SUPPORTING INFORMATION

Interception of Secondary Amide Ylide with Sulfonamides: Catalyst Controlled Synthesis of *N*-sulfonyl Amidines Derivatives

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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, HRMS, GC, and X-ray were performed by the State-authorized Analytical Center in Soochow University.

General procedures for reactions

(a) The procedure for the synthesis of diazo compounds[1]

The corresponding alcohol (20 mmol) and $NaHCO_3$ (5.0 g, 60 mmol) were dissolved in acetonitrile (50 mL) and bromoacetyl bromide (2.6 mL, 30 mmol) was added slowly at 0 ℃. After stirring 30 min at the temperature, the reaction was quenched with H_2O. The solution was extracted with CH_2Cl_2 three times. The organic phase was washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was used in the next reaction without purification. The bromoacetate thus obtained and N, N'-ditosylhydrazine (13.6 g, 40 mmol) were dissolved in THF (50 mL) and cooled to 0 ℃. DBU (60 mL, 40 mmol) was added dropwise and stirred at the temperature for 30 minutes. After the quenching of the reaction by the addition of saturated $NaHCO_3$ solution, it was extracted with Et_2O three times. The organic phase was washed with brine, dried over Na_2SO_4 and evaporated to give the crude product. The crude product thus obtained was purified by chromatography over a column of silica gel using petroleum and ethyl acetate as eluent to afford the desired product.

(b) The procedure for the synthesis of *N*-sulfonyl amidines under manganese catalysis

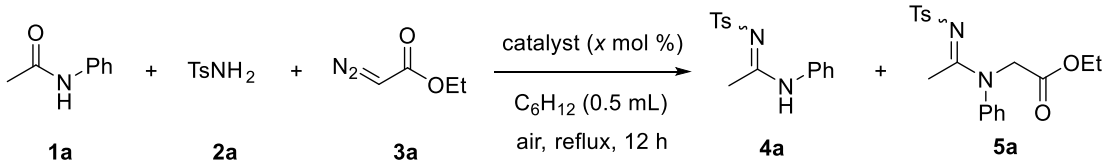
$Mn(ClO_4)_2 \cdot 6H_2O$ (0.02 mmol), secondary amides (0.2 mmol), and sulfamides (0.2 mmol) were added to a 20 mL test tube with a stirring bar. Cyclohexane (0.5 mL), diazo compounds (0.4 mmol) were added via syringe. The reaction mixture was heated in an oil bath at reflux (Tips: severe reflux, recommendation temperature: 90 ^oC) for 12 h under air (Tips: sometimes the solvent might evaporate, but the yield of *N*-sulfonyl amidines will barely be affected). 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.

(c) The procedure for the synthesis of *N*-sulfonyl amidines under znic catalysis

$Zn(OTf)_2$ (0.06 mmol), secondary amides (0.2 mmol), and sulfamides (0.2 mmol) were added to a 20 mL test tube with a stirring bar. Cyclohexane (0.5 mL) and diazo compounds (1.2 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: sometimes the solvent might evaporate, but the yield of *N*-sulfonyl amidines will barely be affected). 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, *N*-sulfonyl amidines slightly soluble in ethyl acetate, soluble in dichloromethane)

Table S1. Optimization of the Reaction Conditions [a]

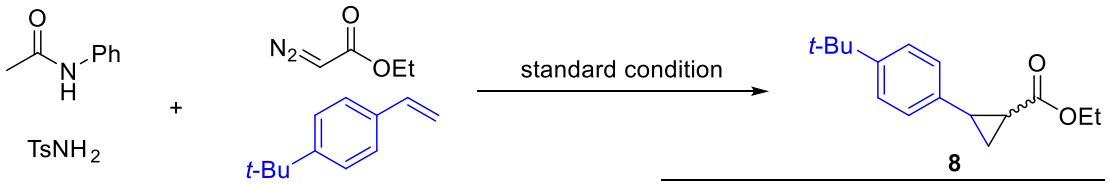


1a **2a** **3a** **4a** **5a**

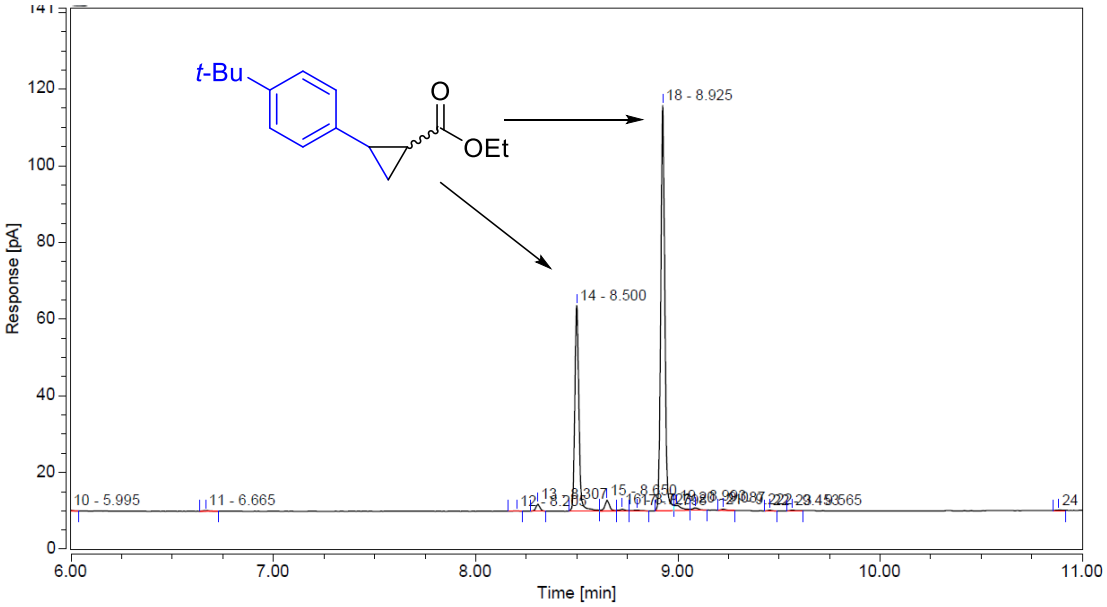
entry	catalyst	*x*	**3a** (equiv)	**4a** yield (%)[b]	**5a** yield (%)[b]
1	$Zn(OTf)_2$	10	2	29	30
2	$ZnCl_2$	10	2	21	< 5
3	$ZnBr_2$	10	2	21	< 5
4	$Cu(acac)_2$	10	2	19	< 5
5	$Co(BF_4)_2{\cdot}6H_2O$	10	2	38	8
6	AgOTf	10	2	24	< 5
7	$Fe(OTf)_3$	10	2	44	21
8	$Mn(ClO_4)_2{\cdot}6H_2O$	10	2	63	< 5
9	$Ni(ClO_4)_2{\cdot}6H_2O$	10	2	21	< 5
10	$Zn(ClO_4)_2{\cdot}6H_2O$	10	2	47	< 5
11	$AgClO_4$	10	2	< 5	< 5
12	$Zn(OTf)_2$	10	3	11	59
13	$Zn(OTf)_2$	10	4	10	61
14	$Zn(OTf)_2$	20	4	< 5	61
15	$Zn(OTf)_2$	30	4	< 5	56
16	$Zn(OTf)_2$	30	5	< 5	66
17	$Zn(OTf)_2$	30	6	< 5	81
18	—	—	2	< 5	< 5
19	$Zn(OTf)_2$	10	—	< 5	< 5
20	$Mn(ClO_4)_2{\cdot}6H_2O$	10	—	< 5	< 5

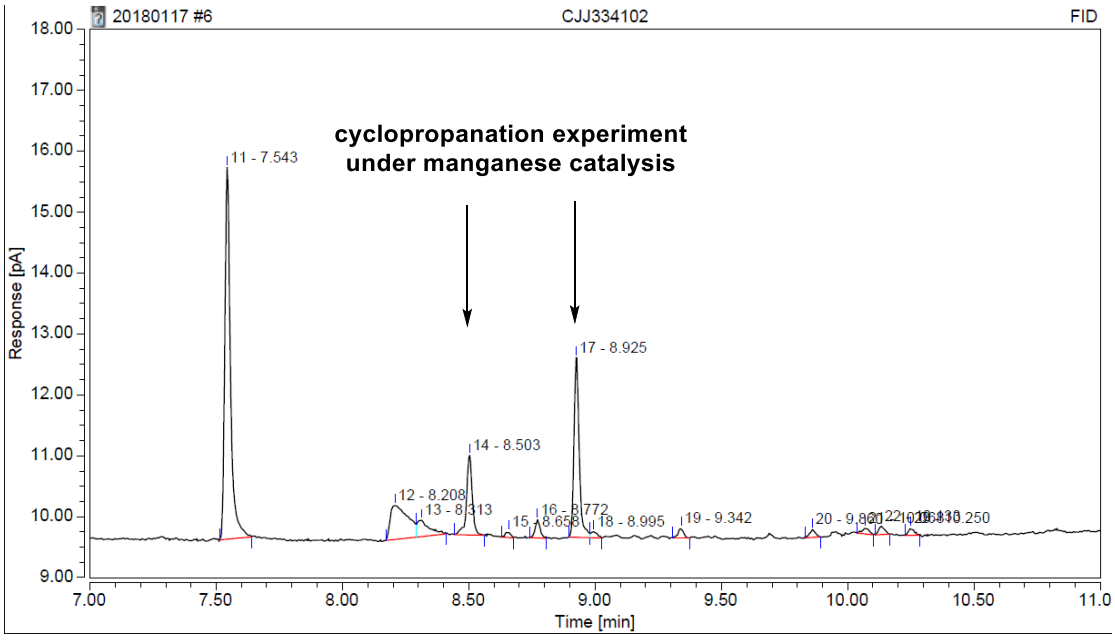
[a]Reaction Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3a**, and catalyst in C_6H_{12} (0.5 mL) at reflux for 12 h under air, isolated yield.

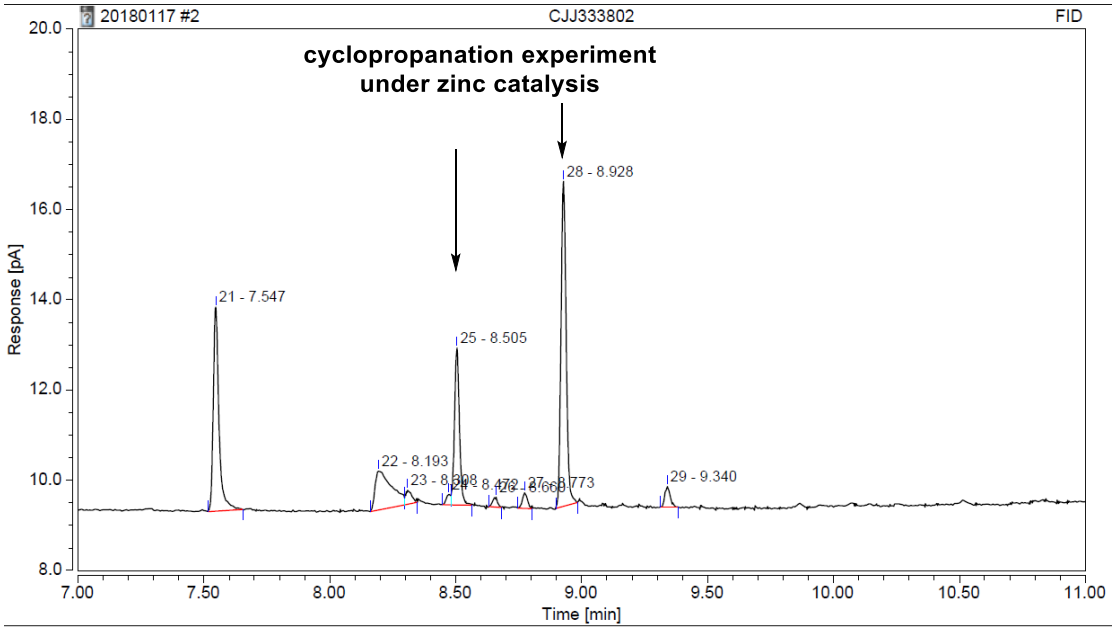
Carbene traps experiment:



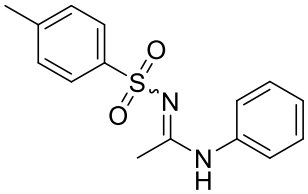
[M]	**8**, detected by GC
$Mn(ClO_4)_2{\cdot}6H_2O$	Yes
$Zn(OTf)_2$	Yes



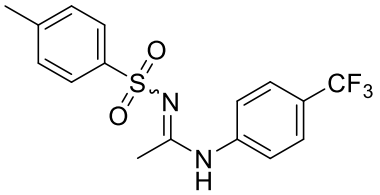



20180117 #2
CJJ333802
FID
cyclopropanation experiment
under zinc catalysis
28 - 8.928
21 - 7.547
25 - 8.505
22 - 8.193
29 - 9.340
Response [pA]
Time [min]

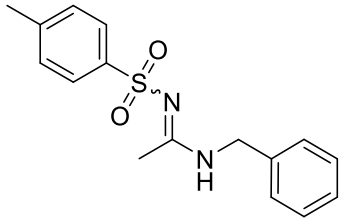
Compound Characterizations



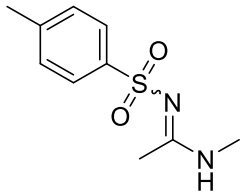
***N*-phenyl-*N*'-tosylacetimidamide (4a)**. Petroleum ether/ ethylacetate = 3:1, white solid, 36.5 mg, 63% yield, *E/Z* = 1:1.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 0.67H), 8.36 (s, 1H), 7.87–7.86 (m, 1.34H), 7.79–7.77 (m, 2H), 7.54–7.52 (m, 2H), 7.43–7.39 (m, 1.33H), 7.36–7.35 (m, 0.66H), 7.32–7.30 (m, 1H), 7.25–7.19 (m, 4H), 7.13–7.06 (m, 2.65H), 2.51 (s, 3H), 2.42 (s, 2H), 2.39 (s, 3H), 2.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 143.3, 142.4, 140.0, 138.8, 137.3, 136.3, 129.6, 129.4, 129.2, 128.6, 128.1, 126.4, 126.23, 126.17, 125.3, 121.8, 21.8, 21.5, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}N_2O_2S+Na^+$: 311.0825, Found: 311.0828; IR (neat, cm-1): υ 3302, 1531, 1268, 1137, 1085, 688.



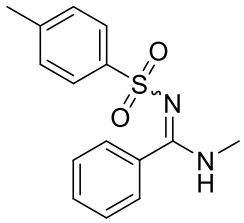
***N*'-tosyl-*N*-(4-(trifluoromethyl)phenyl)acetimidamide (4b)**. Petroleum ether/ ethylacetate = 4:1, 45.3 mg, white solid, 64% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, DMSO) δ 10.27 (s, 1H), 8.09 (s, 1H), 7.77–7.75 (m, 1H), 7.73–7.71 (m, 2H), 7.54–7.50 (m, 1H), 7.36–7.34 (m, 2H), 7.28 (s, 1H), 2.36 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.9, 141.9, 141.5, 140.1, 129.9, 129.3, 125.7, 122.4, 119.3 ((q, *J* = 3 Hz)), 115.0, 24.0, 20.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}F_3N_2O_2S+Na^+$: 357.0879, Found: 357.0871; IR (neat, cm-1): υ 3272, 1676, 1557, 1331, 1157, 662.



***N*-benzyl-*N*'-tosylacetimidamide (4c)**. Petroleum ether/ ethylacetate = 2:1, white solid, 44.8 mg, 74% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.63 (m, 2H), 7.24–7.23 (m, 3H), 7.19–7.17 (m, 4H), 6.99 (s, 1H), 4.39 (d, *J* = 2.1 Hz, 2H), 2.38 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 142.1, 140.3, 136.5, 129.1, 128.5, 128.0, 127.5, 126.1, 45.8, 21.3, 20.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{18}N_2O_2S+Na^+$: 325.0981, Found: 325.0973; IR (neat, cm-1): υ 3304, 1542, 1270, 1143, 1088, 668.

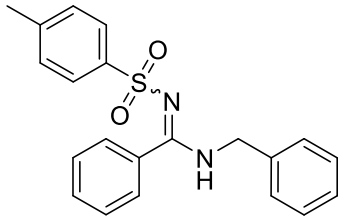


***N*-methyl-*N*'-tosylacetimidamide (4d)**. Petroleum ether/ ethylacetate = 1:1, white solid, 34.6 mg, 77% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.26–7.24 (m, 2H), 7.02 (s, 1H), 2.80 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 142.2, 140.3, 129.2, 126.2, 28.8, 21.4, 20.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{14}N_2O_2S+Na^+$: 249.0668, Found: 249.0658; IR (neat, cm-1): υ 3294, 1554, 1271, 1139, 665.

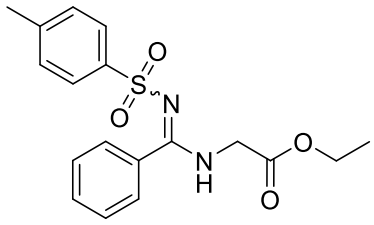


***N*-methyl-*N*'-tosylbenzimidamide (4e)**. Petroleum ether/ ethylacetate = 2:1, white solid, 23.7 mg, 41% yield, *E/Z* = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.84–7.83 (m, 2H), 7.63–7.61 (m, 2H), 7.49–7.41 (m, 9H), 7.35–7.33 (m, 2H), 7.28 (s,

1H), 7.16–7.14 (m, 2H), 5.90 (s, 1H), 2.98 (s, 3H), 2.94 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.3, 142.9, 141.7, 140.8, 139.2, 134.2, 132.5, 131.0, 130.7, 129.3, 128.8, 128.5, 128.1, 128.0, 127.7, 126.42, 126.40, 33.0, 29.5, 21.5, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{16}N_2O_2S+Na^+$: 311.0825, Found: 311.0824; IR (neat, cm-1): υ 3257, 1535, 1268, 1134, 1080, 687.

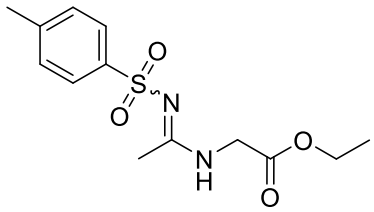


***N*-benzyl-*N*'-tosylbenzimidamide (4f)**. Petroleum ether/ ethylacetate = 3.5:1, colorless liquid, 42.2 mg, 58% yield, *E/Z* = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.80– 7.79 (m, 2H), 7.60– 7.58 (m, 2H), 7.49–7.42 (m, 4H), 7.38–7.24 (m, 16H), 7.15– 7.13 (m, 2H), 7.10–7.09 (m, 2H), 6.01 (s, 1H), 4.57 (d, *J* = 2.2 Hz, 2H), 4.42 (d, *J* = 3.8 Hz, 2H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.3, 143.0, 141.8, 140.7, 139.0, 136.4, 136.3, 134.0, 131.1, 130.9, 129.6, 129.4, 128.9, 128.8, 128.8, 128.6, 128.2, 128.1, 128.0, 127.9, 127.7, 126.8, 126.5, 126.4, 126.4, 49.7, 46.6, 21.5, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{20}N_2O_2S+Na^+$: 387.1138, Found: 387.1137; IR (neat, cm-1): υ 3288, 1531, 1137, 1085, 686.

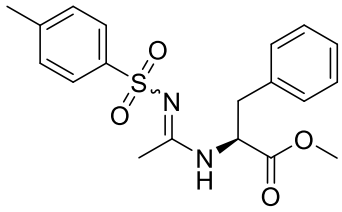


Ethyl (phenyl(tosylimino)methyl)glycinate (4g). Petroleum ether/ ethylacetate = 2.5:1, colorless liquid, 21.4 mg, 88% yield, *E/Z* = 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 0.33H), 7.91 (s, 0.65H), 7.63–7.61 (m, 2H), 7.52–7.46 (m, 2.68H), 7.40–7.37 (m, 2.68H), 7.30–7.28 (m, 0.67H), 7.17–7.15 (m, 2H), 6.23 (s, 1H), 4.23–4.17 (m, 4.67H), 3.98 (s, 0.66H), 2.42 (s, 1H), 2.37 (s, 3H), 1.28–1.25 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 165.2, 142.0, 140.4, 133.5, 131.2, 131.1, 128.9, 128.7, 128.2,

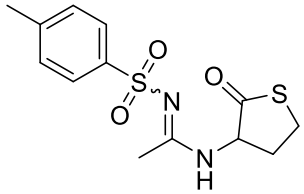
127.9, 127.8, 126.7, 126.5, 61.9, 44.0, 30.9, 21.4, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_4S+Na^+$: 383.1036, Found: 383.1029; IR (neat, cm-1): υ 3304, 1741, 1530, 1139, 1086, 687.



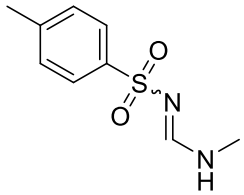
Ethyl (1-(tosylimino)ethyl)glycinate (4h). Petroleum ether/ ethylacetate = 1:1, colorless liquid, 42.8 mg, 72% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.26–7.24 (m, 2H), 6.76 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.02 (d, *J* = 3.4 Hz, 2H), 2.40 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 165.9, 142.3, 140.0, 129.1, 126.2, 61.6, 43.4, 21.3, 20.5, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_4S+Na^+$: 321.0879, Found: 321.0882; IR (neat, cm-1): υ 3290, 1752, 1558, 1139, 1087, 669.



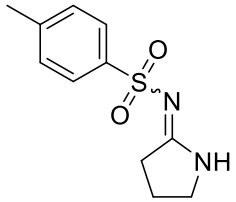
Methyl (1-(tosylimino)ethyl)-*L*-phenylalaninate (4i). Petroleum ether/ ethylacetate = 2:1, colorless liquid, 59.5 mg, 80% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = 40.3 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.27–7.22 (m, 5H), 7.01–7.00 (m, 2H), 6.36 (d, *J* = 6.0 Hz, 1H), 4.83 (q, *J* = 5.8 Hz, 1H), 3.65 (s, 3H), 3.18–3.01 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 165.0, 142.2, 140.1, 135.3, 129.1, 129.0, 128.5, 127.1, 126.2, 55.2, 52.4, 36.7, 21.4, 20.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{22}N_2O_4S+Na^+$: 397.1192, Found: 397.1184; IR (neat, cm-1): υ 3294, 1742, 1540, 1272, 1141, 1089, 697.



***N*-(2-oxotetrahydrothiophen-3-yl)-*N*'-tosylacetimidamide (4j)**. Petroleum ether/ ethylacetate = 2:1, light yellow solid, 34.0 mg, 55% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, DMSO) δ 8.96 (d, *J* = 7.8 Hz, 1H), 7.67–7.65 (m, 2H), 7.34–7.32 (m, 2H), 4.86–4.79 (m, 1H), 3.47–3.40 (m, 1H), 3.32–3.28 (m, 1H), 2.53–2.47 (m, 1H), 2.36 (s, 3H), 2.24 (s, 3H), 2.14–2.06 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 204.1, 166.5, 141.8, 140.7, 129.3, 125.9, 59.8, 29.6, 27.0, 20.9, 19.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{16}N_2O_3S_2$+Na^+: 335.0495, Found: 335.0497; IR (neat, cm-1): υ 3269, 2918, 1697, 1537, 1262, 1086, 665.

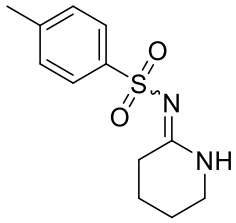


***N*-methyl-*N*'-tosylformimidamide (4k)**. Petroleum ether/ ethylacetate = 1:1, white solid, 37.4 mg, 88% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.73–7.71 (m, 2H), 7.26–7.24 (m, 2H), 7.16 (s, 1H), 2.89 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 142.7, 139.0, 129.4, 126.2, 28.3, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_9H_{12}N_2O_2S$+Na^+: 235.0512, Found: 235.0504; IR (neat, cm-1): υ 3372, 1619, 1266, 1140, 906, 681.

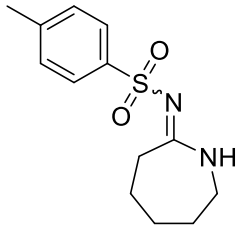


4-Methyl-*N*-(pyrrolidin-2-ylidene)benzenesulfonamide (4l). Petroleum ether/ ethylacetate = 1:1, white solid, 42.6 mg, 90% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.81–7.79 (m, 2H), 7.28–7.26 (m, 2H), 3.57 (t, *J* = 7.1 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.08–2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$)

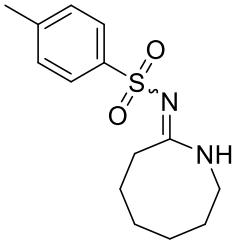
δ 171.6, 142.6, 139.4, 129.2, 126.3, 46.2, 32.6, 21.4, 20.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}N_2O_2S+Na^+$: 261.0668, Found: 261.0660; IR (neat, cm-1): υ 3202, 1611, 1143, 809, 666.



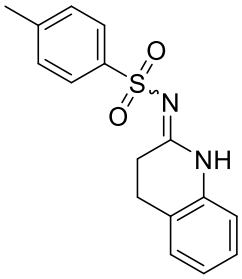
4-Methyl-*N*-(piperidin-2-ylidene)benzenesulfonamide (4m). Petroleum ether/ ethylacetate = 1.5:1, white solid, 35.1 mg, 70% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.81–7.79 (m, 2H), 7.28–7.26 (m, 2H), 3.38 (m, 2H), 2.49 (m, 2H), 2.40 (s, 3H), 1.75 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 142.4, 139.8, 129.2, 126.2, 42.3, 30.4, 21.4, 21.2, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}N_2O_2S+Na^+$: 275.0825, Found: 275.0815; IR (neat, cm-1): υ 3220, 1608, 1273, 1146, 676.



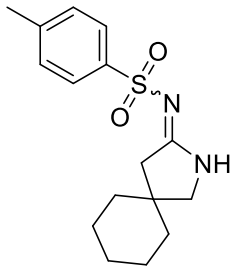
***N*-(azepan-2-ylidene)-4-methylbenzenesulfonamide (4n)**. Petroleum ether/ ethylacetate = 2:1, white solid, 29.8 mg, 56% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.82–7.80 (m, 2H), 7.28–7.26 (m, 2H), 3.36 (m, 2H), 2.50–2.48 (m, 2H), 2.40 (s, 3H), 1.74–1.73 (m, 2H), 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 142.6, 139.4, 129.2, 126.2, 44.6, 36.6, 29.9, 28.5, 23.5, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_2S+Na^+$: 289.0981, Found: 289.0972; IR (neat, cm-1): υ 3333, 2931, 1604, 1266, 892, 685.



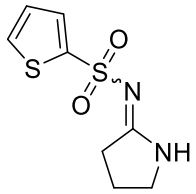
***N*-(azocan-2-ylidene)-4-methylbenzenesulfonamide (4o)**. Petroleum ether/ ethylacetate = 3:1, white solid, 37.2 mg, 66% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.83–7.81 (m, 2H), 7.28–7.29 (m, 2H), 3.43–3.42 (m, 2H), 2.45–2.40 (m, 5H), 1.73 (m, 2H), 1.61 (m, 2H), 1.43–1.40 (m, 2H), 1.37–1.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 142.6, 139.4, 129.1, 126.3, 42.8, 32.3, 31.5, 28.8, 25.2, 24.0, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{20}N_2O_2S+Na^+$: 303.1138, Found: 303.1126; IR (neat, cm-1): υ 2933, 1597, 1278, 1140, 612.



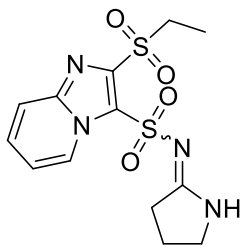
***N*-(3,4-dihydroquinolin-2(1*H*)-ylidene)-4-methylbenzenesulfonamide (4p)**. Petroleum ether/ ethylacetate = 4.5:1, 37.9 mg, white solid, 63% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.88–7.86 (m, 2H), 7.30–7.28 (m, 2H), 7.23–7.20 (m, 1H), 7.15–7.14 (m, 1H), 7.08–7.04 (m, 1H), 6.91–6.89 (m, 1H), 2.90–2.86 (m, 2H), 2.73–2.72 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 143.2, 138.8, 134.8, 129.4, 128.2, 127.8, 126.4, 124.7, 124.2, 116.7, 30.4, 23.8, 21.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{16}N_2O_2S+H^+$: 301.1005, Found: 301.1018; IR (neat, cm-1): υ 3287, 1575, 1275, 1081, 757, 687.



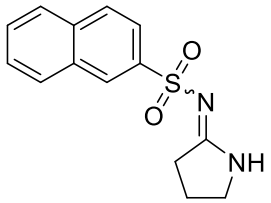
4-Methyl-*N*-(2-azaspiro[4.5]decan-3-ylidene)benzenesulfonamide (4q). Petroleum ether/ ethylacetate = 3.5:1, white solid, 44.0 mg, 72% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.80–7.78 (d, *J* = 7.8 Hz, 2H), 7.28–7.26 (m, 2H), 3.29 (s, 2H), 2.54 (s, 2H), 2.40 (s, 3H), 1.45–1.41 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 142.6, 139.5, 129.2, 126.3, 56.8, 45.1, 39.4, 36.1, 25.3, 22.8, 21.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{22}N_2O_2S+Na^+$: 329.1294, Found: 329.1282; IR (neat, cm-1): υ 2919, 1609, 1150, 816, 667.



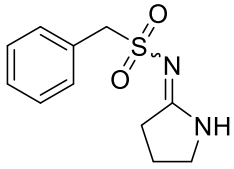
***N*-(pyrrolidin-2-ylidene)thiophene-2-sulfonamide (4r)**. Petroleum ether/ ethylacetate = 1:1, white solid, 45.2 mg, 98% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.614–7.606 (m, 1H), 7.53–7.52 (m, 1H), 7.05–7.03 (m, 1H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.80–2.77 (m, 2H), 2.11–2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 143.6, 130.8, 130.6, 126.9, 46.2, 32.4, 20.0. HRMS (ESI-TOF): Anal. Calcd. For $C_8H_{10}N_2O_2S_2+Na^+$: 253.0076, Found: 353.0078; IR (neat, cm-1): υ 3100, 1607, 1300, 1139, 1013, 722, 664.



2-(Ethylsulfonyl)-*N*-(pyrrolidin-2-ylidene)imidazo[1,2-a]pyridine-3-sulfonamide (4s). Petroleum ether/ ethylacetate = 1:2, white solid, 41.1 mg, 58% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.92–8.90 (m, 1H), 7.87–7.85 (m, 1H), 7.58–7.54 (m, 1H), 7.21–7.18 (m, 1H), 3.75–3.66 (m, 4H), 2.69 (t, *J* = 8.1 Hz, 2H), 2.11–2.03 (m, 2H), 1.40 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 144.3, 143.7, 129.1, 128.0, 122.6, 118.9, 116.1, 50.3, 47.8, 34.3, 19.4, 6.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{16}N_4O_4S_2+H^+$: 357.0686, Found: 357.0697; IR (neat, cm-1): υ 3305, 1609, 1302, 1133, 729.

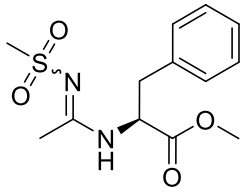


***N*-(pyrrolidin-2-ylidene)naphthalene-2-sulfonamide (4t)**. Petroleum ether/ ethylacetate = 1.5:1, white solid, 41.5 mg, 76% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.40 (s, 1H), 7.95–7.91 (m, 3H), 7.88–7.86 (m, 1H), 7.61–7.54 (m, 2H), 3.55 (m, 2H), 2.72–2.71 (m, 2H), 2.04–2.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 139.2, 134.5, 132.0, 129.1, 129.0, 128.2, 127.7, 127.1, 126.9, 122.4, 46.3, 32.7, 19.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{14}N_2O_2S+Na^+$: 297.0668, Found: 297.0671; IR (neat, cm-1): υ 2969, 1612, 1125, 818, 641.

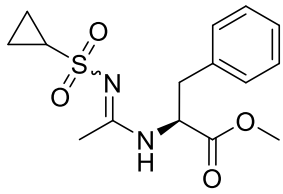


1-Phenyl-*N*-(pyrrolidin-2-ylidene)methanesulfonamide (4u). Petroleum ether/ ethylacetate = 1:1, white solid, 34.8 mg, 73% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.43–7.41 (m, 2H), 7.35–7.34 (m, 3H), 4.25 (s, 2H), 3.24 (t, *J* = 6.1 Hz, 2H), 2.51–2.47 (m, 2H), 1.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 130.9, 129.9, 128.2, 128.2, 59.9, 46.1, 32.7, 19.6. HRMS (ESI-TOF): Anal. Calcd.

For $C_{11}H_{14}N_2O_2S+Na^+$: 261.0668, Found: 261.0675; IR (neat, cm-1): υ 3107, 1618, 1302, 1126, 699.

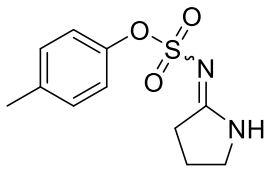


Methyl (1-((methylsulfonyl)imino)ethyl)-*L*-phenylalaninate (4v). Petroleum ether/ ethylacetate = 1.5:1, colourless liquid, 58.2 mg, 97% yield, *E/Z* = 3:1, $[\alpha]_D^{20}$ = 125.9 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 4H), 7.11–7.09 (d, *J* = 7.6 Hz, 2.67H), 6.39–6.37 (m, 1H), 6.18–6.17 (m, 0.33H), 4.86–4.81 (m, 1.33H), 3.73 (s, 3H), 3.71 (s, 1H), 3.23–3.05 (m, 2.67H), 2.95 (s, 3.41H), 2.40 (s, 3H), 1.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 171.2, 169.8, 164.6, 135.7, 135.3, 129.1, 129.0, 128.5, 128.4, 127.2, 127.0, 55.1, 53.1, 52.4, 52.2, 42.8, 37.7, 36.9, 22.9, 20.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_4S+Na^+$: 321.0879, Found: 321.0887; IR (neat, cm-1): υ 3301, 1741, 1543, 1267, 1112, 789.

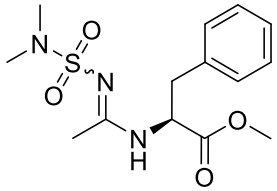


Methyl (1-((cyclopropylsulfonyl)imino)ethyl)-*L*-phenylalaninate (4w). Petroleum ether/ ethylacetate = 2:1, colourless liquid, 60.4 mg, 93% yield, *E/Z* = 2.2:1, $[\alpha]_D^{20}$ = 114.9 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.22 (m, 4.39H), 7.12–7.10 (m, 2.9H), 6.38 (d, *J* = 6.3 Hz, 1H), 6.19 (d, *J* = 6.8 Hz, 0.45H), 4.88–4.81 (m, 1.46H), 3.73 (s, 3H), 3.71 (s, 1.35H), 3.24–3.19 (m, 0.91H), 3.16–3.04 (m, 2H), 2.54–2.49 (m, 1.45H), 2.40 (s, 3H), 1.97 (s, 1.45H), 1.16–1.12 (m, 2.91H), 1.01–0.99 (m, 0.9H), 0.95–0.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 171.3, 169.8, 164.6, 135.7, 135.4, 129.1, 129.0, 128.5, 128.4, 127.1, 127.0, 55.2, 53.1, 52.4, 52.2, 37.7, 36.8, 32.2, 32.1, 22.9, 20.8, 5.8, 5.13, 5.08. HRMS (ESI-TOF): Anal. Calcd. For

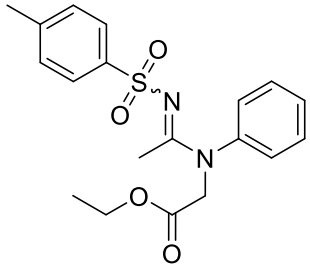
$C_{15}H_{20}N_2O_4S+Na^+$: 347.1036, Found: 347.1026; IR (neat, cm-1): υ 3305, 1741, 1542, 1113, 731, 699.



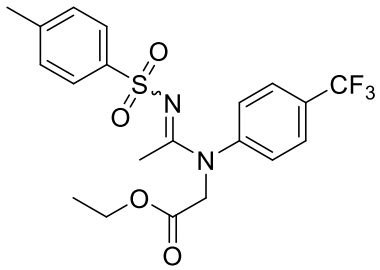
***p*-tolyl pyrrolidin-2-ylidenesulfamate (4x)**. Petroleum ether/ ethylacetate = 2:1, white solid, 32.9 mg, 63% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.27–7.13 (m, 4H), 3.50–3.49 (m, 2H), 2.79–2.76 (m, 2H), 2.33 (s, 3H), 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 148.3, 136.2, 129.9, 121.8, 46.3, 32.3, 20.8, 20.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}N_2O_3S+Na^+$: 277.0617, Found: 277.0613; IR (neat, cm-1): υ 3104, 1629, 1349, 1154, 821.



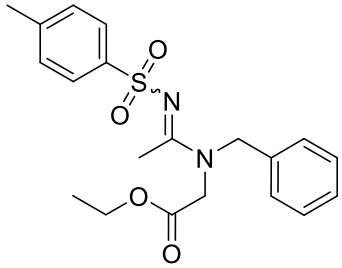
Methyl (1-((*N*,*N*-dimethylsulfamoyl)imino)ethyl)-*L*-phenylalaninate (4y). Petroleum ether/ ethylacetate = 2:1, white solid, 51.1 mg, 78% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = 41.1 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 3H), 7.12–7.10 (m, 2H), 6.12 (d, *J* = 6.0 Hz, 1H), 4.81–4.76 (m, 1H), 3.73 (s, 3H), 3.26–3.21 (m, 1H), 3.13–3.08 (m, 1H), 2.74 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 165.7, 135.3, 129.0, 128.7, 127.3, 55.2, 52.4, 38.8, 38.2, 36.7, 20.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{21}N_3O_4S+Na^+$: 350.1145, Found: 350.1150; IR (neat, cm-1): υ 3316, 1748, 1541, 1145, 716.



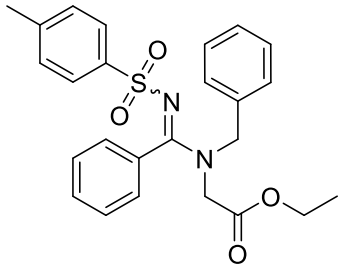
Ethyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5a). Petroleum ether/ ethylacetate = 4:1, light yellow solid, 60.2 mg, 80% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.47–7.37 (m, 3H), 7.33–7.31 (m, 2H), 7.28–7.26 (m, 2H), 4.37 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.2, 142.2, 142.1, 140.4, 130.0, 128.9, 128.9, 127.5, 126.2, 61.2, 53.8, 21.3, 19.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{22}N_2O_4S+Na^+$: 397.1192, Found: 397.1196; IR (neat, cm-1): υ 3332, 2974, 1742, 1536, 1084, 687.



Ethyl *N*-(1-(tosylimino)ethyl)-*N*-(4-(trifluoromethyl)phenyl)glycinate (5b). Petroleum ether/ ethylacetate = 4:1, colourless liquid, 49.4 mg, 56% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.69–7.68 (m, 1H), 7.63–7.62 (m, 2H), 7.59–7.55 (m, 1H), 7.29– 7.27 (m, 2H), 4.37 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 166.0, 142.8, 142.4, 140.1, 131.4, 130.8, 129.1, 126.3, 125.8 (q, *J* = 3.3 Hz), 124.8 (q, *J* = 3.7 Hz), 61.5, 53.8, 21.4, 19.2, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{21}F_3N_2O_4S+H^+$: 443.1247, Found: 443.1258; IR (neat, cm-1): υ 2985, 1743, 1543, 1086, 838.

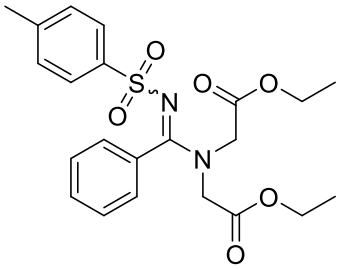


Ethyl *N*-benzyl-*N*-(1-(tosylimino)ethyl)glycinate (5c). Petroleum ether/ ethylacetate = 3:1, colourless liquid, 27.8 mg, 36% yield, *E/Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.77 (m, 2.67H), 7.40–7.28 (m, 4H), 7.25–7.23 (m, 2.69H), 7.21–7.17 (m, 2.67H), 4.75 (s, 1H), 4.69 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 0.67H), 4.08 (s, 7.H), 4.04 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 0.66H), 2.61 (s, 3H), 2.53 (s, 1H), 2.40 (s, 4H), 1.23 (t, *J* = 7.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 167.7, 166.7, 166.6, 142.0, 140.6, 135.1, 134.5, 129.1, 129.1, 129.0, 128.9, 128.7, 128.5, 128.2, 128.0, 126.6, 126.6, 126.2, 126.2, 62.0, 61.3, 53.7, 52.8, 50.4, 49.7, 21.4, 21.2, 18.0, 17.7, 14.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{24}N_2O_4S+H^+$: 411.1349, Found: 411.1347; IR (neat, cm-1): υ 2981, 1741, 1541, 1143, 686.

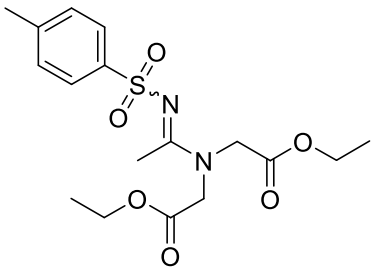


Ethyl *N*-benzyl-*N*-(phenyl(tosylimino)methyl)glycinate (5d). Petroleum ether/ ethylacetate = 3.5:1, colourless liquid, 50.9 mg, 57% yield, *E/Z* = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 0.66H), 7.52–7.50 (m, 2H), 7.44–7.26 (m, 10.66H), 7.19–7.08 (m, 5.22H), 4.92 (s, 0.66H), 4.34 (s, 2H), 4.26–4.20 (q, *J* = 7.2 Hz, 1H), 4.16 (s, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 0.73H), 2.40 (s, 1H), 2.36 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 167.8, 167.5, 167.3, 143.2, 141.8, 140.3, 139.3, 135.0, 134.6, 131.4, 131.2, 130.1, 130.0, 129.5, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 127.3, 127.2, 127.1, 126.45, 126.41, 126.3, 61.7, 61.4, 54.1, 51.7, 50.0, 48.5, 21.4, 21.3, 13.97, 13.95.

HRMS (ESI-TOF): Anal. Calcd. For $C_{25}H_{26}N_2O_4S+H^+$: 451.1686, Found: 451.1681; IR (neat, cm-1): υ 2981, 1740, 1522, 1143, 684.

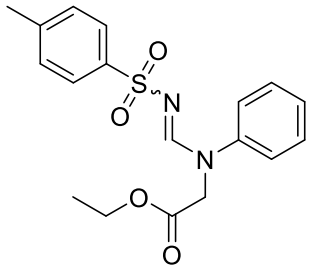


Diethyl 2,2'-((phenyl(tosylimino)methyl)azanediyl)diacetate (5e). Petroleum ether/ ethylacetate = 2.5:1, light yellow solid, 55.2 mg, 62% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.46–7.42 (m, 1H), 7.37–7.34 (m, 2H), 7.20–07.18 (m, 2H), 7.14–7.12 (m, 2H), 4.35 (s, 2H), 4.19–4.09 (m, 4H), 3.87 (s, 2H), 2.36 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 167.7, 167.3, 141.9, 140.1, 130.7, 130.3, 128.7, 128.3, 127.1, 126.4, 61.7, 61.4, 51.9, 50.1, 21.3, 14.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{22}H_{26}N_2O_6S+Na^+$: 469.1404, Found: 469.1414; IR (neat, cm-1): υ 2985, 1741, 1540, 1145, 679.

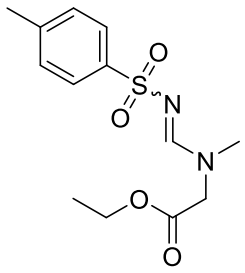


Diethyl 2,2'-((1-(tosylimino)ethyl)azanediyl)diacetate (5f). Petroleum ether/ ethylacetate = 1.5:1, colourless liquid, 42.7 mg, 56% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.25–7.23 (m, 2H), 4.25–4.18 (m, 6H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 167.6, 166.6, 142.1, 140.3, 129.0, 126.2, 62.1, 61.3, 51.6, 51.2, 21.3, 17.4, 14.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For

$C_{17}H_{24}N_2O_6S+Na^+$: 407.1247, Found: 407.1248; IR (neat, cm-1): υ 2978, 1745, 1551, 1209, 684.

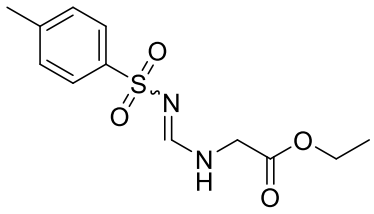


Ethyl *N*-phenyl-*N*-((tosylimino)methyl)glycinate (5g). Petroleum ether/ ethylacetate = 5:1, colourless liquid, 55.6 mg, 77% yield, *E/Z* = 2.8:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.78–7.73 (m, 2.73H), 7.45–7.41 (m, 2H), 7.36–7.32 (m, 1H), 7.31–7.23 (m, 5.44H), 5.34 (d, *J* = 15.3 Hz, 0H), 4.57 (s, 2H), 4.11–4.04 (m, 2.72H), 3.76 (s, 1H), 2.41 (s, 1H), 2.40 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.0, 158.7, 143.6, 142.8, 142.2, 138.4, 136.1, 129.8, 129.6, 129.2, 128.8, 127.7, 127.1, 126.5, 123.0, 119.7, 61.7, 50.7, 44.1, 21.4, 21.4, 13.83, 13.77. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{20}N_2O_4S+H^+$: 361.1217, Found: 367.1218; IR (neat, cm-1): υ 2981, 1743, 1575, 1147, 675.

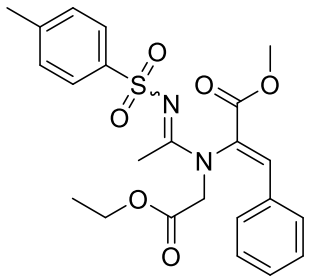


Ethyl *N*-methyl-*N*-((tosylimino)methyl)glycinate (5h). Petroleum ether/ ethylacetate = 1.5:1, light yellow liquid, 29.7 mg, 50% yield, *E/Z* = 1.8:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.18 (s, 0..56H), 7.78–7.76 (m, 1.12H), 7.74–7.72 (m, 2H), 7.28–7.23 (m, 3.12H), 4.23 (q, *J* = 7.1 Hz, 1.28H), 4.17 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 1.12H), 3.20 (s, 3H), 3.05 (s, 1.68H), 2.40 (s, 1.68H), 2.39 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 1.79H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.9, 160.2, 159.9, 142.6, 142.5, 139.0, 138.9, 129.3, 129.2, 126.5, 126.4,

762.0, 61.6, 55.1, 49.1, 40.3, 35.0, 29.6, 21.4, 14.03, 13.92. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_4S+H^+$: 299.1060, Found: 299.1062; IR (neat, cm-1): υ 2923, 1742, 1608, 1144, 1083, 671.

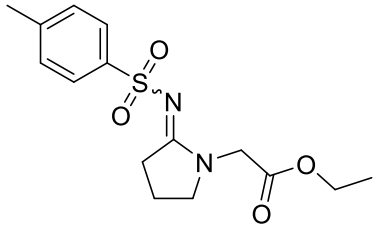


Ethyl ((tosylimino)methyl)glycinate (5i). Petroleum ether/ ethylacetate = 4:1, white solid, 29.0 mg, 51% yield, *E/Z* = 1:5.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 0.17H), 7.78–7.73 (M, 2.34H), 7.40–7.38 (m, 0.34H), 7.32–7.30 (m, 2H), 5.20 (s, 1H), 4.35 (s, 0.17H), 4.27–4.21 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 0.34H), 3.77 (d, *J* = 3.0 Hz, 2H), 2.47 (s, 0.34H), 2.42 (s, 3H), 2.41 (s, 0.5H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 0.51H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 156.5, 143.7, 136.1, 130.4, 129.7, 129.5, 127.9, 127.2, 127.1, 61.8, 61.6, 45.6, 44.1, 21.7, 21.5, 13.9, 13.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}N_2O_4S+Na^+$: 307.0723, Found: 307.0728; IR (neat, cm-1): υ 3221, 1732, 1331, 1154, 659.

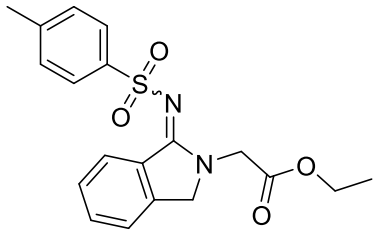


Methyl (2*Z*)-2-(*N*-(2-ethoxy-2-oxoethyl)-*N*'-tosylacetimidamido)-3-phenylacrylate (5j). Petroleum ether/ ethylacetate = 10:1, colourless liquid, 45.1 mg, 50% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.76 (s, 1H), 7.68–7.67 (m, 2H), 7.48–7.40 (m, 3H), 7.29–7.27 (m, 2H), 4.12 (d, *J* = 2.8 Hz, 2H), 4.00–3.90 (m, 2H), 3.87 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 167.1, 164.5, 142.3, 140.0, 139.1, 131.6, 131.0, 130.8, 129.2, 129.0, 128.9, 126.4, 61.1, 53.0, 52.6, 21.4, 18.0, 13.8. HRMS (ESI-TOF): Anal. Calcd.

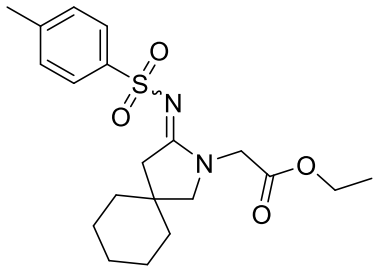
For $C_{23}H_{26}N_2O_6S+Na^+$: 481.1404, Found: 481.1403; IR (neat, cm-1): υ 2981, 1717, 1550, 1147, 683.



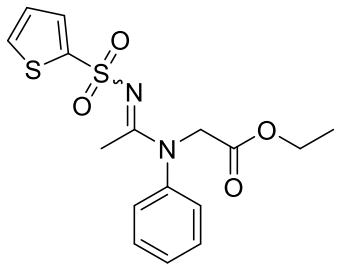
Ethyl 2-(2-(tosylimino)pyrrolidin-1-yl)acetate (5k). Petroleum ether/ ethylacetate = 1.5:1, white solid, 49.9 mg, 77% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.25–7.23 (m, 2H), 4.18–4.12 (m, 4H), 3.54 (t, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 7.9 Hz, 2H), 2.39 (s, 3H), 2.12–2.05 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 167.1, 142.0, 140.0, 128.9, 126.2, 61.3, 50.0, 45.8, 30.2, 21.2, 19.1, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{20}N_2O_4S+Na^+$: 347.1036, Found: 347.1028; IR (neat, cm-1): υ 2972, 1745, 1567, 1144, 670.



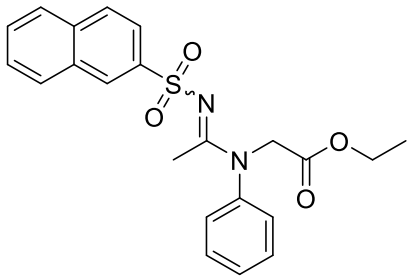
Ethyl 2-(1-(tosylimino)isoindolin-2-yl)acetate (5l). Petroleum ether/ ethylacetate = 2:1, light yellow liquid, 31.2 mg, 42% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90–8.88 (m, 1H), 7.90–7.88 (m, 2H), 7.60–7.56 (m, 1H), 7.54–7.50 (m, 1H), 7.46–7.45 (m, 1H), 7.27–7.25 (m, 2H), 4.66 (s, 2H), 4.38 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.8, 142.1, 141.9, 141.0, 132.2, 129.3, 129.1, 129.0, 128.4, 126.2, 122.3, 61.6, 53.6, 46.2, 21.4, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{20}N_2O_4S+Na^+$: 395.1036, Found: 395.1044; IR (neat, cm-1): υ 2957, 1747, 1562, 914, 684.



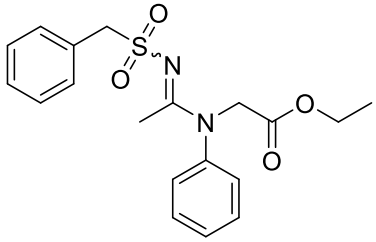
Ethyl 2-(3-(tosylimino)-2-azaspiro[4.5]decan-2-yl)acetate (5m). Petroleum ether/ ethylacetate = 3.5:1, white solid, 70.5 mg, 90% yield, *E/Z* = 4.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.74 (m, 2.39H), 7.31–7.23 (m, 2.42H), 4.17–4.12 (m, 4.88H), 4.03 (s, 0.44H), 3.30 (s, 2H), 3.24 (s, 0.45H), 2.89 (s, 2H), 2.39 (s, 3H), 2.29 (s, 0.66H), 1.54–1.40 (m, 12.26H), 1.29 (t, *J* = 7.1 Hz, 0.48H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 170.1, 168.5, 167.3, 141.9, 140.2, 128.9, 126.2, 61.4, 61.1, 60.6, 45.6, 43.7, 42.9, 38.5, 36.6, 36.3, 36.0, 25.4, 25.2, 22.6, 21.2, 14.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{28}N_2O_4S+H^+$: 393.1843, Found: 393.1842; IR (neat, cm-1): υ 2921, 1748, 1572, 1144, 670.



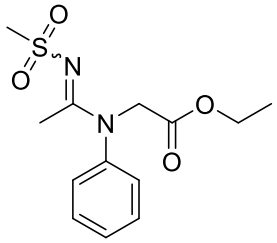
Ethyl *N*-phenyl-*N*-(1-((thiophen-2-ylsulfonyl)imino)ethyl)glycinate (5n). Petroleum ether/ ethylacetate = 4:1, colourless liquid, 50.7 mg, 69% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.62 (m, 1H), 7.52–7.51 (m, 1H), 7.46–7.40 (m, 3H), 7.34–7.29 (m, 2H), 7.05–7.02 (m, 1H), 4.44 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.6, 144.7, 142.0, 130.4, 130.0, 130.0, 129.0, 127.4, 126.6, 61.4, 53.9, 19.1, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{18}N_2O_4S_2+Na^+$: 389.0600, Found: 389.0609; IR (neat, cm-1): υ 2982, 1745, 1540, 1145, 786.



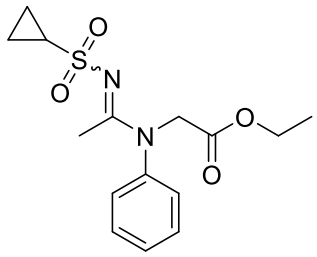
Ethyl *N*-(1-((naphthalen-2-ylsulfonyl)imino)ethyl)-*N*-phenylglycinate (5o). Petroleum ether/ ethylacetate = 4:1, white solid, 52.3 mg, 64% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.97–7.88 (m, 4H), 7.6 –7.56 (m, 2H), 7.46–7.39 (m, 3H), 7.33–7.31 (m, 2H), 4.38 (s, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.4, 142.2, 140.2, 134.4, 132.0, 130.0, 129.1, 129.0, 128.6, 128.1, 127.7, 127.5, 127.0, 126.6, 122.6, 61.3, 54.0, 19.2, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{22}H_{22}N_2O_4S+H^+$: 411.1373, Found: 411.1361; IR (neat, cm-1): υ 2981, 1742, 1537, 1073, 677.



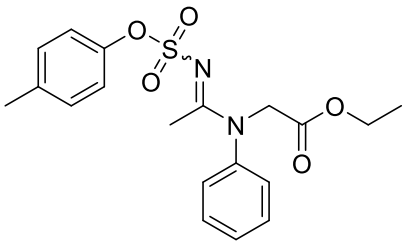
Ethyl *N*-(1-((benzylsulfonyl)imino)ethyl)-*N*-phenylglycinate (5p). Petroleum ether/ ethylacetate = 4:1, colourless liquid, 50.0 mg, 67% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.47 (m, 2H), 7.45–7.35 (m, 6H), 7.27–7.25 (m, 2H), 4.34 (s, 2H), 4.28 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.11 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.9, 142.1, 131.0, 130.3, 130.0, 128.9, 128.3, 128.1, 127.5, 61.4, 60.8, 53.6, 19.1, 14.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{22}N_2O_4S+H^+$: 397.1192, Found: 397.1200; IR (neat, cm-1): υ 2978, 1738, 1544, 1100, 696.



