Decarboxylative sulfinamidation of *N*-sulfinylamines with carboxylic acids via photochemical iron-mediated ligand-to-metal charge transfer process

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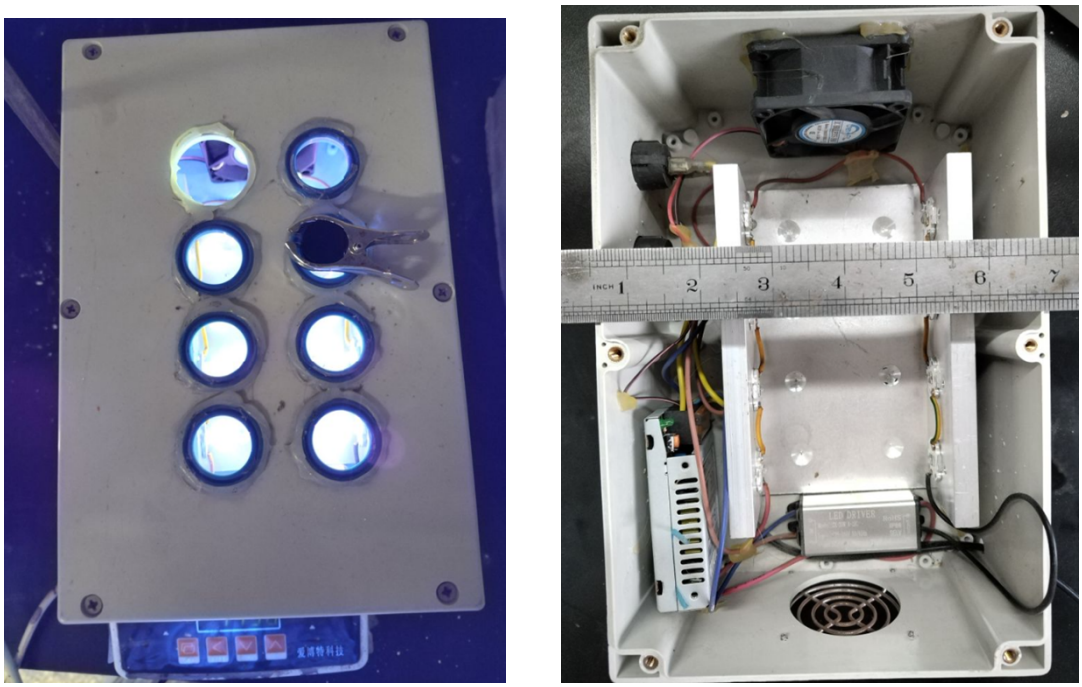
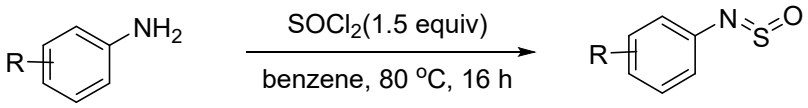
(A) General Information

All reactions and manipulations which are sensitive to moisture or air were performed under inert atmosphere of argon. All chemicals were purchased from J&K, Acros and Aldrich, and were used as received. Anhydrous CH_2Cl_2, THF, DMSO, DMF and MeCN were freshly distilled from calcium hydride. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and chemical shifts are reported in δ (ppm) referenced to residual undeuterated solvent signal for ^1H NMR (7.26 ppm) and ^{13}C NMR (77.00 ppm). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD-MS-MS quadrupole mass spectrometer. The light source for the photocatalytic reaction is manufactured by GeAo chemistry with a power of 40 W, a broad band source (365–375 nm). A fan was used to maintain the reaction temperature at room temperature (about 25-30 ℃). The reactions were carried out in a borosilicate glass vessel and the distance from the light source to the irradiation vessel is about 1 cm.

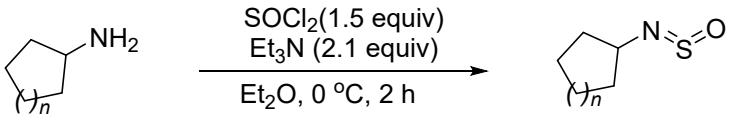


Photoreactor (GeAo)

(B) General procedure for the synthesis of sulfinylamines 1[1]



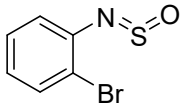
To a solution of amine (10 mmol, 1.0 equiv) in anhydrous benzene (10 mL) was added $SOCl_2$ (15 mmol, 1.1 mL, 1.5 equiv) dropwise at room temperature. The reaction mixture was heated to 80 °C in an oil-bath for 16 h. The reaction mixture was then cooled down to room temperature, evaporation the solvent under reduced pressure, the resulting solid was recrystallized in dry petroleum ether to give the sulfinylamines **1t**-**1aa**.



n = 1, 2

To a solution of cyclic amine (10 mmol, 1.0 equiv) in anhydrous diethyl ether (20 mL) was added Et_3N (1.2 mL, 2.1 equiv) at 0 °C. Then freshly distilled $SOCl_2$ (0.3 mL, 1.1 equiv) was added dropwise to the reaction mixture. The solution was stirred at 0 °C for 2 h. filtered through Celite and washed with diethyl ether. Evaporation of the solvent under reduced pressure at room temperature gave **1ba** and **1ca**, which were used directly without further purification.

((2-bromophenyl)imino)-λ⁴-sulfanone (1aa)



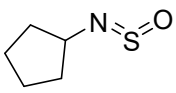
Yellow oil, 1.9 g, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15-8.13 (m, 1H), 7.50-7.47 (m, 1H), 7.19-7.12 (m, 1H), 7.04-6.99(m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.4, 133.1, 130.6, 128.1, 127.8, 119.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for C_6H_5NBrSO: 217.9270; Found: 217.9270.

(cyclopentylimino)-λ⁴-sulfanone (1ba)



Brown solid, 1.1 g, 90% yield.

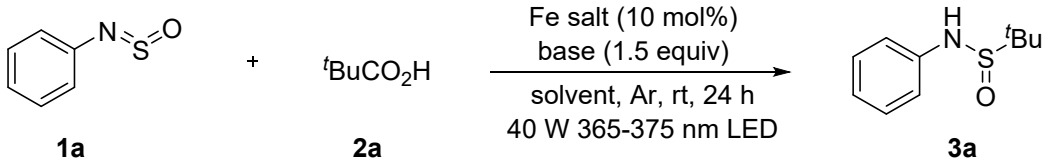
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (s, 1H), 2.05-2.02 (m, 2H), 1.88-1.83 (m, 4H), 1.64-1.62 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 52.7, 31.3, 23.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_5H_{10}NSO$: 132.0478; Found: 132.0487.

(C) Optimization of the reaction conditions.

Table S1. Iron salt screening[a]

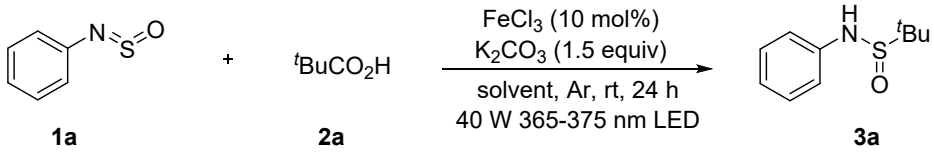


1a **2a** **3a**

entry	Fe salt (10 mol%)	yield (%)[b]
1	$FeCl_3$	22
2	$FeBr_3$	18
3	$Fe_2(SO_4)_3$	0
4	$Fe(OTf)_3$	0
5	$Fe(acac)_3$	0
6	$Fe(NO_3)_3$•$9H_2O$	0
7	$FeSO_4$	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Fe salt (10 mol%), K_2CO_3 (1.5 equiv), MeCN (2 mL), 40 W 365-375 nm LED, Ar, rt, 24 h. [b]isolated yield.

Table S2. Solvent screening[a]

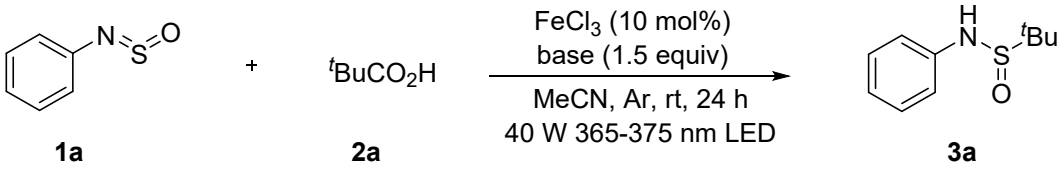


1a **2a** **3a**

entry	solvent	yield (%)[b]
1	MeCN	22
2	CH_2Cl_2	0
3	THF	0
4	EA	0
5	DMF	0
6	DMSO	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $FeCl_3$ (10 mol%), K_2CO_3 (1.5 equiv), solvent (2 mL), 40 W 365-375 nm LED, Ar, rt, 24 h. [b]isolated yield.

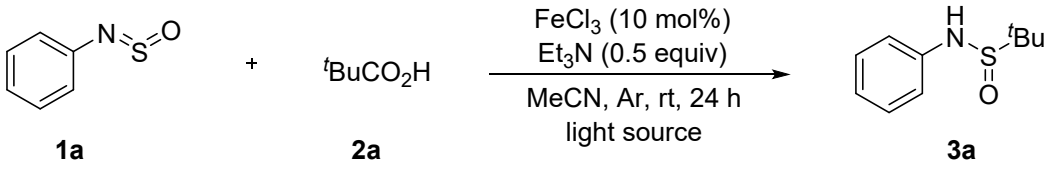
Table S3. Base screening[a]



entry	base (1.5 equiv)	yield (%)[b]
1	K_2CO_3	22
2	Na_2CO_3	0
3	Cs_2CO_3	0
4	$NaHCO_3$	0
5	Na_3PO_4	61
6	K_2HPO_4	0
7	Et_3N	69
8	Pyridine	13
9[c]	Et_3N	81
10[d]	Et_3N	58
11[e]	Et_3N	63

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $FeCl_3$ (10 mol%), base (1.5 equiv), MeCN (2 mL), 40 W 365-375 nm LED, Ar, rt, 24 h. [b]isolated yield. [c]Et_3N (0.5 equiv). [d]Et_3N (1.5 equiv). [e]Et_3N (2 equiv).

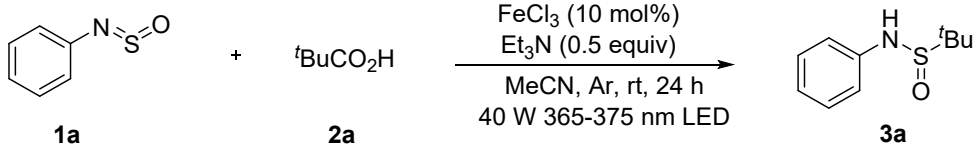
Table S4. Screening of light sources[a]



entry	light souce	yield (%)[b]
1	24 W violet LED (365-375 nm)	81
2	24 W white LED	74
3	40 W green LED (510-520 nm)	0
4	24 W blue LED (450-465 nm)	18

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $FeCl_3$ (10 mol%), Et_3N (1.5 equiv), MeCN (2 mL), light, Ar, rt, 24 h. [b]isolated yield.

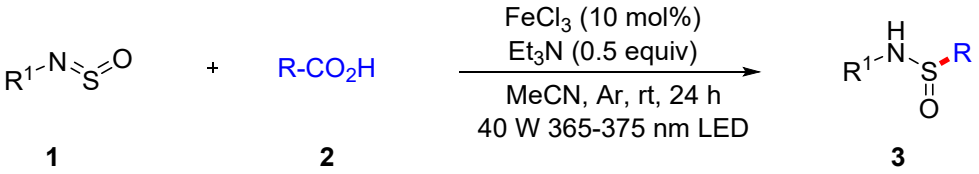
Table S5. Control experiments[a]



entry	control experiments	yield (%)[b]
1	Without Et_3N	15
2	Without Fe_3Cl	0
3	air	13
4	Without light	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $FeCl_3$ (10 mol%), Et_3N (1.5 equiv), MeCN (2 mL), 40 W 365-375 nm LED, Ar, rt, 24 h. [b]isolated yield.

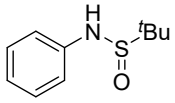
(D) General Procedure for Synthesis of sulfonamides 3



1 **2** **3**

To an 8 mL vial equipped with a magnetic stir bar was added **1** (0.2 mmol), carboxylic acids **2** (0.3 mmol), $FeCl_3$ (0.02 mmol), freshly distilled Et_3N (0.1 mmol) and anhydrous MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon irradiation with 40 W 365–375 nm LED at room temperature for 24 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to provide the desired product **3**.

2-Methyl-*N*-phenylpropane-2-sulfinamide (3a)[2]

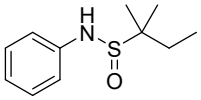


White solid, MP. 93-94 °C, 32mg, 81% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 7.6 Hz, 2H), 7.02-6.98 (m, 3H), 5.78 (s, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 129.3, 122.7, 118.1, 56.5, 22.4.

2-Methyl-*N*-phenylbutane-2-sulfinamide (3b)



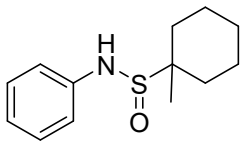
White solid, MP. 68-69 °C, 38 mg, 90% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (t, *J* = 7.6 Hz, 2H), 7.01-6.94 (m, 3H), 6.11 (s, 1H), 1.80-1.71 (m, 1H), 1.67-1.58 (m, 1H), 1.27 (s, 3H), 1.23 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 129.2, 122.4, 117.9, 59.9, 28.6, 18.9, 18.7, 7.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{17}NNaSO$: 234.0923; Found: 234.0921.

1-Methyl-*N*-phenylcyclohexane-1-sulfinamide (3c)



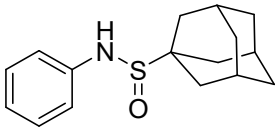
White solid, MP. 116-117 °C, 36 mg, 90% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (t, *J* = 7.6 Hz, 2H), 7.02-6.98 (m, 3H), 5.59 (s, 1H), 1.89-1.37 (m, 10H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 129.3, 122.7, 118.2, 60.0, 32.1, 30.6, 25.5, 21.8, 21.5, 15.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}NNaSO$: 260.1080; Found: 260.1076.

(3s,5s,7s)-*N*-phenyladamantane-1-sulfinamide (3d)



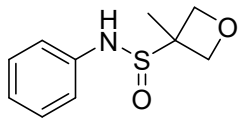
White solid, MP. 163-164 °C, 52 mg, 94% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (t, *J* = 7.6 Hz, 2H), 7.02-6.95 (m, 3H), 6.16 (s, 1H), 2.16-2.15 (m, 3H), 1.95-1.88 (m, 6H), 1.77-1.67 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.4, 129.2, 122.4, 117.9, 58.2, 36.2, 34.6, 28.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{21}NNaSO$: 298.1236; Found: 298.1233.

3-Methyl-*N*-phenyloxetane-3-sulfinamide (3e)



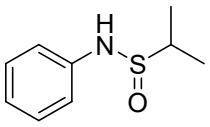
White solid, MP. 124-125 °C, 26mg, 62% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (t, *J* = 7.6 Hz, 2H), 6.99-6.96 (m, 3H), 6.11 (s, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 7.6 Hz, 1H), 4.51-4.89 (m, 2H), 1.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 129.5, 123.5, 118.6, 76.8, 76.5, 60.7, 16.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{14}NSO_2$: 212.0740; Found: 212.0752.

***N*-phenylpropane-2-sulfinamide (3f)**[3]

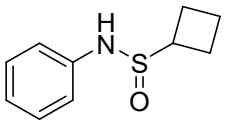


White solid, MP. 75-76 °C, 29.6 mg, 81% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (t, *J* = 7.6 Hz, 2H), 7.14 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 3.14-3.03 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 129.2, 122.5, 117.8, 54.4, 16.1, 15.6.

***N*-phenylcyclobutanesulfinamide (3g)**[3]

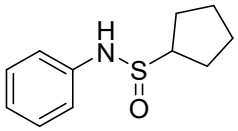


White solid, MP. 126-127 °C, 27mg, 69% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 7.6 Hz, 2H), 7.05-6.97 (m, 3H), 6.76 (s, 1H), 3.79-3.71 (m, 1H), 2.62-2.53 (m, 1H), 2.31-2.16 (m, 3H), 2.04-1.96 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 129.3, 122.7, 118.0, 56.3, 22.8, 21.4, 17.5.

***N*-phenylcyclopentanesulfinamide (3h)**[2]

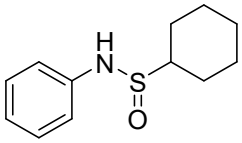


Yellow solid, MP. 76-77 °C, 24 mg, 56% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (s, 1H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 3.52-3.44 (m, 1H), 2.14-2.07 (m, 1H), 1.96-1.85 (m, 2H), 1.76-1.55 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 129.2, 122.4, 117.7, 63.9, 27.4, 27.2, 25.8, 25.7.

***N*-phenylcyclohexanesulfinamide (3i)**[3]

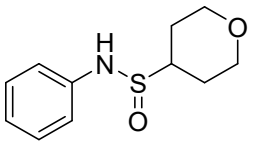


Yellow solid, MP. 113-114 °C, 30 mg, 68% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (t, *J* = 8.4 Hz, 2H), 7.02-6.95 (m, 4H), 2.92-2.85 (m, 1H), 2.16-2.13 (m, 1H), 2.05-2.02 (m, 1H), 1.88-1.81 (m, 2H), 1.67-1.65 (m, 1H), 1.56-1.22 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.0, 129.3, 122.6, 117.9, 62.7, 26.5, 26.2, 25.4, 25.1, 25.0.

***N*-phenyltetrahydro-2H-pyran-4-sulfinamide (3j)**



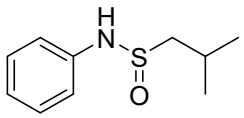
Yellow solid, MP. 140-141 °C, 36 mg, 80% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (s, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.04-6.98 (m, 3H), 4.04-3.98 (m, 2H), 3.34 (td, *J* = 11.2, 2.4 Hz, 1H), 3.20 (td, *J* = 11.6, 2.4 Hz, 1H), 3.14-3.06 (m, 1H), 2.01-1.97 (m, 1H), 1.91-1.87 (m, 1H), 1.85-1.64 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.6, 129.4, 122.9, 117.9, 66.6, 66.5, 59.6, 27.0, 26.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{15}NNaSO$: 248.0716; Found: 248.0723.

2-Methyl-*N*-phenylpropane-1-sulfinamide (3k)[2]

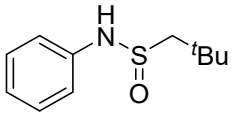


Yellow oil, 26 mg, 67% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.03-7.01(m, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 2.95 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.83 (dd, *J* = 13.2, 8.0 Hz, 1H), 2.15-2.08 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 129.3, 122.6, 117.8, 64.3, 24.5, 22.1, 21.7.

2,2-dimethyl-*N*-phenylpropane-1-sulfinamide (3l)[3]

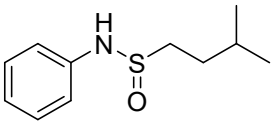


Brown solid, MP. 80-81 °C, 24 mg, 56% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.02-6.94 (m, 3H), 3.08 (d, *J* = 12.8 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.3, 129.3, 122.6, 117.8, 70.1, 30.9, 29.7.

3-Methyl-*N*-phenylbutane-1-sulfinamide (3m)



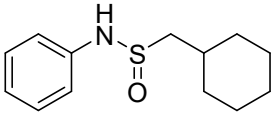
White solid, MP. 86-87 °C, 17 mg, 41% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (s, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.03-6.97 (m, 3H), 3.07-2.95 (m, 2H), 1.68-1.53 (m, 3H), 0.91 (t, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 129.4, 122.8, 118.1, 53.9, 31.8, 27.4, 22.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{17}NNaSO$: 234.0923; Found: 234.0935.

1-cyclohexyl-*N*-phenylmethanesulfinamide (3n)[3]

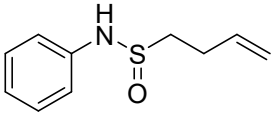


White solid, MP. 85-86 °C, 32 mg, 68% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.03-6.95 (m, 3H), 2.96 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.82 (dd, *J* = 12.8, 8.4 Hz, 1H), 1.94-1.60 (m, 6H), 1.32-0.99 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 129.3, 122.6, 117.8, 63.0, 33.3, 32.8, 32.2, 25.9, 25.8, 29.6.

***N*-phenylbut-3-ene-1-sulfinamide (3o)**[3]

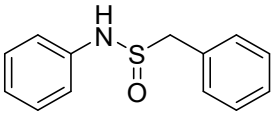


Yellow oil, 30 mg, 77% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.01-6.96 (m, 3H), 5.84-5.74 (m, 1H), 5.13-5.06 (m, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.49-2.43 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 134.6, 129.3, 122.7, 118.0, 117.0, 54.5, 27.5.

***N*,1-diphenylmethanesulfinamide (3p)**[3]



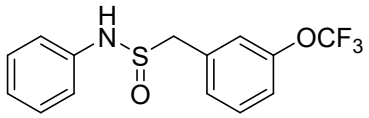
White solid, MP. 111-112 °C, 35 mg, 76% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40-7.34 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.6 Hz,

1H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 4.31 (d, *J* = 12.8 Hz, 1H), 4.15 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 130.7, 129.4, 129.0, 128.9, 128.6, 123.3, 118.8, 61.3.

***N*-phenyl-1-(3-(trifluoromethoxy)phenyl)methanesulfinamide (3q)**



White solid, MP. 130-131 °C, 35 mg, 56% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

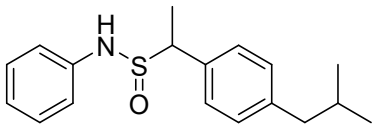
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.28 (m, 1H), 7.19-7.11 (m, 5H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.87-6.77 (m, 3H), 4.24 (d, *J* = 12.8 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 140.7, 131.4, 130.3, 129.5, 128.9, 123.5, 122.9, 120.9, 118.7, 60.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -57.8 (s, 3F).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}NF_3SO_2$: 316.0614; Found: 316.0619.

1-(4-isobutylphenyl)-*N*-phenylethane-1-sulfinamide (3r)



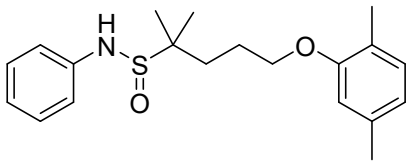
White solid, MP. 112-113 °C, 38 mg, 63% yield. R_f = 0.2 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.19 (m, 6H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 2H), 5.47 (s, 1H), 3.96 (q, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.95-1.85 (m, 1H), 1.76 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 141.0, 130.5, 129.5, 129.3, 129.2, 123.0, 118.6, 62.9, 45.1, 30.1, 22.4, 22.3, 15.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}NNaSO$: 324.1393; Found: 324.1392.

5-(2,5-dimethylphenoxy)-2-methyl-*N*-phenylpentane-2-sulfinamide (3s)



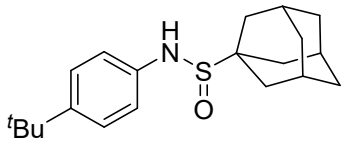
Colorless oil, 59 mg, 86% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (t, *J* = 7.6 Hz, 2H), 7.01-6.96 (m, 4H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.59 (s, 1H), 5.89 (s, 1H), 3.93 (t, *J* = 5.6 Hz, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 1.95-1.76 (m, 4H), 1.32 (d, *J* = 10.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7, 142.1, 136.4, 130.3, 129.3, 123.4, 122.7, 120.8, 118.1, 111.9, 67.5, 59.4, 32.5, 23.8, 21.3, 19.6, 19.3, 15.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{27}NNaSO$: 368.1655; Found: 368.1660.

(3s,5s,7s)-*N*-(4-(*tert*-butyl)phenyl)adamantane-1-sulfinamide (3t)



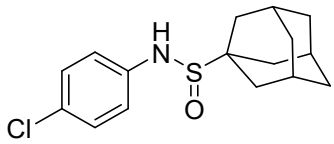
White solid, MP. 168-169 °C, 51 mg, 77% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 2.20-2.19 (m, 3H), 1.97-1.89 (m, 6H), 1.80-1.71 (m, 6H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 139.5, 126.2, 118.2, 58.1, 38.7, 36.5, 36.3, 34.6, 34.2, 34.4, 28.5, 27.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{29}NNaSO$: 354.1862; Found: 354.1869.

(3s,5s,7s)-*N*-(4-chlorophenyl)adamantane-1-sulfinamide (3u)



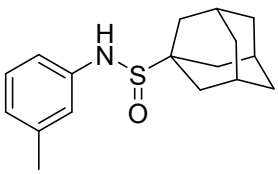
White solid, MP. 150-151 °C, 37 mg, 60% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.35 (s, 1H), 2.18-2.16 (m, 3H), 1.91-1.90 (m, 6H), 1.79-1.68 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2, 129.1, 127.5, 119.1, 58.5, 38.7, 36.4, 36.2, 34.6, 28.5, 27.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NNaSOCl$: 332.0846; Found: 332.0844.

(3s,5s,7s)-*N*-(*m*-tolyl)adamantane-1-sulfinamide (3v)



White solid, MP. 149-150 °C, 39 mg, 68% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

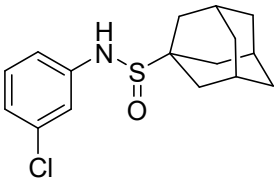
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (t, *J* = 7.6 Hz, 1H), 6.84-6.79 (m, 3H), 6.05 (s, 1H), 2.29 (s,

3H), 2.18-2.17 (m, 3H), 1.96-1.93 (m, 6H), 1.78-1.69 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 139.2, 129.1, 123.4, 118.7, 115.2, 58.1, 38.7, 36.5, 36.3, 34.6, 28.5, 27.9, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}NNaSO$: 312.1393; Found: 312.1398.

(3s,5s,7s)-*N*-(3-chlorophenyl)adamantane-1-sulfinamide (3w)



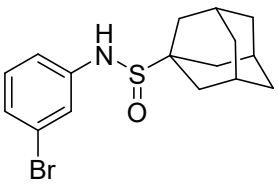
White solid, MP. 153-154 °C, 42 mg, 68% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.94-6.88 (m, 2H), 6.49 (s, 1H), 2.17-2.15 (m, 3H), 1.91-1.90 (m, 6H), 1.77-1.67 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 134.9, 130.2, 122.3, 177.7, 115.7, 58.6, 38.7, 36.5, 36.2, 34.6, 28.5, 27.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NNaSOCl$: 332.0846; Found: 332.0846.

(3s,5s,7s)-*N*-(3-bromophenyl)adamantane-1-sulfinamide (3x)



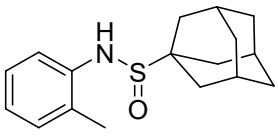
White solid, MP. 172-173 °C, 49.5 mg, 70% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (s, 1H), 7.08 (d, *J* = 4.8 Hz, 2H), 6.95-6.93 (m, 1H), 6.48 (s, 1H), 2.17-2.15 (m, 3H), 1.91-1.90 (m, 6H), 1.77-1.68 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 130.5, 125.2, 123.0, 120.6, 116.1, 58.6, 38.7, 36.4, 36.2, 34.6, 28.5, 27.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NNaSOBr$: 376.0341; Found: 376.0345.

(3s,5s,7s)-*N*-(*o*-tolyl)adamantane-1-sulfinamide (3y)



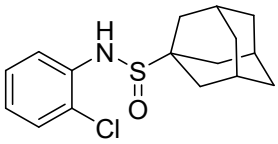
White solid, MP. 147-148 °C, 46 mg, 80% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.13 (m, 3H), 6.98-6.94 (m, 1H), 5.47 (s, 1H), 2.78 (s, 3H), 2.21-2.20 (m, 3H), 2.00-1.88 (m, 6H), 1.81-1.72 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.0, 130.7, 127.5, 127.0, 123.3, 119.0, 58.3, 38.6, 36.4, 36.3, 34.7, 28.5, 27.8, 17.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}NNaSO$: 312.1393; Found: 312.1400.

(3s,5s,7s)-*N*-(2-chlorophenyl)adamantane-1-sulfinamide (3z)



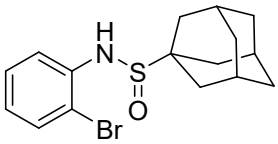
White solid, MP. 126-127 °C, 56 mg, 91% yield. R_f = 0.5 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.27 (m, 2H), 7.19 (td, *J* = 7.6, 1.6 Hz, 1H), 6.92 (td, *J* = 7.6, 1.6 Hz, 1H), 6.23 (s, 1H), 2.24-2.21 (m, 3H), 2.00-1.90 (m, 6H), 1.82-1.70 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 129.5, 127.8, 122.8, 122.6, 117.3, 58.7, 38.6, 36.4, 36.2, 34.5, 28.5, 27.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NNaSOCl$: 332.0846; Found: 332.0854.

(3s,5s,7s)-*N*-(2-bromophenyl)adamantane-1-sulfinamide (3aa)



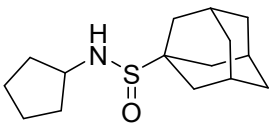
White solid, MP. 128-129 °C, 61 mg, 86% yield. R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 1H), 7.29-7.22 (m, 2H), 6.86 (t, *J* = 7.6, 1H), 6.28 (s, 1H), 2.24-2.22 (m, 3H), 2.01-1.90 (m, 6H), 1.83-1.71 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.9, 132.7, 128.6, 123.3, 117.4, 113.1, 58.8, 38.6, 36.4, 36.2, 34.6, 28.5, 27.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NNaSOBr$: 376.0341; Found: 376.0346.

