Rh-Catalyzed Diastereoselective Addition of Arylboronic Acids to α-Keto *N*-*tert*-Butanesulfinyl Aldimines: Synthesis of α-Amino Ketones

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Supporting Information

Table of Contents

1. General information 2

2. General procedure *1* of synthesis of *N*-Sulfinyl imines 1 3

3. General procedure *2* of synthesis of α-amino ketones 3 10

4. Scale-up synthesis and synthetic applications 30

5. Reference 43

6. Copies of ^{1}H, ^{13}C and ^{19}F Spectra 44

1. General information

All experiments were conducted with a Schlenk tube under an argon atmosphere. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at ambient temperature using Bruker Ascend TM 400 (400 MHz) spectrometer, Bruker AVANCE III 500M spectrometers or JNM-ECZ500R/S1 (500 MHz) spectrometer. ^{1}H NMR chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm), CD_3OD (δ = 3.31 ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, m = multiplet. HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source (Ion Trap). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm). Enantioselectivities were recorded on Waters or Agilent HPLC. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

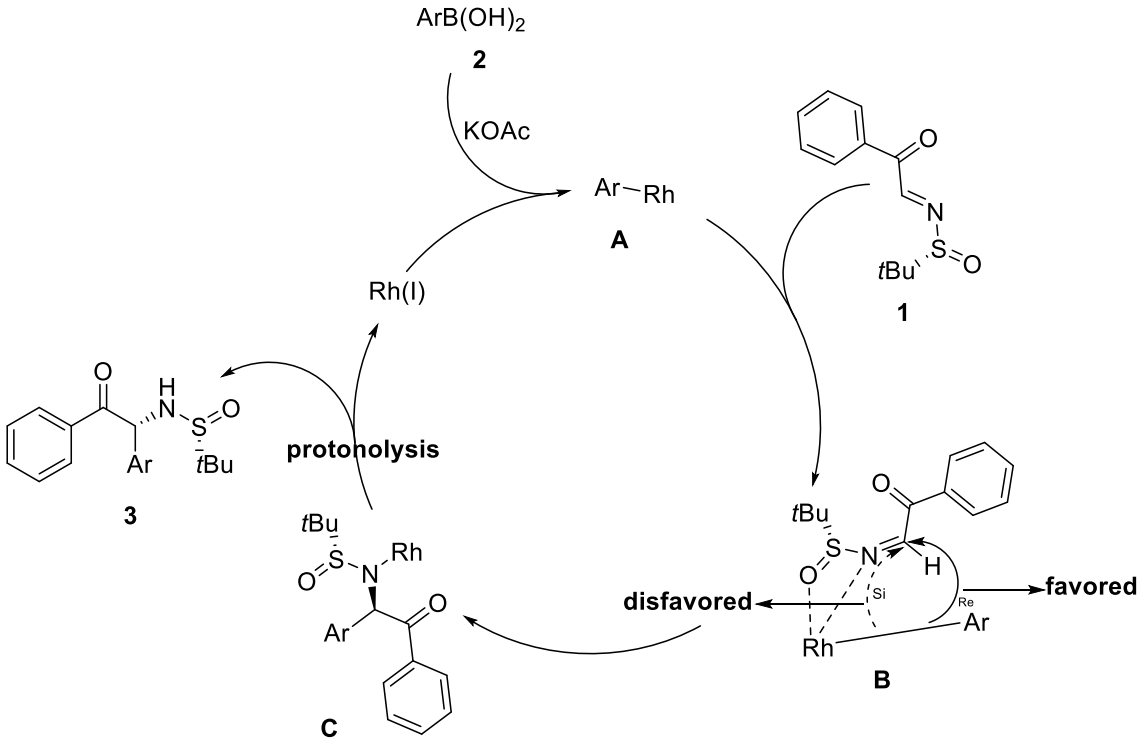
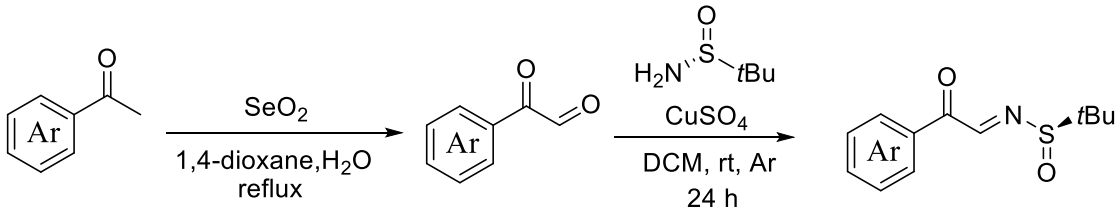


Figure S1. Proposed catalytic cycle.

2. General procedure *1* of synthesis of *N*-Sulfinyl imines 1

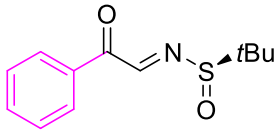


Compound **A** Compound **B** **1**

Step 1: SeO_2 (9 mmol), 1,4-dioxane (9 mL) and water (1 mL) were added to a 100 mL three-necked bottle and fitted it with an condenser. The mixture was heated to 50-55 ℃ and stirred until the solid dissolved. Then followed by addition of Compound **A** (5 mmol) and the reaction was maintained at reflux temperature. After the reaction was complete, as monitored by TLC, the mixture was filtered through a pad of Celite. The filtrate was evaporated to afford a crude product **B**.[1]

Step 2: To a solution of Compound **B** and (*R*)-tert-butanesulfinamide (1.1 equiv) in dry dichloromethane (15 mL) under argon was added anhydrous $CuSO_4$ (2 equiv) and the reaction mixture was stirred at room temperature for 24 h. The solid was filtered off, washed with ethyl acetate (3 × 10 mL) and the organic layer was evaporated .The resulting residue was purified by column chromatography silica gel, to yield pure compounds **1**. Yields, physical and spectroscopic data for these compounds follow.[2]

(*R*)-2-methyl-*N*-(2-oxo-2-phenylethylidene) propane-2-sulfinamide (1a)

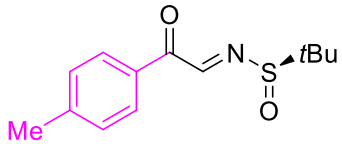


1a

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 65% (750 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v). Known compound.[2]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.12 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.69 – 7.58 (m, 1H), 7.50 (dd, *J* = 8.3, 7.4 Hz, 2H), 1.27 (s, 9H).

(*R*)-2-methyl-*N*-(2-oxo-2-(p-tolyl)ethylidene)propane-2-sulfinamide (1b)



1b

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 60% (750 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

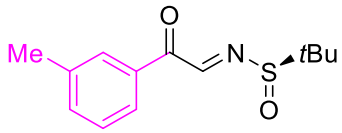
^{1}H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 187.2, 160.8, 145.1, 131.6, 129.8, 129.1, 58.1, 22.2, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}NO_2S^+$ 252.1053; Found: 252.1050.

[α]^{25}D: -54.5 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-(2-oxo-2-(m-tolyl)ethylidene)propane-2-sulfinamide (1c)



1c

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 58% (739 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

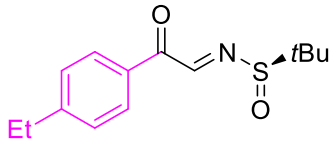
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.94 – 7.90 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 2.42 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.2, 161.0, 138.6, 135.1, 134.5, 130.4, 128.6, 127.4, 58.6, 22.7, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}NO_2S^+$ 252.1053; Found: 252.1051.

[α]^{25}D: -234.5 (c 0.5, Chloroform).

(*R*)-*N*-(2-(4-ethylphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide(1d)



1d

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 60% (750 mg), R_f= 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

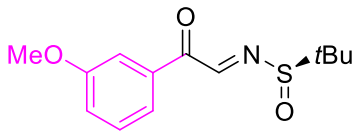
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.31 (d, *J* = 10 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.27 (s, 9H), 1.25 (d, *J* = 7.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.6, 161.1, 151.6, 132.2, 130.3, 128.3, 58.5, 29.0, 22.7, 15.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{20}NO_2S^+$ 266.1209; Found: 266.1206.

[α]^{25}D: -21.2 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(3-methoxyphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1e)



1e

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 60% (761 mg), R_f = 0.65 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).

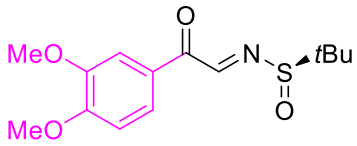
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.58 – 7.53 (m, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.05 – 6.99 (m, 1H), 3.68 (s, 3H), 1.13 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.2, 160.6, 159.3, 135.1, 129.2, 122.4, 120.4, 113.4, 58.0, 54.9, 22.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}NO_3S^+$ 268.1002; Found: 268.1003.

[α]^{25}D: -54.8 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(3,4-dimethoxyphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1f)



1f

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 50% (742 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 10: 1, v/v).

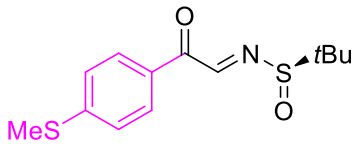
^{1}H NMR (500 MHz, Chloroform-d) δ 8.43 (s, 1H), 7.80 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 186.1, 161.1, 154.4, 149.2, 127.5, 125.8, 111.0, 110.0, 58.3, 56.0, 55.8, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{20}NO_4S^+$ 298.1108; Found: 298.1109.

[α]^{25}D: -16.3 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-(2-(4-(methylthio)phenyl)-2-oxoethylidene)propane-2-sulfinamide (1g)



1g

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 48% (693 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).

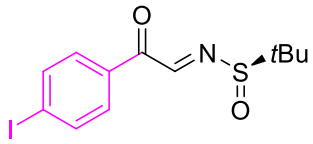
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 2.51 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.8, 161.0, 148.2, 130.7, 130.4, 124.8, 58.5, 22.6, 14.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}NO_2S_2^+$ 284.0773; Found: 284.0771.

[α]^{25}D: 31.0 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(4-iodophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1h)



1h

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 70% (1272 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

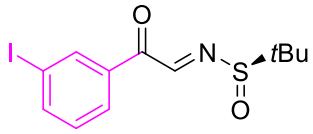
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.85 (d, *J* = 5.0 Hz, 4H), 1.26 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.2, 160.6, 138.0, 133.6, 131.3, 102.9, 58.7, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}INO_2S^+$ 363.9863; Found: 363.9861.

[α]^{25}D: -4.3 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(3-iodophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1i)



1i

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 63% (1143 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

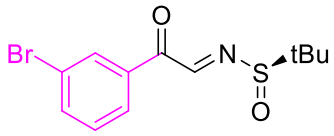
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.48 (t, *J* = 1.8 Hz, 1H), 8.38 (s, 1H), 8.12 – 8.05 (m, 1H), 7.97 – 7.90 (m, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.4, 160.4, 142.8, 138.9, 136.1, 130.3, 129.2, 94.2, 58.9, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}INO_2S^+$ 363.9863; Found: 363.9865.

[α]^{25}D: -31.8 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(3-bromophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1j)



1j

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 60% (946 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

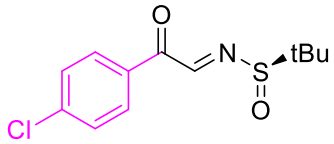
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.28 (t, *J* = 1.8 Hz, 1H), 8.06 (m, 1H), 7.74 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.5, 160.4, 137.0, 136.1, 133.0, 130.2, 128.6 122.8, 58.9, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}BrNO_2S^+$ 316.0001; Found: 315.9995.

[α]^{25}D: -69.2 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(4-chlorophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1k)



1k

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 60% (813 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

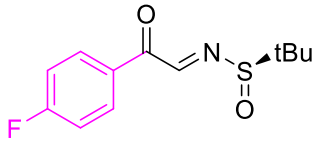
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.7, 160.6, 141.0, 132.7, 131.5, 129.1, 58.8, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}ClNO_2S^+$ 272.0507; Found: 272.0500.

[α]^{25}D: -18.2 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(4-fluorophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1l)



1l

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 61% (770mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 8.20 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.17 (dd, *J* = 9.0, 8.3 Hz, 2H), 1.27 (s, 9H).

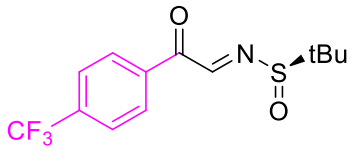
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.4, 166.4 (d, *J* = 257.6 Hz), 160.8, 133.0 (d, *J* = 9.4 Hz), 130.9 (d, *J* = 3.1 Hz), 116.0 (d, *J* = 21.9 Hz), 58.7, 22.7.

^{19}FNMR (471 MHz, Chloroform-*d*) δ -102.17.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}FNO_2S^+$ 256.0802; Found: 256.0800.

[α]^{25}D: -7.2 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)propane-2-sulfinamide (1m)



1m

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 63% (961 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.23 (dd, *J* = 8.9, 0.8 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 1.25 (s, 9H).

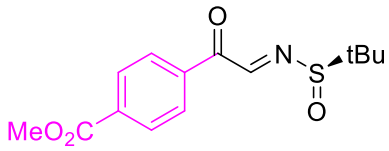
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.9, 160.4, 137.1, 135.1 (q, *J* = 32.8 Hz), 130.4, 125.6 (d, *J* = 3.8 Hz), 58.8, 22.6.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.25.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{15}F_3NO_2S^+$ 303.0770; Found: 303.0768.

[α]^{25}D: -5.4 (*c* 0.5, Chloroform).

methyl (*R*)-4-(2-((tert-butylsulfinyl)imino)acetyl)benzoate (1n)



1n

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 63% (923 mg), R_f = 0.5 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 10: 1, v/v).

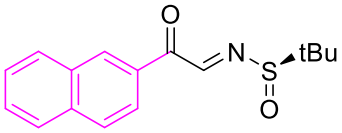
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.13 (d, *J* = 15.2 Hz, 4H), 3.90 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.4, 165.8, 160.4, 137.5, 134.5, 129.9, 129.6, 58.7, 52.4, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{18}NO_4S^+$ 296.0951; Found: 296.0946.

[α]^{25}D: -29.1 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-(2-(naphthalen-2-yl)-2-oxoethylidene)propane-2-sulfinamide (1o)



1o

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 50% (729 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

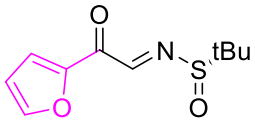
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 8.62 (d, *J* = 2.4 Hz, 1H), 8.14 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.8, 161.1, 136.1, 133.1, 132.3, 131.9, 129.9, 129.4, 128.8, 127.9, 127.08, 124.5, 58.7, 22.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{18}NO_2S^+$ 288.1053; Found: 288.1049.

[α]^{25}D: -4.3 (*c* 0.5, Chloroform).

(*R*)-*N*-(2-(furan-2-yl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1p)



1p

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 65% (750 mg), R_f = 0.6 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).

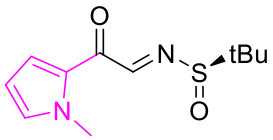
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.76 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.67 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.62 (dd, *J* = 3.7, 1.7 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 159.6, 150.4, 148.9, 123.0, 112.9, 59.0, 22.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{14}NO_3S^+$ 228.0689; Found: 228.0684

[α]^{25}D: -73.8 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-(2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethylidene)propane-2-sulfinamide (1q)



1q

Following the general procedure *1* on 5 mmol scale, yellow oil liquid, yield: 53% (636 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

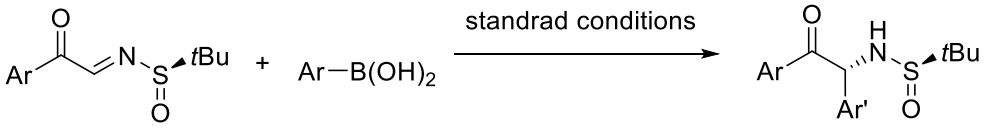
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.35 (dd, *J* = 4.3, 1.7 Hz, 1H), 6.98 (t, *J* = 2.1 Hz, 1H), 6.23 (dd, *J* = 4.3, 2.4 Hz, 1H), 4.02 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.5, 161.0, 133.8, 129.7, 123.4, 109.6, 58.5, 37.9, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{17}N_2O_2S^+$ 241.1005; Found: 241.1001.

[α]^{25}D: -101.0 (*c* 0.5, Chloroform).

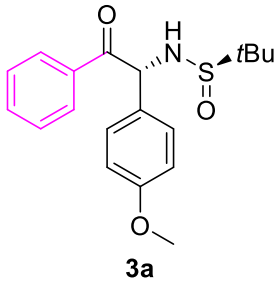
3. General procedure *2* of synthesis of α-amino ketones 3



1 **2** **3**

To a Schlenk tube added $[RhCl(COD)]_2$ (4.5 mg, 0.0125 mmol, 5 mol %) , (*R*)-*N*-tert-butanesulfinyl imines (**1**) (0.2 mmol), arylboronic acids (**2**) (0.4 mmol) and KOAc (0.4 mmol) under nitrogen atmosphere. Then toluene (0.75 mL) and water (0.25 mL) were added and the mixture was stirred at 30 ℃ for 3 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with saturated ammonium chloride aqueous solution and brine. The aqueous layer was extracted with EtOAc (3×15 mLxz). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to isolate the product.

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3a)



3a

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 75% (56 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

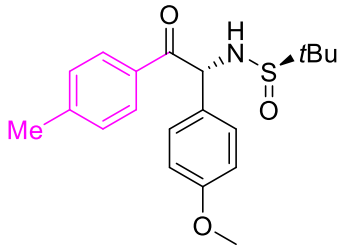
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.91 (d, *J* = 3.8 Hz, 1H), 5.08 (d, *J* = 3.8 Hz, 1H), 3.74 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.3, 159.5, 134.5, 133.4, 129.9, 129.7, 129.0, 128.6, 114.5, 62.6, 55.9, 55.1, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}NO_3S^+$ 346.1471; Found: 346.1474.

[α]^{25}D: -94.4 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-oxo-2-(p-tolyl)ethyl)-2-methylpropane-2-sulfinamide (3b)



3b

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 81% (59 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

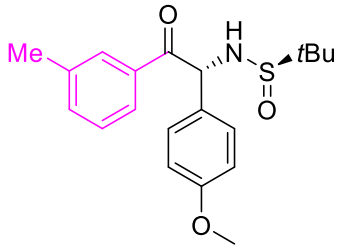
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.77 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 – 7.12 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 3.7 Hz, 1H), 5.10 (d, *J* = 3.7 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.7, 159.4, 144.4, 131.8, 130.2, 129.6, 129.2, 129.1, 114.4, 62.4, 55.8, 55.1, 22.5, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_3S^+$ 360.1628; Found: 360.1621.

[α]^{25}D: -180.2 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-oxo-2-(m-tolyl)ethyl)-2-methylpropane-2-sulfinamide (3c)



3c

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 77% (56 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

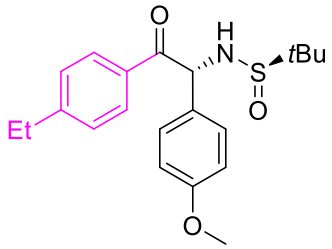
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 (dd, *J* = 8.3, 6.6 Hz, 3H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.91 (d, *J* = 3.8 Hz, 1H), 5.08 (d, *J* = 3.9 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.5, 159.4, 138.4, 134.4, 134.2, 130.0, 129.6, 129.5, 128.3, 126.2, 114.4, 62.5, 55.8, 55.1, 22.5, 21.2

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_3S^+$ 360.1628; Found: 360.1626.

[α]^{25}D: -87.3 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(4-ethylphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3d)



3d

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 72% (54 mg), R_f= 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

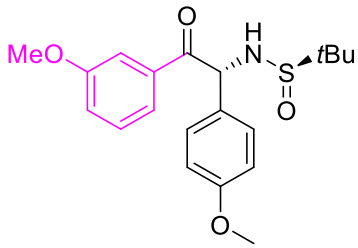
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 3.8 Hz, 1H), 5.09 (d, *J* = 3.8 Hz, 1H), 3.74 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.21 – 1.17 (m, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.8, 159.4, 150.5, 132.0, 130.2, 129.6, 129.3, 128.1, 114.4, 62.4, 55.8, 55.1, 28.8, 22.5, 14.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{28}NO_3S^+$ 374.1784; Found: 374.1778.

[α]^{25}D: -161.3 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(3-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3e)



3e

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 76% (58 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

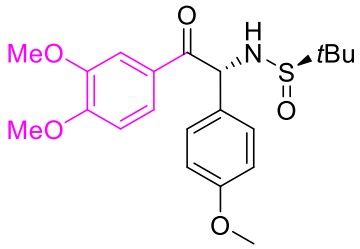
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (m, 1H), 7.41 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.01 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 3.9 Hz, 1H), 5.06 (d, *J* = 3.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.1, 159.6, 159.5, 135.7, 129.9, 129.6, 129.5, 121.6, 120.0, 114.4, 113.25, 62.7, 55.9, 55.3, 55.1, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_4S^+$ 376.1577; Found: 376.1579.

[α]^{25}D: -150.0 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3f)



3f

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 75% (62 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

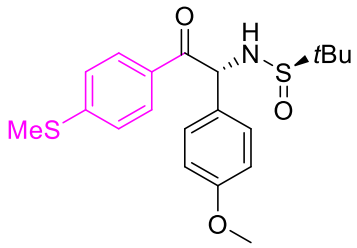
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.86 (d, *J* = 4.0 Hz, 1H), 5.09 (d, *J* = 3.9 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.72 (s, 3H), 1.18 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.6, 159.4, 153.5, 148.8, 130.6, 129.4, 127.2, 123.9, 114.4, 111.1, 110.0, 62.1, 55.9, 55.8, 55.8, 55.1, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{28}NO_5S^+$ 406.1683; Found: 460.1685.

[α]^{25}D: -118.2 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-(4-(methylthio)phenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide(3g)



3g

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 70% (55 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

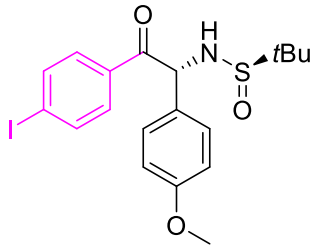
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.86 (d, *J* = 3.7 Hz, 1H), 5.09 (d, *J* = 3.7 Hz, 1H), 3.75 (s, 3H), 2.46 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.1, 159.5, 146.8, 130.5, 130.3, 129.6, 129.4, 124.8, 114.5, 62.4, 55.9, 55.2, 22.6, 14.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_3S_2^+$ 392.1349; Found: 392.1349.

[α]^{25}D: -59.7 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(4-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3h)



3h

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 82% (78 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

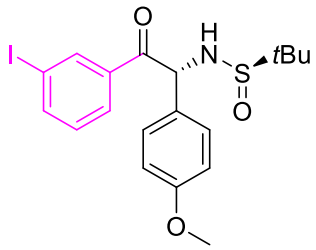
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.83 (d, *J* = 3.8 Hz, 1H), 5.03 (d, *J* = 3.7 Hz, 1H), 3.75 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.6, 159.6, 137.9, 133.6, 130.2, 129.6, 129.4, 114.6, 101.7, 62.5, 55.9, 55.1, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}INO_3S^+$ 472.0438; Found: 472.0434.

[α]^{25}D: -117.0 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(3-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3i)



3i

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 74% (71 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 81: 19

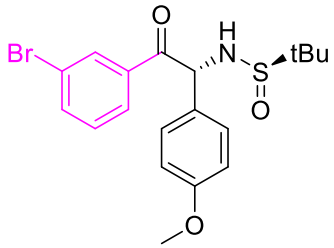
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (t, *J* = 1.7 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.84 (d, *J* = 3.2 Hz, 1H), 5.00 (d, *J* = 3.8 Hz, 1H), 3.75 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.0, 159.6, 142.2, 137.8, 136.1, 130.2, 129.7, 129.2, 128.0, 114.6, 94.3, 62.6, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}INO_3S^+$ 472.0438; Found: 472.0432.

[α]^{25}D: -107.0 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(3-bromophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3j)



3j

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 62% (53 mg), R_f= 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

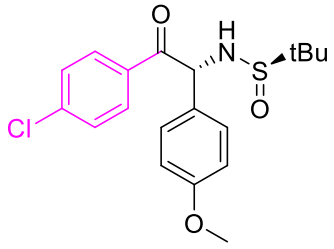
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (t, *J* = 1.8 Hz, 1H), 7.78 (m, 1H), 7.60 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.85 (d, *J* = 3.9 Hz, 1H), 5.00 (d, *J* = 3.9 Hz, 1H), 3.76 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.1, 159.7, 136.3, 136.2, 131.9, 130.1, 129.7, 129.2, 127.5, 122.9, 114.6, 62.7, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}BrNO_3S^+$ 424.0577; Found: 424.0573.

[α]^{25}D: -85.5 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(4-chlorophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3k)



3k

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 78% (60 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 93: 7

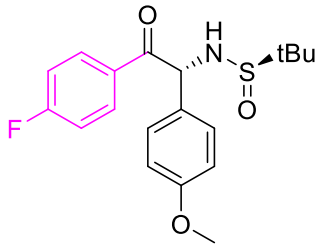
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.86 (d, *J* = 3.8 Hz, 1H), 5.04 (d, *J* = 3.8 Hz, 1H), 3.74 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.1, 159.6, 139.9, 132.7, 130.4, 129.6, 129.5, 128.9, 114.6, 62.6, 55.9, 55.1, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}ClNO_3S^+$ 379.1082; Found: 380.1074.

[α]^{25}D: -132.8 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(4-fluorophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3l)



3l

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 83% (61 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.86 (d, *J* = 4.0 Hz, 1H), 5.05 (d, *J* = 3.9 Hz, 1H), 3.75 (s, 3H), 1.20 (s, 9H).

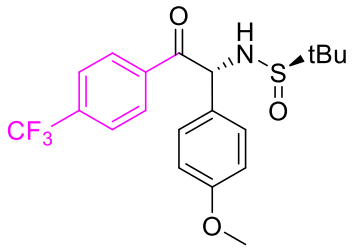
^{13}C NMR (126 MHz, Chloroform-d) δ 194.7, 159.6, 131.7 (d, J = 9.4 Hz), 130.8 (d, J = 2.4 Hz), 129.8, 129.6 115.8 (d, J = 21.9 Hz), 114.6, 62.6, 55.9, 55.2, 22.5.

^{19}F NMR (471 MHz, Chloroform-d) δ -103.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}FNO_3S^+$ 364.1377; Found: 364.1376.

[*α*]^{25}D: -116.0 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-2-methylpropane-2-sulfinamide (3m)



3m

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 65% (54 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.90 (d, *J* = 3.8 Hz, 1H), 5.03 (d, *J* = 3.8 Hz, 1H), 3.75 (s, 3H), 1.21 (s, 9H).

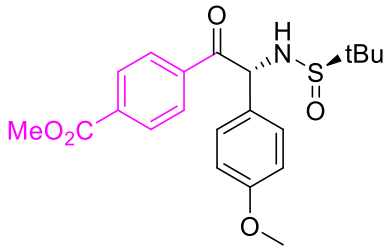
^{13}C NMR (126 MHz, Chloroform-d) δ 195.5, 159.7, 137.2, 135.7, 134.5 (q, J = 33.1 Hz), 129.5 (d, J = 57.2 Hz), 128.9, 125.6 (d, J = 4.2 Hz), 123.3 (d, J = 272.8 Hz), 114.7, 63.0, 56.0, 55.2, 22.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.20.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}F_3NO_3S^+$ 414.1345; Found: 414.1347.

[*α*]^{25}D: -87.1 (*c* 0.5, Chloroform).

methyl 4-((*R*)-2-(((*R*)-tert-butylsulfinyl)amino)-2-(4-methoxyphenyl)acetyl)benzoate (3n)



3n

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 70% (54 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

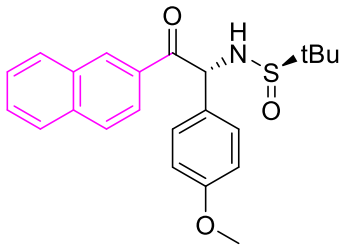
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.91 (d, *J* = 3.7 Hz, 1H), 5.04 (d, *J* = 3.7 Hz, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.0, 166.0, 160.0, 137.8, 134.1, 129.7, 129.7, 129.2, 128.9, 114.6, 63.0, 55.9, 55.2, 52.5, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{26}NO_5S^+$ 384.1805; Found: 384.1796.

[α]^{25}D: -88.6 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3o)



3o

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 66% (66 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

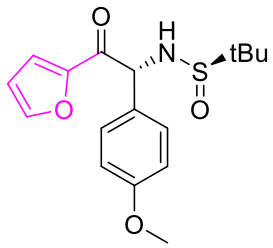
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 7.93 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.55 (m, 1H), 7.49 (m, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.10 (d, *J* = 3.7 Hz, 1H), 5.16 (d, *J* = 3.8 Hz, 1H), 3.71 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.4, 159.6, 135.7, 132.3, 131.9, 131.2, 130.2, 129.8, 128.9, 128.6, 127.8, 127.0, 124.5, 114.6, 62.7, 56.0, 55.2, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}NO_3S^+$ 396.1628; Found: 396.1631.

[α]^{25}D: -48.8 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-2-(furan-2-yl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3p)



3p

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 90% (66 mg), R_f = 0.1 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

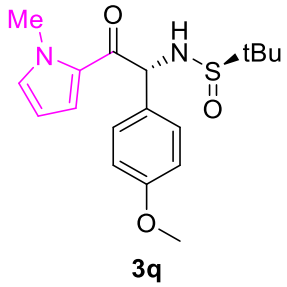
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.14 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.45 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.72 (d, *J* = 4.0 Hz, 1H), 4.96 (d, *J* = 4.0 Hz, 1H), 3.76 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.9, 159.6, 150.4, 147.0, 129.7, 129.4, 119.4, 114.2, 112.5, 62.4, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{22}NO_4S^+$ 336.1264; Found: 336.1255.

[α]^{25}D: -153.0 (*c* 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)-2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3q)



3q

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 83% (53 mg), R_f = 0.1 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v). dr: >98: 2

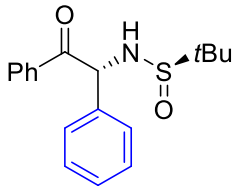
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.94 (dd, *J* = 4.2, 1.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.78 (t, *J* = 2.0 Hz, 1H), 6.06 (dd, *J* = 4.2, 2.4 Hz, 1H), 5.64 (d, *J* = 4.7 Hz, 1H), 5.01 (d, *J* = 4.7 Hz, 1H), 3.90 (s, 3H), 3.76 (s,3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.3, 159.2, 132.0, 131.6, 129.1, 128.2, 120.8, 114.2, 108.7, 62.5, 55.8, 55.1, 37.7, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{25}N_2O_3S^+$ 349.1580; Found: 349.1573.

[α]^{25}D: -139.2 (*c* 0.5, Chloroform).

(*R*)-2-methyl-*N*-((*R*)-2-oxo-1,2-diphenylethyl)propane-2-sulfinamide (3r)



3r

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 61% (39 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

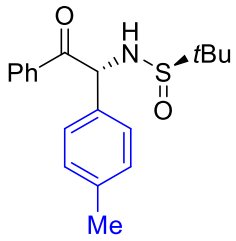
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.27 – 7.22 (m, 1H), 5.96 (d, *J* = 4.0 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 196.2, 138.0, 134.3 133.6, 129.1, 129.0, 128.6, 128.4, 128.3, 63.3, 55.9, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{22}NO_2S^+$ 316.1366; Found: 316.1364.

[α]^{25}D: -314.0 (c 0.5, Chloroform).

(*R*)-2-methyl-*N*-((*R*)-2-oxo-2-phenyl-1-(p-tolyl)ethyl)propane-2-sulfinamide (3s)



3s

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 81% (52 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

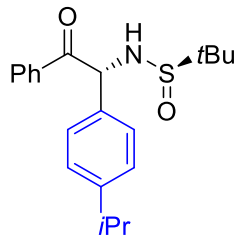
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.20 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 5.92 (d, *J* = 3.3 Hz, 1H), 5.11 (d, *J* = 3.9 Hz, 1H), 2.28 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.3, 138.2, 134.9, 134.4, 133.5, 129.8, 129.0, 128.6, 128.3, 63.0, 55.9, 22.6, 21.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}NO_2S^+$ 330.1522; Found: 330.1523.

[α]^{25}D: -133.6 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-isopropylphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3t)



3t

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 61% (44 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

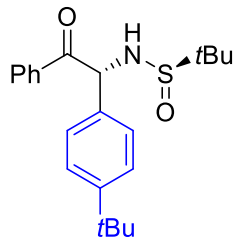
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.94 (d, *J* = 4.4 Hz, 1H), 5.14 (d, *J* = 4.4 Hz, 1H), 2.83 (p, *J* = 6.9 Hz, 1H), 1.21 (s, 9H), 1.18 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.4, 149.0, 135.1, 134.4, 133.5, 129.1, 128.5, 128.2, 127.1, 62.9, 55.9, 33.6, 23.7, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{28}NO_2S^+$ 358.1835; Found: 358.1837.

[α]^{25}D: -150.8 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-(tert-butyl)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3u)



3u

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 53% (40 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

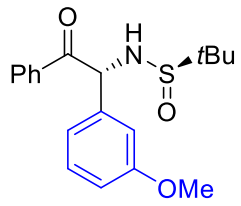
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.50 (m, 1H), 7.38 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 4.6 Hz, 1H), 5.11 (d, *J* = 4.6 Hz, 1H), 1.25 (s, 9H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.5, 151.3, 134.8, 134.5, 133.5, 129.1, 128.6, 127.9, 126.0, 62.8, 55.9, 34.5, 31.2, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H30NO_2S^+$ 372.1992; Found: 372.1998.

[α]^{25}D: -82.2 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(3-methoxyphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3v)



3v

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 53% (37 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

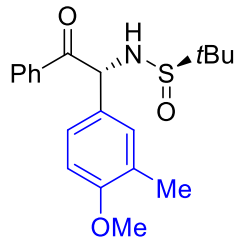
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 10.0 Hz 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 5.92 (d, *J* = 4.1 Hz, 1H), 5.13 (d, *J* = 4.1 Hz, 1H), 3.74 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (126 MHz,) δ 196.1, 160.0, 139.4, 134.4, 133.6, 130.1, 129.0, 128.6, 120.8, 113.9, 113.8, 63.2, 56.0, 55.2, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}NO_3S^+$ 346.1471; Found: 346.1479.

[α]^{25}D: -100.2 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxy-3-methylphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3w)



3w

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 70% (51 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

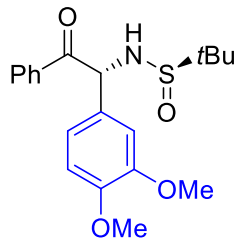
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.87 (d, *J* = 3.3 Hz, 1H), 5.06 (t, *J* = 3.1 Hz, 1H), 3.75 (s, 3H), 2.14 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.4, 157.6, 134.5, 133.4, 130.5, 129.3, 129.0, 128.5, 127.4, 127.1, 110.1, 62.6, 55.8, 55.2, 22.6, 16.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_3S^+$ 360.1628; Found: 360.1629.

[α]^{25}D: -74.5 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(3,4-dimethoxyphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3x)



3x

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 43% (33 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 96: 4

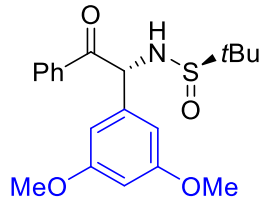
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 8.2, 7.4 Hz, 2H), 6.91 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 5.90 (d, *J* = 3.6 Hz, 1H), 5.05 (d, *J* = 3.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.2, 149.4, 149.0, 134.5, 133.5, 130.2, 128.9, 128.5, 121.3, 111.2, 110.8, 62.8, 55.9, 55.8, 55.7, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_4S^+$ 376.1577; Found: 376.1580.

[α]^{25}D: -122.8 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(3,5-dimethoxyphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3y)



3y

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 57% (43 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

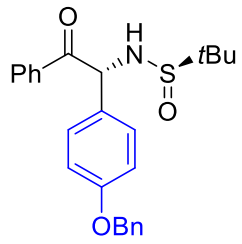
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.55 – 7.43 (m, 1H), 7.38 (dd, *J* = 8.3, 7.4 Hz, 2H), 6.45 (d, *J* = 2.2 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 1H), 5.85 (d, *J* = 4.1 Hz, 1H), 5.11 (d, *J* = 4.1 Hz, 1H), 3.72 (s, 6H), 1.22 (s, 9H).

^{13}C NMR (126 MHz,) δ 196.0, 161.2, 140.1, 134.4, 133.6, 129.0, 128.6, 106.4, 100.1, 63.3, 56.0, 55.3, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{26}NO_4S^+$ 376.1577; Found: 376.1574.

[α]^{25}D: -162.8 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-(benzyloxy)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3z)



3z

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 45% (38 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

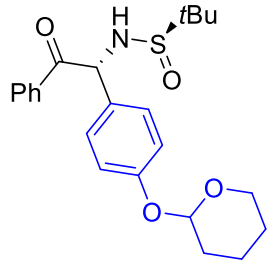
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.34 (m, 6H), 7.32 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.93 (d, *J* = 3.9 Hz, 1H), 5.09 (d, *J* = 3.9 Hz, 1H), 4.98 (s, 2H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.3, 158.7, 136.6, 134.4, 133.5, 130.2, 129.7, 129.0, 128.6, 128.0, 127.5, 115.3, 70.0, 62.6, 55.9, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{28}NO_3S^+$ 422.1784; Found: 422,1781.

[α]^{25}D: -108.2 (c 0.5, Chloroform).

(*R*)-2-methyl-*N*-((1*R*)-2-oxo-2-phenyl-1-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)ethyl)propane-2-sulfinamide (3aa)



3aa

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 65% (54 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 1: 1

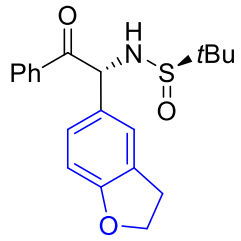
^{1}H NMR (500 MHz,) δ 7.95 – 7.80 (m, 2H), 7.51 – 7.43 (m,1H), 7.36 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.96 (dd, *J* = 8.7, 0.7 Hz, 2H), 5.91 (dd, *J* = 4.0, 1.8 Hz, 1H), 5.33 (q, *J* = 3.6 Hz, 1H), 5.08 (t, *J* = 3.8 Hz, 1H), 3.85 (m, 1H), 3.64 – 3.38 (m, 1H), 1.94 (m, 1H), 1.82 – 1.72 (m, 2H), 1.68 – 1.53 (m, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.3, 157.1, 134.4, 133.5, 130.8, 129.6, 129.5, 129.1, 128.6, 128.5, 116.8, 116.8, 96.4, 96.3, 62.6, 62.6, 62.2, 62.2, 55.9, 30.3, 25.1, 22.6, 18.8, 18.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{30}NO_4S^+$ 416.1890; Found: 416.1887.

[α]^{25}D: -115.6 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(2,3-dihydrobenzofuran-5-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ab)



3ab

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 68% (49 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 93: 7

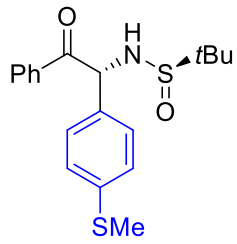
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.48 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.11 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.89 (d, *J* = 3.9 Hz, 1H), 5.05 (d, *J* = 3.9 Hz, 1H), 4.52 (m, 2H), 3.13 (t, *J* = 8.7 Hz, 2H), 1.21 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.4, 160.2, 134.4, 133.5, 129.7, 129.0, 128.7, 128.6, 128.0, 124.9, 109.7, 71.4, 62.8, 55.8, 29.5, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{24}NO_3S^+$ 358.1471; Found: 358.1474.

[α]^{25}D: -81.8 (c 0.5, Chloroform).

(*R*)-2-methyl-*N*-((*R*)-1-(4-(methylthio)phenyl)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3ac)



3ac

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 51% (37 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

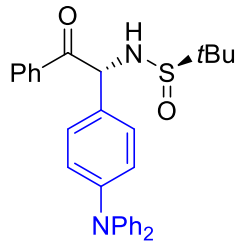
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.92 (d, *J* = 3.8 Hz, 1H), 5.11 (d, *J* = 3.8 Hz, 1H), 2.42 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.0, 139.1, 134.4, 134.3, 133.6, 129.0, 128.8, 128.6, 126.5, 62.7, 55.9, 22.5, 15.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{24}NO_2S_2^+$ 362.1243; Found: 362.1245.

[α]^{25}D: -163.0 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-(diphenylamino)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ad)



3ad

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 55% (41 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v). dr: >98: 2

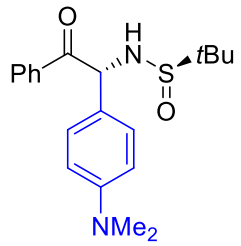
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.23 (dd, *J* = 8.8, 7.1 Hz, 4H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.06 – 6.99 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 2H), 5.91 (d, *J* = 4.4 Hz, 1H), 5.08 (d, *J* = 4.4 Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.3, 147.8, 147.2, 134.5, 133.6, 130.9, 129.3, 129.1, 129.1, 128.6, 124.8, 123.4, 122.8, 62.6, 55.9, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{31}N_2O_2S^+$ 483.2101; Found: 483.2108.

[α]^{25}D: -54.3 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-(dimethylamino)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ae)



3ae

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 35% (25 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

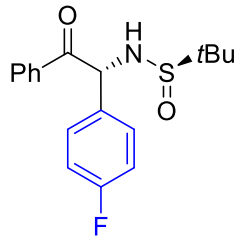
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.85 (m, 2H), 7.49 – 7.42 (m, 1H), 7.35 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 5.87 (d, *J* = 3.9 Hz, 1H), 5.02 (d, *J* = 4.0 Hz, 1H), 2.89 (s, 6H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.5, 150.2, 134.7, 133.3, 129.4, 129.0, 128.5, 124.8, 112.5, 62.7, 55.8, 40.2, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{27}N_2O_2S^+$ 359.1788; Found: 359.1785.

[α]^{25}D: -152.8 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-fluorophenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3af)



3af

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 79% (53 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.38 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.30 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.96 (d, *J* = 3.7 Hz, 1H), 5.12 (d, *J* = 3.7 Hz, 1H), 1.20 (s, 9H).

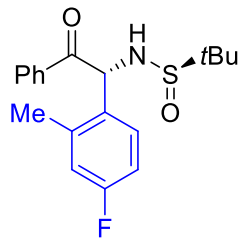
^{13}C NMR (126 MHz, Chloroform-d) δ 196.0, 162.5 (d, J = 248.0 Hz), 134.2, 133.9, 133.9, 133.7, 130.2 (d, J = 8.3 Hz), 128.8 (d, J = 41.5 Hz), 116.1 (d, J = 21.7 Hz), 62.3, 56.0, 22.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{21}FNO_2S^+$ 334.1272; Found: 334.1269.

[*α*]^{25}D: -67.6 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-fluoro-2-methylphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ag)



3ag

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 55% (38 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.35 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.10 (dd, *J* = 8.6, 5.7 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.83 – 6.77 (m, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.11 (d, *J* = 3.9 Hz, 1H), 2.47 (s, 3H), 1.20 (s, 9H).

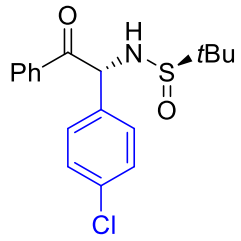
^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.8, 162.33 (d, *J* = 247.6 Hz), 139.1 (d, *J* = 8.0 Hz), 134.5, 133.6, 132.1, 132.0, 130.9 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 4.8 Hz), 118.2 (d, *J* = 21.4 Hz), 113.6 (d, *J* = 21.2 Hz), 60.8, 55.9, 22.5, 19.6.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -113.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}FNO_2S^+$ 348.1428; Found: 348.1420.

[α]^{25}D: -54.4 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-chlorophenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ah)



3ah

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 53% (37 mg), R_f = 0.35 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

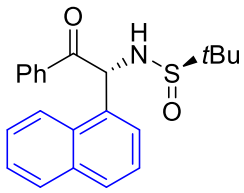
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.27 (d, *J* = 2.8 Hz, 4H), 5.94 (d, *J* = 3.7 Hz, 1H), 5.13 (d, *J* = 3.7 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (126 MHz,) δ 195.8, 136.5, 134.4, 134.1, 133.8, 129.7, 129.4, 129.0, 128.7, 62.4, 56.0, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{21}ClNO_2S^+$ 350.0976; Found: 350.0968.

[α]^{25}D: -54.6 (c 0.5, Chloroform).

(*R*)-2-methyl-*N*-((*R*)-1-(naphthalen-1-yl)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3ai）



3ai

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 51% (22 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

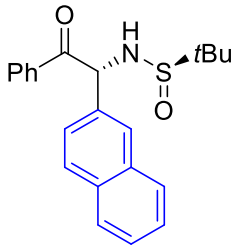
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.80 (m, 3H), 7.60 (m, 1H), 7.52 (m, 1H), 7.43 – 7.34 (m, 3H), 7.27 – 7.23 (m, 2H), 6.50 (d, *J* = 4.6 Hz, 1H), 5.27 (d, *J* = 4.6 Hz, 1H), 1.14 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.2, 134.5, 134.4, 133.7, 133.5, 130.9, 129.5, 129.1, 128.8, 128.5, 127.8, 127.0, 126.1, 125.4, 123.4, 61.5, 56.0, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{24}NO_2S^+$ 366.1522; Found: 366.1523.

[α]^{25}D: -108.3 (c 0.5, Chloroform).

(*R*)-2-methyl-*N*-((*R*)-1-(naphthalen-2-yl)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3aj)



3aj

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 51% (34 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

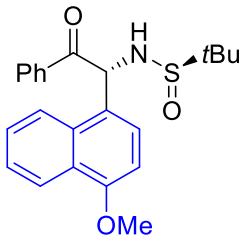
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.84 (s, 1H), 7.81 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.78 (dd, *J* = 8.5, 3.8 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.34 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.14 (d, *J* = 3.7 Hz, 1H), 5.23 (d, *J* = 3.8 Hz, 1H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.1, 135.3, 134.3, 133.6, 133.3, 133.0, 129.2, 129.1, 128.6, 128.1, 128.0, 127.7, 126.6, 126.5, 125.4, 63.4, 56.0, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{24}NO_2S^+$ 366.1522; Found: 366.1525.

[*α*]^{25}D: -54.9 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(4-methoxynaphthalen-1-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ak)



3ak

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 63% (50 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

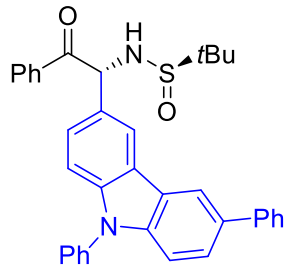
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.35 – 8.26 (m, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.59 (m, 1H), 7.50 (m, 1H), 7.45 – 7.36 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.22 (m, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 4.7 Hz, 1H), 5.18 (d, *J* = 4.7 Hz, 1H), 3.94 (s, 3H), 1.14 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.5, 156.0, 134.7, 133.3, 131.9, 128.7, 128.4, 127.4, 126.4, 125.4, 125.4, 123.2, 122.8, 103.2, 61.5, 55.9, 55.4, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}NO_3S^+$ 396.1628; Found: 396.1619.

[*α*]^{25}D: -241.8 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(6,9-diphenyl-9H-carbazol-3-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3al)



3al

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 65% (73 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

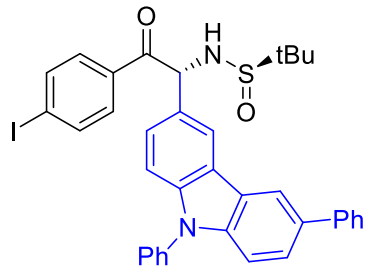
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 1.5 Hz, 1H), 8.00 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.72 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.66 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.59 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.52 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.51 – 7.46 (m, 3H), 7.46 – 7.41 (m, 2H), 7.40 – 7.33 (m,5H), 6.21 (d, *J* = 3.6 Hz, 1H), 5.26 (d, *J* = 3.7 Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.3, 141.6, 141.0, 140.6, 137.2, 134.5, 133.8, 133.4, 129.9, 129.5, 129.1, 128.8, 128.5, 127.6, 127.2, 126.8, 126.7, 126.4, 125.8, 124.0, 123.4, 120.6, 118.9, 110.6, 110.2, 63.5, 55.8, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{36}H_{33}N_2O_2S^+$ 557.2257; Found: 557.2250.

[α]^{25}D: -114.0 (c 0.5, Chloroform).

(*R*)-*N*-((*R*)-1-(6,9-diphenyl-9H-carbazol-3-yl)-2-(4-iodophenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3am)



3am

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 58% (79 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.34 (dd, *J* = 1.8, 0.6 Hz, 1H), 8.12 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.69 (d, *J* = 7.2 Hz, 3H), 7.67 – 7.65 (m, 1H), 7.60 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.55 – 7.52 (m, 2H), 7.49 (dd, *J* = 8.3, 7.0 Hz, 3H), 7.43 (dd, *J* = 8.6, 0.7 Hz, 1H), 7.39 – 7.30 (m, 3H), 6.12 (d, *J* = 3.5 Hz, 1H), 5.20 (d, *J* = 3.5 Hz, 1H), 1.22 (s, 9H).

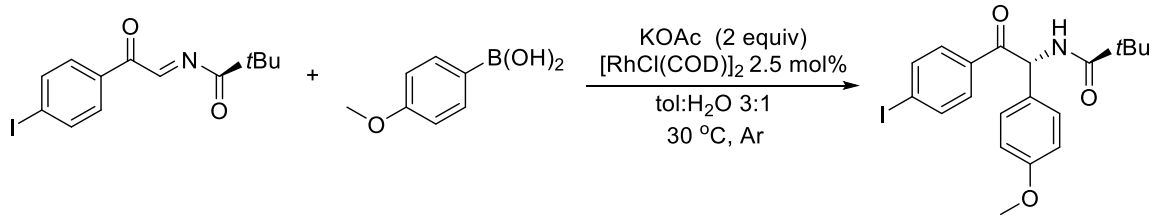
^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.7, 141.6, 141.1, 140.7, 137.9, 137.2, 133.9, 133.7, 130.4, 129.9, 129.1, 128.8, 127.8, 127.3, 126.9, 126.7, 126.4, 126.0, 124.1, 123.3, 120.6, 118.9, 110.8, 110.2, 101.6, 63.5, 55.9, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{36}H_{32}IN_2O_2S^+$ 683.1224; Found: 683.1221.

[α]^{25}D: -94.4 (c 0.5, Chloroform).

4. Scale-up synthesis and synthetic applications

Scale-up synthesis

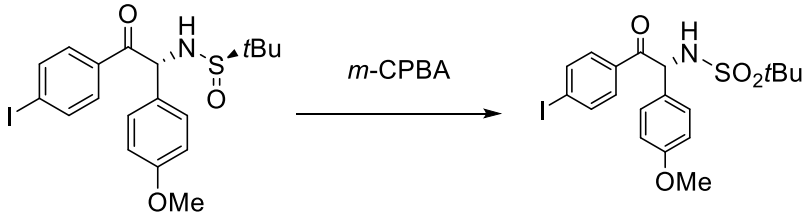


1h **2a** **3h**

To a Schlenk tube added $[RhCl(COD)]_2$ (35 mg, 0.0125 mmol, 2.5 mol %) , *N*-Sulfinyl imine (**1h**) (3 mmol), arylboronic acid (**2a**) (6 mmol) and KOAc (6 mmol) under nitrogen atmosphere. Then toluene (3 mL) and water (1 ml) were added and the mixture was stirred at 30 ℃ for 3 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with saturated ammonium chloride aqueous solution and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 3: 1) to isolate the product **3h** (1074 mg, >98: 2 dr) as yellow oil.

Synthetic applications

The synthesis of (*R*)-*N*-(2-(4-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfonamide (4)

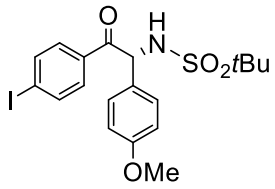


3h **4**

In a Schlenk tube, *m*-CPBA (0.4 mmol, 2 equiv) was added to the solution of **3h** (0.2 mmol) in DCM (1.5 mL) at 0 ℃. The mixture was stirred for 1 h at rt and subsequently quenched with a aqueous solution containing both sodium bicarbonate and sodium metabisulfite. The reaction mixture was poured into a separatory funnel containing a mixture of water and diethyl ether. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure and dried in

vacuo to provide the crude product. The crude reaction product was purified by flash column chromatography (PE/EA, 4: 1) to get product **4**. [3]

(*R*)-*N*-(2-(4-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfonamide (4)



4

White solid (mp: 150-153 °C), yield: 90% (87 mg), R_f = 0.5 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

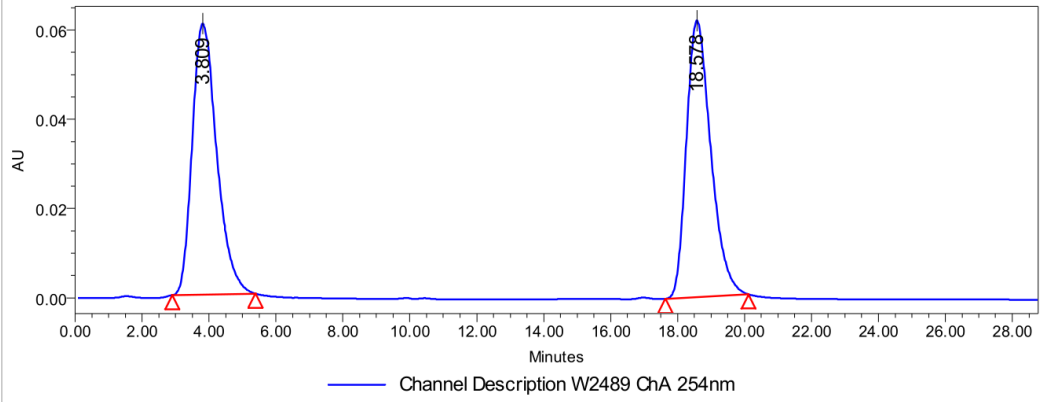
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.03 (d, *J* = 7.3 Hz, 1H), 5.68 (dd, *J* = 7.3, 1.3 Hz, 1H), 3.73 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.1, 159.7, 138.0, 133.2, 130.3, 129.3, 128.9, 114.7, 102.1, 61.7, 59.8, 55.2, 24.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}INO_4S^+$ 488.0387; Found: 488.0383.

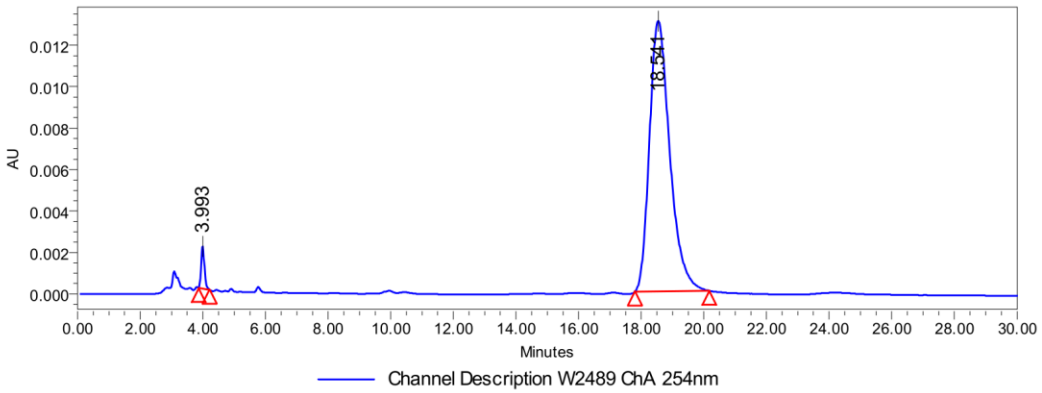
HPLC analysis: DAICEL CHIRALCEL OD-H, hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 3.993 min, t_R (major) = 18.541 min, 95% ee.

[α]^{25}D: -12.00 (c 0.5, Chloroform)**.**



Peak Result

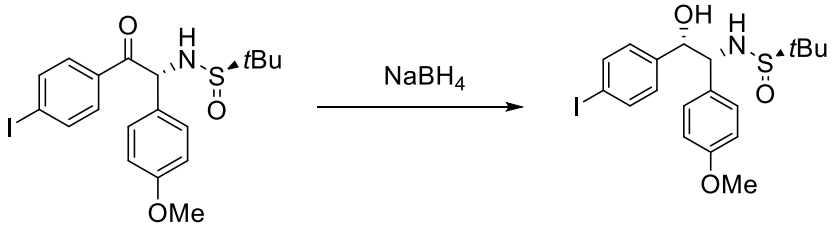
	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	3.809	BB	149.000	3093301	60751	49.60
2	18.578	BB	149.000	3143380	61993	50.40



Peak Result

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	3.993	BB	21.000	15097	2035	2.50
2	18.541	Bb	142.000	589364	13048	97.50

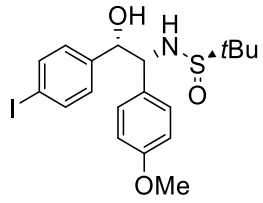
The synthesis of (*R*)-*N*-((1*R*,2*S*)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (5)



3h **5**

To a Schlenk tube added **3h** (94.2 mg, 0.2 mmol, 1.0 equiv) and MeOH (0.5 mL, 0.4 M). The resulting solution was cooled to 0 ^{o}C and $NaBH_4$ was added in one portion (9 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was stirred at 0 ^{o}C for 1 h. The reaction mixture was diluted with EtOAc (3 mL) and was washed with distilled water. The aqueous layer was extracted with EtOAc (3 x 10 ml), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 2: 1) to isolate the product **5** (74 mg, >98: 2 dr) as white solid.[4]

(*R*)-*N*-((1*R*,2*S*)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (5)



5

White solid (mp: 210-214 ^{o}C), yield: 78% (73 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

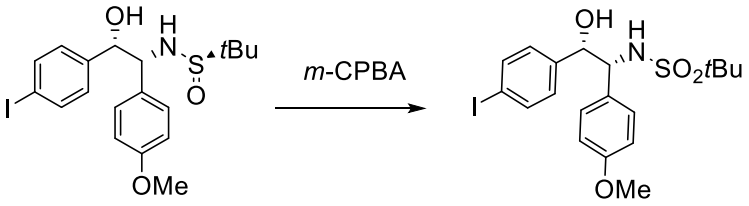
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 4.1 Hz, 1H), 4.68 (dd, *J* = 6.3, 4.0 Hz, 1H), 4.06 (d, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.0, 138.6, 136.7, 129.5, 129.1, 128.9, 113.5, 93.3, 76.8, 64.4, 56.0, 55.1, 22.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}INO_4S^+$ 474.0594; Found: 474.0597.

[α]^{25}D: -58.00 (c 0.5, Chloroform)**.**

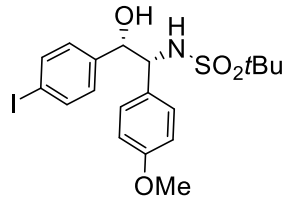
The synthesis of *N*-((1*R*, 2*S*)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6)



5 **6**

To a Schlenk tube add *m*-CPBA (2 equiv) was added to the solution of **5** in anhydrous DCM (1.5 mL) at 0 ℃. The mixture was stirred for 1 h at rt and subsequently quenched with a aqueous solution containing both sodium bicarbonate and sodium metabisulfite. The reaction mixture was poured into a separatory funnel containing a mixture of water and diethyl ether. The organic layer was separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure and dried in vacuo to provide the crude product. The crude reaction product was purified by flash column chromatography (PE/EA, 4: 1) to get product **6**.[3]

***N*-((1*R*, 2*S*)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6)**



6

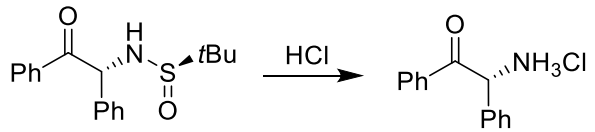
White solid (mp: 179-181 ^{o}C), yield: 83% (60 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.08 (t, *J* = 4.1 Hz, 1H), 4.65 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.77 (s, 3H), 3.17 (d, *J* = 4.8 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.0, 139.2, 137.0, 129.0, 128.5, 128.4, 113.5, 93.4, 77.4, 63.1, 60.0, 55.1, 24.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}INO_4S^+$ 490.0543; Found: 490.0539.