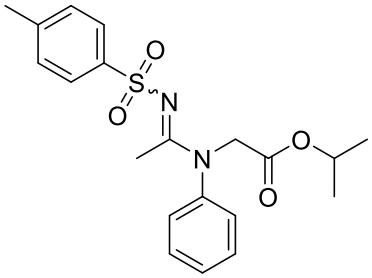
Ethyl *N*-(1-((methylsulfonyl)imino)ethyl)-*N*-phenylglycinate (5q). Petroleum ether/ ethylacetate = 3:1, white solid, 37.4 mg, 63% yield, *E/Z* = 3.3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.25–7.23 (m, 2H), 4.24–4.18 (m, 6H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 167.6, 166.6, 142.1, 140.3, 129.0, 126.2, 62.1, 61.3, 51.6, 51.2, 21.3, 17.4, 14.0, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{18}N_2O_4S+Na^+$: 321.0879, Found: 321.0890; IR (neat, cm-1): υ 3287, 1736, 1550, 1104, 801.



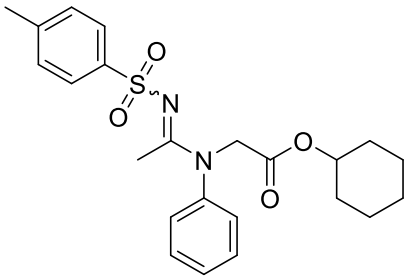
Ethyl *N*-(1-((cyclopropylsulfonyl)imino)ethyl)-*N*-phenylglycinate (5r). Petroleum ether/ ethylacetate = 3.5:1, colourless liquid, 44.3 mg, 68% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 3H), 7.34–7.32 (m, 2H), 4.40 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.60–2.54 (m, 1H), 2.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20–1.16 (m, 2H), 0.98–0.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 165.9, 142.3, 130.0, 128.8, 127.5, 61.3, 53.8, 32.3, 19.3, 14.1, 5.3, 5.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{20}N_2O_4S+H^+$: 325.1217, Found: 325.1228; IR (neat, cm-1): υ 2983, 1743, 1546, 1132, 699.



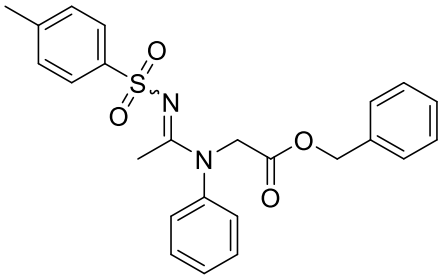
Ethyl *N*-phenyl-*N*-(1-(((p-tolyloxy)sulfonyl)imino)ethyl)glycinate (5s). Petroleum ether/ ethylacetate = 7:1, colourless liquid, 52.5 mg, 67% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.40 (m, 3H), 7.33–7.31 (m, 1H), 7.25–7.22 (m, 2H), 7.20–7.16 (m, 3H), 4.41 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.27 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.5, 148.7, 142.0, 136.1, 130.2, 129.8, 129.2, 127.3, 121.9, 61.7, 53.8, 20.8, 19.0, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{22}N_2O_5S+Na^+$: 413.1142, Found: 413.1144; IR (neat, cm-1): υ 2985, 1744, 1501, 1147, 790.



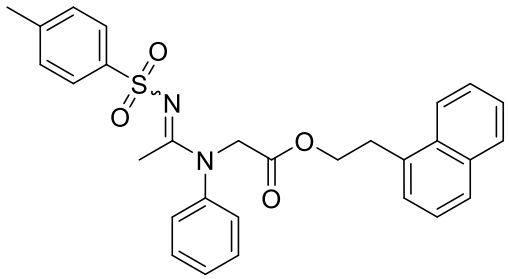
Isopropyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5t). Petroleum ether/ ethylacetate = 4.5:1, light yellow solid, 52.5 mg, 68% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.46–7.39 (m, 3H), 7.33–7.31 (m, 2H), 7.27–7.25 (m, 2H), 4.97–4.89 (m, 1H), 4.35 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.2, 142.2, 142.0, 140.4, 129.9, 128.9, 128.8, 127.4, 126.2, 69.1, 54.0, 21.5, 21.3, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{24}N_2O_4S+H^+$: 389.1530, Found: 389.1544; IR (neat, cm-1): υ 2979, 1745, 1540, 1082, 683.



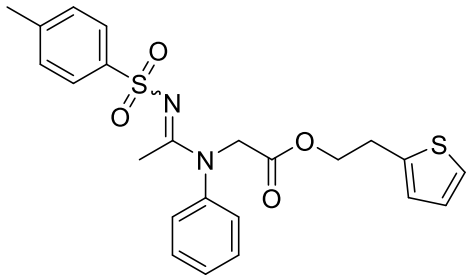
Cyclohexyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5u). Petroleum ether/ ethylacetate = 4.5:1, yellow liquid, 49.4 mg, 58% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.46–7.37 (m, 3H), 7.33–7.31 (m, 2H), 7.27–7.25 (m, 2H), 4.69–4.65 (m, 1H), 4.35 (s, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 1.69–1.65 (m, 4H), 1.53–1.51 (m, 1H), 1.31–1.26 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.1, 142.3, 142.0, 140.4, 129.9, 128.9, 128.8, 127.4, 126.2, 74.0, 54.0, 31.2, 25.0, 23.5, 21.3, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{28}N_2O_4S+Na^+$: 451.1662, Found: 461.1669; IR (neat, cm-1): υ 2937, 1739, 1544, 1089, 684.



Benzyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5v). Petroleum ether/ ethylacetate = 4.5:1, yellow liquid, 50.1 mg, 57% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.43–7.37 (m, 2H), 7.34–7.32 (m, 4H), 7.29–7.27 (m, 2H), 7.25–7.23 (m, 2H), 7.21–7.19 (m, 2H), 5.01 (s, 2H), 4.42 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 166.3, 142.1, 140.3, 134.9, 130.0, 129.0, 128.9, 128.4, 128.3, 128.0, 127.4, 126.2, 67.0, 53.8, 21.3, 19.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{24}H_{24}N_2O_4S+H^+$: 437.1530, Found: 437.1520; IR (neat, cm-1): υ 3062, 1749, 1548, 1088, 700.

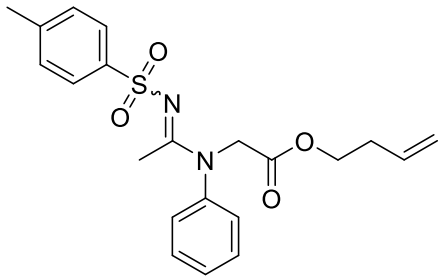


2-(Naphthalen-1-yl)ethyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5w). Petroleum ether/ ethylacetate = 4:1, colourless liquid, 74.9 mg, 75% yield, *E/Z* = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.04 (m, 0.25H), 7.99–7.97 (m, 1H), 7.87–7.79 (m, 4H), 7.76–7.74 (m, 1H), 7.54–7.45 (m, 2.57H), 7.40–7.32 (m, 6.51H), 7.2– 7.26 (m, 1H), 7.24–7.14 (m, 4H), 5.00 (s, 0.5H), 4.48 (*J* = 7.2 Hz, 0.52H), 4.36 *J* = 13.6, 6.1 Hz4.31 (m, 4H), 3.42 (t, *J* = 7.4 Hz, 0.51H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 0.75H), 2.32 (s, 3H), 2.24 (s, 3H), 1.90 (s, 0.75H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 169.1, 167.9, 166.3, 142.2, 142.2, 140.4, 133.8, 133.2, 131.9, 130.0, 129.7, 129.6, 129.1, 128.9, 128.8, 128.7, 128.2, 127.8, 127.4, 127.0, 127.0, 126.4, 126.3, 126.21, 126.16, 125.65, 125.60, 125.5, 125.4, 123.45, 123.40, 65.1, 54.0, 51.2, 32.0, 31.8, 22.1, 21.4, 21.3, 19.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{29}H_{28}N_2O_4S+Na^+$: 523.1662, Found: 523.1649; IR (neat, cm-1): υ 2924, 1742, 1539, 1086, 776.

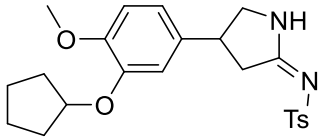


2-(Thiophen-2-yl)ethyl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5x). Petroleum ether/ ethylacetate = 4.5:1, light yellow liquid, 58.6 mg, 64% yield, *E/Z* = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.43–7.32 (m, 4H), 7.28–7.25 (m, 3H), 7.23–7.20 (m, 3H), 7.15–7.13 (m, 3H), 6.93–6.91 (m, 1.5H), 6.84–6.70 (m, 1.5H), 4.37–4.34 (m, 4H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.16 (t, *J* = 6.8 Hz, 1H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3.64H), 1.91 (s, 1.51H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 168.9, 167.6, 166.2, 143.1, 142.1, 142.1, 140.3, 139.5, 139.3, 130.0, 129.6,

129.0, 128.8, 128.1, 127.7, 127.4, 126.8, 126.8, 126.2, 125.49, 125.48, 123.93, 123.90, 65.18, 65.16, 53.9, 51.1, 29.0, 28.9, 22.0, 21.3, 19.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{24}N_2O_4S_2$+Na^+: 479.1070, Found: 479.1072; IR (neat, cm-1): υ 2955, 1743, 1540, 1147, 698.

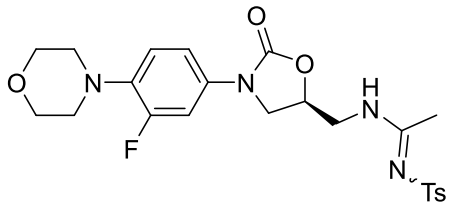


Dut-3-en-1-yl *N*-phenyl-*N*-(1-(tosylimino)ethyl)glycinate (5y). Petroleum ether/ ethylacetate = 4.5:1, yellow liquid, 39.0 mg, 49% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.46–7.38 (m, 3H), 7.32–7.26 (m, 4H), 5.74–7.64 (m, 1H), 5.08–5.05 (m, 2H), 4.37 (s, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 2.26 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.2, 142.2, 142.1, 140.4, 133.5, 130.0, 129.0, 128.9, 127.5, 126.2, 117.3, 64.2, 53.8, 32.7, 21.4, 19.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{24}N_2O_4S$+Na^+: 423.1349, Found: 423.1355; IR (neat, cm-1): υ 2919, 1747, 1544, 1149, 1089, 702.

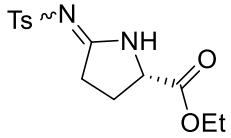


***N*-(4-(3-(cyclopentyloxy)-4-methoxyphenyl)pyrrolidin-2-ylidene)-4-methylbenzen esulfonamide (6a)**. Petroleum ether/ ethylacetate = 2.5:1, light yellow liquid, 52.5 mg, 61% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.83–7.81 (m, 2H), 7.28–7.26 (m, 2H), 6.80–6.77 (m, 1H), 6.68–6.67 (m, 2H), 4.72–4.70 (m, 1H), 3.97–3.90 (m, 1H), 3.81 (s, 3H), 3.57–3.50 (m, 2H), 3.13–3.08 (m, 1H), 2.86–2.79 (m, 1H), 2.40 (s, 3H), 1.91–1.79 (m, 6H), 1.63–1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 149.2, 147.8, 142.7, 139.3, 133.0, 129.3, 126.4, 118.7, 113.5, 112.1, 80.4, 60.3, 56.0, 39.2, 32.7, 23.9, 21.4, 14.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{28}N_2O_4S$

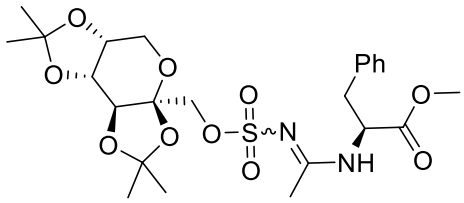
+H^+: 429.1843, Found: 429.1831; IR (neat, cm-1): υ 2954, 1599, 1256, 1137, 810, 666.



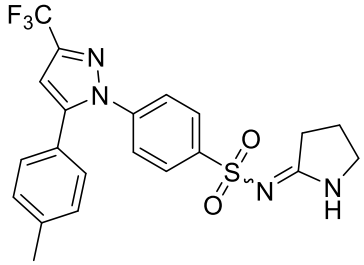
(*S*)-*N*-((3-(3-fluoro-4-morpholinophenyl)-2-oxooxazolidin-5-yl)methyl)-*N*'-tosylacetimidamide (6b). Petroleum ether/ ethylacetate = 1:3, white solid, 31.1 mg, 32% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = 454.8 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.33–7.29 (m, 2H), 7.26–7.24 (m, 2H), 7.00–6.98 (m, 1H), 6.92–6.88 (m, 1H), 4.812–8.809 (m, 1H), 3.99–3.97 (m, 1H), 3.88–3.86 (m, 4H), 3.77–3.64 (m, 3H), 3.05 (m, 4H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 154.5, 142.6, 140.0, 129.3, 126.4, 118.9, 114.1, 107.7, 107.5, 71.0, 66.8, 60.4, 51.0, 47.9, 44.1, 21.4, 20.6, 14.1. HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{27}FN_4O_5S$+H^+: 491.1759, Found: 491.1747; IR (neat, cm-1): υ 3288, 1749, 1514, 1085, 661.



Ethyl (*S*)-5-(tosylimino)pyrrolidine-2-carboxylate (6c). Petroleum ether/ ethylacetate = 1.5:1, colourless liquid, 38.7 mg, 63% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = 35.4 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.83–7.80 (m, 2H), 7.28–7.26 (m, 2H), 4.47–4.44 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.76–2.73 (m, 2H), 2.45–2.36 (m, 4H), 2.18–2.09 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 170.7, 142.8, 139.0, 129.2, 126.4, 61.9, 59.3, 31.3, 29.5, 21.4, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{18}N_2O_4S$+Na^+: 333.0879, Found: 333.0872; IR (neat, cm-1): υ 3365, 2922, 1737, 1594, 1139, 810.

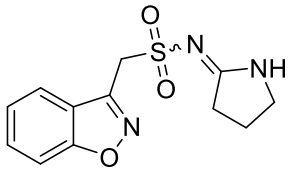


Methyl (1-(((((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)sulfonyl)imino)ethyl)-*L*-phenylalaninate (6d). Petroleum ether/ ethylacetate = 2:1, colourless liquid, 41.5 mg, 48% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = 411.1 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 3H), 7.06–7.05 (m, 2H), 6.21 (d, *J* = 6.0 Hz, 1H), 4.94–4.92 (m, 1H), 4.64–4.61 (dd, *J* = 7.8, 2.6 Hz, 1H), 4.45 (d, *J* = 2.6 Hz, 1H), 4.25 (s, 1H), 4.25–4.22 (m, 2H), 3.92 (dd, *J* = 12.9, 1.7 Hz, 1H), 3.76 (s, 3H), 3.75–3.73 (m, 1H), 3.27 (dd, *J* = 13.9, 5.8 Hz, 1H), 3.13 (dd, *J* = 13.9, 4.9 Hz, 1H), 2.41 (s, 3H), 1.54 (s, 3H), 1.46 (s, 3H), 1.44 (s, 4H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 166.5, 134.9, 129.1, 128.7, 127.4, 109.0, 101.0, 70.7, 70.0, 69.9, 69.4, 61.3, 55.0, 52.6, 36.5, 30.9, 26.5, 25.8, 25.3, 24.0, 20.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{24}H_{34}N_2O_{10}S+Na^+$: 565.1826, Found: 565.1827; IR (neat, cm-1): υ 3325, 2989, 1744, 1548, 1154, 701.

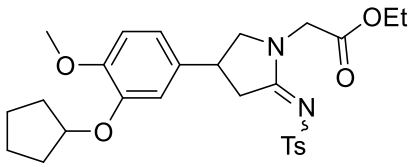


***N*-(pyrrolidin-2-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (6e)**. Petroleum ether/ ethylacetate = 1.2:1, white solid, 77.5 mg, 86% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.91–7.89 (m, 2H), 7.44–7.42 (m, 2H), 7.17–7.15 (m, 2H), 7.12–7.10 (m, 2H), 6.73 (s, 1H), 3.60 (m, 2H), 2.72 (m, 2H), 2.37 (s, 3H), 2.10–2.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 145.0, 144.3, 143.9, 143.5, 143.1, 141.9, 141.8, 139.5, 129.6, 128.6, 127.4, 125.6, 125.1, 125.0, 122.3, 119.6, 117.0, 106.0, 46.4, 32.8, 21.2, 19.9. ^{19}F NMR (376 MHz,

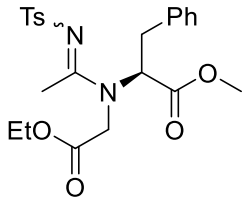
$CDCl_3$) δ -62.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{19}F_3N_4O_2S+Na^+$: 471.1073, Found: 471.1065; IR (neat, cm-1): υ 2969, 1600, 1235, 1133, 627.



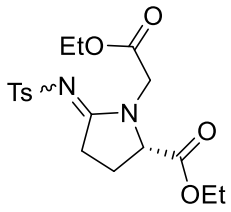
1-(Benzo[*d*]isoxazol-3-yl)-*N*-(pyrrolidin-2-ylidene)methanesulfonamide (6f). Petroleum ether/ ethylacetate = 1:1, white solid, 39.3 mg, 70% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, DMSO) δ 8.97 (s, 1H), 8.01–7.88 (m, 1H), 7.77–7.74 (m, 1H), 7.68–7.64 (m, 1H), 7.44–7.40 (m, 1H), 4.81 (s, 2H), 3.31 (t, *J* = 8.0 Hz, 3H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.91–1.83 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 172.8, 162.6, 151.0, 130.4, 123.8, 123.6, 121.0, 109.5, 49.9, 44.8, 31.4, 20.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}N_3O_3S+Na^+$: 302.0570, Found: 302.0581; IR (neat, cm-1): υ 3119, 1632, 1605, 1294, 1139, 750.



Ethyl 2-(4-(3-(cyclopentyloxy)-4-methoxyphenyl)-2-(tosylimino)pyrrolidin-1-yl)acetate (7a). Petroleum ether/ ethylacetate = 2.5:1, light yellow liquid, 82.28 mg, 81% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2H), 7.27–7.23 (m, 2H), 6.79–6.77 (m, 1H), 6.73–6.69 (m, 2H), 4.75 (s, 1H), 4.30–4.26 (m, 1H), 4.21–4.13 (m, 3H), 3.87 (m, 1H), 3.81 (s, 3H), 3.63–3.54 (m, 3H), 3.09–3.06 (m, 1H), 2.39 (s, 3H), 1.89–1.82 (m, 6H), 1.60 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 167.2, 149.1, 147.8, 142.1, 139.9, 133.3, 129.0, 126.3, 118.6, 113.4, 112.0, 80.3, 61.5, 57.1, 55.9, 45.8, 38.3, 38.2, 32.6, 32.5, 23.8, 21.2, 13.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{27}H_{34}N_2O_6S$ $+H^+$: 515.2210, Found: 515.2218; IR (neat, cm-1): υ 2926, 1742, 1570, 1141, 670.

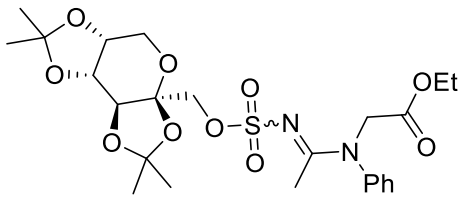


Methyl *N*-(2-ethoxy-2-oxoethyl)-*N*-(1-(tosylimino)ethyl)-*L*-phenylalaninate (7b). Petroleum ether/ ethylacetate = 2.5:1, light yellow liquid, 38.2 mg, 42% yield, *E/Z* = 1:1, $[\alpha]_D^{20}$ = -88.9 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.73–7.71 (m, 2H), 7.32–7.27 (m, 5H), 7.22–7.17 (m, 8H), 7.08–7.06 (m, 1H), 5.13 (t, *J* = 6.8 Hz, 1H), 4.68 (t, *J* = 7.2 Hz, 1H), 4.15–4.13 (m, 4H), 4.09–4.05 (m, 2H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.55 (s, 3H), 3.23–3.15 (m, 2H), 3.09–3.00 (m, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 2.39 (d, *J* = 1.2 Hz, 6H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.1, 167.6, 167.5, 166.4, 165.7, 142.2, 142.0, 140.3, 140.2, 136.3, 135.4, 129.0, 128.88, 128.86, 128.7, 128.5, 128.4, 127.4, 126.8, 126.2, 126.1, 61.9, 61.4, 61.1, 61.0, 52.7, 52.2, 46.9, 36.1, 35.0, 30.8, 21.4, 21.3, 18.0, 17.4, 13.9, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{28}N_2O_6S$+Na^+: 483.1560, Found: 483.1545; IR (neat, cm-1): υ 2922, 1738, 1542, 1145, 686.

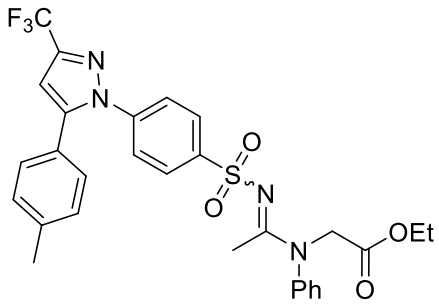


Ethyl (*S*)-1-(2-ethoxy-2-oxoethyl)-5-(tosylimino)pyrrolidine-2-carboxylate (7c). Petroleum ether/ ethylacetate = 2:1, colourless liquid, 66.4 mg, 84% yield, *E/Z* = 3.3:1, $[\alpha]_D^{20}$ = 30.4 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.26–7.24 (m, 2H), 4.70 (d, *J* = 17.8 Hz, 1H), 4.62 (d, *J* = 18.0 Hz, 0.3H), 4.48–4.41 (m, 1.3H), 4.22–4.07 (m, 5.32H), 3.84 (d, *J* = 17.8 Hz, 1H), 3.71 (d, *J* = 18.0 Hz, 0.3H), 3.21–3.02 (m, 2H), 2.56–2.43 (m, 1.9H), 2.42–2.40 (m, 3.56H), 2.25–2.11 (m, 1.32H), 1.27 (t, *J* = 7.1 Hz, 4.81H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

175.4, 171.3, 171.2, 170.0, 168.6, 167.4, 142.3, 139.6, 129.0, 126.3, 61.9, 61.6, 61.4, 61.2, 59.3, 45.0, 42.8, 29.0, 28.8, 24.3, 22.6, 21.3, 14.0, 13.94, 13.89, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{24}N_2O_6S+H^+$: 397.1428, Found: 397.1425; IR (neat, cm-1): υ 2982, 1737, 1566, 1145, 671.

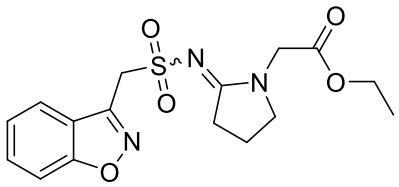


Ethyl *N*-phenyl-*N*-((*E*)-1-(((((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)sulfonyl)imino)ethyl)glycinate (7d). Petroleum ether/ ethylacetate = 3.5:1, colourless liquid, 61.5 mg, 57% yield, *E/Z* > 99:1, $[\alpha]_D^{20}$ = -51.7 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.41 (m, 3H), 7.35–7.33 (m, 2H), 4.63 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.58 (d, *J* = 16.8 Hz, 1H), 4.46 (d, *J* = 2.6 Hz, 1H), 4.37 (d, *J* = 16.9 Hz, 1H), 4.26–4.19 (m, 5H), 3.93 (dd, *J* = 13.0, 1.7 Hz, 1H), 3.75 (d, *J* = 12.9 Hz, 1H), 2.30 (s, 3H), 1.55 (s, 3H), 1.51 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz,, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 167.4, 142.1, 130.1, 129.1, 127.4, 109.0, 108.9, 101.0, 70.7, 70.0, 69.9, 69.4, 61.6, 61.2, 53.6, 26.4, 25.8, 25.2, 24.0, 18.9, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{24}H_{34}N_2O_{10}S+Na^+$: 565.1826, Found: 565.1822; IR (neat, cm-1): υ 2988, 1745, 1548, 1158, 701.



Ethyl *N*-phenyl-*N*-(1-(((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfon

yl)imino)ethyl)glycinate (7e). Petroleum ether/ ethylacetate = 5:1, colourless liquid, 60.7 mg, 52% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.48–7.40 (m, 5H), 7.33–7.31 (m, 2H), 7.19–7.17 (m, 2H), 7.13–7.11 (m, 2H), 6.74 (s, 1H), 4.38 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.8, 145.0, 143.9, 143.5, 142.8, 142.0, 141.6, 139.5, 130.1, 129.6, 129.1, 128.6, 127.4, 127.3, 125.7, 125.1, 125.0, 122.4, 119.7, 117.0, 105.9, 105.9, 61.5, 53.9, 21.2, 19.3, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{29}H_{27}F_3N_4O_4S+Na^+$: 607.1597, Found: 607.1583; IR (neat, cm-1): υ 2984, 1744, 1540, 1088, 787.

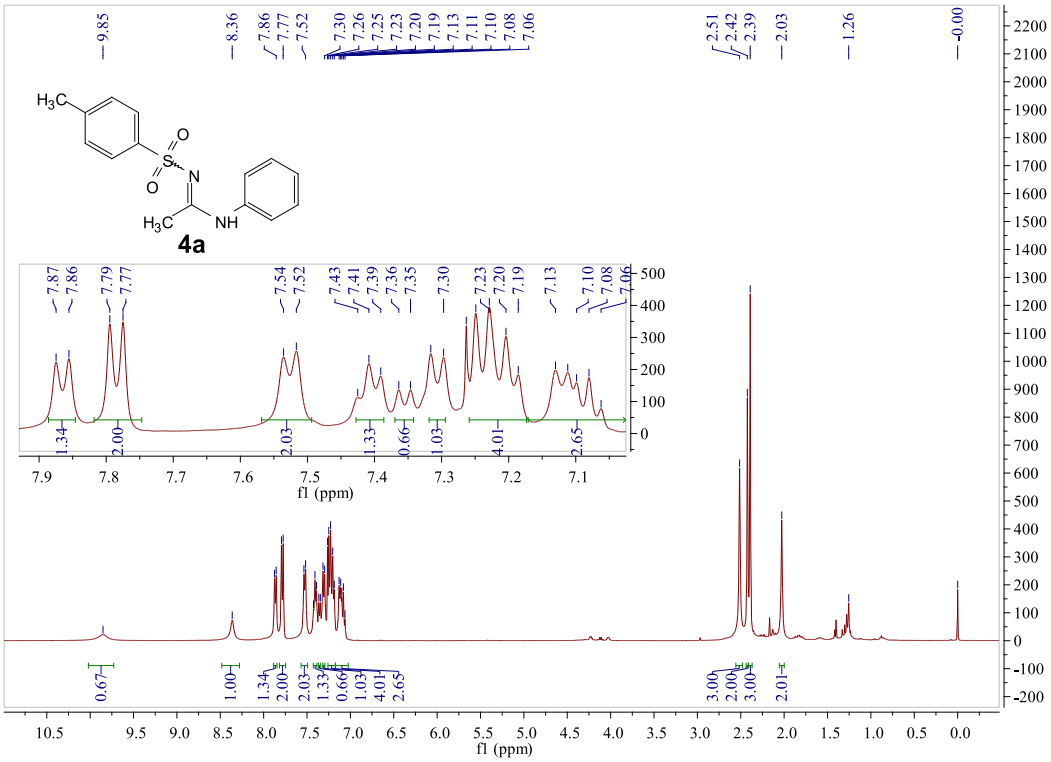


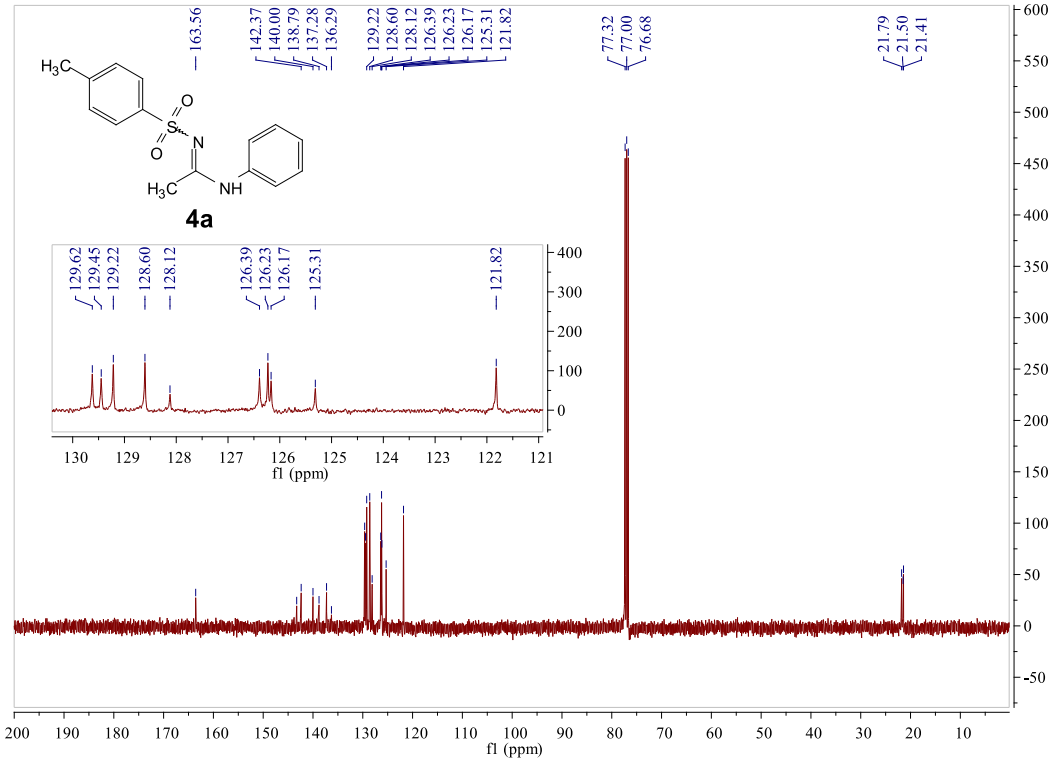
Ethyl 2-(2-(((benzo[*d*]isoxazol-3-ylmethyl)sulfonyl)imino)pyrrolidin-1-yl)acetate (7f). Petroleum ether/ ethylacetate = 1.5:1, light yellow solid, 23.3 mg, 32% yield, *E/Z* > 99:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 1H), 7.59–7.54 (m, 2H), 7.37–7.33 (m, 1H), 4.70 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 3.52–3.51 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.04–2.00 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 166.9, 163.4, 150.4, 130.0, 123.8, 122.8, 121.1, 109.6, 61.7, 51.1, 50.2, 45.9, 30.9, 19.3, 14.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{19}N_3O_5S$ +Na^+: 388.0938, Found: 388.0935; IR (neat, cm-1): υ 2923, 1733, 1572, 1295, 1125, 751.

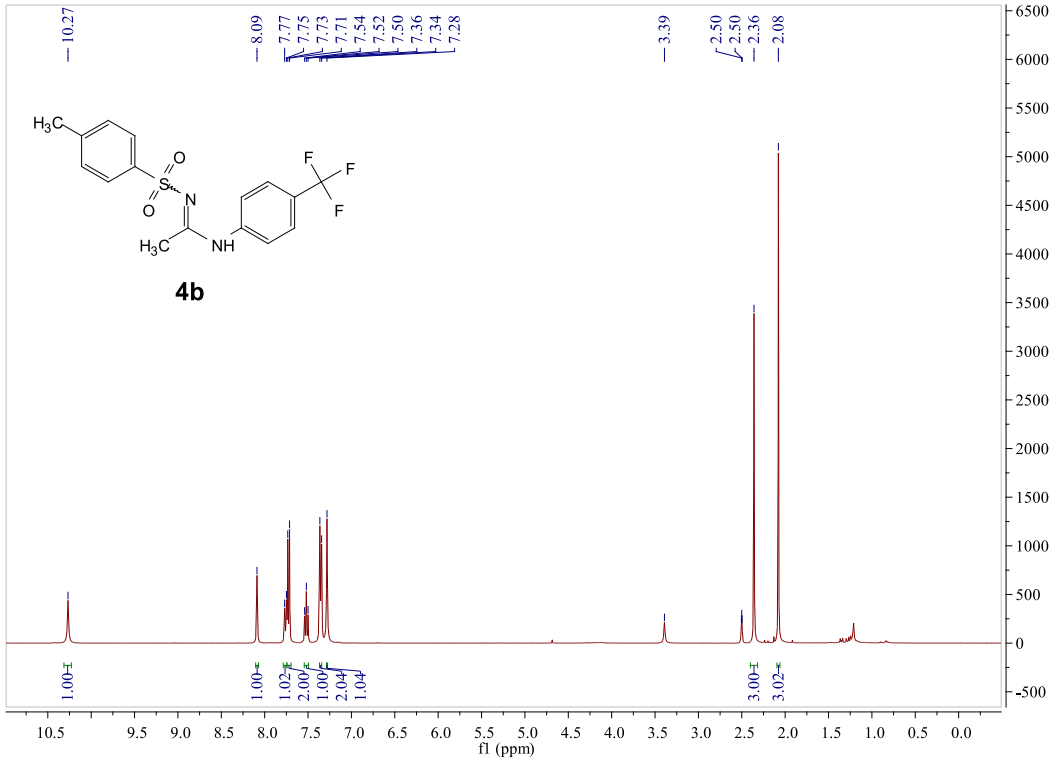
References

(1) Toma, T.; Shimokawa, J.; Fukuyama, T. *Org. Lett.* **2007**, *9*, 3195.