(3s,5s,7s)-*N*-cyclopentyladamantane-1-sulfinamide (3ba)



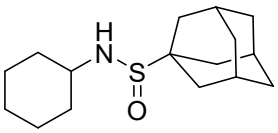
Brown solid, MP. 87-88 °C, 27 mg, 51% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.73 (q, *J* = 5.2 Hz, 1H), 3.28 (d, *J* = 4.4 Hz, 1H), 2.12-2.10 (m, 3H), 1.95-1.44 (m, 20H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.8, 56.3, 38.7, 36.5, 36.3, 34.6, 33.2, 28.5, 27.9, 23.4, 23.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{25}NNaSO$: 290.1549; Found: 290.1555.

(3s,5s,7s)-*N*-cyclohexyladamantane-1-sulfinamide (3ca)



Brown solid, MP. 105-106 °C, 23 mg, 41% yield. R_f = 0.3 (petroleum ether/ethyl acetate = 3:1).

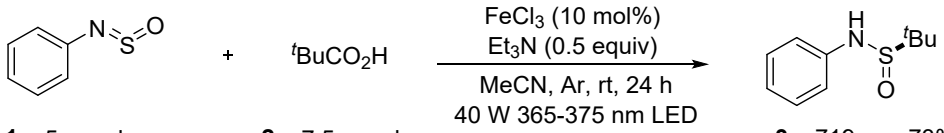
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.15-3.09 (m, 2H), 2.09-2.07 (m, 3H), 1.91-1.88 (m, 2H), 1.79-1.61 (m, 14H), 1.55-1.51 (m, 1H), 1.28-1.09 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.8, 53.9, 36.4, 35.2, 34.7, 34.0, 28.5, 25.5, 24.7, 24.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{28}NSO$: 282.1886; Found: 282.1891.

(E) Scale-up reaction and synthetic transformations

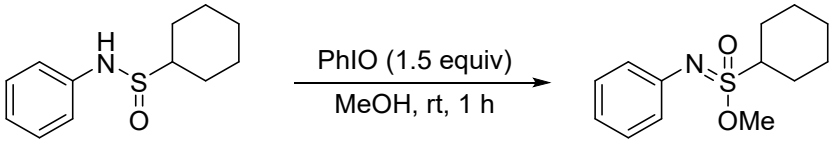
(a) Scale-up reaction



1a, 5 mmol + **2a**, 7.5 mmol → **3a**, 719 mg, 73%

To a 50 mL over-dried schleck tube with a magnetic stir bar was added **1a** (695 mg, 5 mmol), ^{t}BuCO$_2$H **2a** (765 mg, 7.5 mmol), $FeCl_3$ (81 mg, 0.5 mmol), freshly distilled Et_3N (0.35 mL, 2.5 mmol) and anhydrous MeCN (10 mL) under argon atmosphere. Then the reaction mixture was stirred upon irradiation with 40 W 365−375 nm LED at room temperature for 24 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography (petroleum ether/ethyl acetate = 2:1) affording the desired sulfonamide **3a** (719 mg, 73%) as a white solid.

(b) Synthetic transformations

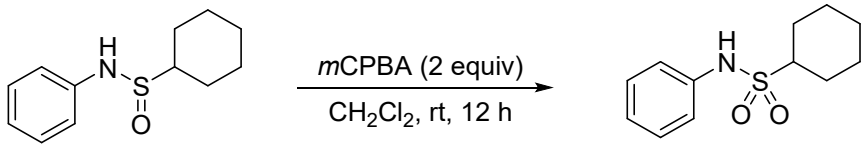


3i → **4**

To a solution of **3i** (110 mg, 0.49 mmol) in anhydrous methanol (5 mL) was added iodosylbenzene (163 mg, 0.74 mmol) at room temperature. The reaction mixture was stirred for 1 h. After the starting materials consumed, the solvent was concentrated in vacuo and the residue was purified by a column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1), delivering the corresponding product **4** (98 mg, 78%) as a colorless oil.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.11-3.05 (m, 1H), 2.24-2.14 (m, 2H), 1.84-1.81 (m, 2H), 1.63-1.56 (m, 3H), 1.26-1.11 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 128.9, 123.1, 122.0, 60.8, 55.4, 26.6, 26.0, 25.0, 24.9 (2).



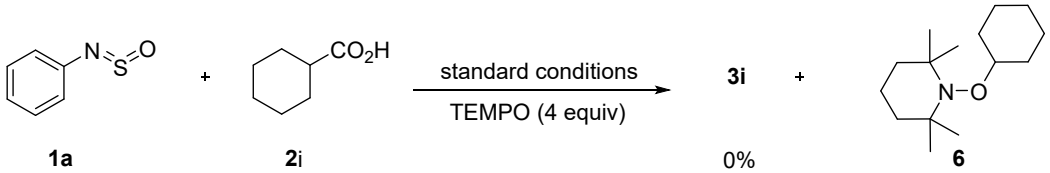
3i **5**

To a solution of **3i** (100 mg, 0.45 mmol) in anhydrous CH_2Cl_2 (5 mL) was added *meta*-chloroperbenzoic acid (*m*CPBA) (155 mg, 0.9 mmol) at room temperature. The reaction mixture was stirred for 12 h. After the starting materials consumed, 40% sodium bisulfite (5 mL) was added to the reaction mixture and stirred for 5 min. The mixture was extracted with CH_2Cl_2 (3 x 10 mL), the organic phase was washed with saturated $NaHCO_3$ (3 x 10 mL), dried with Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by a column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1), delivering the corresponding product **5** (56 mg, 52%) as a white solid.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.17 (m, 5H), 7.05 (t, *J* = 7.2 Hz, 1H), 2.97-2.91 (m, 1H), 2.11-2.08 (m, 2H), 1.78-1.76 (m, 2H), 1.59-1.45 (m, 3H), 1.18-1.04 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.3, 129.5, 124.5, 119.8, 60.2, 26.2, 25.0, 24.9.

(F) TEMPO trapping experiment

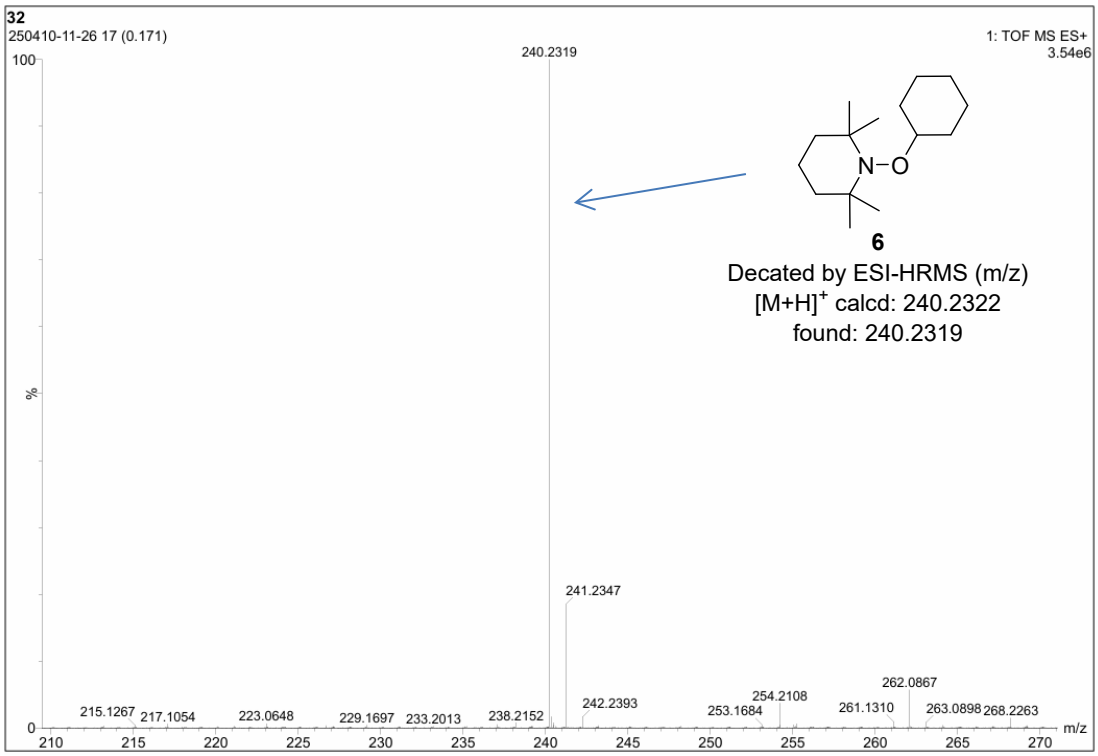


1a **2i** 0% **6**

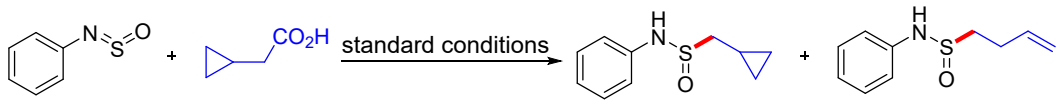
Decated by ESI-HRMS (m/z)
$[M+H]^+$ calcd: 240.2322
found: 240.2319

To an 8 mL vial equipped with a magnetic stir bar was added **1a** (28 mg, 0.2 mmol), carboxylic acids **2i** (38.4 mg, 0.3 mmol), $FeCl_3$ (0.02 mmol), TEMPO (124.8 mg, 0.8 mmol),

freshly distilled Et_3N (0.1 mmol) and anhydrous MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon irradiation with 40 W 365–375 nm LED at room temperature for 24 h. the analysis of the crude reaction mixture by high resolution mass spectrometry (HRMS) identified 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine adduct **6**. HRMS (ESI) m/z: compound **6**, [**6**+H]$^+$ calcd for $C_{15}H_{30}NO$: 240.2322; found: 240.2319.



(G) Radical clock experiment



1a **2t** **3t + 3t'** (30%)

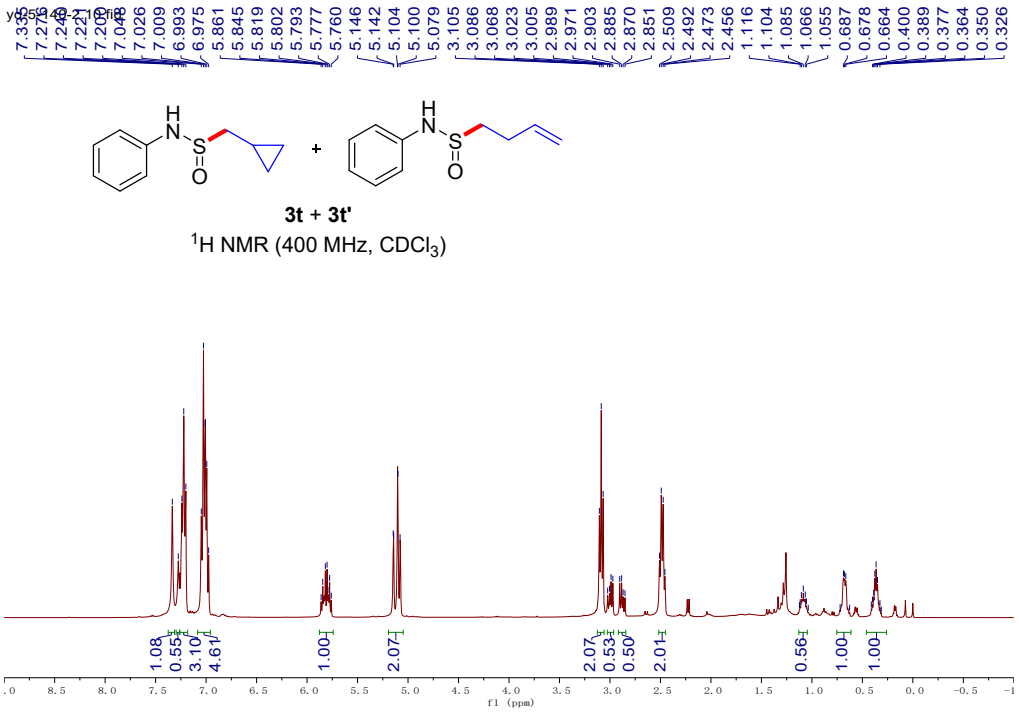
To an 8 mL vial equipped with a magnetic stir bar was added **1a** (28 mg, 0.2 mmol), carboxylic acid **2t** (30 mg, 0.3 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol), freshly distilled Et_3N (13.9 uL, 0.1 mmol) and anhydrous MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon irradiation with 40 W 365–375 nm LED at room temperature for 24 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to provide the inseparable mixture of product **3t** and **3t'** (12 mg, 30% yield) as a colorless liquid.

3t: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 0.55H), 7.24-7.20 (m, 3H), 3.00 (dd, *J* = 13.6, 7.2 Hz,

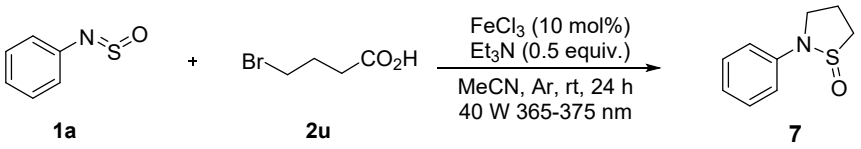
0.5H), 2.88 (dd, *J* = 13.6, 7.2 Hz, 0.5H), 1.12-1.04 (m, 0.6H), 0.72-0.62 (m, 1H), 0.41-0.31 (m, 1H).

3t': ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (s, 1H), 7.05-6.98 (m, 4.5H), 5.86-5.76 (m, 1H), 5.15-5.08 (m, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.51-2.46 (m, 2H).

The spectral date are consistent with the literature.[4]



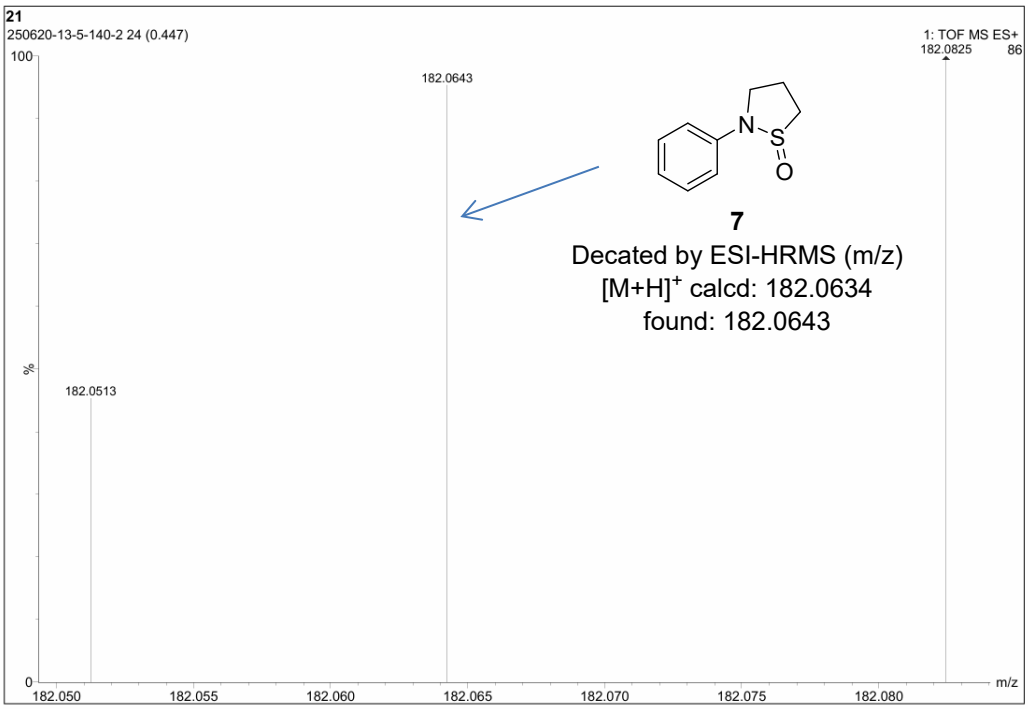
(H) Anion trapping experiment



1a + **2u** → **7**

Decated by ESI-HRMS (m/z)
$[M+H]^+$ calcd: 182.0634
found: 182.0643

To an 8 mL vial equipped with a magnetic stir bar was added **1a** (28 mg, 0.2 mmol), 4-bromobutyric acid **2u** (49.8 mg, 0.3 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol), freshly distilled Et_3N (13.9 uL, 0.1 mmol) and anhydrous MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon irradiation with 40 W 365–375 nm LED at room temperature for 24 h. the analysis of the crude reaction mixture by high resolution mass spectrometry (HRMS) identified cyclic sulfinamide **7**. HRMS (ESI) m/z: compound **7**, $[7+H]^+$ calcd for $C_9H_{12}NOS$: 182.0634; found: 182.0643.



(I) Computational details

DFT calculations were performed with Gaussian 16 program.[5] All molecular geometries were optimized in gas phase at the PBE0-D3BJ[6]/def2SVP[7] level of theory at 298.15 K and 1 atm. Optimized minima were verified by harmonic vibrational analysis that have no imaginary frequency. To refine calculated energies, single point calculations with larger basis set def2TZVP[7] were then performed based on these optimized structures by using the same PBE0-D3BJ functional using SMD model[8] to account for solvation energies in MeCN

(J) Mechanistic Insights into the Role of $FeCl_3$ in Catalyzing Nucleophilic Attack: A DFT Study

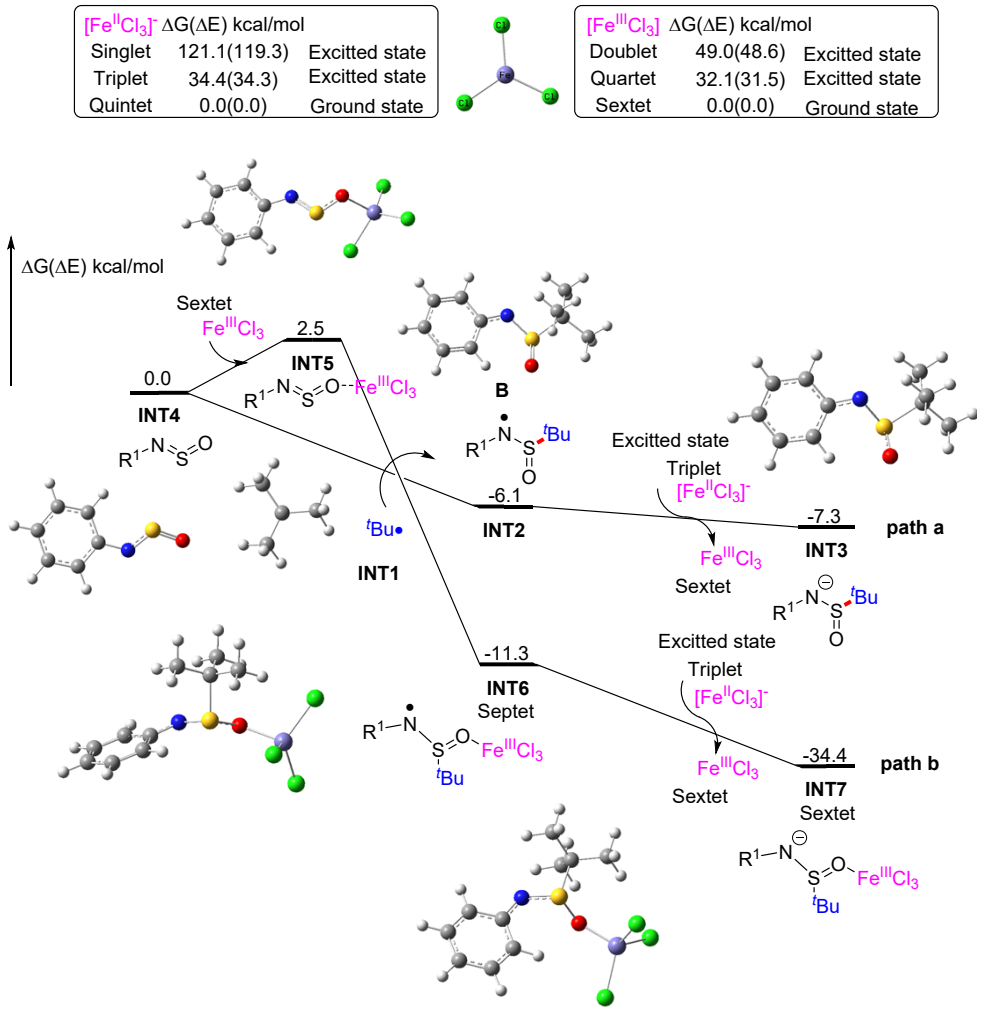


Figure S1. Free energy profile of mechanism.

Density functional theory (DFT) computations have elucidated the catalytic influence of $FeCl_3$ as a Lewis acid in facilitating nucleophilic attack processes. Specifically, in path b, the interaction between intermediate **INT4** and $FeCl_3$ yields intermediate **INT5** with a minimal energy increment of 2.5 kcal/mol. Subsequent attack by the ^{t}Bu• on the sulfur atom generates intermediate **INT6**, accompanied by an exothermic release of 11.3 kcal/mol. This is followed by an outer-sphere electron transfer from Fe(II) to Fe(III), resulting in an additional exothermic release of 34.4 kcal/mol. Collectively, path b is characterized by a lower overall energy barrier and a more pronounced exothermic profile.

Conversely, in the absence of $FeCl_3$ (path a), the combination of intermediate **INT4** with the ^{t}Bu• forms intermediate **INT2**, with an energy stabilization at 6.1 kcal/mol. The subsequent outer-sphere electron transfer from Fe(II) to Fe(III) stabilizes the system to -7.3 kcal/mol. This comparative analysis underscores the pivotal role of $FeCl_3$ in enhancing the thermodynamic and

kinetic feasibility of the nucleophilic attack pathway.

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(K) Cartesian Coordinates of the Optimized Structures

$FeCl_3$-Fe(III)Doublet

0 2

Fe	0.00001700	-0.00016100	0.06697500
Cl	-1.76873200	-1.14229600	-0.03414800
Cl	1.87391000	-0.96013500	-0.03414900
Cl	-0.10520400	2.10267600	-0.03413600

$FeCl_3$-Fe(III)Quartet

0 4

Fe	0.12793500	-0.00043300	0.00000000
Cl	-1.22665300	-1.62866300	0.00000000
Cl	2.25407300	-0.00141400	0.00000000
Cl	-1.22308600	1.63073800	0.00000000

$FeCl_3$-Fe(III)Sextet

0 6

Fe	0.00000200	0.00000200	-0.00000300
Cl	-2.03399000	-0.66767200	0.00000100
Cl	1.59522000	-1.42763200	0.00000100
Cl	0.43876700	2.09530100	0.00000100

$FeCl_3$-Fe(II)Singlet

-1 1

Fe	-0.00001000	-0.00000400	-0.00001500
Cl	0.87723000	1.92912000	0.00000800
Cl	-2.10930700	-0.20487300	0.00000800
Cl	1.23209200	-1.72424000	0.00000800

$FeCl_3$-Fe(II)Triplet

-1 3

Fe	0.00135500	0.02295900	0.00000000
Cl	-0.04654400	-2.21050800	0.00000000
Cl	1.98145000	1.04908300	0.00000000
Cl	-1.93697900	1.12631000	0.00000000

$FeCl_3$-Fe(II)Quintet

-1 5

Fe	-0.00000600	0.00000000	0.00000100
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Cl	-1.21042400	-1.89022300	0.00000000
Cl	2.24222000	-0.10313500	0.00000000

INT1 Doublet

0 2

C	0.00000700	0.00000600	-0.14343500
C	1.47784200	0.10877200	0.01385900
H	2.00301600	-0.74750400	-0.43963900
H	1.87196900	1.03282600	-0.43941500
H	1.78185800	0.13099900	1.08276800
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H	-1.64899700	-1.36078000	-0.43935500
H	-0.04170800	-2.13754800	-0.43969300
H	-0.77717300	-1.60876700	1.08276600

INT2 Doublet

0 2

N	-0.08825300	0.56037300	-0.46986600
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C	2.03551000	0.38213100	1.68462600
C	3.68223300	-0.55990600	0.03023200
C	-1.38484000	0.26707000	-0.22637500
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C	-2.28175800	1.37536600	-0.20595500
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H	2.92270800	1.65810700	-1.44766100
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H	-5.19812800	-0.22902600	0.49689800

H	-4.29847100	2.05904400	0.06831400
H	-1.86494000	2.36523100	-0.40213500

INT3

-1 1

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C	2.60135300	0.66253700	1.42080800
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C	-1.99178400	-1.01415800	-0.11081500
C	-3.36915800	-1.16819800	-0.22456900
C	-4.24111500	-0.08043600	-0.12630400
C	-3.68340300	1.18467900	0.10279700
C	-2.31192200	1.35774700	0.20944000
H	3.40068300	2.19772100	-0.80936300
H	2.37145000	1.34256300	-1.99158200
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H	3.56392100	1.13868300	1.68070500
H	2.49241400	-0.27622900	1.98686800
H	1.76990300	1.32507000	1.70145300
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H	3.60121700	-0.81498300	-1.56216800
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H	-3.77478700	-2.17499300	-0.37862700
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H	-4.33908700	2.05825600	0.19655700
H	-1.88327200	2.34906100	0.38241400

INT4

0 1

N	1.05761800	-0.59780900	-0.33212100
S	2.17505100	0.2898000	0.25887300
O	3.52344900	-0.17256000	-0.08835100
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C	-1.20476800	-1.30951900	-0.03599900
C	-2.55789200	-1.04031800	0.13094700
C	-3.02056000	0.27681900	0.13257700
C	-2.11780200	1.32635200	-0.03948700
C	-0.76021500	1.06860600	-0.19722900
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H	-4.08654000	0.48447700	0.24974200
H	-2.47580600	2.35842500	-0.06509500
H	-0.06279900	1.89152200	-0.37316000

INT5 Sextet

0 6

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C	3.96119800	-1.31119400	0.43978700
C	5.30939600	-1.08843000	0.18818800
C	5.73483400	0.15392500	-0.28248500
C	4.80831800	1.17874900	-0.50435800
C	3.46240800	0.97321700	-0.24358700
Fe	-2.34781700	-0.06465100	-0.06470500
Cl	-1.26839600	1.23041800	-1.52626400
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Cl	-2.97913900	-1.97769400	-0.84530400
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H	6.03194100	-1.89122500	0.34983500
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H	2.73830600	1.76635500	-0.44839700

INT6 Septet

0 7

Fe	2.42877100	-0.62826100	-0.02073300
Cl	2.01844800	-0.56415700	2.14731200
Cl	3.73791600	1.00684500	-0.68524700
Cl	2.94786500	-2.58968100	-0.79066400
N	-1.81838200	-0.02082100	-0.92292600
S	-0.55750100	0.33063200	0.13694700
O	0.65390400	-0.11822700	-0.70307600
C	-2.98929700	-0.43810300	-0.41909900
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C	-5.27418500	-1.09863400	-0.98908100
C	-5.55304000	-1.30121200	0.37109900
C	-4.55544700	-1.08772300	1.33582800
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H	-6.04991500	-1.27637400	-1.73719800
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H	-0.18994100	3.65070400	-1.55419100
H	0.71175500	2.13134600	-1.78894100
C	0.59933800	2.64166300	0.90846000
H	0.44127500	2.31160600	1.94594200
H	1.57657300	2.26881400	0.56842900
H	0.64149100	3.74250000	0.89969000

INT7 Sextet

-1 6

Fe	1.94698100	-0.86666100	-0.06358900
Cl	2.22439700	-0.54041900	2.11946000
Cl	3.67799200	-0.05946300	-1.20819900
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N	-2.01615700	1.06541300	-0.40548300
S	-0.61037600	0.98263700	0.33716800
O	0.46056000	0.16390300	-0.55323700
C	-2.90513700	0.02785400	-0.21150200
C	-4.28214000	0.30333000	-0.37993400
C	-5.24437200	-0.68283400	-0.20704000
C	-4.87787400	-1.98791700	0.13564700
C	-3.52256600	-2.28262600	0.28368600
C	-2.54783700	-1.30441500	0.10371800
H	-4.56474900	1.32530000	-0.64484300
H	-6.30113300	-0.42941600	-0.33946700
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H	-0.61630400	4.68435400	0.59135700
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H	-1.00080900	2.79622600	-1.90670600
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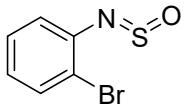
H	0.69072200	2.22497200	-1.99114800
C	1.41526800	2.78363400	0.58970900
H	1.43753600	2.47272300	1.64571600
H	2.12377600	2.14940000	0.03737100
H	1.77143600	3.82515000	0.52698400

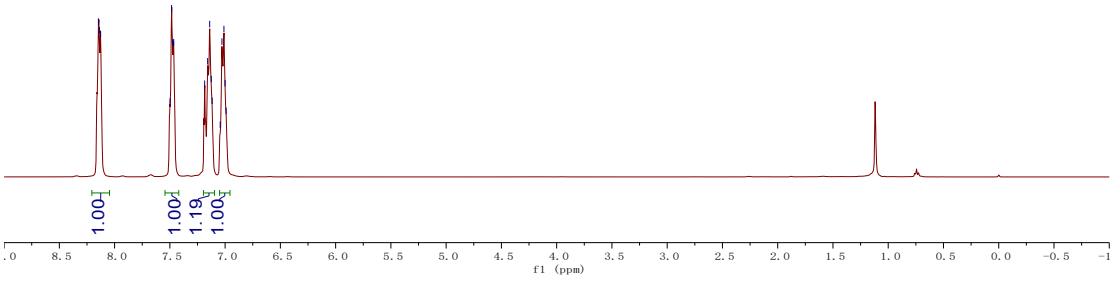
(L) NMR spectra of new compounds

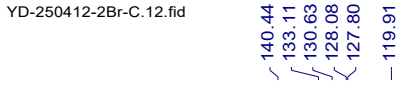
((2-bromophenyl)imino)-λ^4-sulfanone (1aa)

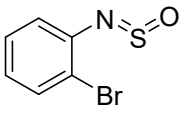


1aa

^{1}H NMR (400 Hz, $CDCl_3$)

