Supporting information

Rh(III)-catalyzed *ortho* C−H functionalization of aromatic amides with bis(phenylsulfonyl)diazomethane and *α*-diazosulfones

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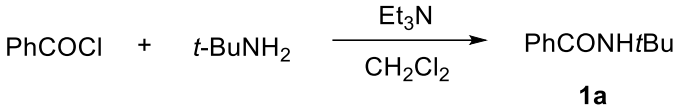
1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 MHz or 500 MHz spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane. Chemical shifts of carbon are referenced to the center line of a triplet at 77.0 ppm of chloroform-d_3, a heptet at 39.5 ppm of dimethyl sulfoxide-d_6 or a heptet at 29.8 ppm of acetone-d_6. Peaks are labeled as single (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), double doublet (dd), triple doublet (td), multiplet (m). Melting points were determined with a commercially available melting point apparatus. High-resolution mass spectra (HRMS) were acquired using an electron spray ionization time-of flight (ESI-TOF) mass spectrometer in positive mode. All reagents were used without further purification as received from commercial suppliers unless otherwise noted. All solvents were dried and distilled prior to use according to the standard protocols.

2. General procedure for the preparation of substrates

2.1 Preparation of amides 1 and 3 (taking 1a as an example)[1]

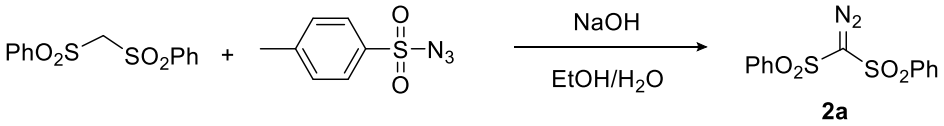


Scheme S1. Preparation of **1a**

To a stirring solution of *tert*-butylamine (1.26 mL, 12 mmol), Et_3N (1.67 mL, 12 mmol) in CH_2Cl_2 (20 mL) was added benzoyl chloride (1.16 mL, 10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 minutes. Then, the reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction, the reaction mixture was washed with saturated $NaHCO_3$ solution, saturated brine, and dried over $MgSO_4$. The organic layer was concentrated and recrystallized by PE/DCM, affording the expected compound **1a** (1.17 g, 66%) as a yellow solid.

Amides **1i**[2] and **1j**[3] were prepared by according to the reported procedures.

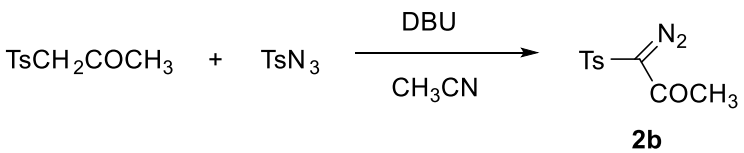
2.2 Preparation of bis(phenylsulfonyl)diazomethane 2a[4]



Scheme S2. Preparation of **2a**

To a stirring solution of 4-methylbenzenesulfonyl azide (5.3 g, 20.0 mmol, 75 % w/w in ethyl acetate,) in EtOH (30 mL) was added bis(phenylsulfonyl)methane (3.0 g, 10.0 mmol) in the mixture of EtOH (24 mL), H_2O (16 mL), and NaOH (1.0 g, 12 mmol). The reaction mixture was stirred at -5 °C for 1 h. After the completion of the reaction, the reaction mixture was quenched by water (40 mL) and then extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 12/1) to give the expected compound **2** (2.12 g, 66 %) as a yellow solid.

2.3 Preparation of 2b–2d (taking 2b as an example)[5]

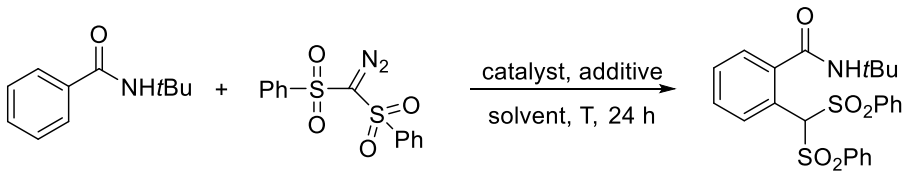


Scheme S3. Preparation of **2b**

To a stirring solution of 1-tosylpropan-2-one (2.12 g, 10 mmol) and tosyl azide (75 % w/w in ethyl acetate, 3.16g, 12 mmol) in acetonitrile (20 mL) was added DBU (1.80 mL, 12 mmol) at 0 °C. The reaction mixture was stirred for 3h. After the completion of the reaction, the reaction mixture was quenched by water (40 mL) and then extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography to give the expected compound **2b** (1.52 g, 64 %) as a yellow solid.

3. General experimental procedure

3.1 Optimization of reaction conditions[a]



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

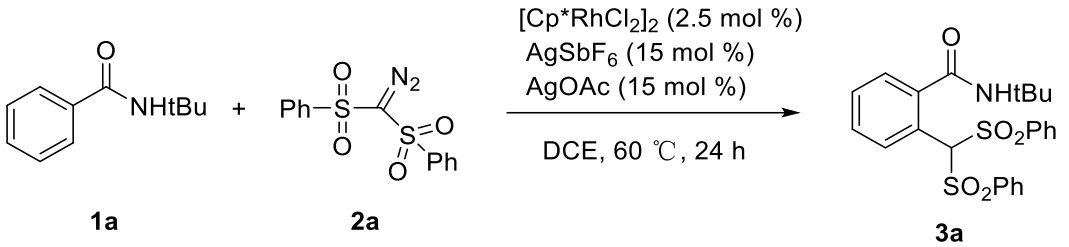
Entry	Catalyst (mol%)	Additive (mol%)	solvent	T (°C)	Yield[b] (%)
1	$[Cp^*IrCl_2]_2$ (2)	$AgNTf_2$ (8)/AgOAc (4)	DCE	90	30
2	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)	DCE	60	27
3	$[Cp^*RhCl_2]_2$ (2.5)	AgOAc (15)	DCE	60	0
4	$[Cp^*RhCl_2]_2$ (2.5)	$AgNTf_2$ (15)	DCE	60	25
5	$[Cp^*RhCl_2]_2$ (2.5)	AgOTf (15)	DCE	60	24
6	$[Cp^*RhCl_2]_2$ (2.5)	$AgBF_4$ (15)	DCE	60	20
7	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	DCE	60	88(83[c])
8	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	DCE	90	68
9	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	DCE	30	85
10	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/KOAc (15)	DCE	60	0
11	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/HOAc (15)	DCE	60	13
12	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (10)/AgOAc (10)	DCE	60	86
13	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (20)/AgOAc (20)	DCE	60	85
14	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	DMSO	60	0
15	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	CH_3CN	60	0
16	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	MeOH	60	48
17	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	EA	60	67
18	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	dioxane	60	71
19	$[Cp^*RhCl_2]_2$ (2.5)	$AgSbF_6$ (15)/AgOAc (15)	toluene	60	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), solvent (2.0 mL), 24 h, under a N_2 atmosphere.

[b]Yield determined by ^1H NMR using 1, 3, 5-trimethoxybenzene as the internal standard.

[c]Isolated yield after column chromatography.

3.2 General procedure for the synthesis of 3, 5 and 6 (taking 3a as an example)



Scheme S4. Preparation of **3a**.

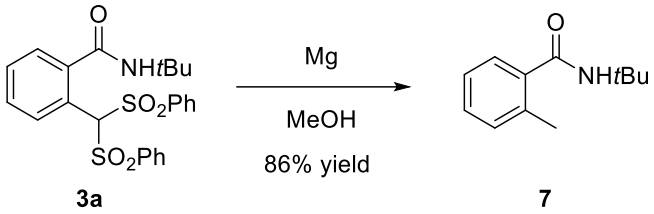
A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (6.2 mg, 2.5 mol%), $AgSbF_6$ (20.6 mg, 15 mol%), AgOAc (10.0 mg, 15 mol%), **1a** (70.9 mg, 0.4 mmol), and DCE (2 mL). To the mixture was then added bis(phenylsulfonyl)diazomethane **2a** (154.7 mg, 0.48 mmol) in DCE (2 mL). The reaction mixture was stirred at 60 ℃ under a N_2 atmosphere for 24 h. The crude mixture was filtered through Celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography (petroleum ether (PE): ethyl acetate (EA) = 4:1–2:1) to give the desired product **3a** (156.8 mg, 83%) as a white solid.

3.3 Gram Scale Experiment

A 50 mL flask equipped with a magnetic stirrer were charged with $[Cp^*RhCl_2]_2$ (77.3 mg, 2.5 mol%), $AgSbF_6$ (257.7 mg, 15 mol%), AgOAc (125.2 mg, 15 mol%), **1a** (886.2 mg, 5.0 mmol), and DCE (10 mL). To the mixture was then added bis(phenylsulfonyl)diazomethane **2a** (1.93 g, 6.0 mmol) in DCE (10 mL). The reaction mixture was stirred at 60 ℃ under a N_2 atmosphere for 24 h. The crude mixture was filtered through Celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography to give the desired product **3a** (1.72 g, 73%) as a white solid.

4. Transformations of products

4.1 Preparation of 7

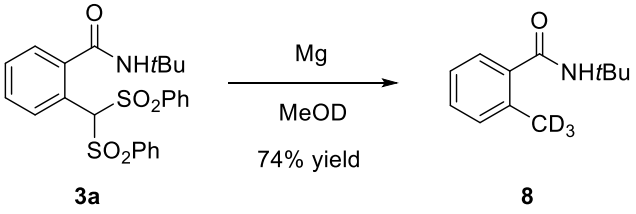


3a 7

Scheme S5. Preparation of **7**.

To a 25 mL flask equipped with a magnetic stirrer were added **3a** (94.3 mg, 0.2 mmol), freshly activated Mg turnings (580 mg, 20 mmol, 100 equiv), and anhydrous MeOH (10 mL) under a N_2 atmosphere. The reaction mixture was stirred at 50 ℃ for 2 h. Filtrating the reaction mixture through a short pad of silica gel and concentrating the filtrate gave the crude product, which was purified by flash chromatography to give the expected compound **7** (30.6 mg, 86%) as a white solid.

4.2 Preparation of 8

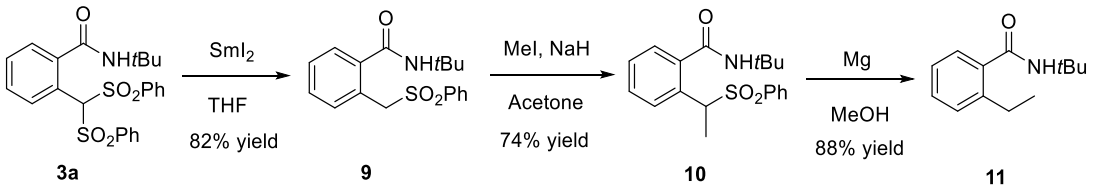


3a 8

Scheme S6. Preparation of **8**.

To a 25 mL flask equipped with a magnetic stirrer were added **3a** (94.3 mg, 0.2 mmol), freshly activated Mg turnings (580 mg, 20 mmol, 100 equiv.), and anhydrous MeOD (10 mL) under a N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 12 h. Filtrating the reaction mixture through a short pad of silica gel and concentrating the filtrate gave the crude product, which was purified by flash chromatography to give the expected compound **8** (28.9 mg, 74%) as a white solid.

4.3 Preparation of 9, 10 and 11



3a 9 10 11

Scheme S7. Preparation of **9, 10** and **11**.

(1) Preparation of 9

To a 50 mL flask equipped with a magnetic stirrer were added HMPA (1mL) and SmI_2 (0.1 mol/L in THF, 20 mL, 20 equiv) under a N_2 atmosphere. After stirring for 10 minutes, **3a** (94.3 mg, 0.2 mmol) in THF (5 mL) was added dropwise. After stirring for 2 h at room temperature, the reaction was quenched with saturated $NaHCO_3$ solution (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was concentrated in vacuo. The crude product was purified by flash chromatography to give the expected compound **9** (54.4 mg, 82%) as a white solid.

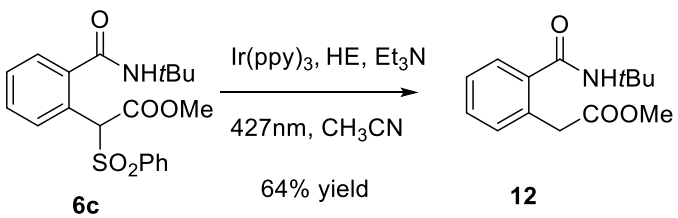
(2) Preparation of 10

To a 25 mL reaction tube equipped with a magnetic stirrer were added **8** (66.3 mg, 0.2 mmol), NaH (60% dispersion in mineral oil, 8 mg, 0.2 mmol), and CH_3COCH_3 (1 mL) under an air atmosphere. After stirring for 10 minutes, CH_3I (12.5 μL, 0.2 mmol) in CH_3COCH_3 (1 mL) was added to the mixture. The reaction mixture was stirred at room temperature for 12 h, then quenched with water (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was concentrated in vacuo. The crude product was purified by flash chromatography to give the expected compound **10** (51.2 mg, 74%) as a white solid.

(3) Preparation of 11

To a 25 mL flask equipped with a magnetic stirrer were added **10** (34.5 mg, 0.1 mmol), freshly activated Mg turnings (120 mg, 5 mmol, 50 equiv), and anhydrous MeOH (5 mL) under a N_2 atmosphere. The reaction mixture was stirred at 50 ℃ for 2 h. Filtrating the reaction mixture through a short pad of silica gel and concentrating the filtrate gave the crude product, which was purified by flash chromatography to give the expected compound **11** (18.0 mg, 88%) as a white solid.

4.4 Preparation of 12



6c **12**

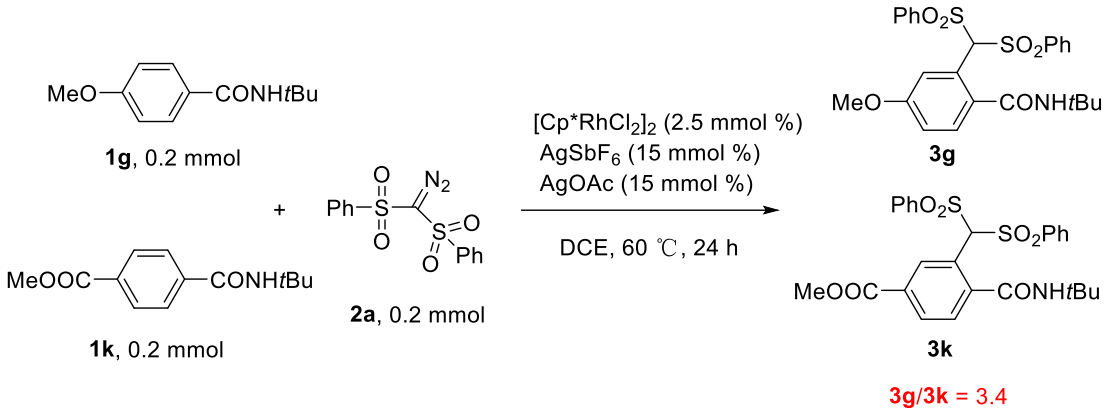
Scheme S8 Preparation of **12**.

To a 20 mL quartz tube equipped with a magnetic stirrer were added **6c** (38.9 mg, 0.1 mmol), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.025 equiv), Et_3N (139.0 μL, 1.0 mmol, 10 equiv), Hantzsch ester (50.7 mg, 0.2

mmol) and anhydrous MeCN (2 mL) under a N_2 atmosphere. The reaction mixture was stirred at room temperature under irradiation with Blue LED (427 nm, 40W) for 24 h. The reaction mixture then quenched with water (10 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was concentrated in vacuo. The crude product was purified by flash chromatography to give the expected compound **12** (16.0 mg, 64%) as a colorless oil.

5. Control experiments

5.1 Electronic effect



Scheme S9 Competition experiment of **1g**, **1k** with **2a**.

A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 15 mol %), AgOAc (5.0 mg, 15 mol%), **1g** (41.5 mg, 0.2 mmol),**1k** (47.1 mg, 0.2 mmol), and DCE (1 mL). To the mixture was added bis(phenylsulfonyl)diazomethane **2a** (64.5 mg, 0.2 mmol) in DCE (1mL). The reaction mixture was stirred at 60 ℃ under a N_2 atmosphere for 24 h. The crude mixture was filtered through Celite and concentrated in vacuo. The residue was then purified by flash column chromatography. The mixture of **3g** and **3k** were combinedly isolated. The ratio of **3g** and **3k** was determined to be 3.4: 1 by ^{1}H NMR analysis.

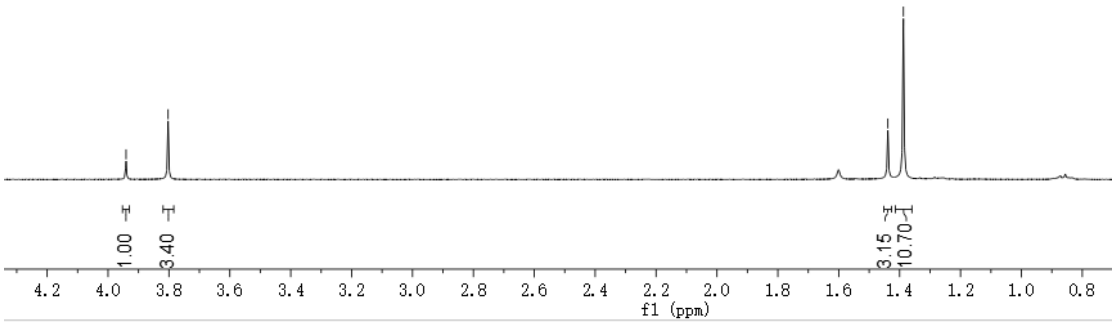
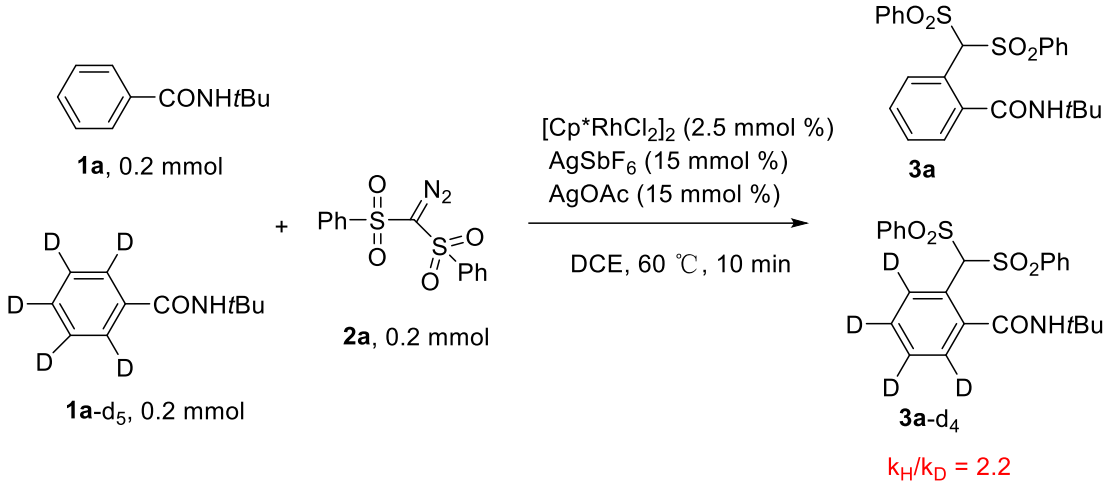


Figure S1 ^{1}H NMR spectra of the mixture of **3g** and **3k**.

5.2 Determination of KIE from Intermolecular Competition Experiment



Scheme S10 Intermolecular competition experiment of **1a**, **1a**-d_5 with **2a**.

A 25 mL reaction tube equipped with a magnetic stirrer bar were charged with $[Cp^*RhCl_2]_2$ (3.1mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 15 mol %), AgOAc (5.0 mg, 15 mol%), **1a** (35.4 mg, 0.2 mmol), **1a**-d_5 (36.4 mg, 0.2 mmol), and DCE (1 mL). To the mixture was added bis(phenylsulfonyl)diazomethane **2a** (64.5 mg, 0.2 mmol) in DCE (1 mL). The reaction mixture was stirred at 60 ℃ under a N_2 atmosphere for 10 min. The crude mixture was filtered through Celite and concentrated under reduced pressure. The residue was then purified by flash column chromatography to afford the mixture of **3a and 3a**-d_4. The ratio of **3a** and **3a**-d_4 was determined to be 0.69: 0.31 by ^{1}H NMR analysis. The KIE value is equal to 2.2.

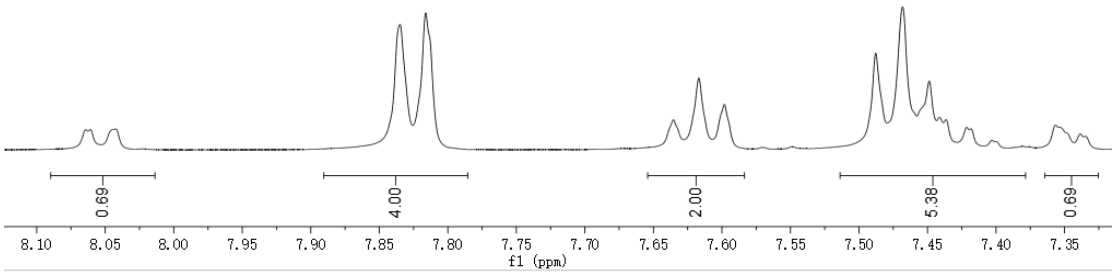
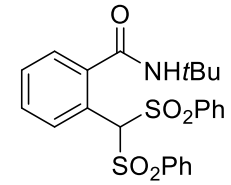


Figure S2 ^{1}H NMR spectra of the mixture of **3a** and **3a**-d_4.

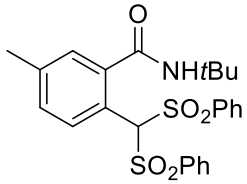
6. Characterization data for products

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)benzamide (3a)



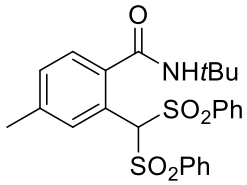
White solid (156.8 mg, 83% yield); **Mp:** 172–174 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 7.7 Hz, 4H), 7.60 (t, J = 7.4 Hz, 2H), 7.43 (m, 6H), 7.33 (d, J = 7.1 Hz, 1H), 7.09 (s, 1H), 5.75 (s, 1H), 1.41 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 139.3, 138.4, 134.3, 131.5, 130.4, 129.9, 129.4, 128.8, 127.3, 123.4, 81.3, 52.1, 28.5; **HRMS** (ESI): calculated for $C_{24}H_{26}NO_5S_2$ $[M+H]^+$: 472.1247, found: 472.1247.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-methylbenzamide (3c)



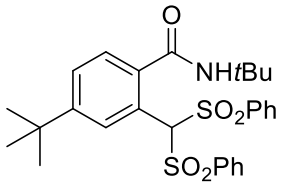
White solid (97.0 mg, 50% yield); **Mp:** 176–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.7 Hz, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.44 (t, J = 7.6 Hz, 4H), 7.24 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 7.02 (s, 1H), 5.75 (s, 1H), 2.34 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 140.9, 139.3, 138. 5, 134.2, 131.3, 130.6, 129.4, 128.8, 128.0, 120.1, 81.4, 52.0, 28.5, 21.2; **HRMS** (ESI): calculated for $C_{25}H_{28}NO_5S_2$ $[M+H]^+$: 486.1403, found: 486.1403.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-methylbenzamide (3d)



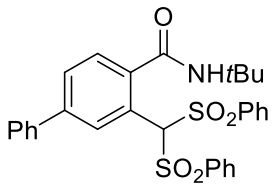
White solid (187.0 mg, 96% yield); **Mp:** 166–168 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 4H), 7.74 (s, 1H), 7.59 (t, J = 7.3 Hz, 2H), 7.45 (t, J = 7.7 Hz, 4H), 7.27–7.15 (m, 3H), 5.71 (s, 1H), 2.34 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 140.3, 138.5, 136.4, 134.2, 132.1, 130.9, 129.4, 128.7, 127.3, 123.4, 81.2, 51.9, 28.6, 21.4; **HRMS** (ESI): calculated for $C_{25}H_{28}NO_5S_2$ $[M+H]^+$: 486.1403, found: 486.1406.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-*tert*-butyl benzamide (3e)



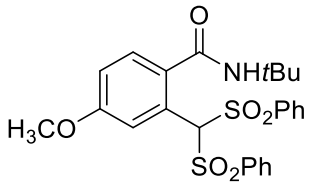
White solid (209.1 mg, 99% yield); **Mp:** 180–182 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 7.5 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.8 Hz, 4H), 7.35 (dd, J = 8.1, 1.8 Hz, 1H), 7.27–7.23 (m, 1H), 7.17 (s, 1H), 5.81 (s, 1H), 1.43 (s, 9H), 1.25 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 153.0, 138.3, 136.4, 134.2, 129.6, 128.8, 128.7, 127.2, 127.1, 123.1, 81.6, 52.0, 34.8, 30.8, 28.6; **HRMS** (ESI): calculated for $C_{28}H_{33}NO_5S_2Na$ $[M+Na]^+$: 550.1692, found: 550.1697.

2-(Bis(phenylsulfonyl)methyl)-*N*-(tert-butyl)-4-phenylbenzamide (3f)



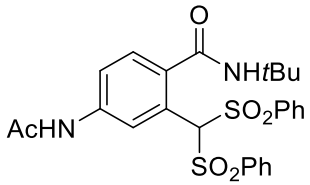
White solid (210.0 mg, 96% yield); **Mp:** 230–232 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.27 (d, J = 1.8 Hz, 1H), 7.87–7.78 (m, 5H), 7.76–7.69 (m, 3H), 7.64–7.51 (m, 9H), 7.45 (t, J = 7.3 Hz, 1H), 7.12 (s, 1H), 1.41 (s, 9H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 168.4, 142.8, 140.2, 139.9, 137.7, 135.2, 130.7, 130.0, 130.0, 129.9, 129.8, 129.2, 128.8, 127.7, 126.2, 81.4, 52.5, 28.8; **HRMS** (ESI): calculated for $C_{30}H_{30}NO_5S_2$ $[M+H]^+$: 548.1560, found: 548.1557.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-methoxybenzamide (3g)



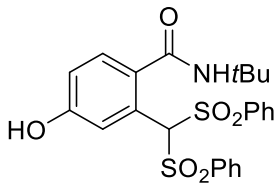
White solid (198.0 mg, 99% yield); **Mp:** 197–199°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 4H), 7.60 (t, J = 7.4 Hz, 2H), 7.53 (d, J = 2.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 4H), 7.37 (s, 1H), 7.29–7.24 (m, 1H), 6.89 (dd, J = 8.6, 2.4 Hz, 1H), 5.64 (s, 1H), 3.80 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 160.2, 138.5, 134.2, 131.4, 129.4, 128.8, 128.8, 125.5, 116.6, 116.1, 80.7, 55.5, 51.9, 28.6; **HRMS** (ESI): calculated for $C_{25}H_{28}NO_6S_2$ $[M+H]^+$: 502.1353, found:502.1352.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-acetamidobenzamide (3h)



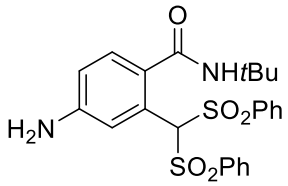
White solid (166.0 mg, 78% yield); **Mp:** 238–240 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.66 (s, 1H), 8.14 (dd, J = 8.6, 2.1 Hz, 1H), 7.88–7.82 (m, 2H), 7.76 (dd, J = 8.4, 1.1 Hz, 4H), 7.72–7.66 (m, 2H), 7.54 (t, J = 7.9 Hz, 4H), 7.44 (d, J = 8.6 Hz, 1H), 6.87 (s, 1H), 2.17 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 169.5, 168.2, 141.6, 140.4, 135.0, 133.1, 129.9, 129.8, 129.8, 126.3, 122.3, 120.6, 80.8, 52.2, 28.7, 24.3; **HRMS** (ESI): calculated for $C_{26}H_{28}N_2O_6S_2Na$ $[M+Na]^+$: 551.1281, found: 551.1285.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-hydroxybenzamide (3i)



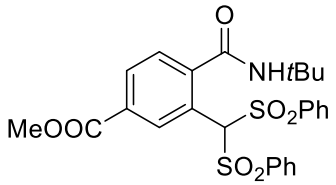
White solid (63.0 mg, 32% yield); **Mp:** 210–212 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.08 (s, 1H), 7.93 (s, 1H), 7.77 (d, J = 7.5 Hz, 4H), 7.70 (t, J = 7.1 Hz, 2H), 7.61–7.47 (m, 5H), 7.39 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.76 (s, 1H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 168.5, 159.2, 140.5, 135.0, 130.8, 130.2, 129.8, 127.4, 119.3, 117.2, 80.8, 52.1, 28.8; **HRMS** (ESI): calculated for $C_{24}H_{26}NO_6S_2$ $[M+H]^+$: 488.1196, found: 486.1202.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-aminobenzamide (3j)



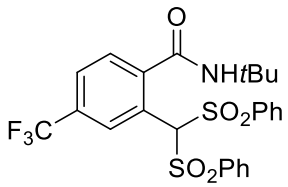
White solid (62.0 mg, 32% yield); **Mp:** 270–272 °C; **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.11 (s, 1H), 7.77 (d, J = 7.3 Hz, 4H), 7.67 (t, J = 7.5 Hz, 2H), 7.52 (t, J = 7.9 Hz, 4H), 7.31 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 6.63 (dd, J = 8.5, 2.4 Hz, 1H), 6.50 (s, 1H), 5.35 (s, 2H), 1.32 (s, 9H); **^{13}C NMR** (126 MHz, Acetone-d_6) δ 168.9, 150.8, 140.9, 134.8, 130.4, 129.7, 129.6, 127.1, 126.1, 117.6, 115.0, 80.6, 51.8, 28.9; **HRMS** (ESI): calculated for $C_{24}H_{27}N_2O_5S_2$ $[M+H]^+$: 487.1356, found: 487.1359.

