Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Interception of Amide Ylides with Sulfonamides: Synthesis of (*E*)-*N*-Sulfonyl Amidines Catalyzed by $Zn(OTf)_2$

Jijun Chen, Wenhao Long, Shangwen Fang, Yonggang Yang,* and Xiaobing Wan*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

Email: *wanxb@suda.edu.cn*

List of Contents

General Information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400MHz) and ^{13}C NMR (100MHz) data were recorded using $CDCl_3$ as solvent at room temperature unless specified otherwise. ^{19}F NMR (376 MHz) data was recorded using $CDCl_3$ as solvent at room temperature The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. IR, MS, HRMS, and GC-MS were performed by the State-authorized Analytical Center in Soochow University.

General procedures for reactions

(a) The procedure for the synthesis of *N*-arylpyrrolidone[1]

A flame-dried resealable Schlenk tube was charged with $Pd(OAc)_2$ (8.8 mg, 0.04 mmol, 1 mol%), Xantphos (34.8 mg, 0.06 mmol, 1.5 mol%), the solid reactant(s) (4.0 mmol of the aryl halide/triflate and 4.8 mmol of the amide), and Cs_2CO_3 (1824 mg, 5.6 mmol). The Schlenk tube was capped with a rubber septum, evacuated and backfilled with argon; this evacuation/backfill sequence was repeated one additional time. The liquid reactant(s) and 1,4-dioxane (4 mL) were added through the septum. The septum was replaced with a teflon screwcap. The Schlenk tube was sealed, and the mixture was stirred at the indicated temperature (45-110 ^{o}C) for 24h. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (20 mL),

filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to give corresponding the desired *N*-arylpyrrolidone.

(b) The procedure for the synthesis of benzamide derivatives[2]

Aryl acyl chloride (20 mmol) was added dropwise to a solution of amine (22 mmol), Et_3N (25 mmol) and dichloromethane (100mL) at room temperature. The reaction mixture was stirred for 12 h at room temperature and then was diluted with dichloromethane. The solution was transferred to a separation funnel and was washed with 1N HCl. The organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to give corresponding the desired benzamide derivatives.

(c) The procedure for the synthesis of alkyl amide derivatives[3]

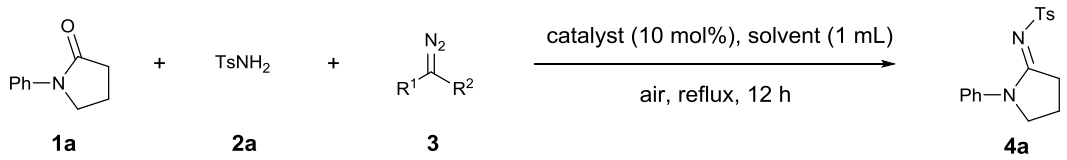
To a solution of amine (20 mmol) in dichloromethane (100 mL) was added Et_3N (25 mmol). Acyl chloride (22 mmol) was then added dropwise to the mixture at room temperature. The reaction mixture was stirred for 12 h at room temperature and then was diluted with dichloromethane. The solution was transferred to a separation funnel and was washed with 1N HCl. The organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to give corresponding the desired benzamide derivatives.

(d) The procedure for the synthesis of (*E*)-*N*-Sulfonyl Amidines

$Zn(OTf)_2$ (0.02 mmol), amides (0.2 mmol), and sulfamides (0.2 mmol) were added to a 20 mL test tube with a stirring bar. Cyclohexane (1.0 mL), diazo compounds (0.4 mmol) were added via syringe. The reaction mixture was heated in an oil bath at reflux (Tips: severe reflux, recommendation temperature: 90 ^oC) for 12 h under air (Tips: even if solvent volatilization, still no problem). After, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ ethylacetate to give the desired products.

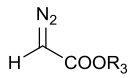
(Tips: In many cases, (*E*)-*N*-Sulfonyl Amidines slightly soluble in ethyl acetate, soluble in dichloromethane)

Table S1. Optimization of the Reaction Conditions [a]

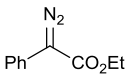


1a **2a** **3** **4a**

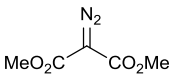
Entry	Catalyst	Diazo (equiv)	Solvent	Yield (%)[b]
1	$Cu(OAc)_2$	**3a** (0.5)	C_6H_{12}	trace
2	$Cu(OAc)_2$	**3a** (1.0)	C_6H_{12}	9
3	$Cu(OAc)_2$	**3a** (2.0)	C_6H_{12}	18
4	CuI	**3a** (2.0)	C_6H_{12}	19
5	$Co(BF_4)_2{\cdot}6H_2O$	**3a** (2.0)	C_6H_{12}	56
6	$Rh_2(OAc)_4$	**3a** (2.0)	C_6H_{12}	25
7	$Pd(OAc)_2$	**3a** (2.0)	C_6H_{12}	< 5
8	Ag_2CO_3	**3a** (2.0)	C_6H_{12}	24
9	$Zn(OTf)_2$	**3a** (2.0)	C_6H_{12}	98
10[c]	$Zn(OTf)_2$	**3a** (2.0)	EA	60
11[c]	$Zn(OTf)_2$	**3a** (2.0)	DCE	66
12[c]	$Zn(OTf)_2$	**3a** (2.0)	^{i}PrOH	< 5
13[c]	$Zn(OTf)_2$	**3a** (2.0)	DME	< 5
14[c]	$Zn(OTf)_2$	**3a** (2.0)	PhH	79
15[c]	$Zn(OTf)_2$	**3a** (2.0)	DMSO	< 5
16	—	**3a** (2.0)	C_6H_{12}	< 5
17	$Zn(OTf)_2$	—	C_6H_{12}	< 5
18	$Zn(OTf)_2$	**3b** (2.0)	C_6H_{12}	98
19	$Zn(OTf)_2$	**3c** (2.0)	C_6H_{12}	93
20	$Zn(OTf)_2$	**3d** (2.0)	C_6H_{12}	30
21	$Zn(OTf)_2$	**3e** (2.0)	C_6H_{12}	< 5
22	$Zn(OTf)_2$	**3f** (2.0)	C_6H_{12}	11



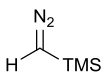
3a, R_3 = Et
3b, R_3 = ^{i}Pr
3c, R_3 = Ph



3d



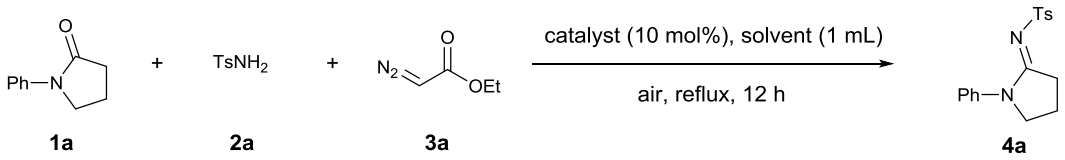
3e



3f

[a]Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3** (2.0 equiv), catalyst (10 mol%) in C_6H_{12} was stirred at reflux for 12 h under air. [b]Isolated yields. [c]80 °C.

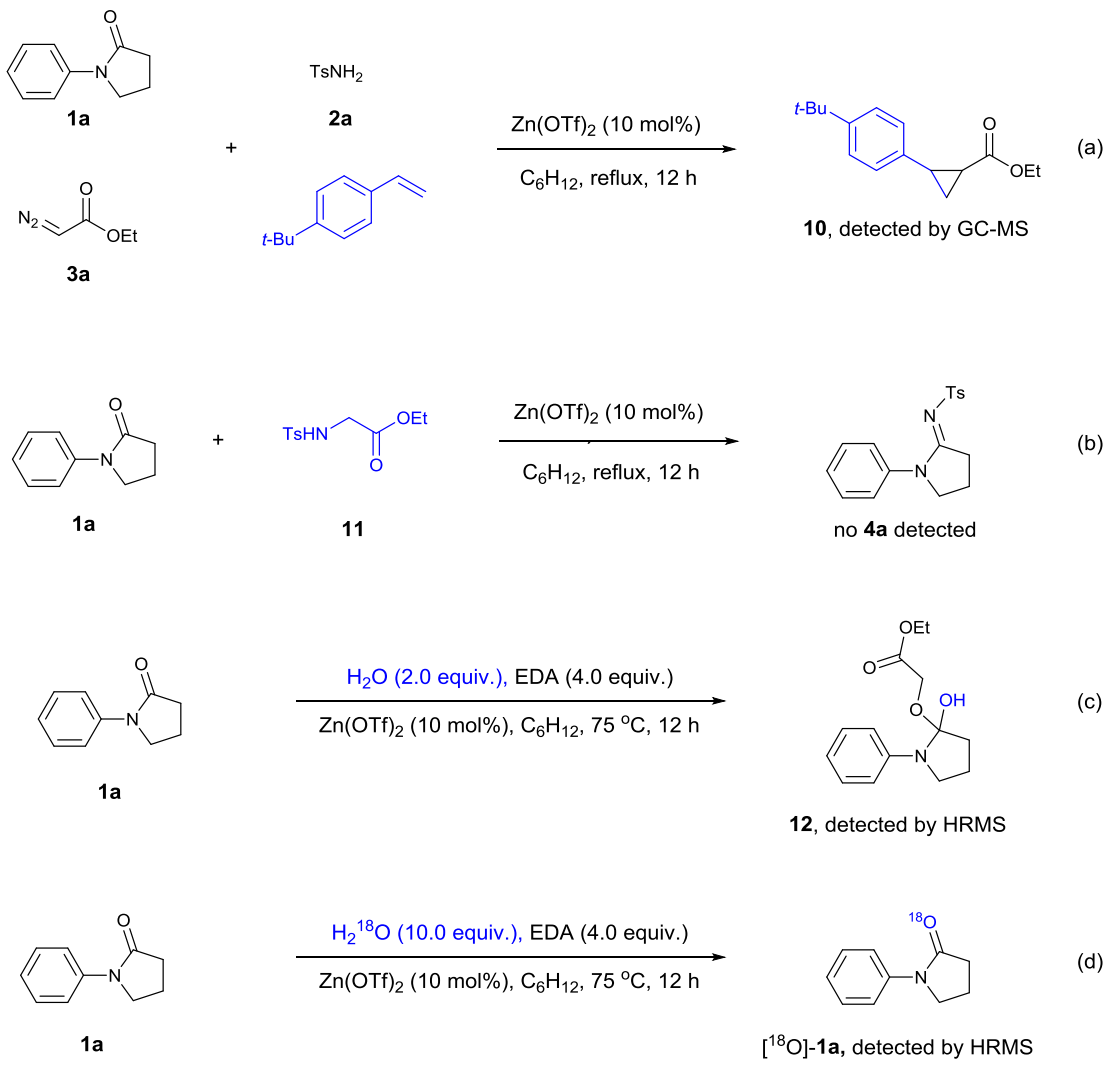
Table S2. Screening of the Reaction Catalysts [a]



1a **2a** **3a** **4a**

entry	catalyst	diazo (equiv)	solvent	yield (%)[b]
1	$Cu(OAc)_2$	**3a** (2.0)	C_6H_{12}	18
2	CuI	**3a** (2.0)	C_6H_{12}	19
3	CuO	**3a** (2.0)	C_6H_{12}	< 5
4	$Co(acac)_2$	**3a** (2.0)	C_6H_{12}	< 5
5	$Co(BF_4)_2{\cdot}6H_2O$	**3a** (2.0)	C_6H_{12}	56
6	$Rh_2(OAc)_4$	**3a** (2.0)	C_6H_{12}	25
7	$Pd(OAc)_2$	**3a** (2.0)	C_6H_{12}	< 5
8	Ag_2CO_3	**3a** (2.0)	C_6H_{12}	24
9	$Zn(OTf)_2$	**3a** (2.0)	C_6H_{12}	98
10	$Cu(OTf)_2$	**3a** (2.0)	C_6H_{12}	< 5
11	AgOTf	**3a** (2.0)	C_6H_{12}	42
12	$Ni(OTf)_2$	**3a** (2.0)	C_6H_{12}	39
13	$Bi(OTf)_3$	**3a** (2.0)	C_6H_{12}	62
14	$In(OTf)_3$	**3a** (2.0)	C_6H_{12}	34
15	$Sc(OTf)_3$	**3a** (2.0)	C_6H_{12}	31
16	$Mg(OTf)_2$	**3a** (2.0)	C_6H_{12}	60
17	$ZnCl_2$	**3a** (2.0)	C_6H_{12}	30
18	$Zn(OAc)_2{\cdot}2H_2O$	**3a** (2.0)	C_6H_{12}	26
19	ZnI_2	**3a** (2.0)	C_6H_{12}	26
20	ZnF_2	**3a** (2.0)	C_6H_{12}	28
21	ZnO	**3a** (2.0)	C_6H_{12}	< 5

[a]Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), catalyst (10 mol%) in C_6H_{12} was stirred at reflux for 12 h under air.



Scheme S1. Mechanistic probes.

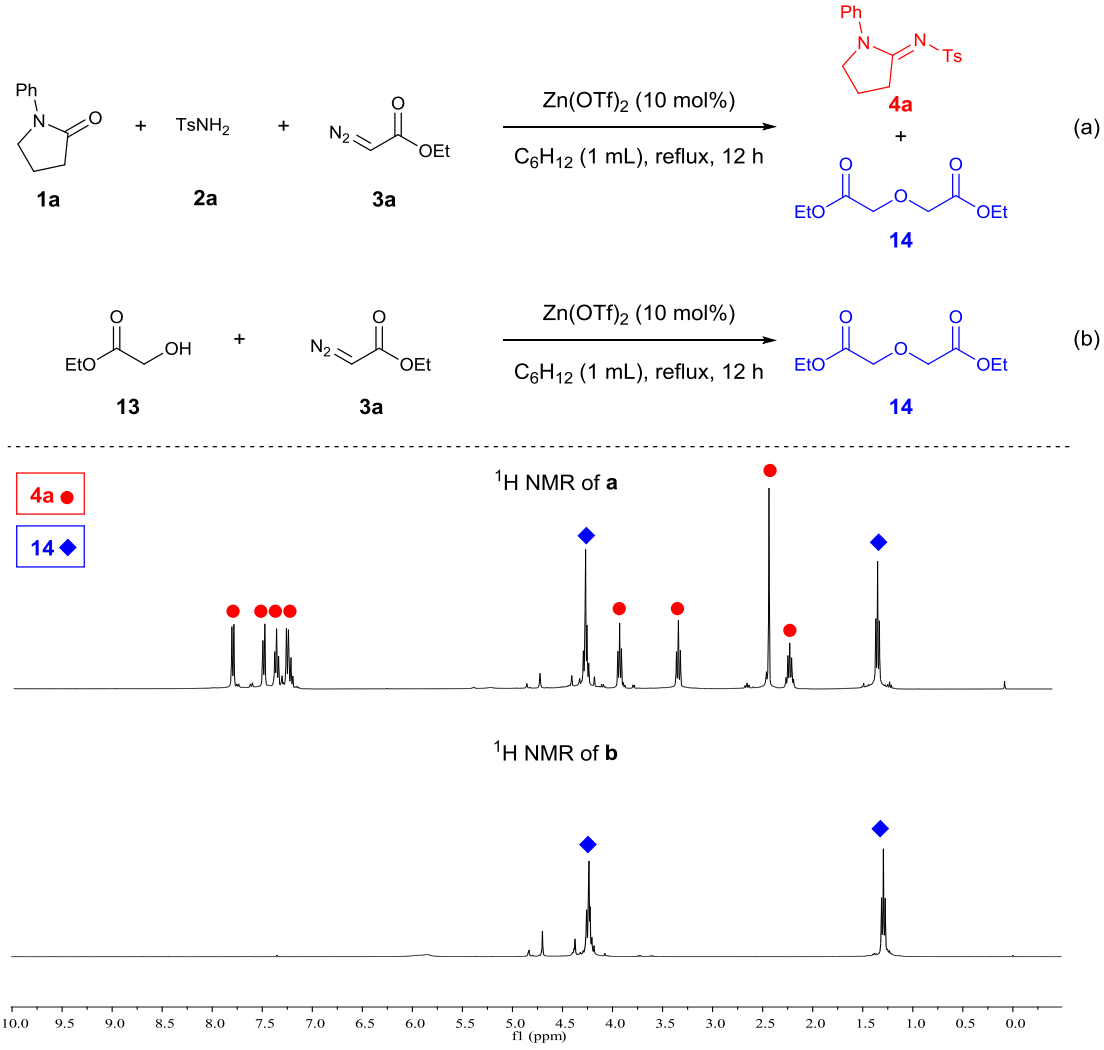
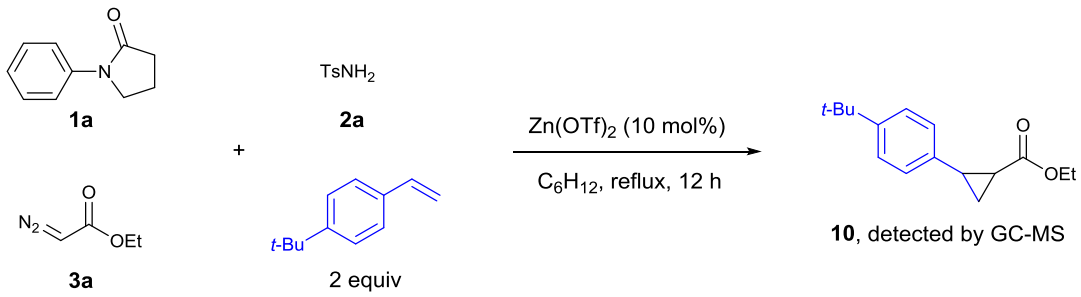
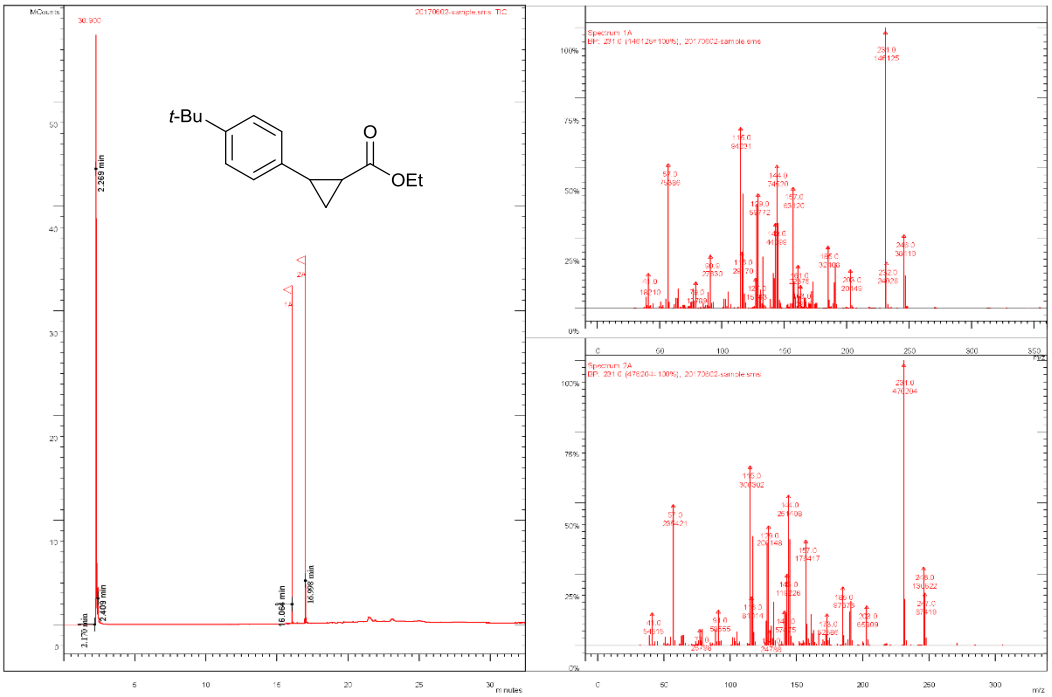


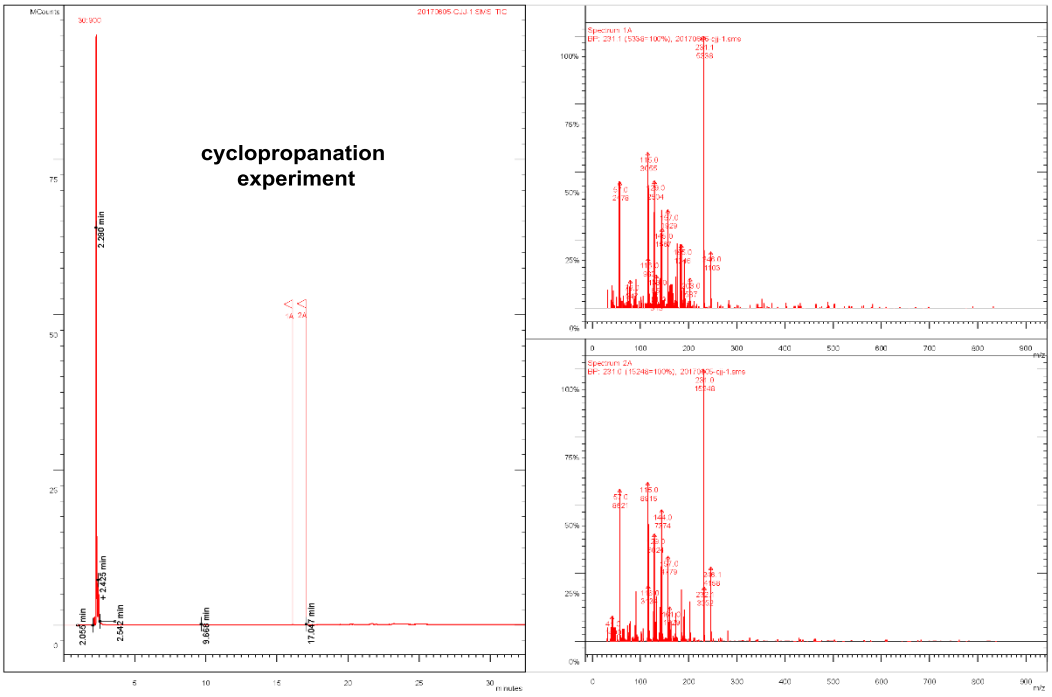
Figure S1. The Outcome of EDA.

Mechanistic Probes

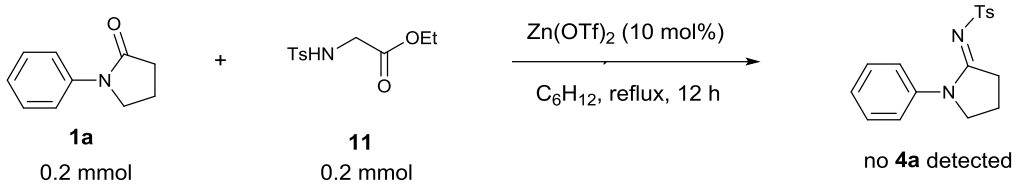
(a) Cyclopropanation experiment (carbene traps experiment):




t-Bu
O
OEt
2.269 min
2.409 min
16.084 min
16.998 min


cyclopropanation
experiment
2.260 min
2.425 min
2.542 min
9.667 min
17.047 min

(b) Control reaction:

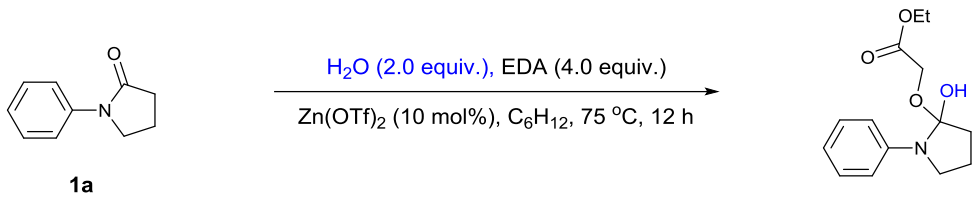


1a
0.2 mmol

11
0.2 mmol

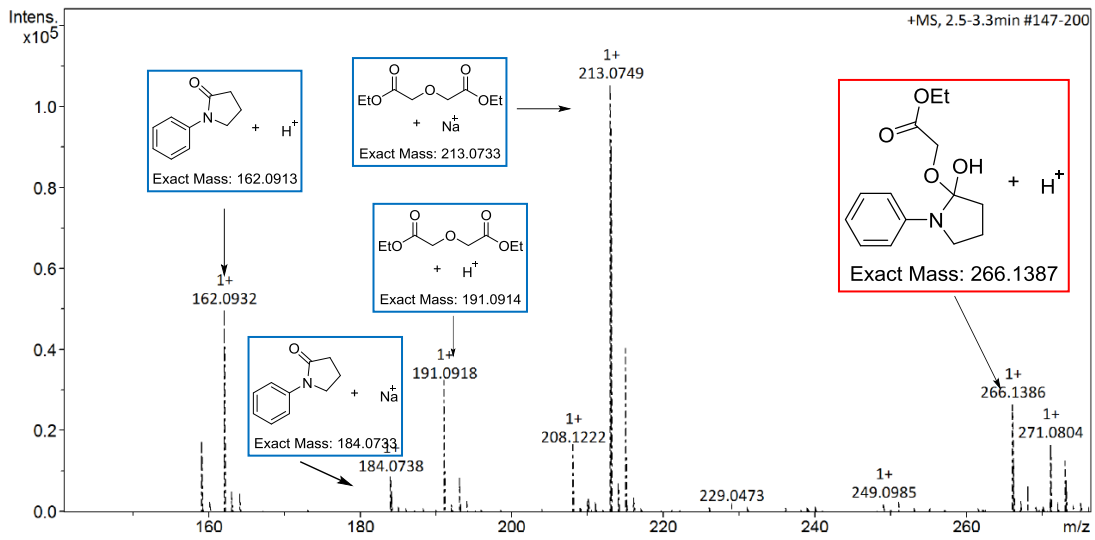
no **4a** detected

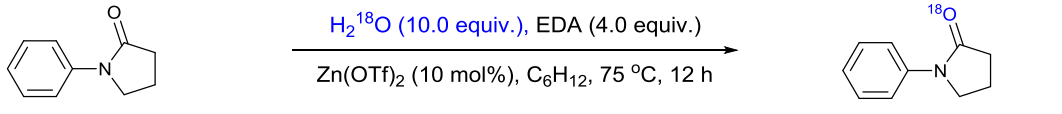
(c) High-resolution mass spectrometry (HRMS) analysis:



1a

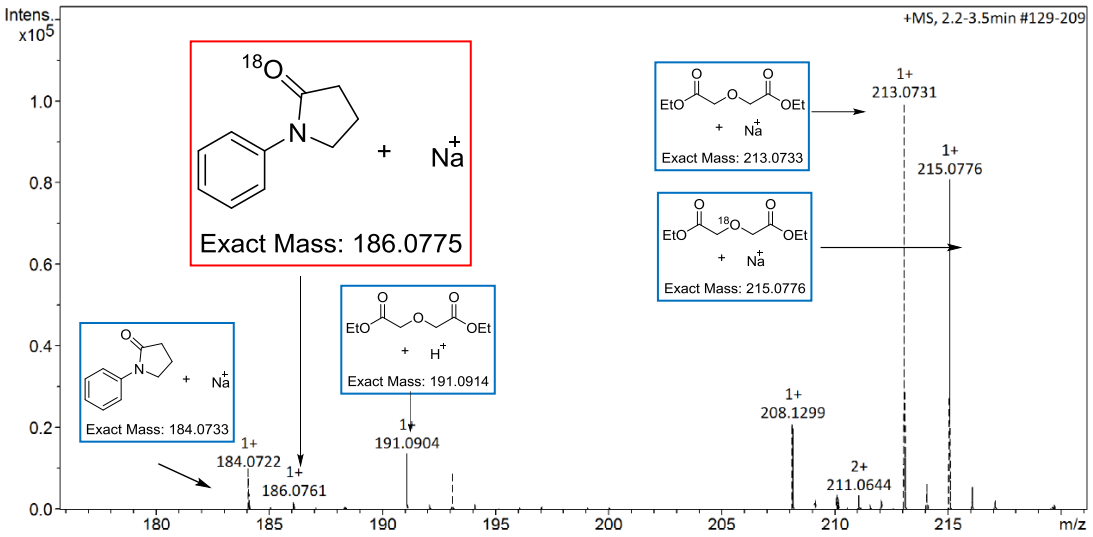
12, detected by HRMS



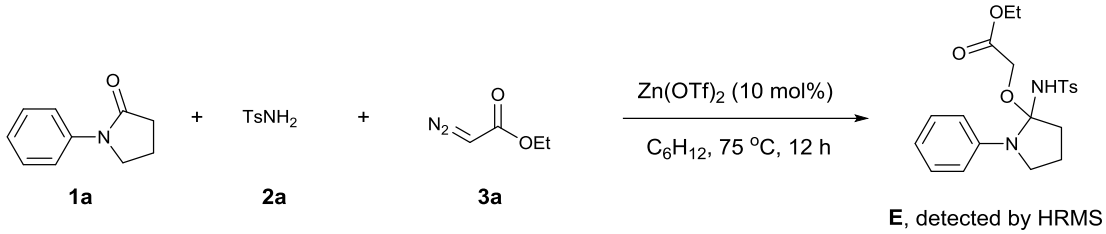


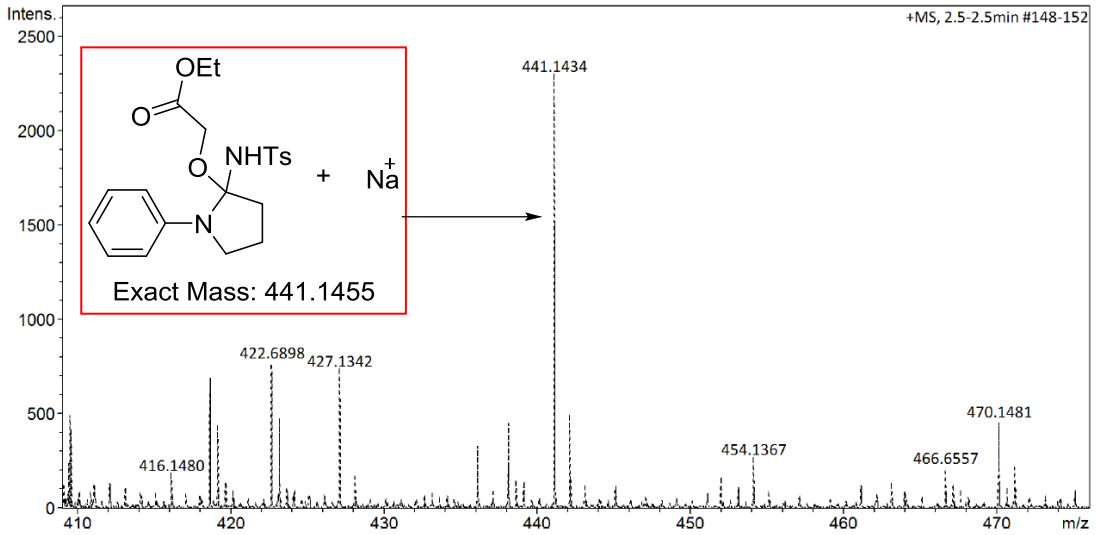
1a

[^{18}O]-**1a,** detected by HRMS

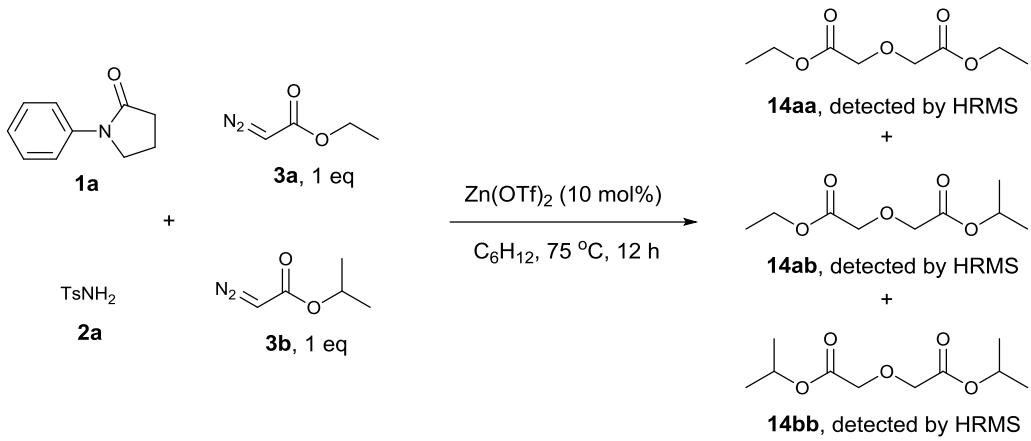


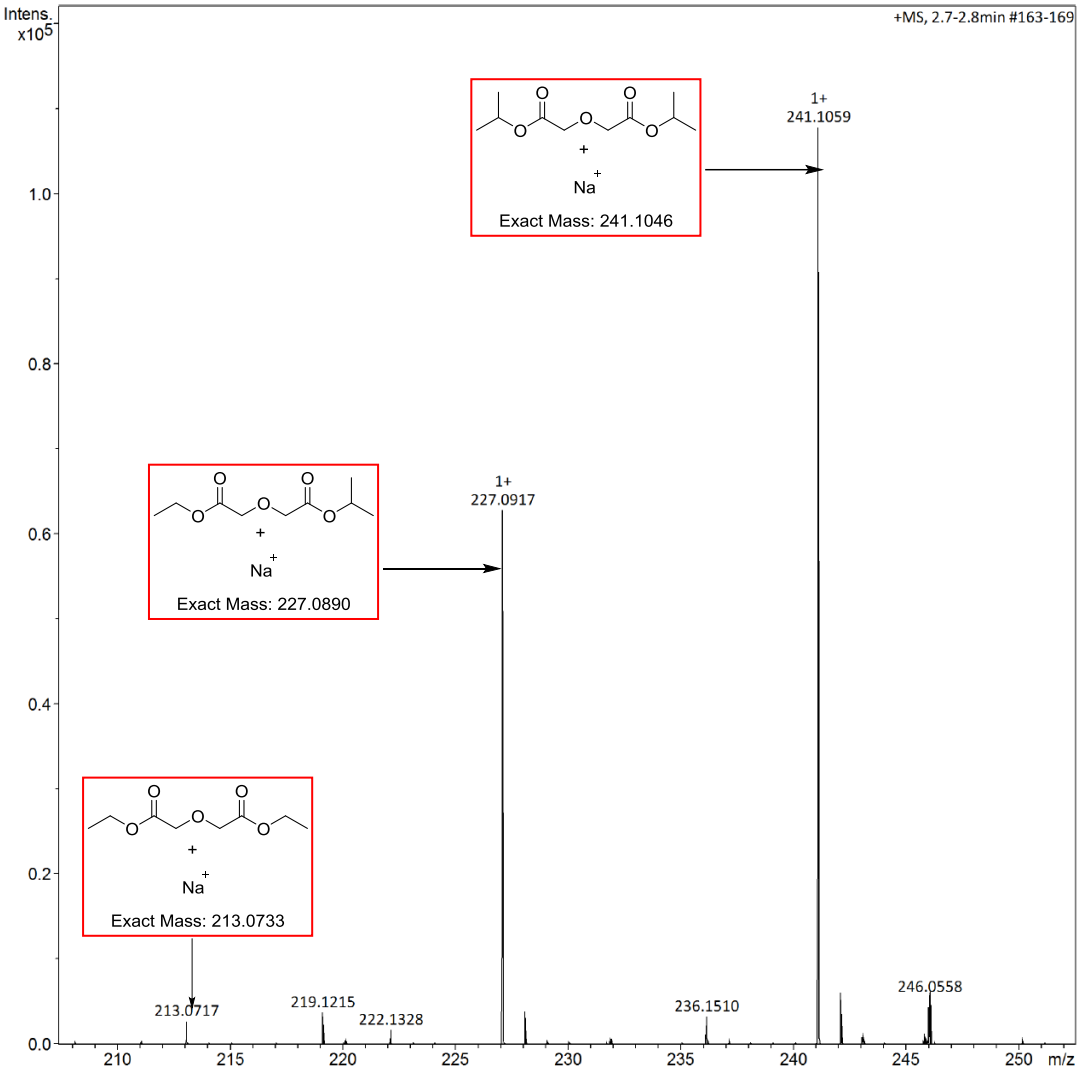
(d) Trapping of intermediate:



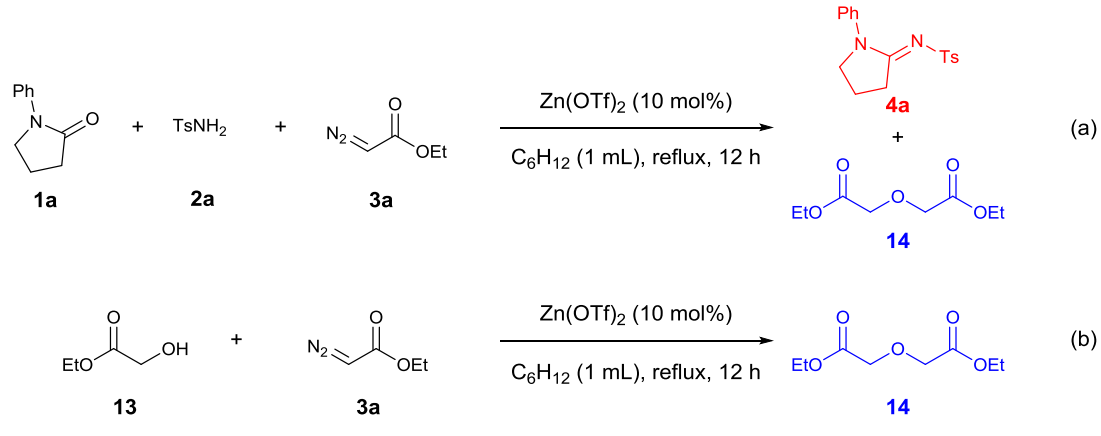


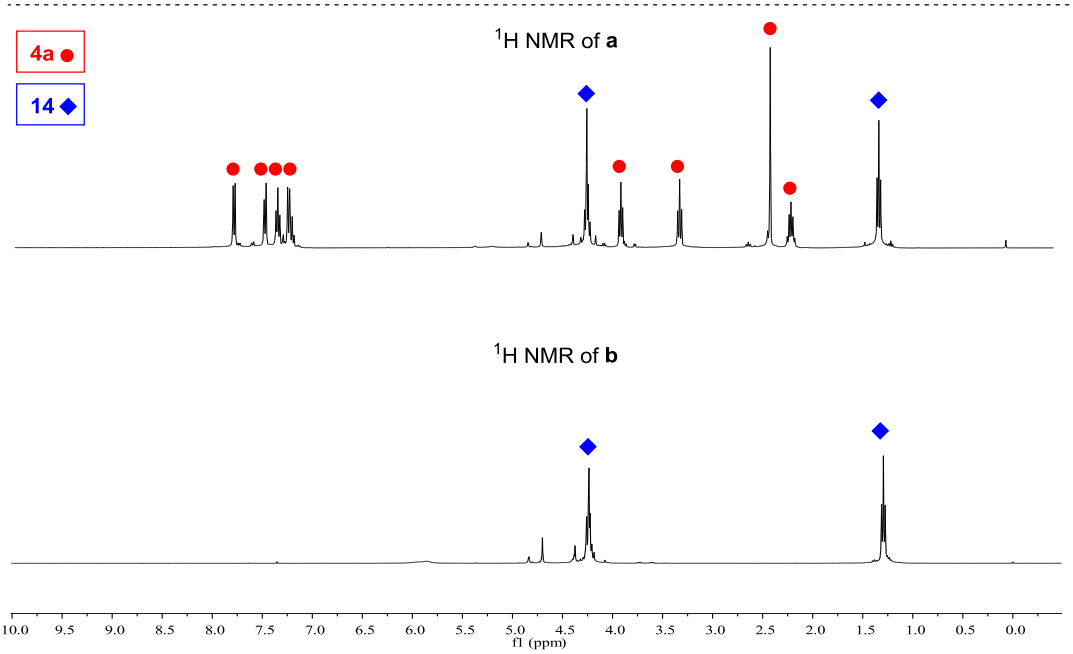
(e) Identify the outcome of EDA:


1a
3a, 1 eq
TsNH2
2a
3b, 1 eq
Zn(OTf)2 (10 mol%)
C6H12, 75 °C, 12 h
14aa, detected by HRMS
+
14ab, detected by HRMS
+
14bb, detected by HRMS

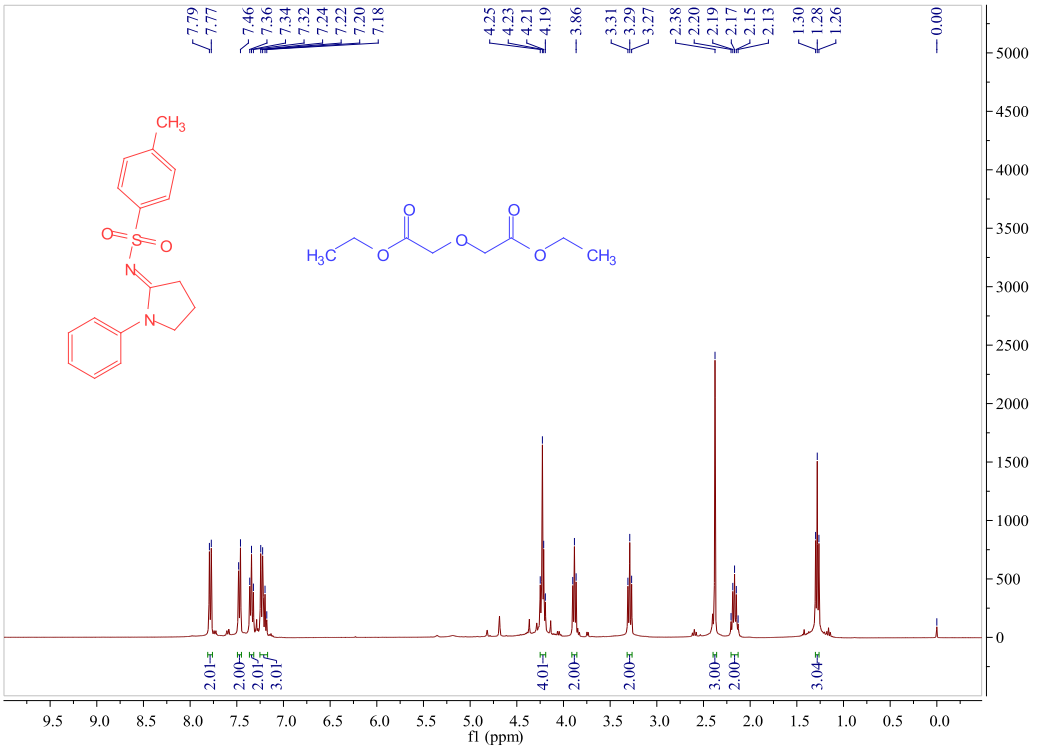

+MS, 2.7-2.8min #163-169
Intens.
x10^5
1.0
0.8
0.6
0.4
0.2
0.0
1+
241.1059
Na+
Exact Mass: 241.1046
1+
227.0917
Na+
Exact Mass: 227.0890
Na+
Exact Mass: 213.0733
213.0717
219.1215
222.1328
236.1510
246.0558
210
215
220
225
230
235
240
245
250
m/z

(f) NMR study on the model reaction to identify the outcome of EDA:

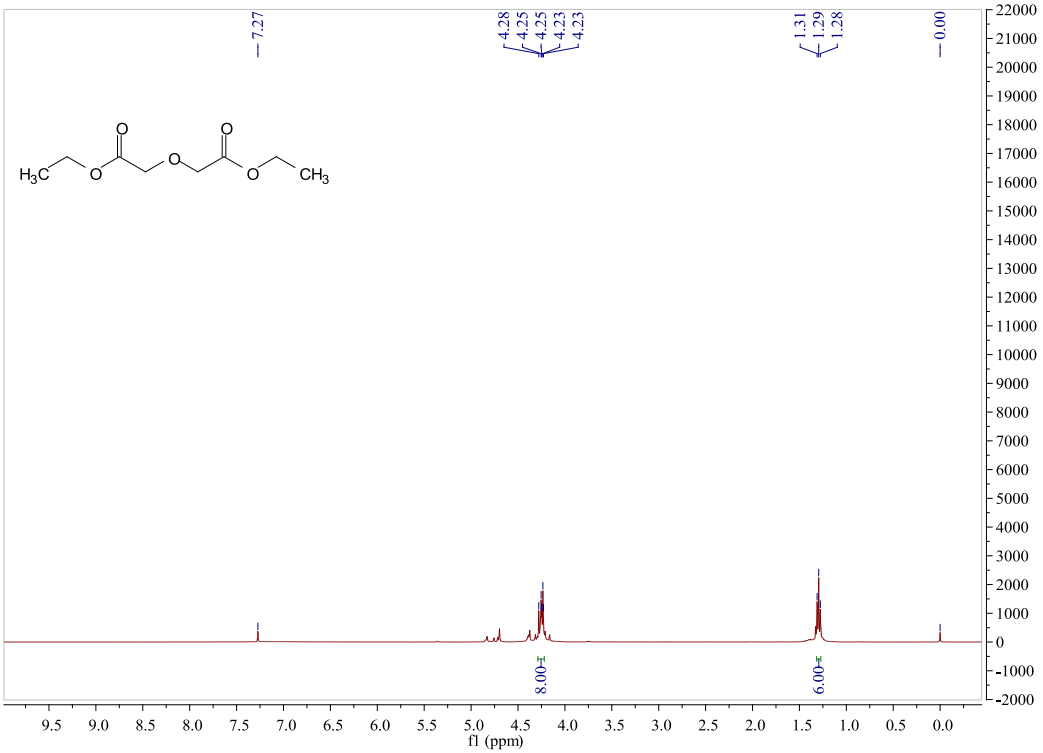




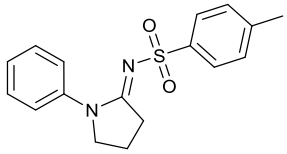
f(a) ^{1}H NMR:



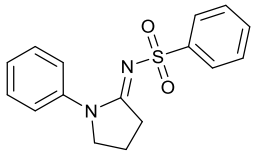
f(b) ^{1}H NMR:



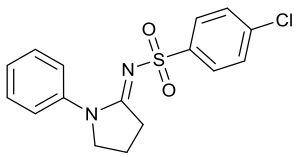
Compound Characterizations



(*E*)-4-Methyl-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4a). Petroleum ether/ ethylacetate = 3:1, white solid, 61.4 mg, 98% yield, mp: 124.5−125.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.48–7.46 (m, 2H), 7.36–7.32 (m, 2H), 7.24–7.18 (m, 3H), 3.88 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.20–2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.1, 140.1, 138.5, 129.1, 128.7, 126.30, 126.27, 122.9, 52.0, 31.9, 21.3, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_2S+H^+$: 315.1162, Found: 315.1169; IR (neat, cm-1): υ 2917, 2849, 1743, 1536, 1300, 1146, 824, 651.

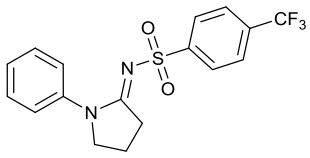


(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)benzenesulfonamide (4b). Petroleum ether/ ethylacetate = 3:1, white solid, 57.4 mg, 96% yield, mp: 137.3−139.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.50–7.41 (m, 5H), 7.36–7.32 (m, 2H), 7.22–7.19 (m, 1H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.22–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 142.9, 138.5, 131.6, 128.7, 128.5, 126.4, 126.3, 123.0, 52.1, 32.0, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{16}N_2O_2S+H^+$: 301.1005, Found: 301.1011; IR (neat, cm-1): υ 2924, 2852, 1742, 1536, 1300, 1146, 855, 690.

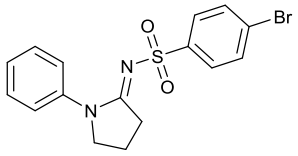


(*E*)-4-Chloro-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4c). Petroleum ether/ ethylacetate = 3:1, white solid, 65.5 mg, 98% yield, mp: 136.3−137.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.45–7.33 (m, 6H), 7.24–7.20 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.33 (t, *J* = 8.0 Hz, 2H), 2.25–2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.5, 138.3, 137.8,

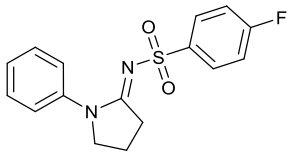
128.8, 128.7, 127.8, 126.6, 123.0, 52.2, 32.1, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}{}^{35}ClN_2O_2S+Na^+$: 357.0435, $C_{16}H_{15}{}^{37}ClN_2O_2S+Na^+$: 359.0405, Found: 357.0438, 359.0396; IR (neat, cm-1): υ 2919, 2849, 1745, 1530, 1298, 1147, 752, 619.



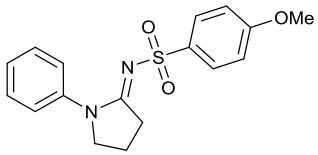
(*E*)-*N*-(1-phenylpyrrolidin-2-ylidene)-4-(trifluoromethyl)benzenesulfonamide (4d). Petroleum ether/ ethylacetate = 3:1, white solid, 67.3 mg, 92% yield, mp: 149.8−151.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H), 7.70–7.68 (m, 2H), 7.44–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.27–7.22 (m, 1H), 3.94 (t, *J* = 7.2 Hz, 2H), 3.36 (t, *J* = 8.0 Hz, 2H), 2.27 – 2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 146.4, 138.2, 133.24 (q, *J* = 32 Hz), 128.8, 126.84, 126.81, 125.7 (q, *J* = 4 Hz), 123.4 (q, *J* = 271 Hz), 123.2, 52.4, 32.3, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{15}F_3N_2O_2S+H^+$: 369.0879, Found: 369.0884; IR (neat, cm-1): υ 2919, 2849, 1748, 1547, 1304, 1103, 689.



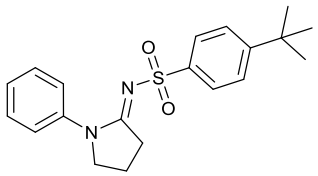
(*E*)-4-Bromo-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4e). Petroleum ether/ ethylacetate = 3:1, white solid, 70.8 mg, 94% yield, mp: 141.1−142.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.57–7.55 (m, 2H), 7.44–7.42 (m, 2H), 7.37–7.33 (m, 2H), 7.24–7.20 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.24–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 142.1, 138.3, 131.7, 128.8, 128.0, 126.6, 126.3, 123.1, 52.2, 32.1, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}{}^{79}BrN_2O_2S+Na^+$: 400.9930, $C_{16}H_{15}{}^{81}BrN_2O_2S+Na^+$: 402.9909, Found: 400.9941, 402.9943; IR (neat, cm-1): υ 2920, 2850, 1737, 1533, 1147, 742, 608.



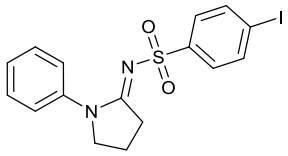
(*E*)-4-Fluoro-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4f). Petroleum ether/ ethylacetate = 3:1, white solid, 62.1 mg, 98% yield, mp: 108.4−109.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.89 (m, 2H), 7.46–7.44 (m, 2H), 7.37–7.33 (m, 2H), 7.23–7.20 (m, 1H), 7.13–7.08 (m, 2H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.33 (t, *J* = 8.0 Hz, 2H), 2.25–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 164.4 (d, *J* = 251 Hz), 139.14 (d, *J* = 3 Hz), 138.4, 128.9 (d, *J* = 9 Hz), 128.8, 126.5, 123.0, 115.6 (d, *J* = 23 Hz), 52.2, 32.1, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}FN_2O_2S+Na^+$: 341.0730, Found: 341.0740; IR (neat, cm-1): υ 2918, 2849, 1748, 1536, 1305, 1148, 844, 671.



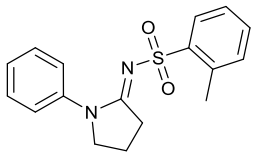
(*E*)-4-Methoxy-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4g). Petroleum ether/ ethylacetate = 2:1, white solid, 58.3 mg, 88% yield, mp: 68.2−69.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.48–7.46 (m, 2H), 7.36–7.32 (m, 2H), 7.21–7.17 (m, 1H), 6.92–6.90 (m, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.20–2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 162.0, 138.5, 135.0, 128.7, 128.3, 126.2, 122.9, 113.6, 55.4, 52.0, 31.9, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_3S+H^+$: 331.1111, Found: 331.1109; IR (neat, cm-1): υ 2923, 2849, 1748, 1546, 1142, 672.



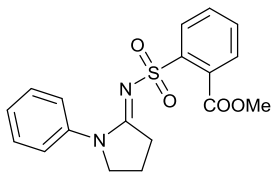
(*E*)-4-(*tert*-butyl)-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4h). Petroleum ether/ ethylacetate = 3:1, white solid, 66.4 mg, 94% yield, mp: 113.9−115.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.50–7.49 (m, 2H), 7.46–7.44 (m, 2H), 7.37–7.33 (m, 2H), 7.22–7.18 (m, 1H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.21–2.14 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 155.1, 140.0, 138.6, 128.7, 126.3, 126.1, 125.5, 122.9, 52.0, 34.9, 32.0, 31.0, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{24}N_2O_2S+Na^+$: 379.1451, Found: 379.1464; IR (neat, cm-1): υ 2961, 2923, 1749, 1551, 1150, 760, 628.



(*E*)-4-Iodo-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4i). Petroleum ether/ ethylacetate = 3:1, white solid, 81.5 mg, 96% yield, mp: 132.7−133.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2H), 7.62–7.60 (m, 2H), 7.44–7.42 (m, 2H), 7.37–7.33 (m, 2H), 7.23–7.20 (m, 1H), 3.90 (t, *J* = 7.2 Hz, 2H), 3.31 (t, *J* = 8.0 Hz, 2H), 2.23–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 142.7, 138.3, 137.6, 128.8, 127.9, 126.6, 123.0, 98.6, 52.2, 32.1, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}IN_2O_2S+Na^+$: 448.9791, Found: 448.9798; IR (neat, cm-1): υ 3043, 2941, 1736, 1532, 1298, 1148, 737.

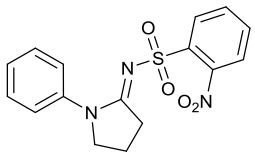


(*E*)-2-Methyl-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4j). Petroleum ether/ ethylacetate = 3:1, white solid, 61.4 mg, 98% yield, mp: 118.7−119.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.01 (m, 1H), 7.45–7.44 (m, 2H), 7.38–7.32 (m, 3H), 7.26–7.19 (m, 3H), 3.87 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 2.21–2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 140.8, 138.5, 137.4, 132.0, 131.7, 128.7, 127.5, 126.5, 125.4, 123.2, 52.1, 32.0, 20.3, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_2S+H^+$: 315.1162, Found: 315.1168; IR (neat, cm-1): υ 2923, 2852, 1745, 1558, 1273, 1115, 692.

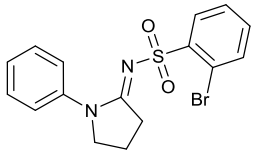


Methyl (*E*)-2-(*N*-(1-phenylpyrrolidin-2-ylidene)sulfamoyl)benzoate (4k). Petroleum ether/ ethylacetate = 2:1, white solid, 41.7 mg, 59% yield, mp: 117.4−118.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.06 (m, 1H), 7.54–7.51 (m, 3H), 7.47–7.45 (m, 2H), 7.35–7.31 (m, 2H), 7.22–7.18 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.23–2.16 (m, 2H). ^{13}C NMR

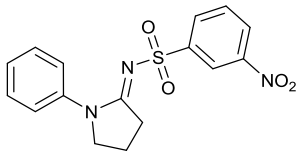
(100 MHz, $CDCl_3$) δ 169.0, 168.1, 140.7, 138.4, 131.6, 131.4, 130.3, 128.7, 128.7, 128.3, 126.5, 123.3, 52.6, 52.3, 32.3, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{18}N_2O_4S+H^+$: 359.1060, Found: 359.1063; IR (neat, cm-1): υ 2920, 2850, 1732, 1542, 1289, 1152, 759.



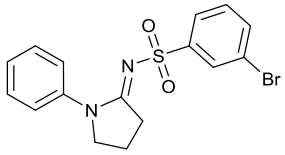
(*E*)-2-nitro-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4l). Petroleum ether/ ethylacetate = 3:1, light yellow solid, 68.1 mg, 99% yield, mp: 104.5−107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17– 8.13 (m, 1H), 7.65–7.55 (m, 3H), 7.39–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.22–7.18 (m, 1H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 8.0 Hz, 2H), 2.28–2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 147.5, 138.1, 135.7, 132.5, 131.9, 129.6, 128.8, 126.9, 124.1, 123.6, 52.7, 32.9, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}N_3O_4S+H^+$: 346.0856, Found: 346.0864; IR (neat, cm-1): υ 2923, 2852, 1745, 1531, 1300, 1149, 733.



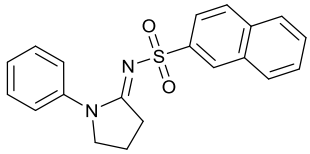
(*E*)-2-bromo-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4m). Petroleum ether/ ethylacetate = 3:1, white solid, 66.9 mg, 89% yield, mp: 107.1−108.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.15 (m, 1H), 7.68–7.66 (m, 1H), 7.50–7.48 (m, 2H), 7.37–7.27 (m, 4H), 7.20–7.16 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 2H), 2.24–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 141.5, 138.3, 134.9, 132.7, 129.7, 128.7, 127.2, 126.5, 123.3, 120.3, 52.3, 32.7, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}{}^{79}BrN_2O_2S+Na^+$: 400.9930, $C_{16}H_{15}{}^{81}BrN_2O_2S+Na^+$: 402.9909, Found: 400.9941, 402.9945; IR (neat, cm-1): υ 2921, 2850, 1736, 1532, 1300, 1146, 740.



(*E*)-3-Nitro-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4n). Petroleum ether/ ethylacetate = 3:1, white solid, 68.5 mg, 99% yield, mp: 132.7−133.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74–8.73 (m, 1H), 8.33–8.30 (m, 1H), 8.22–8.20 (m, 1H), 7.66–7.62 (m, 1H), 7.44–7.36 (m, 4H), 7.27–7.23 (m, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 3.39 (t, *J* = 8.0 Hz, 2H), 2.31–2.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 147.8, 145.1, 138.0, 131.9, 129.9, 128.9, 127.0, 126.0, 123.3, 121.7, 52.5, 32.4, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}N_3O_4S+H^+$: 346.0856, Found: 346.0859; IR (neat, cm-1): υ 2920, 2850, 1749, 1528, 1306, 1154, 661.

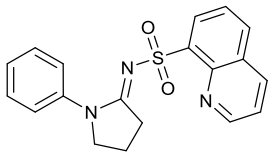


(*E*)-3-Bromo-*N*-(1-phenylpyrrolidin-2-ylidene)benzenesulfonamide (4o). Petroleum ether/ ethylacetate = 20:1, white solid, 74.7 mg, 99% yield, mp: 109.2−110.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83–7.81 (m, 1H), 7.61–7.59 (m, 1H), 7.45–7.43 (m, 2H), 7.39–7.35 (m, 2H), 7.33–7.29 (m, 1H), 7.25–7.21 (m, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.25–2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 144.8, 138.2, 134.6, 130.1, 129.4, 128.8, 126.7, 124.8, 123.1, 122.3, 52.3, 32.2, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}{}^{79}BrN_2O_2S+H^+$: 379.0110, $C_{16}H_{15}{}^{81}BrN_2O_2S+H^+$: 381.0090, Found: 371.0109, 381.0100; IR (neat, cm-1): υ 2920, 2850, 1747, 1546, 1305, 1149, 654.

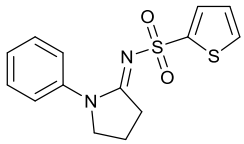


(*E*)-*N*-(1-phenylpyrrolidin-2-ylidene)naphthalene-2-sulfonamide (4p). Petroleum ether/ ethylacetate = 2:1, white solid, 62.6 mg, 90% yield, mp: 180.9−182.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.91–7.84 (m, 4H), 7.59 – 7.52 (m, 2H), 7.47–7.45 (m, 2H), 7.35–7.31 (m 2H), 7.21–7.17 (m, 1H), 3.87 (t, *J* = 7.2 Hz, 2H), 3.35 (t, *J* = 8.0 Hz, 2H), 2.20–2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 139.9, 138.4, 134.3, 132.0, 129.1, 128.8, 128.7, 128.1, 127.7, 127.0, 126.7, 126.4, 123.0, 122.6, 52.1, 32.1, 19.4. HRMS (ESI-TOF): Anal. Calcd. For

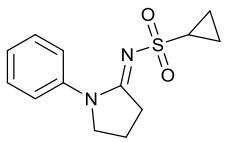
$C_{20}H_{18}N_2O_2S+H^+$: 351.1162, Found: 351.1163; IR (neat, cm-1): υ 2920, 2849, 1733, 1560, 1267, 1139, 671.



(*E*)-*N*-(1-phenylpyrrolidin-2-ylidene)quinoline-8-sulfonamide (4q). Petroleum ether/ ethylacetate = 1:2, light yellow solid, 50.7 mg, 72% yield, mp: 173.5−175.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08–9.07 (m, 1H), 8.55–8.53 (m, 1H), 8.22–8.20 (m, 1H), 7.98–7.96 (m, 1H), 7.60–7.56 (m, 1H), 7.50–7.47 (m, 1H), 7.38–7.37 (m, 2H), 7.17–7.13 (m, 2H), 7.08–7.04 (m, 1H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.70 (t, *J* = 7.9 Hz, 2H), 2.32–2.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 150.7, 147.5, 144.0, 138.7, 136.4, 132.7, 130.3, 128.9, 128.5, 126.0, 125.4, 122.9, 121.5, 52.1, 32.8, 19.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{17}N_3O_2S+Na^+$: 374.0934, Found: 374.0932; IR (neat, cm-1): υ 2959, 2921, 2852, 1733, 1544, 1277, 1138, 609.

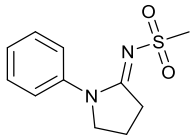


(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)thiophene-2-sulfonamide (4r). Petroleum ether/ ethylacetate = 20:1, white solid, 60.7 mg, 99% yield, mp: 112.3−113.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.58 (m, 1H), 7.50–7.46 (m, 3H), 7.39–7.35 (m, 2H), 7.25–7.21 (m, 1H), 7.0–6.98 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.23–2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 144.5, 138.2, 130.4, 130.1, 128.8, 126.7, 126.6, 123.1, 52.3, 32.0, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{14}N_2O_2S_2+Na^+$: 329.0389, Found: 329.0398; IR (neat, cm-1): υ 3094, 2901, 1539, 1292, 1138, 722.

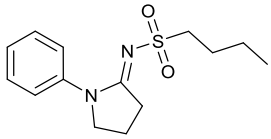


(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)cyclopropanesulfonamide (4s). Petroleum ether/ ethylacetate = 2:1, white solid, 52.2 mg, 99% yield, mp: 69.4−70.7 °C. ^{1}H NMR (400 MHz,

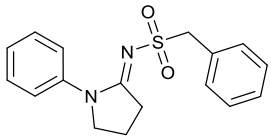
$CDCl_3$) δ 7.55–7.53 (m, 2H), 7.41–7.37 (m, 2H), 7.28–7.21 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.57–2.49 (m, 1H), 2.24–2.16 (m, 2H), 1.16– 1.12 (m, 2H), 0.94–0.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 138.7, 128.7, 126.1, 122.8, 51.9, 32.2, 31.8, 19.5, 5.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{16}N_2O_2S+H^+$: 265.1005, Found: 265.1018; IR (neat, cm-1): υ 2923, 2851, 1750, 1549, 1272, 1136, 733.



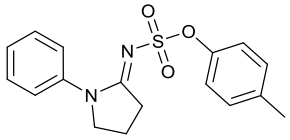
(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)methanesulfonamide (4t) Petroleum ether/ ethylacetate = 2:1, white solid, 41.2 mg, 87% yield, mp: 103.0−103.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.41–7.38 (m, 2H), 7.28–7.22 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.33 (t, *J* = 8.0 Hz, 2H), 2.98 (s, 3H), 2.25–2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.6, 128.7, 126.3, 123.0, 52.0, 42.6, 32.0, 19.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}N_2O_2S+Na^+$: 261.0668, Found: 261.0679; IR (neat, cm-1): υ 2920, 2850, 1746, 1555, 1270, 1131, 759.



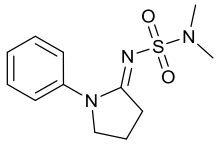
(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)butane-1-sulfonamide (4u). Petroleum ether/ ethylacetate = 3:1, white solid, 51.8 mg, 93% yield, mp: 68.0−69.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.41–7.37 (m, 2H), 7.25–7.22 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.25–2.17 (m, 2H), 1.85–1.77 (m, 2H), 1.47–1.37 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 138.6, 128.6, 126.2, 122.9, 54.2, 51.8, 32.1, 25.6, 21.4, 19.6, 13.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{20}N_2O_2S+H^+$: 281.1318, Found: 281.1319; IR (neat, cm-1): υ 2955, 2918, 1749, 1562, 1263, 1129, 860, 695.



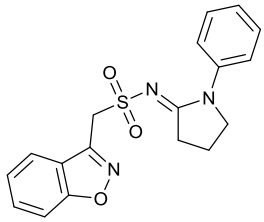
(*E*)-1-Phenyl-*N*-(1-phenylpyrrolidin-2-ylidene)methanesulfonamide (4v). Petroleum ether/ ethylacetate = 2:1, white solid, 55.7 mg, 89% yield, mp: 128.7−129.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 10H), 4.21 (s, 2H), 3.80 (t, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 7.9 Hz, 2H), 2.08–2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 138.4, 131.0, 130.3, 128.6, 128.1, 128.0, 126.4, 123.3, 60.2, 52.0, 32.0, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_2S+Na^+$: 337.0981, Found: 337.0993; IR (neat, cm-1): υ 2920, 2849, 1735, 1566, 1099, 690.



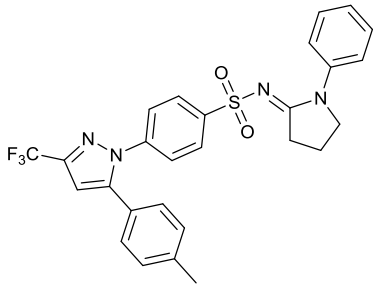
***p*-Tolyl (*E*)-(1-phenylpyrrolidin-2-ylidene)sulfamate (4w).** Petroleum ether/ ethylacetate = 4:1, white solid, 53.9 mg, 82% yield, mp: 75.7−76.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 4H), 7.30–7.25 (m, 1H), 7.16–7.09 (m, 4H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.22–2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 148.6, 138.0, 136.0, 129.7, 128.8, 127.0, 123.5, 122.0, 52.9, 32.2, 20.8, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_3S+Na^+$: 353.0930, Found: 353.0937; IR (neat, cm-1): υ 2917, 2848, 1700, 1557, 1146, 826.



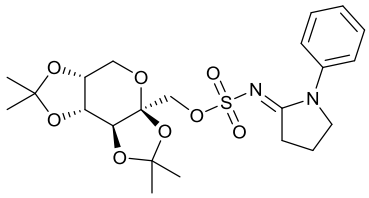
***N*,*N*-Dimethyl (*E*)-(1-phenylpyrrolidin-2-ylidene)sulfamate (4x).** Petroleum ether/ ethylacetate = 4:1, colourless liquid, 33.4 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.41–7.37 (m, 2H), 7.24–7.21 (m, 1H), 3.93 (t, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.72 (s, 6H), 2.25–2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 138.9, 128.6, 126.0, 122.8, 52.0, 38.9, 32.0, 19.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{17}N_3O_2S+Na^+$: 290.0934, Found: 290.0924; IR (neat, cm-1): υ 2961, 2878, 1749, 1563, 1302, 1138, 712.