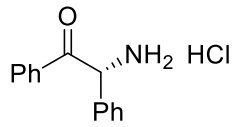
$[\alpha]^{25}$D: 29.20 (c 0.5, Chloroform)**.**



3r **7**

3r (63 mg, 0.2 mmol, 1.0 equiv) was taken up in MeOH (1.3 mL, 0.15 M) and was treated with 4.0 M HCl in dioxane (0.25 mL, 5.0 equiv. HCl) at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the amine hydrochloride (40 mg, 80%) as white solid.[4]

(*R*)-2-amino-1,2-diphenylethan-1-one hydrochloride (7)



7

White solid (mp: >230 ^{o}C), yield: 70% (34 mg), Known compound.[5]

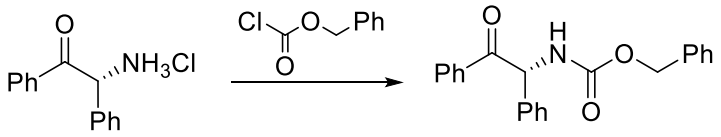
^{1}H NMR (500 MHz, Methanol-d_4) δ 8.02 – 7.97 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.42 (m, 5H), 6.22 (s, 1H).

^{13}C NMR (151 MHz, Methanol-d4) δ 194.0, 135.4, 134.3, 133.4, 131.1, 130.7, 130.1, 129.8, 129.8, 60.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{14}ClNNaO^+$ 270.0656; Found: 270.0660.

[α]^{25}D: -102.6 (c 0.5, CH_3OH).

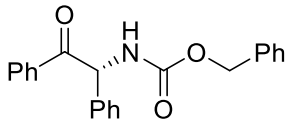
Benzyl (*R*)-(2-oxo-1,2-diphenylethyl)carbamate (8)



7 8

In a Schlenk tube, 2-Oxo-1,2- diphenylethan-1-aminium chloride **7** (50 mg, 0.2 mmol, 1.0 equiv) was suspended in tetrahydrofuran (THF, 1 mL) and cooled to 0 °C in an ice−salt bath. Triethylamine (131 mg, 180 µl, 1.3 mmol, 6.5 equiv) was added dropwise to the reaction mixture and stirred at the same temperature for 30 min. During the addition of triethylamine, the initially cloudy reaction mixture became clear. To the reaction mixture, benzyl chloroformate (34 mg, 0.4 mmol, 2.0 equiv) in THF (1 mL) was added dropwise and the resulting reaction mixture was stirred at 0 ℃ for 30 min followed by overnight stirring at rt. Once the reaction was complete (assessed by TLC), water (15 mL) and DCM (5 mL) were added and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. The crude material was purified by column chromatography (PE/EA, 5: 1) to afford product **8** as a white solid (0.410 g, 1.31 mmol, 94%).[5]

benzyl (*R*)-(2-oxo-1,2-diphenylethyl)carbamate (8)



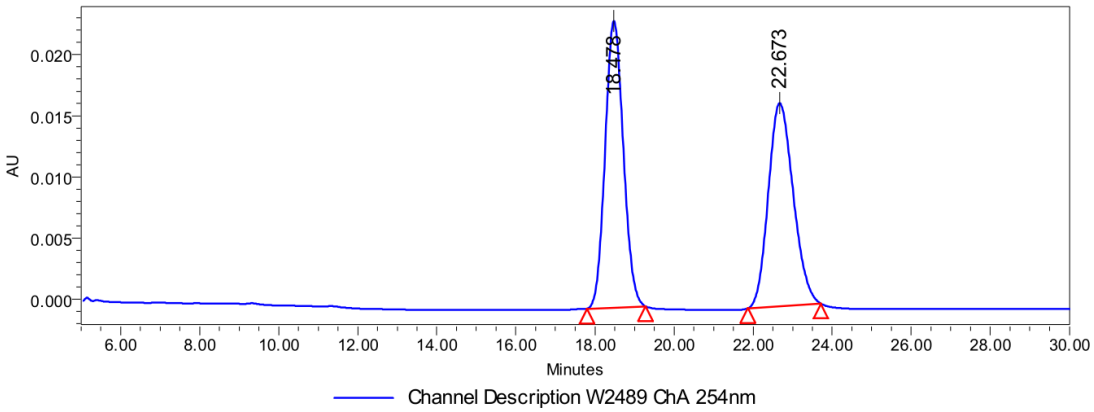
8

White solid (mp: 92-94 ^oC), yield: 94% (64 mg), R_f = 0.4 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 5: 1, v/v). Known compound.[5]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.90 (m, 2H), 7.57 – 7.46 (m, 1H), 7.44 – 7.37 (m, 4H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.30 (m, 4H), 7.27 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 7.4 Hz, 1H), 5.39 – 4.68 (m, 2H).

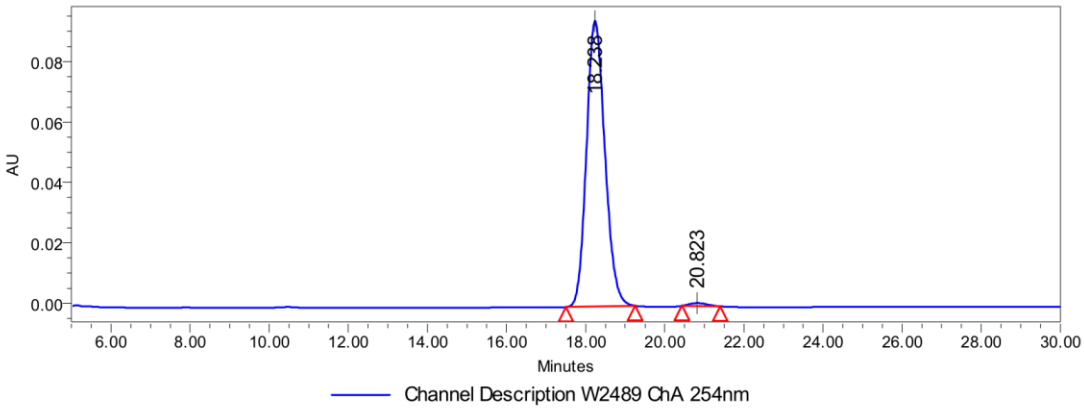
HPLC analysis: DAICEL CHIRALCEL OD-H, hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (major) = 18.23 min, t_R (minor) = 20.82 min, 98% ee.

[α]^{25}D: -162.2 (c 0.5, Chloroform).



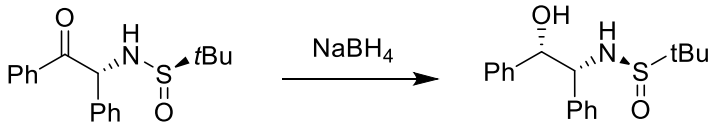
Peak Result

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	18.478	BB	89.000	750637	23433	50.79
2	22.673	BB	111.000	727269	16611	49.21



Peak Result

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	18.238	BB	105.000	3063732	94549	98.98
2	20.823	Bb	58.000	31573	992	1.02

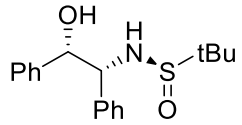


3r **9**

To a Schlenk tube added **3r** (126 mg, 0.4 mmol, 1.0 equiv) in MeOH (0.5 mL, 0.4 M). The resulting solution was cooled to 0 ^{o}C and $NaBH_4$ was added in one portion (18 mg, 0.48 mmol, 1.2 equiv). The

reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was diluted with EtOAc (3 mL) and was washed with distilled water. The aqueous layer was extracted with EtOAc (3 x 10 ml), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 2: 1) to isolate the product **9**.[4]

(*R*)-*N*-((1R,2S)-2-hydroxy-1,2-diphenylethyl)-2-methylpropane-2-sulfinamide (9)



9

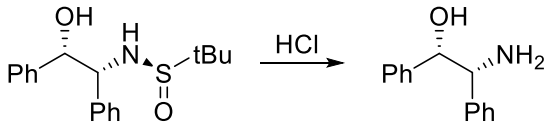
White solid (mp: >320 °C), yield: 80% (101 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 3H), 7.24 – 7.21 (m, 3H), 7.09 (dd, *J* = 7.5, 2.1 Hz, 2H), 6.99 – 6.95 (m, 2H), 5.07 (d, *J* = 4.3 Hz, 1H), 4.78 (dd, *J* = 7.2, 4.3 Hz, 1H), 3.88 (d, *J* = 7.3 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.45, 138.40, 128.22, 127.96, 127.88, 127.69, 127.61, 127.24, 77.62, 65.53, 56.02, 22.71.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{24}NO_2S^+$ 318.1522; Found: 318.1516.

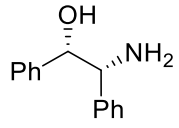
[α]^{25}D: -87.9 (c 0.5, Chloroform).



9 **10**

To the solution of t-butanesulfinamide **9** (0.32 mmol) in MeOH (0.42 ml) was added HCl in 1,4-dioxane 4.0 M (0.64 mmol, 0.16 ml). The solution was stirred for 1 h, then Et_2O was added. The precipitate was filtered off and washed with diethyl ether to afford the amine hydrochloride. The amine hydrochloride was basified with 1 M NaOH (30 ml) and extracted with EtOAc (15 ml x 2). The EtOAc layers were combined, washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo .**10** was obtained as a white solid.

(1S,2R)-2-amino-1,2-diphenylethan-1-ol (10)



10

white solid (mp: 142 – 145 °C), yield: 80% (54 mg), R_f = 0.3 (silica gel, EA), column chromatography (silica gel, PE: DCM = 1: 1, v/v). Known compound.[7]

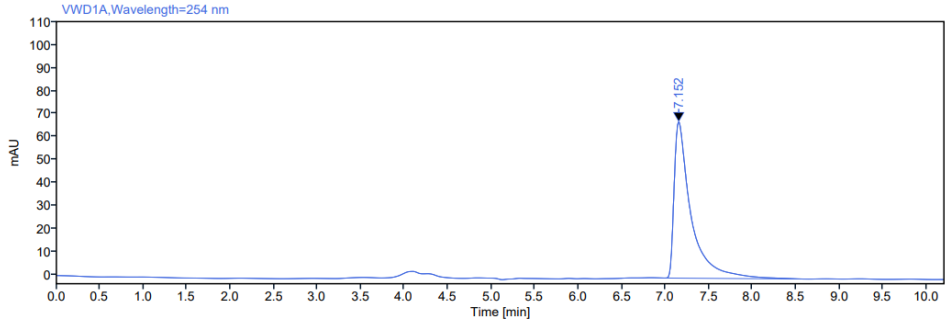
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 6H), 7.26 – 7.20 (m, 4H), 4.73 (d, *J* = 6.3 Hz, 1H), 4.15 (d, *J* = 6.3 Hz, 1H).

HPLC analysis: DAICEL CHIRALCEL OJ-H, hexane/isopropanol = 95/5, 1mL/min, λ = 254 nm,

Absolute configurations were determined by HPLC compared with commercial (1S,2R)-2-amino-1,2-diphenylethan-1-ol

HPLC diagram of commercial (1*S*, 2*R*) - 2-amino-1,2-diphenylethane-1-alcohol

Data file:	SR-OJH-100595.dx		
Sequence Name:	LC1260-2021-11-03 16-12-36+08-00	**Project Name:**	WH
Sample name:	SR-OJH-100595	**Operator:**	SYSTEM
Instrument:	LC1260	**Injection date:**	2021-11-03 16:13:33+08:00
Inj. volume:	10.000 µL	**Location:**	P1-F3
Acq. method:	P2 10 0595 30min.amx	**Type:**	Sample
Processing method:	GC_LC Area Percent_DefaultMethod.pmx	**Sample amount:**	0.00
Manually modified:	Manual Integration		

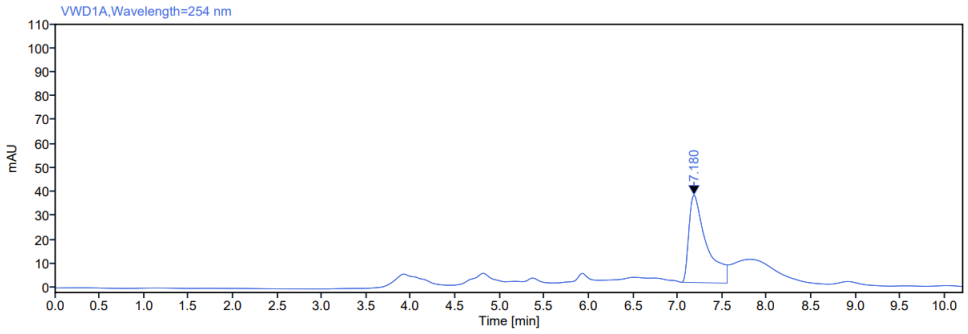


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.152	MM m	1.60	924.46	68.06	100.00	
		Sum	**924.46**			

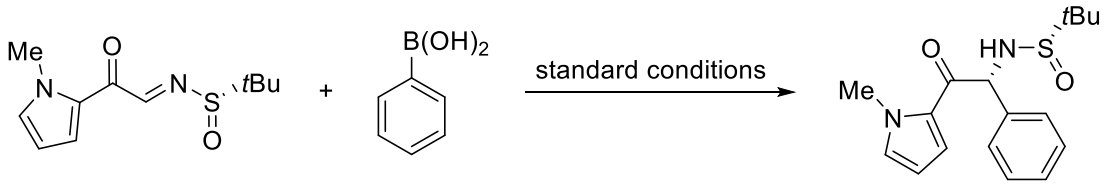
HPLC diagram of **10**

Data file:	MAKE-OJH-100595.dx		
Sequence Name:	LC1260-2021-11-03 15-56-16+08-00	**Project Name:**	WH
Sample name:	MAKE-OJH-100595	**Operator:**	SYSTEM
Instrument:	LC1260	**Injection date:**	2021-11-03 15:57:12+08:00
Inj. volume:	10.000 µL	**Location:**	P1-F2
Acq. method:	P2 10 0595 30min.amx	**Type:**	Sample
Processing method:	GC_LC Area Percent_DefaultMethod.pmx	**Sample amount:**	0.00
Manually modified:	Manual Integration		



Signal:	VWD1A,Wavelength=254 nm					
RT [min]	**Type**	**Width [min]**	**Area**	**Height**	**Area%**	**Name**
7.180	MM m	0.51	504.04	36.44	100.00	
		Sum	**504.04**			

(*R*)-2-methyl-*N*-((*R*)-2-(1-methyl-1H-pyrrol-2-yl)-2-oxo-1-phenylethyl)propane-2-sulfinamide



12 **2b** **13**, 70%, >98:2 dr

Following the general procedure *2* on 0.2 mmol scale, yellow oil liquid, yield: 70% (43 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

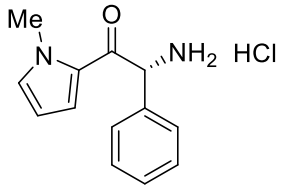
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 6.97 (dd, *J* = 4.2, 1.6 Hz, 1H), 6.79 (t, *J* = 2.0 Hz, 1H), 6.07 (dd, *J* = 4.3, 2.4 Hz, 1H), 5.68 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 5.0 Hz, 1H), 3.91 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.1, 139.6, 132.2, 128.8, 128.2, 128.0, 127.9, 121.0, 108.7, 63.2, 55.9, 37.7, 22.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}N_2O_2S^+$ 319.1475; Found: 319.1468.

[α]^{25}D: -188.6 (*c* 0.5, Chloroform).

(*R*)-2-amino-1-(1-methyl-1H-pyrrol-2-yl)-2-phenylethan-1-one hydrochloride (14)

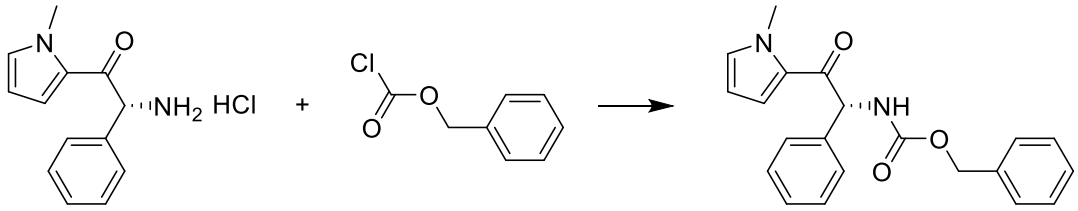


14

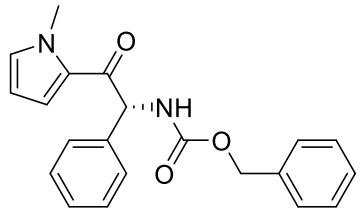
13 (50.0 mg, 0.2 mmol, 1.0 equiv) was taken up in MeOH (1.3 mL, 0.15 M) and was treated with 4.0 M HCl in dioxane (0.25 mL, 5.0 equiv. HCl) at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the amine hydrochloride (40 mg, 80%) as gray solid.[4] Known compound.[6]

HPLC analysis: DAICEL CHIRALCEL OZ-3, hexane/isopropanol = 85/15, 1 mL/min, λ = 254 nm, t_R (major) = 20.9 min, t_R (minor) = 26.1 min, >99% ee. (The ee value was determined after an amidation with benzyl chloroformate）

^{1}H NMR (500 MHz, Methanol-d_4) δ 7.58 – 7.50 (m, 2H), 7.48 – 7.36 (m, 3H), 7.10 (dd, *J* = 4.3, 1.7 Hz, 1H), 7.07 (t, *J* = 2.0 Hz, 1H), 6.12 (dt, *J* = 4.3, 2.1 Hz, 1H), 5.83 (d, *J* = 1.8 Hz, 1H), 3.96 (d, *J* = 1.7 Hz, 3H).



In a Schlenk tube, hydrochloride **14** (50 mg, 0.2 mmol, 1.0 equiv) was suspended in DCM (10 ml) and cooled to 0 °C in an ice−salt bath. Triethylamine (131 mg, 180 µl, 1.3 mmol, 6.5 equiv) was added dropwise to the reaction mixture and stirred at the same temperature for 30 min. During the addition of triethylamine, the initially cloudy reaction mixture became clear. To the reaction mixture, Benzyl chloroformate (34 mg, 0.4 mmol, 2.0 equiv) in DCM (1 mL) was added dropwise and the resulting reaction mixture was stirred at 0 ℃ for 30 min followed by overnight stirring at rt. Once the reaction was complete (assessed by TLC), water (15 mL) and DCM (15 mL) were added and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product. The crude material was purified by column chromatography (PE/EA, 5: 1) to afford product as colorless liquid.[5]

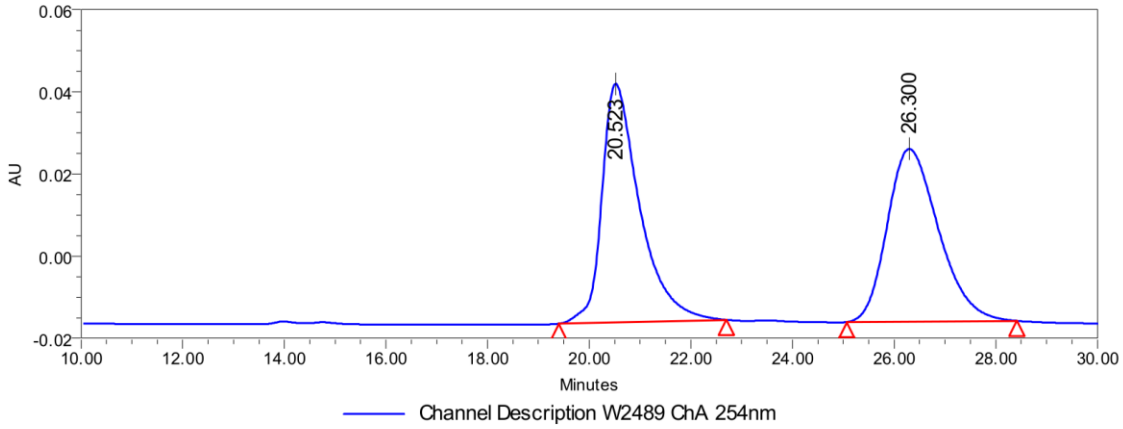


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 2H), 7.34 (d, *J* = 4.4 Hz, 4H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.28 – 7.23 (m, 1H), 7.07 (dd, *J* = 4.3, 1.7 Hz, 1H), 6.80 (t, *J* = 2.0 Hz, 1H), 6.33 (d, *J* = 7.6 Hz, 1H), 6.10 (dd, *J* = 4.3, 2.4 Hz, 1H), 6.04 (d, *J* = 7.5 Hz, 1H), 5.24 – 4.95 (dd, *J* = 45.1 Hz ,*J* = 12.3 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.3, 155.4, 138.8, 136.4, 132.2, 128.9, 128.5, 128.5, 128.3, 128.0, 127.58, 126.9, 121.1, 108.8, 66.8, 59.9, 37.6.

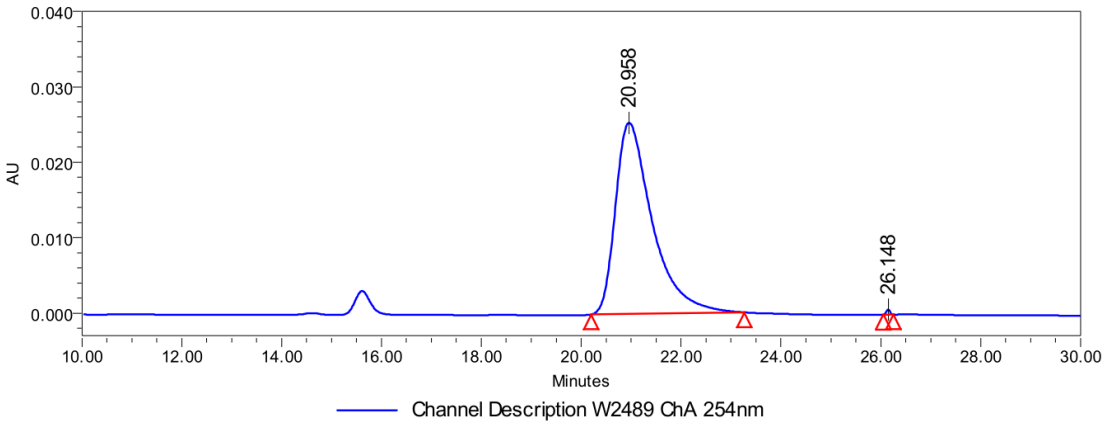
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{21}N_2O_3^+$ 349.1547; Found: 349.1540.

[α]^{25}D: -176.0 (*c* 0.5, Chloroform).



Peak Result

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	20.523	Bb	198.000	3006282	58085	50.48
2	26.300	Bb	201.000	2949180	42017	49.52



Peak Result

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	20.958	Bb	184.000	1300857	25362	99.75
2	26.148	bb	12.000	3304	669	0.25

5. Reference

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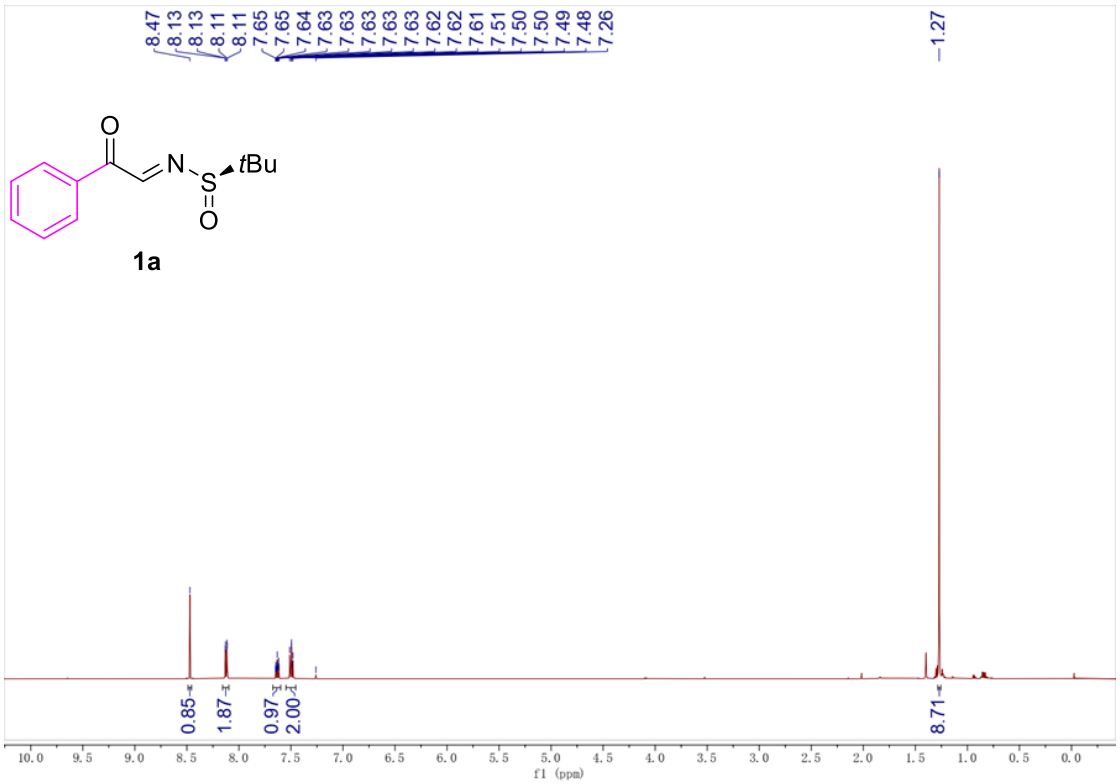
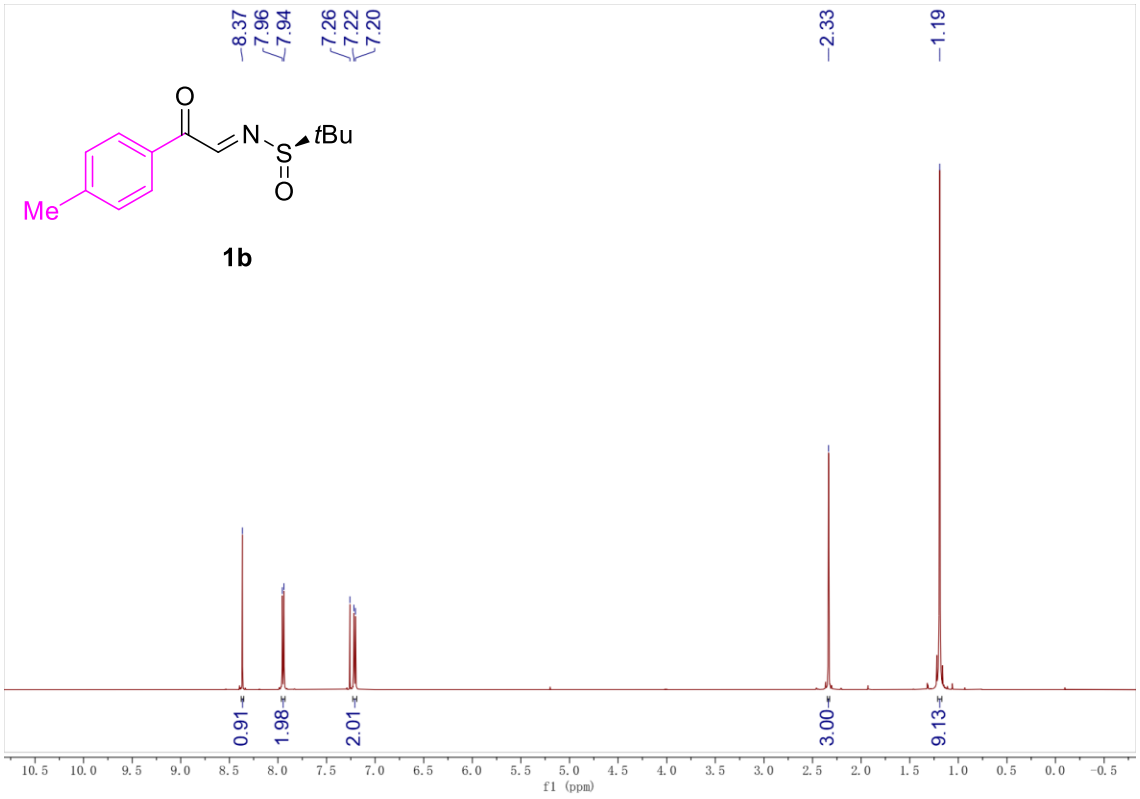
6. Copies of ^{1}H, ^{13}C and ^{19}F Spectra

