 7.38 (t, 1H, ArH, *J* = 5.6 Hz), 7.20 (t, 1H, ArH, *J* = 7.6 Hz), 7.06 (s, 1H, ArH), 2.52 (s, 3H, CH_3), 2.50 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 137.1, 128.9, 127.9, 125.5, 123.7, 123.0, 120.4, 119.4, 119.3, 117.8, 110.7, 21.4, 16.9.



2-Methyl-6-(trifluoromethyl)-9H-carbazole (2r)[7]

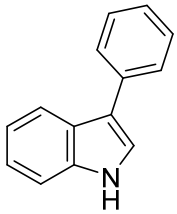
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 60/1) as a white solid in 91% yield (226.6 mg). Mp 202-204°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, ArH), 8.08 (s, 1H, NH), 7.96 (d, 1H, ArH, *J* = 8.0 Hz), 7.60 (d, 1H, ArH, *J* = 8.4 Hz), 7.41 (d, 1H, ArH, *J* = 8.4 Hz) 7.22 (s, 1H, ArH), 7.11 (d, 1H, ArH, *J* = 8.0 Hz), 2.53 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.4, 137.2, 126.6, 123.9, 123.1, 122.2(2), 122.1(2), 121.9, 121.5, 120.6, 120.2, 117.6(2), 117.5(2), 111.1, 110.5, 22.1. ^{19}F NMR (376MHz, $CDCl_3$): δ -60.1.

5. General procedure for the synthesis of indoles 4



In a 10-mL reaction vial, equipped with a magnetic stirring bar, alkenylaniline **3** (1.0 mmol), indolin-2-one (13.3 mg, 10 mol%) and $FeBr_3$ (59.2 mg, 20 mol%) were added to DMAc (2.0 mL). Then the vial was placed in a pre-heated metal block at 100 ºC under an air balloon. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled and quenched with cold water (20 mL) and extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (30/1−4/1, v/v) as eluent to afford the pure products.

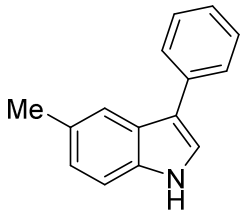
6. Characterization data of indoles 4



3-Phenyl-1H-indole (4a)[8]

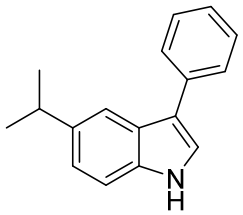
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a yellow solid in 91% yield (175.8 mg). Mp 106-108°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ

11.37 (s, 1H, NH), 7.87 (d, 1H, CH, *J* = 8.0 Hz), 7.72-7.65 (m, 3H, ArH), 7.47-7.41 (m, 3H, ArH), 7.25-7.21 (m, 1H, ArH), 7.18-7.14 (m, 1H, ArH), 7.11-7.08 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.4, 136.4, 129.2, 127.0, 125.7, 125.4, 123.9, 121.9, 120.1, 119.5, 116.1, 112.4.



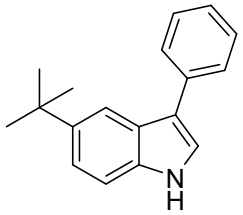
5-Methyl-3-phenyl-1H-indole (4b)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a brown solid in 83% yield (172.0 mg). Mp 102-105°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H, NH) 7.72 (s, 1H, ArH), 7.64 (d, 2H, ArH, *J* = 7.6 Hz), 7.43 (t, 2H, ArH, *J* = 7.6 Hz), 7.28-7.16 (m, 3H, ArH), 7.05 (d, 1H, ArH, *J* = 8.4 Hz), 2.46 (s, 3H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 135.0, 129.7, 128.8, 127.6, 126.0 (2), 124.1, 122.1, 119.5, 117.8, 111.2, 21.7.



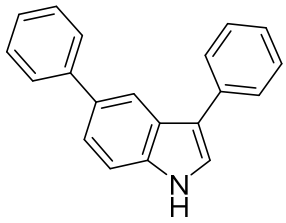
5-Isopropyl-3-phenyl-1H-indole (4c)[9]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a brown oil in 91% yield (214.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H, NH), 7.76 (s, 1H, ArH), 7.66 (d, 2H, ArH, *J* = 7.6 Hz), 7.44 (t, 2H, ArH, *J* = 7.6 Hz), 7.30-7.24 (m, 3H, ArH), 7.14 (d, 1H, ArH), 3.07-3.00 (m, 1H, CH), 1.31 (d, 6H, CH, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 135.9, 135.3, 128.8, 127.6, 125.9, 125.9, 122.1, 121.6, 118.1, 116.7, 111.3, 34.5, 24.8.



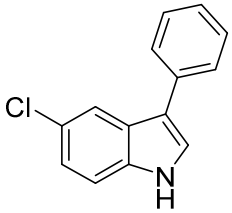
5-(Tert-butyl)-3-phenyl-1H-indole (4d)[9]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a brown oil in 56% yield (139.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H, NH), 7.92 (s, 1H, ArH), 7.67 (d, 2H, ArH, *J* = 7.6 Hz), 7.46 (t, 2H, ArH, *J* = 7.6 Hz), 7.38-7.28 (m, 4H, ArH), 1.40 (s, 9H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 135.8, 134.8, 128.8, 1276, 125.9, 125.5, 122.0, 120.8, 118.5, 115.4, 110.9, 34.7, 32.0.



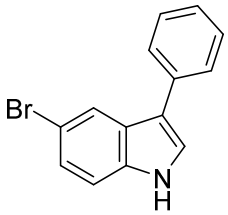
3,5-Diphenyl-1H-indole (4e)[10]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a brown oil in 69% yield (185.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s. 1H, NH), 8.13 (t, 1H, ArH, *J* = 0.8 Hz), 7.70-7.64 (m, 4H, ArH), 7.51-7.41 (m, 6H, ArH), 7.34 (d, 1H, ArH, *J* = 1.6 Hz), 7.33-7.28 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 136.2, 135.4, 134.1, 128.9, 128.7, 127.6, 127.5, 126.5, 126.3, 126.1, 122.5, 122.4, 118.8, 118.4, 111.7.



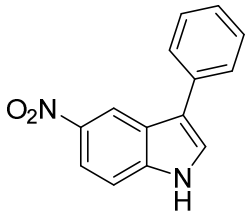
5-Chloro-3-phenyl-1H-indole (4f)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a yellow solid in 88% yield (200.3 mg). Mp100-102°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H, NH), 7.89 (s, 1H, ArH), 7.61 (d, 2H, ArH, *J* = 7.6 Hz), 7.45 (t, 2H, ArH, *J* = 7.6 Hz), 7.36 (s, 1H, ArH), 7.34-7.29 (m, 2H, ArH), 7.20 (d, 1H, ArH, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.8, 128.9, 127.5, 126.9, 126.3, 126.2, 123.0, 122.8, 119.3, 118.3, 112.4.



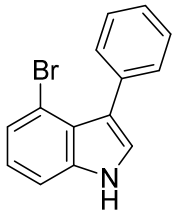
5-Bromo-3-phenyl-1H-indole (4g)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a brown oil in 76% yield (206.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (br s, 1H, NH), 8.03 (d, *J* = 2.0 Hz, 1H, ArH), 7.59-7.57 (m, 2H, ArH), 7.45-7.41 (m, 2H, ArH), 7.31-7.27 (m, 3H, ArH), 7.22 (d, *J* = 8.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 134.8, 128.9, 128.3, 127.5, 126.4, 125.3, 123.0, 122.4, 118.1, 113.7, 112.9.



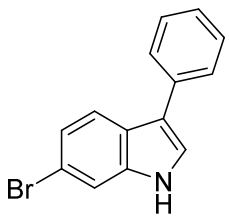
5-Nitro-3-phenyl-1H-indole(4h)[11]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 6/1) as a yellow solid in 84% yield (199.9 mg). Mp 185-186°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.13 (s, 1H, NH), 8.73 (s, 1H, ArH), 8.08 (d, 1H, CH, *J* = 8.8 Hz), 7.98 (s, 1H, ArH), 7.72 (d, 2H, ArH, *J* = 7.2 Hz), 7.65 (d, 1H, ArH, *J* = 8.8 Hz), 7.51 (t, 1H, ArH, *J* = 7.2 Hz), 7.34 (t, 1H, ArH, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.1, 139.9, 134.1, 129.0, 127.1, 126.9, 126.3, 124.3, 118.3, 116.8, 116.0, 112.5.



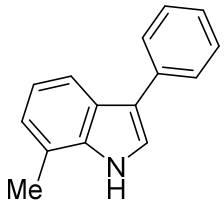
4-Bromo-3-phenyl-1H-indole (4i)[12]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a yellow oil in 68% yield (184.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (br s, 1H, NH), 7.52-7.49 (m, 2H, ArH), 7.41-7.35 (m, 4H, ArH), 7.32 (d, *J* = 7.2 Hz, 1H, ArH), 7.18 (d, *J* = 2.4 Hz, 1H, ArH), 7.06 (t, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.8, 131.5, 127.2, 126.7, 124.9, 124.7, 124.6, 123.1, 119.8, 114.5, 110.6.



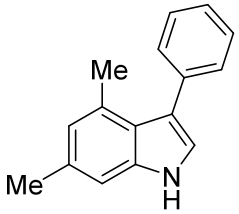
6-Bromo-3-phenyl-1H-indole (4j)[13]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 30/1) as a yellow oil in 78% yield (212.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (br s, 1H, NH), 7.69 (d, *J* = 8.8 Hz, 1H, ArH), 7.54-7.51 (m, 2H, ArH), 7.44 (d, *J* = 2.0 Hz, 1H, ArH), 7.36 (t, *J* = 7.6 Hz, 2H, ArH), 7.23-7.22 (m, 1H, ArH), 7.20-7.18 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.9, 128.9, 127.5, 126.3, 124.7, 123.6, 122.3, 121.1, 118.5, 115.9, 114.3.



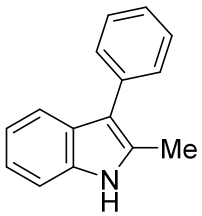
3,5-Diphenyl-1H-indole (4k)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a brown oil in 88% yield (182.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.32 (s. 1H, NH), 7.70-7.67 (m, 4H, ArH), 7.42 (t, 2H, ArH, *J* = 7.2 Hz), 7.22 (t, 1H, ArH, *J* = 7.6 Hz), 7.03-6.95 (m, 2H, ArH), 2.50 (s. 3H, CH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.8, 136.5, 129.2, 127.0, 125.7, 125.1, 123.6, 122.4, 121.6, 120.3, 117.1, 116.6, 17.3.



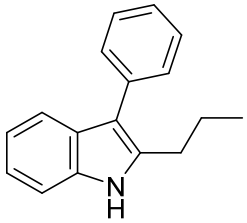
4,6-Dimethyl-3-phenyl-1H-indole (4l)[10]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a brown oil in 54% yield (119.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s. 1H, NH), 7.43-7.41 (m, 2H, ArH), 7.37-7.33 (m, 2H, ArH), 7.32-7.27 (m, 1H, ArH), 6.94 (s. 1H, ArH), 6.91 (d. 1H, ArH, *J* = 2.4 Hz), 6.73 (s. 1H, ArH), 2.41 (s. 3H, CH_3), 2.24 (s. 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.8, 132.3, 130.9, 130.7, 127.7, 126.4, 123.6, 123.2, 122.5, 119.5, 109.1, 21.6, 20.9.



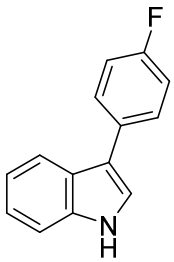
2-Methyl-3-phenyl-1H-indole (4m)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 30/1) as a yellow oil in 86% yield (178.2 mg). 1H NMR (400 MHz, CDCl3): δ 7.79 (br s, 1H, NH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.60 (d, *J* = 8.0 Hz, 2H, ArH), 7.54 (t, *J* = 7.6 Hz, 2H, ArH), 7.40-7.34 (m, 2H, ArH), 7.27-7.18 (m, 2H, ArH), 2.52 (s, 3H, CH_3). 13C NMR (100 MHz, $CDCl_3$): δ 135.5, 135.3, 131.6, 129.5, 128.6, 127.9, 125.9, 121.6, 120.0, 118.9, 114.5, 110.4, 12.6.



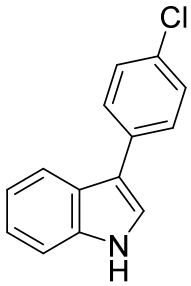
3-Phenyl-2-propyl-1H-indole (4n)[14]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 30/1) as a yellow oil in 84% yield (197.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H, NH), 7.65 (t, *J* = 6.8 Hz, 1H, ArH), 7.49-7.46 (m, 2H, ArH), 7.44-7.40 (m, 2H, ArH), 7.29-7.25 (m, 1H, ArH), 7.20 (d, *J* = 7.2 Hz, 1H, ArH), 7.17-7.07 (m, 2H, ArH), 2.70 (t, *J* = 7.6 Hz, 2H, CH_2), 1.64-1.54 (m, 2H, CH_2), 0.88 (dt, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.7, 135.4, 129.9, 128.7, 128.1, 126.1, 121.7, 120.1, 119.1, 114.6, 110.7, 28.5, 23.4, 14.2.



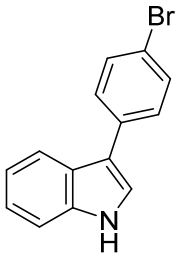
3-(4-Fluorophenyl)-1H-indole(4o)[15]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 8/1) as a yellow solid in 93% yield (196.4 mg). Mp 98-99°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H, NH), 7.87 (d, 1H, ArH, *J* = 8.0 Hz), 7.62-7.59 (m, 2H, ArH), 7.43 (d, 1H, ArH, *J* = 8.0 Hz), 7.31 (d, 1H, ArH, *J* = 2.0 Hz), 7.26 (t, 1H, ArH, *J* = 5.6 Hz), 7.20 (t, 1H, ArH, *J* = 7.2 Hz), 7.13 (t, 2H, ArH, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 160.3, 136.6, 131.6, 131.5, 129.0, 128.9, 125.7, 122.5, 121.6, 120.4, 119.5, 117.5, 115.7, 115.5, 111.5. ^{19}F NMR (376Hz, $CDCl_3$): δ -117.0.



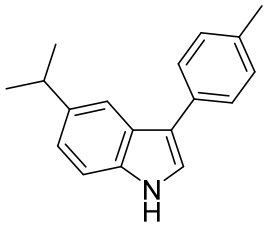
3-(4-Chlorophenyl)-1H-indole (4p)[8]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 8/1) as a light yellow solid in 89% yield (202.5 mg). Mp 130-133°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H, NH), 7.86 (d, J = 7.6 Hz, 1H, CH), 7.76 (d, J = 2.4 Hz, 1H, ArH), 7.72 (d, J = 8.8 Hz, 2H, ArH), 7.49-7.45 (m, 3H, ArH), 7.18 (t, J = 7.2 Hz, 1H, ArH), 7.11 (t, J = 6.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO): δ 137.4, 135.3, 130.0, 129.2, 128.4, 125.2, 124.4, 122.0, 120.3, 119.3, 114.8, 112.5.



3-(4-Bromophenyl)-1H-indole (4q)[16]

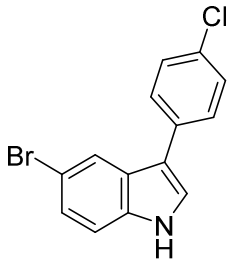
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a light brown solid in 82% yield (222.9 mg). Mp 125-128°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (br s, 1H, NH), 7.86 (d, J = 8.0 Hz, 1H, CH), 7.54-7.48 (m, 4H, ArH), 7.36 (d, J = 7.6 Hz, 1H, ArH), 7.25-7.16 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 134.6, 131.9, 129.0, 125.5, 122.7, 122.0, 120.6, 119.7, 119.6, 117.2, 111.6.



5-Isopropyl-3-(p-tolyl)-1H-indole (4r)

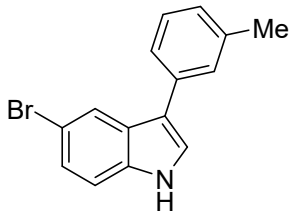
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a brown oil in 91% yield (226.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s. 1H, NH),

7.74 (s, 1H, ArH), 7.54 (d, 2H, ArH, J = 8.0 Hz), 7.25 (d, 3H, ArH, J = 8.4 Hz), 7.17 (s, 1H, ArH), 7.12 (d, 1H, ArH, J = 8.4 Hz), 3.05-2.99 (m, 1H, CH), 2.39 (s, 3H, CH_3), 1.30 (d, 6H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 135.6, 135.3, 132.9, 129.6, 127.6, 125.9, 121.9, 121.5, 118.1, 116.8, 111.3, 34.5, 24.8, 21.3. HRMS (ESI) m/z: calcd for $C_{18}H_{20}N^+$ ([M+H]$^+$), 250.1590; found, 250.1589.



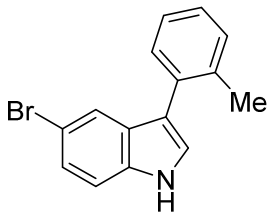
5-Bromo-3-(4-chlorophenyl)-1H-indole (4s)[17]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a yellow oil in 77% yield (236.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (br s, 1H, NH), 7.86 (d, J = 2.0 Hz, 1H, ArH), 7.39 (d, J = 8.8 Hz, 2H, ArH), 7.28 (d, J = 8.8 Hz, 2H, ArH), 7.22-7.20 (m, 1H, ArH), 7.17 (d, J = 2.8 Hz, 1H, ArH), 7.14 (d, J = 8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.3, 132.0, 129.0, 128.6, 127.3, 125.5, 123.0, 122.1, 116.9, 113.9, 113.0.



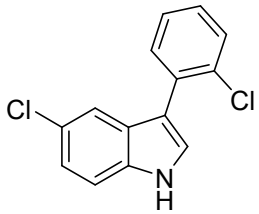
5-Bromo-3-(m-tolyl)-1H-indole (4t)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 6/1) as a yellow oil in 78% yield (223.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s. 1H, NH), 8.03 (d, 1H, ArH, J = 1.6 Hz), 7.41-7.40 (m, 2H, ArH), 7.35 (d, 1H, ArH, J = 7.6 Hz), 7.33-7.30 (m, 2H, ArH), 7.26 (d, 1H, ArH, J = 8.4 Hz), 7.13 (d, 1H, ArH, J = 7.2 Hz), 2.43 (s, 3H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.2, 134.7, 128.8, 128.2, 127.6, 127.2, 125.3, 124.6, 122.8, 122.4, 118.2, 113.6, 112.8, 21.6. HRMS (ESI) m/z: calcd for $C_{15}H_{13}BrN^+$ ([M+H]$^+$), 286.0226; found, 286.0228.



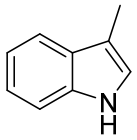
5-Bromo-3-(o-tolyl)-1H-indole (4u)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as an orange oil in 78% yield (223.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (br s, 1H, NH), 7.63 (s, 1H, ArH), 7.33-7.24 (m, 7H, ArH), 7.17 (s, 1H, ArH), 2.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 134.5, 133.6, 130.8, 130.4, 129.0, 127.1, 125.8, 125.1, 123.9, 122.6, 117.2, 113.3, 112.7, 20.7. HRMS (ESI) m/z: calcd for $C_{15}H_{13}BrN^+$ ($[M+H]^+$), 286.0226; found, 286.0224.



5-Chloro-3-(2-chlorophenyl)-1H-indole (4v)[18]

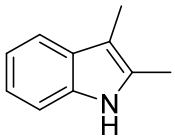
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 4/1) as a brown liquid in 85% yield (222.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (br s, 1H, NH), 7.59 (d, J = 2.0 Hz, 1H, ArH) 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.43 (s, 1H, ArH), 7.35-7.31 (m, 2H, ArH), 7.26 (t, J = 7.6 Hz, 1H, ArH), 7.18 (d, J = 7.2 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 133.3, 133.1, 131.8, 130.2, 128.0, 127.7, 126.8, 126.1, 125.4, 122.7, 119.6, 114.7, 112.4.



3-Methyl-1H-indole (4w)[19]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a pale brown solid in 90% yield (117.9 mg). Mp 94-95°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H, NH), 7.58 (d, 1H, ArH, J = 8.0 Hz), 7.33 (d, 1H, ArH, J = 8.0 Hz), 7.19 (t, 1H, ArH, J

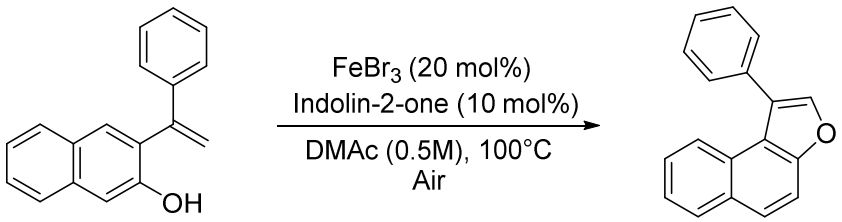
= 6.8 Hz), 7.12 (t, 1H, ArH, *J* = 7.2 Hz), 6.95 (s, 1H, ArH), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 128.3, 121.9, 121.6, 119.1, 118.9, 111.8, 111.0, 9.7.



2,3-Dimethyl-1H-indole (4x)[20]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a yellow solid in 35% yield (50.8 mg). Mp 104-105°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H, NH), 7.45 (d, 1H, ArH, *J* = 6.4 Hz), 7.17-7.15 (m, 1H, ArH), 7.10-7.04 (m, 2H, ArH), 2.26 (s, 3H, CH_3), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 130.9, 129.5, 120.9, 119.0, 118.0, 110.2, 107.0, 11.5, 8.5.

7. Synthetic procedure and characterization data of benzofuran 6



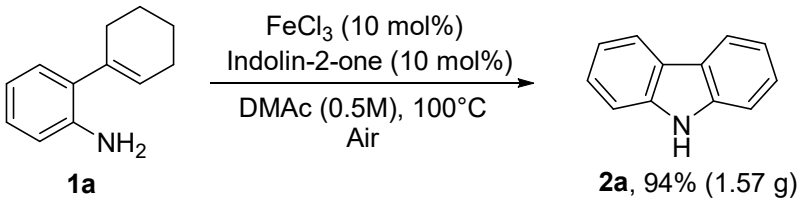
5 **6**, 72%

1-Phenylnaphtho[2,1-b]furan (6)[21]

In a 10-mL reaction vial, equipped with a magnetic stirring bar, alkenylaniline **5** (1.0 mmol), indolin-2-one (13.3 mg, 10 mol%,) and $FeBr_3$ (59.2 mg, 20 mol%,) were added to DMAc (2.0 mL). Then the vial was placed in a pre-heated metal block at 100 ºC under an air balloon. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled and quenched with cold water (20 mL) and extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (30/1, v/v) as eluent to afford the pure product **6** as a yellow solid (175.8 mg, 72% yield). Mp 112-113°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, ArH, *J* = 8.0 Hz), 7.94 (d, 1H, ArH, *J* = 8.4 Hz), 7.77 (d, 1H, ArH, *J* = 8.8 Hz), 7.70 (d, 2H, ArH, *J* = 9.2), 7.61 (d, 2H, ArH, *J* = 6.4 Hz), 7.53-7.47 (m, 3H, ArH), 7.43 (t, 1H, ArH, *J* = 7.2 Hz), 7.37-7.32 (m, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 141.7, 133.1, 130.8, 129.9, 128.9, 128.6, 128.3, 127.9, 126.4, 126.0, 124.5, 124.4, 123.4, 120.7, 112.7.

8. The procedure for gram-scale synthesis of 2a, 4a and 4w

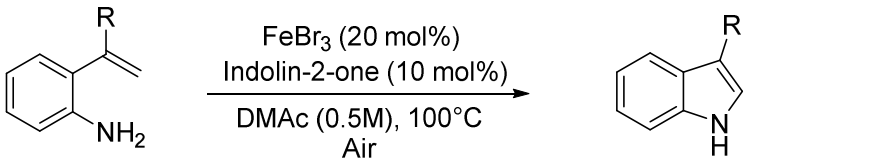
8.1 Gram-scale preparation for carbazole **4a**



1a **2a**, 94% (1.57 g)

In a 50-mL reaction vial, equipped with a magnetic stirring bar, 2-cyclohexenyl aminoarene **1a** (1.73 g, 10.0 mmol), indolin-2-one (133 mg, 10 mol%) and $FeCl_3$ (162 mg, 10 mol%,) were added to DMAc (20.0 mL). Then the vial was placed in a pre-heated oil bath at 100 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled and quenched with cold water (200 mL) and extracted with ethyl acetate (3×150 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (10/1, v/v) as eluent to afford the pure product **2a** in 94% yield (1.57 g).

8.2 Gram-scale preparation for indoles **4a** and **4w**

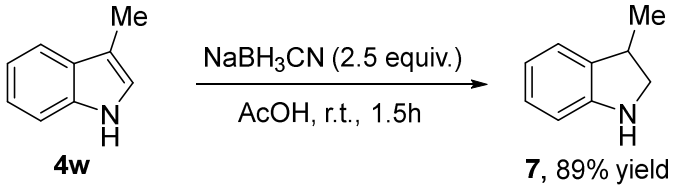


3

4a, R = Ph, 91% (1.76 g)
4w, R = Me, 88% (1.15 g)

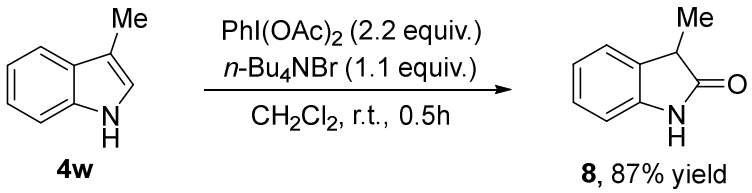
In a 50-mL reaction vial, equipped with a magnetic stirring bar, alkenylaniline **3** (10.0 mmol), indolin-2-one (133 mg, 10 mol%) and $FeBr_3$ (296 mg, 10 mol%) were added to DMAc (20.0 mL). Then the vial was placed in a pre-heated oil bath at 100 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was cooled and quenched with cold water (200 mL) and extracted with ethyl acetate (3×150 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (10/1−4/1, v/v) as eluent to afford the pure products.

9. Product transformations processes for compounds 7-14



3-Methylindoline (7)[22]

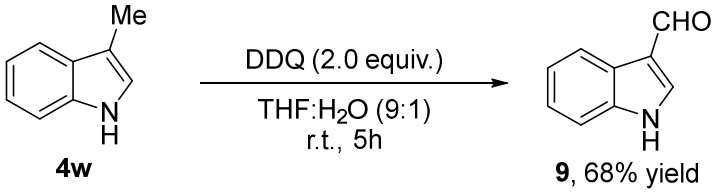
To a stirred solution of 3-methyl-indole (131.2 mg, 1.0 mmol, 1 equiv.) in acetic acid (2 mL) was added $NaBH_3CN$ (157 mg, 2.5 mmol, 2.5 equiv.). The reaction was allowed to stir at room temperature and reaction progress was monitored by TLC. After the reaction was judged to be complete, the reaction mixture was diluted with water (30 mL), brought to pH~9 with NaOH pellets and extracted with EtOAc (3×10 mL). The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (40:1, v/v) to afford 3-methylindoline **7** as a colourless liquid (118.5 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, J = 7.6 Hz, 1H, ArH), 6.93 (t, J = 8.0 Hz, 1H, ArH), 6.65 (t, J = 7.2 Hz, 1H, ArH), 6.54 (d, J = 7.6 Hz, 1H, ArH), 3.58 (m, 2H, CH_2 and NH), 3.31-3.22 (m, 1H, CH), 3.00 (t, J = 8.4 Hz, 2H, CH_2), 1.22 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 134.4, 127.3, 123.4, 118.8, 109.6, 55.4, 36.7, 18.7.



3-Methylindolin-2-one (8)[23]

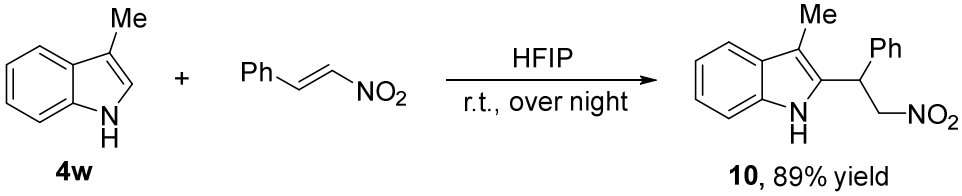
To the solution of 3-methyl-indole (131.2 mg, 1 mmol, 1 equiv.) and n-Bu_4NBr (354.6 mg, 1.1 mmol, 1.1 equiv.) in DCM (5 mL) was added dropwise $PhI(OAc)_2$ (708.6 mg, 2.2 mmol, 2.2 equiv.) at room temperature. The resulting solution was stirred for further 30 min. After the reaction was judged to be complete, the reaction mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (10:1, v/v) to afford 3-methylindolin-2-one **8** as a pale solid (128.0 mg, 87% yield). Mp 120-121°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H, NH), 7.20 (t, J = 7.6 Hz, 2H, ArH), 7.02 (t, J = 7.6 Hz,

1H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 3.50-3.44 (m, 1H, CH), 1.50 (d, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 141.5, 131.3, 127.9, 123.7, 122.3, 110.0, 41.3, 15.3.



1H-Indole-3-carbaldehyde (9)[24]

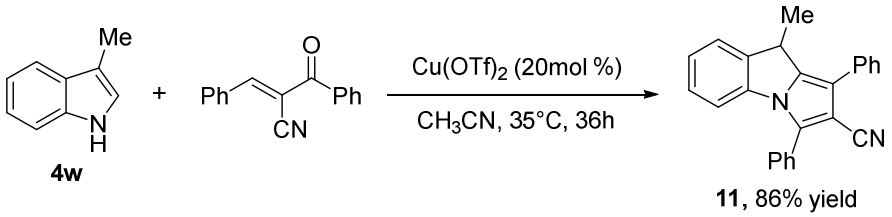
To the solution of 3-methyl-indole (65.6 mg, 0.5 mmol, 1 equiv.) in THF:H_2O (9:1, 10 mL) was added DDQ (227.0 mg, 1.0 mmol, 2 equiv.) and the reaction mixture was stirred at room temperature for 5 h. After completion of the reaction (monitored by TLC), NaOH aq (2 N, 3 mL) was added and the mixture was extracted with EtOAc (3×6 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (40:1, v/v) to afford 1H-indole-3-carbaldehyde **9** as a light-brown solid (49.4 mg, 68% yield). Mp 196-198°C. ^1H NMR (400 MHz, DMSO-d_6): δ 12.13 (br s, 1H, NH), 9.97 (s, 1H, C(O)H), 8.31 (s, 1H, ArH), 8.14 (d, *J* = 7.2 Hz, 1H, ArH), 7.54 (d, J = 7.6 Hz, 1H, ArH), 7.30-7.22 (m, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.4, 138.9, 137.5, 124.6, 123.9, 122.6, 121.3, 118.6, 112.9.



3-Methyl-2-(2-nitro-1-phenylethyl)-1H-indole (10)[25]

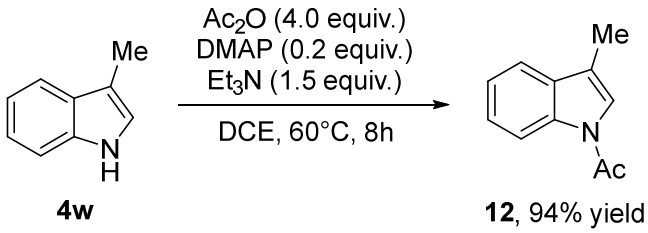
In a 10-mL reaction vial, equipped with a magnetic stirring bar, 3-methyl-indole (65.6 mg, 0.5 mmol, 1 equiv.), β-nitroalkene (74.6 mg, 0.5 mmol, 1 equiv.) were added to HFIP (2.0 mL) under air. The resulting solution was stirred over night. After the reaction was judged to be complete, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (40/1, v/v) as eluent to afford the pure product **10** as a yellow solid (124.7 mg, 89% yield). Mp 141-142°C. ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$ (v/v = 1:3)): δ 10.81 (s, 1H, NH), 7.40 (d, *J* = 7.6 Hz, 3H, ArH),

7.32-7.27 (m, 3H, ArH), 7,21 (t, J = 6.4 Hz, 1H, ArH), 7.05 (t, J = 6.8 Hz, 1H, ArH), 6.96 (t, J = 7.6 Hz, 1H, ArH), 5.38-5.26 (m, 2H, CH), 5.13 (t, J = 7.2 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$ (v/v = 1:3)) δ 138.9, 136.1, 132.3, 129.0, 128.6, 127.7, 127.5, 121.5, 118.8, 118.4, 111.1, 107.6, 77.7, 41.2, 8.7.



9-Methyl-1,3-diphenyl-9H-pyrrolo[1,2-a]indole-2-carbonitrile (11)[26]

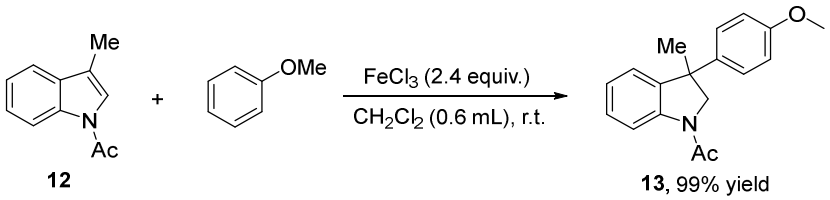
In a 10-mL reaction vial, equipped with a magnetic stirring bar, 3-methyl-indole (26.2 mg, 0.2 mmol, 1 equiv.), aromatic aldehyde-derived oxodiene (46.7 mg, 0.2 mmol, 1 equiv.), $Cu(OTf)_2$ (14.5 mg, 0.04 mmol), and 1.2 mL of CH_3CN. Then the vial was placed in a pre-heated metal block at 35 ºC in the presence of ambient air. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was directly concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1, v/v) as eluent to afford the pure product **11** as a white solid (59.6 mg, 86% yield). Mp 173-175°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.67 (m, 4H, ArH), 7.57-7.52 (m, 3H, ArH), 7.46 (t, 2H, ArH, J = 7.6 Hz), 7.42 (d, 1H, ArH, J = 7.2 Hz), 7.33 (t, 1H, ArH, J = 8.0 Hz), 7.19 (t, 1H, ArH, J = 7.6 Hz), 7.14 (t, 1H, ArH, J = 7.6 Hz), 7.02 (d, 1H, ArH, J = 7.6 Hz), 4.49-4.43 (m, 1H, CH), 1.45 (d. 3H, CH_3, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 139.1, 138.4, 135.1, 132.3, 129.8, 129.6, 128.9 (2), 127.6, 127.5, 127.2, 125.3, 125.0, 120.4, 117.1, 112.7, 96.1, 36.0, 35.9, 16.9.



1-(3-Methyl-1H-indol-1-yl)ethan-1-one (12)[27]

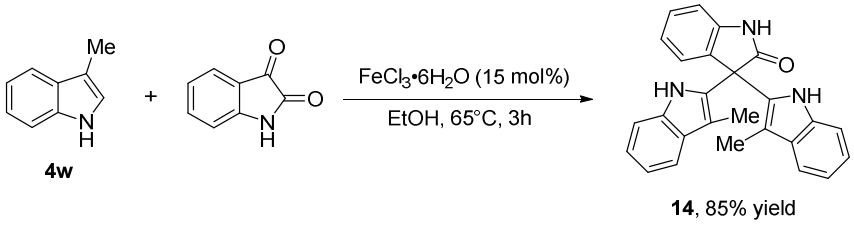
To the solution of 3-methyl-indole (65.6 mg, 0.5 mmol), DMAP (12.2 mg, 0.1 mmol) and Et_3N (75.8 mg, 0.75 mmol) in DCE (5 mL) was added Ac_2O (204.2 mg, 2.0 mmol). Then the resulting mixture was stirred at 60 ºC (oil bath) for 8 h. After completion of the reaction (monitored by TLC), a saturated NH_4Cl aqueous solution (5 mL) was added and the mixture was extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4,

filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1, v/v) as eluent to afford the pure product **12** as a yellow oil (81.4 mg, 94% yield). Mp 66-68°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H, ArH), 7.48 (d, 1H, ArH, *J* = 7.6 Hz), 7.34 (t, 1H, ArH, *J* = 7.2 Hz), 7.28 (t, 1H, ArH, *J* = 7.2 Hz), 7.14 (s, 1H, ArH), 2.56 (s. 3H, CH_3), 2.26 (d, 1H, CH_3, *J* = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 135.8, 131.4, 125.1, 123.4, 122.2, 118.8, 118.4, 116.6, 24.0, 9.7.



1-(3-(4-Methoxyphenyl)-3-methylindolin-1-yl)ethan-1-one (13)[28]

In a 10-mL reaction vial, equipped with a magnetic stirring bar, 1-(3-methyl-1H-indol-1-yl)ethan-1-one **12** (52.0 mg, 0.3 mmol, 1 equiv.), anisole (64.9 mg, 0.6 mmol, 2 equiv.), $FeCl_3$ (116.8 mg, 0.72 mmol, 2.4 equiv.) and 0.6 mL of DCM. Then the resulting mixture was stirred at room temperature. The formation of the products was monitored by TLC. After completion of the reaction (monitored by TLC), a saturated NH_4Cl aqueous solution (6 mL) was added and diluted with EtOAc (5 mL). The organic and aqueous phases were separated. The aqueous phase was then extracted with EtOAc (2×5 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (10/1, v/v) as eluent to afford the pure product **13** as a white solid (83.5 mg, 99% yield). Mp 98-100°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 1H, ArH, *J* = 8.4 Hz), 7.25 (t, 1H, ArH, *J* = 8.4 Hz), 7.15 (d, 2H, ArH, *J* = 8.8 Hz), 7.04 (t, 1H, ArH, *J* = 7.2 Hz), 6.97 (d, 1H, ArH, *J* = 7.2 Hz), 6.83 (d, 2H, ArH, *J* = 8.8 Hz), 4.10 (d, 1H, CH_2, *J* = 10.4 Hz), 4.00 (d, 1H, CH_2, *J* = 10.4 Hz), 3.77 (s. 3H, CH_3), 2.17 (s. 3H, CH_3), 1.74 (s. 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 158.3, 142.2, 139.7, 138.9, 128.0, 127.5, 124.1, 123.8, 117.0, 113.8, 65.9, 55.3, 47.3, 27.3, 24.2.



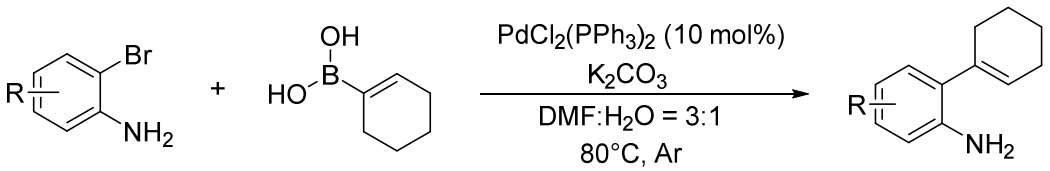
3,3''-Dimethyl-[2,3':3',2''-terindolin]-2'-one (14)[29]

A 10-mL round bottomed flask was charged with 3-methyl-indole (65.6 mg, 0.5 mmol, 1 equiv.), isatin (147.1 mg, 1.0 mmol, 2 equiv.), $FeCl_3$•$6H_2O$ (20.3 mg, 15 mol%) and ethanol (2.0 mL). Then the mixture was heated to 65°C and stirred for 3 h. The formation of the products was monitored by TLC. After completion of the reaction, cool the mixture to room temperature, and the insoluble crude product was isolated by filtration, washed with H_2O (2×10 mL). The crude product was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (4/1, v/v) as eluent to afford the pure product **14** as a white solid (166.4 mg, 85% yield). Mp. 302-303°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.81 (br s, 1H, NH), 10.45 (s, 2H, NH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 7.36-7.33 (m, 3H, ArH), 7.27 (t, J = 8.0 Hz, ArH), 7.06-6.95 (m, 6H, ArH), 1.93 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.4, 142.0, 135.8, 132.2, 131.6, 129.6, 129.2, 126.1, 122.7, 121.4, 118.8, 118.3, 111.9, 110.5, 107.8, 55.1, 9.4.

10. General procedure for the synthesis of alkenylaniline 1, 3 and 5

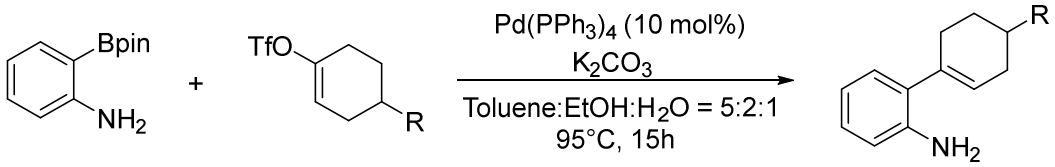
The alkenylanilines of **1a-1n** and **1q** were prepared according to method **A**. The alkenylanilines of **1o**, **1p** and **1r** were prepared according to method **B**. The alkenylanilines of **3a**, **3g**, **3h**, **3m-3q**, **3v** and **3x** were prepared according to method **C**. The alkenylanilines of **3b-3f**, **3i-3l**, **3r-3u** were prepared according to method **D**. The alkenylaniline **3w** was purchased and used as received.

Method A[30]:



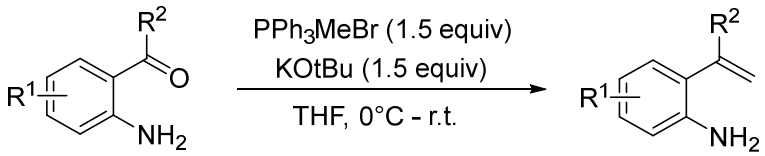
To a mixture of 2-bromoaniline (2.0 mmol, 1.0 equiv), the corresponding cycloolefin boric acid (2.4 mmol, 1.2 equiv.) under nitrogen was added potassium carbonate (8.0 mmol, 4.0 equiv), bis(triphenylphosphine)palladium(II) chloride (140.4 mg, 0.2 mmol, 10 mol%), DMF/H_2O (8 mL 3/1, v/v) and the mixture was stirred at 80°C over night. The mixture was cooled to room temperature, poured into ethyl acetate (40 mL), washed with saturated salt water (40 mL). The aqueous phase was then extracted with EtOAc (3×30 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (10/1, v/v) as eluent to afford the product.

Method B[31]:



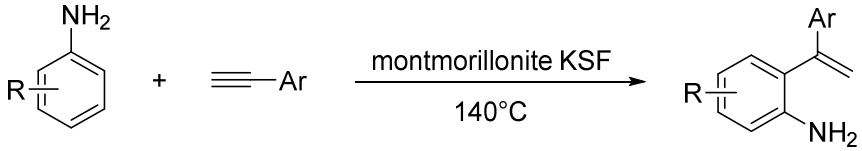
A cyclohex-1-en-1-yltrifluoromethanesulfonate (2.0 mmol, 1.0 equiv), 2-aminophenylboronic acid pinacolate ester (657 mg, 3.0 mmol, 1.5 equiv), K_2CO_3 (8.0 mmol, 4.0 equiv) and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol, 10 mol%) were dissolved in a mixture of toluene/water/ethanol (5:2:1, 0.06 M). The resulting mixture was heated to 95 °C for 15 hours. After cooling to room temperature, the biphasic solution was diluted with saturated aqueous NH_4Cl and CH_2Cl_2 and the phases were separated. The aqueous phase was extracted twice with CH_2Cl_2 (30 mL) and the combined organic phases were washed with demin. water (30 mL) and brine (30 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum ether / ethyl acetate 10:1) afforded the products.

Method C[32]:



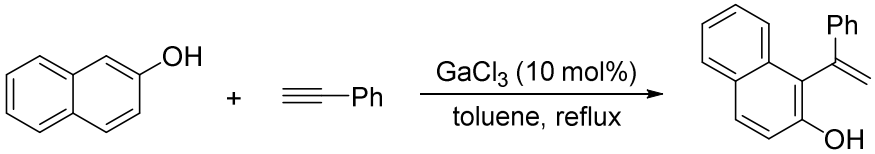
To a suspension of PPh_3MeBr (15 mmol, 1.5 equiv.) in dry THF (30 mL) at 0 °C was added KOtBu (15 mmol, 1.5 equiv) in two portions over 10 min. The resulting yellow mixture was allowed to stir for 30 minutes at room temperature before it was cooled to 0°C again and the corresponding 2′-aminoacetophenone or 2-aminobenzophenone (10 mmol, 1 equiv) was added. After five minutes the cooling bath was removed and the mixture was allowed to warm to ambient temperature. After completion of the reaction the mixture was diluted with EtOAc (20 mL) and sat. $NaHCO_3$ (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (2×30 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was loaded on silica and purified via column chromatography to afford the product.

Method D[33]:



An arylamine (10.0 mmol, 1 equiv.), a phenylacetylene (10.0 mmol, 1 equiv.) and montmorillonite KSF (1 g) were added to a round-bottom flask. The resulting mixture was stirred at 140 °C under reflux for 7 h. After being allowed to cool to room temperature, the reaction mixture was dissolved in CH_2Cl_2, and then filtered through Celite. The filtrate was concentrated in vacuo, and then the residue was purified by column chromatography to afford the product.

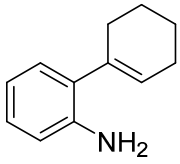
Method for the synthesis of 1-(1-phenylvinyl)naphthalen-2-ol (5)[34]



5

A mixture of the naphthalen-2-ol (2.0 mmol, 1 equiv.), phenylacetylene (2.4 mmol, 1.2 equiv.), and $GaCl_3$ (0.2 mmol) in toluene (4 mL) was stirred under reflux for 5h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled and quenched with H_2O (20 mL) and extracted with EtOAc (3×15 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (15/1, v/v) as eluent to afford the pure product **5** as a white solid (349.7 mg, 71% yield). Mp 112-113°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.45 (s, 1H, OH), 7.82-7.79 (m, 2H, ArH), 7.57 (d, 1H, ArH, J = 8.4 Hz), 7.33-7.21 (m, 9H, ArH), 6.18 (s, 1H, CH), 5.22 (s, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.3, 143.2, 140.4, 133.8, 129.1, 128.8, 128.4, 128.3, 127.9, 126.7, 126.3, 124.5, 122.9, 121.1, 118.8, 117.3.

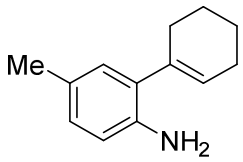
11. Characterization data of alkenylaniline 1 and 3



2',3',4',5'-Tetrahydro-[1,1'-biphenyl]-2-amine (1a)[31]

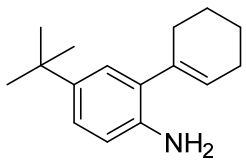
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 71% yield (245.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (t, 1H, ArH, J = 7.6 Hz), 6.95 (d, 1H, ArH, J = 7.6 Hz), 6.69 (t, 1H, ArH, J = 7.2 Hz), 6.62 (d, 1H, ArH, J = 8.0 Hz), 5.73-5.72 (m, 1H, CH), 3.70 (s, 2H, NH_2), 2.23-2.20 (m, 2H, CH_2), 2.16-2.13 (m, 2H, CH_2),

1.77-1.71 (m, 2H, CH_2), 1.68-1.63 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 136.6, 130.5, 128.7, 127.6, 126.9, 118.3, 115.5, 29.5, 25.6, 23.3, 22.3.



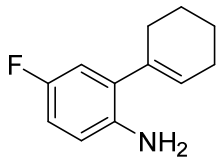
5-Methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1b)[35]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a red oil in 86% yield (321.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 6.84 (dd, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.0 Hz), 6.80 (s, 1H, ArH), 6.60 (d, 1H, ArH, J = 8.0 Hz), 5.74-5.71 (m, 1H, CH), 3.58 (s, 2H, NH_2), 2.25-2.21 (m, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.18-2.14 (m, 2H, CH_2), 1.79-1.73 (m, 2H, CH_2), 1.70-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 136.6, 130.6, 129.2, 128.0, 127.5, 126.7, 115.6, 29.5, 25.5, 23.2, 22.2, 20.5.



5-(Tert-butyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1c)

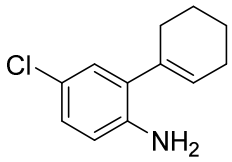
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a red oil in 88% yield (403.4 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.0 Hz), 6.99 (d, 1H, ArH, J = 2.0 Hz), 6.63 (d, 1H, ArH, J = 8.4 Hz), 5.76-5.73 (m, 1H, CH), 3.53 (s, 2H, NH_2), 2.25-2.23 (m, 2H, CH_2), 2.18-2.16 (m, 2H, CH_2), 1.80-1.75 (m, 2H, CH_2), 1.71-1.65 (m, 2H, CH_2), 1.27 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 140.5, 136.9, 130.1, 126.7, 125.5, 124.3, 115.2, 34.0, 31.6, 29.6, 25.5, 23.3, 22.2. HRMS (ESI) m/z: calcd for $C_{16}H_{24}N^+$ ($[M+H]^+$), 230.1903; found, 230.1906.



5-Fluoro-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1d)

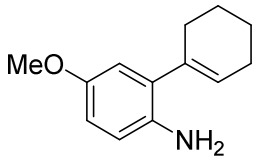
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 64% yield (244.6 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 6.76-6.69 (m, 2H, ArH), 6.62-6.59 (m, 1H, ArH), 5.78-5.75 (m, 1H, CH), 3.55 (s, 2H, NH_2), 2.23-2.15 (m, 4H, CH_2),

1.79-1.73 (m, 2H, CH_2), 1.70-1.65 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 155.0, 139.1, 135.7, 131.7, 131.6, 127.5, 116.2, 116.1, 115.1, 113.8, 113.6, 29.1, 25.4, 23.1, 22.0. ^{19}F NMR (376MHz, $CDCl_3$): δ -127.1. HRMS (ESI) m/z: calcd for $C_{12}H_{15}FN^+$ ($[M+H]^+$), 192.1183; found, 192.1186.



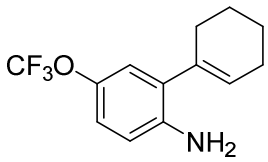
5-Chloro-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1e)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 83% yield (344.6 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 6.98-6.94 (m, 2H, ArH), 6.59 (d, 1H, ArH, J = 8.4 Hz), 5.76-5.74 (m, 1H, CH), 3.65 (s, 2H, NH_2), 2.22-2.15 (m, 4H, CH_2), 1.78-1.72 (m, 2H, CH_2), 1.70-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 135.5, 131.8, 128.4, 127.7, 127.2, 122.8, 116.4, 29.2, 25.4, 23.1, 22.0. HRMS (ESI) m/z: calcd for $C_{12}H_{15}ClN^+$ ($[M+H]^+$), 208.0888; found, 208.0890.



5-Methoxy-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1f)[35]

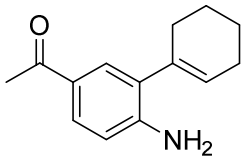
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 62% yield (251.8 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 6.64 (s, 1H, ArH), 6.63 (s, 1H, ArH), 6.58 (t, 1H, ArH, J = 2.0 Hz), 5.76-5.73 (m, 1H, CH), 3.73 (s, 3H, CH_3), 3.45 (s, 2H, NH_2), 2.25-2.22 (m, 2H, CH_2), 2.18-2.15 (m, 2H, CH_2), 1.79-1.73 (m, 2H, CH_2), 1.71-1.65 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 136.7, 136.5, 131.7, 127.0, 116.6, 114.2, 113.2, 55.7, 29.3, 25.4, 23.2, 22.2.



5-(Trifluoromethoxy)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1g)

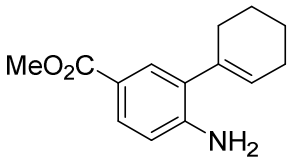
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a red oil in 91% yield (467.8 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 6.89-6.85 (m, 2H, ArH),

6.60 (d, 1H, ArH, J = 8.4 Hz), 5.78-5.76 (m, 1H, CH), 3.73 (s, 2H, NH_2), 2.22-2.13 (m, 4H, CH_2), 1.78-1.72 (m, 2H, CH_2), 1.70-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 141.1, 141.0, 135.4, 131.1, 127.8, 124.5, 122.0, 121.6, 120.3, 119.5, 116.9, 115.6, 29.1, 25.3, 23.0, 22.0. ^{19}F NMR (376MHz, $CDCl_3$): δ -58.3. HRMS (ESI) m/z: calcd for $C_{13}H_{15}F_3NO^+$ ($[M+H]^+$), 258.1100; found, 258.1102.



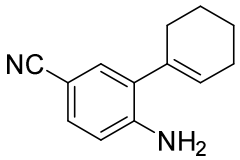
1-(6-Amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (1h)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 71% yield (305.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.4 Hz), 7.63 (d, 1H, ArH, J = 2.0 Hz), 6.65 (d, 1H, ArH, J = 8.4 Hz), 5.78-5.76 (m, 1H, CH), 4.30 (s, 2H, NH_2), 2.50 (s, 3H, CH_3), 2.24-2.21 (m, 2H, CH_2), 2.18-2.15 (m, 2H, CH_2), 1.79-1.75 (m, 2H, CH_2), 1.70-1.67 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 148.4, 135.5, 129.8, 129.0 (2), 127.8, 127.3, 114.0, 29.3, 26.1, 25.4, 23.1, 22.0. HRMS (ESI) m/z: calcd for $C_{14}H_{18}NO^+$ ($[M+H]^+$), 216.1383; found, 216.1387.



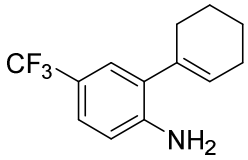
Methyl 6-amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-3-carboxylate (1i)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a colourless oil in 86% yield (397.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.0 Hz), 7.68 (d, 1H, ArH, J = 1.6 Hz), 6.63 (d, 1H, ArH, J = 8.4 Hz), 5.77-5.74 (m, 1H, CH), 4.16 (s, 2H, NH_2), 3.83 (s, 3H, CH_3), 2.24-2.20 (m, 2H, CH_2), 2.16-2.14 (m, 2H, CH_2), 1.78-1.73 (m, 2H, CH_2), 1.69-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 147.9, 135.5, 130.6, 129.6, 129.1, 127.6, 119.1, 114.1, 51.6, 29.3, 25.4, 23.1, 22.1. HRMS (ESI) m/z: calcd for $C_{14}H_{18}NO_2^+$ ($[M+H]^+$), 232.1332; found, 232.1334.



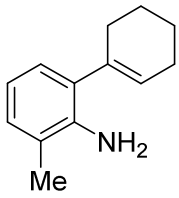
6-Amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-3-carbonitrile (1j)[36]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a white solid in 66% yield (261.7 mg). Mp 126-128°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 1H, ArH, *J* = 8.0 Hz), 7.23 (s, 1H, ArH), 6.65 (d, 1H, ArH, *J* = 8.4 Hz), 5.78 (s, 1H, CH), 4.09 (s, 2H, NH_2), 2.19-2.17 (m, 4H, CH_2), 1.78-1.74 (m, 2H, CH_2), 1.71-1.67 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 134.5, 132.8, 131.8, 130.0, 128.6, 128.5, 120.4, 114.7, 99.8, 29.1, 25.3, 23.0, 21.9.



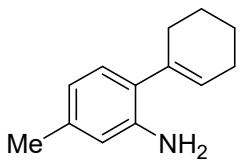
5-(Trifluoromethyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1k)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a colourless oil in 85% yield (409.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H, ArH), 6.62 (d, 1H, ArH, *J* = 8.4 Hz), 5.77-5.74 (m, 1H, CH), 3.98 (s, 2H, NH_2), 2.21-2.17 (m, 2H, CH_2), 2.16-2.13 (m, 2H, CH_2), 1.78-1.72 (m, 2H, CH_2), 1.69-1.63 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 135.4, 129.7, 129.1, 128.0, 126.4, 125.9, 125.8, 125.8, 125.8, 124.7, 124.7, 124.6, 124.6, 123.7, 121.0, 120.1, 119.8, 119.5, 119.2, 114.5, 29.2, 25.4, 23.0, 22.0. ^{19}F NMR (376MHz, $CDCl_3$): δ -60.9. HRMS (ESI) m/z: calcd for $C_{13}H_{15}F_3N^+$ ($[M+H]^+$), 242.1151; found, 242.1154.



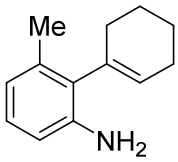
3-Methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1l)[37]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 82% yield (307.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, 1H, ArH, *J* = 7.2 Hz), 6.85 (d, 1H, ArH, *J* = 7.2 Hz), 6.65 (dt, 1H, ArH, J_1 = 2.0 Hz, J_2 = 7.2 Hz), 5.74-5.72 (m, 1H, CH), 3.68 (s, 2H, NH_2), 2.22 (s, 2H, CH_2), 2.17-2.14 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.77-1.73 (m, 2H, CH_2), 1.70-1.66 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 136.9, 130.3, 128.8, 126.9, 126.5, 122.4, 117.9, 29.7, 25.6, 23.4, 22.3, 18.0.



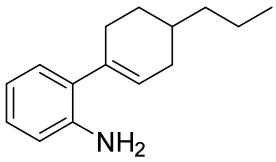
4-Methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1m)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as an orange oil in 71% yield (265.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, 1H, ArH, J = 7.6 Hz), 6.53 (d, 1H, ArH, J = 7.6 Hz), 6.47 (s, 1H, ArH), 5.72-5.70 (m, 1H, CH), 3.65 (s, 2H, NH_2), 2.22 (s, 3H, CH_3), 2.21-2.19 (m, 2H, CH_2), 2.15-2.13 (m, 2H, CH_2), 1.77-1.71 (m, 2H, CH_2), 1.68-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 137.3, 136.4, 128.6, 127.8, 126.8, 126.6, 119.2, 119.2, 116.3, 116.2, 29.7, 25.6, 23.4, 22.3, 21.3. HRMS (ESI) m/z: calcd for $C_{13}H_{18}N^+$ ([M+H]$^+$), 188.1434; found, 188.1435.



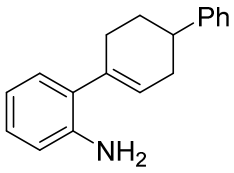
6-Methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1n)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 77% yield (287.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (t, 1H, ArH, J = 7.6 Hz), 6.61 (d, 1H, ArH, J = 7.6 Hz), 6.56 (d, 1H, ArH, J = 8.0 Hz), 5.63-5.61 (m, 1H, CH), 3.60 (br s, 2H, NH_2), 2.18 (s, 3H, CH_3), 2.20-2.03 (m, 4H, CH_2), 1.79-1.76 (m, 2H, CH_2), 1.73-1.69 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 135.2, 134.6, 129.2, 126.3, 126.0, 118.9, 111.5, 27.2, 24.5, 22.1, 21.2, 18.4. HRMS (ESI) m/z: calcd for $C_{13}H_{18}N^+$ ([M+H]$^+$), 188.1434; found, 188.1436.



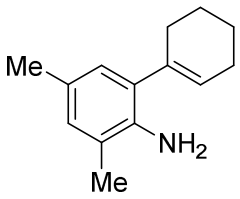
4'-Propyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1o)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a colourless oil in 78% yield (335.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (dt, 1H, ArH, J_1 = 1.2 Hz, J_2 = 8.0 Hz), 6.96 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 7.6 Hz), 6.70 (dt, 1H, ArH, J_1 = 1.2 Hz, J_2 = 7.6 Hz), 6.65 (dd, 1H, ArH, J_1 = 0.4 Hz, J_2 = 8.0 Hz), 5.72-5.71 (m, 1H, CH), 3.71 (s, 2H, NH_2), 2.29-2.24 (m, 3H, CH_2), 1.88-1.75 (m, 2H, CH_2), 1.67-1.57 (m, 1H, CH), 1.43-1.27 (m, 5H, CH_2), 0.93 (t, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 136.4, 130.3, 128.7, 127.5, 126.5, 126.4, 118.3, 115.4, 38.9, 33.0, 32.3, 29.6, 20.2, 14.6, 14.5. HRMS (ESI) m/z: calcd for $C_{15}H_{22}N^+$ ([M+H]$^+$), 216.1747; found, 216.1744.



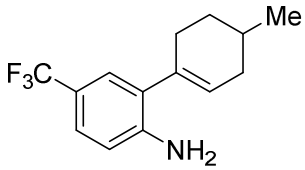
2',3',4',5'-Tetrahydro-[1,1':4',1''-terphenyl]-2-amine (1p)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a waxy in 72% yield (358.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 4H, ArH), 7.23-7.18 (m, 1H, ArH), 7.07-7.00 (m, 2H, ArH), 6.74 (dt, 1H, ArH, J_1 = 1.2 Hz, J_2 = 7.6 Hz), 6.69 (dd, 1H, ArH, J_1 = 0.8 Hz, J_2 = 8.0 Hz), 5.86-5.84 (m, 1H, CH), 3.82 (s, 2H, NH_2), 2.94-2.87 (m, 1H, CH), 2.49-2.43 (m, 2H, CH_2), 2.38-2.28 (m, 2H, CH_2), 2.09-2.02 (m, 1H, CH), 1.97-1.87 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 143.1, 136.5, 129.9, 128.7, 128.5, 127.7, 127.0, 126.4, 126.2, 118.5, 115.6, 39.8, 33.7, 30.4, 30.1. HRMS (ESI) m/z: calcd for $C_{18}H_{20}N^+$ ($[M+H]^+$), 250.1590; found, 250.1588.



3,5-Dimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1q)

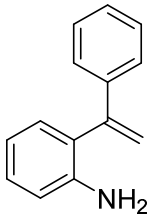
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a yellow oil in 92% yield (370.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (s, 1H, ArH), 6.68 (s, 1H, ArH), 5.72-5.70 (m, 1H, CH), 3.54 (s, 2H, NH_2), 2.23-2.21 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.16-2.14 (m, 2H, CH_2), 2.11 (s, 3H, CH_3), 1.78-1.72 (m, 2H, CH_2), 1.68-1.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 137.1, 130.5, 129.6, 127.0, 126.9, 126.7, 122.5, 29.7, 25.6, 23.4, 22.4, 20.5, 18.0. HRMS (ESI) m/z: calcd for $C_{14}H_{20}N^+$ ($[M+H]^+$), 202.1590; found, 202.1589.



4'-Methyl-5-(trifluoromethyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-amine (1r)

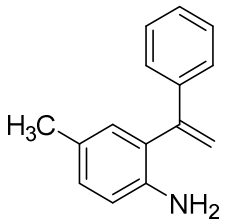
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 10/1) as a waxy in 57% yield (291.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 1H, ArH, J = 8.4 Hz), 7.21 (s, 1H, ArH), 6.68 (d, 1H, ArH, J = 8.0 Hz), 5.76-5.74 (m, 1H, CH), 4.06 (s, 2H,

NH_2), 2.35-2.21 (m, 3H, CH), 1.86-1.72 (m, 3H, CH), 1.43-1.33 (m, 1H, CH), 1.02 (d, 3H, CH_3, J = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 135.0, 129.5, 127.5, 125.8 (q, J_{C-F} = 3.8 Hz), 124.9 (q, J_{C-F} = 269.0 Hz), 124.6 (q, J_{C-F} = 3.7 Hz), 119.9 (q, J_{C-F} = 32.3 Hz), 114.5, 33.9, 31.2, 29.2, 28.0, 21.7. ^{19}F NMR (376MHz, $CDCl_3$) δ -61.0 (s, 3F, CF_3).



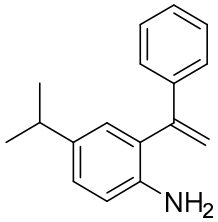
2-(1-Phenylvinyl)aniline (3a)[32]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a white solid in 60% yield (1.17 g). Mp 70-72°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H, ArH), 7.23-7.19 (m, 3H, ArH), 7.09-7.04 (m, 2H, ArH), 6.71 (t, 1H, ArH, J = 7.2 Hz), 6.53 (d, 1H, ArH, J = 8.0 Hz), 5.70 (s, 1H, CH), 5.27 (s, 1H, CH_3), 3.39 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.45, 144.3, 140.0, 131.1, 129.1, 128.9, 128.4, 127.5, 127.0, 118.5, 116.4, 115.9.



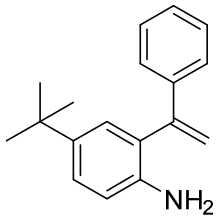
4-Methyl-2-(1-phenylvinyl)aniline (3b)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a yellow oil in 62% yield (1.29 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 5H, ArH), 6.94-6.91 (m, 2H, ArH), 6.54 (d, 1H, ArH, J = 8.0 Hz), 5.74 (s, 1H, CH), 5.30 (s, 1H, CH), 3.35 (s, 2H, NH_2), 2.22 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 141.6, 139.9, 131.4, 129.5, 128.7, 128.2, 127.6, 126.8, 116.1, 115.9, 20.6.



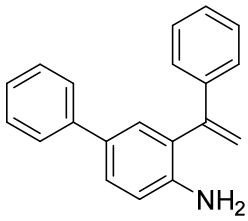
4-Isopropyl-2-(1-phenylvinyl)aniline (3c)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a brown oil in 78% yield (1.85 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.28 (m, 5H, ArH), 7.03 (d, 1H, ArH, *J* = 8.0 Hz), 6.98 (s, 1H, ArH), 6.67 (d, 1H, ArH, *J* = 8.0 Hz), 5.79 (s, 1H, CH), 5.35 (s, 1H, CH) 3.52 (s, 2H, NH_2), 2.88-2.77 (m, 1H, CH), 1.22 (d, 6H, CH_3, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 141.2, 139.8, 139.3, 128.8, 128.5, 128.0, 127.6, 126.7, 126.6, 116.0, 100.0, 33.2, 24.2.



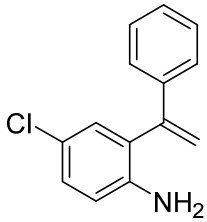
4-(Tert-butyl)-2-(1-phenylvinyl)aniline (3d)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a red oil in 91% yield (2.28 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, 2H, ArH, J_1 = 2.0 Hz, J_2 = 8.4 Hz), 7.31-7.25 (m, 3H, ArH), 7.17 (dd, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.4 Hz), 7.12 (d, 1H, ArH, *J* = 2.4 Hz), 6.61 (d, 1H, ArH, *J* = 8.4 Hz), 5.78 (s, 1H, CH), 5.33 (s, 1H, CH), 3.39 (s, 2H, NH_2), 1.29 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 141.4, 141.3, 139.8, 128.6, 128.1, 127.7, 127.1, 126.8, 125.7, 116.0, 115.5, 34.0, 31.7.



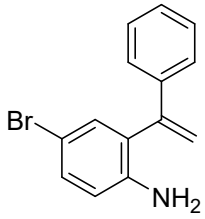
3-(1-Phenylvinyl)-[1,1'-biphenyl]-4-amine (3e)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a yellow oil in 81% yield (2.19 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 2H, ArH, *J* = 7.2 Hz), 7.43-7.22 (m, 10H, ArH), 6.74 (d, 1H, ArH, *J* = 8.4 Hz), 5.82 (s, 1H, CH), 5.40 (s, 1H, CH), 3.28 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.5, 141.0, 139.5, 131.4, 129.5, 128.7 (2), 128.3, 127.7, 127.4, 126.7, 126.4 (2), 116.4, 116.1.



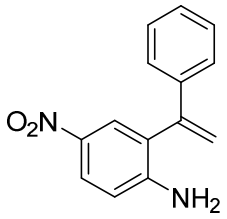
4-Chloro-2-(1-phenylvinyl)aniline (3f)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a brown oil in 57% yield (1.31 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 5H, ArH), 7.10-7.09 (m, 2H, ArH), 6.60 (d, 1H, ArH, J = 9.2 Hz), 5.79 (s, 1H, CH), 5.34 (s, 1H, CH), 3.53 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 142.5, 138.9, 130.3, 128.7 (2), 128.6, 128.4, 126.6, 122.9, 116.8 (2).



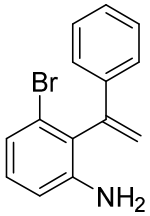
4-Bromo-2-(1-phenylvinyl)aniline(3g)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 120/1) as a yellow oil in 87% yield (2.38 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.37-7.29 (m, 5H, ArH), 7.21 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.03 (d, J = 2.4 Hz, 1H, ArH), 6.67 (d, J = 8.6 Hz, 1H, ArH), 5.84 (s, 1H, CH), 5.30 (s, 1H, CH), 4.74 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO): δ 145.3, 144.9, 138.8, 131.8, 130.8, 128.5, 128.0, 127.6, 126.3, 116.7, 116.7, 106.5.



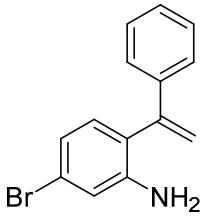
4-Nitro-2-(1-phenylvinyl)aniline (3h)[32]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15:1) as yellow solid in 81% yield (1.95 g). Mp 85-87°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8,05 (m, 2H, ArH), 7.34 (s, 5H, ArH), 6.65 (d, 1H, ArH, J = 9.6 Hz), 5.88 (s, 1H, CH), 5.43 (s, 1H, CH), 4.35 (br s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 145.1, 138.8, 138.1, 128.9, 128.8, 127.3, 126.5, 125.8, 125.5, 117.9, 114.0.



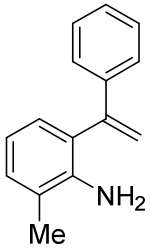
3-Bromo-2-(1-phenylvinyl)aniline (3i)[38]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 50/1) as a yellow oil in 26% yield (0.71 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H, ArH), 7.30-7.25 (m, 3H, ArH), 7.01-6.99 (m, 1H, ArH), 6.94 (t, 1H, ArH, *J* = 7.8 Hz), 6.62-6.60 (m, 1H, ArH), 6.04 (s, 1H, CH), 5.30 (s, 1H, CH), 3.74 (br s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 145.0, 137.9, 129.5, 128.7, 128.3, 127.6, 126.1, 124.6, 122.2, 117.5, 114.1.



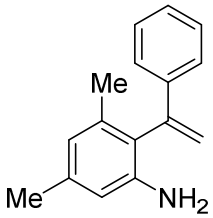
5-Bromo-2-(1-phenylvinyl)aniline (3j)[38]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 50/1) as a yellow oil in 31% yield (0.85 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.19 (m, 5H, ArH), 6.85 (d, 1H, ArH, *J* = 8.0 Hz), 6.79-6.77 (m, 1H, ArH), 6.71 (d, 1H, ArH, *J* = 2.0 Hz), 5.68 (s, 1H, CH), 5.23 (s, 1H, CH), 3.50 (br s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 145.4, 139.1, 132.2, 128.7, 128.4, 126.7, 126.1, 122.4, 121.2, 118.1, 116.6.



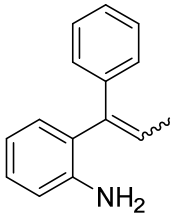
2-Methyl-6-(1-phenylvinyl)aniline (3k)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a red oil in 63% yield (1.32 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.28 (m, 5H, ArH), 7.06 (d, 1H, ArH, *J* = 7.2 Hz), 6.99 (d, 1H, ArH, *J* = 7.6 Hz), 6.72 (t, 1H, ArH, *J* = 8.0 Hz), 5.80 (s, 1H, CH), 5.34 (s, 1H, CH), 3.49 (s, 2H, NH_2), 2.16 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 142.0, 139.8, 129.9, 128.7, 128.6, 128.1, 127.2, 126.7, 122.5, 117.9, 116.2, 17.8.



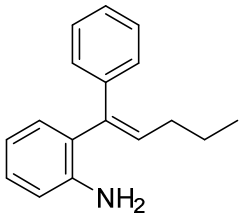
3,5-Dimethyl-2-(1-phenylvinyl)aniline (3l)[33]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a red oily liquid in 81% yield (1.81 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, 2H, ArH, *J* = 7.6 Hz), 7.28-7.22 (m, 3H, ArH), 6.49 (s, 1H, ArH), 6.41 (s, 1H, ArH), 6.00 (s, 1H, CH), 5.23 (s, 1H, CH), 3.53 (s, 2H, NH_2), 2.25 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.0, 139.2, 137.8, 137.1, 128.7, 128.0, 126.0, 124.6, 121.0, 116.3, 113.6, 21.4, 20.1.



2-(1-Phenylprop-1-en-1-yl)aniline (3m)[33]

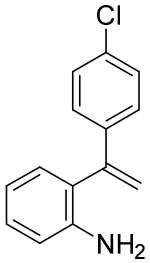
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 30/1) as a red oil in 51% yield (1.07 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.13 (m, 6H, ArH), 6.97 (d, 1H, ArH, *J* = 7.2 Hz), 6.79 (t, 1H, ArH, *J* = 7.2 Hz), 6.74 (d, 1H, ArH, *J* = 8.0 Hz), 6.38-6.33 (m, 1H, ArH), 3.51 (br s, 2H, NH_2), 1.74 (s, 3H, CH_3), 1.68* (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.9, 138.9, 130.9, 128.5, 128.4, 127.1, 126.2, 126.0, 125.1, 118.4, 115.4, 15.6.



(Z)-2-(1-Phenylprop-1-en-1-yl)aniline (3n)[39]

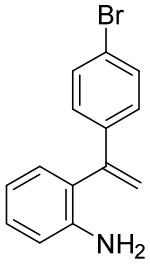
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a waxy in 37% yield (0.88 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.17 (m, 2H, ArH), 7.14-7.10 (m, 2H, ArH), 7.08-7.05 (m, 1H, ArH), 7.02 (t, *J* = 7.6 Hz, 1H, ArH), 6.87 (dd, J_1 = 7.4

Hz, J_2 = 1.4 Hz, 1H, ArH), 6.66 (t, J = 7.2 Hz, 1H, ArH), 6.58 (d, J = 8.0 Hz, 1H, ArH), 6.17 (t, J = 7.4 Hz, 1H, CH), 3.37 (s, 2H, NH_2), 1.91 (q, J = 7.4 Hz, 2H, CH_2), 1.34 (h, J = 7.4 Hz, 2H, CH_2), 0.78 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 140.9, 138.2, 131.8, 131.0, 128.6, 128.4, 127.2, 126.4, 125.4, 118.3, 115.4, 32.0, 23.0, 14.1.



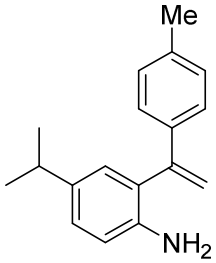
2-(1-(4-Chlorophenyl)vinyl)aniline (3p)[40]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 120/1) as a yellow oil in 66% yield (1.52 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 4H, ArH), 7.17 (t, J = 7.6 Hz, 1H, ArH), 7.08 (d, J = 7.6 Hz, 1H, ArH), 6.79 (t, J = 7.6 Hz, 1H, ArH), 6.71 (d, J = 8.0 Hz, 1H, ArH), 5.78 (s, 1H, CH), 5.36 (s, 1H, CH), 3.58 (br s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 143.6, 138.1, 134.0, 130.8, 129.0, 128.7, 128.0, 126.9, 118.6, 116.6, 115.8.



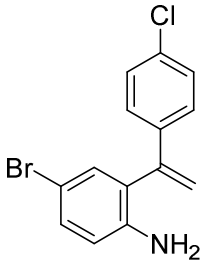
2-(1-(4-bromophenyl)vinyl)aniline (3q)[40]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 120/1) as a yellow oil in 93% yield (2.55 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.52 (d, J_1 = 8.2 Hz, 2H, ArH), 7.26 (d, J = 8.2 Hz, 2H, ArH), 7.08 (t, J = 7.2 Hz, 1H, ArH), 6.92 (d, J = 7.2 Hz, 1H, ArH), 6.73 (d, J = 8.0 Hz, 1H, ArH), 6.61 (t, J = 7.4 Hz, 1H, ArH), 5.85 (s, 1H, CH), 5.30 (s, 1H, CH), 4.55 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO): δ 145.6, 145.3, 138.6, 131.3, 130.0, 128.6, 128.5, 125.0, 121.1, 116.6, 116.2, 114.9.



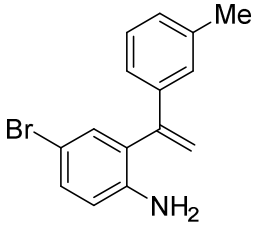
4-Isopropyl-2-(1-(p-tolyl)vinyl)aniline (3r)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as a red oil in 44% yield (1.11 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, 2H, ArH, J = 8.0 Hz), 7.12 (d, 2H, ArH, J = 8.0 Hz), 7.01 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.0 Hz), 6.97 (d, 1H, ArH, J = 2.0 Hz), 6.65 (d, 1H, ArH, J = 8.4 Hz), 5.75 (s, 1H, CH), 5.29 (s, 1H, CH), 3.45 (s, 2H, NH_2), 2.88-2.77 (m, 1H, CH), 2.34 (s, 3H, CH_3), 1.22 (d, 6H, CH_3, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 141.4, 139.1, 137.9, 136.9, 129.3, 128.8, 127.7, 126.6, 126.5, 115.8, 115.1, 33.2, 24.3, 21.2. HRMS (ESI) m/z: calcd for $C_{18}H_{22}N^+$ ([M+H]$^+$), 252.1747; found, 252.1744.



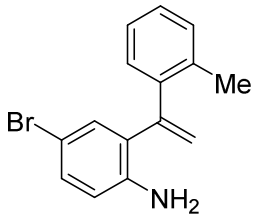
4-Bromo-2-(1-(4-chlorophenyl)vinyl)aniline (3s)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a yellow oil in 39% yield (1.20 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 4H, ArH), 7.25-7.22 (m, 1H, ArH), 7.20-7.19 (m, 1H, ArH), 6.56 (d, J = 8.4 Hz, 1H, ArH), 5.78 (s, 1H, CH), 5.35 (s, 1H, CH), 3.55 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.0, 137.3, 134.3, 133.1, 131.7, 128.9, 128.5, 127.9, 117.4, 117.2, 110.0. HRMS (ESI) m/z: calcd for $C_{14}H_{12}BrClN^+$ ([M+H]$^+$), 307.9836; found, 307.9837.