Spectroscopic data for products



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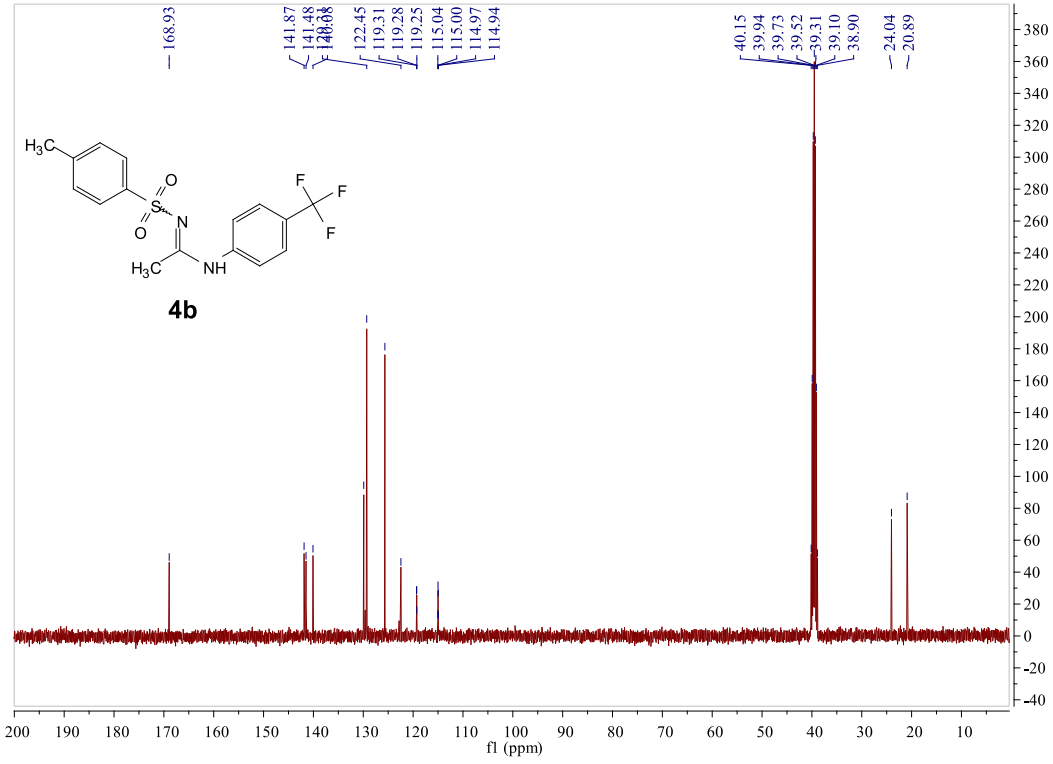
fl (ppm)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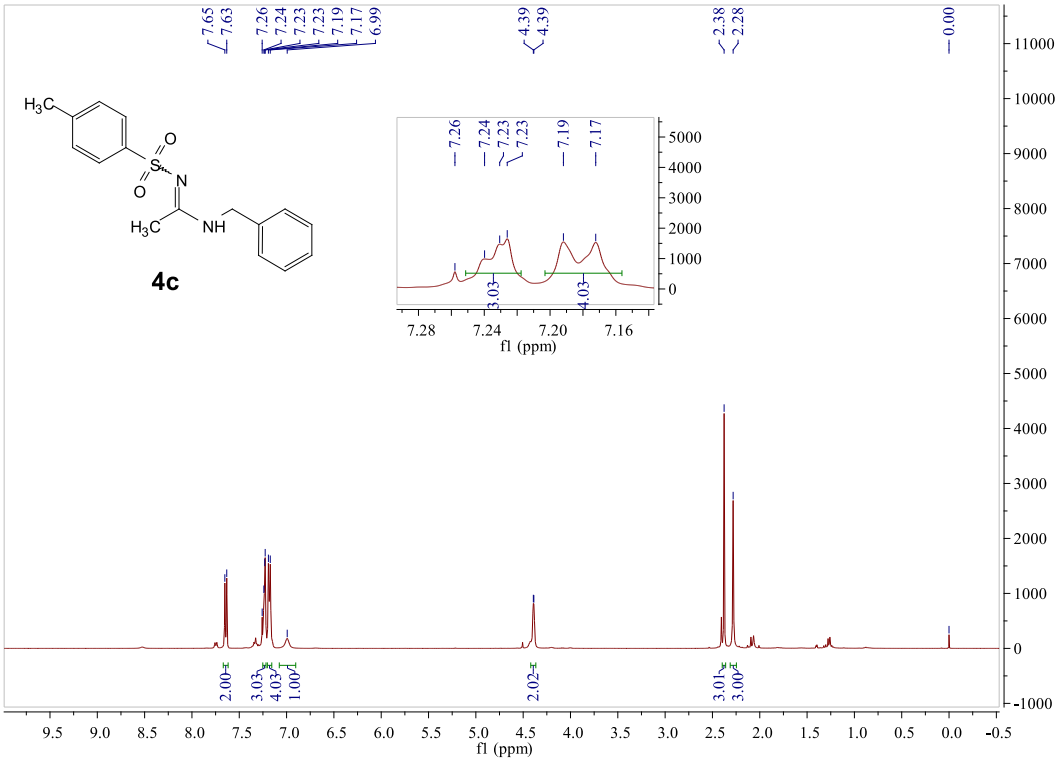
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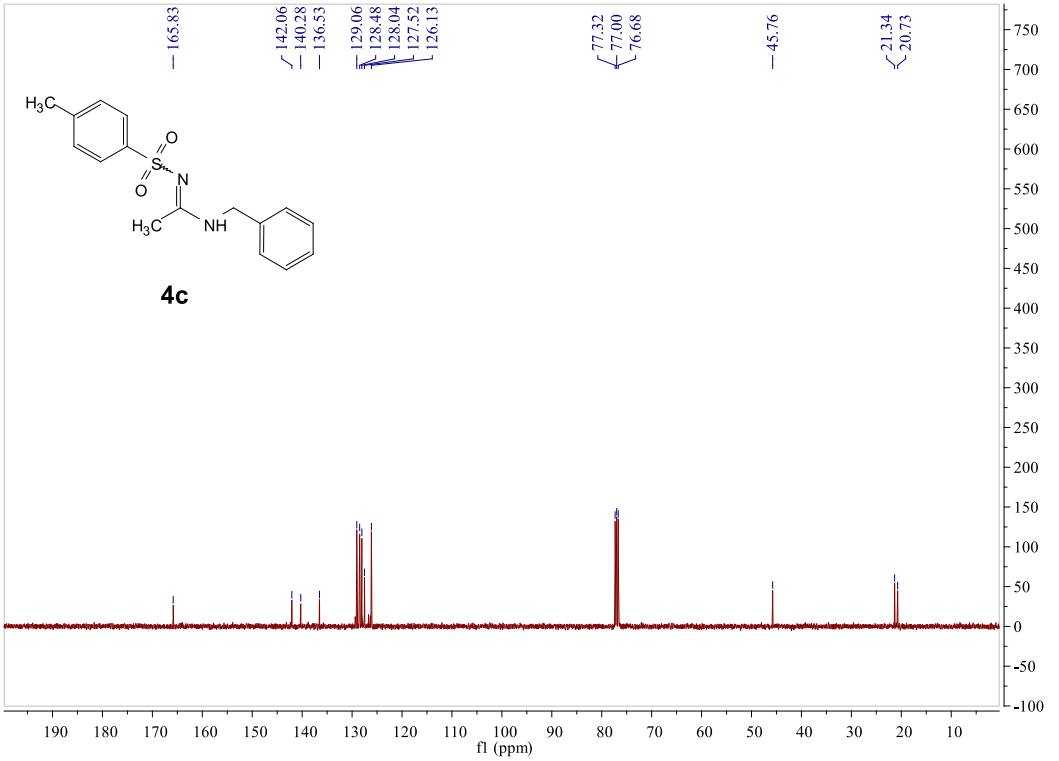
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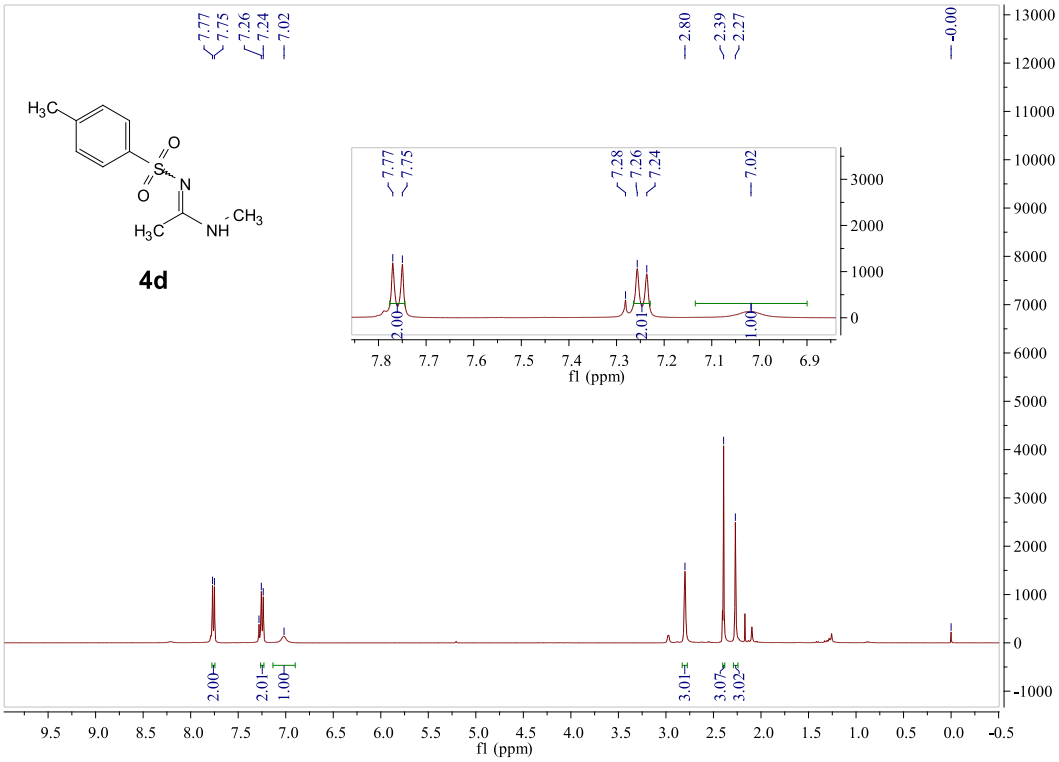
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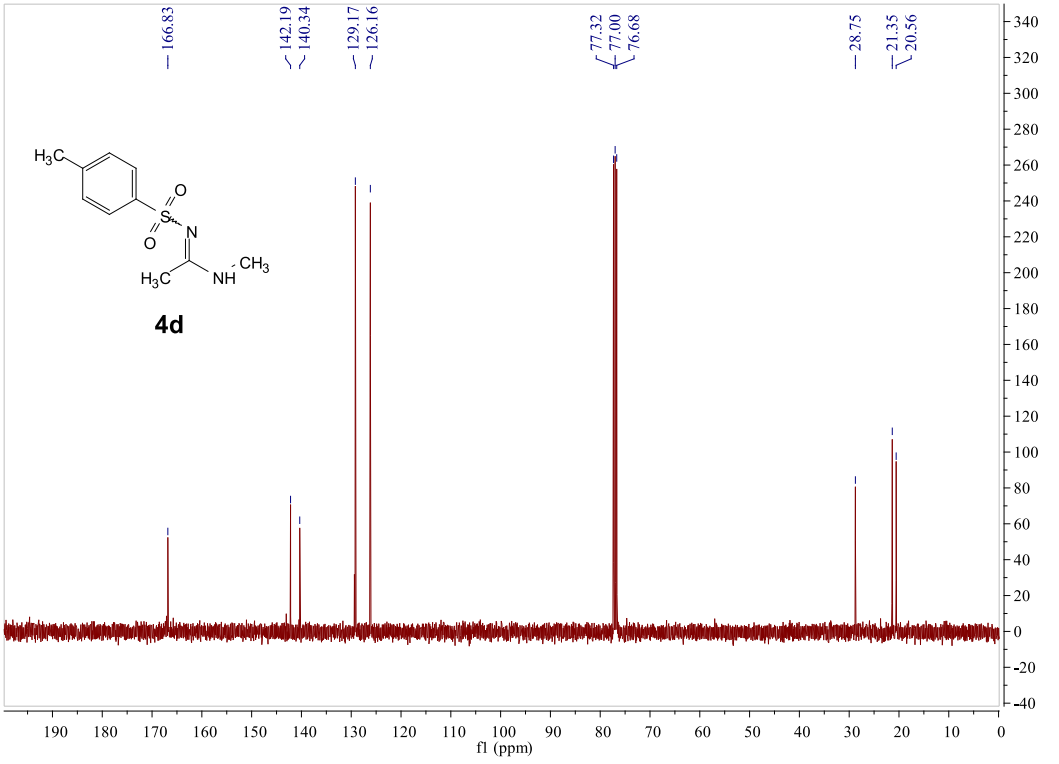
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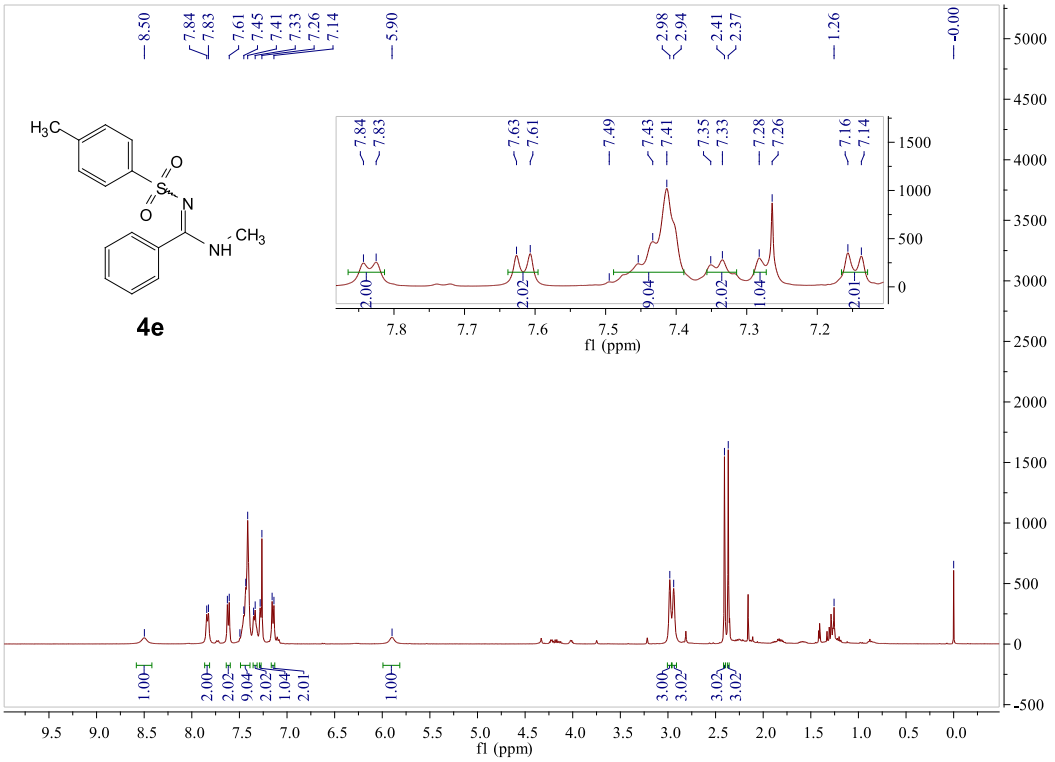
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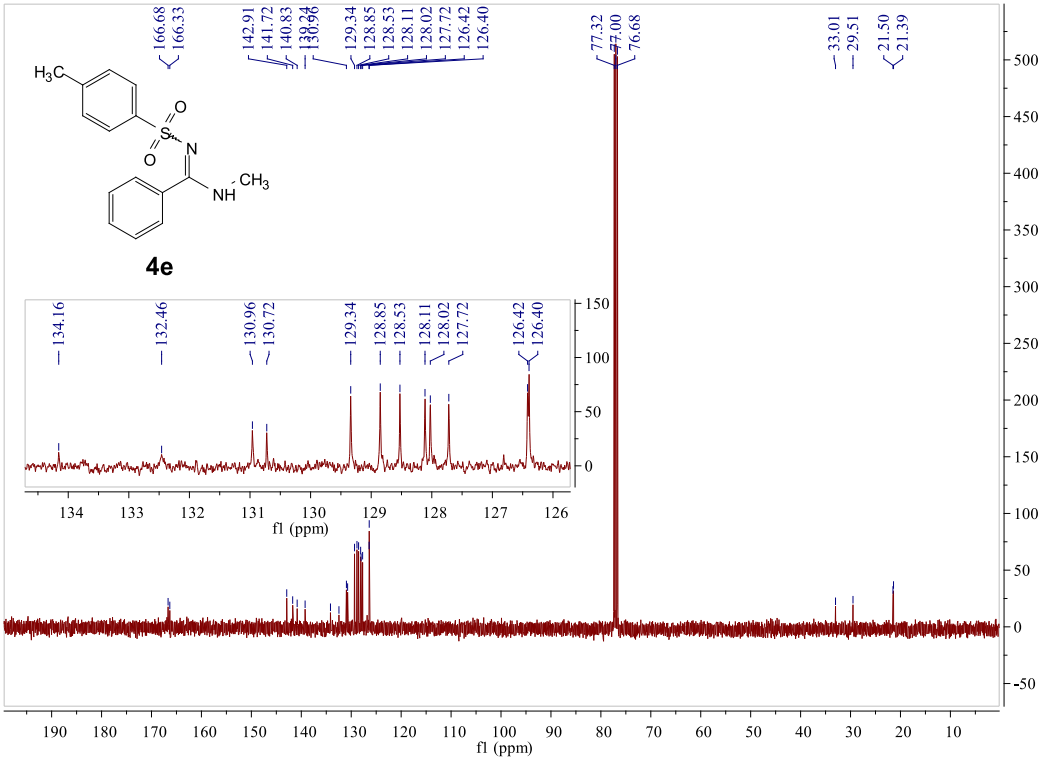
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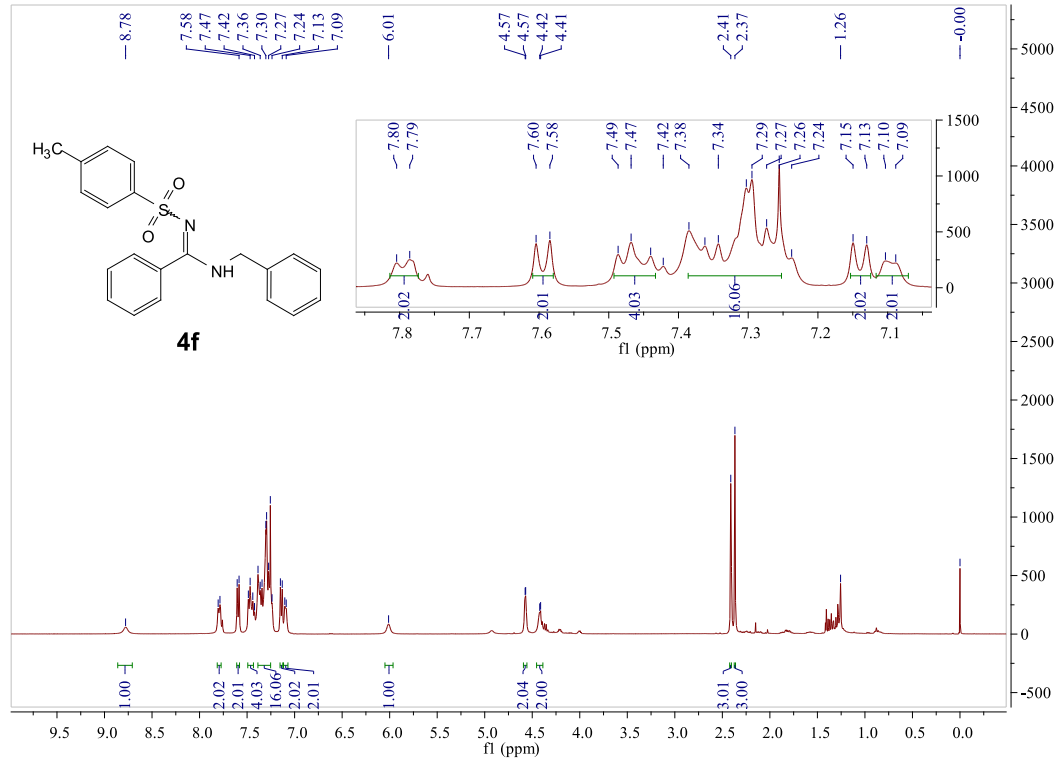
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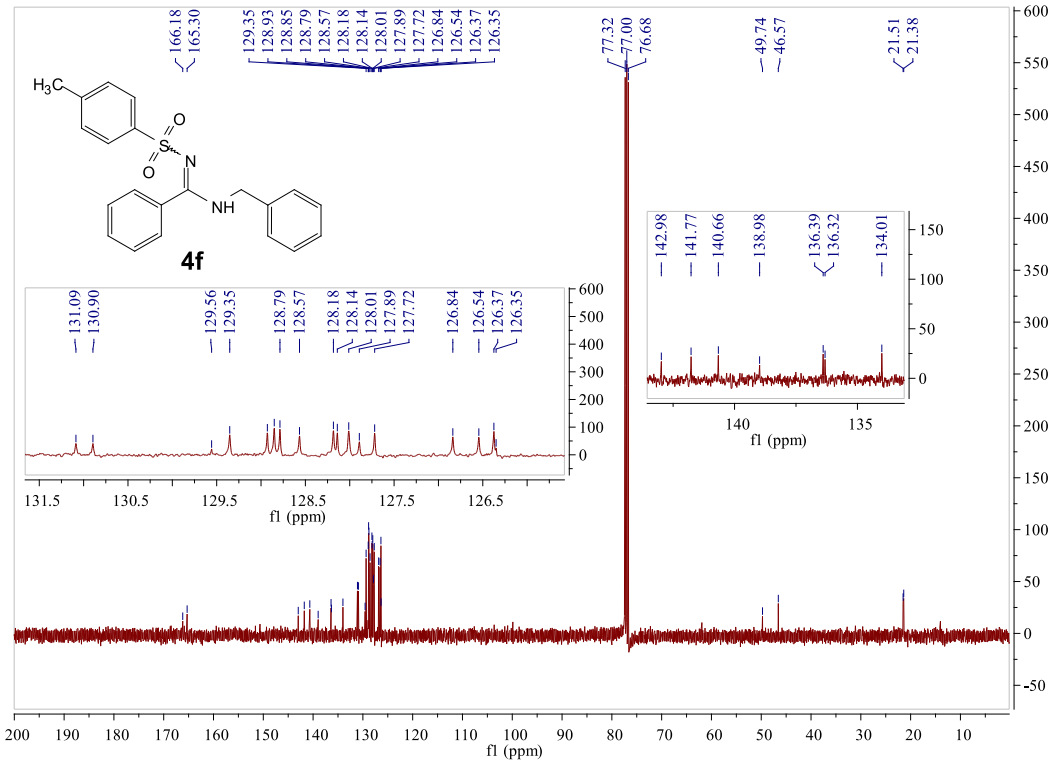
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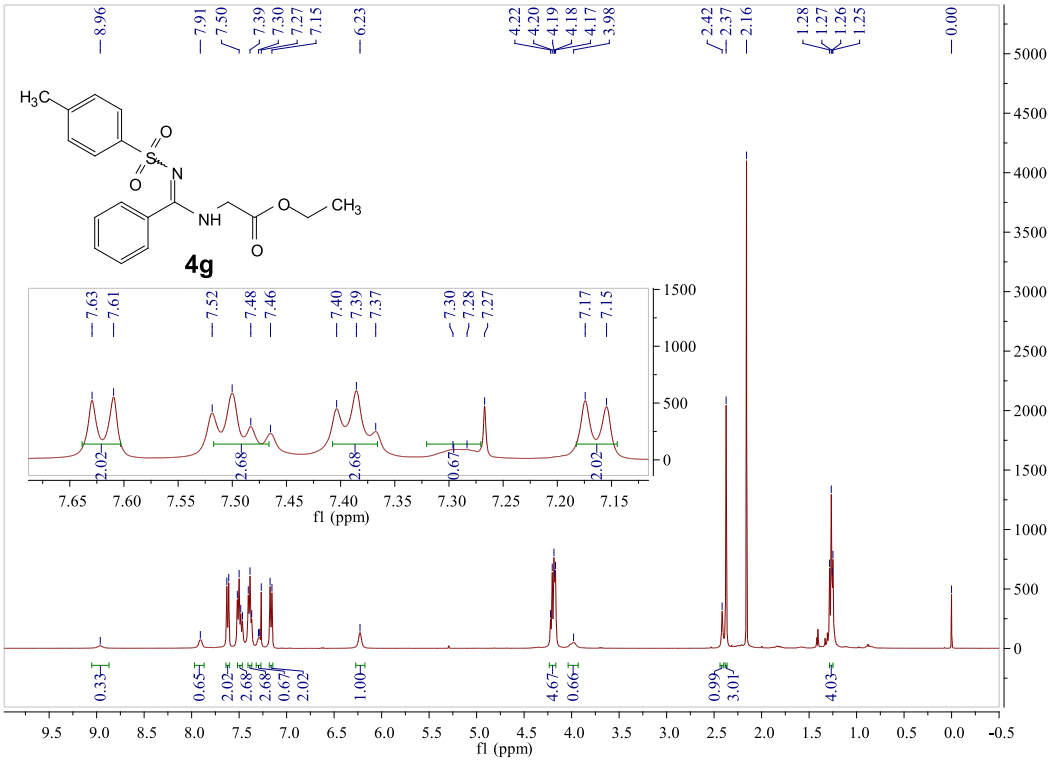
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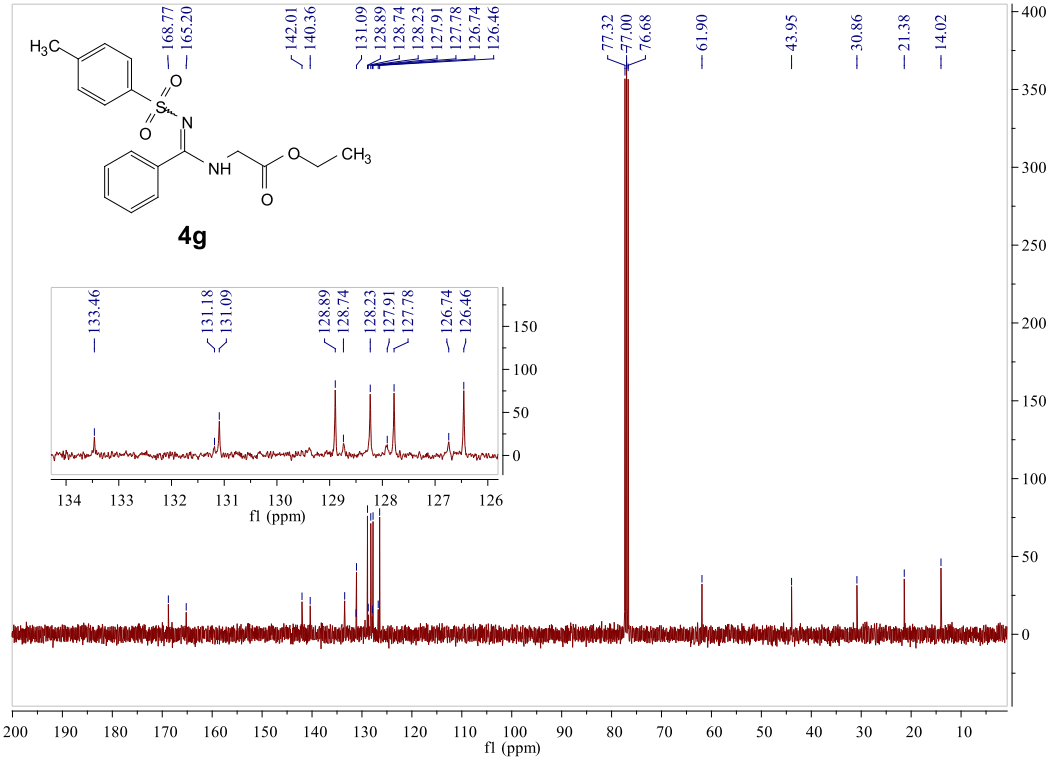
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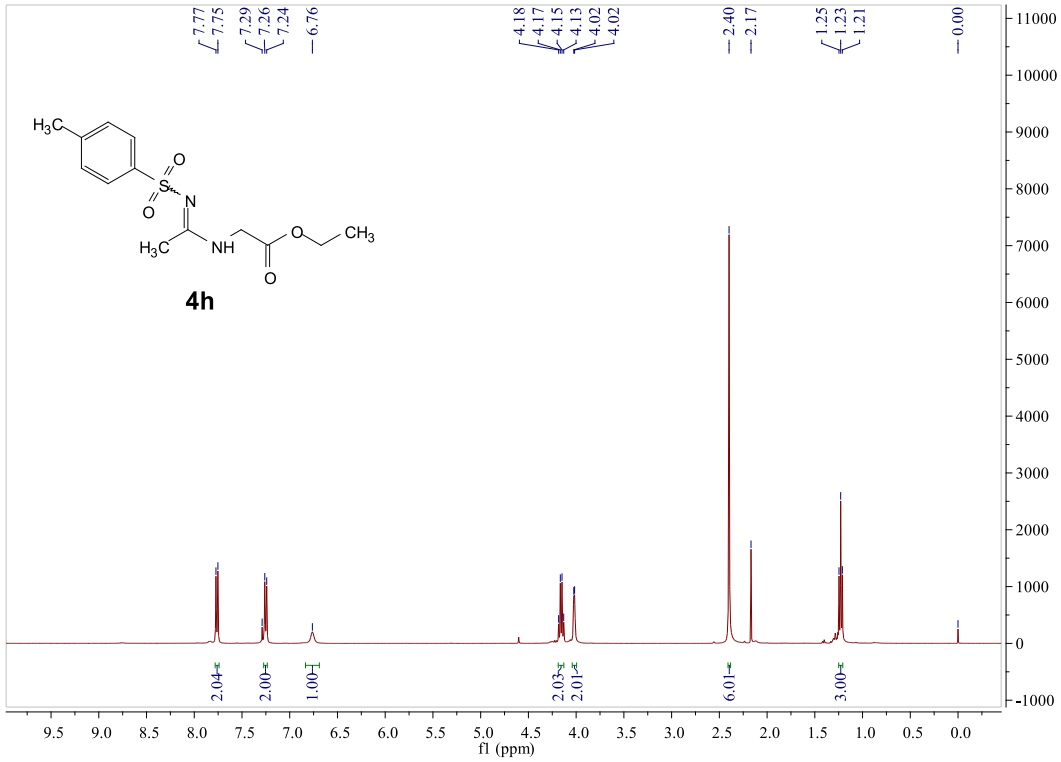
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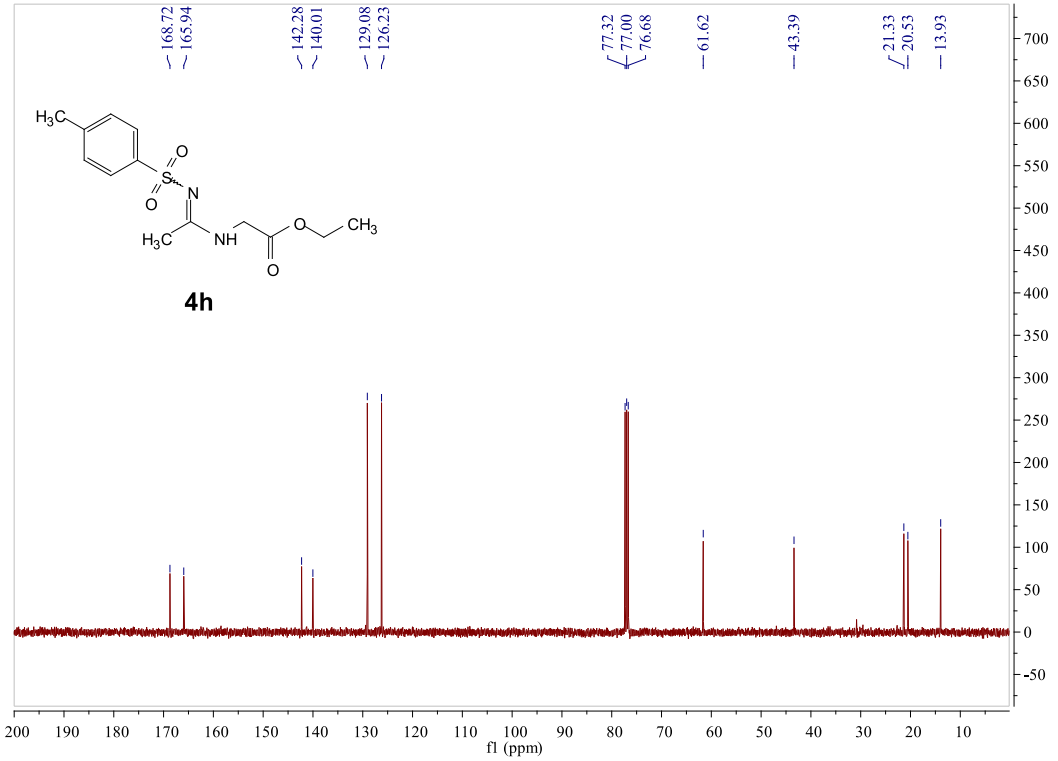
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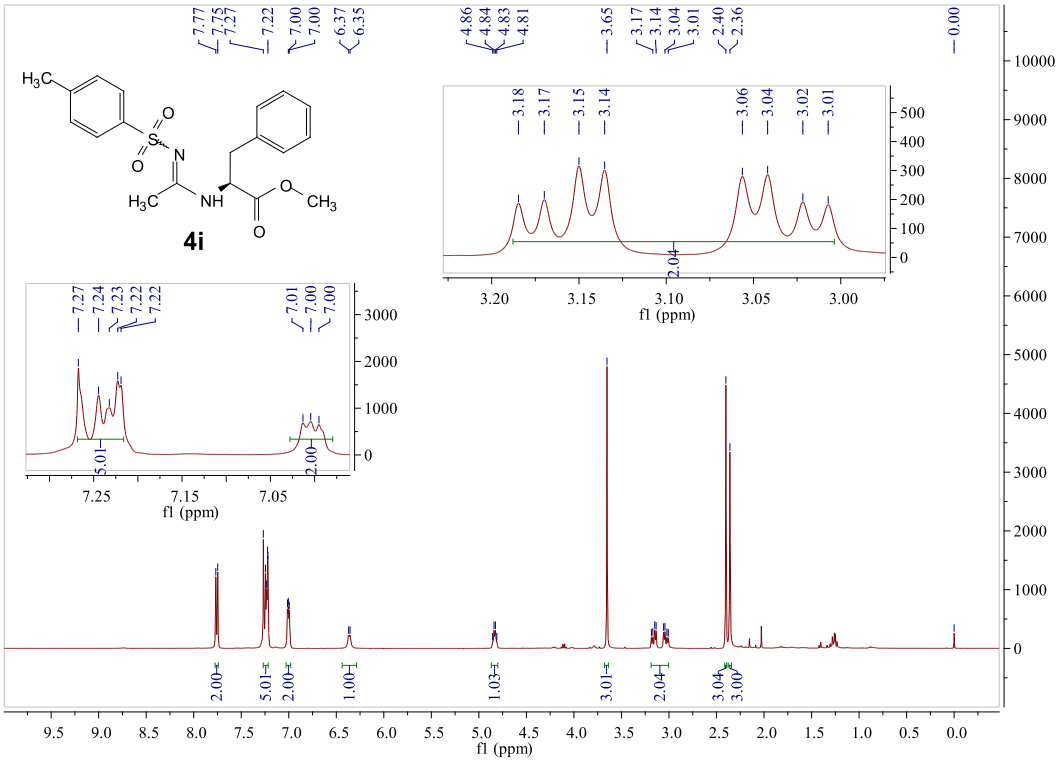
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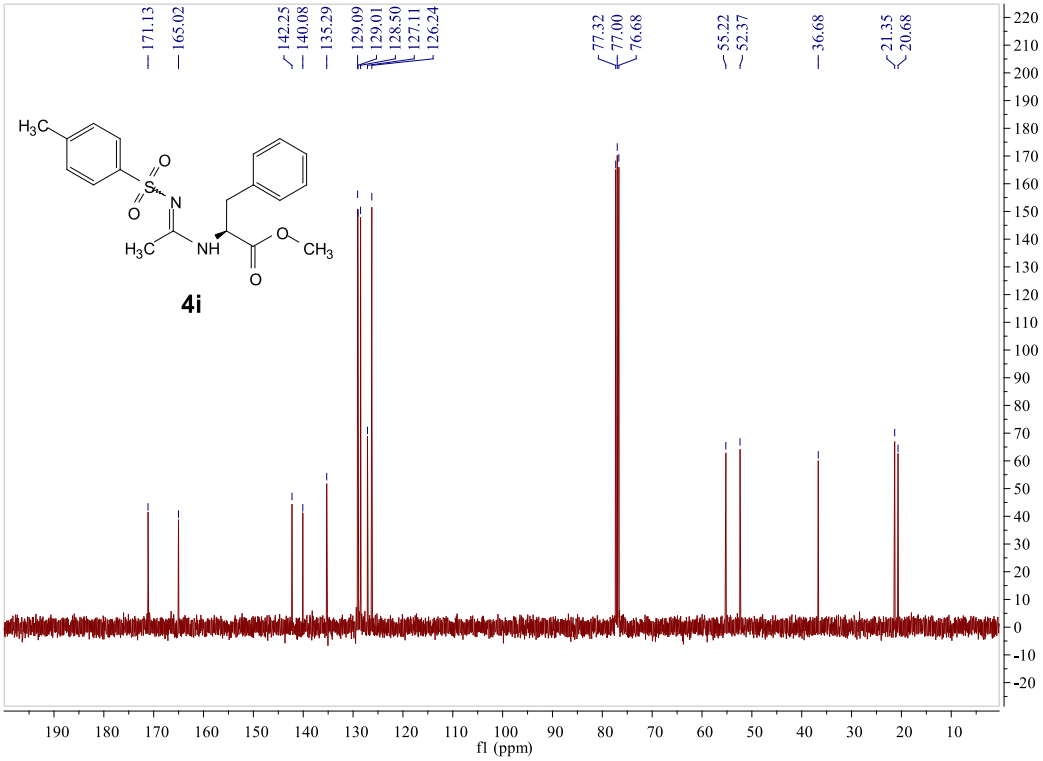
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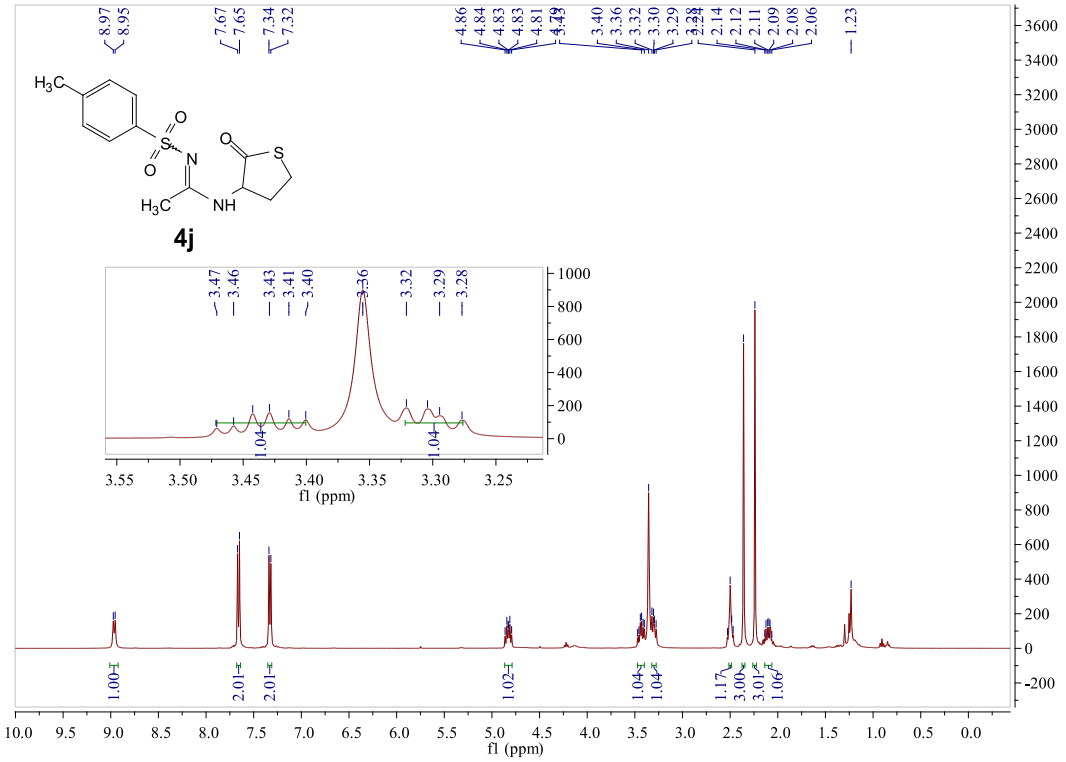
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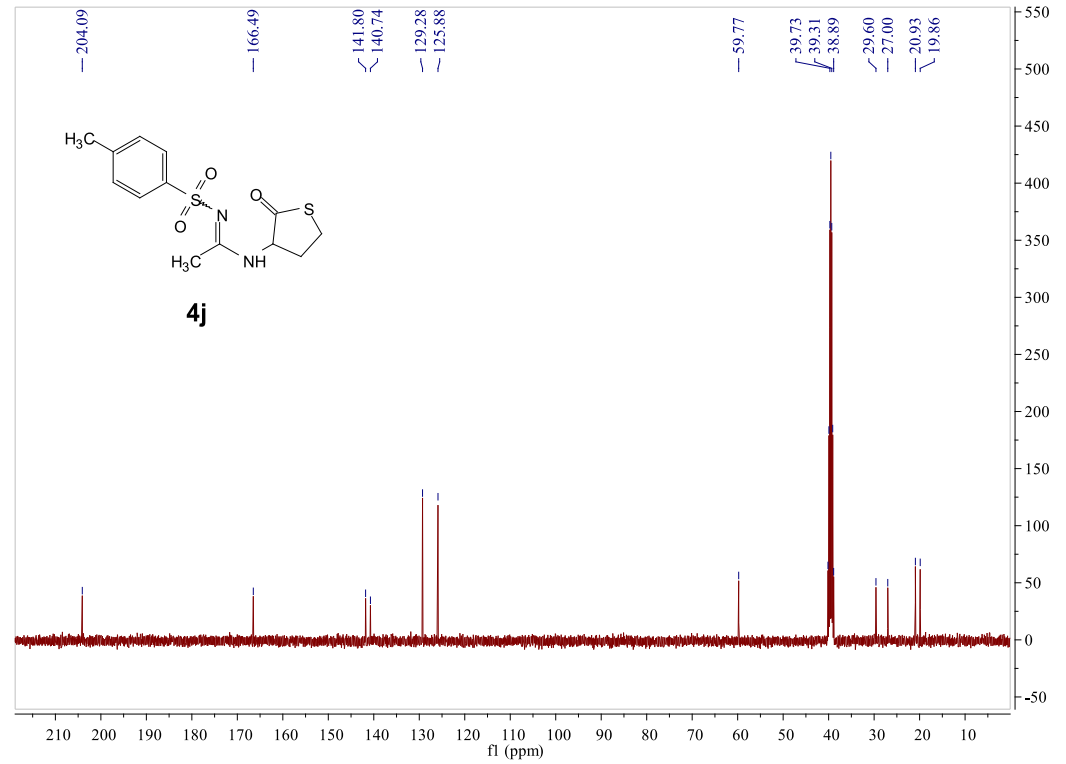
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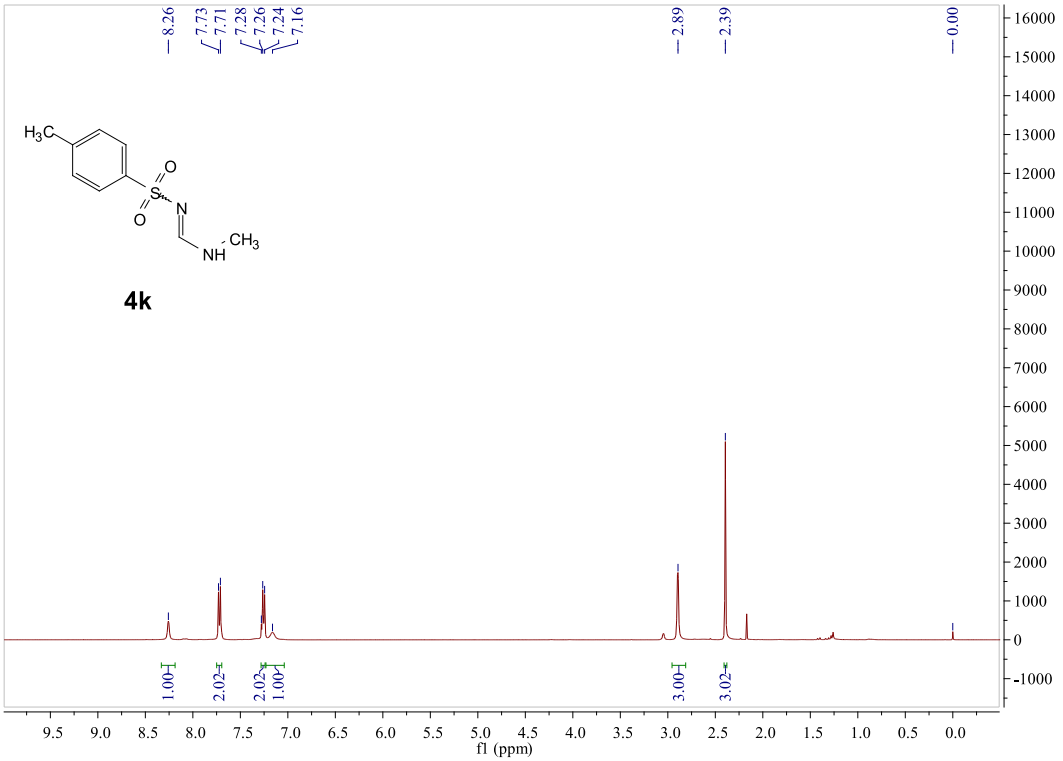
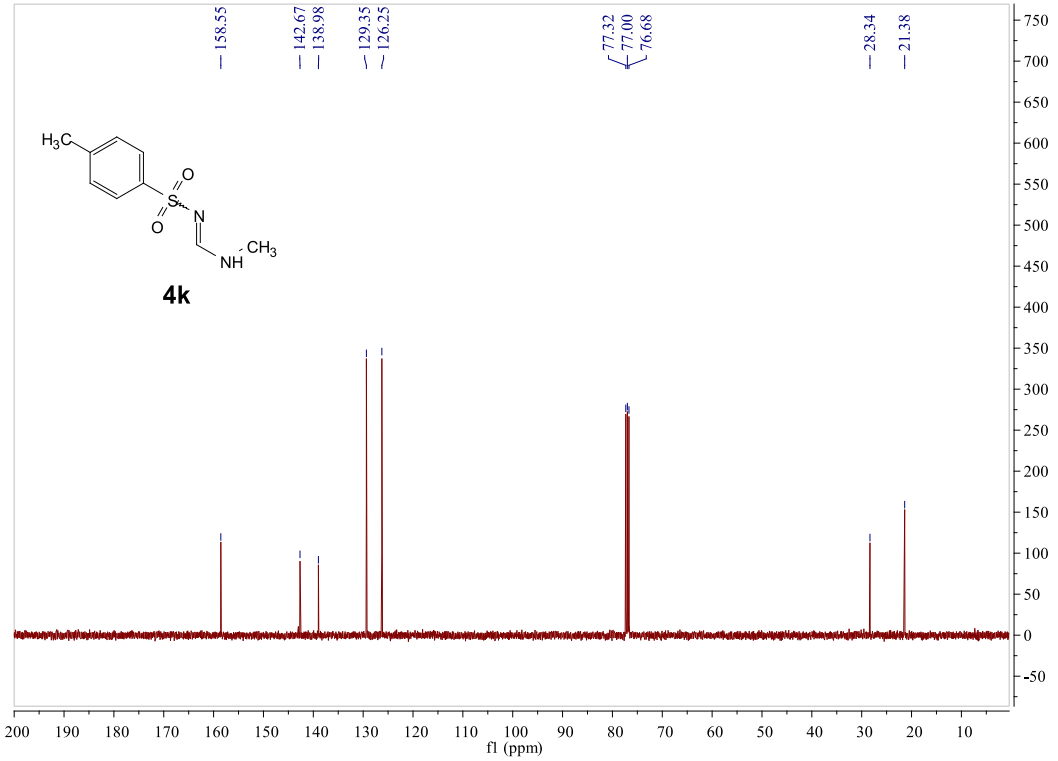
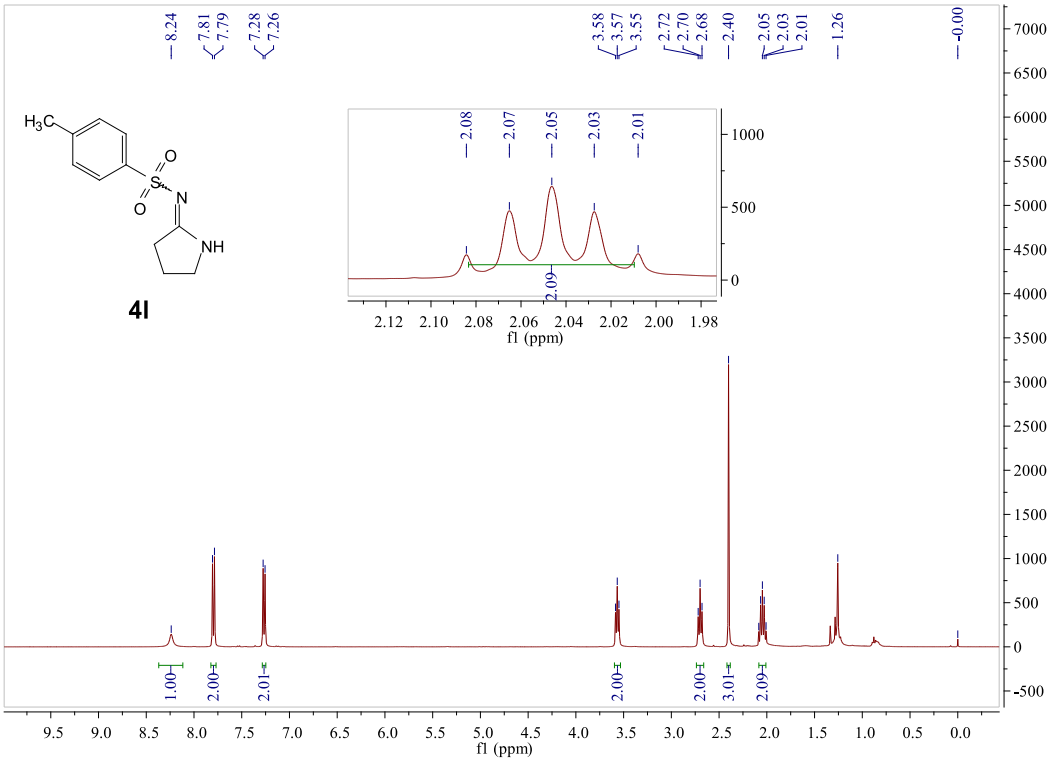
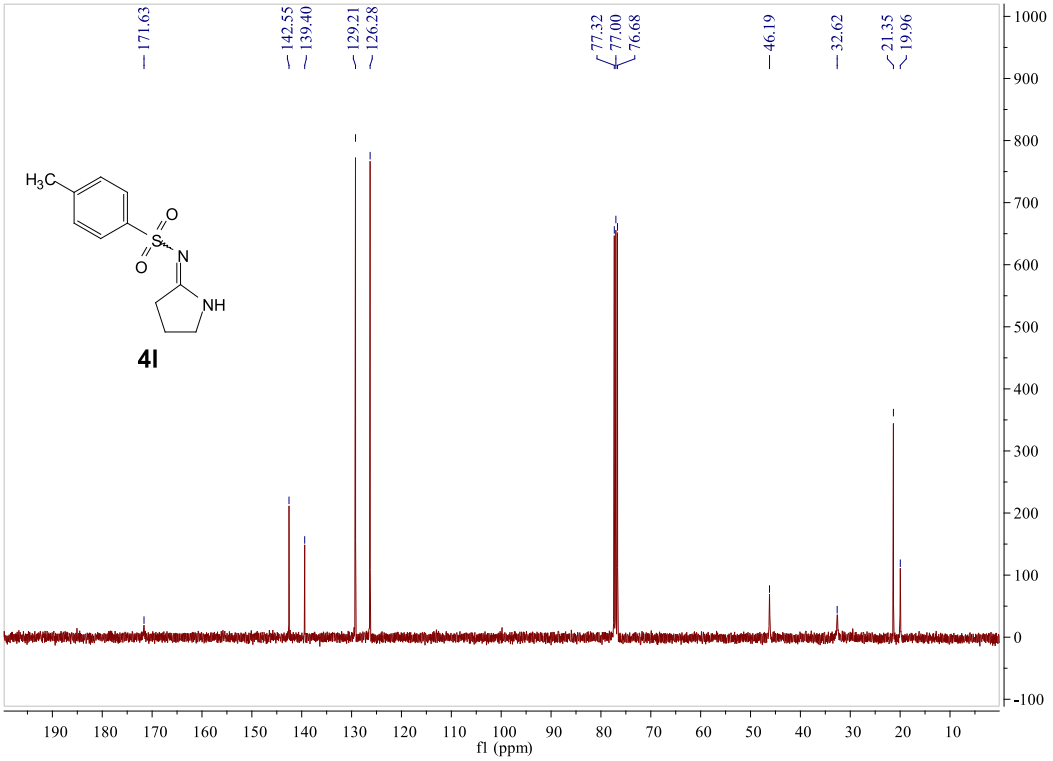
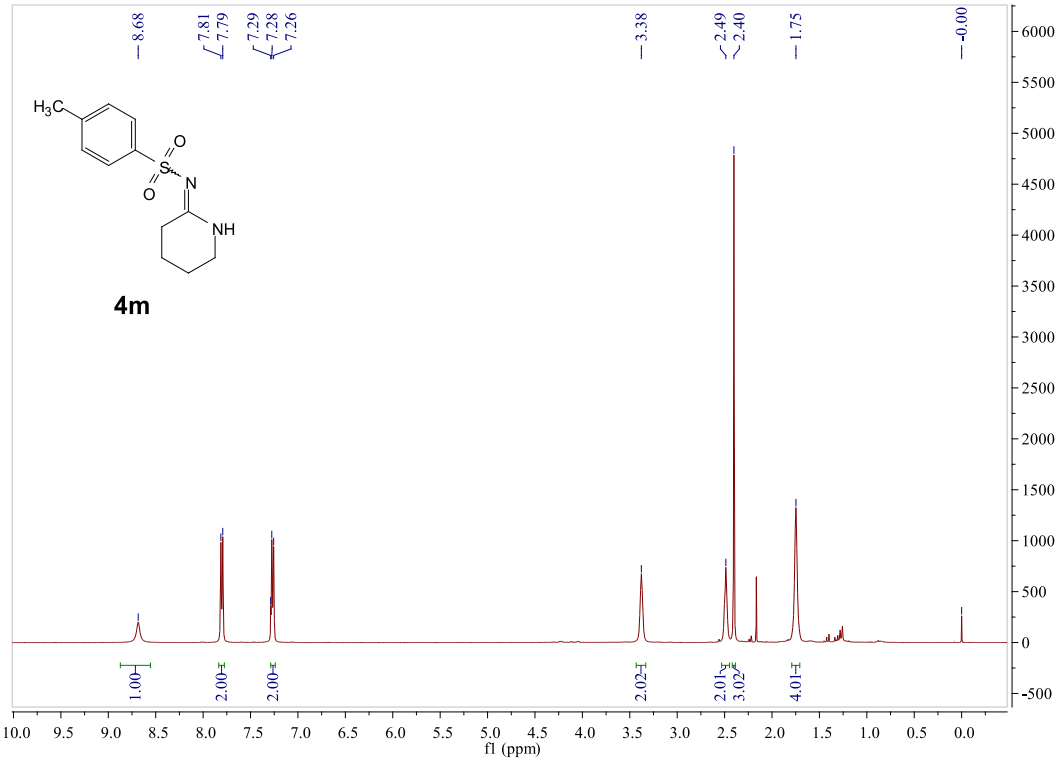
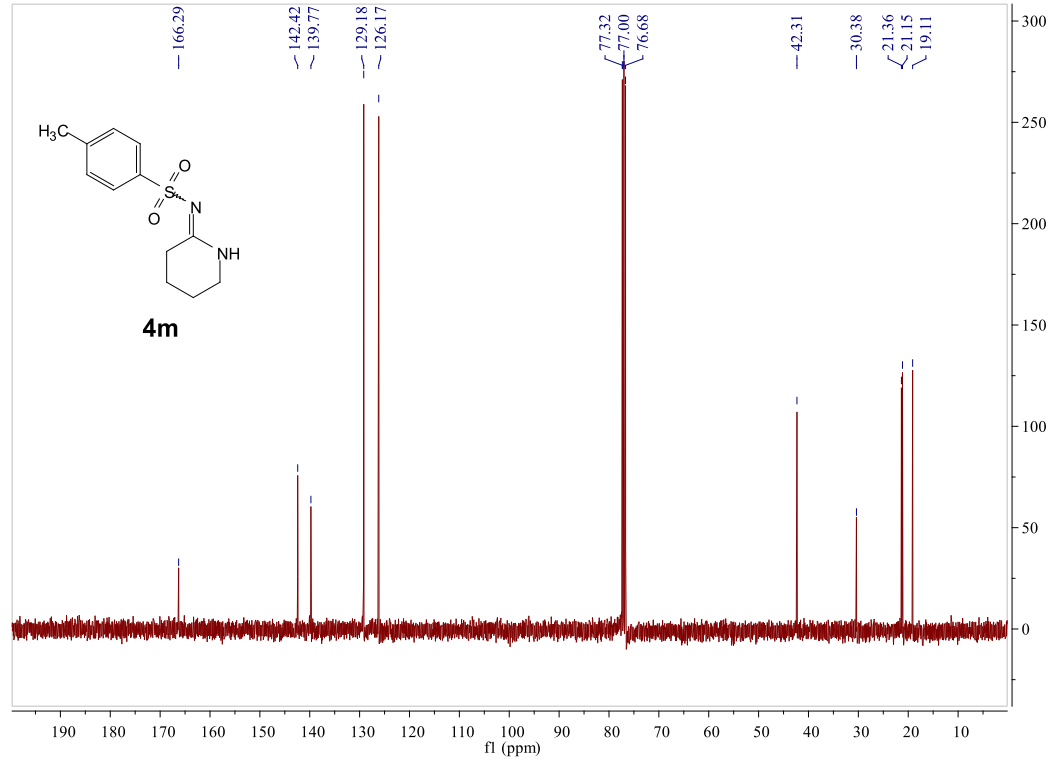

8.26
7.73
7.71
7.28
7.26
7.24
7.16
2.89
2.39
0.00
H3C
O
S
O
N
NH
CH3
4k
1.00
2.02
2.02
1.00
3.00
3.02
fl (ppm)

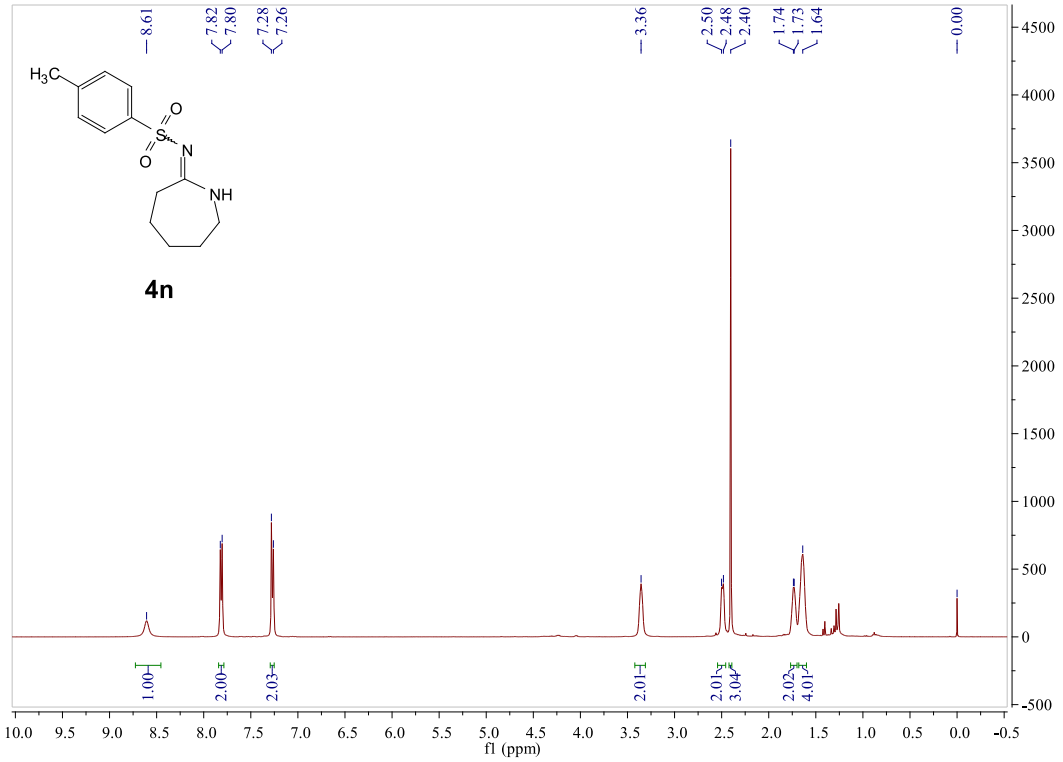

158.55
142.67
138.98
129.35
126.25
77.32
77.00
76.68
28.34
21.38
H3C
O
S
O
N
NH
CH3
4k
fl (ppm)


8.24
7.81
7.79
7.28
7.26
3.58
3.57
3.55
2.72
2.70
2.68
2.40
2.05
2.03
2.01
1.26
-0.00
2.08
2.07
2.05
2.03
2.01
2.09
fl (ppm)
1.00
2.00
2.01
2.00
2.00
3.01
2.09
fl (ppm)
4l

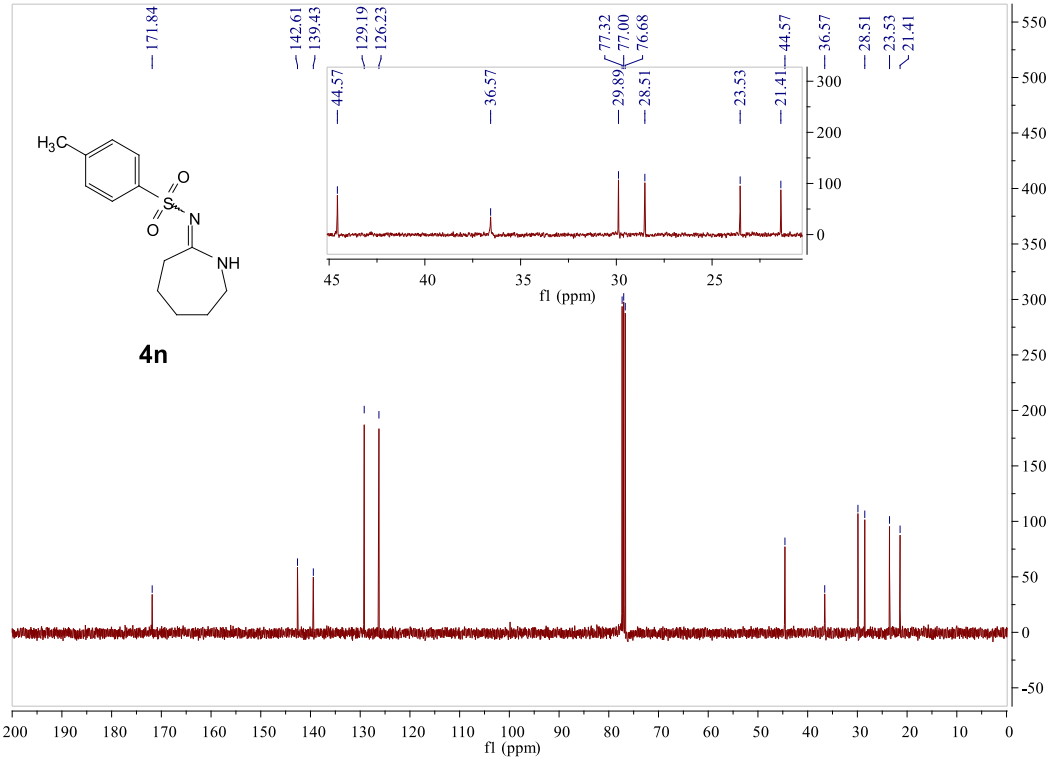

171.63
142.55
139.40
129.21
126.28
77.32
77.00
76.68
46.19
32.62
21.35
19.96
fl (ppm)
4l


8.68
7.81
7.79
7.29
7.28
7.26
3.38
2.49
2.40
1.75
0.00
H3C
O
S
O
N
NH
4m
1.00
2.00
2.00
2.02
2.01
3.02
4.01
fl (ppm)

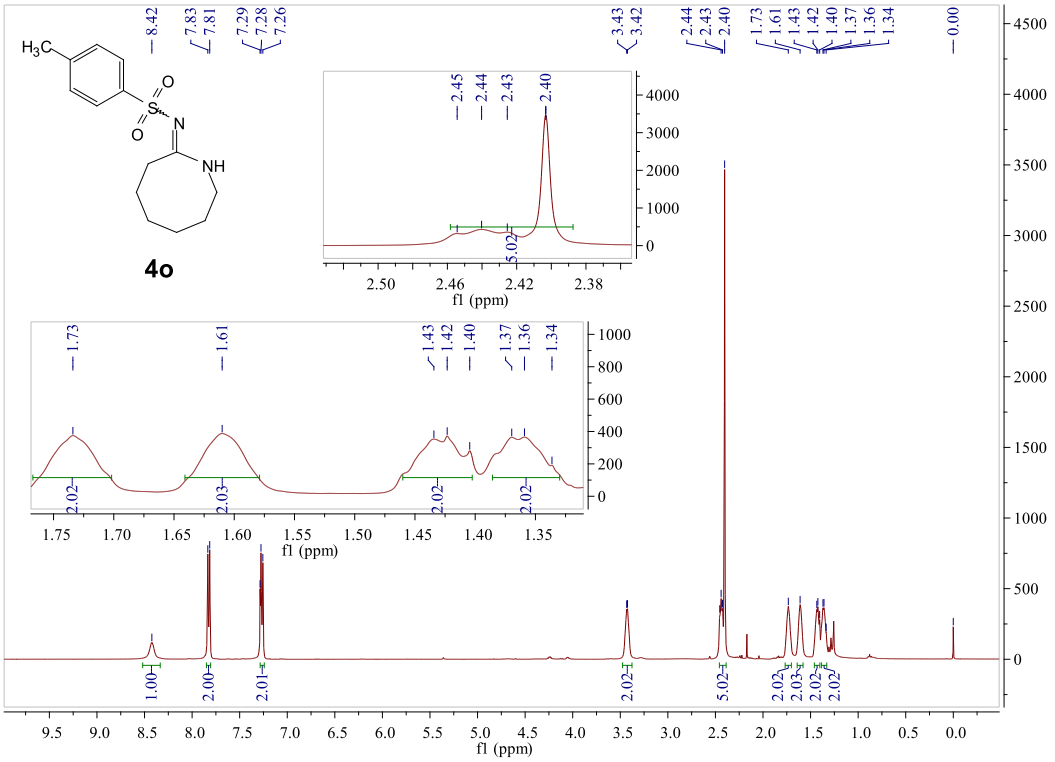

166.29
142.42
139.77
129.18
126.17
77.32
77.00
76.68
42.31
30.38
21.36
21.15
19.11
H3C
O
S
O
N
NH
4m
fl (ppm)

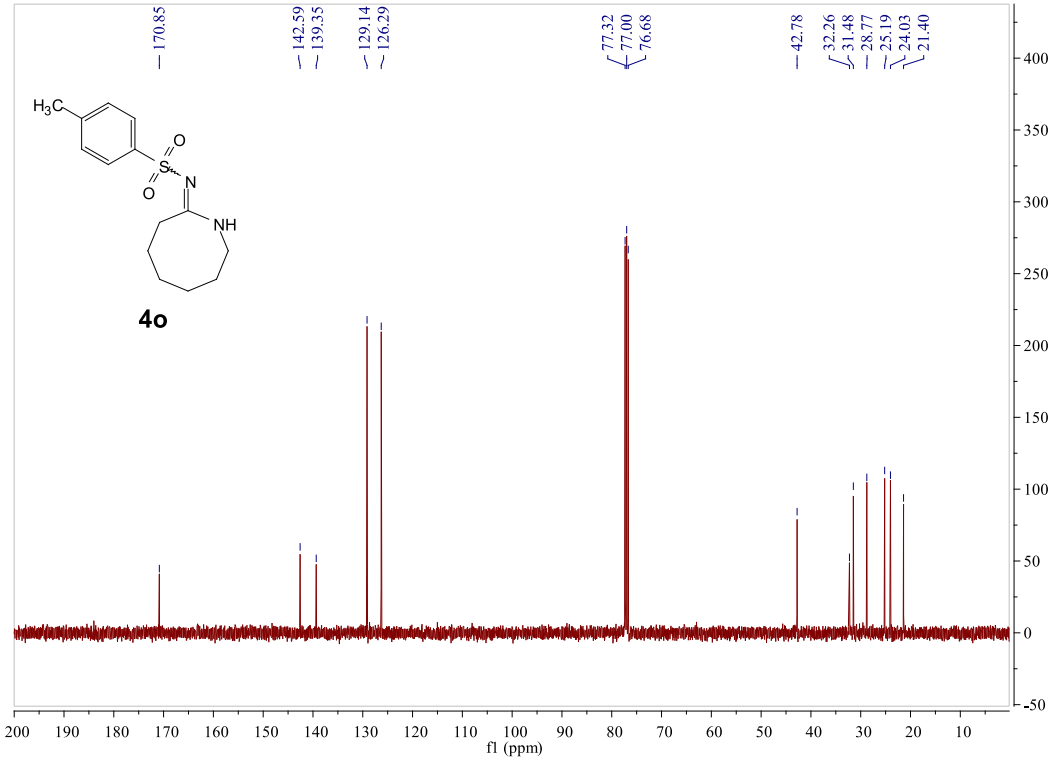

8.61
7.82
7.80
7.28
7.26
3.36
2.50
2.48
2.40
1.74
1.73
1.64
0.00
1.00
2.00
2.03
2.01
2.01
3.04
2.02
4.01
fl (ppm)

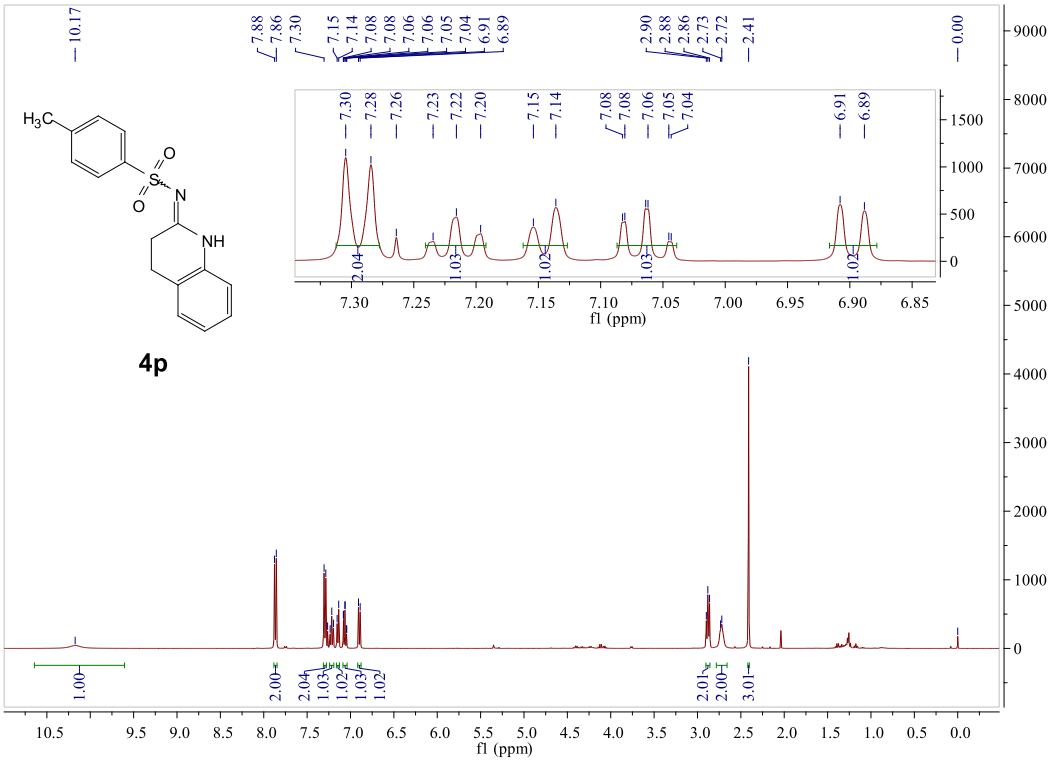
4n

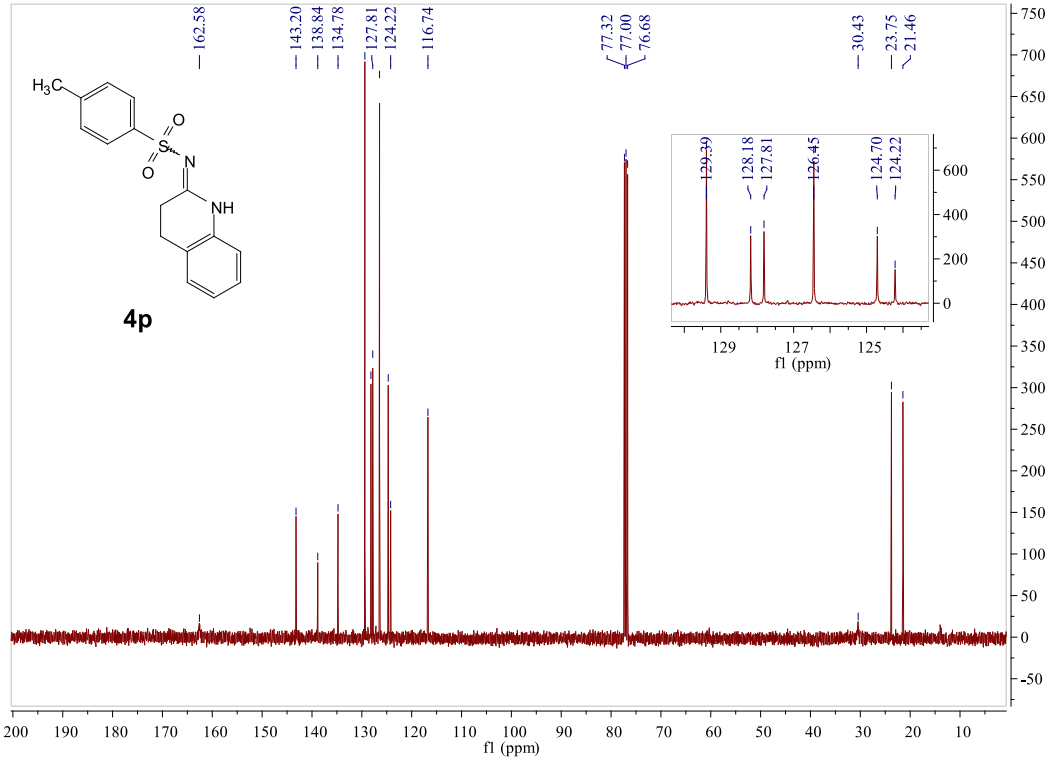

171.84
142.61
139.43
129.19
126.23
77.32
77.00
76.68
44.57
36.57
28.51
23.53
21.41
fl (ppm)

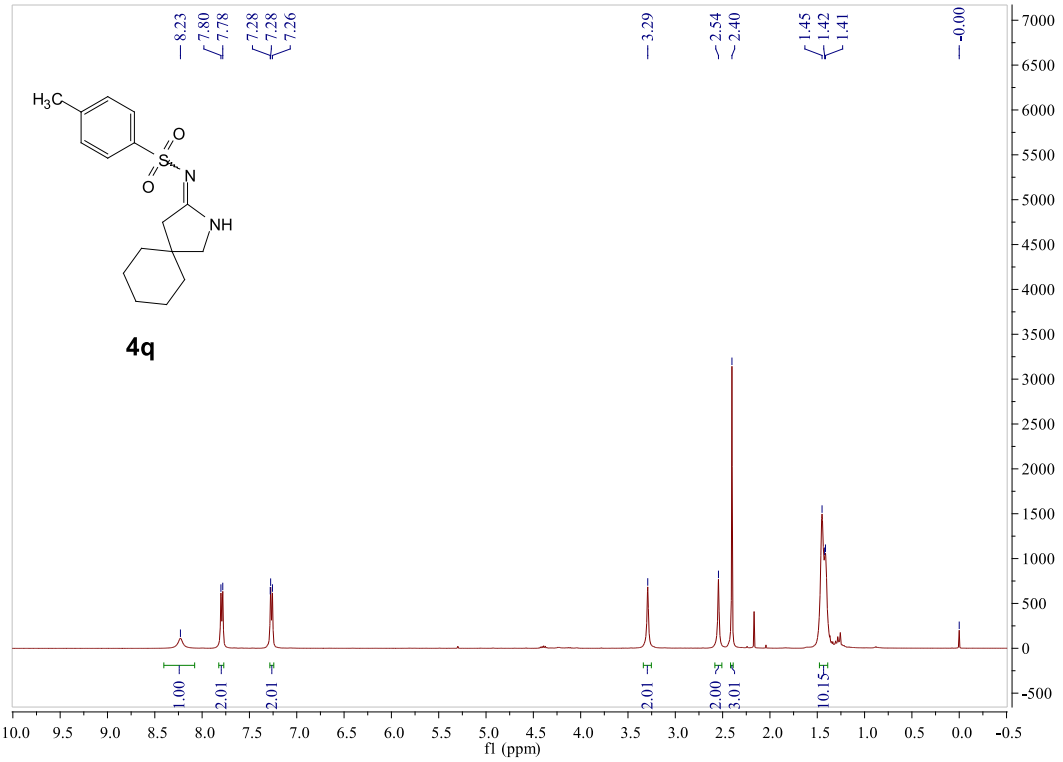
4n

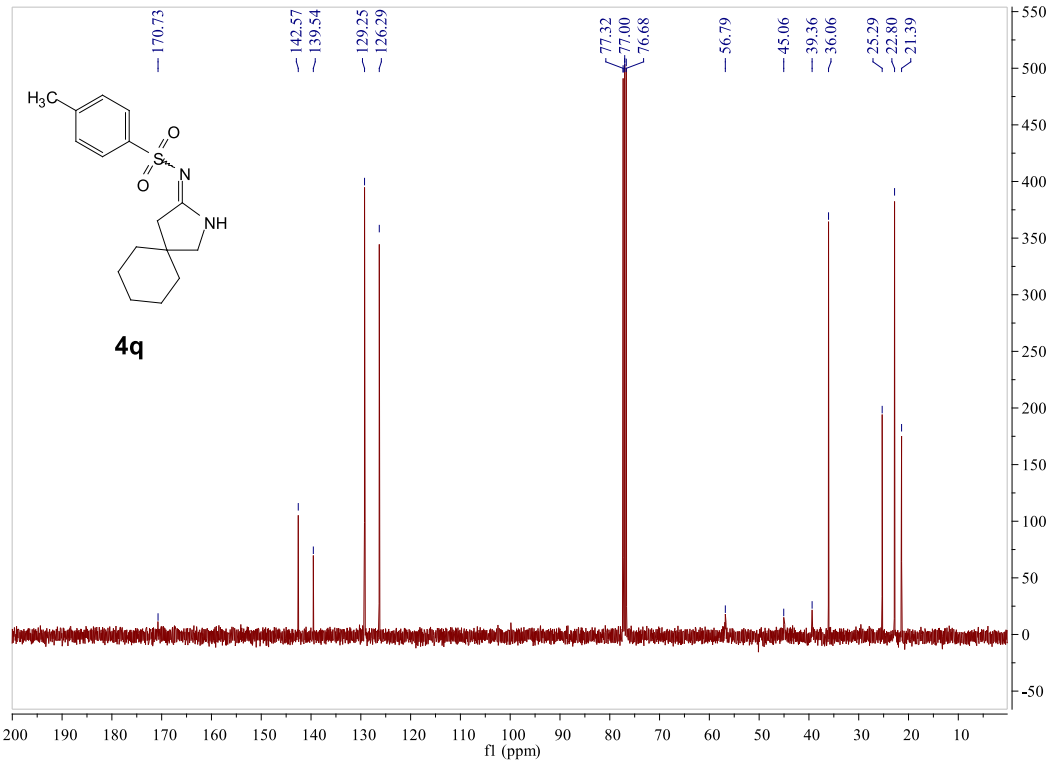

4o
fl (ppm)