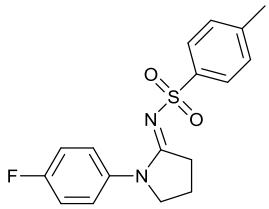
(*E*)-1-(Benzo[*d*]isoxazol-3-yl)-*N*-(1-phenylpyrrolidin-2-ylidene)methanesulfonamide (5a). Petroleum ether/ ethylacetate = 2:1, white solid, 46.6 mg, 66% yield, mp: 126.9−128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 1H), 7.58–7.50 (m, 2H), 7.38–7.32 (m, 4H), 7.26–7.19 (m, 2H), 4.71 (s, 2H), 3.83 (t, *J* = 7.2 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.13–2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 163.5, 150.3, 138.1, 129.9, 128.8, 126.8, 123.8, 123.3, 122.9, 121.0, 109.6, 52.3, 51.3, 32.3, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}N_3O_3S+Na^+$: 378.0883, Found: 378.0871; IR (neat, cm-1): υ 2921, 2850, 1748, 1557, 1294, 860, 749.



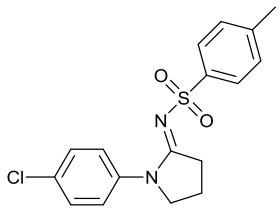
(*E*)-*N*-(1-Phenylpyrrolidin-2-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (5b). Petroleum ether/ ethylacetate = 3:1, white solid, 95.8 mg, 90% yield, mp: 171.7−172.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.43–7.38 (m, 4H), 7.36–7.32 (m, 2H), 7.26–7.21 (m, 1H), 7.16–7.14 (m, 2H), 7.10–7.08 (m, 2H), 6.72 (s, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.9 Hz, 2H), 2.36 (s, 3H), 2.25–2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 145.0, 142.6, 141.5, 139.5, 138.2, 129.6, 128.8, 128.6, 127.4, 126.6, 125.6, 125.1, 123.1, 105.9, 52.3, 32.1, 21.2, 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35. HRMS (ESI-TOF): Anal. Calcd. For $C_{27}H_{23}F_3N_4O_2S+Na^+$: 547.1386, Found: 347.1398; IR (neat, cm-1): υ 3141, 2922, 2852, 1741, 1550, 1147, 968,636.



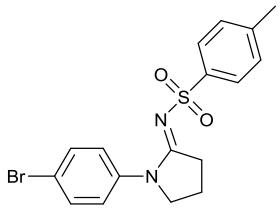
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl ((*E*)-1-phenylpyrrolidin-2-ylidene)sulfamate (5c). Petroleum ether/ ethylacetate = 3:1, colorless sticky liquid, 94.1 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.40–7.36 (m, 2H), 7.26-7.23 (m, 1H), 4.55 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.38 (d, *J* = 1.7 Hz, 1H), 4.22 (d, *J* = 8.2 Hz, 1H), 4.17 (d, *J* = 4.7 Hz, 2H), 3.96 (t, *J* = 7.2 Hz, 2H), 3.89 (d, *J* = 12.9 Hz, 1H), 3.73 (d, *J* = 13.0 Hz, 1H), 3.31 (t, *J* = 7.9 Hz, 2H), 2.26–2.19 (m, 2H), 1.52 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 138.1, 128.8, 126.7, 123.2, 108.9, 108.8, 101.0, 70.6, 69.9, 69.4, 61.1, 52.8, 32.0, 26.4, 25.7, 25.1, 23.9, 19.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{22}H_{30}N_2O_8S+Na^+$: 505.1615, Found: 505.1616; IR (neat, cm-1): υ 2988, 2934, 1557, 1156, 862, 606.



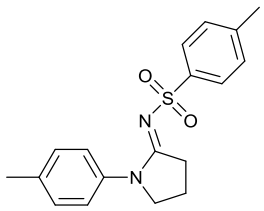
(*E*)-*N*-(1-(4-fluorophenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6a). Petroleum ether/ ethylacetate = 3:1, light yellow solid, 65.9 mg, 99% yield, mp: 128.2−129.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2H), 7.46–7.41 (m, 2H), 7.27–7.23 (m, 2H), 7.06–7.00 (m, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.22–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 160.4 (d, *J* = 245 Hz), 142.2, 134.0, 134.54 (d, *J* = 4 Hz), 129.1, 126.3, 124.9 (d, *J* = 8 Hz), 115.6 (d, *J* = 22 Hz), 52.2, 31.8, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}FN_2O_2S+H^+$: 333.1068, Found: 333.1058; IR (neat, cm-1): υ 2920, 2850, 1738, 1503, 1146, 824, 656.



(*E*)-*N*-(1-(4-chlorophenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6b). Petroleum ether/ ethylacetate = 3:1, white solid, 65.8 mg, 95% yield, mp: 142.5−143.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.77 (m, 2H), 7.46–7.42 (m, 2H), 7.3–7.27 (m, 2H), 7.26–7.24 (m, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.22–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.3, 139.8, 137.1, 131.5, 129.2, 128.8, 126.3, 124.0, 51.8, 31.9, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}{}^{35}ClN_2O_2S+H^+$: 349.0772, $C_{17}H_{17}{}^{37}ClN_2O_2S+H^+$: 351.0743, Found: 349.0767, 351.0762; IR (neat, cm-1): υ 2920, 2850, 1721, 1545, 1145, 831, 658.

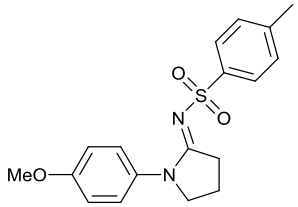


(*E*)-*N*-(1-(4-bromophenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6c). Petroleum ether/ ethylacetate = 3:1, white solid, 78.1 mg, 99% yield, mp: 147.1−148.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.78 (m, 2H), 7.45–7.43 (m, 2H), 7.39–7.37 (m, 2H), 7.26–7.24 (m, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.21–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.4, 139.8, 137.6, 131.7, 129.2, 126.3, 124.3, 119.3, 51.7, 31.9, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}{}^{79}BrN_2O_2S+H^+$: 393.0267, $C_{17}H_{17}{}^{81}BrN_2O_2S+H^+$: 395.0246, Found: 393.0256, 395.0251; IR (neat, cm-1): υ 2918, 2849, 1716, 1297, 1144, 827.

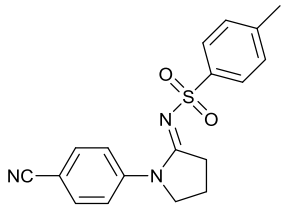


(*E*)-4-methyl-*N*-(1-(*p*-tolyl)pyrrolidin-2-ylidene)benzenesulfonamide (6d). Petroleum ether/ ethylacetate = 3:1, white solid, 65.0 mg, 99% yield, mp: 75.8−76.7 °C. ^{1}H NMR

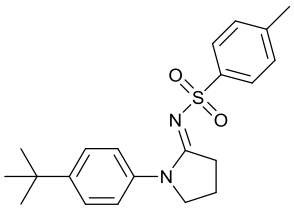
(400 MHz, $CDCl_3$) δ 7.79–7.77 (m, 2H), 7.35–7.33 (m, 2H), 7.24–7.21 (m, 2H), 7.15–7.13 (m, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 2.19–2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 142.0, 140.2, 136.2, 136.0, 129.2, 129.1, 126.3, 122.8, 52.1, 31.9, 21.3, 20.9, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_2S+H^+$: 329.1318, Found: 329.1319; IR (neat, cm-1): υ 2921, 2853, 1708, 1540, 1147, 815, 665.



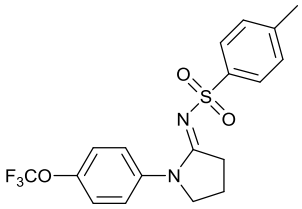
(*E*)-*N*-(1-(4-methoxyphenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6e). Petroleum ether/ ethylacetate = 2:1, white solid, 67.9 mg, 99% yield, mp: 111.2−112.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79–7.77 (m, 2H), 7.38–7.35 (m, 2H), 7.24–7.22 (m, 2H), 6.88–6.84 (m, 2H), 3.84 (t, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.20–2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 157.7, 142.0, 140.3, 131.5, 129.1, 126.3, 124.5, 113.9, 55.4, 52.4, 31.8, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_3S+H^+$: 345.1267, Found: 345.1279; IR (neat, cm-1): υ 2924, 2851, 1707, 1146, 834, 666.



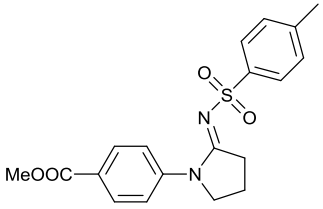
(*E*)-*N*-(1-(4-cyanophenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6f). Petroleum ether/ ethylacetate = 2:1, white solid, 67.3 mg, 99% yield, mp: 161.4−162.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.71–7.68 (m, 2H), 7.62–7.59 (m, 2H), 7.28–7.26 (m, 2H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.35 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 2.26–2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.8, 142.4, 139.4, 132.6, 129.3, 126.4, 122.4, 118.2, 108.8, 51.3, 32.1, 21.4, 19.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}N_3O_2S+H^+$: 340.1114, Found: 340.1132; IR (neat, cm-1): υ 2921, 2852, 2222, 1299, 1149, 836, 665.



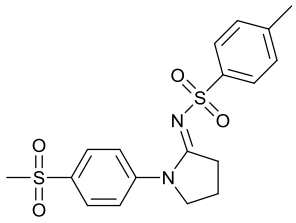
(*E*)-*N*-(1-(4-(*tert*-butyl)phenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6g). Petroleum ether/ ethylacetate = 3:1, white solid, 56.8 mg, 77% yield, mp: 138.3−140.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–8.79 (m, 2H), 7.42–7.40 (m, 2H), 7.36–7.34 (m, 2H), 7.25–7.23 (m, 2H), 3.87 (t, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.19–2.11 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 149.2, 142.1, 140.2, 135.9, 129.1, 126.4, 125.6, 122.4, 52.1, 34.4, 31.9, 31.2, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{26}N_2O_2S+H^+$: 371.1788, Found: 371.1783; IR (neat, cm-1): υ 2947, 2862, 1709, 1539, 1301, 1150, 656.



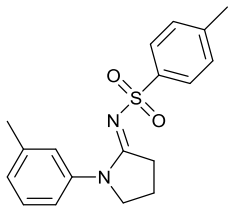
(*E*)-4-methyl-*N*-(1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-ylidene)benzenesulfonamide (6h). Petroleum ether/ ethylacetate = 3:1, white solid, 43.6 mg, 55% yield, mp: 131.2−132.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.77 (m, 2H), 7.55–7.52 (m, 2H), 7.27–7.24 (m, 2H), 7.20–7.18 (m, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.24–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.5, 139.8, 137.1, 129.2, 126.4, 124.2, 121.2, 52.0, 31.9, 21.4, 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.96. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}F_3N_2O_3S+Na^+$: 421.0804, Found: 421.0800; IR (neat, cm-1): υ 2924, 2853, 1713, 1551, 1147, 674.



Methyl (*E*)-4-(2-(tosylimino)pyrrolidin-1-yl)benzoate (6i). Petroleum ether/ ethylacetate = 3:1, white solid, 39.2 mg, 53% yield, mp: 122.6−123.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.81–7.79 (m, 2H), 7.63–7.61 (m, 2H), 7.27–7.25 m, 2H), 3.94 (t, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 3.36 (t, *J* = 7.9 Hz, 2H), 2.40 (s, 3H), 2.25–2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.2, 142.5, 142.5, 139.7, 130.1, 129.2, 127.2, 126.4, 121.9, 52.1, 51.6, 32.2, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{20}N_2O_4S+H^+$: 373.1217, Found: 373.1223; IR (neat, cm-1): υ 2922, 2852, 1710, 1278, 1148, 664.

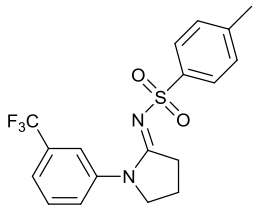


(*E*)-4-methyl-*N*-(1-(4-(methylsulfonyl)phenyl)pyrrolidin-2-ylidene)benzenesulfonamide (6j). Petroleum ether/ ethylacetate = 1:1, white solid, 63.0 mg, 81% yield, mp: 181.0−182.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.81–7.79 (m, 2H), 7.76–7.74 (m, 2H), 7.29–7.27 (m, 2H), 3.95 (t, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 7.9 Hz, 2H), 3.03 (s, 3H), 2.41 (s, 3H), 2.27–2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 143.2, 142.8, 139.4, 136.9, 129.3, 128.0, 126.3, 122.6, 51.5, 44.4, 32.0, 21.4, 19.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_4S_2+H^+$: 393.0937, Found: 393.0942; IR (neat, cm-1): υ 2922, 2852, 1709, 1548, 1144, 698

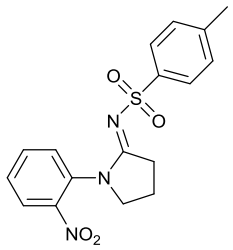


(*E*)-4-methyl-*N*-(1-(m-tolyl)pyrrolidin-2-ylidene)benzenesulfonamide (6k). Petroleum ether/ ethylacetate = 3:1, white solid, 65.0 mg, 99% yield, mp: 95.0−96.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.27–7.20 (m, 5H), 7.02–7.01 (m, 1H), 3.86 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 2.20–2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 142.0, 140.2, 138.5, 138.4, 129.0, 128.5, 127.1, 126.2, 123.7, 120.0, 52.1, 31.9,

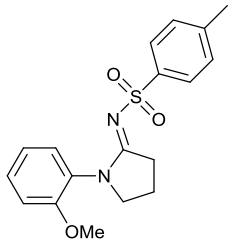
21.3, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_2S+H^+$: 329.1318, Found: 329.1306; IR (neat, cm-1): υ 2921, 2853, 1752, 1546, 1144, 669.



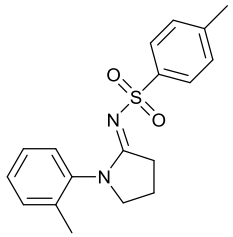
(*E*)-4-methyl-*N*-(1-(3-(trifluoromethyl)phenyl)pyrrolidin-2-ylidene)benzenesulfonamide (6l). Petroleum ether/ ethylacetate = 3:1, colorless sticky liquid, 61.3 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.49–7.42 (m, 2H), 7.26–7.24 (m, 2H), 3.92 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.26–2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.5, 139.8, 139.1, 131.0 (q, *J* = 32 Hz), 129.3, 129.2, 127.65 (q, *J* = 271 Hz), 126.2, 125.4, 122.5 (q, *J* = 4 Hz), 119.7 (q, *J* = 4 Hz), 51.5, 32.0, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}F_3N_2O_2S+H^+$: 383.1036, Found: 383.1044; IR (neat, cm-1): υ 2922, 2851, 1558, 1327, 1146, 691.



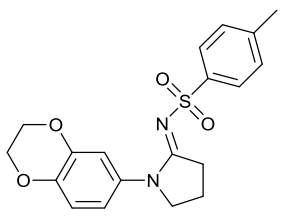
(*E*)-4-methyl-*N*-(1-(2-nitrophenyl)pyrrolidin-2-ylidene)benzenesulfonamide (6m). Petroleum ether/ ethylacetate = 1:1, yellow solid, 69.9 mg, 98% yield, mp: 187.5−189.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.94 (m, 1H), 7.66–7.64 (m, 3H), 7.47–7.44 (m, 1H), 7.34–7.32 (m, 1H), 7.24–7.22 (m, 2H), 3.89 (t, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 7.9 Hz, 2H), 2.39 (s, 3H), 2.32–2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 145.4, 142.4, 139.2, 134.3, 131.8, 129.0, 128.5, 126.4, 125.6, 125.4, 52.8, 30.9, 21.4, 20.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}N_3O_4S+H^+$: 360.1013, Found: 360.1001; IR (neat, cm-1): υ 2922, 2852, 1698, 1527, 1144, 666.



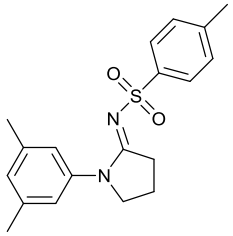
(*E*)-*N*-(1-(2-methoxyphenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6n). Petroleum ether/ ethylacetate = 2:1, white solid, 55.3 mg, 81% yield, mp: 150.0−151.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.70 (m, 2H), 7.30–7.25 (m, 1H), 7.20–7.15 (m, 3H), 6.96–6.91 (m, 2H), 3.76–3.72 (m, 5H), 3.20 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.22–2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.1, 141.7, 140.5, 129.4, 128.9, 128.2, 126.6, 126.2, 120.6, 112.0, 55.4, 52.0, 30.9, 21.3, 20.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_3S+H^+$: 345.1267, Found: 345.1264; IR (neat, cm-1): υ 2918, 2848, 1749, 1557, 1145, 751, 668.



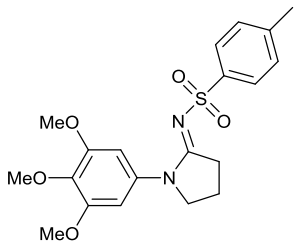
(*E*)-4-methyl-*N*-(1-(o-tolyl)pyrrolidin-2-ylidene)benzenesulfonamide (6o). Petroleum ether/ ethylacetate = 2:1, white solid, 49.7 mg, 76% yield, mp: 125.1−126.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.67 (m, 2H), 7.22–7.17 (m, 5H), 7.07–7.05 (m, 1H), 3.71 (t, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.26–2.19 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 141.9, 140.3, 137.0, 134.9, 131.1, 129.0, 128.4, 126.8, 126.3, 126.2, 52.9, 30.9, 21.3, 20.2, 17.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_2S+H^+$: 329.1318, Found: 329.1307; IR (neat, cm-1): υ 2920, 2850, 1751, 1283, 1149, 668.



(*E*)-*N*-(1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6p). Petroleum ether/ ethylacetate = 2:1, white solid, 73.5 mg, 99% yield, mp: 153.2−155.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.25–7.22 (m, 2H), 6.99–6.97 (m, 1H), 6.94–6.91 (m, 1H), 6.82–6.79 (m, 1H), 4.22 (s, 4H), 3.81 (t, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.18–2.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 143.2, 142.0, 142.0, 140.2, 131.9, 129.1, 126.3, 117.0, 116.5, 112.6, 64.2, 52.4, 31.8, 21.3, 19.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{20}N_2O_4S+H^+$: 373.1217, Found: 373.1214; IR (neat, cm-1): υ 2919, 2850, 1749, 1506, 1273, 1145, 662.

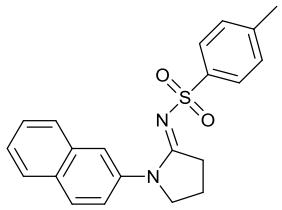


(*E*)-*N*-(1-(3,5-dimethylphenyl)pyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (6q). Petroleum ether/ ethylacetate = 3:1, white solid, 67.6 mg, 99% yield, mp: 59.1−60.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.24–7.22 (m, 2H), 7.06 (s, 2H), 6.85 (s, 1H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.27 (s, 6H), 2.19–2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 142.0, 140.4, 138.3, 138.3, 129.0, 128.1, 126.2, 120.9, 52.2, 31.9, 21.3, 21.2, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{22}N_2O_2S+H^+$: 343.1475, Found: 343.1473; IR (neat, cm-1): υ 2917, 2849, 1748, 1549, 1144, 668.

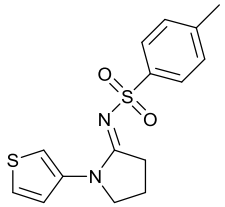


(*E*)-4-methyl-*N*-(1-(3,4,5-trimethoxyphenyl)pyrrolidin-2-ylidene)benzenesulfonamide (6r). Petroleum ether/ ethylacetate = 1:1, white solid, 67.2 mg, 84% yield, mp: 151.6−152.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.25–7.23 (m, 2H), 6.73 (s, 2H), 3.90 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.70 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.24–2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 152.8, 142.2, 140.2, 136.1, 134.3, 129.0, 126.3, 100.7, 60.8, 55.9,

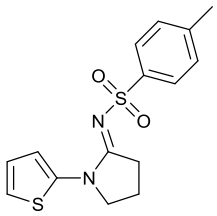
52.2, 32.1, 21.3, 19.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{24}N_2O_5S+H^+$: 405.1479, Found: 405.1480; IR (neat, cm-1): υ 2919, 2848, 1558, 1120, 665.



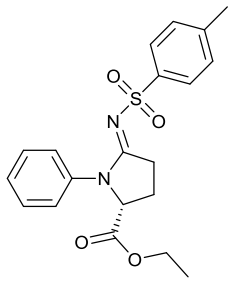
(*E*)-4-methyl-*N*-(1-(naphthalen-2-yl)pyrrolidin-2-ylidene)benzenesulfonamide (6s). Petroleum ether/ ethylacetate = 2:1, white solid, 72.0 mg, 99% yield, mp: 116.5−117.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–8.77 (m, 5H), 7.75–7.72 (m, 1H), 7.69–7.66 (m, 1H), 7.48–7.42 (m, 2H), 7.22–7.20 (m, 2H), 3.94 (t, *J* = 7.2 Hz, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.21–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.1, 140.1, 136.1, 133.0, 131.4, 129.1, 128. 4, 127.7, 127.5, 126.5, 126.3, 126.1, 121.7, 120.8, 52.2, 32.0, 21.3, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{20}N_2O_2S+H^+$: 365.1318, Found: 365.1314; IR (neat, cm-1): υ 2919, 2849, 1714, 1549, 1146, 706.



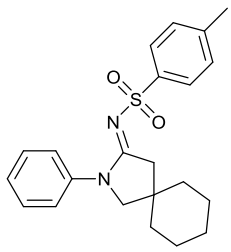
(*E*)-4-methyl-*N*-(1-(thiophen-3-yl)pyrrolidin-2-ylidene)benzenesulfonamide (6t). Petroleum ether/ ethylacetate = 3:1, white solid, 61.9 mg, 97% yield, mp: 136.2−137.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.53–7.52 (m, 1H), 7.38–7.36 (m, 1H), 7.28–7.23 (m, 3H), 3.91 (t, *J* = 7.3 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.22–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 142.3, 140.0, 136.8, 129.2, 126.4, 124.6, 121.3, 113.2, 51.6, 31.7, 21.4, 19.2. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}N_2O_2S_2+H^+$: 321.0726, Found: 321.0736; IR (neat, cm-1): υ 2919, 2850, 1736, 1521, 1279, 666.



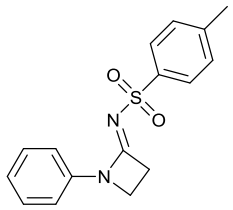
(*E*)-4-methyl-*N*-(1-(thiophen-2-yl)pyrrolidin-2-ylidene)benzenesulfonamide (6u). Petroleum ether/ ethylacetate = 3:1, white solid, 57.3 mg, 90% yield, mp: 136.3−137.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.53–7.52 (m, 1H), 7.38–7.36 (m, 1H), 7.28–7.23 (m, 3H), 3.91 (t, *J* = 7.4 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.22–2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 142.3, 140.0, 136.8, 129.2, 126.4, 124.6, 121.3, 113.2, 51.6, 31.7, 21.4, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}N_2O_2S_2$+H^+: 321.0726, Found: 321.0727; IR (neat, cm-1): υ 2921, 2852, 1736, 1520, 1279, 666.



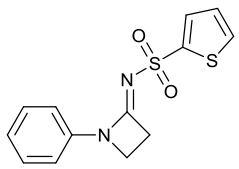
Ethyl (*R*,*E*)-1-phenyl-5-(tosylimino)pyrrolidine-2-carboxylate (7a). Petroleum ether/ ethylacetate = 3:1, white solid, 74.7 mg, 97% yield, mp: 120.6−121.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.34–7.33 (m, 4H), 7.23–7.21 (m, 3H), 4.74–4.70 (m, 1H), 4.17–4.05 (m, 2H), 3.47–3.39 (m, 1H), 3.31–3.22 (m, 1H), 2.59–2.49 (m, 1H), 2.37 (s, 3H), 2.27–2.19 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.7, 142.2, 139.8, 137.3, 129.1, 128.8, 127.2, 126.2, 124.7, 64.5, 61.8, 30.3, 24.9, 21.3, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{22}N_2O_4S$+Na^+: 409.1192, Found: 409.1196; IR (neat, cm-1): υ 2965, 2922, 2852, 1728, 1560, 1082, 699.



(*E*)-4-methyl-*N*-(2-phenyl-2-azaspiro[4.5]decan-3-ylidene)benzenesulfonamide (7b). Petroleum ether/ ethylacetate = 5:1, white solid, 58.6 mg, 77% yield, mp: 148.3−149.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.48–7.47 (m, 2H), 7.36–7.32 (m, 2H), 7.24–7.17 (m, 3H), 3.65 (s, 2H), 3.16 (s, 2H), 2.38 (s, 3H), 1.55–1.45 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 142.1, 140.2, 138.8, 129.1, 128.7, 126.3, 126.2, 122.8, 62.6, 44.2, 38.0, 36.0, 25.4, 22.8, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{22}H_{26}N_2O_2S+H^+$: 383.1788, Found: 383.1772; IR (neat, cm-1): υ 2919, 2850, 1747, 1558, 1150, 681.

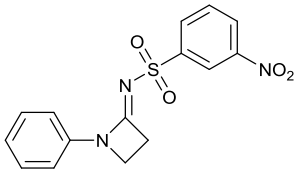


(*E*)-4-methyl-*N*-(1-phenylazetidin-2-ylidene)benzenesulfonamide (7c). Petroleum ether/ ethylacetate = 3:1, light yellow solid, 35.5 mg, 60% yield, mp: 105.9−107.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.84 (m, 2H), 7.44–7.42 (m, 2H), 7.35–7.31 (m, 2H), 7.29–7.27 (m, 2H), 7.15–7.11 (m, 1H), 3.98 (t, *J* = 4.1 Hz, 2H), 3.50 (t, *J* = 4.1 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 142.8, 139.5, 137.8, 129.3, 129.1, 126.6, 125.1, 117.3, 45.0, 32.3, 21.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{16}N_2O_2S+Na^+$: 323.0825, Found: 323.0830; IR (neat, cm-1): υ 2923, 2853, 1734, 1610, 1147, 895, 681.

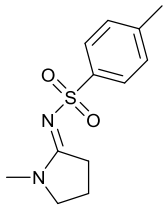


(*E*)-*N*-(1-phenylazetidin-2-ylidene)thiophene-2-sulfonamide (7d). Petroleum ether/ ethylacetate = 1:3, white solid, 50.2 mg, 86% yield, mp: 128.8−129.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.67 (m, 1H), 7.55–7.53 (m, 1H), 7.48–7.45 (m, 2H), 7.38–7.34 (m, 2H), 7.18–7.15 (m, 1H), 7.07–7.05 (m, 1H), 4.02 (t, *J* = 4.1 Hz, 2H), 3.53 (t, *J* = 4.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 143.7, 137.7, 131.1, 131.0, 129.2, 127.0, 125.4, 117.5, 45.2, 32.2. HRMS

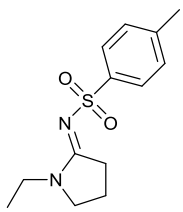
(ESI-TOF): Anal. Calcd. For $C_{13}H_{12}N_2O_2S_2+H^+$: 293.0413, Found: 293.0417; IR (neat, cm-1): υ 2920. 1735, 1307, 1138, 1015, 891, 681.



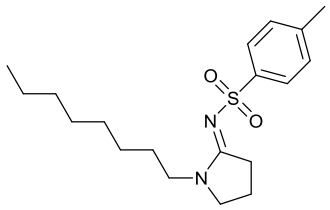
(*E*)-3-nitro-*N*-(1-phenylazetidin-2-ylidene)benzenesulfonamide (7e). Petroleum ether/ ethylacetate = 1:3, white solid, 43.8 mg, 66% yield, mp: 160.6−161.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.805–8.796 (m, 1H), 8.40–8.38 (m, 1H), 8.32–8.30 (m, 1H), 7.74–7.70 (m, 1H), 7.44–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.19–7.16 (m, 1H), 4.08 (t, *J* = 4.1 Hz, 2H), 3.58 (t, *J* = 4.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 148.1, 144.4, 137.5, 132.3, 130.2, 129.2, 126.6, 125.7, 121.9, 117.5, 45.3, 32.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{13}N_3O_4S+H^+$: 332.0700, Found: 332.0697; IR (neat, cm-1): υ 2919, 1576, 1347, 1013, 895, 762, 677.



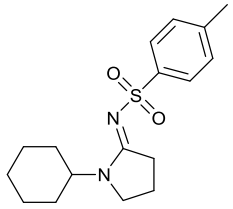
(*E*)-4-methyl-*N*-(1-methylpyrrolidin-2-ylidene)benzenesulfonamide (7f). Petroleum ether/ ethylacetate = 1:1, white solid, 46.8 mg, 93% yield, mp: 157.8−159.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.26–7.24 (m, 2H), 3.45 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.96 (s, 3H), 2.39 (s, 3H), 2.08–2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 141.9, 140.5, 129.1, 126.4, 51.6, 31.9, 30.6, 21.4, 18.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}N_2O_2S+Na^+$: 275.0825, Found: 375.0834; IR (neat, cm-1): υ 2922, 2852, 1733, 1596, 1278, 668.



(*E*)-*N*-(1-ethylpyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (7g). Petroleum ether/ ethylacetate = 1:1, white solid, 38.5 mg, 73% yield, mp: 106.0−107.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.26–7.24 (m, 2H), 3.49–3.43 (m, 4H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.07–2.00 (m, 2H), 1.13 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 141.9, 140.6, 129.1, 126.4, 48.8, 39.6, 31.0, 21.4, 19.0, 11.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_2S+Na^+$: 289.0981, Found: 289.0989; IR (neat, cm-1): υ 2922, 2852, 1729, 1579, 1280, 1142, 666.

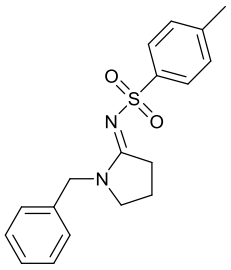


(*E*)-4-methyl-*N*-(1-octylpyrrolidin-2-ylidene)benzenesulfonamide (7h). Petroleum ether/ ethylacetate = 3:1, white solid, 53.0 mg, 76% yield, mp: 81.2−82.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.25–7.23 (m, 2H), 3.45–3.38 (m, 4H), 3.04 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.07–1.99 (m, 2H), 1.56–1.50 (m, 2H), 1.34–1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 141.8, 140.7, 129.0, 126.3, 49.4, 44.8, 31.7, 31.0, 29.1, 29.0, 26.6, 26.5, 22.5, 21.4, 19.1, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{30}N_2O_2S+Na^+$: 373.1920, Found: 373.1921; IR (neat, cm-1): υ 2925, 2852, 1732, 1580, 1303, 1143, 672.

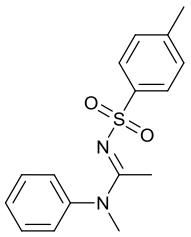


(*E*)-*N*-(1-cyclohexylpyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (7i). Petroleum ether/ ethylacetate = 4:1, white solid, 37.4 mg, 59% yield, mp: 188.6−190.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.26–7.24 (m, 2H), 4.20–4.13 (m, 1H), 3.40 (t, *J* = 7.3 Hz, 2H), 3.01 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.02–1.95 (m, 2H), 1.80–1.66 (m, 5H), 1.43–1.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 141.8, 140.8, 129.1, 126.4, 52.8, 45.0, 31.3, 29.6, 25.3, 25.1,

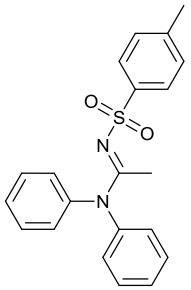
21.4, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{24}N_2O_2S+Na^+$: 343.1451, Found: 343.1461; IR (neat, cm-1): υ 2921, 2849, 1733, 1556, 1137, 666.



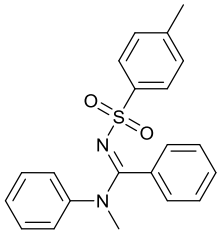
(*E*)-*N*-(1-benzylpyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (7j). Petroleum ether/ ethylacetate = 3:1, white solid, 56.4 mg, 86% yield, mp: 137.7−139.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.31–7.25 (m, 5H), 7.21–7.18 (m, 2H), 4.58 (s, 2H), 3.34 (t, *J* = 7.3 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.04–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 142.0, 140.4, 134.9, 129.1, 128.7, 128.3, 127.9, 126.4, 48.8, 48.6, 30.9, 21.4, 18.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_2S+Na^+$: 351.1138, Found: 351.1147; IR (neat, cm-1): υ 2923, 2854, 1749, 1571, 1140, 667.



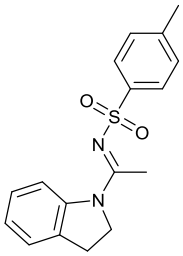
(*E*)-*N*-methyl-*N*-phenyl-*N'*-tosylacetimidamide (8a). Petroleum ether/ ethylacetate = 5:1, white solid, 59.2 mg, 98% yield, mp: 78.5−79.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.46–7.42 (m, 2H), 7.40–7.36 (m, 1H), 7.30–7.28 (m, 2H), 7.16–7.14 (m, 2H), 3.34 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 143.1, 142.0, 140.8, 130.0, 129.1, 128.5, 126.7, 126.3, 40.3, 21.4, 19.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{18}N_2O_2S+H^+$: 303.1162, Found: 303.1170; IR (neat, cm-1): υ 2921, 2869, 1745, 1537, 1270, 1083, 770, 681.



(*E*)-*N*,*N*-diphenyl-*N′*-tosylacetimidamide (8b). Petroleum ether/ ethylacetate = 4:1, light yellow solid, 71.5 mg, 99% yield, mp: 147.9−148.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.35–7.21 (m, 10H), 7.15–7.13 (m, 2H), 2.53 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 141.8, 140.4, 129.6, 129.4, 128.8, 127.1, 126.3, 126.0, 21.3, 20.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{20}N_2O_2S+H^+$: 365.1318, Found: 365.1315; IR (neat, cm-1): υ 2917, 2849, 1743, 1489, 1271, 1088, 684.

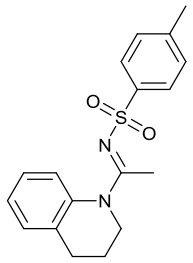


(*E*)-*N*-methyl-*N*-phenyl-*N′*-tosylbenzimidamide (8c). Petroleum ether/ ethylacetate = 4:1, white solid, 40.7 mg, 56% yield, mp: 104.7−106.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.19–7.05 (m, 10H), 6.95–6.93 (m, 2H), 3.52 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 143.3, 141.7, 140.7, 132.3, 129.4, 129.1, 128.8, 128.7, 127.4, 127.3, 127.3, 126.5, 40.8, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{20}N_2O_2S+Na^+$: 387.1138, Found: 387.1139; IR (neat, cm-1): υ 3355, 3260, 2921, 2851, 1741, 1522, 1147, 679.

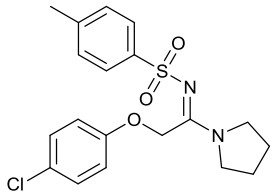


(*E*)-*N*-(1-(indolin-1-yl)ethylidene)-4-methylbenzenesulfonamide (8d). Petroleum ether/ ethylacetate = 2:1, white solid, 58.1 mg, 93% yield, mp: 177.5−178.6 °C. ^{1}H NMR (400 MHz,

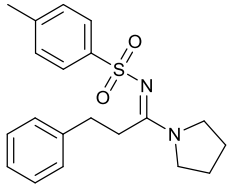
$CDCl_3$) δ 8.20–8.18 (m, 1H), 7.87–8.86 (m, 2H), 7.28–7.26 (m, 2H), 7.17–7.15 (m, 1H), 7.10–7.01 (m, 2H), 4.03 (t, *J* = 8.2 Hz, 2H), 3.15 (t, *J* = 8.1 Hz, 2H), 2.63 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 142.1, 141.7, 140.6, 132.7, 129.2, 127.4, 126.3, 125.0, 124.6, 119.3, 49.7, 27.1, 21.4, 20.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{18}N_2O_2S+H^+$: 315.1162, Found: 315.1169; IR (neat, cm-1): υ 2918, 2849, 1734, 1132, 754, 660.



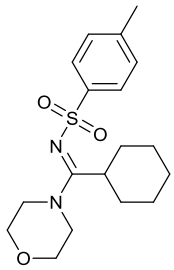
(*E*)-*N*-(1-(3,4-dihydroquinolin-1(2*H*)-yl)ethylidene)-4-methylbenzenesulfonamide (8e). Petroleum ether/ ethylacetate = 5:1, white solid, 63.6 mg, 97% yield, mp: 104.5−107.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.29–7.27 (m, 2H), 7.22–7.18 (m, 3H), 7.03–7.02 (m, 1H), 3.87 (t, *J* = 6.9 Hz, 2H), 2.67 (t, *J* = 6.5 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H), 1.97–1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 142.0, 140.6, 137.5, 129.0, 128.3, 127.0, 126.4, 126.2, 126.1, 124.8, 45.8, 26.4, 23.7, 21.3, 20.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_2S+H^+$: 329.1318, Found: 329.1326; IR (neat, cm-1): υ 2922, 2851, 1749, 1492, 1082, 753.



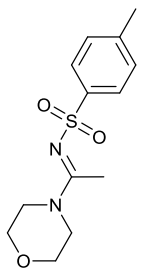
(*E*)-*N*-(2-(4-chlorophenoxy)-1-(pyrrolidin-1-yl)ethylidene)-4-methylbenzenesulfonamide (8f). Petroleum ether/ ethylacetate = 3:1, white solid, 53.2 mg, 68% yield, mp: 118.8−120.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.23– 7.21 (m, 4H), 6.89–6.87 (m, 2H), 5.26 (s, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.53 (t, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 1.98–1.91 (m, 2H), 1.88–1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.7, 142.0, 140.8, 129.4, 129.0, 126.8, 126.2, 115.8, 64.2, 49.4, 48.7, 26.0, 23.5, 21.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{21}{}^{35}ClN_2O_3S+H^+$: 393.1034, $C_{19}H_{21}{}^{37}ClN_2O_3S+H^+$: 395.1005, Found: 393.1024, 395.0978; IR (neat, cm-1): υ 2921, 2851, 1541, 1082, 837, 696.



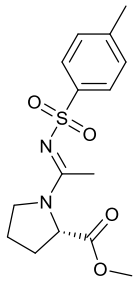
(*E*)-4-methyl-*N*-(3-phenyl-1-(pyrrolidin-1-yl)propylidene)benzenesulfonamide (8g). Petroleum ether/ ethylacetate = 4:1, white solid, 39.5 mg, 56% yield, mp: 126.6−128.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.31–7.19 (m, 7H), 3.49 (t, *J* = 6.5 Hz, 2H), 3.30 (t, *J* = 6.2 Hz, 2H), 3.15–3.11 (m, 2H), 3.08–3.04 (m, 2H), 2.39 (s, 3H), 1.86–1.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 141.7, 141.6, 140.1, 129.0, 128.5, 128.5, 126.5, 126.1, 48.6, 47.5, 34.8, 32.8, 25.7, 24.1, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{24}N_2O_2S+H^+$: 357.1631, Found: 357.1624; IR (neat, cm-1): υ 2919, 2850, 1747, 1541, 1252, 697.



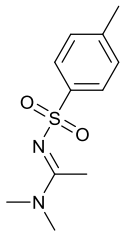
(*E*)-*N*-(cyclohexyl(morpholino)methylene)-4-methylbenzenesulfonamide (8h). Petroleum ether/ ethylacetate = 2:1, white solid, 31.5 mg, 45% yield, mp: 133.9−135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.26–7.24 (m, 2H), 3.72–3.62 (m, 9H), 2.40 (s, 3H), 1.87–1.70 (m, 6H), 1.61–1.52 (m, 2H), 1.19–1.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 141.7, 141.6, 129.0, 126.1, 66.6, 47.6, 43.4, 40.2, 29.6, 29.2, 28.3, 26.0, 25.7, 25.4, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{26}N_2O_3S+H^+$: 351.1737, Found: 351.1725; IR (neat, cm-1): υ 2922, 2850, 1740, 1534, 1138, 870, 667.



(*E*)-4-methyl-*N*-(1-morpholinoethylidene)benzenesulfonamide (8i). Petroleum ether/ ethylacetate = 1:1, white solid, 49.2 mg, 88% yield, mp: 116.7−117.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.27–7.25 (m, 2H), 3.75–3.73 (m, 2H), 3.72–3.69 (m, 2H), 3.67–3.65 (m, 2H), 3.53–3.50 (m, 2H), 2.52 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 142.0, 140.7, 129.1, 126.2, 66.2, 66.2, 46.5, 44.5, 21.4, 17.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_3S+Na^+$: 305.0930, Found: 309.0940; IR (neat, cm-1): υ 2921, 2856, 1730, 1535, 1260, 675.

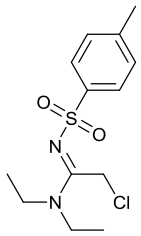


Methyl (*E*)-(1-(tosylimino)ethyl)-*L*-prolinate (8j). Petroleum ether/ ethylacetate = 1:1, colorless sticky liquid, 42.0 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.73 (m, 2H), 7.24–7.22 (m, 2H), 4.53–4.50 (m, 1H), 3.71–3.66 (m, 1H), 3.59–3.55 (m, 1H), 3.53 (s, 3H), 2.51 (s, 3H), 2.39 (s, 3H), 2.25–2.10 (m, 2H), 2.04–2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 164.0, 141.8, 140.7, 128.9, 126.1, 60.7, 52.0, 48.4, 29.2, 24.3, 21.4, 18.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{20}N_2O_4S+H^+$: 325.1217, Found: 325.1203; IR (neat, cm-1): υ 2923, 2852, 1741, 1538, 114, 704.

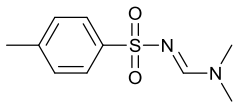


(*E*)-*N*,*N*-dimethyl-*N′*-tosylacetimidamide (8k). Petroleum ether/ ethylacetate = 1:1, white solid, 32.2 mg, 68% yield, mp: 105.6−107.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.26–7.24 (m, 2H), 3.09 (s, 3H), 3.07 (s, 3H), 2.49 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.8, 141.1, 129.1, 126.2, 38.8, 38.8, 21.4, 18.0. HRMS (ESI-TOF): Anal. Calcd. For

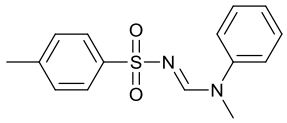
$C_{11}H_{16}N_2O_2S+Na^+$: 263.0825, Found: 263.0831; IR (neat, cm-1): υ 2921, 2851, 1729, 1572, 1251, 683.



(*E*)-2-chloro-*N*,*N*-diethyl-*N′*-tosylacetimidamide (8l). Petroleum ether/ ethylacetate = 3:1, yellow solid, 24.7 mg, 40% yield, mp: 68.5−69.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.27–7.24 (m, 2H), 4.71 (s, 2H), 3.51–3.44 (m, 4H), 2.40 (s, 3H), 1.28 (t, *J* = 8.0 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 142.1, 140.5, 129.0, 126.2, 43.6, 43.5, 34.4, 21.4, 14.1, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{19}{}^{35}ClN_2O_2S+H^+$: 325.0748, $C_{13}H_{19}{}^{37}ClN_2O_2S+H^+$: 327.0718, Found: 325.0758, 327.0714; IR (neat, cm-1): υ 2978, 2874, 1733, 1556, 1143, 669.

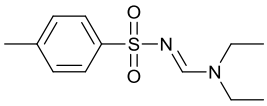


(*E*)-*N*,*N*-dimethyl-*N′*-tosylformimidamide (9a). Petroleum ether/ ethylacetate = 1:1, white solid, 44.4 mg, 98% yield, mp: 124.3−125.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.78–7.76 (m, 2H), 7.26–7.24 (m, 2H), 3.12 (s, 3H), 3.00 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 142.3, 139.5, 129.2, 126.4, 41.4, 35.4, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{14}N_2O_2S+Na^+$: 249.0668, Found: 249.0676; IR (neat, cm-1): υ 2922, 2852, 1619, 1278, 1143, 910, 667.

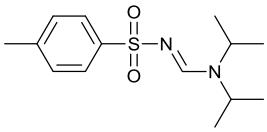


(*E*)-*N*-methyl-*N*-phenyl-*N′*-tosylformimidamide (9b). Petroleum ether/ ethylacetate = 5:1, white solid, 56.9 mg, 99% yield, mp: 94.7−96.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.84–7.82 (m, 2H), 7.45–7.41 (m, 2H), 7.34–7.28 (m, 3H), 7.20–7.19 (m, 2H), 3.44 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.1, 142.8, 138.8, 129.8, 129.3, 127.2, 126.6, 122.0,

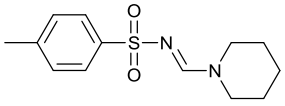
35.9, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}N_2O_2S+H^+$: 289.1005, Found: 289.1016; IR (neat, cm-1): υ 2921, 2851, 1743, 1566, 1143, 763, 672.



(*E*)-*N*,*N*-diethyl-*N′*-tosylformimidamide (9c). Petroleum ether/ ethylacetate = 2:1, white solid, 50.2 mg, 99% yield, mp: 54.5−55.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.77–7.75 (m, 2H), 7.26–7.24 (m, 2H), 3.47 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 142.1, 139.7, 129.2, 126.2, 46.9, 40.8, 21.3, 14.4, 12.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{18}N_2O_2S+Na^+$: 277.0981, Found: 277.0976; IR (neat, cm-1): υ 2984, 2875, 1748, 1607, 1280, 1142, 670.

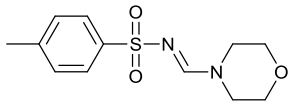


(*E*)-*N*,*N*-diisopropyl-*N′*-tosylformimidamide (9d). Petroleum ether/ ethylacetate = 5:1, white solid, 55.0 mg, 98% yield, mp: 103.6−104.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.76–7.74 (m, 2H), 7.26–7.24 (m, 2H), 4.52 (dt, *J* =13.6, 6.8 Hz, 1H), 3.69 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.39 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 142.0, 139.8, 129.1, 126.1, 48.4, 47.8, 23.5, 21.3, 19.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{22}N_2O_2S+H^+$: 283.1475, Found: 283.1478; IR (neat, cm-1): υ 2925, 2854, 1747, 1595, 1146, 669.



(*E*)-4-methyl-*N*-(piperidin-1-ylmethylene)benzenesulfonamide (9e). Petroleum ether/ ethylacetate = 3:1, white solid, 52.7 mg, 99% yield, mp: 150.3−151.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.77–7.75 (m, 2H), 7.26–7.24 (m, 2H), 3.58 (t, *J* = 5.0 Hz, 2H), 3.41 (t, *J* = 5.0 Hz, 2H), 2.39 (s, 3H), 1.70–1.66 (m, 4H), 1.59–1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.2, 139.6, 129.2, 126.3, 51.8, 44.5, 26.3, 24.7, 23.8, 21.3. HRMS (ESI-TOF): Anal. Calcd.

For $C_{13}H_{18}N_2O_2S+H^+$: 267.1162, Found: 267.1170; IR (neat, cm-1): υ 2924, 2856, 1732, 1603, 1145, 670.

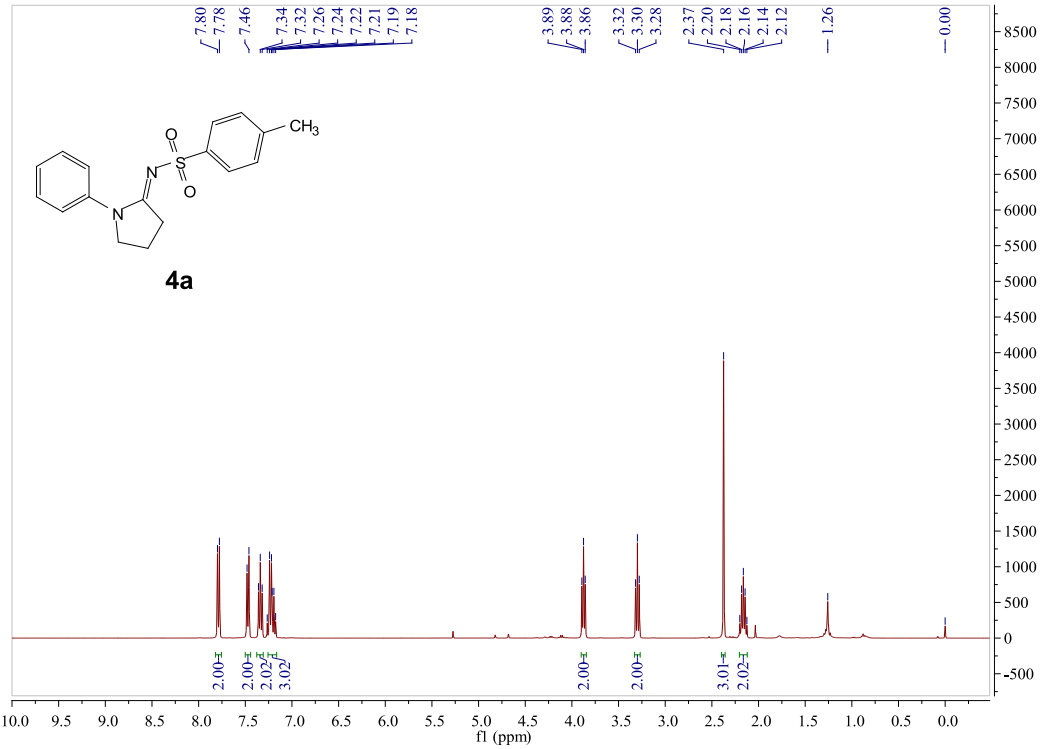


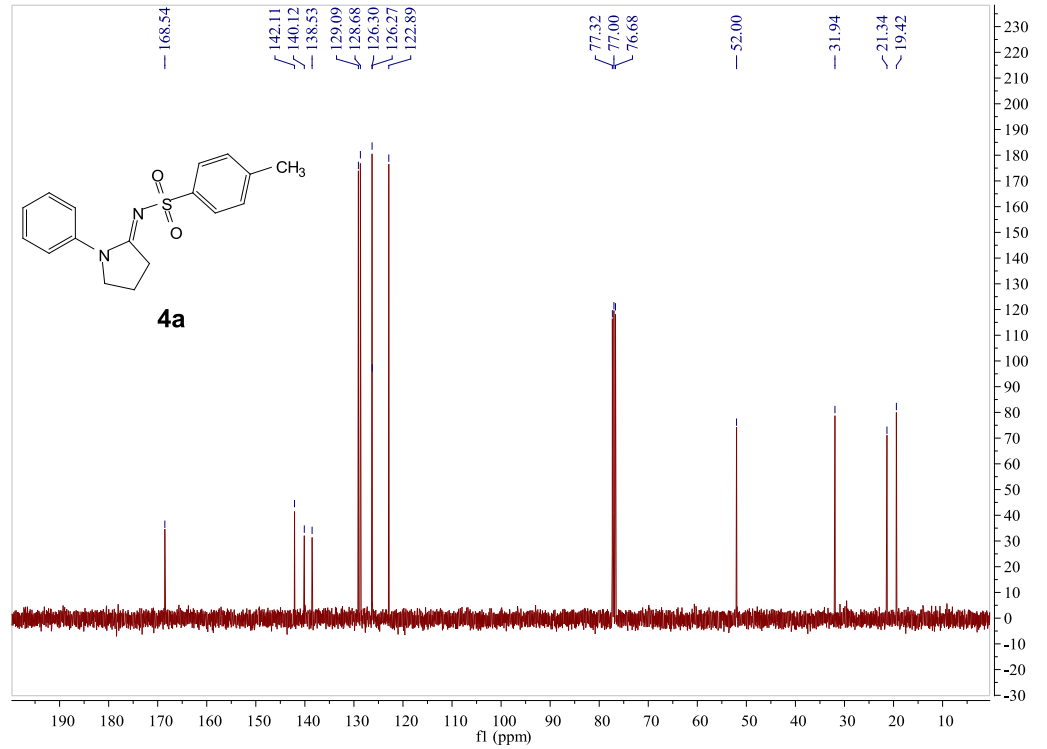
(*E*)-4-methyl-*N*-(morpholinomethylene)benzenesulfonamide (9f). Petroleum ether/ ethylacetate = 1:1, white solid, 52.9 mg, 99% yield, mp: 164.1−165.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.77–7.75 (m, 2H), 7.28–7.26 (m, 2H), 3.75–3.72 (m, 2H), 3.66 (s, 4H), 3.51–3.49 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 142.5, 139.1, 129.3, 126.4, 66.7, 65.8, 50.2, 44.1, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}N_2O_3S+H^+$: 269.0954, Found: 269.0961; IR (neat, cm-1): υ 2922, 2851, 1735, 1605, 853, 668.

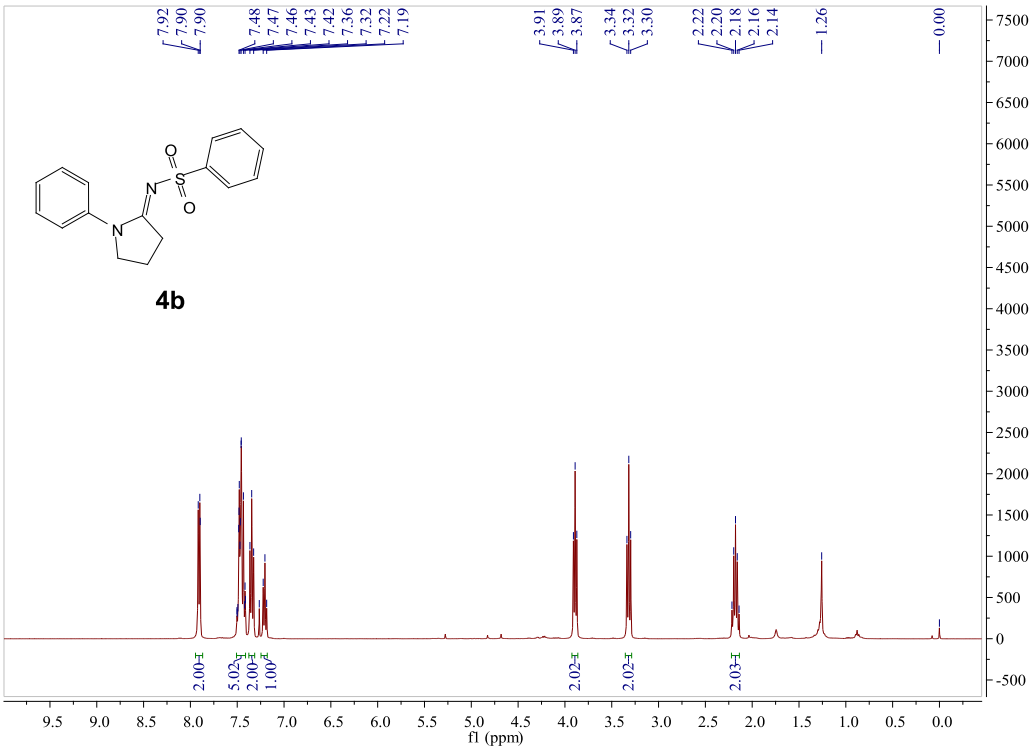
References

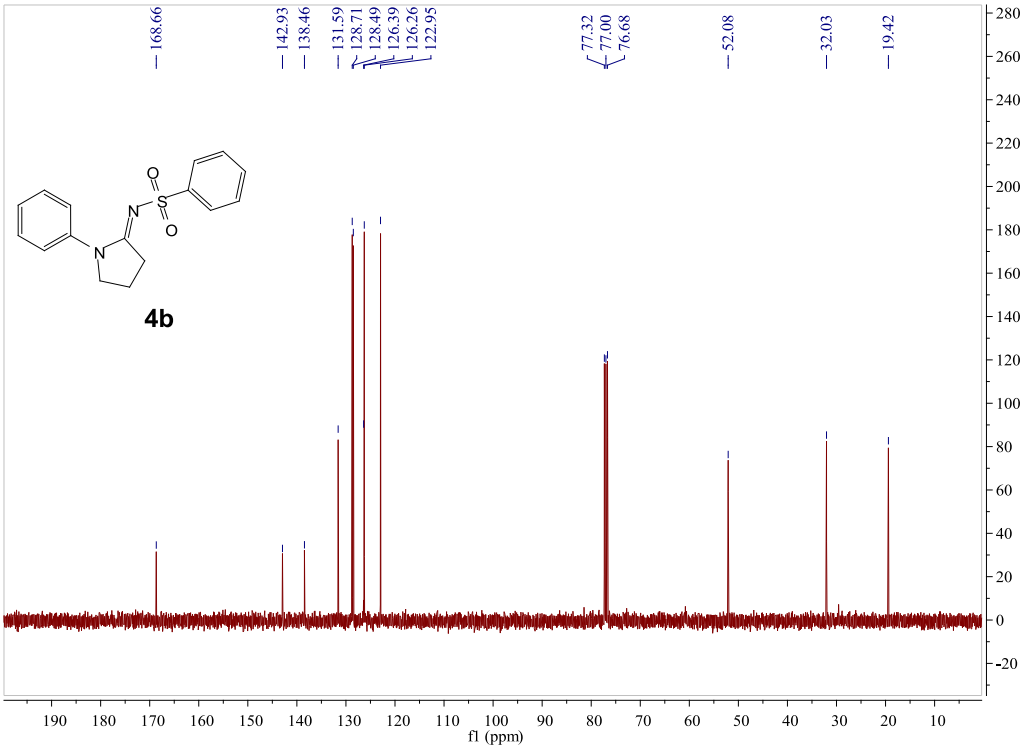
1. J. Yin and S. L. Buchwald, *Org. Lett.*, **2000**, *2*, 1101.
2. G. Barbe and A. B. Charette, *J. Am. Chem. Soc.*, **2008**, *130*, 18.
3. B. Peng, D. Geerdink, C. Farès and N. Maulide, *Angew. Chem. Int. Ed.*, **2014**, *53*, 5462.

