Iridium(III)-Catalyzed One-Pot Access to 1,2-Disubstituted Benzimidazoles Starting from Imidamides and Sulfonyl Azides

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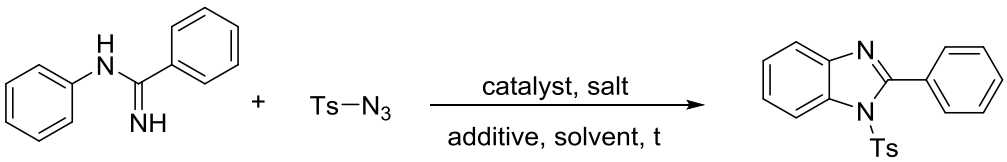
Context

1. General information

All manipulations were conducted with a standard Schlenk technique under air atmosphere. Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: ^{1}H d 7.27, ^{13}C d 77.0). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F_{254}). Starting materials **1**[1] and **2**[2] were prepared according to the literatures.

2. Optimization of the reaction conditions



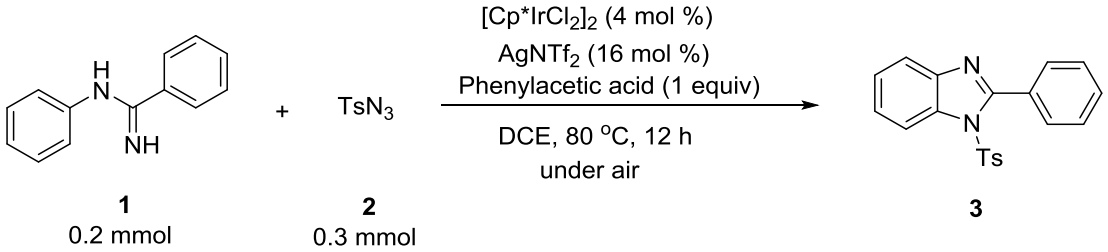
1a **2a** **3aa**

entry	catalyst	salt	acid(equiv)	solvent	yield (%)[b]
1	[Cp*IrCl2]2	AgNTf2	-	DCE	32
2	[Cp*IrCl2]2	AgNTf2	HOAc（0.5）	DCE	45
3	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	DCE	61
4	[Cp*IrCl2]2	AgNTf2	HOAc（1.5）	DCE	47
5	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	$CHCl_3$	48
6	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	dioxane	26
7	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	IPA	45
8	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	DMF	N.R.
9	[Cp*IrCl2]2	AgNTf2	HOAc（1.0）	toluene	28
10	[Cp*IrCl2]2	AgNTf2	PivOH（1.0）	DCE	54
11	[Cp*IrCl2]2	AgNTf2	Benzoic acid（1.0）	DCE	35
12	[Cp*IrCl2]2	AgNTf2	TsOH（1.0）	DCE	N.R.
13	[Cp*IrCl2]2	AgNTf2	phenylacetic acid（1.0）	DCE	80
14[c]	**[Cp*IrCl2]2**	**AgNTf2**	**phenylacetic acid（1.0）**	**DCE**	**97**

15[c]	[Cp*IrCl2]2	$AgSbF_6$	phenylacetic acid（1.0）	DCE	87
16[c]	[Cp*IrCl2]2	AgOAc	phenylacetic acid（1.0）	DCE	54
17[c]	[Cp*IrCl2]2	NaOAc	phenylacetic acid（1.0）	DCE	45
18[c]	[Cp*IrCl2]2	KO^{t}Bu	phenylacetic acid（1.0）	DCE	42
19[c]	[Cp*IrCl2]2	-	phenylacetic acid（1.0）	DCE	45
20[d]	[Cp*IrCl2]2	AgNTf2	phenylacetic acid（1.0）	DCE	62
21[c]	-	AgNTf2	phenylacetic acid（1.0）	DCE	N.R.
22[c]	[Cp*RhCl2]2	AgNTf2	phenylacetic acid（1.0）	DCE	N.R.
23[c]	[Cp*CoCl2]2	AgNTf2	phenylacetic acid（1.0）	DCE	N.R.
24[c]	[Ru(p-cymene)Cl2	AgNTf2	phenylacetic acid（1.0）	DCE	18

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), [Cp*IrCl2]2 (2.5 mol %), salt (10 mol %), acid, solvent (2 mL), 80 °C, 12 h, under air. [b] Isolated yield. [c] [Cp*IrCl2]2 (4 mol %), salt (16 mol %). [d] [Cp*IrCl2]2 (4 mol %), 70 °C. IPA = *iso*-propyl alcohol. TsOH = 4-methylbenzene acid. N.R. = no reaction.

3. General catalytic procedure



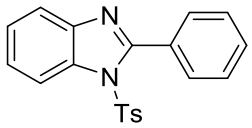
1 0.2 mmol + **2** 0.3 mmol → **3**

A reaction tube (25 mL) equipped with a magnetic stirrer bar was charged with N-phenylbenzimidamide **1** (0.2 mmol), sulfonyl azide **2** (0.3 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 equiv) and 1,2-dichloroethane (2 mL). The reaction mixture was stirred at 80 °C for 12 h under air. After cooled to room temperature, the resulting mixture was diluted by moderate ethyl acetate, then extracted with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was removed under reduced pressure and the residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 8:1) to afford the desired product **3**.

Procedure for the synthesis of product 3aa at a 1 mmol scale

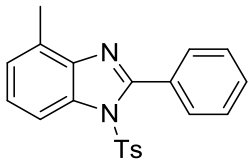
A reaction tube equipped with a magnetic stirrer bar was charged with N-phenylbenzimidamide **1a** (1 mmol), TsN_3 **2a** (1.5 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 equiv) and 1,2-dichloroethane (10 mL). The reaction mixture was stirred at 80 °C for 12 h under air. After cooled to room temperature, the resulting mixture was diluted by moderate ethyl acetate, then extracted with saturated $NaHCO_3$. The organic phase was removed under reduced pressure and the residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 8:1) to afford the desired product **3aa** (330.6 mg, 95%).

4. Characterization of the Products



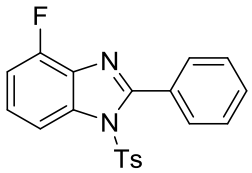
2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3aa**)[3]

Light brown crystal, 67.5 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.54 (dd, *J* = 11.2, 4.5 Hz, 1H), 7.48 – 7.36 (m, 4H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.03, 145.64, 142.61, 135.02, 133.87, 130.82, 130.47, 130.04, 129.66, 127.61, 126.96, 125.41, 125.23, 120.36, 115.13, 21.57.



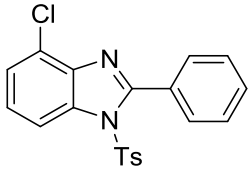
4-methyl-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ba**)

White solid, 21.7 mg, 30% yield, mp: 147 – 148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.33 (dd, *J* = 14.2, 8.2 Hz, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.61 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.92, 145.52, 141.65, 135.10, 133.41, 130.85, 130.44, 130.30, 129.64, 127.60, 126.98, 125.70, 125.22, 112.34, 21.58, 16.60. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1159.



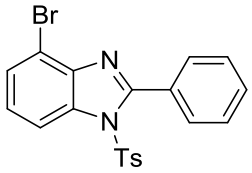
4-fluoro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ca**)

White solid, 45.4 mg, 62% yield, mp: 156 – 158 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (td, *J* = 8.3, 5.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.22, 153.65 (d, *J* = 254.8 Hz), 145.98, 136.24 (d, *J* = 6.6 Hz), 134.61, 131.37 (d, *J* = 16.7 Hz), 130.92, 130.67, 129.72, 129.47, 127.58, 126.96, 125.88 (d, *J* = 7.1 Hz), 111.06 (d, *J* = 2.7 Hz), 110.96 (d, *J* = 10.0 Hz), 21.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.02 (dd, *J* = 9.7, 4.9 Hz). HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}FN_2O_2S$: 367.0911 , found 367.0909.



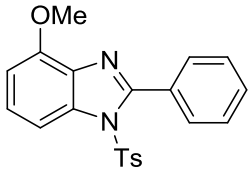
4-chloro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3da**)

White solid, 53.5 mg, 70% yield, mp: 166 – 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.48 – 7.39 (m, 1H), 7.36 (td, *J* = 8.0, 1.0 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.33 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.56, 146.02, 139.85, 134.81, 134.71, 131.01, 130.67, 129.76, 129.49, 127.59, 127.04, 125.83, 125.22, 125.19, 113.63, 21.59. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}ClN_2O_2S$: 383.0616 , found 383.0616.



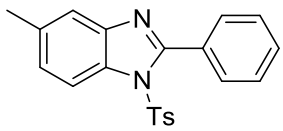
4-bromo-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ea**)

White solid, 51.1 mg, 60% yield, mp: 169 – 170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (dt, *J* = 8.0, 3.9 Hz, 3H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.42, 146.02, 141.22, 134.69, 134.30, 131.01, 130.65, 129.76, 129.47, 128.26, 127.57, 127.03, 126.16, 114.18, 113.70, 21.59. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}BrN_2O_2S$: 427.0110 , found 427.0109.



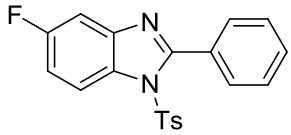
4-methoxy-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3fa**)

White solid, 42.3 mg, 56% yield, mp: 143 – 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.54 – 7.49 (m, 1H), 7.42 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.98 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.80, 151.30, 145.59, 135.20, 134.89, 132.62, 130.99, 130.27, 129.98, 129.59, 127.36, 126.90, 126.16, 107.59, 105.98, 55.80, 21.52. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_3S$: 379.1111 , found 379.1107.



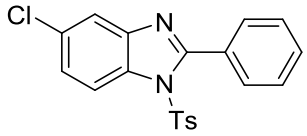
5-methyl-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ga**)

Yellow solid, 54.3 mg, 75% yield, mp: 72 – 75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.52 (dd, *J* = 14.1, 6.7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.05, 145.48, 142.74, 135.18, 134.88, 131.75, 130.75, 130.37, 130.03, 129.56, 127.53, 126.81, 126.69, 120.16, 114.59, 21.49, 21.34. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1162.



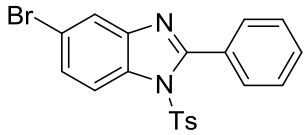
5-fluoro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ha**)

Yellow crystal, 36.6 mg, 50% yield, mp: 154 – 156 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (td, *J* = 9.1, 2.6 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.64 (d, *J* = 242.4 Hz), 155.72, 145.88, 143.41 (d, *J* = 12.4 Hz), 134.69, 130.81, 130.73, 130.24 (d, *J* = 1.3 Hz), 129.72, 129.64, 127.67, 126.92, 115.93 (d, *J* = 9.7 Hz), 113.36 (d, *J* = 25.3 Hz), 106.49 (d, *J* = 24.4 Hz), 21.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.62. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}FN_2O_2S$: 367.0911 , found 367.0915.



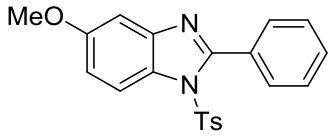
5-chloro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ia**)

White solid, 75.6 mg, 99% yield, mp: 139 – 142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.32, 145.97, 143.46, 134.64, 132.47, 130.85, 130.82, 130.77, 129.75, 129.50, 127.69, 126.94, 125.69, 120.20, 115.97, 21.60. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}ClN_2O_2S$: 383.0616 , found 383.0617.



5-bromo-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ja**)

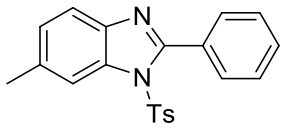
White solid, 78.4 mg, 92% yield, mp: 144 – 146 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 1.7 Hz, 1H), 7.56 (ddd, *J* = 10.6, 8.5, 4.4 Hz, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.14, 145.98, 143.83, 134.63, 132.89, 130.83, 130.77, 129.76, 129.46, 128.37, 127.69, 126.94, 123.25, 118.32, 116.35, 21.60. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}BrN_2O_2S$: 427.0110 , found 427.0110.



5-methoxy-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ka**)

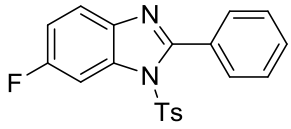
Light yellow solid, 60.5 mg, 80% yield, mp: 146 – 148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d,

J = 9.0 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.52 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.09 – 7.02 (m, 3H), 3.84 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.92, 154.82, 145.54, 143.73, 134.81, 130.81, 130.49, 129.94, 129.59, 127.95, 127.58, 126.83, 115.72, 114.46, 102.75, 55.63, 21.53. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_3S$: 379.1111 , found 379.1099.



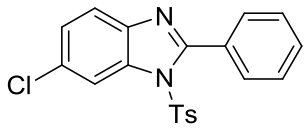
6-methyl-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3la**)

Brown solid, 63.0 mg, 87% yield, mp: 128 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.54 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 145.46, 140.51, 135.56, 134.92, 133.95, 130.66, 130.23, 130.02, 129.52, 127.46, 126.76, 126.52, 119.66, 114.95, 21.94, 21.44. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1161.



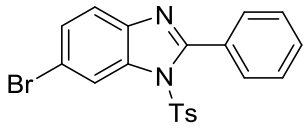
6-fluoro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3ma**)

White solid, 55.0 mg, 75% yield, mp: 136 – 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.65 (dd, *J* = 8.8, 5.0 Hz, 1H), 7.56 (dd, *J* = 15.2, 7.3 Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.09 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.69 (d, *J* = 243.0 Hz), 154.31 (d, *J* = 3.5 Hz), 145.93, 138.81 (d, *J* = 1.2 Hz), 134.66, 134.09 (d, *J* = 13.7 Hz), 130.73, 130.55, 129.74, 129.64, 127.63, 126.96, 121.01 (d, *J* = 10.0 Hz), 113.37 (d, *J* = 24.9 Hz), 102.49 (d, *J* = 29.9 Hz), 21.57. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.53 (td, *J* = 9.2, 5.0 Hz). HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}FN_2O_2S$: 367.0911 , found 367.0913.



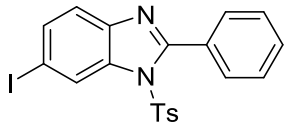
6-chloro-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3na**)

White solid, 74.1 mg, 97% yield, mp: 163 – 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.51, 145.98, 141.07, 134.66, 134.40, 131.14, 130.76, 130.65, 129.76, 129.49, 127.65, 126.99, 125.85, 121.03, 115.25, 21.58. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}ClN_2O_2S$: 383.0616 , found 383.0613.



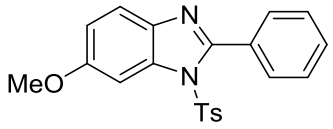
6-bromo-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3oa**)

White solid, 66.5 mg, 78% yield, mp: 164 – 165 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 0.9 Hz, 1H), 7.53 (ddd, *J* = 12.0, 9.9, 4.7 Hz, 5H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.40, 146.00, 141.46, 134.77, 134.66, 130.76, 130.67, 129.77, 129.45, 128.59, 127.66, 127.01, 121.44, 118.74, 118.12, 21.60. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}BrN_2O_2S$: 427.0110 , found 427.0110.



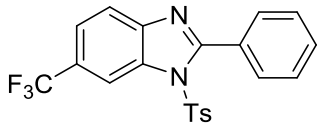
6-iodo-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3pa**)

White solid, 73.8 mg, 78% yield, mp: 151 – 153 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.3 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.55 (t, *J* = 7.1 Hz, 3H), 7.48 – 7.42 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.17, 145.99, 142.05, 135.07, 134.65, 134.33, 130.77, 130.68, 129.77, 129.39, 127.67, 127.01, 123.88, 121.88, 89.33, 21.62. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}IN_2O_2S$: 474.9972 , found 474.9974.



6-methoxy-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3qa**)

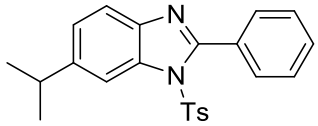
Brown solid, 45.4 mg, 60% yield, mp: 126 – 127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 7.9, 5.2 Hz, 3H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.99 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.92 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 152.84, 145.57, 136.72, 134.87, 134.65, 130.70, 130.21, 130.01, 129.58, 127.50, 126.80, 120.60, 113.90, 99.12, 55.90, 21.49. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_3S$: 379.1111 , found 379.1110.



2-phenyl-1-tosyl-6-(trifluoromethyl)-1H-benzo[d]imidazole (**3ra**)

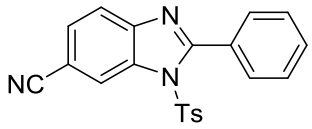
White solid, 58.2 mg, 70% yield, mp: 153 – 154 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.29, 146.21, 144.65, 134.52, 133.55, 130.94, 130.82, 129.84, 129.29, 127.76, 127.98 – 126.94 (m), 127.08, 124.30 (q, *J* = 272.2 Hz), 122.34 – 122.15 (m), 120.76, 112.94 (q, *J* = 4.3 Hz), 21.63.

^{19}F NMR (376 MHz, $CDCl_3$) δ -60.91. HRMS: $[M + H]^+$ calculated for $C_{21}H_{16}F_3N_2O_2S$: 417.0879 , found 417.0878.



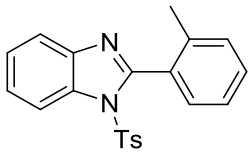
6-isopropyl-2-phenyl-1-tosyl-1H-benzo[d]imidazole (**3sa**)

Light yellow solid, 62.6 mg, 80% yield, mp: 99 – 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.61 (dd, *J* = 13.1, 4.9 Hz, 3H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.12 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.31 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.66, 146.91, 145.51, 140.94, 134.96, 134.00, 130.75, 130.32, 130.20, 129.57, 127.56, 126.92, 124.10, 119.88, 112.62, 34.65, 24.40, 21.54. HRMS: $[M + H]^+$ calculated for $C_{23}H_{23}N_2O_2S$: 391.1475 , found 391.1472.



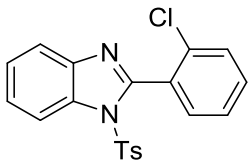
2-phenyl-1-tosyl-1H-benzo[d]imidazole-6-carbonitrile (**3ta**)

White solid, 52.8 mg, 70% yield, mp: 171 – 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.82 (s, 1H), 7.67 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.51 – 7.46 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 146.47, 145.24, 134.28, 133.62, 131.15, 130.79, 129.93, 128.88, 128.72, 127.80, 127.10, 121.32, 119.72, 119.08, 108.48, 21.64. HRMS: $[M + H]^+$ calculated for $C_{21}H_{16}N_3O_2S$: 374.0958 , found 374.0955.



2-(o-tolyl)-1-tosyl-1H-benzo[d]imidazole (**3aaa**)

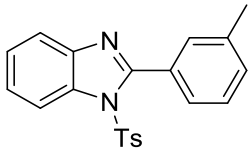
White crystal, 57.9 mg, 80% yield, mp: 156 – 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.37 (m, 5H), 7.20 (ddd, *J* = 20.4, 12.7, 7.2 Hz, 5H), 2.35 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.34, 145.80, 142.25, 138.93, 135.20, 133.11, 130.62, 130.28, 129.81, 129.76, 129.68, 127.28, 125.32, 124.84, 124.73, 120.38, 114.38, 21.59, 19.82. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1162.



2-(2-chlorophenyl)-1-tosyl-1H-benzo[d]imidazole (**3aab**)[3]

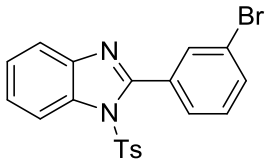
White crystal, 75.6 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.79

(d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.41 (dddd, *J* = 10.1, 7.9, 6.7, 1.8 Hz, 4H), 7.19 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.57, 145.96, 142.20, 135.12, 134.96, 132.81, 132.27, 131.54, 129.93, 129.84, 129.36, 127.32, 125.90, 125.66, 124.96, 120.70, 114.15, 21.63. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}ClN_2O_2S$: 383.0616 , found 383.0614.



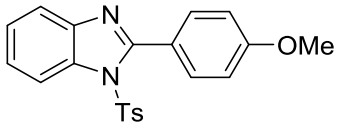
2-(m-tolyl)-1-tosyl-1H-benzo[d]imidazole (**3aac**)

Brown crystal, 52.9 mg, 73% yield, mp: 109 – 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 1H), 7.75 – 7.68 (m, 1H), 7.45 – 7.37 (m, 3H), 7.36 – 7.32 (m, 5H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.17, 145.56, 142.52, 137.28, 135.03, 133.82, 131.16, 131.14, 129.85, 129.57, 127.94, 127.48, 126.99, 125.30, 125.14, 120.28, 115.05, 21.53, 21.24. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1161.



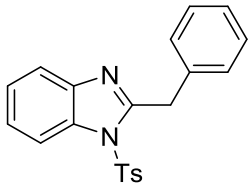
2-(3-bromophenyl)-1-tosyl-1H-benzo[d]imidazole (**3aad**)

Brown solid, 44.3 mg, 52% yield, mp: 106 – 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 5.8 Hz, 2H), 7.48 – 7.32 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.09, 145.98, 142.36, 134.88, 133.79, 133.39, 133.26, 131.89, 129.80, 129.58, 129.15, 126.93, 125.74, 125.35, 121.57, 120.49, 115.02, 21.59. HRMS: $[M + H]^+$ calculated for $C_{20}H_{16}BrN_2O_2S$: 427.0110 , found 427.0110.



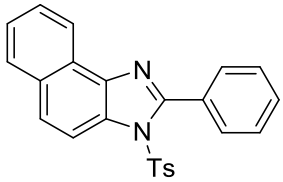
2-(4-methoxyphenyl)-1-tosyl-1H-benzo[d]imidazole (**3aae**)

White solid, 55.2 mg, 73% yield, mp: 123 – 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.69 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.43 – 7.34 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.95 (m, 2H), 3.90 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.42, 154.25, 145.53, 142.69, 134.89, 133.89, 132.46, 129.59, 126.86, 125.23, 125.14, 122.12, 120.09, 115.27, 113.07, 55.34, 21.53. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_3S$: 379.1111 , found 379.1110.



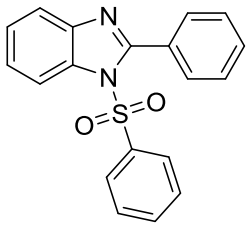
2-benzyl-1-tosyl-1H-benzo[d]imidazole (**3aaf**)[4]

Colorless crystal, 71.7 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 1H), 7.73 – 7.68 (m, 1H), 7.37 (s, 1H), 7.36 – 7.31 (m, 3H), 7.28 (ddd, *J* = 11.6, 6.7, 2.1 Hz, 5H), 7.05 (d, *J* = 8.3 Hz, 2H), 4.64 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.93, 145.54, 141.84, 135.90, 134.94, 132.94, 129.82, 129.17, 128.55, 126.87, 126.82, 124.85, 124.57, 120.07, 113.60, 35.65, 21.49. HRMS: $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2S$: 363.1162 , found 363.1163.



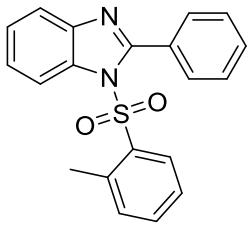
2-phenyl-3-tosyl-3H-naphtho[1,2-d]imidazole (**3aag**)

Brown solid, 20.7 mg, 26% yield, mp: 146 – 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 9.1 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.55 (qd, *J* = 7.2, 1.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.49, 145.71, 138.46, 135.08, 131.37, 131.09, 130.40, 130.34, 130.25, 129.70, 128.13, 127.67, 126.97, 126.94, 126.35, 126.11, 125.82, 122.32, 114.21, 21.57. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}N_2O_2S$: 399.1162 , found 399.1159.



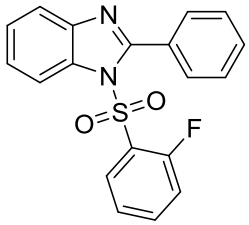
2-phenyl-1-(phenylsulfonyl)-1H-benzo[d]imidazole (**3ab**)

Yellow crystal, 66.1 mg, 99% yield, mp: 104 – 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.57 – 7.37 (m, 8H), 7.30 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92, 142.53, 137.85, 134.33, 133.83, 130.77, 130.51, 129.85, 129.03, 127.63, 126.85, 125.49, 125.32, 120.38, 115.07. HRMS: $[M + H]^+$ calculated for $C_{19}H_{15}N_2O_2S$: 335.0849 , found 335.0846.



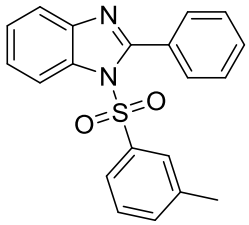
2-phenyl-1-(o-tolylsulfonyl)-1H-benzo[d]imidazole (**3ac**)

Colorless crystal, 52.2 mg, 75% yield, mp: 211 - 212 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 1H), 7.79 (dt, *J* = 6.6, 2.9 Hz, 1H), 7.45 – 7.38 (m, 5H), 7.36 – 7.28 (m, 4H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.24, 141.71, 138.02, 136.97, 134.80, 134.08, 132.45, 130.38, 130.18, 129.97, 129.64, 127.70, 125.88, 125.36, 124.88, 120.52, 115.05, 19.51. HRMS: $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2S$: 349.1005 , found 349.1005.



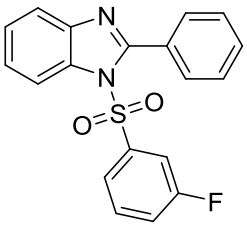
1-((2-fluorophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3ad**)

Beown crystal, 69.0 mg, 98% yield, mp: 124 – 126 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 1H), 7.82 – 7.74 (m, 1H), 7.59 – 7.44 (m, 5H), 7.43 – 7.34 (m, 4H), 7.06 (dt, *J* = 18.7, 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.14 (d, *J* = 259.9 Hz), 153.63, 142.13, 136.76 (d, *J* = 8.6 Hz), 133.81, 130.62, 130.54, 130.36, 129.84, 127.65, 126.20 (d, *J* = 13.7 Hz), 125.40, 125.17, 124.15 (d, *J* = 3.8 Hz), 120.45, 117.29 (d, *J* = 20.4 Hz), 114.85 (d, *J* = 1.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.72. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}FN_2O_2S$: 353.0755 , found 353.0751.



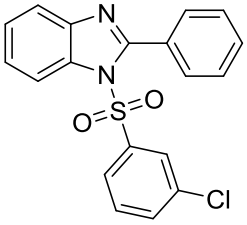
2-phenyl-1-(m-tolylsulfonyl)-1H-benzo[d]imidazole (**3ae**)

Brown crystal, 68.2 mg, 98% yield, mp: 118 – 121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 1H), 7.76 – 7.71 (m, 1H), 7.59 – 7.52 (m, 3H), 7.48 – 7.36 (m, 4H), 7.30 – 7.23 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.81, 142.44, 139.32, 137.62, 135.11, 133.85, 130.80, 130.42, 129.89, 128.88, 127.54, 127.31, 125.41, 125.19, 123.94, 120.30, 115.04, 21.06. HRMS: $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2S$: 349.1005 , found 349.1005.



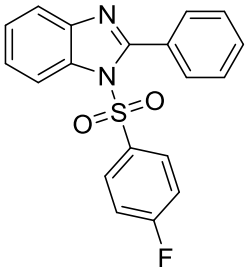
1-((3-fluorophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3af**)

Colorless crystal, 65.5 mg, 93% yield, mp: 96 – 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 1H), 7.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.51 – 7.40 (m, 4H), 7.30 (td, *J* = 8.0, 5.1 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.13 – 7.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.86 (d, *J* = 253.4 Hz), 153.82, 142.57, 139.50 (d, *J* = 7.1 Hz), 133.69, 130.96 (d, *J* = 7.8 Hz), 130.80, 130.75, 129.60, 127.75, 125.74, 125.60, 122.69 (d, *J* = 3.5 Hz), 121.69 (d, *J* = 21.2 Hz), 120.56, 115.02, 114.45 (d, *J* = 25.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.21. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}FN_2O_2S$: 353.0755 , found 353.0751.



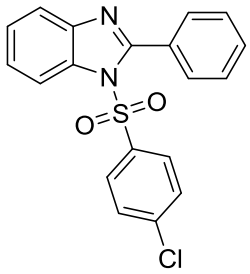
1-((3-chlorophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3ag**)

Brown crystal, 72.9 mg, 99% yield, mp: 97 – 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 1H), 7.78 – 7.71 (m, 1H), 7.62 – 7.55 (m, 3H), 7.45 (dddd, *J* = 18.9, 14.8, 7.3, 1.7 Hz, 5H), 7.35 – 7.29 (m, 2H), 7.25 (dd, *J* = 8.7, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.71, 142.51, 139.21, 135.24, 134.48, 133.66, 130.80, 130.77, 130.36, 129.52, 127.76, 127.16, 125.74, 125.58, 124.86, 120.55, 115.00. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}ClN_2O_2S$: 369.0459 , found 369.0459.



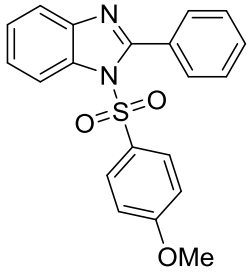
1-((4-fluorophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3ah**)

Light yellow crystal, 57.7 mg, 82% yield, mp: 104 – 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.16 (m, 1H), 7.77 – 7.70 (m, 1H), 7.64 – 7.53 (m, 3H), 7.44 (tdd, *J* = 12.5, 10.2, 4.4 Hz, 6H), 7.01 – 6.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93 (d, *J* = 258.5 Hz，1C), 153.87, 142.60, 133.84 (d, *J* = 3.3 Hz, 1C), 133.77, 130.84, 130.68, 129.88 (d, *J* = 9.8 Hz, 2C), 129.74, 127.74, 125.64, 125.51, 120.54, 116.47 (d, *J* = 22.9 Hz, 2C), 115.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.21. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}FN_2O_2S$: 353.0755 , found 353.0757.



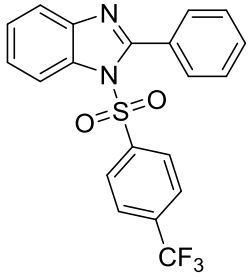
1-((4-chlorophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3ai**)

Colorless crystal, 66.2 mg, 90% yield, mp: 140 – 141 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.64 – 7.59 (m, 2H), 7.55 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.49 – 7.37 (m, 4H), 7.35 – 7.31 (m, 2H), 7.25 (dd, *J* = 8.9, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.79, 142.57, 141.12, 136.09, 133.64, 130.79, 130.65, 129.64, 129.34, 128.24, 127.69, 125.61, 125.51, 120.52, 115.01. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}ClN_2O_2S$: 369.0459 , found 369.0460.



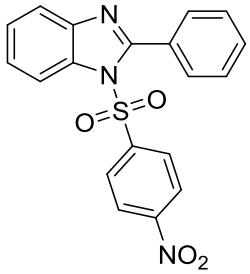
1-((4-methoxyphenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3aj**)

Brown solid, 54.6 mg, 75% yield, mp: 126 – 127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 10.9, 4.0 Hz, 1H), 7.48 – 7.34 (m, 6H), 6.73 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.16, 154.00, 142.54, 133.87, 130.81, 130.44, 130.06, 129.37, 129.29, 127.61, 125.36, 125.16, 120.31, 115.11, 114.20, 55.64. HRMS: $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_3S$: 365.0954 , found 365.0955.



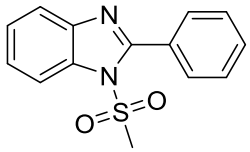
2-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1H-benzo[d]imidazole (**3ak**)

Brown solid, 43.4 mg, 54% yield, mp: 182 – 186 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.52 (m, 7H), 7.45 (dt, *J* = 16.5, 7.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.79, 142.66, 141.11, 135.87 (q, *J* = 33.4 Hz), 133.67, 130.86, 130.83, 129.55, 127.82, 127.50, 126.24 (q, *J* = 3.7 Hz), 125.85, 125.78, 122.70 (d, *J* = 273.3 Hz), 120.71, 115.05. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.44. HRMS: $[M + H]^+$ calculated for $C_{20}H_{14}F_3N_2O_2S$: 403.0723 , found 403.0722.



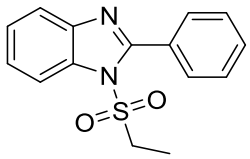
1-((4-nitrophenyl)sulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3al**)

Yellow solid, 47.8 mg, 63% yield, mp: 175 – 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 15.6, 8.0 Hz, 5H), 7.46 (ddd, *J* = 16.6, 13.9, 7.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.74, 150.82, 142.83, 142.71, 133.52, 131.02, 130.88, 129.33, 128.25, 127.90, 126.02, 124.24, 120.84, 115.03. HRMS: $[M + H]^+$ calculated for $C_{19}H_{14}N_3O_4S$: 380.0700 , found 380.0700.



1-(methylsulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3am**)

Colorless crystal, 53.9 mg, 99% yield, mp: 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.87 – 7.82 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.43 (m, 5H), 3.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.56, 142.50, 133.58, 130.75, 130.59, 129.61, 127.94, 125.70, 125.53, 120.68, 114.40, 41.89. HRMS: $[M + H]^+$ calculated for $C_{14}H_{13}N_2O_2S$: 273.0692 , found 273.0691.

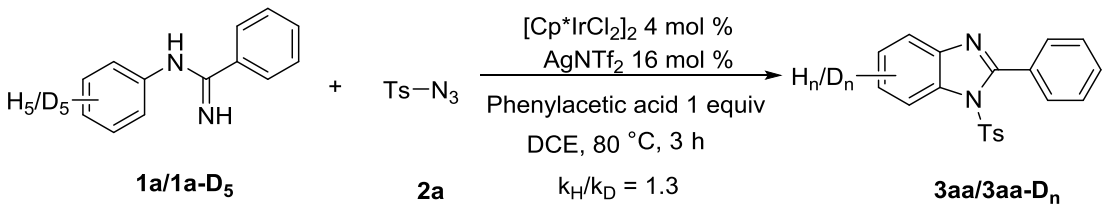


1-(ethylsulfonyl)-2-phenyl-1H-benzo[d]imidazole (**3an**)[5]

Colorless crystal, 45.8 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 1H), 7.88 – 7.80 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.40 (m, 5H), 3.14 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.16, 142.32, 133.92, 130.67, 130.63, 129.71, 127.80, 125.59, 125.39, 120.62, 114.36, 49.32, 7.53.

