Supporting Information

Transition-Metal-Free Arene C–H Functionalization for the Synthesis of Sulfoximines

Wenbo Zhang[a], Xinyu Li[a], Yanchuan Zhao[b,*], and Bing Gao[a,c,*]

[a]State Key Laboratory of Chemo and Biosensing, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

[b]Key Laboratory of Fluorine and Nitrogen Chemistry and Advanced Materials, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Ling-Ling Road, Shanghai 200032, China

[c]Institute of Drug Discovery and Design, College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, Zhejiang 310058, China

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1. Genaral information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. ^{1}H (400 MHz), ^{13}C (101MHz) and ^{19}F (376 MHz) NMR spectra were recorded on a Bruker AM-400 instrument. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 298 K in $CDCl_3$, DMSO-d_6, CD_3OD and the chemical shifts (δ) were given in parts per million (ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Data for ^{13}C and ^{19}F NMR spectra were reported in a similar manner, except that singlet peaks in the ^{13}C NMR spectra were reported with their chemical shifts only. For ^{1}H NMR, the chemical shift is calibrated relative to the residual of undeuterated solvents ($CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm; CD_3OD, 3.31 ppm). Spectroscopic data of the ^{13}C NMR spectra were calibrated in reference to the deuterated solvents ($CDCl_3$, 77.2 ppm; DMSO-d_6, 39.5 ppm; CD_3OD, 49.0 ppm). High-resolution mass spectrometry (HRMS) was performed on a Waters G2-XS QTOF instrument with real-time direct analysis (ESI) ionization mode. Thin layer chromatography (TLC) was performed using TLC silica gel plates HSG F254 and visualized using UV light, iodine, potassium permanganate. Silica gel column chromatography was carried out using 300-400 mesh silica gel.

2. Preparation of starting materials

2.1 Preparation of diaryliodonium salts

All diaryliodonium salts were synthesized according to the reported procedures.[1-3] Compounds **1a**, **1c**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1m**, **1n** and **1o** were reported in previous literature. Therefore, their preparation and characterization data are not presented in this file.

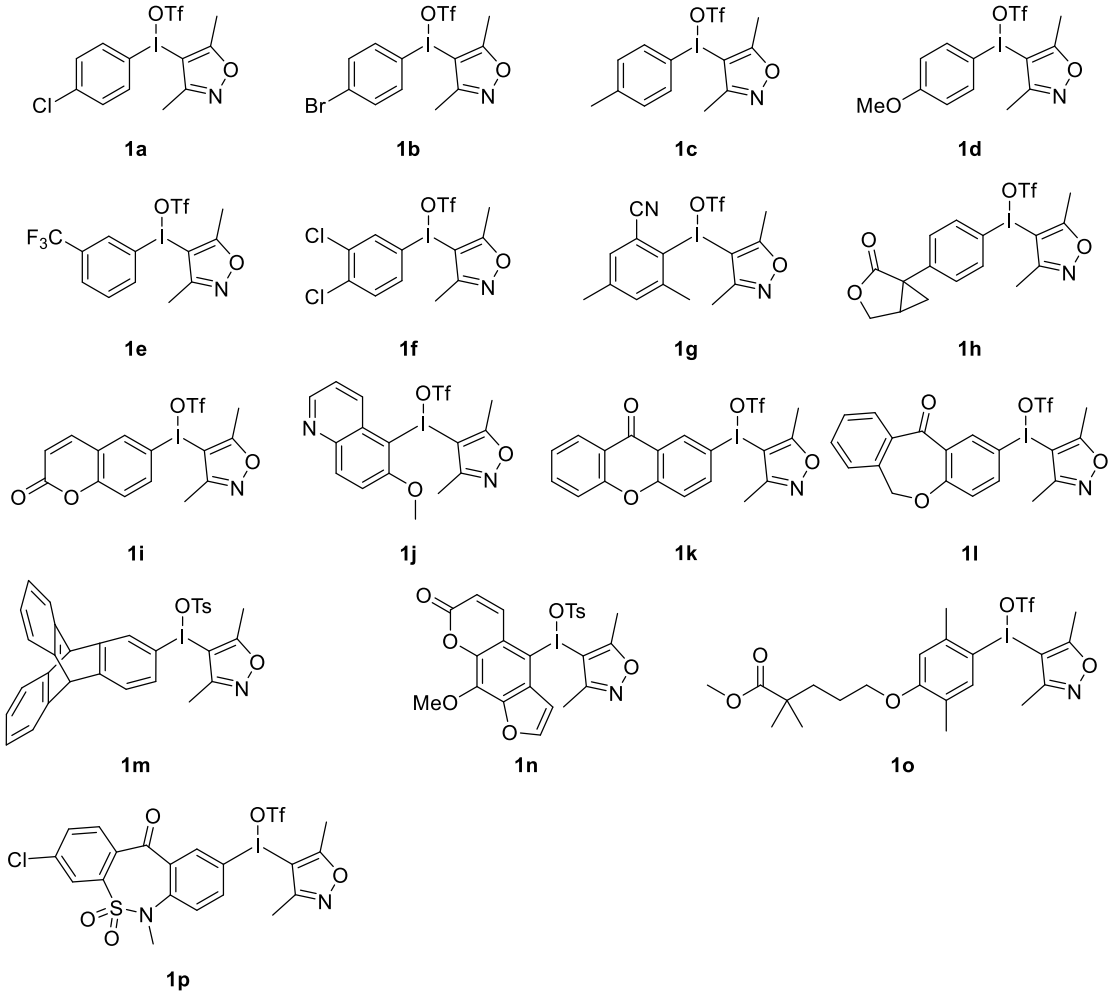
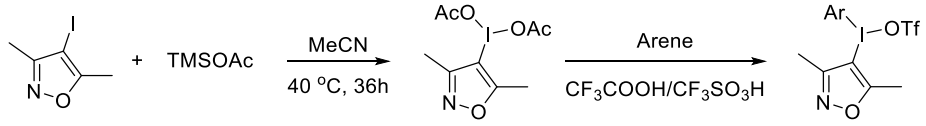
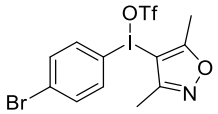


Figure S1. Diaryliodonium Salts



General procedure A: (3,5-dimethylisoxazol-4-yl)-λ^3-iodanediyl diacetate was synthesized according to the literature procedures. To a suspension of hypervalent iodine intermediates (1.0 mmol) in CF_3CO_2H (2.0 mL) and CF_3SO_3H (0.2 mL) was added Arene (1.0 mmol) at room temperature. Then the reaction mixture was stirred at room temperature and monitored by TLC. The solution was concentrated under vacuum and the crude product was precipitated in Et_2O. The crude product was filtered, washed with Et_2O, and dried under vacuum to give the product as a yellow to white solid.

(4-bromophenyl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (1b)



According to **General Procedure A** (2.0 mmol scale), **1d** was obtained as a white solid (908 mg, 86% yield).

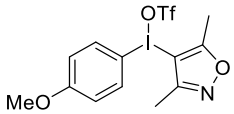
^{1}H NMR (400 MHz, CD_3OD) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 2.76 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 178.2, 161.6, 137.7, 136.5, 128.8, 121.7 (q, *J* = 318.6 Hz), 114.6, 84.8, 12.7, 11.2.

^{19}F NMR (376 MHz, CD_3OD) δ -80.03 (s, 3F).

HRMS (ESI): Calcd. for $[C_{11}H_{10}BrINO]^+$: 377.8985; Found: 377.9011.

(3,5-Dimethylisoxazol-4-yl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (1d)



According to **General Procedure A** (2.0 mmol scale), **1a** was obtained as a grey solid (480 mg, 50% yield).

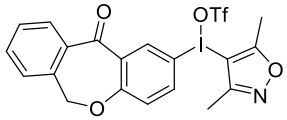
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.69 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 162.8, 160.3, 136.5, 120.0 (q, *J* = 321 Hz), 118.0, 103.5, 84.0, 55.9, 12.8, 11.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.02 (s, 3F).

HRMS (ESI): Calcd. for $[C_{12}H_{13}INO_2]^+$: 329.9985; Found: 329.9985.

(3,5-Dimethylisoxazol-4-yl)(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)iodonium trifluoromethanesulfonate (1l)



According to **General Procedure A** (2.0 mmol scale), **1l** was obtained as a white solid (885 mg, 76% yield).

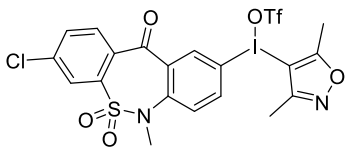
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 5.23 (s, 2H), 2.77 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 176.8, 163.9, 160.4, 140.2, 139.6, 139.2, 134.7, 133.8, 130.0, 129.8, 128.4, 127.9, 125.4, 119.9 (q, *J* = 319.4 Hz), 105.8, 83.4, 74.0, 12.9, 11.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.48 (s, 3F).

HRMS (ESI): Calcd. for $[C_{19}H_{15}INO_3]^+$: 432.0091; Found: 432.0097.

(3-Chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepin-9-yl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (1p)



According to **General Procedure A** (1.0 mmol scale), **1p** was obtained as a white solid (359 mg, 53% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (d, J = 2.3 Hz, 1H), 8.46 (dd, J = 8.8, 2.3 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.70 (d, J = 8.9 Hz, 1H), 3.40 (s, 3H), 2.74 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 188.9, 176.3, 160.7, 143.9, 140.5, 138.1, 137.4, 137.3, 134.5, 133.8, 133.6, 131.4, 127.5, 124.5, 120.8 (q, J = 322.2 Hz), 113.0, 87.0, 38.6, 12.6, 11.1.

^{19}F NMR (377 MHz, DMSO-d_6) δ -77.75.

HRMS (ESI): Calcd. for $[C_{19}H_{15}ClIN_2O_4S]^+$: 528.9480; Found: 528.9489.

2.2 Preparation of *N*-((aryl/alkyl)sulfinyl)pivalamides.

The *N*-((aryl/alkyl)sulfinyl)pivalamides were prepared based on reported procedures.[4-8] Compounds **2a**, **2c**, **2e**, **2f**, **2l**, **2n**, **2o**, **2p**, **2q**, **2r**, **2s** and **2t** were reported in our previous studies. Therefore, their preparation and characterization data are not presented in this file.

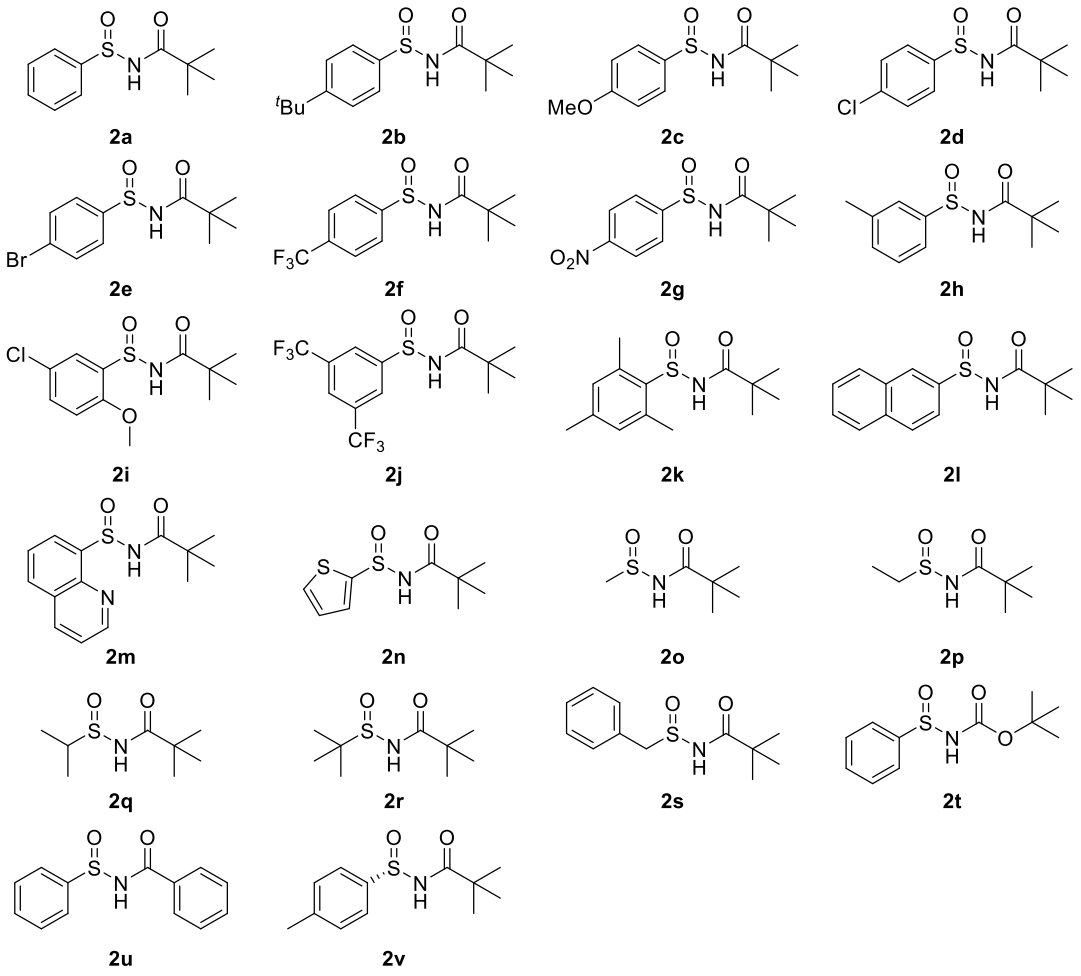
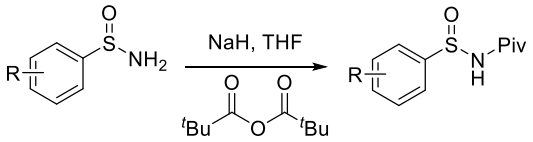
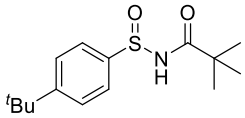


Figure S2. *N*-((aryl/alkyl)sulfinyl)pivalamides



General Procedure B: To a suspension of aryl or alkyl sulfinamides (1.0 equiv) in THF (c = 0.5 M) was added NaH (2.5 equiv) at 0 ºC. The mixture was stirred for 1.0 h at room temperature, then cooled to 0 ºC. The trimethylacetic anhydride (1.2 equiv) was added dropwise into the mixture reaction and the resulting reaction mixture was stirred overnight at room temperature. Thereafter, it was quenched by saturated NH_4Cl (aq.) and extracted with ethyl acetate for three times. The combined organic layer was washed with saturated brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by column chromatography or recrystallizing with ethyl acetate and petroleum ether.

***N*-((4-(tert-Butyl)phenyl)sulfinyl)pivalamide (2b)**



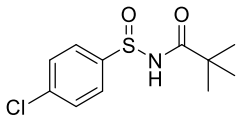
According to **General Procedure B** (4-(*tert*-butyl)benzenesulfinamide, 1.22 g, 6.2 mmol), **2b** was obtained as a white solid (842 mg, 49% yield). R_f = 0.5 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 1.34 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 155.7, 141.0, 126.6, 124.7, 39.8, 35.2, 31.3, 27.2.

HRMS (ESI): Calcd. for $[C_{15}H_{23}NO_2S+Na]^+$: 304.1342; Found: 304.1348.

***N*-((4-Chlorophenyl)sulfinyl)pivalamide (2d)**



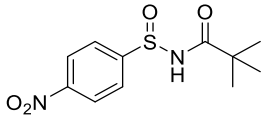
According to **General Procedure B** (4-chlorobenzenesulfinamide, 1.40 g, 8.0 mmol), **2d** was obtained as a white solid (1.46 g, 70% yield). R_f= 0.5 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 142.7, 138.3, 129.7, 126.4, 39.8, 27.1.

HRMS (ESI): Calcd. for $[C_{11}H_{14}ClNO_2S+Na]^+$: 282.0326; Found: 282.0336.

***N*-((4-Nitrophenyl)sulfinyl)pivalamide (2g)**



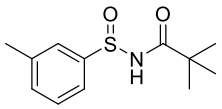
According to **General Procedure B** (4-nitrobenzenesulfinamide, 1.12 g, 6.0 mmol), **2g** was obtained as a yellow solid (878 mg, 54% yield). R_f= 0.3 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.8 Hz, 2H), 8.16 (s, 1H), 7.88 (d, J = 8.8 Hz, 2H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 151.0, 145.0, 126.4, 124.5, 40.0, 27.1.

HRMS (ESI): Calcd. for $[C_{11}H_{14}N_2O_2S+Na]^+$: 293.0566; Found: 293.0577.

***N*-(*m*-Tolylsulfinyl)pivalamide (2h)**



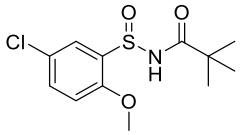
According to **General Procedure B** (3-methylbenzenesulfinamide, 512 mg, 3.3 mmol), **2h** was obtained as a white solid (300 mg, 38% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.51 (s, 1H), 7.46 – 7.37 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 143.8, 139.8, 132.8, 129.3, 125.1, 121.9, 39.7, 27.1, 21.5.

HRMS (ESI): Calcd. for $[C_{12}H_{17}NO_2S+H]^+$: 240.1053; Found: 240.1055.

***N*-((5-Chloro-2-methoxyphenyl)sulfinyl)pivalamide (2i)**



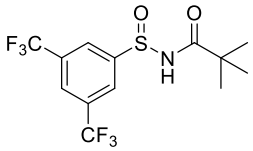
According to **General Procedure B** (5-chloro-2-methoxybenzenesulfinamide, 1.03 g, 5.0 mmol), **2i** was obtained as a white solid (1.15 g, 79% yield). R_f= 0.3 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.71 (m, 2H), 7.46 – 7.38 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H), 1.20 – 1.16 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 154.8, 133.3, 132.4, 126.8, 126.4, 112.9, 56.3, 39.7, 27.1.

HRMS (ESI): Calcd. for $[C_{12}H_{16}ClNO_3S+Na]^+$: 312.0432; Found: 312.0433.

***N*-((3,5-Bis(trifluoromethyl)phenyl)sulfinyl)pivalamide (2j)**



According to **General Procedure B** (3,5-bis(trifluoromethyl)benzenesulfinamide, 1.94 g, 7.0 mmol), **2j** was obtained as a white solid (1.79g, 71% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

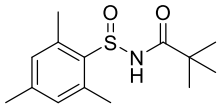
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 7.83 (m, 4H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 147.8, 133.2 (q, *J* = 34.3 Hz), 125.68, 125.65, 122.7 (q, *J* = 275 Hz), 40.1, 27.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99 (s, 6F).

HRMS (ESI): Calcd. for $[C_{13}H_{13}F_6NO_2S+H]^+$: 362.0644; Found: 362.0648.

***N*-(Mesitylsulfinyl)pivalamide (2k)**



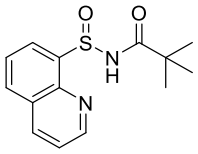
According to **General Procedure B** (2,4,6-trimethylbenzenesulfinamide, 1.28 g, 7.0 mmol), **2k** was obtained as a white solid (1.03 g, 55% yield). R_f= 0.6 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 6.85 (s, 2H), 2.55 (s, 6H), 2.26 (s, 3H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 142.1, 137.8, 136.2, 131.1, 39.7, 27.2, 21.13, 19.2.

HRMS (ESI): Calcd. for $[C_{14}H_{21}NO_2S+H]^+$: 268.1366; Found: 268.1374.

***N*-(Quinolin-8-ylsulfinyl)pivalamide (2m)**



According to **General Procedure B** (quinoline-5-sulfinamide, 5.0 mmol), **2m** was obtained as a white solid (490 mg, 36% yield). R_f= 0.2 (PE/EA= 2/1).

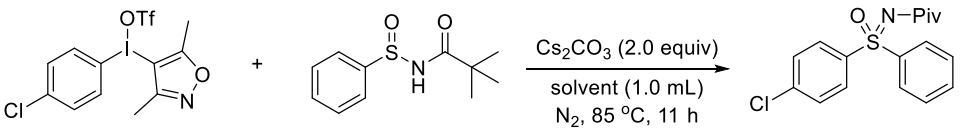
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 8.97 – 8.95 (m, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.26 – 8.19 (m, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.57 (dd, *J* = 8.6, 4.3 Hz, 1H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 150.7, 144.3, 139.7, 137.5, 132.5, 130.4, 129.3, 126.4, 122.5, 39.9, 27.2.

HRMS (ESI): Calcd. for $[C_{14}H_{16}N_2O_2S+H]^+$: 277.1005; Found: 277.1010.

3. Optimization of the reaction conditions

Table S1. Evaluation of solvents

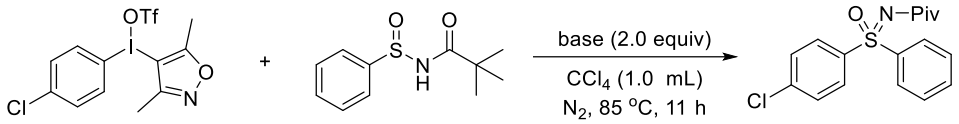


1a **2a** **3aa**

Entry	Solvent	yield (%)[a]
1	DCM	51
2	$CHCl_3$	41
3	DCE	42
4	CCl_4	79
5	PhCl	62
6	Toluene	70
7	Xylene	70
8	$PhCF_3$	55
9	m-xylene	71
10	Benzene	68
11	THF	trace
12	MeCN	4
13	DMSO	0
14	DMF	0
15	NMP	0
16	Acetone	6

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), Cs_2CO_3 (0.1 mmol), solvent (1.0 mL), 85 °C,11 h. Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

Table S2. Evaluation of bases

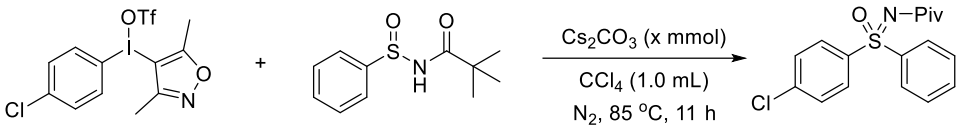


1a **2a** **3aa**

Entry	Base	yield (%)[a]
1	Cs_2CO_3	79
2	K_2CO_3	28
3	Na_2CO_3	35
4	K_2HPO_4	36
5	K_3PO_4	34
6	CsF	39
7	$NaHCO_3$	0
8	DBU	11
9	NaOH	34

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), base (0.1 mmol), CCl_4 (1.0 mL), 85 °C,11 h.Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

Table S3. Evaluation of the ratio of base

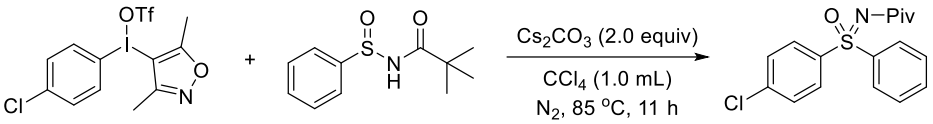


1a **2a** **3aa**

Entry	x mmol	yield (%)[a]
1	0.05	65
2	0.075	72
3	0.10	79
4	0.15	67
5	0.20	42
6	0.30	55

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), Cs_2CO_3 (x mmol), CCl_4 (1.0 mL), 85 °C,11 h. Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

Table S4. Evaluation of the substrate ratio

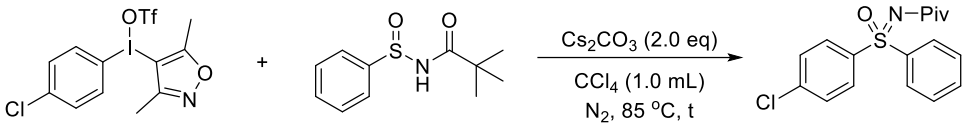


1a **2a** **3aa**

Entry	1c/2a	yield (%)[a]
1	0.5	49
2	1.0	48
3	1.5	60
4	2.0	79
5	2.5	74
6	3.0	75

[a]Reaction conditions: 0.05 mmol scale, Cs_2CO_3 (0.1 mmol), CCl_4 (1.0 mL), 85 °C,11 h. Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

Table S5. Evaluation of time

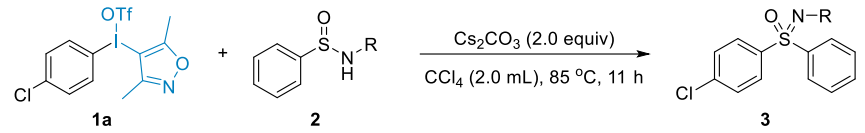


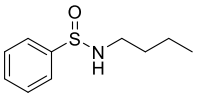
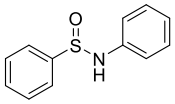
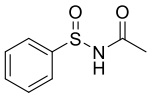
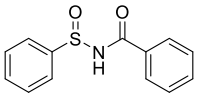
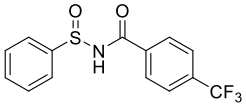
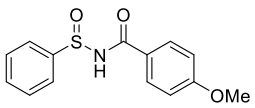
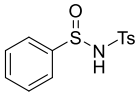
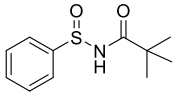
1a **2a** **3aa**

Entry	t (h)	yield (%)[a]
1	6.0	55
2	11	79
3	18	71
4	24	72

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), Cs_2CO_3 (0.1 mmol), CCl_4 (1.0 mL), 85 °C, t/h. Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

Table S6. Evaluation of *N*-substituents on sulfinamides.

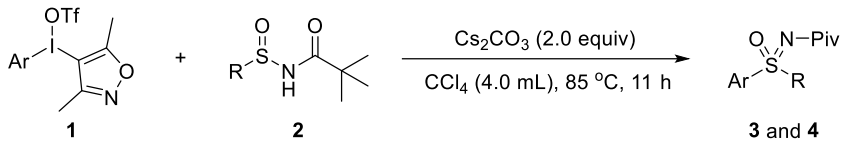


			
Failed	Failed	yield: 12%	yield: 43%
			
yield: 28%	yield: 41%	Failed	yield: 79%

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), Cs_2CO_3 (0.2 mmol), CCl_4 (2.0 mL), 85 °C. Yield was determined by ^1H NMR with CH_2Br_2 (0.10 mmol) as the internal standard.

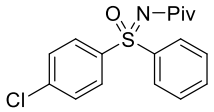
4. Substrate scope

4.1 Synthesis of sulfoximines 3aa-3pa



General Procedure C: To an oven-dried Schlenk flask was charged with sulfinamide (0.2 mmol, 1.0 equiv), diaryliodonium salt (0.4 mmol, 2.0 equiv), Cs_2CO_3 (2.0 equiv) and CCl_4 (4.0 mL). The reaction mixture was stirred at 85 °C for 11 h. The resulting mixture was concentrated and then purified by column chromatography on silica gel to afford the corresponding product.

***N*-(Pivaloyl)-*S,S*-(4-chlorophenyl)phenylsulfoximine (3aa)**



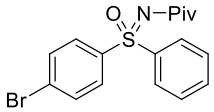
According to **General Procedure C** (**1a**, 193 mg, 0.4 mmol), **3aa** was obtained as a white solid (49.7 mg, 74% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.49 (m, 3H), 7.46 (d, *J* = 8.6 Hz, 2H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 139.9, 139.8, 138.9, 133.5, 129.9, 129.7, 129.0, 127.7, 41.8, 27.8.

HRMS (ESI): Calcd. for $[C_{17}H_{18}ClNO_2S+H]^+$: 336.0820; Found: 336.0826.

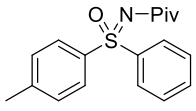
***N*-(Pivaloyl)-*S,S*-(4-bromophenyl)phenylsulfoximine (3ba)**[7]



According to **General Procedure C** (**1b**, 211 mg, 0.4 mmol), **3ba** was obtained as a white solid (52.6 mg, 69% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.48 (m, 3H), 1.27 (s, 9H).

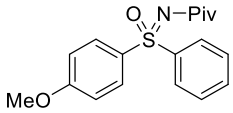
***N*-(Pivaloyl)-*S,S*-(4-methylphenyl)phenylsulfoximine (3ca)**[8]



According to **General Procedure C** (**1c**, 185 mg, 0.4 mmol), **3ca** was obtained as a white solid (32.4 mg, 51% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.55-7.47 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 1.28 (s, 9H).

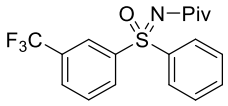
***N*-(Pivaloyl)-*S,S*-(4-methoxyphenyl)phenylsulfoximine (3da)**[8]



According to **General Procedure C** (**1d**, 191 mg, 0.4 mmol), **3da** was obtained as a colorless oil (20.0 mg, 30% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.46 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.27 (s, 9H).

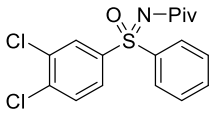
***N*-(Pivaloyl)-*S*,*S*-(3-trifluoromethylphenyl)phenylsulfoximine (3ea)[7]**



According to **General Procedure C** (**1e**, 207 mg, 0.4 mmol), **3ea** was obtained as a white solid (50.0 mg, 68% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.61 – 7.50 (m, 3H), 1.28 (s, 9H).

***N*-(Pivaloyl)-*S*,*S*-(3,4-dichlorophenyl)phenylsulfoximine (3fa)**



According to **General Procedure C** (**1f**, 207 mg, 0.4 mmol), **3fa** was obtained as a white solid (36.6 mg, 49% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

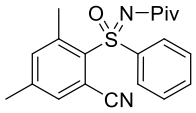
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.72 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.64 – 7.51 (m, 4H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 140.4, 139.2, 138.2, 134.3, 133.8, 131.6, 129.8, 129.5, 127.8, 126.5, 41.9, 27.8.

HRMS (ESI): Calcd. for $[C_{17}H_{17}Cl_2NO_2S+H]^+$: 370.0430; Found: 370.0430.

IR (neat) ν 3055, 2988, 2305, 1421, 1266, 896, 750, 734, 704 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(2-cyano-4,6-dimethylphenyl)phenylsulfoximine (3ga)**



According to **General Procedure C** (**1g**, 201 mg, 0.4 mmol), **3ga** was obtained as a white solid (29.7 mg, 42% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 2/1).

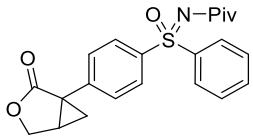
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.47 (s, 1H), 7.28 (s, 1H), 2.66 (s, 3H), 2.36 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 143.5, 141.6, 139.2, 138.6, 137.1, 135.8, 134.0, 129.3, 128.6, 116.8, 113.0, 42.2, 27.9, 22.0, 20.9.

HRMS (ESI): Calcd. for $[C_{20}H_{22}N_2O_2S+H]^+$: 355.1475; Found: 355.1484.

IR (neat) ν 3055, 2986, 2305, 1421, 1266, 896, 743, 738, 705 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(4-(2-oxo-3-oxabicyclo[3.1.0]hexan-1-yl)phenyl)phenylsulfoximine (3ha)**



According to **General Procedure C** (**1h**, 218 mg, 0.4 mmol), **3ha** was obtained as a colorless oil (46.0 mg, 58% yield) after purification by silica gel flash chromatography. R_f = 0.2 (PE/EA= 2/1).

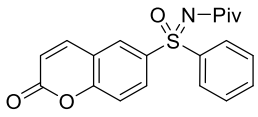
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.47 (m, 5H), 4.47 – 4.40 (m, 1H), 4.30 (d, *J* = 9.4 Hz, 1H), 2.64 (dq, *J* = 8.6, 4.4 Hz, 1H), 1.70 – 1.63 (m, 1H), 1.44 (td, *J* = 5.0, 1.7 Hz, 1H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 175.1, 139.8, 139.4 (d, *J* = 2.7 Hz), 133.4, 129.6, 129.1, 129.0, 127.9, 127.7, 68.1, 41.8, 31.3, 27.8, 25.9 (d, *J* = 15.8 Hz), 21.2 (d, *J* = 5.0 Hz).

HRMS (ESI): Calcd. for $[C_{22}H_{23}NO_4S+H]^+$: 398.1421; Found: 398.1421.

IR (neat) ν 3055, 2986, 2307, 1770, 1641, 1422, 1265, 1169, 896, 743, 705 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(2-oxo-2H-chromen-6-yl)phenylsulfoximine (3ia)**



According to **General Procedure C** (**1i**, 218 mg, 0.4 mmol), **3ia** was obtained as a white solid (18.1 mg, 25% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 2/1).

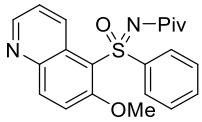
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.3 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.95 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.74 (d, *J* = 9.7 Hz, 1H), 7.64 – 7.49 (m, 3H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.52 (d, *J* = 9.6 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 159.3, 156.7, 142.6, 139.5, 136.6, 133.7, 130.2, 129.8, 128.2, 127.8, 119.4, 118.6, 118.5, 41.9, 27.8.

HRMS (ESI): Calcd. for $[C_{20}H_{19}NO_4S+H]^+$: 370.1108; Found: 370.1110.

IR (neat) ν 3055, 2986, 2305, 1743, 1421, 1266, 896, 738, 705 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(6-methoxyquinolin-5-yl)phenylsulfoximine (3ja)**



According to **General Procedure C** (**1j**, 212 mg, 0.4 mmol), **3ja** was obtained as a white solid (50.4 mg, 66% yield) after purification by silica gel flash chromatography. R_f = 0.2 (PE/EA = 2/1).

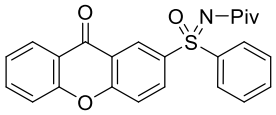
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, *J* = 9.0 Hz, 1H), 8.85 (d, *J* = 4.1 Hz, 1H), 8.26 (d, *J* = 9.3 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 9.3 Hz, 1H), 3.56 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 155.5, 149.0, 143.8, 142.3, 138.2, 133.4, 133.0, 129.5, 128.5, 128.0, 123.1, 119.6, 115.9, 56.2, 41.7, 27.9.

HRMS (ESI): Calcd. for $[C_{21}H_{22}N_2O_3S+H]^+$: 383.1424; Found: 383.1424.

IR (neat) ν 3053, 2988, 2305, 1421, 1276, 1255, 896, 766, 715, 688 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(9-oxo-9H-xanthen-2-yl)phenylsulfoximine (3ka)**



According to **General Procedure C** (**1k**, 227 mg, 0.4 mmol), **3ka** was obtained as a white solid (63.0 mg, 75% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 2/1).

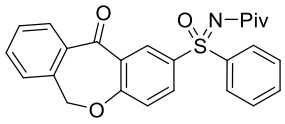
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.4 Hz, 1H), 8.35 – 8.26 (m, 2H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.59 – 7.48 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 175.9, 158.5, 156.0, 139.7, 136.2, 135.8, 133.6, 133.0, 129.8, 127.8, 127.6, 126.9, 125.1, 122.2, 121.7, 120.0, 118.2, 41.9, 27.8.

HRMS (ESI): Calcd. for $[C_{24}H_{21}NO_4S+H]^+$: 420.1264; Found: 420.1264.

IR (neat) ν 3055, 2988, 2305, 1422, 1266, 896, 750, 704 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)phenylsulfoximine (3la)**



According to **General Procedure C** (**1l**, 233 mg, 0.4 mmol), **3la** was obtained as a yellow solid (48.2 mg, 56% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 2/1).

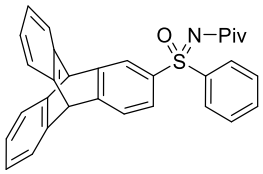
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.5 Hz, 1H), 8.05 – 7.99 (m, 3H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.42 (m, 5H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 5.22 (s, 2H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 188.2, 164.3, 140.2, 140.1, 134.6, 133.8, 133.44, 133.37, 133.3, 132.9, 129.8, 129.7, 129.6, 128.3, 127.7, 125.7, 122.7, 73.7, 41.9, 27.9.

HRMS (ESI): Calcd. for $[C_{25}H_{23}N_2O_2S+H]^+$: 434.1421; Found: 434.1423.

IR (neat) ν 3055, 2986, 2305, 1422, 1266, 896, 740, 705 cm^{-1}.

***N*-(((9r,10r)-9,10-Dihydro-9,10-[1,2]benzenoanthracen-2-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)pivalamide (3ma)**



According to **General Procedure C** (**1m**, 259 mg, 0.4 mmol), **3ma** was obtained as a yellow solid (68.8 mg, 72% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

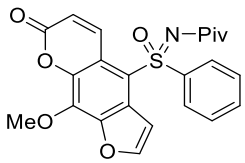
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.38 (m, 8H), 7.06 – 7.01 (m, 4H), 5.52 (s, 1H), 5.50 (s, 1H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 150.9, 147.0, 144.2, 144.1, 143.9, 143.83, 140.3, 136.7, 133.0, 129.5, 127.5, 125.8, 125.73, 125.71, 125.4, 124.5, 124.2, 124.07, 124.05, 124.02, 122.4, 54.0, 53.9, 41.7, 27.8.

HRMS (ESI): Calcd. for $[C_{31}H_{27}NO_2S+H]^+$: 478.1835; Found: 478.1844.

IR (neat) ν 3055, 2986, 2686, 2305, 1422, 1265, 896, 743, 705 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(9-methoxy-7-oxo-7*H*-furo[3,2-*g*]chromen-4-yl) phenylsulfoximine (3na)**



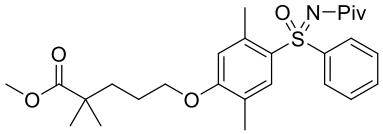
According to **General Procedure C** (**1n**, 243 mg, 0.4 mmol), **3na** was obtained as a white solid (65.0 mg, 74% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 10.2 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.78 (d, *J* = 2.2 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.39 (d, *J* = 10.2 Hz, 1H), 4.42 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 158.6, 148.5, 145.9, 143.4, 140.7, 139.3, 137.0, 134.0, 129.8, 128.4, 127.1, 118.2, 116.9, 115.0, 107.5, 61.5, 42.1, 27.8.

HRMS (ESI): Calcd. for $[C_{23}H_{21}NO_6S+H]^+$: 440.1163; Found: 440.1170.

Methyl 5-(2,5-dimethyl-4-(N-pivaloylphenylsulfonimidoyl)phenoxy)-2,2-dimethylpentanoate (3oa)



According to **General Procedure C** (**1o**, 254 mg, 0.4 mmol), **3oa** was obtained as a colorless oil (25.3 mg, 26% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

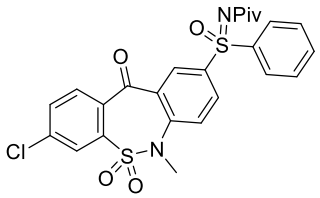
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.45 (m, 2H), 6.53 (s, 1H), 3.92 (t, *J* = 5.6 Hz, 2H), 3.65 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.73 – 1.64 (m, 4H), 1.26 (s, 9H), 1.21 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 178.3, 161.0, 140.6, 137.2, 132.8, 132.3, 129.1, 127.8, 127.4, 125.3, 114.6, 68.4, 51.9, 42.2, 41.9, 37.1, 28.0, 25.3, 25.1, 20.4, 16.1.

HRMS (ESI): Calcd. for $[C_{27}H_{37}NO_5S+H]^+$: 488.2465; Found: 488.2466.

IR (neat) ν 3055, 2986, 2686, 2305, 1553, 1422, 1278, 1253, 1160, 896, 764, 717, 691 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(3-chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepin-9-yl)phenylsulfoximine (3pa)**



According to **General Procedure C** (**1p**, 272 mg, 0.4 mmol), **3pa** was obtained as a yellow solid (73.1 mg, 69% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.90 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.42 (d, *J* = 8.7 Hz, 1H), 3.42 (s, 3H), 1.29 (s, 9H).

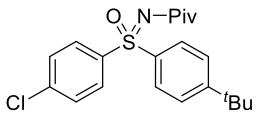
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 188.2, 144.8, 139.2, 139.1, 138.1, 137.6, 134.0, 133.9, 133.8, 133.2, 133.0, 131.8, 130.7, 129.9, 127.9, 124.9, 124.4, 41.9, 38.5, 27.8.

HRMS (ESI): Calcd. for $[C_{25}H_{23}ClN_2O_5S_2+H]^+$: 531.0810; Found: 531.0814.

IR (neat) ν 3055, 2986, 2305, 1422, 1265, 896, 747, 705 cm^{-1}.

4.2 Synthesis of products (4ab-4au)

***N*-(Pivaloyl)-*S,S*-(4-(*tert*-butyl)phenyl)-4-chlorophenylsulfoximine (4ab)**



According to **General Procedure C** (**2b**, 56.3 mg, 0.2 mmol), **4ab** was obtained as a white solid (66.7 mg, 85% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

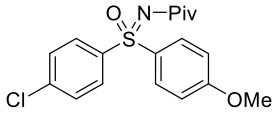
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 1.30 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 157.4, 139.6, 139.2, 136.5, 129.8, 129.0, 127.5, 126.8, 41.8, 35.3, 31.1, 27.8.

HRMS (ESI): Calcd. for $[C_{21}H_{26}ClNO_2S+H]^+$: 392.1446; Found: 392.1451.

IR (neat) ν 3055, 2988, 2307, 1422, 1274, 1258, 896, 764, 715, 695 cm^{-1}.

***N*-(Pivaloyl)-*S,S*-(4-methoxyphenyl)-4-chlorophenylsulfoximine (4ac)**



According to **General Procedure C** (**2c**, 51.1 mg, 0.2 mmol), **4ac** was obtained as a white solid (58.6 mg, 80% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

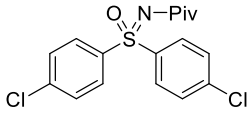
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 4H), 7.44 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 163.7, 139.6, 139.5, 130.6, 129.9, 129.7, 128.8, 115.0, 55.8, 41.8, 27.8.

HRMS (ESI): Calcd. for $[C_{18}H_{20}ClNO_3S+H]^+$: 366.0925; Found: 366.0934.

IR (neat) ν 3055, 2986, 2305, 1422, 1265, 896, 745, 707 cm^{-1}.

***N*-(Pivaloyl)-*S,S*-bis(4-chloro)phenylsulfoximine (4ad)**



According to **General Procedure C** (**2d**, 26.0 mg, 0.1 mmol), **4ad** was obtained as a white solid (26.0 mg, 70% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

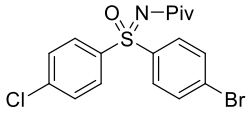
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 4H), 7.51 – 7.46 (m, 4H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 140.3, 138.4, 130.0, 129.1, 41.9, 27.8.

HRMS (ESI): Calcd. for $[C_{17}H_{17}Cl_2NO_2S+H]^+$: 370.0430; Found: 370.0433.

IR (neat) ν 3055, 2986, 2305, 1265, 896, 738, 705 cm^{-1}.

***N*-(Pivaloyl)-*S,S*-(4-bromophenyl)-4-chlorophenylsulfoximine (4ae)**



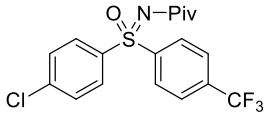
According to **General Procedure C** (**2e**, 60.8 mg, 0.2 mmol), **4ae** was obtained as a white solid (55.4 mg, 67% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 140.3, 139.0, 138.3, 133.0, 130.0, 129.1, 129.1, 128.8, 41.8, 27.7.

HRMS (ESI): Calcd. for $[C_{17}H_{17}BrClNO_2S+H]^+$: 413.9925; Found: 413.9935.

***N*-(Pivaloyl)-*S*,*S*-(4-(trifluoromethyl)phenyl)-4-chlorophenylsulfoximine (4af)**



According to **General Procedure C** (**2f**, 58.7 mg, 0.2 mmol), **4af** was obtained as a white solid (51.2 mg, 63% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 1.28 (s, 9H).

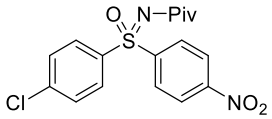
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 143.9, 140.7, 137.7, 135.0 (q, *J* = 33.3 Hz), 130.2, 129.3, 128.2, 126.8 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 275 Hz), 41.9, 27.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.24 (3F).

HRMS (ESI): Calcd. for $[C_{18}H_{17}ClF_3NO_2S+H]^+$: 404.0694; Found: 404.0704.

IR (neat) ν 3055, 2988, 2305, 1421, 1266, 896, 748, 704 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(4-nitrophenyl)-4-chlorophenylsulfoximine (4ag)**



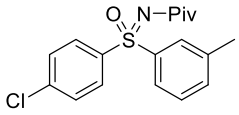
According to **General Procedure C** (**2g**, 54.1 mg, 0.2 mmol), **4ag** was obtained as a white solid (17.7 mg, 23% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 150.5, 146.4, 141.1, 137.1, 130.4, 129.5, 128.9, 124.9, 41.9, 27.7.

HRMS (ESI): Calcd. for $[C_{17}H_{17}ClN_2O_4S+H]^+$: 381.0671; Found: 381.0676.

***N*-(Pivaloyl)-*S*,*S*-(3-methylphenyl)-4-chlorophenylsulfoximine (4ah)**



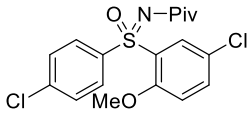
According to **General Procedure C** (**2h**, 47.9 mg, 0.2 mmol), **4ah** was obtained as a white solid (36.7 mg, 53% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.74 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.38 (m, 2H), 2.40 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 140.0, 139.8, 139.6, 139.1, 134.3, 129.8, 129.5, 129.0, 127.9, 124.8, 41.8, 27.8, 21.6.

HRMS (ESI): Calcd. for $[C_{18}H_{20}ClNO_2S+H]^+$: 350.0976; Found: 350.0981.