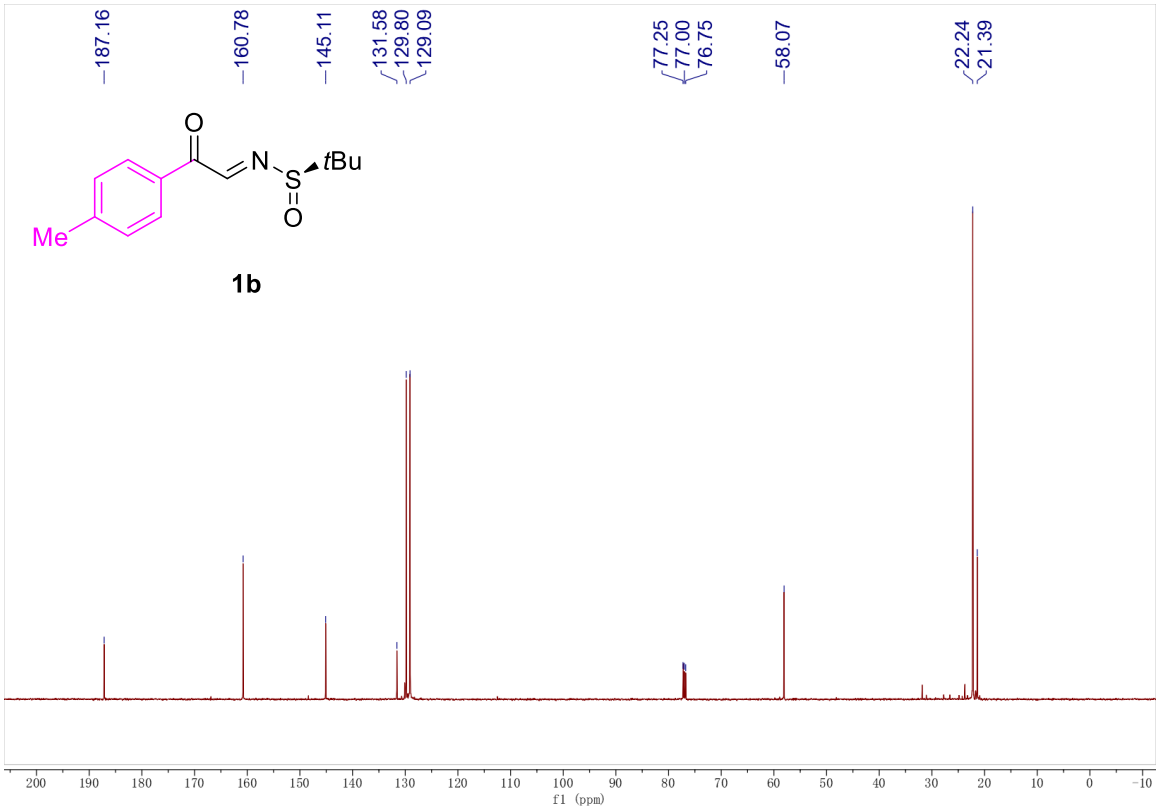
^{1}H NMR spectrum of 1a



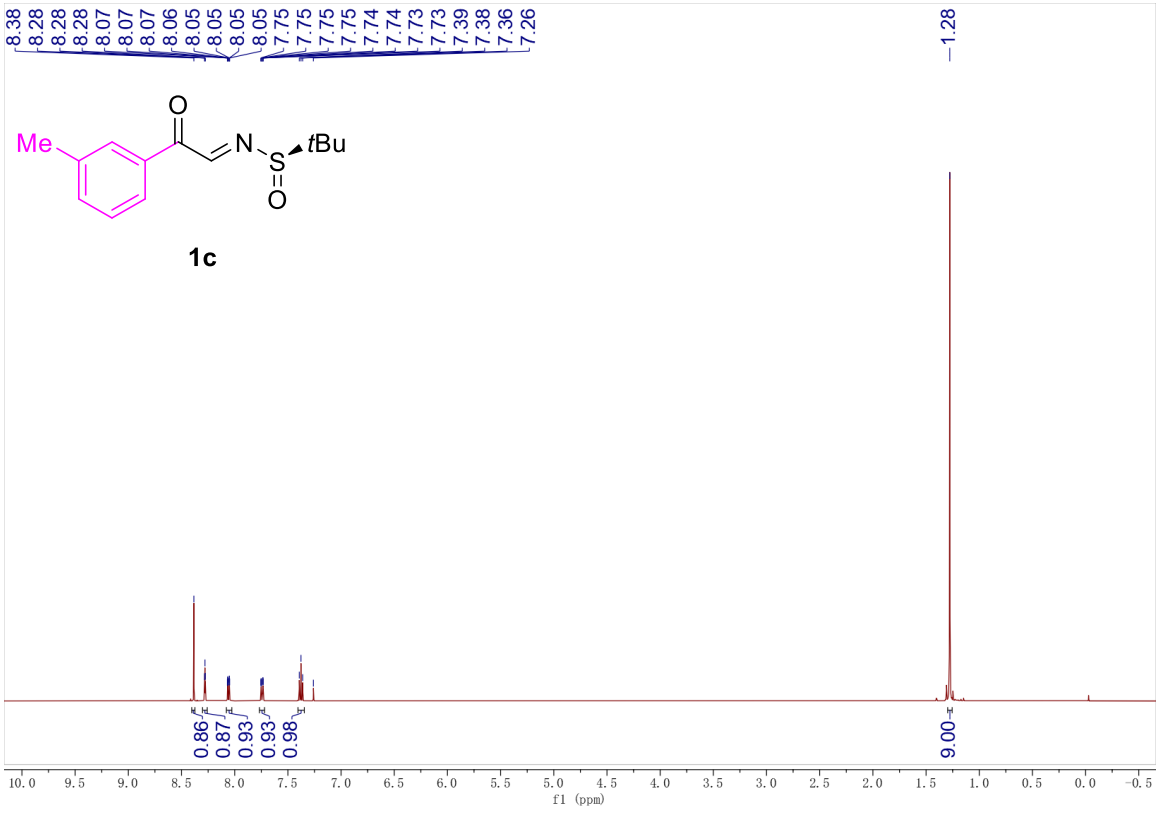
^{1}H NMR spectrum of 1b



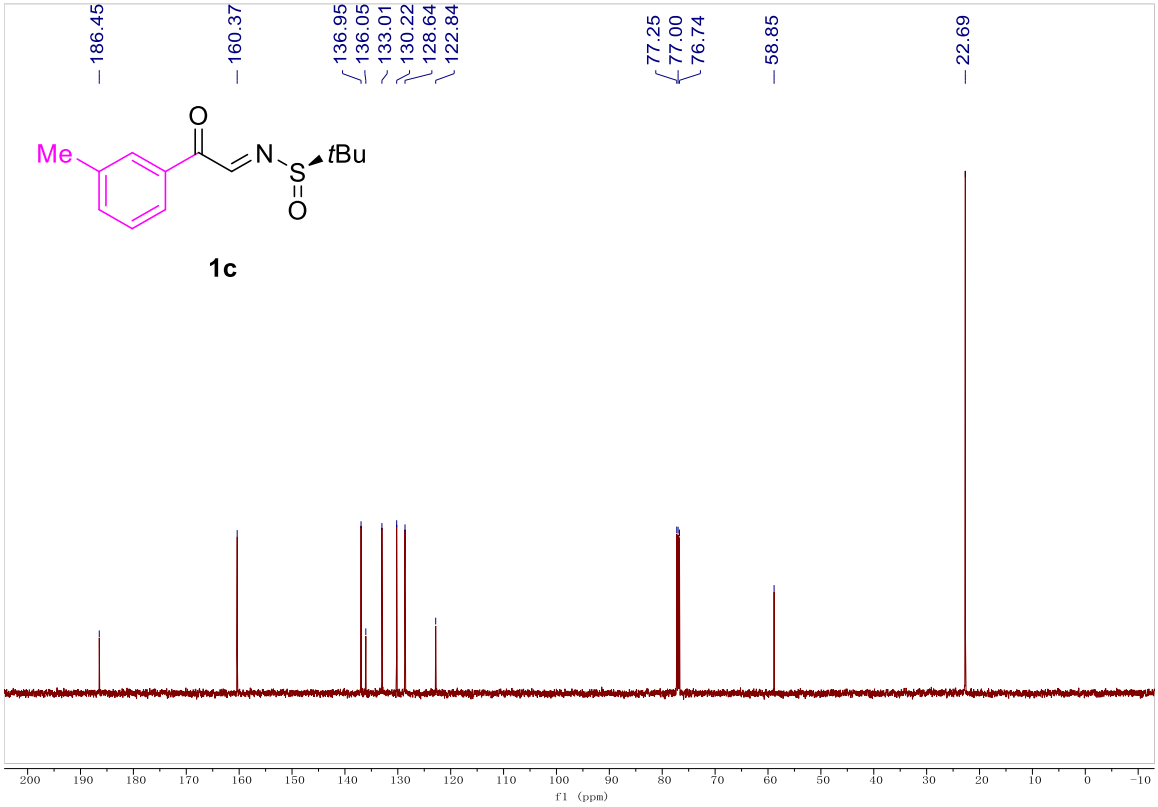
^{13}C NMR spectrum of 1b



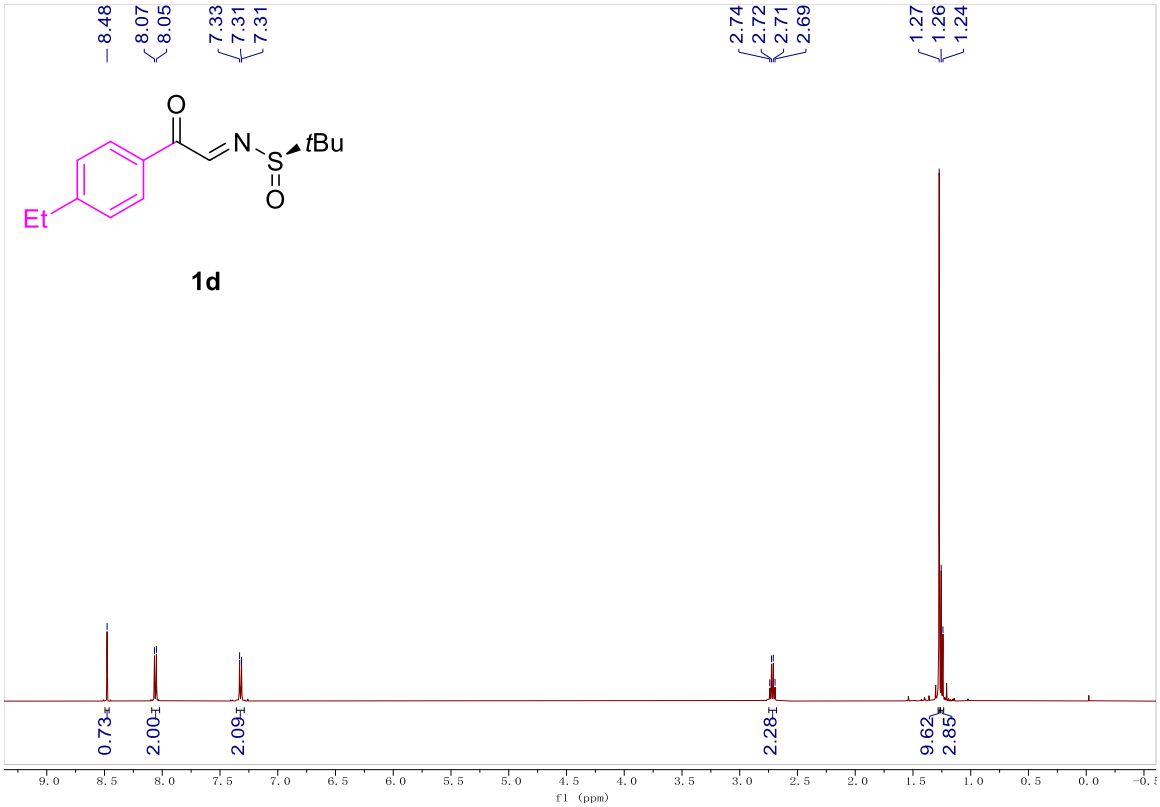
^{1}H NMR spectrum of 1c



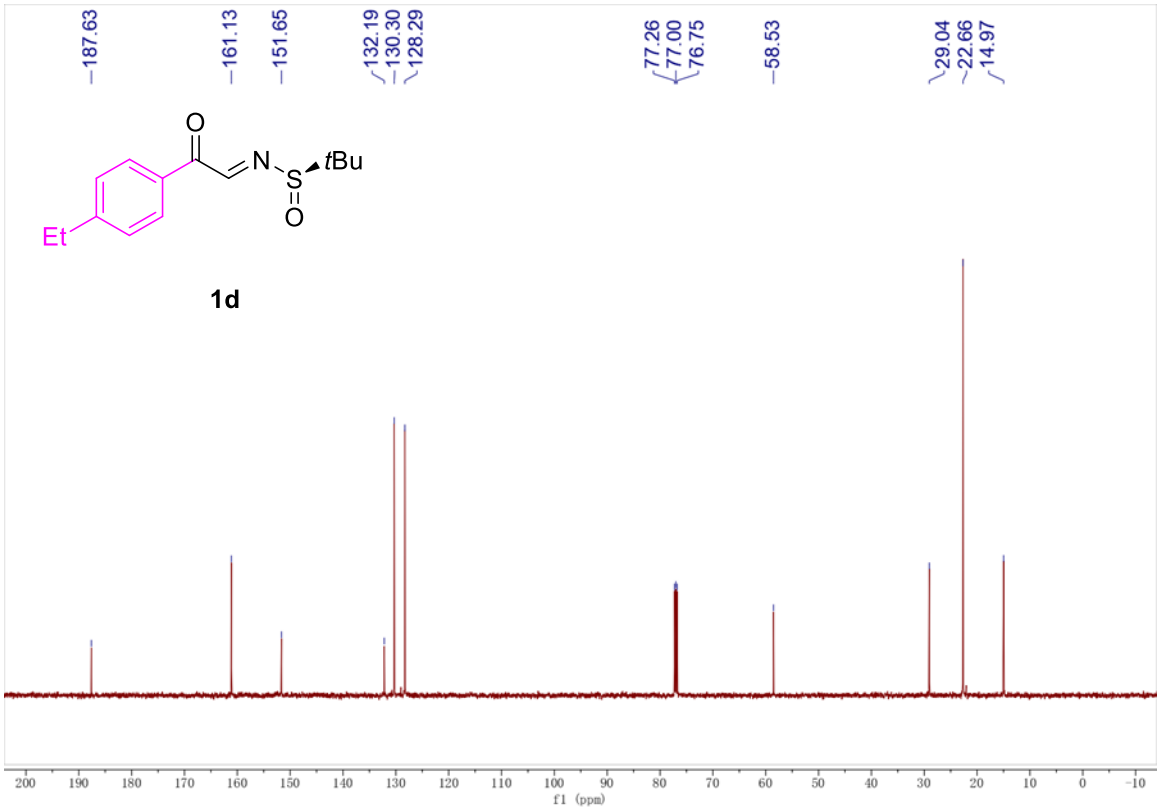
^{13}C NMR spectrum of 1c



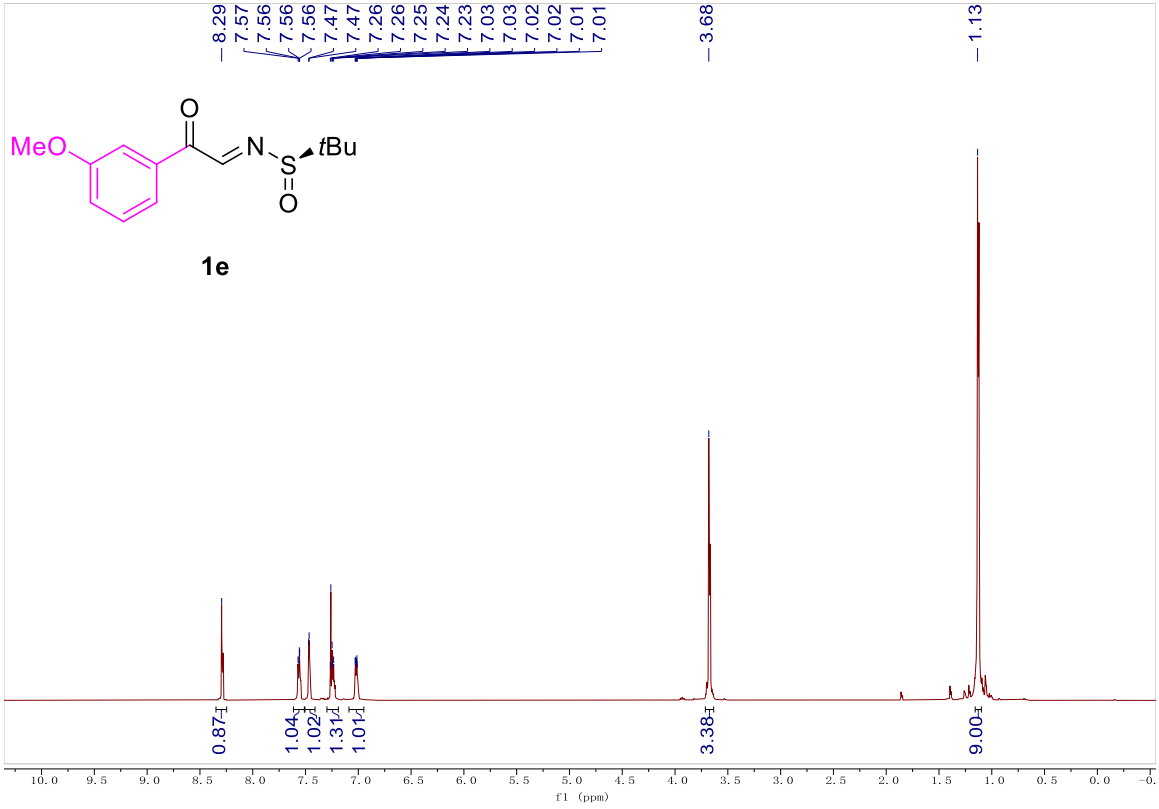
^{1}H NMR spectrum of 1d



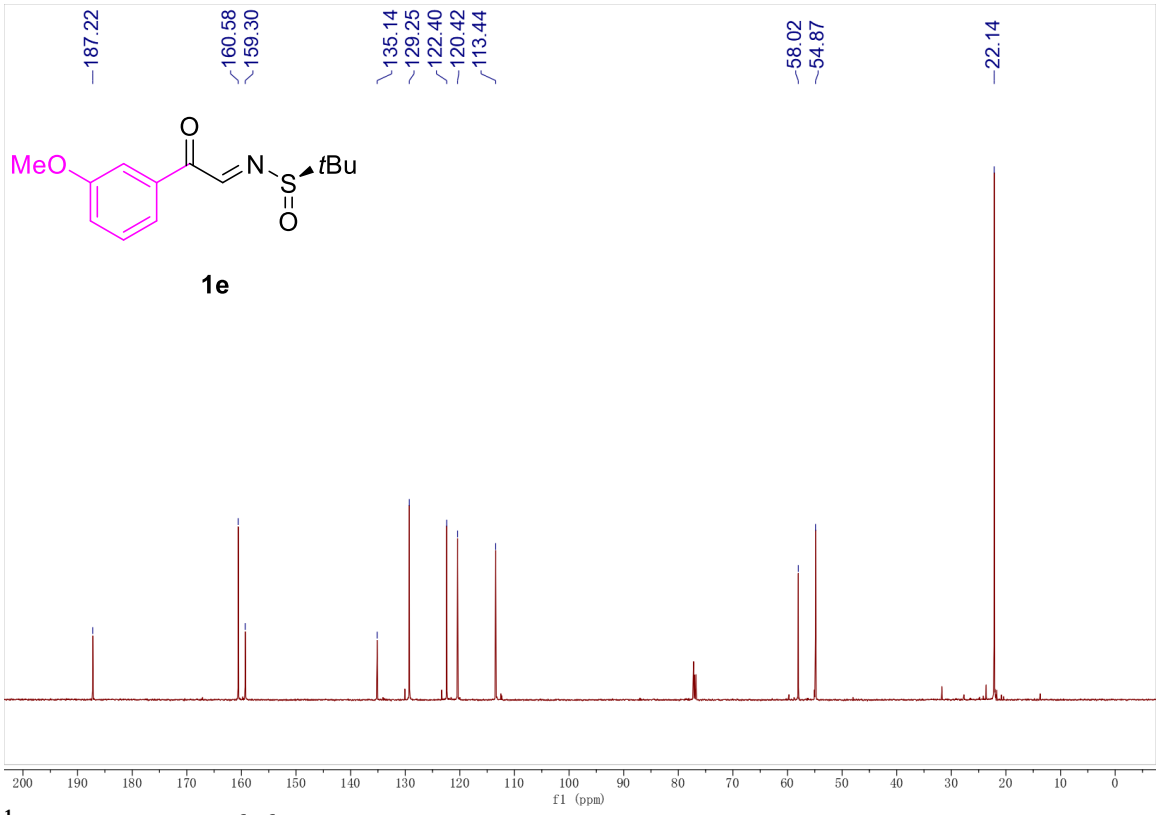
^{13}C NMR spectrum of 1d



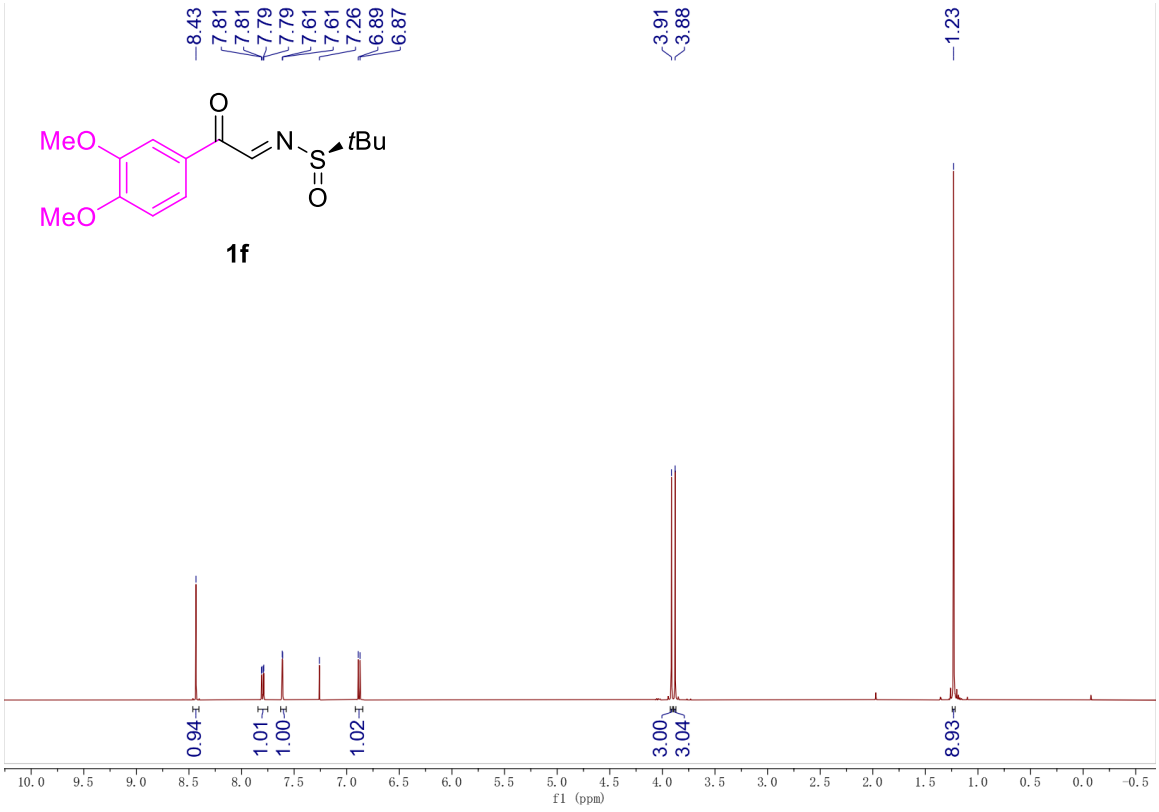
^{1}H NMR spectrum of 1e



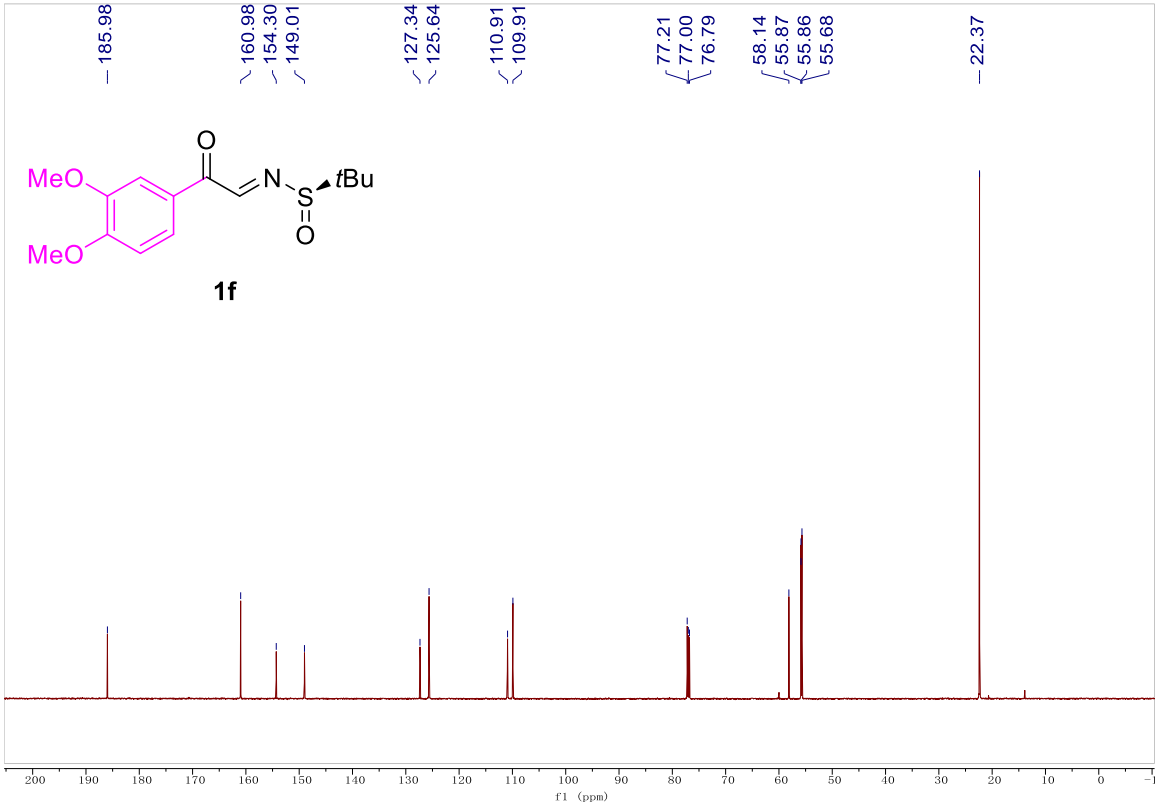
^{13}C NMR spectrum of 1e



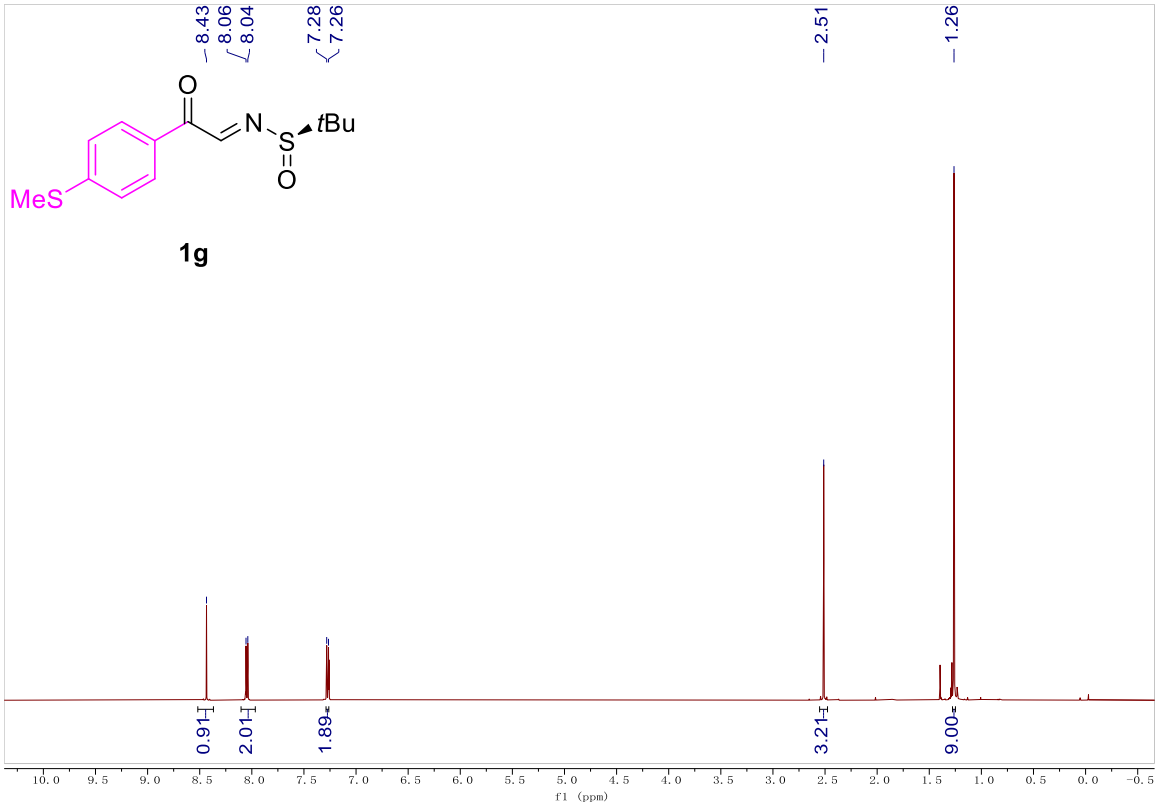
^{1}H NMR spectrum of 1f



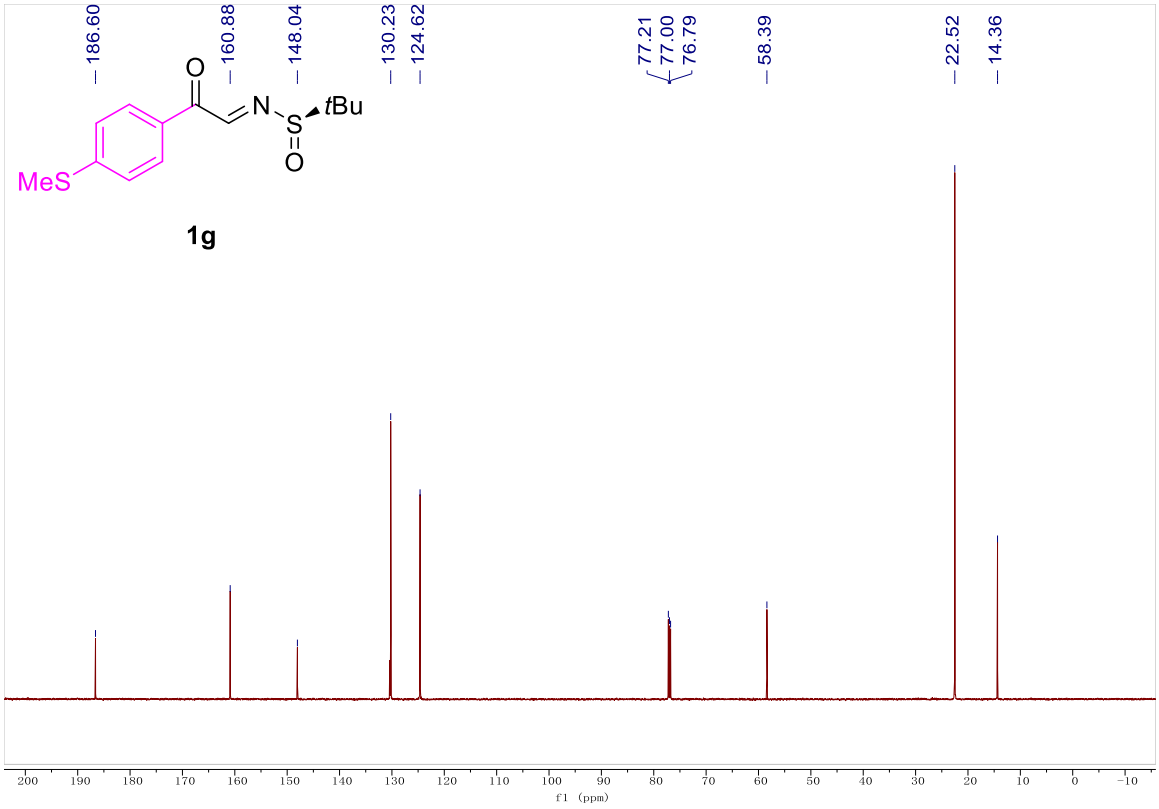
^{13}C NMR spectrum of 1f



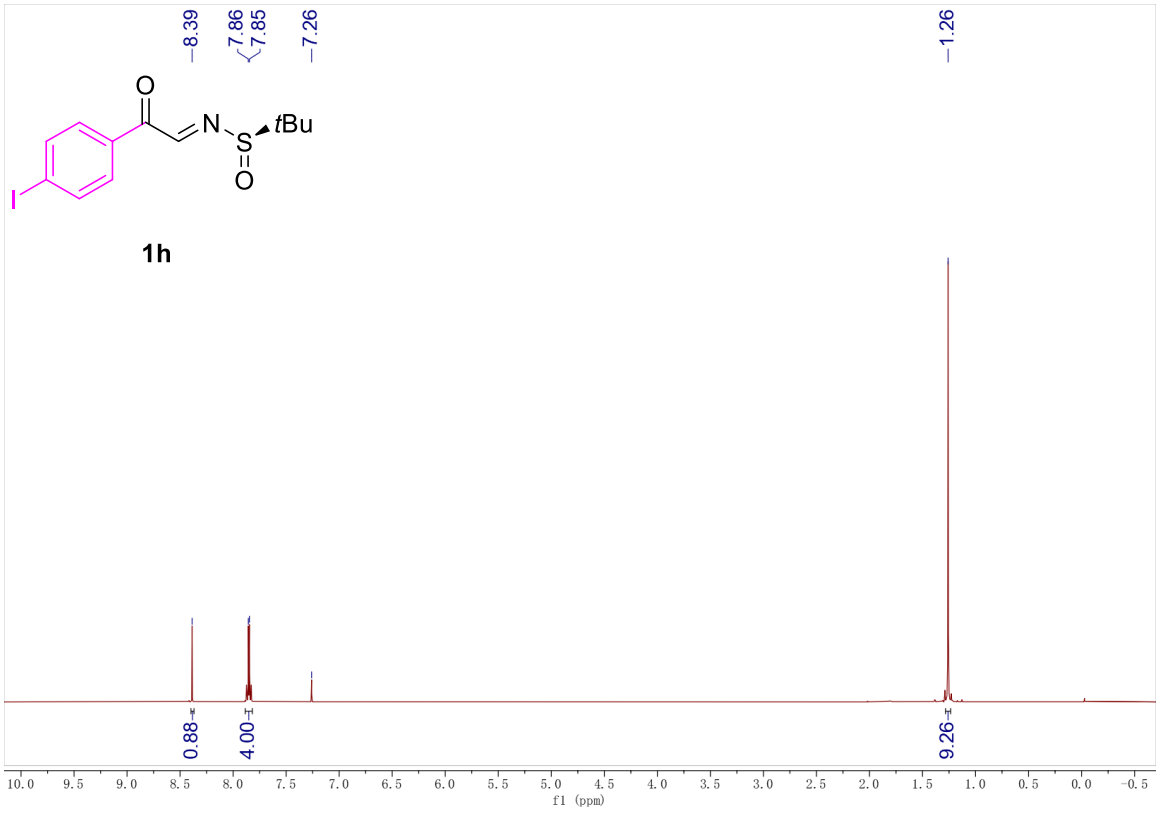
^{1}H NMR spectrum of 1g



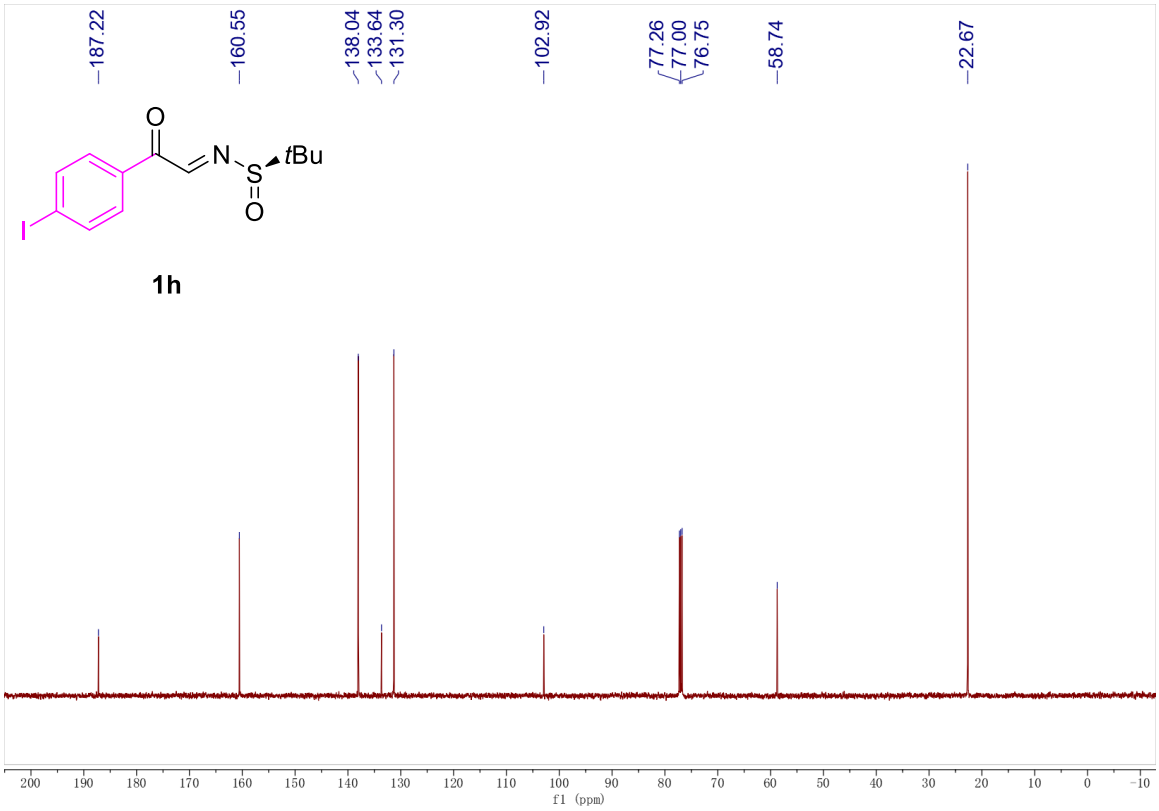
^{13}C NMR spectrum of 1g



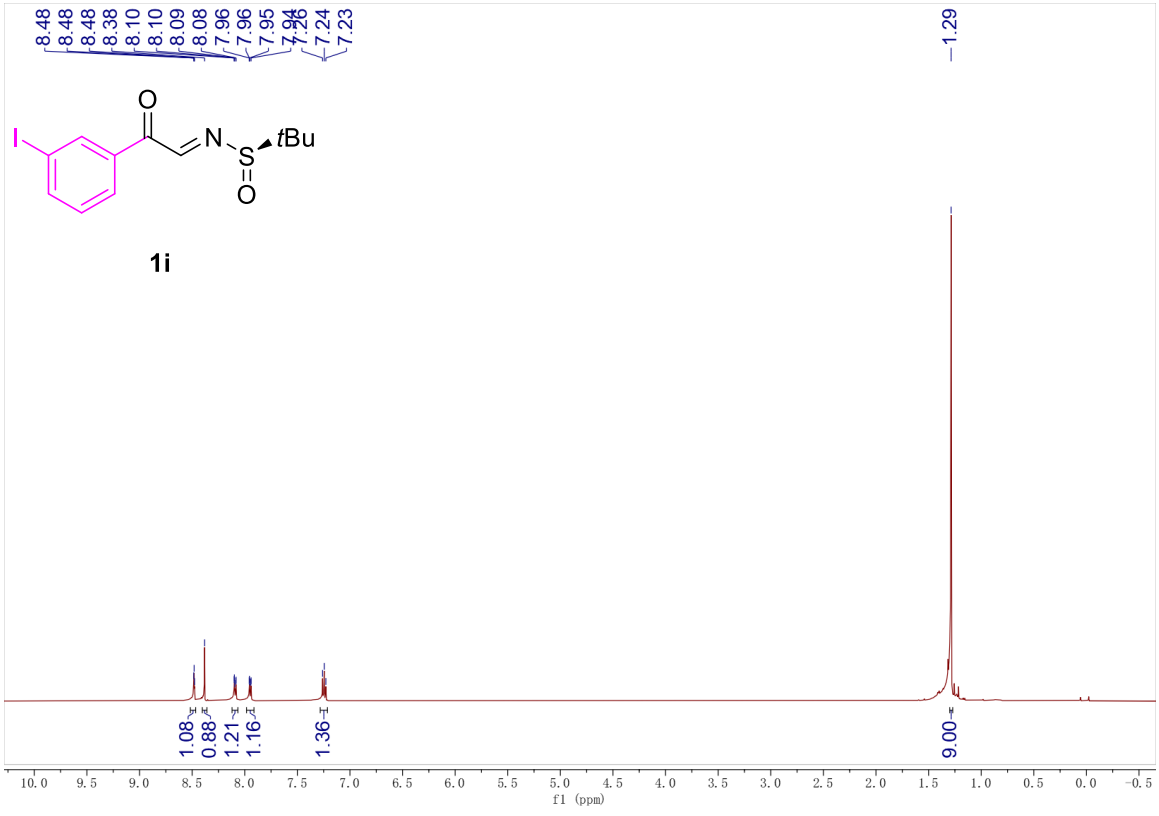
^{1}H NMR spectrum of 1h



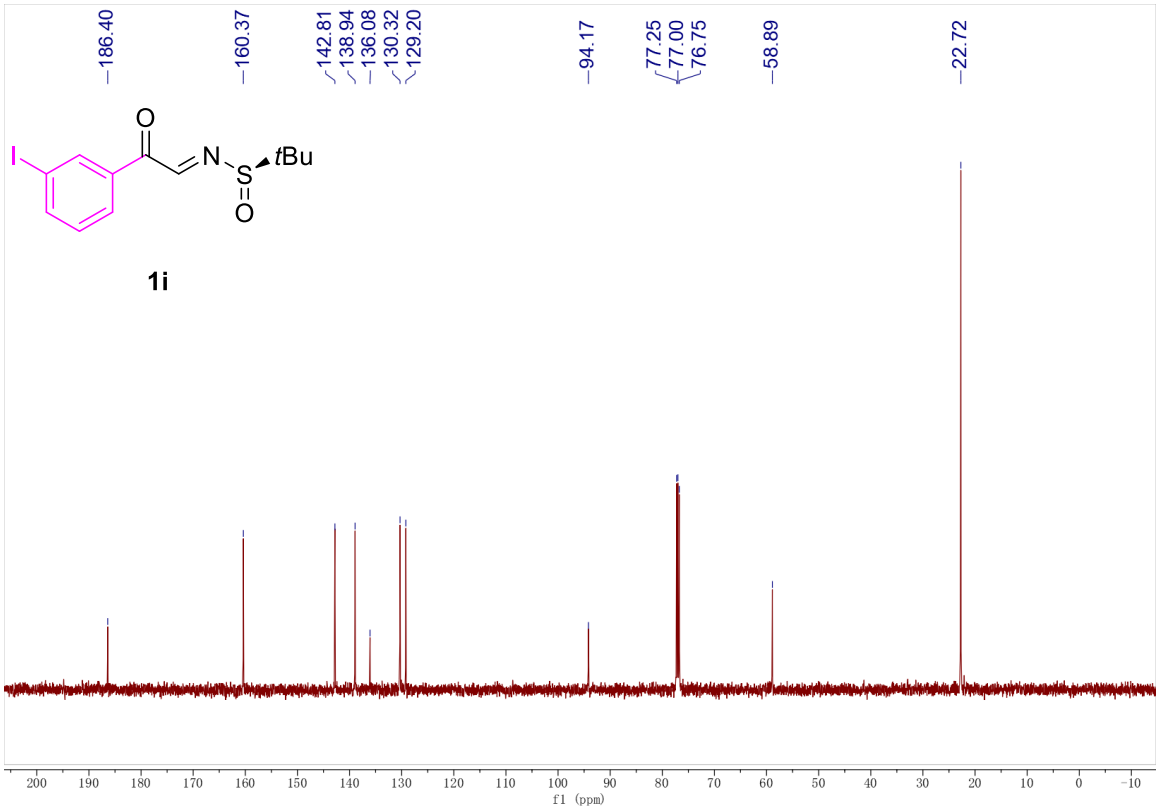
^{13}C NMR spectrum of 1h



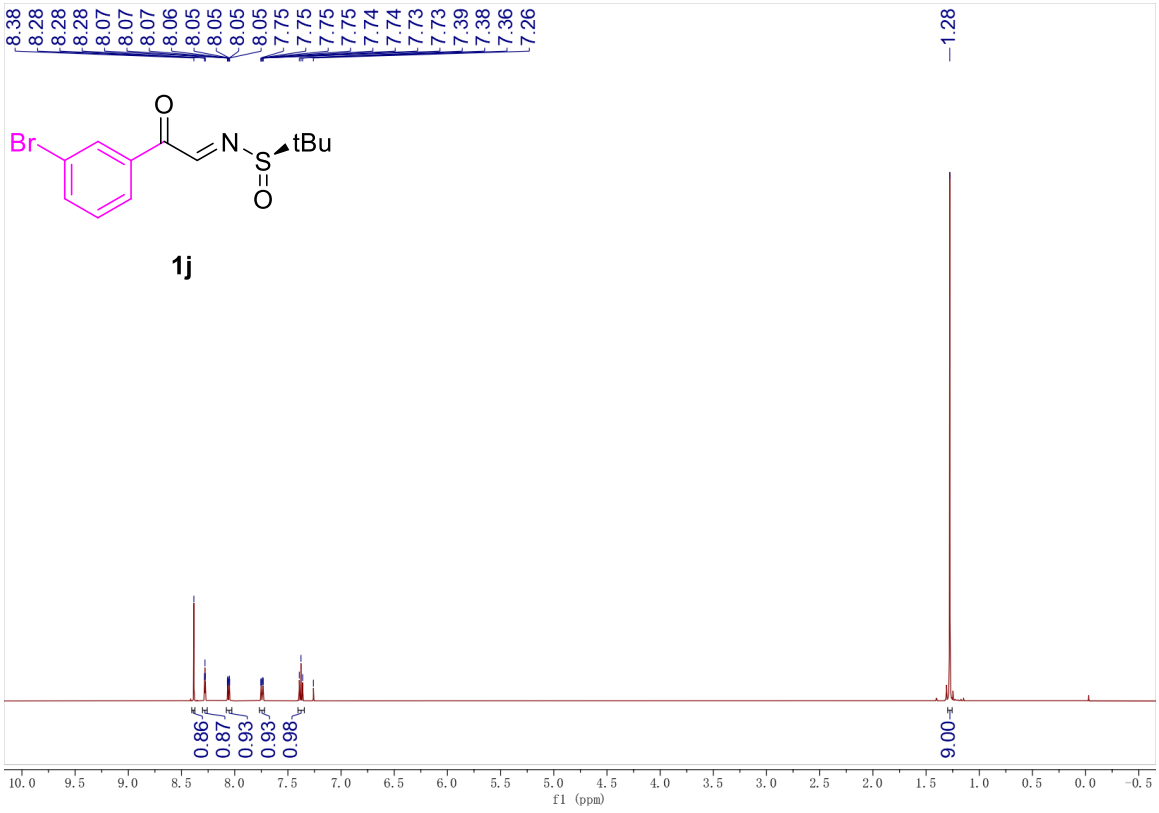
^{1}H NMR spectrum of 1i



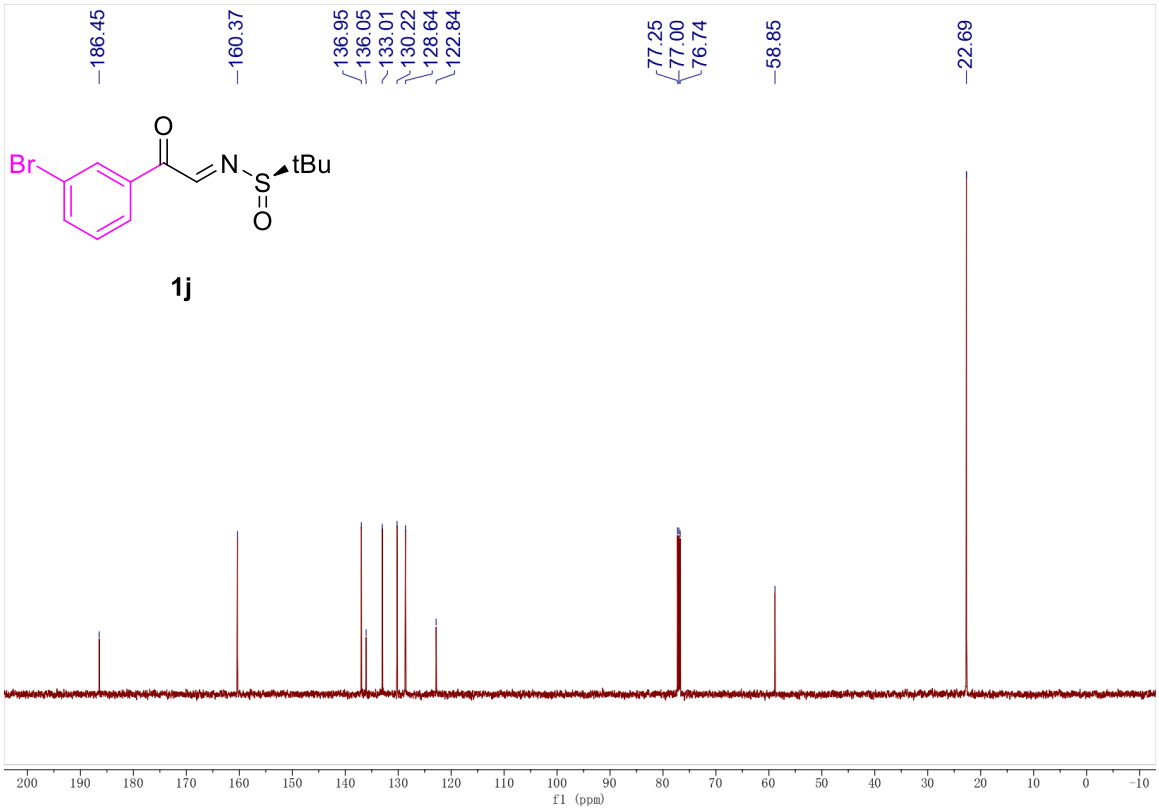
^{13}C NMR spectrum of 1i



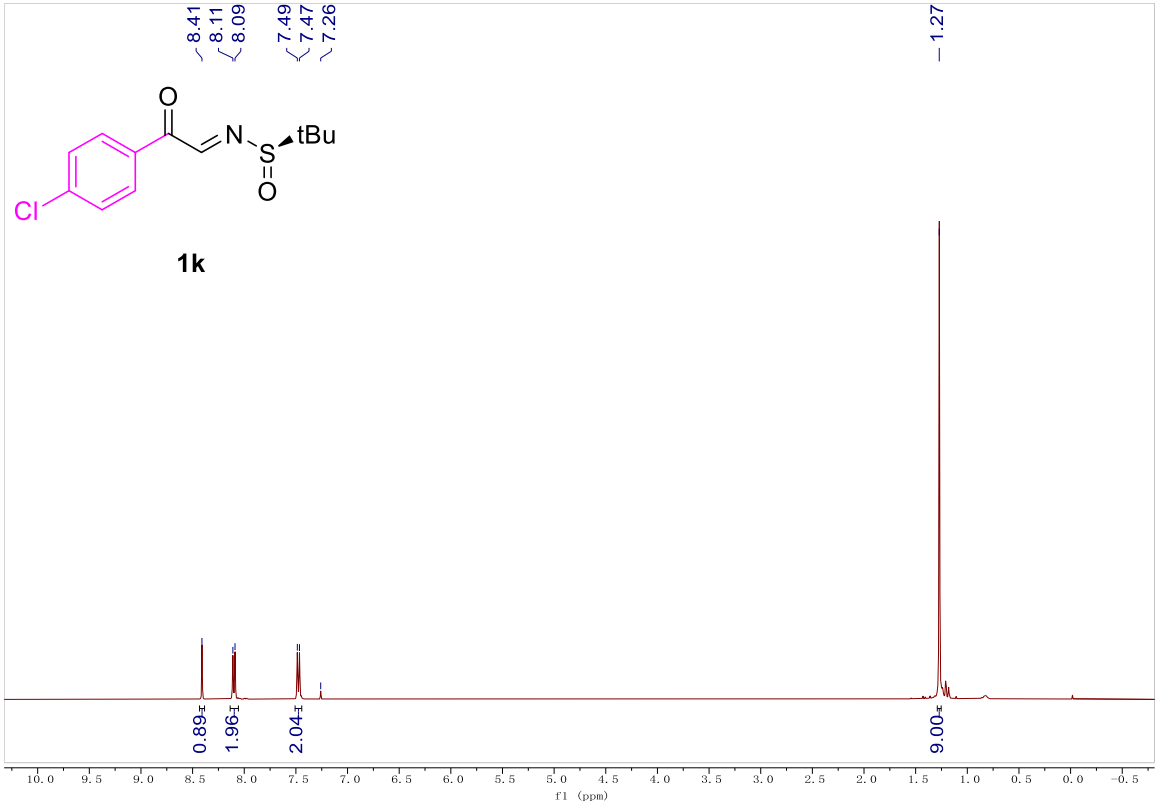
^{1}H NMR spectrum of 1j



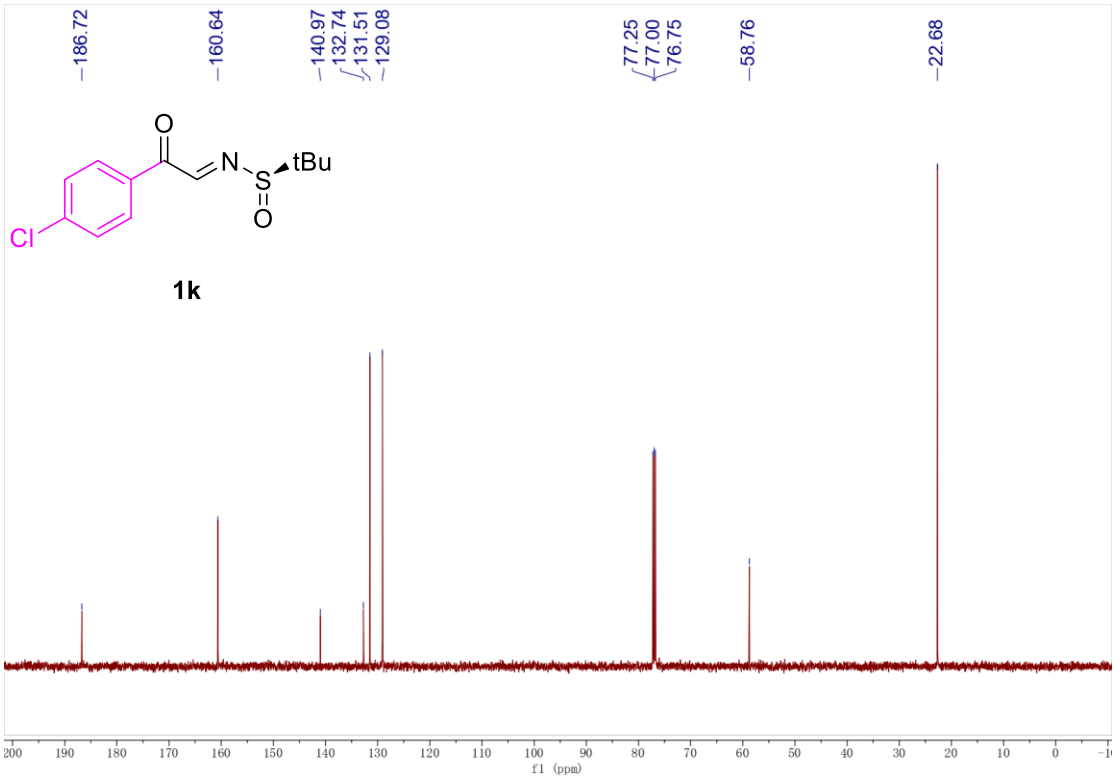
^{13}C NMR spectrum of 1j



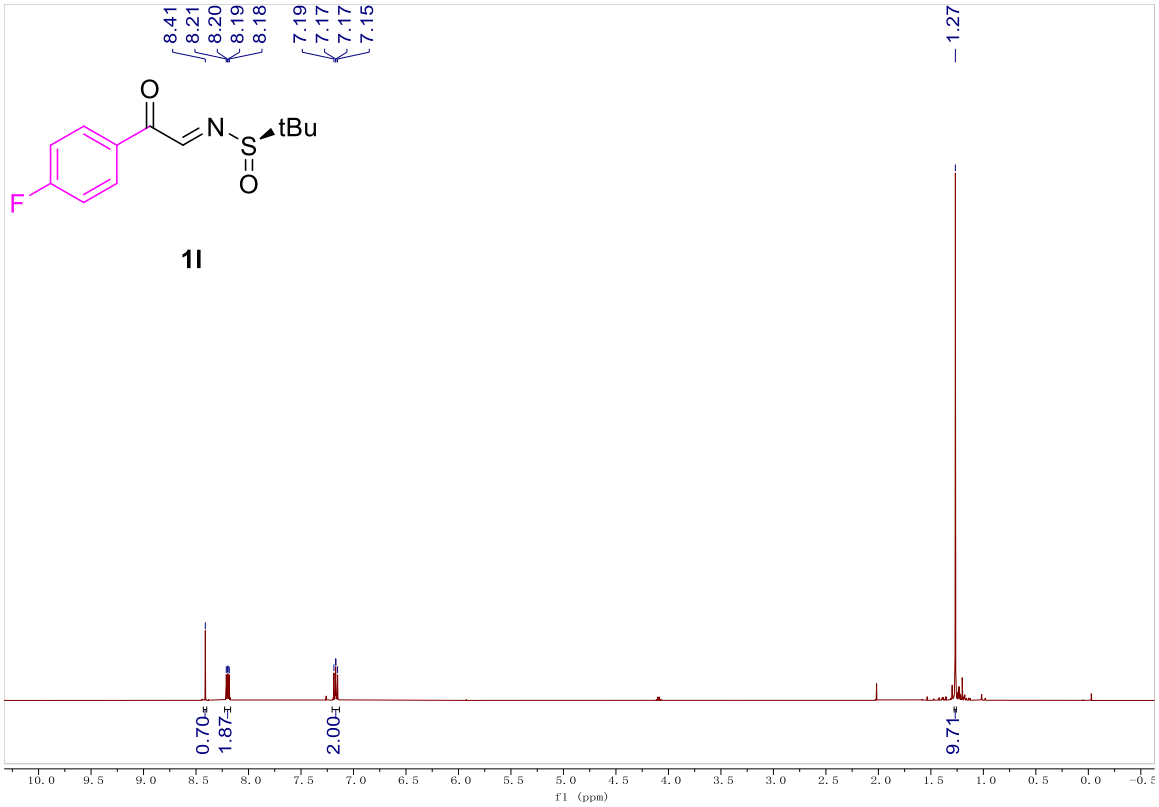
^{1}H NMR spectrum of 1k



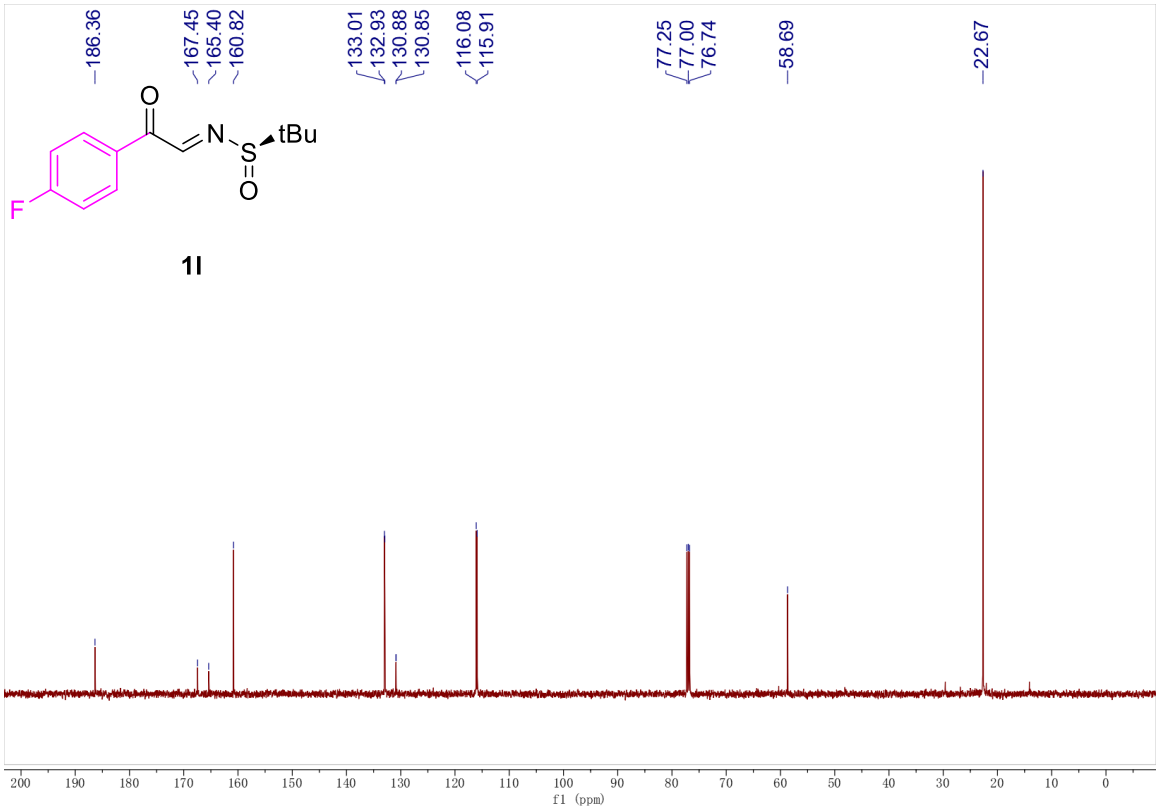
^{13}C NMR spectrum of 1k



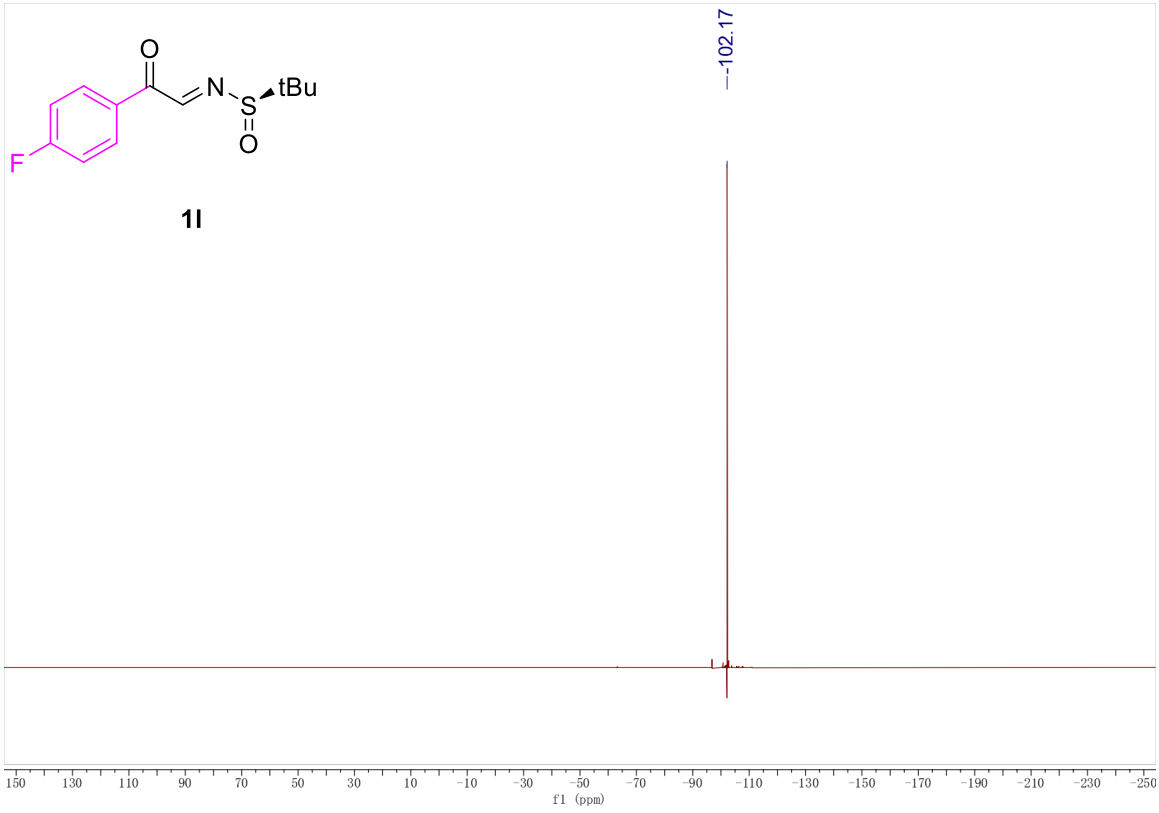
^{1}H NMR spectrum of 1l



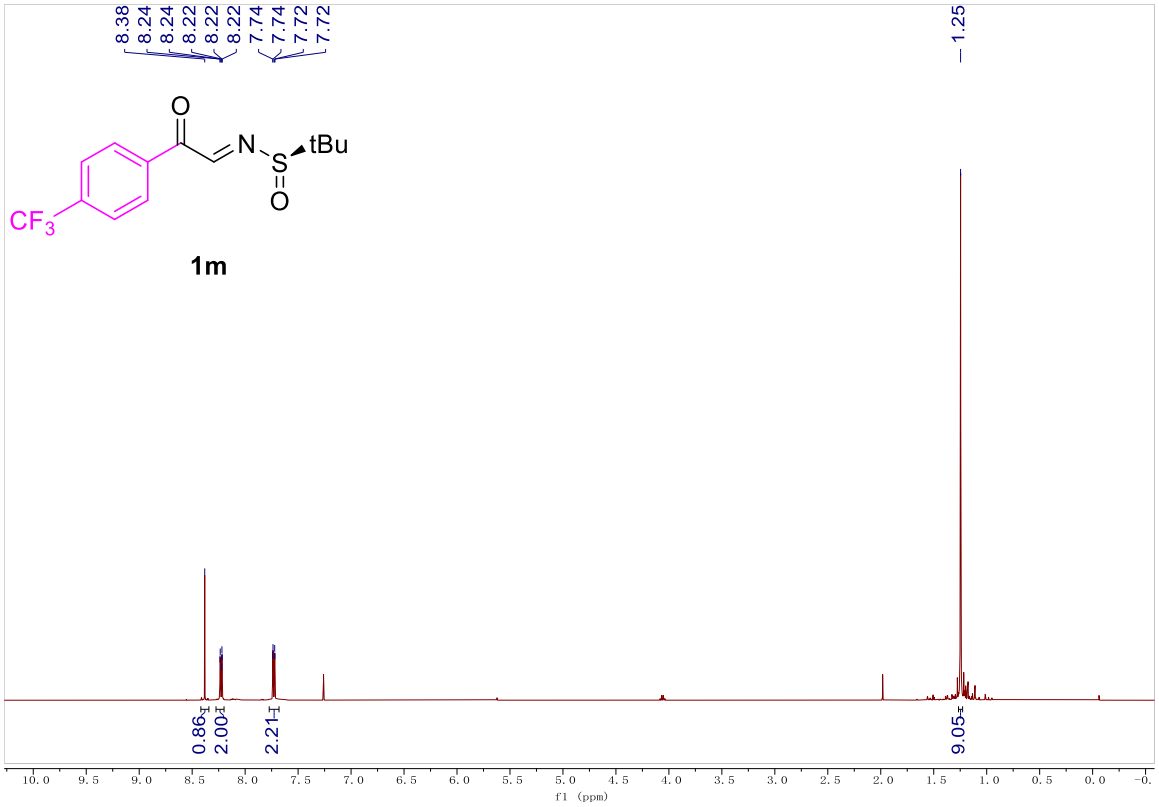
^{13}C NMR spectrum of 1l



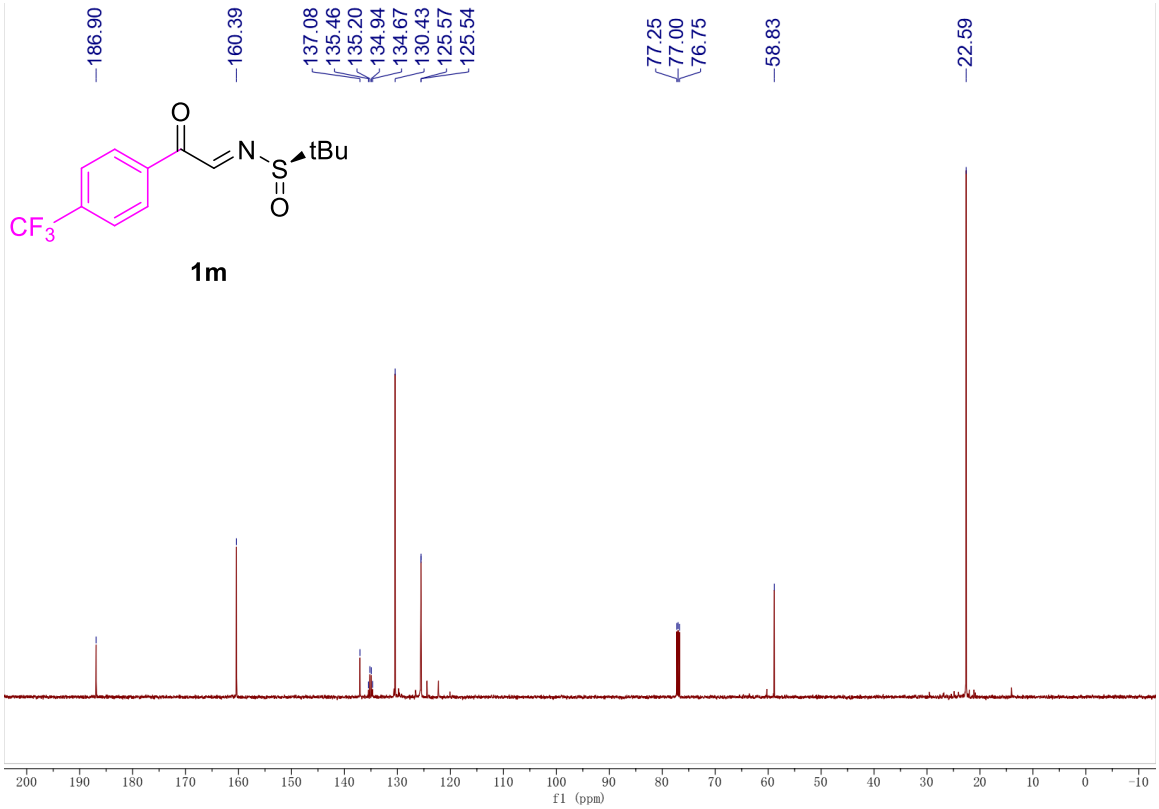
^{19}F NMR spectrum of 1l



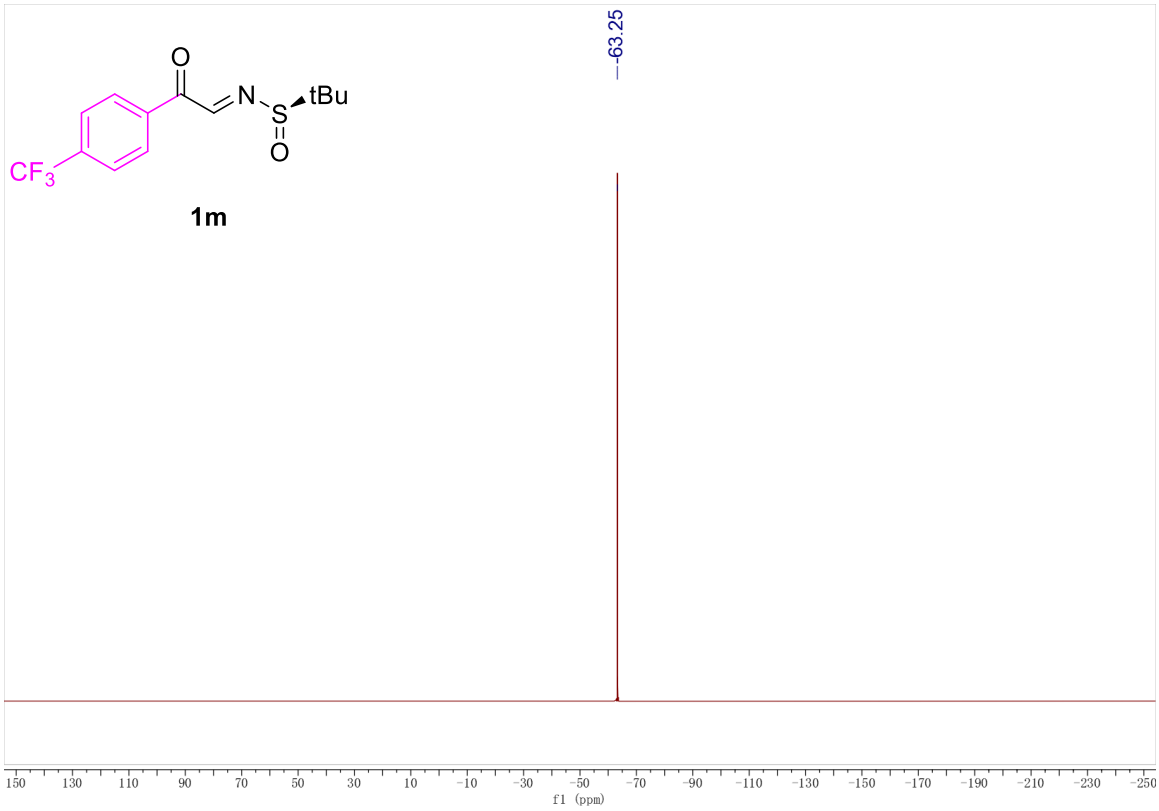
^{1}H NMR spectrum of 1m



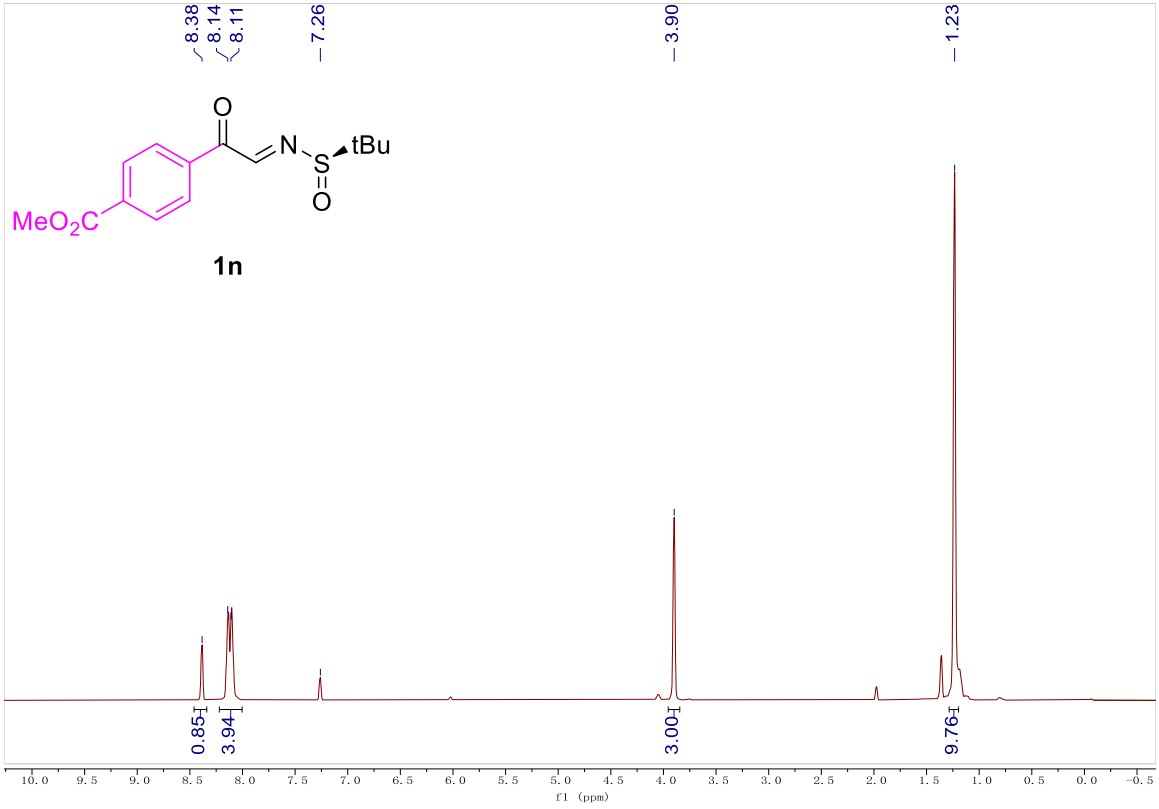
^{13}C NMR spectrum of 1m



^{19}F NMR spectrum of 1m



^{1}H NMR spectrum of 1n



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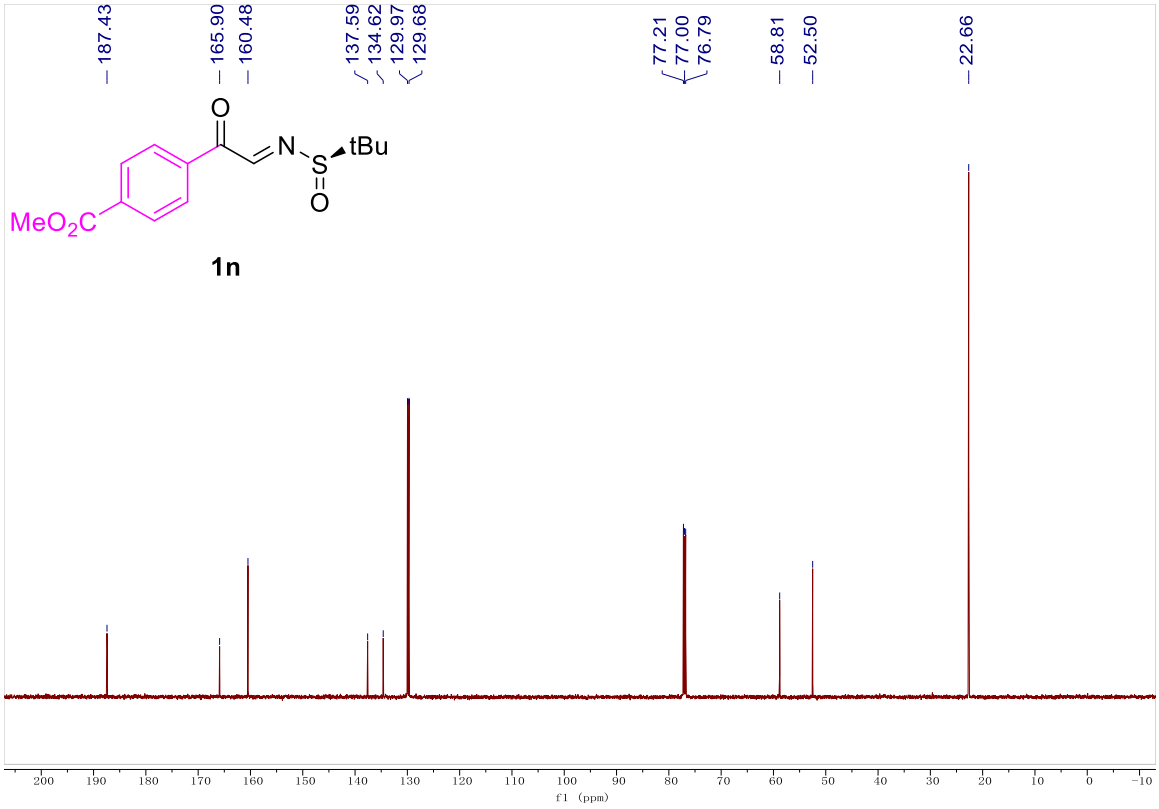

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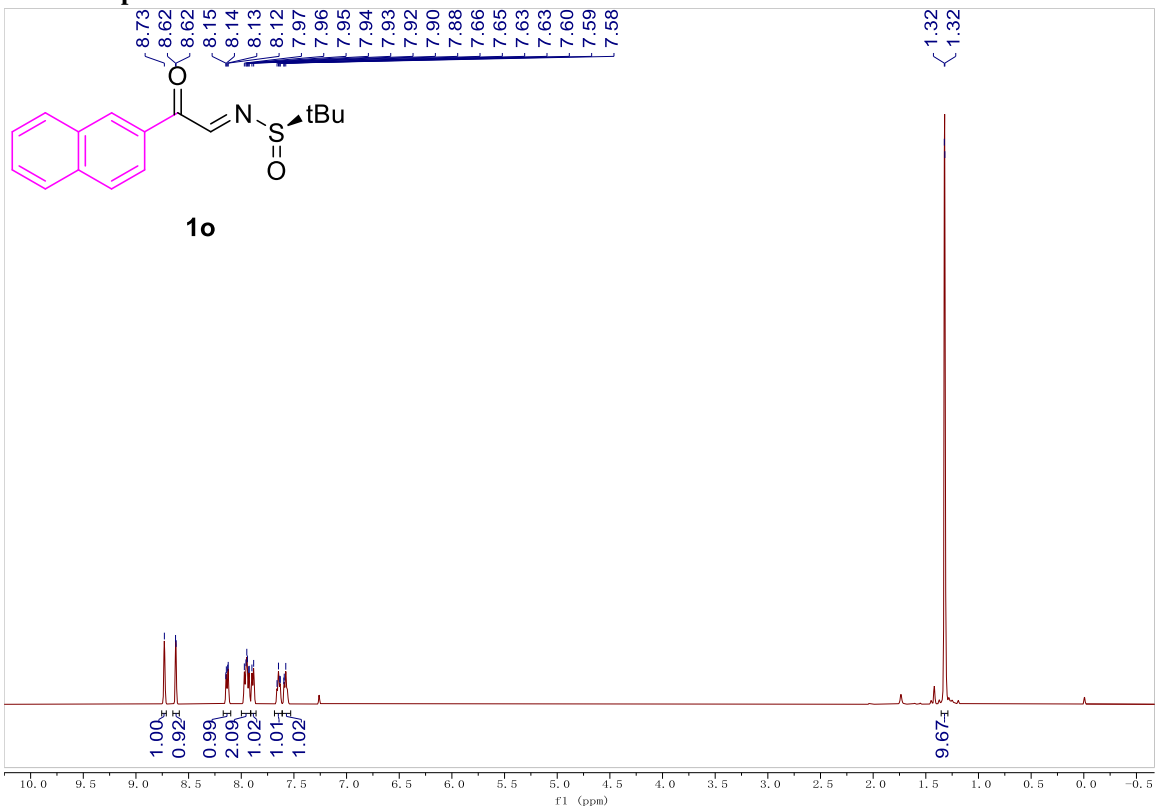
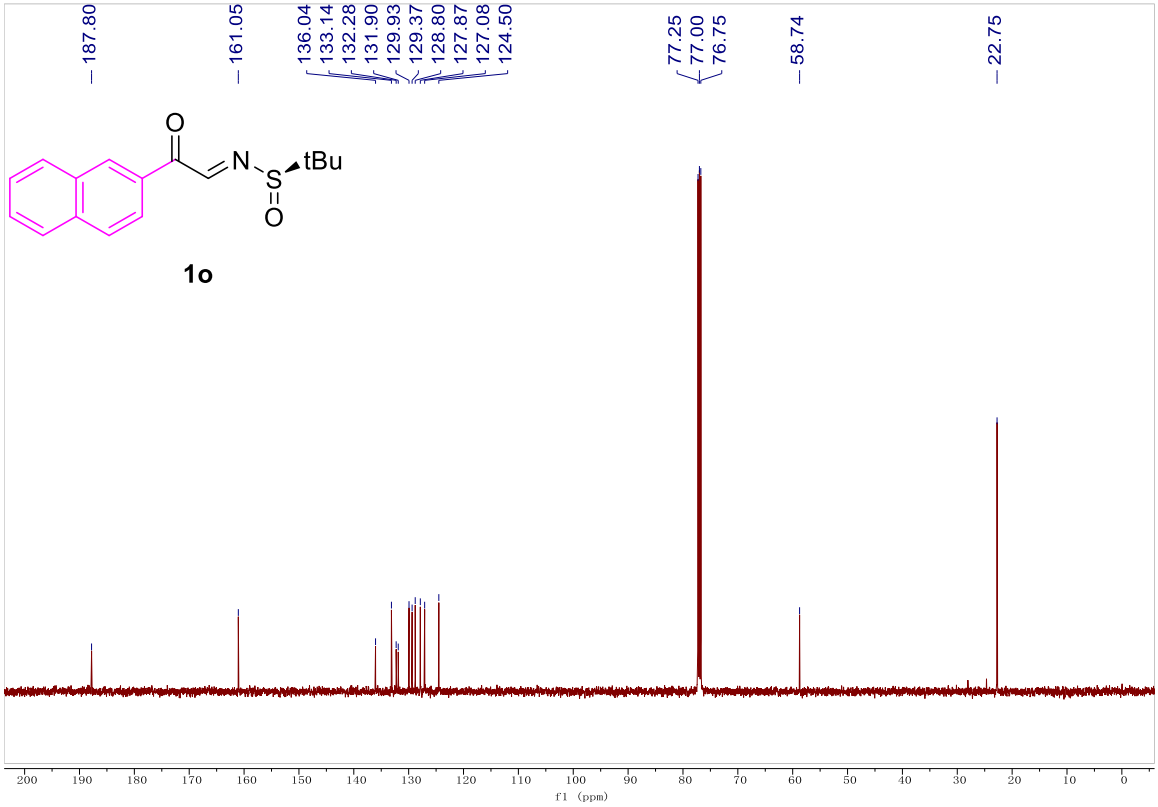
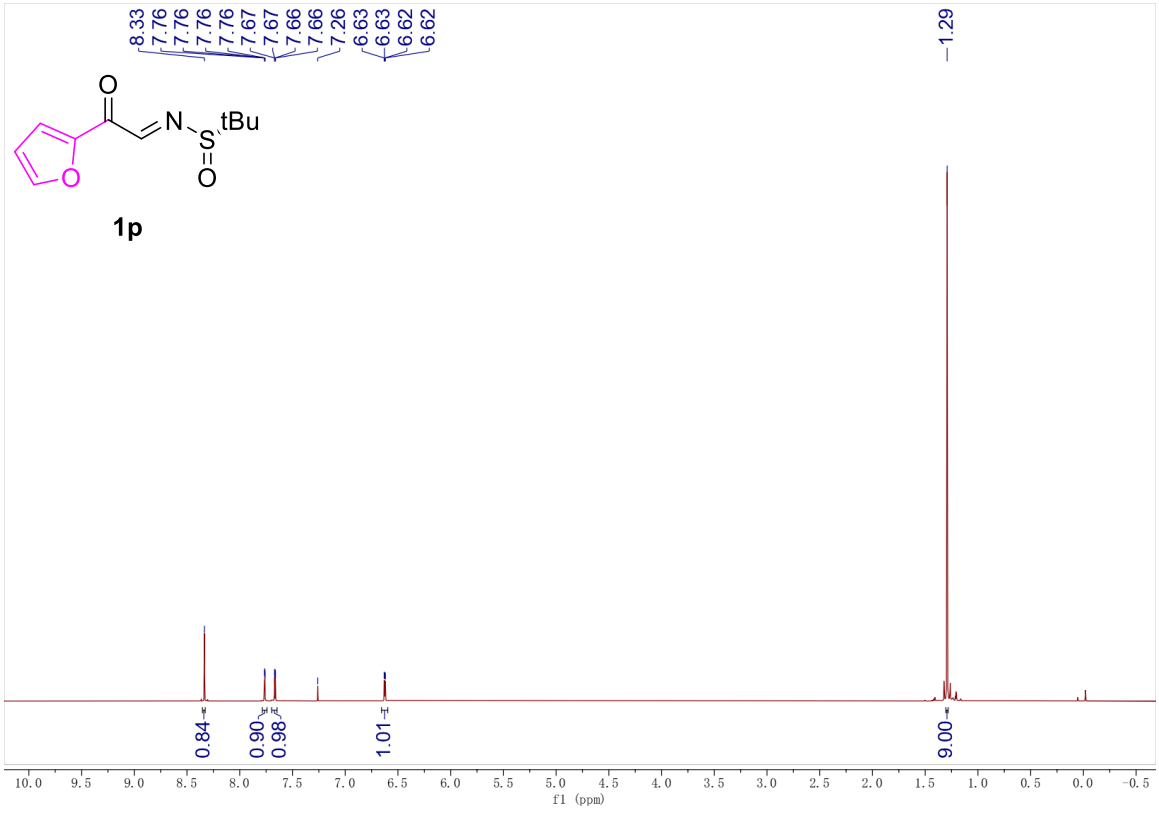