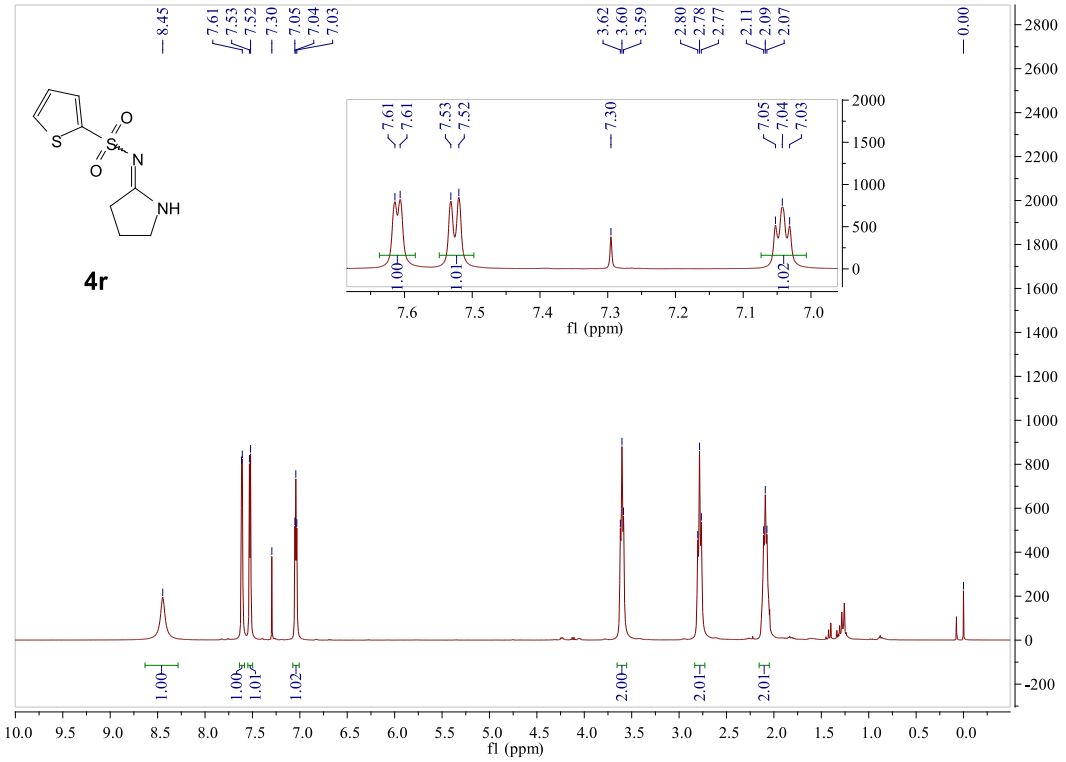

4o
fl (ppm)

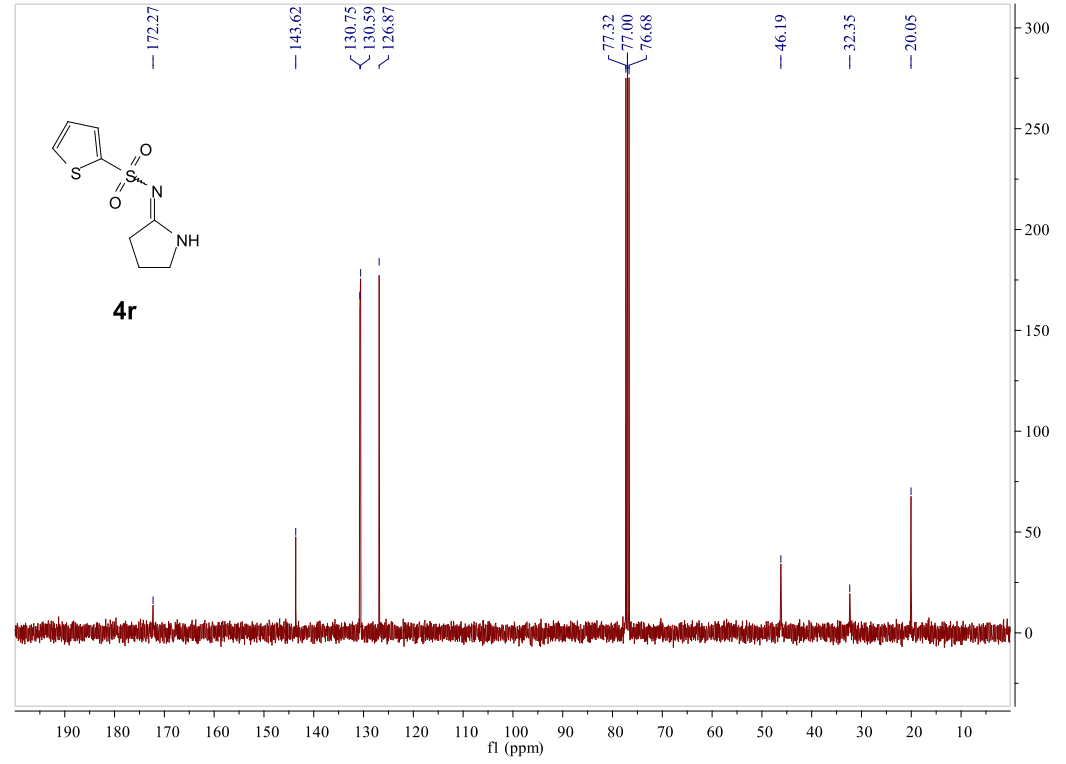

4p
fl (ppm)

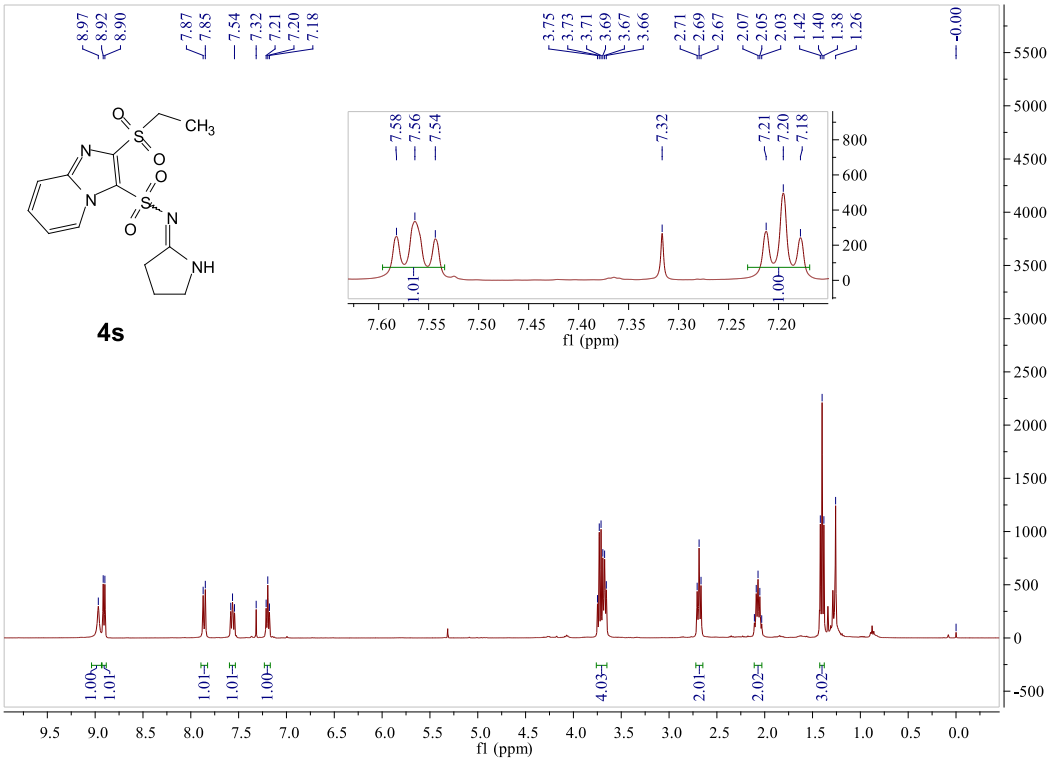

4p
fl (ppm)

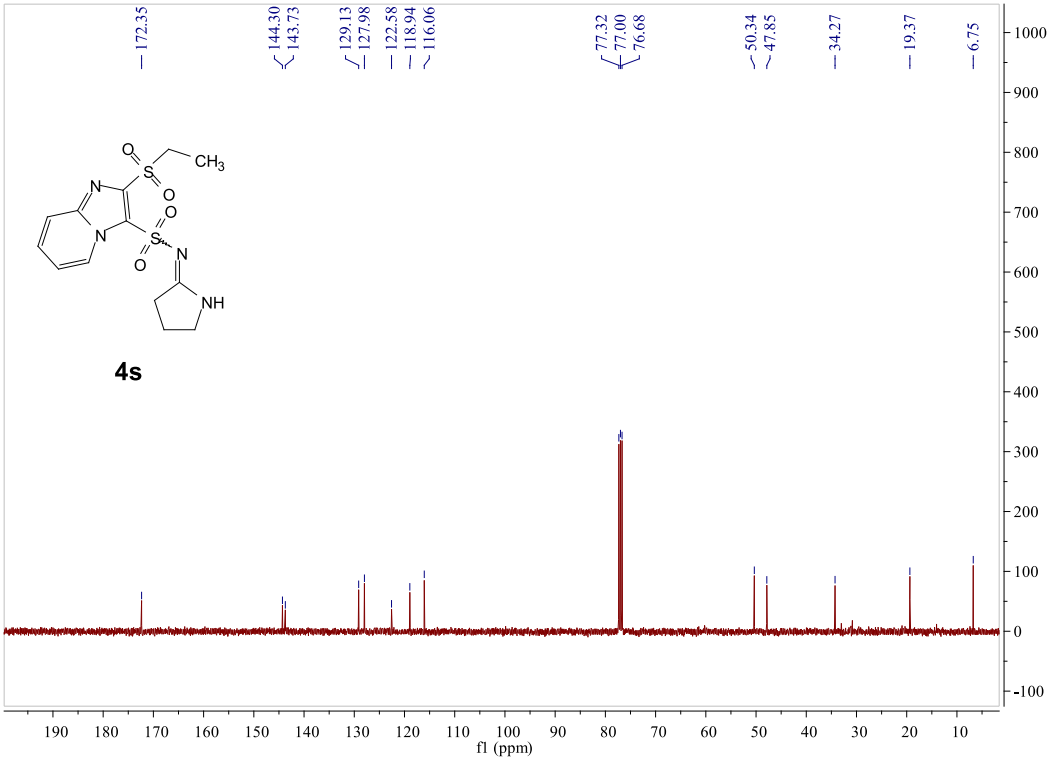

8.23
7.80
7.78
7.28
7.28
7.26
3.29
2.54
2.40
1.45
1.42
1.41
0.00
1.00
2.01
2.01
2.01
2.00
3.01
10.15
f1 (ppm)
4q

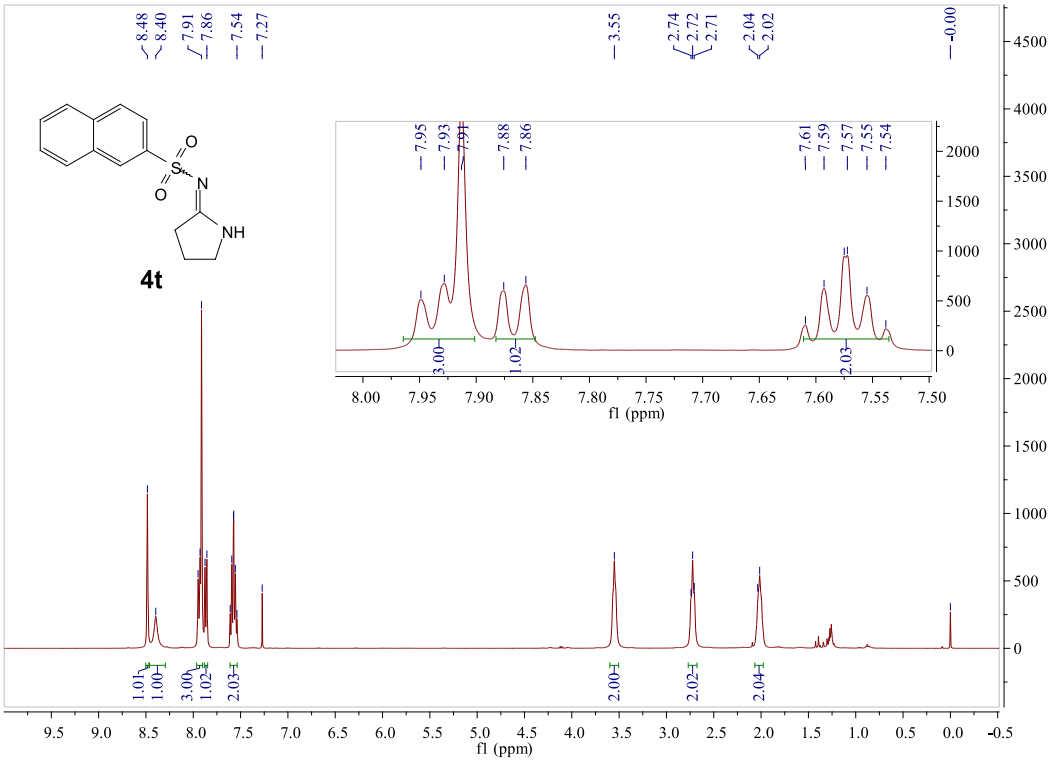

170.73
142.57
139.54
129.25
126.29
77.32
77.00
76.68
56.79
45.06
39.36
36.06
25.29
22.80
21.39
f1 (ppm)
4q

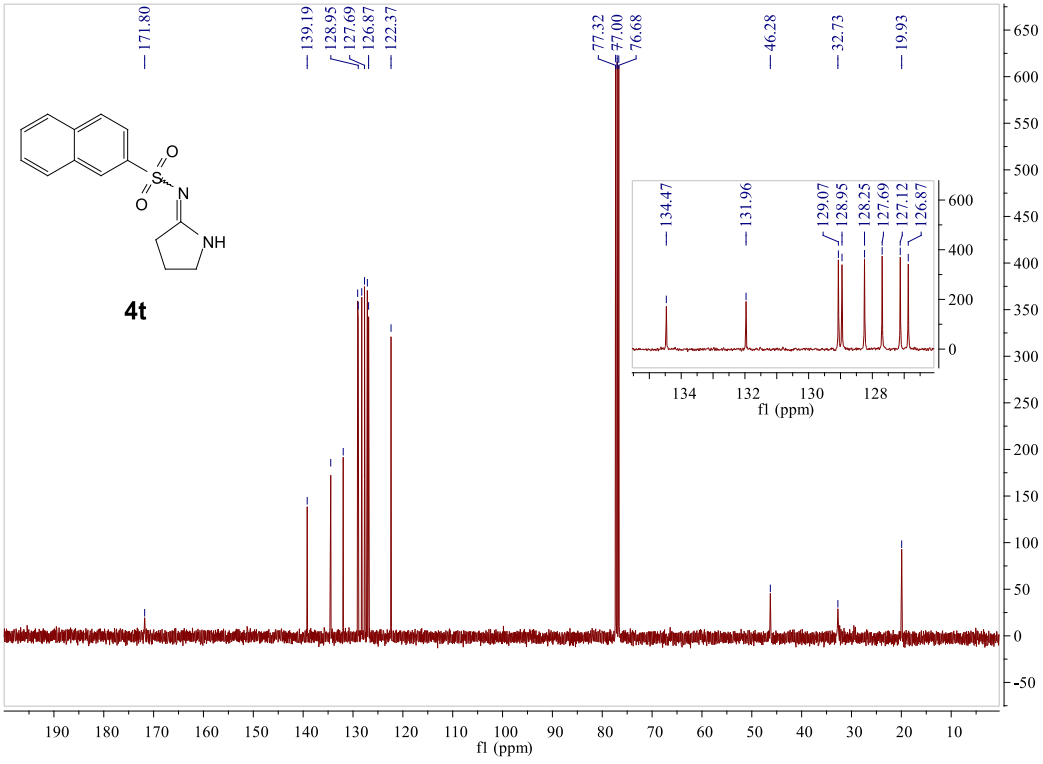

8.45
7.61
7.53
7.52
7.30
7.05
7.04
7.03
3.62
3.60
3.59
2.80
2.78
2.77
2.11
2.09
2.07
0.00
4r
fl (ppm)


172.27
143.62
130.75
130.59
126.87
77.32
77.00
76.68
46.19
32.35
20.05
4r
fl (ppm)


8.97
8.92
8.90
7.87
7.85
7.54
7.32
7.21
7.20
7.18
3.75
3.73
3.71
3.69
3.67
3.66
2.71
2.69
2.67
2.07
2.05
2.03
1.42
1.40
1.38
1.26
0.00
7.58
7.56
7.54
7.32
7.21
7.20
7.18
1.01
1.00
fl (ppm)
4s
1.00
1.01
1.01
1.01
1.00
4.03
2.01
2.02
3.02
fl (ppm)


172.35
144.30
143.73
129.13
127.98
122.58
118.94
116.06
77.32
77.00
76.68
50.34
47.85
34.27
19.37
6.75
4s
fl (ppm)


8.48
8.40
7.91
7.86
7.54
7.27
3.55
2.74
2.72
2.71
2.04
2.02
0.00
4t
7.95
7.93
7.91
7.88
7.86
7.61
7.59
7.57
7.55
7.54
3.00
1.02
2.03
f1 (ppm)
1.01
1.00
3.00
1.02
2.03
2.00
2.02
2.04
f1 (ppm)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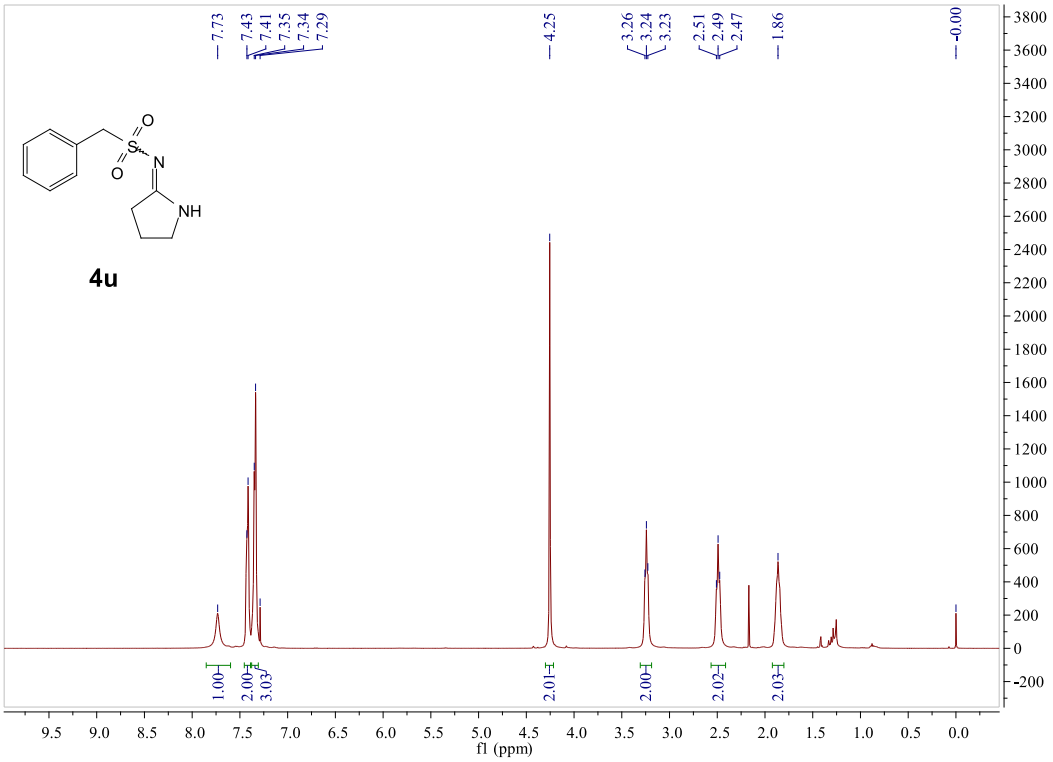
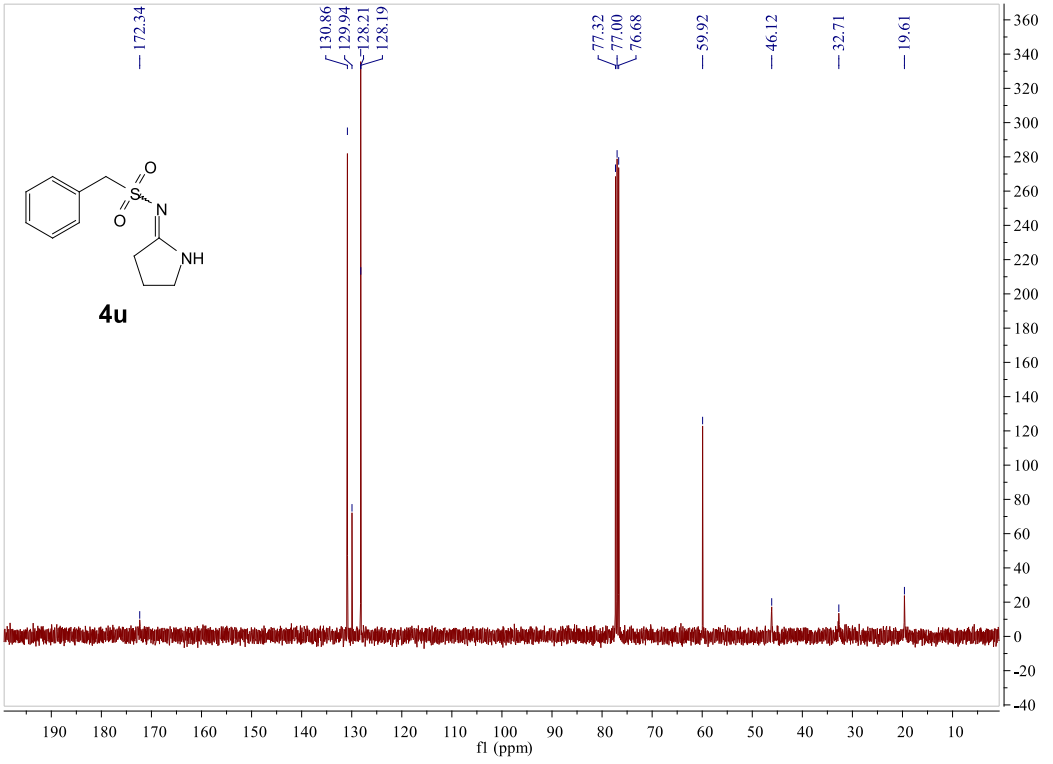
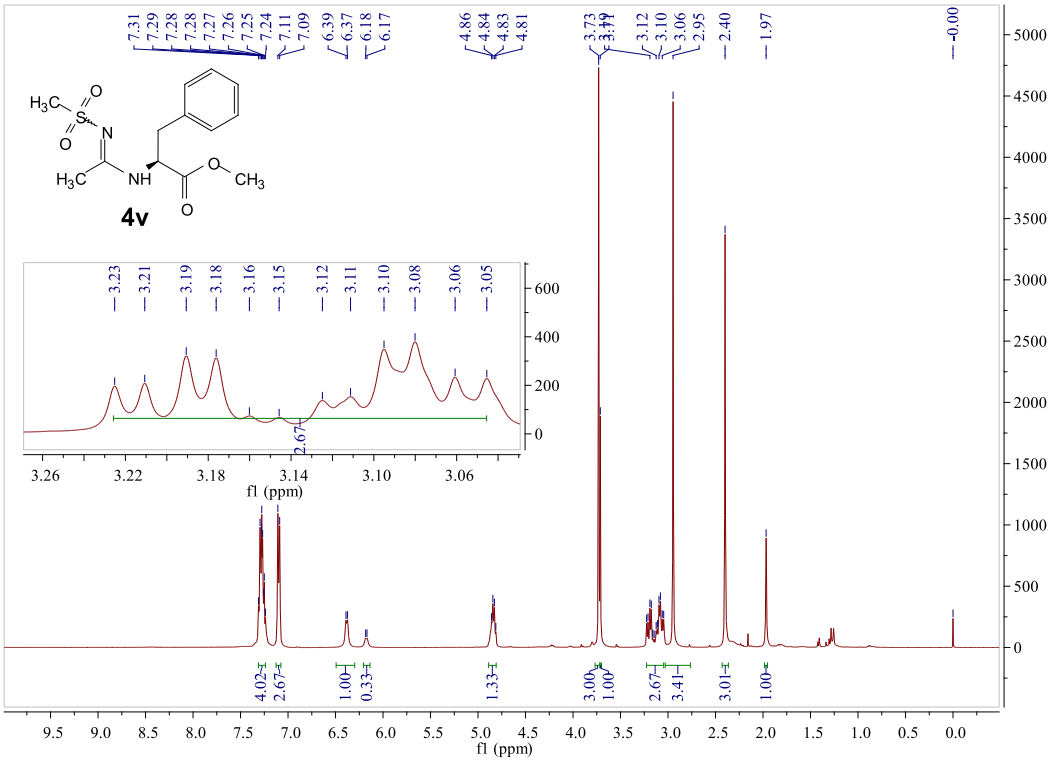
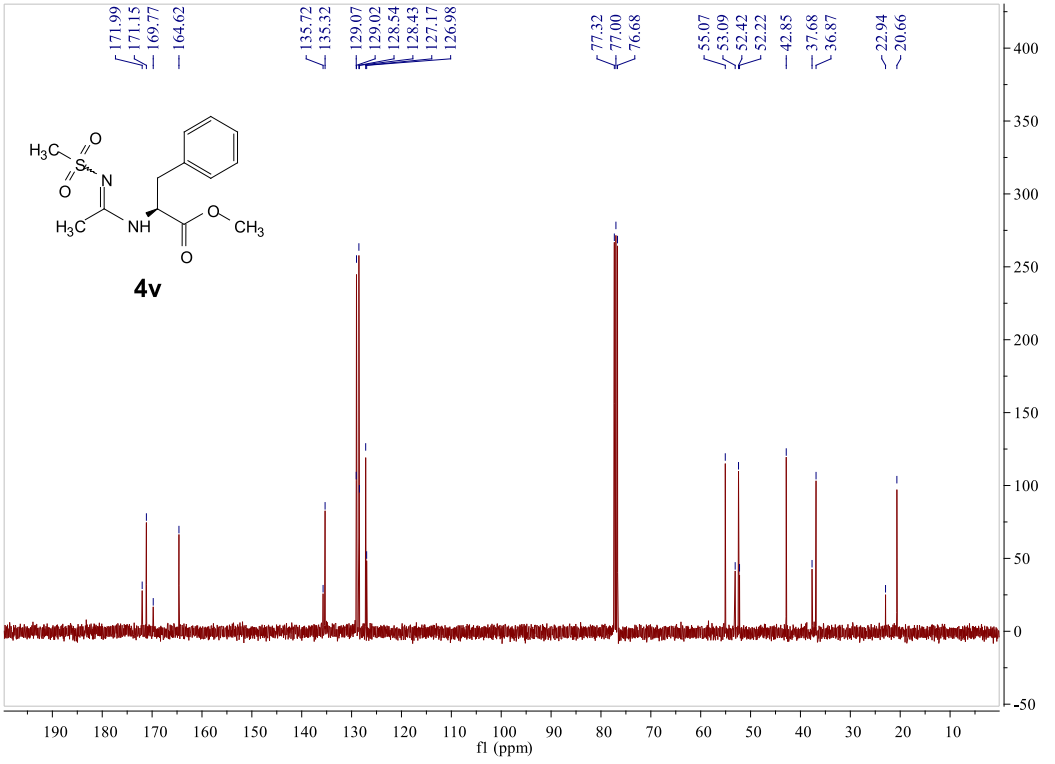
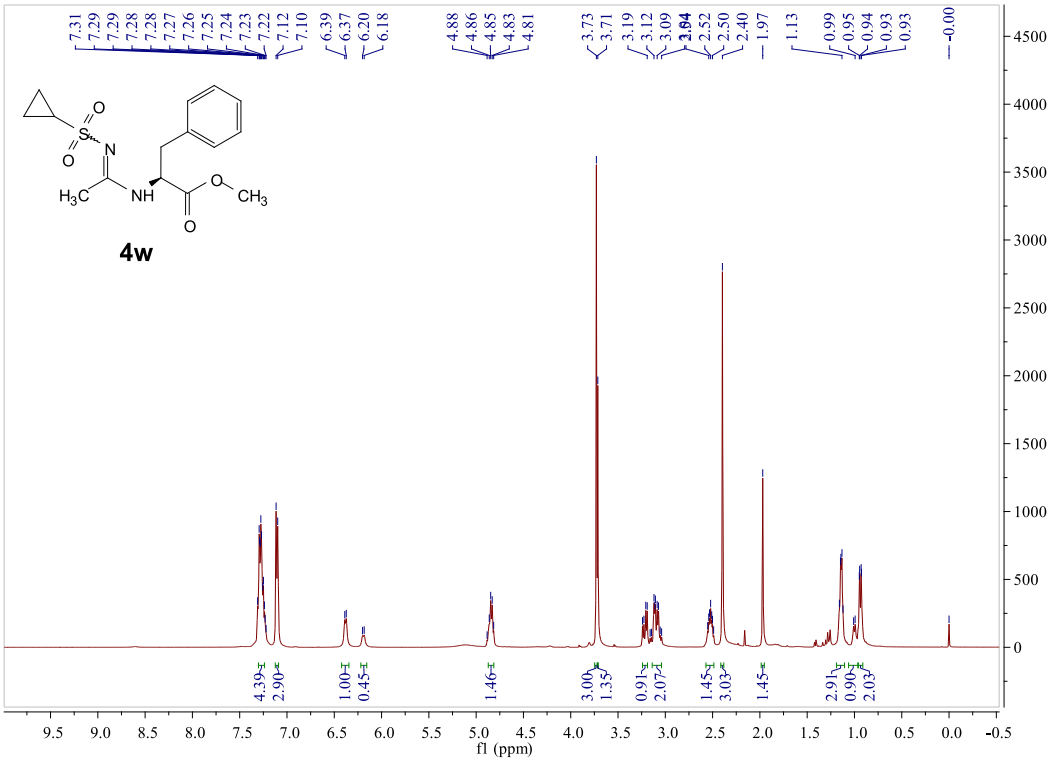
139.19
128.95
127.69
126.87
122.37
77.32
77.00
76.68
46.28
32.73
19.93
4t
134.47
131.96
129.07
128.95
128.25
127.69
127.12
126.87
f1 (ppm)
f1 (ppm)

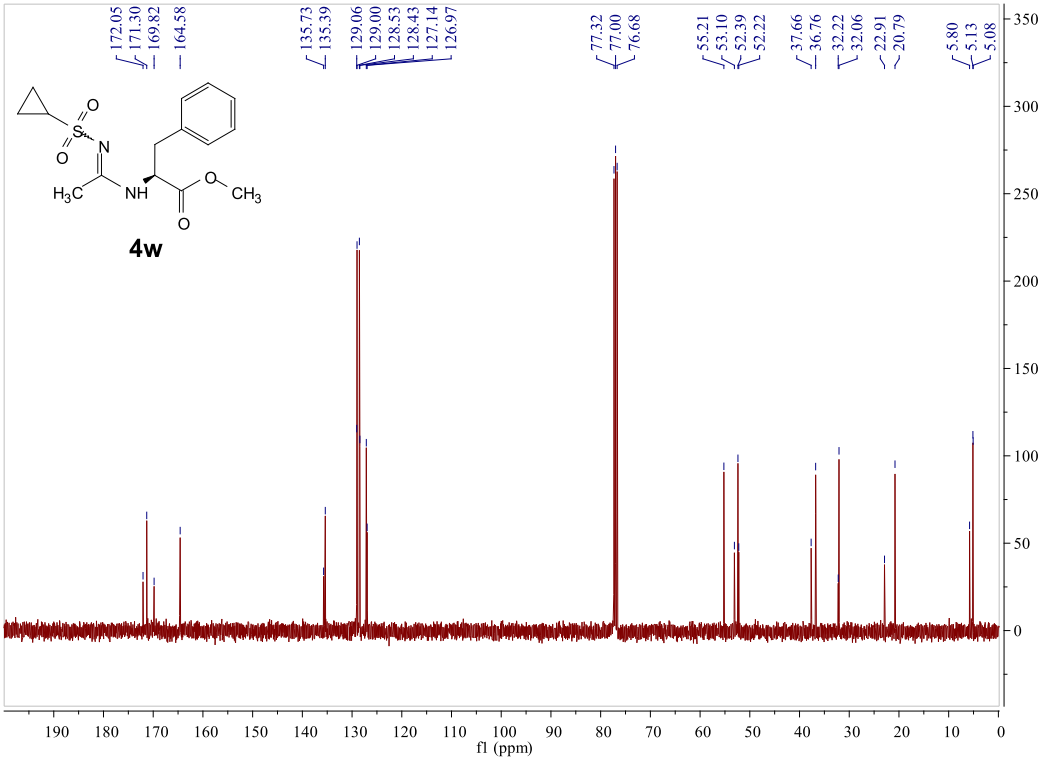

7.73
7.43
7.41
7.35
7.34
7.29
4.25
3.26
3.24
3.23
2.51
2.49
2.47
1.86
0.00
1.00
2.00
3.03
2.01
2.00
2.02
2.03
f1 (ppm)
4u

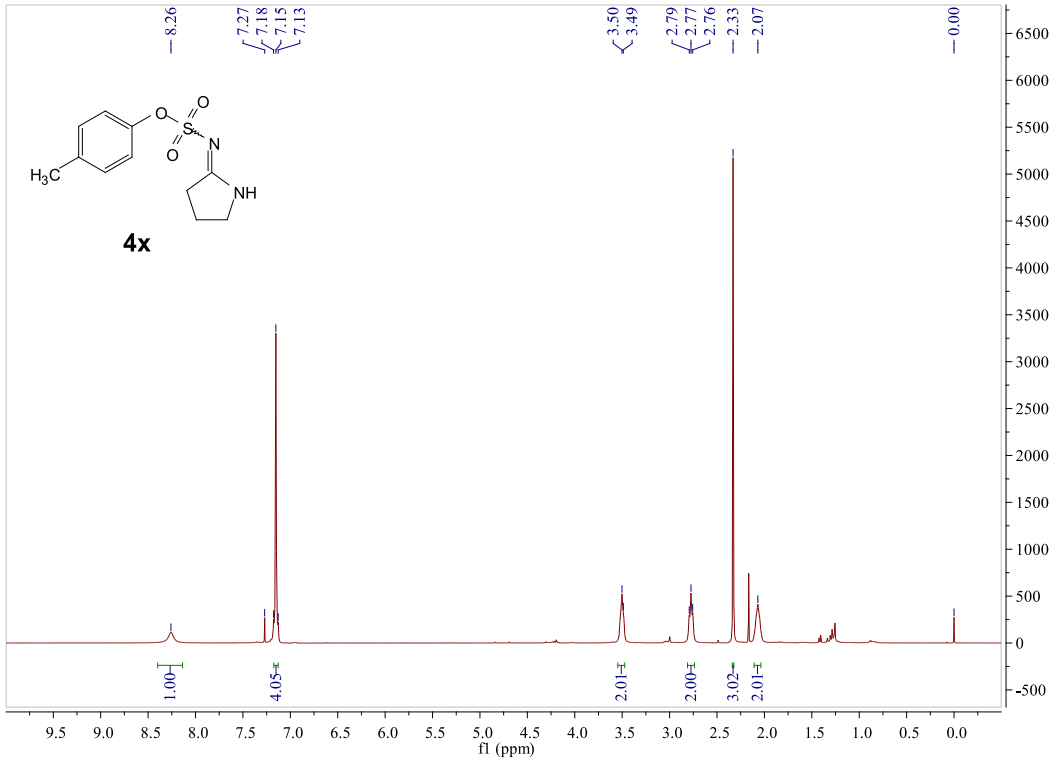

172.34
130.86
129.94
128.21
128.19
77.32
77.00
76.68
59.92
46.12
32.71
19.61
f1 (ppm)
4u

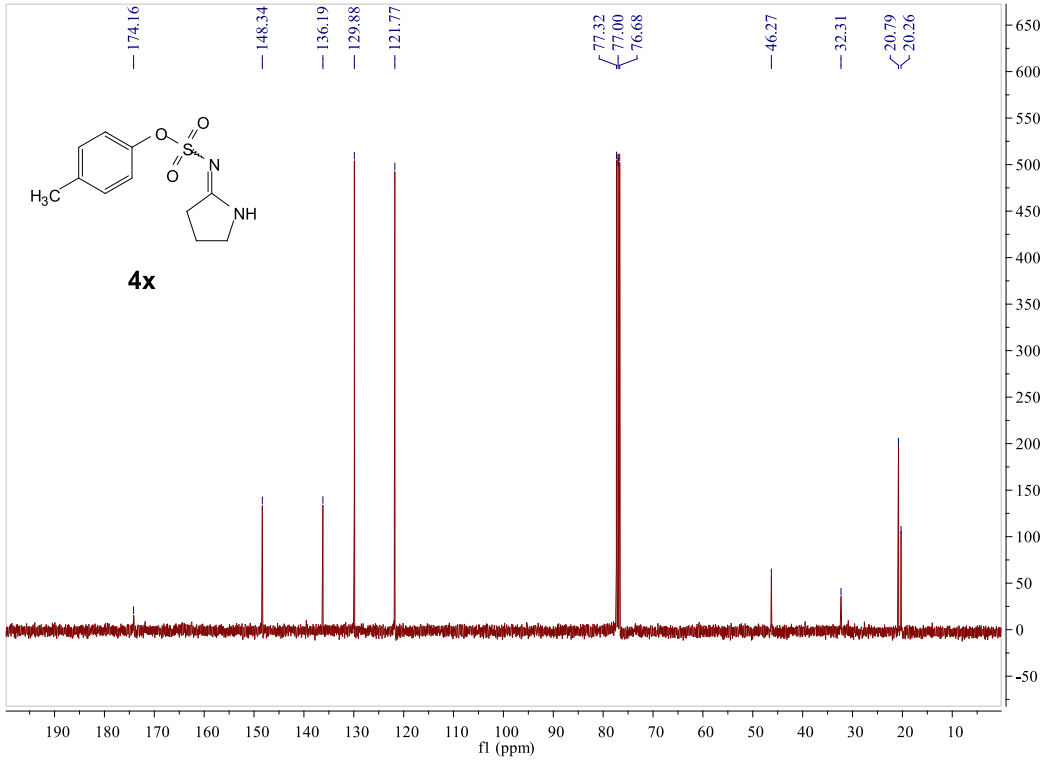

4v
f1 (ppm)

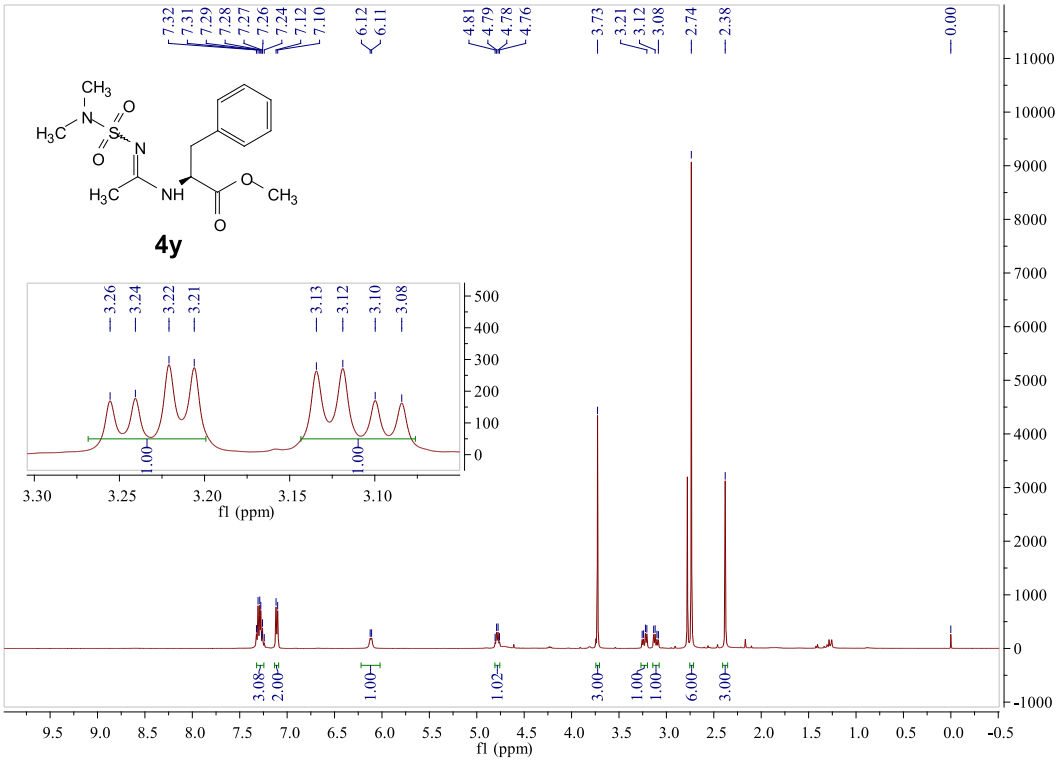

4v
f1 (ppm)

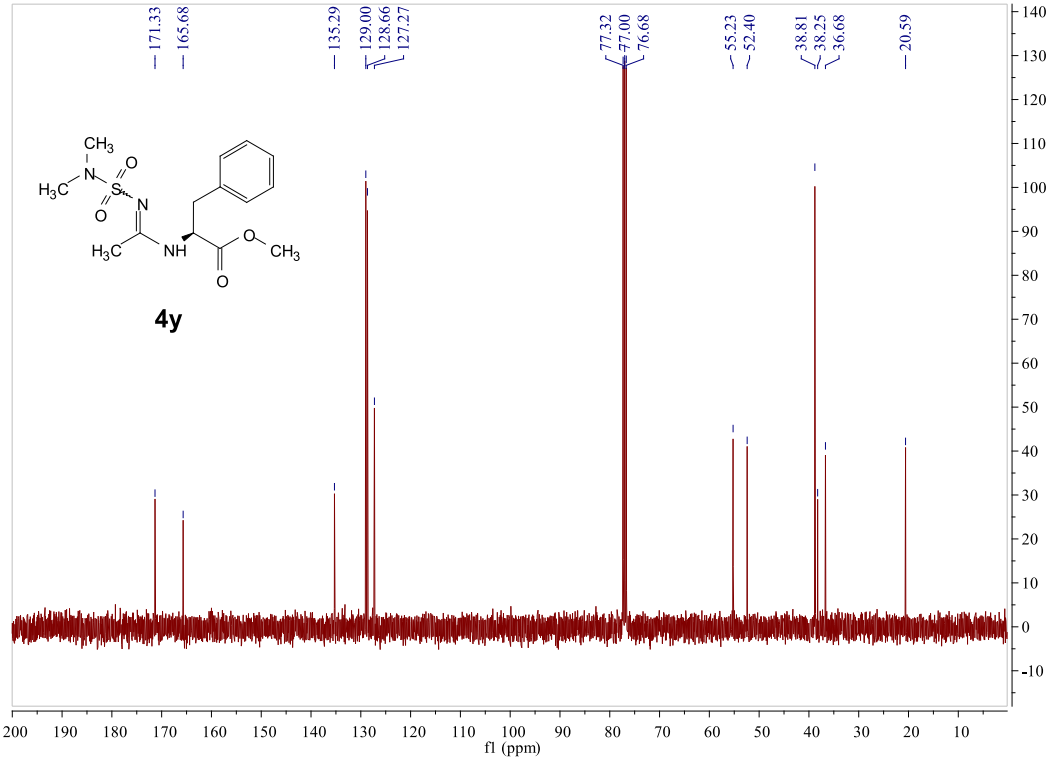

4w
f1 (ppm)

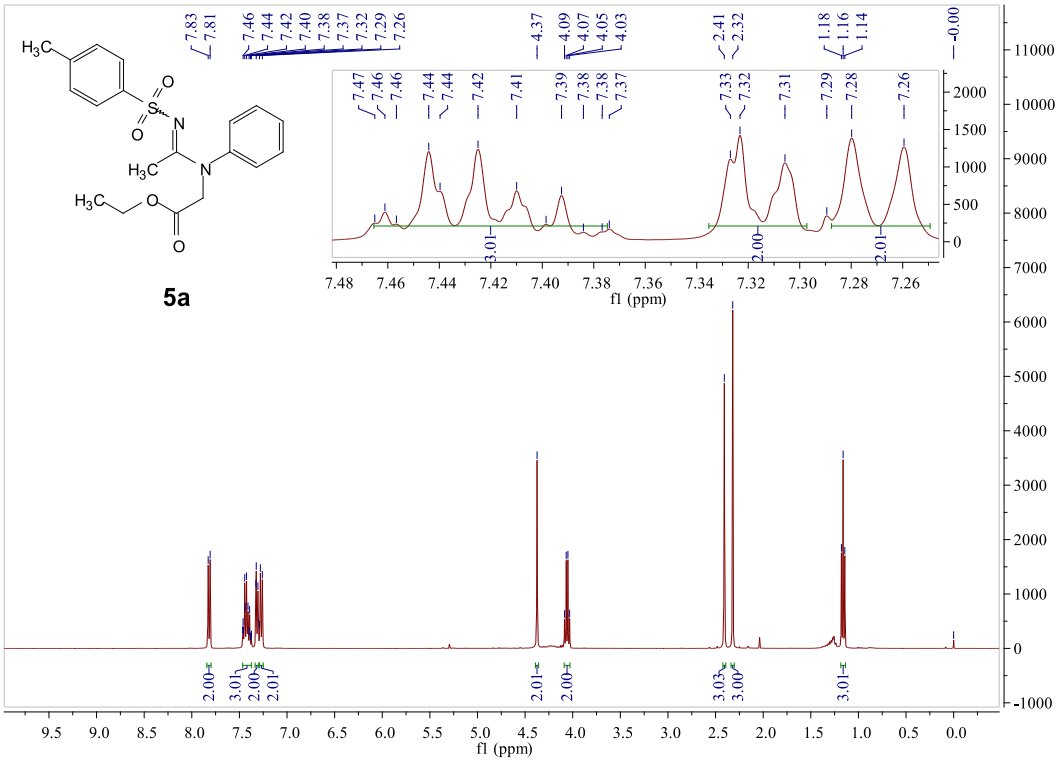

4w
f1 (ppm)

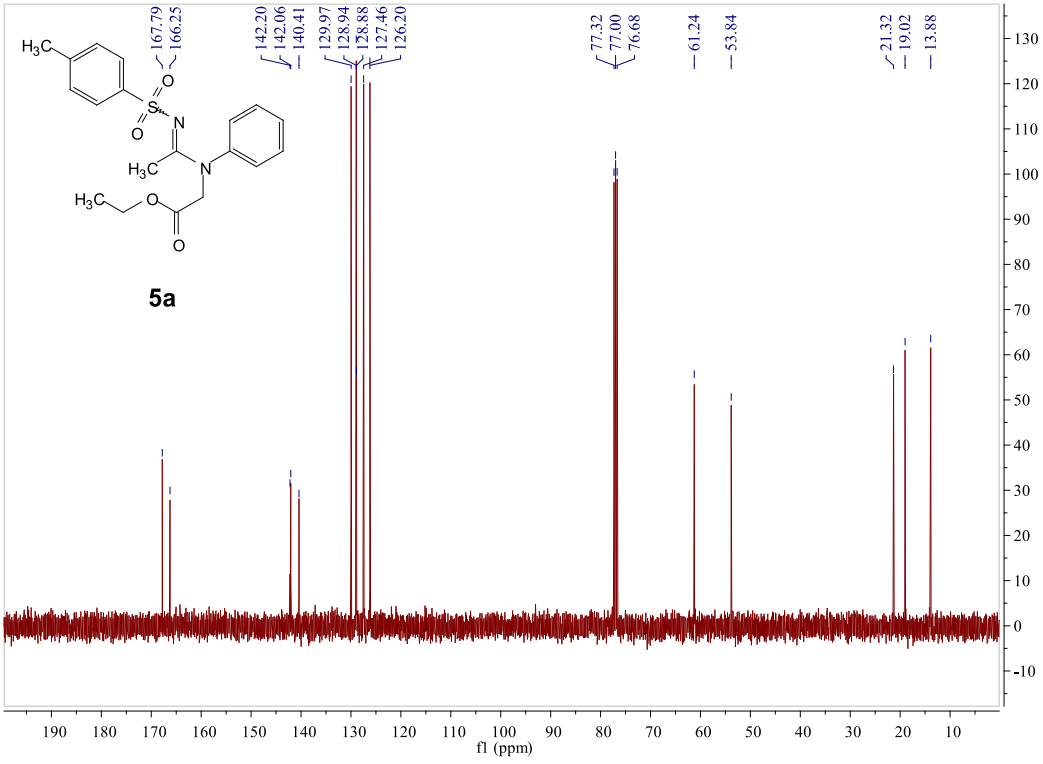

8.26
7.27
7.18
7.15
7.13
3.50
3.49
2.79
2.77
2.76
2.33
2.07
0.00
4x
1.00
4.05
2.01
2.00
3.02
2.01
f1 (ppm)

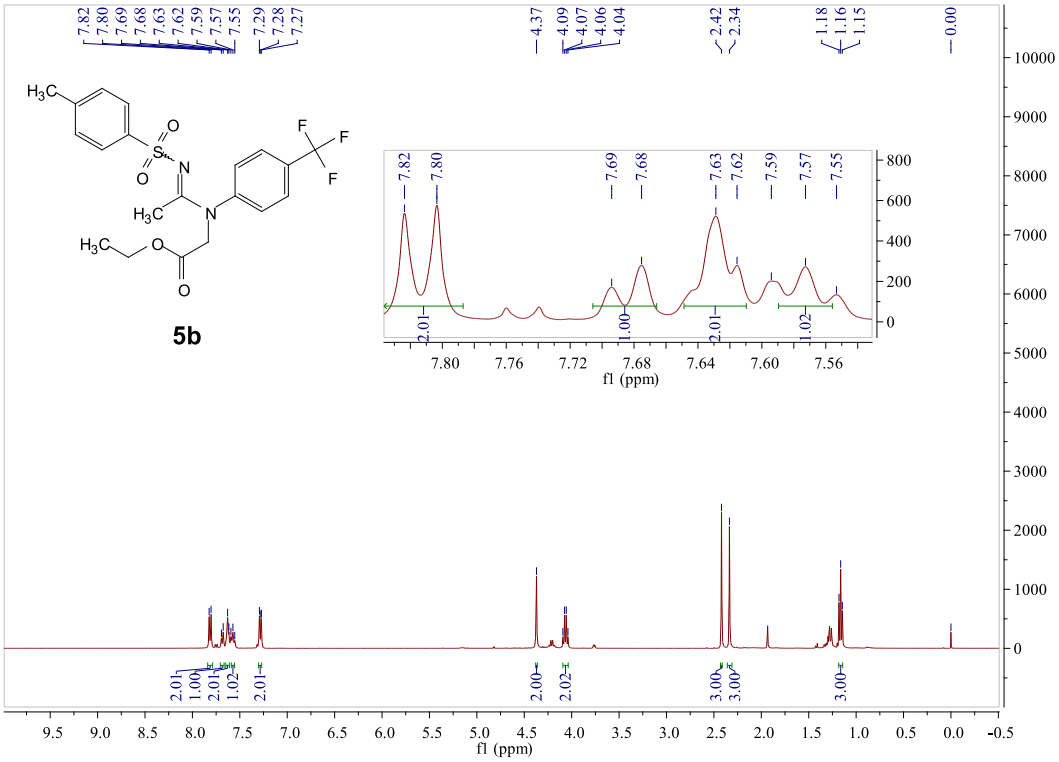

174.16
148.34
136.19
129.88
121.77
77.32
77.00
76.68
46.27
32.31
20.79
20.26
4x
f1 (ppm)

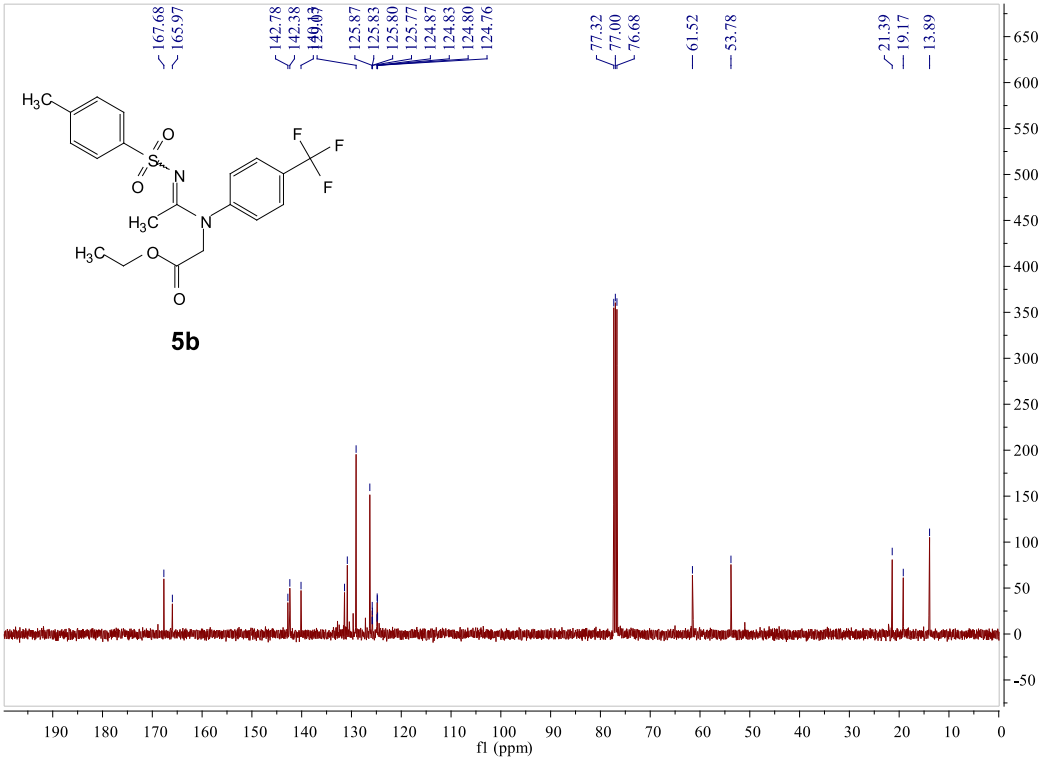

7.32
7.31
7.29
7.28
7.27
7.26
7.24
7.12
7.10
6.12
6.11
4.81
4.79
4.78
4.76
3.73
3.21
3.12
3.08
2.74
2.38
0.00
4y
3.26
3.24
3.22
3.21
3.13
3.12
3.10
3.08
1.00
1.00
fl (ppm)
3.08
2.00
1.00
1.02
3.00
1.00
1.00
6.00
3.00
fl (ppm)