***N*-(Pivaloyl)-*S*,*S*-(5-chloro-2-methoxyphenyl)-4-chlorophenylsulfoximine (4ai)**



According to **General Procedure C** (**2i**, 58.0 mg, 0.2 mmol), **4ai** was obtained as a white solid (42.8 mg, 54% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

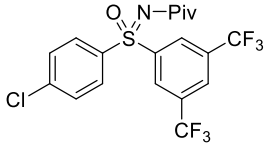
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 3H), 6.80 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 154.7, 140.1, 137.6, 135.3, 130.7, 130.2, 129.2, 128.4, 126.6, 113.8, 56.1, 41.8, 27.8.

HRMS (ESI): Calcd. for $[C_{18}H_{19}Cl_2NO_3S+H]^+$: 400.0536; Found: 400.0544.

IR (neat) ν 3055, 2986, 2307, 1422, 1266, 896, 741, 707 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(3,5-bis(trifluoromethyl)phenyl)-4-chlorophenylsulfoximine (4aj)**



According to **General Procedure C** (**2j**, 72.2 mg, 0.2 mmol), **4aj** was obtained as a white solid (42.0 mg, 45% yield) after purification by silica gel flash chromatography. R_f = 0.7 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.05 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 1.28 (s, 9H).

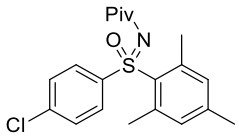
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 143.7, 141.4, 136.7, 133.7 (q, *J* = 34.6 Hz), 130.6, 129.5, 127.8 – 127.6 (m), 127.2 – 126.9 (m), 122.4 (q, *J* = 273.6 Hz), 42.0, 27.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99 (s, 6F).

HRMS (ESI): Calcd. for $[C_{19}H_{16}ClF_6NO_2S+H]^+$: 472.0567; Found: 472.0569.

IR (neat) ν 3055, 2988, 2305, 1421, 1266, 896, 745, 705 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(mesityl)-4-chlorophenylsulfoximine (4ak)**



According to **General Procedure C** (**2k**, 53.5 mg, 0.2 mmol), **4ak** was obtained as a white solid (47.6 mg, 63% yield) after purification by silica gel flash chromatography. R_f = 0.6 (PE/EA= 5/1).

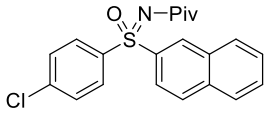
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 2H), 2.47 (s, 6H), 2.28 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 143.2, 140.7, 140.2, 139.6, 132.6, 132.2, 129.4, 128.7, 41.8, 28.0, 22.7, 21.1.

HRMS (ESI): Calcd. for $[C_{20}H_{24}ClNO_2S+H]^+$: 378.1289; Found: 378.1296.

IR (neat) ν 3055, 2988, 2305, 1419, 1276, 1255, 896, 766, 715, 690 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(naphthalen-2-yl)-4-chlorophenylsulfoximine (4al)**



According to **General Procedure C** (**2l**, 55.1 mg, 0.2 mmol), **4al** was obtained as a white solid (40.9 mg, 53% yield) after purification by silica gel flash chromatography. R_f = 0.5 (PE/EA= 5/1).

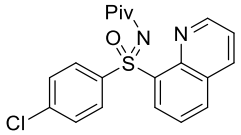
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.95 (m, 4H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.62 (p, *J* = 7.0 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 139.9, 138.9, 136.5, 135.2, 132.5, 130.1, 129.9, 129.6, 129.5, 129.5, 129.2, 128.1, 127.9, 122.1, 41.9, 27.9.

HRMS (ESI): Calcd. for $[C_{21}H_{20}ClNO_2S+H]^+$: 386.0976; Found: 386.0975.

IR (neat) ν 3055, 2986, 2305, 1422, 1265, 896, 745, 707 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(quinolin-8-yl)-4-chlorophenylsulfoximine (4am)**



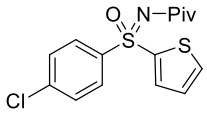
According to **General Procedure C** (**2m**, 55.3 mg, 0.2 mmol), **4am** was obtained as a white solid (38.5 mg, 50% yield) after purification by silica gel flash chromatography. R_f = 0.2 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 7.6 Hz, 1H), 8.82 (d, *J* = 4.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 8.6, 3.7 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 150.5, 143.2, 139.6, 138.5, 136.5, 136.3, 134.5, 133.3, 131.0, 129.0, 128.7, 126.1, 122.2, 41.9, 27.9.

HRMS (ESI): Calcd. for $[C_{20}H_{19}ClN_2O_2S+H]^+$: 387.0929; Found: 387.0934.

***N*-(Pivaloyl)-*S*,*S*-(thiophen-2-yl)-4-chlorophenylsulfoximine (4an)**



According to **General Procedure C** (**2n**, 46.3 mg, 0.2 mmol), **4an** was obtained as a white solid (26.9 mg, 39% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

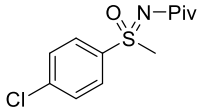
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 4.7 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 4.5 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 140.7, 140.0, 139.5, 134.9, 133.9, 129.9, 128.8, 128.7, 41.8, 27.7.

HRMS (ESI): Calcd. for $[C_{15}H_{16}ClNO_2S_2+H]^+$: 342.0384; Found: 342.0387.

IR (neat) ν 3055, 2988, 2307, 1421, 1272, 1259, 896, 761, 715, 698 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(methyl)-4-chlorophenylsulfoximine (4ao)**



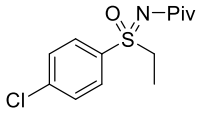
According to **General Procedure C** (**2o**, 32.6 mg, 0.2 mmol), **4ao** was obtained as a white solid (25.5 mg, 47% yield) after purification by silica gel flash chromatography. R_f = 0.2 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 3.30 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 140.5, 138.0, 130.0, 128.7, 44.3, 41.5, 27.7.

HRMS (ESI): Calcd. for $[C_{12}H_{16}ClNO_2S+H]^+$: 274.0663; Found: 274.0663.

***N*-(Pivaloyl)-*S*,*S*-(ethyl)-4-chlorophenylsulfoximine (4ap)**



According to **General Procedure C** (**2p**, 35.5 mg, 0.2 mmol), **4ap** was obtained as a white solid (31.3 mg, 54% yield) after purification by silica gel flash chromatography. R_f = 0.25 (PE/EA= 5/1).

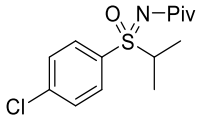
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 3.45 (m, 2H), 1.25 – 1.18 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 140.5, 135.6, 129.9, 129.4, 50.4, 41.6, 27.8, 7.3.

HRMS (ESI): Calcd. for $[C_{13}H_{18}ClNO_2S+H]^+$: 288.0820; Found: 288.0829.

IR (neat) ν 3055, 2988, 2305, 1419, 1266, 896, 740, 704 cm^{-1}.

***N*-(Pivaloyl)-*S*,*S*-(isopropyl)-4-chlorophenylsulfoximine (4aq)**



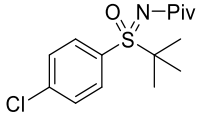
According to **General Procedure C** (**2q**, 38.3 mg, 0.2 mmol), **4aq** was obtained as a white solid (25.8 mg, 43% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 3.65 – 3.54 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.25 – 1.19 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 140.4, 133.8, 130.2, 129.8, 56.1, 41.7, 27.8, 15.9, 15.4.

HRMS (ESI): Calcd. for $[C_{14}H_{20}ClNO_2S+H]^+$: 302.0976; Found: 302.0984.

***N*-(Pivaloyl)-*S*,*S*-(*tert*-butyl)-4-chlorophenylsulfoximine (4ar)**



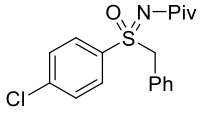
According to **General Procedure C** (**2r**, 41.0 mg, 0.2 mmol), **4ar** was obtained as a white solid (27.6 mg, 44% yield) after purification by silica gel flash chromatography. R_f = 0.45 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 1.38 (s, 9H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 140.3, 132.3, 131.2, 129.6, 61.5, 41.8, 27.9, 23.3.

HRMS (ESI): Calcd. for $[C_{15}H_{22}ClNO_2S+H]^+$: 316.1136; Found: 316.1133.

***N*-(Pivaloyl)-*S*,*S*-(benzyl)-4-chlorophenylsulfoximine (4as)**



According to **General Procedure C** (**2s**, 47.9 mg, 0.2 mmol), **4as** was obtained as a white solid (37.1 mg, 53% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1);

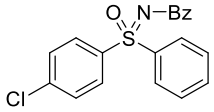
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 4.88 (d, *J* = 13.6 Hz, 1H), 4.64 (d, *J* = 13.6 Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 140.5, 134.5, 131.3, 130.0, 129.3, 129.3, 128.5, 127.4, 61.9, 41.6, 27.7.

HRMS (ESI): Calcd. for $[C_{18}H_{20}ClNO_2S+H]^+$: 350.0976; Found: 350.0979.

IR (neat) ν 3055, 2986, 2305, 1422, 1266, 896, 741, 705 cm^{-1}.

***N*-(benzoyl)-*S*,*S*-(benzyl)-4-chlorophenylsulfoximine (4au)**



According to **General Procedure C** (**2u**, 46.3 mg, 0.2 mmol), **4au** was obtained as a white solid (10.0 mg, 14% yield) after purification by silica gel flash chromatography. R_f = 0.3 (PE/EA= 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.21 (m, 2H), 8.09 – 8.05 (m, 2H), 8.02 – 7.96 (m, 2H), 7.65 – 7.59 (m, 1H), 7.59 – 7.48 (m, 5H), 7.48 – 7.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 140.2, 139.6, 138.7, 135.7, 133.7, 132.5, 130.0, 129.8, 129.7, 129.2, 128.3, 127.8.

HRMS (ESI): Calcd. for $[C_{19}H_{14}ClNO_2S+Na]^+$: 378.0335; Found: 378.0326.

5. Mechanism discussion

Four potential reaction pathways or intermediates have been evaluated in our reaction, 1) the SNAr pathway; 2) aryne intermediate; 3) aryl radical intermediate; 4) ligand coupling pathway. The first three were excluded based on experimental results and the knowledge of previous reports.

1) the SNAr pathway was not likely involved for the following reasons:

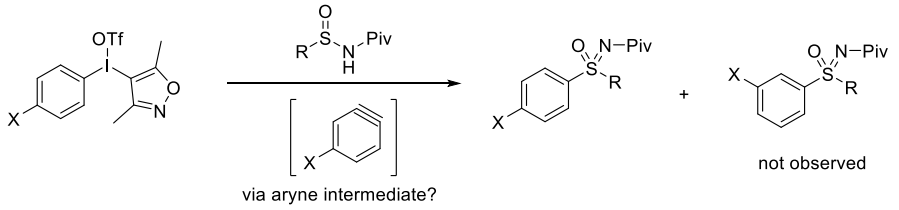
(i) Solvent Effects: SNAr reactions typically require polar aprotic solvents to stabilize transition states and intermediates. However, polar aprotic solvents provided poor yields in this reaction (Table 1 in the manuscript and Table S1 in this file). The experimental observation of solvent effects align with results observed in previous well-defined ligand coupling reactions at hypervalent iodine(III) centers (*Angew. Chem. Int. Ed.,* **2016**, *55*, 13335-13339).

(ii) Electronic Effects: SNAr mechanisms generally require electron-withdrawing groups to activate the aromatic ring for nucleophilic substitution. In contrast, the substrate scope of this reaction accommodates electron-donating groups, such as 4-alkyl and 4-methoxy substituents (**3ca**, **3ma**, and **3da**, Scheme 2 in the main text). The low yields observed for these products are likely due to the strong electron-donating effects, which alter the electronic properties of the iodine(III) center, thereby reducing the efficiency of the ligand coupling process (*Org. Lett.* **2025**, *27*, 1130-1135).

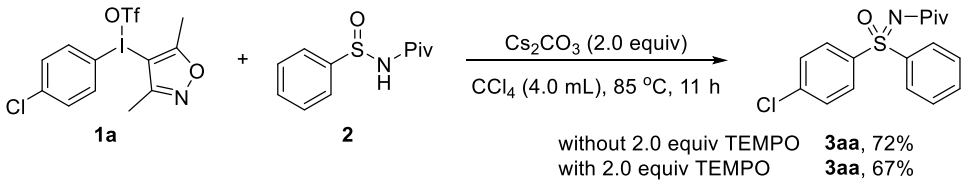
(iii) Steric Effects: Sterically congested substrates bearing ortho substitutions are generally poor candidates for SNAr reactions. However, these aryl iodonium salts provided moderate to good yields in our reactions (**3ga**, **3ja**, and **3oa**, Scheme 2 in the manuscript).

2) aryne intermediates were not likely involved for the following reasons

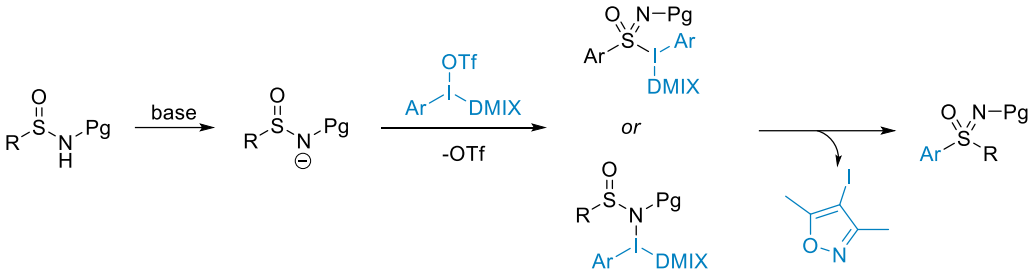
The site-specific formation of *ipso*-substitution products in this reaction suggests that an aryne intermediate is unlikely to be involved. For instance, the 4-Br substrate failed to generate regioselective products (**3ba**), which contrasts with previously reports via aryne intermediates (*Org. Biomol. Chem.* **2016**, *14*, 10185-10188; *Org. Lett.* **2025**, 27, 1130-1135). Additionally, the formation of products **3ga** and **3ja** could not proceed via an aryne intermediate, further supporting its exclusion from the reaction pathway.



3) aryl radical intermediates were excluded based on the radical trapping experiment. The reaction was little affected when the radical scavenger TEMPO was added.

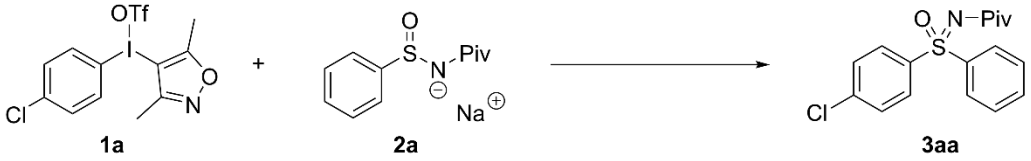


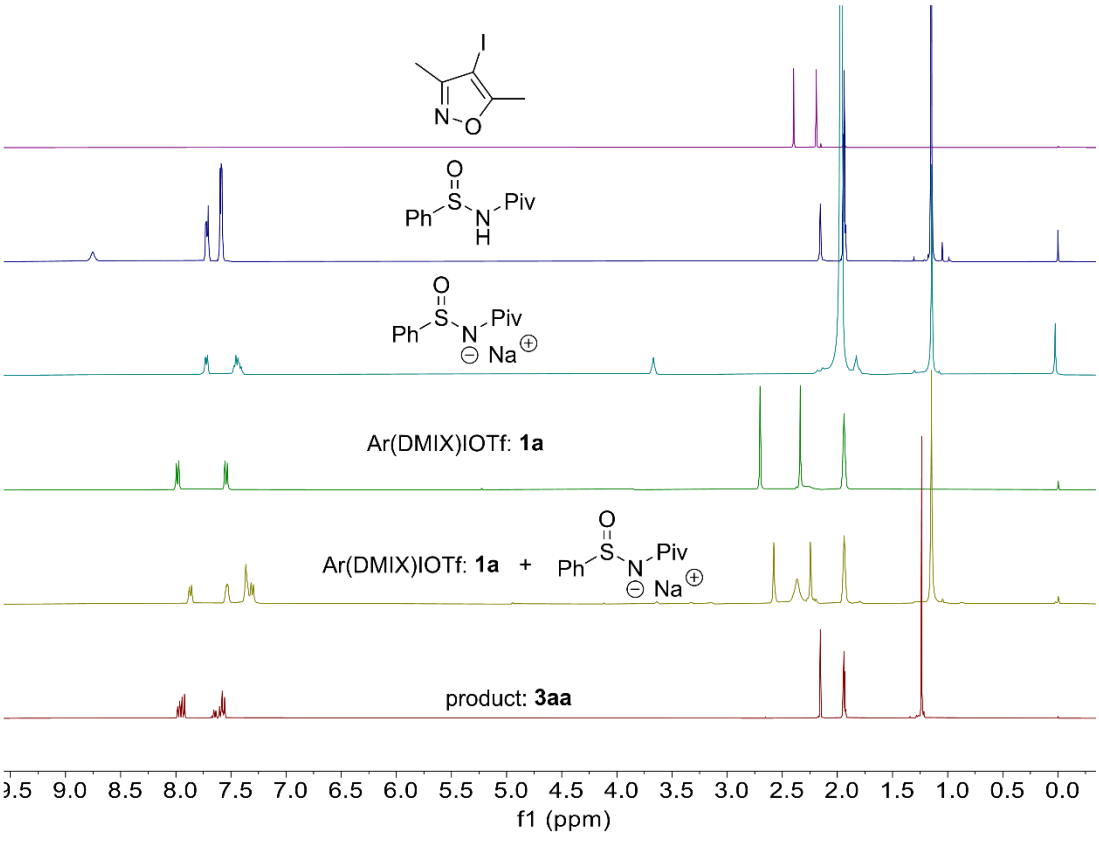
4) ligand coupling pathway was proposed based experimental results and knowledge from previous reports. However, no solid evidence has been obtained at the current stage.



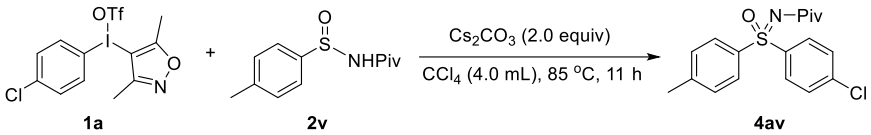
The following experiment aimed to capture the potential iodine(III) intermediate formed in situ by deprotonated sodium salt of sulfinamide (**2a**) and the DMIX-iodonium reagent (**1a**). We did observe the chemical shift by monitoring their mixture in CD_3CN using ^1H NMR at room temperature, indicating the formation of a new species. However, the new species could not be isolated or characterized as the proposed iodine(III) intermediate of ligand coupling reaction. The mixture was then heated in CCl_4 that resulted in the product **3aa** in moderate yield.

^1H NMR experiment (in CD_3CN)

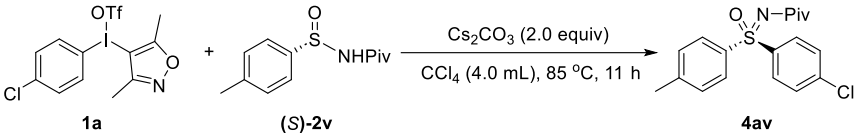




6. Gram scale experiment and synthetic application.



According to **General Procedure C** (**2v**, 4.9 mmol), **4av** was obtained as a white solid (1.0 g mg, 58% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).



According to **General Procedure C** ((*S*)**-2v**, 23.9 mg, 0.1 mmol), **4av** was obtained as a white solid (26.2 mg, 75% yield) after purification by silica gel flash chromatography. R_f = 0.4 (PE/EA= 5/1).

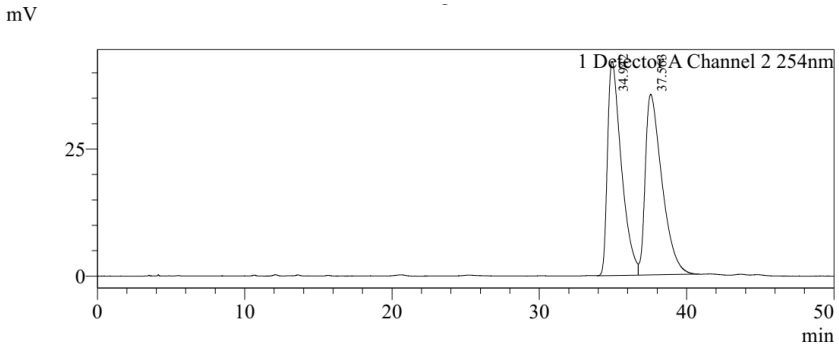
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 144.6, 139.7, 139.2, 136.5, 130.3, 129.8, 128.9, 127.7, 41.8, 27.8, 21.6.

HRMS (ESI): Calcd. for $[C_{18}H_{20}ClNO_2S+H]^+$: 350.0976; Found: 350.0980.

[α]D^{20} = -13.4 (*c* = 1.0, $CHCl_3$). **HPLC** analysis: Daicel CHIRALCEL OD column, 1% *i*-PrOH in hexanes, 1.0 mL/min, λ = 254 nm, retention time: 35.0 min (minor) and 36.7 min (major).

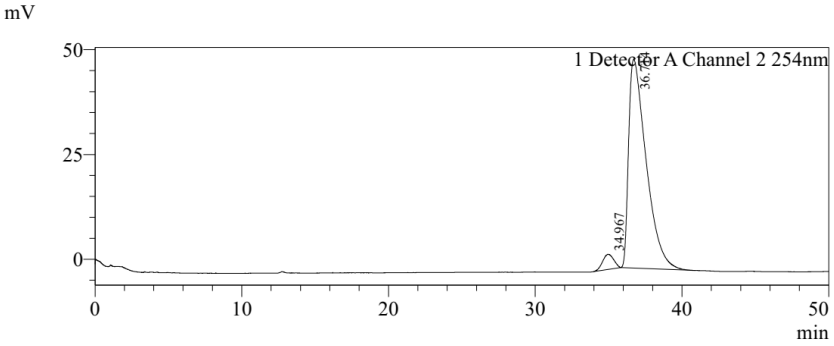
Racemic **4av**



Detector A Channel 2 254nm

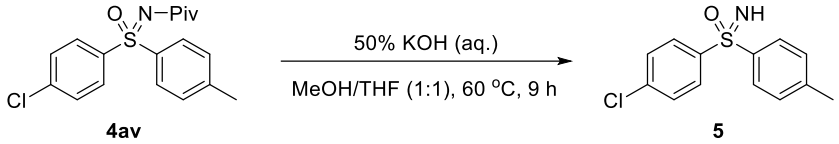
Peak#	Ret. Time	USP Width	Area	Height	Area%
1	34.942	1.703	2756413	42119	49.506
2	37.563	2.060	2811476	35536	50.494

enantio-enriched **4av**



Detector A Channel 2 254nm

Peak#	Ret. Time	USP Width	Area	Height	Area%
1	34.967	1.436	188378	3597	4.358
2	36.714	2.203	4134403	49775	95.642



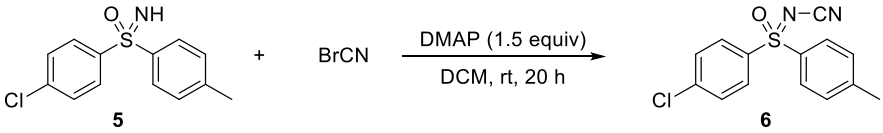
4av **5**

Following the literature reported method. An oven-dried 25 mL flask equipped with a magnetic stir bar was charged with **4ct** (102 mg, 0.3 mmol, 1.0 equiv), 50% KOH aq. (1.1 mL), MeOH (3.0 mL) and THF (3.0 mL). The reaction mixture was stirred for 9 h at 60 °C. The reaction mixture was quenched with 1 M NaH_2PO_4 aq. and basified with sat. $NaHCO_3$ aq. The aqueous layer was extracted with DCM for three times. The combined organic layer was washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford compound **5** as white solid (60.7 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.90 – 7.86 (m, 2H), 7.43 – 7.38 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 2.99 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 142.3, 140.0, 139.1, 130.0, 129.4, 129.4, 128.0, 21.5.

HRMS (ESI): Calcd. For $[C_{13}H_{12}ClNOS+H]^+$: 266.0401; Found: 266.0406.



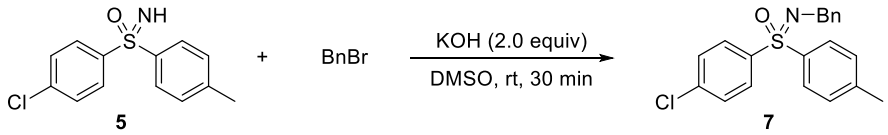
5 **6**

An over-dried 10 mL Schlenk tube equipped with magnetic stir bar was added **5** (26.3 mg, 0.1 mmol, 1.0 equiv) and DMAP (18.3 mg, 0.15 mmol, 1.5 equiv). The DCM (1.0 mL, 0.1 M) and BrCN (0.15 mmol, 1.5 equiv) were then added under nitrogen atmosphere at 0 °C. The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was quenched with H_2O and extracted with DCM for three times. The combined organic layer was washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford compound **6** as solid (22.2 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.88 – 7.84 (m, 2H), 7.58 – 7.53 (m, 2H), 7.42 – 7.38 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 141.8, 136.4, 133.8, 130.9, 130.4, 129.3, 128.1, 111.9, 21.8.

HRMS (ESI): Calcd. For $[C_{14}H_{11}ClN_2OS+H]^+$: 291.0353; Found: 291.0358.



An over-dried 10 mL Schlenk tube equipped with magnetic stir bar was added **5** (26.3 mg, 0.1 mmol, 1.0 equiv) and KOH (11.2 mg, 0.2 mmol, 2.0 equiv). The DMSO (1.0 mL, 0.1 M) and BnBr (25.7 mg, 0.15 mmol, 1.5 equiv) were then added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with H_2O and extracted with EA for three times. The combined organic layer was washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford compound **7** as solid (27.7 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.90 – 7.85 (m, 2H), 7.46 – 7.40 (m, 4H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 4.27 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 141.4, 139.7, 139.1, 137.3, 130.1, 130.1, 129.5, 128.8, 128.4, 127.5, 126.7, 47.2, 21.6.

HRMS (ESI): Calcd. For $[C_{20}H_{18}ClNOS+H]^+$: 356.0870; Found: 356.0878.

7. References

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(6) Aota, Y.; Kano, T.; Maruoka, K. Asymmetric Synthesis of Chiral Sulfoximines via the *S*-Arylation of Sulfinamides. *J. Am. Chem. Soc.* **2019**, *141*, 19263-19268.

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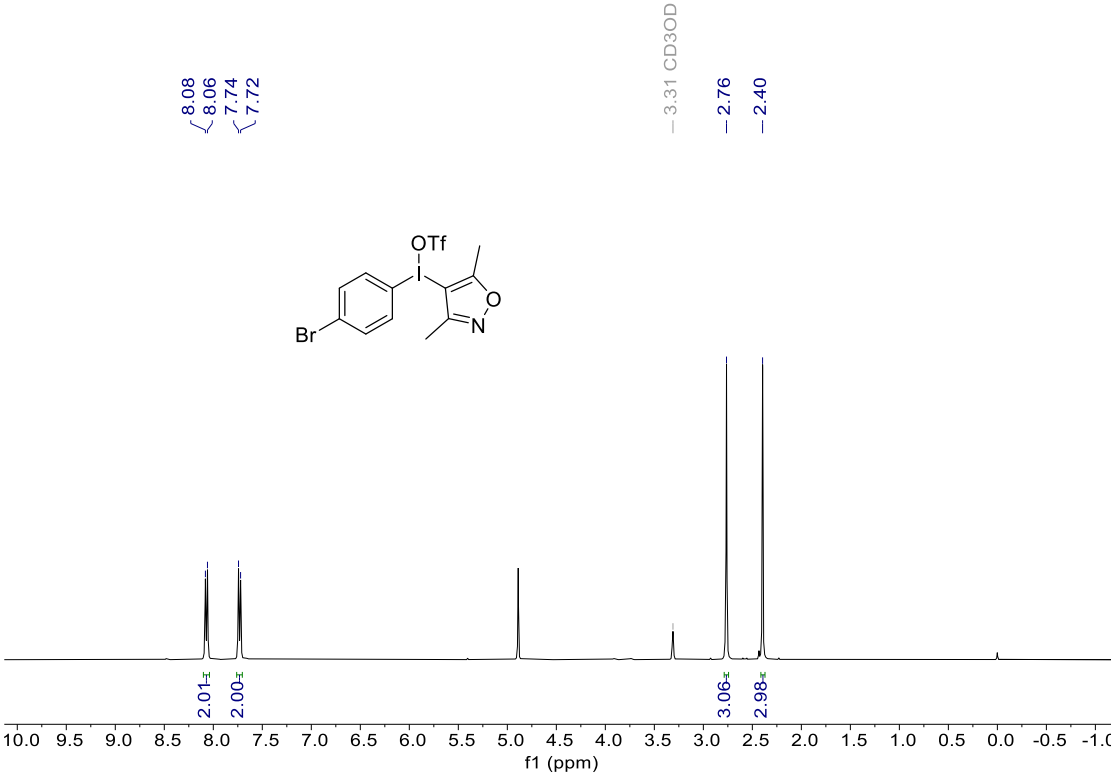
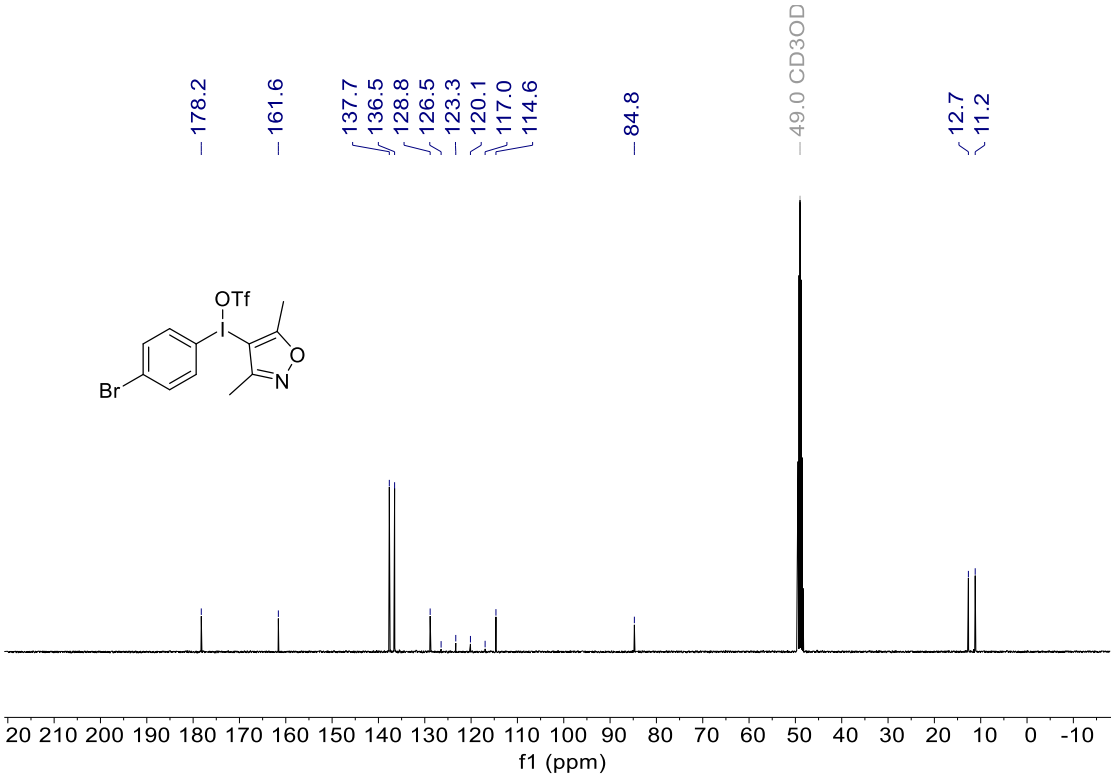
8. NMR spectra of related compounds

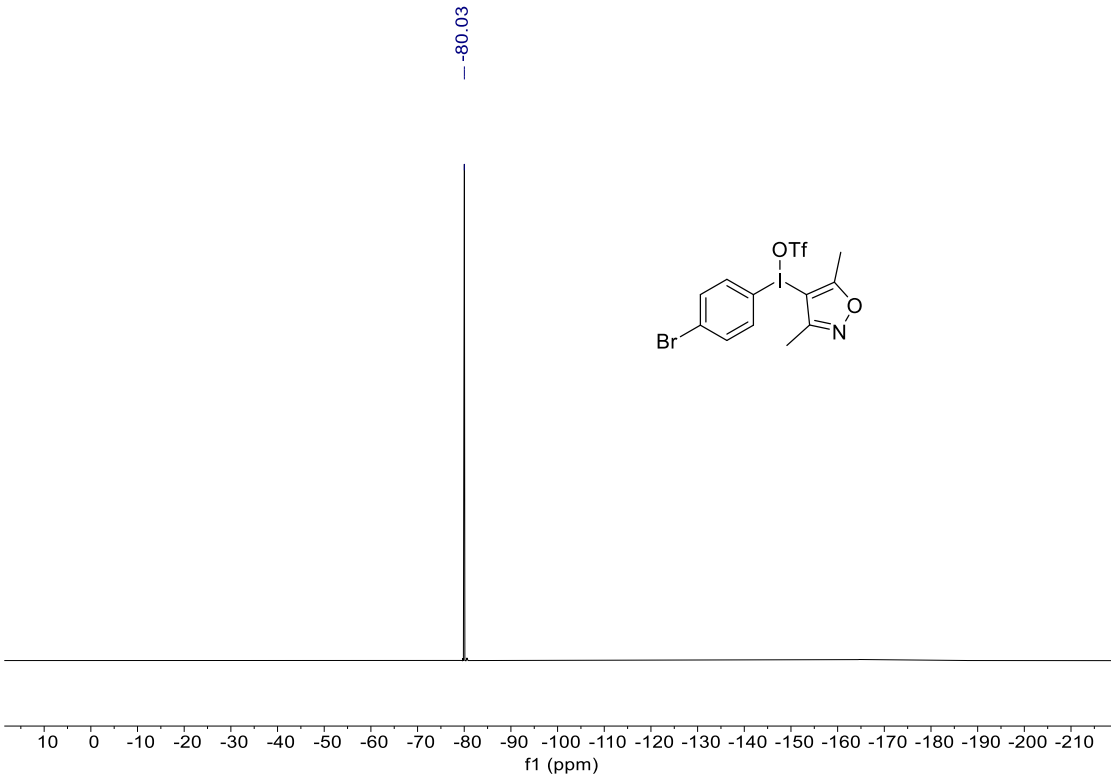
1b, ^{1}H NMR (400 MHz, CD_3OD)



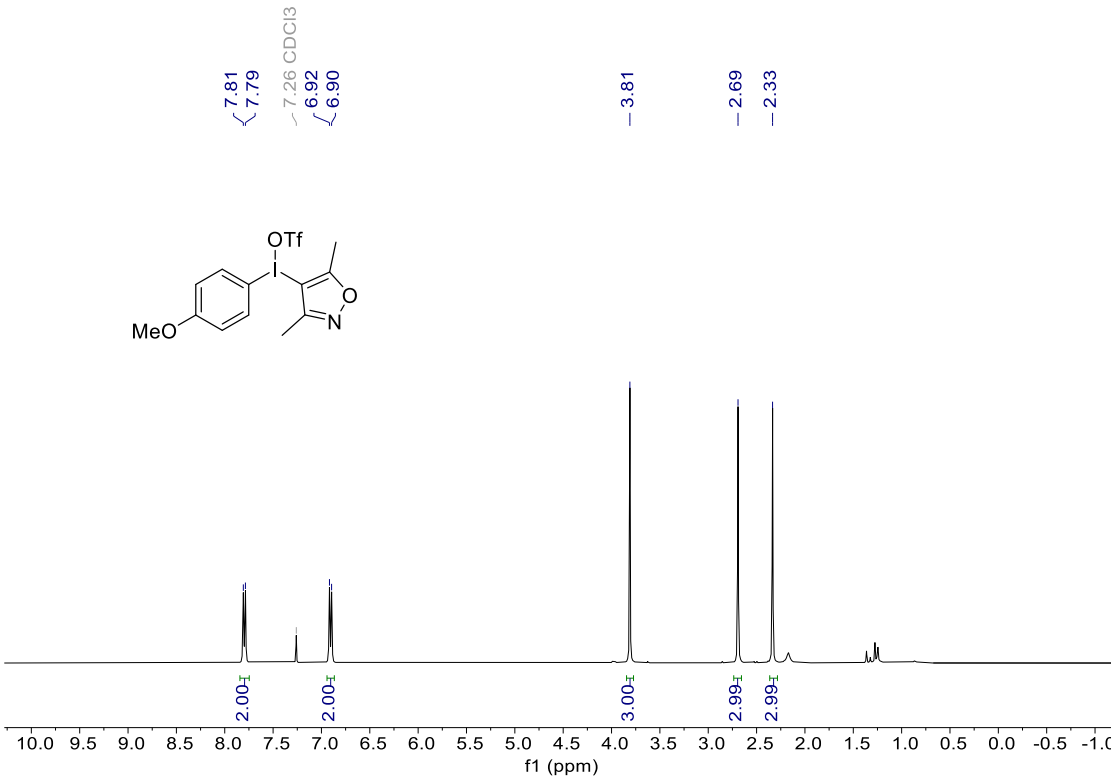
1b, ^{13}C NMR (101 MHz, CD_3OD)



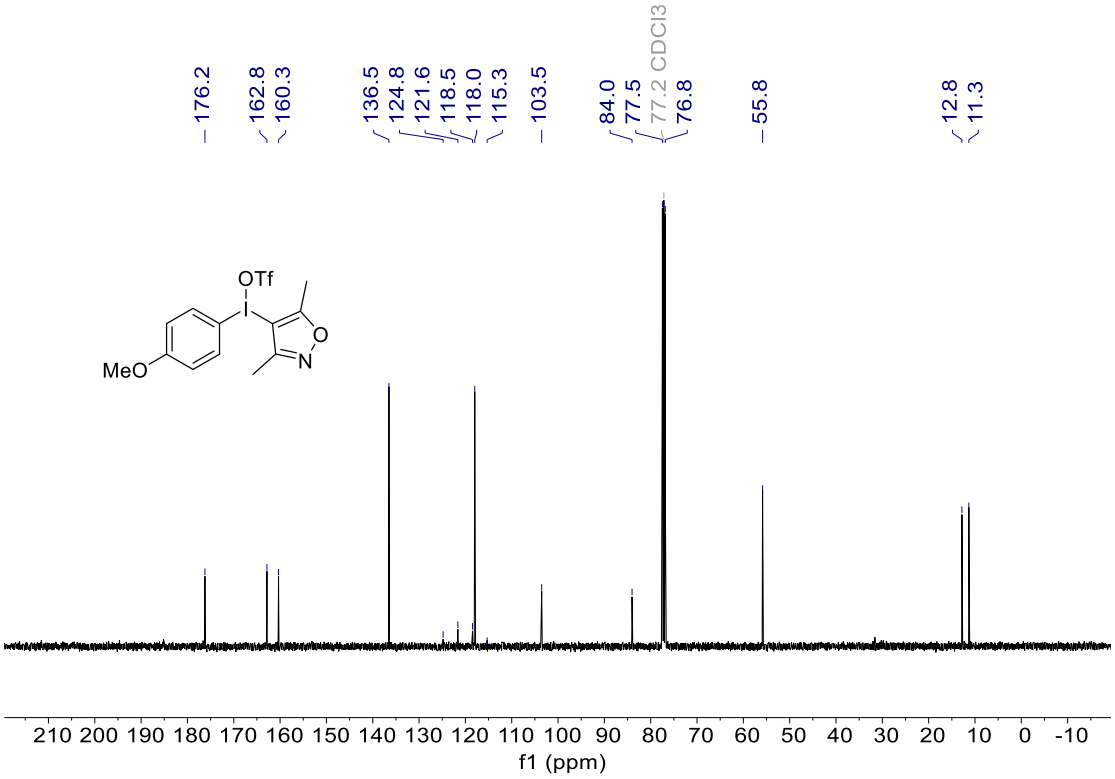
1b, ^{19}F NMR (376 MHz, CD_3OD)



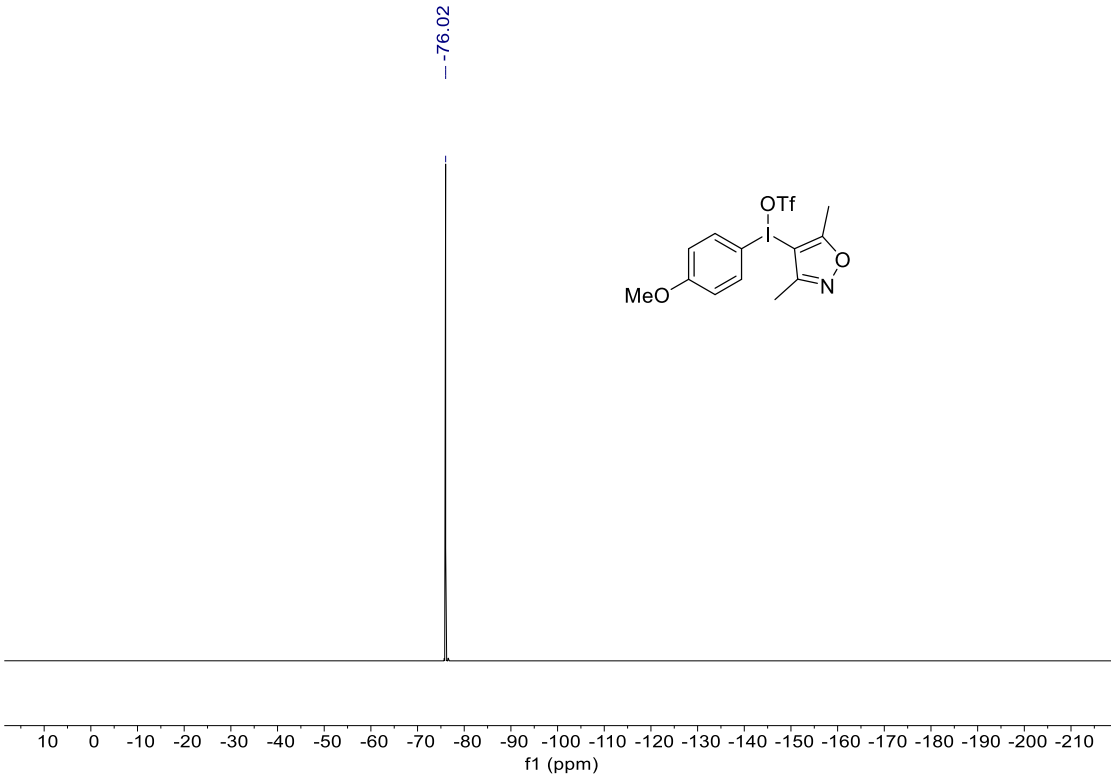
1d, ^{1}H NMR (400 MHz, $CDCl_3$)



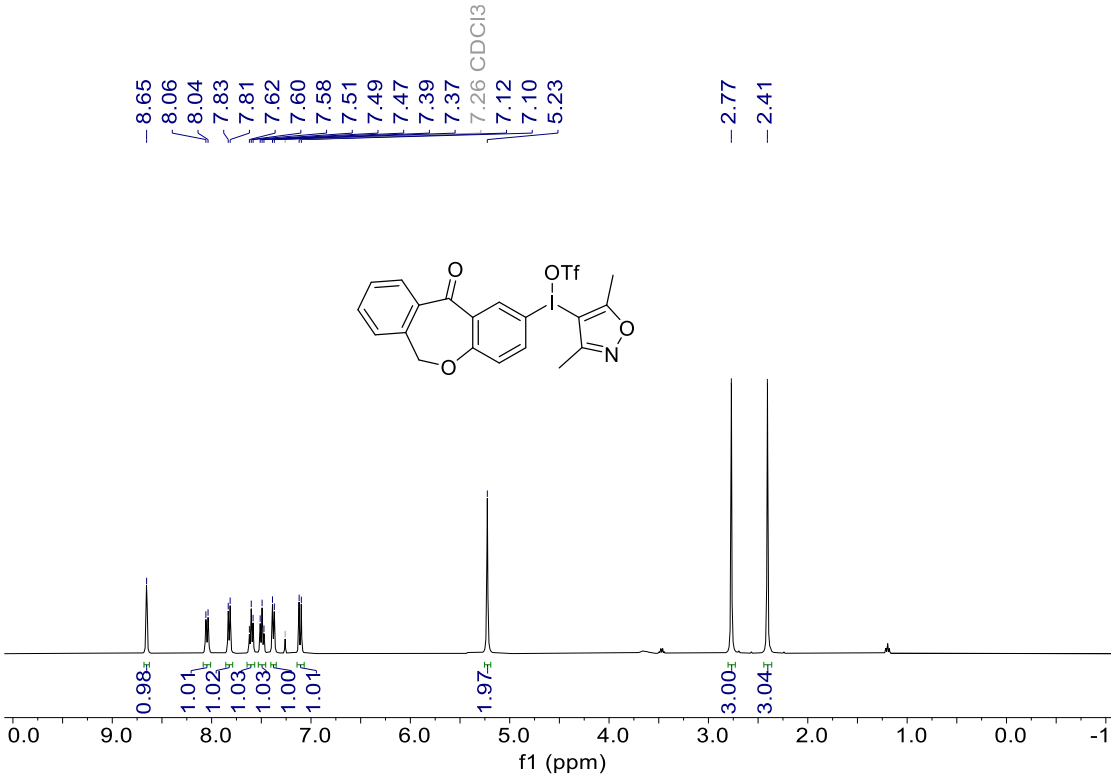
1d, ^{13}C NMR (101 MHz, $CDCl_3$)