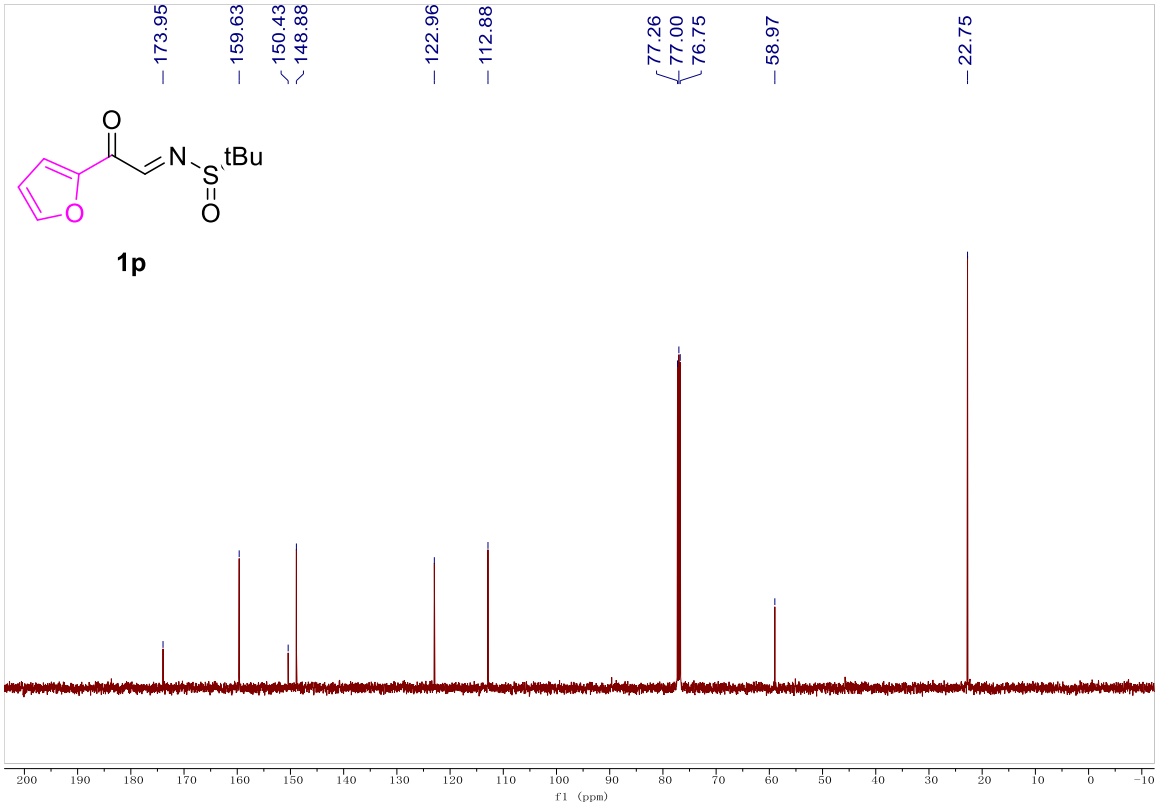
^{13}C NMR spectrum of 1o



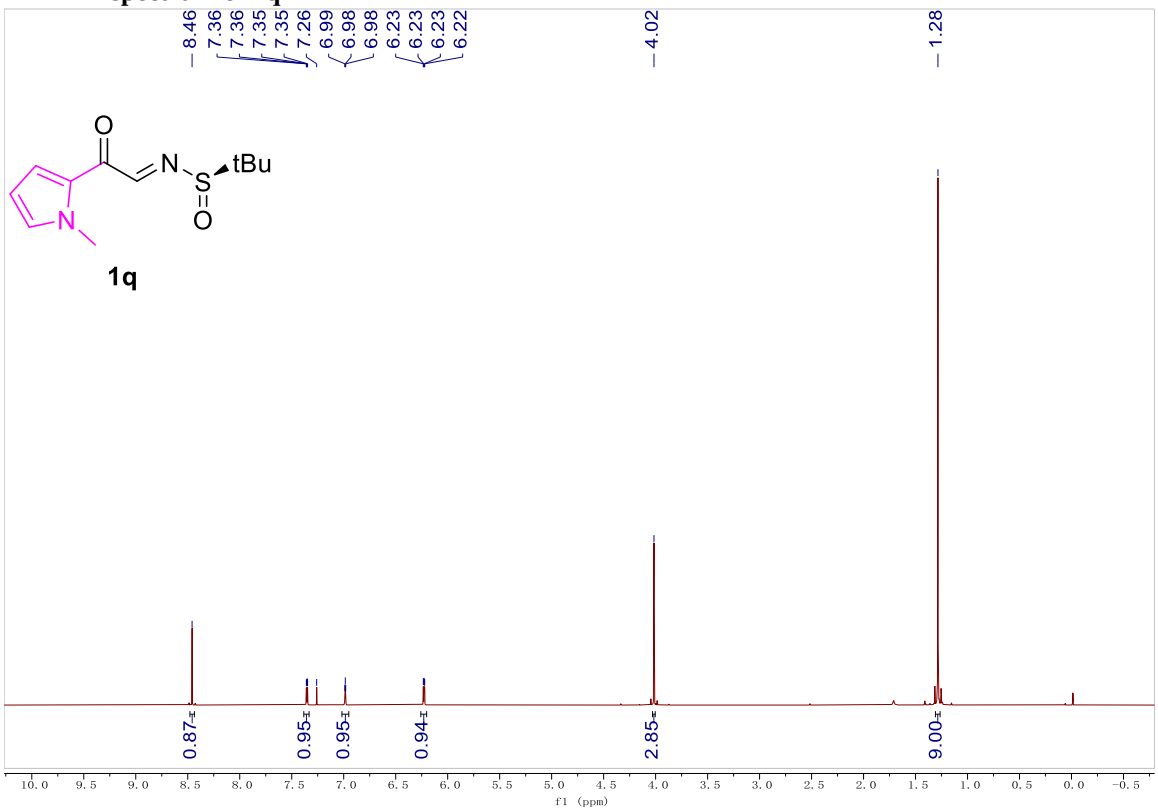
^{1}H NMR spectrum of 1p



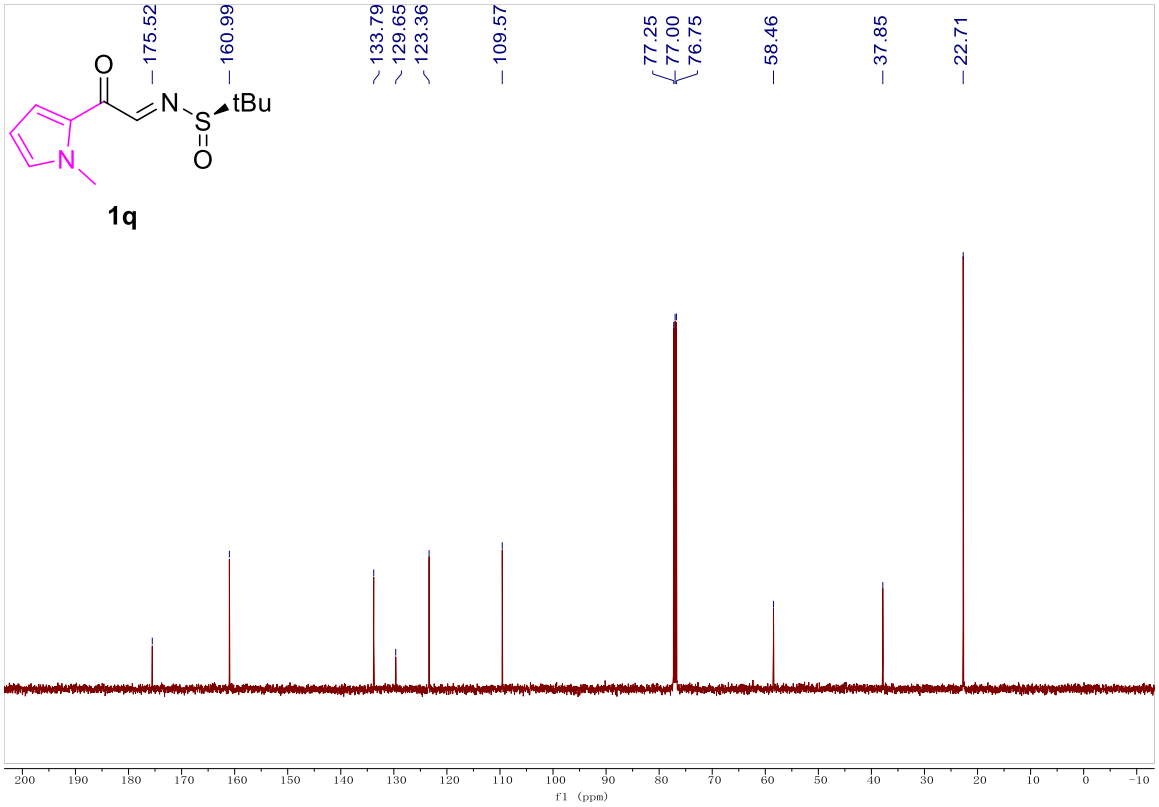
^{13}C NMR spectrum of 1p



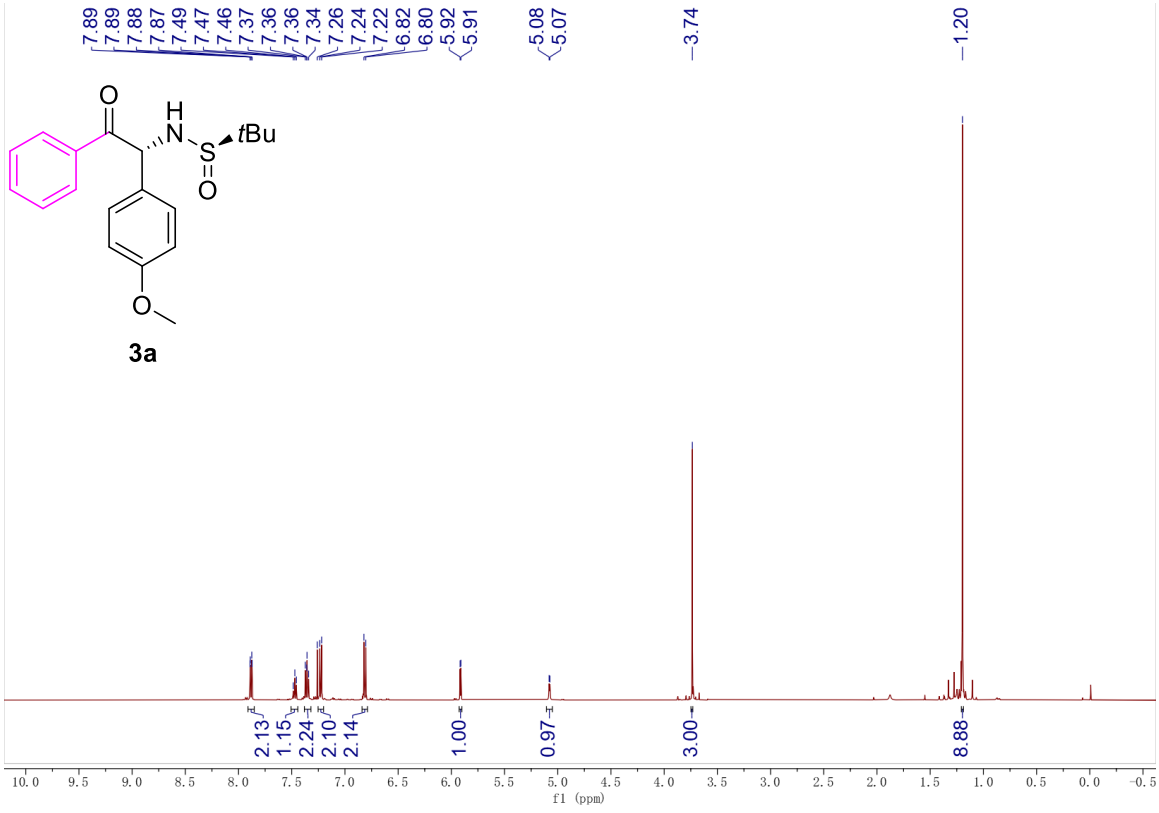
^{1}H NMR spectrum of 1q



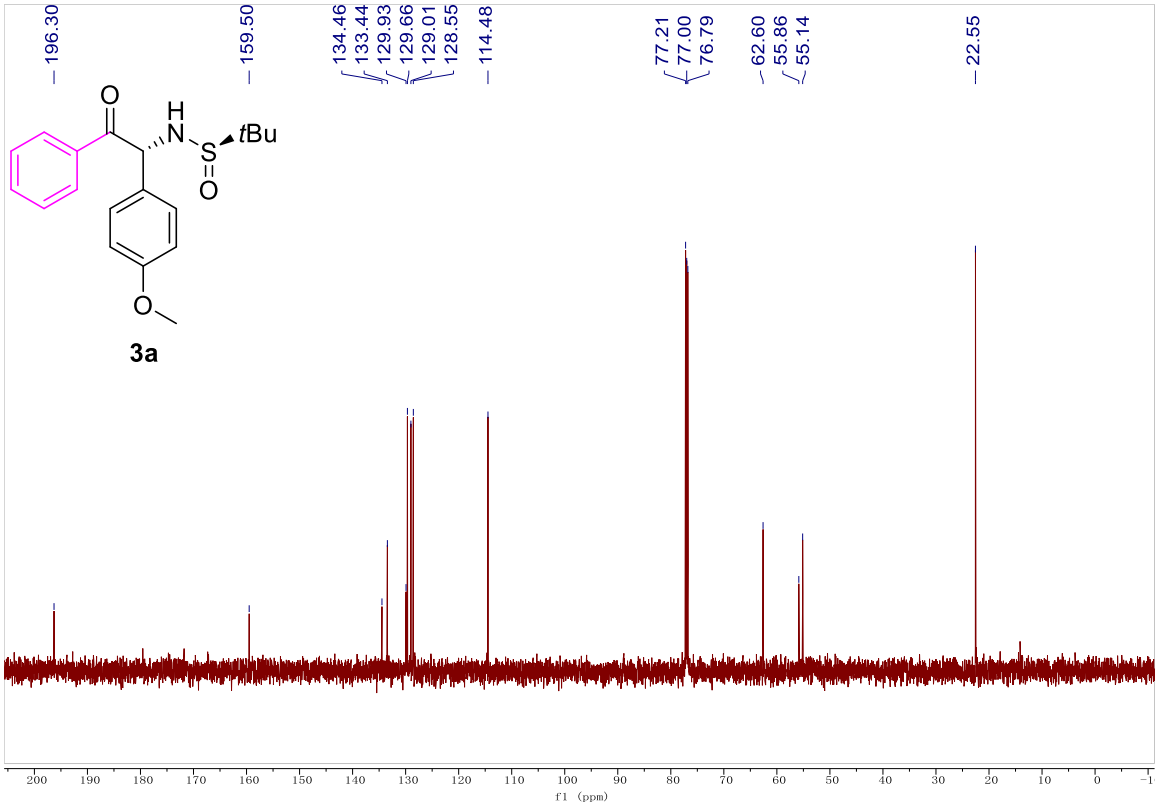
^{13}C NMR spectrum of 1q



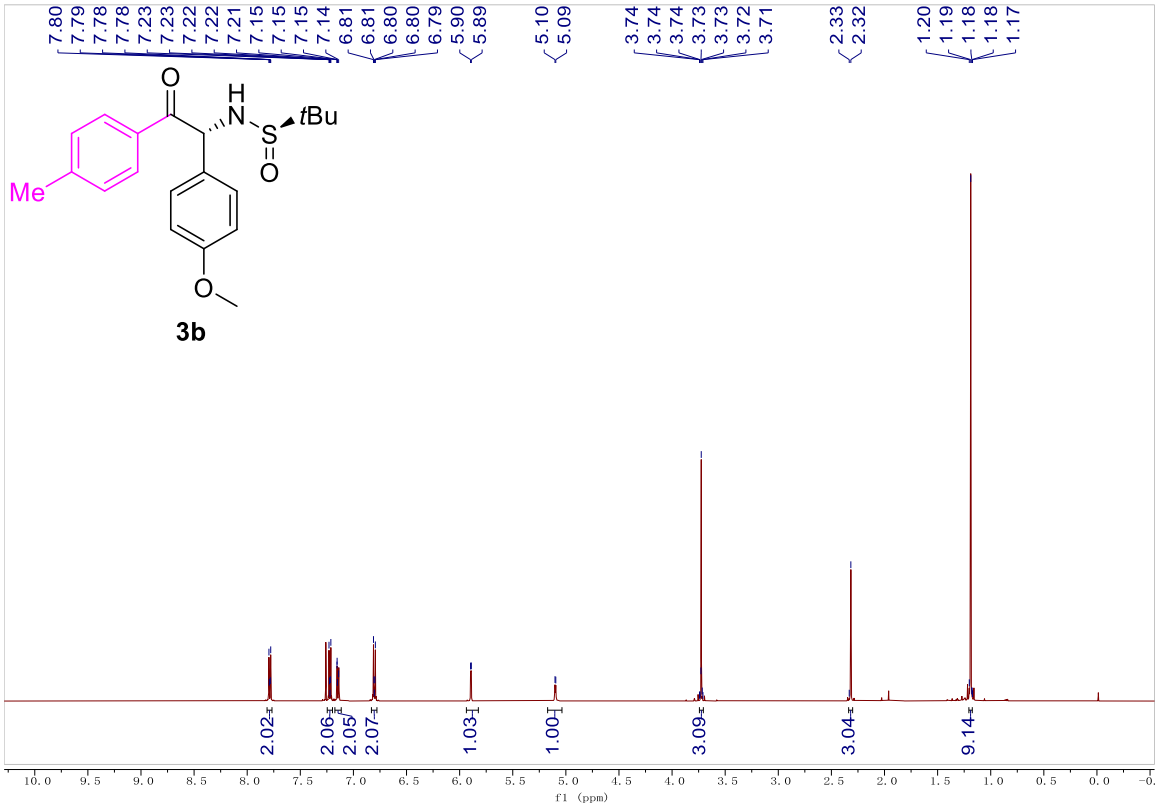
^{1}H NMR spectrum of 3a



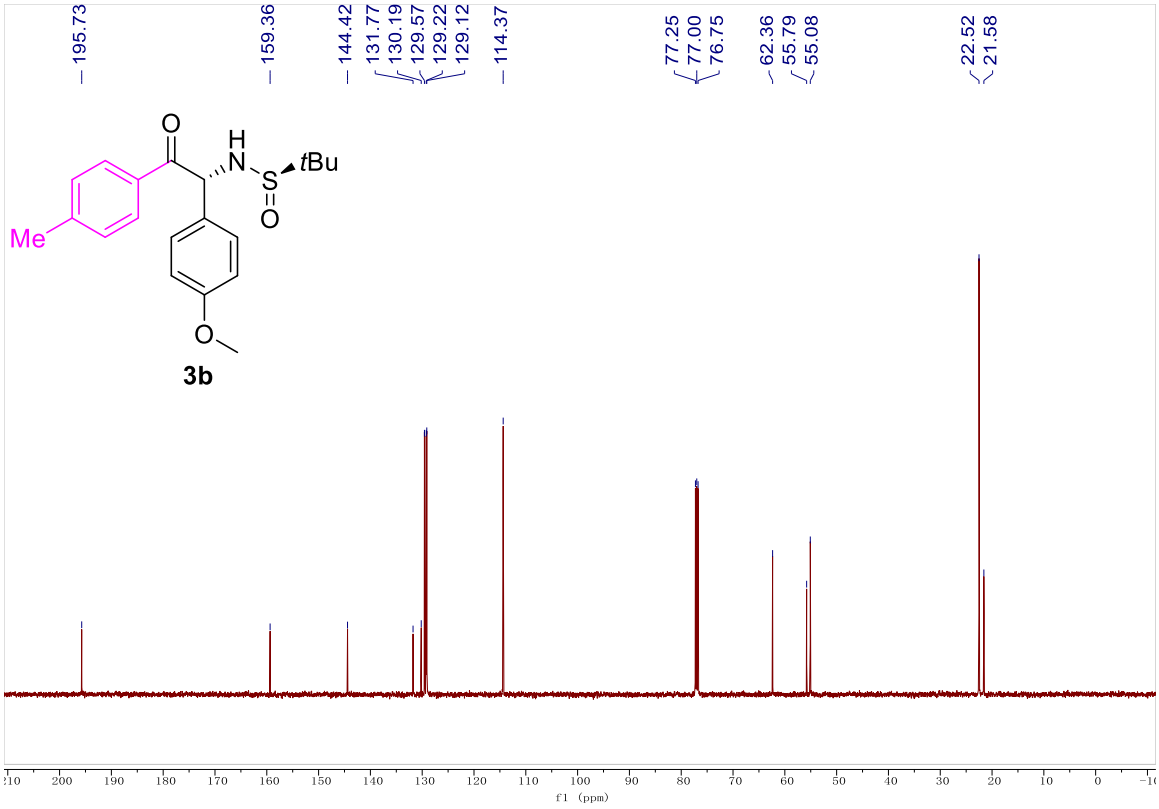
^{13}C NMR spectrum of 3a



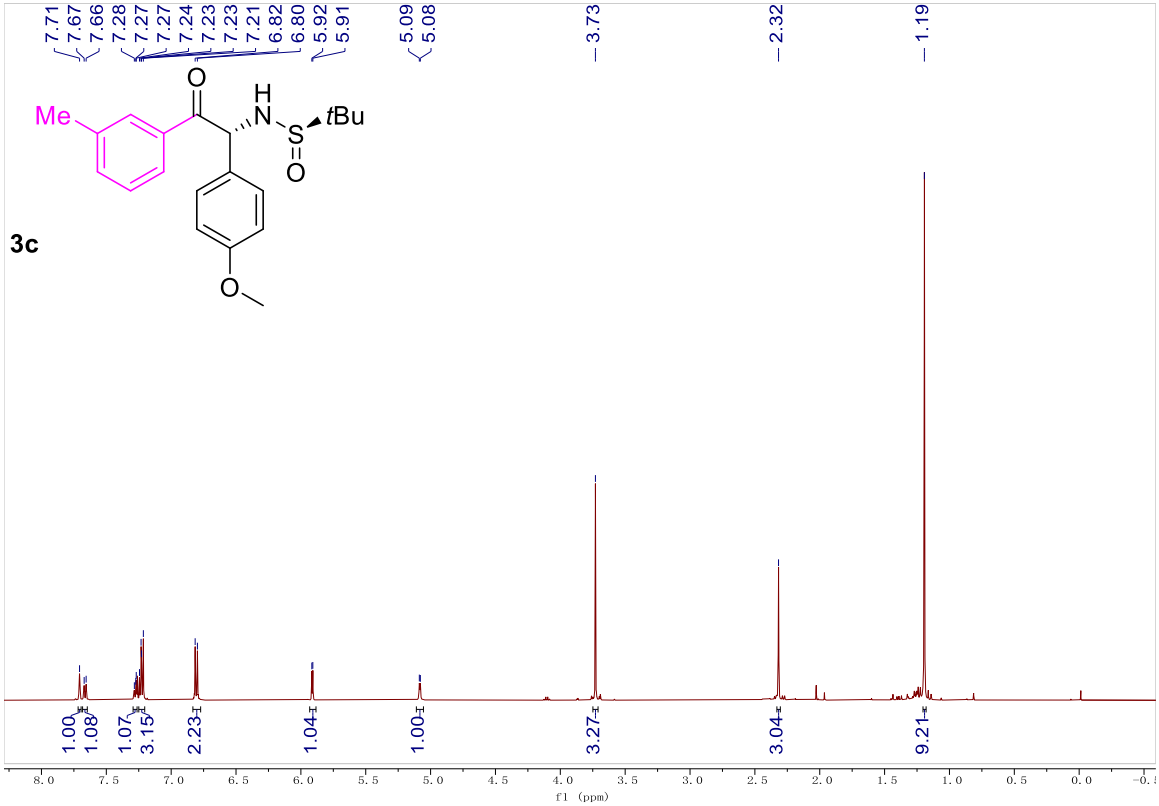
^{1}H NMR spectrum of 3b



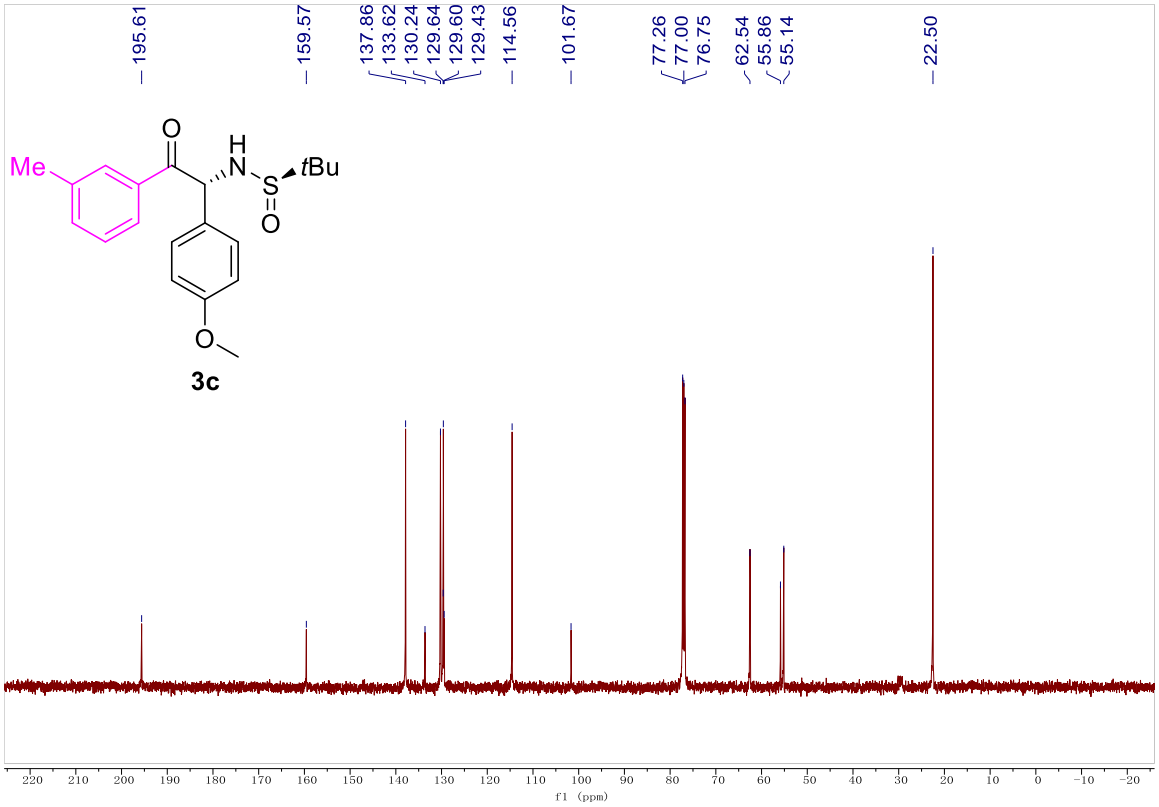
^{13}C NMR spectrum of 3b



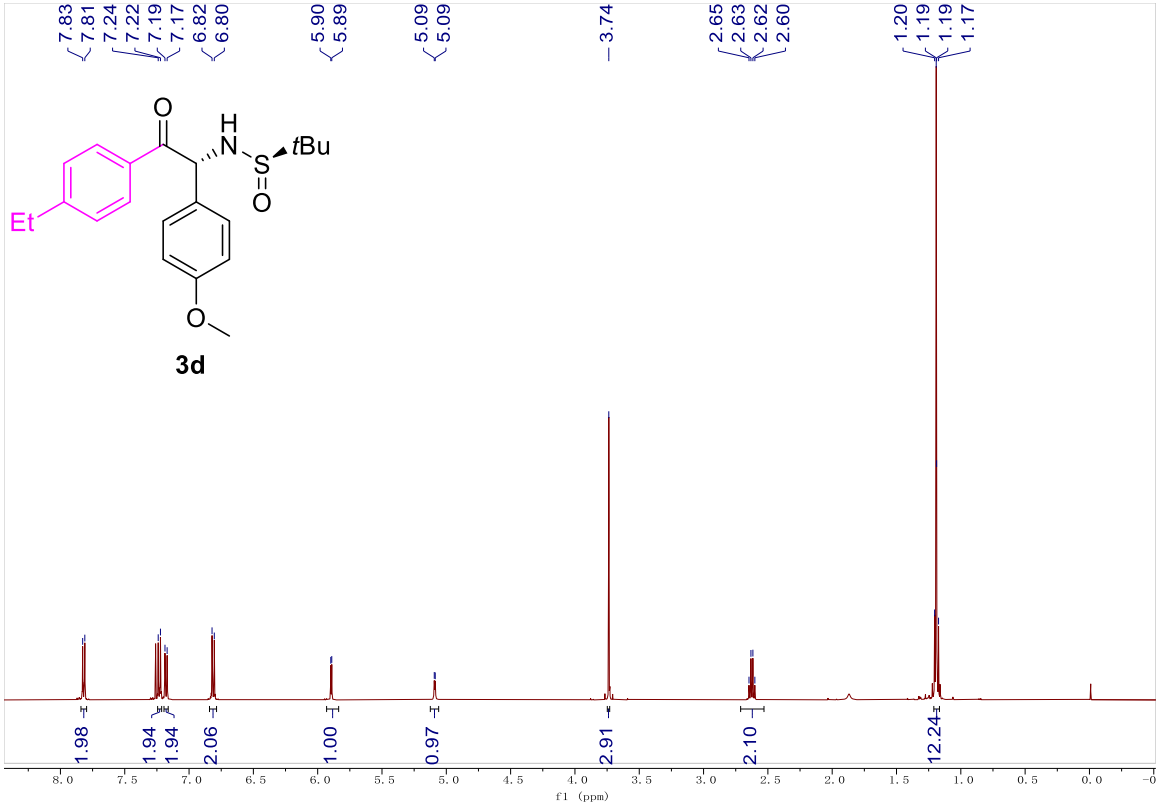
^{1}H NMR spectrum of 3c



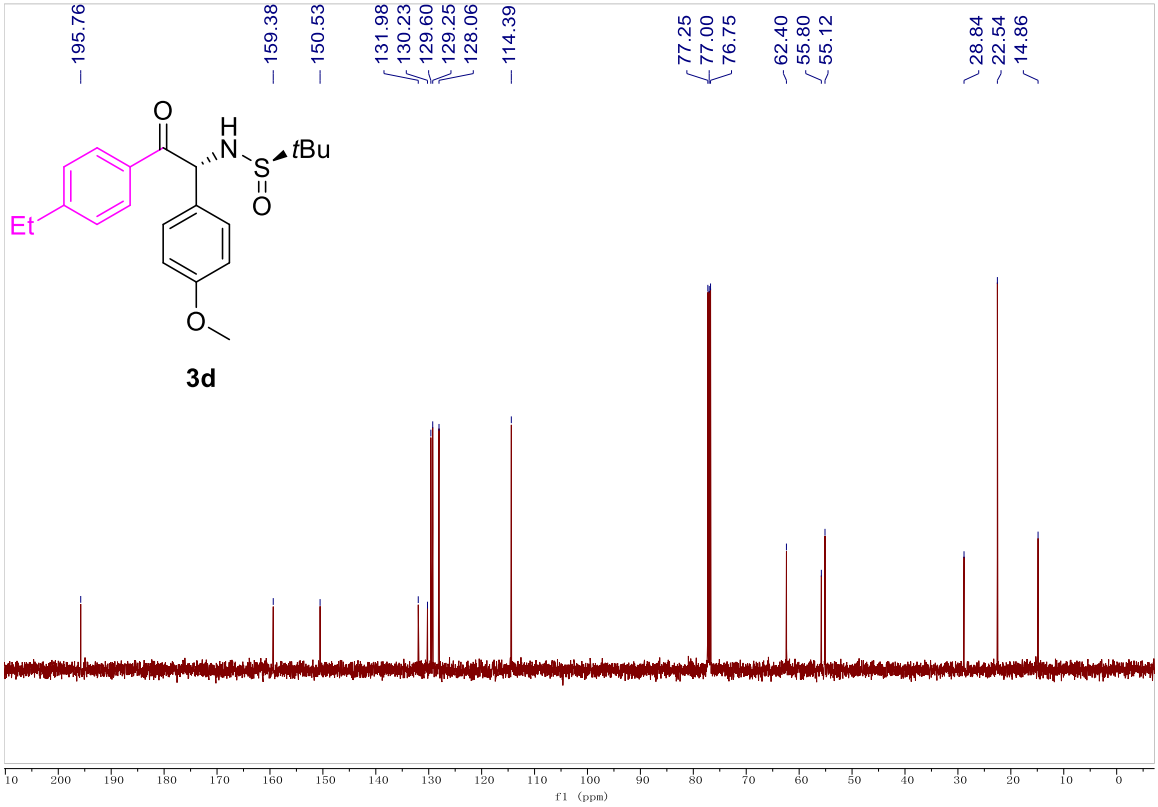
^{13}C NMR spectrum of 3c



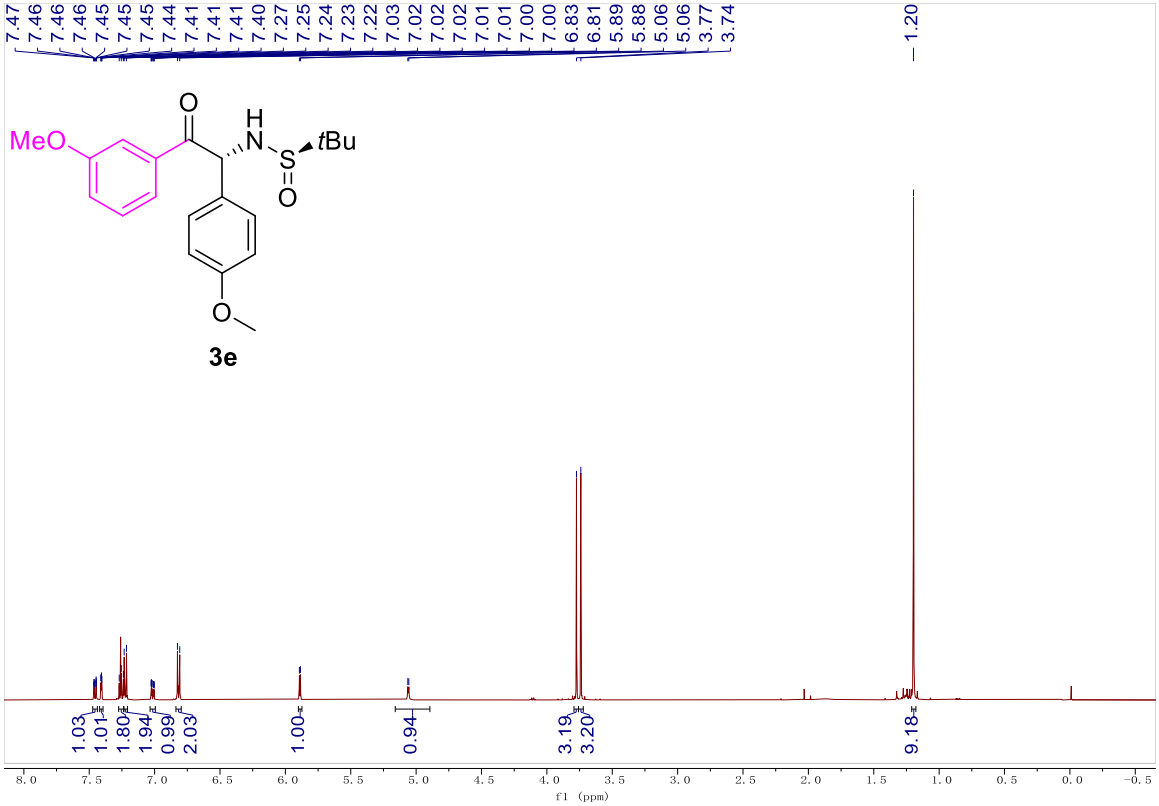
^{1}H NMR spectrum of 3d



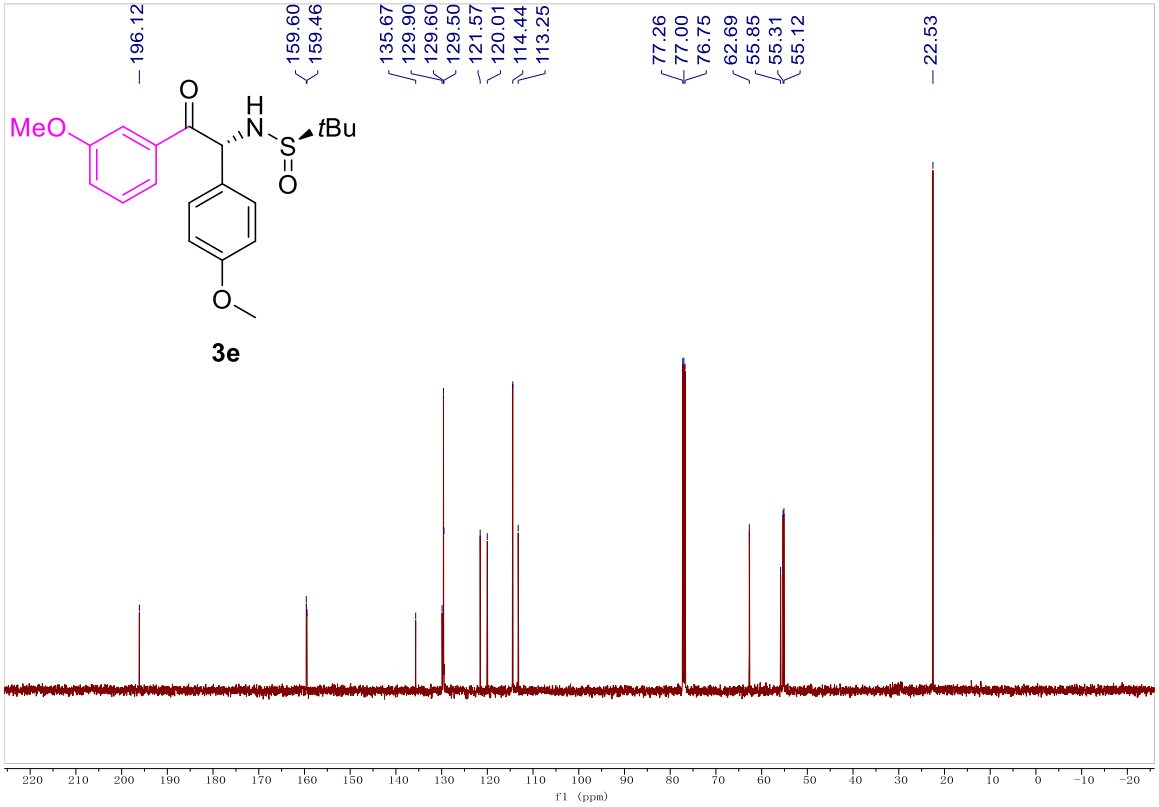
^{13}C NMR spectrum of 3d



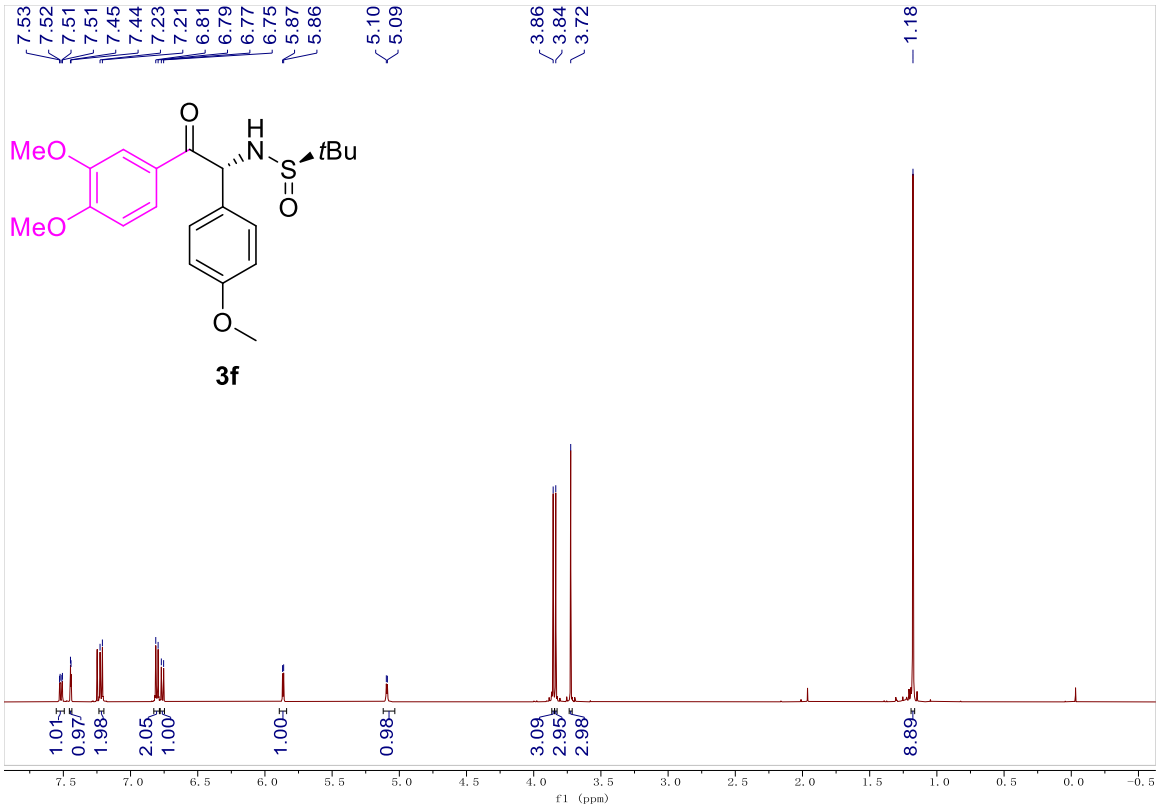
^{1}H NMR spectrum of 3e



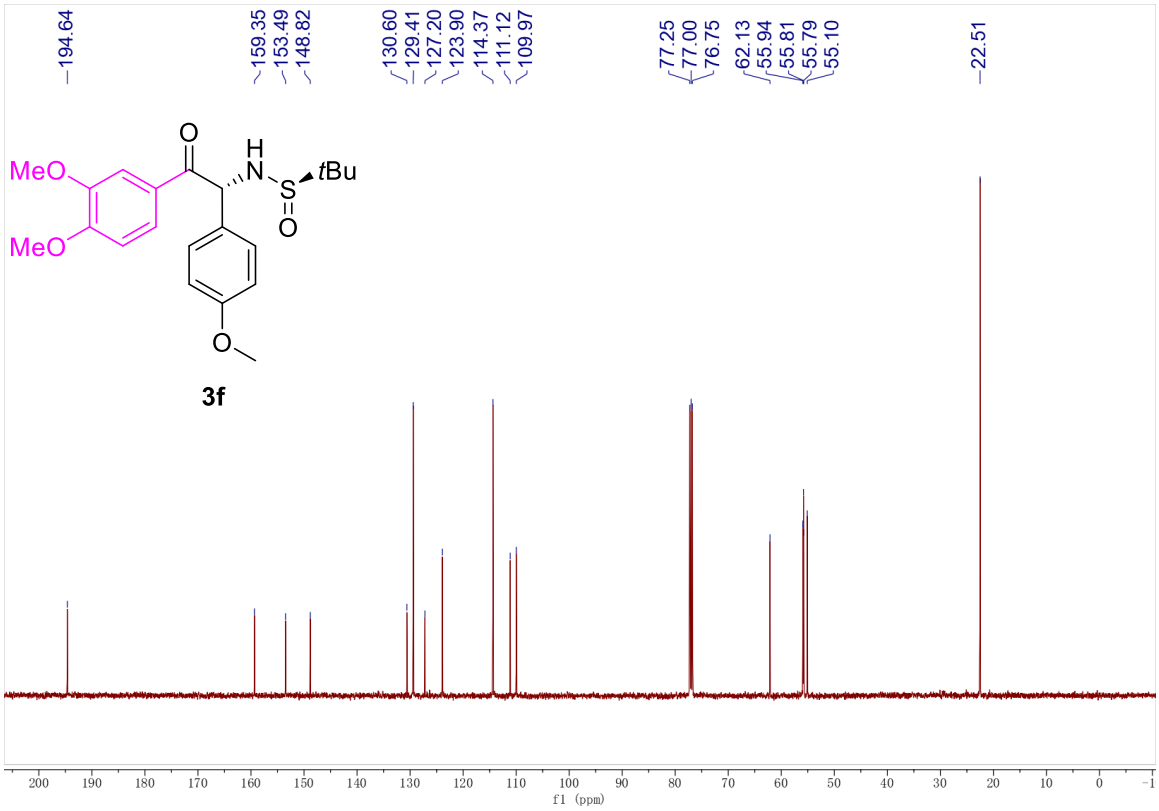
^{13}C NMR spectrum of 3e



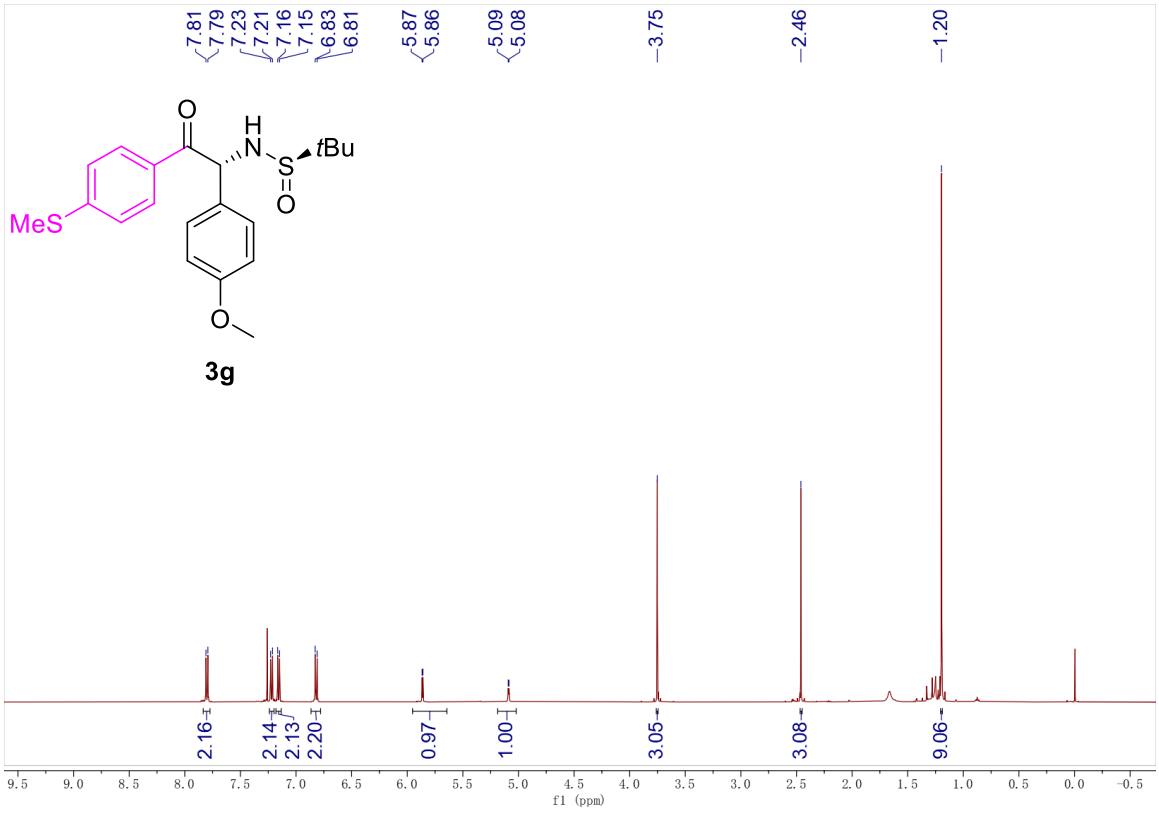
^{1}H NMR spectrum of 3f



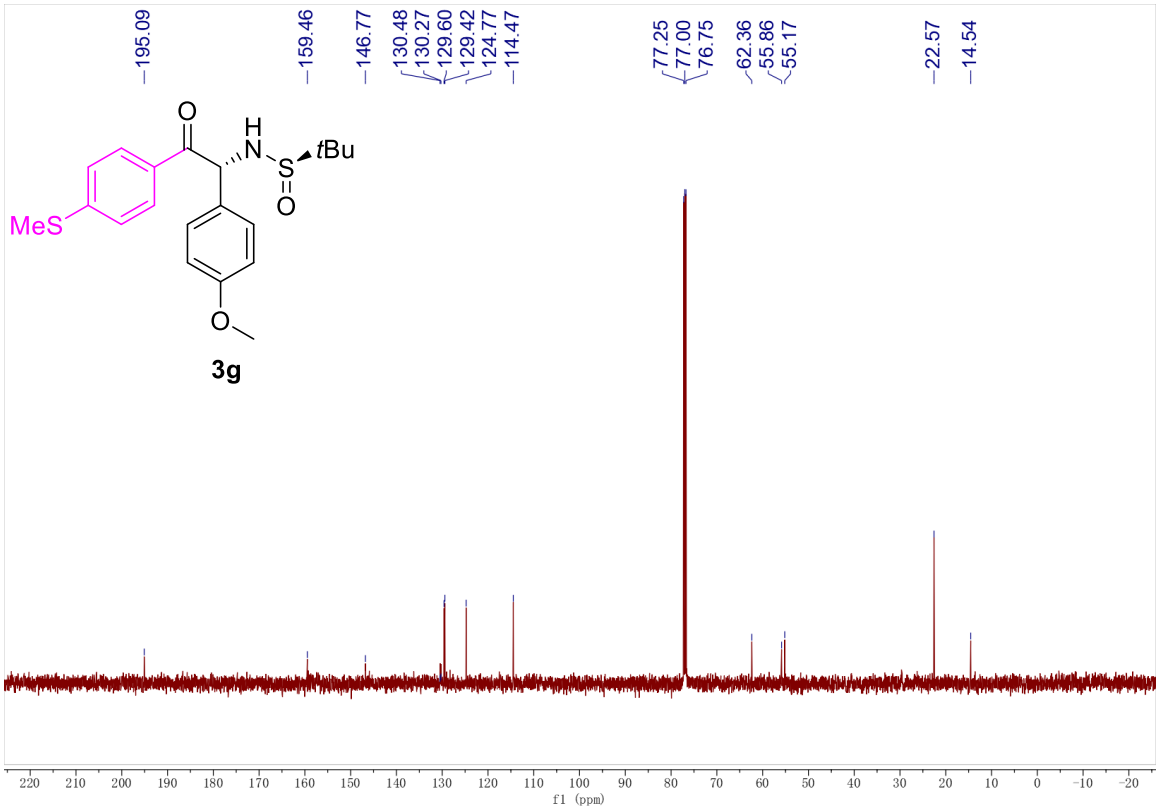
^{13}C NMR spectrum of 3f



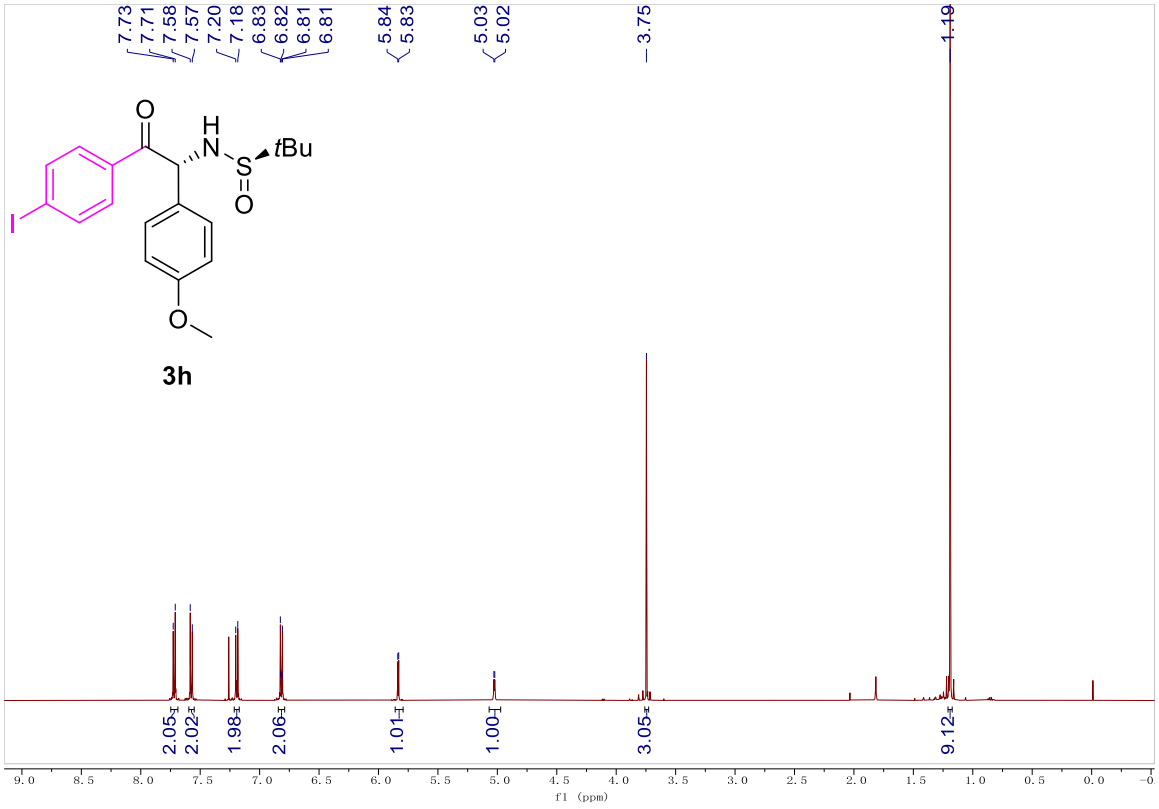
^{1}H NMR spectrum of 3g



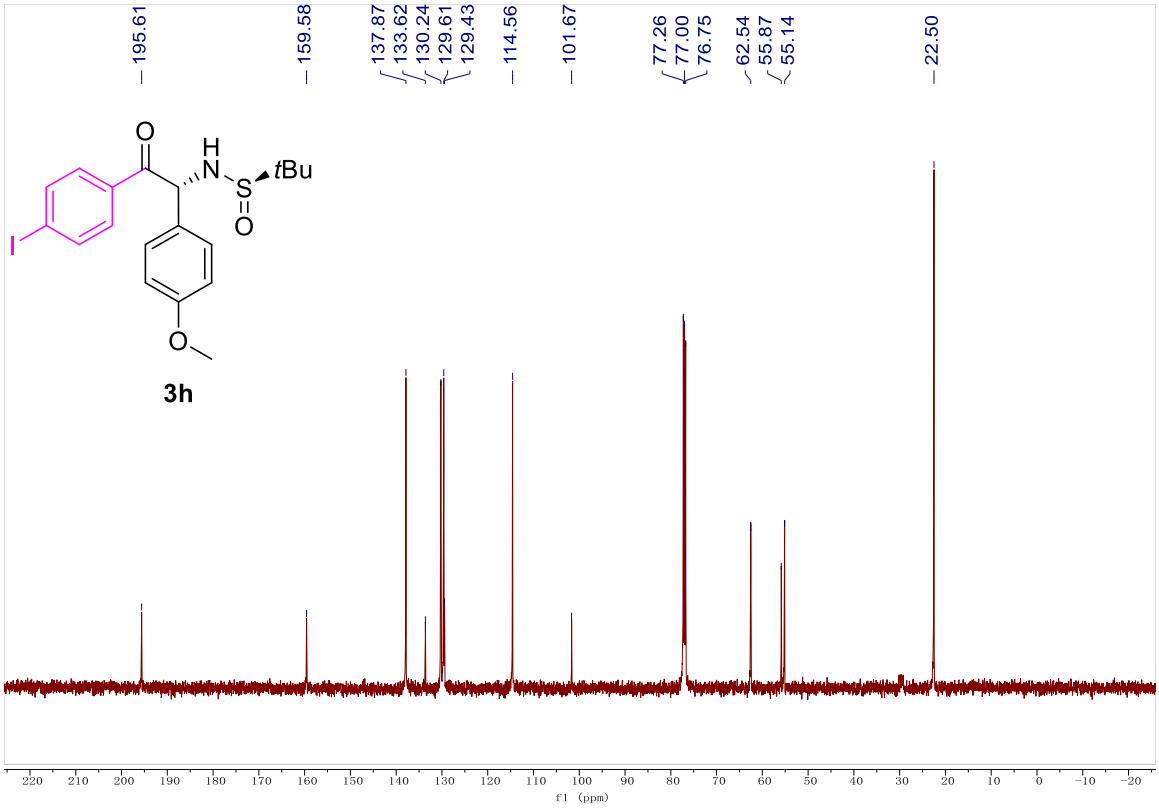
^{13}C NMR spectrum of 3g



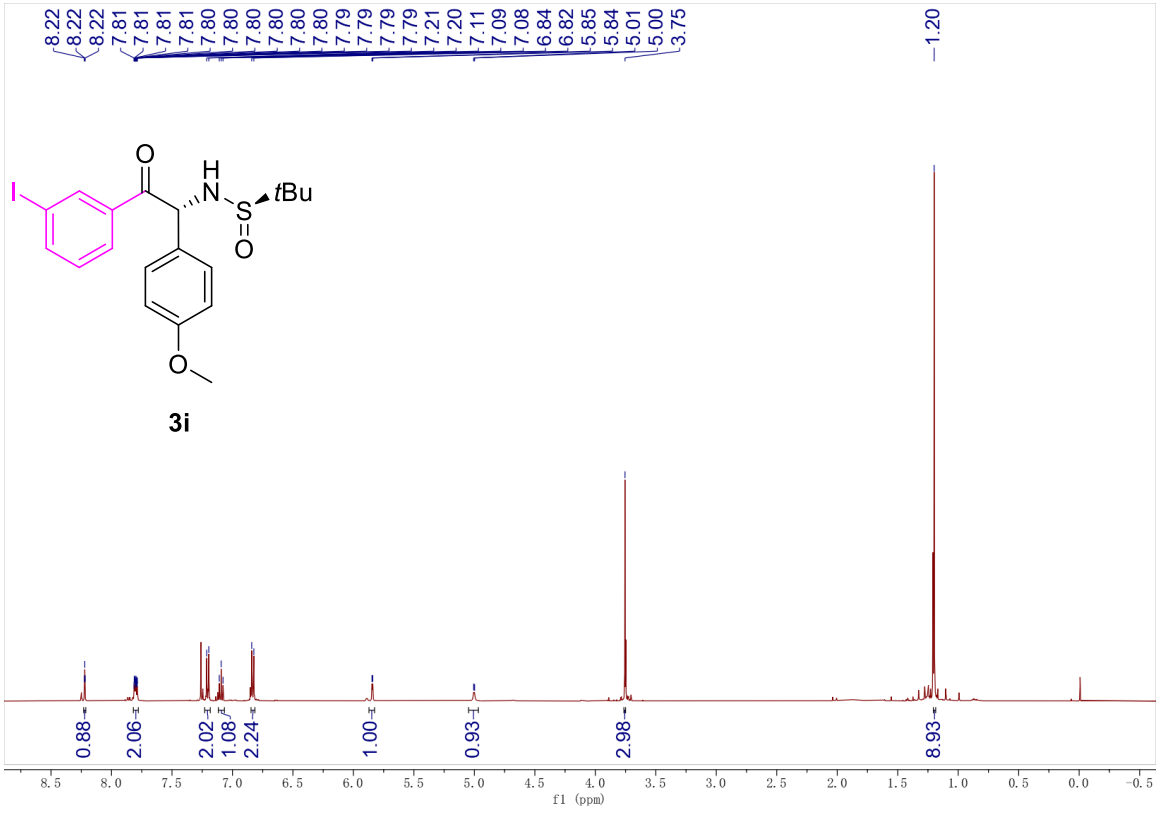
^{1}H NMR spectrum of 3h



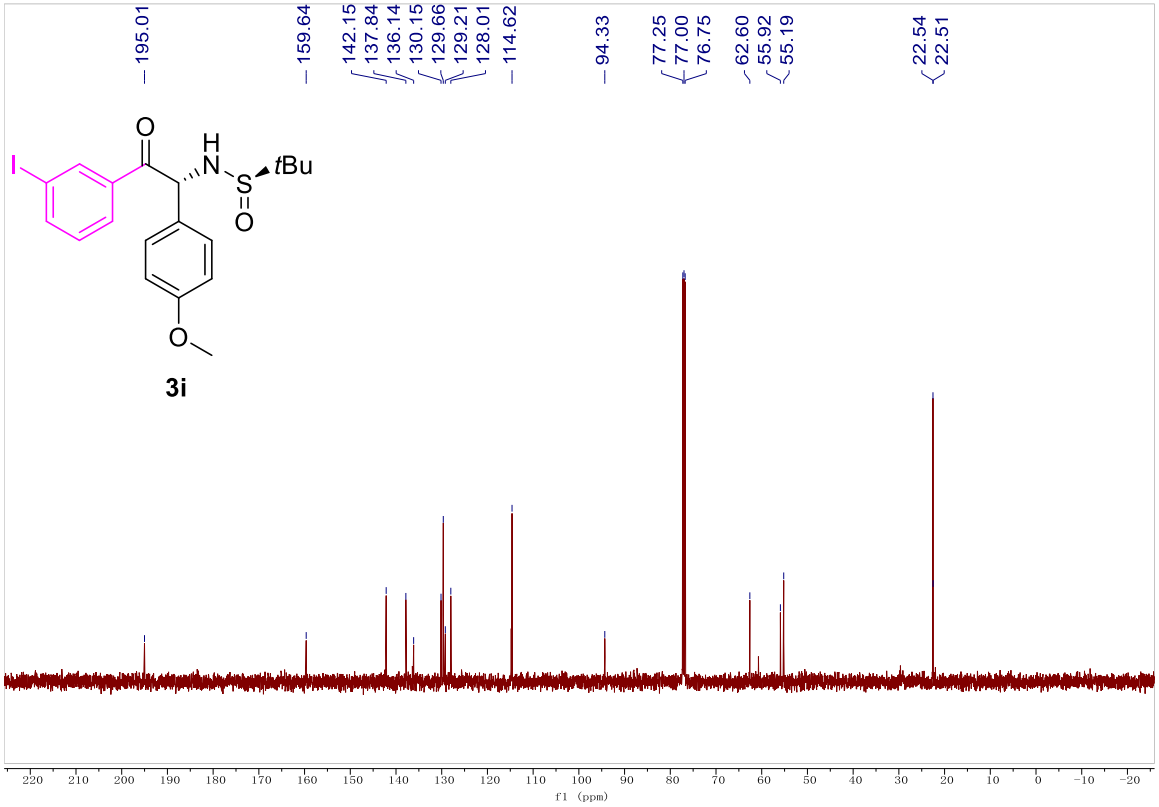