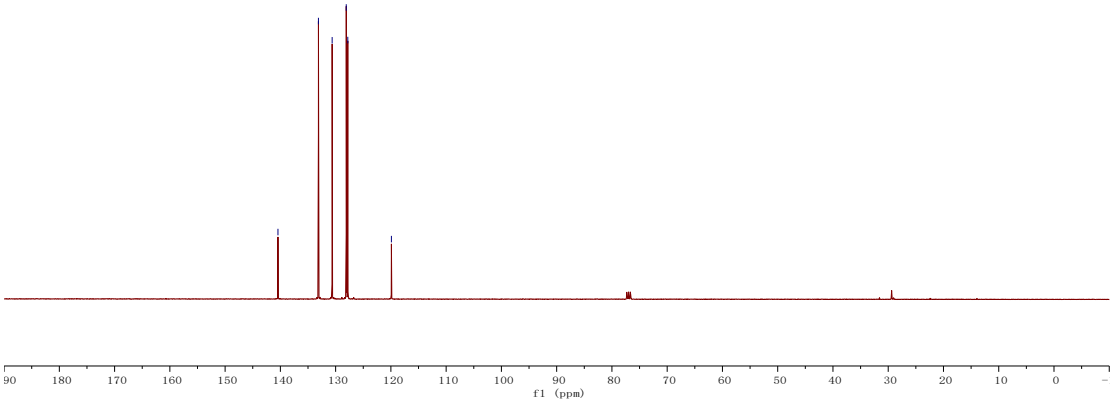






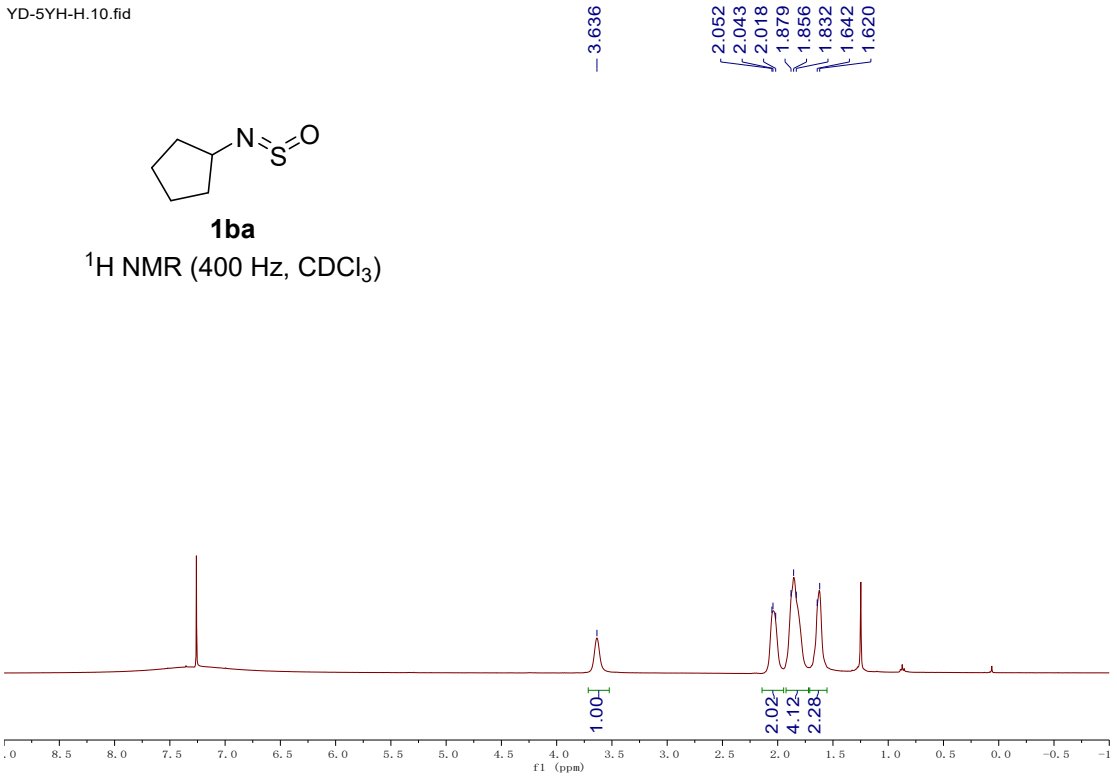
1aa

^{13}C NMR (100 Hz, $CDCl_3$)



(cyclopentylimino)-λ⁴-sulfanone (1ba)

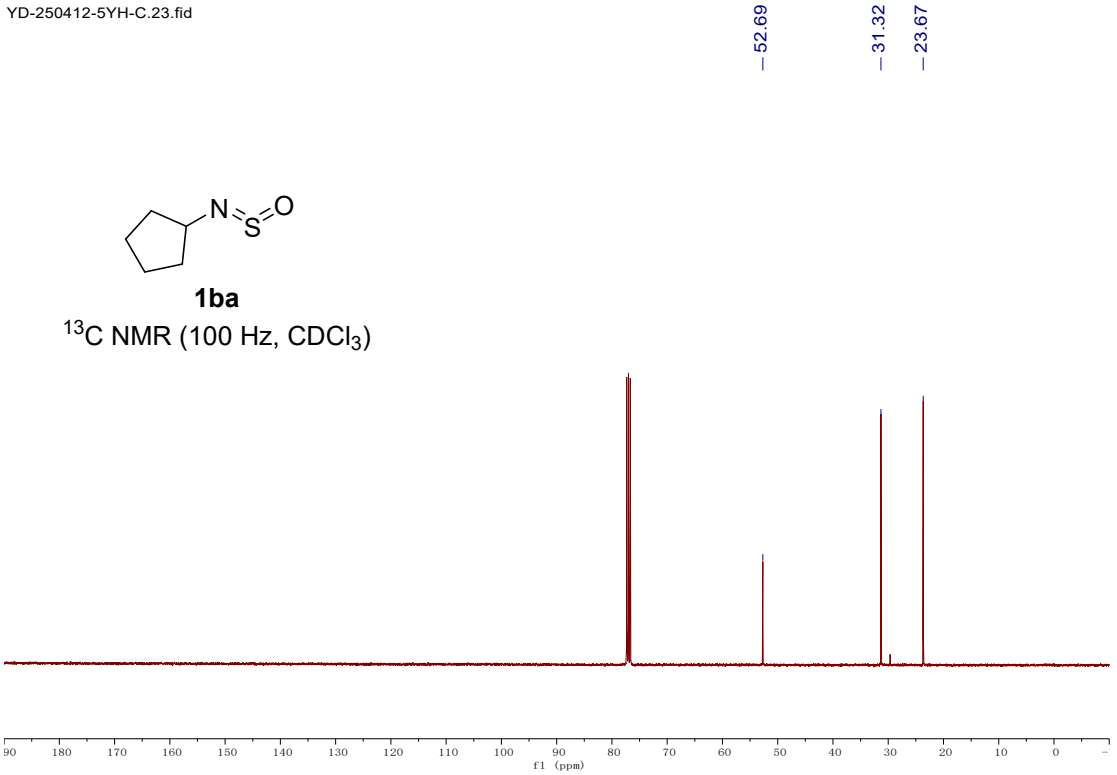
YD-5YH-H.10.fid



1ba

^{1}H NMR (400 Hz, $CDCl_3$)

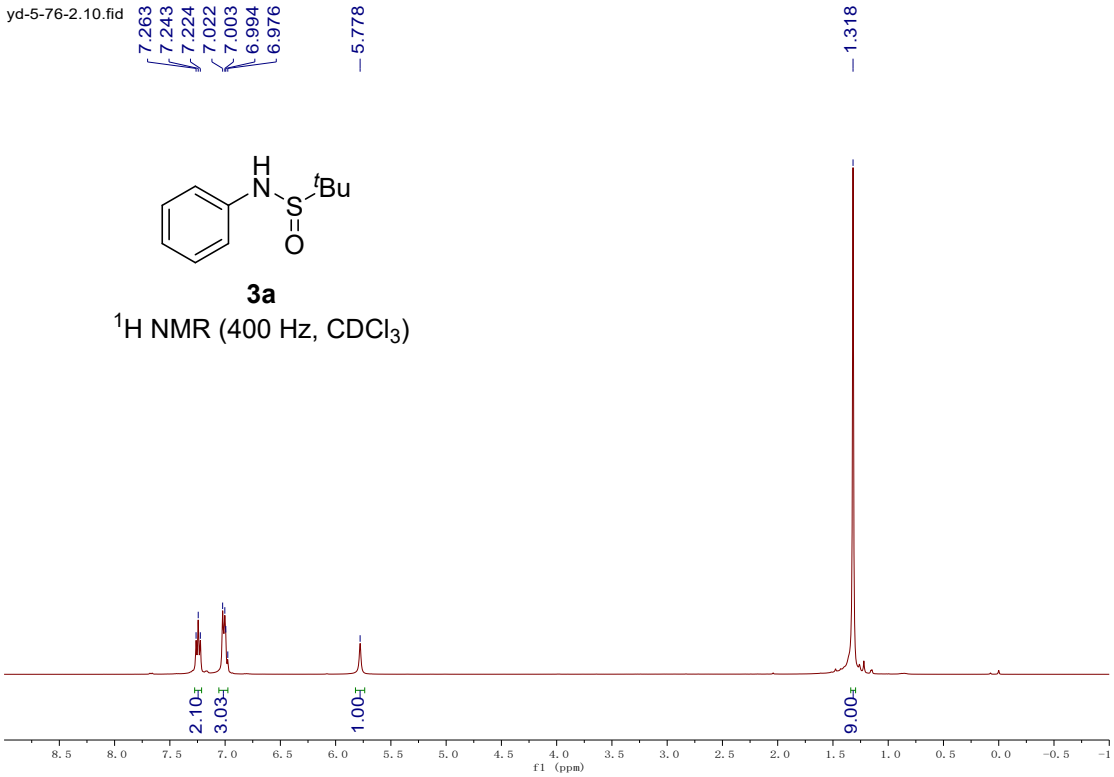
YD-250412-5YH-C.23.fid



1ba

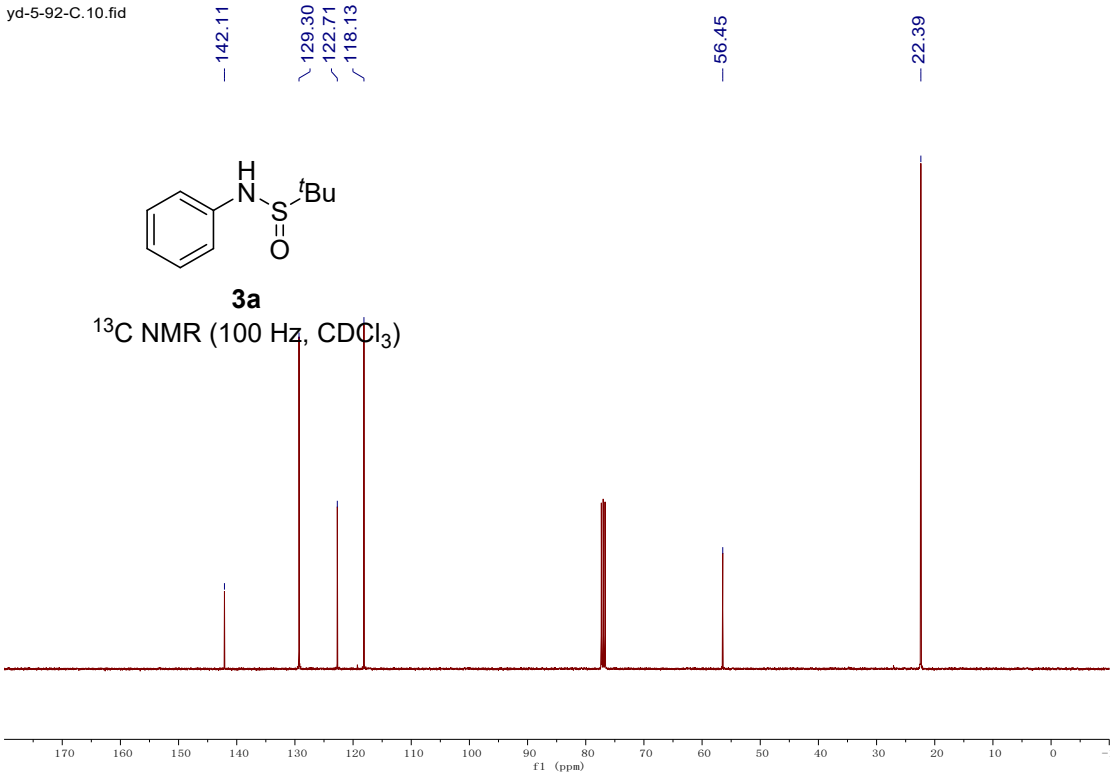
^{13}C NMR (100 Hz, $CDCl_3$)

2-Methyl-*N*-phenylpropane-2-sulfinamide (3a)



3a

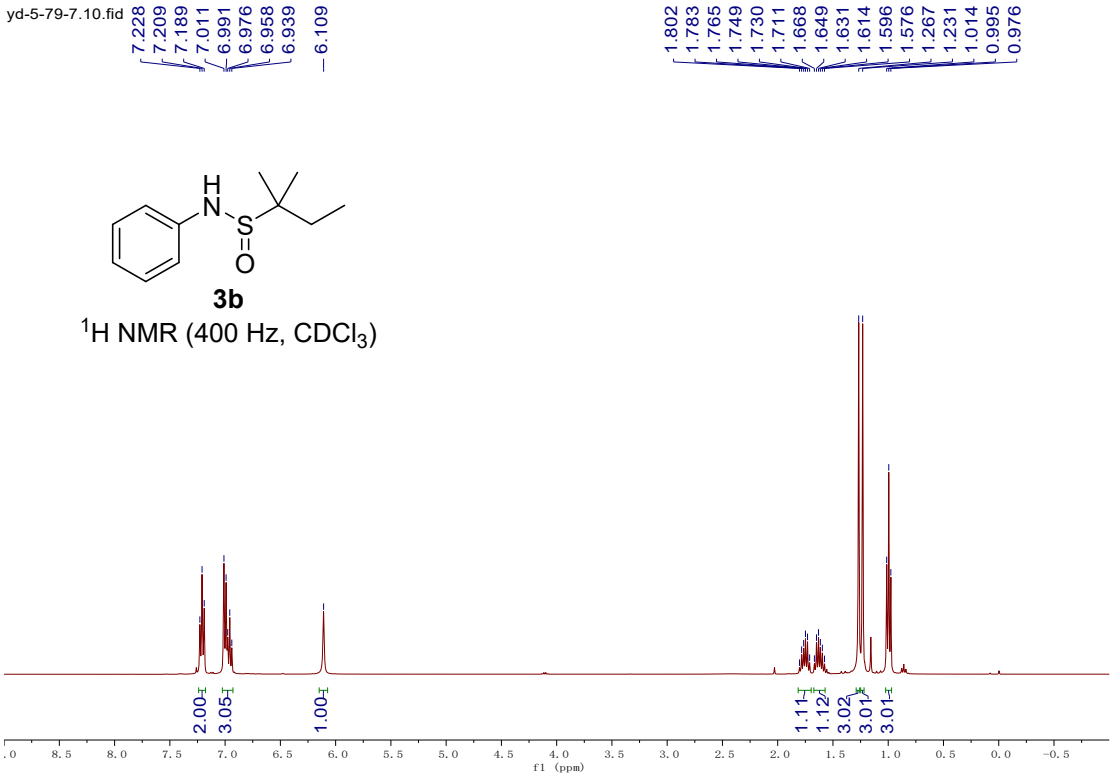
^{1}H NMR (400 Hz, $CDCl_3$)

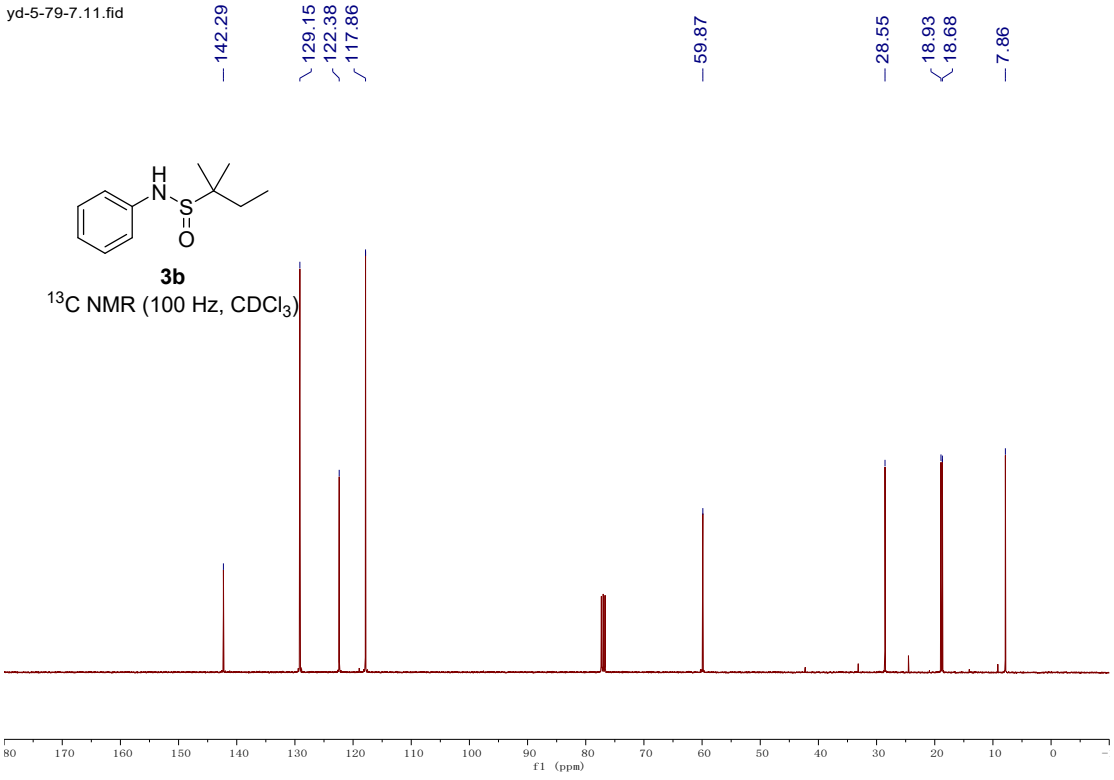


3a

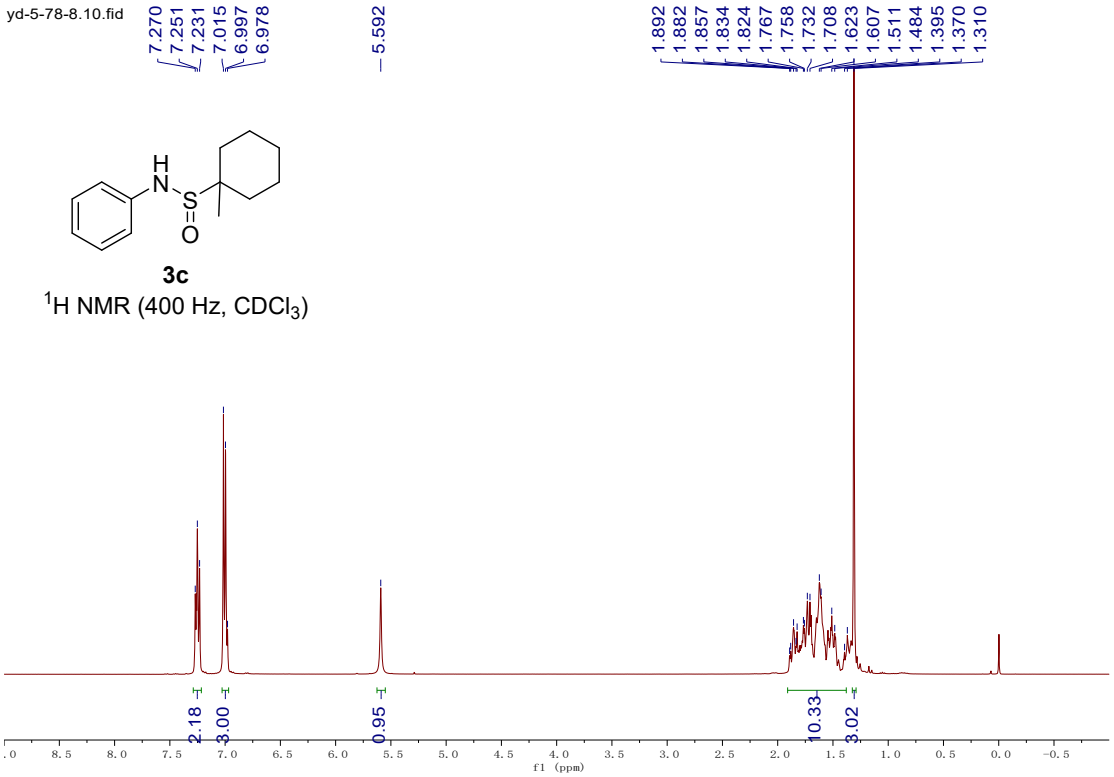
^{13}C NMR (100 Hz, $CDCl_3$)

2-Methyl-*N*-phenylbutane-2-sulfinamide (3b)



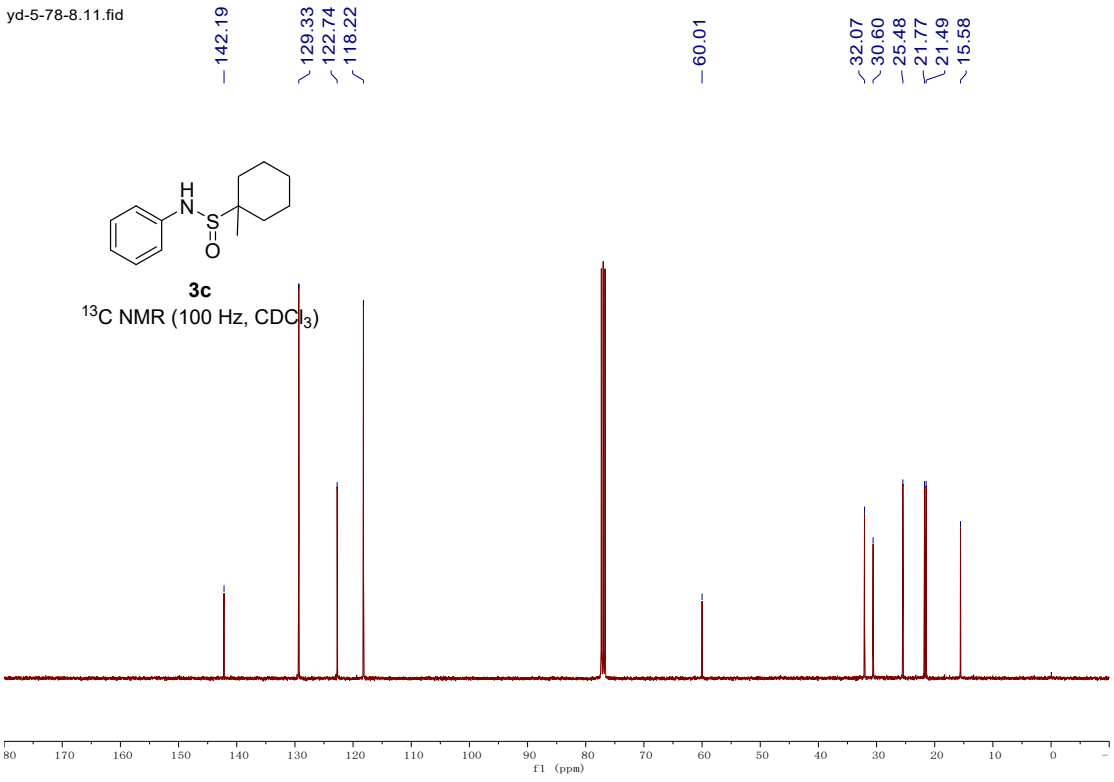


1-Methyl-*N*-phenylcyclohexane-1-sulfinamide (3c)



3c

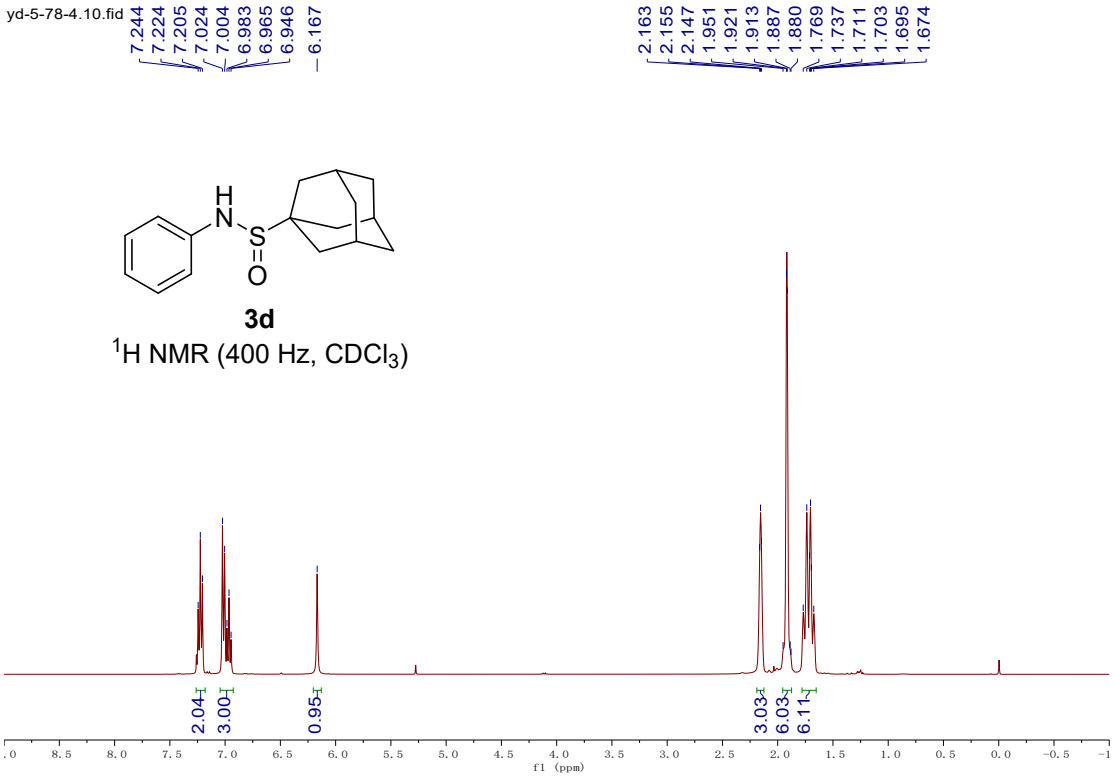
^{1}H NMR (400 Hz, $CDCl_3$)

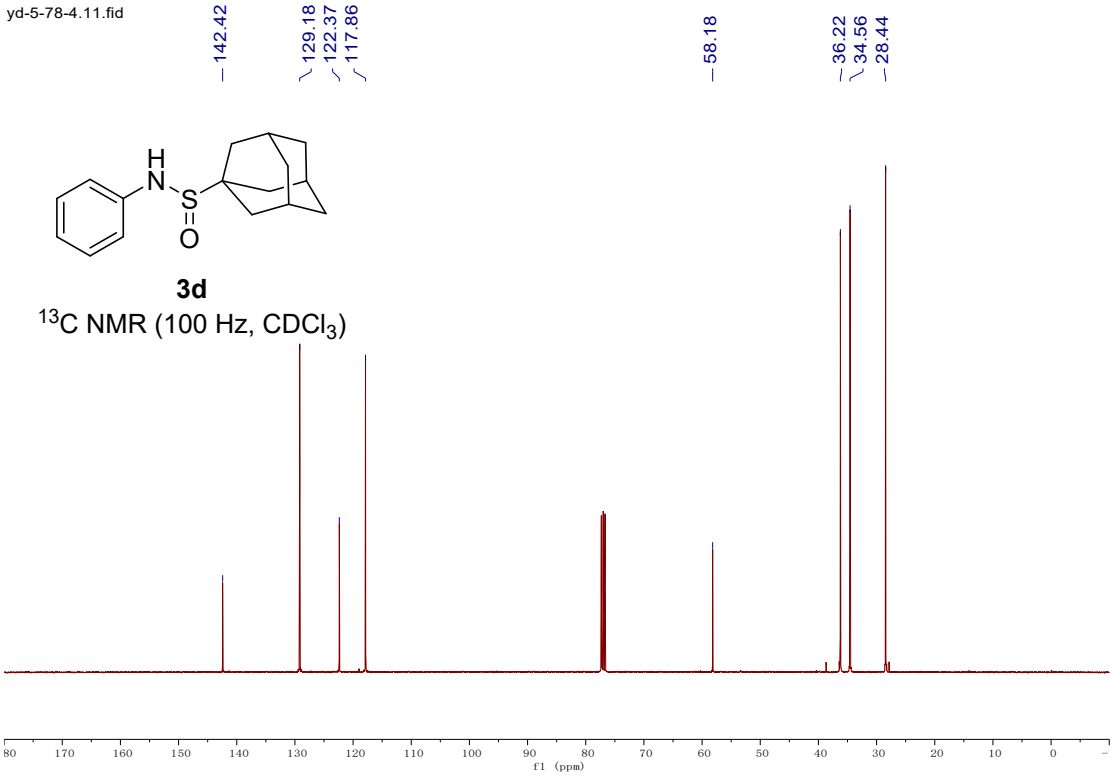


3c

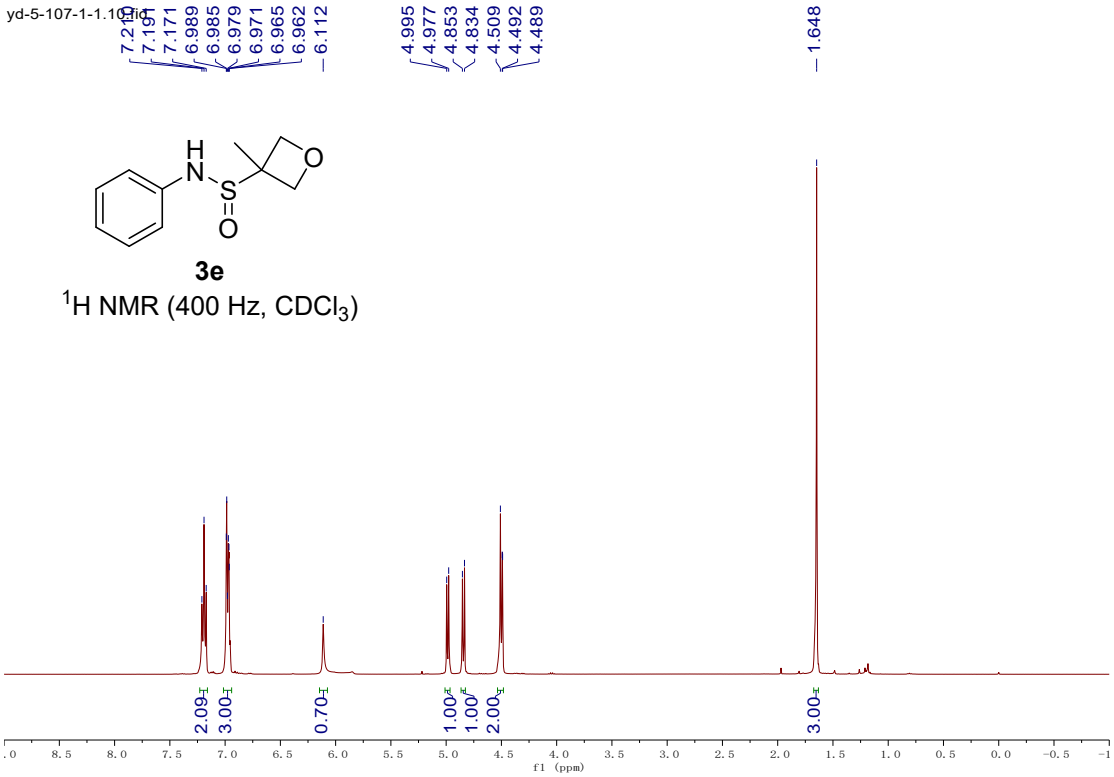
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-phenyladamantane-1-sulfinamide (3d)