Methyl 3-(bis(phenylsulfonyl)methyl)-4-(*tert*-butylcarbamoyl)benzoate (3k)



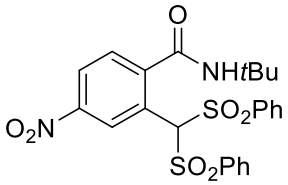
White solid (152.0 mg, 72% yield); **Mp:** 190–192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.9 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.42 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 5.88 (s, 1H),3.94 (s, 3H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 165.4, 143.1, 137.9, 134.5, 132.2, 131.5, 131.3, 129.5, 128.9, 127.5, 123.9, 81.3, 52.6, 52.4, 28.5; **HRMS** (ESI): calculated for $C_{26}H_{28}NO_7S_2$ $[M+H]^+$: 530.1302, found: 530.1302.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-(trifluoromethyl)benzamide (3l)



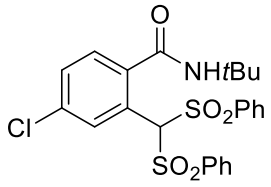
White solid (140.2 mg, 65% yield); **Mp:** 206–208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.81 (d, J = 7.7 Hz, 4H), 7.64 (t, J = 7.4 Hz, 3H), 7.54–7.43 (m, 5H), 6.92 (s, 1H), 5.96 (s, 1H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 142.7, 137.4, 134.7, 131.6 (q, $J_{C\text{-}C\text{-}F}$ = 33.7 Hz), 129.6, 129.0, 128.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.0 Hz), 128.0, 127.1 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.0 Hz), 124.6, 123.0(q, $J_{C\text{-}F}$ = 273.7 Hz), 81.5, 52.6, 28.5; **^{19}F NMR** (376 MHz, CDCl3) δ -63.12; **HRMS** (ESI): calculated for $C_{25}H_{25}F_3NO_5S_2$ $[M+H]^+$: 540.1121, found: 540.1121.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-nitrobenzamide (3m)



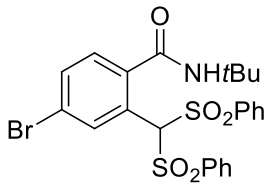
White solid (148.6 mg, 72% yield); **Mp:** 230–232 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 2.1 Hz, 1H), 8.22 (dd, J = 8.4, 2.1 Hz, 1H), 7.82 (d, J = 7.6 Hz, 4H), 7.66 (t, J = 7.5 Hz, 2H), 7.56–7.46 (m, 5H), 6.87 (s, 1H), 6.02 (s, 1H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 147.8, 144.8, 137.3, 134.9, 129.5, 129.2, 128.5, 126.2, 125.5, 125.1, 81.2, 52.8, 28.5; **HRMS** (ESI): calculated for $C_{24}H_{25}N_2O_7S_2$ $[M+H]^+$: 517.1098, found: 517.1098.

2-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-4-chlorobenzamide (3n)



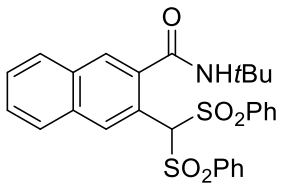
White solid (198.4 mg, 98% yield); **Mp:** 206–208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 1.8 Hz, 1H), 7.81 (d, J = 7.6 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.8 Hz, 4H), 7.39–7.32 (m, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.08 (s, 1H), 5.79 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 137.9, 137.6, 136.0, 134.5, 131.4, 130.4, 129.5, 128.9, 128.6, 125.4, 80.9, 52.3, 28.5; **HRMS** (ESI): calculated for $C_{24}H_{25}ClNO_5S_2$ $[M+H]^+$: 506.0857, found: 506.0856.

2-(Bis(phenylsulfonyl)methyl)-4-bromo-*N*-(*tert*-butyl)benzamide (3o)



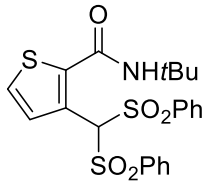
White solid (209.2 mg, 98% yield); **Mp:** 190–192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 7.4 Hz, 4H), 7.63 (t, J = 7.5 Hz, 2H), 7.55–7.46 (m, 5H), 7.20 (d, J = 8.2 Hz, 1H), 7.00 (s, 1H), 5.81 (s, 1H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 138.0, 137.8, 134.6, 134.2, 133.4, 129.5, 128.9, 128.7, 125.5, 124.0, 80.3, 52.3, 28.5; **HRMS** (ESI): calculated for $C_{24}H_{25}BrNO_5S_2$ $[M+H]^+$: 550.0352, found: 550.0352.

3-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)-2-naphthamide (3p)



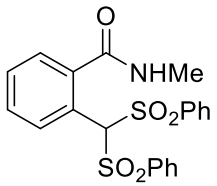
White solid (106.0 mg, 51% yield); **Mp:** 197–199 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.90–7.86 (m, 1H), 7.86–7.79 (m, 6H), 7.64–7.54 (m, 4H), 7.42 (t, J = 7.8 Hz, 4H), 7.33 (s, 1H), 5.87 (s, 1H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 138.4, 135.4, 134.2, 132.8, 132.7, 132.5, 129.5, 128.8, 128.4, 128.0, 127.8, 127.3, 120.1, 81.0, 52.1, 28.6; **HRMS** (ESI): calculated for $C_{28}H_{28}NO_5S_2$ $[M+H]^+$: 522.1403, found: 522.1405.

3-(Bis(phenylsulfonyl)methyl)-*N*-(*tert*-butyl)thiophene-2-carboxamide (3q)



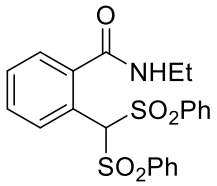
White solid (145.0 mg, 76% yield); **Mp:** 177–179 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 4H), 7.71 (d, J = 5.2 Hz, 1H), 7.60 (t, J = 7.4 Hz, 3H), 7.45 (t, J = 7.8 Hz, 4H), 7.32 (d, J = 5.2 Hz, 1H), 5.51 (s, 1H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 138.5, 138.2, 134.2, 130.6, 129.1, 128.8, 128.1, 125.7, 79.1, 52.2, 28.6; **HRMS** (ESI): calculated for $C_{22}H_{23}NO_5S_3Na$ $[M+Na]^+$: 500.0631, found: 500.0632.

2-(Bis(phenylsulfonyl)methyl)-*N*-methylbenzamide (5a)



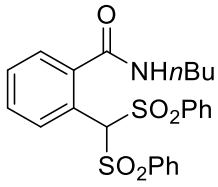
White solid (140.8 mg, 82% yield); **Mp:** 235–237 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.5 Hz, 4H), 7.59 (t, J = 7.0 Hz, 2H), 7.55–7.39 (m, 6H), 7.36–7.28 (m, 2H), 5.70 (s, 1H), 2.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 138.7, 137.1, 134.2, 131.9, 130.5, 129.3, 128.8, 127.2, 124.3, 80.6, 26.9; **HRMS** (ESI): calculated for $C_{21}H_{20}NO_5S_2$ $[M+H]^+$: 430.0777, found: 430.0781.

2-(Bis(phenylsulfonyl)methyl)-*N*-ethylbenzamide (5b)



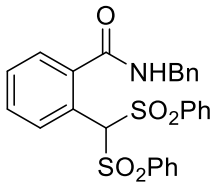
White solid (129.6 mg, 73% yield); **Mp:** 220–222 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.4 Hz, 4H), 7.59 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.48–7.40 (m, 5H), 7.33 (d, J = 7.6 Hz, 1H), 7.30 (s, 1H), 5.75 (s, 1H), 3.37–3.23 (m, 2H), 1.17 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 138.6, 137.4, 134.2, 131.9, 130.4, 130.4, 129.3, 128.8, 127.2, 124.2, 80.7, 35.0, 14.5; **HRMS** (ESI): calculated for $C_{22}H_{22}NO_5S_2$ $[M+H]^+$: 444.0934, found: 444.0930.

2-(Bis(phenylsulfonyl)methyl)-*N*-butylbenzamide (5c)



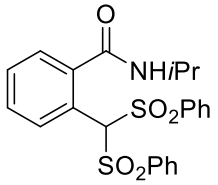
White solid (128.1 mg, 68% yield); **Mp:** 176–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.54–7.40 (m, 6H), 7.33 (d, J = 7.4 Hz, 1H), 7.29 (s, 1H), 5.77 (s, 1H), 3.34–3.20 (m, 2H), 1.57–1.47 (m, 2H), 1.44–1.32 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 138.6, 137.7, 134.2, 131.8, 130.4, 130.3, 129.4, 128.8, 127.2, 124.1, 80.8, 39.9, 31.4, 20.1, 13.7; **HRMS** (ESI): calculated for $C_{24}H_{25}NO_5S_2Na$ $[M+Na]^+$: 494.1066, found: 494.1065.

***N*-Benzyl-2-(bis(phenylsulfonyl)methyl)benzamide (5d)**



White solid (153.6 mg, 76% yield); **Mp:** 185–187 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.7 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46–7.29 (m, 11H), 7.22 (s, 1H), 6.18 (s, 1H), 4.47 (d, J = 5.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 138.4, 137.5, 137.3, 134.2, 131.9, 130.5, 130.5, 129.3, 128.9, 128.8, 127.9, 127.8, 127.4, 124.1, 80.8, 44.1; **HRMS** (ESI): calculated for $C_{27}H_{24}NO_5S_2$ $[M+H]^+$: 506.1090, found: 506.1094.

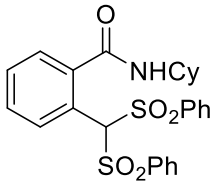
2-(Bis(phenylsulfonyl)methyl)-*N*-isopropylbenzamide (5e)



White solid (145.0 mg, 90% yield); **Mp:** 187–189 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.51–7.38 (m, 6H), 7.34 (d, J = 9.7 Hz, 2H), 5.76 (d, J = 7.2 Hz, 1H), 4.15–4.01 (m, 1H), 1.19 (d, J = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 138.5, 137.8, 134.2, 131.8, 130.4, 130.3, 129.4, 128.8, 127.3, 124.0, 80.9, 42.1, 22.5; **HRMS** (ESI):

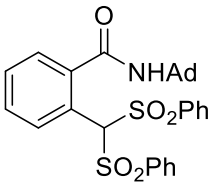
calculated for $C_{23}H_{24}NO_5S_2$ [M+H]$^+$: 458.1090, found: 458.1090.

2-(Bis(phenylsulfonyl)methyl)-*N*-cyclohexylbenzamide (5f)



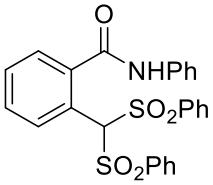
White solid (161.0 mg, 81% yield); **Mp:** 148–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.7 Hz, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.50–7.38 (m, 6H), 7.34 (d, J = 7.4 Hz, 1H), 7.30 (s, 1H), 5.80 (d, J = 7.5 Hz, 1H), 3.79 (d, J = 7.9 Hz, 1H), 2.05–1.85 (m, 2H), 1.81–1.58 (m, 3H), 1.48–1.30 (m, 2H), 1.26–1.09 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 138.4, 137.9, 134.3, 131.7, 130.4, 130.2, 129.4, 128.8, 127.4, 124.0, 81.0, 77.3, 77.0, 76.7, 48.9, 32.8, 25.4, 24.7; **HRMS** (ESI): calculated for $C_{26}H_{28}NO_5S_2$ [M+H]$^+$: 498.1403, found: 498.1405.

***N*-Adamantanyl-2-(bis(phenylsulfonyl)methyl)benzamide (5g)**



White solid (214.7 mg, 98% yield); **Mp:** 195–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 6.7 Hz, 1H), 7.82 (d, J = 7.7 Hz, 4H), 7.61 (t, J = 7.3 Hz, 2H), 7.52–7.37 (m, 6H), 7.36–7.30 (m, 1H), 7.08 (s, 1H), 5.61 (s, 1H), 2.13 (s, 3H), 2.06 (s, 6H), 1.72 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 139.5, 138.3, 134.3, 131.4, 130.4, 129.8, 129.5, 128.8, 127.4, 123.3, 81.4, 52.8, 41.3, 36.2, 29.4; **HRMS** (ESI): calculated for $C_{30}H_{31}NO_5S_2Na$ [M+Na]$^+$: 572.1536, found: 572.1536.

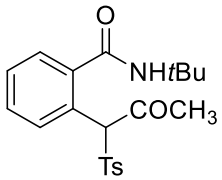
2-(Bis(phenylsulfonyl)methyl)-*N*-phenylbenzamide (5h)



White solid (40.0 mg, 20% yield); **Mp:** 228–230 °C; **^{1}H NMR** (500 MHz, Acetone-d_6) δ 9.21 (s, 1H), 8.16 (d, J = 7.1 Hz, 1H), 7.75 (d, J = 6.9 Hz, 4H), 7.71–7.54 (m, 8H), 7.53–7.45 (m, 4H), 7.42–7.32 (m, 2H), 7.22–7.12 (m, 1H); **^{13}C NMR** (126 MHz, Acetone-d_6) δ167.1, 140.2, 139.6, 137.9, 135.2, 132.6, 131.3, 131.0, 129.9, 129.8, 129.4, 129.0, 126.1, 125.1, 121.3, 81.3; **HRMS** (ESI): calculated for

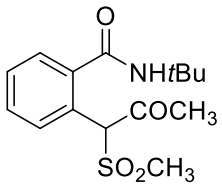
$C_{26}H_{21}NO_5S_2Na$ $[M+Na]^+$: 514.0753, found: 514.0751.

***N*-(*tert*-Butyl)-2-(2-oxo-1-tosylpropyl)benzamide (6a)**



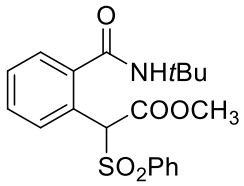
Colorless oil (120.0 mg, 77% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.56–7.50 (m, 1H), 7.46–7.38 (m, 3H), 7.31–7.24 (m, 2H), 6.36 (s, 1H), 5.94 (s, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.3, 168.6, 145.0, 139.9, 134.9, 130.7, 129.9, 129.7, 129.5, 129.4, 127.4, 125.3, 74.0, 52.1, 31.0, 28.6, 21.6; **HRMS** (ESI): calculated for $C_{21}H_{26}NO_4S$ $[M+H]^+$: 388.1577, found: 388.1579.

***N*-(*tert*-Butyl)-2-(1-(methylsulfonyl)-2-oxopropyl)benzamide (6b)**



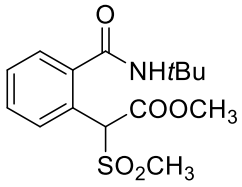
Colorless oil (119.6 mg, 96% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 1H), 7.55–7.51 (m, 1H), 7.50–7.45 (m, 2H), 6.24 (s, 1H), 6.16 (s, 1H), 3.01 (s, 3H), 2.32 (s, 3H), 1.49 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 168.6, 139.9, 130.2, 129.8, 129.6, 128.0, 125.3, 73.5, 52.3, 39.8, 30.9, 28.6; **HRMS** (ESI): calculated for $C_{15}H_{22}NO_4S$ $[M+H]^+$: 312.1264, found: 312.1265.

Methyl 2-(2-(*tert*-butylcarbamoyl)phenyl)-2-(phenylsulfonyl)acetate (6c)



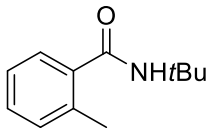
White solid (74.0 mg, 47% yield); **Mp**: 122–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.72 (m, 3H), 7.66 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.48–7.37 (m, 3H), 6.32 (s, 1H), 6.07 (s, 1H), 3.63 (s, 3H), 1.50 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 165.5, 139.6, 137.2, 134.2, 130.9, 129.7, 129.7, 129.6, 128.8, 127.5, 124.9, 68.8, 53.1, 52.2, 28.6; **HRMS** (ESI): calculated for $C_{20}H_{24}NO_5S$ $[M+H]^+$: 390.1370, found: 390.1372.

Methyl 2-(2-(*tert*-butylcarbamoyl)phenyl)-2-(methylsulfonyl)acetate (6d)



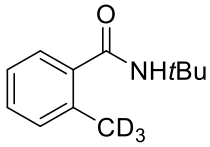
White solid (64.5 mg, 49% yield); **Mp**: 138–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.2 Hz, 1H), 7.60–7.40 (m, 3H), 6.23–6.05 (m, 2H), 3.82 (s, 3H), 3.07 (s, 3H), 1.47 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 165.9, 139.4, 130.1, 129.9, 129.8, 127.8, 125.5, 68.0, 53.5, 52.3, 39.5, 28.6; **HRMS** (ESI): calculated for $C_{15}H_{22}NO_5S$ $[M+H]^+$: 328.1213, found: 328.1215.

***N*-(*tert*-Butyl)-2-methylbenzamide (7)**



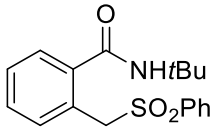
White solid (20.6 mg, 86% yield); **Mp:** 80–82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 2H), 7.22–7.13 (m, 2H), 5.57 (s, 1H), 2.43 (s, 3H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 137.9, 135.4, 130.8, 129.4, 126.4, 125.6, 51.7, 28.8, 19.5; **HRMS** (ESI): calculated for $C_{24}H_{20}NO_5S_2Na$ $[M+Na]^+$: 214.1202, found: 214.1205.

***N*-(*tert*-Butyl)-2-(methyl-d_3)benzamide (8)**



White solid (28.9 mg, 74% yield); **Mp:** 78–80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 2H), 7.23–7.13 (m, 2H), 5.58 (s, 1H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 137.9, 135.3, 130.8, 129.4, 126.4, 125.6, 51.7, 28.8, 18.7 (septet, J = 19.2 Hz); **HRMS** (ESI): calculated for $C_{24}H_{21}N_2O_4S_2$ Na $[M+Na]^+$: 217.1391, found: 217.1394.

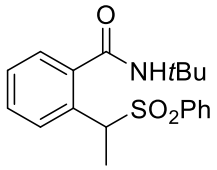
***N*-(*tert*-Butyl)-2-((phenylsulfonyl)methyl)benzamide (9)**



White solid (54.4 mg, 82% yield); **Mp:** 146–148 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz,

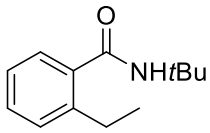
2H), 7.67 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.35 (s, 1H), 4.68 (s, 2H), 1.50 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 139.9, 138.8, 133.9, 132.5, 129.5, 129.2, 129.0, 128.3, 128.0, 124.6, 59.0, 52.0, 28.7; **HRMS** (ESI): calculated for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332.1315, found: 332.1316.

***N*-(*tert*-Butyl)-2-(1-(phenylsulfonyl)ethyl)benzamide (10)**



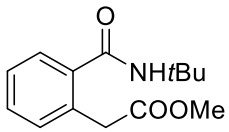
White solid (51.2 mg, 74% yield); **Mp:** 178–180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.56–7.47 (m, 3H), 7.44–7.33 (m, 3H), 6.05 (s, 1H), 5.15 (q, J = 7.0 Hz, 1H), 1.63 (d, J = 7.0 Hz, 3H), 1.48 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 139.9, 137.4, 133.6, 130.7, 129.7, 129.1, 129.0, 129.0, 128.7, 127.4, 60.4, 52.0, 28.7, 15.6; **HRMS** (ESI): calculated for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1471, found: 346.1472.

***N*-(*tert*-Butyl)-2-ethylbenzamide (11)**



White solid (18.0 mg, 88% yield); **Mp:** 78–80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.23 (d, J = 7.1 Hz, 1H), 7.20–7.14 (m, 1H), 5.57 (s, 1H), 2.79 (q, J = 7.6 Hz, 2H), 1.46 (s, 9H), 1.24 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 141.8, 137.6, 129.5, 129.3, 126.5, 125.6, 51.7, 28.8, 26.2, 15.8; **HRMS** (ESI): calculated for $C_{13}H_{20}NO$ $[M+H]^+$: 206.1539, found: 206.1541.

Methyl 2-(2-(*tert*-butylcarbamoyl)phenyl)acetate (12)



Colorless oil (16.0 mg, 64% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.4, 1.1 Hz, 1H), 7.38–7.28 (m, 2H), 7.22 (d, J = 7.5 Hz, 1H), 6.22 (s, 1H), 3.87 (s, 2H), 3.71 (s, 3H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 167.0, 138.3, 131.4, 130.9, 129.8, 127.6, 127.5, 52.1, 51.8, 38.7, 28.7; **HRMS** (ESI): calculated for $C_{14}H_{20}NO_3$ $[M+H]^+$:250.1438, found: 250.1439.

7. References

[1] M. Chong, Y. X. Hu, W. J. Lu, *Synthesis* **2018***, 50,* 2999–3005.

[2] M. N. Esfahani, M. Montazerozohori, Z. Karami, *Org. Prep. Proced. Int.* **2016**, *48*, 321–327.

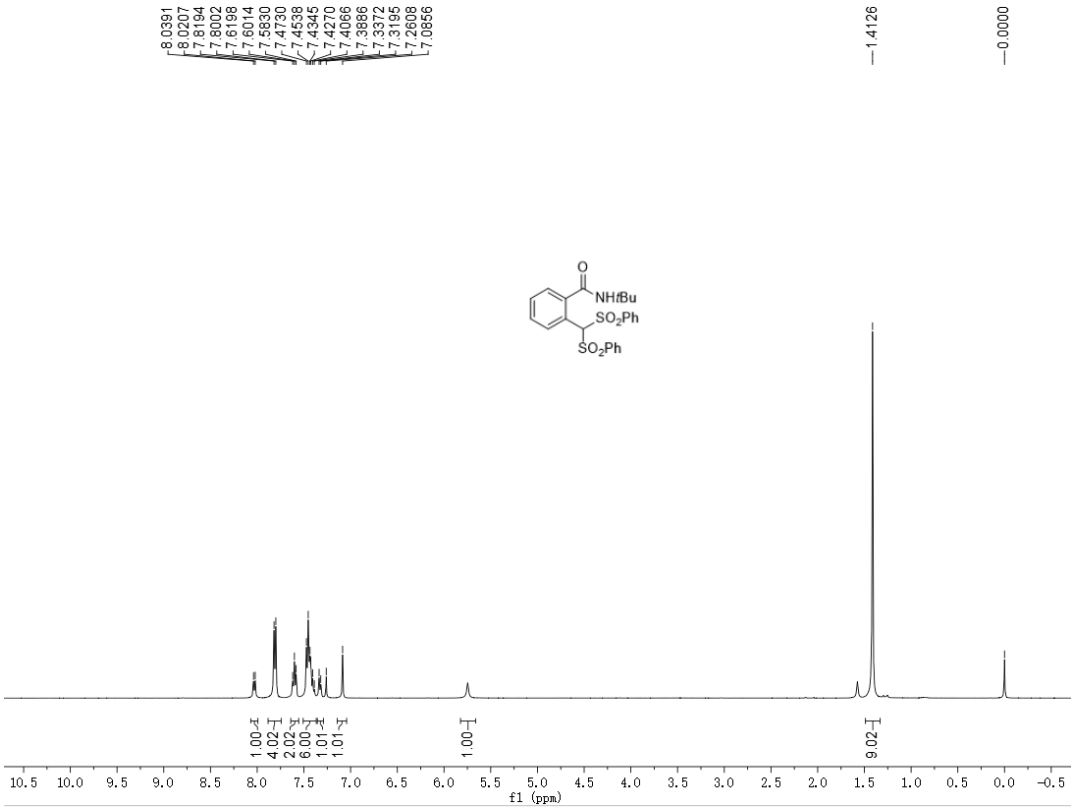
[3] R. F. Sun, Z. W. Wang, Y. Q. Li, L. X. Xiong, Y. X. Liu, Q. M. Wang, *J. Agric. Food Chem.* **2013**, *61*, 517–522.

[4] G. Heyes, G. Holt, *J. Chem. Soc. Perkin I.* **1973**, 189–193.

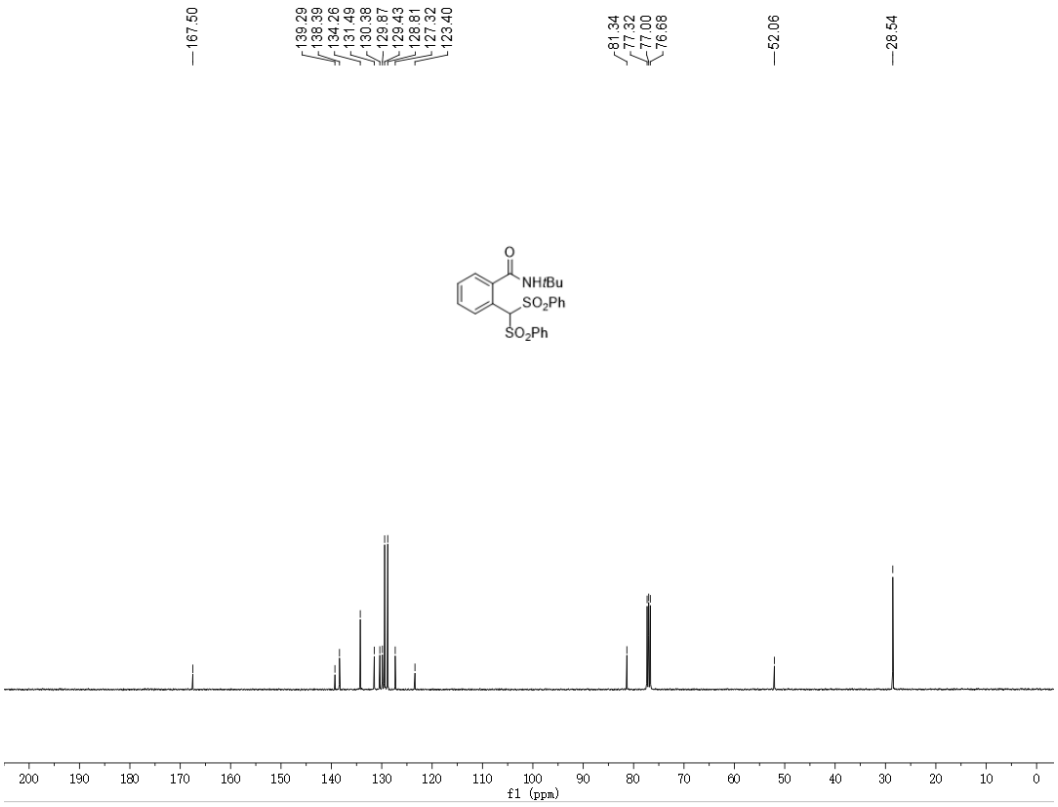
[5] Y. Dong, J. J. Chen, H. Xu, *Chem. Commun.* **2019**, *55*, 2027–2030.

8. NMR spectra of products

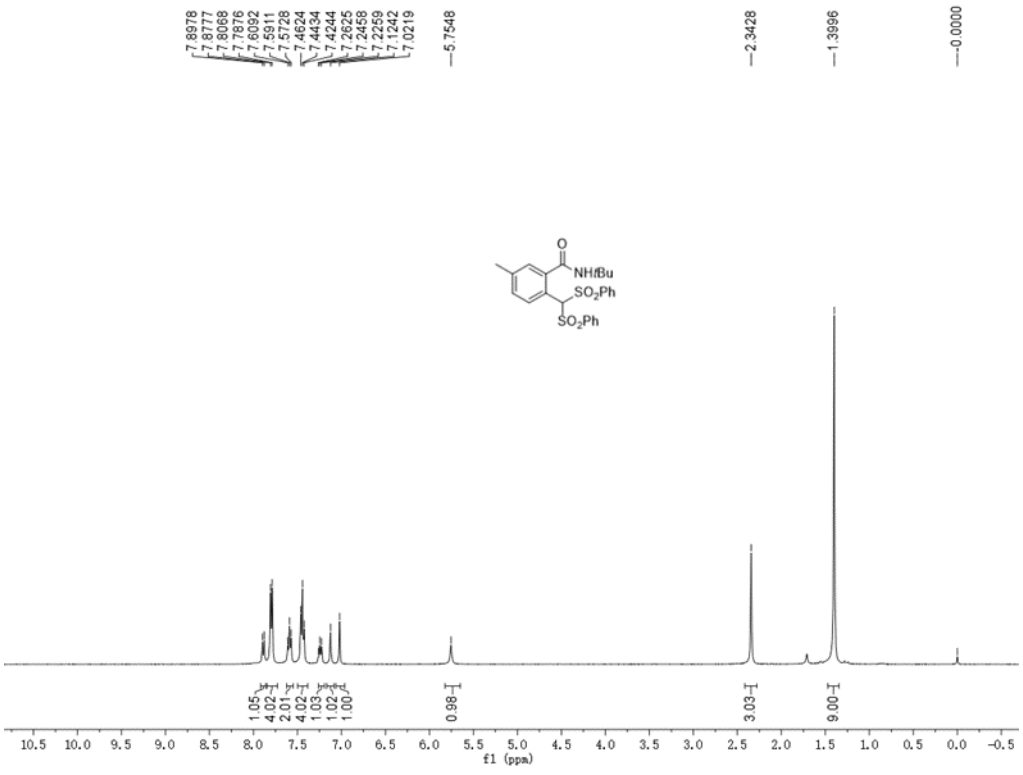
^{1}H NMR (400 MHz) Spectrum of 3a in $CDCl_3$



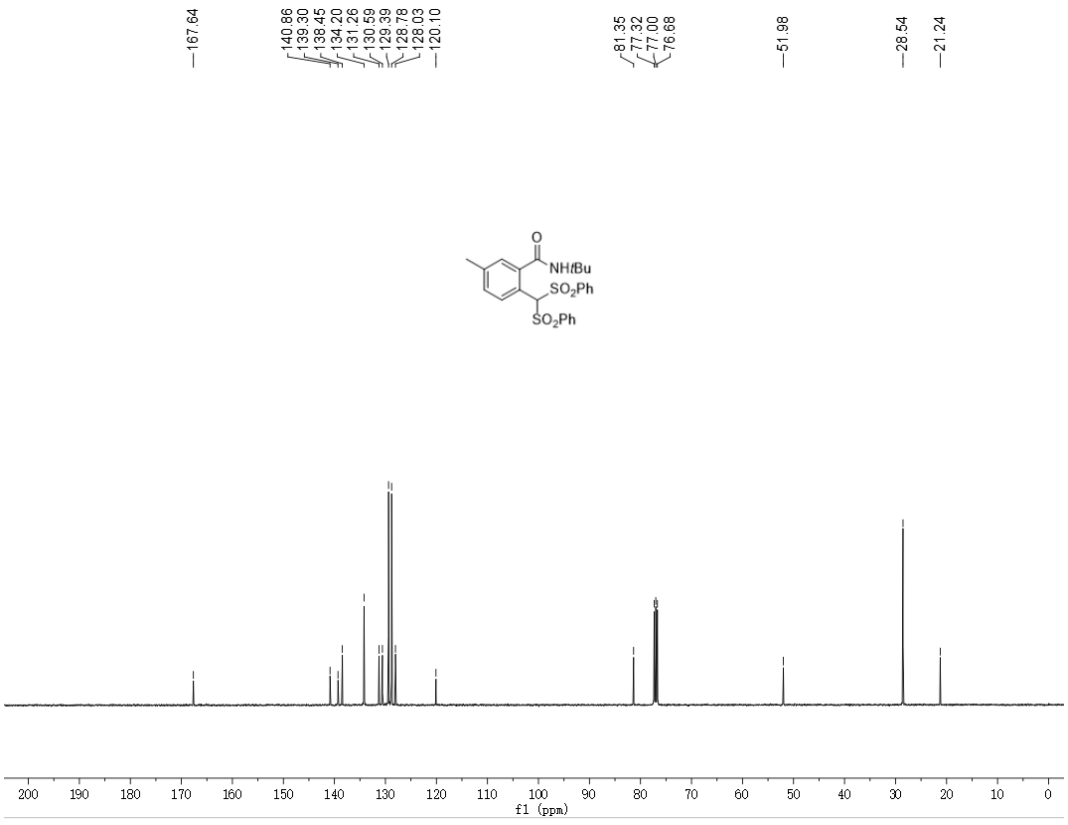
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3a in $CDCl_3$