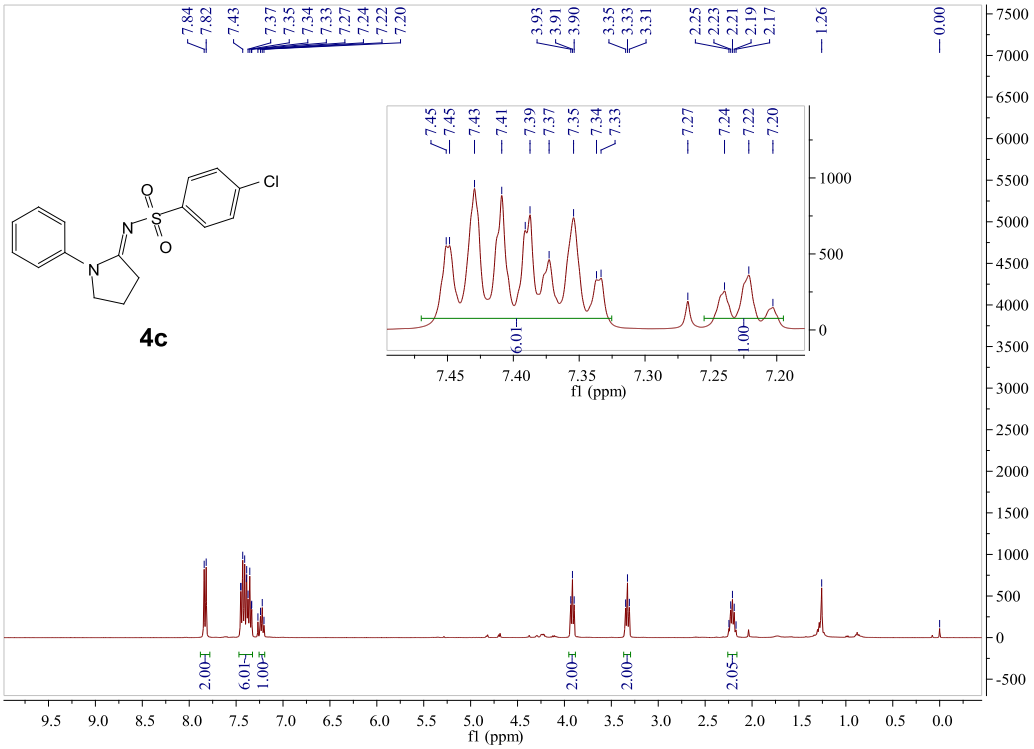
Spectroscopic data for products

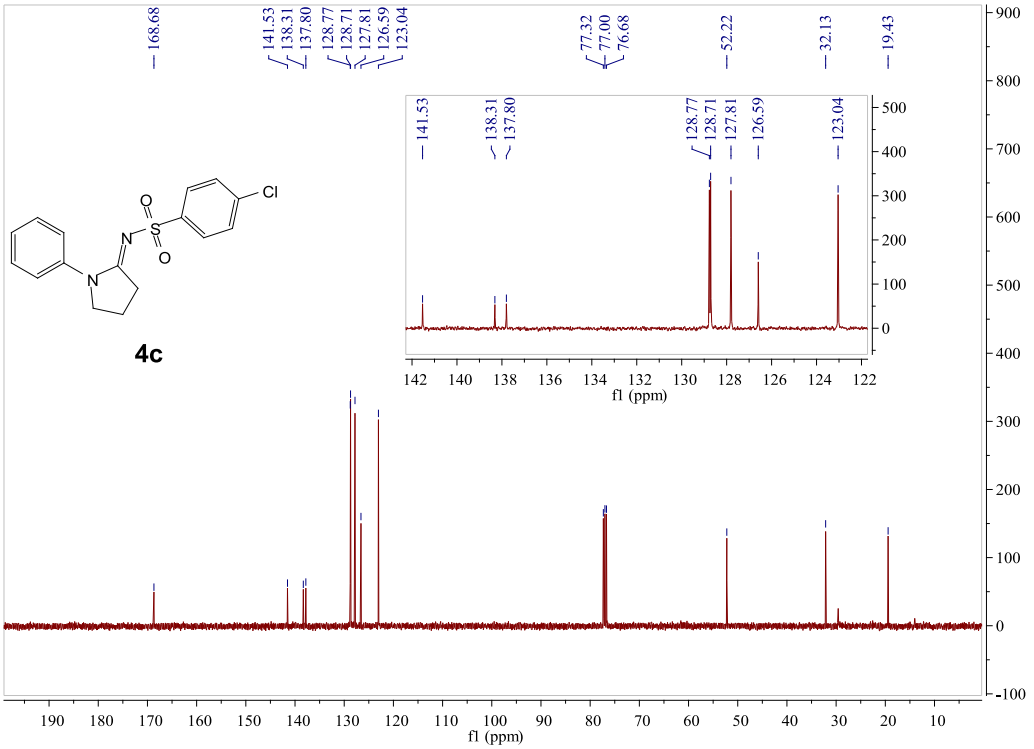


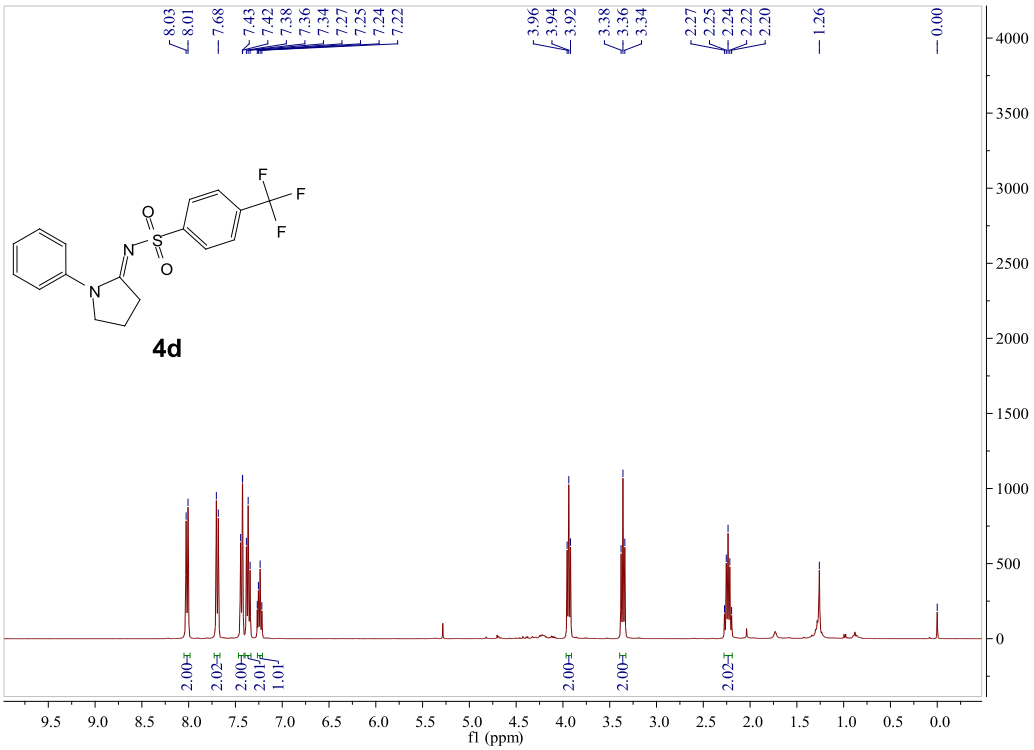


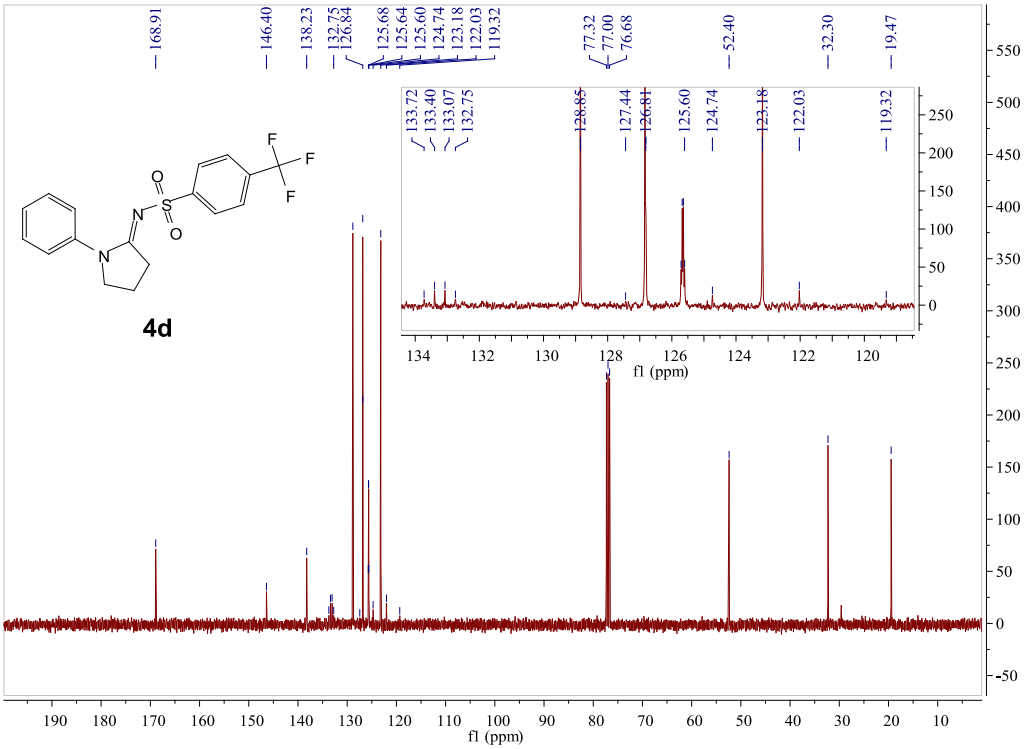

7.92
7.90
7.90
7.48
7.47
7.46
7.43
7.42
7.36
7.32
7.22
7.19
3.91
3.89
3.87
3.34
3.32
3.30
2.22
2.20
2.18
2.16
2.14
1.26
0.00
4b
2.00
5.02
2.00
1.00
2.02
2.02
2.03
fl (ppm)

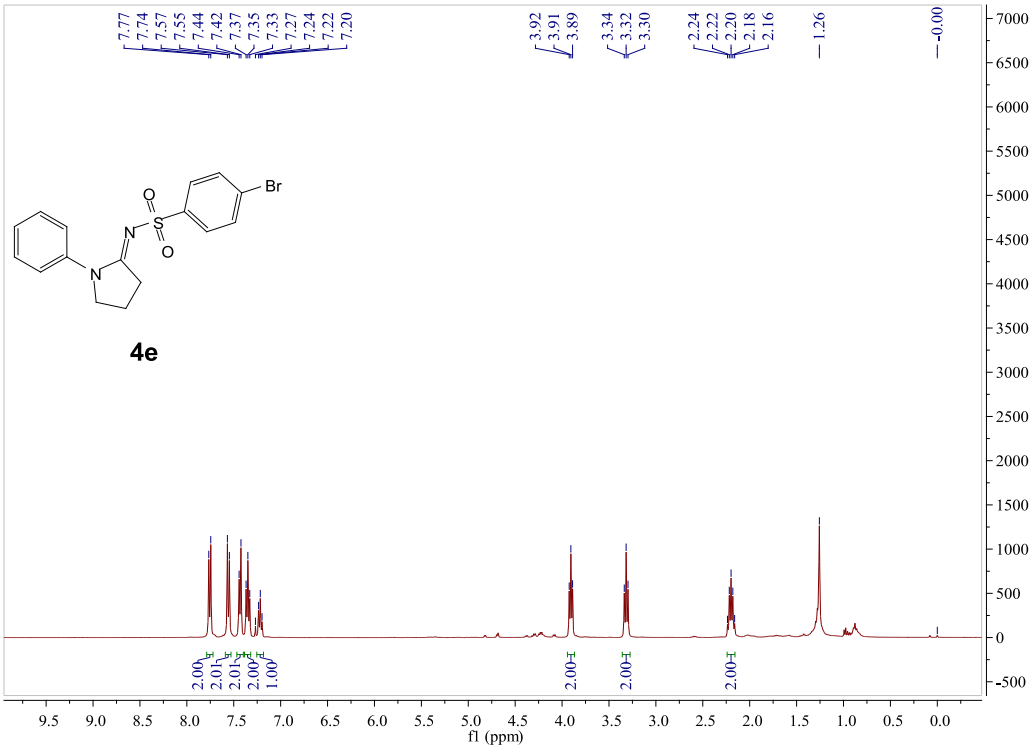

168.66
142.93
138.46
131.59
128.71
128.49
126.39
126.26
122.95
77.32
77.00
76.68
52.08
32.03
19.42
4b
fl (ppm)

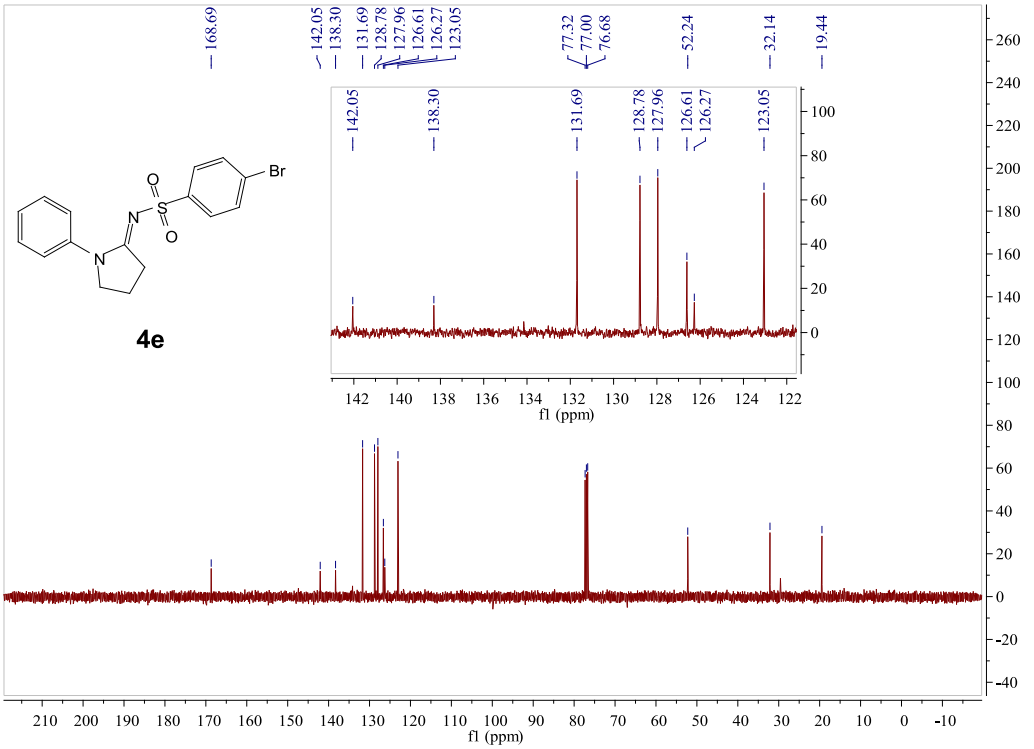

7.84
7.82
7.43
7.37
7.35
7.34
7.33
7.27
7.24
7.22
7.20
3.93
3.91
3.90
3.35
3.33
3.31
2.25
2.23
2.21
2.19
2.17
1.26
0.00
Cl
O
N
S
O
N
4c
7.45
7.45
7.43
7.41
7.39
7.37
7.35
7.34
7.33
7.27
7.24
7.22
7.20
6.01
1.00
fl (ppm)
2.00
6.01
1.00
2.00
2.00
2.05
fl (ppm)

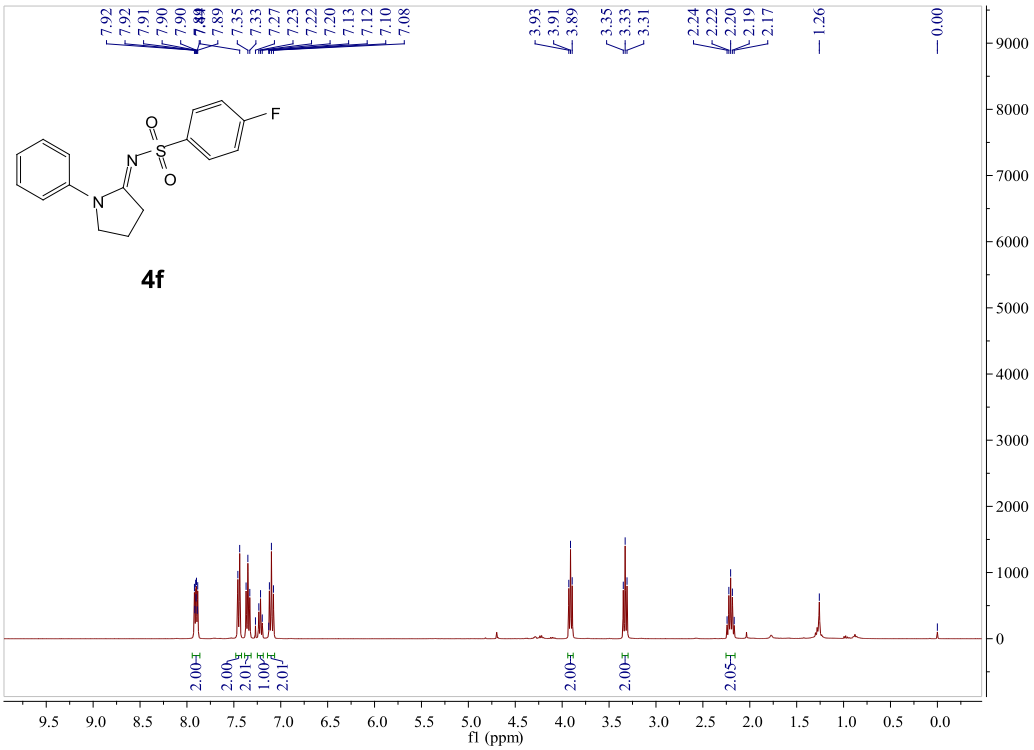

168.68
141.53
138.31
137.80
128.77
128.71
127.81
126.59
123.04
77.32
77.00
76.68
52.22
32.13
19.43
Cl
O
N
S
O
N
4c
141.53
138.31
137.80
128.77
128.71
127.81
126.59
123.04
fl (ppm)
fl (ppm)

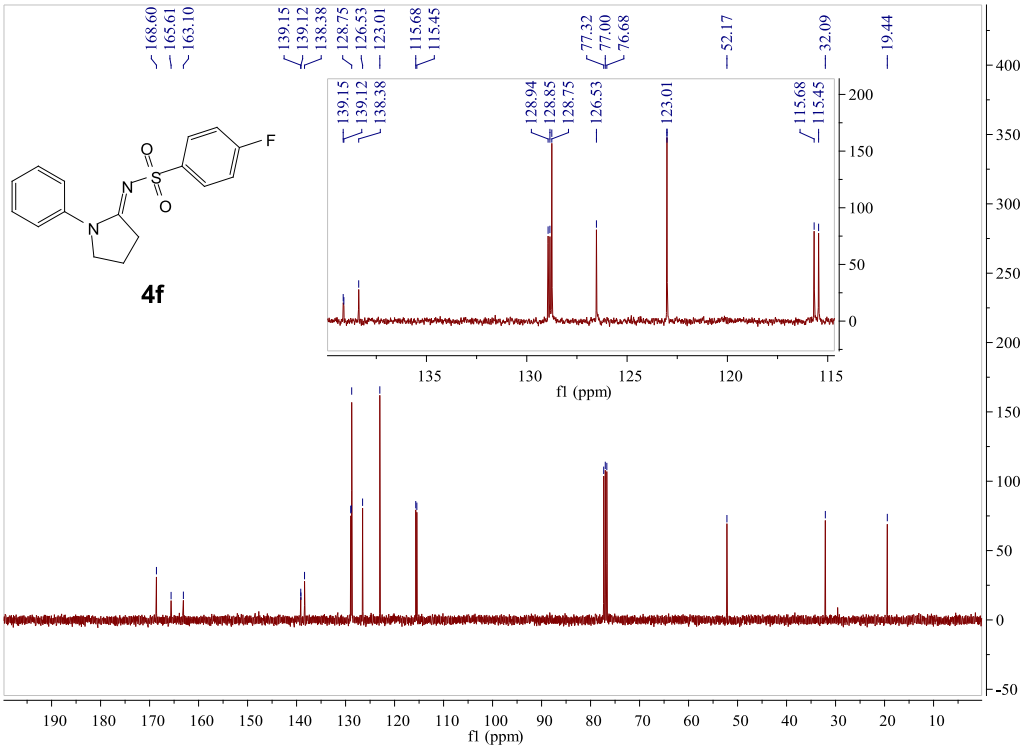

8.03
8.01
7.68
7.43
7.42
7.38
7.36
7.34
7.27
7.25
7.24
7.22
3.96
3.94
3.92
3.38
3.36
3.34
2.27
2.25
2.24
2.22
2.20
1.26
0.00
F
F
F
O
N
S
O
N
4d
2.00
2.02
2.00
2.01
1.01
2.00
2.00
2.02
fl (ppm)

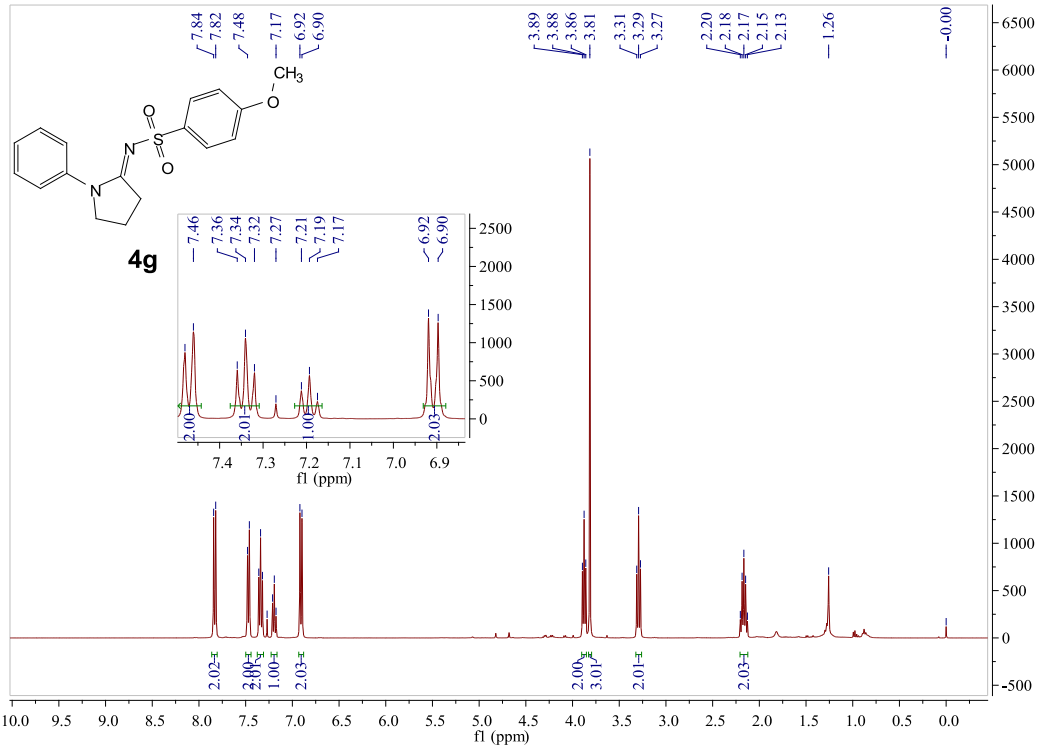

168.91
146.40
138.23
132.75
126.84
125.68
125.64
125.60
124.74
123.18
122.03
119.32
77.32
77.00
76.68
52.40
32.30
19.47
133.72
133.40
133.07
132.75
128.85
127.44
126.81
125.60
124.74
123.18
122.03
119.32
F
F
F
O
N
S
O
N
4d
fl (ppm)
fl (ppm)

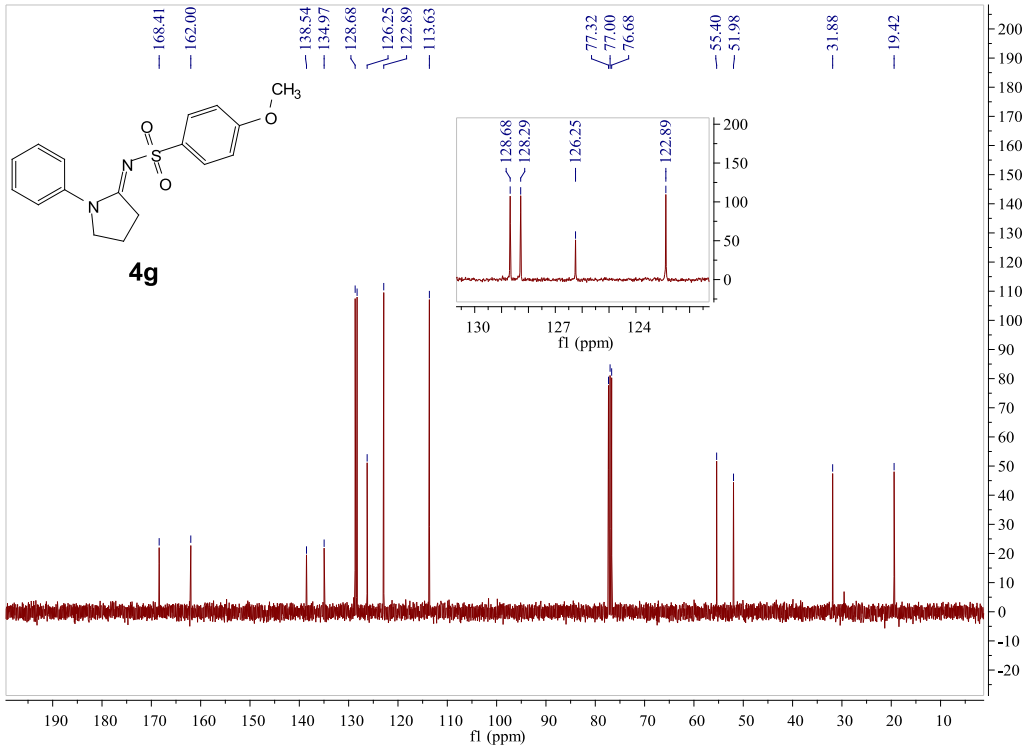

7.77
7.74
7.57
7.55
7.44
7.42
7.37
7.35
7.33
7.27
7.24
7.22
7.20
3.92
3.91
3.89
3.34
3.32
3.30
2.24
2.22
2.20
2.18
2.16
1.26
-0.00
Br
O
N
S
O
N
4e
2.00
2.01
2.01
2.00
1.00
2.00
2.00
2.00
fl (ppm)

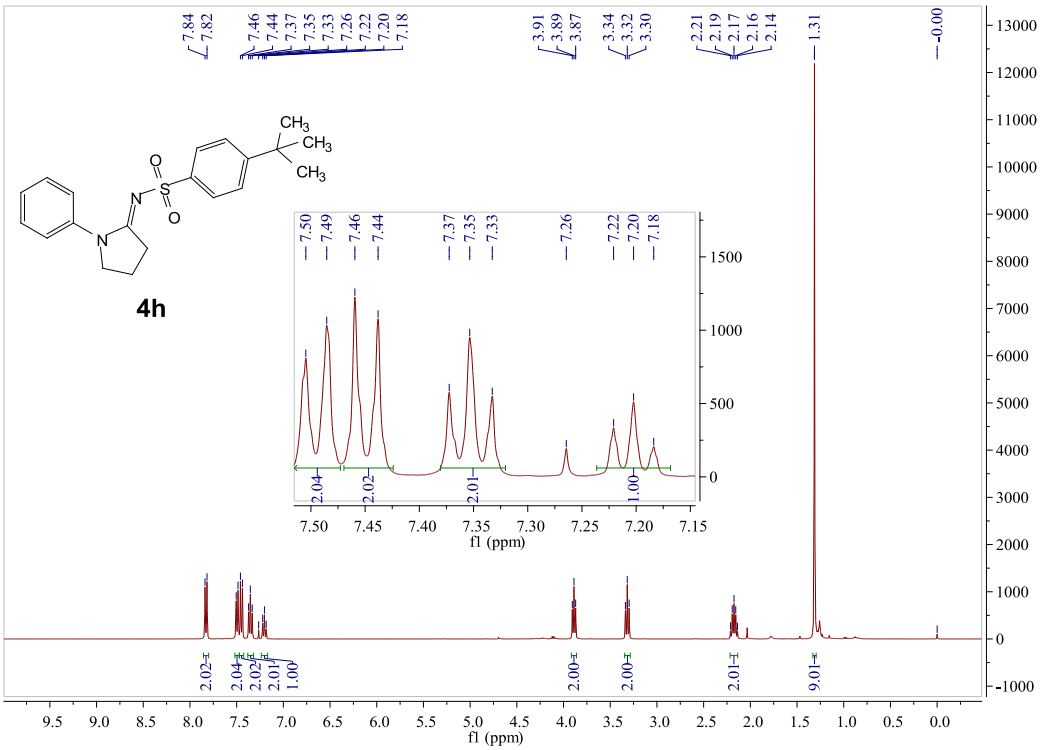

168.69
142.05
138.30
131.69
128.78
127.96
126.61
126.27
123.05
77.32
77.00
76.68
52.24
32.14
19.44
Br
O
N
S
O
N
4e
fl (ppm)
fl (ppm)

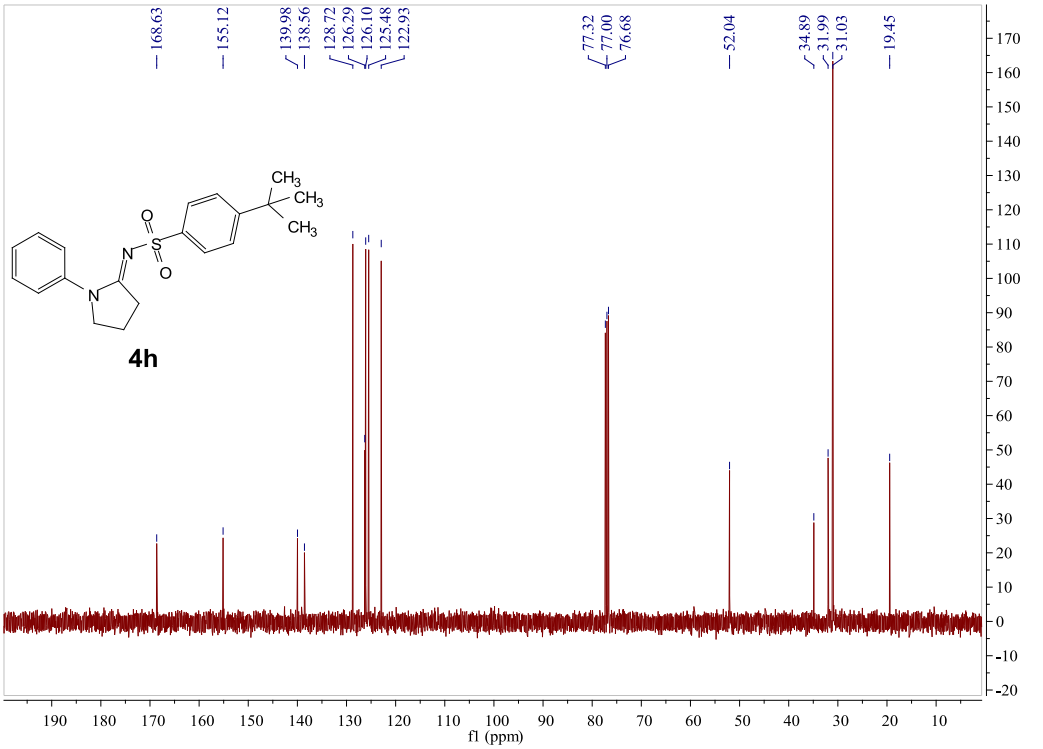

7.92
7.92
7.91
7.90
7.90
7.89
7.35
7.33
7.27
7.23
7.22
7.20
7.13
7.12
7.10
7.08
3.93
3.91
3.89
3.35
3.33
3.31
2.24
2.22
2.20
2.19
2.17
1.26
0.00
F
O
S
O
N
N
4f
2.00
2.00
2.01
1.00
2.01
2.00
2.00
2.05
f1 (ppm)

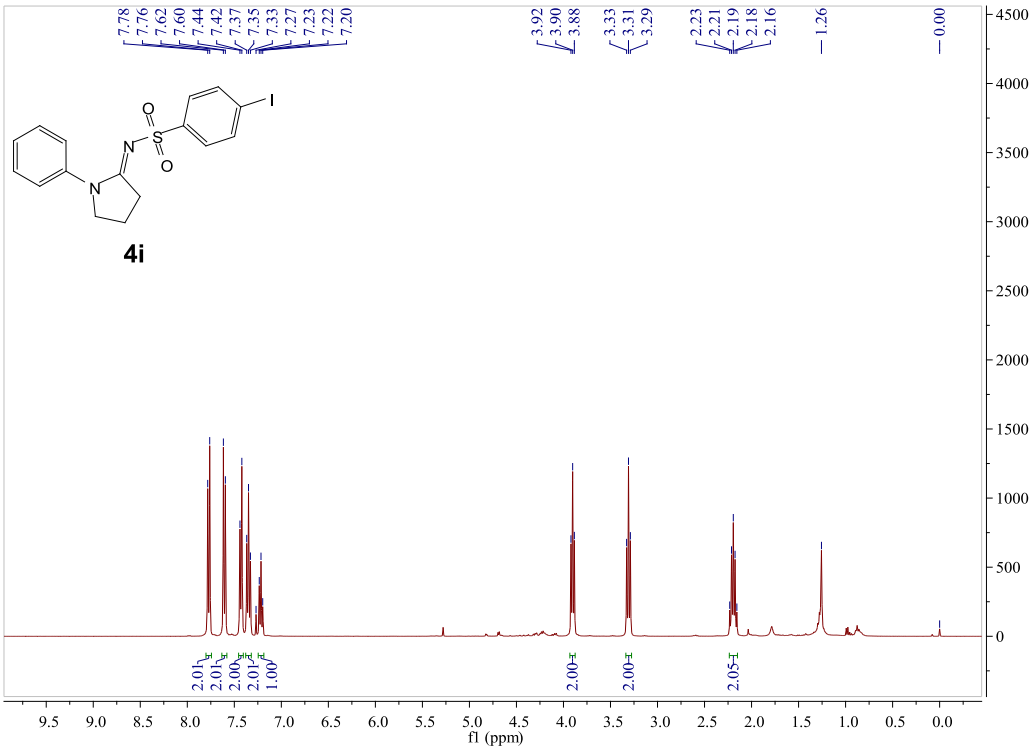

168.60
165.61
163.10
139.15
139.12
138.38
128.75
126.53
123.01
115.68
115.45
77.32
77.00
76.68
52.17
32.09
19.44
F
O
S
O
N
N
4f
f1 (ppm)

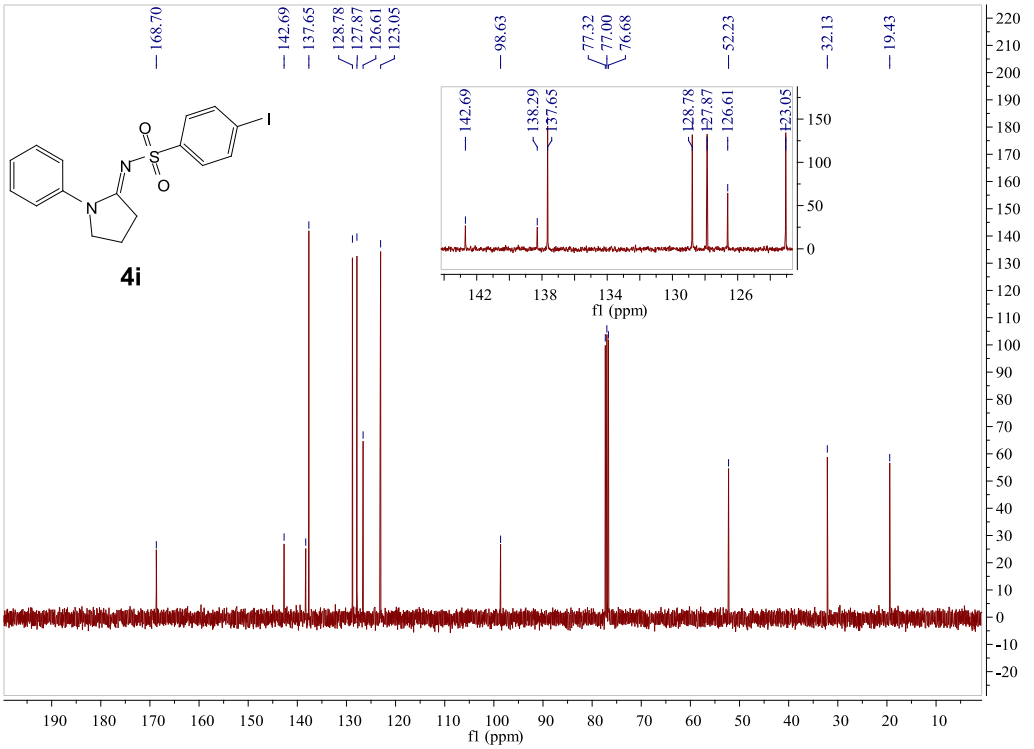

4g
fl (ppm)

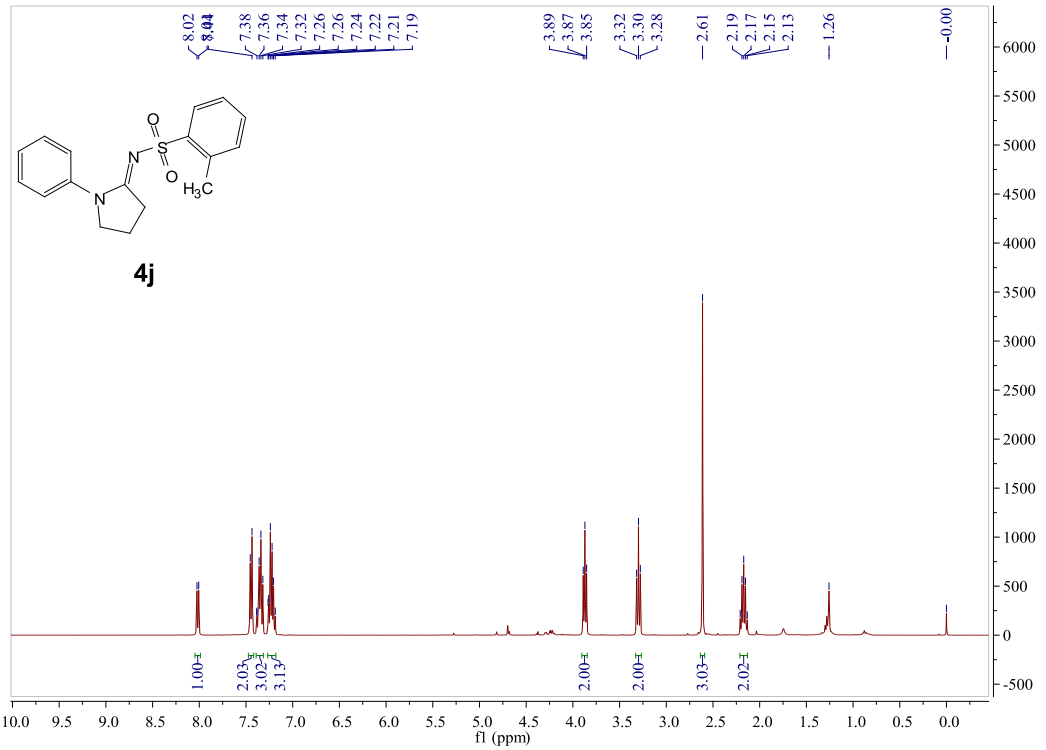

4g
fl (ppm)

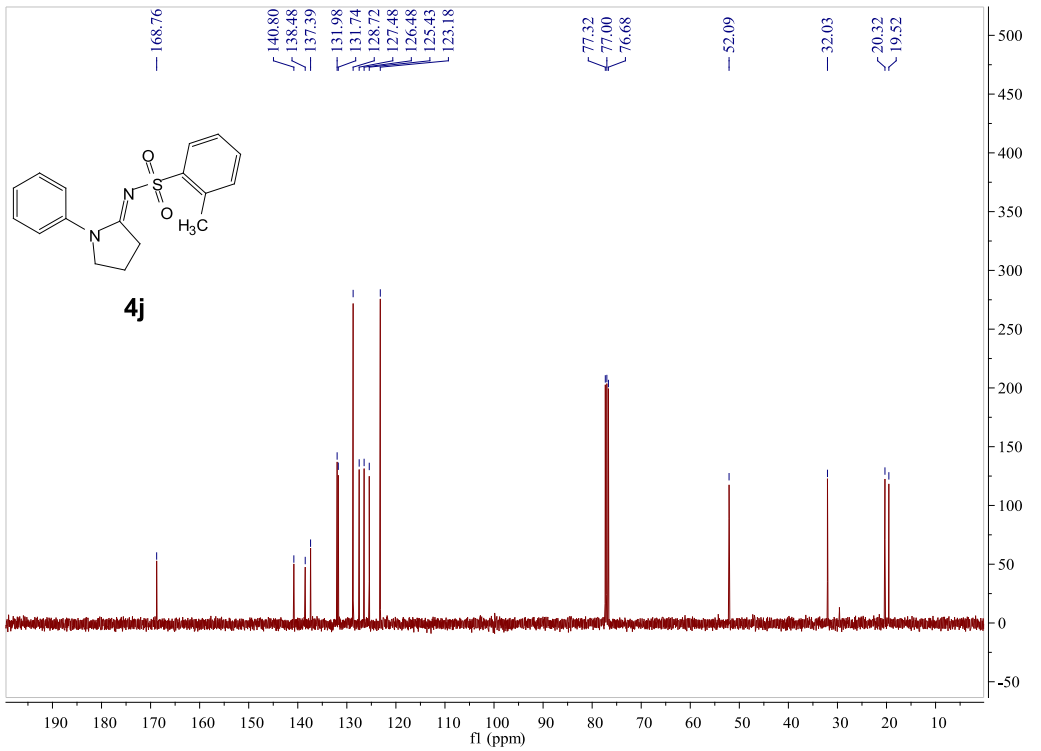

7.84
7.82
7.46
7.44
7.37
7.35
7.33
7.26
7.22
7.20
7.18
3.91
3.89
3.87
3.34
3.32
3.30
2.21
2.19
2.17
2.16
2.14
1.31
-0.00
4h
fl (ppm)

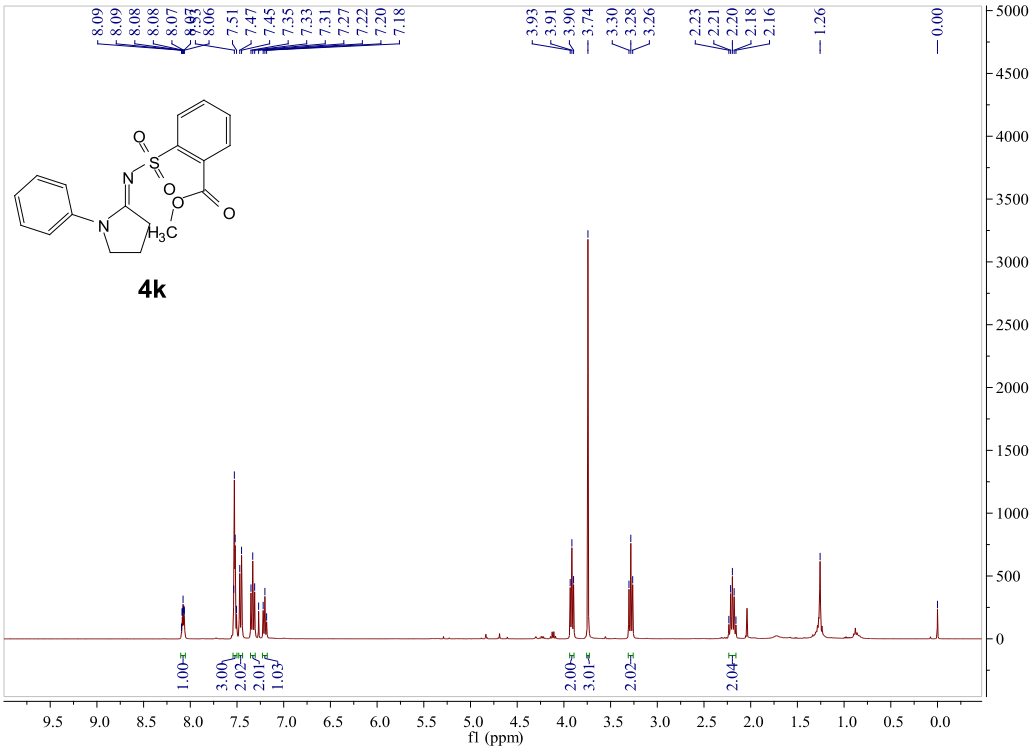

168.63
155.12
139.98
138.56
128.72
126.29
126.10
125.48
122.93
77.32
77.00
76.68
52.04
34.89
31.99
31.03
19.45
4h
fl (ppm)

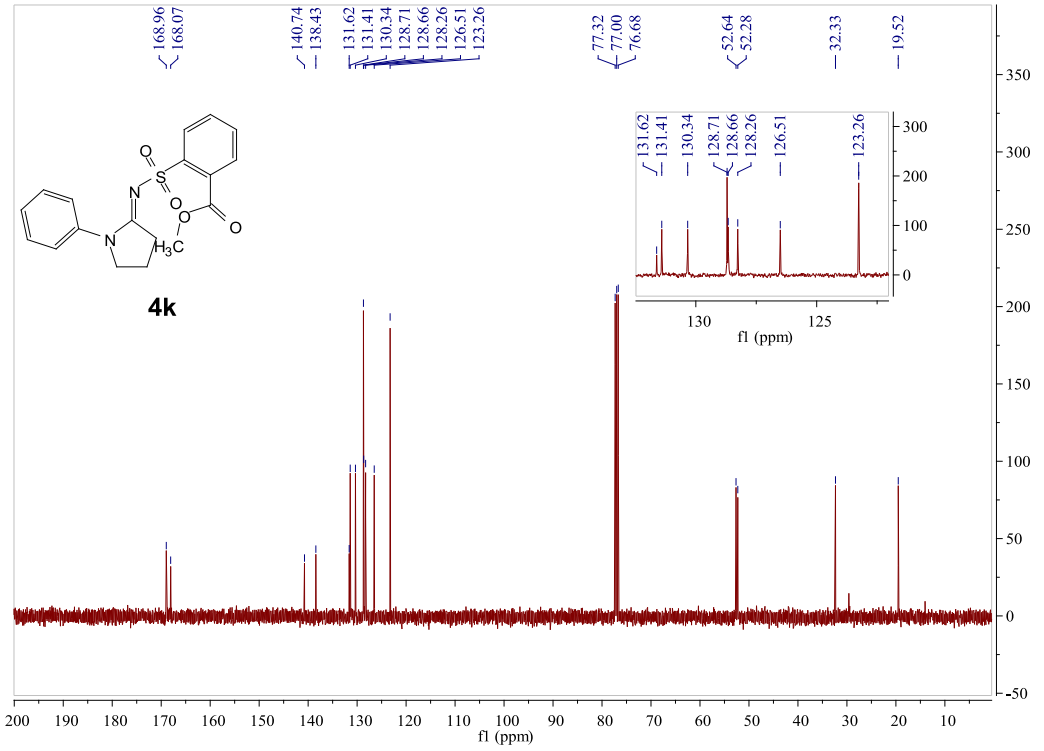

7.78
7.76
7.62
7.60
7.44
7.42
7.37
7.35
7.33
7.27
7.23
7.22
7.20
3.92
3.90
3.88
3.33
3.31
3.29
2.23
2.21
2.19
2.18
2.16
1.26
0.00
I
O
N
S
O
N
4i
2.01
2.01
2.00
2.01
1.00
2.00
2.00
2.05
f1 (ppm)

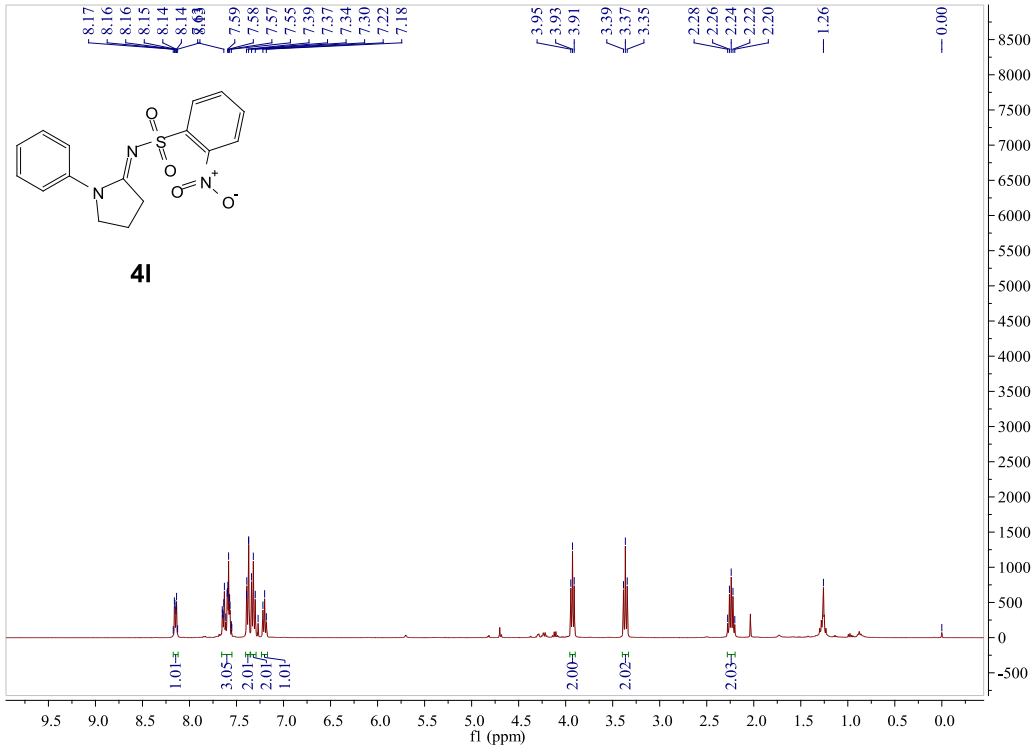

168.70
142.69
137.65
128.78
127.87
126.61
123.05
98.63
77.32
77.00
76.68
52.23
32.13
19.43
I
O
N
S
O
N
4i
142.69
138.29
137.65
128.78
127.87
126.61
123.05
f1 (ppm)
f1 (ppm)

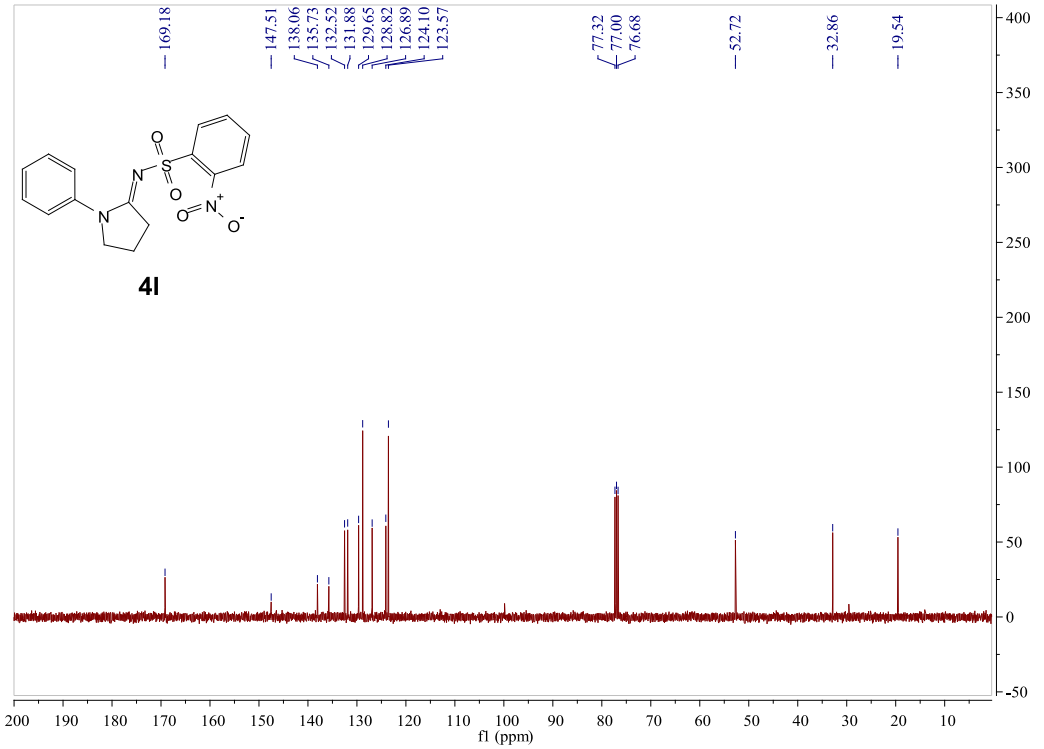

8.02
7.38
7.36
7.34
7.32
7.26
7.24
7.22
7.21
7.19
3.89
3.87
3.85
3.32
3.30
3.28
2.61
2.19
2.17
2.15
2.13
1.26
-0.00
1.00
2.03
3.02
3.13
2.00
2.00
3.03
2.02
fl (ppm)

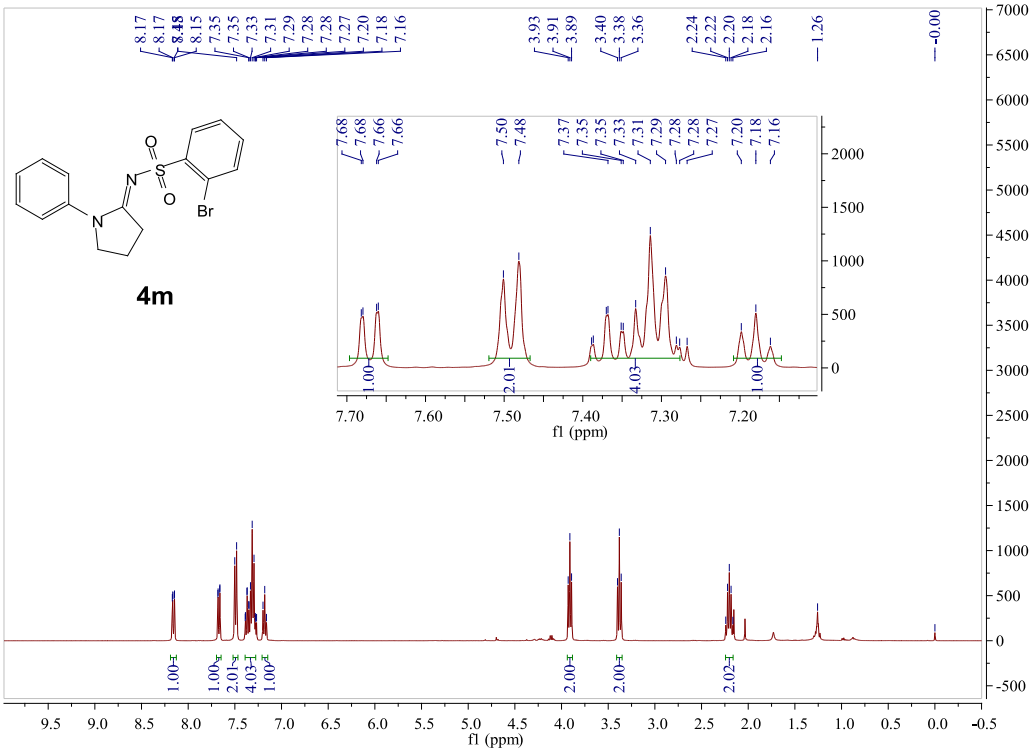

168.76
140.80
138.48
137.39
131.98
131.74
128.72
127.48
126.48
125.43
123.18
77.32
77.00
76.68
52.09
32.03
20.32
19.52
fl (ppm)

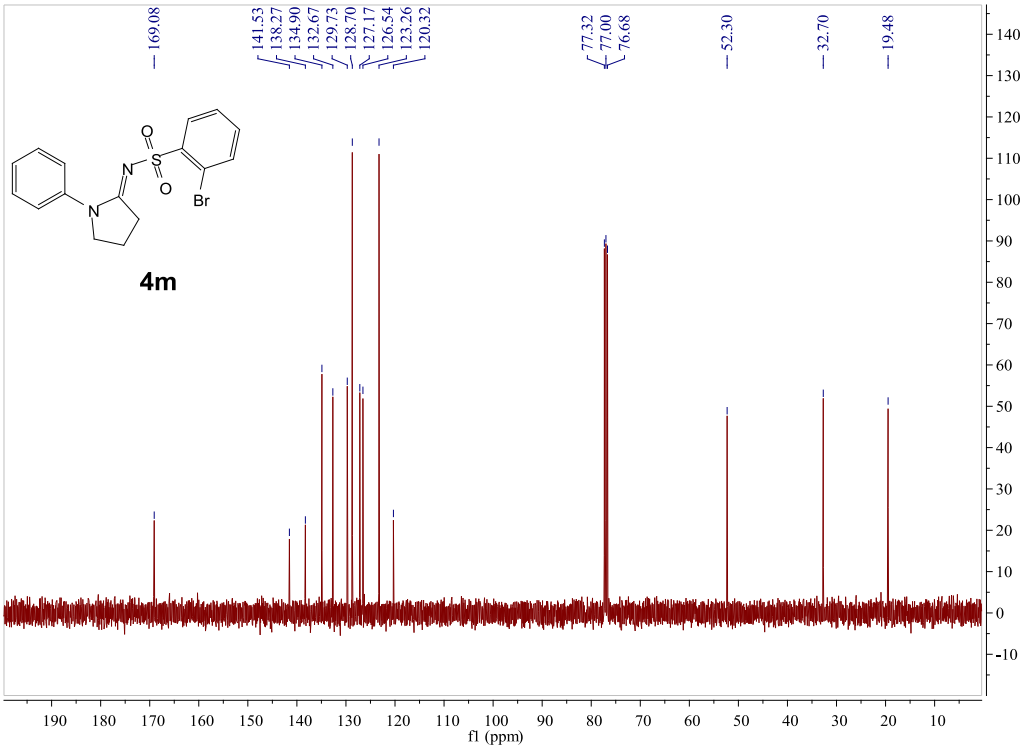

8.09
8.09
8.08
8.08
8.07
8.07
8.06
7.51
7.47
7.45
7.35
7.33
7.31
7.27
7.22
7.20
7.18
3.93
3.91
3.90
3.74
3.30
3.28
3.26
2.23
2.21
2.20
2.18
2.16
1.26
0.00
1.00
3.00
2.02
2.01
1.03
2.00
3.01
2.02
2.04
4k
fl (ppm)

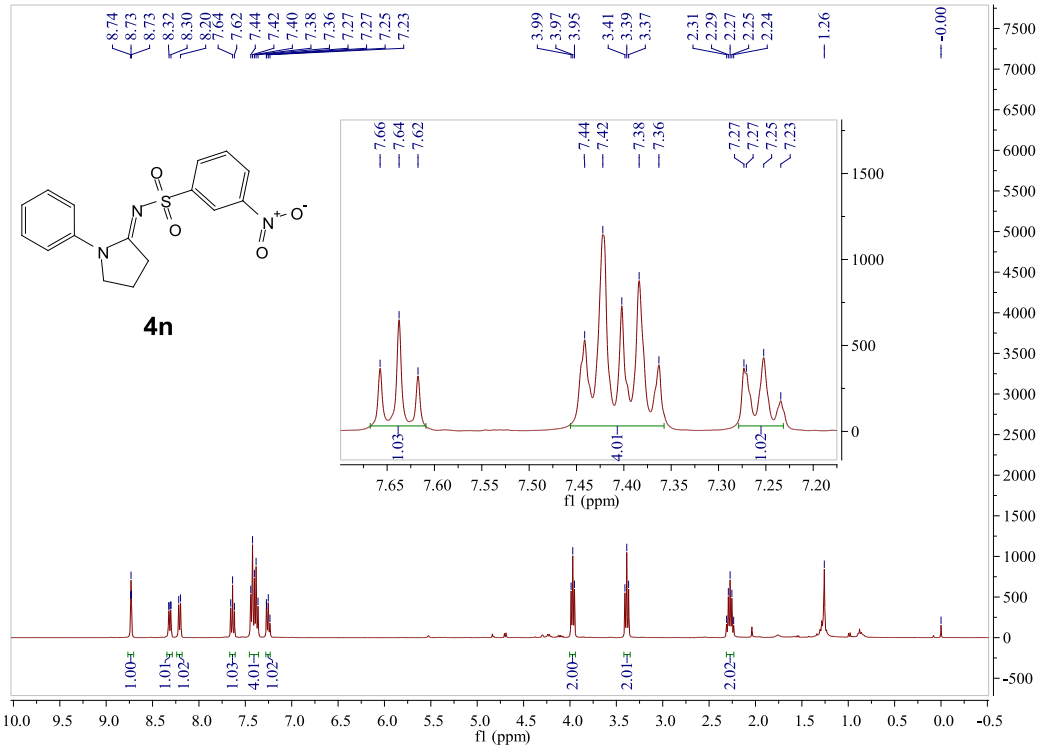

168.96
168.07
140.74
138.43
131.62
131.41
130.34
128.71
128.66
128.26
126.51
123.26
77.32
77.00
76.68
52.64
52.28
32.33
19.52
4k
fl (ppm)

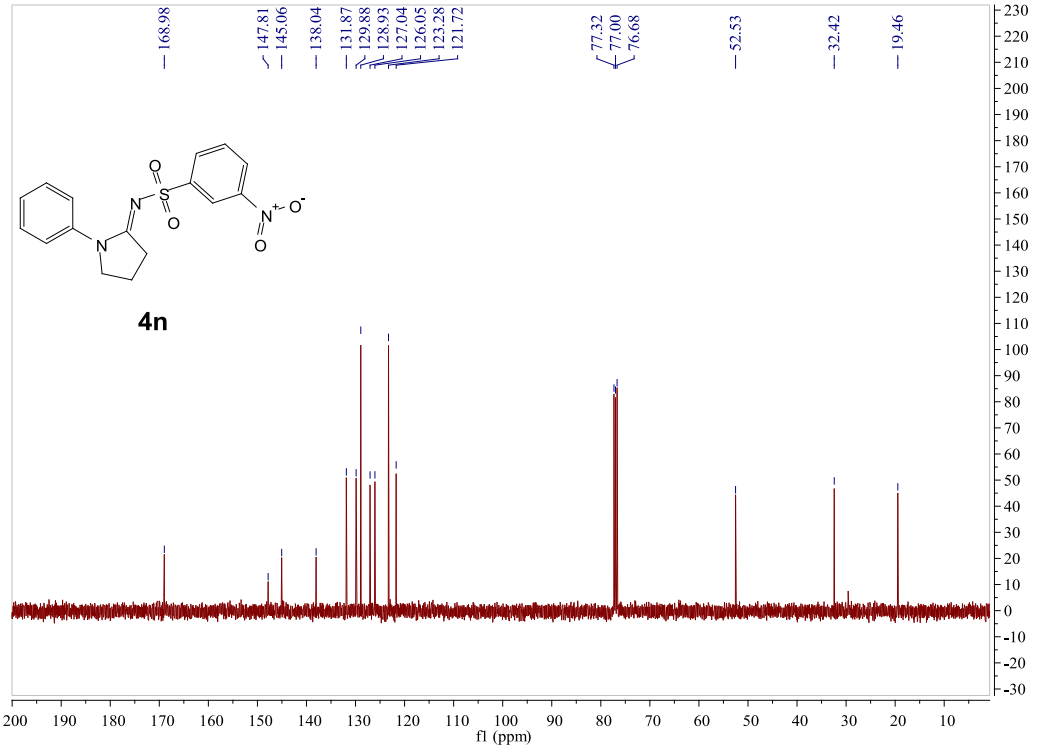

8.17
8.16
8.16
8.15
8.14
8.14
7.59
7.58
7.57
7.55
7.39
7.37
7.34
7.30
7.22
7.18
3.95
3.93
3.91
3.39
3.37
3.35
2.28
2.26
2.24
2.22
2.20
1.26
0.00
4l
1.01
3.05
2.01
2.01
1.01
2.00
2.02
2.03
f1 (ppm)

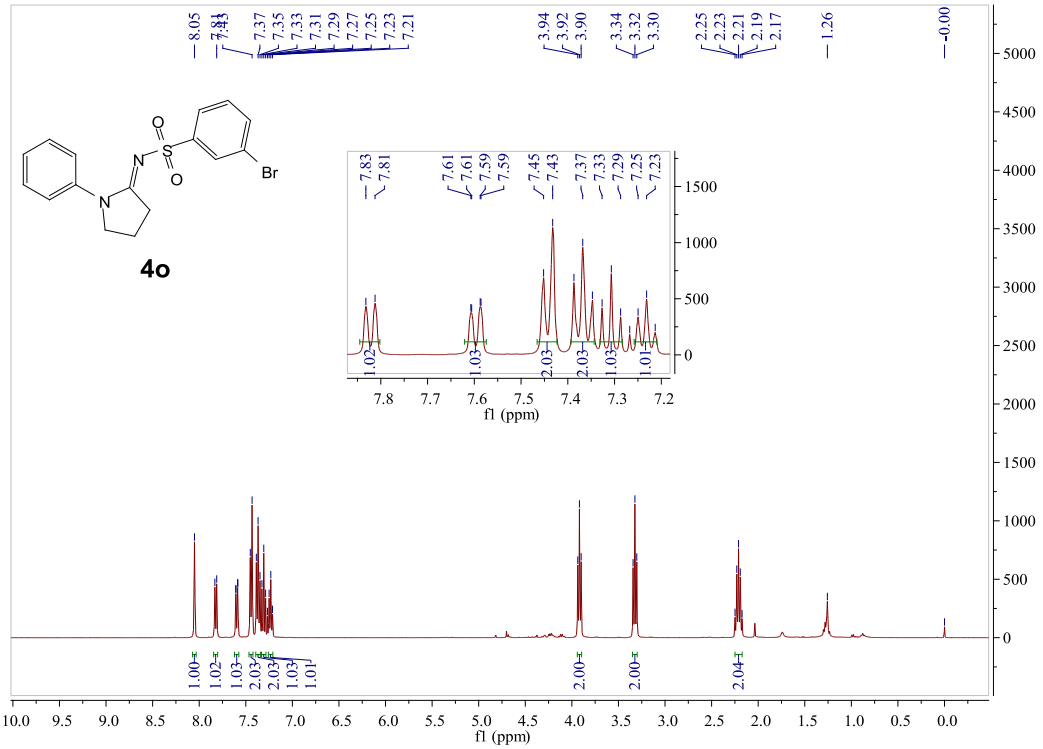

169.18
147.51
138.06
135.73
132.52
131.88
129.65
128.82
126.89
124.10
123.57
77.32
77.00
76.68
52.72
32.86
19.54
4l
f1 (ppm)

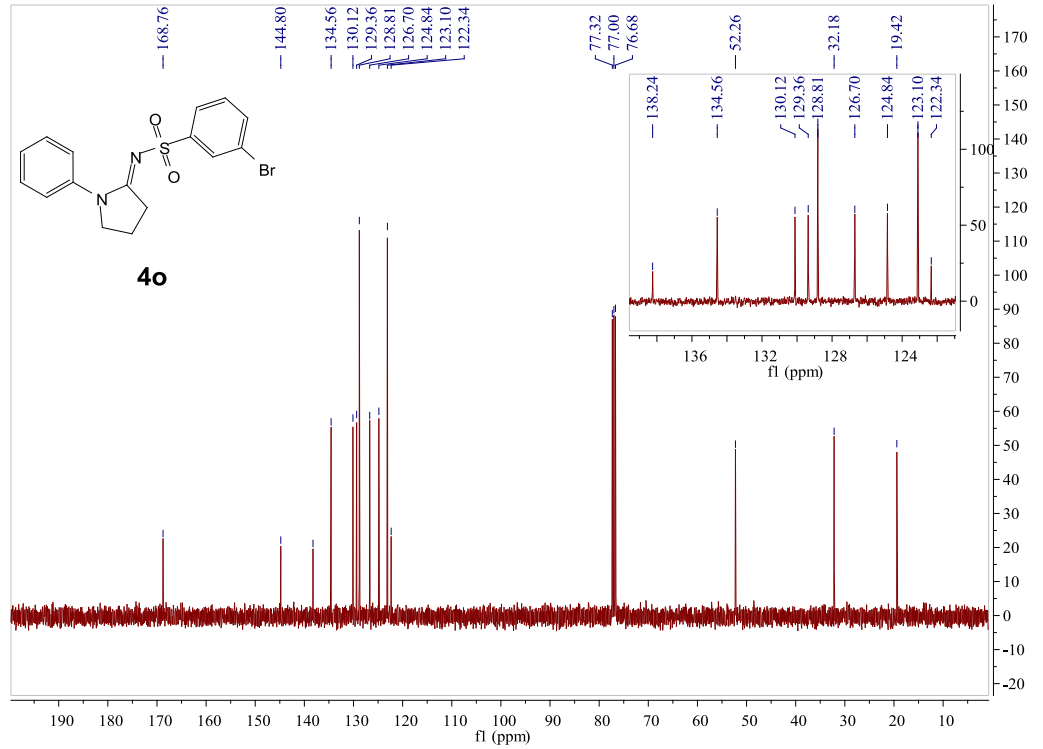

4m
fl (ppm)

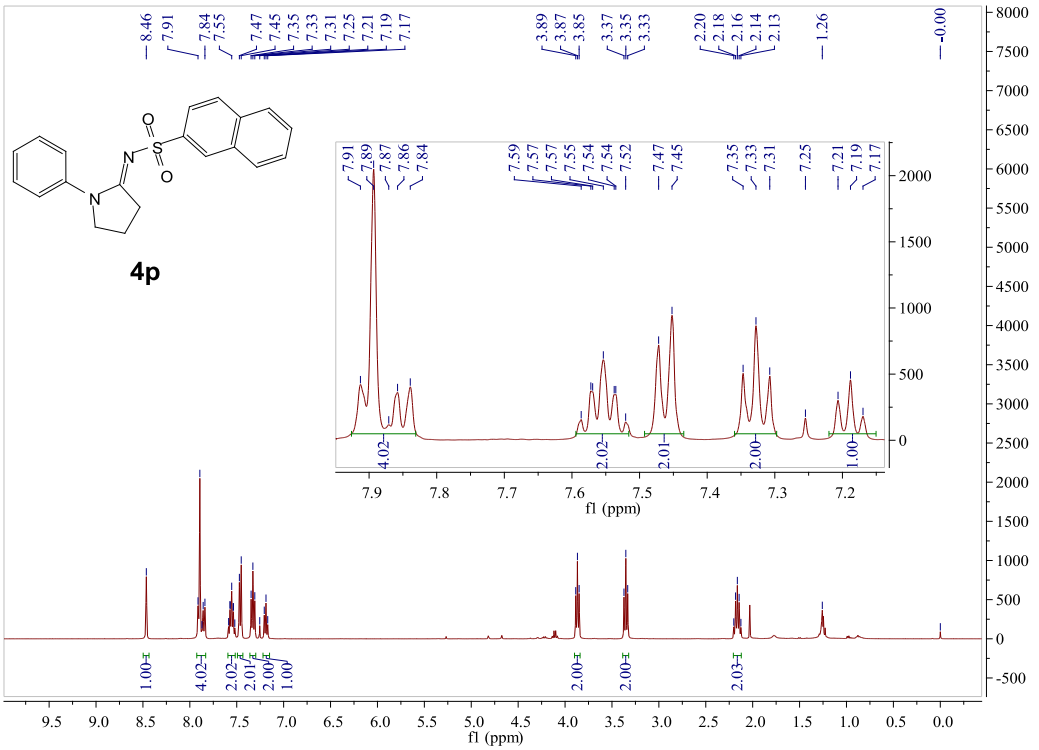

4m
fl (ppm)

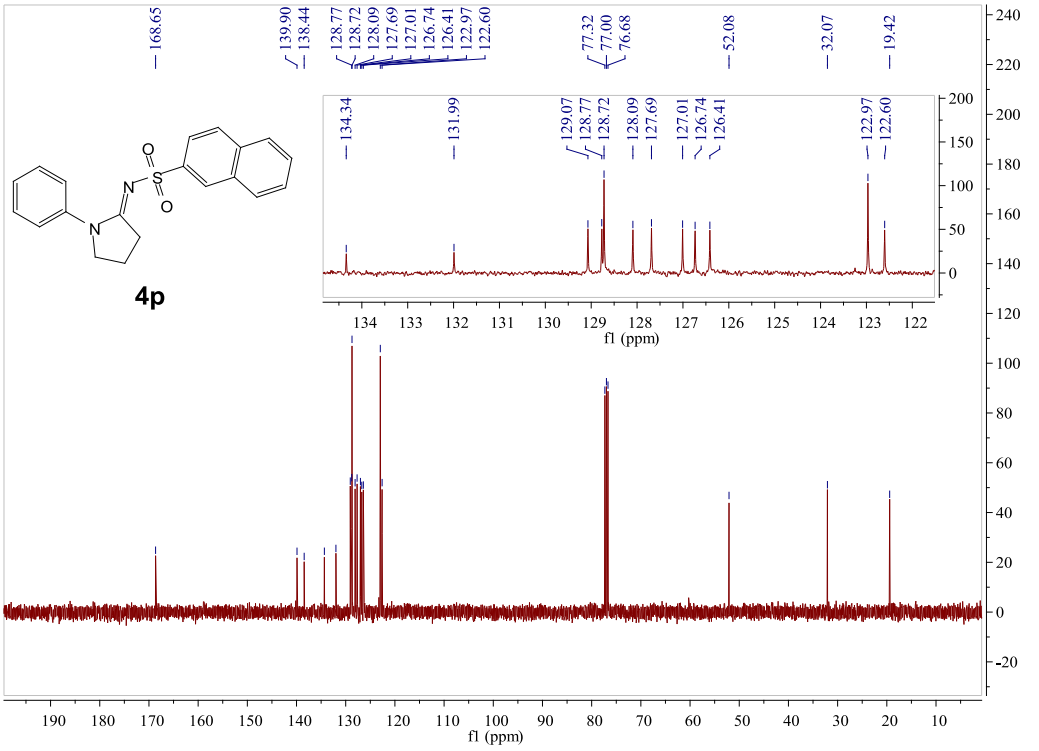

8.74
8.73
8.73
8.32
8.30
8.20
7.64
7.62
7.44
7.42
7.40
7.38
7.36
7.27
7.27
7.25
7.23
3.99
3.97
3.95
3.41
3.39
3.37
2.31
2.29
2.27
2.25
2.24
1.26
0.00
4n
1.00
1.01
1.02
1.03
4.01
1.02
2.00
2.01
2.02
f1 (ppm)

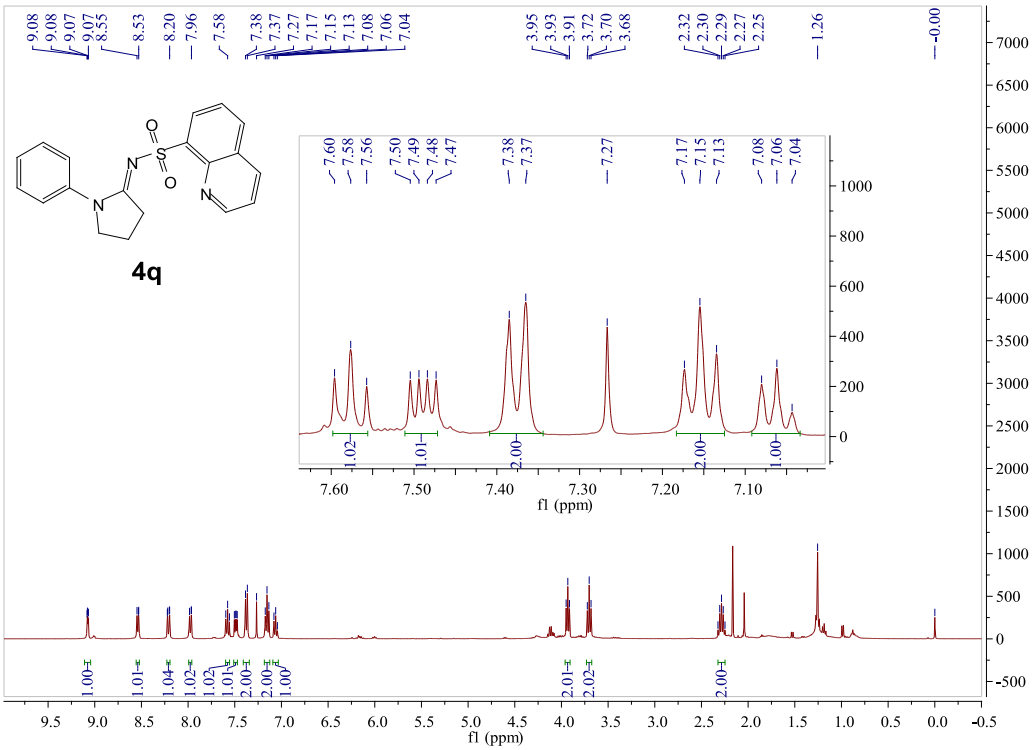

168.98
147.81
145.06
138.04
131.87
129.88
128.93
127.04
126.05
123.28
121.72
77.32
77.00
76.68
52.53
32.42
19.46
4n
f1 (ppm)