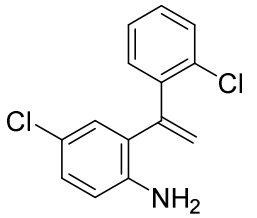
4-Bromo-2-(1-(m-tolyl)vinyl)aniline (3t)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 15/1) as an orange oil in 43% yield (1.23 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 3H, ArH), 7.16-7.11 (m, 3H, ArH), 6.57 (d, 1H, ArH, J = 8.8 Hz), 5.77 (s, 1H, CH), 5.32 (s, 1H, CH), 3.56 (s, 2H, NH_2), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 142.9, 138.9, 138.3, 133.0, 131.4, 129.4, 129.2, 128.6, 127.2, 123.8, 117.2, 116.8, 110.1, 21.5. HRMS (ESI) m/z: calcd for $C_{15}H_{15}BrN^+$ ([M+H]$^+$), 288.0382; found, 288.0381.



4-Bromo-2-(1-(o-tolyl)vinyl)aniline (3u)

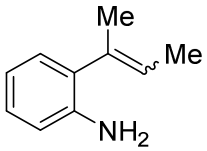
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a reddish brown oil in 63% yield (1.82 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.2 Hz, 1H, ArH), 7.22 (t, J = 7.4 Hz, 2H, ArH), 7.17-7.13 (m, 3H, ArH), 6.54 (d, J = 8.4 Hz, 1H, ArH), 5.60 (s, 1H, CH), 5.46 (s, 1H, CH), 3.69 (br s, 2H, NH_2), 2.12 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 142.7, 140.9, 135.8, 132.3, 131.1, 130.8, 129.6, 129.2, 128.1, 126.2, 119.7, 117.5, 110.1, 20.5. HRMS (ESI) m/z: calcd for $C_{15}H_{15}BrN^+$ ([M+H]$^+$), 288.0382; found, 288.0381.



4-Chloro-2-(1-(2-chlorophenyl)vinyl)aniline (3v)[32]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a yellow oil in 76% yield (2.01 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.45-7.41 (m, 2H, ArH), 7.36-7.32 (m, 2H, ArH), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.78 (d, J = 8.8 Hz, 1H, ArH), 6.75 (d, J = 2.4 Hz, 1H, ArH), 5.70 (s, 1H, CH), 5.57 (s, 1H, CH), 5.01 (s, 2H, NH_2).

^{13}C NMR (100 MHz, DMSO): δ 144.4, 143.8, 140.3, 131.5, 131.1, 129.7, 129.4, 128.2, 127.8, 127.3, 126.3, 120.7, 119.4, 116.8.



2-(But-2-en-2-yl)aniline (3x)[32]

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a red oil in 41% yield (0.60 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (t, 1H, ArH, *J* = 7.6 Hz), 6.96 (d, 1H, ArH, *J* = 7.6 Hz), 6.71 (t, 1H, ArH, *J* = 7.2 Hz), 6.66 (d, 1H, ArH, *J* = 7.6 Hz), 5.57-5.52 (m, 1H, CH), 3.56 (br s, 2H, NH_2), 1.93 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.76* (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 134.4, 131.8, 128.8, 127.5, 124.6, 118.3, 115.4, 17.1, 14.0.

12. Characterization data of compound 15

3-(2,6-di-tert-butyl-4-methylphenoxy)indolin-2-one (15)

The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 20/1) as a yellow solid. Mp 171-172°C. ^{1}H NMR (400MHz, DMSO-d_6): δ 0.90 (s, 9H, CH_3), 1.22 (s, 9H, CH_3), 1.52 (s, 3H, CH_3), 3.65 (s, 1H, CH), 6.37 (d, 1H, ArH, *J* = 2.8 Hz), 6.76 (t, 2H, ArH, *J* = 8.0 Hz), 6.81 (d, 1H, ArH, *J* = 2.8 Hz), 6.92 (d, 1H, ArH, *J* = 7.6 Hz), 7.10 (t, 1H, ArH, *J* = 7.6 Hz), 10.49 (s, 1H, NH). ^{13}C NMR (100MHz, DMSO-d_6): δ 185.1, 176.3, 146.4, 145.2, 145.1, 142.6, 142.0, 128.1, 126.2, 125.3, 120.1, 108.7, 52.1, 42.6, 34.4, 34.0, 29.1, 28.8, 22.2. HRMS (ESI) m/z: calcd for $C_{23}H_{29}NNaO_2^+$ ($[M+Na]^+$), 374.2091; found, 374.2088.

13. References

[1] C. Suzuki, K. Hirano, T. Satoh, M. Miura. *Org. Lett*. **2015**, *17*, 1597.

[2] Z. Qu, X. Ji, S. Tang, G.-J. Deng, H. Huang. *Org. Lett.* **2022**, *24*, 7173.

[3] M. E. Budén, V. A. Vaillard, S. E. Martin, R. A. Rossi. *J. Org. Chem.* **2009**, *74*, 4490.

[4] L. Yang, Y. Zhang, X. Zou, H. Lu, G. Li. *Green Chem.* **2018**, *20*, 1362.

[5] T. Chatterjee, G. Roh, M. A. Shoaib, C.-H. Suhl, J. S. Kim, C.-G. Cho, E. J. Cho. *Org. Lett.* **2017**, *19*, 1906.

[6] S. Parisien-Collette, C. Cruché, X. Abel-Snape, S. K. Collins. *Green Chem.* **2017**, *19*, 4798.

[7] T. Watanabe, S. Oishi, N. Fujii, H. Ohno. *J. Org. Chem.* **2009**, *74*, 4720.

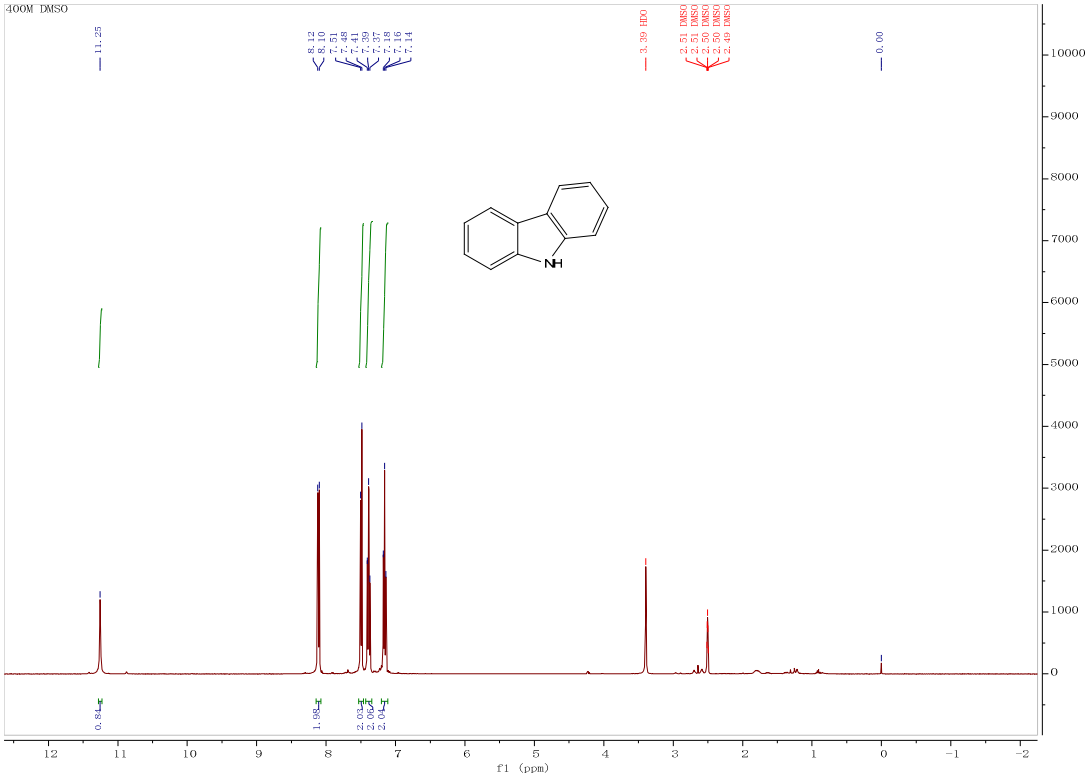
[8] Y. Mohr, M. Renom-Carrasco, C. Demarcy, E. A. Quadrelli, C. Camp, F. M. Wisser, E. Clot, C. Thieuleux, J. Canivet. *ACS Catal.* **2020**, *10*, 2713.

[9] M. Wu, R. Yan. *Synlett* **2017**, *28*, 729.

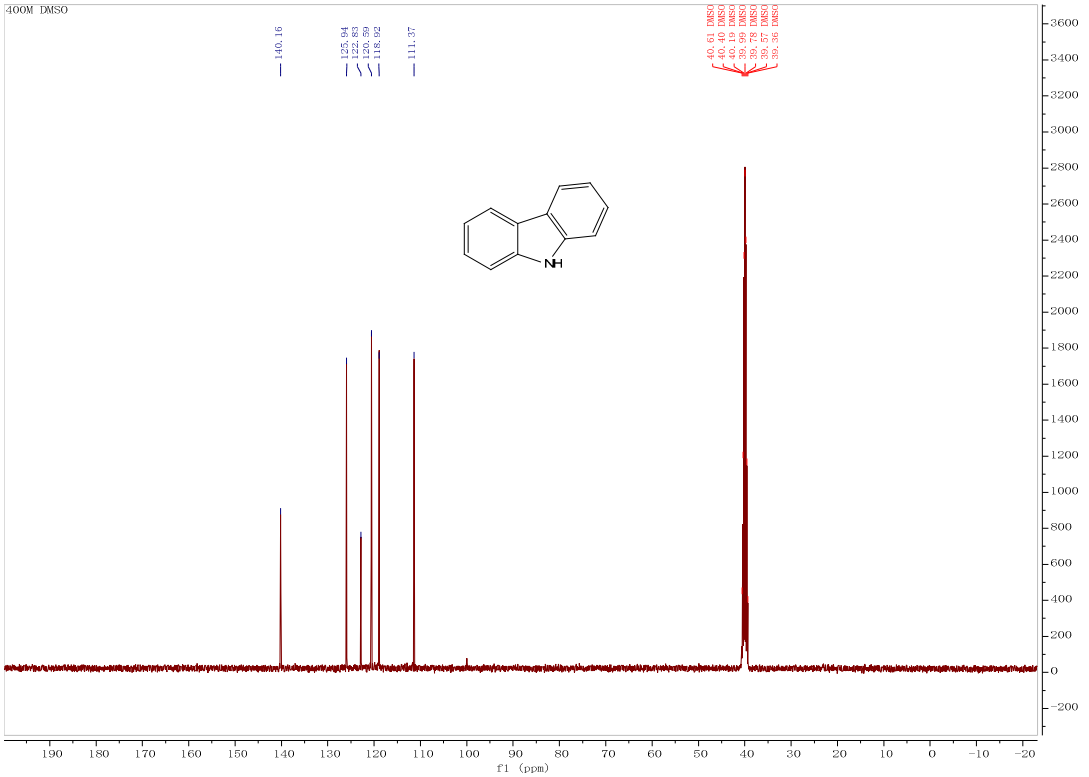
[10] R. Yang, J.-T. Yu, S. Sun, Q. Zheng, J. Cheng. *Tetrahedron Lett.* **2017**, *58*, 445.
[11] N. Batail, A. Bendjeriou, T. Lomberget, R. Barret, V. Dufaud, L. Djakovitch. *Adv. Syn. Catal.* **2009**, *351*, 2055.
[12] S. Perato, B. Large, Q. Lu, A. Gaucher, D. Prim. *ChemCatChem* **2017**, *9*, 389.
[13] M. Jin, N. Perl, A. Kohlmann, N. Yin, J. T. Lowe, J. Y. Ahn, M. J. Mulvihill, E. S. Koltun, A. L. Gill. *PCT Int. Appl.* **2020**, WO 2020132597.
[14] S. M. A. Rahman, B. C. G. Söderberg. *Tetrahedron* **2021**, *94*, 132331.
[15] M. Wang, Y. Li, Q.-A. Wu, S. Luo, Y. Li. *Synthesis* **2019**, *51*, 3085.
[16] Y. Chen, S. Guo, K. Li, J. Qu, H. Yuan, Q. Hua, B. Chen. *Adv. Syn. Catal.* **2013**, *355*, 711.
[17] Y.-P. Zhang, X.-L. Feng, Y.-S. Yang, B.-X. Cao. *Tetrahedron Lett.* **2016**, *57*, 2298.
[18] J. Rheinheimer, R. Rath, S. Kulkarni, C. Rosenbaum, C. Wiebe, L. Brahm, I. Siepe, E. Haden, F. Roehl, S. Khanna, S. Khanna, H. Schiffer, D. Kremzow-Graw, M. Poonoth. *PCT Int. Appl.* **2019**, WO 2019057660 A1 20190328.
[19] Y. Kim, D. Kim, S. Chang. *Chem. Commun.* **2021**, *57*, 12309.
[20] Y. Li, T. Yan, K. Junge, M. Beller. *Angew. Chem. Int. Ed.* **2014**, *53*, 10476.
[21] M. J. Moure, R. SanMartin, E. Dominguez. *Angew. Chem. Int. Ed*. **2012**, *51*, 3220.
[22] Y. Yang, C. Wang. *Chem. Eur. J*. **2019**, *25*, 8245.
[23] P. Liang, H. Zhao, T. Zhou, K. Zeng, W. Jiao, Y. Pan, Y. Liu, D. Fang, X. Ma, H. Shao. *Adv. Synth. Catal*. **2021**, *363*, 3532.
[24] Y. Oikawa, O. Yonemitsu. *J. Org. Chem*. **1977**, *42*, 1213.
[25] R.-J. Tang, T. Milcent, B. Crousse. *RSC Adv.* **2018**, *8*, 10314.
[26] Y.-S. Zhu, B.-B. Yuan, J.-M. Guo, S.-J. Jin, H.-H. Dong, Q.-L. Wang, Z.-W. Bu. *J. Org. Chem*. **2017**, *82*, 5669.
[27] S. Pan, N. Ryu, T. Shibata. *J. Am. Chem. Soc.* **2012**, *134*, 17474.
[28] R. Beaud, R. Guillot, C. Kouklovsky, G. Vincent. *Angew. Chem. Int. Ed*. **2012**, *51*, 12546.
[29] K.-X. Wu, Y.-Z. Xu, L. Cheng, R.-S. Wu, P.-Z. Liu, D.-Z. Xu. *Green Chem.* **2021**, *23*, 8448.
[30] H. Fan, P. Pan, Y. Zhang, W. Wang. *Org. Lett*. **2018**, *20*, 7929.
[31] I. T. Alt, C. Guttroff, B. Plietker. *Angew. Chem. Int. Ed*. **2017**, *56*, 10582.
[32] A. Boelke, L. D. Caspers, B. J. Nachtsheim. *Org. Lett*. **2017**, *19*, 5344.
[33] J. Ni, Y. Jiang, Z. An, R. Yan. *Org. Lett*. **2018**, *20*, 1534.
[34] J. S. Yadav, B. V. S. Reddy, S. Sengupta, S. K. Biswas. *Synthesis* **2009**, *41*, 1301.
[35] Q. Nguyen, K. Sun, T. G. Driver. *J. Am. Chem. Soc.* **2012**, *134*, 7262.
[36] C. R. Illig, C. L. Manthey, S. K. Meegalla, M. J. Wall, J. Chen, K. J. Wilson, R. L. DesJarlais, S. K. Ballentine, C. Schubert, C. S. Crysler, Y. Chen, C. J. Molloy, M. A. Chaikin, R. R. Donatelli, E. Yurkow, Z. Zhou, M. R. Player, B. E. Tomczuk. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 6363.
[37] B. Liu, K. K. Moffett, R. W. Joseph, B. D. Dorsey. *Tetrahedron Lett.* **2005**, *46*, 1779.
[38] J. Yuan, J.-T. Yu, Y. Jiang, J. Cheng. *Org. Biomol. Chem.* **2017**, *15*, 1334.
[39] H.-M. Zhang, Z.-H. Gao, L. Yi, S. Ye. *Chem. Asian J.* **2016**, *11*, 2671.
[40] K. Sun, Y. Zhang, M. Tian, Z. Wang, D. Zhao, S. Wang, S. Tang, Z. Zhang. *Chem. Commun.* **2022**, *58,* 9658.

14. Spectroscopic data for carbazoles 2

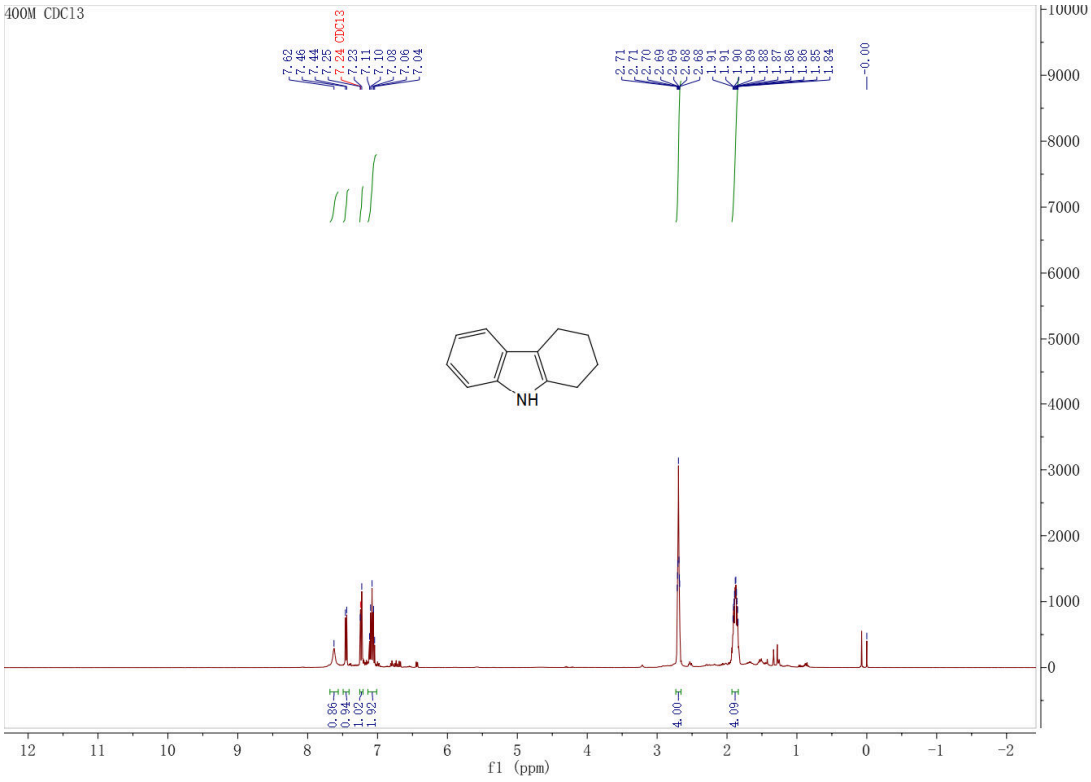
^{1}H NMR spectrum of Compound 2a (DMSO-d_6, 400 MHz)



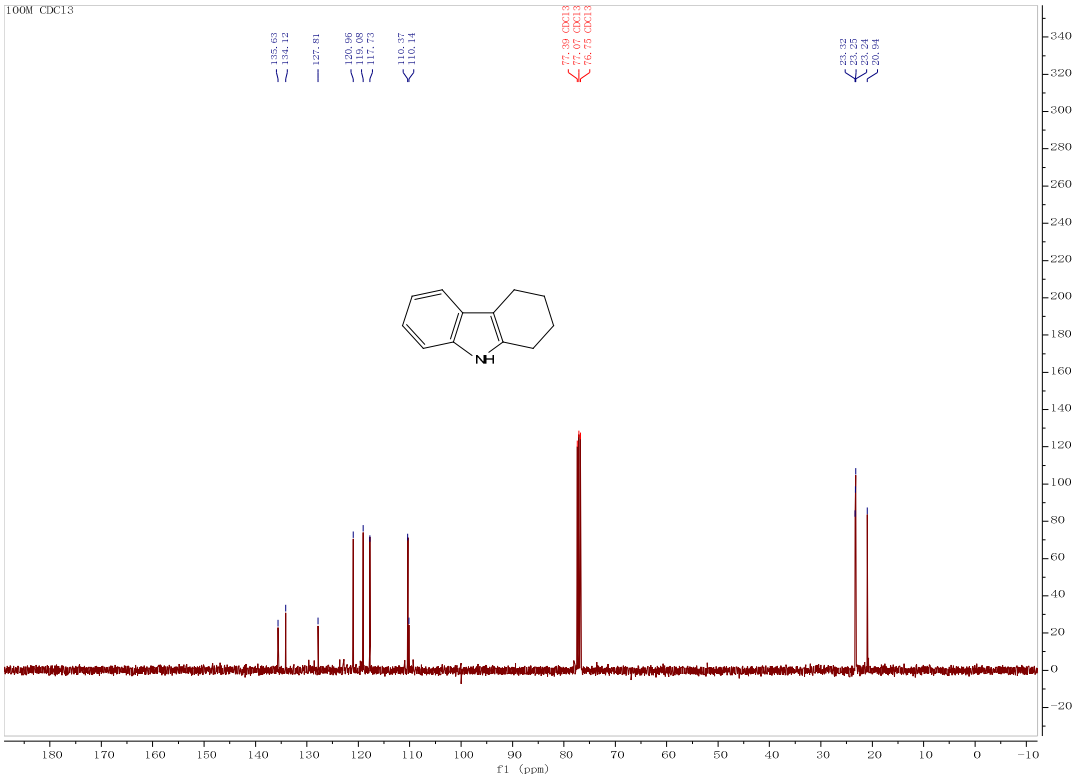
^{13}C NMR spectrum of Compound 2a (DMSO-d_6, 100 MHz)



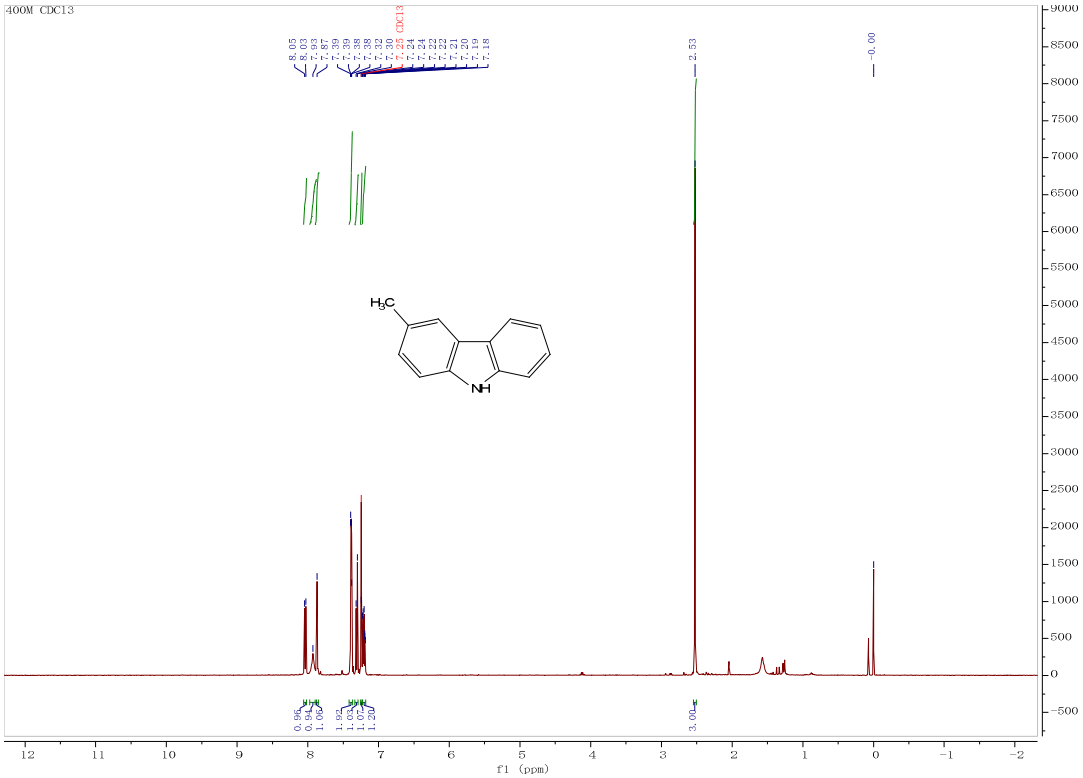
^{1}H NMR spectrum of Compound 2a′ ($CDCl_3$, 400 MHz)



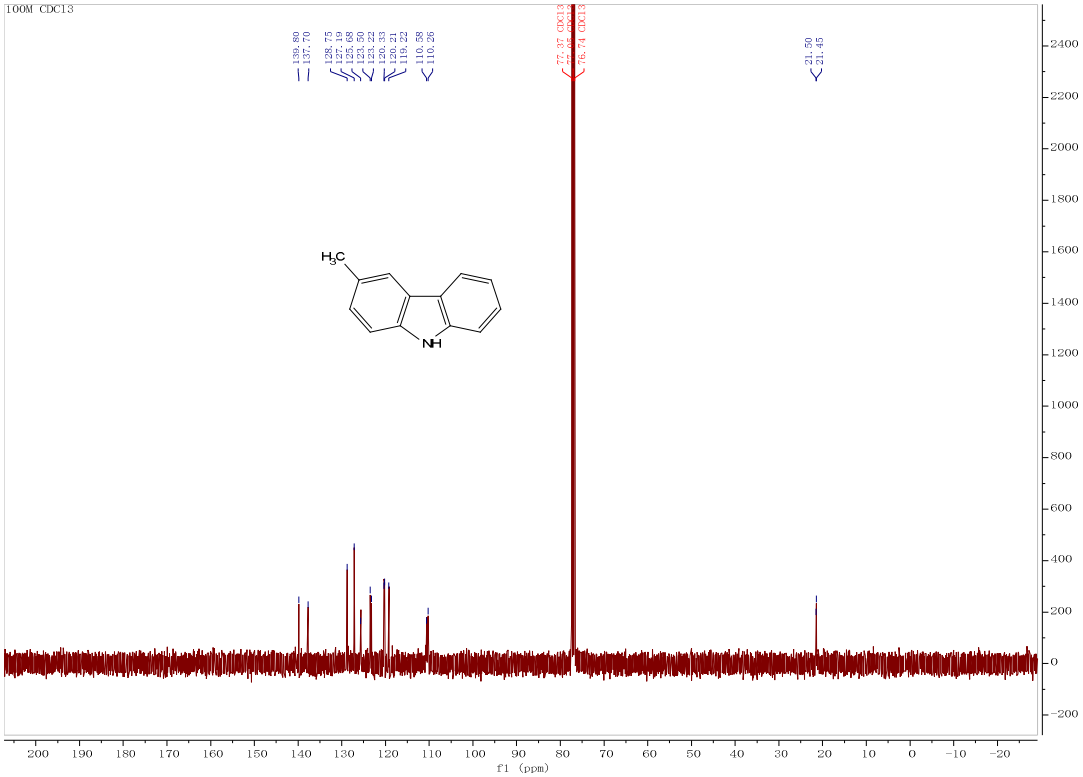
^{13}C NMR spectrum of Compound 2a′ ($CDCl_3$, 100 MHz)



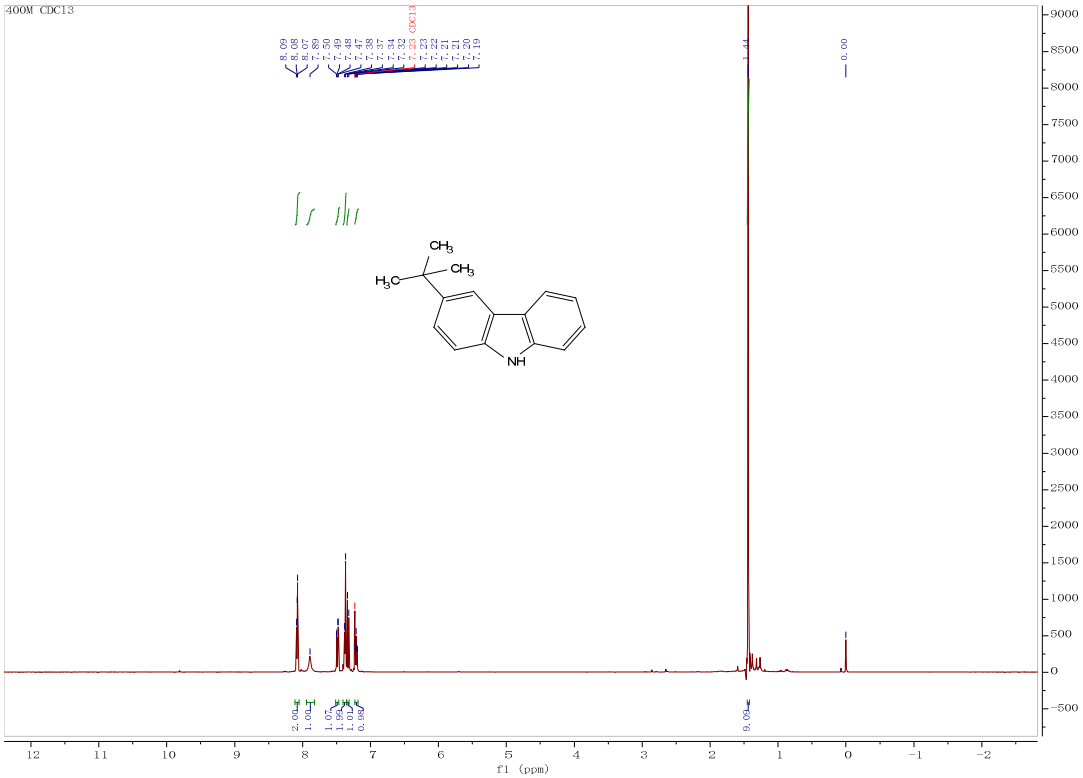
^{1}H NMR spectrum of Compound 2b ($CDCl_3$, 400 MHz)



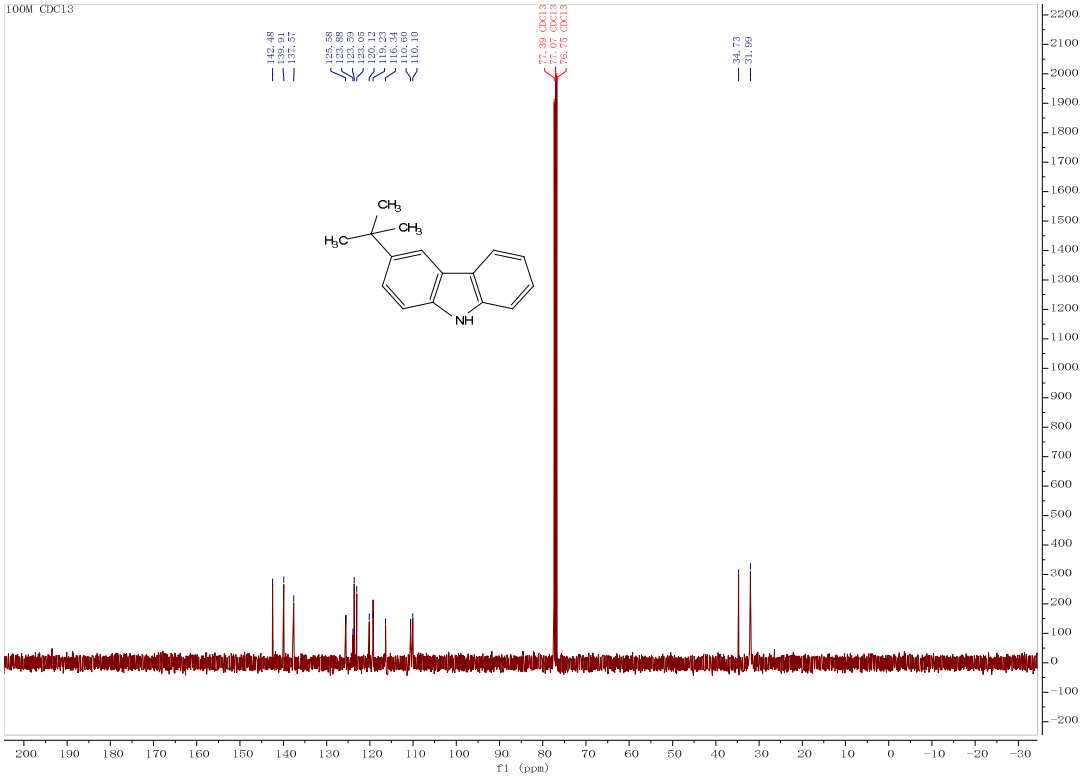
^{13}C NMR spectrum of Compound 2b ($CDCl_3$, 100 MHz)



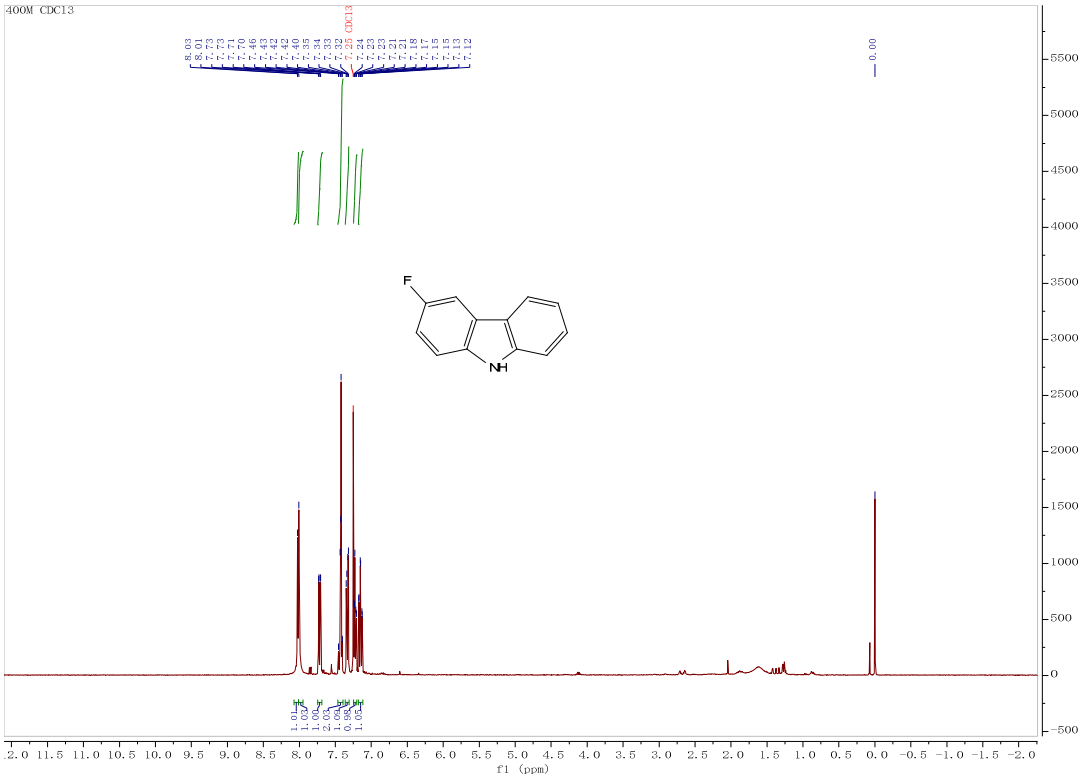
^{1}H NMR spectrum of Compound 2c ($CDCl_3$, 400 MHz)



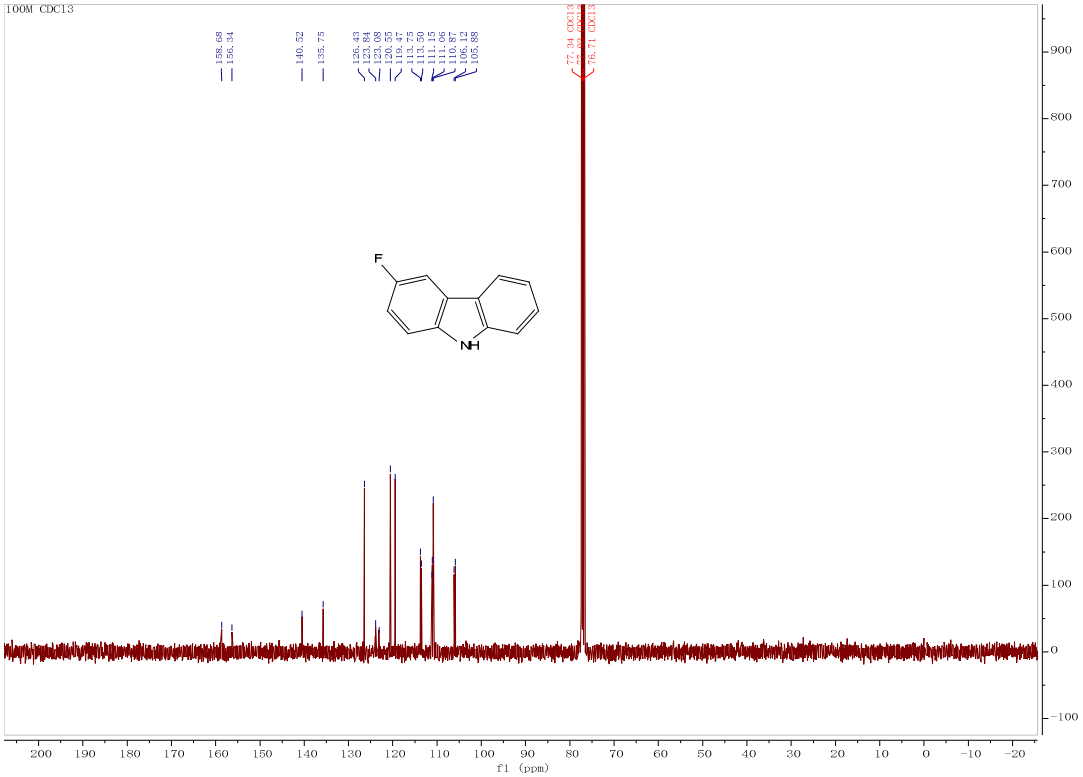
^{13}C NMR spectrum of Compound 2c ($CDCl_3$, 100 MHz)



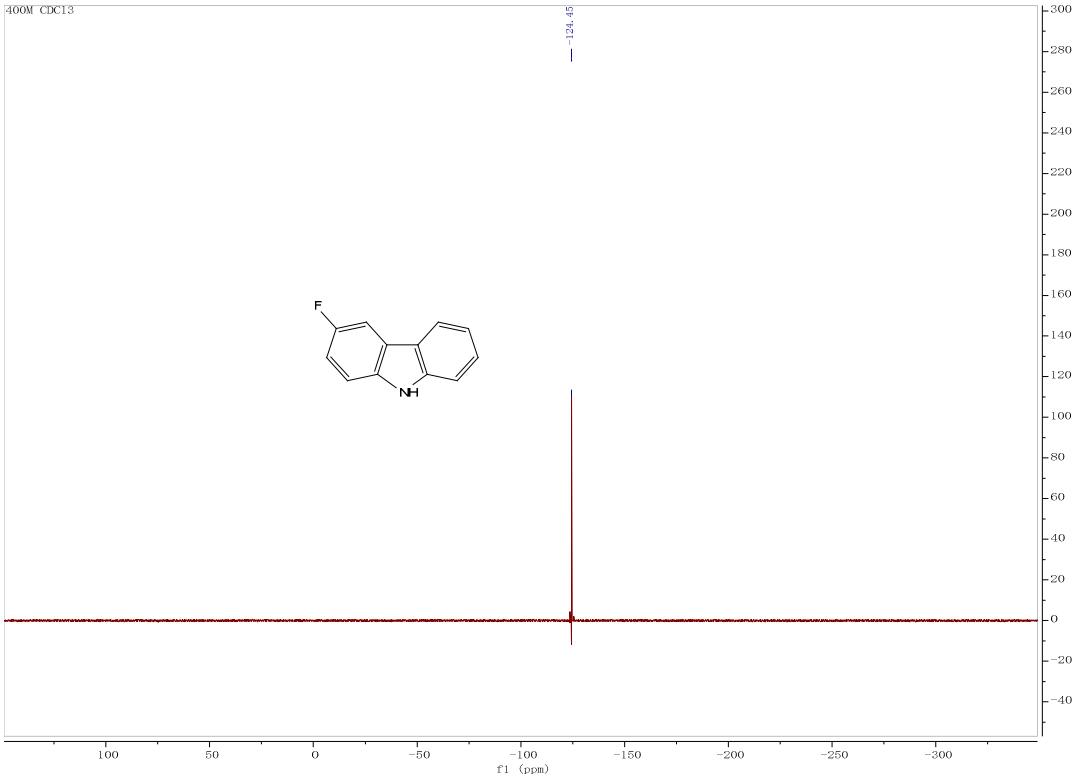
^{1}H NMR spectrum of Compound 2d ($CDCl_3$, 400 MHz)



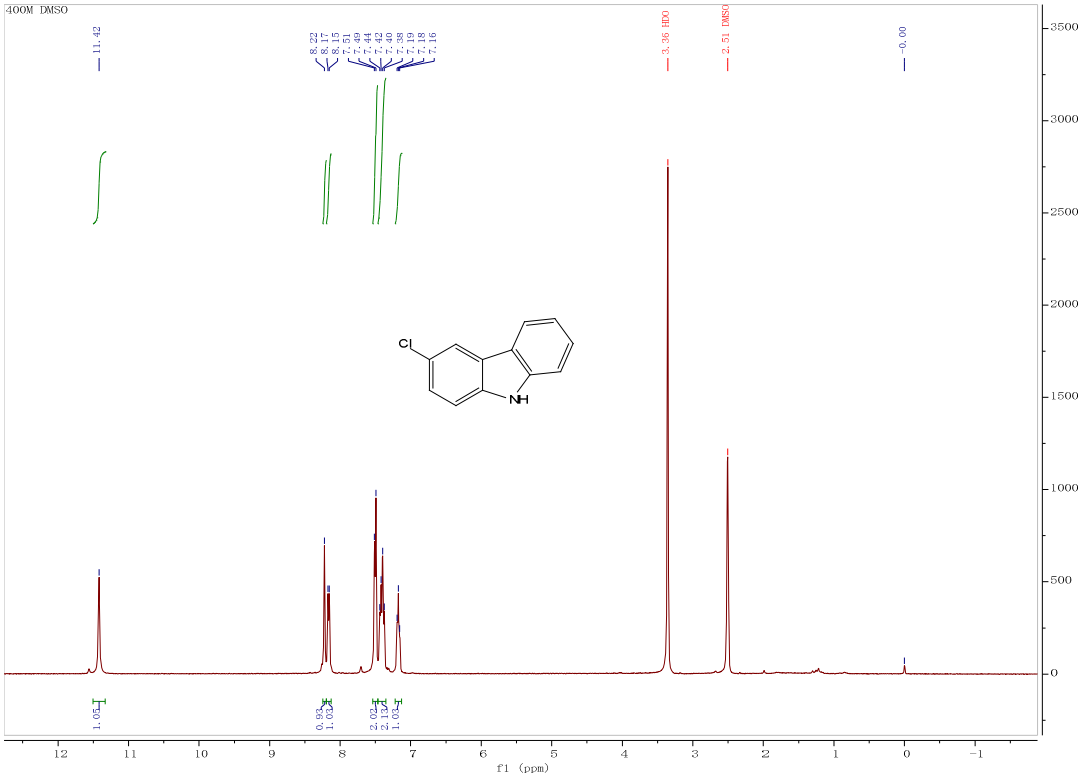
^{13}C NMR spectrum of Compound 2d ($CDCl_3$, 100 MHz)



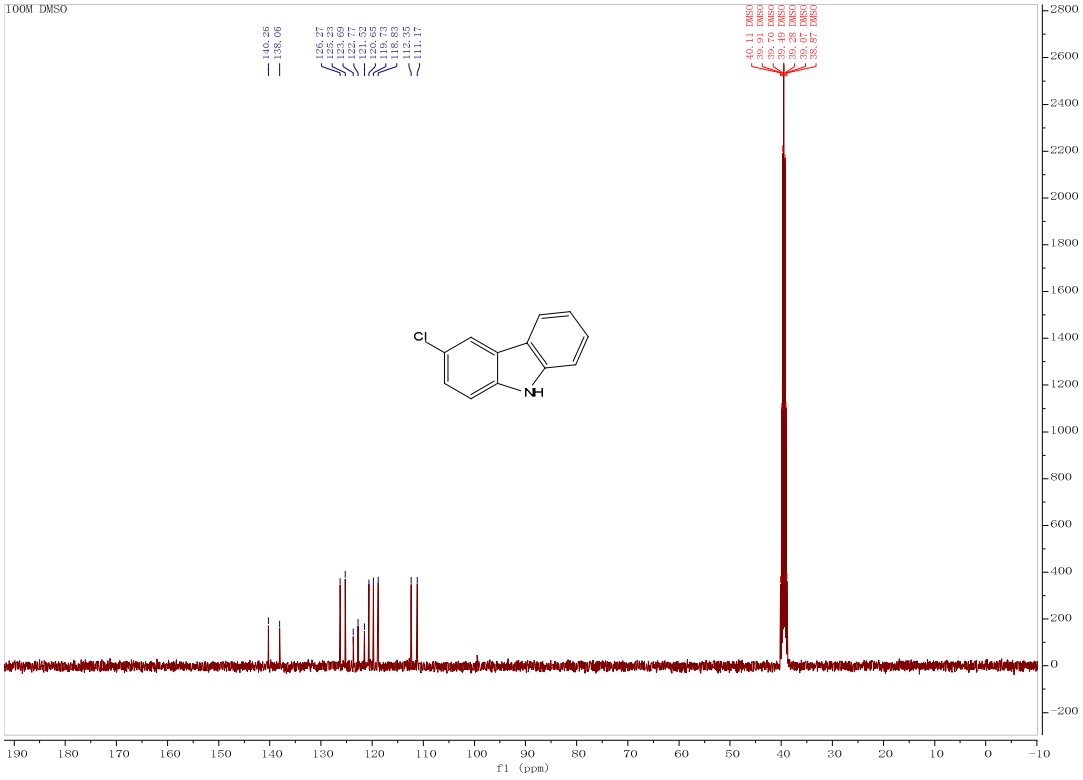
^{19}F NMR spectrum of Compound 2d ($CDCl_3$, 376 MHz)



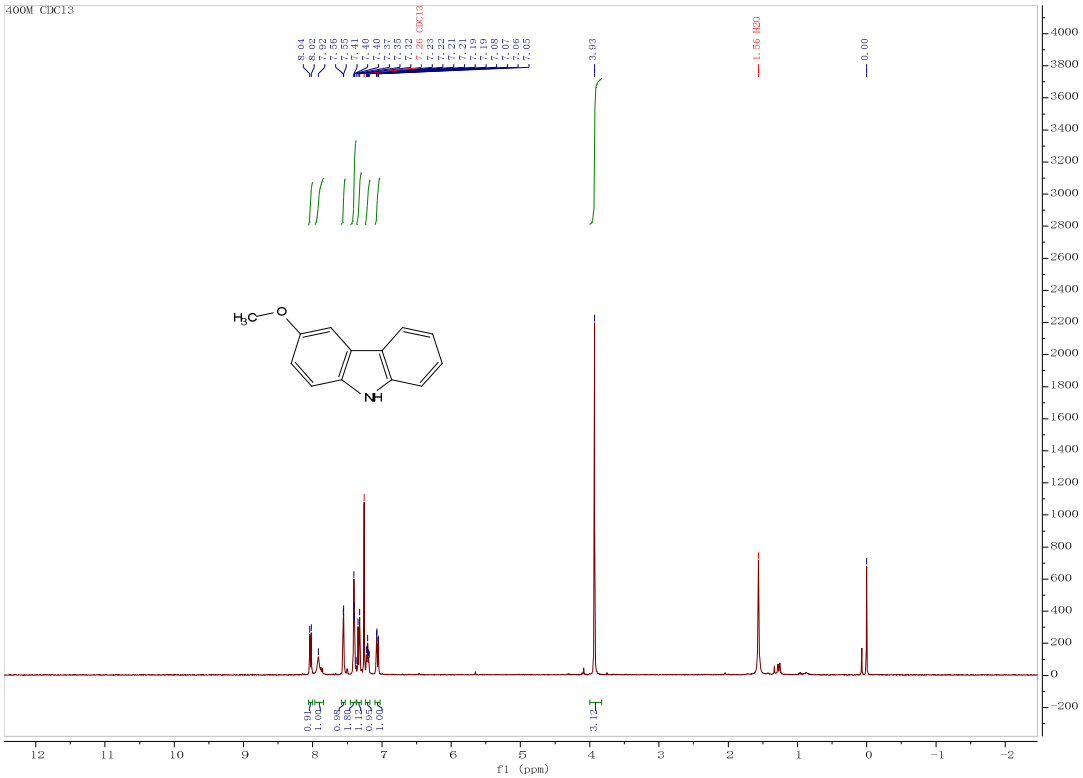
^{1}H NMR spectrum of Compound 2e (DMSO-d_6, 400 MHz)



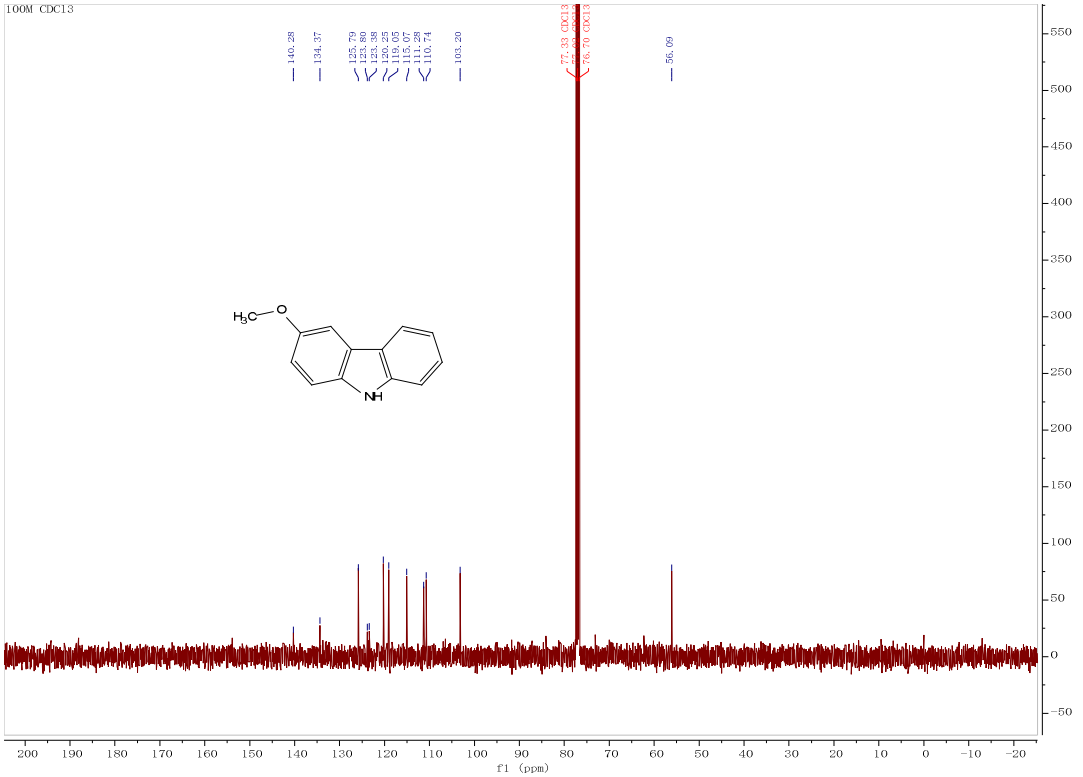
^{13}C NMR spectrum of Compound 2e (DMSO-d_6, 100 MHz)



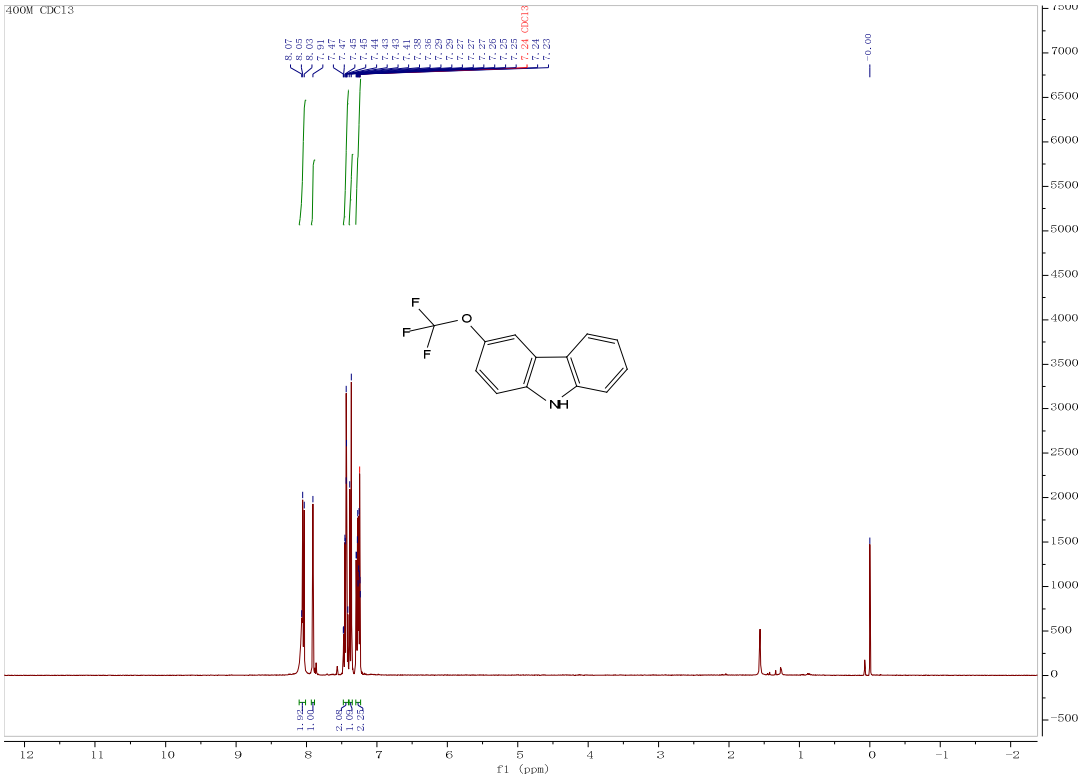
^{1}H NMR spectrum of Compound 2f ($CDCl_3$, 400 MHz)



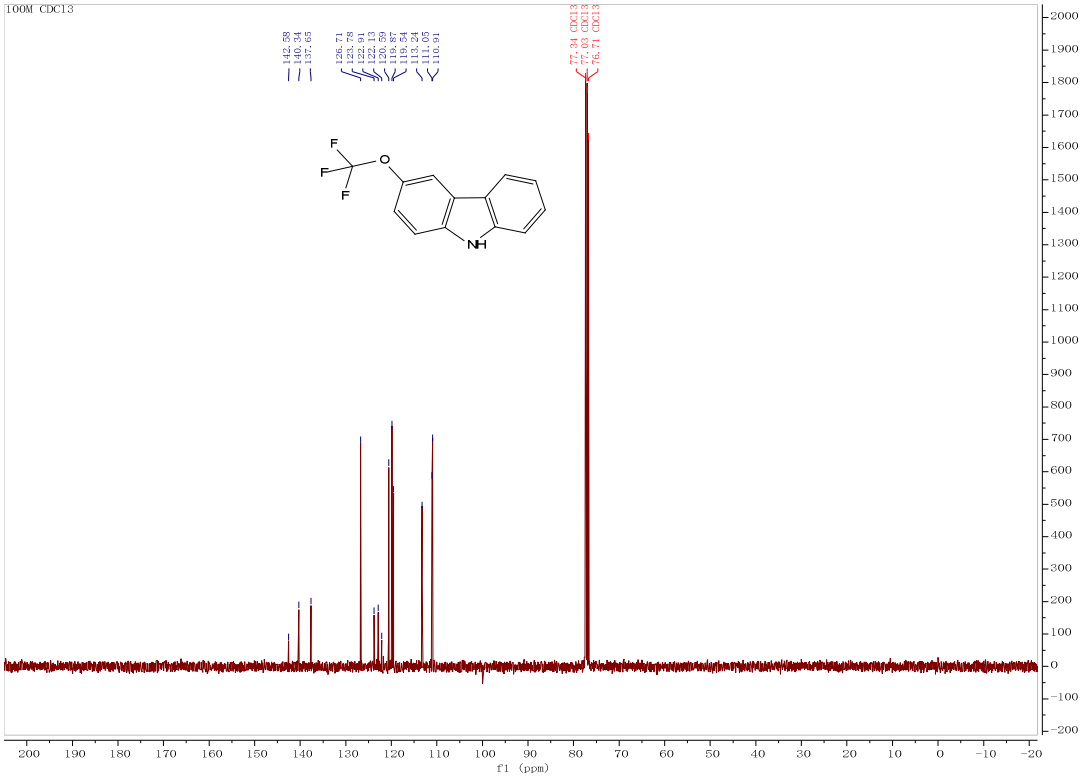
^{13}C NMR spectrum of Compound 2f ($CDCl_3$, 100 MHz)



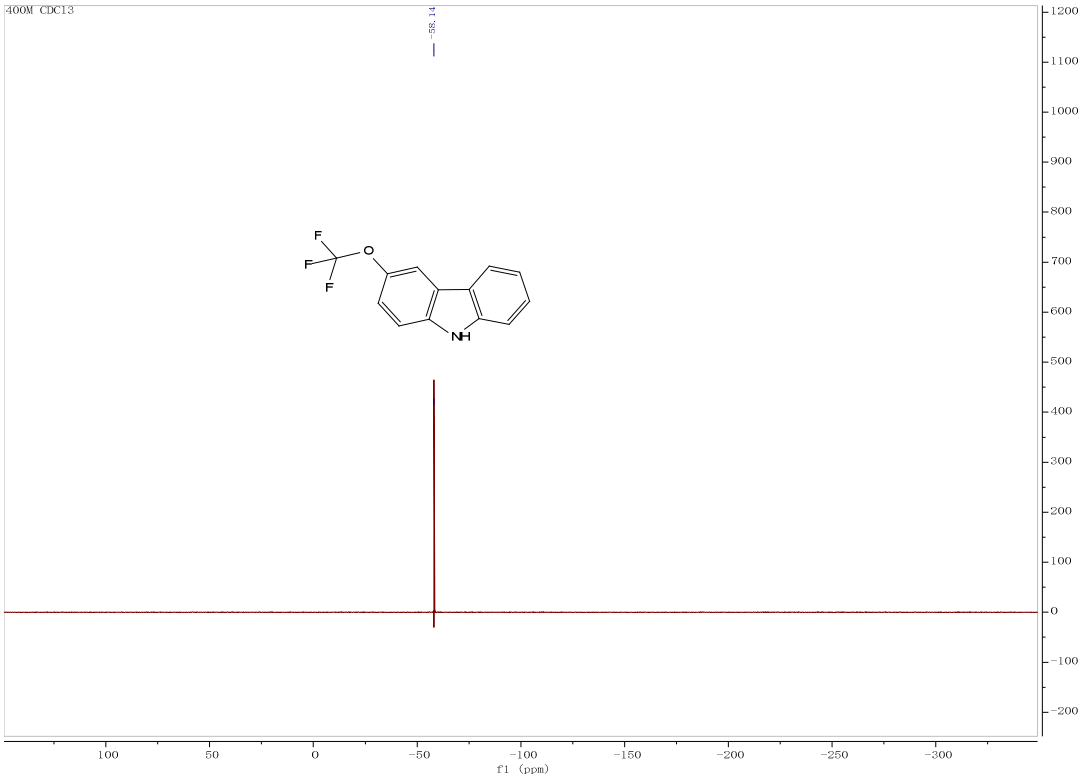
^{1}H NMR spectrum of Compound 2g ($CDCl_3$, 400 MHz)



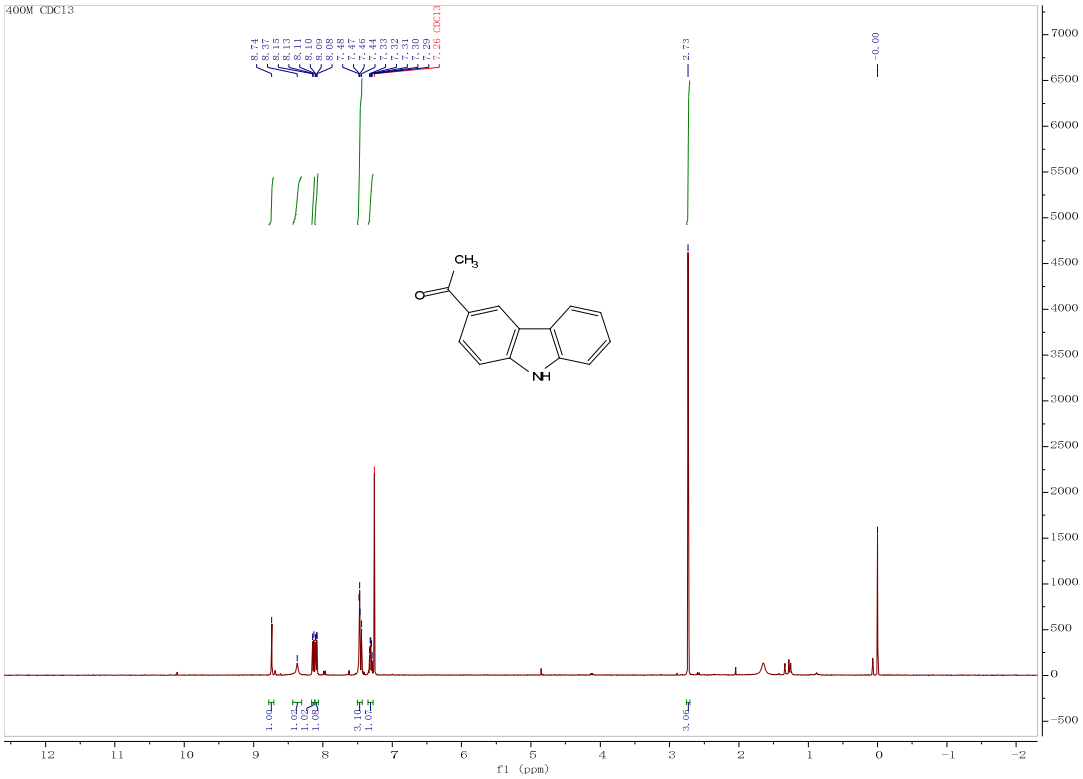
^{13}C NMR spectrum of Compound 2g ($CDCl_3$, 100 MHz)



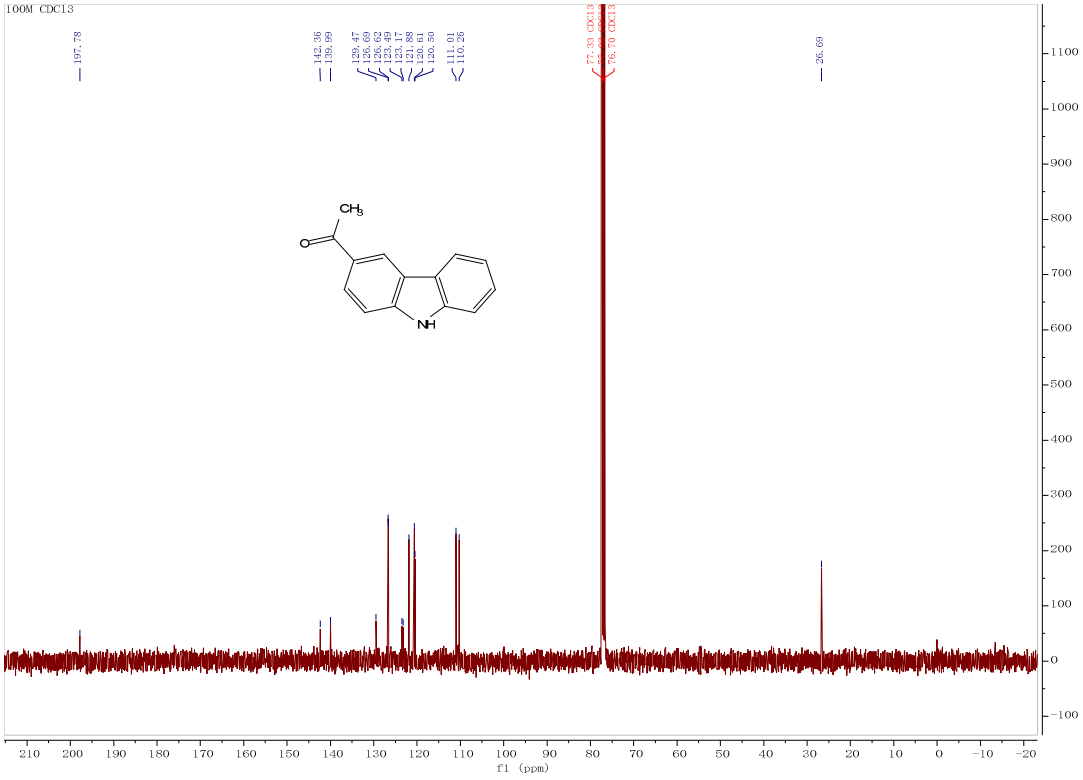
^{19}F NMR spectrum of Compound 2g ($CDCl_3$, 376 MHz)



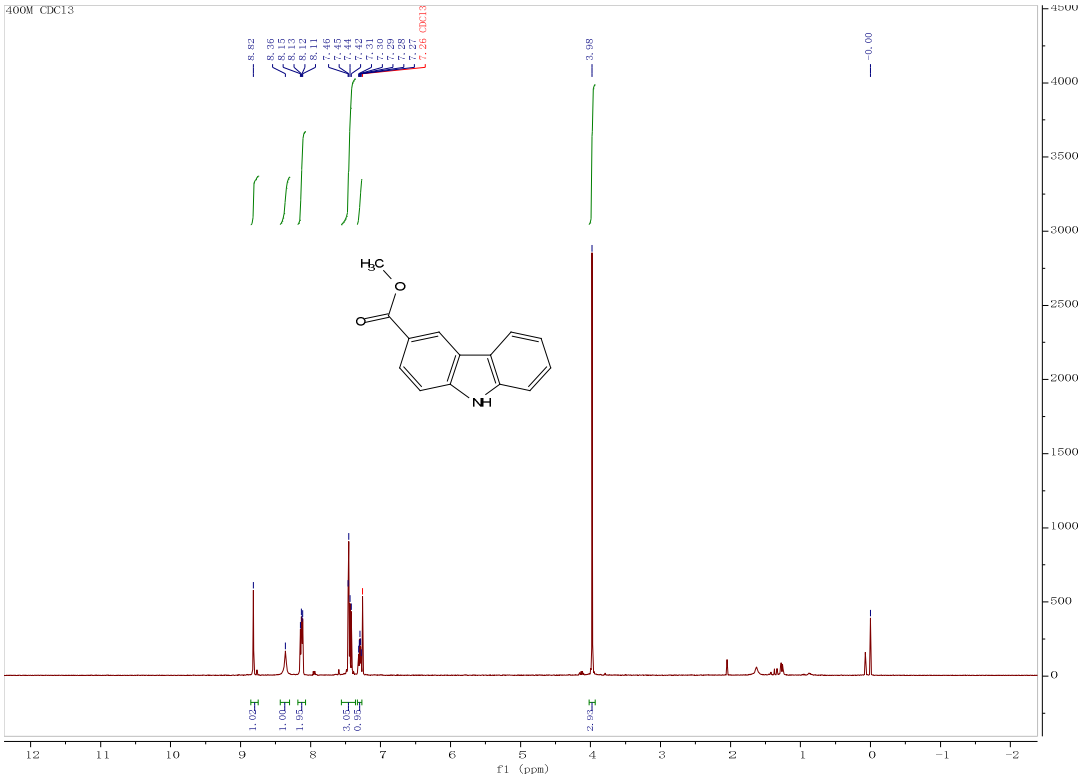
^{1}H NMR spectrum of Compound 2h ($CDCl_3$, 400 MHz)



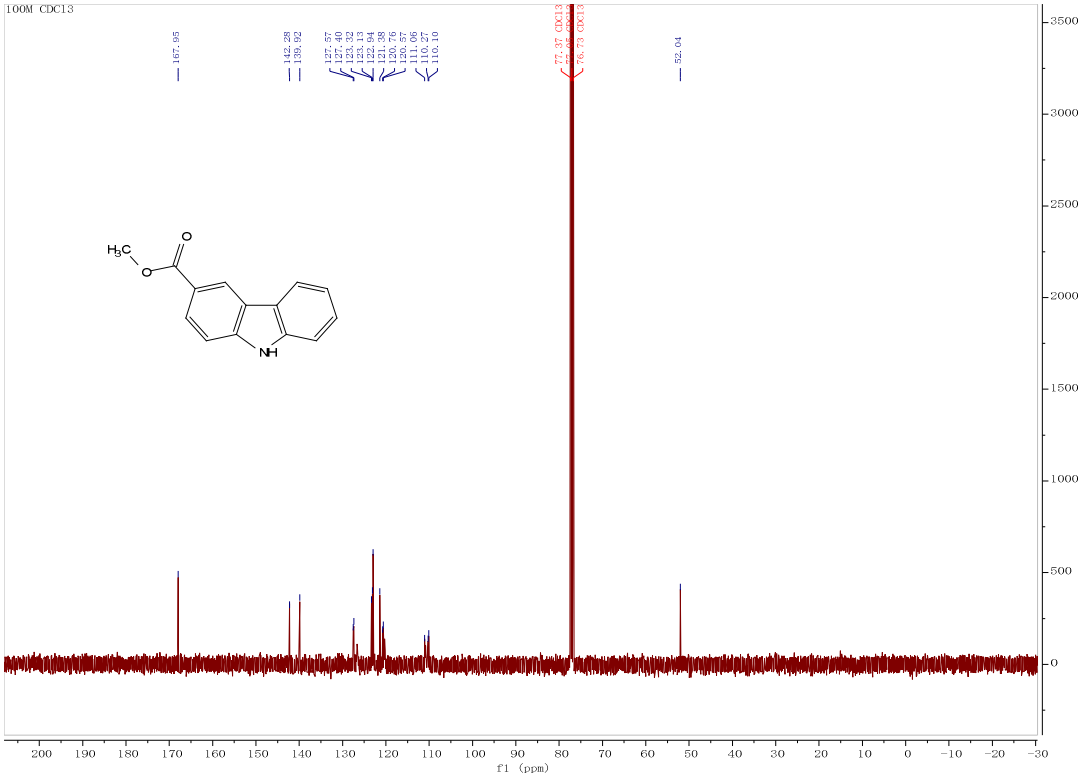
^{13}C NMR spectrum of Compound 2h ($CDCl_3$, 100 MHz)



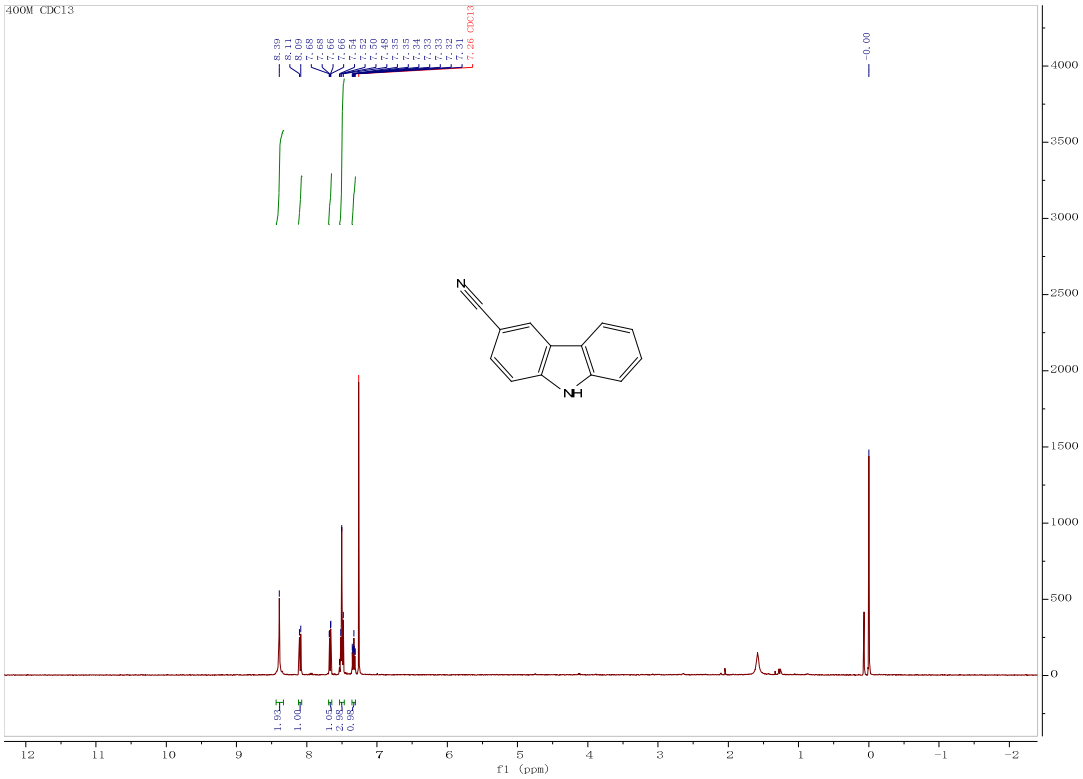
^{1}H NMR spectrum of Compound 2i ($CDCl_3$, 400 MHz)



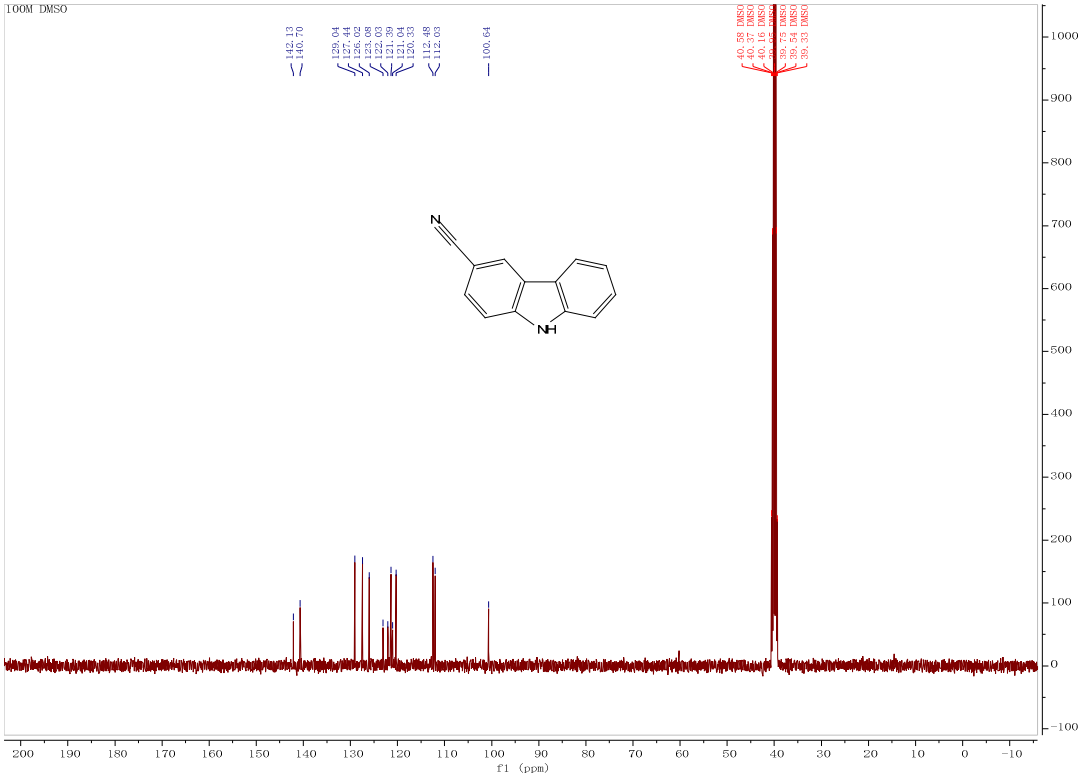
^{13}C NMR spectrum of Compound 2i ($CDCl_3$, 100 MHz)



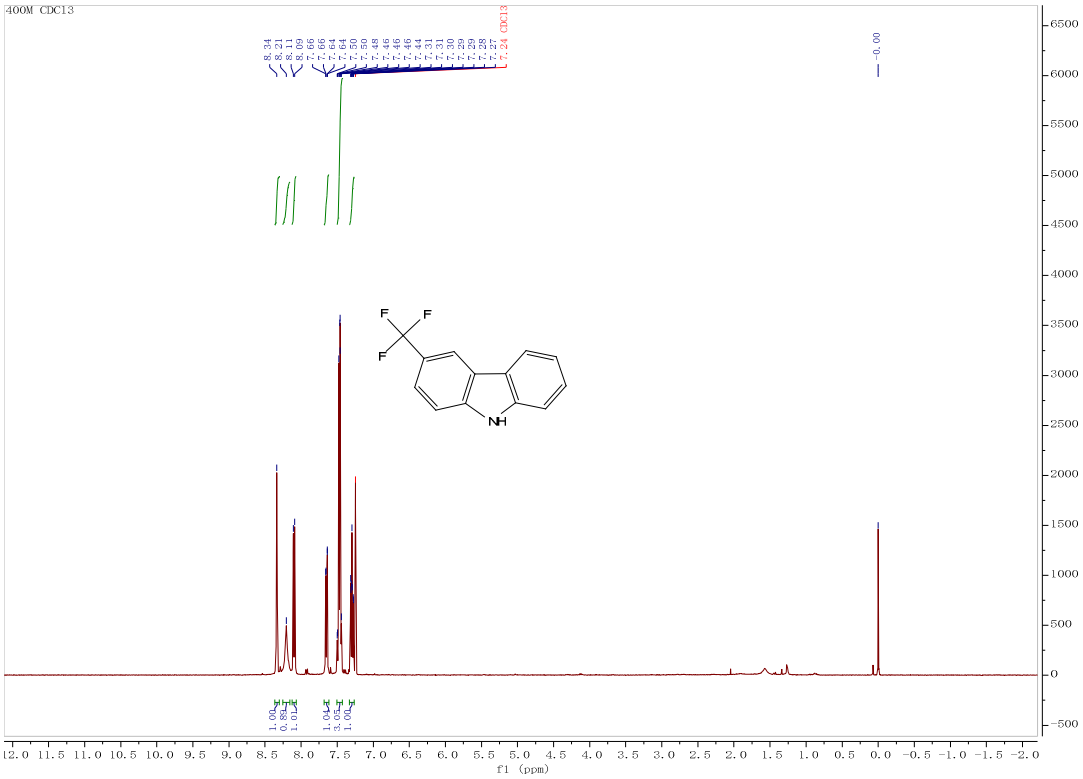
^{1}H NMR spectrum of Compound 2j ($CDCl_3$, 400 MHz)