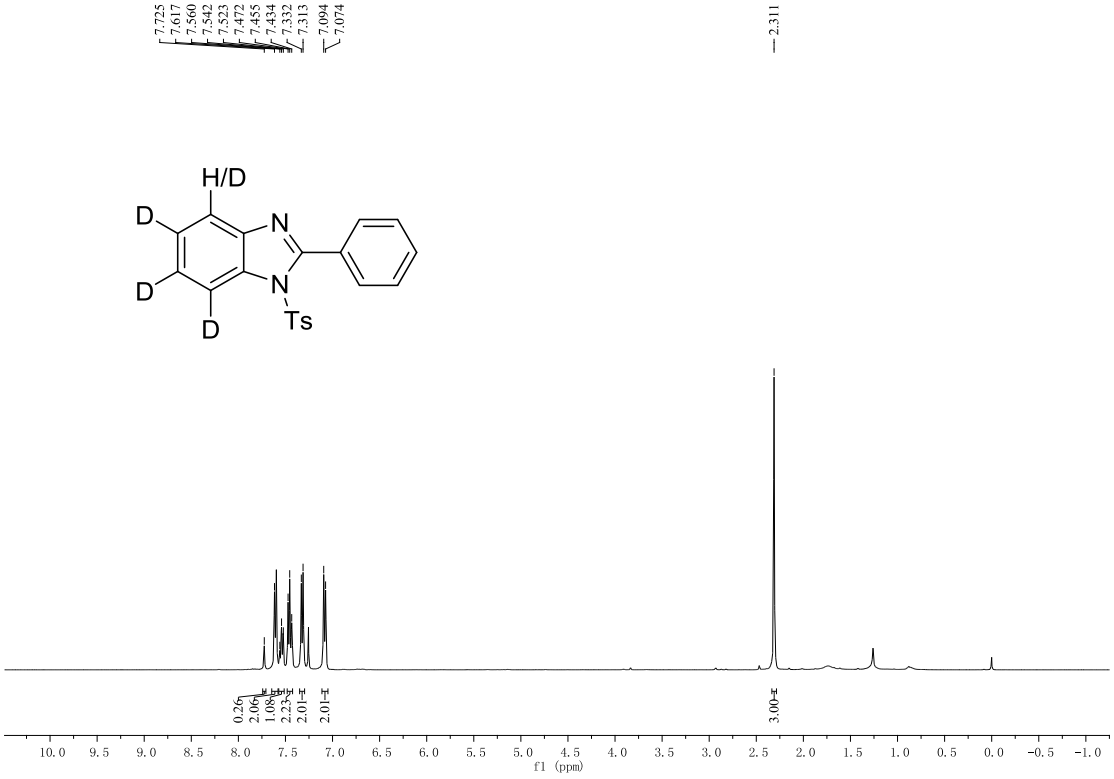
5. Experiments with mechanism studies

(a) KIE studies

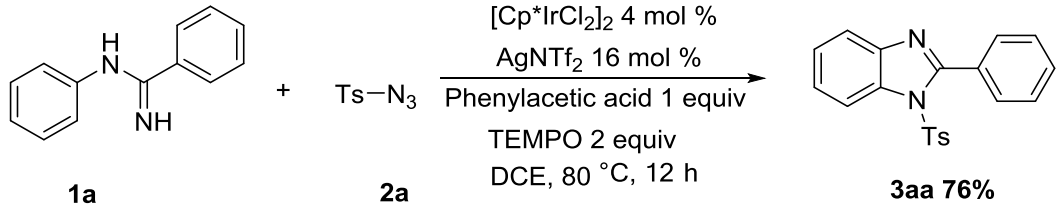


1a/1a-D$_5$ **2a** **3aa/3aa-D$_n$**

To a flask charged with N-phenylbenzimidamide **1a** or **1a-D_5** (0.2 mmol), sulfonyl azide **2a** (0.3 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 euqiv) and 1, 2-dichloroethane (2 mL). The reaction mixture was stirred at 80 ^oC for 3 h. After cooled to room temperature, the resulting mixture was diluted by moderate ethyl acetate, then extracted with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was removed under reduced pressure, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1) to give the desired product 38.7 mg of **3aa** and 30.6 mg of **3aa-D_n**. The KIE value of k_H/k_D = 1.3 was determined on the basis of the product yield of **3aa** and **3aa-D_n**. ^1H NMR analysis of the product **3aa-D_n** revealed 26% hydrogen at the ortho-position (4-position of the benzimidazole).



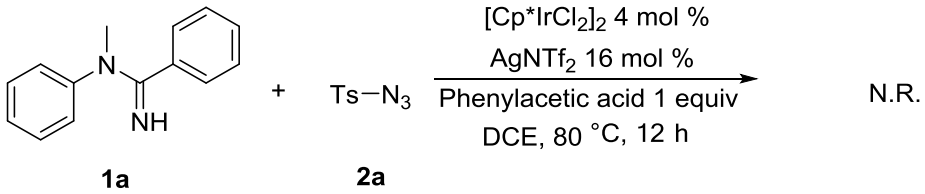
(b) Radical trapping experiment



To a flask charged with N-phenylbenzimidamide **1a** (0.2 mmol), sulfonyl azide **2a** (0.3 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 euqiv), TEMPO (2 equiv) and 1,2-dichloroethane (2 mL). The reaction mixture was stirred at 80 ^oC for 12 h. After cooled to room temperature, the resulting mixture was diluted by moderate ethyl acetate, then extracted with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was removed under reduced pressure, and the residue was purified by

chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1) to give the desired product **3aa** 54.3 mg.

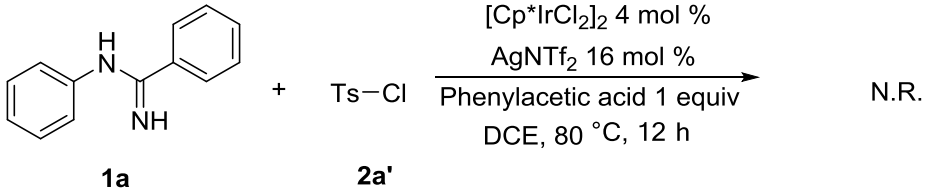
(c)



1a **2a**

To a flask charged with N-methyl-N-phenylbenzimidamide **3a** (0.2 mmol), sulfonyl azide **2a** (0.3 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 euqiv) and 1,2-dichloroethane (2 mL). The reaction mixture was stirred at 80 ^oC for 12 h. No product was detected by TLC. The reaction clarified the proposed mechanism suggesting the need of free N-H group.

(d)



1a **2a'**

To a flask charged with N-phenylbenzimidamide **1a** (0.2 mmol), TsCl(4-methyl-benzenesulfonyl chloride) **2a'** (0.3 mmol), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), phenylacetic acid (1 euqiv) and 1,2-dichloroethane (2 mL). The reaction mixture was stirred at 80 ^oC for 12 h. No product was detected. The control experiment suggested that the nitrogen attached to Ts in the **3aa** might come from **2a**.

6. Reference

1. (a) Brasche, G.; Buchwald, S. L. Angew. Chem. **2008**, *120*, 1958-1960. (b) Jihui, L.; Luc N. Org. Lett. **2013**, *15*, 1752-1755.

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4. Jin, H.; Xu, X.; Gao, J.; Zhong, J.; Wang, Y. Adv. Synth. Catal. **2010**, *352*, 347-350.

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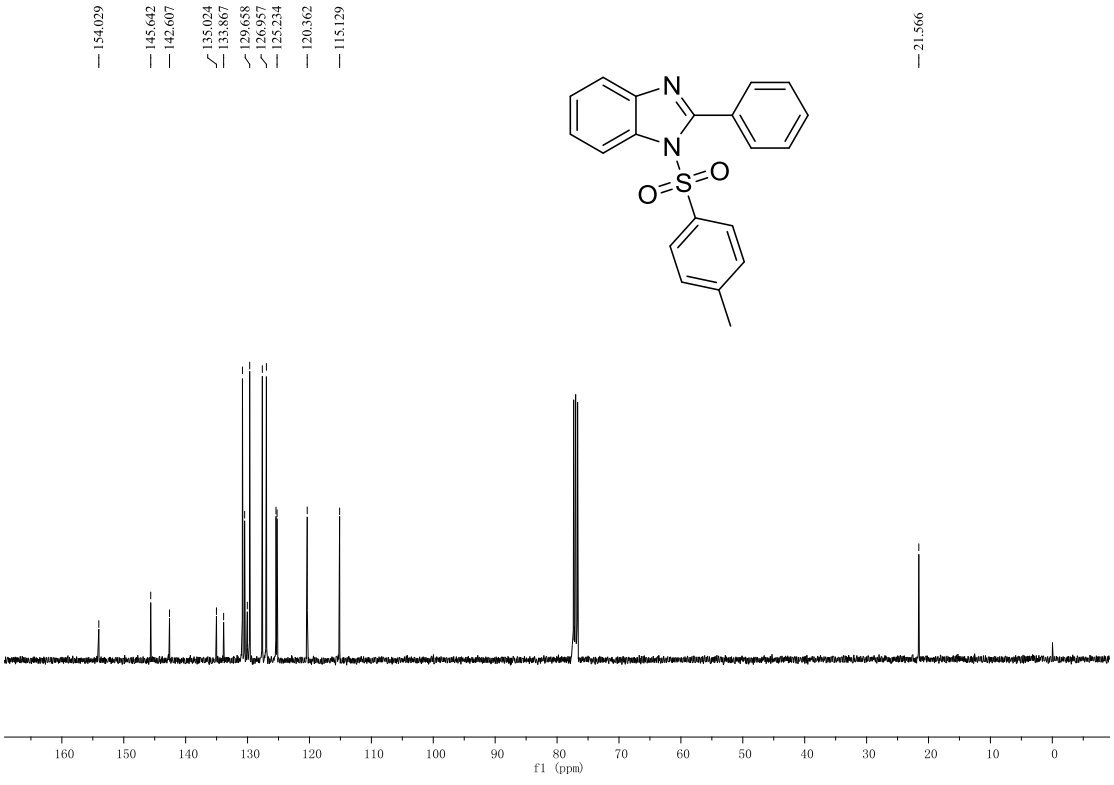
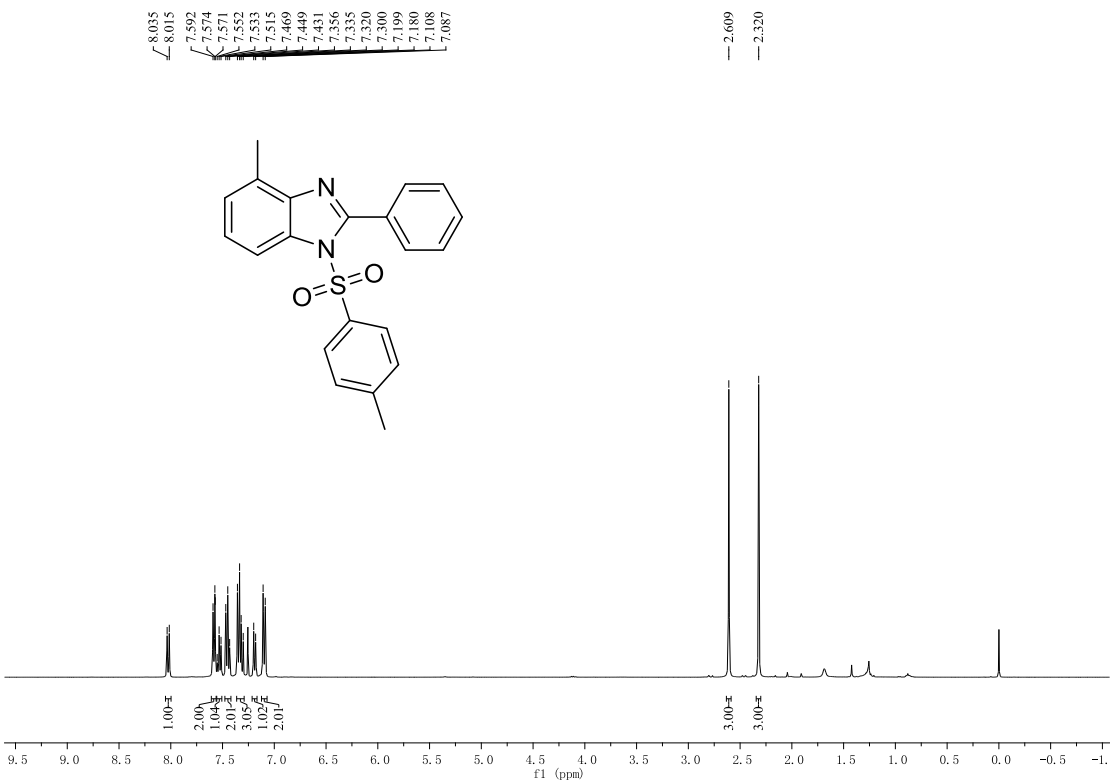
7. NMR spectra of products