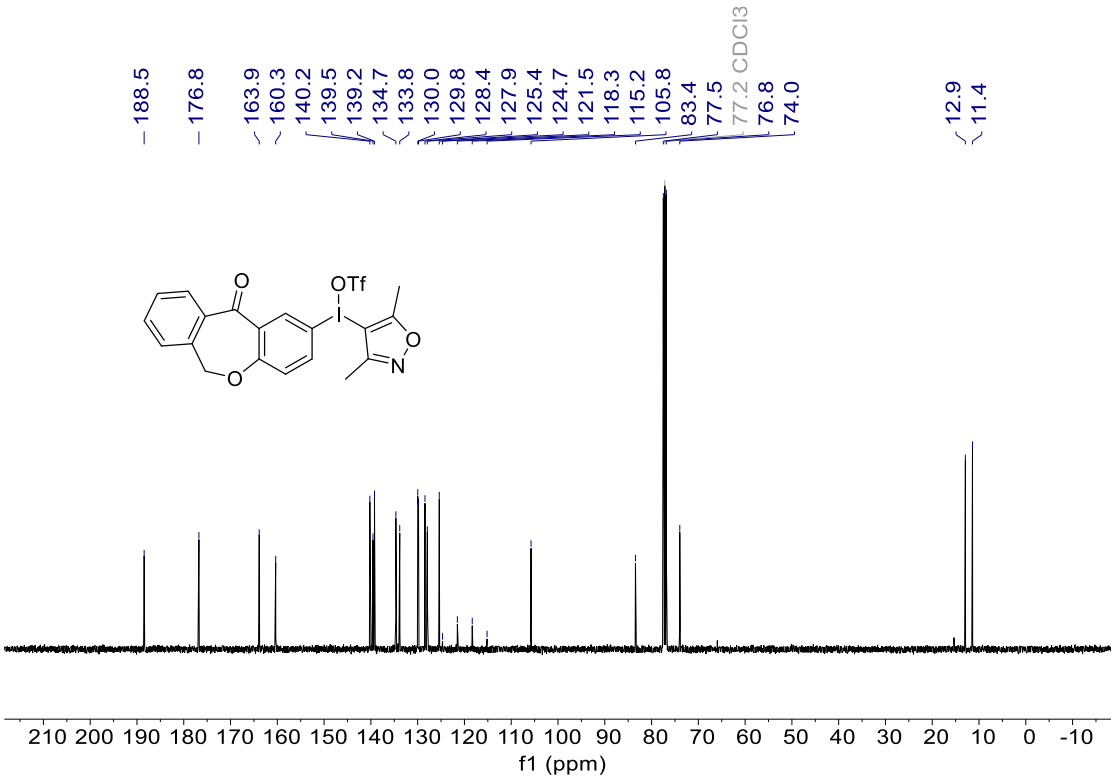
1d, ^{19}F NMR (376 MHz, $CDCl_3$)



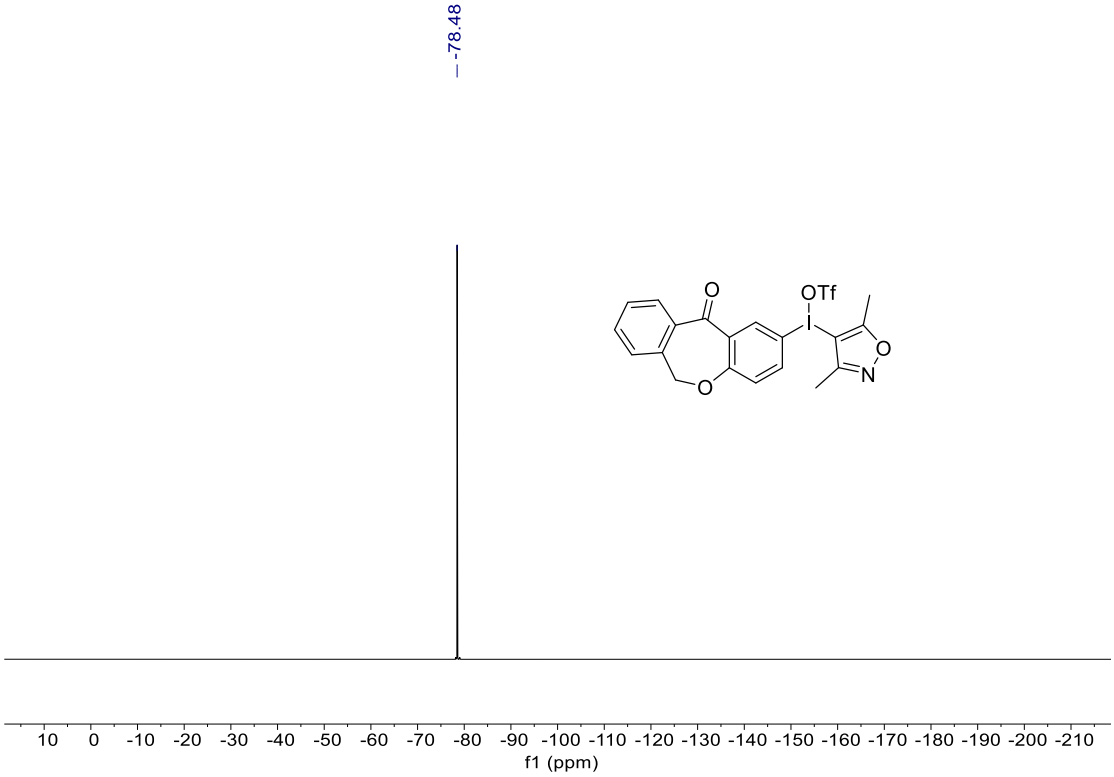
1l, ^{1}H NMR (400 MHz, $CDCl_3$)



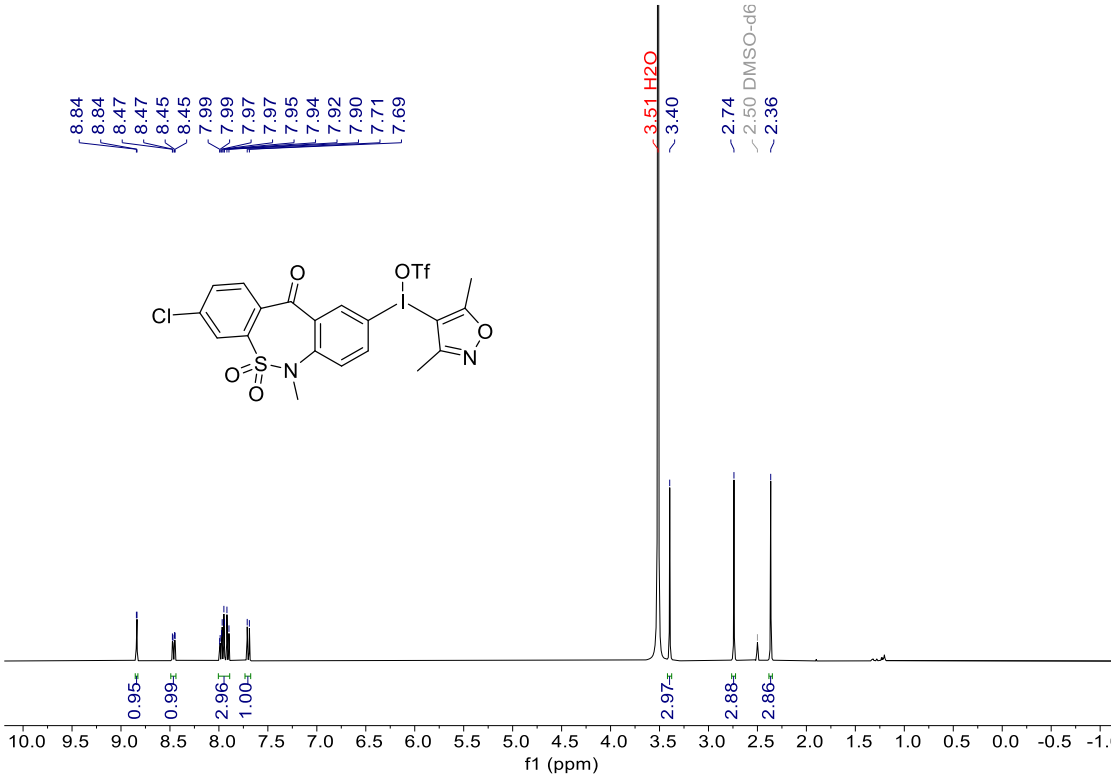
1l, ^{13}C NMR (101 MHz, $CDCl_3$)



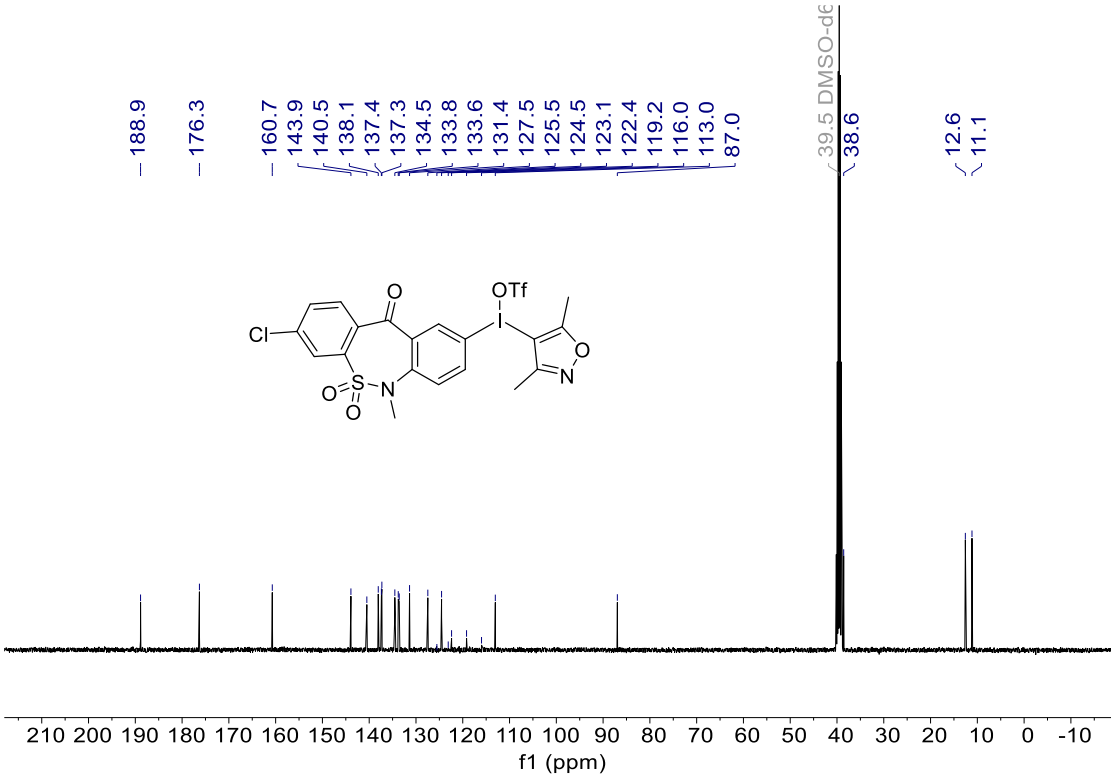
1l, ^{19}F NMR (376 MHz, $CDCl_3$)



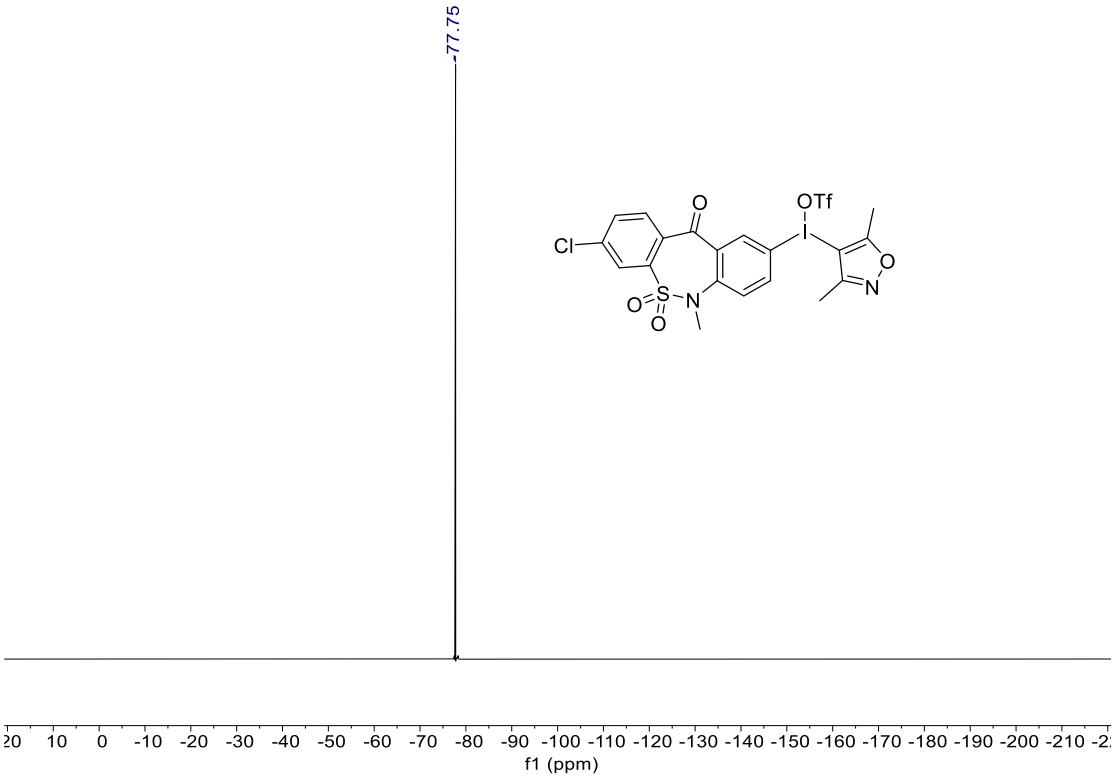
1p, ^{1}H NMR (400 MHz, DMSO-d_6)



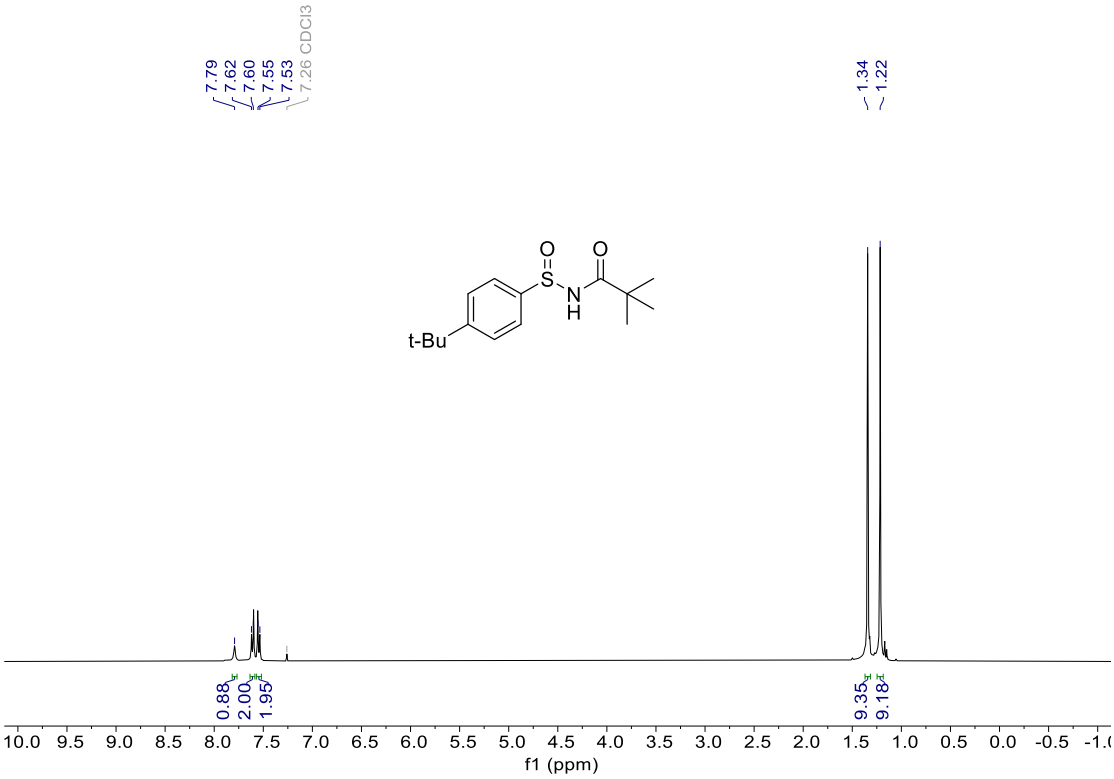
1p, ^{13}C NMR (101 MHz, DMSO-d_6)



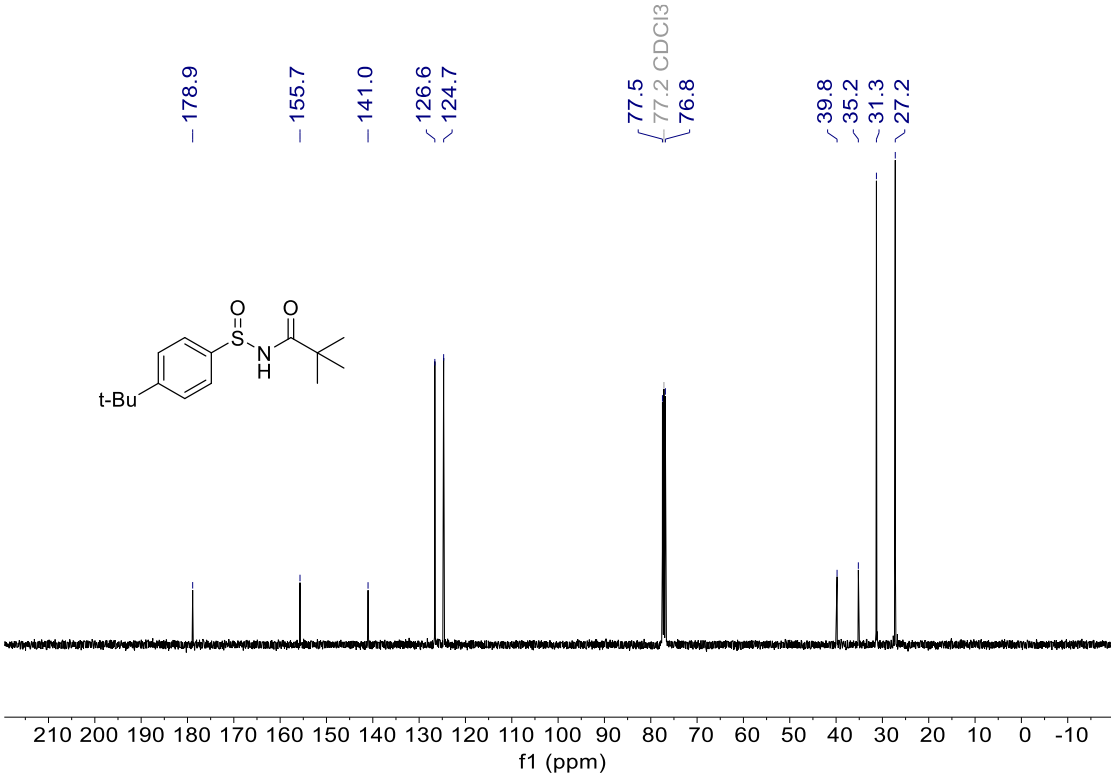
1p, ^{19}F NMR (376 MHz, DMSO-d_6)



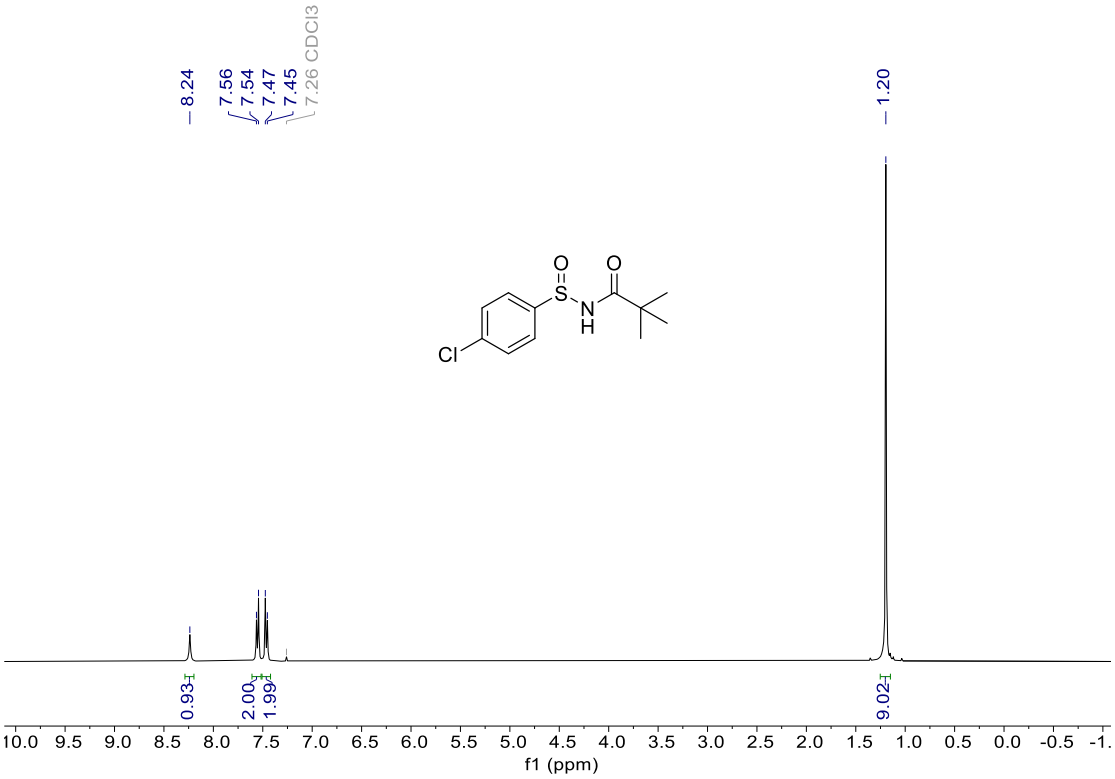
2c, ^{1}H NMR (400 MHz, $CDCl_3$)



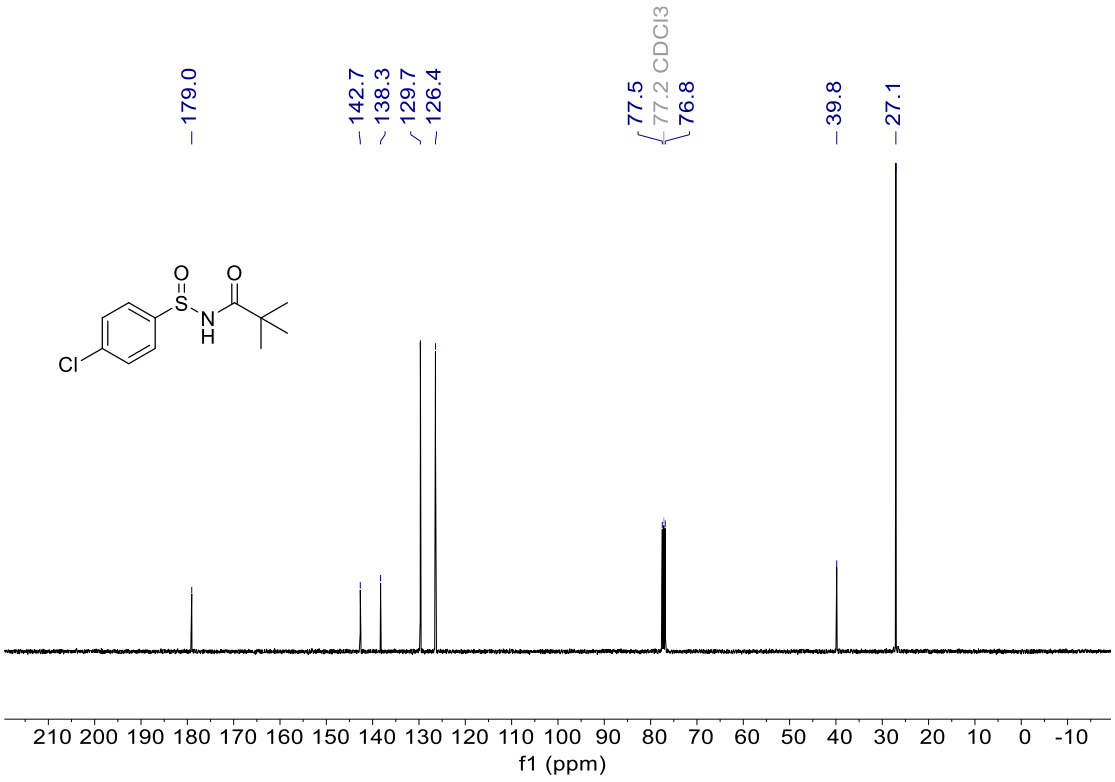
2c, ^{13}C NMR (101 MHz, $CDCl_3$)



2e, ^{1}H NMR (400 MHz, $CDCl_3$)



2e, ^{13}C NMR (101 MHz, $CDCl_3$)



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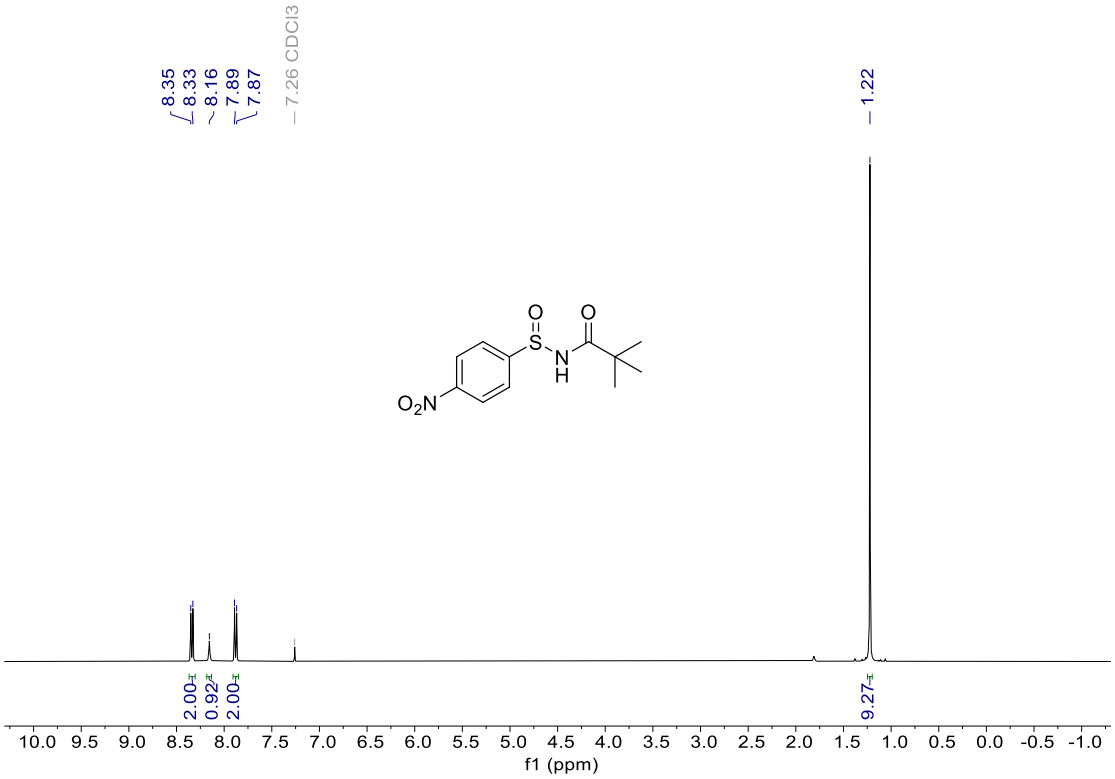
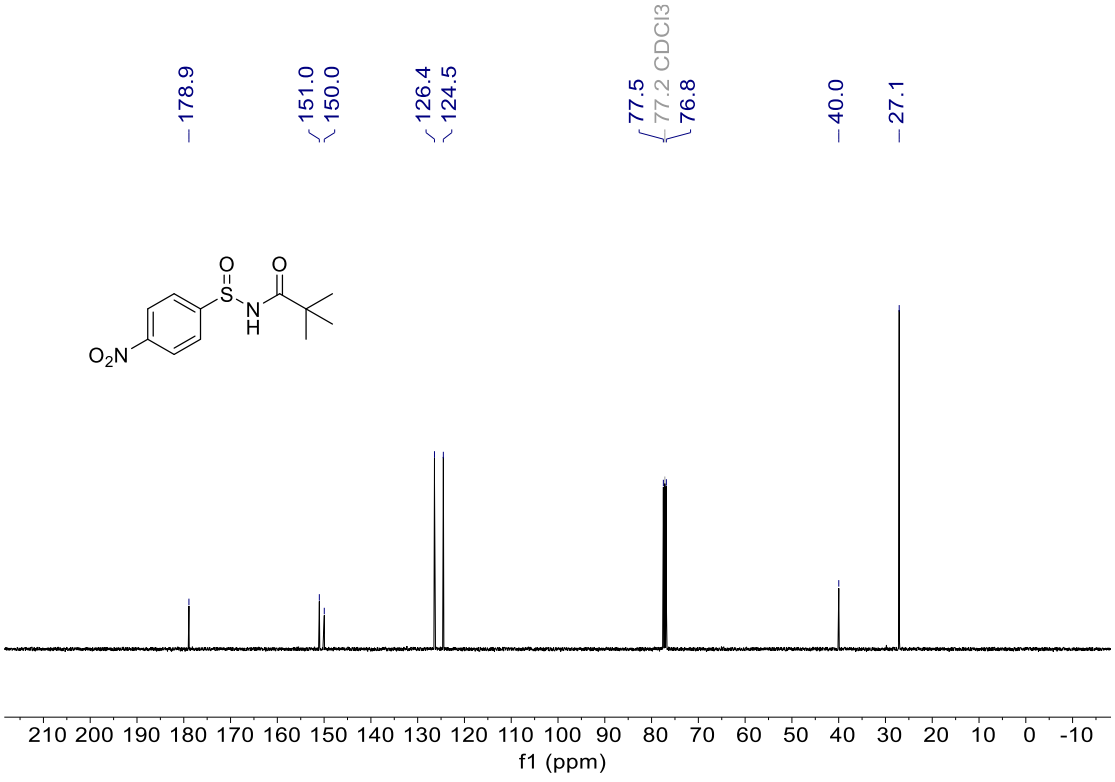
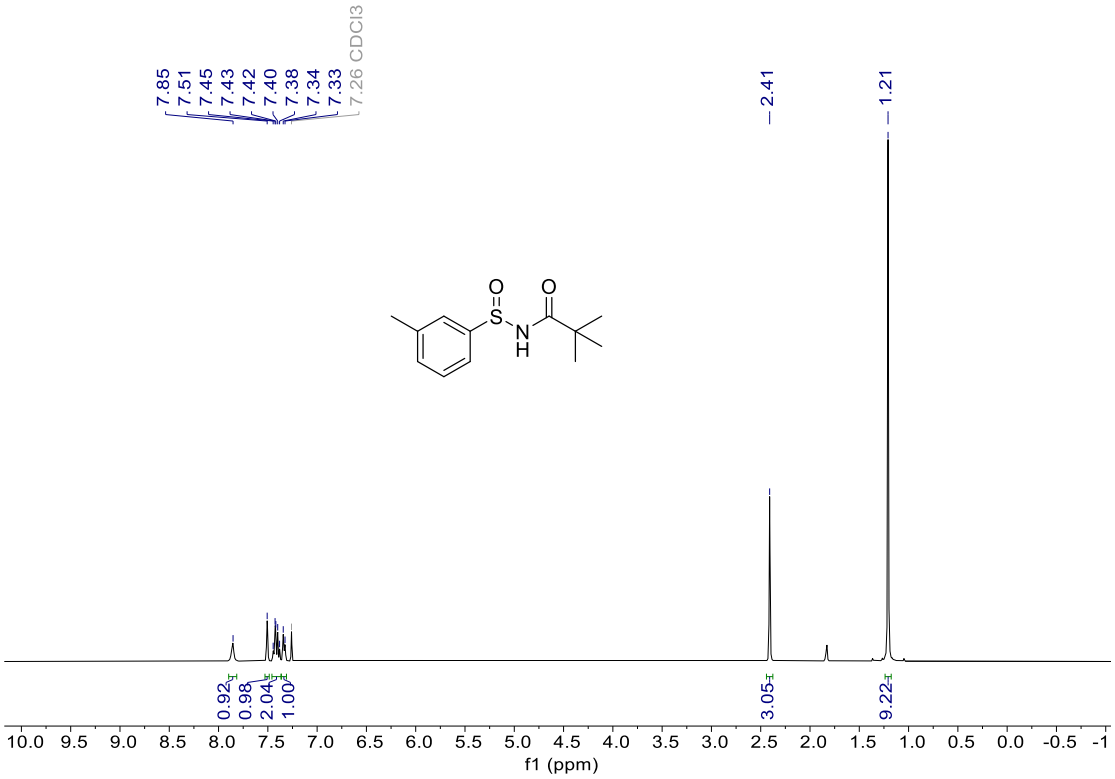


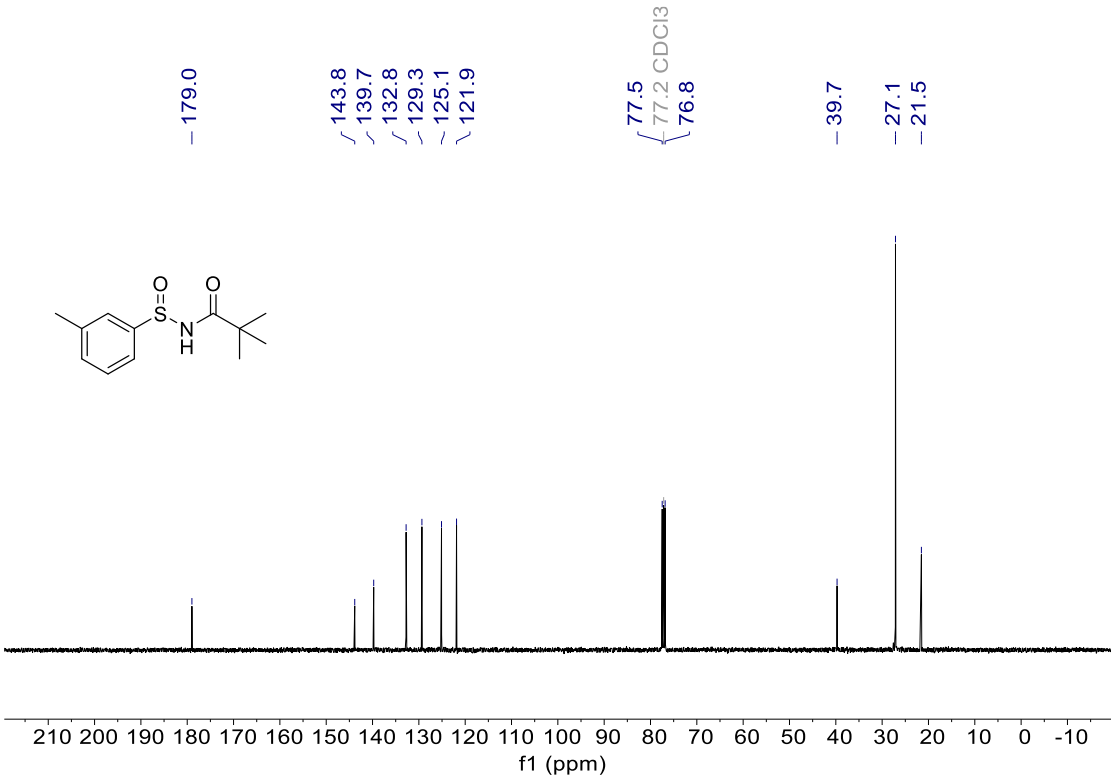
2h, ^{13}C NMR (101 MHz, $CDCl_3$)



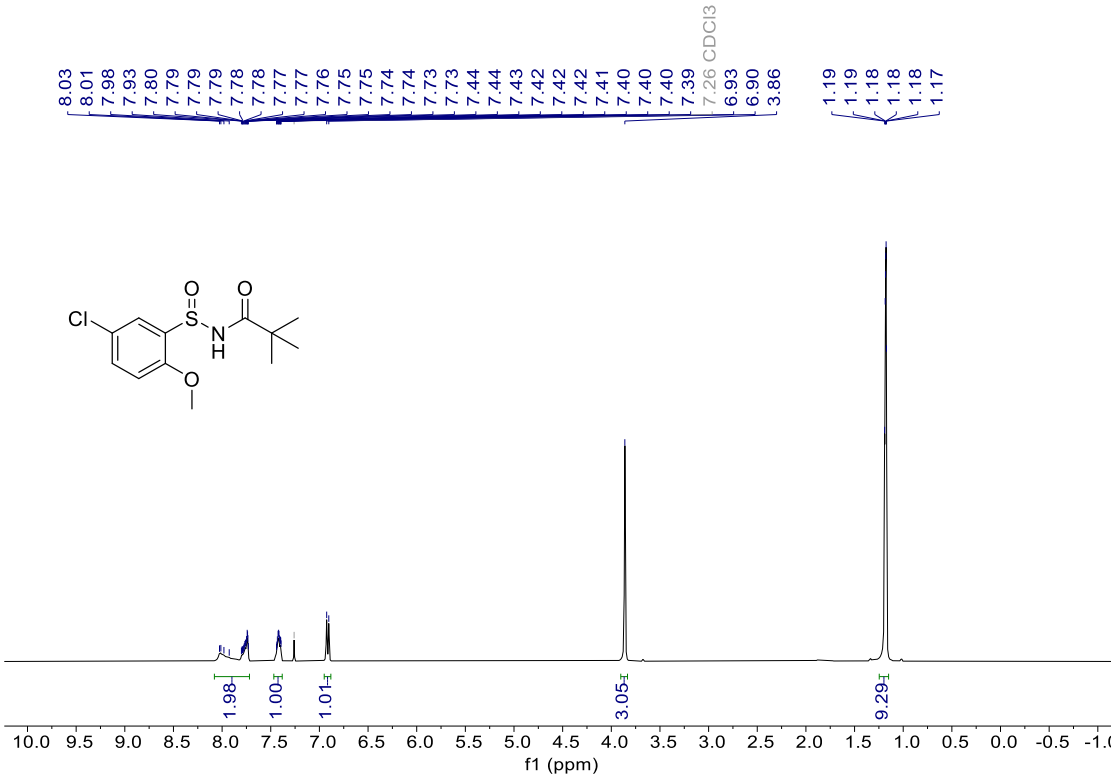
2i, ^{1}H NMR (400 MHz, $CDCl_3$)



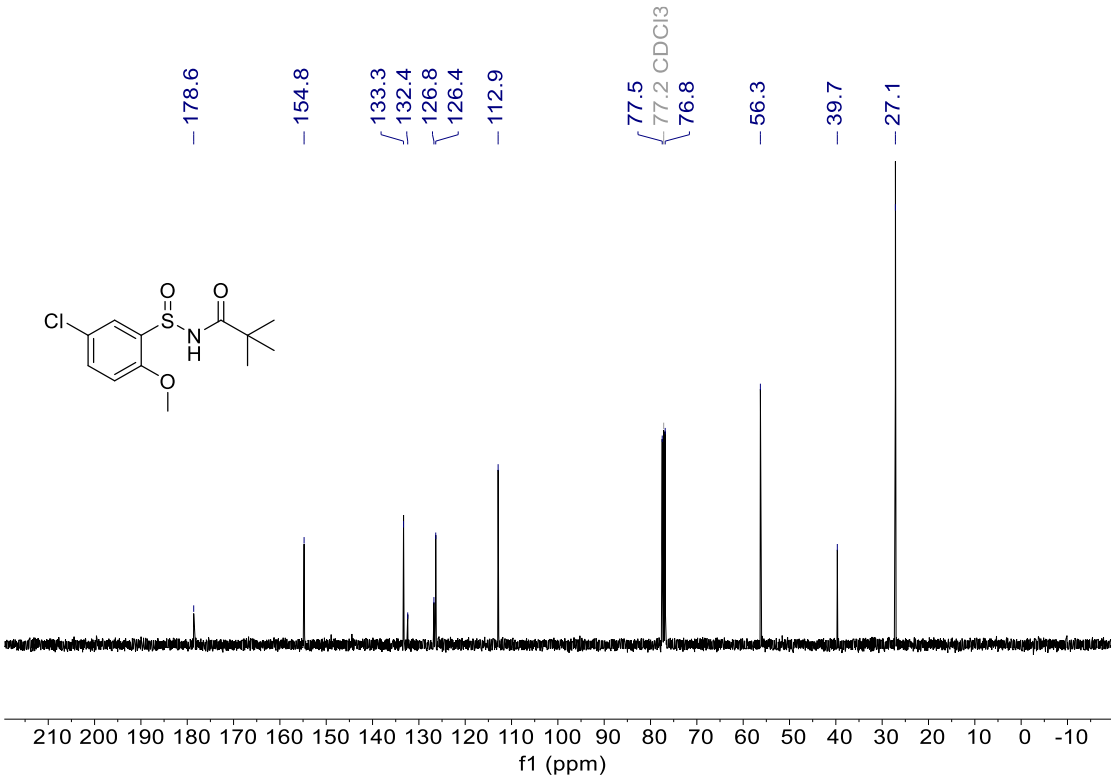
2i, ^{13}C NMR (101 MHz, $CDCl_3$)



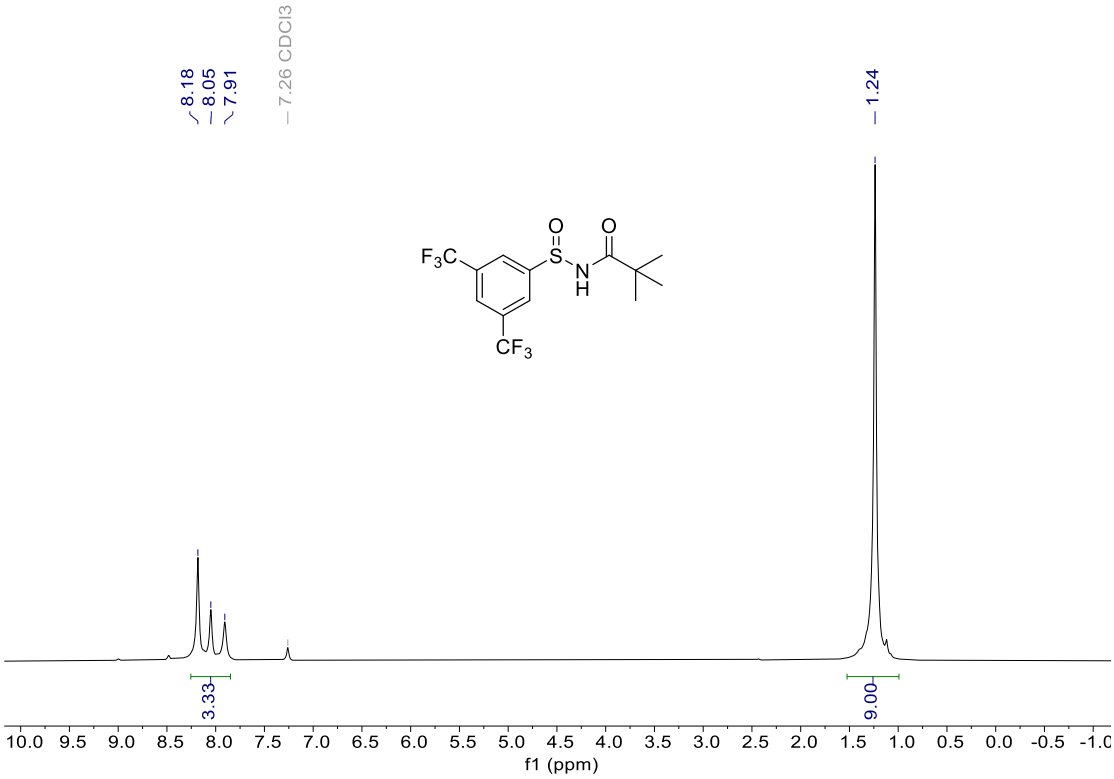
2j, ^{1}H NMR (400 MHz, $CDCl_3$)



