Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Conversion of racemic alcohols to optically pure amine precursors enabled by catalyst dynamic kinetic resolution: experiment and computation

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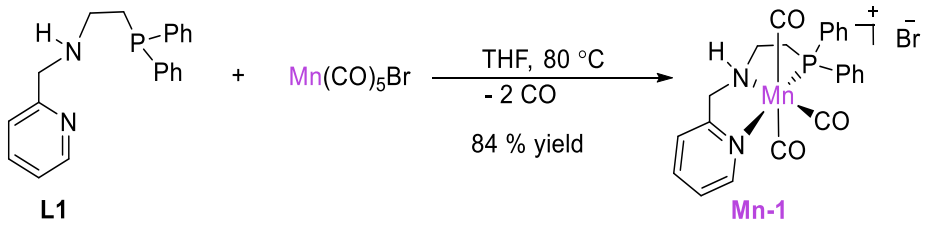
General Information

All reactions were carried out under an argon atmosphere using oven-dried glassware. The dry and degassed dioxane, t-amyl alcohol and 2-methyl-THF were distilled from sodium benzophenone under nitrogen. Toluene were obtained from MBRAUN Solvent Purification System. All other chemicals were used as purchased without further purification. ^{1}H, ^{13}C and ^{31}P spectra were recorded in $CDCl_3$ using Varian VNMR 600 MHz and 400MHz spectrometer. The signals were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra (EI-MS, 70 eV) were conducted on a Finnigan SSQ 7000 spectrometer. HRMS were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 pre-coated aluminium plates (Macherey-Nagel 0.20 mm thickness) with a fluorescent indicator UV254. Visualization was performed with standard phosphomolybdic acid stain (10g in 100 mL EtOH) or UV light.

Synthesis of the Manganese Complex Mn-1[1]



A 50 mL Schlenk tube was charged with the PNN pincer ligand L1 (300 mg, 1.07 mmol, 1 eq.) and $Mn(CO)_5Br$ (293 mg, 1.07 mmol, 1.0 eq.). The Schlenk tube was evacuated and backfilled with argon for several time. Afterwards, 15 mL of degassed THF was added and the reaction mixture was stirred at 80 °C for 20 h. The suspension was allowed to cool to room temperature and the yellow precipitate was filtered off and washed with diethyl ether and n-hexane. The remaining solid was dried under vacuum to afford the complex **Mn-1** as a yellow powder (0.49 g, 84% yield).

Crystals suitable for X-ray diffraction were obtained on the following way, in an inner vial was placed the complex followed by toluene, DCM and triethylamine (the solution was filtered to get it clear) in the outer vial toluene was placed. Upon standing at RT for 48 h yellow crystals were formed. The supernatant solution was removed with a help of syringe and the crystals were immediately covered with PARATONE® and mounted on the diffractometer. The data were collected on SuperNova single crystal X-ray diffractometer equipped with a cooling device.

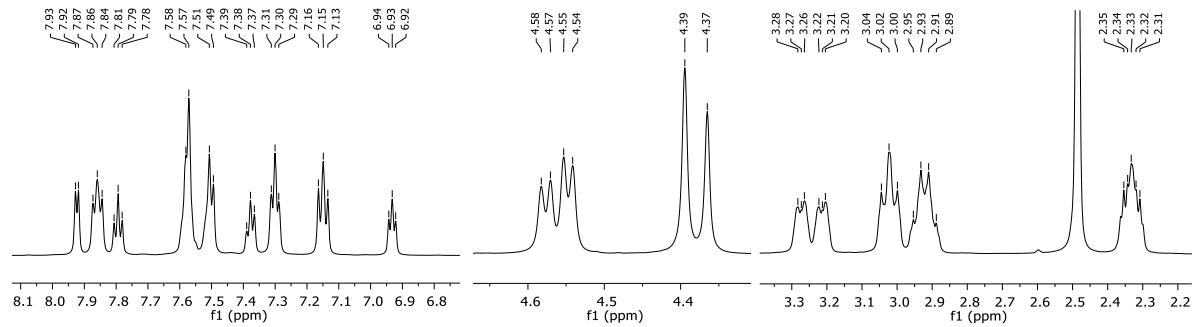
^{1}H NMR: (600 MHz, DMSO-*d6*): δ 7.93 – 7.92 (m, 1H), 7.87 – 7.84 (m, 2H), 7.81-7.78 (m, 1H), 7.58-7.49 (m, 4H), 7.39 – 7.37 (m, 1H), 7.31 – 7.29 (m, 2H), 7.20 – 7.09 (m, 2H), 6.94 – 6.92 (m, 1H), 4.58 – 4.54 (m, 1H), 4.38 (m, 1H), 3.28 – 3.20 (m, 1H), 3.04 – 3.00 (m, 1H), 2.95-2.89 (m, 1H), 2.40 – 2.27 (m, 1H).

^{13}C NMR: (151 MHz, DMSO-*d6*): δ 221.2, 219.9, 215.3, 162.1, 153.0, 139.2, 132.4, 132.0, 131.1, 131.0, 130.9, 130.8, 129.9, 129.8, 129.6, 125.0, 122.4, 59.8, 53.8 (d, J = 8.8 Hz), 22.7 (d, J = 22.7 Hz).

^{31}P NMR: (242 MHz, DMSO-*d6*): δ 65.86.

IR (ATR): ν 3045, 2891, 2024, 1914, 1843, 1477, 1434, 1099, 892, 752, 693 cm^{-1}

HRMS (ESI): calc. for $C_{23}H_{21}MnN_2O_3P$ $[M-Br]^+$: 459.0665, found 459.0675.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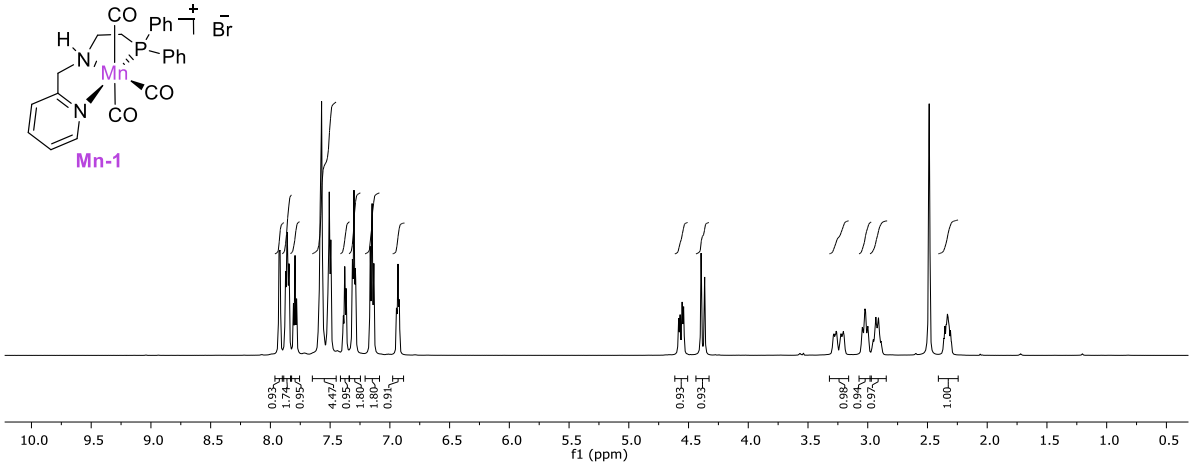
7.87
7.86
7.84
7.81
7.79
7.78
7.58
7.57
7.51
7.49
7.39
7.38
7.37
7.31
7.30
7.29
7.16
7.15
7.13
6.94
6.93
6.92
4.58
4.57
4.55
4.54
4.39
4.37
3.28
3.27
3.26
3.22
3.21
3.20
3.04
3.02
3.00
2.95
2.93
2.91
2.89
2.35
2.34
2.33
2.32
2.31
f1 (ppm)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Ph
Br
H
N
P
Ph
Mn
CO
N
CO
Mn-1
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1.74
0.95
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0.95
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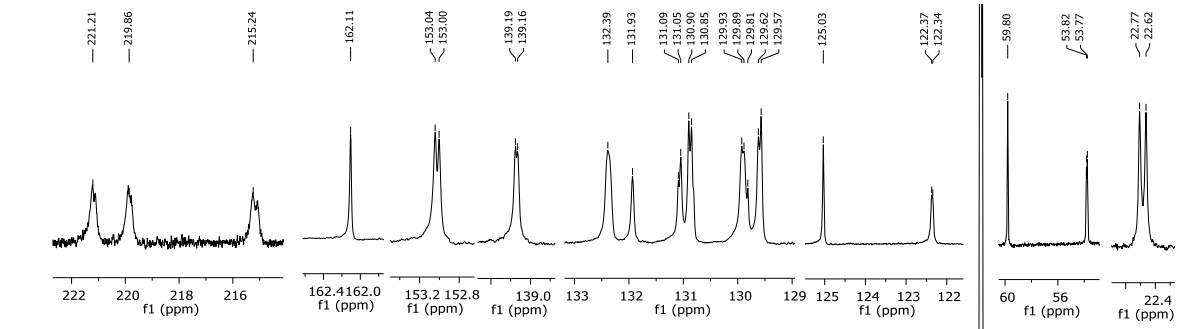
1.80
0.91
0.93
0.93
0.98
0.94
0.97
1.00
f1 (ppm)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130.85
129.93
129.89
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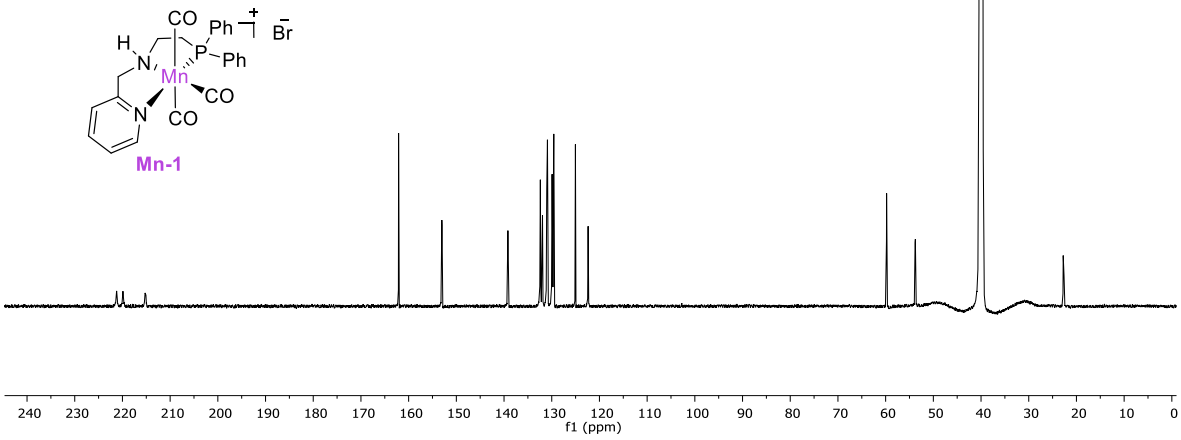
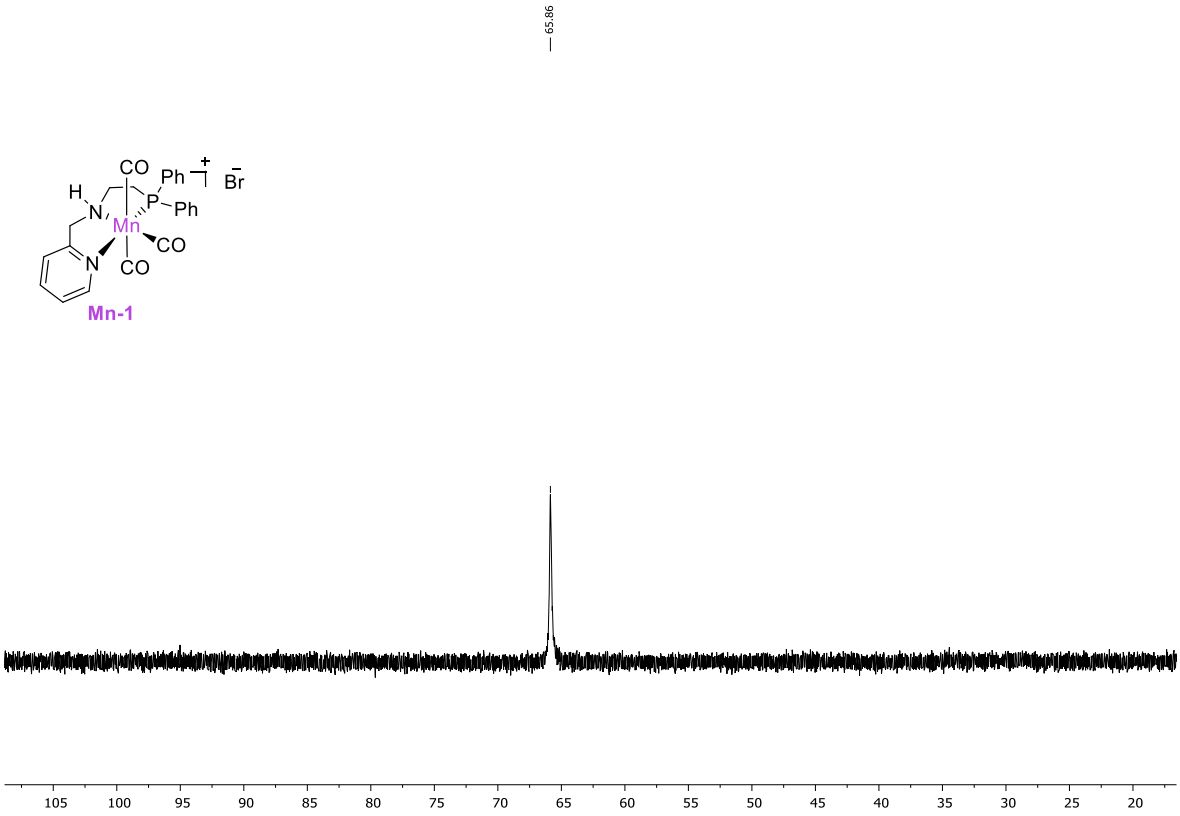
53.77
22.77
22.62
f1 (ppm)


CO
Ph
Br
H
N
P
Ph
Mn
CO
N
CO
Mn-1
f1 (ppm)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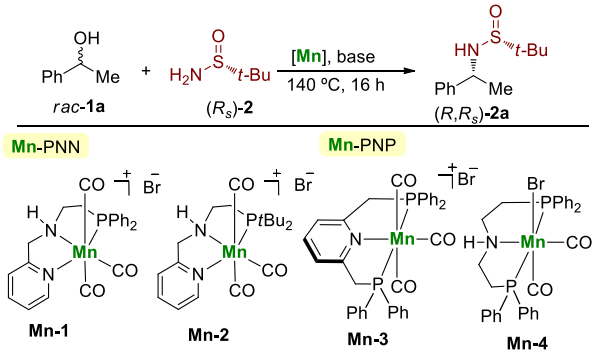
Ph
P
Ph
H
N
Mn
CO
N
CO
Br
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20

Mn-1

Optimization of the reaction conditions

Table 1. Optimization of the Reaction Conditions.[a]



entry	[**Mn**] (mol%)	base (mol %)	yield of **2a** (%)	dr
1	**Mn-1** (2.5)	*t*-BuOK (10)	33	98:02
2	**Mn-2** (2.5)	*t*-BuOK (10)	9	nd
3	**Mn-3** (2.5)	*t*-BuOK (10)	<5	nd
4	**Mn-4** (2.5)	*t*-BuOK (10)	10	nd
5[b]	**Mn-1** (2.5)	*t*-BuOK (10)	27	98:02
6[c]	**Mn-1** (2.5)	*t*-BuOK (10)	14	nd
7[d]	**Mn-1** (2.5)	*t*-BuOK (10)	39	99:01
8[d]	**Mn-1** (2.5)	KOH (10)	41	99:01
9[d]	**Mn-1** (2.5)	K_2CO_3 (10)	18	97:03
10[d]	**Mn-1** (2.5)	Cs_2CO_3 (10)	45	99:01
11[d]	**Mn-1** (2.5)	Cs_2CO_3 (5)	48	99:01
12[d,e]	**Mn-1** (5)	Cs_2CO_3 (10)	**85**	**99:01**

[a]Reaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), [**Mn**] and base in toluene (1 mL) at 140 °C in a glass tube under an inert atmosphere for 16 h. yields were determined by the H^1 NMR analysis of the crude reaction mixture using mesitylene as an internal standard. [b]Reaction in 1,4-dioxane. [c]Reaction in 2-Me-THF. [d]Reaction in *t*-amyl alcohol. [e]Isolated yield. nd = not determined

To our delight, preliminary experiments with 1-phenylethanol (**1a**) and the sulfinamide (*R*)-**2** in the presence of **Mn-1** (2.5 mol %) and *t*-BuOK (10 mol %) resulted in the desired product in 33% yield and a good diastereomeric ratio of 98:2 (Table 1, entry 1). When the complex **Mn-2** bearing aliphatic phosphine was tested, significant decrease in the reactivity was observed (Table 1, entry 2). Next, we decided to test the reactivity of pincer manganese complexes bearing different types of PNP ligands. However, the pyridyl-based complex **Mn-3** as well as the aliphatic NH-bridged complex **Mn-4** showed unsatisfactory results (Table 1, entries 3-4).Based on these results, the reaction condition was further optimized with **Mn-1**. Accordingly, the effect of replacing toluene by other solvents was examined. The polar aprotic solvents such as 1,4-dioxane and Me-THF proved not to be suitable for this reaction (Table 1, entries 5, 6). However, a slightly better result (39% yield) was obtained when the reaction was performed in the polar protic *t*-amyl alcohol (Table 1, entry 7).
Next, different bases were investigated for this reaction. Potassium hydroxide showed similar results if compared to KO*t*Bu, while potassium carbonate resulted in lower yields (Table 1, entries 8, 9). After careful investigations, we found that the use of Cs_2CO_3 in combination with *t*-amyl alcohol is the optimal combination for this reaction (Table 1, entries 10, 11). Finally, increasing the catalyst loading resulted in complete conversion with 85% isolated yield (Table 1, entry 12).

Experimental Procedure and Characterizations of the Products

General procedure for the asymmetric amination of secondary alcohols.

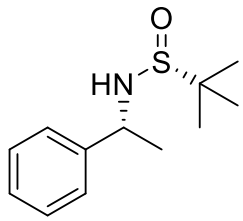
An oven dried 25 mL Schlenk tube equipped a stir bar was charged with secondary alcohol **1** (0.75 mmol), (*R*)-2-methyl-2-propanesulfinamide (61 mg, 0.5 mmol), **Mn-1** (5-10 mol %) and Cs_2CO_3 (10-20 mol %). Then the tube was evacuated and backfilled with argon for three times and degassed *t*-amyl alcohol (1 mL) was added. The reaction mixture was stirred at 140 °C in aluminum block for 16-48 h. Upon cooling down to room temperature the residue was directly purified by flash column chromatography using silica gel and EtOAc/hexanes mixtures as eluent to give the pure *N*-alkylated sulfinamide (*R*, R_s)-**3**.

Diastereomeric ratio was determined by ^{1}H NMR analysis of crude reaction mixture.

For the known compounds, we compared our data with the literature reports; (*JACS*, *119*, 9913), (*JACS*, *136*, 12548) and (*JOC*, *71*, 6859).

For the other compounds, authentic samples of the (*S*, R_s) diasteroisomers were prepared by the reduction of the corresponding sulfinamide imine with L-selectride (*JOC 70*, 7342)

(*R*)-2-methyl-*N*-((*R*)-1-phenylethyl)propane-2-sulfinamide ((*R*, *R*$_s$)-3a)



Yield: 85%, colorless oil

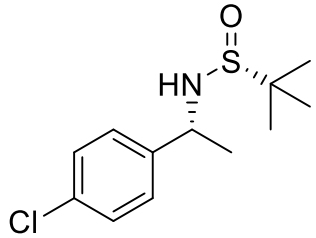
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.37-7.25 (m, 4H), 7.29-7.26 (m, 1H), 4.54 (qd, *J*=6.5, 2.6 Hz, 1H), 3.43 (br s, 1H), 1.50 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 144.0, 128.7, 127.8, 126.6, 55.4, 53.8, 53.8, 22.8, 22.6.

MS (EI): m/z = 225.0 $[M]^+$

IR (ATR): *v* = 3208, 2972, 2325, 2086, 1453, 1365, 1310, 1201, 1181, 1055, 919, 851, 762, 699cm^{-1}.

(*R*)-*N*-((*R*)-1-(4-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, *R*$_s$)-3b)



Yield: 80%, colorless solid

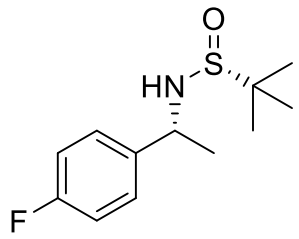
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 4H), 4.49 – 4.46 (m, 1H), 3.40 (d, *J* = 3.4 Hz, 1H), 1.45 (d, *J* = 6.7 Hz, 3H), 1.18 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 142.5, 133.4, 128.8, 128.0, 55.5, 53.4, 53.4, 22.8, 22.5.

MS (EI): m/z = 259.9 $[M]^+$

IR (ATR): *v* =3278, 2980, 1488, 1417, 1365, 1289, 1203, 1177, 1121, 1087, 1045, 938, 820, 783, 717, 658 cm^{-1}.

(*R*)-*N*-((*R*)-1-(4-fluorophenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3c)



Yield: 65%, colorless solid

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.52 – 4.48 (m, 1H), 3.38 (br s, 1H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.20 (s, 9H).

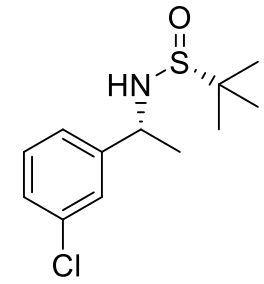
^{13}C NMR: (151 MHz, $CDCl_3$) δ 163.0, 161.3, 139.8 (d, *J* = 3.0 Hz), 128.2 (d, *J* = 8.1 Hz), 115.6, 115.5, 55.5, 53.4 (d, *J* = 1.8 Hz), 22.9, 22.5.

^{19}F NMR: (282 MHz, $CDCl_3$) δ -114.5.

MS (EI): m/z = 243.0 $[M]^+$

IR (ATR): *v* = 3213, 2978, 2956, 2925, 2868, 1603, 1509, 1456, 1423, 1363, 1281, 1219, 1160, 1119, 1088, 1043, 941, 863, 830, 733 cm^{-1}.

(*R*)-*N*-((*R*)-1-(3-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3d)



Yield: 74%, white solid

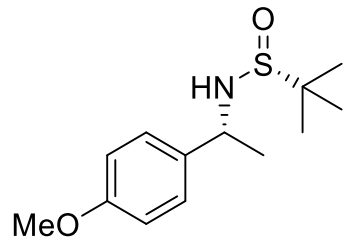
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.26 – 7.16 (m, 3H), 4.47 (qd, *J* = 6.5, 3.2 Hz, 1H), 3.41 (d, *J* = 2.1 Hz, 1H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.19 (s, 9H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 146.0, 134.5, 130.0, 127.9, 126.6, 124.9, 55.5, 53.6, 22.8, 22.5.

MS (EI): m/z = 259.9 $[M]^+$

IR (ATR): *v* =3160, 2960, 1579, 1433, 1366, 1204, 1125, 1041, 947, 879, 832, 781, 693 cm^{-1}.

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, *Rs*)-3e)



Yield: 87%, white solid

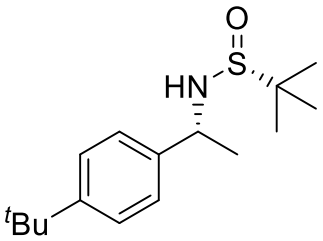
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.47 (qd, *J* = 6.4, 2.3 Hz, 1H), 3.75 (s, 3H), 3.36 (s, 1H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.19 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 159.1, 136.1, 127.7, 114.0, 55.3, 55.2, 53.3, 22.7, 22.6.

MS (EI): m/z = 255.0 $[M]^+$

IR (ATR): *v* =3216, 2963, 2324, 2083, 1611, 1512, 1458, 1366, 1304,1281, 1244, 1177, 1044, 913, 830, 731, 683, 662 cm^{-1}.

(*R*)-*N*-((*R*)-1-(4-(tert-butyl)phenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, *R$_s$*)-3f)



Yield:85%, colorless oil

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.52 (qd, *J* = 6.5, 2.6 Hz, 1H), 3.42 (d, *J* = 1.0 Hz, 1H), 1.48 (d, *J* = 6.7 Hz, 3H), 1.30 (s, 9H), 1.21 (s, 9H).

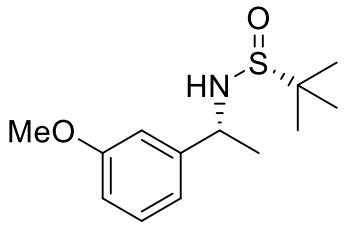
^{13}C NMR: (151 MHz, $CDCl_3$) δ 150.6, 141.0, 126.3, 125.6, 55.4, 53.5, 34.5, 31.3, 22.6.

MS (EI): m/z = 281.0 $[M]^+$

IR (ATR): *v* = 3287, 2960, 2867,1511, 1469, 1421, 1365, 1271, 1208, 1119, 1041, 946, 829 cm^{-1}.

HRMS (ESI): calc. for $C_{16}H_{28}ONS$ $[M + H]^+$: 282.1886, found 282.1889.

(*R*)-*N*-((*R*)-1-(3-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3g)



Yield: 83%, yellow oil

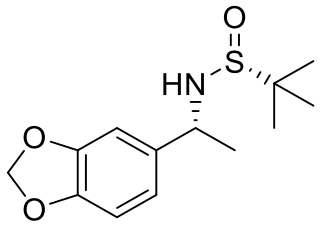
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.22-7.26 (m, 1H), 6.94 – 6.86 (m, 2H), 6.80-6.82 (m, 1H), 4.50 (qd, *J* = 6.4, 2.7 Hz, 1H), 3.79 (s, 3H), 3.41 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.22 (s, 9H)

^{13}C NMR: (101 MHz, $CDCl_3$) δ 159.8, 145.7, 129.8, 118.8, 112.9, 112.4, 55.4, 55.2, 53.8, 22.7, 22.6.

MS (EI): m/z = 256.1 $[M+H]^+$

IR (ATR): *v* = 3214, 2968, 2326, 2162, 1711, 1598, 1458, 1365, 1313, 1256, 1165, 1047, 940, 874, 784, 699 cm^{-1}.

(*R*)-*N*-((*R*)-1-(benzo[d][1,3]dioxol-5-yl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3h)



Yield: 95%, light yellow solid

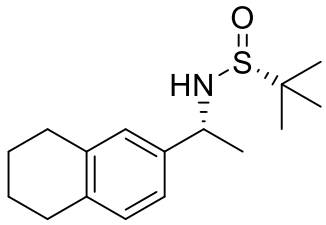
^{1}H NMR: (600 MHz, $CDCl_3$) δ 6.80-6.77 (m, 1H), 6.76-6.73 (m, 1H), 6.71-6.68 (m, 1H), 5.88 (s, 2H), 4.41 (qd, *J* = 6.5, 2.7 Hz, 1H), 3.36 (d, *J* = 1.6 Hz, 1H), 1.41 (d, *J* = 6.7 Hz, 3H), 1.17 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 147.8, 147.0, 138.0, 119.9, 108.2, 106.8, 101.0, 55.4, 53.7, 22.8, 22.6.

MS (EI): m/z = 269.9 $[M]^+$

IR (ATR): *v* = 3304, 2970, 2879, 1610, 1485, 1441, 1376, 1305, 1236, 1097, 1040, 920, 815, 728, 671 cm^{-1}.

(*R*)-2-methyl-*N*-((*R*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethyl)propane-2-sulfinamide ((*R*, R_s)-3i)



Yield:70%, white solid

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.08 – 6.98 (m, 3H), 4.46 (qd, *J* = 6.5, 2.5 Hz, 1H), 3.35 (s, 1H), 2.74-2.73 (m, 4H), 1.81 – 1.74 (m, 4H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H).

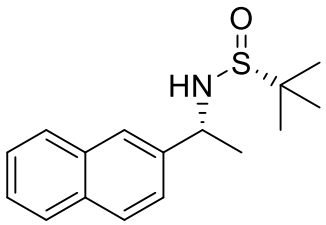
^{13}C NMR: (101 MHz, $CDCl_3$) δ 141.1, 137.4, 136.8, 129.5, 127.3, 123.6, 55.3, 53.6, 29.4, 29.1, 23.1, 22.6.

MS (EI): m/z = 280.2 $[M+H]^+$

IR (ATR): *v* = 3227, 2920, 1435, 1365, 1162, 1135, 1036, 948, 812, 706 cm^{-1}.

HRMS (ESI): calc. for $C_{16}H_{26}ONS$ $[M + H]^+$: 280.1730, found 280.1730.

(*R*)-2-methyl-*N*-((*R*)-1-(naphthalen-2-yl)ethyl)propane-2-sulfinamide ((*R*, R_s)-3J)



Yield: 76%, light yellow solid

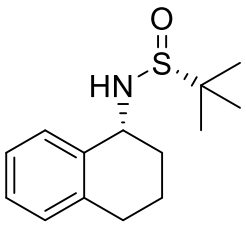
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 4H), 7.51 – 7.44 (m, 3H), 4.72 (qd, *J* = 6.5, 2.8 Hz, 1H), 3.55 (d, *J* = 1.4 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.25 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 141.3, 133.3, 133.0, 128.6, 128.0, 127.7, 126.3, 126.1, 125.3, 124.7, 55.5, 54.0, 22.6.

MS (EI): m/z = 275.2 $[M]^+$

IR (ATR): *v* =3254, 2979, 2953, 2900, 2867, 2113, 2078, 1983, 1925, 1727, 1603, 1509, 1466, 1363, 1307, 1177, 1059, 1015, 913, 866, 821, 750, 674 cm^{-1}.

(*R*)-2-methyl-*N*-((*R*)-1,2,3,4-tetrahydronaphthalen-1-yl)propane-2-sulfinamide ((*R*, *R*$_s$)-3k)



Yield: 84%, yellow solid

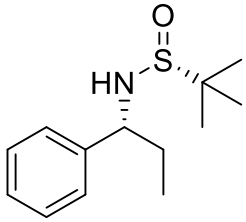
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H), 7.20 – 7.15 (m, 2H), 7.10 – 7.07 (m, 1H), 4.56-4.54 (m, 1H), 3.26 (d, *J* = 3.1 Hz, 1H), 2.83 – 2.77 (m, 1H), 2.75 – 2.68 (m, 1H), 2.02 – 1.95 (m, 1H), 1.95 – 1.84 (m, 2H), 1.78 – 1.71 (m, 1H), 1.20 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 137.7, 136.9, 129.6, 129.2, 127.5, 126.5, 55.4, 52.8, 30.6, 29.1, 22.6, 18.2.

MS (EI): m/z = 251.0 $[M]^+$

IR (ATR): *v* = 3188, 2935, 2859, 2325, 1726, 1456, 1361,1289, 1190, 1028, 898, 742 cm^{-1}.

(*R*)-2-methyl-*N*-((*R*)1-phenylpropyl)propane-2-sulfinamide ((*R*, *R*$_s$)-3l)



Yield: 80%, white solid

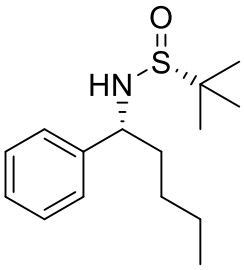
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40 – 7.16 (m, 5H), 4.28-4.24 (m, 1H), 3.37 (d, *J* = 2.4 Hz, 1H), 2.16 – 1.92 (m, 1H), 1.85 – 1.62 (m, 1H), 1.21 (s, 9H), 0.77 (t, *J* = 7.4 Hz, 9H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 142.2, 128.6, 127.7, 127.2, 60.3, 55.6, 29.3, 22.6, 10.0.

MS (EI): m/z = 239.1 $[M]^+$

IR (ATR): *v* = 3193, 2929, 2867, 1602, 1455, 1362, 1185, 1047, 893, 752, 696 cm^{-1}.

(*R*)-2-methyl-*N*-((*R*)-1-phenylpentyl)propane-2-sulfinamide ((*R*, R_s)-3m)



Yield: 86%, colorless oil

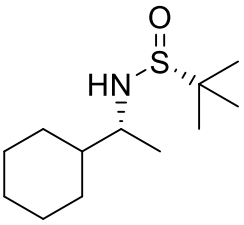
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 4.34-4.31 (m, 1H), 3.38 (d, *J* = 3.1 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.76 – 1.67 (m, 1H), 1.33-1.17 (m, 3H), 1.22 (s, 9H), 1.12 – 1.01 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 142.6, 128.6, 127.8, 127.2, 59.1, 55.6, 36.2, 27.8, 22.6, 22.5, 14.0.

MS (EI): m/z = 267.1 $[M]^+$

IR (ATR): *v* = 3215, 2939, 2867, 2326, 2100, 1887, 1743, 1601, 1459, 1368, 1185, 1052, 916, 703 cm^{-1}.

(*R*)-*N*-((*R*)-1-cyclohexylethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3n)



Yield: 55%, colorless oil

^{1}H NMR: (600 MHz, $CDCl_3$) δ 3.23 – 3.16 (m, 1H), 3.10 (d, *J* = 4.2 Hz, 1H), 1.77 – 1.59 (m, 5H), 1.40 – 1.32 (m, 1H), 1.26 – 1.17 (m, 2H), 1.16 (s, 9H), 1.12-1.09 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.04 – 0.93 (m, 2H).

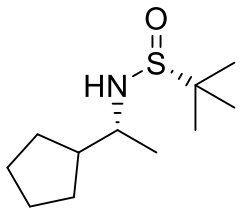
^{13}C NMR: (151 MHz, $CDCl_3$) δ 55.5, 55.3, 44.2, 29.3, 27.9, 26.4, 26.3, 26.2, 22.6, 17.8.

MS (EI): m/z = 231.0 $[M]^+$

IR (ATR): *v* = 3238, 3176, 2920, 2851, 1730, 1447, 1365, 1152, 1043, 957, 906, 846 cm^{-1}.

HRMS (ESI): calc. for $C_{12}H_{26}ONS$ $[M + H]^+$: 232.1730, found 232.1729.

(*R*)-*N*-((*R*)-1-cyclopentylethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3o)



Yield: 74%, colorless oil

^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.26 – 3.17 (m, 1H), 3.13 (d, *J* = 2.6 Hz, 1H), 1.91 – 1.46 (m, 7H), 1.37 – 1.20 (m, 2H), 1.18 (s, 9H), 1.15 (d, *J* = 6.3 Hz, 3H).

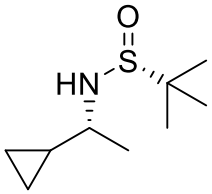
^{13}C NMR: (101 MHz, $CDCl_3$) δ 57.8, 55.2, 55.1, 46.8, 29.5, 29.3, 25.6, 25.4, 22.5, 20.1.

MS (EI): m/z = 217.1 $[M]^+$

IR (ATR): *v* = 3456, 3219, 2949, 2869, 2326, 2156, 1736, 1647, 1457, 1369, 1321, 1180, 1128, 1050, 909, 847, 796 cm^{-1}.

HRMS (ESI): calc. for $C_{11}H_{23}ONS$ $[M + Na]^+$: 240.1393, found 240.1389.

(*R*)-*N*-((*R*)-1-cyclopropylethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3p)



Yield: 89%, colorless oil.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.23 (s, 1H), 2.54 – 2.44 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.13 (s, 9H), 0.83 – 0.72 (m, 1H), 0.52 – 0.41 (m, 2H), 0.28 – 0.13 (m, 2H).

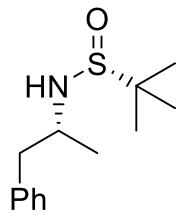
^{13}C NMR: (101 MHz, $CDCl_3$) δ 56.2, 55.0, 22.4, 20.9, 18.8, 4.1, 3.5.

MS (EI): m/z = 189.0 $[M]^+$

IR (ATR): *v* = 3461, 3215, 2964, 2338, 2094, 1722, 1538, 1460, 1370, 1311, 1187, 1051, 949, 819, 682 cm^{-1}.

HRMS (ESI): calc. for $C_9H_{19}ONNaS$ $[M + Na]^+$: 212.1080, found 212.1082.

(*R*)-2-methyl-*N*-((*R*)-1-phenylpropan-2-yl)propane-2-sulfinamide ((*R*, R_s)-3q)



Yield: 78%, colorless oil

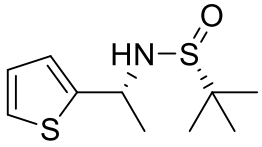
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 5H), 3.67 – 3.57 (m, 1H), 3.00 (d, *J* = 6.5 Hz, 1H), 2.84 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.70 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.11 (s, 9H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 138.3, 129.5, 128.3, 126.4, 55.7, 53.8, 44.5, 22.6, 22.5.

MS (EI): m/z = 240.1 $[M+H]^+$

IR (ATR): *v* =3211, 2965, 1605, 1456, 1367, 1320, 1131, 1047, 960, 878, 744, 699 cm^{-1}.

(*R*)-2-methyl-*N*-((*R*)-1-(thiophen-2-yl)ethyl)propane-2-sulfinamide ((*R*, R_s)-3r)



Yield: 86%, yellow oil

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.23-7.22 (m, 1H), 7.03 (d, *J* = 3.4 Hz, 1H) 6.95-6.94 (m, 1H), 4.86-4.82 (m, 1H), 3.51 (d, *J* = 1.7 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H).

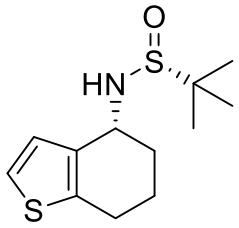
^{13}C NMR: (151 MHz, $CDCl_3$) δ 147.9, 126.7, 124.7, 124.5, 55.6, 50.1, 23.8, 22.6.

MS (EI): m/z = 231.9 $[M]^+$

IR (ATR): *v* = 3202, 2967, 2160, 1660, 1456, 1371, 1302, 1231, 1181, 1051, 908, 843, 698 cm^{-1}.

HRMS (ESI): calc. for $C_{10}H_{18}ONS_2$ $[M + H]^+$: 232.0824, found 232.0828.

(*R*)-2-methyl-*N*-((*R*)-4,5,6,7-tetrahydrobenzo[b]thiophen-4-yl)propane-2-sulfinamide ((*R*, R_s)-3s)



Yield: 78%, white solid

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 2H), 4.53-4.50 (m, 1H), 3.30 (d, *J* = 4.7 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.04 – 1.80 (m, 4H), 1.22 (s, 9H).

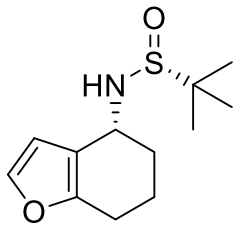
^{13}C NMR: (101 MHz, $CDCl_3$) δ 138.9, 135.9, 127.3, 122.7, 55.5, 51.0, 31.2, 24.8, 22.6, 19.9.

MS (EI): m/z = 257.0 $[M]^+$

IR (ATR): *v* = 3216, 2935, 2859, 1567, 1459, 1431, 1359, 1298, 1251, 1182, 1141, 1083, 1031, 929, 898, 870, 717, 674 cm^{-1}.

HRMS (ESI): calc. for $C_{12}H_{19}ONS_2$ $[M + Na]^+$: 280.0800, found 280.0797.

(*R*)-2-methyl-*N*-((*R*)-4,5,6,7-tetrahydrobenzofuran-4-yl)propane-2-sulfinamide ((*R*, R_s)-3t)



Yield: 83%

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.3 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 4.40 (dd, *J* = 8.8, 4.7 Hz, 1H), 3.22 (d, *J* = 5.1 Hz, 1H), 2.63-2.49 (m, 2H), 1.99 – 1.74 (m, 4H), 1.20 (s, 9H)

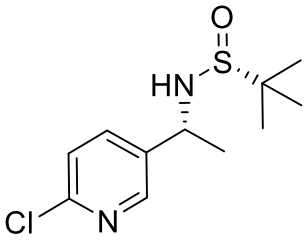
^{13}C NMR: (101 MHz, $CDCl_3$) δ 152.4, 141.0, 118.6, 109.6, 55.5, 49.5, 31.5, 22.8, 22.6, 19.3.

MS (EI): m/z = 241.1 $[M]^+$

IR (ATR): *v* =3227, 2940, 2864, 1739, 1623, 1432, 1360, 1224, 1184, 1141, 1035, 955, 903, 842, 723 cm^{-1}.