^{1}H NMR spectrum of **3aa**

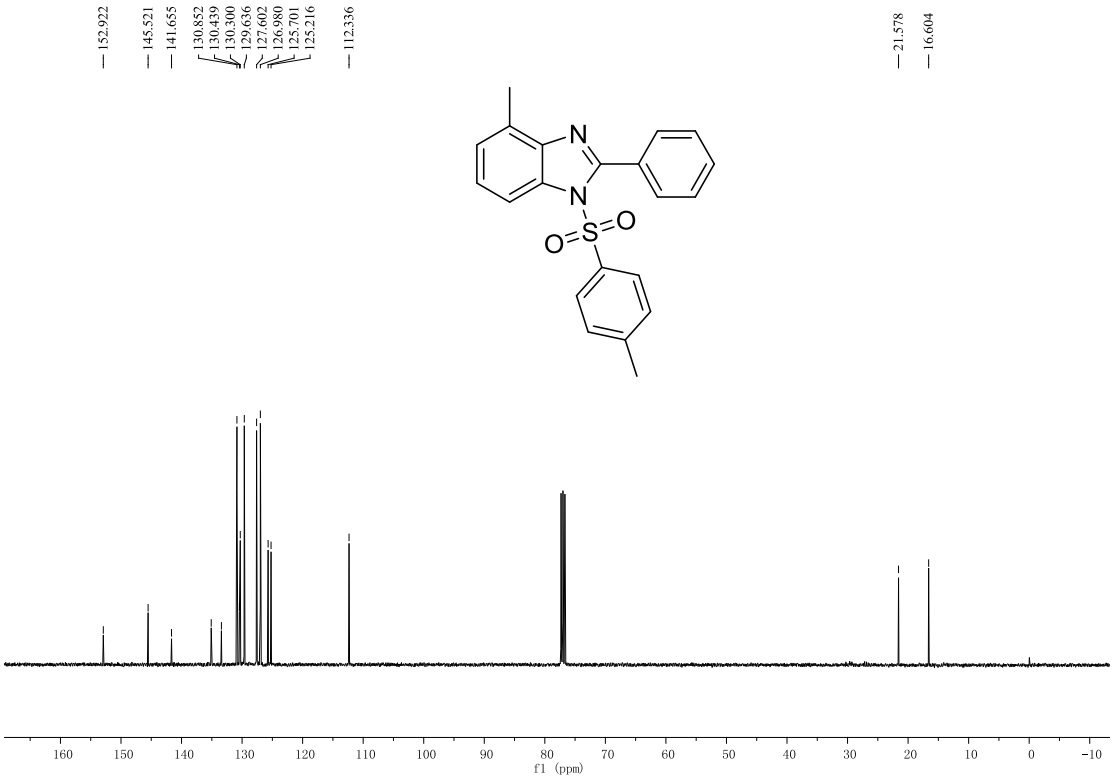
^{13}C NMR spectrum of **3aa**



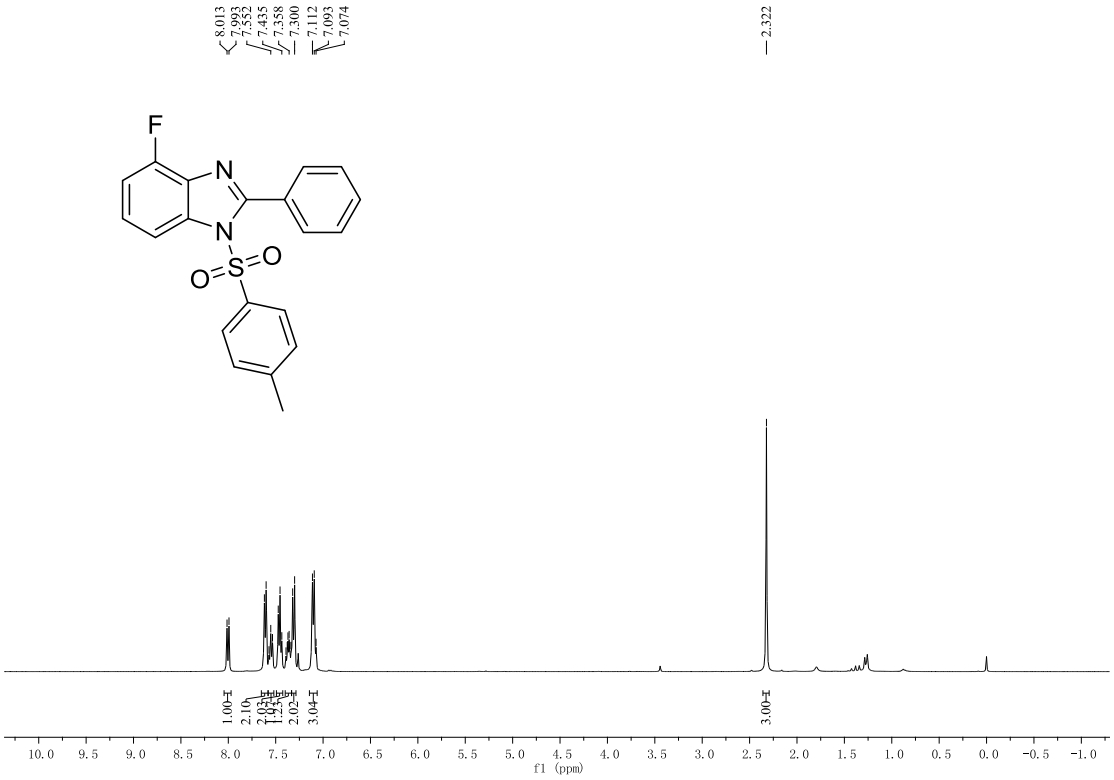
^{1}H NMR spectrum of **3ba**



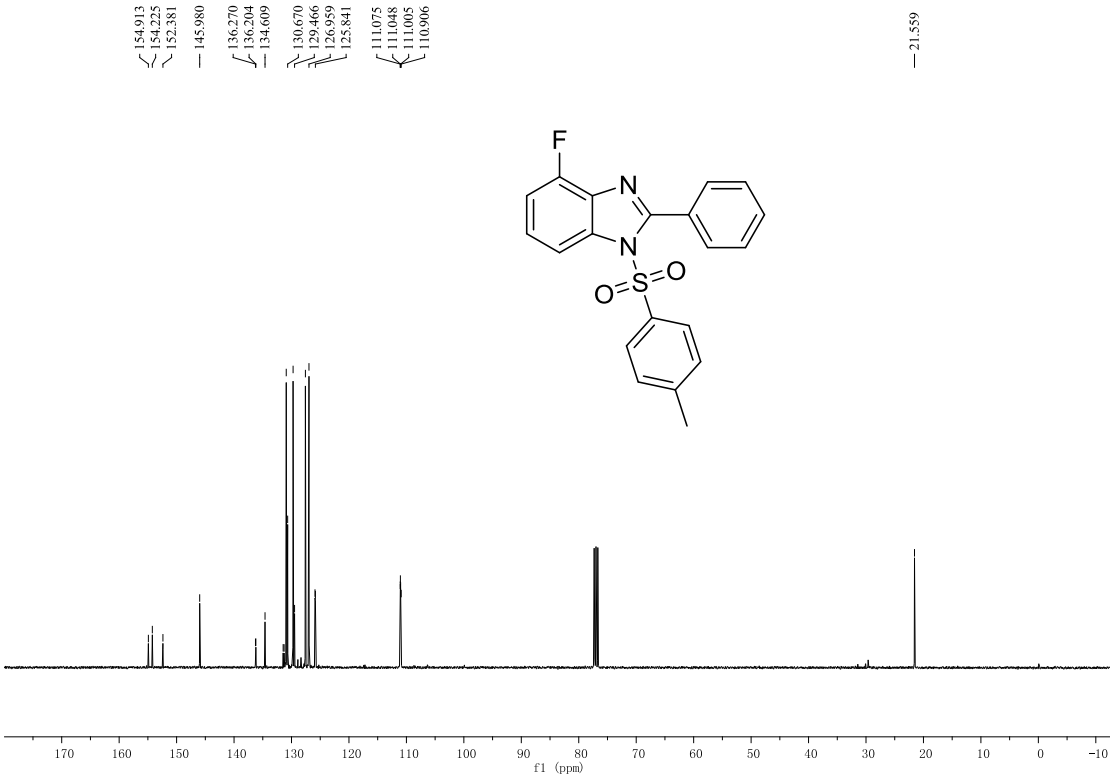
^{13}C NMR spectrum of **3ba**



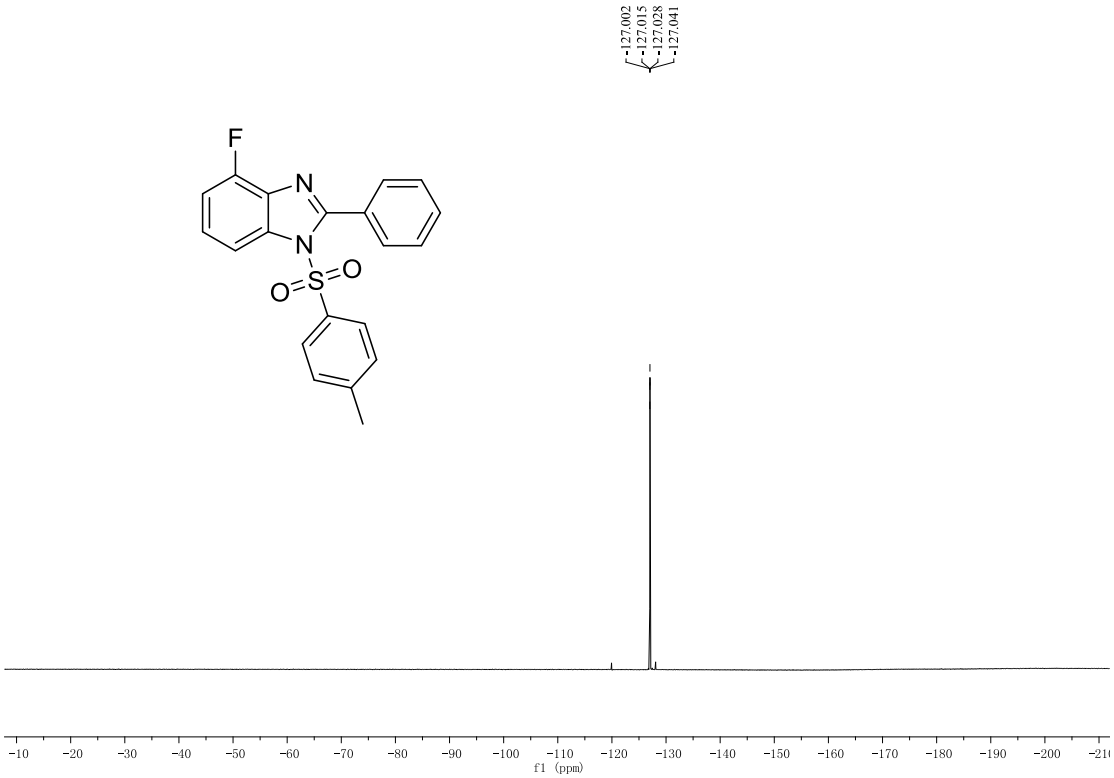
^{1}H NMR spectrum of **3ca**



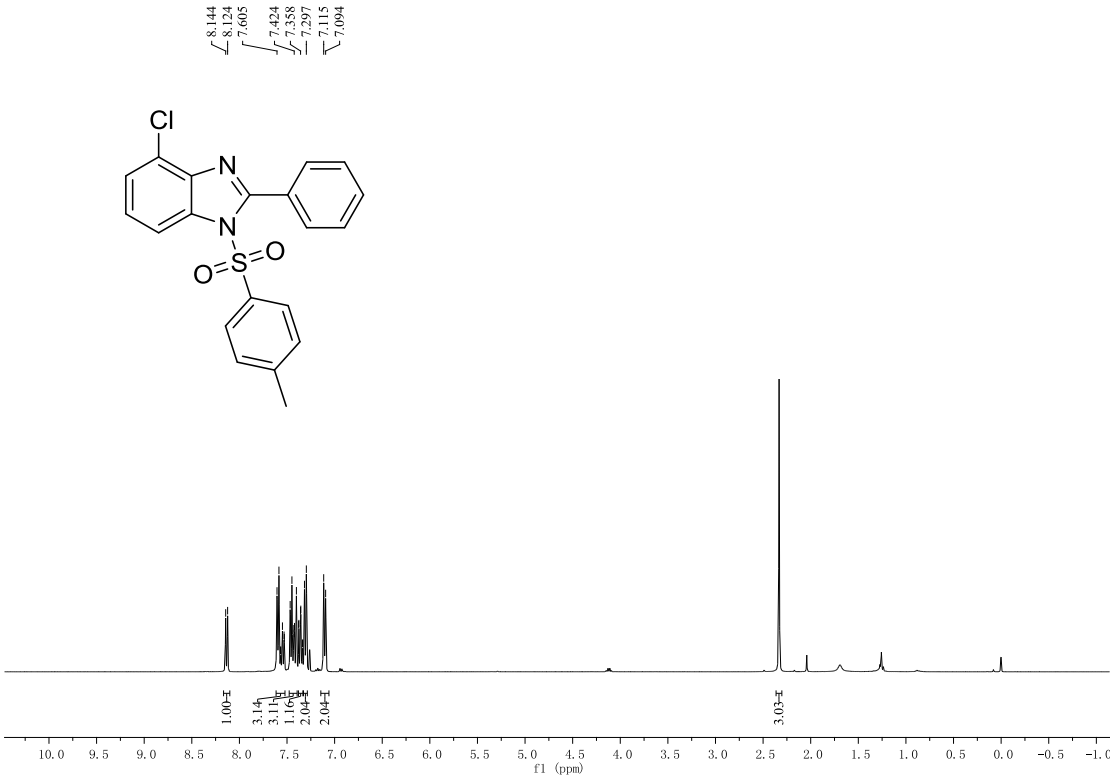
^{13}C NMR spectrum of **3ca**



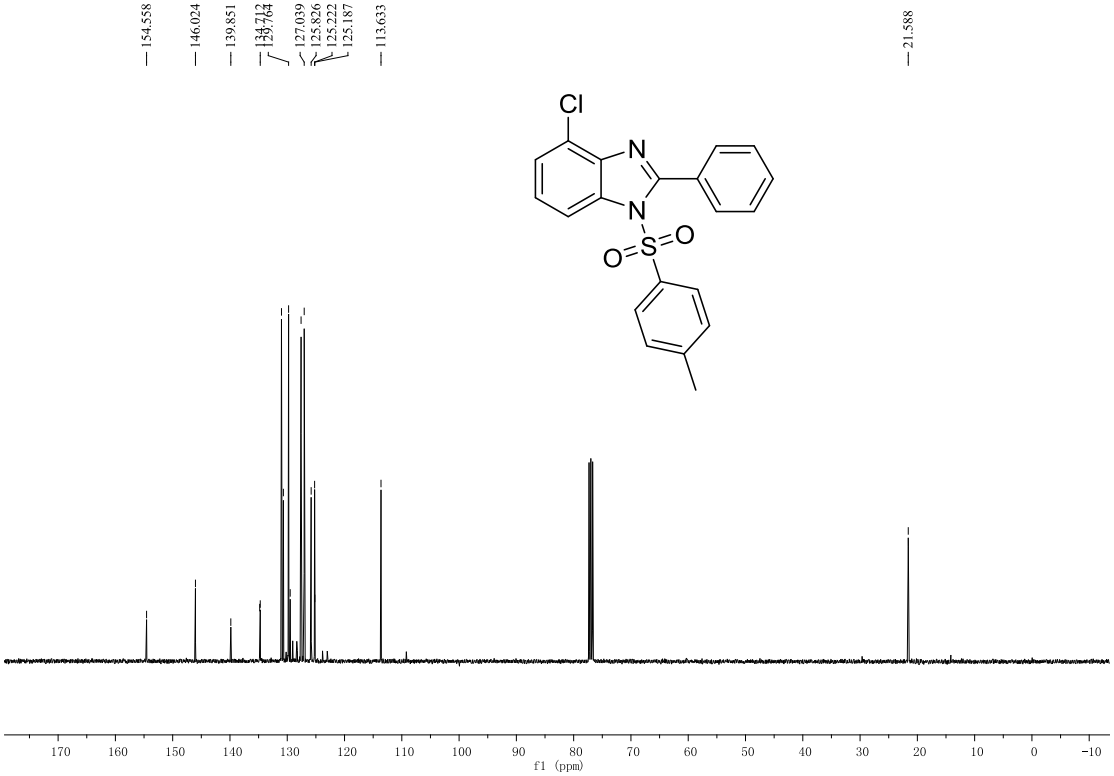
^{19}F NMR spectrum of **3ca**



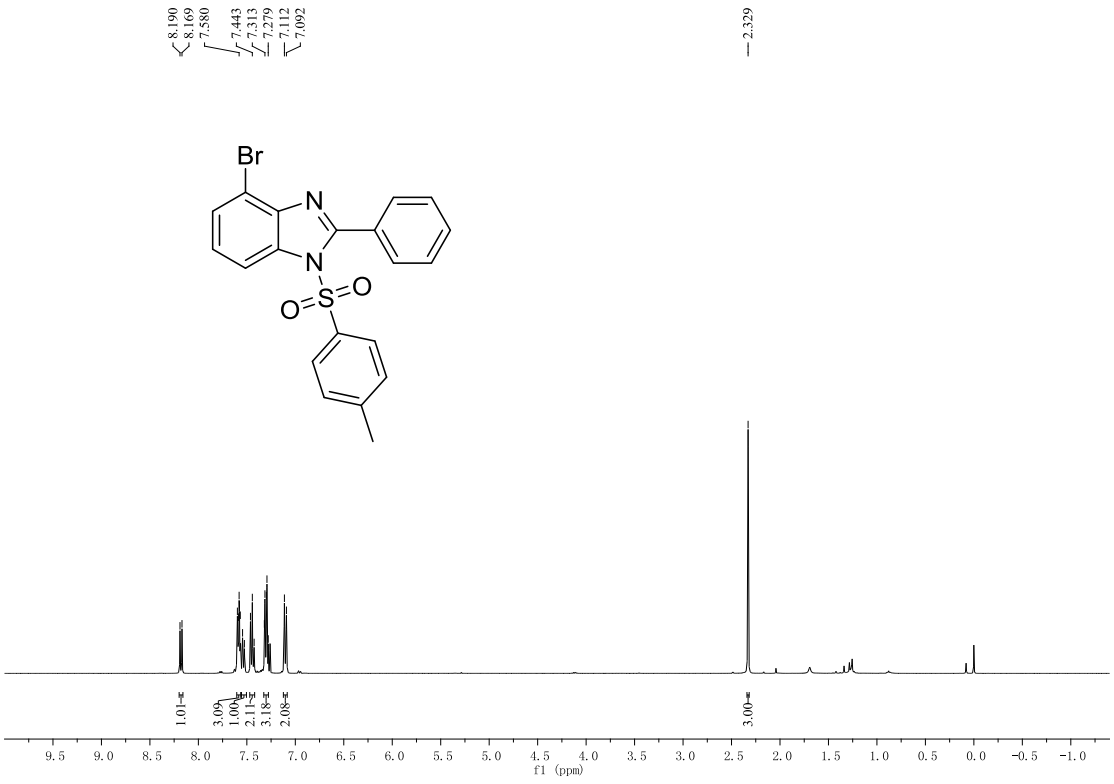
^{1}H NMR spectrum of **3da**



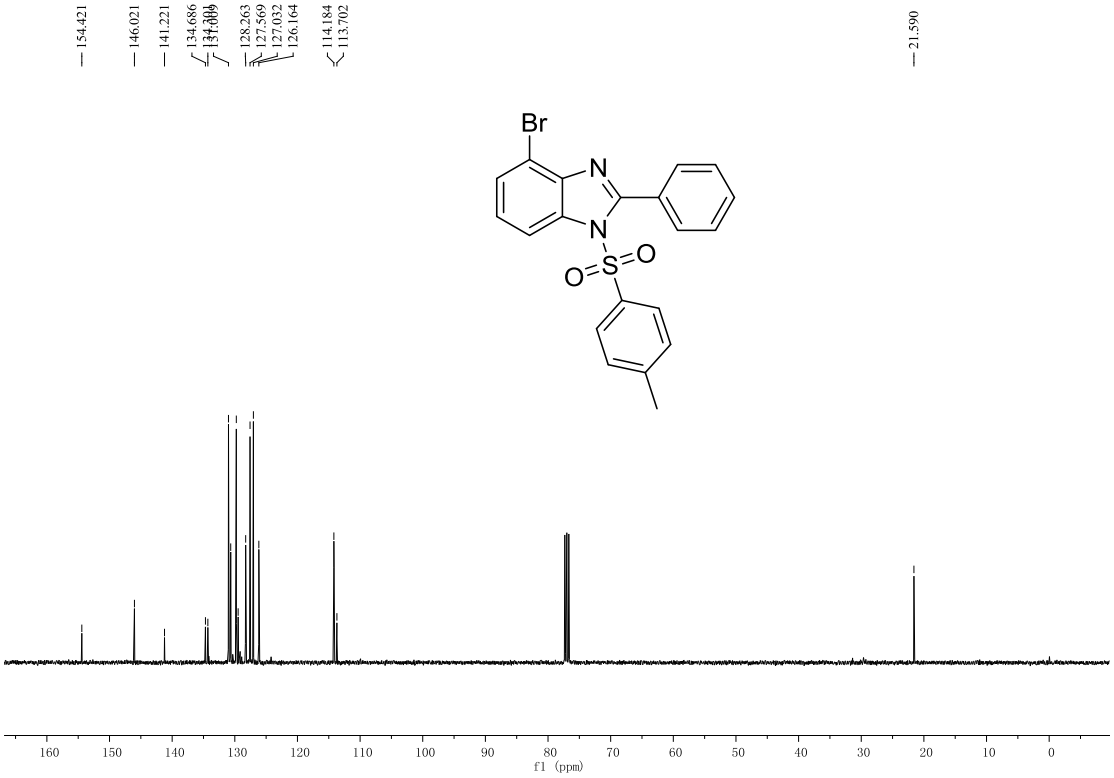
^{13}C NMR spectrum of **3da**



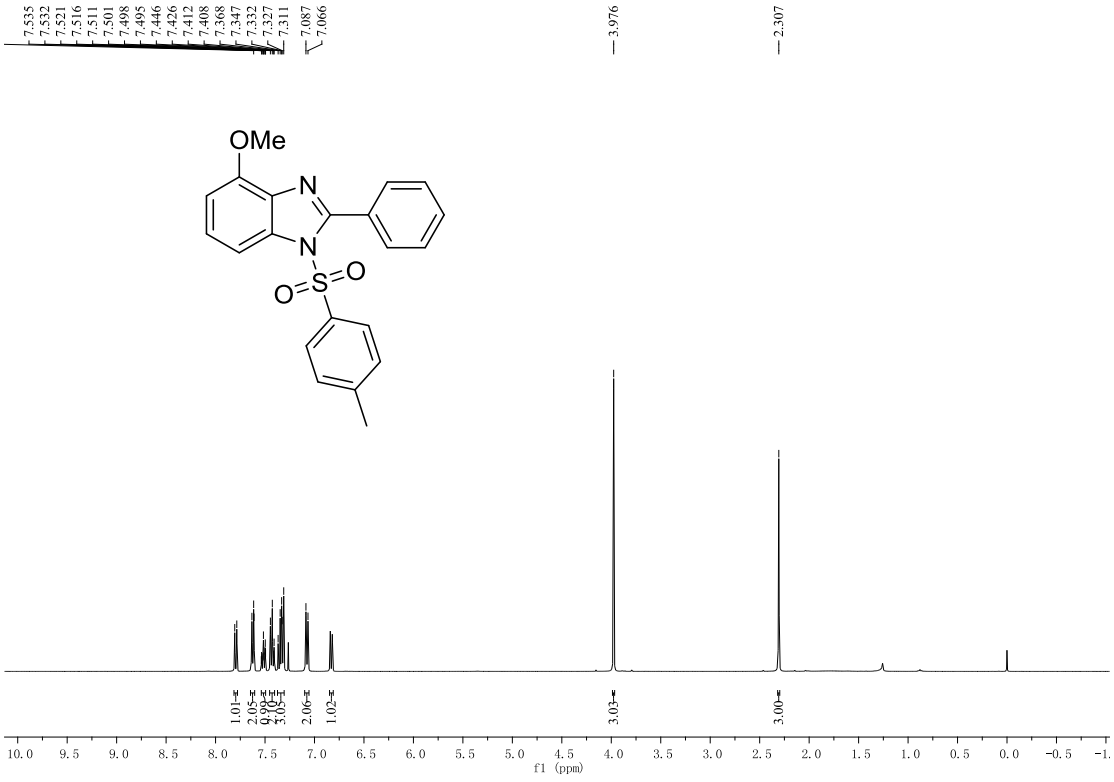
^{1}H NMR spectrum of **3ea**



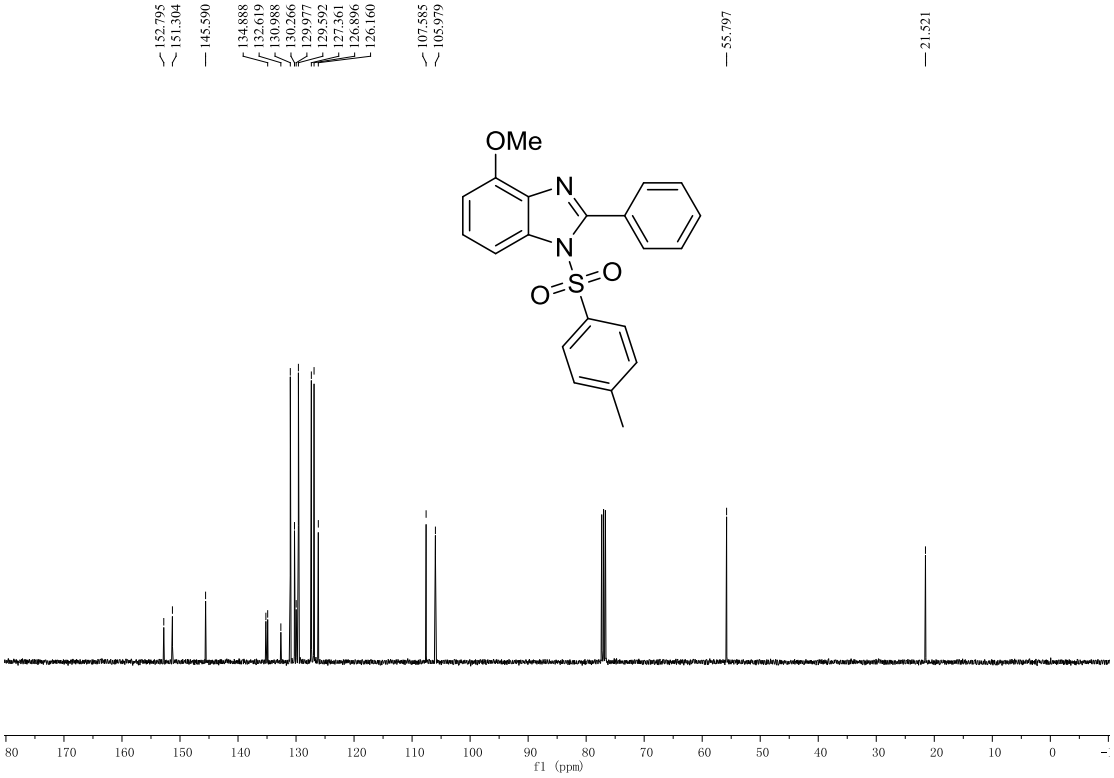
^{13}C NMR spectrum of **3ea**



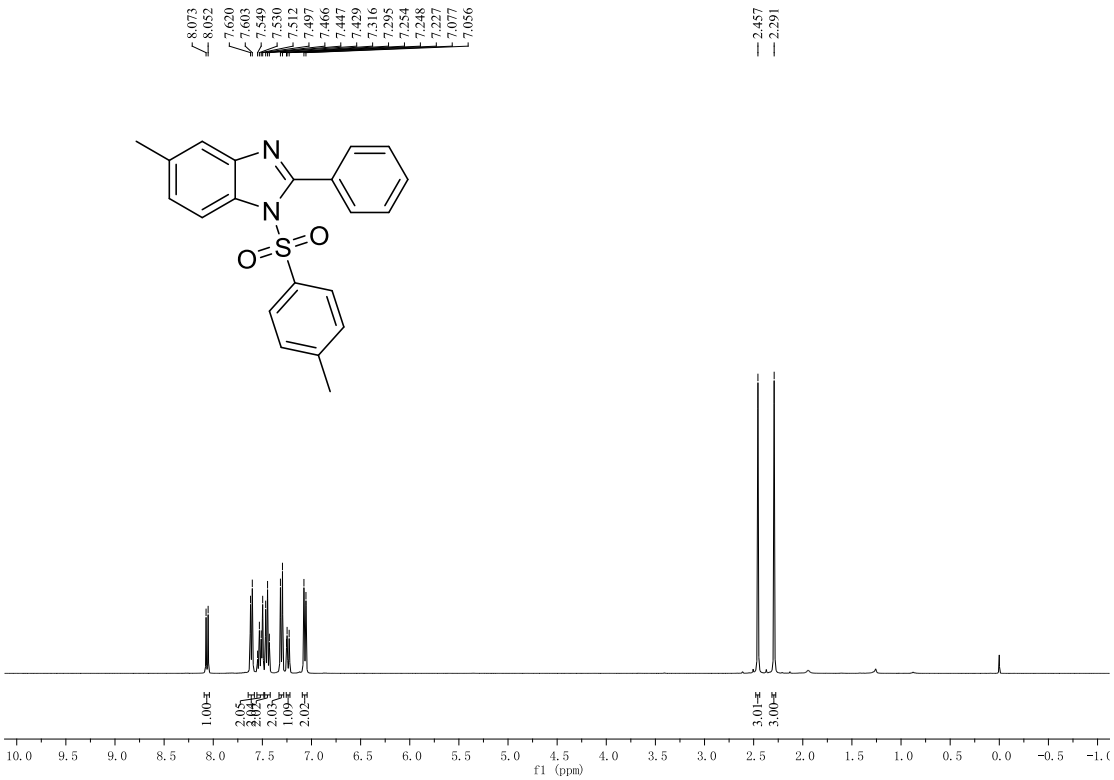
^{1}H NMR spectrum of **3fa**



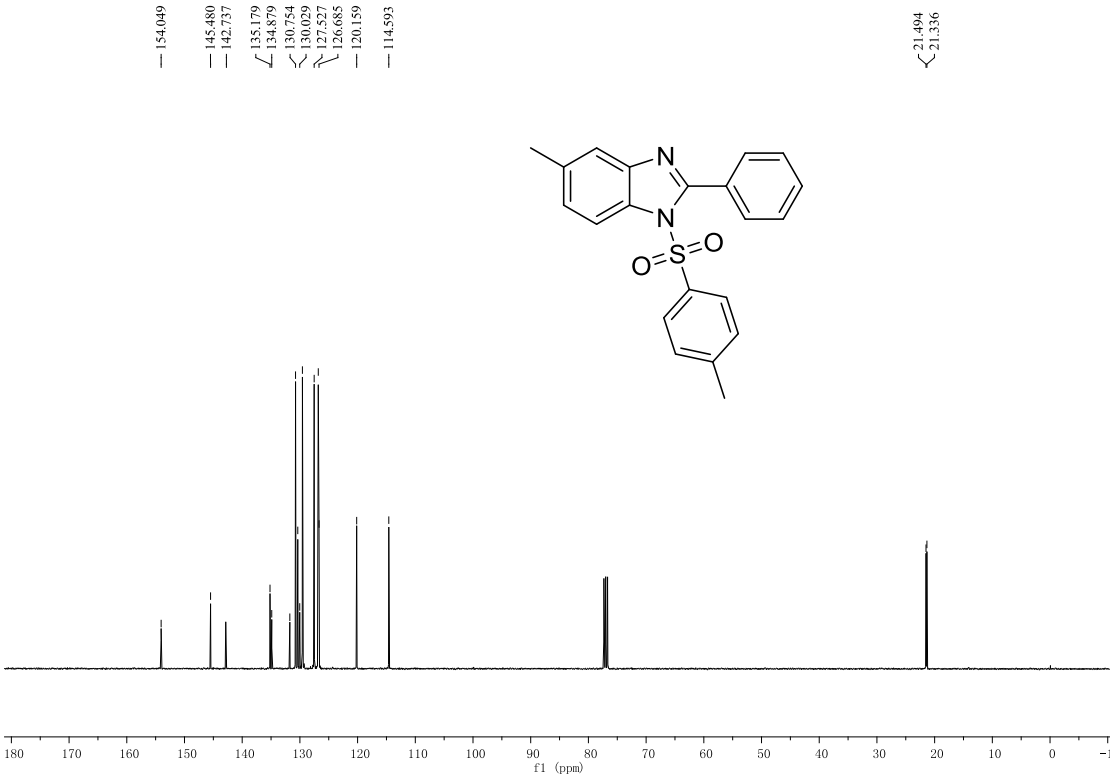
^{13}C NMR spectrum of **3fa**



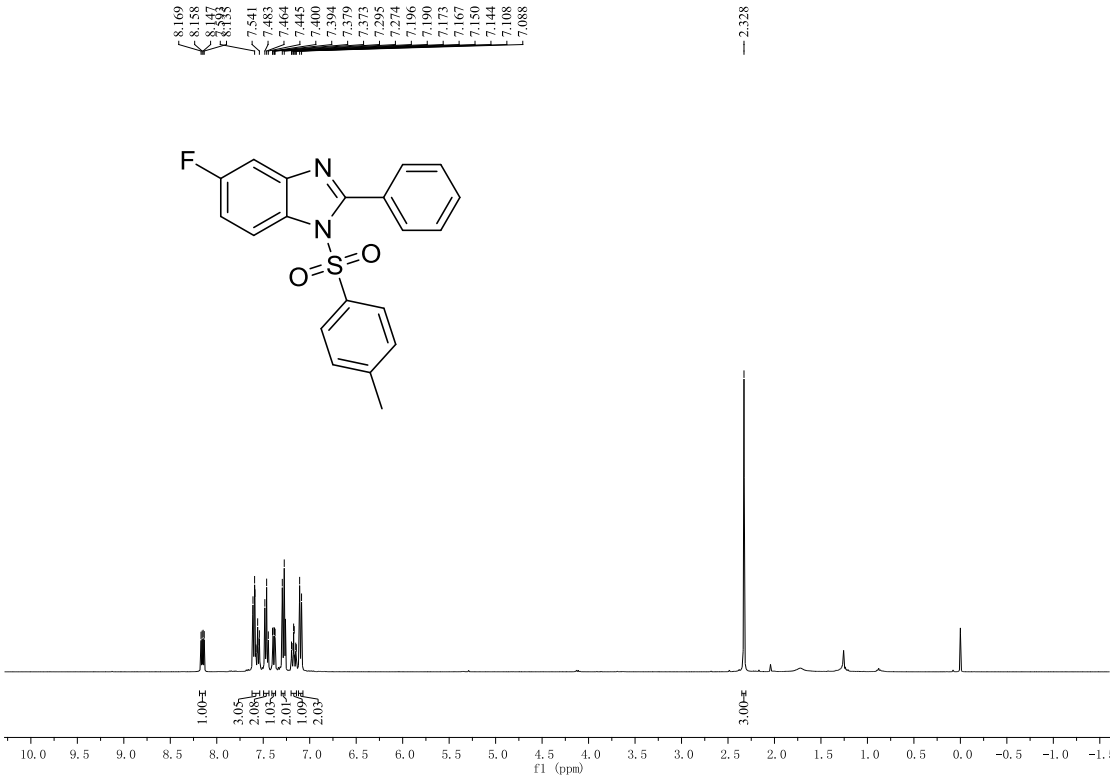
^{1}H NMR spectrum of **3ga**



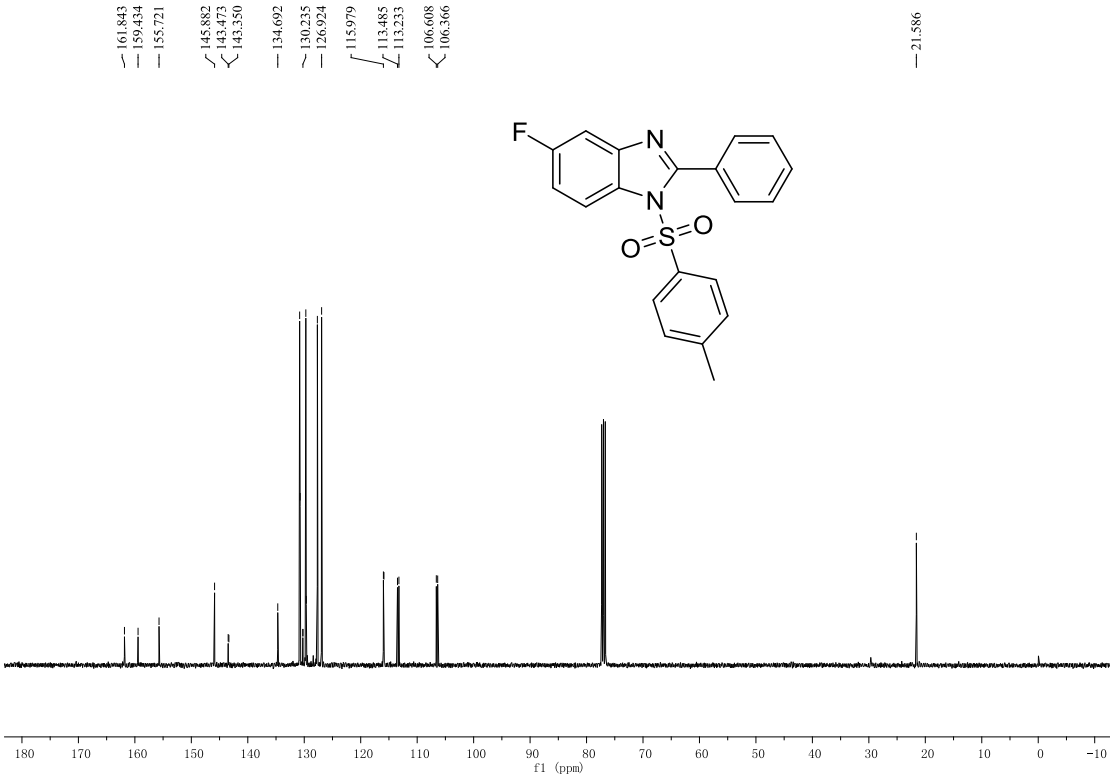