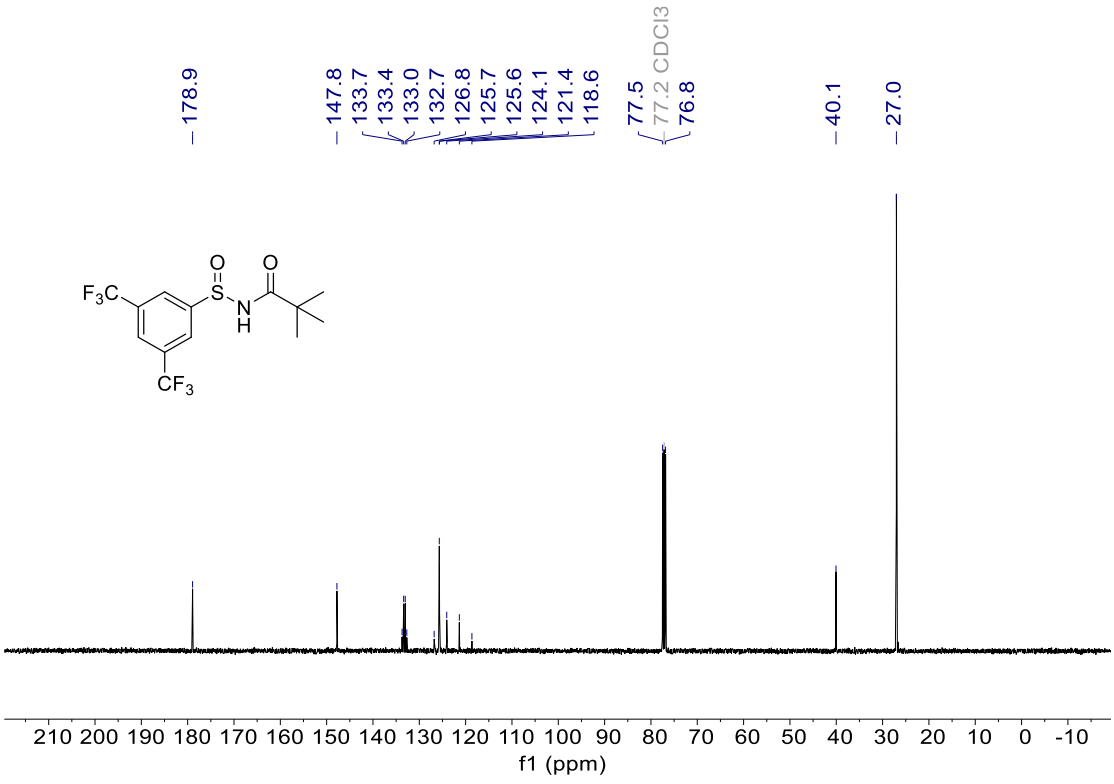
2j, ^{13}C NMR (101 MHz, $CDCl_3$)



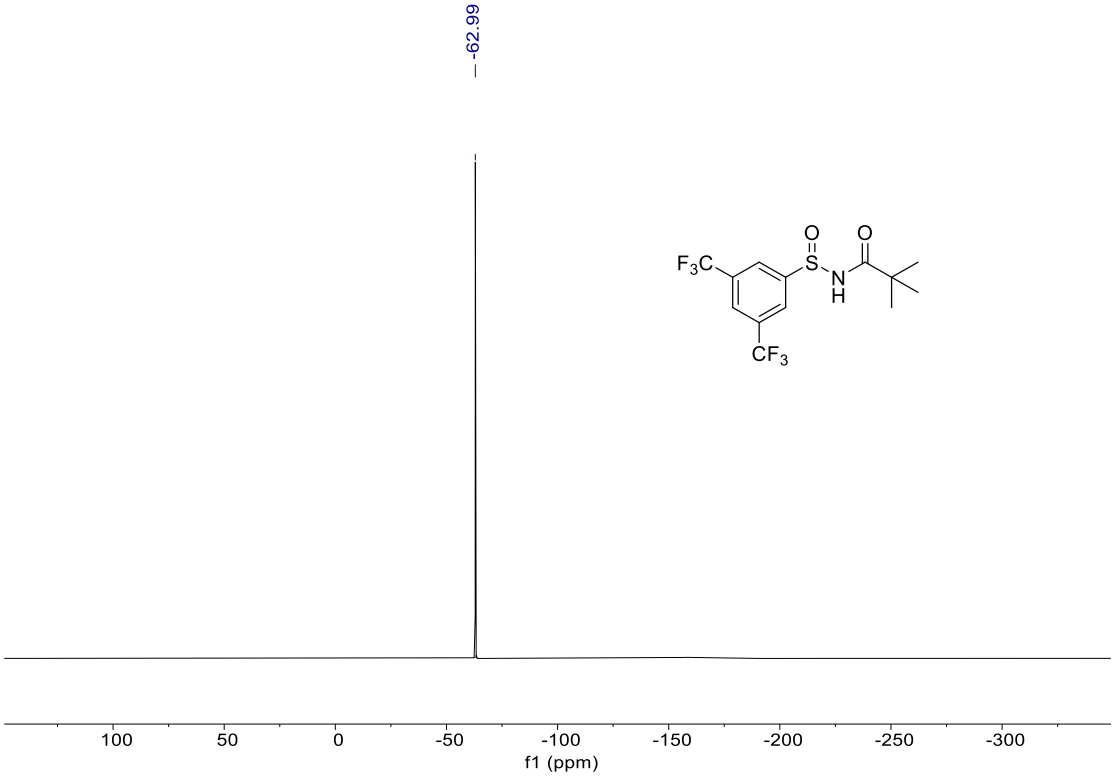
2k, ^{1}H NMR (400 MHz, $CDCl_3$)



2k, ^{13}C NMR (101 MHz, $CDCl_3$)



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



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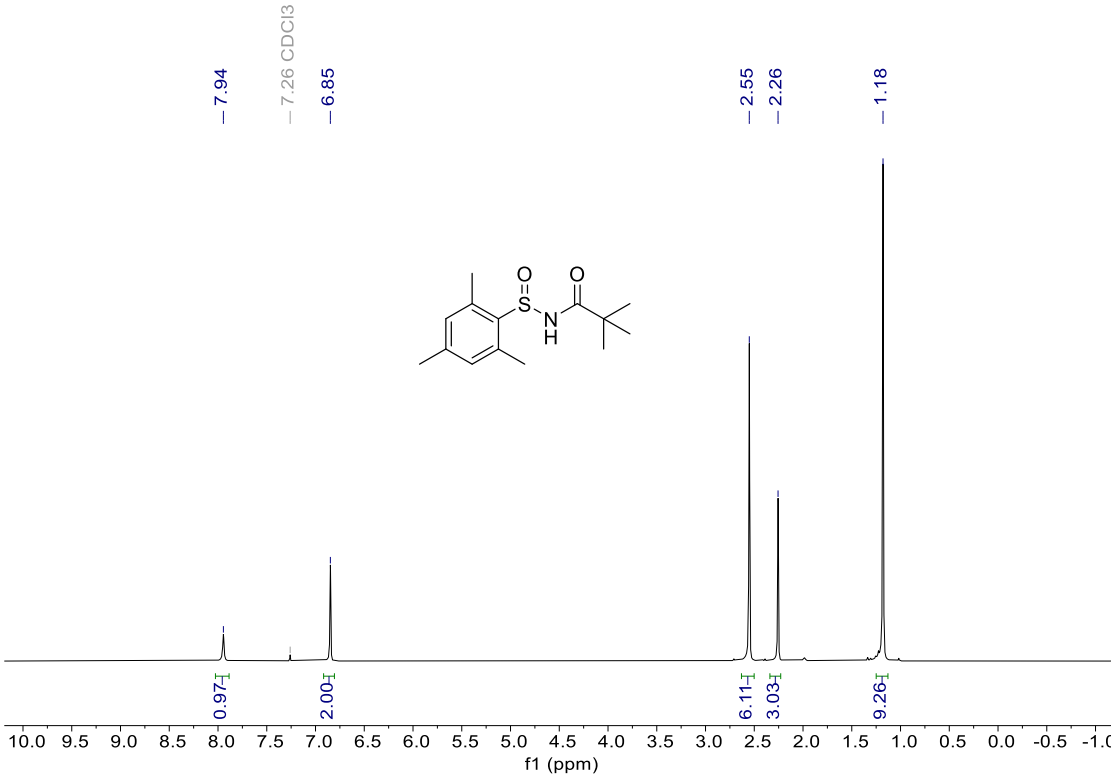

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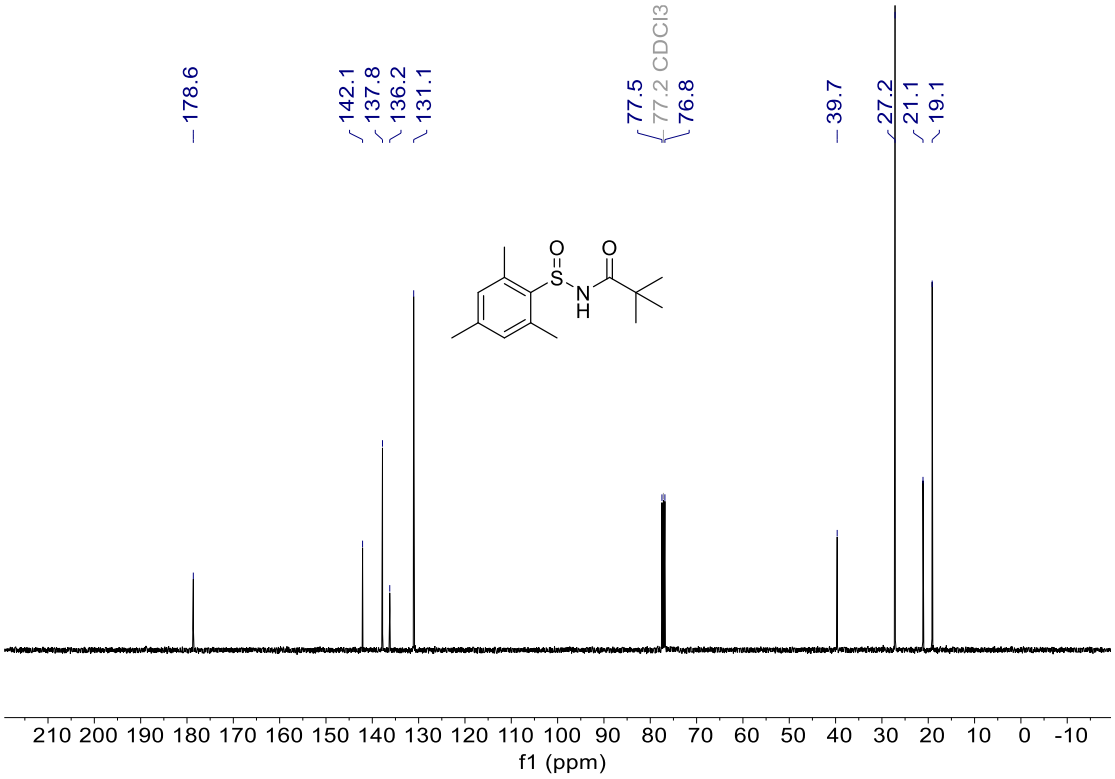
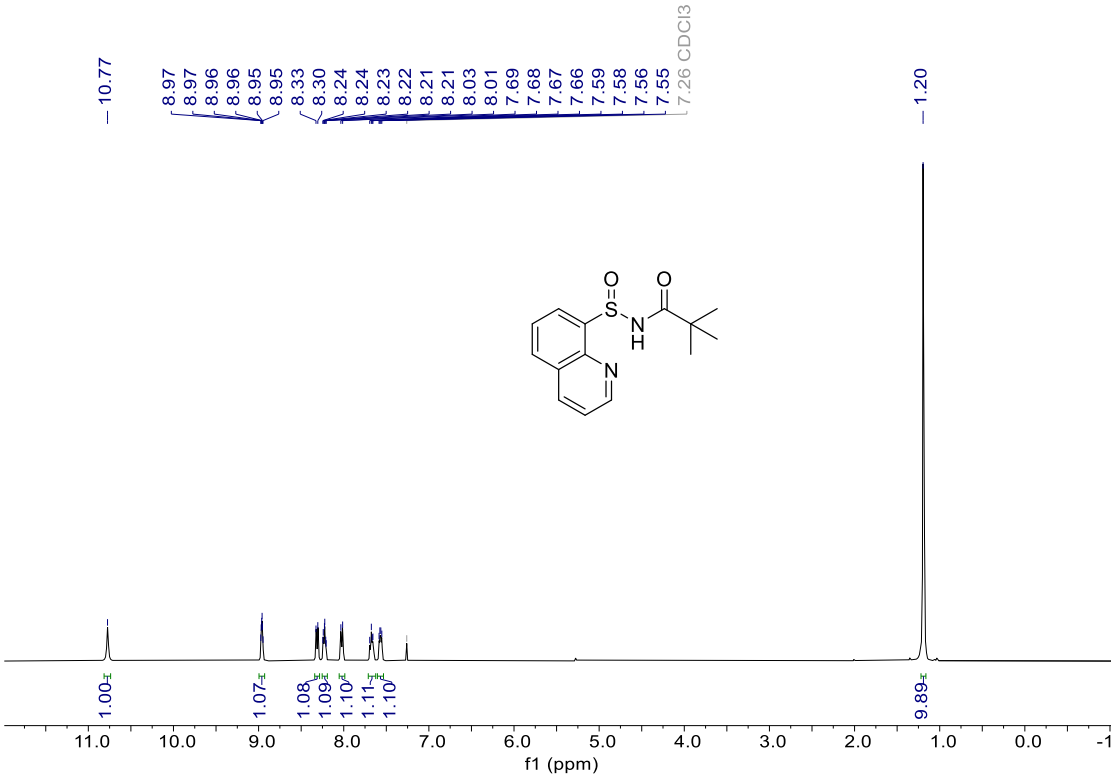
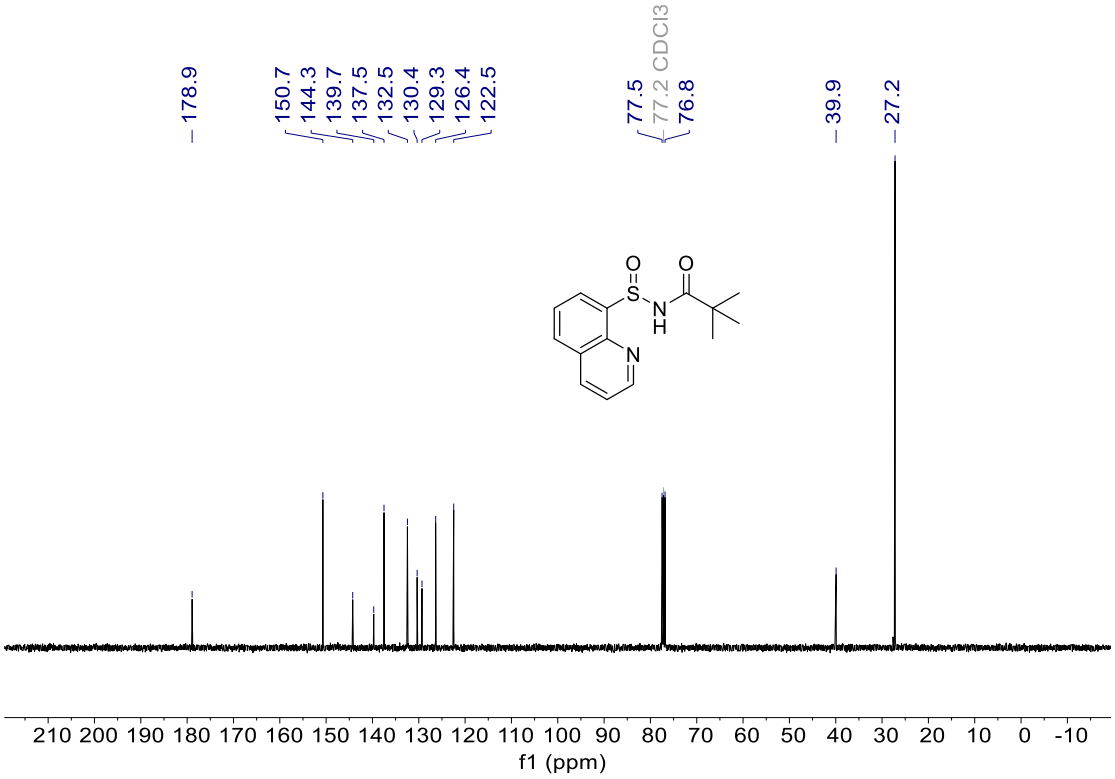


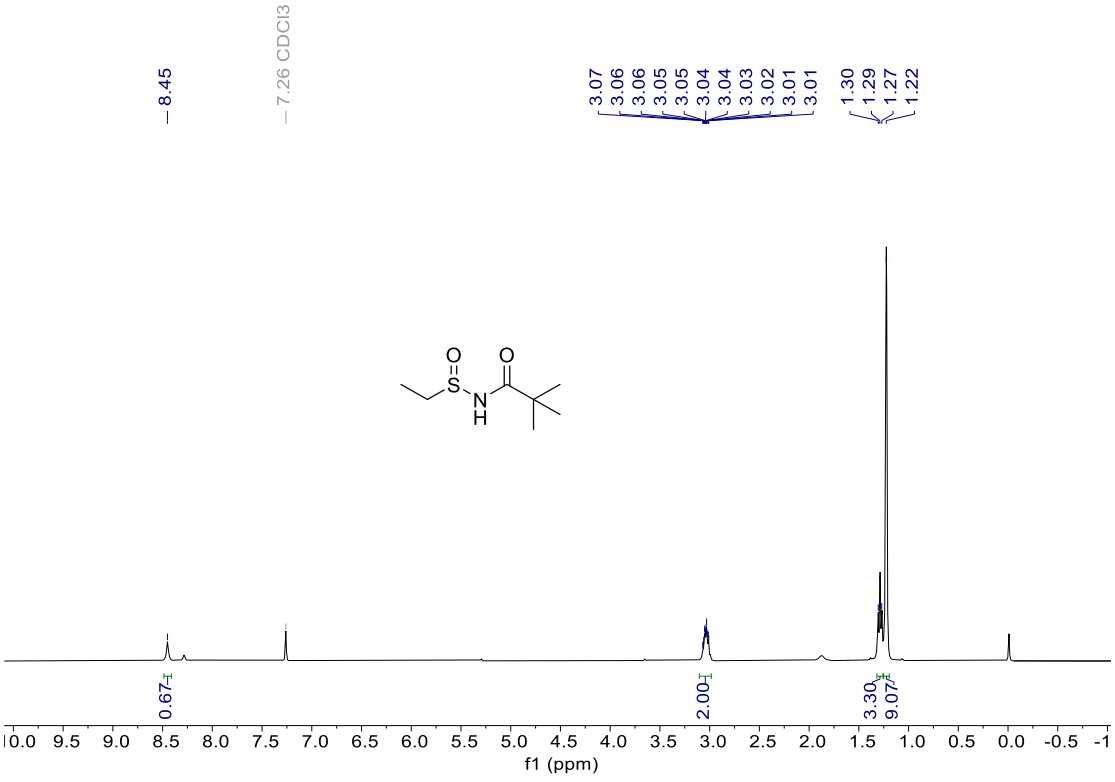
2n, ^{1}H NMR (400 MHz, $CDCl_3$)



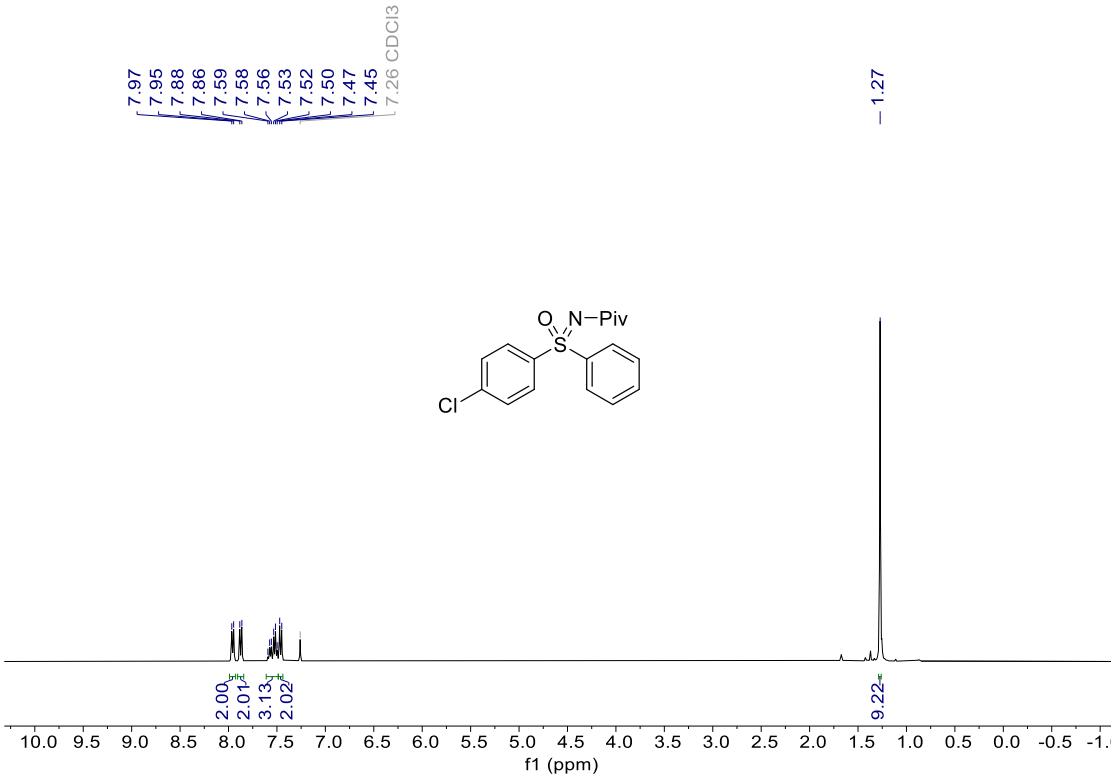
2n, ^{13}C NMR (101 MHz, $CDCl_3$)



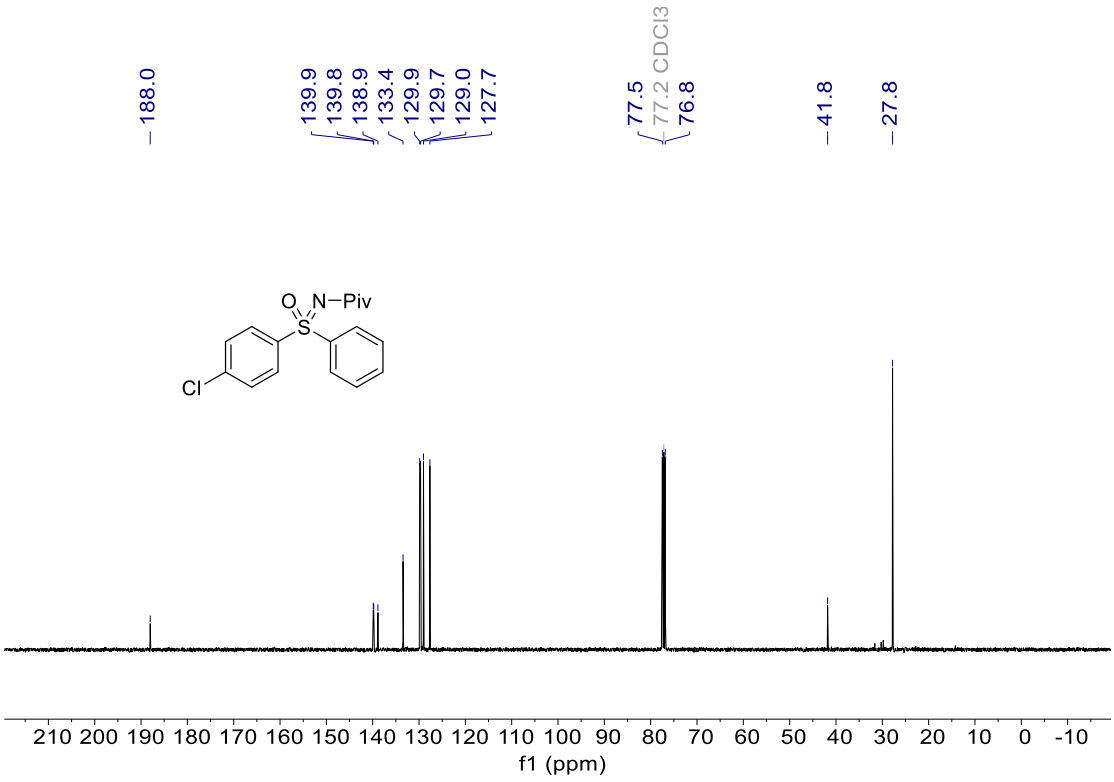
2q, ^{1}H NMR (400 MHz, $CDCl_3$)



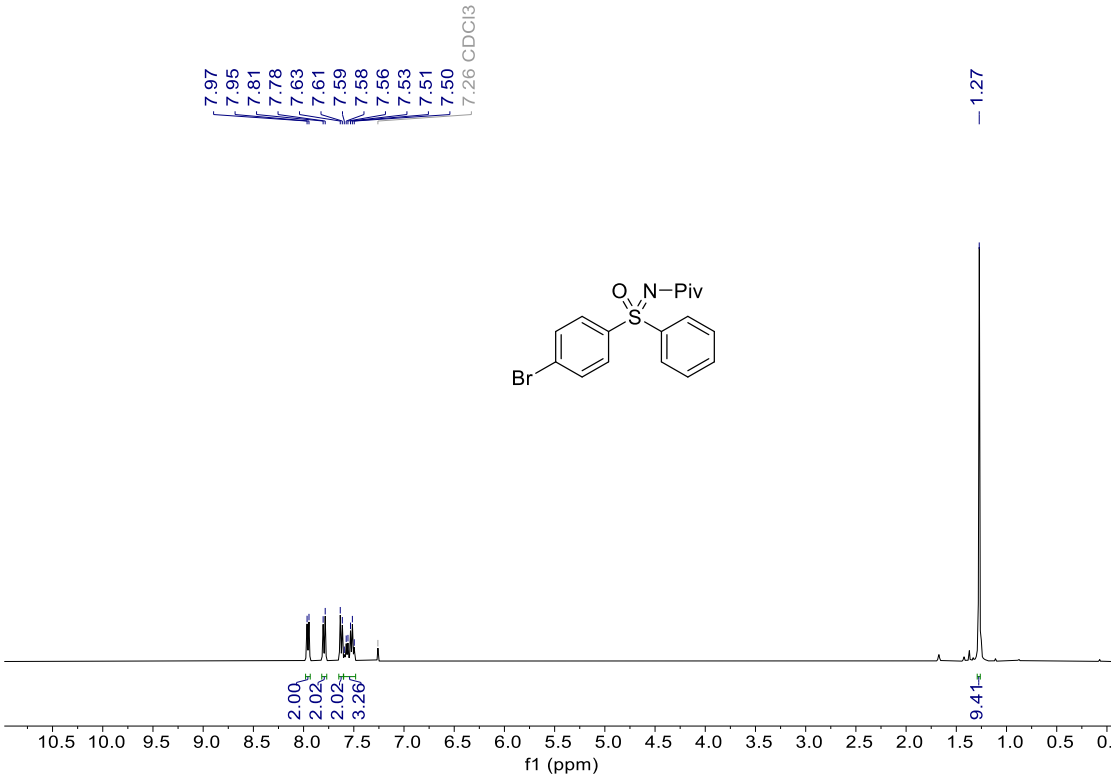
3aa, ^{1}H NMR (400 MHz, $CDCl_3$)



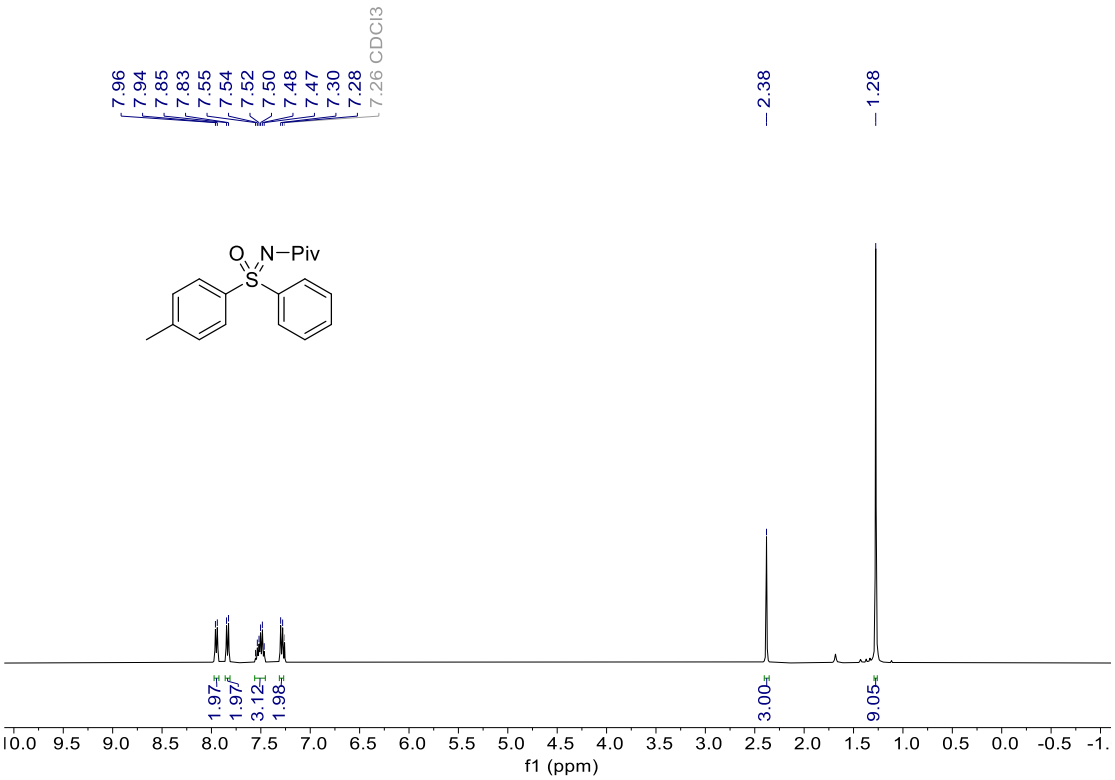
3aa, ^{13}C NMR (101 MHz, $CDCl_3$)



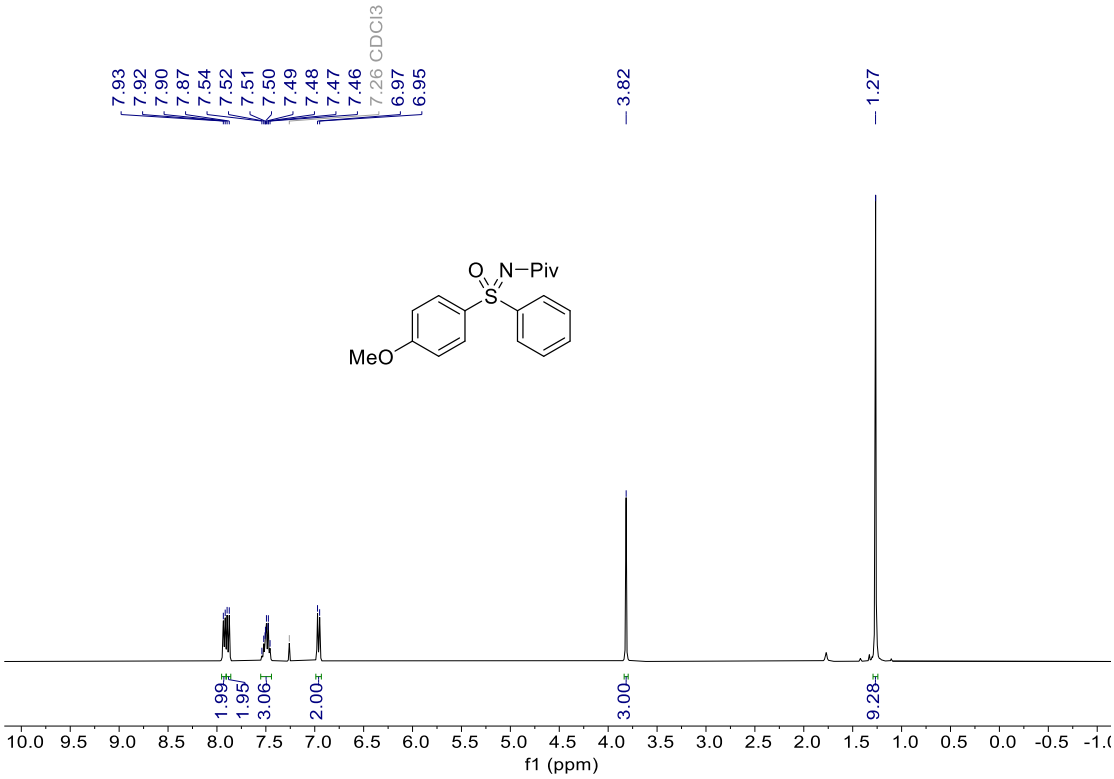
3ba, ^{1}H NMR (400 MHz, $CDCl_3$)



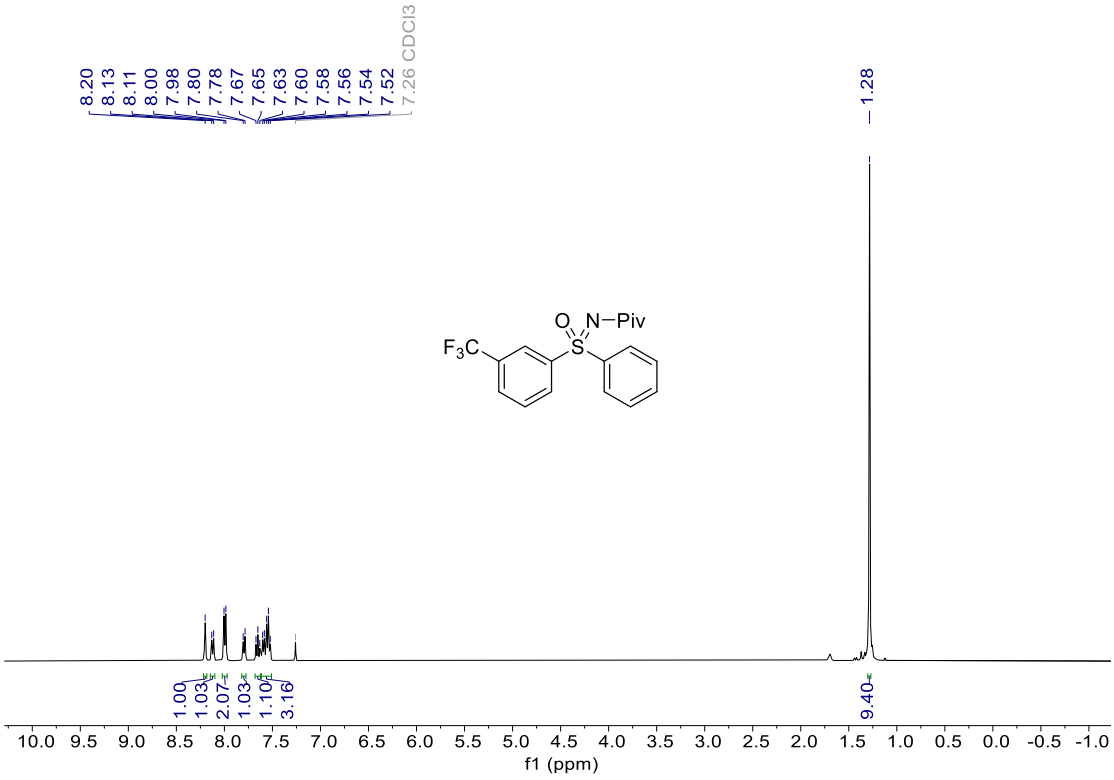
3ca, ^{1}H NMR (400 MHz, $CDCl_3$)



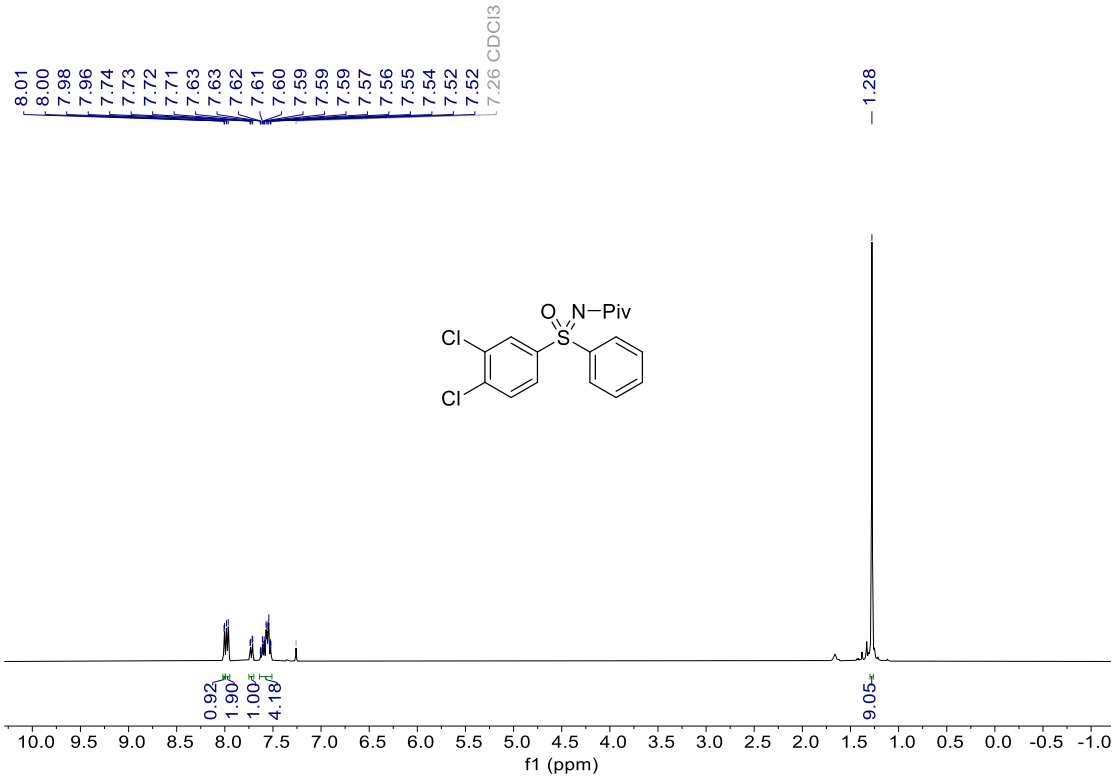
3da, ^{1}H NMR (400 MHz, $CDCl_3$)



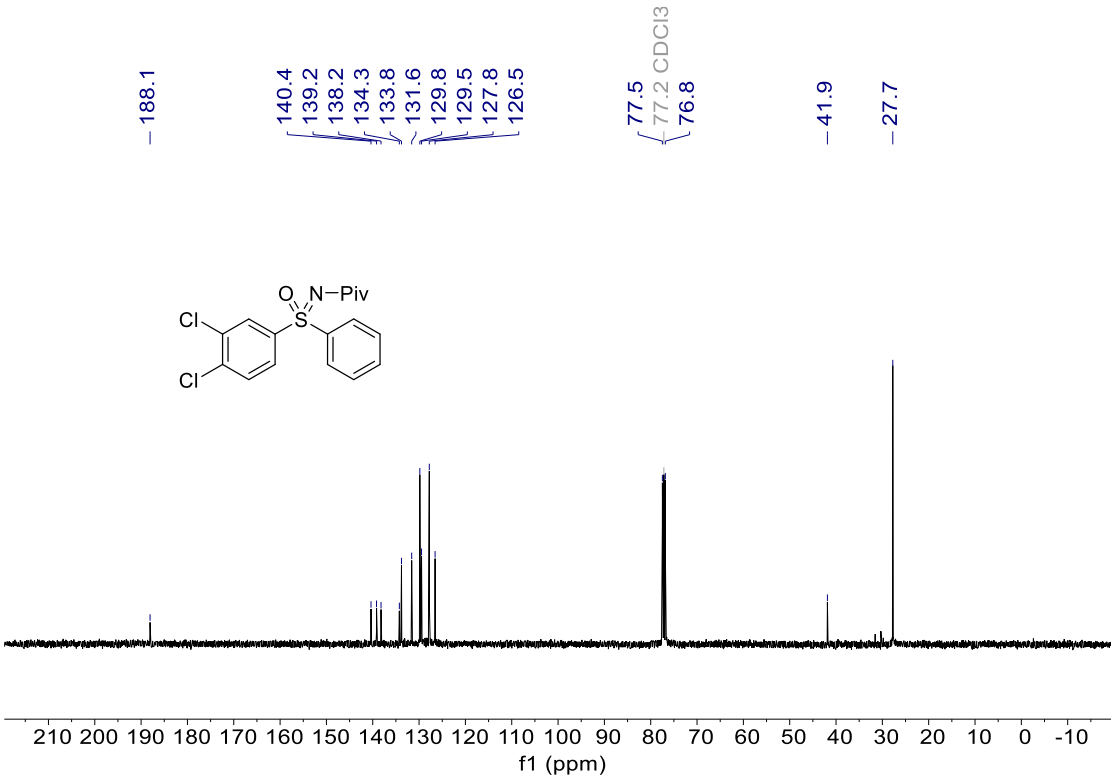
3ea, ^{1}H NMR (400 MHz, $CDCl_3$)



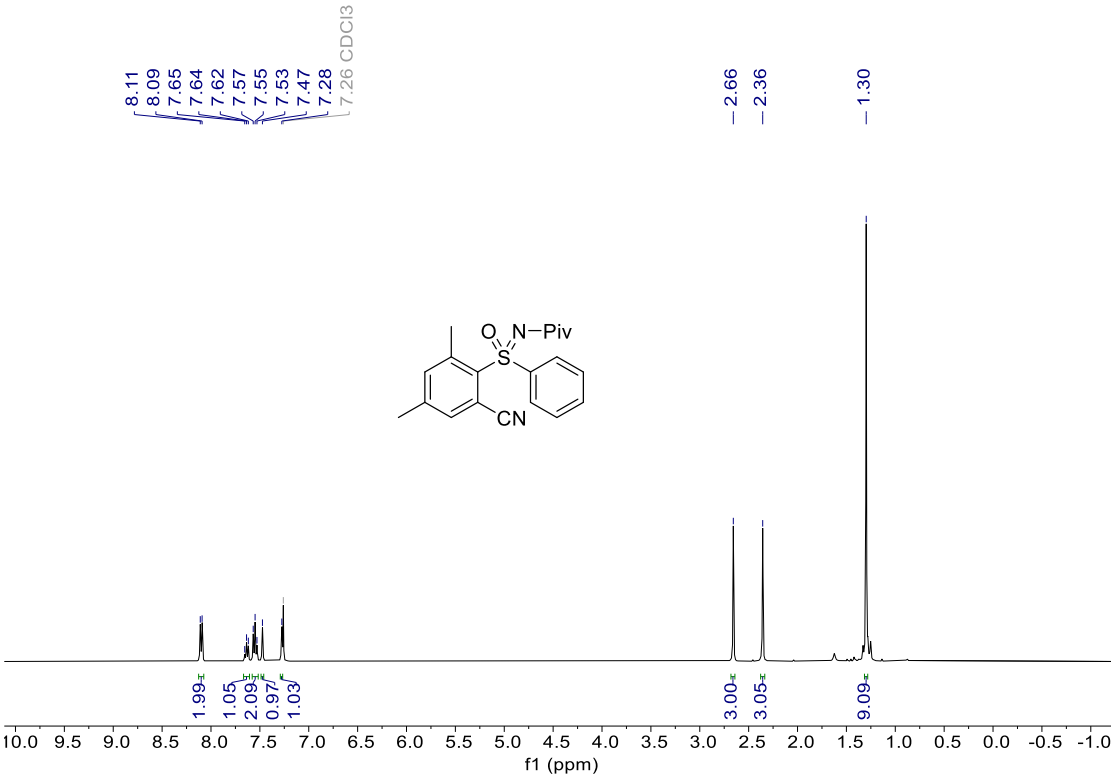
3fa, ^{1}H NMR (400 MHz, $CDCl_3$)



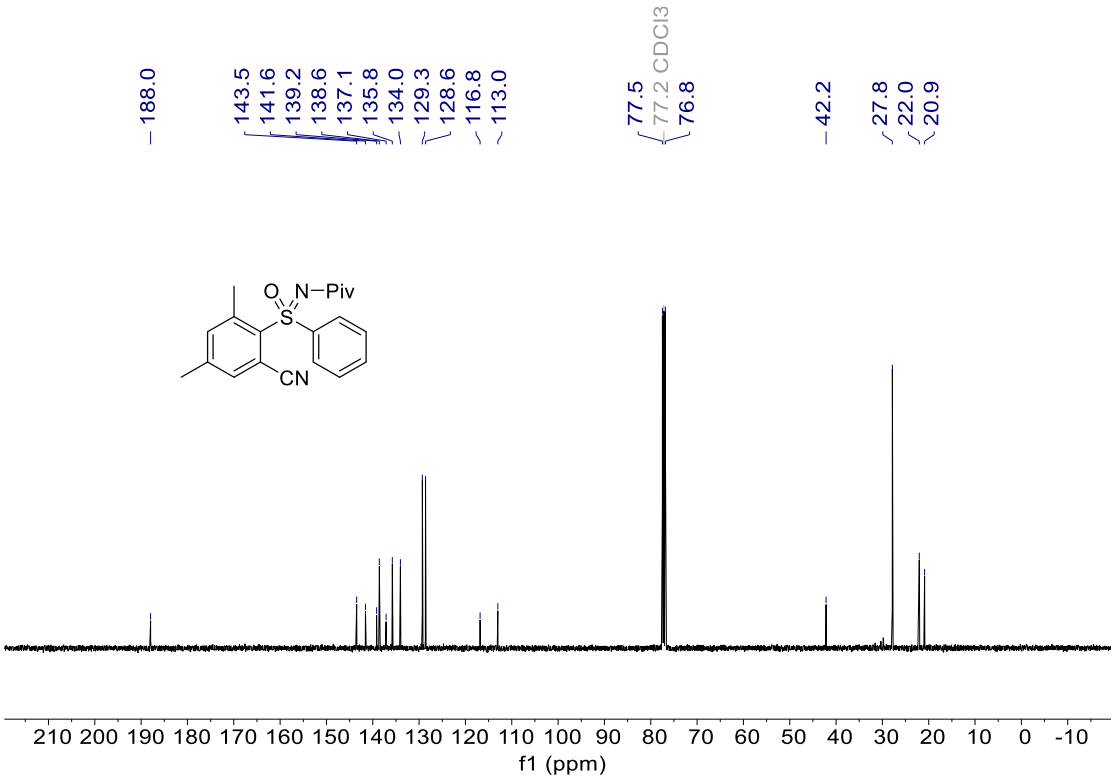
3fa, ^{13}C NMR (101 MHz, $CDCl_3$)