HRMS (ESI): calc. for $C_{12}H_{26}ONS$ $[M + Na]^+$: 264.1029, found 264.1028.

(*R*)-*N*-((*R*)-1-(6-chloropyridin-3-yl)ethyl)-2-methylpropane-2-sulfinamide ((*R*, R_s)-3u)



Yield: 65%, white solid

^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.4 Hz, 1H), 7.65 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 4.55 (qd, *J* = 6.7, 3.9 Hz, 1H), 3.41 (d, *J* = 2.8 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.21 (s, 9H).

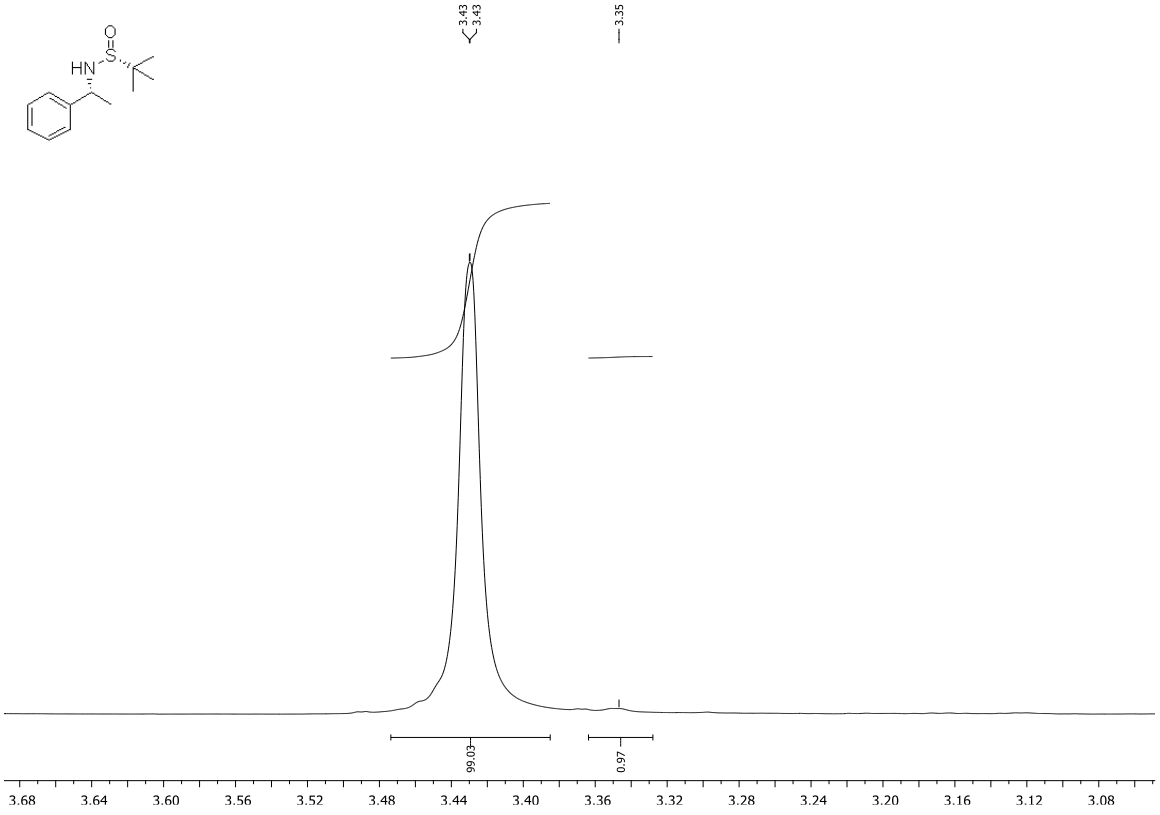
^{13}C NMR: (101 MHz, $CDCl_3$) δ 148.2, 138.2, 137.3, 124.3, 55.8, 51.5, 22.6, 22.5.

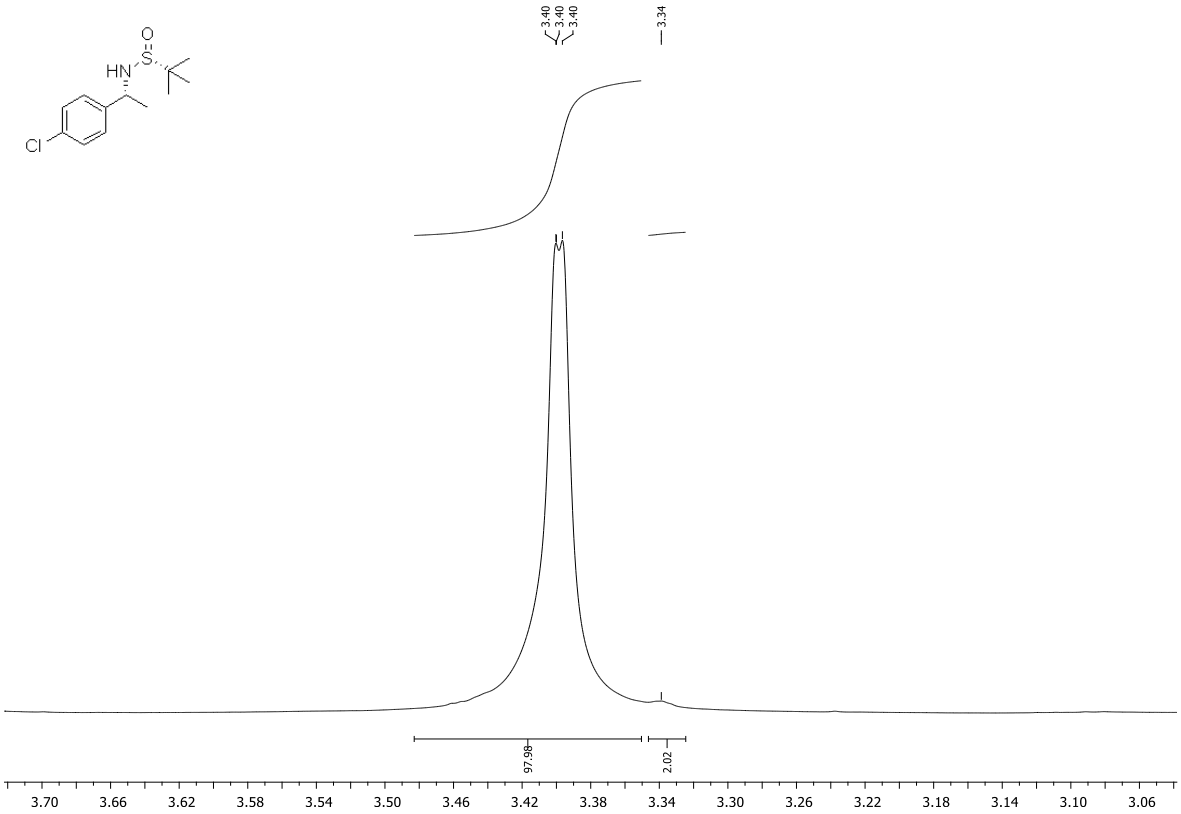
MS (EI): m/z = 261.0 $[M+H]^+$

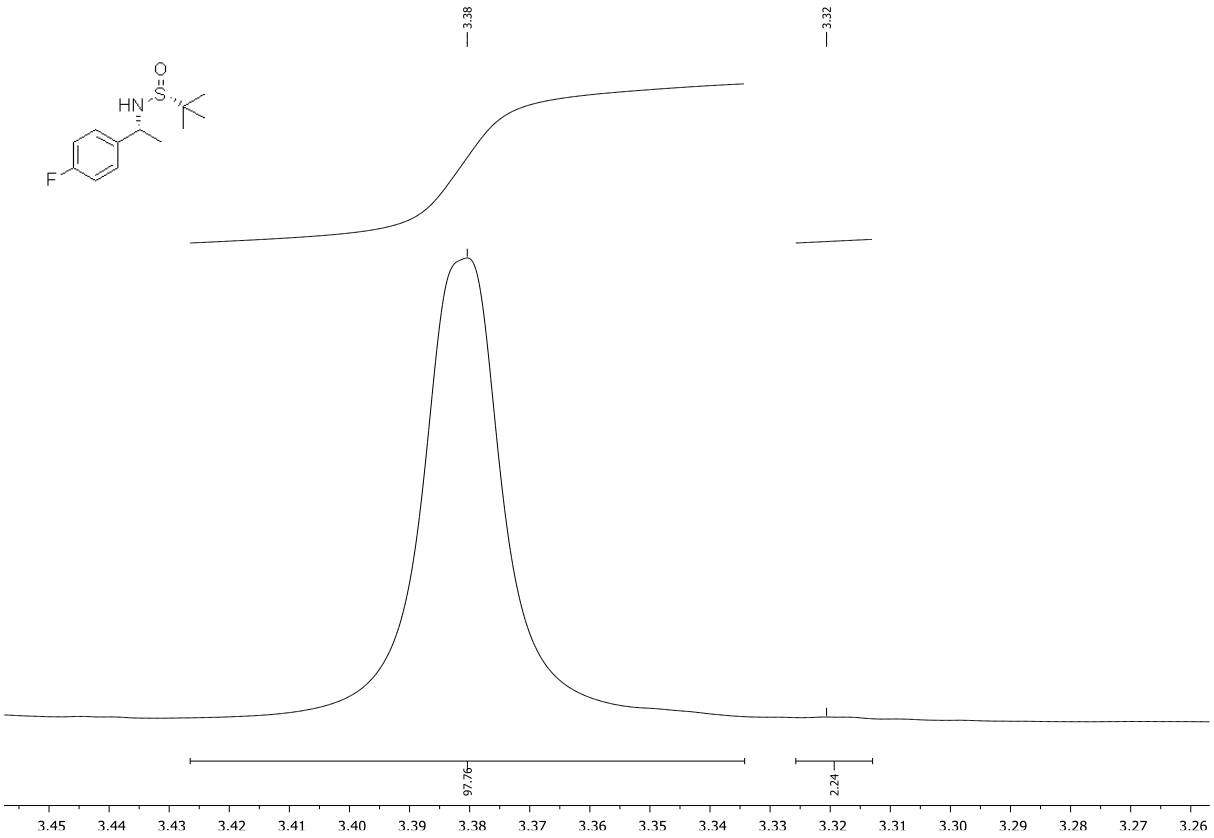
IR (ATR): *v* =3217, 2962, 1733, 1575, 1458, 1373, 1283, 1204, 1099, 1029, 940, 841, 797 cm^{-1}.

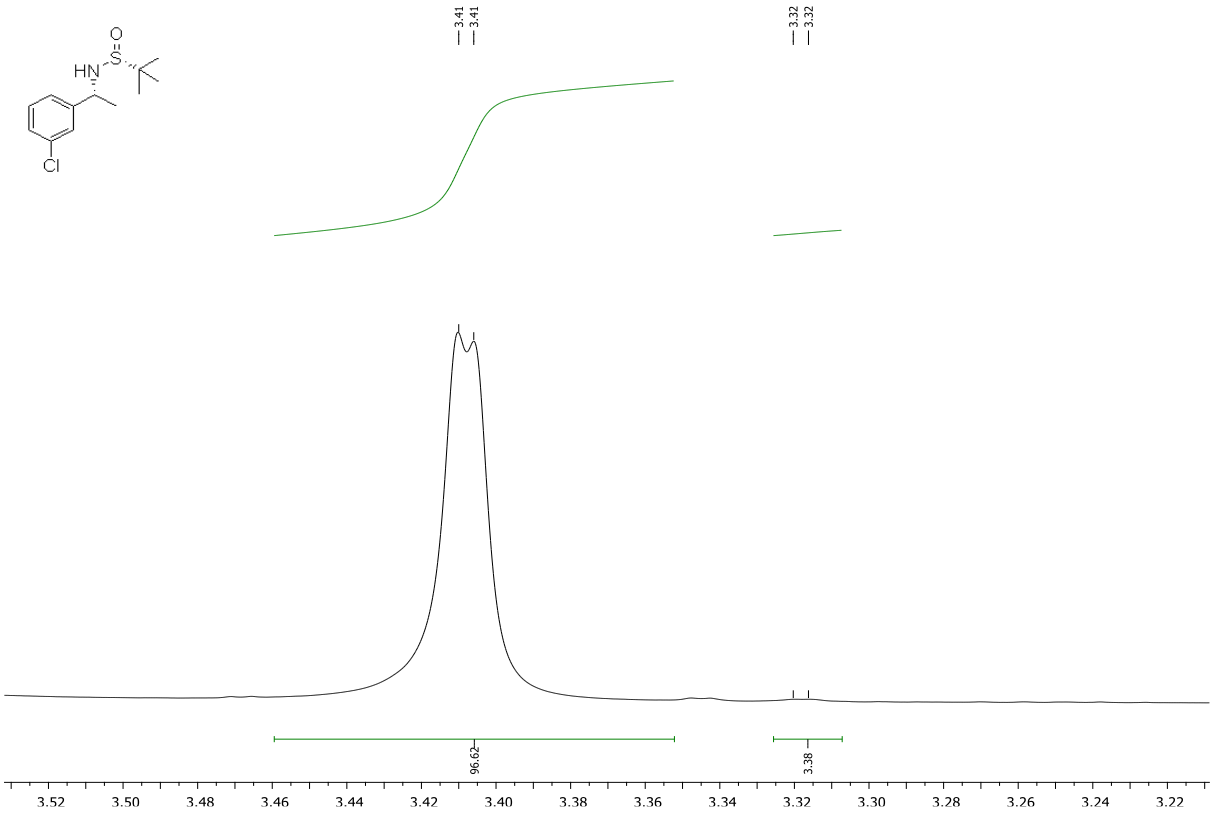
HRMS (ESI): calc. for $C_{11}H_{18}ON_2ClS$ $[M + H]^+$: 261.0823, found 261.0820.

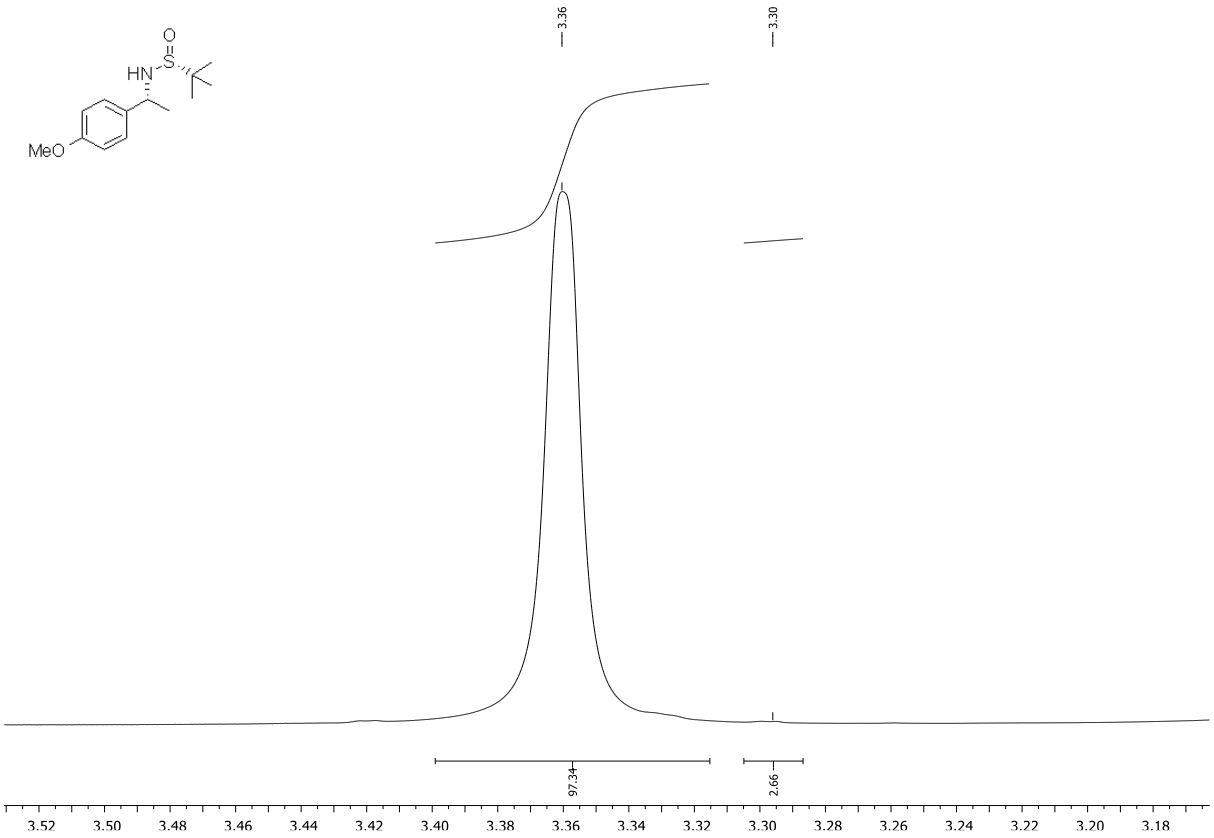
NMR Spectra for the Crude Reaction Mixtures

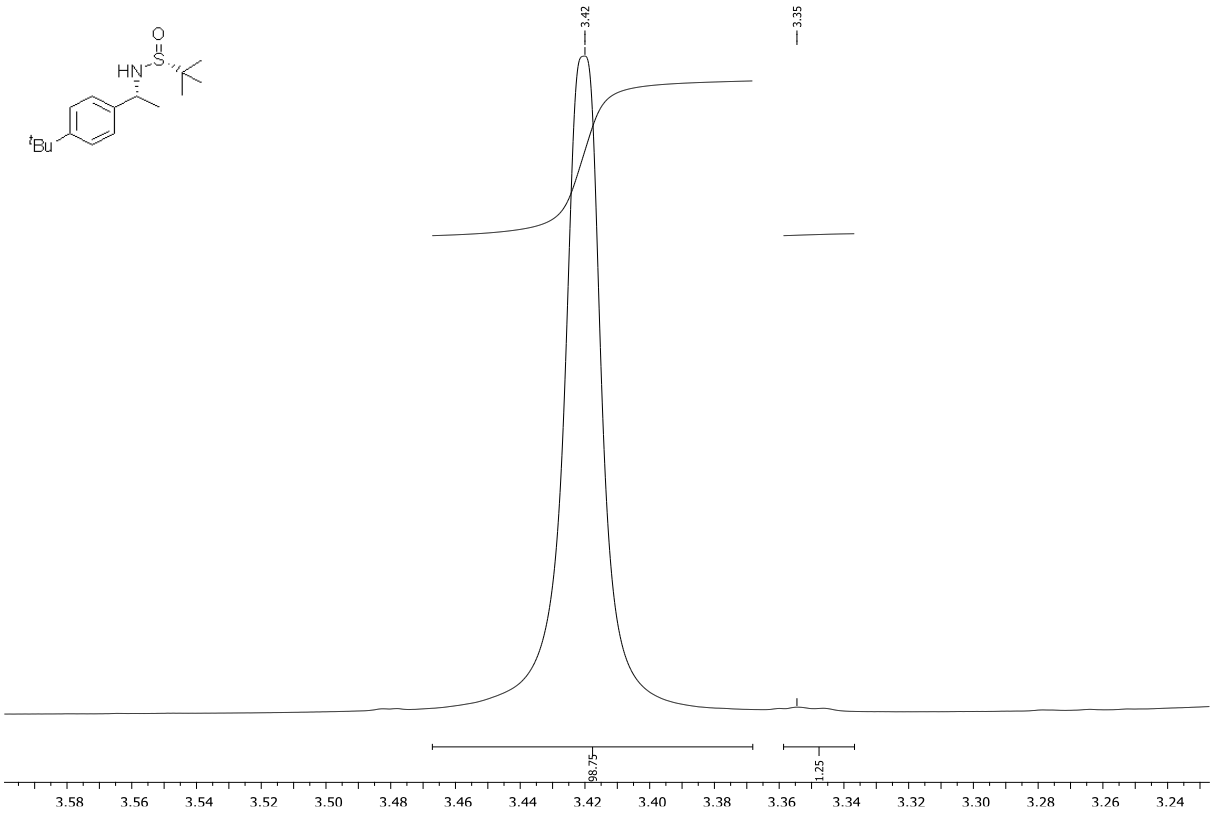


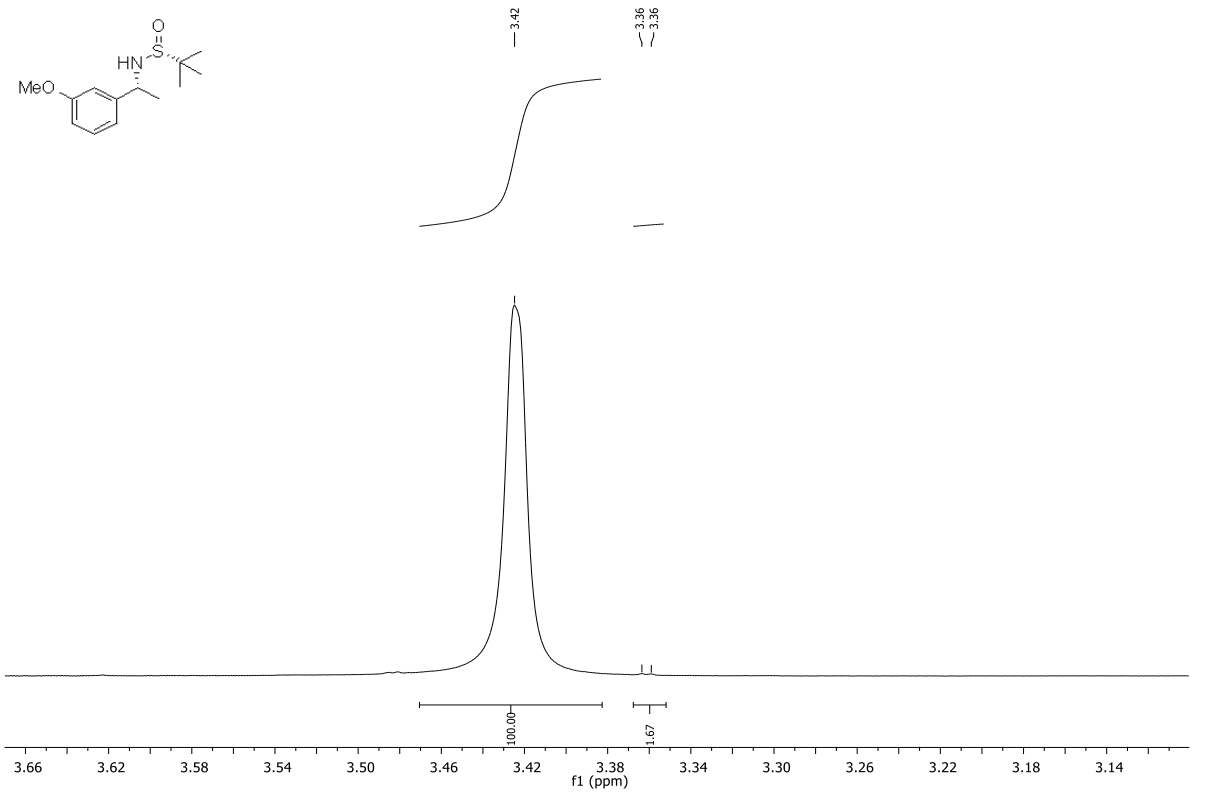


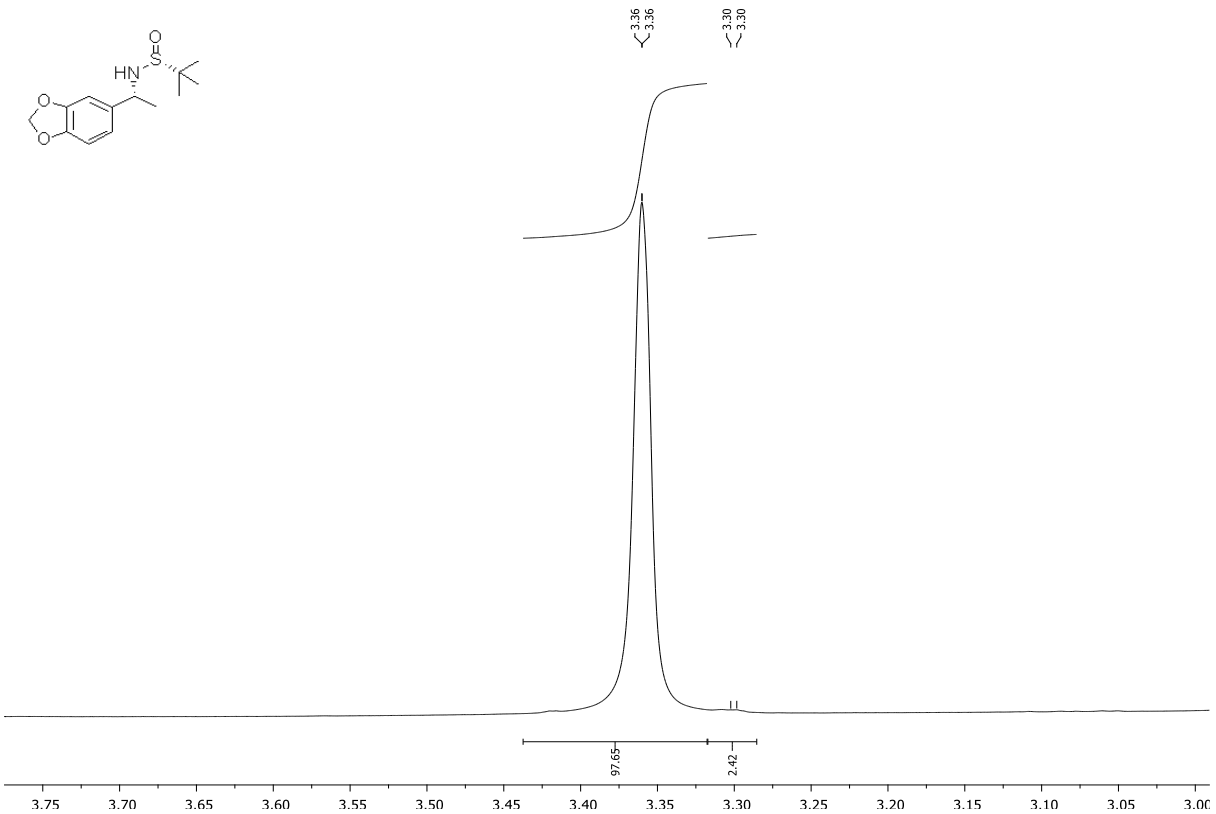

3.38
3.32
HN
S
O
F
97.76
2.24
3.45 3.44 3.43 3.42 3.41 3.40 3.39 3.38 3.37 3.36 3.35 3.34 3.33 3.32 3.31 3.30 3.29 3.28 3.27 3.26


3.41
3.41
3.32
3.32
HN
S
O
Cl
96.62
3.38
3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34 3.32 3.30 3.28 3.26 3.24 3.22


MeO
HN
O
S
3.36
3.30
97.34
2.66
3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34 3.32 3.30 3.28 3.26 3.24 3.22 3.20 3.18


tBu
HN
O
S
3.42
3.35
98.75
1.25
3.58 3.56 3.54 3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34 3.32 3.30 3.28 3.26 3.24


MeO
HN
O
S
3.42
3.36
3.36
100.00
1.67
3.66
3.62
3.58
3.54
3.50
3.46
3.42
3.38
3.34
3.30
3.26
3.22
3.18
3.14
f1 (ppm)


HN
O
S
O
O
3.36
3.36
3.30
3.30
97.65
2.42
3.75
3.70
3.65
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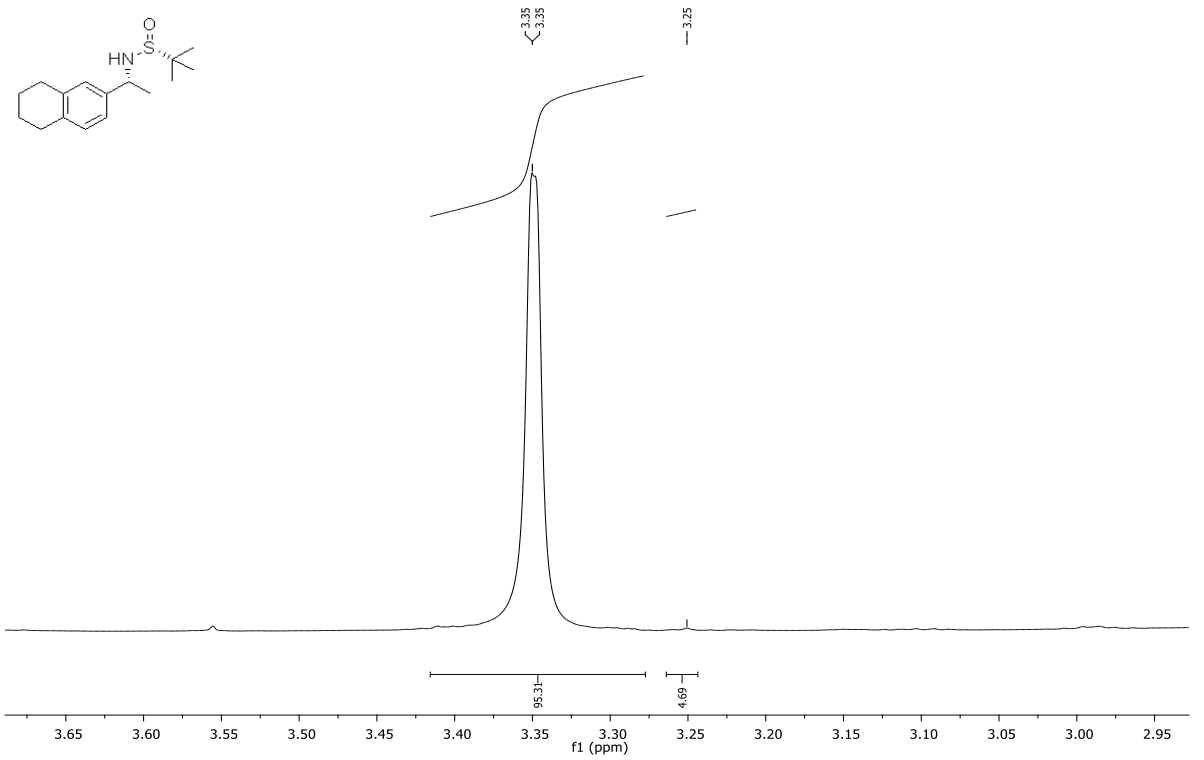
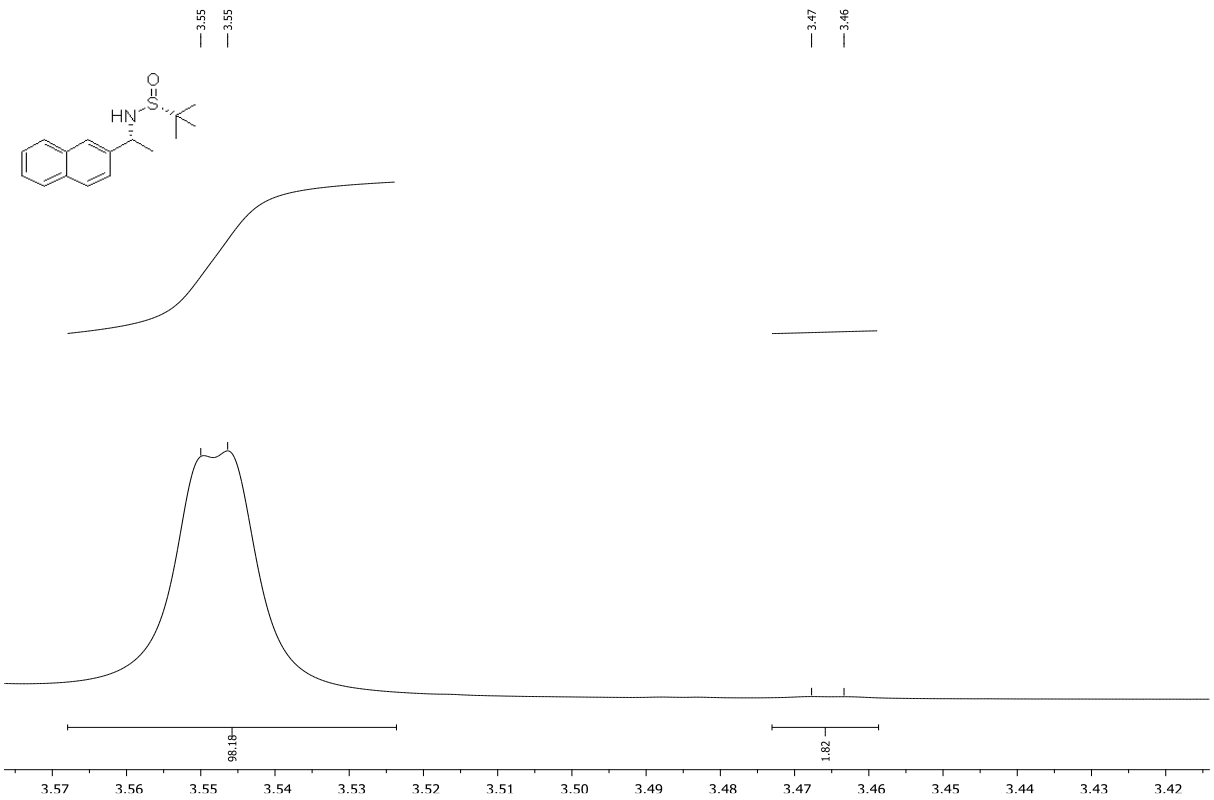
3.30
3.25
3.20
3.15
3.10
3.05


HN
O
O
3.35
3.35
3.25
95.31
4.69
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
3.15
3.10
3.05
3.00
2.95
f1 (ppm)


HN
O
O
3.55
3.55
3.47
3.46
98.18
1.82
3.57
3.56
3.55
3.54
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3.50
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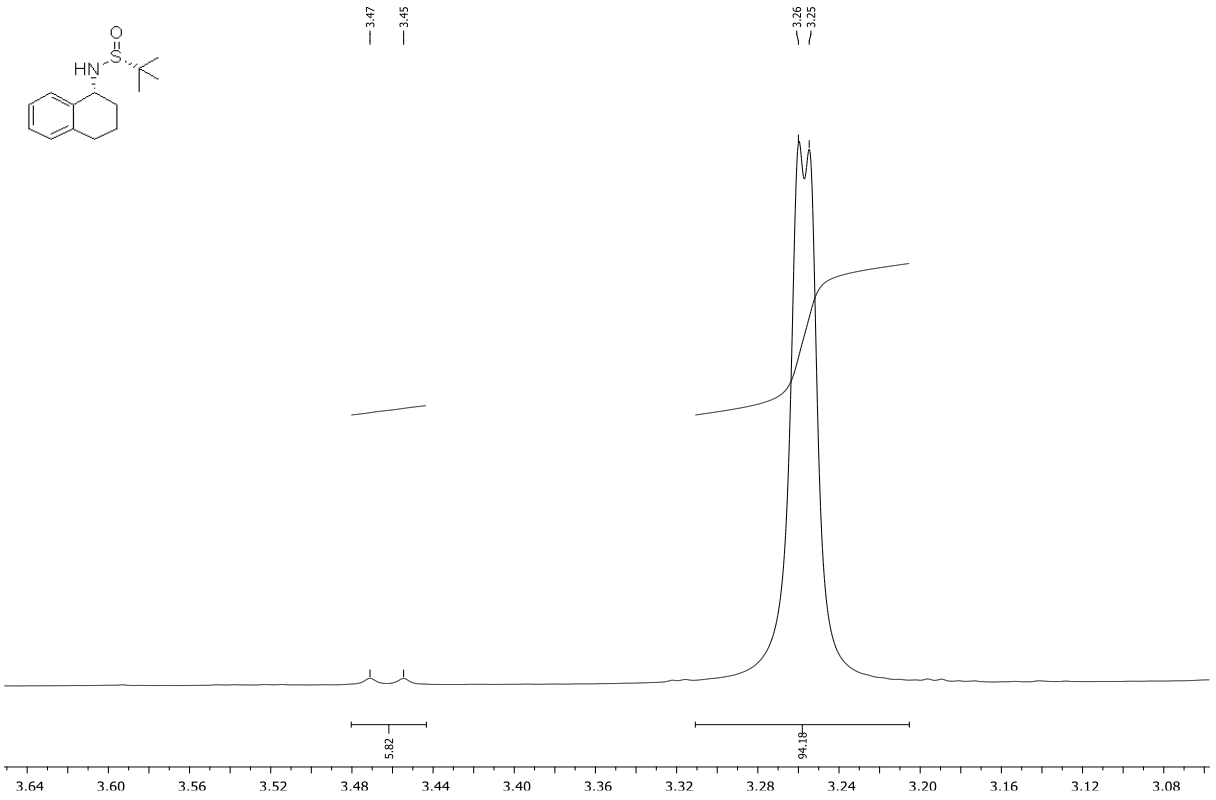
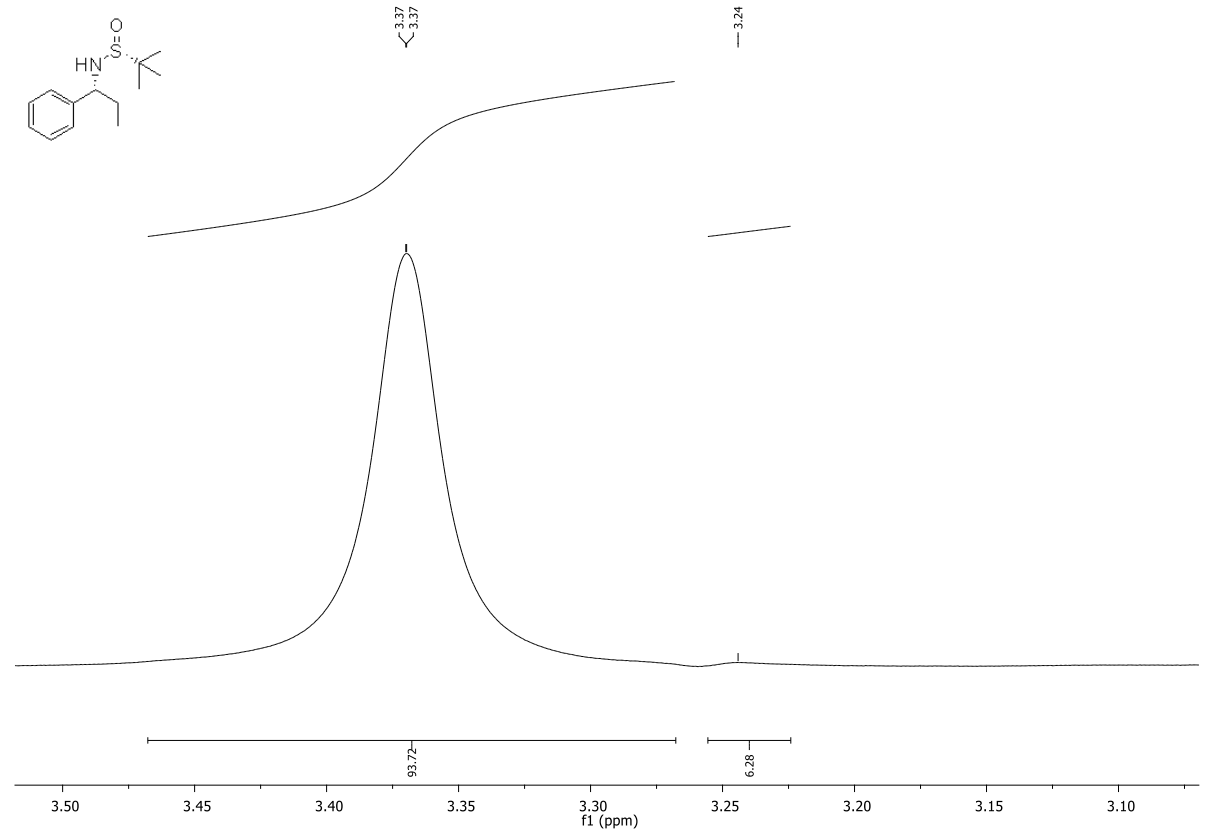
3.48
3.47
3.46
3.45
3.44
3.43
3.42