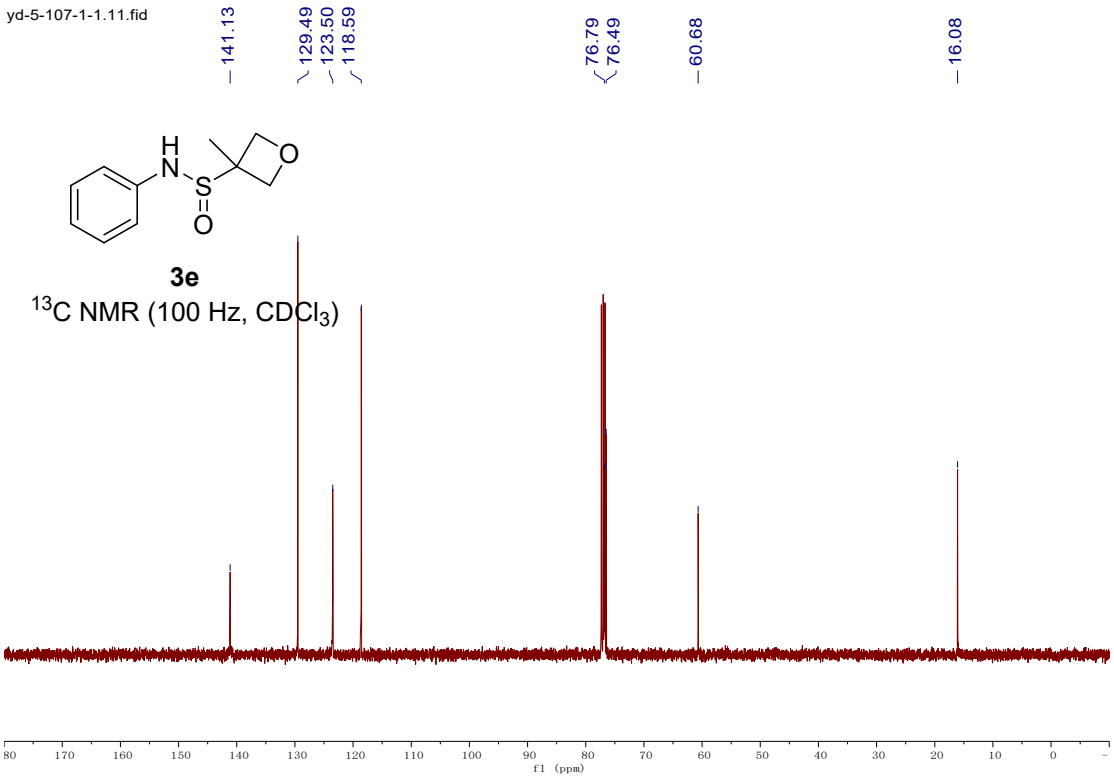


3-Methyl-*N*-phenyloxetane-3-sulfinamide (3e)



3e

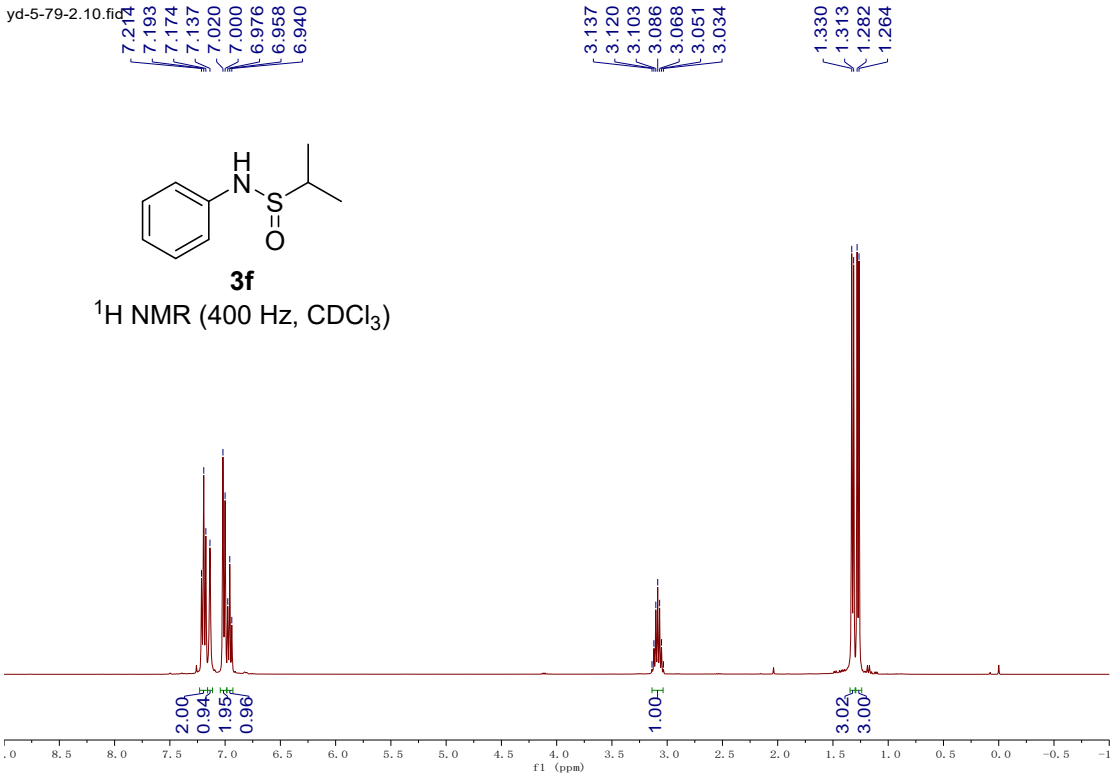
^{1}H NMR (400 Hz, $CDCl_3$)



3e

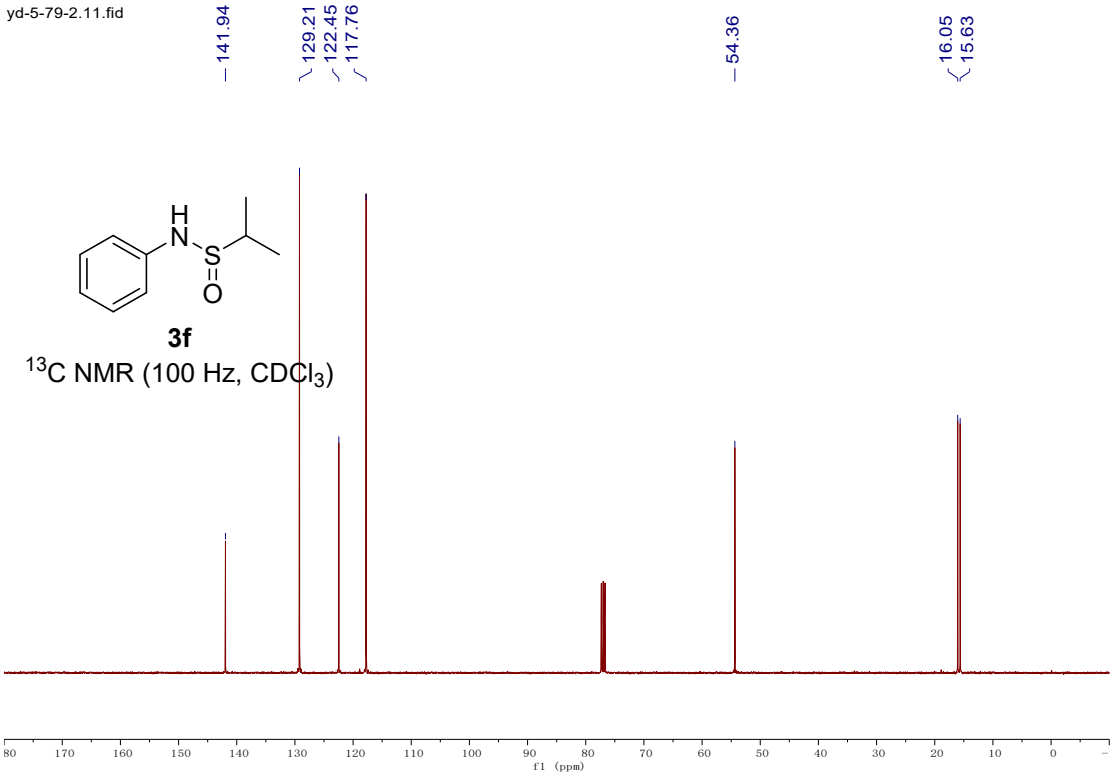
^{13}C NMR (100 Hz, $CDCl_3$)

N-phenylpropane-2-sulfinamide (3f)



3f

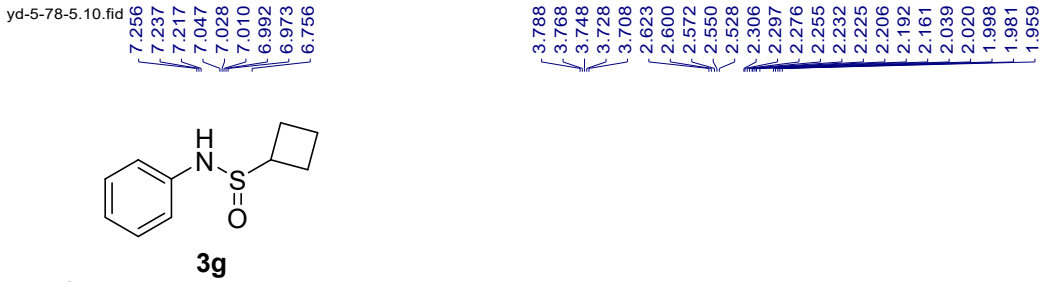
^{1}H NMR (400 Hz, $CDCl_3$)



3f

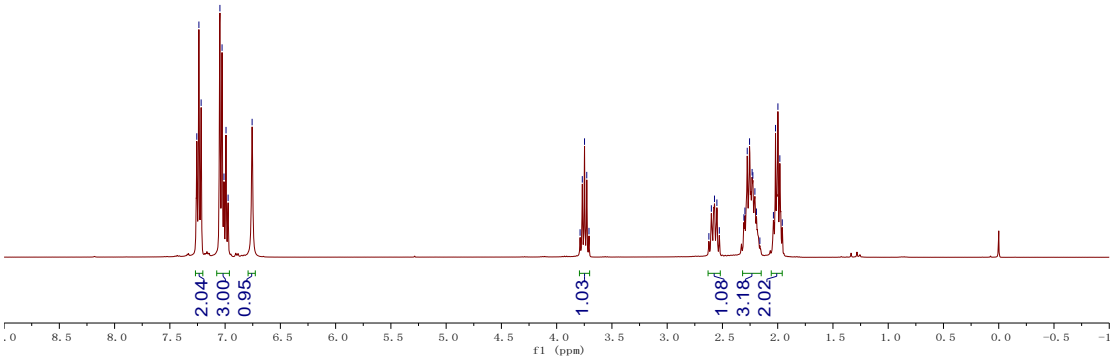
^{13}C NMR (100 Hz, $CDCl_3$)

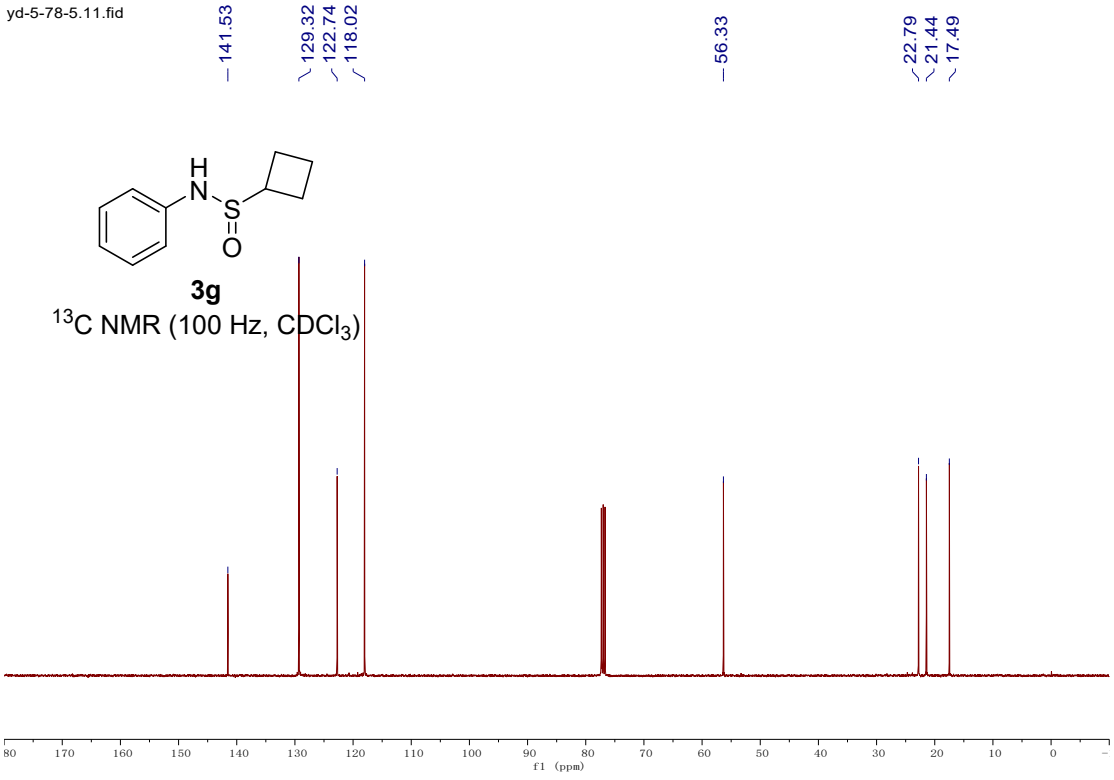
N-phenylcyclobutanesulfinamide (3g)



3g

^{1}H NMR (400 Hz, $CDCl_3$)

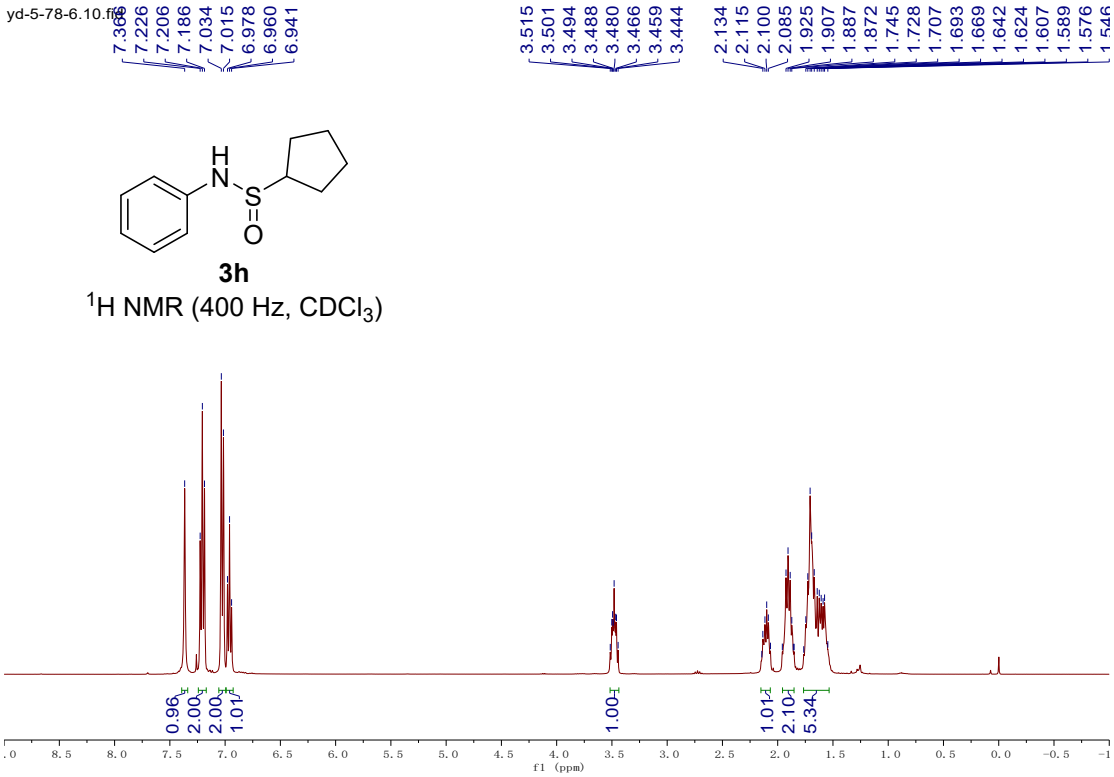




3g

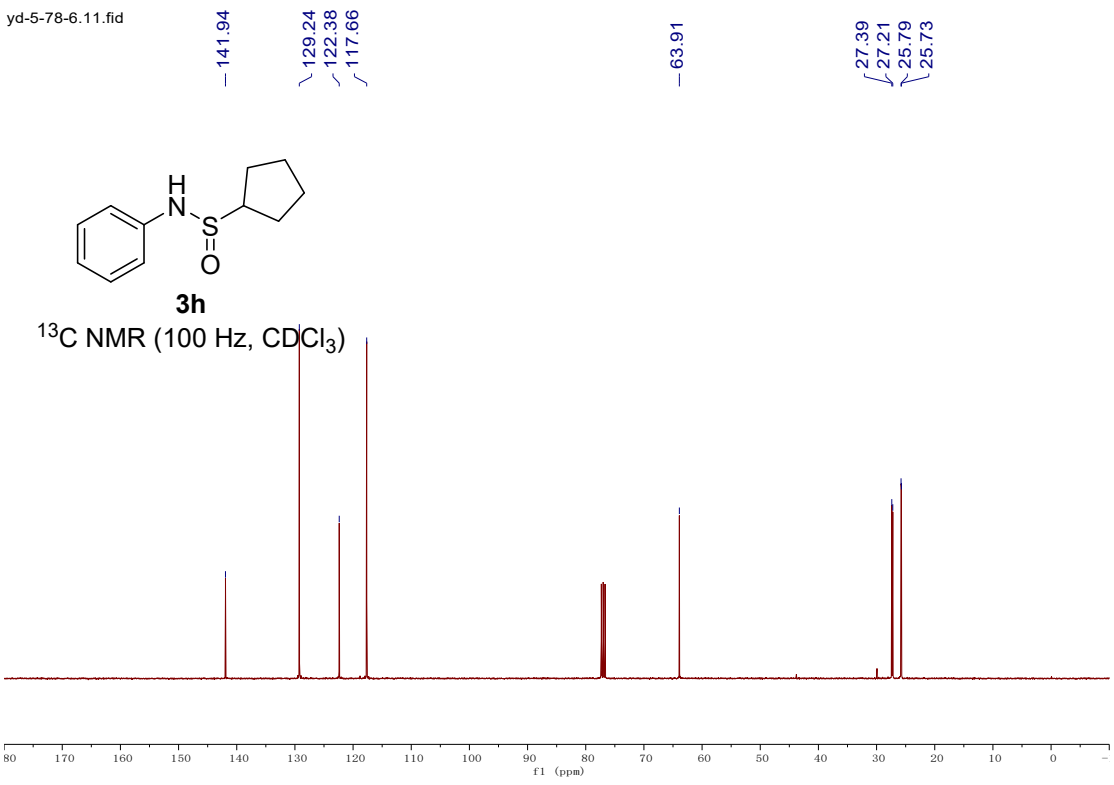
^{13}C NMR (100 Hz, $CDCl_3$)

N-phenylcyclopentanesulfinamide (3h)



3h

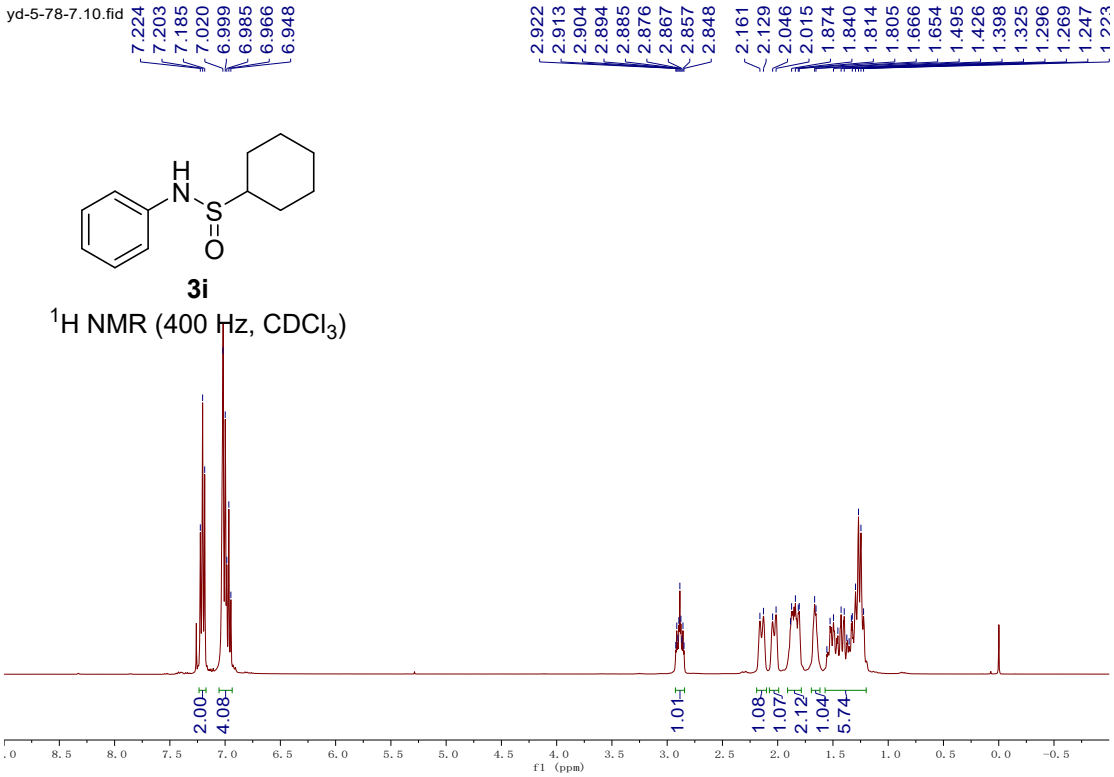
^{1}H NMR (400 Hz, $CDCl_3$)

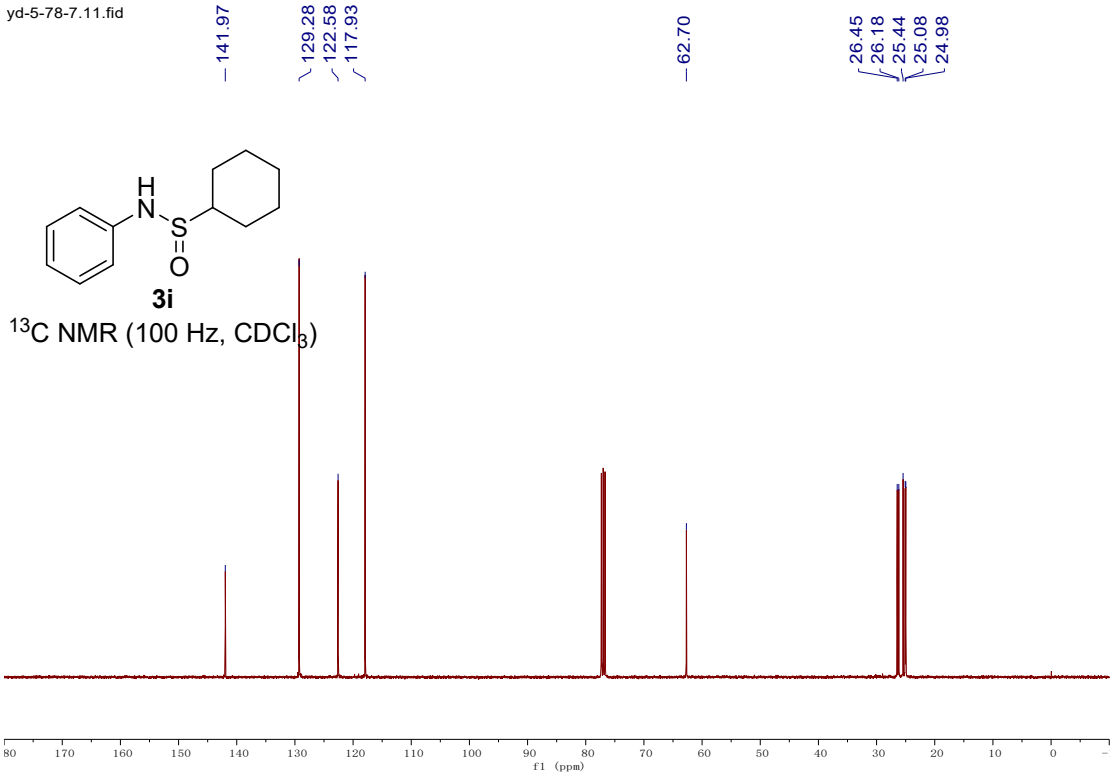


3h

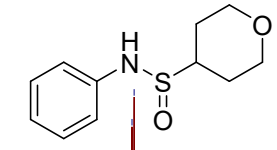
^{13}C NMR (100 Hz, $CDCl_3$)

N-phenylcyclohexanesulfinamide (3i)



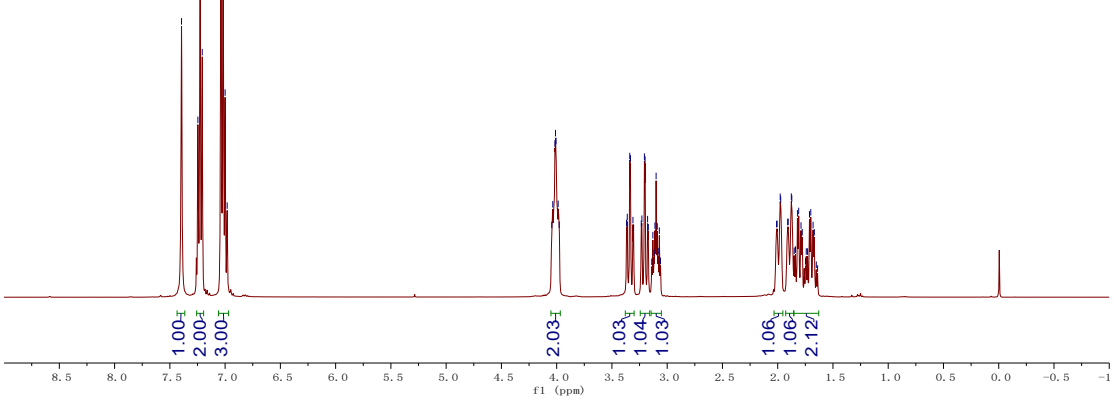


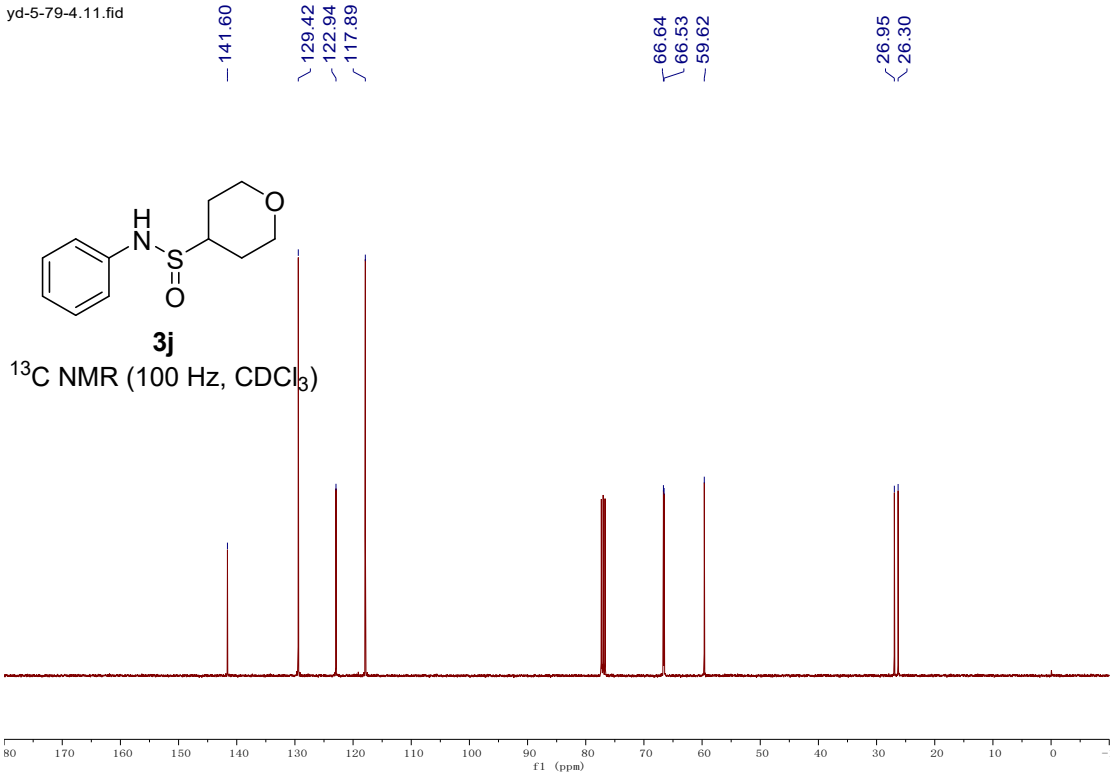
N-phenyltetrahydro-2H-pyran-4-sulfinamide (3j)