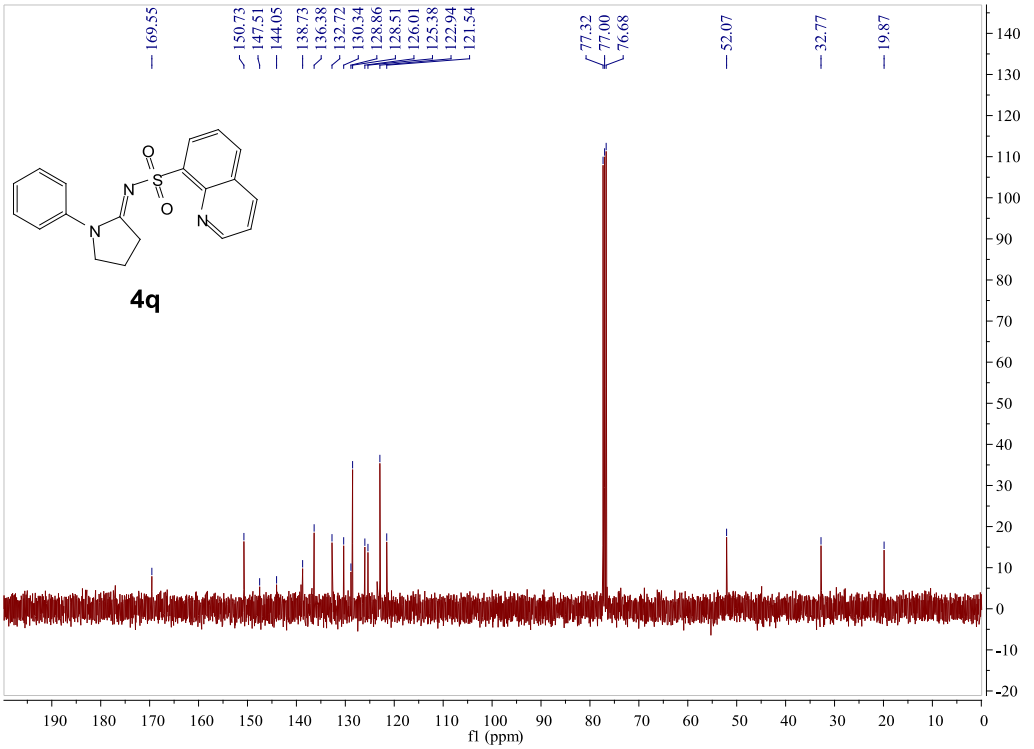

8.05
7.81
7.37
7.35
7.33
7.31
7.29
7.27
7.25
7.23
7.21
3.94
3.92
3.90
3.34
3.32
3.30
2.25
2.23
2.21
2.19
2.17
1.26
-0.00
Br
4o
fl (ppm)
1.00
1.02
1.03
2.03
2.03
1.03
1.01
2.00
2.00
2.04

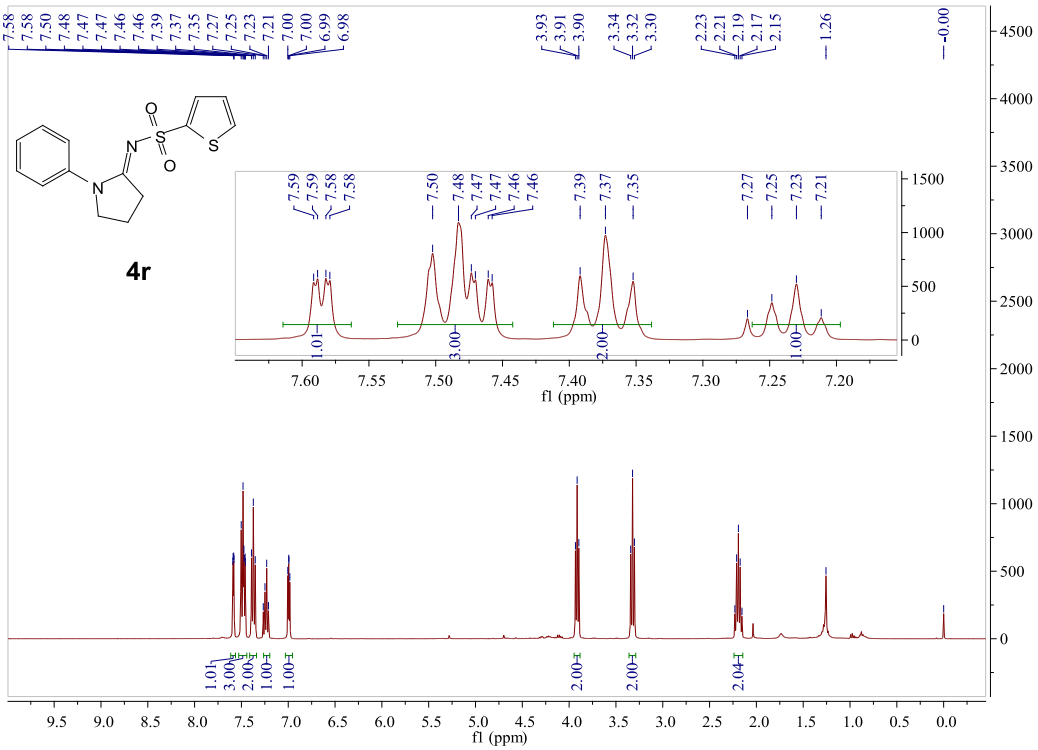

168.76
144.80
134.56
130.12
129.36
128.81
126.70
124.84
123.10
122.34
77.32
77.00
76.68
52.26
32.18
19.42
Br
4o
fl (ppm)

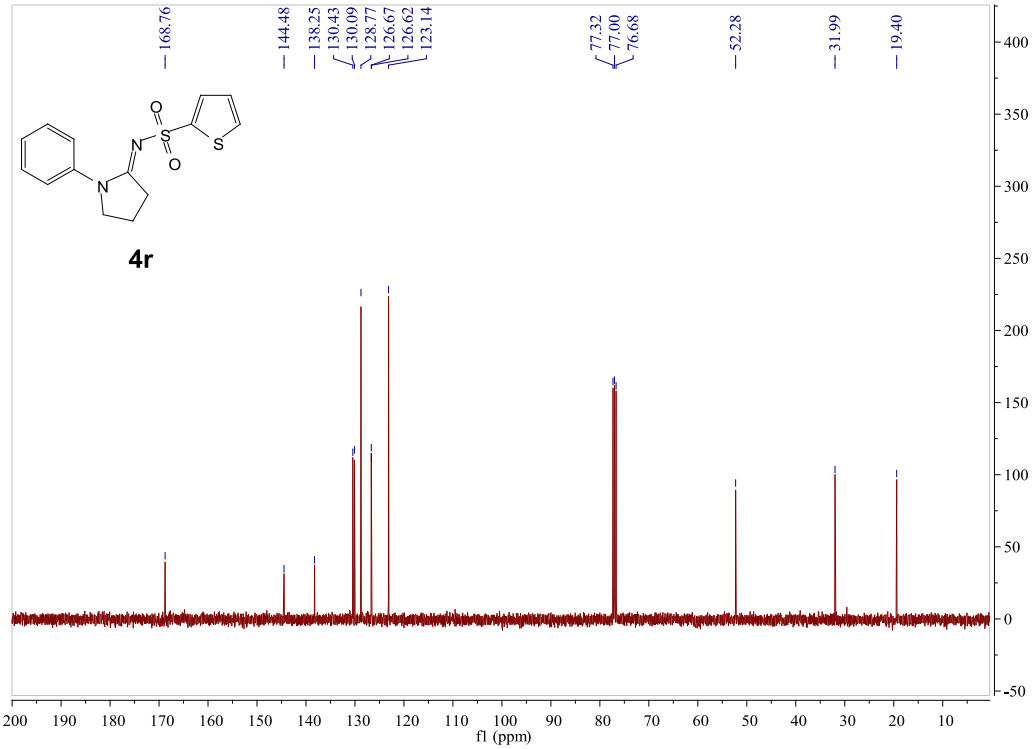

8.46
7.91
7.84
7.55
7.47
7.45
7.35
7.33
7.31
7.25
7.21
7.19
7.17
3.89
3.87
3.85
3.37
3.35
3.33
2.20
2.18
2.16
2.14
2.13
1.26
-0.00
4p
fl (ppm)
1.00
4.02
2.02
2.01
2.00
1.00
2.00
2.00
2.03

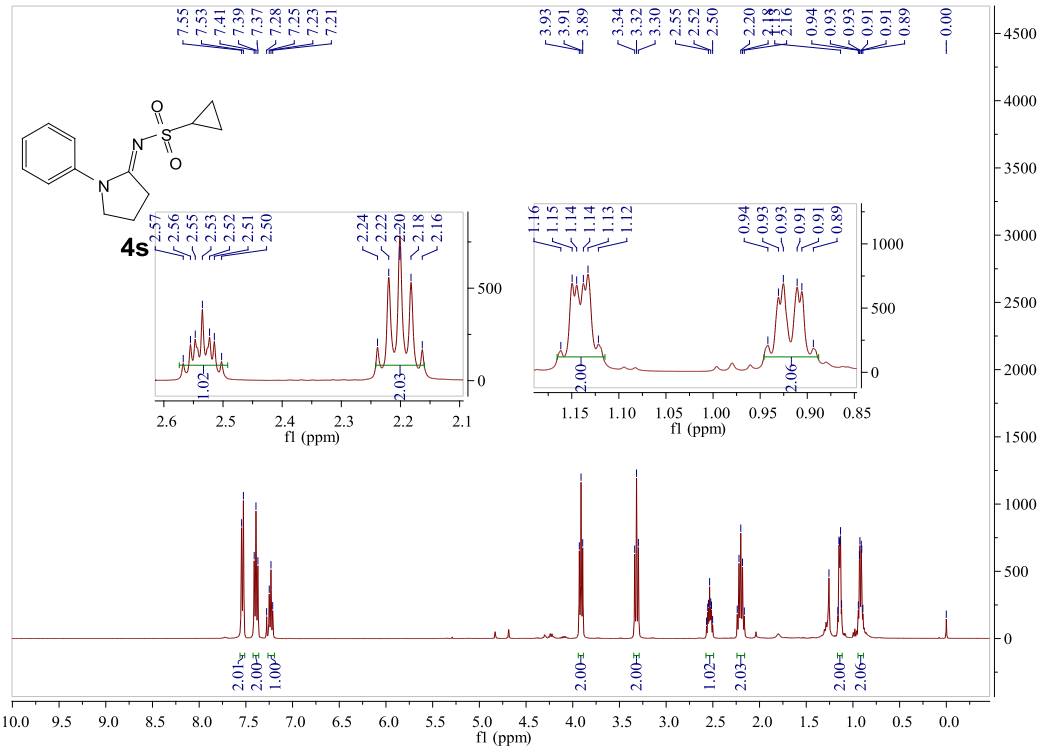

168.65
139.90
138.44
128.77
128.72
128.09
127.69
127.01
126.74
126.41
122.97
122.60
77.32
77.00
76.68
52.08
32.07
19.42
4p
fl (ppm)

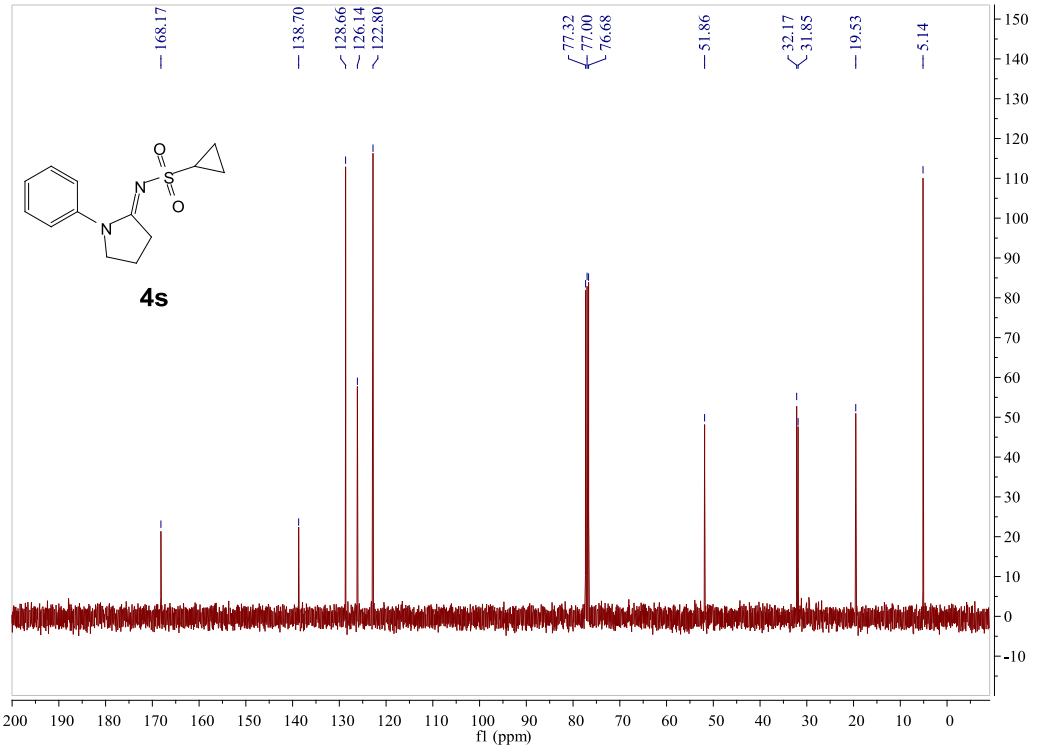

4q
fl (ppm)

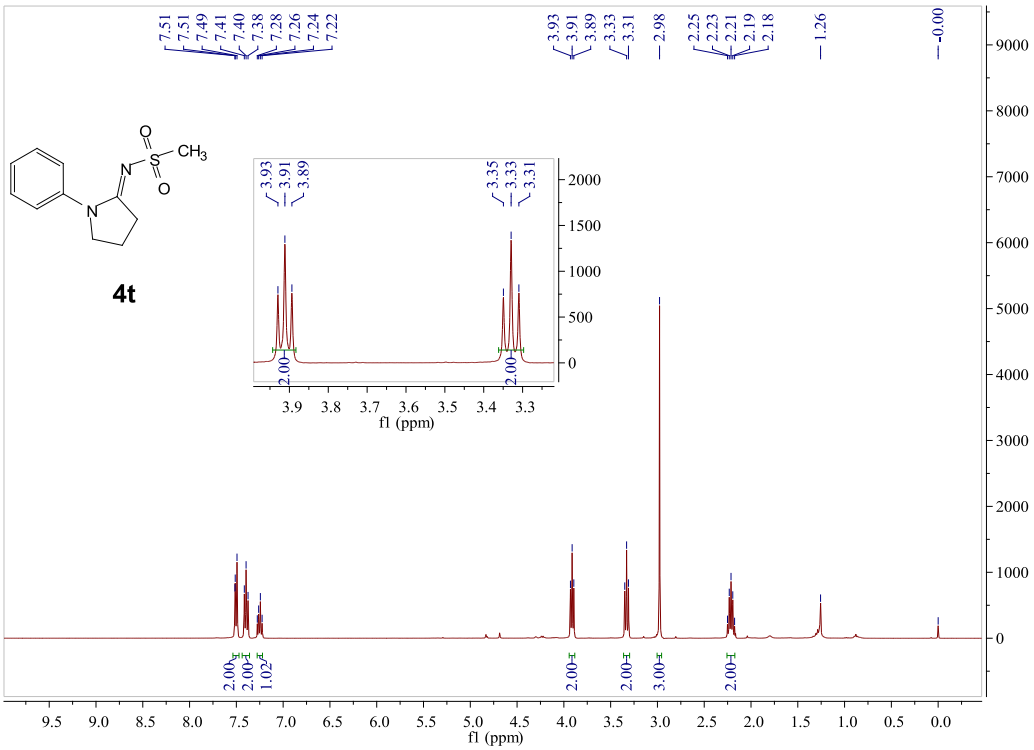

4q
fl (ppm)

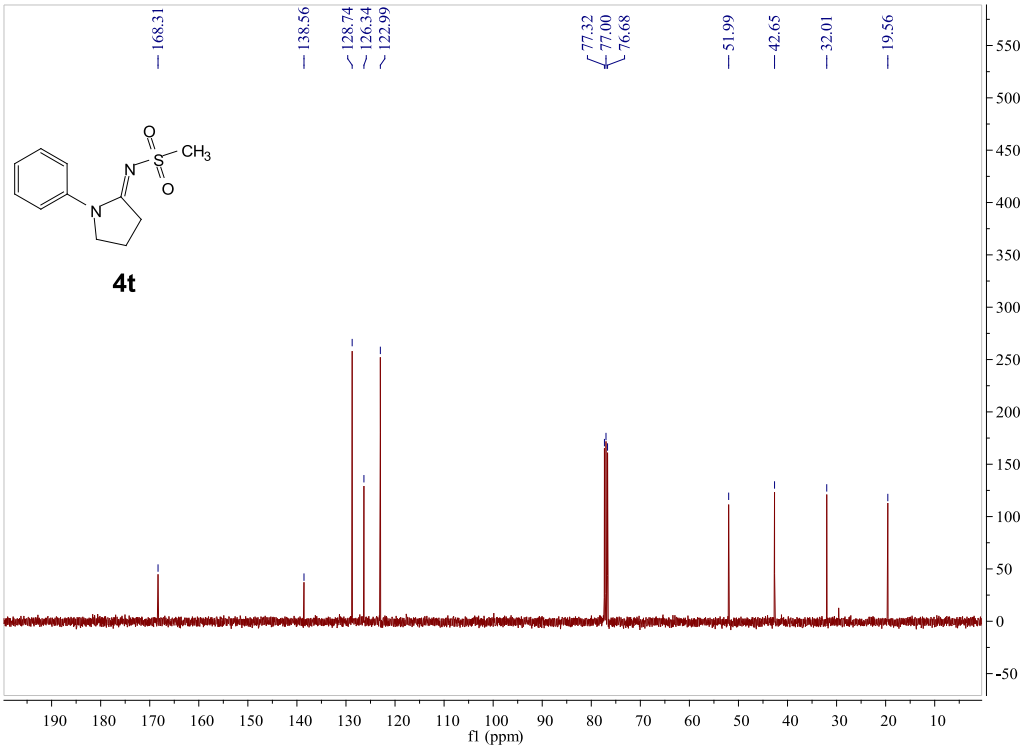

4r
fl (ppm)

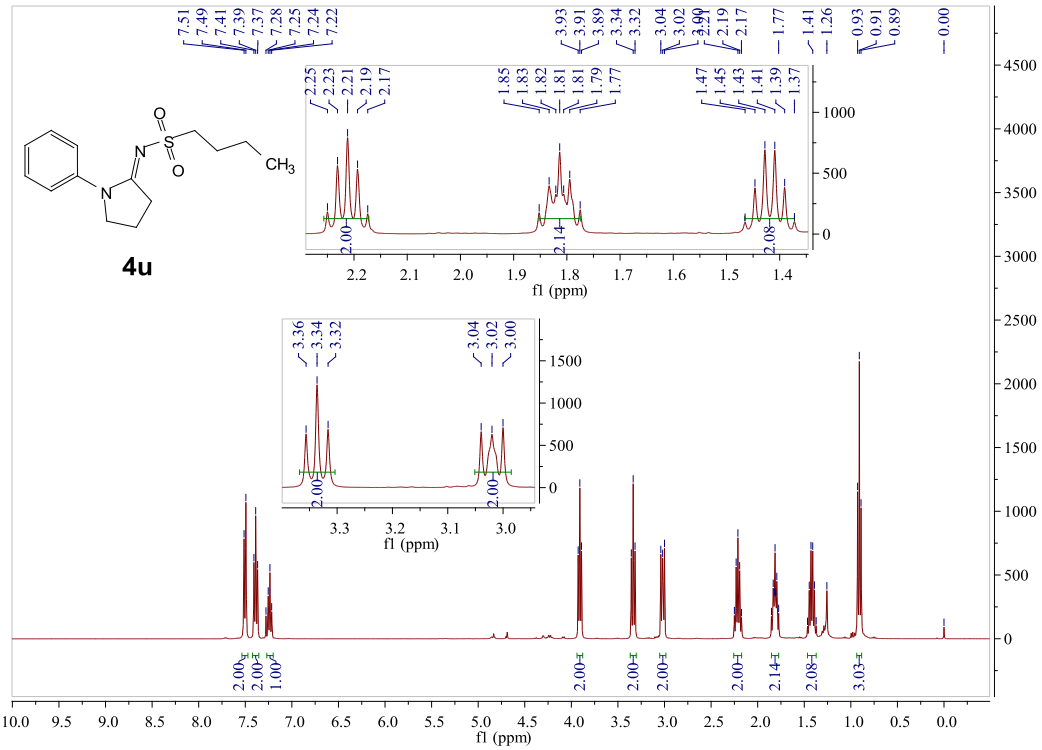

4r
fl (ppm)

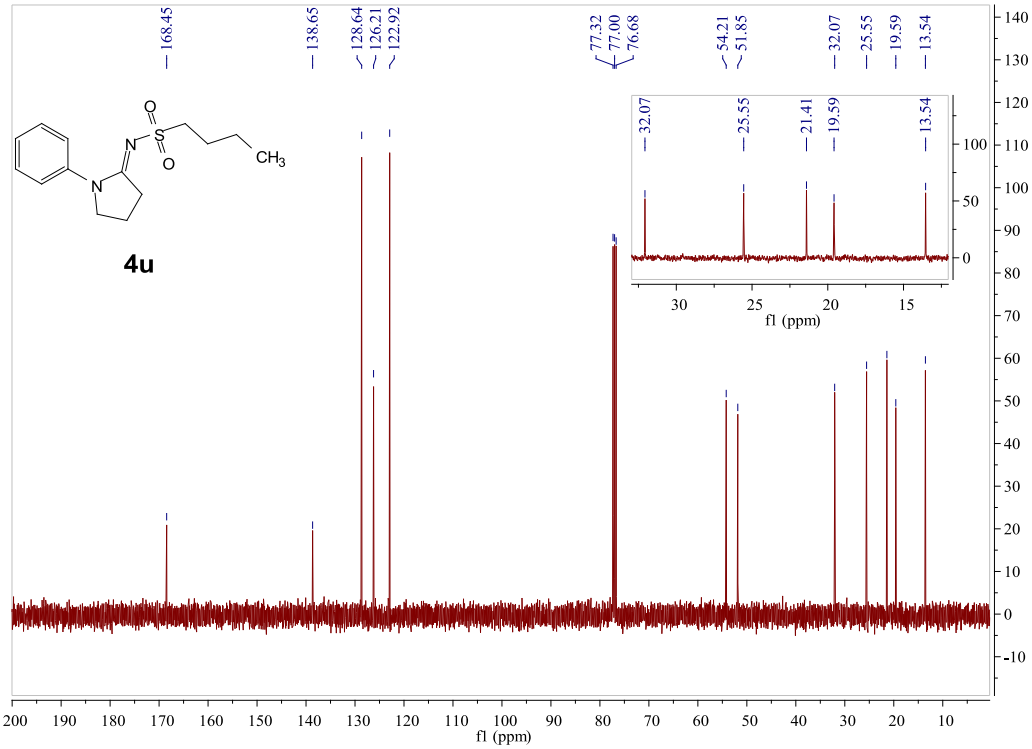

4s
fl (ppm)

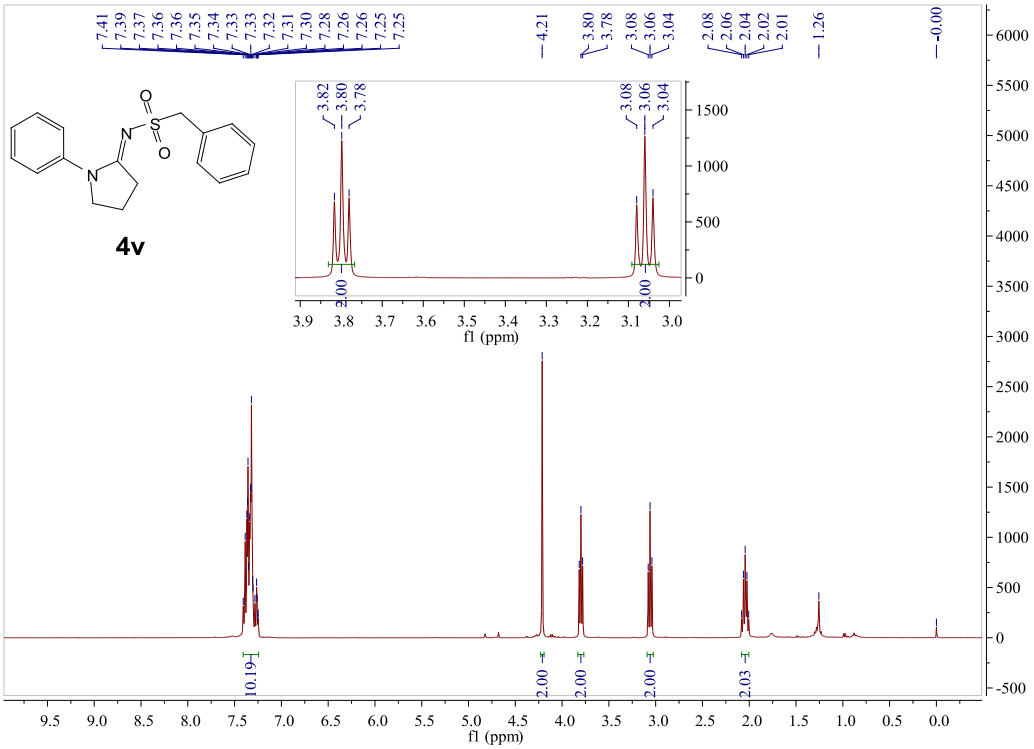

4s
fl (ppm)

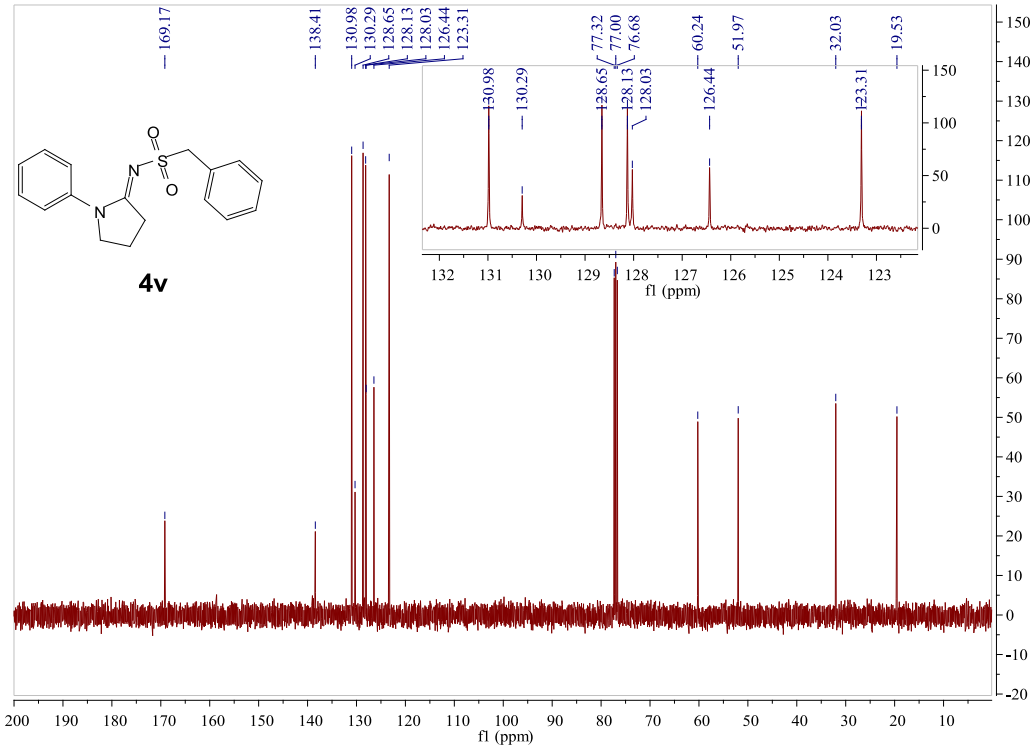

7.51
7.51
7.49
7.41
7.40
7.38
7.28
7.26
7.24
7.22
3.93
3.91
3.89
3.33
3.31
2.98
2.25
2.23
2.21
2.19
2.18
1.26
-0.00
4t
fl (ppm)

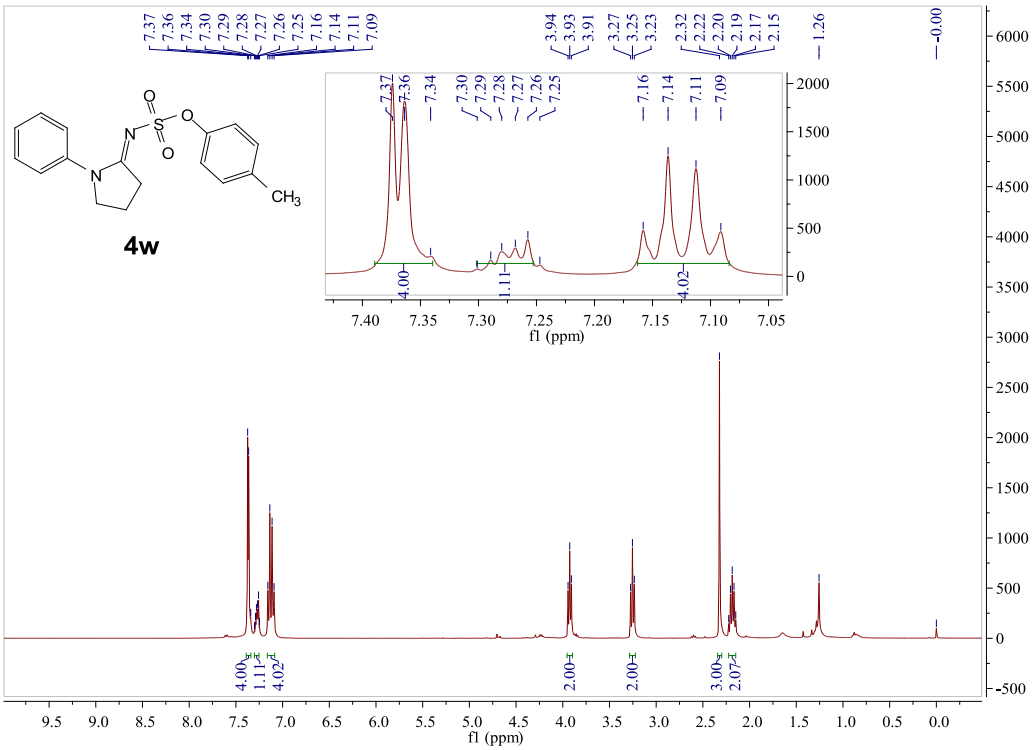

168.31
138.56
128.74
126.34
122.99
77.32
77.00
76.68
51.99
42.65
32.01
19.56
4t
fl (ppm)

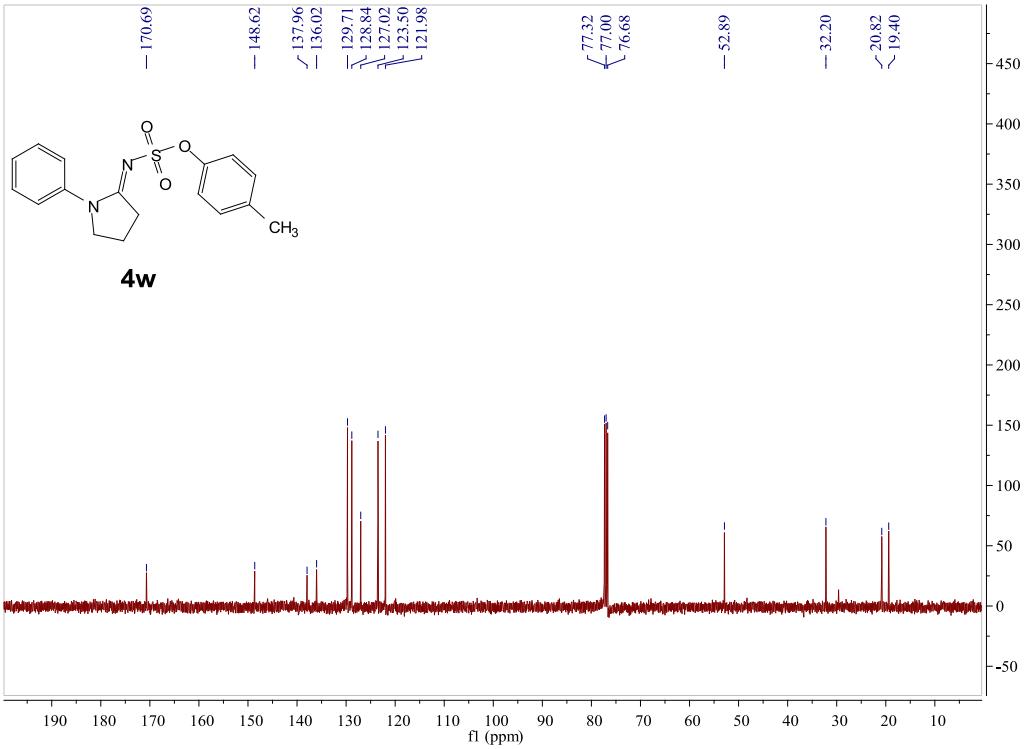

4u
fl (ppm)

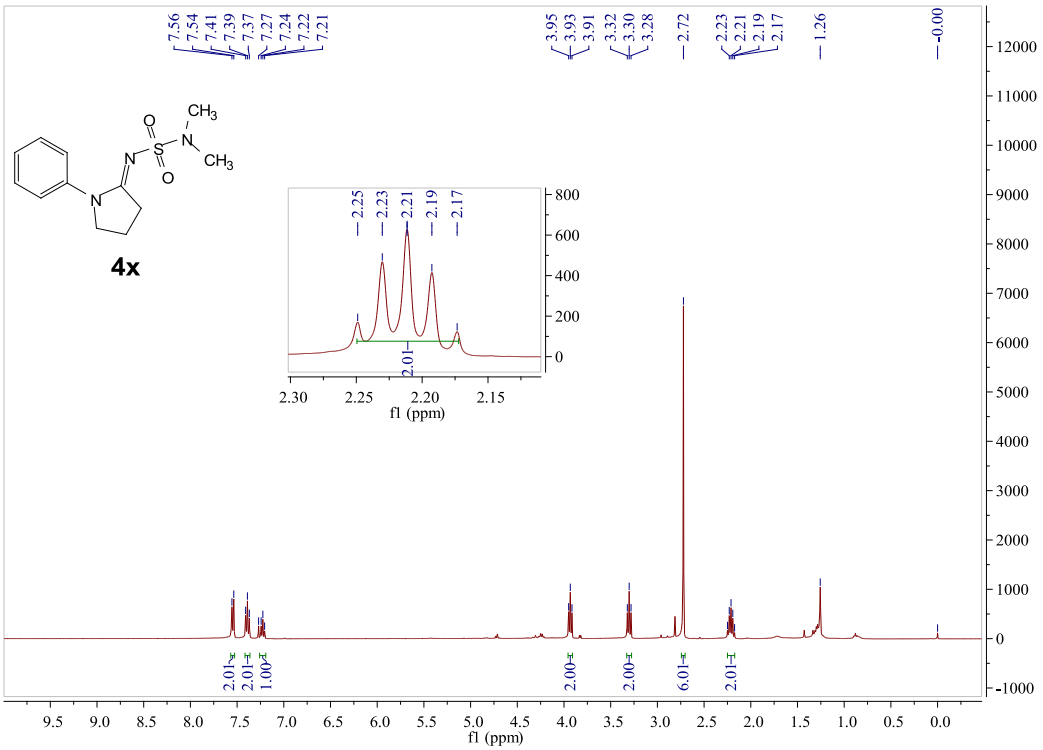

4u
fl (ppm)

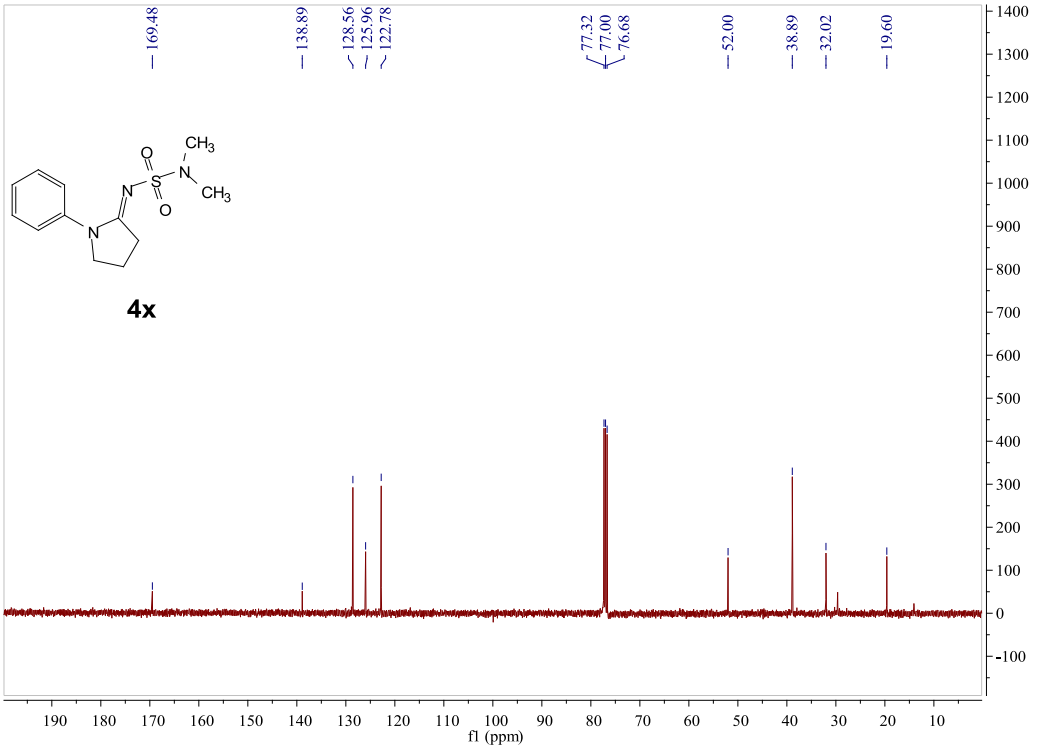

4v
fl (ppm)

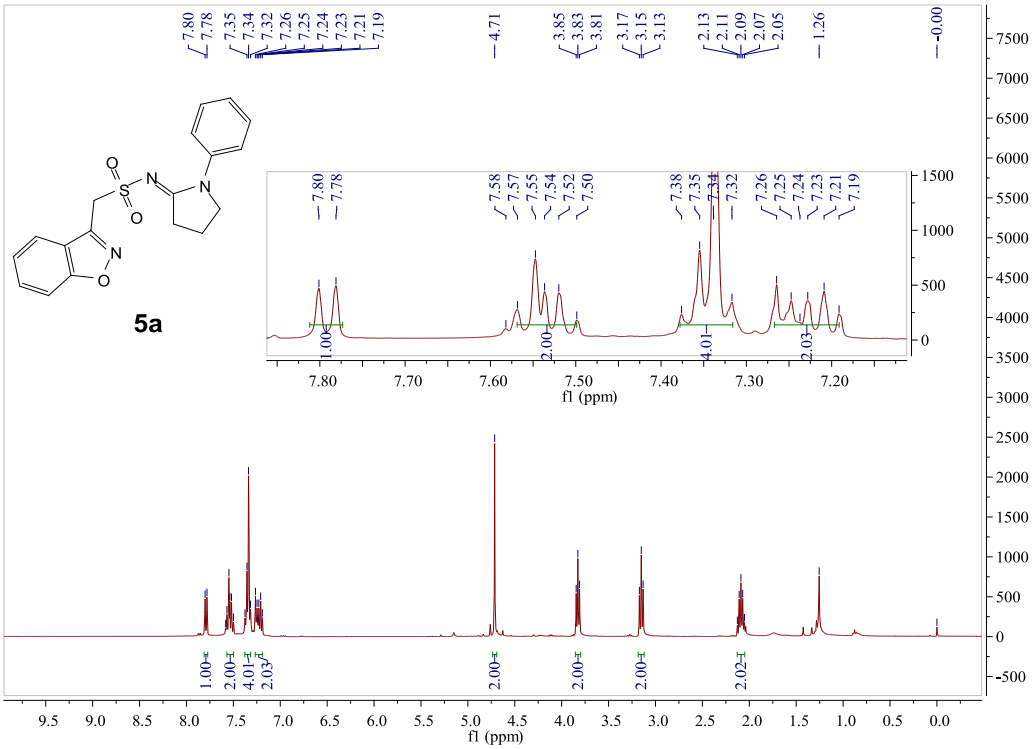

4v
fl (ppm)

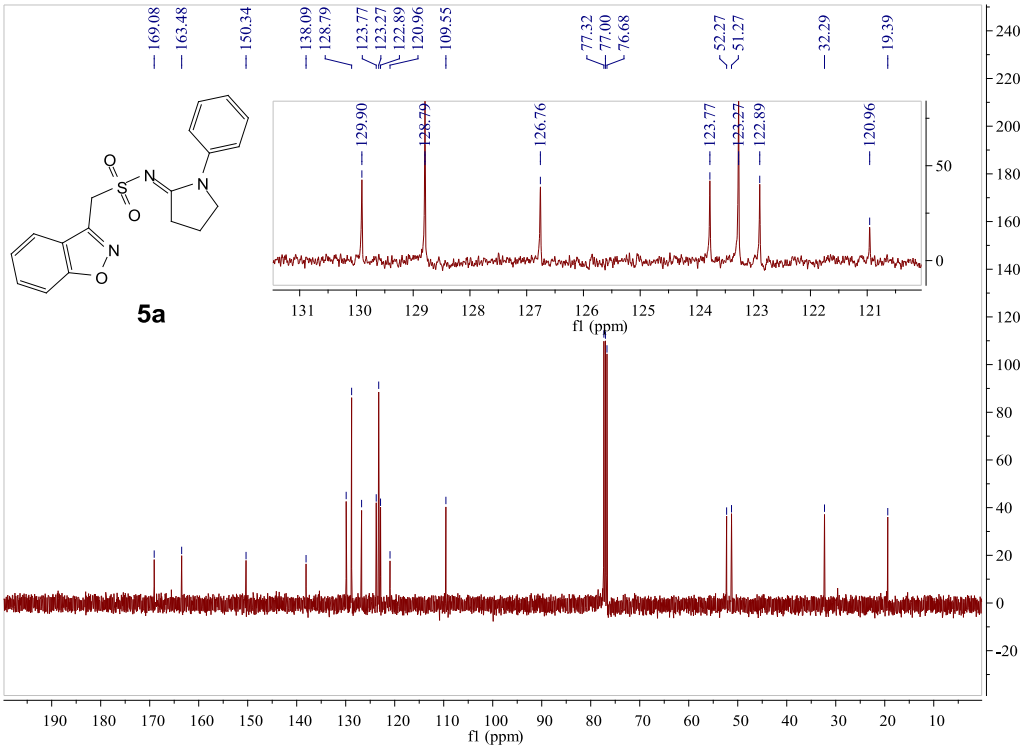

7.37
7.36
7.34
7.30
7.29
7.28
7.27
7.26
7.25
7.16
7.14
7.11
7.09
3.94
3.93
3.91
3.27
3.25
3.23
2.32
2.22
2.20
2.19
2.17
2.15
1.26
0.00
4w
fl (ppm)
fl (ppm)

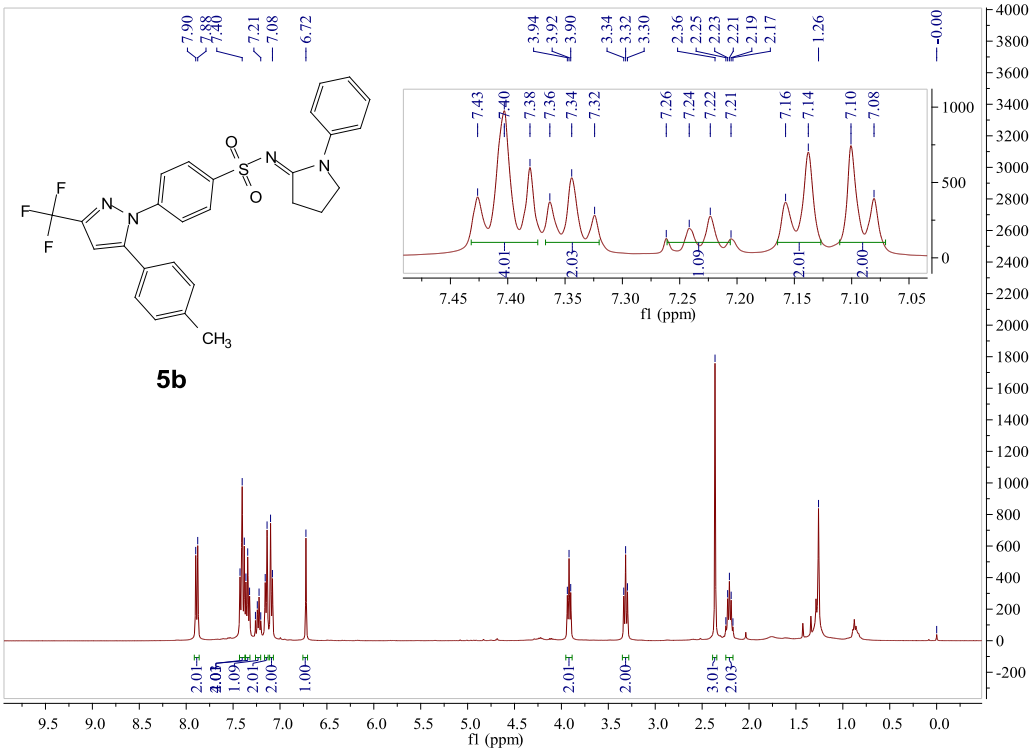

170.69
148.62
137.96
136.02
129.71
128.84
127.02
123.50
121.98
77.32
77.00
76.68
52.89
32.20
20.82
19.40
4w
fl (ppm)

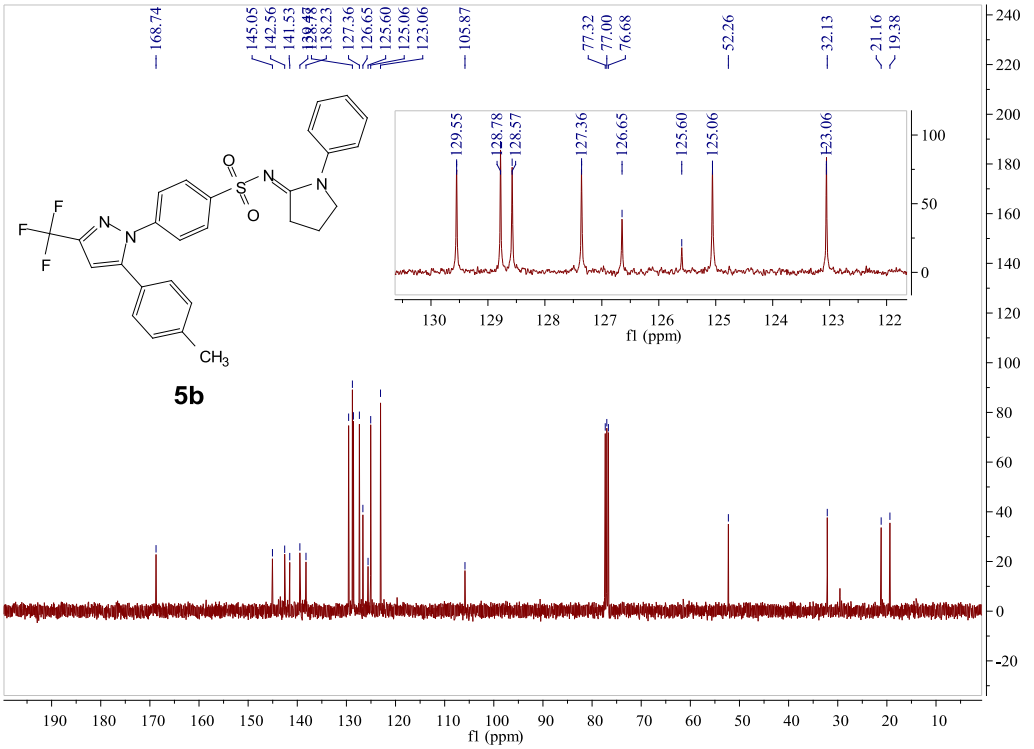

7.56
7.54
7.41
7.39
7.37
7.27
7.24
7.22
7.21
3.95
3.93
3.91
3.32
3.30
3.28
2.72
2.23
2.21
2.19
2.17
1.26
0.00
2.25
2.23
2.21
2.19
2.17
2.01
2.30
2.25
2.20
2.15
f1 (ppm)
2.01
2.01
1.00
2.00
2.00
6.01
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
CH3
O
N
S
N
CH3
O
N
4x

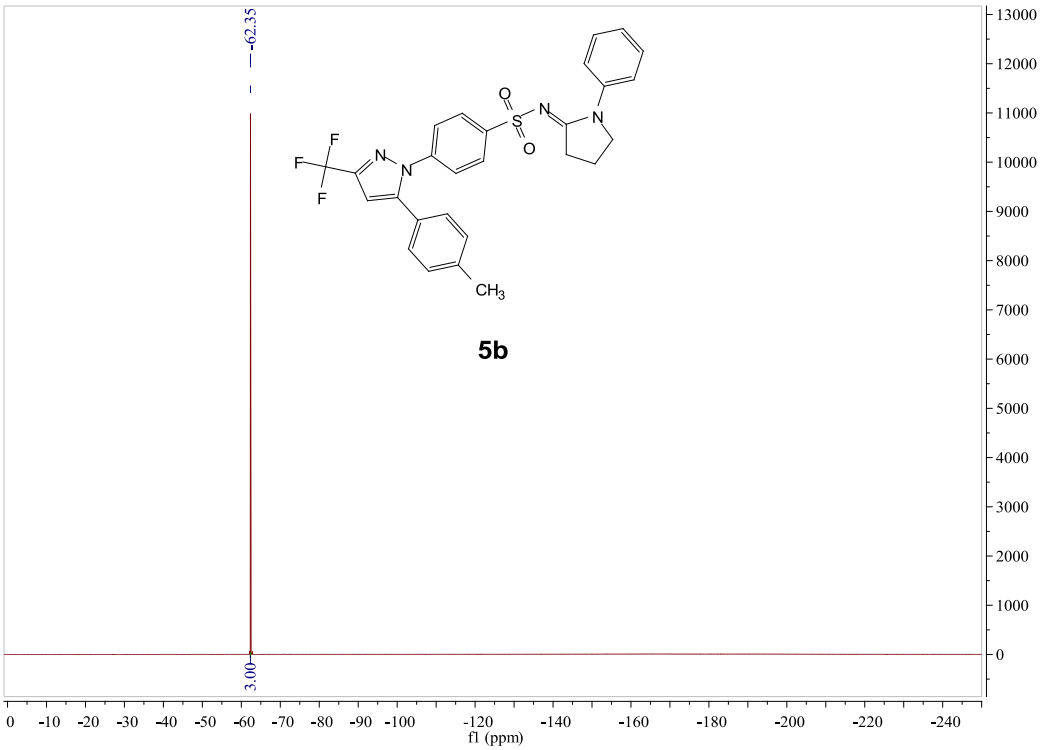

169.48
138.89
128.56
125.96
122.78
77.32
77.00
76.68
52.00
38.89
32.02
19.60
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
CH3
O
N
S
N
CH3
O
N
4x


5a
fl (ppm)

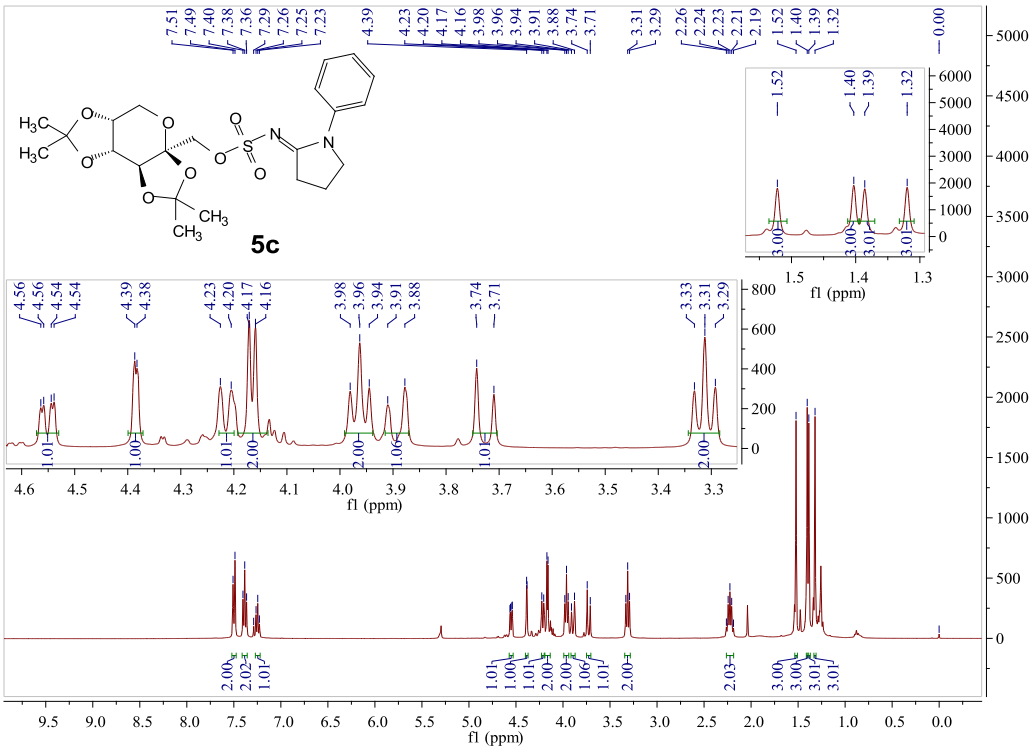

5a
fl (ppm)

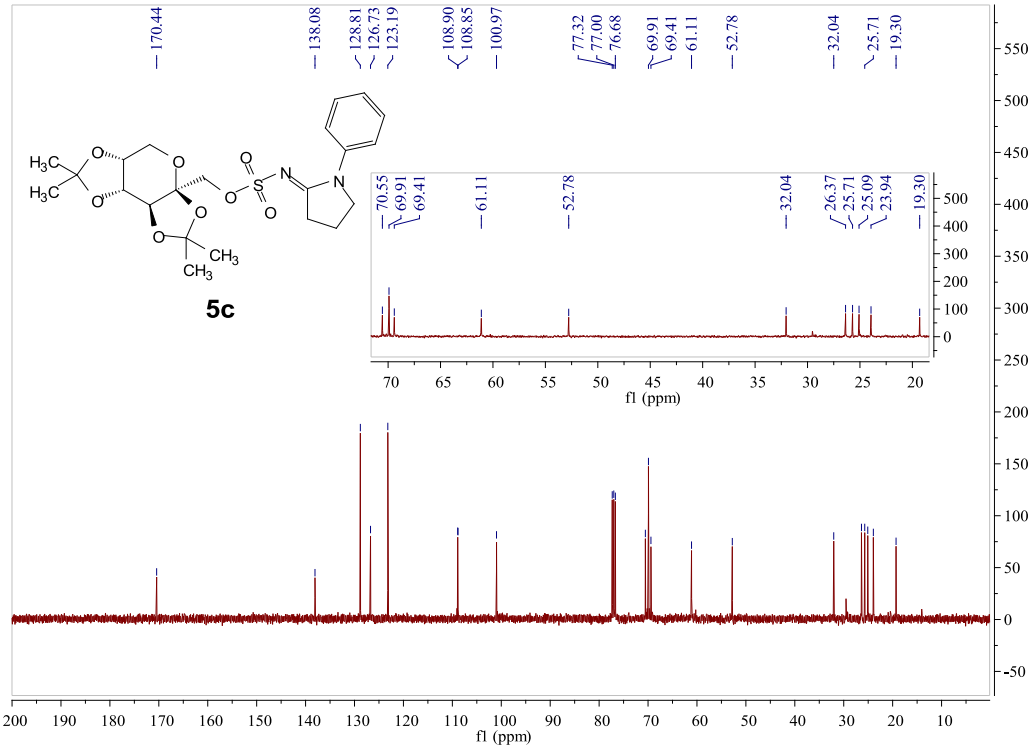

5b
fl (ppm)

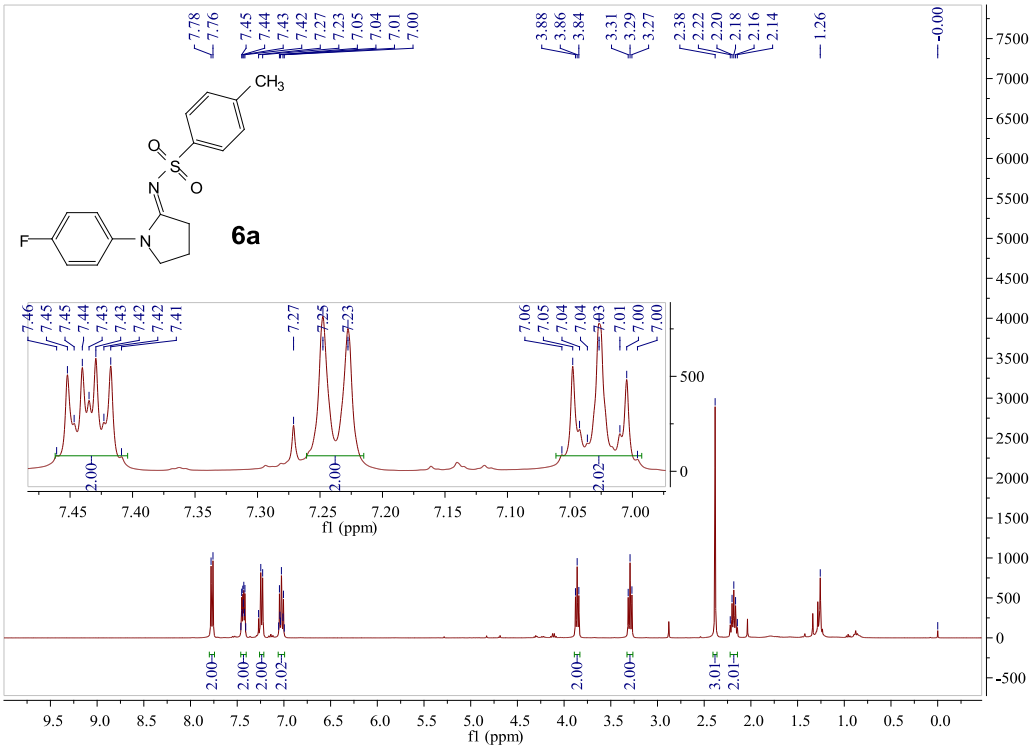

5b
fl (ppm)

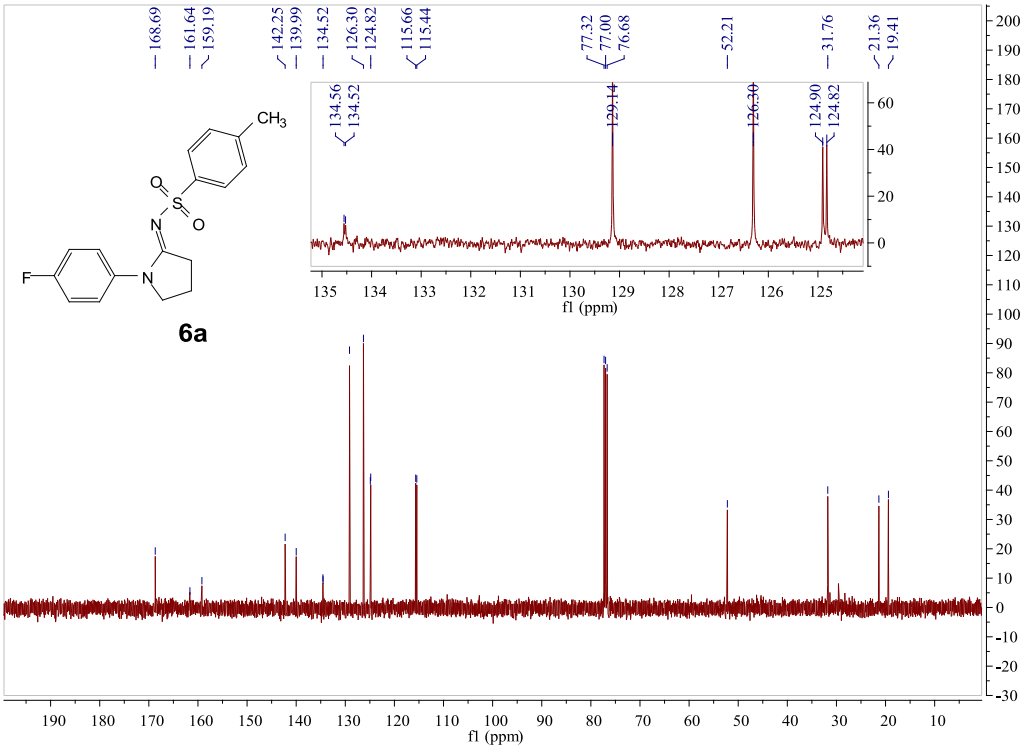

-62.35
3.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)
F
F
F
N
N
O
S
O
N
N
CH3

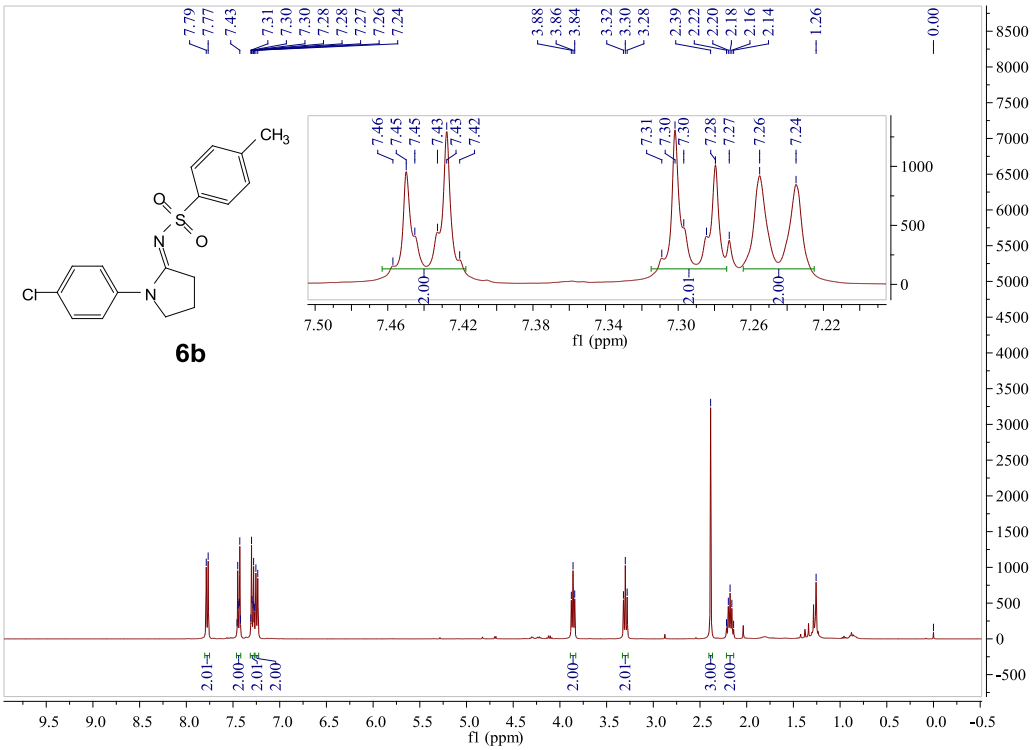
5b

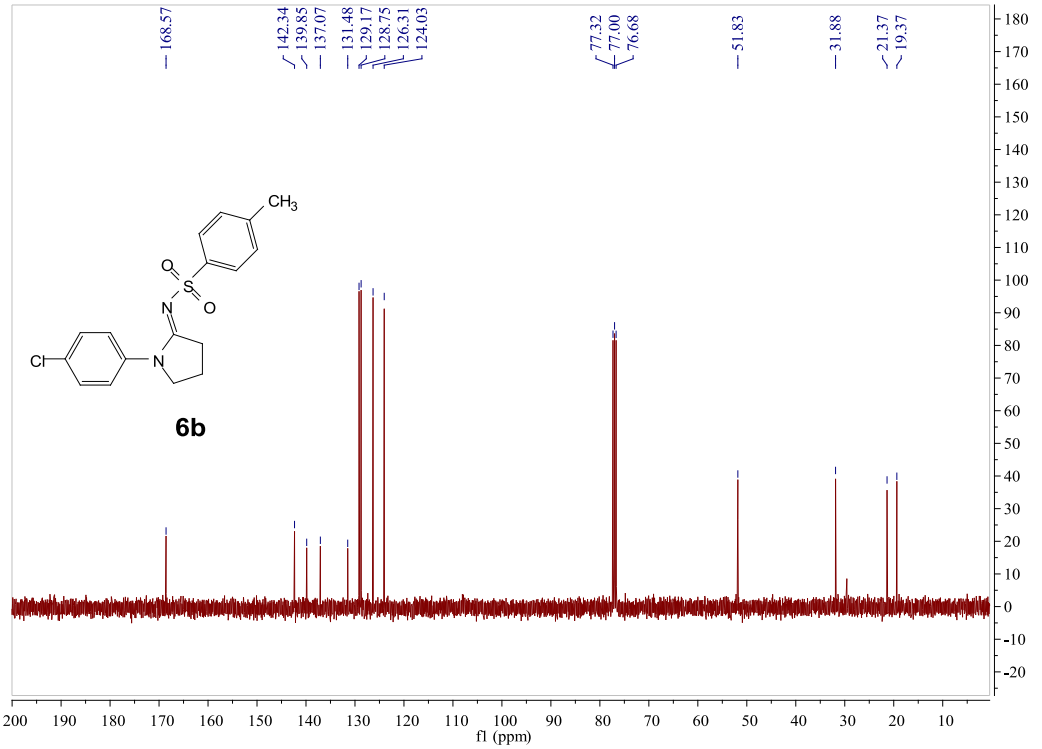

5c
fl (ppm)