3.47
3.45
3.26
3.25
HN
S
O
5.82
94.18
3.64
3.60
3.56
3.52
3.48
3.44
3.40
3.36
3.32
3.28
3.24
3.20
3.16
3.12
3.08


3.37
3.37
3.24
HN
S
O
93.72
6.28
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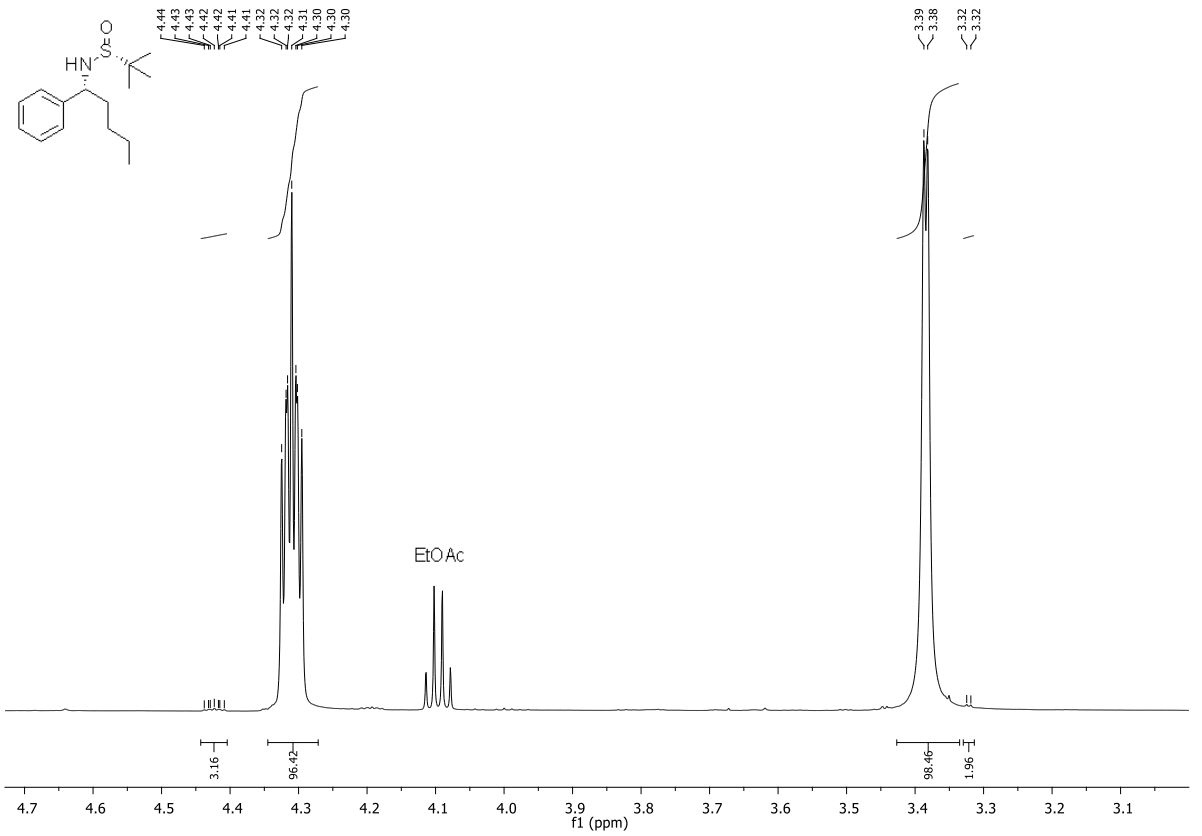
3.40
3.35
3.30
3.25
3.20
3.15
3.10
f1 (ppm)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4.41
4.32
4.32
4.32
4.31
4.30
4.30
4.30
3.39
3.38
3.32
3.32
EtOAc
3.16
96.42
98.46
1.96
4.7
4.6
4.5
4.4
4.3
4.2
4.1
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3.8
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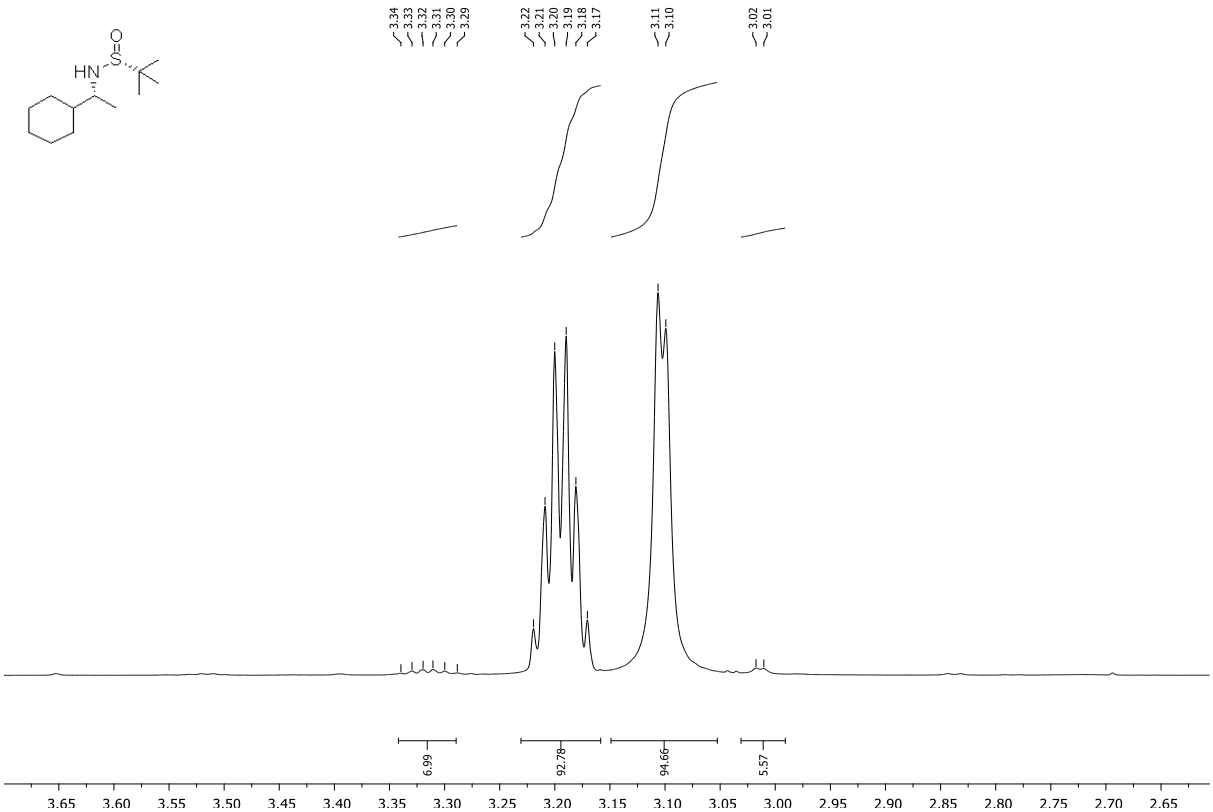
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)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3.21
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3.18
3.17
3.11
3.10
3.02
3.01
6.99
92.78
94.66
5.57
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
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3.10
3.05
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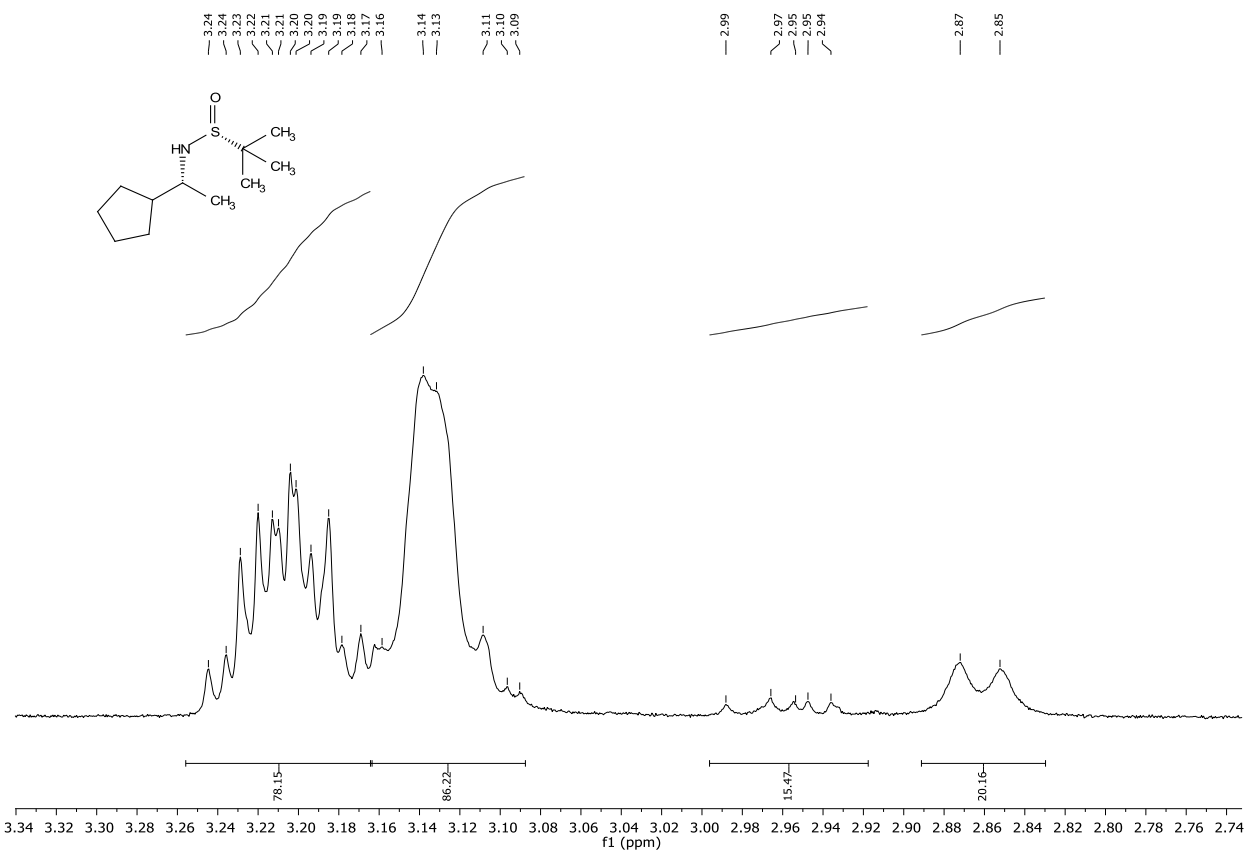
2.90
2.85
2.80
2.75
2.70
2.65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3.20
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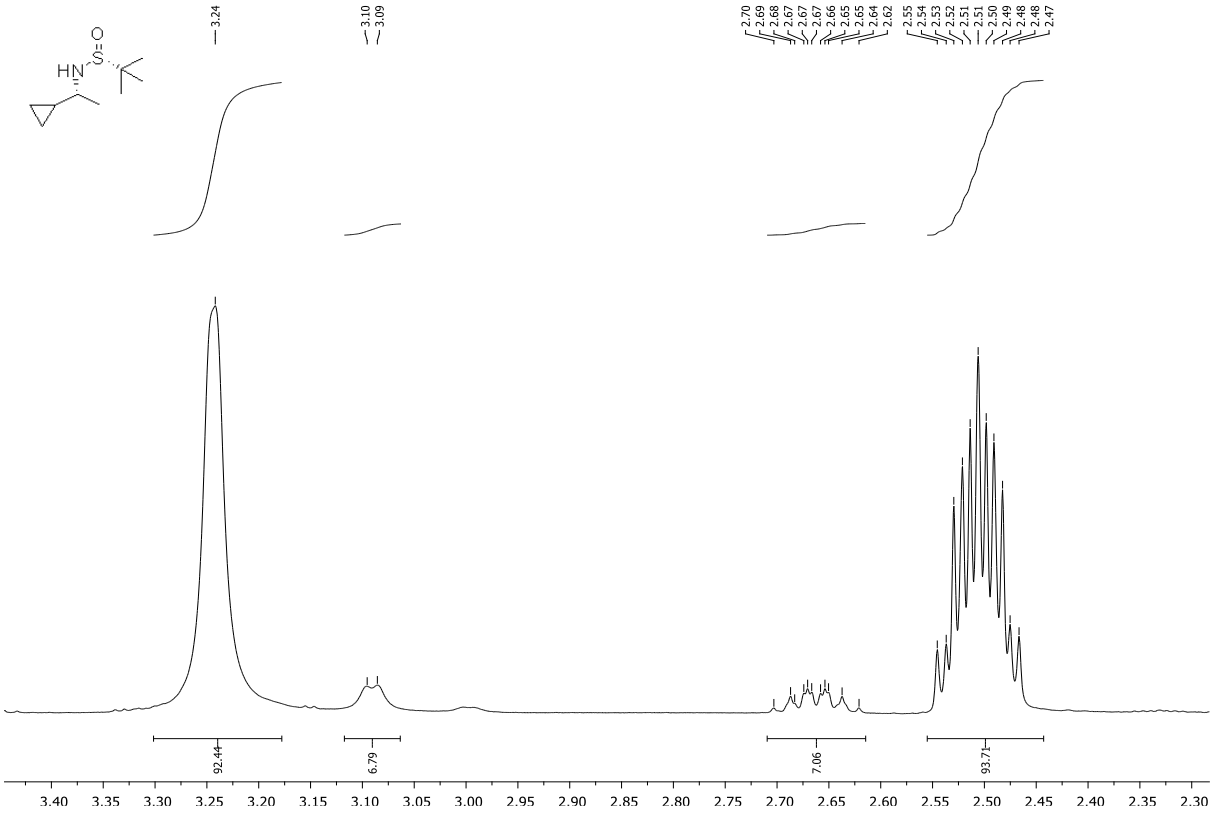
3.19
3.18
3.17
3.16
3.14
3.13
3.11
3.10
3.09
2.99
2.97
2.95
2.95
2.94
2.87
2.85
O
S
HN
CH3
CH3
CH3
CH3
78.15
86.22
15.47
20.16
f1 (ppm)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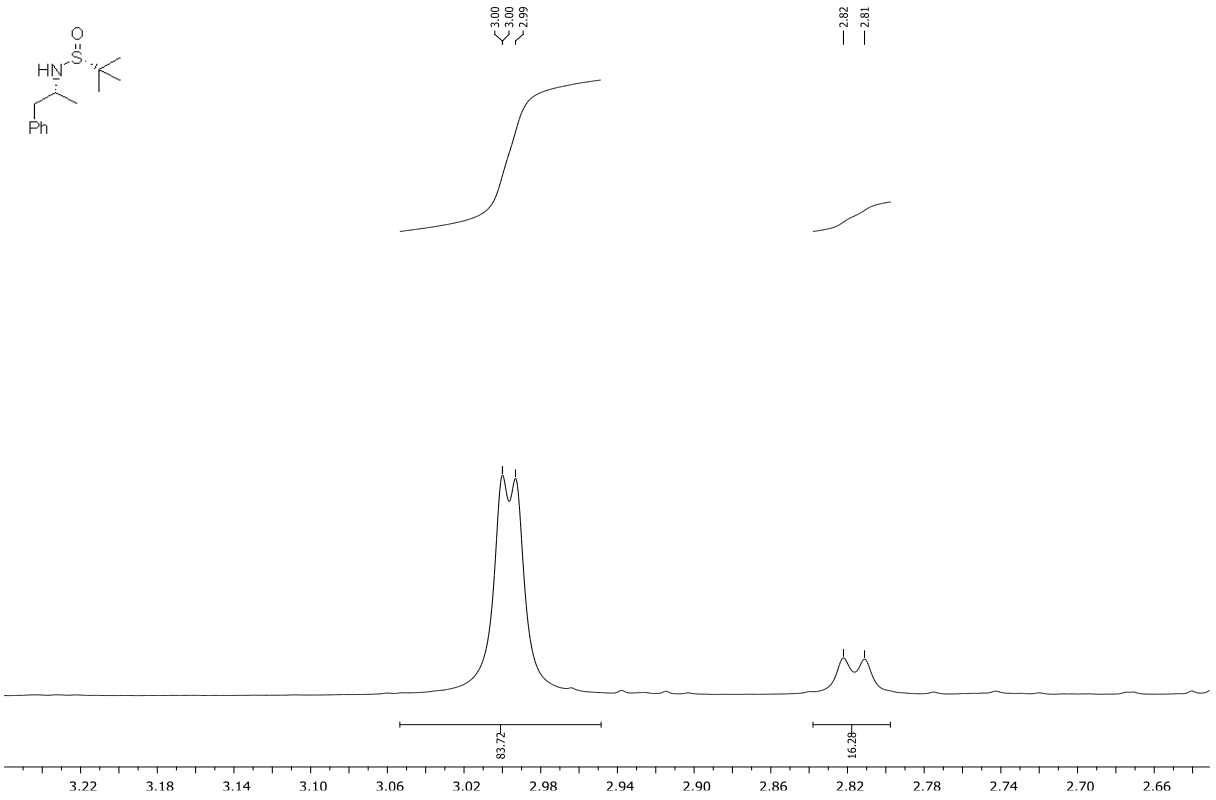
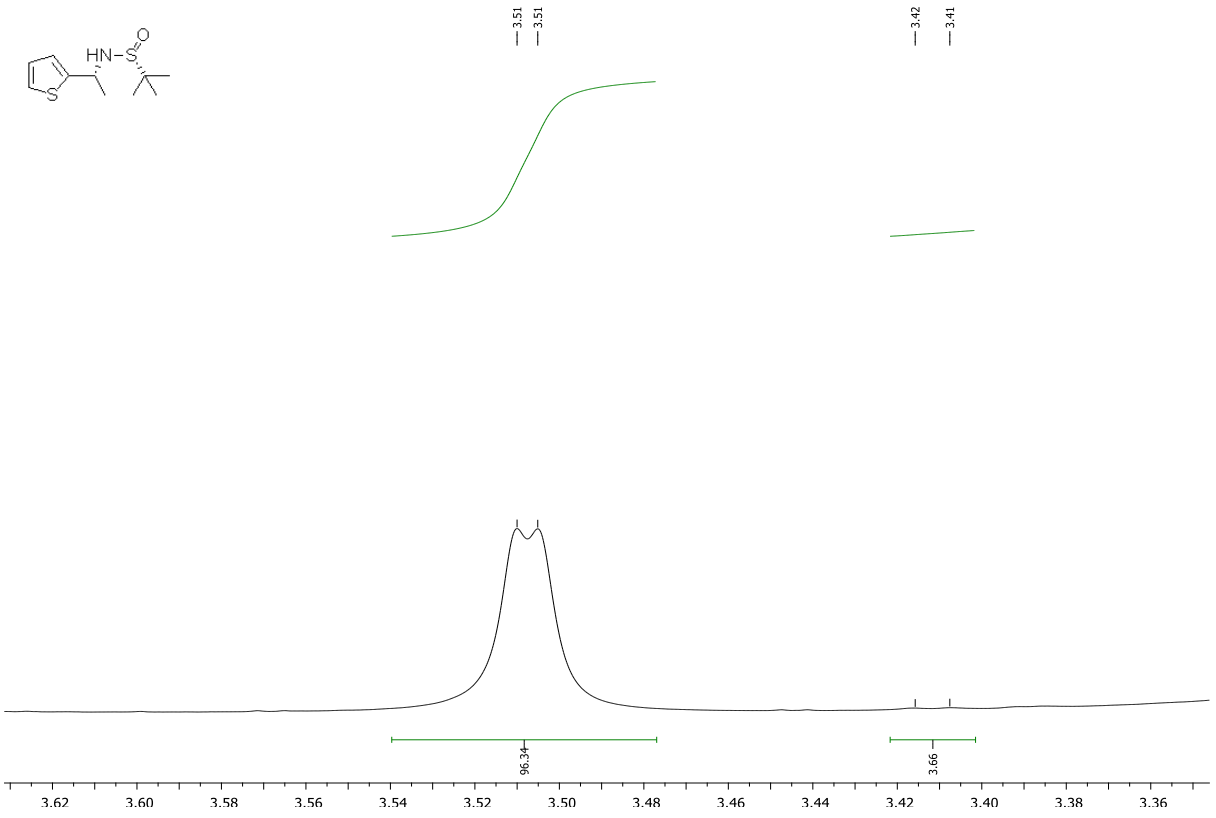
2.69
2.68
2.67
2.67
2.67
2.66
2.65
2.65
2.64
2.62
2.55
2.54
2.53
2.52
2.51
2.51
2.50
2.49
2.48
2.48
2.47
HN
O
92.44
6.79
7.06
93.71


HN
O
S
Ph
3.00
3.00
2.99
2.82
2.81
83.72
16.28
3.22
3.18
3.14
3.10
3.06
3.02
2.98
2.94
2.90
2.86
2.82
2.78
2.74
2.70
2.66


HN
O
S
S
3.51
3.51
3.42
3.41
96.34
3.66
3.62
3.60
3.58
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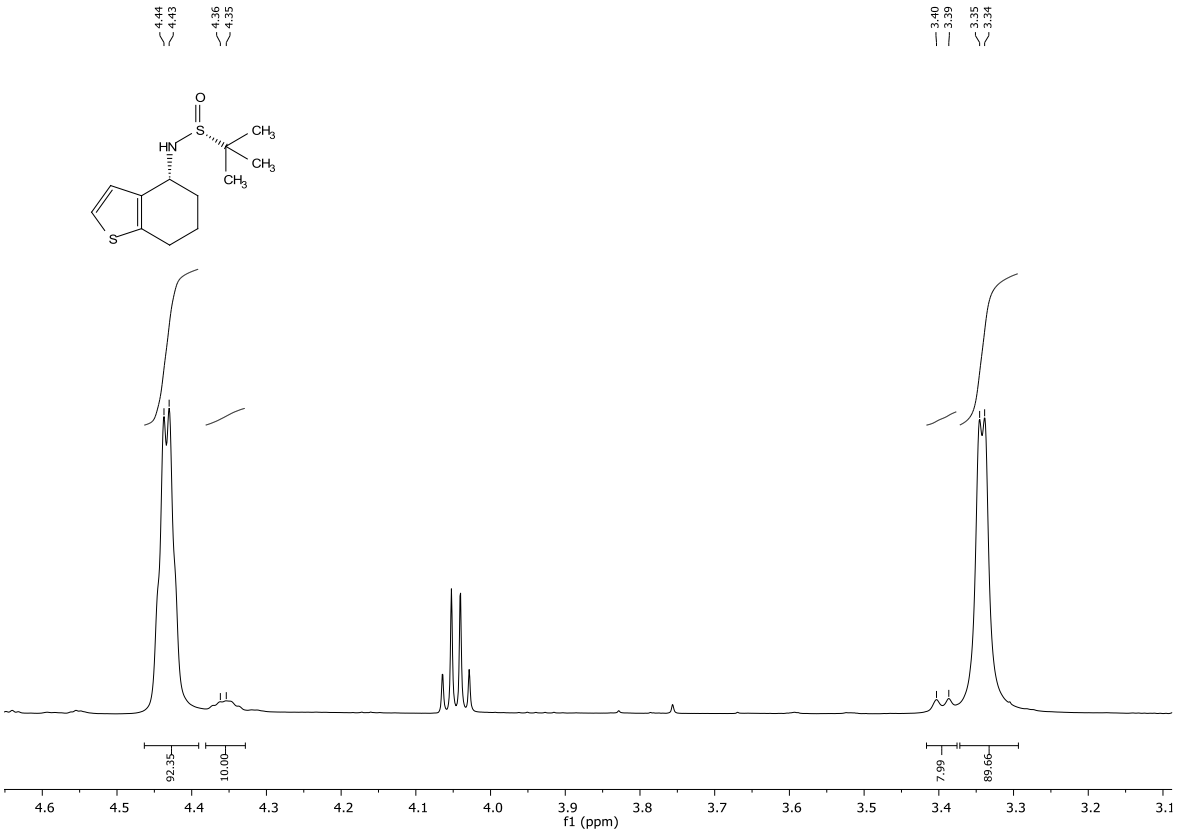
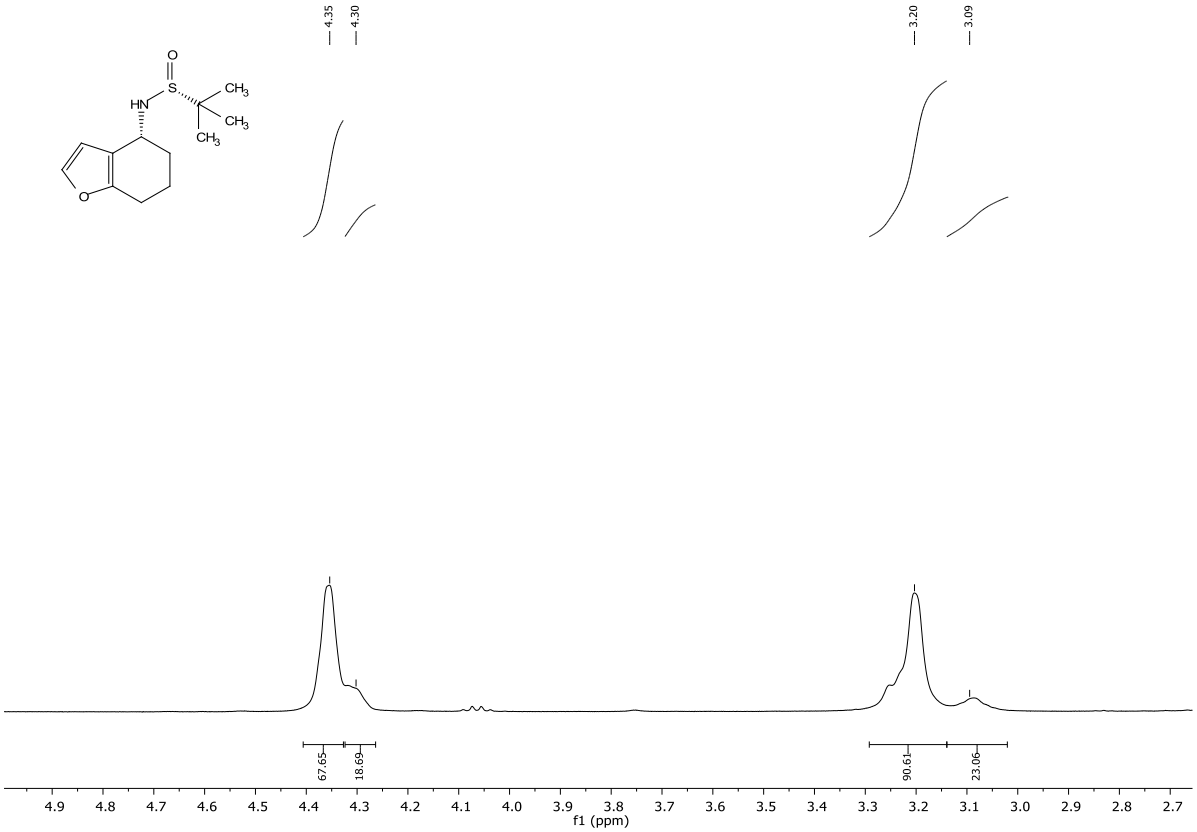
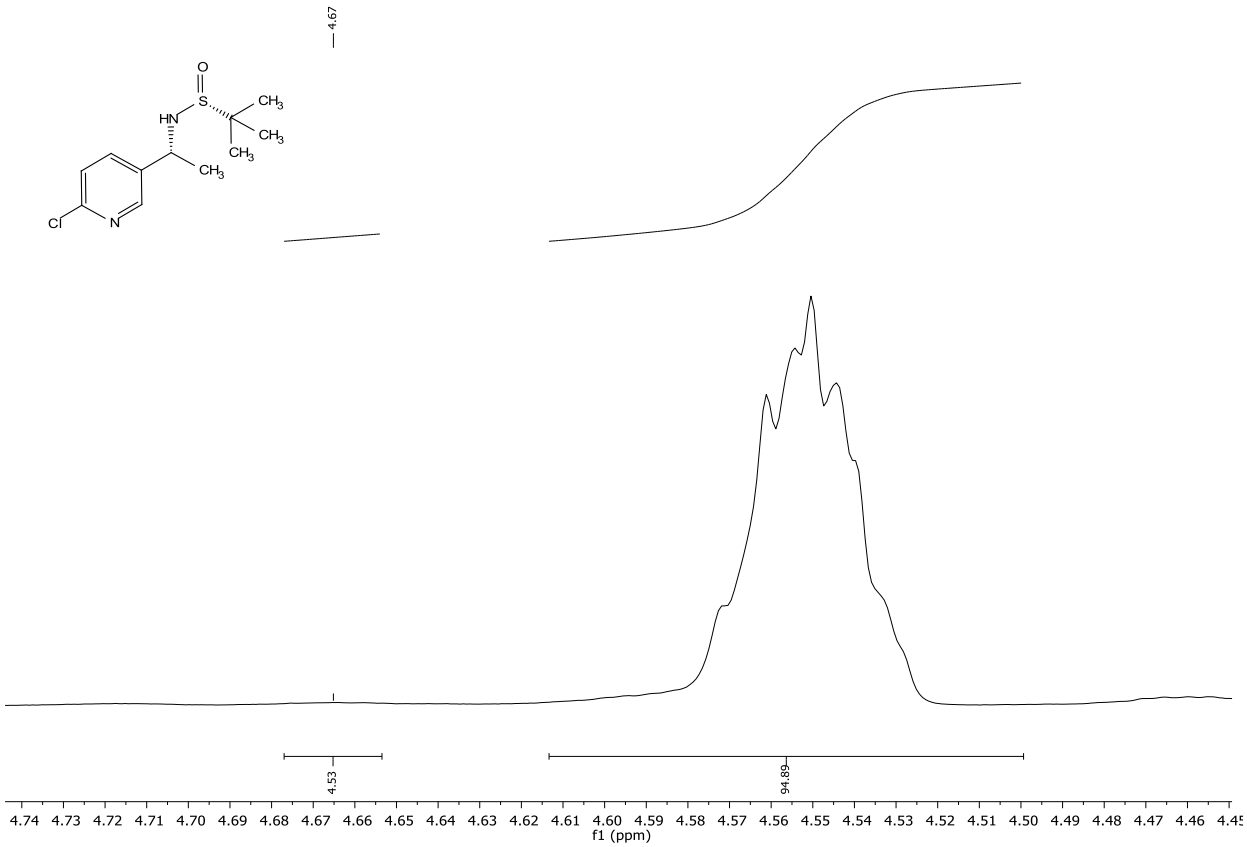
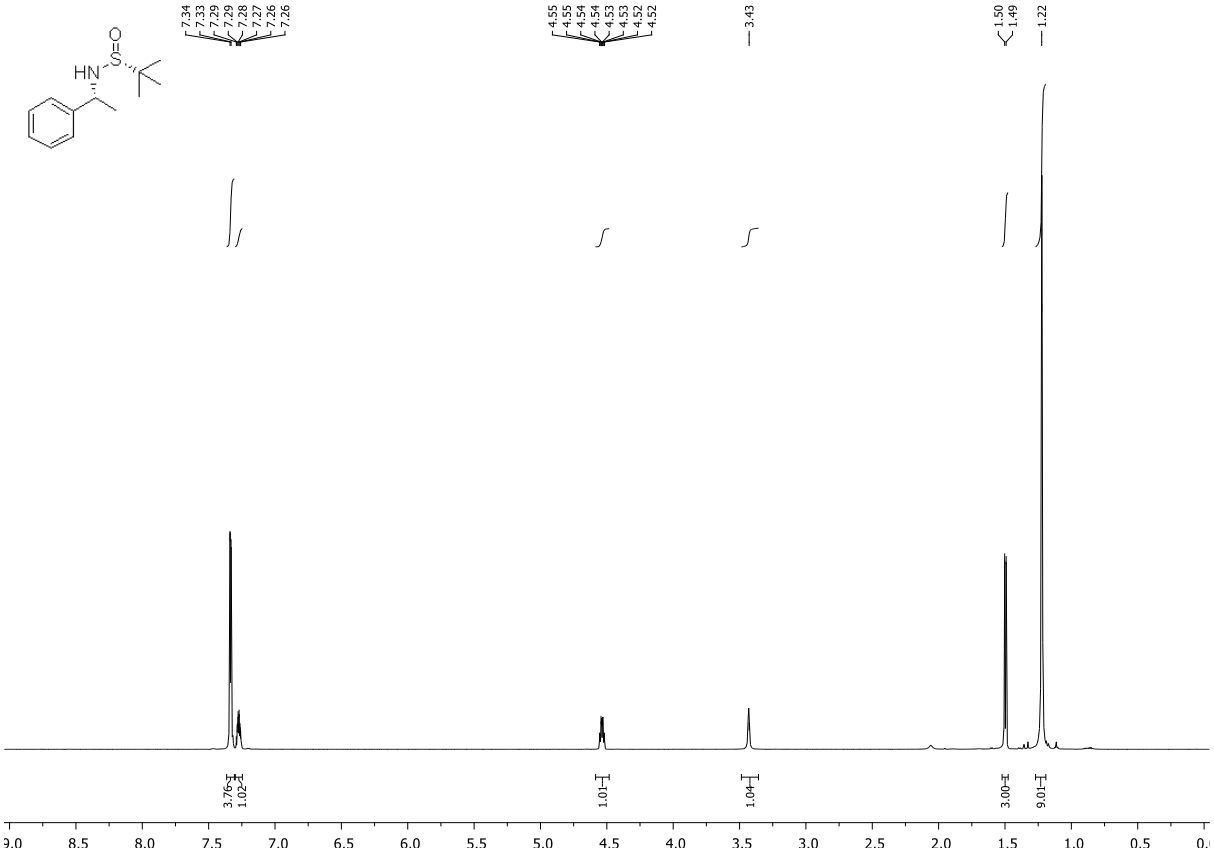
3.46
3.44
3.42
3.40
3.38
3.36

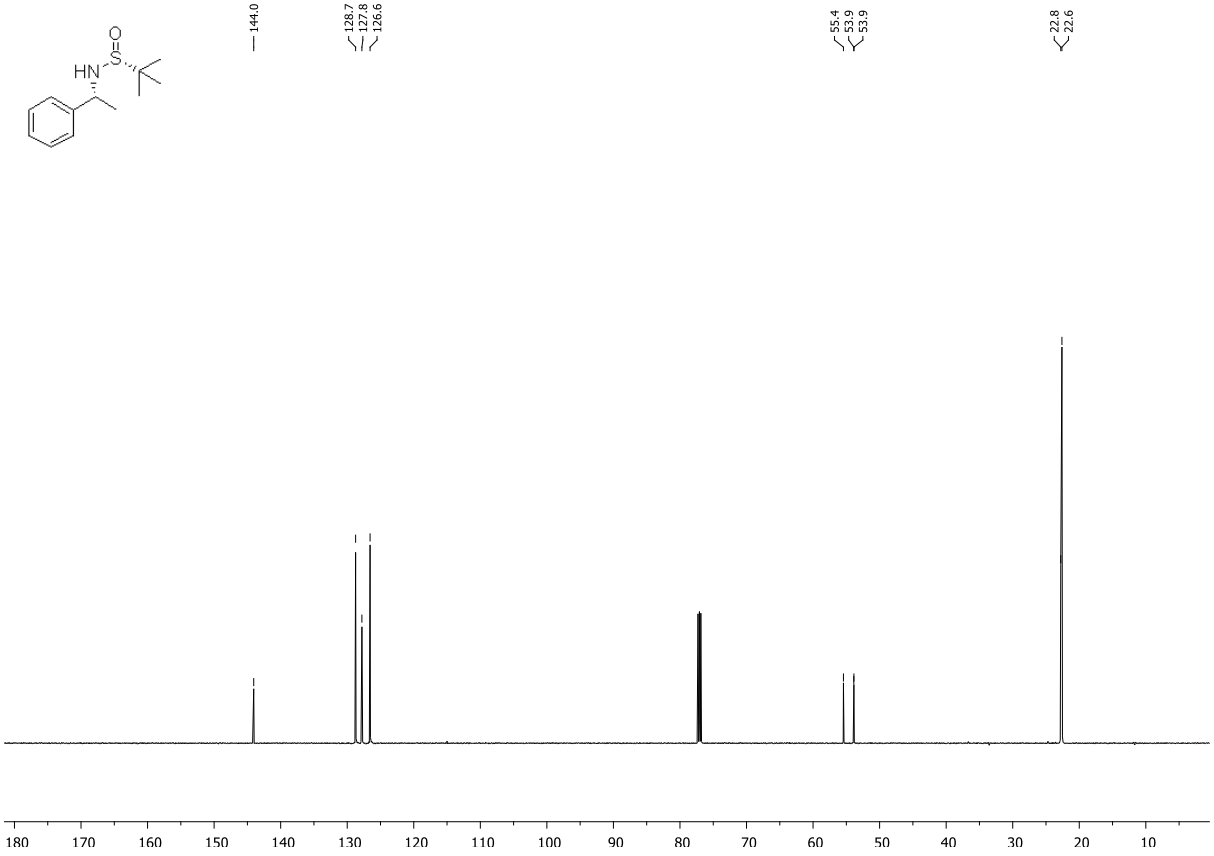

4.44
4.43
4.36
4.35
3.40
3.39
3.35
3.34
O
S
HN
CH3
CH3
CH3
S
92.35
10.00
7.99
89.66
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)

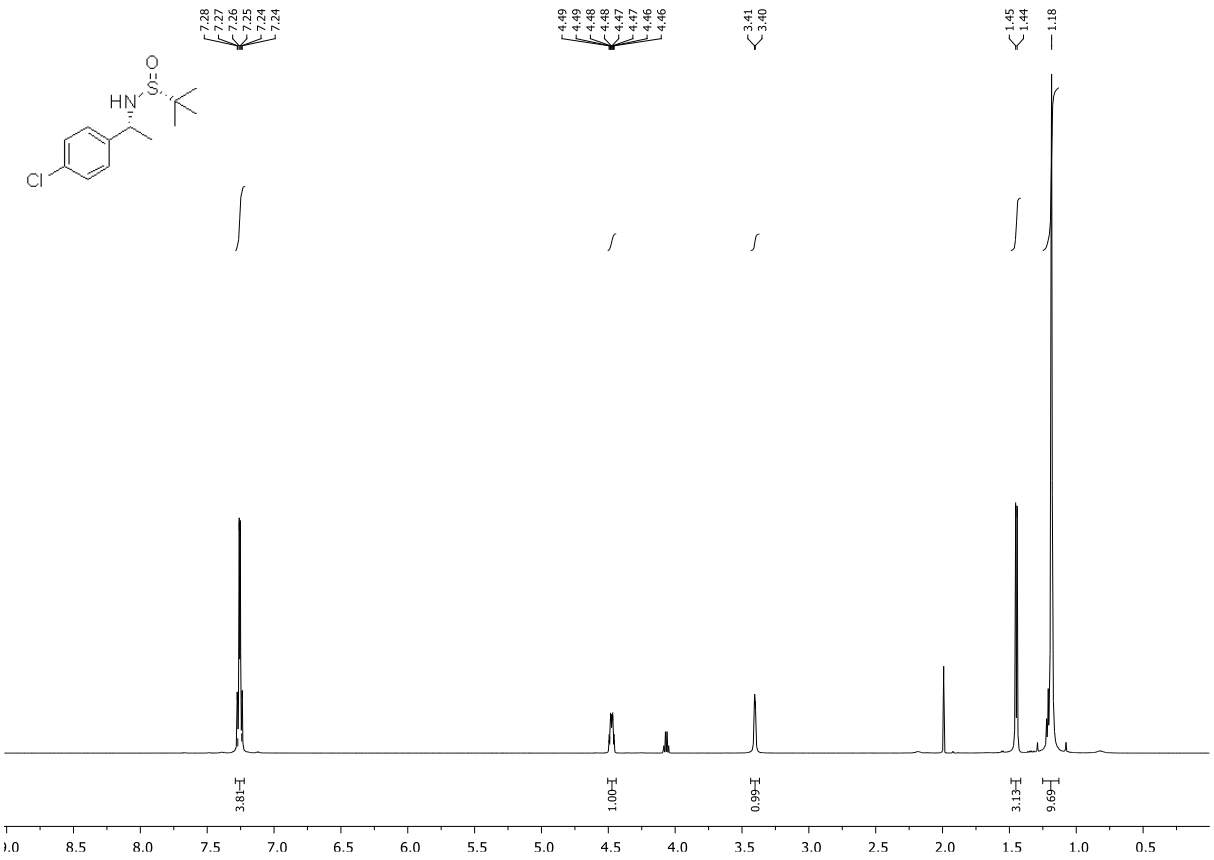

4.35
4.30
3.20
3.09
O
S
HN
CH3
CH3
CH3
O
67.65
18.69
90.61
23.06
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
f1 (ppm)