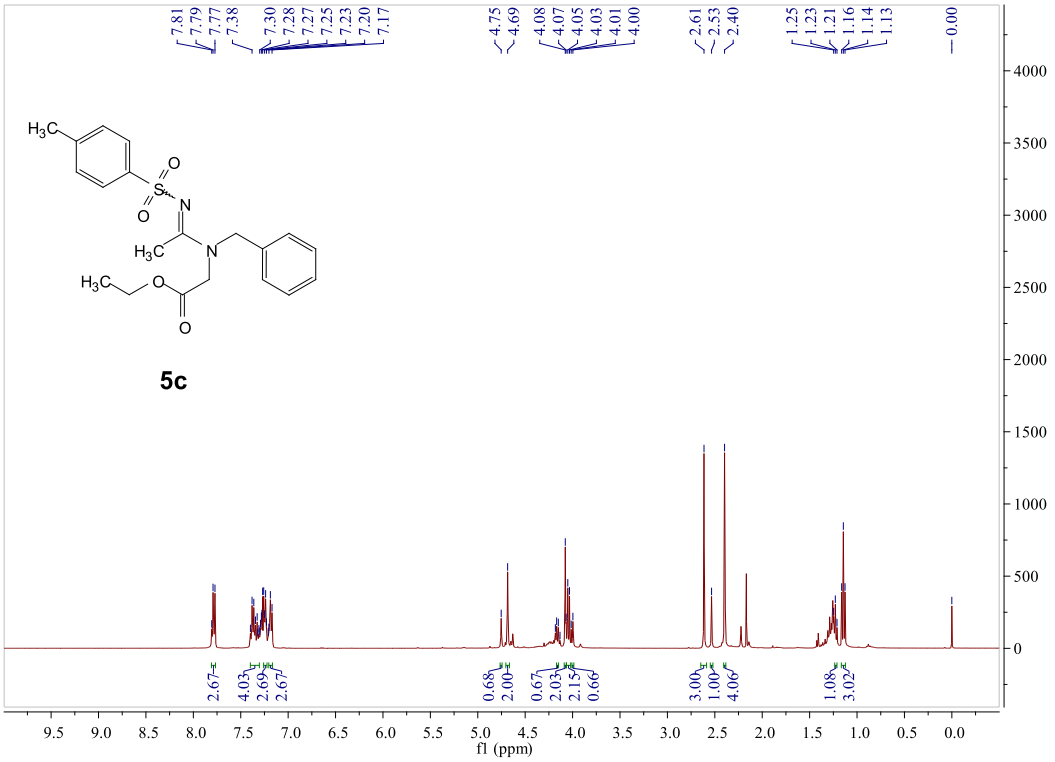

171.33
165.68
135.29
129.00
128.66
127.27
77.32
77.00
76.68
55.23
52.40
38.81
38.25
36.68
20.59
4y
fl (ppm)

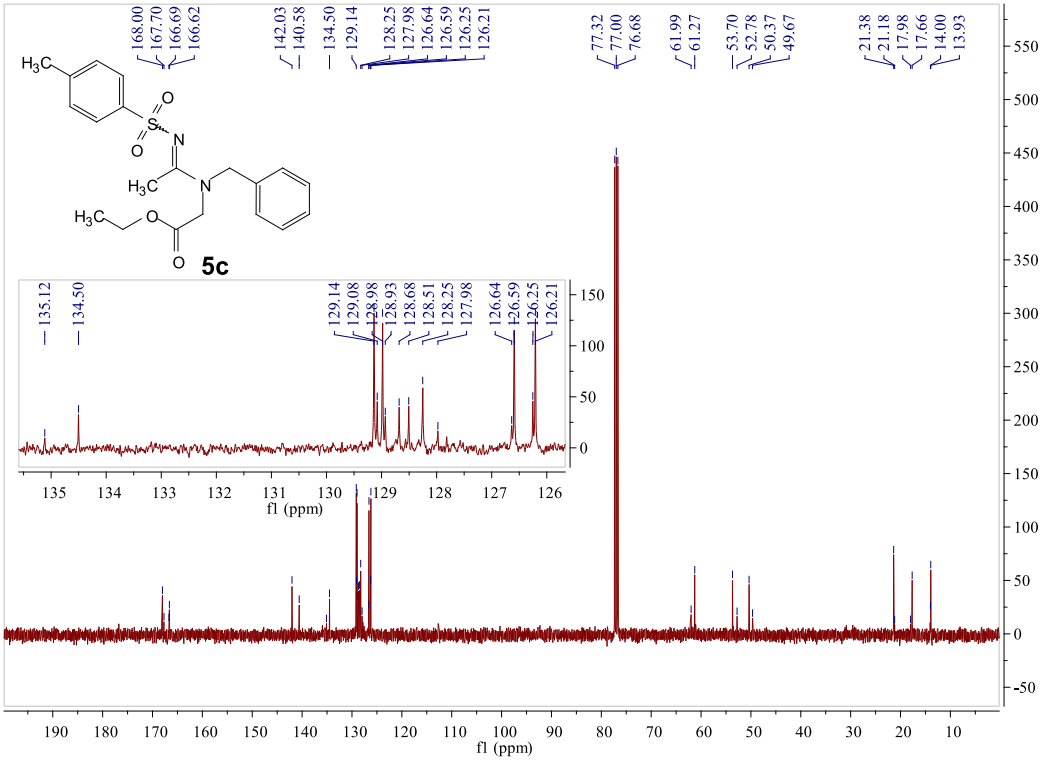

5a
fl (ppm)

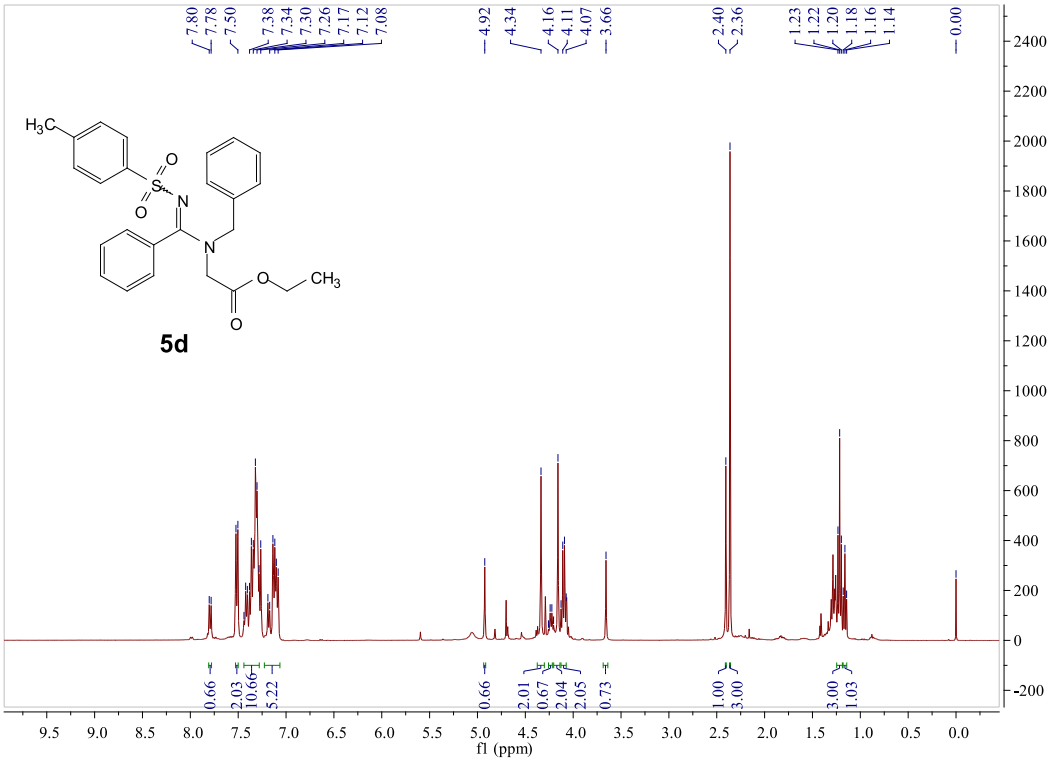

5a
fl (ppm)

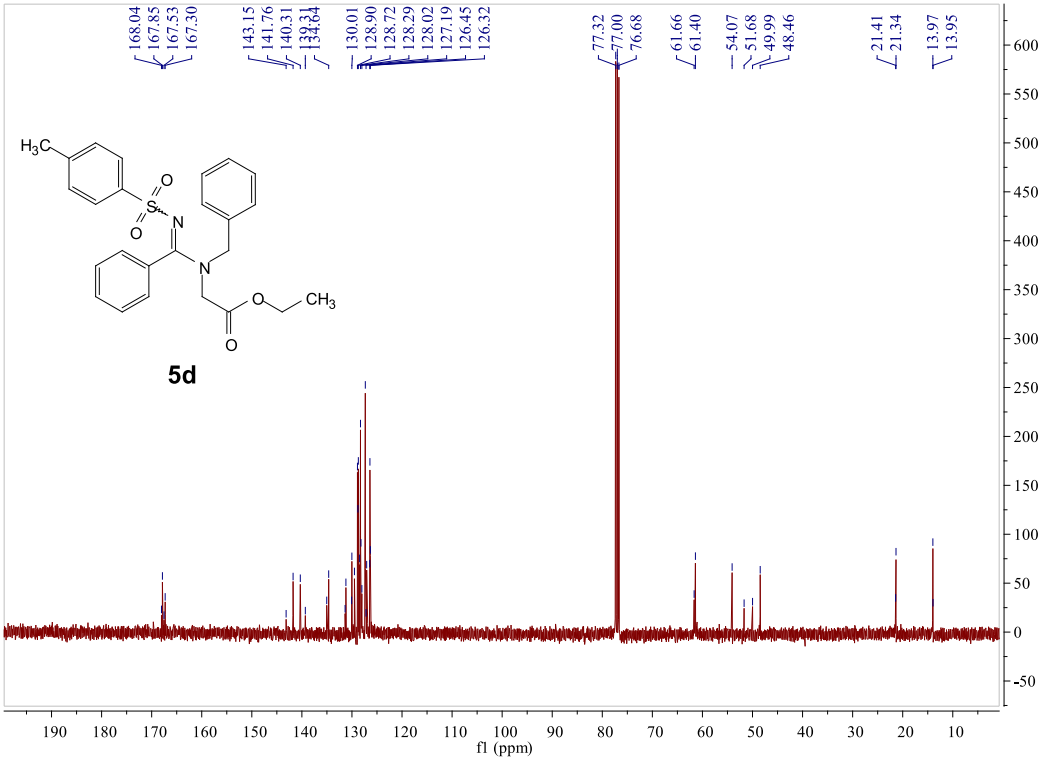

7.82
7.80
7.69
7.68
7.63
7.62
7.59
7.57
7.55
7.29
7.28
7.27
4.37
4.09
4.07
4.06
4.04
2.42
2.34
1.18
1.16
1.15
0.00
5b
fl (ppm)
fl (ppm)

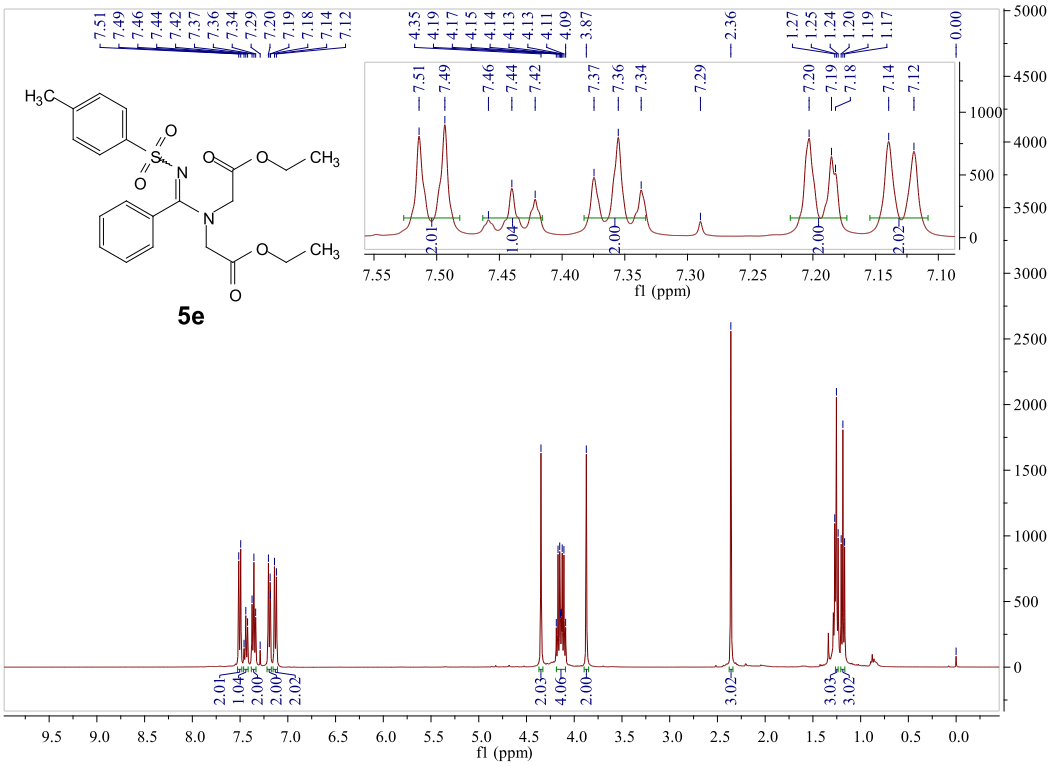

167.68
165.97
142.78
142.38
125.87
125.83
125.80
125.77
124.87
124.83
124.80
124.76
77.32
77.00
76.68
61.52
53.78
21.39
19.17
13.89
5b
fl (ppm)

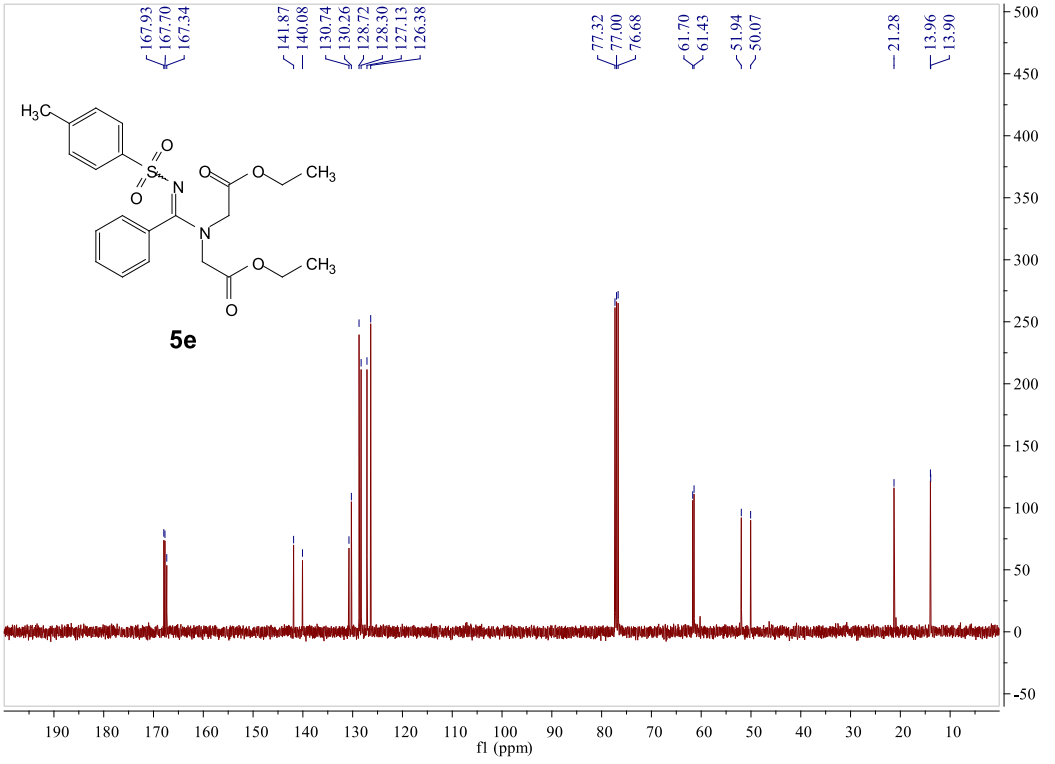

7.81
7.79
7.77
7.38
7.30
7.28
7.27
7.25
7.23
7.20
7.17
4.75
4.69
4.08
4.07
4.05
4.03
4.01
4.00
2.61
2.53
2.40
1.25
1.23
1.21
1.16
1.14
1.13
0.00
H3C
O
S
O
N
O
H3C
N
H3C
O
O
5c
2.67
4.03
2.69
2.67
0.68
2.00
0.67
2.03
2.15
0.66
3.00
1.00
4.06
1.08
3.02
fl (ppm)

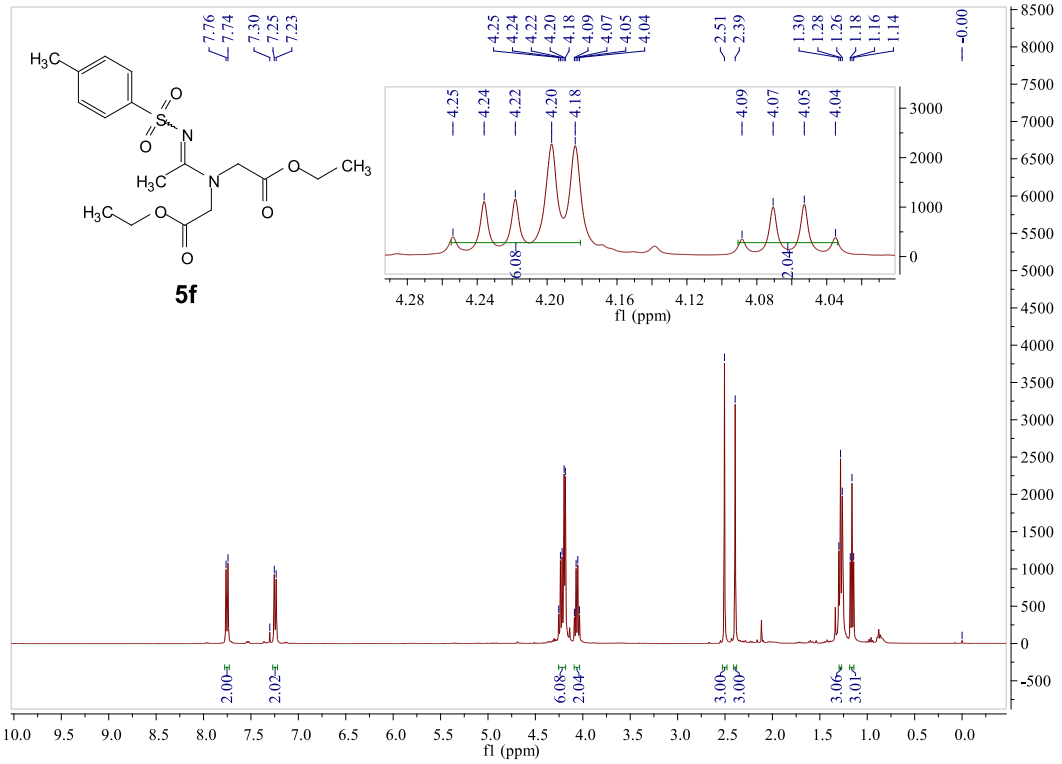

168.00
167.70
166.69
166.62
142.03
140.58
134.50
129.14
128.25
127.98
126.64
126.59
126.25
126.21
77.32
77.00
76.68
61.99
61.27
53.70
52.78
50.37
49.67
21.38
21.18
17.98
17.66
14.00
13.93
H3C
O
S
O
N
O
H3C
N
H3C
O
O
5c
135.12
134.50
129.14
129.08
128.98
128.93
128.68
128.51
128.25
127.98
126.64
126.59
126.25
126.21
fl (ppm)
fl (ppm)

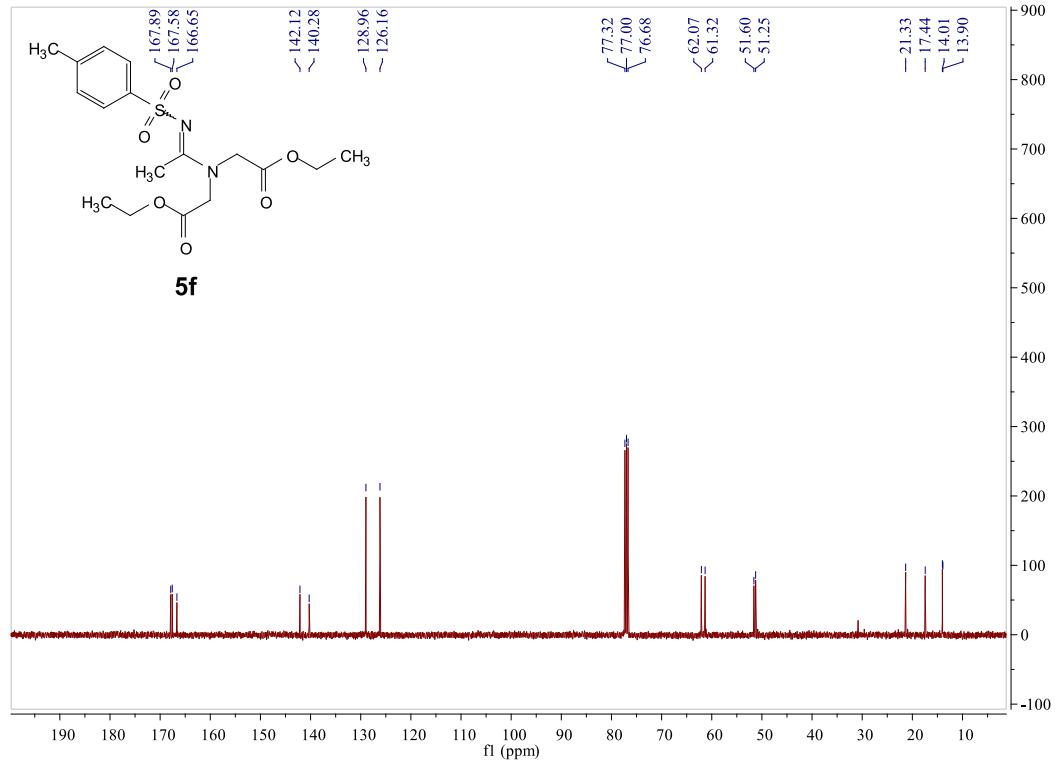

7.80
7.78
7.50
7.38
7.34
7.30
7.26
7.17
7.12
7.08
4.92
4.34
4.16
4.11
4.07
3.66
2.40
2.36
1.23
1.22
1.20
1.18
1.16
1.14
0.00
H3C
O
S
O
N
N
O
CH3
O
5d
0.66
2.03
10.66
5.22
0.66
2.01
0.67
2.04
2.05
0.73
1.00
3.00
3.00
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

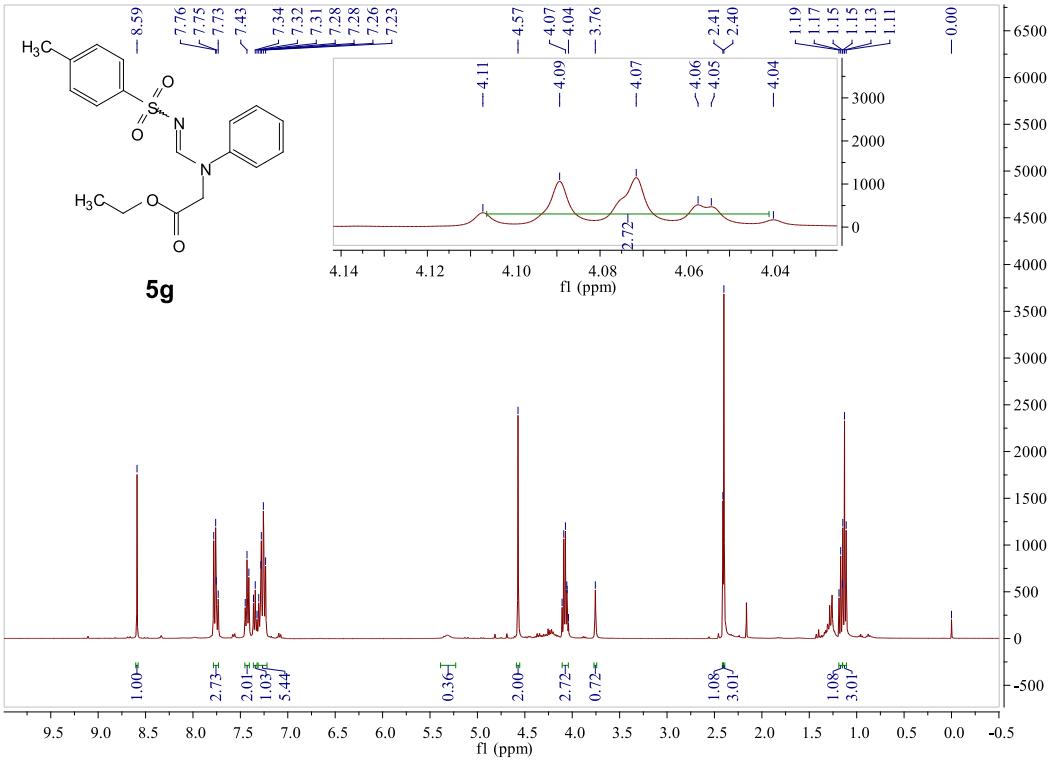

168.04
167.85
167.53
167.30
143.15
141.76
140.31
139.31
134.64
130.01
128.90
128.72
128.29
128.02
127.19
126.45
126.32
77.32
77.00
76.68
61.66
61.40
54.07
51.68
49.99
48.46
21.41
21.34
13.97
13.95
H3C
O
S
O
N
N
O
CH3
O
5d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

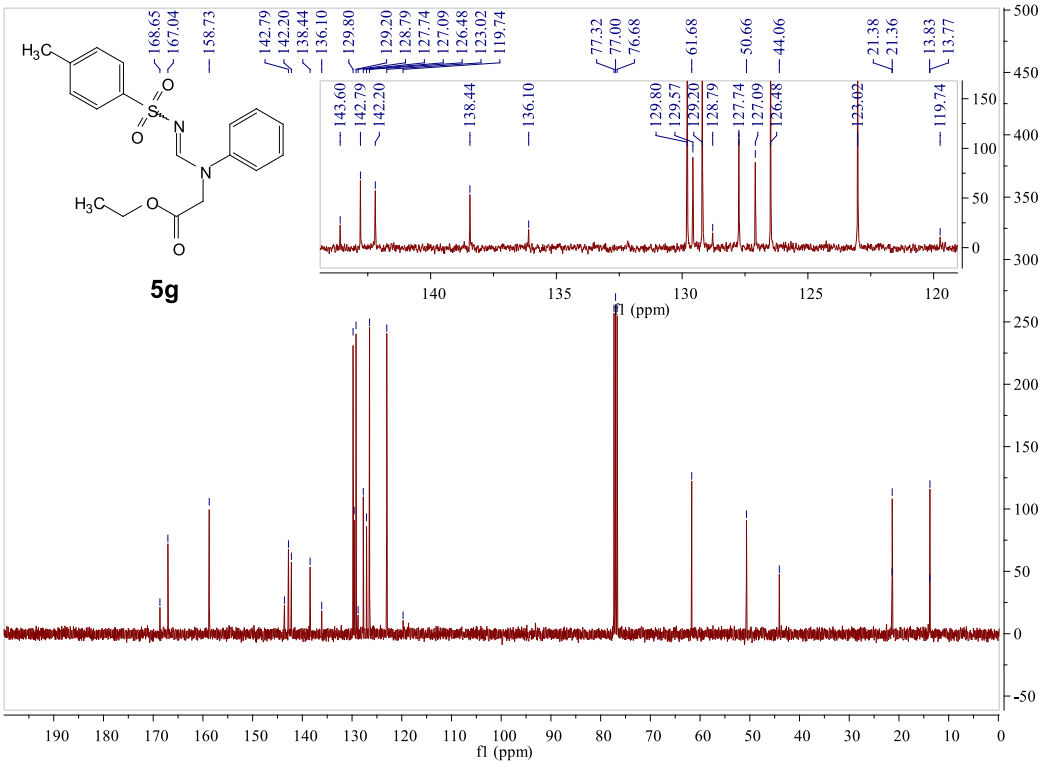

5e
f1 (ppm)

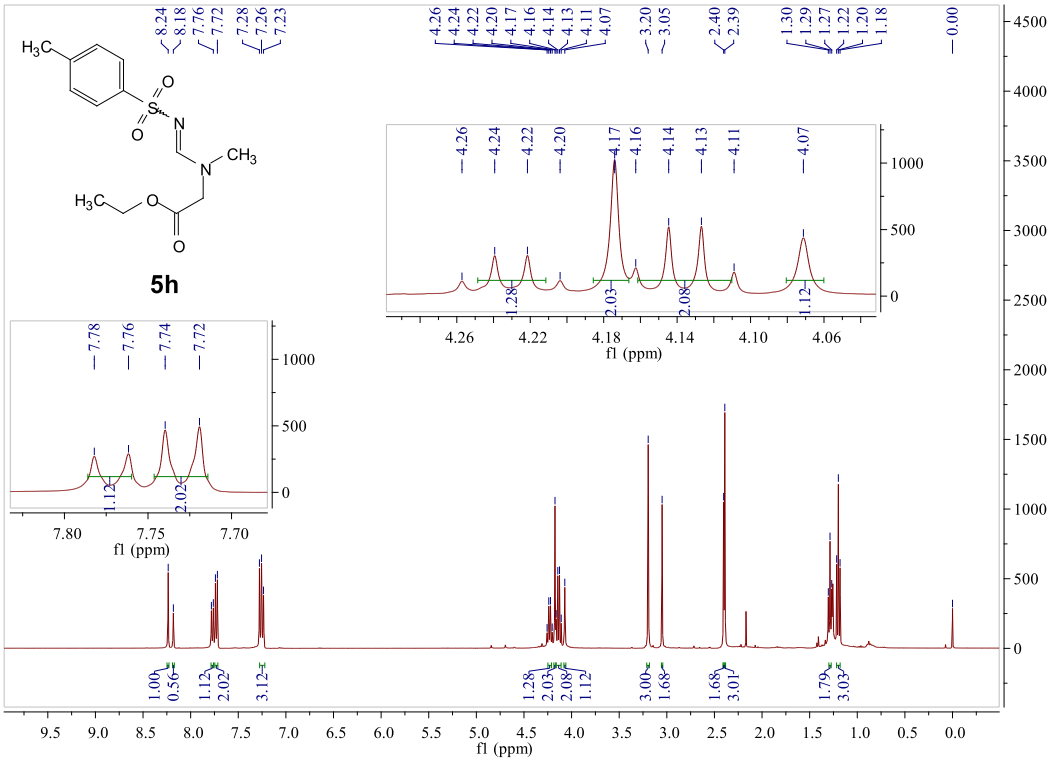

5e
f1 (ppm)

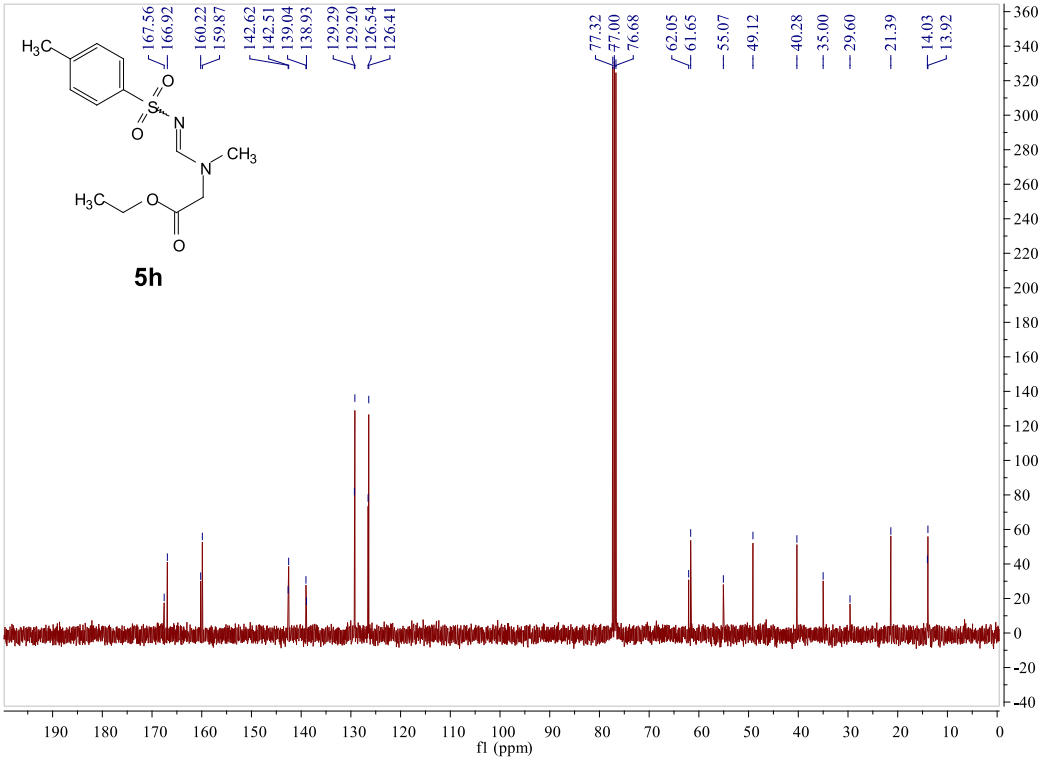

5f
fl (ppm)

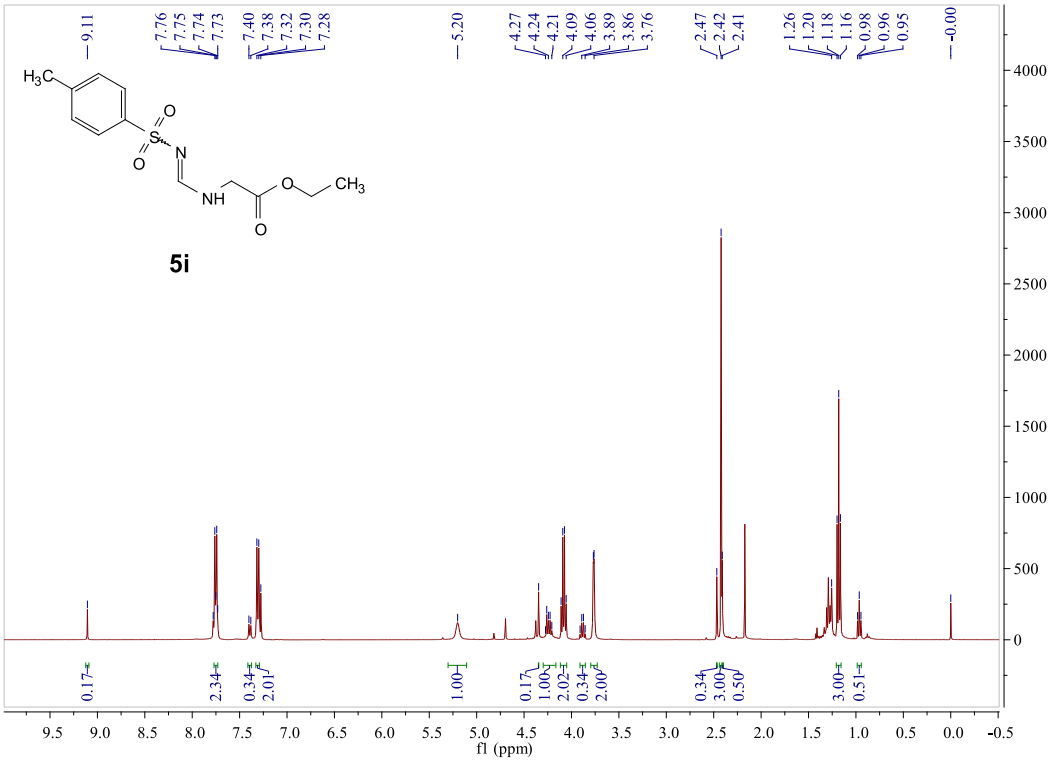

5f
fl (ppm)

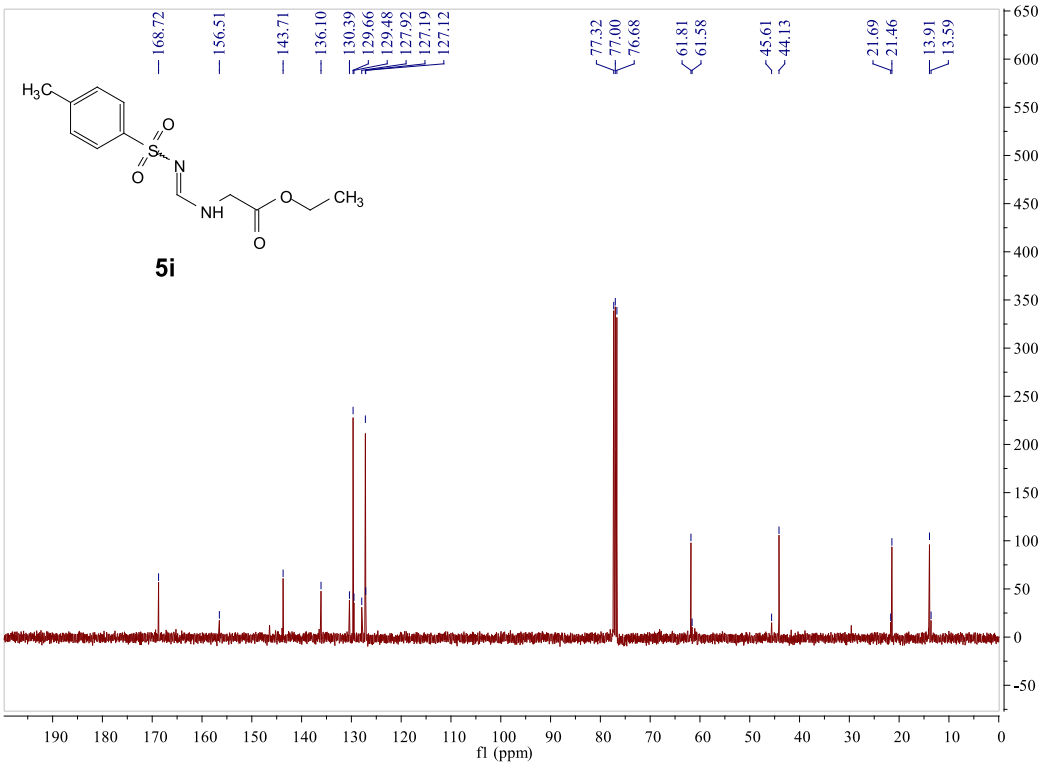

5g
fl (ppm)

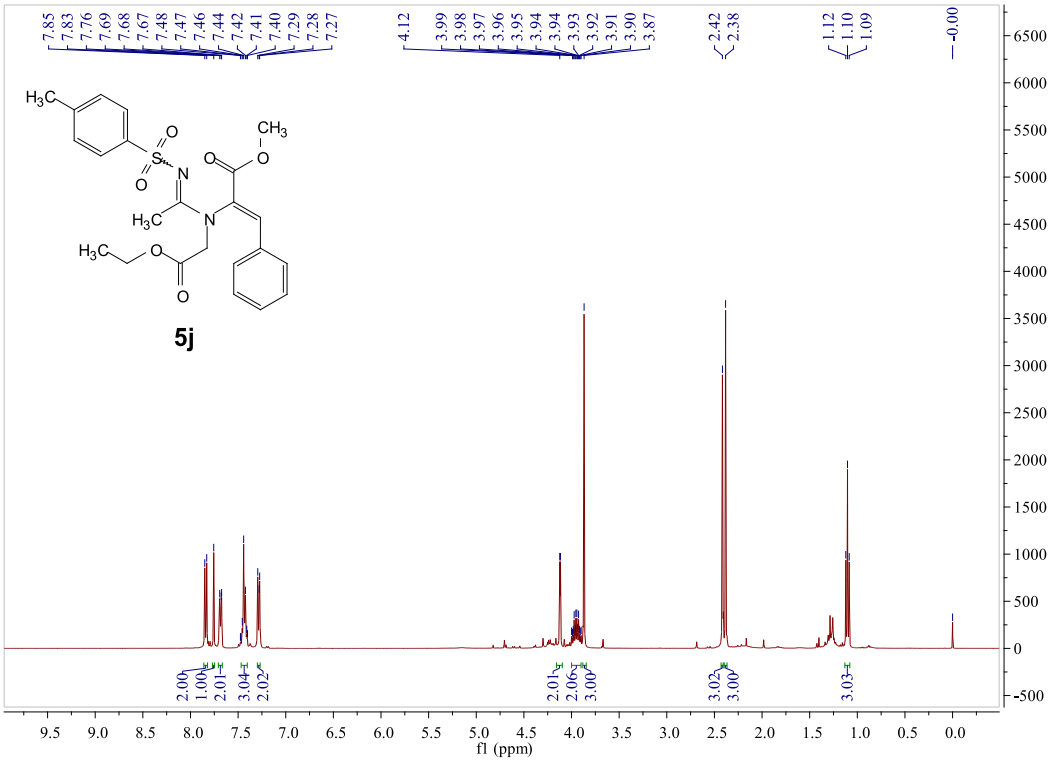

5g
fl (ppm)

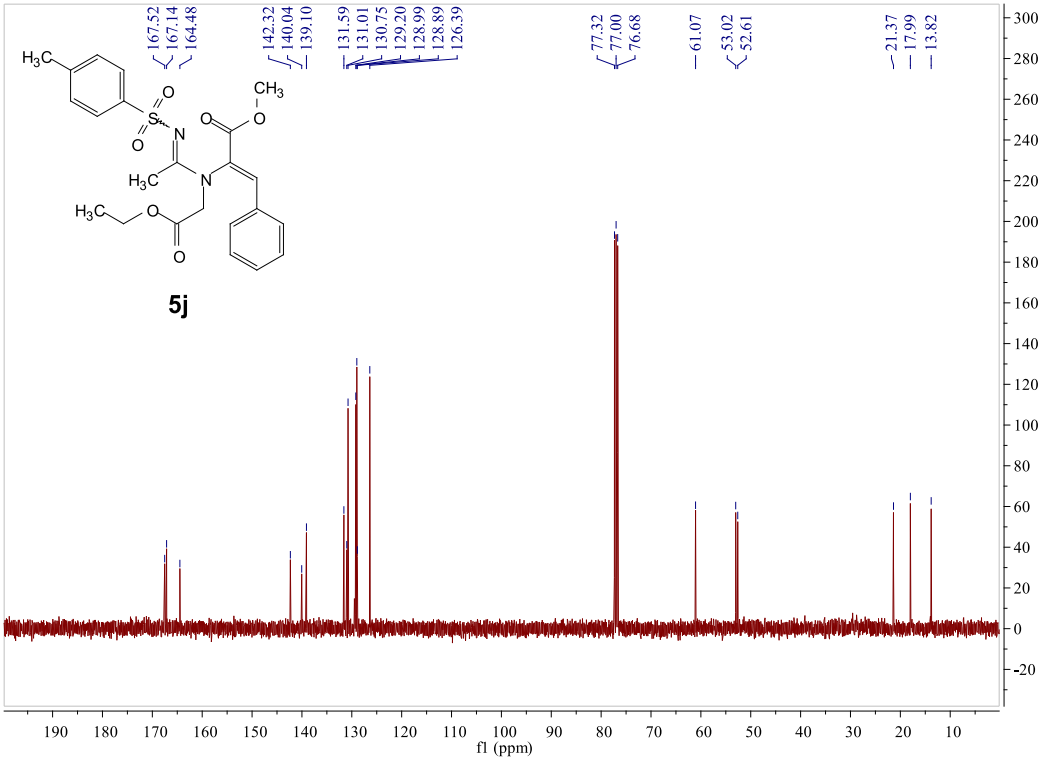

5h
fl (ppm)

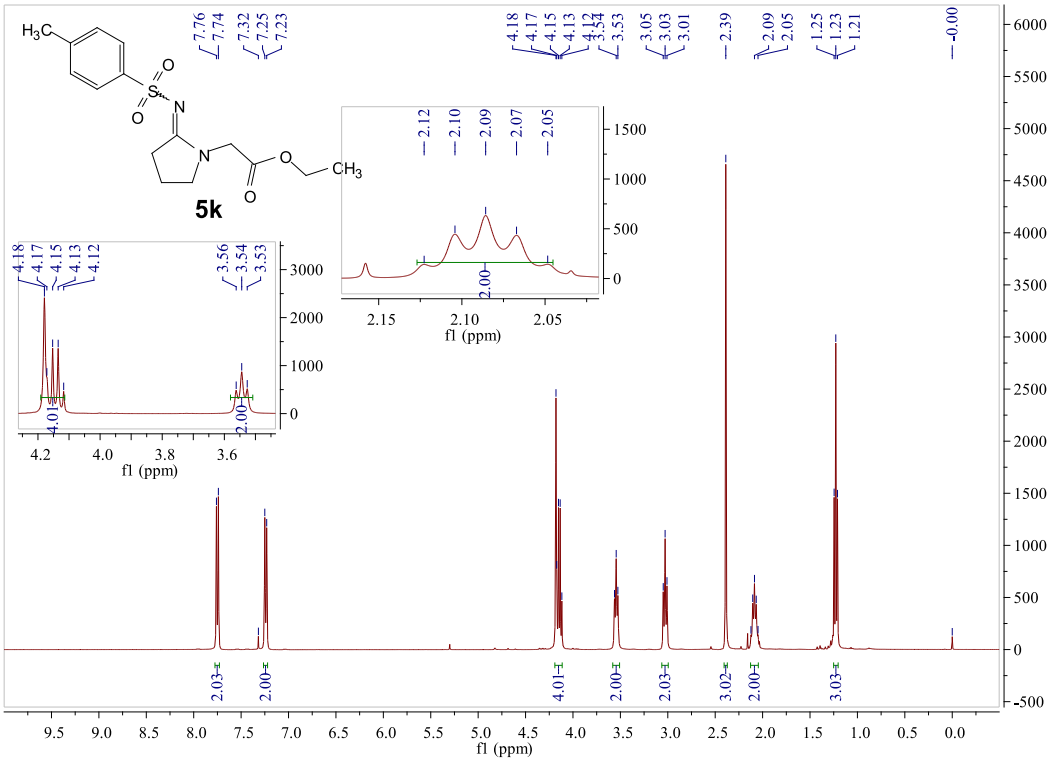

5h
fl (ppm)

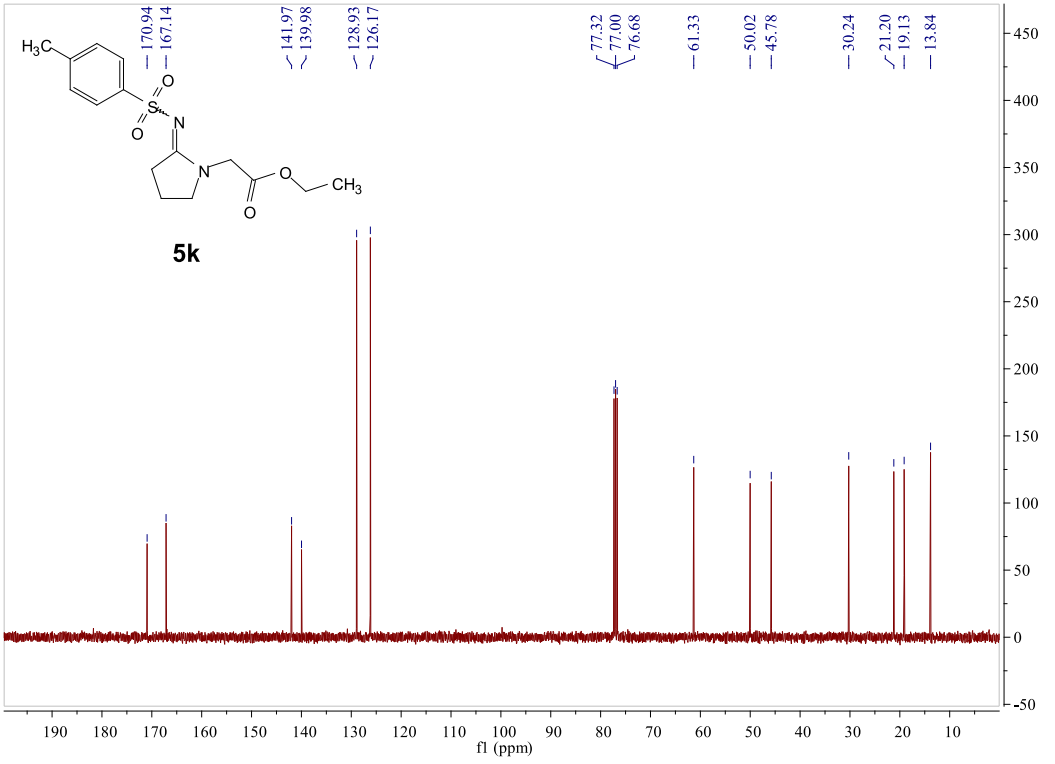

9.11
7.76
7.75
7.74
7.73
7.40
7.38
7.32
7.30
7.28
5.20
4.27
4.24
4.21
4.09
4.06
3.89
3.86
3.76
2.47
2.42
2.41
1.26
1.20
1.18
1.16
0.98
0.96
0.95
0.00
H3C
O
S
O
N
NH
O
O
CH3
5i
0.17
2.34
0.34
2.01
1.00
0.17
1.00
2.02
0.34
2.00
0.34
3.00
0.50
3.00
0.51
f1 (ppm)

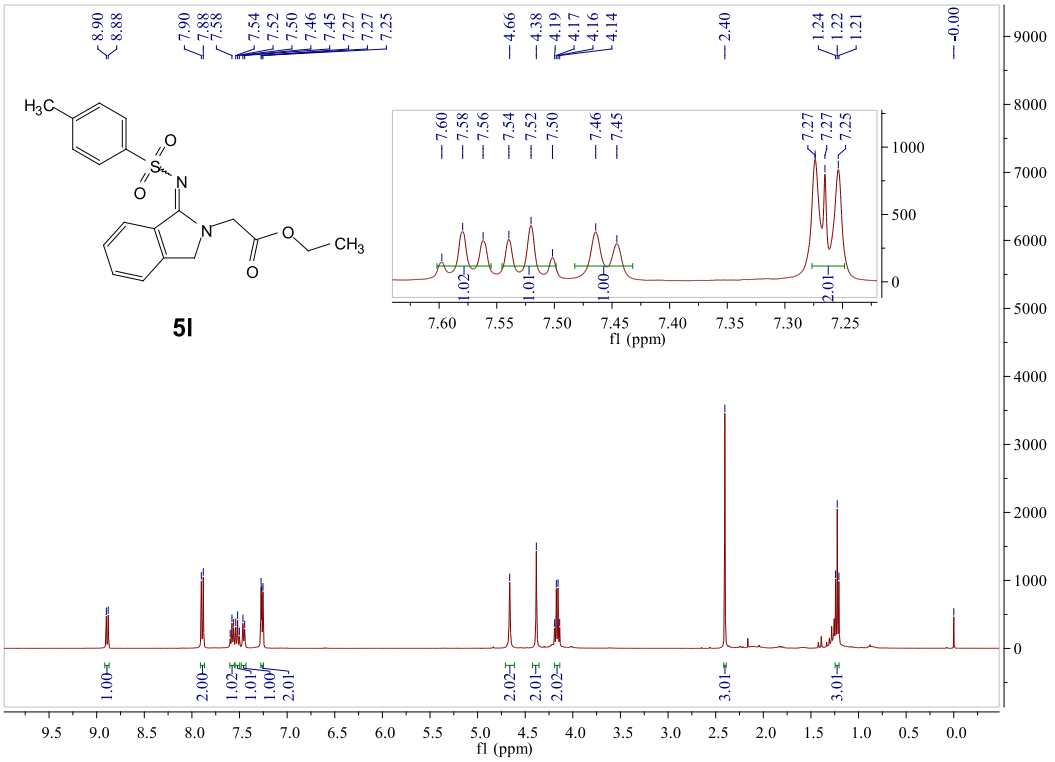

168.72
156.51
143.71
136.10
130.39
129.66
129.48
127.92
127.19
127.12
77.32
77.00
76.68
61.81
61.58
45.61
44.13
21.69
21.46
13.91
13.59
H3C
O
S
O
N
NH
O
O
CH3
5i
f1 (ppm)

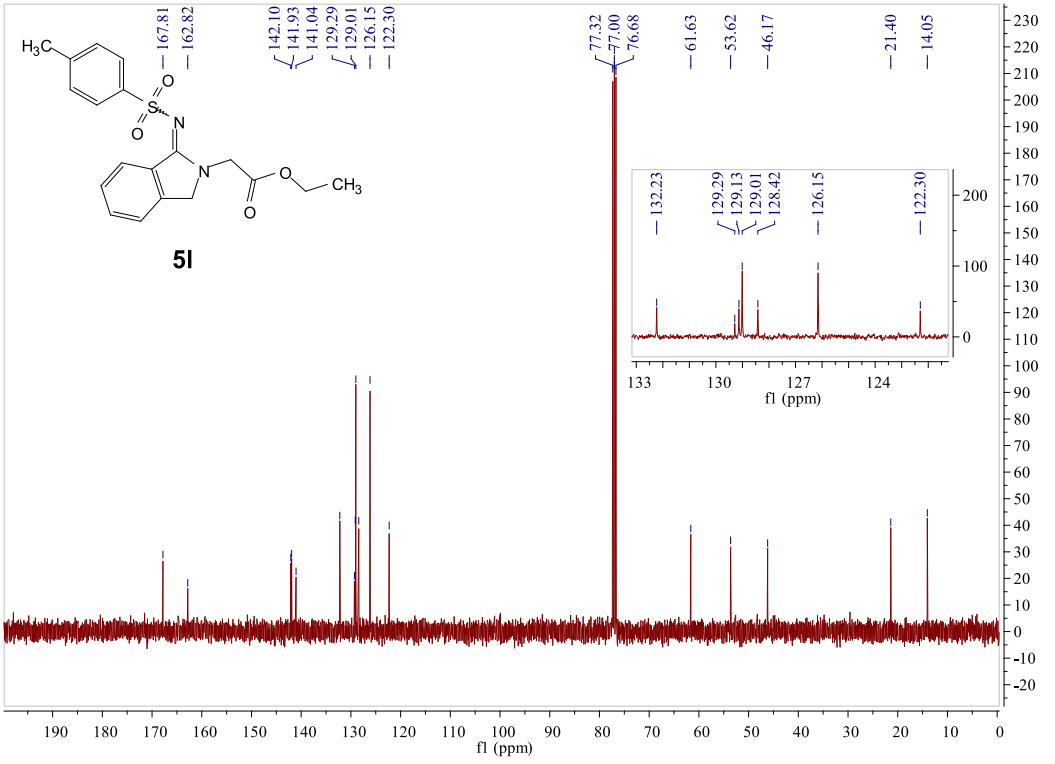

7.85
7.83
7.76
7.69
7.68
7.67
7.48
7.47
7.46
7.44
7.42
7.41
7.40
7.29
7.28
7.27
4.12
3.99
3.98
3.97
3.96
3.95
3.94
3.94
3.93
3.92
3.91
3.90
3.87
2.42
2.38
1.12
1.10
1.09
0.00
5j
2.00
1.00
2.01
3.04
2.02
2.01
2.06
3.00
3.02
3.00
3.03
fl (ppm)