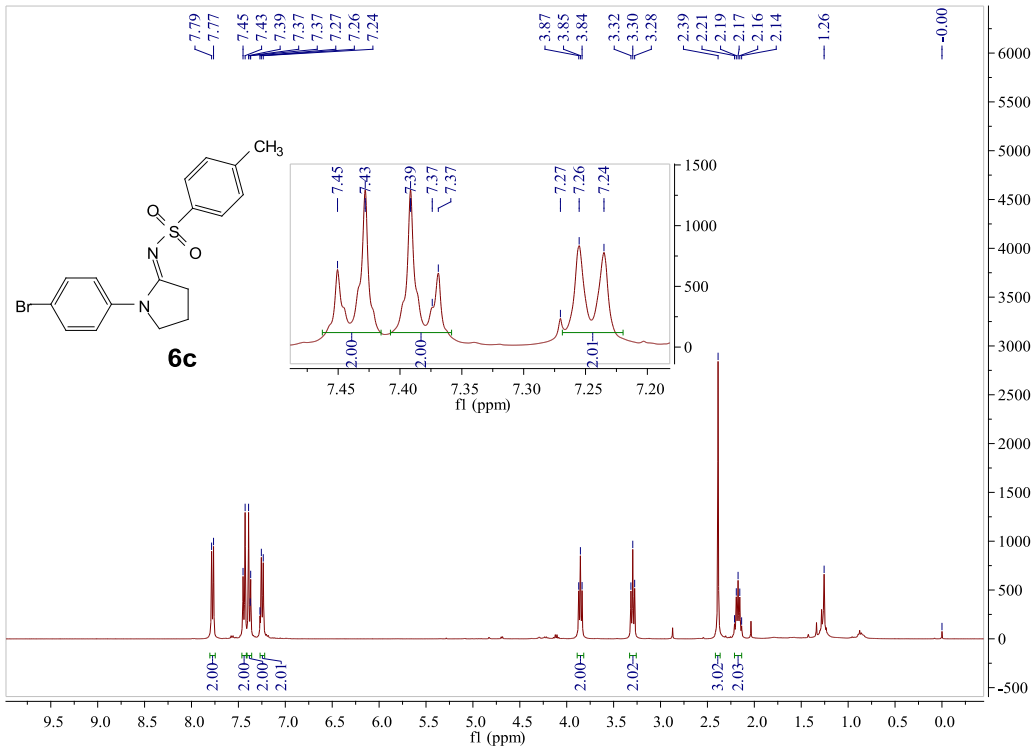

5c
fl (ppm)

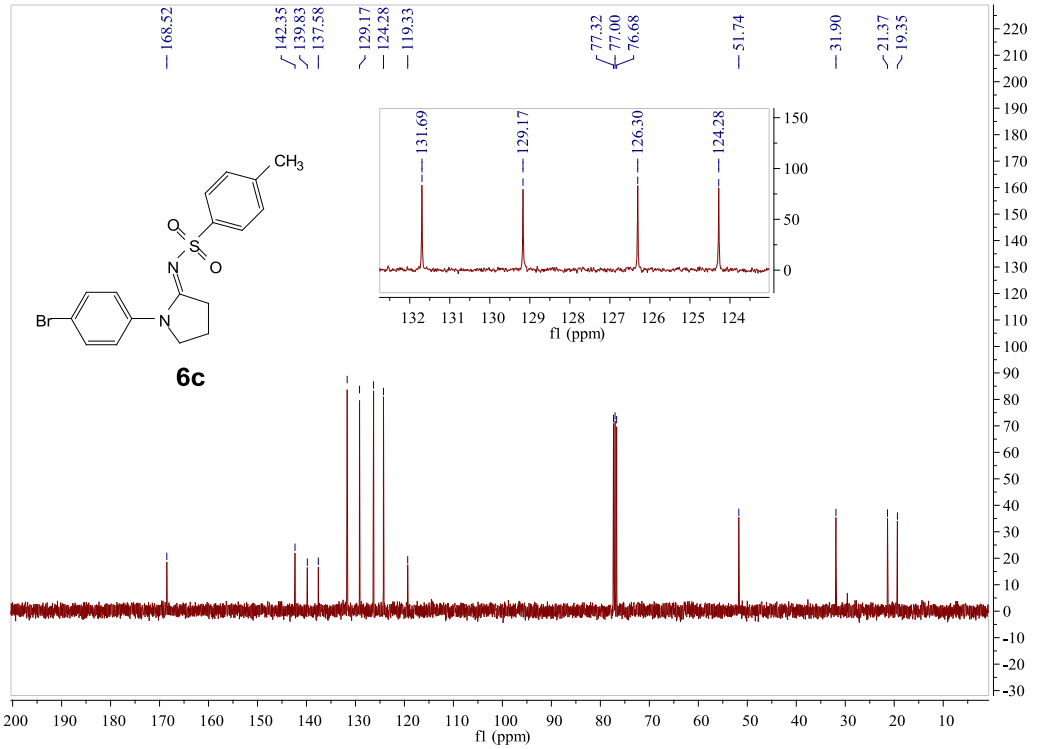

6a
fl (ppm)

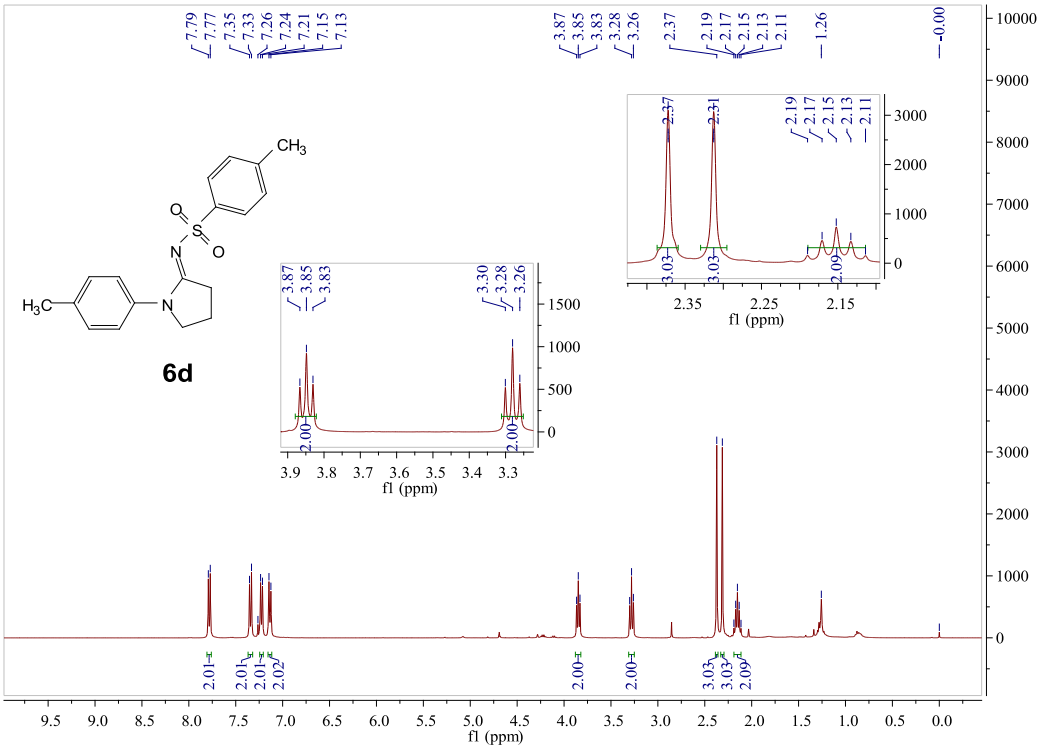

6a
fl (ppm)

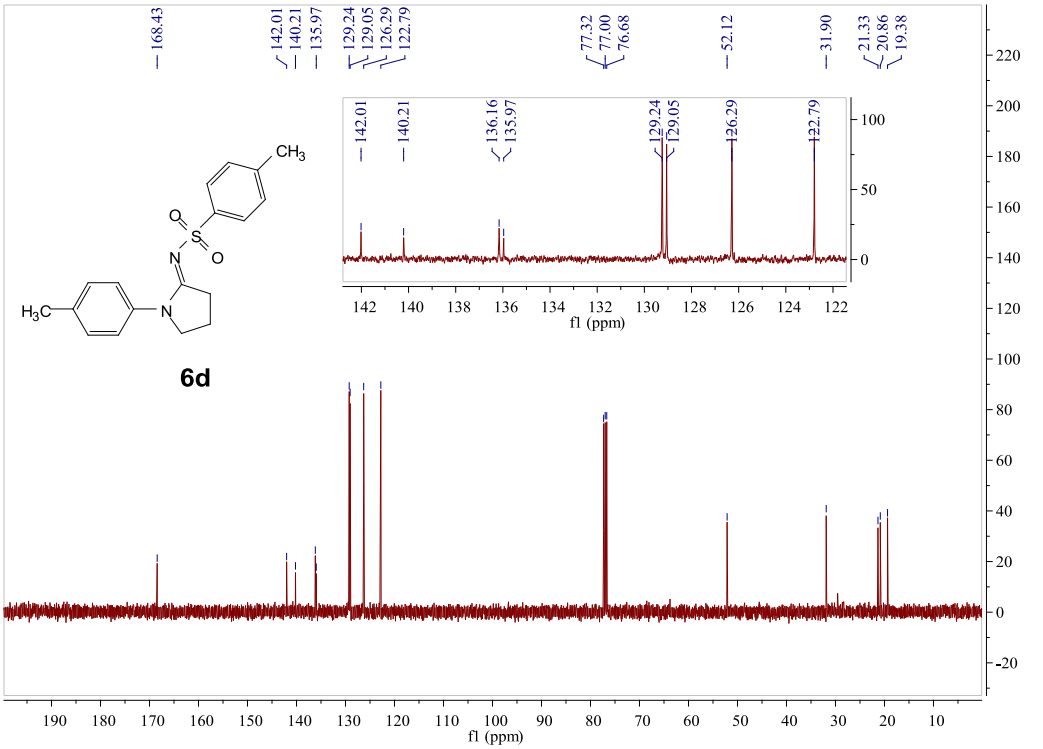

7.79
7.77
7.43
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.24
3.88
3.86
3.84
3.32
3.30
3.28
2.39
2.22
2.20
2.18
2.16
2.14
1.26
0.00
CH3
O
S
O
N
Cl
N
6b
7.46
7.45
7.45
7.43
7.43
7.42
7.31
7.30
7.30
7.28
7.27
7.26
7.24
2.00
2.01
2.00
7.50
7.46
7.42
7.38
7.34
7.30
7.26
7.22
f1 (ppm)
2.01
2.00
2.01
2.00
2.00
2.01
3.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

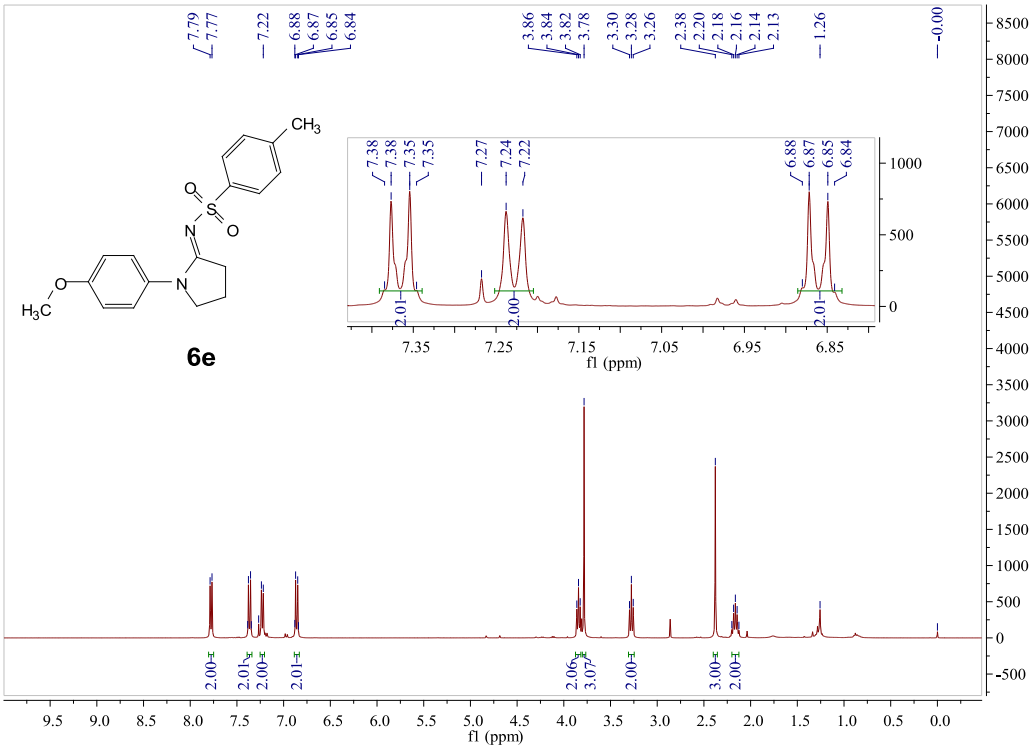

168.57
142.34
139.85
137.07
131.48
129.17
128.75
126.31
124.03
77.32
77.00
76.68
51.83
31.88
21.37
19.37
CH3
O
S
O
N
Cl
N
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

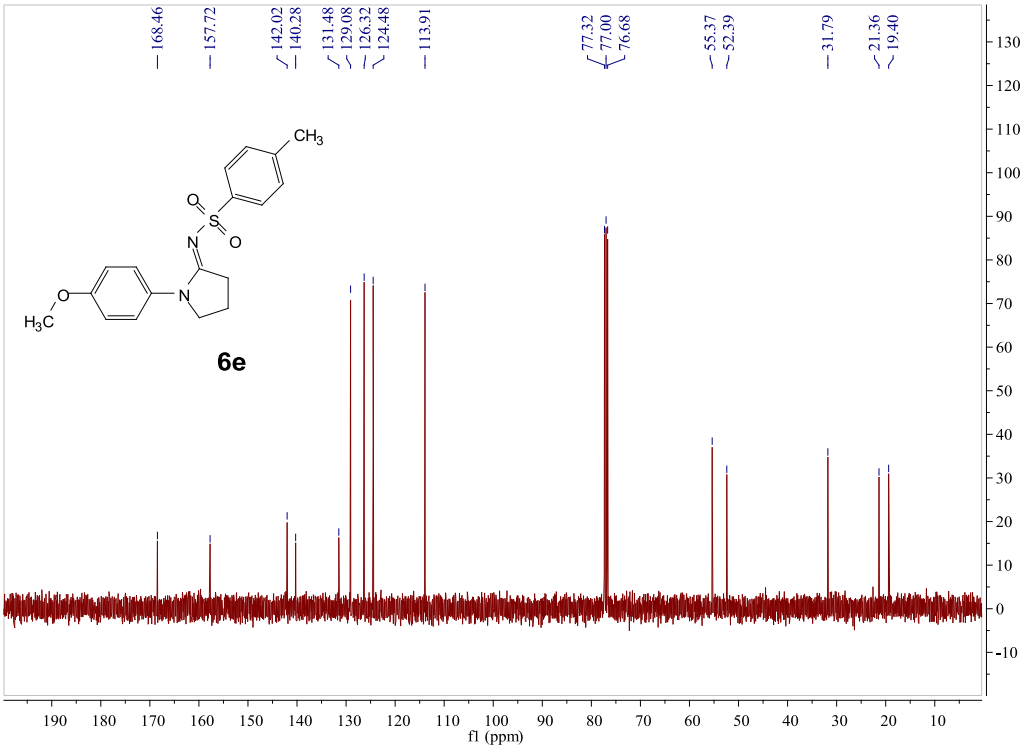

7.79
7.77
7.45
7.43
7.39
7.37
7.37
7.27
7.26
7.24
3.87
3.85
3.84
3.32
3.30
3.28
2.39
2.21
2.19
2.17
2.16
2.14
1.26
-0.00
CH3
O
S
O
N
Br
N
6c
7.45
7.43
7.39
7.37
7.37
7.27
7.26
7.24
2.00
2.00
2.01
f1 (ppm)
2.00
2.00
2.00
2.01
2.00
2.02
3.02
2.03
f1 (ppm)

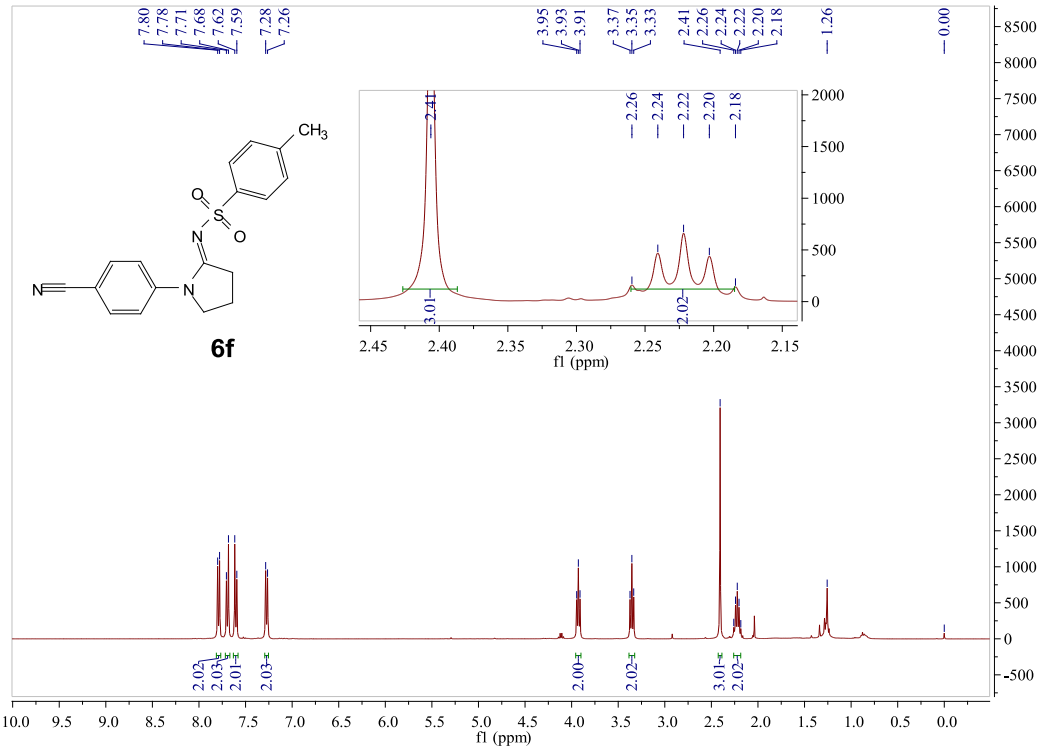

168.52
142.35
139.83
137.58
129.17
124.28
119.33
77.32
77.00
76.68
51.74
31.90
21.37
19.35
CH3
O
S
O
N
Br
N
6c
131.69
129.17
126.30
124.28
f1 (ppm)
f1 (ppm)

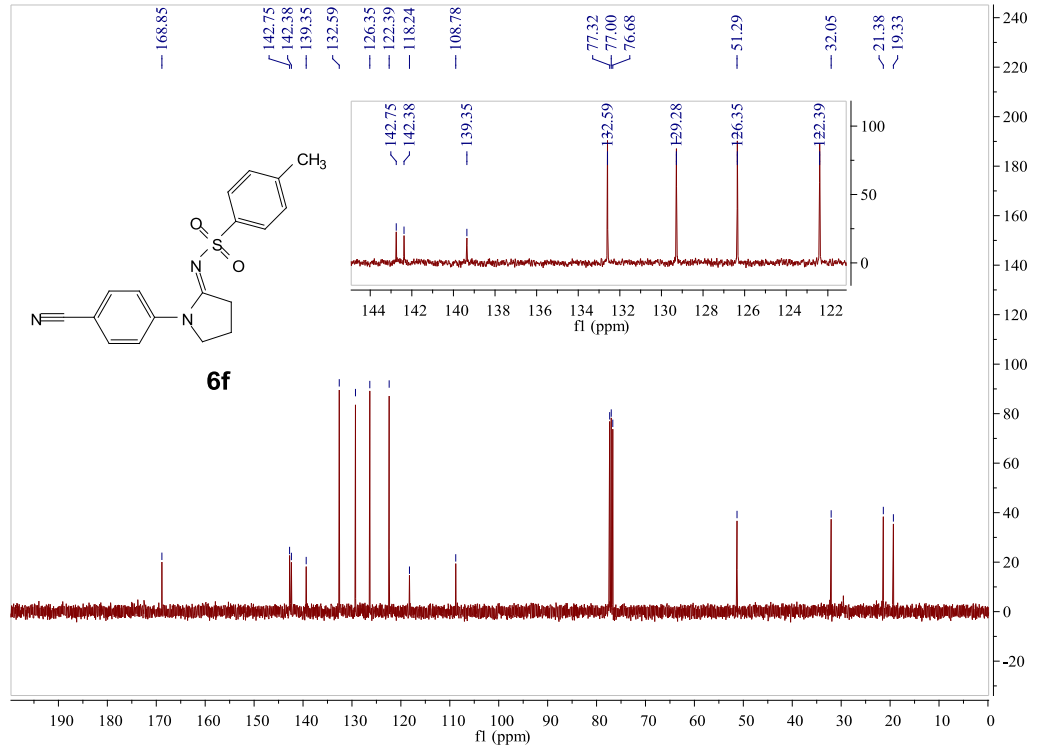

7.79
7.77
7.35
7.33
7.26
7.24
7.21
7.15
7.13
3.87
3.85
3.83
3.28
3.26
2.37
2.19
2.17
2.15
2.13
2.11
1.26
-0.00
CH3
O
S
O
N
H3C
N
6d
f1 (ppm)

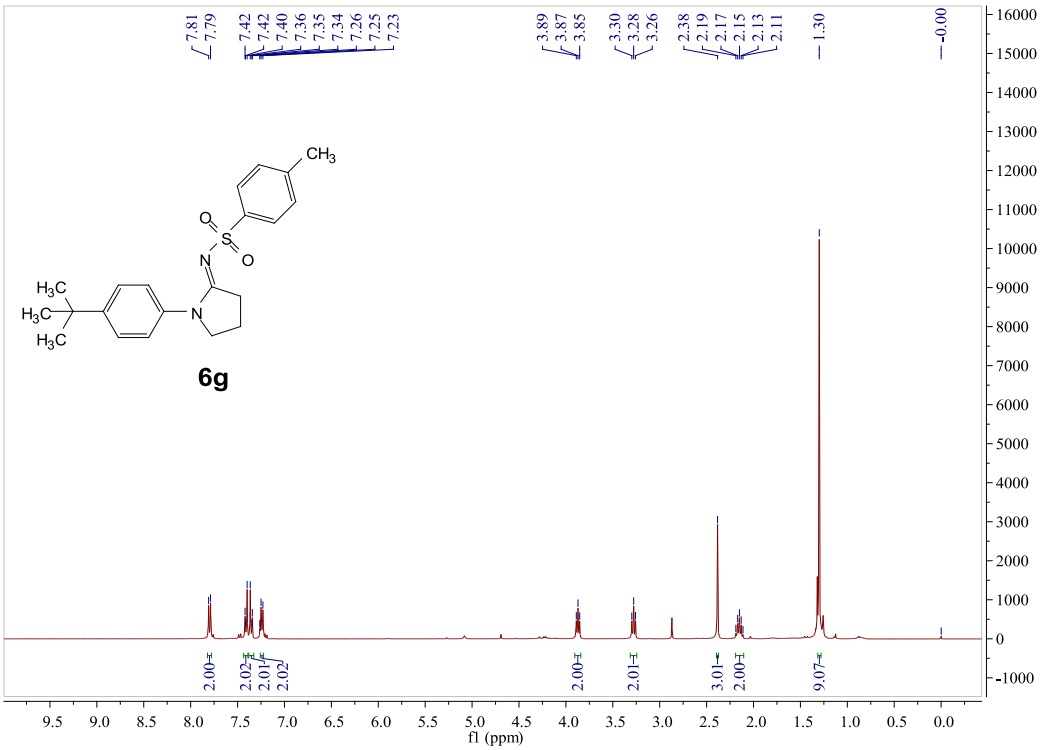

168.43
142.01
140.21
135.97
129.24
129.05
126.29
122.79
77.32
77.00
76.68
52.12
31.90
21.33
20.86
19.38
CH3
O
S
O
N
H3C
N
6d
f1 (ppm)

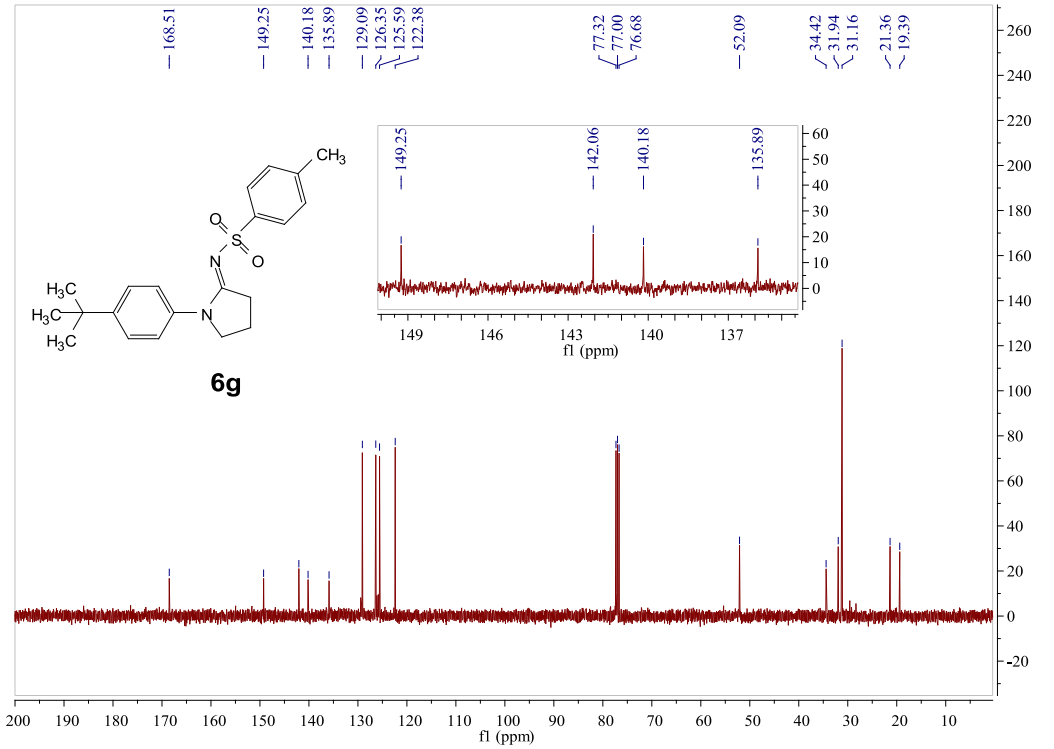

7.79
7.77
7.22
6.88
6.87
6.85
6.84
3.86
3.84
3.82
3.78
3.30
3.28
3.26
2.38
2.20
2.18
2.16
2.14
2.13
1.26
-0.00
CH3
O
S
O
N
O
N
O
H3C
6e
7.38
7.38
7.35
7.35
7.27
7.24
7.22
6.88
6.87
6.85
6.84
2.01
2.00
2.01
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
2.00
2.01
2.00
2.01
2.06
3.07
2.00
3.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

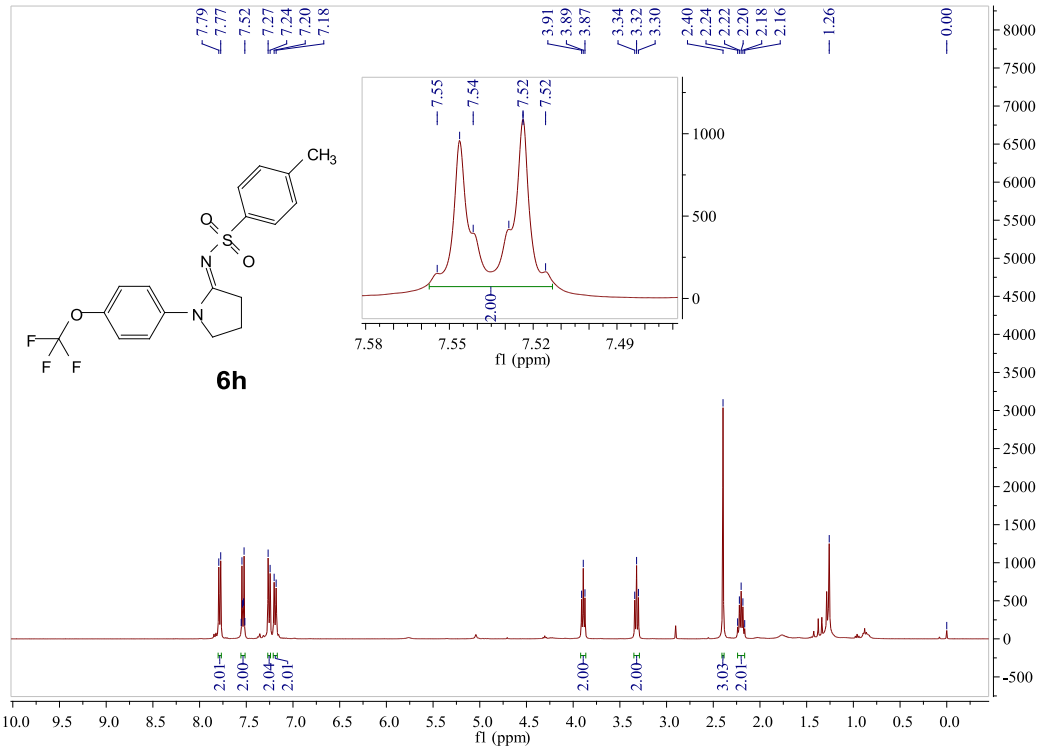

168.46
157.72
142.02
140.28
131.48
129.08
126.32
124.48
113.91
77.32
77.00
76.68
55.37
52.39
31.79
21.36
19.40
CH3
O
S
O
N
O
N
O
H3C
6e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

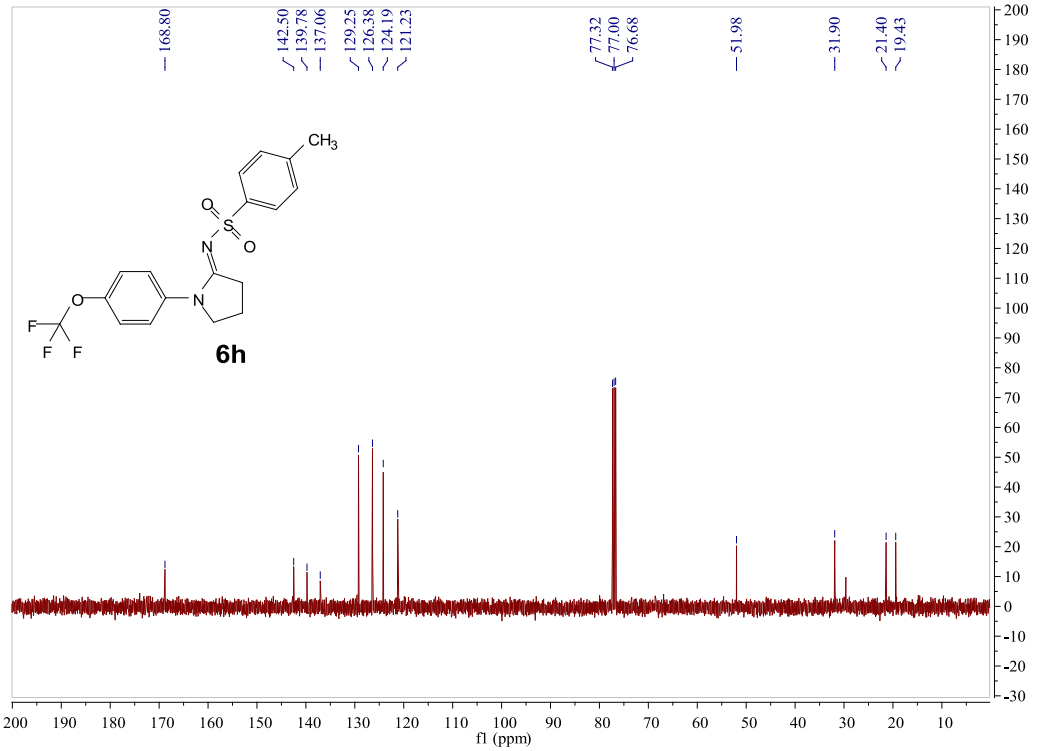

7.80
7.78
7.71
7.68
7.62
7.59
7.28
7.26
3.95
3.93
3.91
3.37
3.35
3.33
2.41
2.26
2.24
2.22
2.20
2.18
1.26
0.00
CH3
O
S
O
N
N
N
6f
3.01
2.02
fl (ppm)
2.02
2.03
2.01
2.03
2.00
2.02
3.01
2.02
fl (ppm)

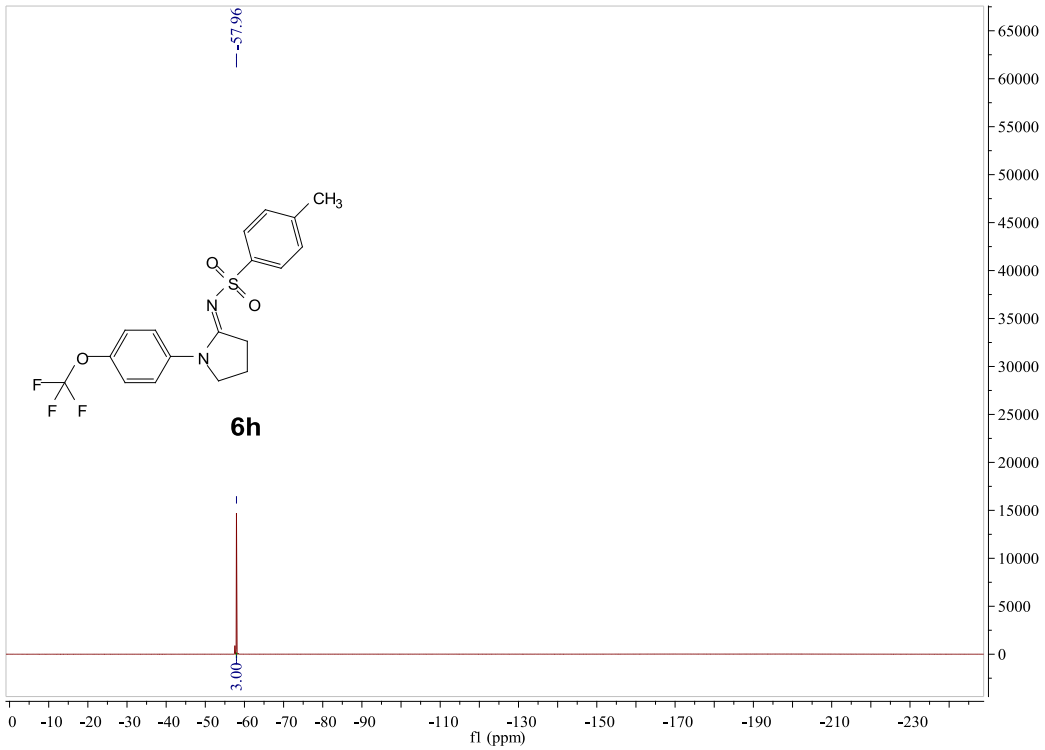

168.85
142.75
142.38
139.35
132.59
126.35
122.39
118.24
108.78
77.32
77.00
76.68
51.29
32.05
21.38
19.33
CH3
O
S
O
N
N
N
6f
142.75
142.38
139.35
132.59
129.28
126.35
122.39
fl (ppm)
fl (ppm)

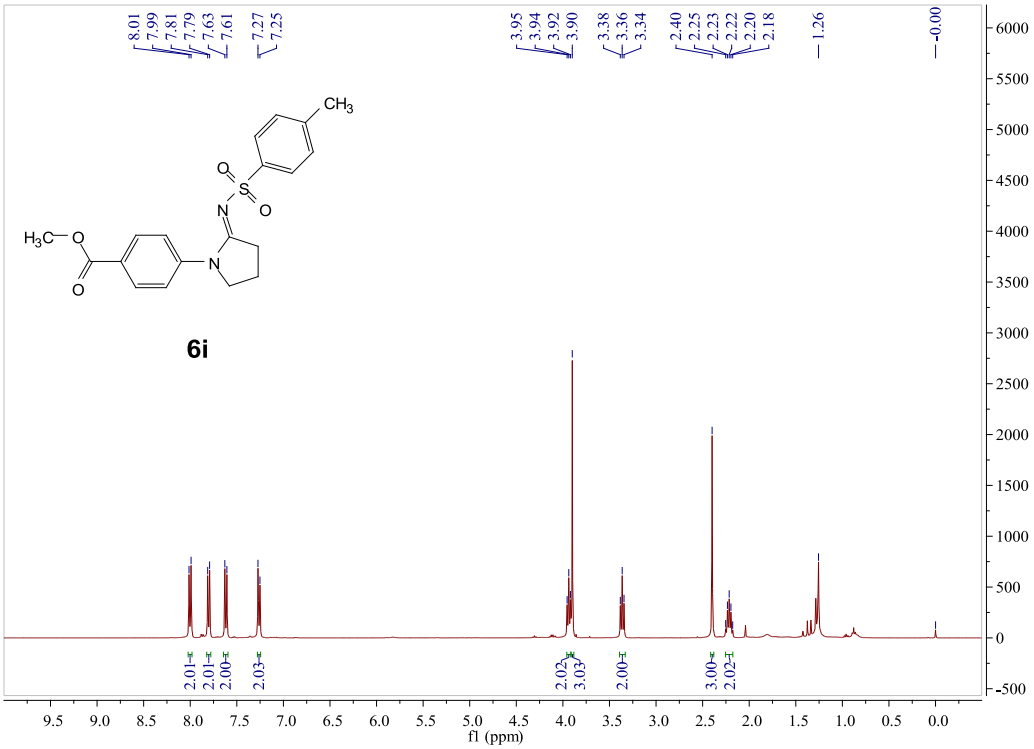

7.81
7.79
7.42
7.42
7.40
7.36
7.35
7.34
7.26
7.25
7.23
3.89
3.87
3.85
3.30
3.28
3.26
2.38
2.19
2.17
2.15
2.13
2.11
1.30
-0.00
2.00
2.02
2.01
2.02
2.00
2.01
3.01
2.00
9.07
f1 (ppm)
6g

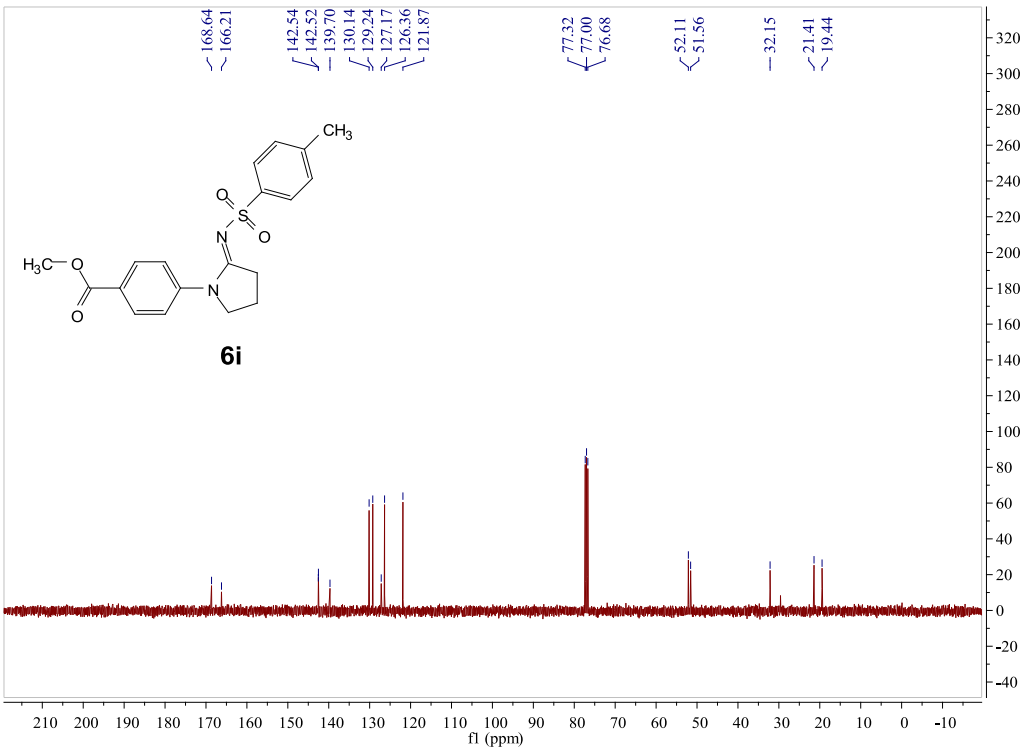

168.51
149.25
140.18
135.89
129.09
126.35
125.59
122.38
77.32
77.00
76.68
52.09
34.42
31.94
31.16
21.36
19.39
149.25
142.06
140.18
135.89
f1 (ppm)
f1 (ppm)
6g

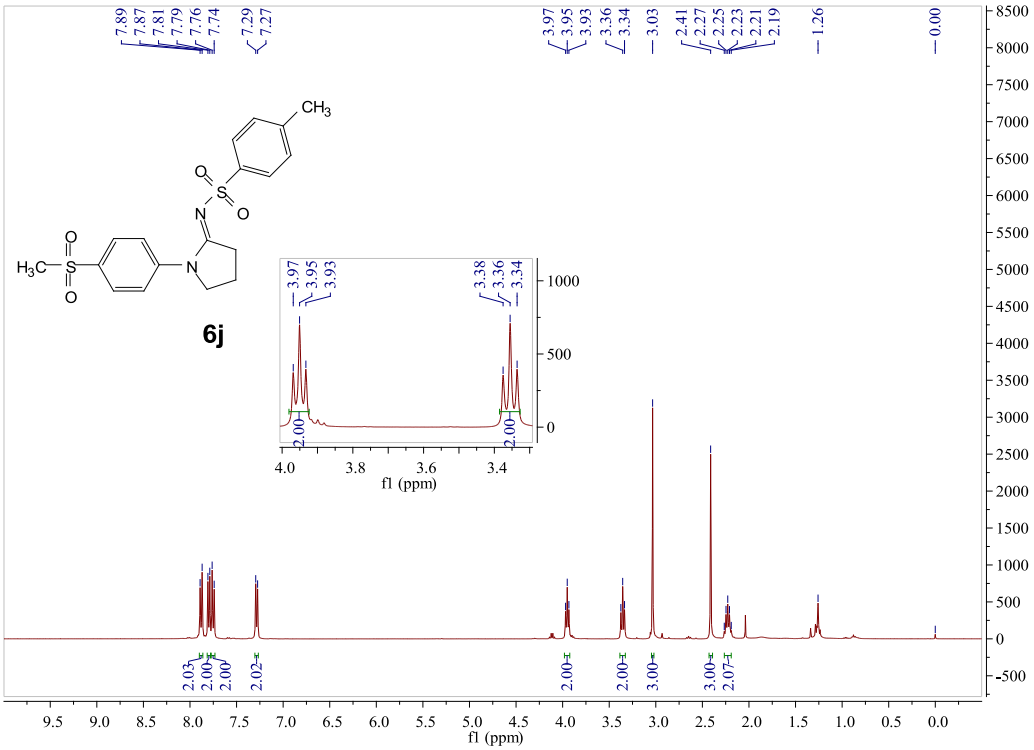

7.79
7.77
7.52
7.27
7.24
7.20
7.18
3.91
3.89
3.87
3.34
3.32
3.30
2.40
2.24
2.22
2.20
2.18
2.16
1.26
0.00
7.55
7.54
7.52
7.52
2.00
7.58
7.55
7.52
7.49
f1 (ppm)
6h
2.01
2.00
2.04
2.01
2.00
2.00
3.03
2.01
f1 (ppm)

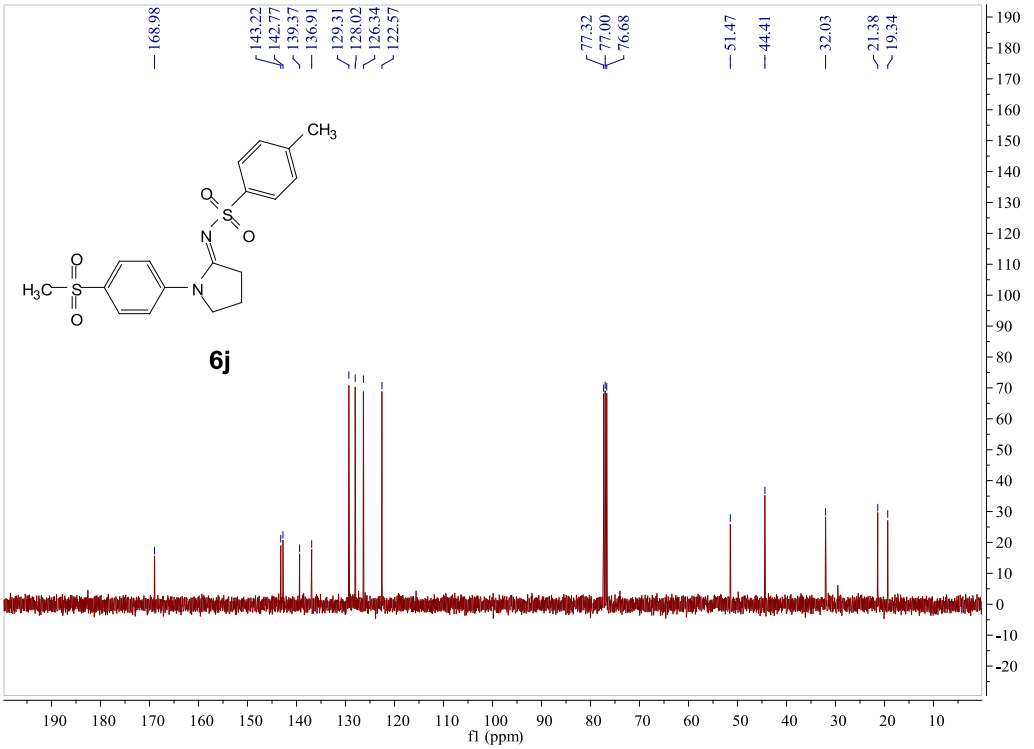

168.80
142.50
139.78
137.06
129.25
126.38
124.19
121.23
77.32
77.00
76.68
51.98
31.90
21.40
19.43
6h
f1 (ppm)

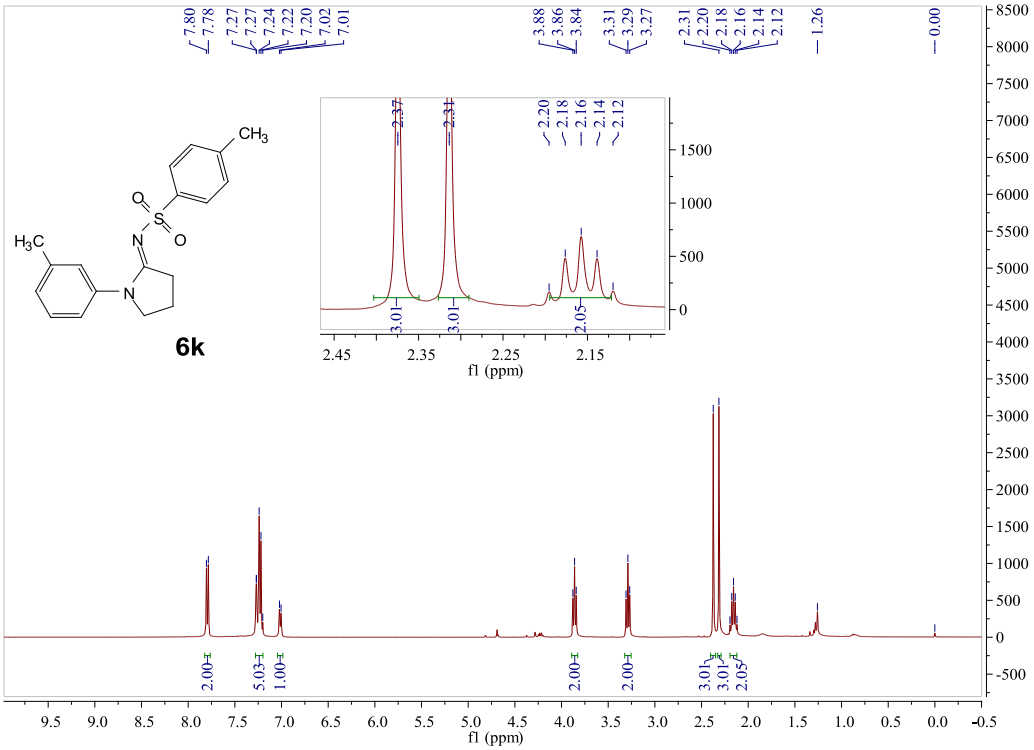

-57.96
CH3
O
S
O
N
O
N
F
F
F
6h
3.00
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

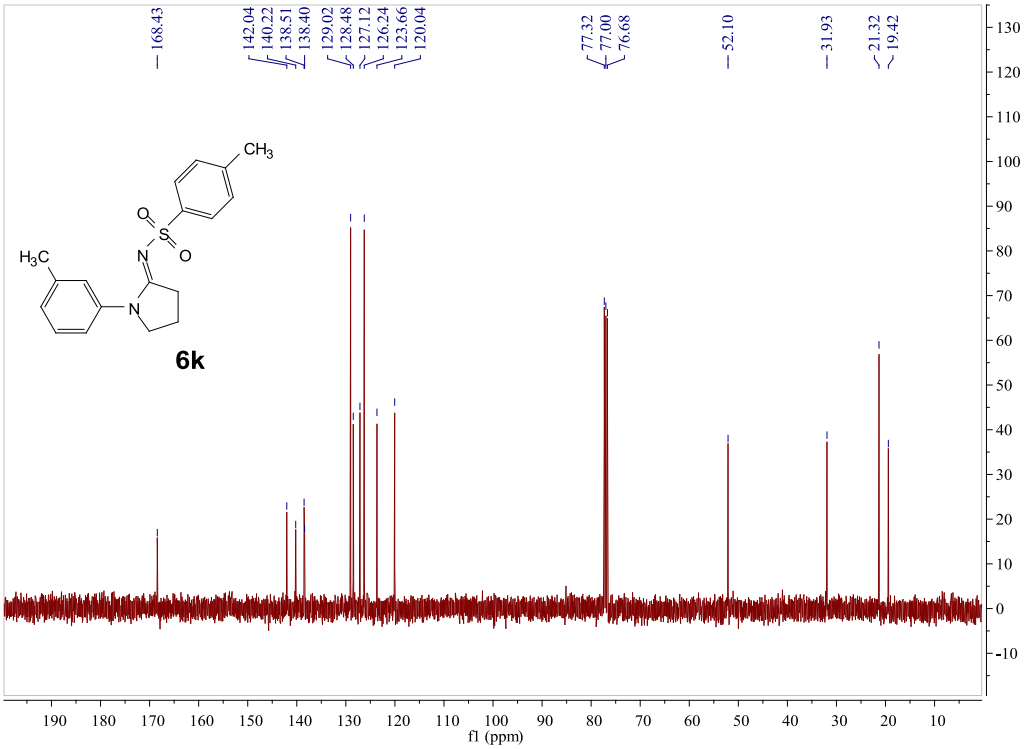

8.01
7.99
7.81
7.79
7.63
7.61
7.27
7.25
3.95
3.94
3.92
3.90
3.38
3.36
3.34
2.40
2.25
2.23
2.22
2.20
2.18
1.26
-0.00
CH3
O
S
O
N
H3C
O
O
N
6i
2.01
2.01
2.00
2.03
2.02
3.03
2.00
3.00
2.02
fl (ppm)

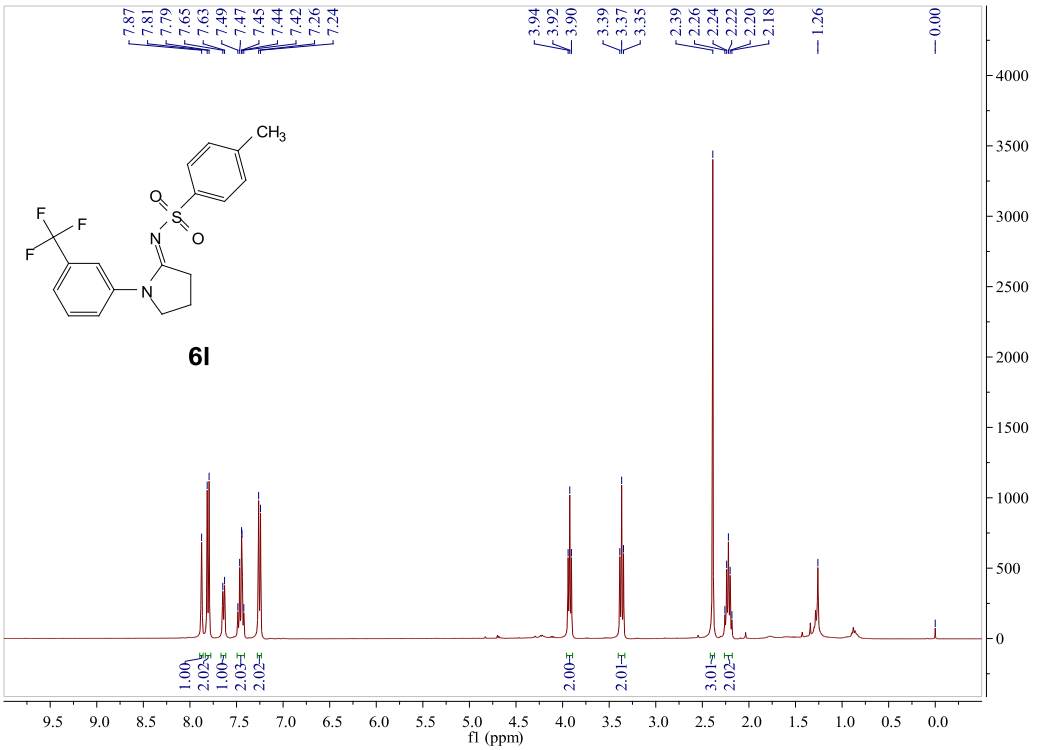

168.64
166.21
142.54
142.52
139.70
130.14
129.24
127.17
126.36
121.87
77.32
77.00
76.68
52.11
51.56
32.15
21.41
19.44
CH3
O
S
O
N
H3C
O
O
N
6i
fl (ppm)

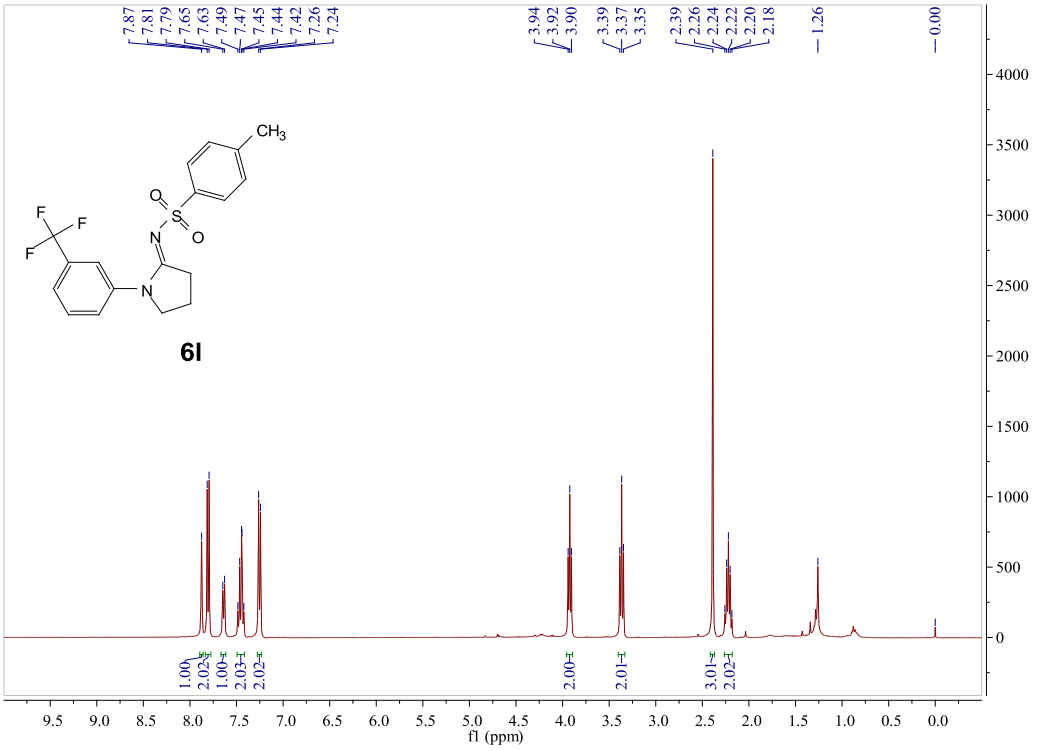

7.89
7.87
7.81
7.79
7.76
7.74
7.29
7.27
3.97
3.95
3.93
3.36
3.34
3.03
2.41
2.27
2.25
2.23
2.21
2.19
1.26
0.00
CH3
O
S
N
H3C
6j
3.38
2.00
fl (ppm)
2.03
2.00
2.00
2.02
2.00
2.00
3.00
3.00
2.07
fl (ppm)

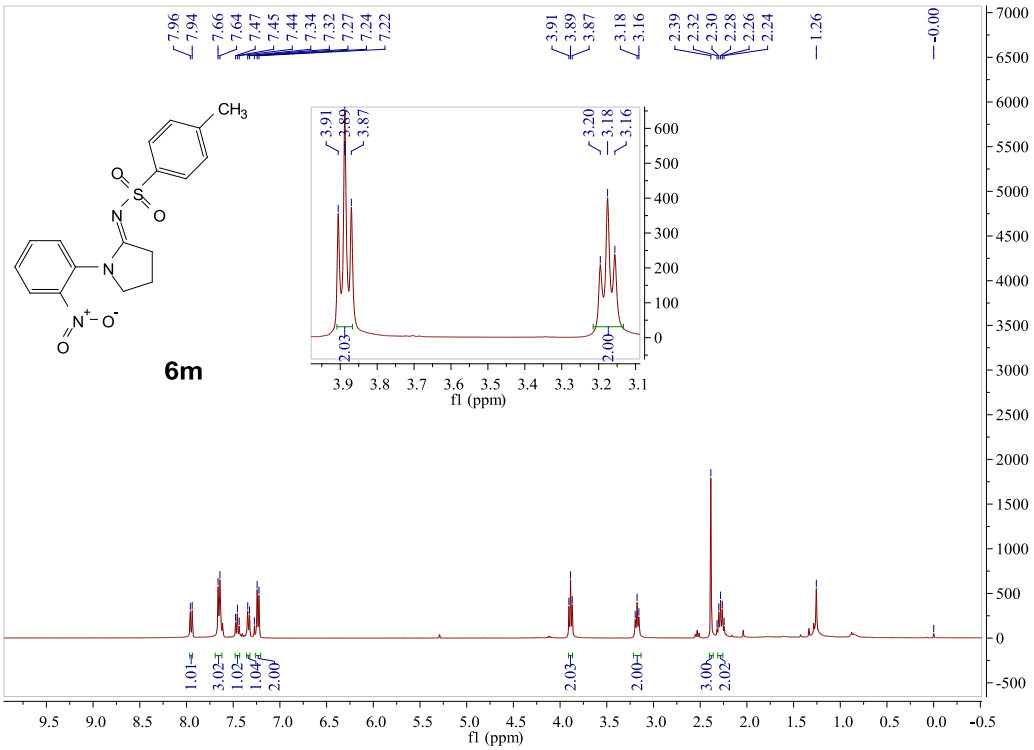

168.98
143.22
142.77
139.37
136.91
129.31
128.02
126.34
122.57
77.32
77.00
76.68
51.47
44.41
32.03
21.38
19.34
CH3
O
S
N
H3C
6j
fl (ppm)

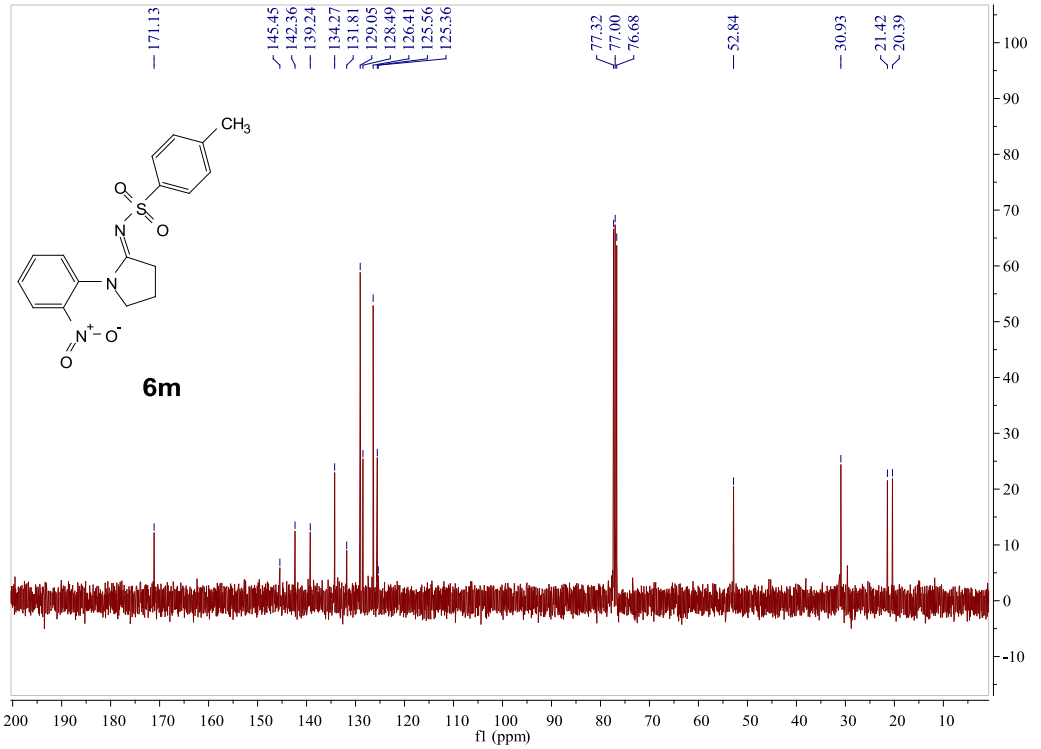

7.80
7.78
7.27
7.27
7.24
7.22
7.20
7.02
7.01
3.88
3.86
3.84
3.31
3.29
3.27
2.31
2.20
2.18
2.16
2.14
2.12
1.26
0.00
CH3
O
S
O
N
H3C
N
6k
2.37
2.31
2.20
2.18
2.16
2.14
2.12
3.01
3.01
2.05
f1 (ppm)
2.00
5.03
1.00
2.00
2.00
3.01
3.01
2.05
f1 (ppm)

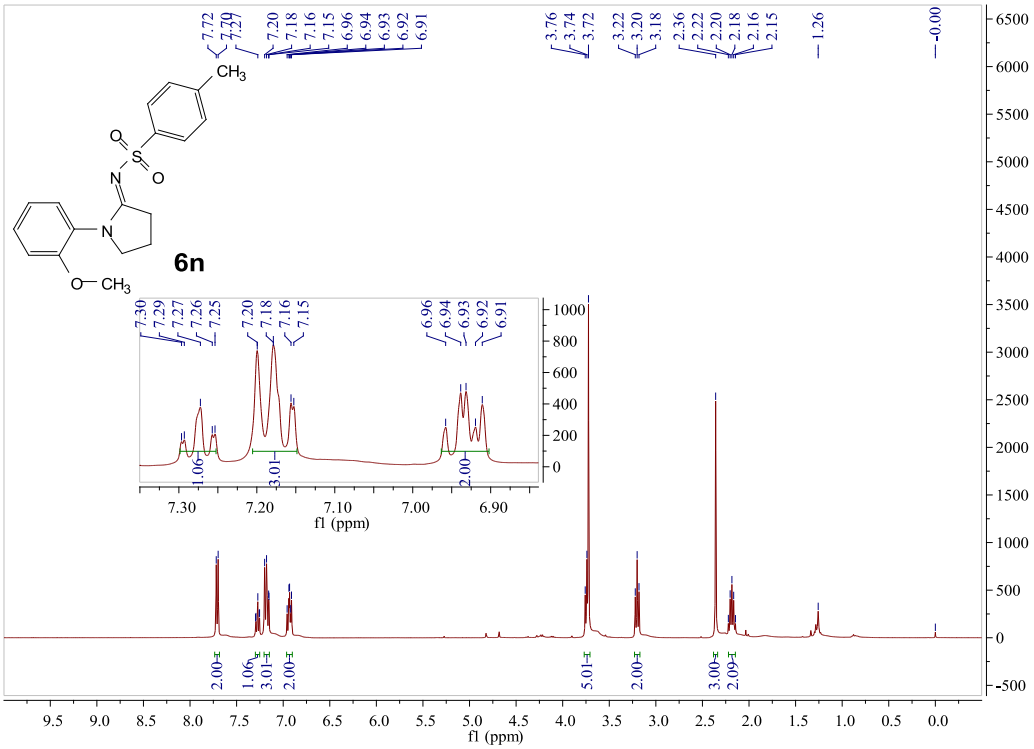

168.43
142.04
140.22
138.51
138.40
129.02
128.48
127.12
126.24
123.66
120.04
77.32
77.00
76.68
52.10
31.93
21.32
19.42
CH3
O
S
O
N
H3C
N
6k
f1 (ppm)

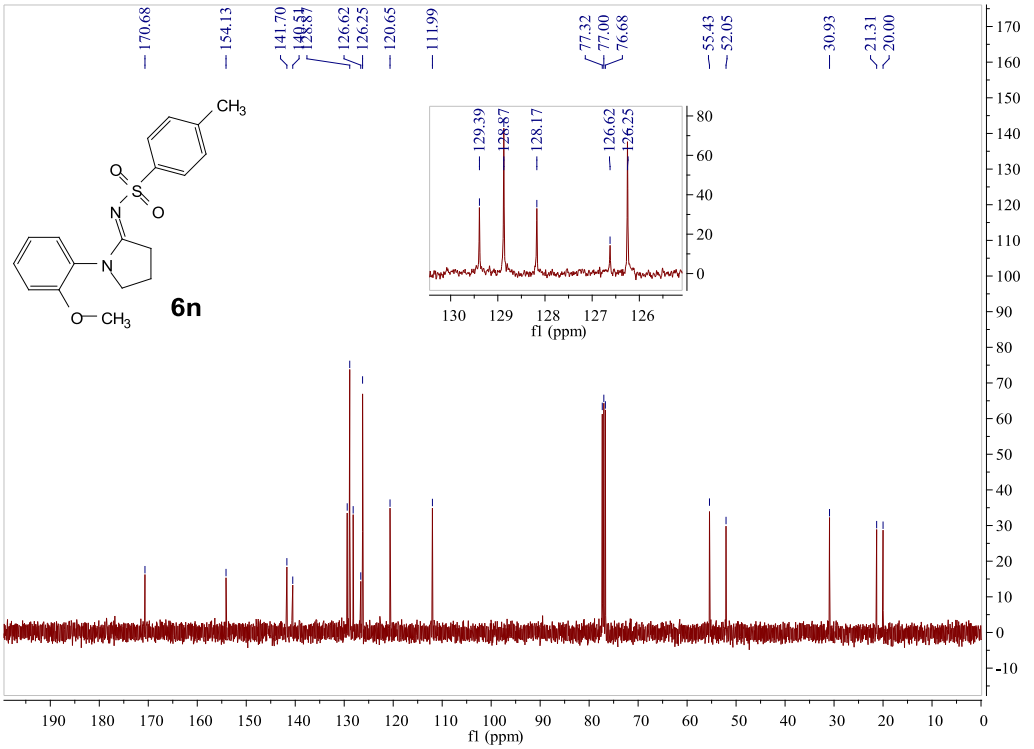

7.87
7.81
7.79
7.65
7.63
7.49
7.47
7.45
7.44
7.42
7.26
7.24
3.94
3.92
3.90
3.39
3.37
3.35
2.39
2.26
2.24
2.22
2.20
2.18
1.26
0.00
CH3
O
S
O
N
F
F
F
N
6l
1.00
2.02
1.00
2.03
2.02
2.00
2.01
3.01
2.02
fl (ppm)