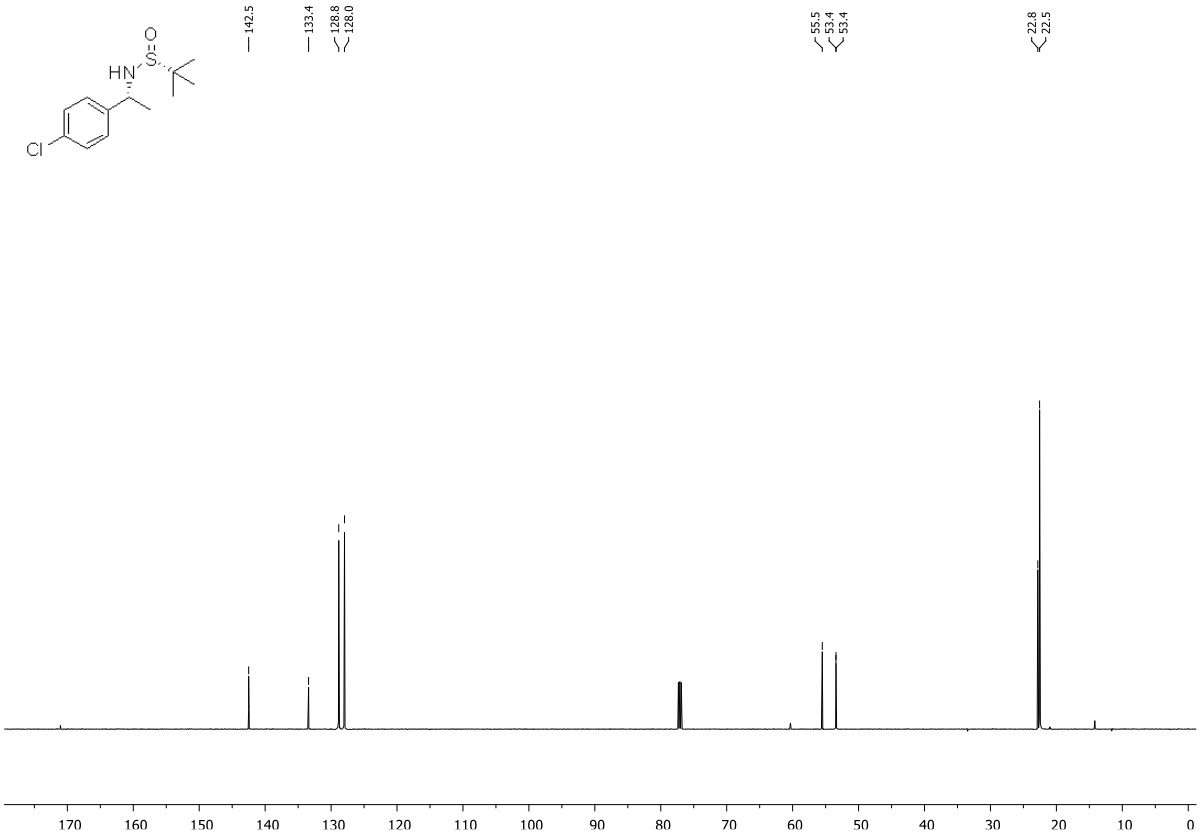

4.67
O
S
HN
CH3
CH3
CH3
CH3
Cl
N
4.53
94.89
4.74 4.73 4.72 4.71 4.70 4.69 4.68 4.67 4.66 4.65 4.64 4.63 4.62 4.61 4.60 4.59 4.58 4.57 4.56 4.55 4.54 4.53 4.52 4.51 4.50 4.49 4.48 4.47 4.46 4.45
f1 (ppm)

NMR Spectra of Isolated Products






7.28
7.27
7.26
7.25
7.24
7.24
4.49
4.49
4.48
4.48
4.47
4.47
4.46
4.46
3.41
3.40
1.45
1.44
1.18
HN
S
O
O
Cl
3.81
1.00
0.99
3.13
9.69
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


142.5
133.4
128.8
128.0
55.5
53.4
53.4
22.8
22.5
HN
S
O
O
Cl
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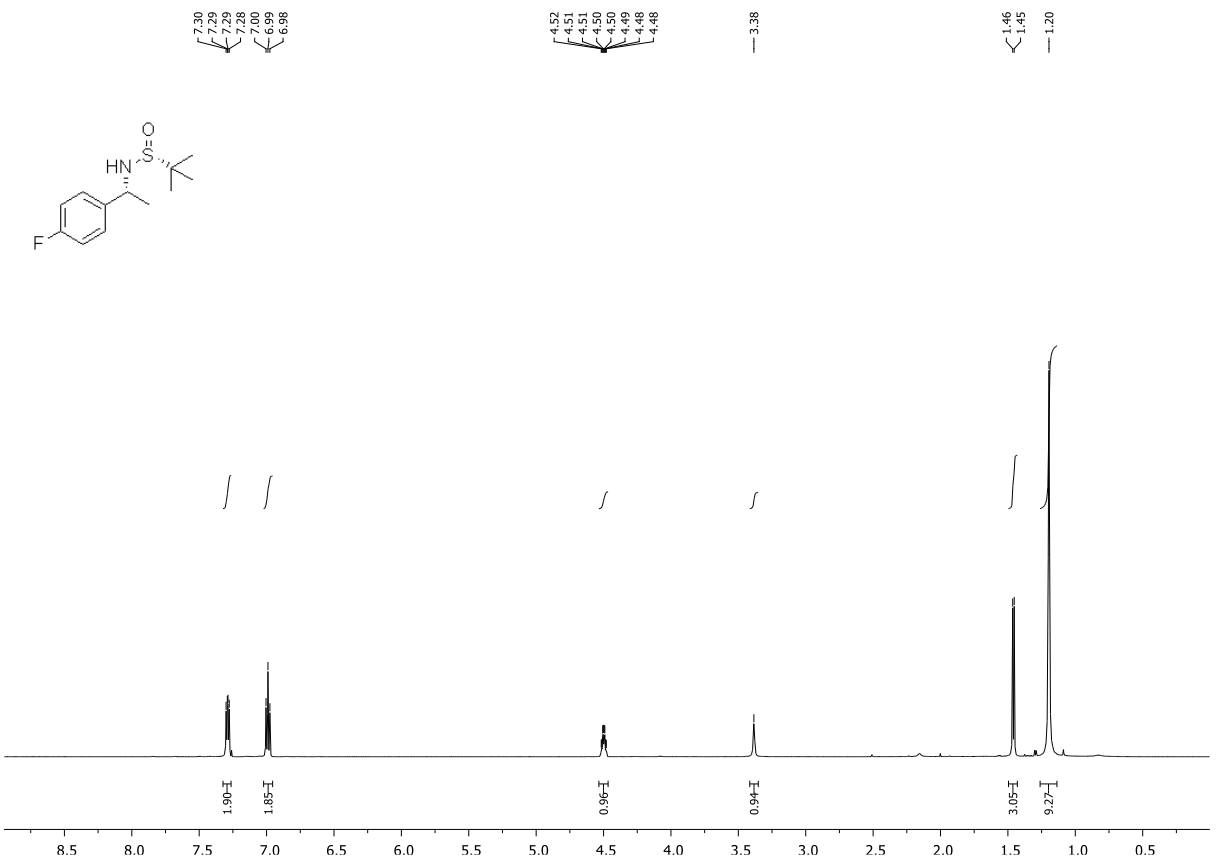
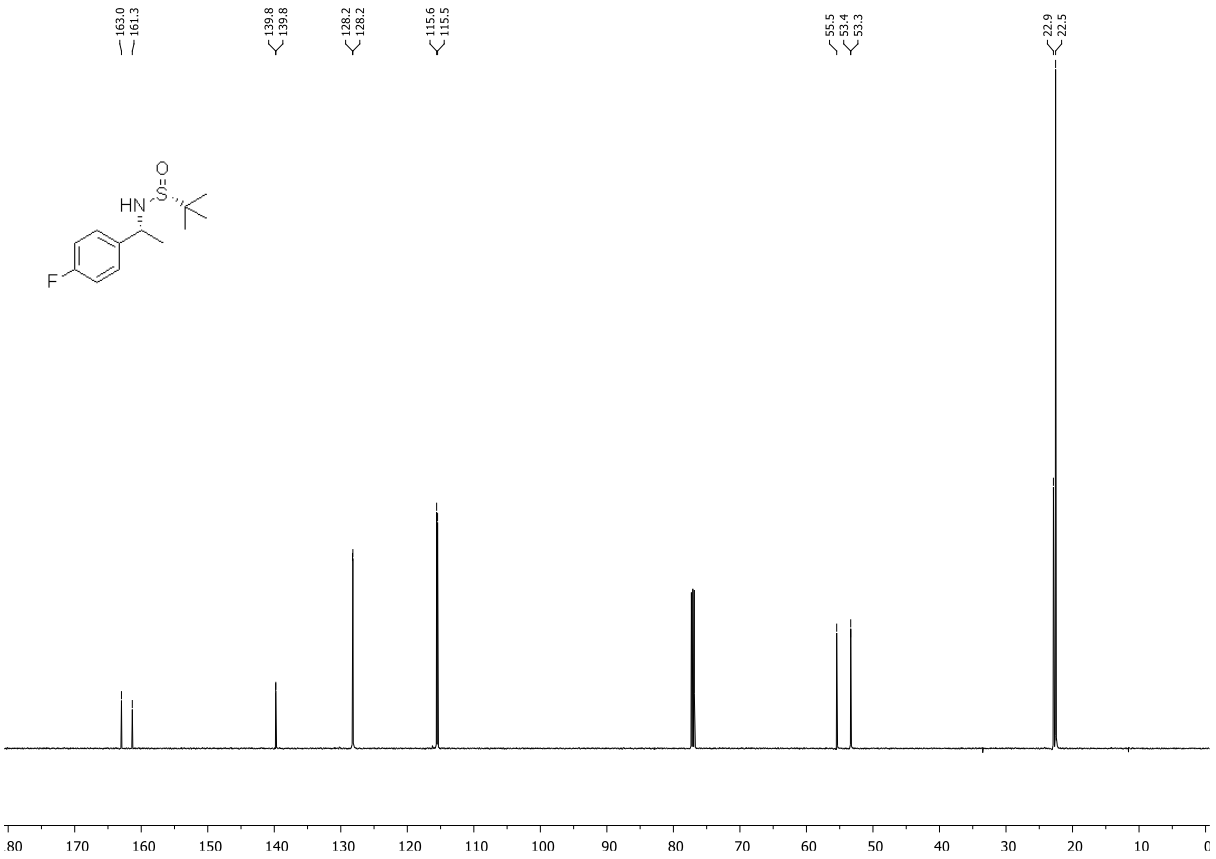
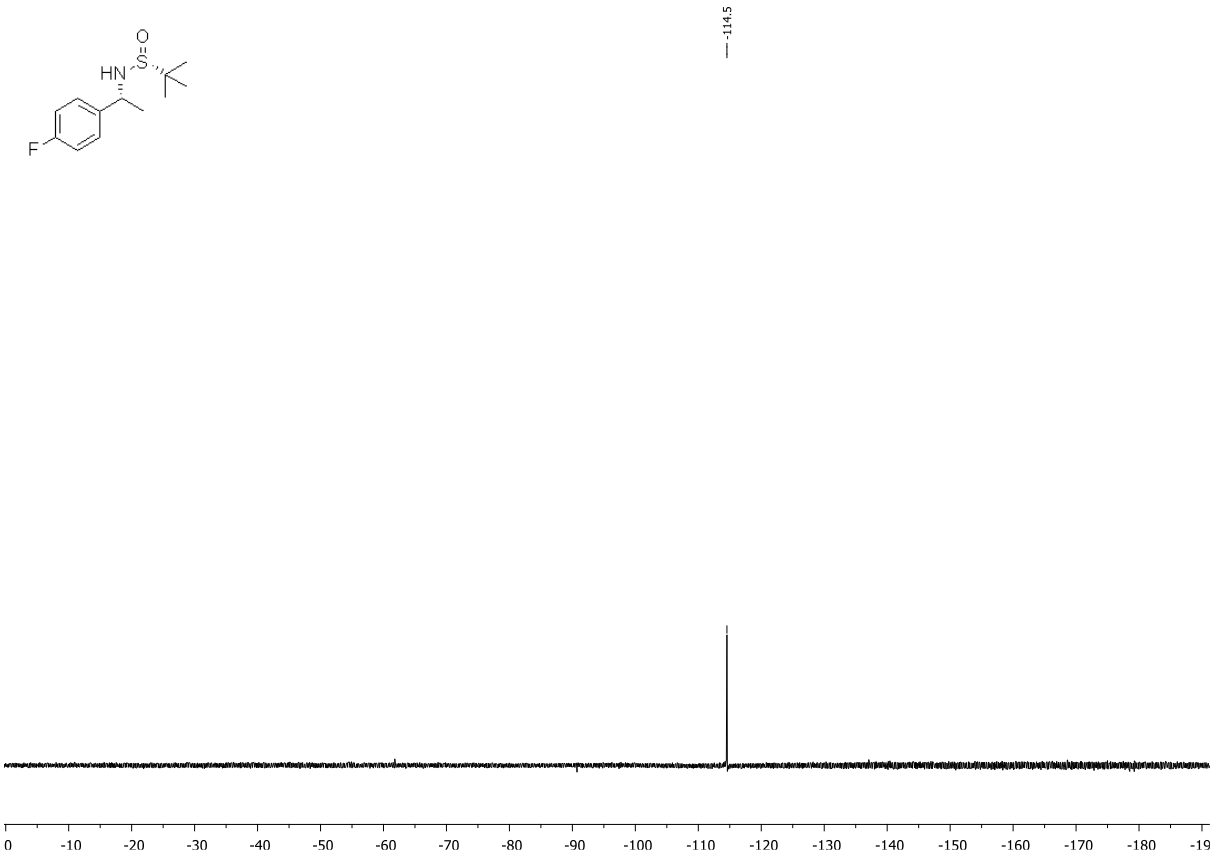
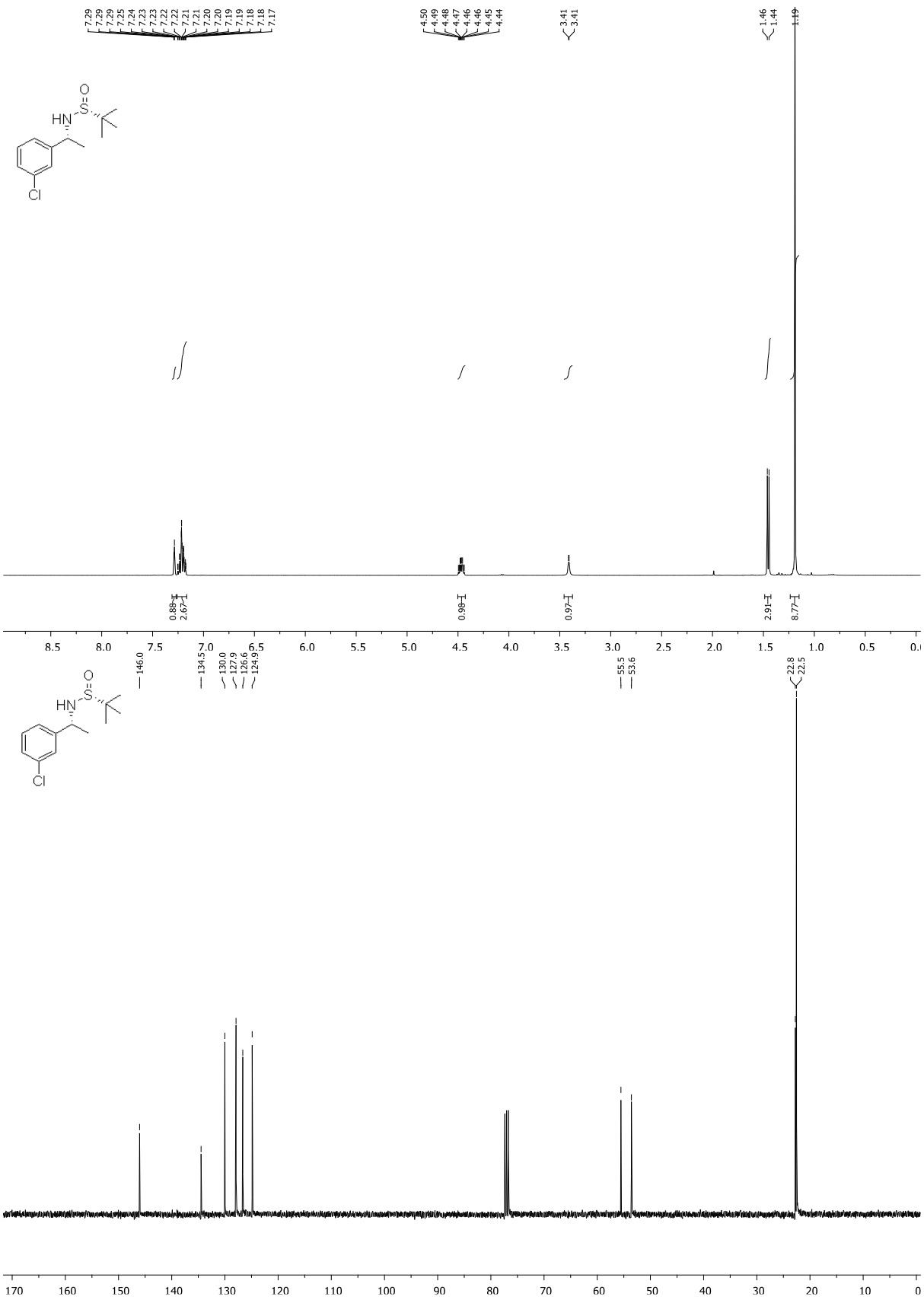
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.30
7.29
7.29
7.28
7.00
6.99
6.98
4.52
4.51
4.51
4.50
4.50
4.49
4.48
4.48
3.38
1.46
1.45
1.20
HN
O
S
F
1.90
1.85
0.96
0.94
3.05
9.27
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


163.0
161.3
139.8
139.8
128.2
128.2
115.6
115.5
55.5
53.4
53.3
22.9
22.5
HN
O
S
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-114.5
HN
S
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19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7.29
7.29
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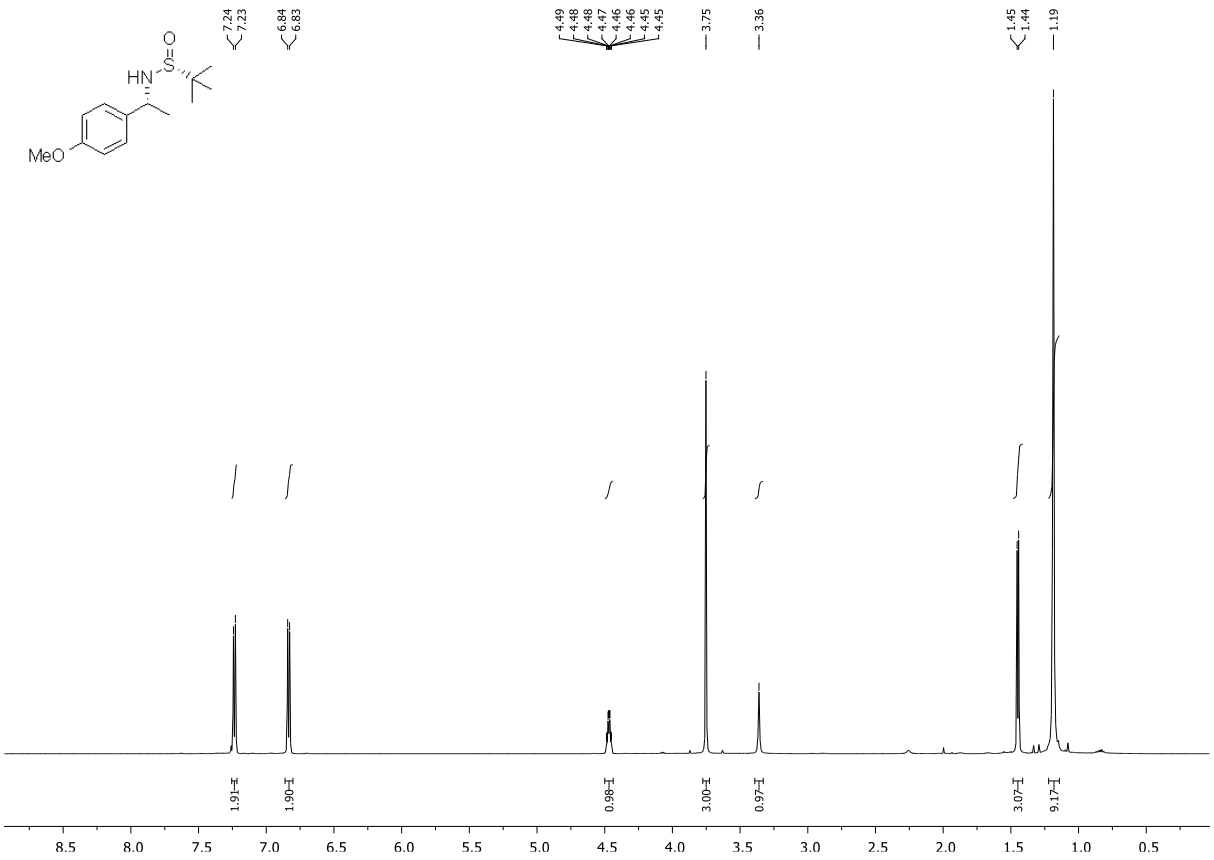
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
4.50
4.49
4.48
4.47
4.46
4.46
4.45
4.44
3.41
3.41
1.46
1.44
1.19
HN
O
S
Cl
0.88
2.67
0.98
0.97
2.91
8.77
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
146.0
134.5
130.0
127.9
126.6
124.9
55.5
53.6
22.8
22.5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6.83
4.49
4.48
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4.47
4.46
4.46
4.45
4.45
3.75
3.36
1.45
1.44
1.19
HN
S
O
MeO
1.91
1.90
0.98
3.00
0.97
3.07
9.17
8.5
8.0
7.5
7.0
6.5
6.0
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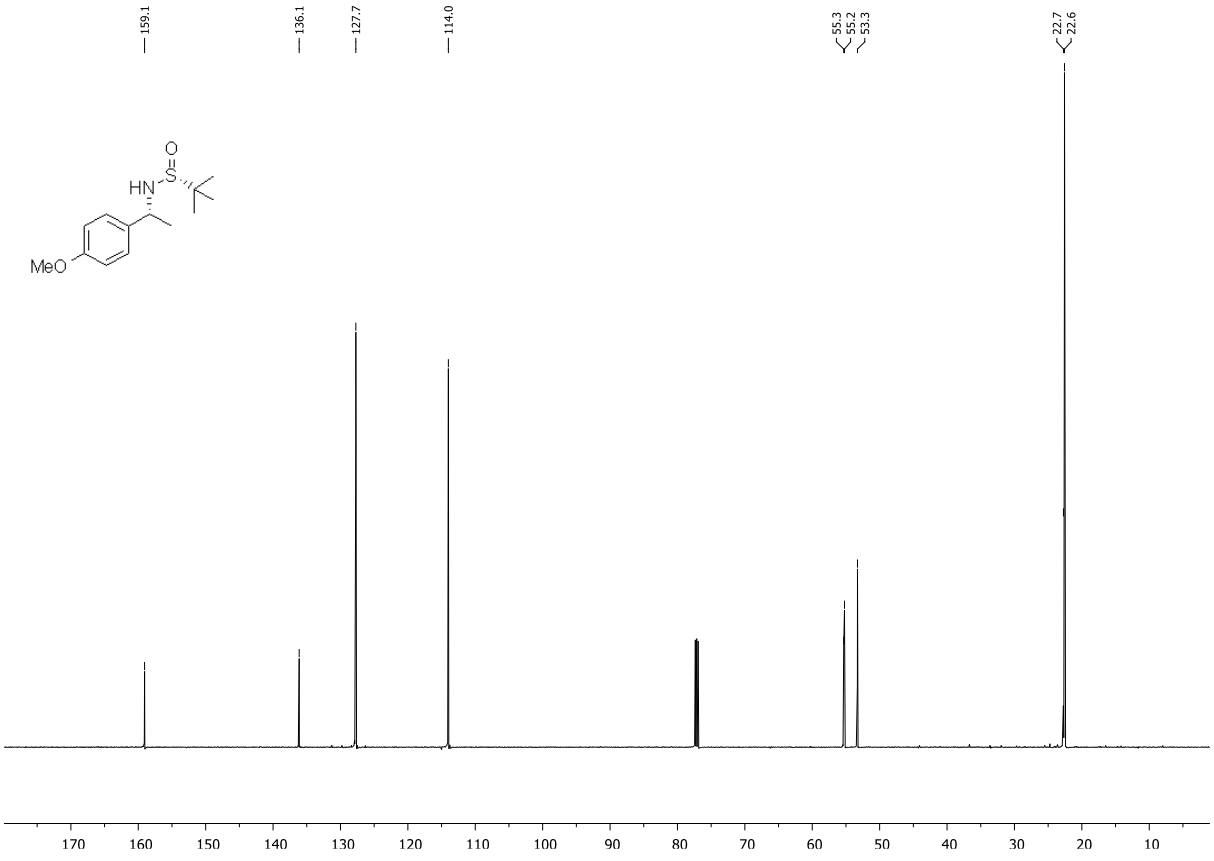
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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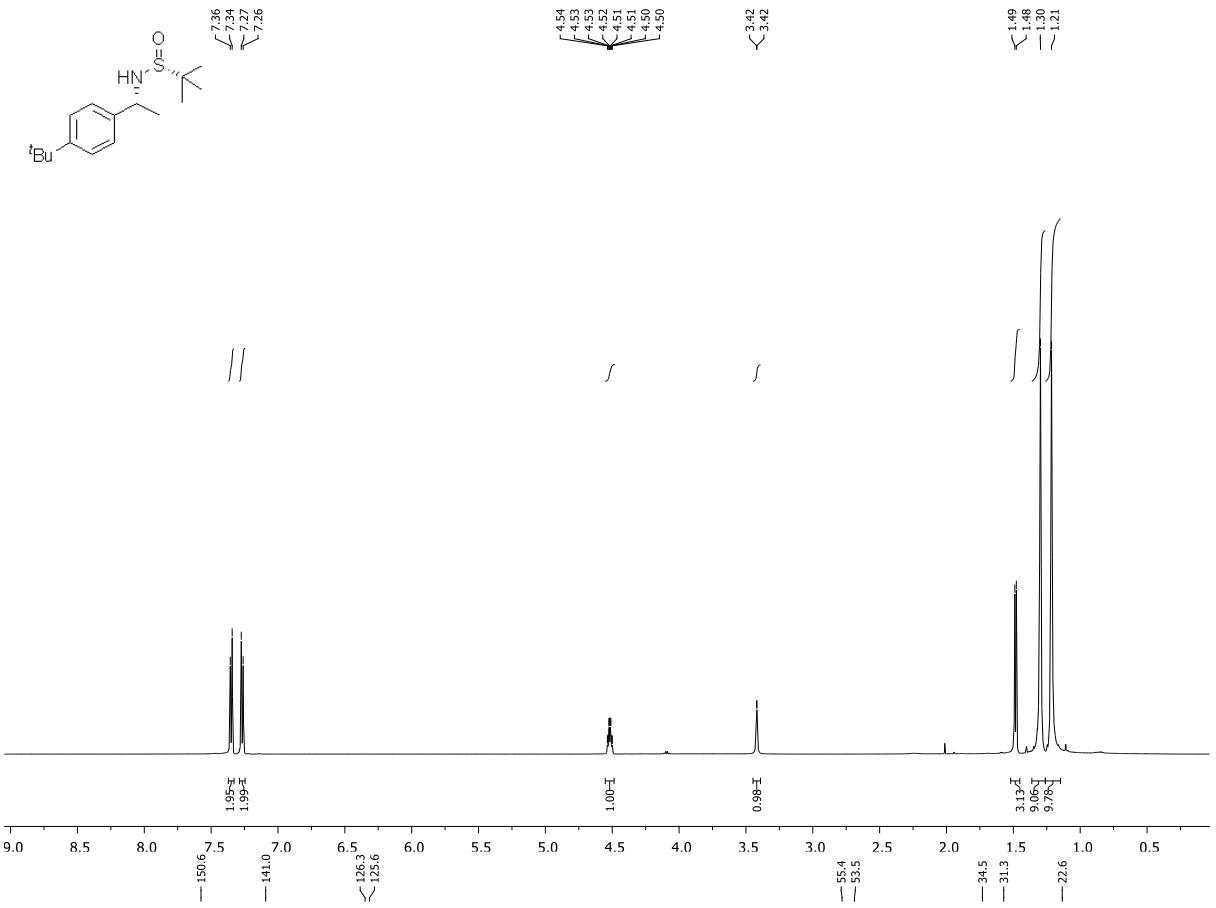
136.1
127.7
114.0
55.3
55.2
53.3
22.7
22.6
HN
S
O
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.36
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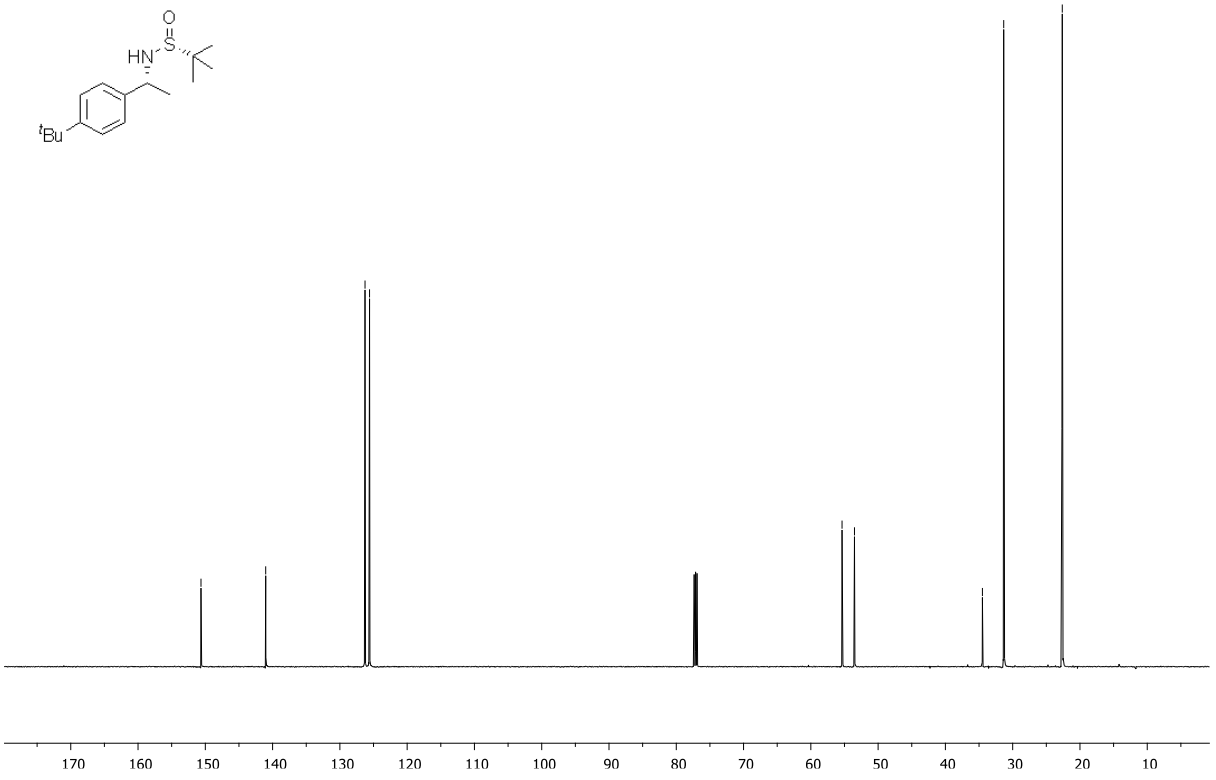
7.27
7.26
4.54
4.53
4.53
4.52
4.51
4.51
4.50
4.50
3.42
3.42
1.49
1.48
1.30
1.21
HN
O
S
tBu
1.95
1.99
1.00
0.98
3.13
9.06
9.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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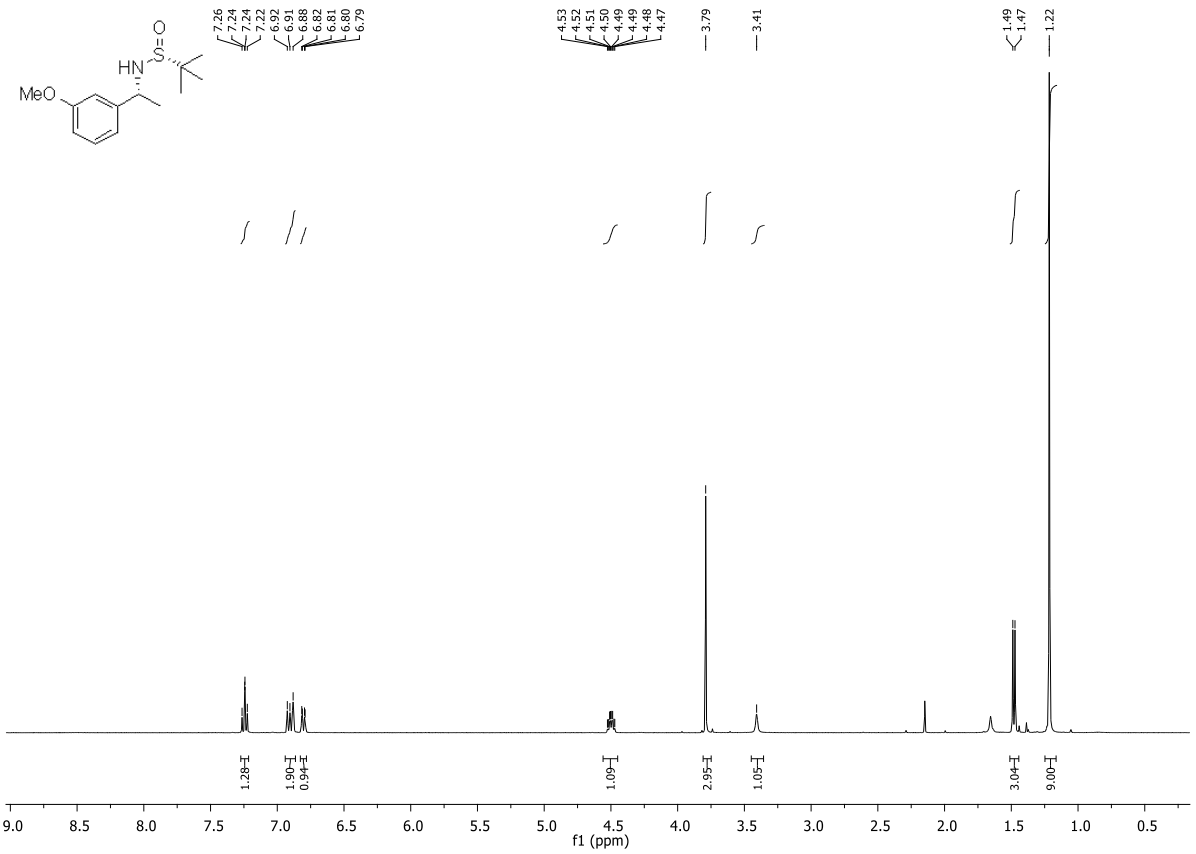
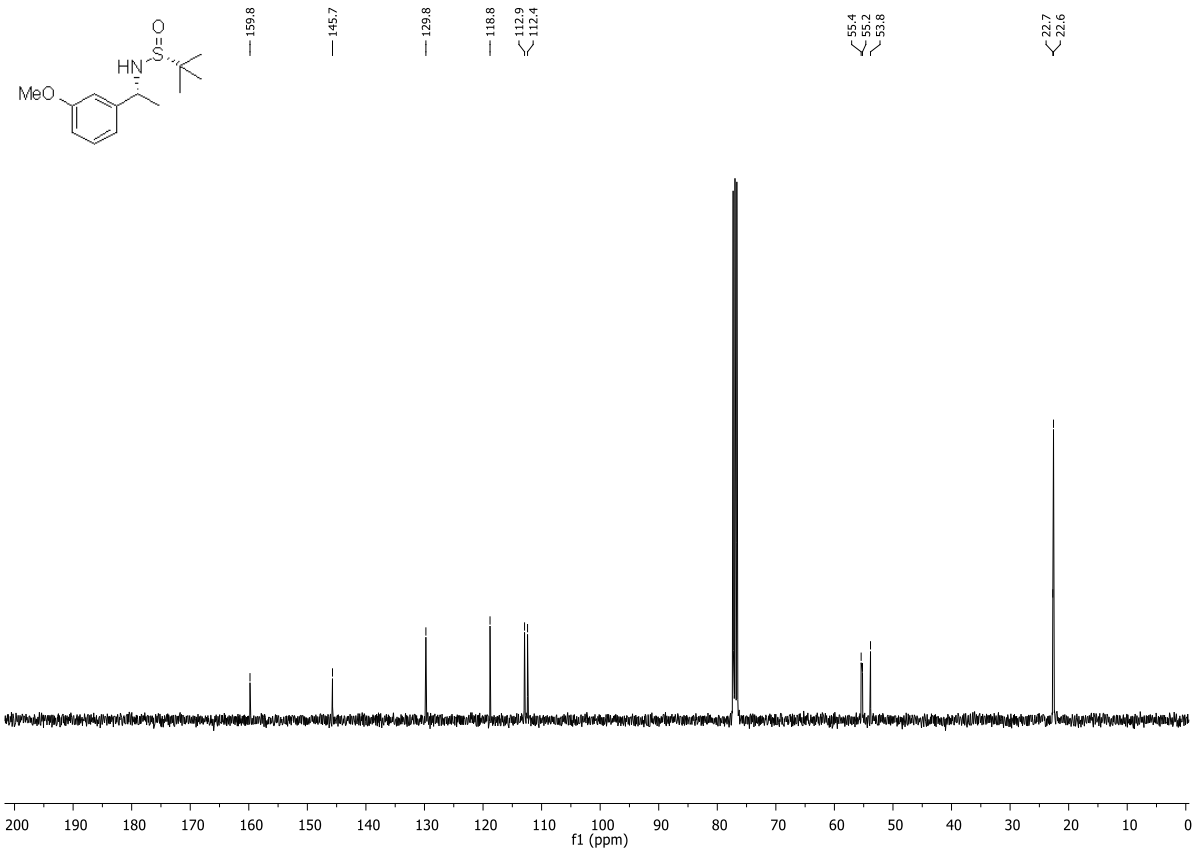
141.0
126.3
125.6
55.4
53.5
34.5
31.3
22.6
HN
O
S
tBu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


MeO
HN
S
O
7.26
7.24
7.24
7.22
6.92
6.91
6.88
6.82
6.81
6.80
6.79
4.53
4.52
4.51
4.50
4.49
4.49
4.48
4.47
3.79
3.41
1.49
1.47
1.22
1.28
1.90
0.94
1.09
2.95
1.05
3.04
9.00
f1 (ppm)