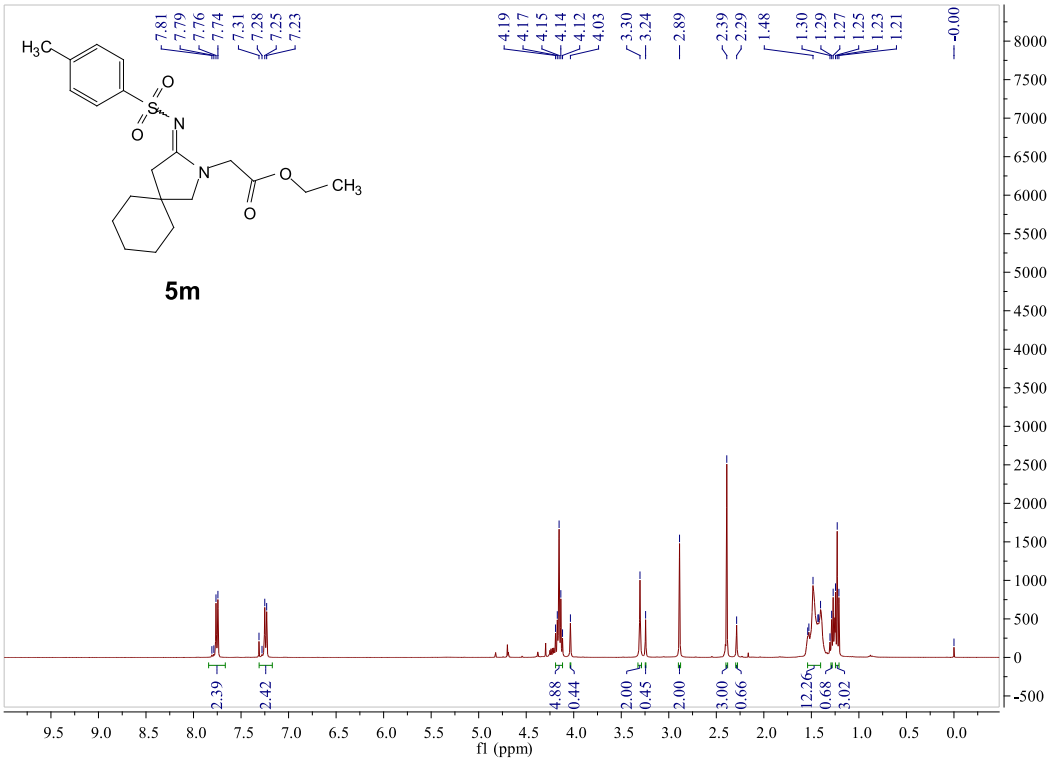

167.52
167.14
164.48
142.32
140.04
139.10
131.59
131.01
130.75
129.20
128.99
128.89
126.39
77.32
77.00
76.68
61.07
53.02
52.61
21.37
17.99
13.82
5j
fl (ppm)

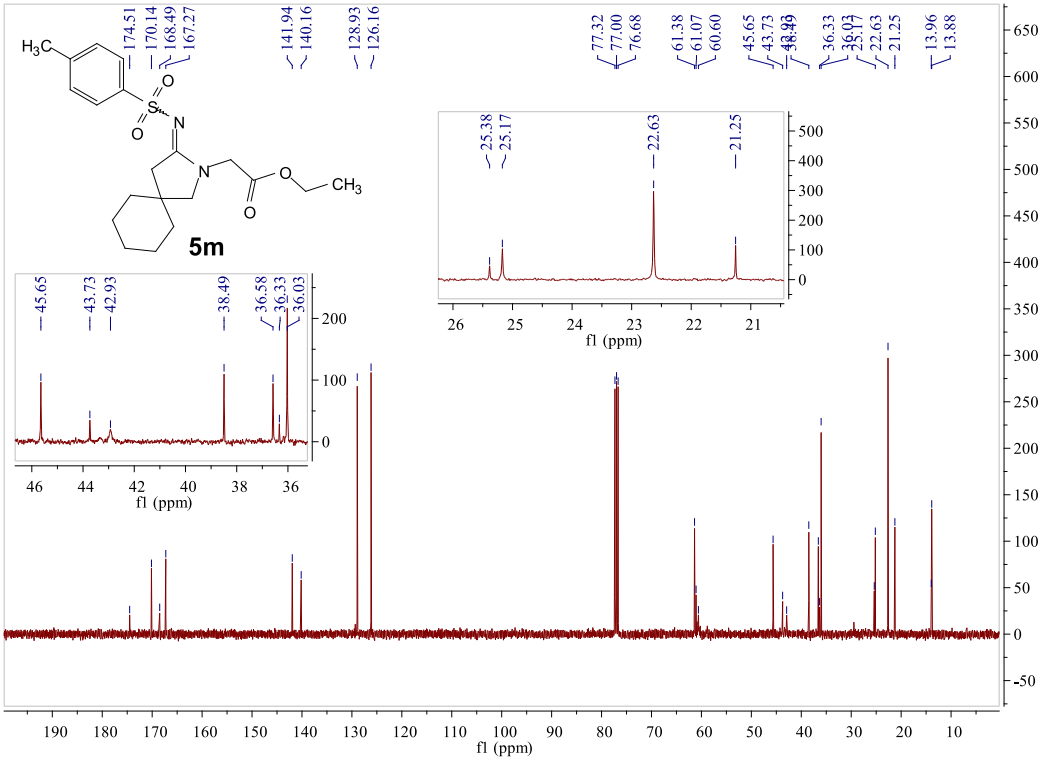

5k
fl (ppm)

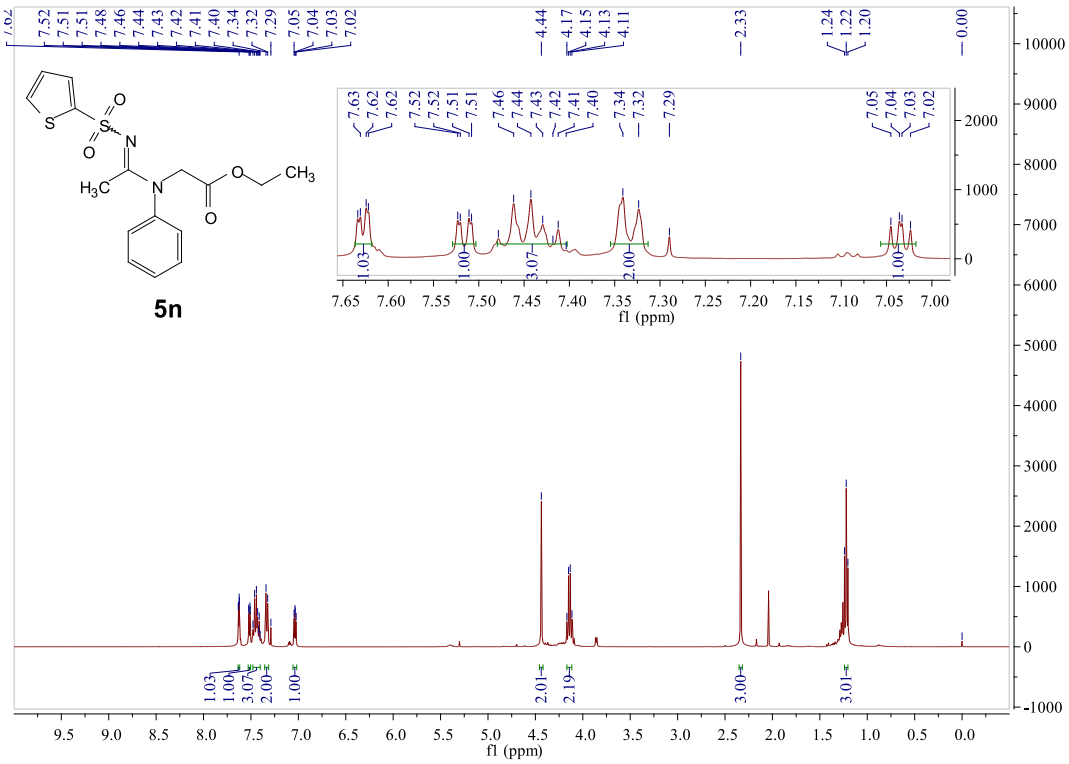

5k
fl (ppm)

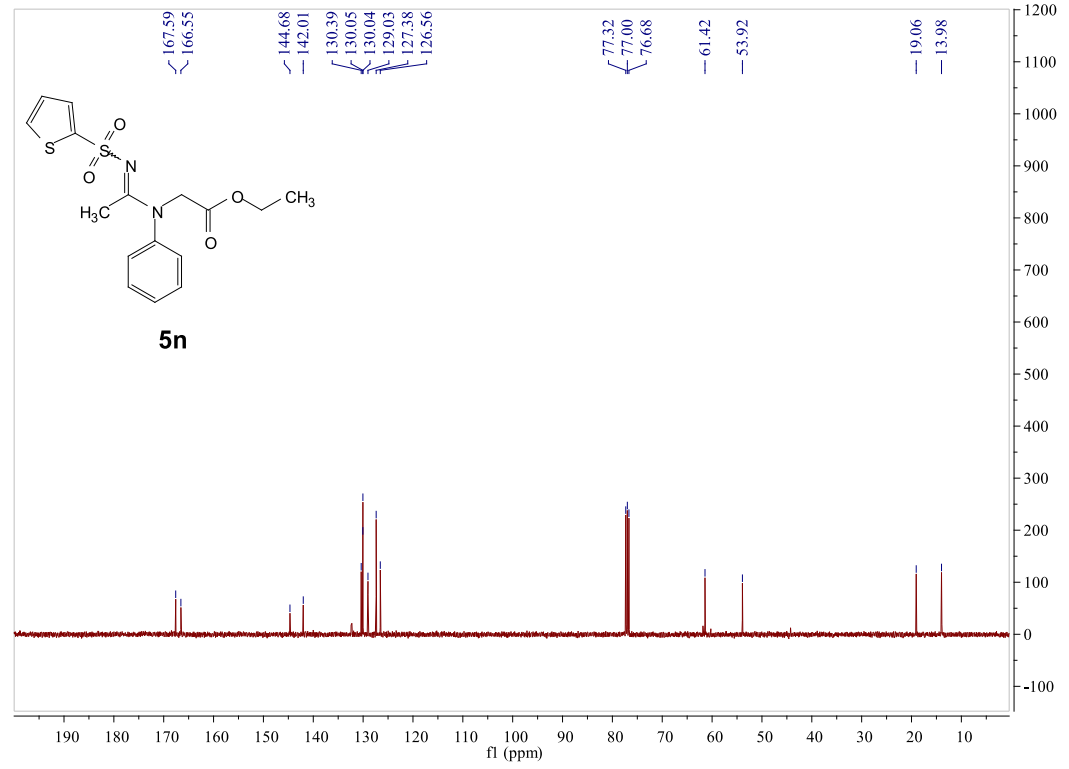

8.90
8.88
7.90
7.88
7.58
7.54
7.52
7.50
7.46
7.45
7.27
7.25
4.66
4.38
4.19
4.17
4.16
4.14
2.40
1.24
1.22
1.21
0.00
H3C
O
S
O
N
N
O
O
CH3
O
5l
7.60
7.58
7.56
7.54
7.52
7.50
7.46
7.45
7.27
7.27
7.25
1.02
1.01
1.00
2.01
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
1.00
2.00
1.02
1.01
1.00
2.01
2.02
2.01
2.02
3.01
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)

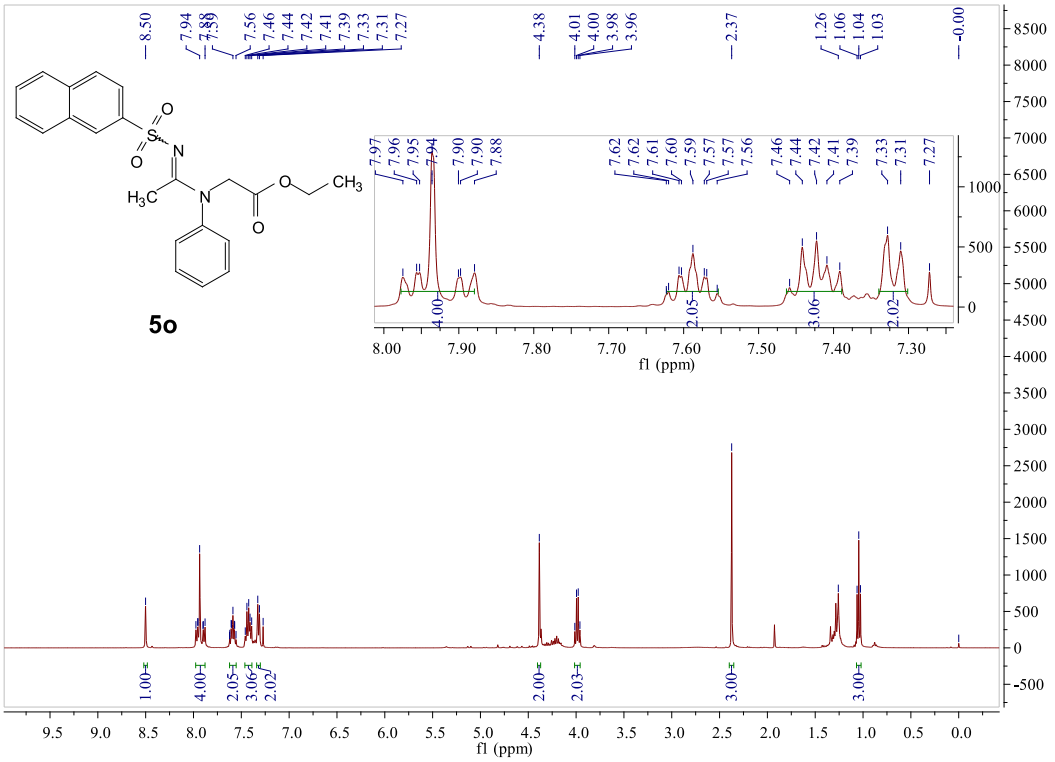

167.81
162.82
142.10
141.93
141.04
129.29
129.01
126.15
122.30
77.32
77.00
76.68
61.63
53.62
46.17
21.40
14.05
H3C
O
S
O
N
N
O
O
CH3
O
5l
132.23
129.29
129.13
129.01
128.42
126.15
122.30
133 130 127 124
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

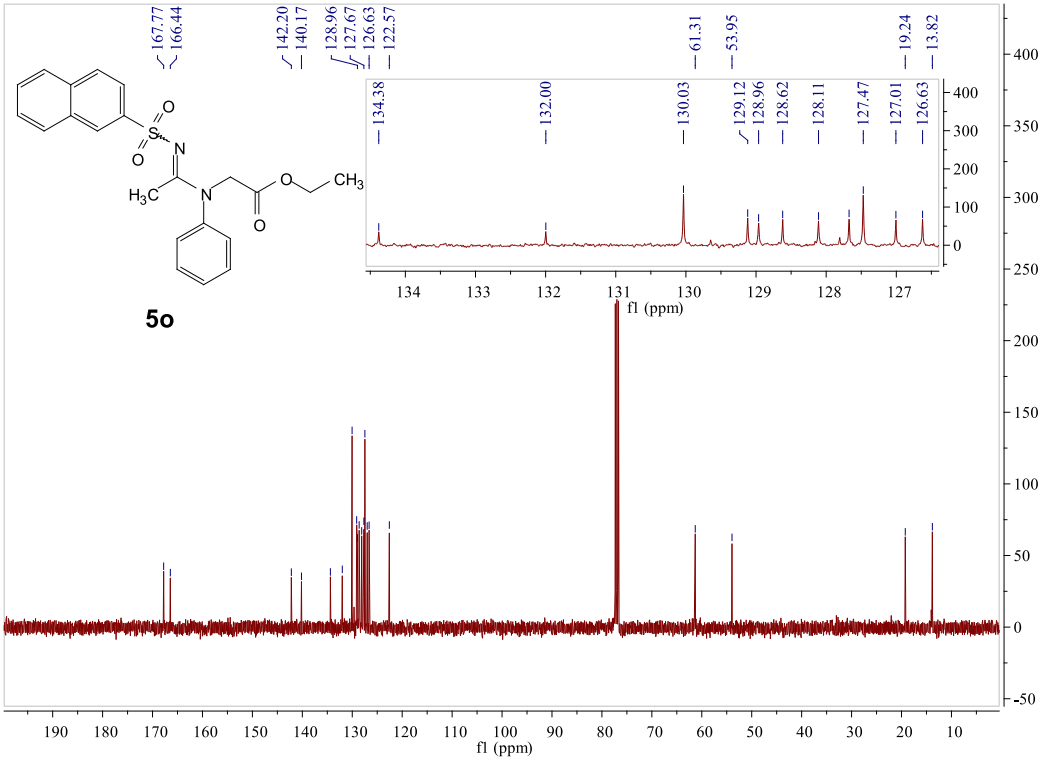

7.81
7.79
7.76
7.74
7.31
7.28
7.25
7.23
4.19
4.17
4.15
4.14
4.12
4.03
3.30
3.24
2.89
2.39
2.29
1.48
1.30
1.29
1.27
1.25
1.23
1.21
0.00
5m
2.39
2.42
4.88
0.44
2.00
0.45
2.00
3.00
0.66
12.26
0.68
3.02
f1 (ppm)

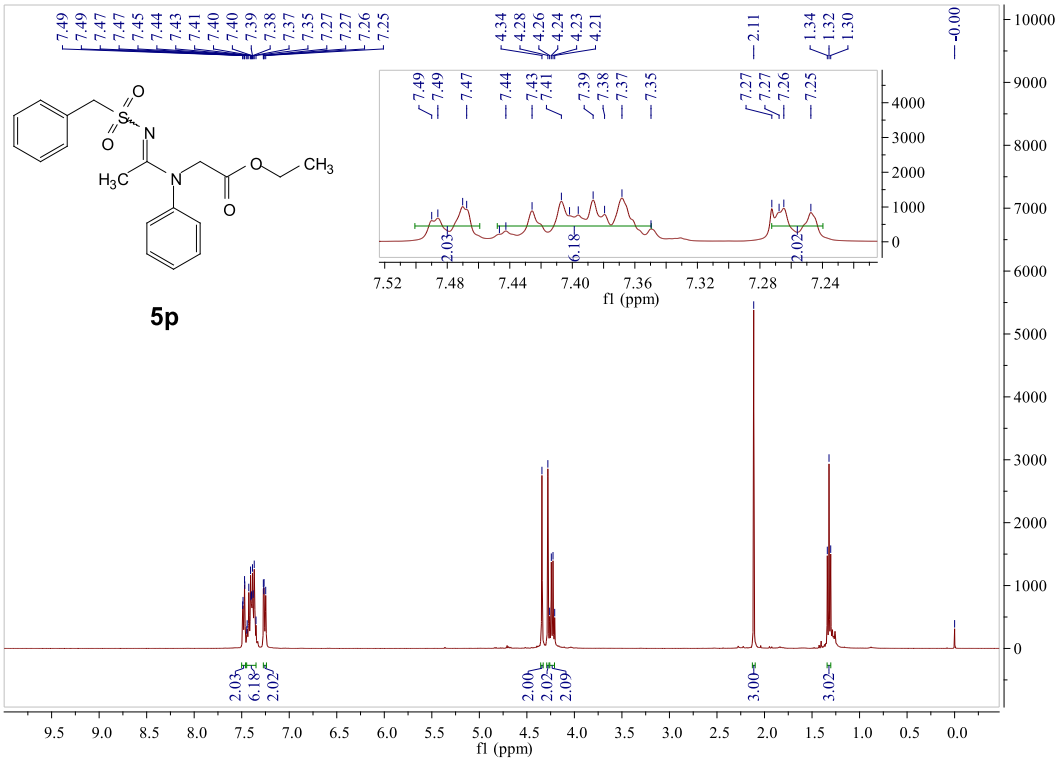

174.51
170.14
168.49
167.27
141.94
140.16
128.93
126.16
77.32
77.00
76.68
61.38
61.07
60.60
45.65
43.73
42.93
38.49
36.33
36.07
36.03
25.38
25.17
22.63
21.25
13.96
13.88
5m
f1 (ppm)

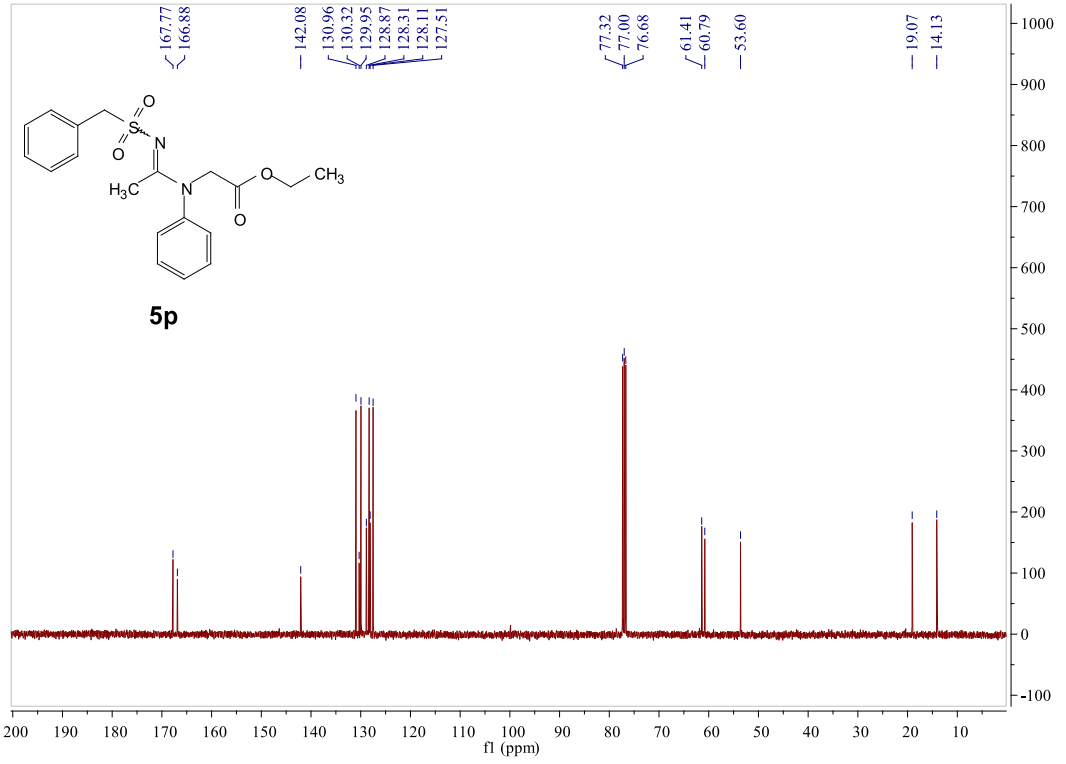

5n
fl (ppm)

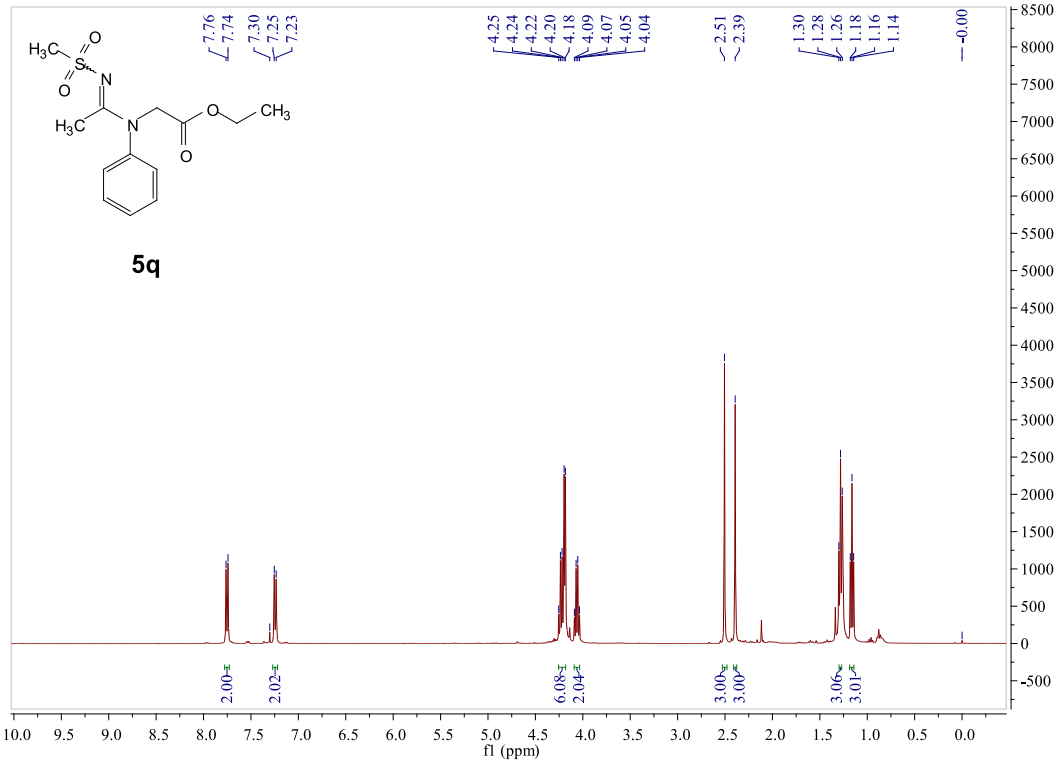

5n
fl (ppm)


5o
fl (ppm)

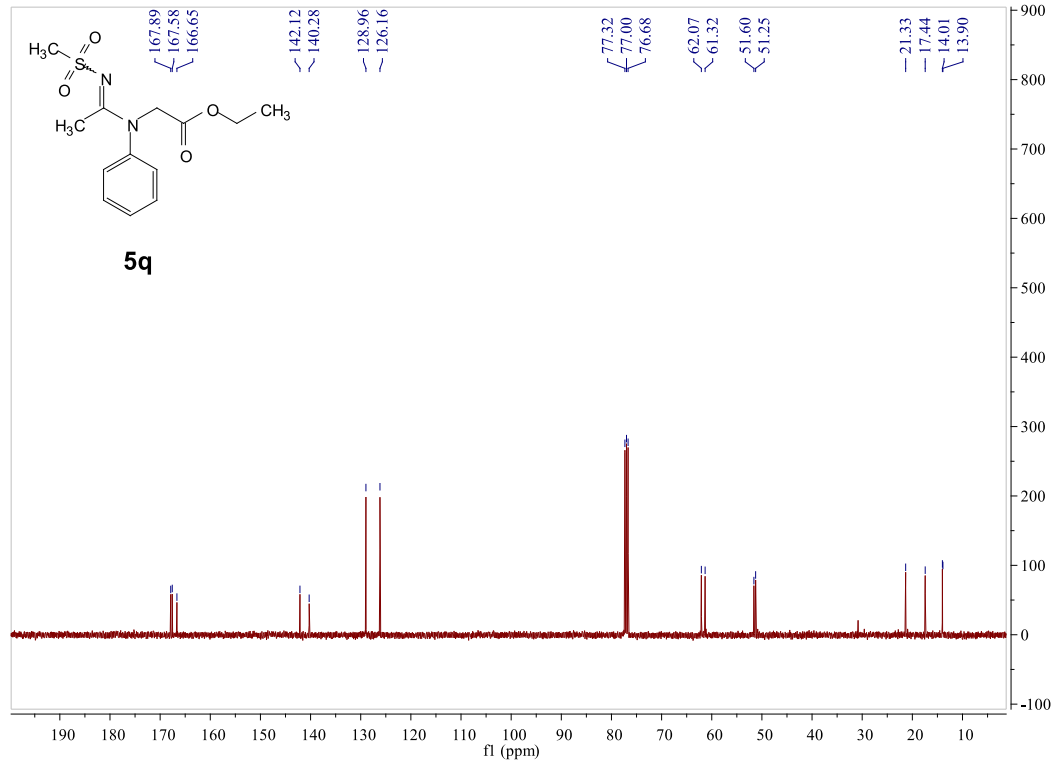

5o
fl (ppm)


5p
fl (ppm)

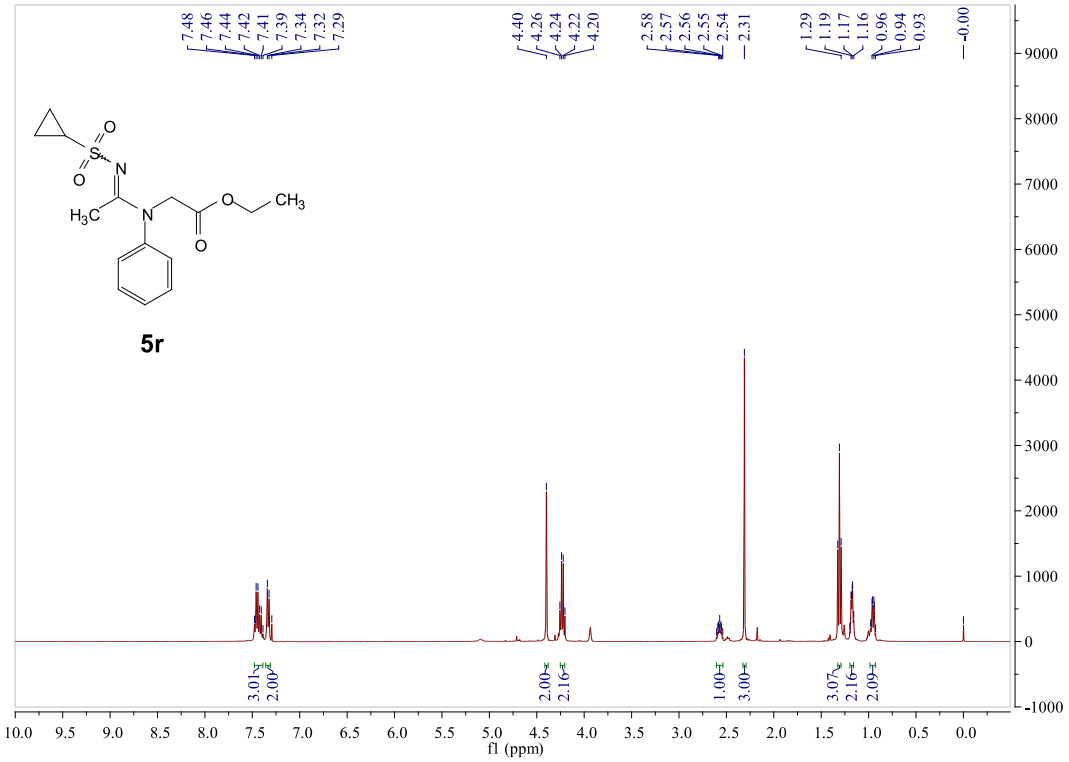

5p
fl (ppm)


7.76
7.74
7.30
7.25
7.23
4.25
4.24
4.22
4.20
4.18
4.09
4.07
4.05
4.04
2.51
2.39
1.30
1.28
1.26
1.18
1.16
1.14
0.00
2.00
2.02
6.08
2.04
3.00
3.00
3.06
3.01
fl (ppm)

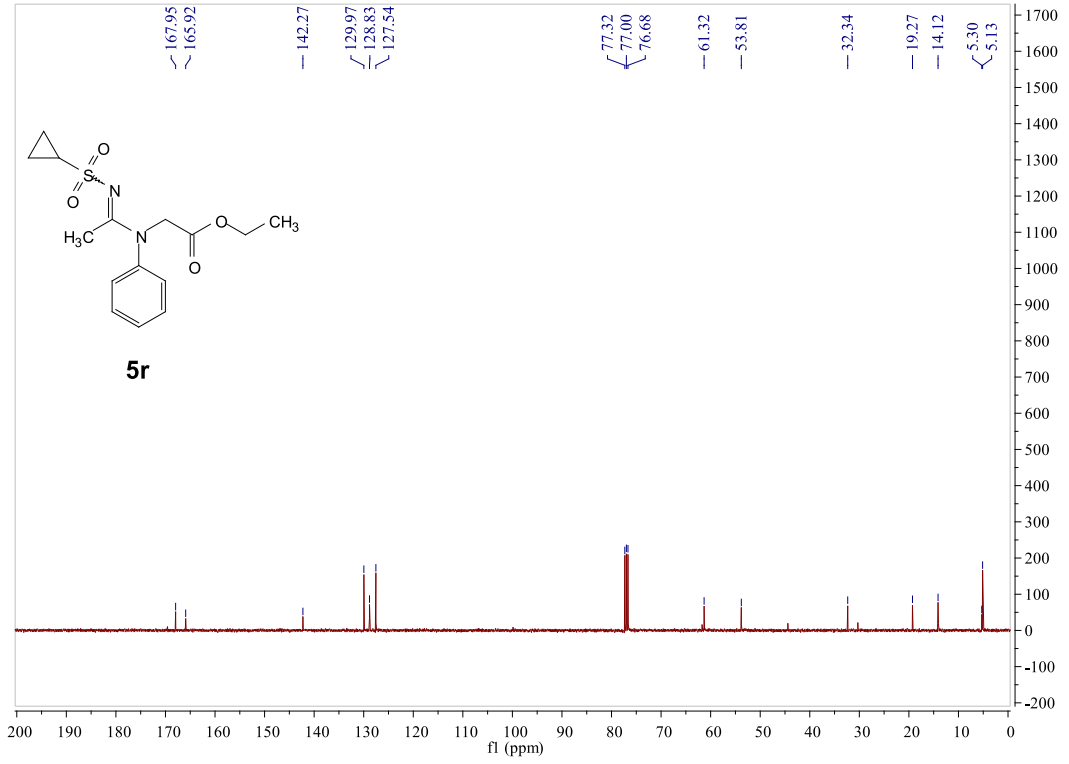
5q


167.89
167.58
166.65
142.12
140.28
128.96
126.16
77.32
77.00
76.68
62.07
61.32
51.60
51.25
21.33
17.44
14.01
13.90
fl (ppm)

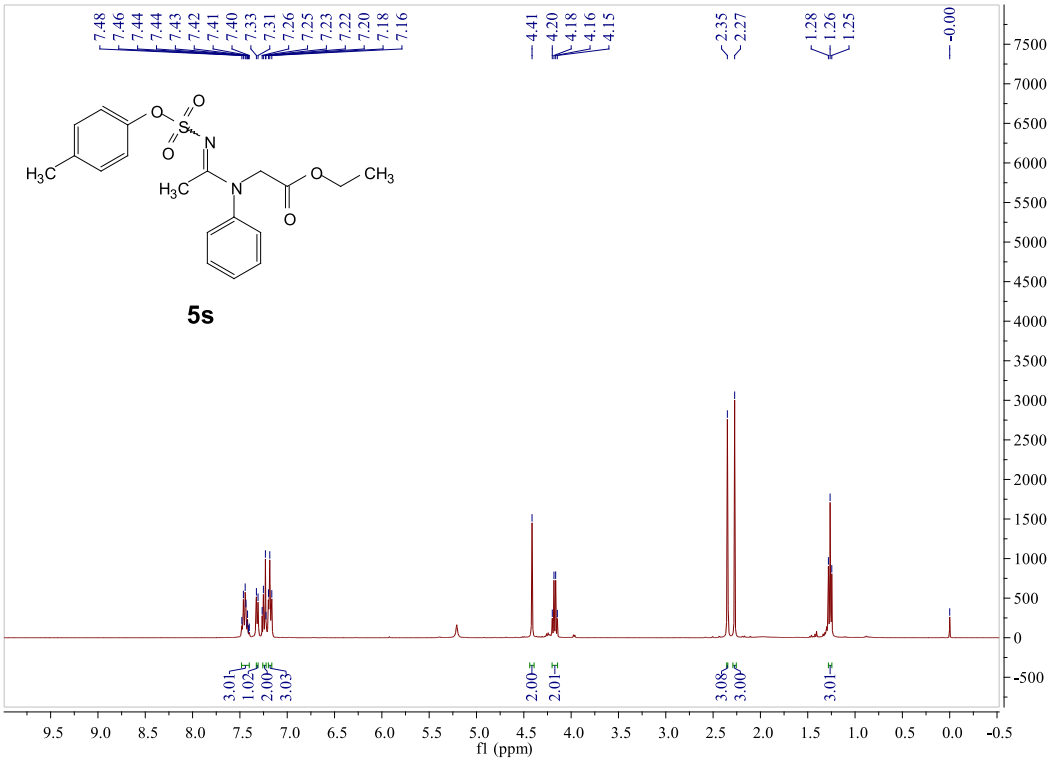
5q


7.48
7.46
7.44
7.42
7.41
7.39
7.34
7.32
7.29
4.40
4.26
4.24
4.22
4.20
2.58
2.57
2.56
2.55
2.54
2.31
1.29
1.19
1.17
1.16
0.96
0.94
0.93
0.00
3.01
2.00
2.00
2.16
1.00
3.00
3.07
2.16
2.09
fl (ppm)

5r


167.95
165.92
142.27
129.97
128.83
127.54
77.32
77.00
76.68
61.32
53.81
32.34
19.27
14.12
5.30
5.13
fl (ppm)

5r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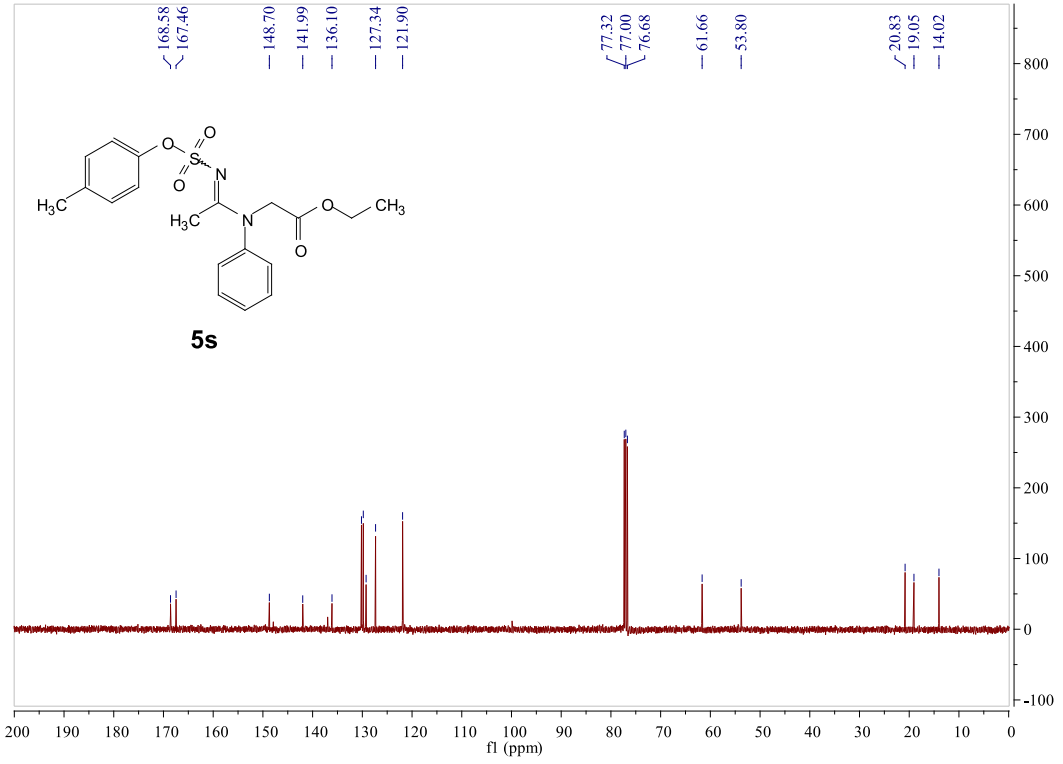
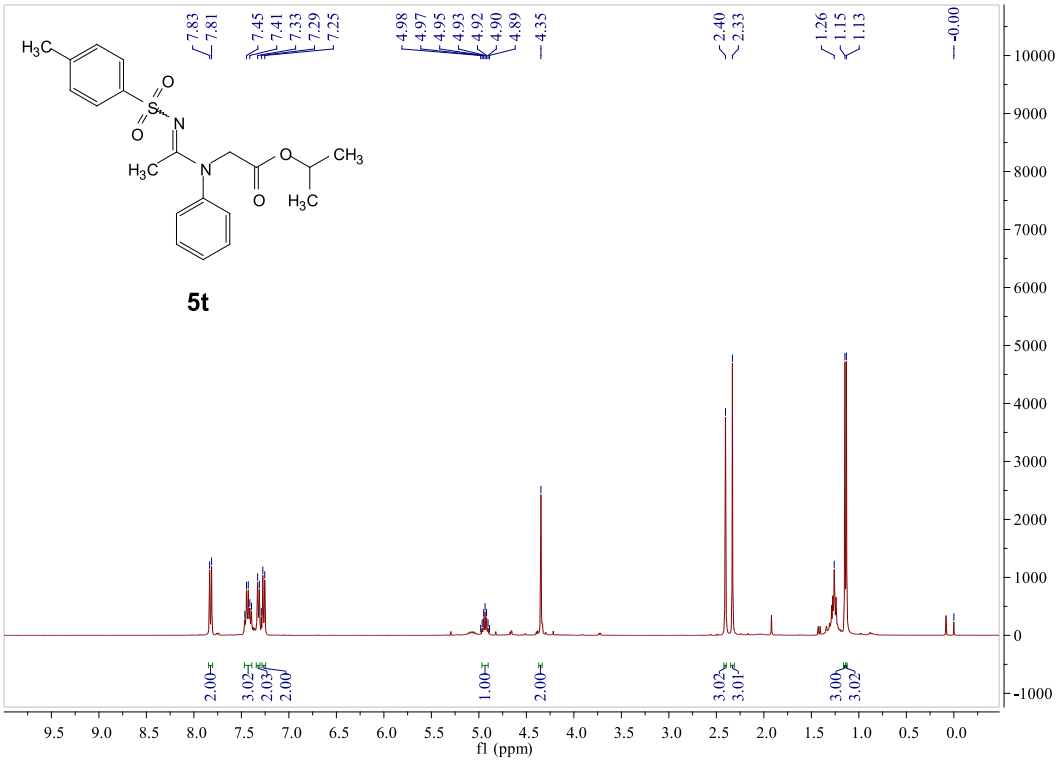
7.46
7.44
7.44
7.43
7.42
7.41
7.40
7.33
7.31
7.26
7.25
7.23
7.22
7.20
7.18
7.16
4.41
4.20
4.18
4.16
4.15
2.35
2.27
1.28
1.26
1.25
0.00
5s
3.01
1.02
2.00
3.03
2.00
2.01
3.08
3.00
3.01
fl (ppm)


168.58
167.46
148.70
141.99
136.10
127.34
121.90
77.32
77.00
76.68
61.66
53.80
20.83
19.05
14.02
5s
fl (ppm)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7.81
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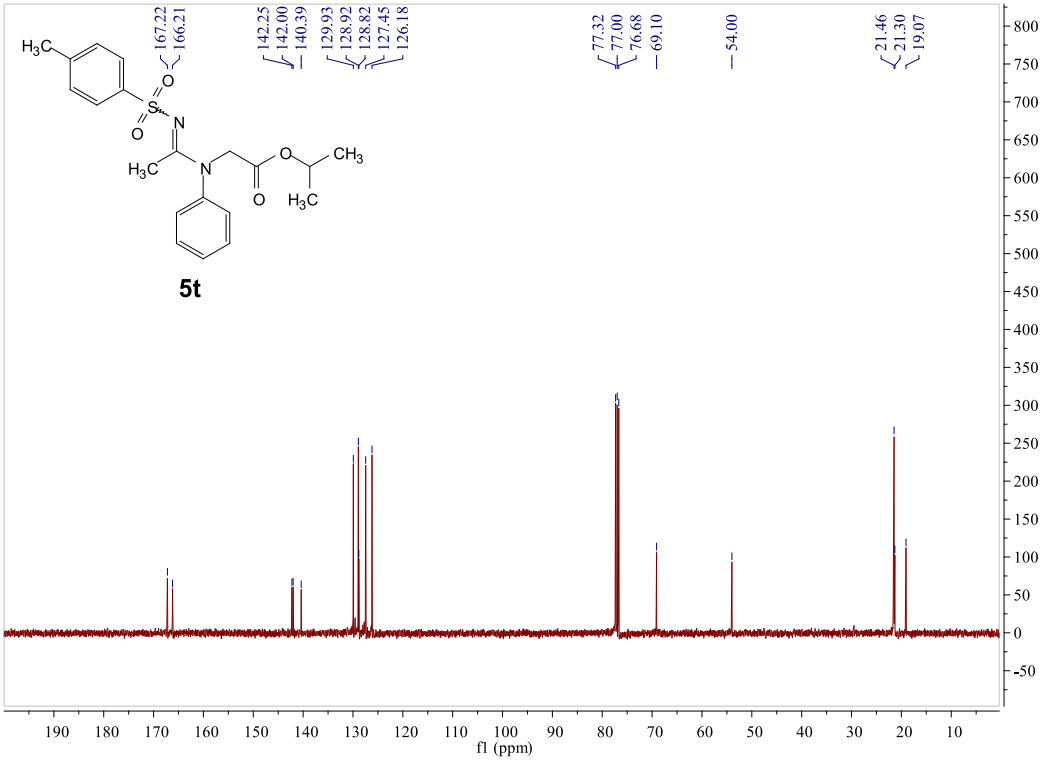
7.41
7.33
7.29
7.25
4.98
4.97
4.95
4.93
4.92
4.90
4.89
4.35
2.40
2.33
1.26
1.15
1.13
0.00
2.00
3.02
2.03
2.00
1.00
2.00
3.02
3.01
3.00
3.02
fl (ppm)

5t


167.22
166.21
142.25
142.00
140.39
129.93
128.92
128.82
127.45
126.18
77.32
77.00
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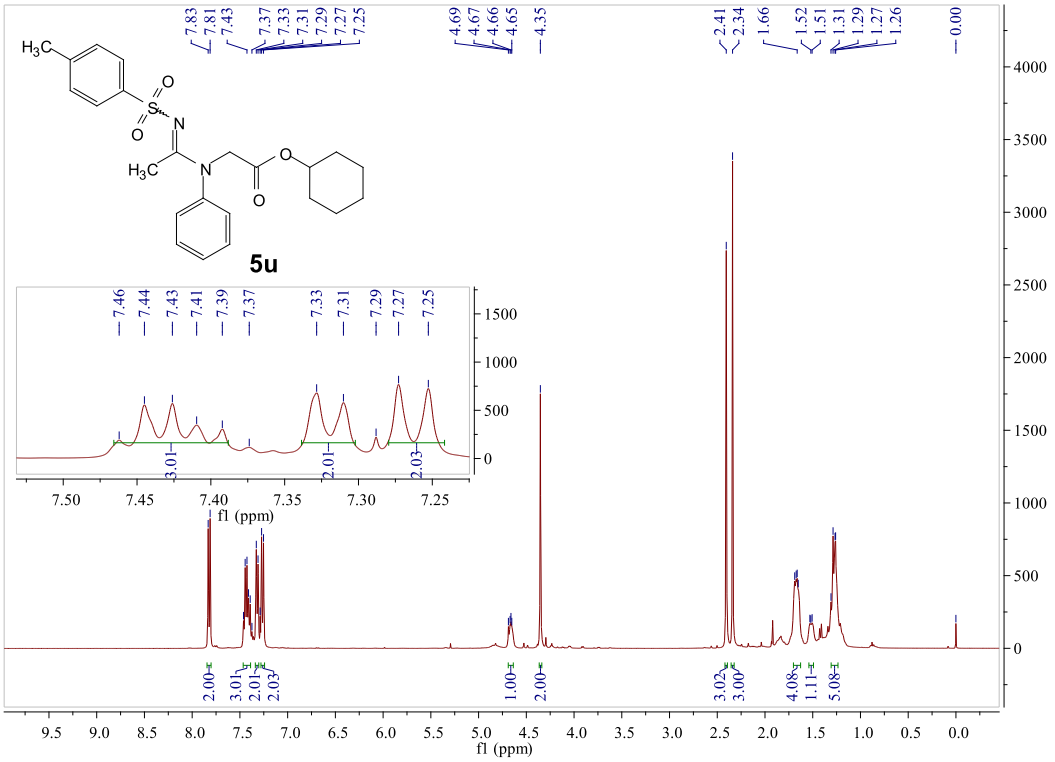
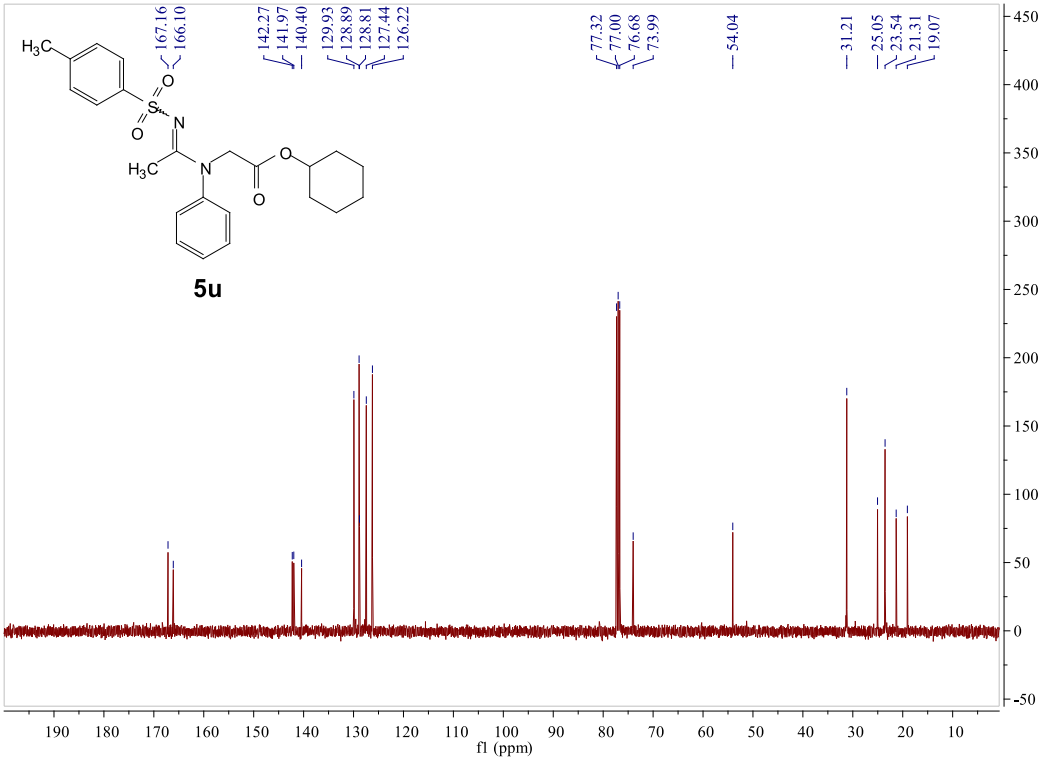
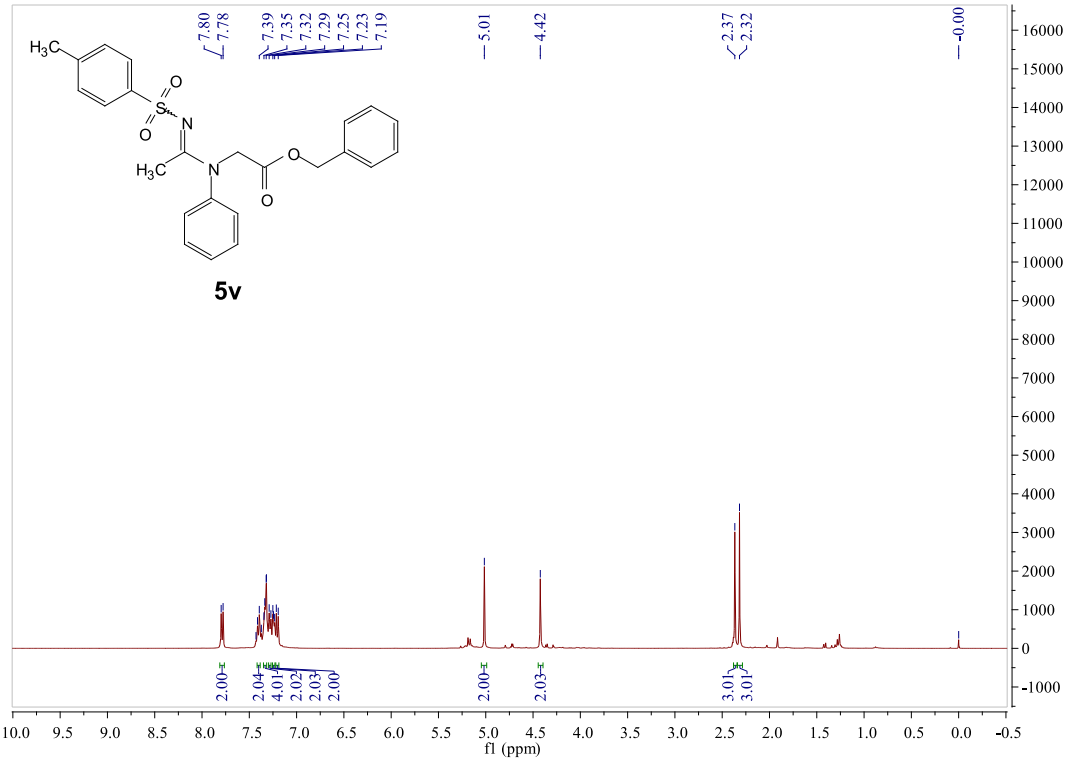
69.10
54.00
21.46
21.30
19.07
fl (ppm)

5t


5u
fl (ppm)