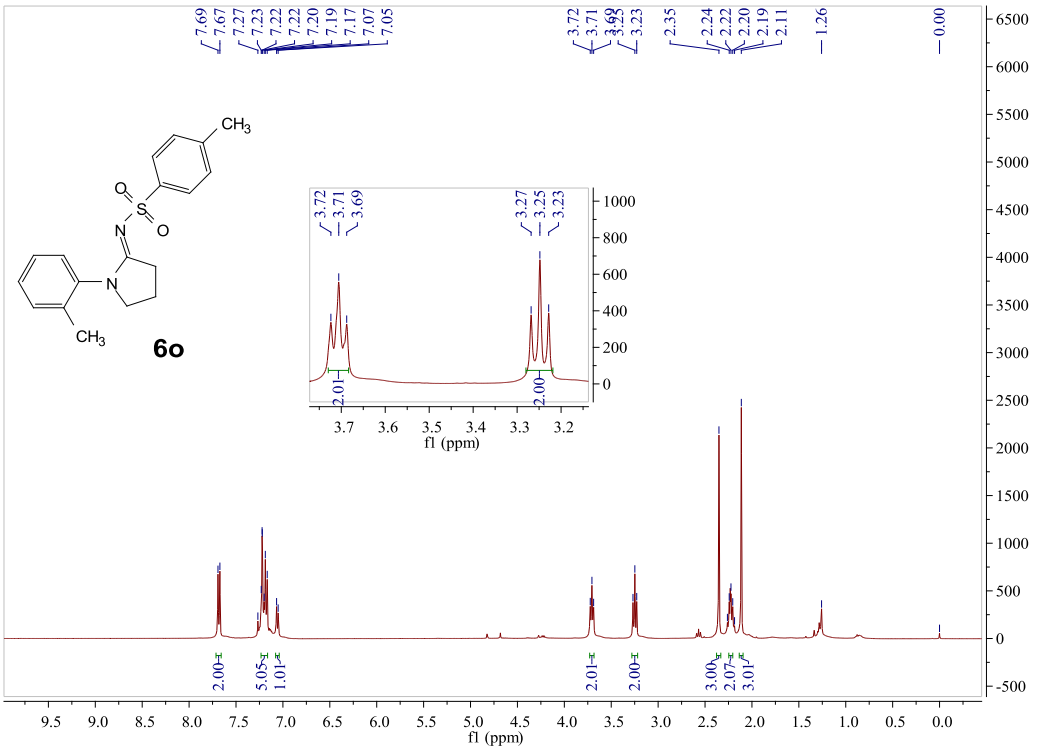

7.87
7.81
7.79
7.65
7.63
7.49
7.47
7.45
7.44
7.42
7.26
7.24
3.94
3.92
3.90
3.39
3.37
3.35
2.39
2.26
2.24
2.22
2.20
2.18
1.26
0.00
CH3
O
S
O
N
F
F
F
N
6l
1.00
2.02
1.00
2.03
2.02
2.00
2.01
3.01
2.02
fl (ppm)

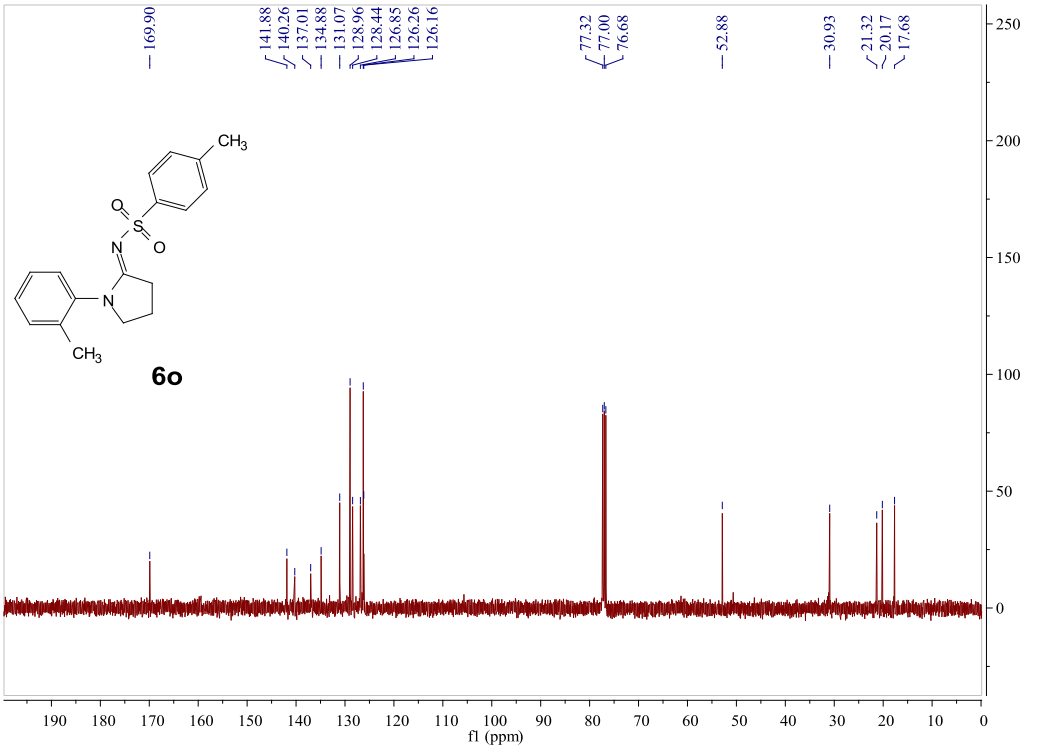

7.96
7.94
7.66
7.64
7.47
7.45
7.44
7.34
7.32
7.27
7.24
7.22
3.91
3.89
3.87
3.18
3.16
2.39
2.32
2.30
2.28
2.26
2.24
1.26
-0.00
CH3
O
S
N
O
N
N+
O-
O
6m
3.91
3.89
3.87
3.20
3.18
3.16
2.03
2.00
f1 (ppm)
1.01
3.02
1.02
1.04
2.00
2.03
2.00
3.00
2.02
f1 (ppm)

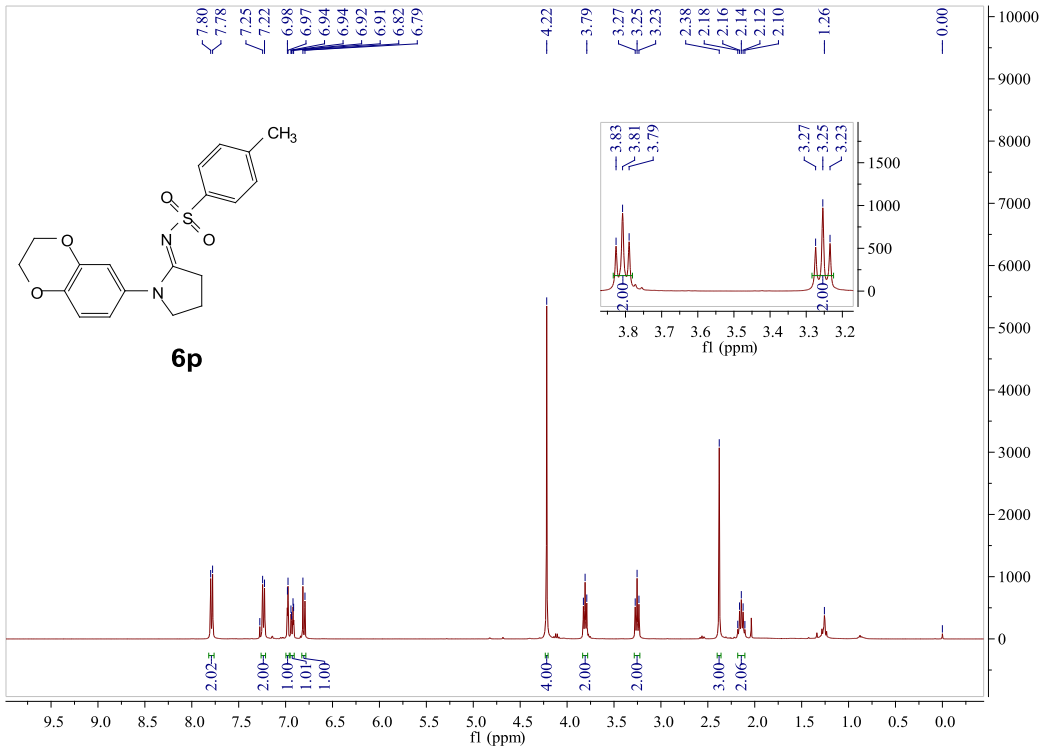

171.13
145.45
142.36
139.24
134.27
131.81
129.05
128.49
126.41
125.56
125.36
77.32
77.00
76.68
52.84
30.93
21.42
20.39
CH3
O
S
N
O
N
N+
O-
O
6m
f1 (ppm)

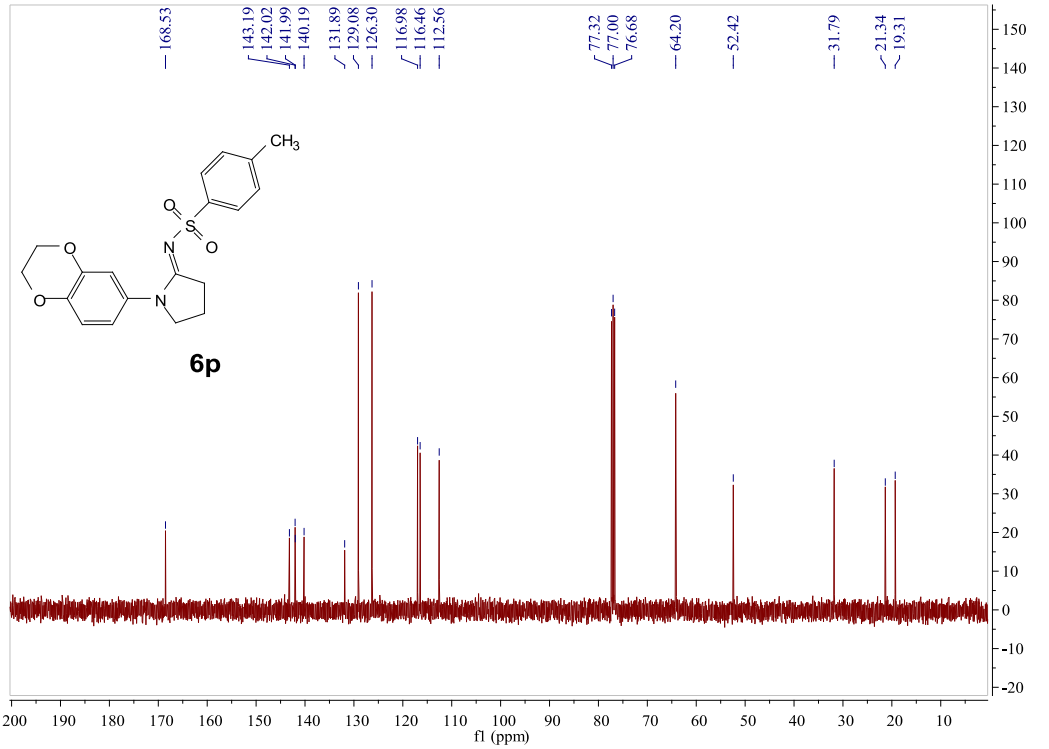

6n
fl (ppm)

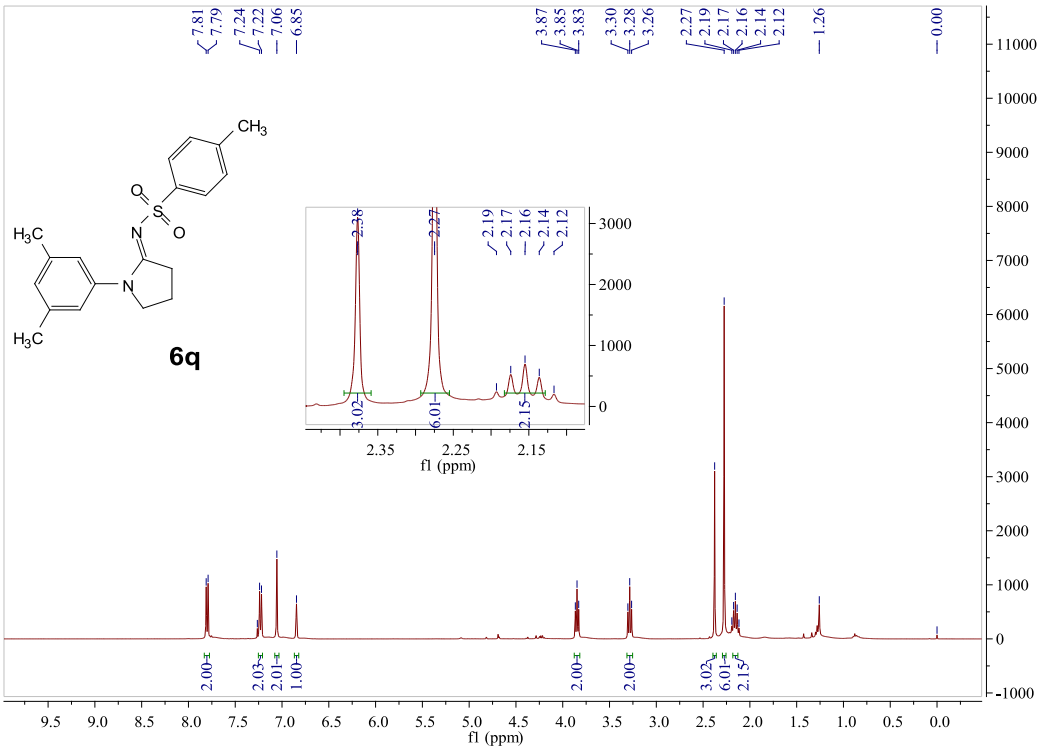

6n
fl (ppm)

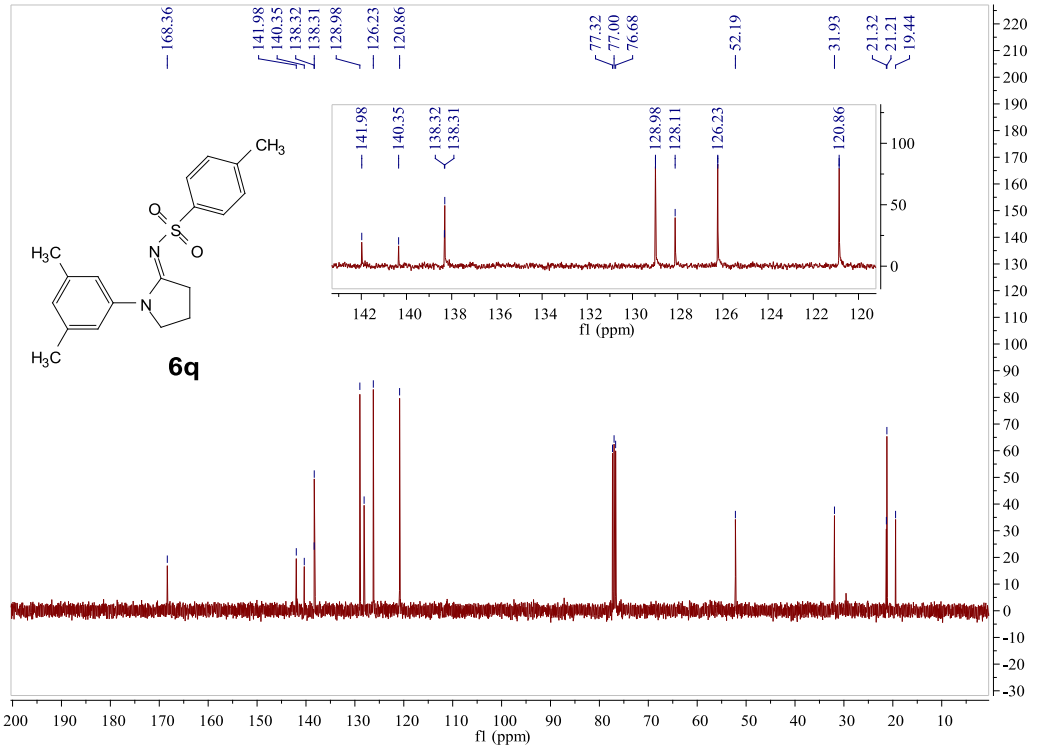

7.69
7.67
7.27
7.23
7.22
7.22
7.20
7.19
7.17
7.07
7.05
3.72
3.71
3.69
3.27
3.25
3.23
2.35
2.24
2.22
2.20
2.19
2.11
1.26
0.00
CH3
O
S
N
O
N
CH3
6o
2.00
5.05
1.01
2.01
2.00
3.00
2.07
3.01
f1 (ppm)

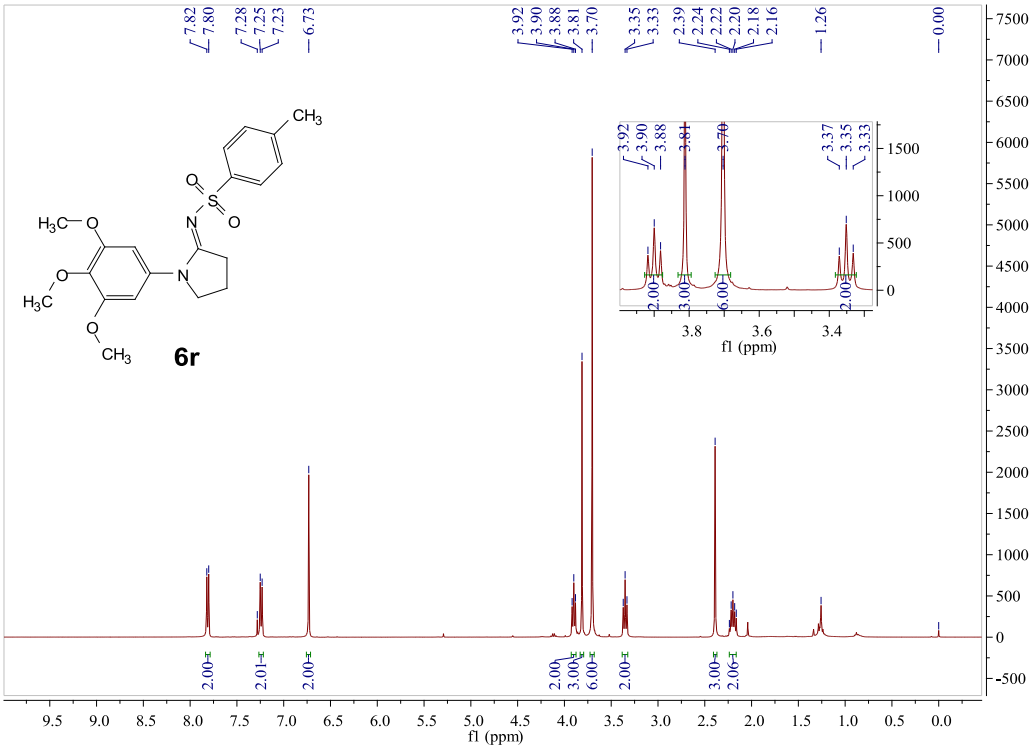

169.90
141.88
140.26
137.01
134.88
131.07
128.96
128.44
126.85
126.26
126.16
77.32
77.00
76.68
52.88
30.93
21.32
20.17
17.68
CH3
O
S
N
O
N
CH3
6o
f1 (ppm)

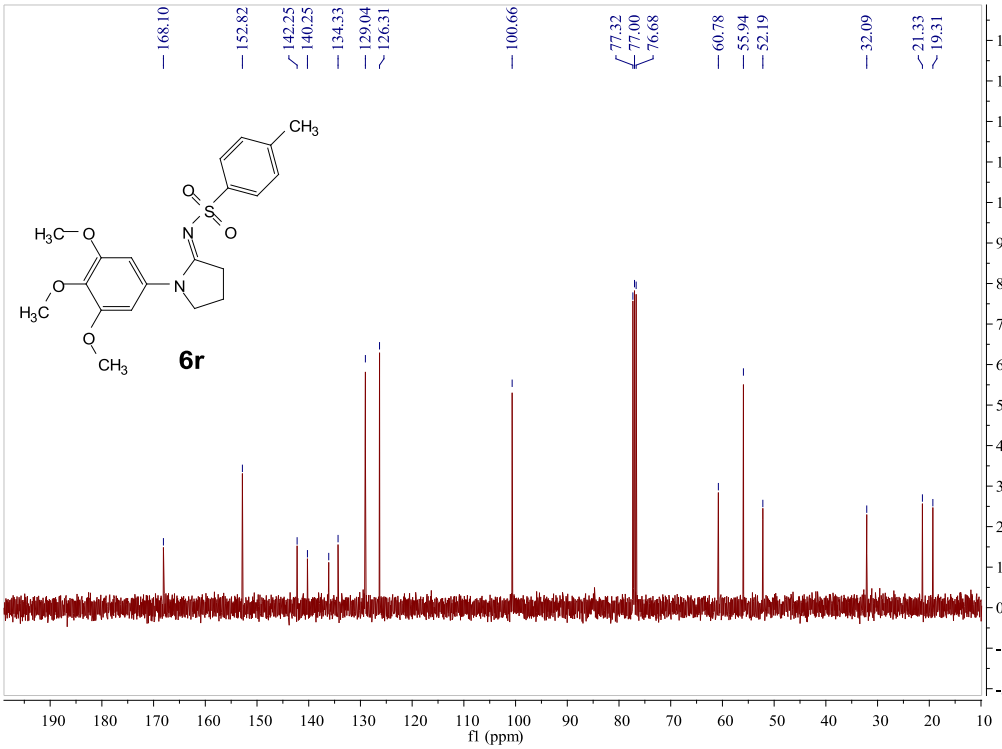

7.80
7.78
7.25
7.22
6.98
6.97
6.94
6.94
6.92
6.91
6.82
6.79
4.22
3.79
3.27
3.25
3.23
2.38
2.18
2.16
2.14
2.12
2.10
1.26
0.00
3.83
3.81
3.79
3.27
3.25
3.23
2.00
2.00
3.8 3.7 3.6 3.5 3.4 3.3 3.2
f1 (ppm)
CH3
O
S
O
N
O
O
N
6p
2.02
2.00
1.00
1.01
1.00
4.00
2.00
2.00
3.00
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

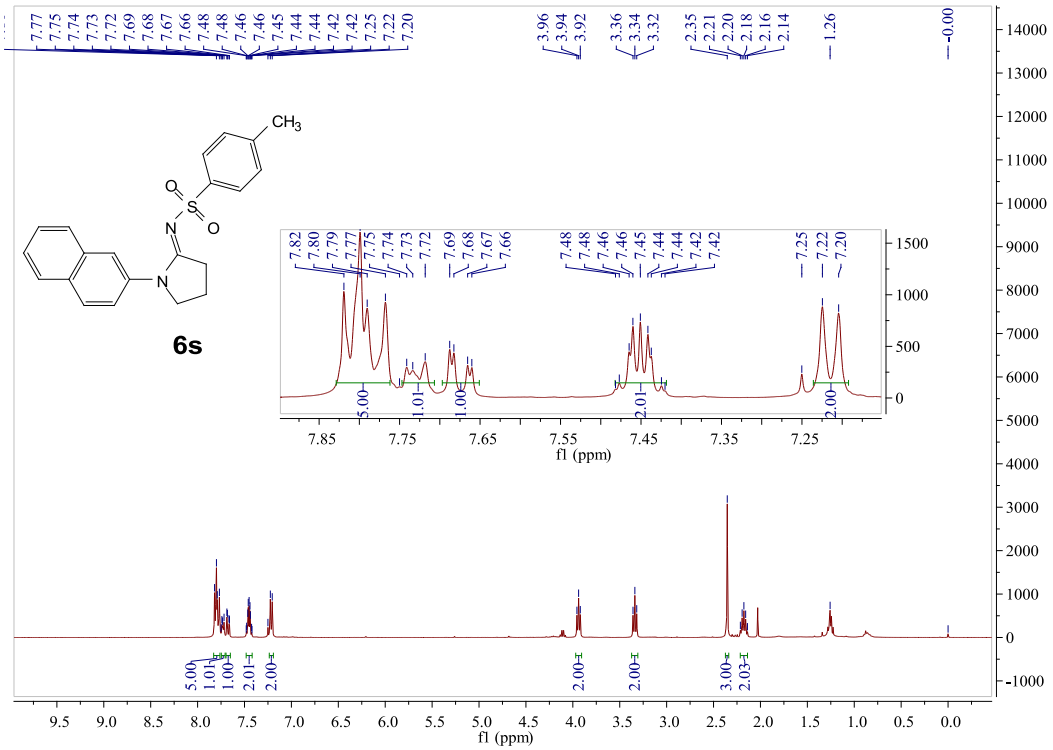

168.53
143.19
142.02
141.99
140.19
131.89
129.08
126.30
116.98
116.46
112.56
77.32
77.00
76.68
64.20
52.42
31.79
21.34
19.31
CH3
O
S
O
N
O
O
N
6p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

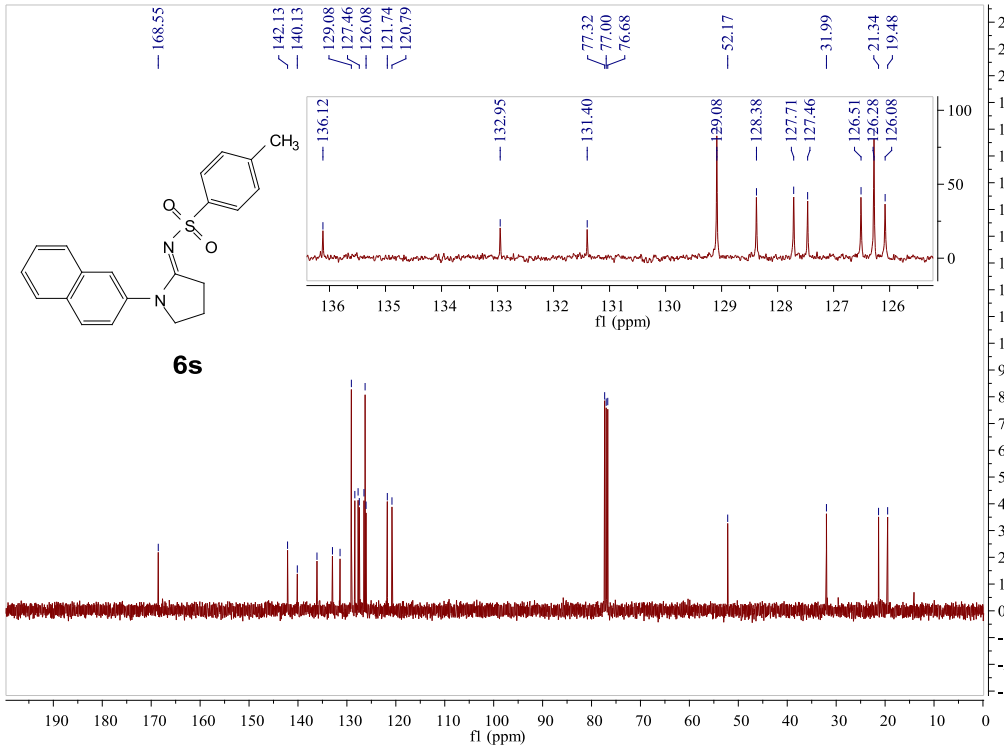

7.81
7.79
7.24
7.22
7.06
6.85
3.87
3.85
3.83
3.30
3.28
3.26
2.27
2.19
2.17
2.16
2.14
2.12
1.26
0.00
CH3
O
S
N
O
H3C
N
H3C
6q
2.38
2.37
2.19
2.17
2.16
2.14
2.12
3.02
6.01
2.15
2.35
2.25
2.15
f1 (ppm)
2.00
2.03
2.01
1.00
2.00
2.00
3.02
6.01
2.15
f1 (ppm)

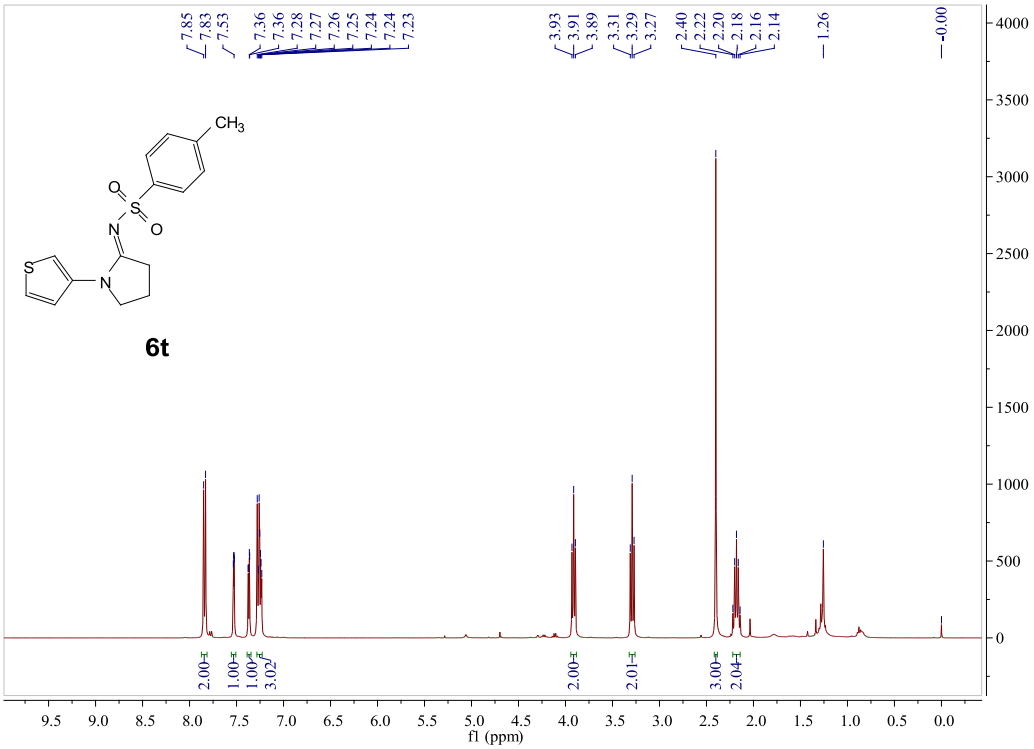

168.36
141.98
140.35
138.32
138.31
128.98
126.23
120.86
77.32
77.00
76.68
52.19
31.93
21.32
21.21
19.44
CH3
O
S
N
O
H3C
N
H3C
6q
141.98
140.35
138.32
138.31
128.98
128.11
126.23
120.86
142
140
138
136
134
132
130
128
126
124
122
120
f1 (ppm)
f1 (ppm)

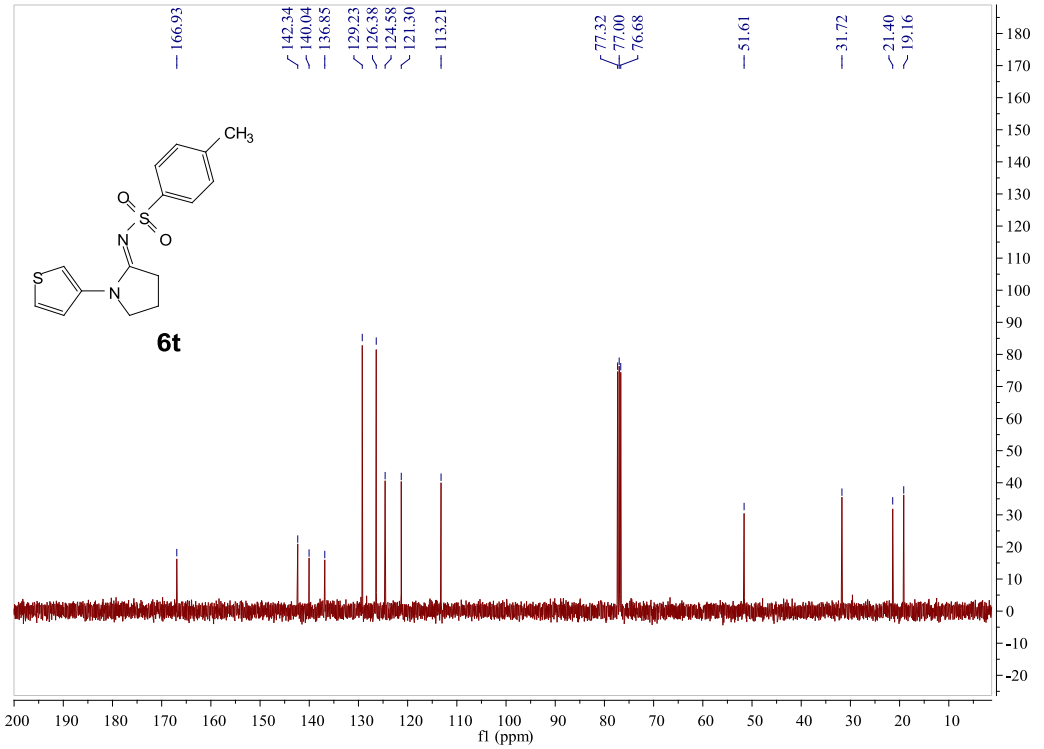

7.82
7.80
7.28
7.25
7.23
6.73
3.92
3.90
3.88
3.81
3.70
3.35
3.33
2.39
2.24
2.22
2.20
2.18
2.16
1.26
0.00
6r
fl (ppm)

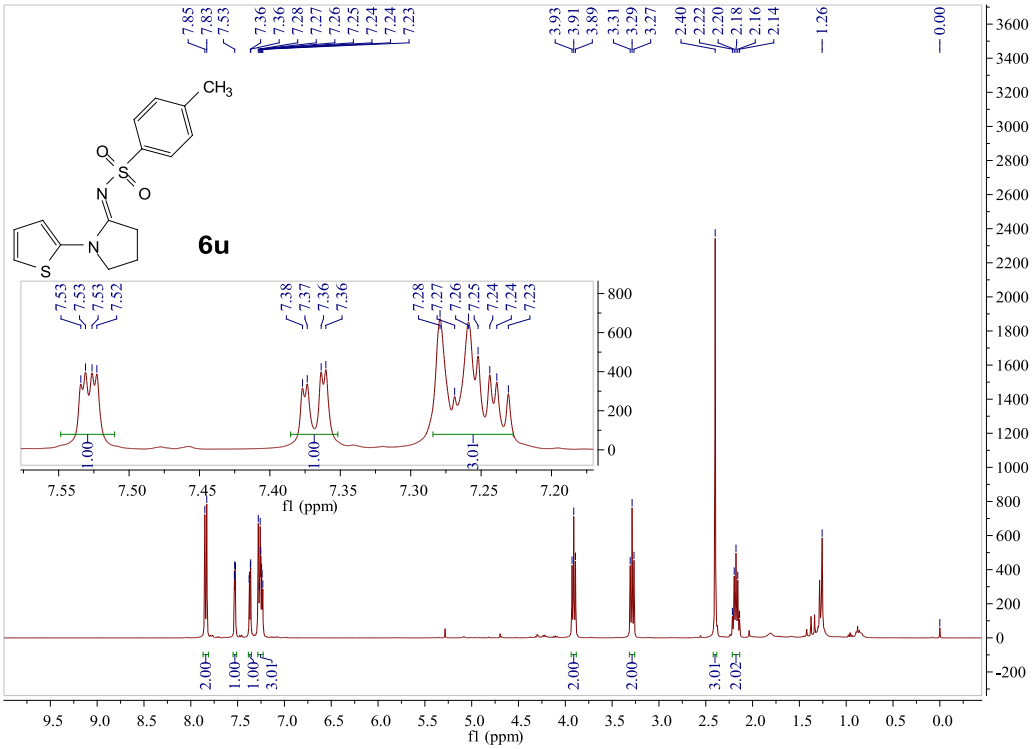

168.10
152.82
142.25
140.25
134.33
129.04
126.31
100.66
77.32
77.00
76.68
60.78
55.94
52.19
32.09
21.33
19.31
6r
fl (ppm)

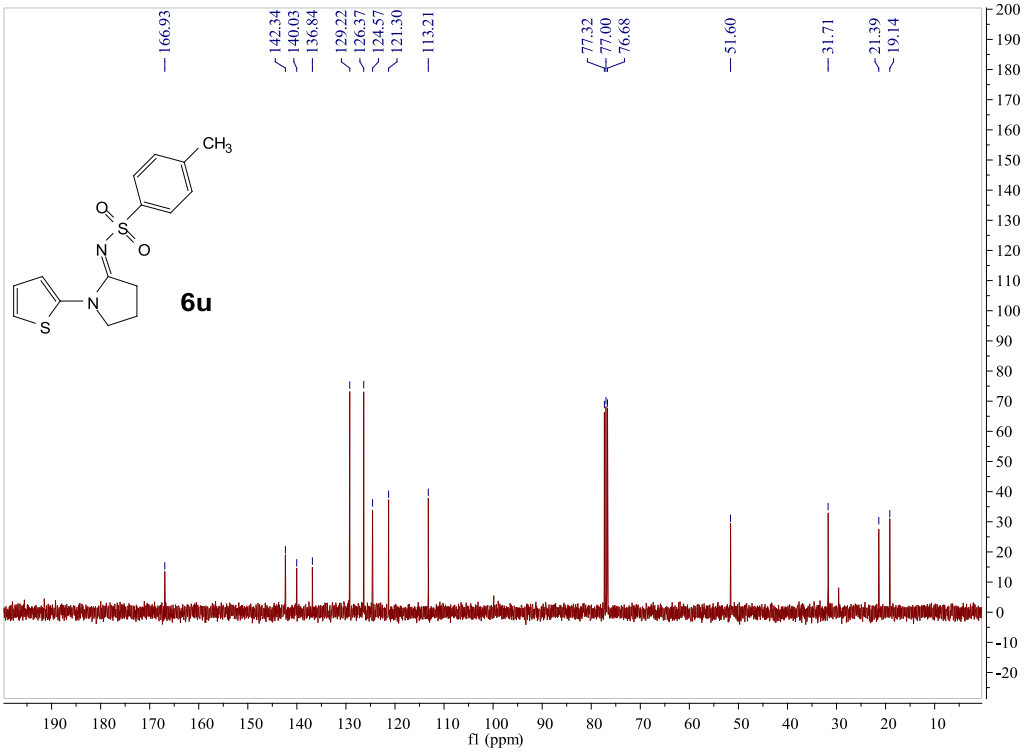

6s
f1 (ppm)

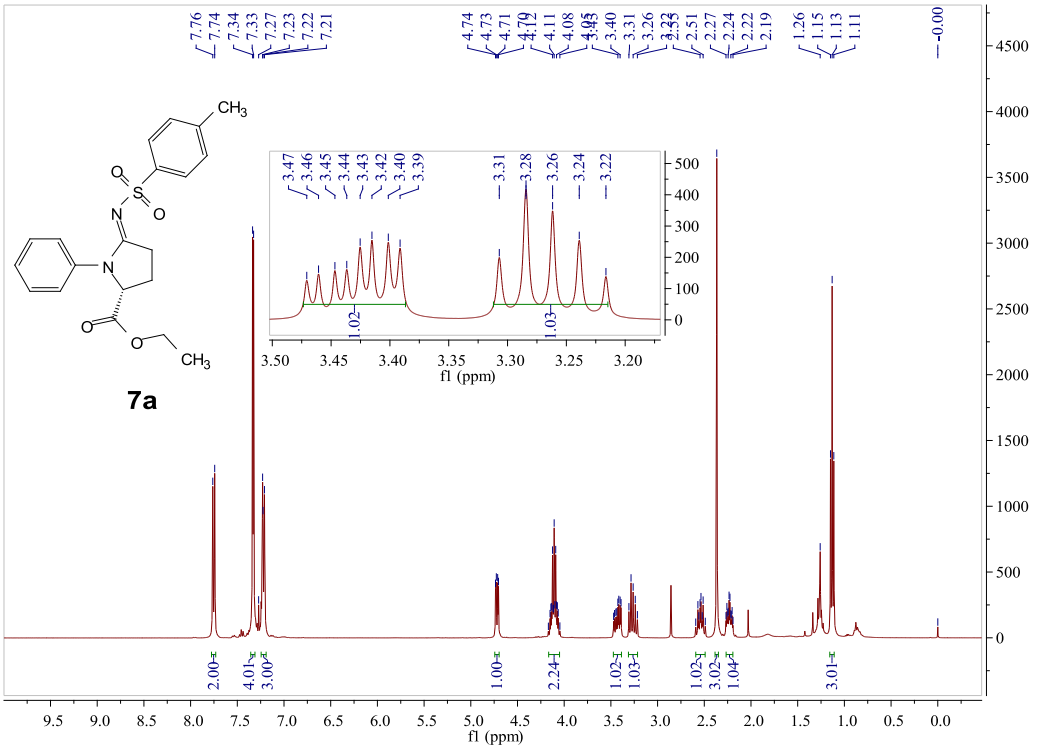

6s
f1 (ppm)

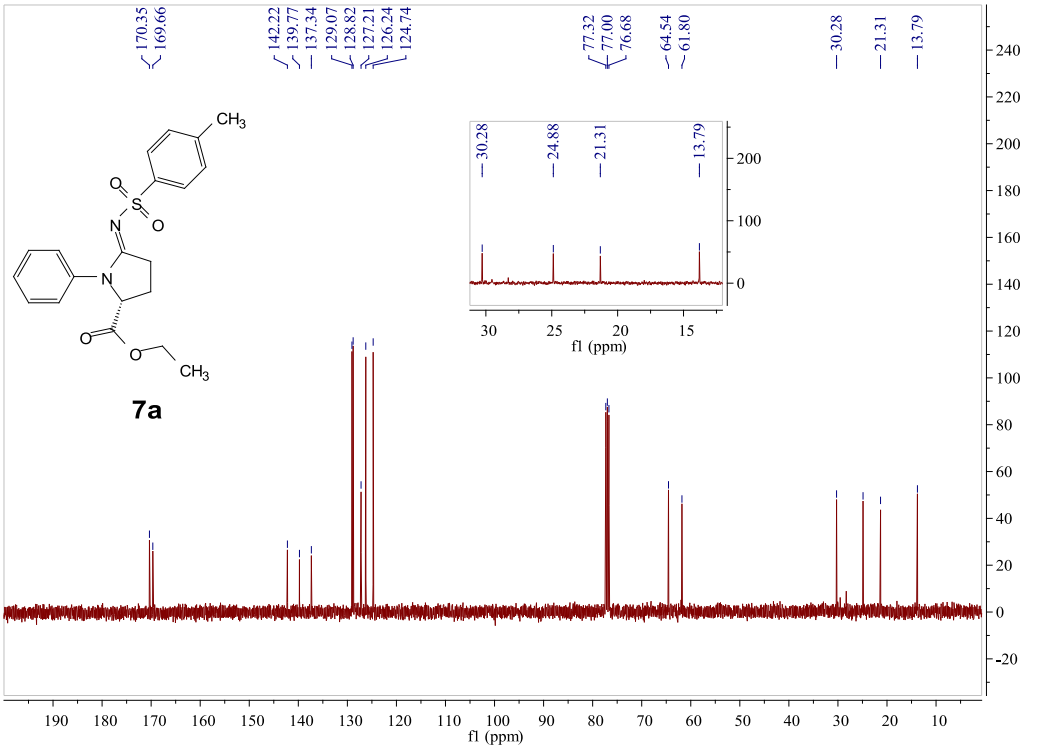

7.85
7.83
7.53
7.36
7.36
7.28
7.27
7.26
7.25
7.24
7.24
7.23
3.93
3.91
3.89
3.31
3.29
3.27
2.40
2.22
2.20
2.18
2.16
2.14
1.26
0.00
CH3
O
S
O
N
S
N
6t
2.00
1.00
1.00
3.02
2.00
2.01
3.00
2.04
f1 (ppm)

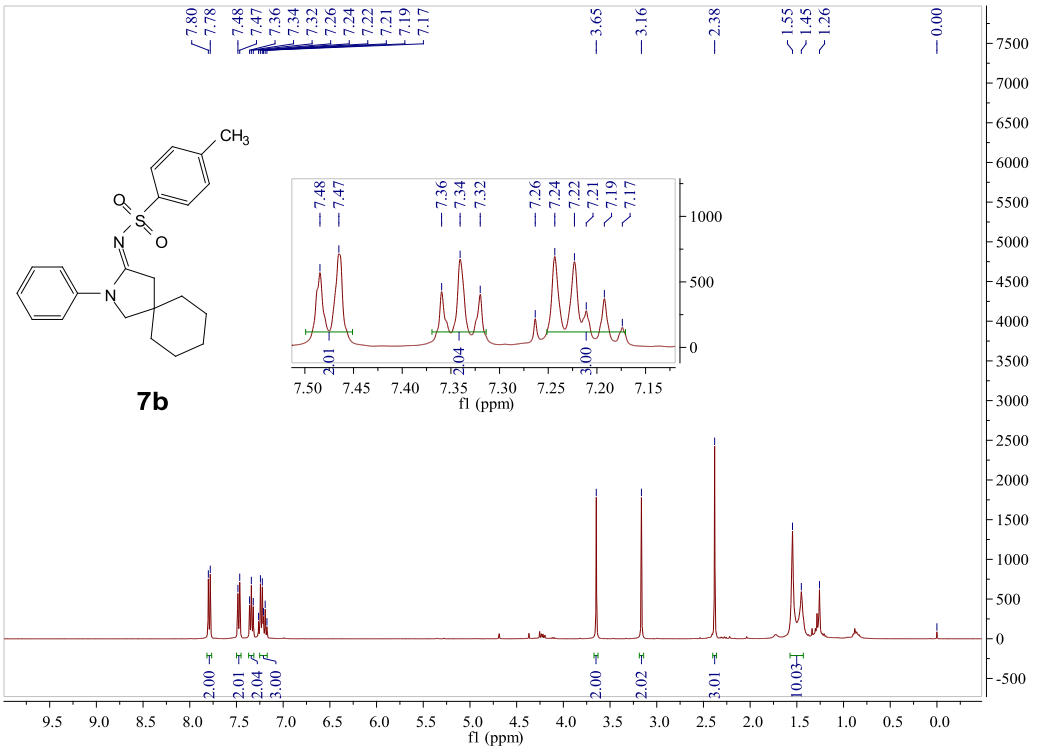

166.93
142.34
140.04
136.85
129.23
126.38
124.58
121.30
113.21
77.32
77.00
76.68
51.61
31.72
21.40
19.16
CH3
O
S
O
N
S
N
6t
f1 (ppm)

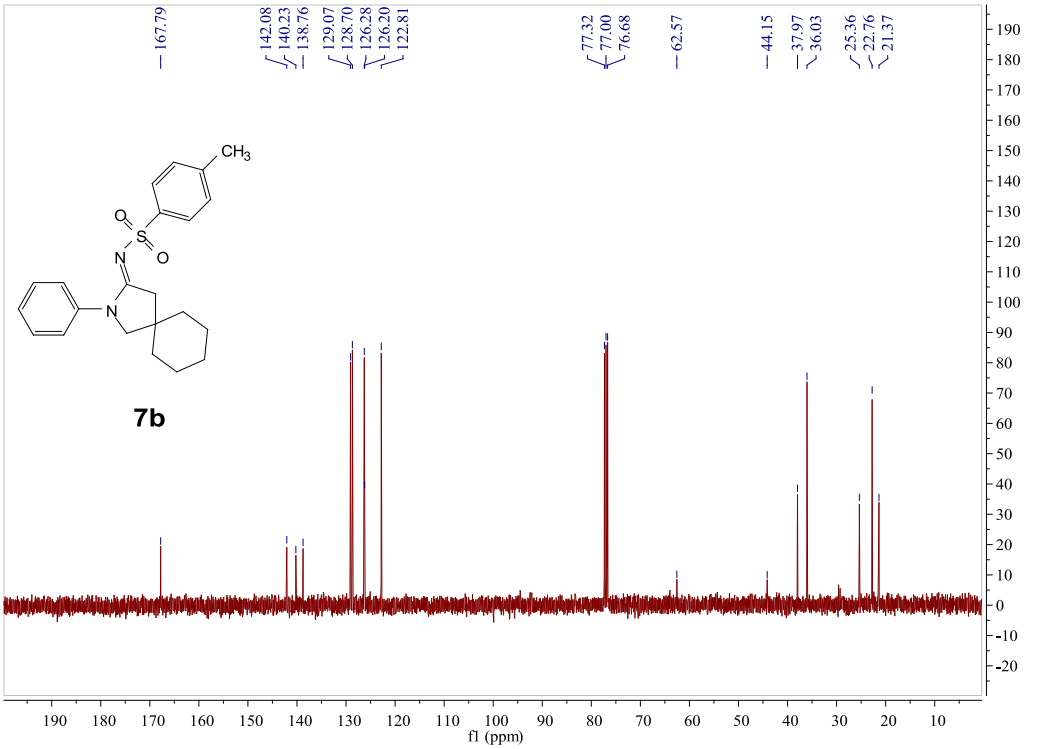

7.85
7.83
7.53
7.36
7.36
7.28
7.27
7.26
7.25
7.24
7.24
7.23
3.93
3.91
3.89
3.31
3.29
3.27
2.40
2.22
2.20
2.18
2.16
2.14
1.26
0.00
CH3
O
S
O
N
N
S
6u
7.53
7.53
7.53
7.52
7.38
7.37
7.36
7.36
7.28
7.27
7.26
7.25
7.24
7.24
7.23
1.00
1.00
3.01
fl (ppm)
2.00
1.00
1.00
3.01
2.00
2.00
3.01
2.02
fl (ppm)

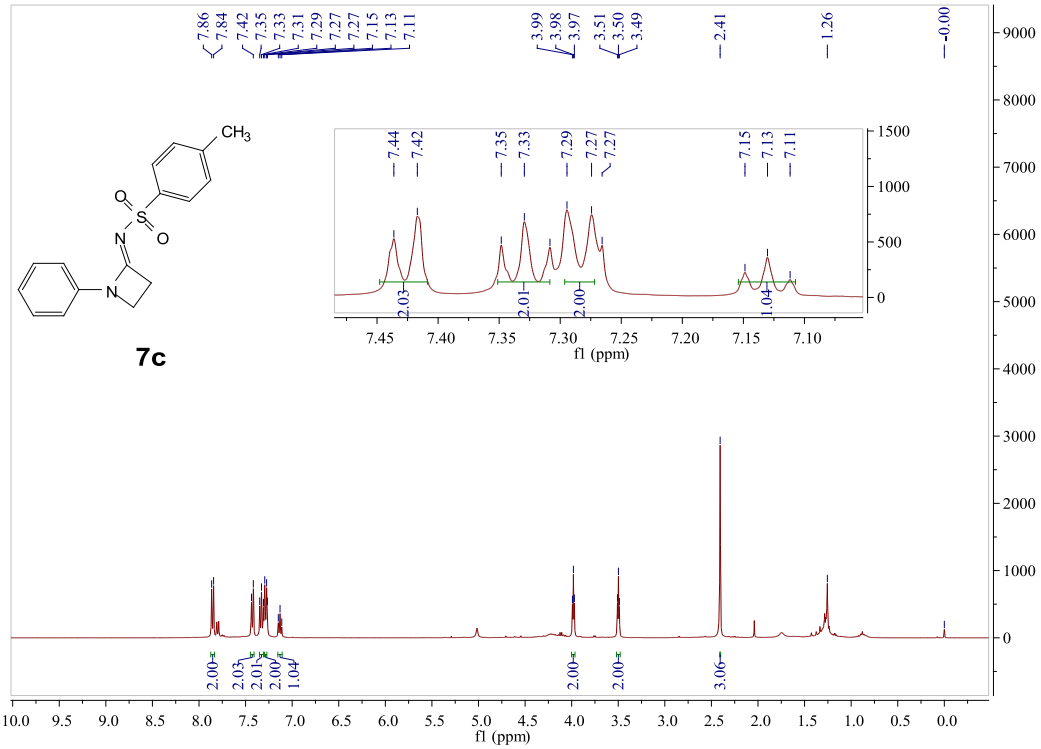

166.93
142.34
140.03
136.84
129.22
126.37
124.57
121.30
113.21
77.32
77.00
76.68
51.60
31.71
21.39
19.14
CH3
O
S
O
N
N
S
6u
fl (ppm)

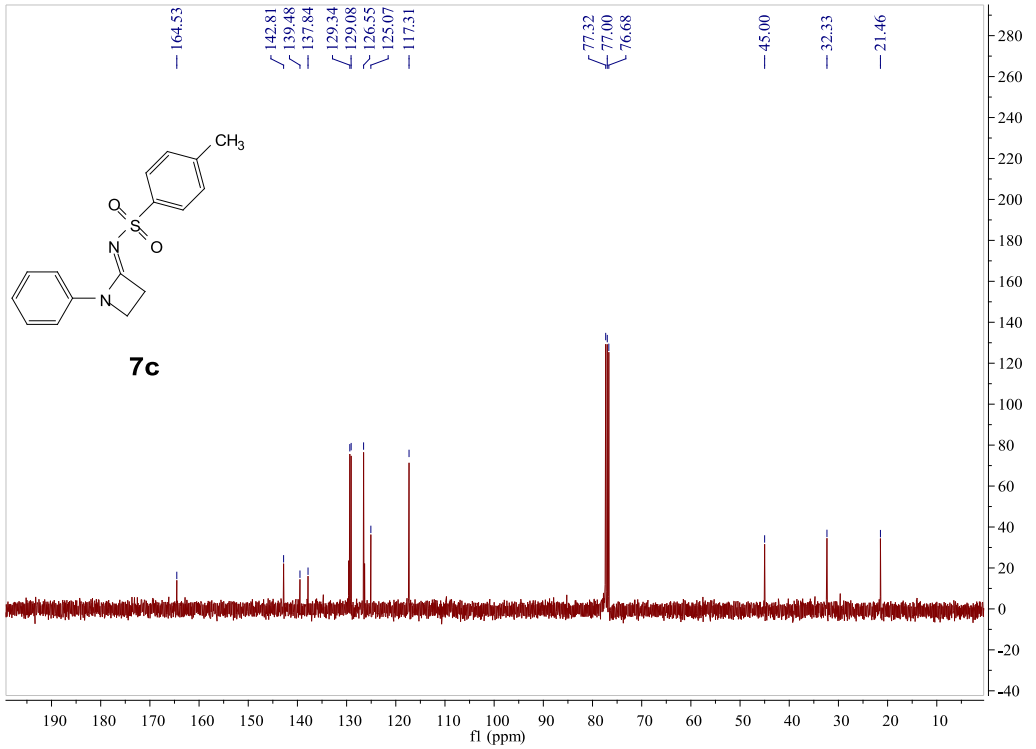

7.76
7.74
7.34
7.33
7.27
7.23
7.22
7.21
4.74
4.73
4.71
4.11
4.08
3.40
3.31
3.26
2.51
2.27
2.24
2.22
2.19
1.26
1.15
1.13
1.11
-0.00
3.47
3.46
3.45
3.44
3.43
3.42
3.40
3.39
3.31
3.28
3.26
3.24
3.22
1.02
1.03
3.50 3.45 3.40 3.35 3.30 3.25 3.20
f1 (ppm)
CH3
O
S
N
O
N
O
O
CH3
7a
2.00
4.01
3.00
1.00
2.24
1.02
1.03
1.02
3.02
1.04
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

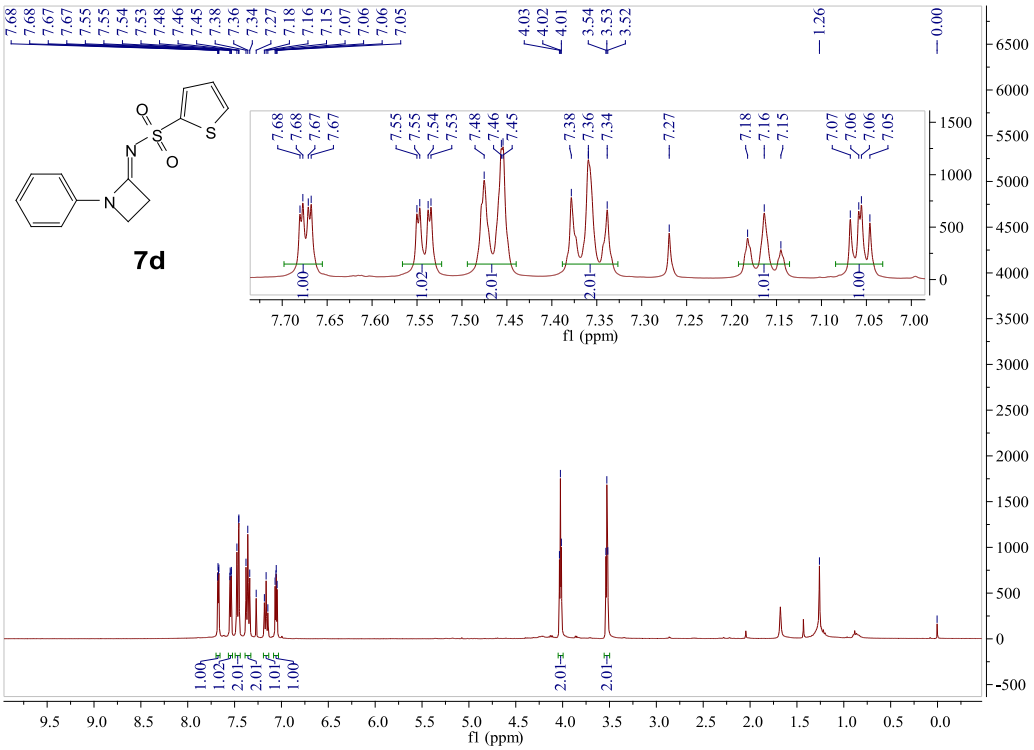

170.35
169.66
142.22
139.77
137.34
129.07
128.82
127.21
126.24
124.74
77.32
77.00
76.68
64.54
61.80
30.28
21.31
13.79
30.28
24.88
21.31
13.79
30 25 20 15
f1 (ppm)
CH3
O
S
N
O
N
O
O
CH3
7a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

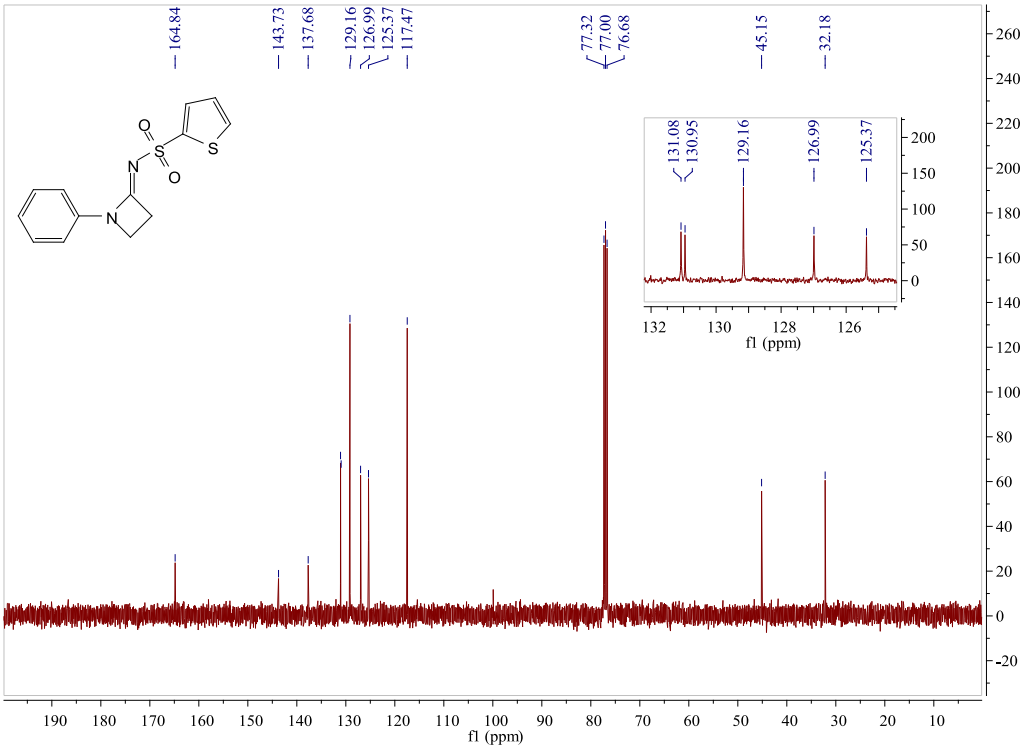

7.80
7.78
7.48
7.47
7.36
7.34
7.32
7.26
7.24
7.22
7.21
7.19
7.17
3.65
3.16
2.38
1.55
1.45
1.26
0.00
CH3
O
S
O
N
N
7b
fl (ppm)
2.00
2.01
2.04
3.00
2.00
2.02
3.01
10.03

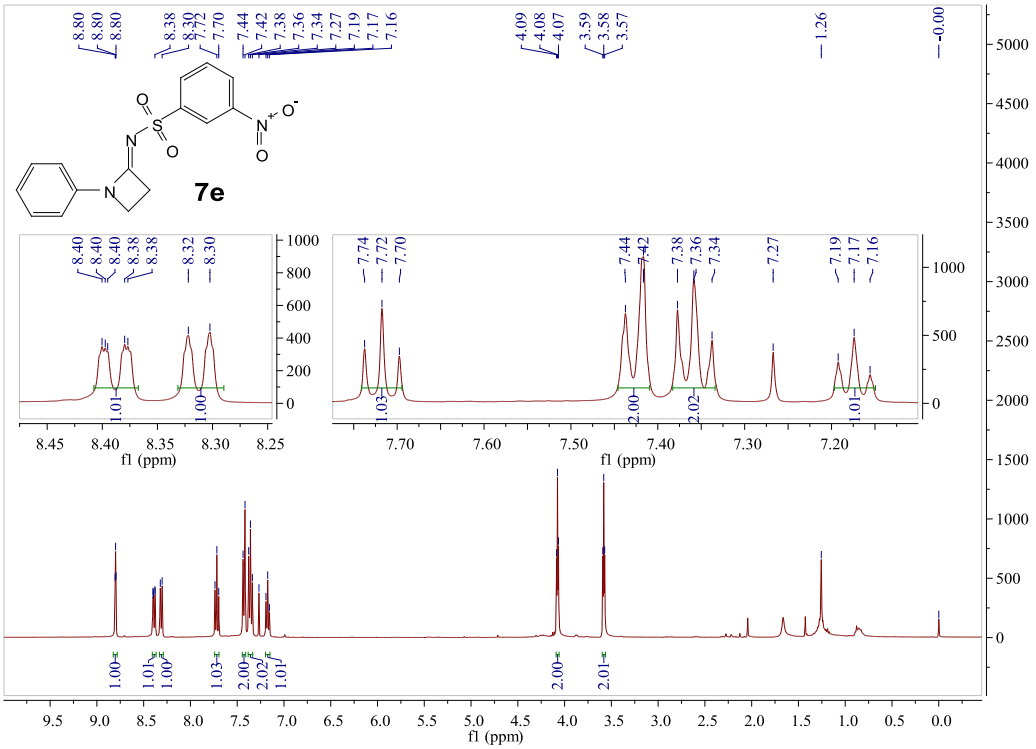

167.79
142.08
140.23
138.76
129.07
128.70
126.28
126.20
122.81
77.32
77.00
76.68
62.57
44.15
37.97
36.03
25.36
22.76
21.37
CH3
O
S
O
N
N
7b
fl (ppm)

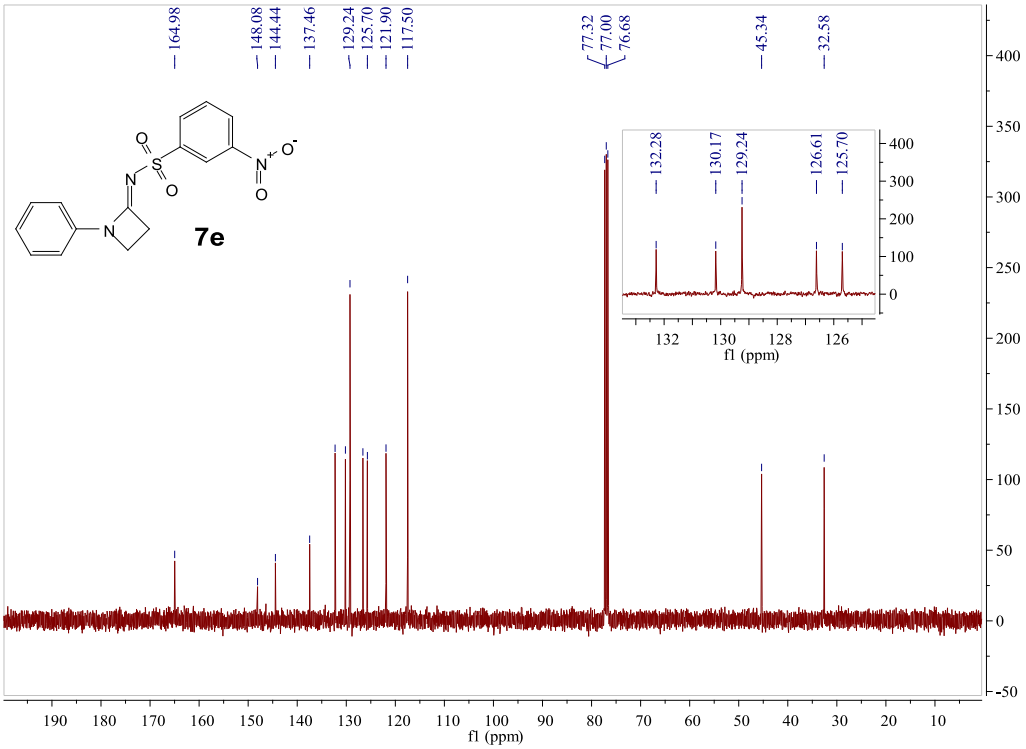

7.86
7.84
7.42
7.35
7.33
7.31
7.29
7.27
7.27
7.15
7.13
7.11
3.99
3.98
3.97
3.51
3.50
3.49
2.41
1.26
-0.00
CH3
O
S
O
N
N
7c
7.44
7.42
7.35
7.33
7.29
7.27
7.27
7.15
7.13
7.11
2.03
2.01
2.00
1.04
f1 (ppm)
2.00
2.03
2.01
2.00
1.04
2.00
2.00
3.06
f1 (ppm)