^{13}C NMR spectrum of **3ga**



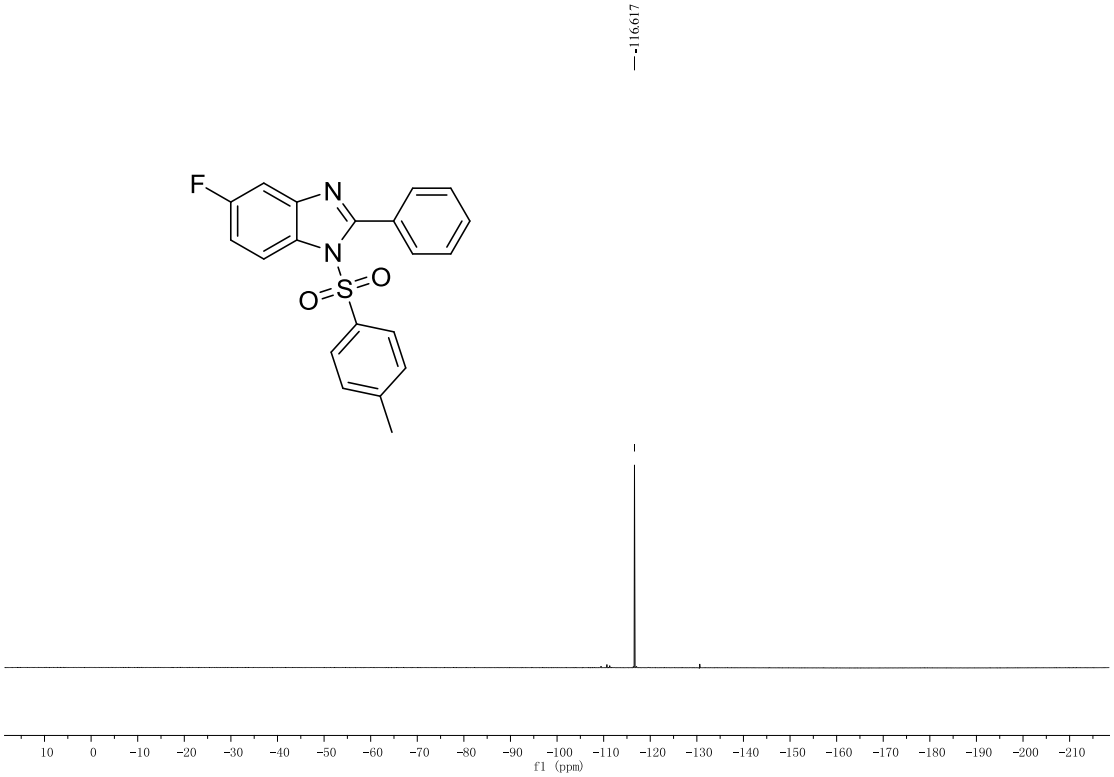
^{1}H NMR spectrum of **3ha**



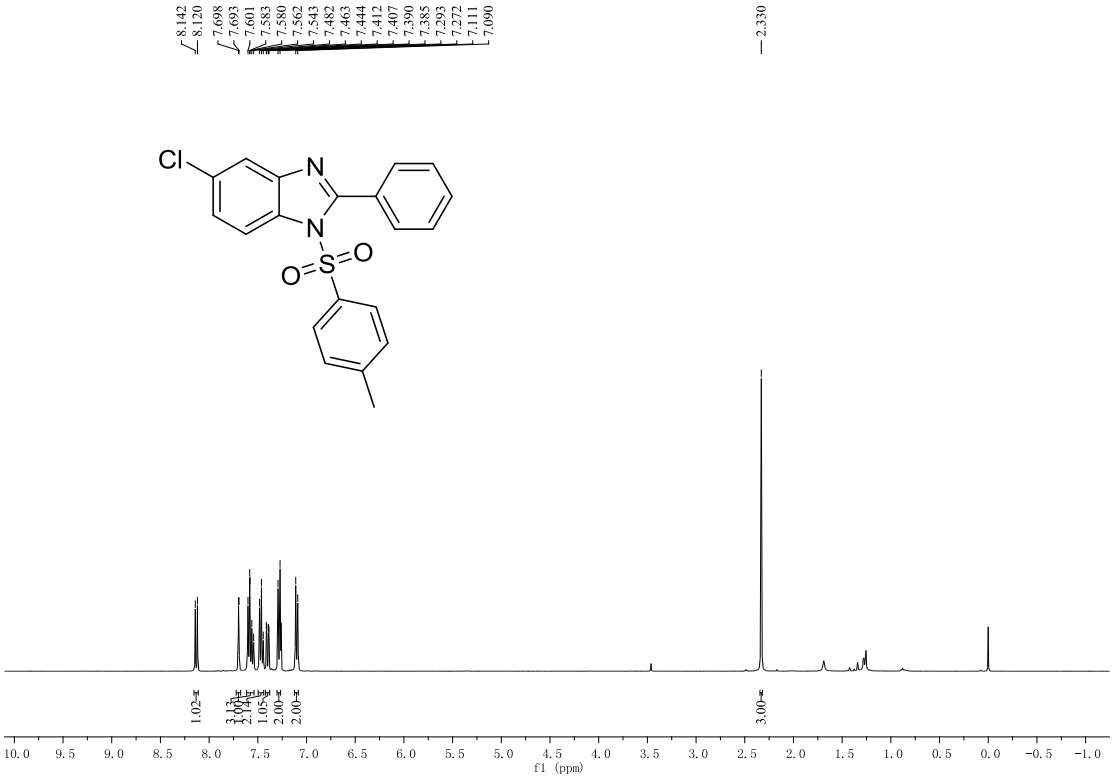
^{13}C NMR spectrum of **3ha**



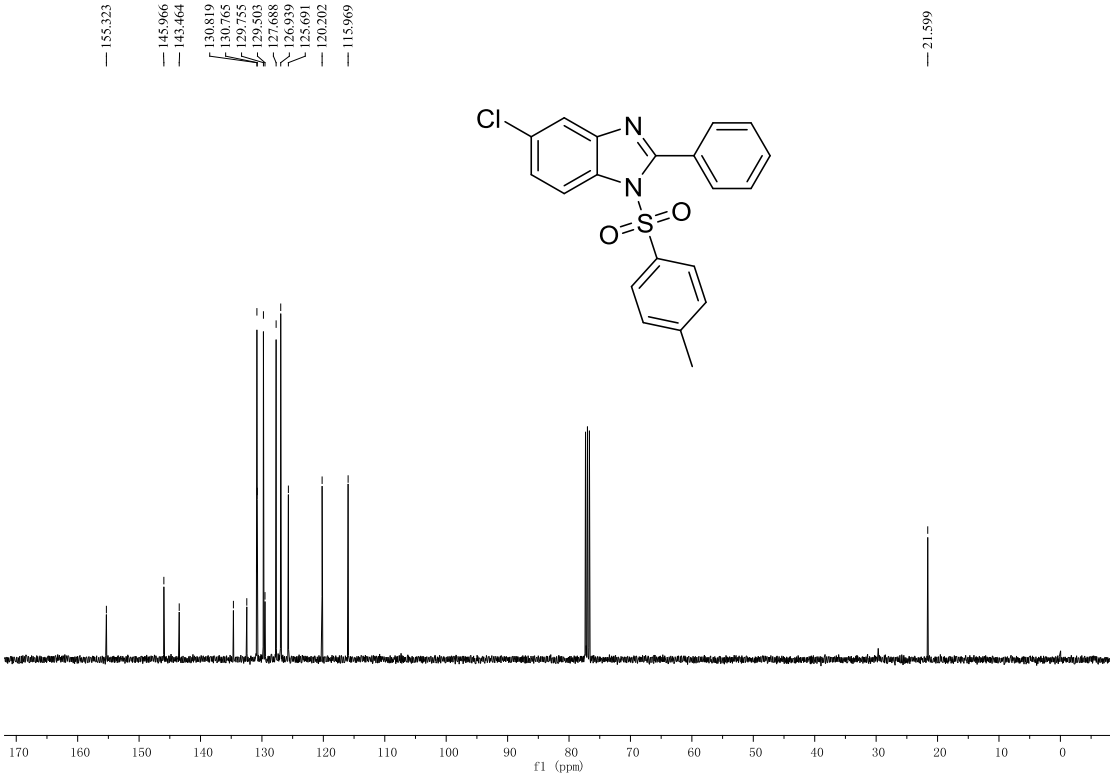
^{19}F NMR spectrum of **3ha**



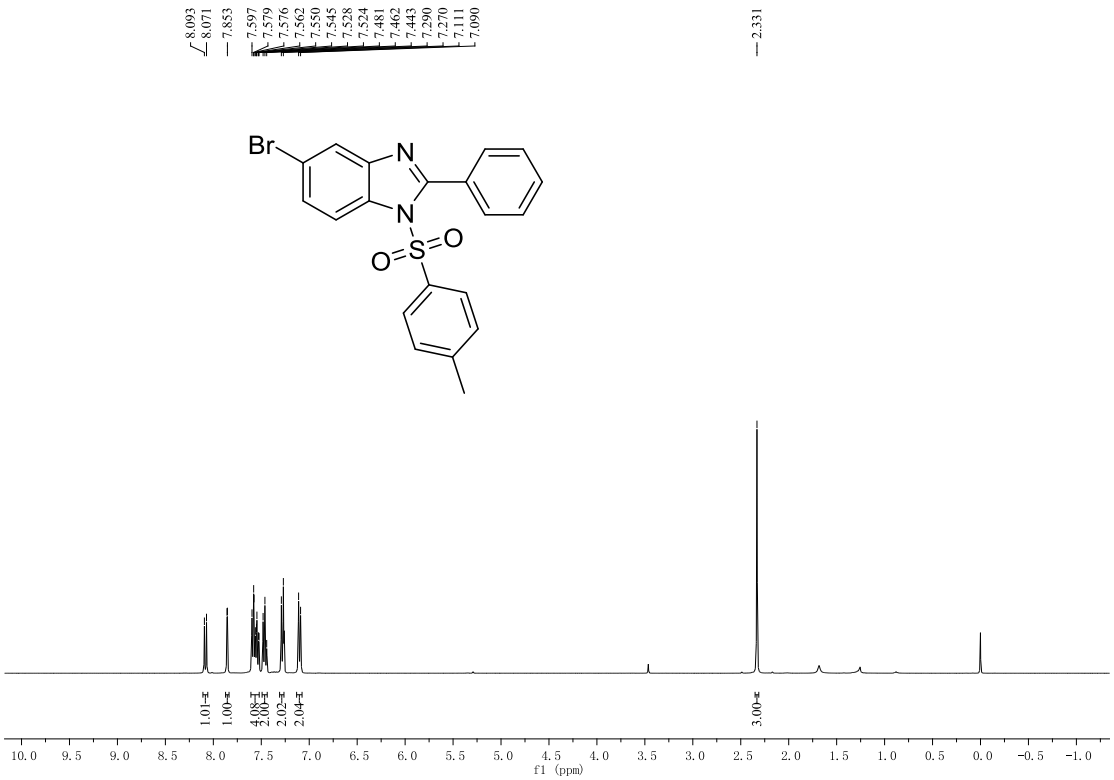
^{1}H NMR spectrum of **3ia**



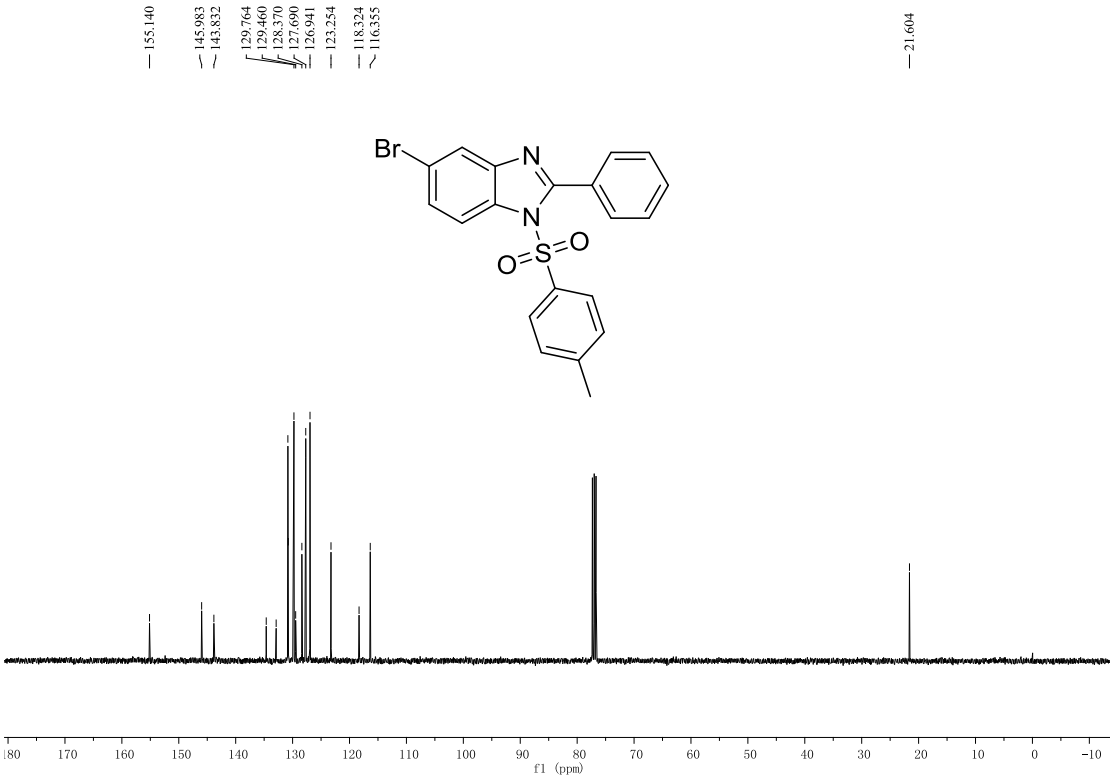
^{13}C NMR spectrum of **3ia**



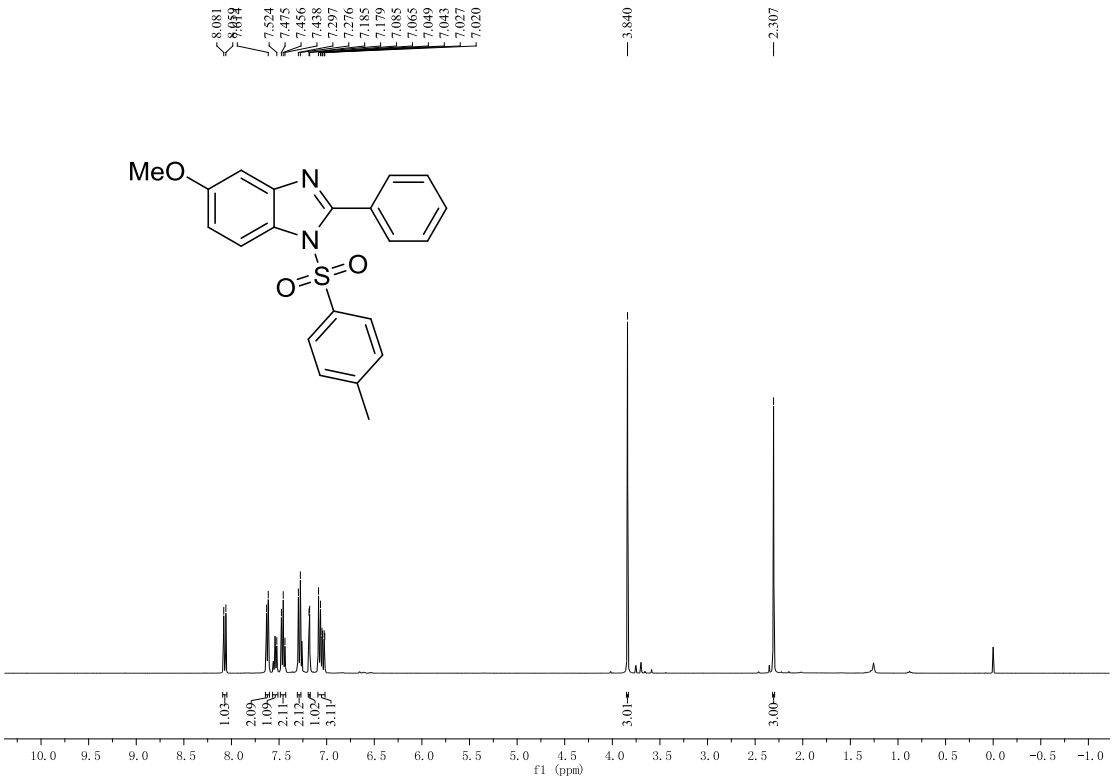
^{1}H NMR spectrum of **3ja**



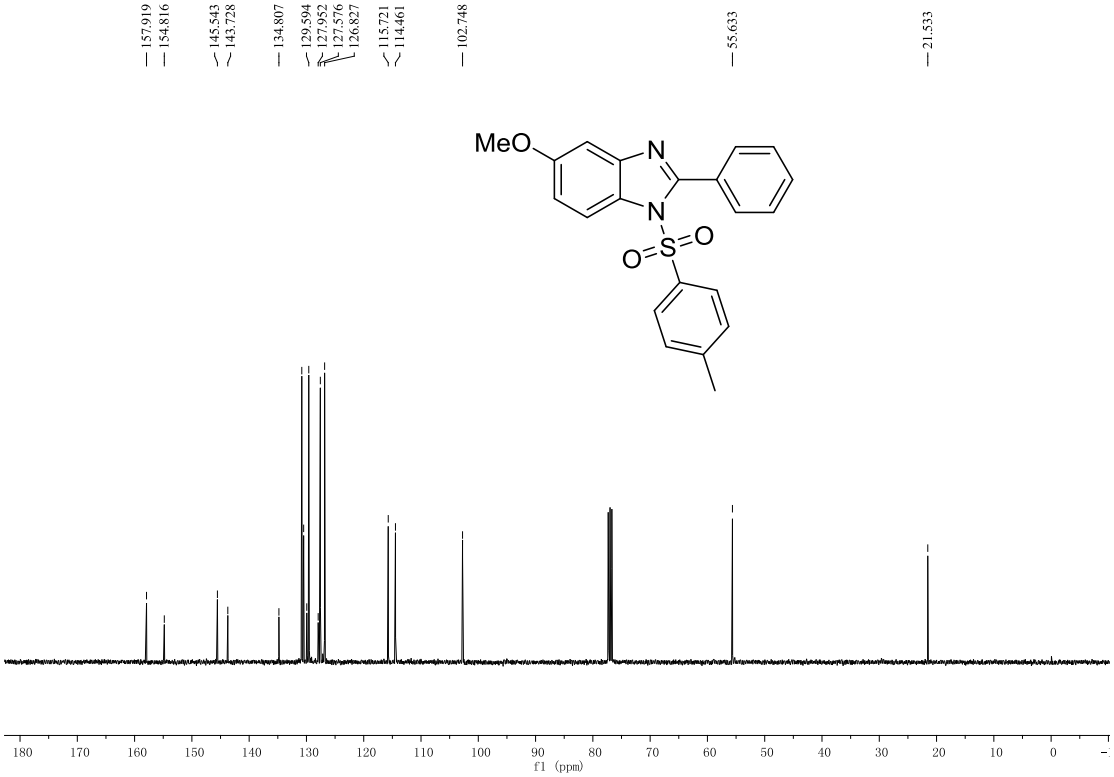
^{13}C NMR spectrum of **3ja**



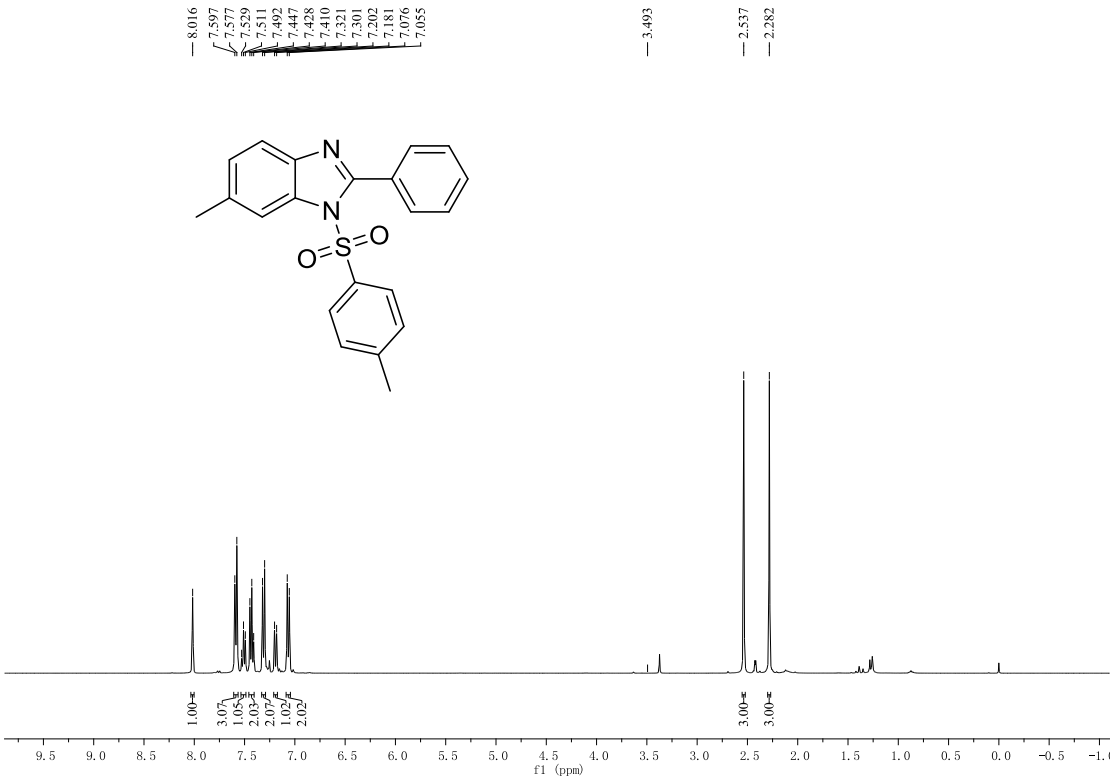
^{1}H NMR spectrum of **3ka**



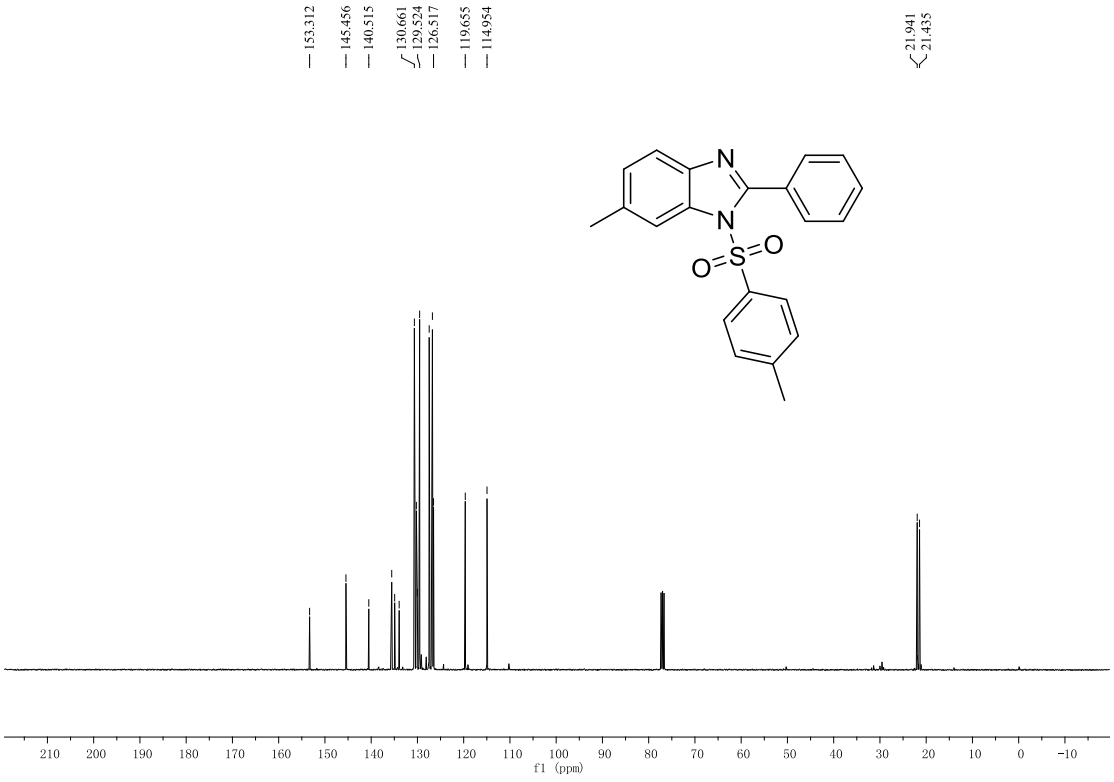
^{13}C NMR spectrum of **3ka**



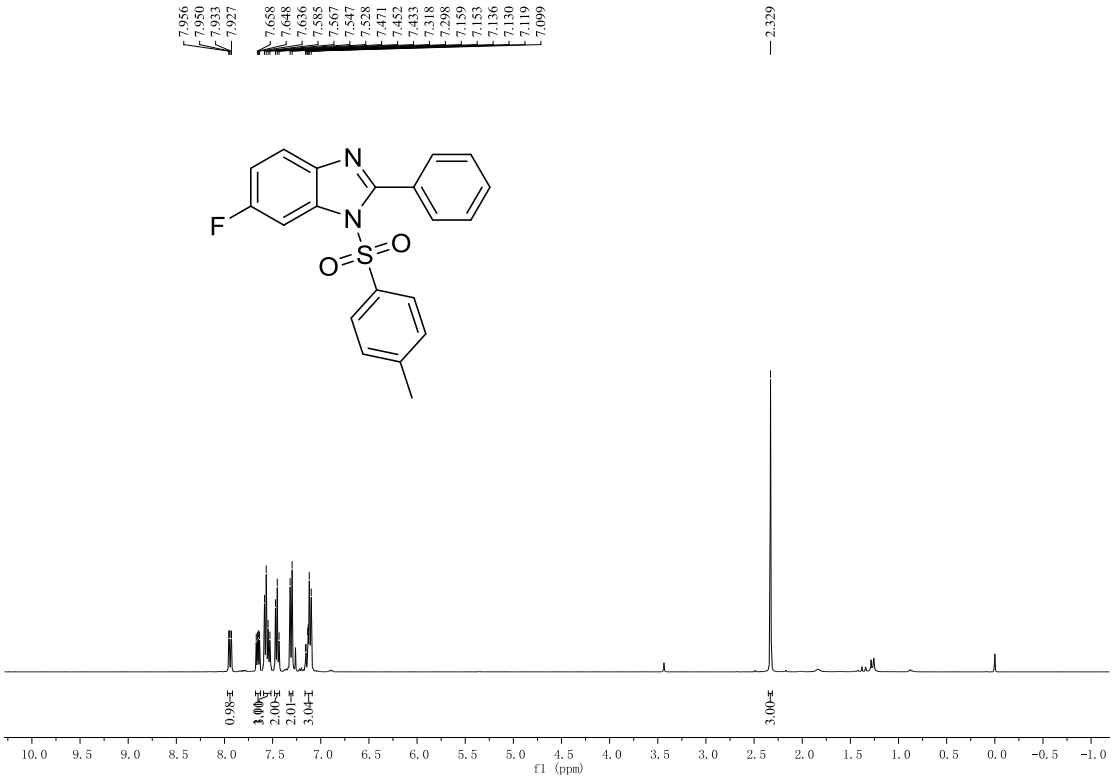
^{1}H NMR spectrum of **3la**



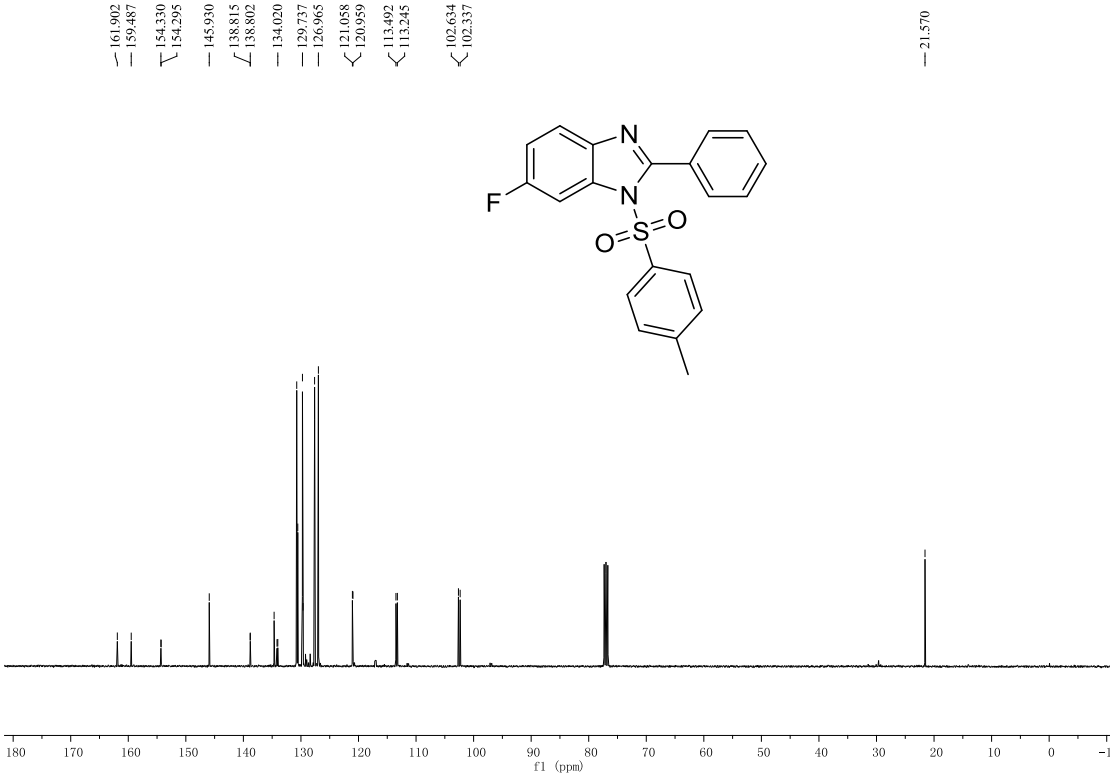
^{13}C NMR spectrum of **3la**



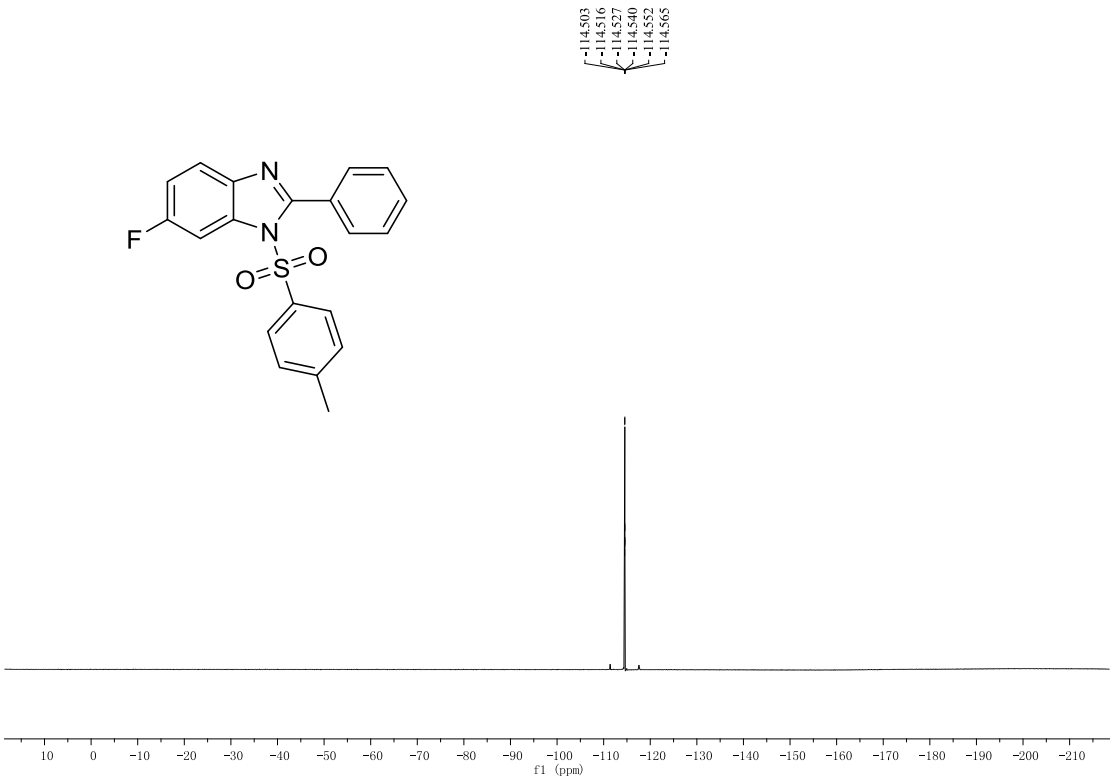
^{1}H NMR spectrum of **3ma**



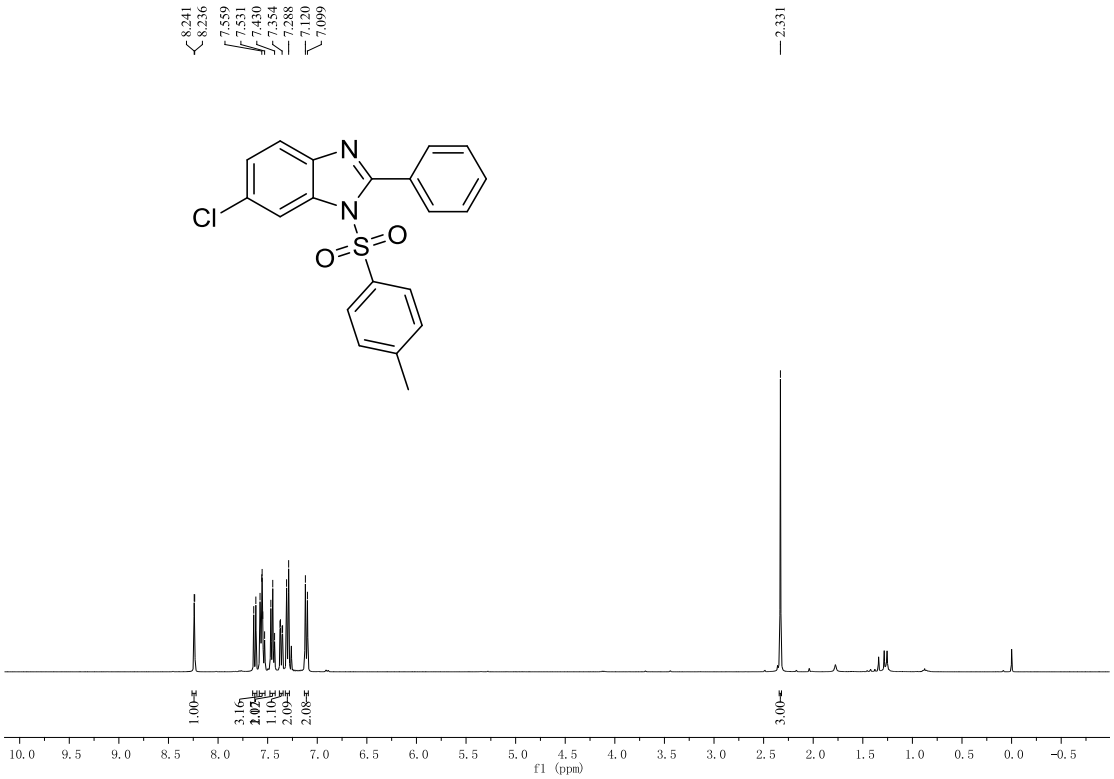
^{13}C NMR spectrum of **3ma**



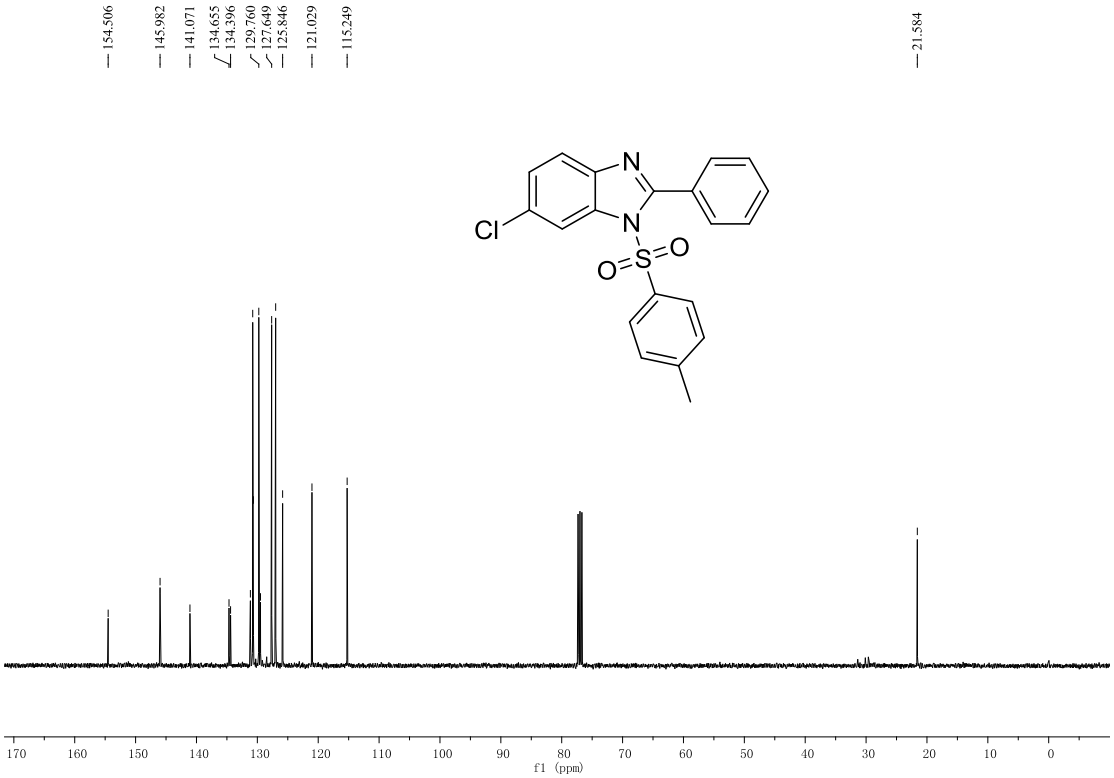
^{19}F NMR spectrum of **3ma**