MeO
HN
S
O
159.8
145.7
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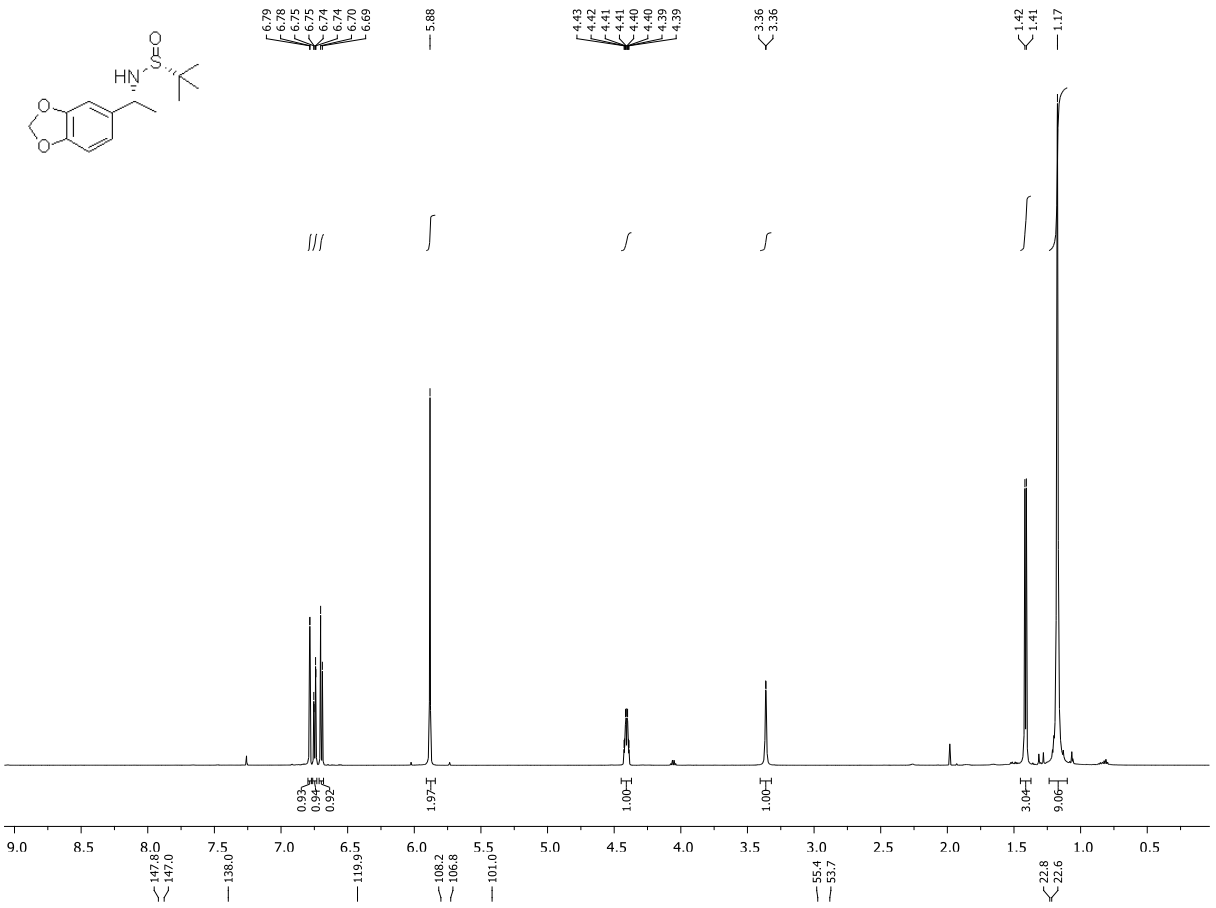
112.9
112.4
55.4
55.2
53.8
22.7
22.6
f1 (ppm)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6.75
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6.74
6.70
6.69
5.88
4.43
4.42
4.41
4.41
4.40
4.40
4.39
4.39
3.36
3.36
1.42
1.41
1.17
0.93
0.94
0.92
1.97
1.00
1.00
3.04
9.06
147.8
147.0
138.0
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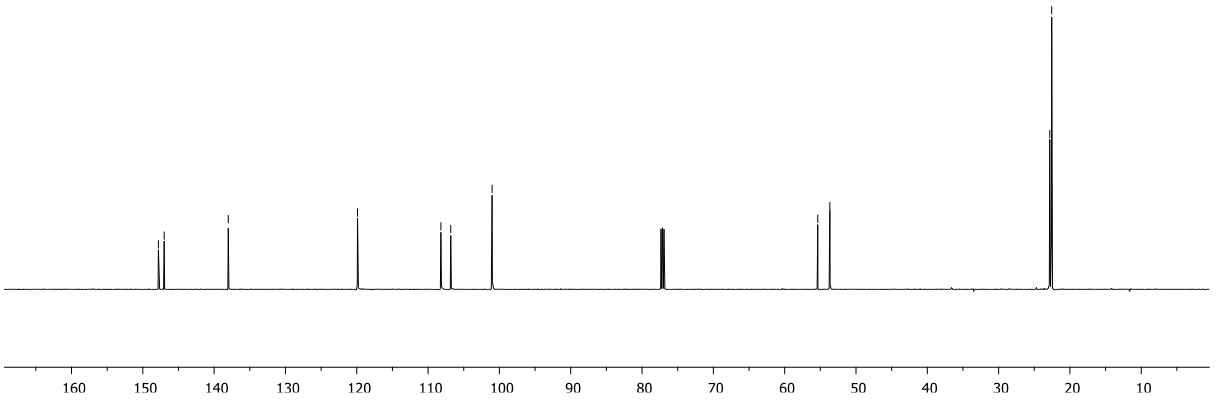
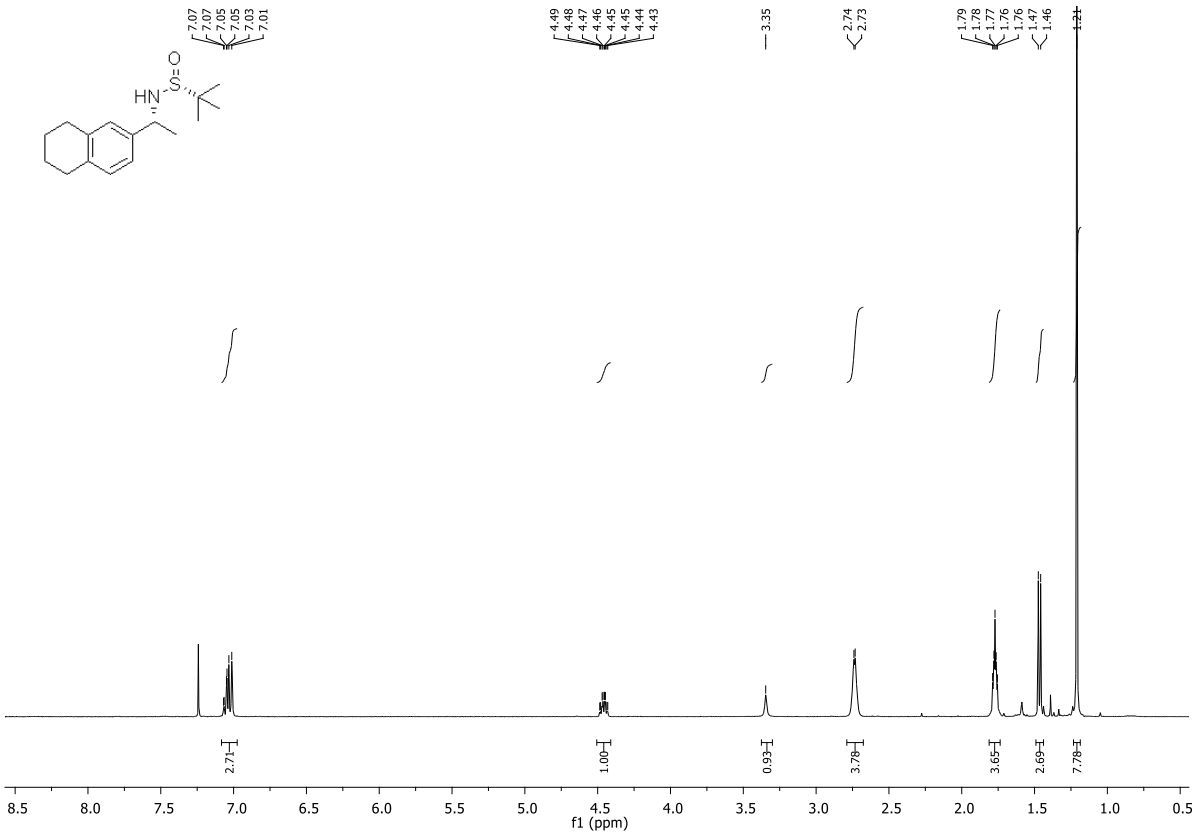
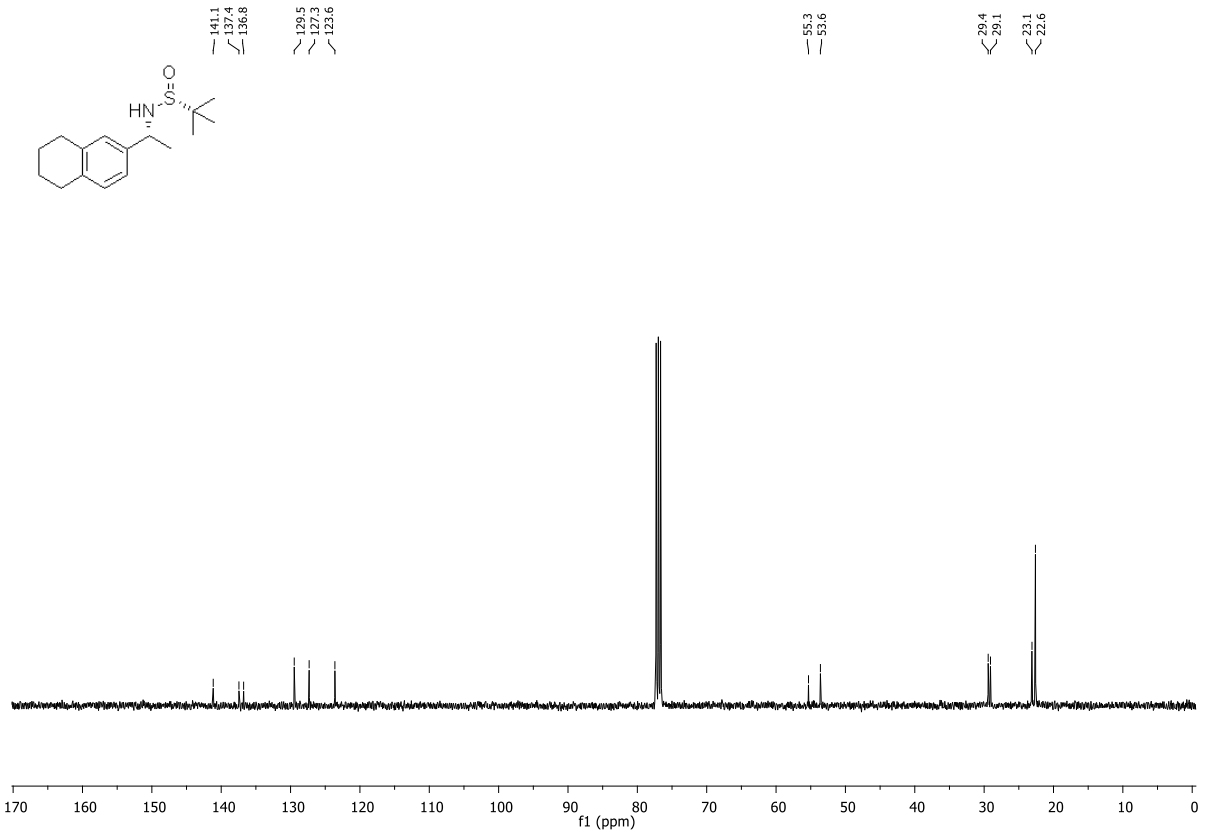
108.2
106.8
101.0
55.4
53.7
22.8
22.6




7.07
7.07
7.05
7.05
7.03
7.01
4.49
4.48
4.47
4.46
4.45
4.45
4.44
4.43
3.35
2.74
2.73
1.79
1.78
1.77
1.76
1.76
1.47
1.46
1.21
HN
O
S
2.71
1.00
0.93
3.78
3.65
2.69
7.78
f1 (ppm)


141.1
137.4
136.8
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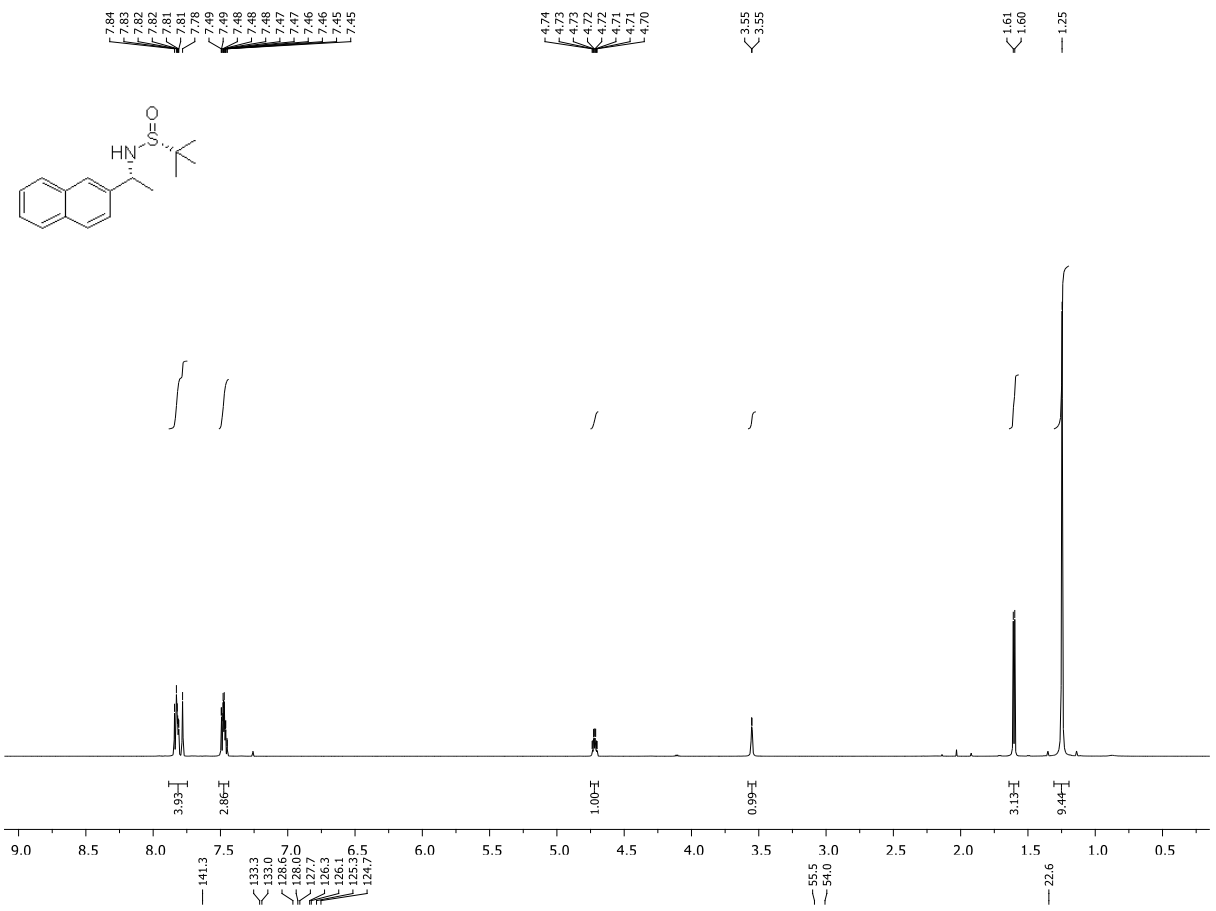
127.3
123.6
55.3
53.6
29.4
29.1
23.1
22.6
HN
O
S
f1 (ppm)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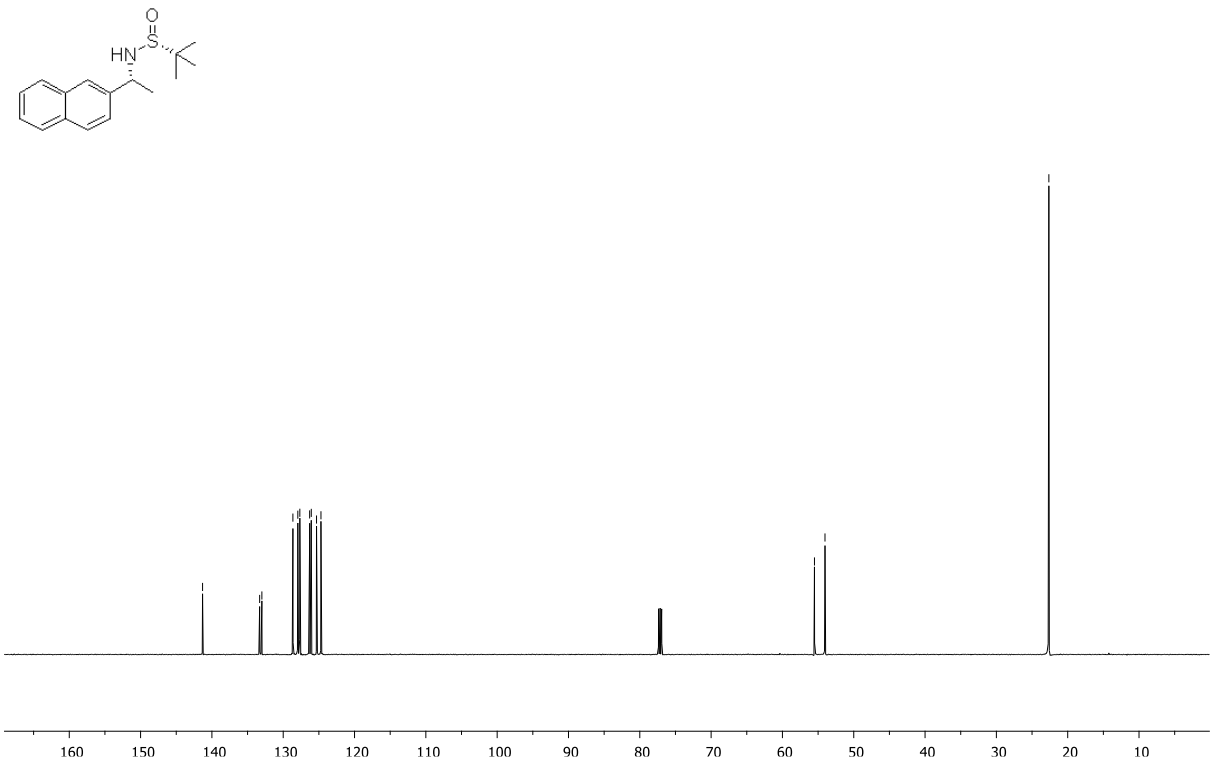
7.81
7.78
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
4.74
4.73
4.73
4.72
4.72
4.71
4.71
4.70
3.55
3.55
1.61
1.60
1.25
HN
S
O
3.93
2.86
1.00
0.99
3.13
9.44
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
141.3
133.3
133.0
128.6
128.0
127.7
126.3
126.1
125.3
124.7
55.5
54.0
22.6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O
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130
120
110
100
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80
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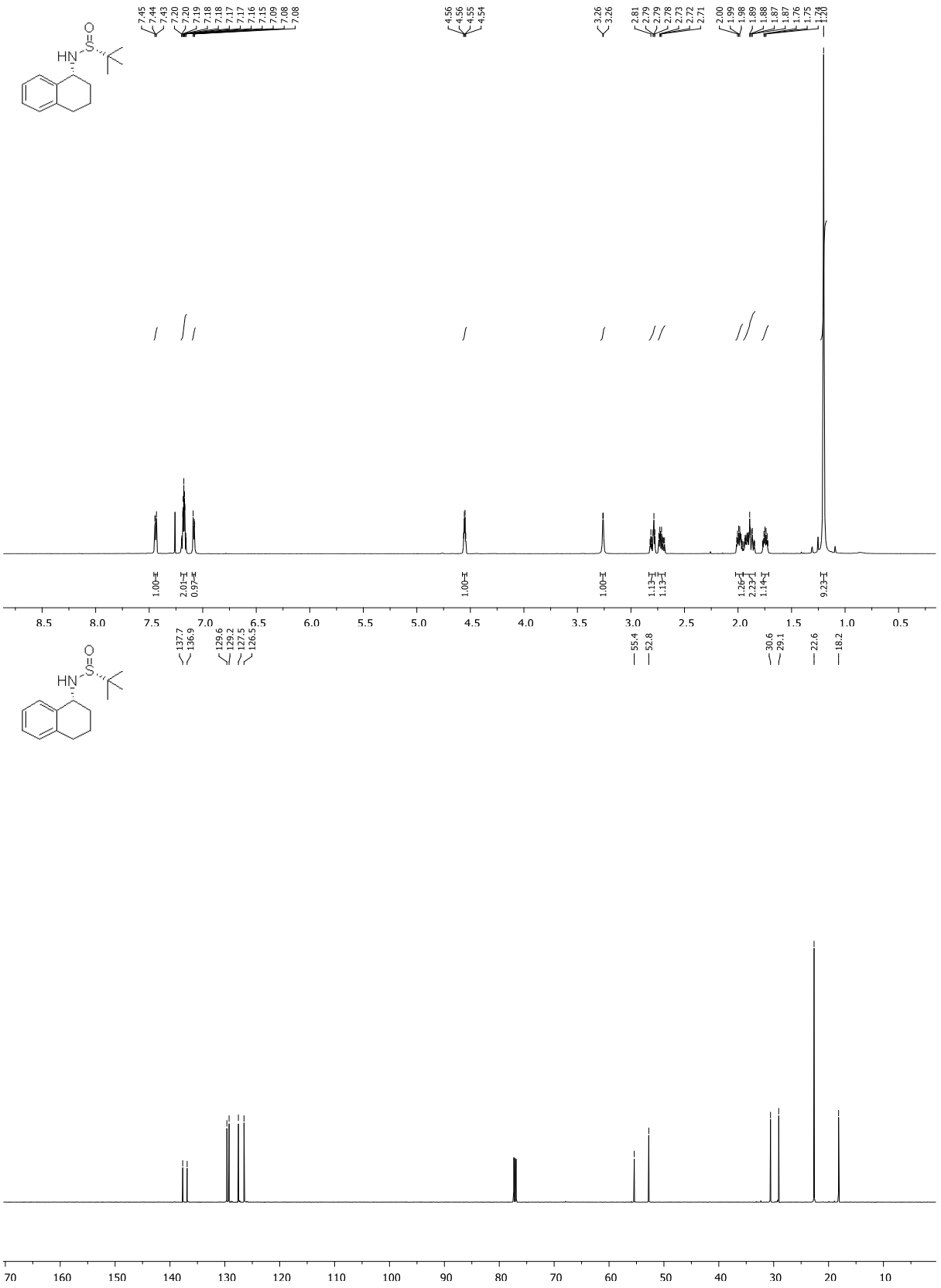
10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7.18
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7.15
7.09
7.08
7.08
4.56
4.56
4.55
4.54
3.26
3.26
2.81
2.79
2.79
2.78
2.73
2.72
2.71
2.00
1.99
1.98
1.89
1.88
1.87
1.87
1.76
1.75
1.74
1.20
1.00
2.01
0.97
1.00
1.00
1.13
1.13
1.26
2.23
1.14
9.23
137.7
136.9
129.6
129.2
127.5
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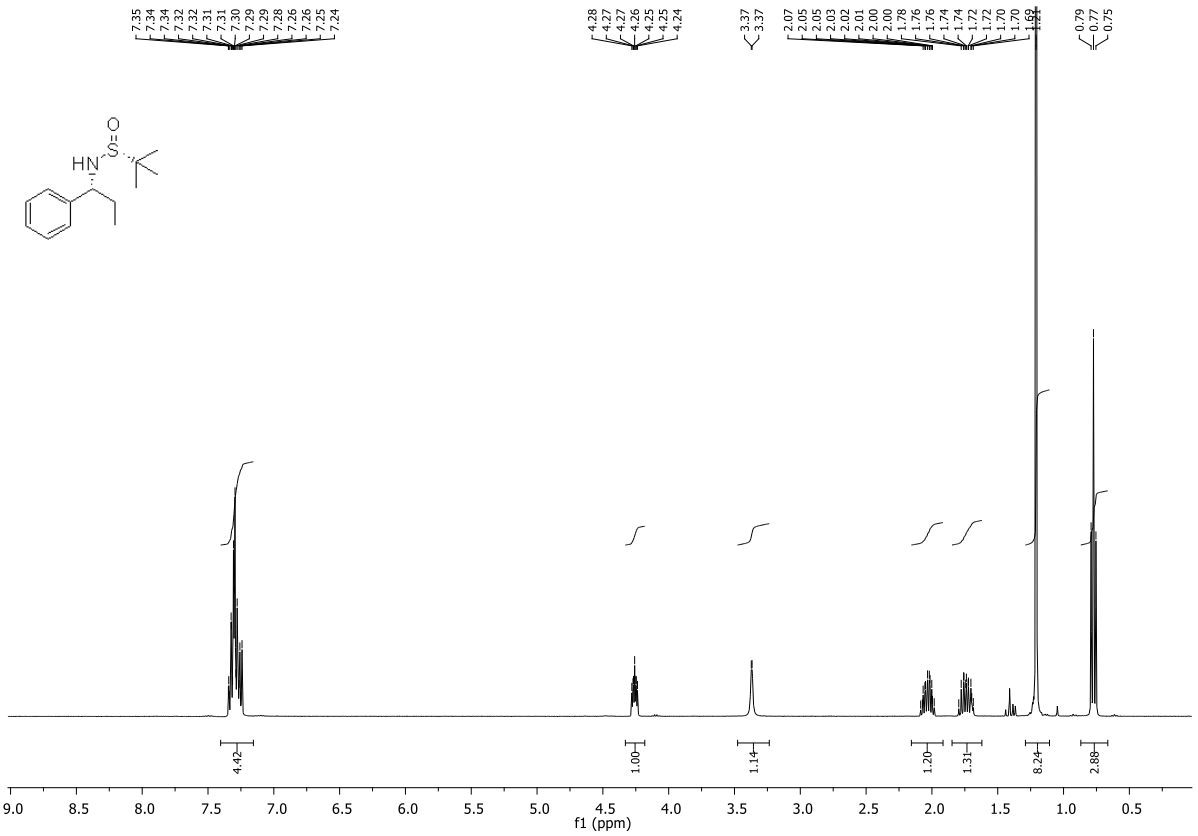
55.4
52.8
30.6
29.1
22.6
18.2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7.34
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7.31
7.31
7.30
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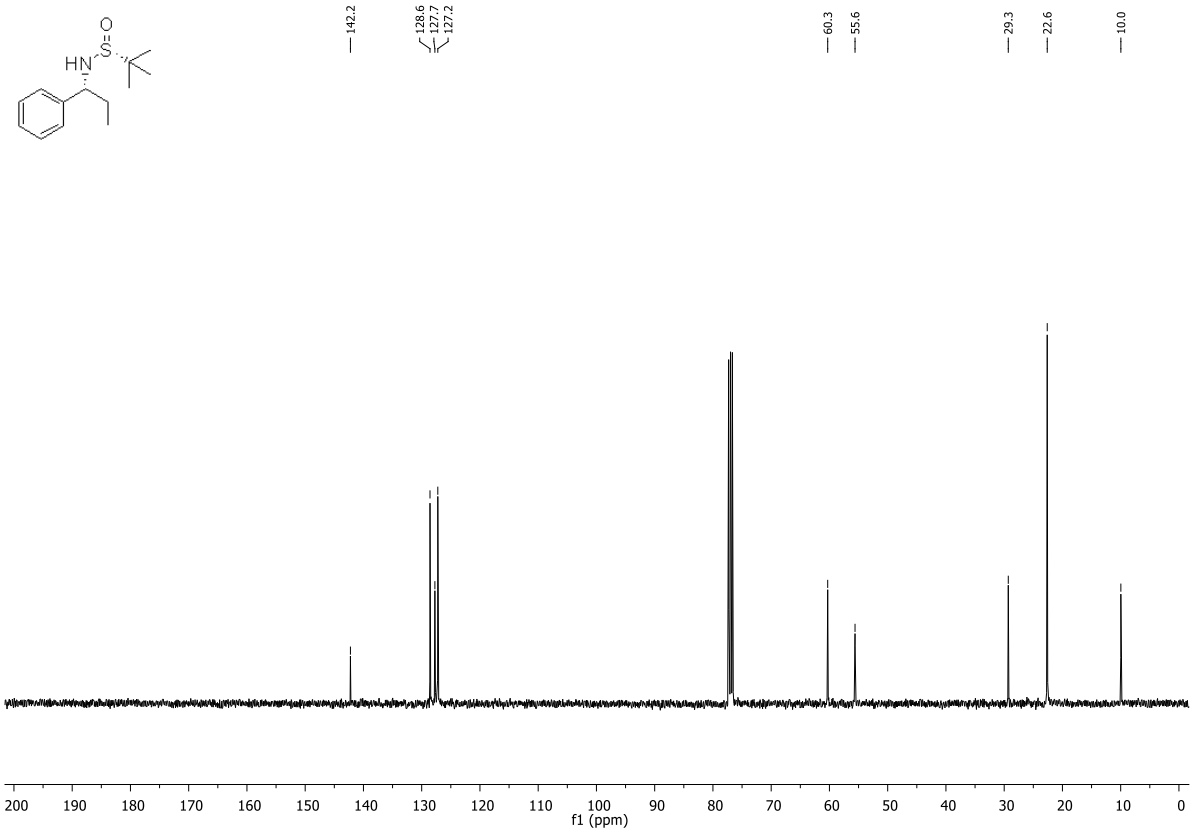
7.29
7.28
7.26
7.26
7.25
7.24
4.28
4.27
4.27
4.26
4.26
4.25
4.25
4.24
3.37
3.37
2.07
2.05
2.05
2.03
2.02
2.01
2.00
2.00
1.78
1.76
1.76
1.74
1.74
1.72
1.72
1.70
1.70
1.69
0.79
0.77
0.75
HN
S
O
4.42
1.00
1.14
1.20
1.31
8.24
2.88
f1 (ppm)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128.6
127.7
127.2
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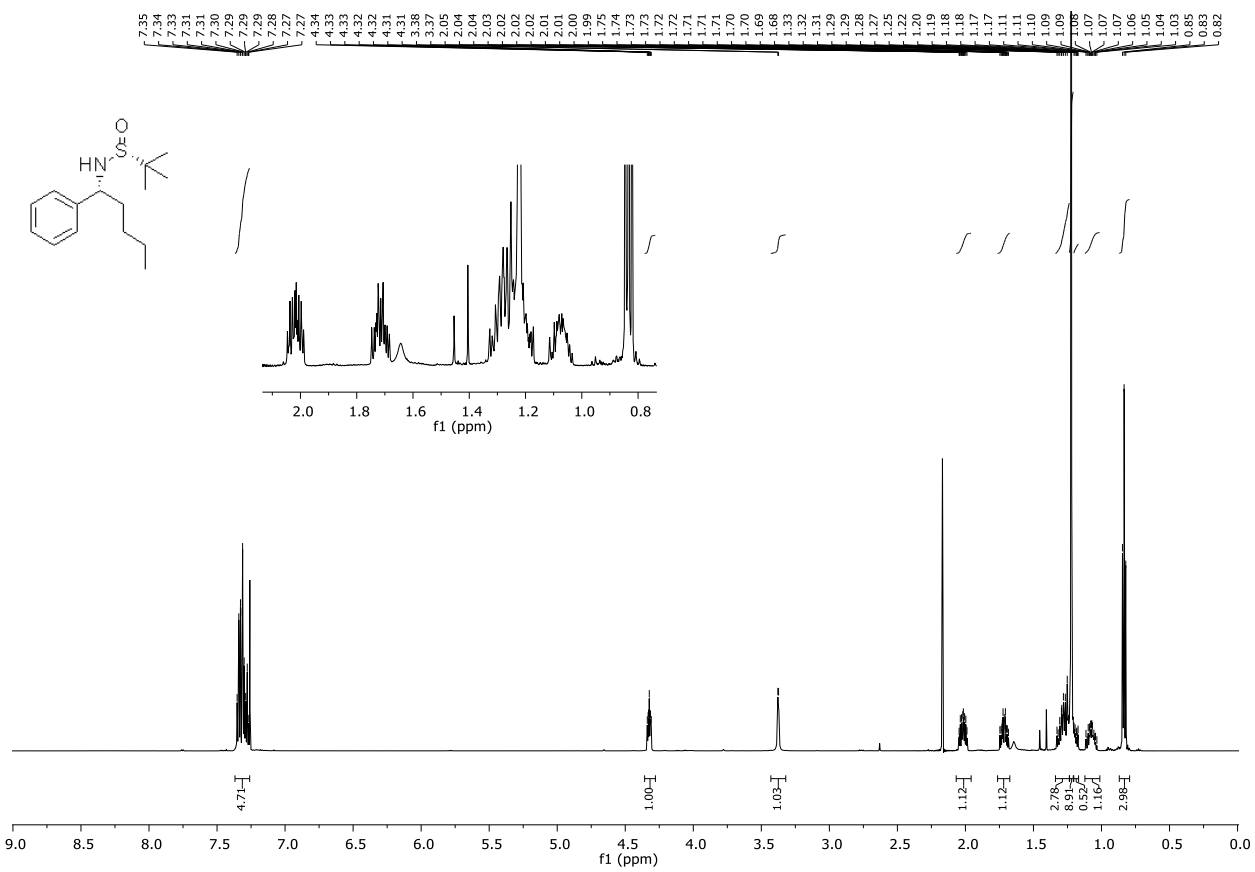
55.6
29.3
22.6
10.0
HN
S
O
f1 (ppm)


HN
O
f1 (ppm)
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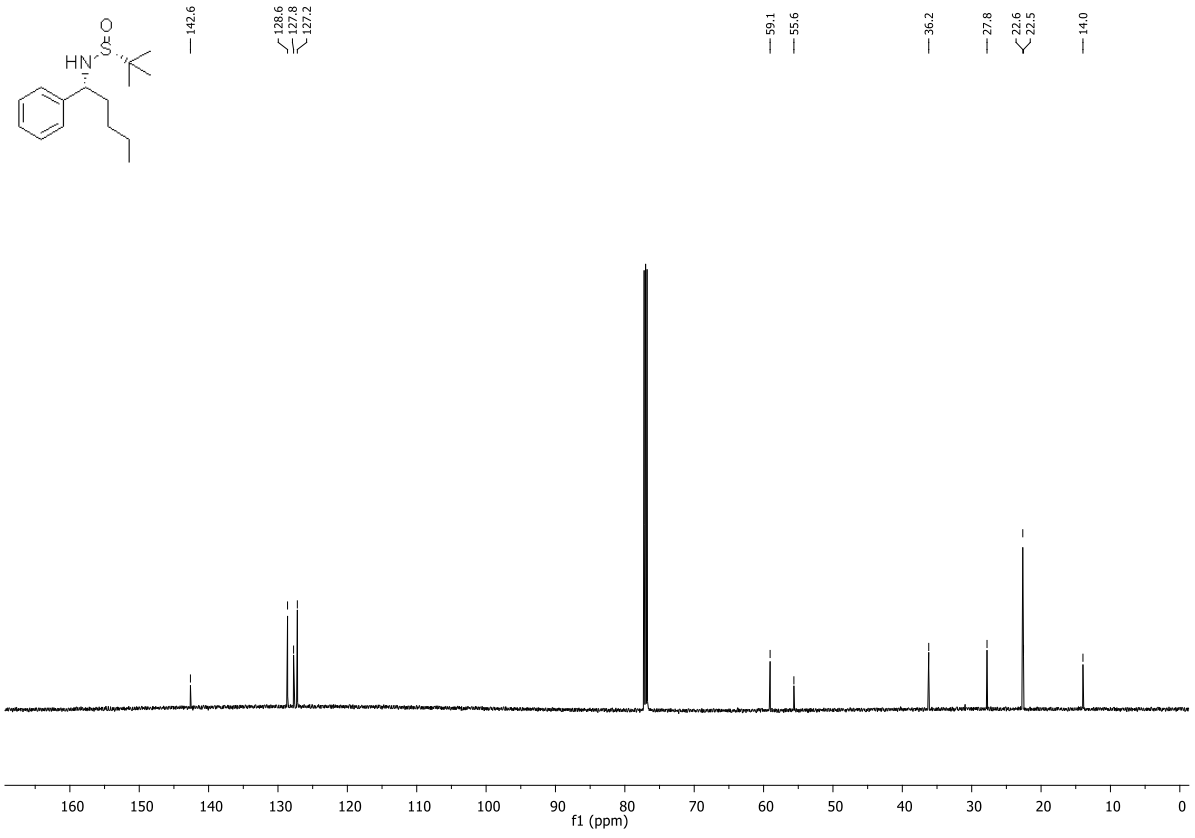
1.00
1.03
1.12
1.12
2.78
8.91
0.52
1.16
2.98