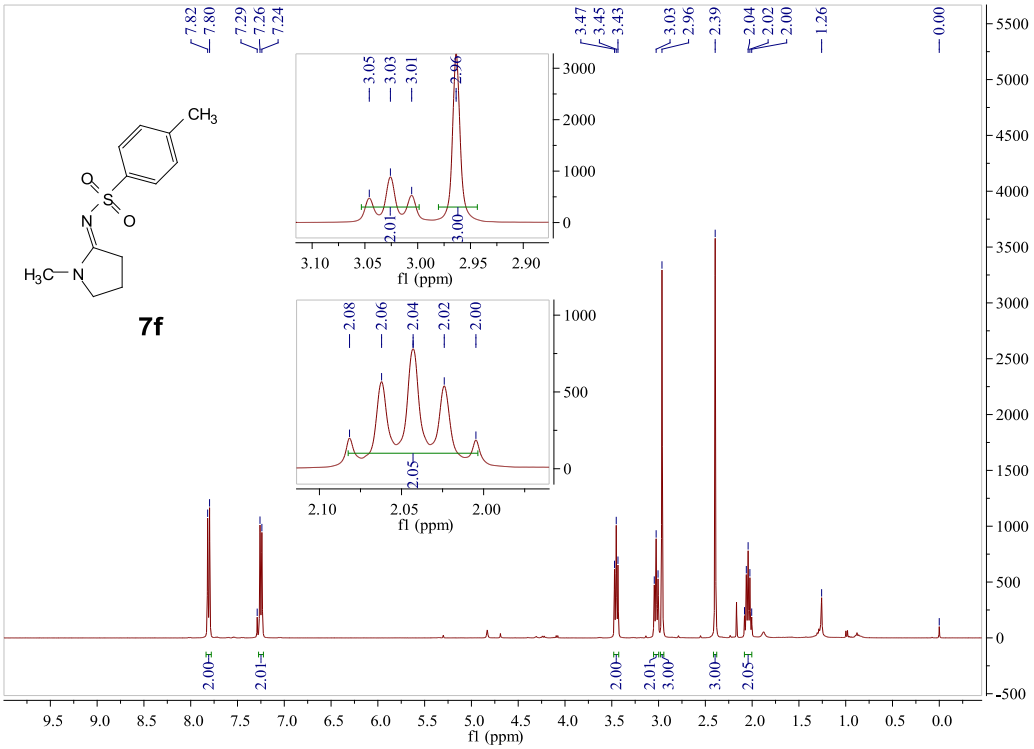

164.53
142.81
139.48
137.84
129.34
129.08
126.55
125.07
117.31
77.32
77.00
76.68
45.00
32.33
21.46
CH3
O
S
O
N
N
7c
f1 (ppm)

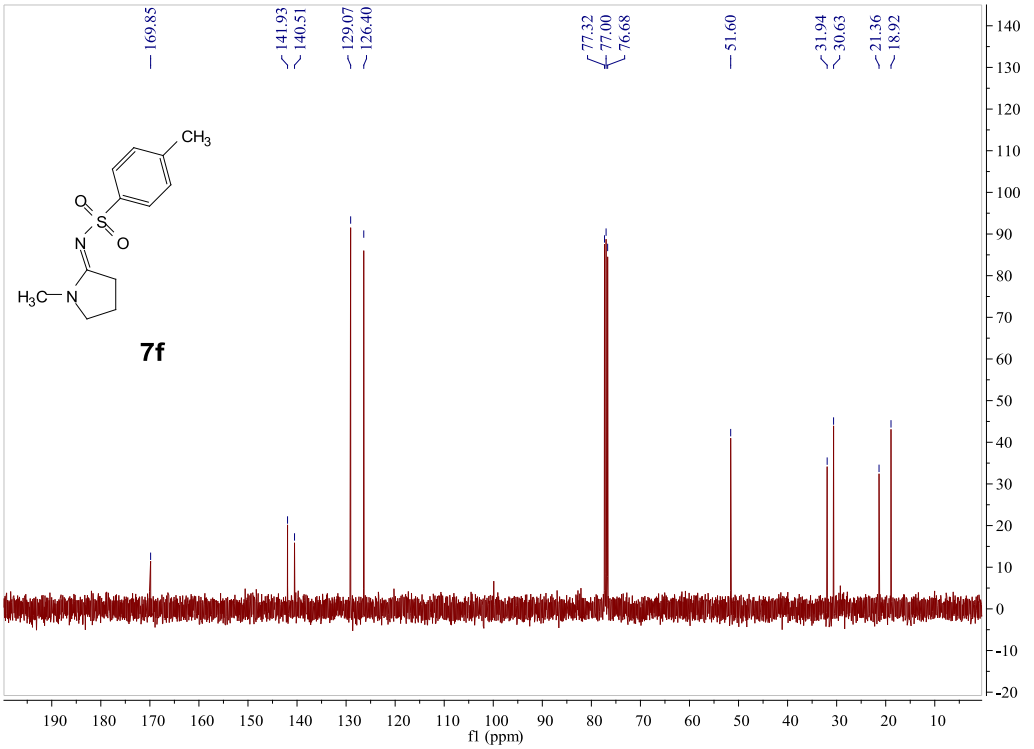

7.68
7.68
7.67
7.67
7.55
7.55
7.54
7.53
7.48
7.46
7.45
7.38
7.36
7.34
7.27
7.18
7.16
7.15
7.07
7.06
7.06
7.05
4.03
4.02
4.01
3.54
3.53
3.52
1.26
0.00
7d
fl (ppm)

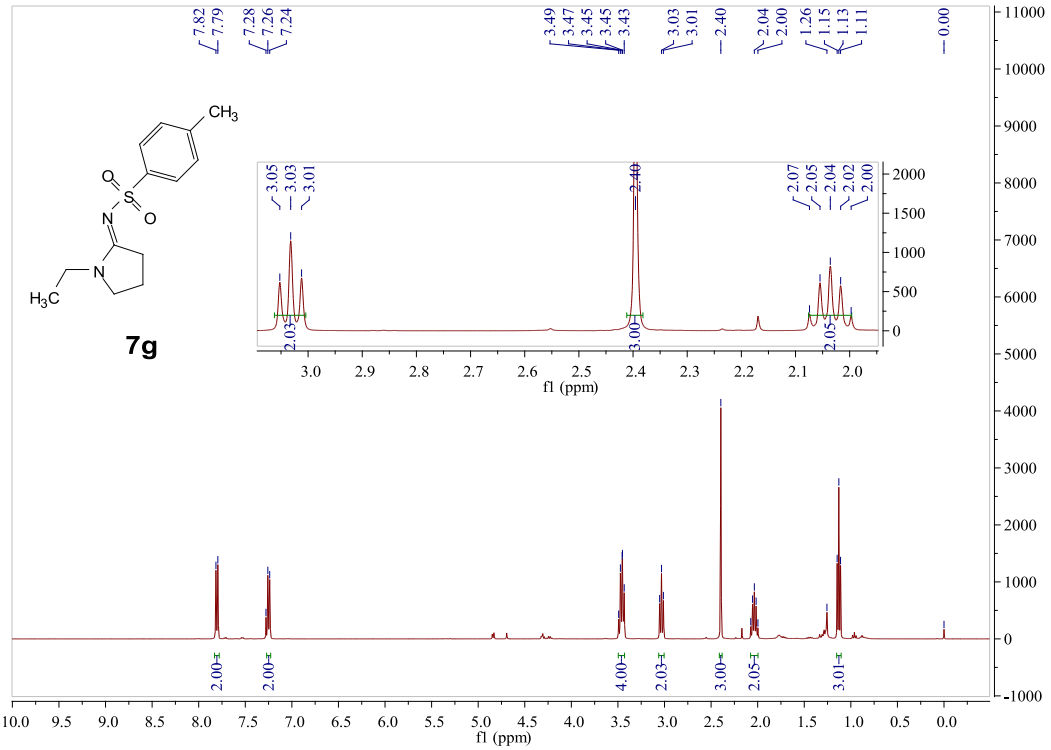

164.84
143.73
137.68
129.16
126.99
125.37
117.47
77.32
77.00
76.68
45.15
32.18
131.08
130.95
129.16
126.99
125.37
fl (ppm)

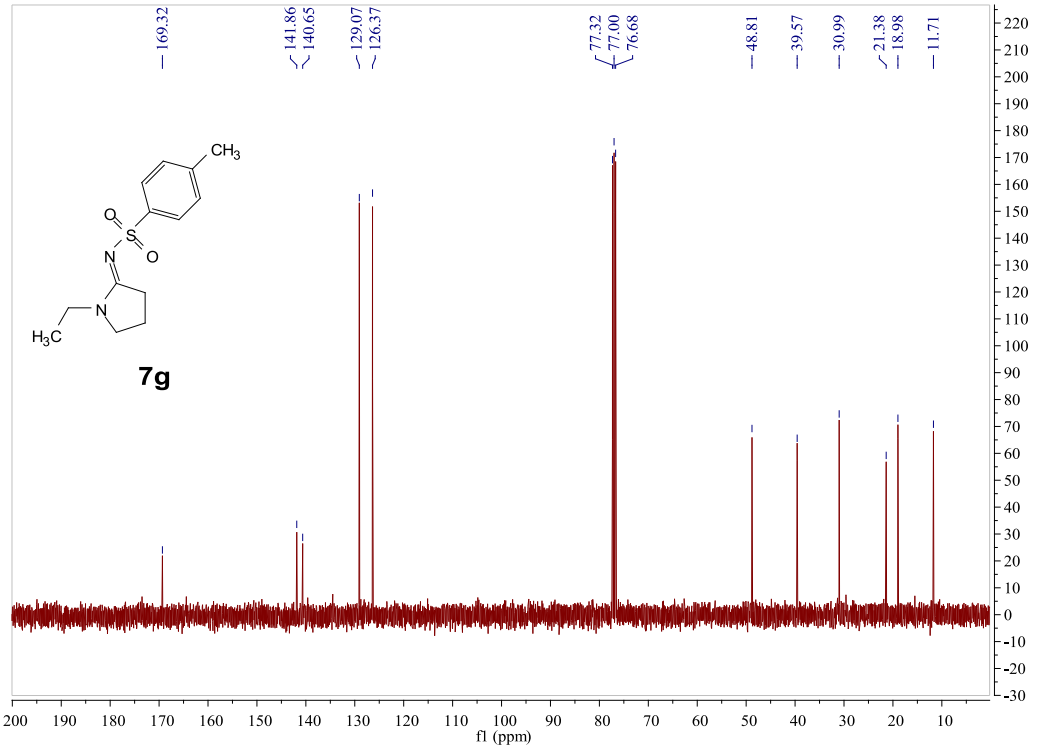

7e
fl (ppm)

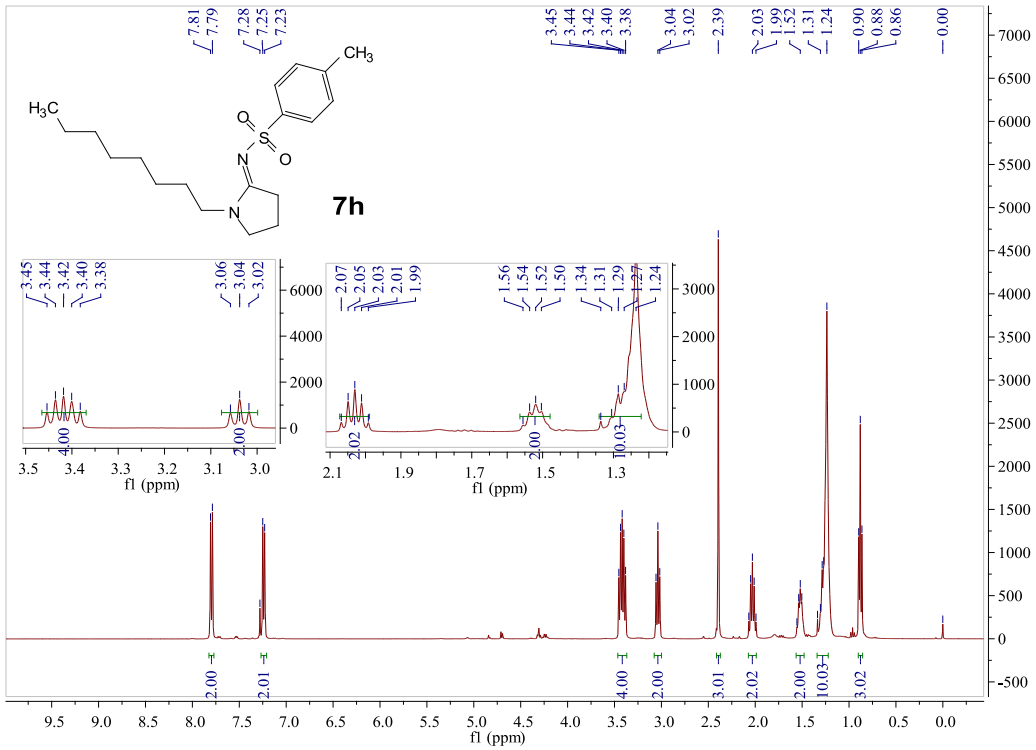

7e
fl (ppm)

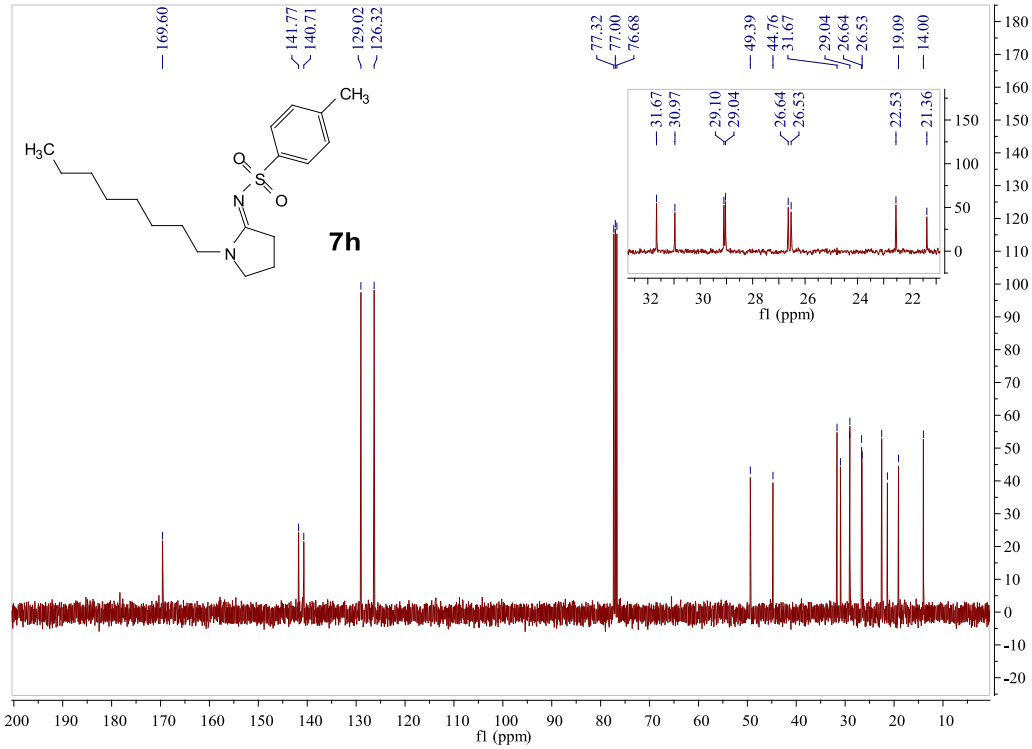

7.82
7.80
7.29
7.26
7.24
3.47
3.45
3.43
3.03
2.96
2.39
2.04
2.02
2.00
1.26
0.00
3.05
3.03
3.01
2.96
2.01
3.00
3.10 3.05 3.00 2.95 2.90
f1 (ppm)
2.08
2.06
2.04
2.02
2.00
2.05
2.10 2.05 2.00
f1 (ppm)
2.00
2.01
2.00
2.01
3.00
3.00
2.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
CH3
O
S
O
N
H3C
N
7f

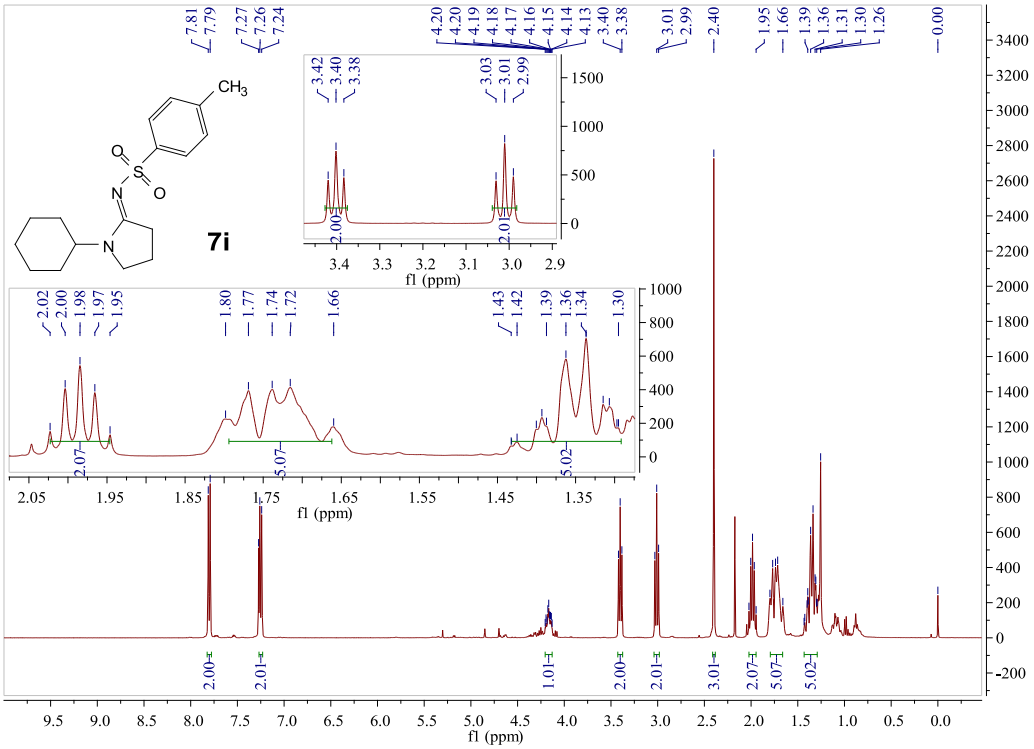

169.85
141.93
140.51
129.07
126.40
77.32
77.00
76.68
51.60
31.94
30.63
21.36
18.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
CH3
O
S
O
N
H3C
N
7f

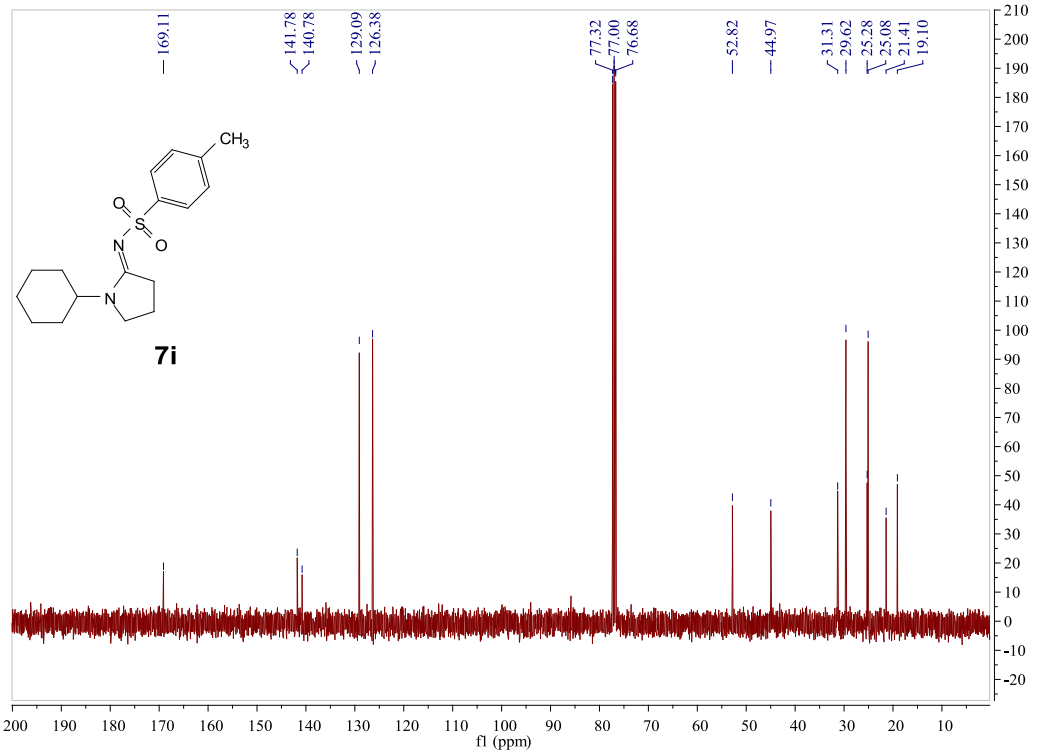

7.82
7.79
7.28
7.26
7.24
3.49
3.47
3.45
3.45
3.43
3.03
3.01
2.40
2.04
2.00
1.26
1.15
1.13
1.11
0.00
CH3
O
S
O
N
N
H3C
7g
3.05
3.03
3.01
2.40
2.07
2.05
2.04
2.02
2.00
fl (ppm)
2.00
2.00
4.00
2.03
3.00
2.05
3.01
fl (ppm)

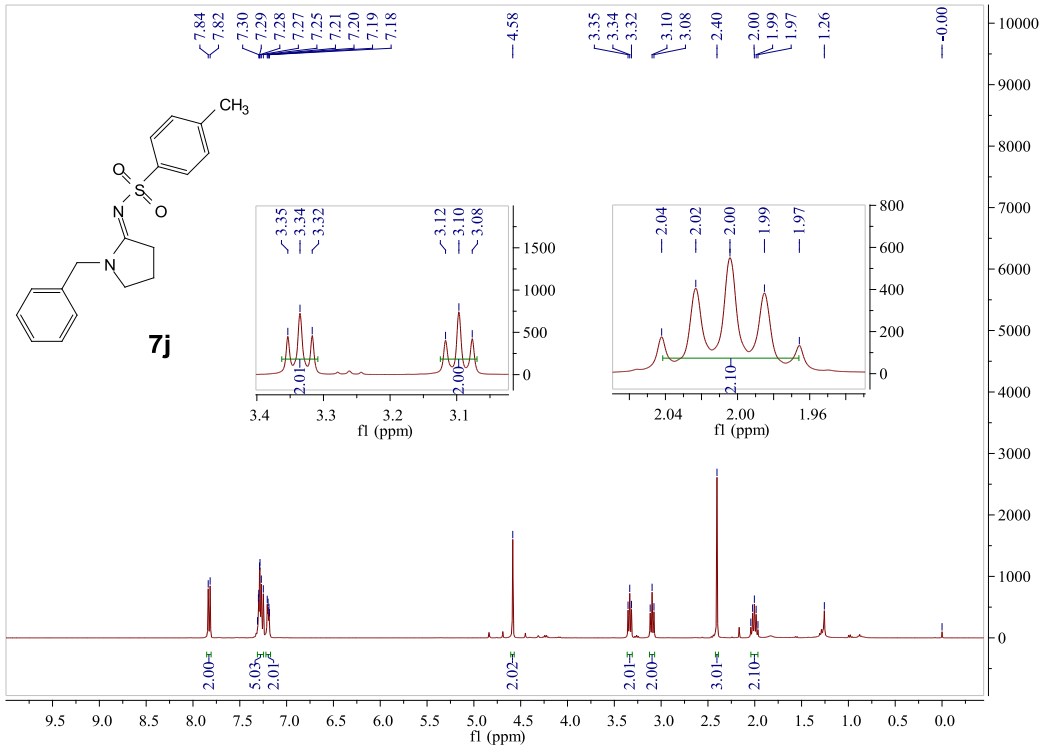

169.32
141.86
140.65
129.07
126.37
77.32
77.00
76.68
48.81
39.57
30.99
21.38
18.98
11.71
CH3
O
S
O
N
N
H3C
7g
fl (ppm)

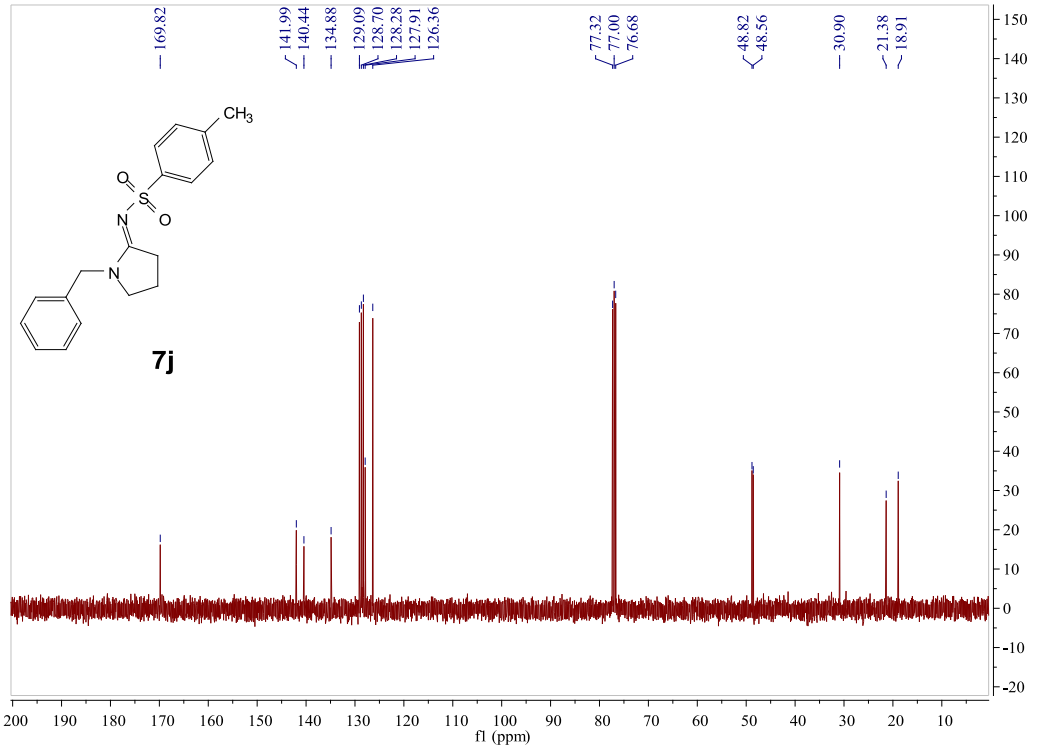

7h
fl (ppm)

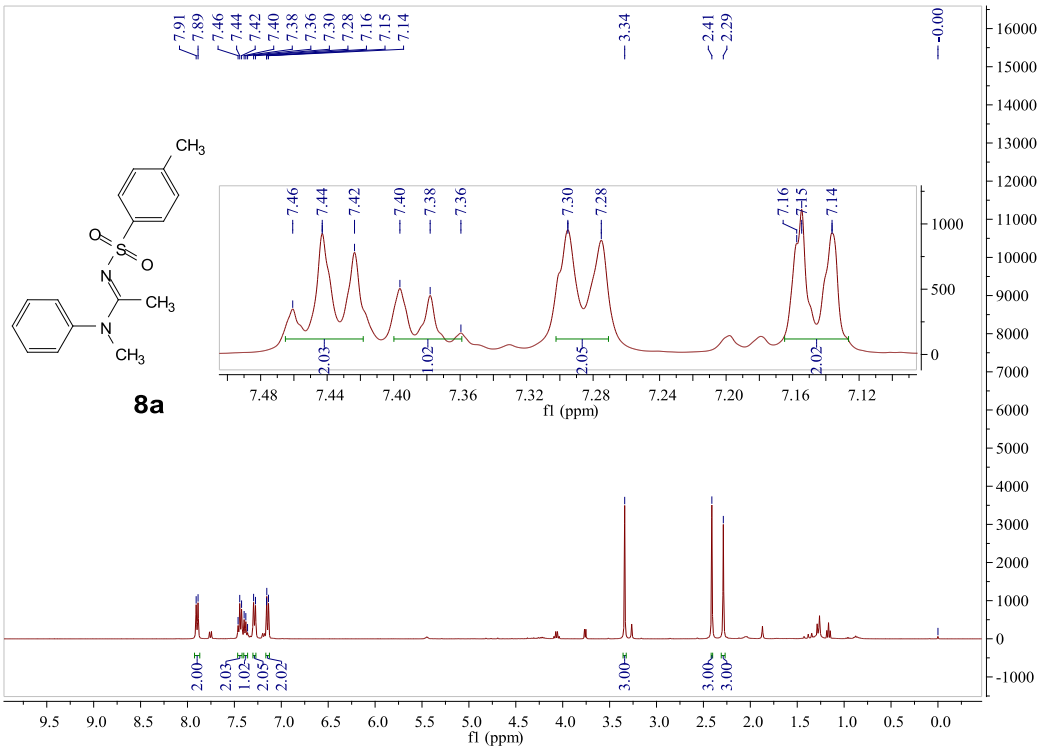

7h
fl (ppm)

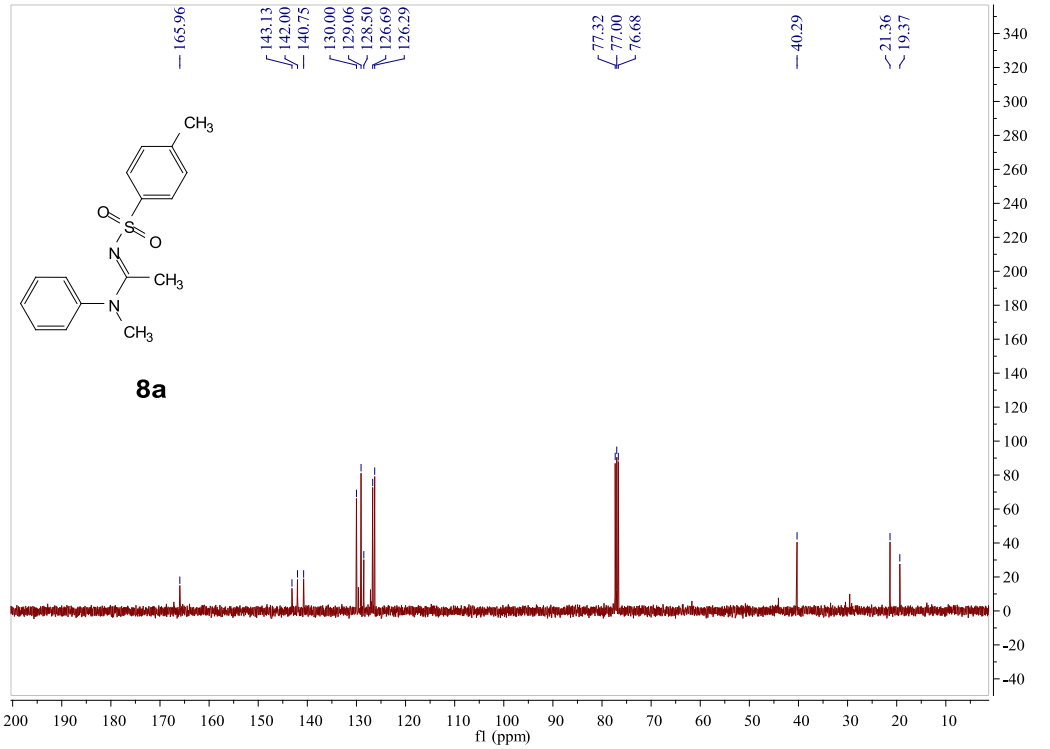

7i
fl (ppm)

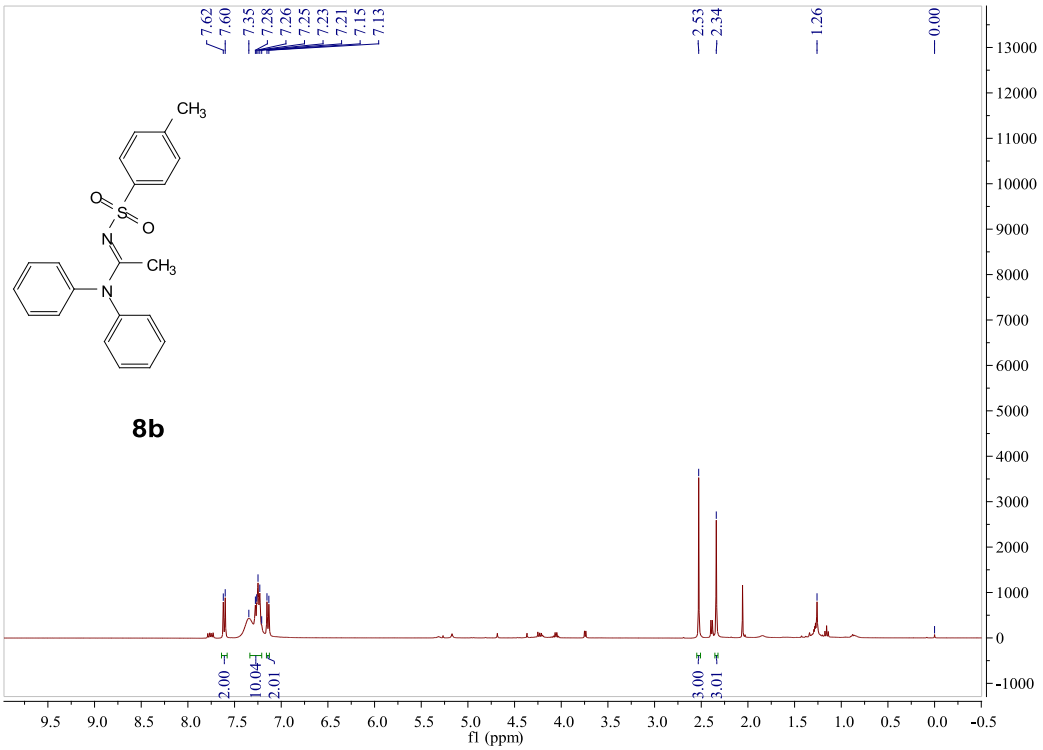

7i
fl (ppm)

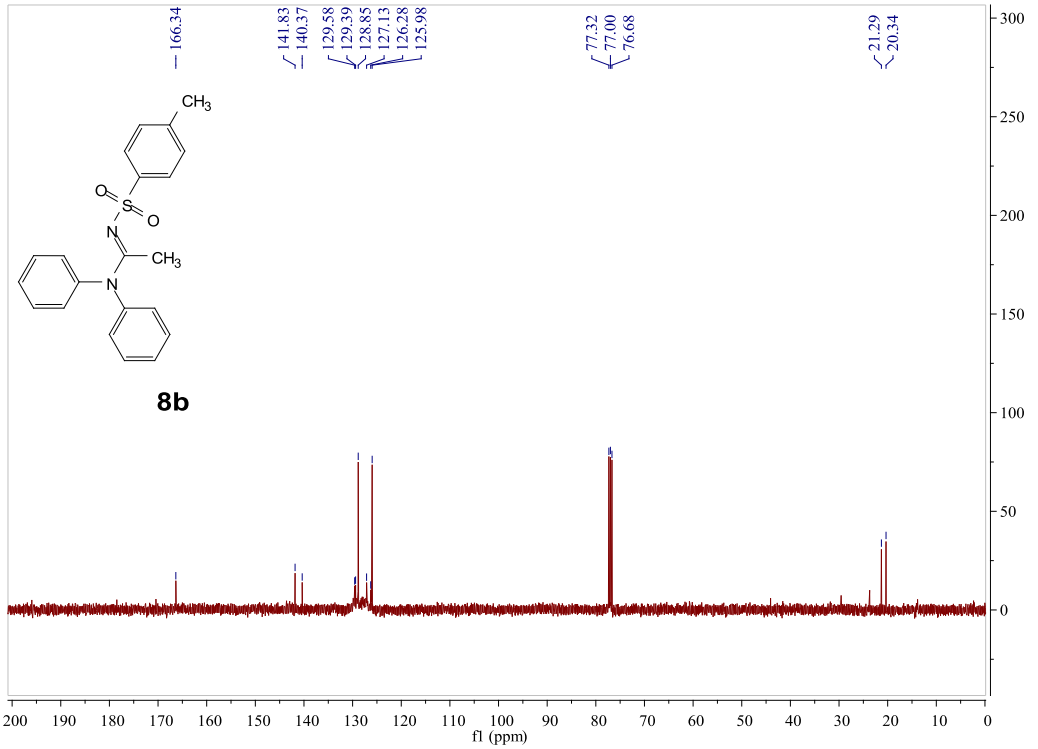

7.84
7.82
7.30
7.29
7.28
7.27
7.25
7.21
7.20
7.19
7.18
4.58
3.35
3.34
3.32
3.10
3.08
2.40
2.00
1.99
1.97
1.26
-0.00
CH3
O
S
N
O
N
7j
3.35
3.34
3.32
3.12
3.10
3.08
2.01
2.00
3.4
3.3
3.2
3.1
f1 (ppm)
2.04
2.02
2.00
1.99
1.97
2.10
2.04
2.00
1.96
f1 (ppm)
2.00
5.03
2.01
2.02
2.01
2.00
3.01
2.10
f1 (ppm)

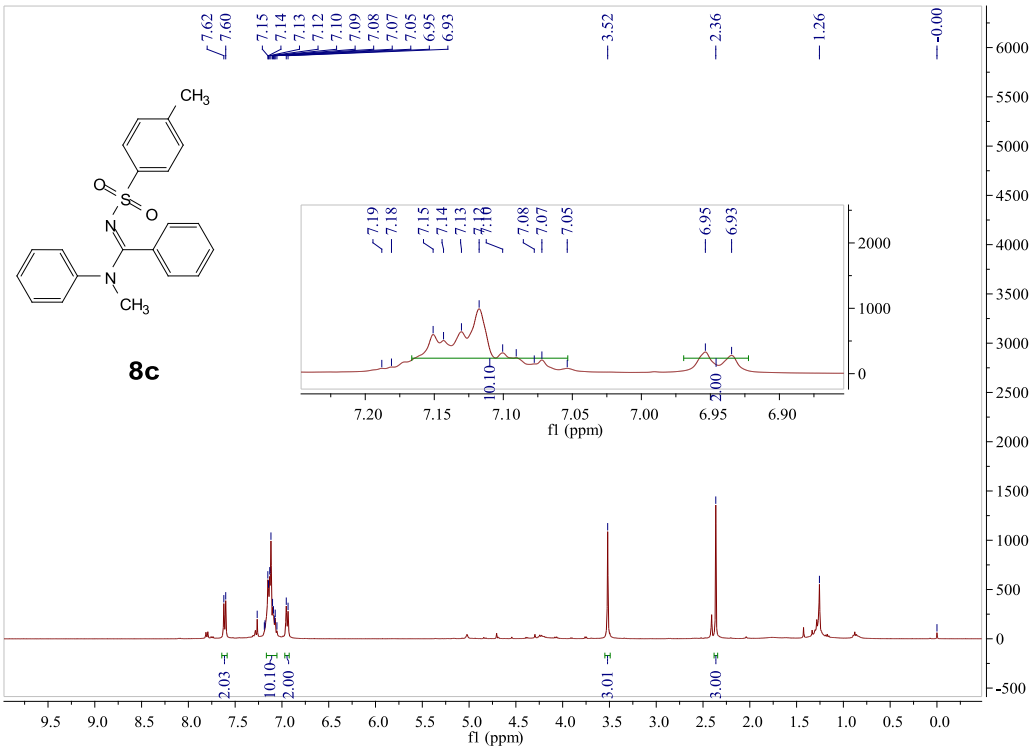

169.82
141.99
140.44
134.88
129.09
128.70
128.28
127.91
126.36
77.32
77.00
76.68
48.82
48.56
30.90
21.38
18.91
CH3
O
S
N
O
N
7j
f1 (ppm)

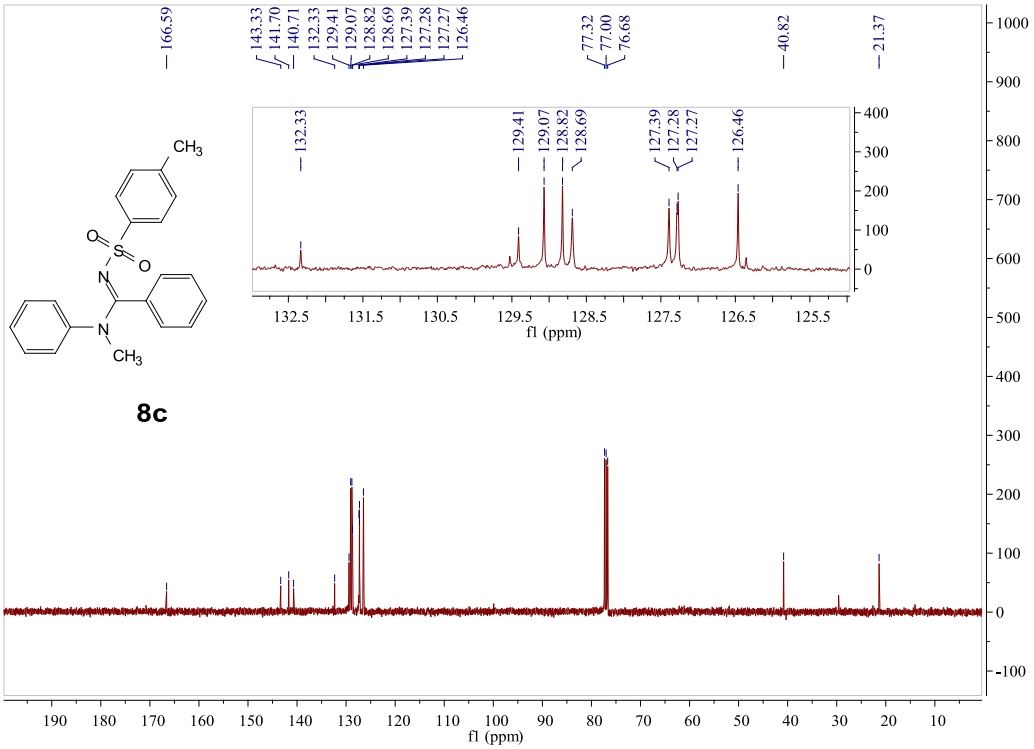

7.91
7.89
7.46
7.44
7.42
7.40
7.38
7.36
7.30
7.28
7.16
7.15
7.14
3.34
2.41
2.29
-0.00
CH3
O
S
O
N
CH3
N
CH3
8a
2.03
1.02
2.05
2.02
2.00
3.00
3.00
3.00
f1 (ppm)

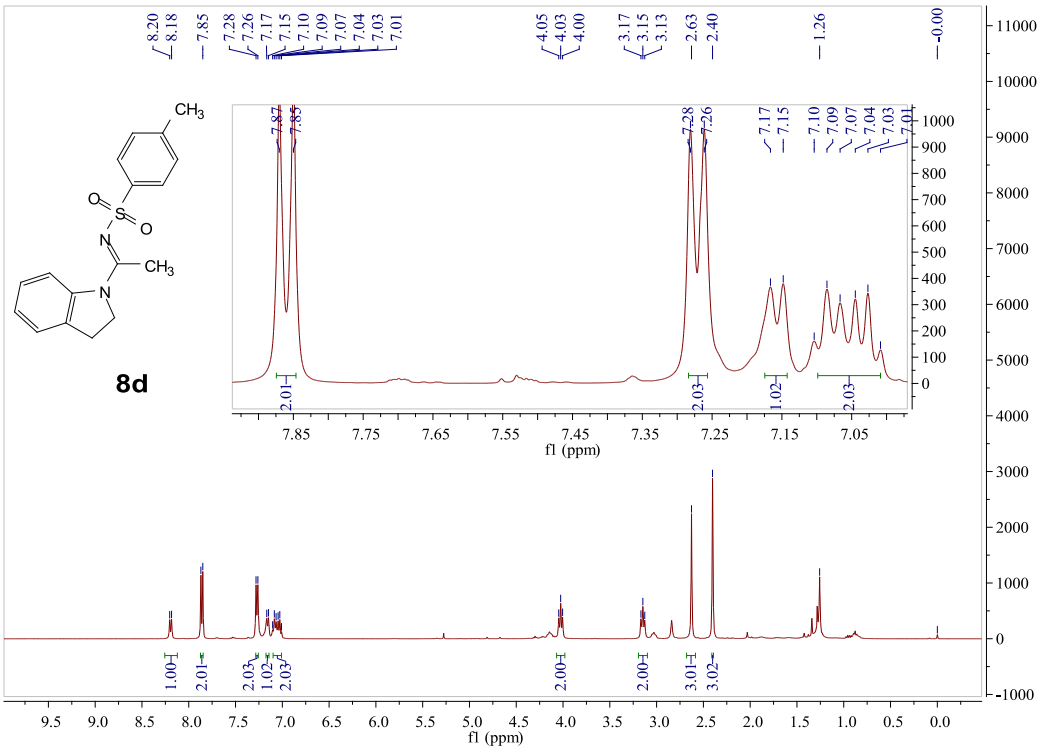

165.96
143.13
142.00
140.75
130.00
129.06
128.50
126.69
126.29
77.32
77.00
76.68
40.29
21.36
19.37
CH3
O
S
O
N
CH3
N
CH3
8a
f1 (ppm)

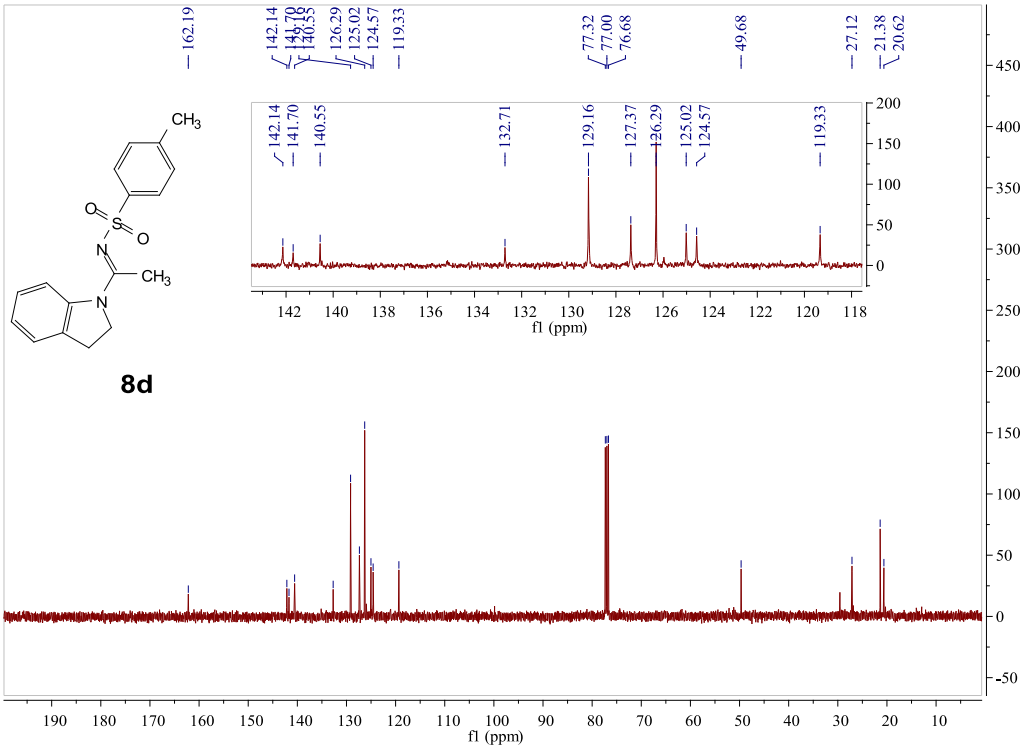

7.62
7.60
7.35
7.28
7.26
7.25
7.23
7.21
7.15
7.13
2.53
2.34
1.26
0.00
CH3
O
S
O
N
CH3
N
8b
2.00
10.04
2.01
3.00
3.01
fl (ppm)

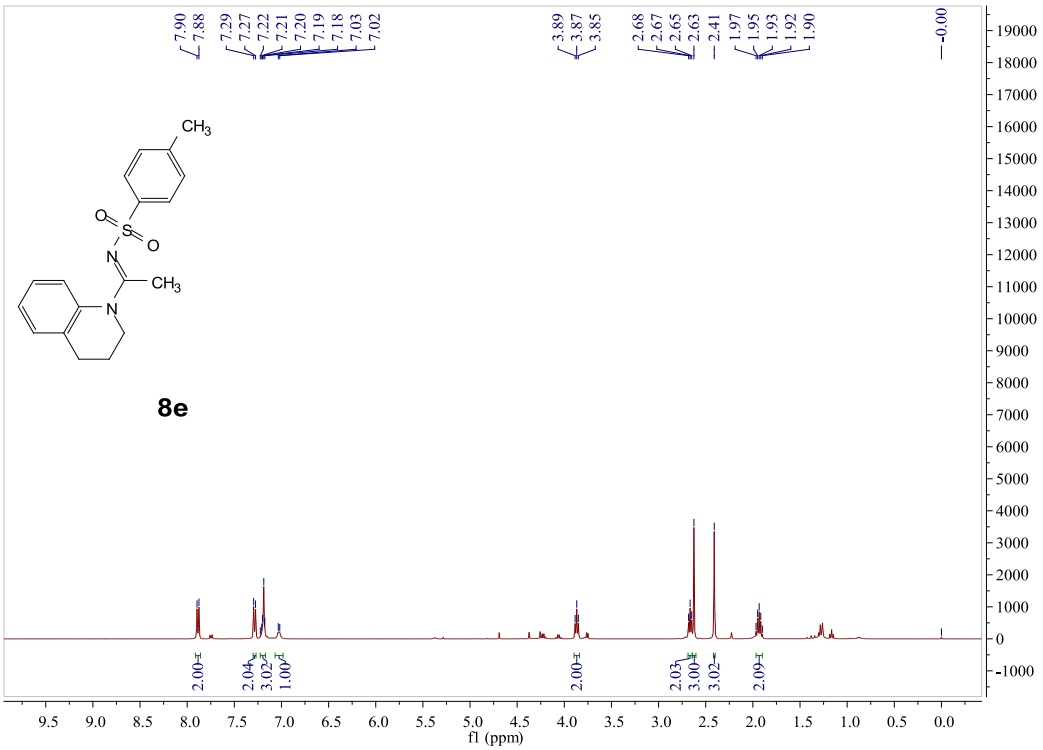

166.34
141.83
140.37
129.58
129.39
128.85
127.13
126.28
125.98
77.32
77.00
76.68
21.29
20.34
CH3
O
S
O
N
CH3
N
8b
fl (ppm)

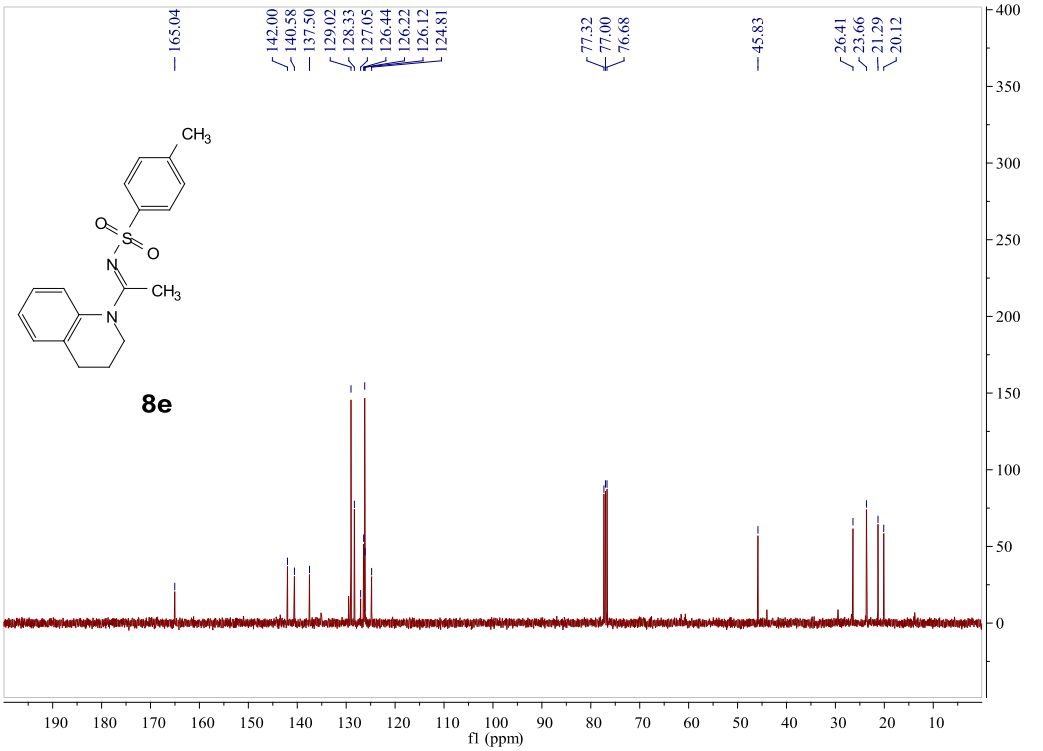

7.62
7.60
7.15
7.14
7.13
7.12
7.10
7.09
7.08
7.07
7.05
6.95
6.93
3.52
2.36
1.26
0.00
CH3
O
S
O
N
N
CH3
8c
7.19
7.18
7.15
7.14
7.13
7.12
7.10
7.08
7.07
7.05
6.95
6.93
10.10
2.00
7.20
7.15
7.10
7.05
7.00
6.95
6.90
f1 (ppm)
2.03
10.10
2.00
3.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

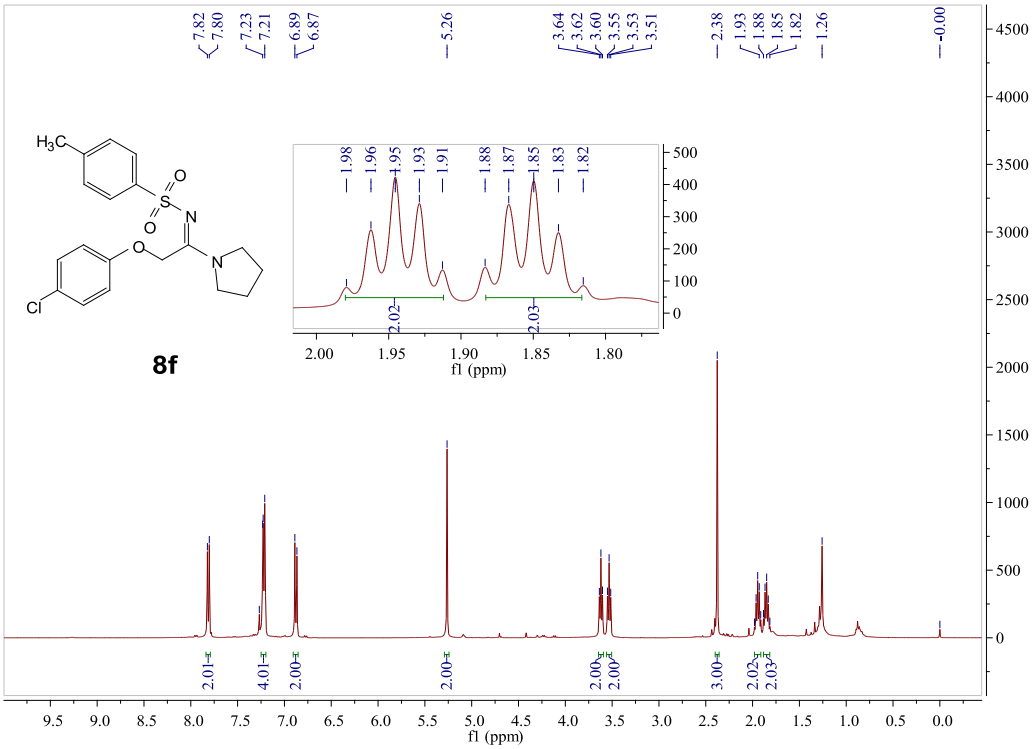

166.59
143.33
141.70
140.71
132.33
129.41
129.07
128.82
128.69
127.39
127.28
127.27
126.46
77.32
77.00
76.68
40.82
21.37
CH3
O
S
O
N
N
CH3
8c
132.33
129.41
129.07
128.82
128.69
127.39
127.28
127.27
126.46
132.5
131.5
130.5
129.5
128.5
127.5
126.5
125.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

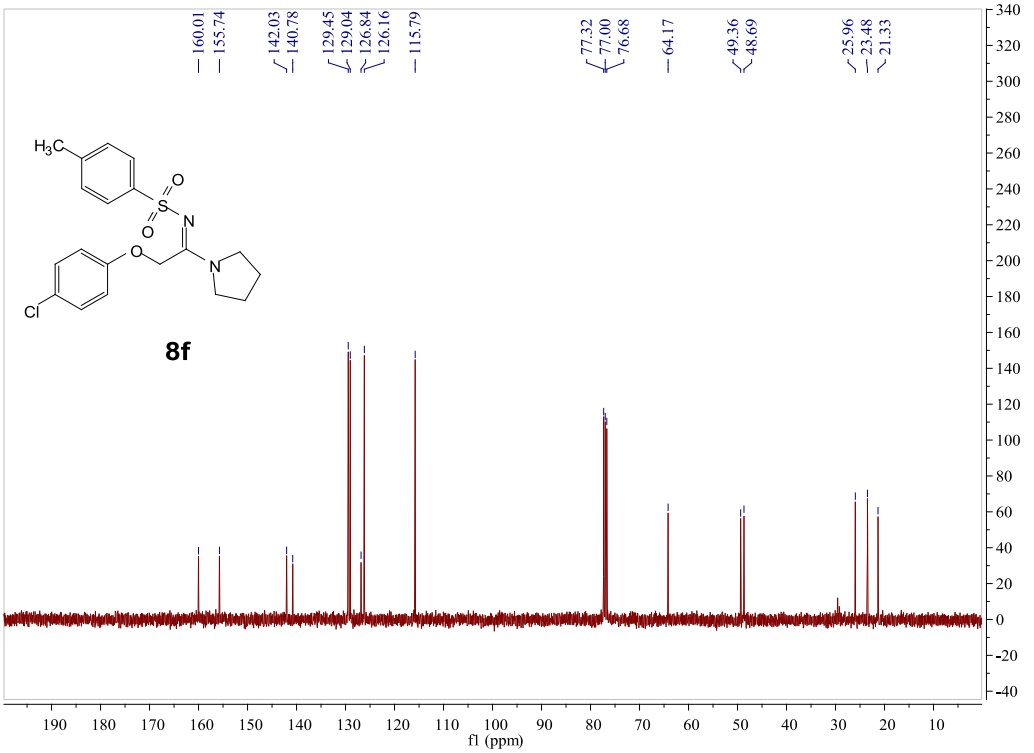

8.20
8.18
7.85
7.28
7.26
7.17
7.15
7.10
7.09
7.07
7.04
7.03
7.01
4.05
4.03
4.00
3.17
3.15
3.13
2.63
2.40
1.26
0.00
CH3
O
S
O
N
CH3
N
8d
2.01
2.03
1.02
2.03
fl (ppm)
1.00
2.01
2.03
1.02
2.03
2.00
2.00
3.01
3.02
fl (ppm)

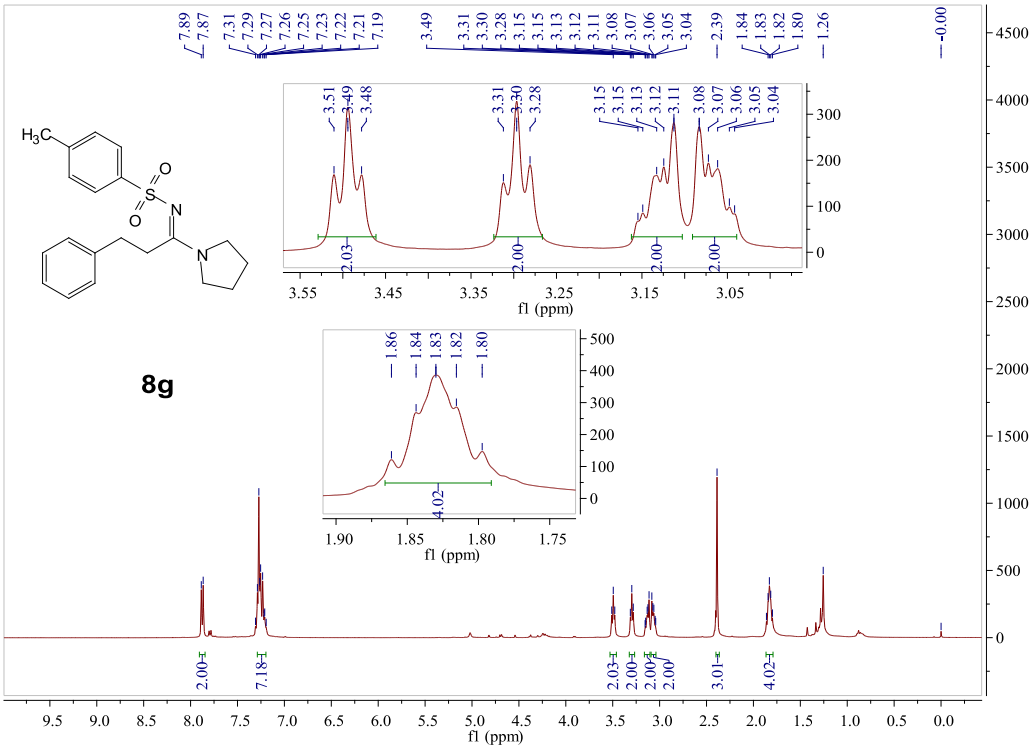

162.19
142.14
141.70
140.55
126.29
125.02
124.57
119.33
77.32
77.00
76.68
49.68
27.12
21.38
20.62
CH3
O
S
O
N
CH3
N
8d
fl (ppm)
fl (ppm)

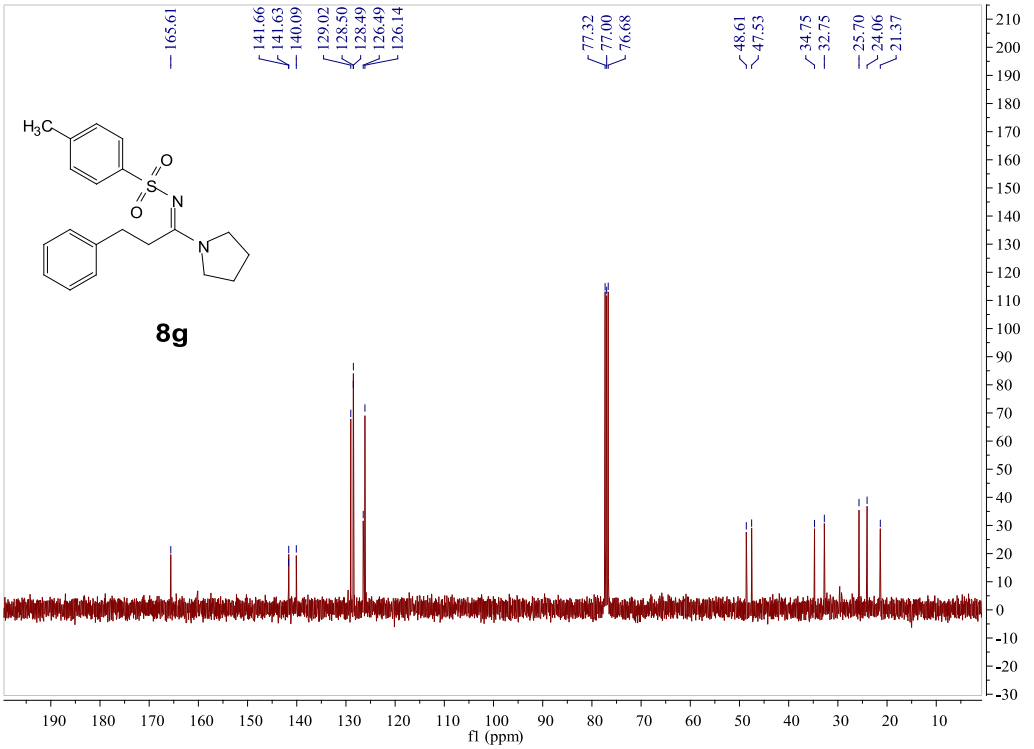

7.90
7.88
7.29
7.27
7.22
7.21
7.20
7.19
7.18
7.03
7.02
3.89
3.87
3.85
2.68
2.67
2.65
2.63
2.41
1.97
1.95
1.93
1.92
1.90
-0.00
CH3
O
S
O
N
CH3
N
8e
2.00
2.04
3.02
1.00
2.00
2.03
3.00
3.02
2.09
f1 (ppm)

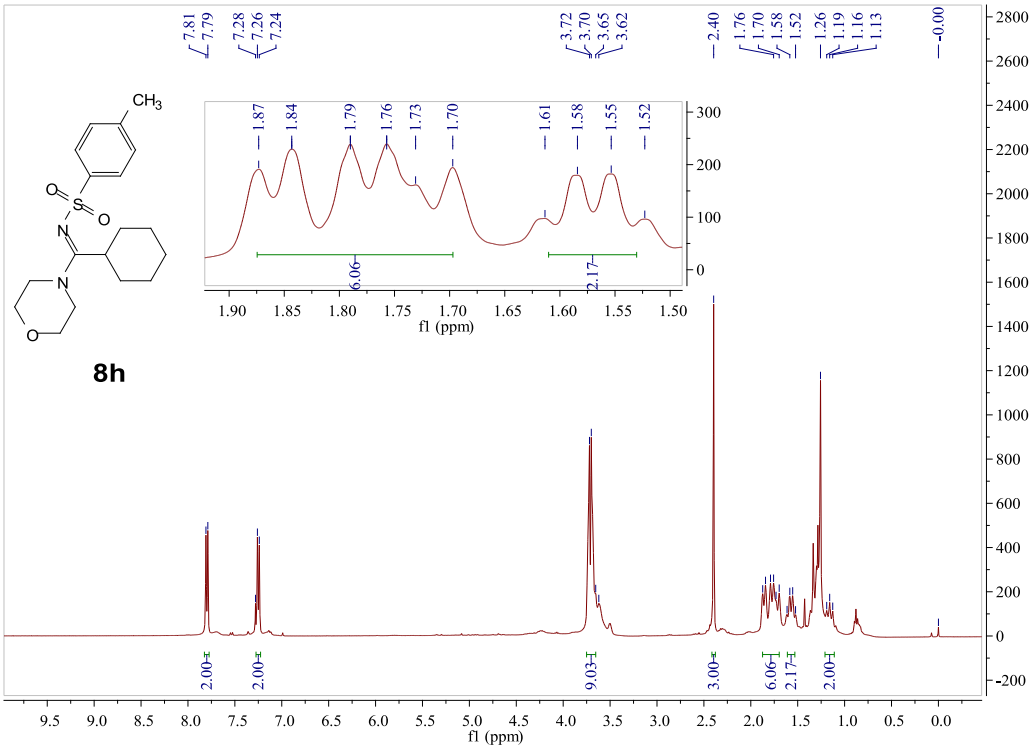

165.04
142.00
140.58
137.50
129.02
128.33
127.05
126.44
126.22
126.12
124.81
77.32
77.00
76.68
45.83
26.41
23.66
21.29
20.12
CH3
O
S
O
N
CH3
N
8e
f1 (ppm)