3j

^{1}H NMR (400 Hz, $CDCl_3$)

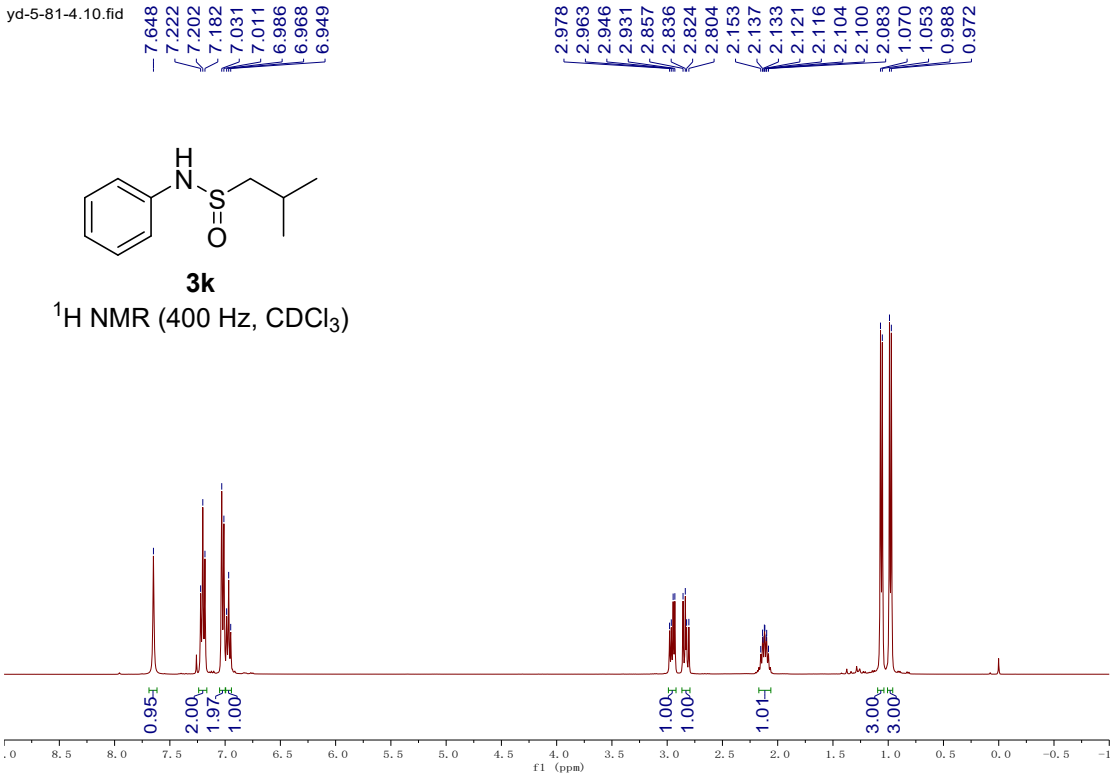




3j

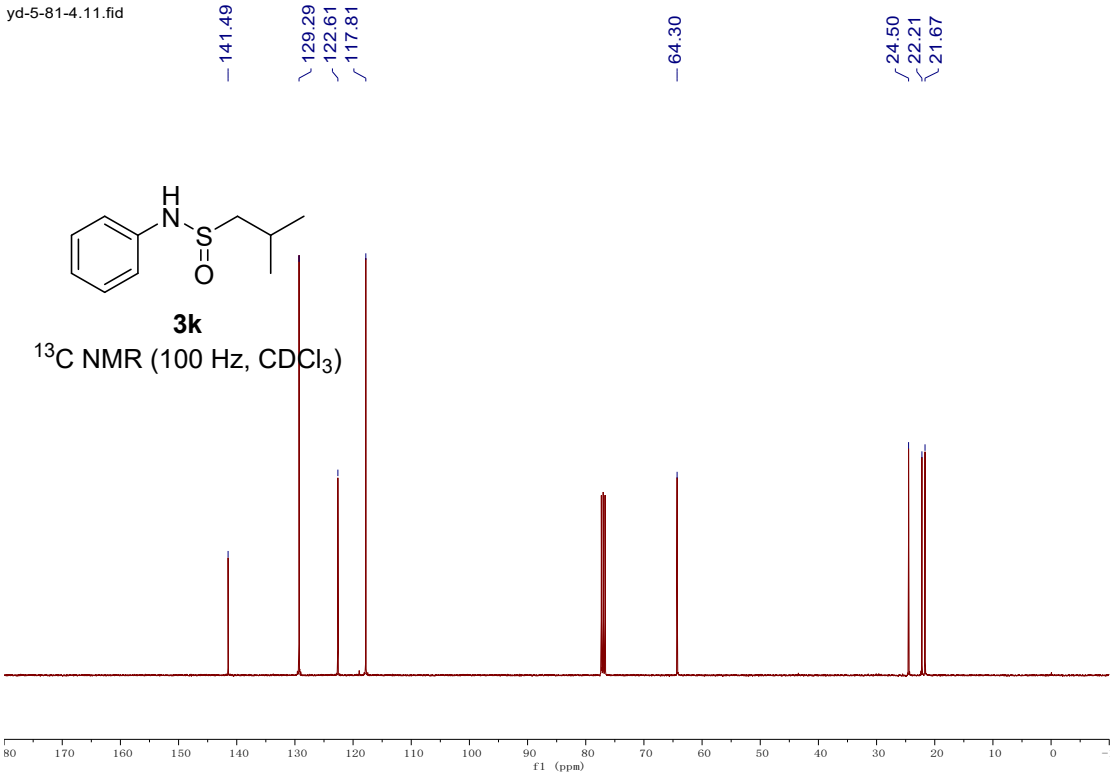
^{13}C NMR (100 Hz, $CDCl_3$)

2-Methyl-*N*-phenylpropane-1-sulfinamide (3k)



3k

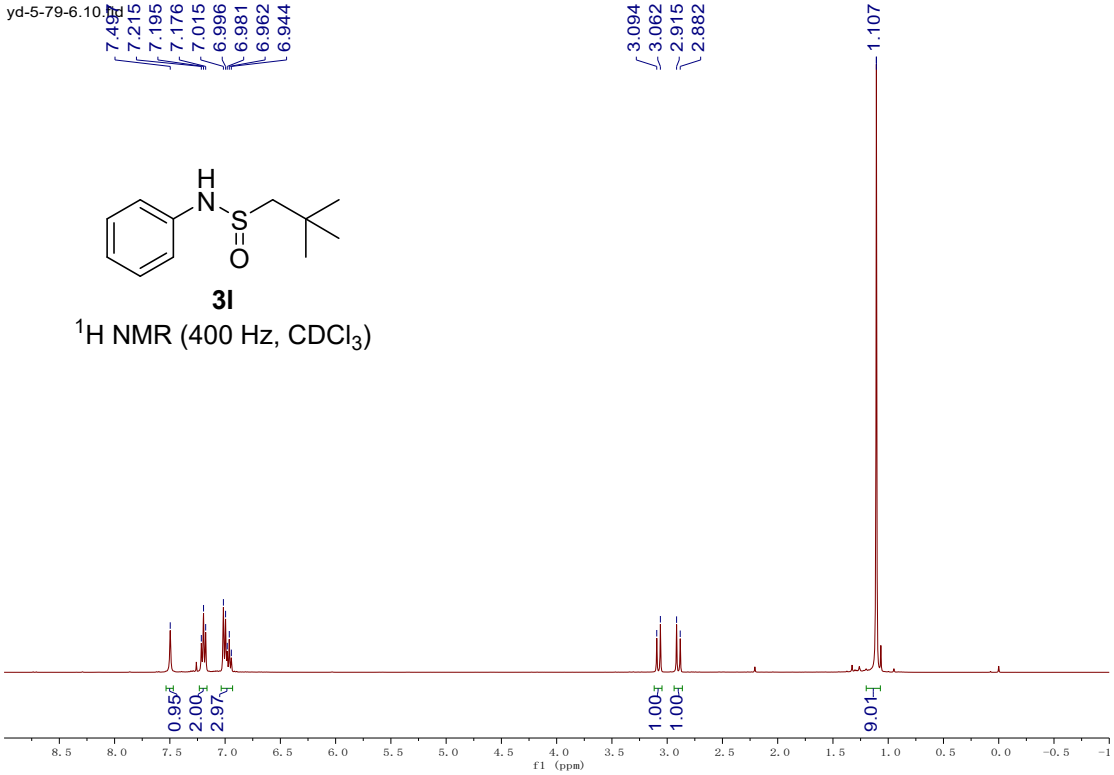
^{1}H NMR (400 Hz, $CDCl_3$)



3k

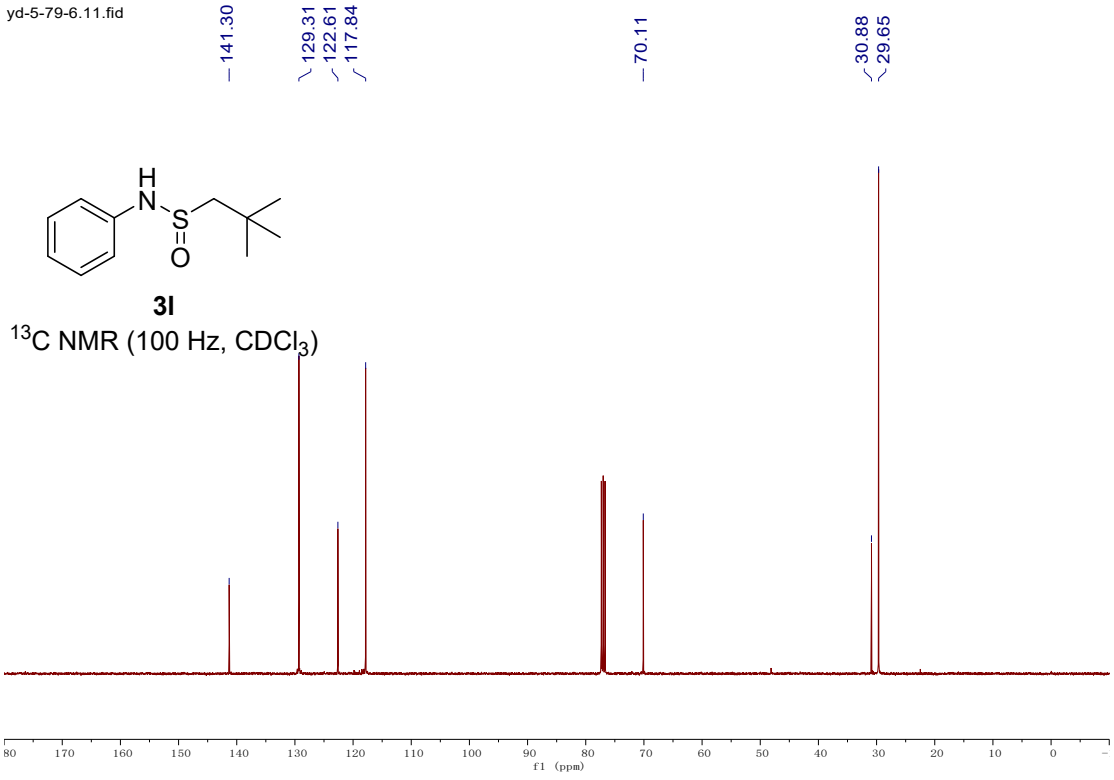
^{13}C NMR (100 Hz, $CDCl_3$)

2,2-dimethyl-*N*-phenylpropane-1-sulfinamide (3l)



3l

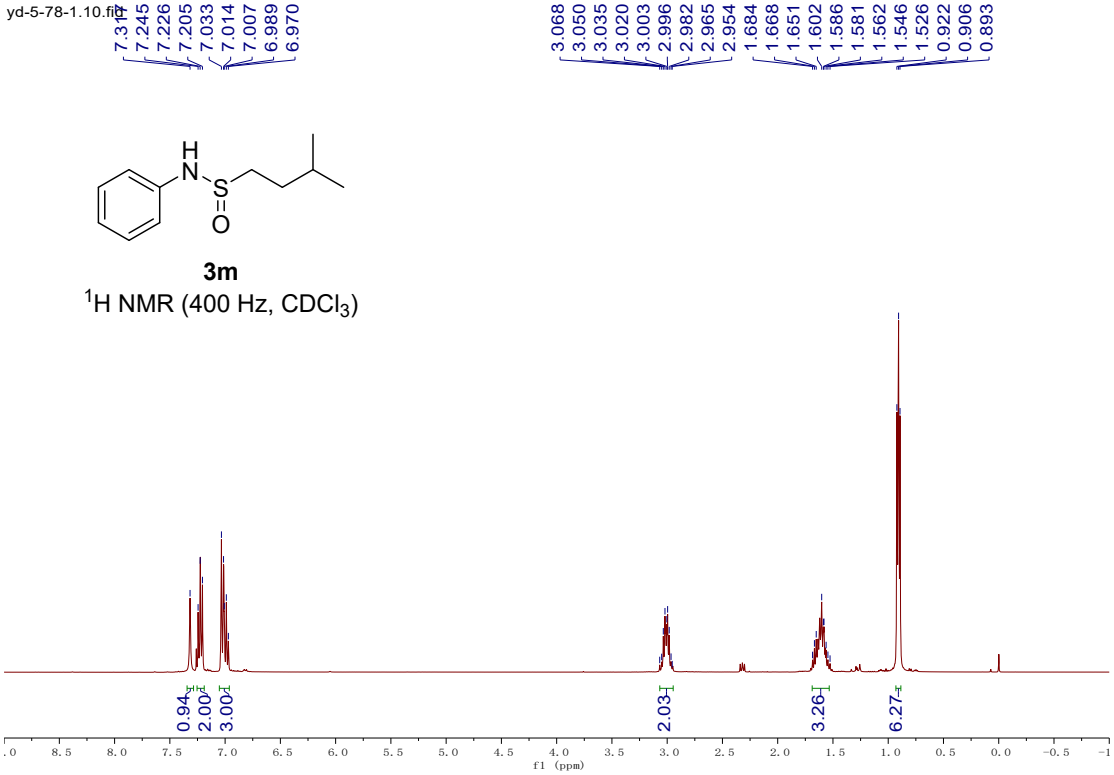
^{1}H NMR (400 Hz, $CDCl_3$)



3l

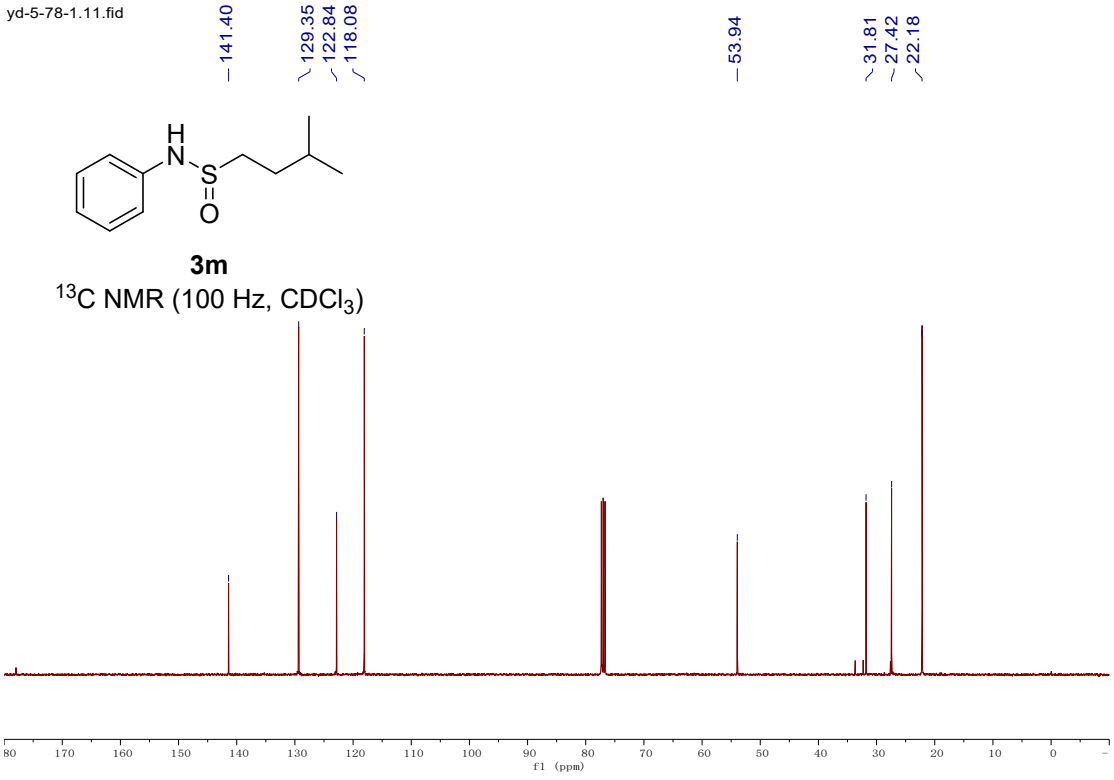
^{13}C NMR (100 Hz, $CDCl_3$)

3-Methyl-*N*-phenylbutane-1-sulfinamide (3m)



3m

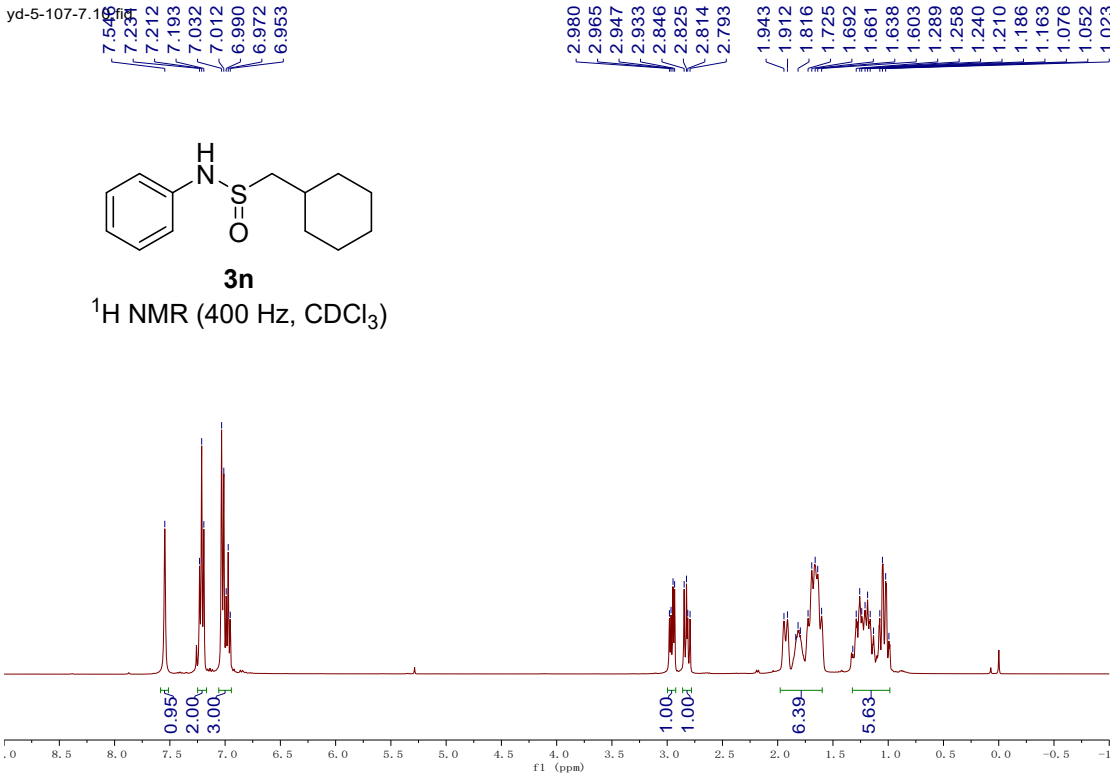
^{1}H NMR (400 Hz, $CDCl_3$)



3m

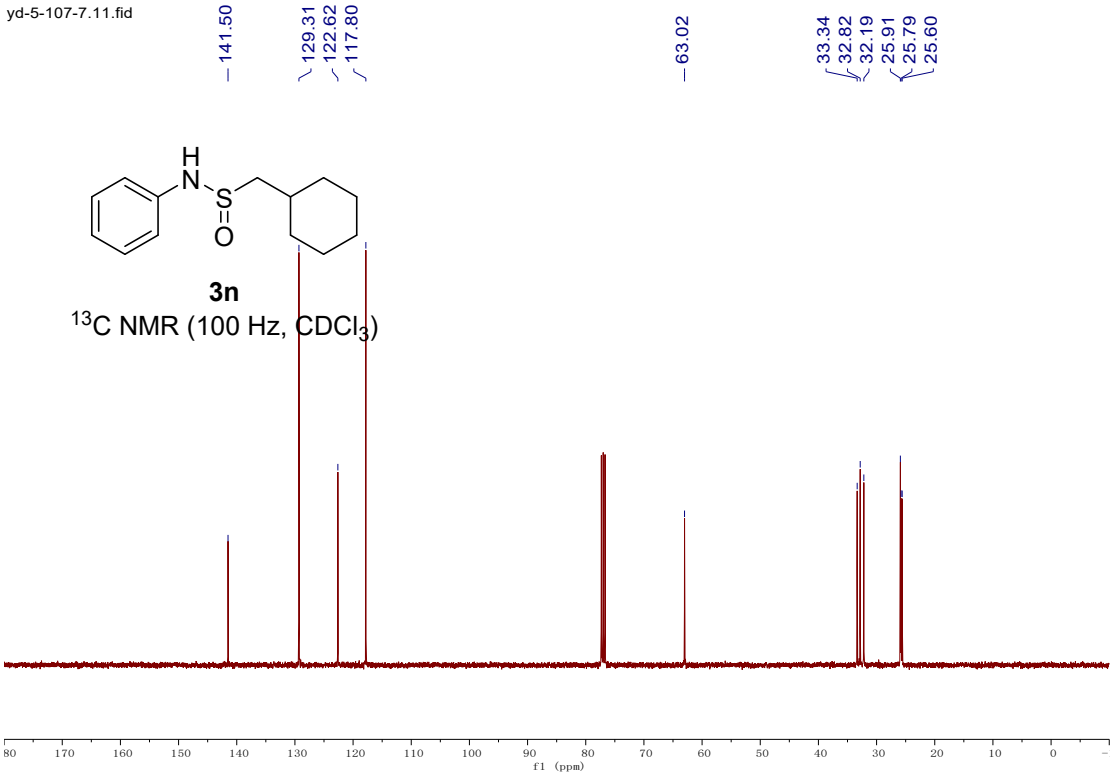
^{13}C NMR (100 Hz, $CDCl_3$)

1-cyclohexyl-*N*-phenylmethanesulfinamide (3n)



3n

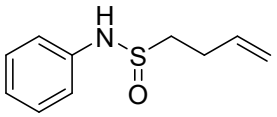
^{1}H NMR (400 Hz, $CDCl_3$)



3n

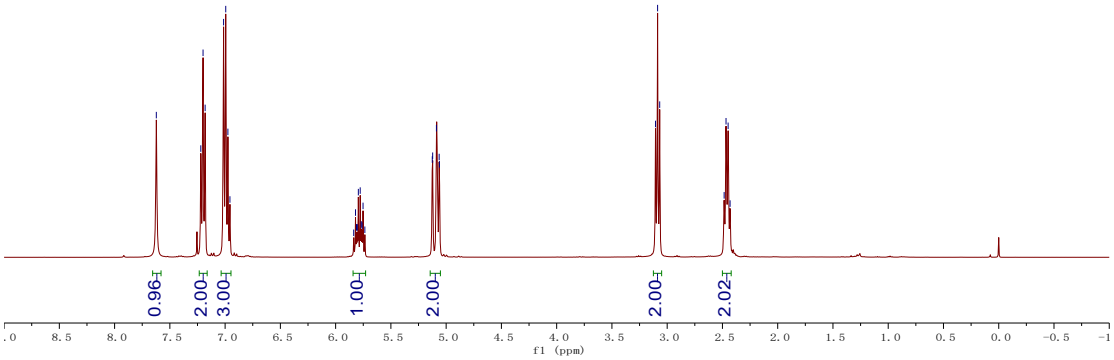
^{13}C NMR (100 Hz, $CDCl_3$)

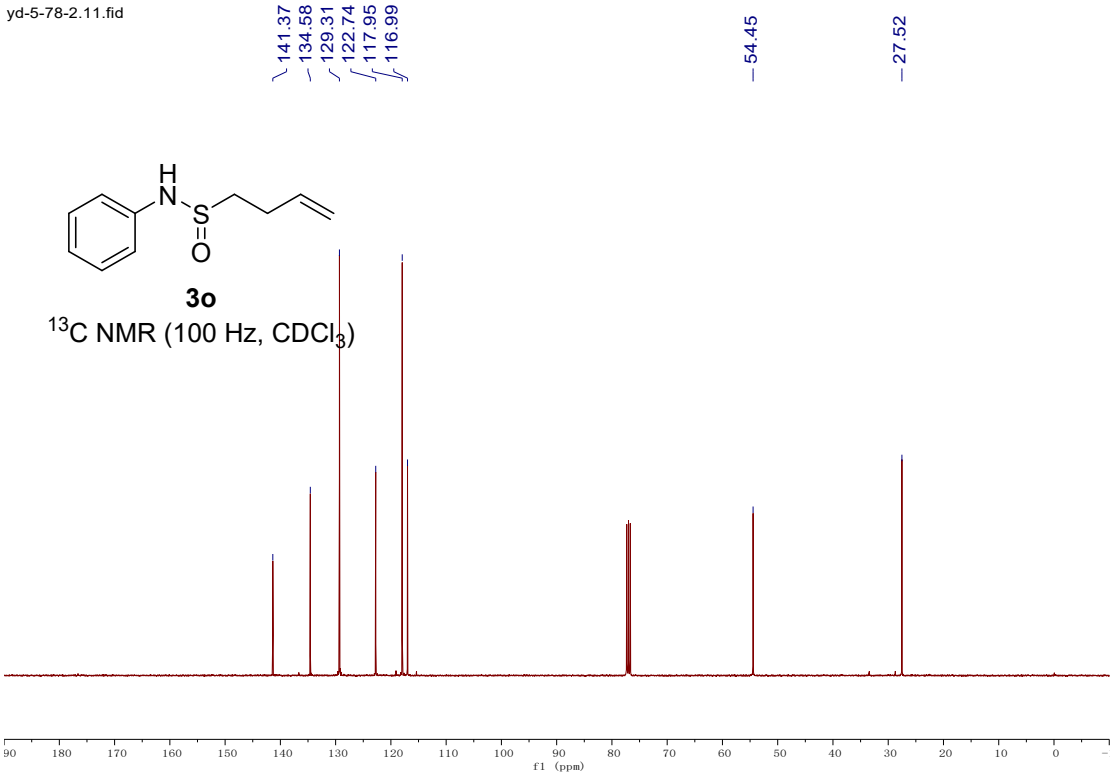
N-phenylbut-3-ene-1-sulfinamide (3o)



3o

^{1}H NMR (400 Hz, $CDCl_3$)

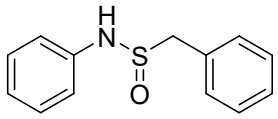




3o

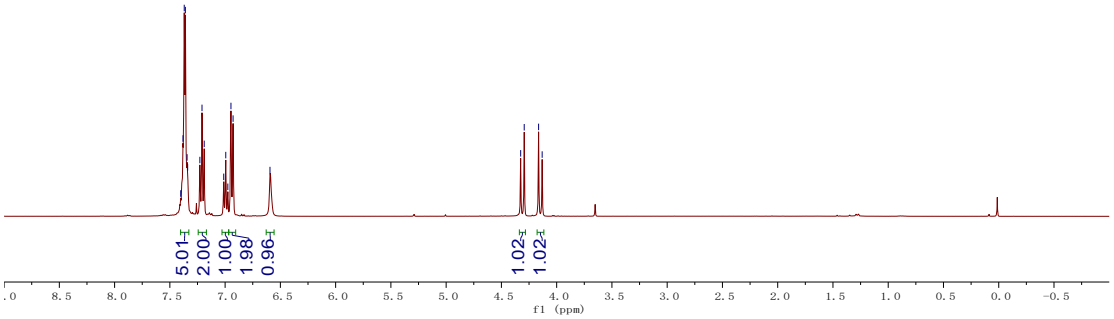
^{13}C NMR (100 Hz, $CDCl_3$)