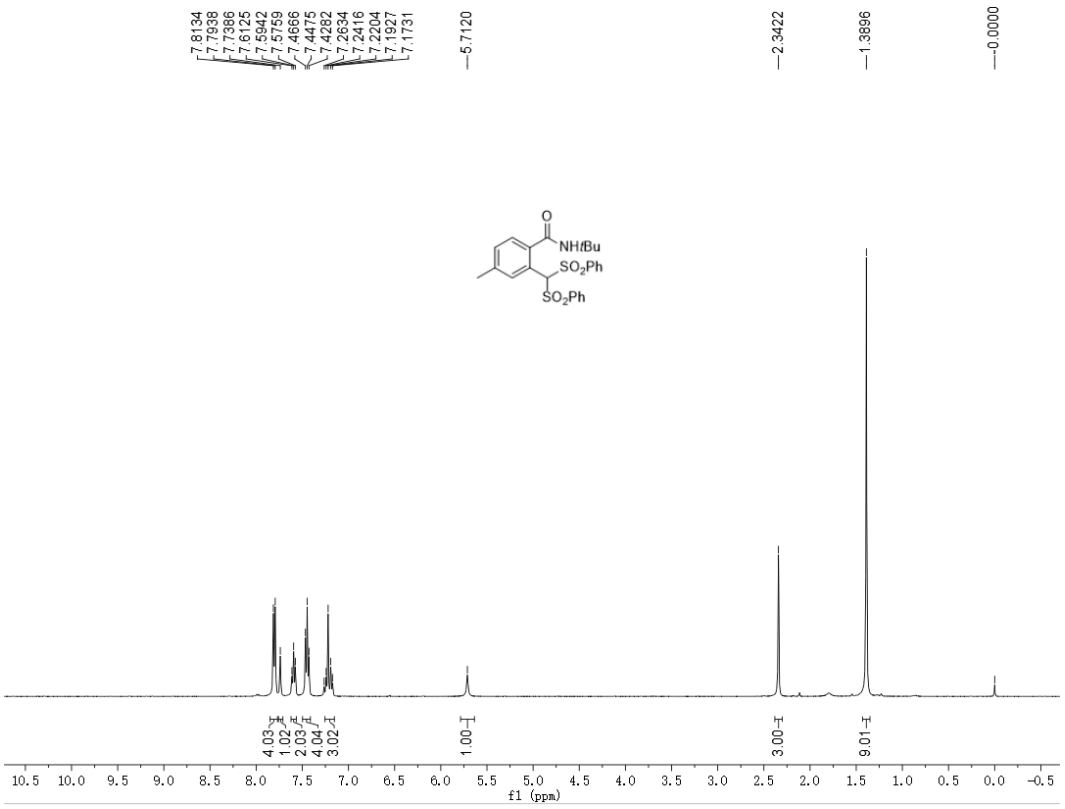
^{1}H NMR (400 MHz) Spectrum of 3c in $CDCl_3$



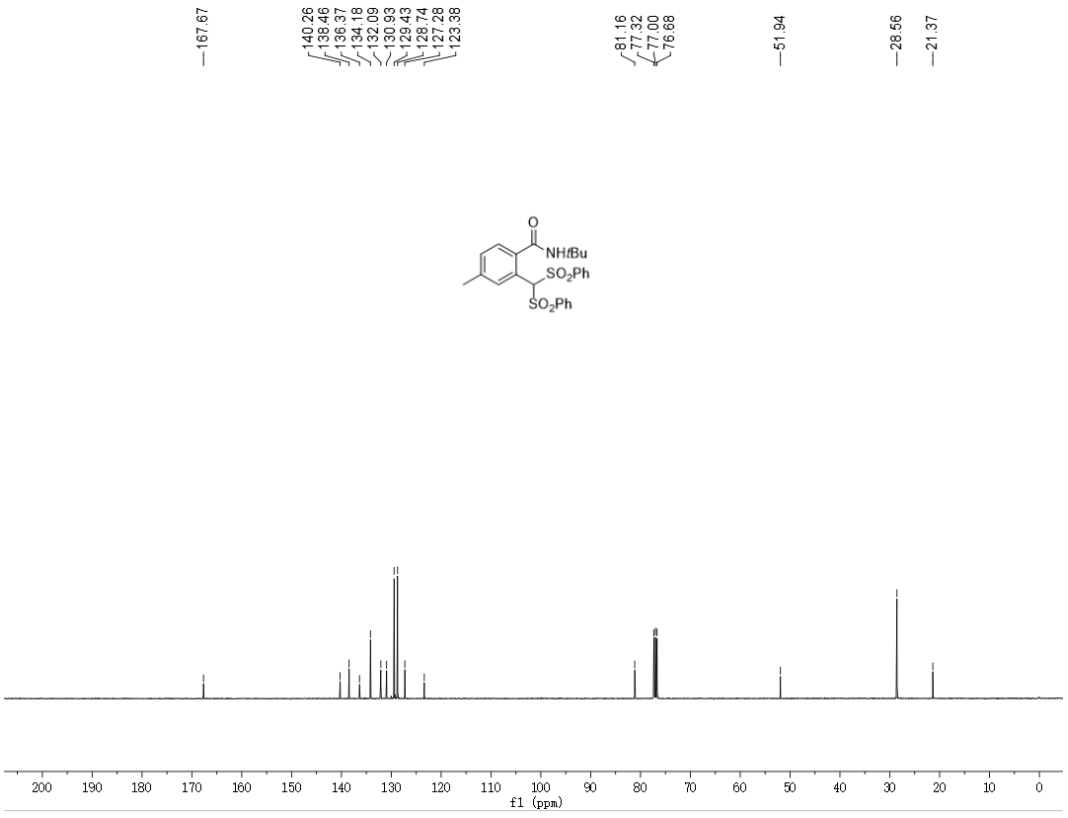
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3c in $CDCl_3$



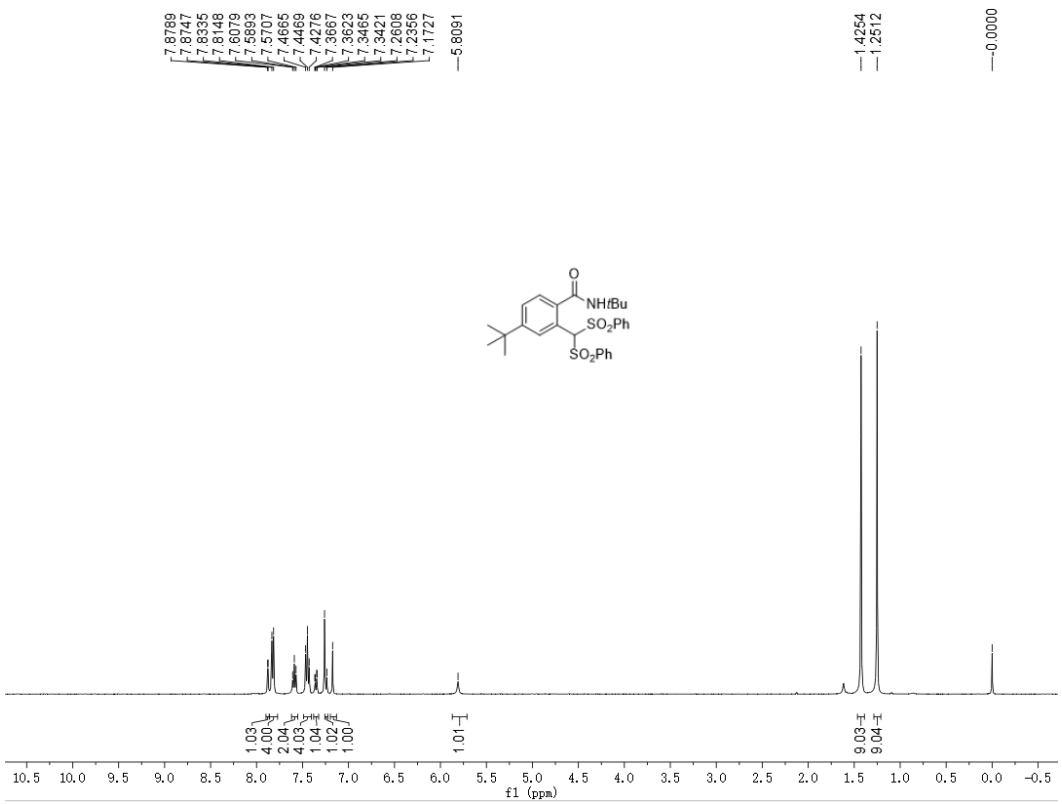
^{1}H NMR (400 MHz) Spectrum of 3d in $CDCl_3$



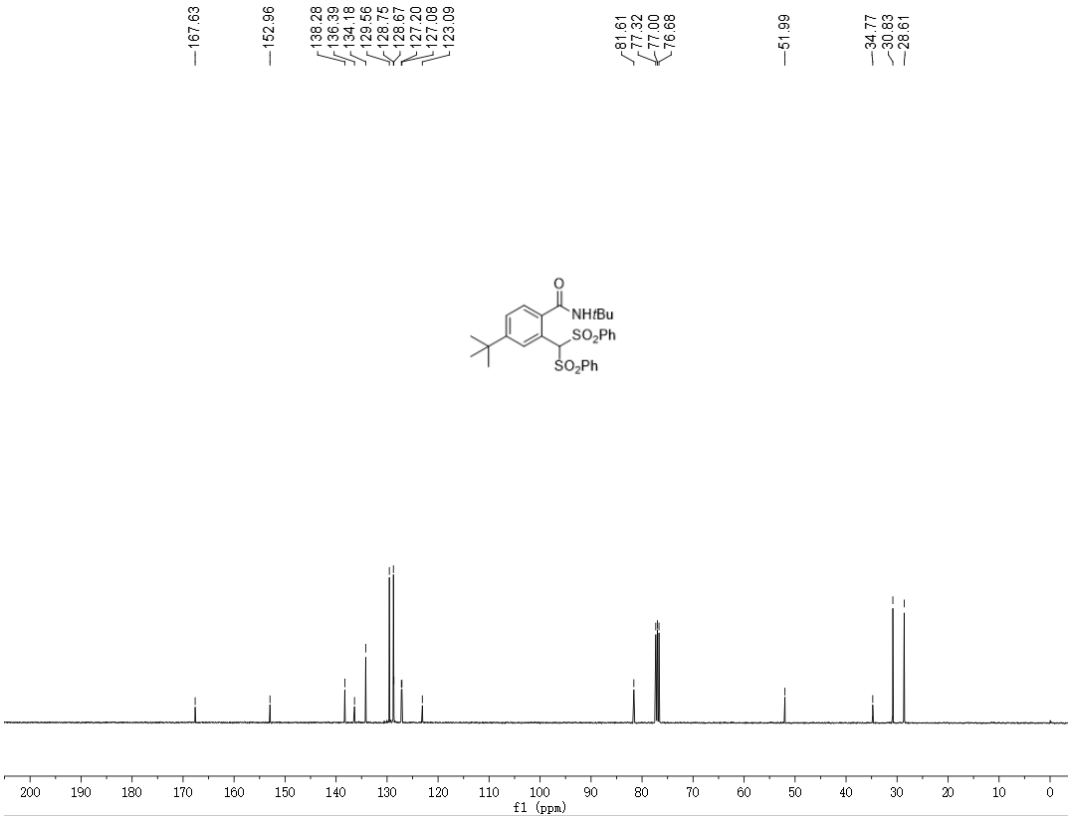
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3d in $CDCl_3$



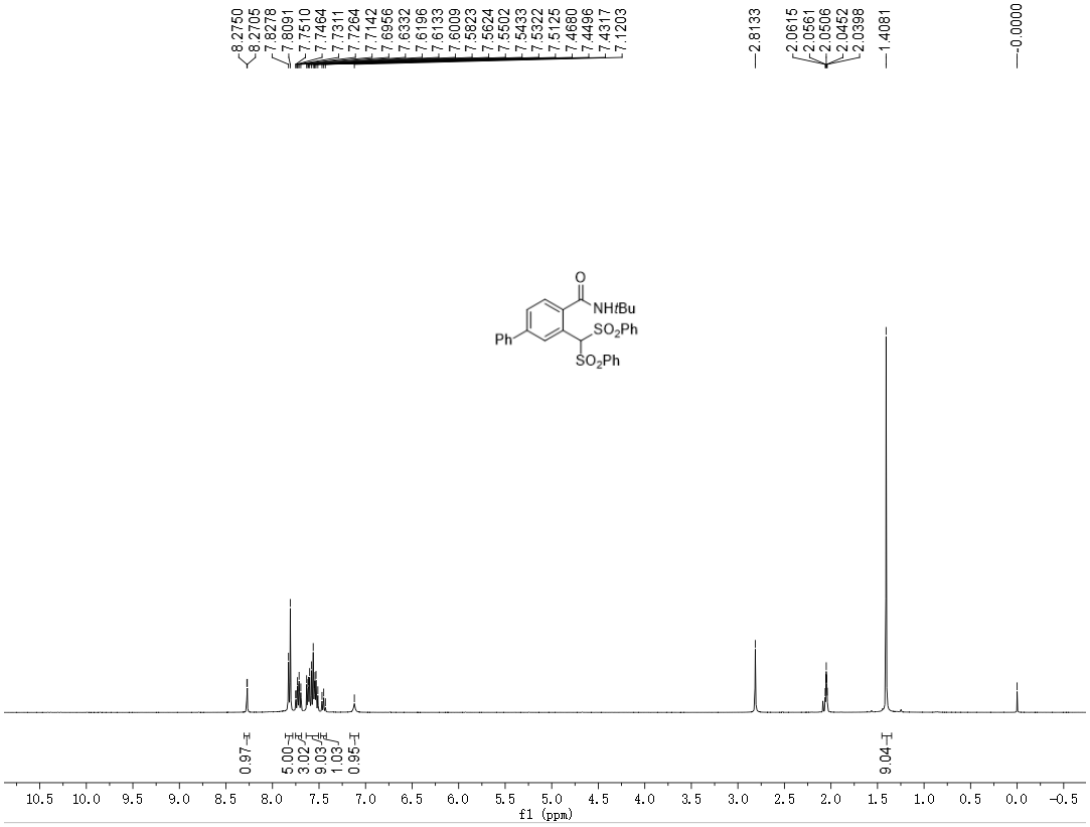
^{1}H NMR (400 MHz) Spectrum of 3e in $CDCl_3$



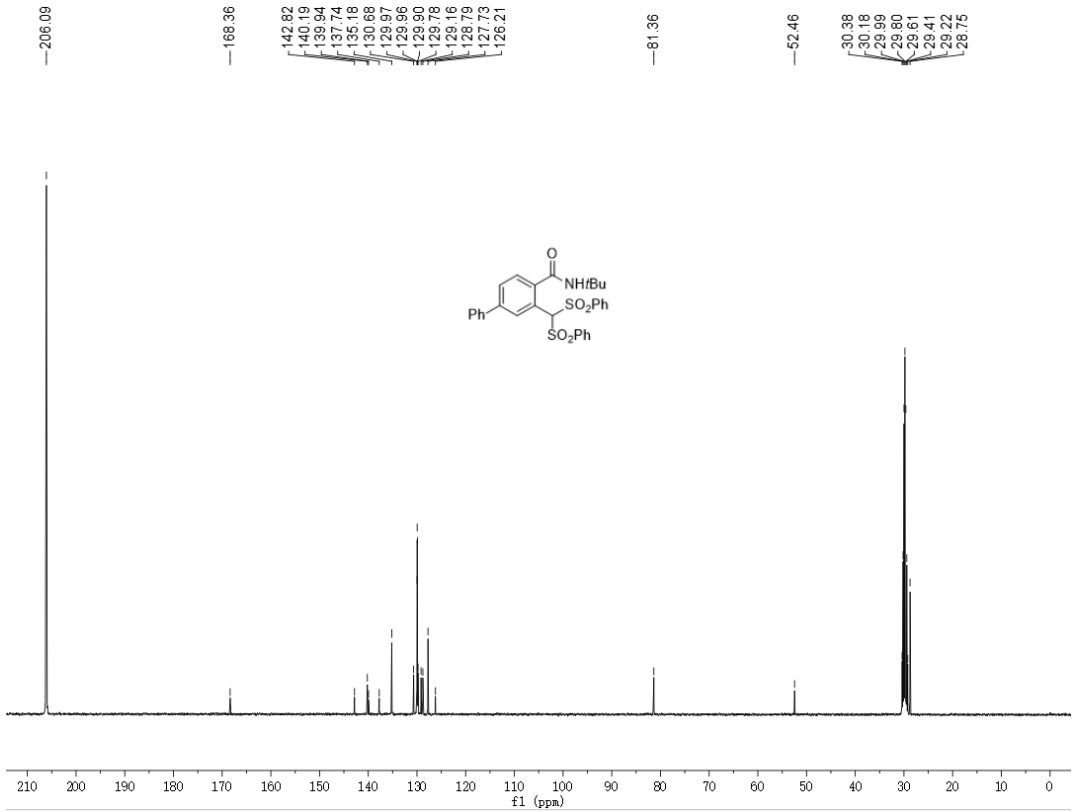
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3e in $CDCl_3$



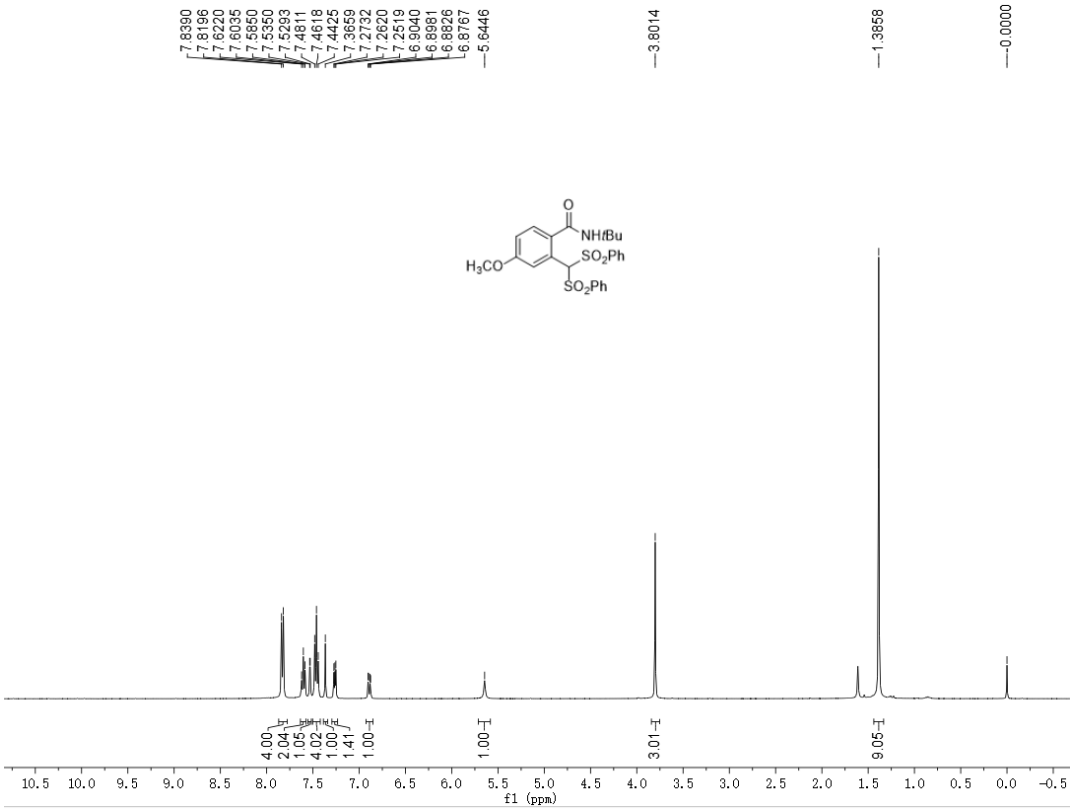
^{1}H NMR (400 MHz) Spectrum of 3f in acetone-d_6



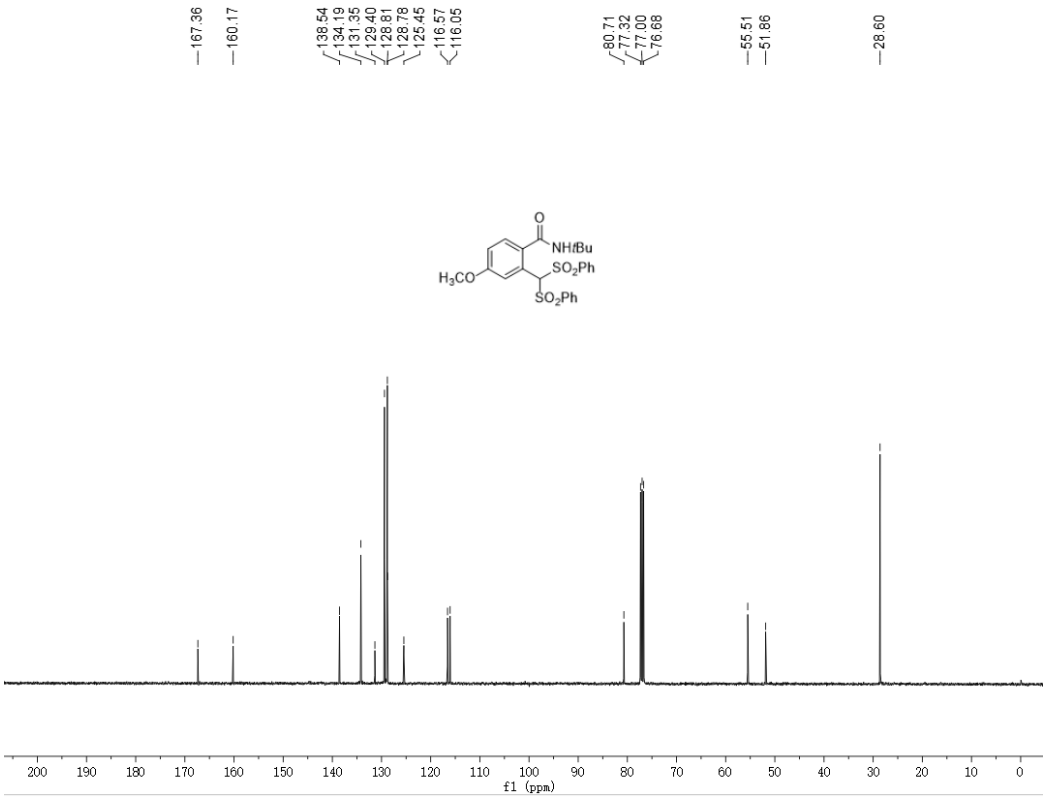
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3f in acetone-d_6



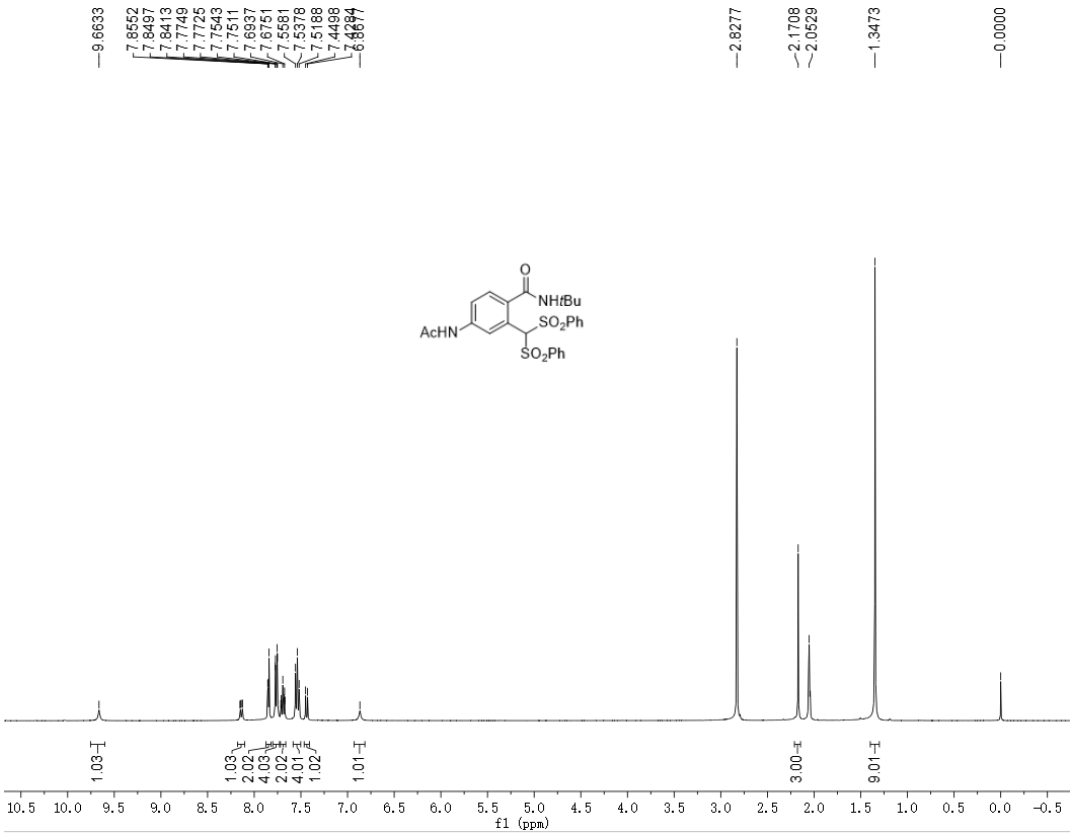
^{1}H NMR (400 MHz) Spectrum of 3g in $CDCl_3$



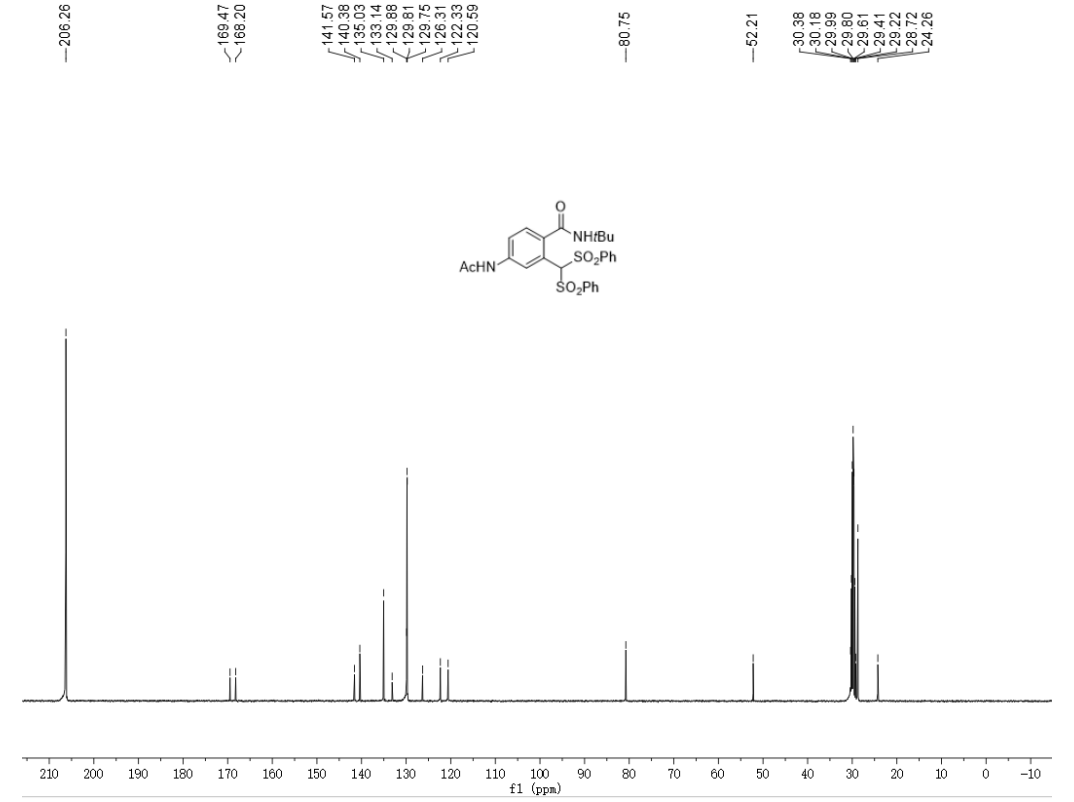
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3g in $CDCl_3$



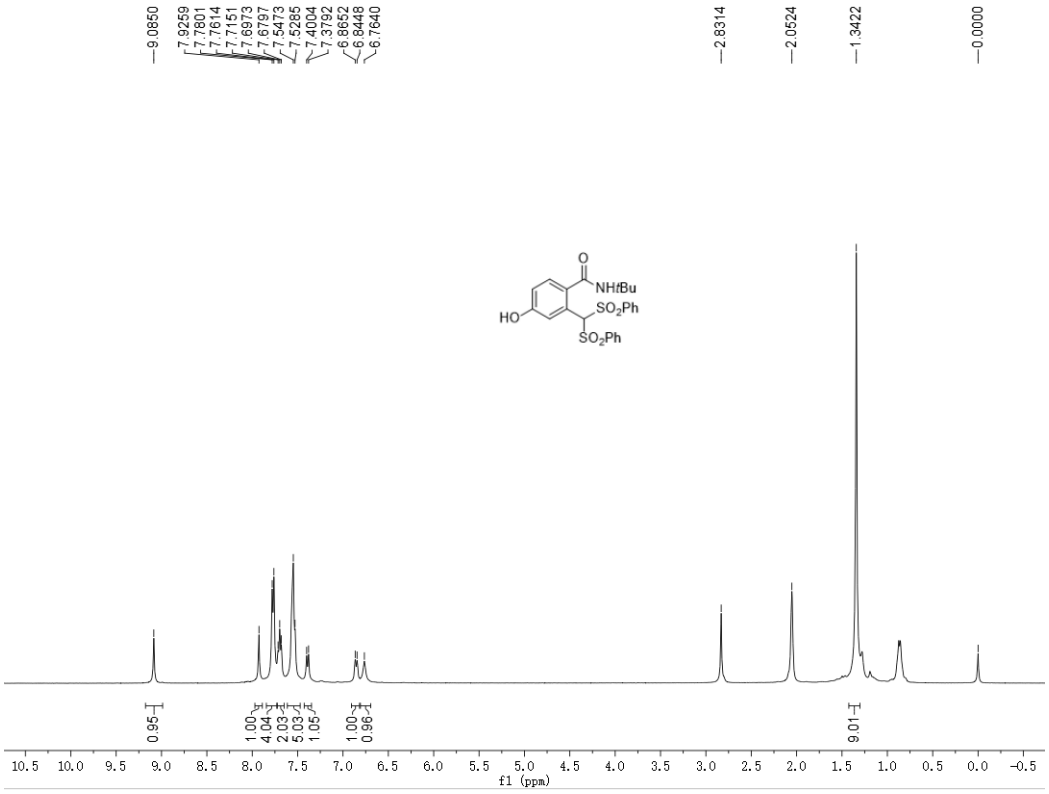
^{1}H NMR (400 MHz) Spectrum of 3h in acetone-*d*$_6$