5u
fl (ppm)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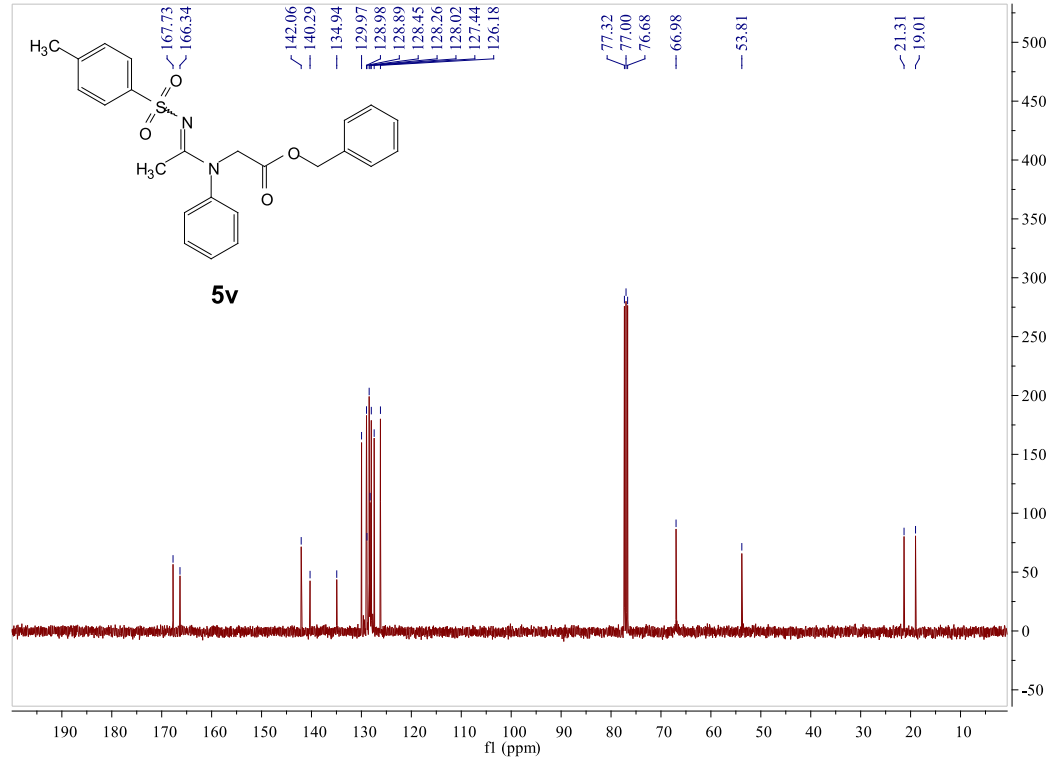
7.32
7.29
7.25
7.23
7.19
5.01
4.42
2.37
2.32
0.00
5v
2.00
2.04
4.01
2.02
2.03
2.00
2.00
2.03
3.01
3.01
fl (ppm)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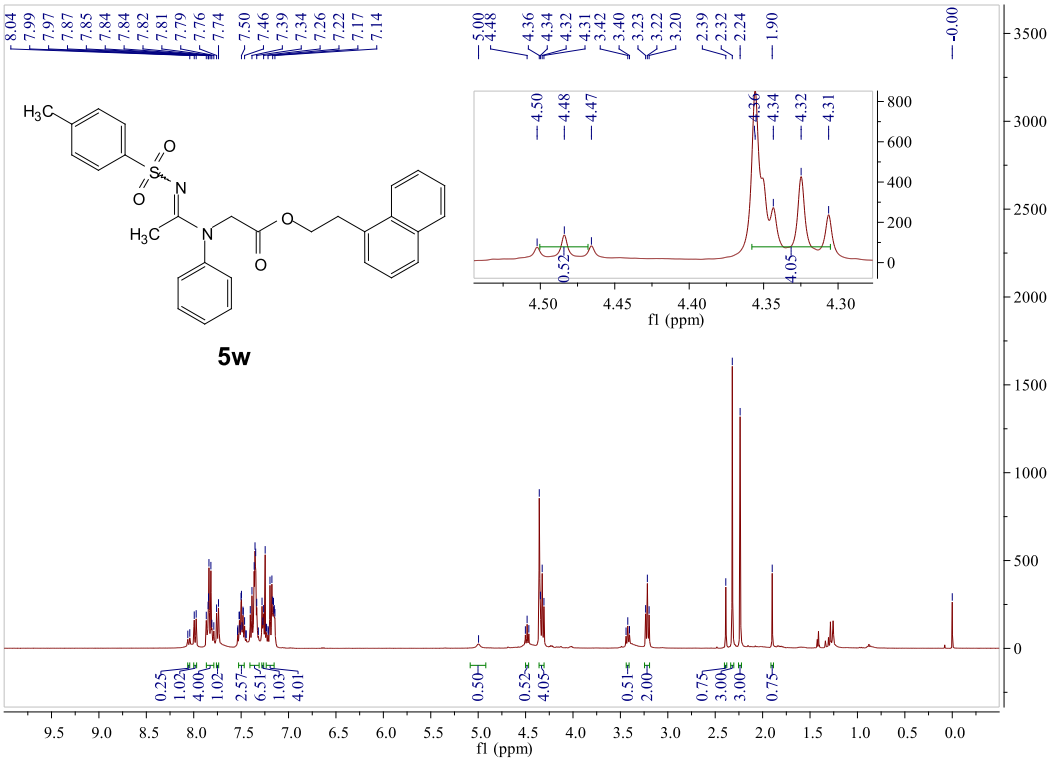
76.68
66.98
53.81
21.31
19.01
5v
fl (ppm)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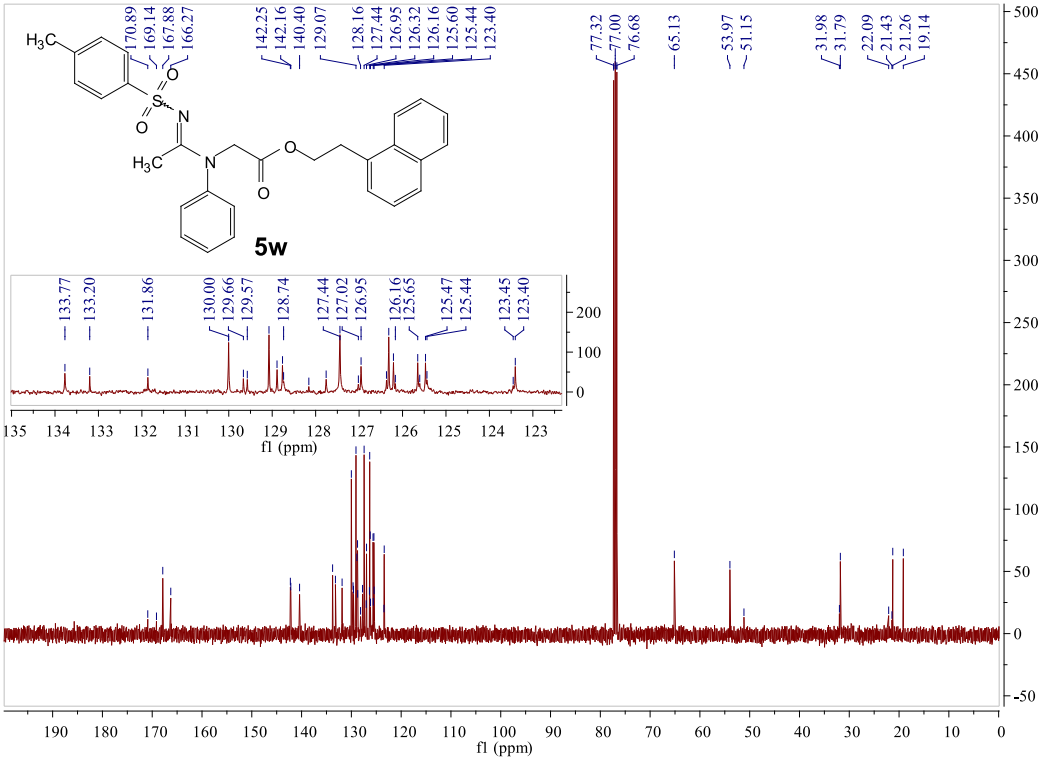
fl (ppm)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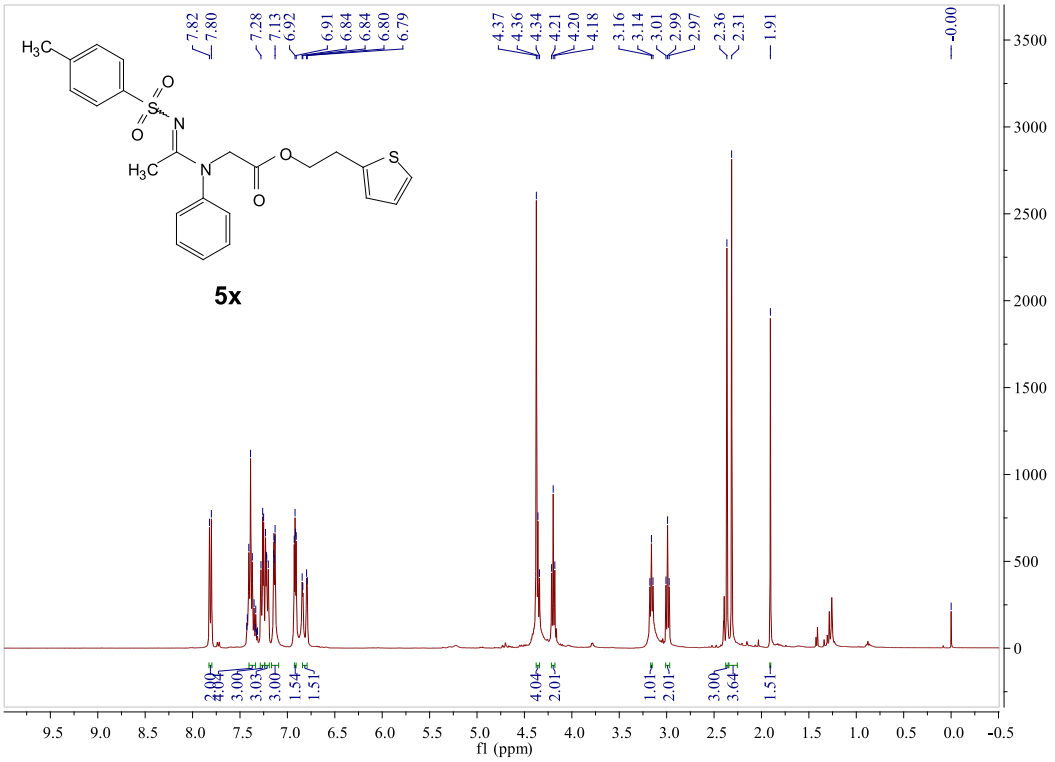
fl (ppm)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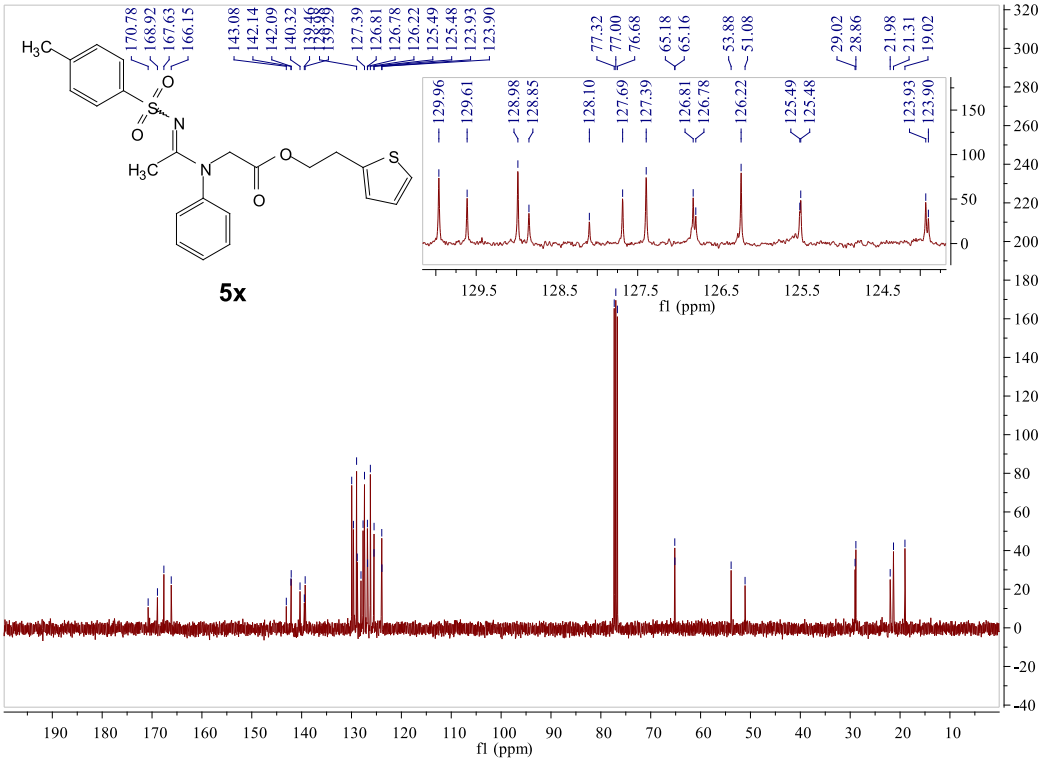
fl (ppm)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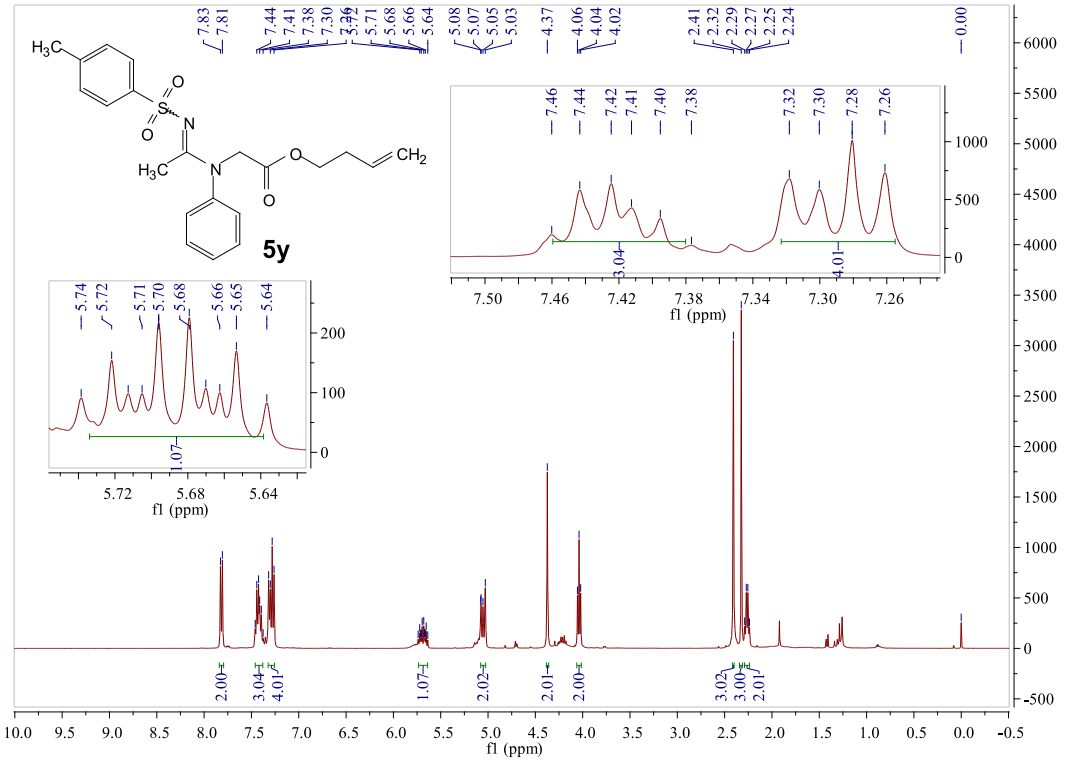
fl (ppm)
fl (ppm)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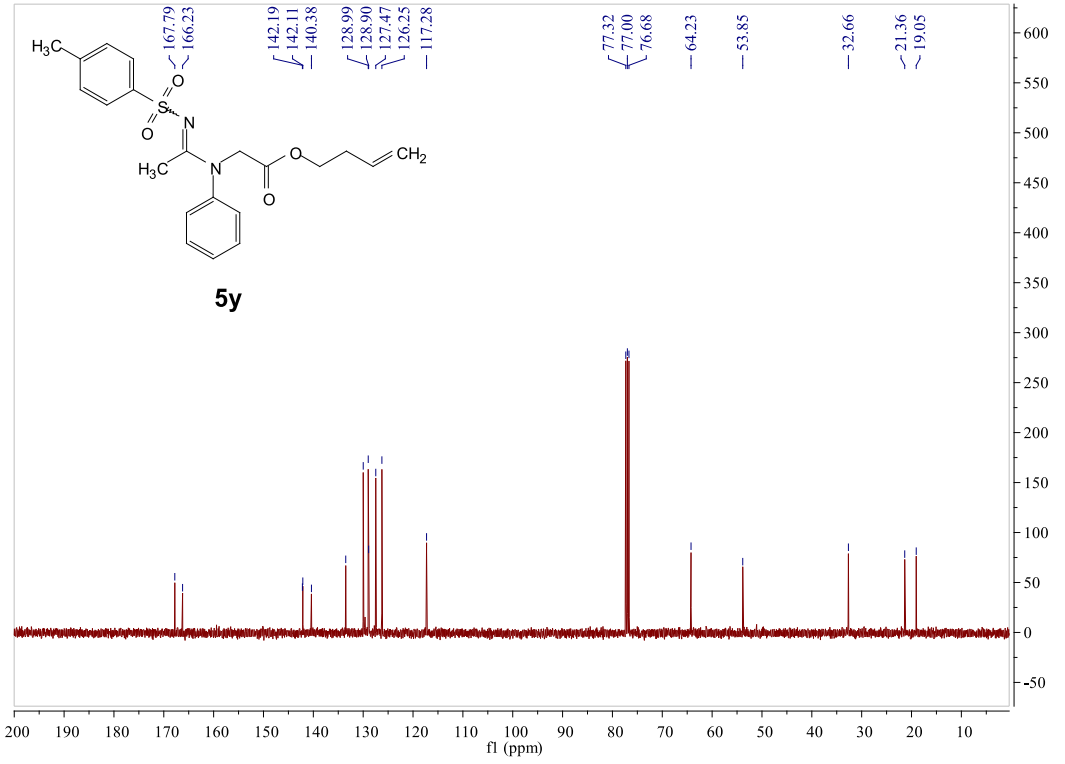
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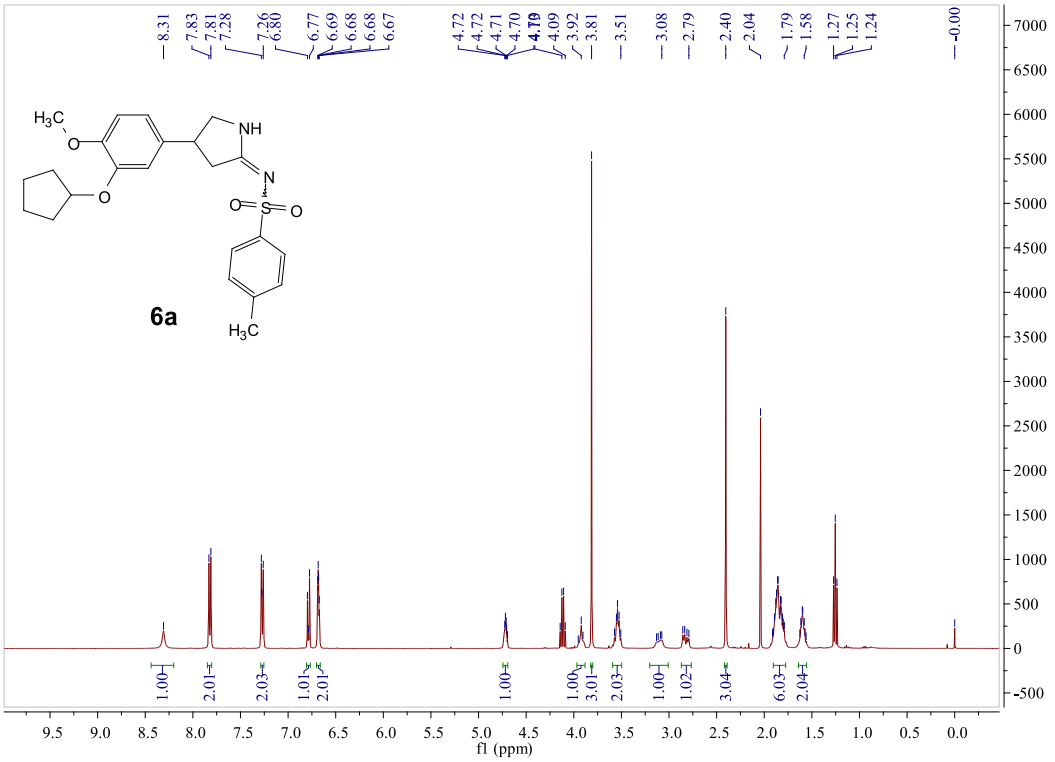
fl (ppm)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6.77
6.69
6.68
6.68
6.67
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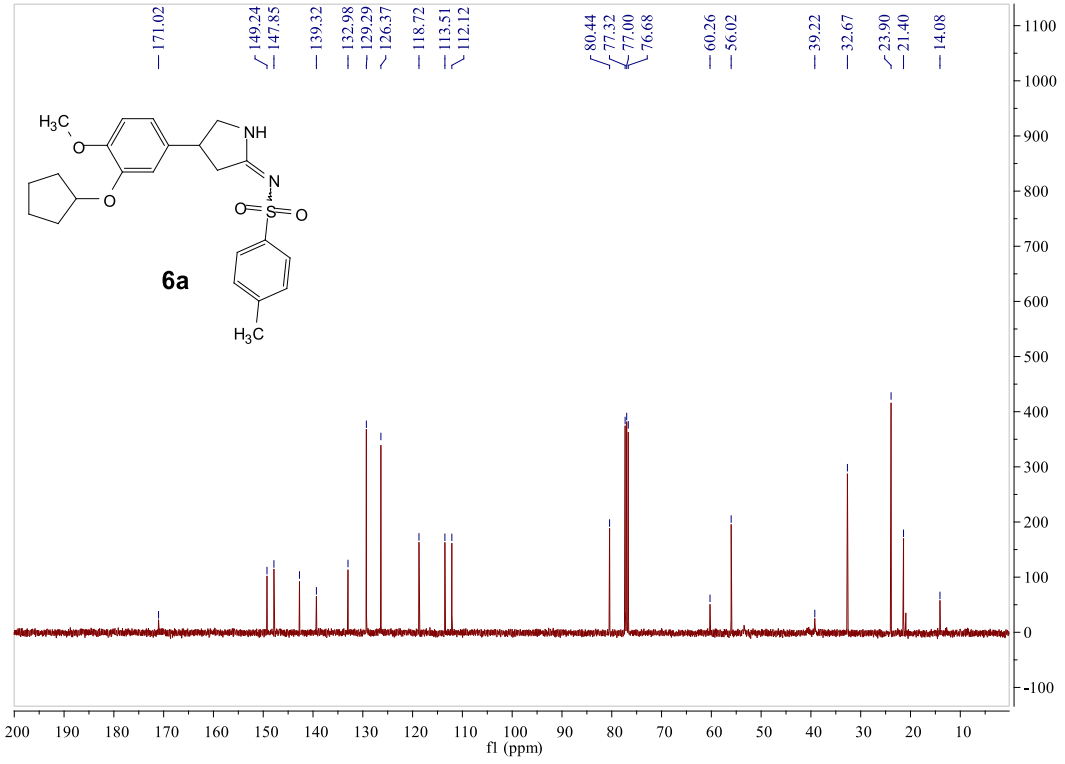
4.71
4.70
4.09
3.92
3.81
3.51
3.08
2.79
2.40
2.04
1.79
1.58
1.27
1.25
1.24
0.00
1.00
2.01
2.03
1.01
2.01
1.00
1.00
3.01
2.03
1.00
1.02
3.04
6.03
2.04
6a
f1 (ppm)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147.85
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129.29
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118.72
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80.44
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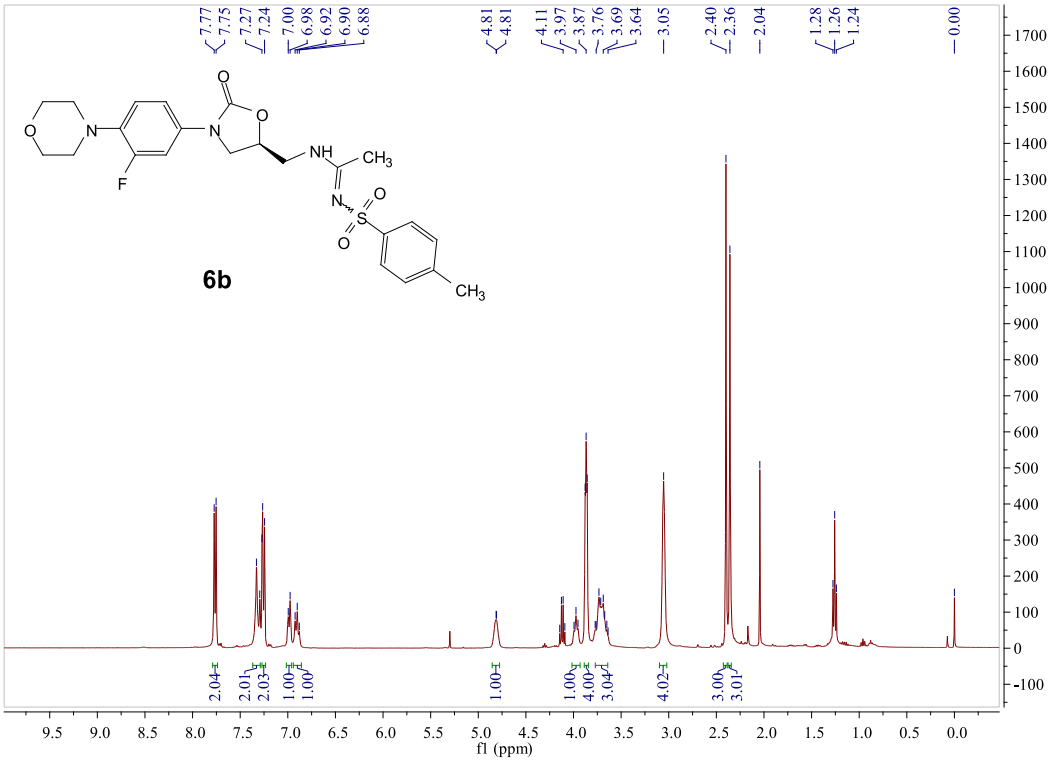
56.02
39.22
32.67
23.90
21.40
14.08
6a
f1 (ppm)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4.81
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3.97
3.87
3.76
3.69
3.64
3.05
2.40
2.36
2.04
1.28
1.26
1.24
0.00
6b
2.04
2.01
2.03
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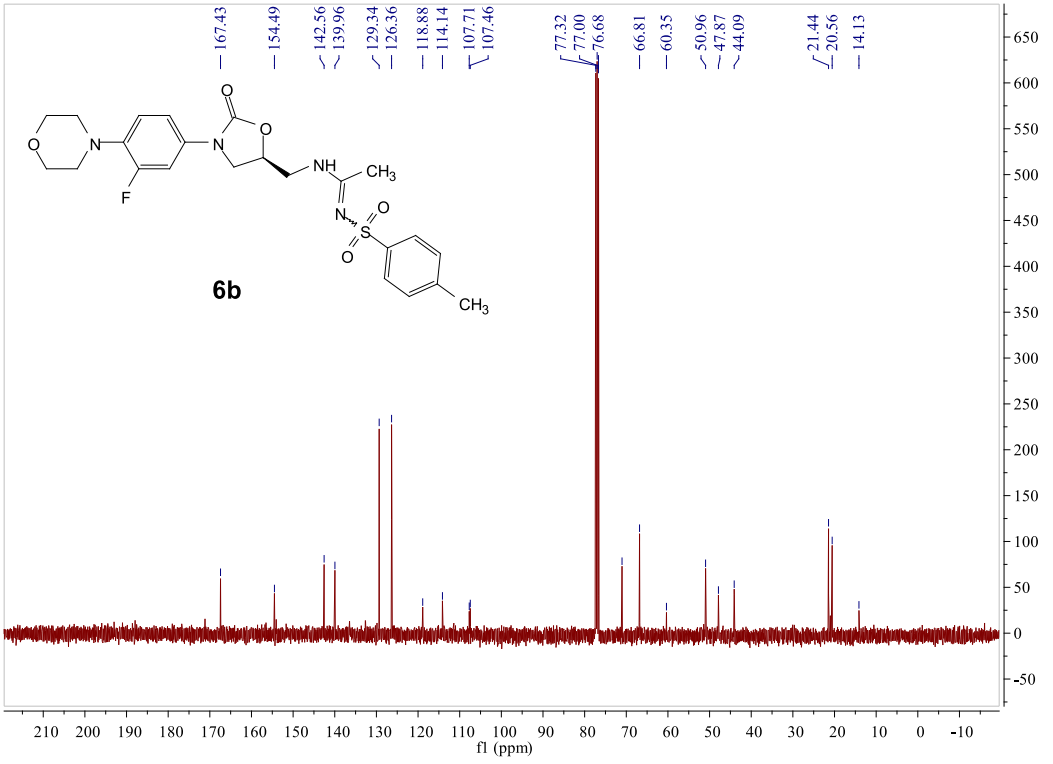
1.00
1.00
1.00
4.00
3.04
4.02
3.00
3.01
f1 (ppm)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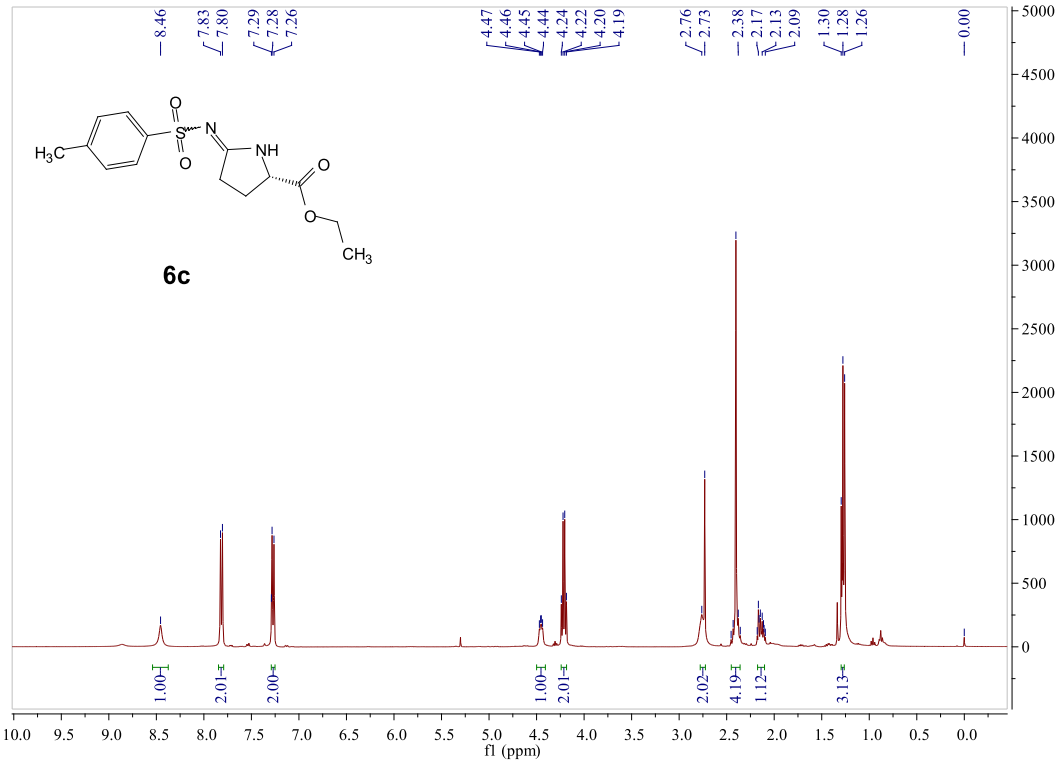
66.81
60.35
50.96
47.87
44.09
21.44
20.56
14.13
6b
f1 (ppm)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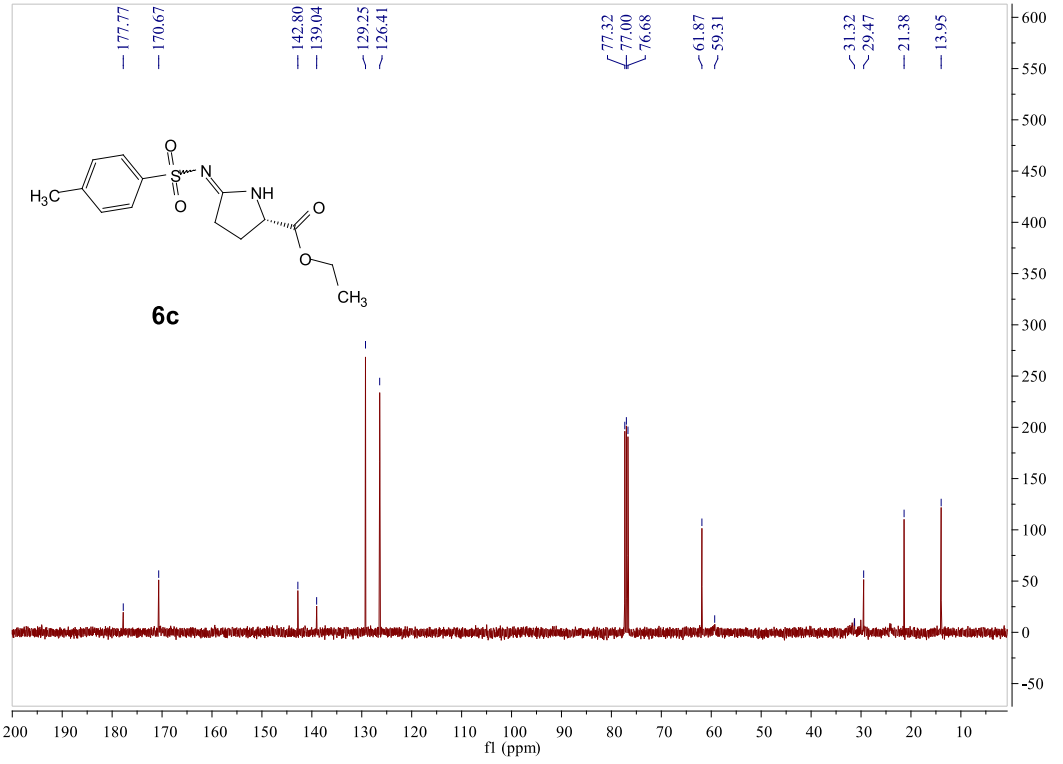
7.29
7.28
7.26
4.47
4.46
4.45
4.44
4.24
4.22
4.20
4.19
2.76
2.73
2.38
2.17
2.13
2.09
1.30
1.28
1.26
0.00
1.00
2.01
2.00
1.00
2.01
2.02
4.19
1.12
3.13
f1 (ppm)
6c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61.87
59.31
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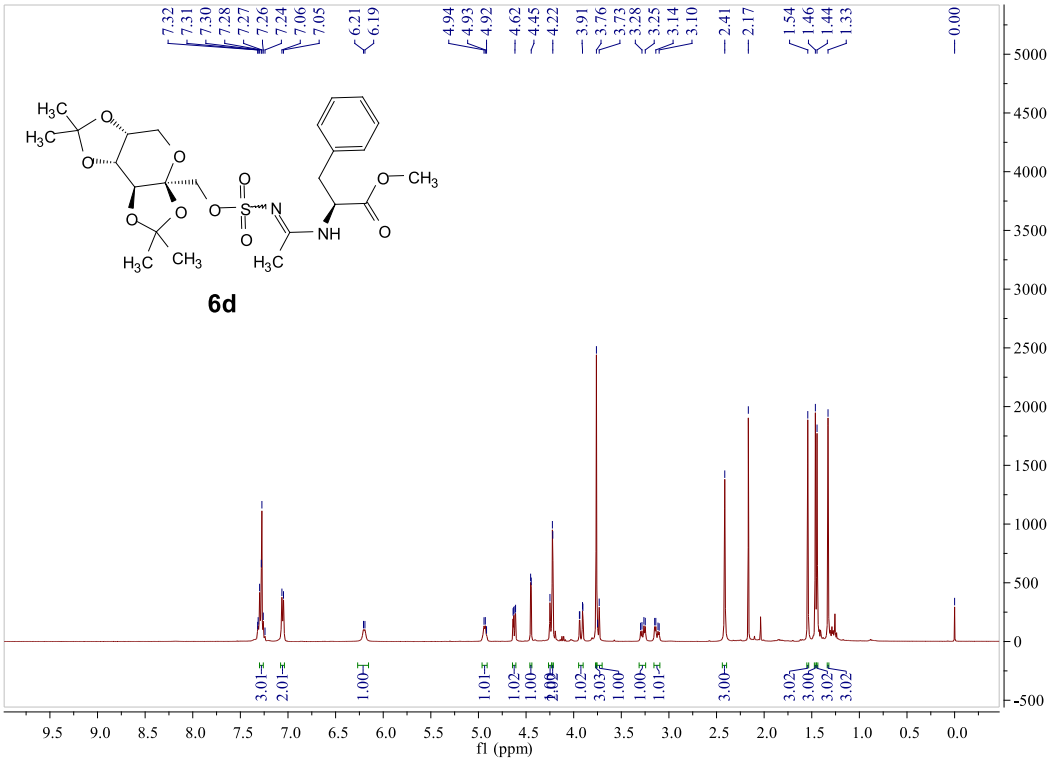
29.47
21.38
13.95
f1 (ppm)
6c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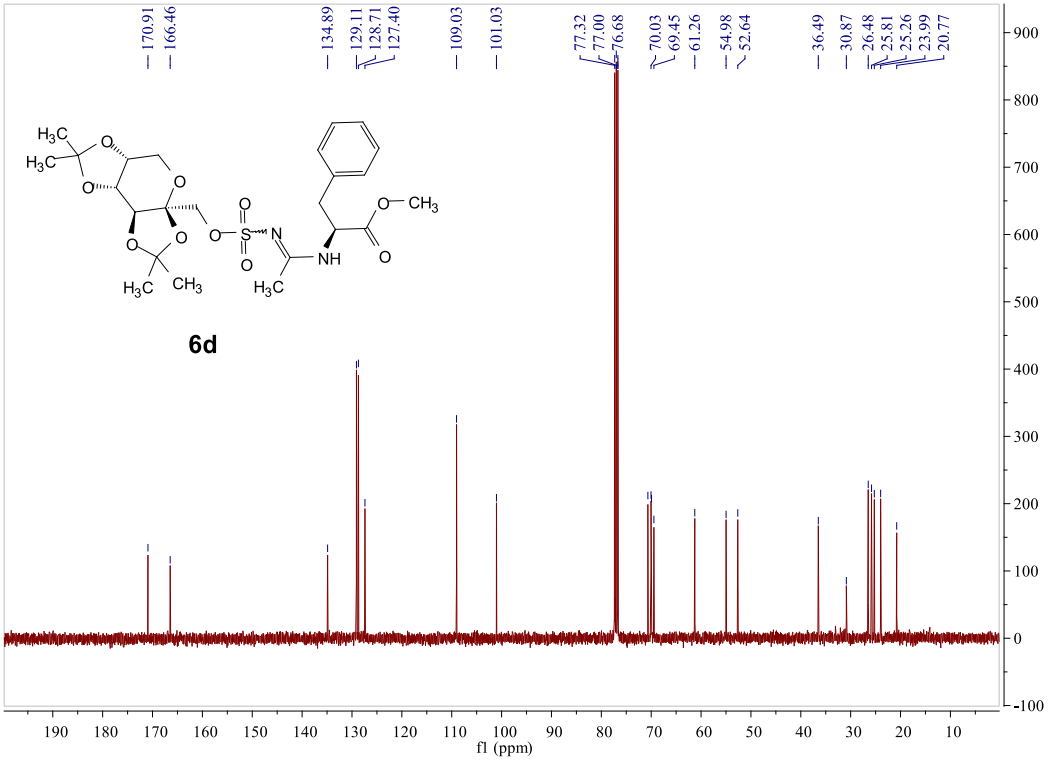
7.26
7.24
7.06
7.05
6.21
6.19
4.94
4.93
4.92
4.62
4.45
4.22
3.91
3.76
3.73
3.28
3.25
3.14
3.10
2.41
2.17
1.54
1.46
1.44
1.33
0.00
6d
fl (ppm)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70.03
69.45
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36.49
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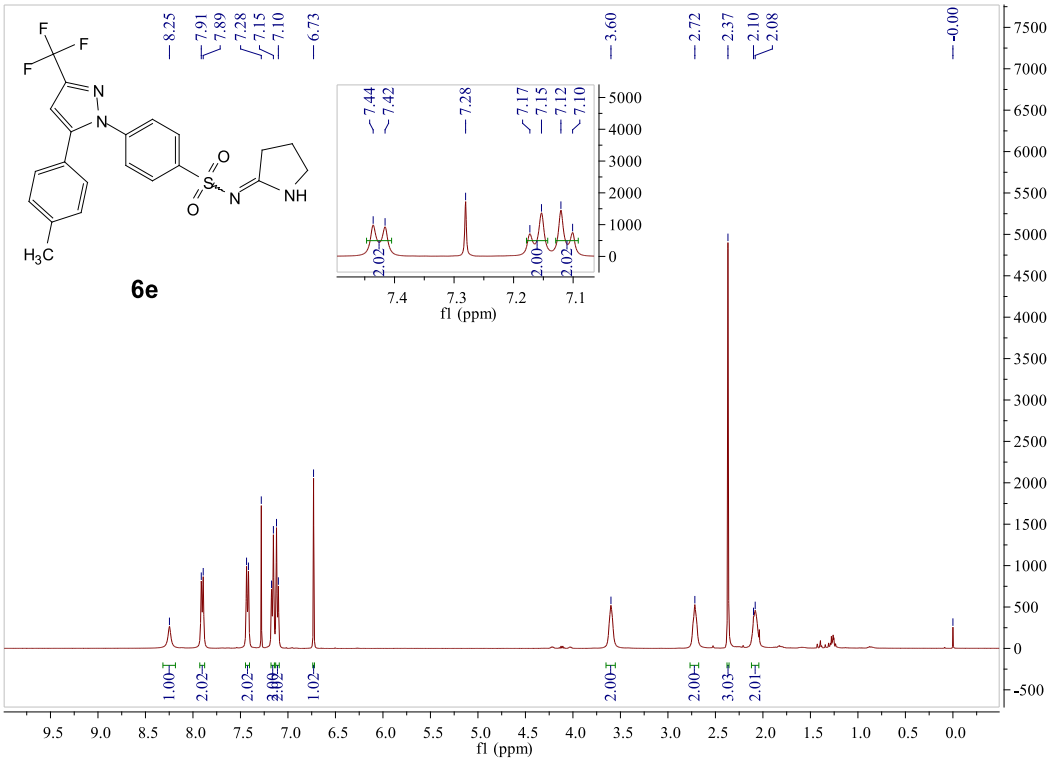
25.26
23.99
20.77
6d
fl (ppm)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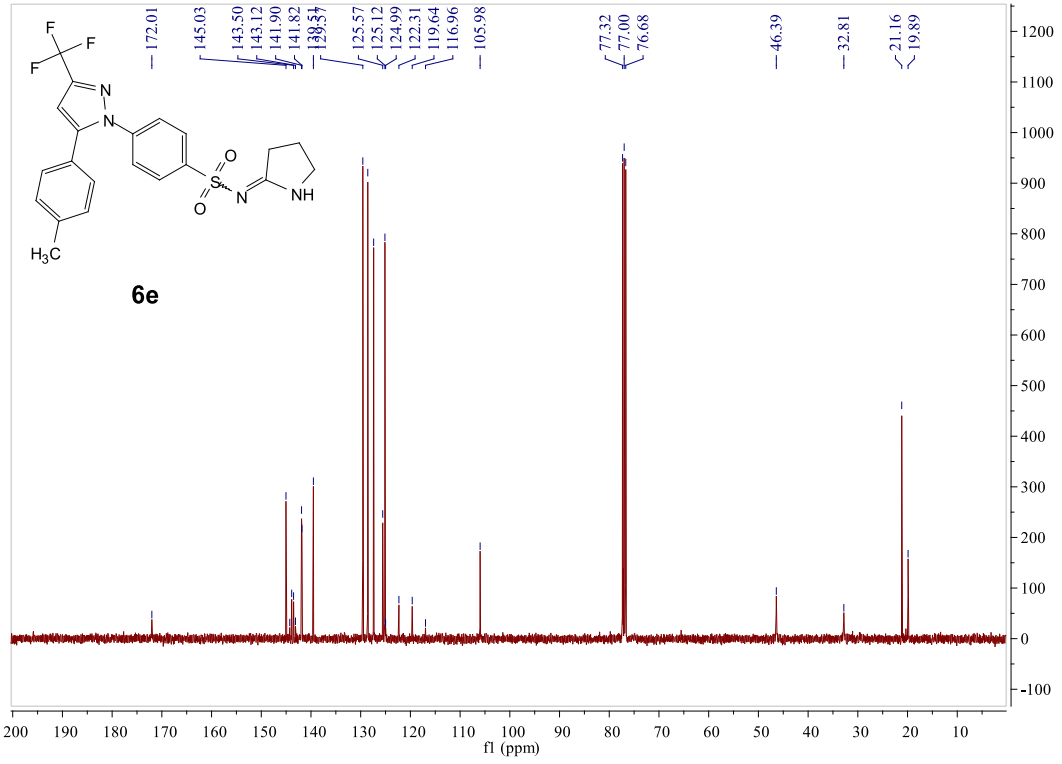
7.89
7.28
7.15
7.10
6.73
3.60
2.72
2.37
2.10
2.08
0.00
7.44
7.42
7.28
7.17
7.15
7.12
7.10
fl (ppm)


6e
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145.03
143.50
143.12
141.90
141.82
125.57
125.12
124.99
122.31
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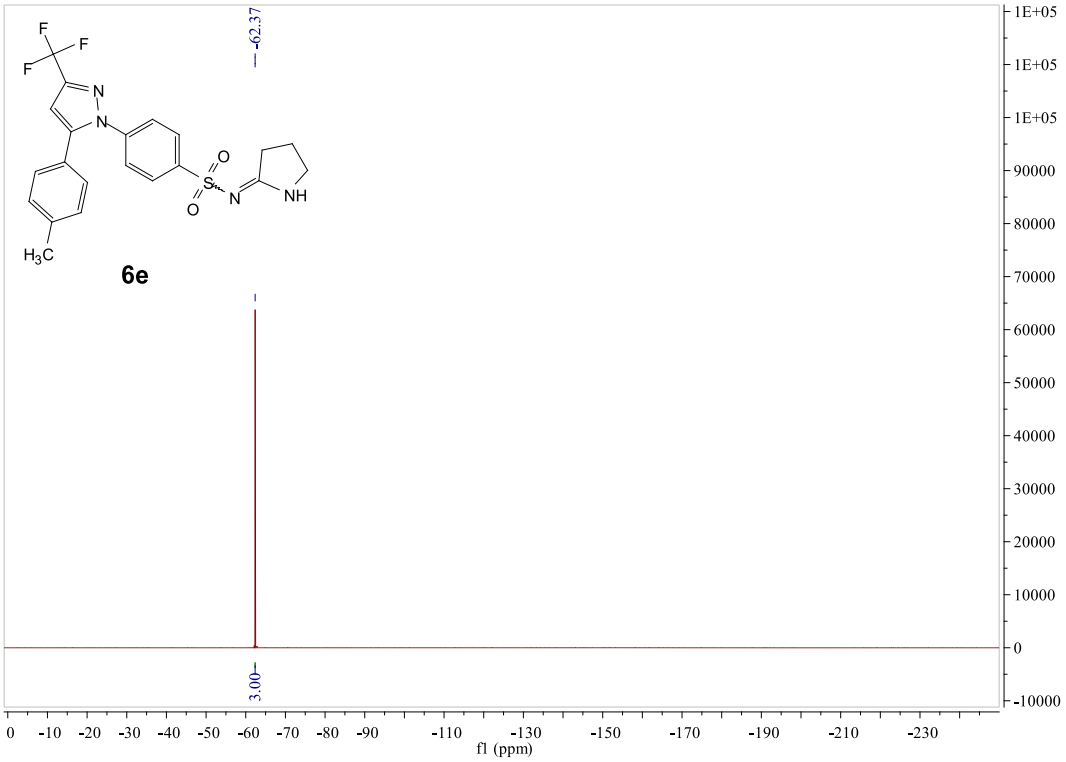
116.96
105.98
77.32
77.00
76.68
46.39
32.81
21.16
19.89
fl (ppm)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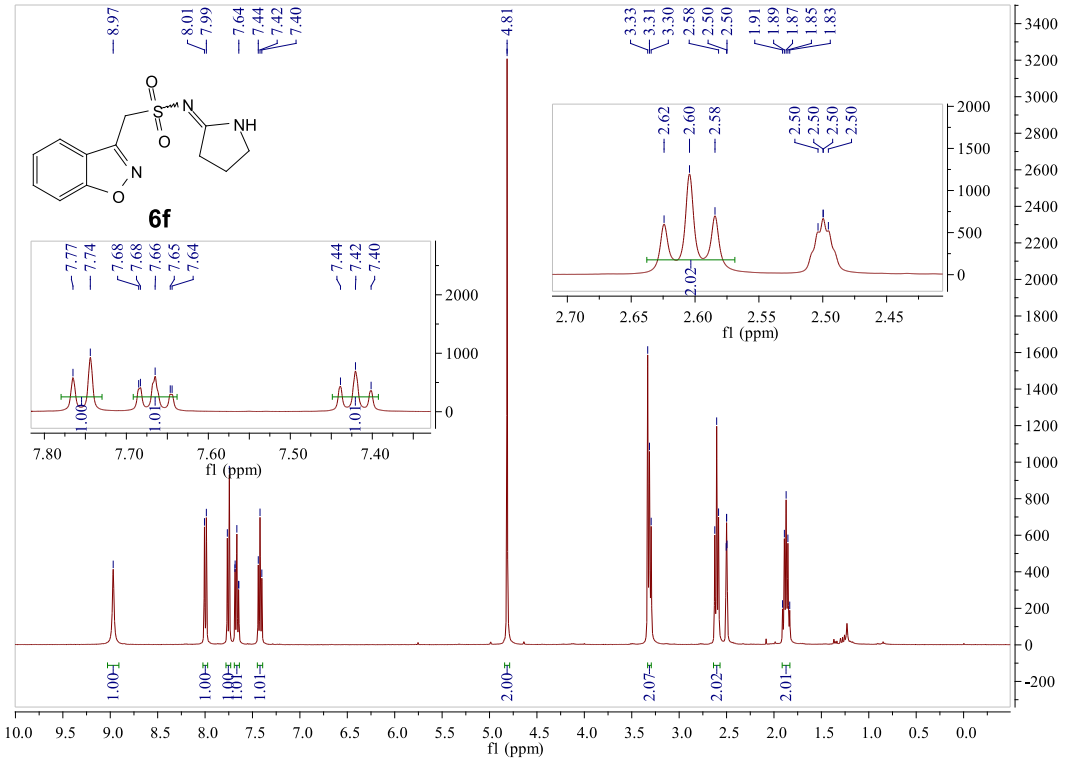
6e
3.00
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)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4.81
3.33
3.31
3.30
2.58
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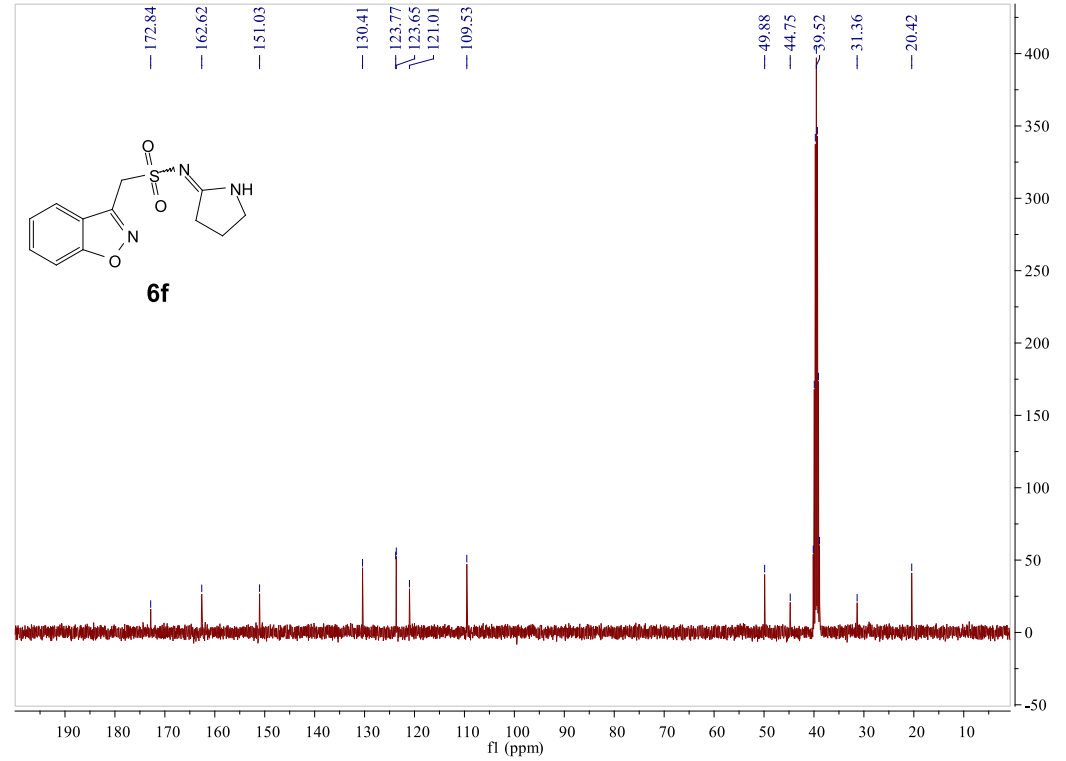
2.50
1.91
1.89
1.87
1.85
1.83
O
S
N
NH
O
N
O
6f
2.62
2.60
2.58
2.50
2.50
2.50
2.50
2.02
fl (ppm)
7.77
7.74
7.68
7.68
7.66
7.65
7.64
7.44
7.42
7.40
1.00
1.01
1.01
fl (ppm)
1.00
1.00
1.00
1.01
2.00
2.07
2.02
2.01
fl (ppm)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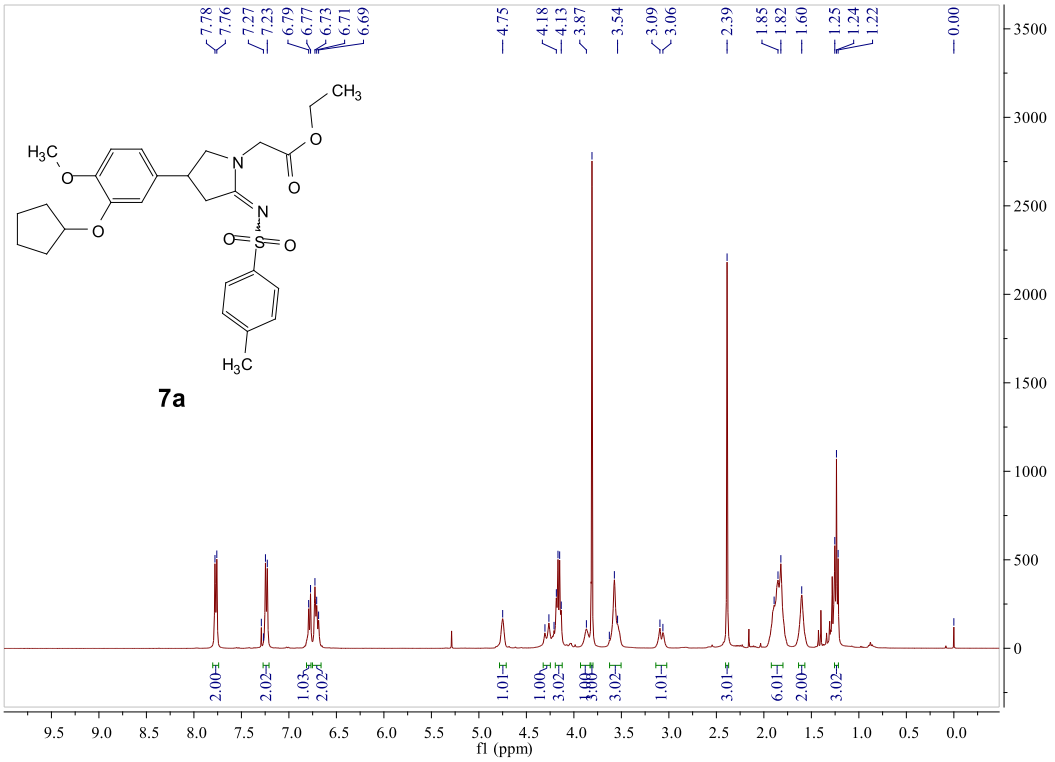
39.52
31.36
20.42
O
S
N
NH
O
N
O
6f
fl (ppm)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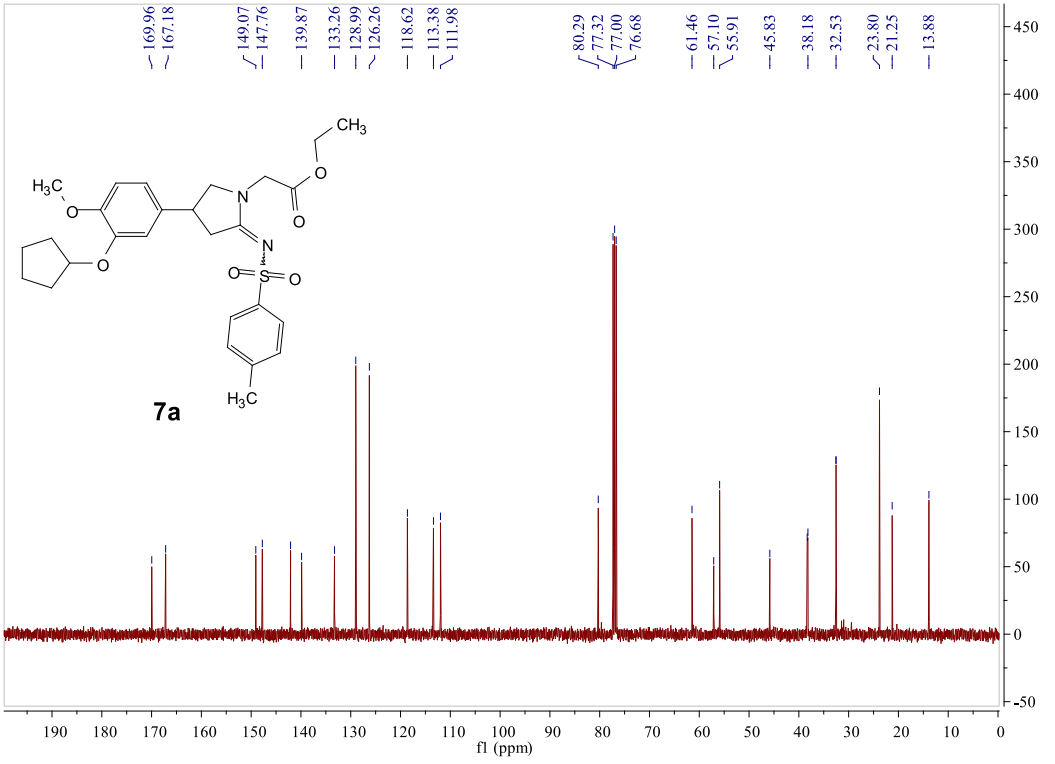
3.87
3.54
3.09
3.06
2.39
1.85
1.82
1.60
1.25
1.24
1.22
0.00
2.00
2.02
1.03
2.02
1.01
1.00
3.02
3.00
3.02
1.01
3.01
6.01
2.00
3.02
fl (ppm)
7a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118.62
113.38
111.98
80.29
77.32
77.00
76.68
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57.10
55.91
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38.18
32.53
23.80
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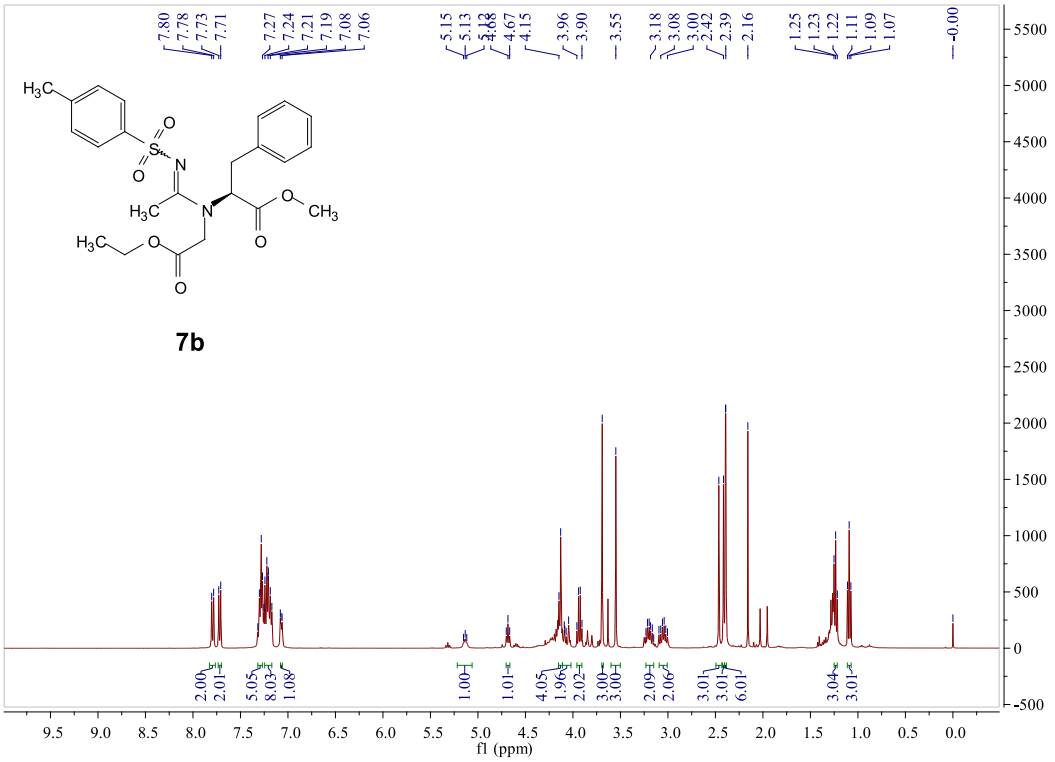
13.88
fl (ppm)
7a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7.19
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7.06
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5.13
4.67
4.15
3.96
3.90
3.55
3.18
3.08
3.00
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2.16
1.25
1.23
1.22
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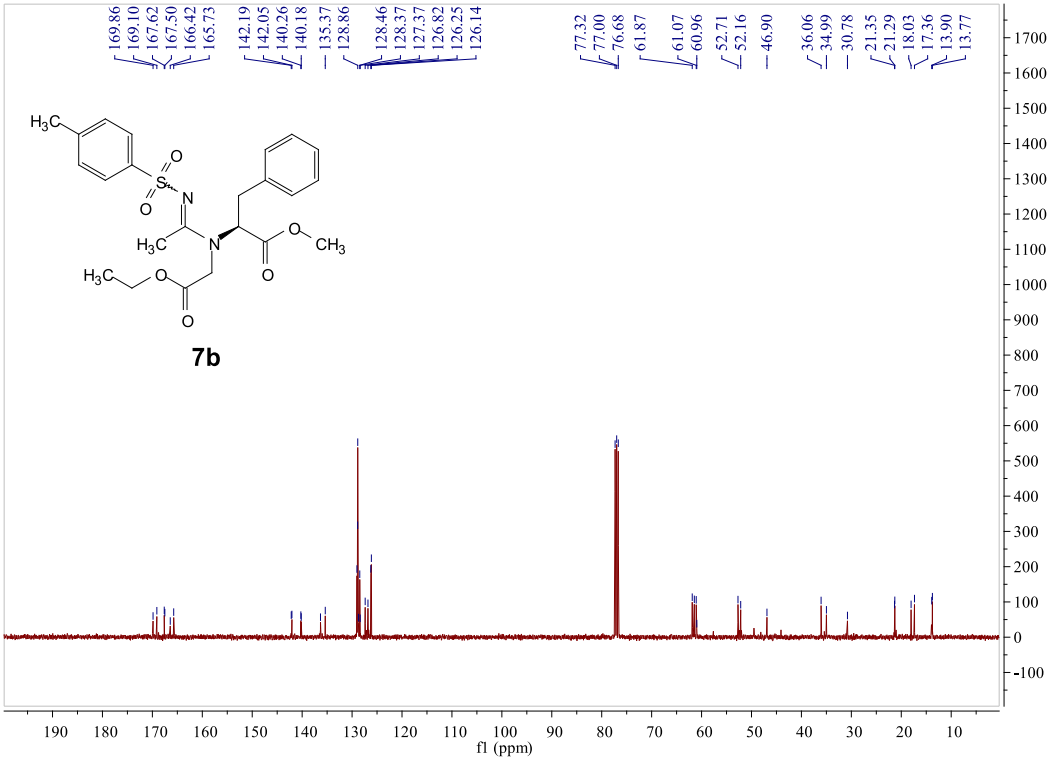
1.09
1.07
0.00
7b
fl (ppm)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142.05
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140.18
135.37
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128.46
128.37
127.37
126.82
126.25
126.14
77.32
77.00
76.68
61.87
61.07
60.96
52.71
52.16
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30.78
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17.36
13.90
13.77
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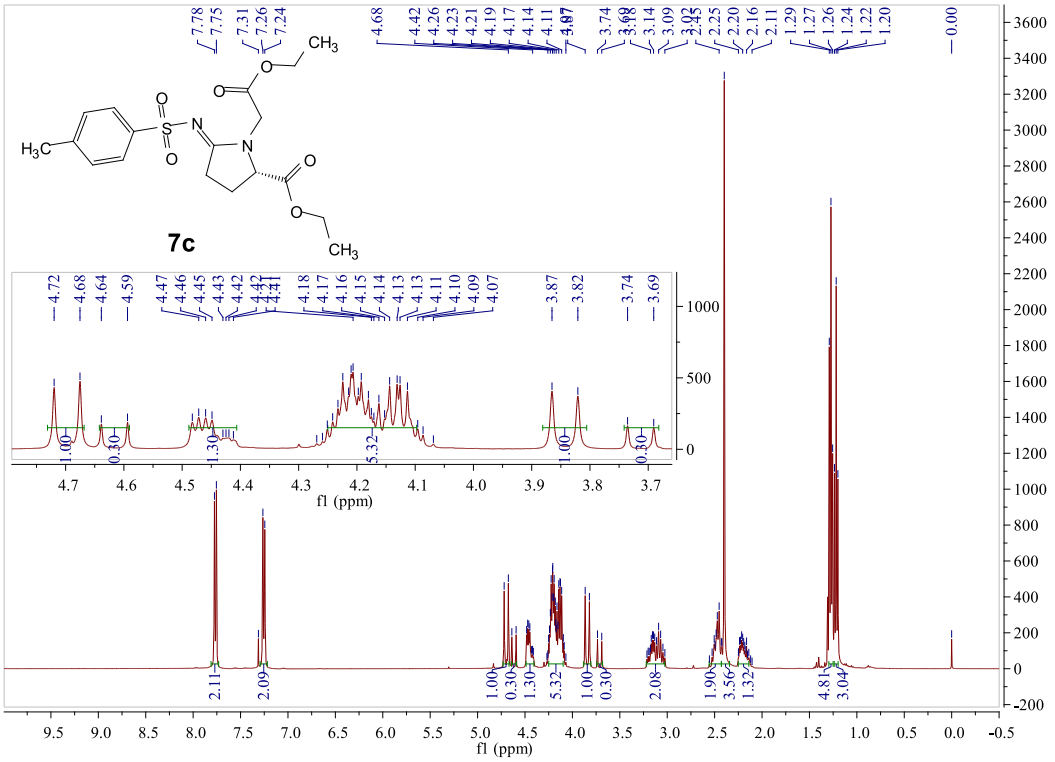
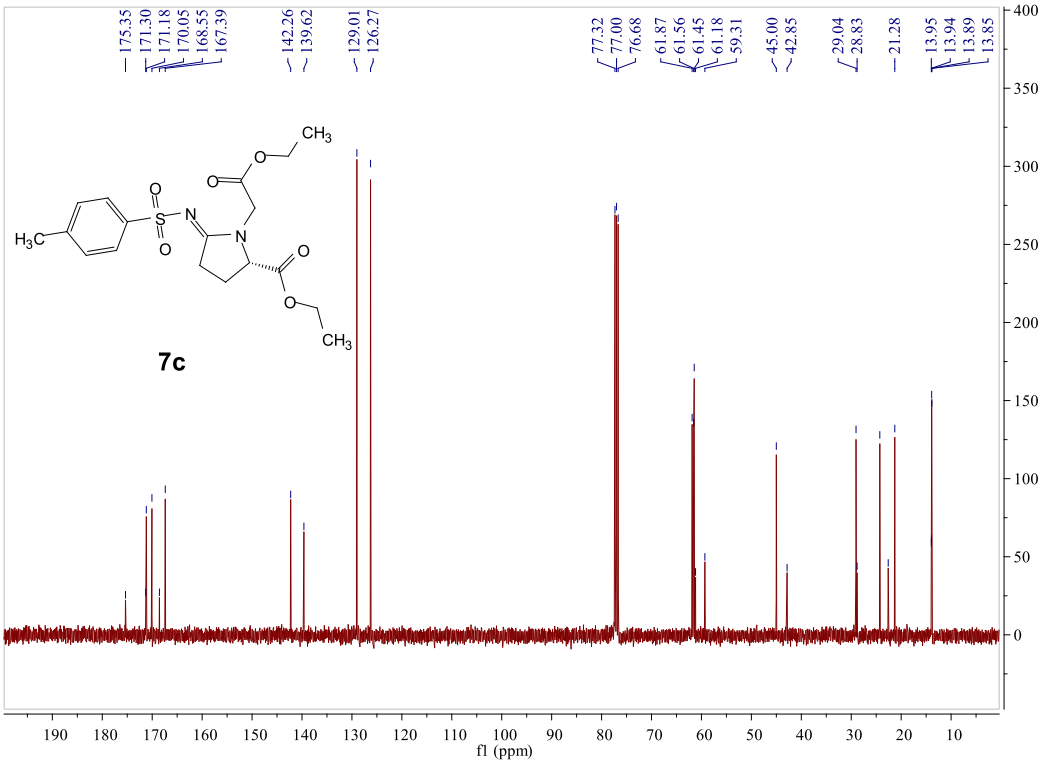
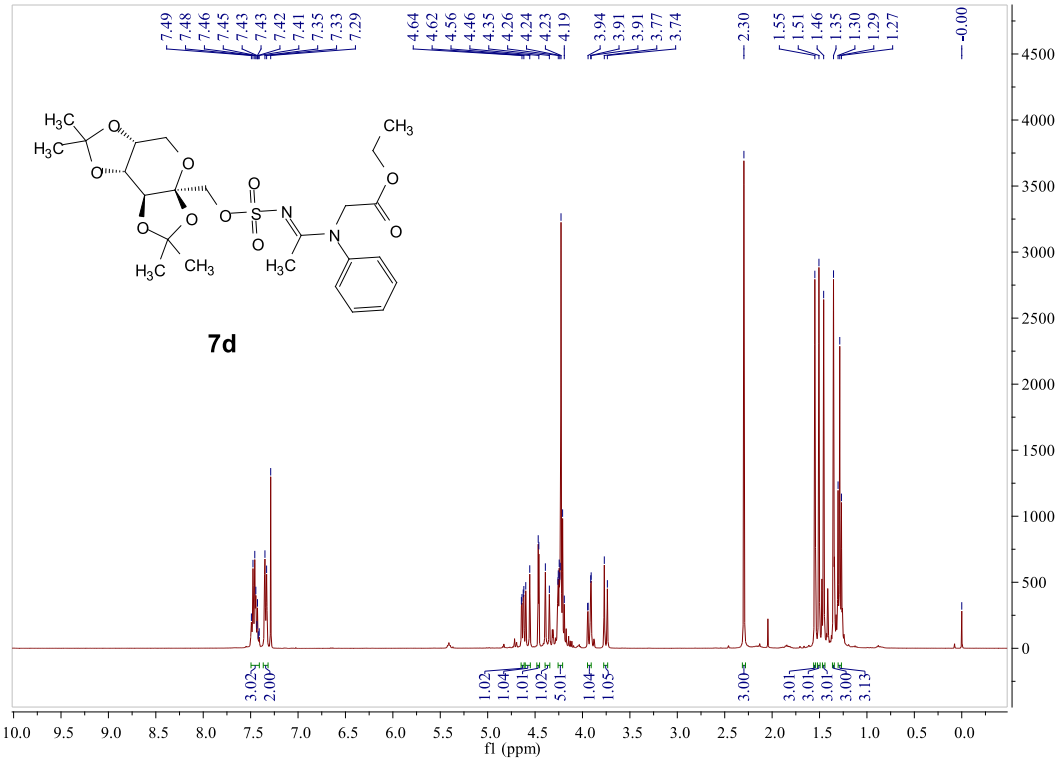
fl (ppm)