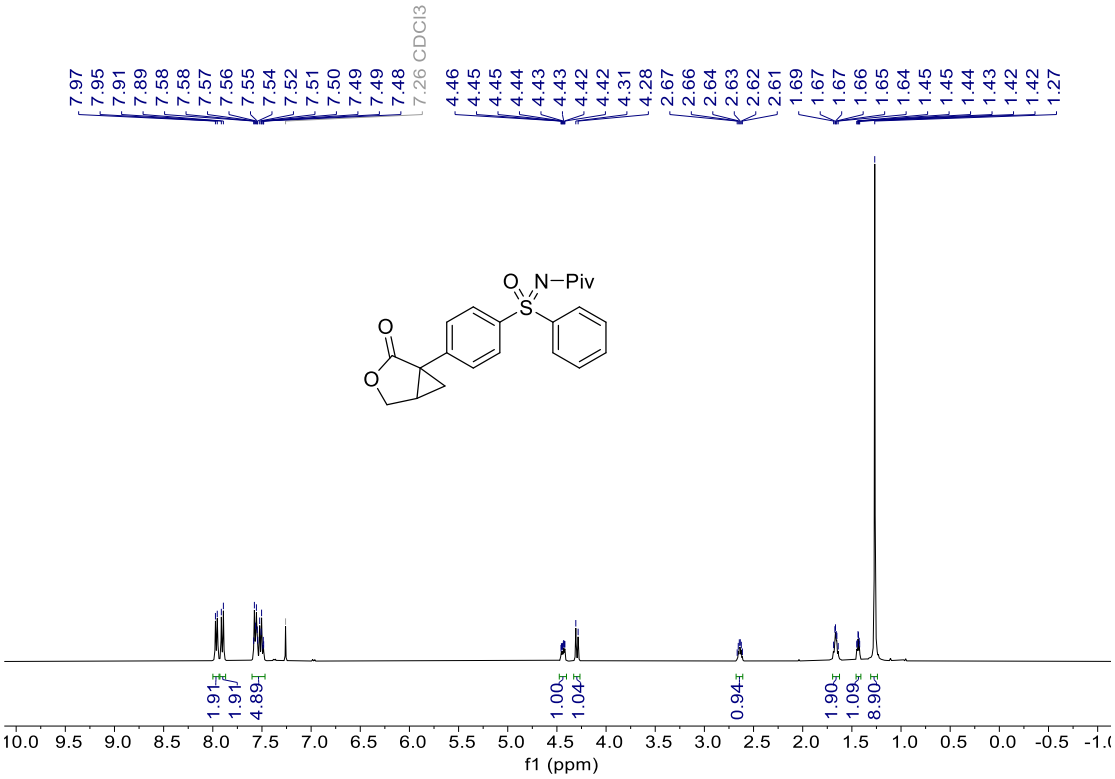
3ga, ^{1}H NMR (400 MHz, $CDCl_3$)



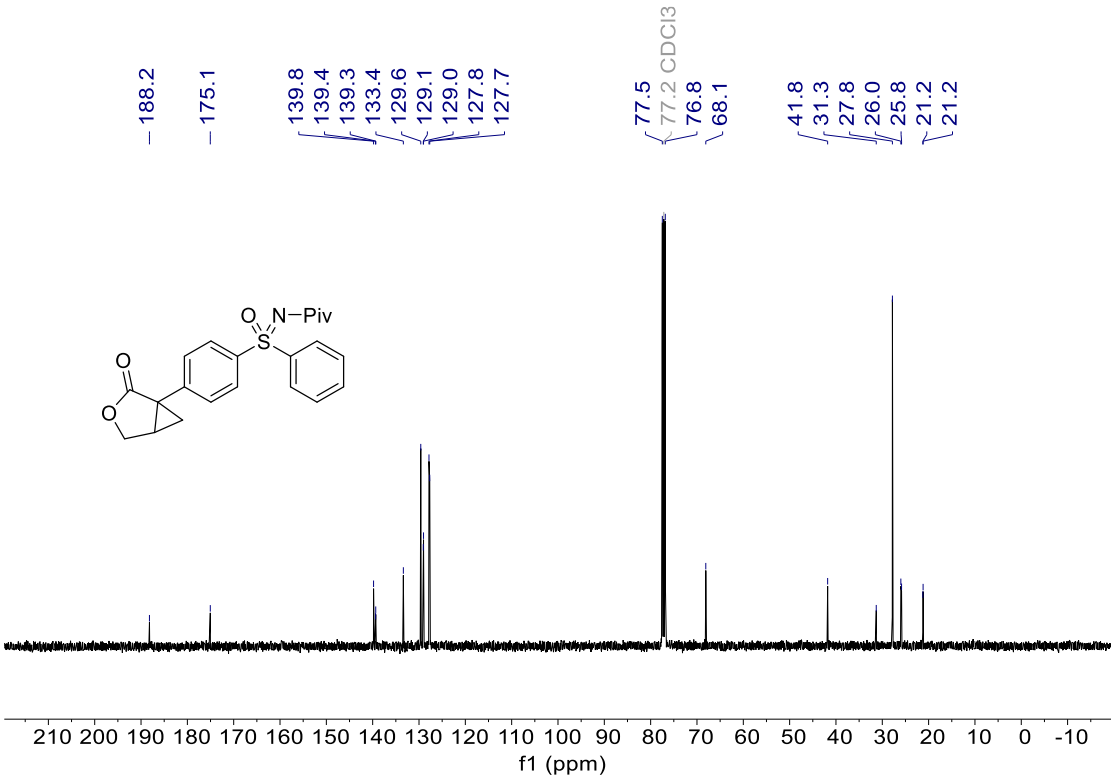
3ga, ^{13}C NMR (101 MHz, $CDCl_3$)



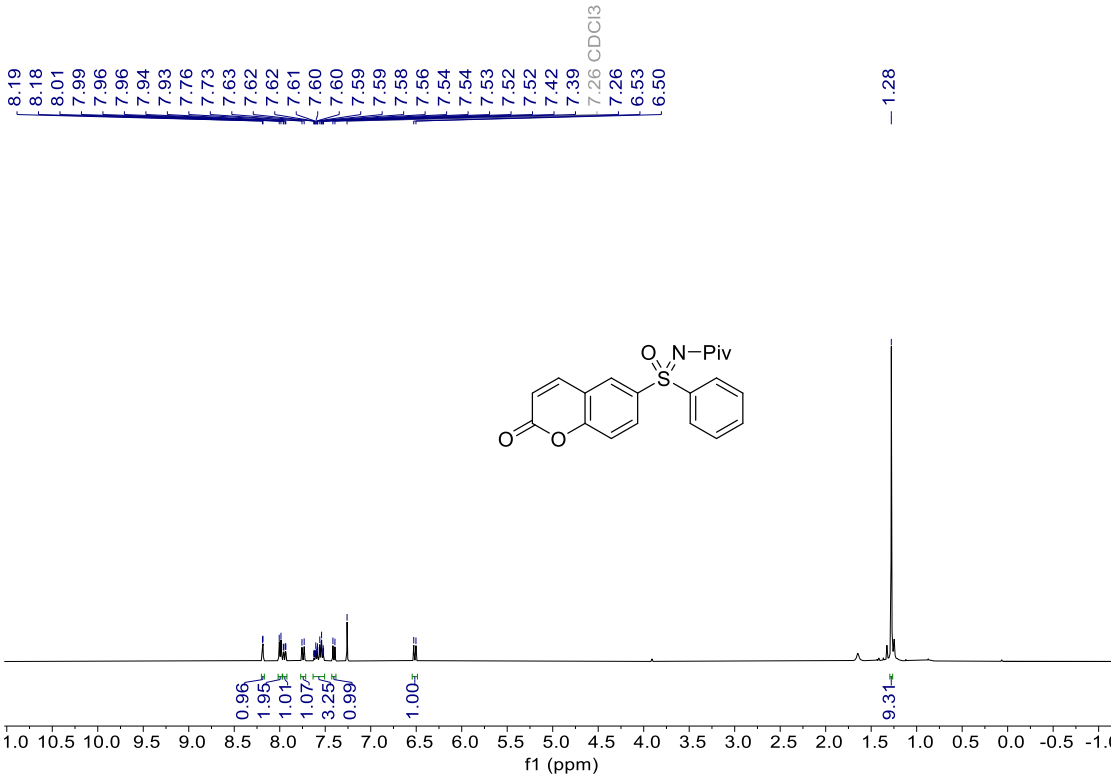
3ha, ^{1}H NMR (400 MHz, $CDCl_3$)



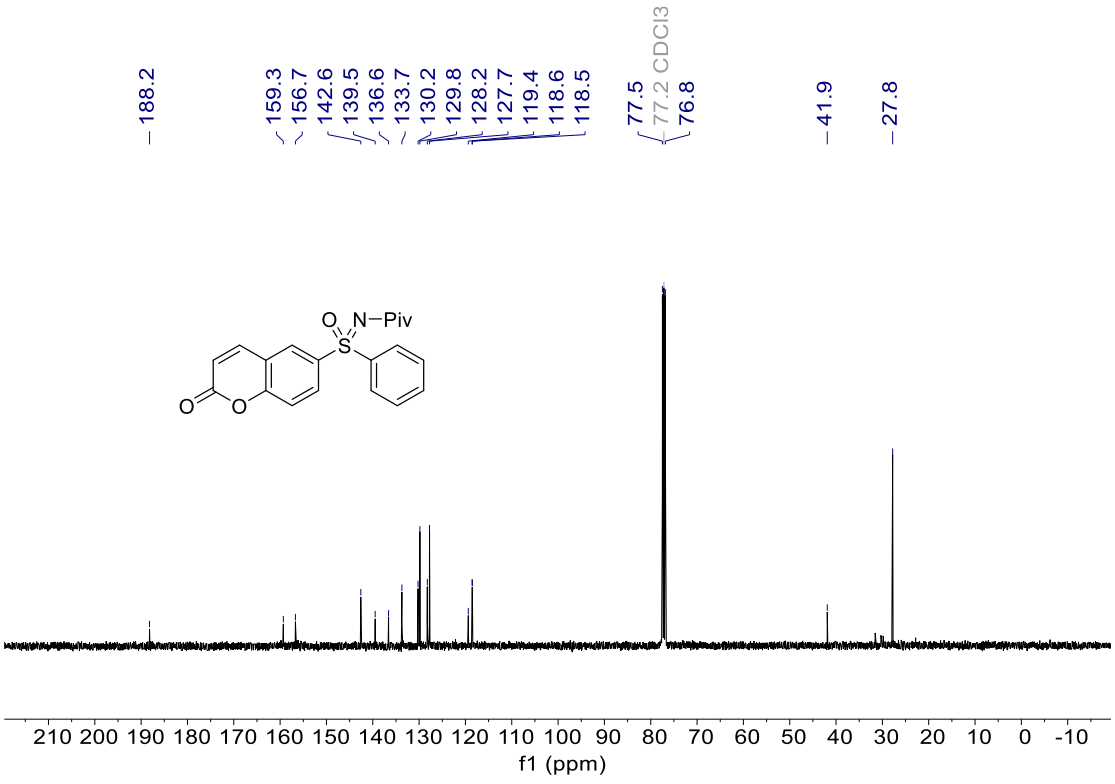
3ha, ^{13}C NMR (101 MHz, $CDCl_3$)



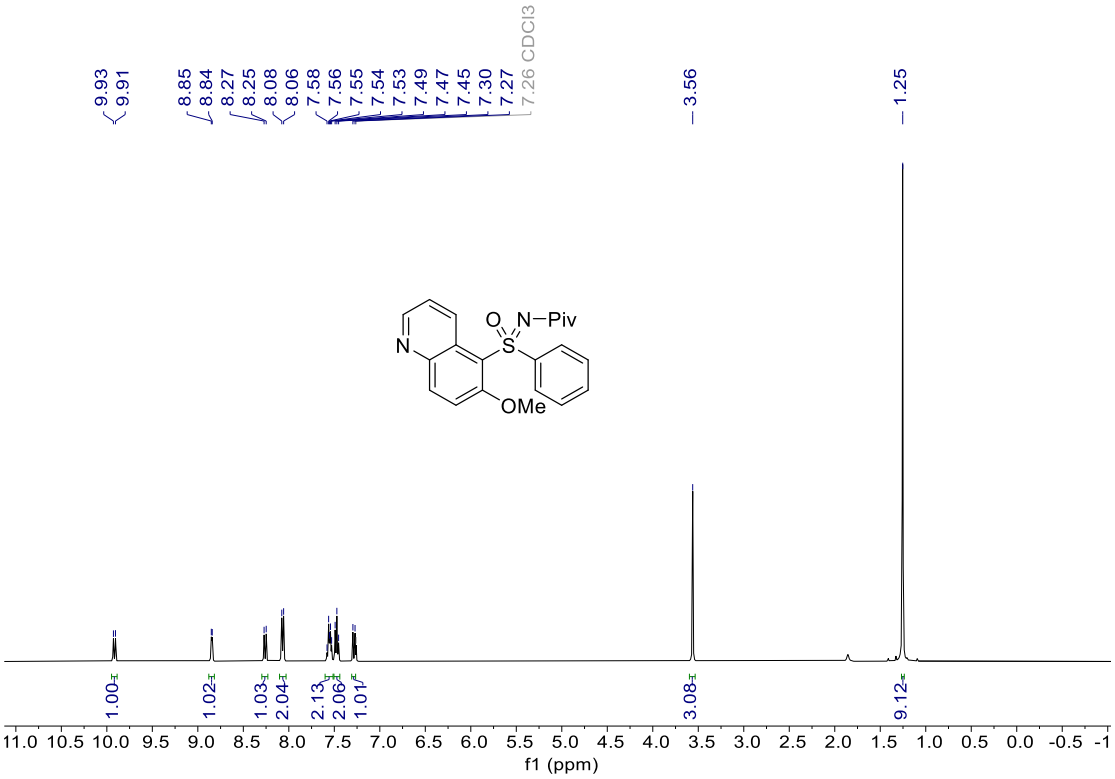
3ia, ^{1}H NMR (400 MHz, $CDCl_3$)



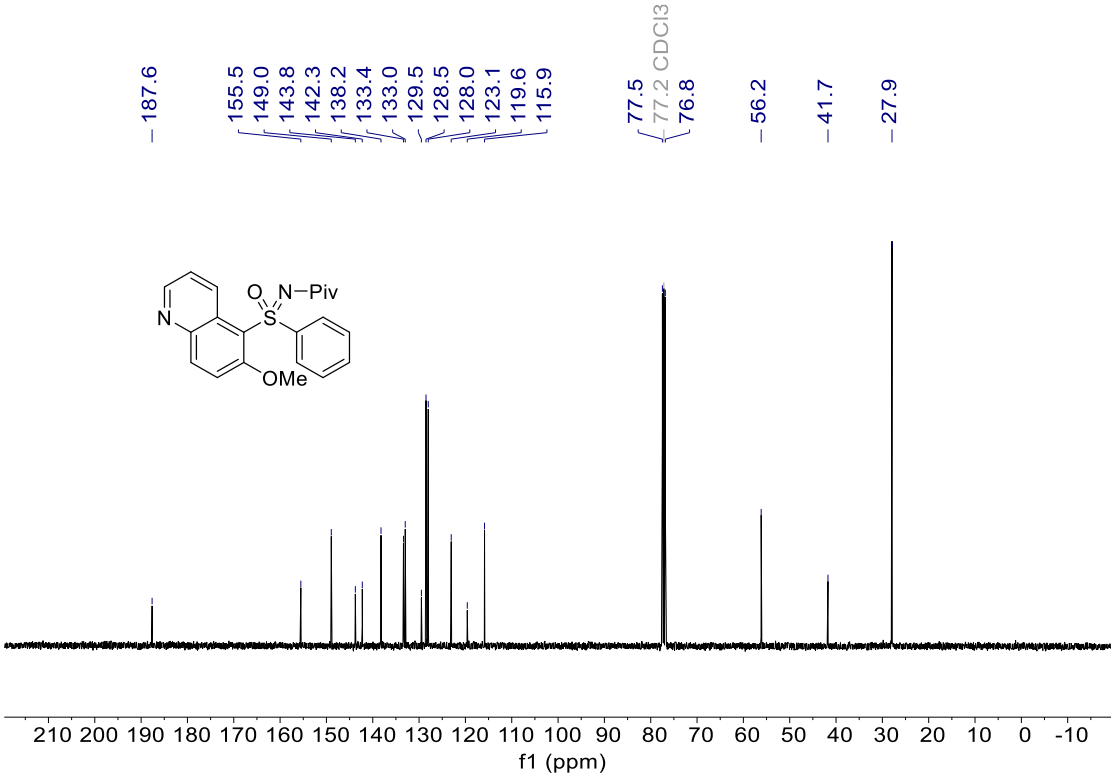
3ia, ^{13}C NMR (101 MHz, $CDCl_3$)



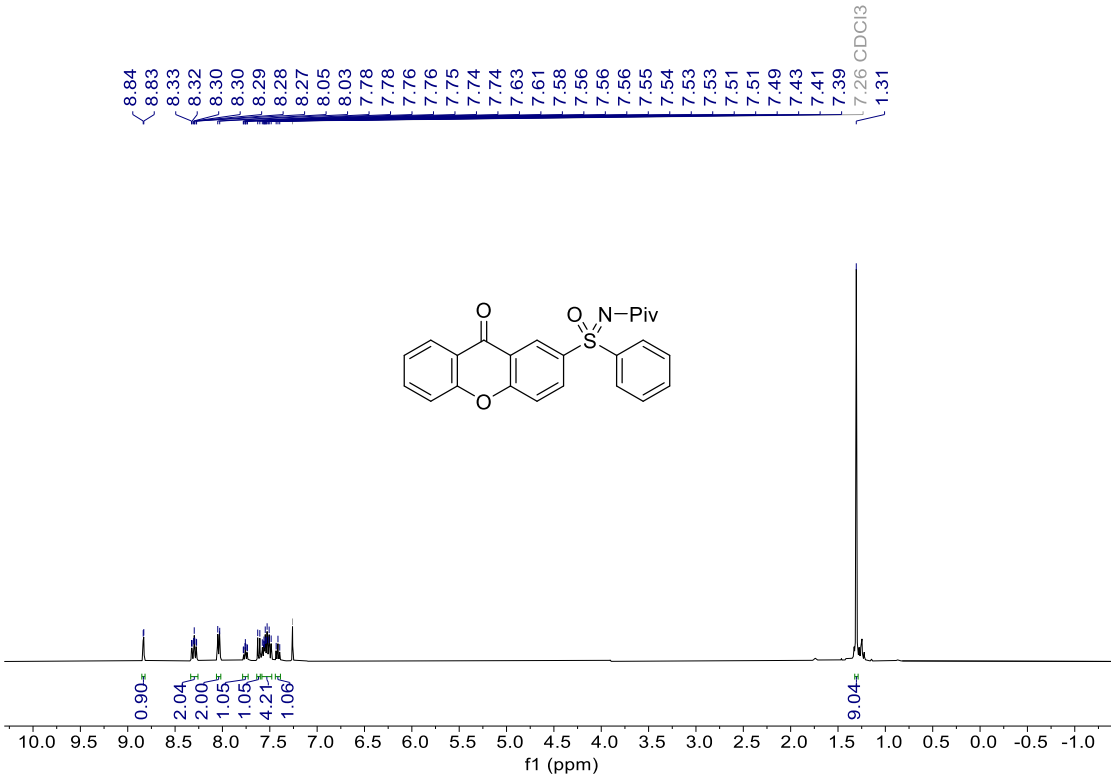
3ja, ^{1}H NMR (400 MHz, $CDCl_3$)



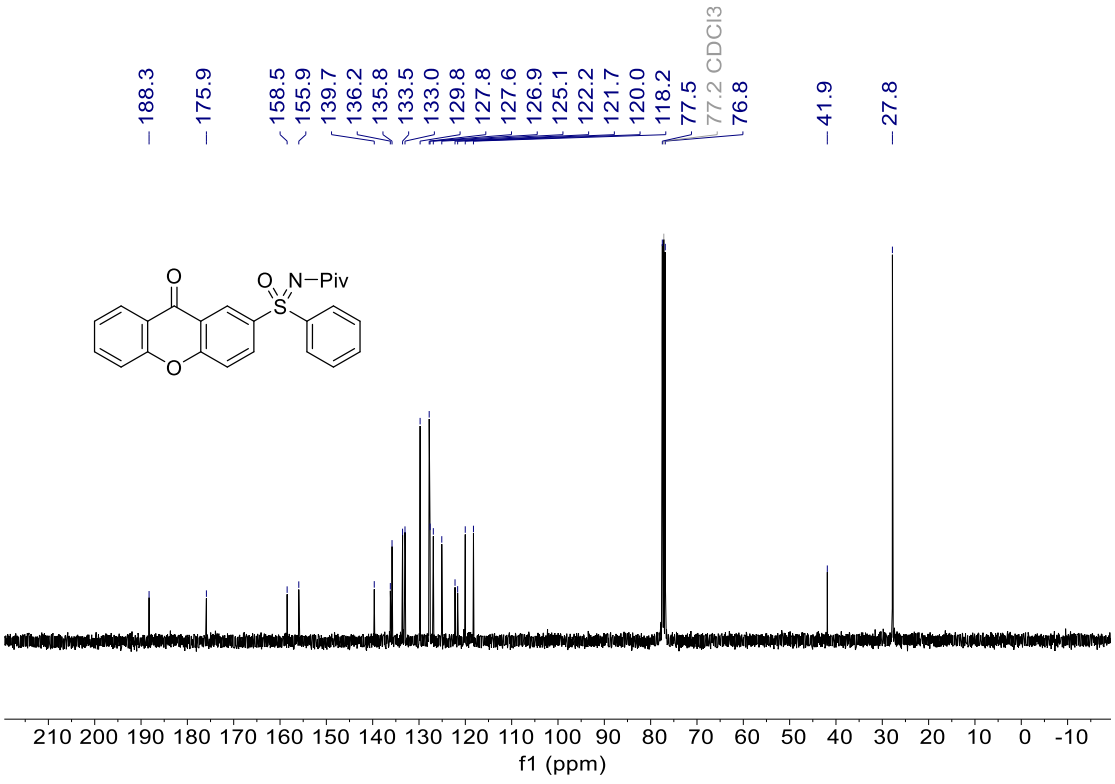
3ja, ^{13}C NMR (101 MHz, $CDCl_3$)



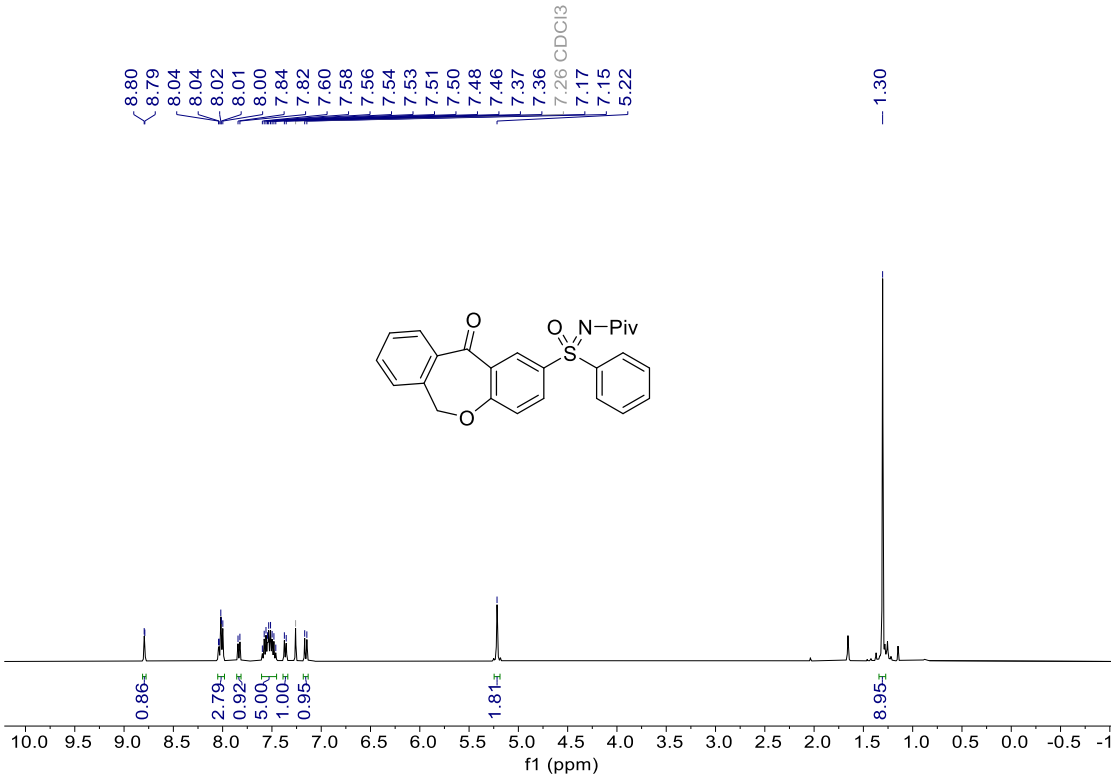
3ka, ^{1}H NMR (400 MHz, $CDCl_3$)



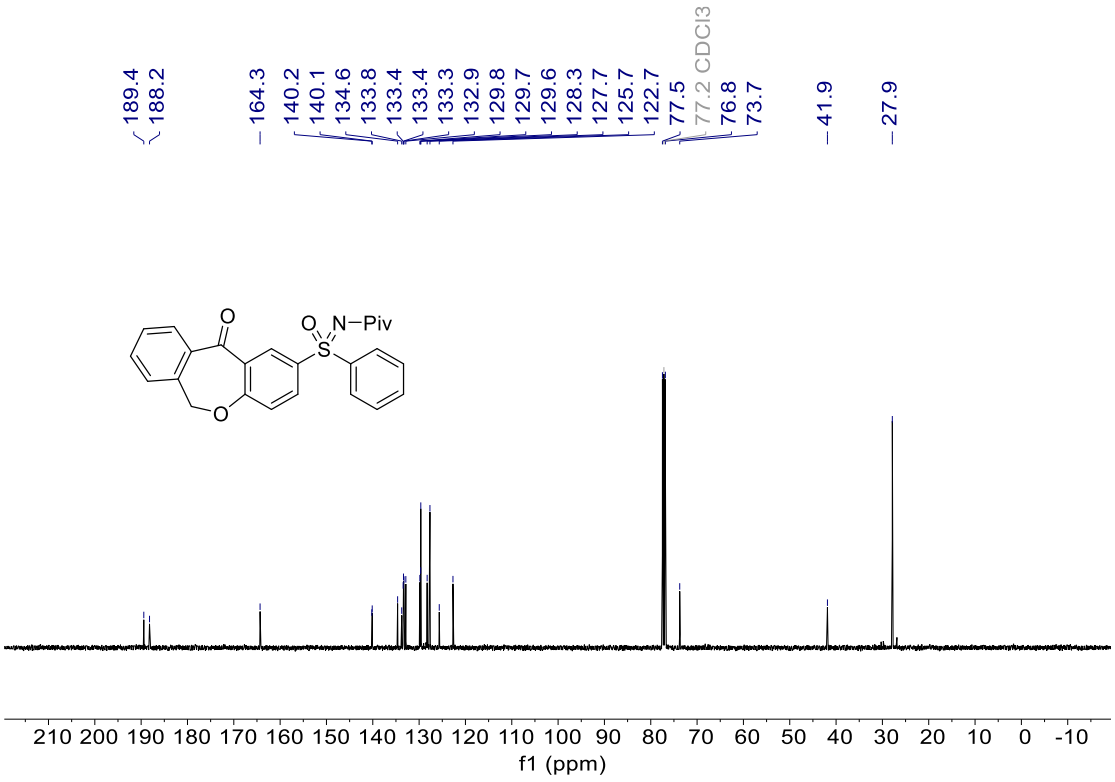
3ka, ^{13}C NMR (101 MHz, $CDCl_3$)



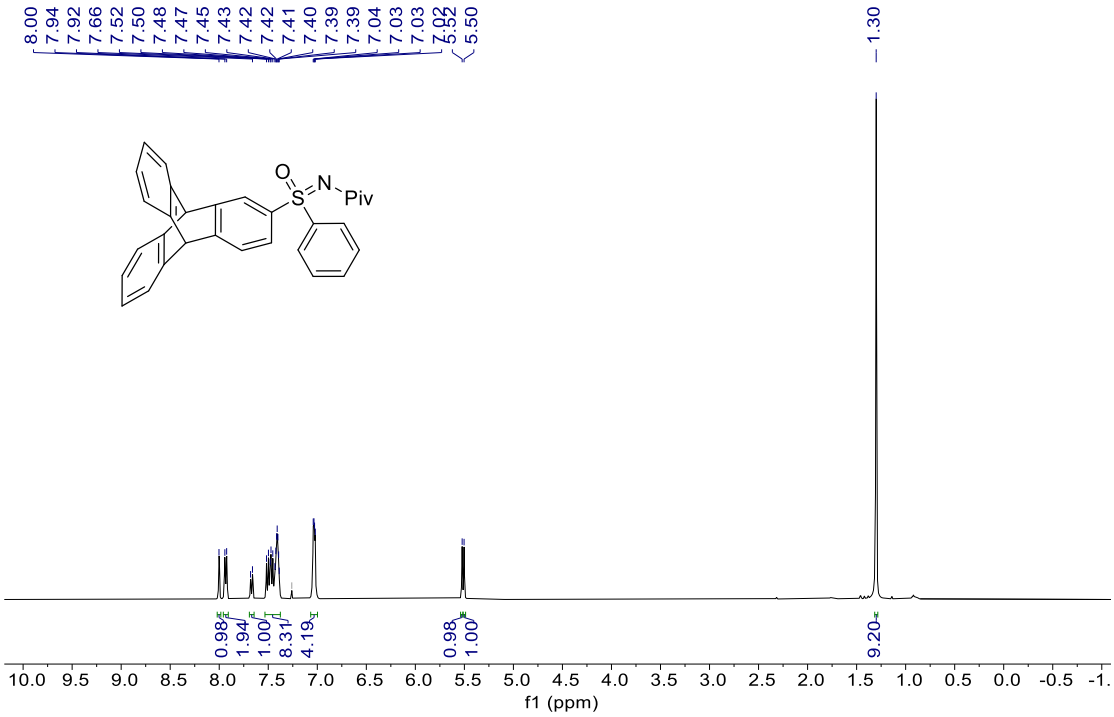
3la, ^{1}H NMR (400 MHz, $CDCl_3$)



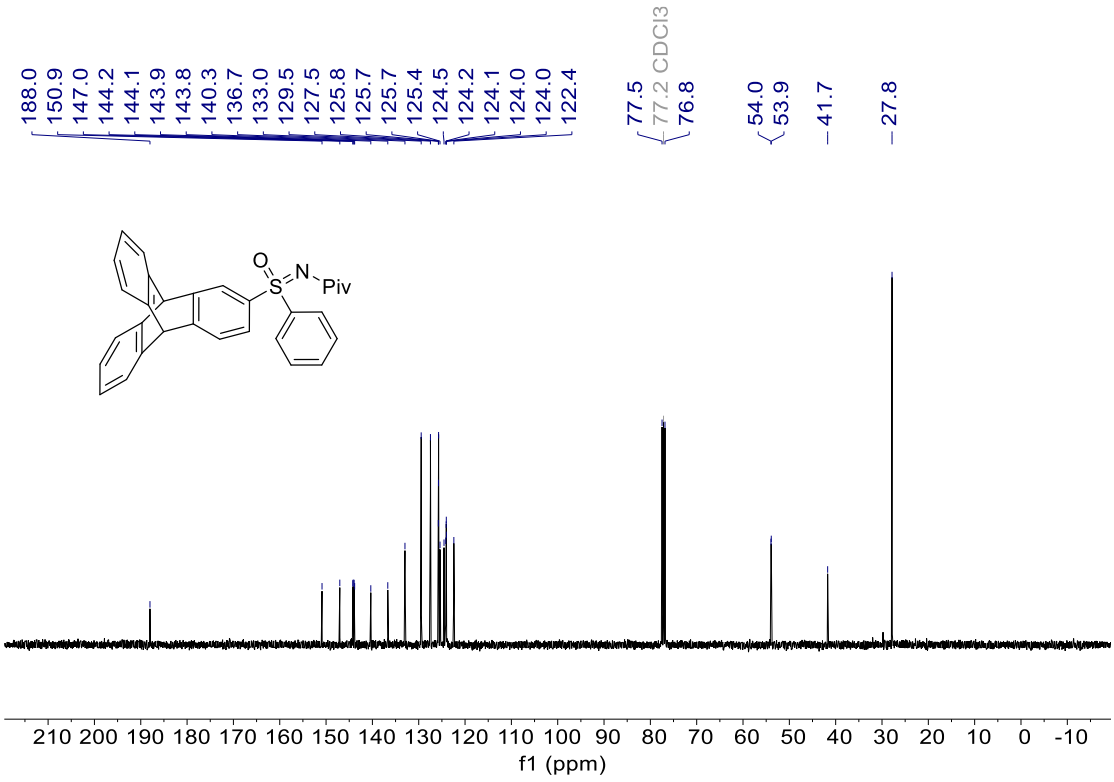
3la, ^{13}C NMR (101 MHz, $CDCl_3$)



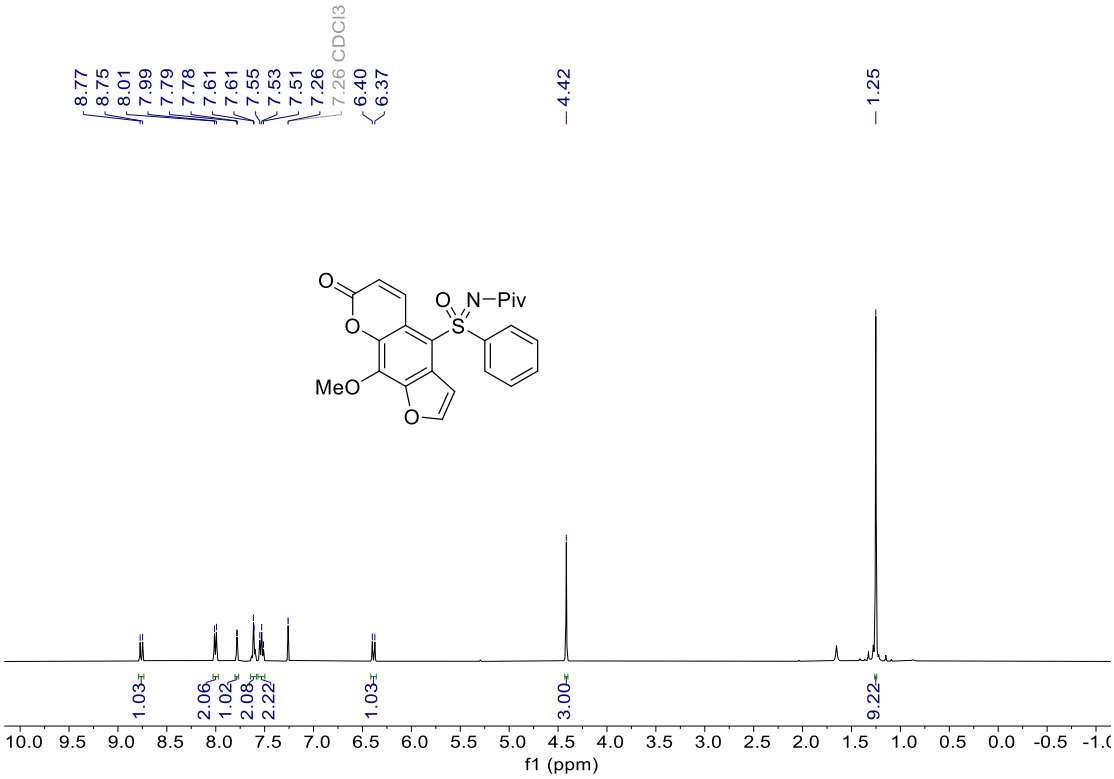
3ma, ^{1}H NMR (400 MHz, $CDCl_3$)



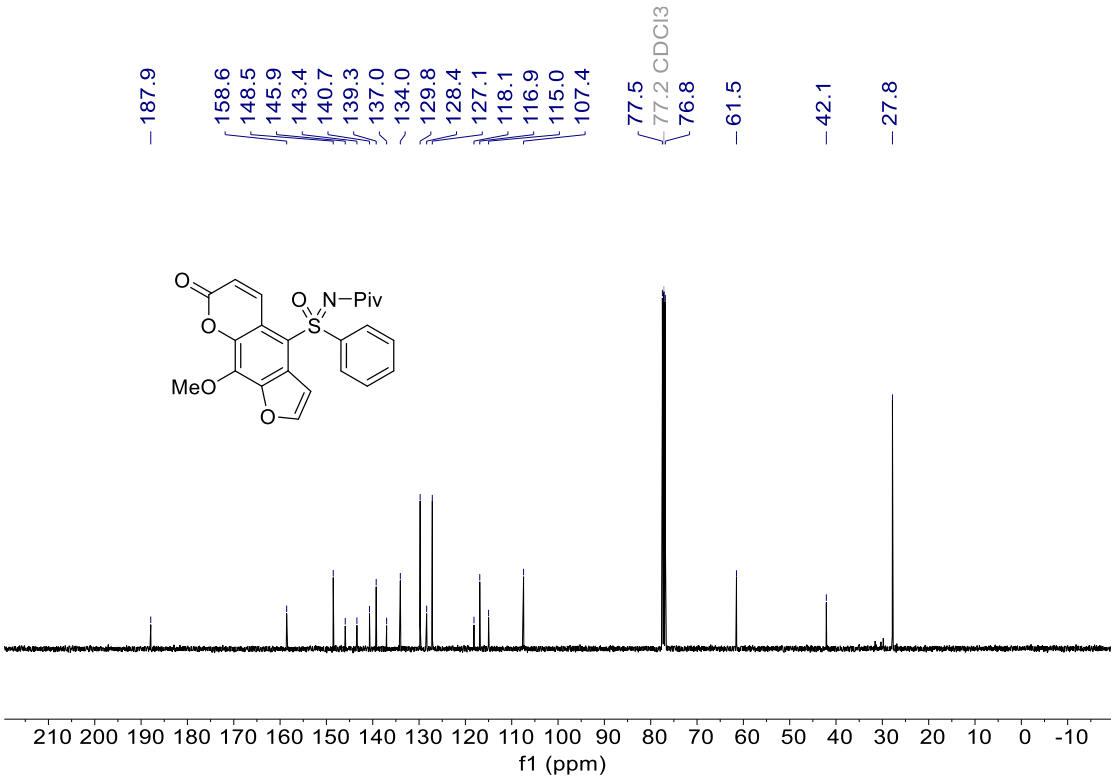
3ma, ^{13}C NMR (101 MHz, $CDCl_3$)



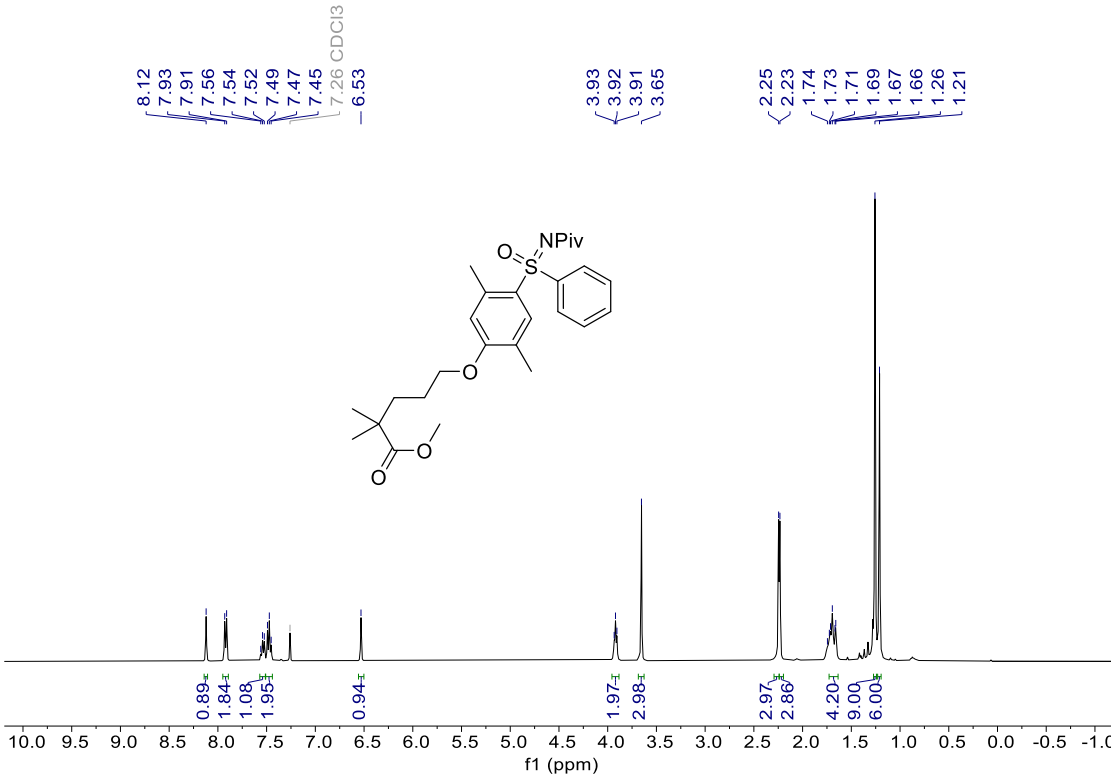
3na, ^{1}H NMR (400 MHz, $CDCl_3$)



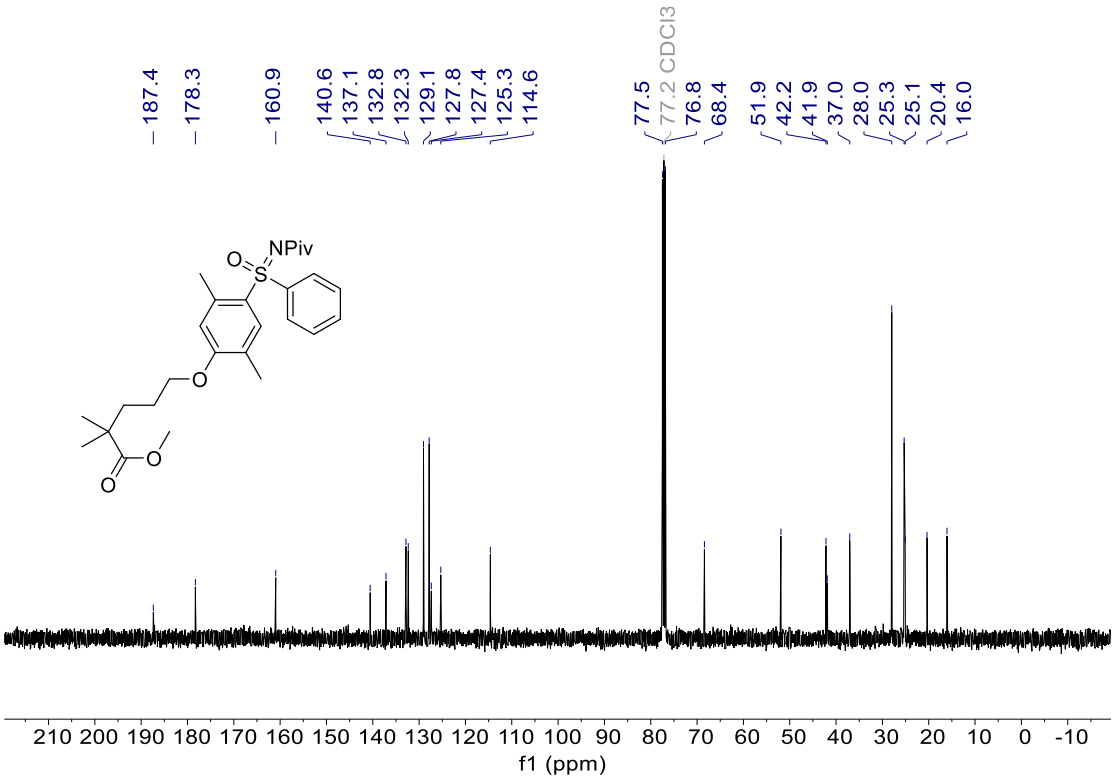
3na, ^{13}C NMR (101 MHz, $CDCl_3$)