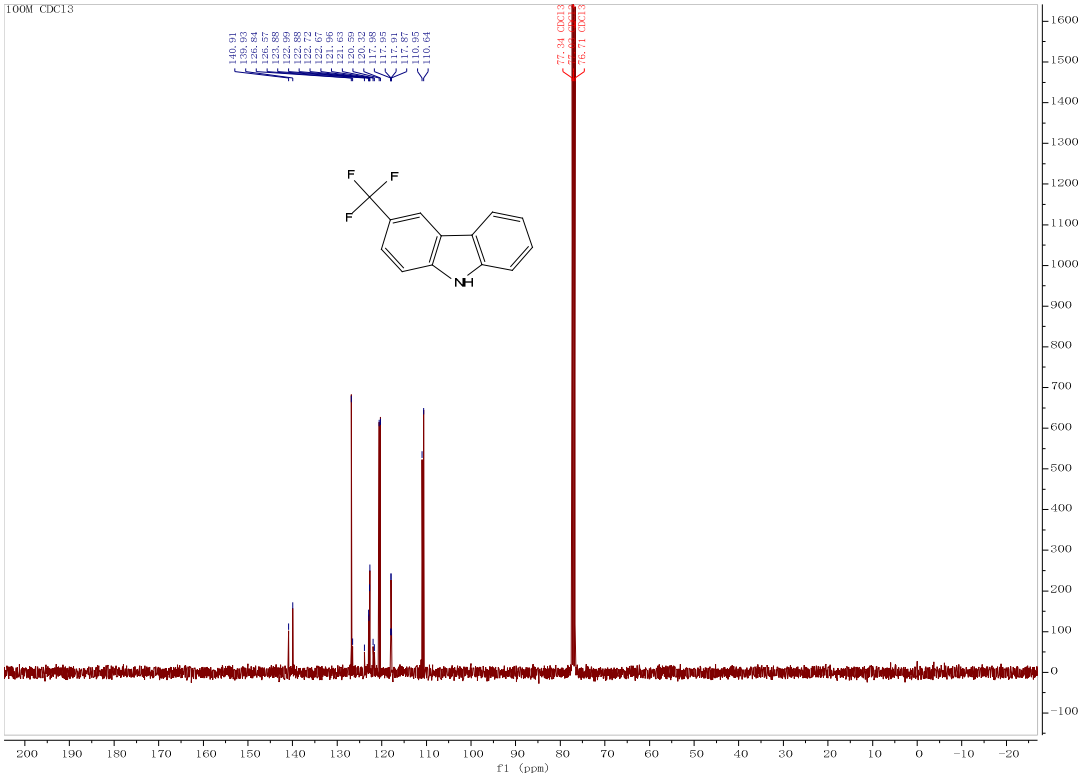
^{13}C NMR spectrum of Compound 2j (DMSO-d_6, 100 MHz)



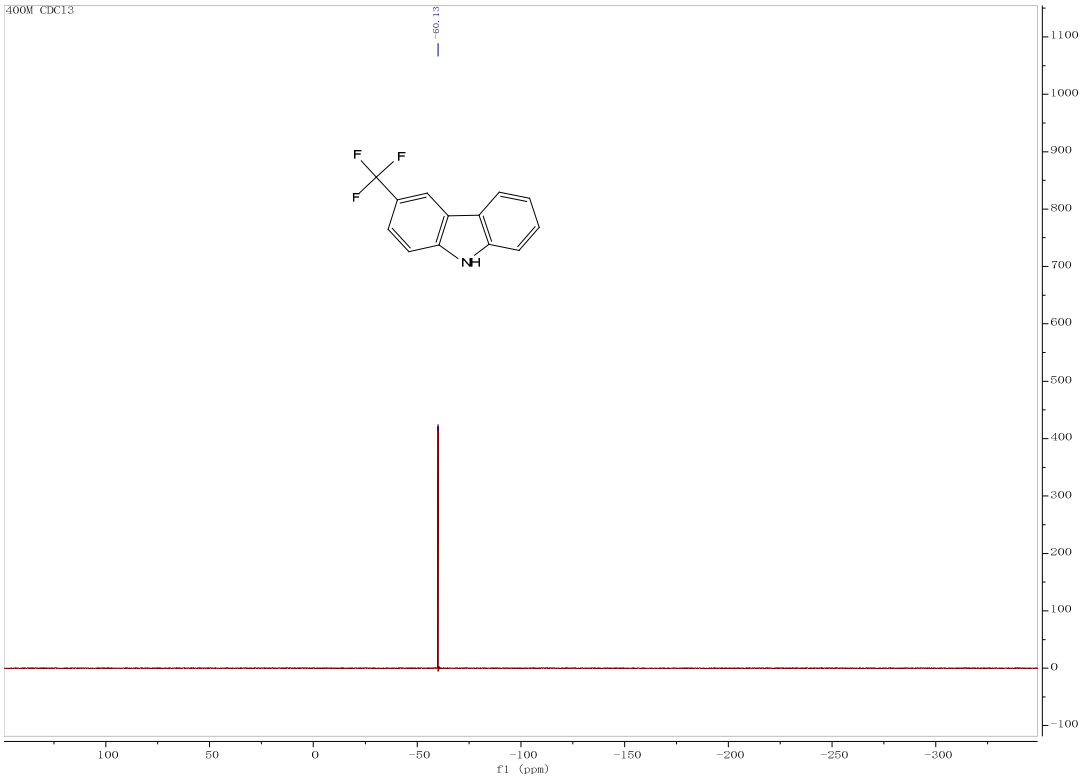
^{1}H NMR spectrum of Compound 2k ($CDCl_3$, 400 MHz)



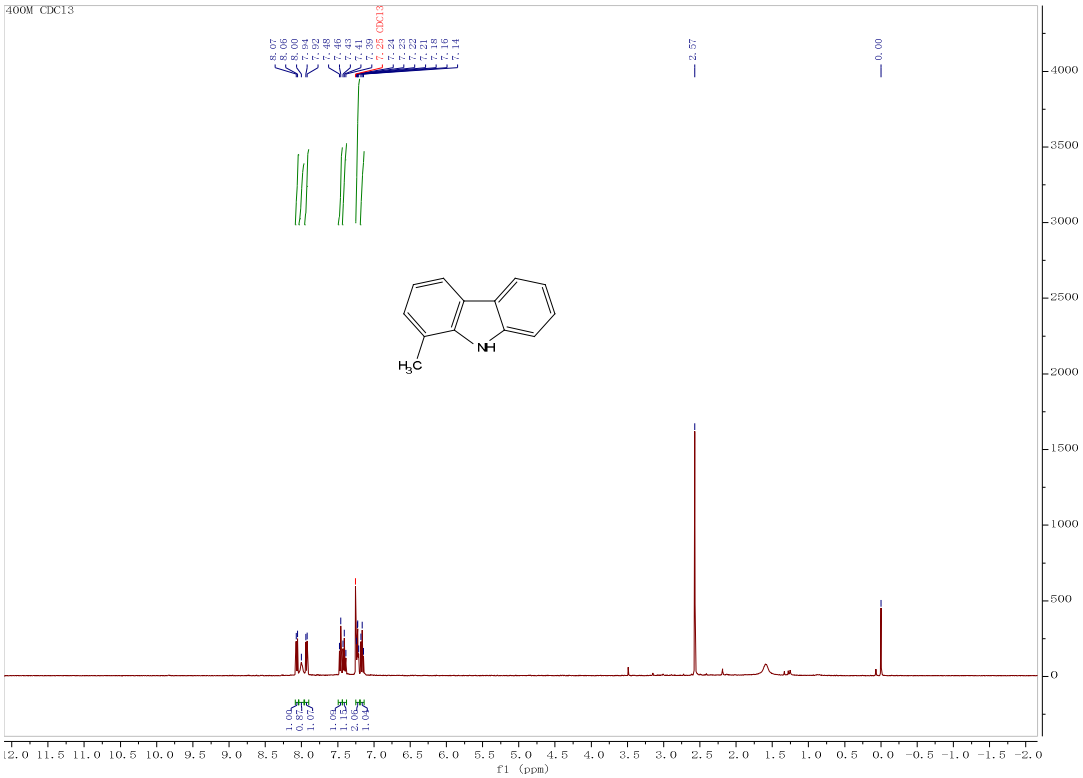
^{13}C NMR spectrum of Compound 2k ($CDCl_3$, 100 MHz)



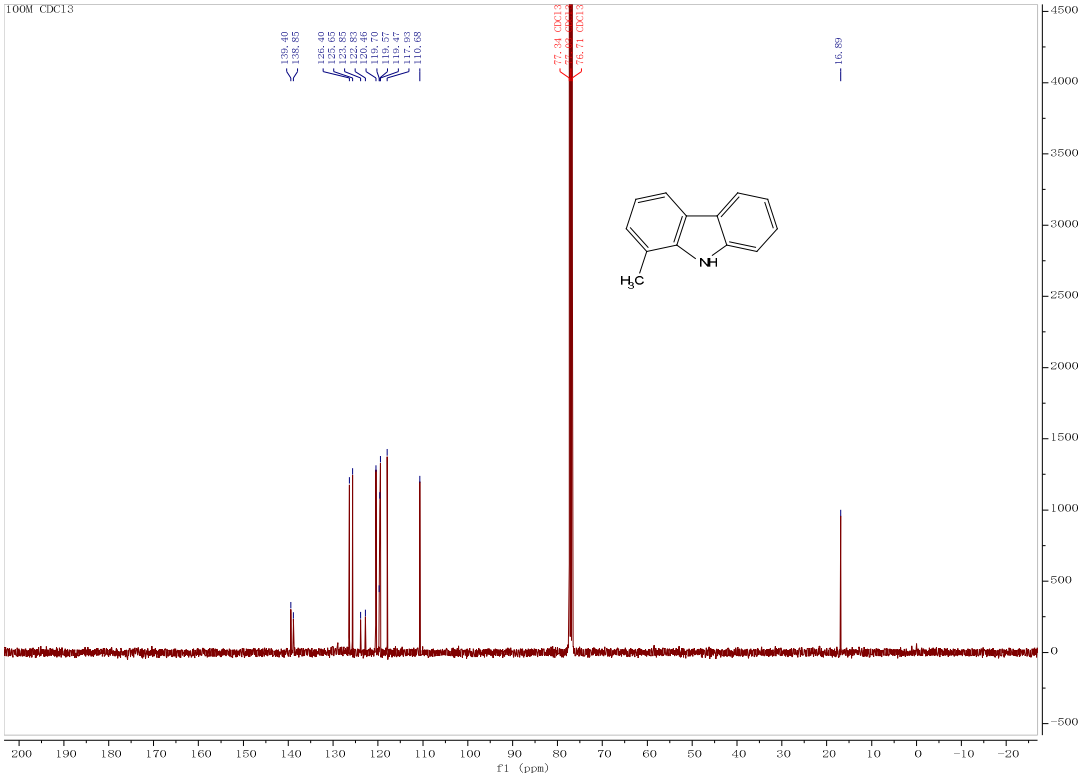
^{19}F NMR spectrum of Compound 2k ($CDCl_3$, 376 MHz)



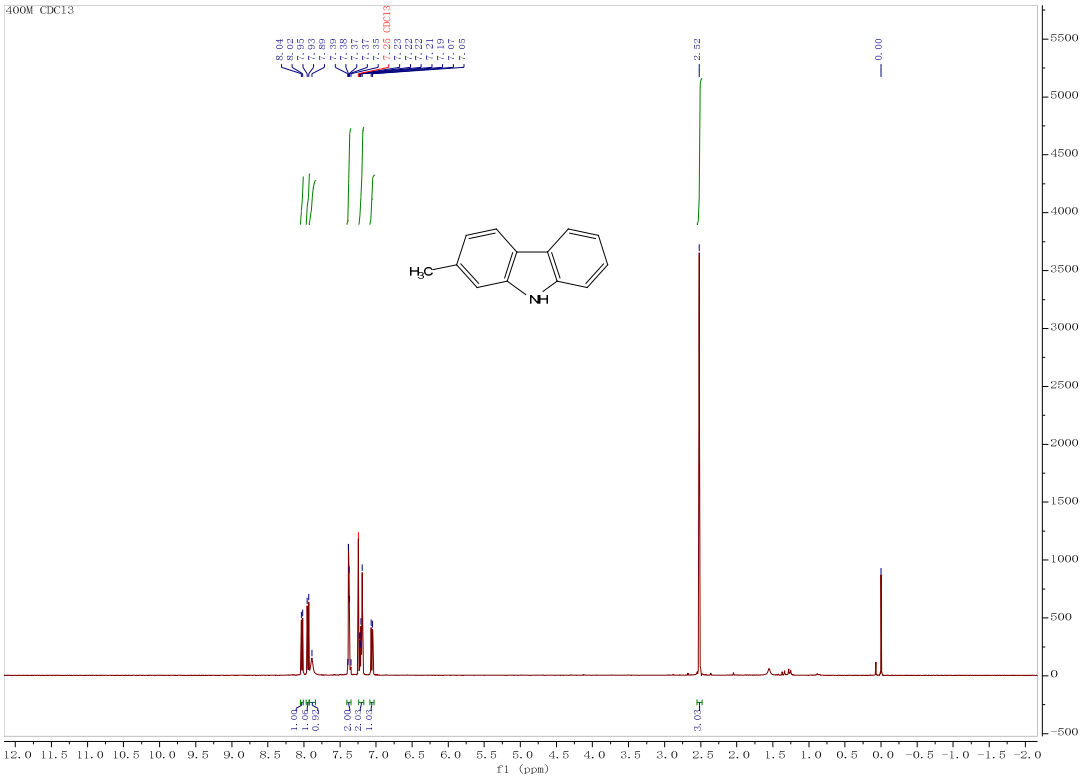
^{1}H NMR spectrum of Compound 2l ($CDCl_3$, 400 MHz)



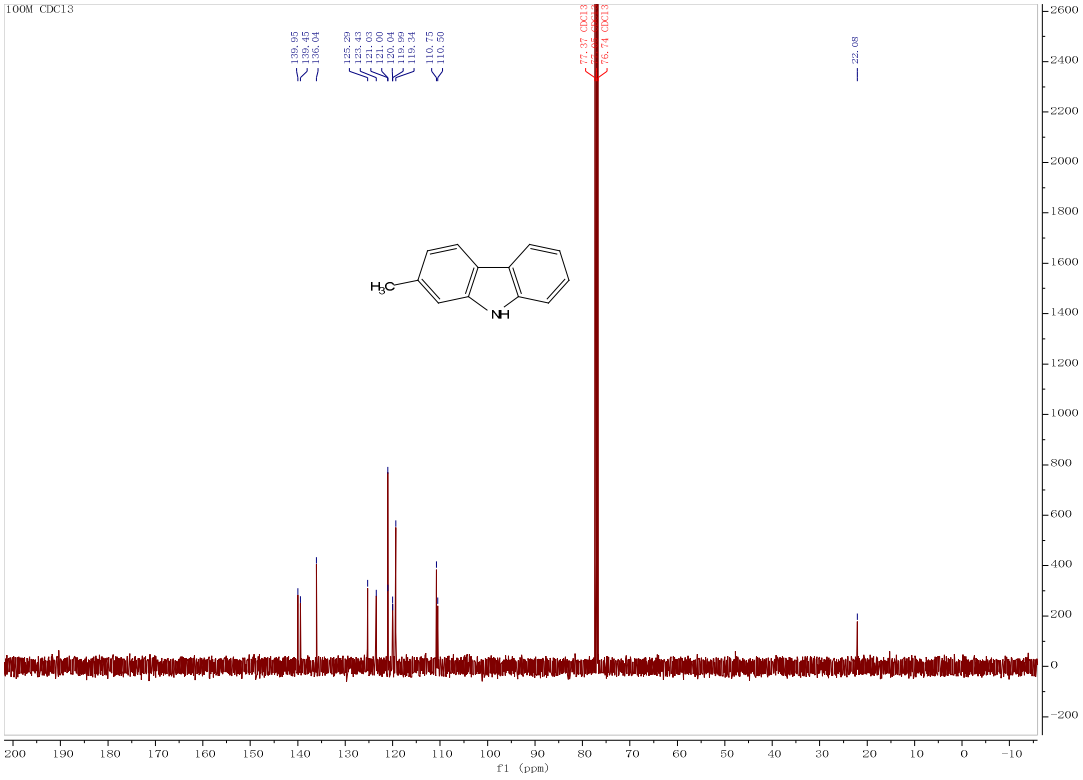
^{13}C NMR spectrum of Compound 2l ($CDCl_3$, 100 MHz)



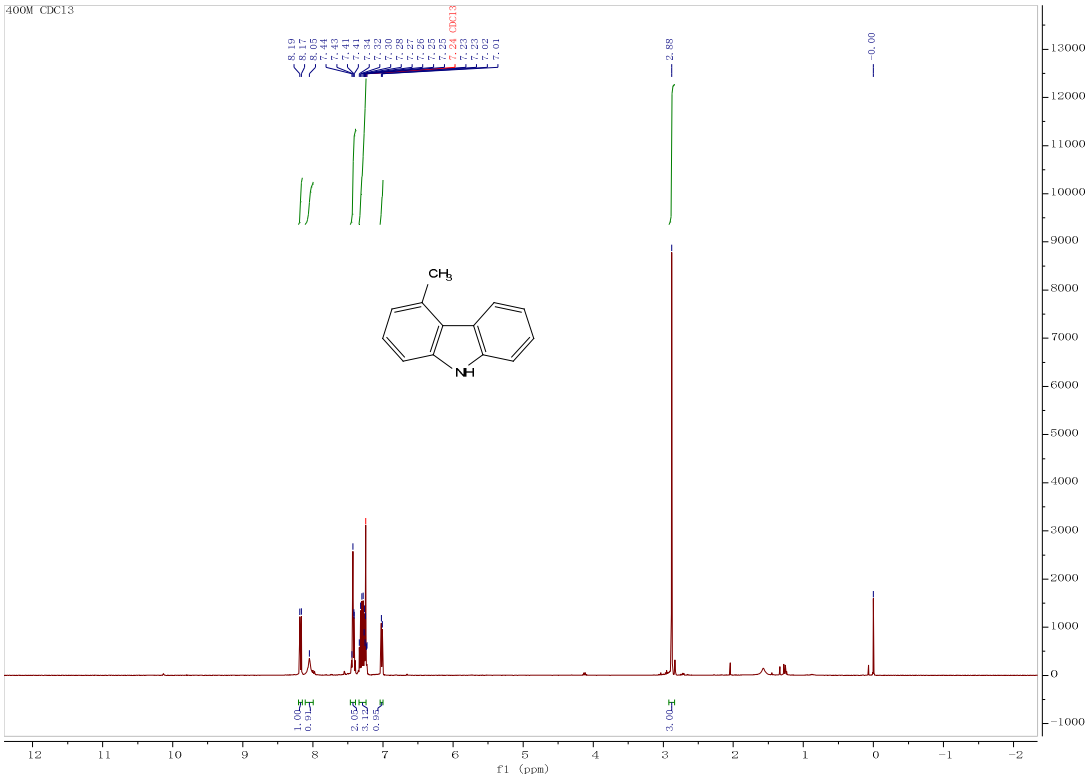
^{1}H NMR spectrum of Compound 2m ($CDCl_3$, 400 MHz)



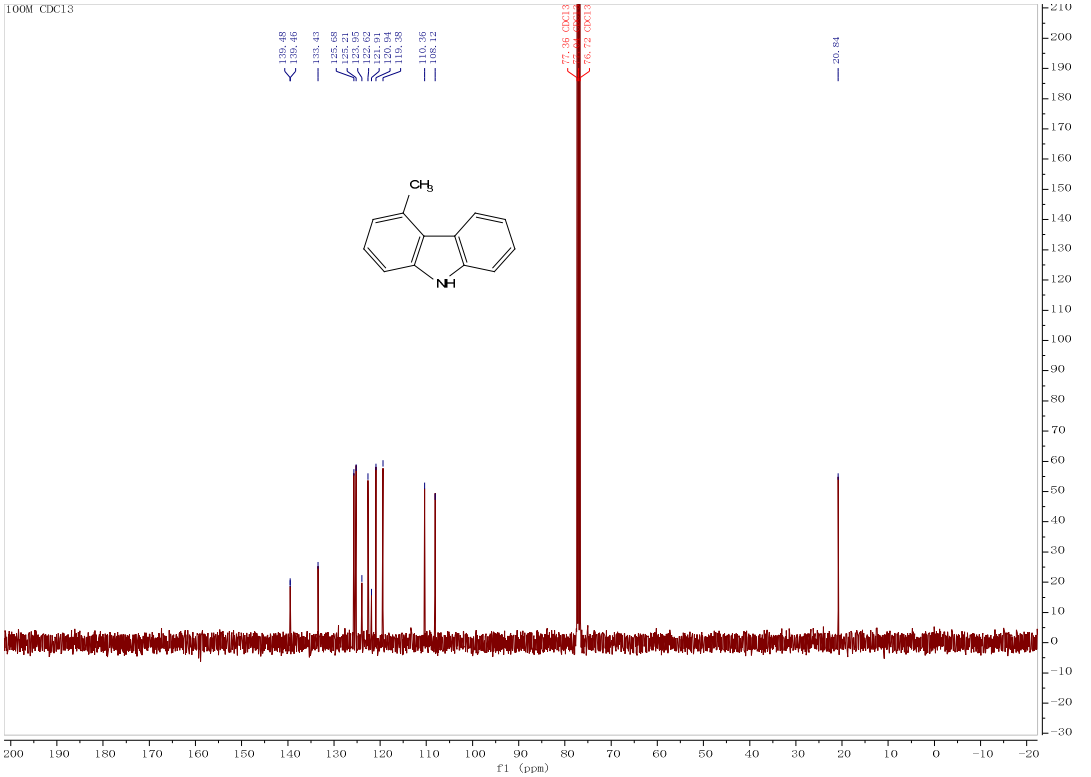
^{13}C NMR spectrum of Compound 2m ($CDCl_3$, 100 MHz)



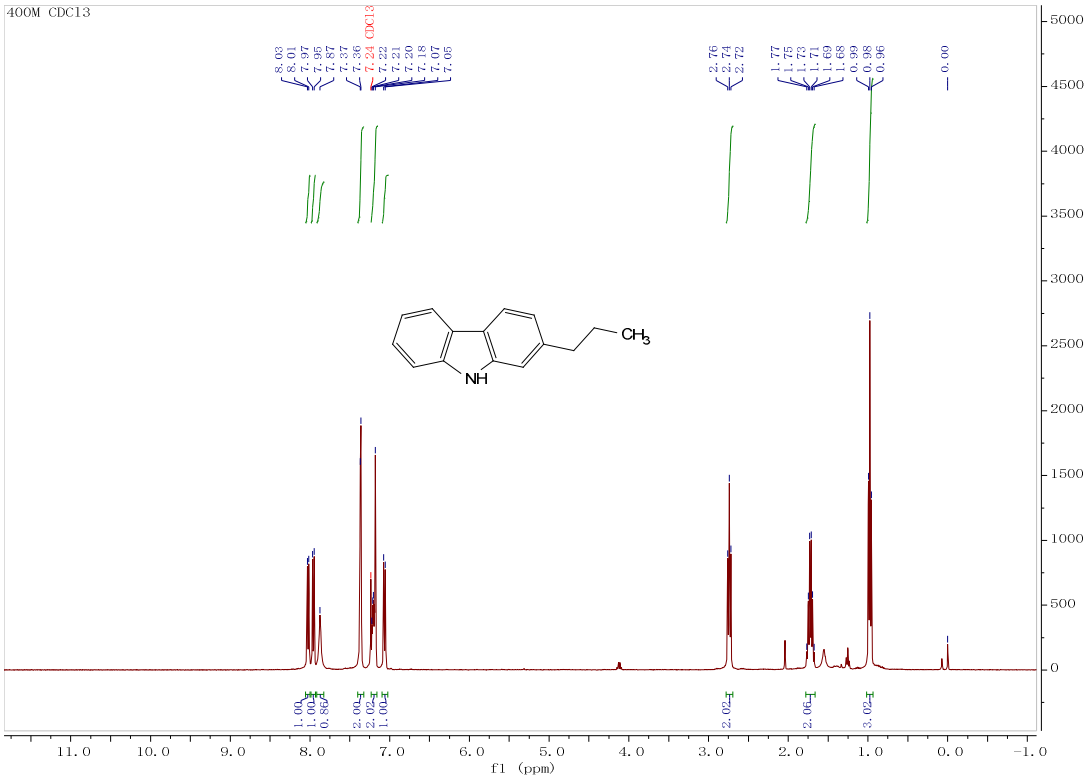
^{1}H NMR spectrum of Compound 2n ($CDCl_3$, 400 MHz)



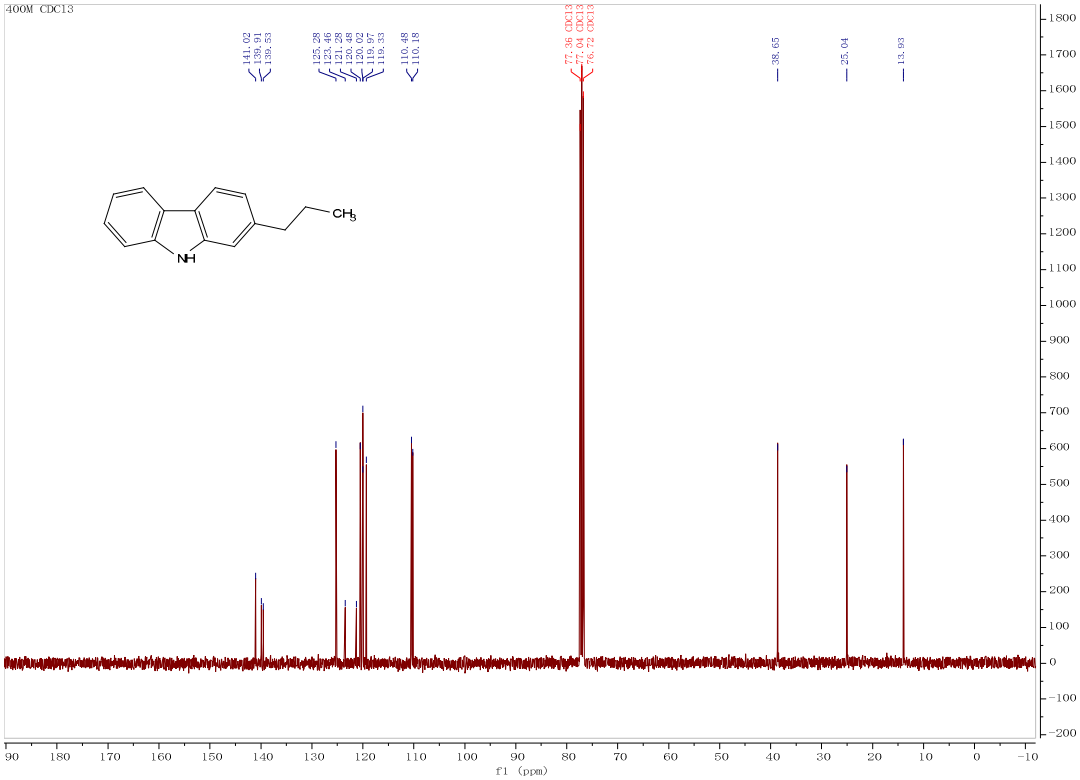
^{13}C NMR spectrum of Compound 2n ($CDCl_3$, 100 MHz)



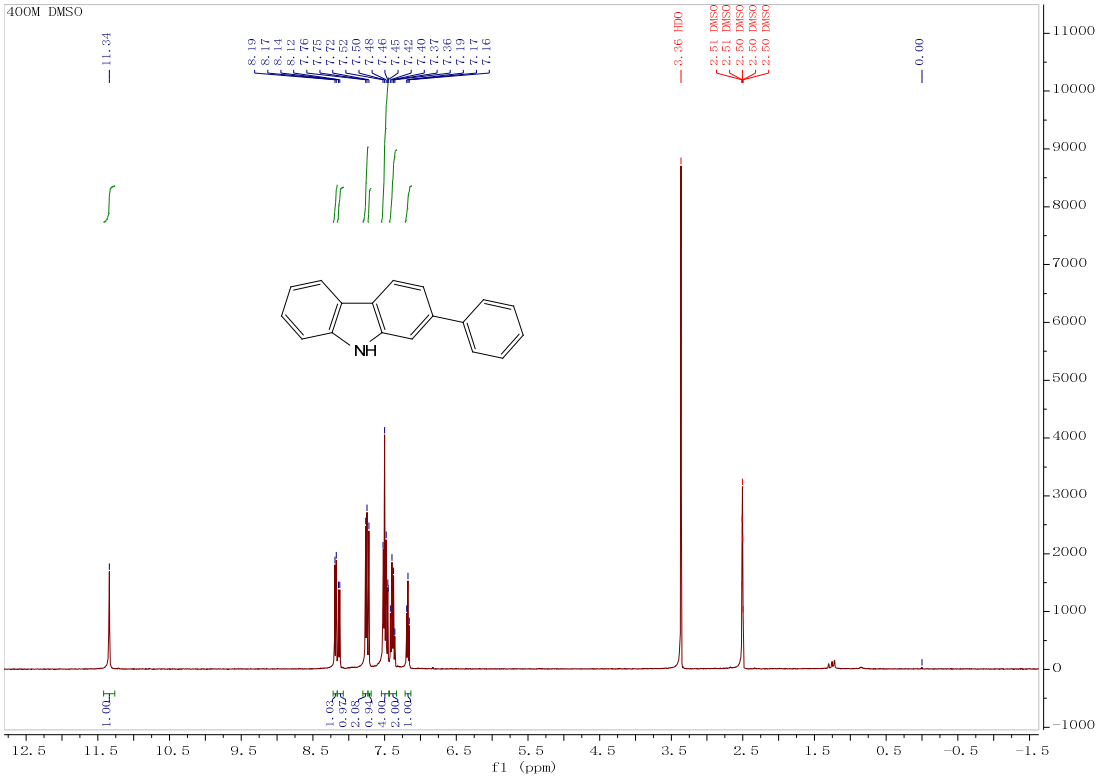
^{1}H NMR spectrum of Compound 2o ($CDCl_3$, 400 MHz)



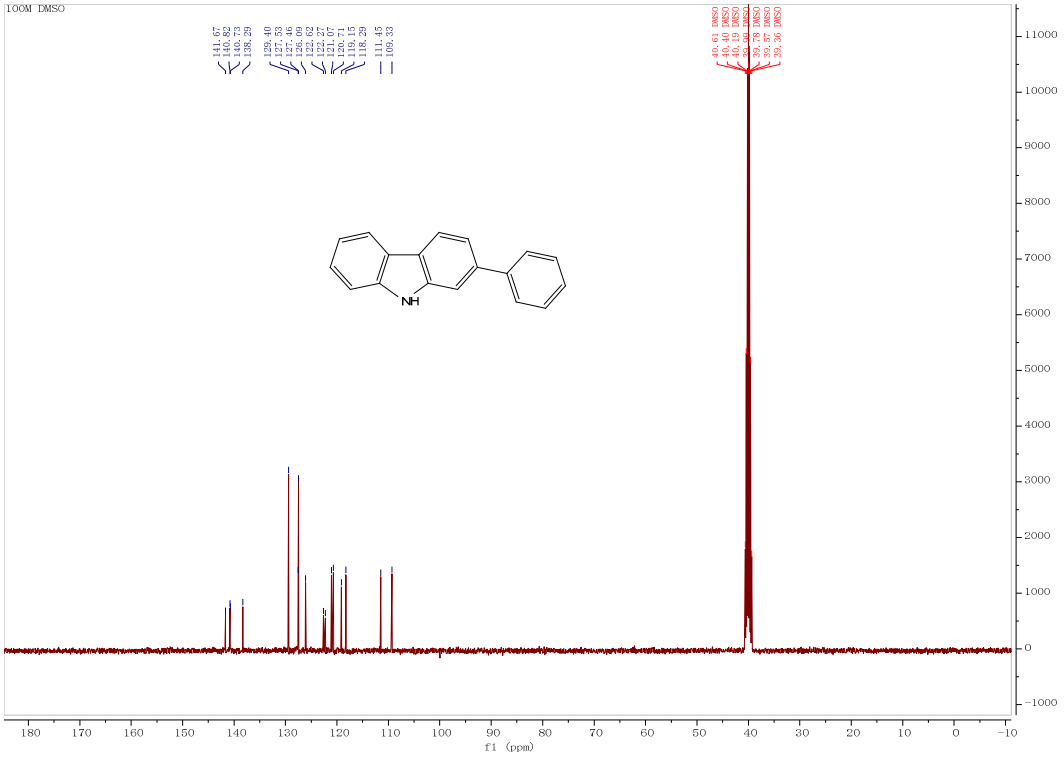
^{13}C NMR spectrum of Compound 2o ($CDCl_3$, 100 MHz)



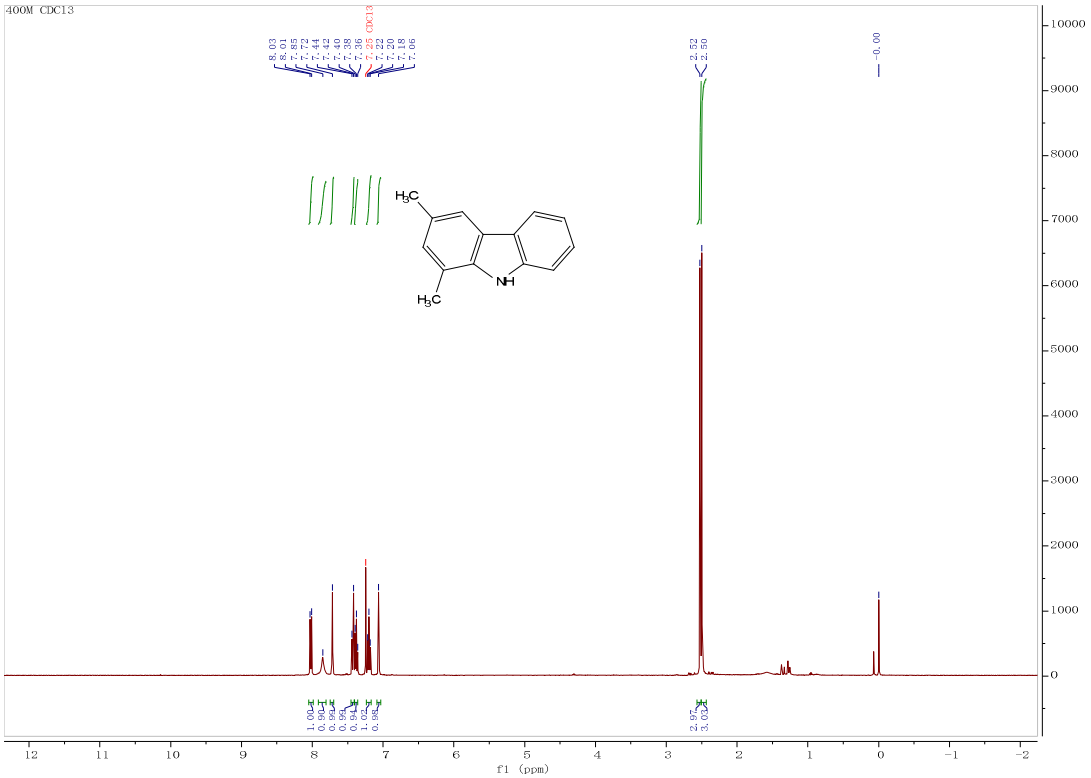
^{1}H NMR spectrum of Compound 2p (DMSO-d_6, 400 MHz)



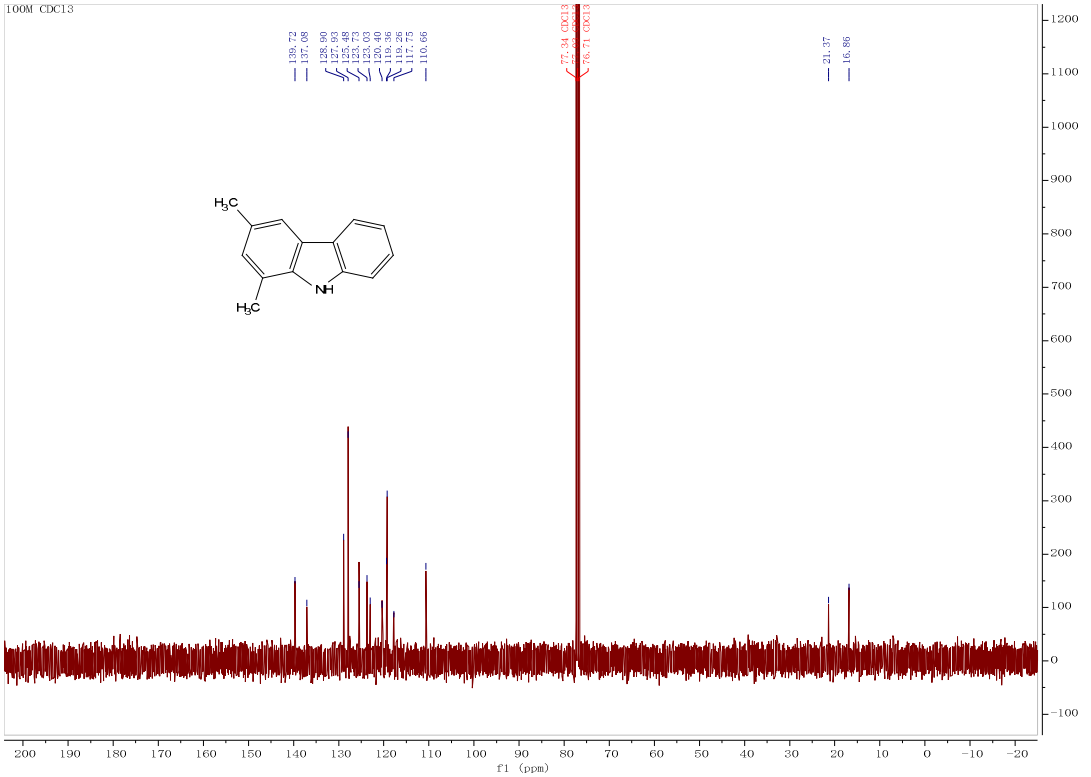
^{13}C NMR spectrum of Compound 2p (DMSO-d_6, 100 MHz)



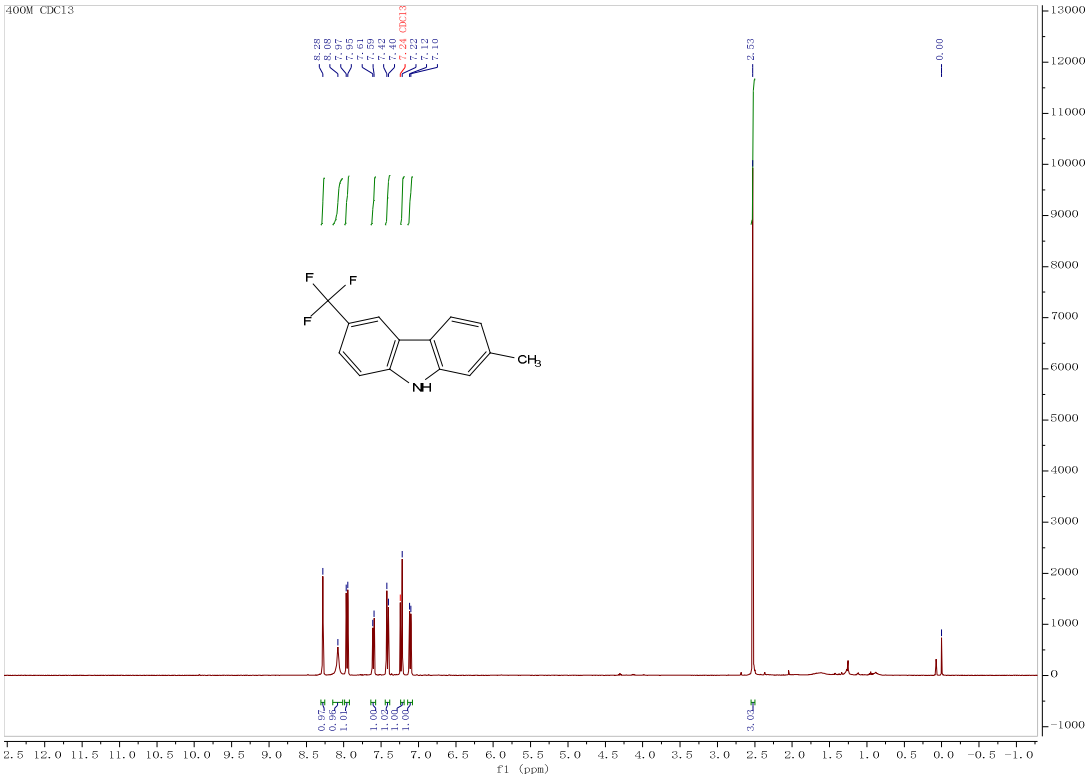
^{1}H NMR spectrum of Compound 2q ($CDCl_3$, 400 MHz)



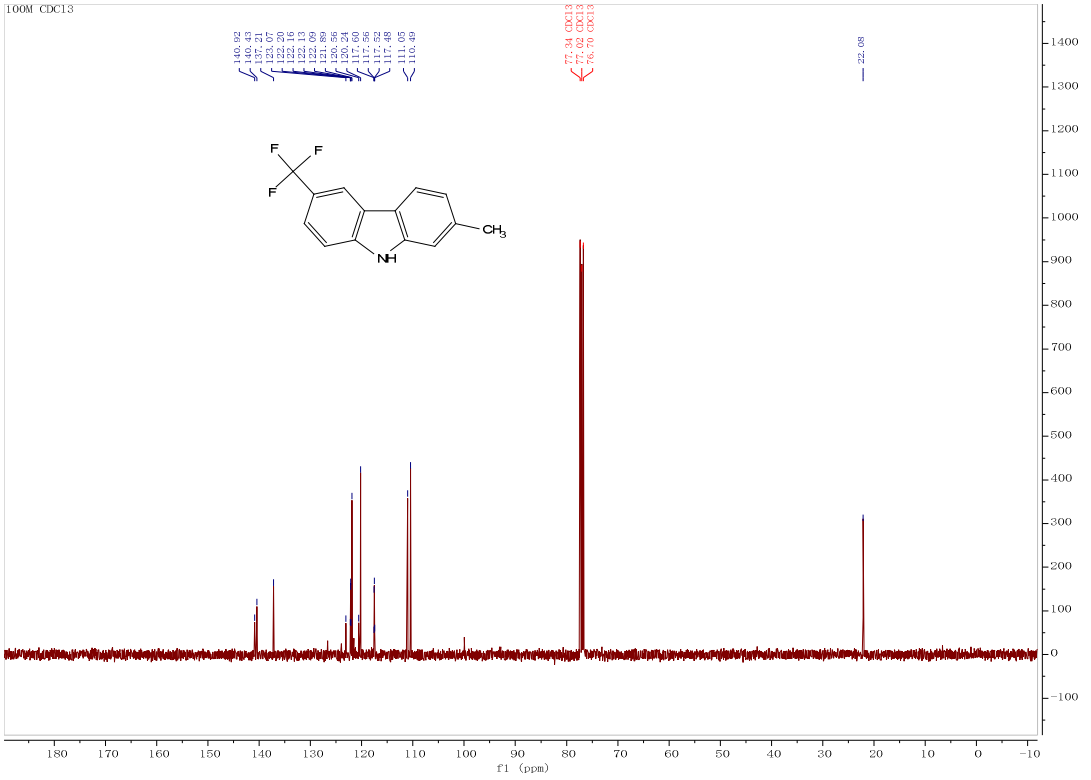
^{13}C NMR spectrum of Compound 2q ($CDCl_3$, 100 MHz)



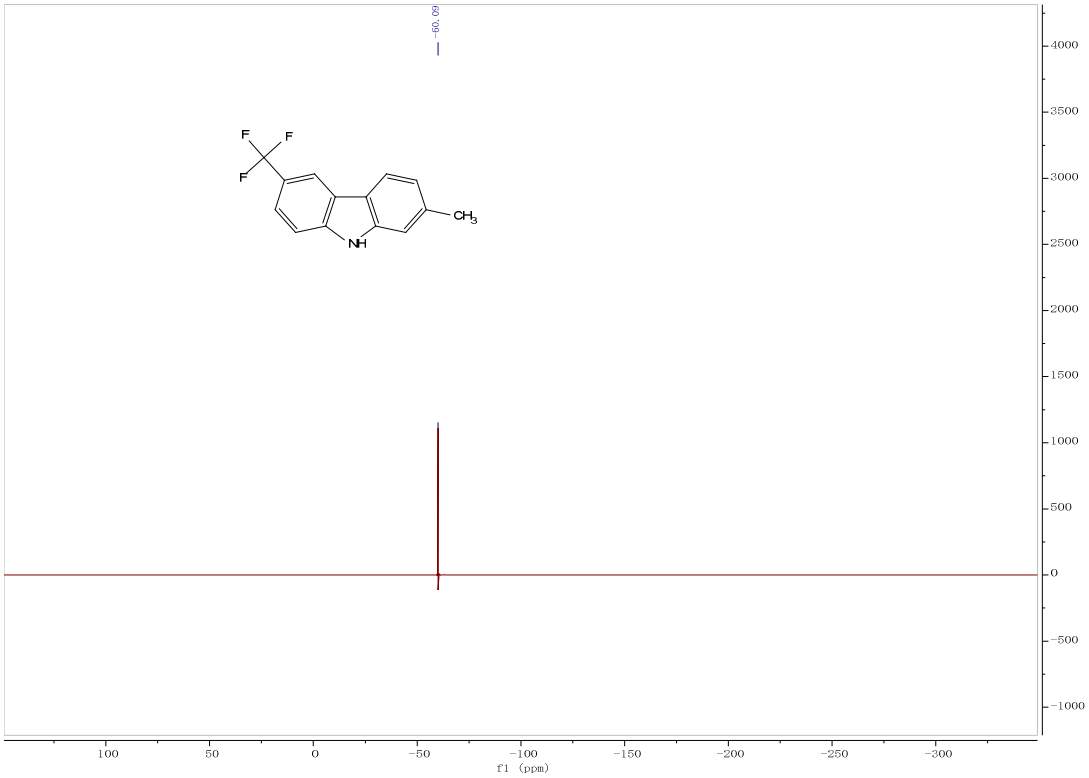
^{1}H NMR spectrum of Compound 2r ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of Compound 2r ($CDCl_3$, 100 MHz)

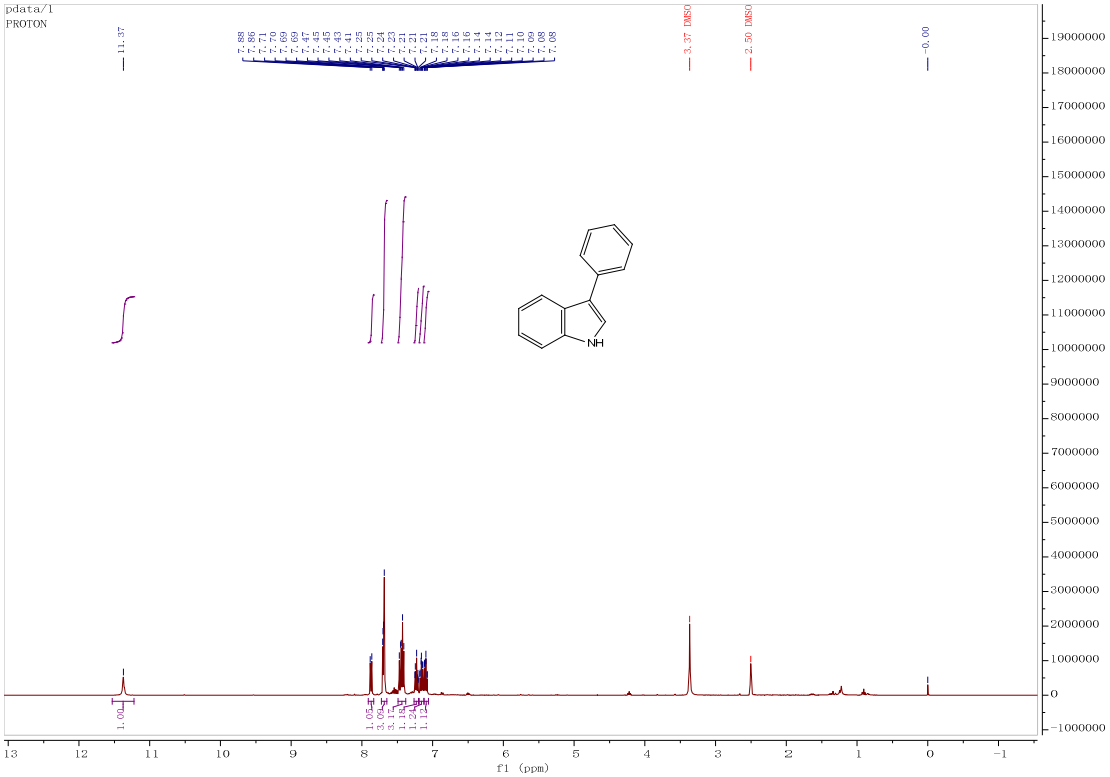


^{19}F NMR spectrum of Compound 2r ($CDCl_3$, 376 MHz)

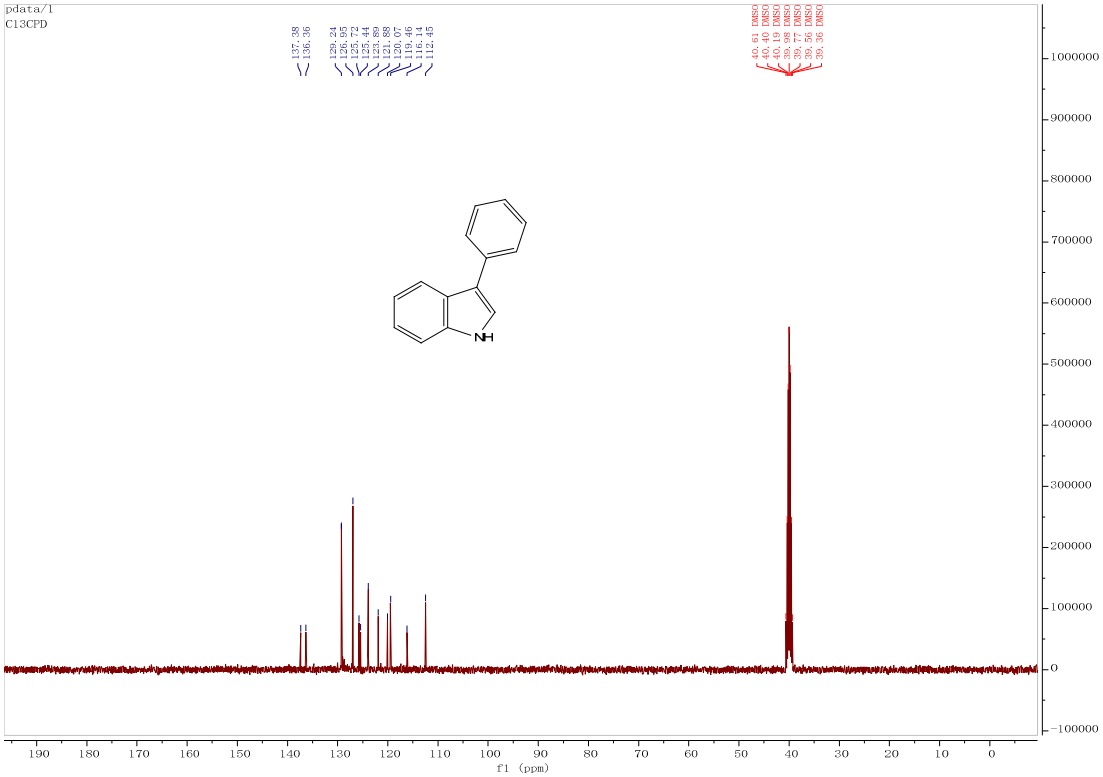


15. Spectroscopic data for indoles 4

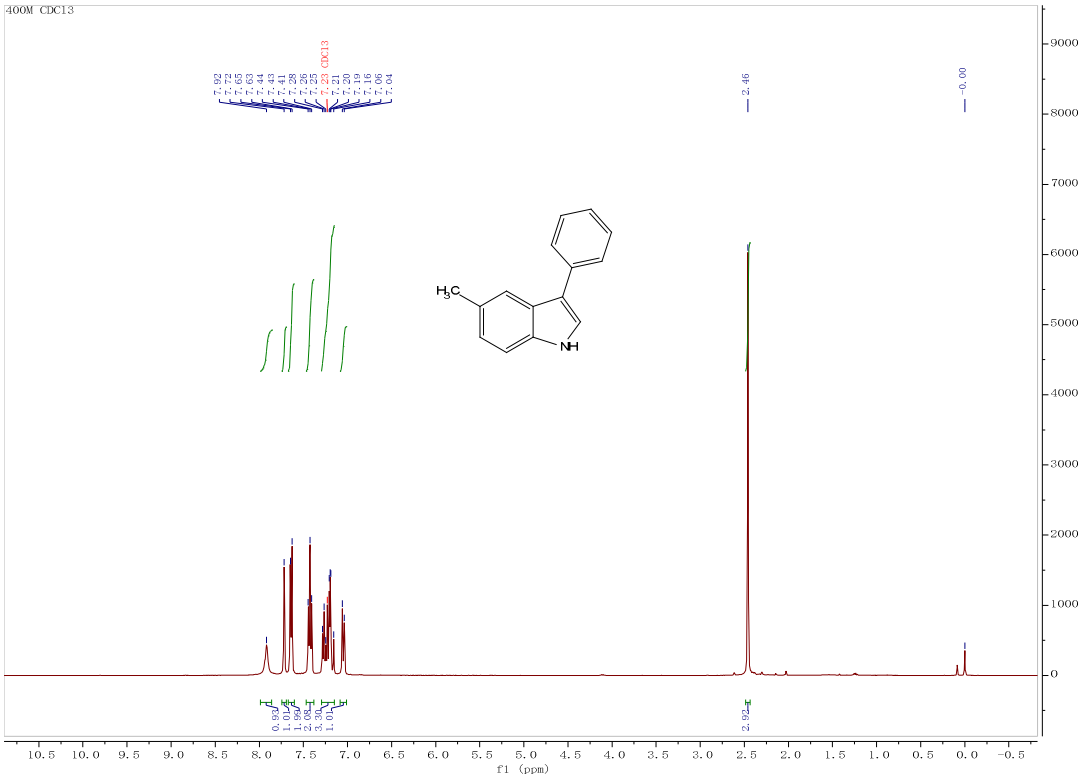
^{1}H NMR spectrum of Compound 4a (DMSO-d_6, 400 MHz)



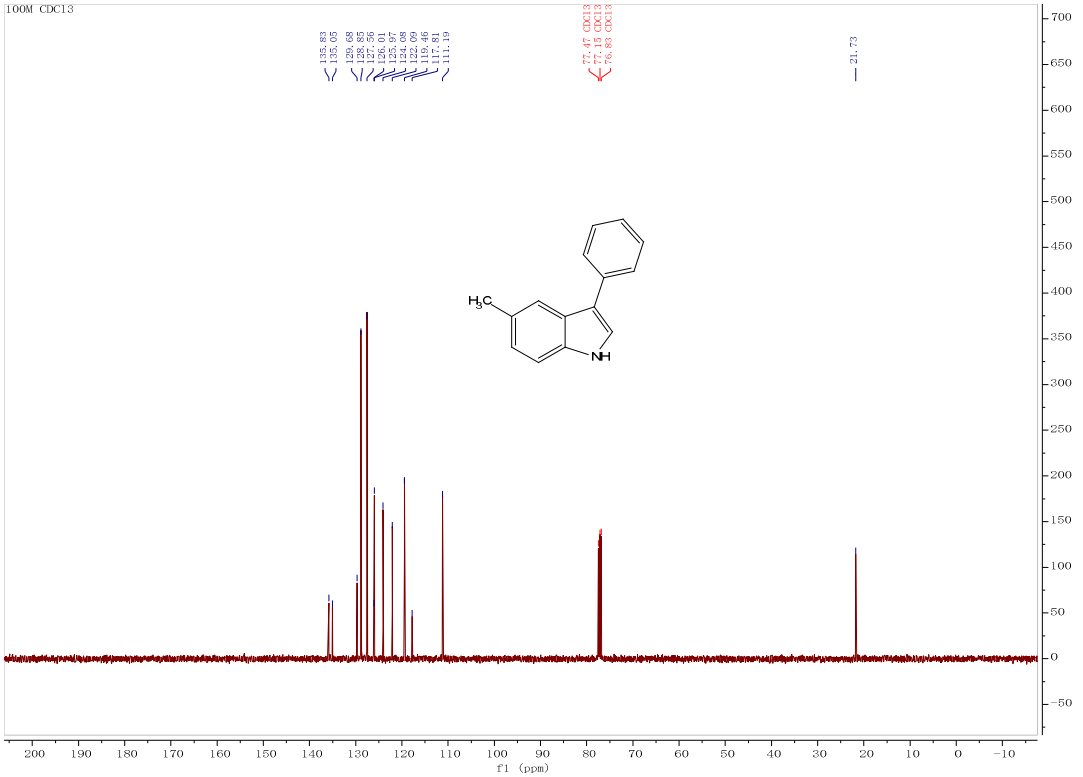
^{13}C NMR spectrum of Compound 4a (DMSO-d_6, 100 MHz)



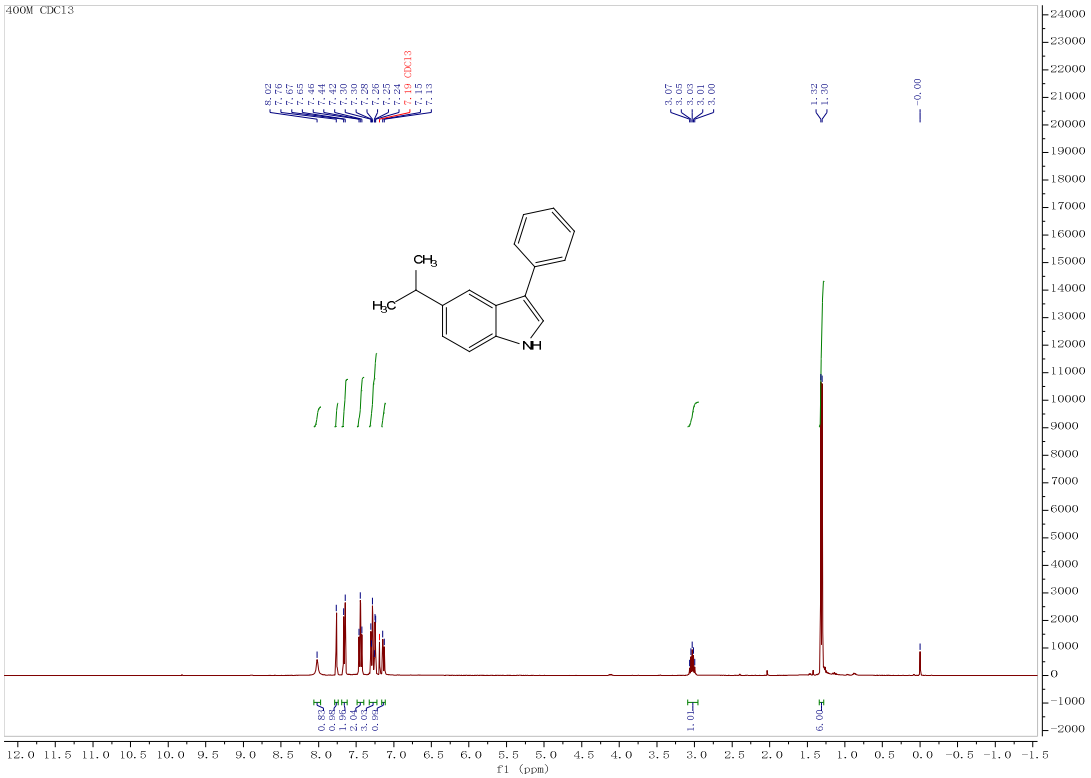
^{1}H NMR spectrum of Compound 4b ($CDCl_3$, 400 MHz)



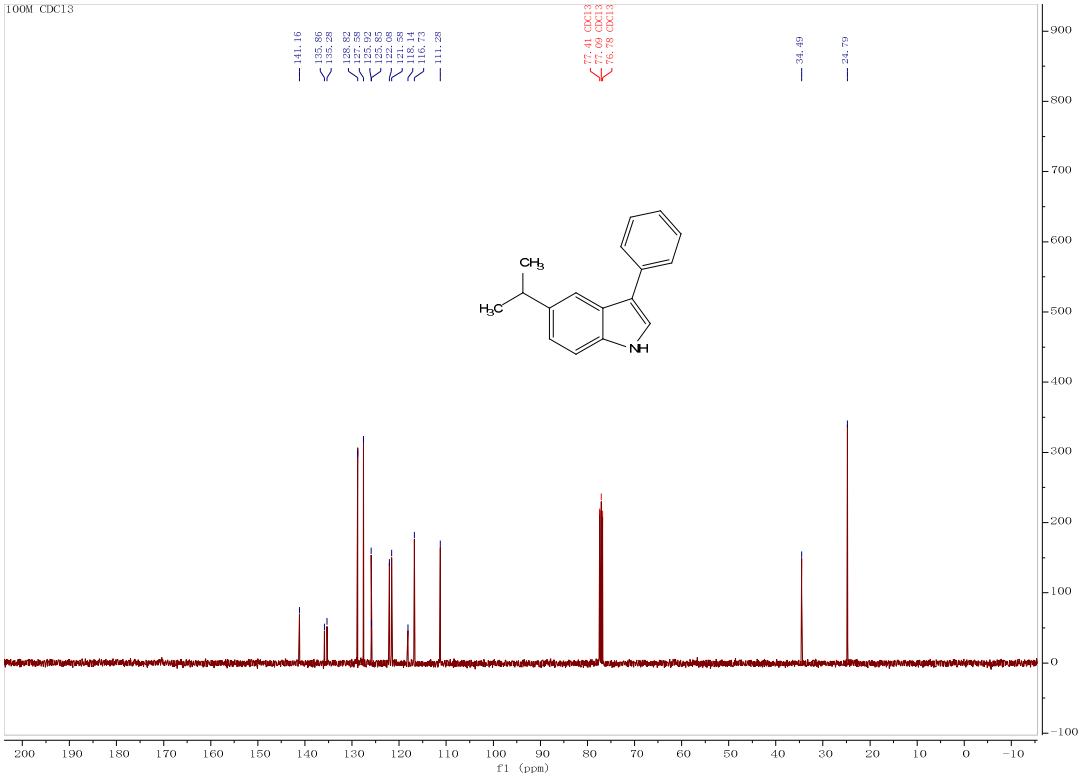
^{13}C NMR spectrum of Compound 4b ($CDCl_3$, 100 MHz)



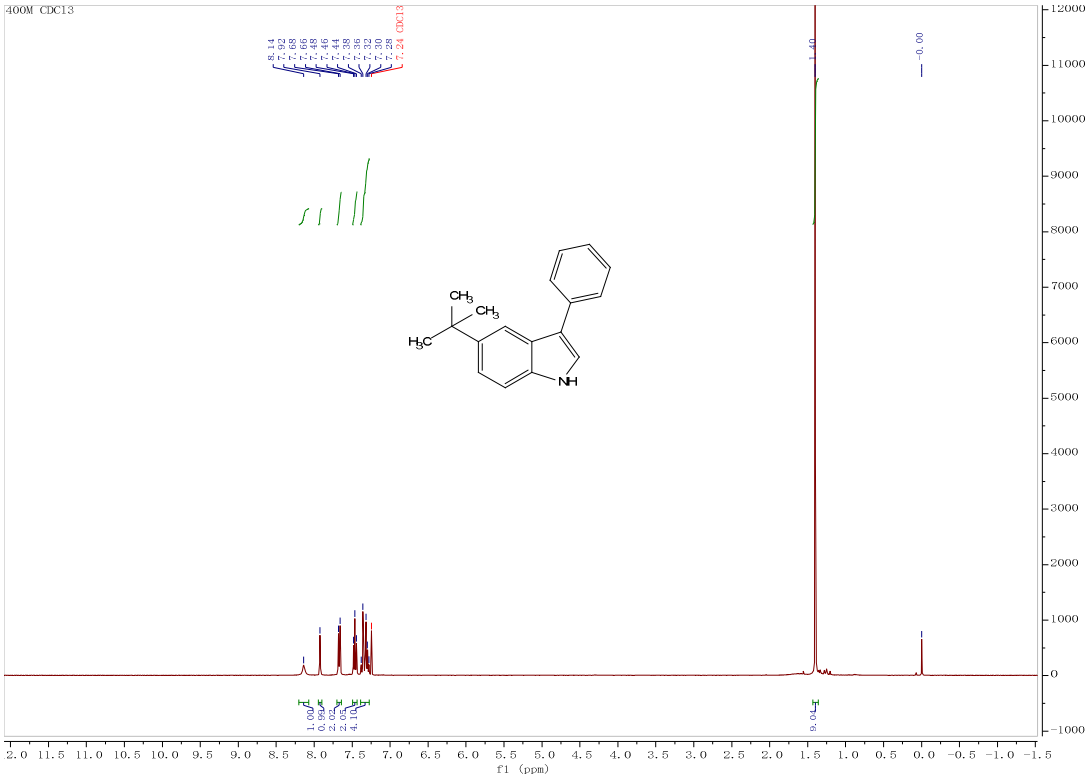
^{1}H NMR spectrum of Compound 4c ($CDCl_3$, 400 MHz)



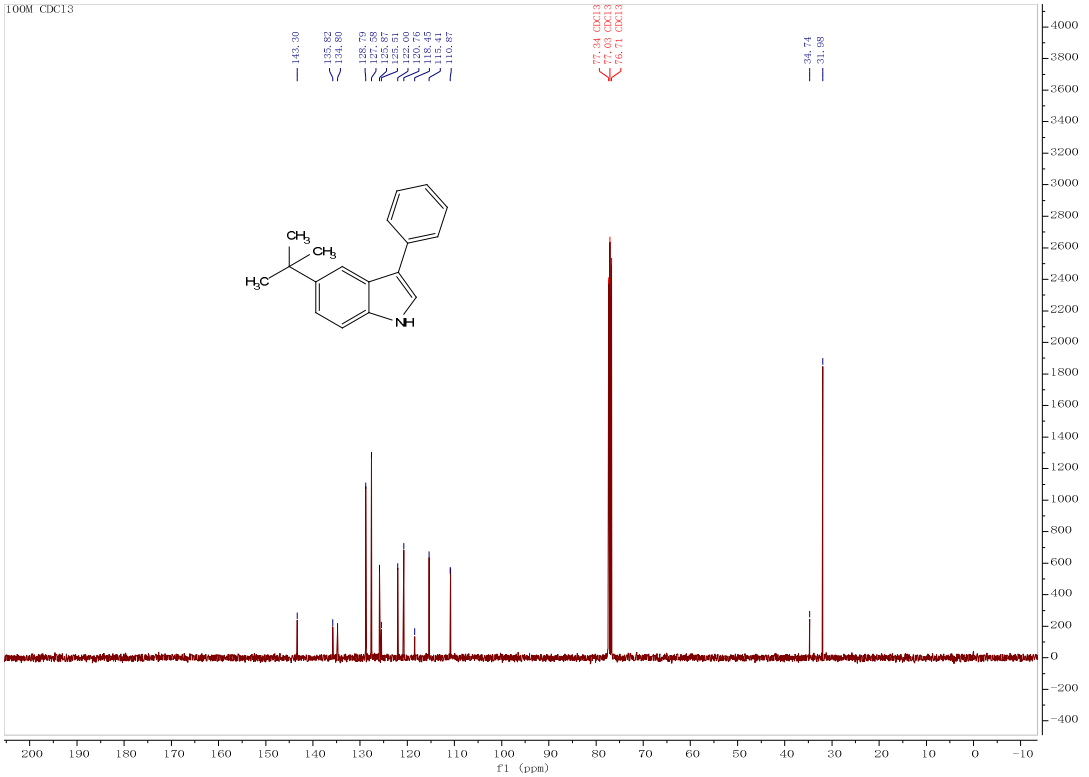
^{13}C NMR spectrum of Compound 4c ($CDCl_3$, 100 MHz)



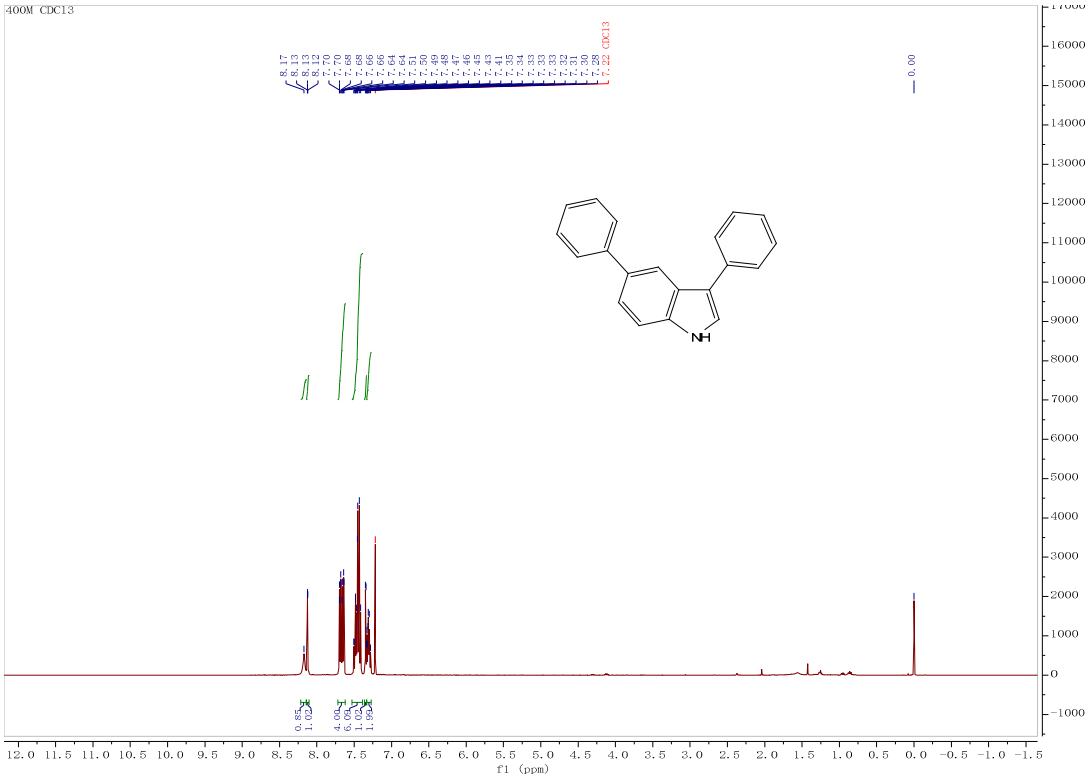
^{1}H NMR spectrum of Compound 4d ($CDCl_3$, 400 MHz)



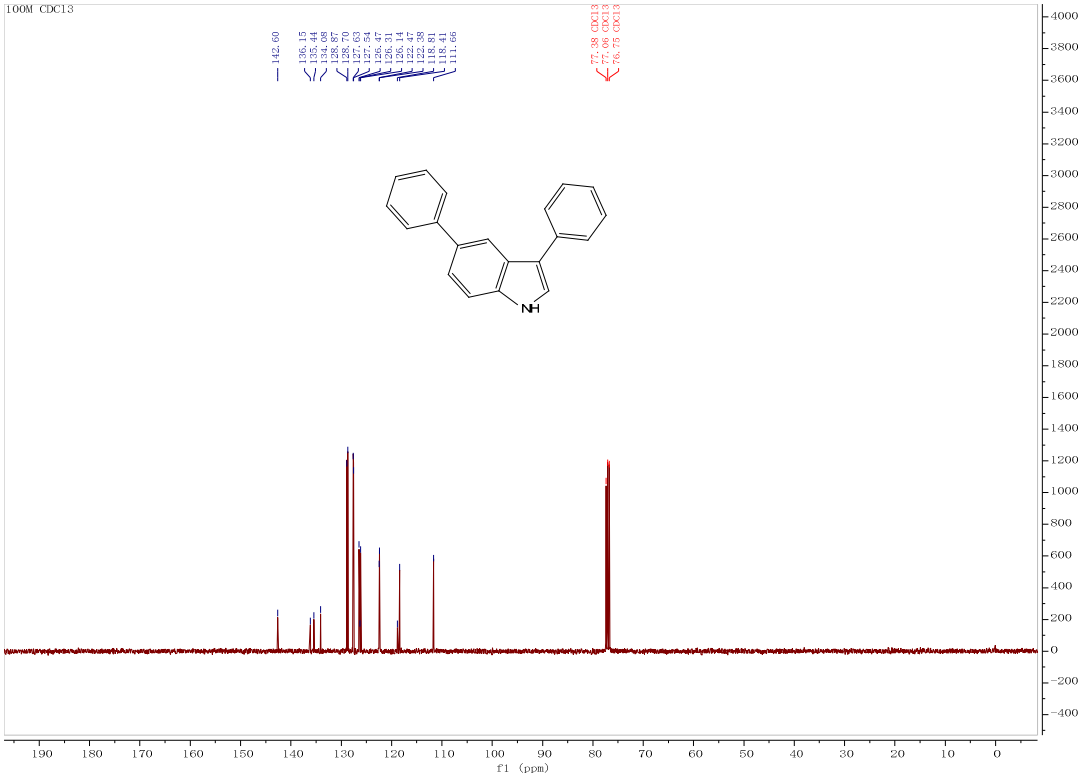
^{13}C NMR spectrum of Compound 4d ($CDCl_3$, 100 MHz)



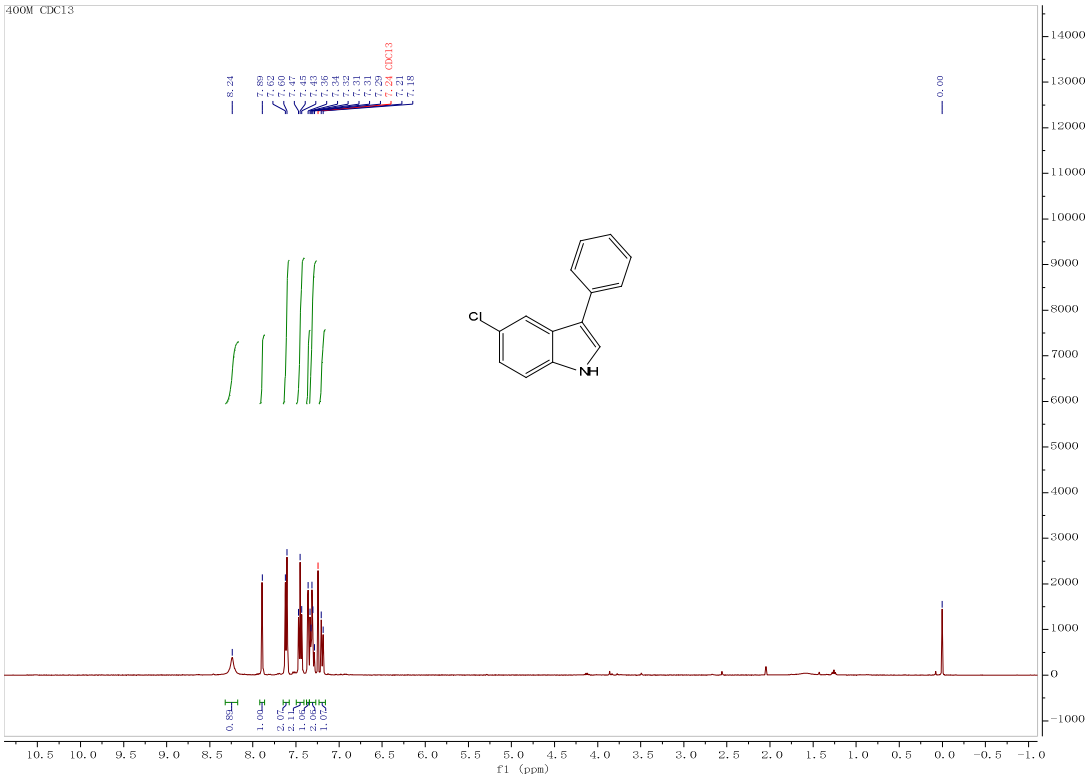
^{1}H NMR spectrum of Compound 4e ($CDCl_3$, 400 MHz)