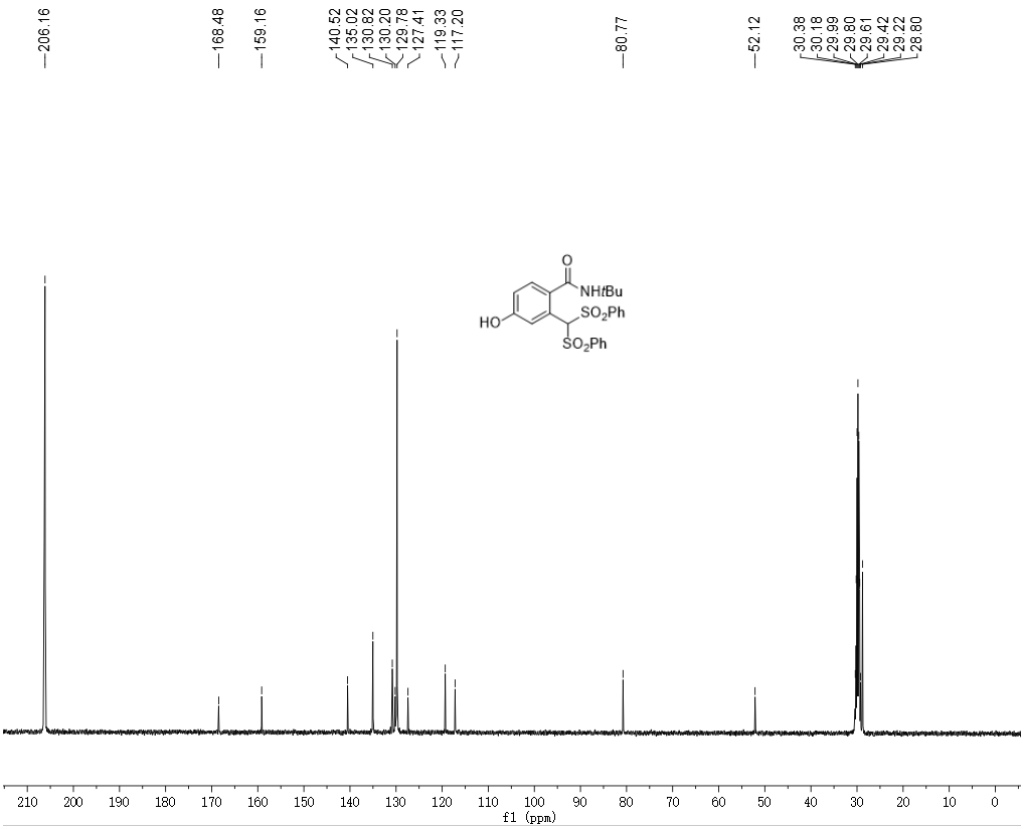
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3h in acetone-*d*$_6$



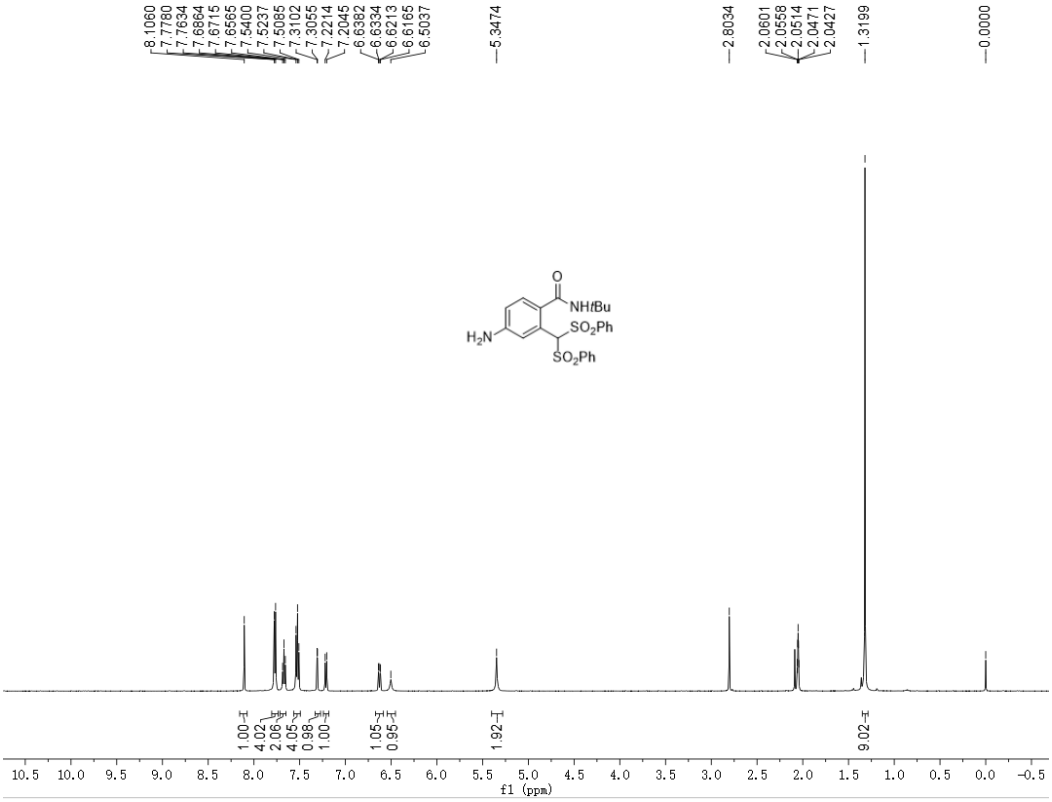
^{1}H NMR (400 MHz) Spectrum of 3i in acetone-d_6



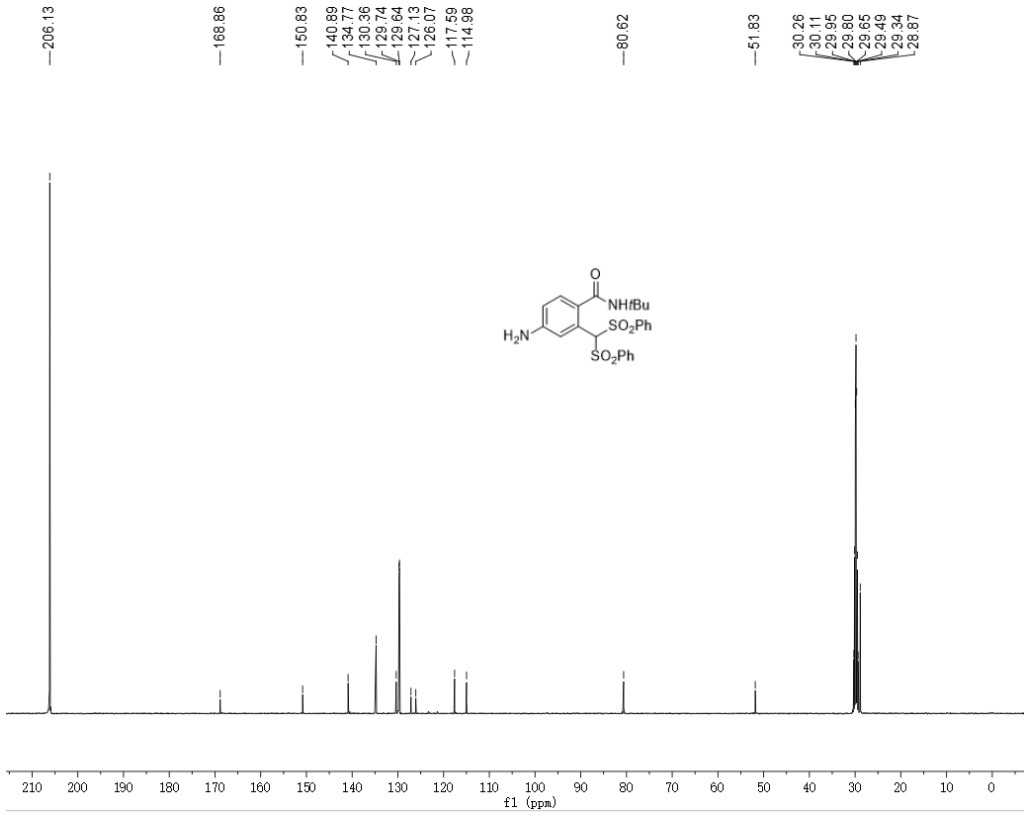
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3i in acetone-d_6



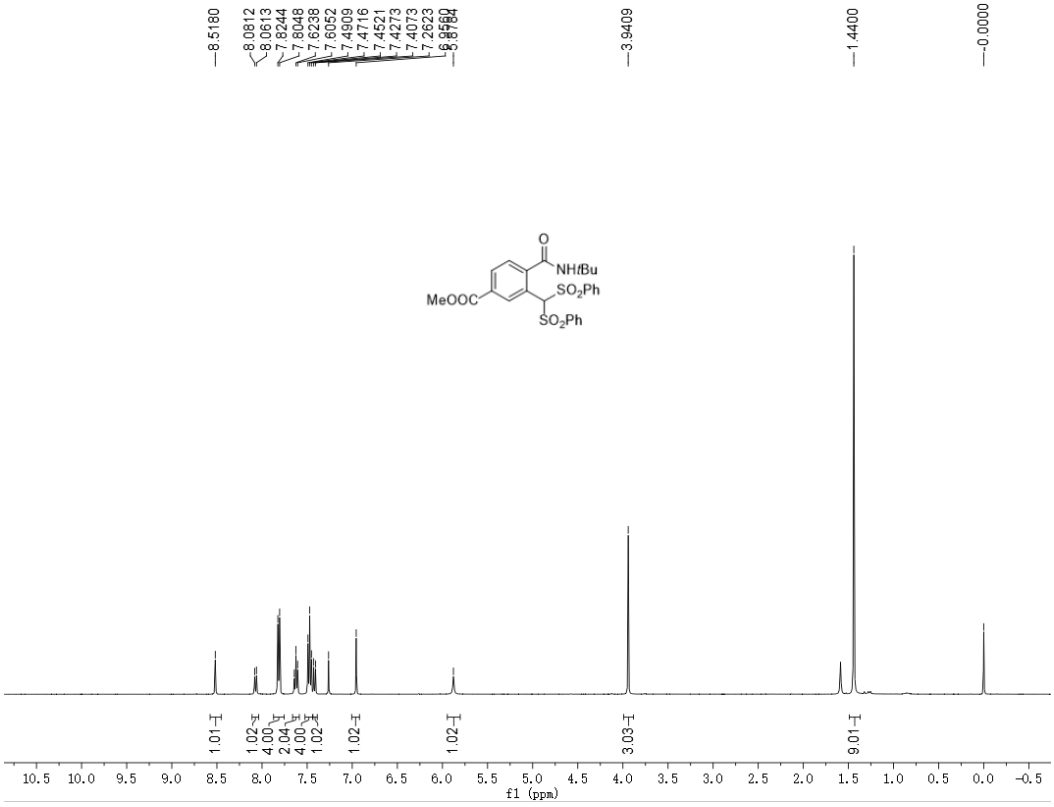
^{1}H NMR (500 MHz) Spectrum of 3j in acetone-d_6



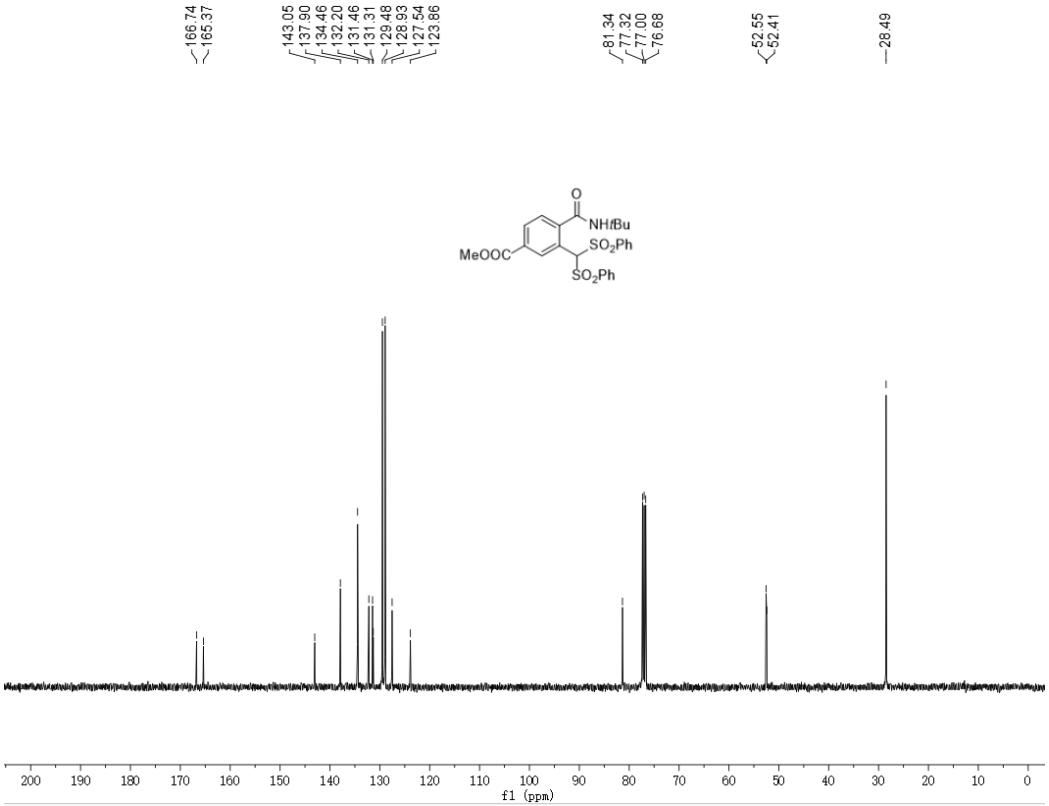
^{13}C{^{1}H} NMR (126 MHz) Spectrum of 3j in acetone-d_6



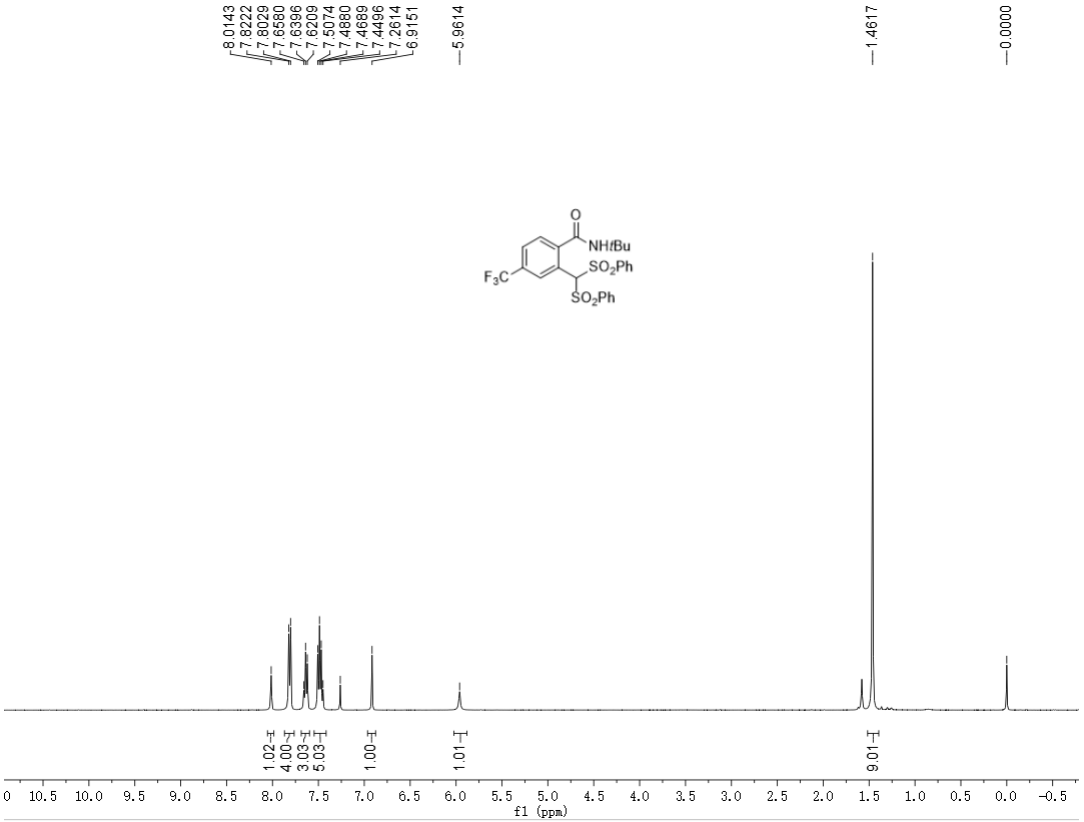
^{1}H NMR (400 MHz) Spectrum of 3k in $CDCl_3$



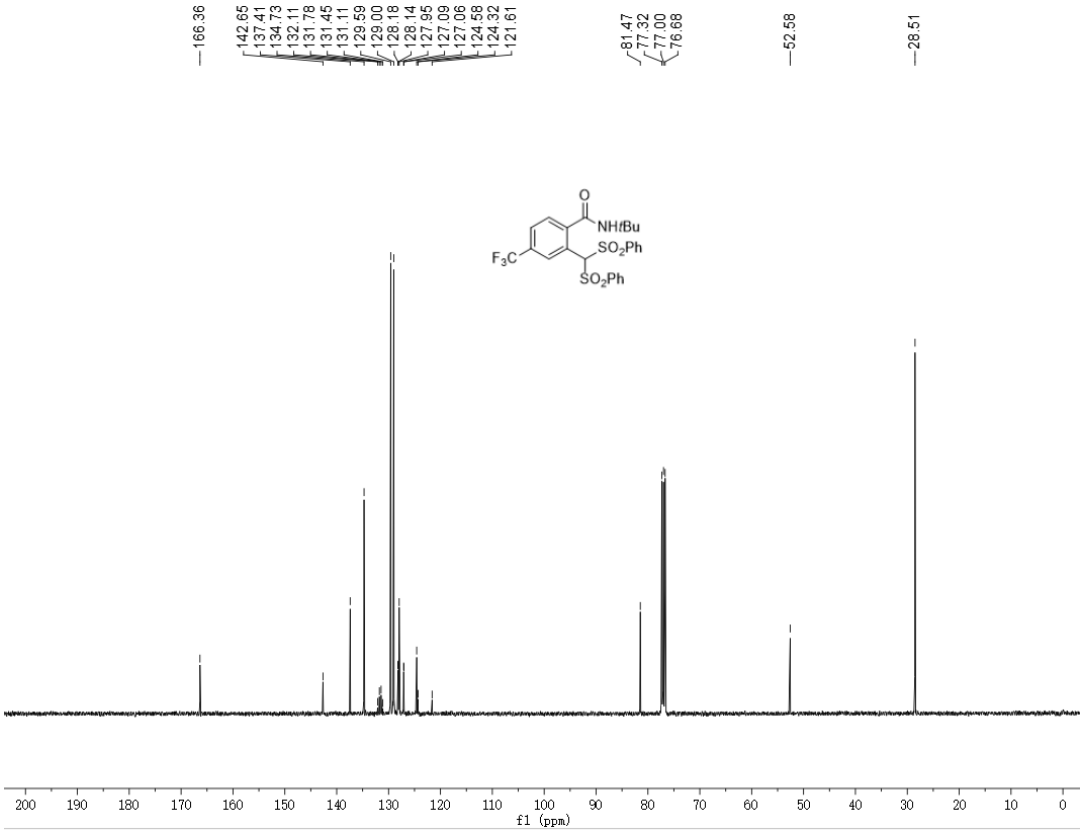
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3k in $CDCl_3$



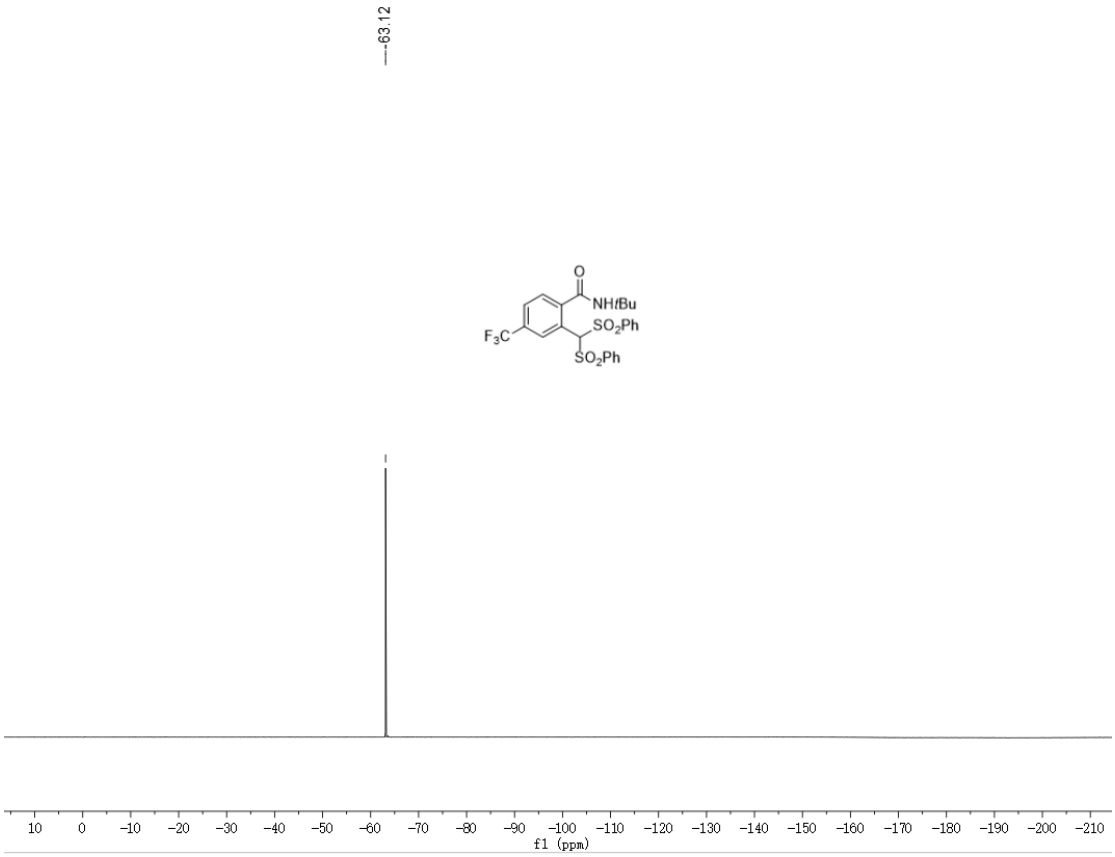
^{1}H NMR (400 MHz) Spectrum of 3l in $CDCl_3$



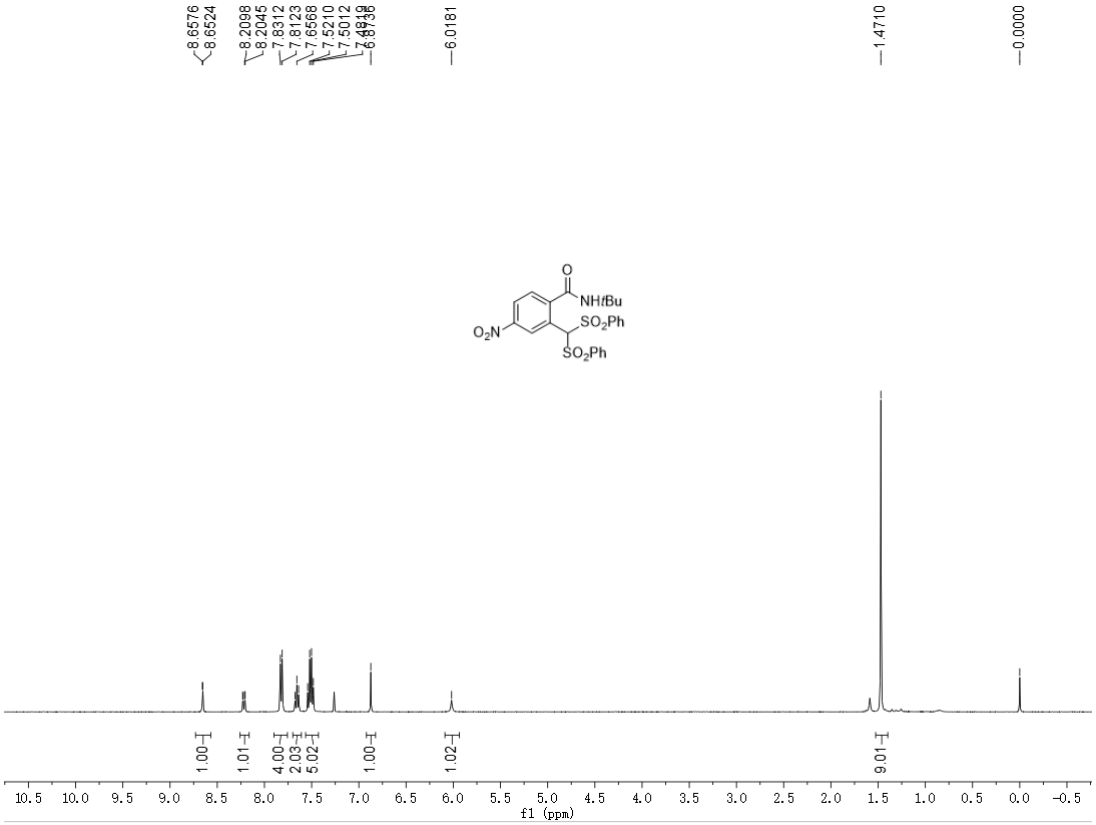
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3l in $CDCl_3$



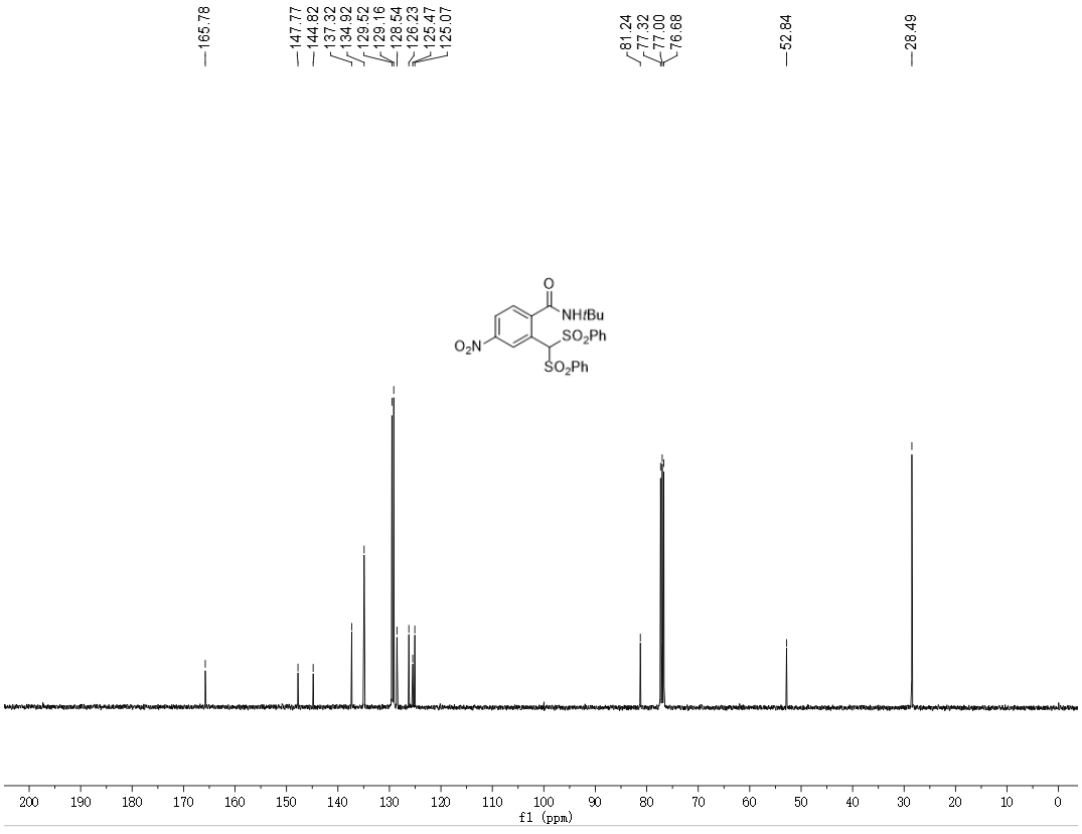
^{19}F NMR (376 MHz) Spectrum of 3l in $CDCl_3$