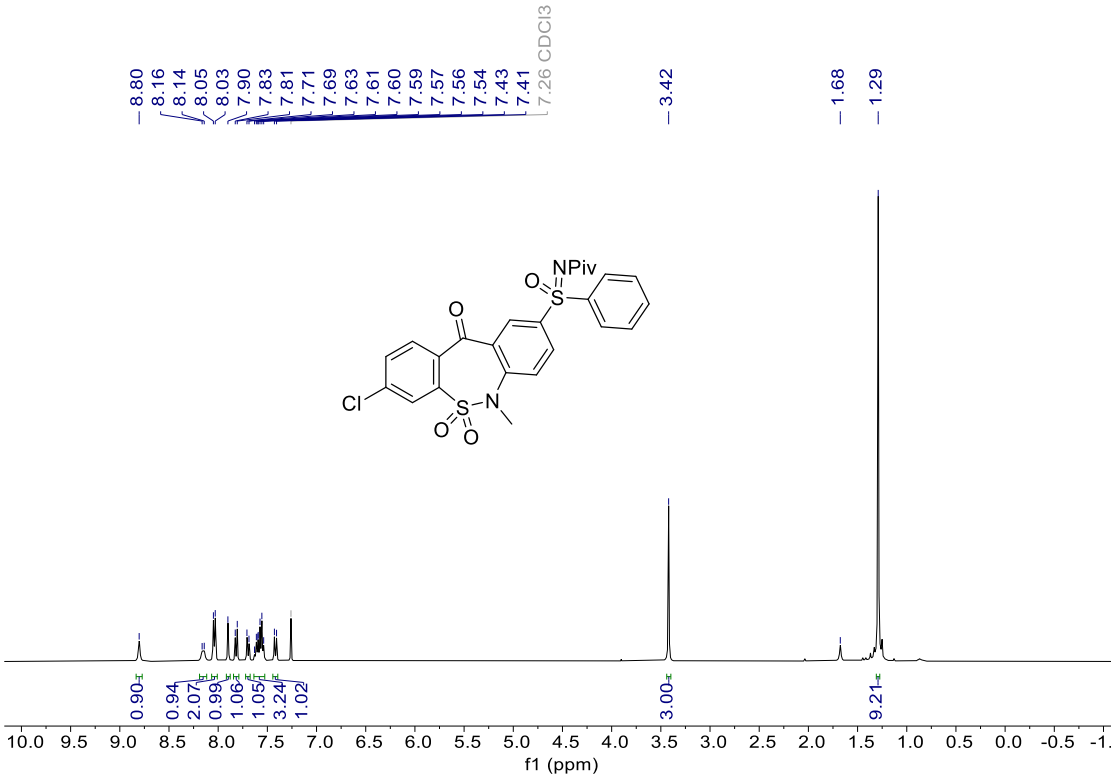
3oa, ^{1}H NMR (400 MHz, $CDCl_3$)



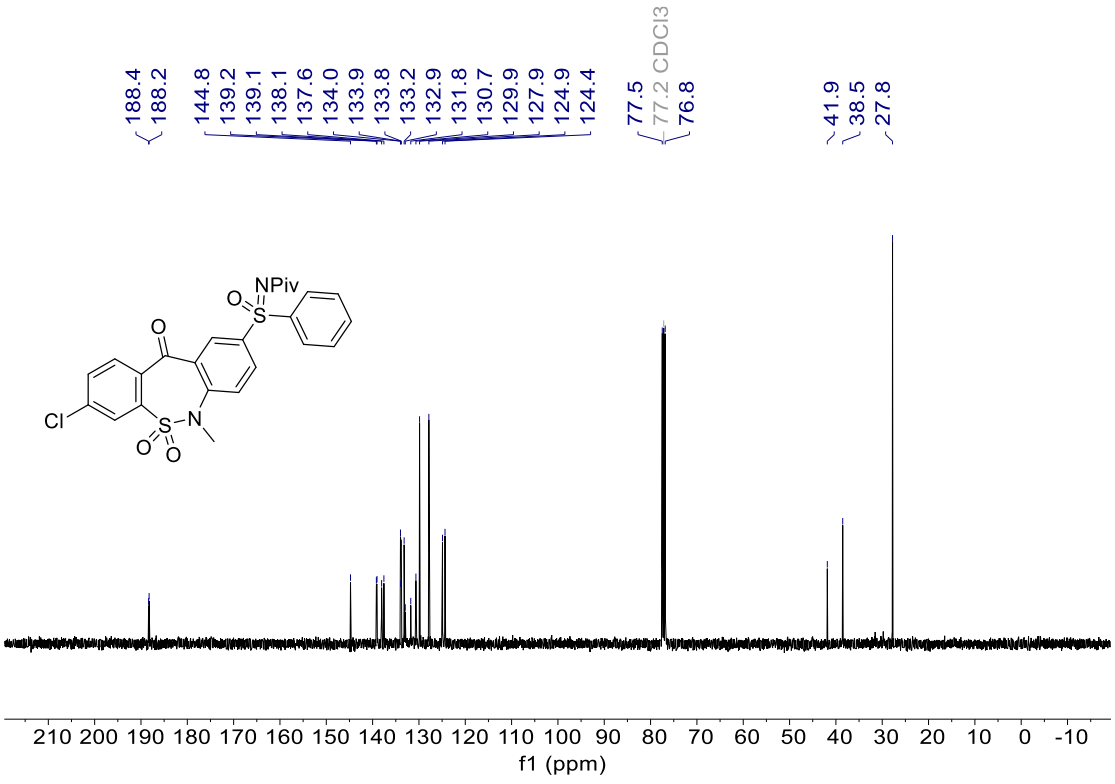
3oa, ^{13}C NMR (101 MHz, $CDCl_3$)



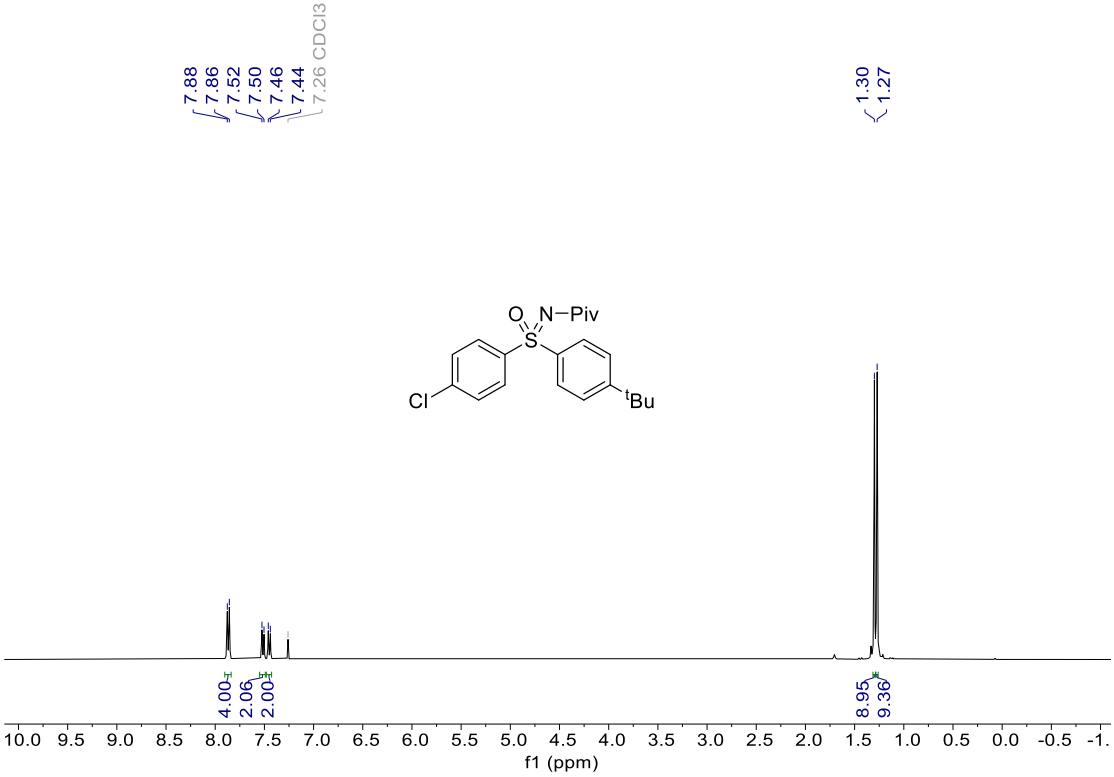
3pa, ^{1}H NMR (400 MHz, $CDCl_3$)



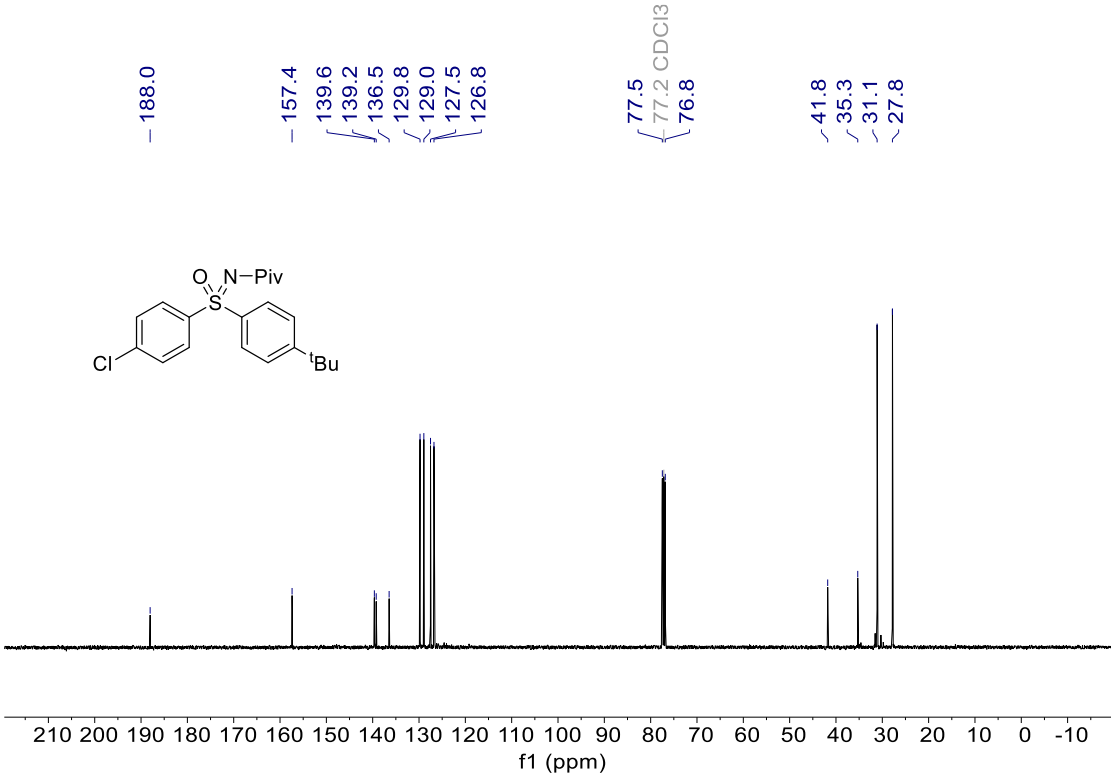
3pa, ^{13}C NMR (101 MHz, $CDCl_3$)



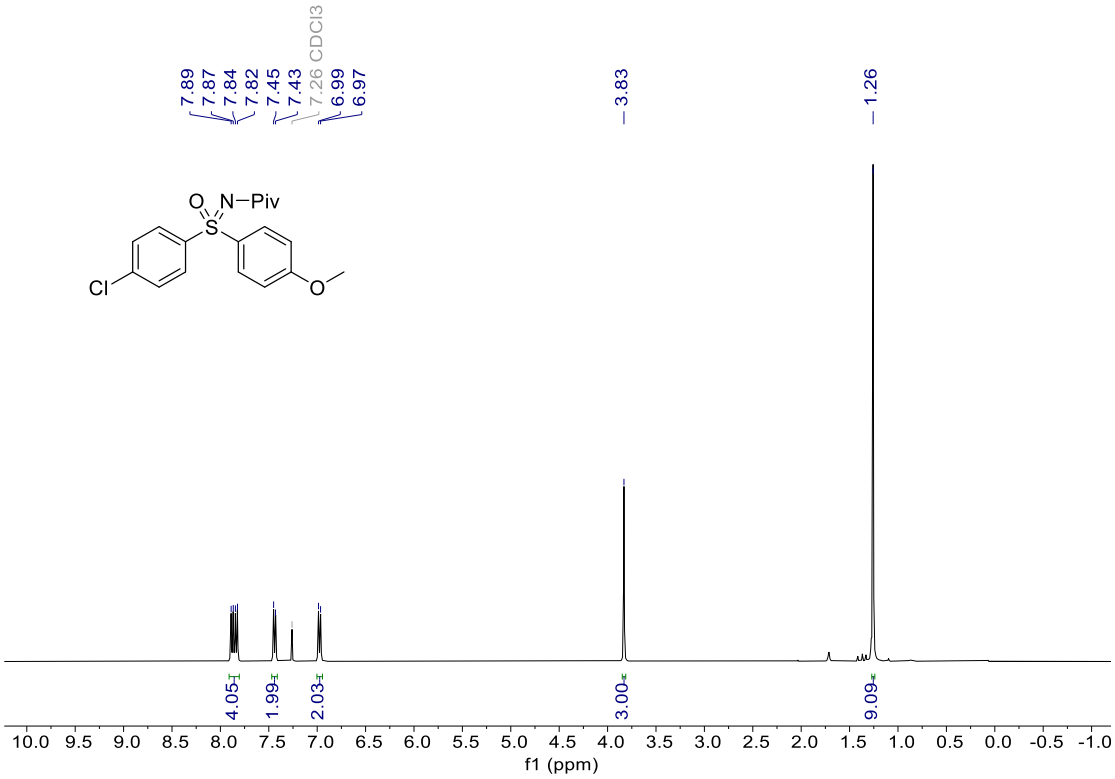
4ab, ^{1}H NMR (400 MHz, $CDCl_3$)



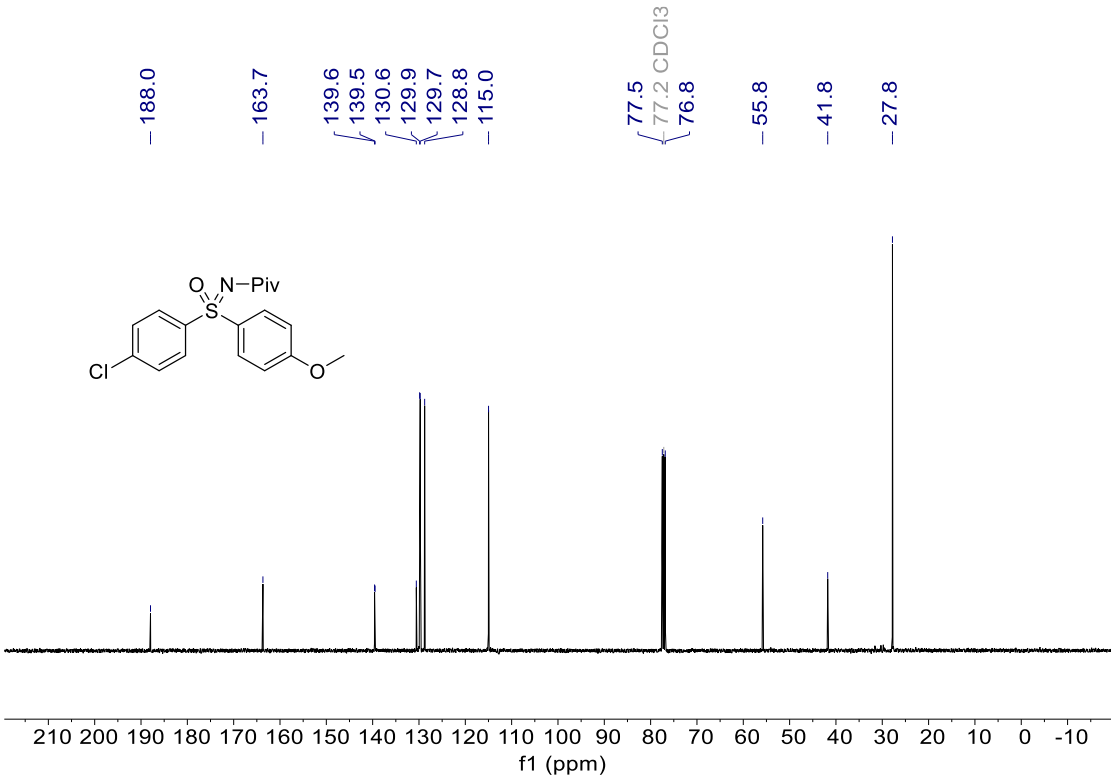
4ab, ^{13}C NMR (101 MHz, $CDCl_3$)



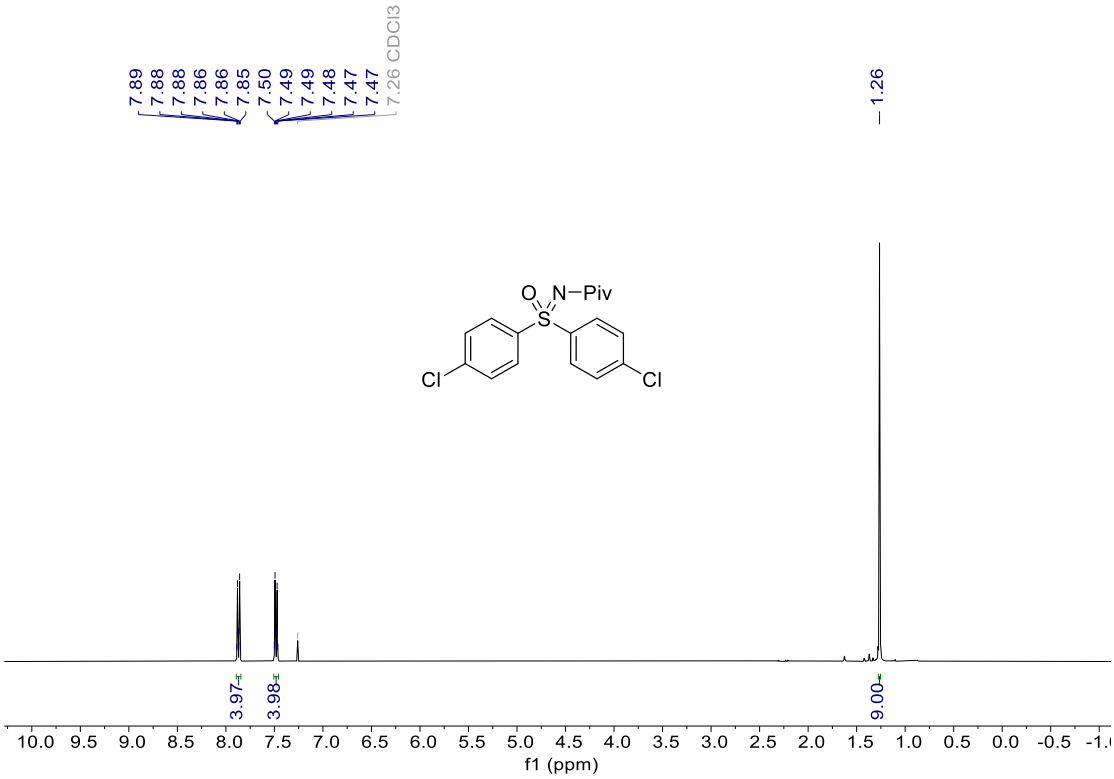
4ac, ^{1}H NMR (400 MHz, $CDCl_3$)



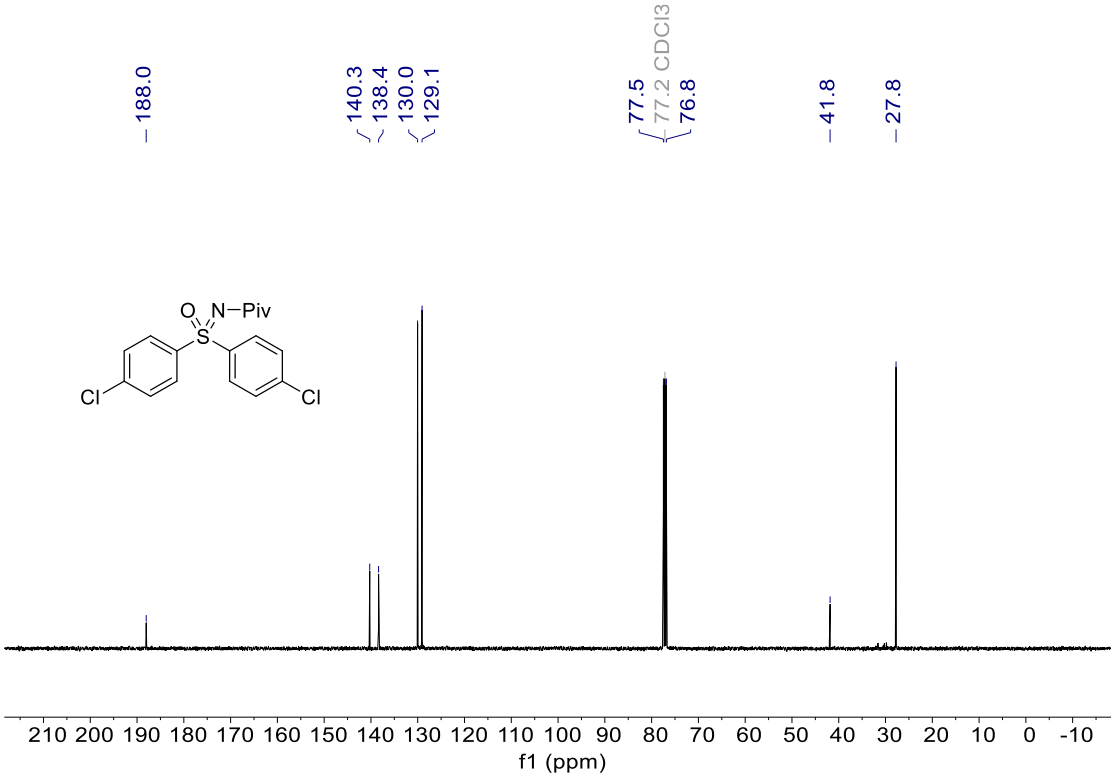
4ac, ^{13}C NMR (101 MHz, $CDCl_3$)



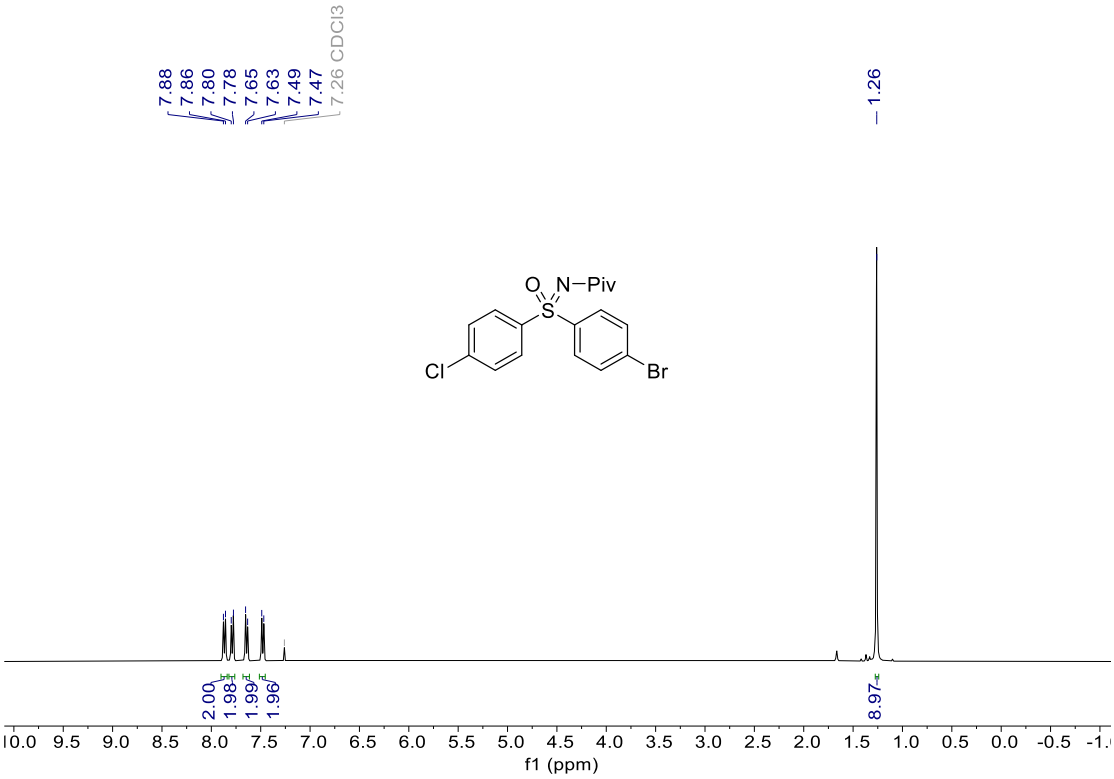
4ad, ^{1}H NMR (400 MHz, $CDCl_3$)



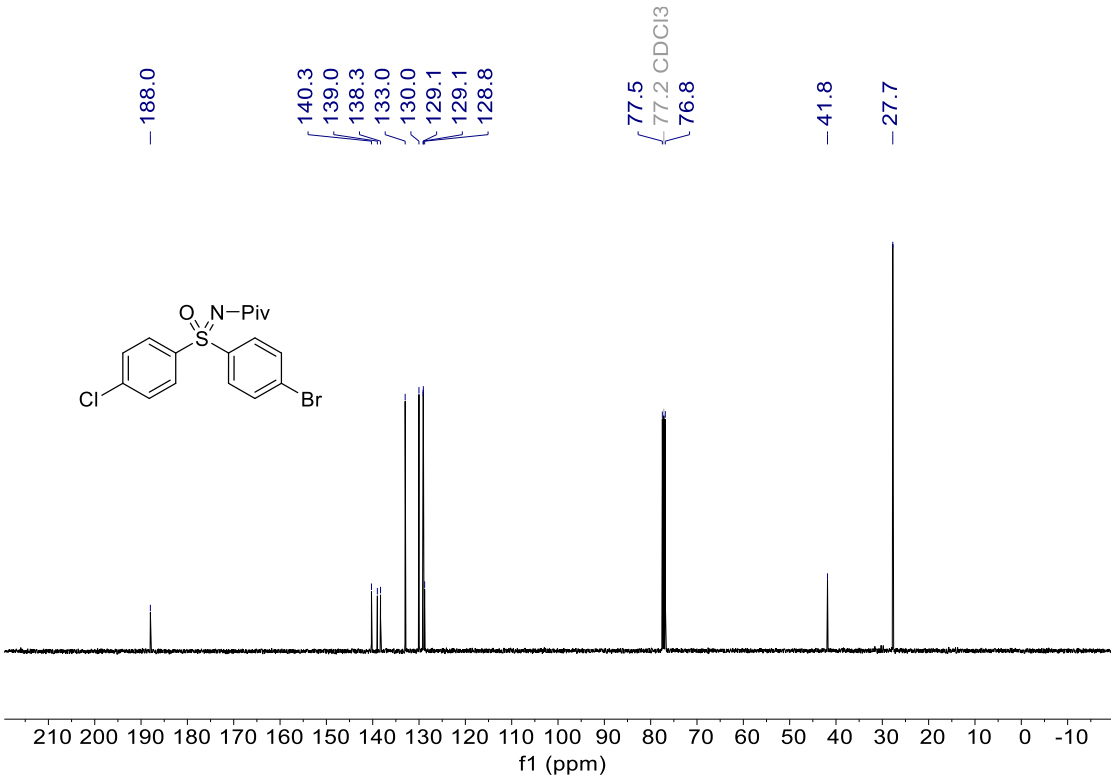
4ad, ^{13}C NMR (101 MHz, $CDCl_3$)



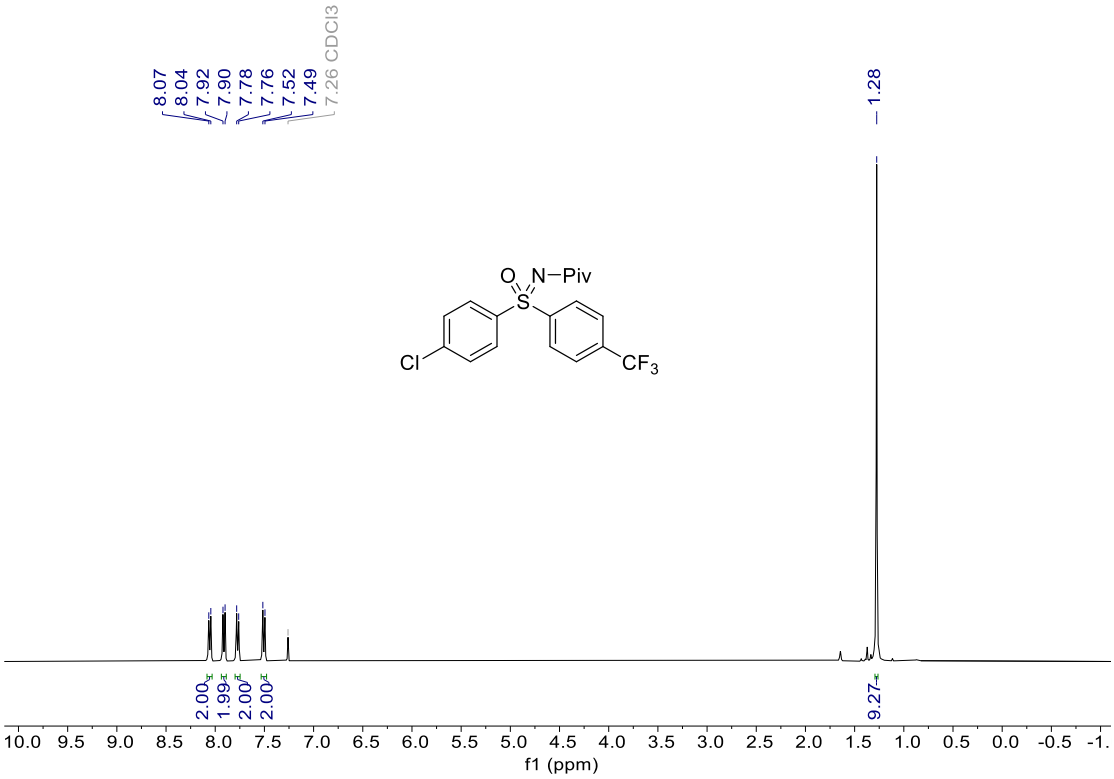
4ae, ^{1}H NMR (400 MHz, $CDCl_3$)



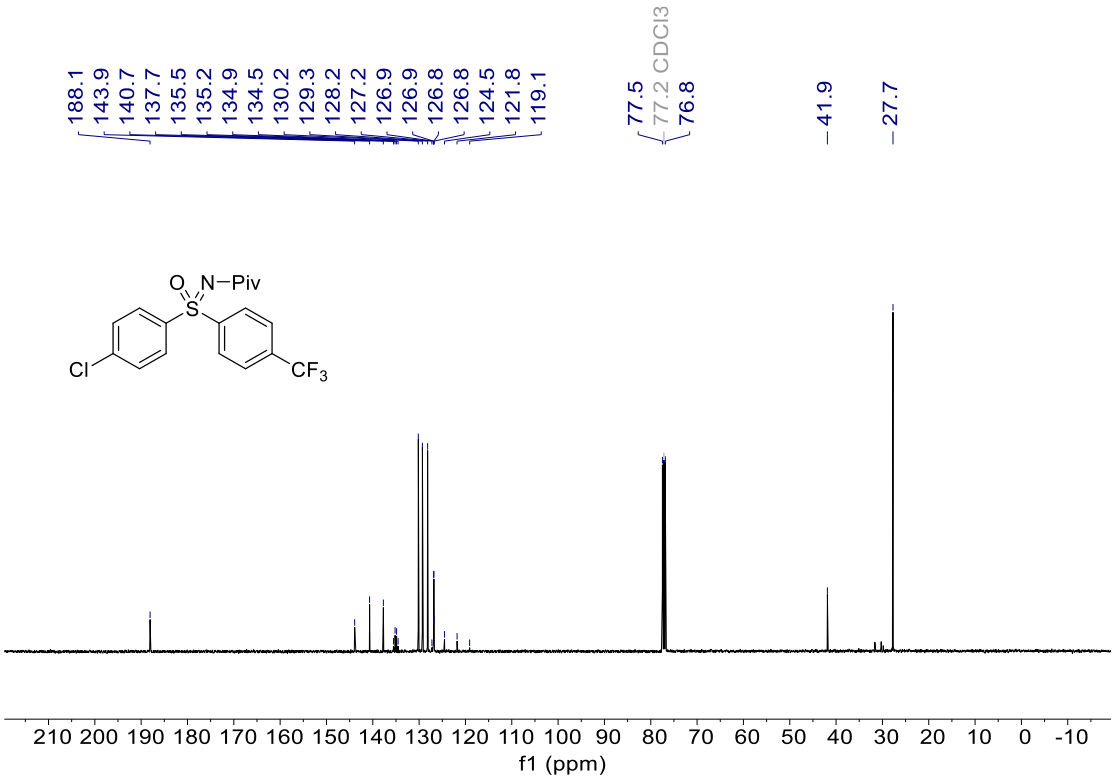
4ae, ^{13}C NMR (101 MHz, $CDCl_3$)



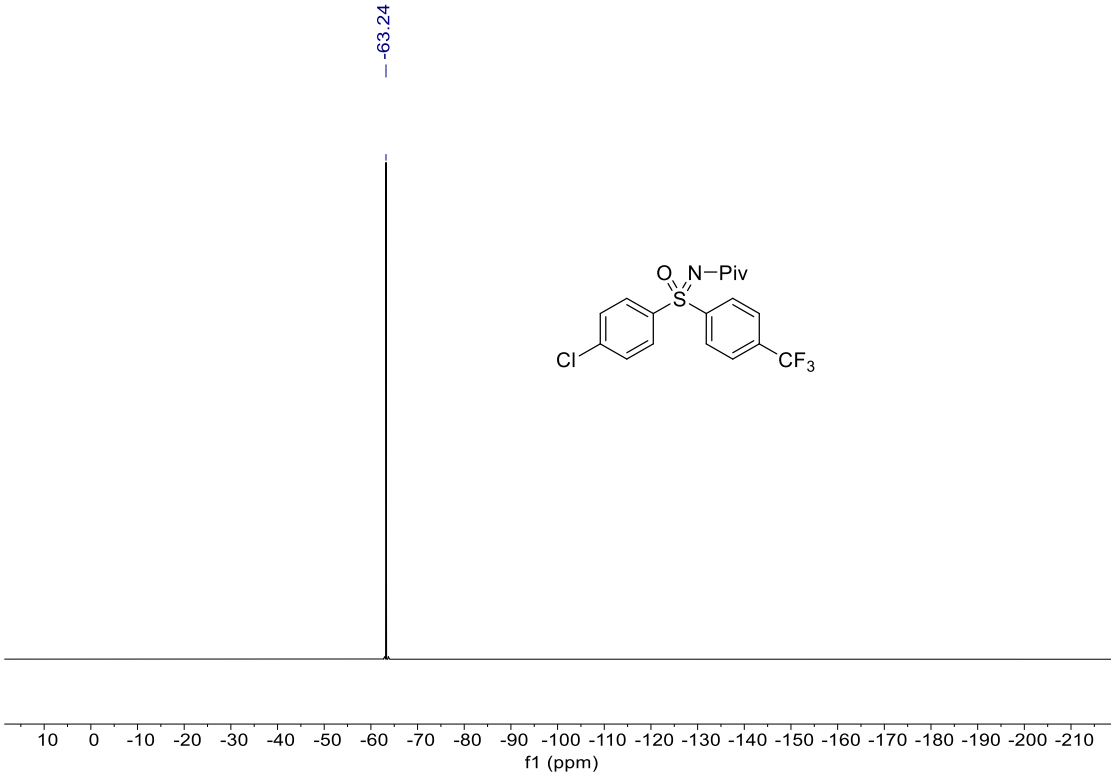
4af, ^{1}H NMR (400 MHz, $CDCl_3$)



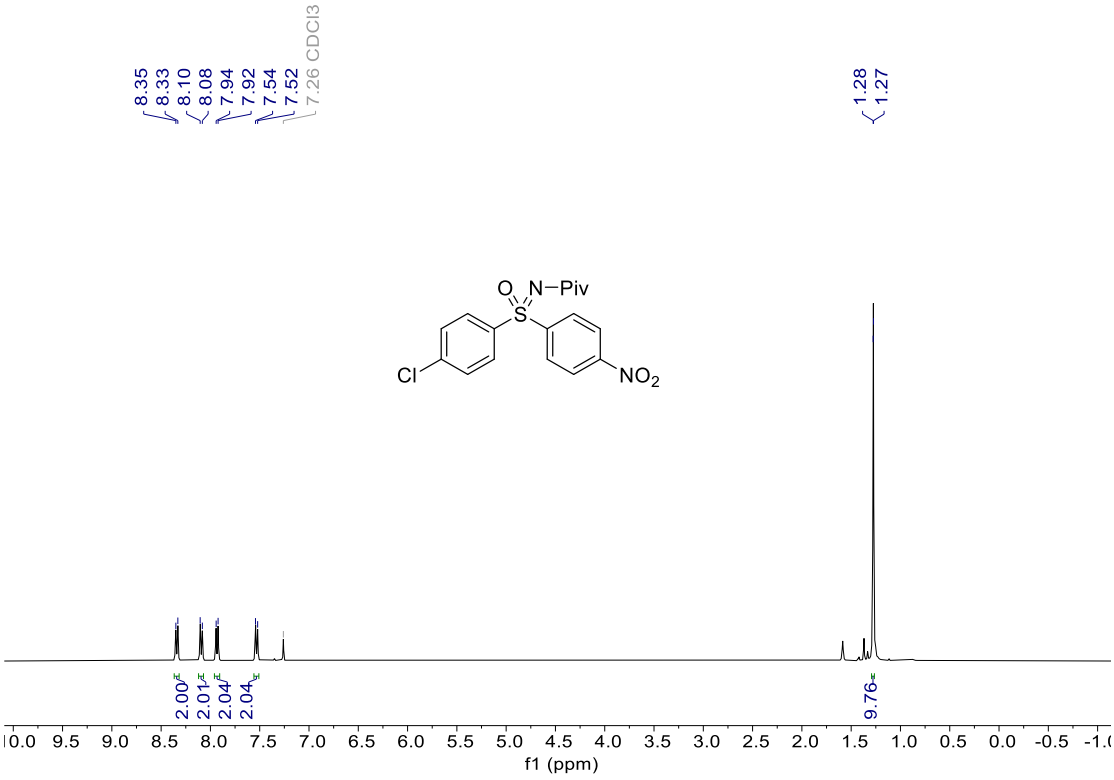
4af, ^{13}C NMR (101 MHz, $CDCl_3$)



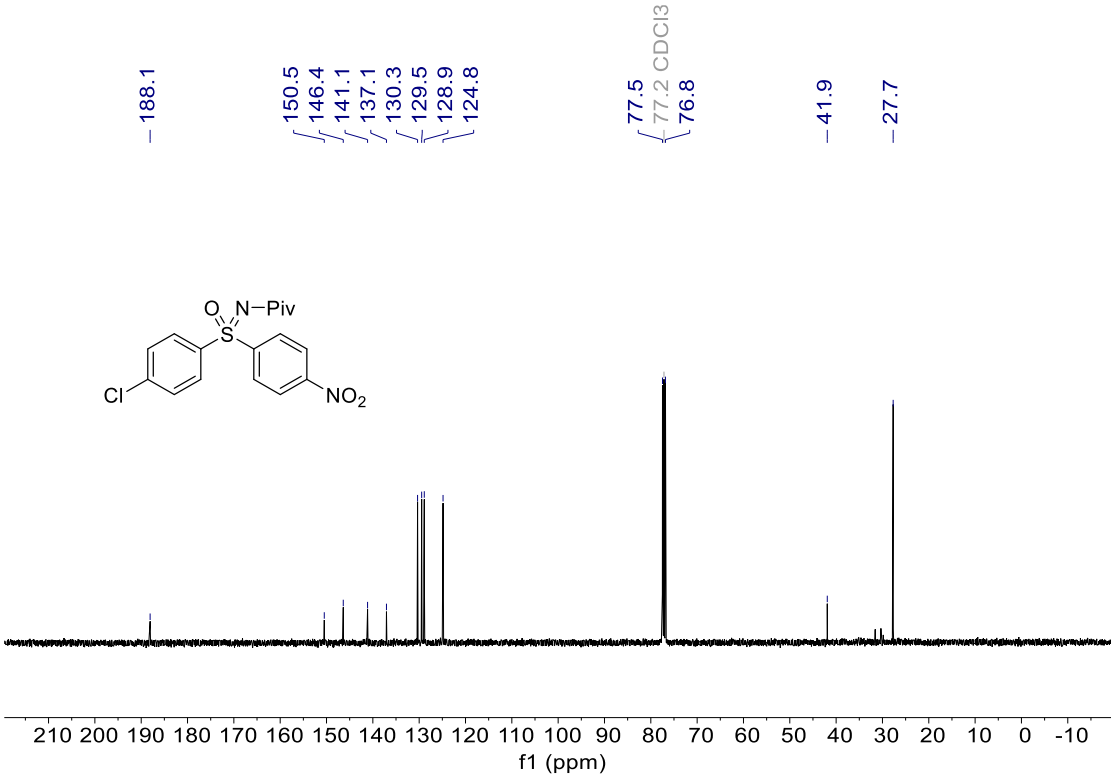
4af, ^{19}F NMR (376 MHz, $CDCl_3$)



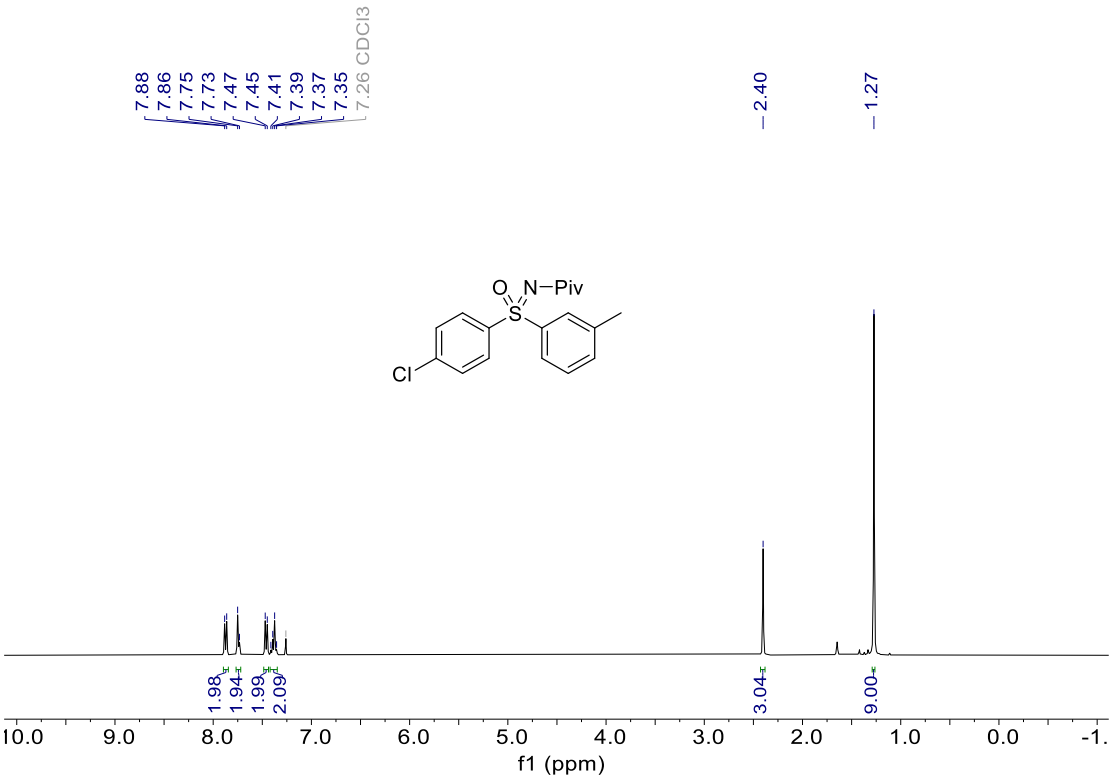
4ag, ^{1}H NMR (400 MHz, $CDCl_3$)