^{13}C NMR spectrum of 3h



^{1}H NMR spectrum of 3i

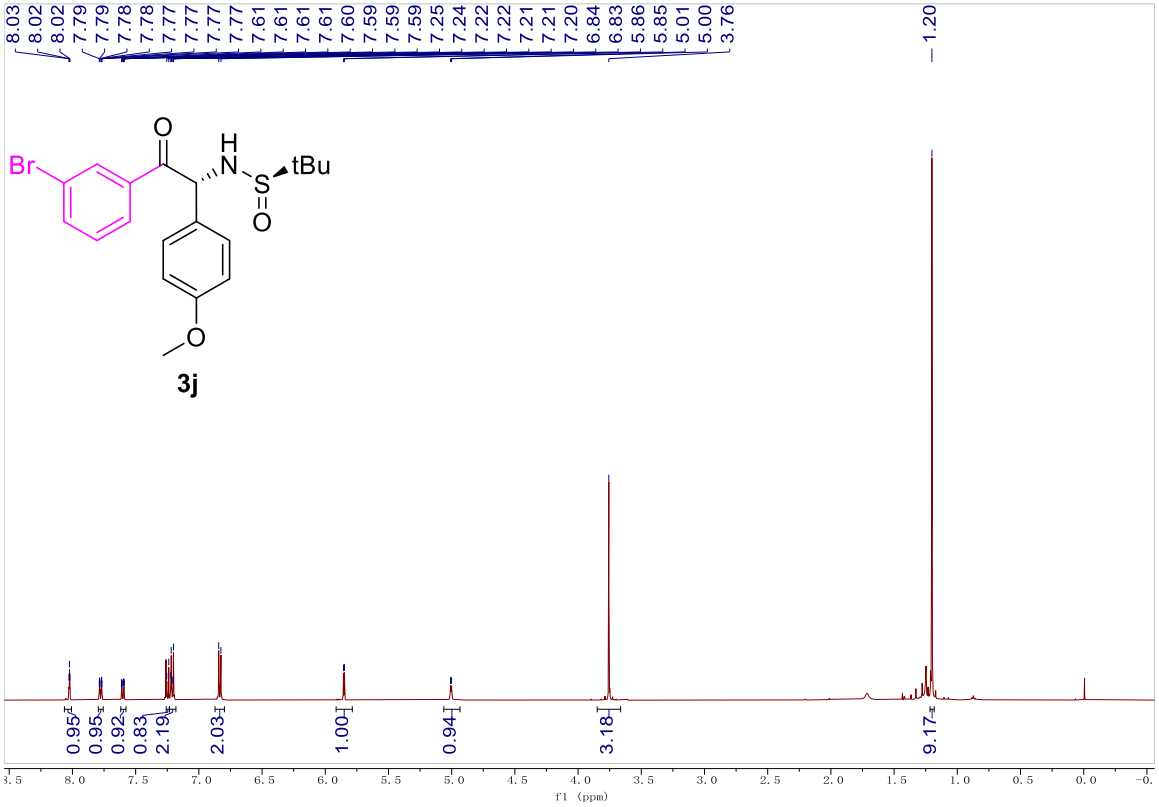


^{13}C NMR spectrum of 3i



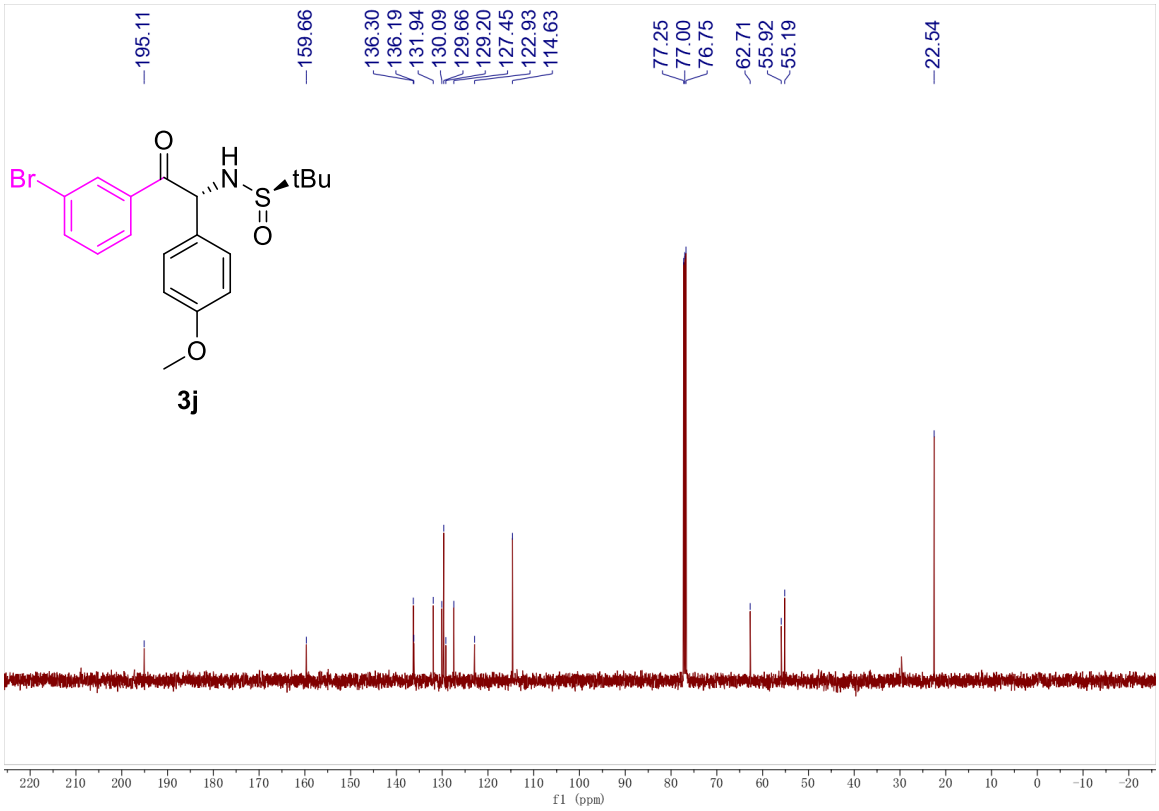
3i

^{1}H NMR spectrum of 3j

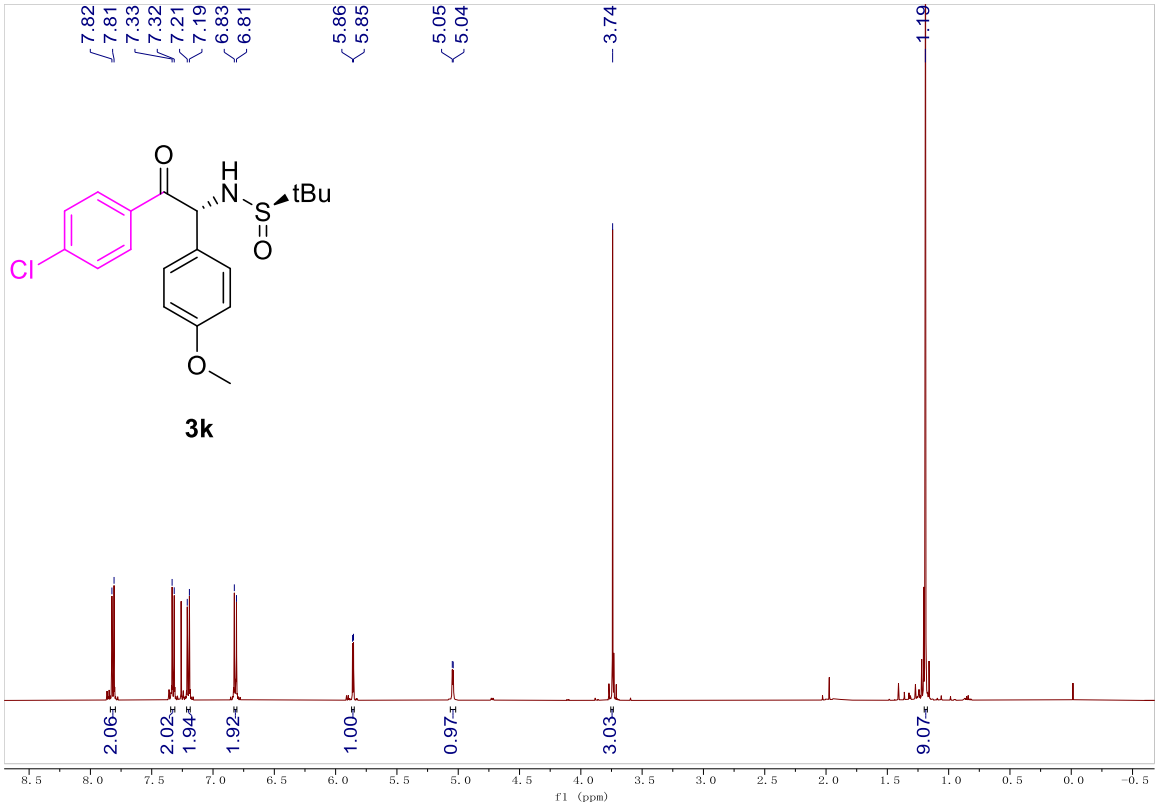


3j

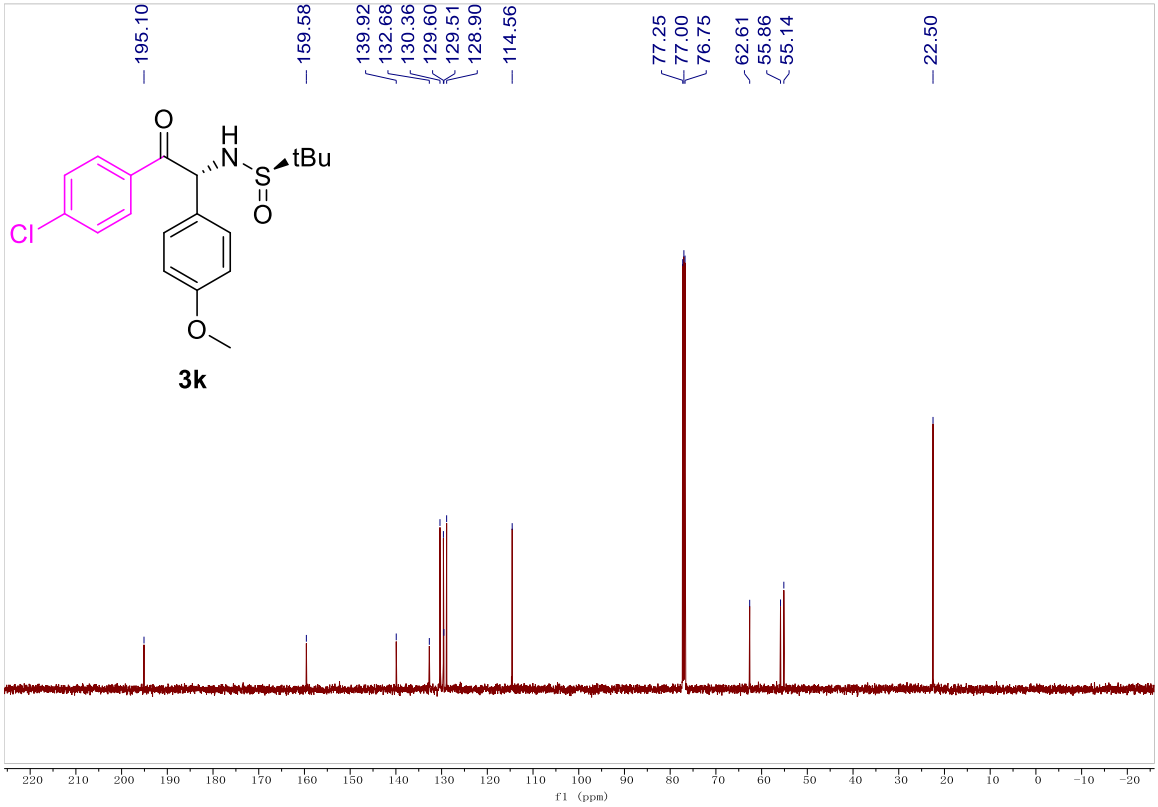
^{13}C NMR spectrum of 3j



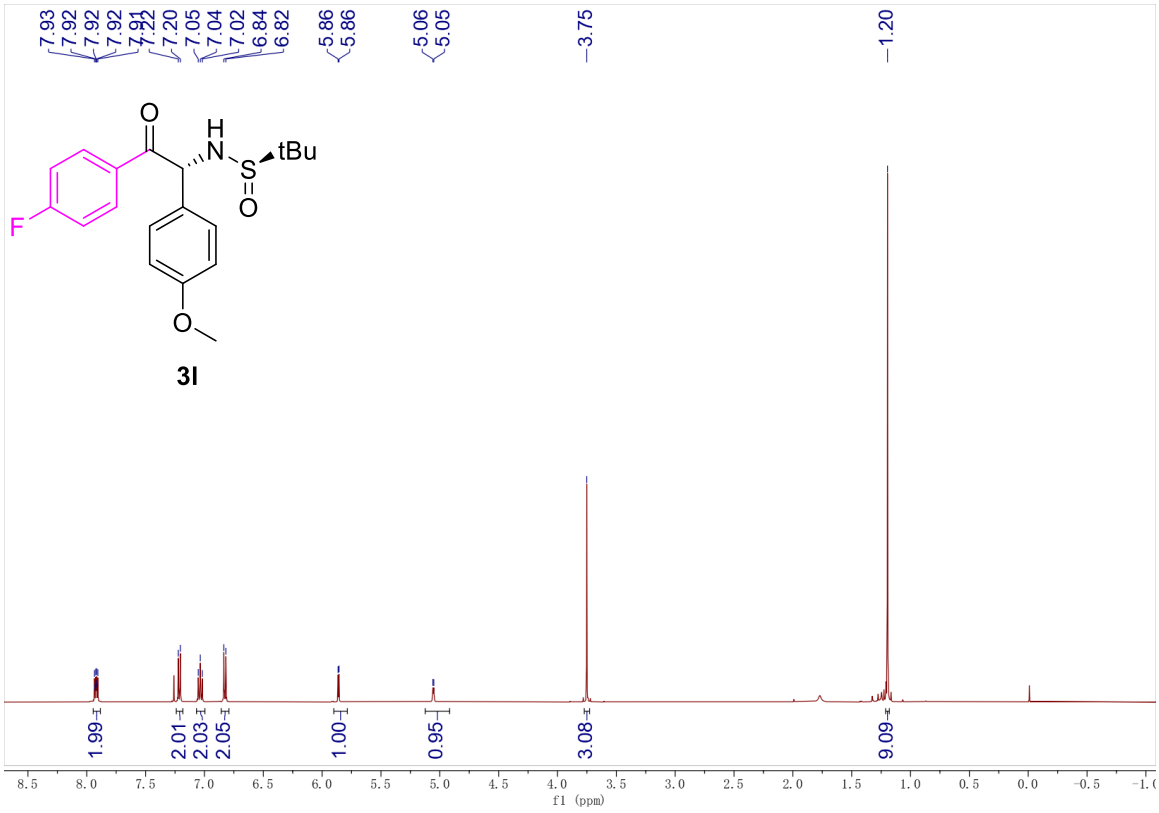
^{1}H NMR spectrum of 3k



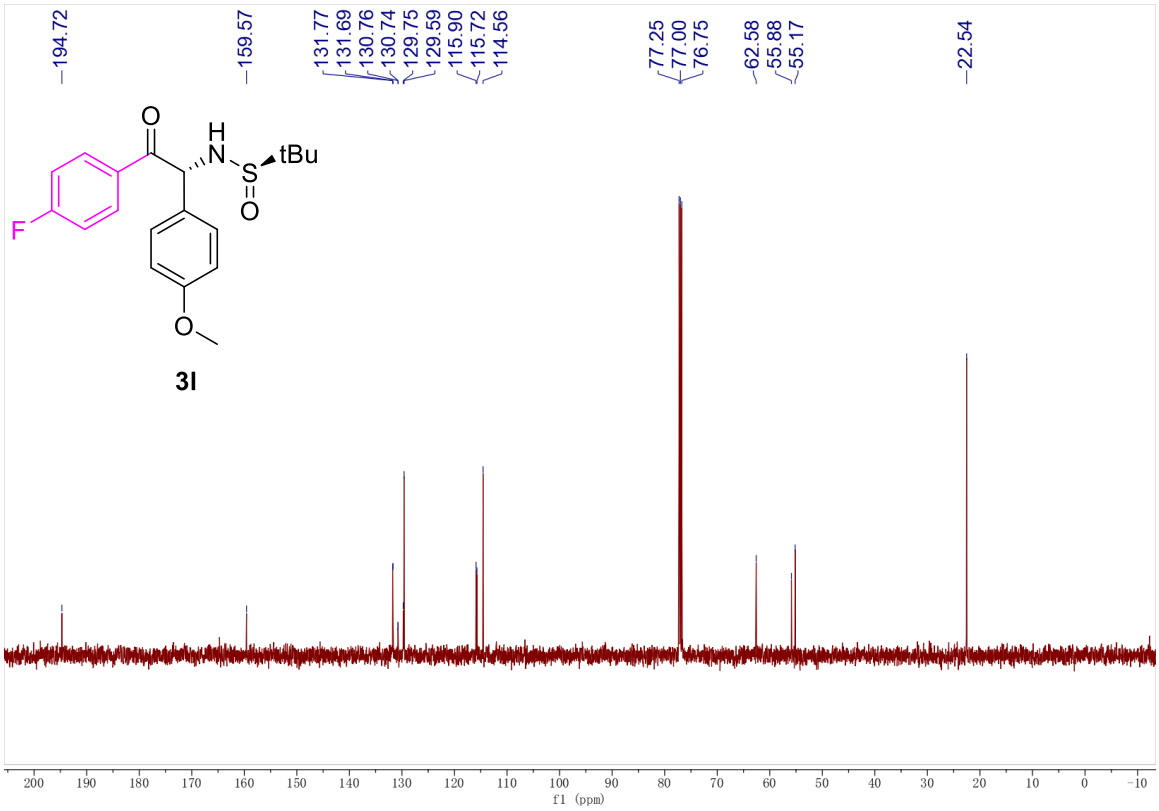
^{13}C NMR spectrum of 3k



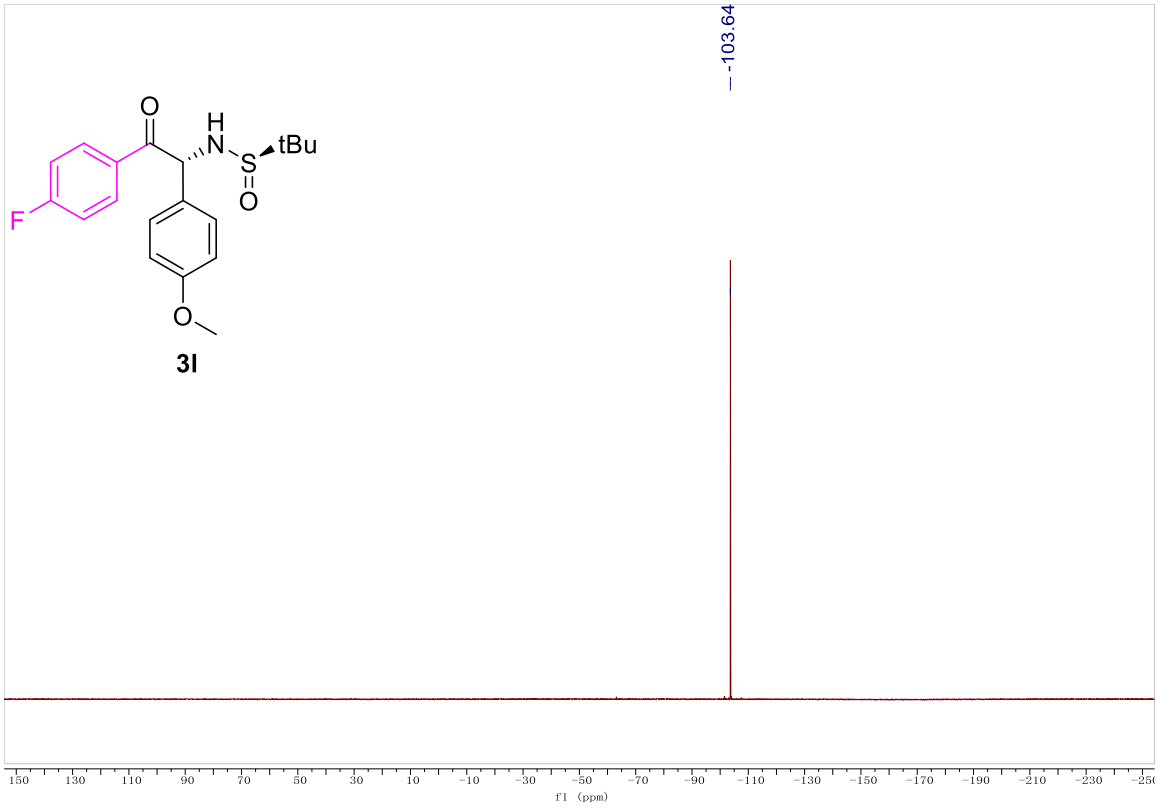
^{1}H NMR spectrum of 3l



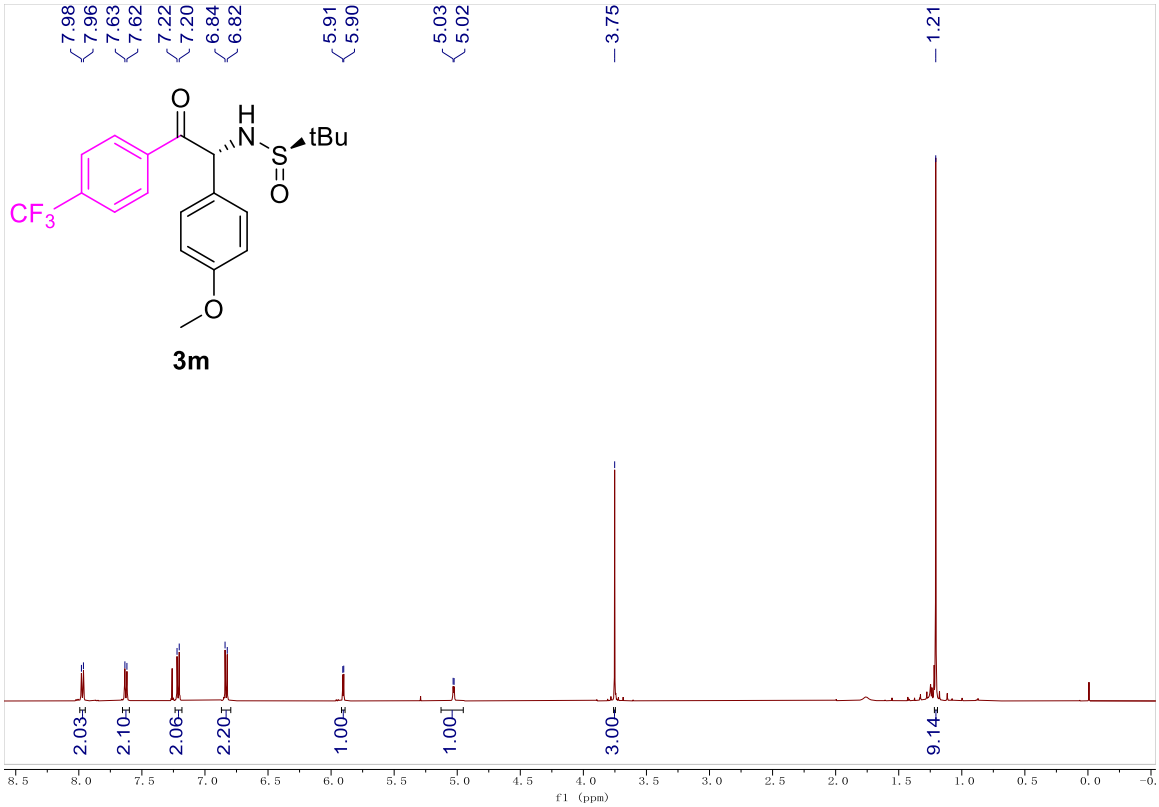
^{13}C NMR spectrum of 3l



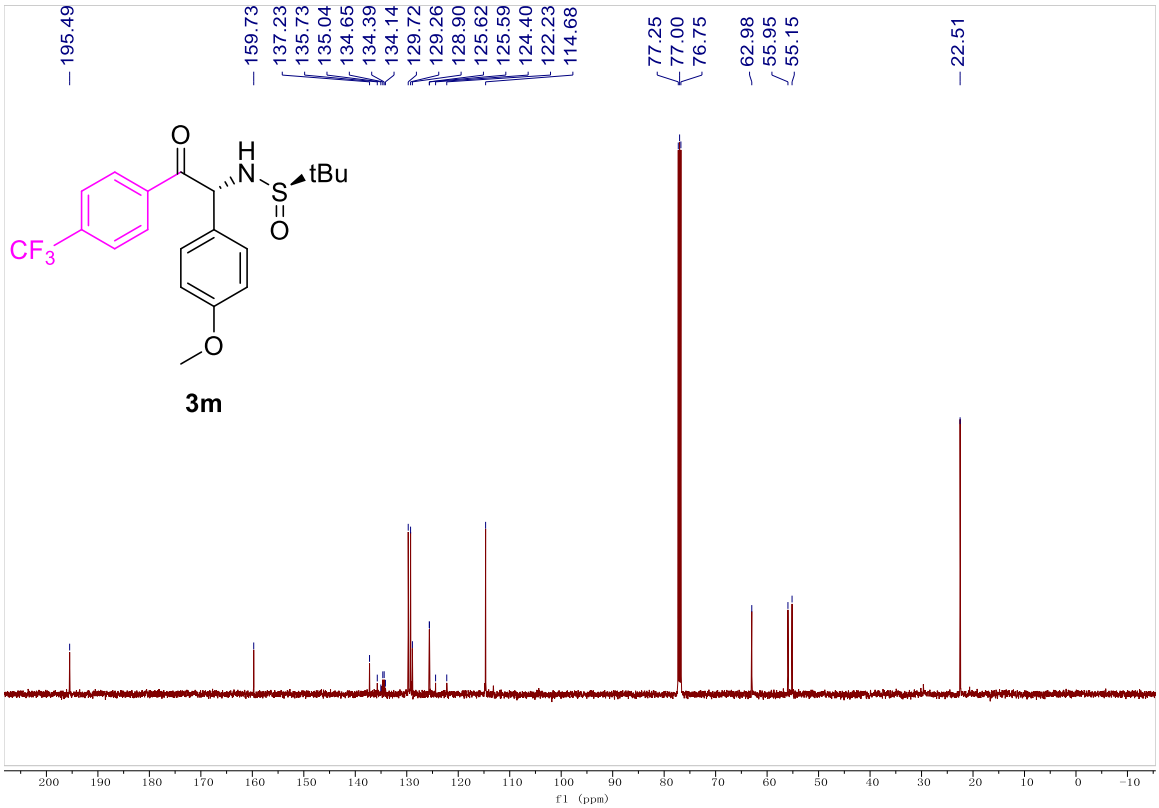
^{19}F NMR spectrum of 3l



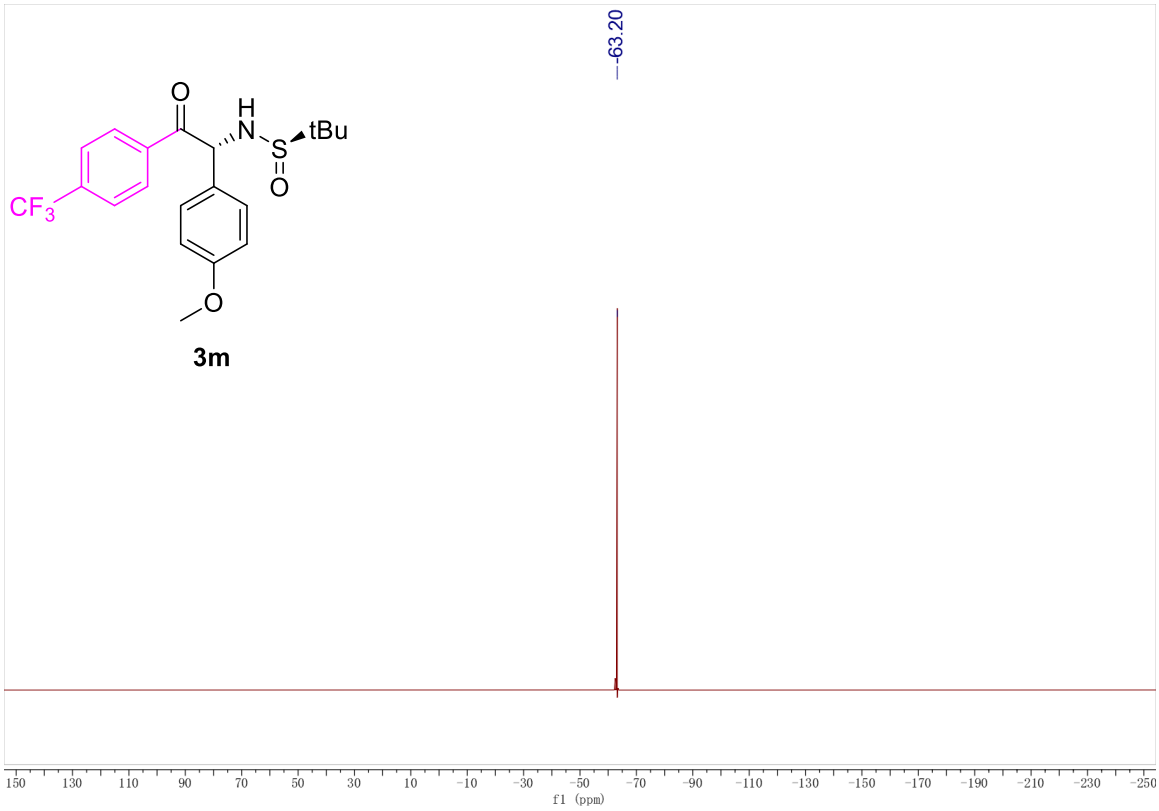
^{1}H NMR spectrum of 3m



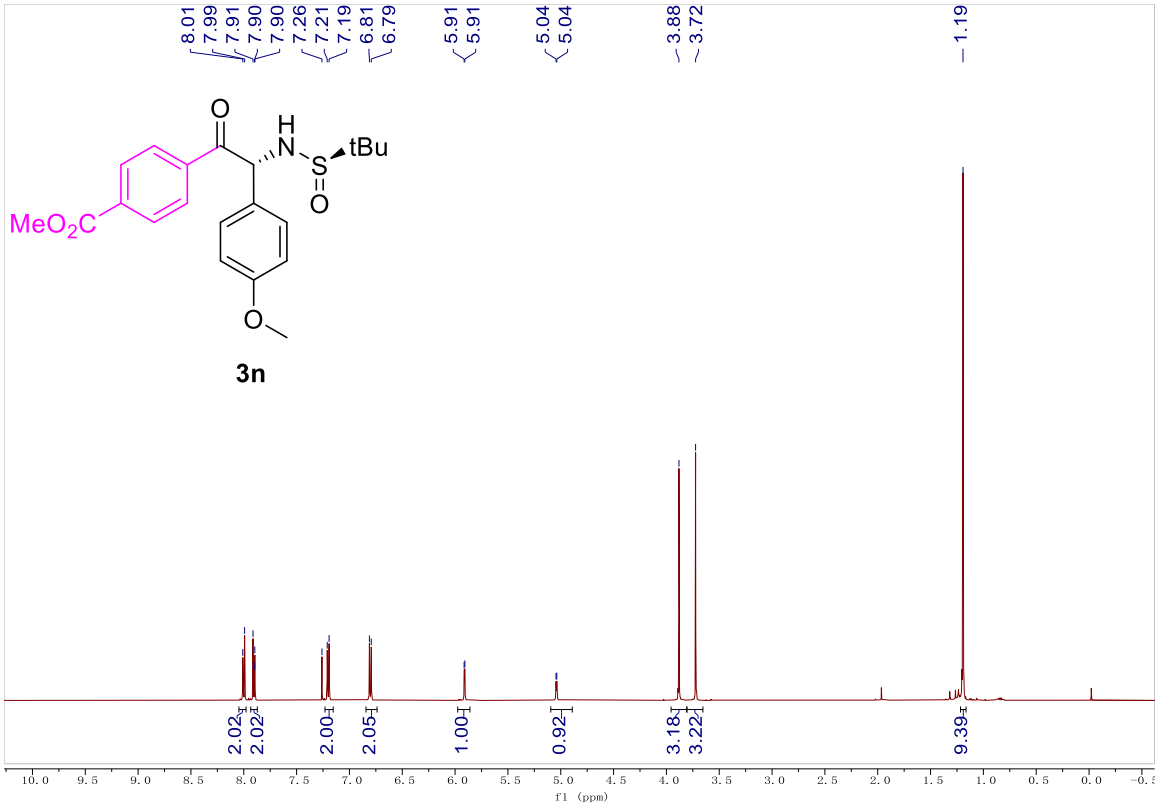
^{13}C NMR spectrum of 3m



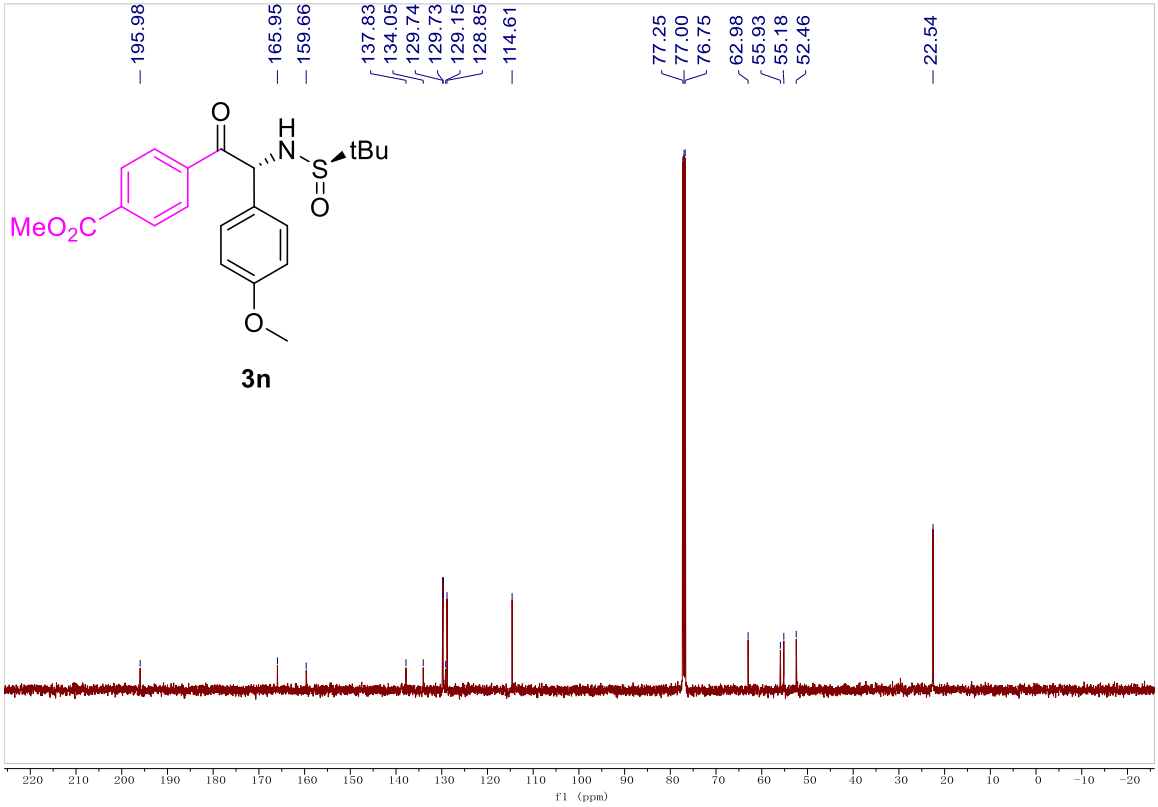
^{19}F NMR spectrum of 3m



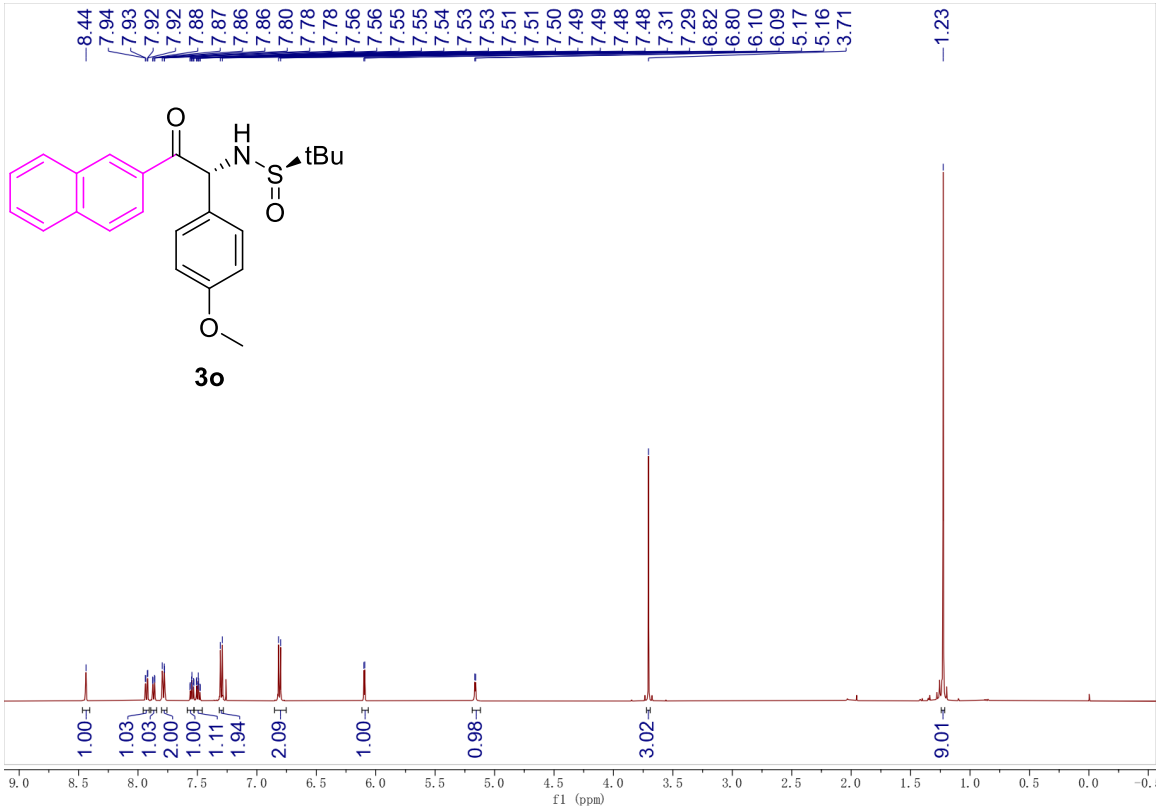
^{1}H NMR spectrum of 3n



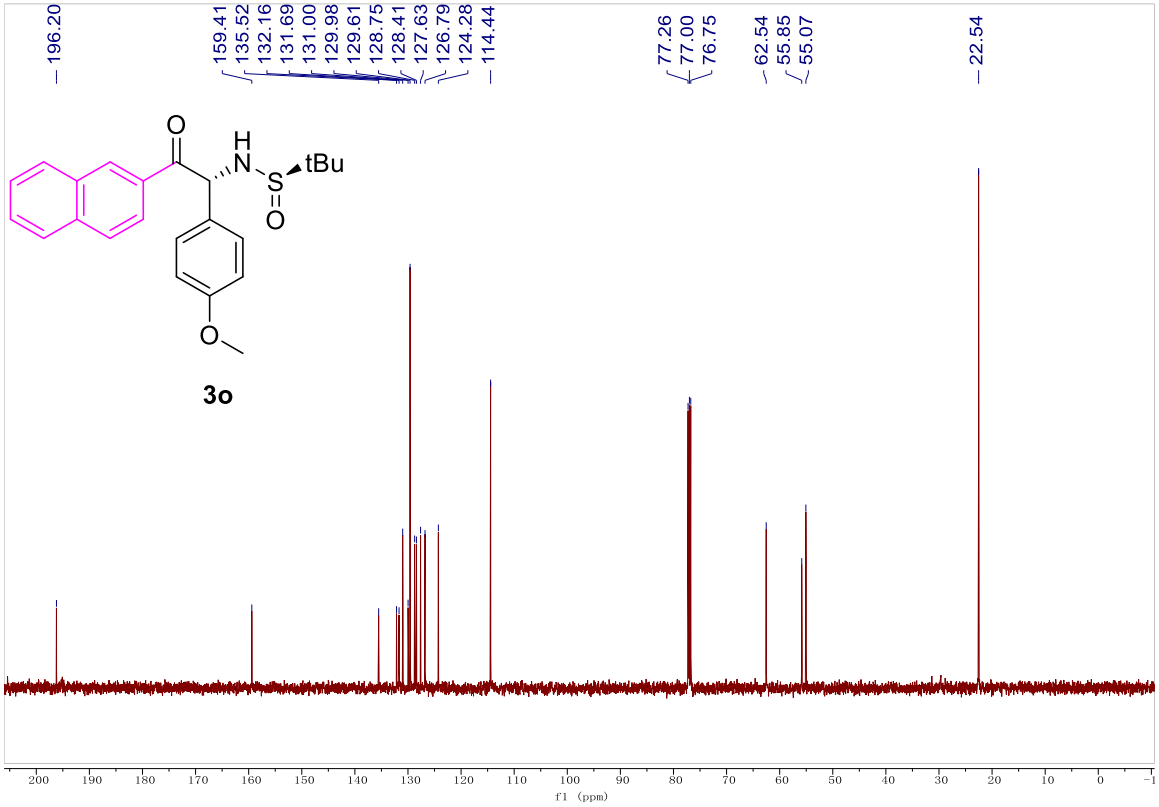
^{13}C NMR spectrum of 3n



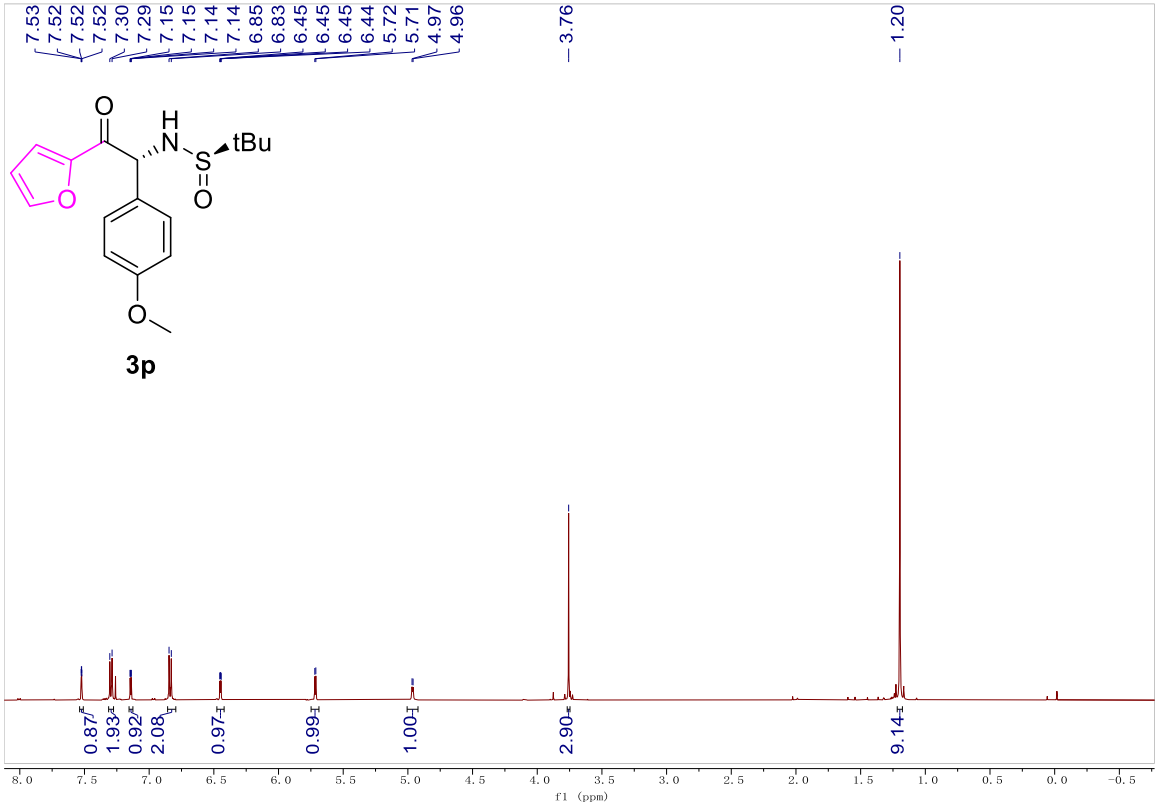
^{1}H NMR spectrum of 3o



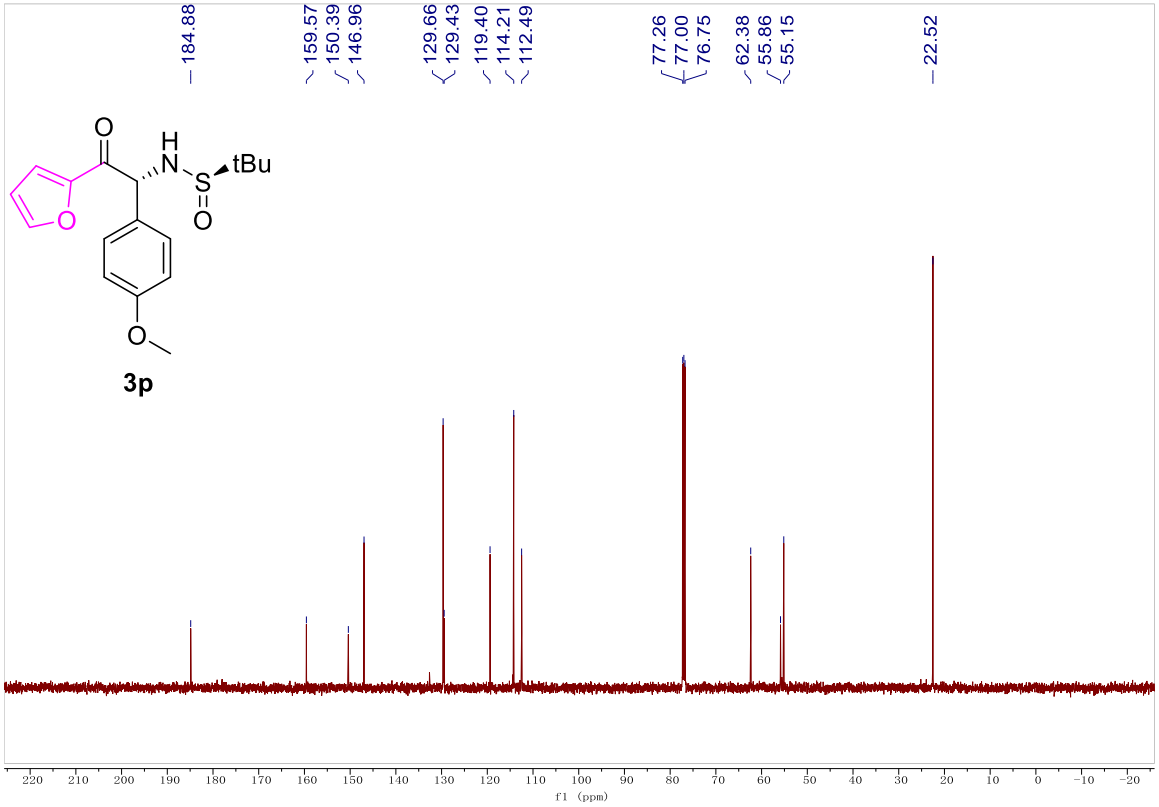
^{13}C NMR spectrum of 3o



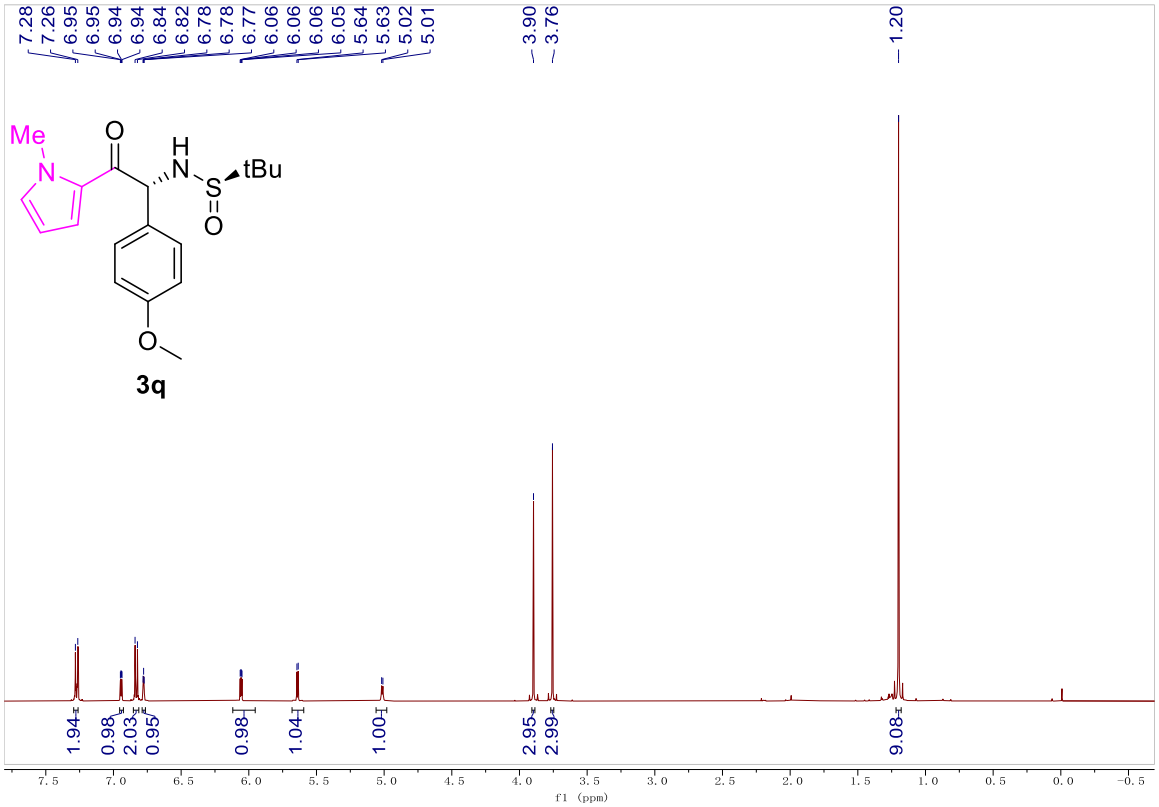
^{1}H NMR spectrum of 3p



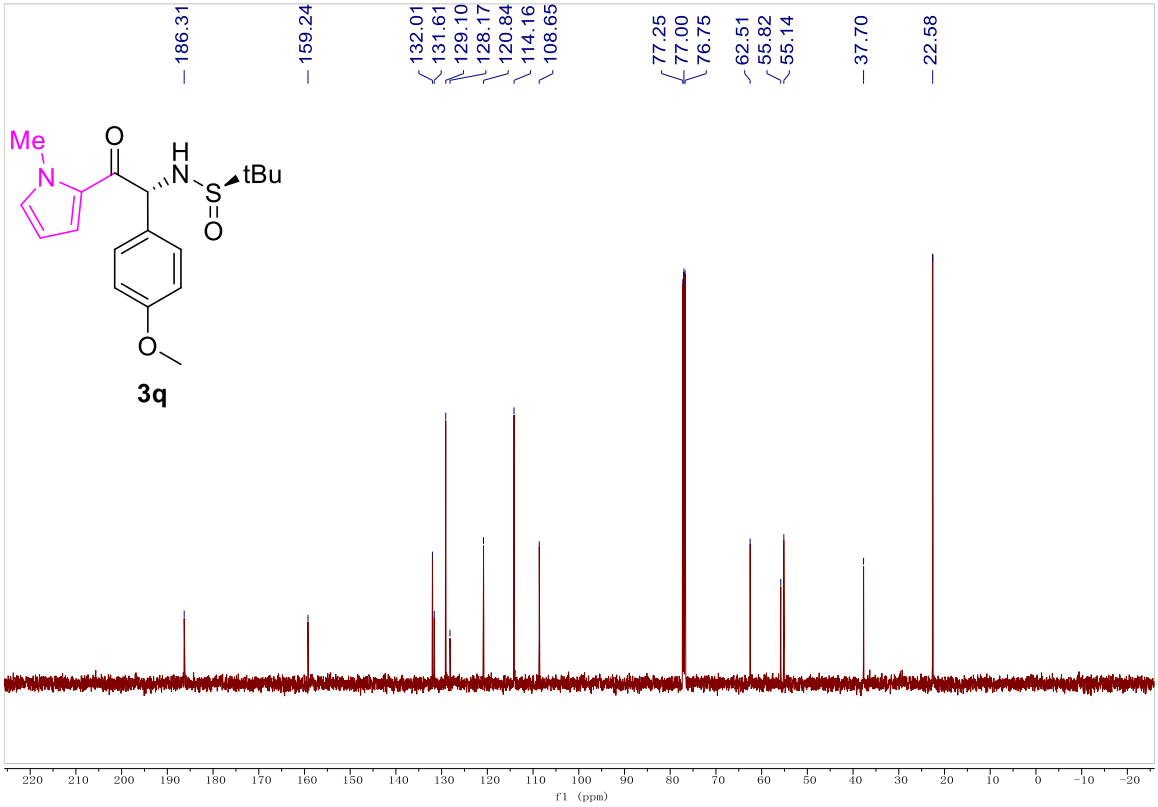
^{13}C NMR spectrum of 3p



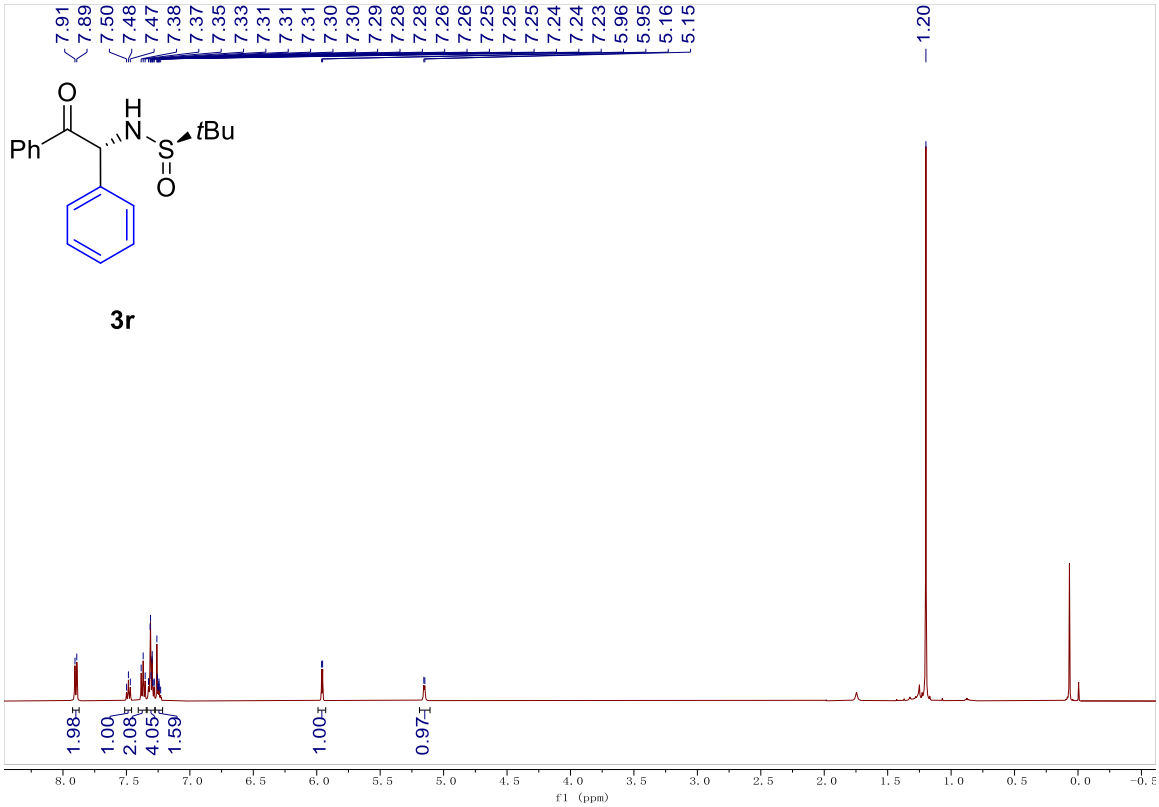
^{1}H NMR spectrum of 3q



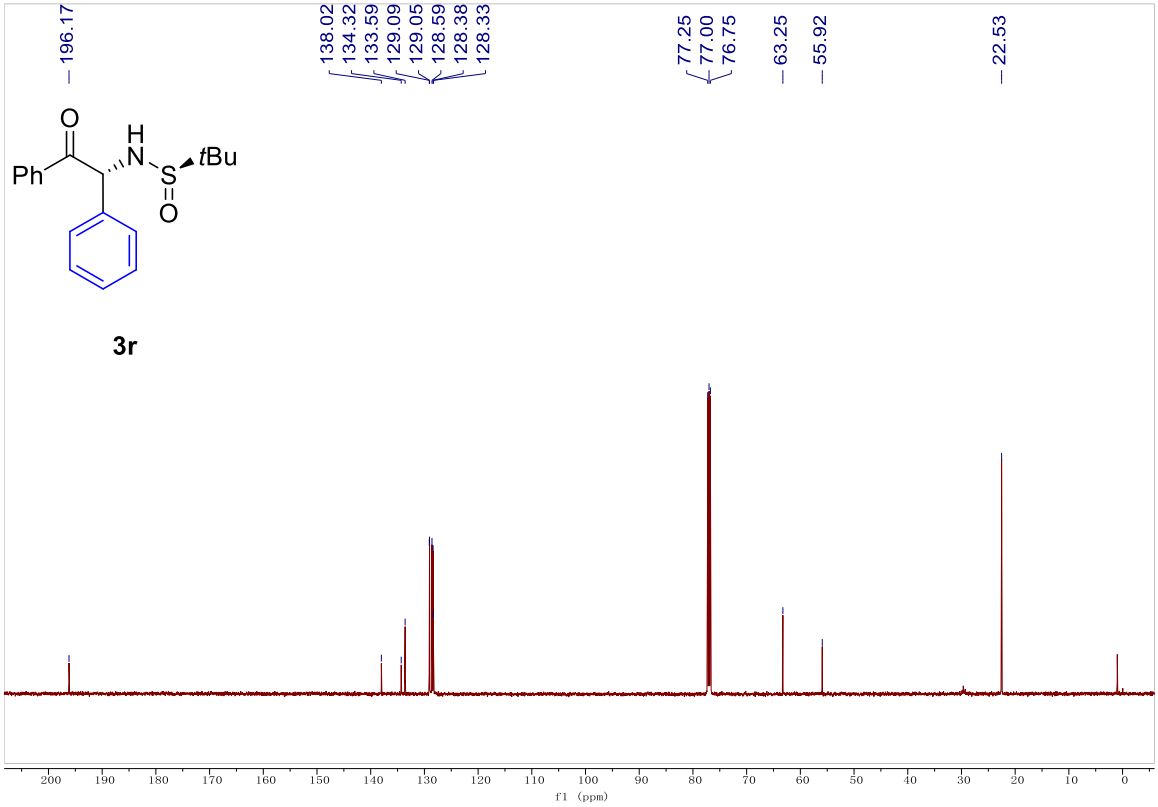
^{13}C NMR spectrum of 3q