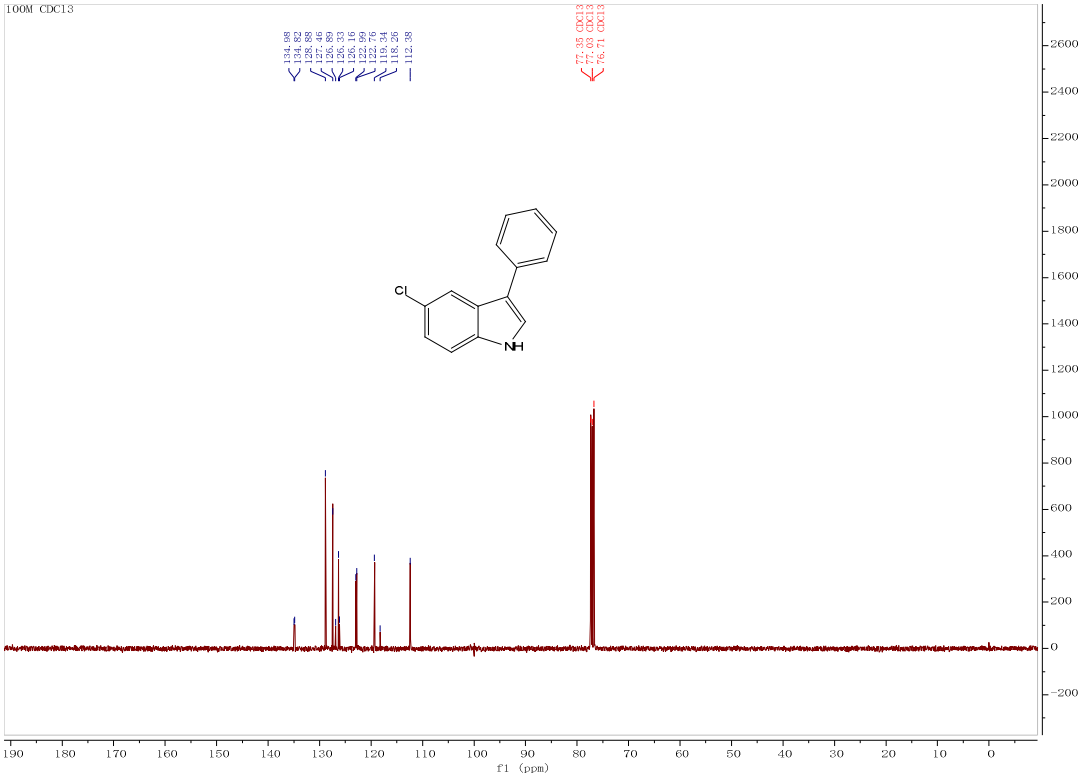
^{13}C NMR spectrum of Compound 4e ($CDCl_3$, 100 MHz)



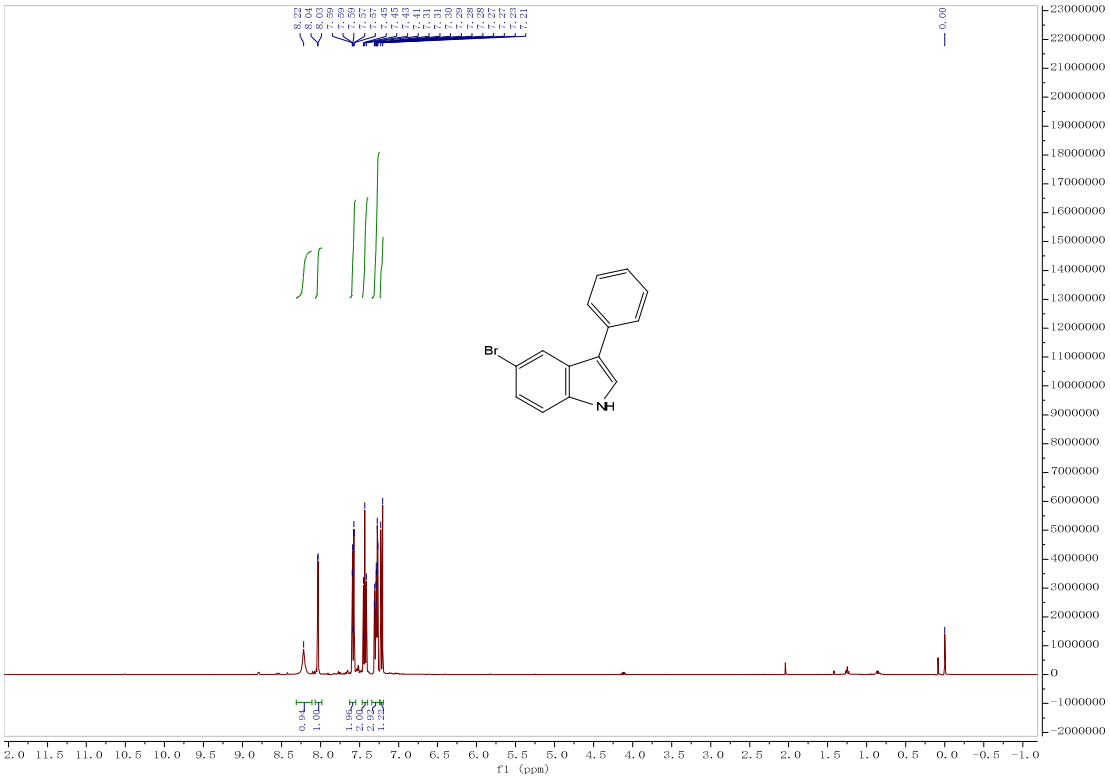
^{1}H NMR spectrum of Compound 4f ($CDCl_3$, 400 MHz)



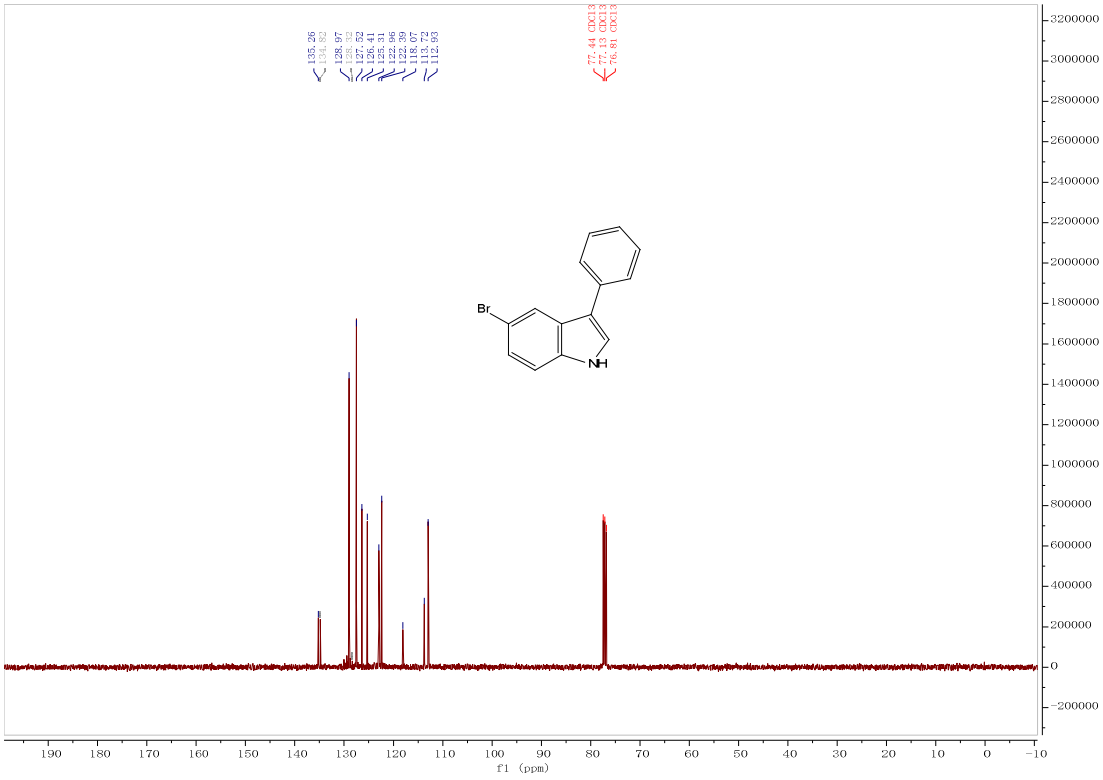
^{13}C NMR spectrum of Compound 4f ($CDCl_3$, 100 MHz)



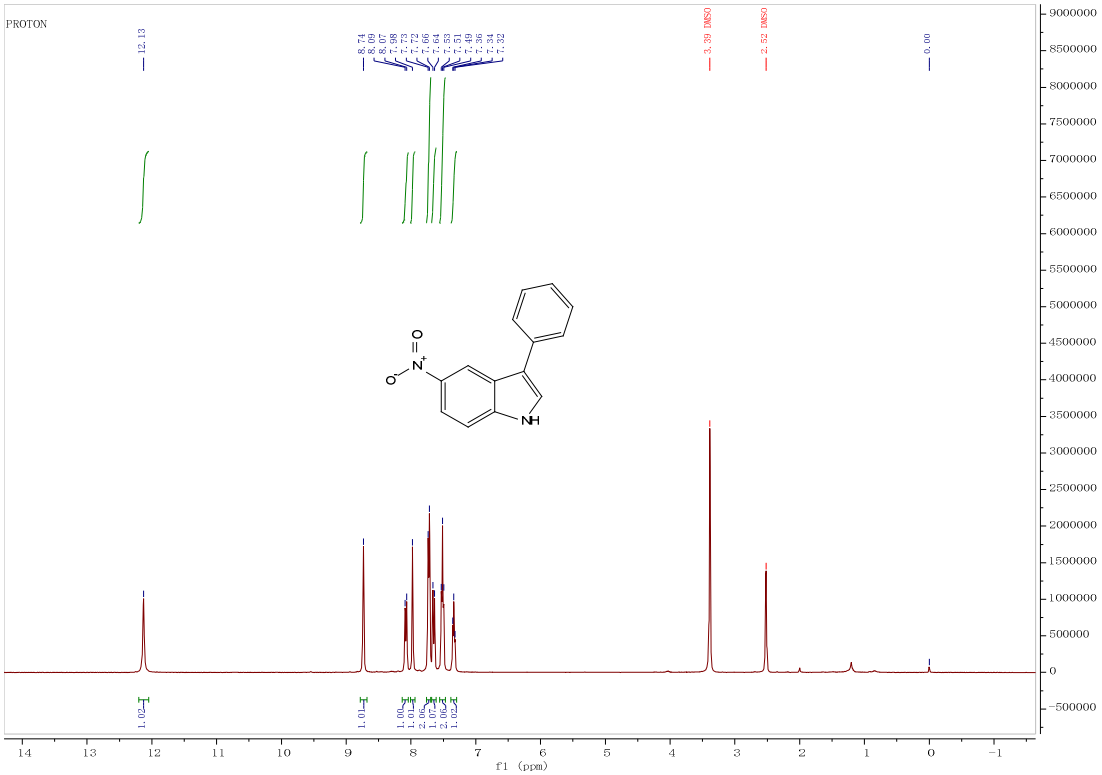
^{1}H NMR spectrum of Compound 4g ($CDCl_3$, 400 MHz)



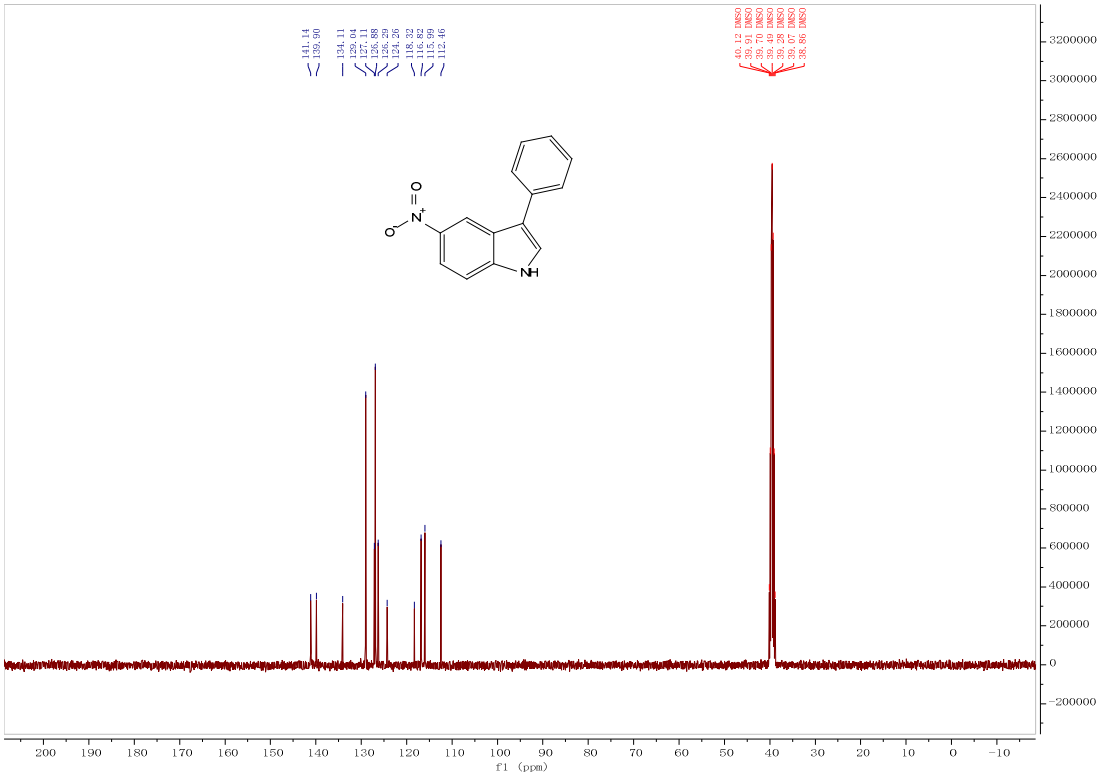
^{13}C NMR spectrum of Compound 4g ($CDCl_3$, 100 MHz)



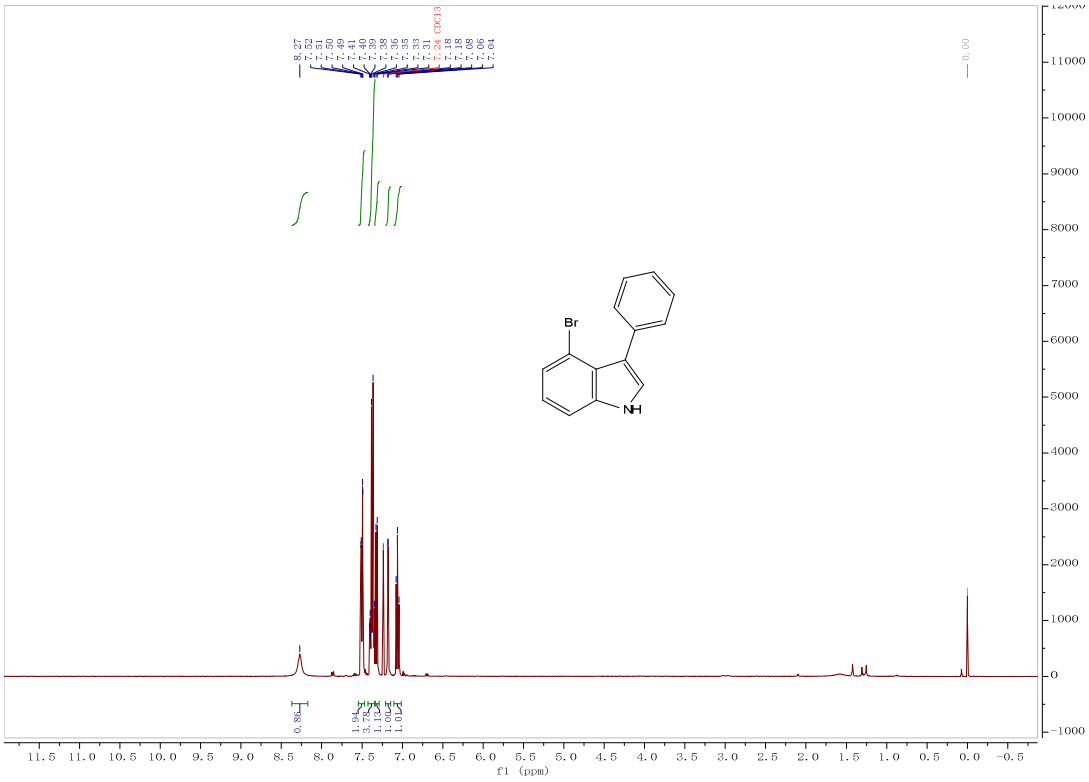
^{1}H NMR spectrum of Compound 4h (DMSO-d_6, 400 MHz)



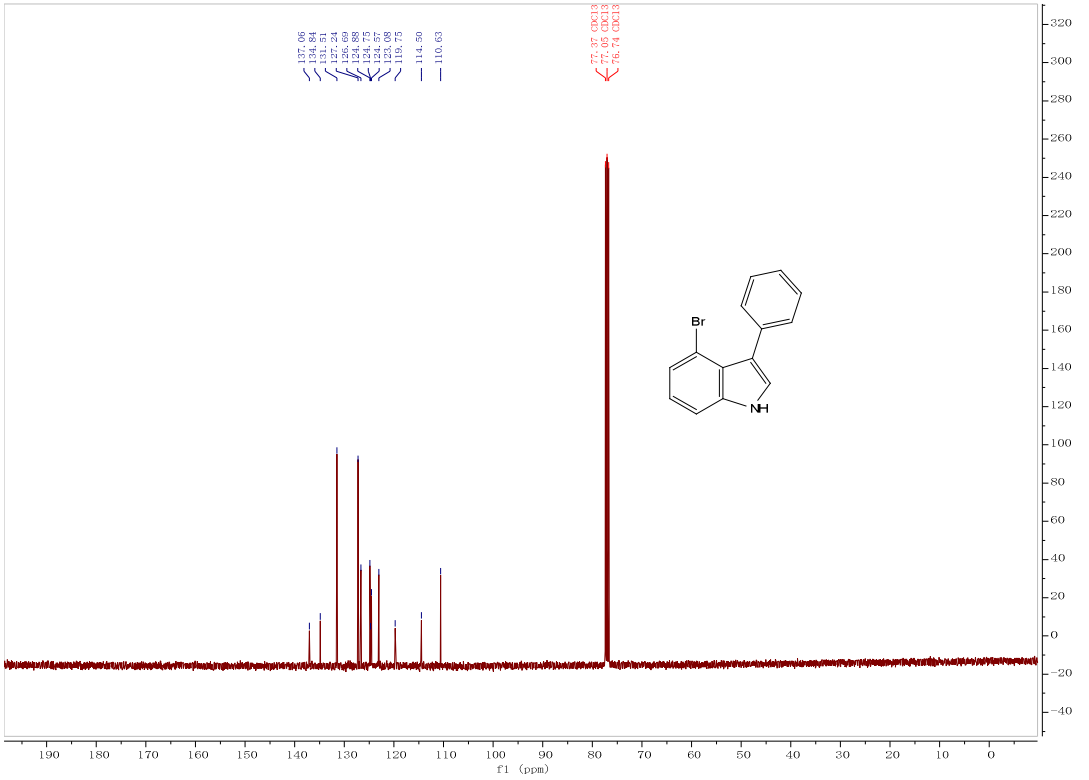
^{13}C NMR spectrum of Compound 4h (DMSO-d_6, 100 MHz)



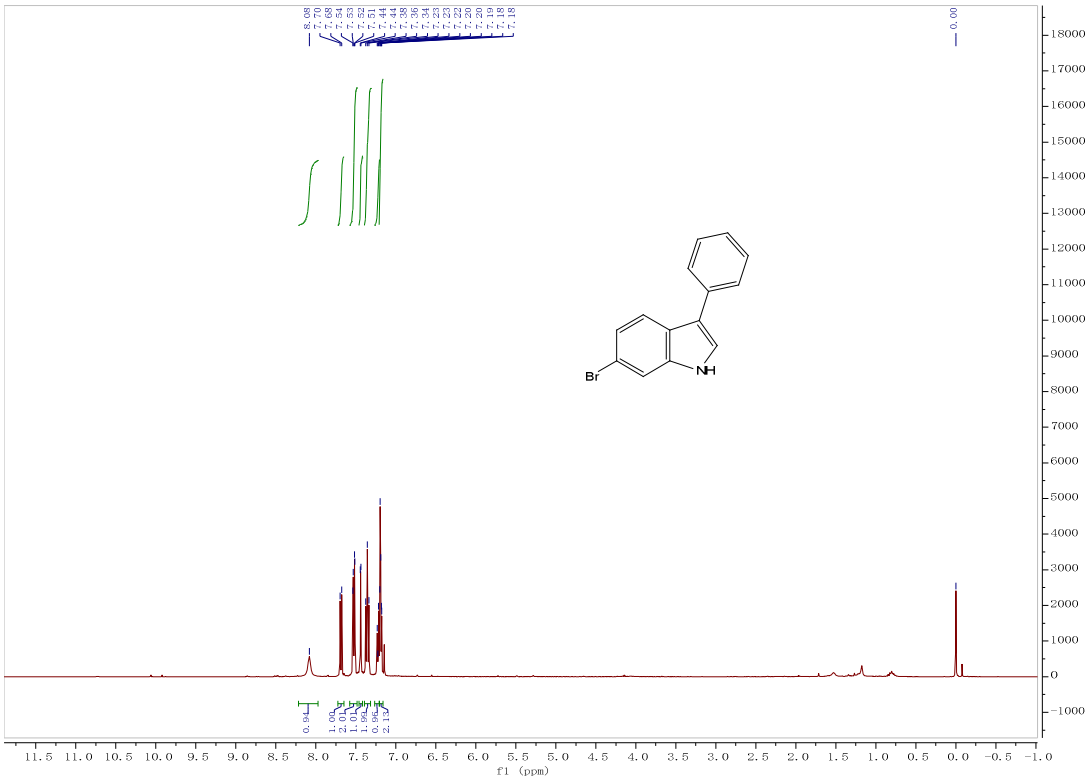
^{1}H NMR spectrum of Compound 4i ($CDCl_3$, 400 MHz)



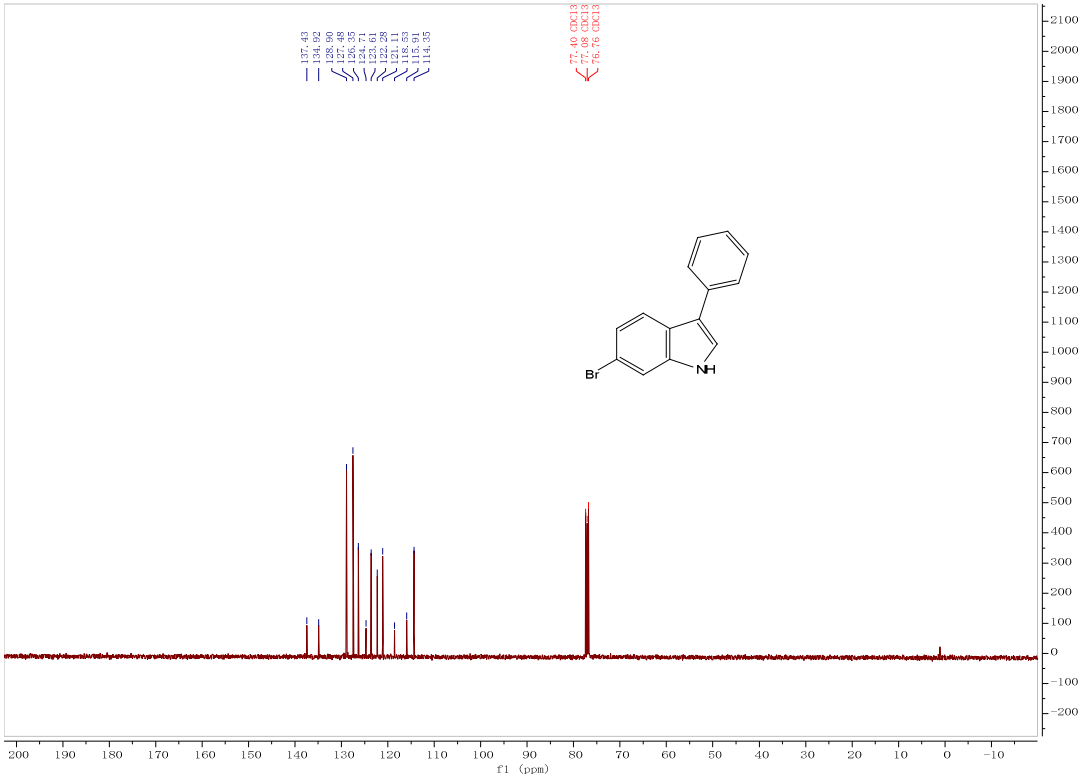
^{13}C NMR spectrum of Compound 4i ($CDCl_3$, 100 MHz)



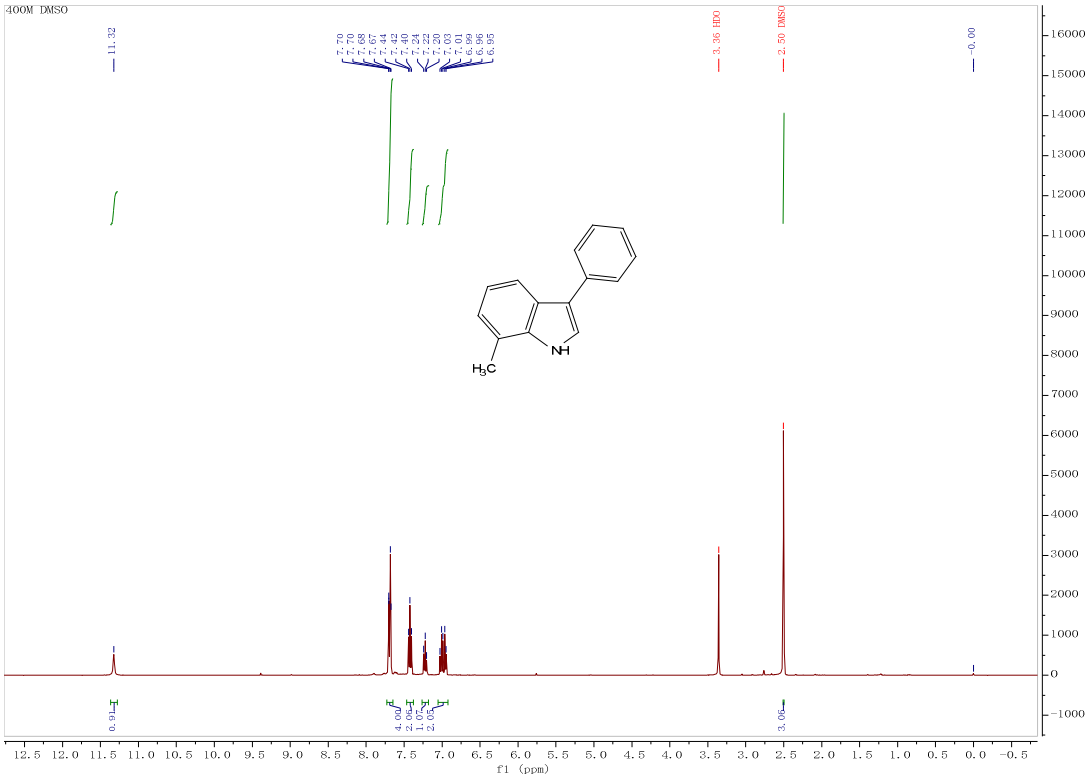
^{1}H NMR spectrum of Compound 4j ($CDCl_3$, 400 MHz)



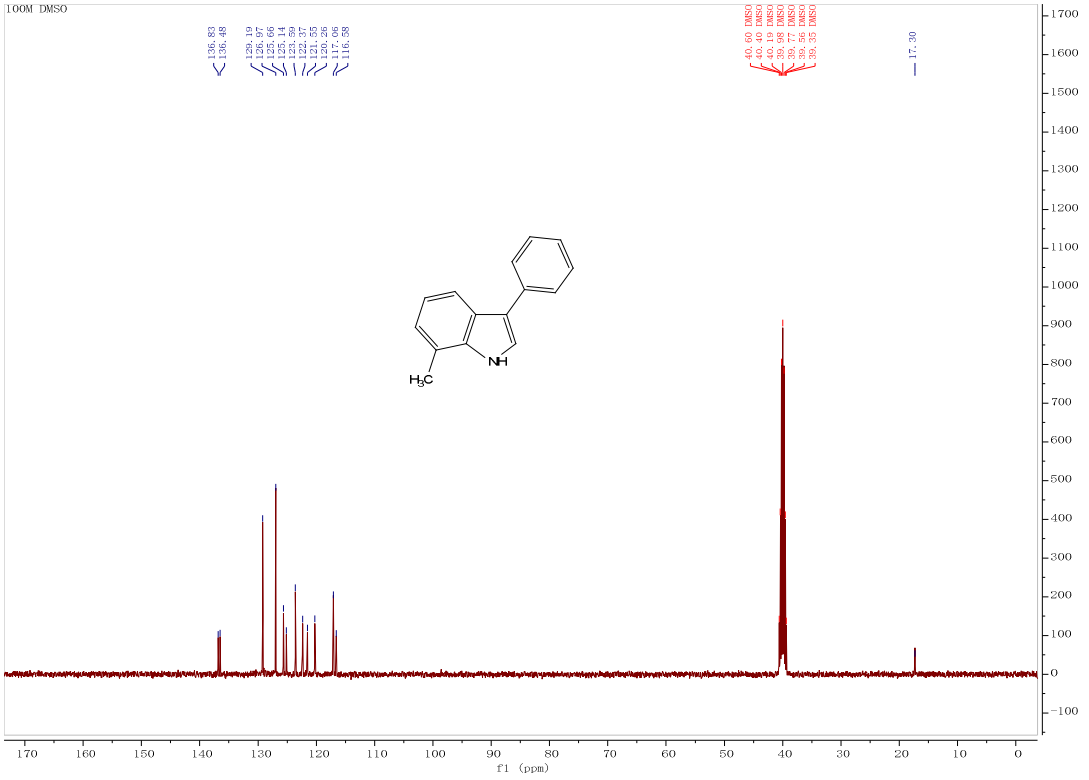
^{13}C NMR spectrum of Compound 4j ($CDCl_3$, 100 MHz)



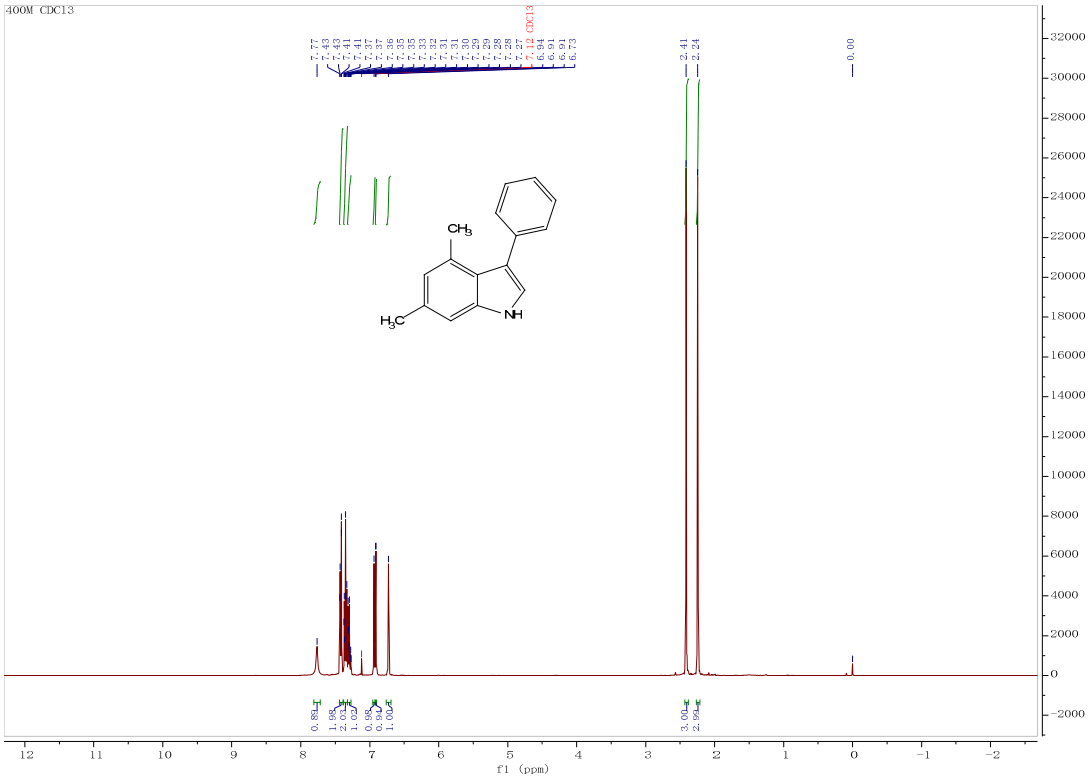
^{1}H NMR spectrum of Compound 4k (DMSO-d_6, 400 MHz)



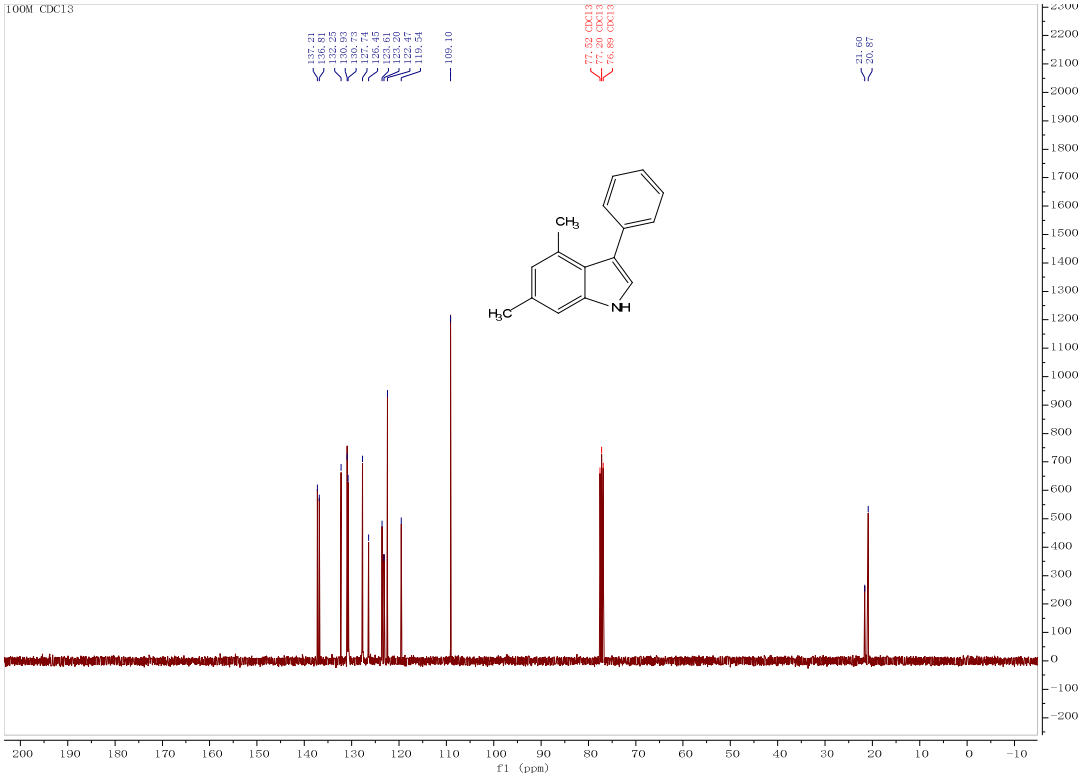
^{13}C NMR spectrum of Compound 4k (DMSO-d_6, 100 MHz)



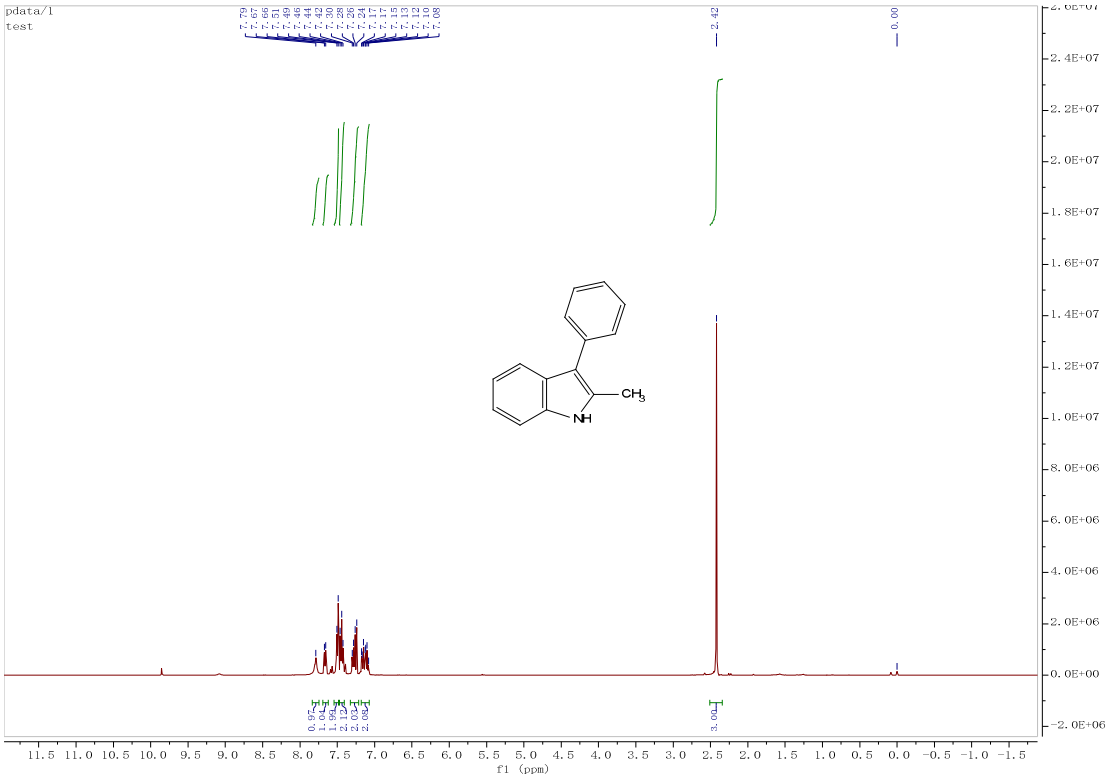
^{1}H NMR spectrum of Compound 4l ($CDCl_3$, 400 MHz)



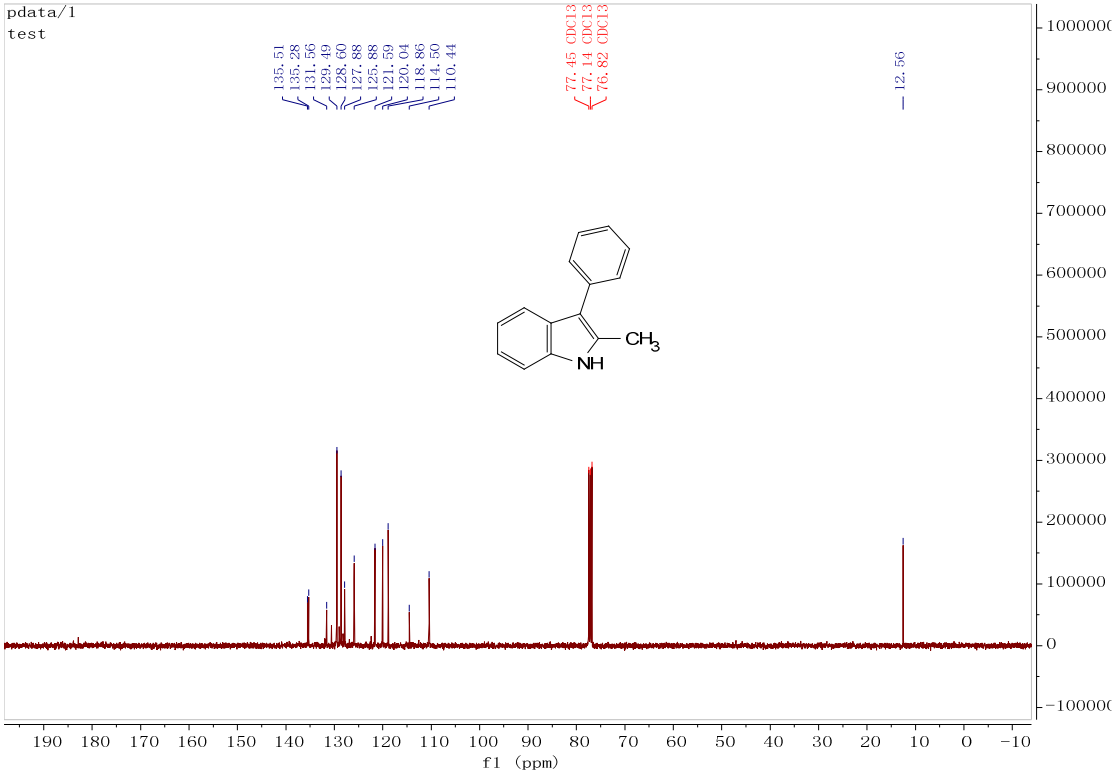
^{13}C NMR spectrum of Compound 4l ($CDCl_3$, 100 MHz)



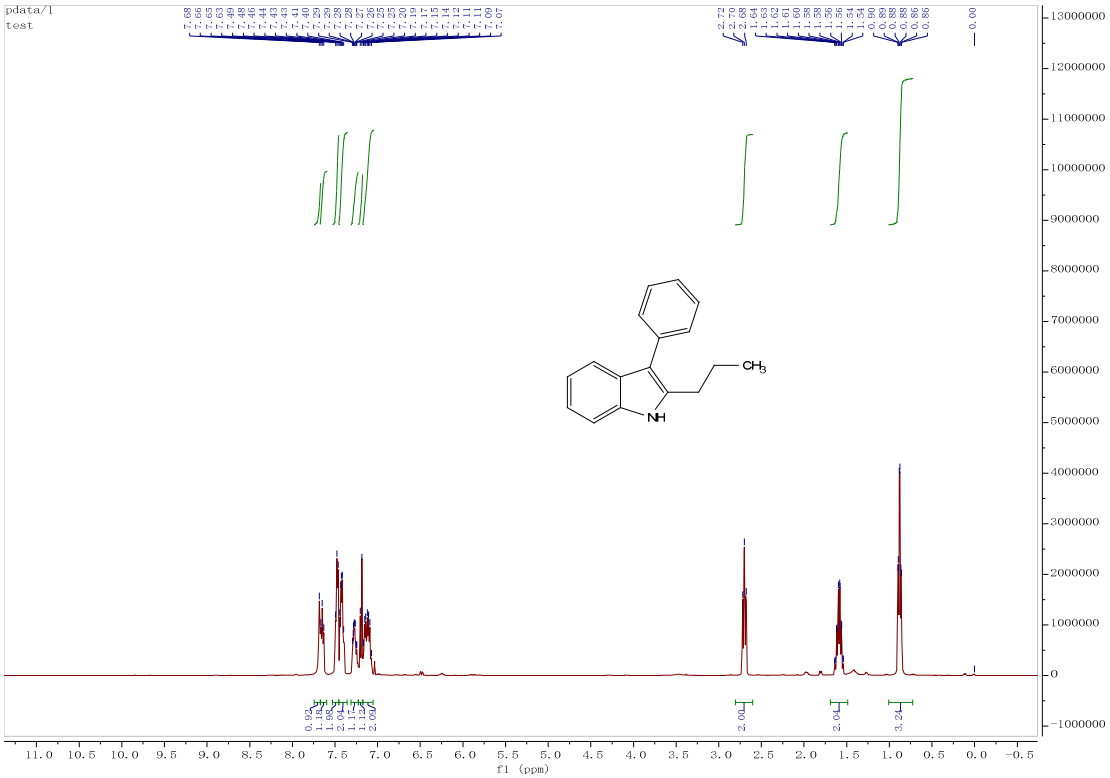
^{1}H NMR spectrum of Compound 4m ($CDCl_3$, 400 MHz)



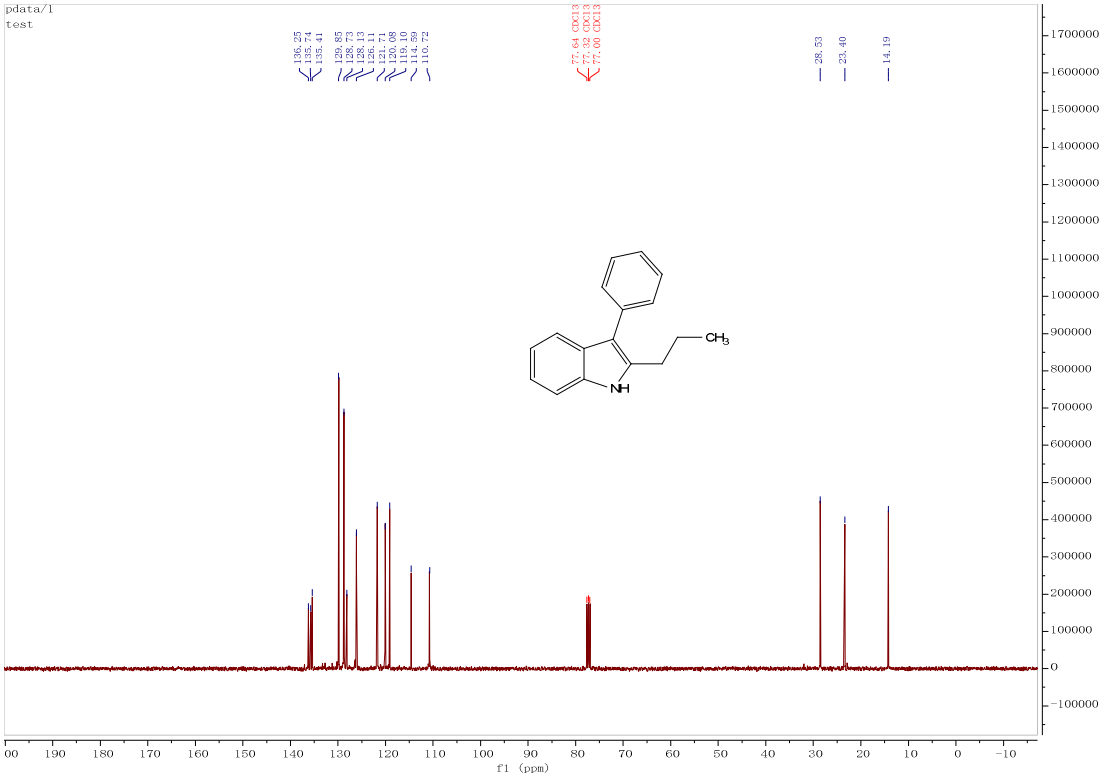
^{13}C NMR spectrum of Compound 4m ($CDCl_3$, 100 MHz)



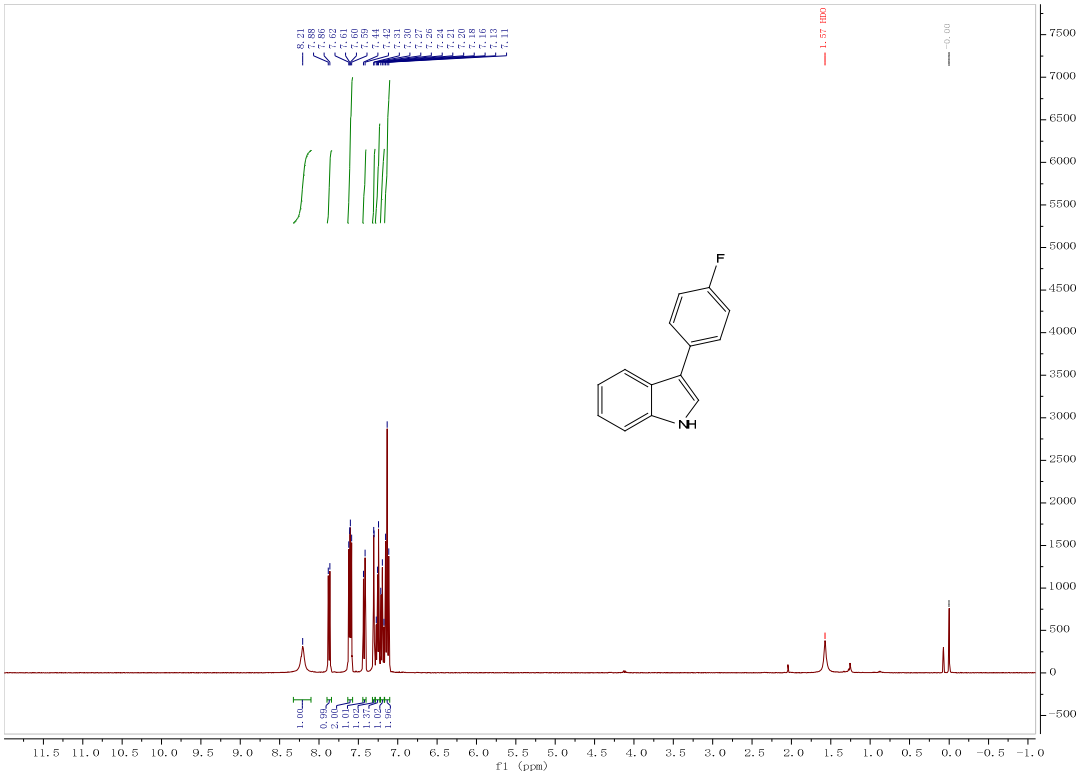
^{1}H NMR spectrum of Compound 4n ($CDCl_3$, 400 MHz)



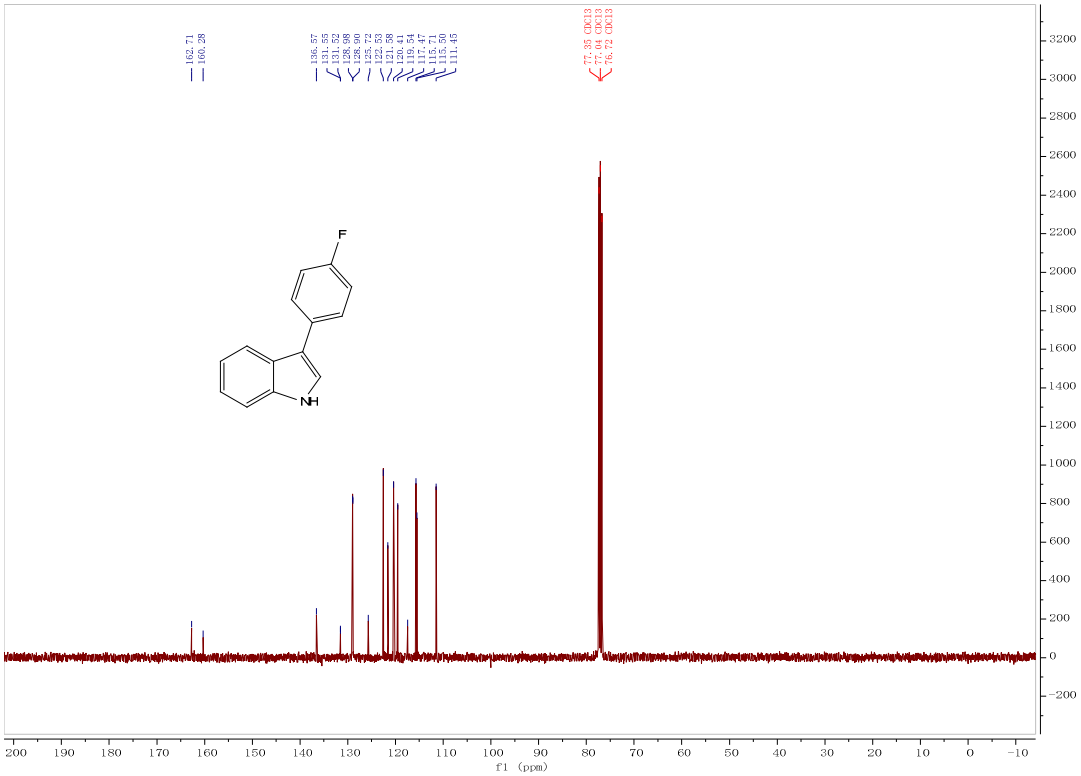
^{13}C NMR spectrum of Compound 4n ($CDCl_3$, 100 MHz)



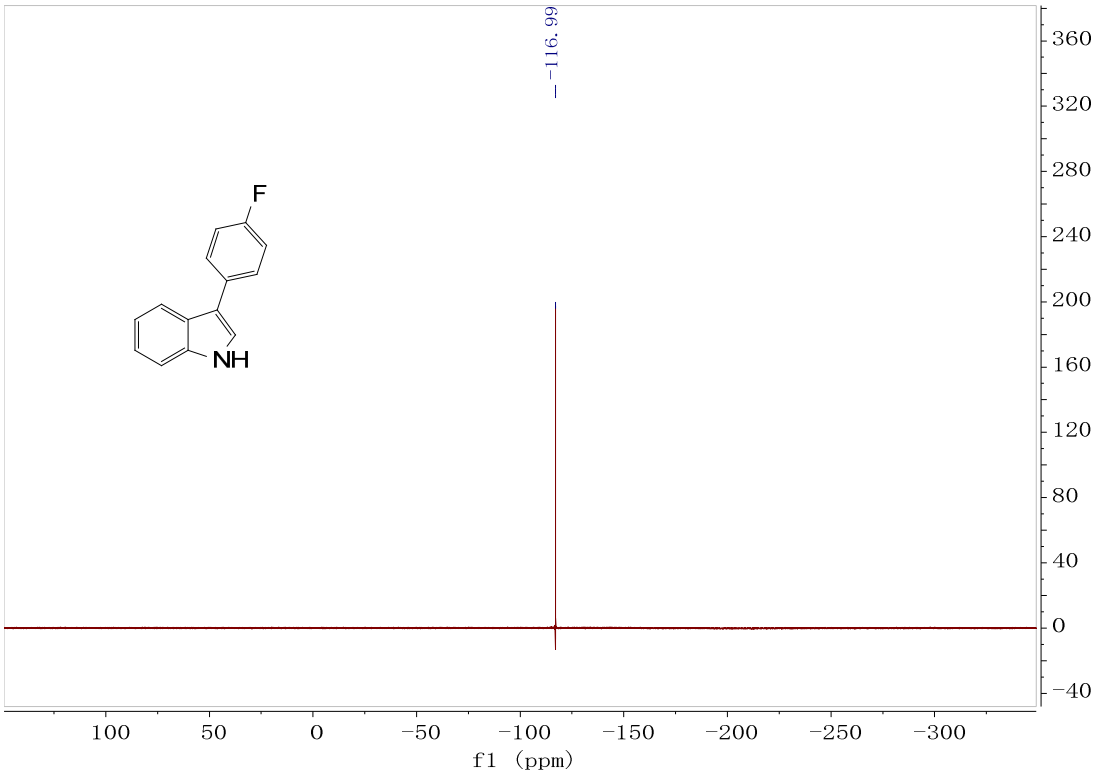
^{1}H NMR spectrum of Compound 4o ($CDCl_3$, 400 MHz)



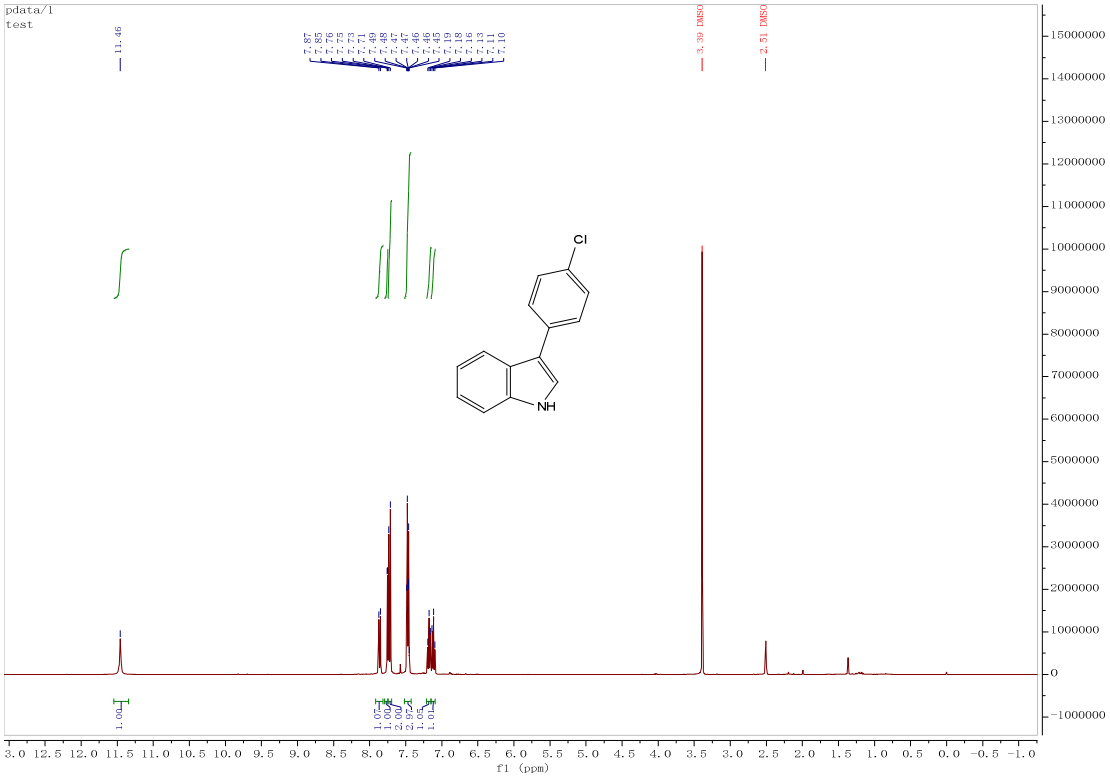
^{13}C NMR spectrum of Compound 4o ($CDCl_3$, 100 MHz)



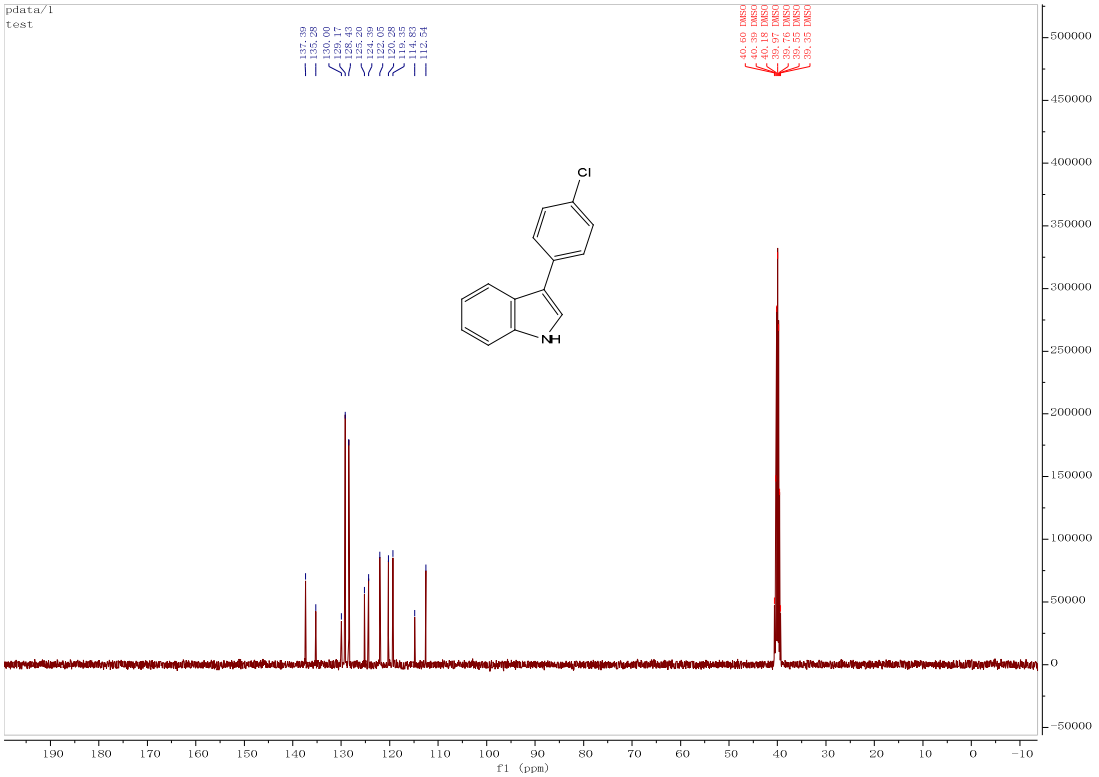
^{19}F NMR spectrum of Compound 4o ($CDCl_3$, 376 MHz)



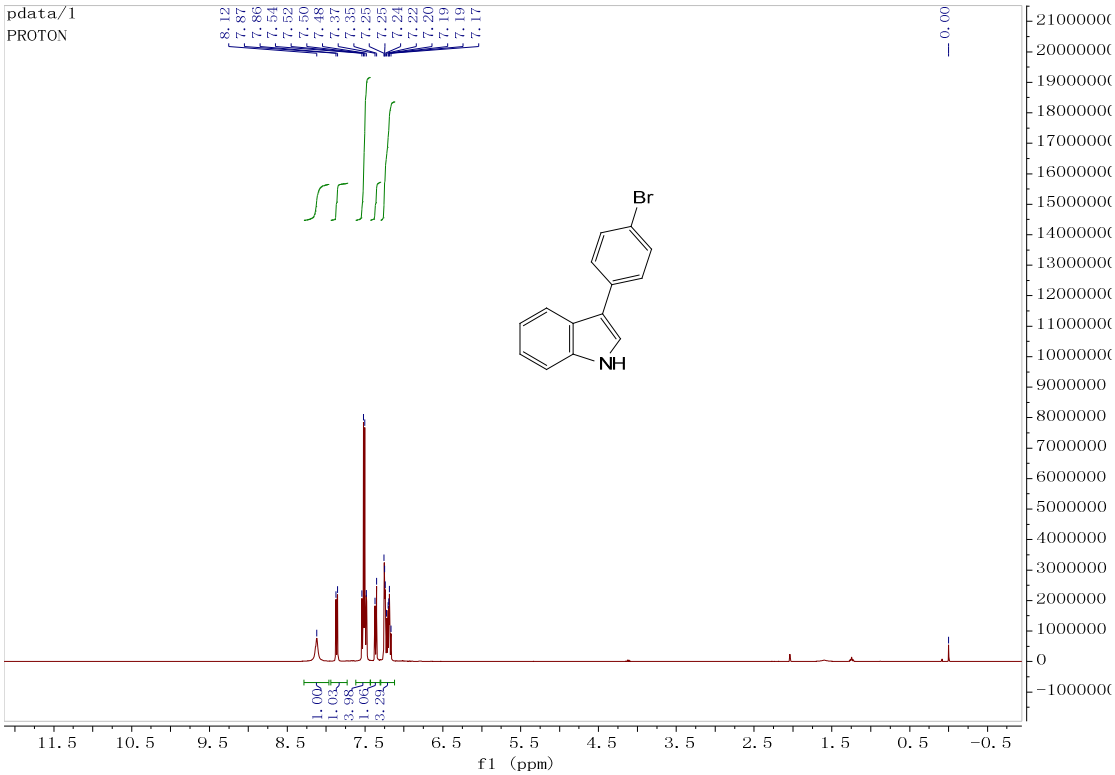
^{1}H NMR spectrum of Compound 4p (DMSO-d_6, 400 MHz)



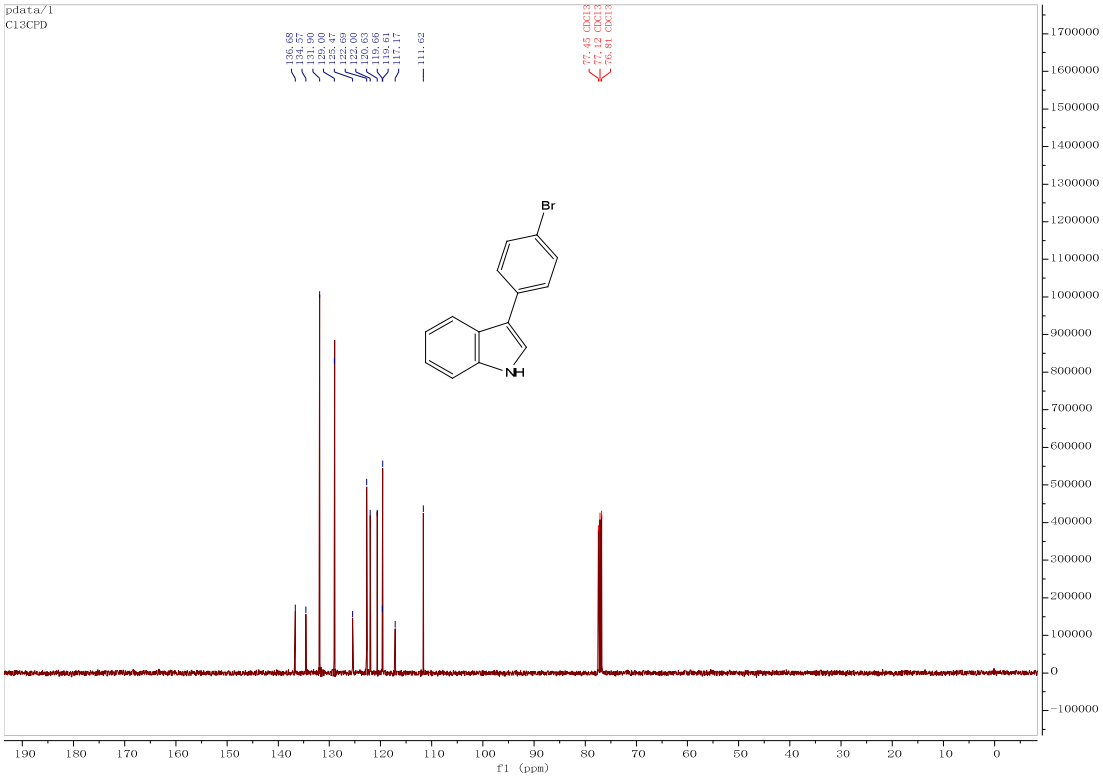
^{13}C NMR spectrum of Compound 4p (DMSO-d_6, 100 MHz)



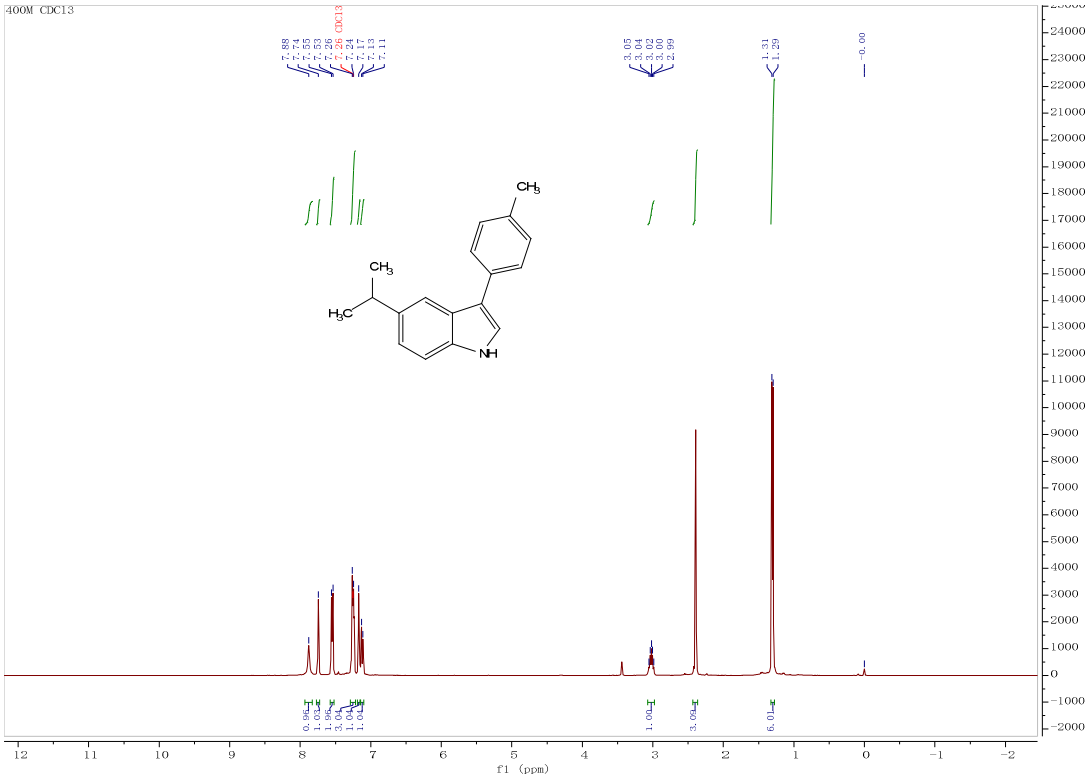
^{1}H NMR spectrum of Compound 4q ($CDCl_3$, 400 MHz)



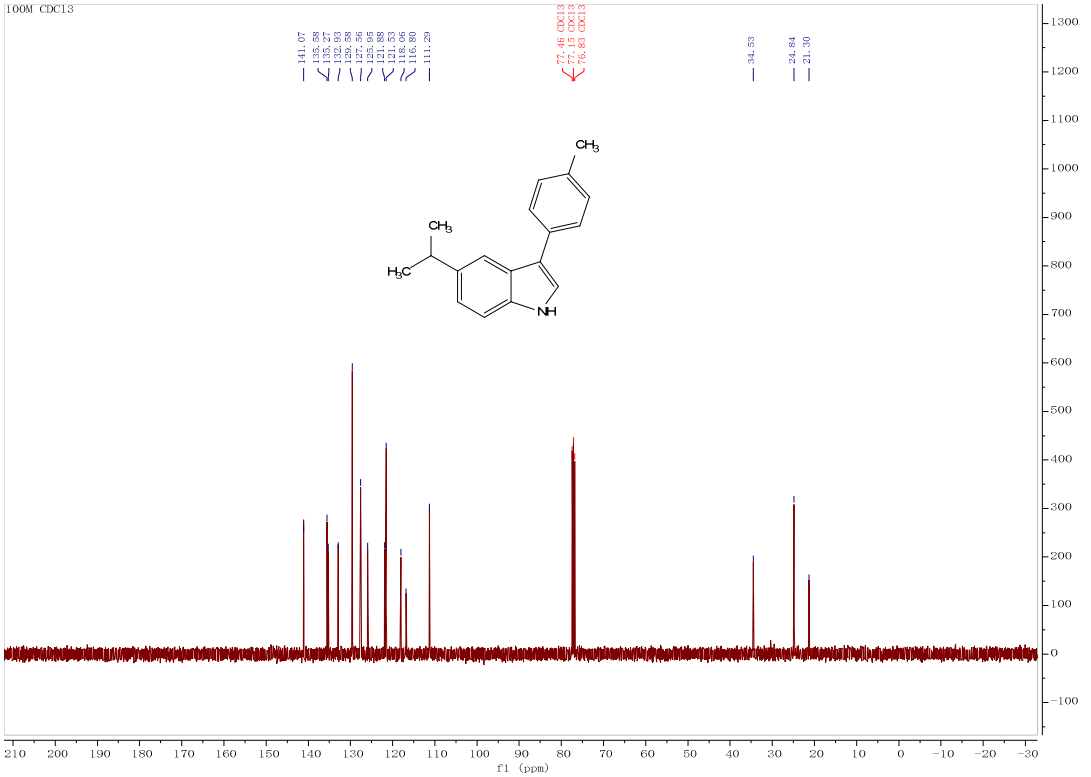
^{13}C NMR spectrum of Compound 4q ($CDCl_3$, 100 MHz)



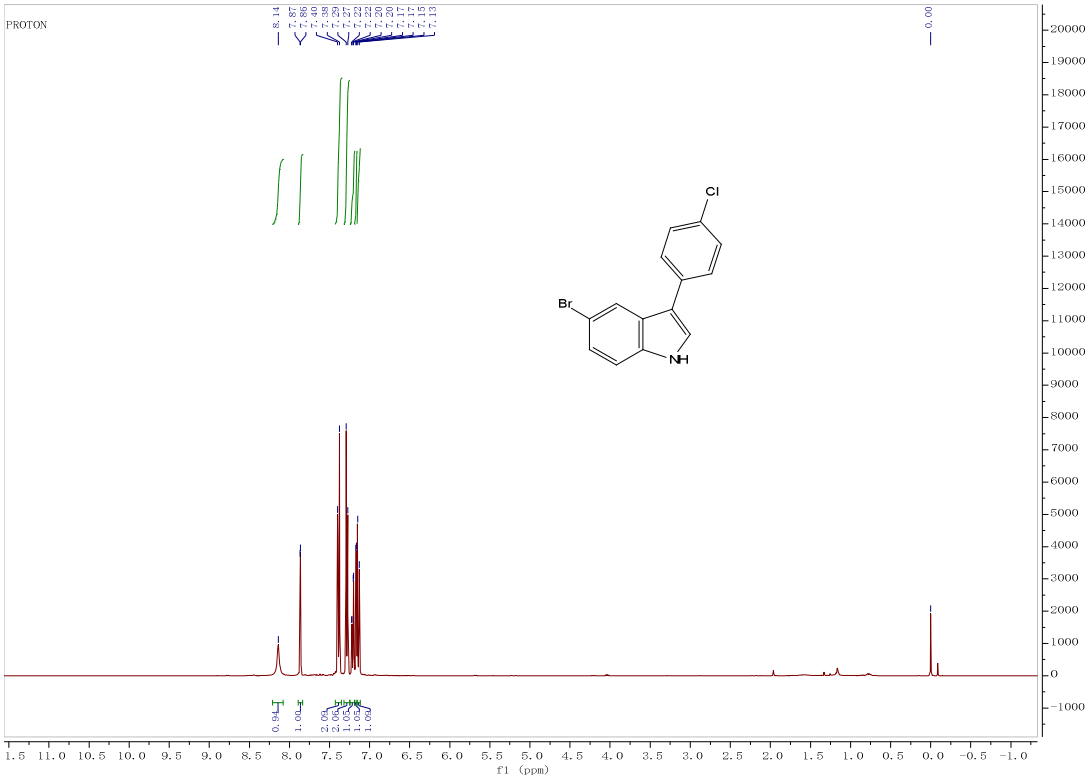
^{1}H NMR spectrum of Compound 4r ($CDCl_3$, 400 MHz)



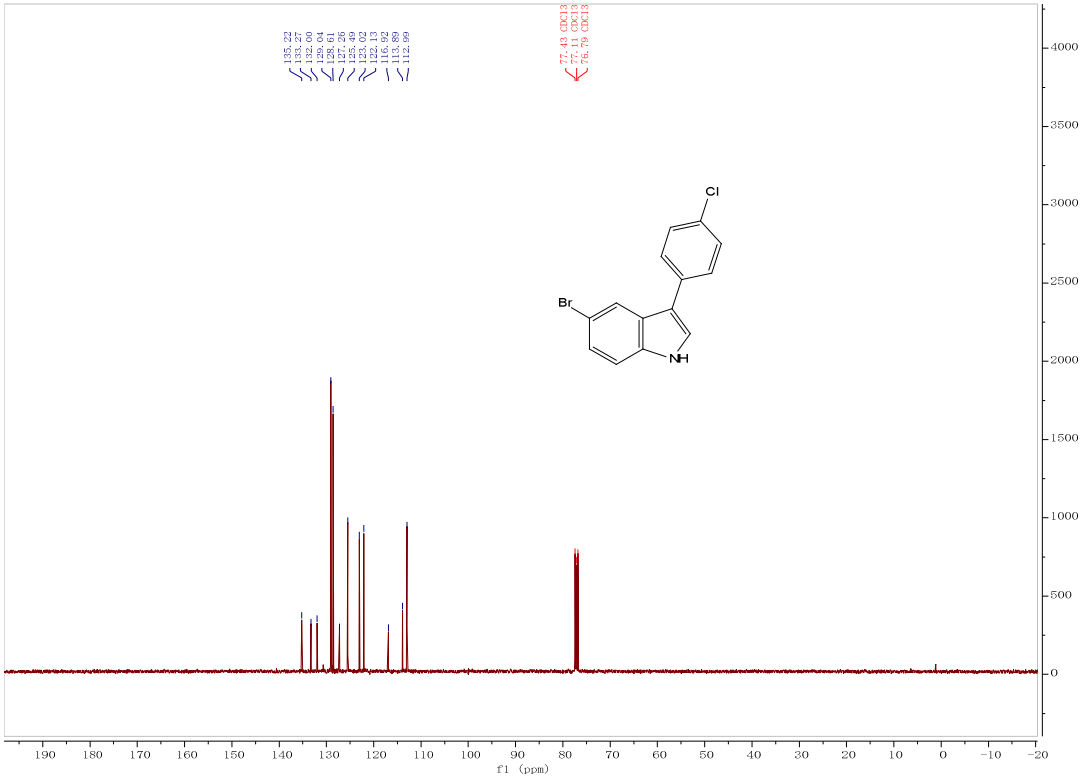
^{13}C NMR spectrum of Compound 4r ($CDCl_3$, 100 MHz)



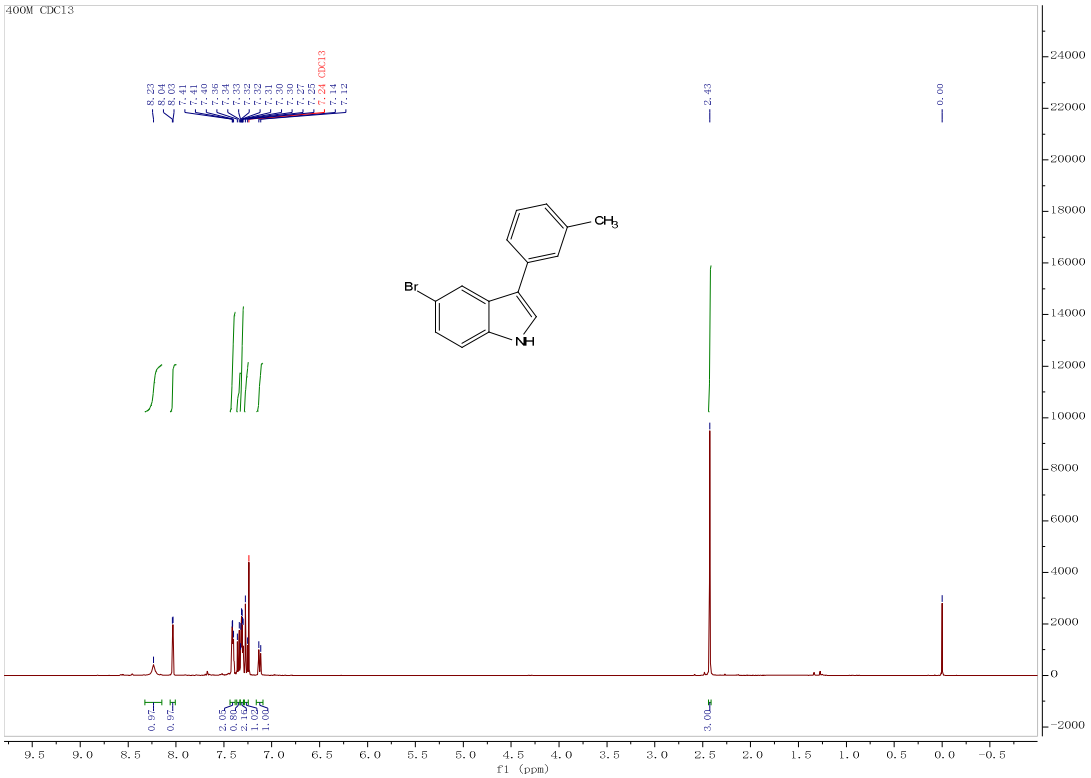
^{1}H NMR spectrum of Compound 4s ($CDCl_3$, 400 MHz)