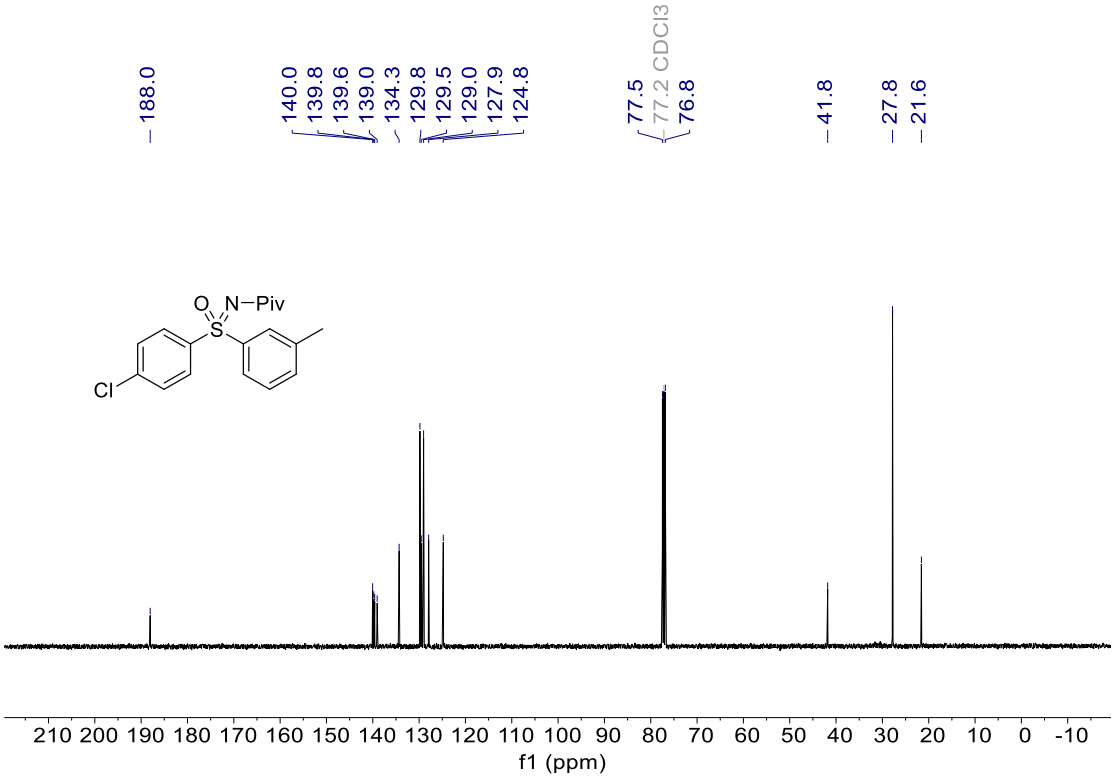
4ag, ^{13}C NMR (101 MHz, $CDCl_3$)



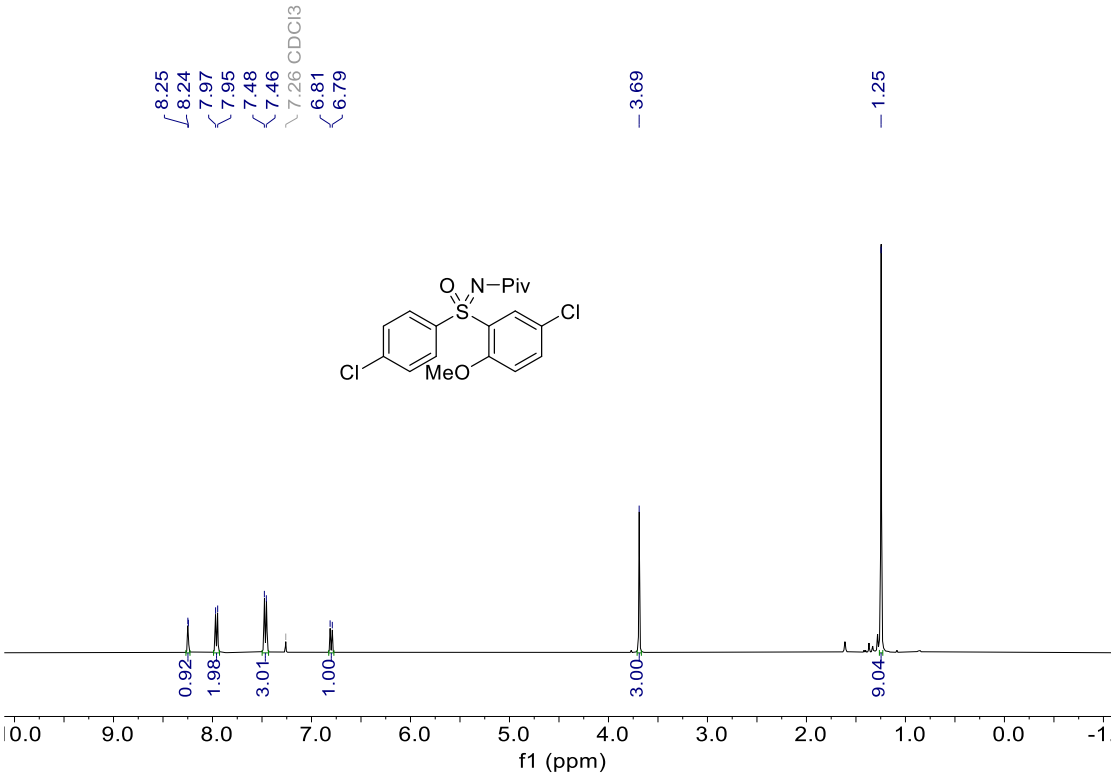
4ah, ^{1}H NMR (400 MHz, $CDCl_3$)



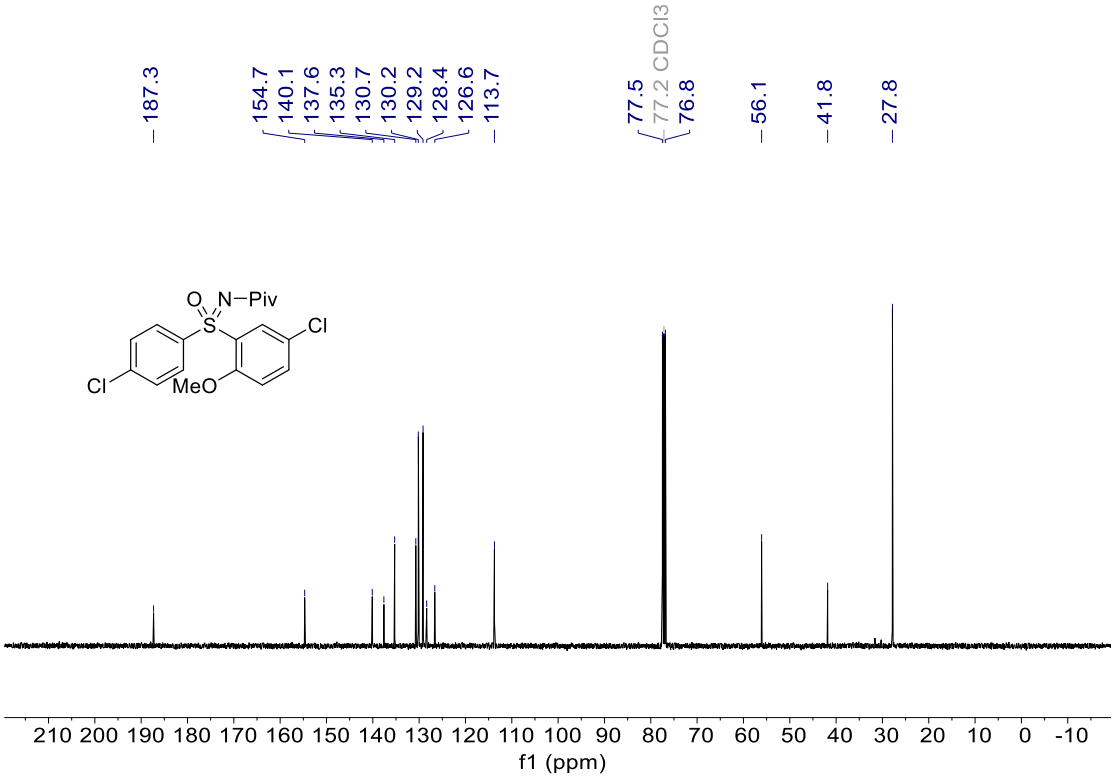
4ah, ^{13}C NMR (101 MHz, $CDCl_3$)



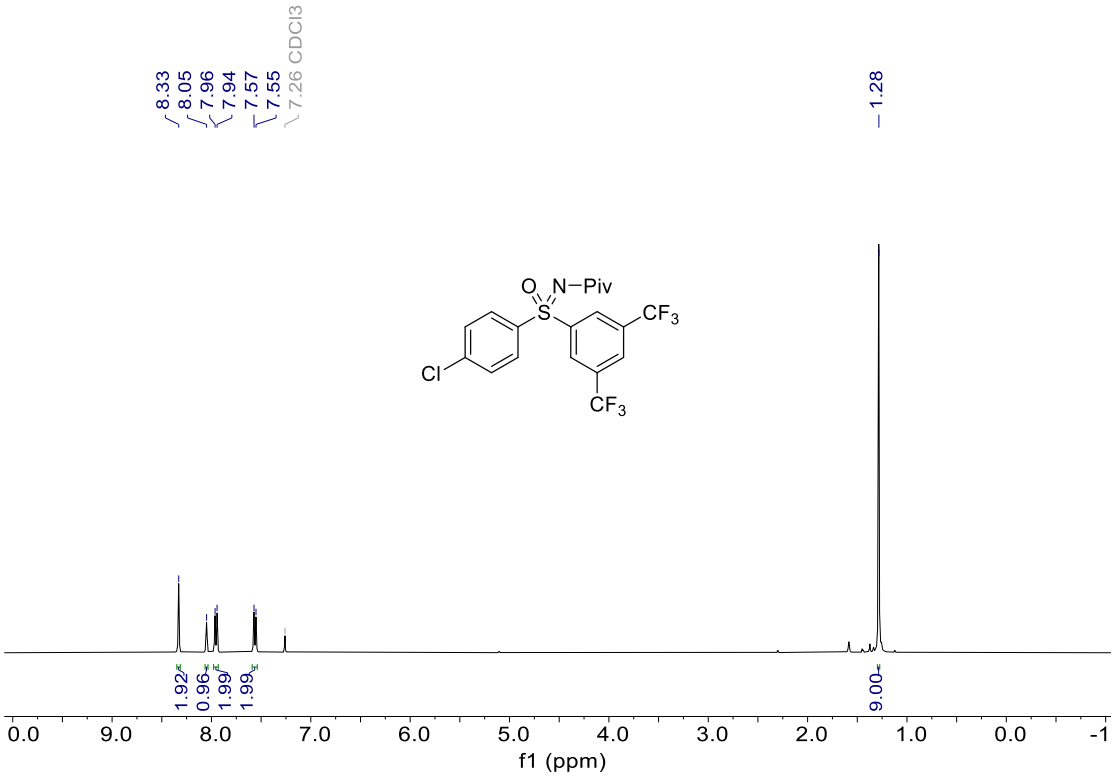
4ai, ^{1}H NMR (400 MHz, $CDCl_3$)



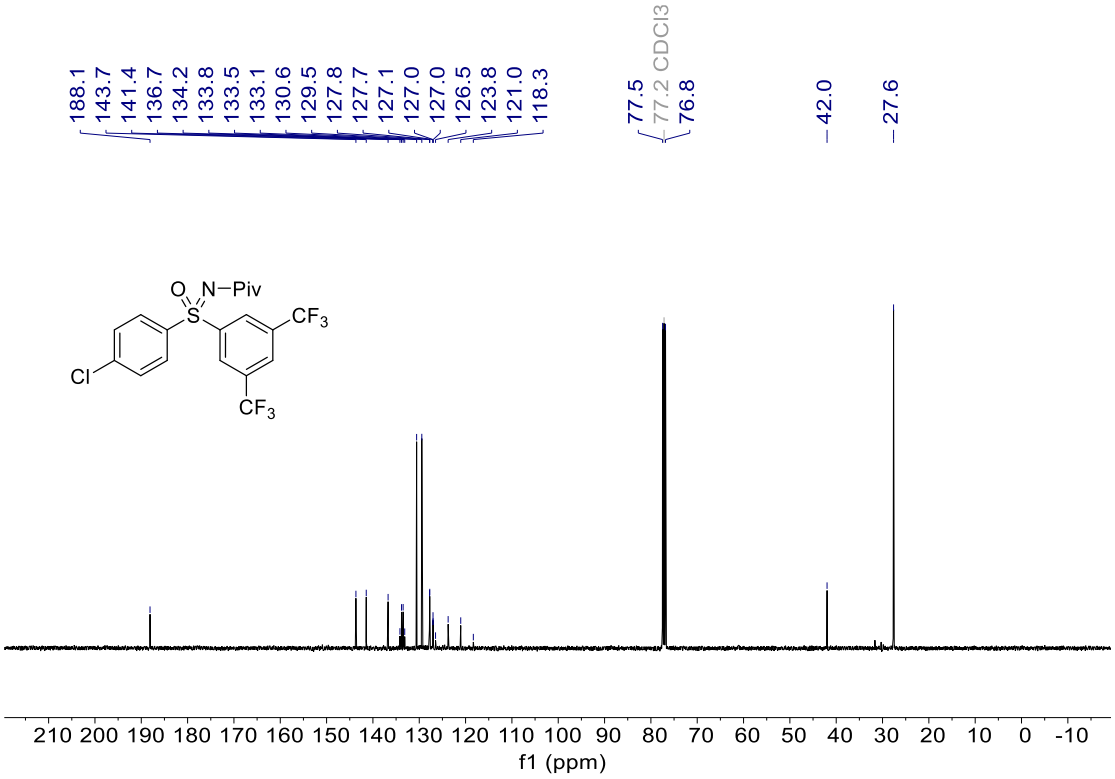
4ai, ^{13}C NMR (101 MHz, $CDCl_3$)



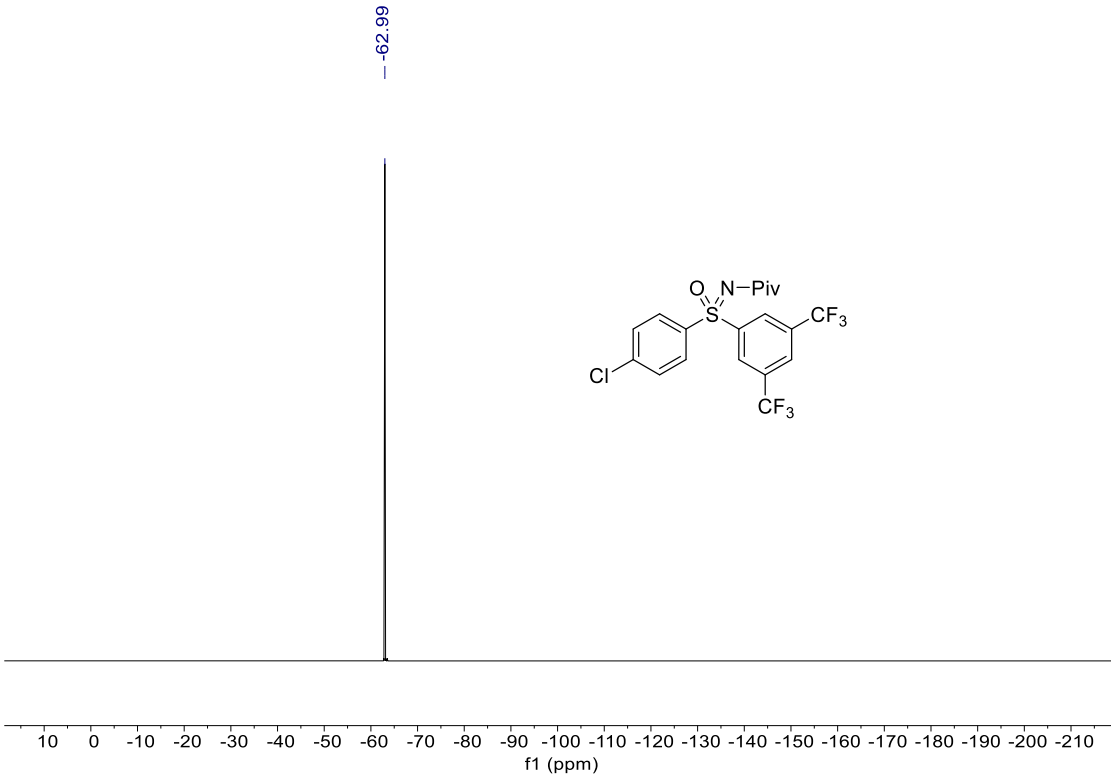
4aj, ^{1}H NMR (400 MHz, $CDCl_3$)



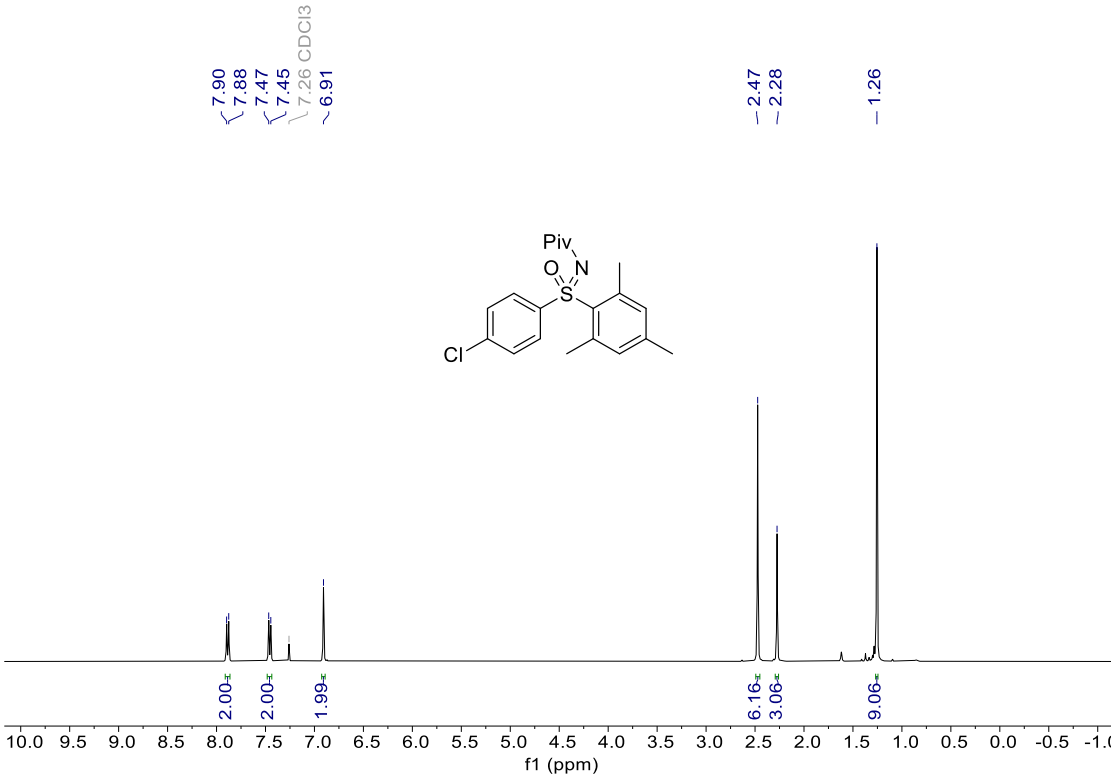
4aj, ^{13}C NMR (101 MHz, $CDCl_3$)



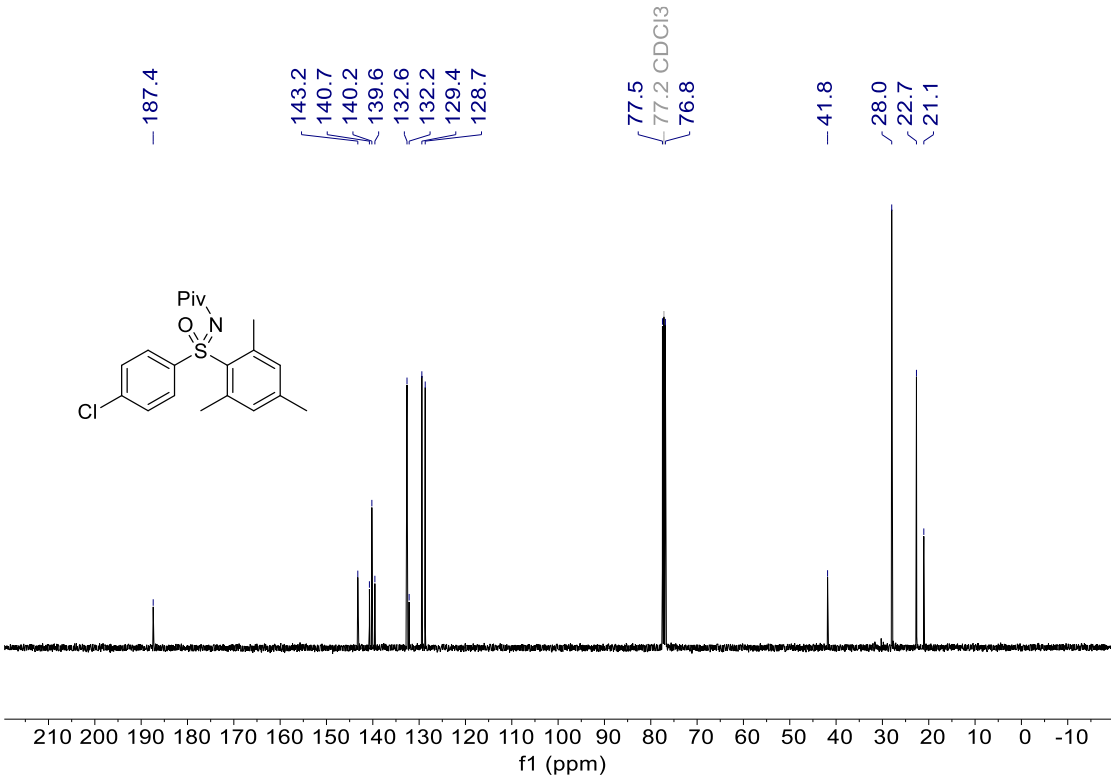
4aj, ^{19}F NMR (376 MHz, $CDCl_3$)



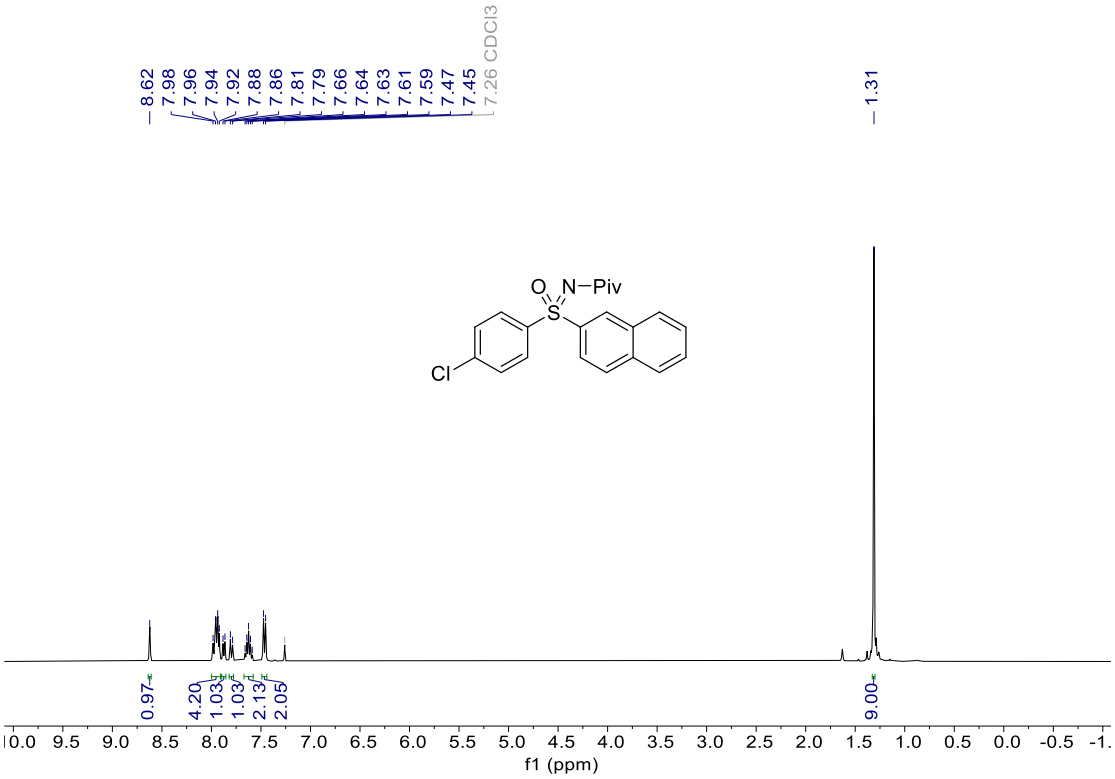
4ak, ^{1}H NMR (400 MHz, $CDCl_3$)



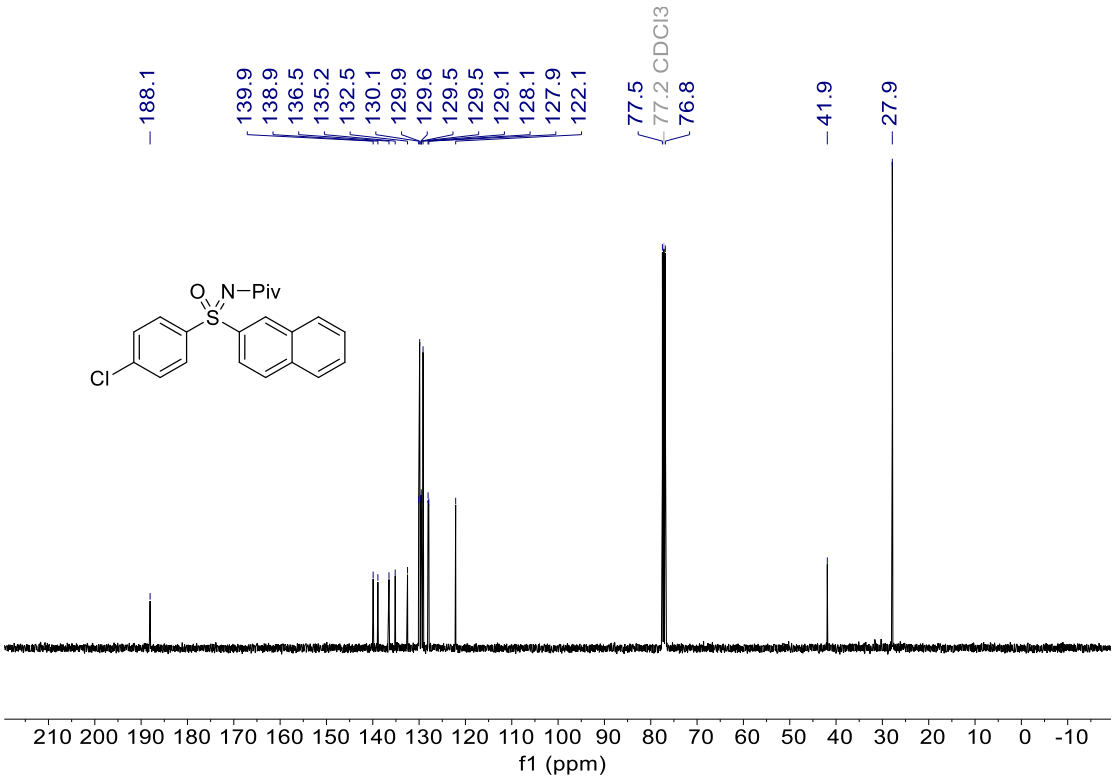
4ak, ^{13}C NMR (101 MHz, $CDCl_3$)



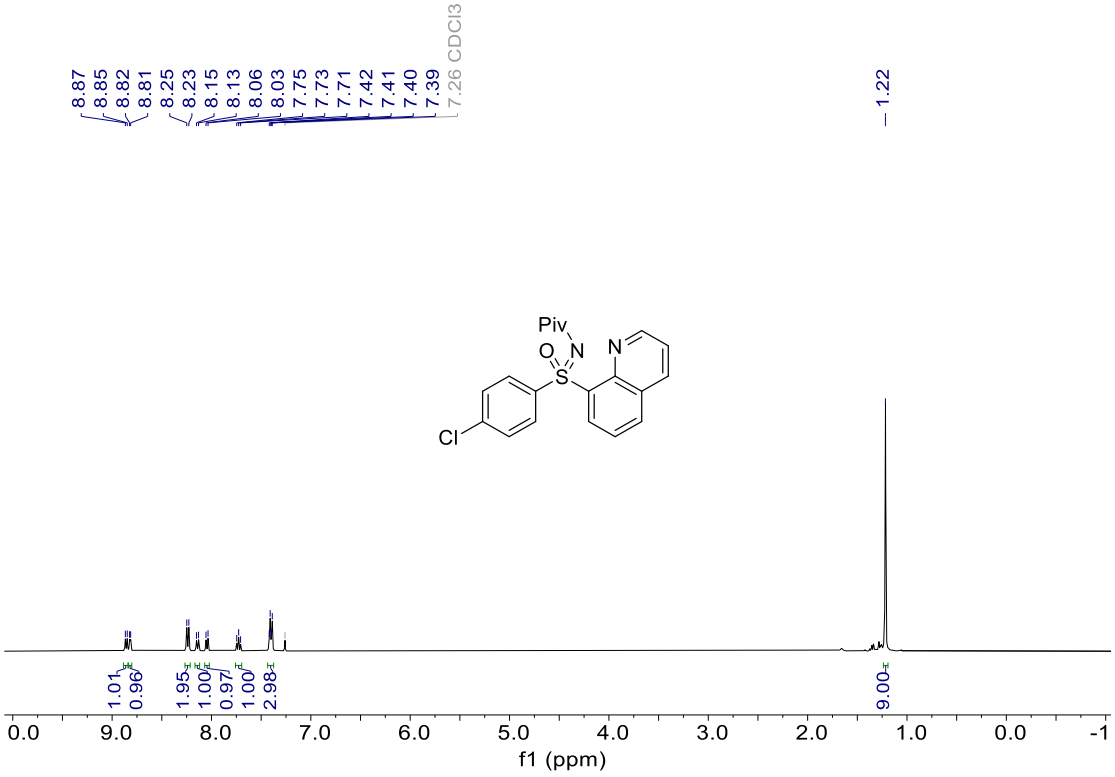
4al, ^{1}H NMR (400 MHz, $CDCl_3$)



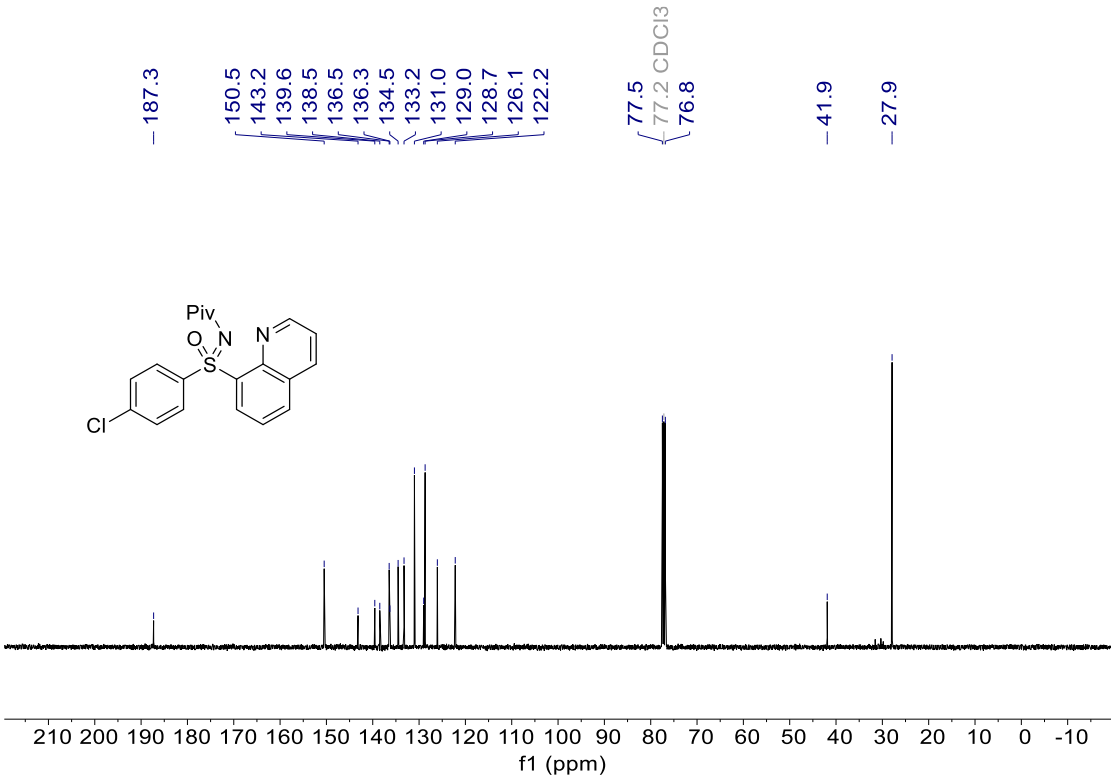
4al, ^{13}C NMR (101 MHz, $CDCl_3$)



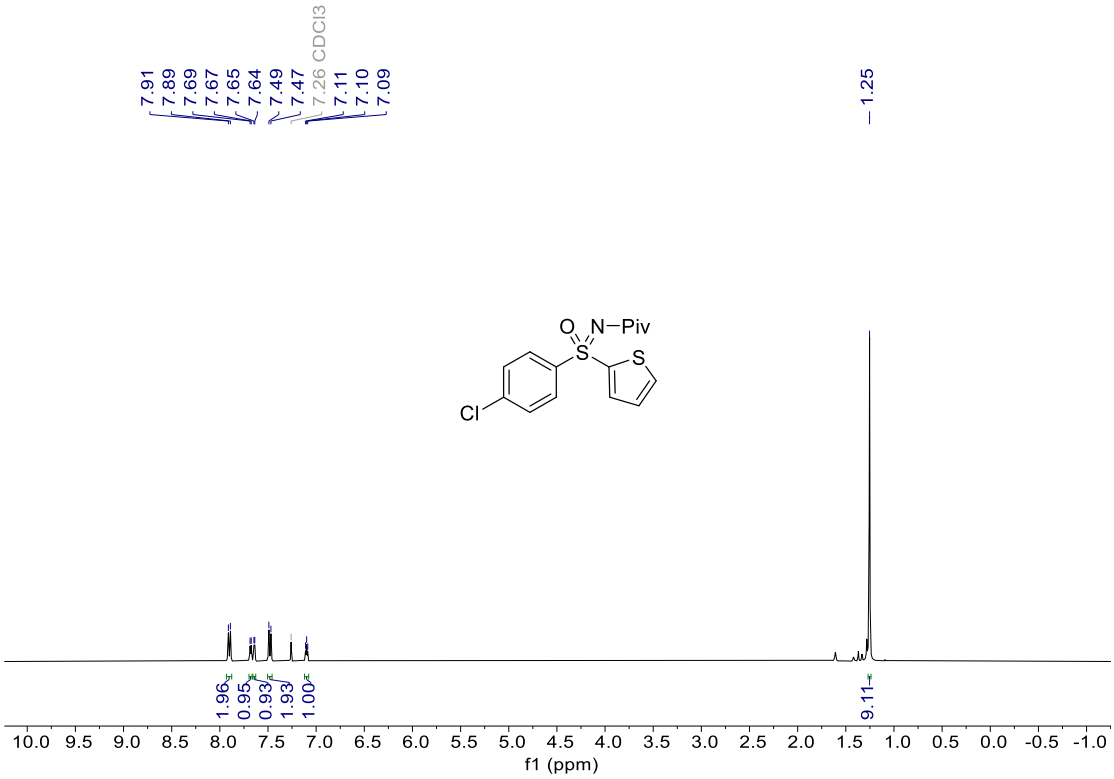
4am, ^{1}H NMR (400 MHz, $CDCl_3$)



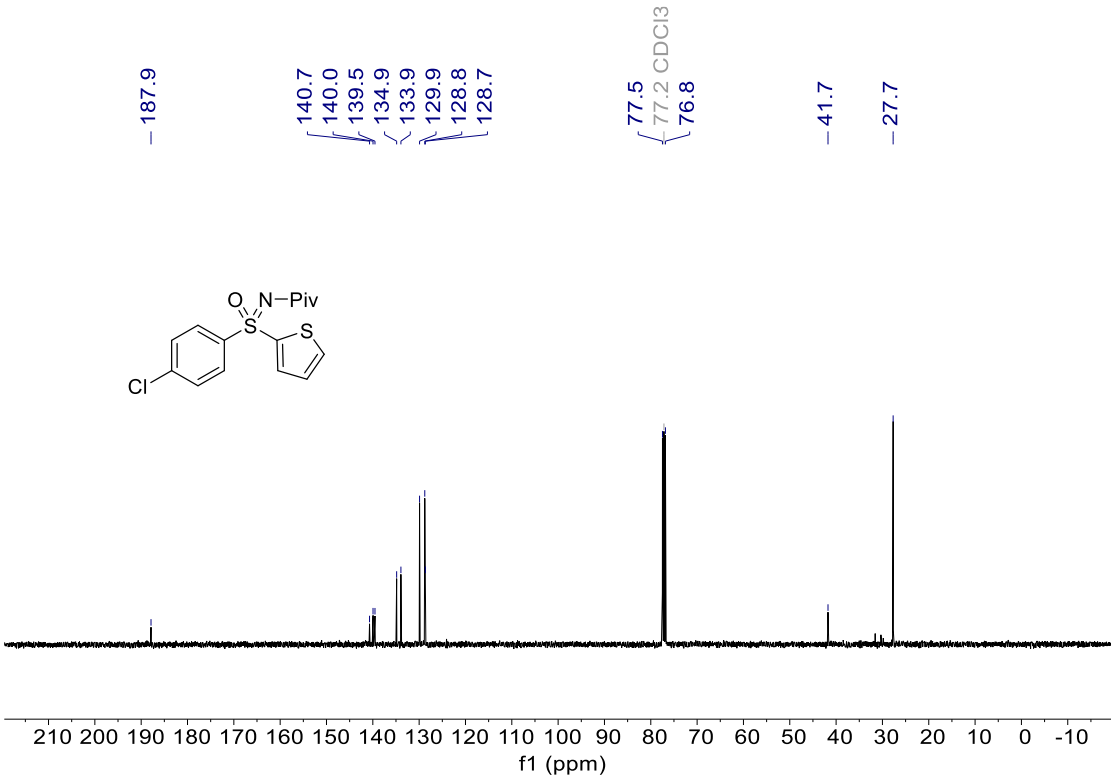
4am, ^{13}C NMR (101 MHz, $CDCl_3$)



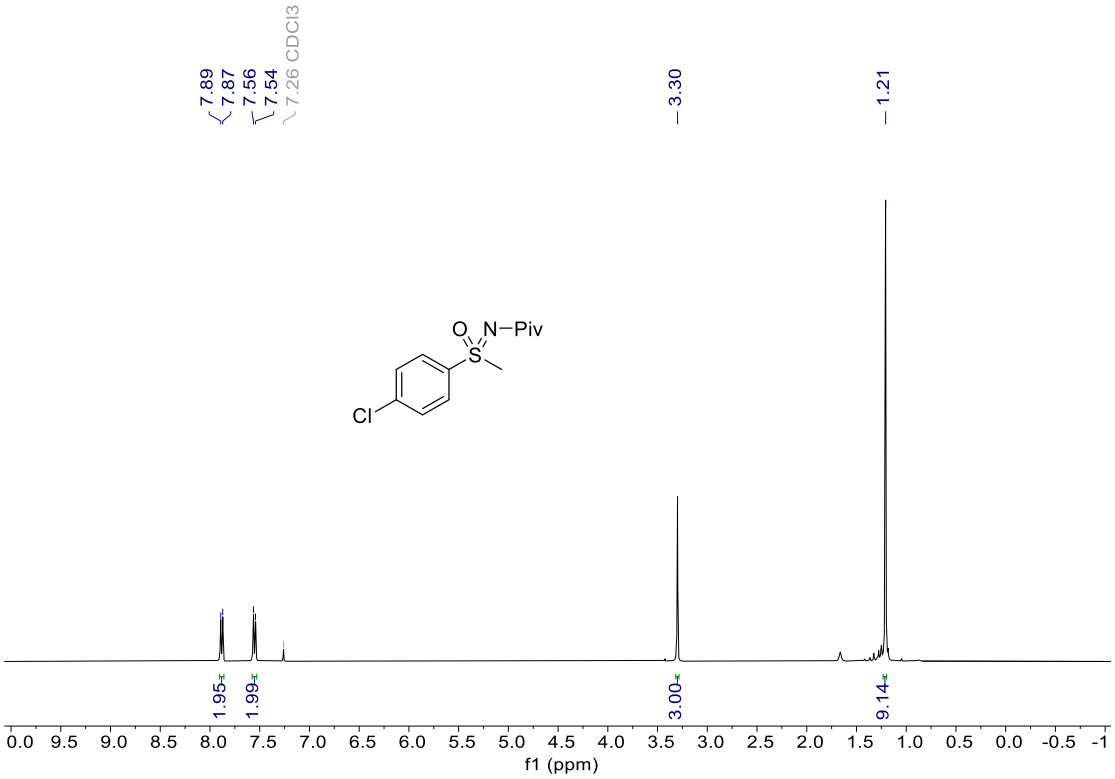
4an, ^{1}H NMR (400 MHz, $CDCl_3$)



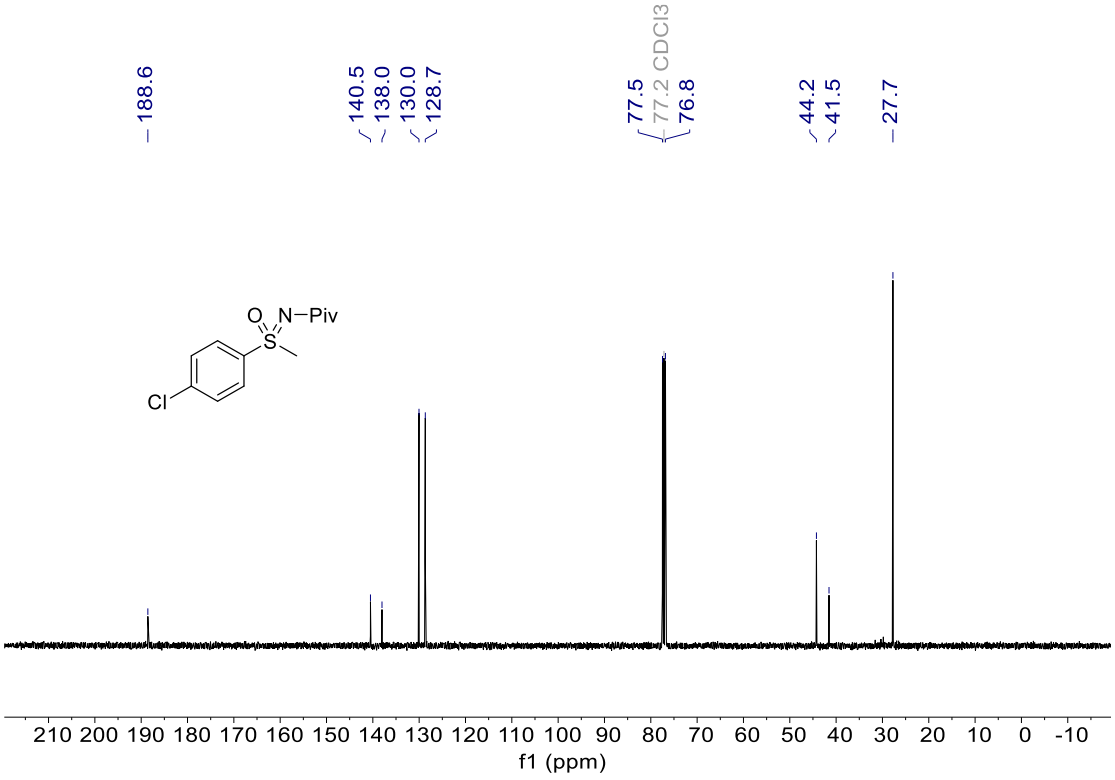
4an, ^{13}C NMR (101 MHz, $CDCl_3$)



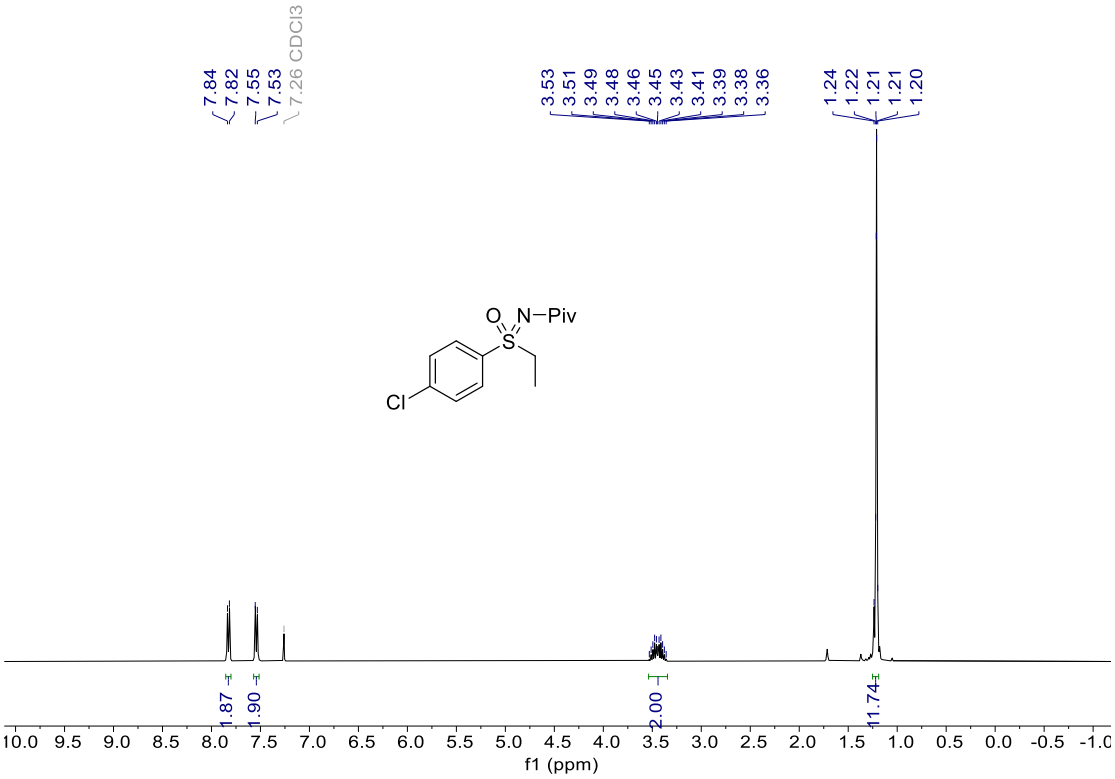
4ao, ^{1}H NMR (400 MHz, $CDCl_3$)