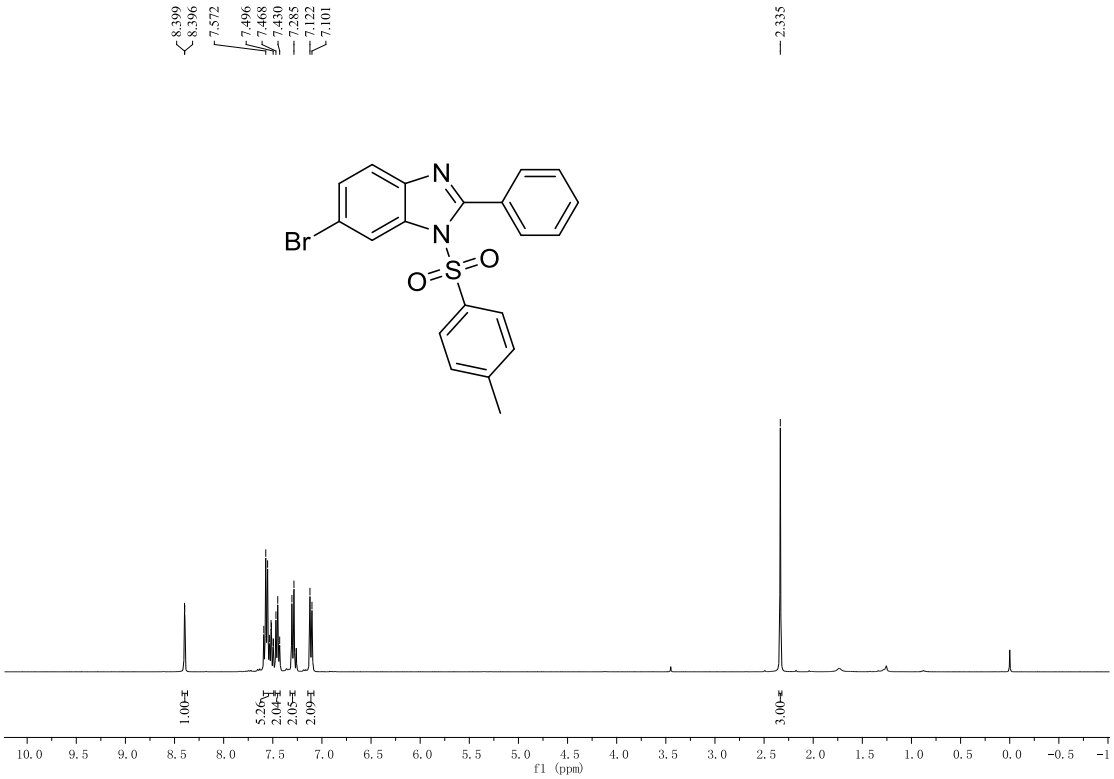
^{1}H NMR spectrum of **3na**



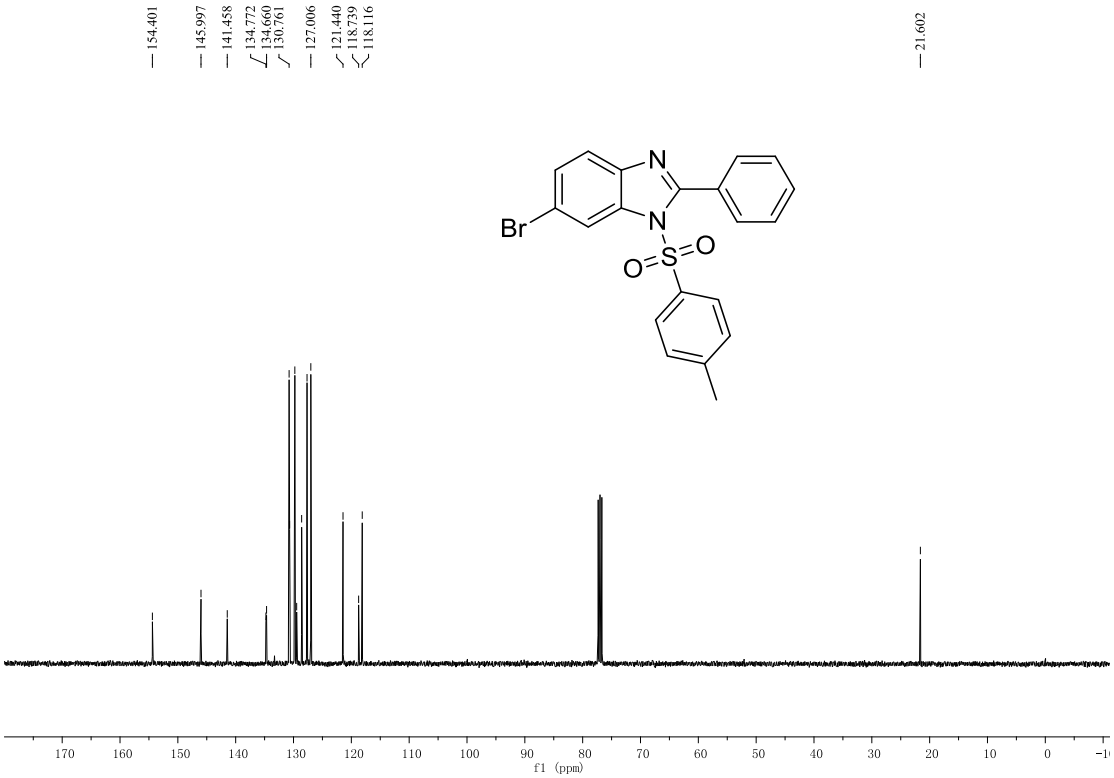
^{13}C NMR spectrum of **3na**



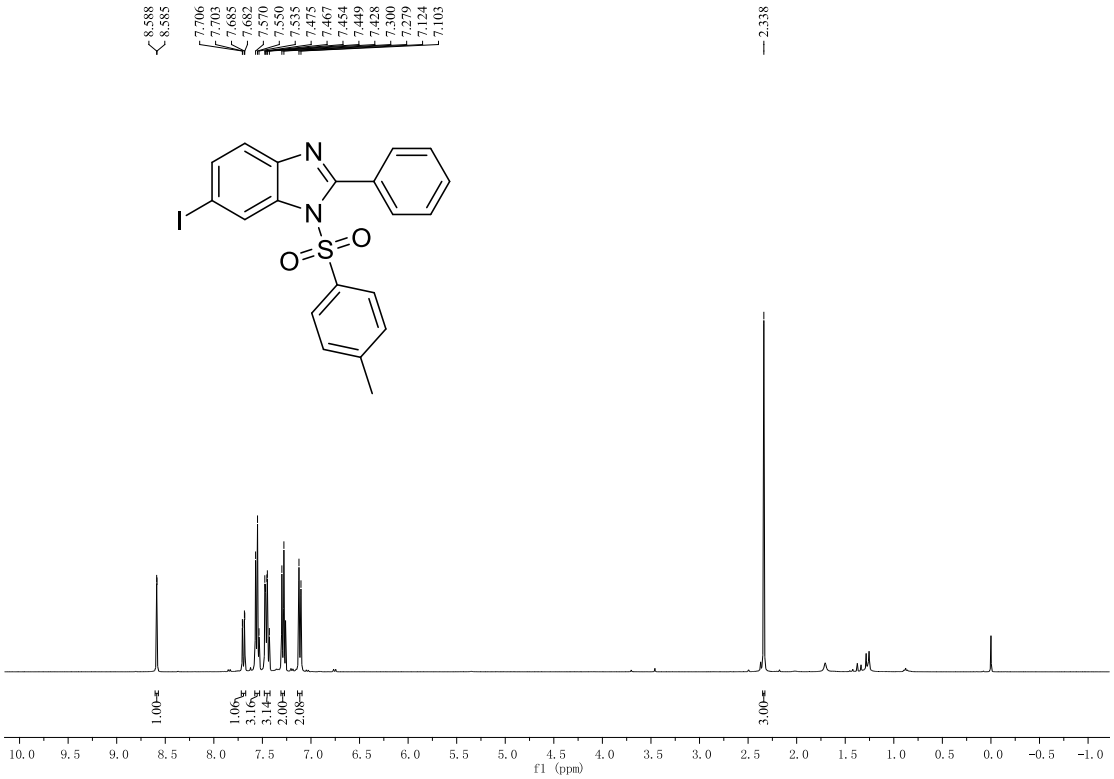
^{1}H NMR spectrum of **3oa**



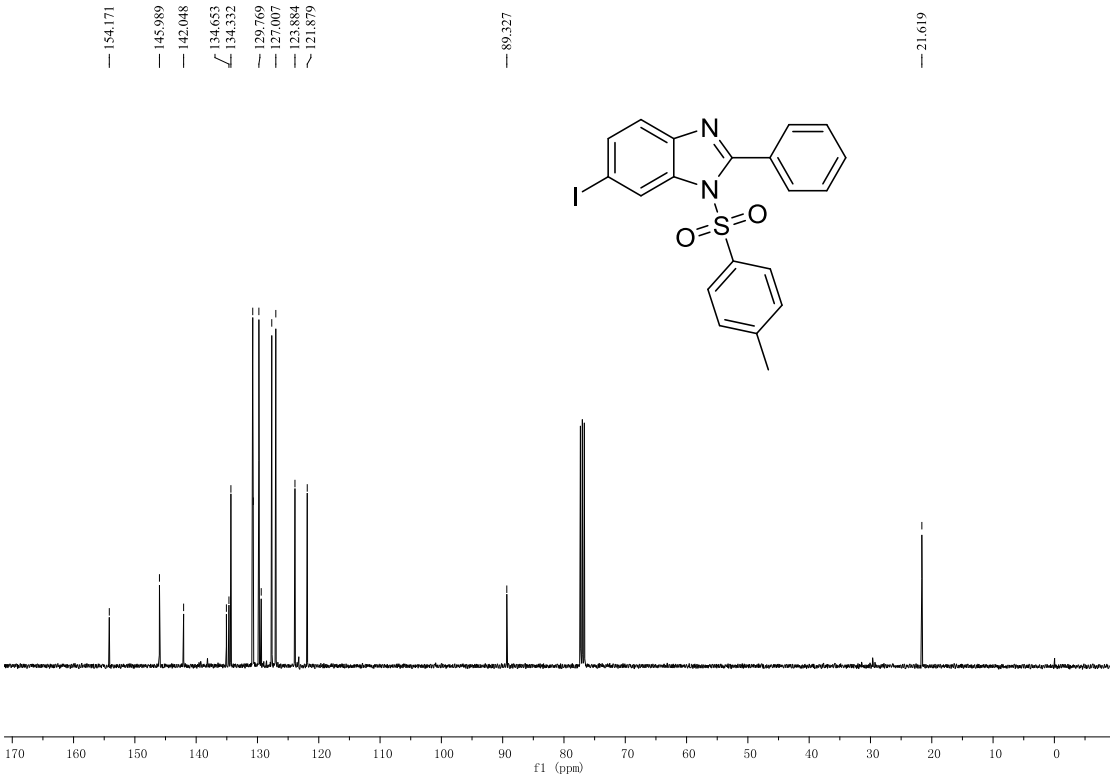
^{13}C NMR spectrum of **3oa**



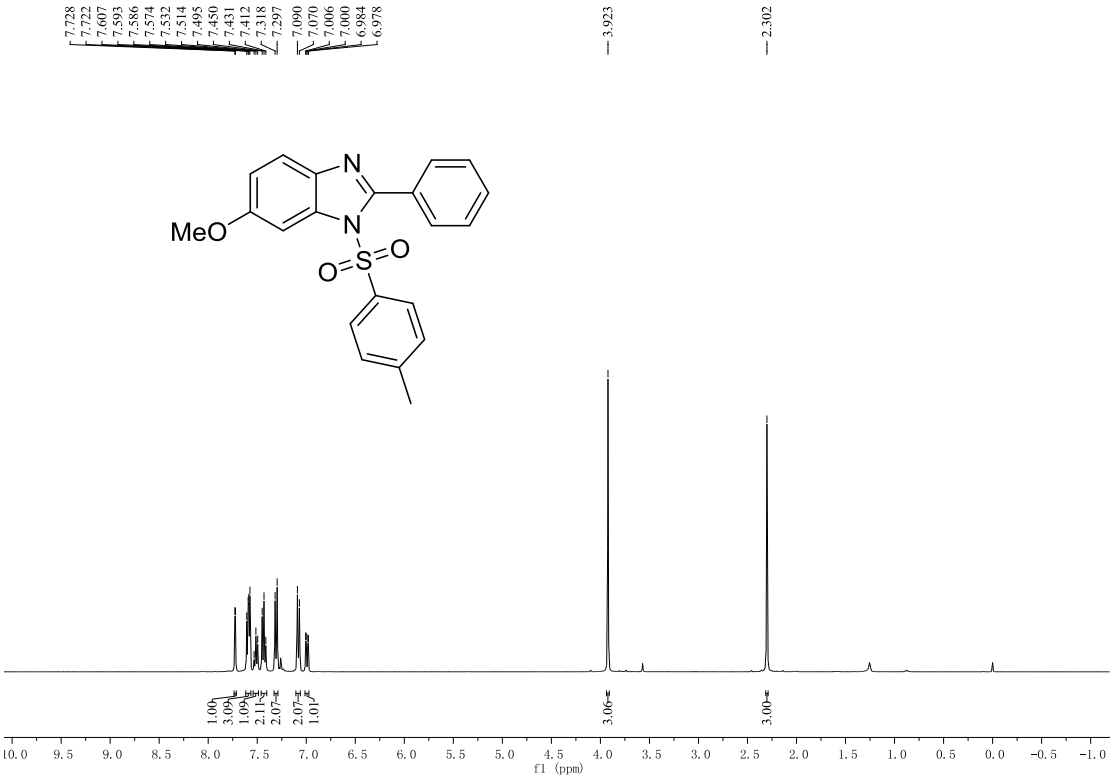
^{1}H NMR spectrum of **3pa**



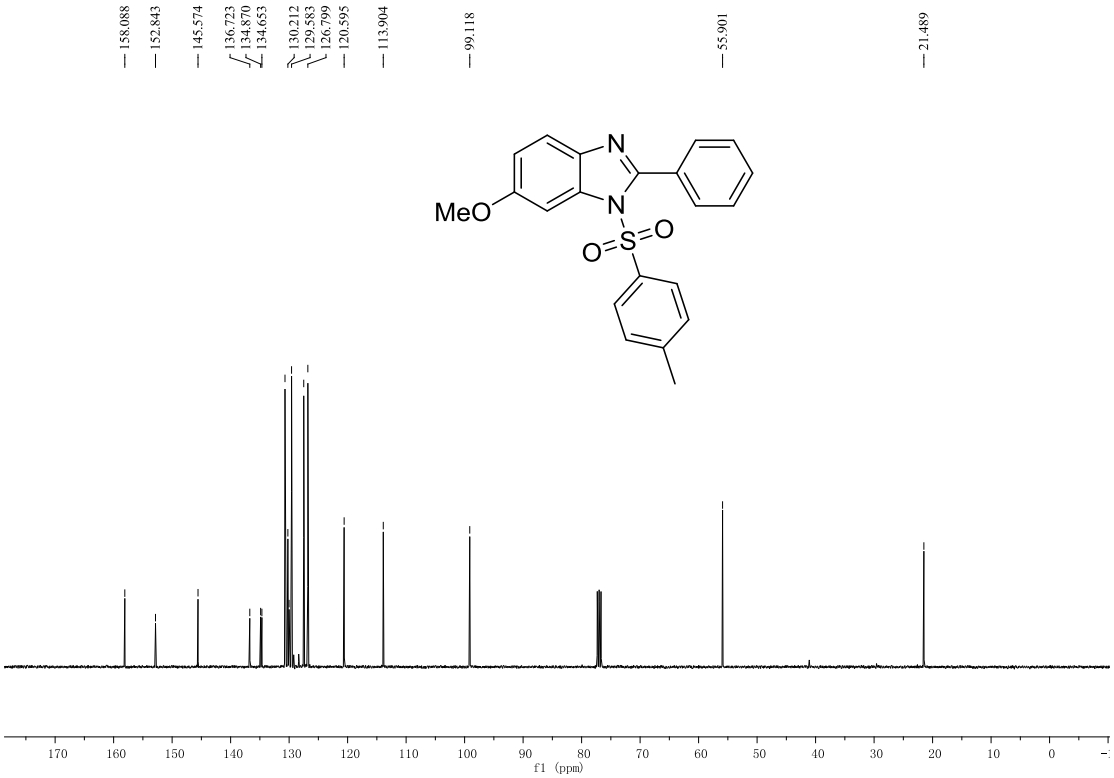
^{13}C NMR spectrum of **3pa**



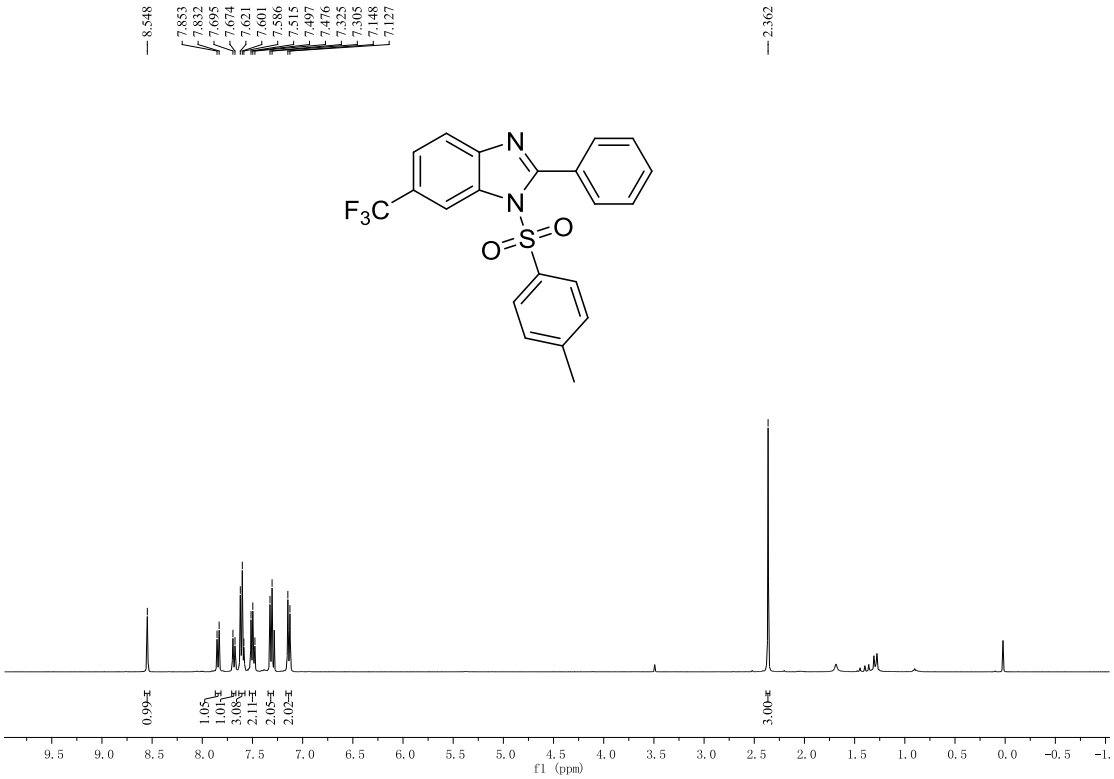
^{1}H NMR spectrum of **3qa**



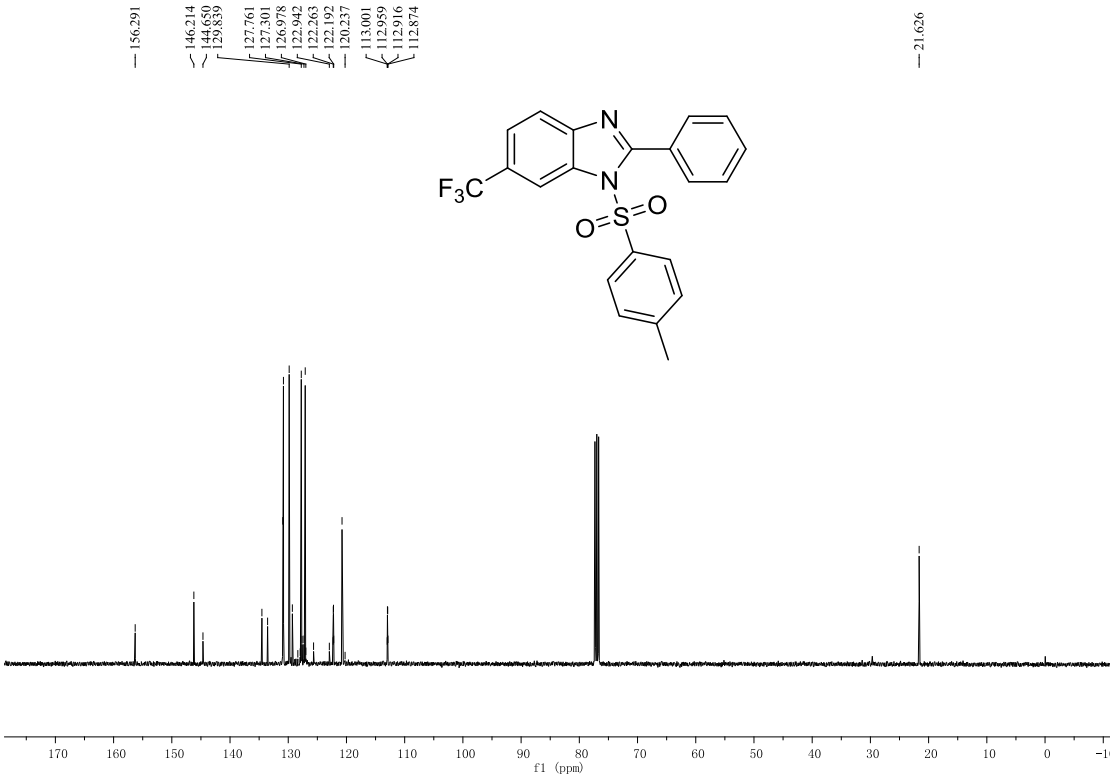
^{13}C NMR spectrum of **3qa**



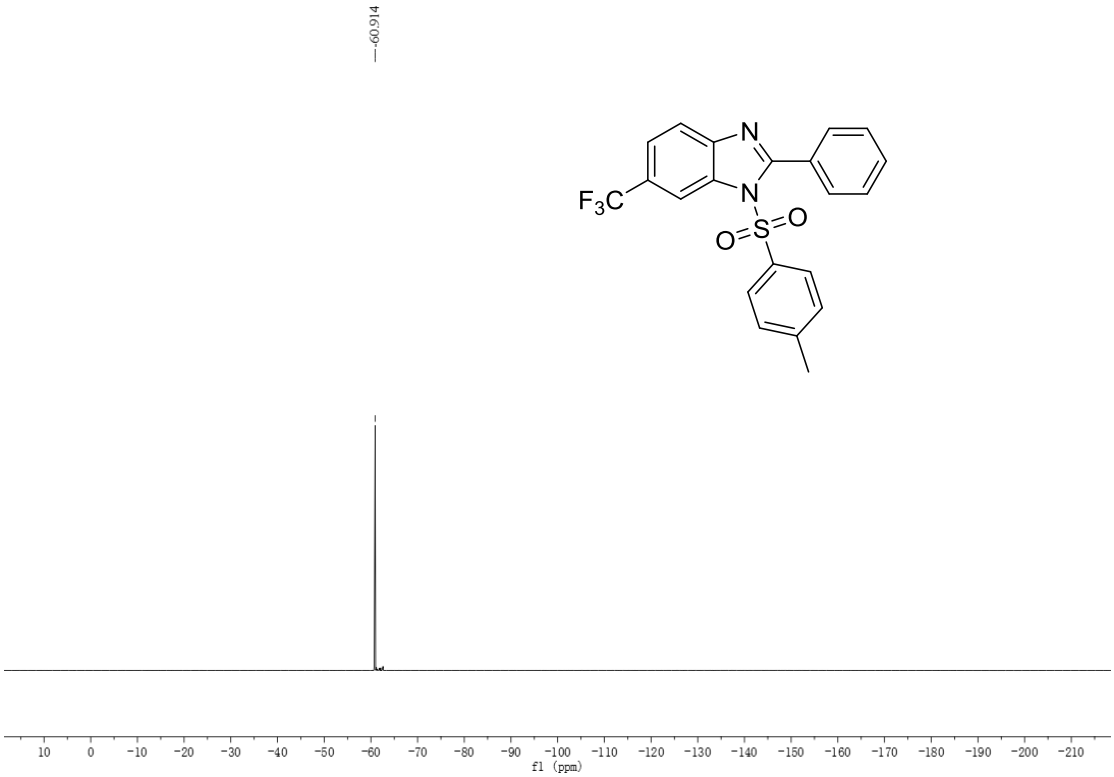
^{1}H NMR spectrum of **3ra**



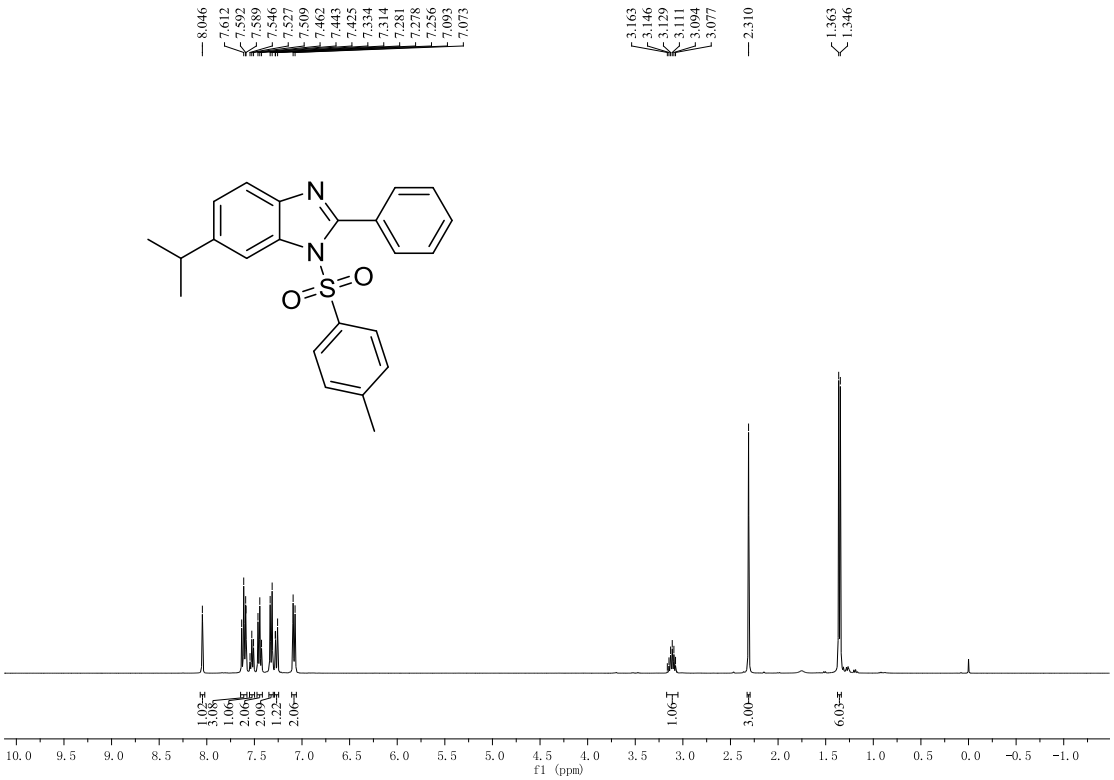
^{13}C NMR spectrum of **3ra**



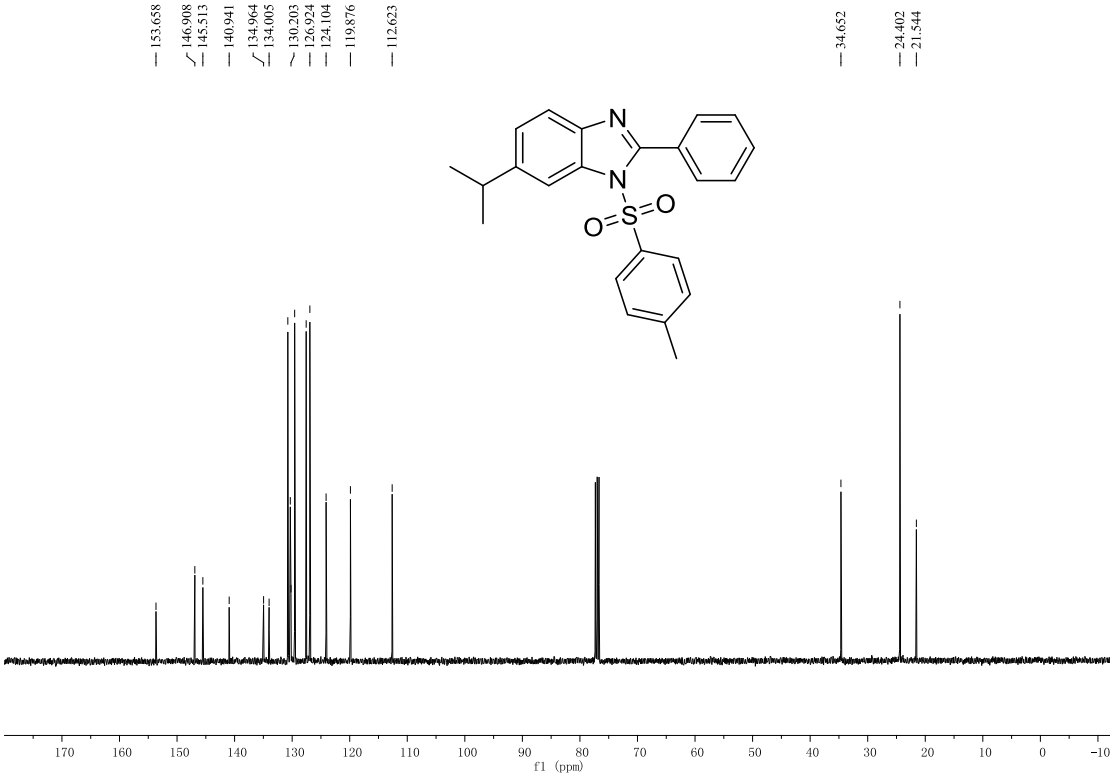
^{19}F NMR spectrum of **3ra**



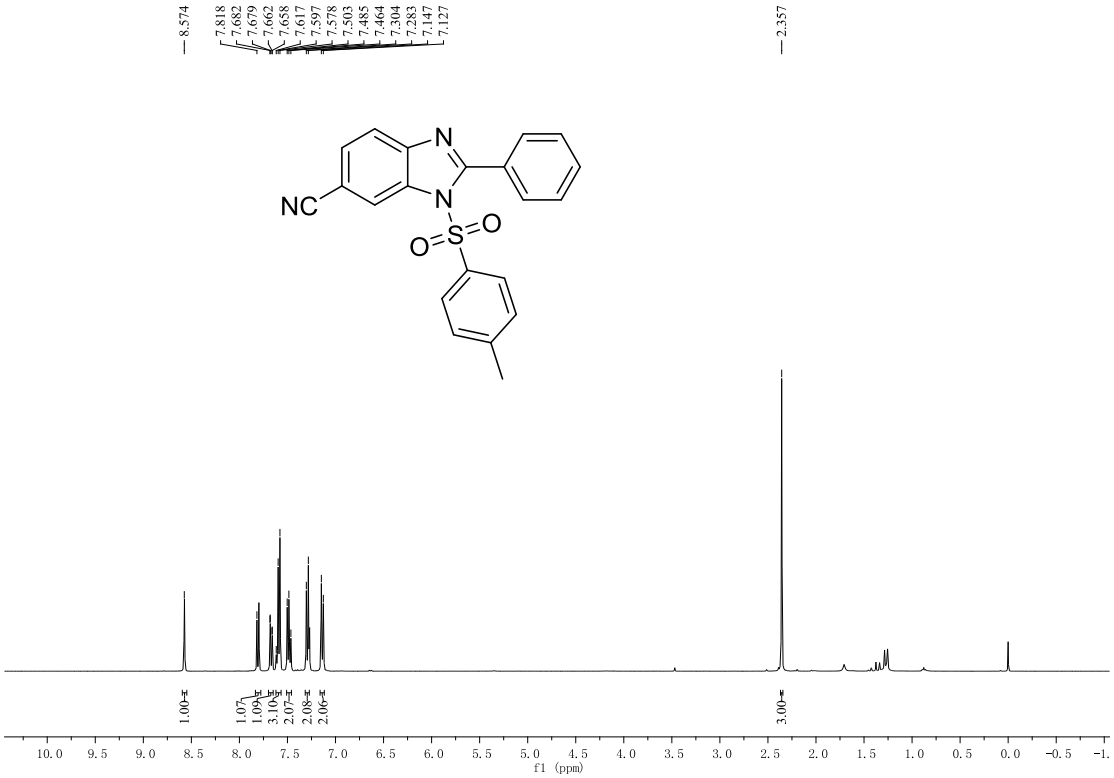
^{1}H NMR spectrum of **3sa**



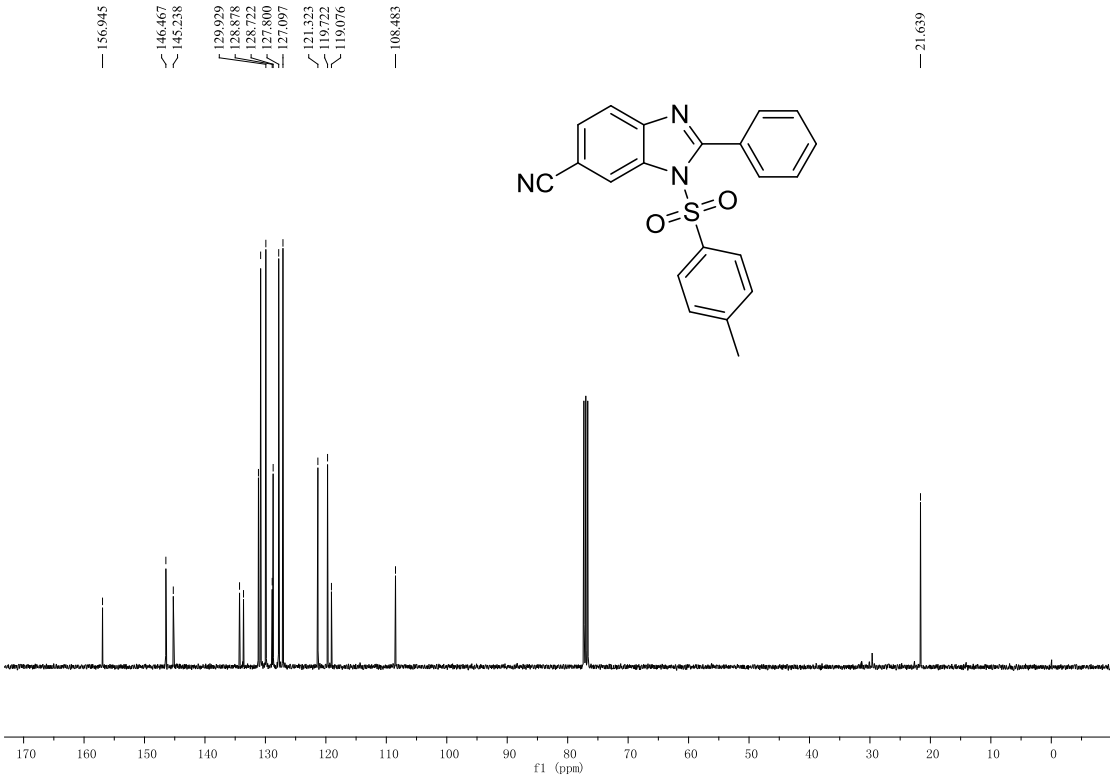
^{13}C NMR spectrum of **3sa**



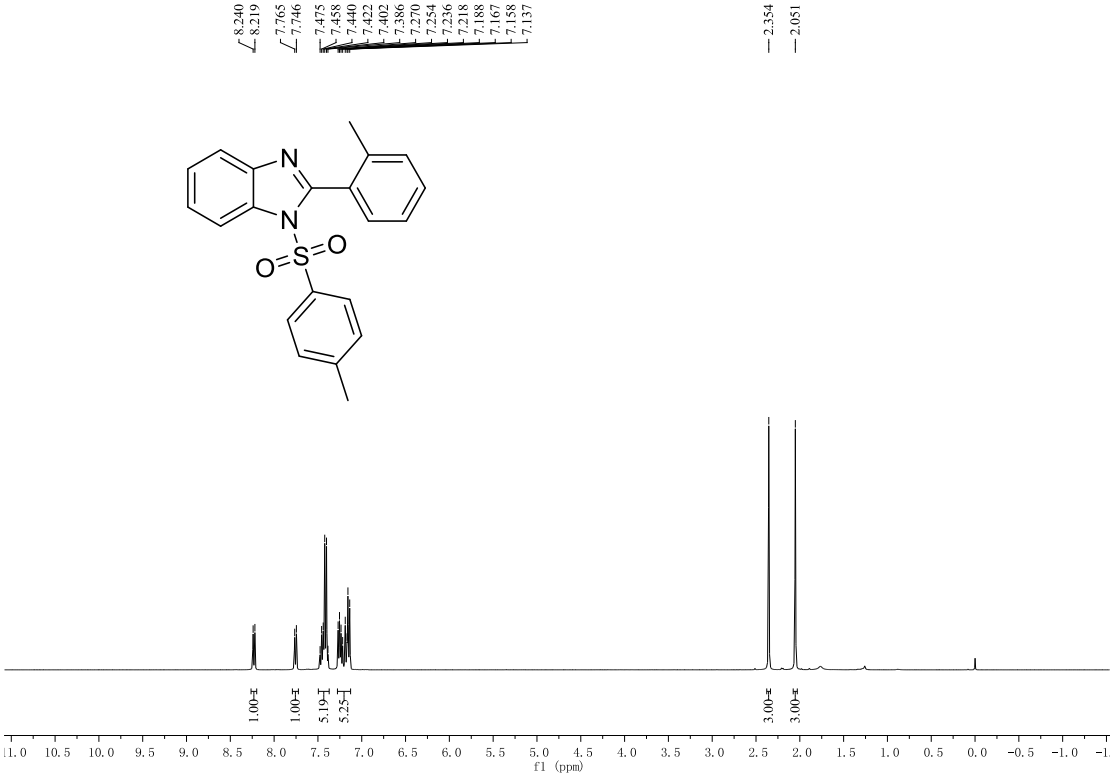
^{1}H NMR spectrum of **3ta**