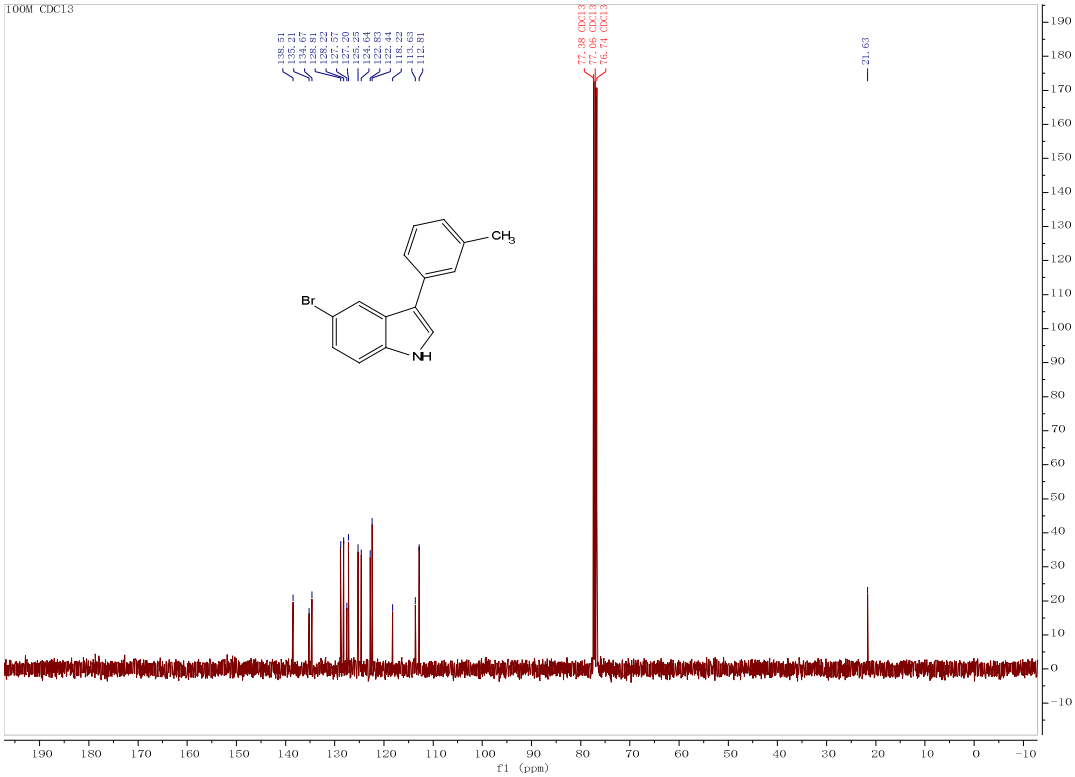
^{13}C NMR spectrum of Compound 4s ($CDCl_3$, 100 MHz)



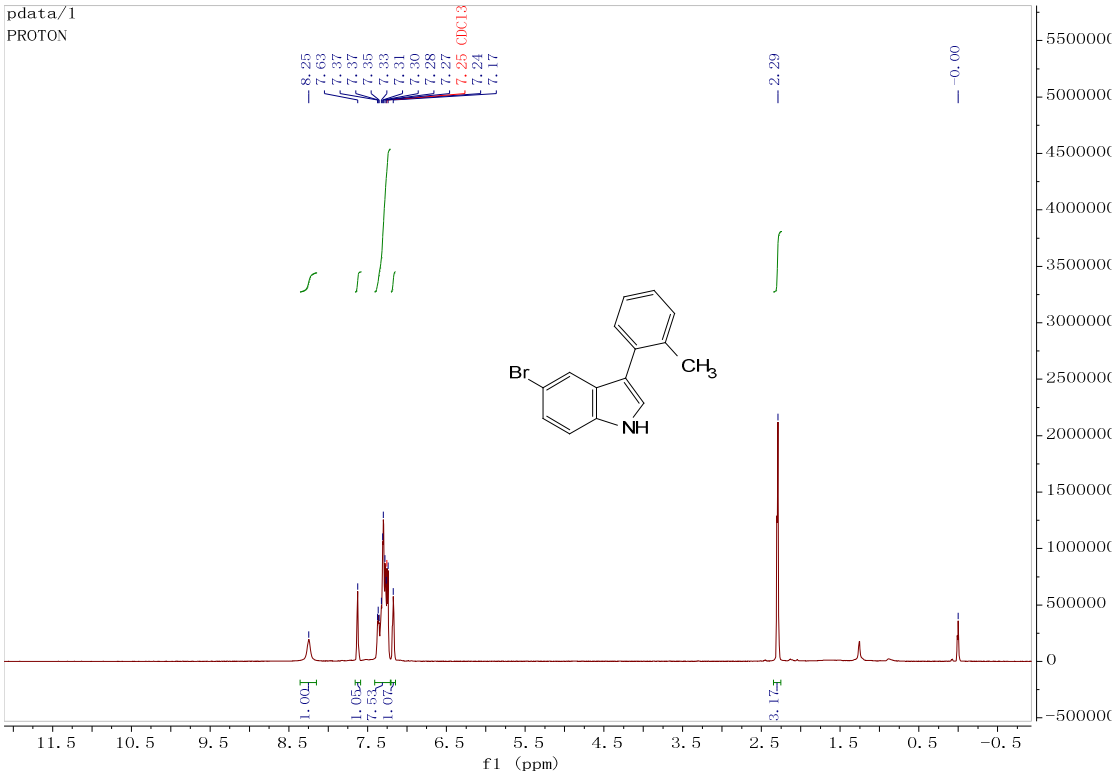
^{1}H NMR spectrum of Compound 4t ($CDCl_3$, 400 MHz)



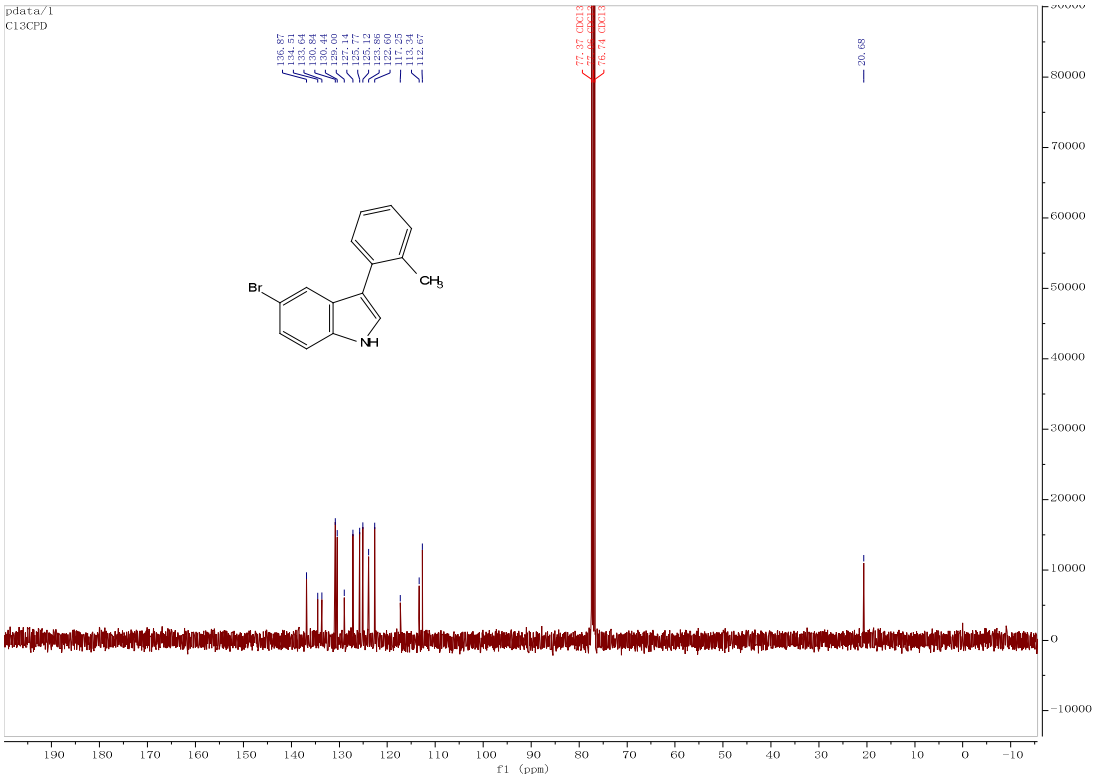
^{13}C NMR spectrum of Compound 4t ($CDCl_3$, 100 MHz)



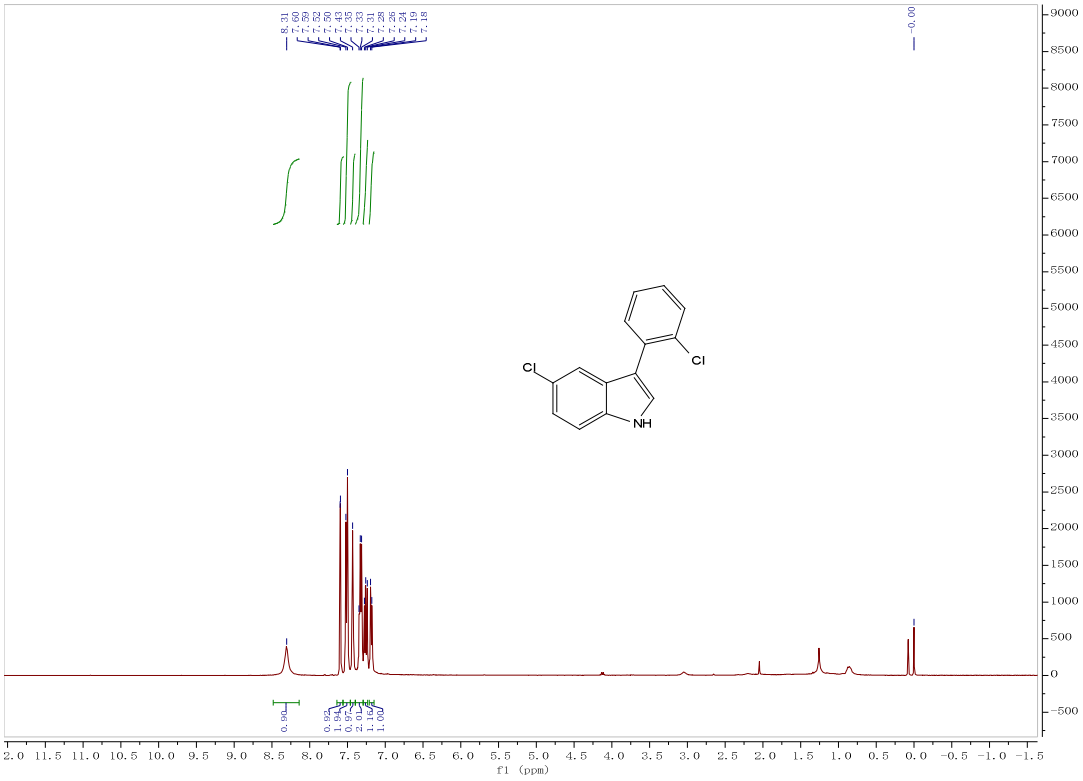
^{1}H NMR spectrum of Compound 4u ($CDCl_3$, 400 MHz)



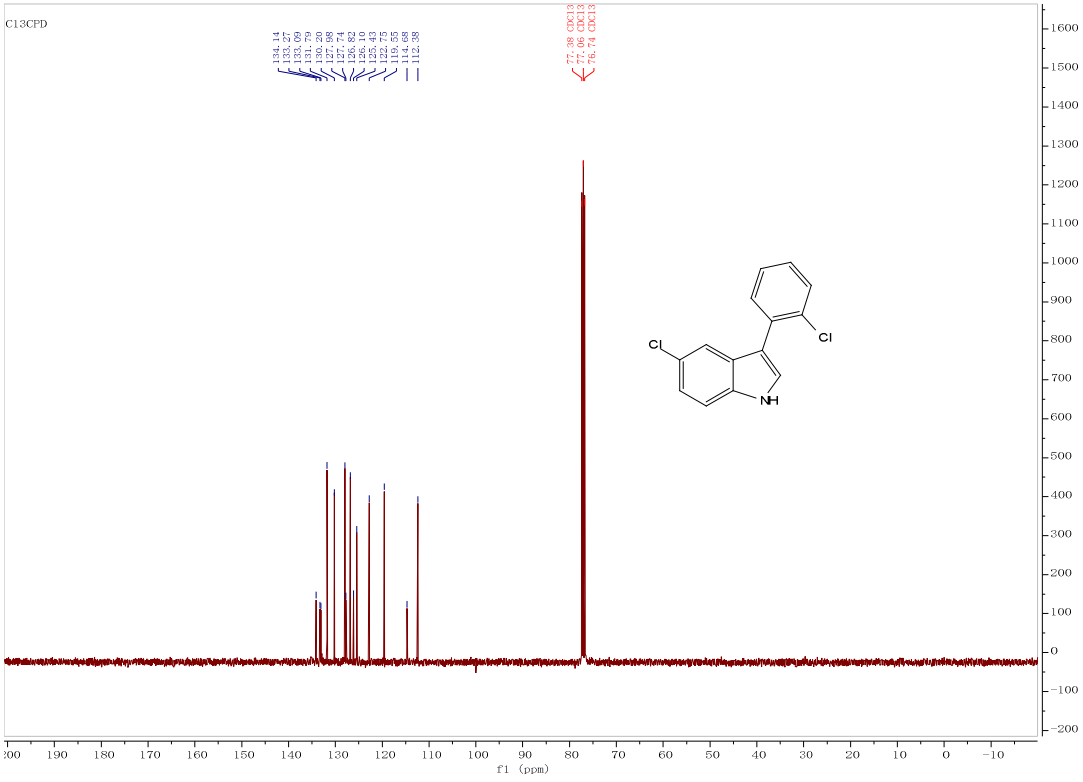
^{13}C NMR spectrum of Compound 4u ($CDCl_3$, 100 MHz)



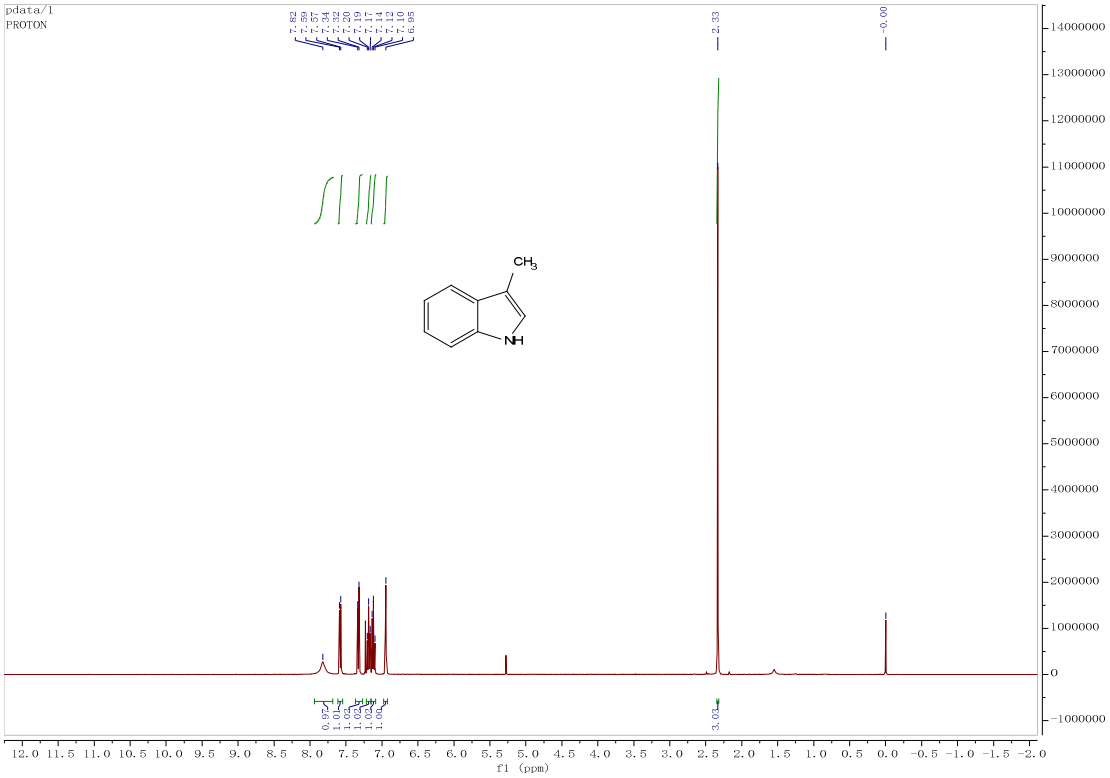
^{1}H NMR spectrum of Compound 4v ($CDCl_3$, 400 MHz)



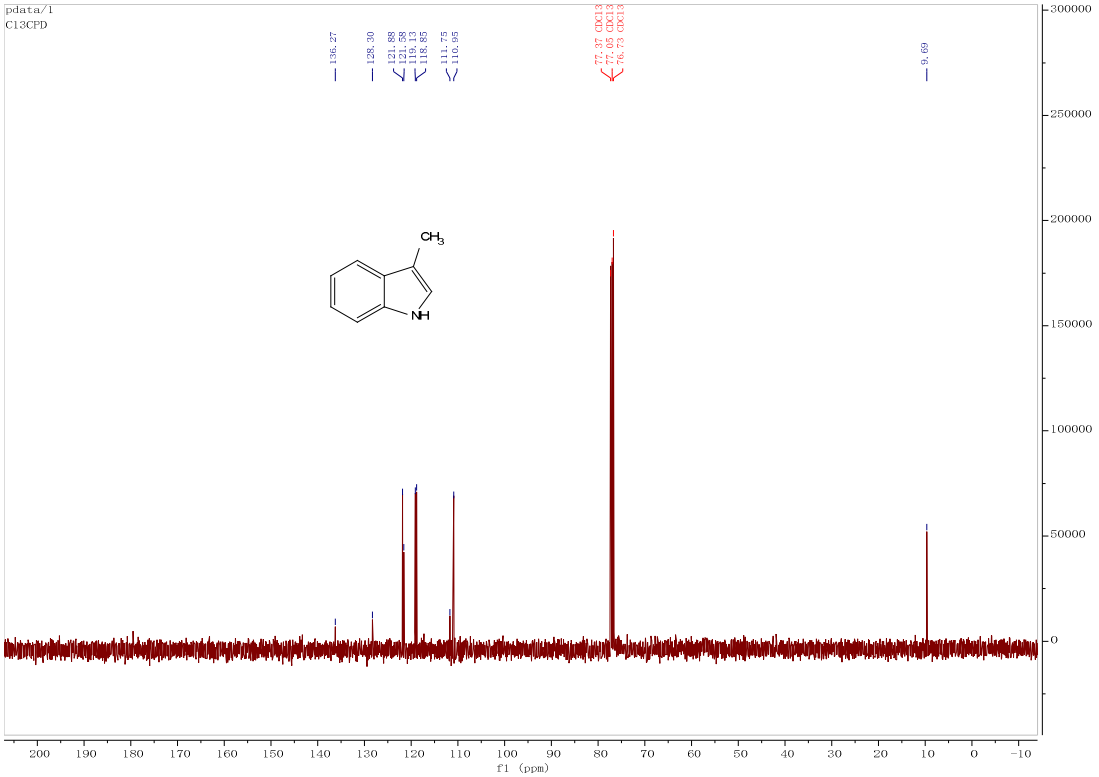
^{13}C NMR spectrum of Compound 4v ($CDCl_3$, 100 MHz)



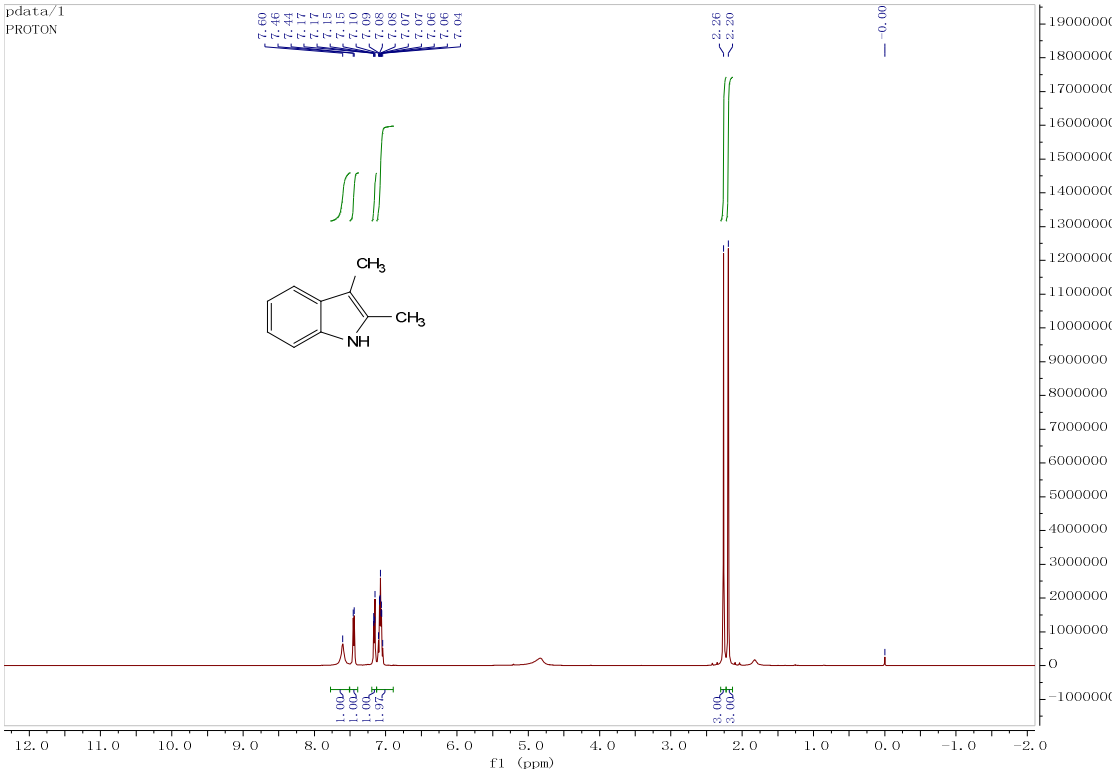
^{1}H NMR spectrum of Compound 4w ($CDCl_3$, 400 MHz)



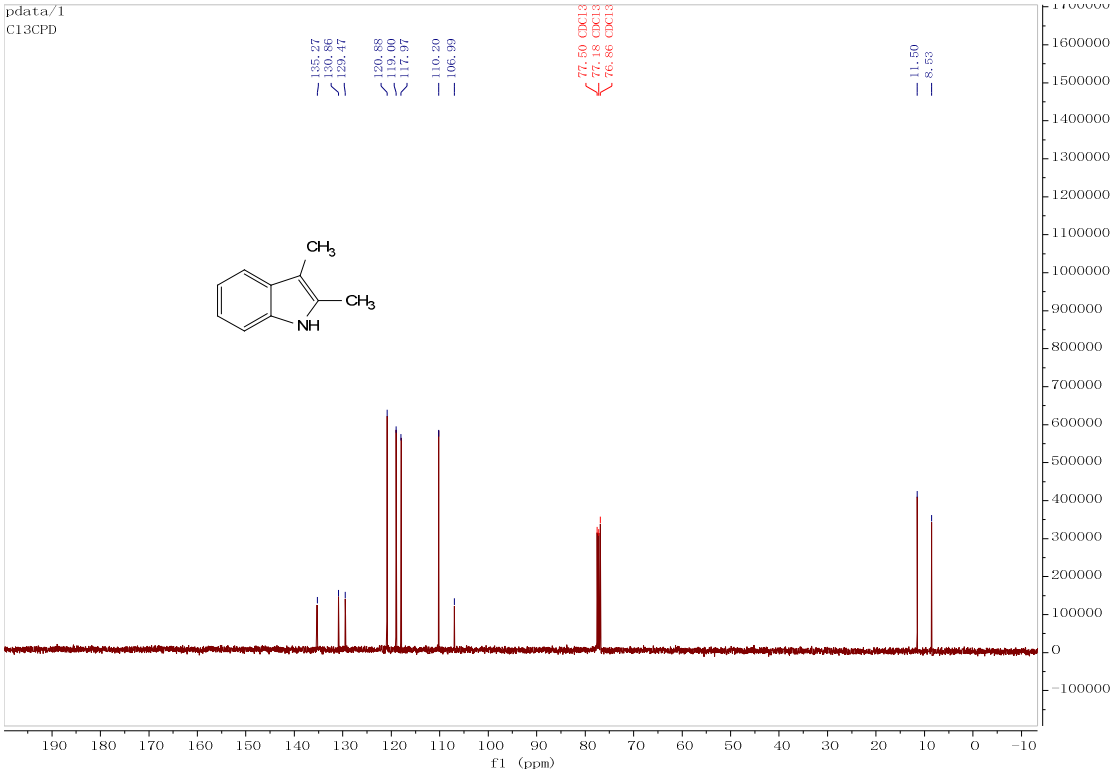
^{13}C NMR spectrum of Compound 4w ($CDCl_3$, 100 MHz)



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

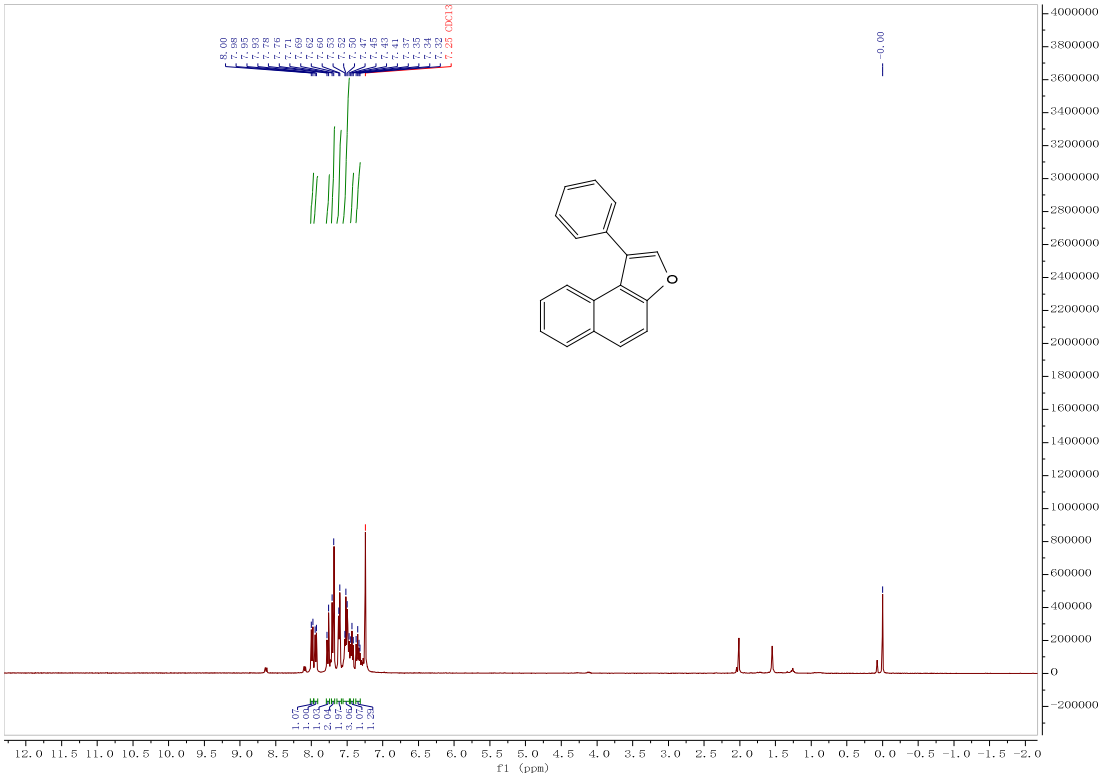


^{13}C NMR spectrum of Compound 4x ($CDCl_3$, 100 MHz)

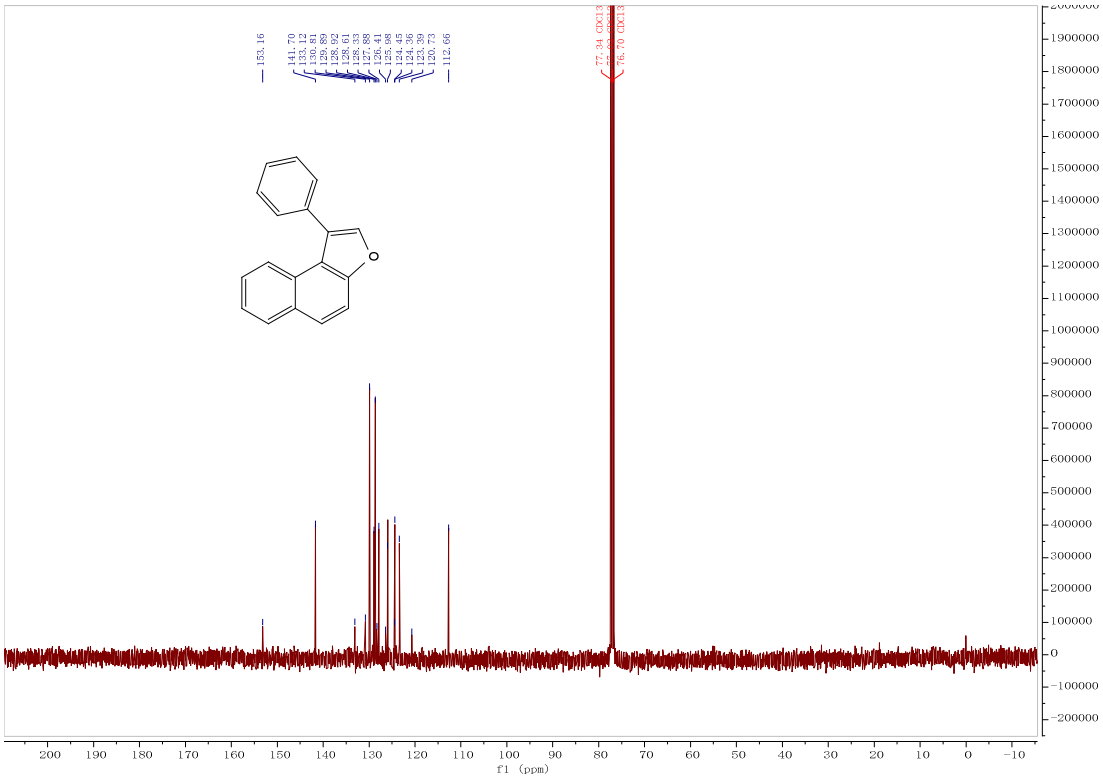


16. Spectroscopic data for benzofuran 6

^{1}H NMR spectrum of Compound 6 ($CDCl_3$, 400 MHz)

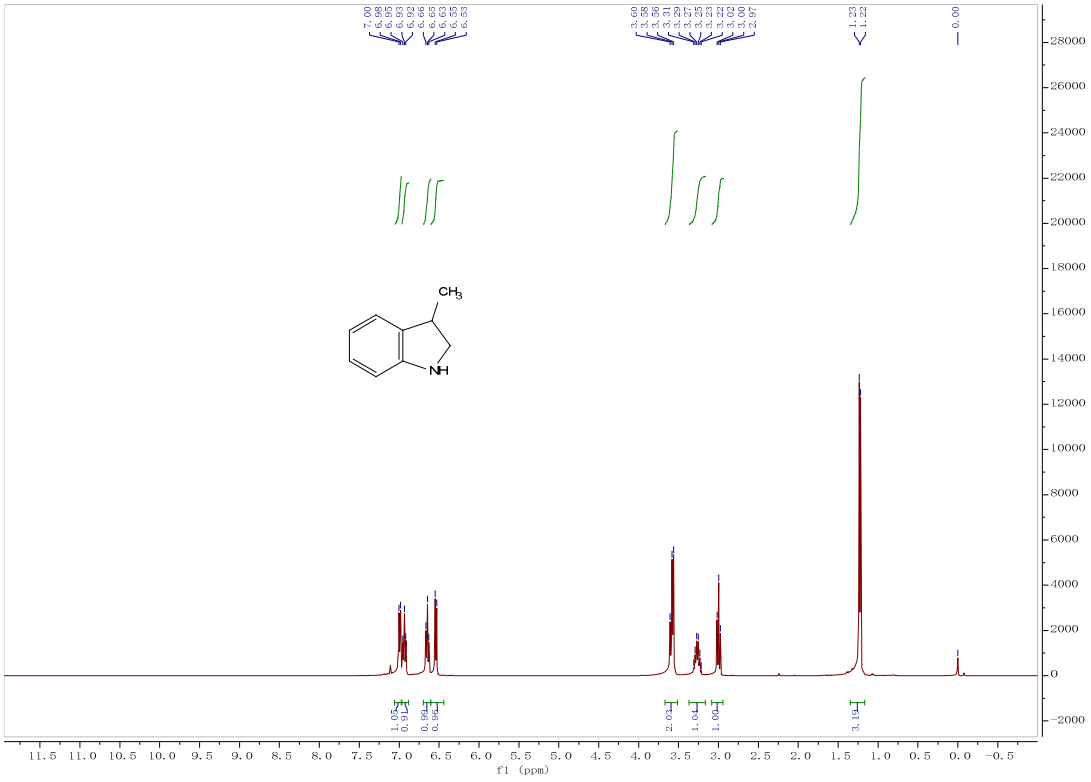


^{13}C NMR spectrum of Compound 6 ($CDCl_3$, 100 MHz)

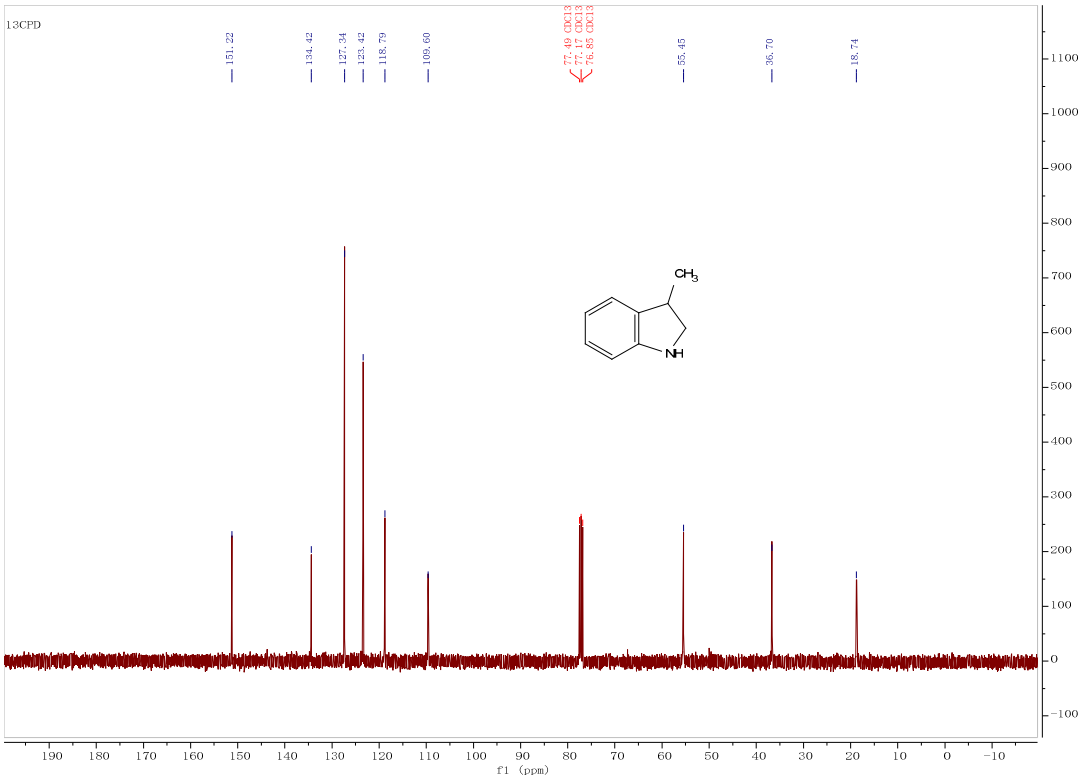


17. Spectroscopic data for compounds 7-14

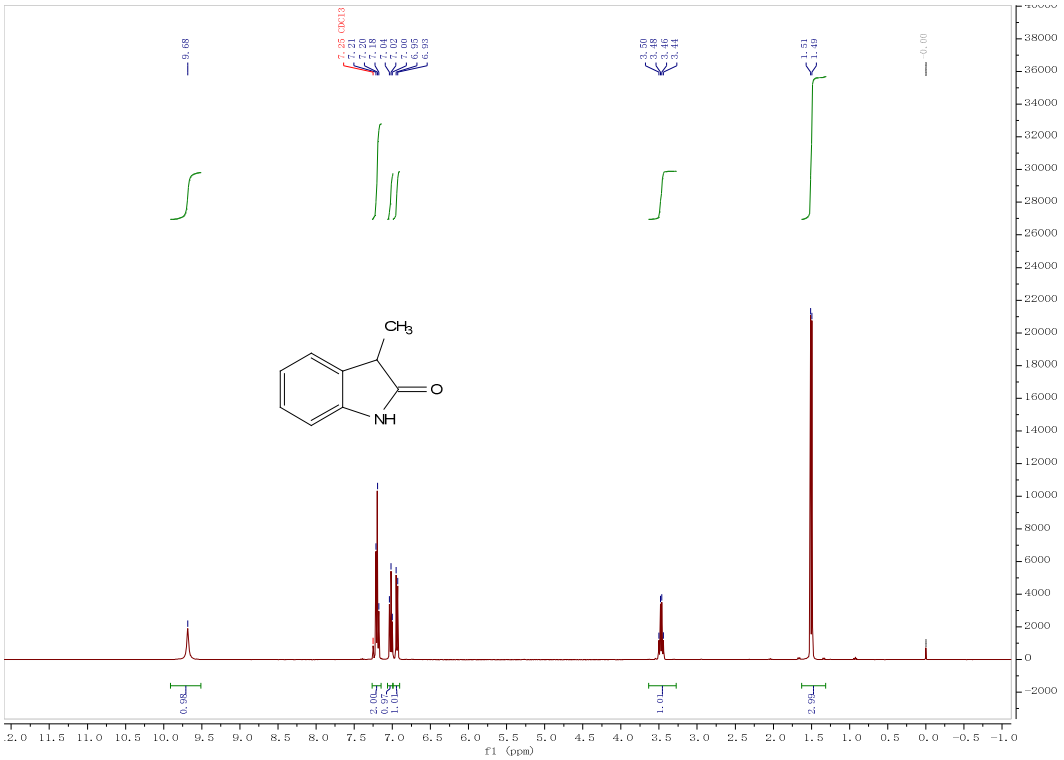
^{1}H NMR spectrum of Compound 7 ($CDCl_3$, 400 MHz)



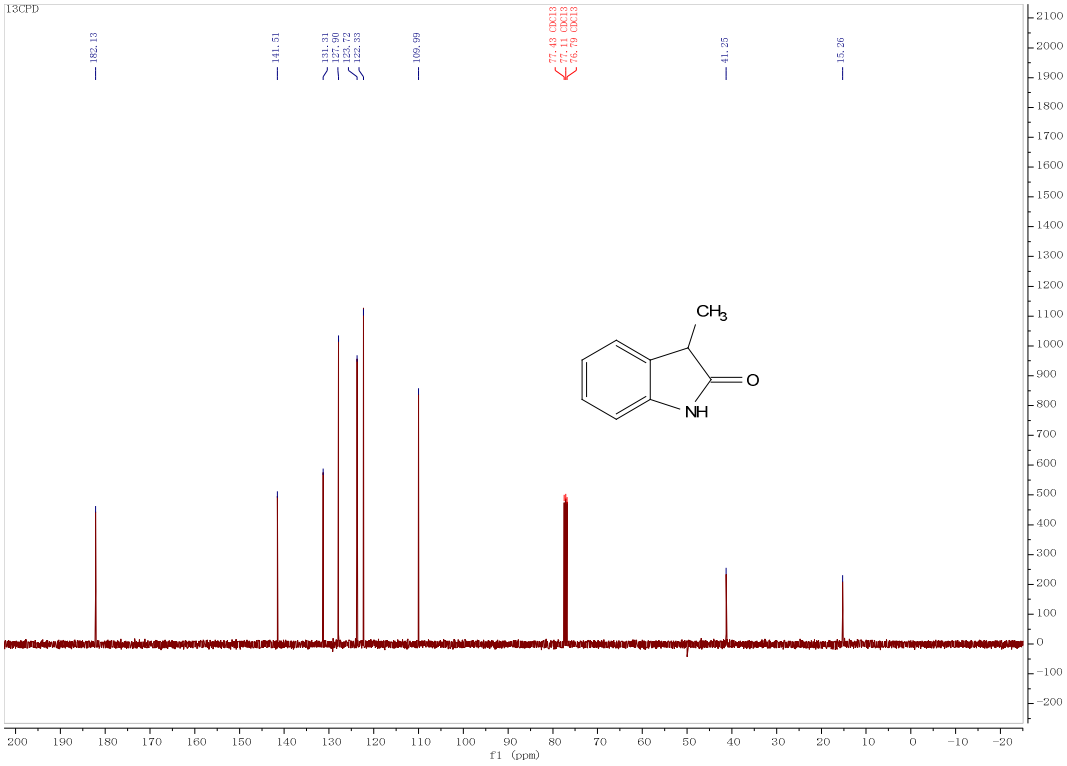
^{13}C NMR spectrum of Compound 7 ($CDCl_3$, 100 MHz)



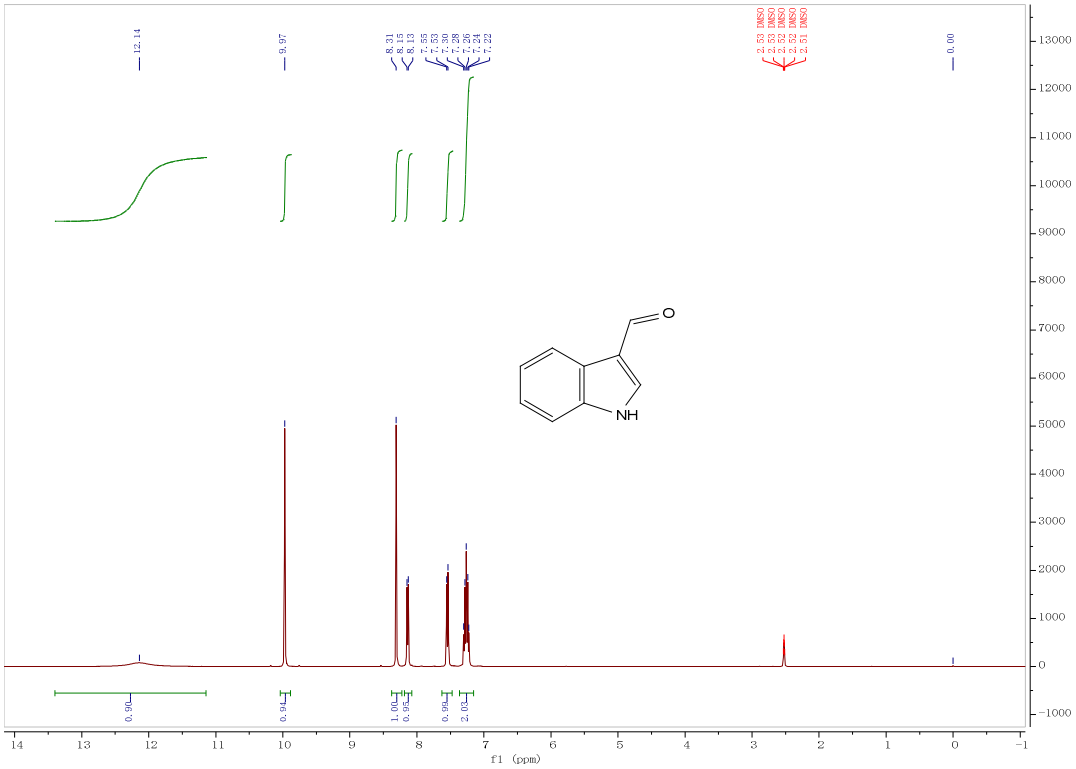
^{1}H NMR spectrum of Compound 8 ($CDCl_3$, 400 MHz)



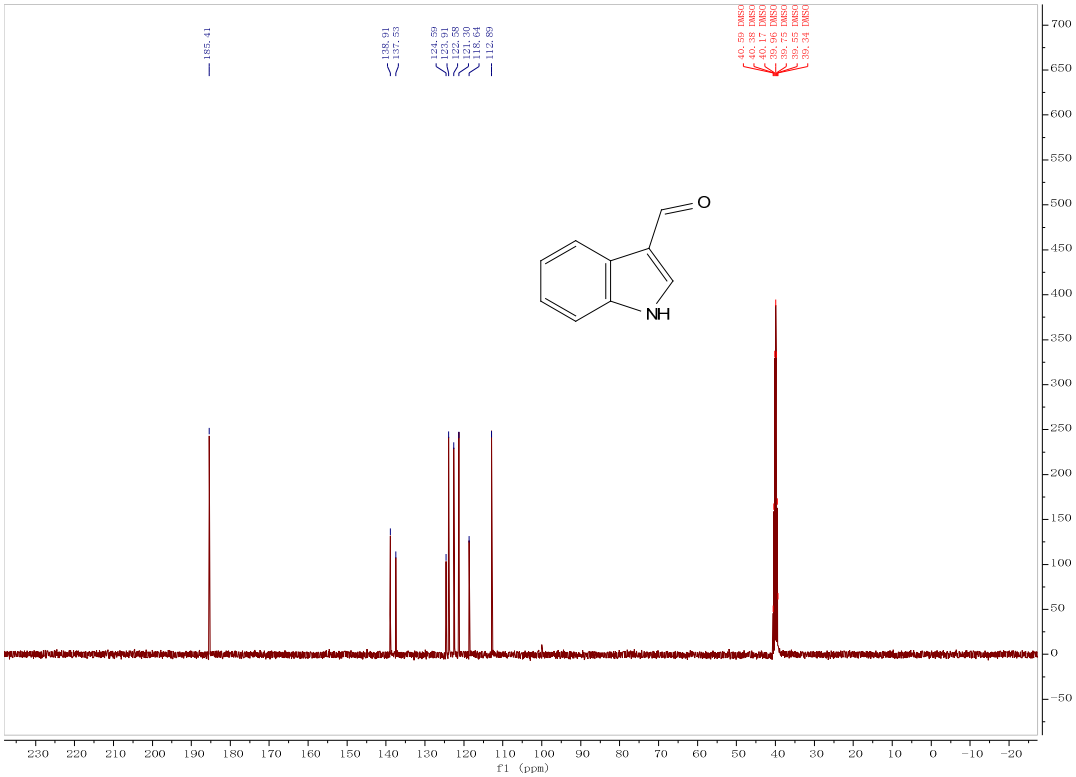
^{13}C NMR spectrum of Compound 8 ($CDCl_3$, 100 MHz)



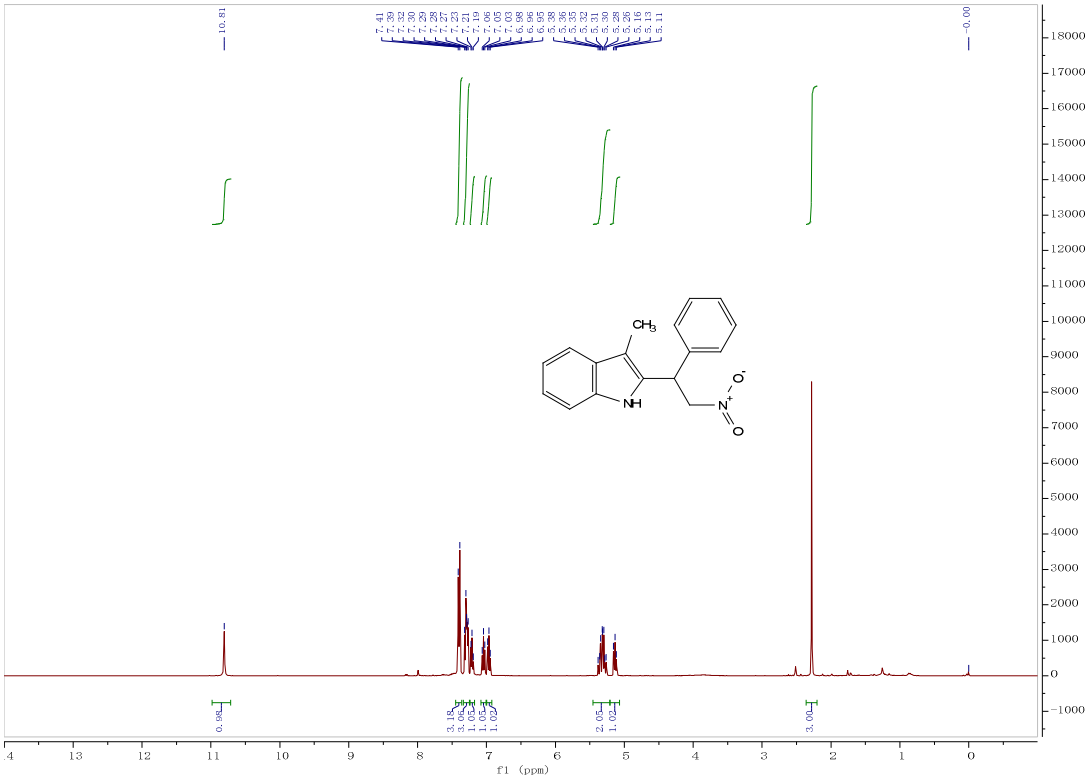
^{1}H NMR spectrum of Compound 9 (DMSO-d_6, 400 MHz)



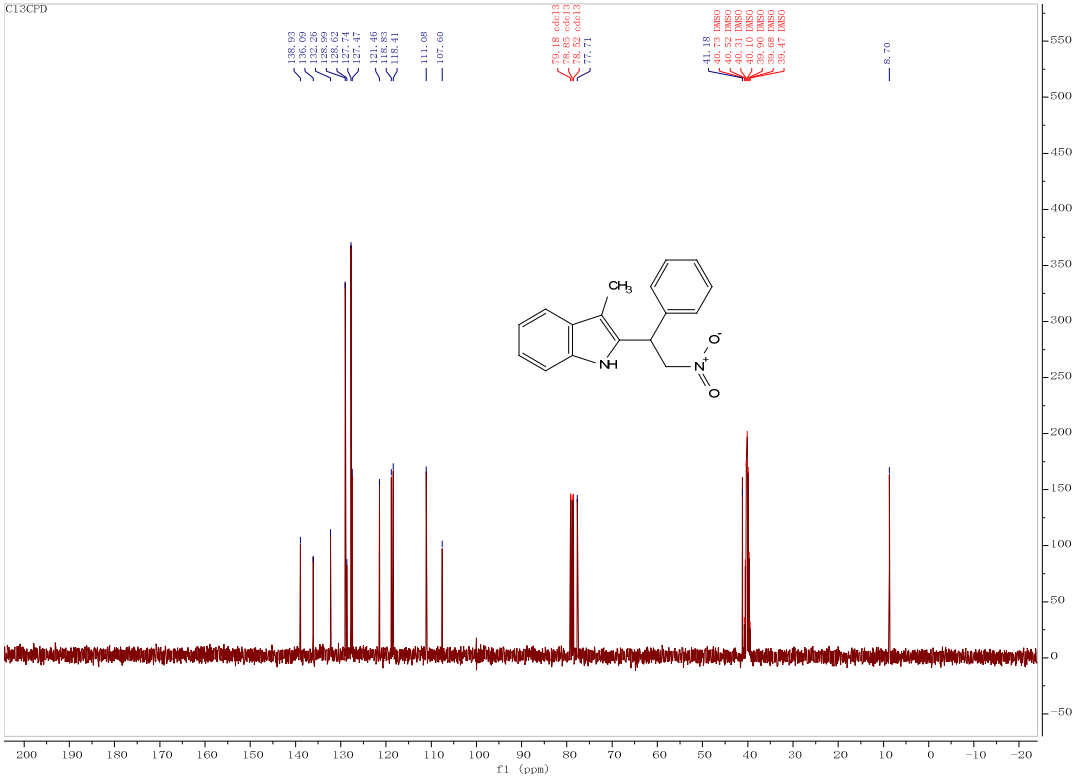
^{13}C NMR spectrum of Compound 9 (DMSO-d_6, 100 MHz)



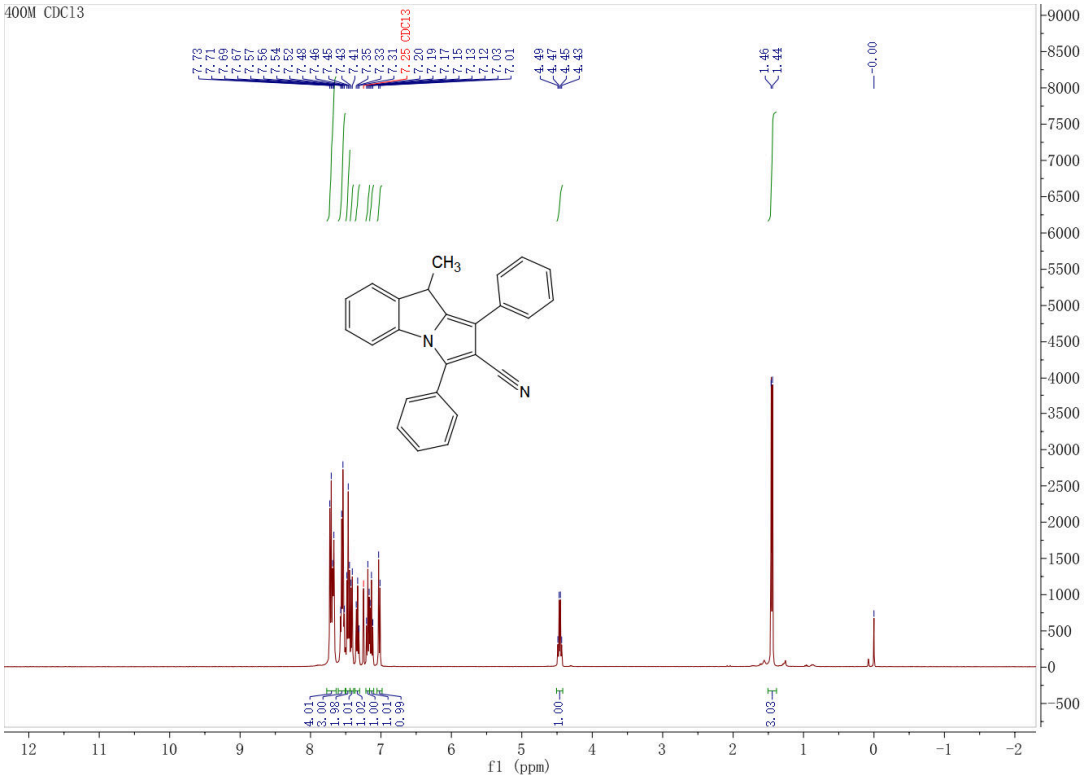
^{1}H NMR spectrum of Compound 10 (DMSO-d_6+ $CDCl_3$ (v/v = 1:3), 400 MHz)



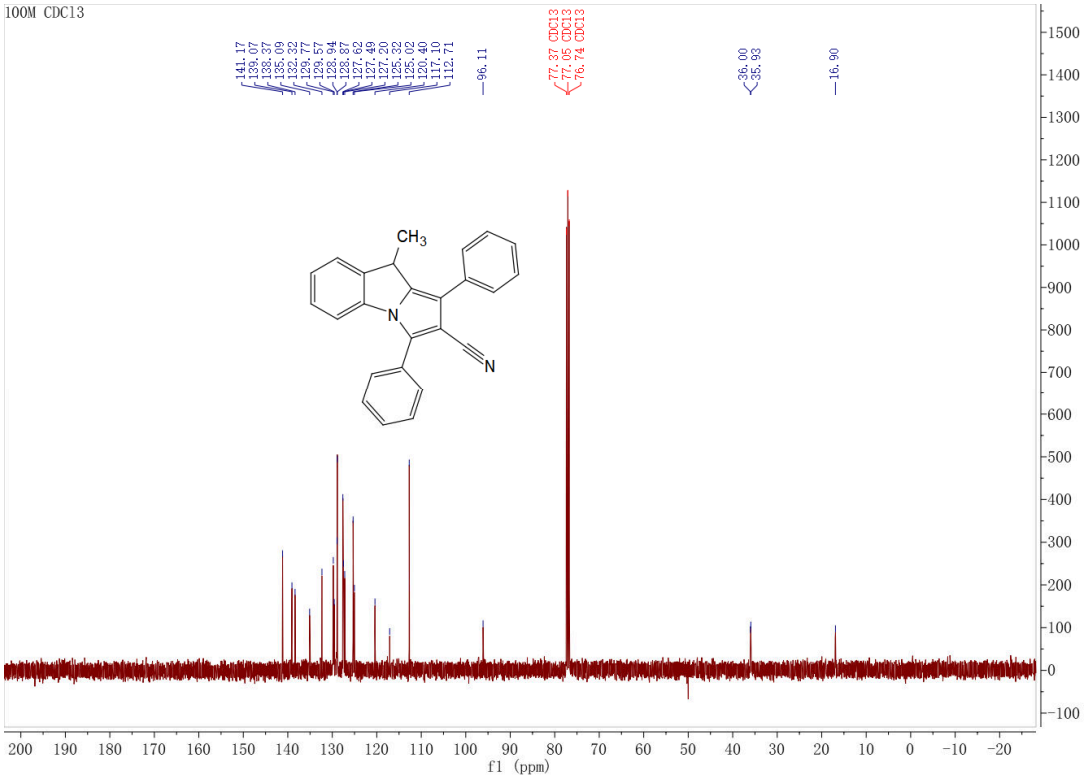
^{13}C NMR spectrum of Compound 10 (DMSO-d_6+ $CDCl_3$ (v/v = 1:3), 100 MHz)



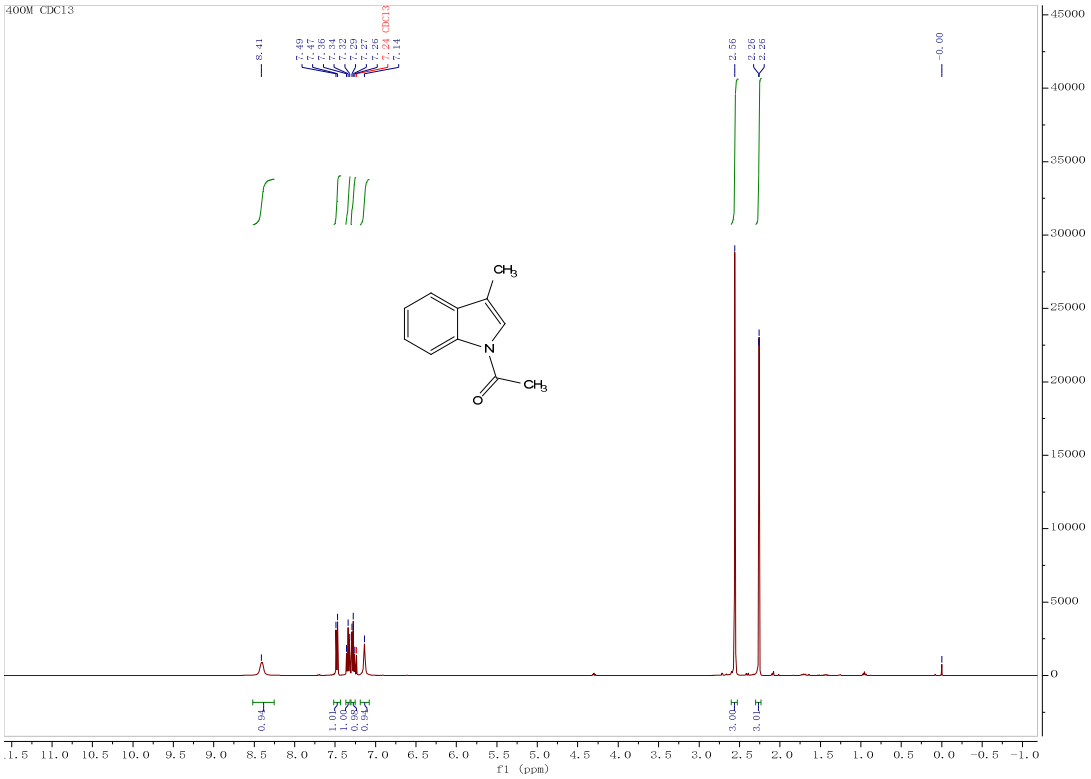
^{1}H NMR spectrum of Compound 11 ($CDCl_3$, 400 MHz)



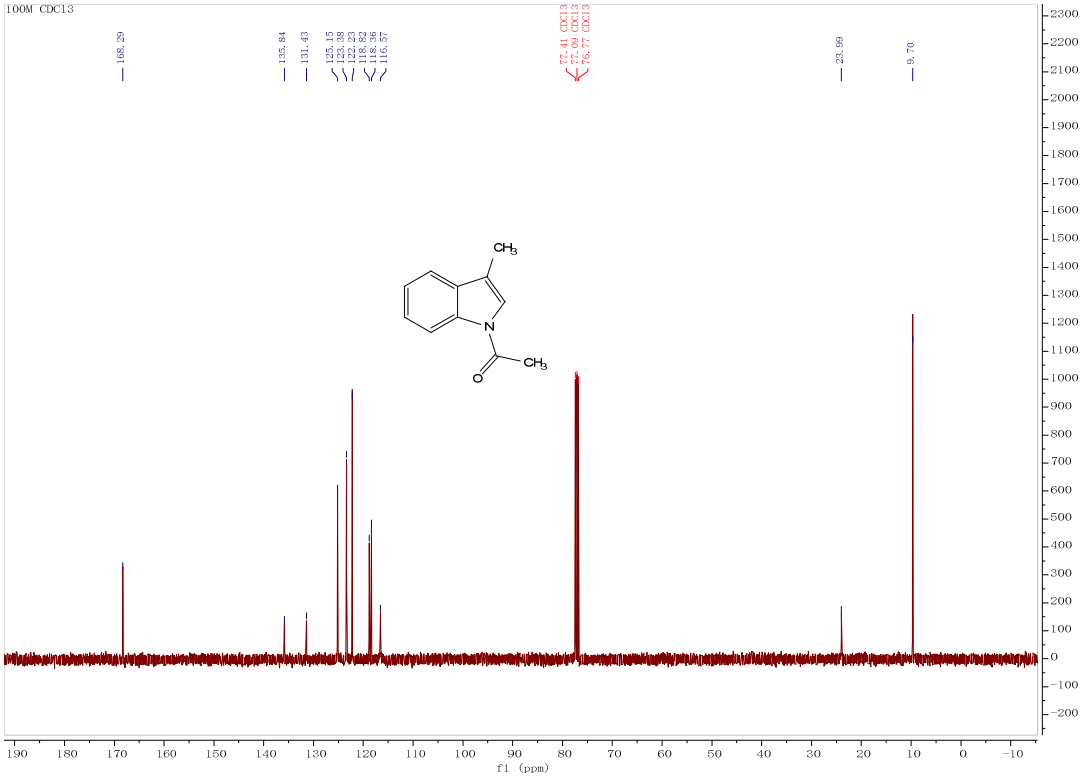
^{13}C NMR spectrum of Compound 11 ($CDCl_3$, 100 MHz)



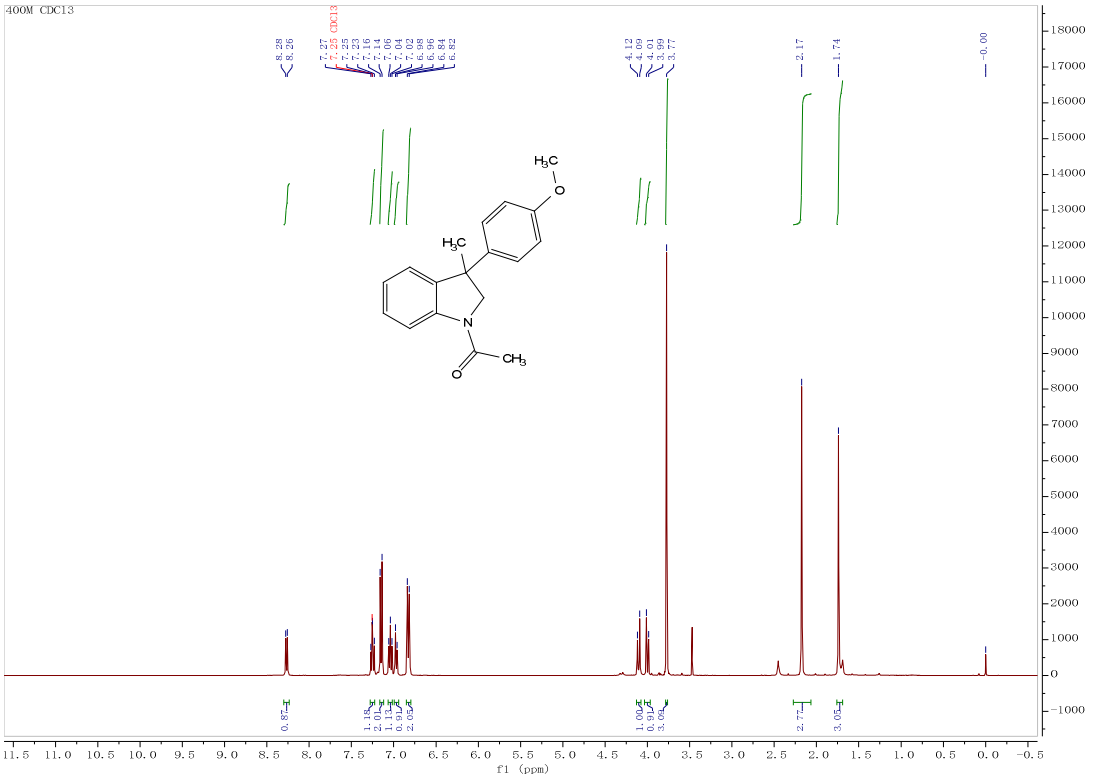
^{1}H NMR spectrum of Compound 12 ($CDCl_3$, 400 MHz)



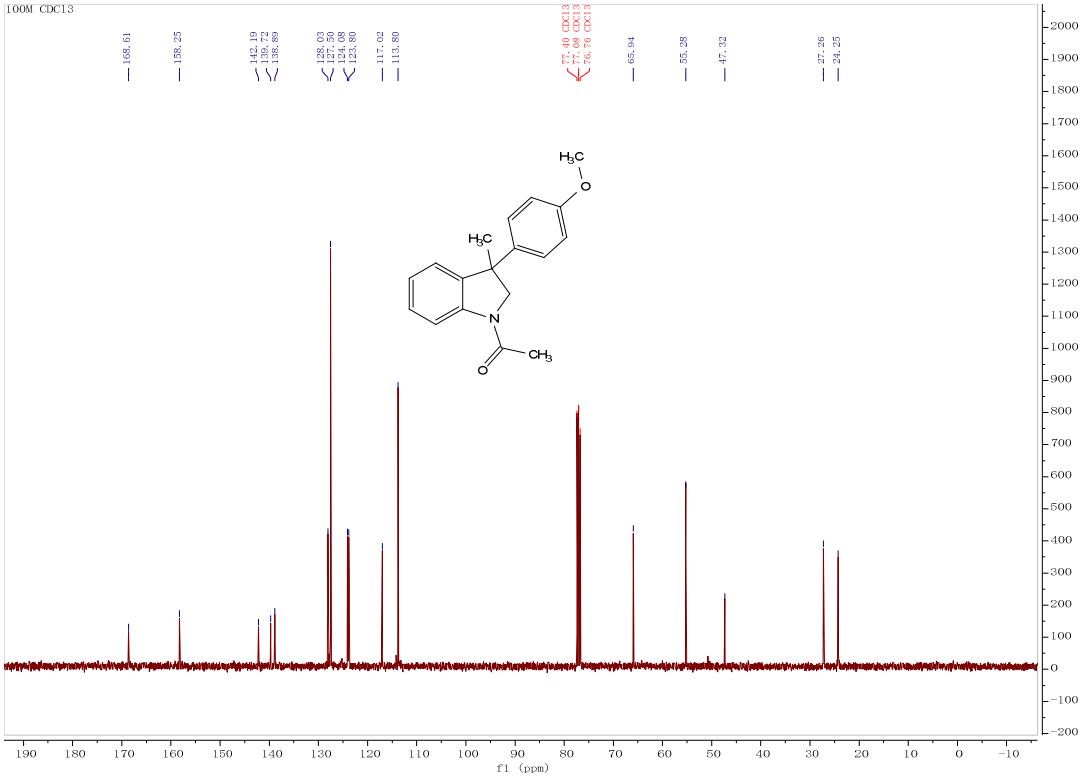
^{13}C NMR spectrum of Compound 12 ($CDCl_3$, 100 MHz)



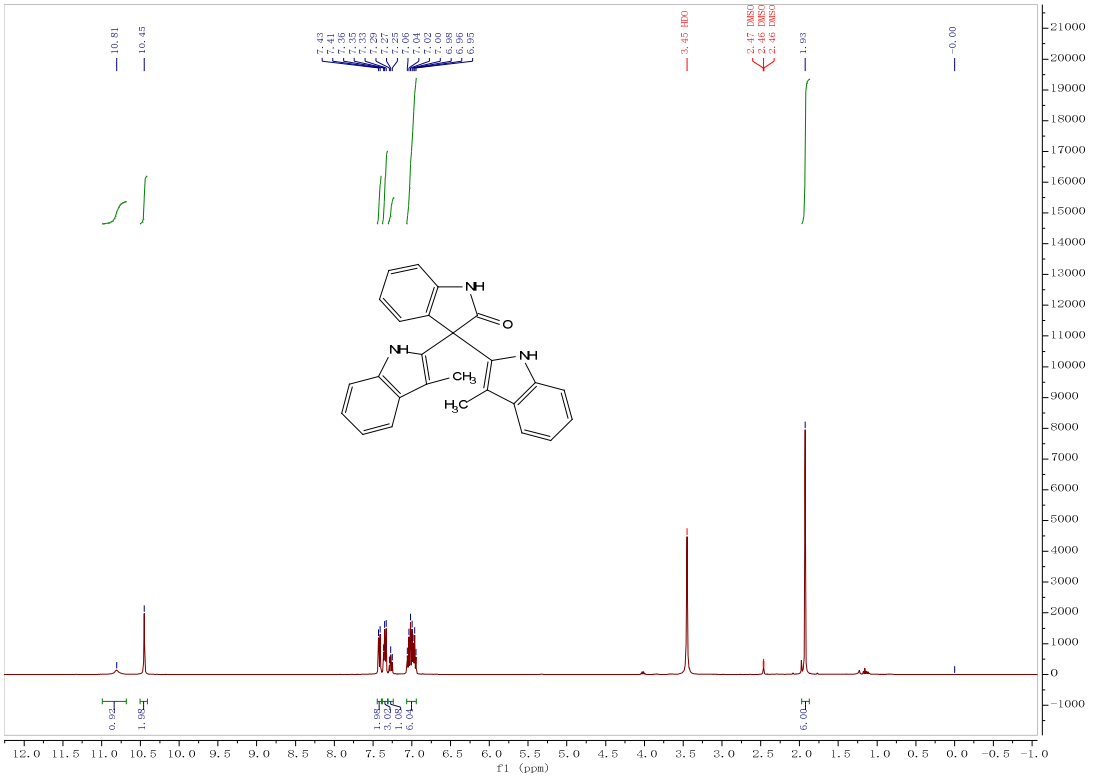
^{1}H NMR spectrum of Compound 13 ($CDCl_3$, 400 MHz)



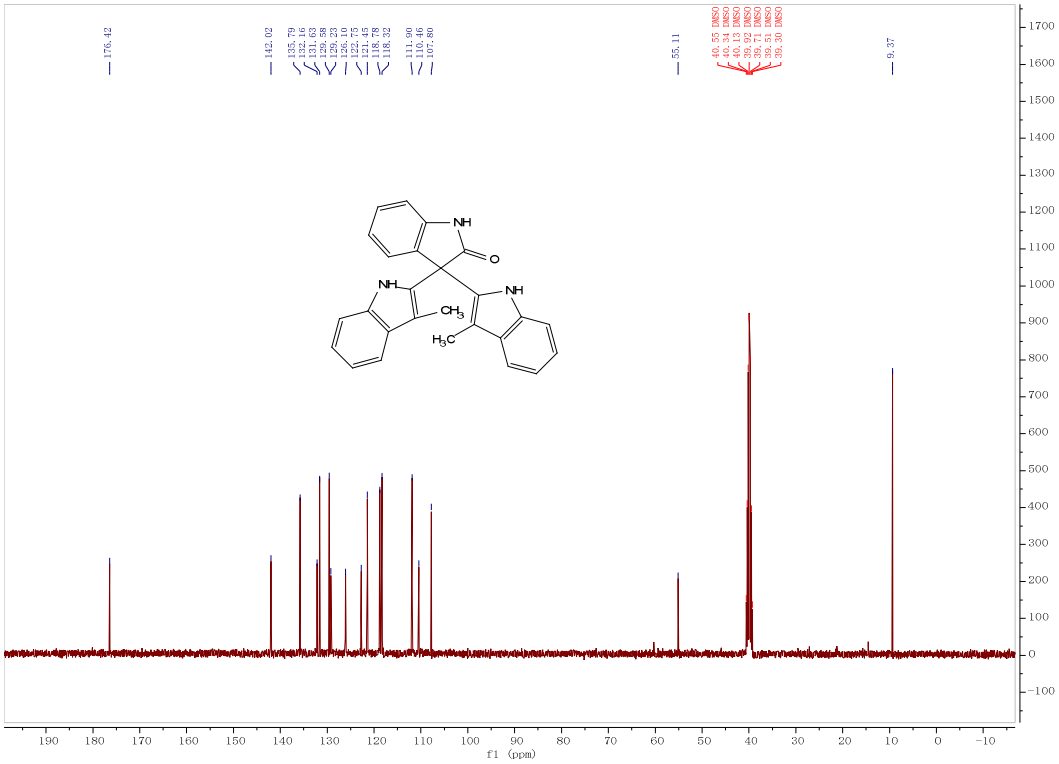
^{13}C NMR spectrum of Compound 13 ($CDCl_3$, 100 MHz)



^{1}H NMR spectrum of Compound 14 (DMSO-d_6, 400 MHz)

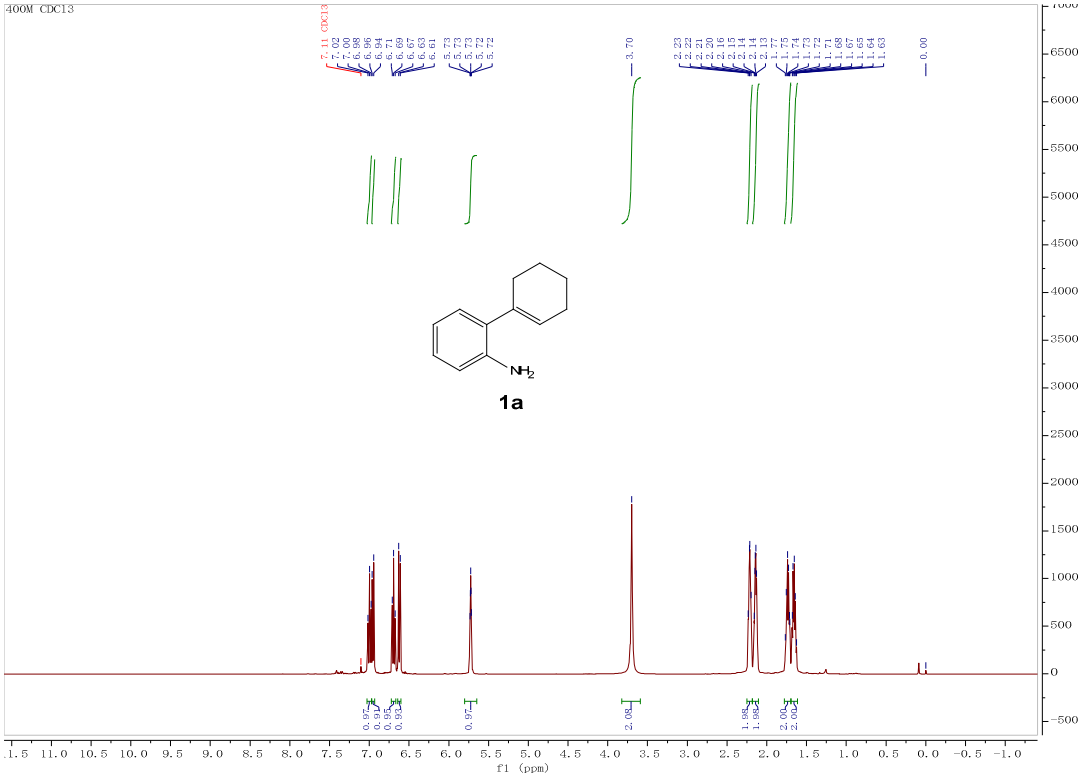


^{13}C NMR spectrum of Compound 14 (DMSO-d_6, 100 MHz)