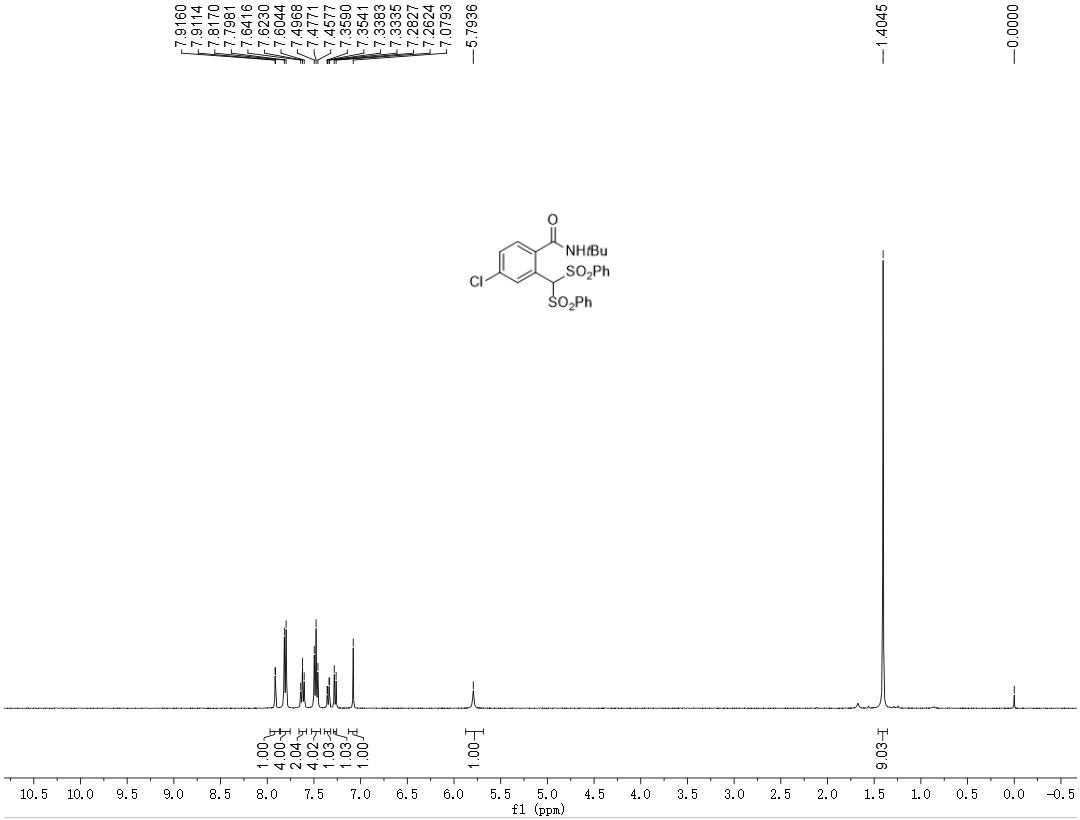
^{1}H NMR (400 MHz) Spectrum of 3m in $CDCl_3$



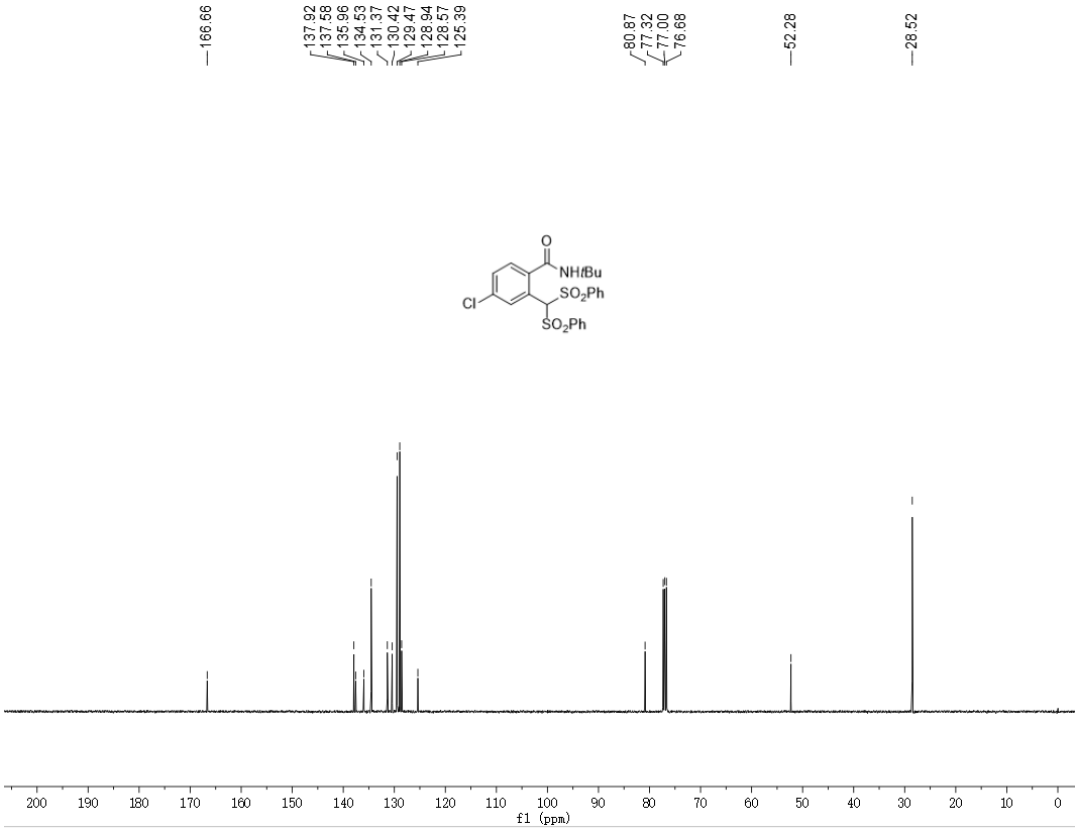
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3m in $CDCl_3$



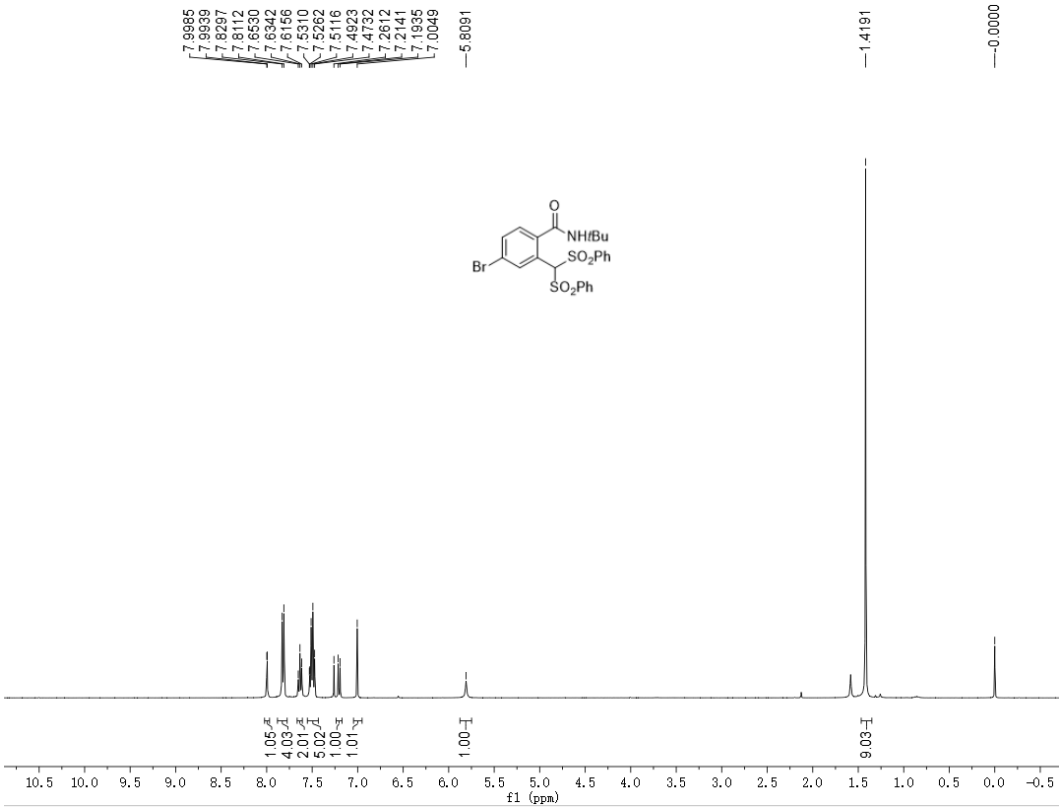
^{1}H NMR (400 MHz) Spectrum of 3n in $CDCl_3$



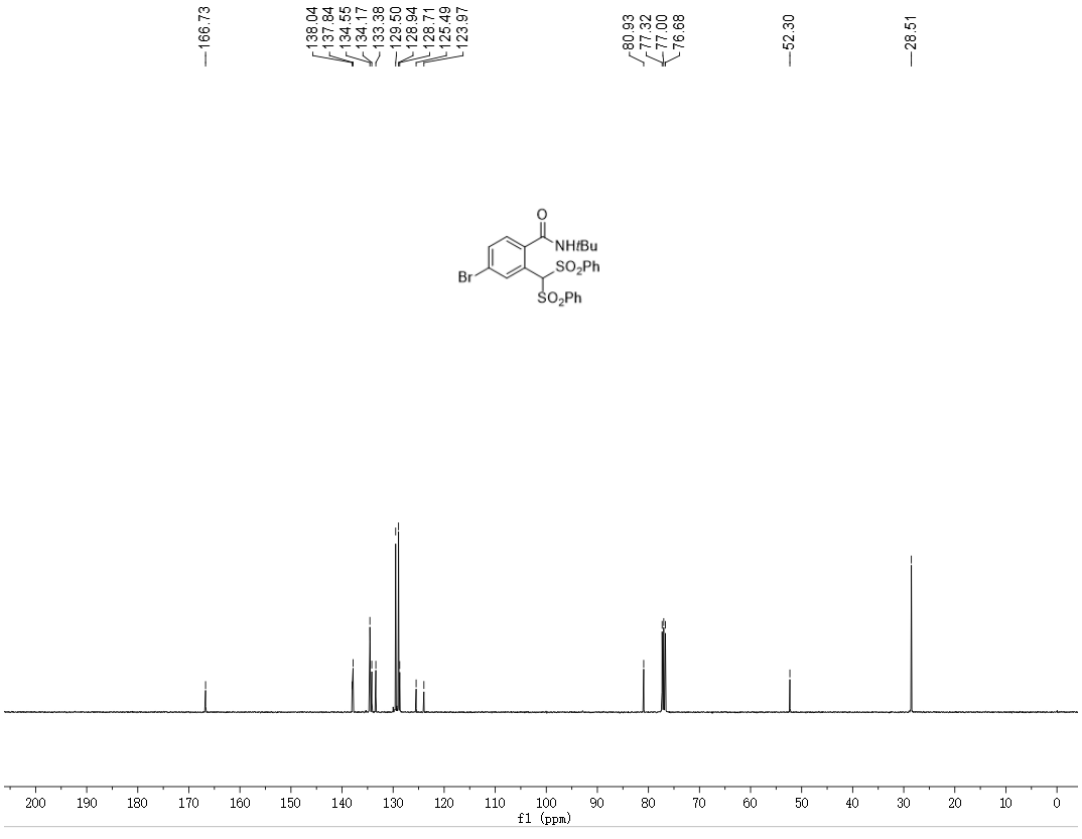
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3n in $CDCl_3$



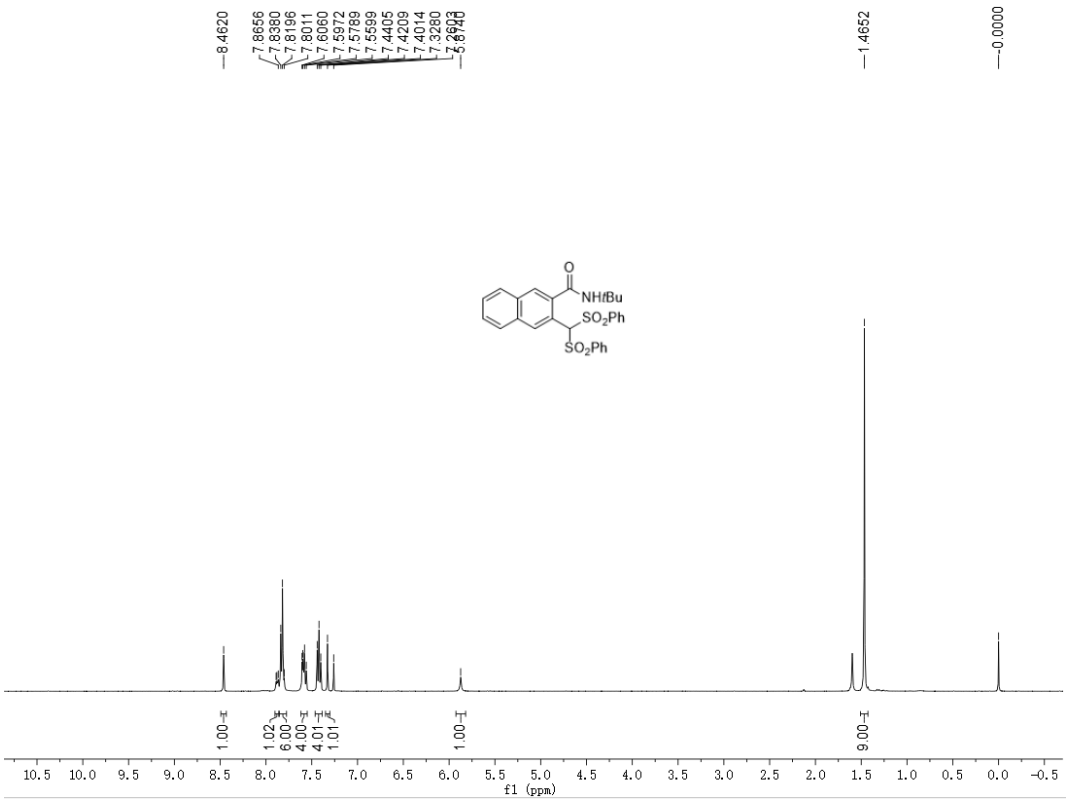
^{1}H NMR (400 MHz) Spectrum of 3o in $CDCl_3$



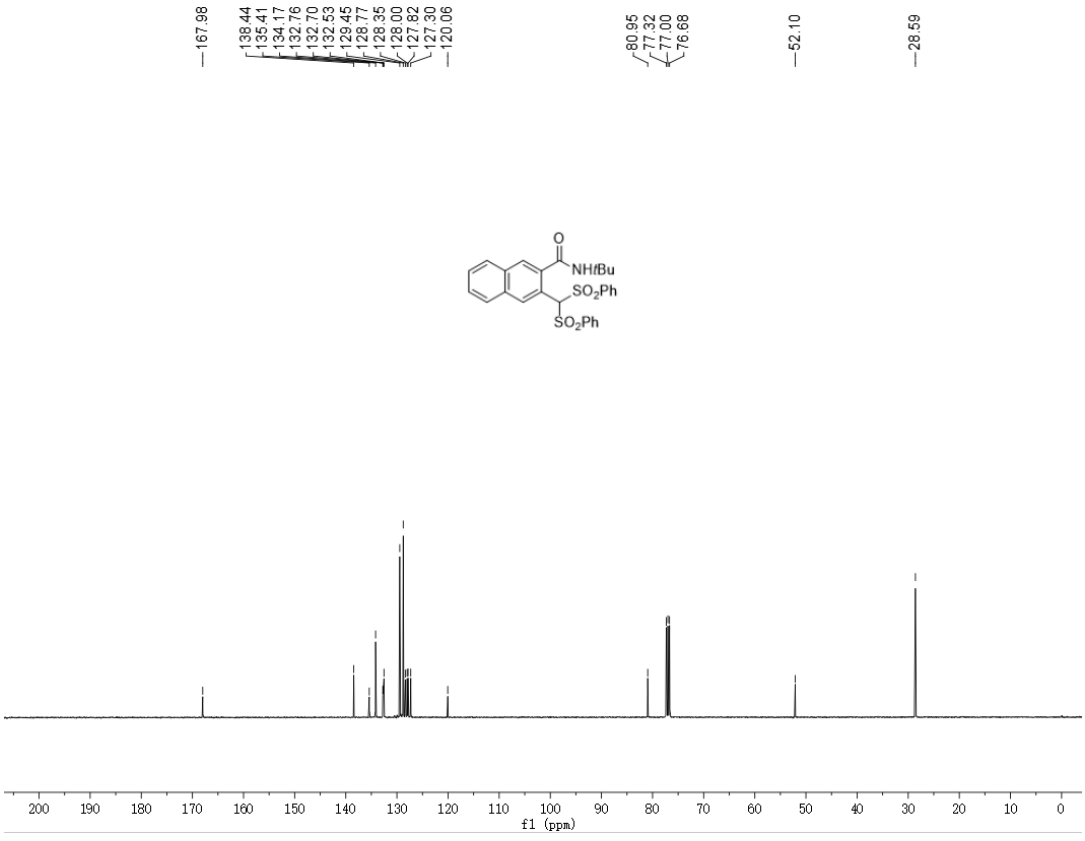
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3o in $CDCl_3$



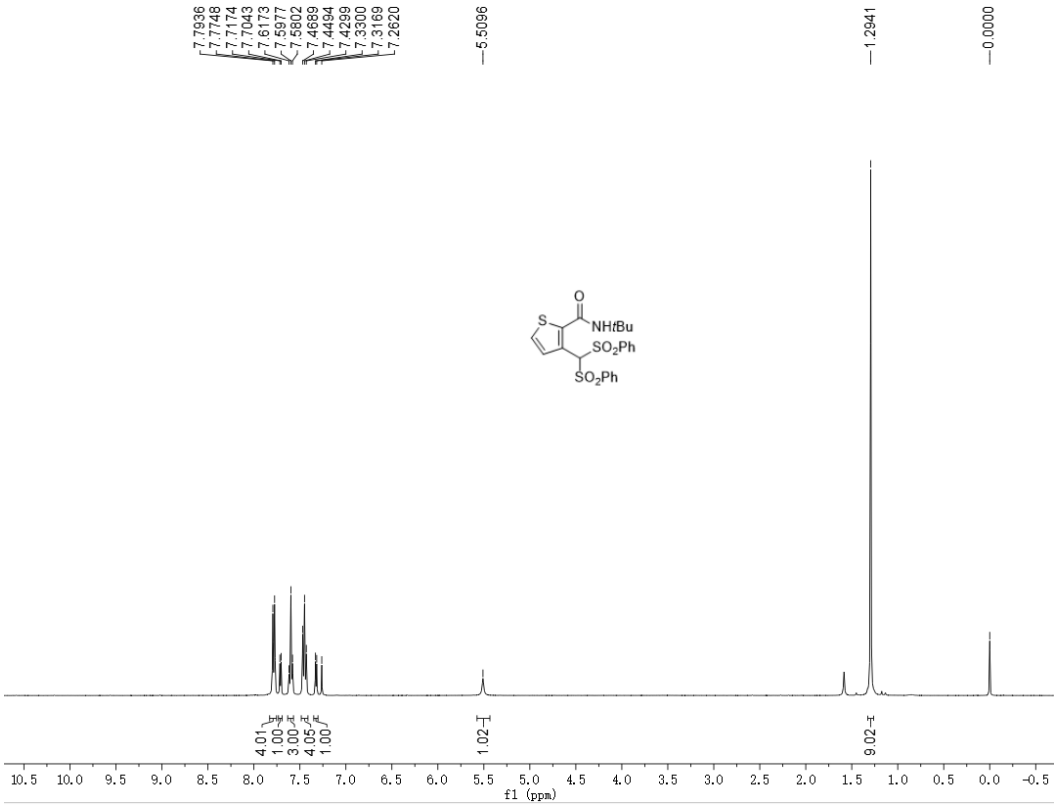
^{1}H NMR (400 MHz) Spectrum of 3p in $CDCl_3$



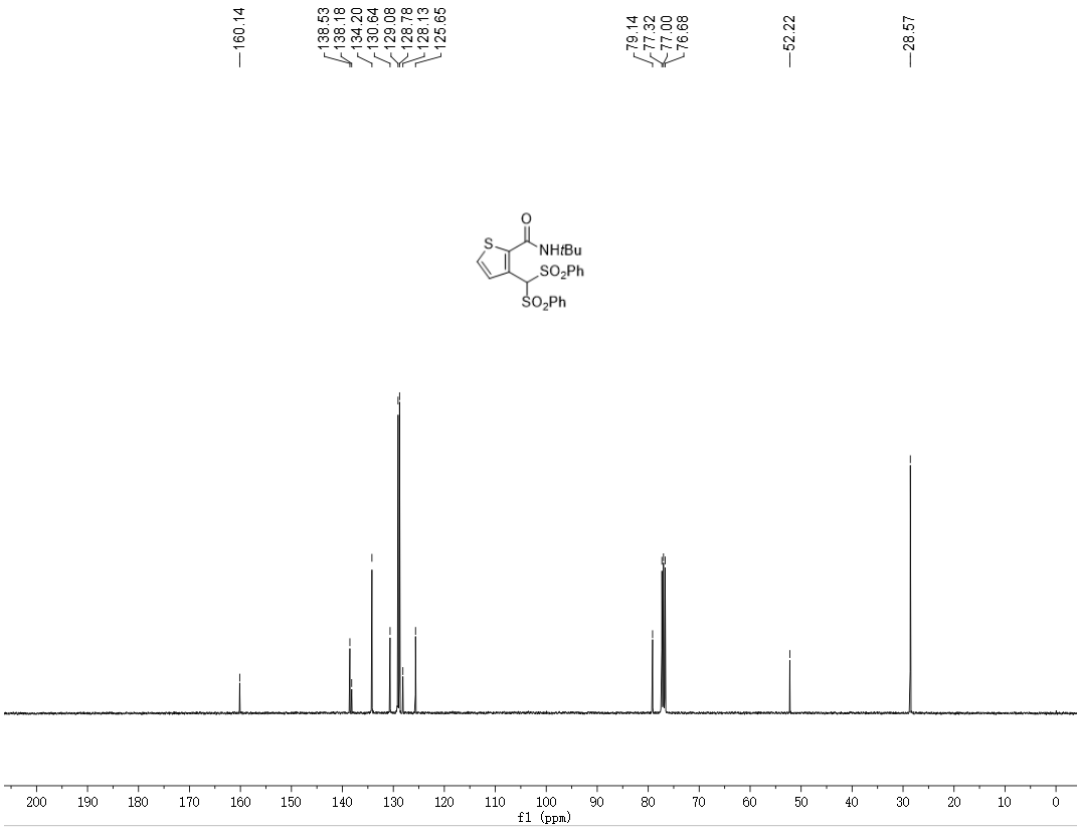
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3p in $CDCl_3$



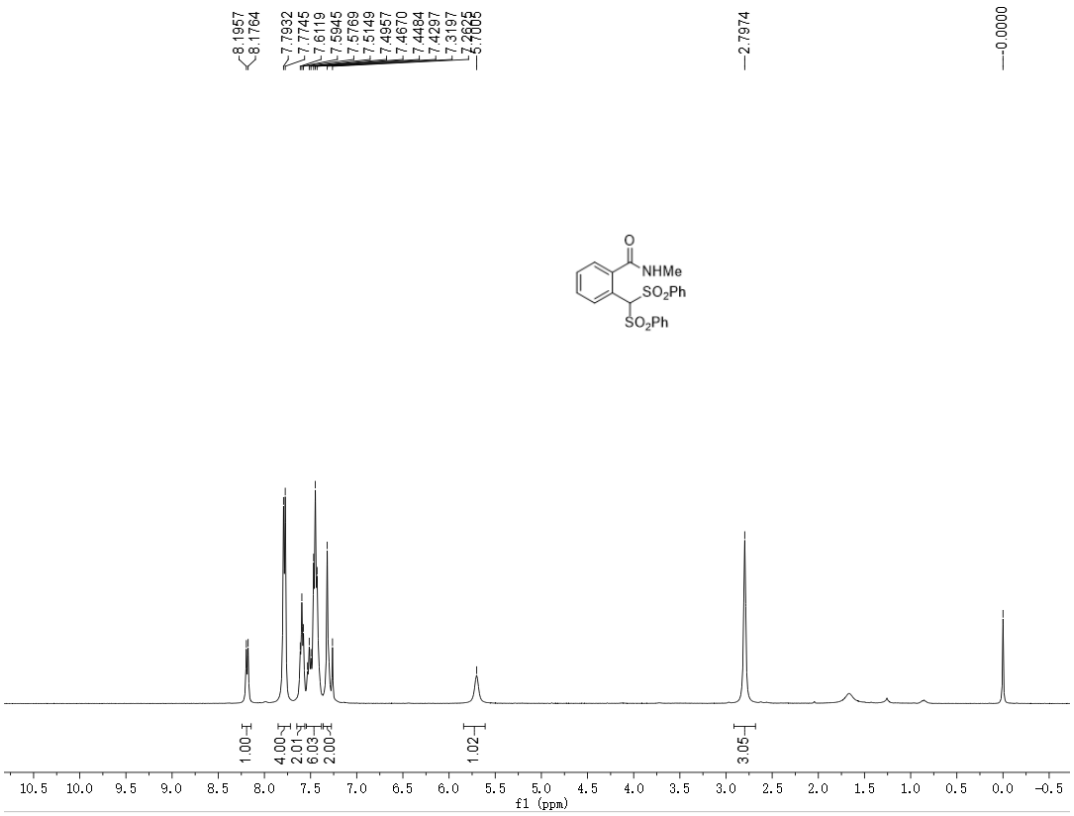
^{1}H NMR (400 MHz) Spectrum of 3q in $CDCl_3$



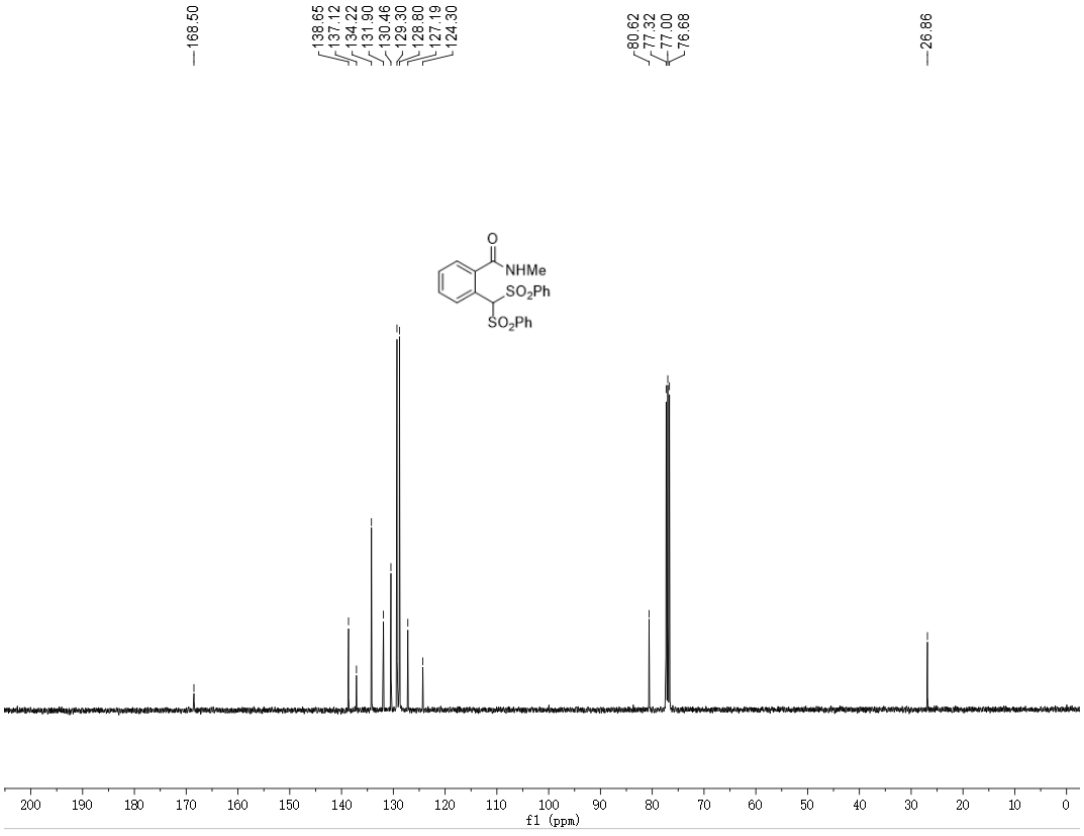
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 3q in $CDCl_3$



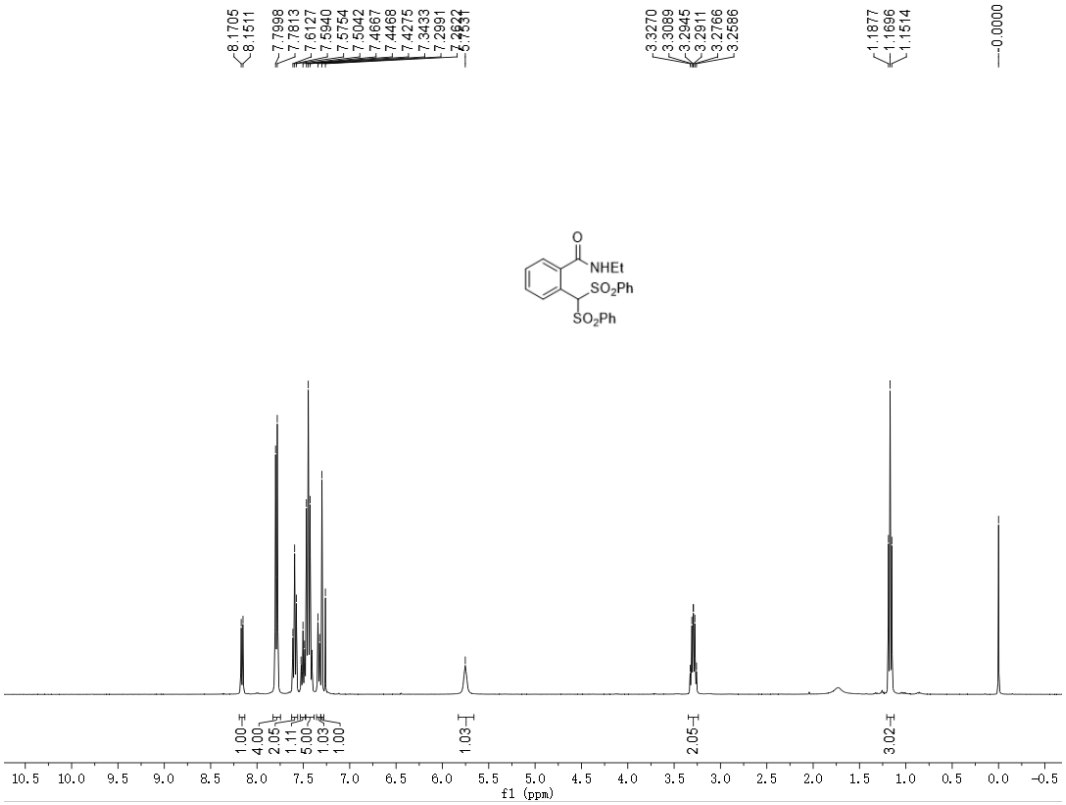
^{1}H NMR (400 MHz) Spectrum of 5a in $CDCl_3$