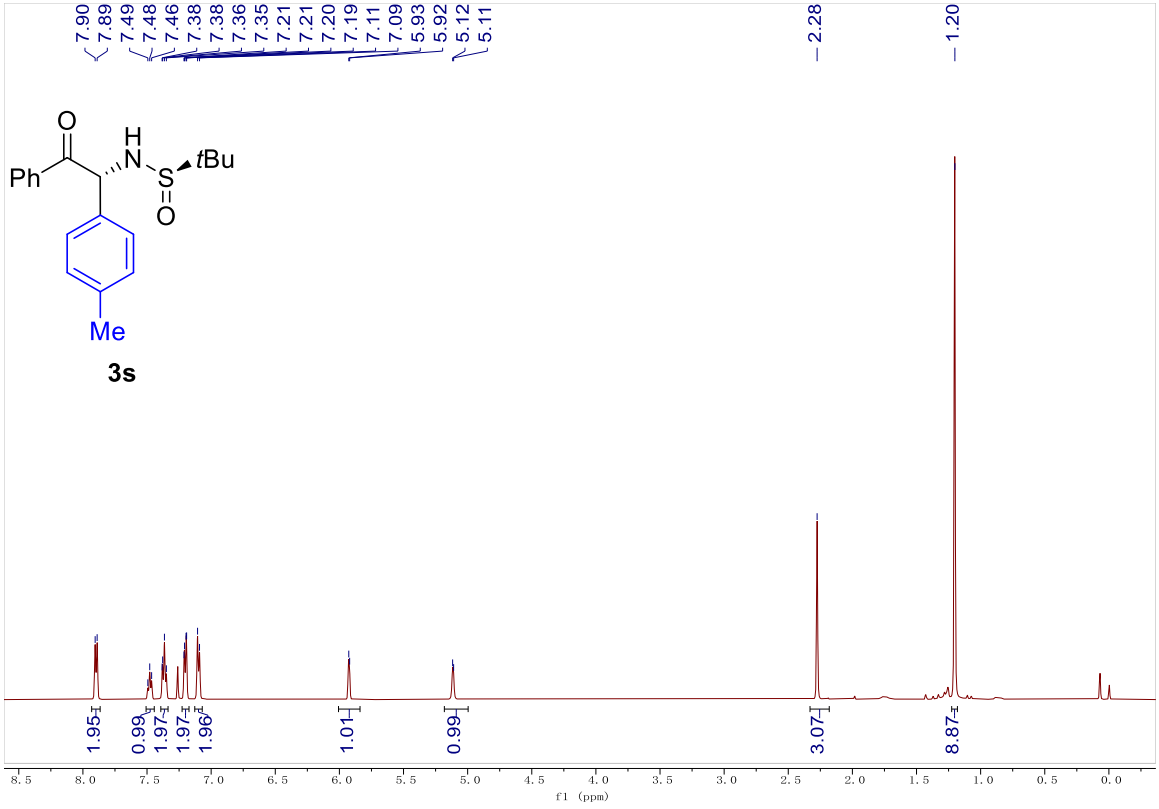
^{1}H NMR spectrum of 3r



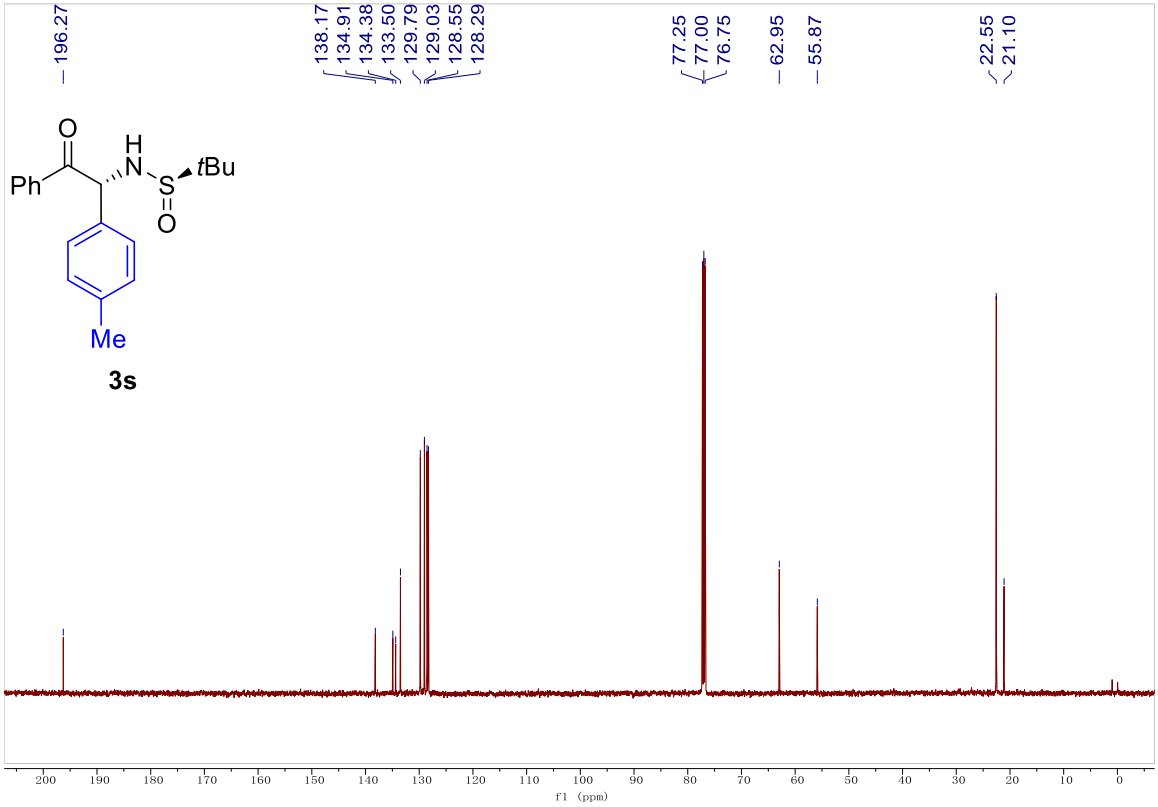
^{13}C NMR spectrum of 3r



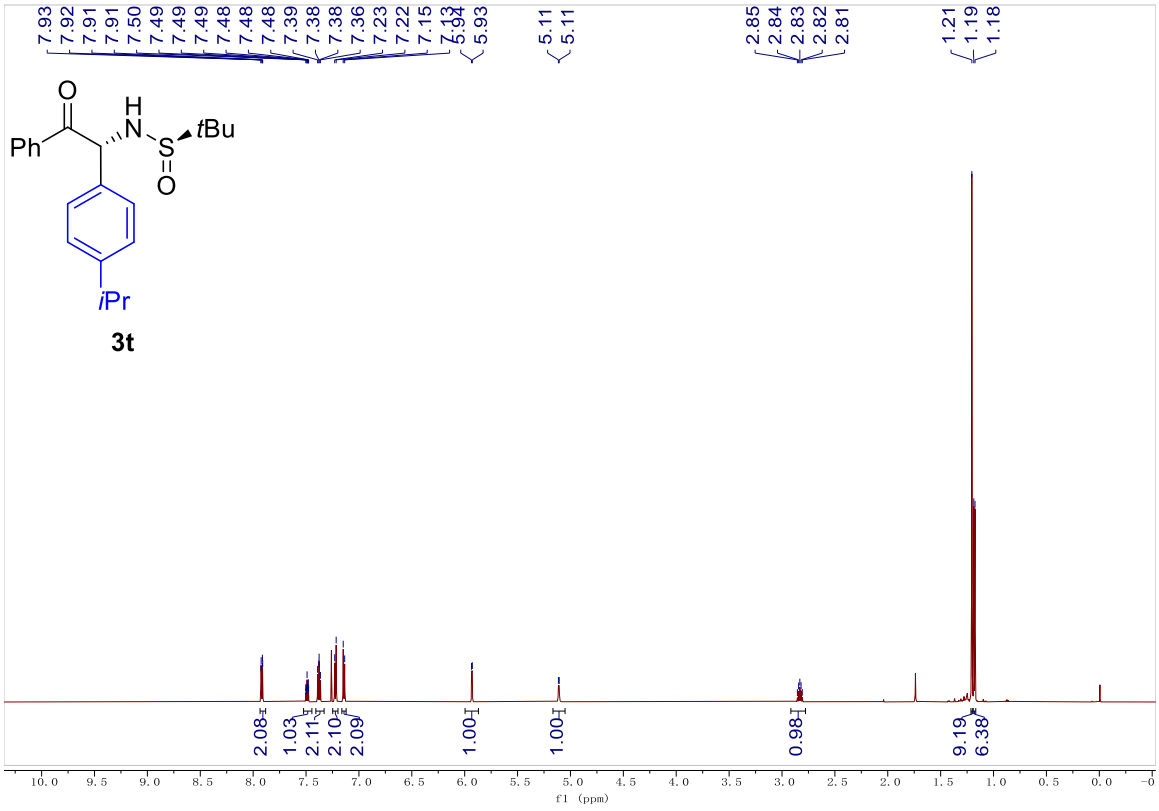
^{1}H NMR spectrum of 3s



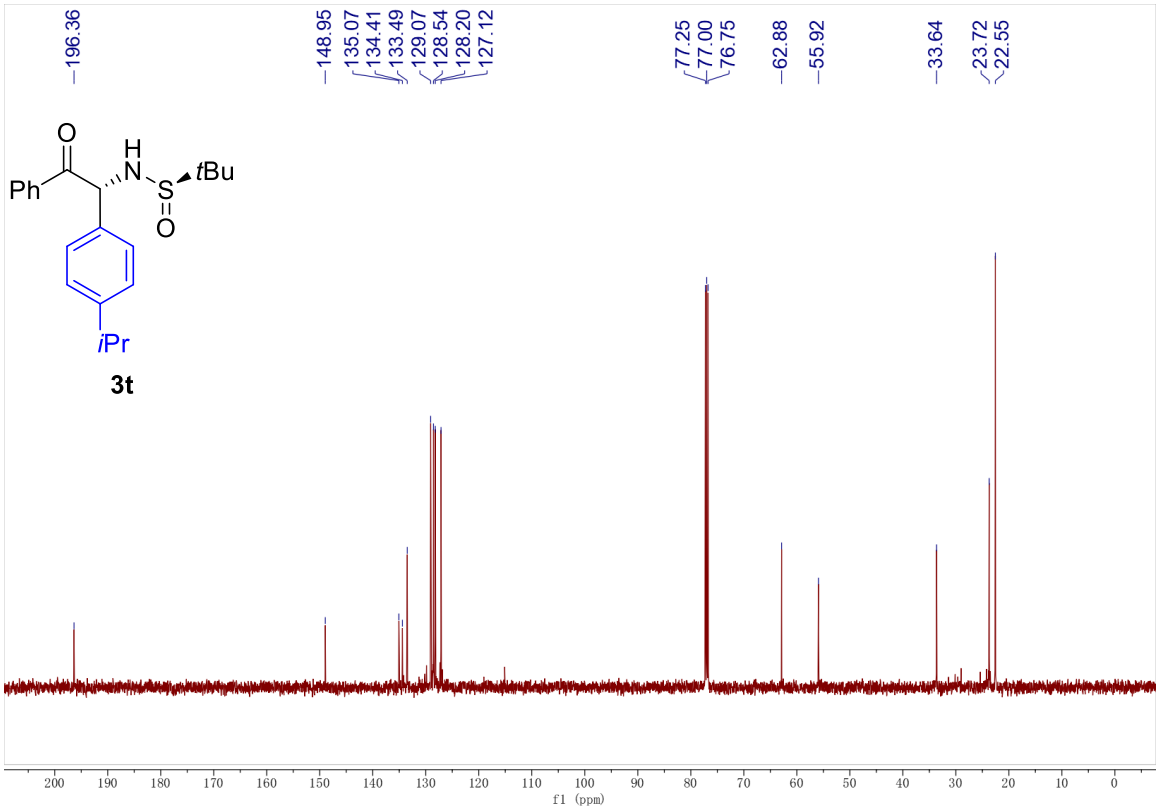
^{13}C NMR spectrum of 3s



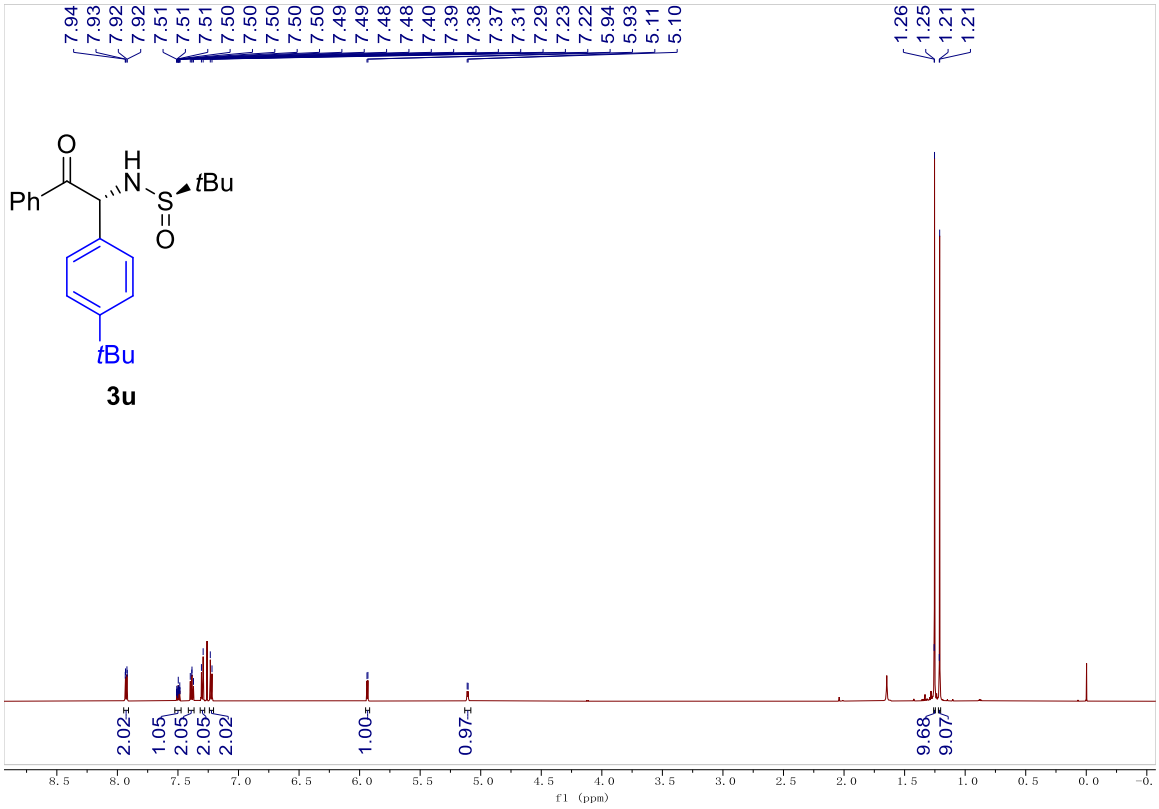
^{1}H NMR spectrum of 3t



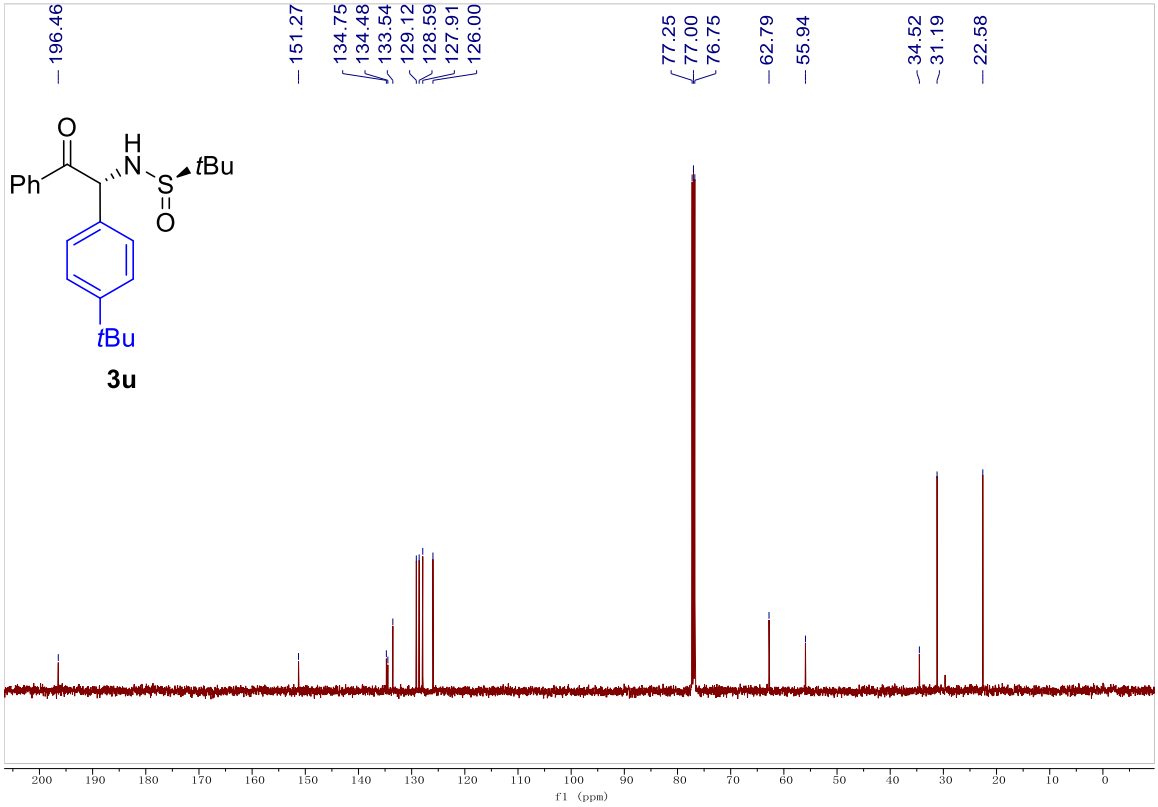
^{13}C NMR spectrum of 3t



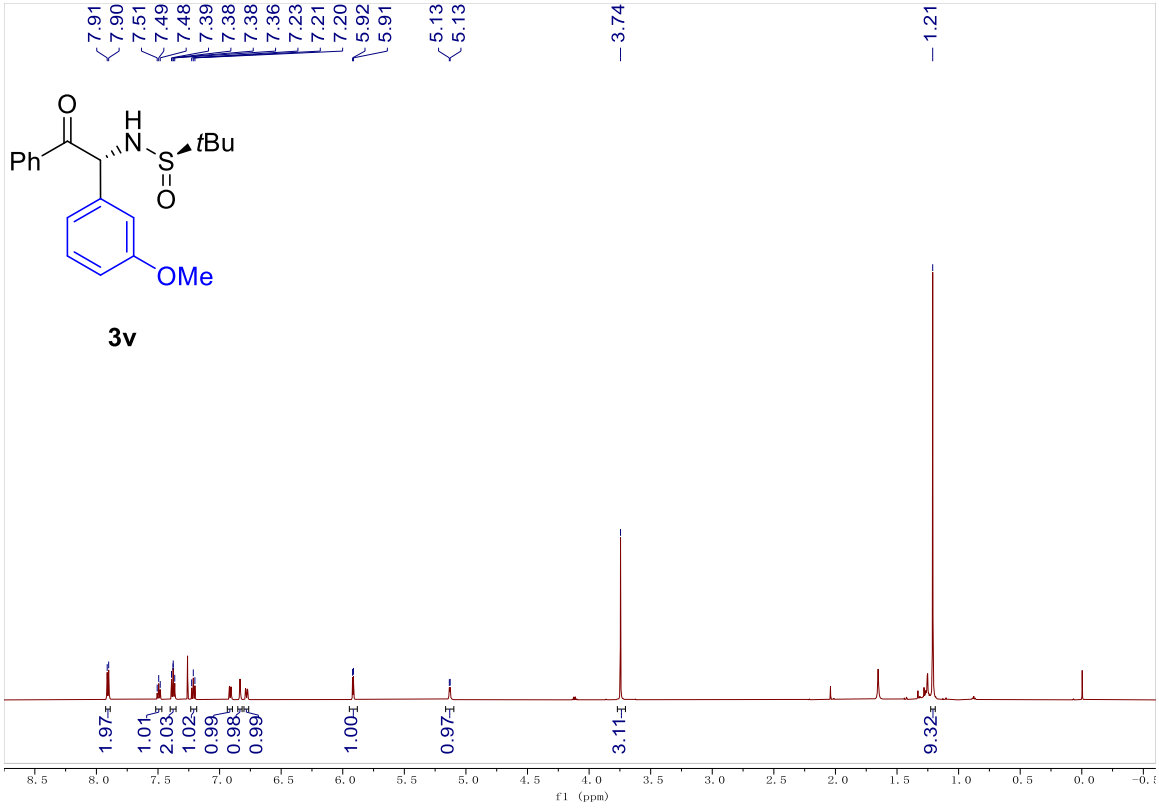
^{1}H NMR spectrum of 3u



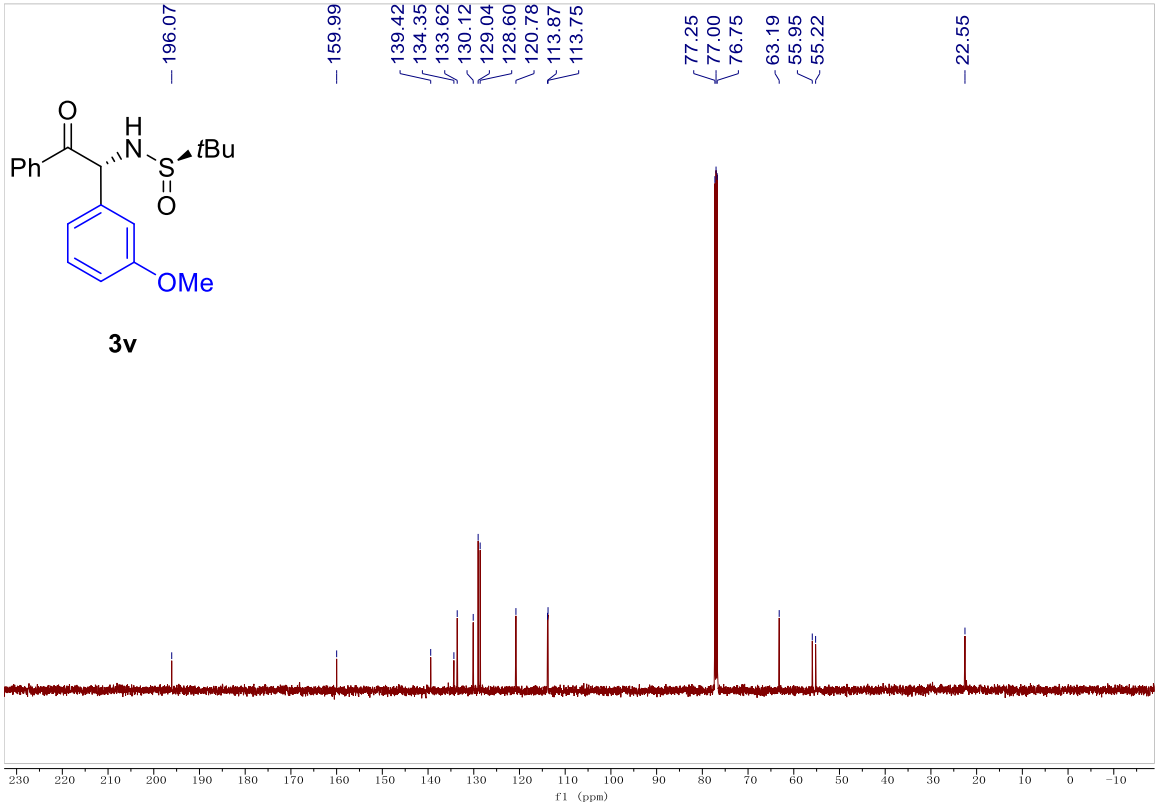
^{13}C NMR spectrum of 3u



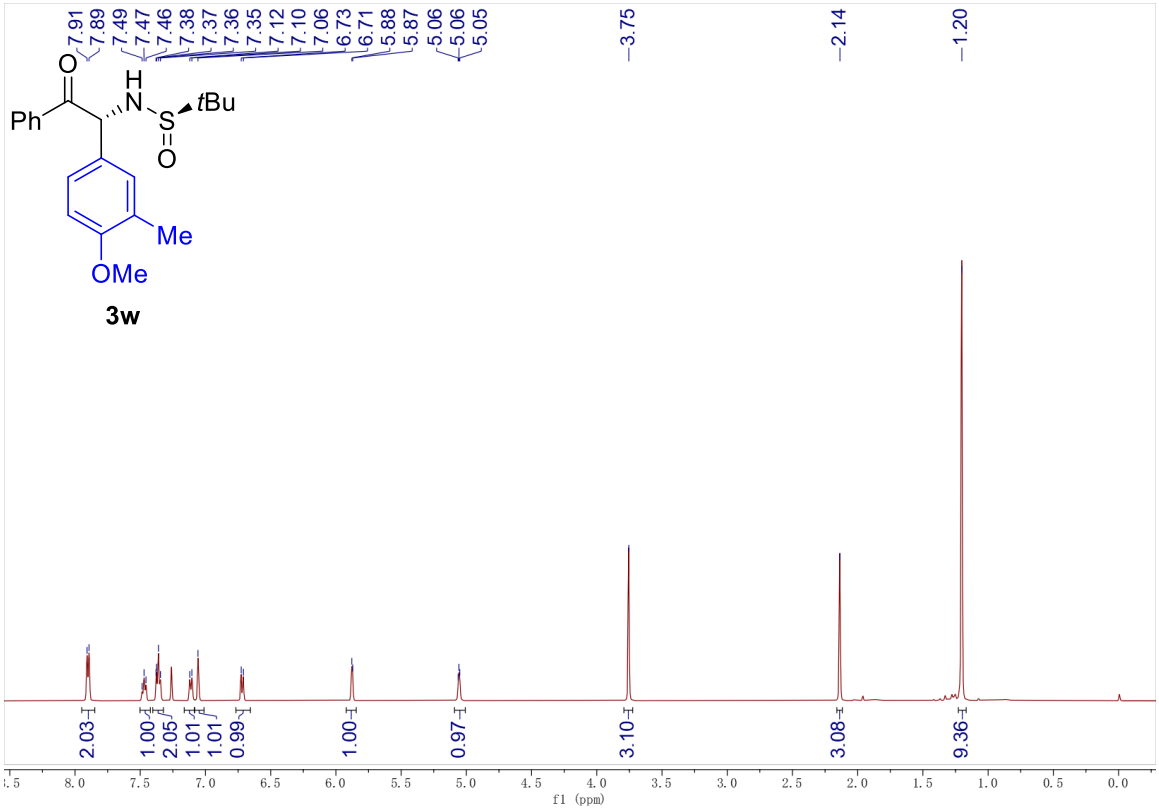
^{1}H NMR spectrum of 3v



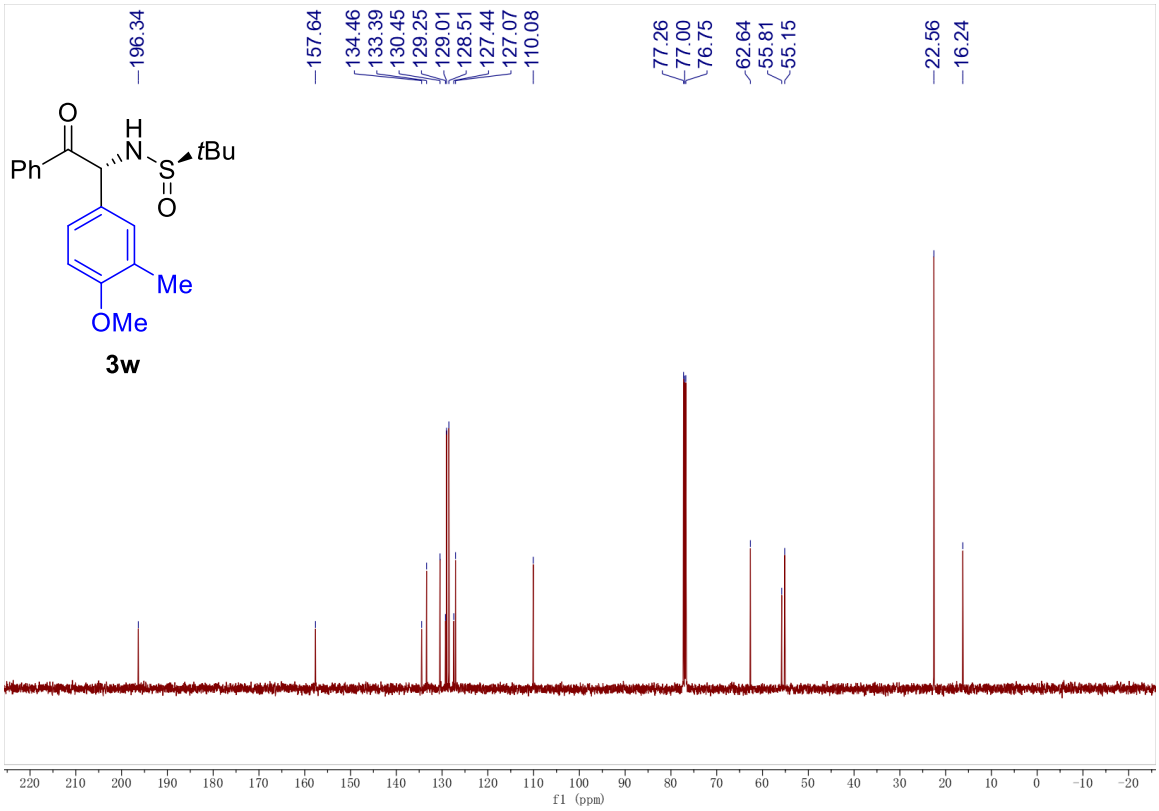
^{13}C NMR spectrum of 3v



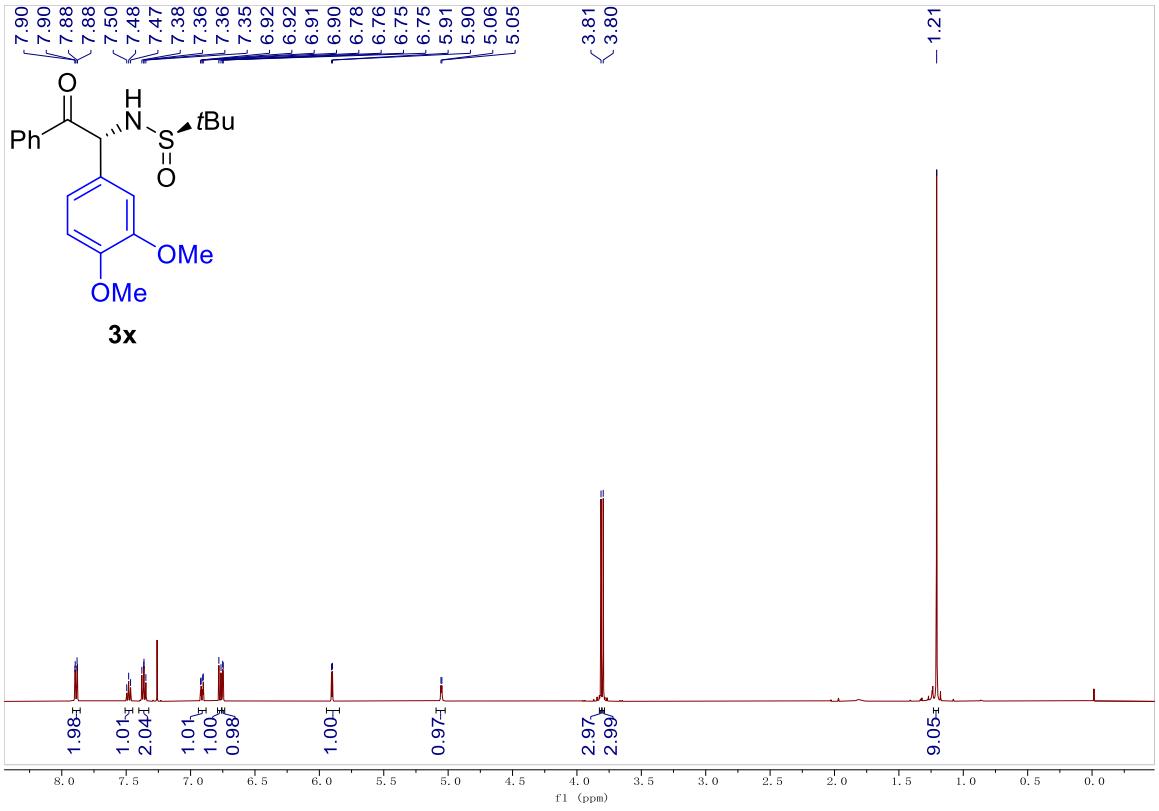
^{1}H NMR spectrum of 3w



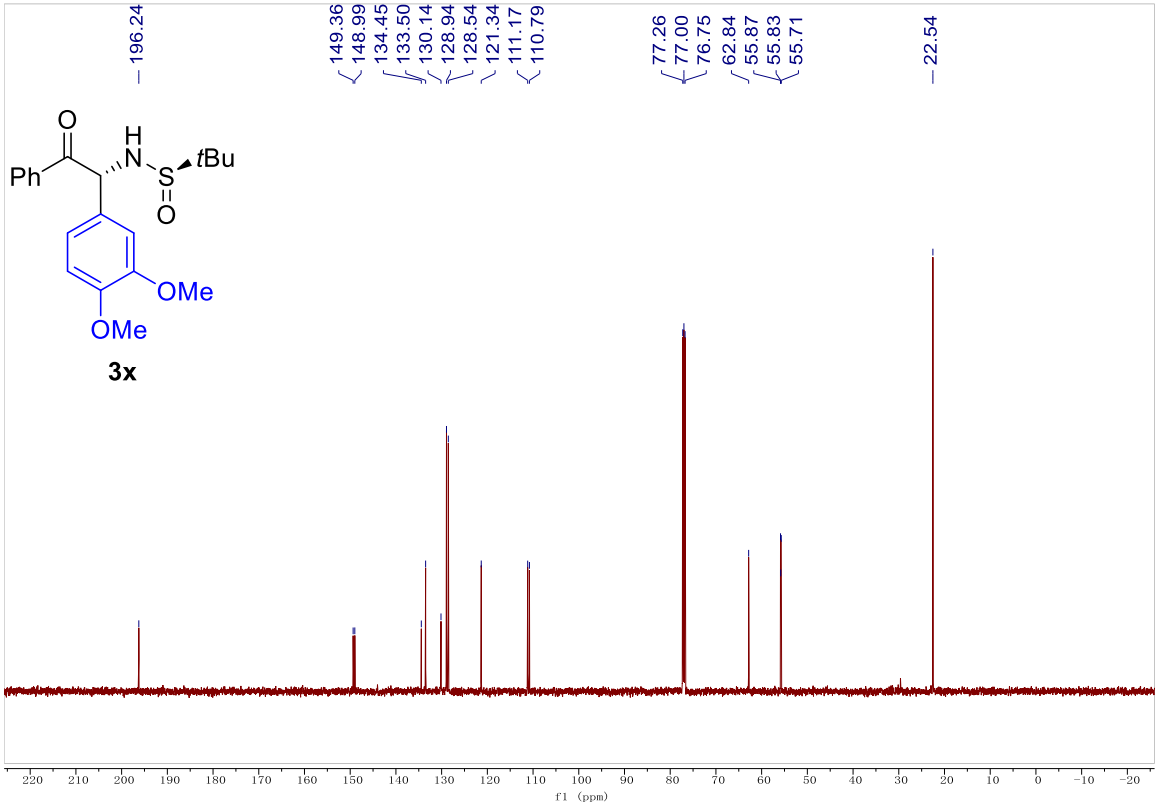
^{13}C NMR spectrum of 3w



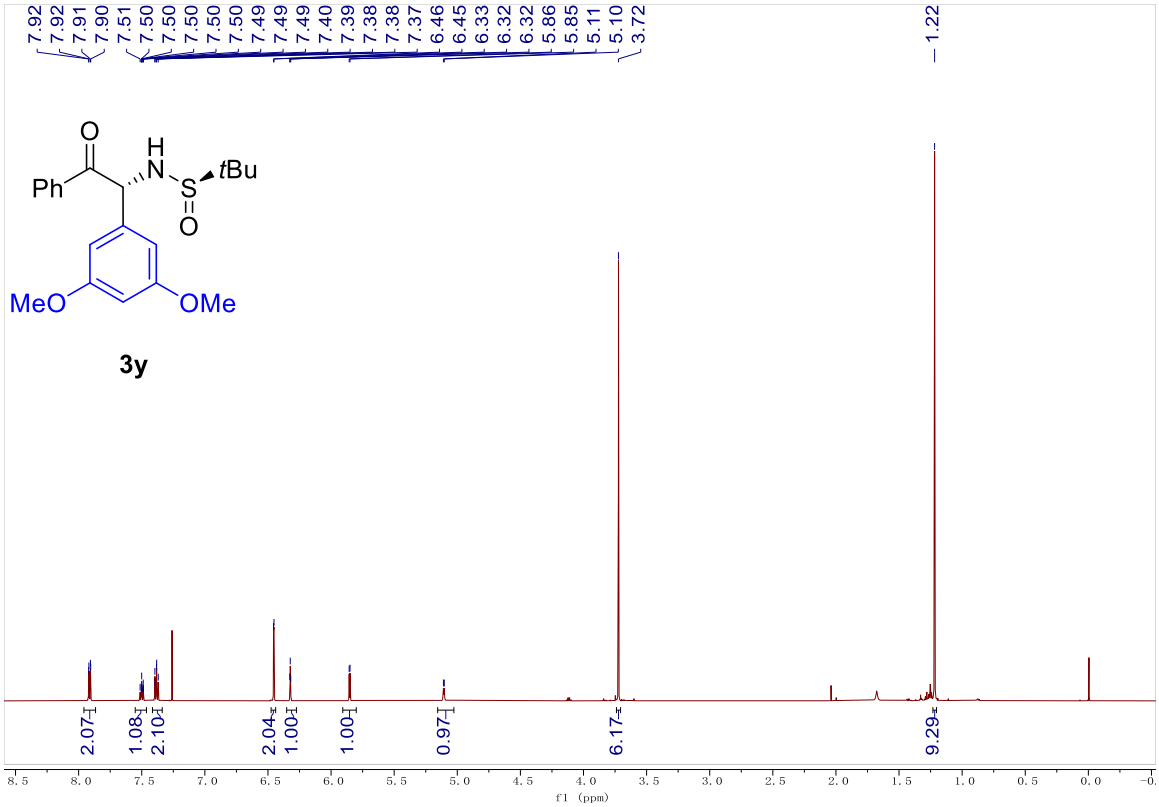
^{1}H NMR spectrum of 3x



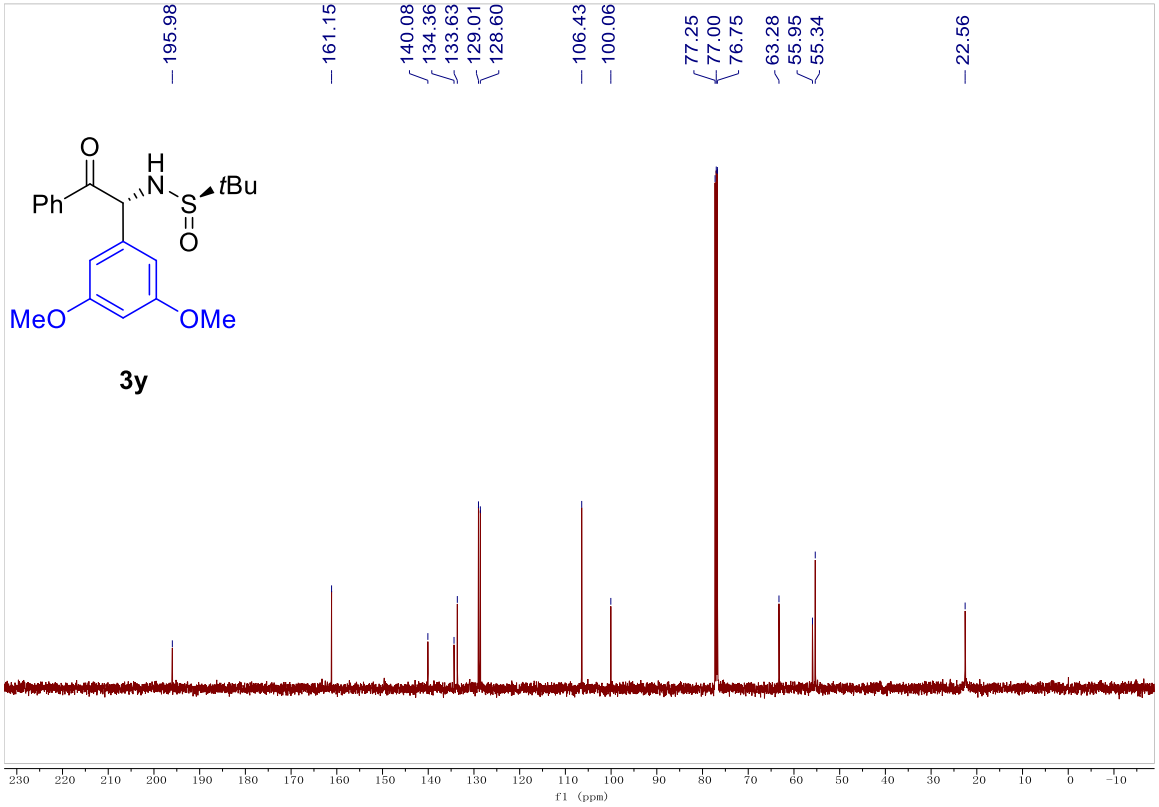
^{13}C NMR spectrum of 3x



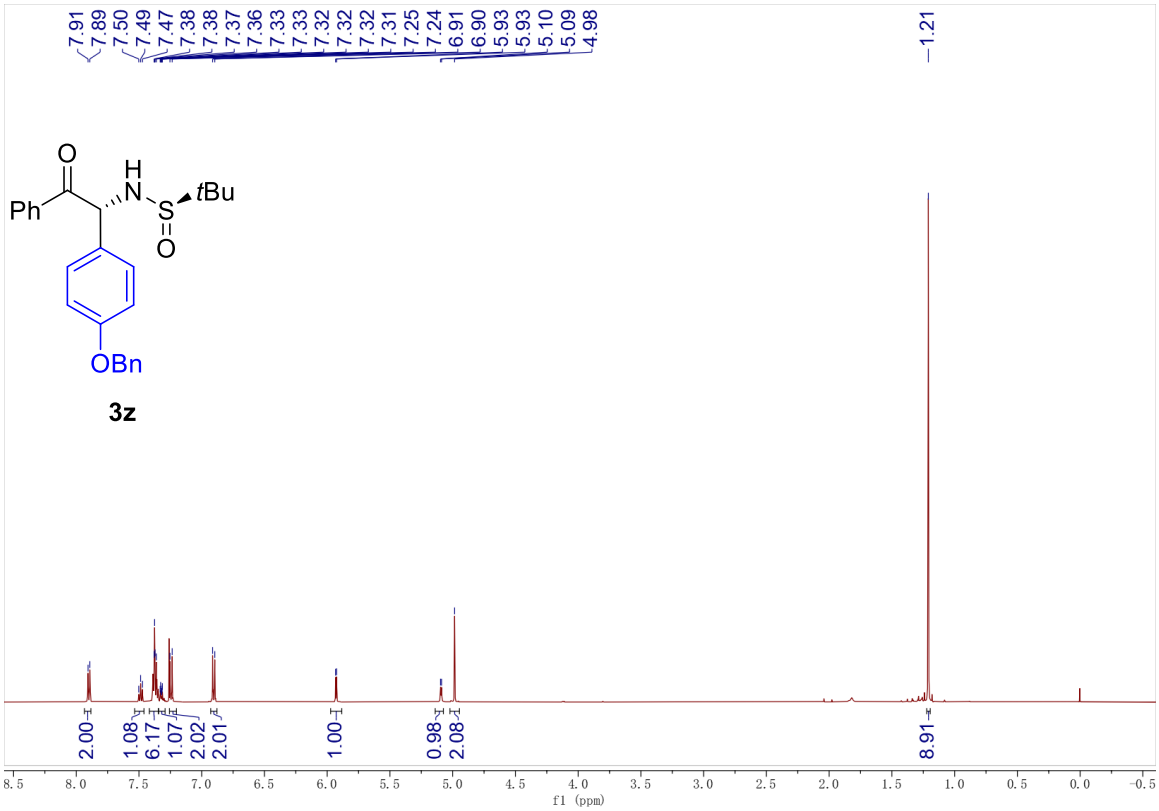
^{1}H NMR spectrum of 3y



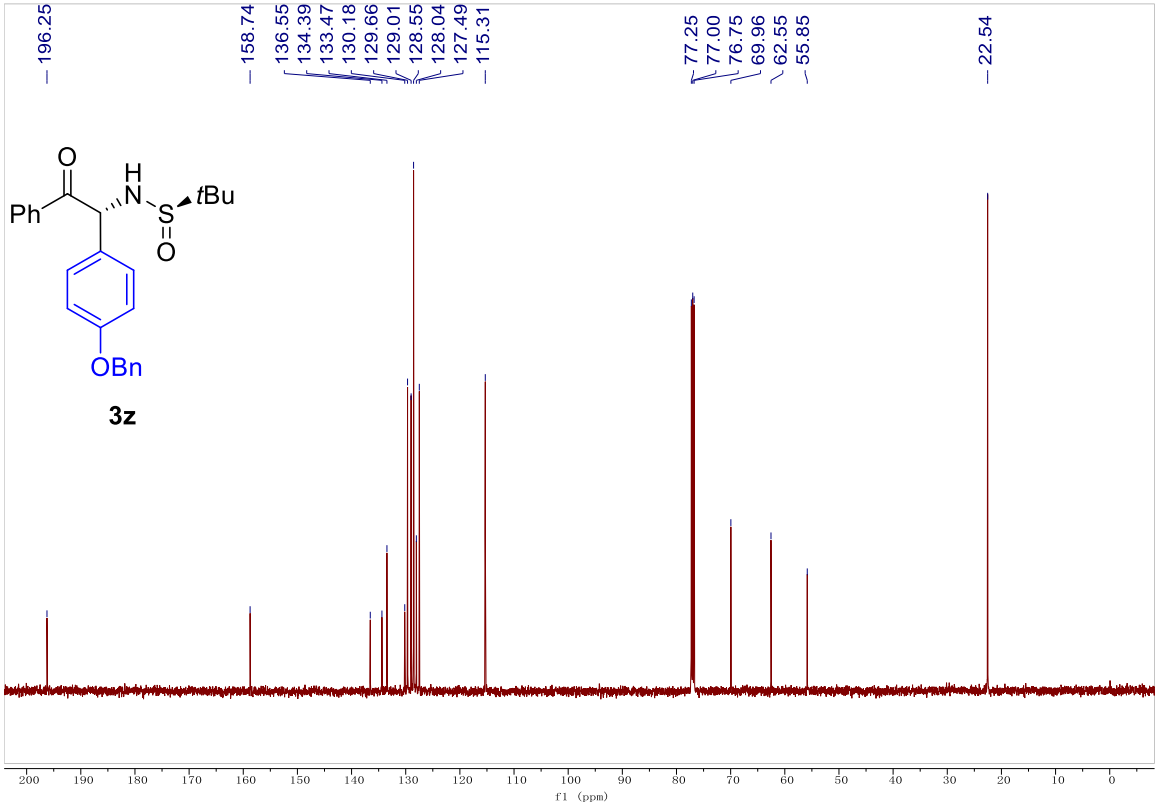
^{13}C NMR spectrum of 3y



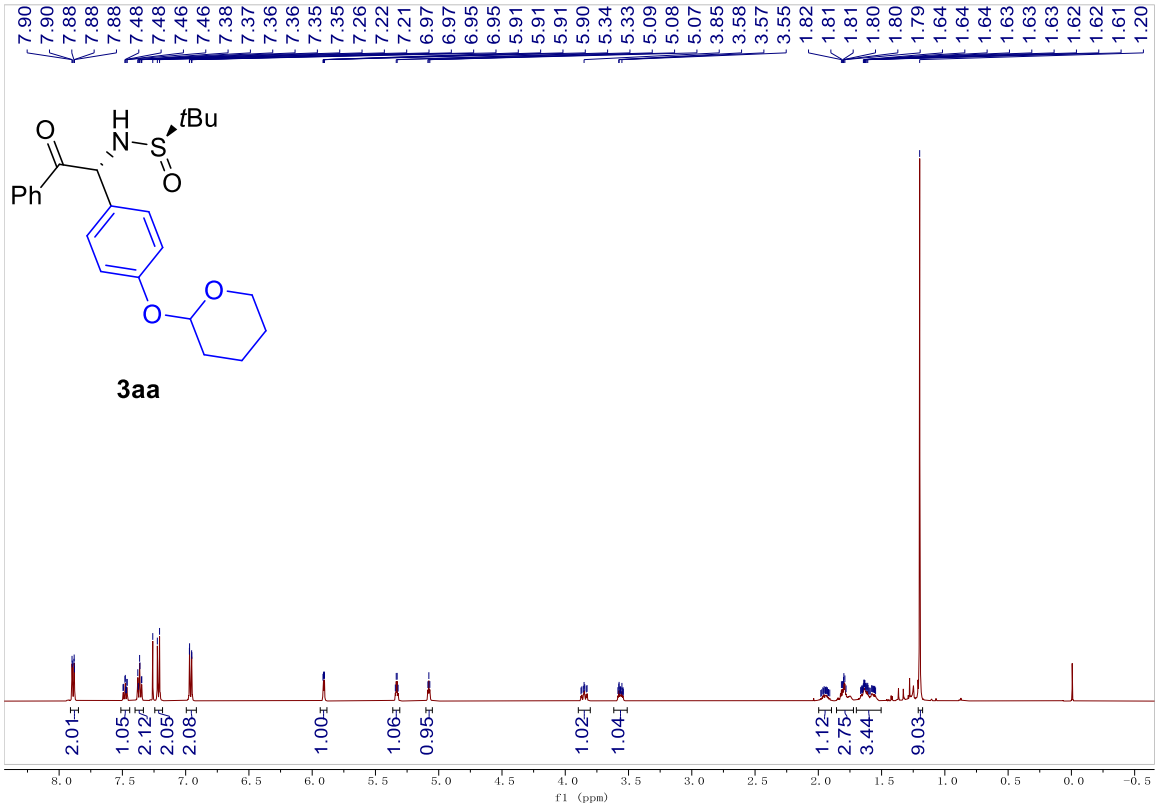
^{1}H NMR spectrum of 3z



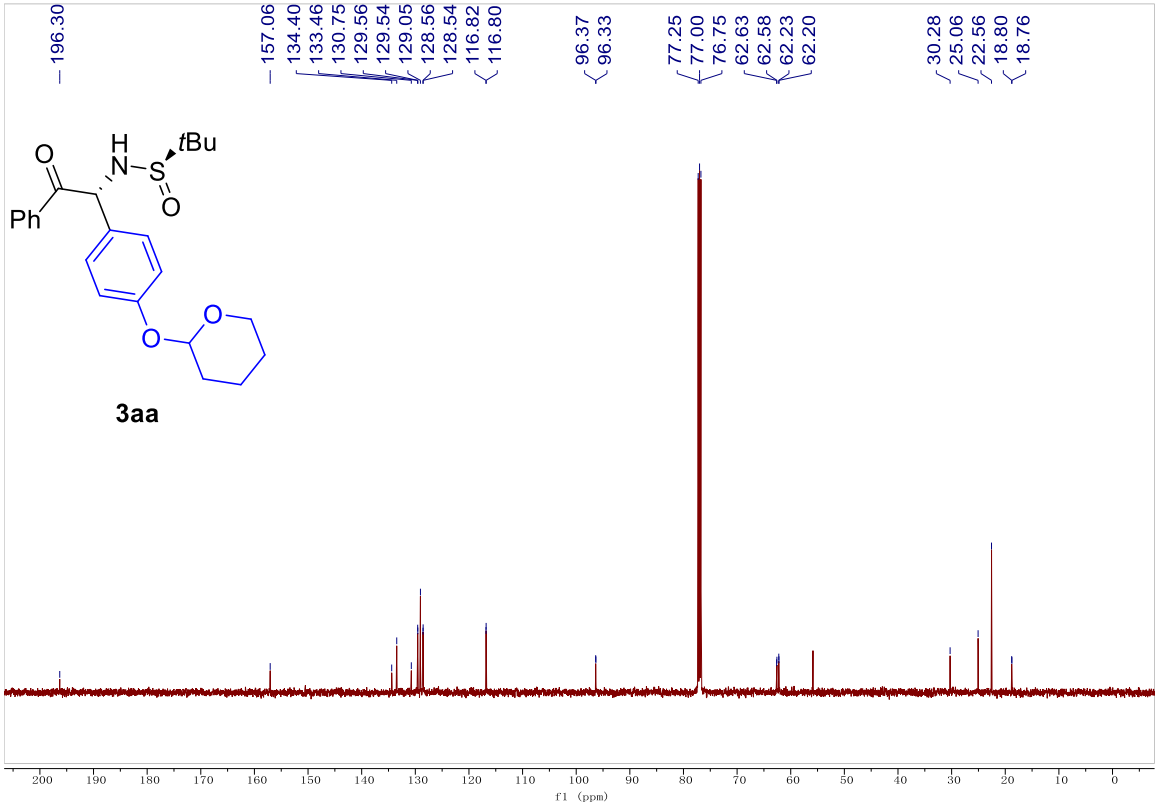
^{13}C NMR spectrum of 3z



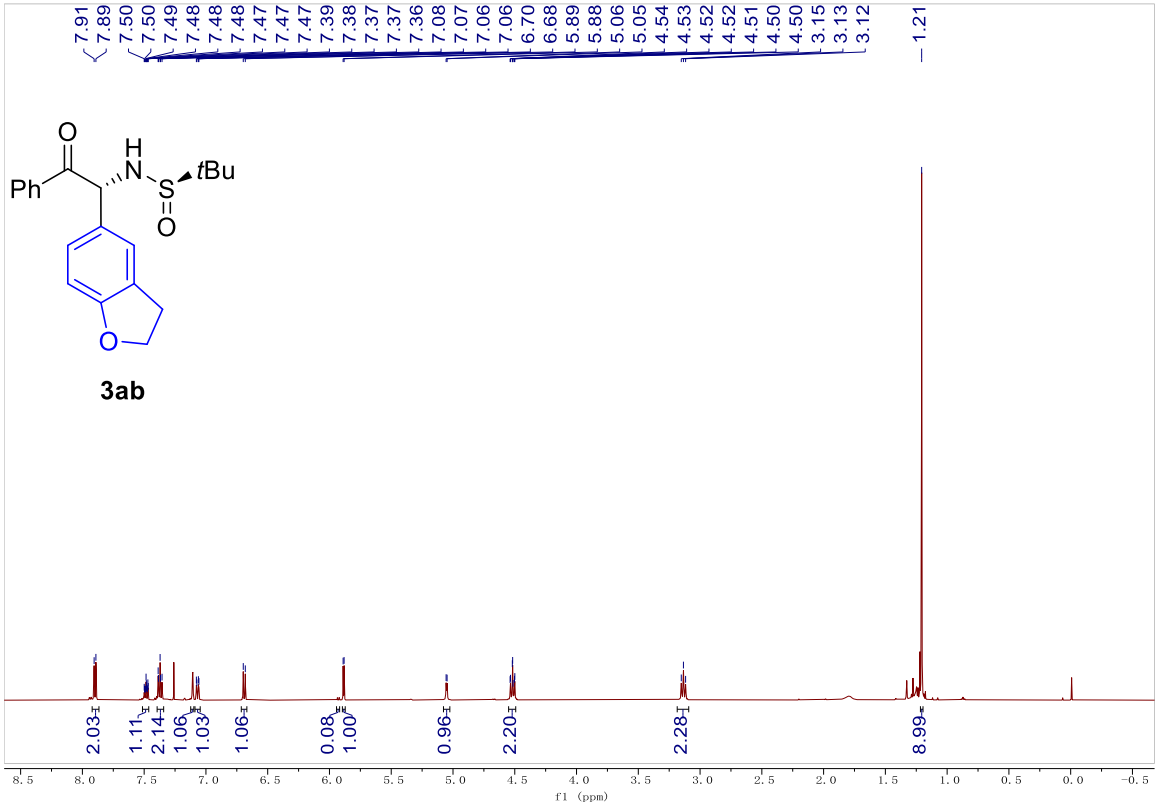
^{1}H NMR spectrum of 3aa



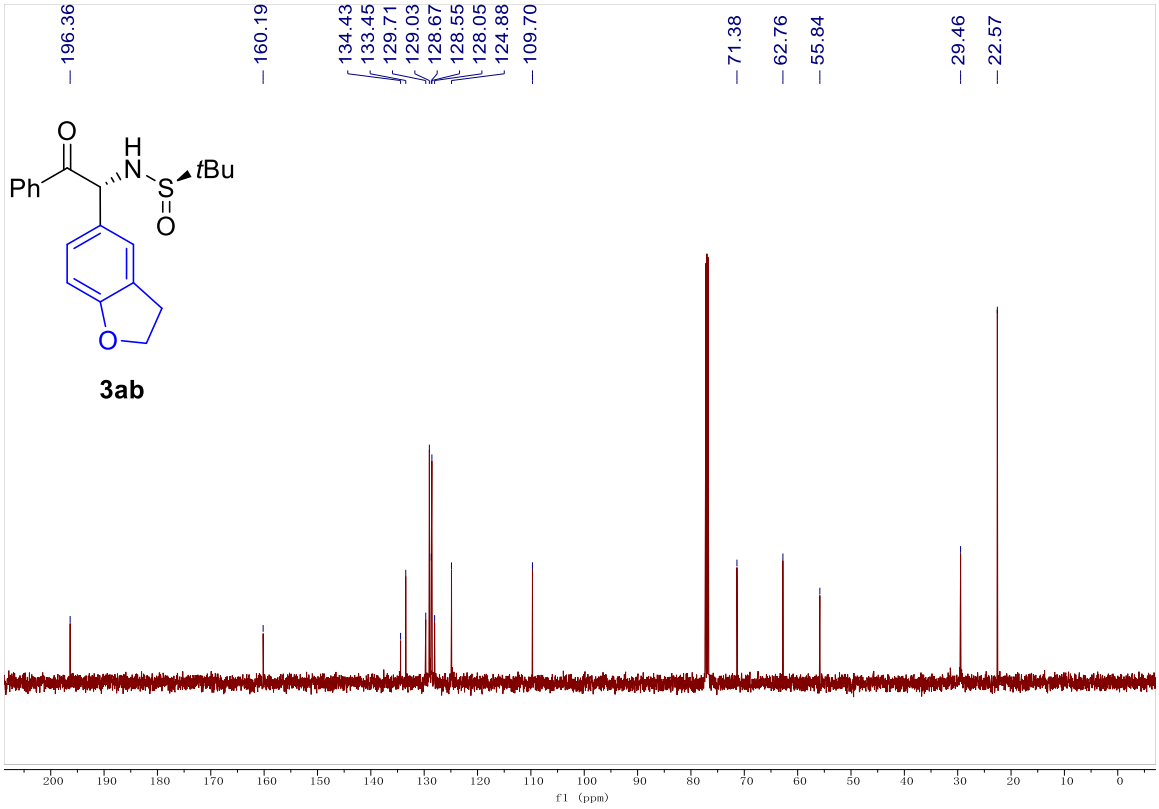
^{13}C NMR spectrum of 3aa