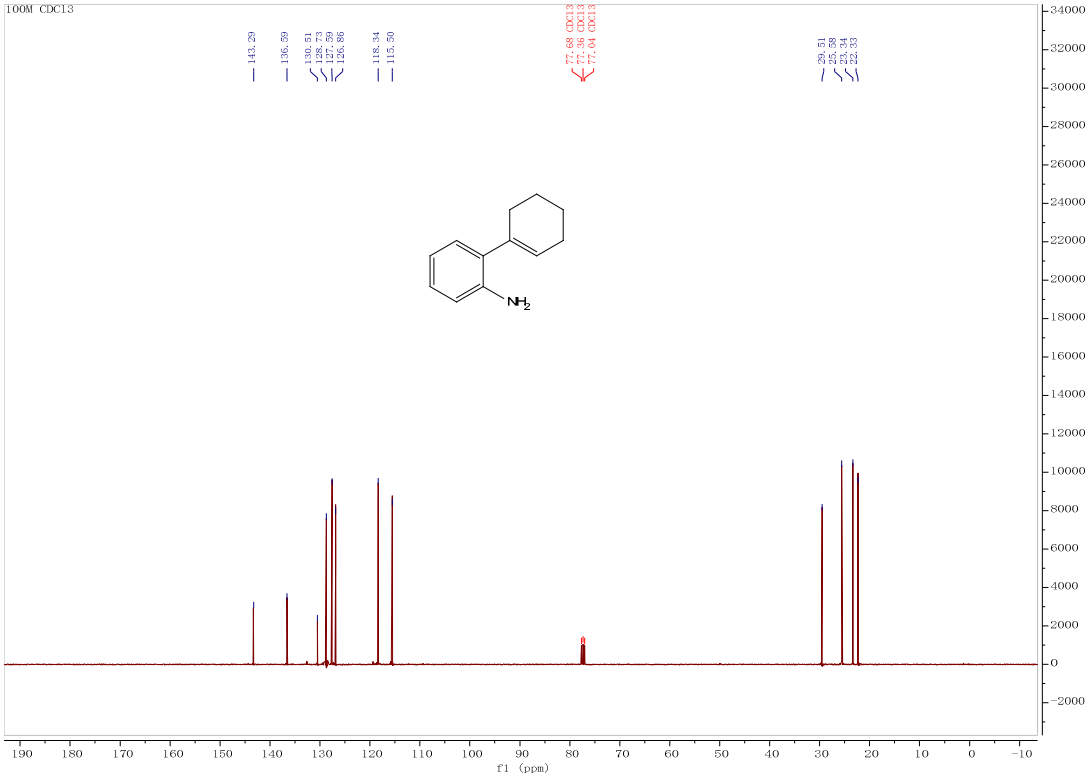


18. Spectroscopic data for alkenylaniline 1, 3 and 5

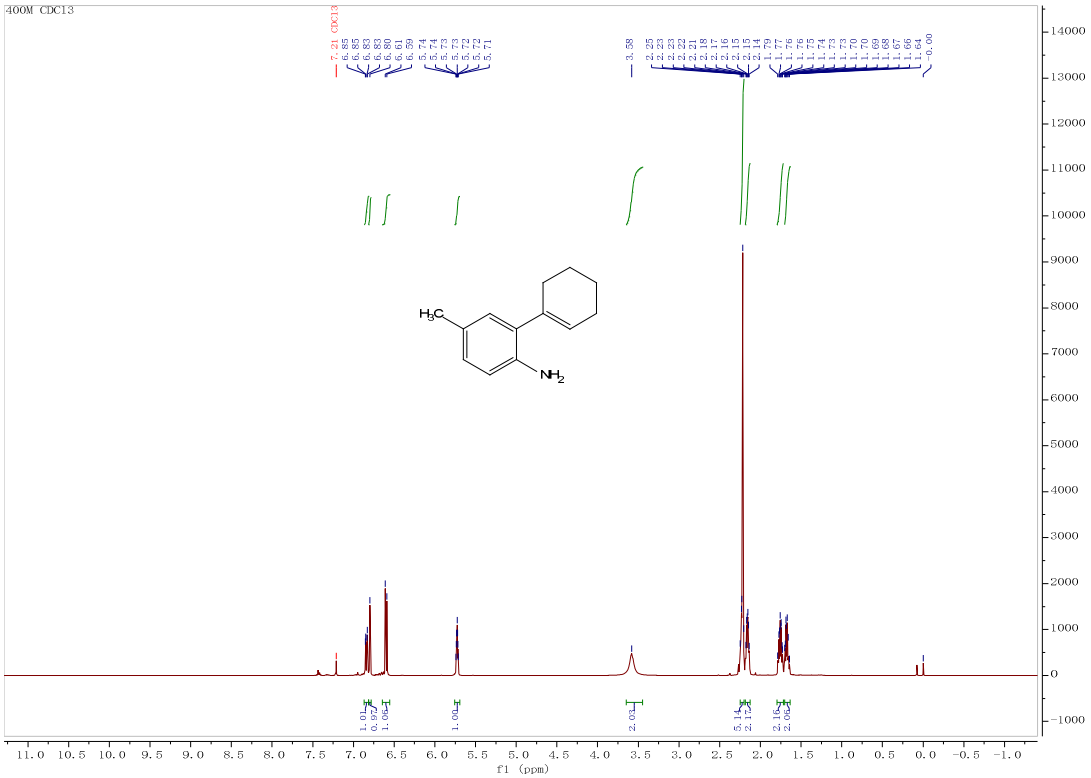
^{1}H NMR spectrum of Compound 1a ($CDCl_3$, 400 MHz)



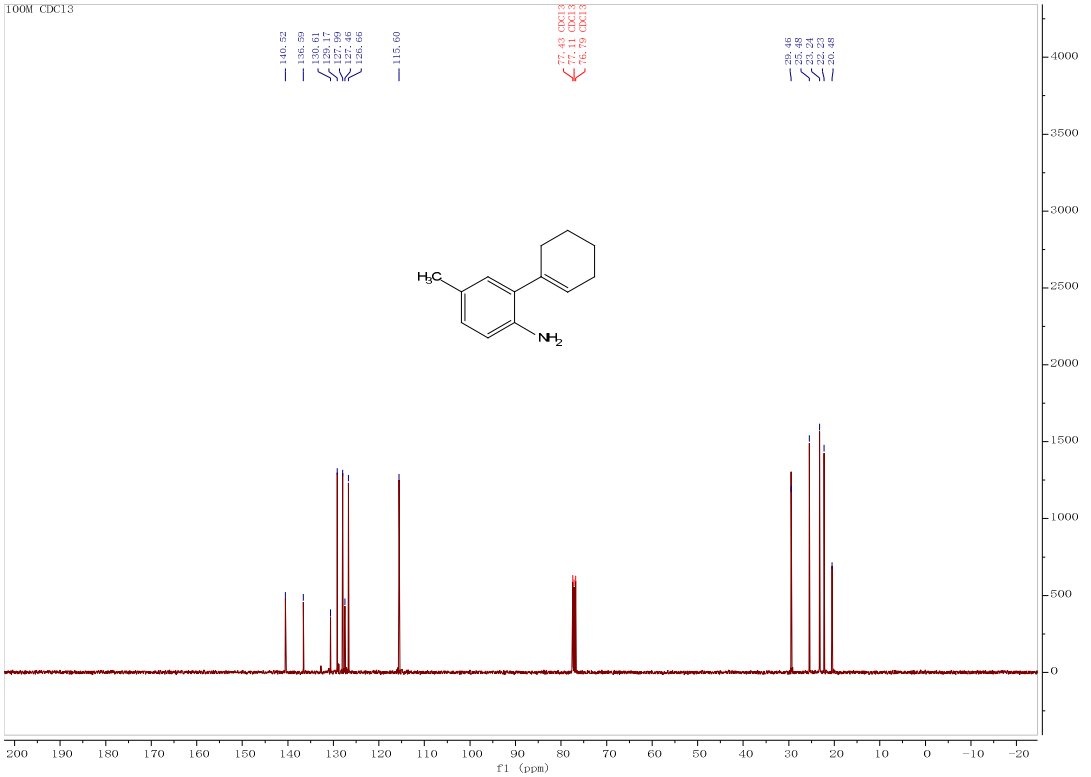
^{13}C NMR spectrum of Compound 1a ($CDCl_3$, 100 MHz)



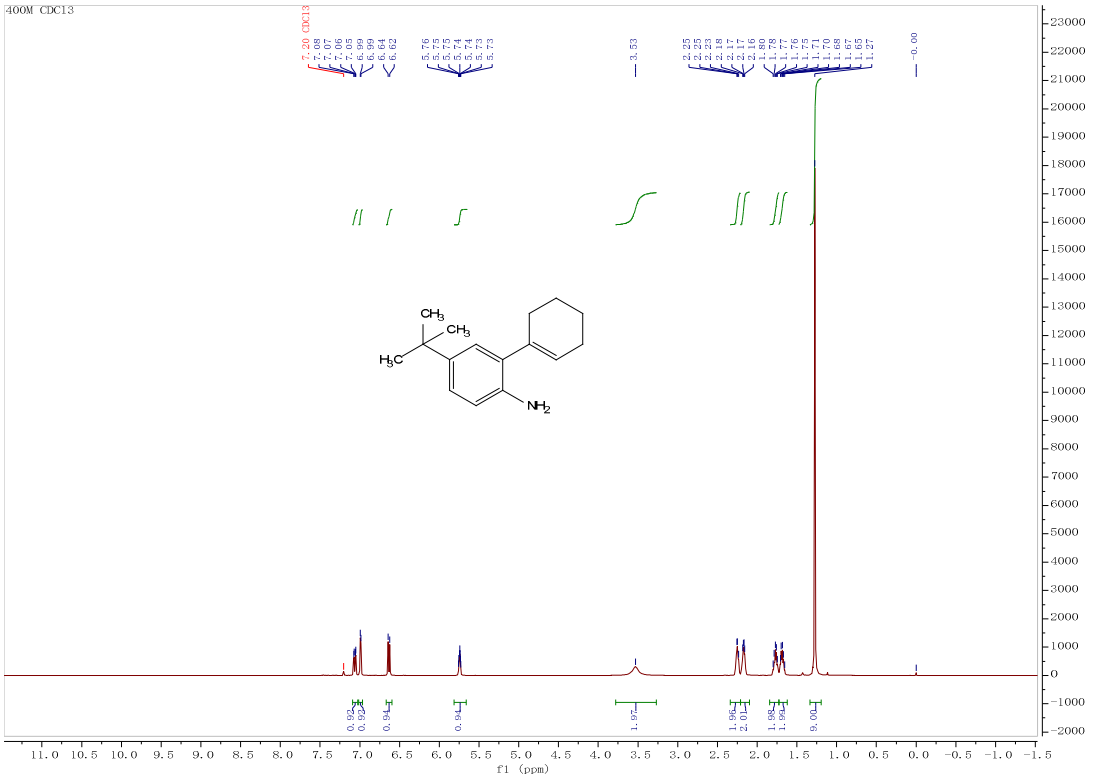
H NMR spectrum of Compound 1b ($CDCl_3$, 400 MHz)



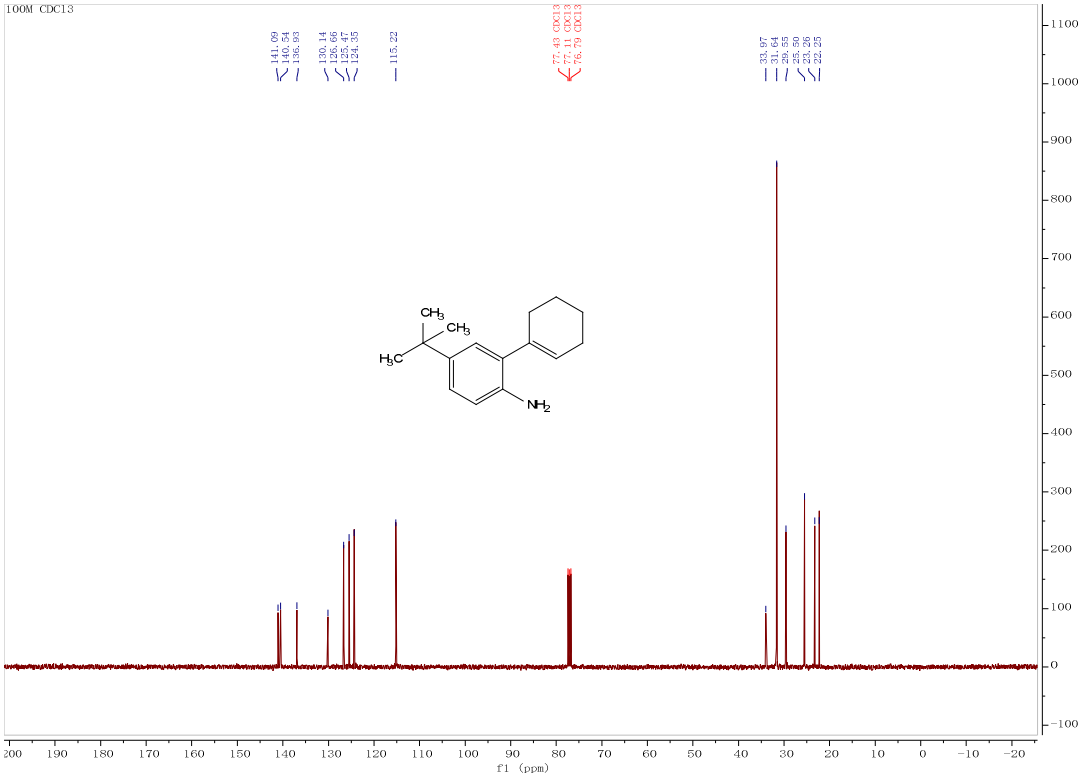
^{13}C NMR spectrum of Compound 1b ($CDCl_3$, 100 MHz)



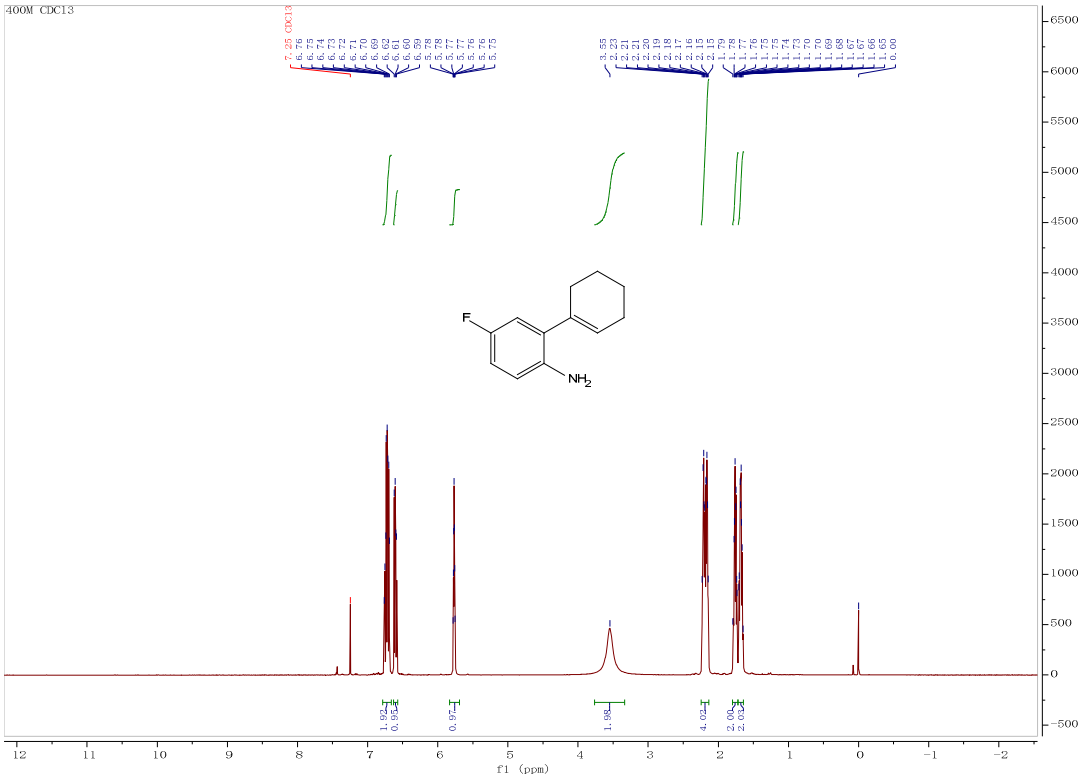
^{1}H NMR spectrum of Compound 1c ($CDCl_3$, 400 MHz)



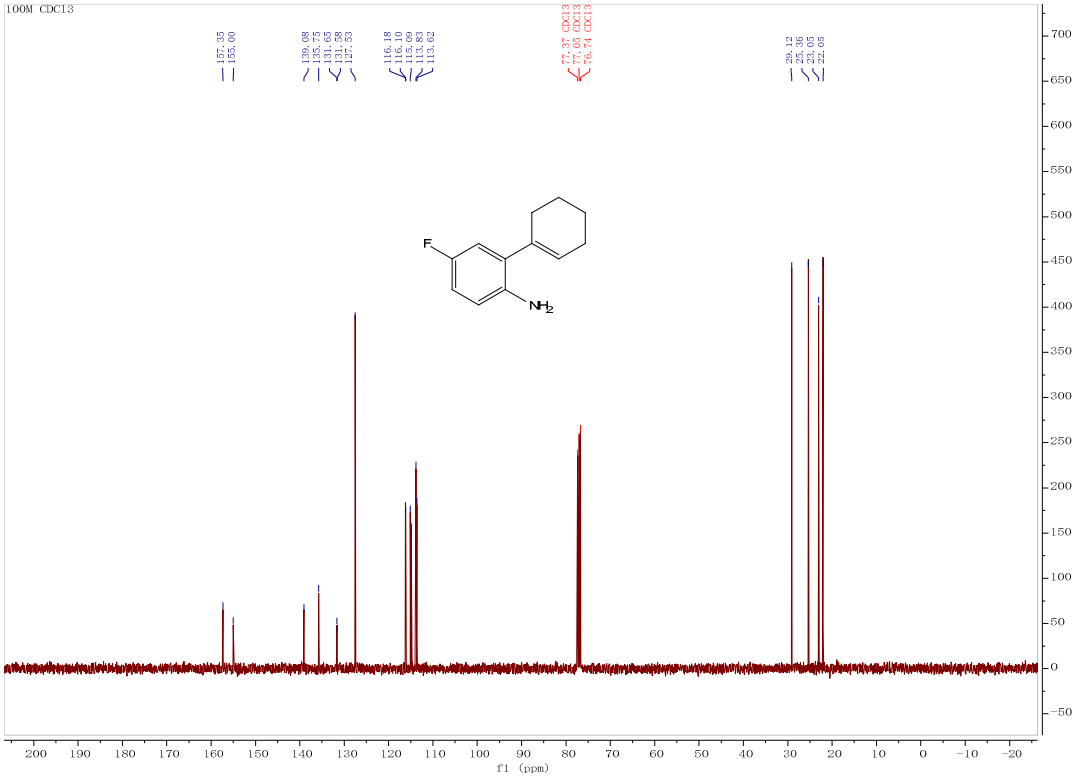
^{13}C NMR spectrum of Compound 1c ($CDCl_3$, 100 MHz)



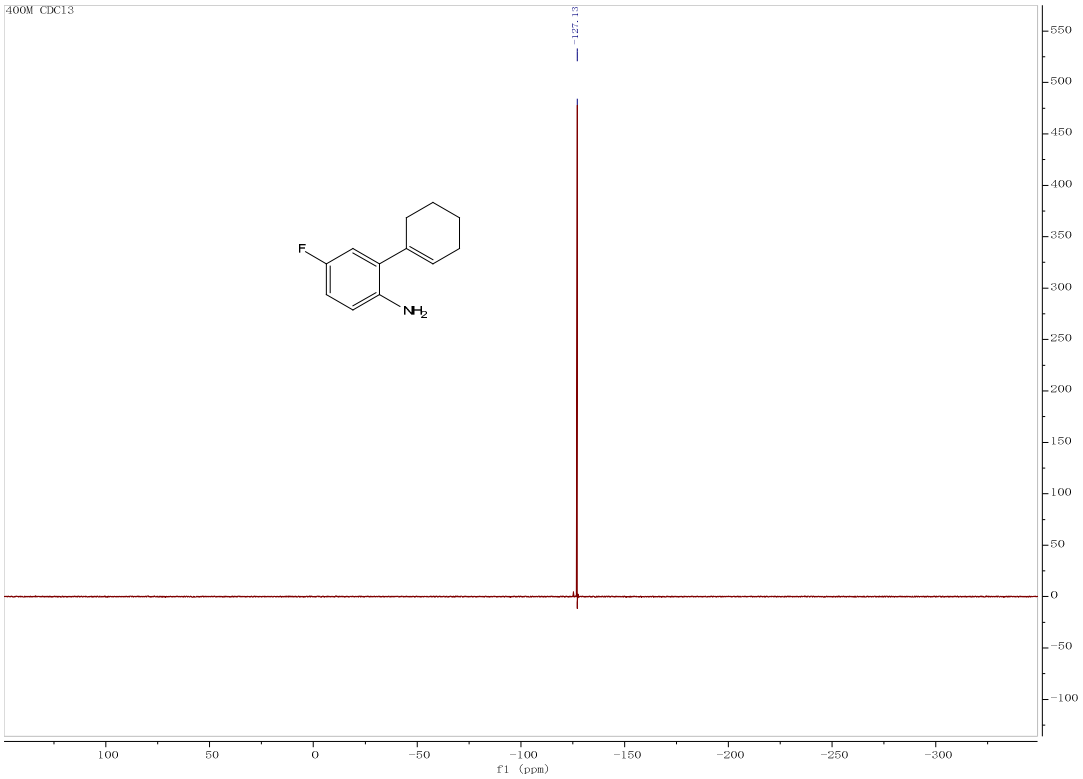
^{1}H NMR spectrum of Compound 1d ($CDCl_3$, 400 MHz)



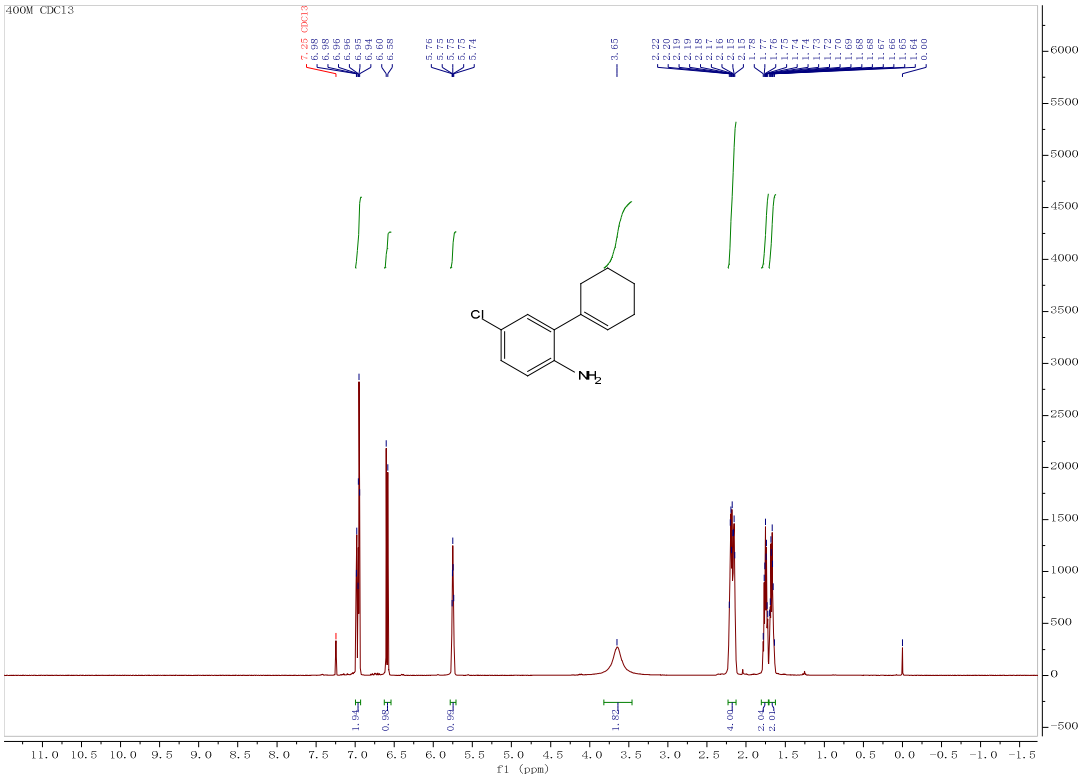
^{13}C NMR spectrum of Compound 1d ($CDCl_3$, 100 MHz)



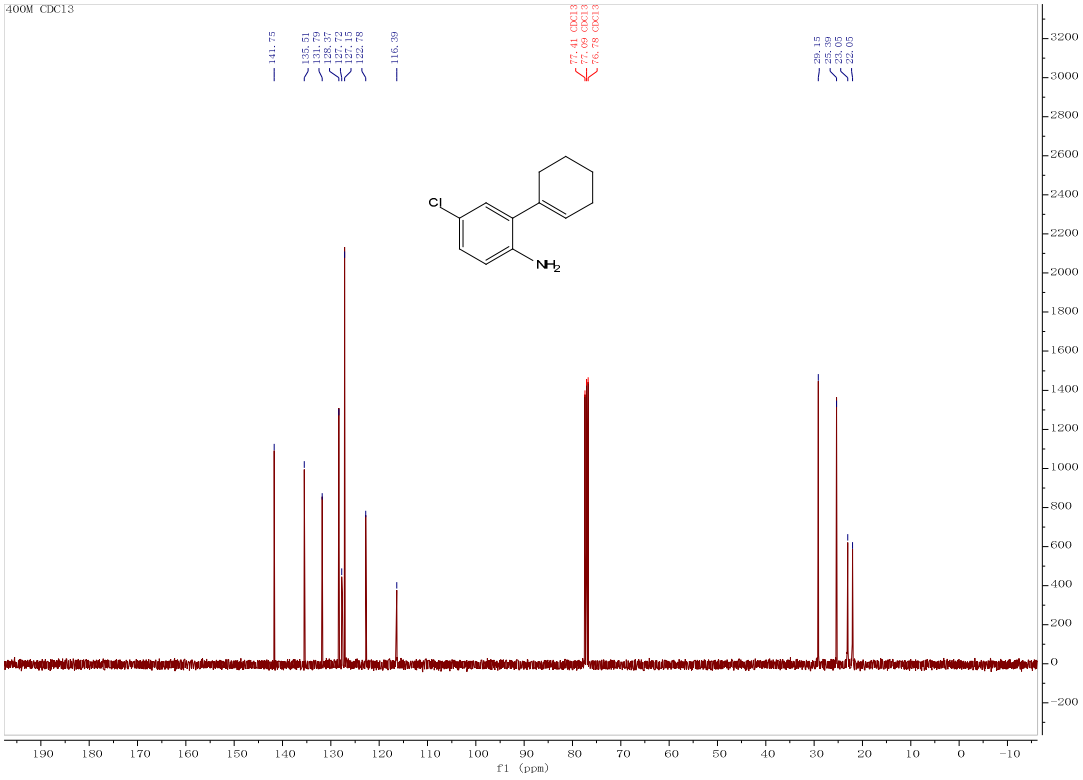
^{19}F NMR spectrum of Compound 1d ($CDCl_3$, 376 MHz)



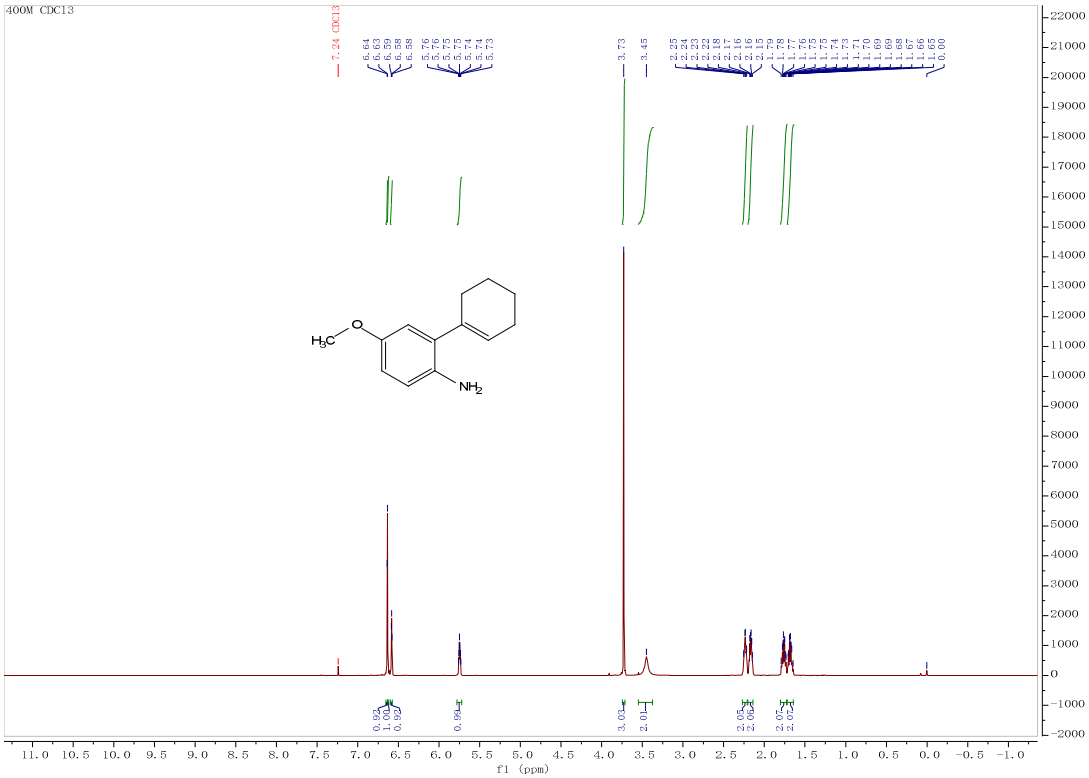
^{1}H NMR spectrum of Compound 1e ($CDCl_3$, 400 MHz)



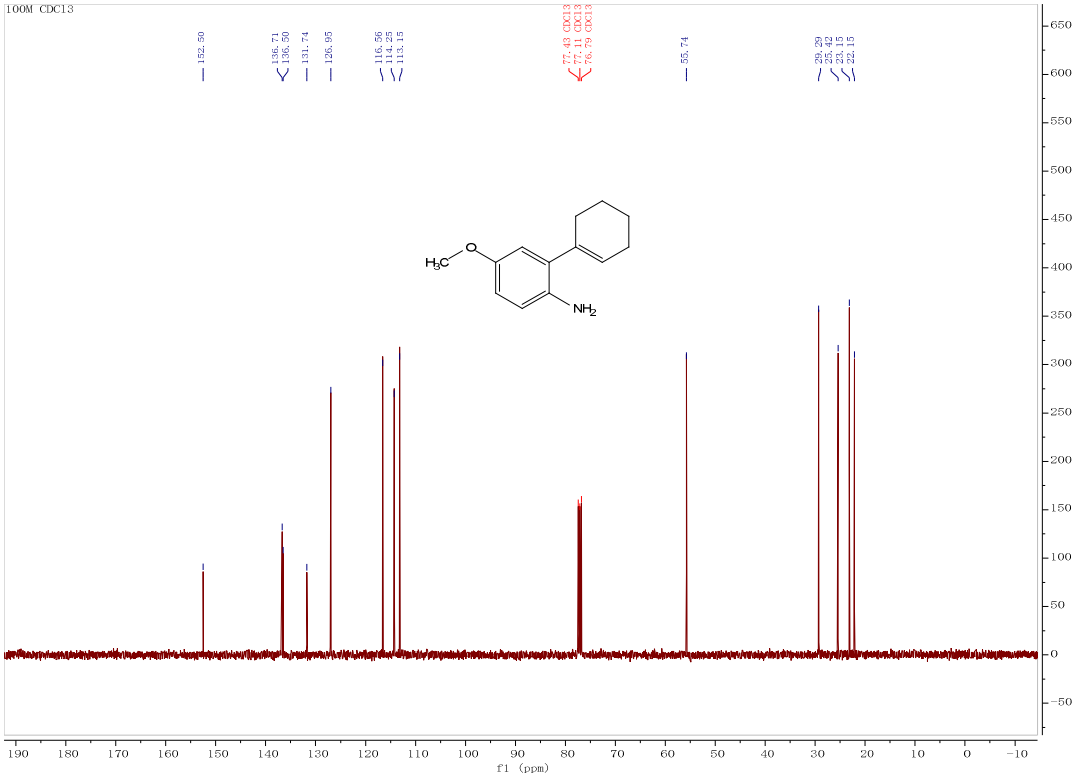
^{13}C NMR spectrum of Compound 1e ($CDCl_3$, 100 MHz)



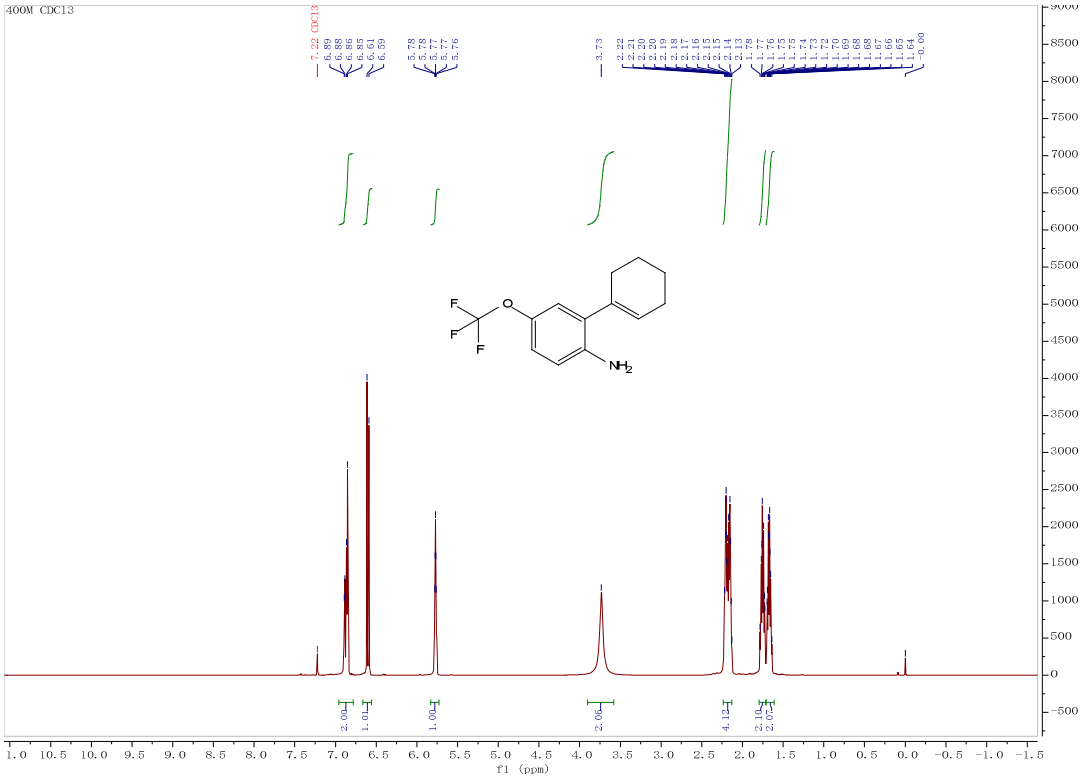
^{1}H NMR spectrum of Compound 1f ($CDCl_3$, 400 MHz)



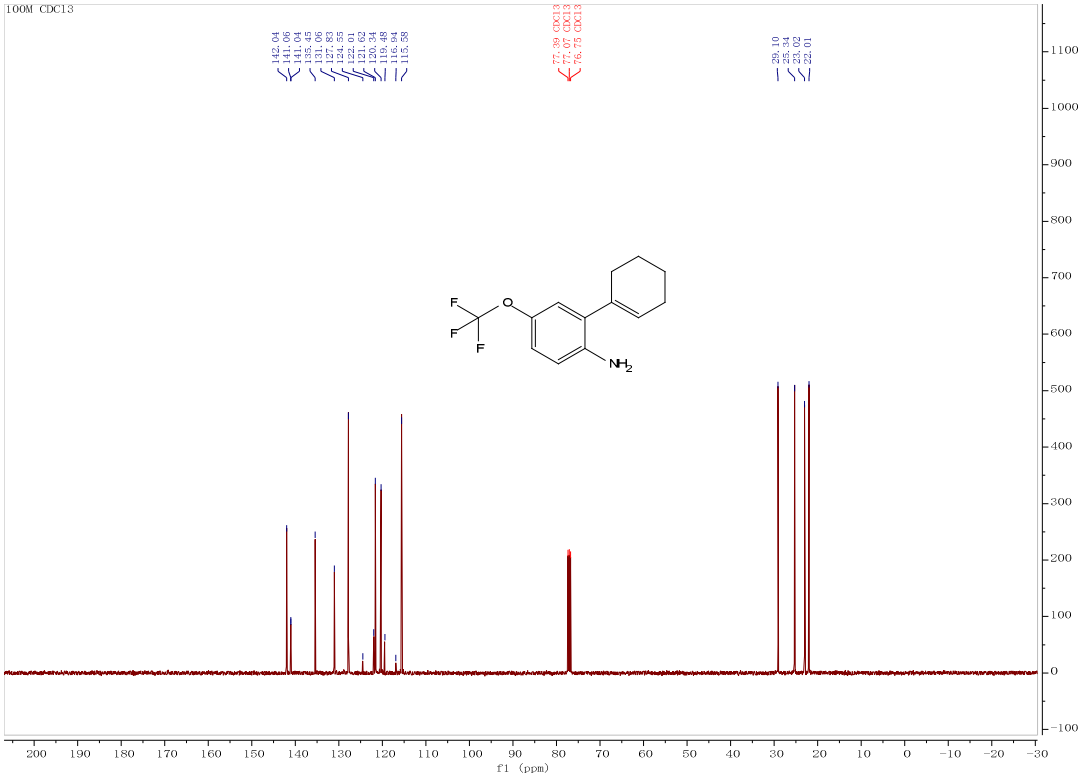
^{13}C NMR spectrum of Compound 1f ($CDCl_3$, 100 MHz)



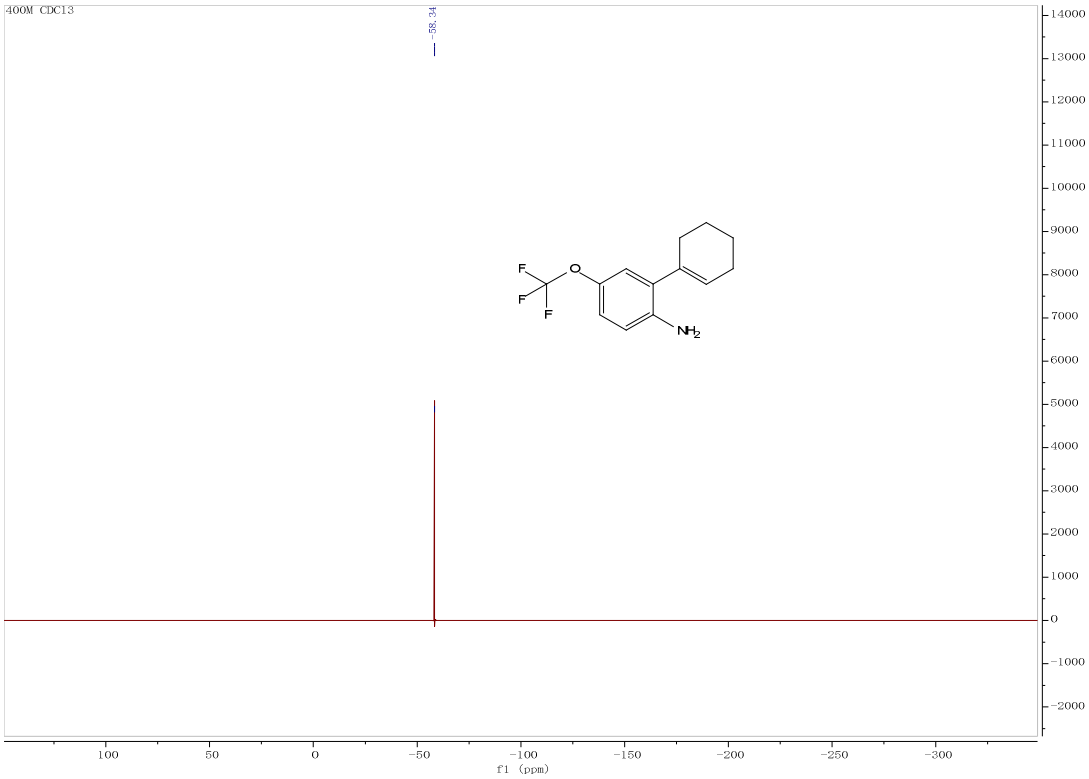
^{1}H NMR spectrum of Compound 1g ($CDCl_3$, 400 MHz)



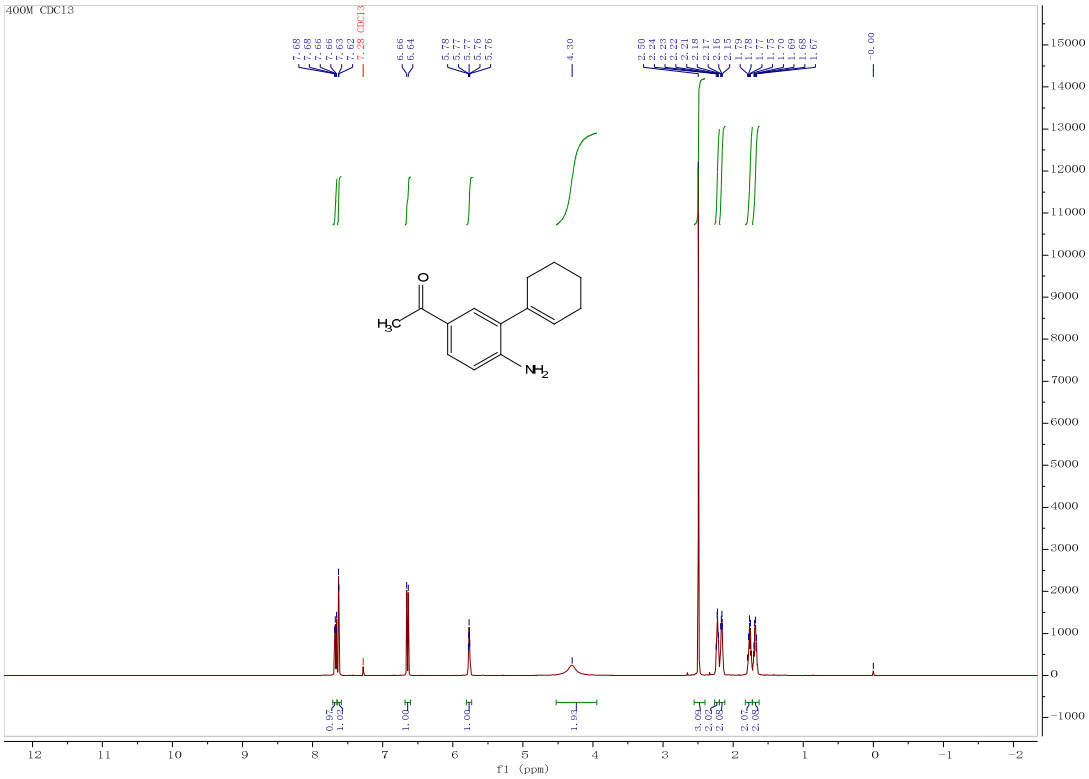
^{13}C NMR spectrum of Compound 1g ($CDCl_3$, 100 MHz)



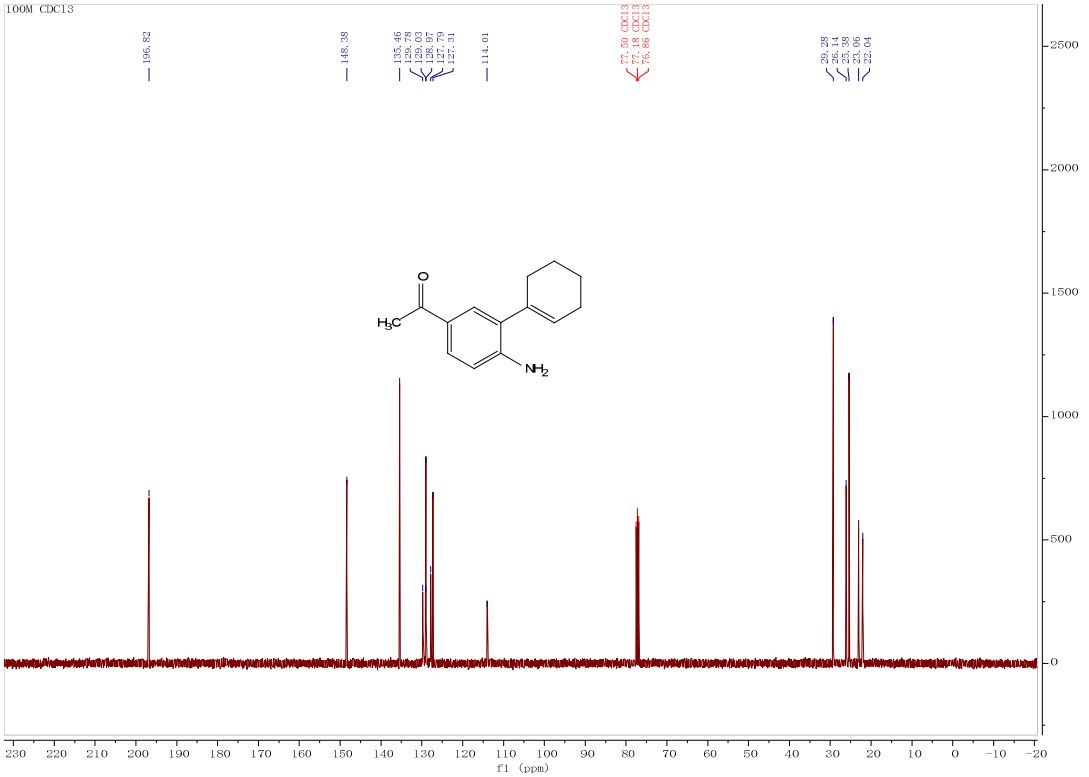
^{19}F NMR spectrum of Compound 1g ($CDCl_3$, 376 MHz)



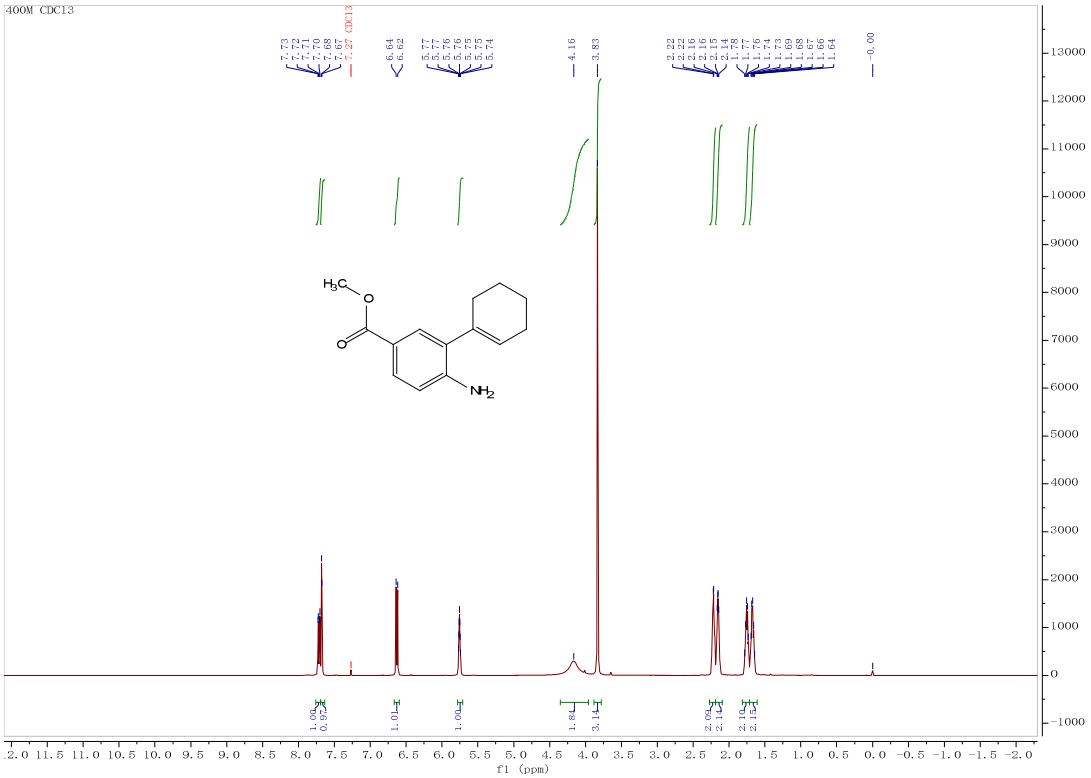
^{1}H NMR spectrum of Compound 1h ($CDCl_3$, 400 MHz)



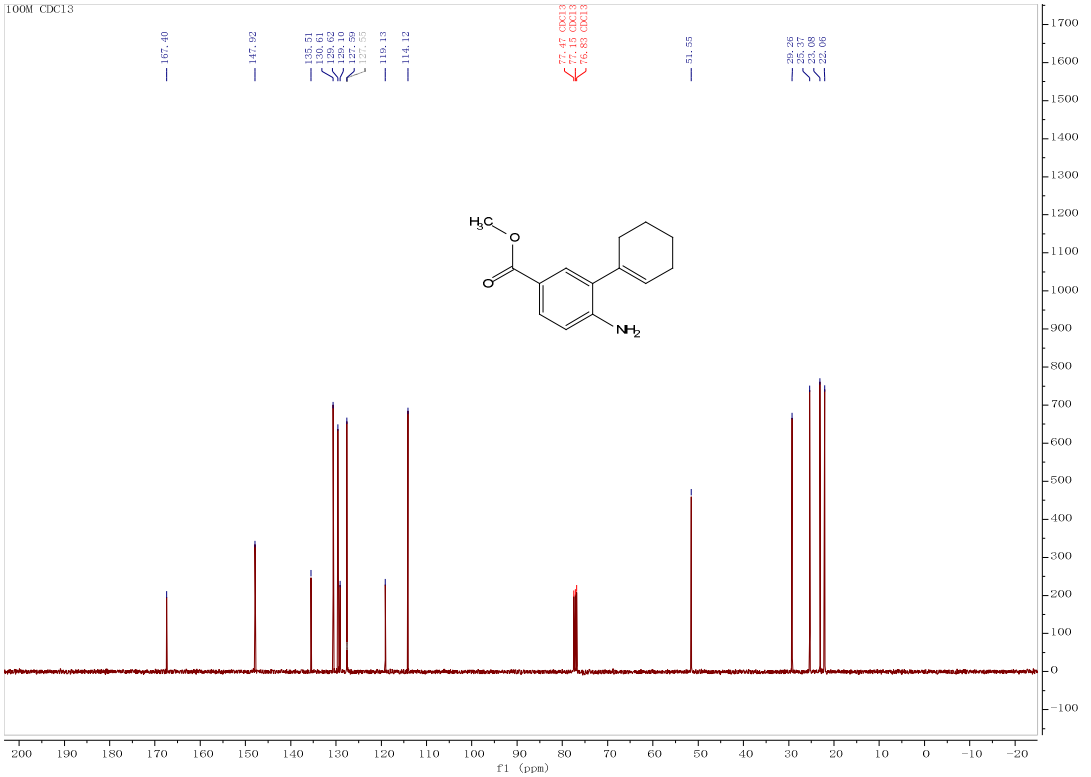
^{13}C NMR spectrum of Compound 1h ($CDCl_3$, 100 MHz)



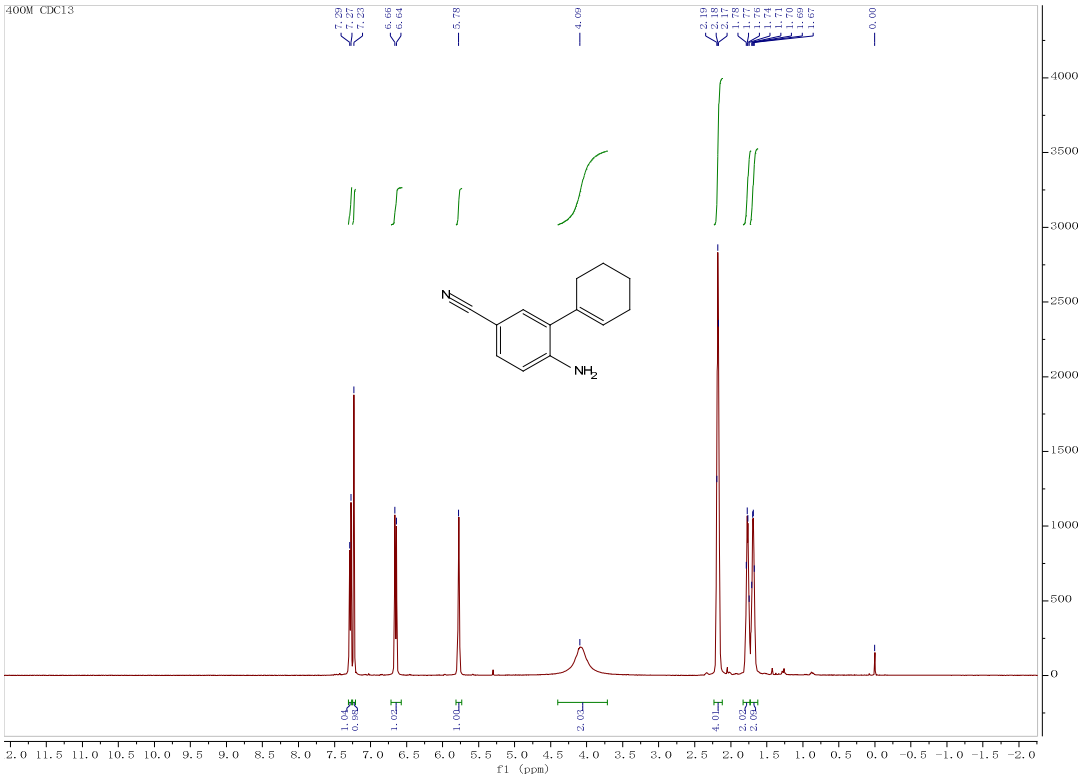
^{1}H NMR spectrum of Compound 1i ($CDCl_3$, 400 MHz)



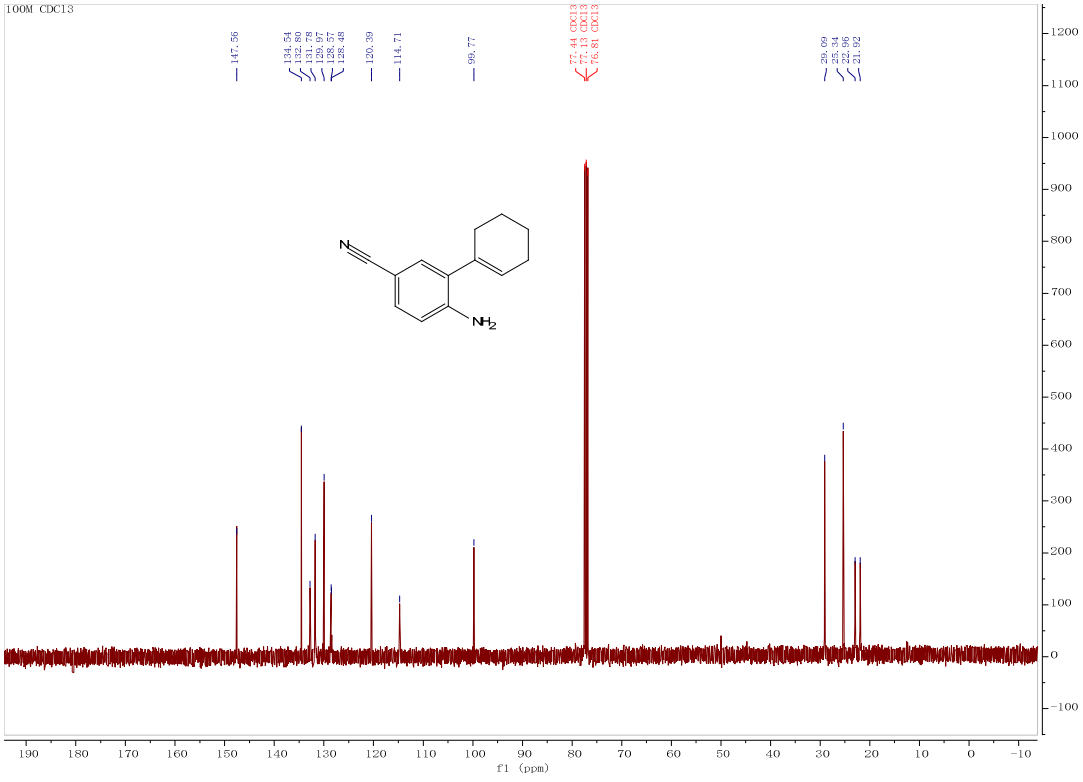
^{13}C NMR spectrum of Compound 1i ($CDCl_3$, 100 MHz)



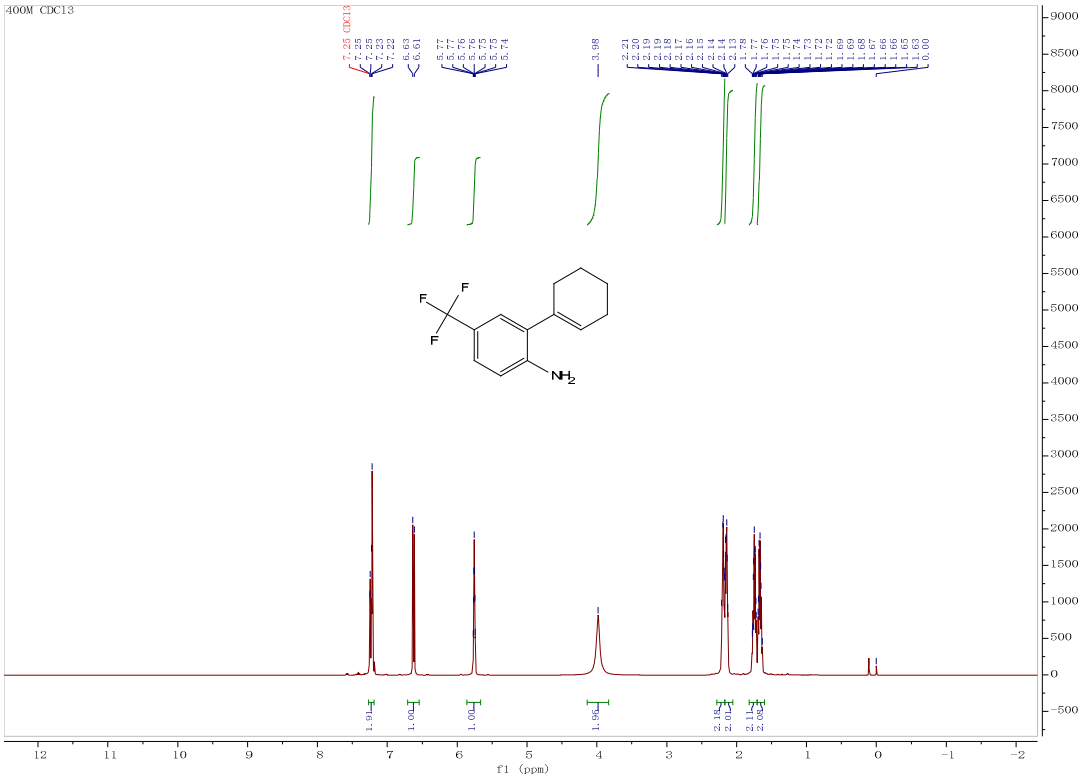
^{1}H NMR spectrum of Compound 1j ($CDCl_3$, 400 MHz)



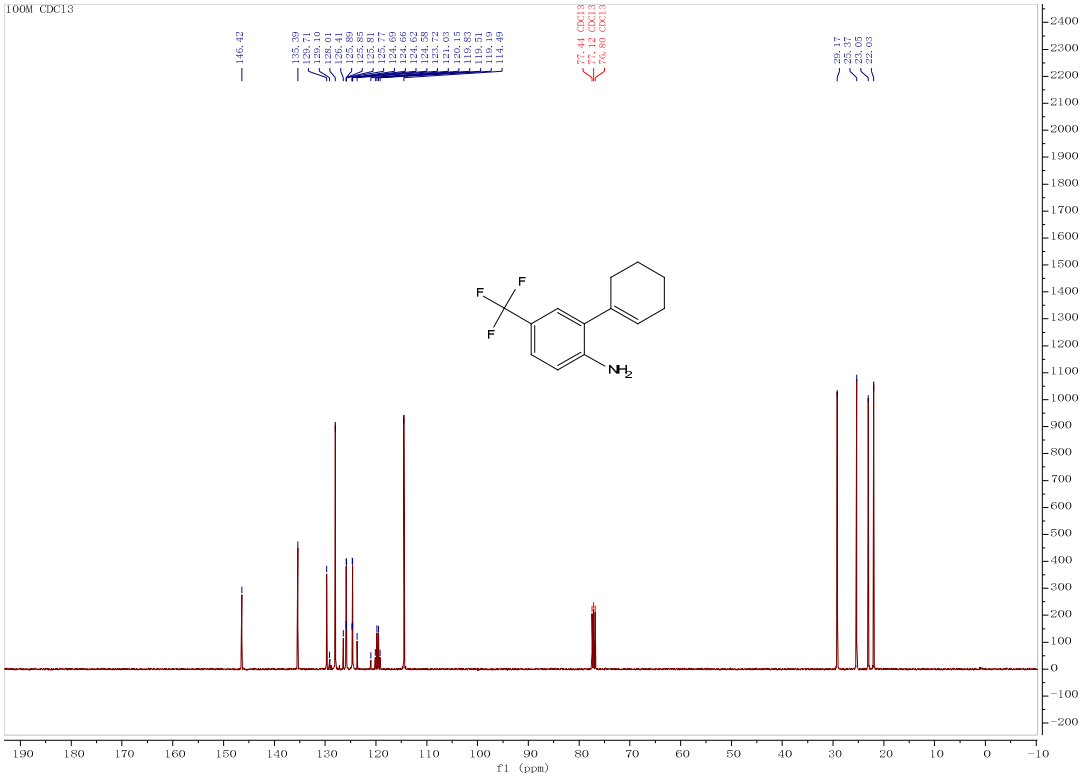
^{13}C NMR spectrum of Compound 1j ($CDCl_3$, 100 MHz)



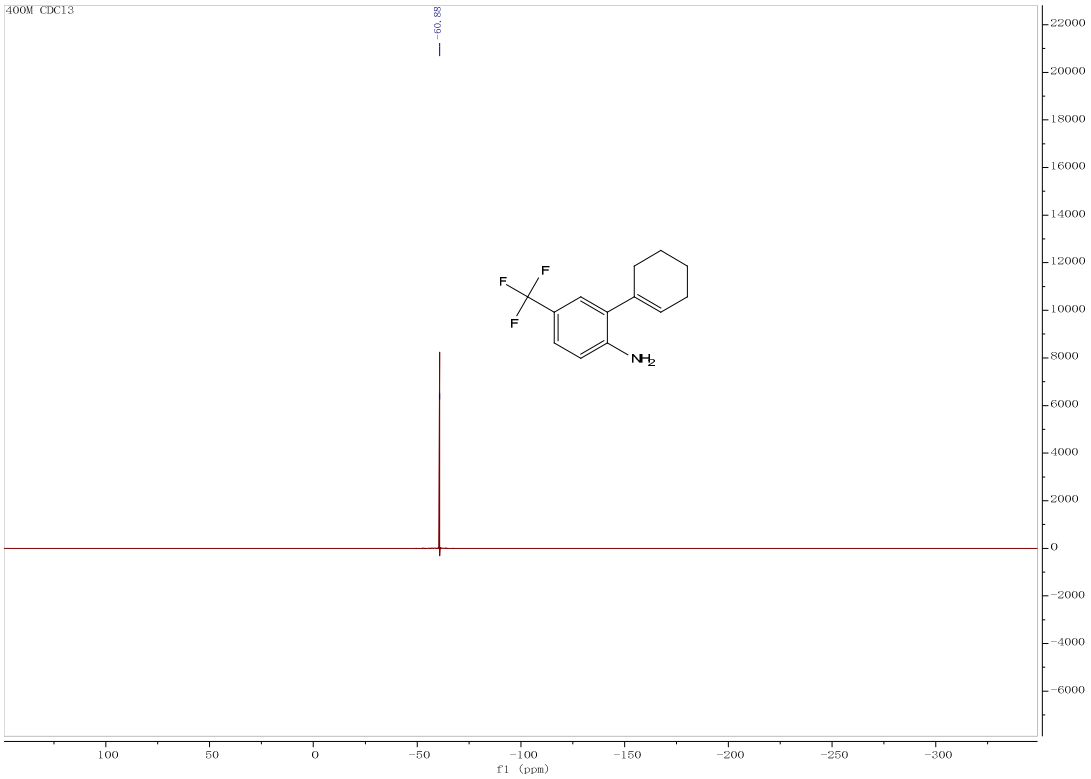
^{1}H NMR spectrum of Compound 1k ($CDCl_3$, 400 MHz)



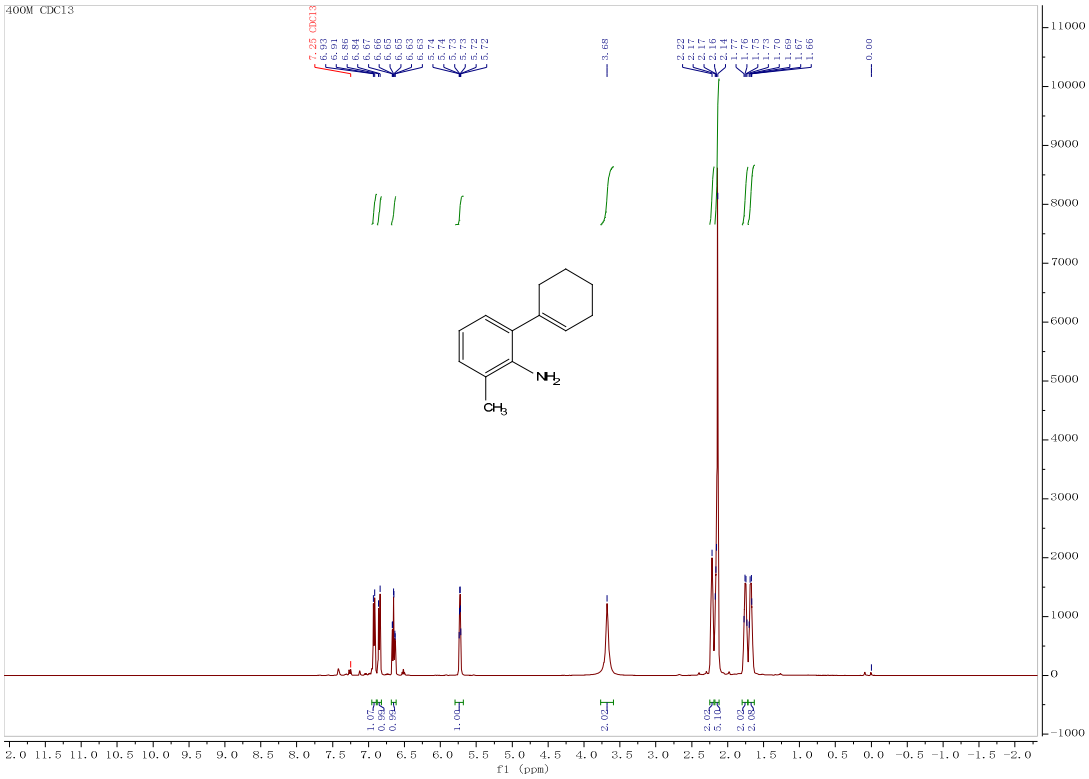
^{13}C NMR spectrum of Compound 1k ($CDCl_3$, 100 MHz)



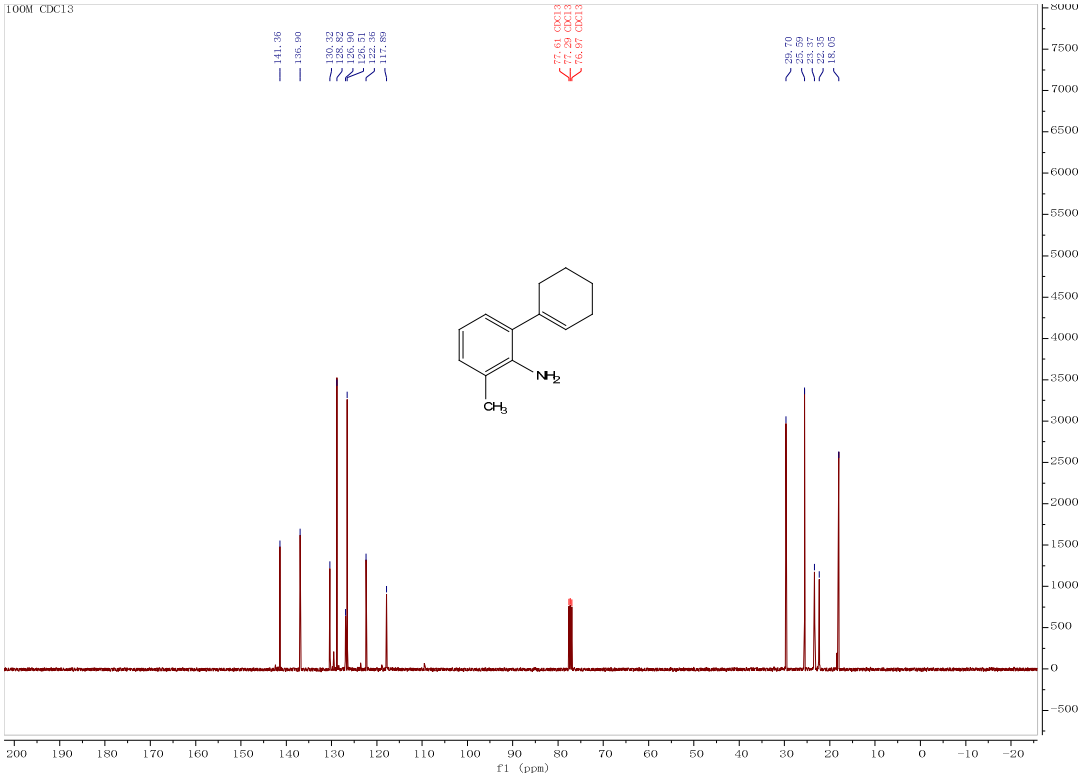
^{19}F NMR spectrum of Compound 1k ($CDCl_3$, 376 MHz)



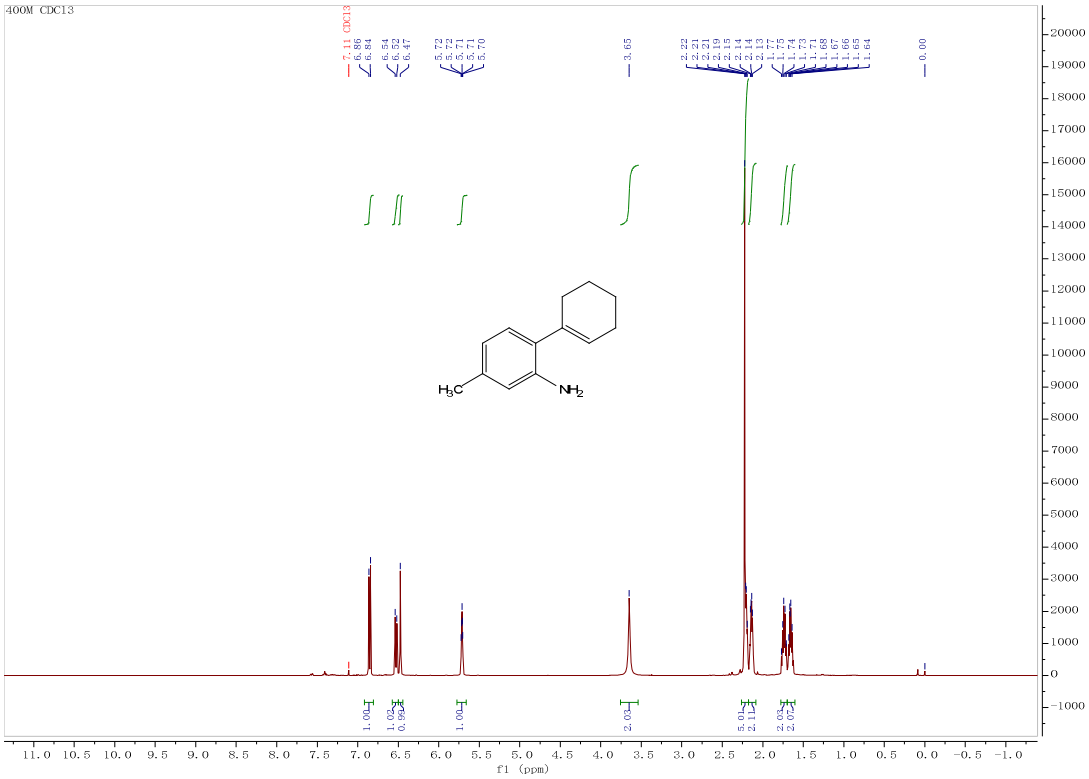
^{1}H NMR spectrum of Compound 1l ($CDCl_3$, 400 MHz)



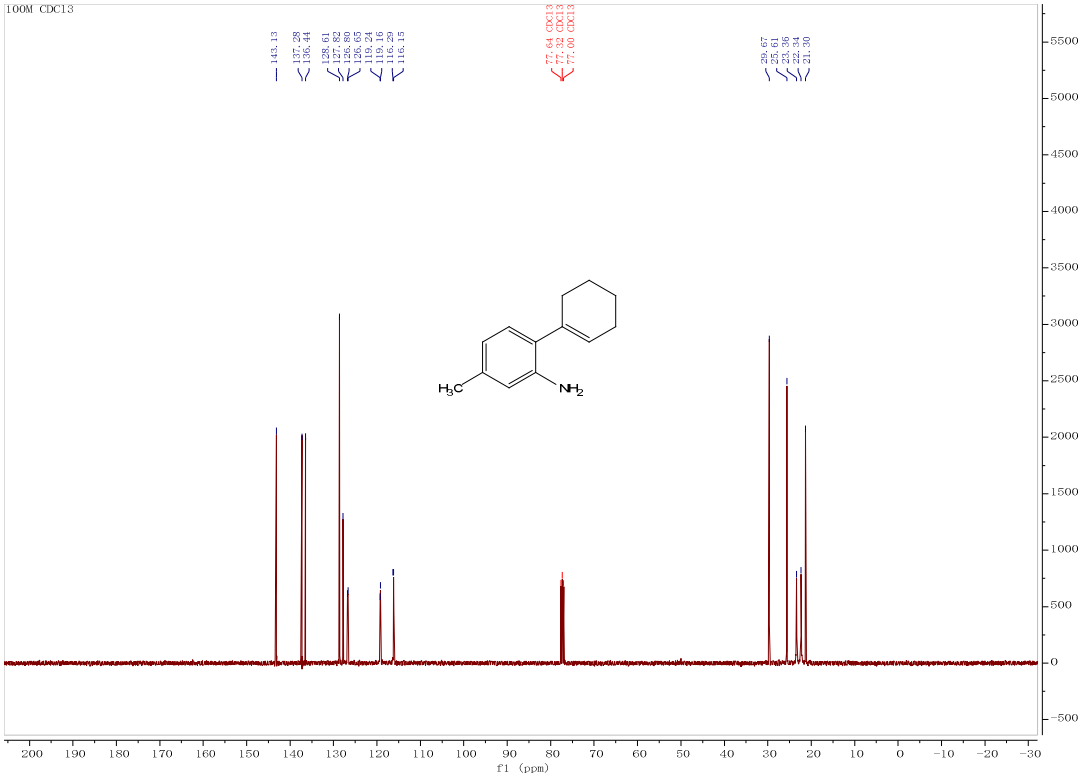
^{13}C NMR spectrum of Compound 1l ($CDCl_3$, 100 MHz)



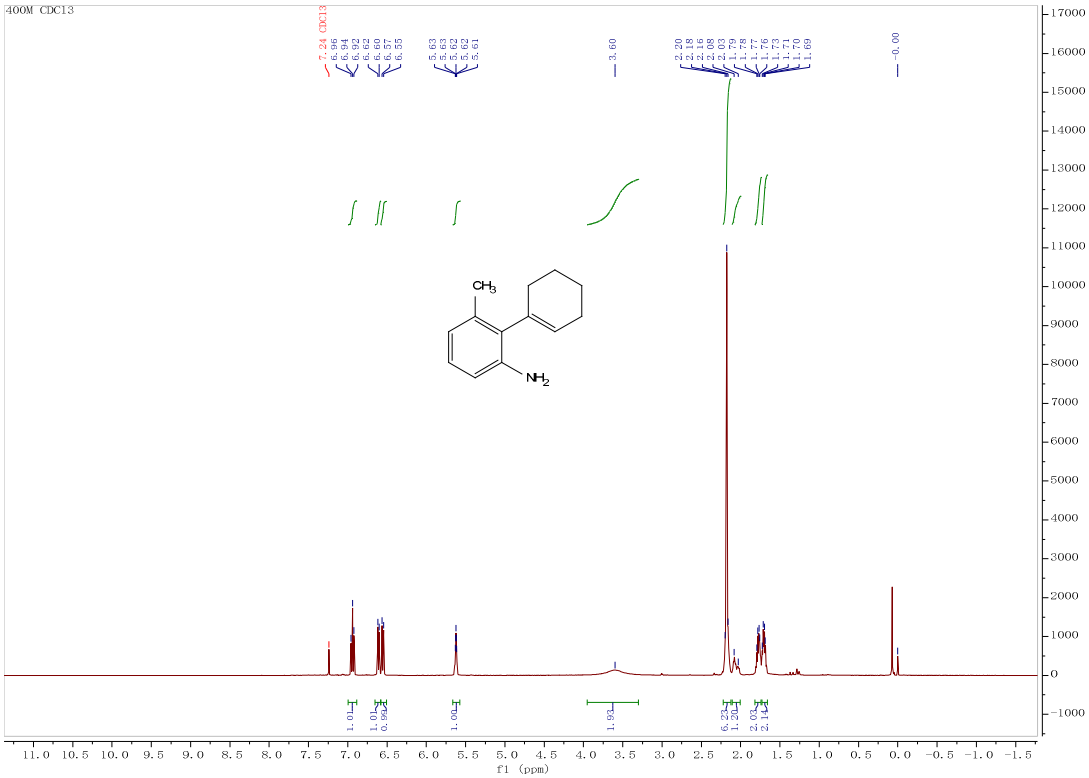
^{1}H NMR spectrum of Compound 1m ($CDCl_3$, 400 MHz)