HN
O
142.6
128.6
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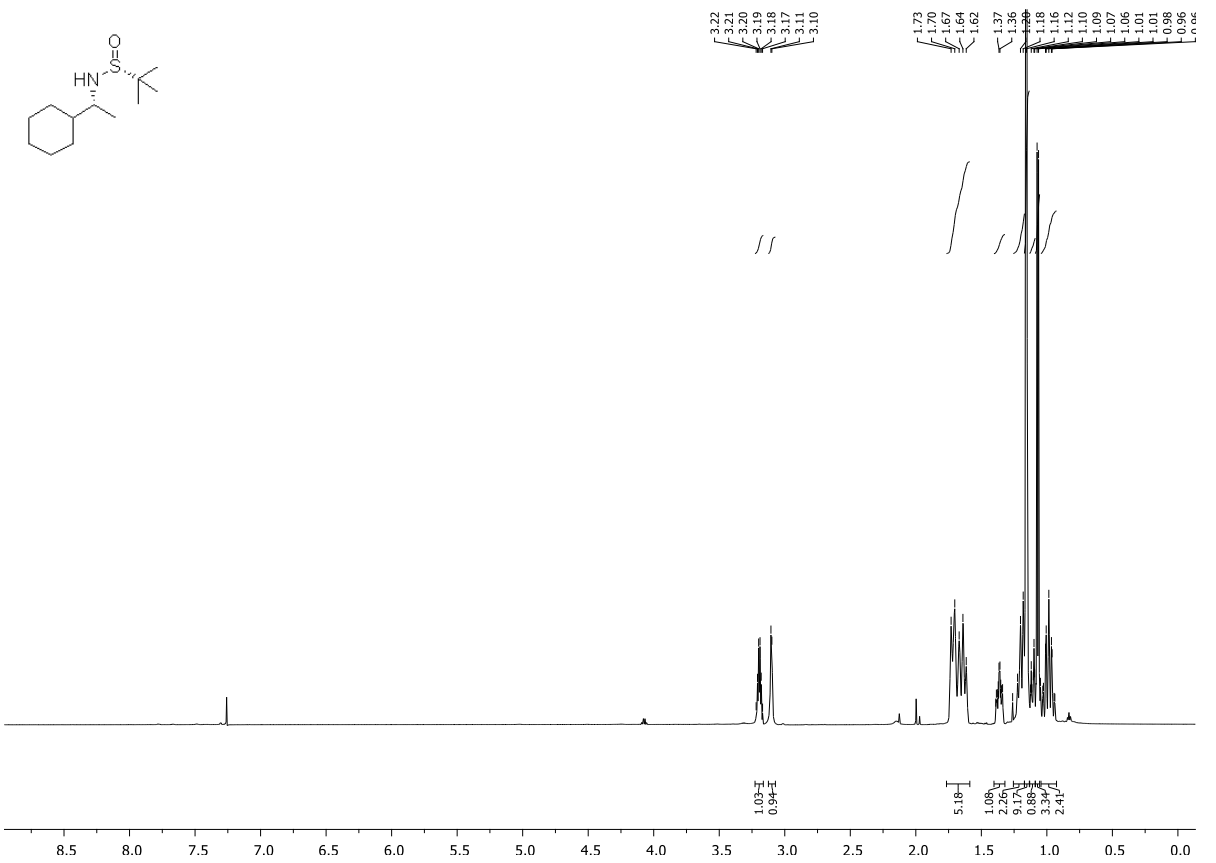
127.2
59.1
55.6
36.2
27.8
22.6
22.5
14.0
f1 (ppm)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3.10
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1.67
1.64
1.62
1.37
1.36
1.20
1.18
1.16
1.12
1.10
1.09
1.07
1.06
1.01
1.01
0.98
0.96
1.03
0.94
5.18
1.08
2.26
9.17
0.88
3.34
2.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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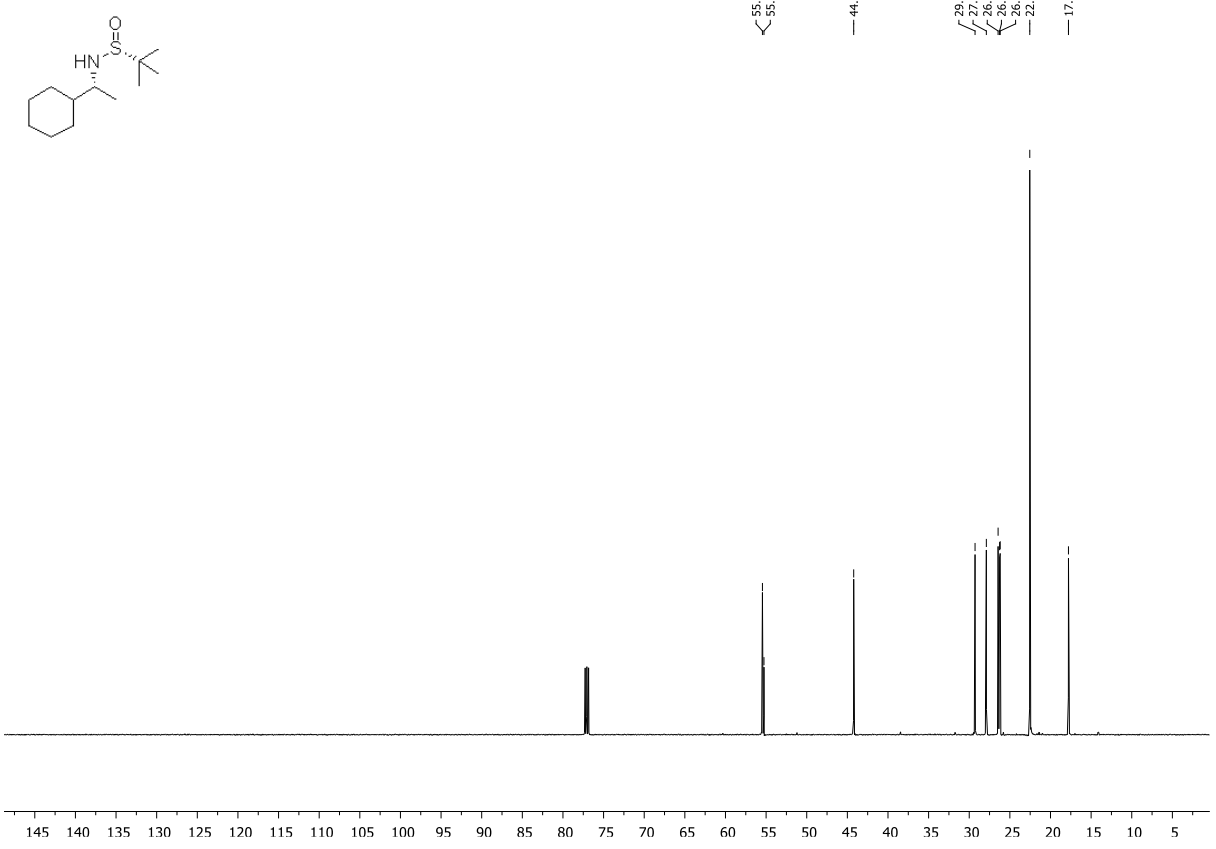
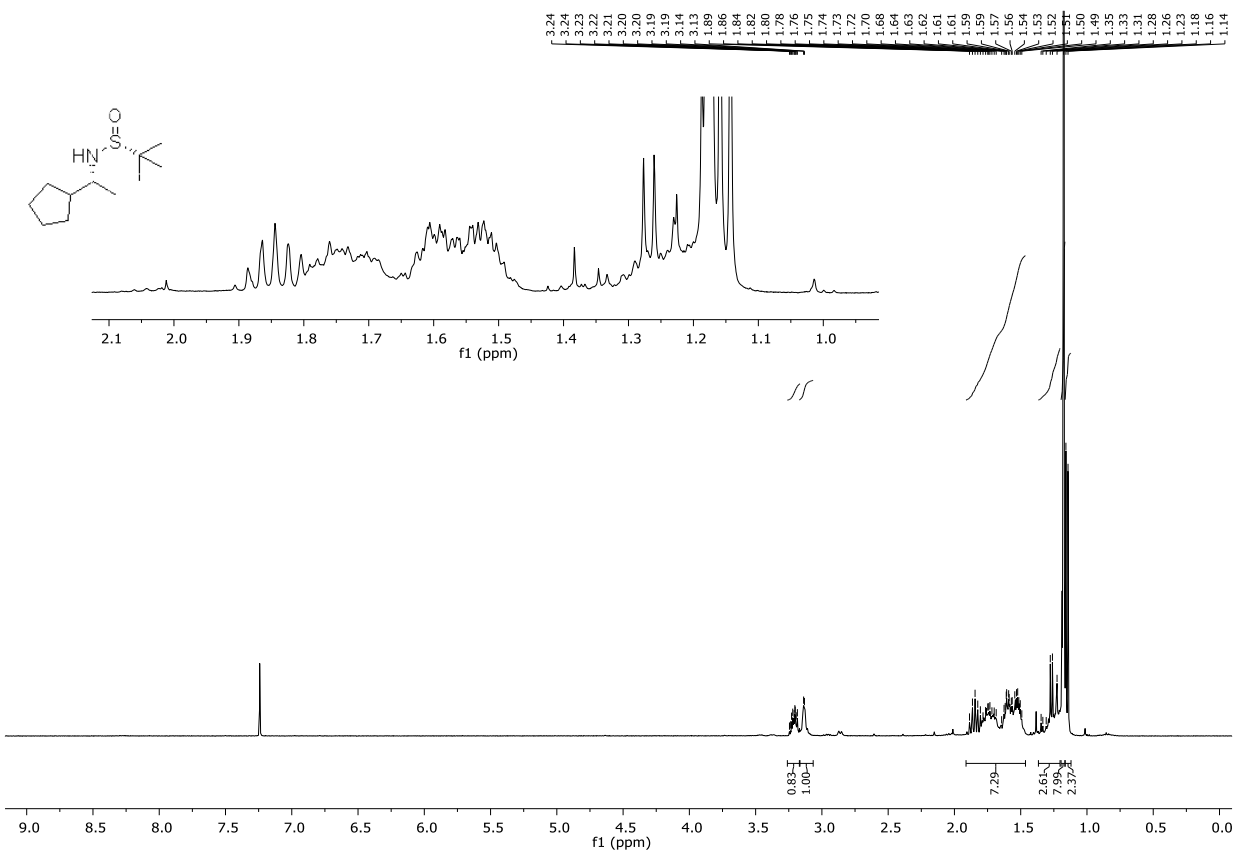
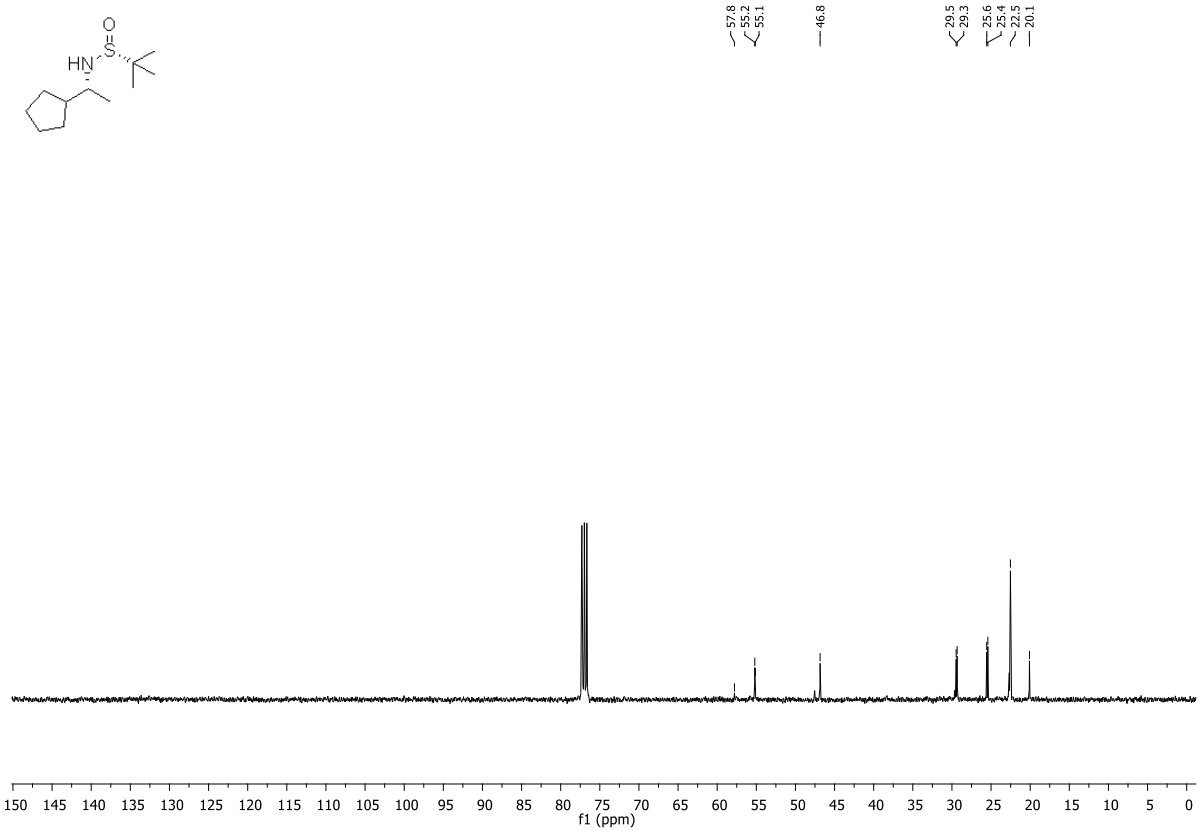
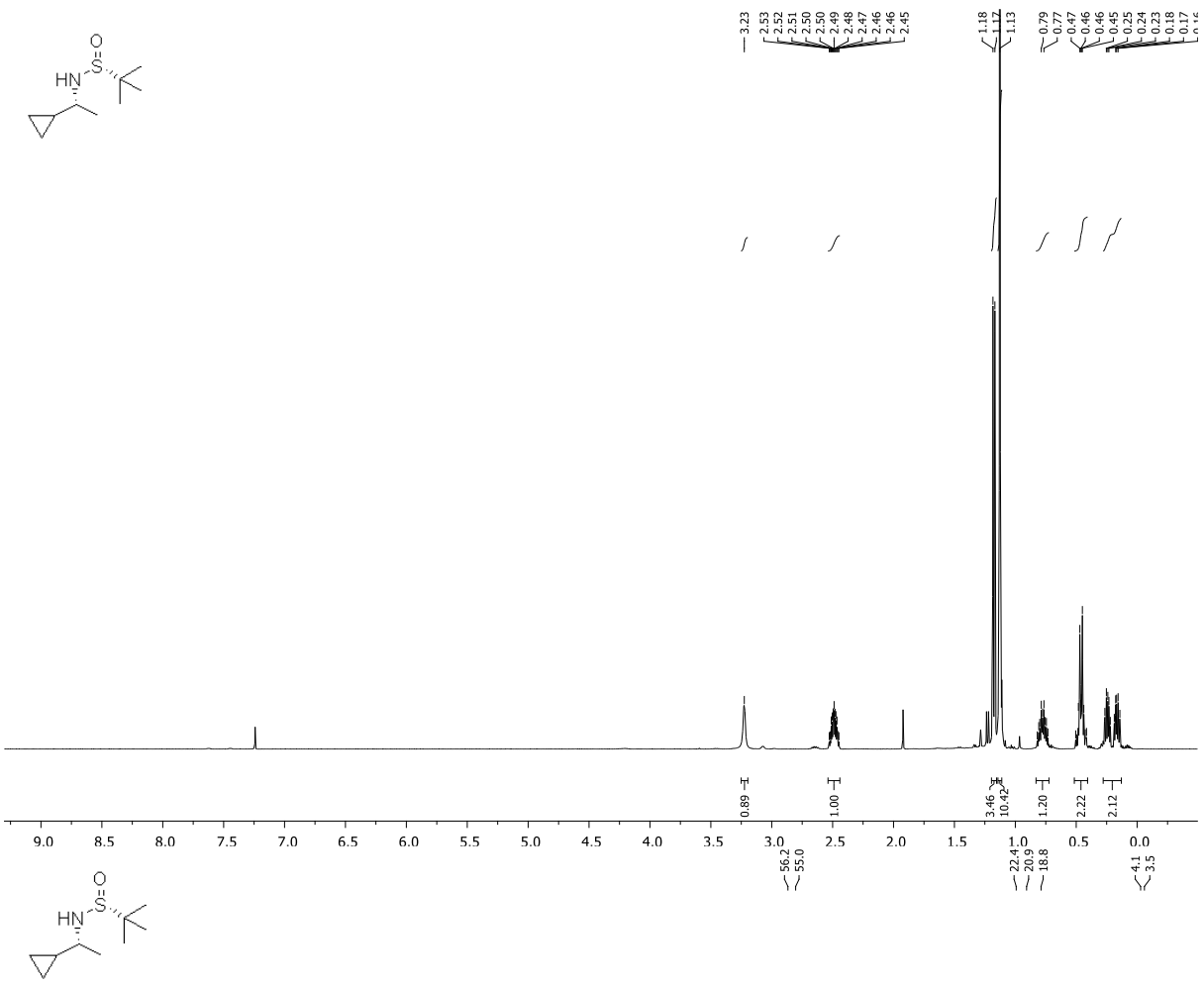
3.0
2.5
2.0
1.5
1.0
0.5
0.0


55.5
55.3
44.2
29.3
27.9
26.4
26.3
26.2
22.6
17.8
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5


HN
S
O
f1 (ppm)
0.83
1.00
7.29
2.61
7.99
2.37


HN
S
O
57.8
55.2
55.1
46.8
29.5
29.3
25.6
25.4
22.5
20.1
f1 (ppm)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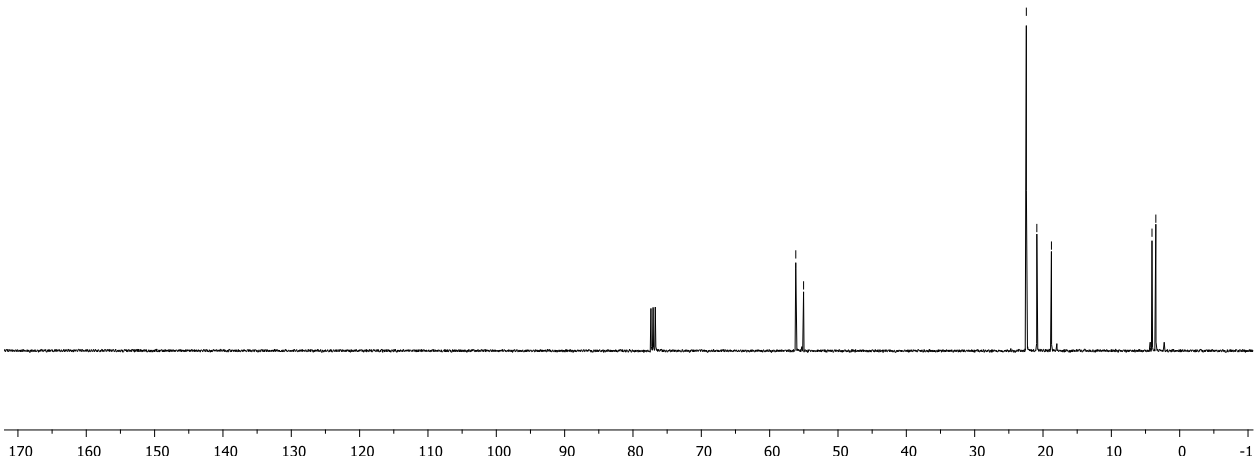
2.52
2.51
2.50
2.50
2.49
2.48
2.47
2.46
2.46
2.45
1.18
1.17
1.13
0.79
0.77
0.47
0.46
0.46
0.45
0.25
0.24
0.23
0.18
0.17
0.89
1.00
3.46
10.42
1.20
2.22
2.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
56.2
55.0
22.4
20.9
18.8
4.1
3.5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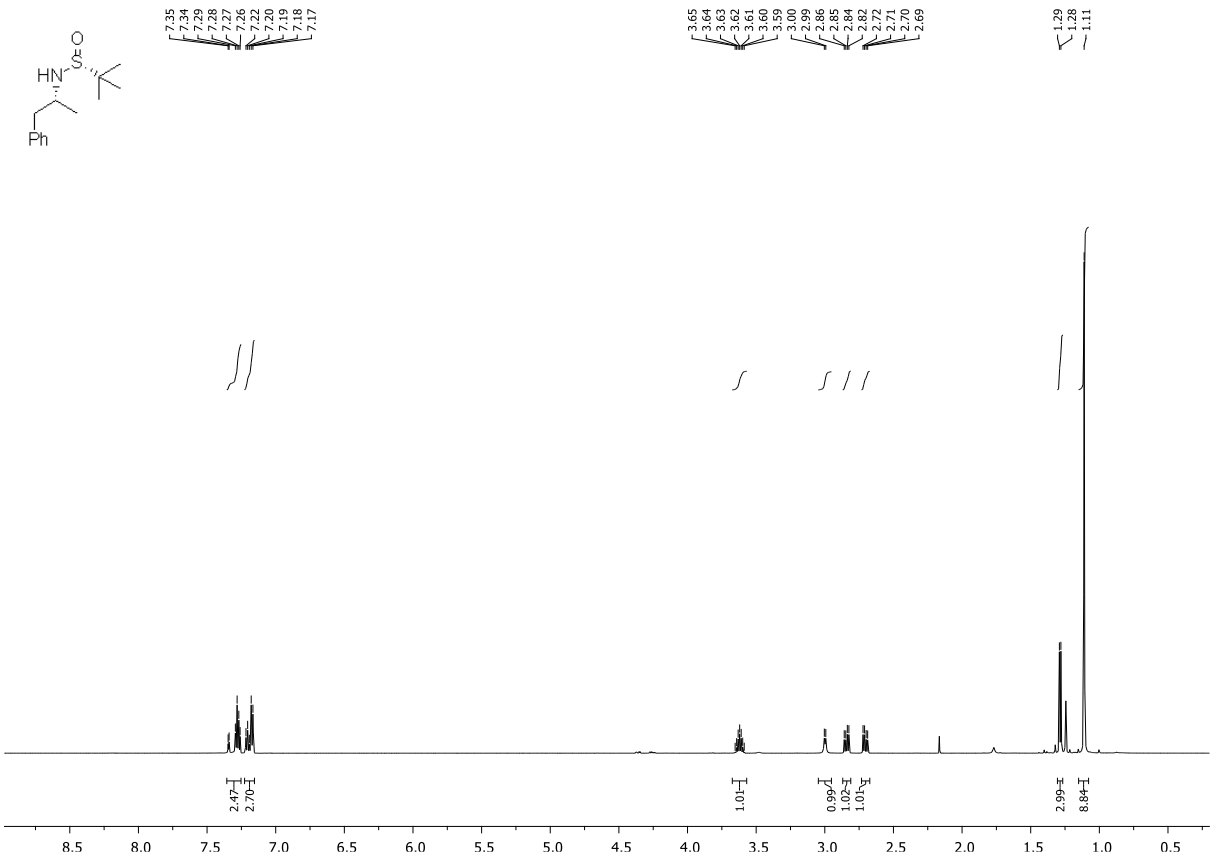
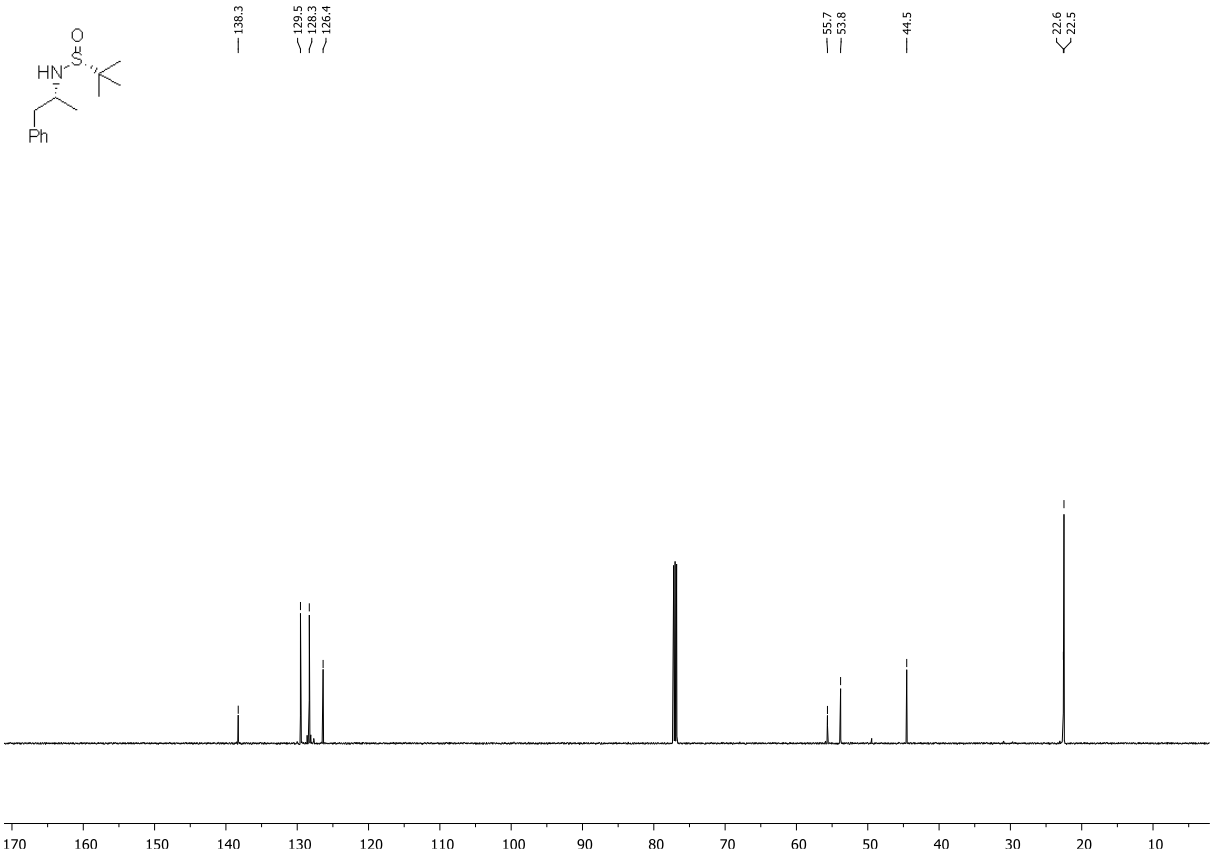
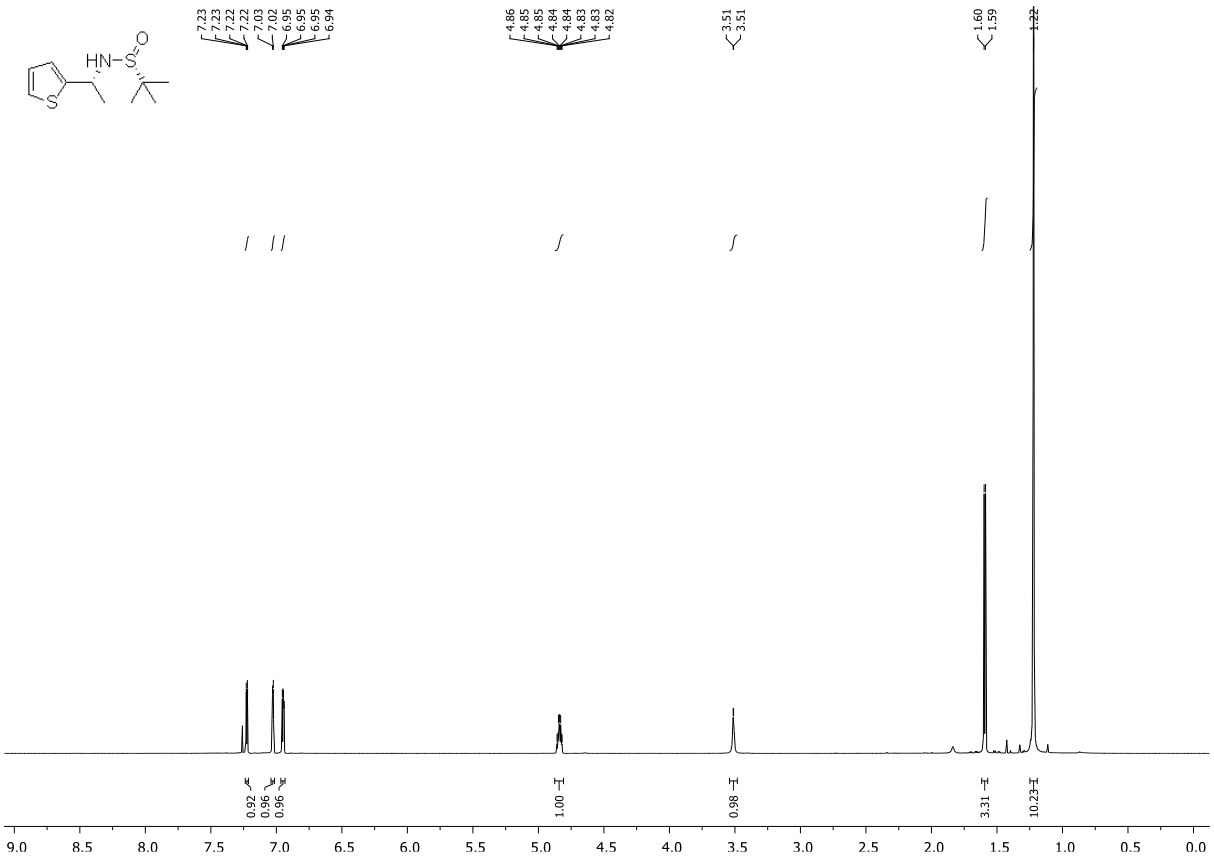
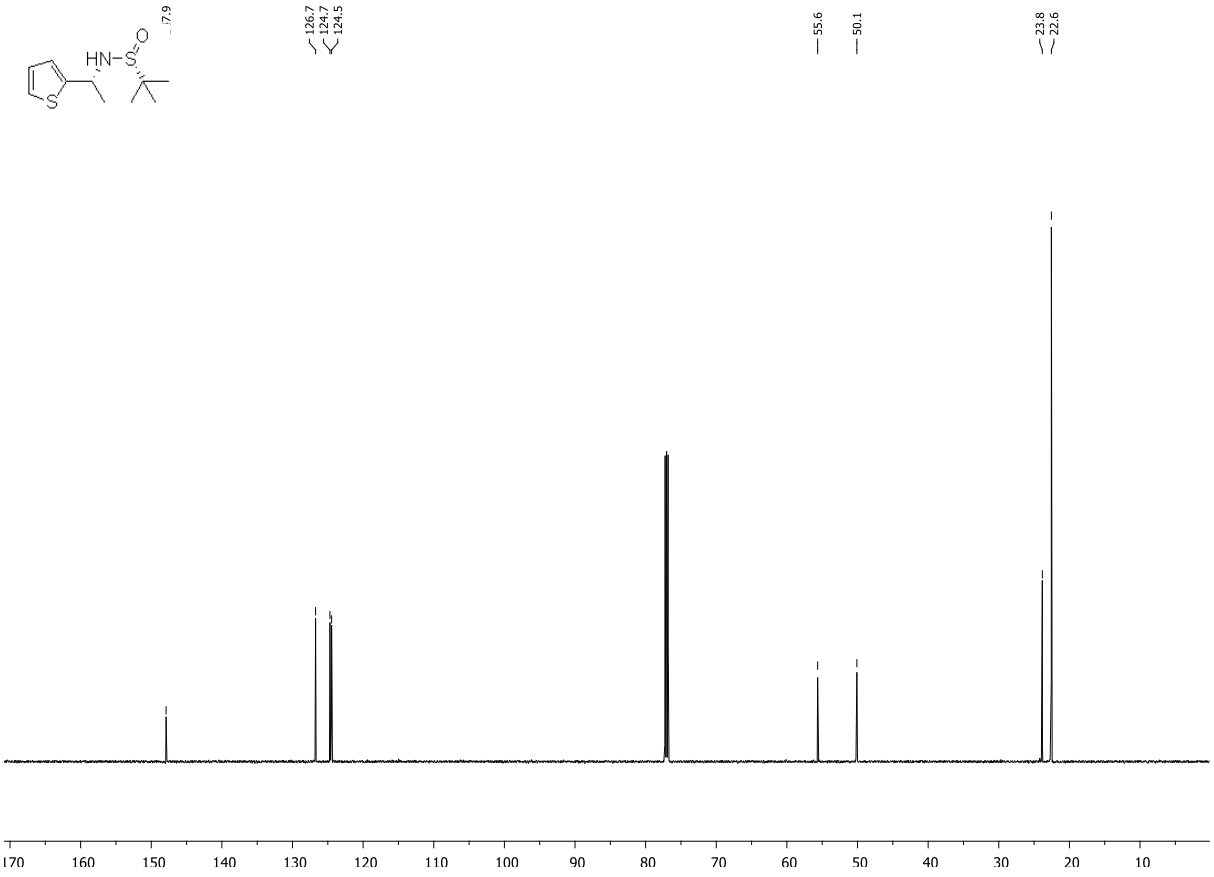
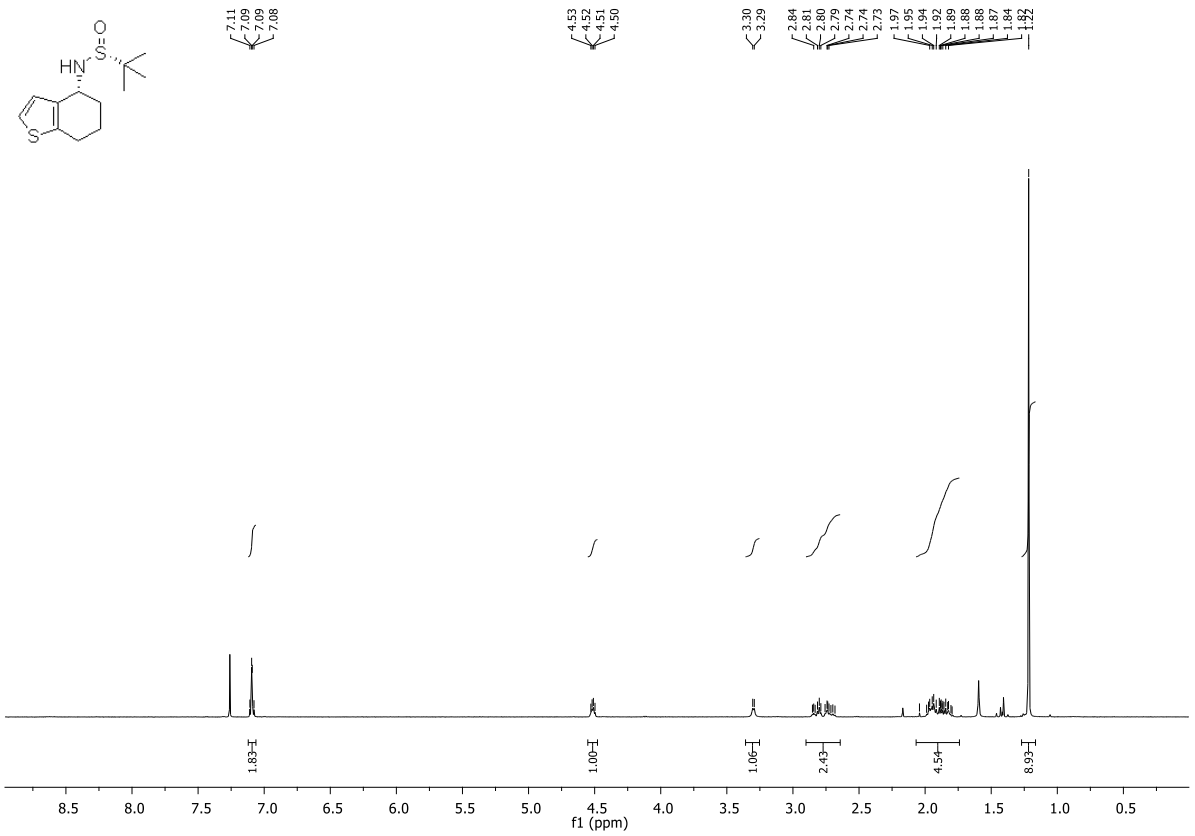
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


7.35
7.34
7.29
7.28
7.27
7.26
7.22
7.20
7.19
7.18
7.17
3.65
3.64
3.63
3.62
3.61
3.60
3.59
3.00
2.99
2.86
2.85
2.84
2.82
2.72
2.71
2.70
2.69
1.29
1.28
1.11
HN
O
S
Ph
2.47
2.70
1.01
0.99
1.02
1.01
2.99
8.84
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


138.3
129.5
128.3
126.4
55.7
53.8
44.5
22.6
22.5
HN
O
S
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HN
S
O
7.23
7.23
7.22
7.22
7.03
7.02
6.95
6.95
6.95
6.94
4.86
4.85
4.85
4.84
4.84
4.83
4.83
4.82
3.51
3.51
1.60
1.59
1.22
0.92
0.96
0.96
1.00
0.98
3.31
10.23
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


HN
S
O
126.7
124.7
124.5
55.6
50.1
23.8
22.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.11
7.09
7.09
7.08
4.53
4.52
4.51
4.50
3.30
3.29
2.84
2.81
2.80
2.79
2.74
2.74
2.73
1.97
1.95
1.94
1.92
1.89
1.88
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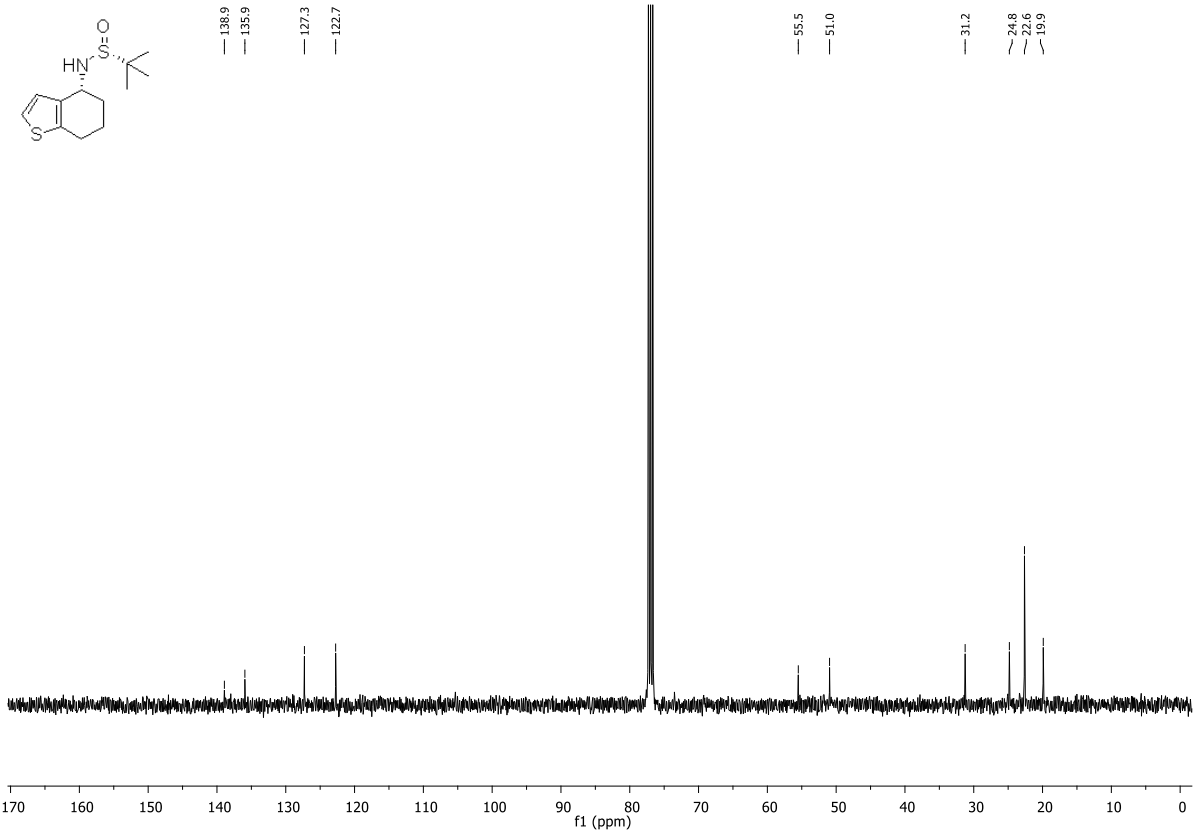
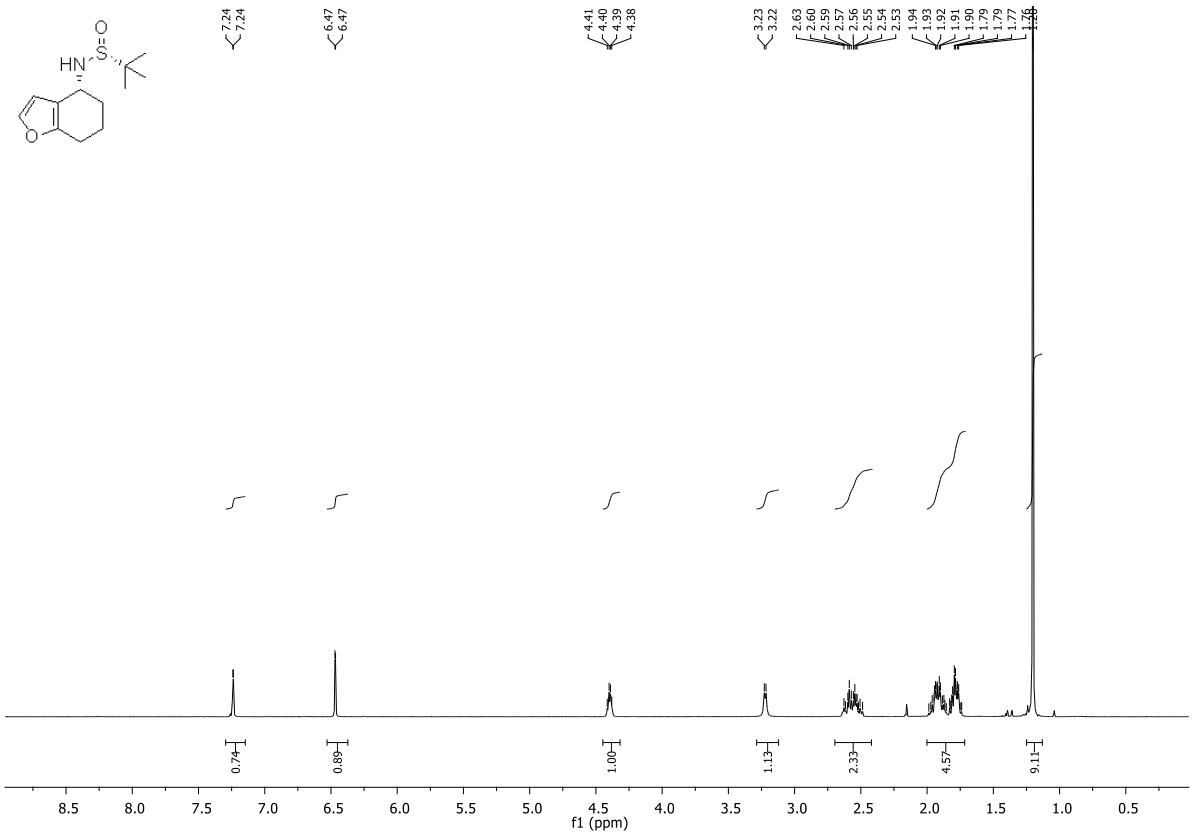
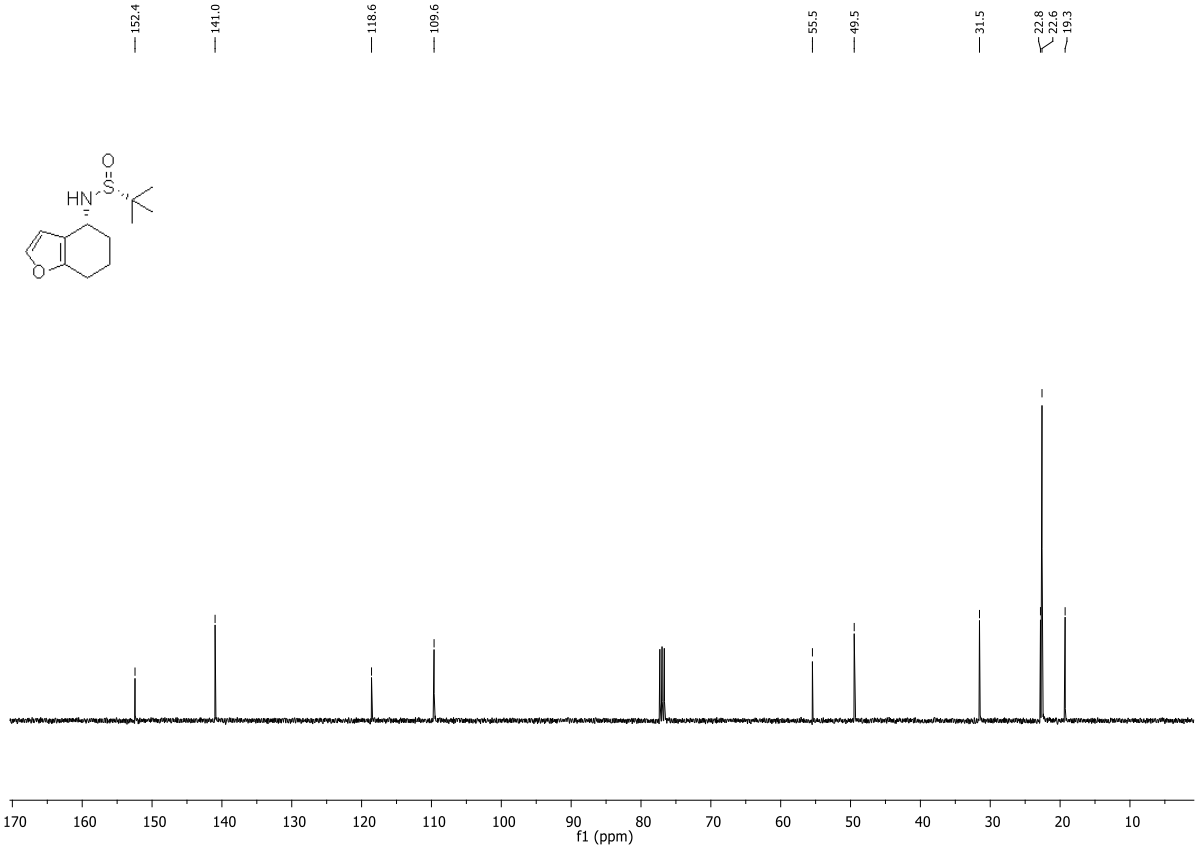
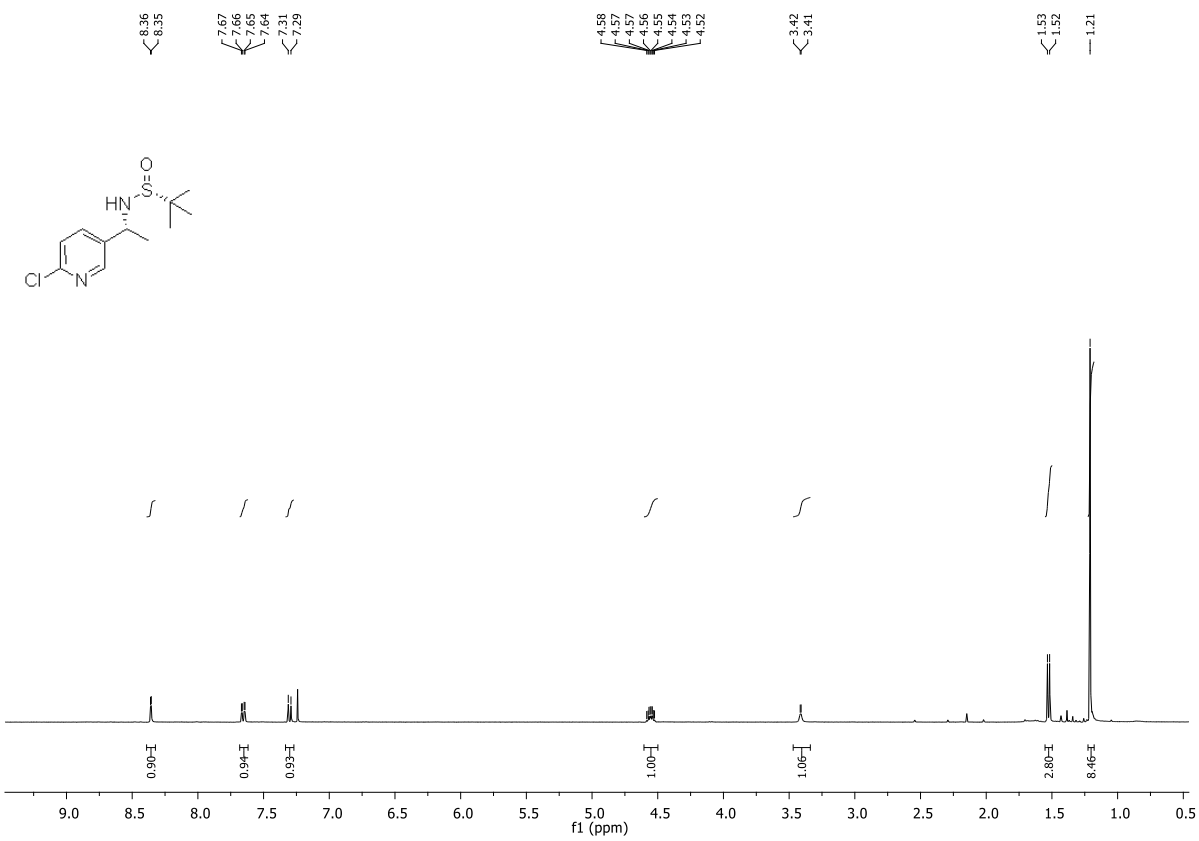
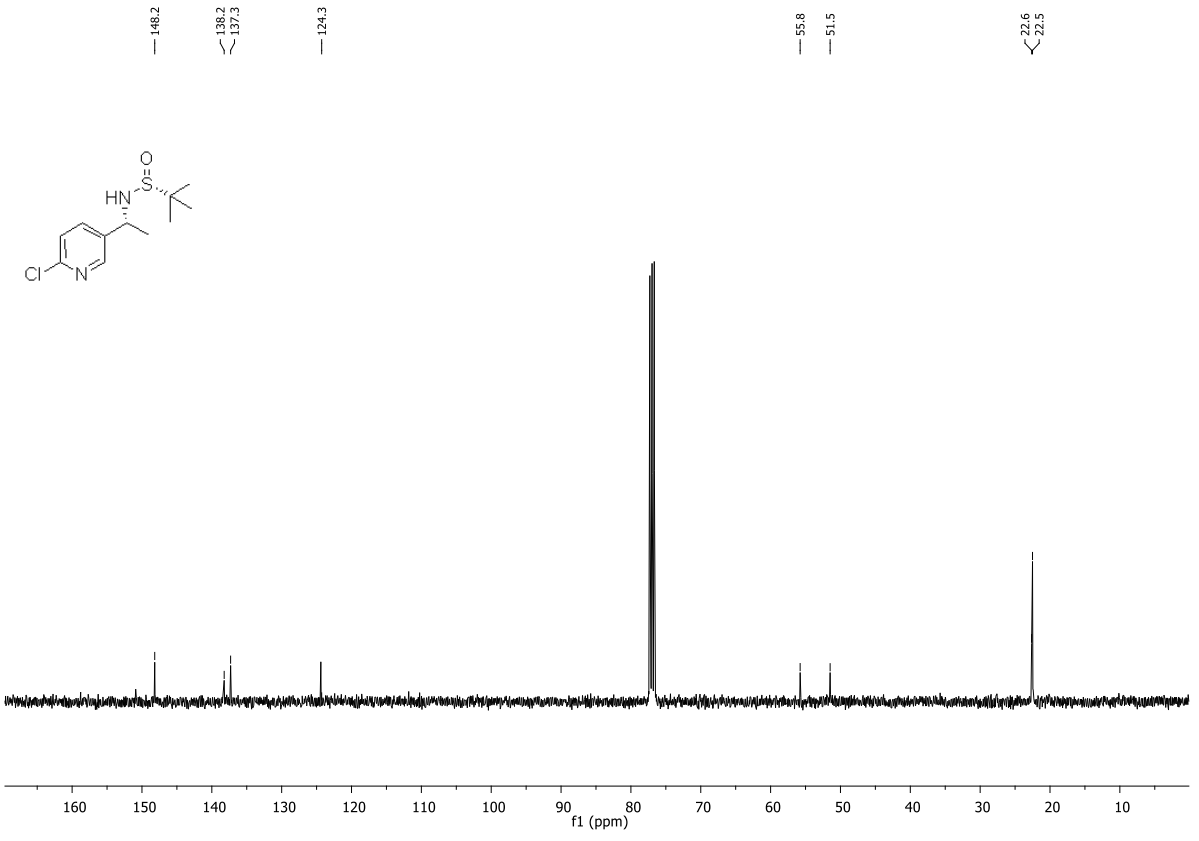
1.06
2.43
4.54
8.93
f1 (ppm)