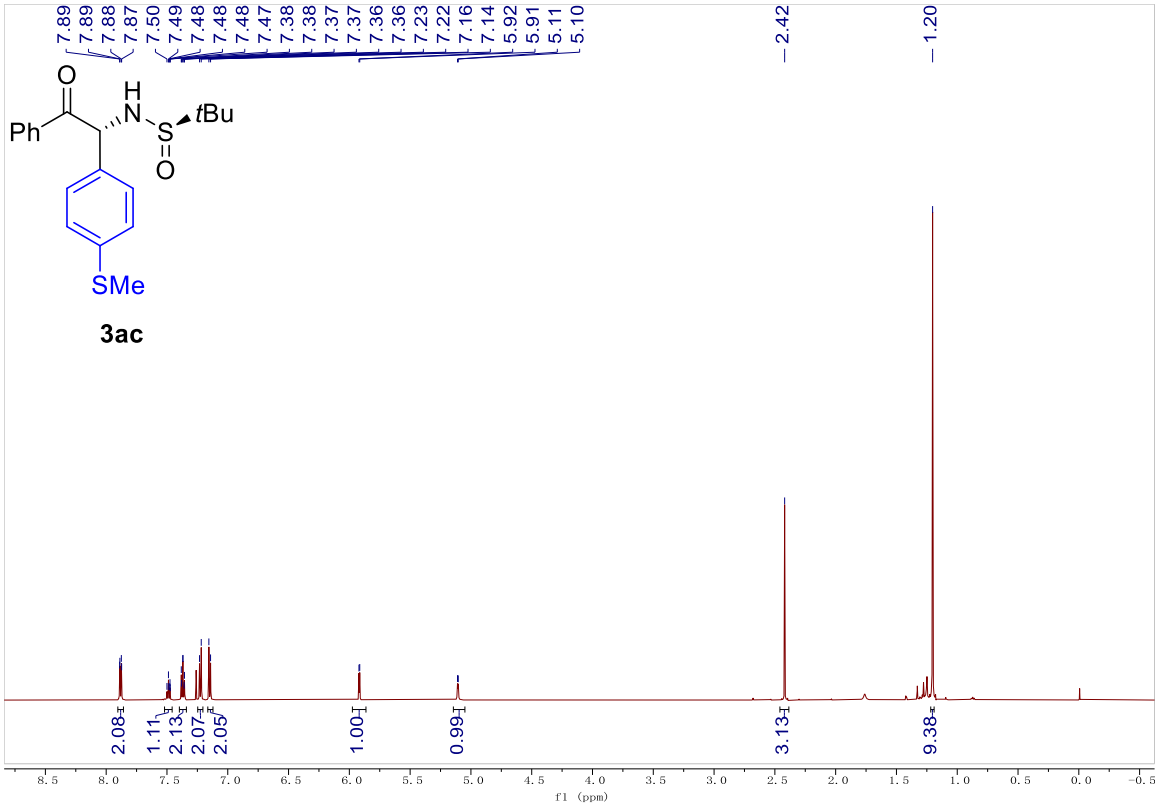
^{1}H NMR spectrum of 3ab



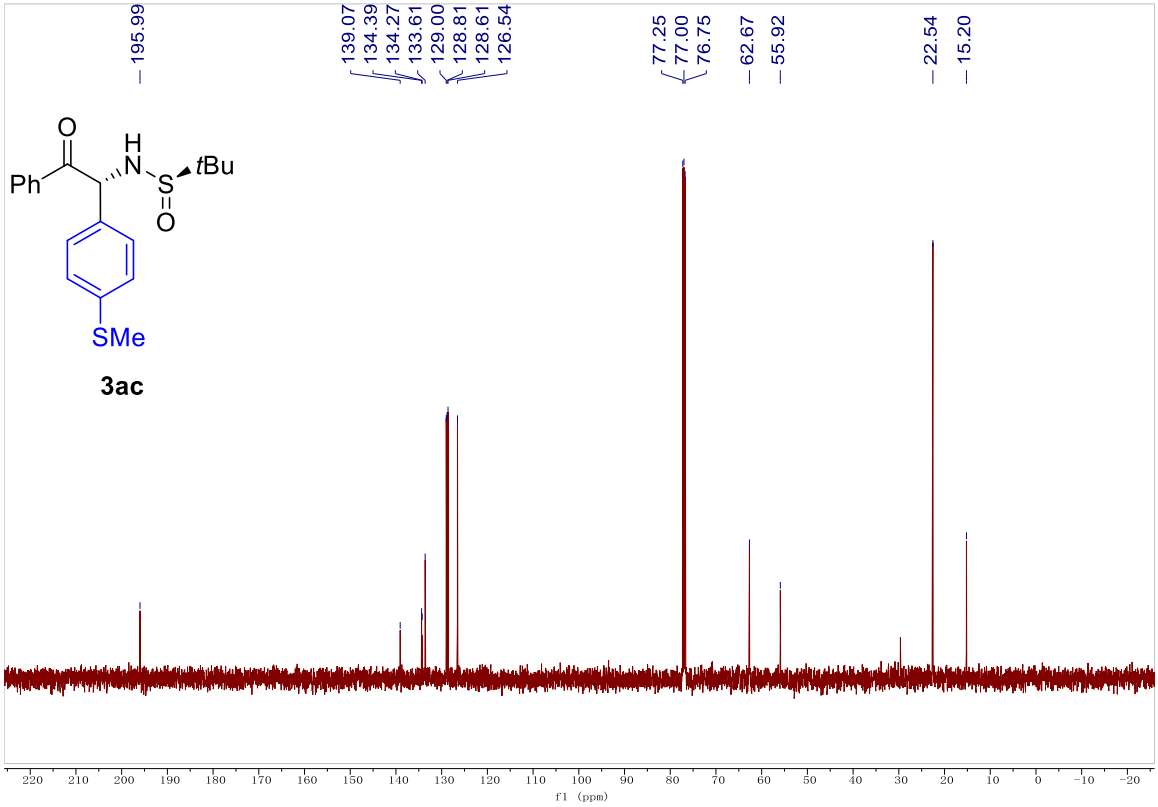
^{13}C NMR spectrum of 3ab



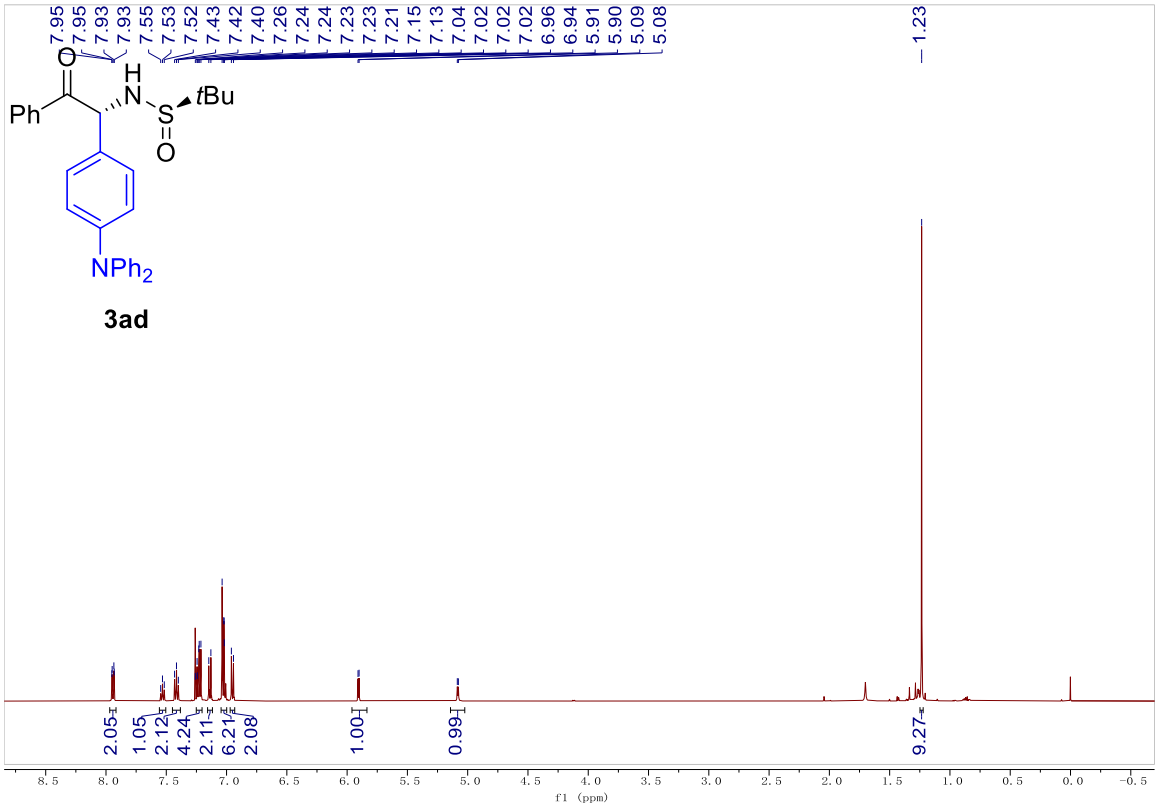
^{1}H NMR spectrum of 3ac



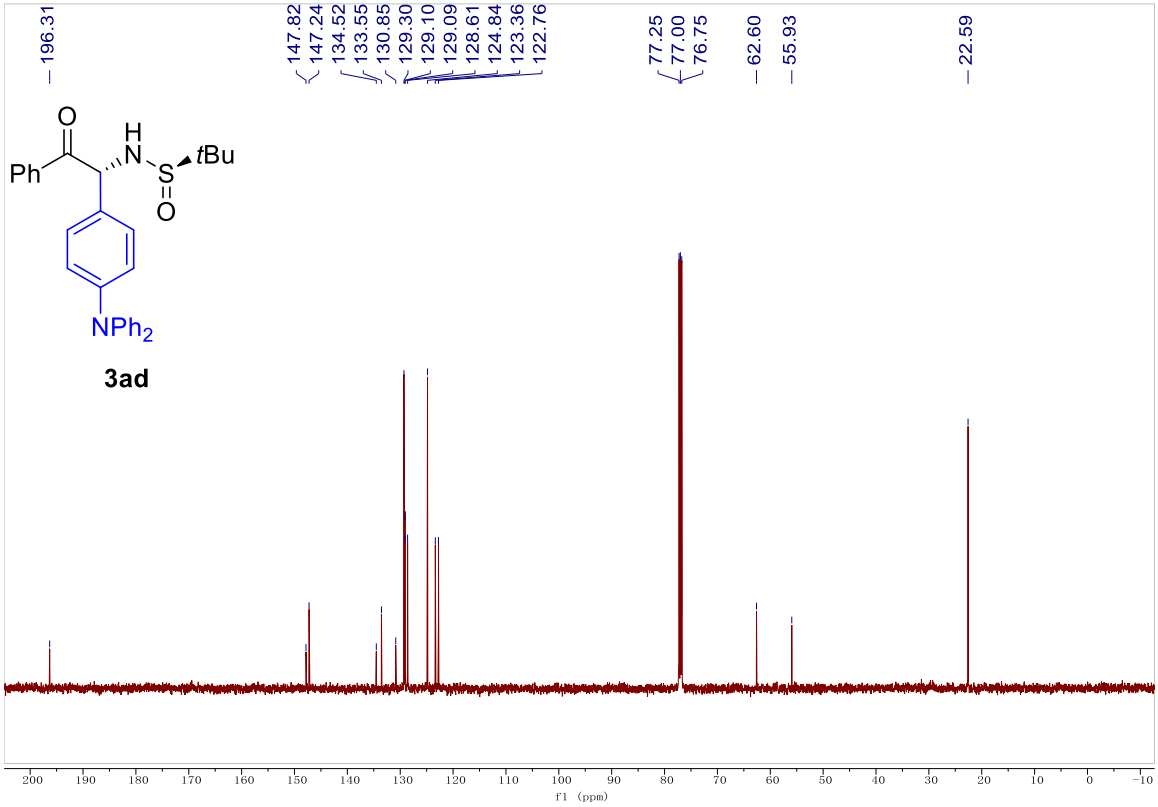
^{13}C NMR spectrum of 3ac



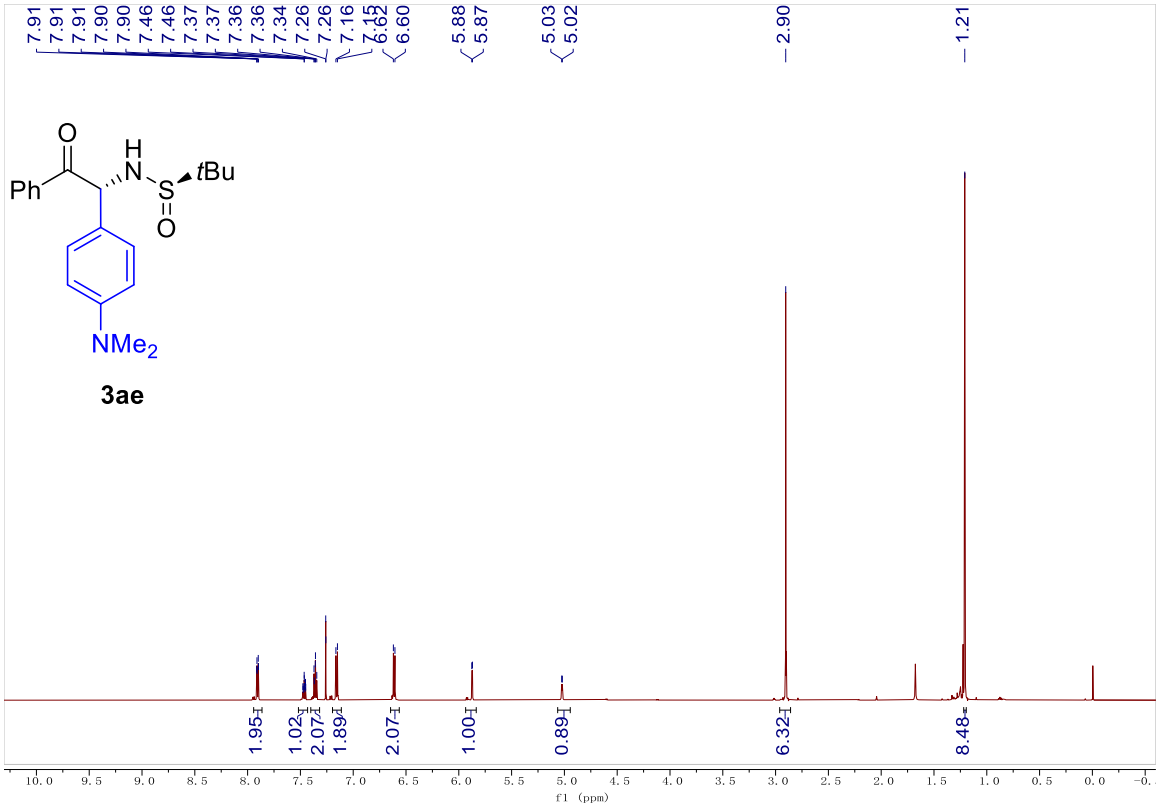
^{1}H NMR spectrum of 3ad



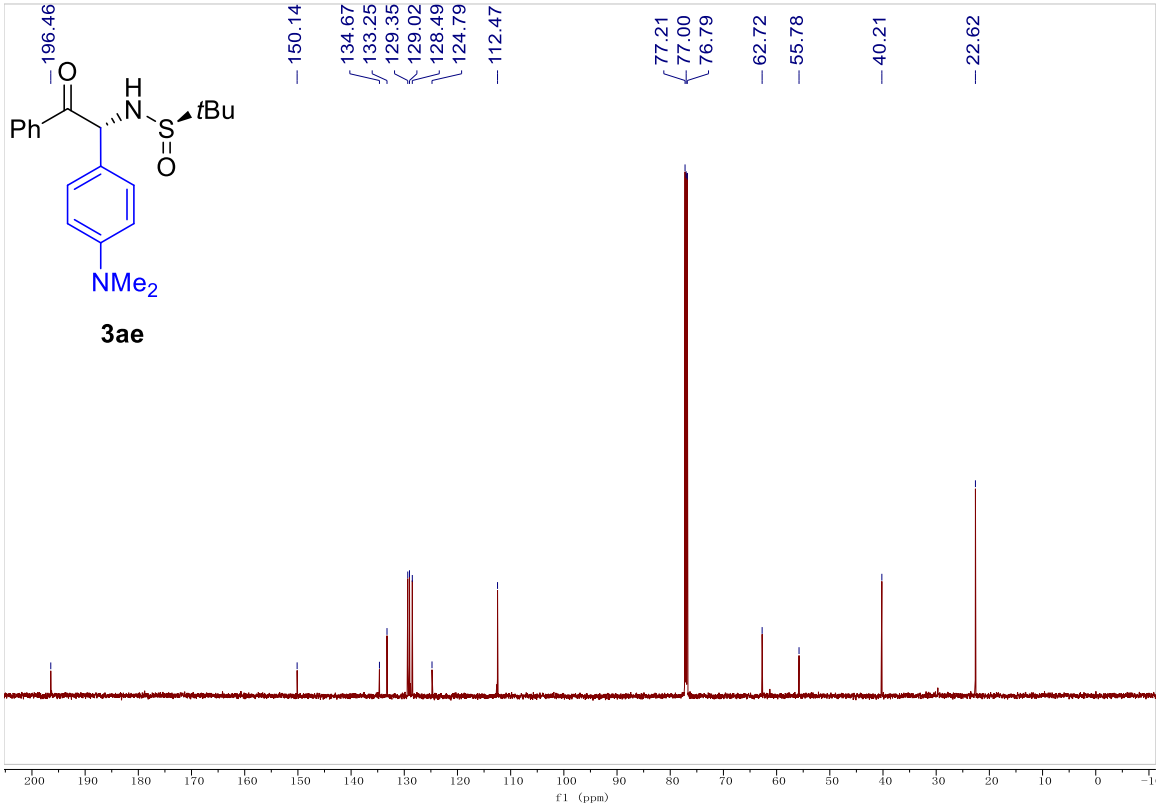
^{13}C NMR spectrum of 3ad



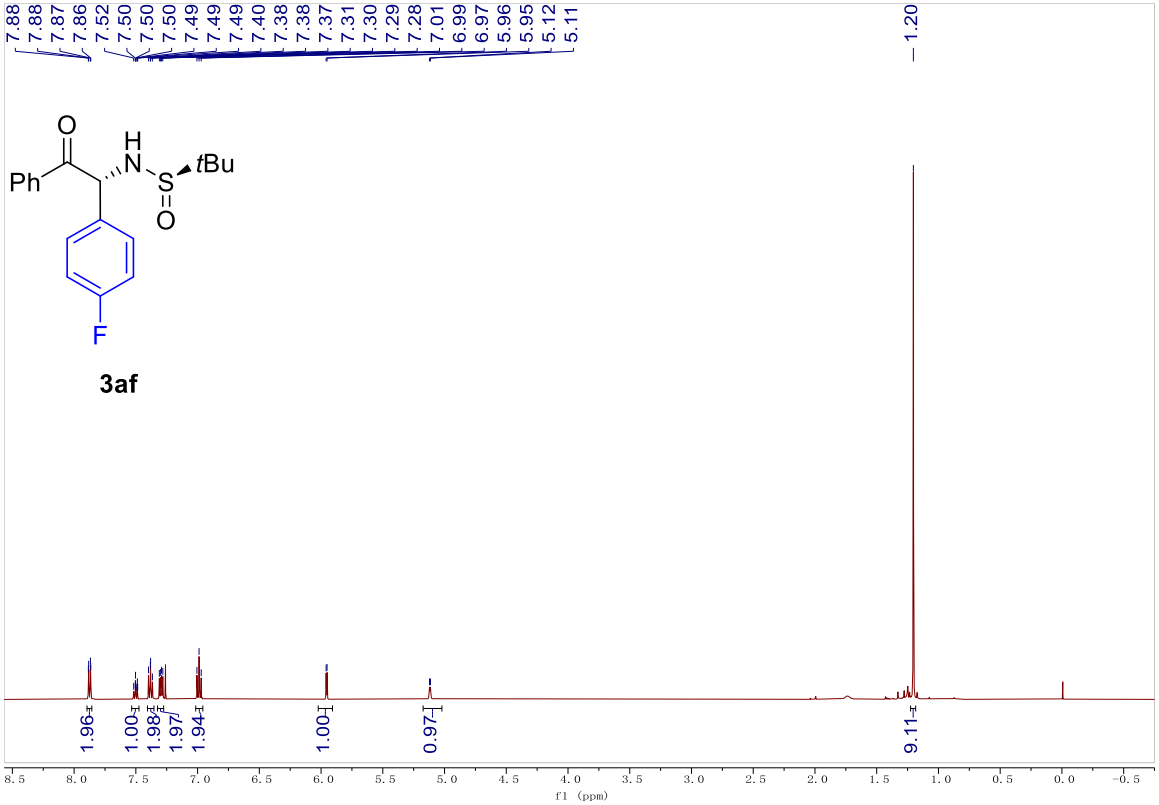
^{1}H NMR spectrum of 3ae



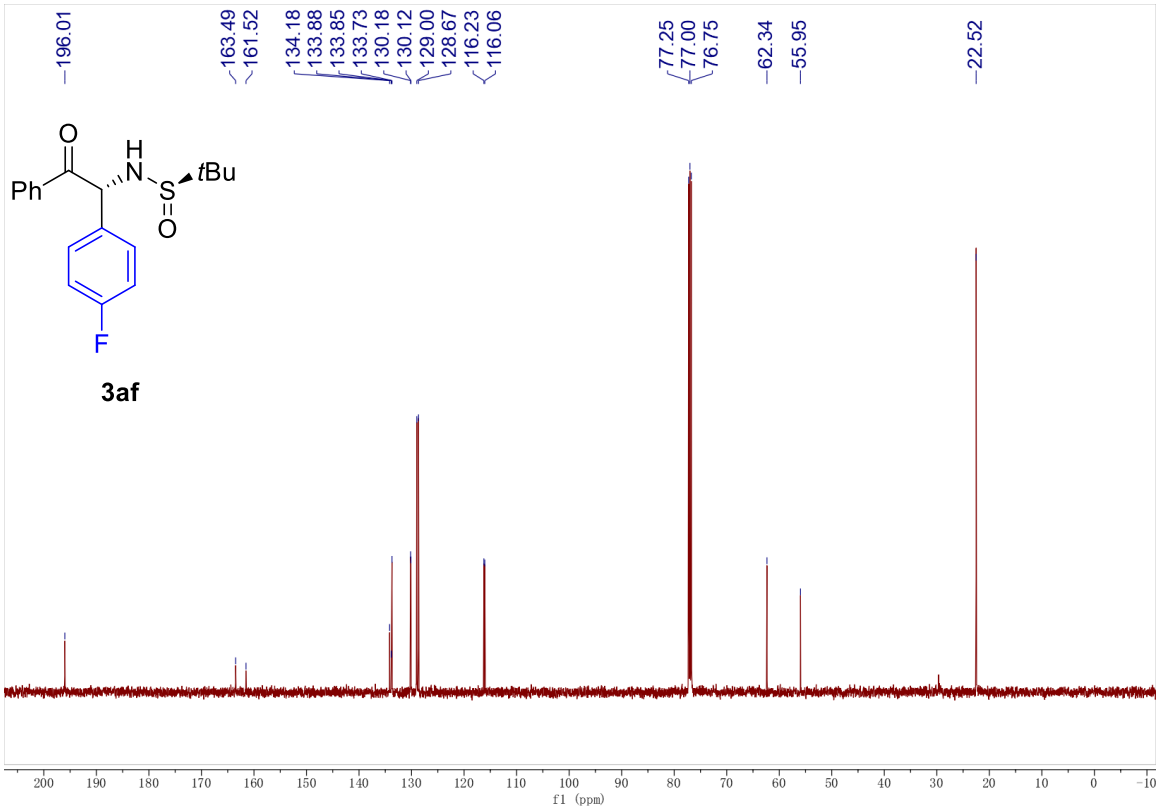
^{13}C NMR spectrum of 3ae



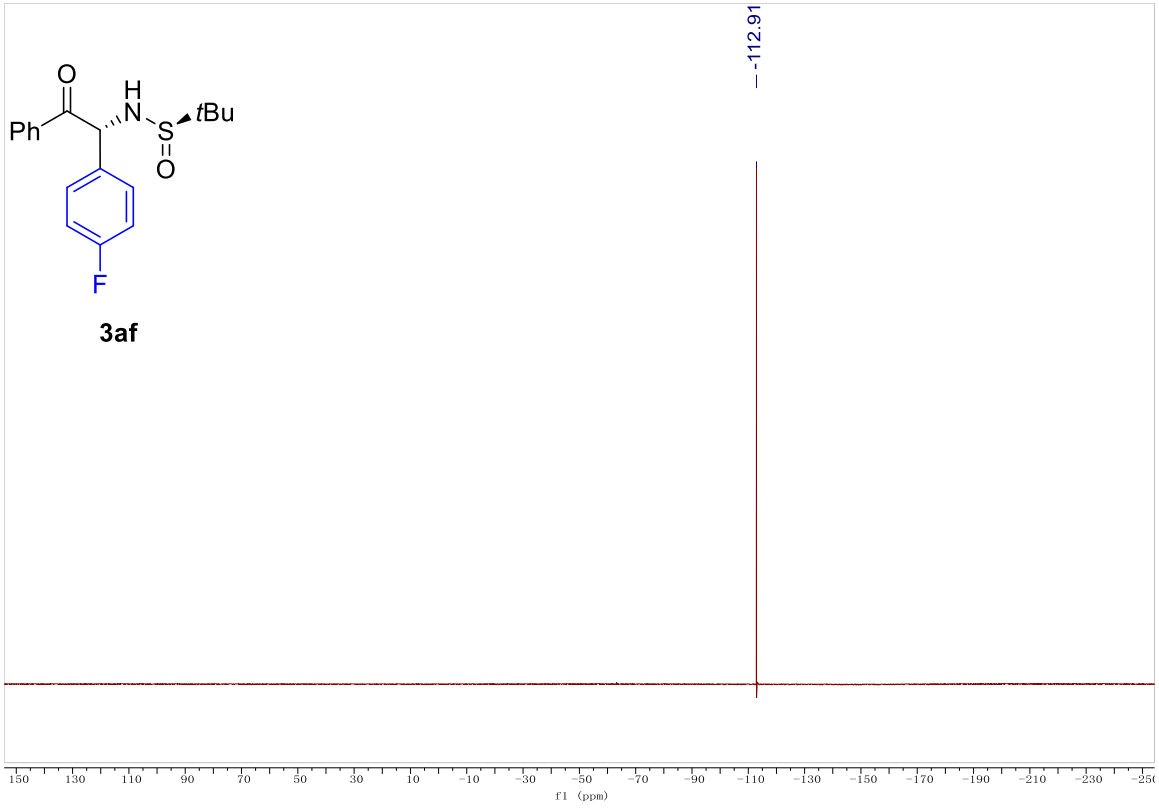
^{1}H NMR spectrum of 3af



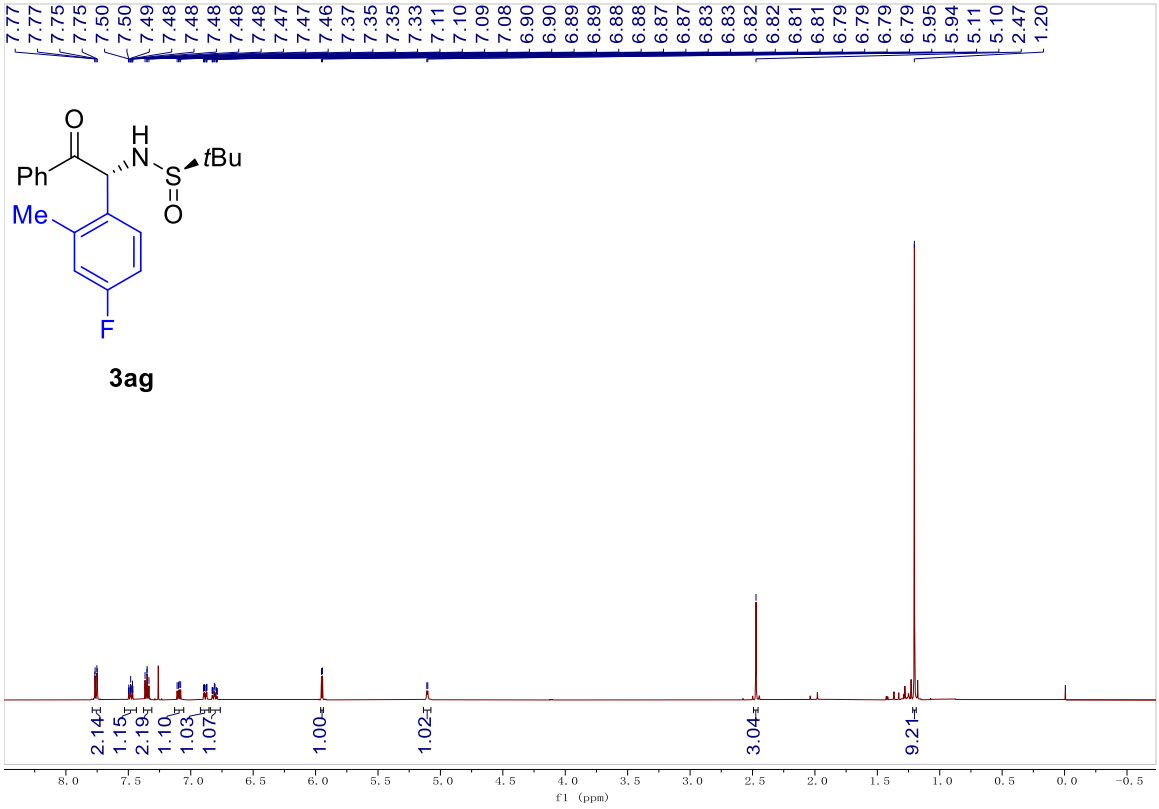
^{13}C NMR spectrum of 3af



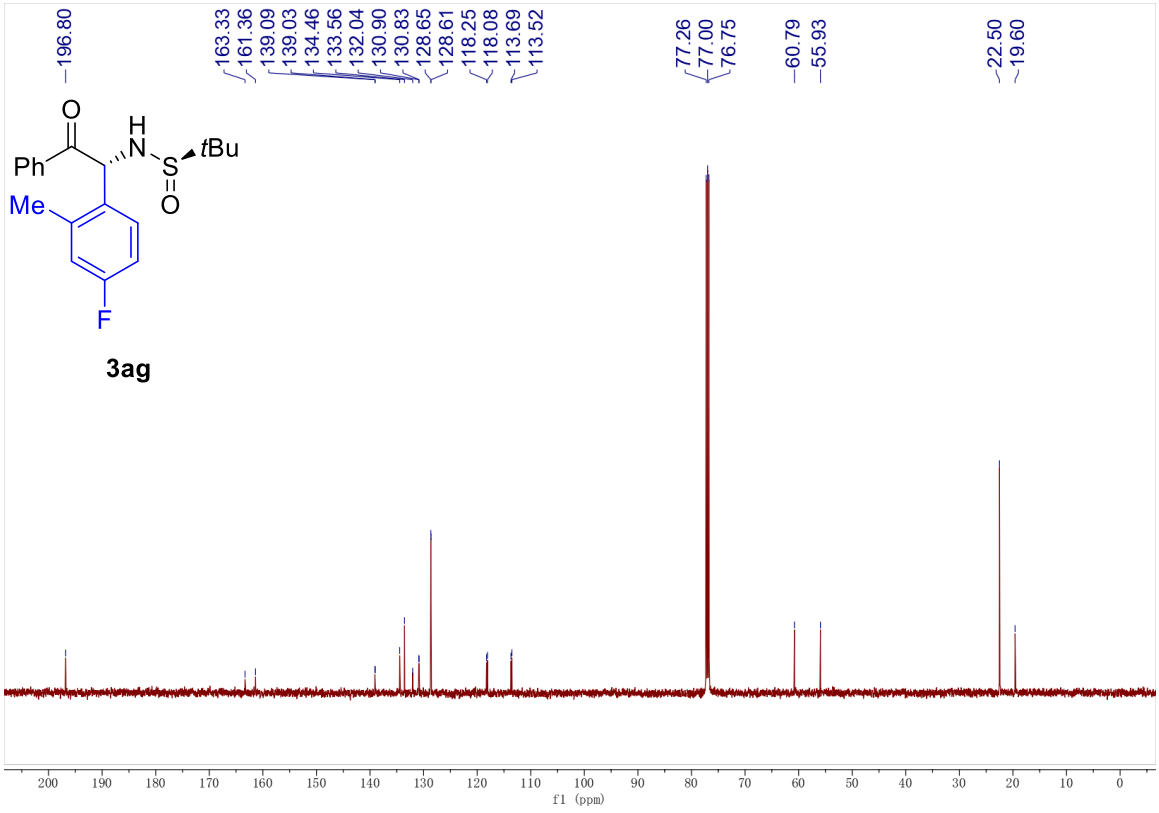
^{19}F NMR spectrum of 3af



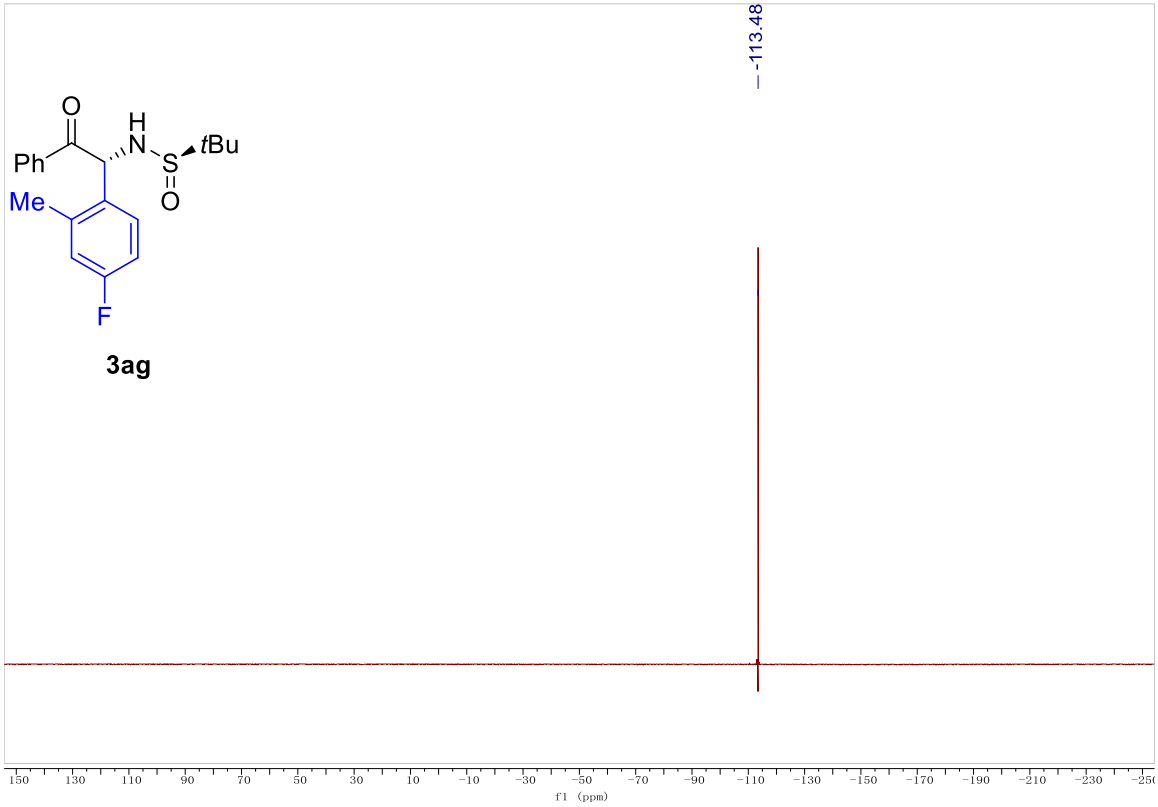
^{1}H NMR spectrum of 3ag



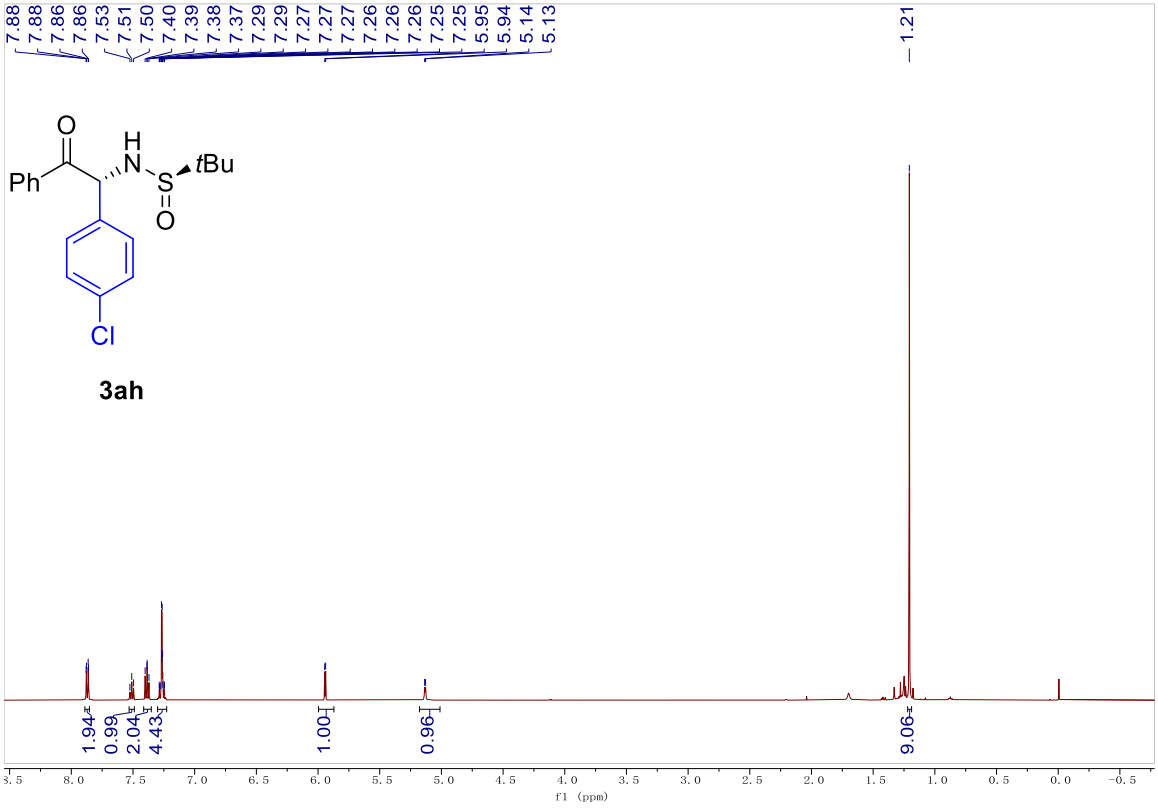
^{13}C NMR spectrum of 3ag



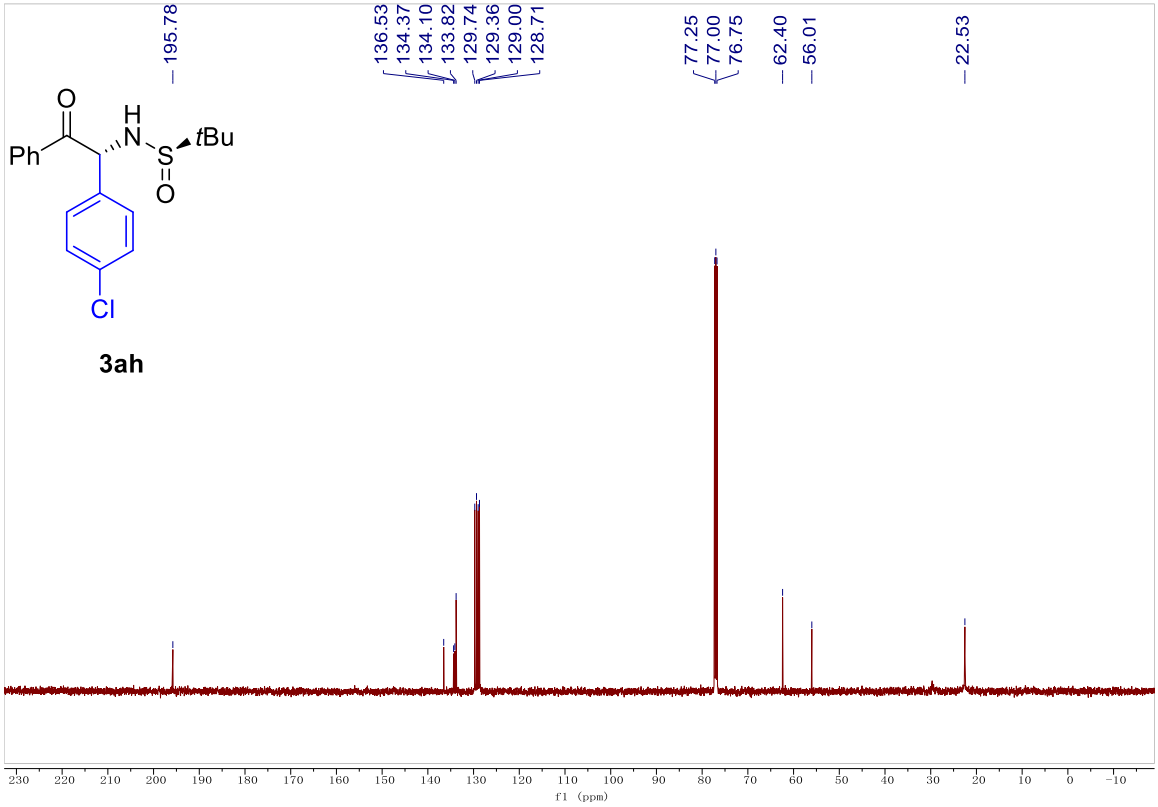
^{19}F NMR spectrum of 3ag



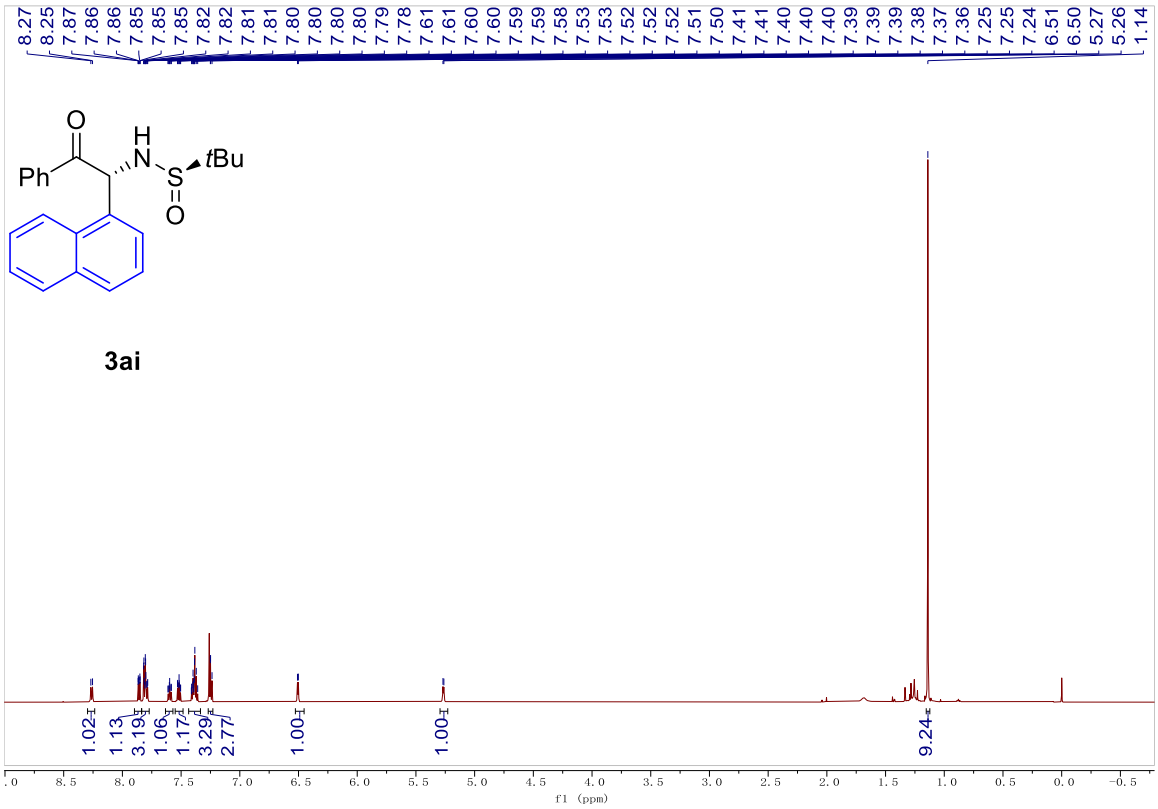
^{1}H NMR spectrum of 3ah



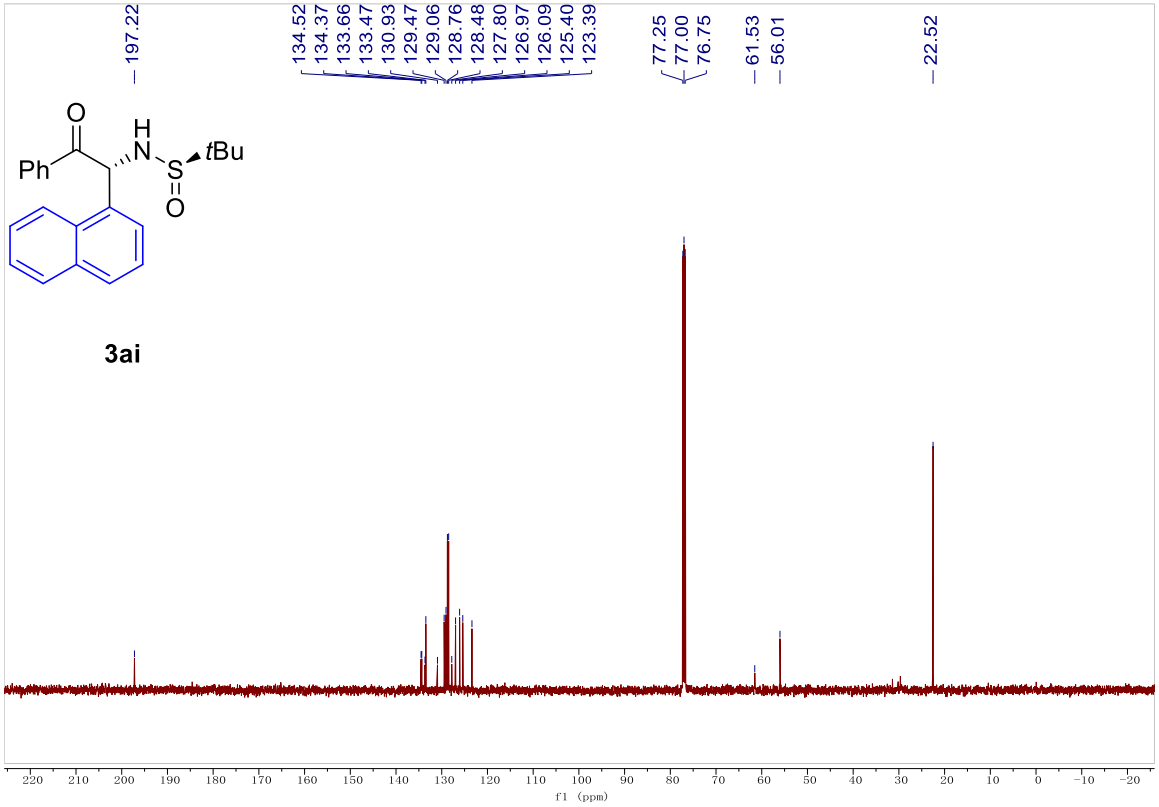
^{13}C NMR spectrum of 3ah



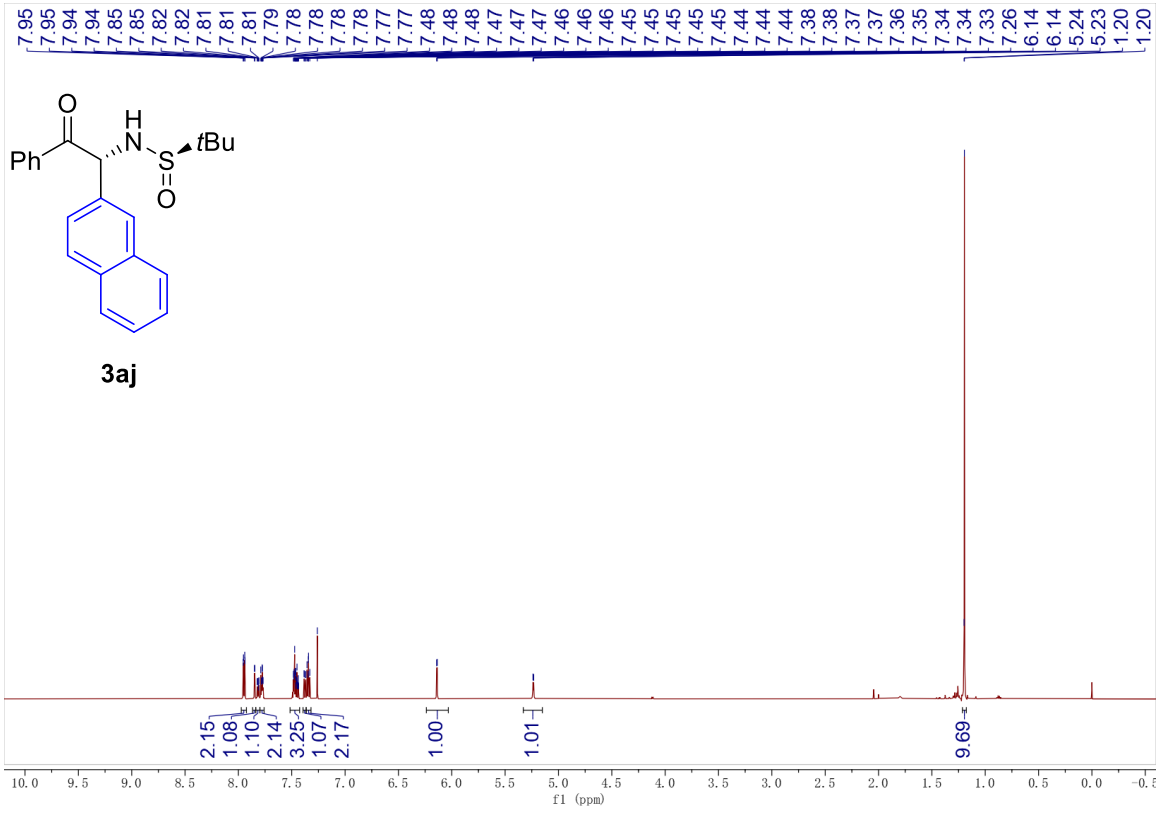
^{1}H NMR spectrum of 3ai



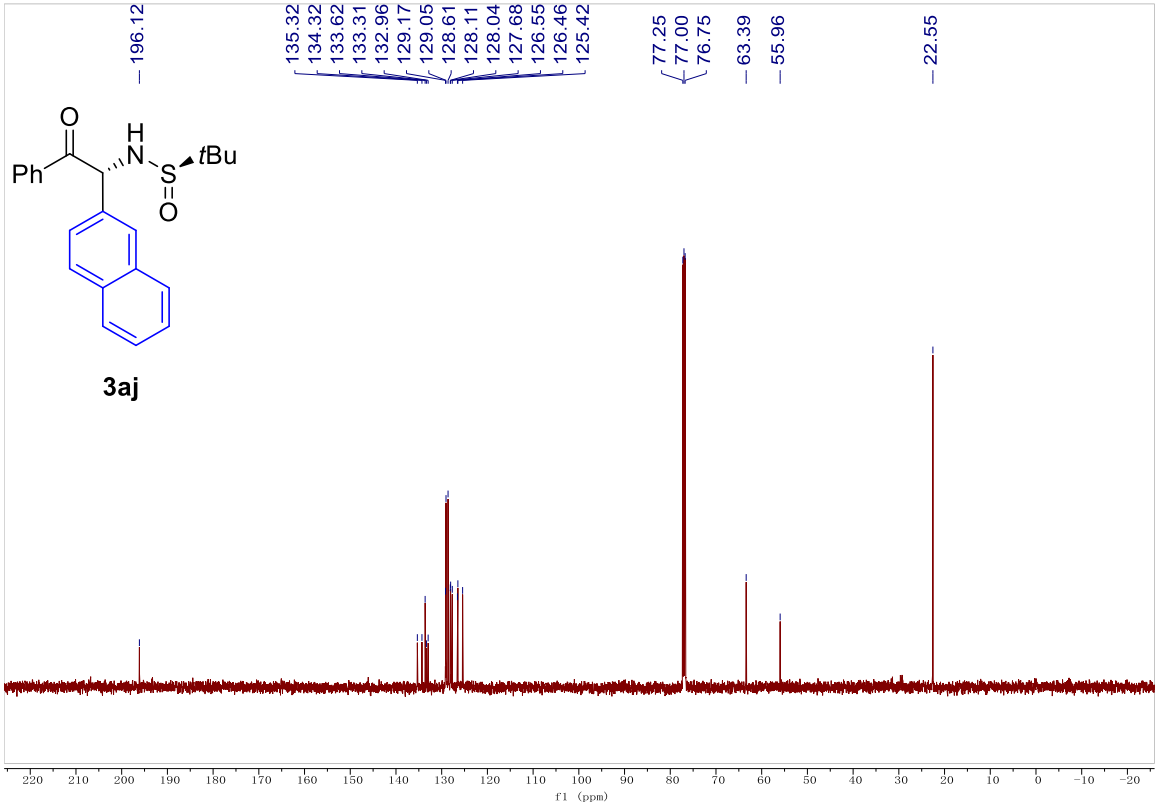
^{13}C NMR spectrum of 3ai



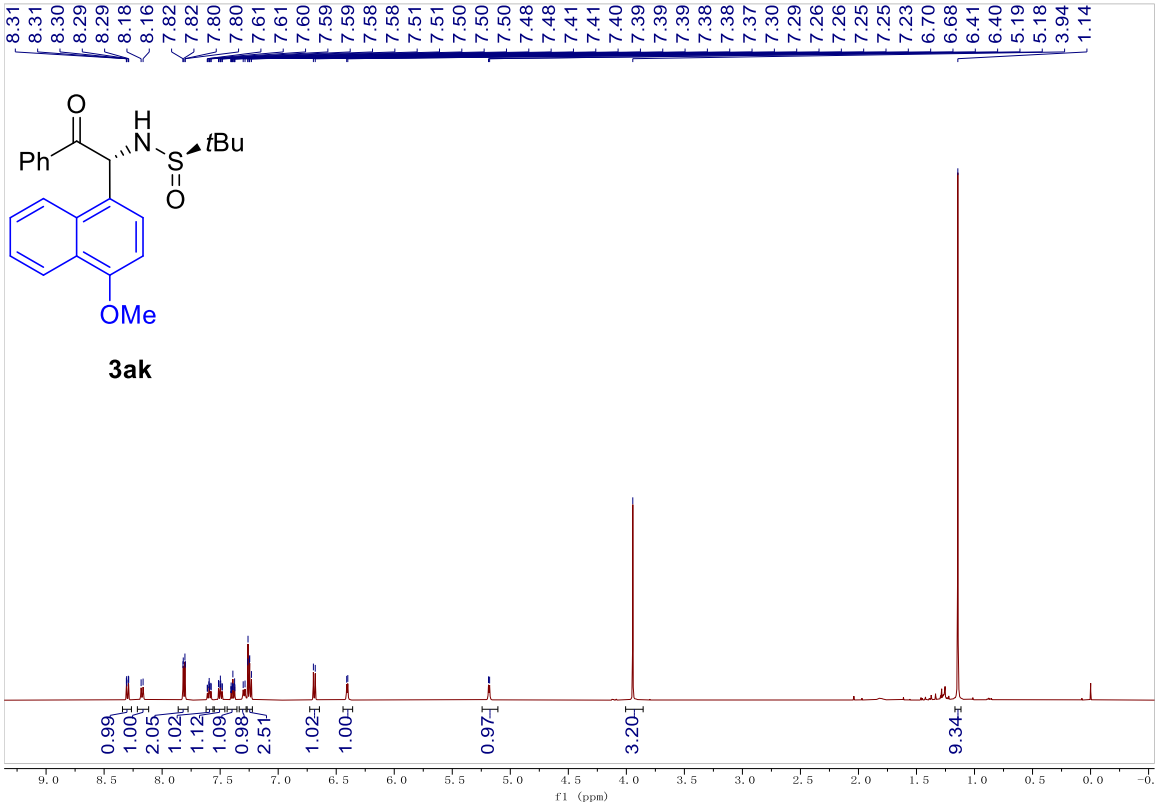
^{1}H NMR spectrum of 3aj



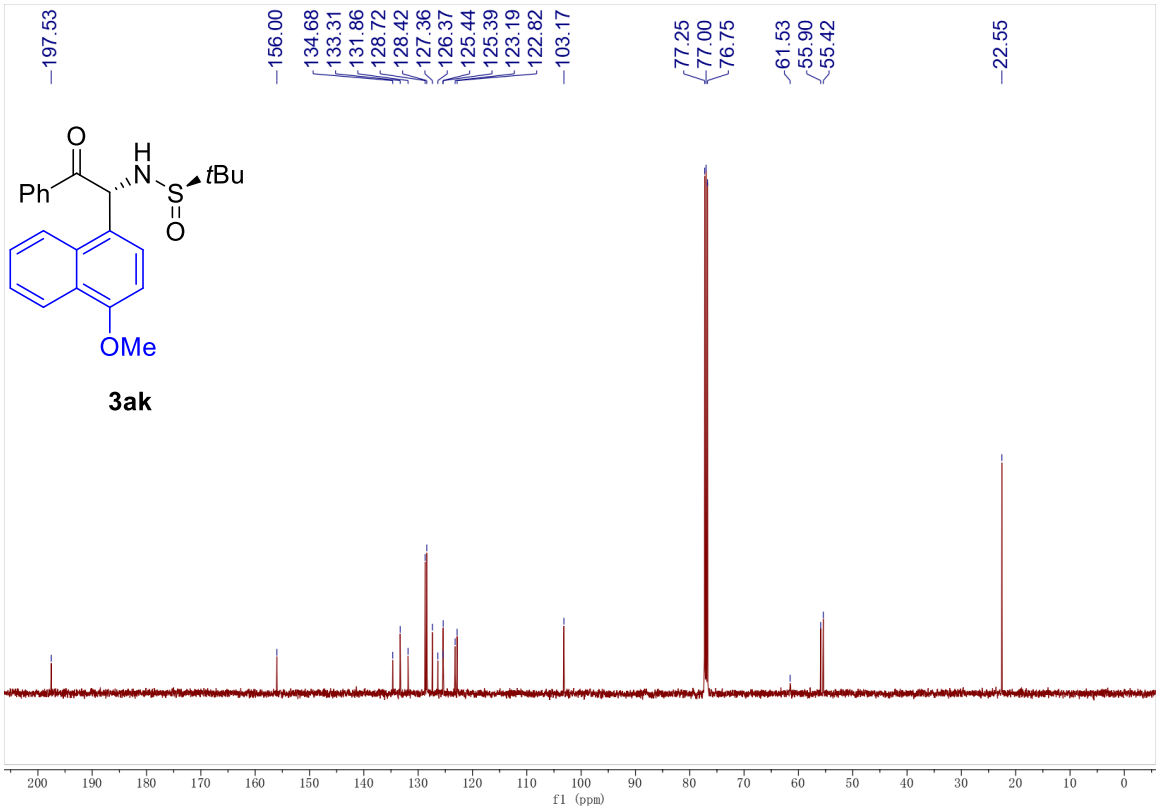
^{13}C NMR spectrum of 3aj



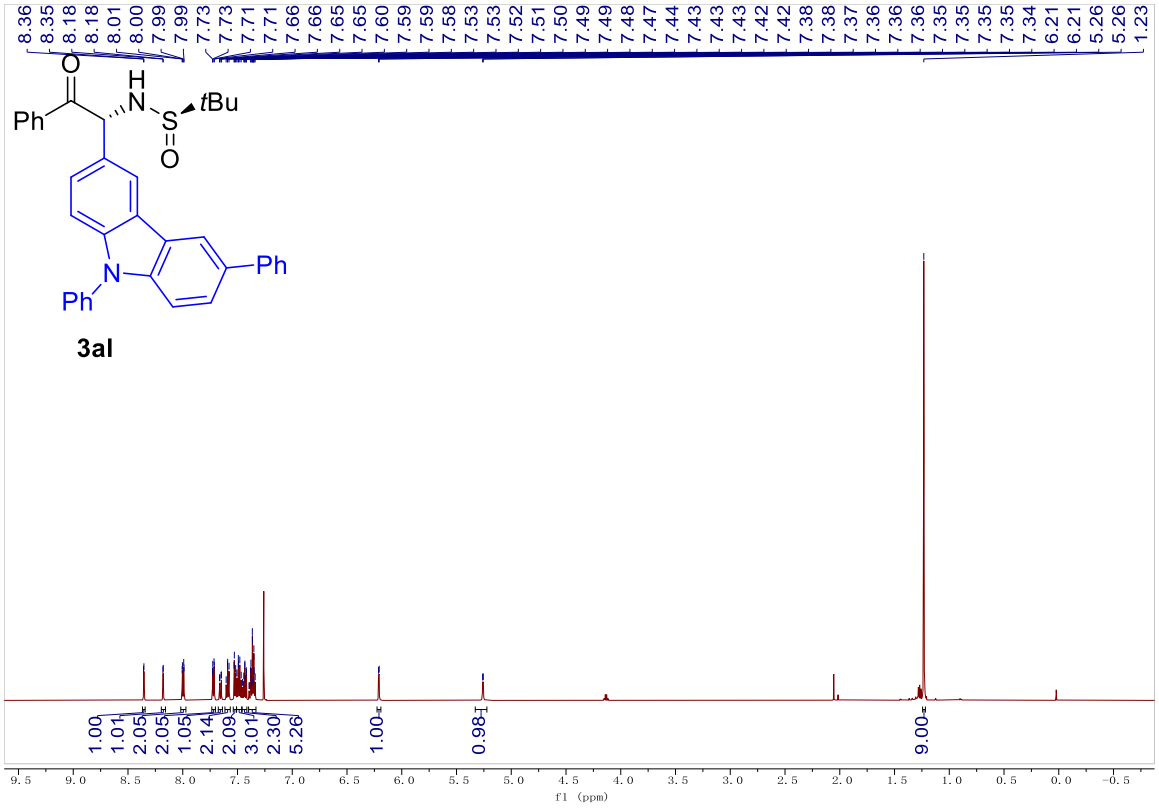