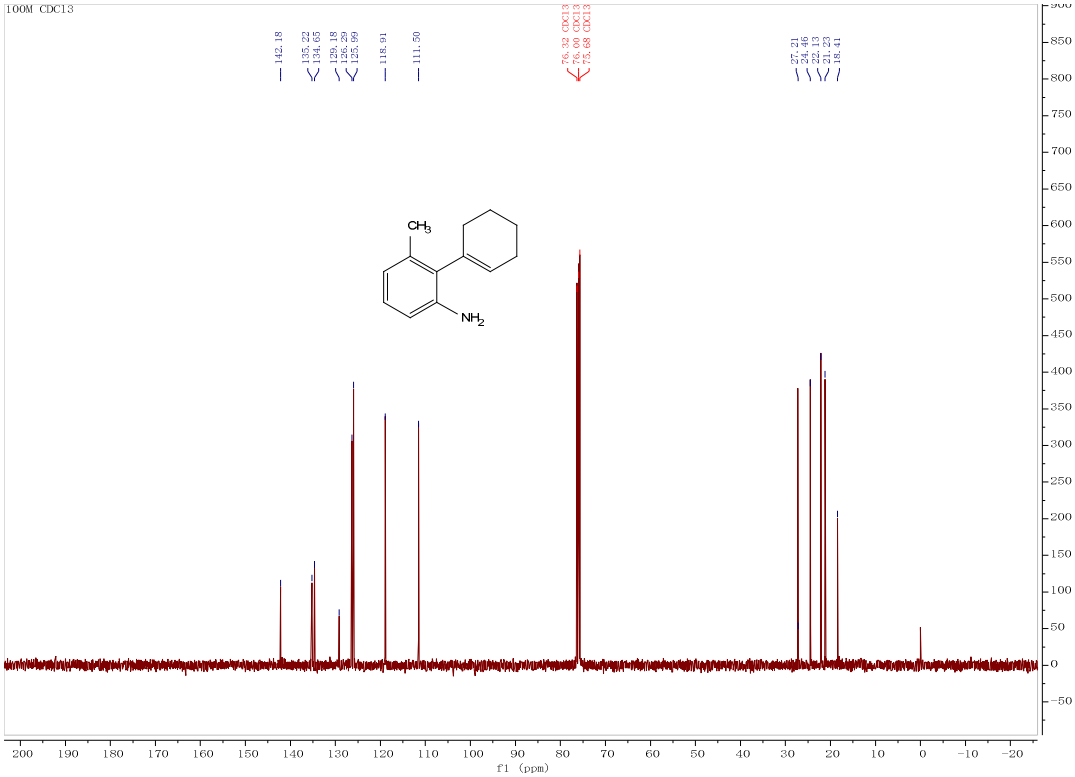
^{13}C NMR spectrum of Compound 1m ($CDCl_3$, 100 MHz)



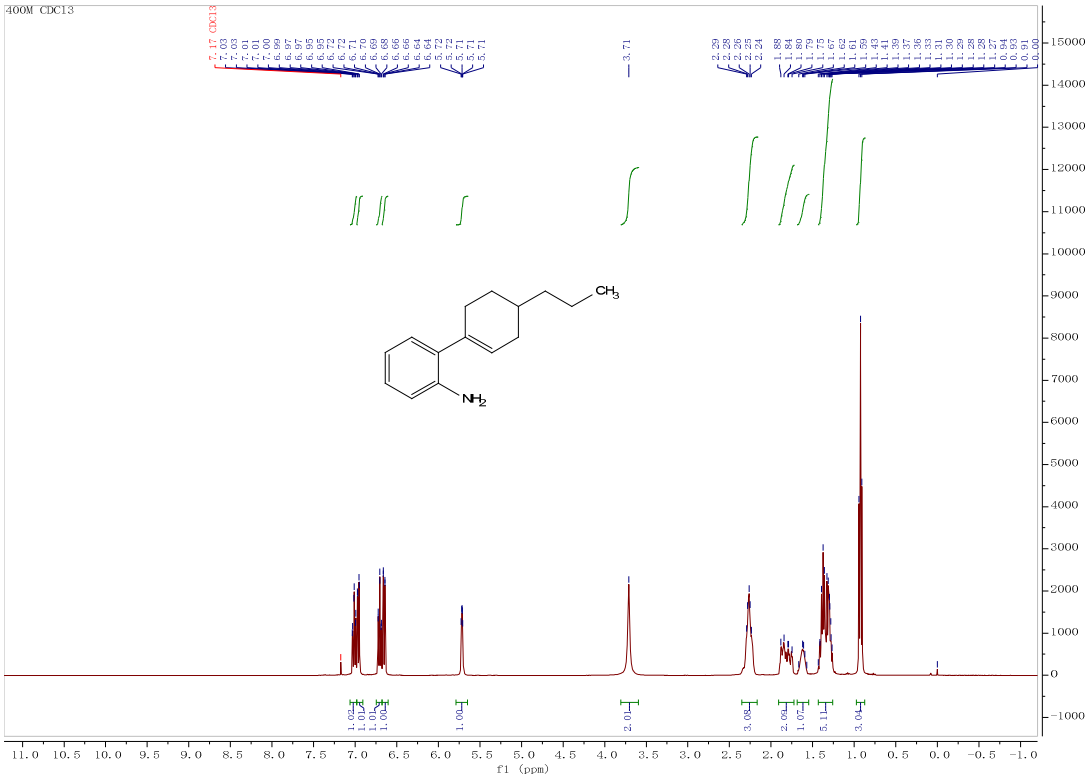
^{1}H NMR spectrum of Compound 1n ($CDCl_3$, 400 MHz)



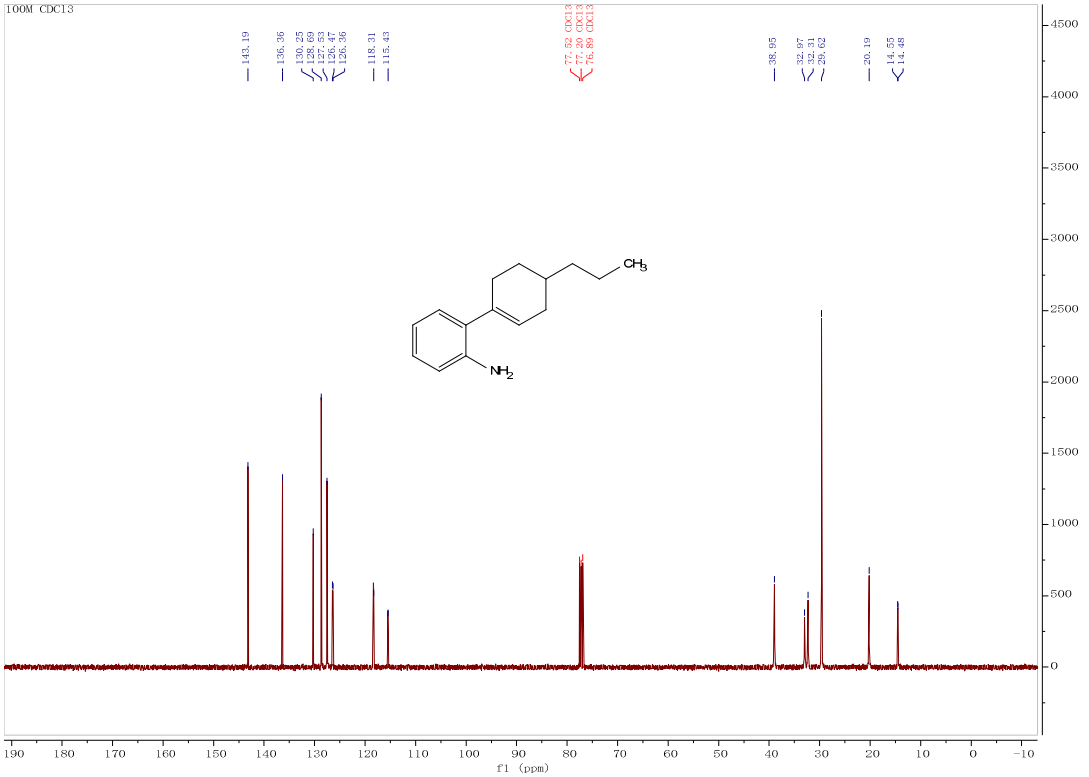
^{13}C NMR spectrum of Compound 1n ($CDCl_3$, 100 MHz)



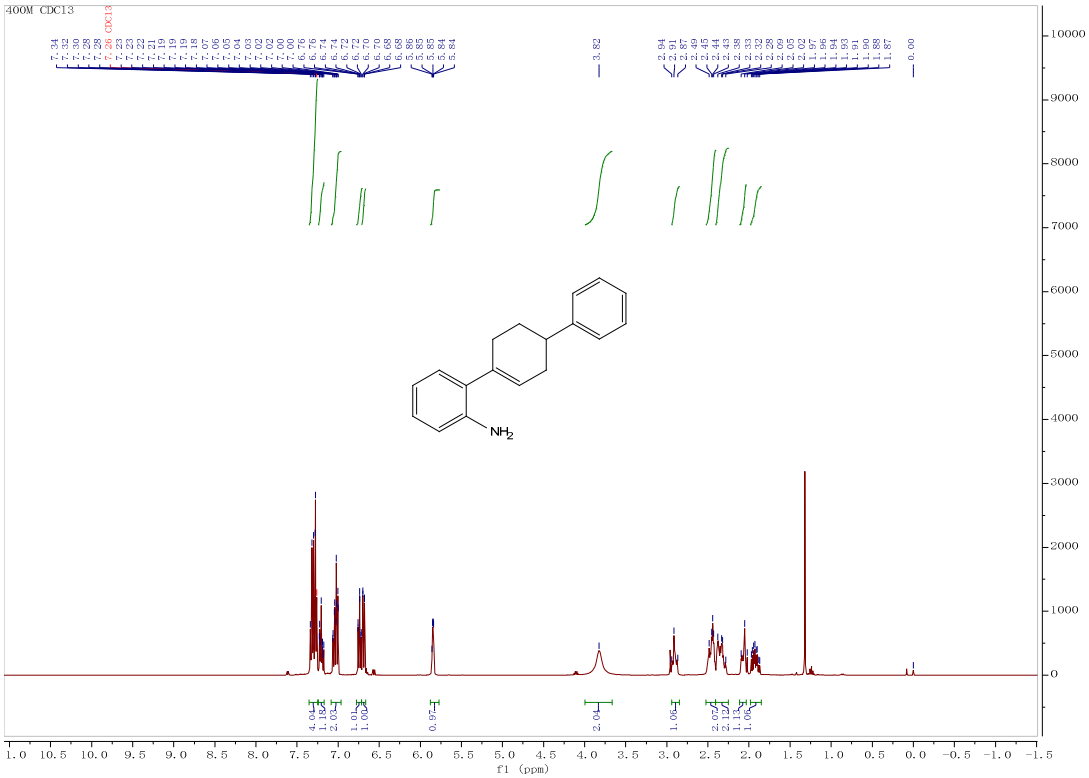
^{1}H NMR spectrum of Compound 1o ($CDCl_3$, 400 MHz)



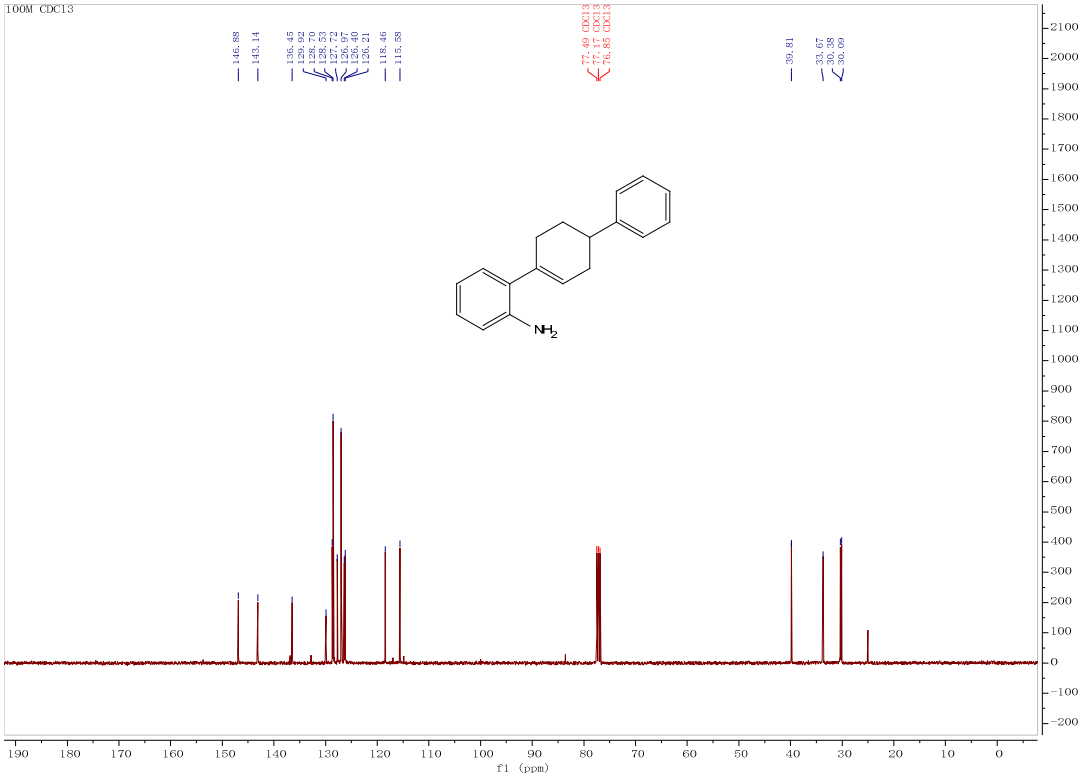
^{13}C NMR spectrum of Compound 1o ($CDCl_3$, 100 MHz)



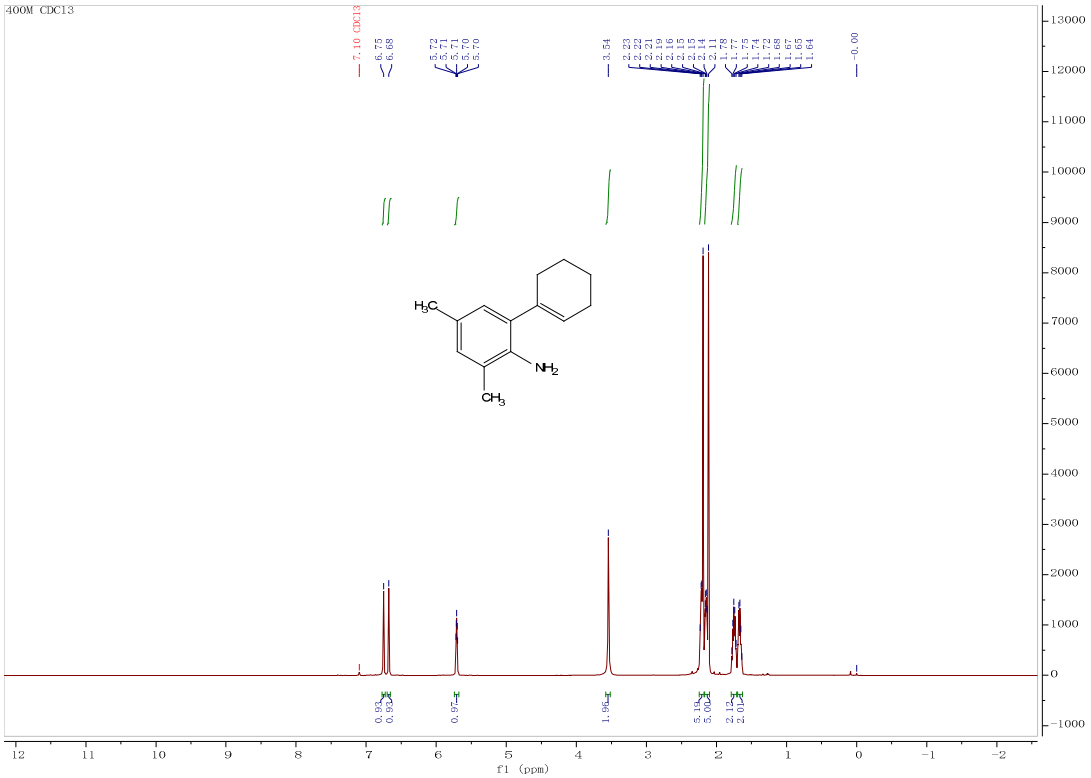
^{1}H NMR spectrum of Compound 1p ($CDCl_3$, 400 MHz)



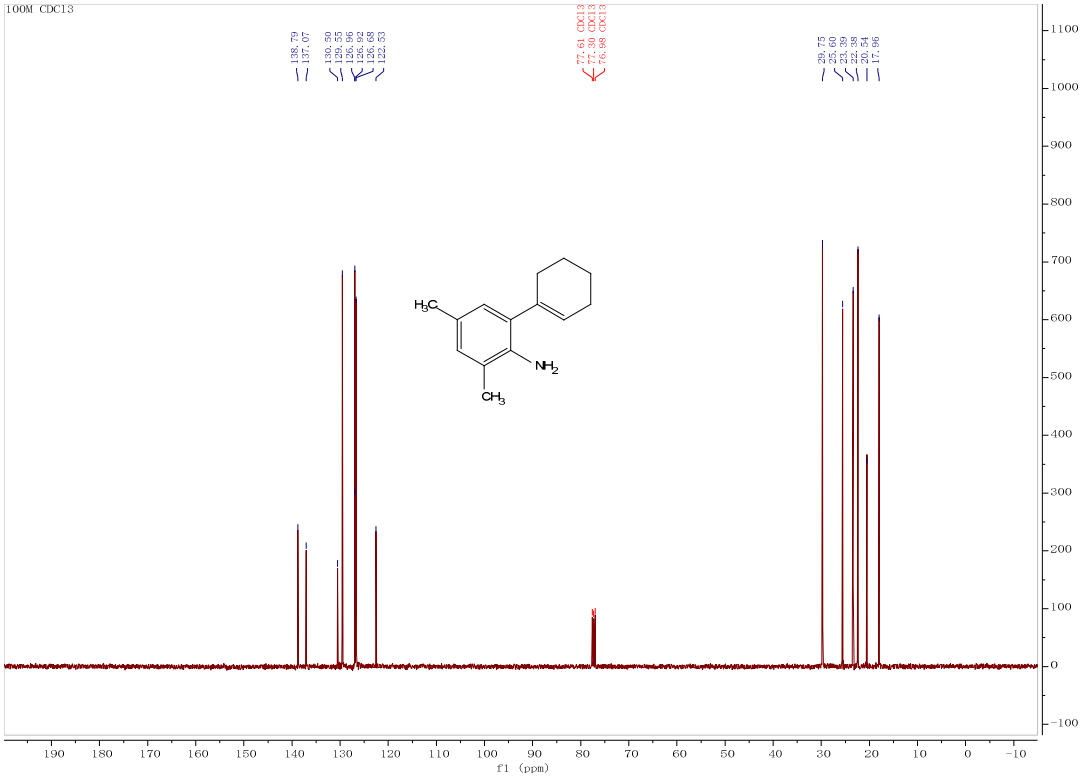
^{13}C NMR spectrum of Compound 1p ($CDCl_3$, 100 MHz)



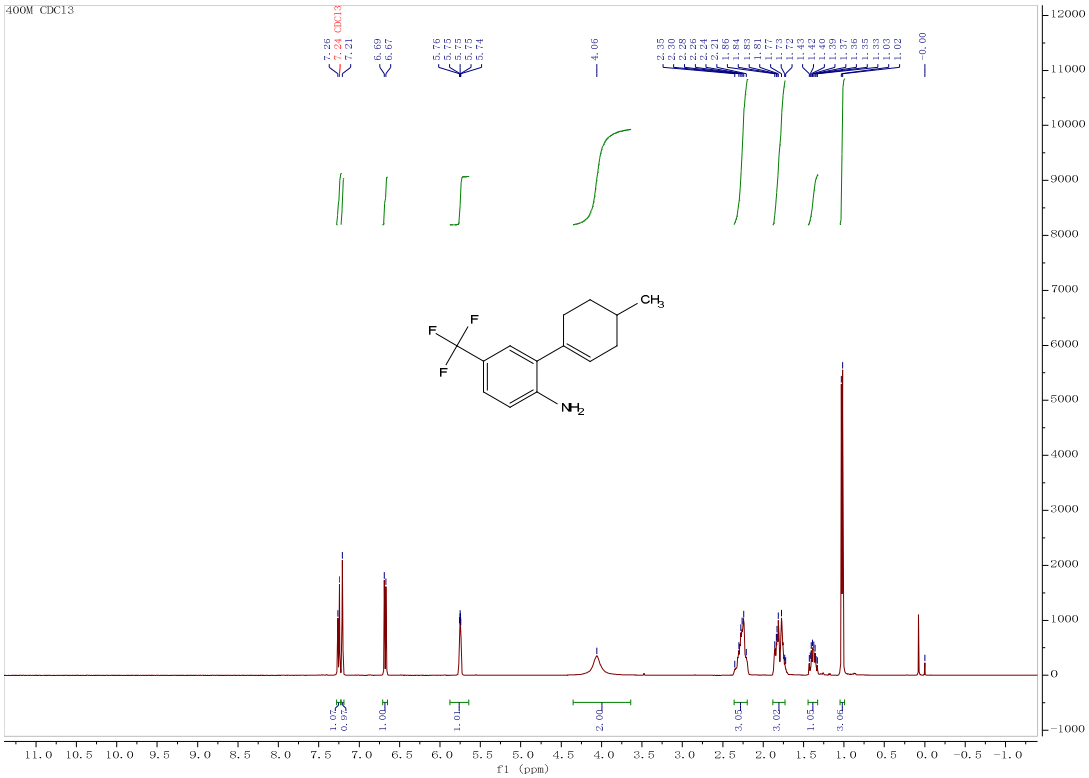
^{1}H NMR spectrum of Compound 1q ($CDCl_3$, 400 MHz)



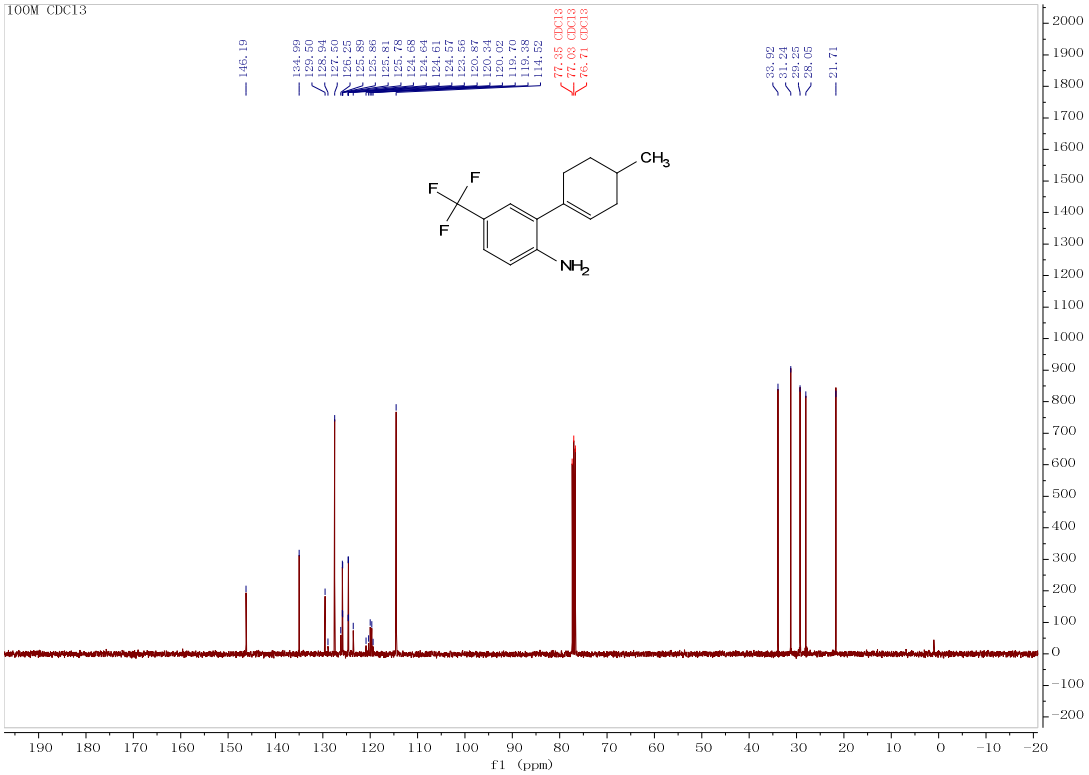
^{13}C NMR spectrum of Compound 1q ($CDCl_3$, 100 MHz)



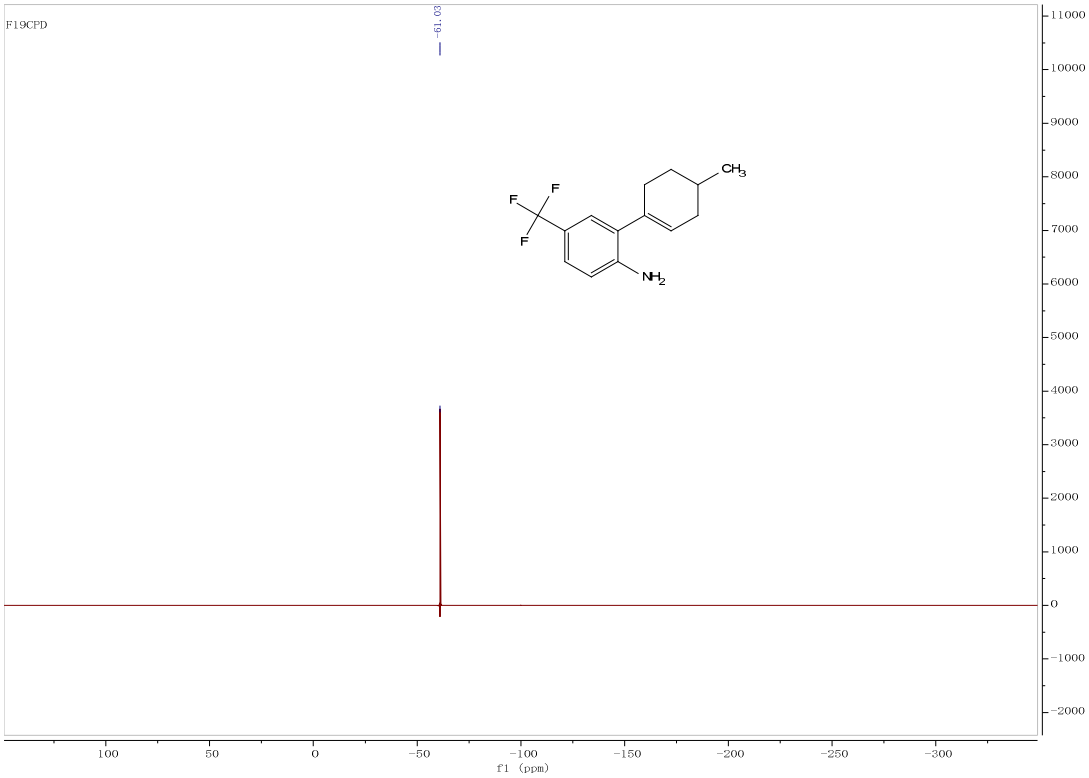
^{1}H NMR spectrum of Compound 1r ($CDCl_3$, 400 MHz)



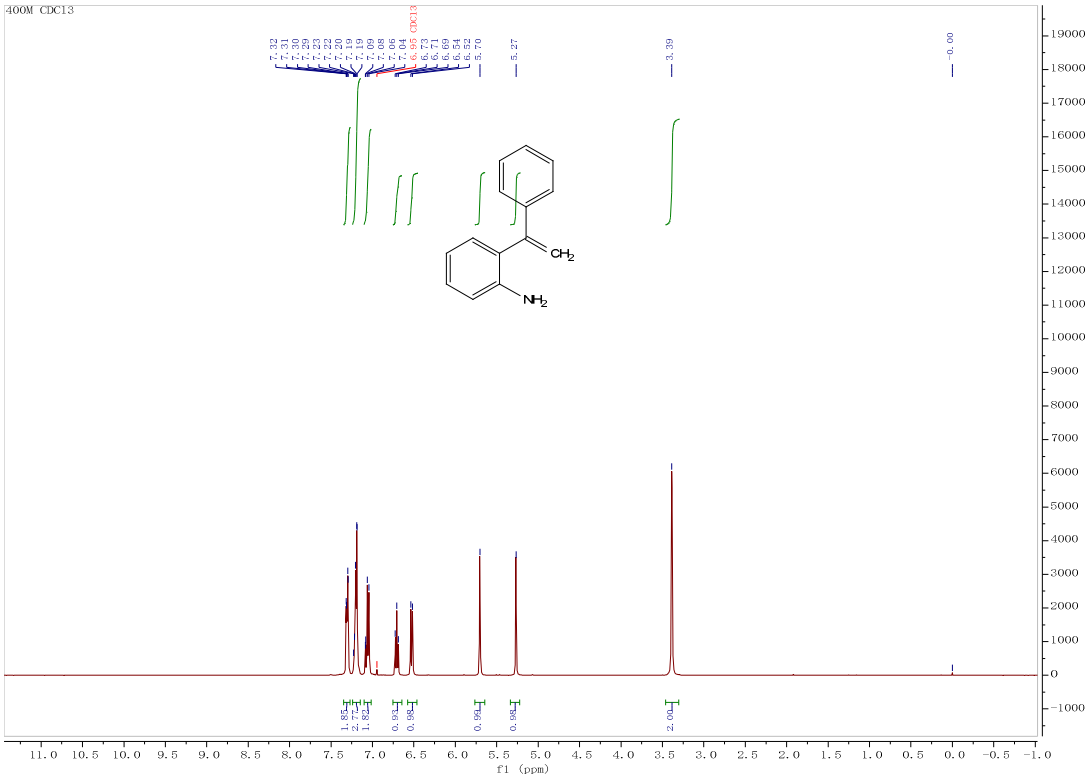
^{13}C NMR spectrum of Compound 1r ($CDCl_3$, 100 MHz)



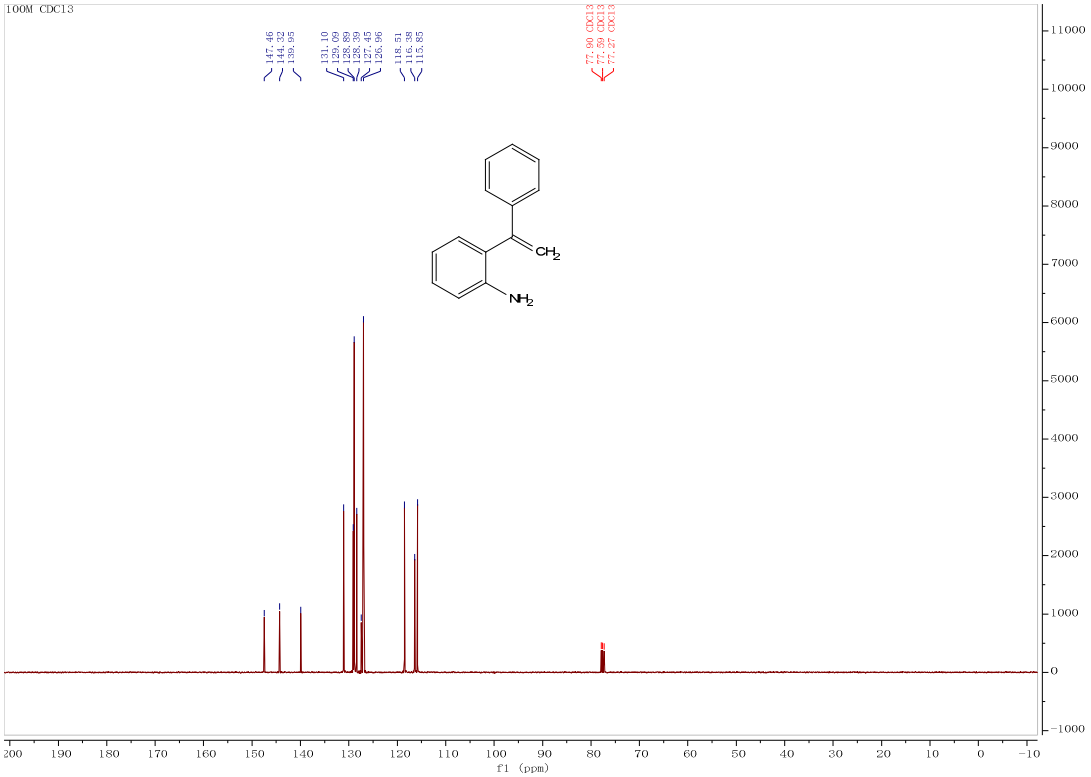
^{19}F NMR spectrum of Compound 1r ($CDCl_3$, 376 MHz)



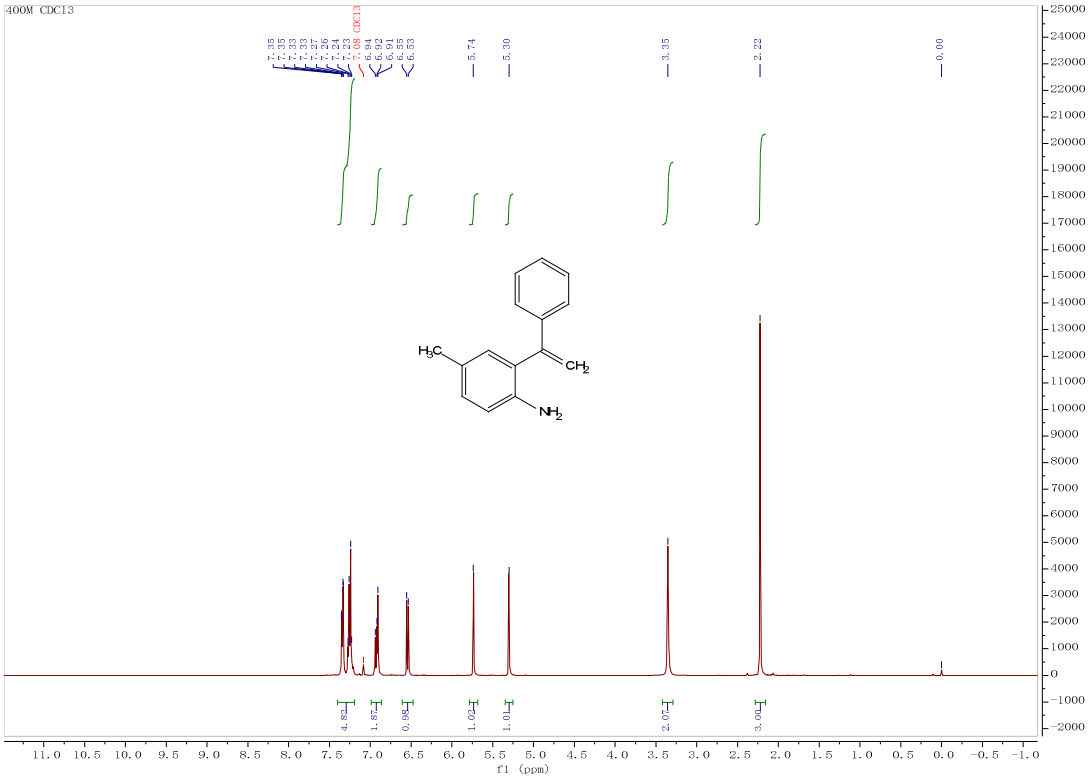
^{1}H NMR spectrum of Compound 3a ($CDCl_3$, 400 MHz)



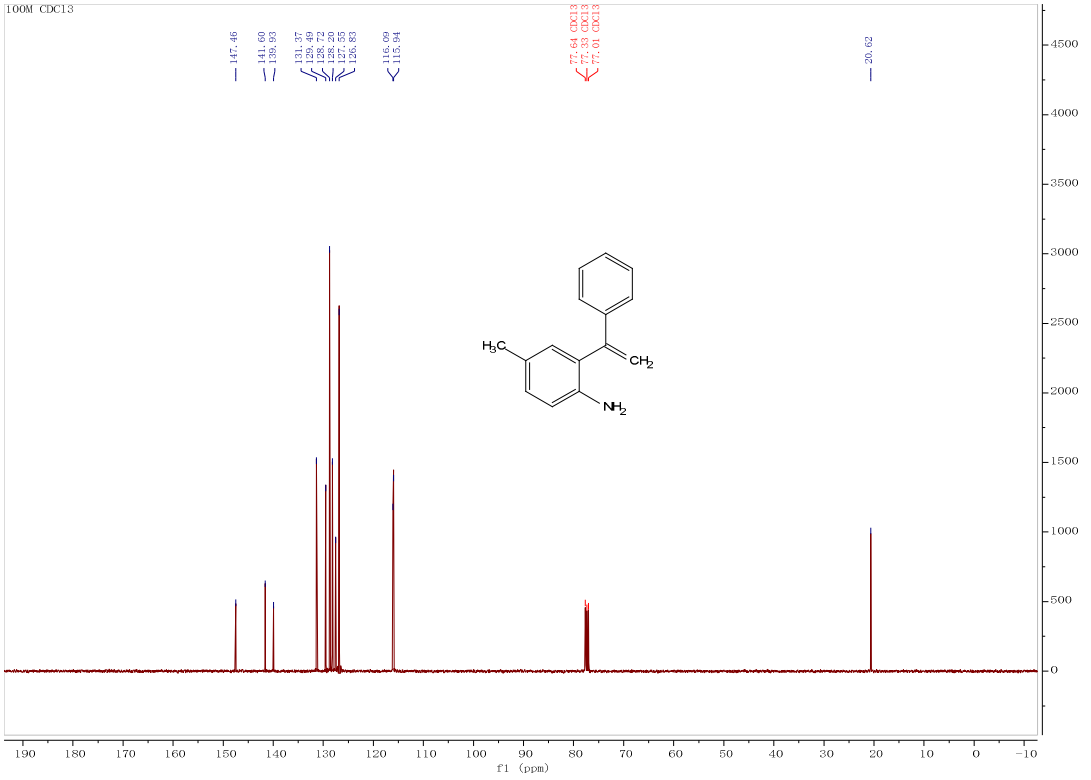
^{13}C NMR spectrum of Compound 3a ($CDCl_3$, 100 MHz)



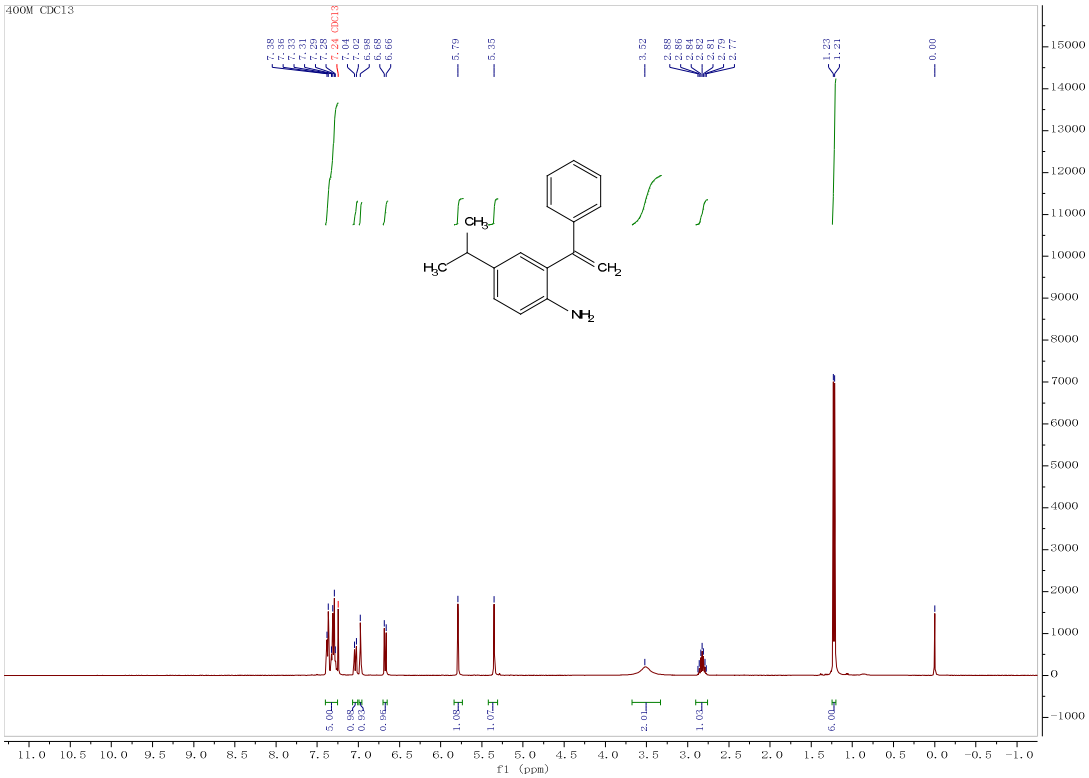
^{1}H NMR spectrum of Compound 3b ($CDCl_3$, 400 MHz)



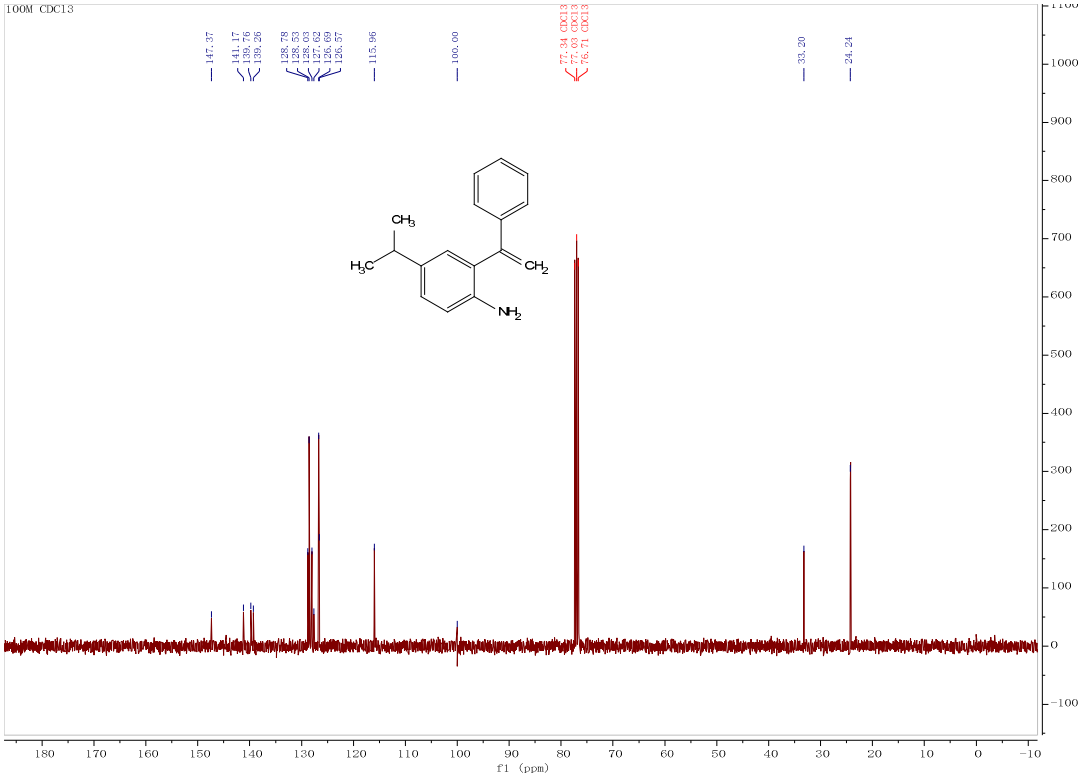
^{13}C NMR spectrum of Compound 3b ($CDCl_3$, 100 MHz)



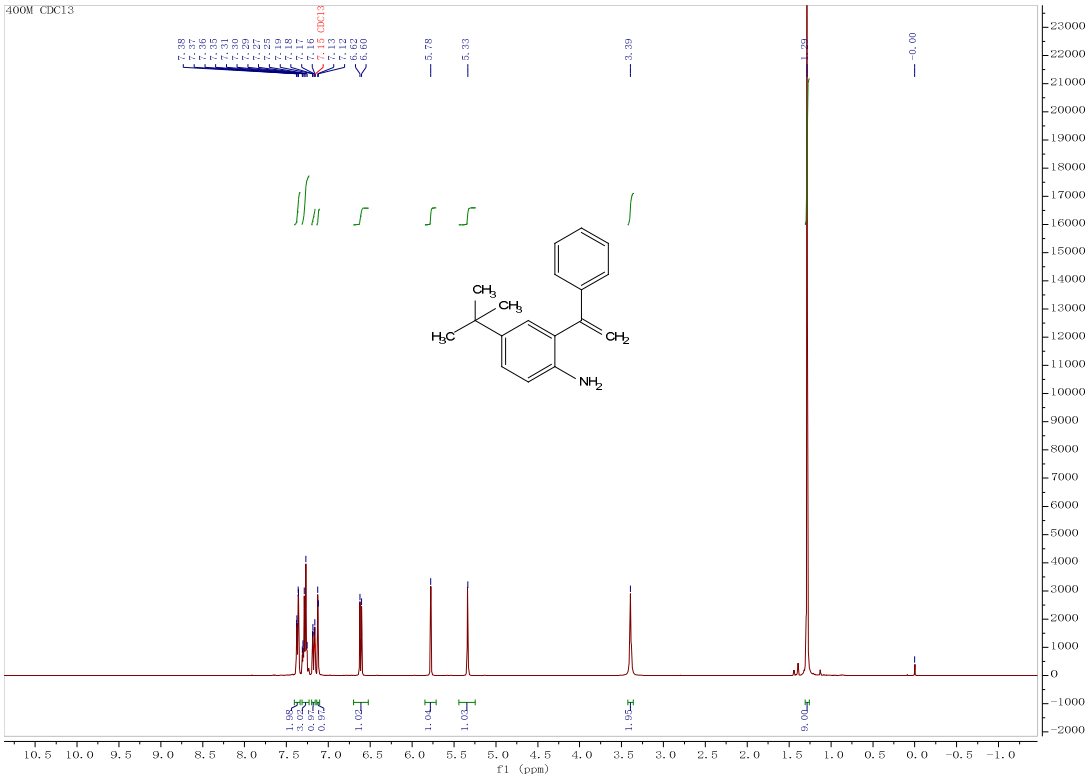
^{1}H NMR spectrum of Compound 3c ($CDCl_3$, 400 MHz)



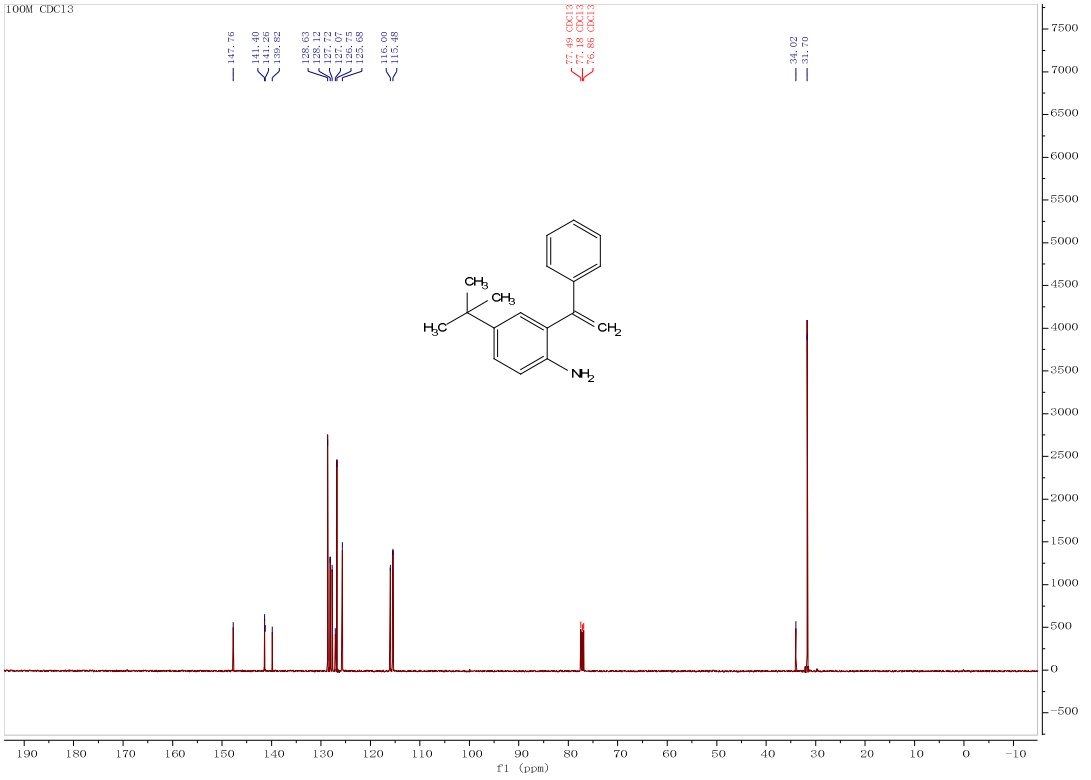
^{13}C NMR spectrum of Compound 3c ($CDCl_3$, 100 MHz)



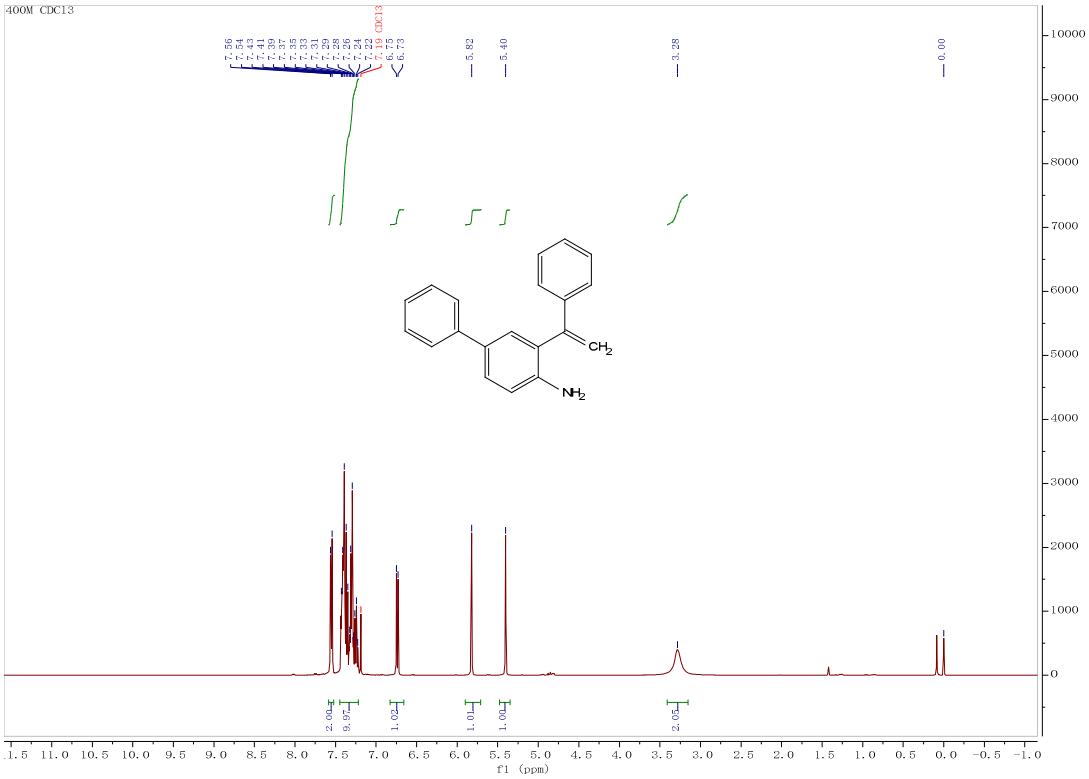
^{1}H NMR spectrum of Compound 3d ($CDCl_3$, 400 MHz)



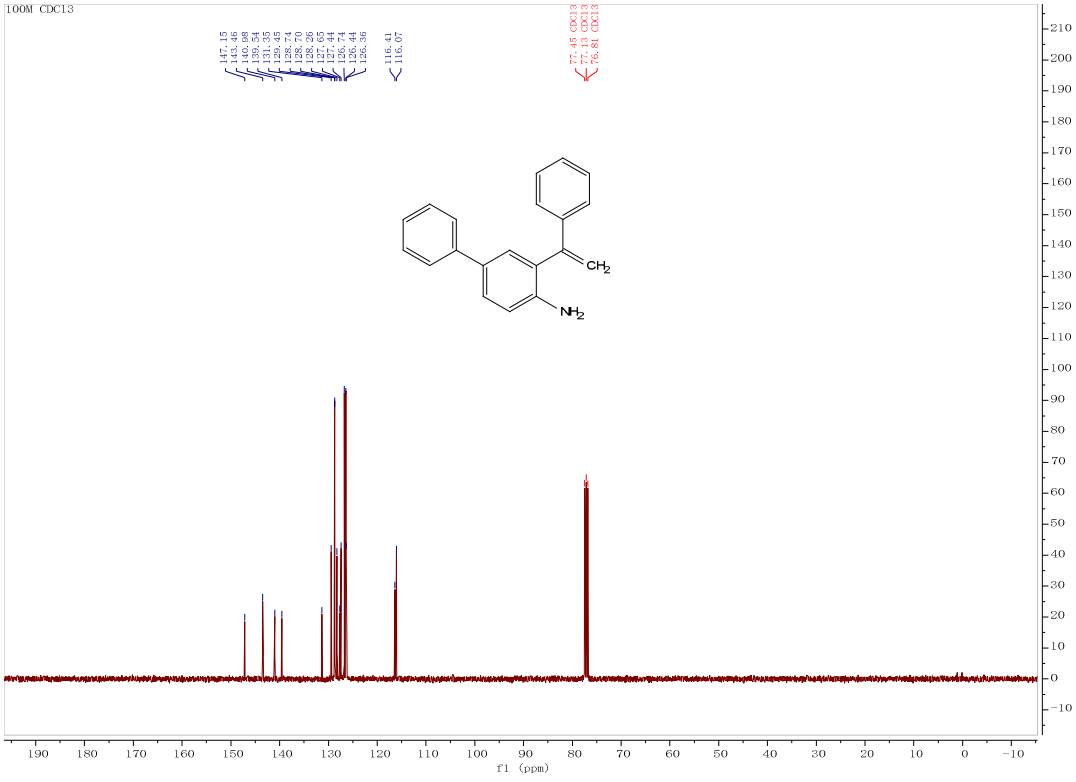
^{13}C NMR spectrum of Compound 3d ($CDCl_3$, 100 MHz)



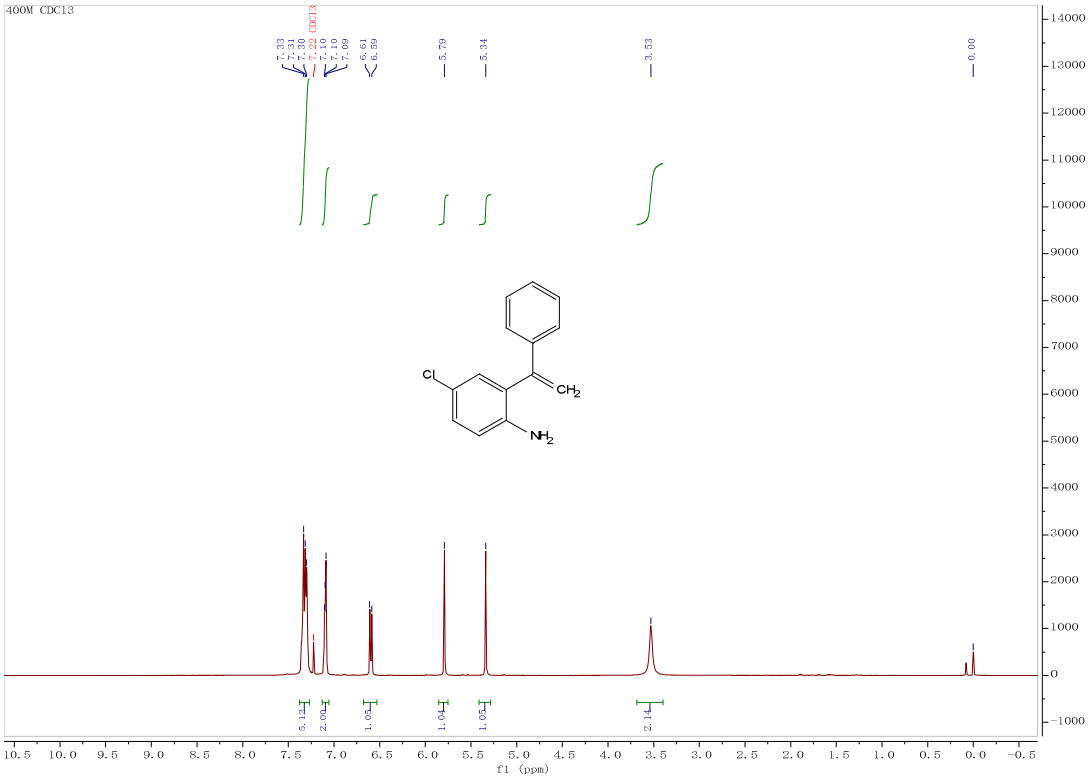
^{1}H NMR spectrum of Compound 3e ($CDCl_3$, 400 MHz)



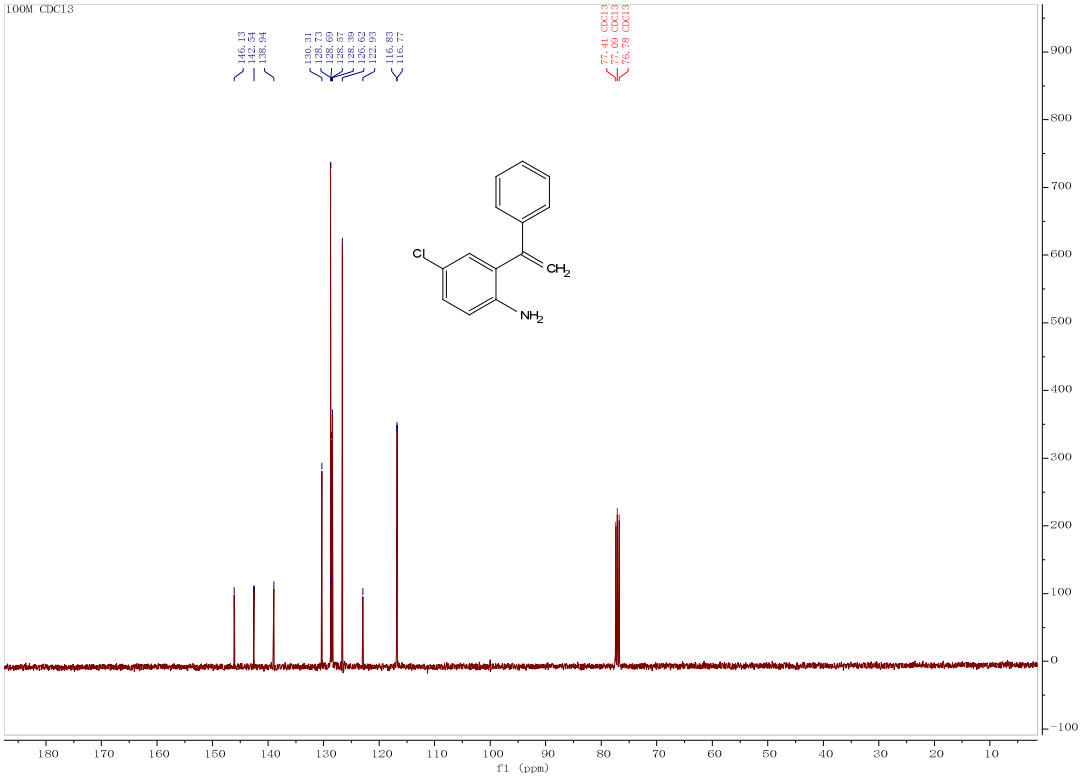
^{13}C NMR spectrum of Compound 3e ($CDCl_3$, 100 MHz)



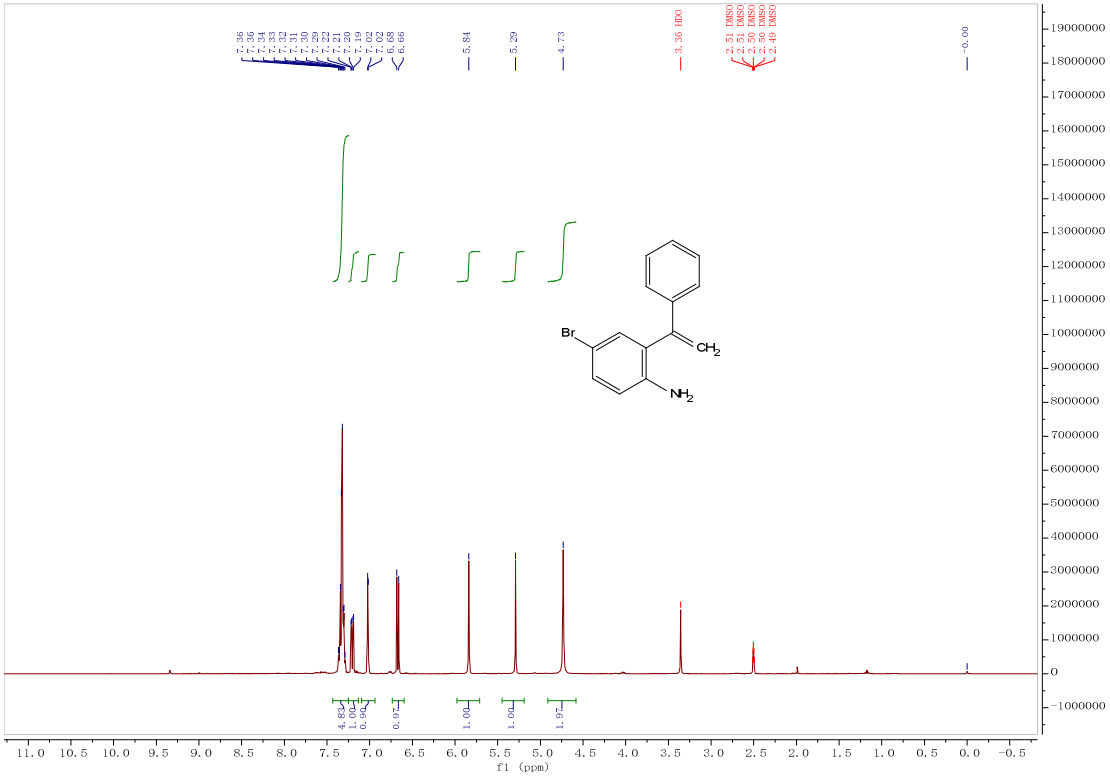
^{1}H NMR spectrum of Compound 3f ($CDCl_3$, 400 MHz)



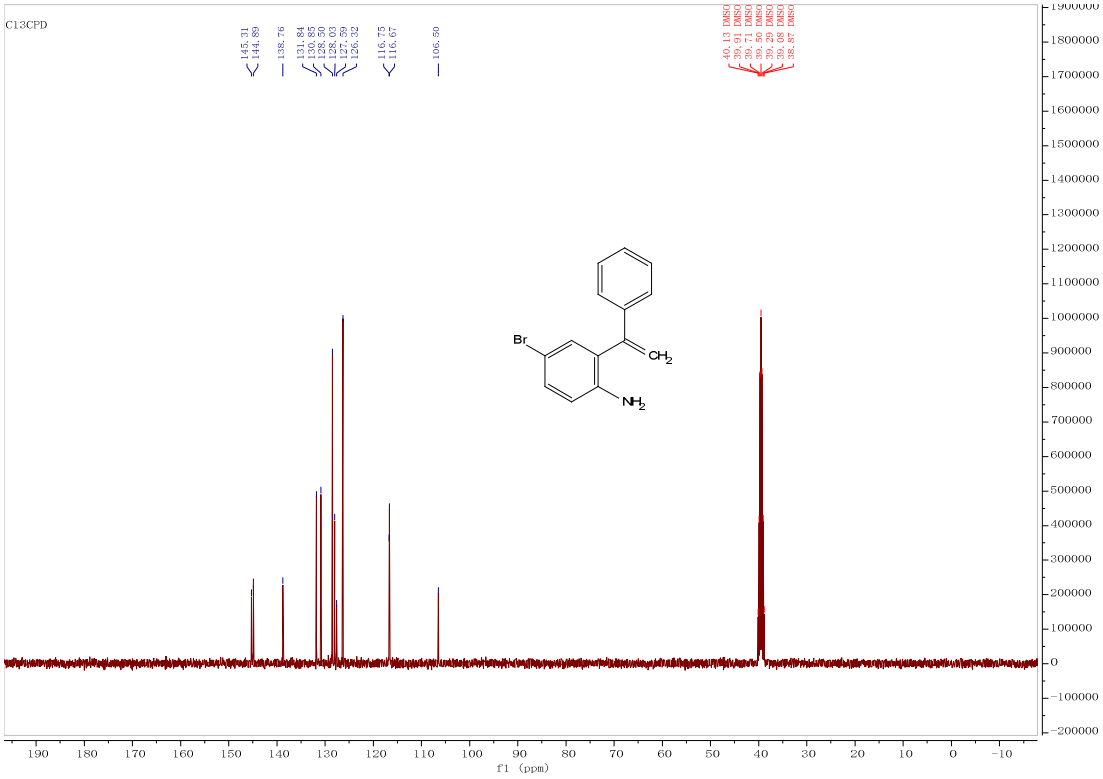
^{13}C NMR spectrum of Compound 3f ($CDCl_3$, 100 MHz)



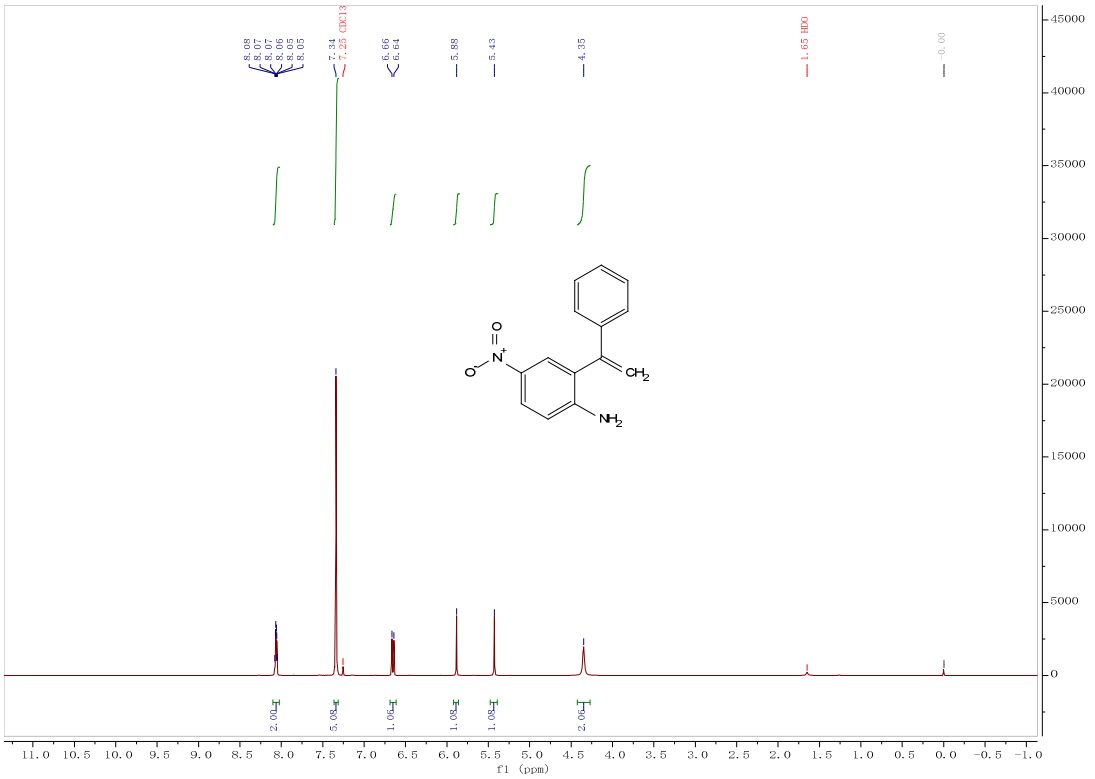
^{1}H NMR spectrum of Compound 3g (DMSO-d_6, 400 MHz)



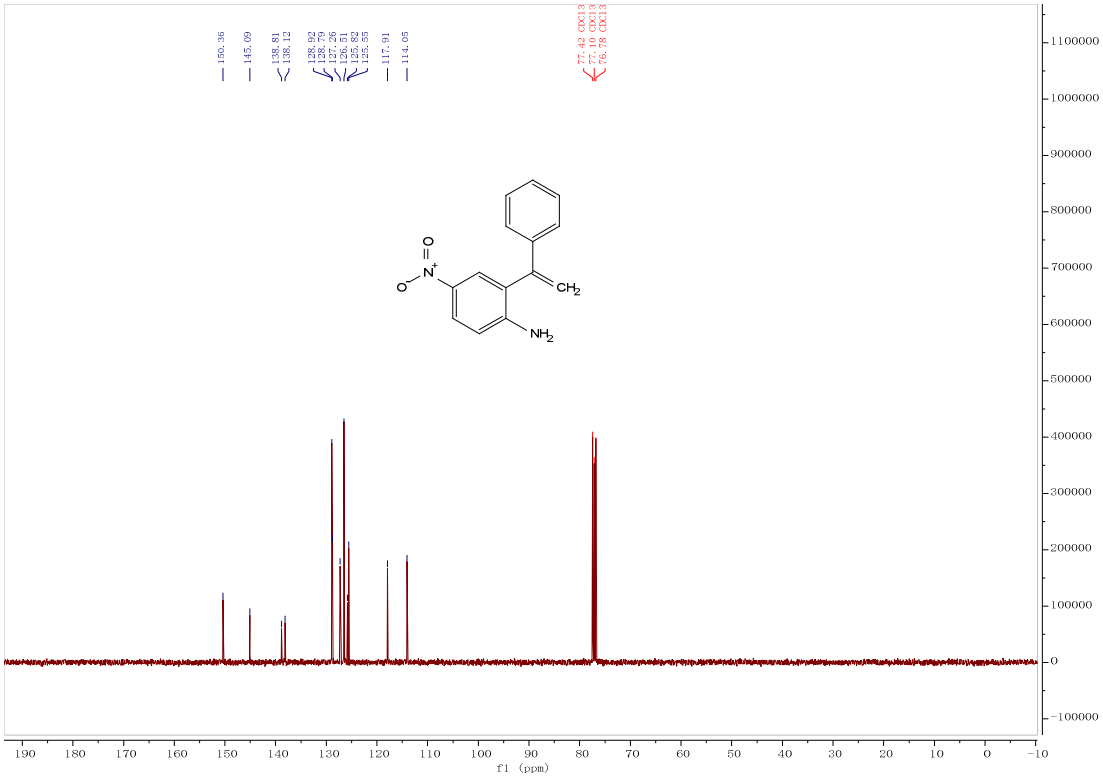
^{13}C NMR spectrum of Compound 3g (DMSO-d_6, 100 MHz)



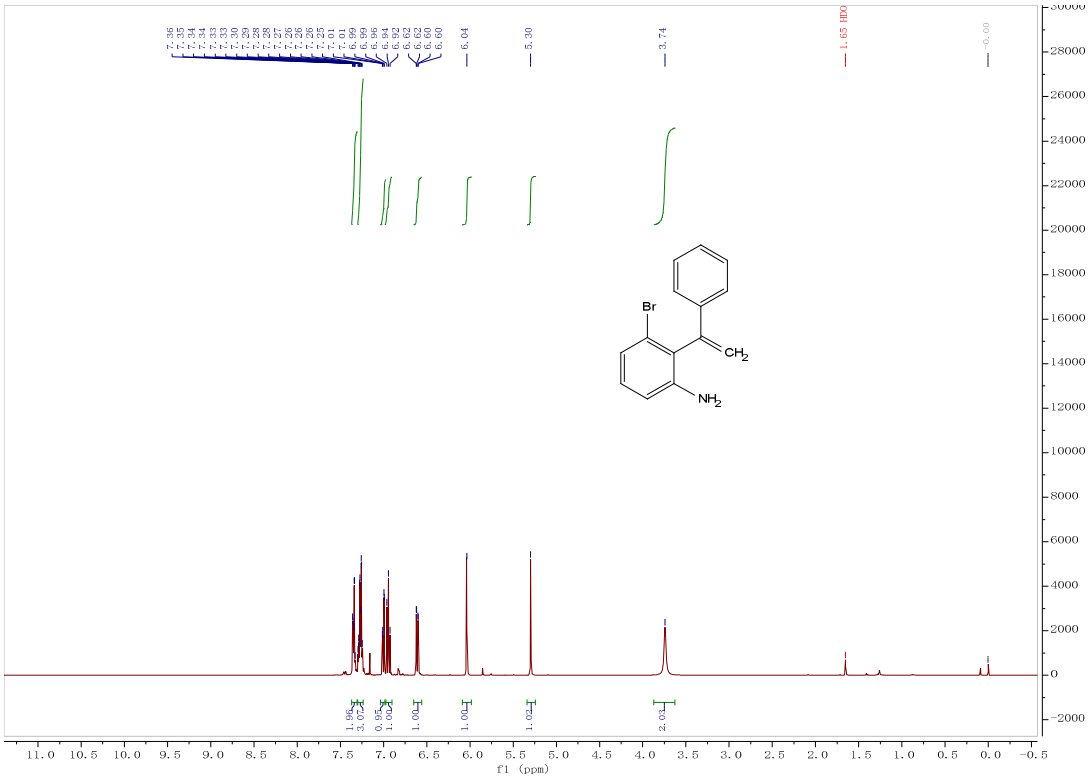
^{1}H NMR spectrum of Compound 3h ($CDCl_3$, 400 MHz)



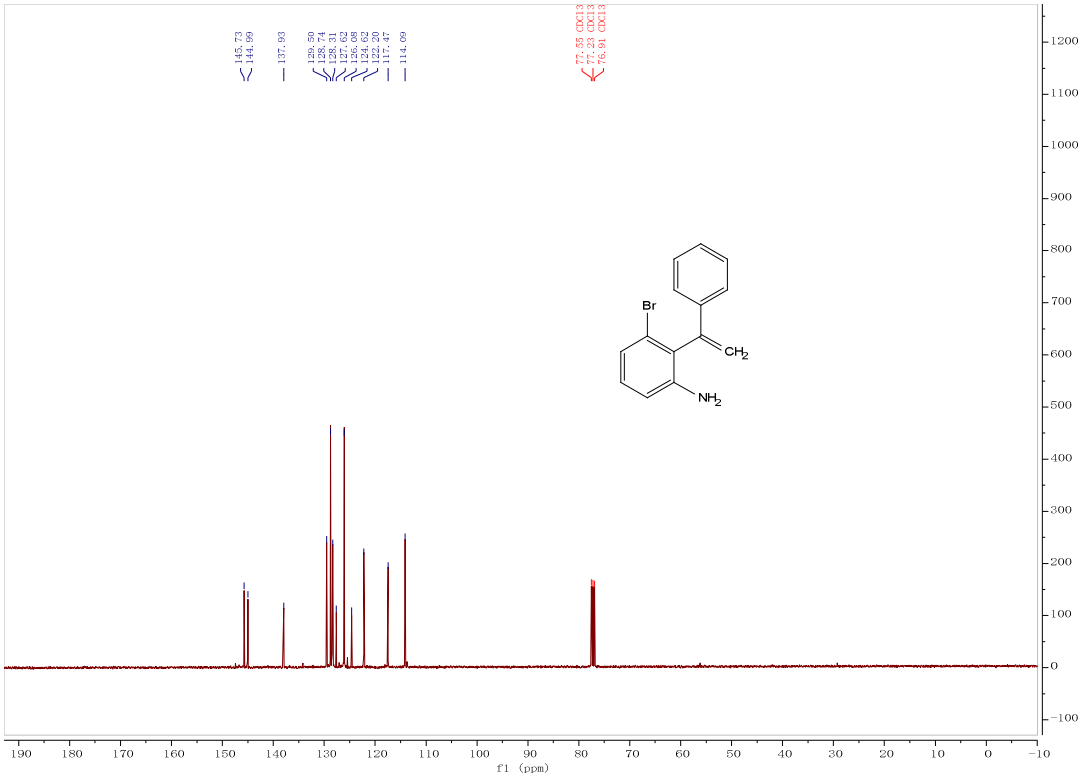
^{13}C NMR spectrum of Compound 3h ($CDCl_3$, 100 MHz)



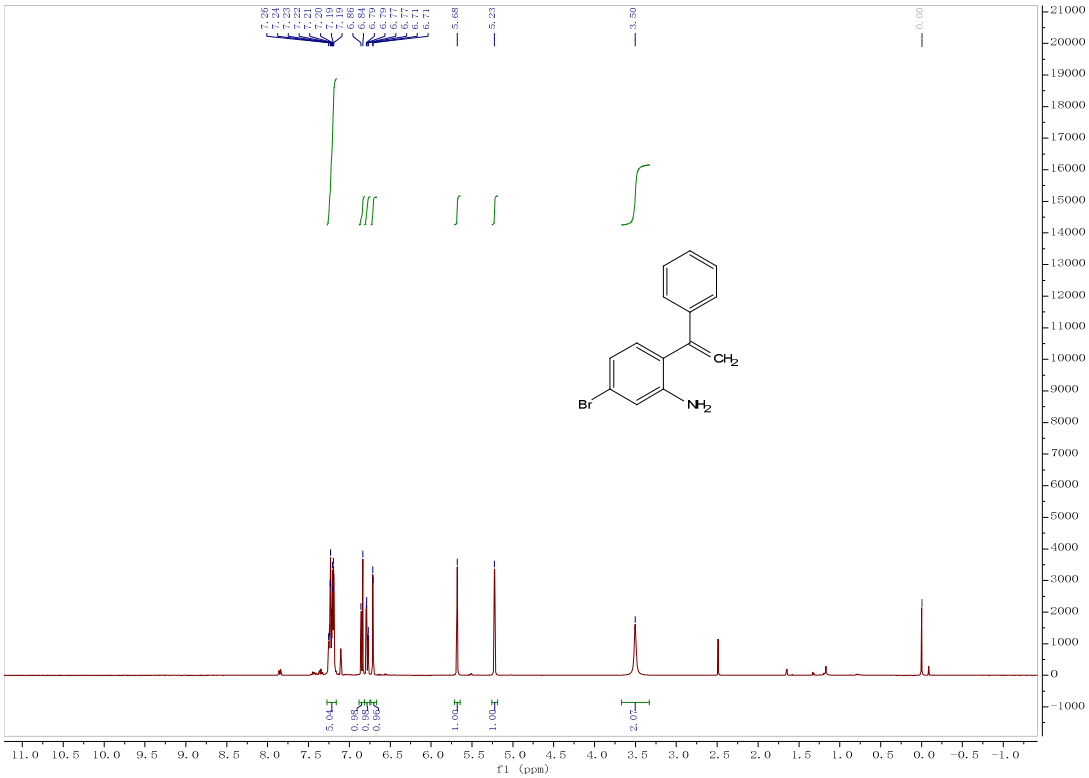
^{1}H NMR spectrum of Compound 3i ($CDCl_3$, 400 MHz)