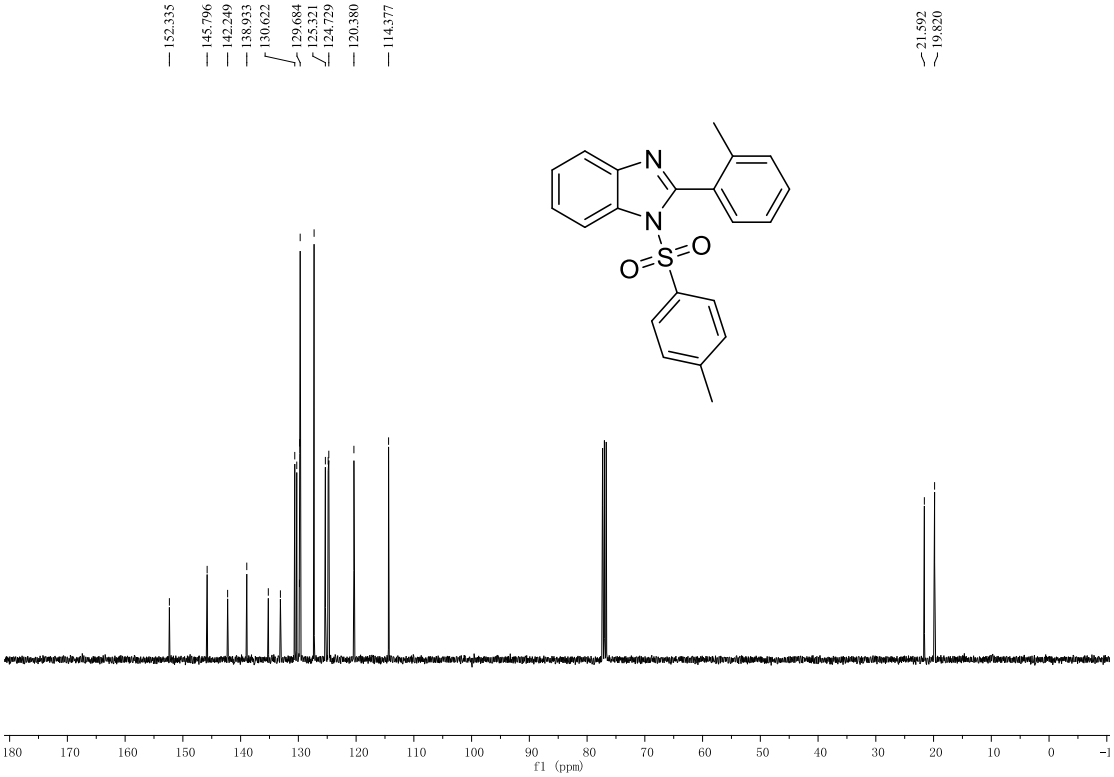
^{13}C NMR spectrum of **3ta**



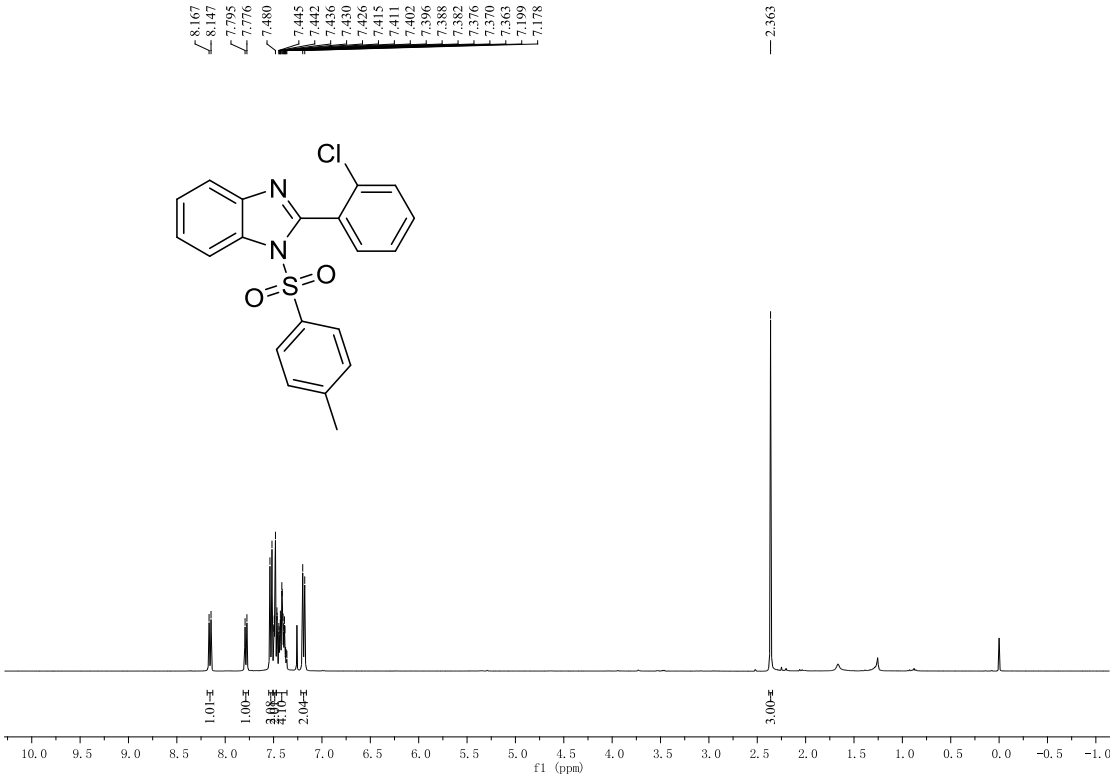
^{1}H NMR spectrum of **3aaa**



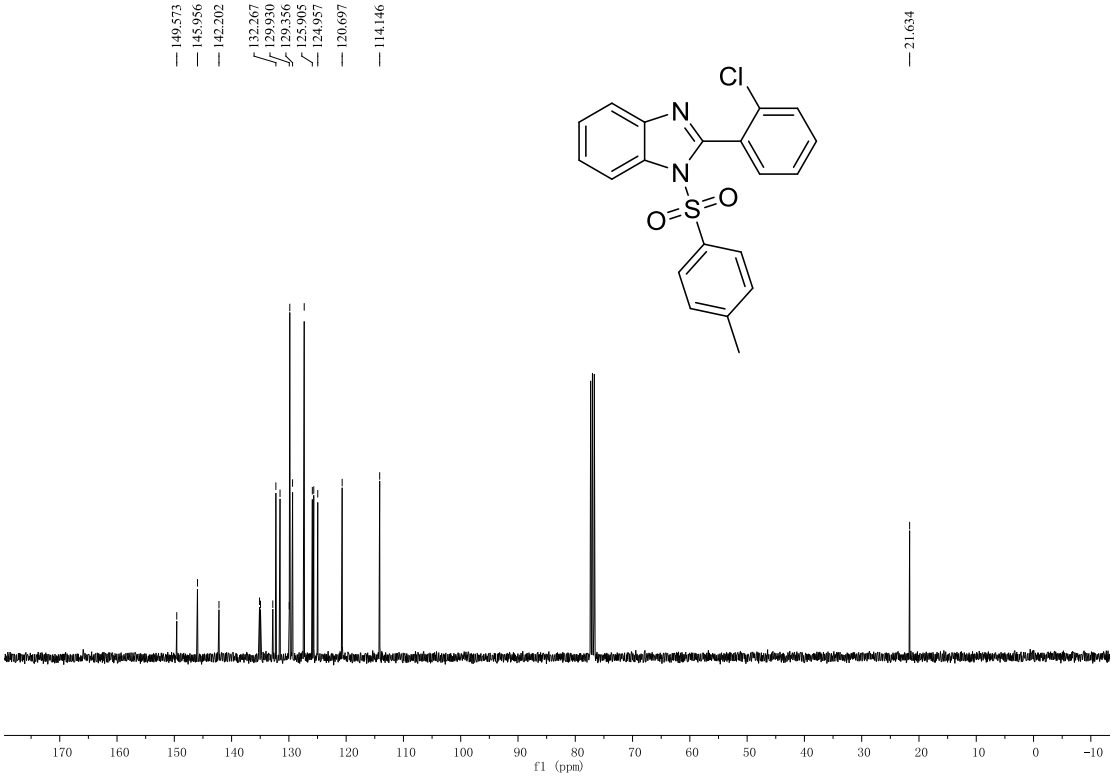
^{13}C NMR spectrum of **3aaa**



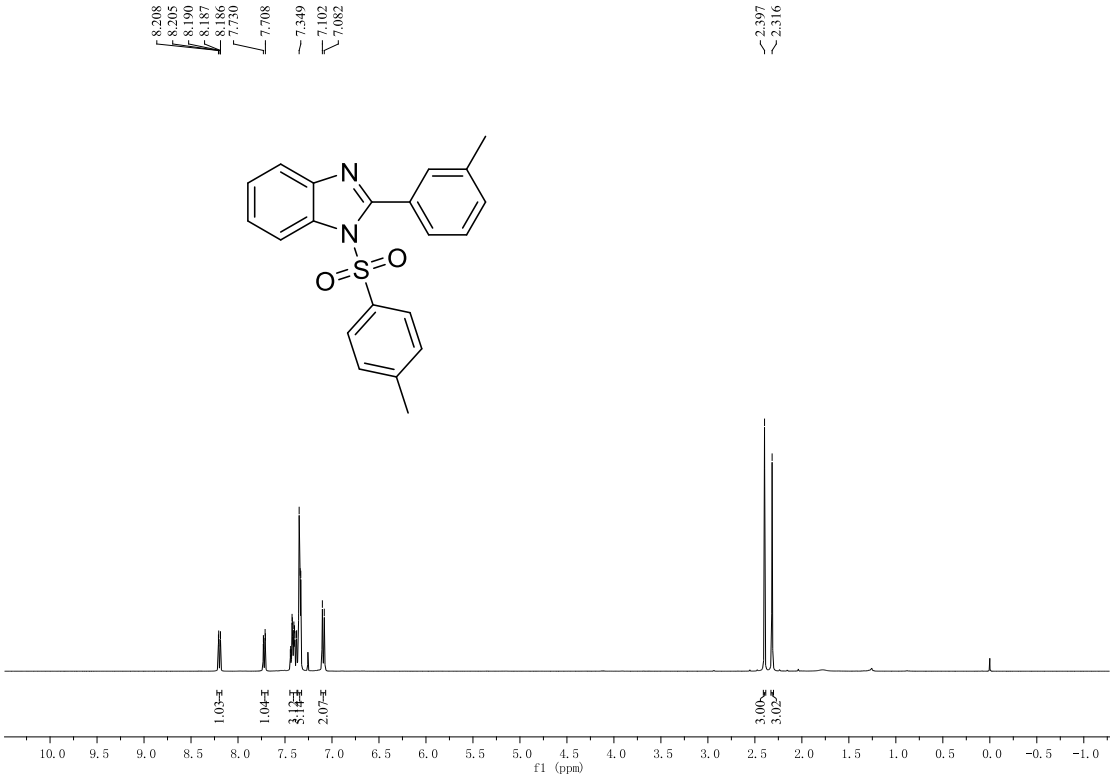
^{1}H NMR spectrum of **3aab**



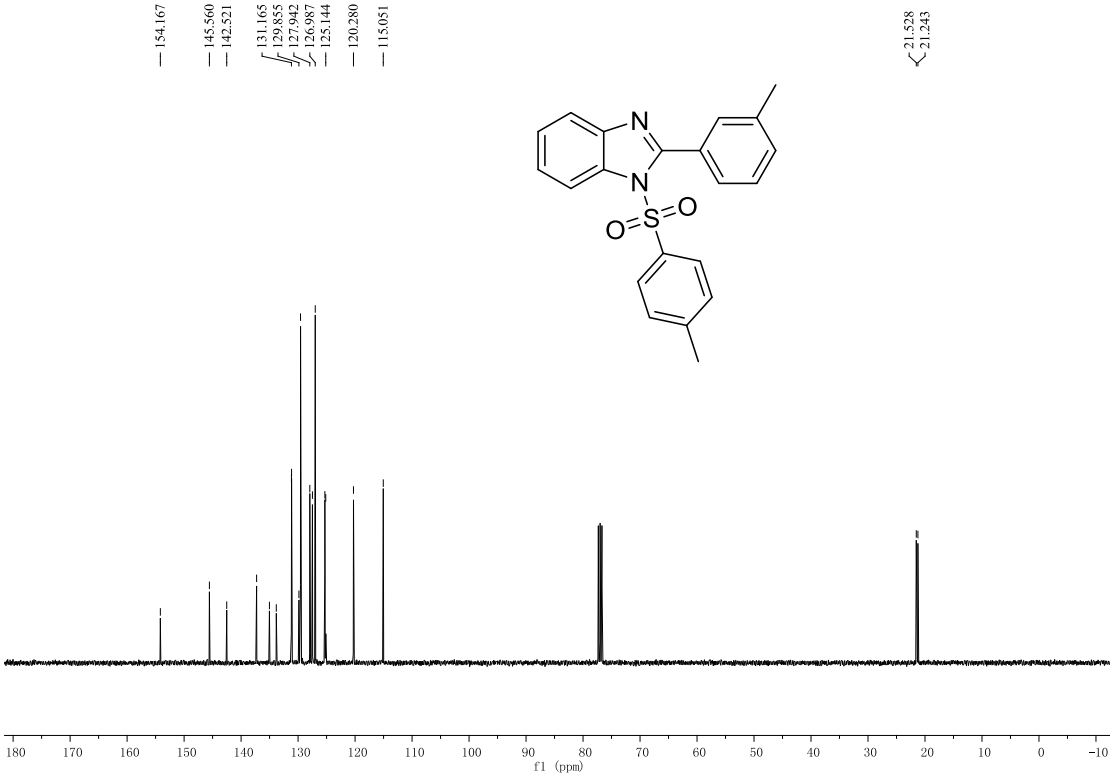
^{13}C NMR spectrum of **3aab**



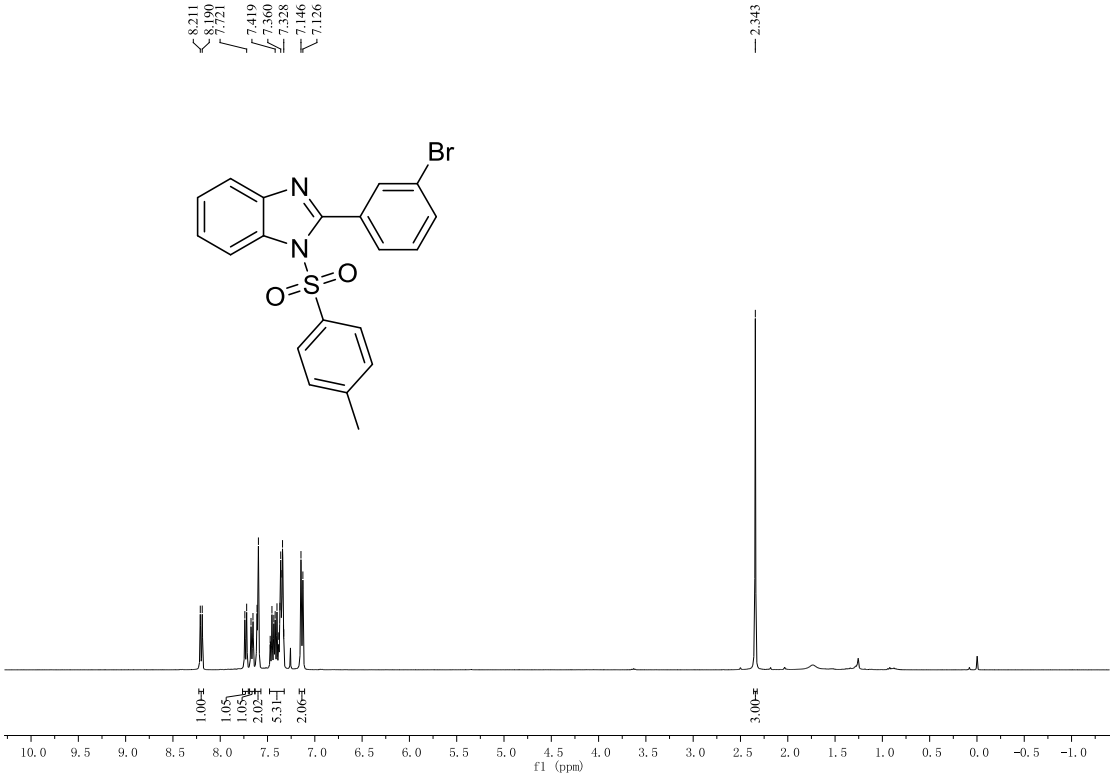
^{1}H NMR spectrum of **3aac**



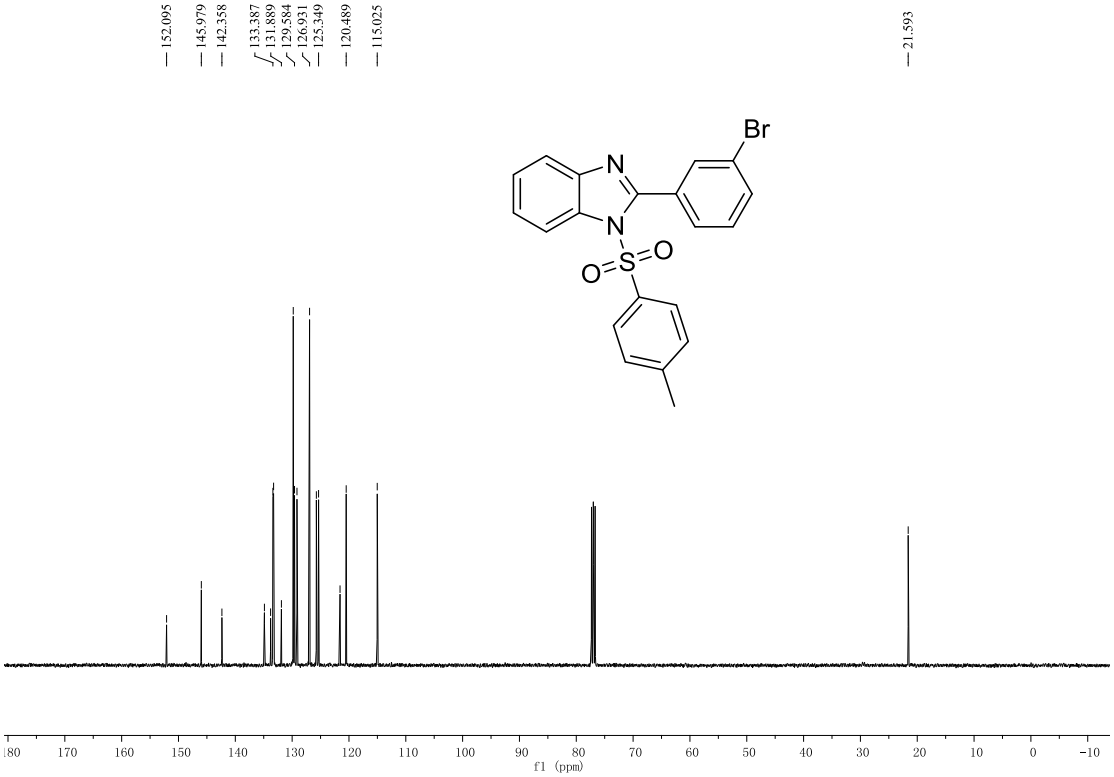
^{13}C NMR spectrum of **3aac**



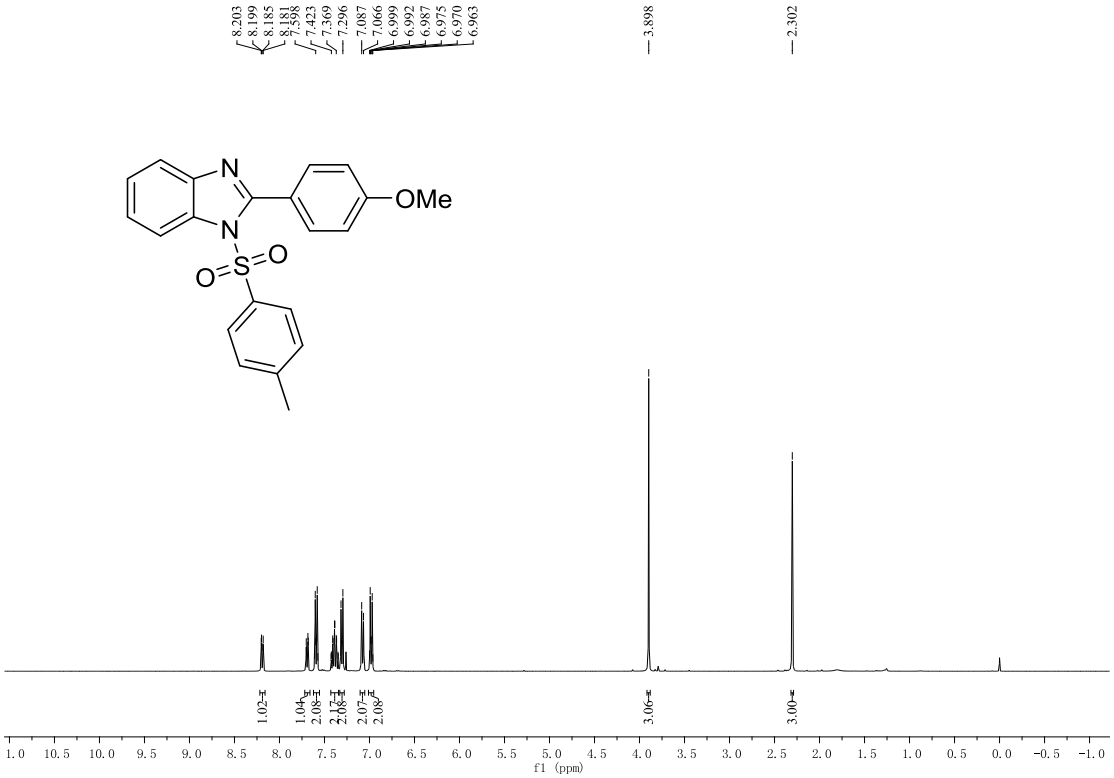
^{1}H NMR spectrum of **3aad**



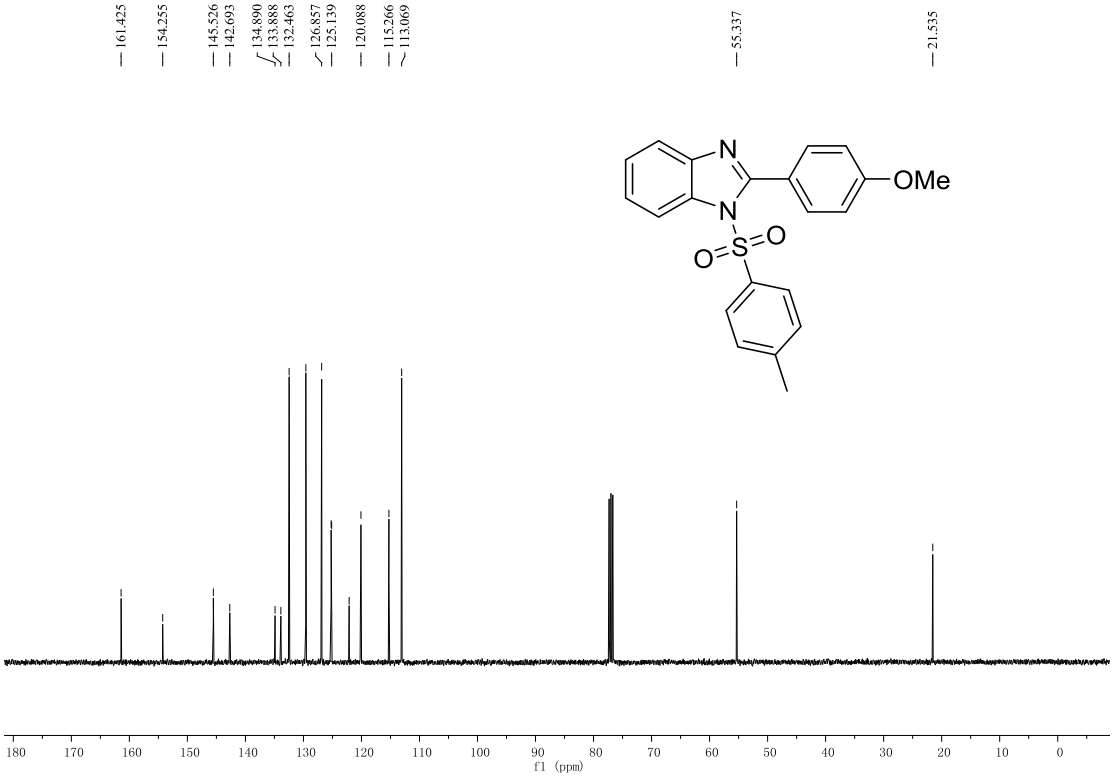
^{13}C NMR spectrum of **3aad**



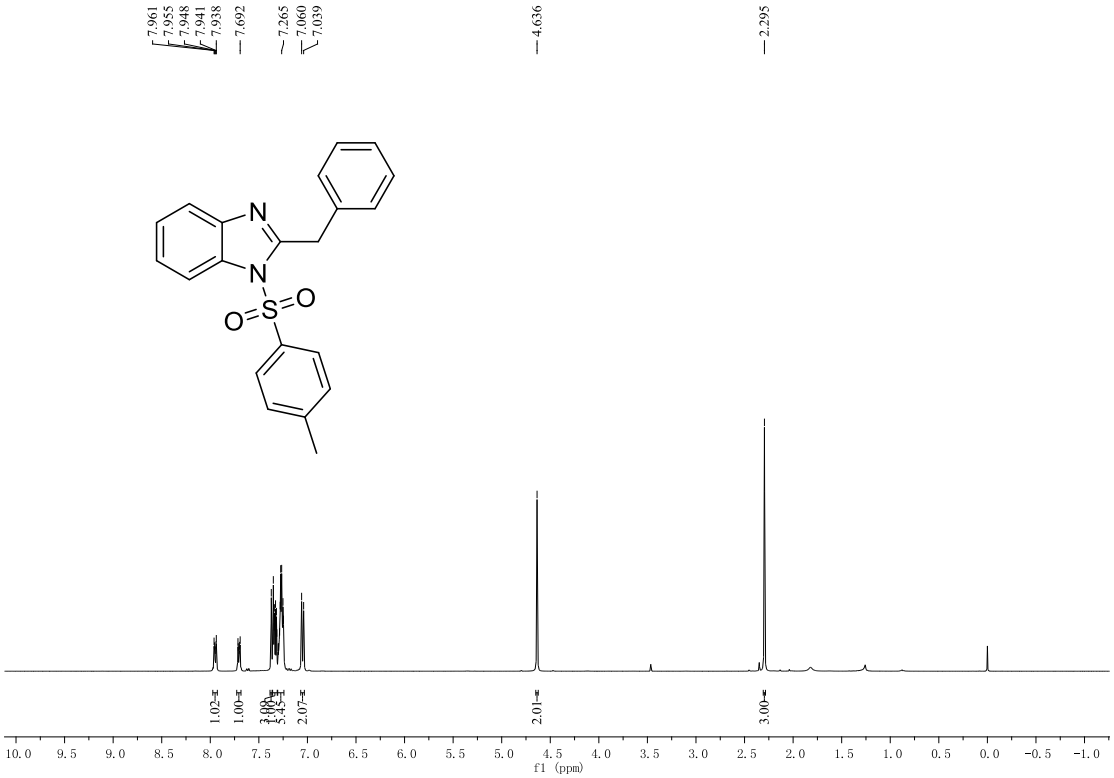
^{1}H NMR spectrum of **3aae**



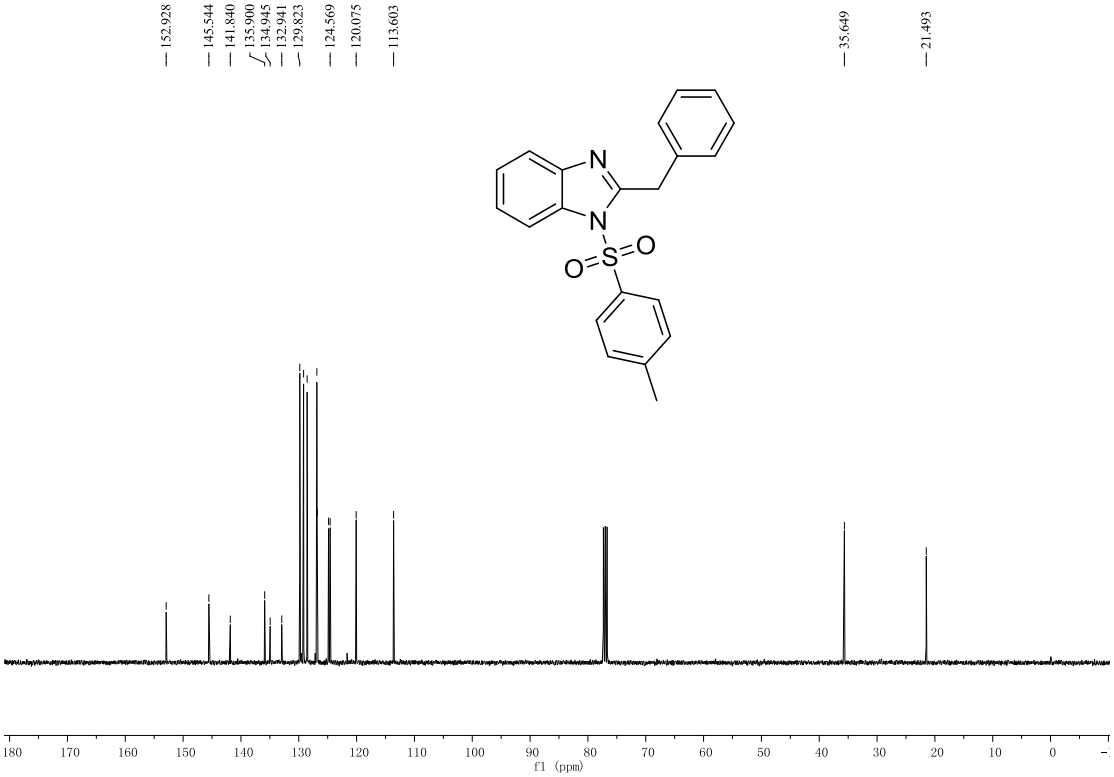
^{13}C NMR spectrum of **3aae**



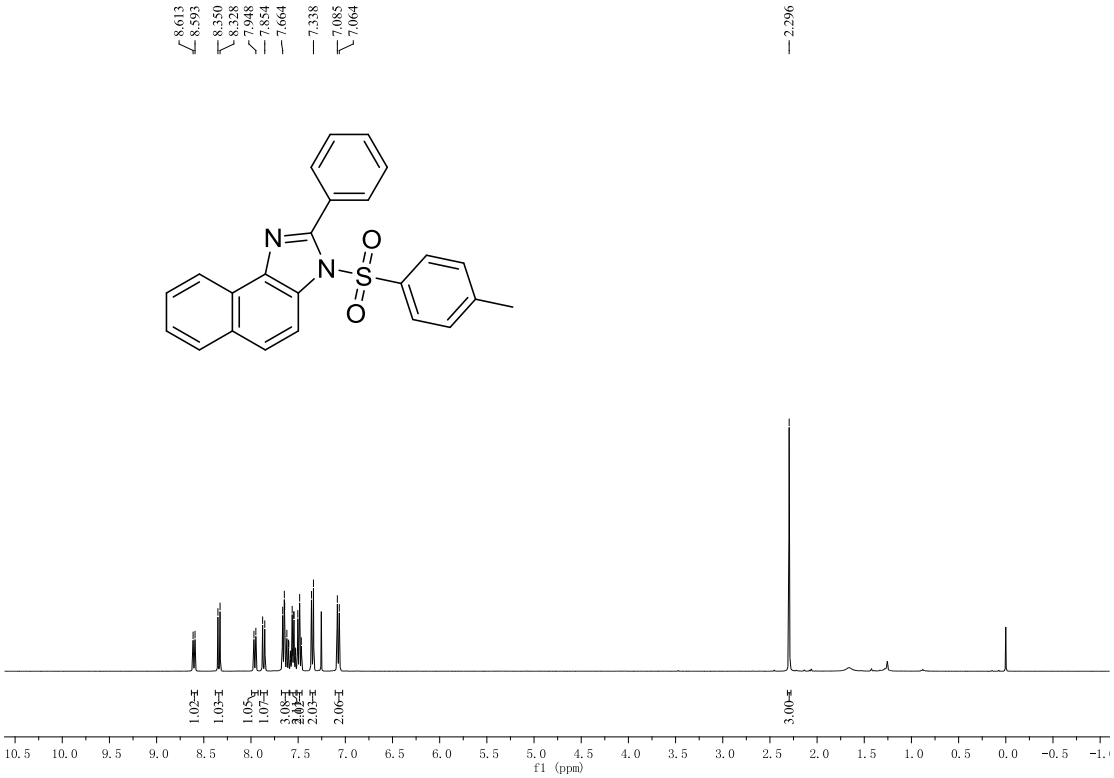
^{1}H NMR spectrum of **3aaf**



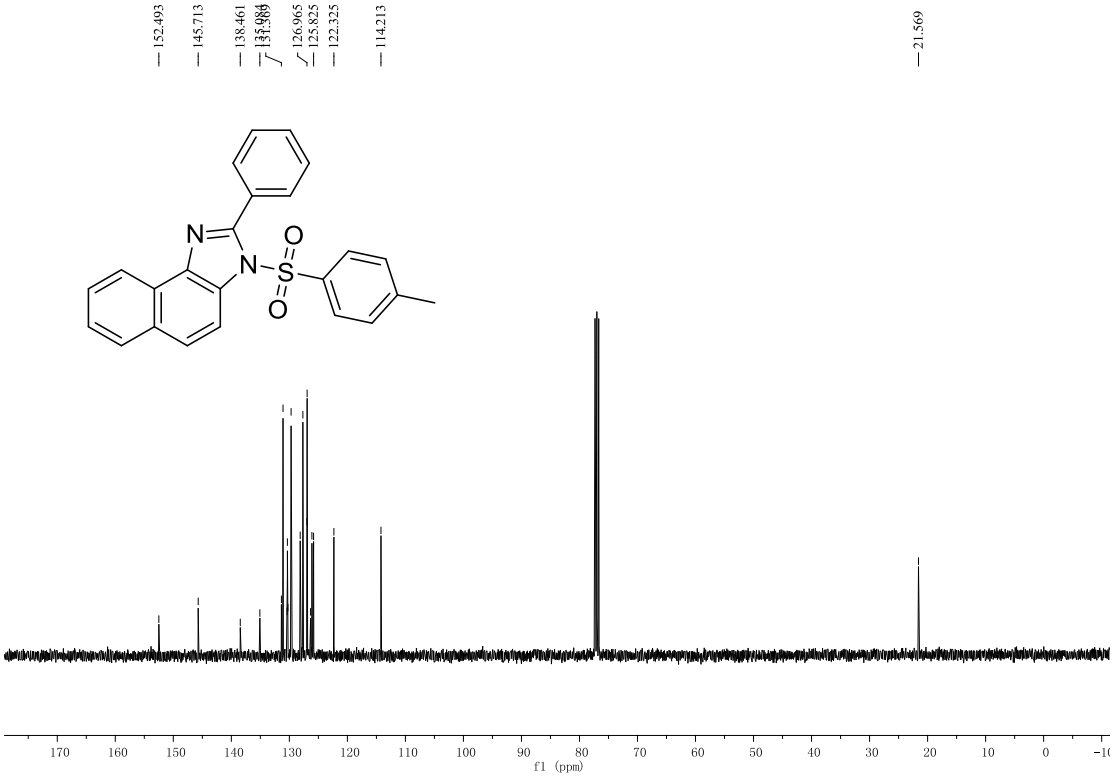
^{13}C NMR spectrum of **3aaf**



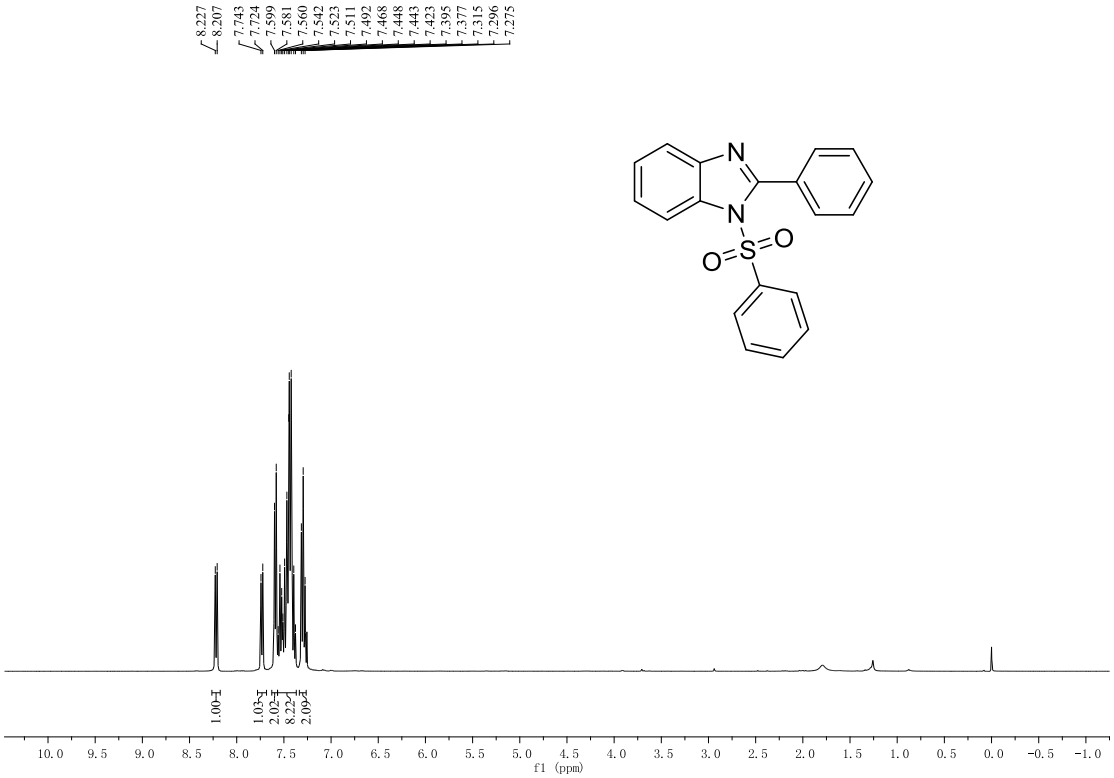
^{1}H NMR spectrum of **3aag**