^{1}H NMR spectrum of 3ak



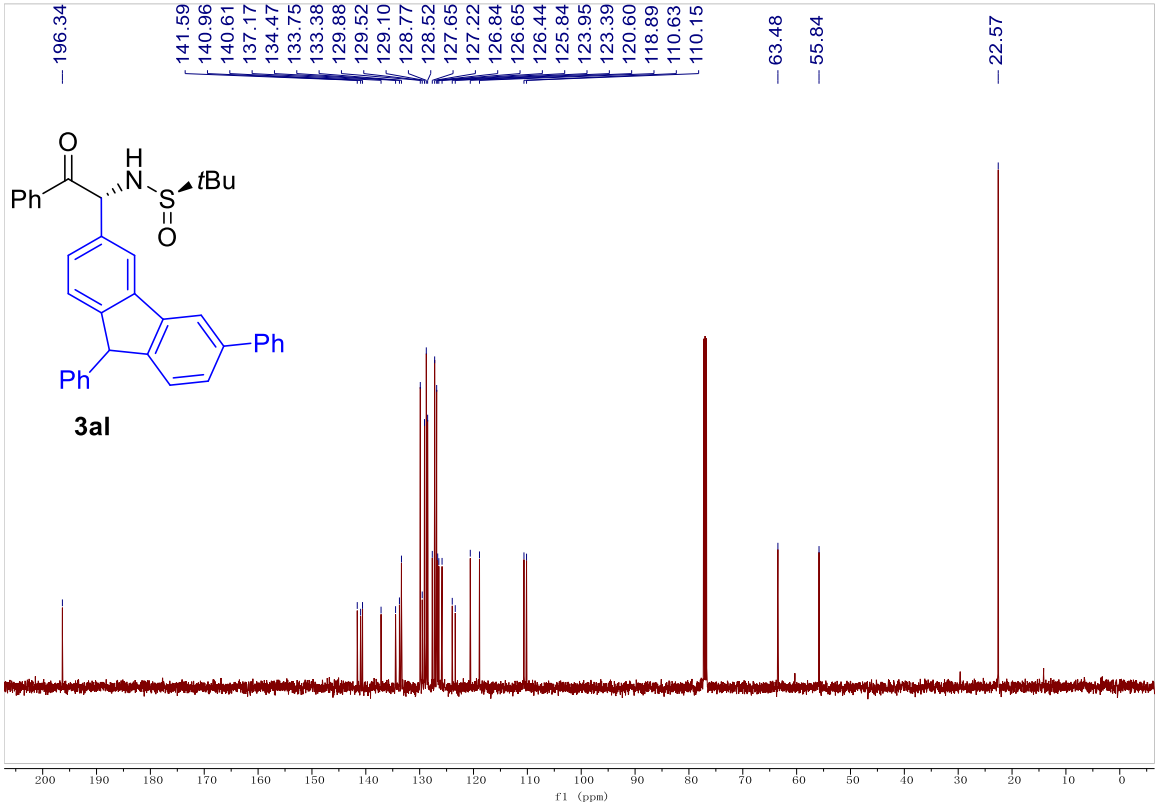
^{13}C NMR spectrum of 3ak



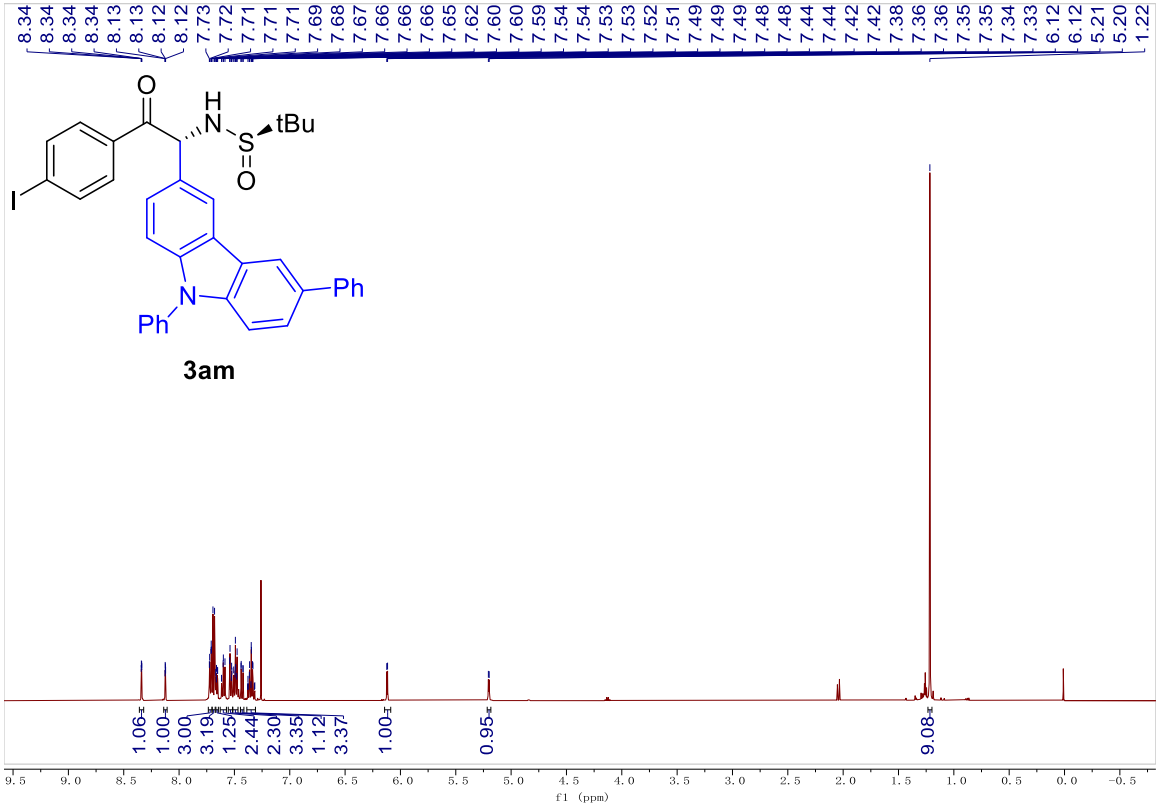
^{1}H NMR spectrum of 3al



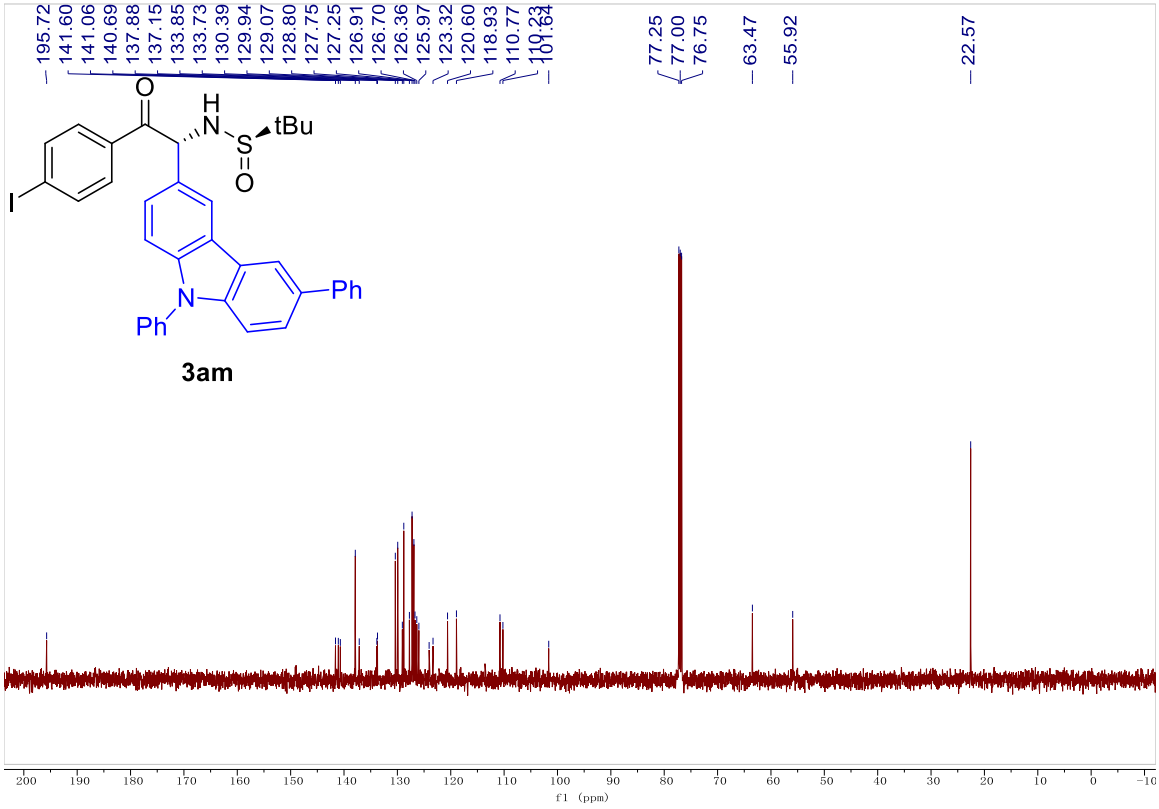
^{13}C NMR spectrum of 3al



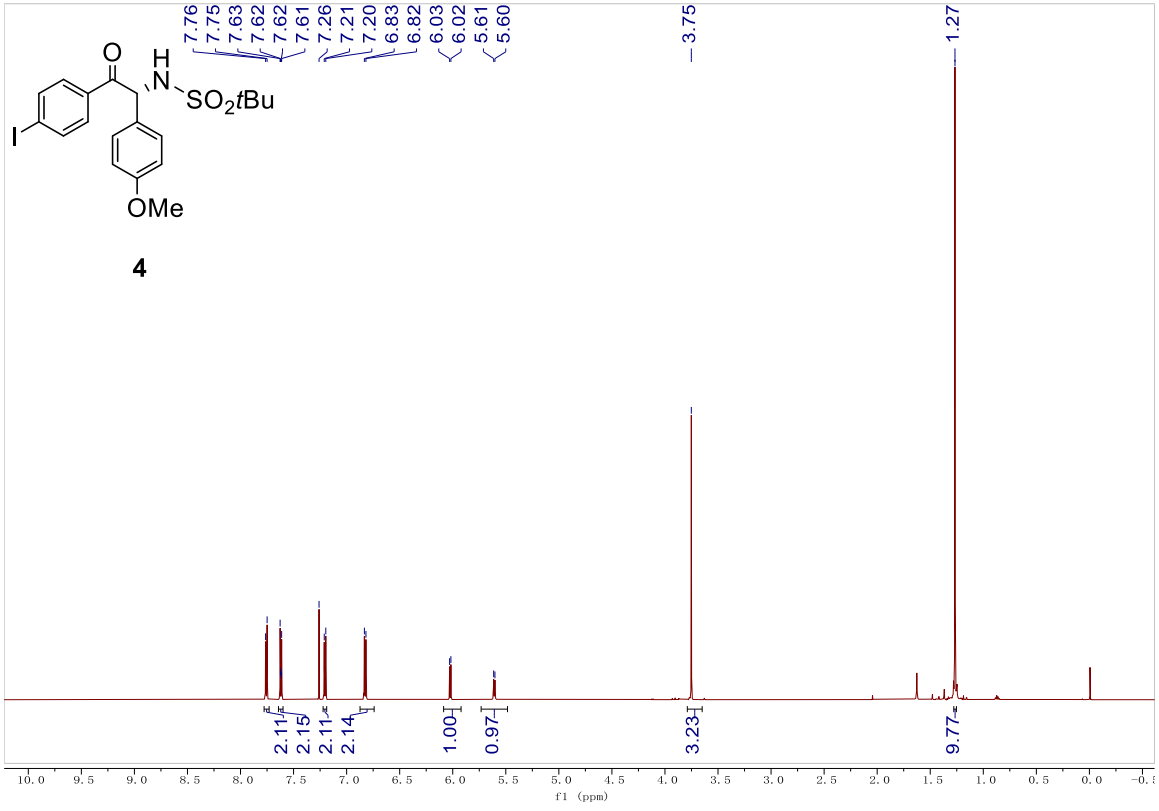
^{1}H NMR spectrum of 3am



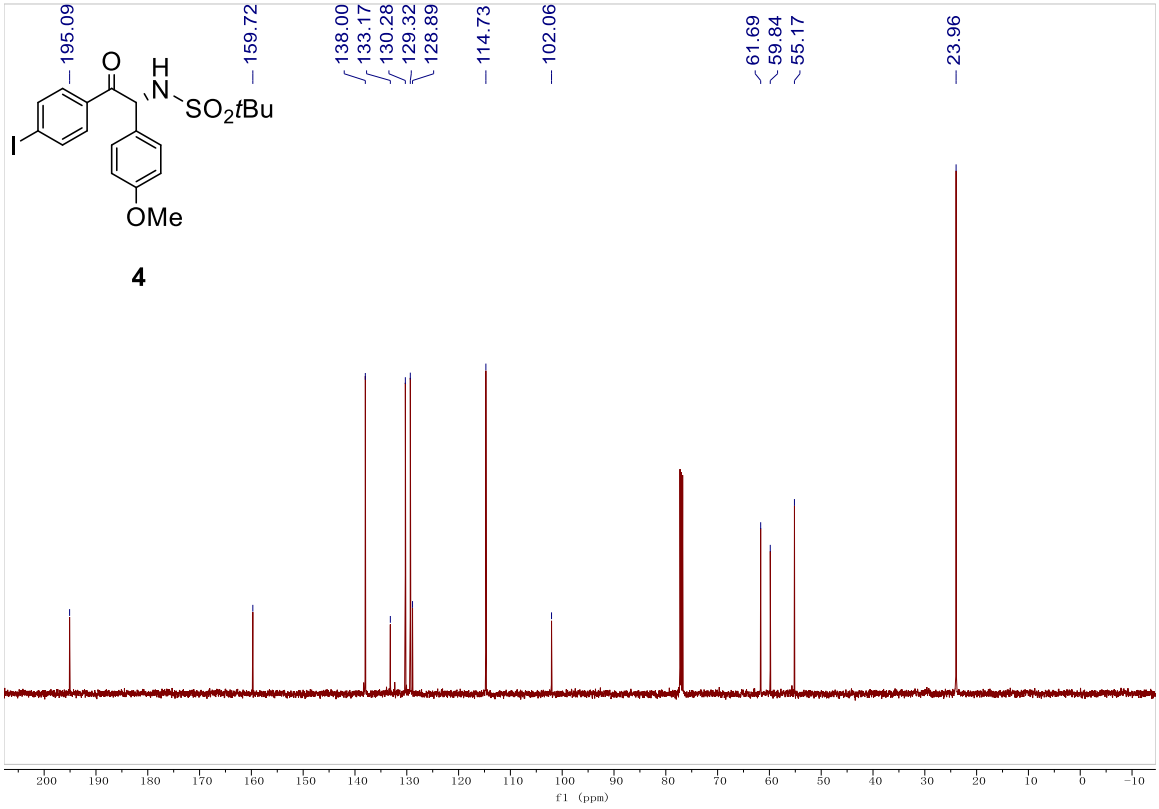
^{13}C NMR spectrum of 3am



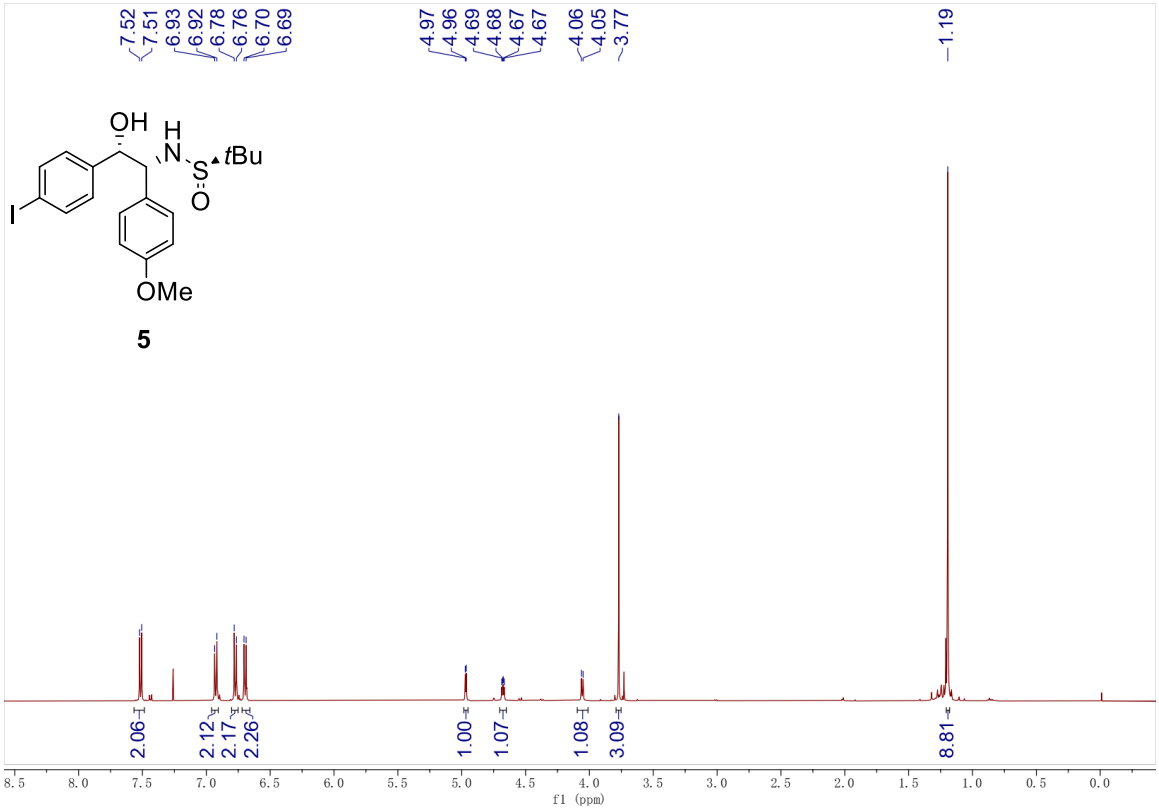
^{1}H NMR spectrum of 4



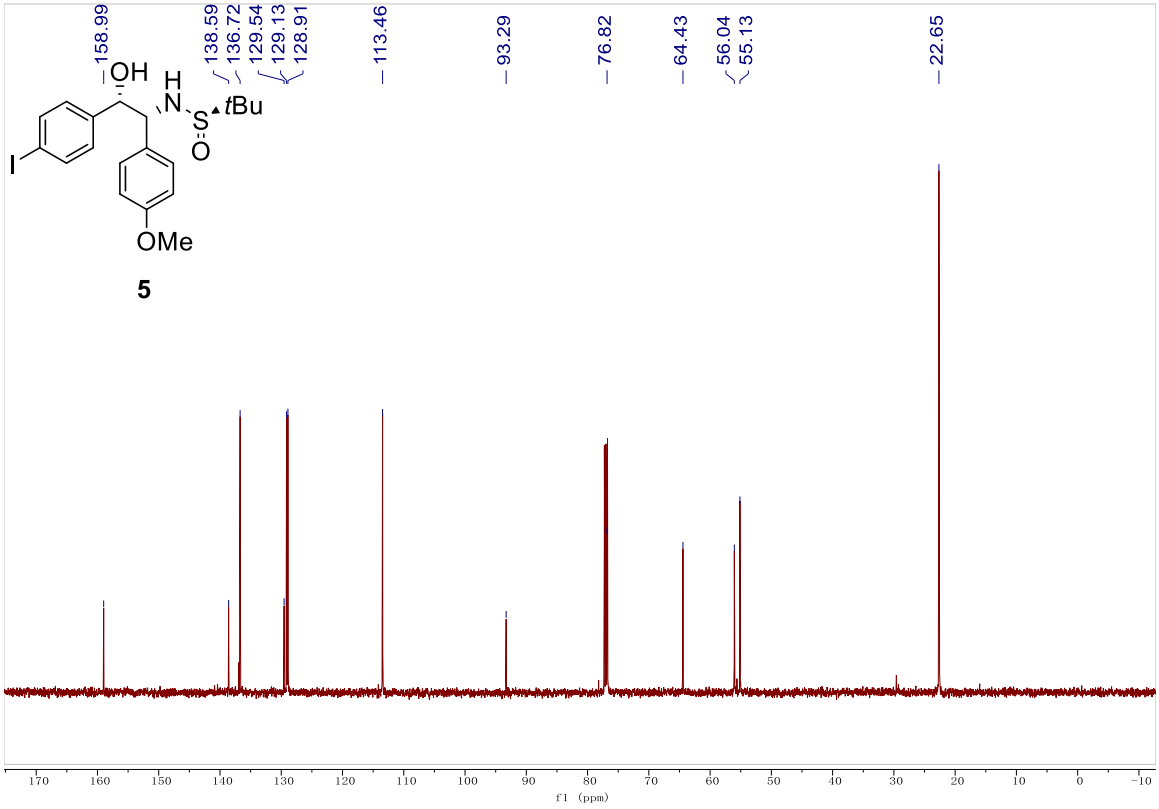
^{13}C NMR spectrum of 4



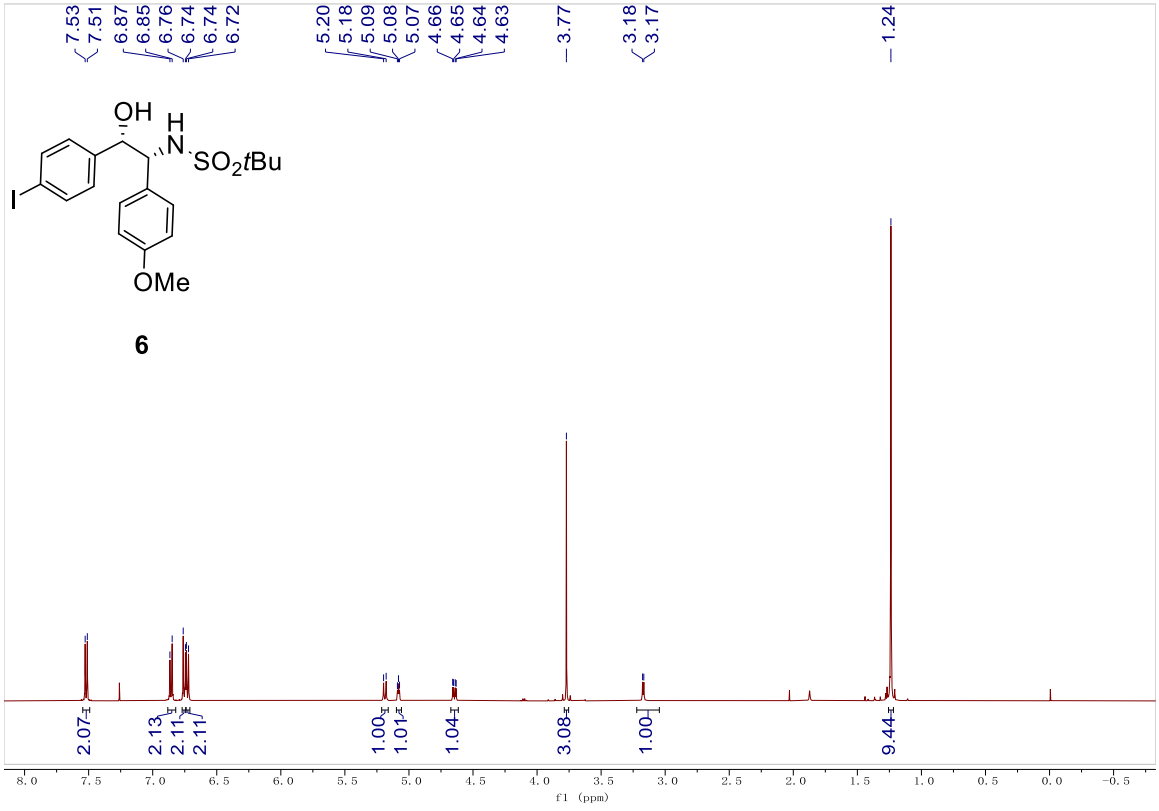
^{1}H NMR spectrum of 5



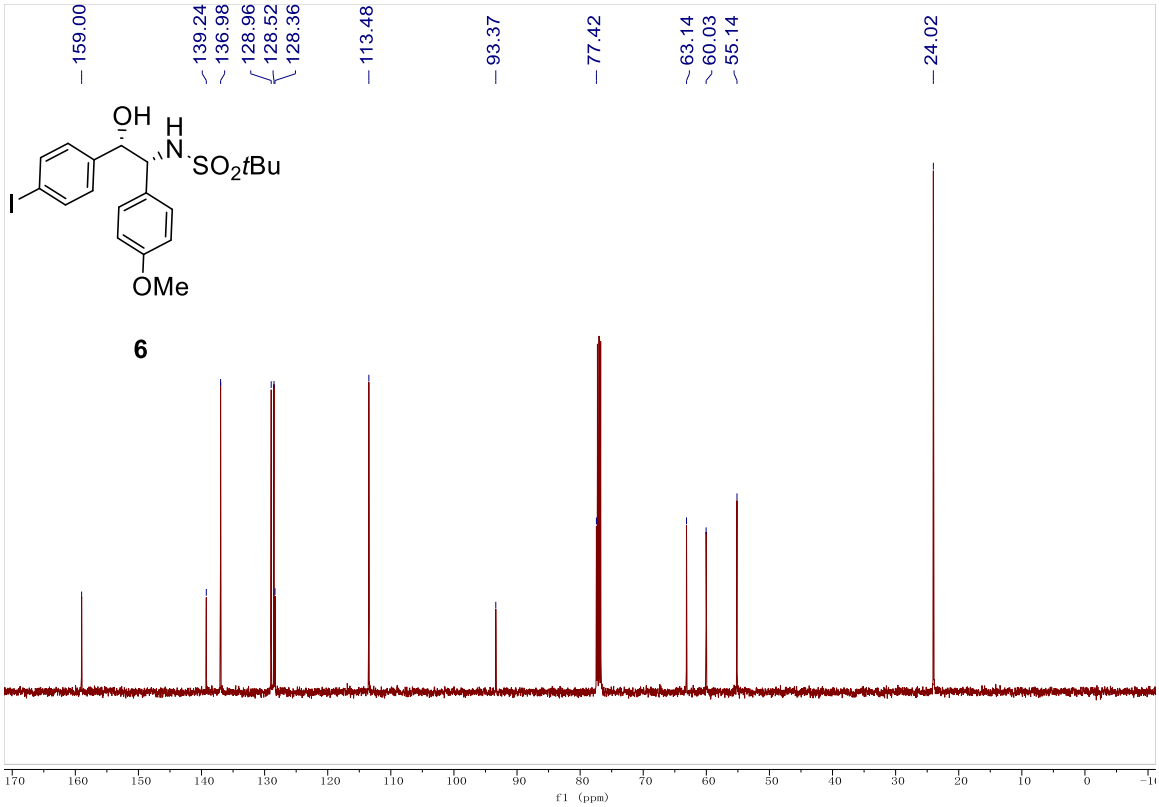
^{13}C NMR spectrum of 5



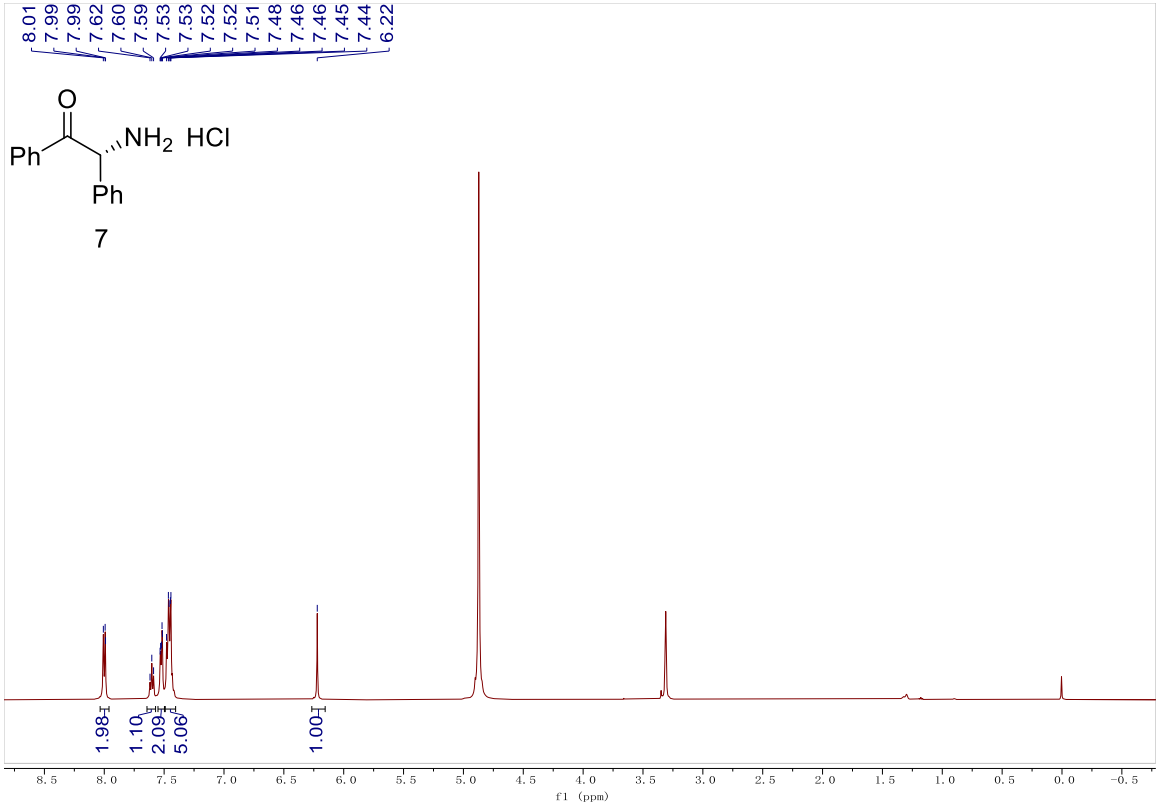
^{1}H NMR spectrum of 6



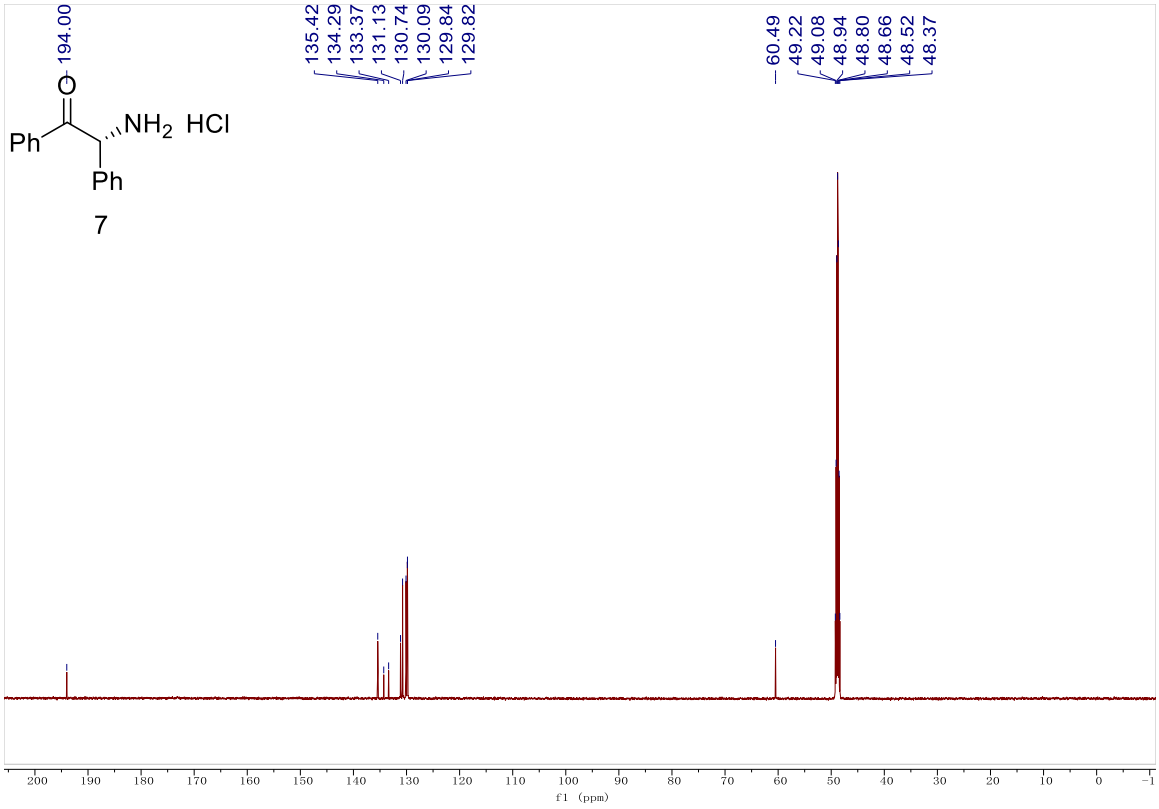
^{13}C NMR spectrum of 6



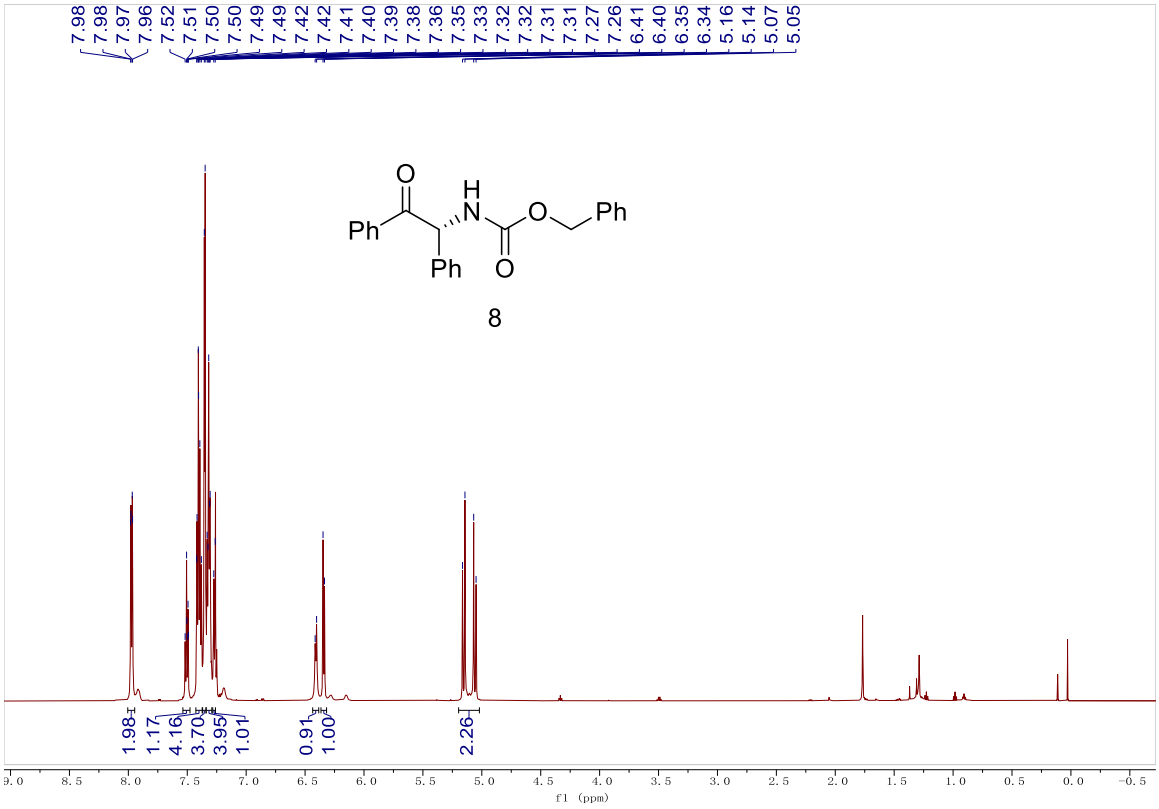
^{1}H NMR spectrum of 7



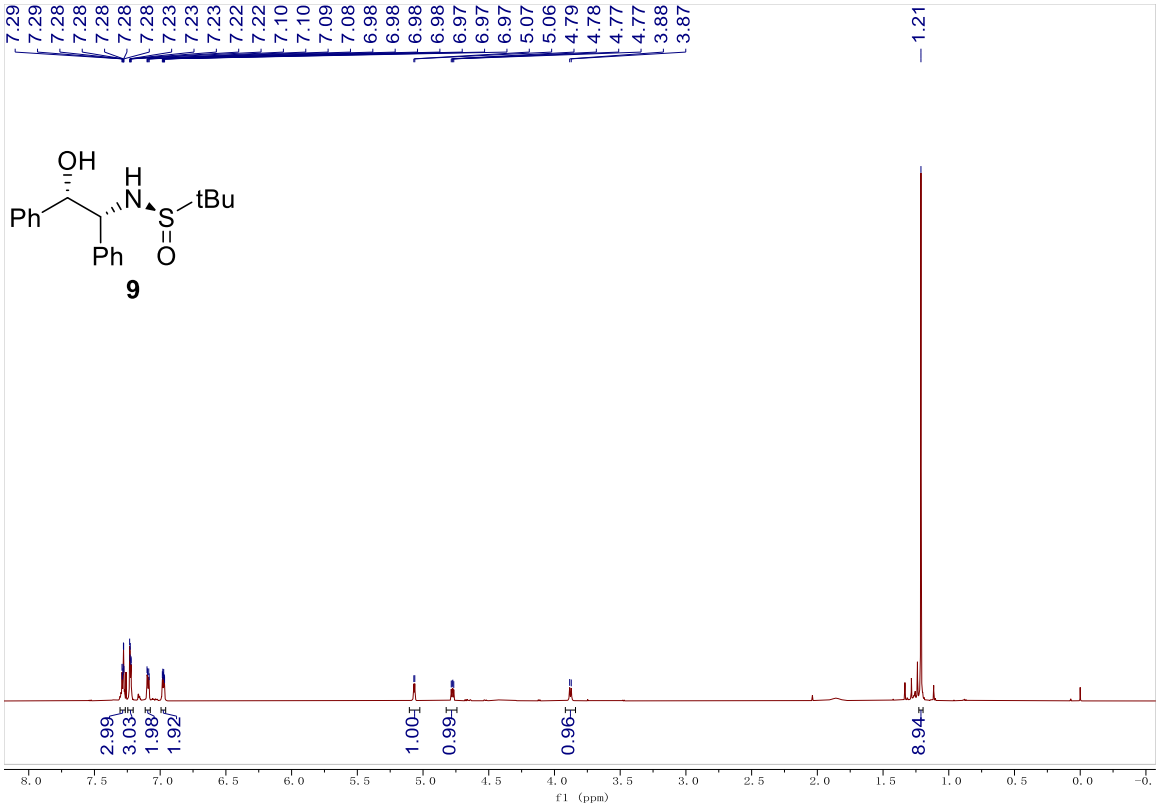
^{13}C NMR spectrum of 7



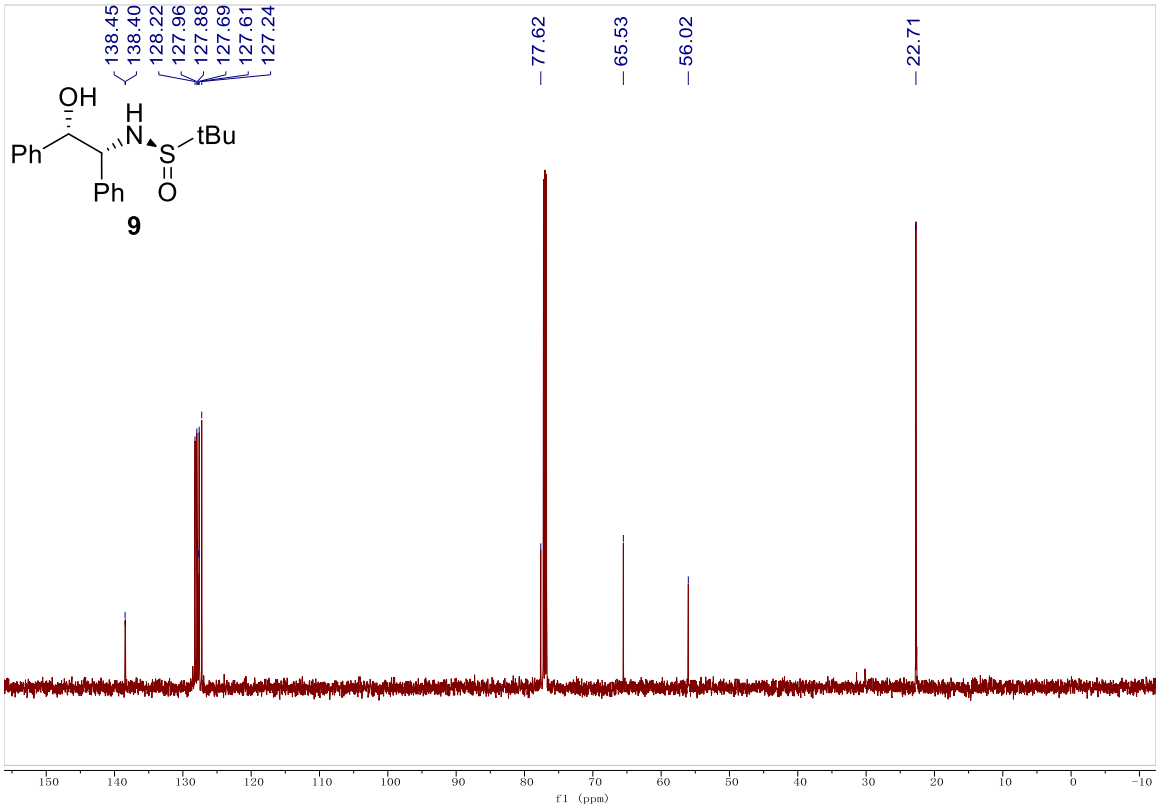
^{1}H NMR spectrum of 8



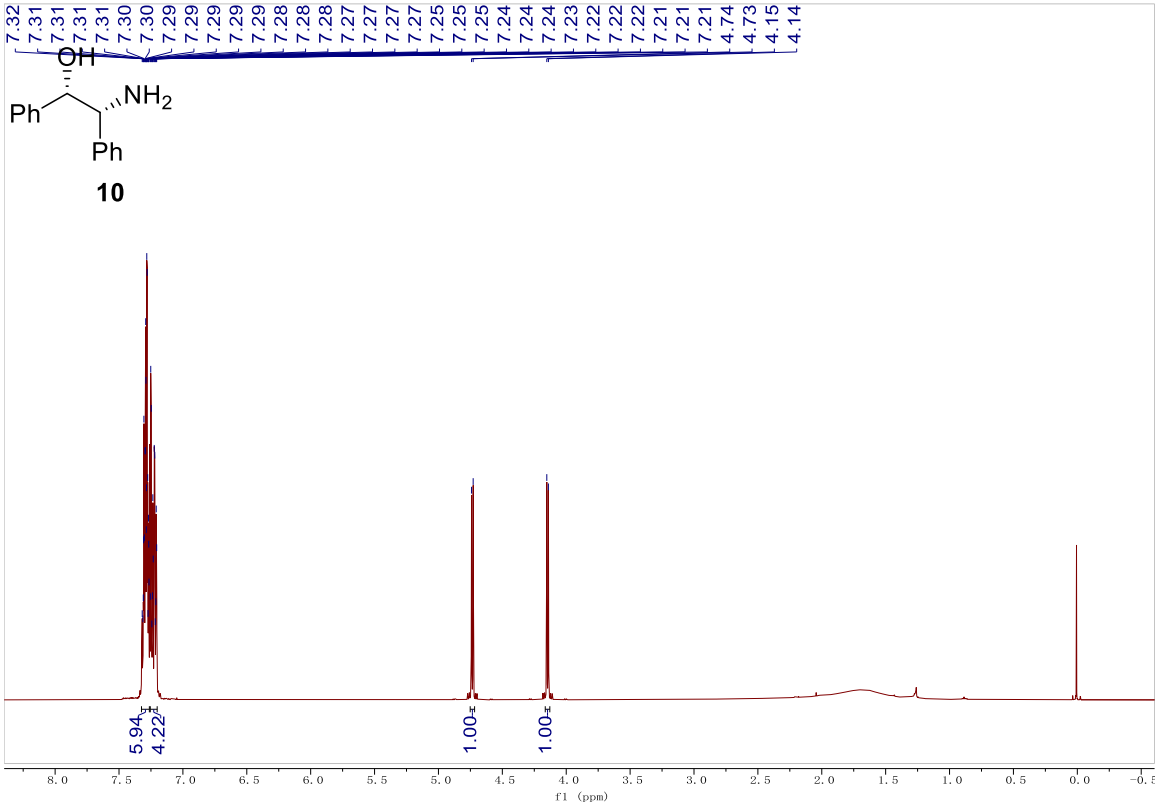
^{1}H NMR spectrum of 9



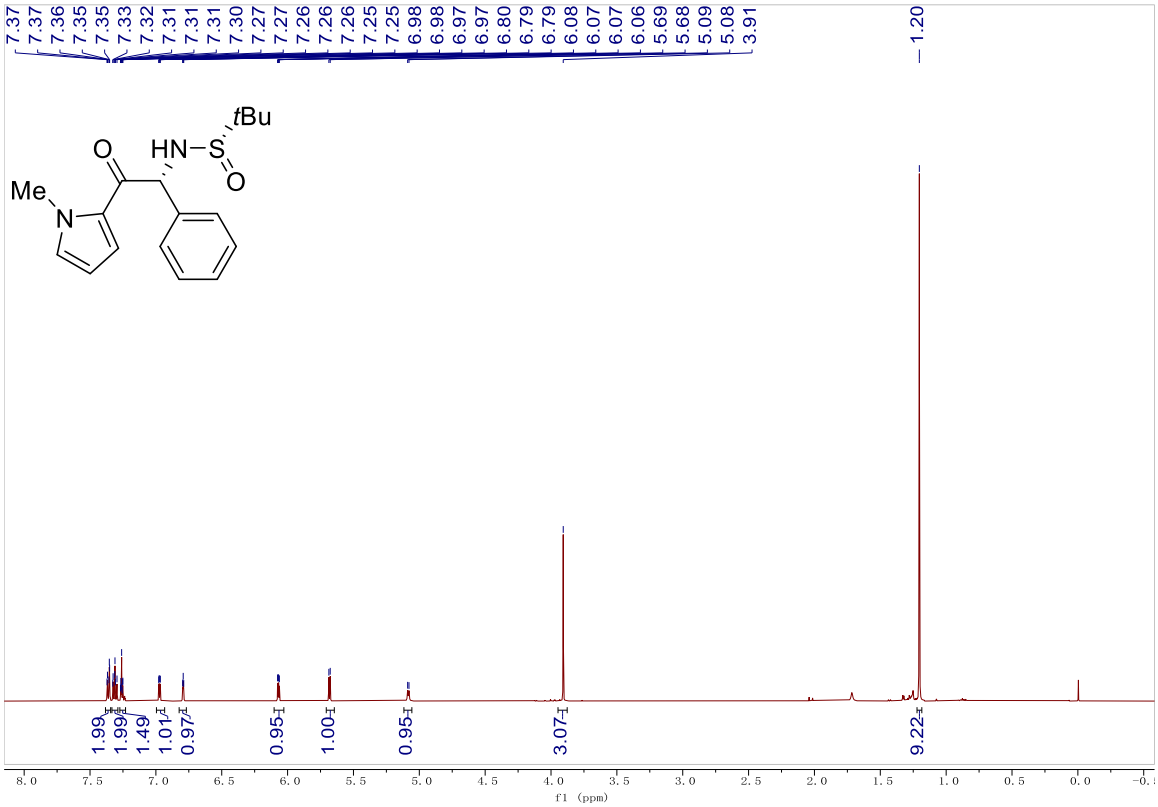
^{13}C NMR spectrum of 9



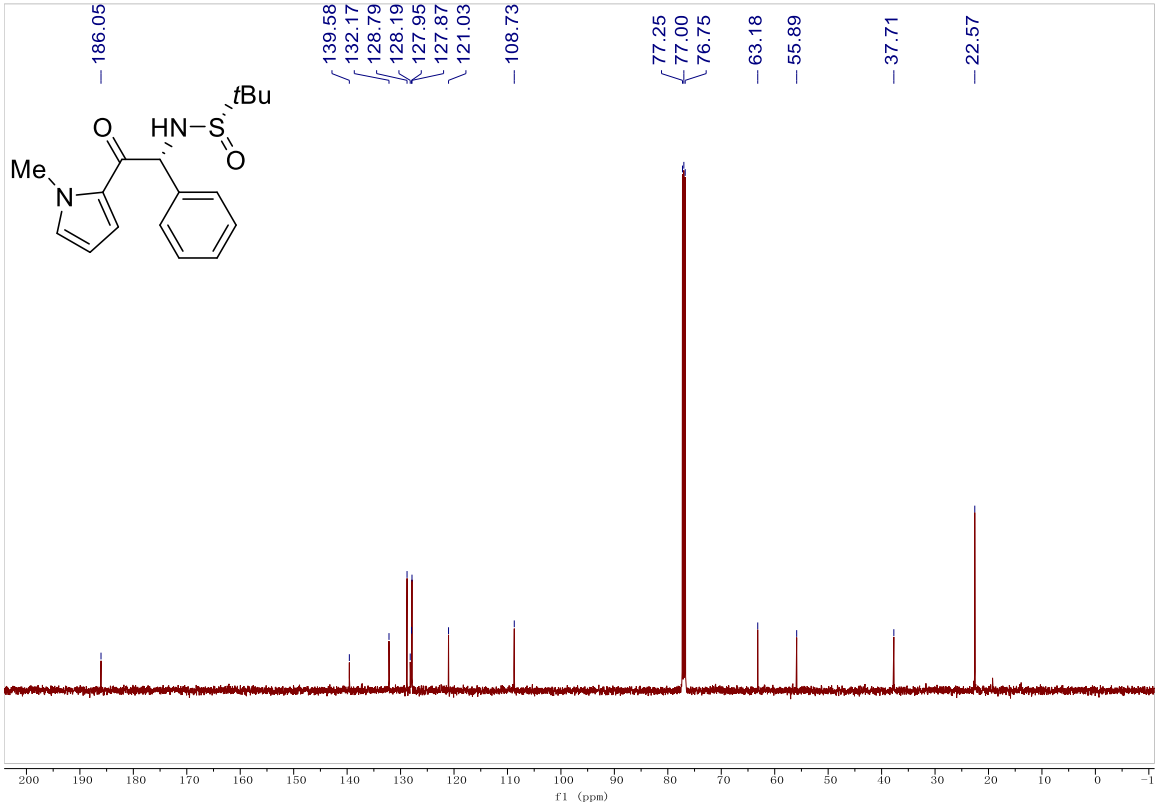
^{1}H NMR spectrum of 10



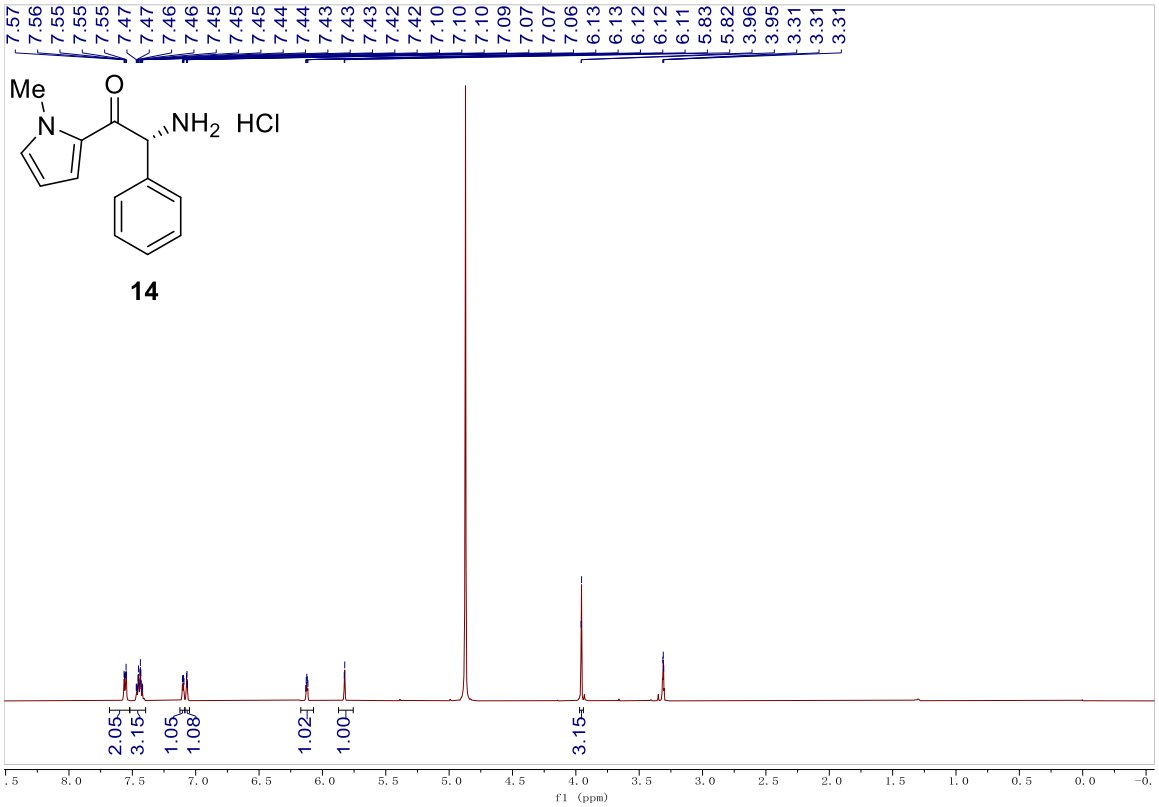
^{1}H NMR spectrum of 13



^{13}C NMR spectrum of 13

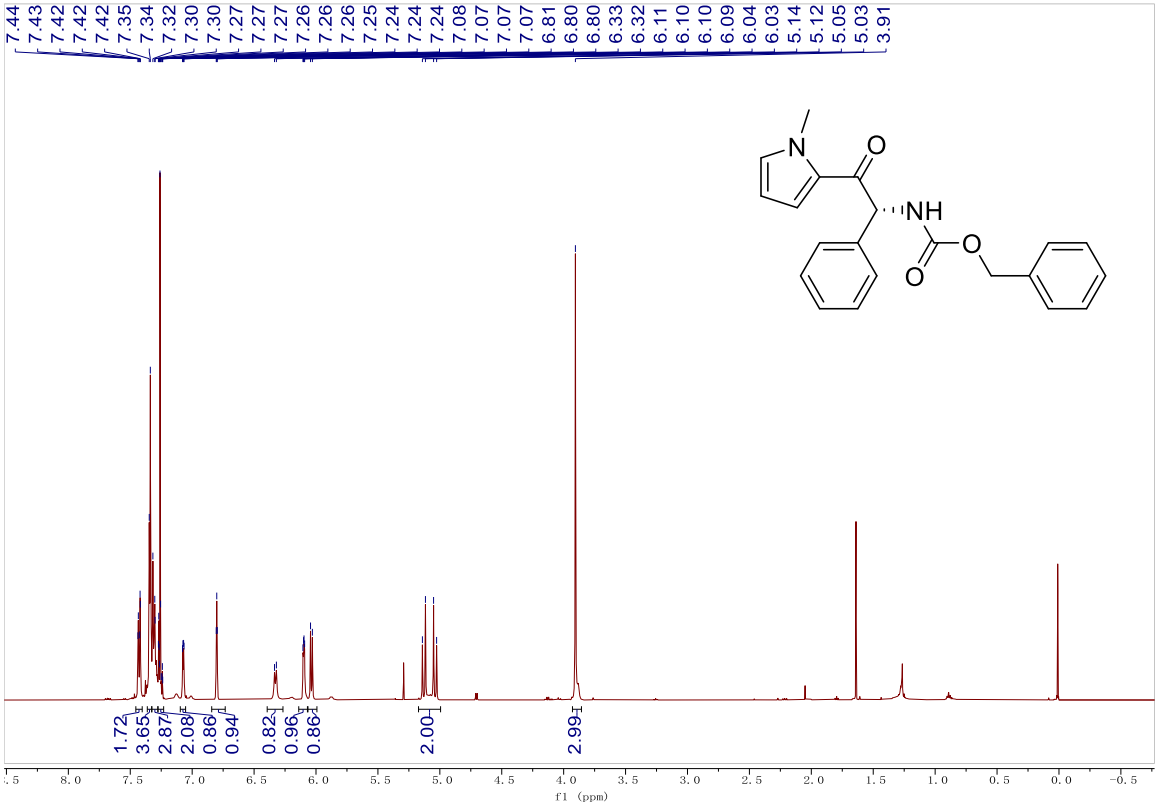


^{1}H NMR spectrum of 14



14

^{1}H NMR spectrum



^{13}C NMR spectrum