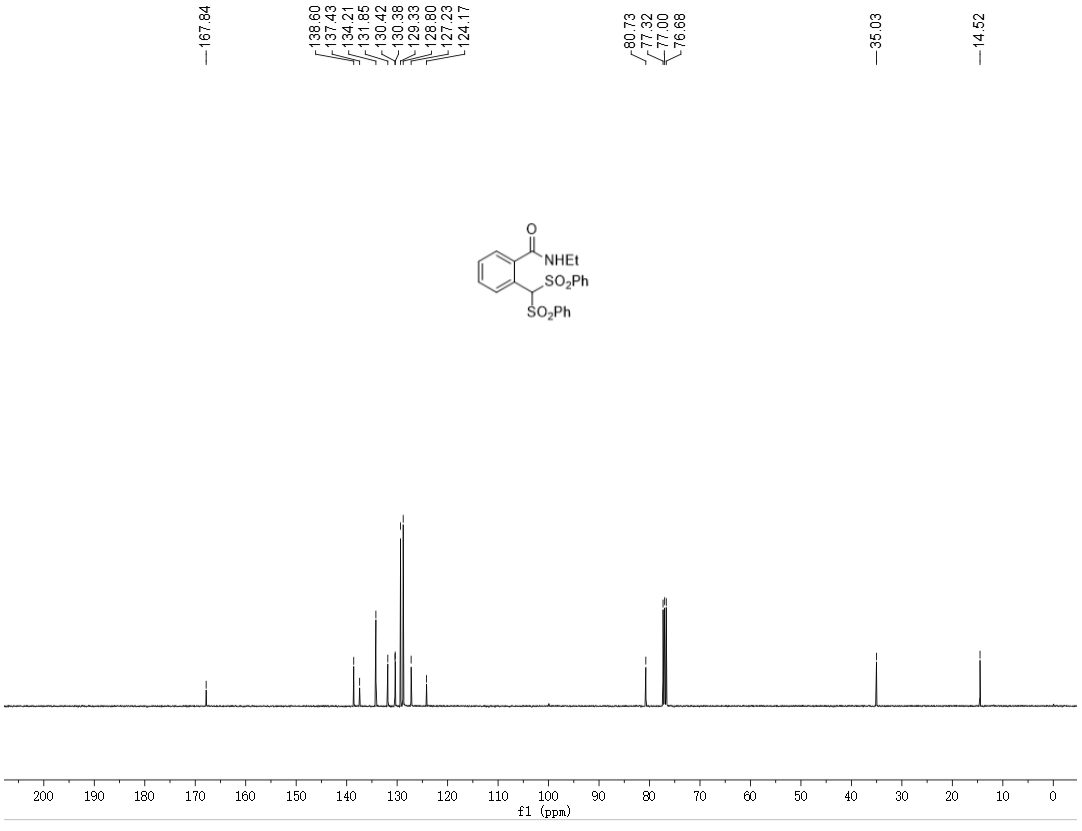
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5a in $CDCl_3$



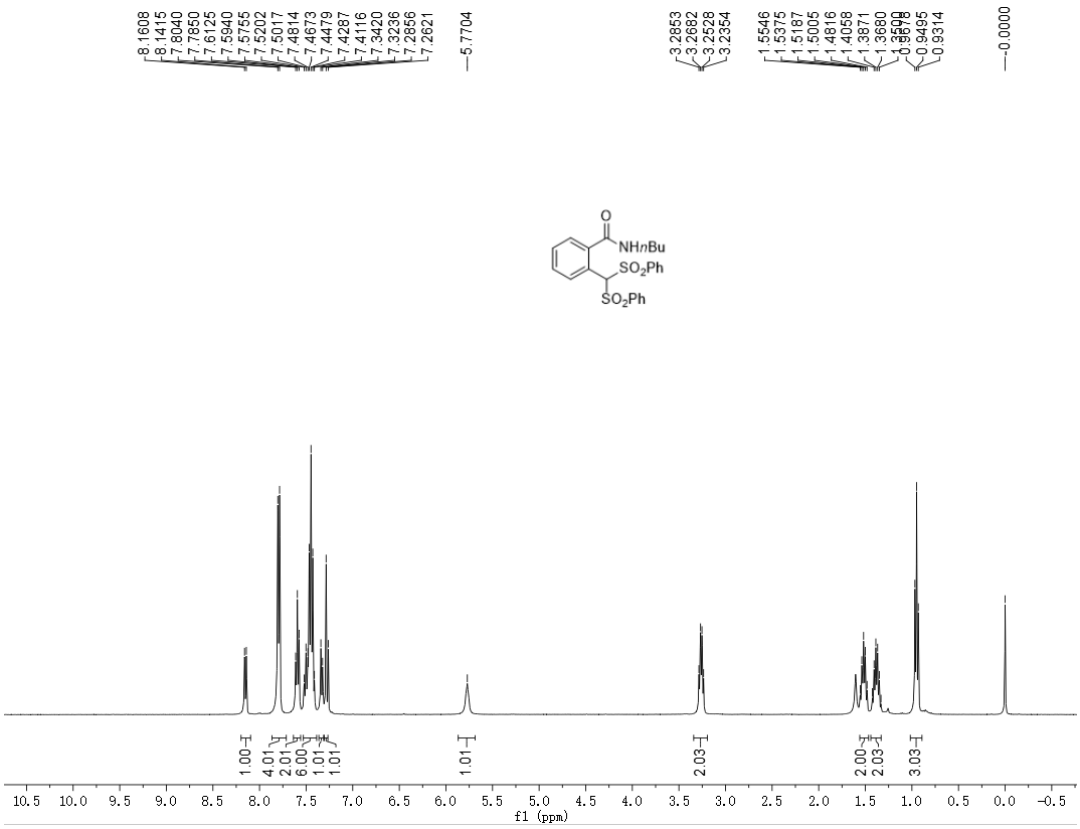
^{1}H NMR (400 MHz) Spectrum of 5b in $CDCl_3$



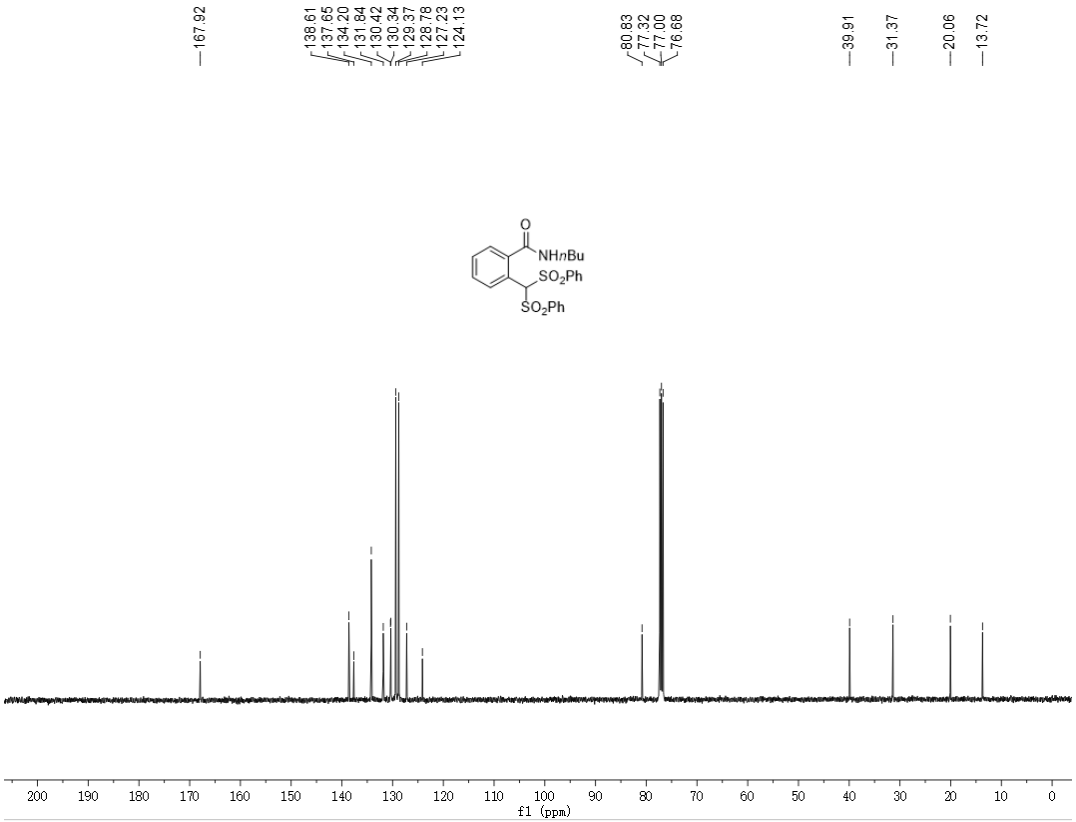
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5b in $CDCl_3$



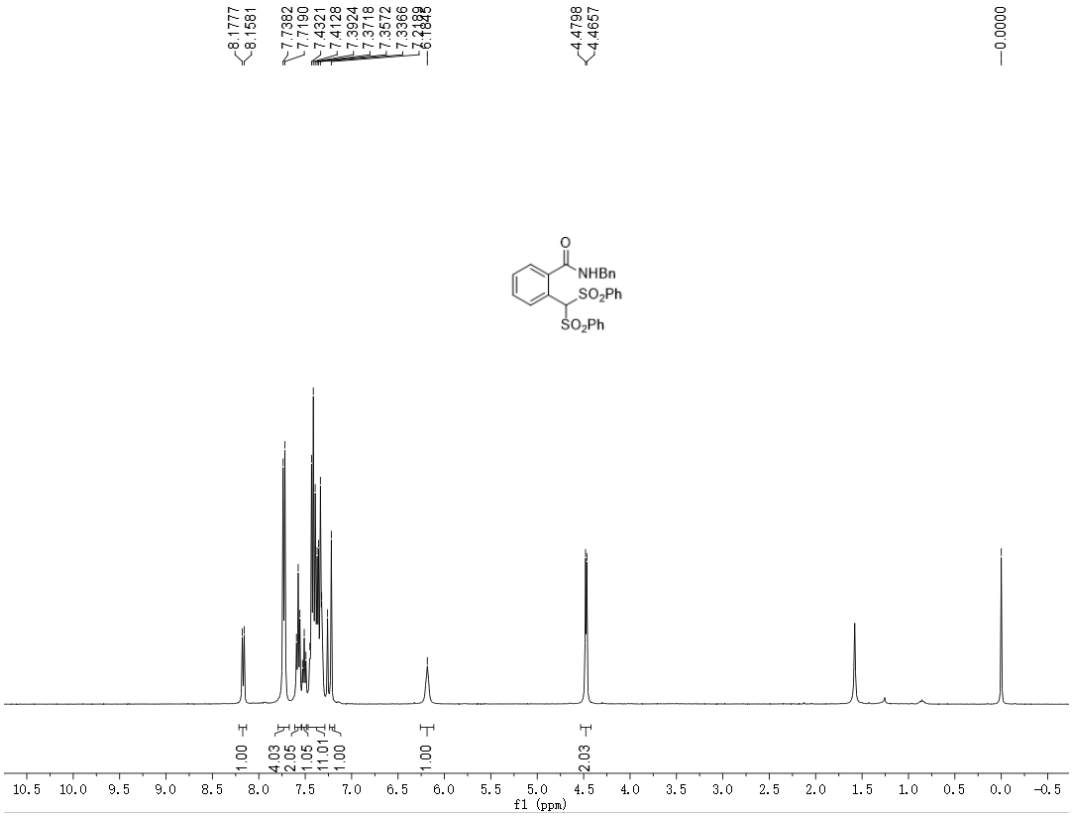
^{1}H NMR (400 MHz) Spectrum of 5c in $CDCl_3$



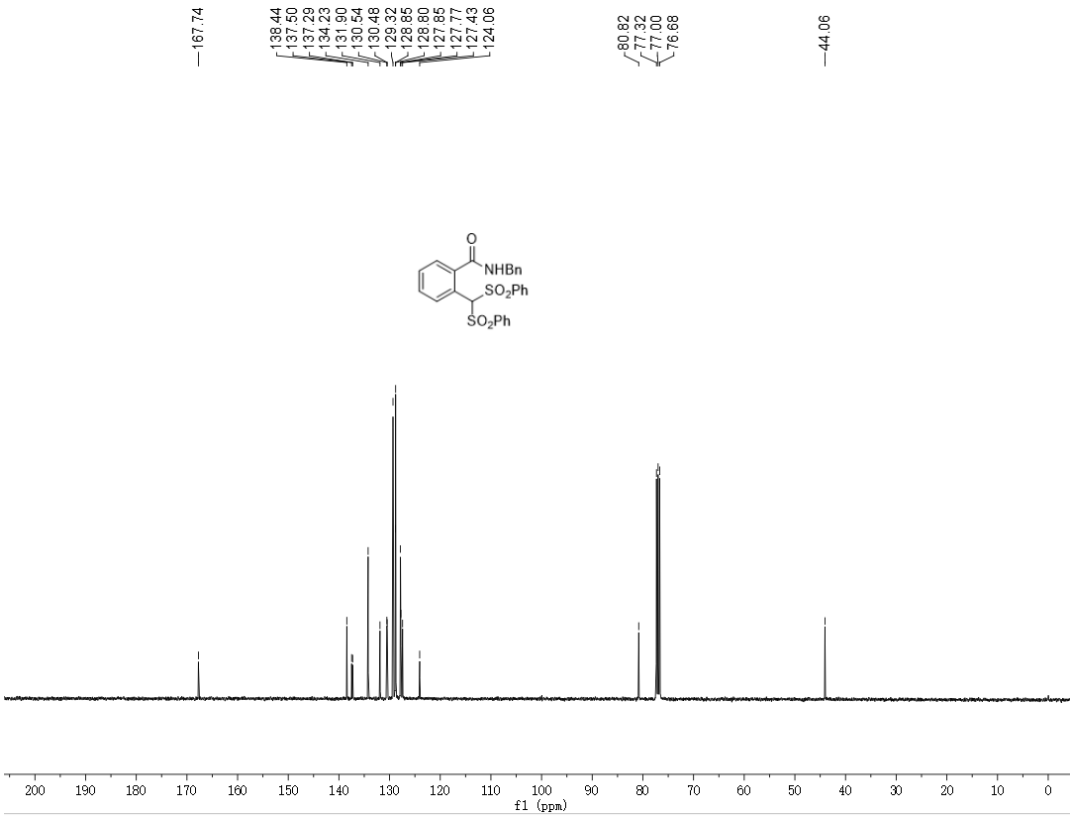
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5c in $CDCl_3$



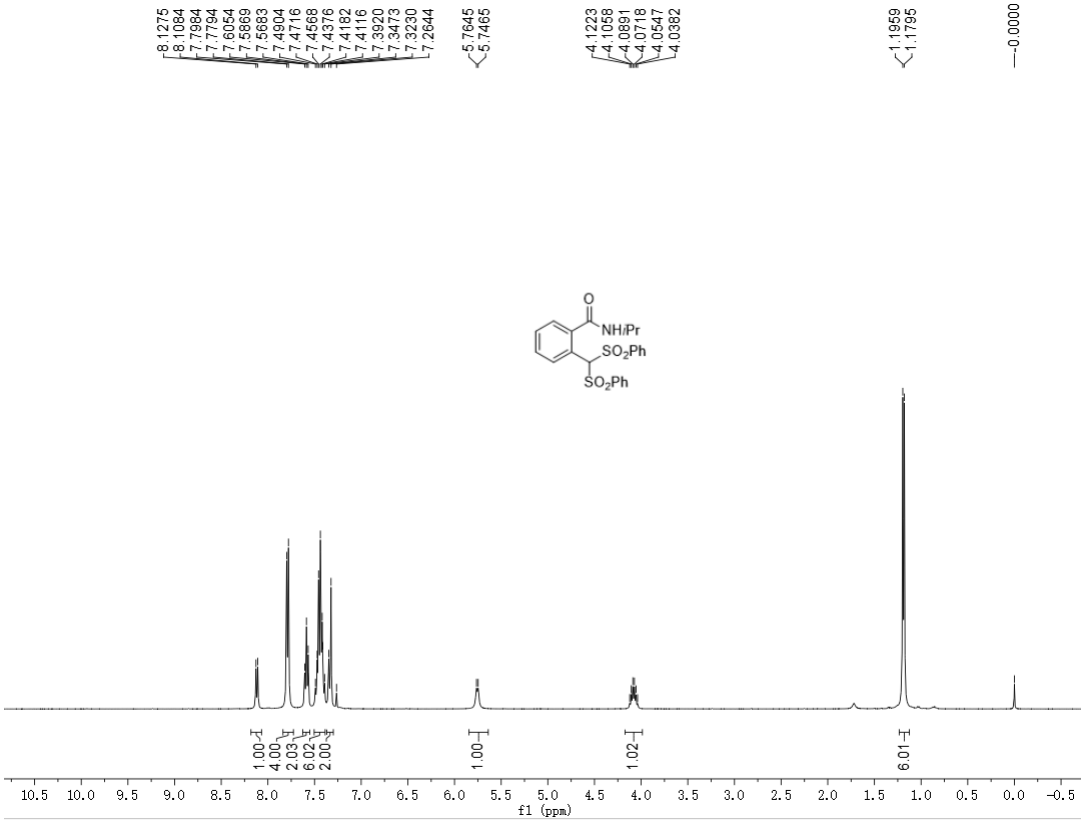
^{1}H NMR (400 MHz) Spectrum of 5d in $CDCl_3$



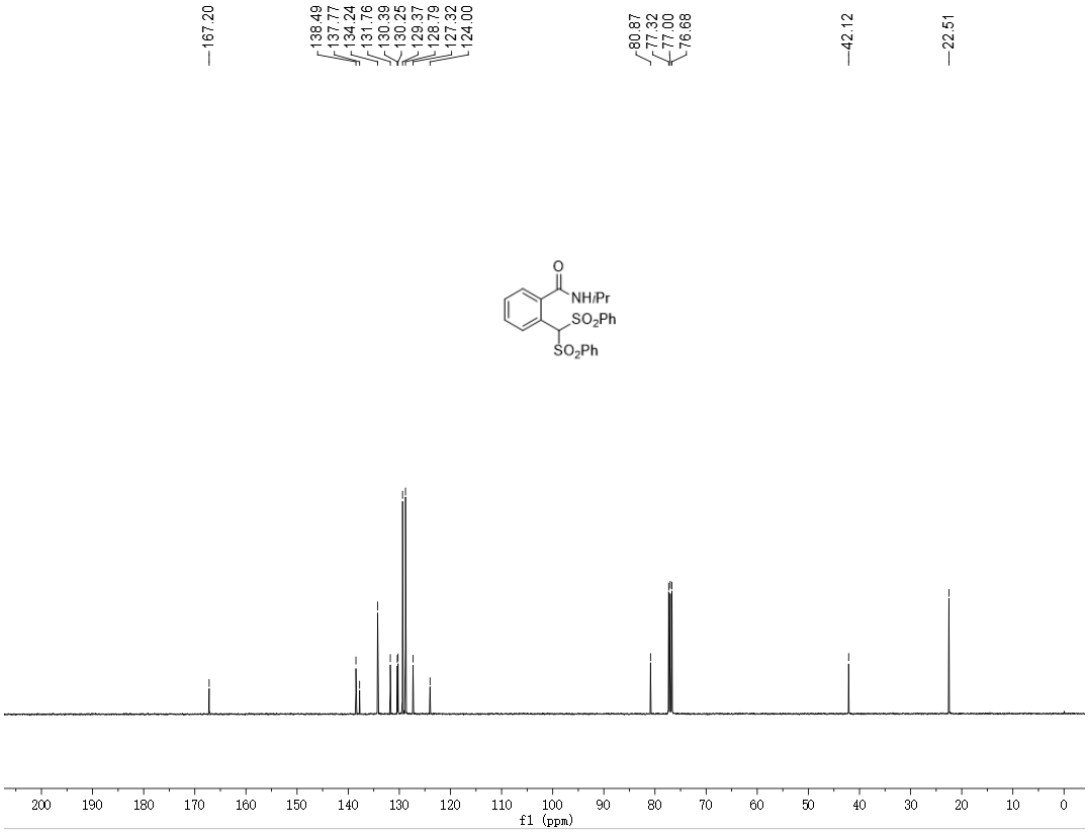
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5d in $CDCl_3$



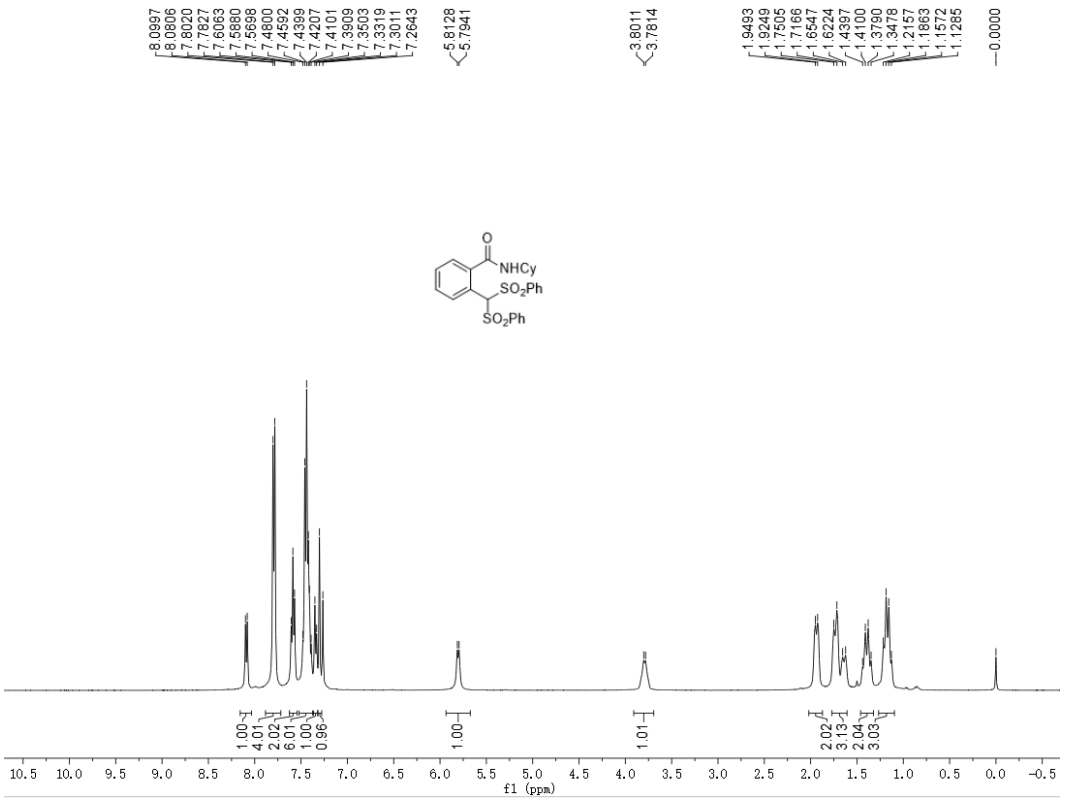
^{1}H NMR (400 MHz) Spectrum of 5e in $CDCl_3$



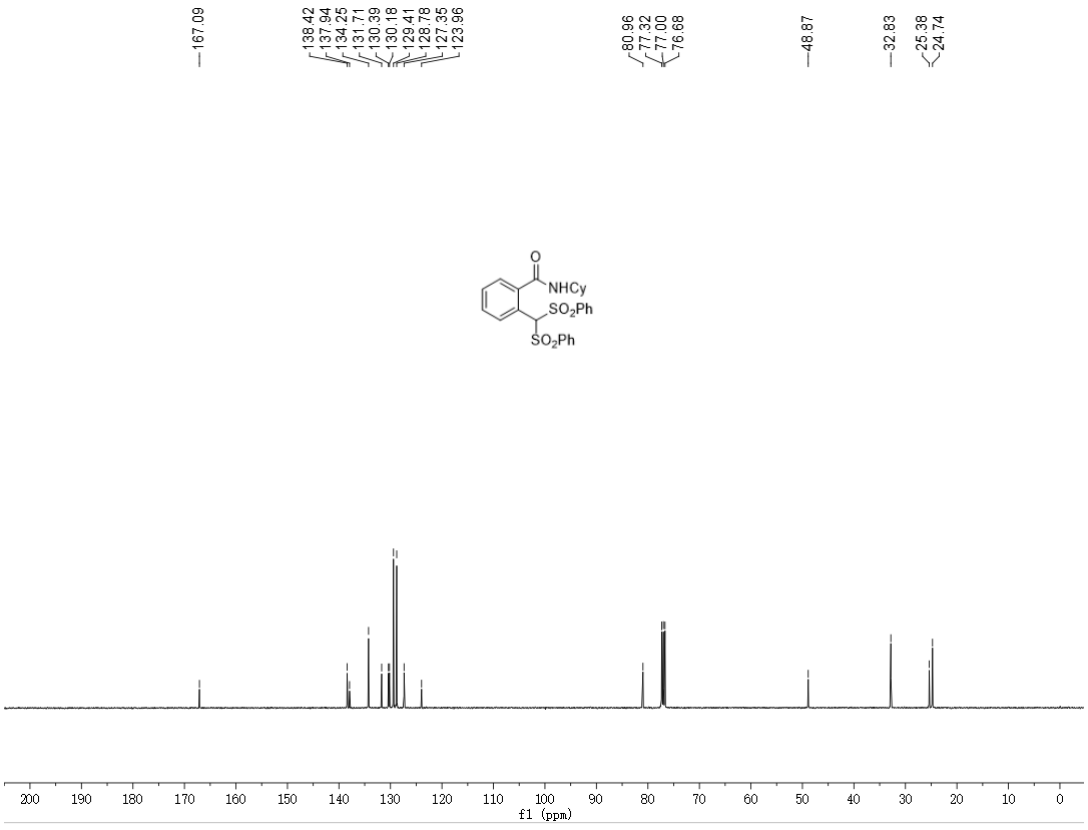
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5e in $CDCl_3$



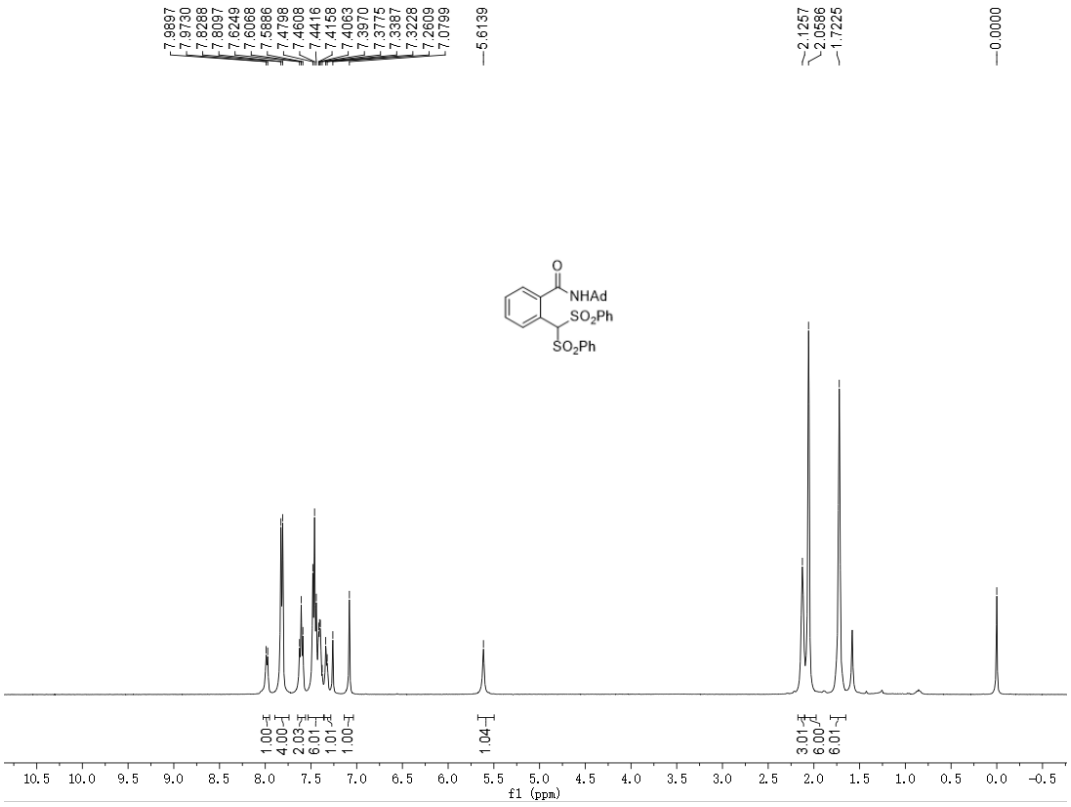
^{1}H NMR (400 MHz) Spectrum of 5f in $CDCl_3$



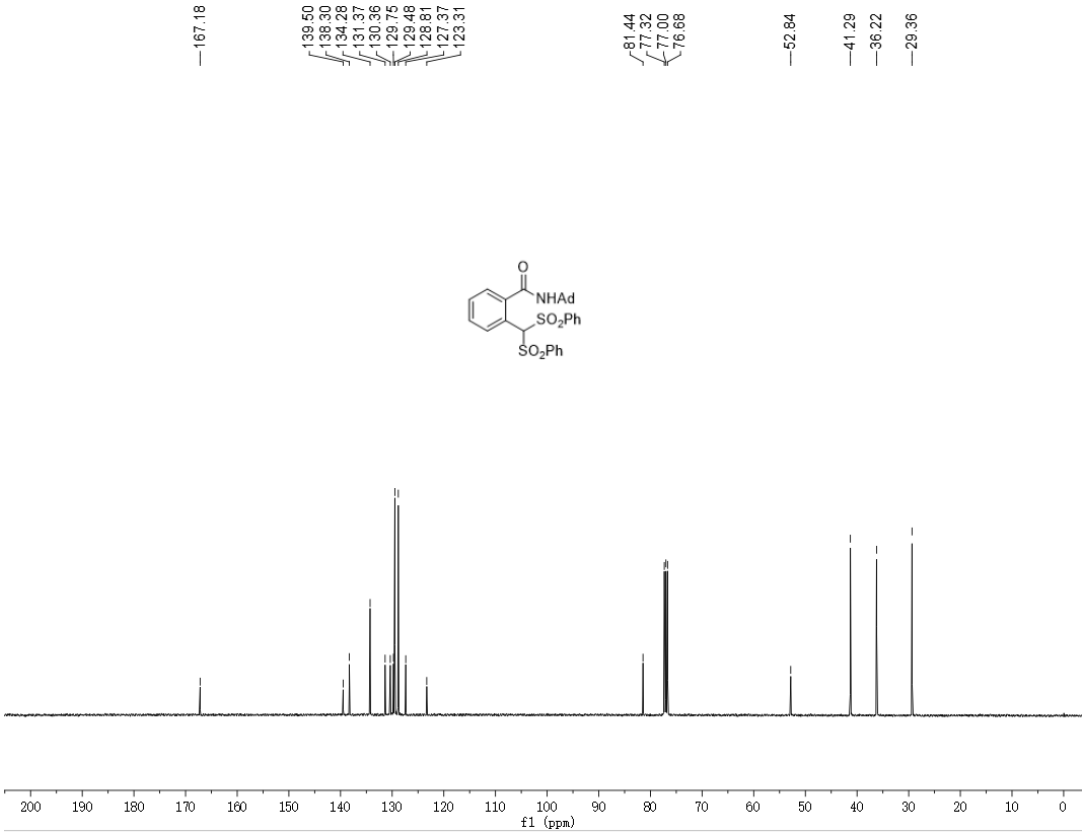
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5f in $CDCl_3$