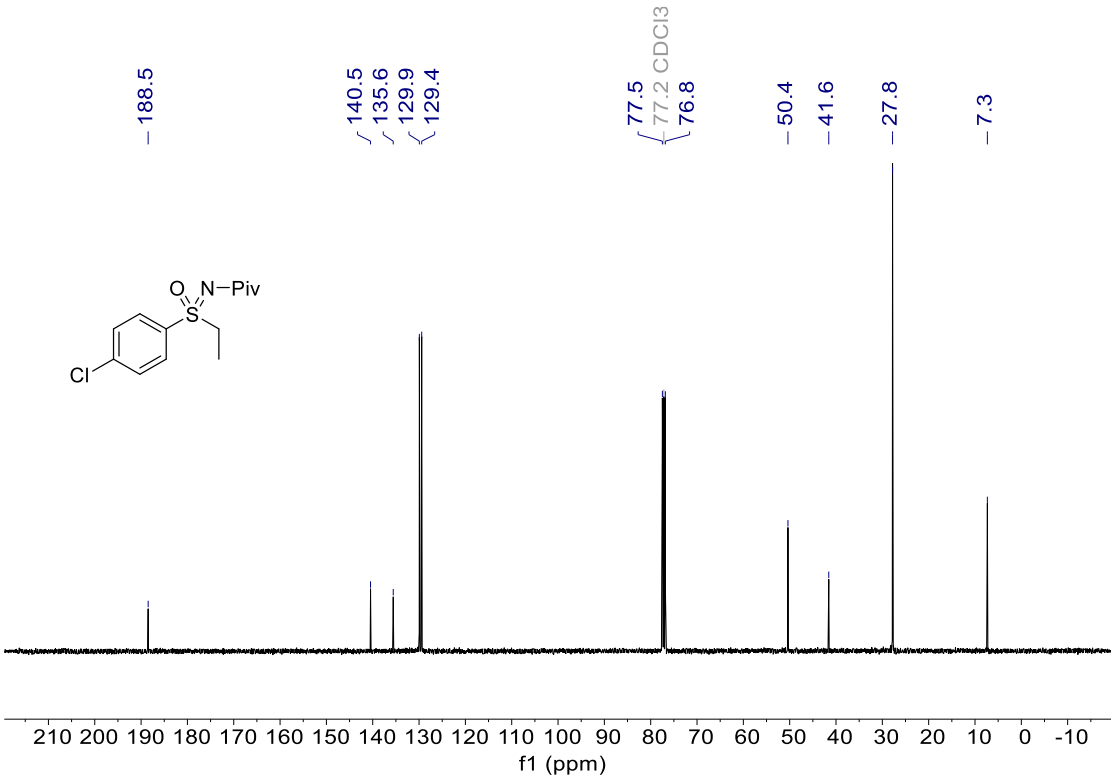
4ao, ^{13}C NMR (101 MHz, $CDCl_3$)



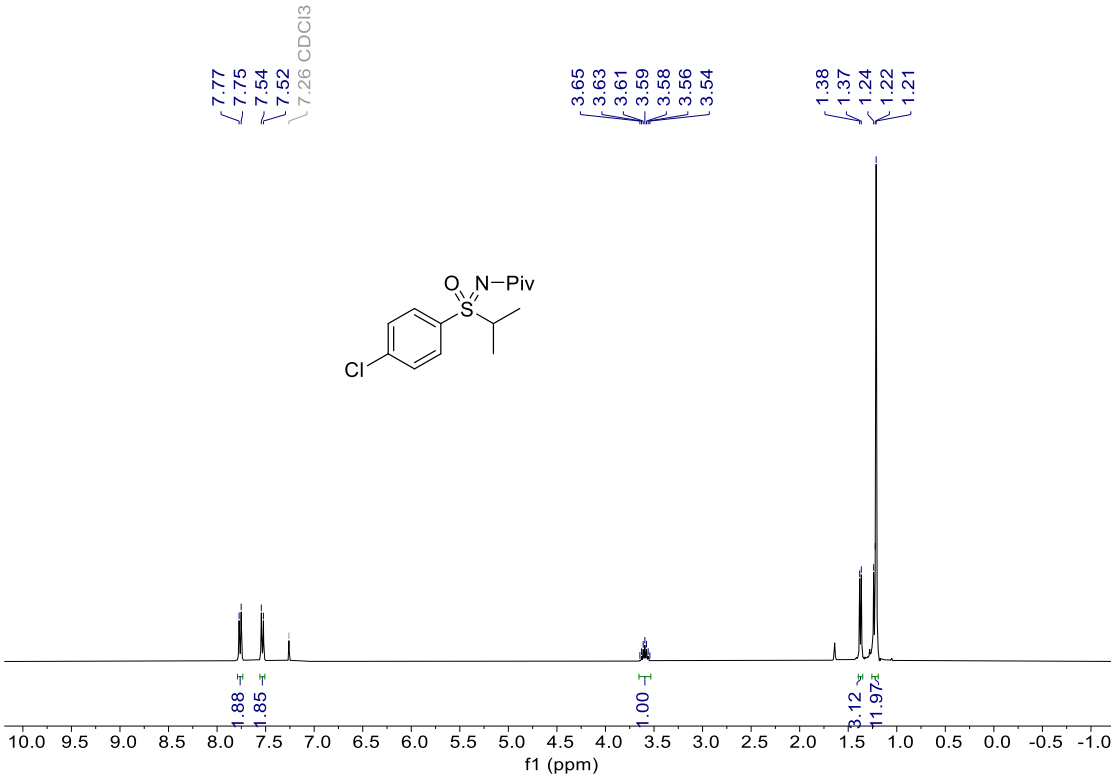
4ap, ^{1}H NMR (400 MHz, $CDCl_3$)



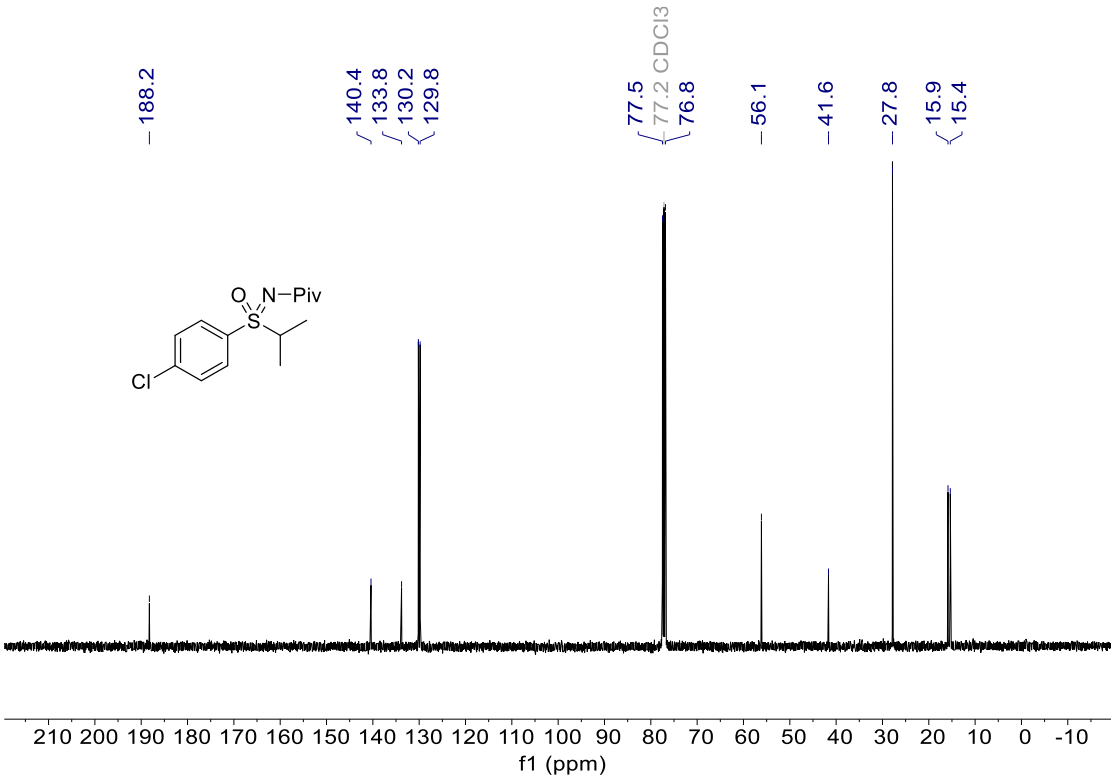
4ap, ^{13}C NMR (101 MHz, $CDCl_3$)



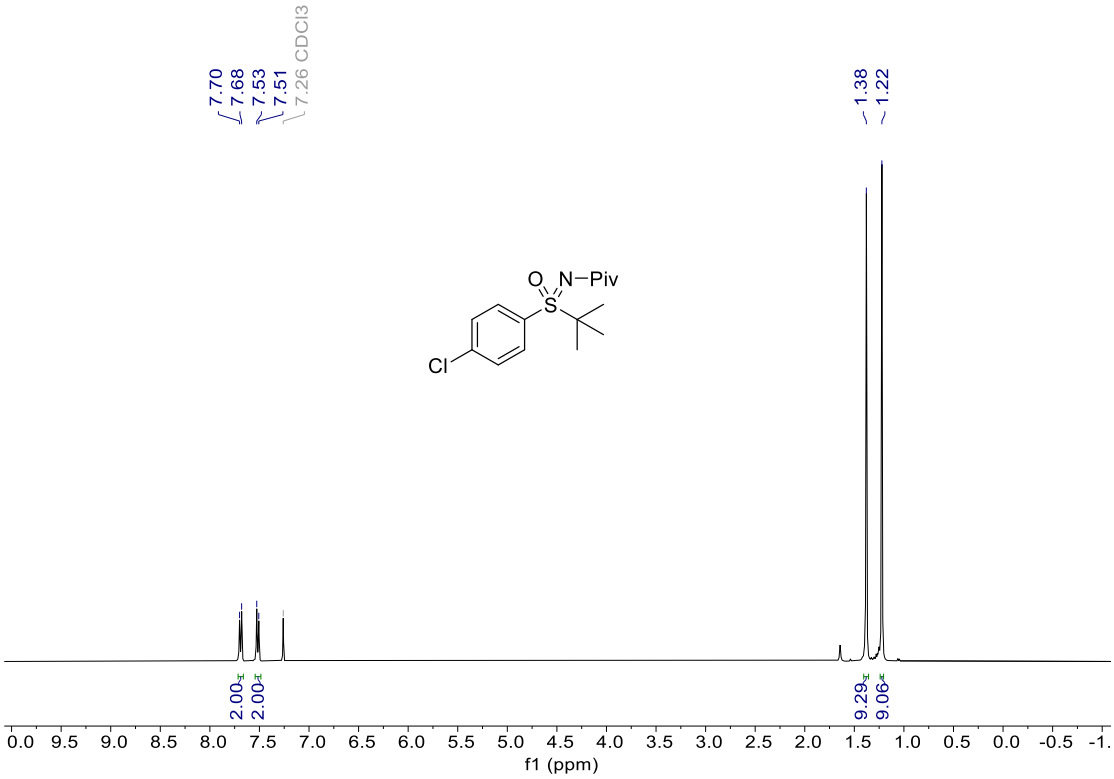
4aq, ^{1}H NMR (400 MHz, $CDCl_3$)



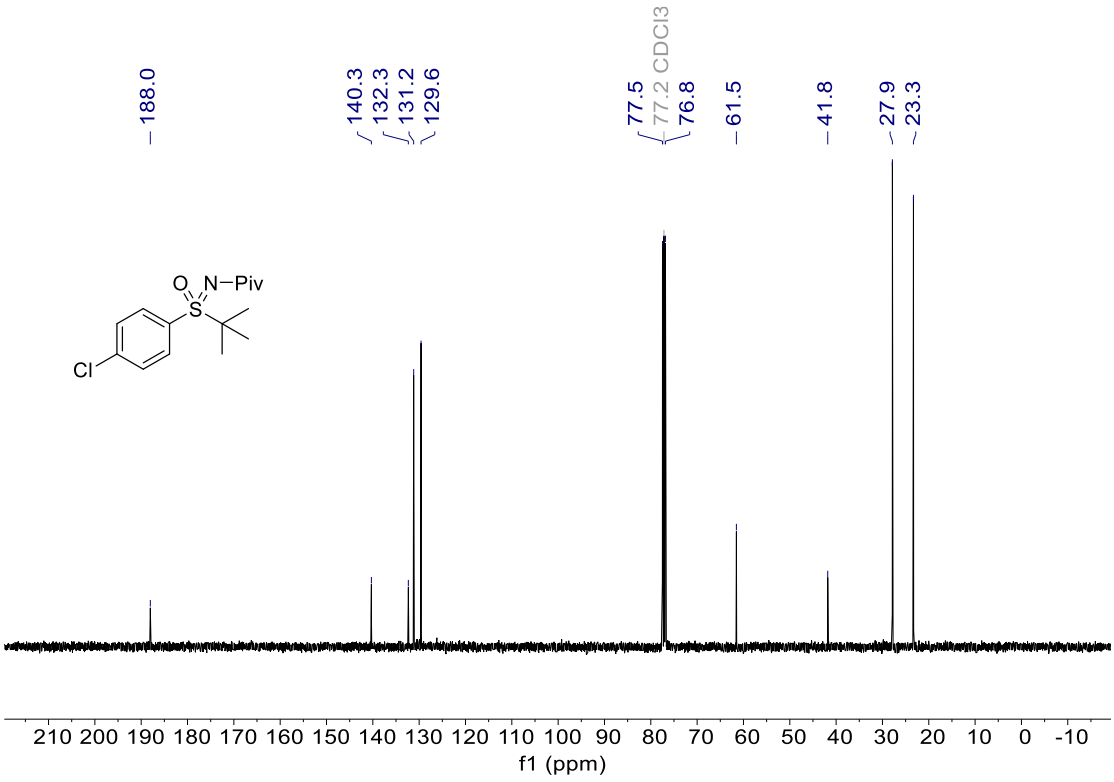
4aq, ^{13}C NMR (101 MHz, $CDCl_3$)



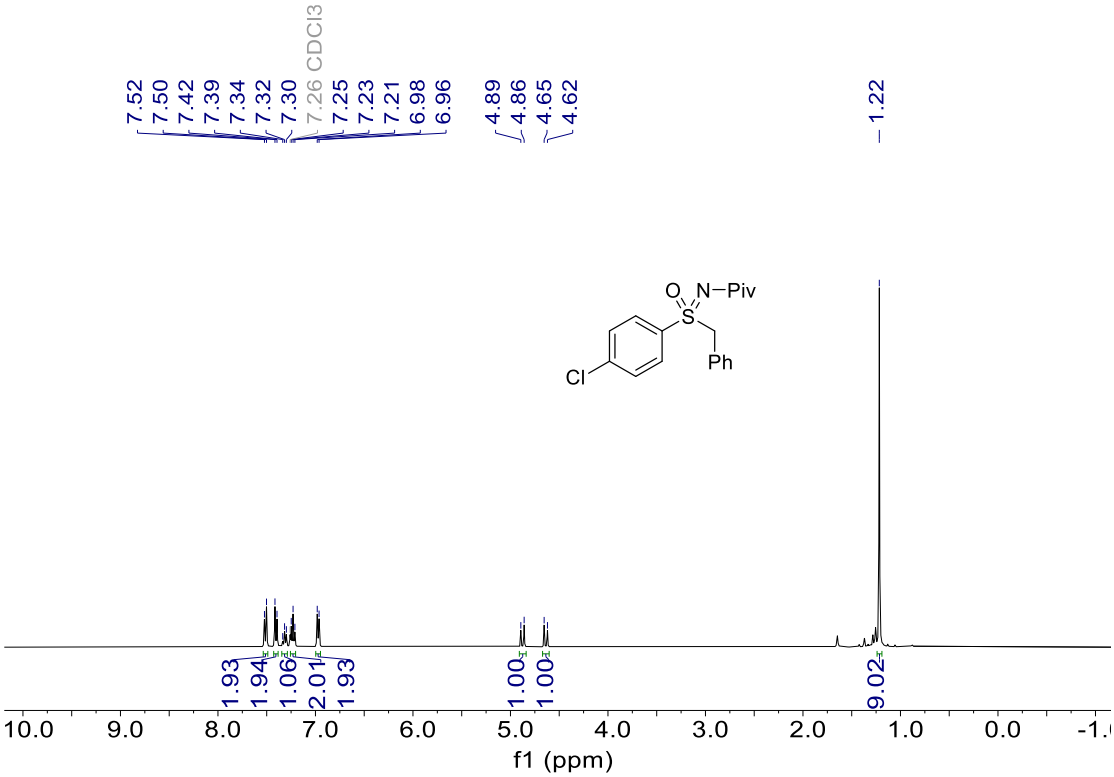
4ar, ^{1}H NMR (400 MHz, $CDCl_3$)



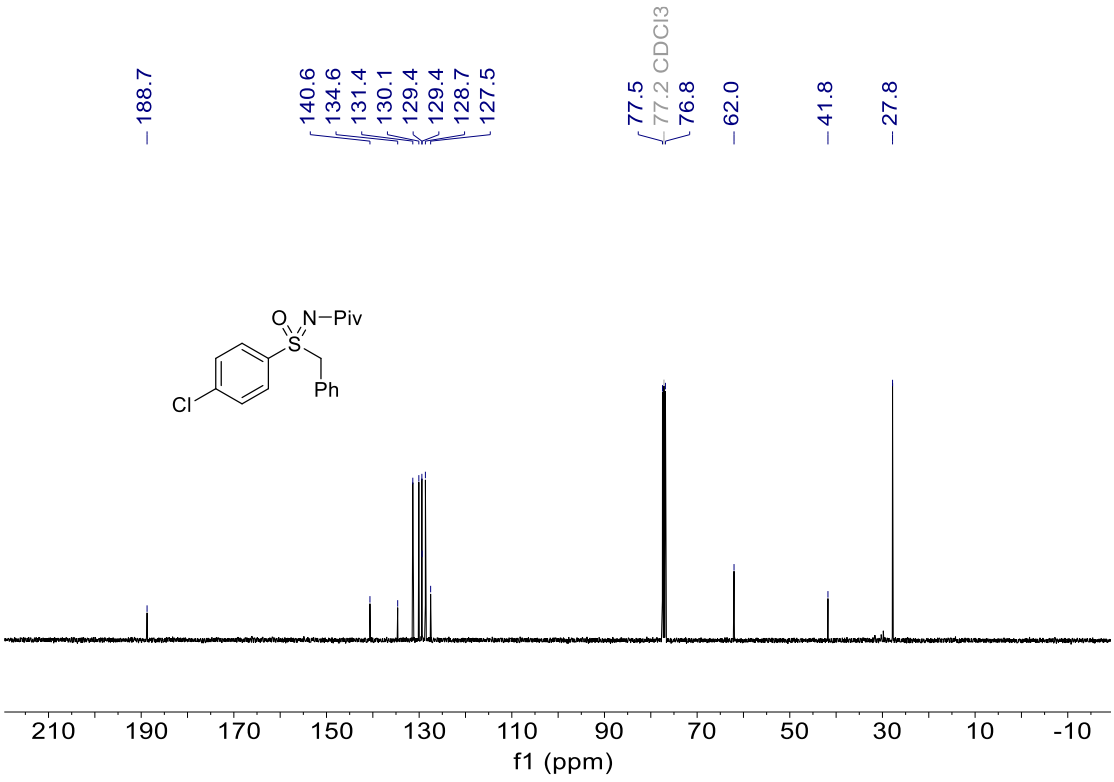
4ar, ^{13}C NMR (101 MHz, $CDCl_3$)



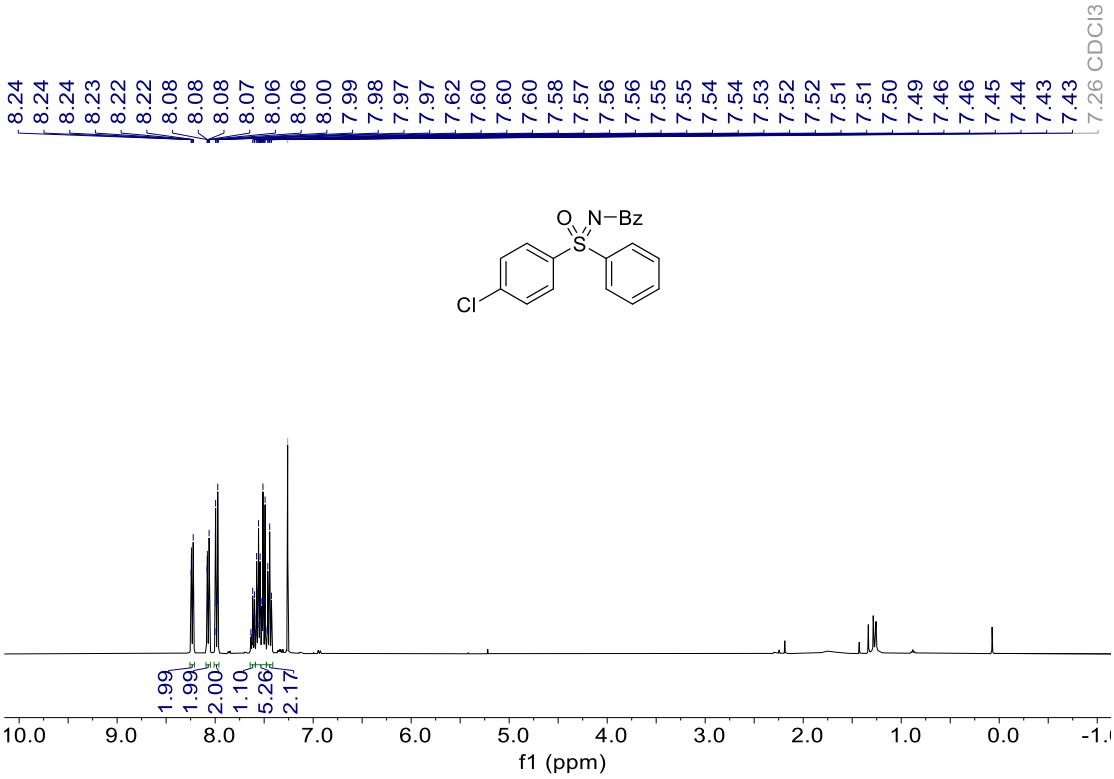
4as, ^{1}H NMR (400 MHz, $CDCl_3$)



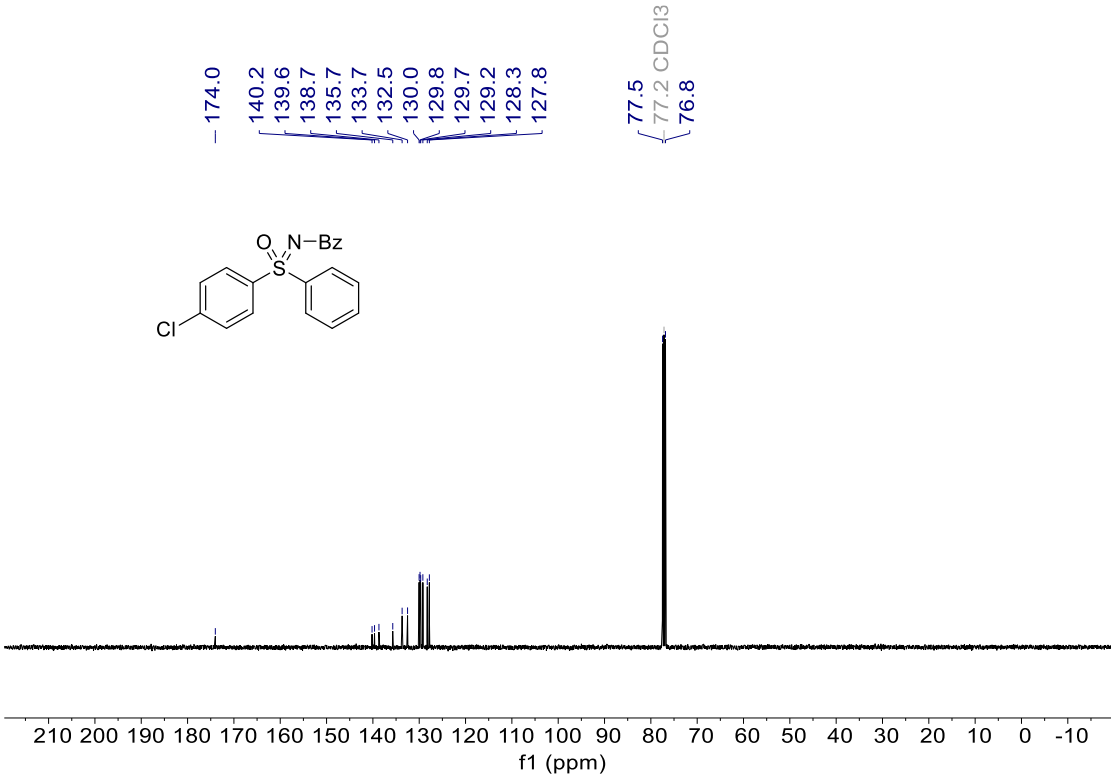
4as, ^{13}C NMR (101 MHz, $CDCl_3$)



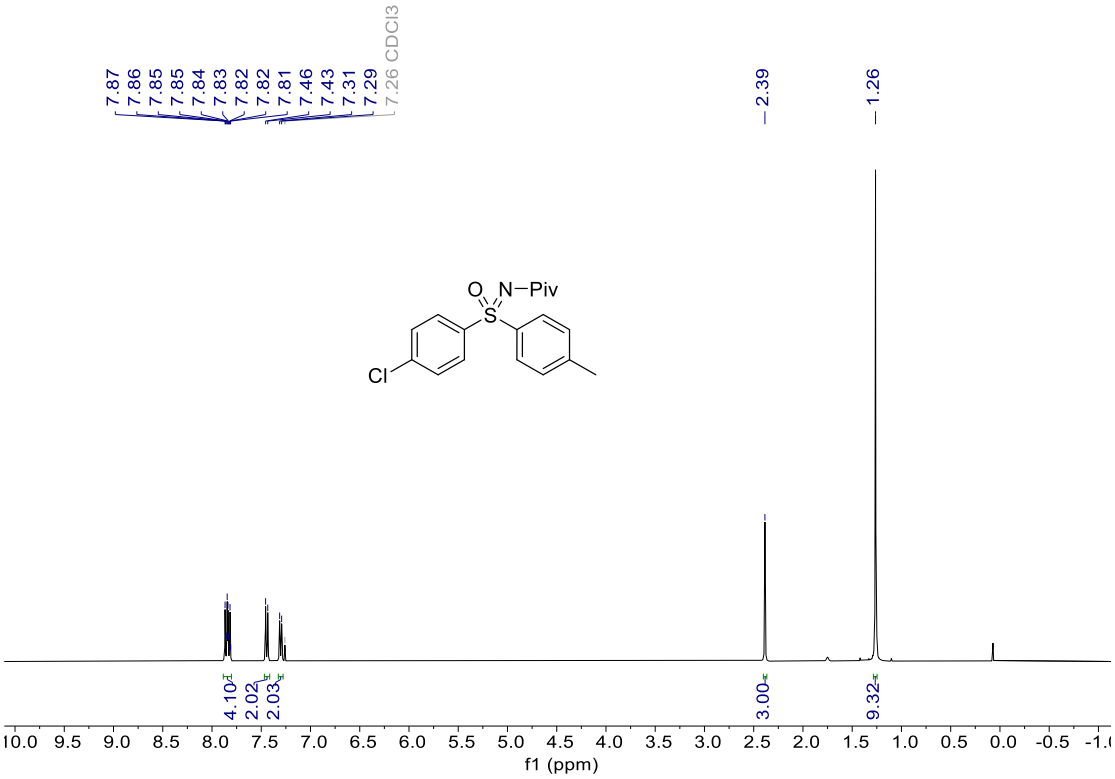
4au, ^{1}H NMR (400 MHz, $CDCl_3$)



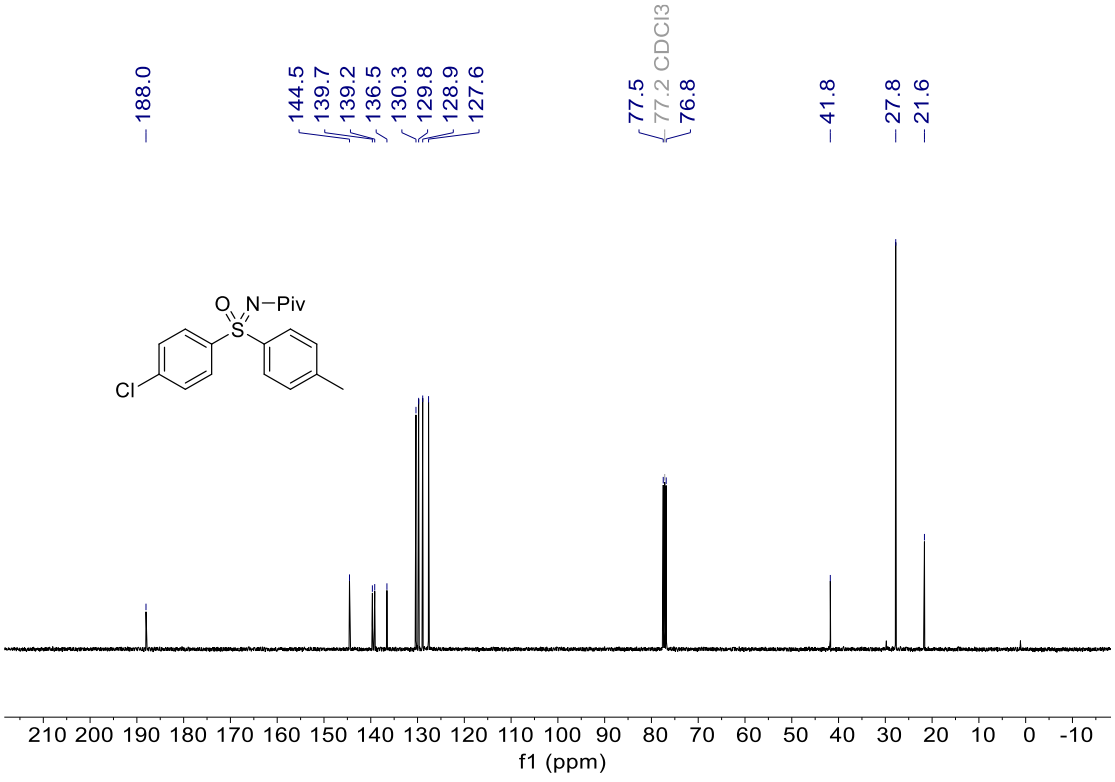
4au, ^{13}C NMR (101 MHz, $CDCl_3$)



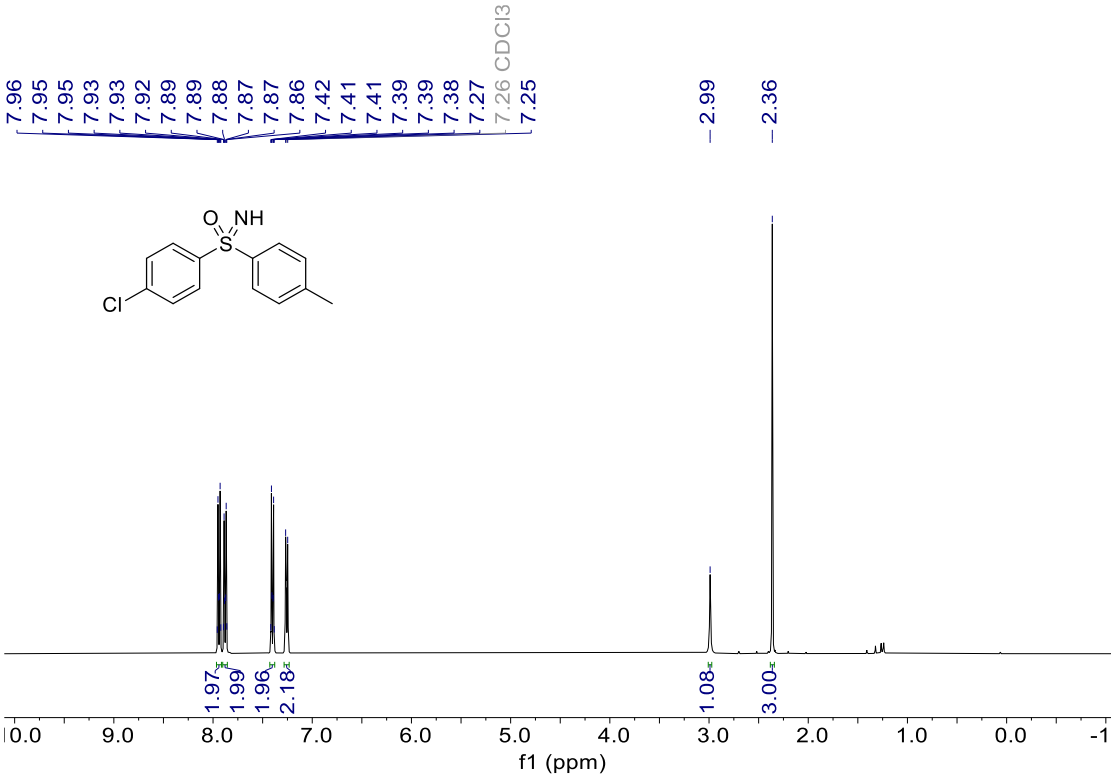
4av, ^{1}H NMR (400 MHz, $CDCl_3$)



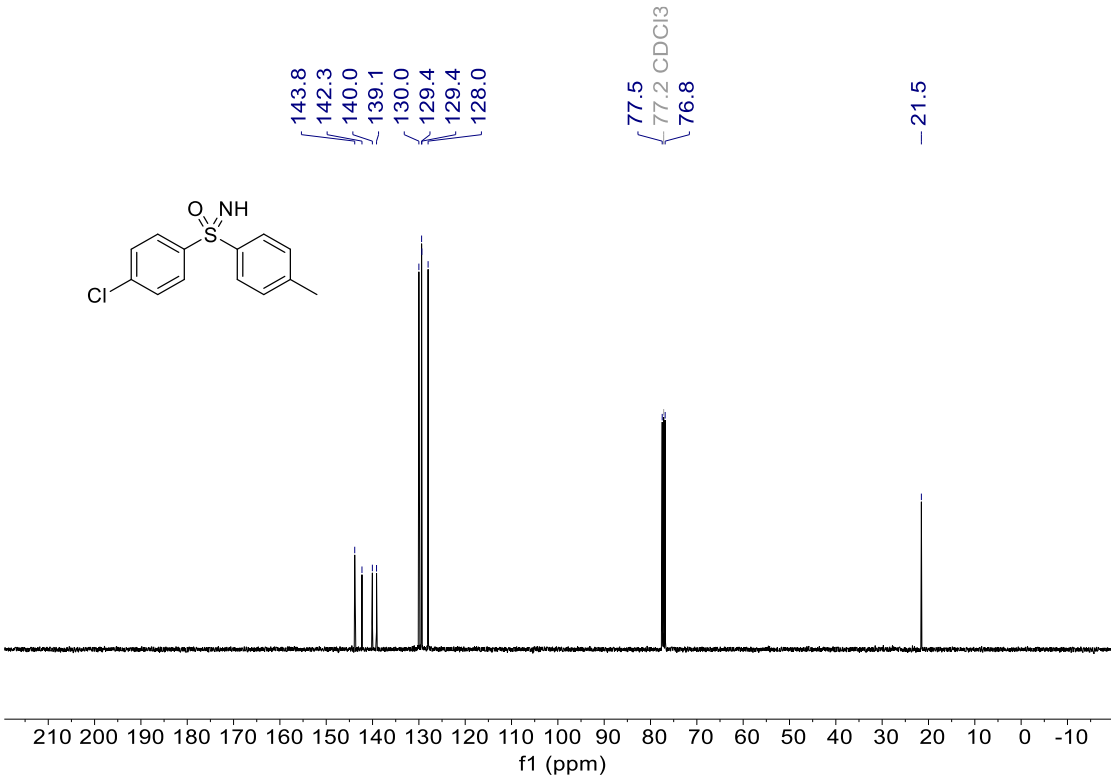
4av, ^{13}C NMR (101 MHz, $CDCl_3$)



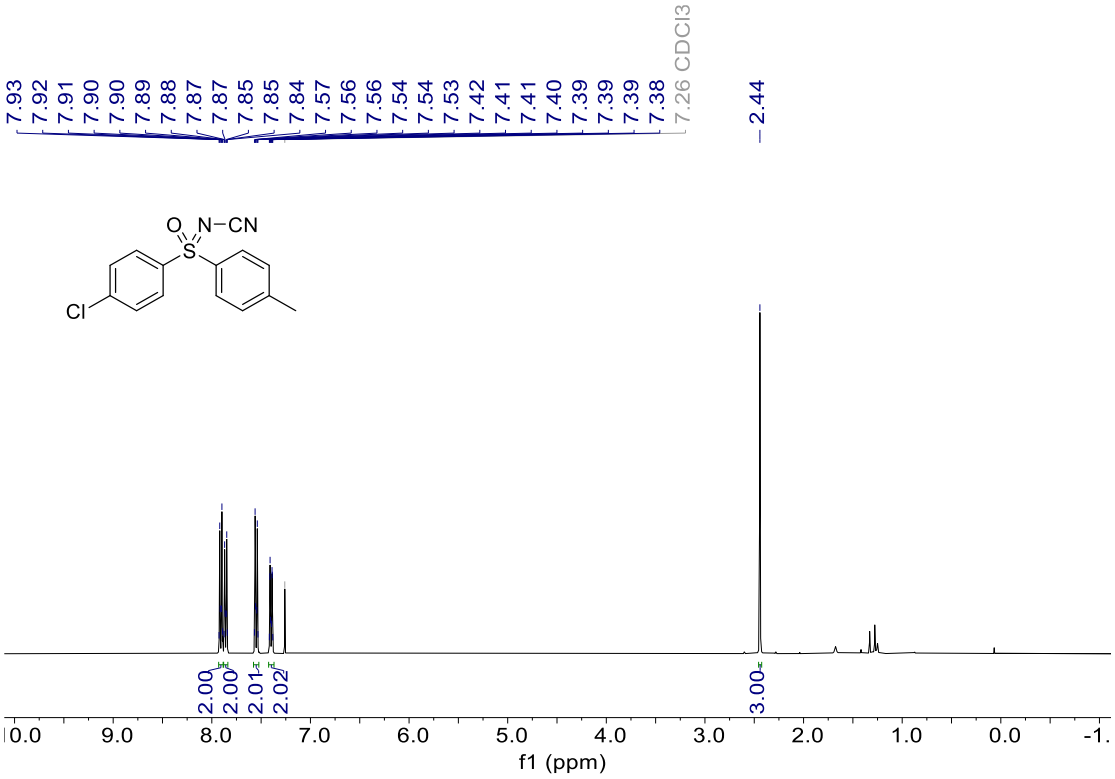
5, ^{1}H NMR (400 MHz, $CDCl_3$)



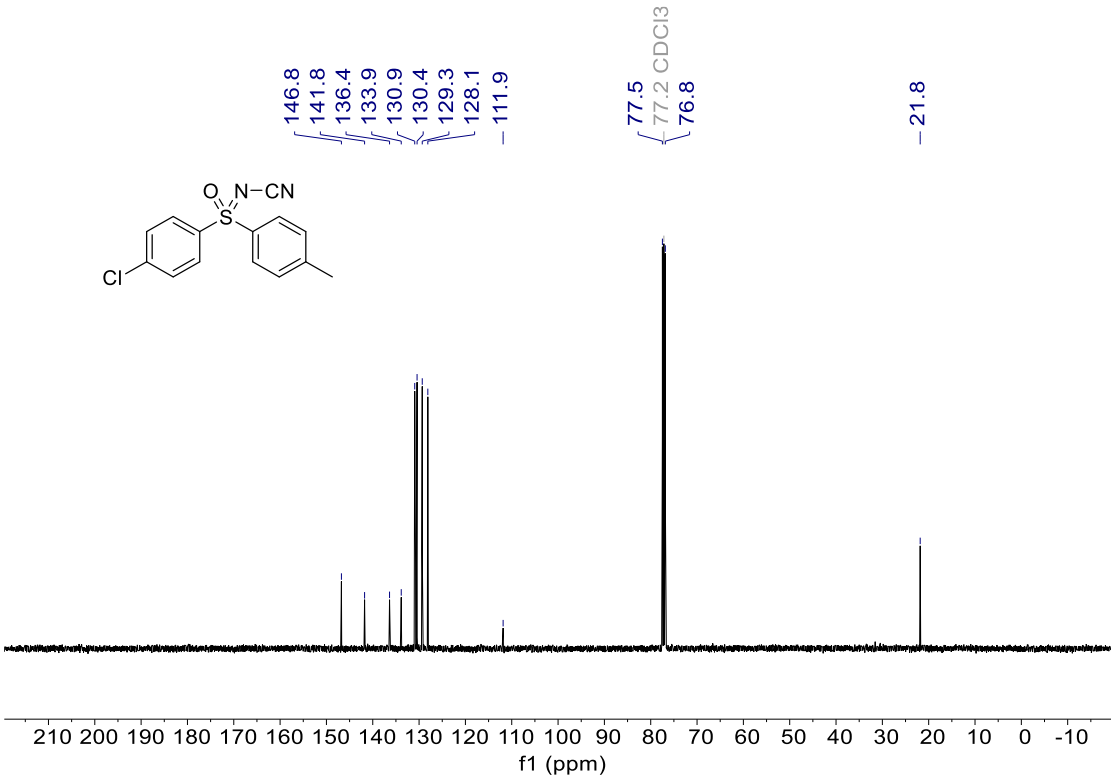
5, ^{13}C NMR (101 MHz, $CDCl_3$)



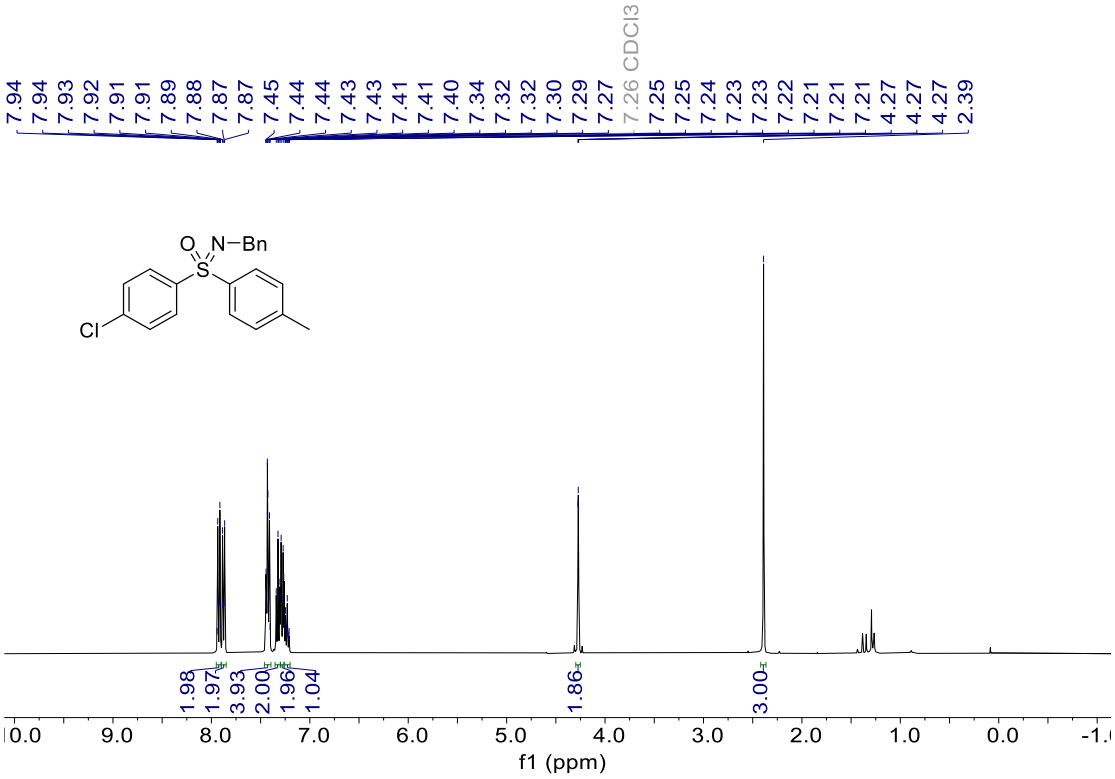
6, ^{1}H NMR (400 MHz, $CDCl_3$)



6, ^{13}C NMR (101 MHz, $CDCl_3$)



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



7, ^{13}C NMR (101 MHz, $CDCl_3$)