7c
fl (ppm)


7c
fl (ppm)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7.42
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7.35
7.33
7.29
4.64
4.62
4.56
4.46
4.35
4.26
4.24
4.23
4.19
3.94
3.91
3.91
3.77
3.74
2.30
1.55
1.51
1.46
1.35
1.30
1.29
1.27
0.00
7d
3.02
2.00
1.02
1.04
1.01
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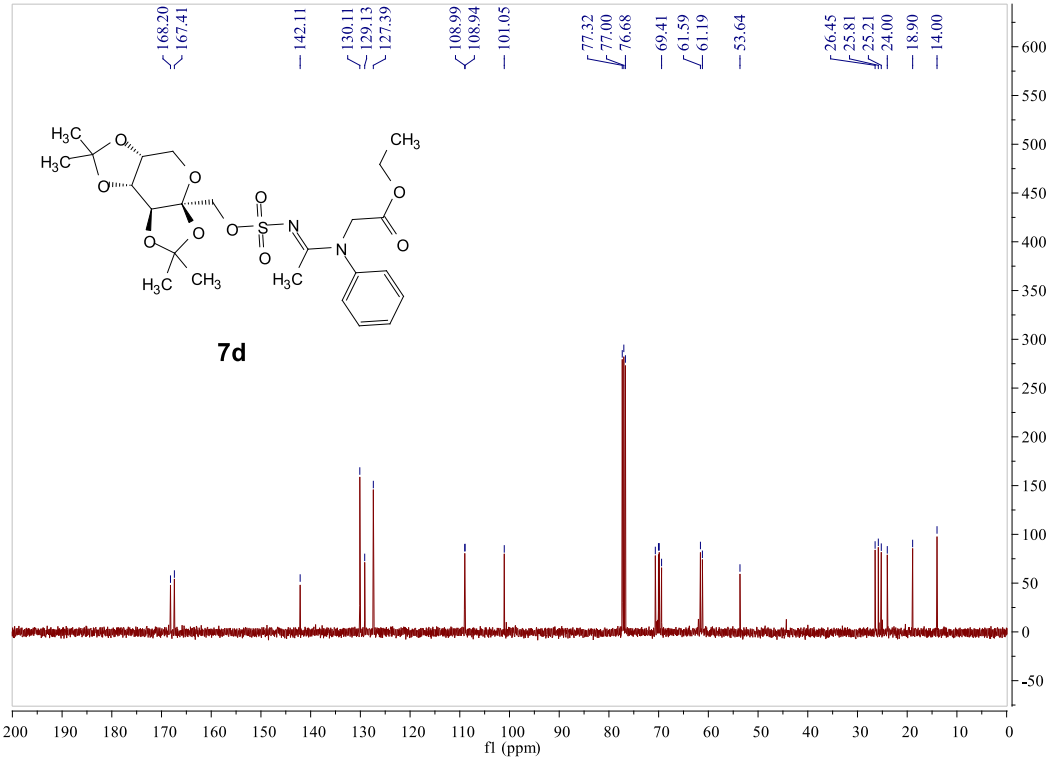
1.04
1.05
3.00
3.01
3.01
3.01
3.00
3.13
f1 (ppm)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77.00
76.68
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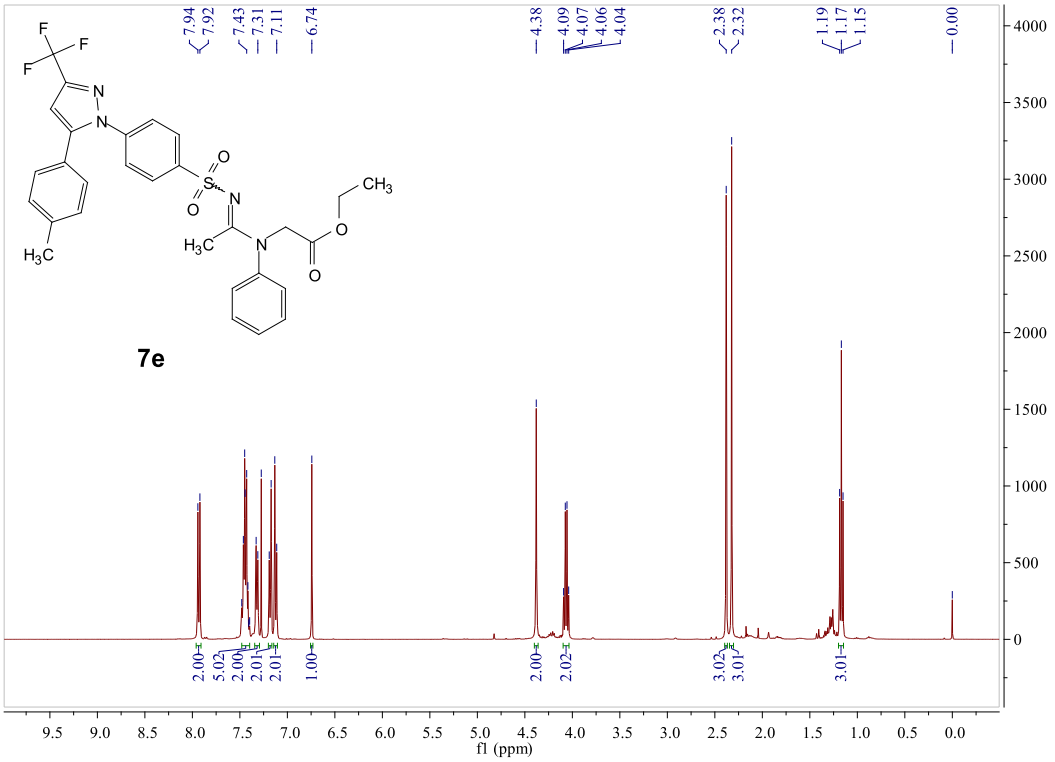
61.19
53.64
26.45
25.81
25.21
24.00
18.90
14.00
7d
f1 (ppm)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7.11
6.74
4.38
4.09
4.07
4.06
4.04
2.38
2.32
1.19
1.17
1.15
0.00
7e
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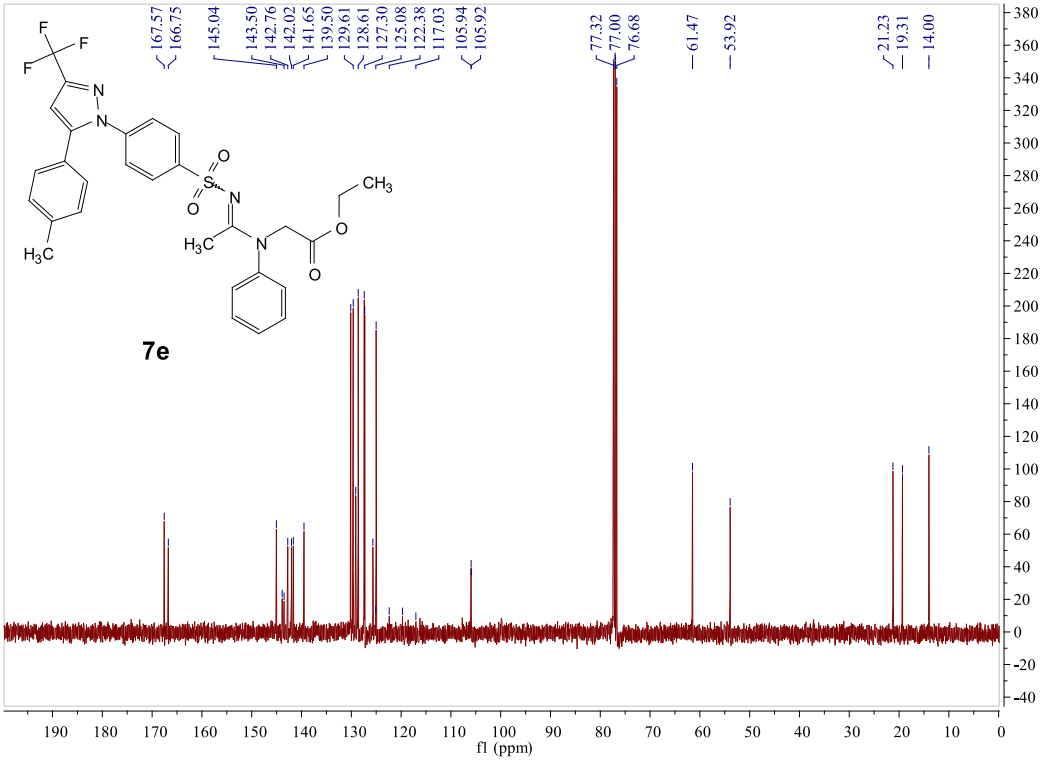
5.02
2.00
2.01
2.01
1.00
2.00
2.02
3.02
3.01
3.01
fl (ppm)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129.61
128.61
127.30
125.08
122.38
117.03
105.94
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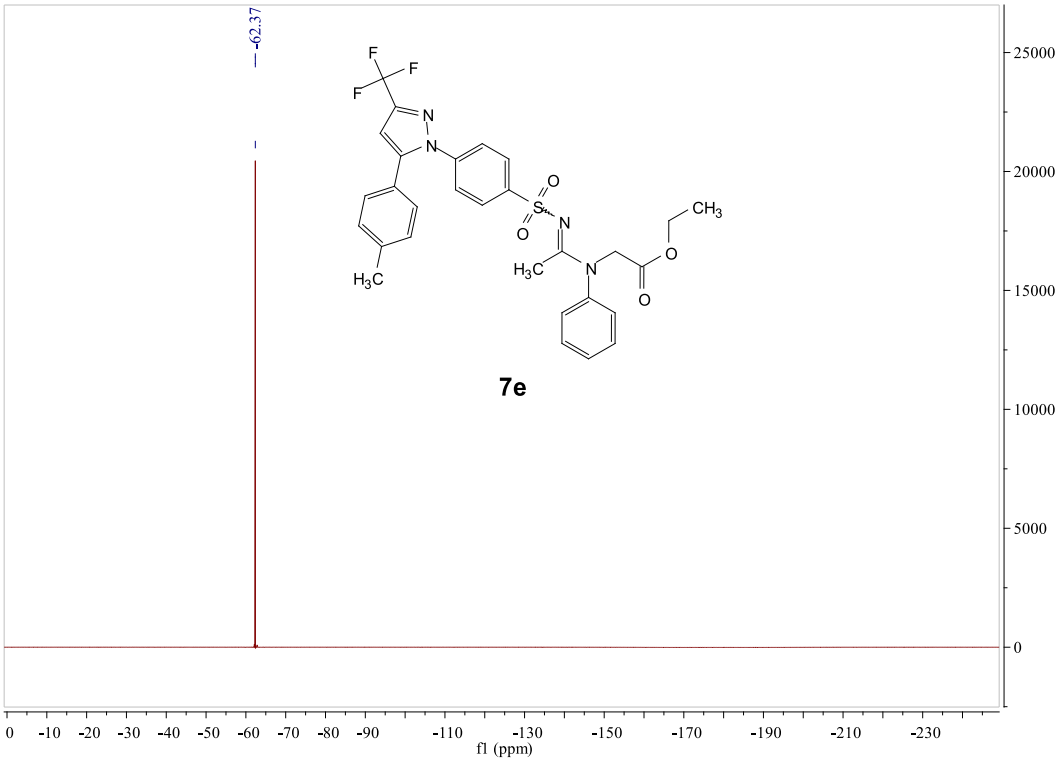
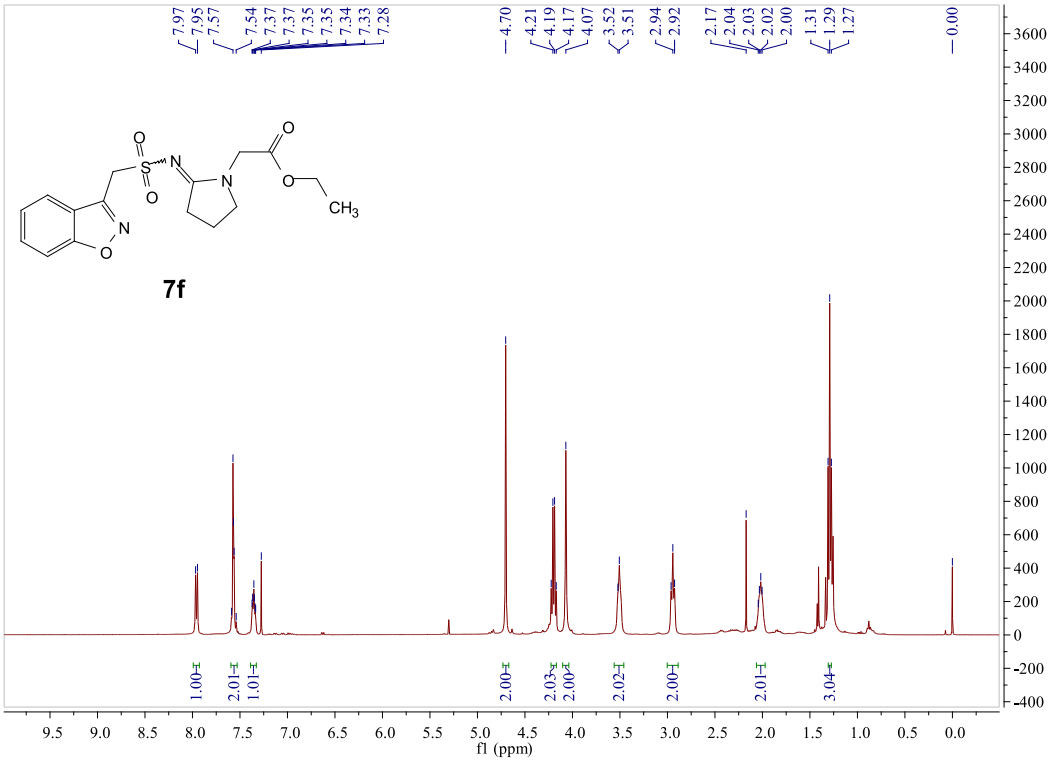
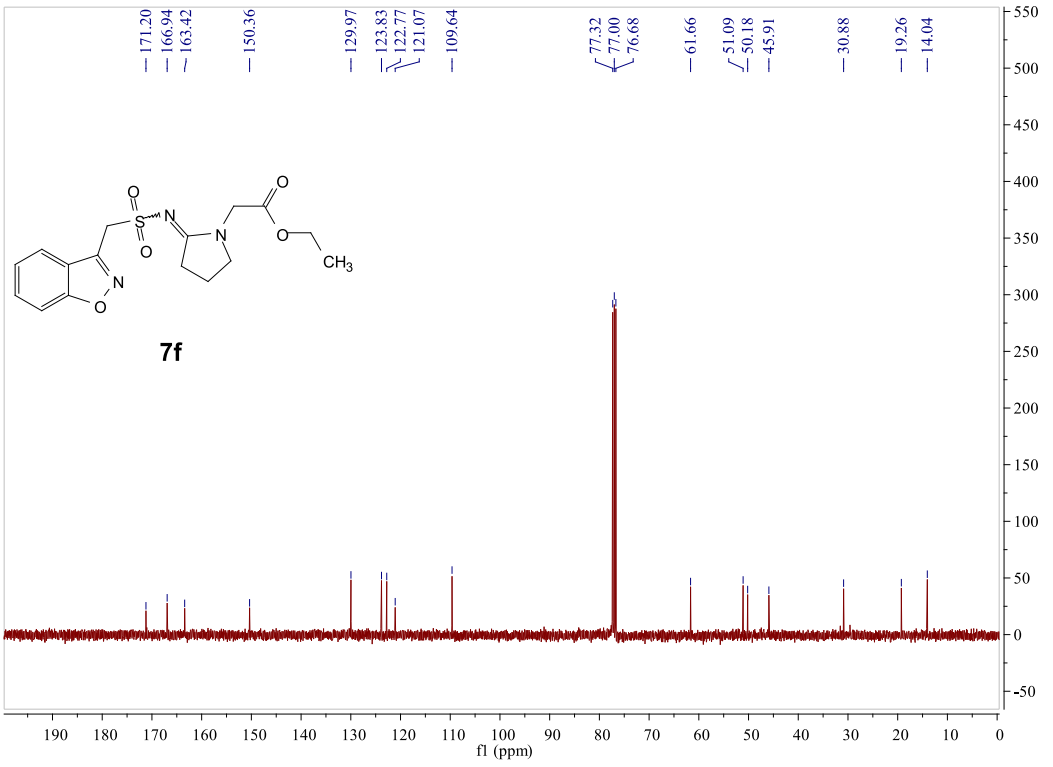
77.32
77.00
76.68
61.47
53.92
21.23
19.31
14.00
7e
fl (ppm)


-62.37
F
F
F
N
N
O
S
O
N
CH3
H3C
H3C
N
O
O
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)

7e





XRD data of the compound 4a

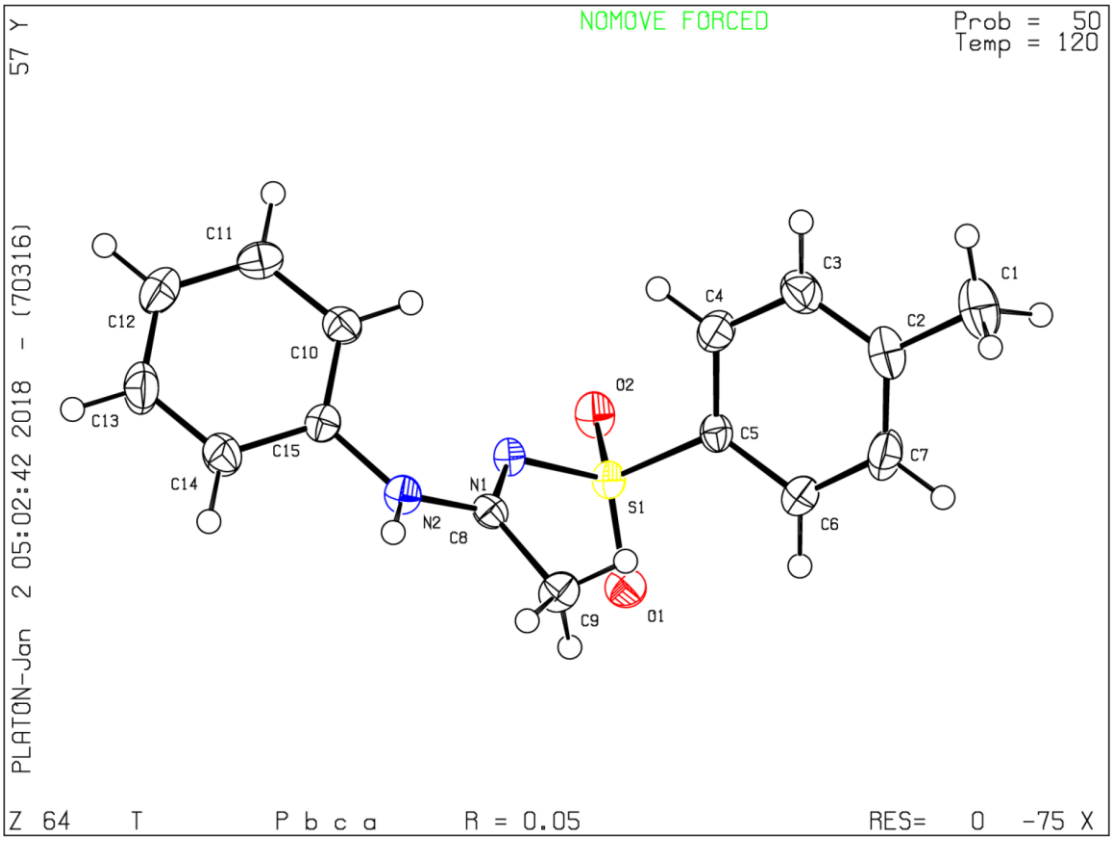


Figure S1. ORTEP structural drawing of **4a**. (CCDC: 1827581)

Table S2. Crystallography data for **4a**.

complex	**4a**
Empirical formula	$C_{15}H_{16}N_2O_2S$
Formula weight(g mol^{-1})	288.36
Temperature	120 (2) K
Crystal system	Orthorhombic
space group	Pbca
Unit cell dimensions	a = 9.6494(8) Å b = 11.5395(7) Å c = 26.2979(15) Å α = 90 ° β = 90 ° γ = 90 °
Volume ($Å^3$)	2928.3(3)
Z	8
ρ(g cm^{-3})	1.308
μ /mm^{-1}	0.224
F(000)	1216.0

Crystal size(mm^3)	0.300 × 0.200 × 0.200
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	6.196 °to 54.996 °
Limiting indices	-12<=h<=7 -14<=k<=14 -31<=l<=34
Reflections collected / unique	14673 / 3350
Data / restraints / parameters	3350 / 0 / 181
GOF	0.802
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0453 *wR2* = 0.1122
R1,*wR2*(all data)	*R1* = 0.0798 *wR2* = 0.1435
Largest diff. peak and hole(e $Å^3$)	0.34 and -0.41

Table S3. Bond lengths [Å] and angles [°] for **4a**.

S(1)-O(2) 1.4394(18)	S(1)-O(1) 1.4403(18)	S(1)-N(1) 1.6132(19)	S(1)-C(5) 1.764(2)
N(1)-C(8) 1.318(3)	N(2)-C(8) 1.336(3)	N(2)-C(15) 1.429(3)	C(1)-C(2) 1.517(4)
C(2)-C(7) 1.384(4)	C(2)-C(3) 1.387(4)	C(3)-C(4) 1.384(4)	C(4)-C(5) 1.381(3)
C(5)-C(6) 1.386(3)	C(6)-C(7) 1.389(4)	C(8)-C(9) 1.495(3)	C(10)-C(15) 1.383(3)
C(10)-C(11) 1.387(3)	C(11)-C(12) 1.379(4)	C(12)-C(13) 1.385(4)	C(13)-C(14) 1.386(4)
C(14)-C(15) 1.391(3)	O(2)-S(1)-O(1) 116.61(11)	O(2)-S(1)-N(1) 104.44(10)	O(1)-S(1)-N(1) 113.52(10)
O(2)-S(1)-C(5) 107.53(11)	O(1)-S(1)-C(5) 107.69(11)	N(1)-S(1)-C(5) 106.48(10)	C(8)-N(1)-S(1) 121.51(17)
C(8)-N(2)-C(15) 128.1(2)	C(7)-C(2)-C(3) 118.5(2)	C(7)-C(2)-C(1) 121.0(3)	C(3)-C(2)-C(1) 120.5(3)
C(4)-C(3)-C(2) 121.0(3)	C(5)-C(4)-C(3) 119.5(2)	C(4)-C(5)-C(6) 120.7(2)	C(4)-C(5)-S(1) 118.54(18)
C(6)-C(5)-S(1) 120.78(19)	C(5)-C(6)-C(7) 118.9(2)	C(2)-C(7)-C(6) 121.4(3)	N(1)-C(8)-N(2) 119.0(2)
N(1)-C(8)-C(9) 125.7(2)	N(2)-C(8)-C(9) 115.4(2)	C(15)-C(10)-C(11) 119.3(2)	C(12)-C(12)-C(10) 121.2(2)
C(11)-C(12)-C(13) 119.2(2)	C(14)-C(13)-C(12) 120.4(2)	C(13)-C(14)-C(15) 119.8(2)	C(10)-C(15)-C(14) 120.1(2)
C(10)-C(15)-N(2) 122.7(2)	C(14)-C(15)-N(2) 117.1(2)		

XRD data of the compound 4l

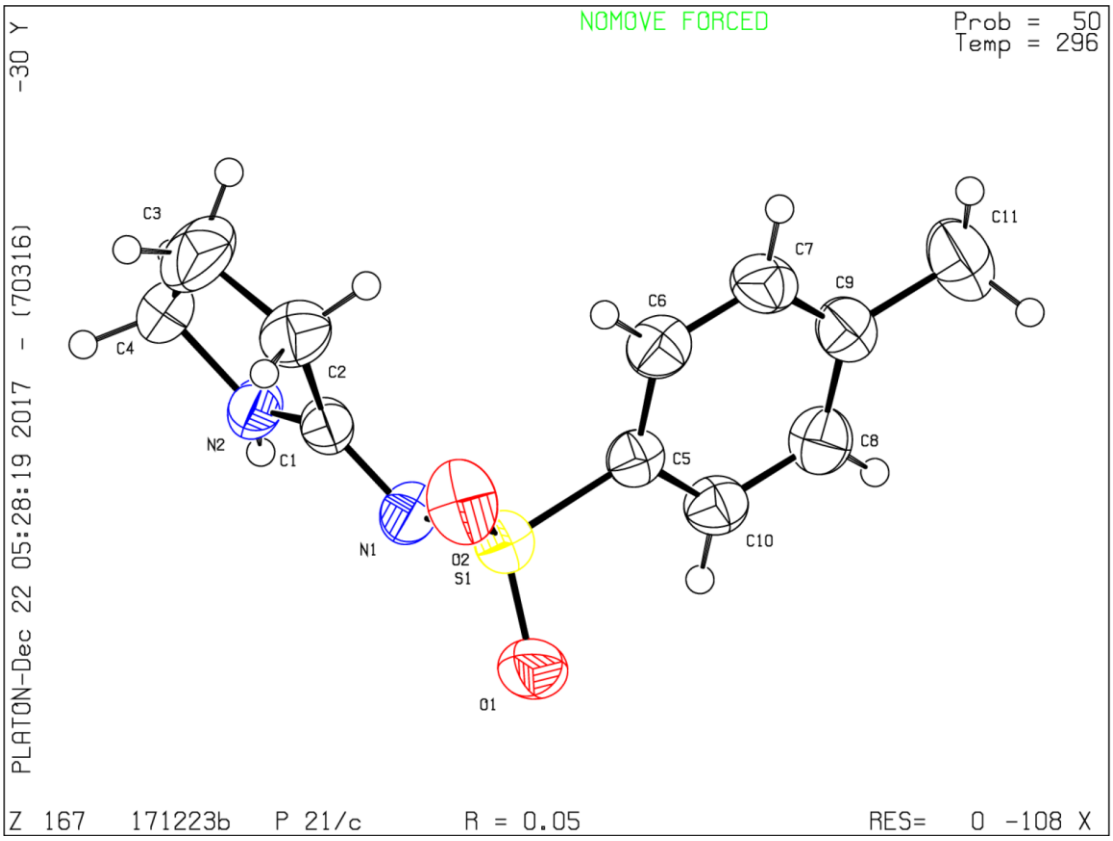


Figure S2. ORTEP structural drawing of **4l**. (CCDC: 1828634)

Table S4. Crystallography data for **4l**.

complex	**4l**
Empirical formula	$C_{11}H_{14}N_2O_2S$
Formula weight(g mol^{-1})	238.30
Temperature	296 (2) K
Crystal system	Monoclinic
space group	P2 (1) /c
Unit cell dimensions	a = 13.4264(17) Å b = 6.7926(9) Å c = 13.5926(17) Å α = 90 ° β = 110.355(3) ° γ = 90 °
Volume ($Å^3$)	1162.2(3)
Z	4
ρ(g cm^{-3})	1.362
μ /mm^{-1}	0.266
F(000)	504.0
Crystal size(mm^3)	0.200 ×0.200 ×0.180

Radiation	MoKα (λ = 0.71073)
Theta range for data collection	6.08 °to 61.514 °
Limiting indices	-12<=h<=17 -9<=k<=9 -18<=l<=14
Reflections collected / unique	8016 / 3195
Data / restraints / parameters	3195 / 0 / 146
GOF	1.016
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0450 *wR2* = 0.1333
R1,*wR2*(all data)	*R1* = 0.0572 *wR2* = 0.1460
Largest diff. peak and hole(e Å^3)	0.34 and -0.35

Table S5. Bond lengths [Å] and angles [°] for **4l**.

C(1)-N(1) 1.3123(19)	C(1)-N(2) 1.313(2)	C(1)-C(2) 1.505(2)	C(2)-C(3) 1.522(3)
C(3)-C(4) 1.507(3)	C(4)-N(2) 1.456(2)	C(5)-C(6) 1.386(2)	C(5)-C(10) 1.389(2)
C(5)-S(1) 1.7565(15)	C(6)-C(7) 1.385(2)	C(7)-C(9) 1.387(3)	C(8)-C(9) 1.383(3)
C(8)-C(10) 1.384(2)	C(9)-C(11) 1.514(2)	N(1)-S(1) 1.6174(13)	O(1)-S(1) 1.4372(13)
O(2)-S(1) 1.4337(13)	N(1)-C(1)-N(2) 119.50(13)	N(1)-C(1)-C(2) 131.68(15)	N(2)-C(1)-C(2) 108.82(14)
C(1)-C(2)-C(3) 104.35(16)	C(4)-C(3)-C(2) 107.22(15)	N(2)-C(4)-C(3) 103.03(15)	C(6)-C(5)-C(10) 120.05(14)
C(6)-C(5)-S(1) 120.75(12)	C(10)-C(5)-S(1) 119.20(11)	C(7)-C(6)-C(5) 119.50(15)	C(6)-C(7)-C(9) 121.35(15)
C(9)-C(8)-C(10) 121.64(16)	C(8)-C(9)-C(7) 118.16(15)	C(8)-C(9)-C(11) 121.46(18)	C(7)-C(9)-C(11) 121.38(17)
C(8)-C(10)-C(5) 119.29(14)	C(1)-N(1)-S(1) 124.36(11)	C(1)-N(2)-C(4) 115.95(14)	O(2)-S(1)-O(1) 117.54(9)
O(2)-S(1)-N(1) 113.06(8)	O(1)-S(1)-N(1) 104.51(7)	O(2)-S(1)-C(5) 108.40(7)	O(1)-S(1)-C(5) 107.52(7)
N(1)-S(1)-C(5) 104.98(7)			

XRD data of the compound 5a

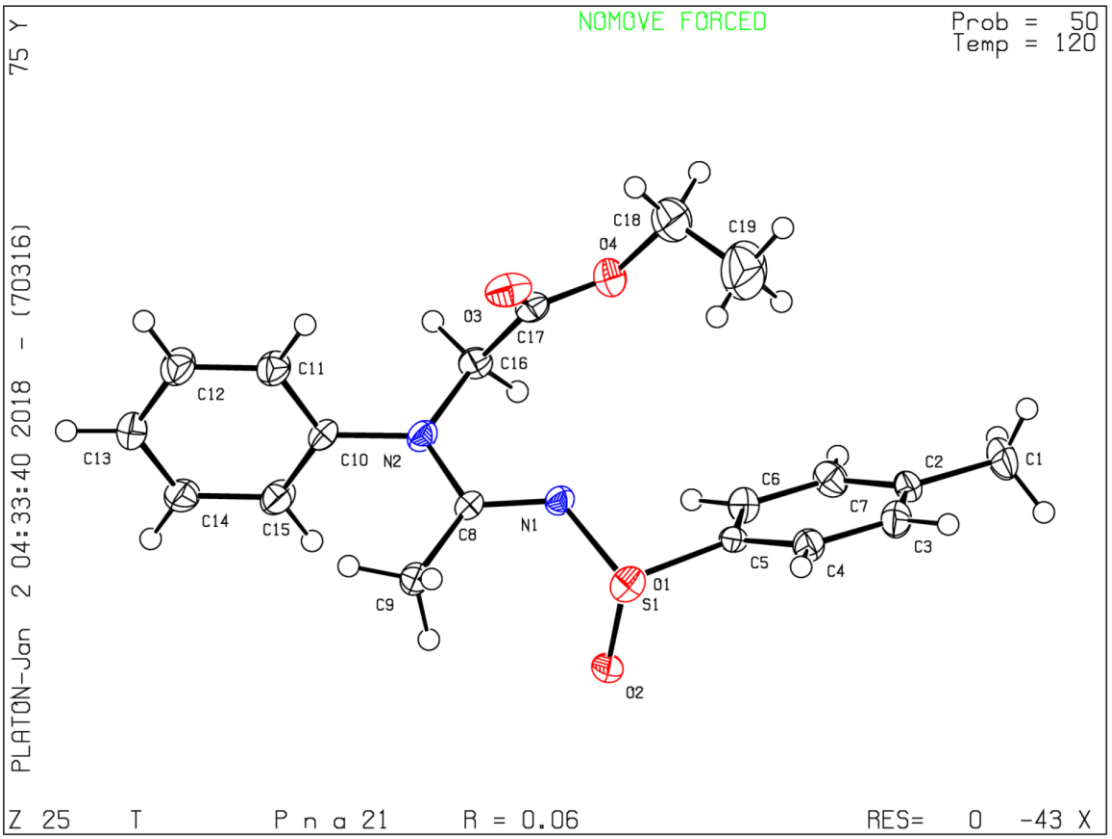


Figure S3. ORTEP structural drawing of **5a**. (CCDC: 1827580)

Table S6. Crystallography data for **5a**.

complex	**5a**
Empirical formula	$C_{19}H_{22}N_2O_4S$
Formula weight(g mol^{-1})	374.44
Temperature	120 (2) K
Crystal system	Orthorhombic
space group	Pna2(1)
Unit cell dimensions	a = 9.7504(5) Å b = 15.8797(9) Å c = 12.1655(8) Å α = 90 ° β = 90 ° γ = 90 °
Volume ($Å^3$)	1883.63(19)
Z	4
ρ(g cm^{-3})	1.320
μ /mm^{-1}	0.198
F(000)	792.0

Crystal size(mm^3)	0.60 × 0.20 × 0.20
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	4.902 °to 54.976 °
Limiting indices	-10<=h<=22 -18<=k<=20 -15<=l<=15
Reflections collected / unique	9778 / 4219
Data / restraints / parameters	4219 / 1 / 235
GOF	1.027
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0566 *wR2* = 0.1493
R1,*wR2*(all data)	*R1* = 0.0620 *wR2* = 0.1567
Largest diff. peak and hole(e $Å^3$)	1.11 and -0.55

Table S7. Bond lengths [Å] and angles [°] for **5a**.

S(1)-O(2) 1.442(3)	S(1)-O(1) 1.449(3)	S(1)-N(1) 1.606(3)	S(1)-C(5) 1.759(5)
N(1)-C(8) 1.311(5)	N(2)-C(8) 1.353(5)	N(2)-C(10) 1.434(5)	N(2)-C(16) 1.464(5)
O(3)-C(17) 1.195(5)	O(4)-C(17) 1.336(6)	O(4)-C(18) 1.455(6)	C(1)-C(2) 1.508(7)
C(2)-C(3) 1.381(7)	C(2)-C(7) 1.400(7)	C(3)-C(4) 1.400(6)	C(4)-C(5) 1.381(6)
C(5)-C(6) 1.393(5)	C(6)-C(7) 1.384(6)	C(8)-C(9) 1.503(6)	C(10)-C(15) 1.384(6)
C(10)-C(11) 1.397(5)	C(11)-C(12) 1.387(6)	C(12)-C(13) 1.392(6)	C(13)-C(14) 1.383(6)
C(14)-C(15) 1.388(6)	C(16)-C(17) 1.521(6)	C(18)-C(19) 1.423(10)	O(2)-S(1)-O(1) 115.46(19)
O(2)-S(1)-N(1) 111.12(19)	O(1)-S(1)-N(1) 113.17(17)	O(2)-S(1)-C(5) 108.29(19)	O(1)-S(1)-C(5) 107.76(19)
N(1)-S(1)-C(5) 99.67(18)	C(8)-N(1)-S(1) 121.9(3)	C(8)-N(2)-C(10) 122.4(4)	C(8)-N(2)-C(16) 118.0(3)
C(10)-N(2)-C(16) 119.5(3)	C(17)-O(4)-C(18) 117.5(4)	C(3)-C(2)-C(7) 118.8(4)	C(3)-C(2)-C(1) 120.9(4)
C(7)-C(2)-C(1) 120.3(4)	C(2)-C(3)-C(4) 120.8(4)	C(5)-C(4)-C(3) 119.7(4)	C(4)-C(5)-C(6) 120.2(4)
C(4)-C(5)-S(1) 119.1(3)	C(6)-C(5)-S(1) 120.6(3)	C(7)-C(6)-C(5) 119.6(4)	C(6)-C(7)-C(2) 120.9(4)
N(1)-C(8)-N(2) 115.6(4)	N(1)-C(8)-C(9) 126.3(4)	N(2)-C(8)-C(9) 118.1(4)	C(15)-C(10)-C(11) 120.5(4)
C(15)-C(10)-N(2) 119.9(4)	C(11)-C(10)-N(2) 119.5(4)	C(12)-C(11)-C(10) 119.2(4)	C(11)-C(12)-C(13) 120.4(4)
C(14)-C(13)-C(12) 119.6(4)	C(13)-C(14)-C(15) 120.6(4)	C(10)-C(15)-C(14) 119.5(4)	N(2)-C(16)-C(17) 111.8(3)

O(3)-C(17)-O(4) 125.8(4)	O(3)-C(17)-C(16) 124.4(4)	O(4)-C(17)-C(16) 109.7(4)	C(19)-C(18)-O(4) 113.4(4)

XRD data of the compound 5k

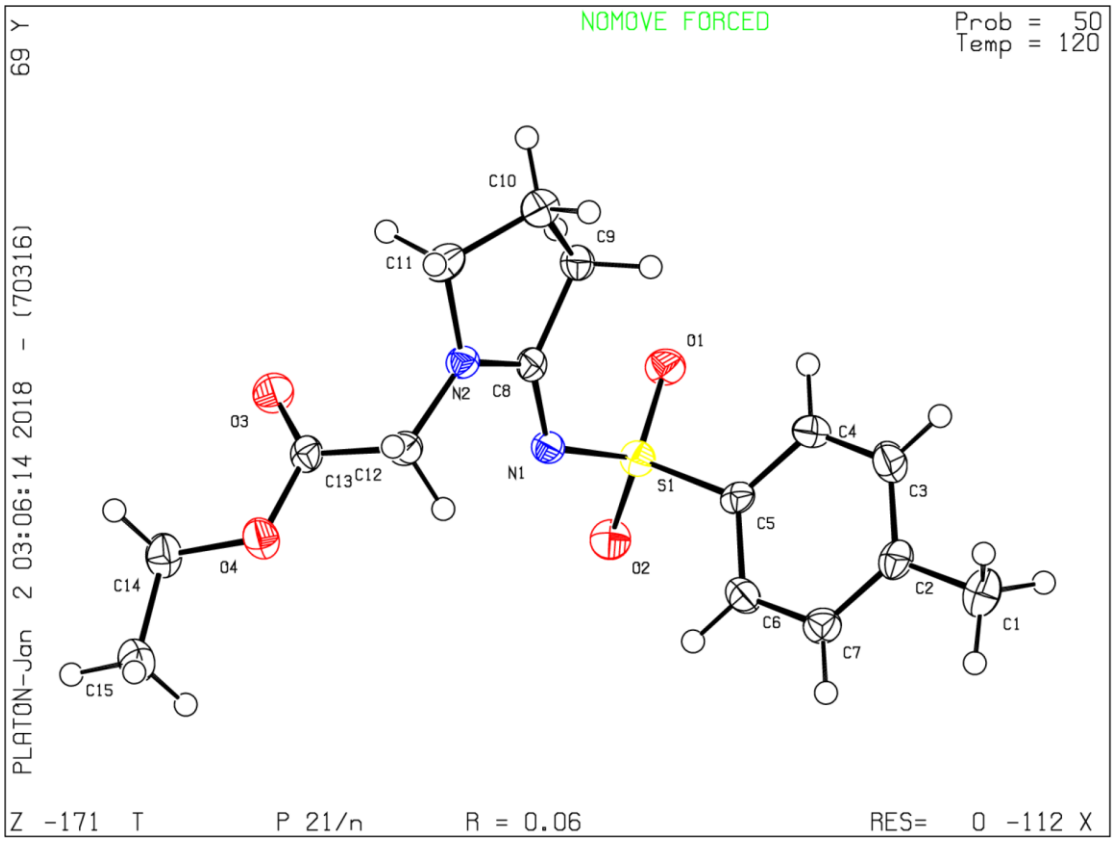


Figure S4. ORTEP structural drawing of **5k**. (CCDC: 1827576)

Table S8. Crystallography data for **5k**.

complex	**5k**
Empirical formula	$C_{15}H_{20}N_2O_4S$
Formula weight(g mol^{-1})	324.39
Temperature	120 (2) K
Crystal system	Monoclinic
space group	P2 (1) /n
Unit cell dimensions	a = 7.6307(7) Å b = 7.7492(8) Å c = 26.486(2) Å α = 90 ° β = 91.851(3) ° γ = 90 °

Volume ($Å^3$)	1565.4(2)
Z	4
ρ(g cm^{-3})	1.376
μ /mm^{-1}	0.226
F(000)	688.0
Crystal size(mm^3)	0.20 ×0.20 ×0.20
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	5.478 °to 55.274 °
Limiting indices	-9<=h<=9 -9<=k<=10 -34<=l<=34
Reflections collected / unique	13904 / 3601
Data / restraints / parameters	3601 / 0 / 199
GOF	0.996
R1,*wR2*[I > 2σ(I)]	*R1* = 0.0605 *wR2* = 0.1212
R1,*wR2*(all data)	*R1* = 0.1491 *wR2* = 0.1599
Largest diff. peak and hole(e $Å^3$)	0.37 and -0.45

Table S9. Bond lengths [Å] and angles [°] for **5k**.

S(1)-O(1) 1.441(2)	S(1)-O(2) 1.440(2)	S(1)-N(1) 1.611(3)	S(1)-C(5) 1.758(3)
N(1)-C(8) 1.315(4)	N(2)-C(8) 1.332(4)	N(2)-C(12) 1.452(4)	N(2)-C(11) 1.1.468(4)
O(3)-C(13) 1.206(4)	O(4)-C(13) 1.338(4)	O(3)-C(14) 1.464(4)	C(1)-C(2) 1.508(5)
C(2)-C(3) 1.394(5)	C(2)-C(7) 1.389(5)	C(3)-C(4) 1.382(5)	C(4)-C(5) 1.389(5)
C(5)-C(6) 1.386(4)	C(6)-C(7) 1.391(5)	C(8)-C(9) 1.512(4)	C(9)-C(10) 1.527(4)
C(10)-C(11) 1.531(5)	C(12)-C(13) 1.509(5)	C(14)-C(15) 1.492(4)	O(1)-S(1)-O(2) 116.87(14)
O(1)-S(1)-N(1) 113.93(14)	O(2)-S(1)-N(1) 105.57(15)	O(1)-S(1)-C(5) 108.04(15)	O(2)-S(1)-C(5) 107.73(14)
N(1)-S(1)-C(5) 103.79(14)	C(8)-N(1)-S(1) 122.2(2)	C(8)-N(2)-C(12) 122.9(3)	C(8)-N(2)-C(11) 113.7(3)
C(12)-N(2)-C(11) 123.1(3)	C(13)-O(4)-C(14) 116.4(2)	C(3)-C(2)-C(7) 118.6(3)	C(3)-C(2)-C(1) 120.2(3)
C(7)-C(2)-C(1) 121.2(3)	C(4)-C(3)-C(2) 120.5(3)	C(3)-C(4)-C(5) 120.4(3)	C(4)-C(5)-C(6) 119.8(3)
C(4)-C(5)-S(1) 120.3(2)	C(6)-C(5)-S(1) 119.9(3)	C(7)-C(6)-C(5) 119.5(3)	C(6)-C(7)-C(2) 121.2(3)

N(1)-C(8)-N(2) 119.7(3)	N(1)-C(8)-C(9) 131.8(3)	N(2)-C(8)-C(9) 108.5(3)	C(8)-C(9)-C(10) 104.1(3)
C(11)-C(10)-C(9) 103.9(3)	N(2)-C(11)-C(10) 102.2(3)	N(2)-C(12)-C(13) 113.2(3)	O(3)-C(13)-O(4) 124.7(3)
O(3)-C(13)-C(12) 126.2(3)	O(4)-C(13)-C(12) 109.2(3)	O(4)-C(14)-C(15) 107.5(3)	