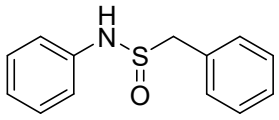
***N*,1-diphenylmethanesulfinamide (3p)**



3p

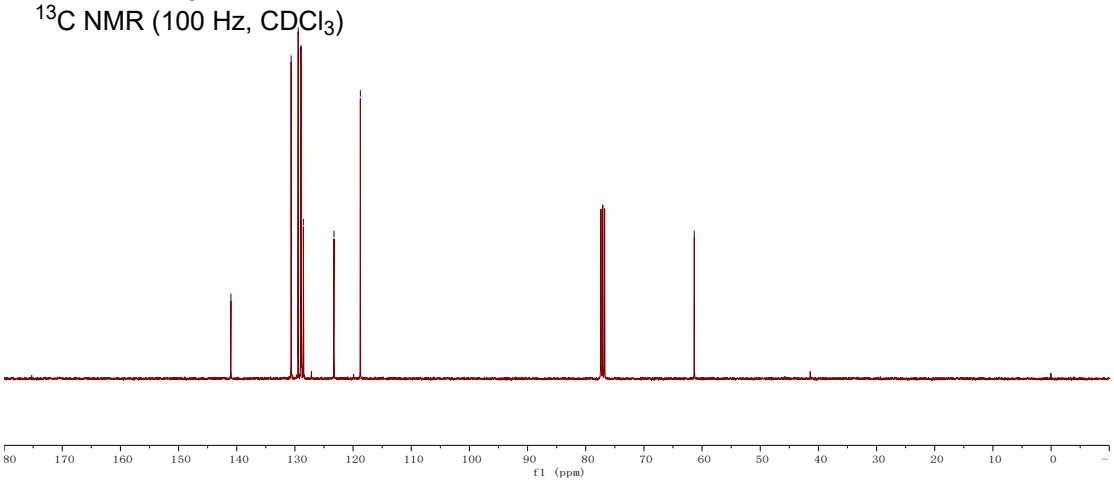
^{1}H NMR (400 Hz, $CDCl_3$)



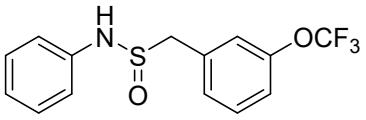


3p

^{13}C NMR (100 Hz, $CDCl_3$)

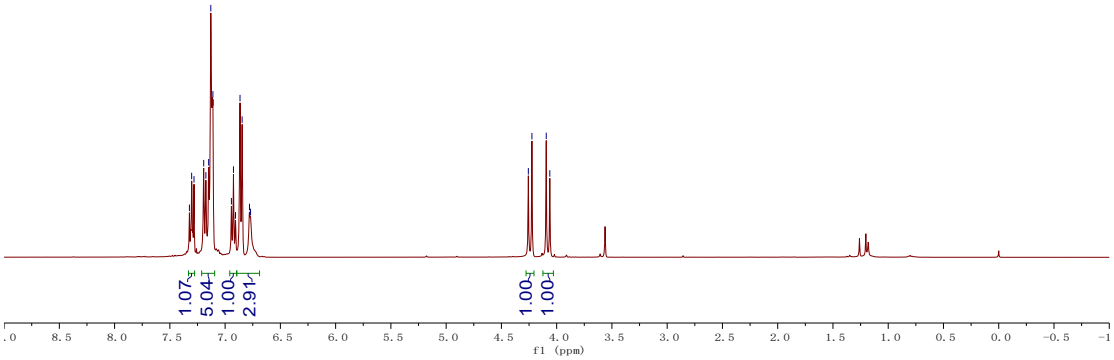


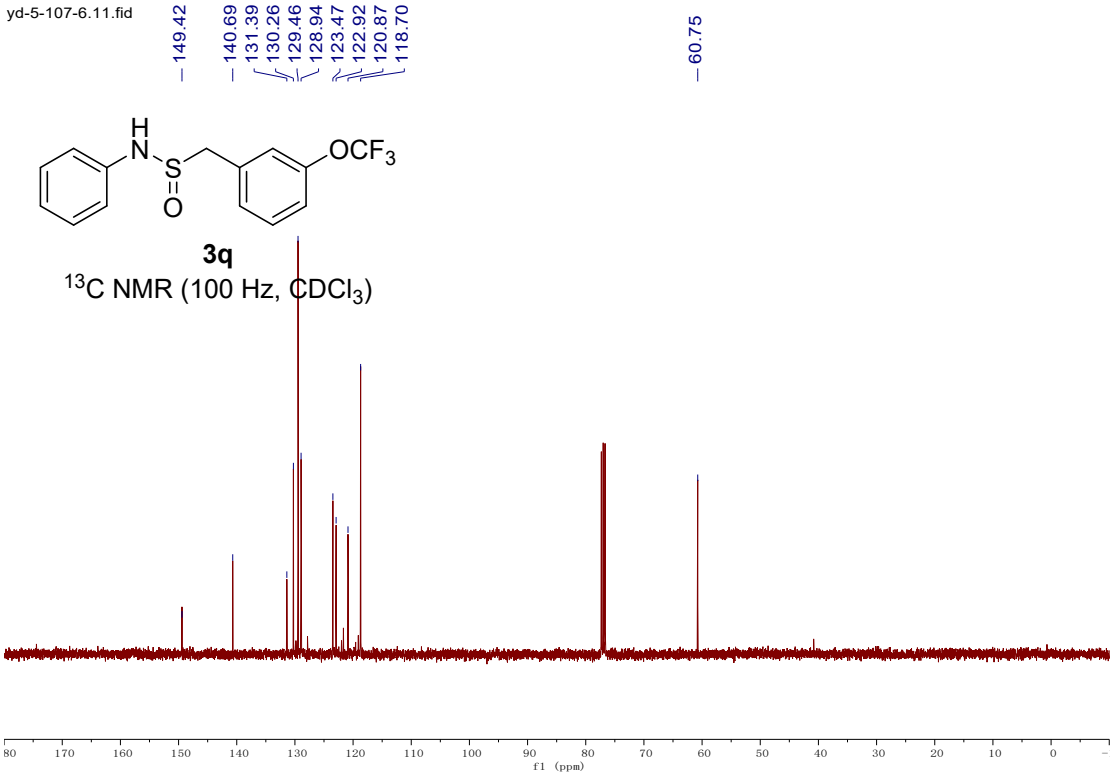
***N*-phenyl-1-(3-(trifluoromethoxy)phenyl)methanesulfinamide (3q)**



3q

^{1}H NMR (400 Hz, $CDCl_3$)

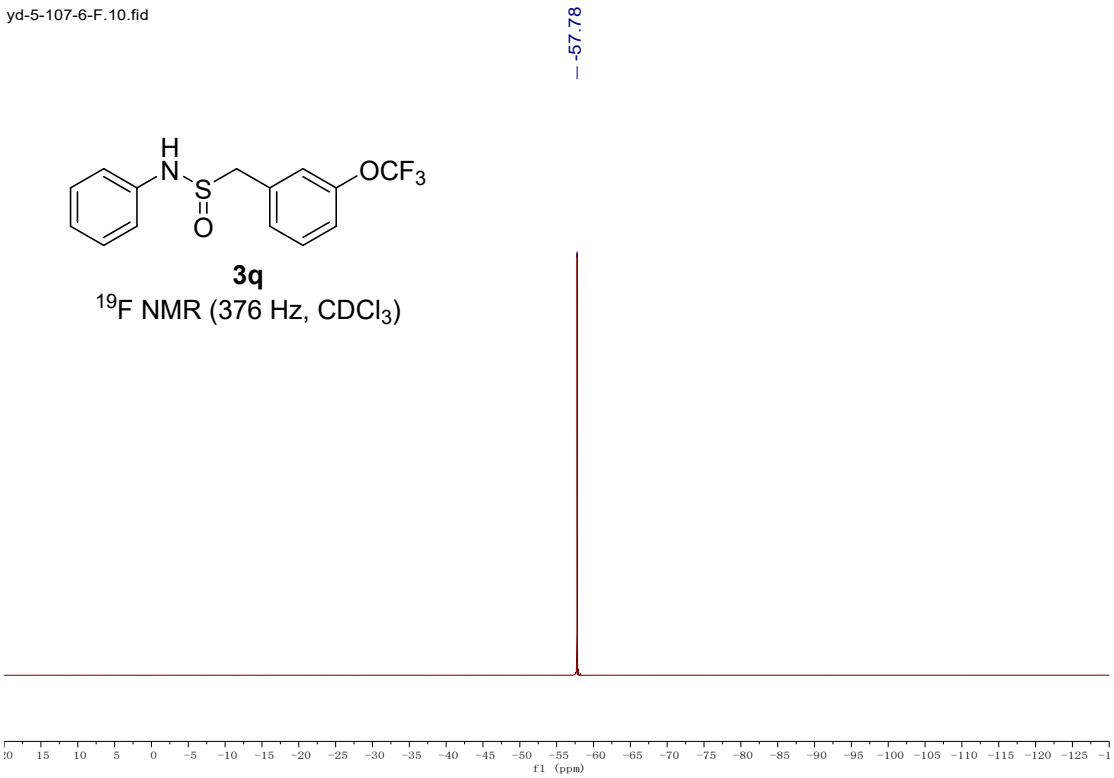




3q

^{13}C NMR (100 Hz, $CDCl_3$)

yd-5-107-6-F.10.fid

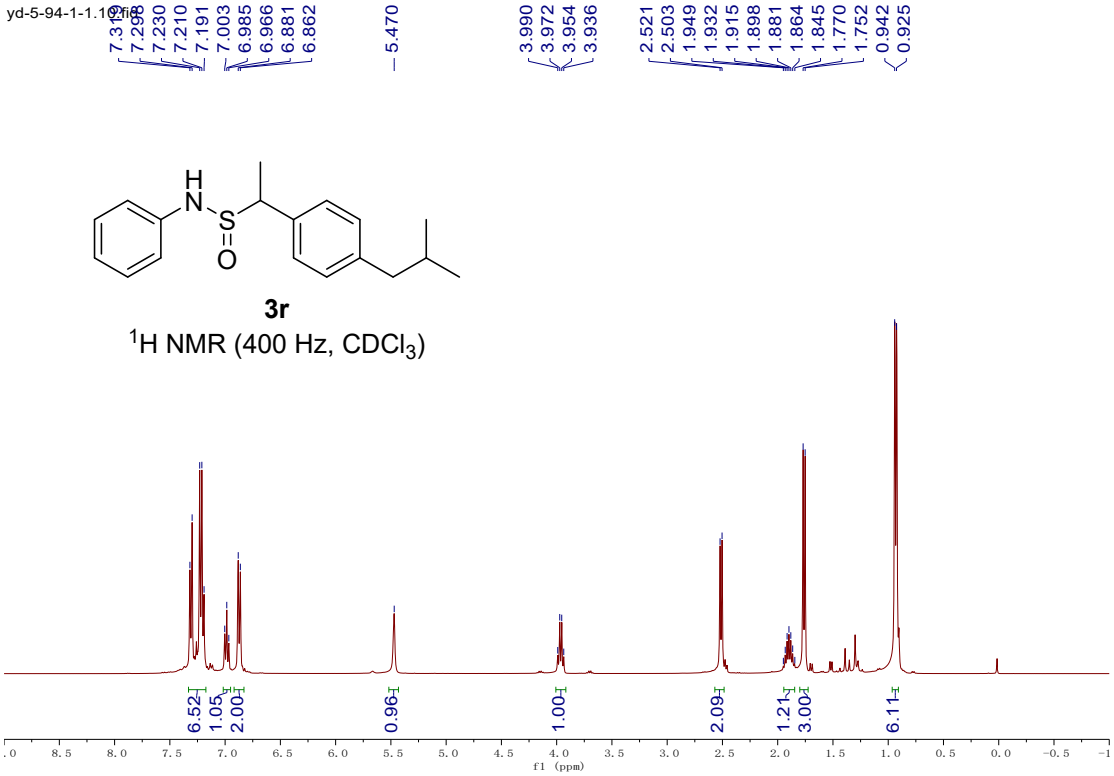


3q

^{19}F NMR (376 Hz, $CDCl_3$)

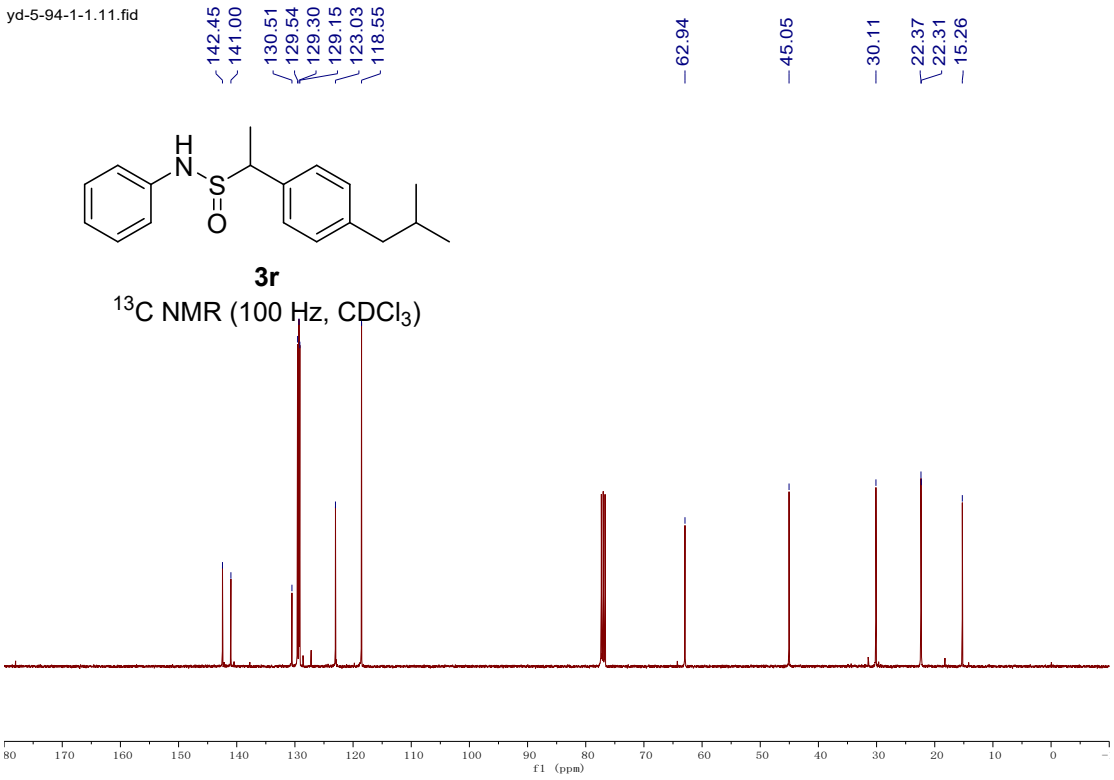
1-(4-isobutylphenyl)-*N*-phenylethane-1-sulfinamide (3r)

yd-5-94-1-1.10.fid



3r

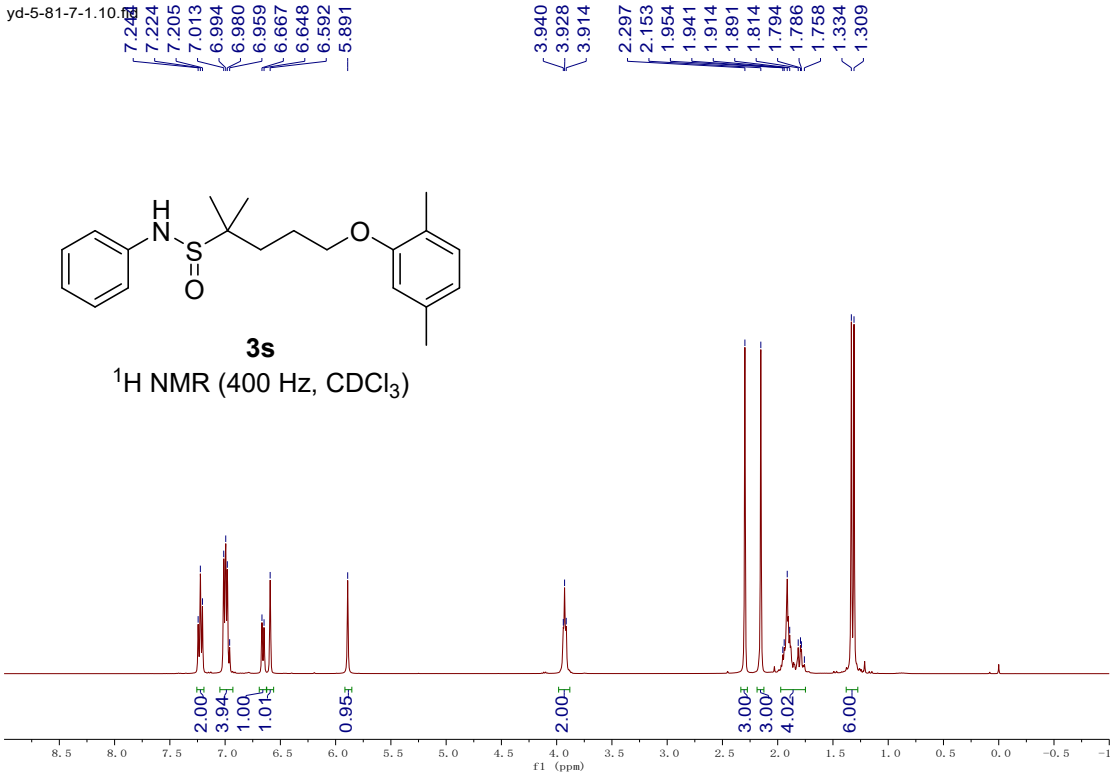
^{1}H NMR (400 Hz, $CDCl_3$)



3r

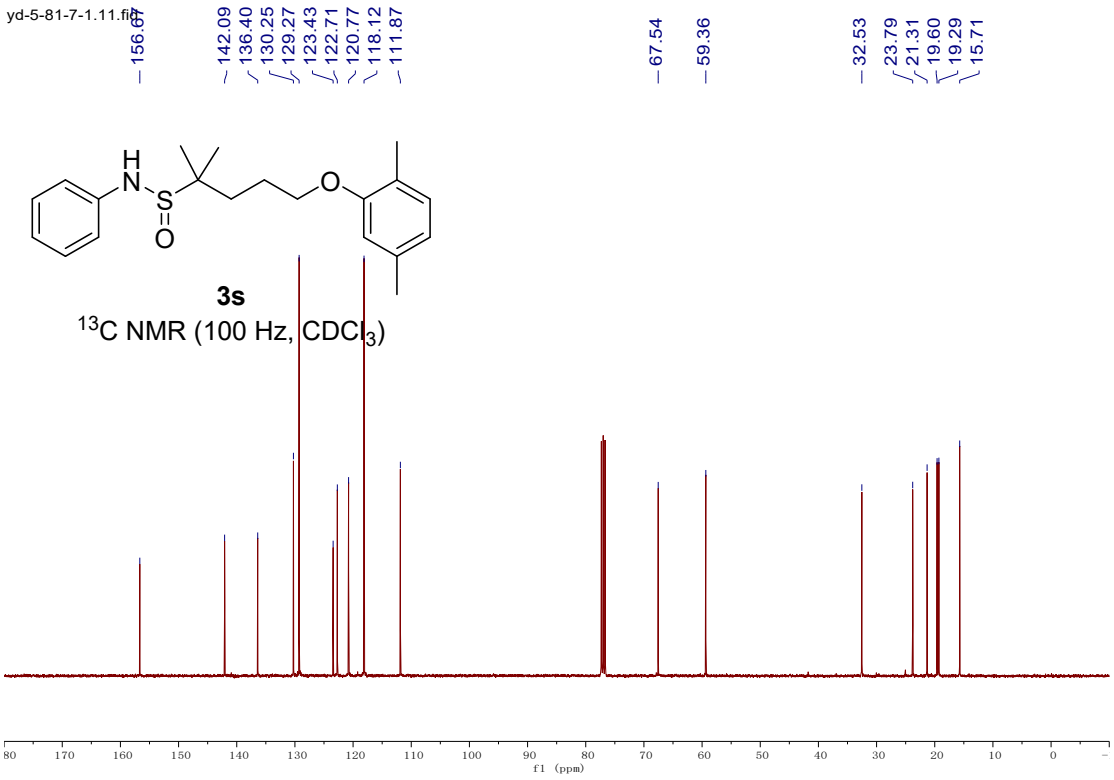
^{13}C NMR (100 Hz, $CDCl_3$)

5-(2,5-dimethylphenoxy)-2-methyl-*N*-phenylpentane-2-sulfinamide (3s)

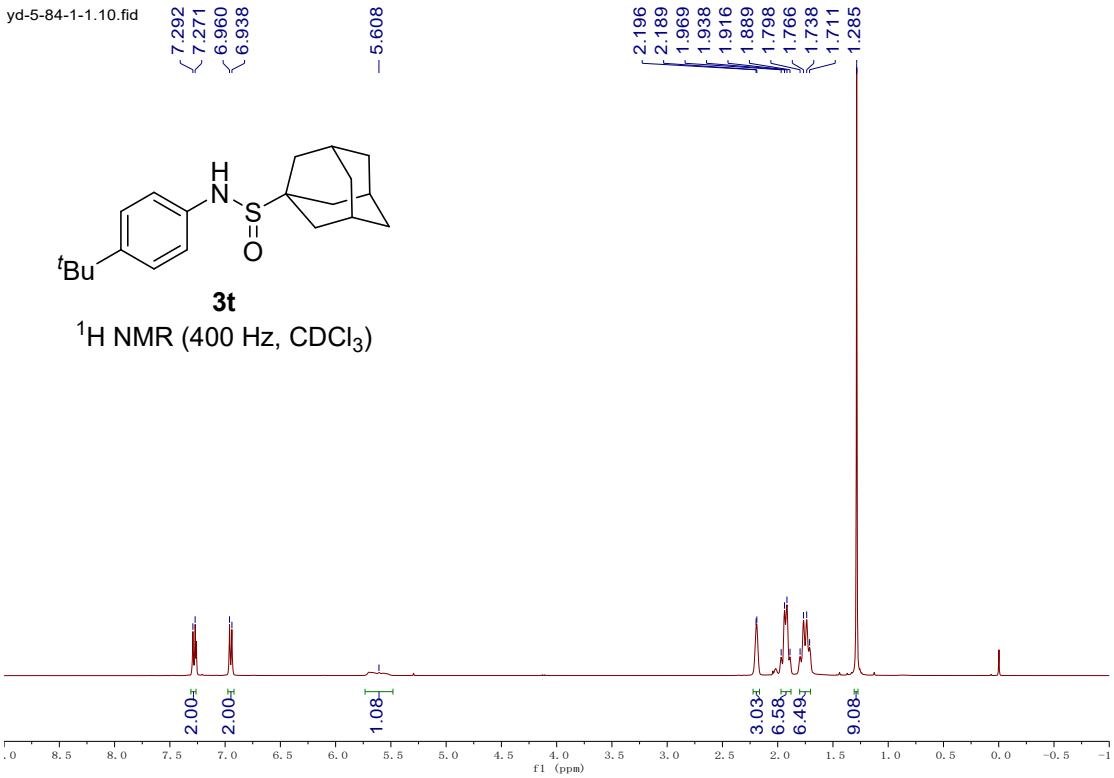


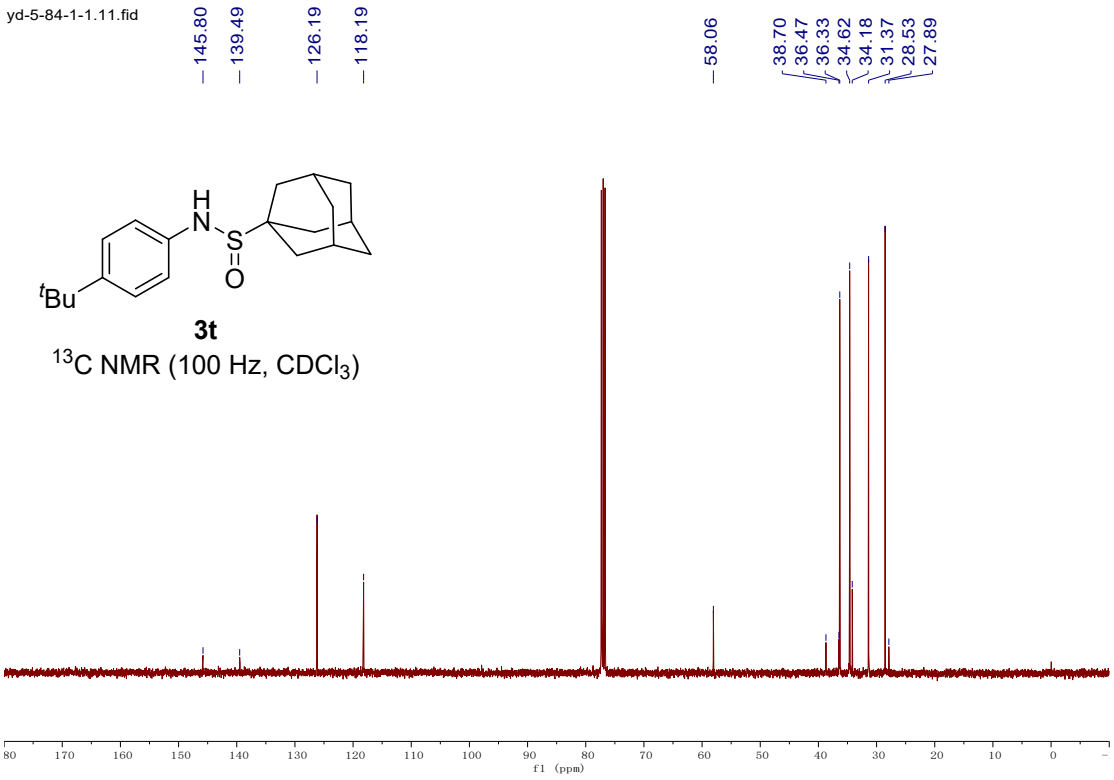
3s

^{1}H NMR (400 Hz, $CDCl_3$)



(3s,5s,7s)-*N*-(4-(*tert*-butyl)phenyl)adamantane-1-sulfinamide (3t)

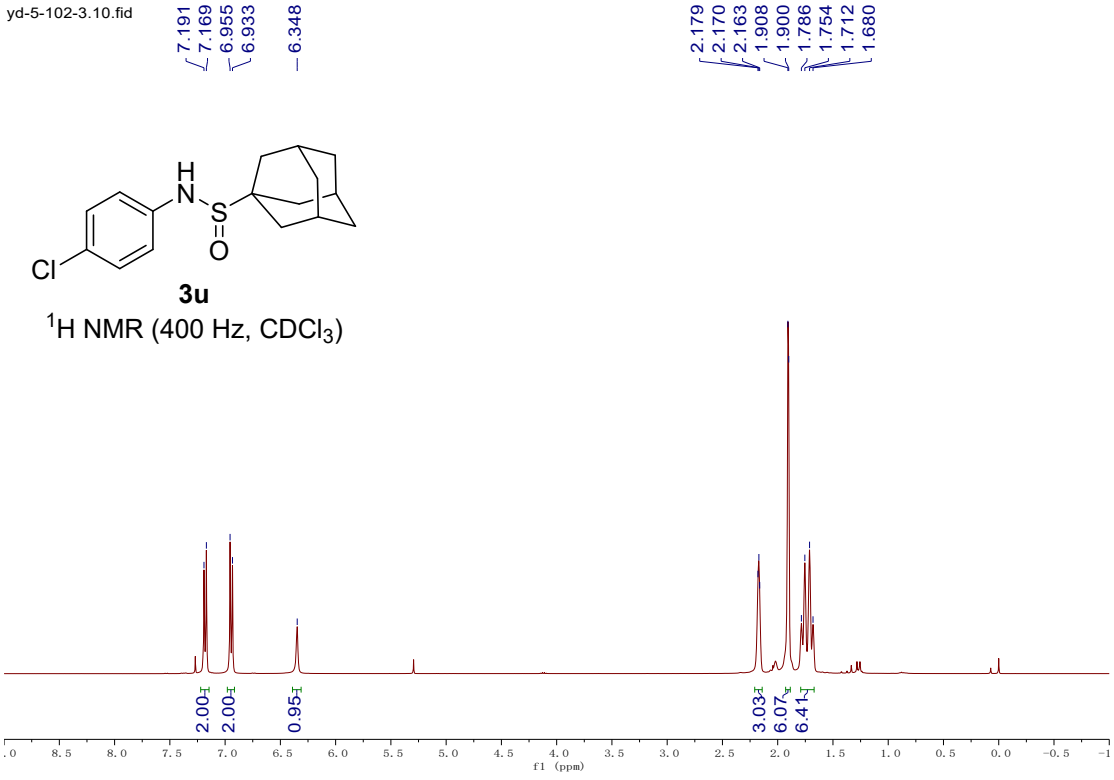




3t

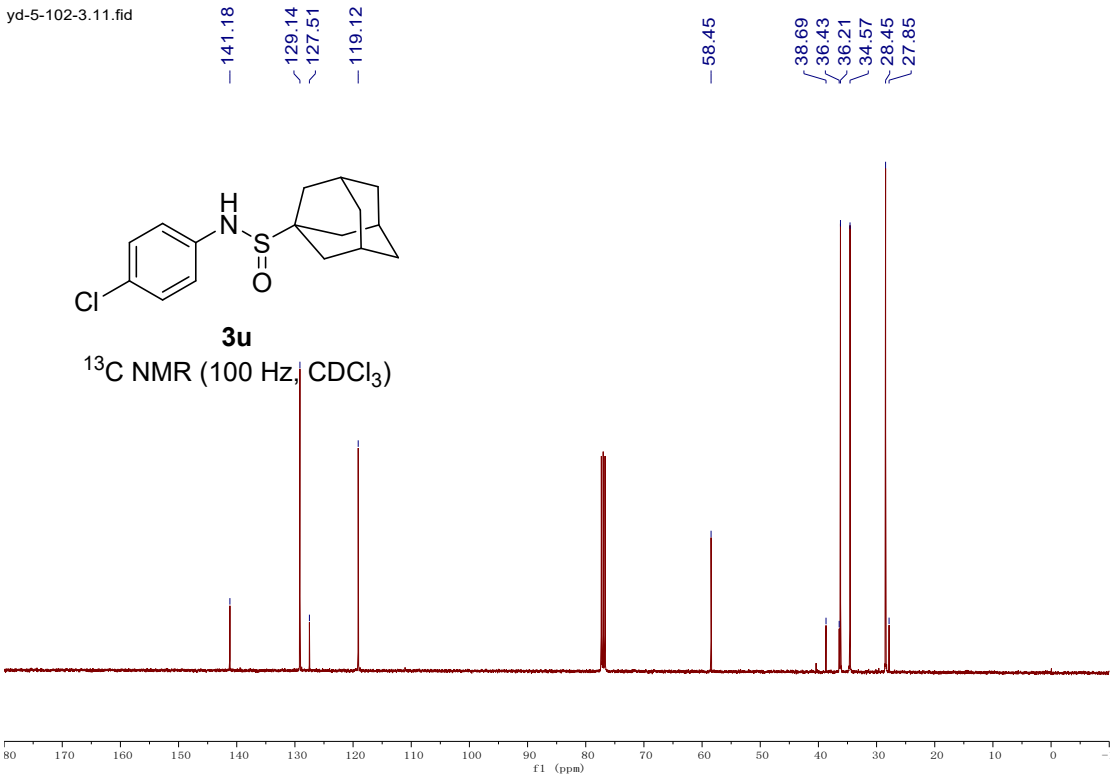
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(4-chlorophenyl)adamantane-1-sulfinamide (3u)