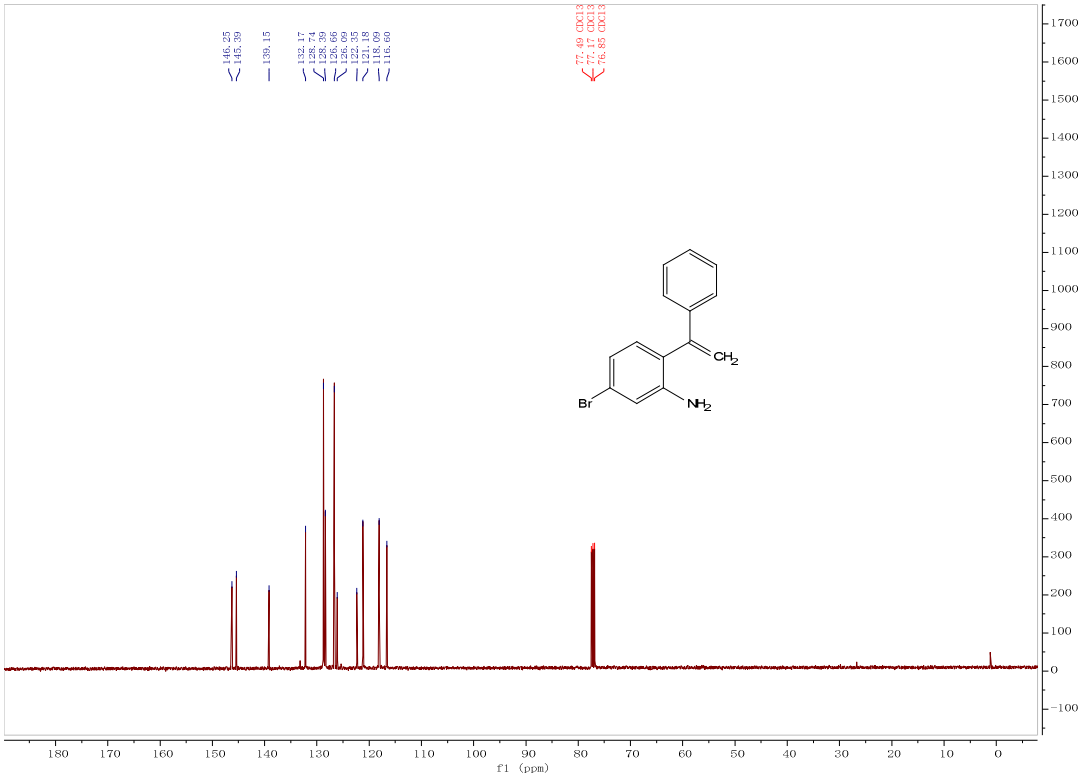
^{13}C NMR spectrum of Compound 3i ($CDCl_3$, 100 MHz)



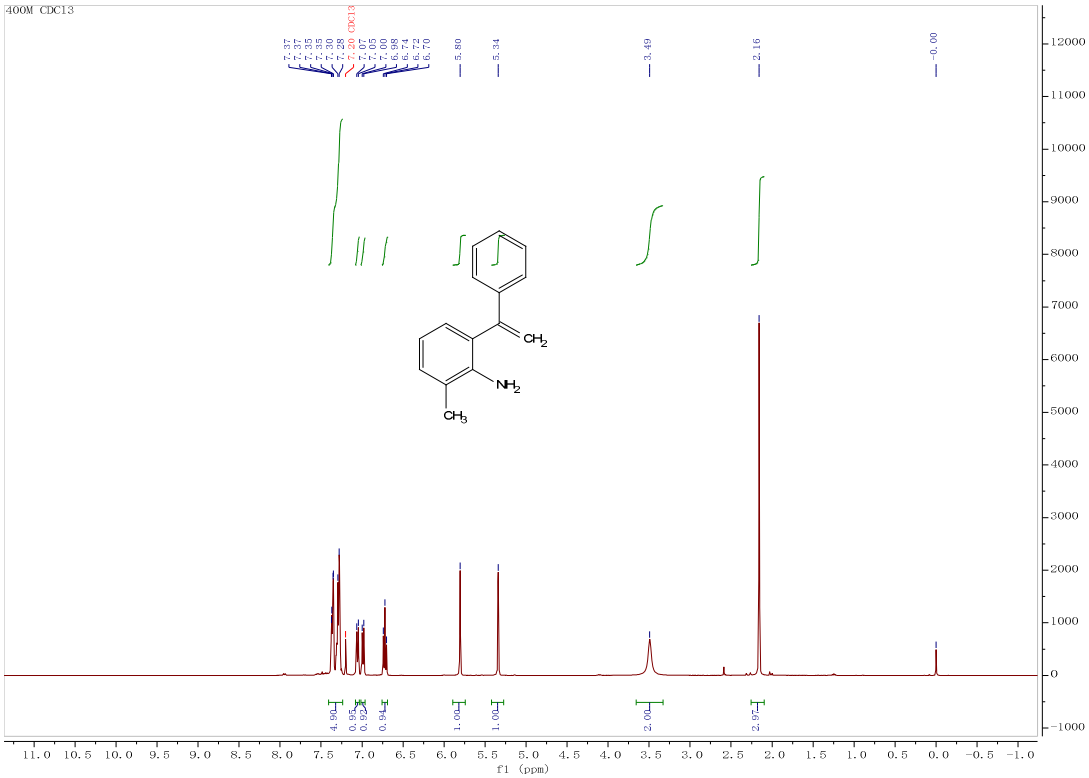
^{1}H NMR spectrum of Compound 3j ($CDCl_3$, 400 MHz)



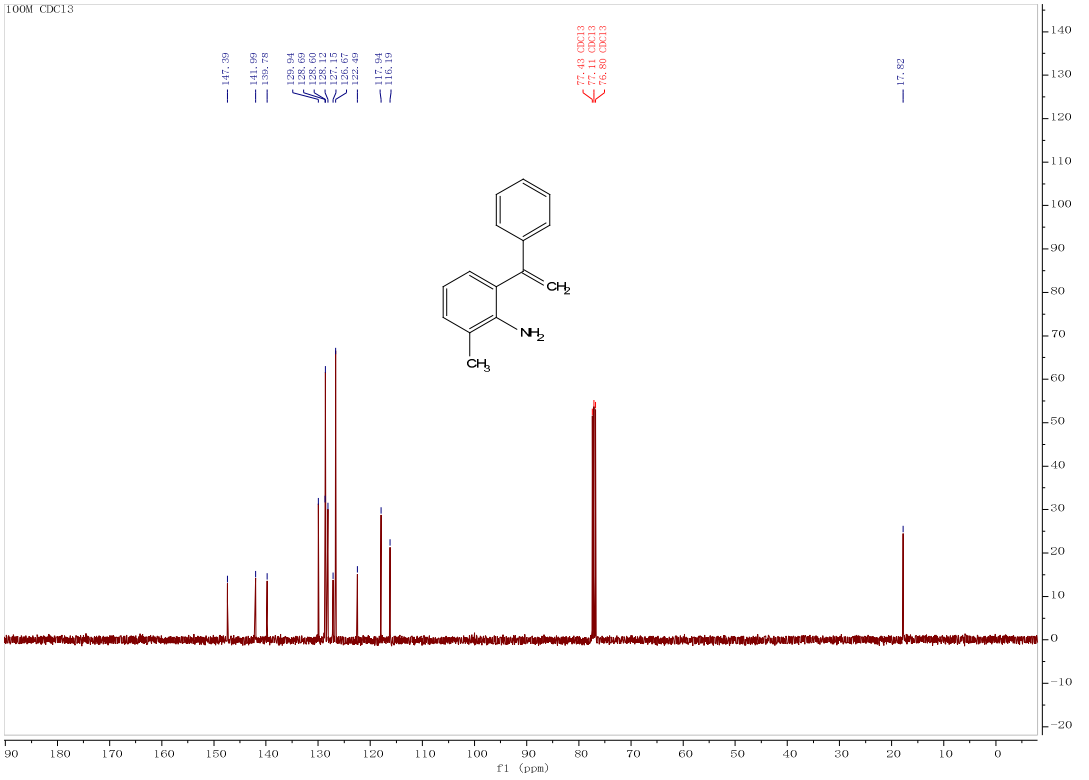
^{13}C NMR spectrum of Compound 3j ($CDCl_3$, 100 MHz)



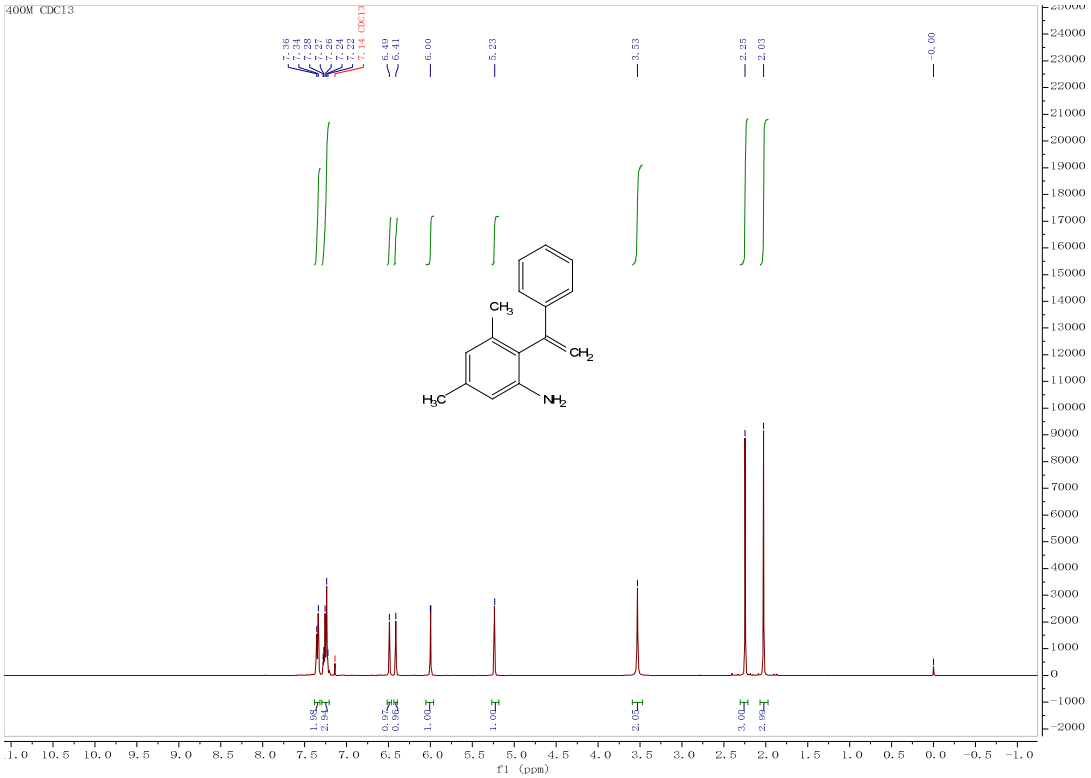
^{1}H NMR spectrum of Compound 3k ($CDCl_3$, 400 MHz)



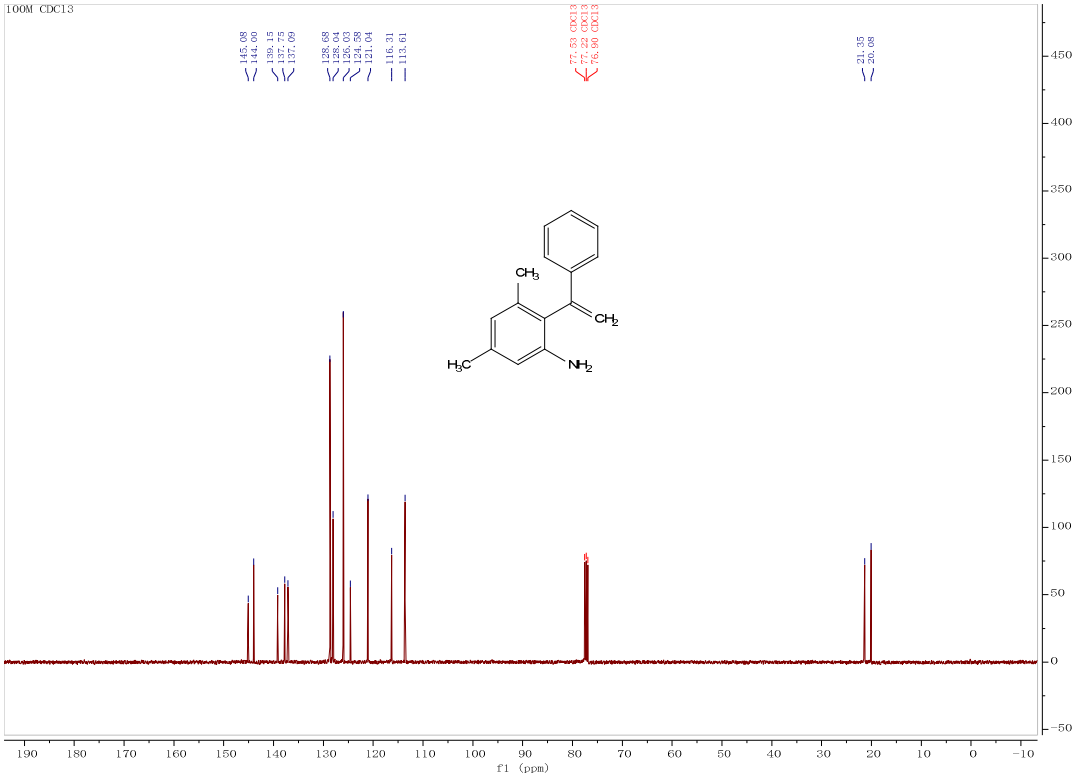
^{13}C NMR spectrum of Compound 3k ($CDCl_3$, 100 MHz)



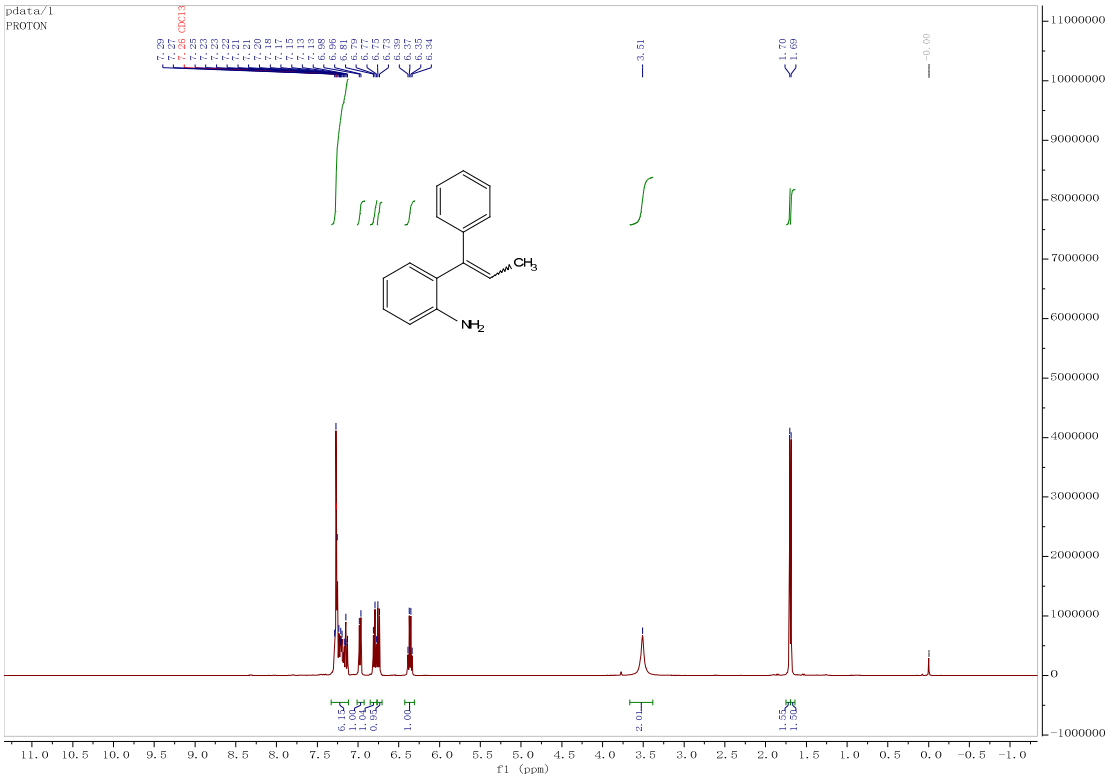
^{1}H NMR spectrum of Compound 3l ($CDCl_3$, 400 MHz)



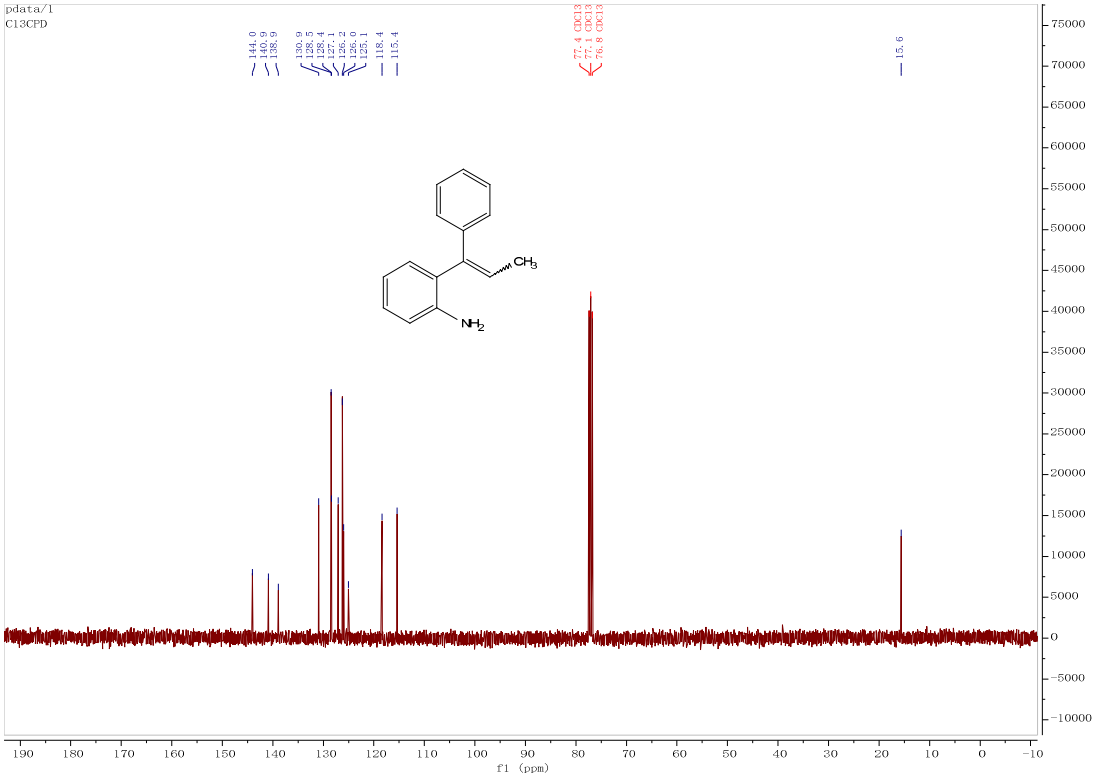
^{13}C NMR spectrum of Compound 3l ($CDCl_3$, 100 MHz)



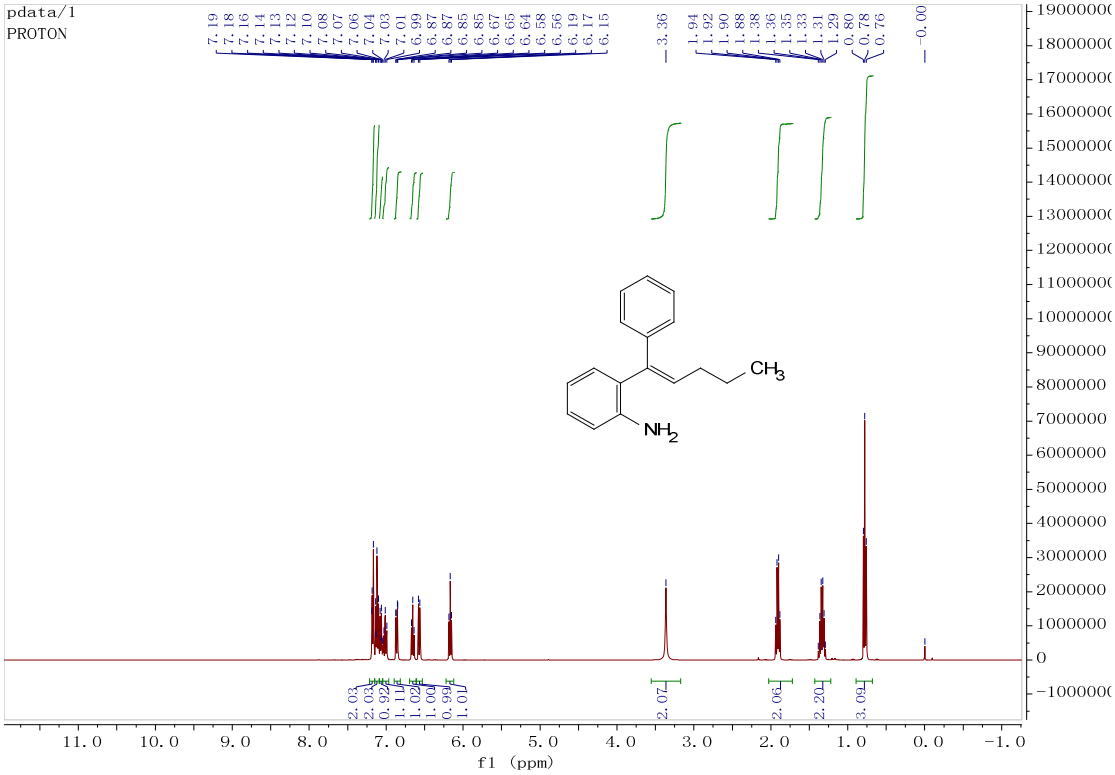
^{1}H NMR spectrum of Compound 3m ($CDCl_3$, 400 MHz)



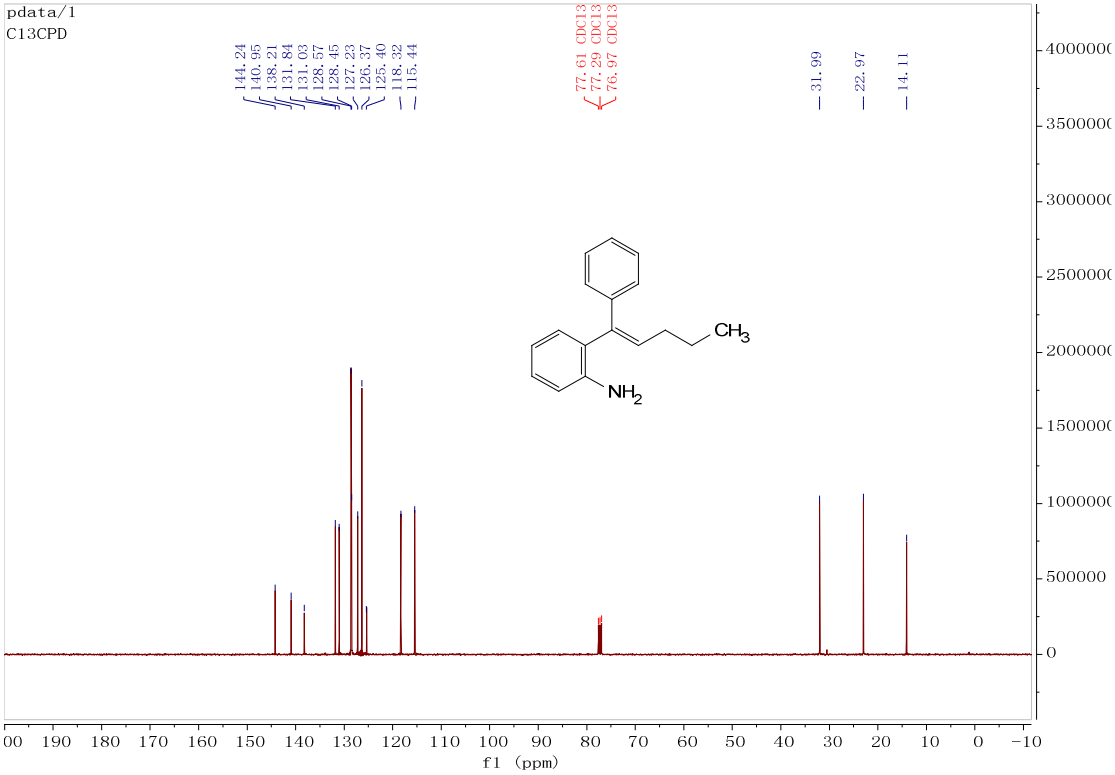
^{13}C NMR spectrum of Compound 3m ($CDCl_3$, 100 MHz)



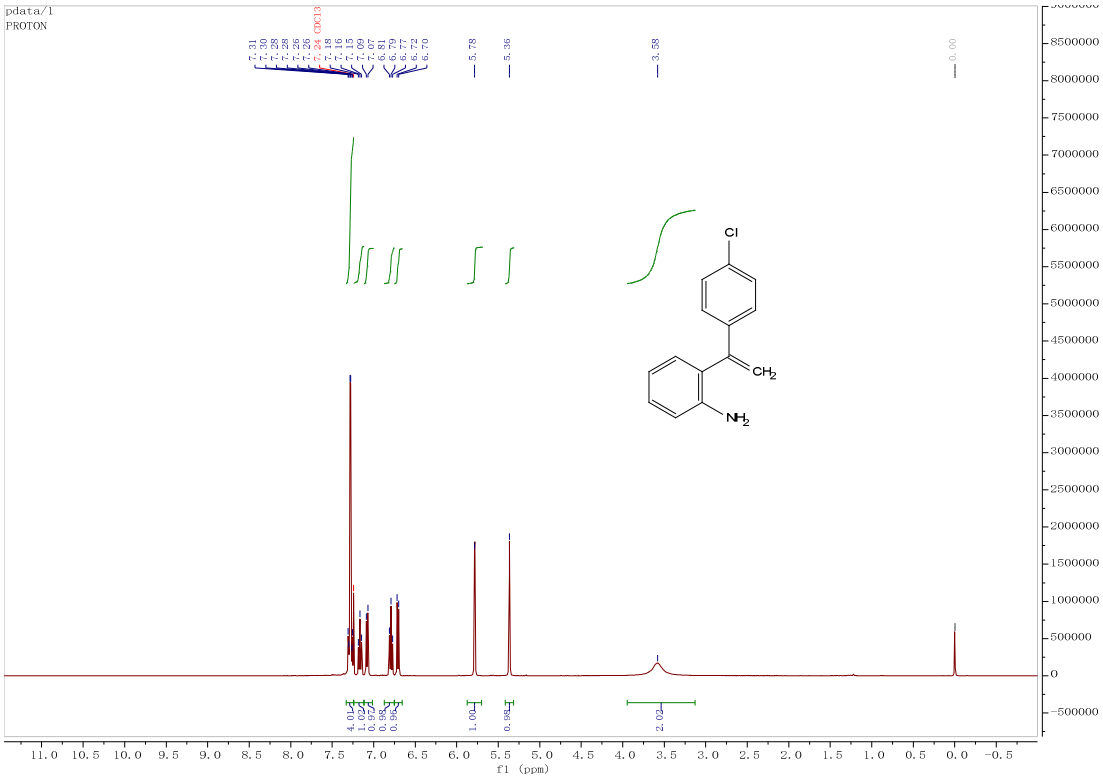
^{1}H NMR spectrum of Compound 3n ($CDCl_3$, 400 MHz)



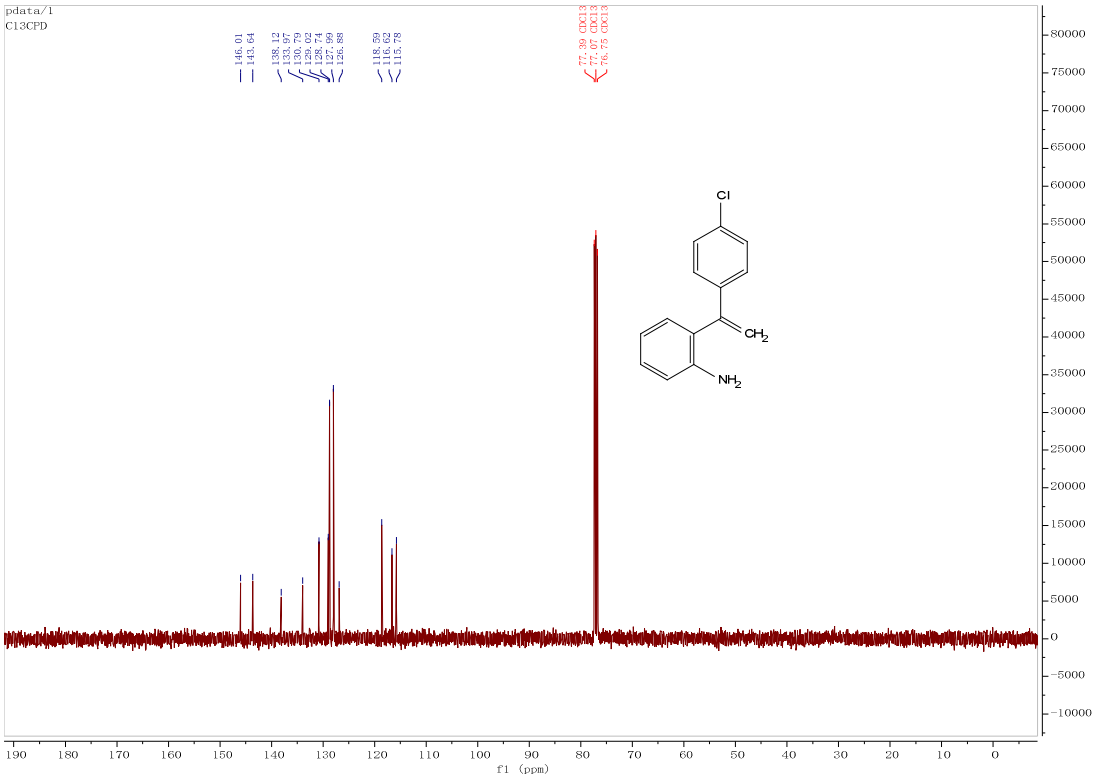
^{13}C NMR spectrum of Compound 3n ($CDCl_3$, 100 MHz)



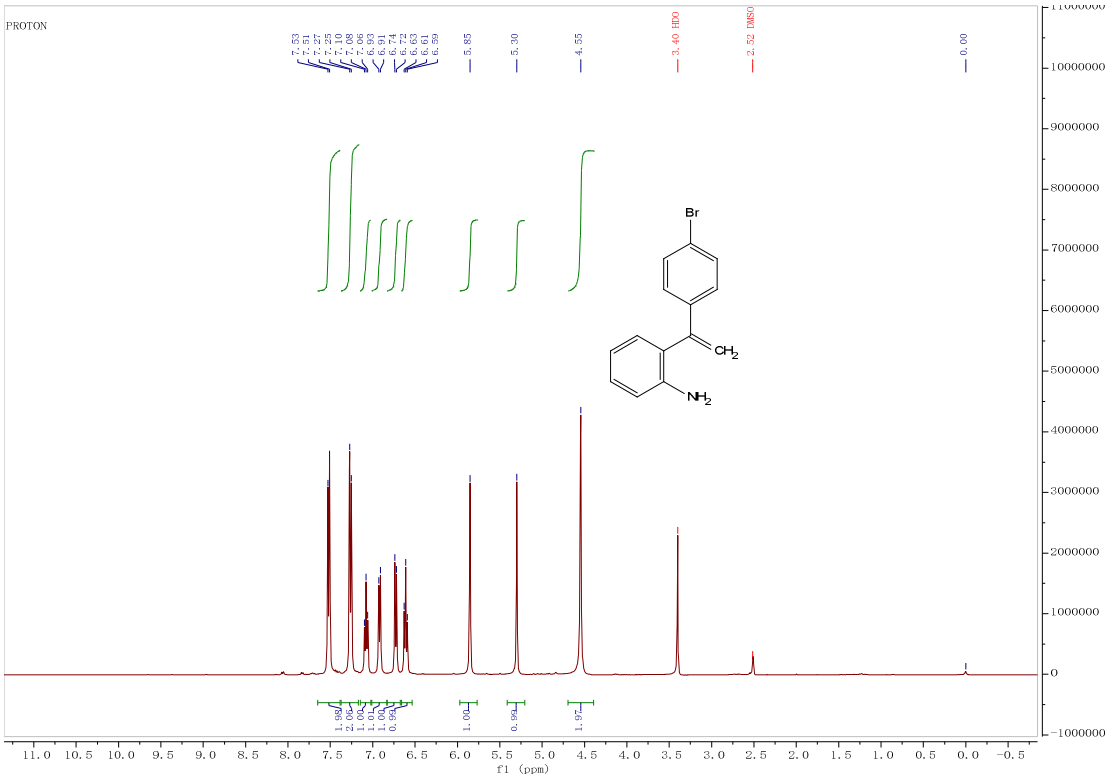
^{1}H NMR spectrum of Compound 3p ($CDCl_3$, 400 MHz)



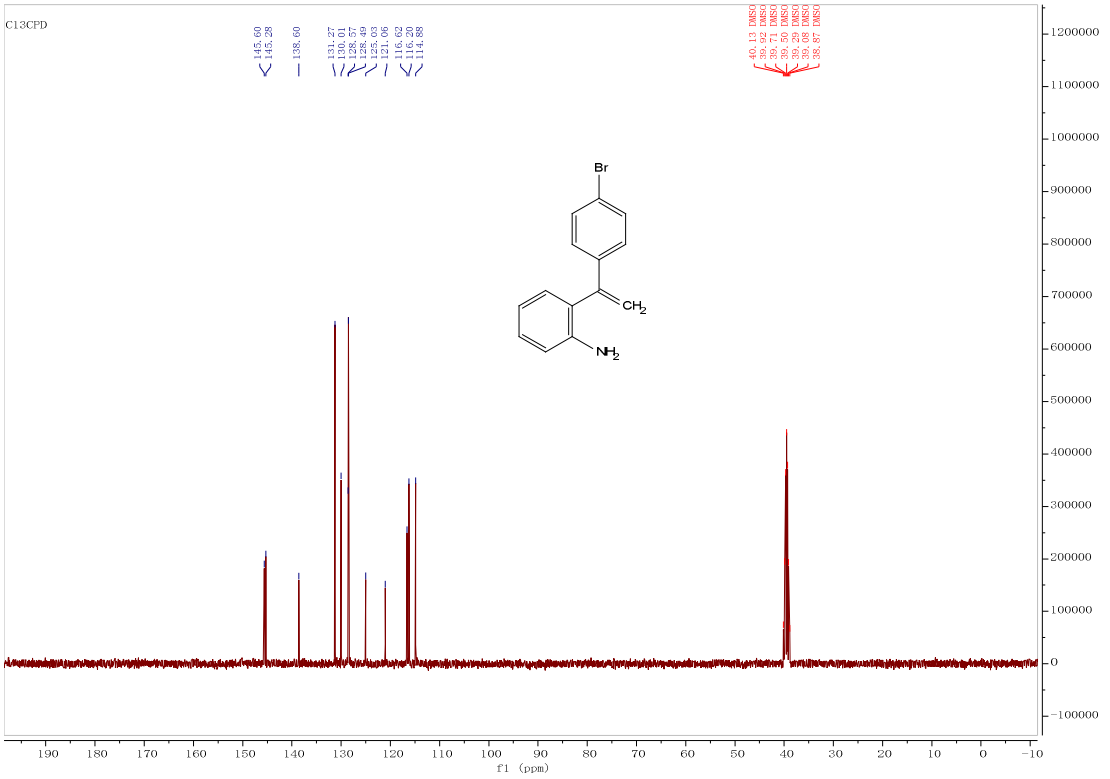
^{13}C NMR spectrum of Compound 3p ($CDCl_3$, 100 MHz)



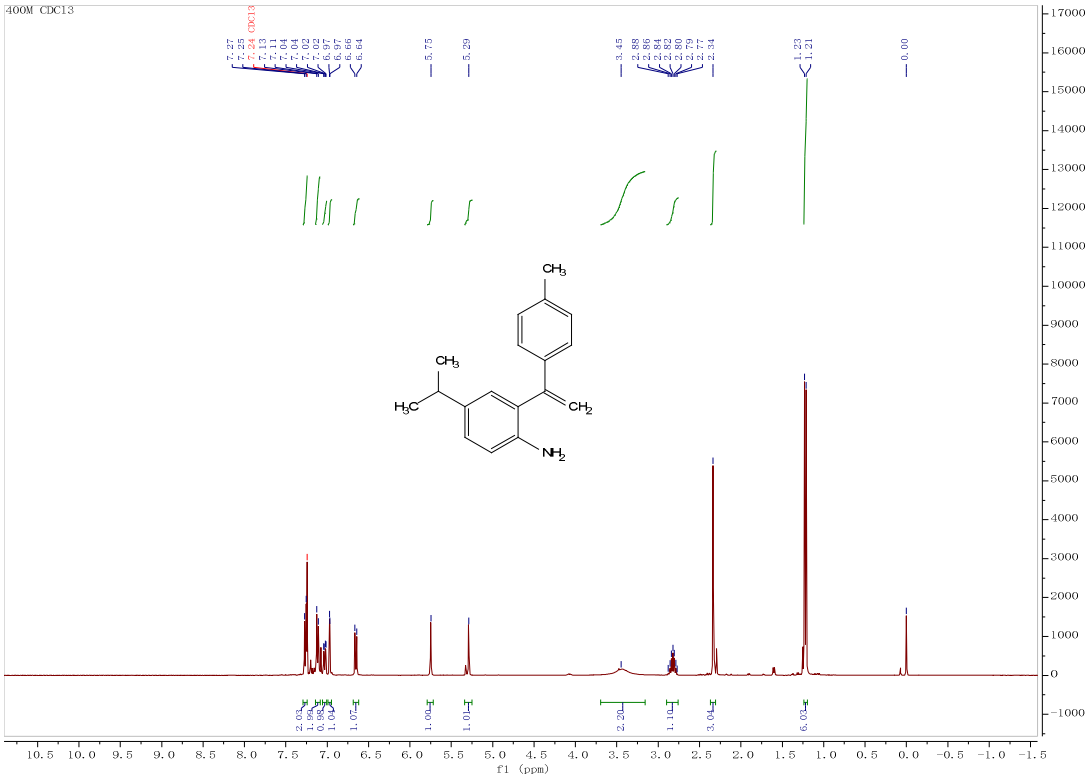
^{1}H NMR spectrum of Compound 3q (DMSO-d_6, 400 MHz)



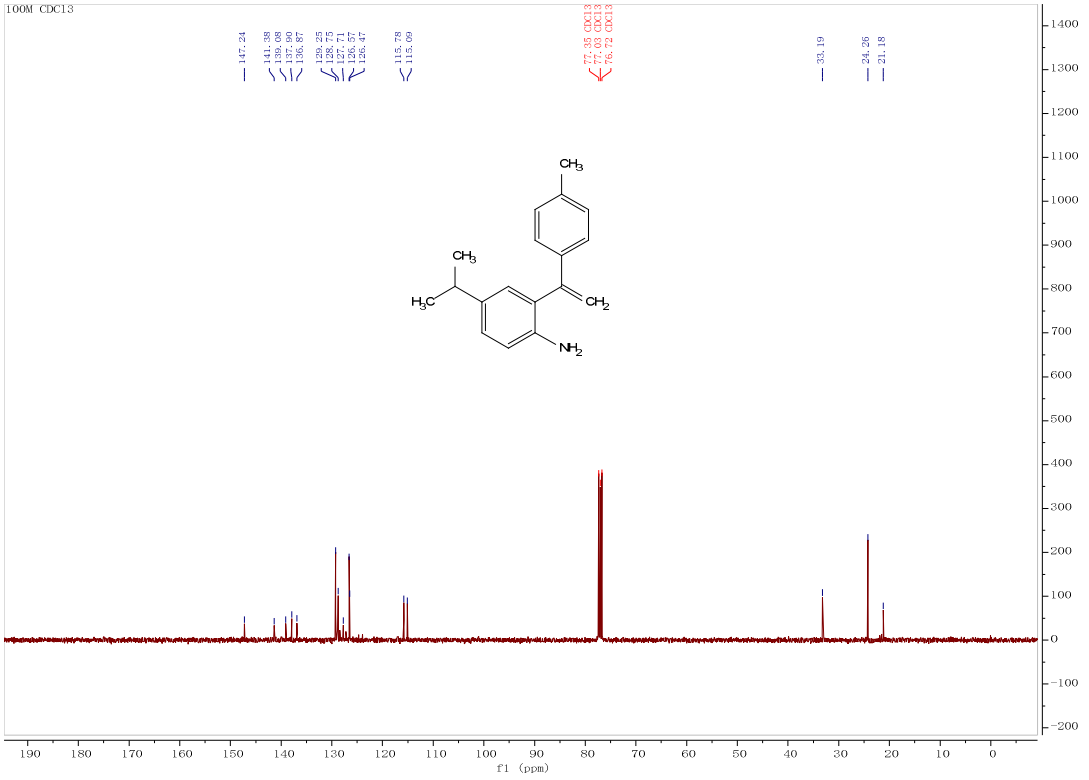
^{13}C NMR spectrum of Compound 3q (DMSO-d_6, 100 MHz)



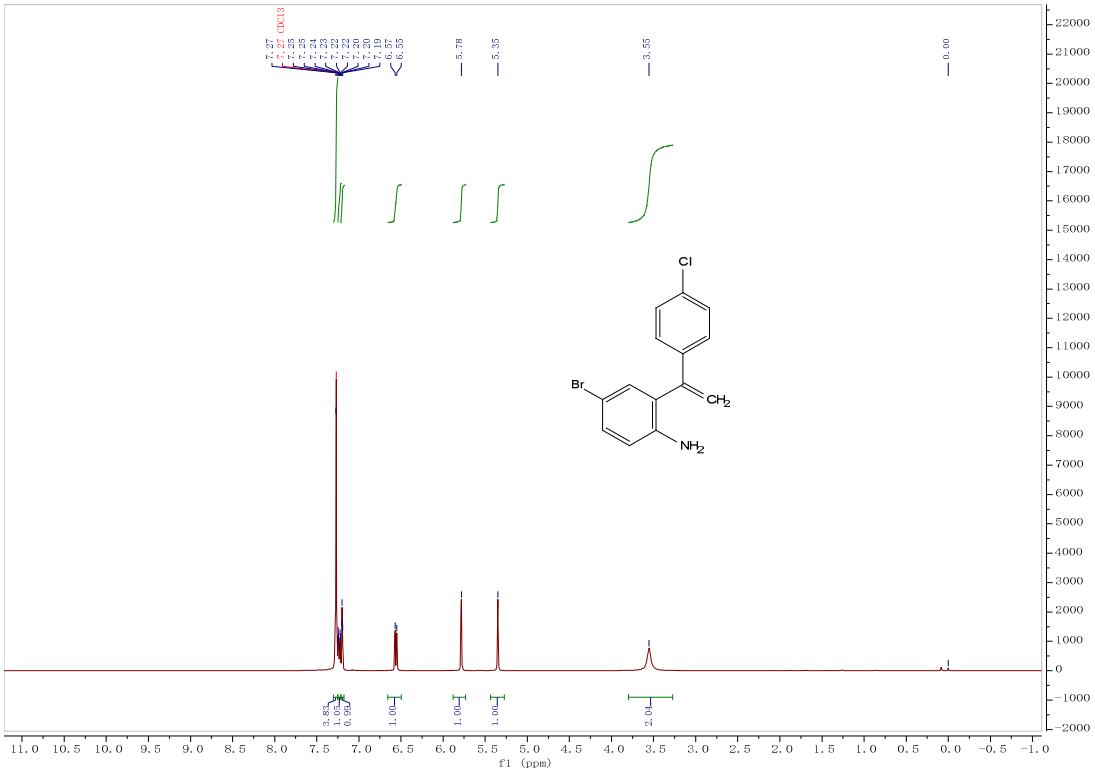
^{1}H NMR spectrum of Compound 3r ($CDCl_3$, 400 MHz)



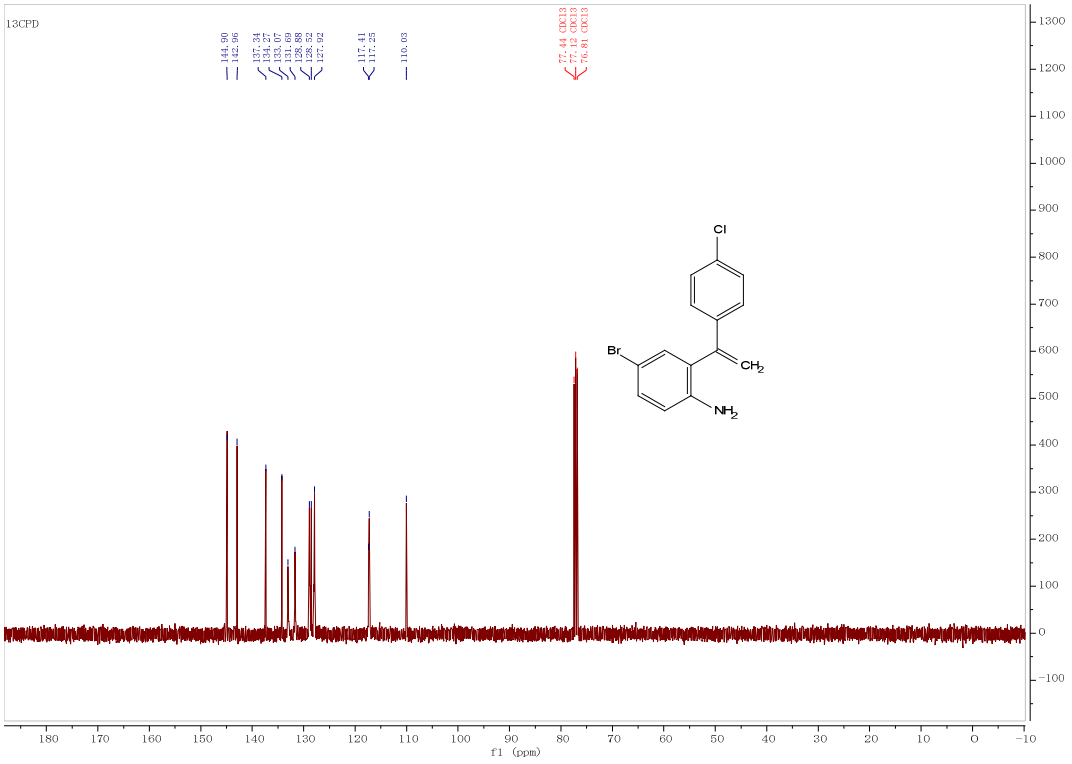
^{13}C NMR spectrum of Compound 3r ($CDCl_3$, 100 MHz)



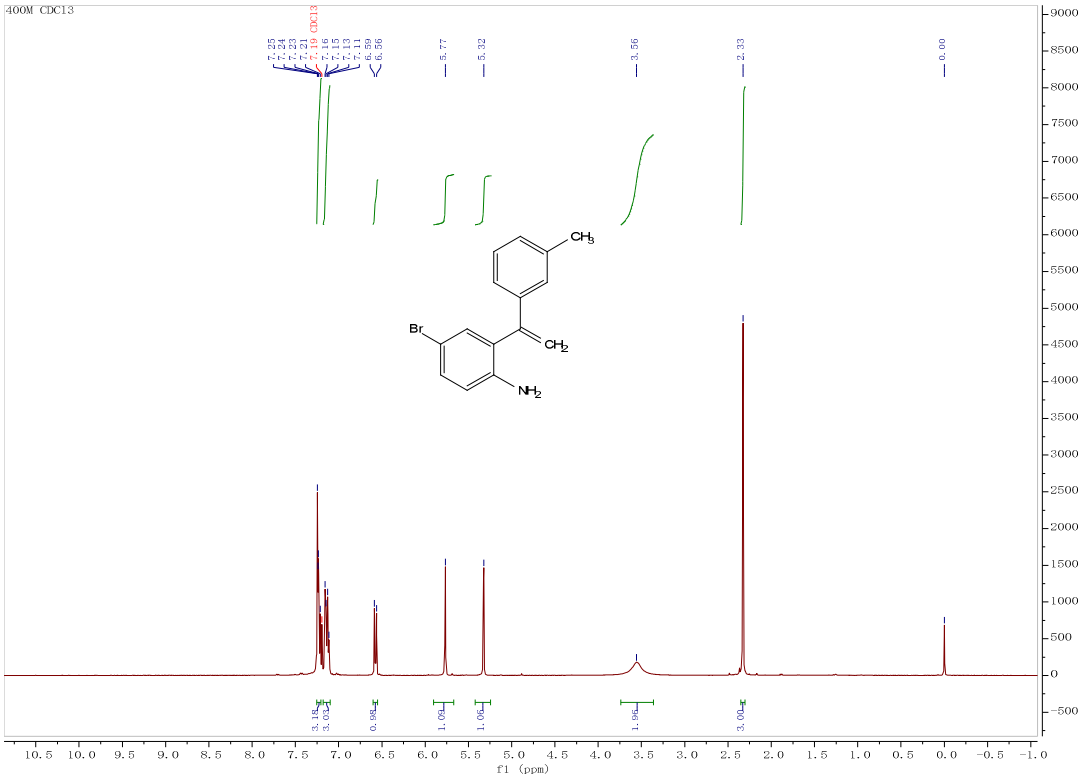
^{1}H NMR spectrum of Compound 3s ($CDCl_3$, 400 MHz)



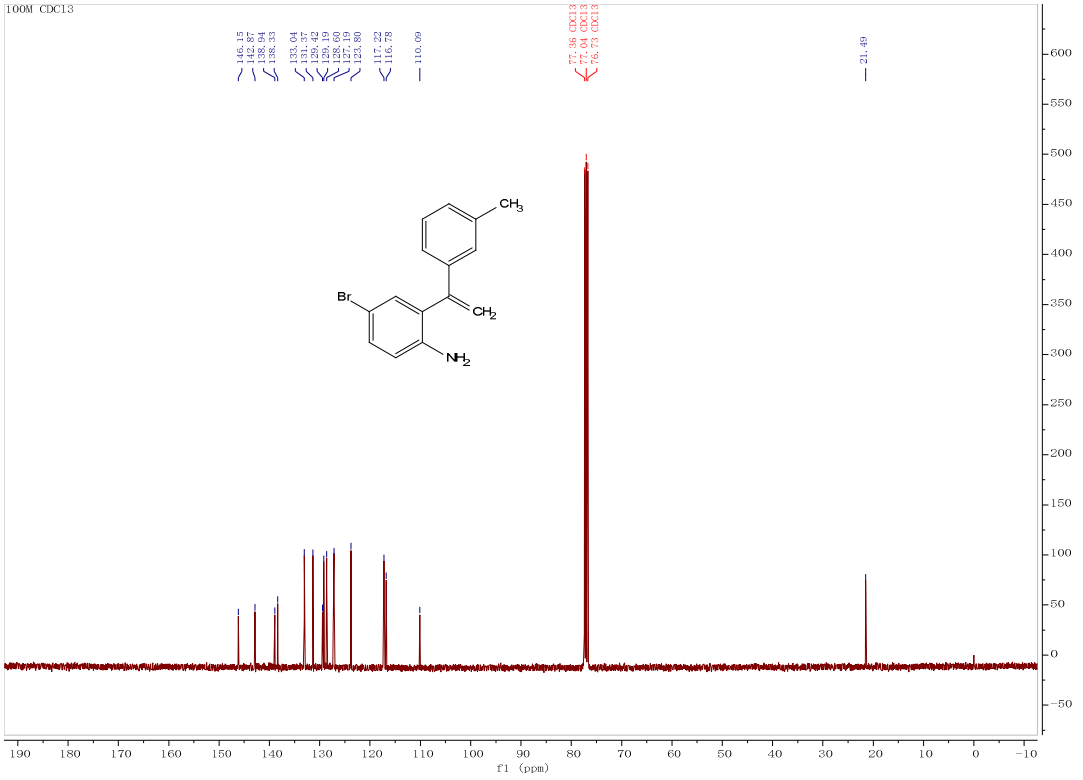
^{13}C NMR spectrum of Compound 3s ($CDCl_3$, 100 MHz)



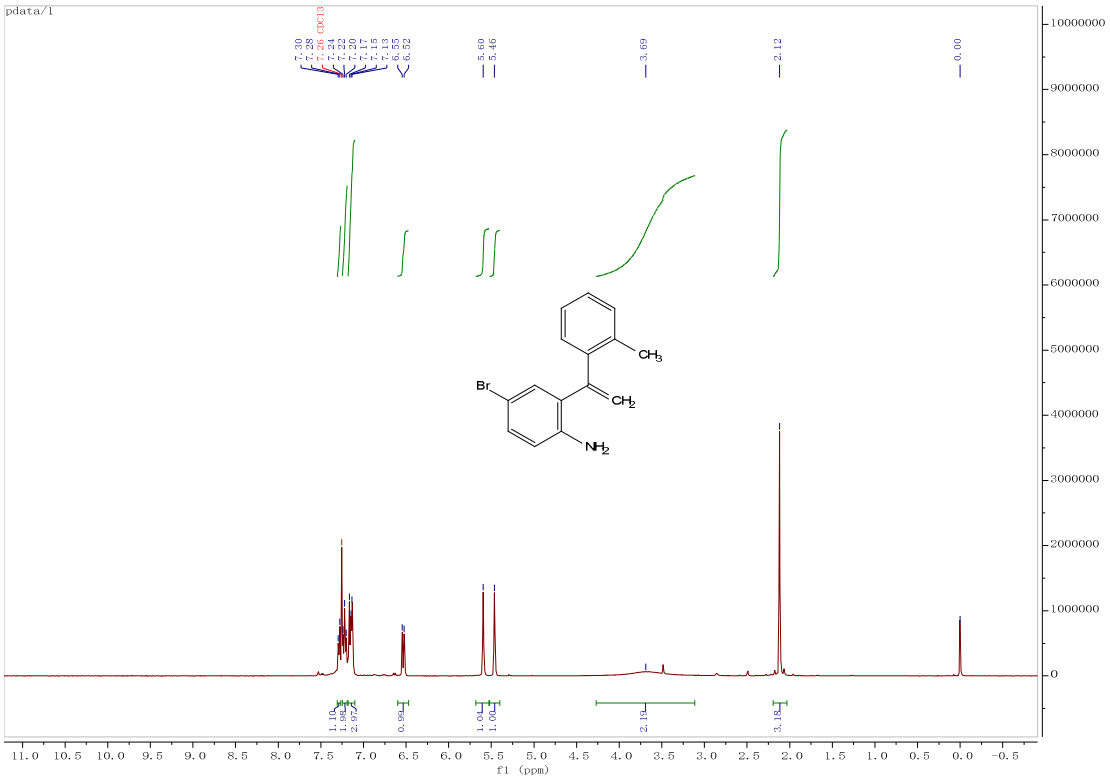
^{1}H NMR spectrum of Compound 3t ($CDCl_3$, 400 MHz)



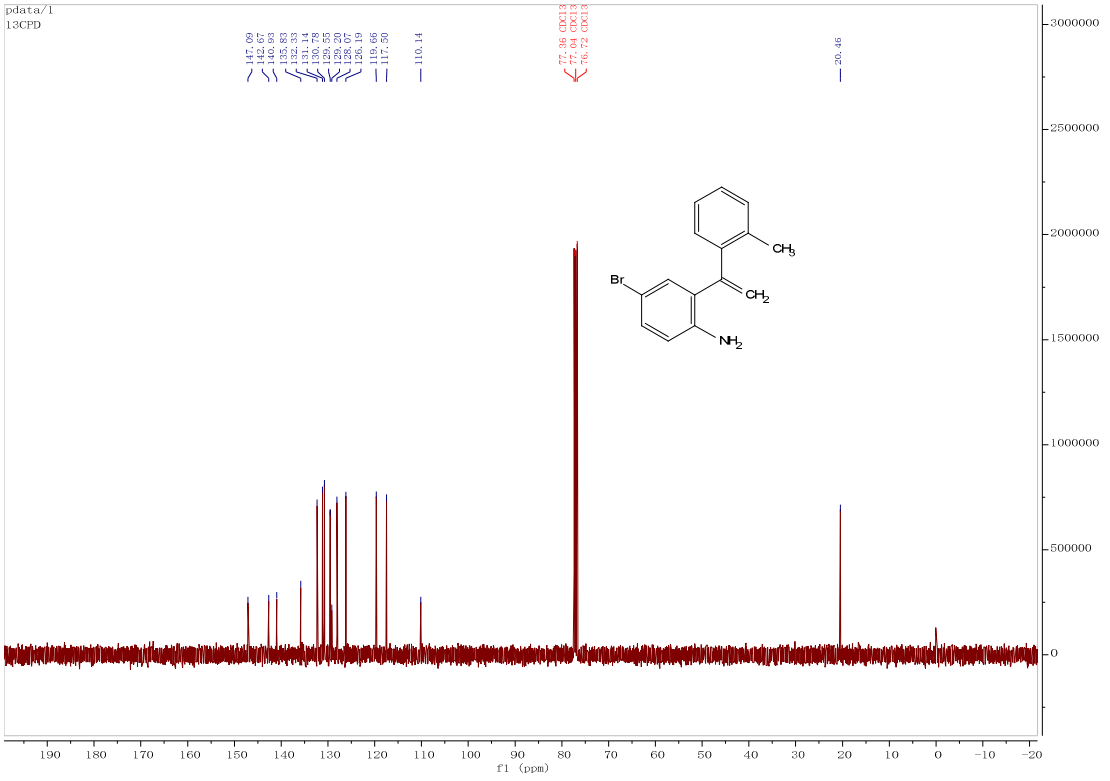
^{13}C NMR spectrum of Compound 3t ($CDCl_3$, 100 MHz)



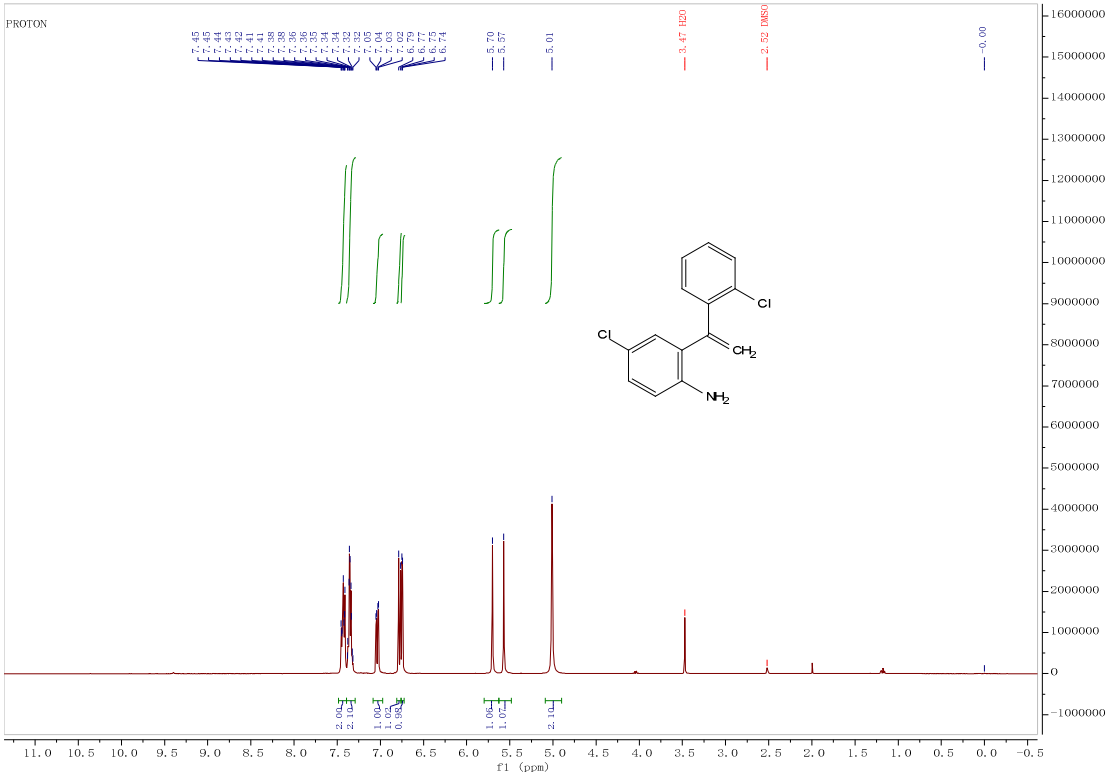
^{1}H NMR spectrum of Compound 3u ($CDCl_3$, 400 MHz)



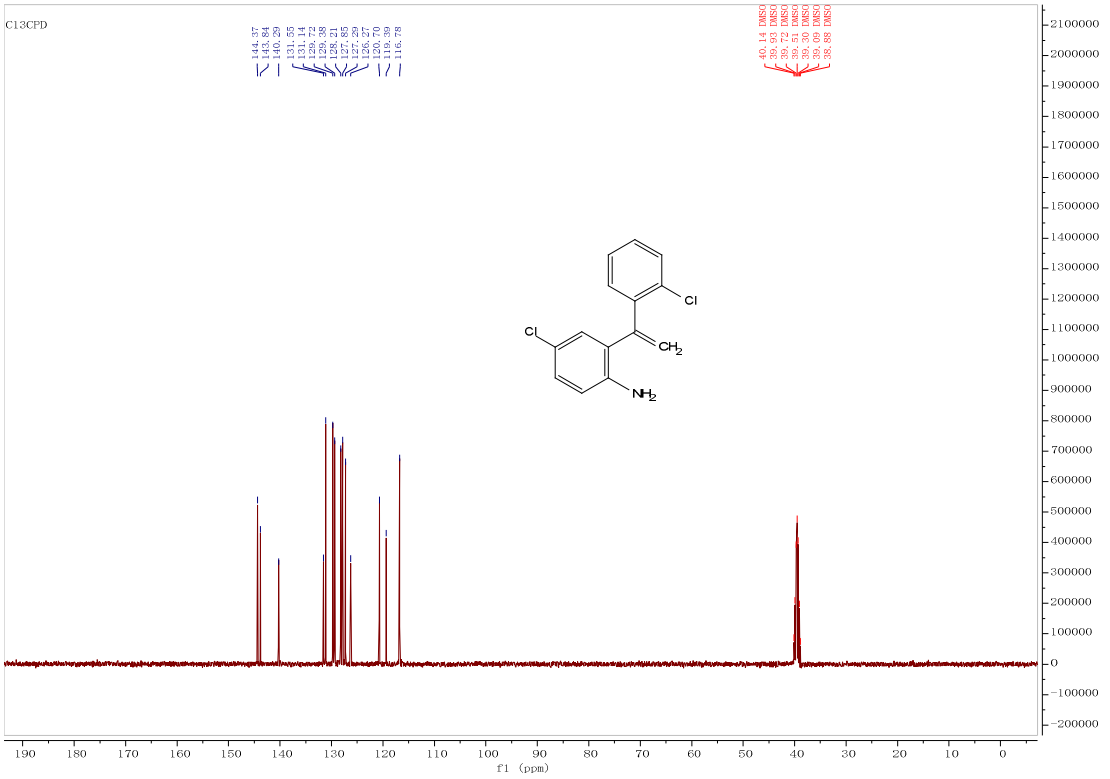
^{13}C NMR spectrum of Compound 3u ($CDCl_3$, 100 MHz)



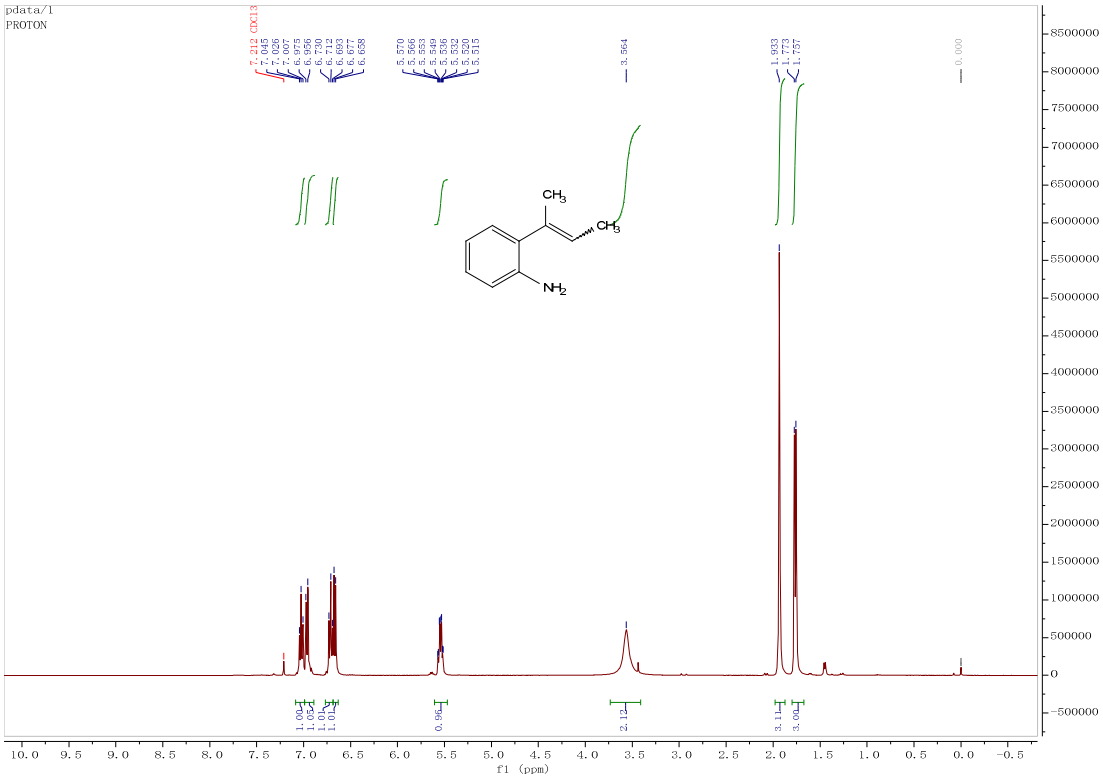
^{1}H NMR spectrum of Compound 3v (DMSO-d_6, 400 MHz)



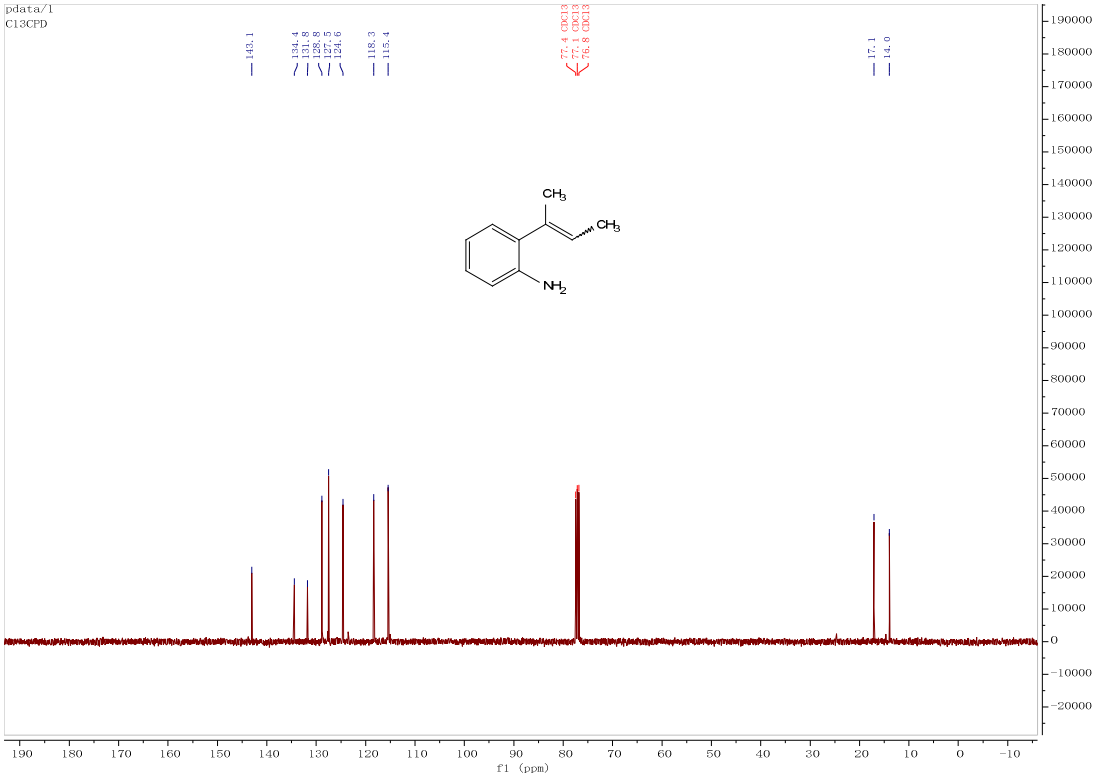
^{13}C NMR spectrum of Compound 3v (DMSO-d_6, 100 MHz)



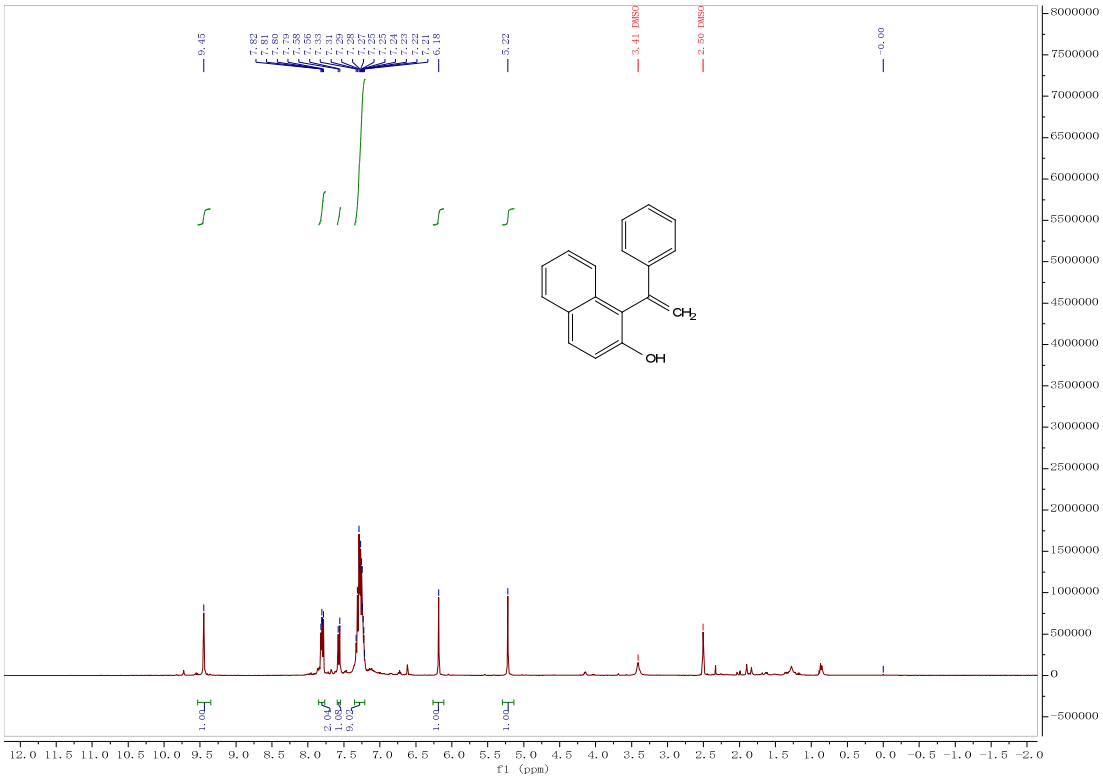
^{1}H NMR spectrum of Compound 3x ($CDCl_3$, 400 MHz)



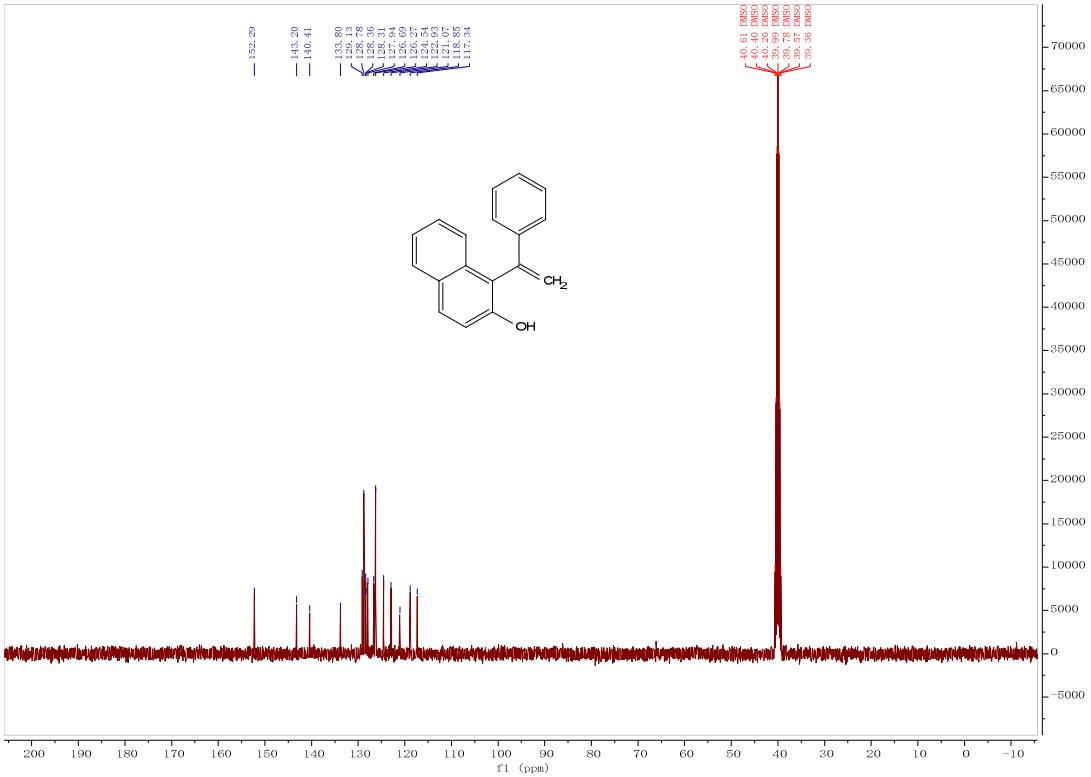
^{13}C NMR spectrum of Compound 3x ($CDCl_3$, 100 MHz)



^{1}H NMR spectrum of Compound 5 (DMSO-d_6, 400 MHz)

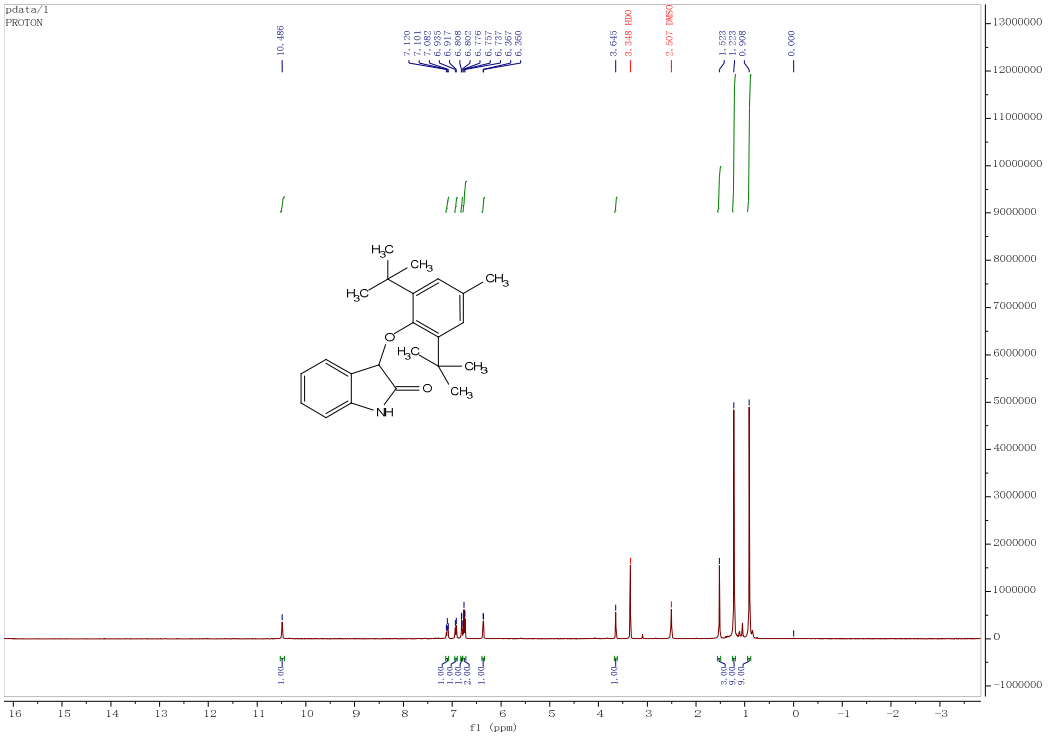


^{13}C NMR spectrum of Compound 5 (DMSO-d_6, 100 MHz)



19. Spectroscopic data for compound 15

^{1}H NMR spectrum of Compound 15 (DMSO-d_6, 400 MHz)



^{13}C NMR spectrum of Compound 15 (DMSO-d_6, 100 MHz)