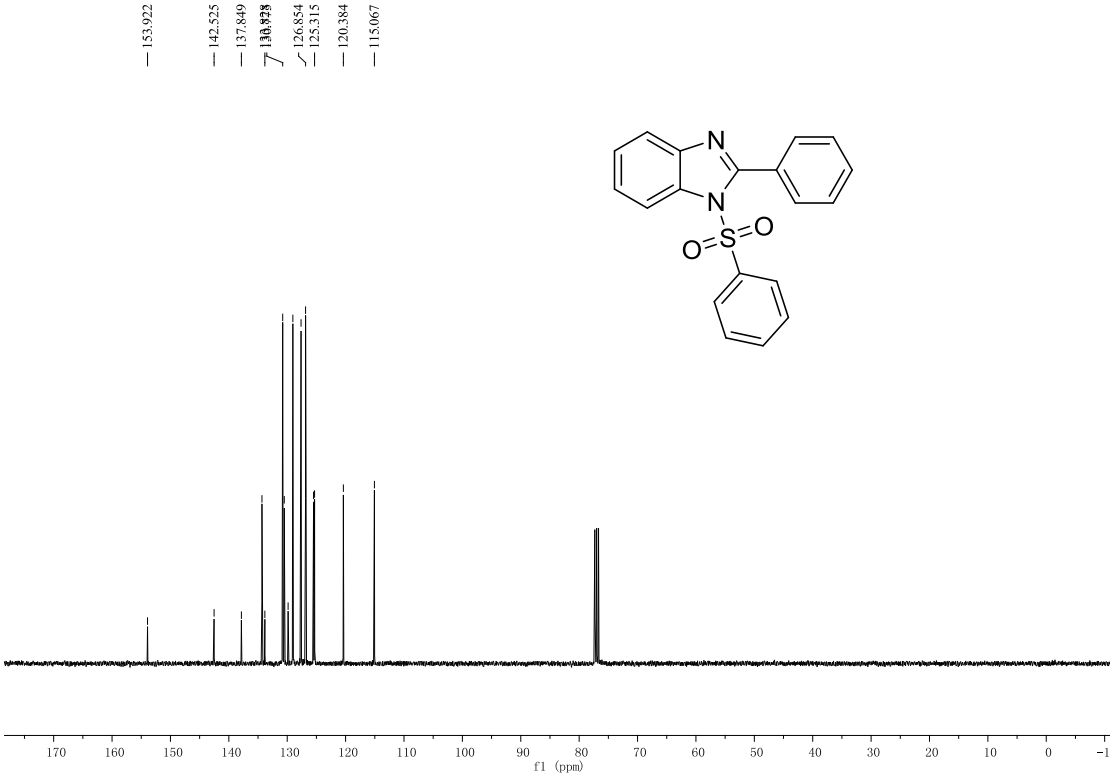
^{13}C NMR spectrum of **3aag**



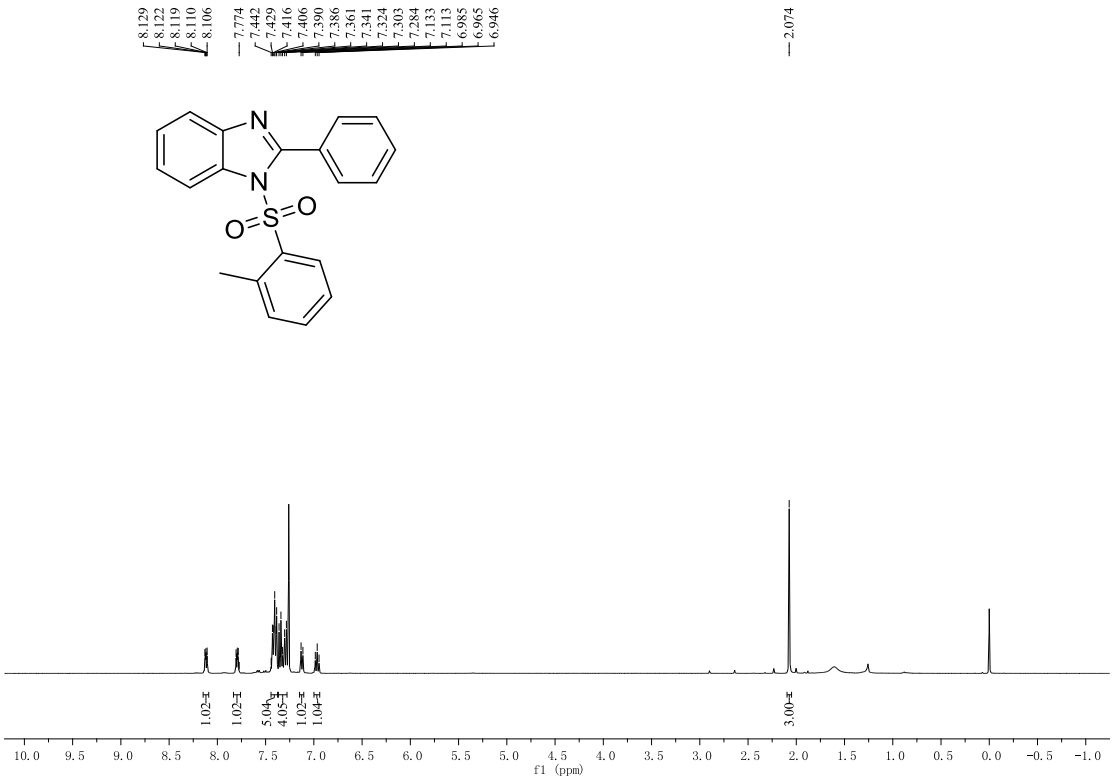
^{1}H NMR spectrum of **3ab**



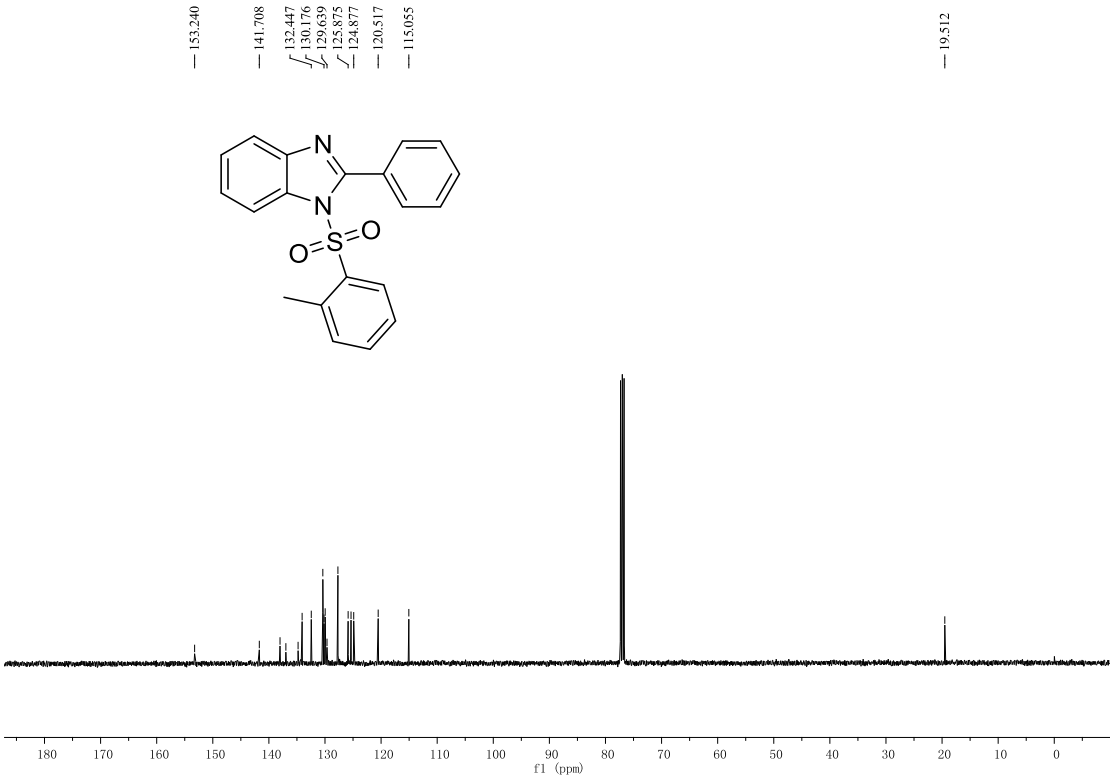
^{13}C NMR spectrum of **3ab**



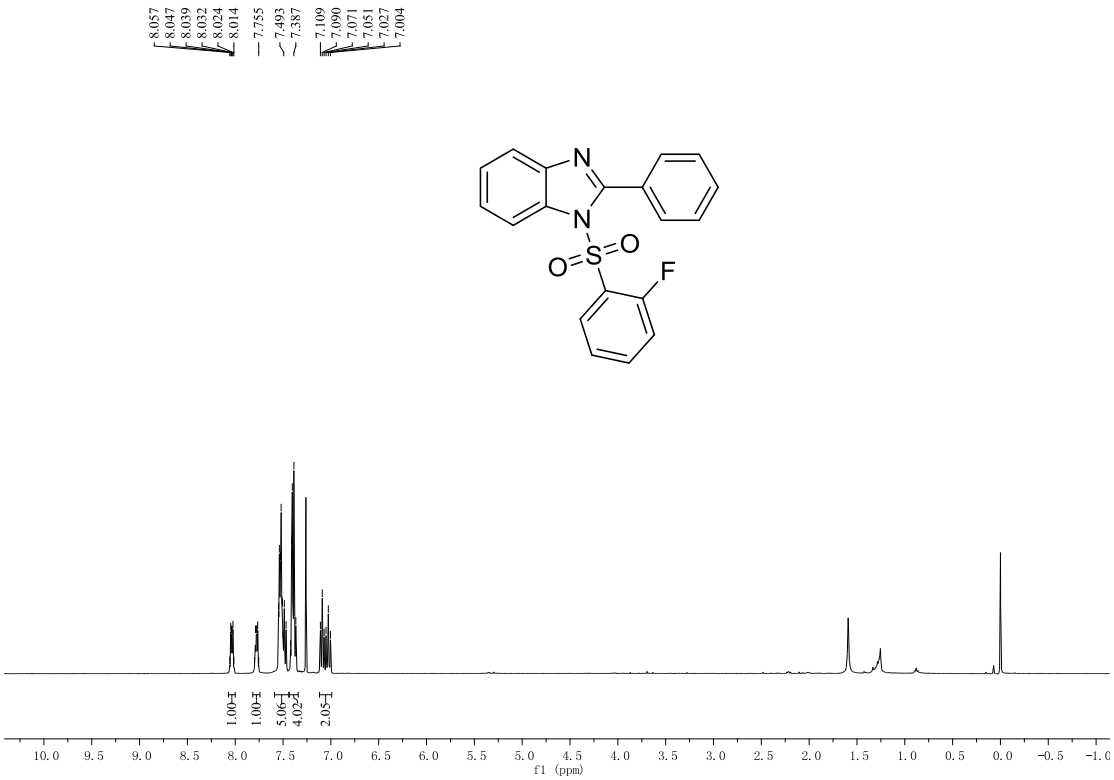
^{1}H NMR spectrum of **3ac**



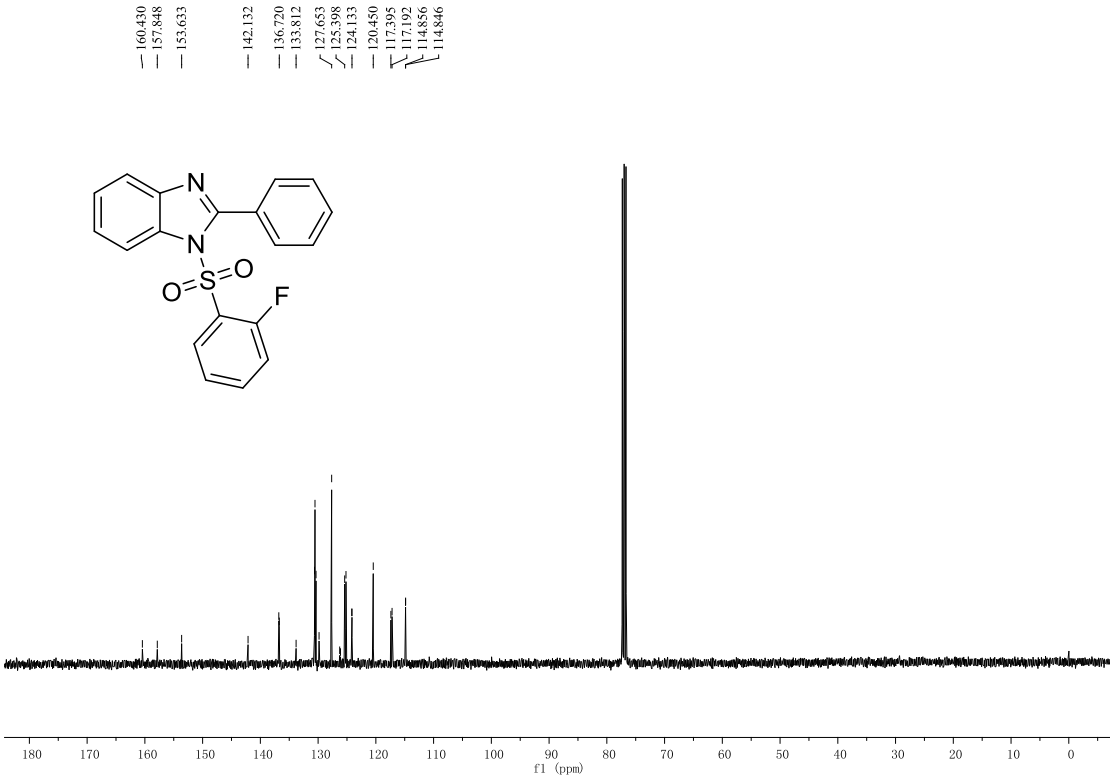
^{13}C NMR spectrum of **3ac**



^{1}H NMR spectrum of **3ad**

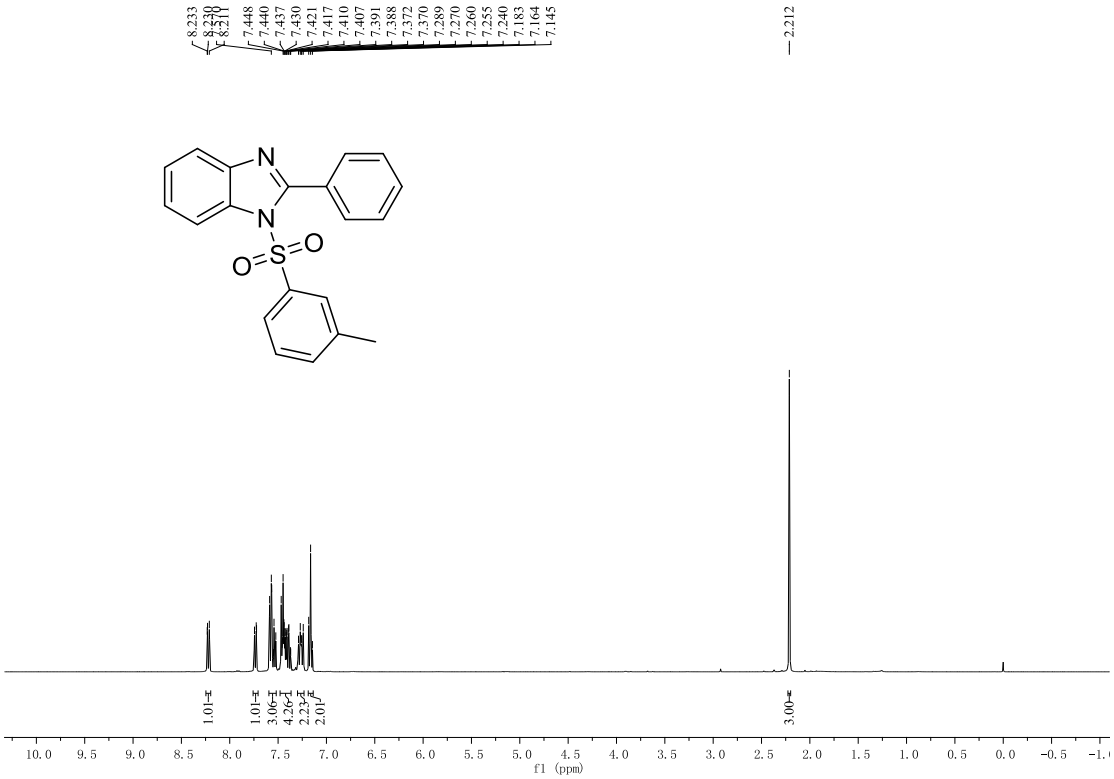


^{13}C NMR spectrum of **3ad**

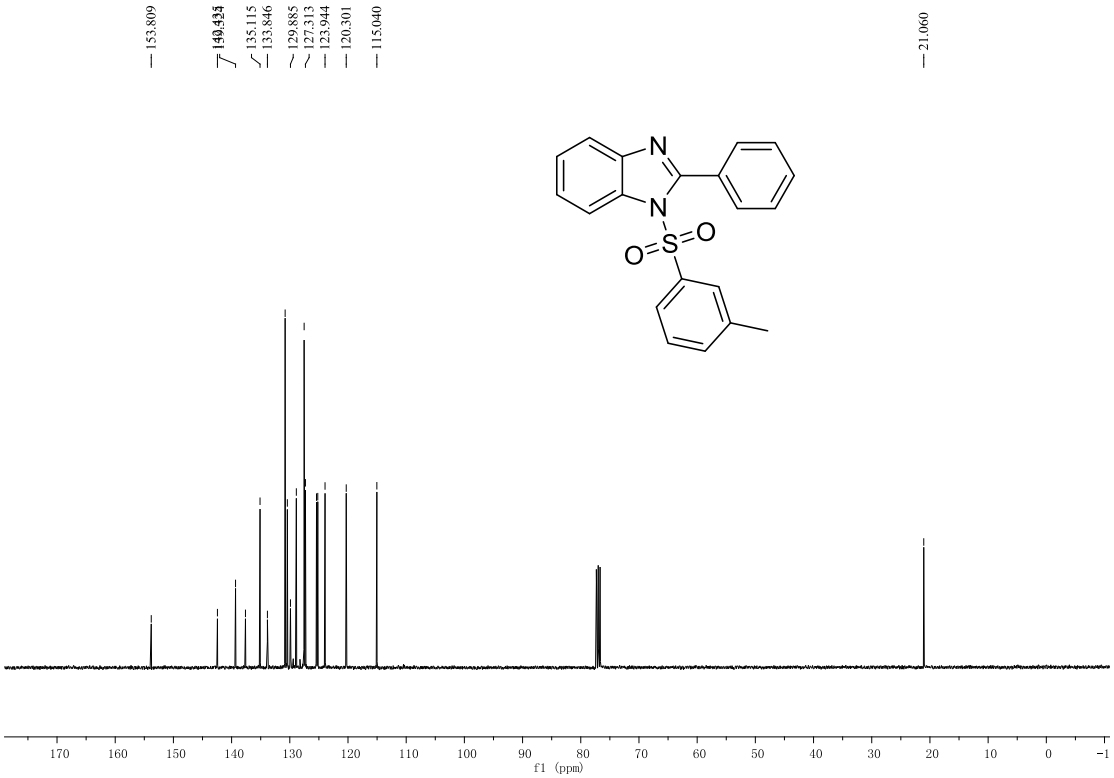


^{19}F NMR spectrum of **3ad**

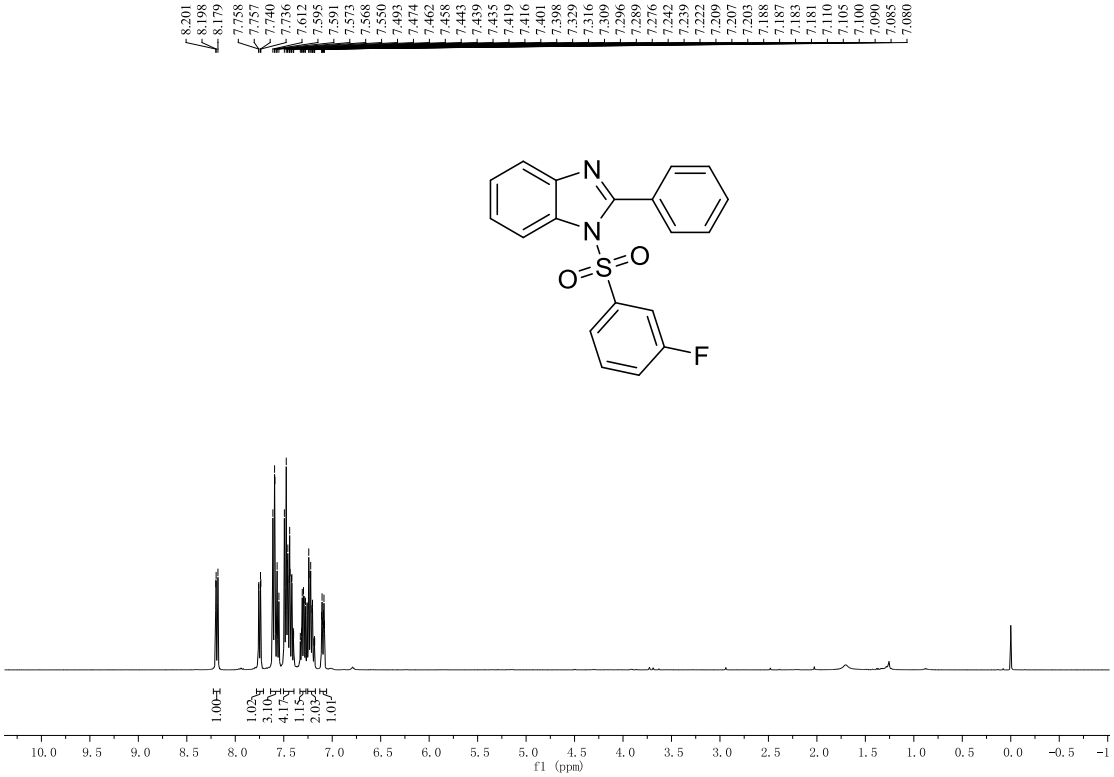
^{1}H NMR spectrum of **3ae**



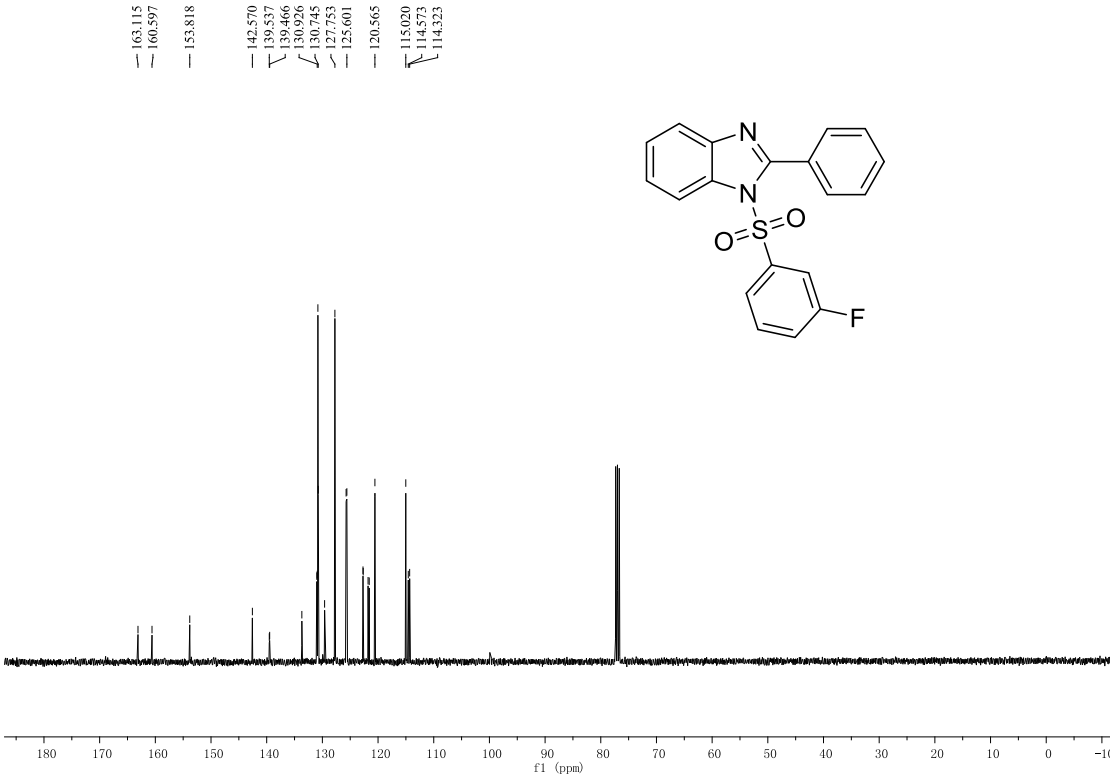
^{13}C NMR spectrum of **3ae**



^{1}H NMR spectrum of **3af**

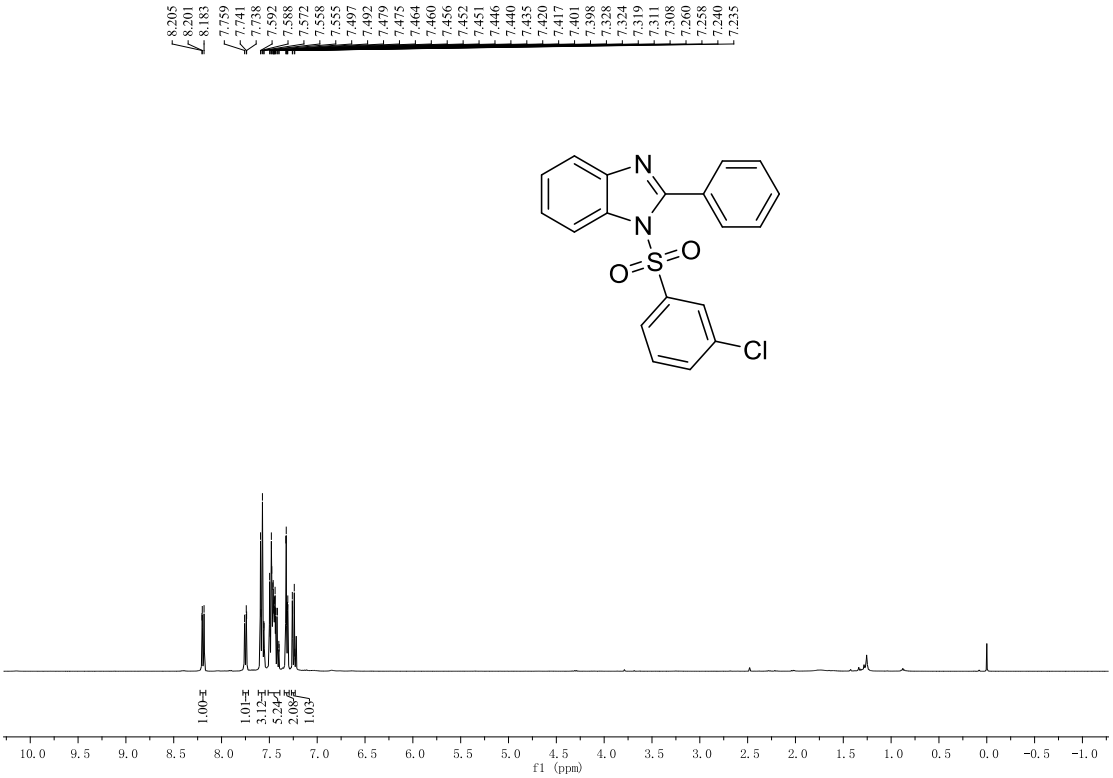


^{13}C NMR spectrum of **3af**

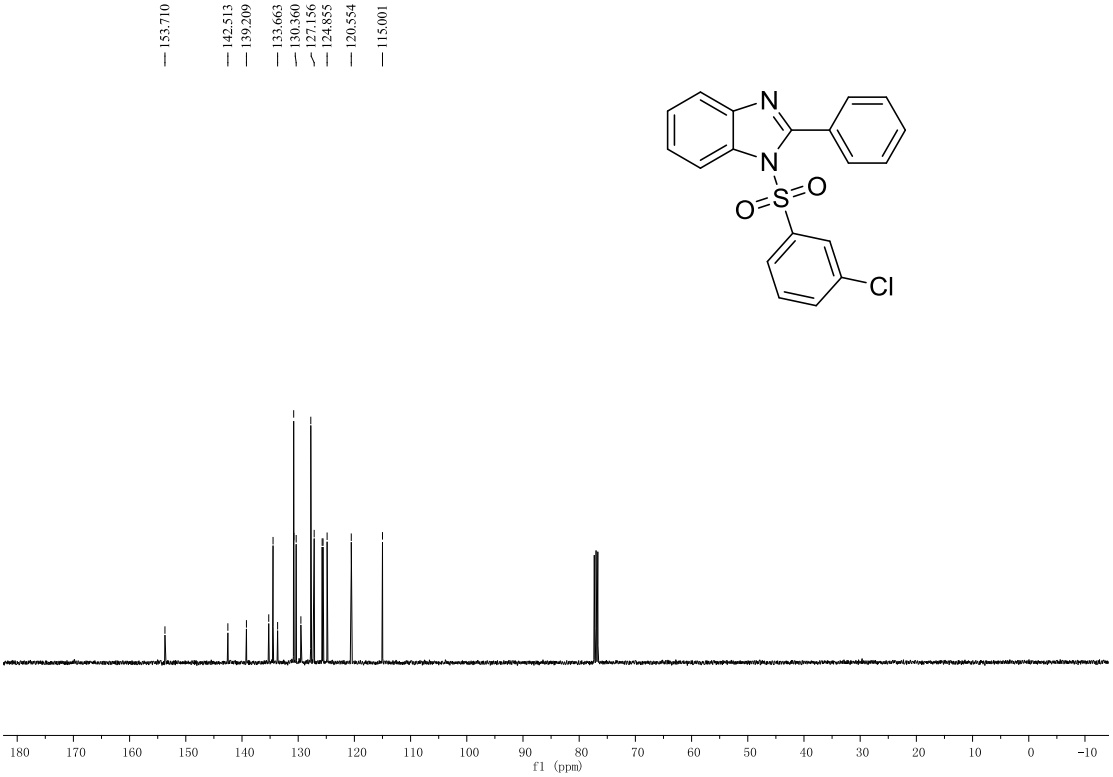


^{19}F NMR spectrum of **3af**

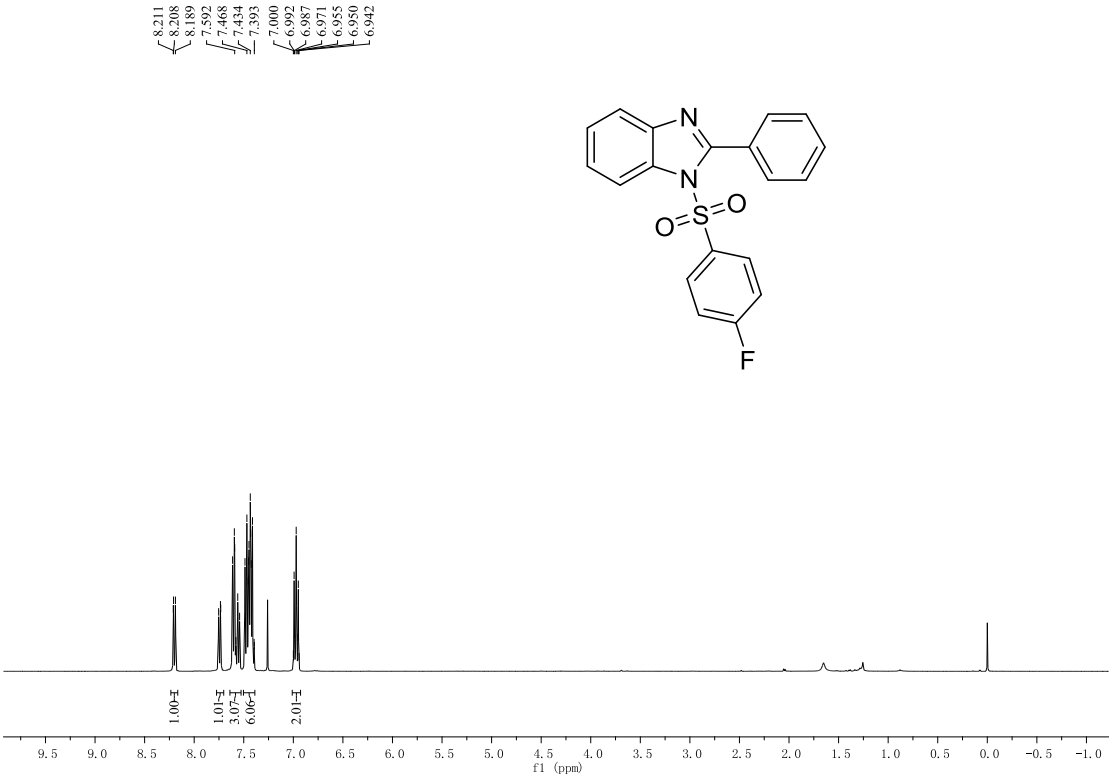
^{1}H NMR spectrum of **3ag**



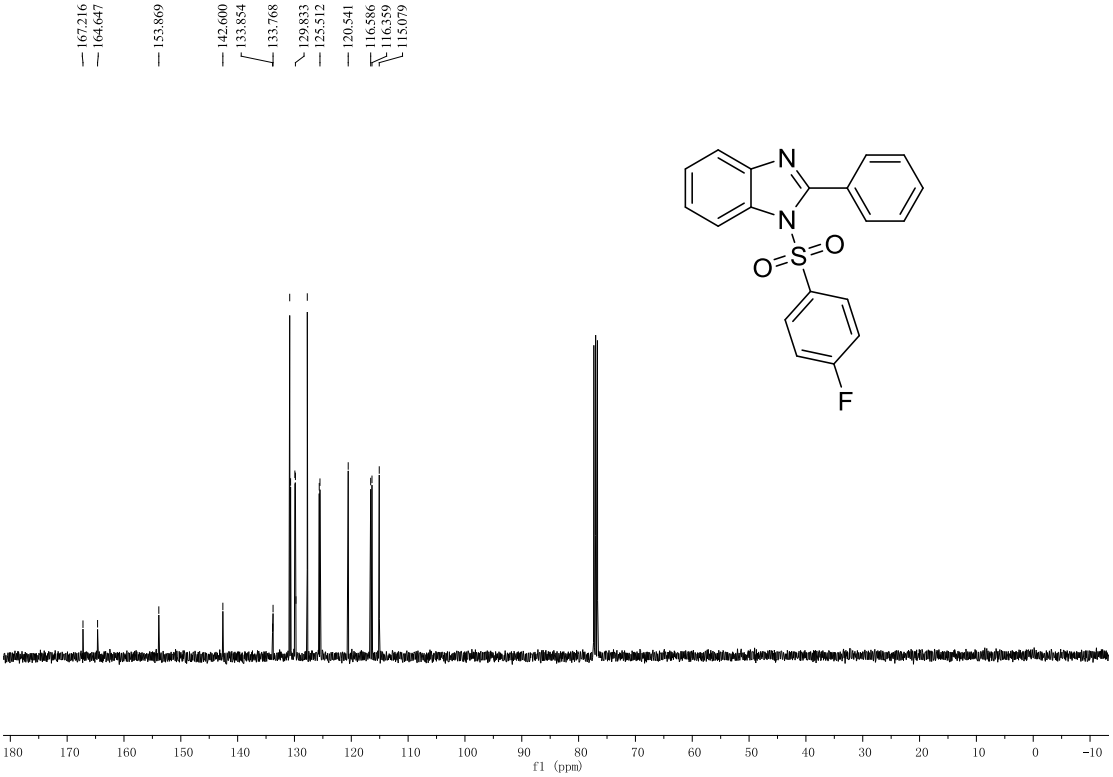
^{13}C NMR spectrum of **3ag**