3u

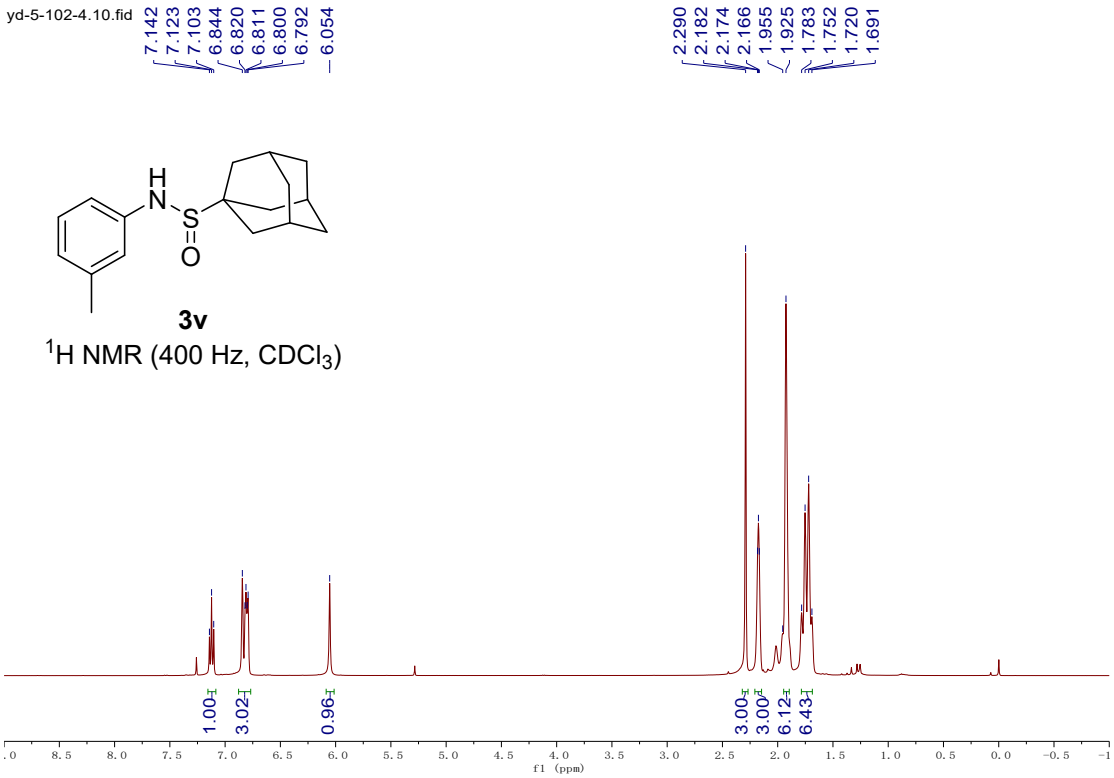
^{1}H NMR (400 Hz, $CDCl_3$)



3u

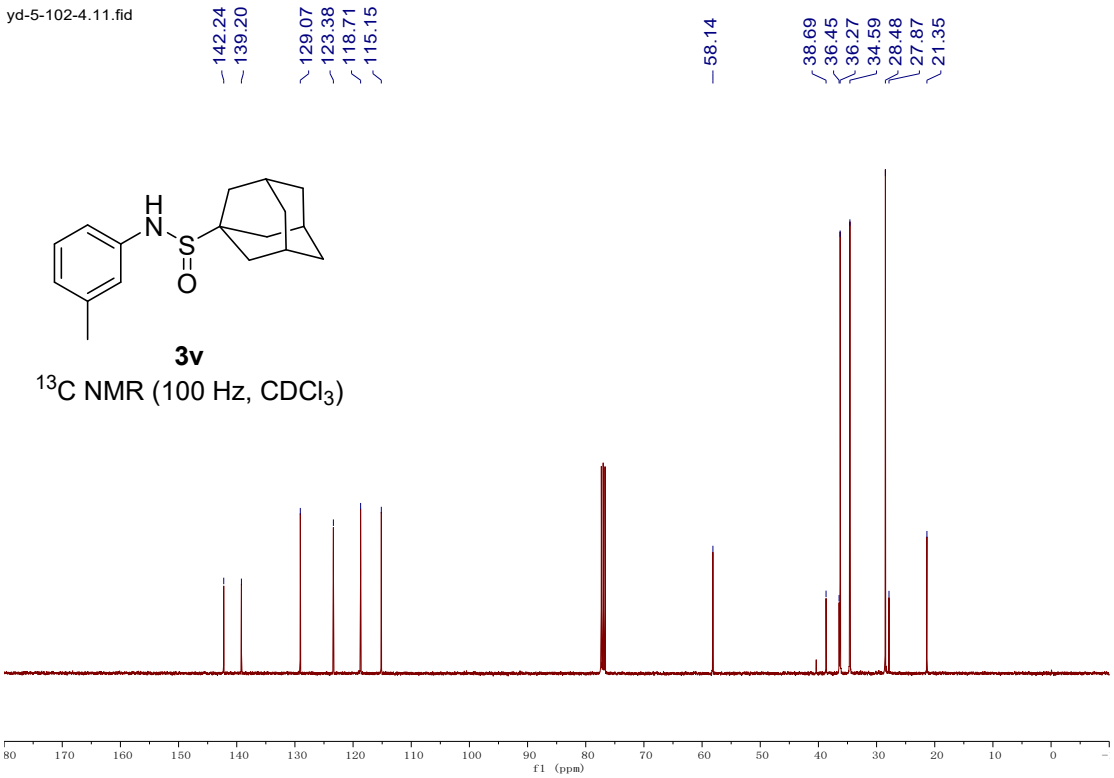
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(*m*-tolyl)adamantane-1-sulfinamide (3v)



3v

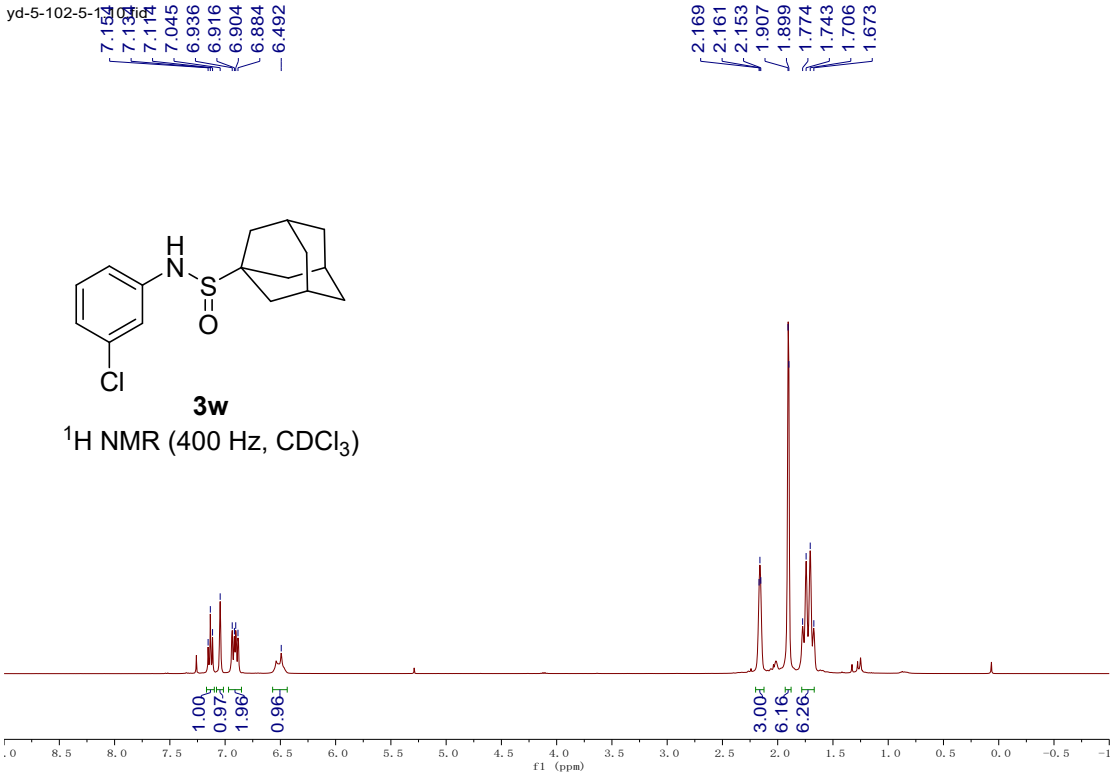
^{1}H NMR (400 Hz, $CDCl_3$)



3v

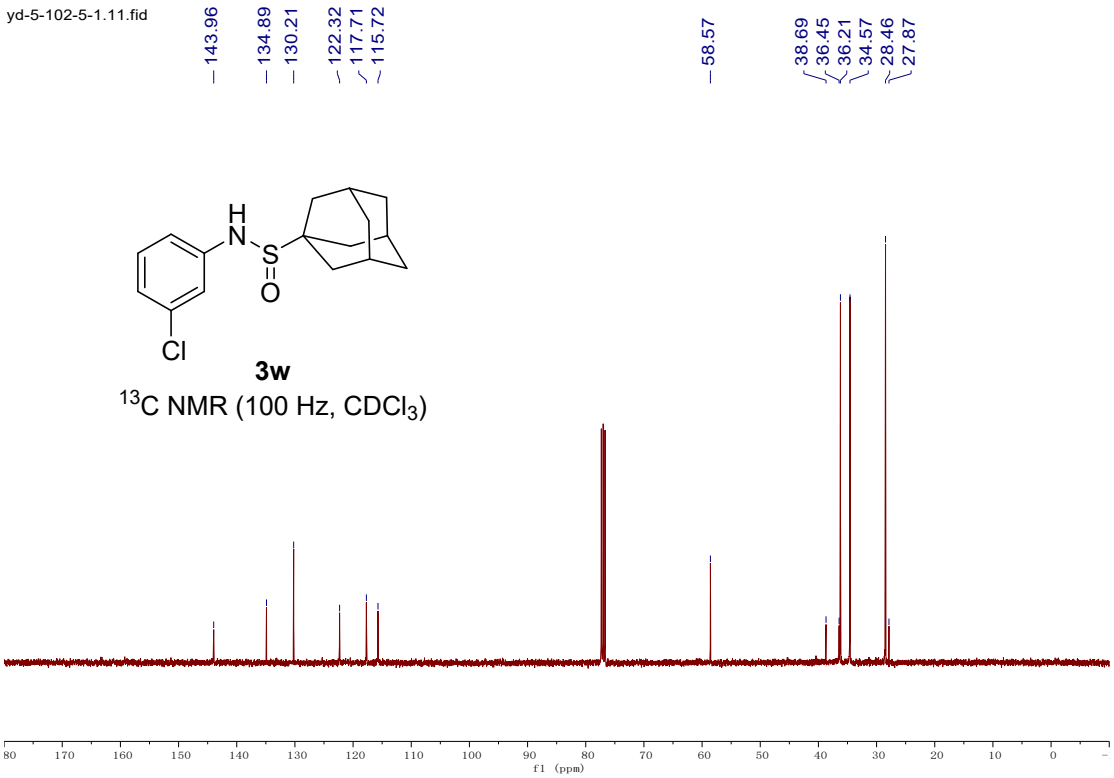
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(3-chlorophenyl)adamantane-1-sulfinamide (3w)



3w

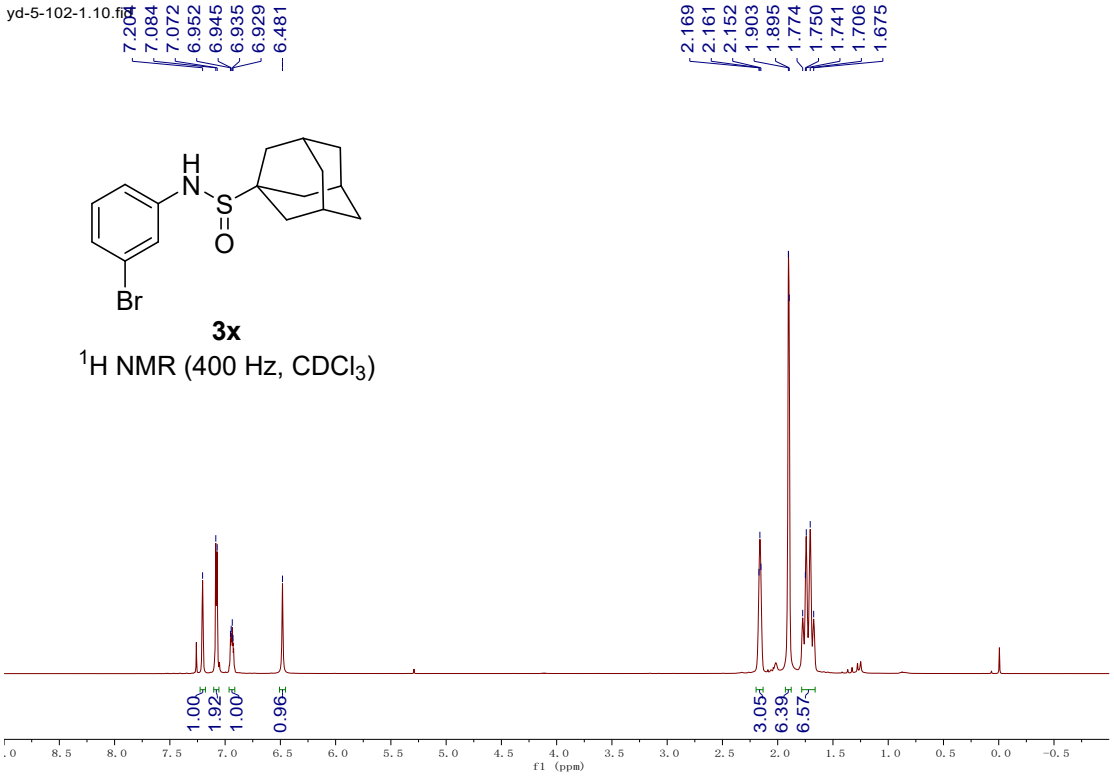
^{1}H NMR (400 Hz, $CDCl_3$)



3w

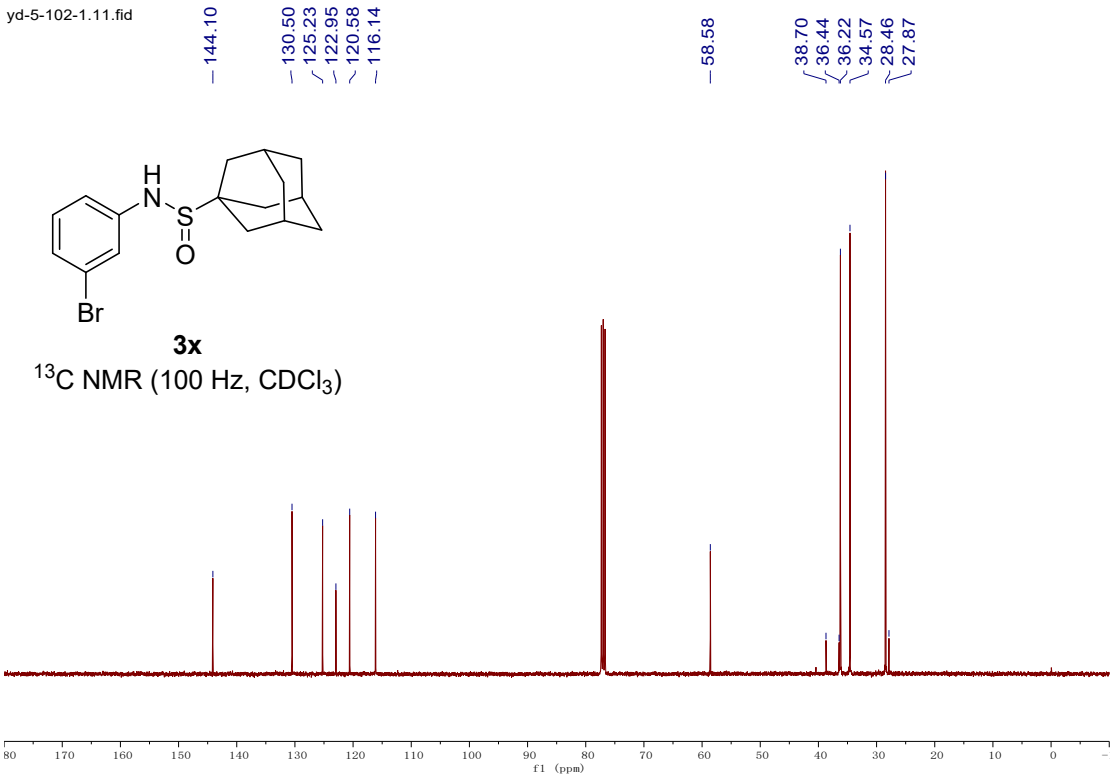
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(3-bromophenyl)adamantane-1-sulfinamide (3x)



3x

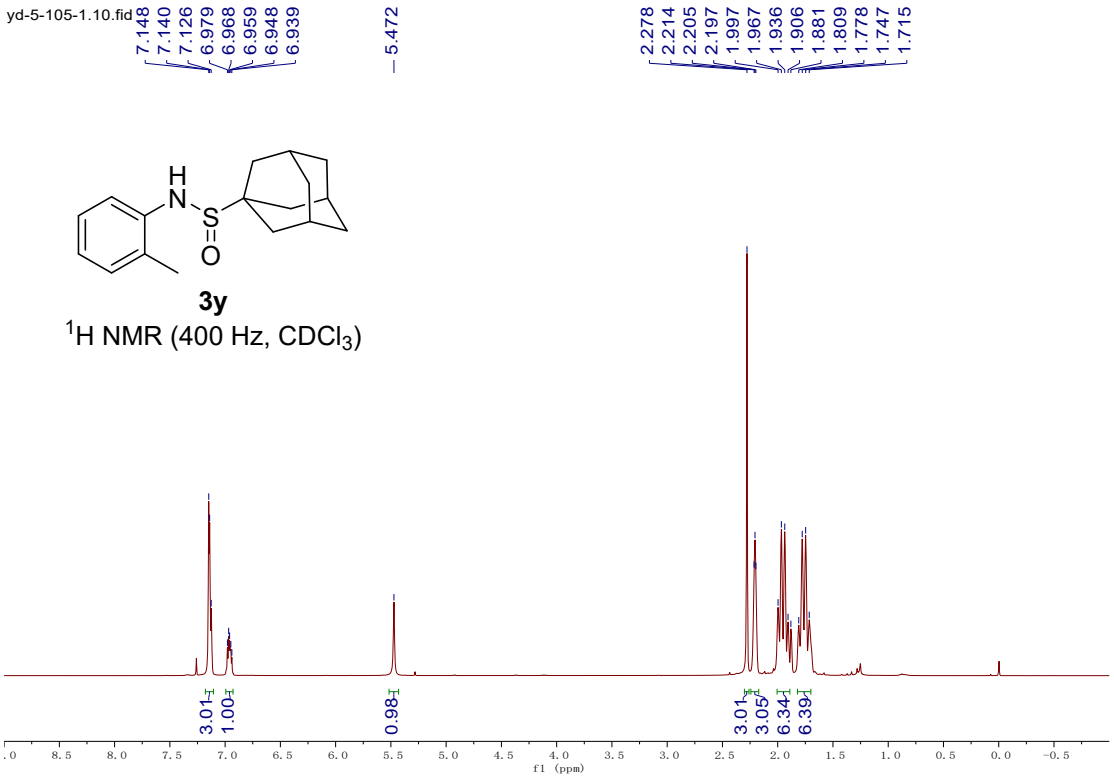
^{1}H NMR (400 Hz, $CDCl_3$)



3x

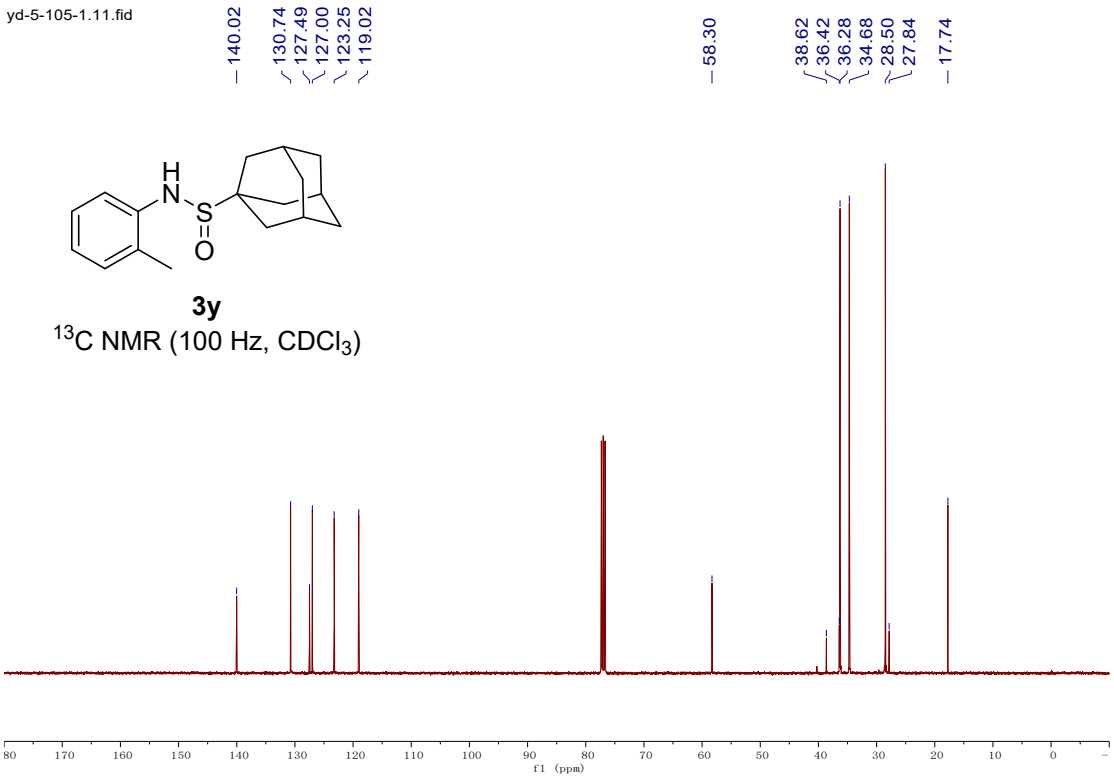
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(o-tolyl)adamantane-1-sulfinamide (3y)



3y

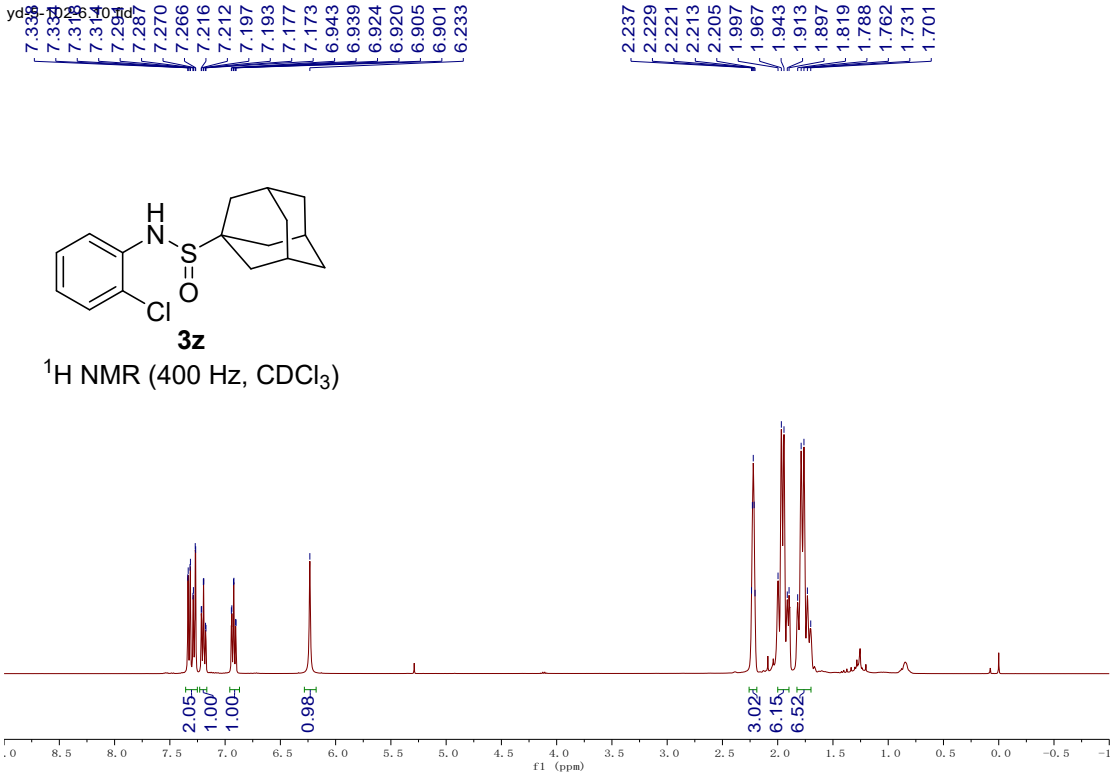
^{1}H NMR (400 Hz, $CDCl_3$)



3y

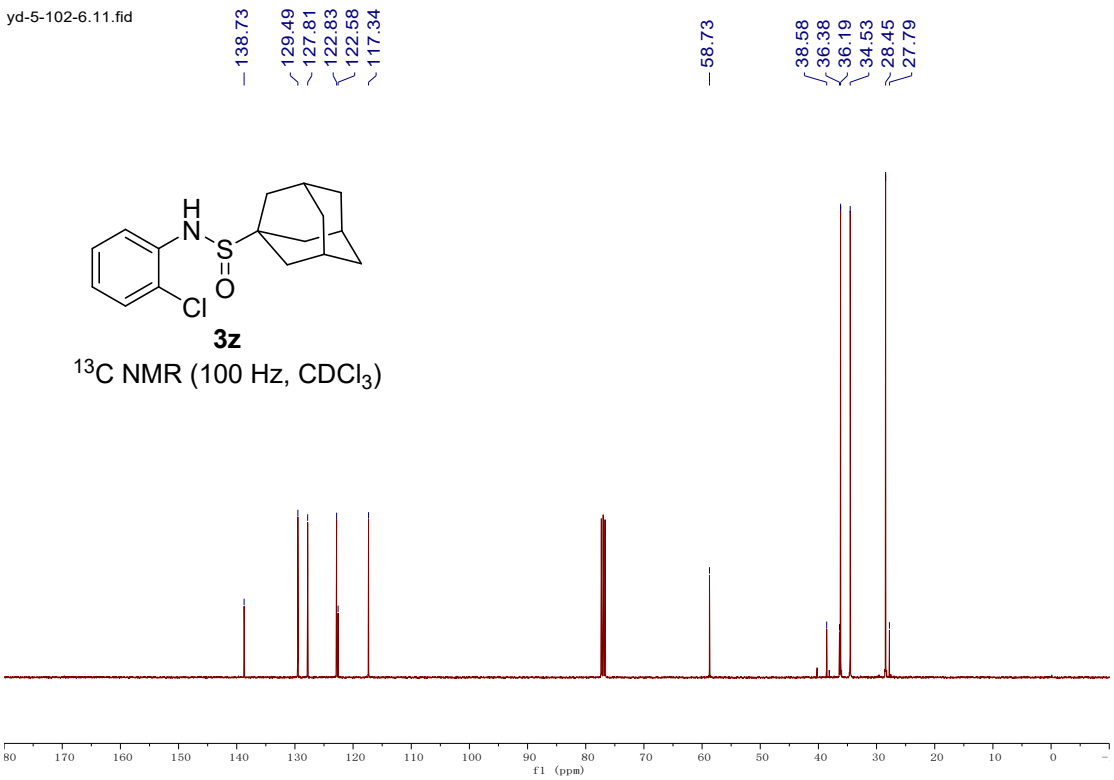
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(2-chlorophenyl)adamantane-1-sulfinamide (3z)