138.9
135.9
127.3
122.7
55.5
51.0
31.2
24.8
22.6
19.9
f1 (ppm)

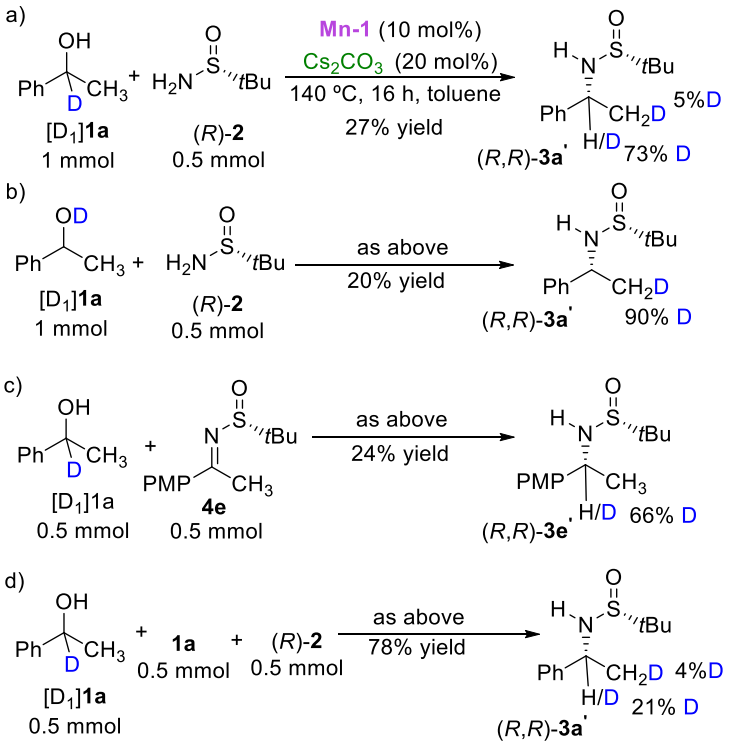

7.24
7.24
6.47
6.47
4.41
4.40
4.39
4.38
3.23
3.22
2.63
2.60
2.59
2.57
2.56
2.55
2.54
2.53
1.94
1.93
1.92
1.91
1.90
1.79
1.79
1.77
1.28
0.74
0.89
1.00
1.13
2.33
4.57
9.11
f1 (ppm)


152.4
141.0
118.6
109.6
55.5
49.5
31.5
22.8
22.6
19.3
f1 (ppm)


8.36
8.35
7.67
7.66
7.65
7.64
7.31
7.29
4.58
4.57
4.57
4.56
4.55
4.54
4.53
4.52
3.42
3.41
1.53
1.52
1.21
HN
O
O
Cl
N
0.90
0.94
0.93
1.00
1.06
2.80
8.46
f1 (ppm)

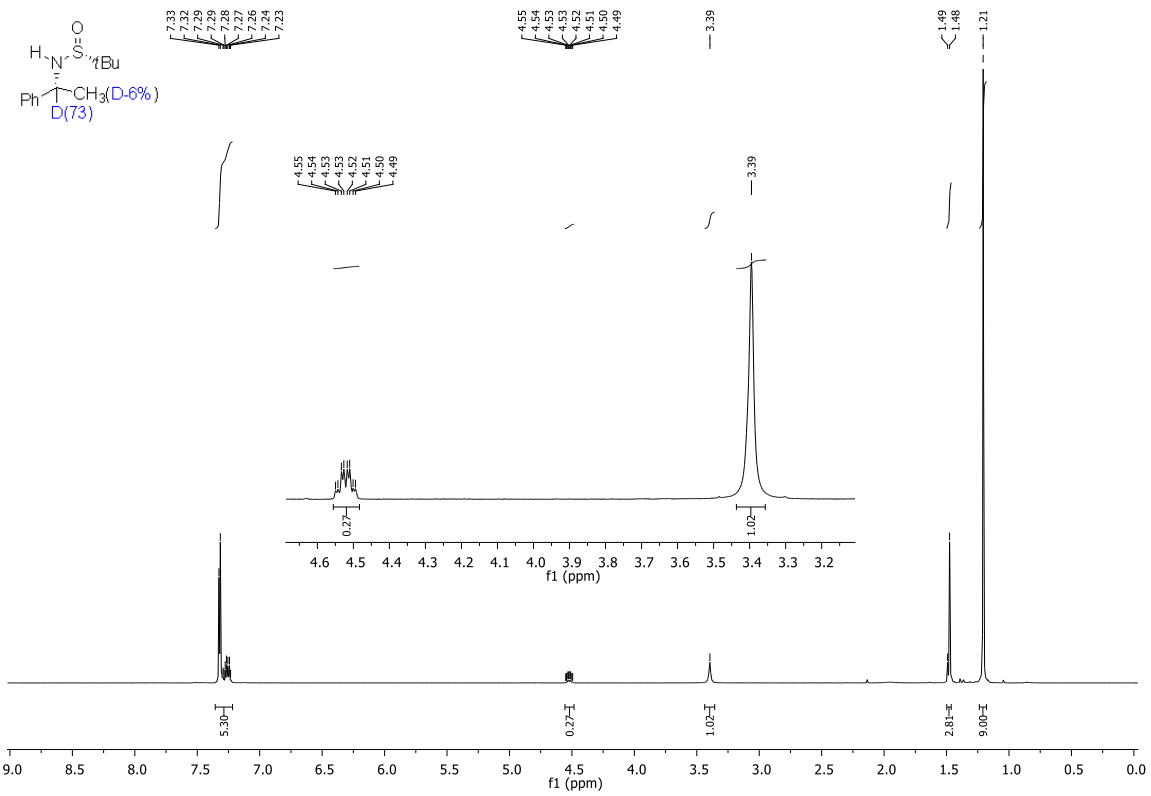

148.2
138.2
137.3
124.3
55.8
51.5
22.6
22.5
HN
O
O
Cl
N
f1 (ppm)

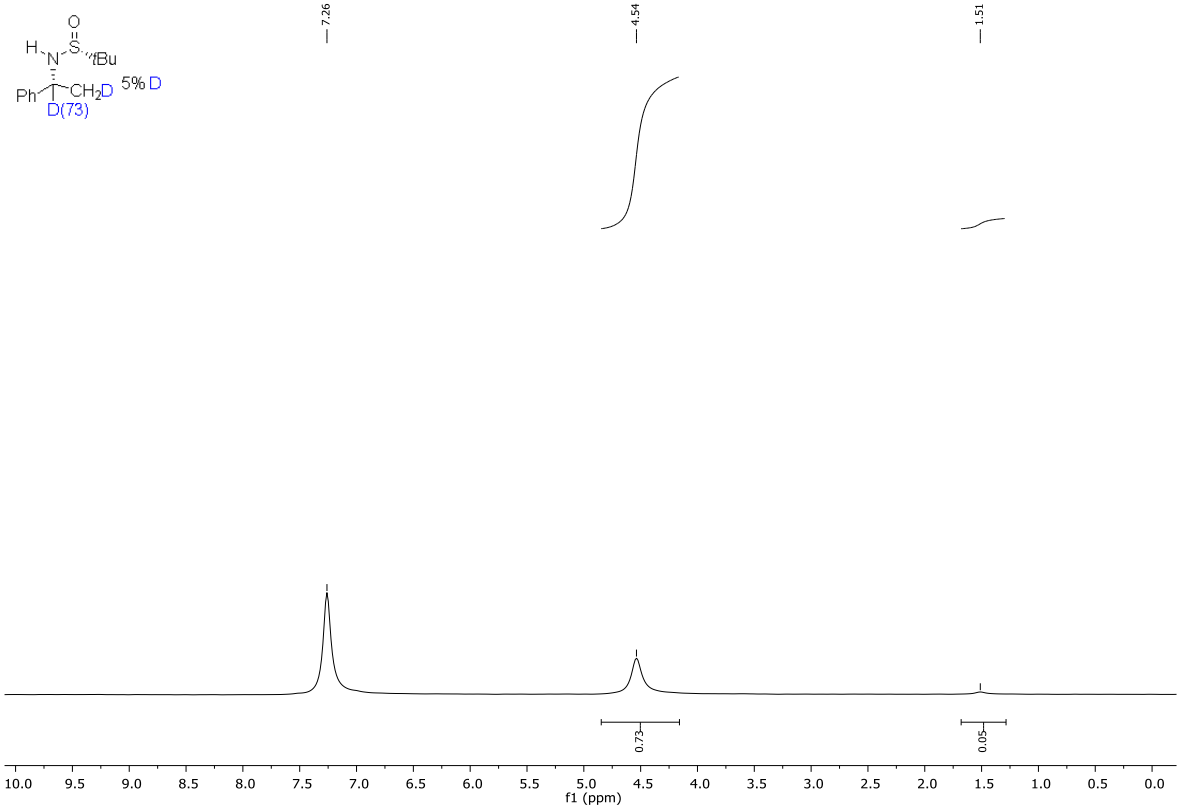
Deuterium labeling experiments

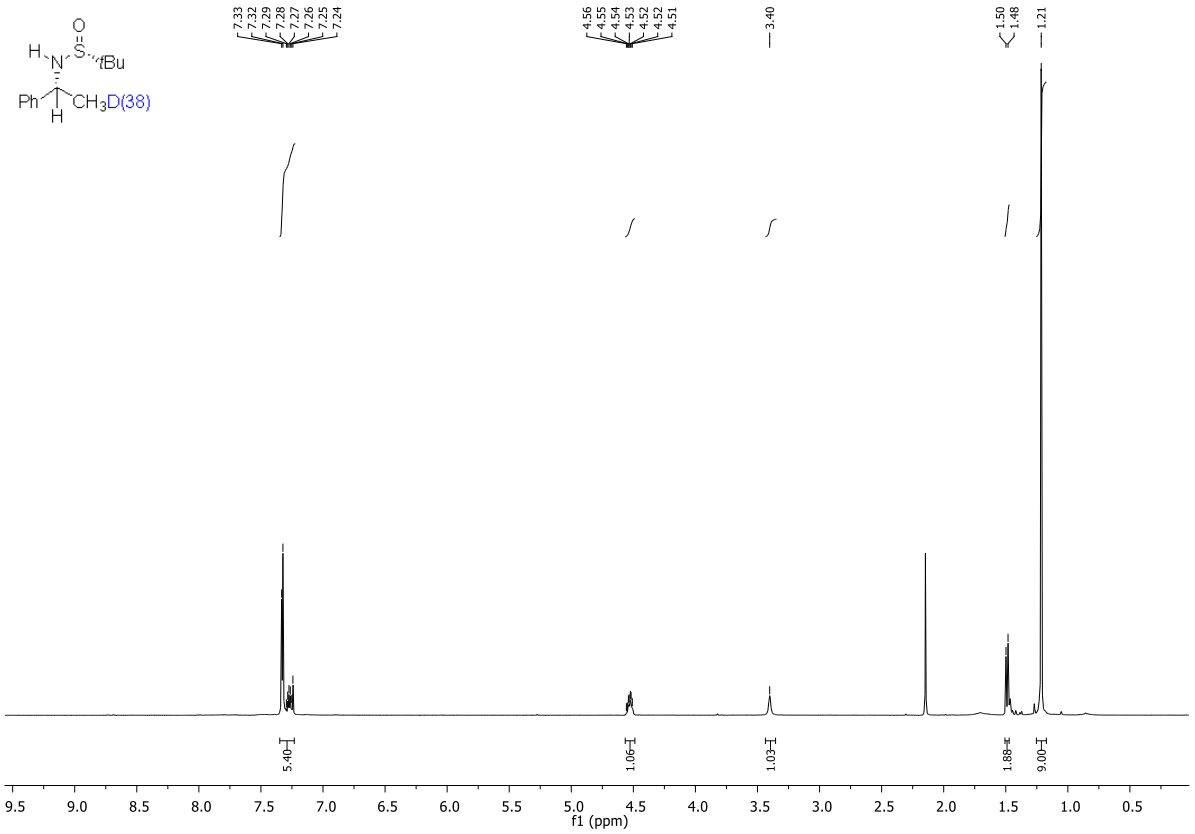


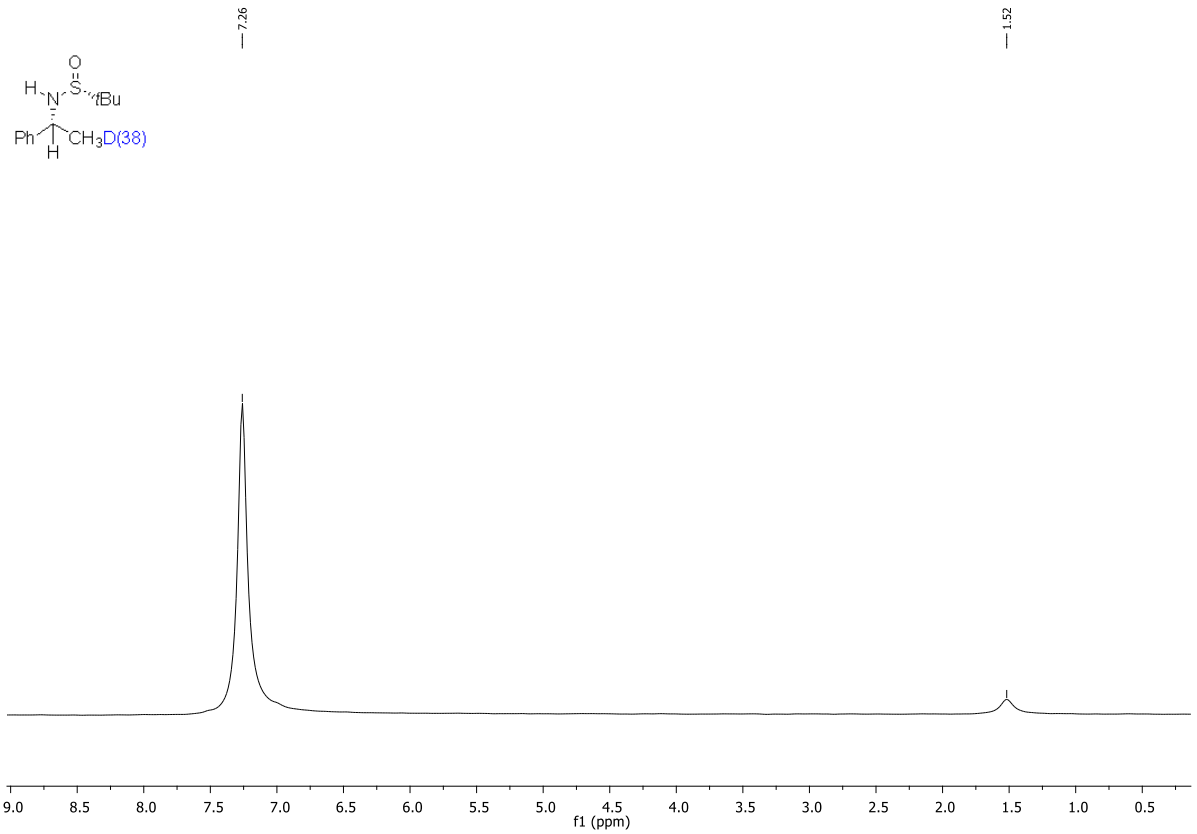
we carried out deuterium-labeling experiments (Scheme 2). To avoid the D/H exchange between the solvent and the substrates, the reactions were carried out in toluene instead of the *t*-amyl alcohol. An experiment with 1-phenylethanol-**α-*d*$_1$** [D$_1$]**1a** provided the desired product (*R*,*R*$_s$)-**3a'** in 27% yield with 73% deuteration at the α-position (Scheme 2a). As complementary experiment, when 1-phenylethanol-OD was subjected to the coupling reaction, we only observed high deuterium incorporation at the methyl group (Scheme 2b). The very low deuterium scrambling between the carbon and the heteroatoms support monohydride mechanism and highlight the involvement of both of the metal and non-innocent ligand in the catalytic pathway[19-20]. Furthermore, in the transfer hydrogenation of the imine **4e** using [D$_1$]**1a** as a hydrogen donor, the desired product (*R*,*R*)-**3e'** was produced in 24% yield and 66% D incorporation at the α-position along with the formation of 28% of acetophenone, which supports the hydrogen transfer pathway (Scheme 2c). Finally, when we performed a competitive experiment between **1a** and [D$_1$]**1a**, a very high KIE was observed (K_H/K_D=2.5) and the desired product was obtained in 78% yield with 21% D incorporation which eliminates the possibility of the nucleophilic substitution pathway.[21]

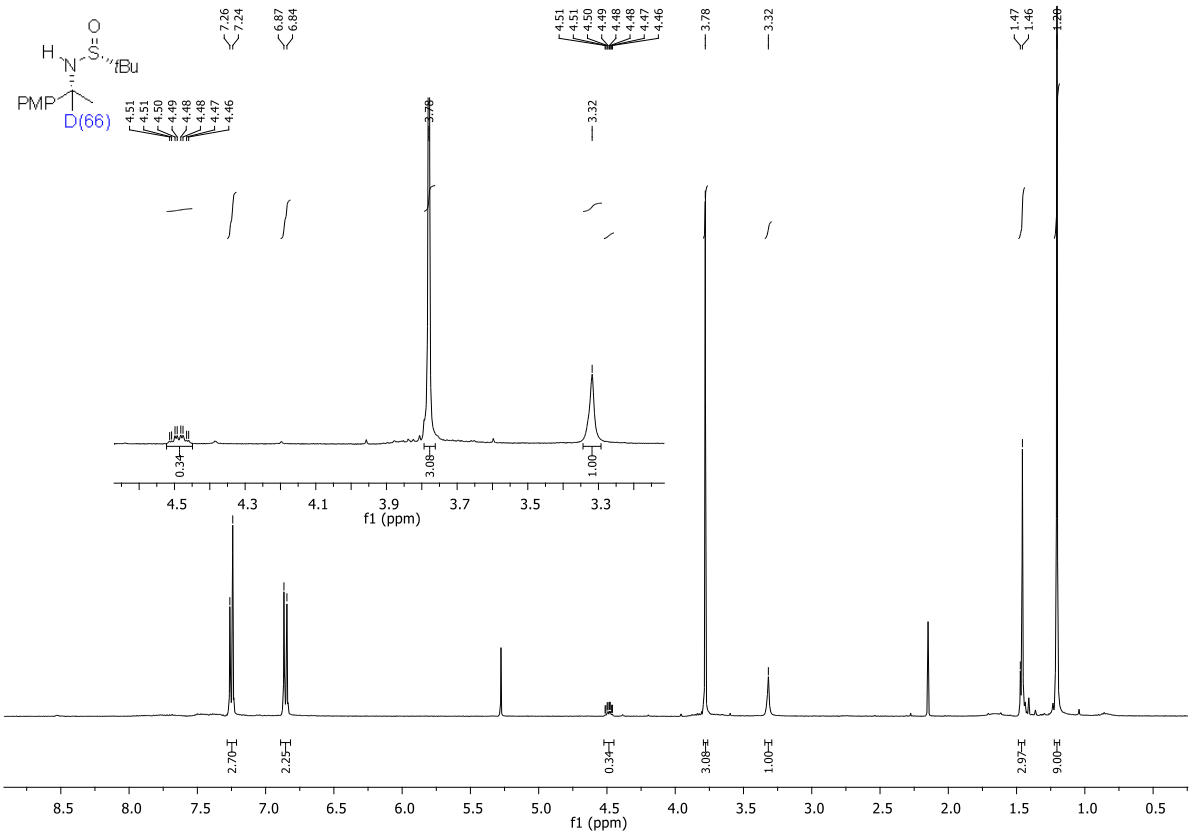
a)

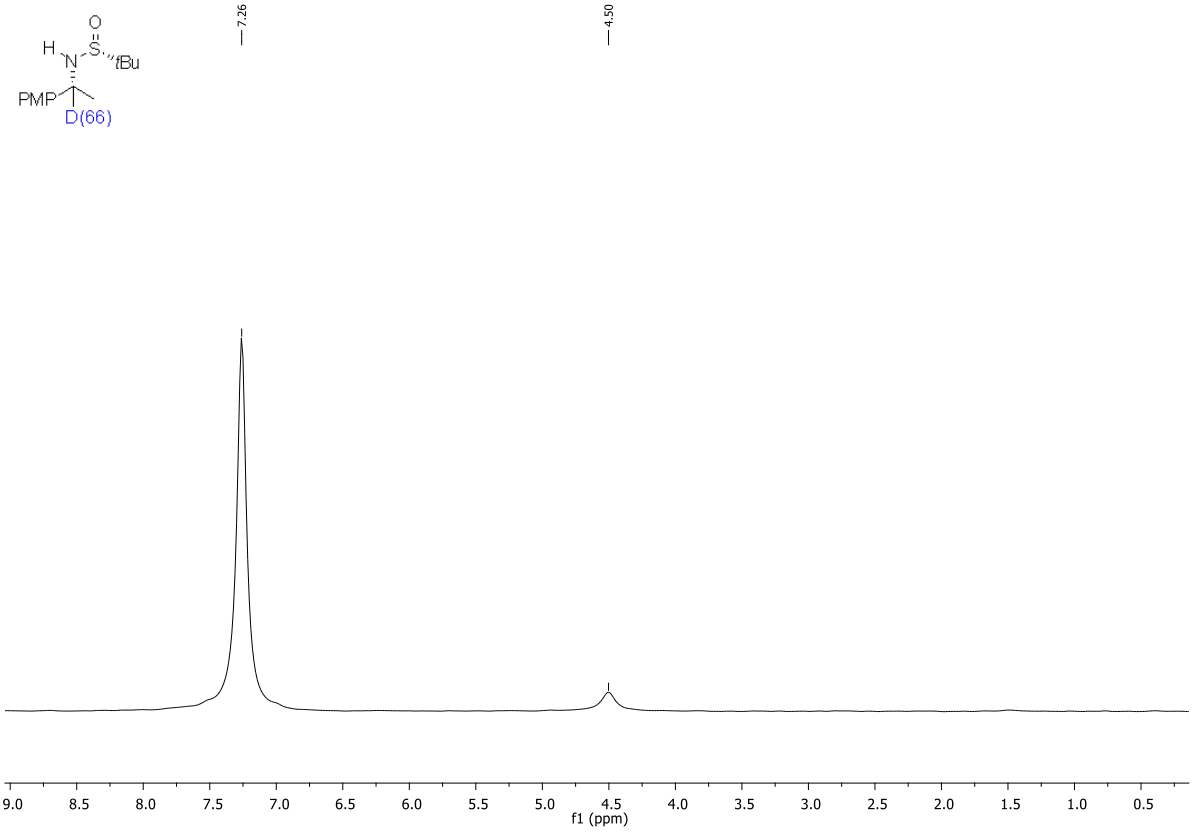

7.33
7.32
7.29
7.29
7.28
7.27
7.26
7.24
7.23
4.55
4.54
4.53
4.53
4.52
4.51
4.50
4.49
3.39
1.49
1.48
1.21
tBu
Ph
CH3(D-6%)
D(73)
0.27
1.02
f1 (ppm)
5.30
0.27
1.02
2.81
9.00

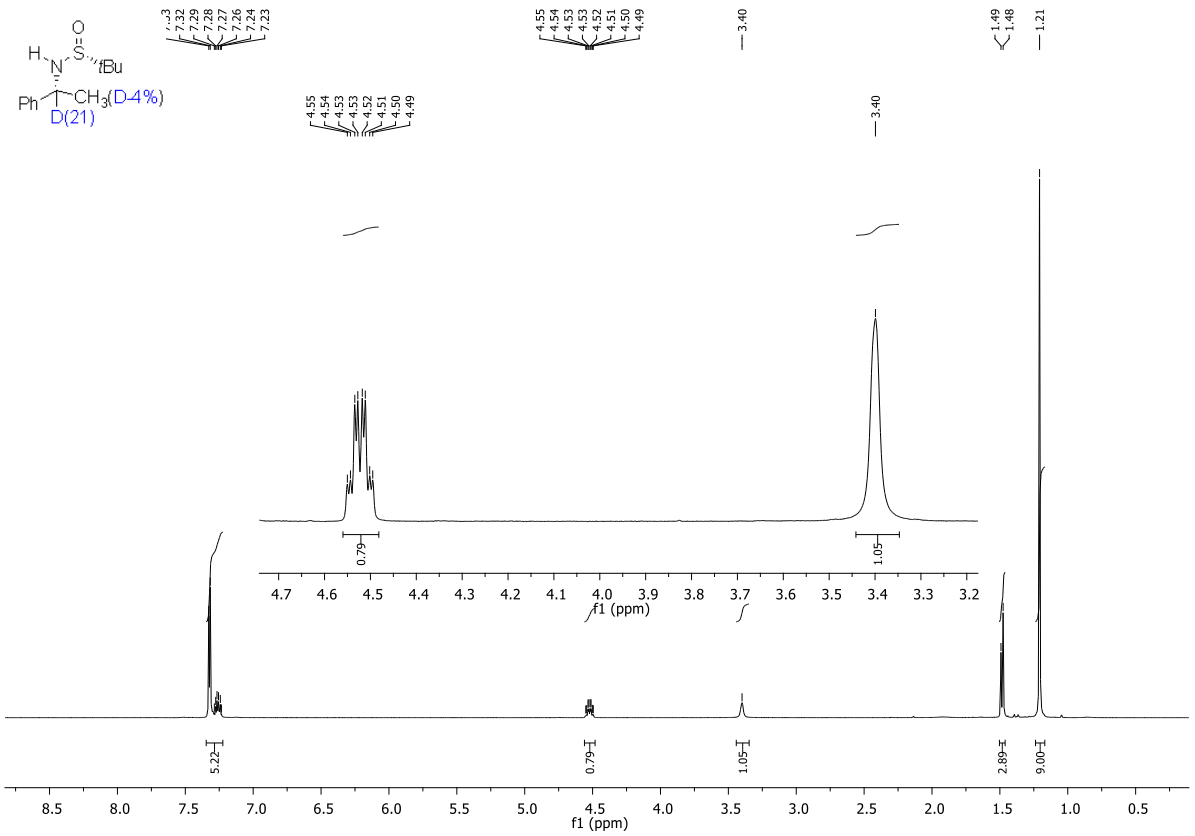

7.26
4.54
1.51
tBu
Ph
CH2D
5% D
D(73)
0.73
0.05
f1 (ppm)

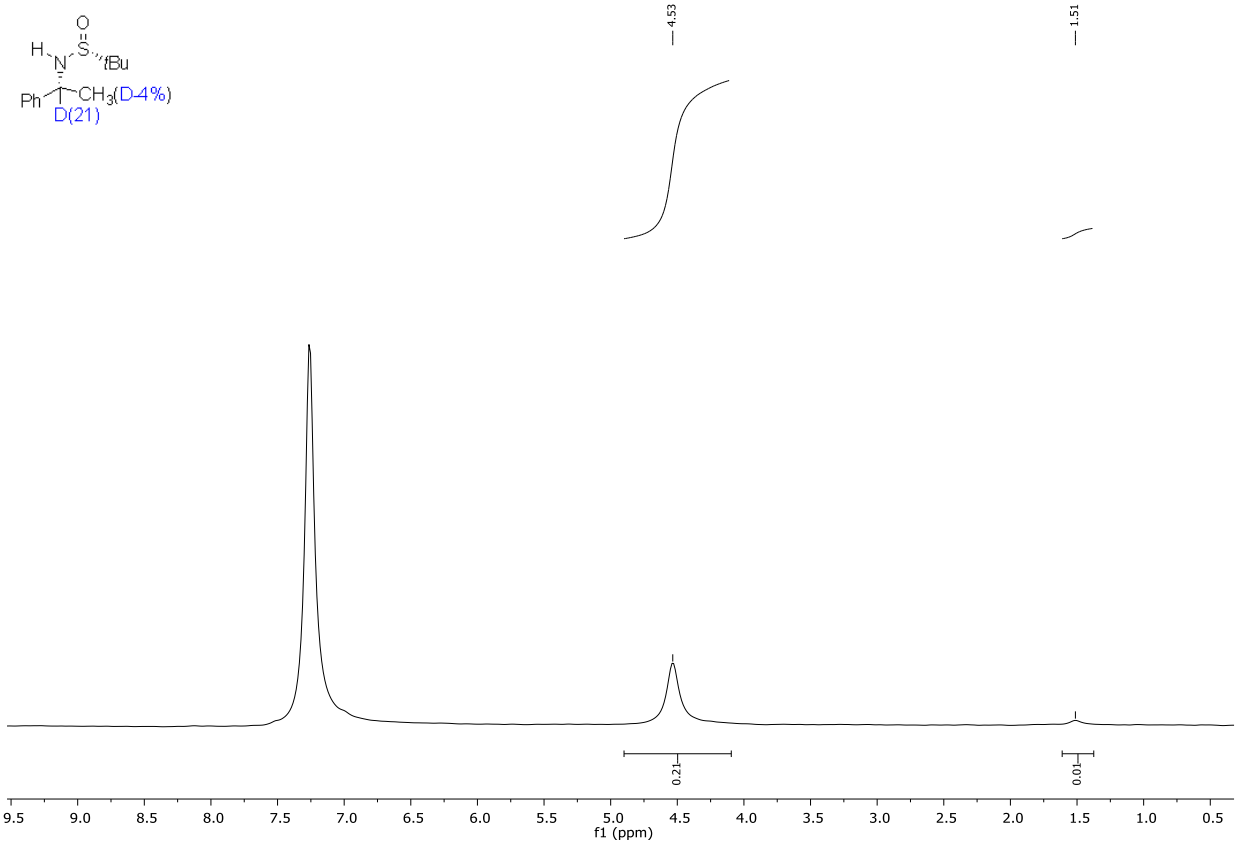

7.33
7.32
7.29
7.28
7.27
7.26
7.25
7.24
4.56
4.55
4.54
4.53
4.52
4.52
4.51
3.40
1.50
1.48
1.21
5.40
1.06
1.03
1.88
9.00
f1 (ppm)


7.26
1.52
f1 (ppm)

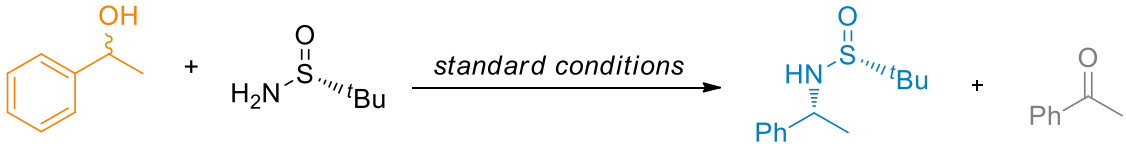

H
N
O
S
tBu
PMP
D(66)
7.26
7.24
6.87
6.84
4.51
4.51
4.50
4.49
4.48
4.48
4.47
4.46
3.78
3.32
1.47
1.46
1.30
3.79
3.32
0.34
3.08
1.00
4.5
4.3
4.1
3.9
3.7
3.5
3.3
f1 (ppm)
2.70
2.25
0.34
3.08
1.00
2.97
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


H
N
O
S
tBu
PMP
D(66)
7.26
4.50
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
f1 (ppm)

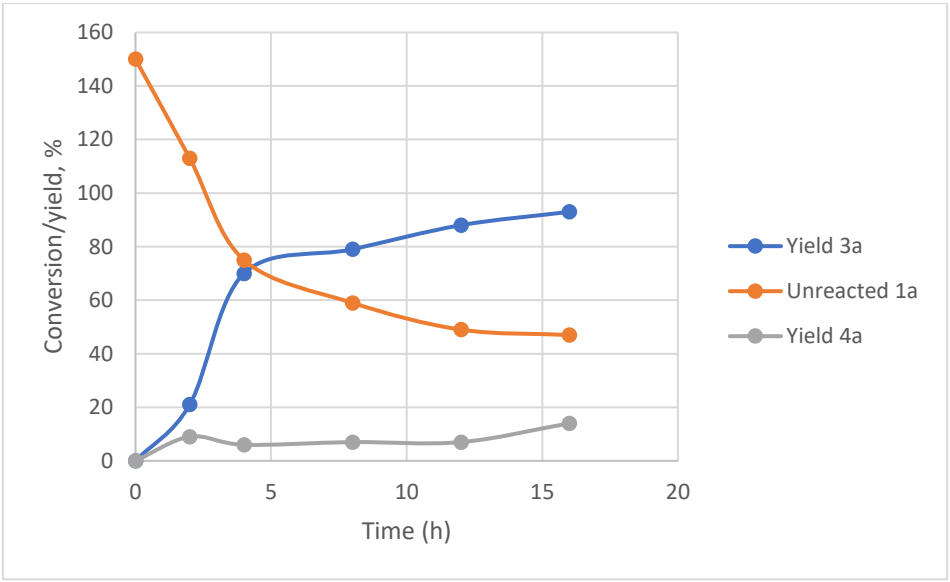

H
N
O
S
tBu
Ph
CH3(D-4%)
D(21)
7.33
7.32
7.29
7.28
7.27
7.26
7.24
7.23
4.55
4.54
4.53
4.52
4.51
4.50
4.49
3.40
1.49
1.48
1.21
0.79
1.05
5.22
0.79
1.05
2.89
9.00
f1 (ppm)


H
N
O
S
tBu
Ph
CH3(D-4%)
D(21)
4.53
1.51
0.21
0.01
f1 (ppm)