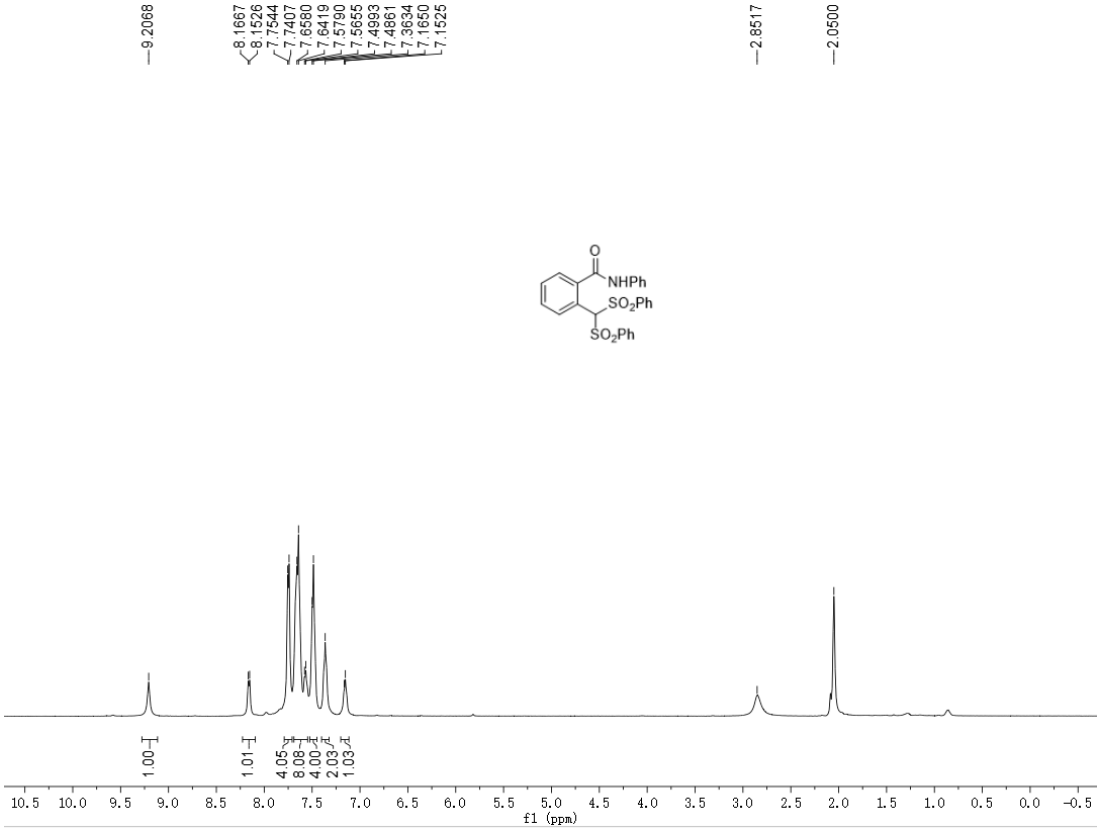
^{1}H NMR (400 MHz) Spectrum of 5g in $CDCl_3$



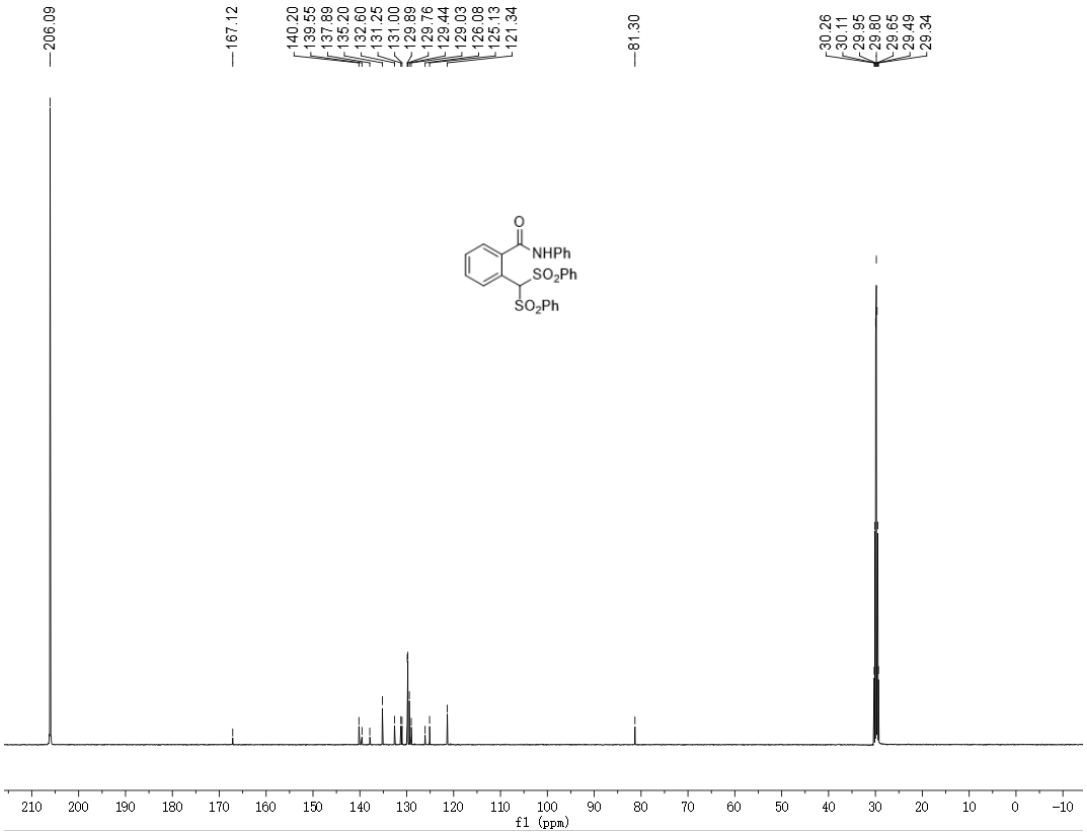
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 5g in $CDCl_3$



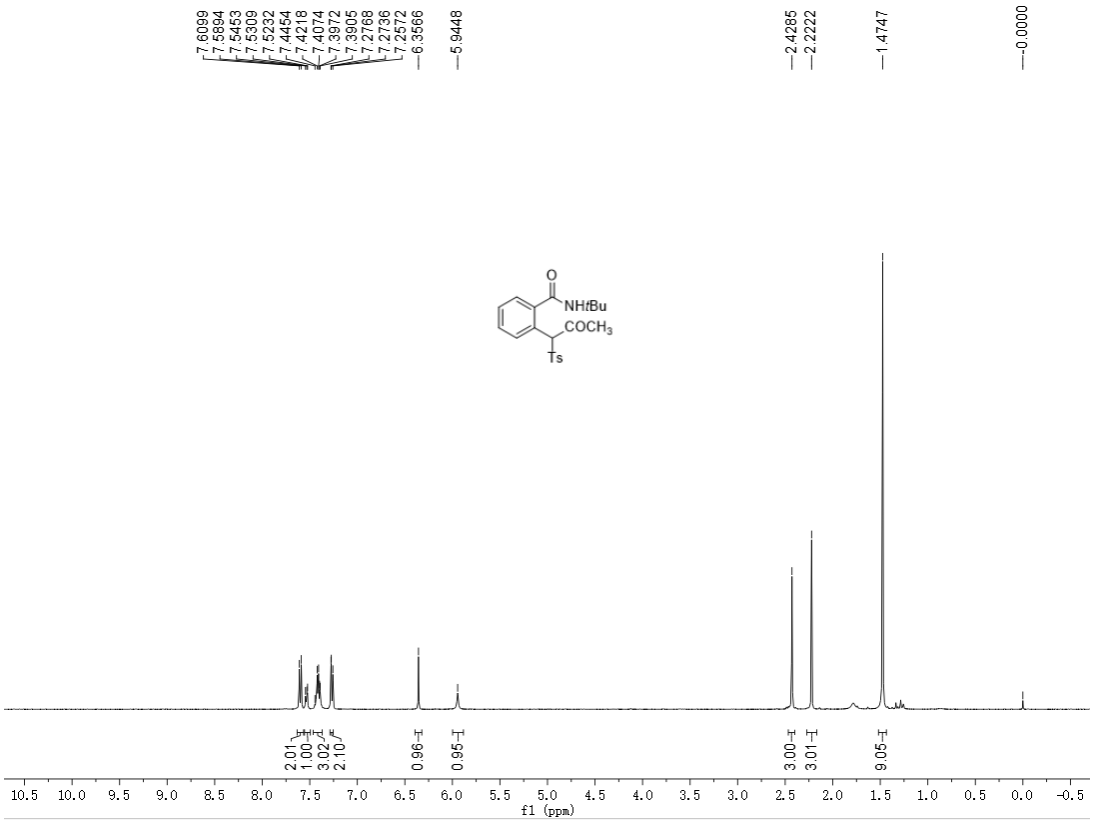
^{1}H NMR (500 MHz) Spectrum of 5h in acetone-d_6



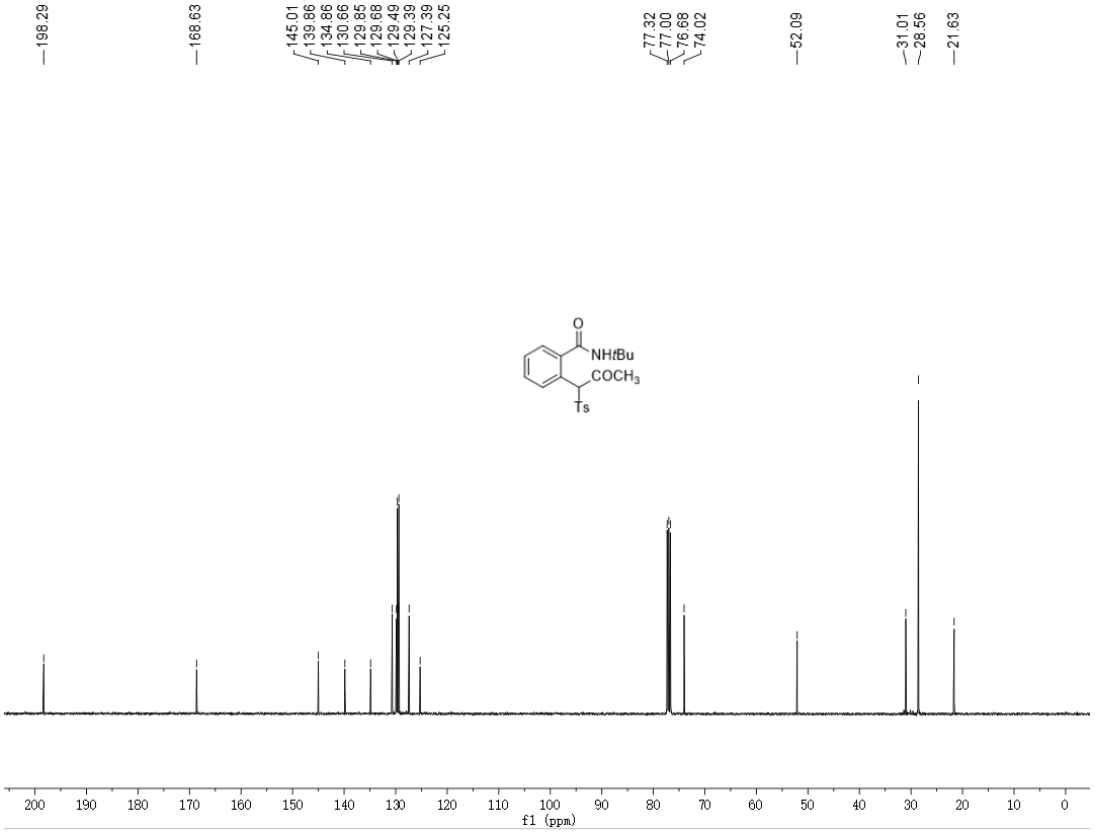
^{13}C{^{1}H} NMR (126 MHz) Spectrum of 5h in acetone-d_6



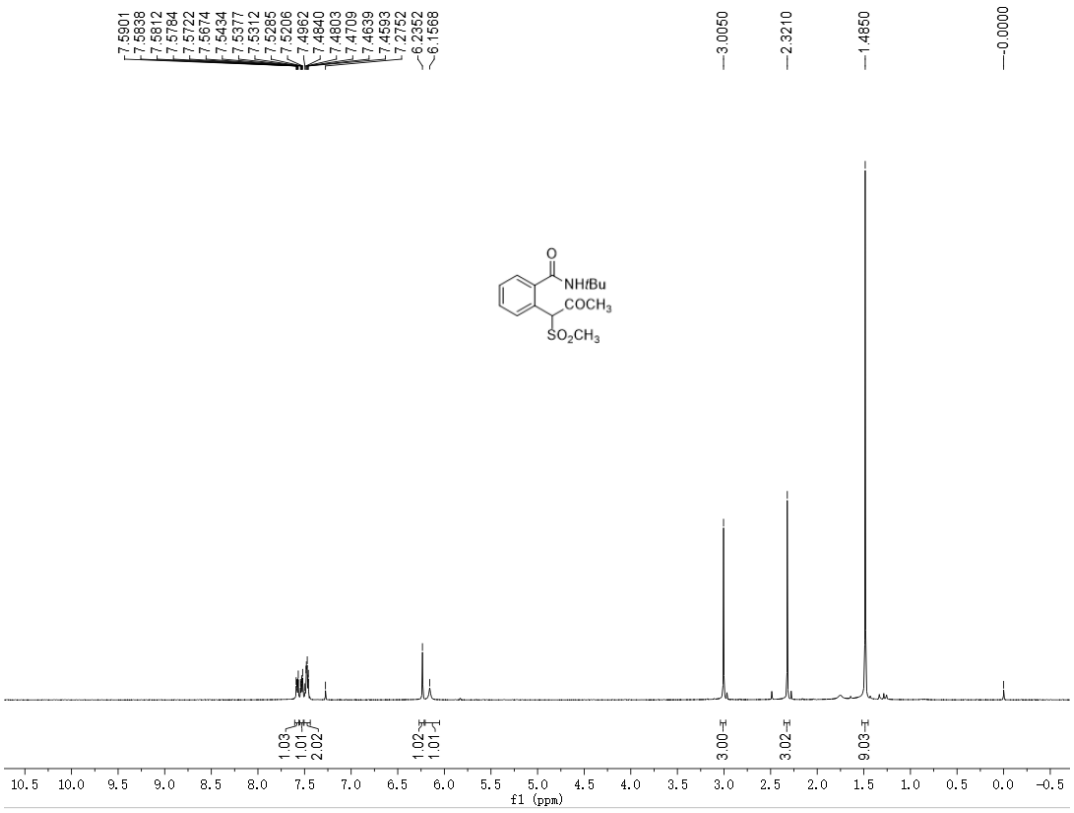
^{1}H NMR (400 MHz) Spectrum of 6a in $CDCl_3$



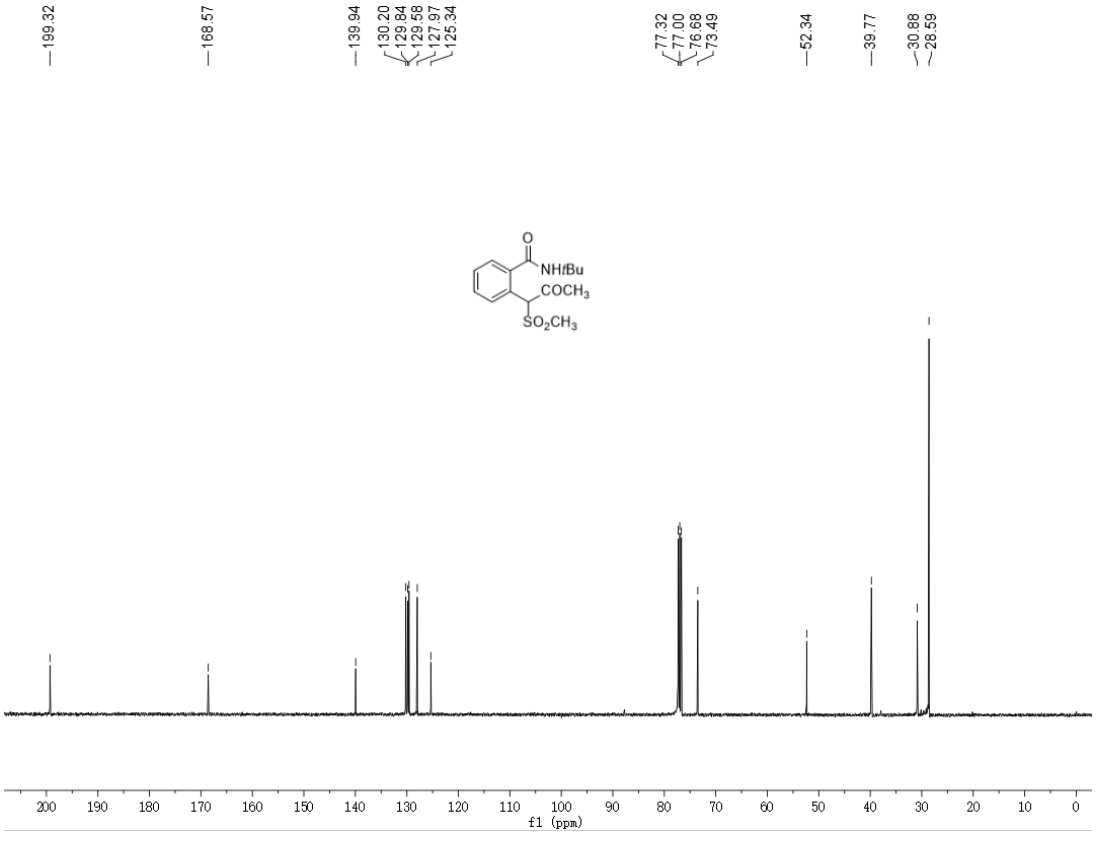
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 6a in $CDCl_3$



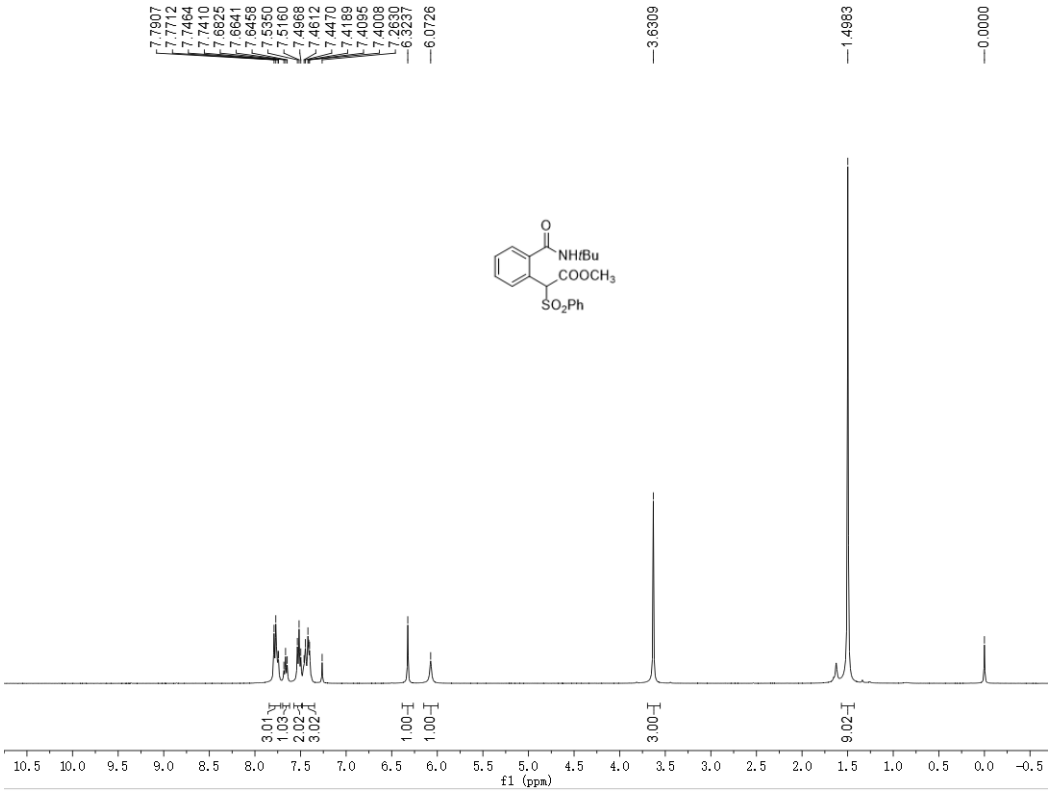
^{1}H NMR (400 MHz) Spectrum of 6b in $CDCl_3$



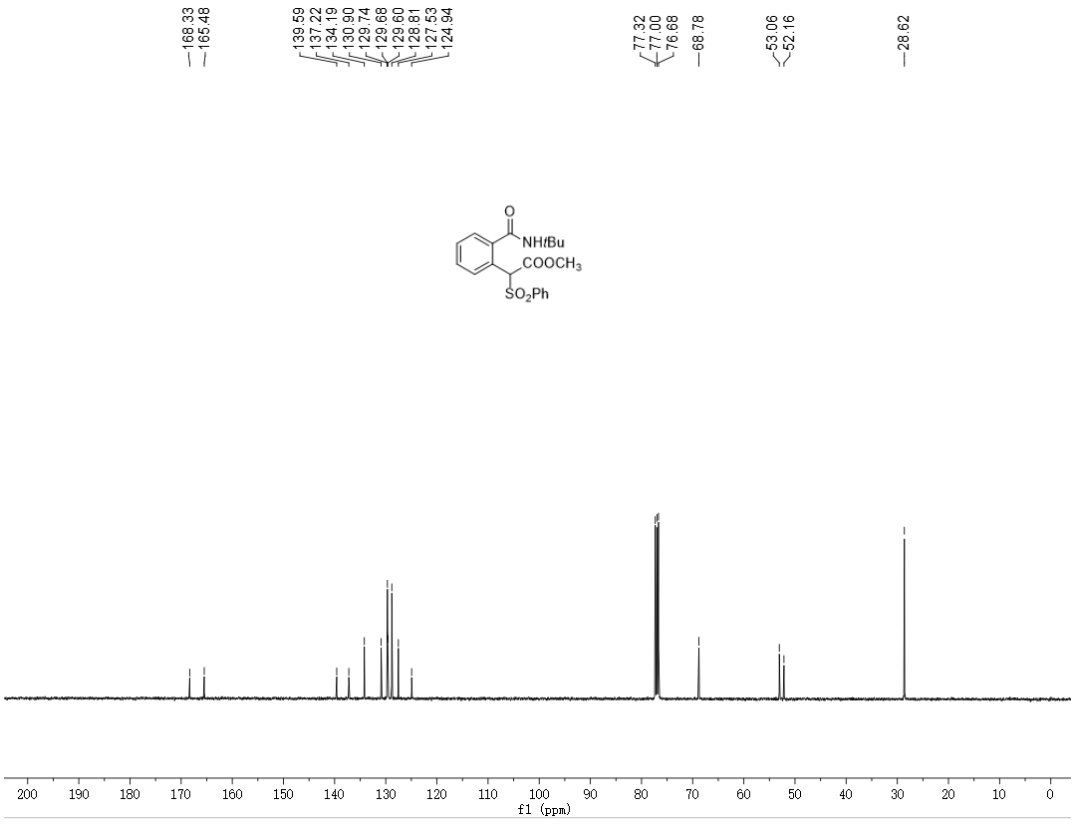
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 6b in $CDCl_3$



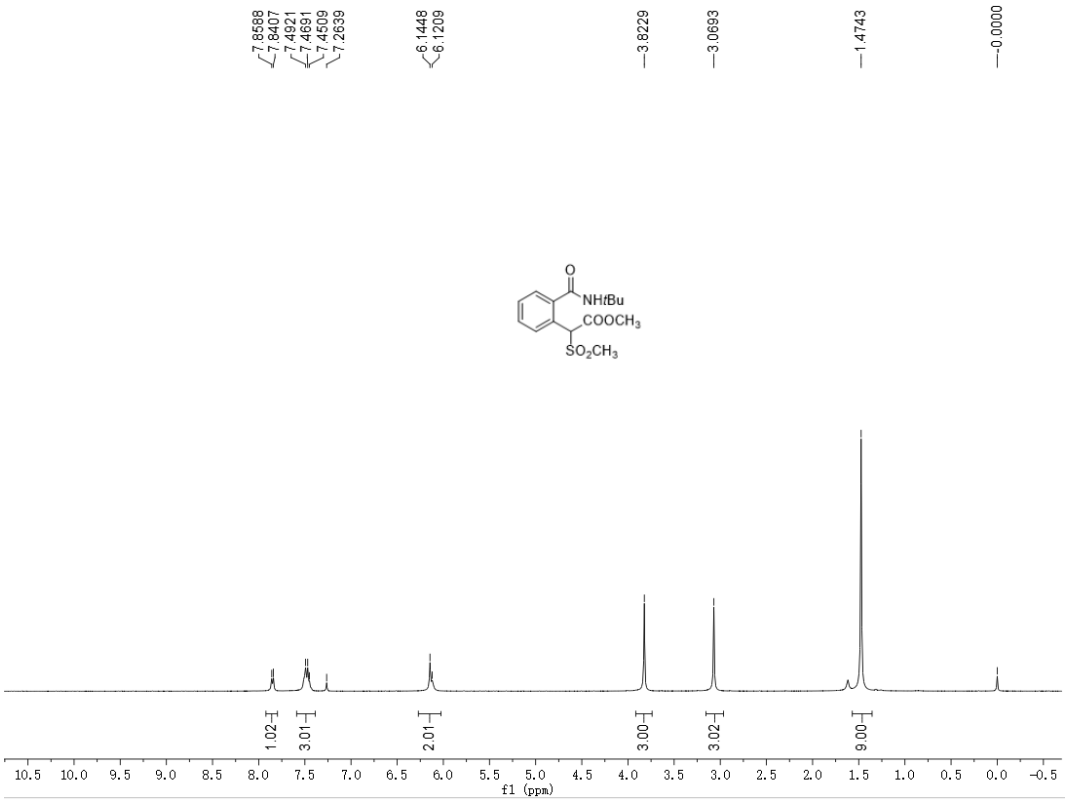
^{1}H NMR (400 MHz) Spectrum of 6c in $CDCl_3$



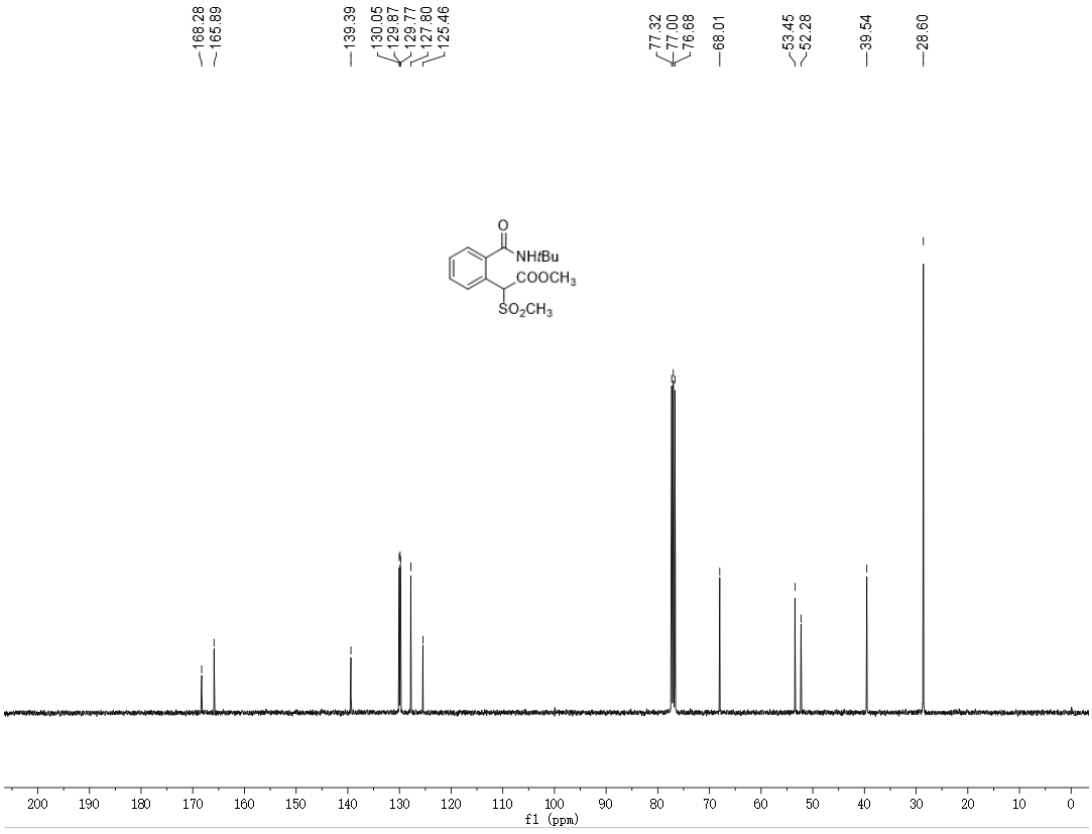
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 6c in $CDCl_3$