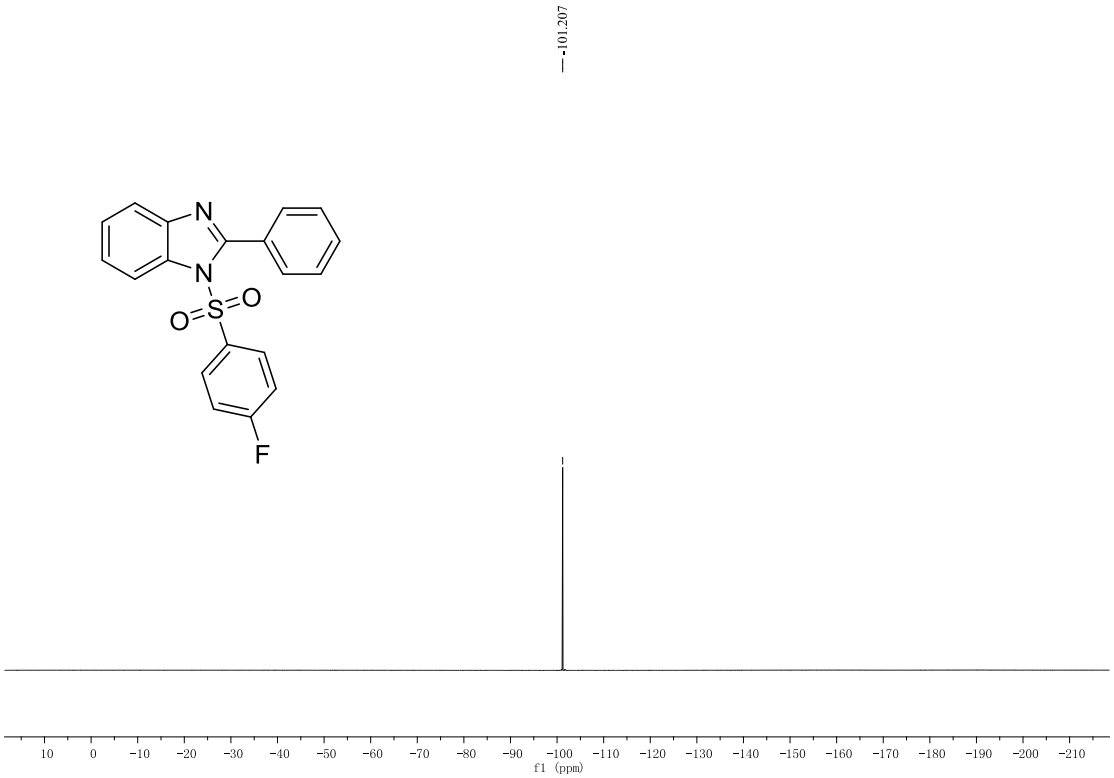
^{1}H NMR spectrum of **3ah**



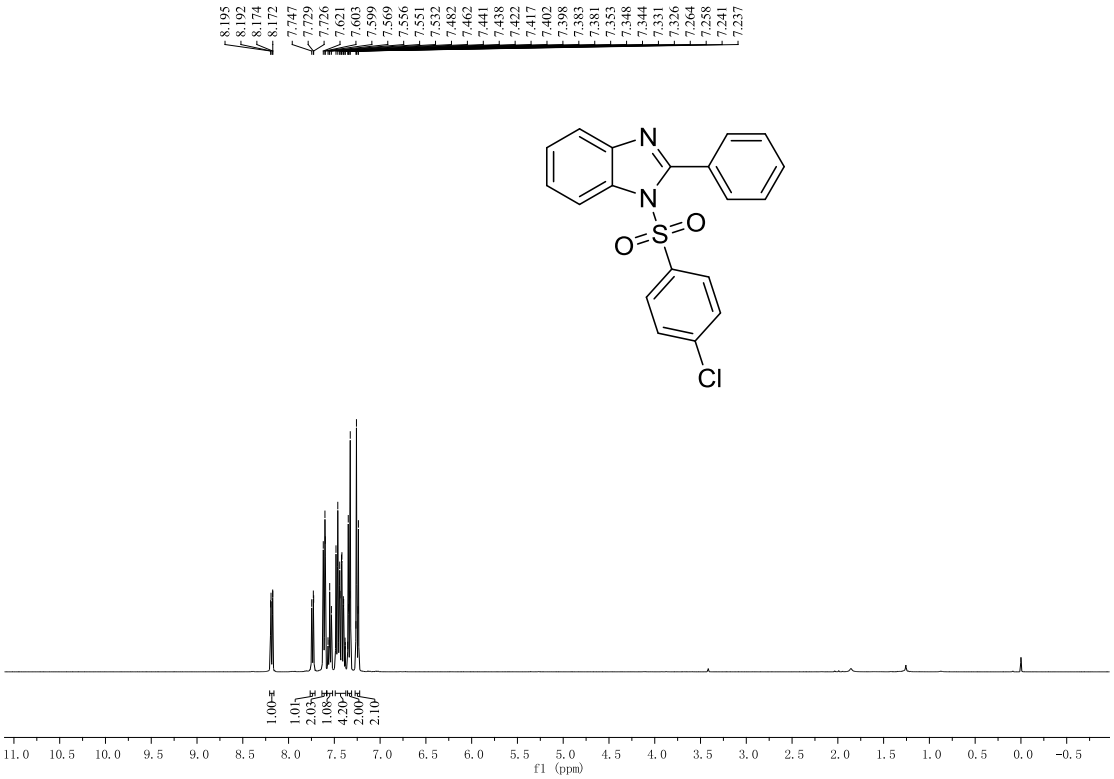
^{13}C NMR spectrum of **3ah**



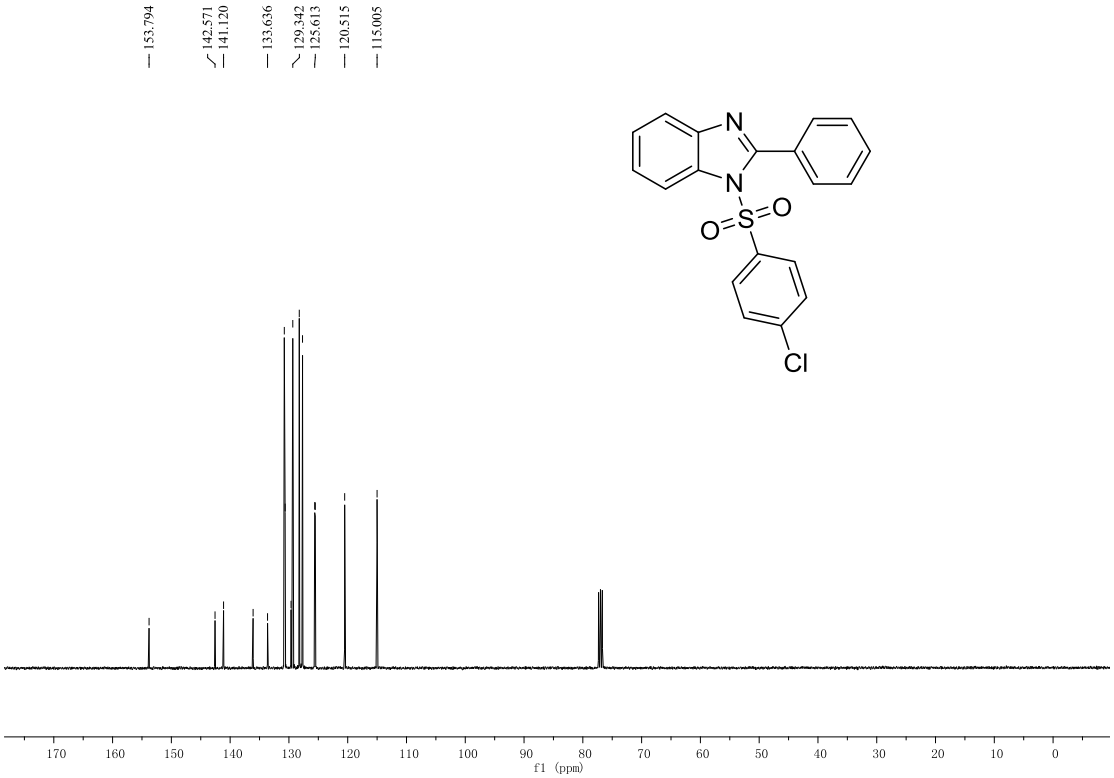
^{19}F NMR spectrum of **3ah**



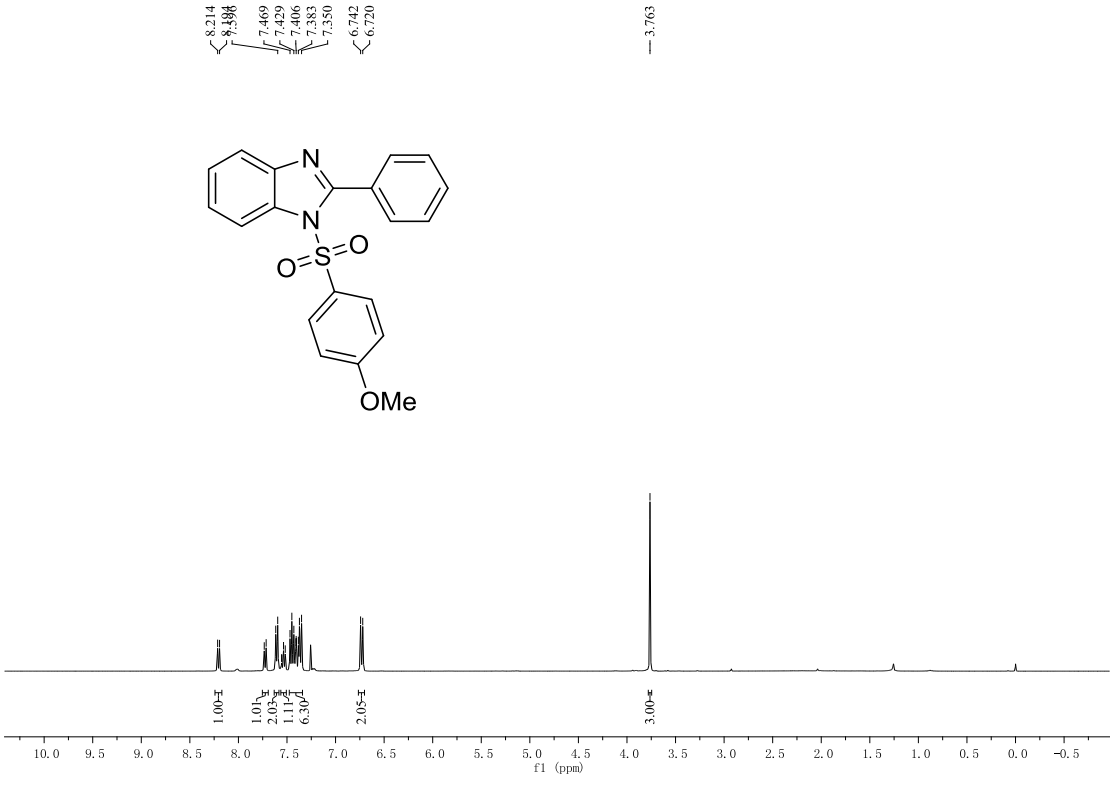
^{1}H NMR spectrum of **3ai**



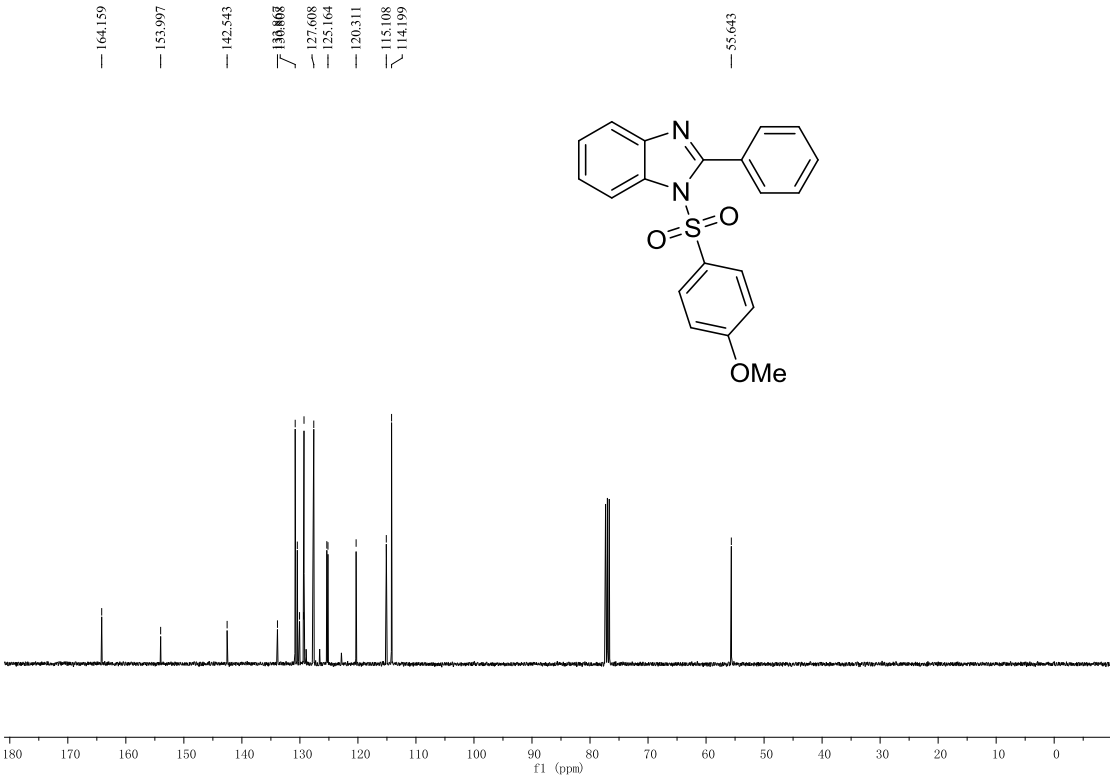
^{13}C NMR spectrum of **3ai**



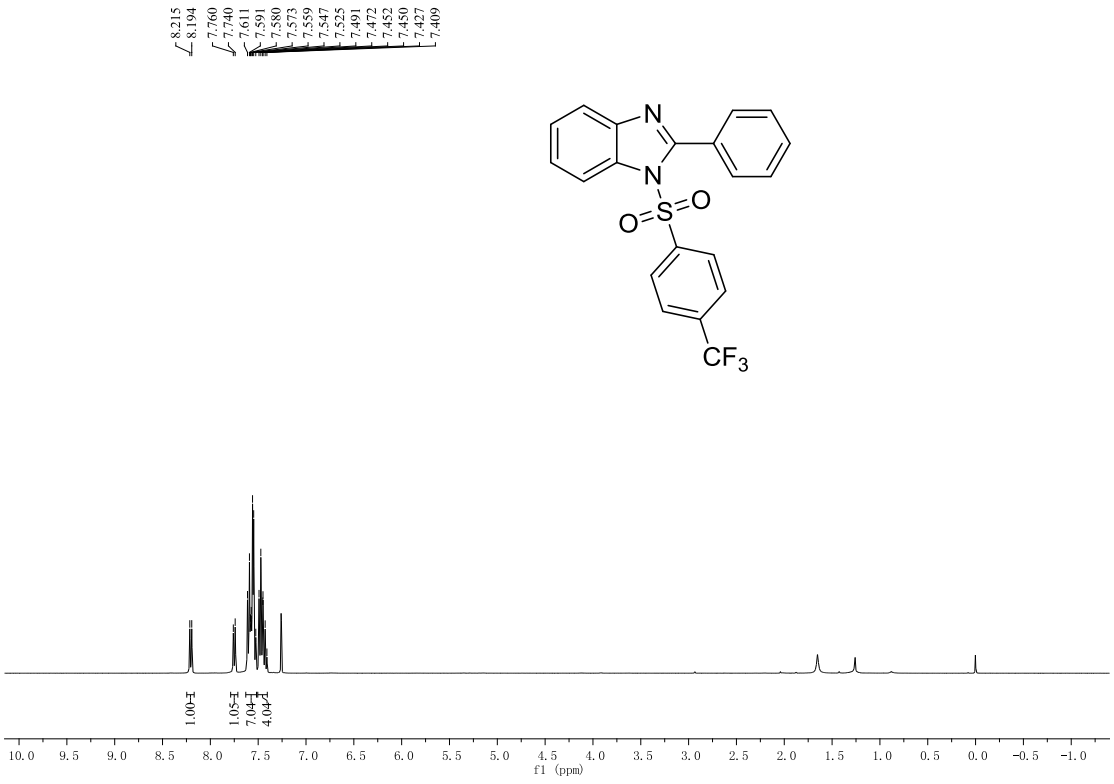
^{1}H NMR spectrum of **3aj**



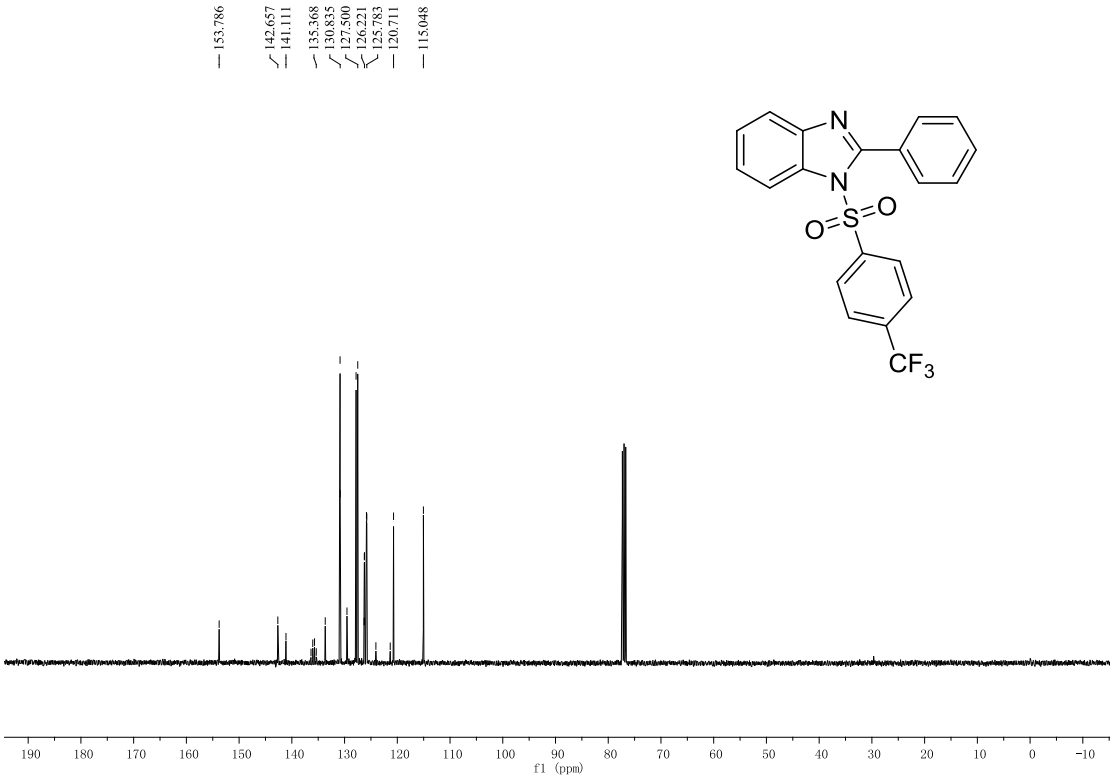
^{13}C NMR spectrum of **3aj**



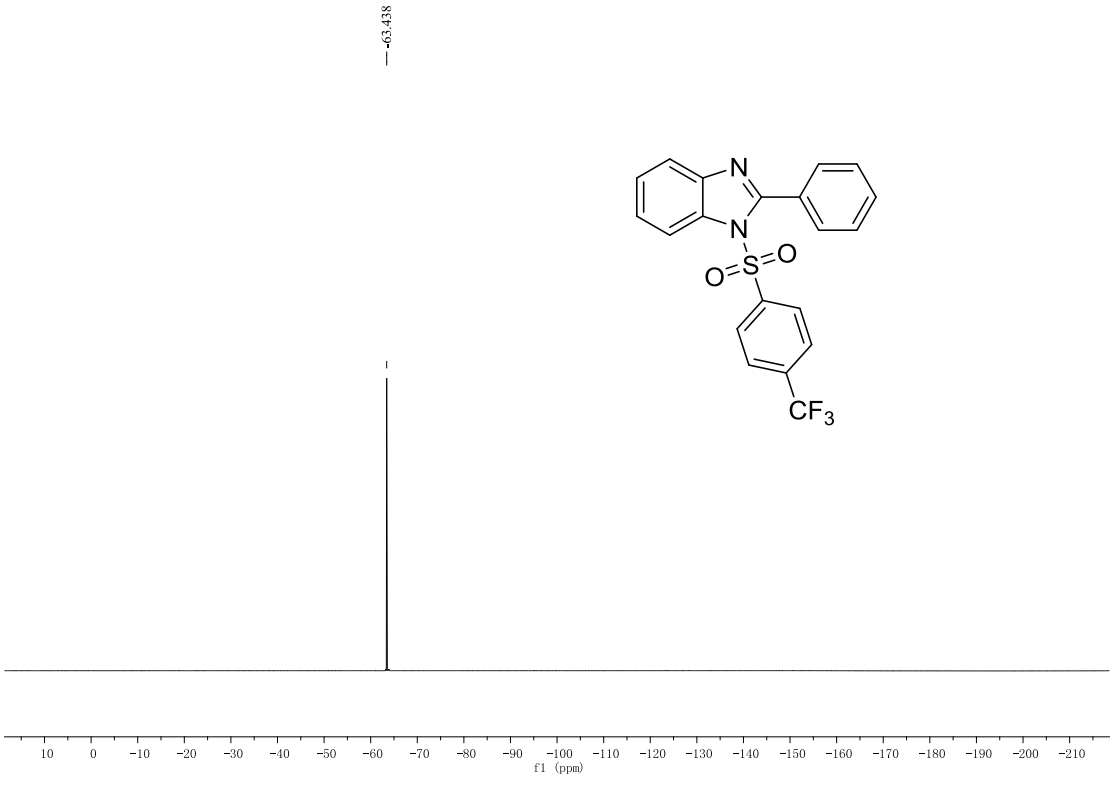
^{1}H NMR spectrum of **3ak**



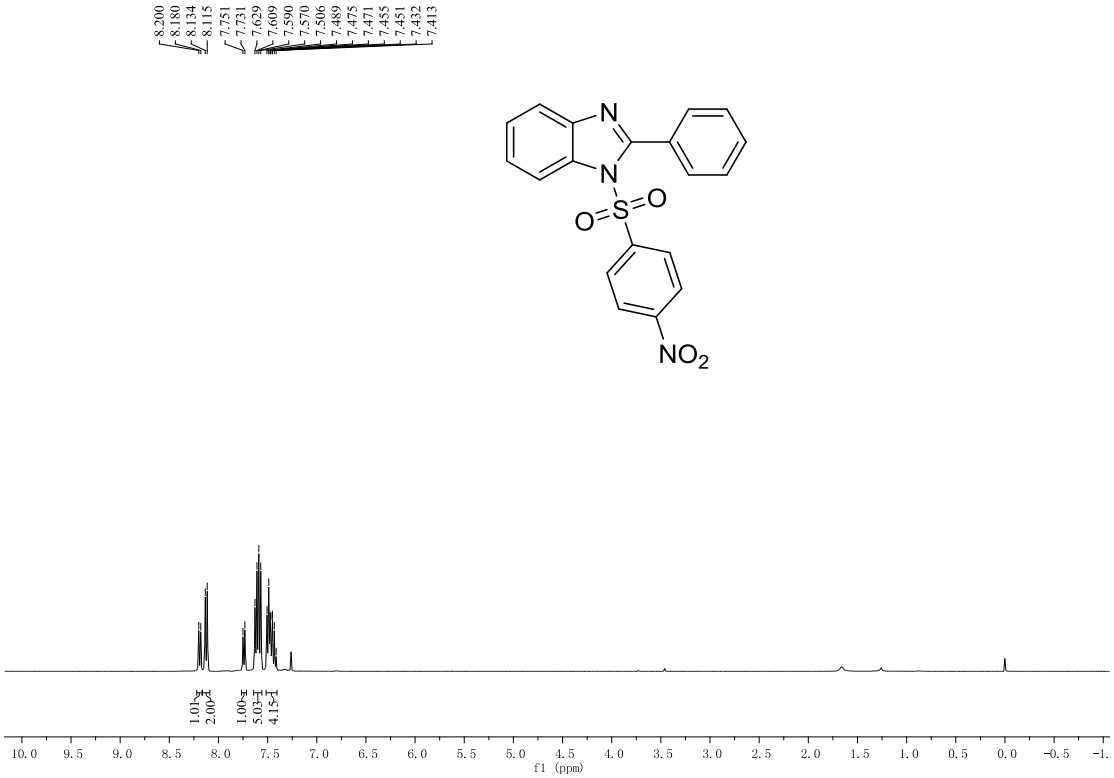
^{13}C NMR spectrum of **3ak**



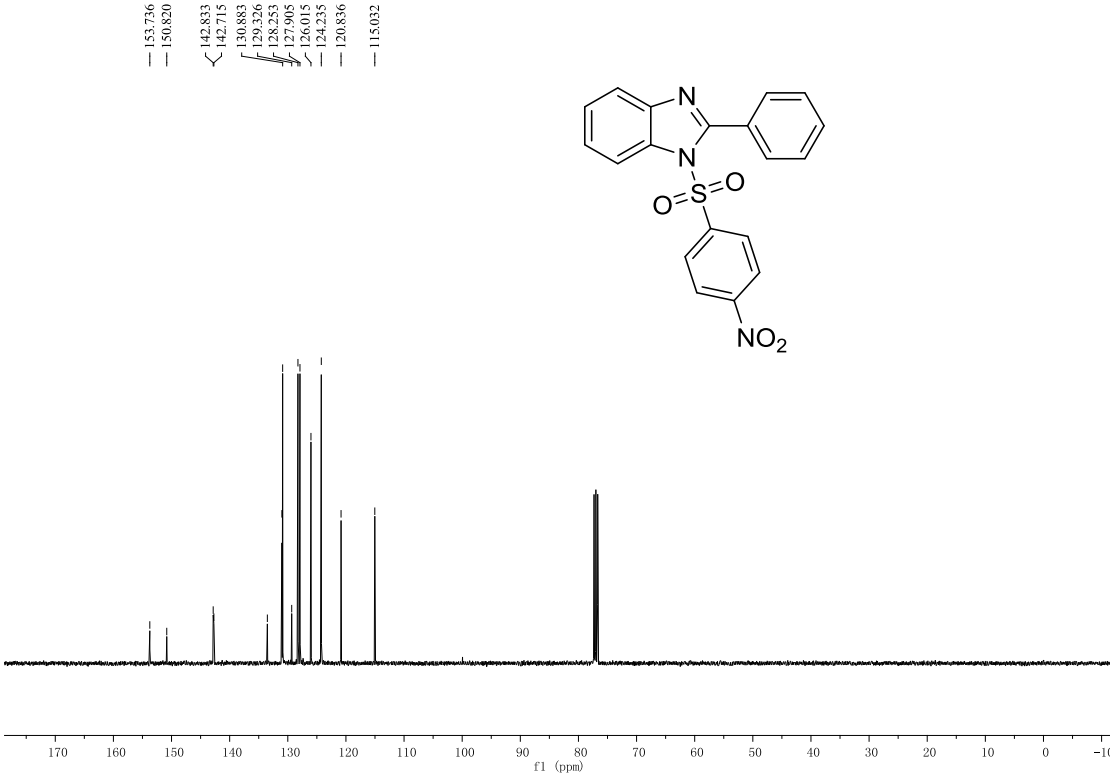
^{19}F NMR spectrum of **3ak**



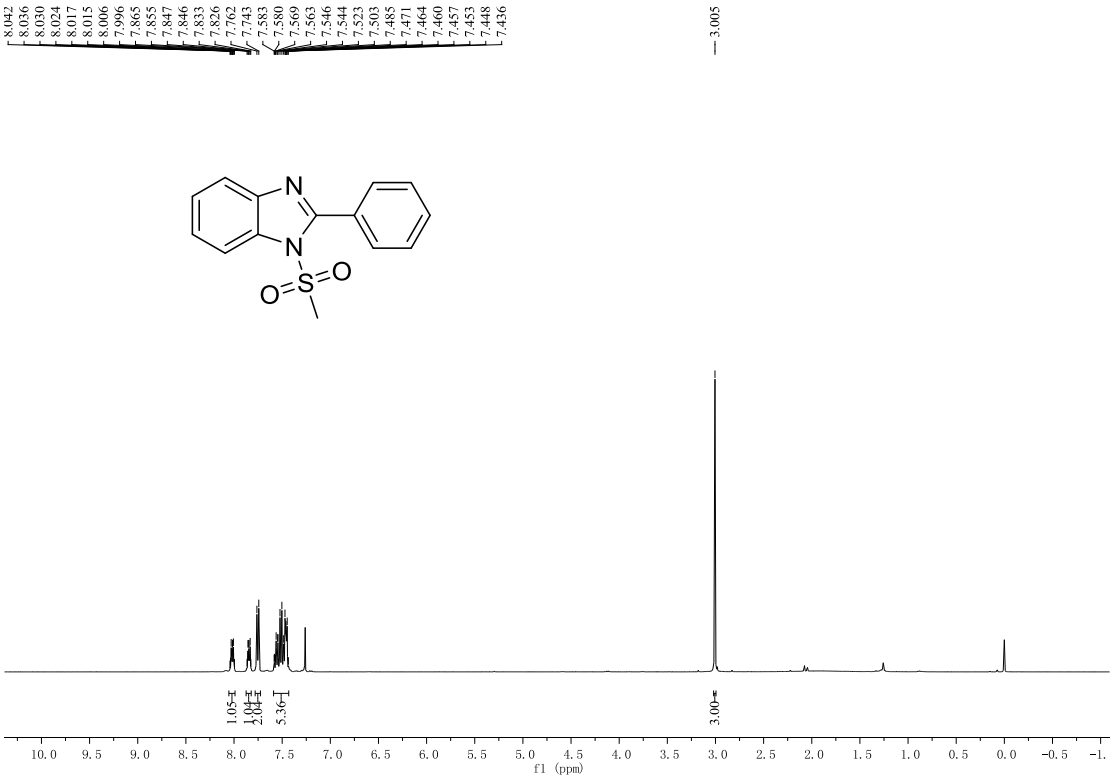
^{1}H NMR spectrum of **3al**



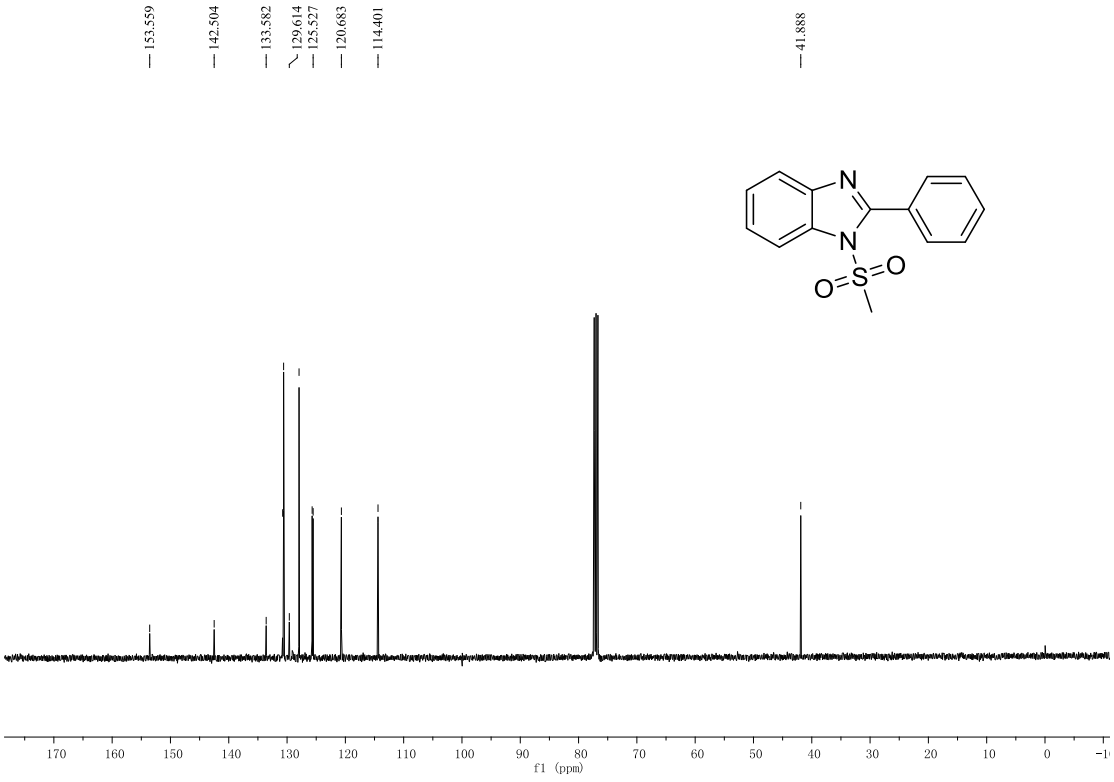
^{13}C NMR spectrum of **3al**



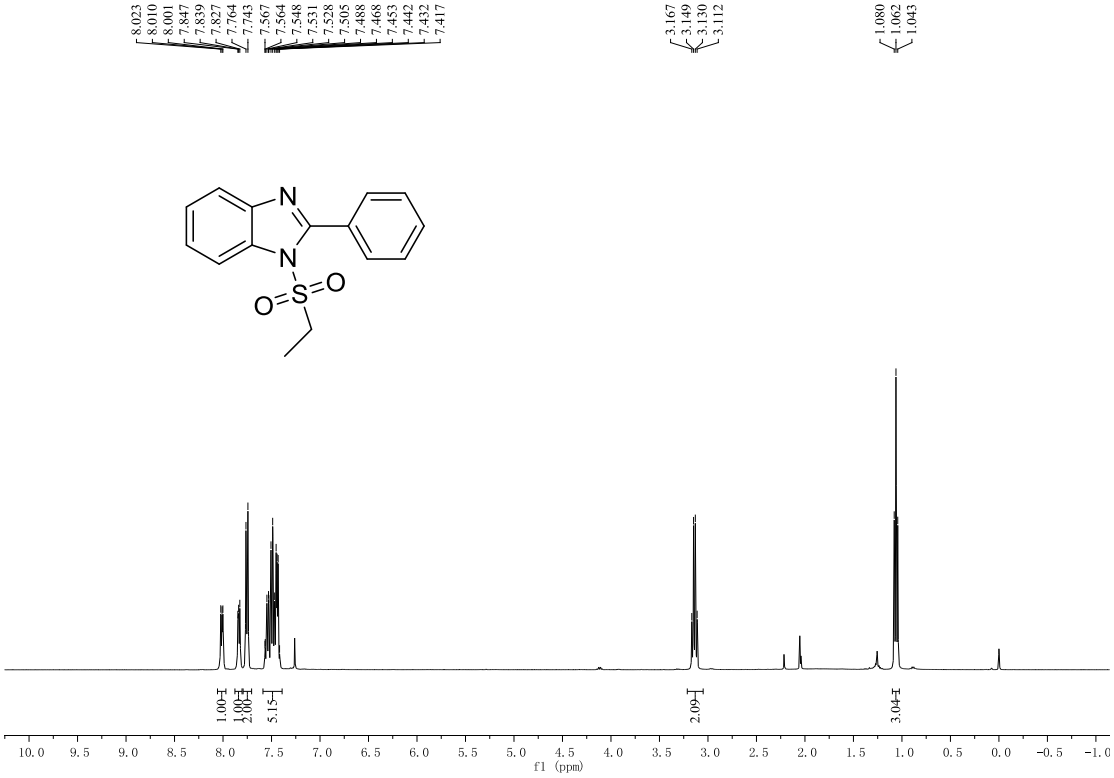
^{1}H NMR spectrum of **3am**



^{13}C NMR spectrum of **3am**



^{1}H NMR spectrum of **3an**



^{13}C NMR spectrum of **3an**