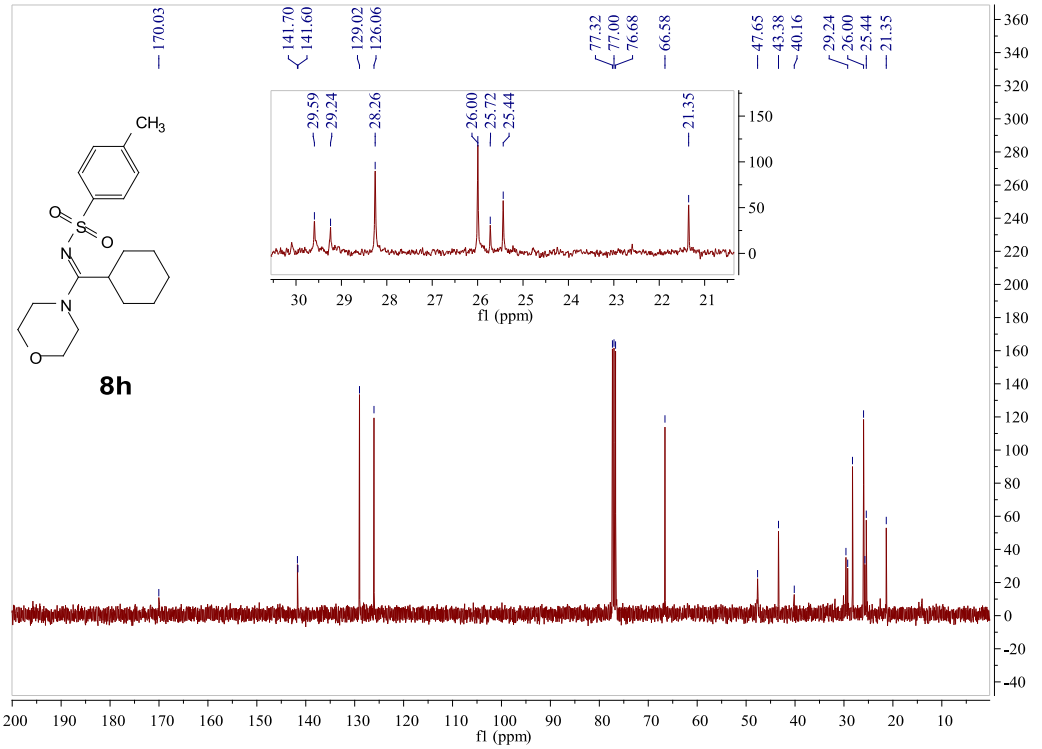

7.82
7.80
7.23
7.21
6.89
6.87
5.26
3.64
3.62
3.60
3.55
3.53
3.51
2.38
1.93
1.88
1.85
1.82
1.26
-0.00
1.98
1.96
1.95
1.93
1.91
1.88
1.87
1.85
1.83
1.82
2.02
2.03
fl (ppm)
8f
2.01
4.01
2.00
2.00
2.00
2.00
3.00
2.02
2.03
fl (ppm)

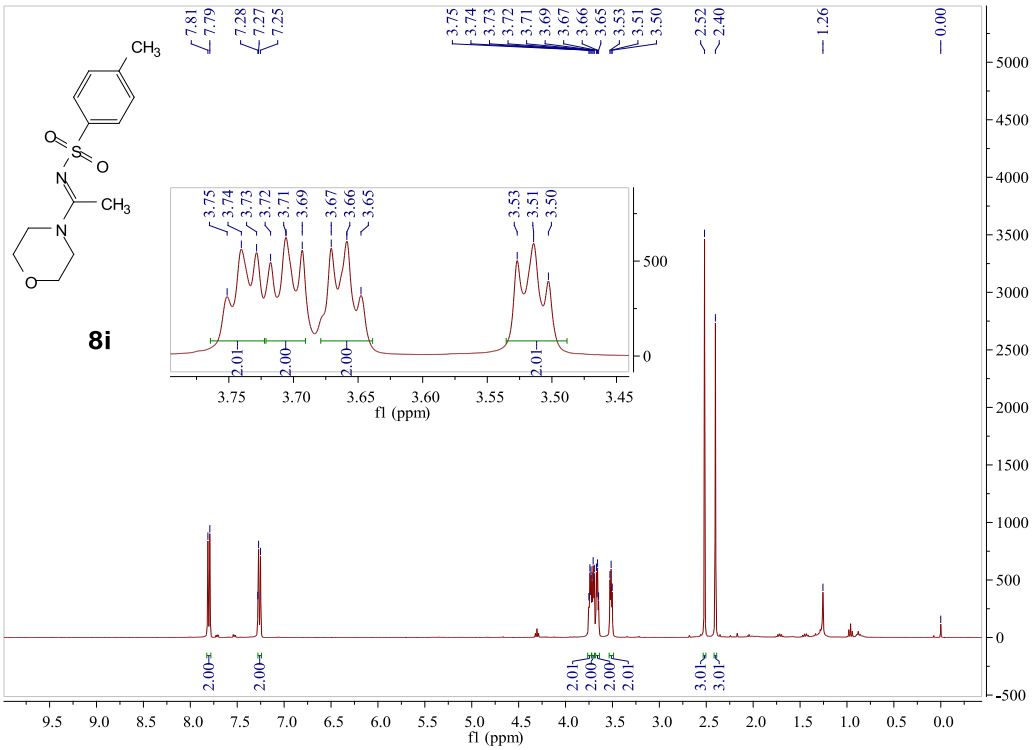

160.01
155.74
142.03
140.78
129.45
129.04
126.84
126.16
115.79
77.32
77.00
76.68
64.17
49.36
48.69
25.96
23.48
21.33
8f
fl (ppm)

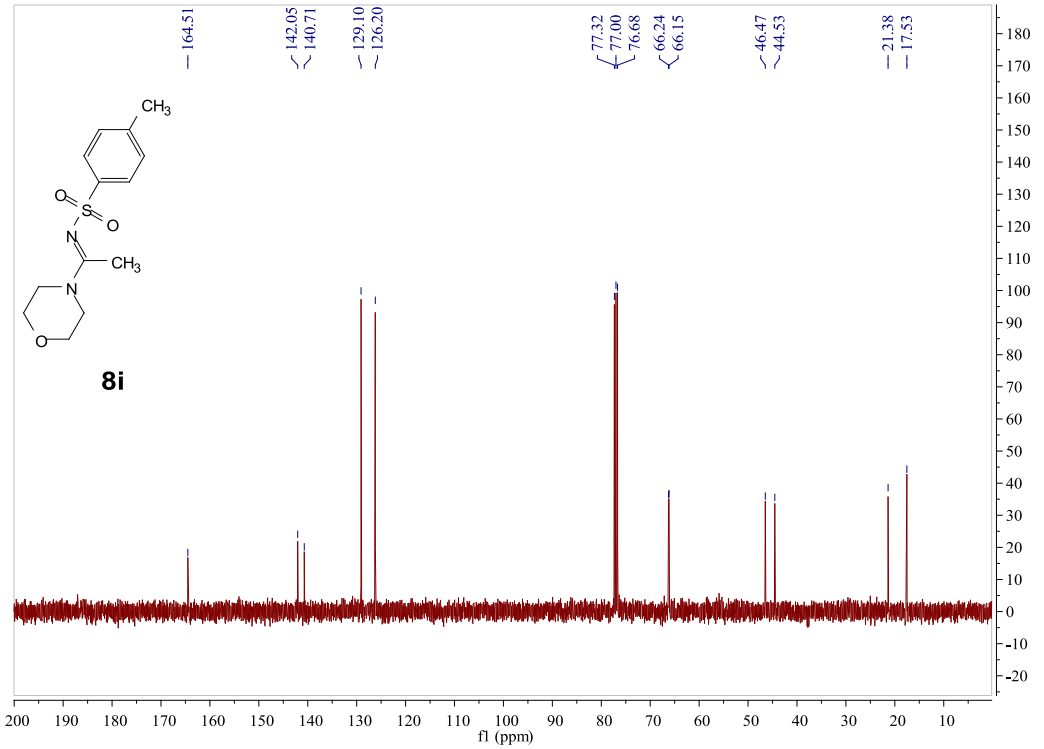

8g
fl (ppm)

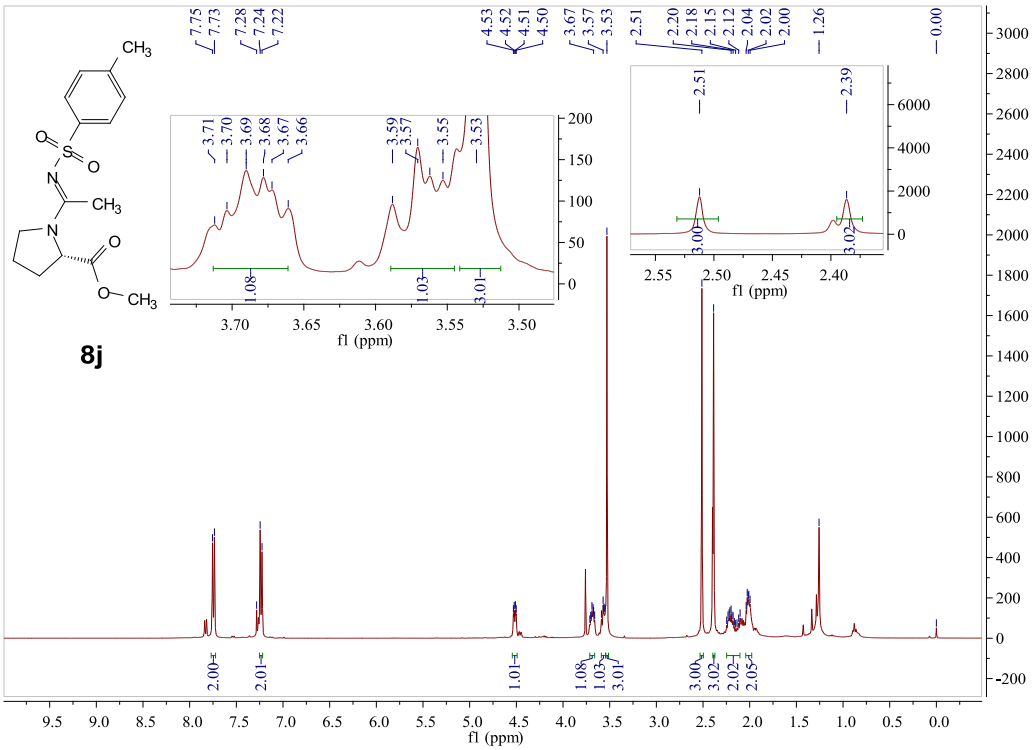

8g
fl (ppm)

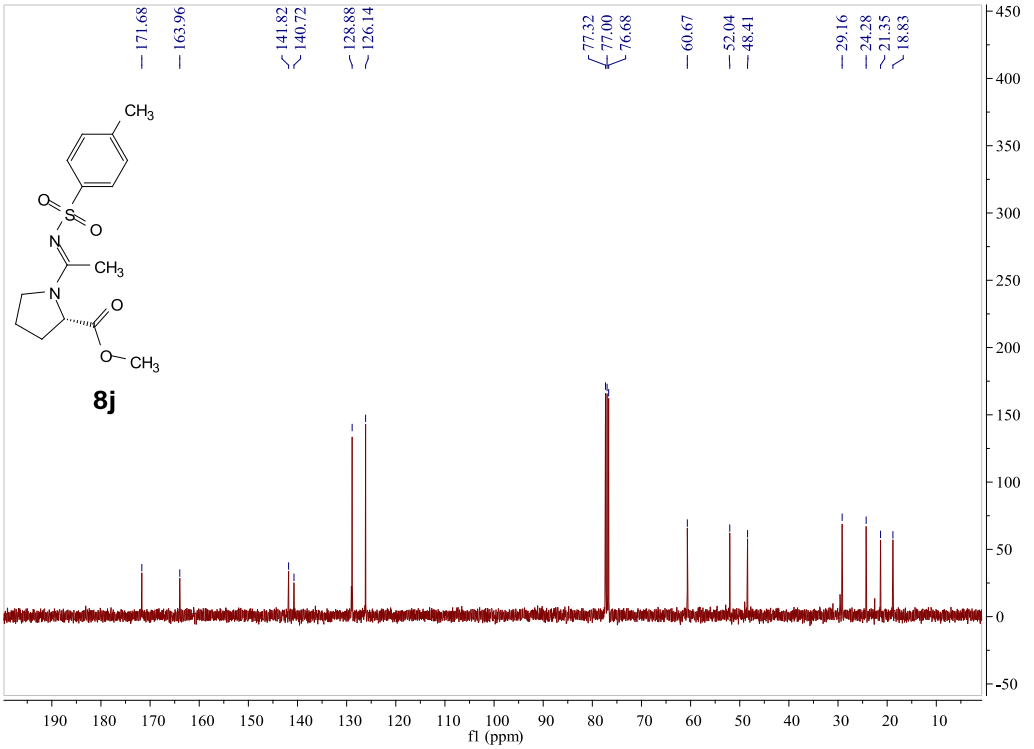

8h
f1 (ppm)

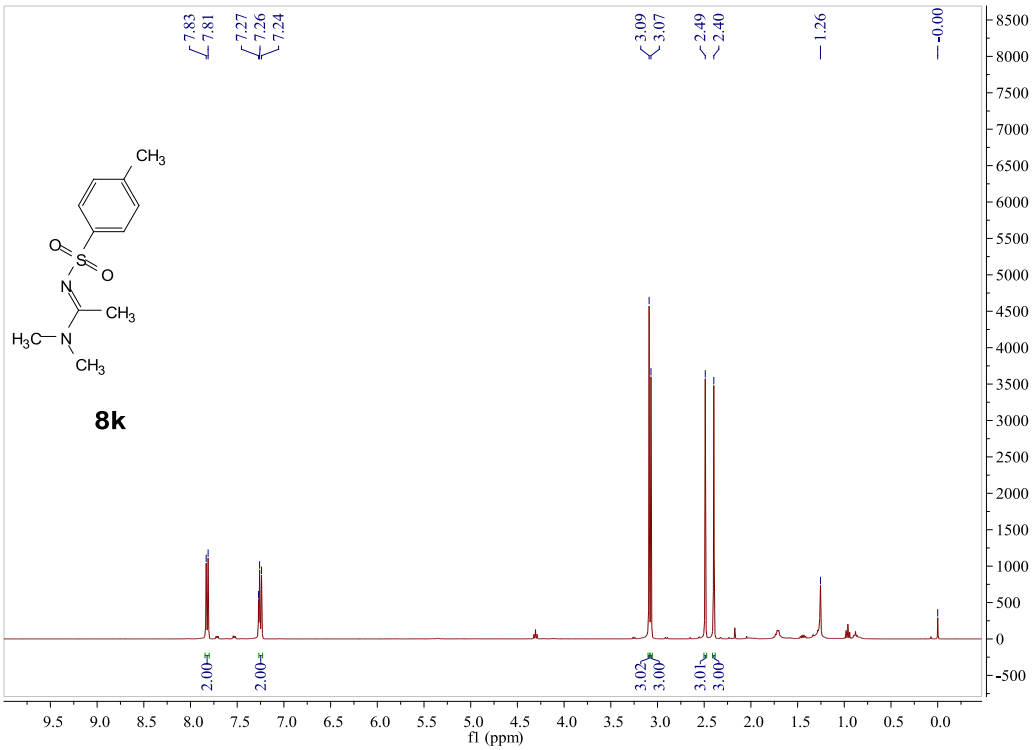

8h
f1 (ppm)

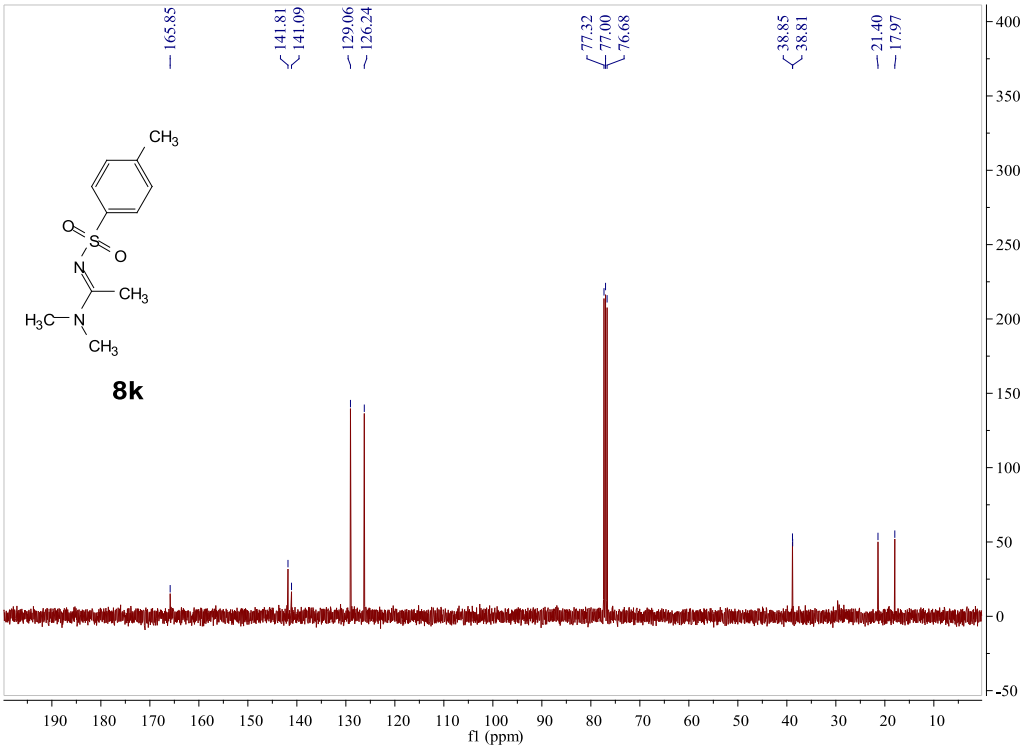

8i
fl (ppm)

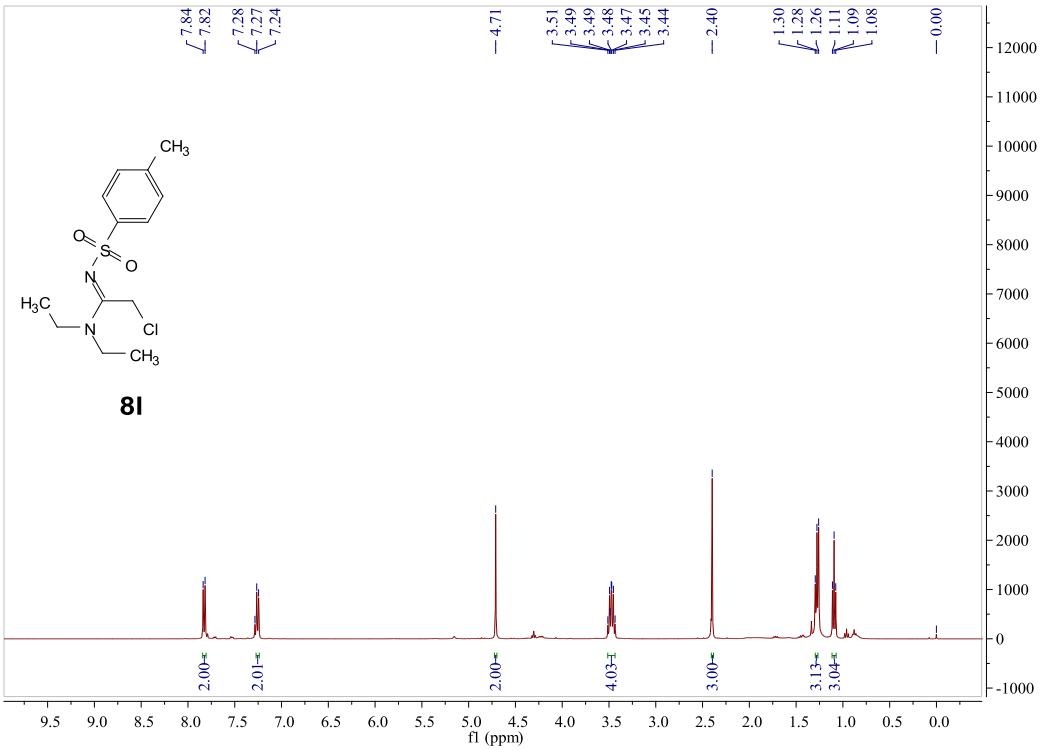

8i
fl (ppm)

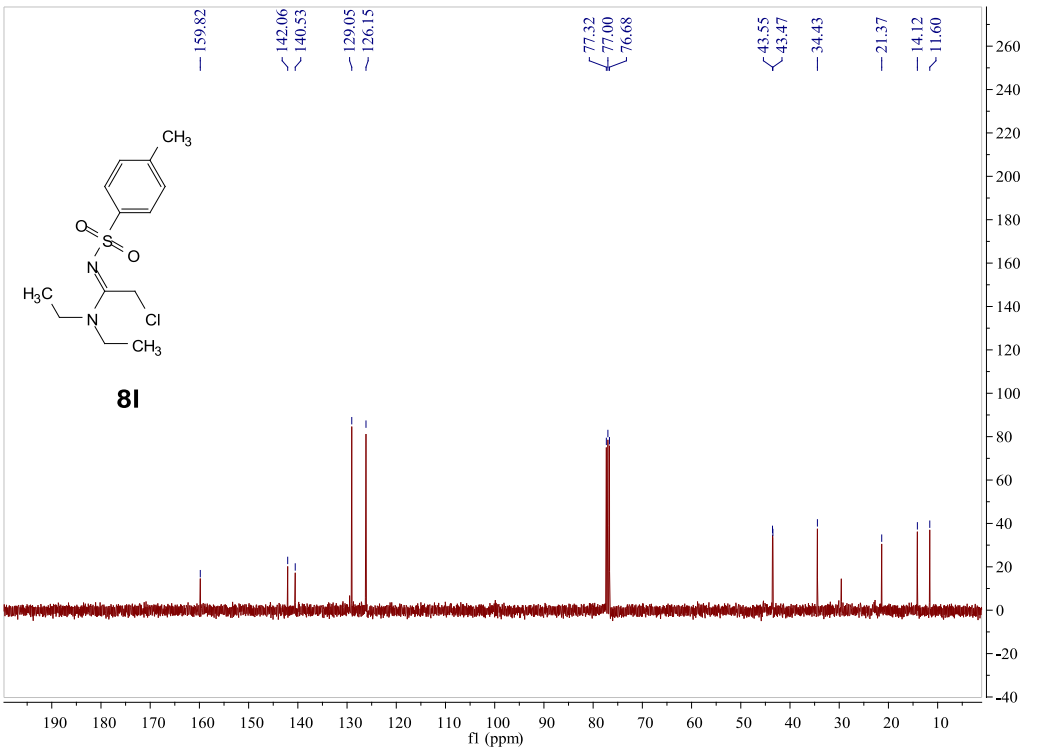

8j
fl (ppm)

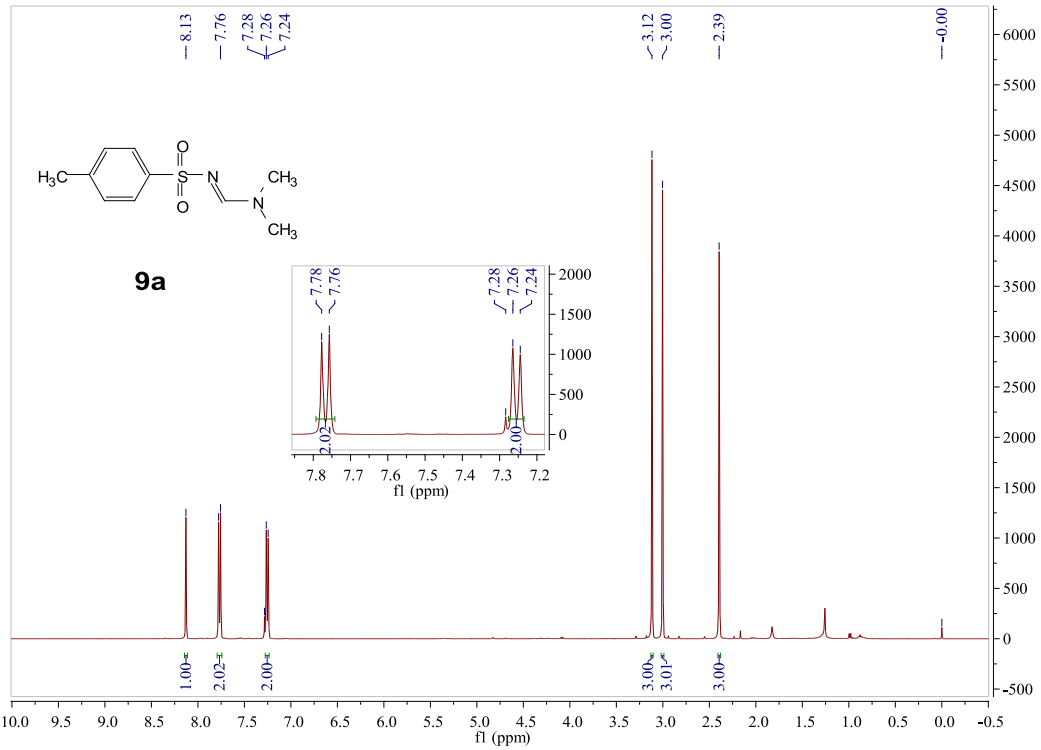

8j
fl (ppm)

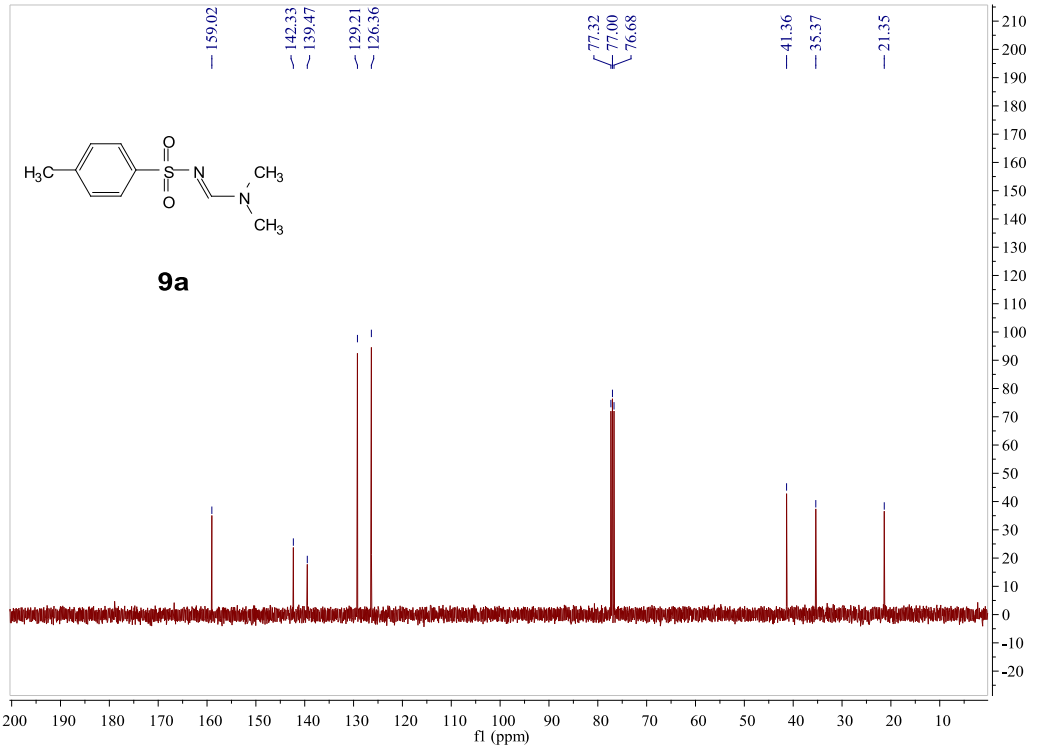

7.83
7.81
7.27
7.26
7.24
3.09
3.07
2.49
2.40
1.26
-0.00
2.00
2.00
3.02
3.00
3.01
3.00
fl (ppm)
8k

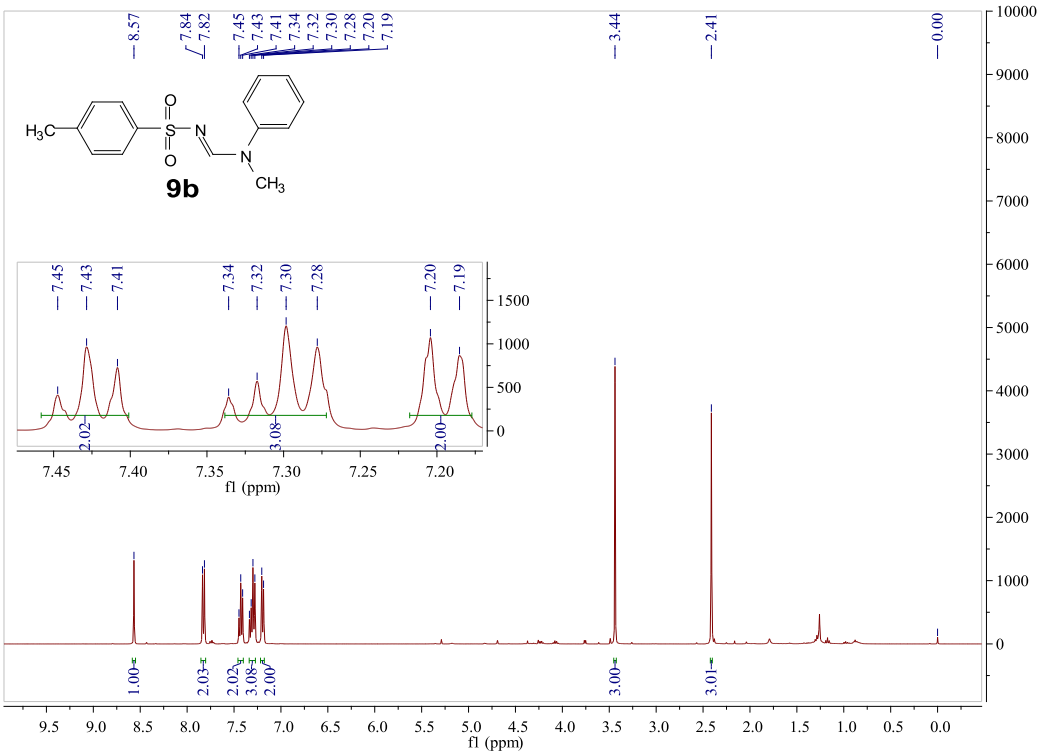

165.85
141.81
141.09
129.06
126.24
77.32
77.00
76.68
38.85
38.81
21.40
17.97
fl (ppm)
8k

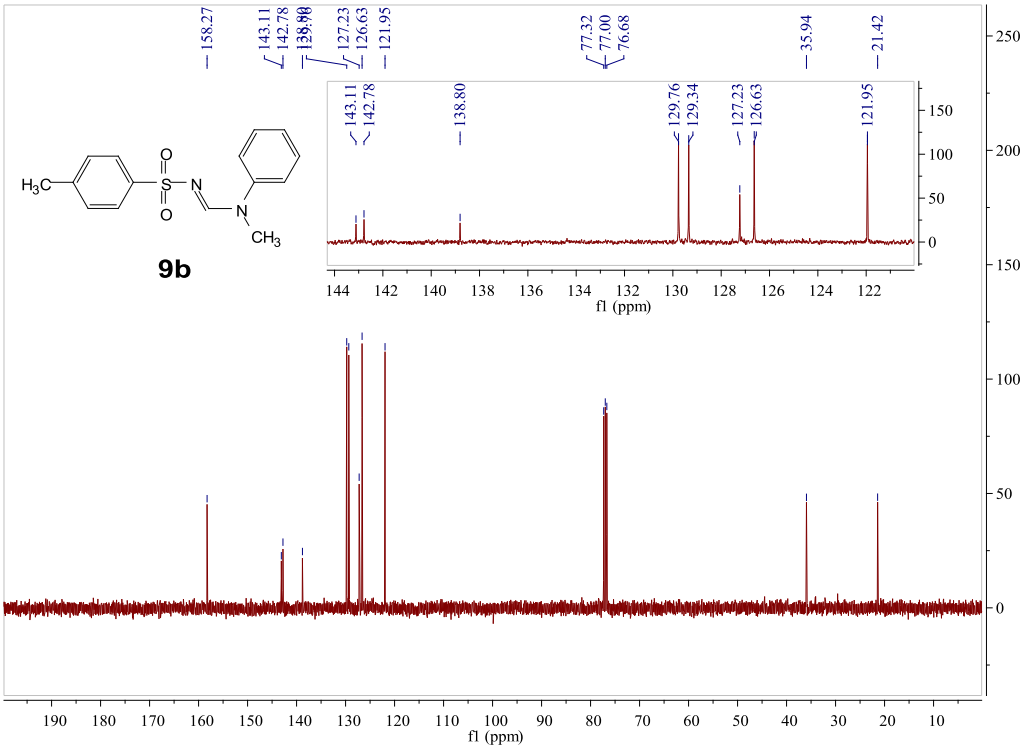

7.84
7.82
7.28
7.27
7.24
4.71
3.51
3.49
3.49
3.48
3.47
3.45
3.44
2.40
1.30
1.28
1.26
1.11
1.09
1.08
0.00
2.00
2.01
2.00
4.03
3.00
3.13
3.04
f1 (ppm)

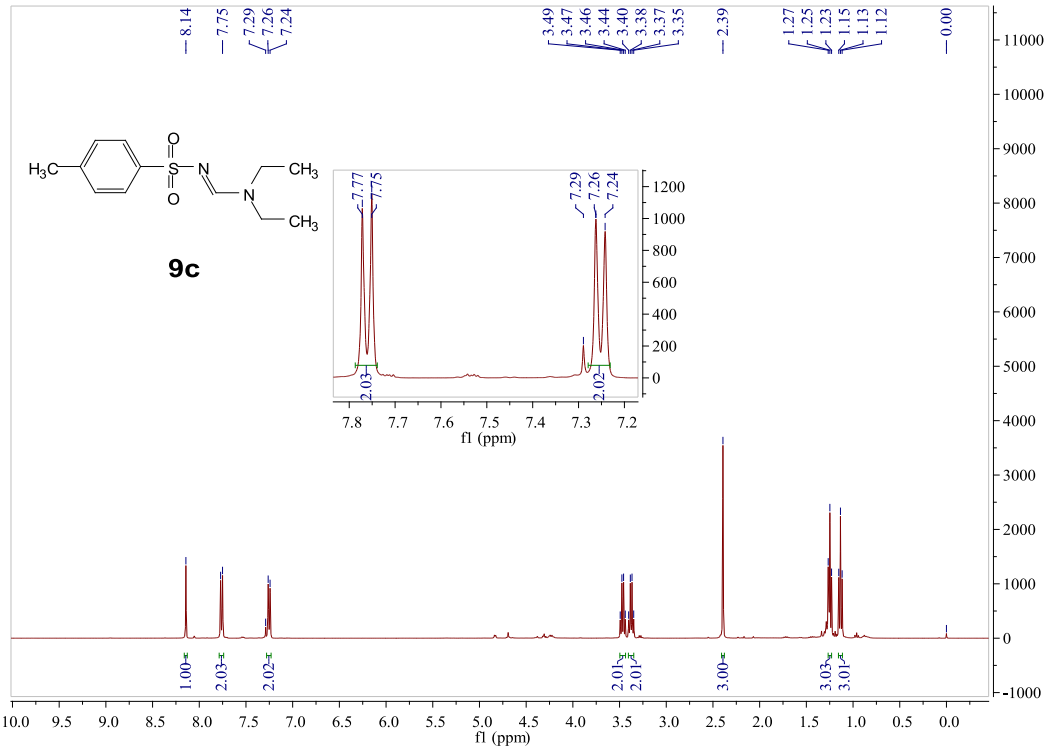

159.82
142.06
140.53
129.05
126.15
77.32
77.00
76.68
43.55
43.47
34.43
21.37
14.12
11.60
f1 (ppm)

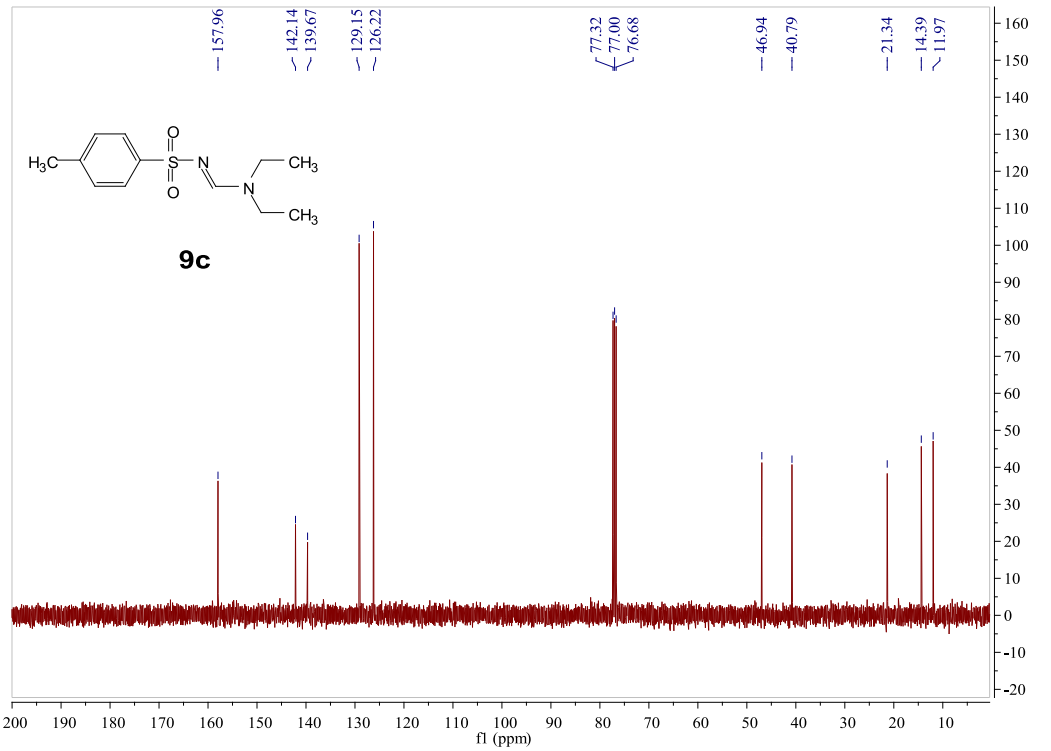

8.13
7.76
7.28
7.26
7.24
3.12
3.00
2.39
0.00
9a
7.78
7.76
7.28
7.26
7.24
2.02
2.00
fl (ppm)
1.00
2.02
2.00
3.00
3.01
3.00
fl (ppm)

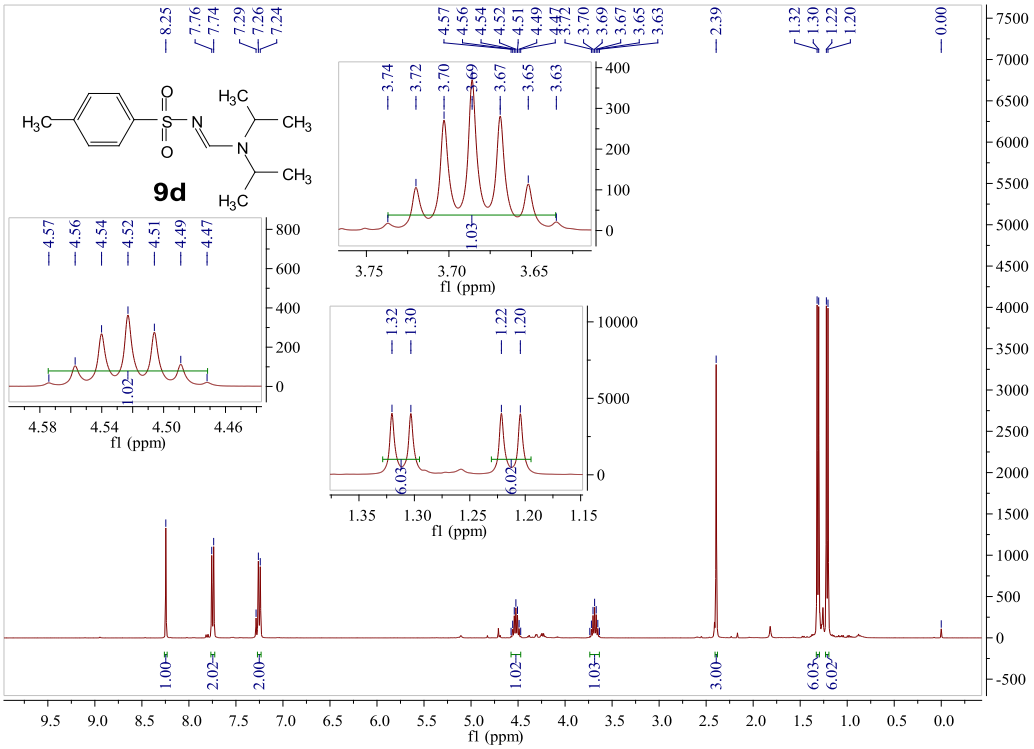

159.02
142.33
139.47
129.21
126.36
77.32
77.00
76.68
41.36
35.37
21.35
9a
fl (ppm)

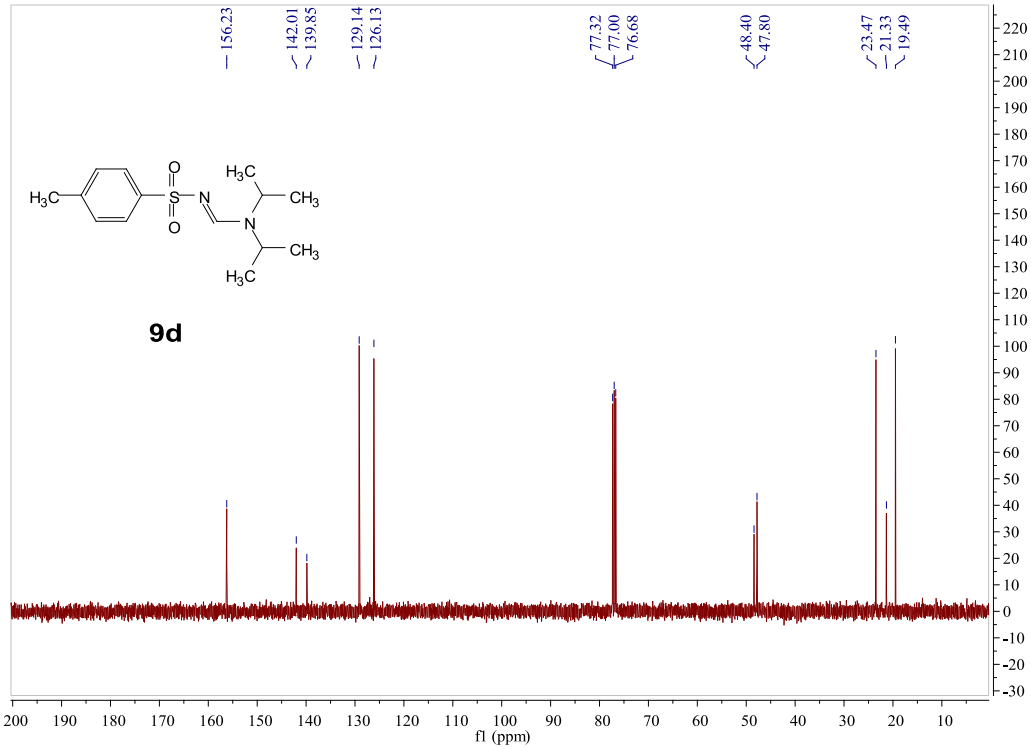

8.57
7.84
7.82
7.45
7.43
7.41
7.34
7.32
7.30
7.28
7.20
7.19
3.44
2.41
0.00
9b
fl (ppm)
1.00
2.03
2.02
3.08
2.00
3.00
3.01

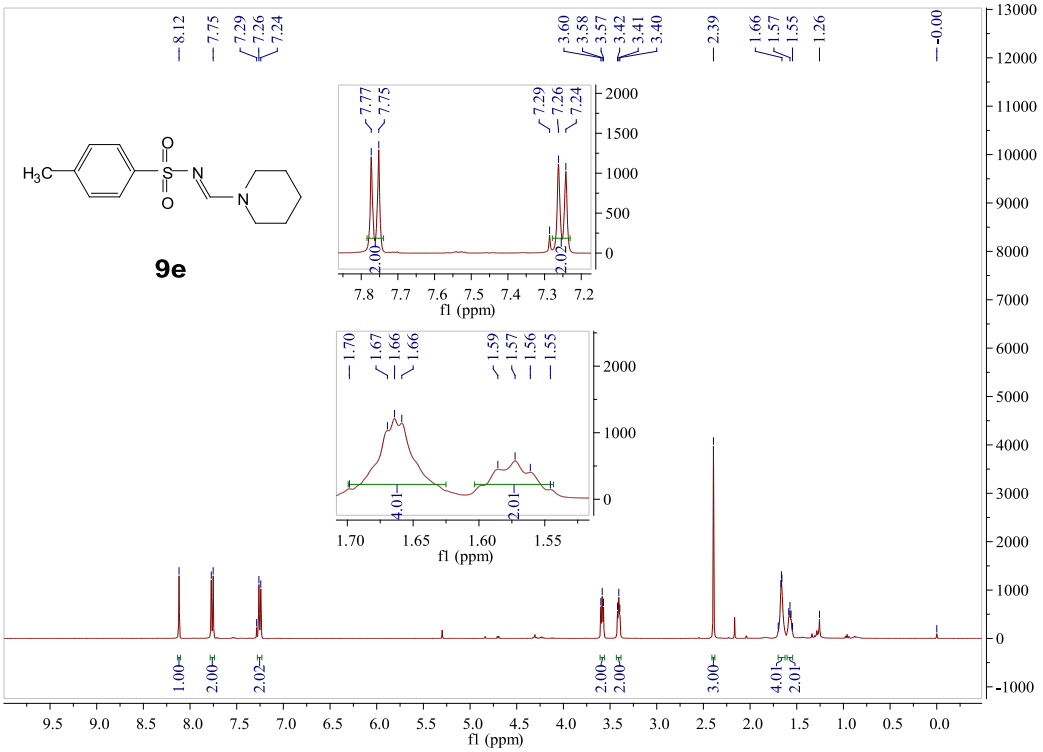

158.27
143.11
142.78
138.80
127.23
126.63
121.95
77.32
77.00
76.68
35.94
21.42
9b
fl (ppm)

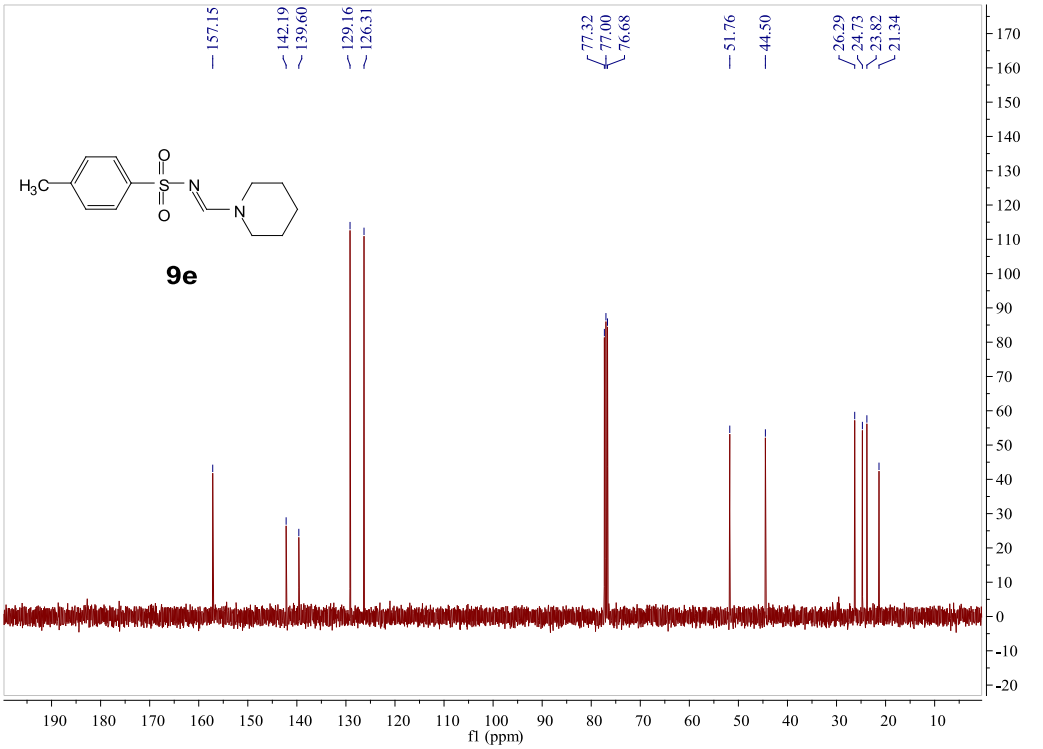

8.14
7.75
7.29
7.26
7.24
3.49
3.47
3.46
3.44
3.40
3.38
3.37
3.35
2.39
1.27
1.25
1.23
1.15
1.13
1.12
0.00
9c
7.77
7.75
7.29
7.26
7.24
2.03
2.02
fl (ppm)
1.00
2.03
2.02
2.01
2.01
3.00
3.03
3.01
fl (ppm)

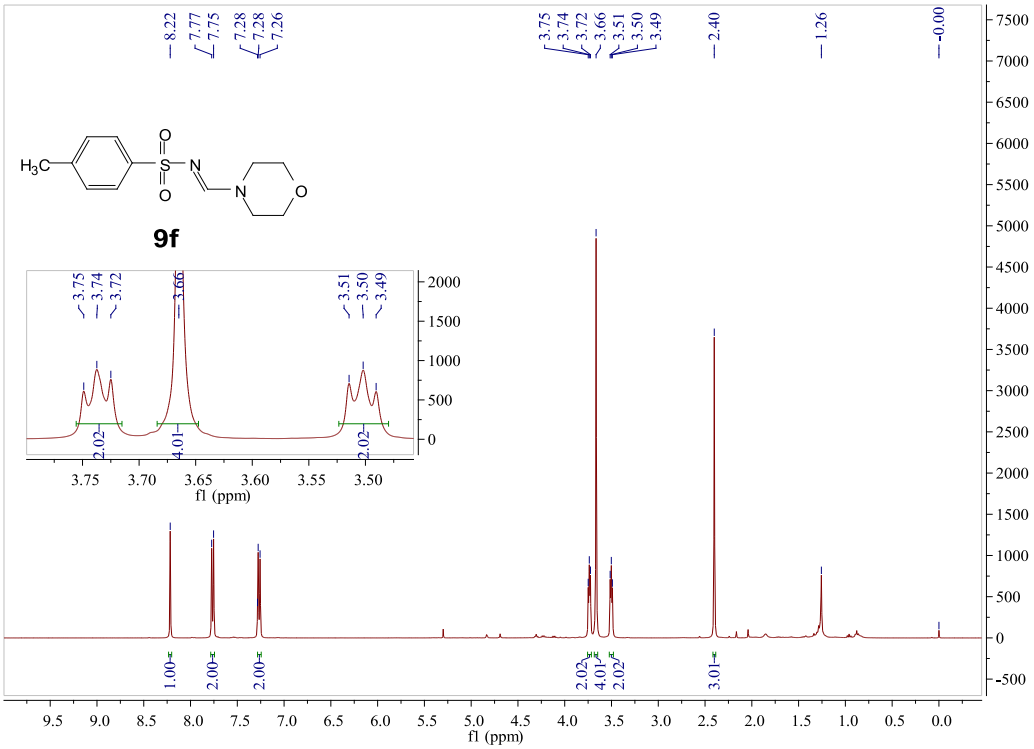

157.96
142.14
139.67
129.15
126.22
77.32
77.00
76.68
46.94
40.79
21.34
14.39
11.97
9c
fl (ppm)

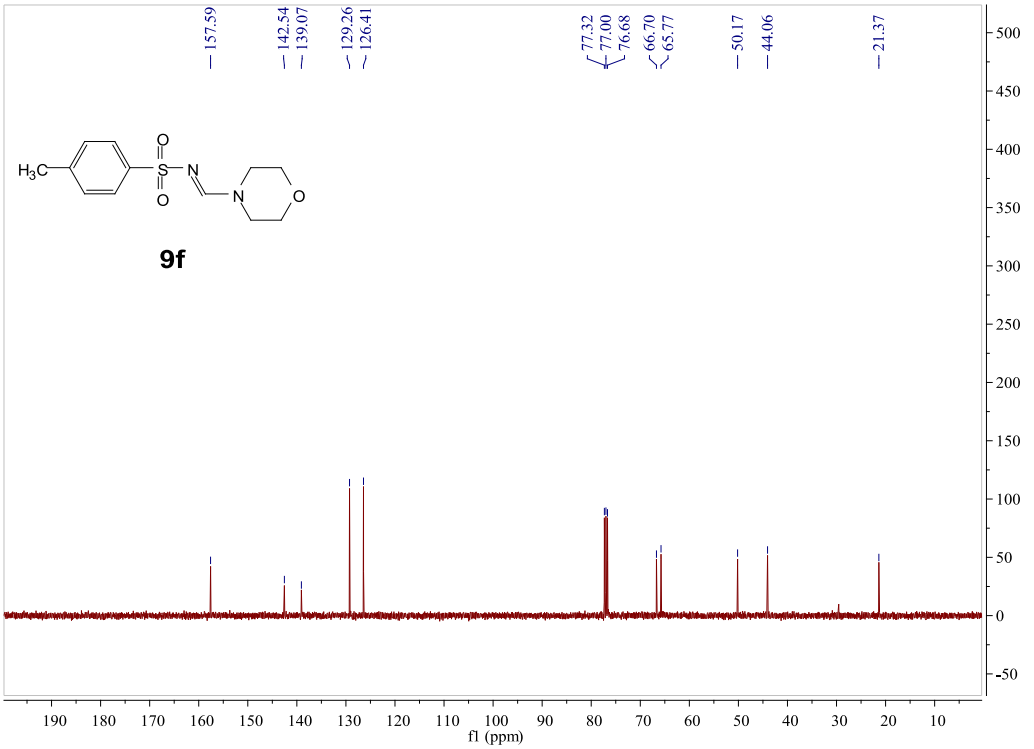

9d
fl (ppm)


9d
fl (ppm)


9e
fl (ppm)


9e
fl (ppm)


8.22
7.77
7.75
7.28
7.28
7.26
3.75
3.74
3.72
3.66
3.51
3.50
3.49
2.40
1.26
-0.00
9f
1.00
2.00
2.00
2.02
4.01
2.02
3.01
f1 (ppm)


157.59
142.54
139.07
129.26
126.41
77.32
77.00
76.68
66.70
65.77
50.17
44.06
21.37
9f
f1 (ppm)

XRD data of the compound 4a

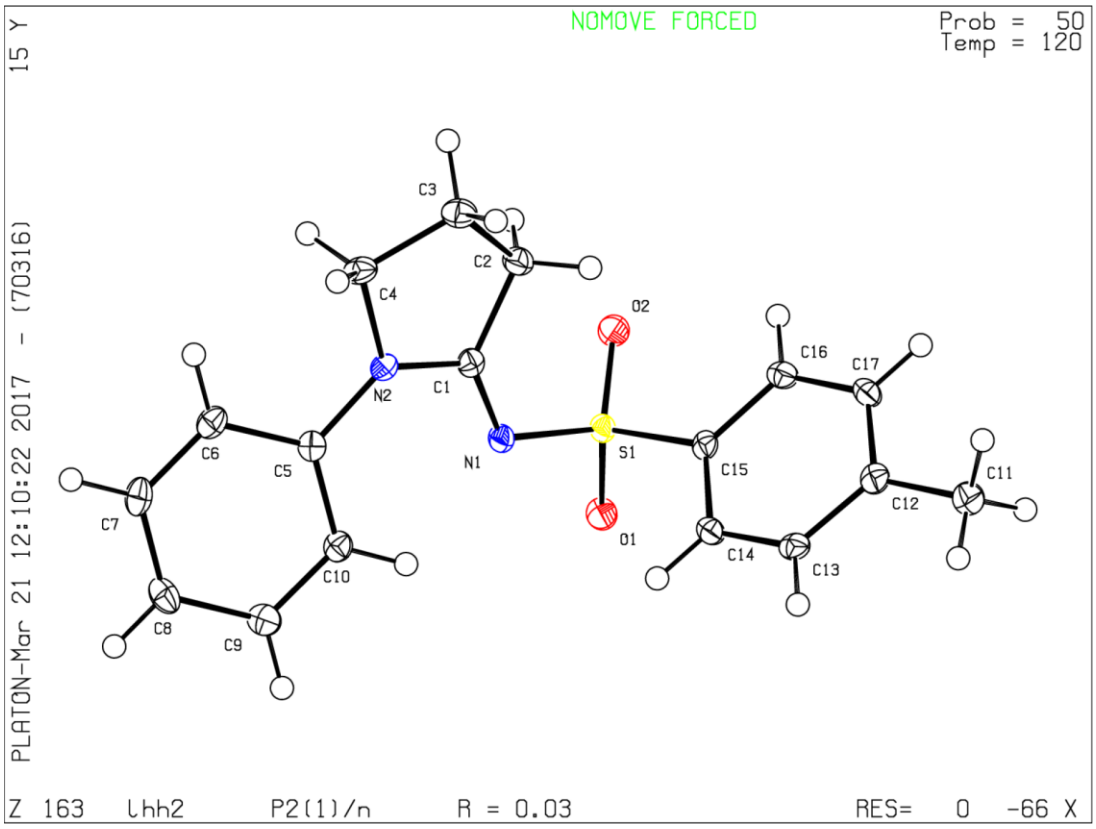


Figure S2. ORTEP structural drawing of **4a**. (CCDC: 1565960)

Table S3. Crystallography data for **4a**.

complex	**4a**
Empirical formula	$C_{17}H_{18}N_2O_2S$
Formula weight(g mol^{-1})	314.39
Temperature	120 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P2 (1) /n
Unit cell dimensions	a = 12.3640 (7) Å b = 7.4331 (4) Å c = 16.5987 (9) Å α = 90 ° β = 105.575 (2) ° γ = 90 °
Volume ($Å^3$)	1469.45 (14)
Z	4
ρ(g cm^{-3})	1.421

F(000)	664
Crystal size(mm^3)	0.20 x 0.15 x 0.10
Theta range for data collection	1.84 °to 25.50 °
Limiting indices	-14<=h<=14 -9<=k<=9 -20<=l<=20
Reflections collected / unique	19816 / 2716
Data / restraints / parameters	2716 / 0 / 200
GOF	1.188
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0328 *wR2* = 0.0940
R1,*wR2*(all data)	*R1* = 0.0395 *wR2* = 0.1085
Largest diff. peak and hole(e $Å^3$)	0.368 and -0.516

Table S4. Bond lengths [Å] and angles [°] for **4a**.

S(1)-O(2) 1.4397(13)	S(1)-O(1) 1.4400(13)	S(1)-N(1) 1.6226(15)	S(1)-C(15) 1.7707(18)
N(1)-C(1) 1.308(2)	N(2)-C(1) 1.353(2)	N(2)-C(5) 1.424(2)	N(2)-C(4) 1.481(2)
C(1)-C(2) 1.503(2)	C(2)-C(3) 1.526(2)	C(3)-C(4) 1.522(3)	C(5)-C(6) 1.395(2)
C(5)-C(10) 1.400(2)	C(6)-C(7) 1.386(3)	C(7)-C(8) 1.387(3)	C(8)-C(9) 1.389(3)
C(9)-C(10) 1.385(3)	C(11)-C(12) 1.507(3)	C(12)-C(17) 1.390(3)	C(12)-C(13) 1.400(3)
C(13)-C(14) 1.380(3)	C(14)-C(15) 1.391(2)	C(15)-C(16) 1.389(2)	C(16)-C(17) 1.392(3)
O(2)-S(1)-O(1) 117.05(8)	O(2)-S(1)-N(1) 113.00(8)	O(1)-S(1)-N(1) 105.37(7)	O(2)-S(1)-C(15) 107.35(8)
O(1)-S(1)-C(15) 107.00(8)	N(1)-S(1)-C(15) 106.47(8)	C(1)-N(1)-S(1) 120.16(12)	C(1)-N(2)-C(5) 127.01(14)
C(1)-N(2)-C(4) 112.40(14)	C(5)-N(2)-C(4) 119.87(14)	N(1)-C(1)-N(2) 121.58(16)	N(1)-C(1)-C(2) 129.36(16)
N(2)-C(1)-C(2) 109.03(15)	C(1)-C(2)-C(3) 104.94(15)	C(4)-C(3)-C(2) 104.48(14)	N(2)-C(4)-C(3) 103.79(14)
C(6)-C(5)-C(10) 119.17(16)	C(6)-C(5)-N(2) 118.42(16)	C(10)-C(5)-N(2) 122.40(15)	C(7)-C(6)-C(5) 120.71(17)
C(6)-C(7)-C(8) 120.02(17)	C(7)-C(8)-C(9) 119.48(17)	C(10)-C(9)-C(8) 120.98(17)	C(9)-C(10)-C(5) 119.61(16)
C(17)-C(12)-C(13) 118.49(17)	C(17)-C(12)-C(11) 120.50(16)	C(13)-C(12)-C(11) 121.01(17)	C(14)-C(13)-C(12) 121.19(17)
C(13)-C(14)-C(15) 119.33(16)	C(16)-C(15)-C(14) 120.72(17)	C(16)-C(15)-S(1) 119.06(14)	C(14)-C(15)-S(1) 120.07(13)
C(15)-C(16)-C(17) 119.16(17)	C(12)-C(17)-C(16) 121.07(16)		

XRD data of the compound 8d

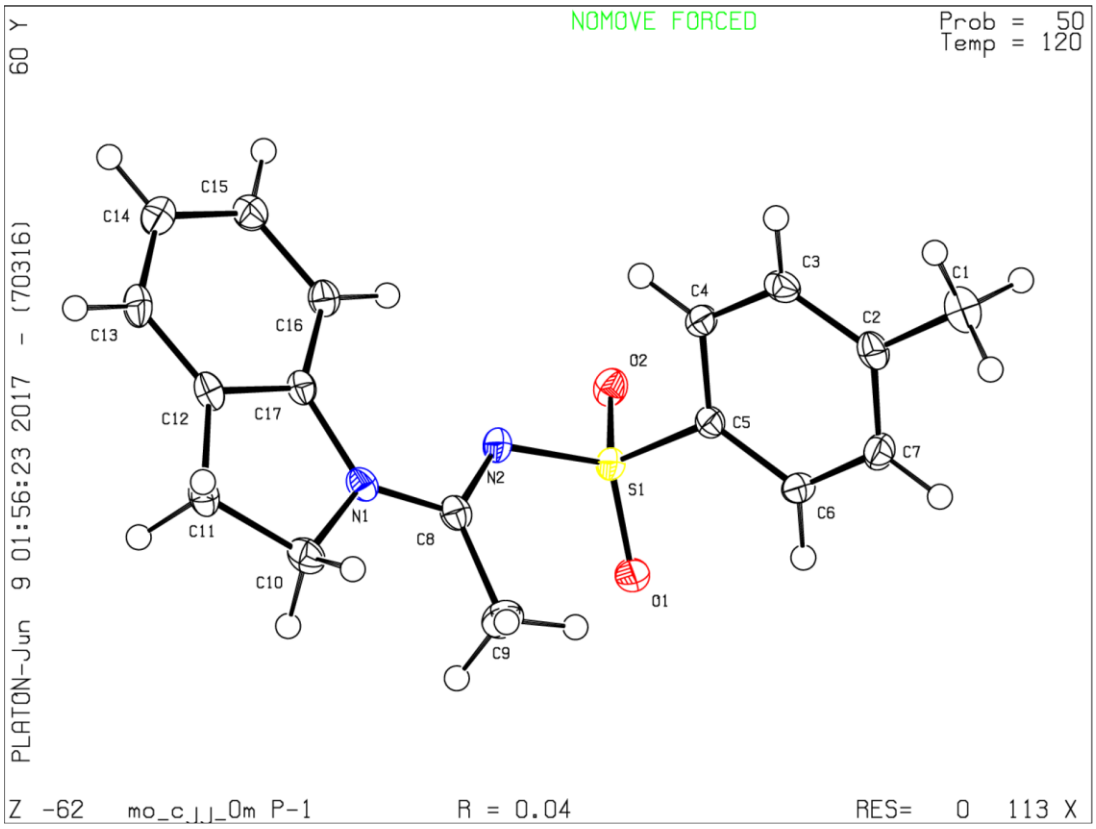


Figure S3. ORTEP structural drawing of **8d**. (CCDC: 1565961)

Table S5. Crystallography data for **8d**.

complex	**8d**
Empirical formula	$C_{17}H_{18}N_2O_2S$
Formula weight(g mol^{-1})	314.39
Temperature	120 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	a = 7.4252 (7) Å b = 9.8673 (10) Å c = 11.2350 (11) Å α = 77.187 (3) ° β = 79.103(3) ° γ = 69.194(3) °
Volume ($Å^3$)	744.80 (13)
Z	2
ρ(g cm^{-3})	1.402
F(000)	332
Crystal size(mm^3)	0.22 x 0.20 x 0.18

Theta range for data collection	1.87 °to 27.55 °
Limiting indices	-9<=h<=9 -12<=k<=12 -14<=l<=14
Reflections collected / unique	15180 / 3404
Data / restraints / parameters	3404 / 0 /201
GOF	1.096
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0418 *wR2* = 0.1133
R1,*wR2*(all data)	*R1* = 0.0558 *wR2* = 0.1321
Largest diff. peak and hole(e Å^3)	0.428 and -0.489

Table S6. Bond lengths [Å] and angles [°] for **8d**.

S(1)-O(2) 1.4378(14)	S(1)-O(1) 1.4426(14)	S(1)-N(2) 1.6123(16)	S(1)-C(5) 1.7663(19)
N(1)-C(8) 1.346(2)	N(1)-C(17) 1.422(2)	N(1)-C(10) 1.487(2)	N(2)-C(8) 1.316(2)
C(1)-C(2) 1.508(3)	C(2)-C(7) 1.388(3)	C(2)-C(3) 1.398(3)	C(3)-C(4) 1.386(3)
C(4)-C(5) 1.393(2)	C(5)-C(6) 1.387(2)	C(6)-C(7) 1.387(3)	C(8)-C(9) 1.500(3)
C(10)-C(11) 1.526(3)	C(11)-C(12) 1.500(3)	C(12)-C(13) 1.377(3)	C(12)-C(17) 1.398(3)
C(13)-C(14) 1.392(3)	C(14)-C(15) 1.386(3)	C(15)-C(16) 1.396(3)	C(16)-C(17) 1.392(3)
O(2)-S(1)-O(1) 116.39(8)	O(2)-S(1)-N(2) 105.08(8)	O(1)-S(1)-N(2) 114.52(8)	O(2)-S(1)-C(5) 107.37(8)
O(1)-S(1)-C(5) 107.82(8)	N(2)-S(1)-C(5) 104.89(9)	C(8)-N(1)-C(17) 128.34(15)	C(8)-N(1)-C(10) 122.03(15)
C(17)-N(1)-C(10) 109.63(14)	C(8)-N(2)-S(1) 124.18(14)	C(7)-C(2)-C(3) 118.37(17)	C(7)-C(2)-C(1) 121.05(17)
C(3)-C(2)-C(1) 120.57(18)	C(4)-C(3)-C(2) 121.43(17)	C(3)-C(4)-C(5) 118.95(17)	C(6)-C(5)-C(4) 120.51(17)
C(6)-C(5)-S(1) 120.12(14)	C(4)-C(5)-S(1) 119.31(13)	C(7)-C(6)-C(5) 119.65(18)	C(6)-C(7)-C(2) 121.05(17)
N(2)-C(8)-N(1) 117.25(16)	N(2)-C(8)-C(9) 126.62(17)	N(1)-C(8)-C(9) 116.14(17)	N(1)-C(10)-C(11) 105.90(15)
C(12)-C(11)-C(10) 104.22(15)	C(13)-C(12)-C(17) 120.31(17)	C(13)-C(12)-C(11) 128.89(17)	C(17)-C(12)-C(11) 110.80(16)
C(12)-C(13)-C(14) 119.42(18)	C(15)-C(14)-C(13) 119.99(18)	C(14)-C(15)-C(16) 121.54(18)	C(17)-C(16)-C(15) 117.60(17)
C(16)-C(17)-C(12) 121.13(17)	C(16)-C(17)-N(1) 129.42(16)	C(12)-C(17)-N(1) 109.44(16)	