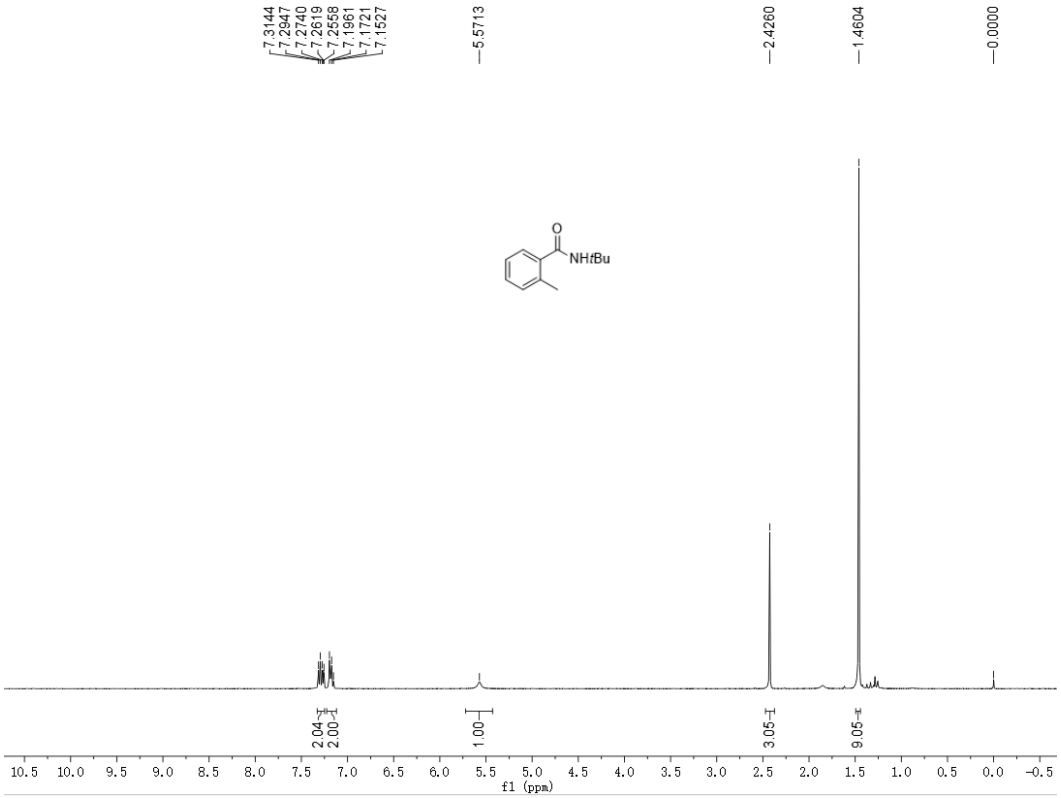
^{1}H NMR (400 MHz) Spectrum of 6d in $CDCl_3$



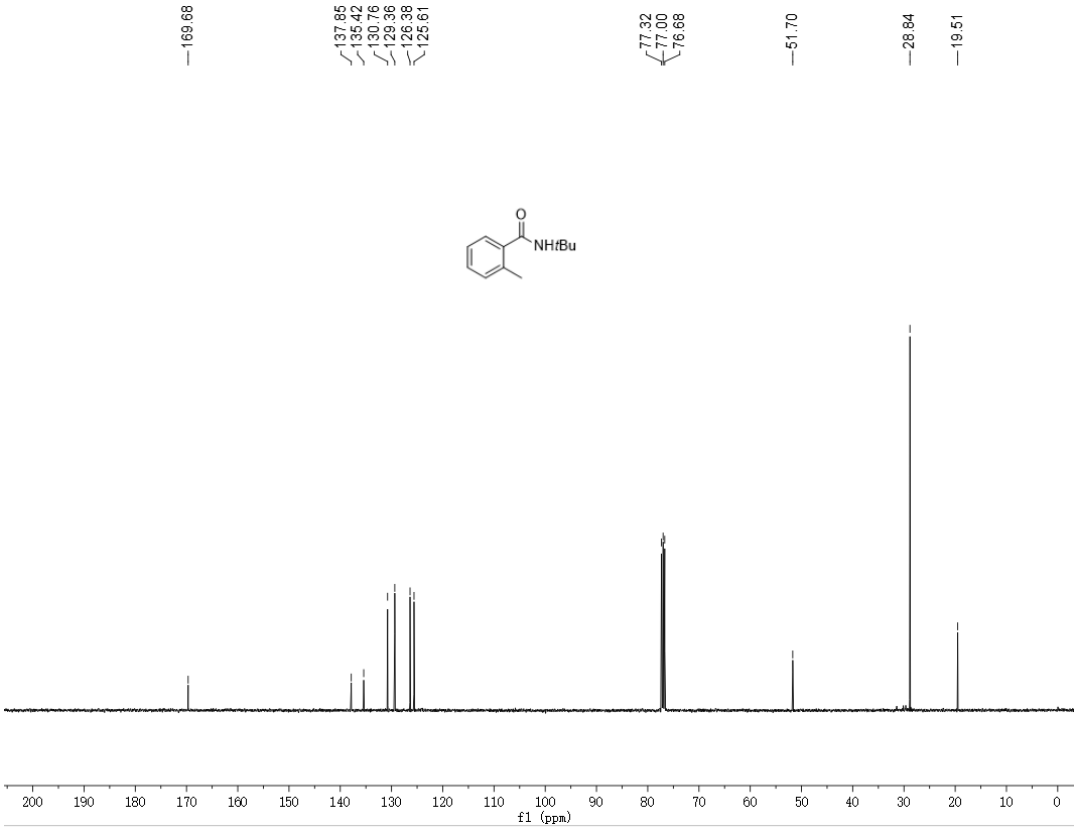
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 6d in $CDCl_3$



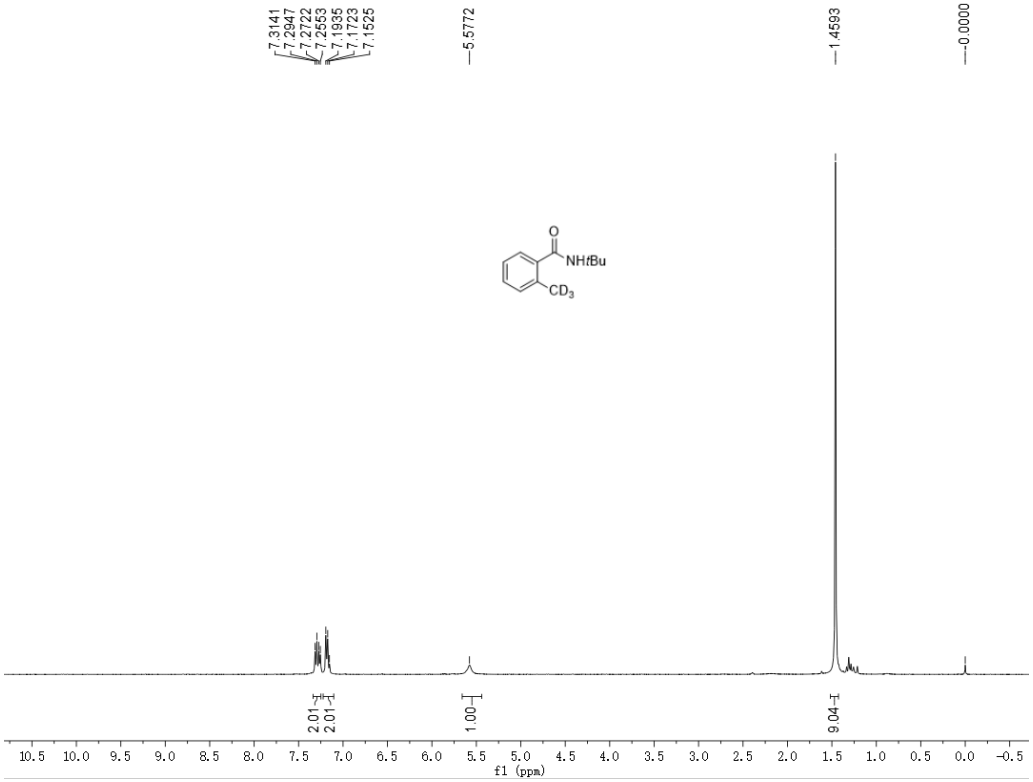
^{1}H NMR (400 MHz) Spectrum of 7 in $CDCl_3$



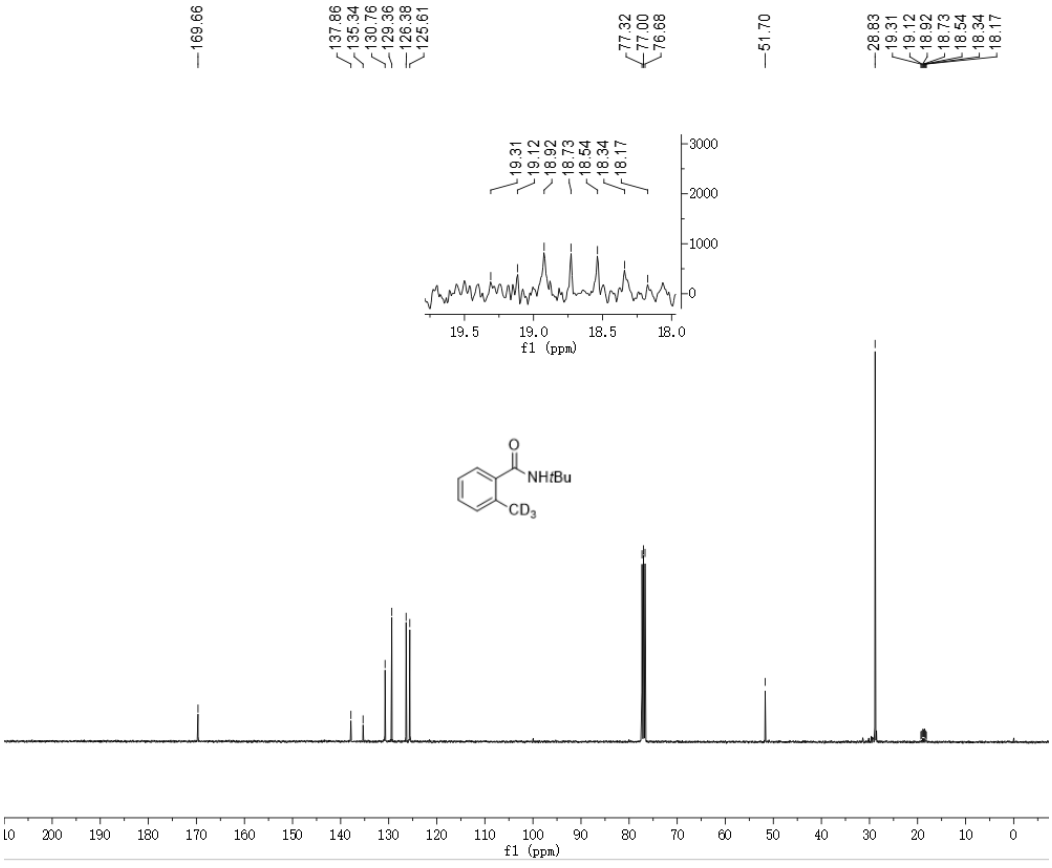
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 7 in $CDCl_3$



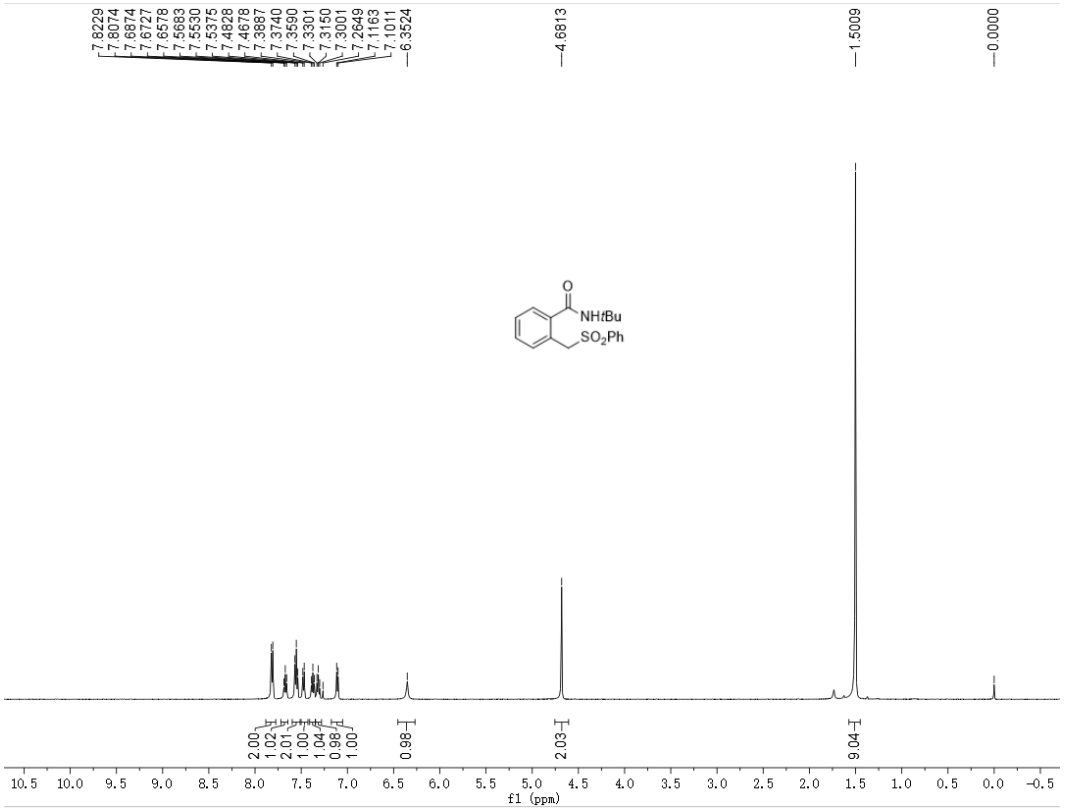
^{1}H NMR (400 MHz) Spectrum of 8 in $CDCl_3$



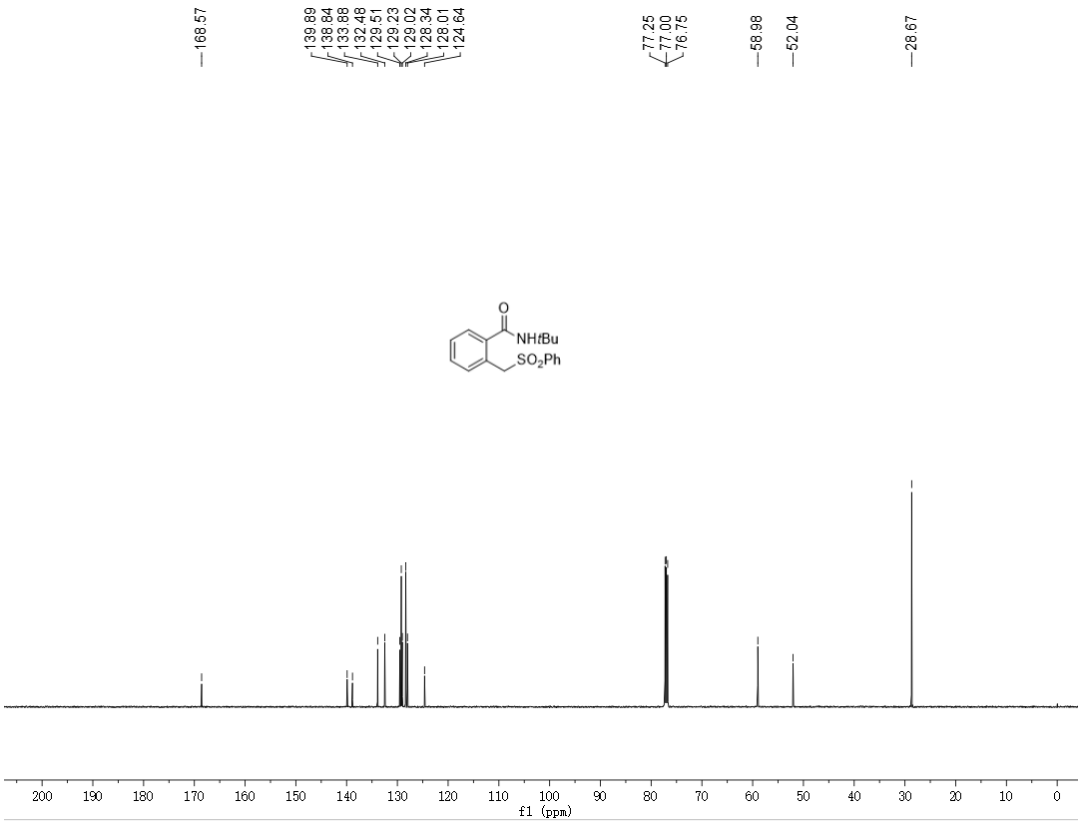
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 8 in $CDCl_3$



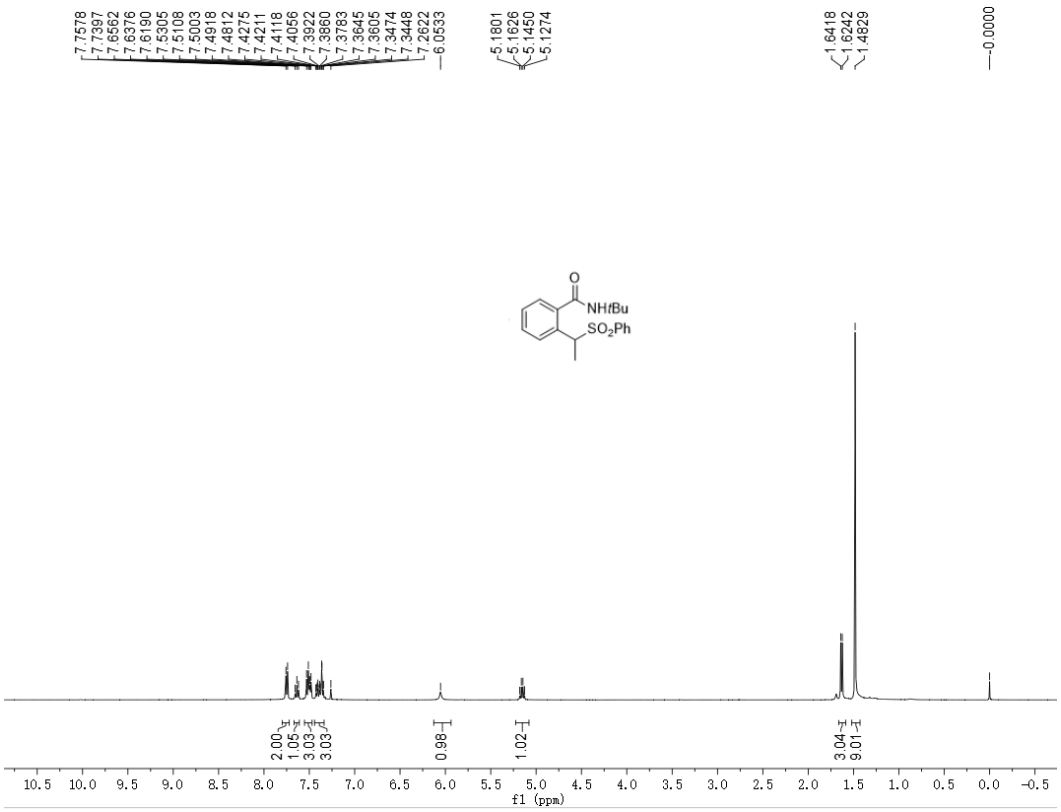
^{1}H NMR (500 MHz) Spectrum of 9 in $CDCl_3$



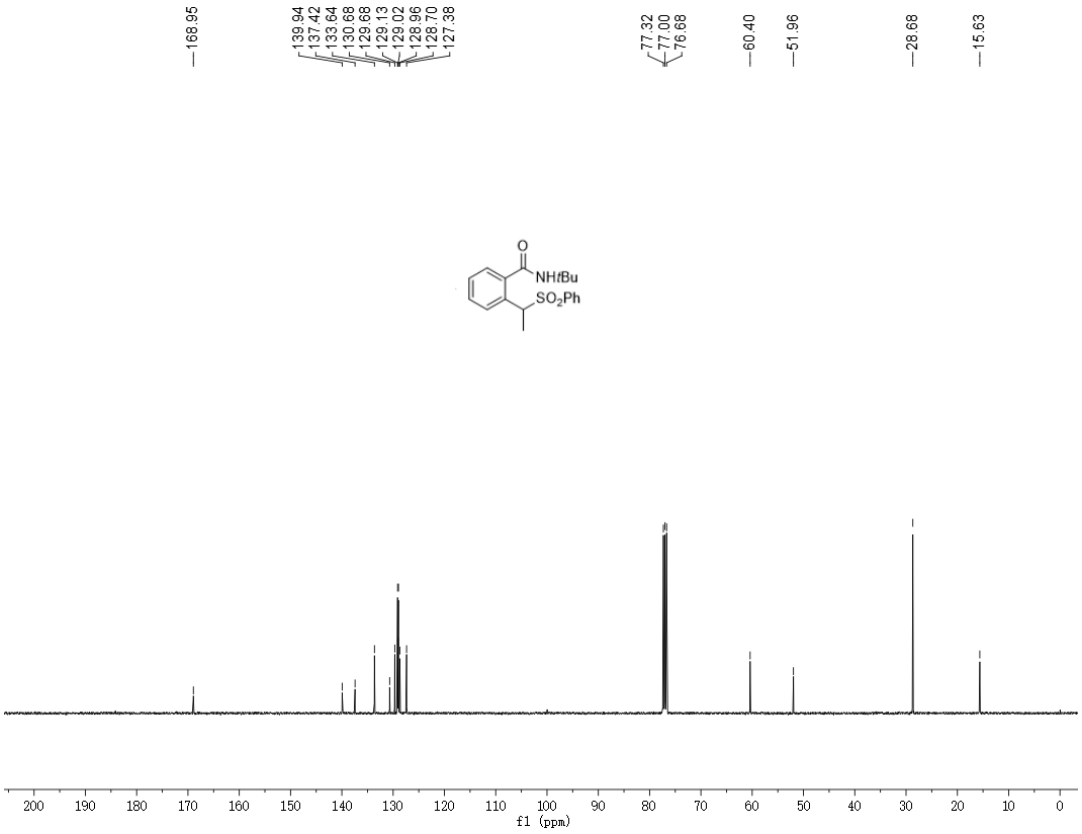
^{13}C{^{1}H} NMR (126 MHz) Spectrum of 9 in $CDCl_3$



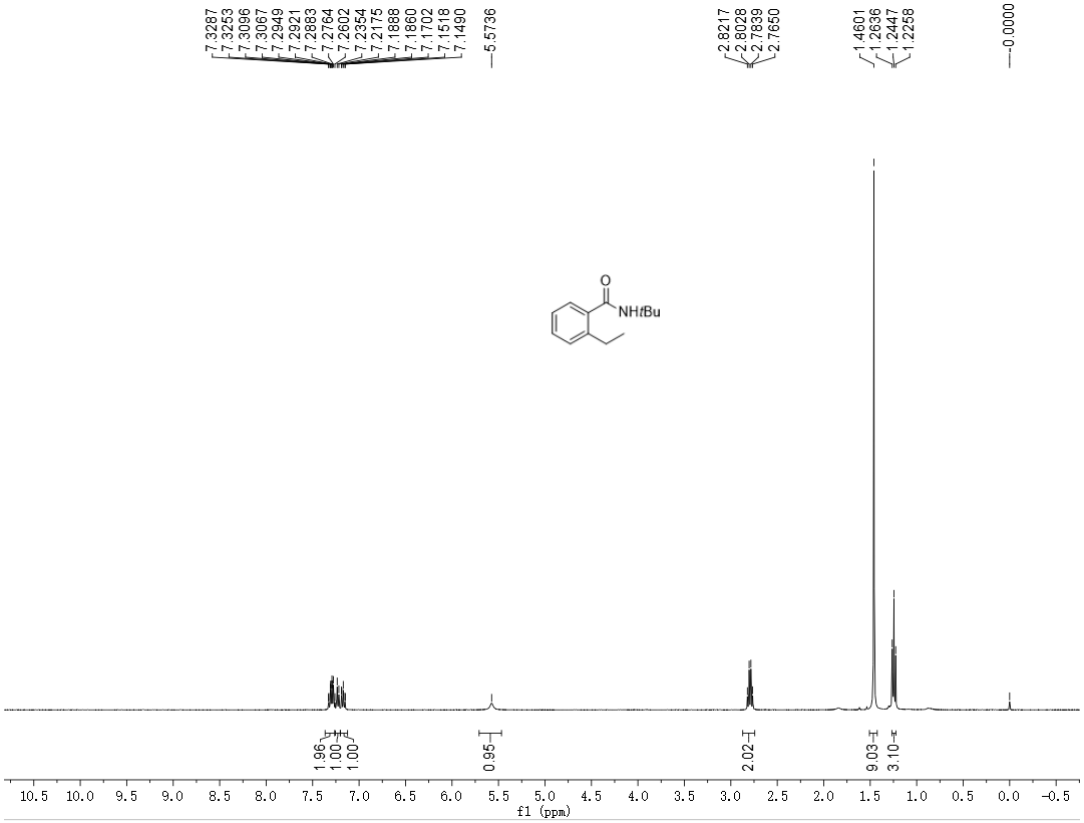
^{1}H NMR (400 MHz) Spectrum of 10 in $CDCl_3$



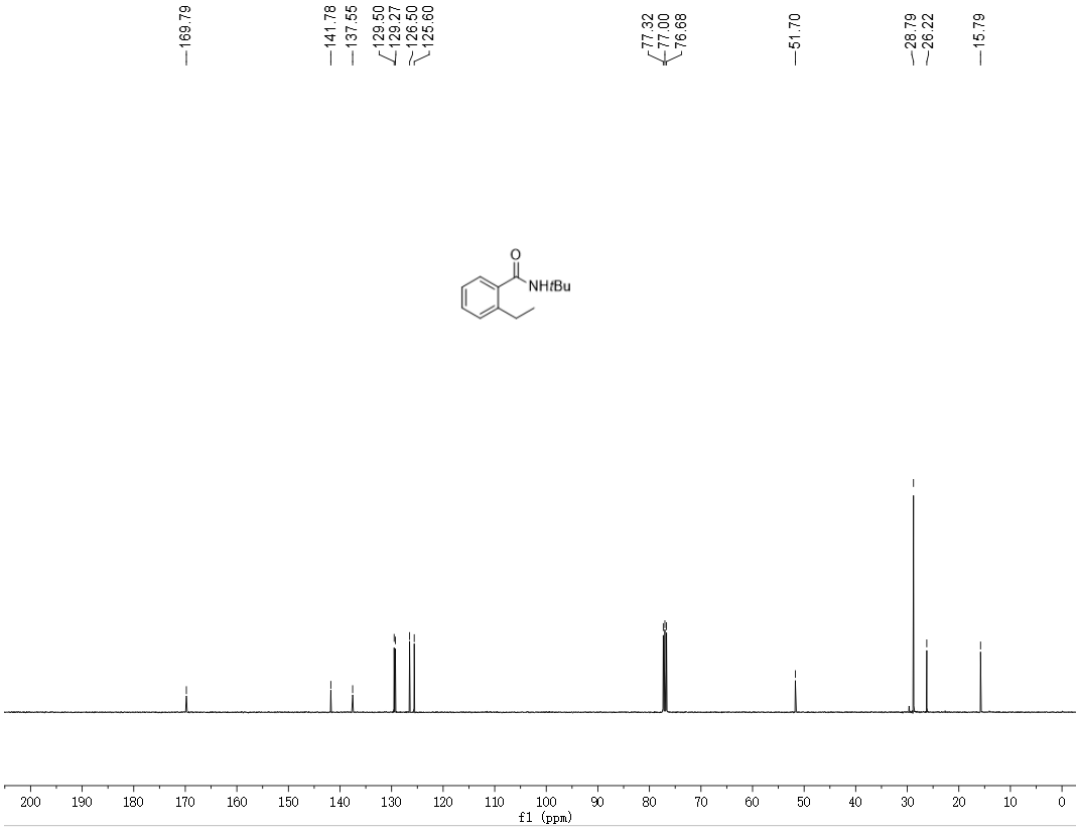
^{13}C{^{1}H} NMR (101 MHz) Spectrum of 10 in $CDCl_3$



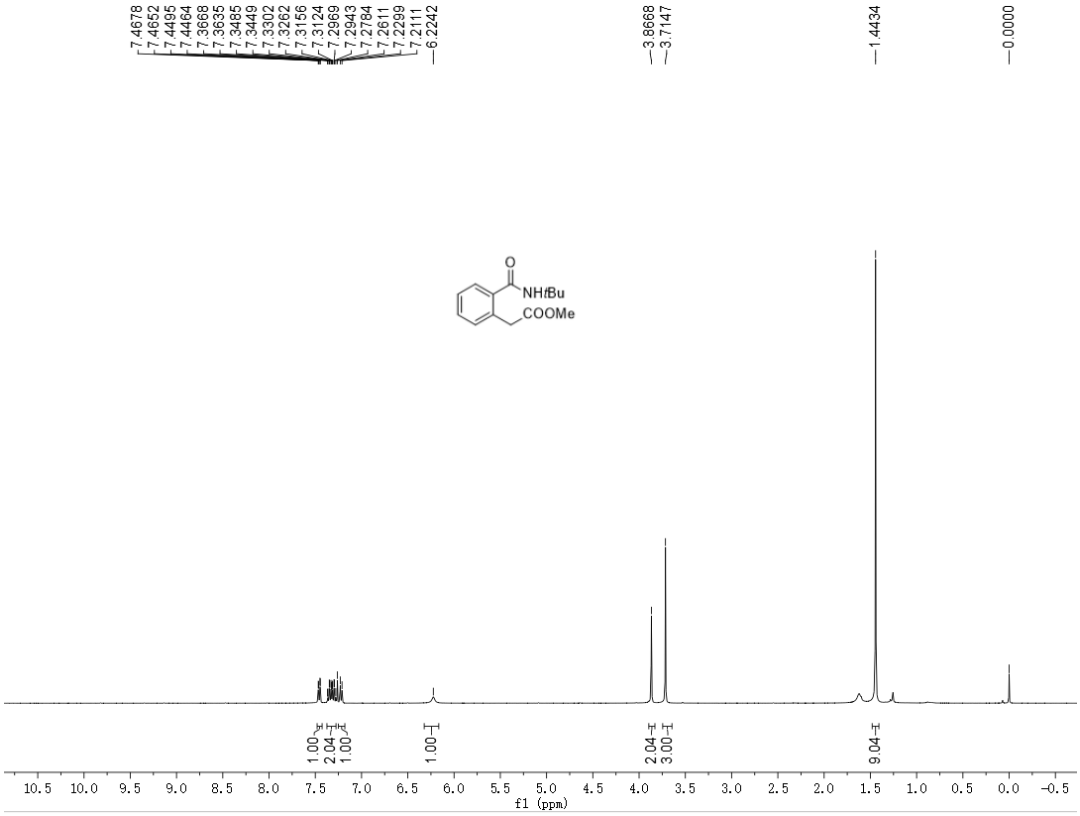
^{1}H NMR (400 MHz) Spectrum of 11 in $CDCl_3$



^{13}C{^{1}H} NMR (101 MHz) Spectrum of 11 in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of 12 in $CDCl_3$



^{13}C{^{1}H} NMR (101 MHz) Spectrum of 12 in $CDCl_3$