3z

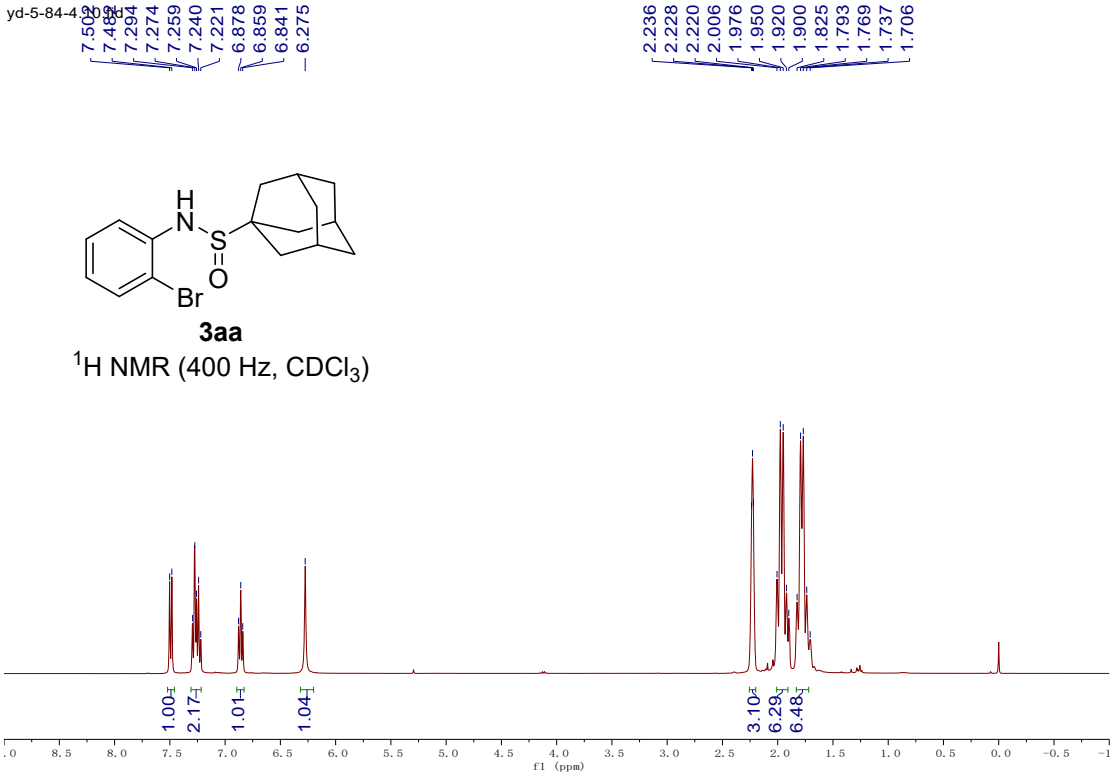
^{1}H NMR (400 Hz, $CDCl_3$)



3z

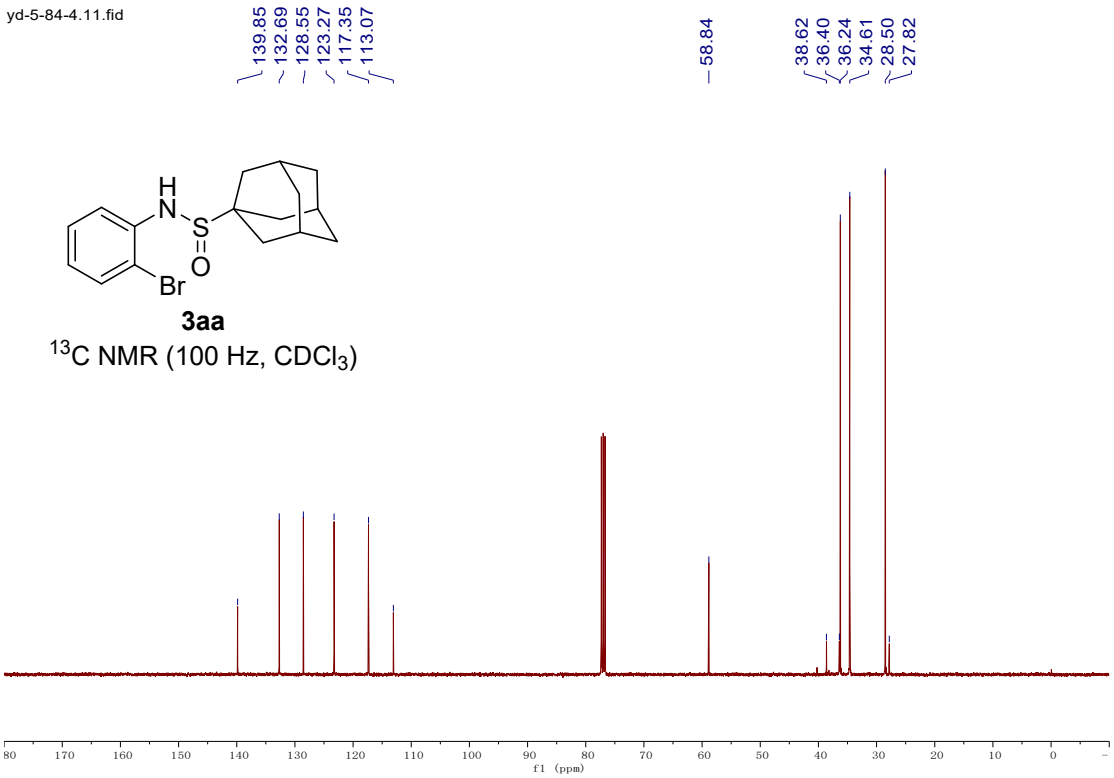
^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-(2-bromophenyl)adamantane-1-sulfinamide (3aa)



3aa

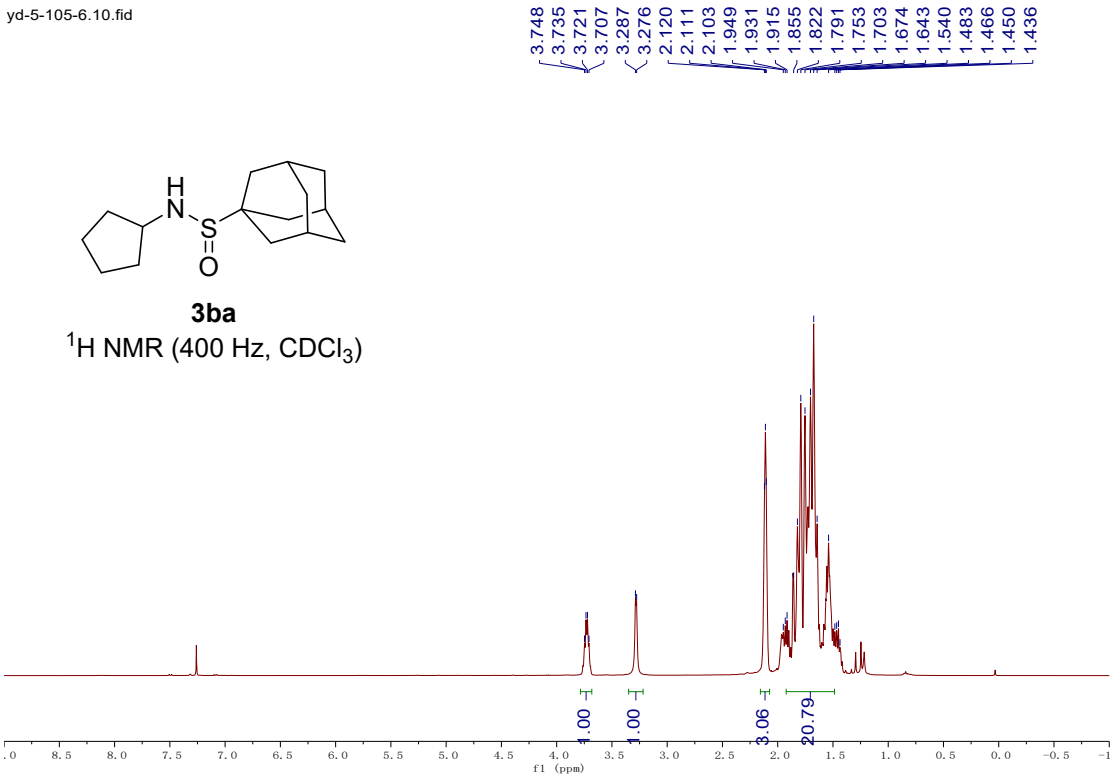
^{1}H NMR (400 Hz, $CDCl_3$)



3aa

^{13}C NMR (100 Hz, $CDCl_3$)

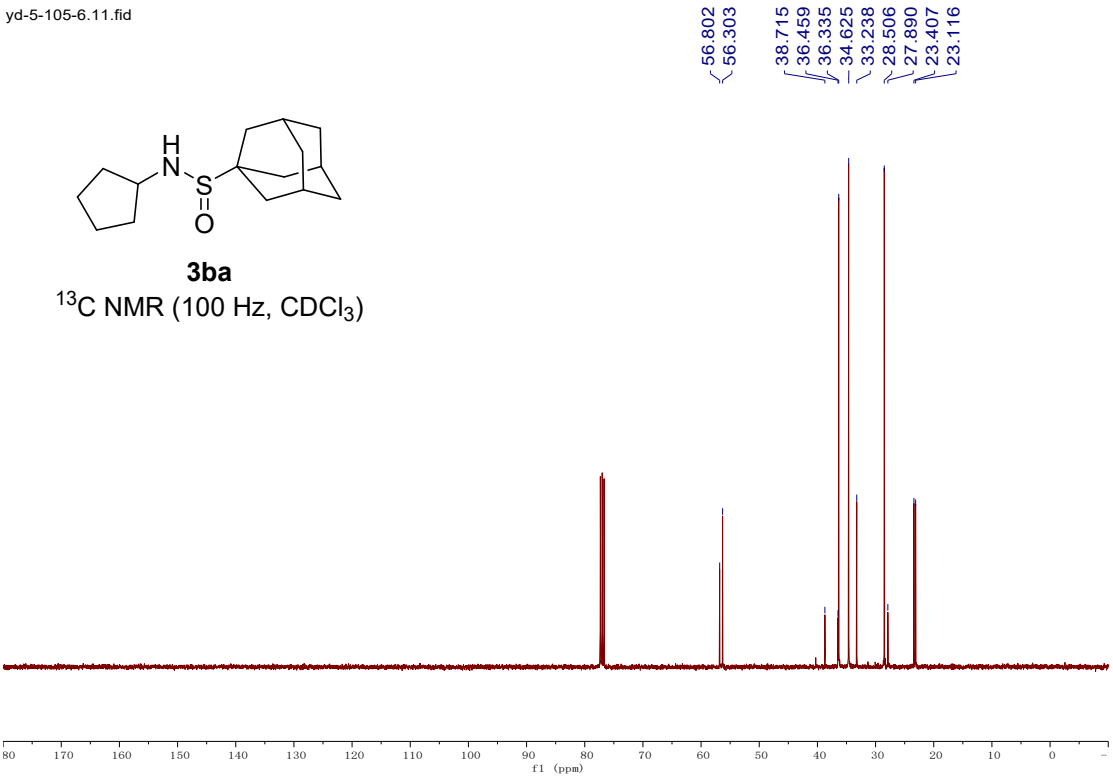
(3s,5s,7s)-*N*-cyclopentyladamantane-1-sulfinamide (3ba)



3ba

^{1}H NMR (400 Hz, $CDCl_3$)

yd-5-105-6.11.fid

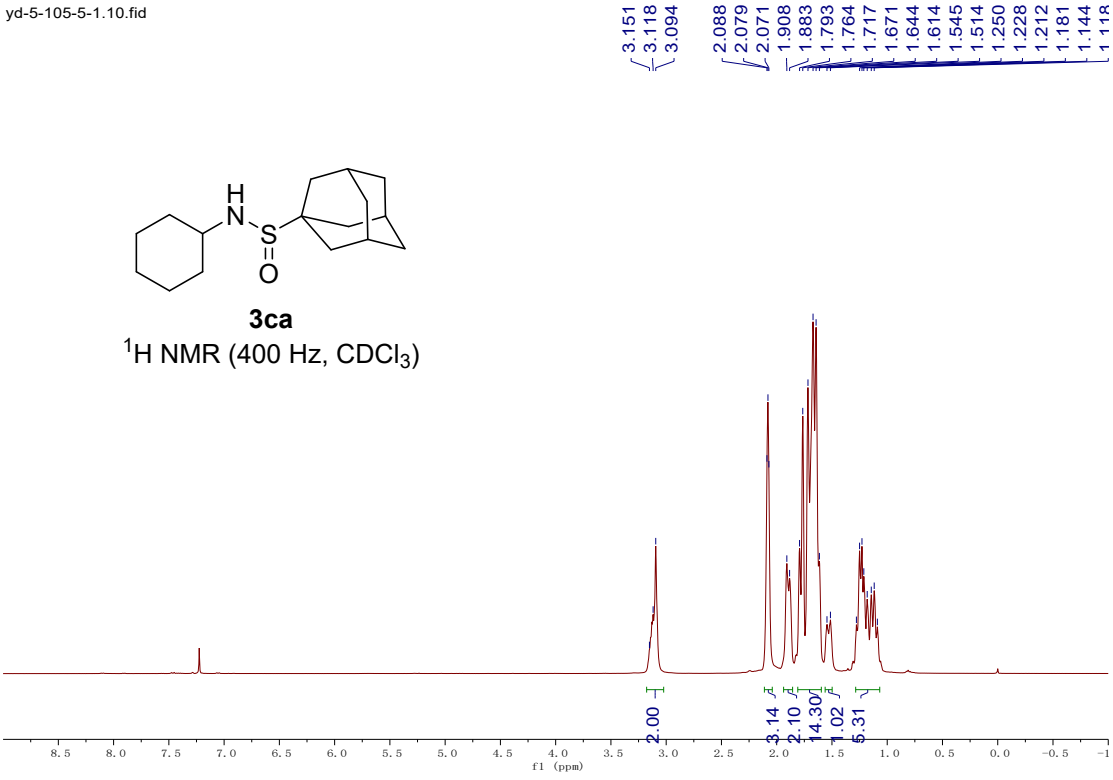


3ba

^{13}C NMR (100 Hz, $CDCl_3$)

(3s,5s,7s)-*N*-cyclohexyladamantane-1-sulfinamide (3ca)

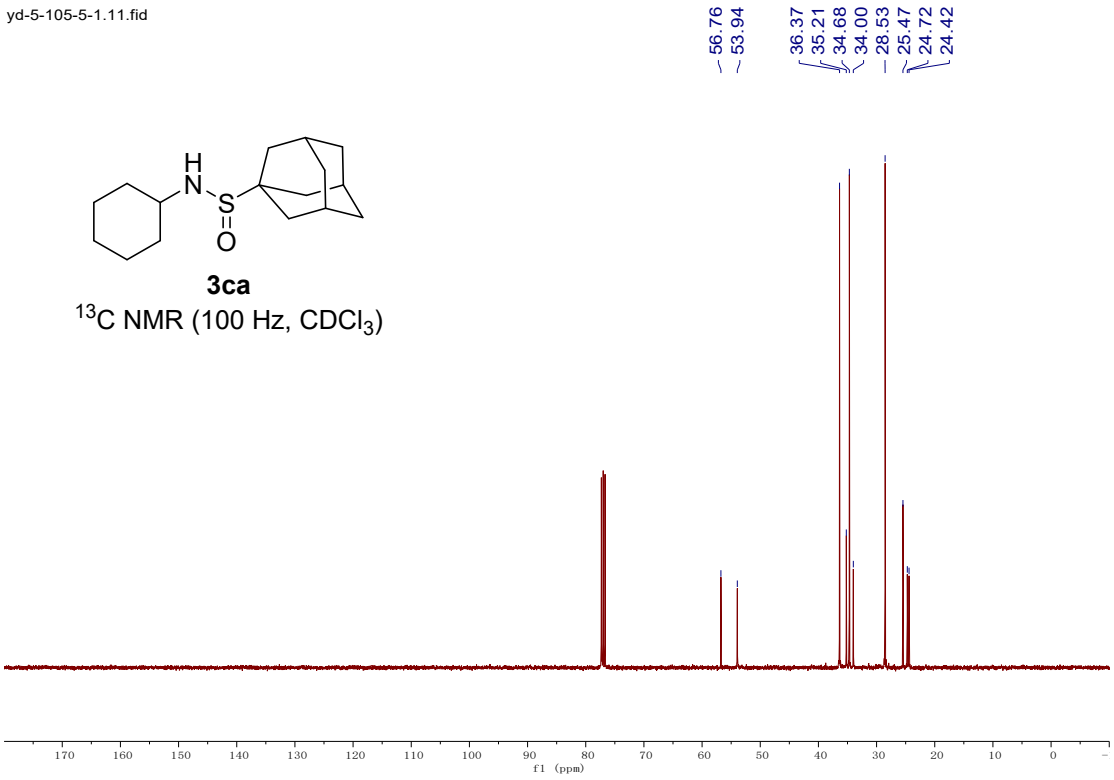
yd-5-105-5-1.10.fid



3ca

^{1}H NMR (400 Hz, $CDCl_3$)

yd-5-105-5-1.11.fid

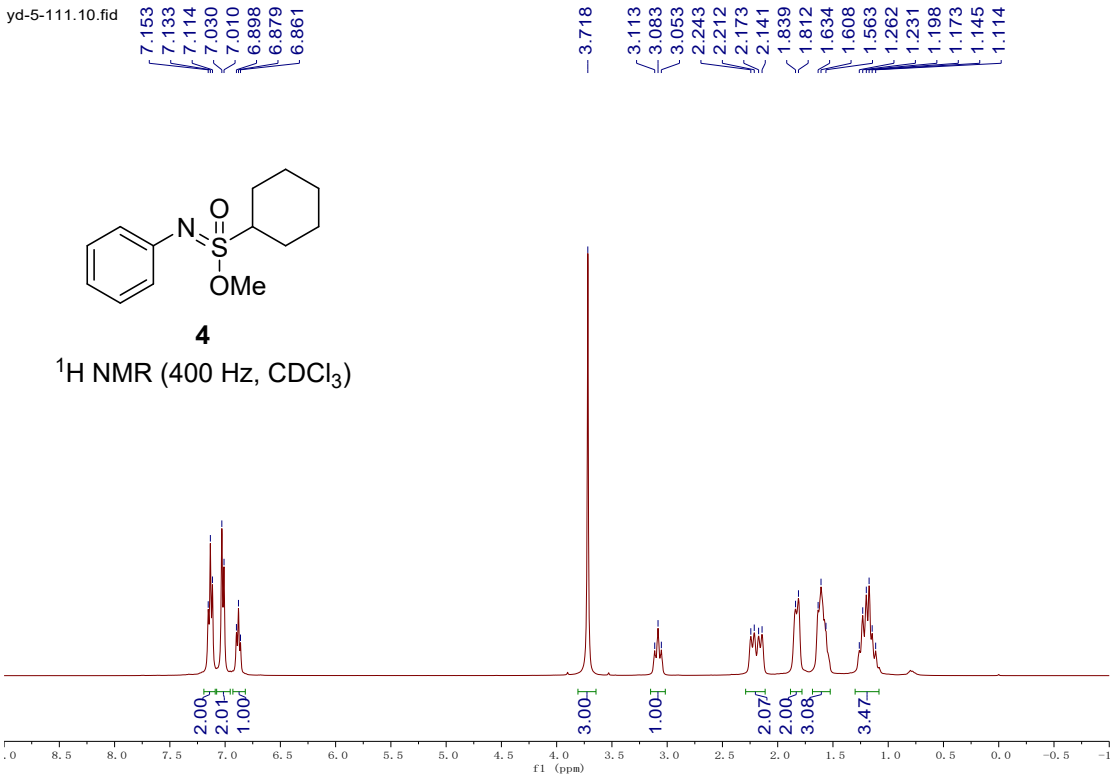


3ca

^{13}C NMR (100 Hz, $CDCl_3$)

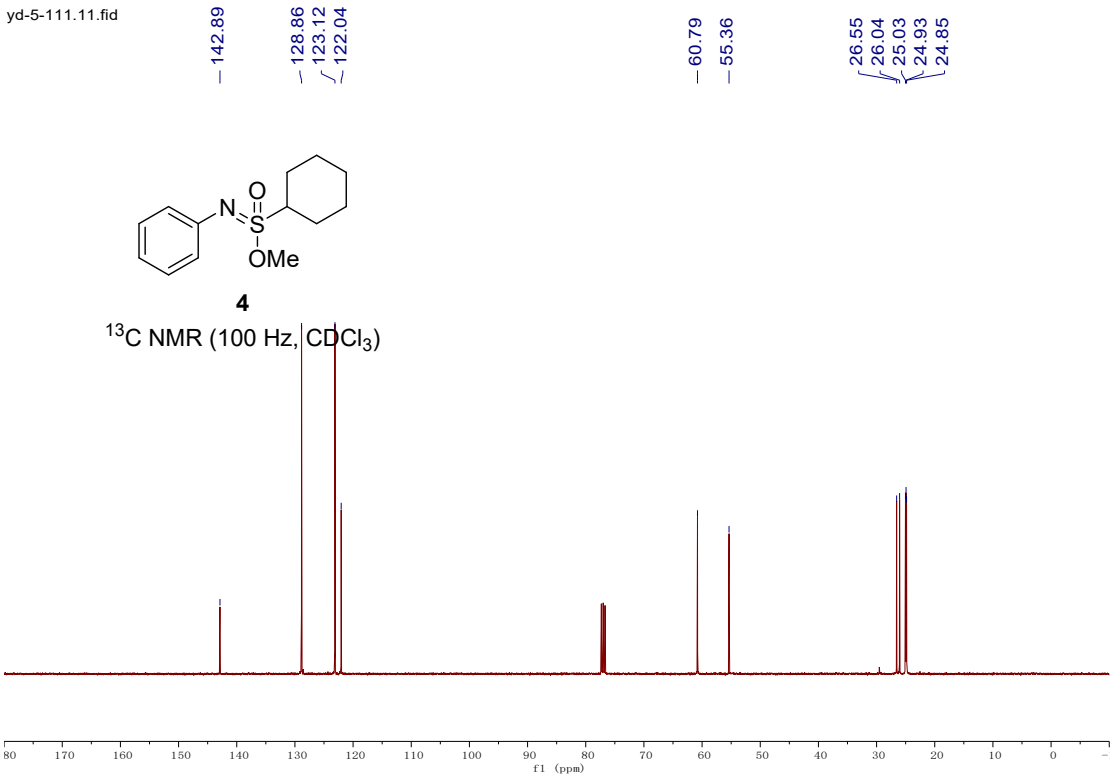
Compound 4

yd-5-111.10.fid

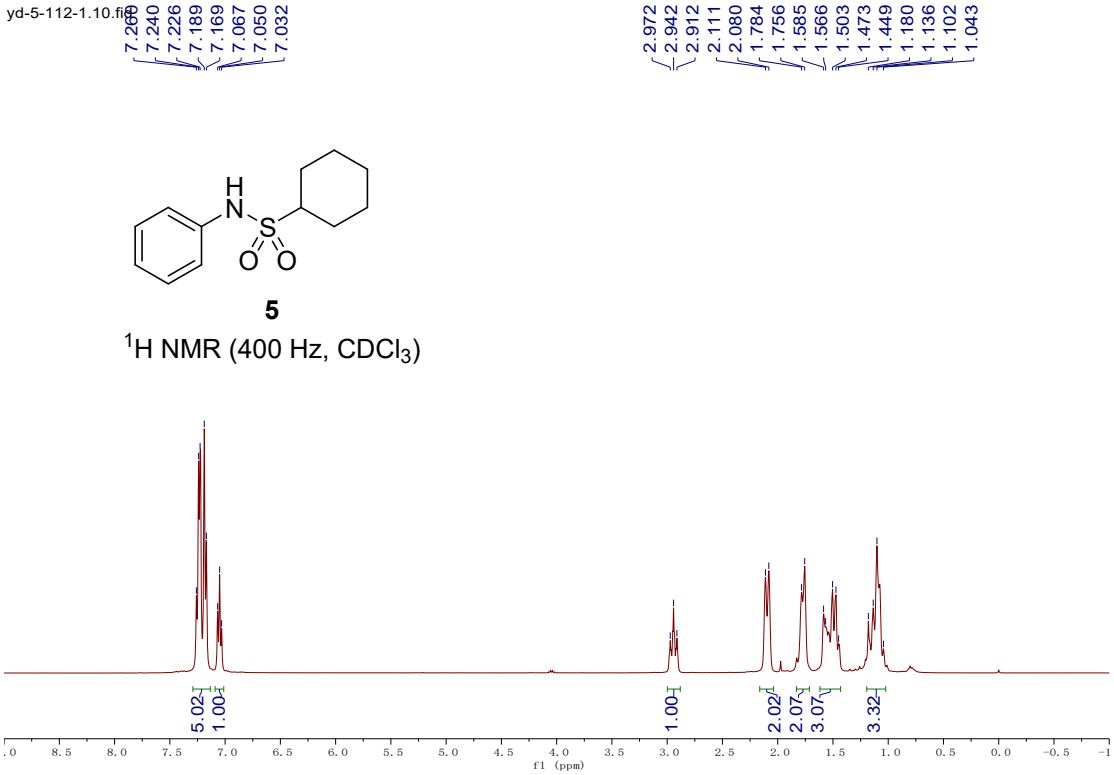


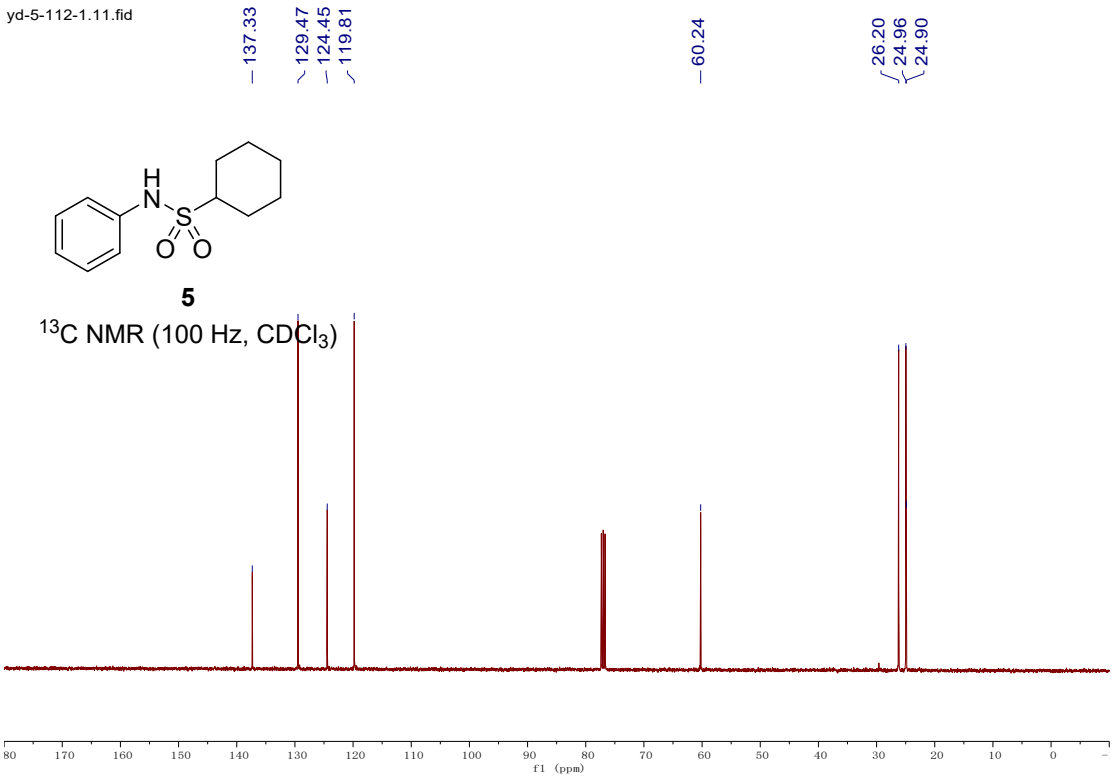
4

^{1}H NMR (400 Hz, $CDCl_3$)


yd-5-111.11.fid
142.89
128.86
123.12
122.04
60.79
55.36
26.55
26.04
25.03
24.93
24.85
N
O
S
OMe
4
13C NMR (100 Hz, CDCl3)
f1 (ppm)

Compound 5


yd-5-112-1.10.fid
7.260
7.240
7.226
7.189
7.169
7.067
7.050
7.032
2.972
2.942
2.912
2.111
2.080
1.784
1.756
1.585
1.566
1.503
1.473
1.449
1.180
1.136
1.102
1.043
H
N
S
O
O
5
1H NMR (400 Hz, CDCl3)
5.02
1.00
1.00
2.02
2.07
3.07
3.32
f1 (ppm)



After density functional theory (DFT) calculations, we found that in mechanism I, $FeCl_3$ as a Lewis acid can more effectively promote the nucleophilic attack process. Specifically, in mechanism I, intermediate INT4 combines with $Fe(III)Cl_3$ to form intermediate INT5, with an energy increase of only 2.5 kcal/mol. Subsequently, the tert-butyl radical attacks the sulfur atom to form intermediate INT6, releasing 11.3 kcal/mol of heat. Then, an outer-sphere electron transfer from Fe(II) to Fe(III) occurs, further releasing 34.4 kcal/mol of heat. Overall, mechanism I has a lower energy barrier and releases more heat.

In contrast, in mechanism II without the participation of $Fe(III)Cl_3$, intermediate INT4 combines with the tert-butyl radical to form intermediate INT2, with an energy stabilization at 6.1 kcal/mol. Subsequently, an outer-sphere electron transfer from Fe(II) to Fe(III) occurs, stabilizing the system to -7.3 kcal/mol.