Reaction Kinetics



1a 1.5 eq. **2** 1 eq. **3a** **4a**



Computational details

The geometries of the minima and transition states (TS) for the reaction mechanism of the asymmetric amination of secondary alcohols catalyzed by a Mn(I)-NNP complex have been studied through the use of Density Functional Theory (DFT) *via* the spin-restricted Kohn-Sham (RKS) formalism and the PBE0 functional,[2] using the SVP basis set for non-metal atoms and the TZVP basis set for Mn.[3] In all cases, the EDIIS/CDIIS procedure[4] was applied for the self-consistent field (SCF) convergence. The Synchronous Transit-Guided Quasi-Newton (STQN)[5] method (QST3) has been used to locate TSs. In all cases, frequency calculations were performed to confirm the nature of the stationary points (minima or first-order TSs with one imaginary frequency). Both optimization and frequency calculations were performed using an ultrafine grid. Empirical dispersion effects have been included through the D3 Grimme's protocol, using the Becke–Johnson dumping function.[6] To simulate the solvent effects, the Polarizable Continuum Model (PCM)[7] has been used applying the standard parameters for toluene (ε = 2.3741). With the aim to obtain more accurate energy values, single point calculations using the M06 functional[8] and the TZVP basis set for all atoms were employed over the previously optimized structures at the PBE0/SVP(H,C,N,O,P,S)/TZVP(Mn) computational level. All calculations were carried out through the facilities provided by the Gaussian09 package (revision D.01).[9]

XYZ Coordinates

	A		
Mn	-1.053346	-0.278291	-0.157087
P	1.085522	-0.034102	0.483870
O	-0.701311	1.027000	-2.752141
O	-0.792052	-2.910734	-1.408629
N	-1.390713	0.348738	1.573677
N	-3.063868	-0.212564	-0.240503
C	0.898748	0.040608	2.316216
C	-0.437709	0.705545	2.603132
C	-2.736394	0.660984	1.952273
C	-3.669147	0.275988	0.855181
C	-5.057246	0.402831	0.934009
C	-5.836552	0.013453	-0.146878
C	-5.201383	-0.494772	-1.282205
C	-3.819367	-0.589628	-1.286296
C	2.434986	-1.261350	0.268942
C	3.776730	-0.891168	0.109422
C	4.768854	-1.865344	0.003296
C	4.434008	-3.217813	0.060043
C	3.100786	-3.594347	0.223341
C	2.106701	-2.623029	0.323337
C	1.880933	1.540631	-0.014465
C	2.149063	2.579088	0.884917
C	2.718153	3.773018	0.438931
C	3.032331	3.940101	-0.908084
C	2.769855	2.909459	-1.812371
C	2.192247	1.722627	-1.370892
C	-0.822716	0.490662	-1.729934
C	-0.883663	-1.854305	-0.933756
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H	1.754605	0.507336	2.826499
H	-0.800651	0.390411	3.602845
H	-0.315713	1.808073	2.663677
H	-2.872249	1.743854	2.168941
H	-3.042394	0.140311	2.886340
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H	-5.768113	-0.815314	-2.157780
H	-3.277249	-0.978977	-2.150271
H	4.050506	0.165542	0.065647
H	5.811434	-1.563127	-0.124150
H	5.212652	-3.979845	-0.026168
H	2.829290	-4.652067	0.264068
H	1.064521	-2.929131	0.437214
H	1.916374	2.467925	1.945659
H	2.918762	4.575627	1.153066
H	3.479963	4.874436	-1.255720
H	3.009723	3.033042	-2.871217
H	1.981366	0.927388	-2.090401
	B(R)		
Mn	0.213657	-1.179375	-0.315705
P	-1.512122	0.062034	0.418374
O	-1.553673	-3.373219	-1.124792
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O	1.425087	0.245699	0.513218
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N	1.850517	-2.376176	-0.390426
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C	-0.747568	-1.474432	2.555911
C	1.061306	-2.987923	1.803831
C	2.097138	-3.095601	0.720419
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C	4.122007	-3.975916	-0.226170
C	3.853668	-3.239230	-1.377247
C	2.708582	-2.453171	-1.415033
C	-1.684066	1.859794	0.130538
C	-2.780391	2.577213	0.630397
C	-2.876954	3.948599	0.408860
C	-1.883799	4.611419	-0.317393
C	-0.797793	3.900369	-0.823582
C	-0.698643	2.527002	-0.601106
C	-3.206564	-0.536912	0.057436

C	-4.078488	-1.060069	1.017378
C	-5.337252	-1.536202	0.644552
C	-5.736717	-1.491506	-0.688977
C	-4.870343	-0.974195	-1.654465
C	-3.613082	-0.507130	-1.285072
C	-0.860496	-2.502026	-0.800300
C	0.224417	-0.539404	-1.968229
C	2.569886	0.771103	-0.042873
C	2.583456	2.293903	0.034479
C	2.098670	2.933202	1.180835
C	3.081799	3.080895	-1.007215
C	2.121461	4.321072	1.289459
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H	-1.501620	-2.254269	2.353237
H	0.311858	-3.786695	1.655576
H	1.519710	-3.154497	2.796092
H	3.401937	-4.456241	1.761317
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H	4.522584	-3.261956	-2.238934
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H	-3.568437	2.058771	1.184605
H	-3.733146	4.504000	0.800309
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H	-0.009249	4.411500	-1.380734
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H	-5.174373	-0.941296	-2.703534
H	-2.932996	-0.115296	-2.047625
H	1.085931	-0.920953	1.758411
H	2.660980	0.510714	-1.122106
H	1.675179	2.315826	1.976676
H	3.449594	2.595001	-1.916795
H	1.731741	4.804178	2.189724
H	3.487694	5.073776	-1.736610
H	2.634638	6.189126	0.323611
H	3.879036	-0.862228	0.566181
H	4.750686	0.661778	0.229158
H	3.791316	0.492653	1.724333
	B(S)		
Mn	0.035914	-0.613457	-0.464284
P	-1.887714	0.156429	0.448197
O	-1.032775	-3.326120	-0.757068
O	-0.686620	0.080956	-3.221258
O	0.873136	1.222721	-0.065785
N	0.650030	-0.773545	1.517259
N	1.914022	-1.352628	-0.716699
C	-1.394084	0.299030	2.229948
C	-0.383545	-0.793488	2.544398
C	1.713737	-1.745682	1.657002
C	2.532818	-1.780765	0.398623
C	3.833708	-2.278250	0.373716
C	4.504430	-2.362928	-0.840697
C	3.850195	-1.942832	-1.995963
C	2.560845	-1.438972	-1.886340
C	-2.625488	1.796378	0.094854
C	-4.005390	2.032986	0.075636
C	-4.488880	3.313238	-0.195568
C	-3.602140	4.360334	-0.447237
C	-2.226242	4.125136	-0.430559
C	-1.735709	2.848408	-0.164947
C	-3.341426	-0.955684	0.398660
C	-4.028082	-1.403763	1.531824
C	-5.127308	-2.254341	1.402456
C	-5.556851	-2.656834	0.139527
C	-4.878742	-2.212911	-0.997070
C	-3.774439	-1.375843	-0.867895
C	-0.632414	-2.244840	-0.631288
C	-0.386349	-0.203352	-2.138638

C	1.982646	1.707892	-0.723401
C	3.271266	1.458873	0.057900
C	3.272916	1.535646	1.456249
C	4.476458	1.169251	-0.588603
C	4.436087	1.303596	2.188604
C	5.644748	0.935795	0.137175
C	5.628206	0.994667	1.530589
C	1.840331	3.208384	-1.004559
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H	-2.243637	0.304903	2.927505
H	0.047227	-0.644468	3.552792
H	-0.865626	-1.786133	2.538212
H	1.261850	-2.743590	1.802898
H	2.361575	-1.551457	2.531546
H	4.309605	-2.589302	1.305279
H	5.525964	-2.746833	-0.884359
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H	2.014338	-1.088207	-2.763484
H	-4.706899	1.217175	0.266952
H	-5.567109	3.492071	-0.211985
H	-3.985686	5.361347	-0.661422
H	-1.527116	4.940797	-0.634421
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H	-3.714361	-1.093008	2.530588
H	-5.651399	-2.601051	2.296620
H	-6.418579	-3.321361	0.039400
H	-5.206030	-2.528965	-1.990482
H	-3.235535	-1.045486	-1.760678
H	1.038577	0.181907	1.398842
H	2.124150	1.215069	-1.711604
H	2.339277	1.786985	1.967323
H	4.494310	1.107751	-1.681021
H	4.415384	1.368448	3.280236
H	6.573168	0.696628	-0.388825
H	6.541134	0.806752	2.101643
H	0.964276	3.386169	-1.646920
H	1.693392	3.752094	-0.057363
H	2.731606	3.619204	-1.504543
	B-C(R)		
Mn	1.043732	0.698482	0.388540
P	-1.073825	0.671066	-0.317085
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O	0.521493	0.435055	3.251430
O	2.230614	-2.185490	-1.206482
N	1.487791	0.378866	-1.618830
N	3.055672	0.526178	0.456901
C	-0.880592	0.173054	-2.086940
C	0.441973	0.746957	-2.570451
C	2.794060	0.959521	-1.884581
C	3.689030	0.641357	-0.725955
C	5.071181	0.519921	-0.841185
C	5.830832	0.292211	0.301401
C	5.174266	0.190295	1.526189
C	3.791179	0.309845	1.557146
C	-2.412225	-0.404276	0.332618
C	-3.441700	-0.876215	-0.490785
C	-4.495478	-1.611664	0.047735
C	-4.540780	-1.871436	1.417366
C	-3.519375	-1.405154	2.243674
C	-2.456073	-0.682374	1.704216
C	-1.976656	2.276820	-0.360882
C	-2.408790	2.905896	-1.532560
C	-3.058039	4.140785	-1.475565
C	-3.286726	4.757315	-0.247691
C	-2.854963	4.138230	0.926898
C	-2.198545	2.912863	0.869150
C	1.091618	2.481849	0.402732
C	0.726153	0.576224	2.113575
C	1.579597	-2.476150	-0.185534
C	0.204889	-3.073732	-0.357735
C	-0.643870	-3.374590	0.714424
C	-0.205749	-3.400419	-1.655982
C	-1.873334	-3.986646	0.491757
C	-1.441068	-4.004606	-1.881639
C	-2.277979	-4.300641	-0.806281

C	2.320810	-2.795042	1.093370
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H	-1.717480	0.464630	-2.737154
H	0.679450	0.380715	-3.586855
H	0.390088	1.847753	-2.620165
H	2.685249	2.057098	-1.954366
H	3.236532	0.605861	-2.833185
H	5.538287	0.603944	-1.824249
H	6.916673	0.193452	0.237528
H	5.720565	0.013679	2.454163
H	3.238832	0.226329	2.494468
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H	-5.371849	-2.441916	1.839781
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H	-1.653198	-0.336414	2.357428
H	-2.243647	2.442987	-2.507910
H	-3.387087	4.621418	-2.400470
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H	1.626402	-0.653208	-1.641520
H	-0.354147	-3.105892	1.732028
H	0.477891	-3.182046	-2.479444
H	-2.531617	-4.201314	1.336079
H	-1.747887	-4.254493	-2.900754
H	-3.248483	-4.773007	-0.977355
H	3.243967	-2.205412	1.127465
H	1.733236	-2.610598	2.000611
H	2.592913	-3.864170	1.063696
	B-C(S)		
Mn	0.170840	-0.799535	-0.302352
P	-1.811277	-0.038052	0.383048
O	-0.835904	-3.468674	-1.025861
O	0.070488	0.235571	-3.033343
O	1.492404	1.352815	2.246934
N	0.500088	-1.139219	1.722893
N	2.104741	-1.390173	-0.310286
C	-1.639905	-0.148704	2.226592
C	-0.713186	-1.316338	2.518079
C	1.474638	-2.210311	1.850862
C	2.527053	-2.023394	0.800954
C	3.826895	-2.503855	0.932557
C	4.719006	-2.343709	-0.122748
C	4.279177	-1.688194	-1.269323
C	2.972142	-1.222137	-1.317959
C	-2.385857	1.684093	0.096023
C	-3.056046	2.421613	1.080286
C	-3.478645	3.725153	0.822417
C	-3.248046	4.301807	-0.426339
C	-2.595144	3.567875	-1.416575
C	-2.162891	2.268468	-1.156678
C	-3.365334	-0.940095	-0.029001
C	-4.455009	-1.037506	0.845369
C	-5.621459	-1.692297	0.453258
C	-5.718553	-2.246111	-0.823484
C	-4.643579	-2.143166	-1.705517
C	-3.473032	-1.498857	-1.308842
C	-0.434718	-2.427089	-0.707415
C	0.092569	-0.207634	-1.956463
C	1.571545	1.870607	1.119862
C	2.847670	1.731689	0.333447
C	2.970222	2.138967	-1.001741
C	3.974329	1.231538	0.994469
C	4.199220	2.066939	-1.651793
C	5.205033	1.159660	0.345069
C	5.323236	1.585178	-0.977475
C	0.682722	3.045174	0.786252
H	-1.145654	0.784796	2.542327
H	-2.590189	-0.236681	2.770879
H	-0.480236	-1.367017	3.598214
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H	0.962155	-3.171771	1.667222
H	1.925518	-2.263799	2.858427

H	4.125571	-3.001445	1.857311
H	5.743329	-2.715176	-0.047191
H	4.940258	-1.521710	-2.120760
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H	-3.991222	4.293156	1.602894
H	-3.578070	5.324000	-0.627586
H	-2.411649	4.012525	-2.397900
H	-1.633991	1.710841	-1.931977
H	-4.408037	-0.594954	1.843386
H	-6.461539	-1.766277	1.148566
H	-6.633840	-2.758257	-1.130638
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H	0.656656	0.750345	-0.002751
H	0.951383	-0.251998	2.027085
H	2.091704	2.490710	-1.546562
H	3.861291	0.914716	2.033295
H	4.280305	2.385273	-2.694223
H	6.078140	0.771213	0.875680
H	6.288541	1.533798	-1.487659
H	1.181933	3.948137	1.178555
H	0.511570	3.184996	-0.286958
H	-0.284468	2.936374	1.289951
	C		
Mn	1.041878	0.152652	-0.254510
P	-1.039498	0.099182	0.477680
O	0.866593	-2.649167	-1.170823
O	0.364505	1.247406	-2.878531
N	1.545333	-0.192614	1.770856
N	3.056193	0.309674	-0.307943
C	-0.814666	-0.094877	2.313743
C	0.487350	-0.846151	2.541410
C	2.831027	-0.874427	1.763966
C	3.713306	-0.209534	0.748928
C	5.099072	-0.154724	0.864335
C	5.842570	0.439017	-0.152284
C	5.161725	0.968192	-1.246252
C	3.775097	0.887096	-1.281146
C	-2.216212	1.506790	0.355632
C	-3.566783	1.357561	0.702120
C	-4.435182	2.444495	0.631396
C	-3.965400	3.688383	0.204874
C	-2.625565	3.840643	-0.149071
C	-1.752721	2.754649	-0.073706
C	-2.116669	-1.299694	-0.032060
C	-2.480084	-2.361498	0.801809
C	-3.236324	-3.425753	0.305640
C	-3.637791	-3.438635	-1.027855
C	-3.273685	-2.385317	-1.869659
C	-2.513466	-1.329190	-1.377640
C	0.982764	-1.564955	-0.769618
C	0.649094	0.781360	-1.851528
H	-0.738085	0.930121	2.711795
H	-1.667944	-0.571795	2.817700
H	0.739246	-0.893166	3.617700
H	0.404690	-1.882433	2.174059
H	2.651872	-1.916977	1.445493
H	3.316062	-0.905754	2.756509
H	5.583898	-0.579259	1.745859
H	6.931610	0.491451	-0.088974
H	5.692840	1.447906	-2.070209
H	3.204655	1.298938	-2.115183
H	-3.944733	0.381117	1.018342
H	-5.486265	2.319272	0.903978
H	-4.649199	4.538934	0.142709
H	-2.255692	4.810351	-0.491842
H	-0.698004	2.855770	-0.343718
H	-2.175747	-2.375366	1.850959
H	-3.511603	-4.249341	0.969434
H	-4.229586	-4.271676	-1.415171
H	-3.577850	-2.391474	-2.919273
H	-2.217241	-0.515333	-2.046566
H	0.994893	1.712910	0.146246
H	1.673510	0.755836	2.123949

C-D(R)

Mn	-0.486491	1.592476	0.381181
S	3.470135	-0.724221	-0.993469
P	-1.625259	0.022049	-0.718480
O	-2.385542	3.748059	-0.246571
O	-1.762668	1.140351	2.974252
O	2.984569	0.498661	-1.776281
N	0.596320	1.741458	-1.396064
N	0.957575	2.891115	0.929785
N	2.193690	-1.378066	-0.124149
C	-0.729573	-0.032635	-2.335300
C	-0.164280	1.355460	-2.582644
C	1.174561	3.074872	-1.451941
C	1.661140	3.438060	-0.082106
C	2.728656	4.302990	0.144492
C	3.064565	4.642781	1.451525
C	2.313002	4.101834	2.492477
C	1.275176	3.231182	2.186926
C	-1.750281	-1.728819	-0.185243
C	-1.469344	-2.808317	-1.030021
C	-1.701206	-4.116569	-0.603383
C	-2.224996	-4.356711	0.664960
C	-2.495209	-3.284931	1.516363
C	-2.251269	-1.980017	1.099216
C	-3.398928	0.288590	-1.154651
C	-3.982773	-0.276557	-2.296072
C	-5.338059	-0.095362	-2.563286
C	-6.132740	0.640507	-1.683061
C	-5.565265	1.190866	-0.535199
C	-4.206115	1.018699	-0.274506
C	-1.626069	2.897510	-0.029773
C	-1.249580	1.329235	1.945936
C	1.899342	-0.805074	1.027572
C	3.621478	-2.069949	-2.264622
C	4.035746	-3.337082	-1.530628
C	2.299870	-2.225882	-2.993356
C	4.719791	-1.574967	-3.200702
C	1.149195	-1.671311	1.995403
C	0.593423	-1.162064	3.175824
C	1.090056	-3.052098	1.770499
C	0.009918	-2.009276	4.112767
C	0.515725	-3.902517	2.711088
C	-0.022047	-3.386149	3.888938
C	2.767960	0.274833	1.629294
H	0.105684	-0.734229	-2.189499
H	-1.336252	-0.389239	-3.179117
H	0.479486	1.357114	-3.481734
H	-0.972849	2.088321	-2.744009
H	0.387079	3.794374	-1.741182
H	1.990500	3.146078	-2.191593
H	3.285753	4.701238	-0.705541
H	3.897769	5.319236	1.654217
H	2.527275	4.340471	3.535536
H	0.668178	2.778540	2.973036
H	-1.072854	-2.640968	-2.033846
H	-1.476197	-4.951374	-1.272208
H	-2.412822	-5.381179	0.996064
H	-2.885403	-3.466011	2.520268
H	-2.451791	-1.148730	1.779617
H	-3.382867	-0.878596	-2.983508
H	-5.778053	-0.537225	-3.460978
H	-7.196303	0.781117	-1.891685
H	-6.181163	1.764284	0.161937
H	-3.766366	1.456065	0.624381
H	0.538314	0.303271	0.764566
H	1.411522	1.097215	-1.360483
H	4.956261	-3.181182	-0.945315
H	3.243017	-3.674956	-0.848742
H	4.233350	-4.137325	-2.261888
H	1.996300	-1.267842	-3.440823
H	2.406619	-2.966933	-3.801730
H	1.515260	-2.565934	-2.302838
H	4.878331	-2.309919	-4.005265
H	4.439472	-0.612919	-3.653823
H	5.675183	-1.443290	-2.667945

H	0.592397	-0.087006	3.356374
H	1.513772	-3.442123	0.844485
H	-0.427726	-1.588186	5.021156
H	0.483029	-4.977607	2.518261
H	-0.474887	-4.052979	4.627261
H	3.713157	-0.193736	1.954186
H	2.999227	1.057923	0.895791
H	2.302417	0.744239	2.500862
	C-D(R)'		
Mn	-0.445983	-1.432418	-0.025722
S	1.355712	2.216620	-1.105564
P	-2.085150	0.037475	-0.352987
O	-2.033924	-3.772580	-0.825925
O	-0.952406	-1.789138	2.829786
O	2.142399	1.209469	-1.954651
N	0.158347	-0.872740	-1.964466
N	1.274250	-2.478984	-0.207483
N	1.422494	2.091429	0.505889
C	-1.738895	0.659091	-2.068213
C	-0.960649	-0.425431	-2.796982
C	0.891200	-1.998964	-2.525941
C	1.751654	-2.605826	-1.460863
C	2.914933	-3.315567	-1.742133
C	3.592661	-3.945673	-0.703117
C	3.084019	-3.830668	0.586944
C	1.932028	-3.082402	0.790878
C	-2.256616	1.525846	0.712310
C	-1.847691	2.811367	0.347704
C	-1.967472	3.872653	1.246351
C	-2.494357	3.662075	2.518338
C	-2.904619	2.380347	2.891491
C	-2.785778	1.322005	1.996125
C	-3.855215	-0.477536	-0.392376
C	-4.828313	0.301255	-1.034624
C	-6.168018	-0.077334	-1.010721
C	-6.556333	-1.232883	-0.329592
C	-5.599531	-2.002213	0.328800
C	-4.255565	-1.627539	0.296117
C	-1.409309	-2.831850	-0.554043
C	-0.766341	-1.684743	1.685537
C	1.478795	1.069243	1.336137
C	2.643342	0.122908	1.423561
C	2.892250	-0.564063	2.624131
C	3.585402	0.000120	0.390257
C	4.057842	-1.307538	2.802300
C	4.736108	-0.763518	0.561661
C	4.991210	-1.406357	1.773599
C	0.744392	1.332571	2.633135
C	2.290577	3.822670	-1.299189
C	3.701864	3.614303	-0.776132
C	2.280587	4.088844	-2.799686
C	1.538542	4.900061	-0.531249
H	-1.109364	1.555382	-1.975440
H	-2.649895	0.937591	-2.616057
H	-0.604483	-0.051663	-3.774997
H	-1.608560	-1.296583	-2.990426
H	0.161812	-2.762883	-2.850787
H	1.491535	-1.717059	-3.408961
H	3.272838	-3.375092	-2.771774
H	4.505272	-4.513514	-0.897269
H	3.577751	-4.298629	1.439271
H	1.511195	-2.956350	1.788320
H	-1.412299	2.999118	-0.634649
H	-1.635329	4.870169	0.947866
H	-2.582890	4.493997	3.221330
H	-3.314824	2.202783	3.888616
H	-3.101541	0.320706	2.301812
H	-4.544050	1.224609	-1.547003
H	-6.915401	0.536677	-1.519638
H	-7.608116	-1.529176	-0.309139
H	-5.896300	-2.903862	0.870122
H	-3.509940	-2.234467	0.812956
H	0.410947	-0.128645	0.638298
H	0.845431	-0.100835	-1.895370
H	2.176292	-0.514686	3.444573

H	3.401885	0.501569	-0.562178
H	4.231692	-1.814452	3.755038
H	5.449195	-0.846707	-0.262702
H	5.907415	-1.986281	1.911285
H	0.339263	0.416847	3.080424
H	-0.080009	2.026282	2.440433
H	1.435231	1.794466	3.357397
H	3.690846	3.372296	0.296606
H	4.201546	2.796924	-1.316773
H	4.289342	4.535004	-0.922960
H	1.253914	4.214275	-3.179905
H	2.835739	5.016065	-3.010789
H	2.755791	3.261608	-3.345790
H	2.031155	5.872561	-0.693474
H	0.497510	4.989469	-0.881047
H	1.524420	4.683433	0.545329
	C-D(S)		
Mn	0.449208	-1.444776	0.051391
S	-2.522604	2.184367	-0.920069
P	2.063604	0.071638	-0.231240
O	2.090451	-3.715898	-0.843129
O	0.966866	-1.904018	2.890838
O	-1.973084	1.334542	-2.076473
N	-0.196991	-0.793016	-1.829594
N	-1.233231	-2.532834	-0.170043
N	-1.455559	2.067463	0.362280
C	1.525597	0.886097	-1.797300
C	0.859166	-0.187571	-2.641257
C	-0.882314	-1.909260	-2.462841
C	-1.696727	-2.632638	-1.431062
C	-2.814496	-3.400206	-1.747217
C	-3.463574	-4.103452	-0.736854
C	-2.983381	-3.992093	0.565272
C	-1.875278	-3.190356	0.805044
C	2.384321	1.439803	0.947803
C	2.264914	2.791647	0.611093
C	2.493641	3.780906	1.568523
C	2.854740	3.429360	2.867726
C	2.991319	2.081839	3.207177
C	2.755314	1.094089	2.255238
C	3.806643	-0.458562	-0.518476
C	4.680374	0.241291	-1.360496
C	6.005160	-0.166865	-1.504256
C	6.478998	-1.271072	-0.795001
C	5.621416	-1.964609	0.057581
C	4.292750	-1.563845	0.190761
C	1.448476	-2.801406	-0.528058
C	0.773631	-1.757493	1.751870
C	-1.549110	1.072709	1.228906
C	-2.737296	0.160901	1.357721
C	-3.222649	-0.160771	2.635104
C	-3.441161	-0.336393	0.247460
C	-4.387424	-0.909619	2.797923
C	-4.610212	-1.072668	0.409948
C	-5.095113	-1.358482	1.685533
C	-0.741177	1.312989	2.479539
C	-2.139116	3.933551	-1.407765
C	-2.547875	4.815110	-0.236216
C	-0.664894	4.061299	-1.740497
C	-3.012854	4.175996	-2.634650
H	0.757038	1.618743	-1.504587
H	2.320899	1.414417	-2.341311
H	0.441596	0.252074	-3.565322
H	1.580434	-0.970727	-2.930581
H	-0.122483	-2.609388	-2.854592
H	-1.513309	-1.594187	-3.313106
H	-3.160827	-3.444826	-2.781661
H	-4.337965	-4.718529	-0.960877
H	-3.464671	-4.507342	1.397619
H	-1.477079	-3.062467	1.812501
H	1.983066	3.086707	-0.400659
H	2.385415	4.833302	1.294085
H	3.030213	4.204773	3.617491
H	3.272765	1.797592	4.224094
H	2.837460	0.041750	2.539121

H	4.335573	1.122432	-1.907045
H	6.673338	0.385036	-2.170314
H	7.518421	-1.589686	-0.906783
H	5.984373	-2.829732	0.617884
H	3.621794	-2.119051	0.850307
H	-0.469316	-0.190443	0.676934
H	-0.894775	-0.036091	-1.695342
H	-2.698921	0.191063	3.524128
H	-3.060526	-0.178083	-0.762261
H	-4.744866	-1.135249	3.805771
H	-5.134617	-1.443058	-0.473757
H	-6.011697	-1.940211	1.811158
H	-0.479482	0.387525	3.005840
H	0.172961	1.852463	2.216410
H	-1.329478	1.959655	3.152453
H	-3.606369	4.664645	0.030950
H	-1.930192	4.599043	0.647253
H	-2.416061	5.874543	-0.509051
H	-0.389185	3.354610	-2.536862
H	-0.451618	5.083429	-2.092429
H	-0.054527	3.857533	-0.850504
H	-2.852207	5.200320	-3.005684
H	-2.759239	3.468399	-3.437551
H	-4.082766	4.064326	-2.396852
	C-D(S)'		
Mn	-0.514928	-1.517529	0.011823
S	1.328070	1.765852	-1.505701
P	-1.867183	0.241483	-0.250417
O	-2.787198	-3.377602	-0.013939
O	-0.394629	-1.417250	2.934391
O	1.573174	0.799278	-2.673896
N	-0.259186	-1.313627	-2.111348
N	0.829834	-3.004037	-0.343233
N	2.215255	1.520325	-0.151715
C	-1.918795	0.481012	-2.098693
C	-1.462169	-0.802626	-2.774313
C	0.183855	-2.601125	-2.626979
C	1.082160	-3.282493	-1.637341
C	2.069047	-4.189549	-2.016443
C	2.795010	-4.857331	-1.034927
C	2.499780	-4.598362	0.301986
C	1.514246	-3.666366	0.601309
C	-1.532305	1.919743	0.406305
C	-2.205888	3.040683	-0.098557
C	-1.964184	4.304331	0.433649
C	-1.065005	4.454868	1.492809
C	-0.401906	3.341589	2.004233
C	-0.623062	2.077820	1.454637
C	-3.632057	0.050158	0.234405
C	-4.546490	-0.609824	-0.595605
C	-5.858113	-0.826177	-0.175435
C	-6.270390	-0.395634	1.084879
C	-5.362707	0.251336	1.923728
C	-4.053160	0.472917	1.502481
C	-1.897067	-2.633167	-0.045643
C	-0.465338	-1.482376	1.777928
C	2.502066	0.311402	0.288563
C	2.769664	0.224048	1.759626
C	3.173746	-0.969295	2.372884
C	2.600687	1.360989	2.562413
C	3.374610	-1.031064	3.750283
C	2.809582	1.303407	3.936526
C	3.190819	0.103467	4.539074
C	3.168638	-0.716992	-0.594849
C	2.100436	3.363146	-2.068507
C	1.933267	4.385824	-0.954637
C	3.555552	3.084076	-2.404466
C	1.299380	3.749847	-3.307336
H	-1.211997	1.293441	-2.321502
H	-2.912729	0.793373	-2.450496
H	-1.276412	-0.622373	-3.849528
H	-2.241129	-1.579549	-2.699328
H	-0.706616	-3.243843	-2.753582
H	0.671371	-2.522549	-3.614711
H	2.258480	-4.365276	-3.077129

H	3.575116	-5.570947	-1.308750
H	3.029149	-5.102587	1.112155
H	1.263568	-3.418334	1.633949
H	-2.931241	2.926009	-0.909049
H	-2.487430	5.175008	0.030213
H	-0.882695	5.444968	1.918295
H	0.301958	3.454758	2.832207
H	-0.081456	1.208015	1.833473
H	-4.239543	-0.971058	-1.580268
H	-6.560205	-1.339876	-0.836913
H	-7.297937	-0.567193	1.414887
H	-5.676068	0.589175	2.914766
H	-3.351158	0.985395	2.165675
H	0.923110	-0.469269	0.280675
H	0.491343	-0.614349	-2.271377
H	3.322728	-1.868714	1.774621
H	2.300552	2.288637	2.072925
H	3.676554	-1.975096	4.210837
H	2.672552	2.201512	4.544644
H	3.346547	0.053805	5.619611
H	4.246465	-0.478975	-0.603733
H	2.801166	-0.639177	-1.623148
H	3.052025	-1.741449	-0.230282
H	0.879116	4.479318	-0.648976
H	2.522023	4.107729	-0.070355
H	2.274684	5.370800	-1.312760
H	3.628723	2.267732	-3.138557
H	4.019626	3.986210	-2.834663
H	4.114844	2.797598	-1.501734
H	1.706226	4.680442	-3.732631
H	1.354994	2.960816	-4.071103
H	0.239946	3.924499	-3.058765
	D(R)		
Mn	0.525560	1.214780	-0.325534
S	-2.223779	0.124410	1.759894
P	1.906172	-0.424226	0.424397
O	2.794945	2.778317	-1.290574
O	0.323374	0.102047	-3.032503
O	-1.105295	0.466892	2.768721
N	0.713474	1.929926	1.630108
N	-0.554125	2.959411	-0.470495
N	-1.545448	0.243836	0.263097
C	2.012091	-0.021218	2.218727
C	1.915752	1.493417	2.336996
C	0.479022	3.358885	1.671334
C	-0.506327	3.757062	0.612687
C	-1.254031	4.930636	0.693004
C	-2.026651	5.321503	-0.395668
C	-2.010981	4.531679	-1.542269
C	-1.262032	3.362172	-1.533703
C	1.660960	-2.236879	0.319419
C	1.914020	-3.097065	1.393415
C	1.744110	-4.472936	1.247836
C	1.332643	-5.004153	0.025853
C	1.096669	-4.153859	-1.054310
C	1.257658	-2.777423	-0.908227
C	3.635187	-0.331982	-0.207494
C	4.758874	-0.261748	0.622236
C	6.041634	-0.211494	0.074839
C	6.216599	-0.240677	-1.307033
C	5.101278	-0.312434	-2.142609
C	3.821164	-0.350701	-1.597401
C	1.924316	2.128417	-0.891113
C	0.352756	0.544759	-1.960017
C	-2.549944	0.487303	-0.784194
C	-3.025778	-0.788286	-1.476244
C	-4.320856	-0.955663	-1.978679
C	-2.116722	-1.840789	-1.642796
C	-4.697994	-2.142970	-2.611480
C	-2.484969	-3.023787	-2.274632
C	-3.784208	-3.183729	-2.761158
C	-3.698544	1.430100	-0.412520
C	-2.538915	-1.678507	2.253161
C	-3.760548	-2.171378	1.492401
C	-1.306716	-2.504633	1.973853

C	-2.846413	-1.603047	3.745243
H	1.110262	-0.460913	2.674333
H	2.899529	-0.424508	2.725536
H	1.878205	1.788632	3.402002
H	2.799579	1.982192	1.889489
H	1.424271	3.887484	1.444589
H	0.149487	3.707237	2.666773
H	-1.212745	5.533224	1.602284
H	-2.620568	6.237301	-0.354750
H	-2.575439	4.805432	-2.434797
H	-1.223288	2.715636	-2.411895
H	2.234597	-2.699501	2.358866
H	1.933068	-5.134213	2.097109
H	1.197825	-6.082786	-0.085408
H	0.781472	-4.562439	-2.017607
H	1.062268	-2.120011	-1.758709
H	4.649430	-0.244673	1.708410
H	6.909217	-0.151086	0.736746
H	7.221614	-0.202756	-1.734340
H	5.227518	-0.328770	-3.227837
H	2.955585	-0.383480	-2.264483
H	-1.993552	1.009982	-1.577043
H	-0.094901	1.432743	2.098290
H	-5.063011	-0.163304	-1.865811
H	-1.118733	-1.720181	-1.222397
H	-5.720203	-2.254733	-2.983286
H	-1.755583	-3.832104	-2.375223
H	-4.082311	-4.114636	-3.250270
H	-3.303736	2.301959	0.128592
H	-4.205685	1.797222	-1.317604
H	-4.452511	0.951620	0.229480
H	-4.611125	-1.479066	1.606337
H	-3.560307	-2.299164	0.421845
H	-4.072238	-3.149472	1.894768
H	-0.448666	-2.119480	2.541415
H	-1.466497	-3.554514	2.270981
H	-1.049251	-2.485944	0.906488
H	-3.115128	-2.606461	4.115949
H	-1.979672	-1.232971	4.308632
H	-3.700004	-0.933872	3.945783
	D(R)'		
Mn	-0.236605	-1.159736	0.195897
S	0.572596	1.613553	-0.947246
P	-2.139274	-0.116236	-0.404824
O	-1.637573	-3.733227	0.206785
O	-0.768206	-0.941133	3.067853
O	1.414024	1.121354	-2.169435
N	0.093446	-1.228487	-1.899598
N	1.554541	-2.140555	0.148596
N	0.863247	0.733294	0.388612
C	-2.043578	-0.088896	-2.254016
C	-1.139901	-1.235616	-2.688377
C	0.966741	-2.357113	-2.176686
C	1.969521	-2.520140	-1.074843
C	3.218279	-3.098824	-1.281507
C	4.051844	-3.326763	-0.191225
C	3.593397	-2.990436	1.077772
C	2.340998	-2.402437	1.198553
C	-2.600075	1.579024	0.111810
C	-3.331815	2.441902	-0.712946
C	-3.720388	3.697045	-0.247150
C	-3.400228	4.092719	1.052691
C	-2.674757	3.235675	1.879135
C	-2.264624	1.989404	1.407705
C	-3.687168	-1.026989	-0.007142
C	-4.390810	-1.787690	-0.946474
C	-5.510775	-2.527540	-0.563802
C	-5.938568	-2.518478	0.761604
C	-5.236336	-1.770072	1.707811
C	-4.117224	-1.035124	1.327779
C	-1.091641	-2.712043	0.174387
C	-0.534957	-1.042078	1.935065
C	1.931123	0.793033	1.381597
C	1.100674	3.422643	-0.909942
C	0.304708	4.156774	0.156874

C	2.607090	3.563021	-0.786766
C	0.647478	3.908825	-2.289648
C	3.375921	0.546119	0.952695
C	4.360032	0.407865	1.946819
C	3.762712	0.368055	-0.378159
C	5.681358	0.110432	1.624588
C	5.088150	0.070724	-0.703063
C	6.054942	-0.060335	0.290510
C	1.807583	1.973251	2.354722
H	-1.580031	0.873146	-2.517914
H	-3.026767	-0.136715	-2.743997
H	-0.920053	-1.156760	-3.769270
H	-1.645658	-2.203398	-2.529439
H	0.357168	-3.279177	-2.205422
H	1.469988	-2.273609	-3.156282
H	3.527882	-3.361611	-2.294686
H	5.042780	-3.764028	-0.330309
H	4.199038	-3.158148	1.969008
H	1.947841	-2.121502	2.176855
H	-3.606246	2.137778	-1.726238
H	-4.284756	4.367084	-0.900554
H	-3.711866	5.074247	1.418180
H	-2.409601	3.544621	2.893226
H	-1.666907	1.334517	2.044350
H	-4.071493	-1.819823	-1.990359
H	-6.049177	-3.116710	-1.310394
H	-6.815385	-3.098224	1.060136
H	-5.559728	-1.761773	2.751601
H	-3.569756	-0.462783	2.081468
H	1.702424	-0.076667	2.017973
H	0.633701	-0.357664	-2.135845
H	-0.775279	4.026911	-0.004272
H	0.535215	3.822059	1.173103
H	0.527240	5.234871	0.095741
H	3.103967	2.950684	-1.552684
H	2.891642	4.616816	-0.944052
H	2.987916	3.251330	0.193494
H	0.847741	4.989649	-2.371160
H	1.183657	3.380948	-3.088742
H	-0.434909	3.754896	-2.430573
H	4.087832	0.516440	3.000343
H	3.016334	0.476573	-1.171163
H	6.423317	0.007120	2.421229
H	5.361977	-0.061136	-1.753710
H	7.091246	-0.293260	0.031732
H	0.754800	2.090259	2.648220
H	2.392019	1.793046	3.268357
H	2.161761	2.918765	1.925789
	D(S)		
Mn	-0.375094	-1.087773	-0.173383
S	1.987464	1.410749	1.029237
P	-2.233278	0.070479	0.345196
O	-1.979220	-3.525588	-0.326805
O	-0.803602	-0.779224	-3.060673
O	1.619444	0.688825	2.345301
N	-0.143956	-1.203873	1.906362
N	1.255608	-2.326241	-0.080276
N	1.227536	0.644314	-0.206084
C	-2.192024	0.097329	2.195176
C	-1.386994	-1.103518	2.669743
C	0.648309	-2.370907	2.256516
C	1.599973	-2.731224	1.155758
C	2.723739	-3.526241	1.379419
C	3.478943	-3.959233	0.294949
C	3.078606	-3.590889	-0.986634
C	1.964332	-2.774264	-1.125593
C	-2.625519	1.782522	-0.165616
C	-3.693855	2.493243	0.397313
C	-3.969505	3.789784	-0.028653
C	-3.192805	4.377931	-1.030528
C	-2.138281	3.668735	-1.602360
C	-1.852235	2.374963	-1.166230
C	-3.807888	-0.760655	-0.104663
C	-4.566327	-1.512687	0.797464
C	-5.712587	-2.183722	0.368565

C	-6.108616	-2.113533	-0.965098
C	-5.351659	-1.371158	-1.873500
C	-4.208008	-0.702278	-1.447550
C	-1.373168	-2.542396	-0.250016
C	-0.592692	-0.895150	-1.926336
C	2.083661	0.550759	-1.408780
C	3.594608	0.485463	-1.168218
C	4.510363	1.238464	-1.909470
C	4.111095	-0.405751	-0.213366
C	5.888502	1.099808	-1.718123
C	5.479452	-0.550754	-0.020638
C	6.381616	0.201846	-0.776991
C	1.701264	1.550410	-2.496568
C	1.279640	3.128423	1.382733
C	1.304011	3.918691	0.089342
C	-0.102003	3.050355	1.990333
C	2.283478	3.688386	2.388297
H	-1.673018	1.026074	2.467353
H	-3.192447	0.131603	2.650435
H	-1.181493	-1.017421	3.753012
H	-1.961391	-2.034604	2.521426
H	-0.026430	-3.237495	2.387884
H	1.189986	-2.237129	3.209148
H	2.987888	-3.806372	2.400838
H	4.364006	-4.580815	0.447345
H	3.624896	-3.914986	-1.873256
H	1.616811	-2.462991	-2.112013
H	-4.316865	2.030605	1.168015
H	-4.798435	4.344715	0.417698
H	-3.414139	5.394424	-1.365472
H	-1.526085	4.126468	-2.383322
H	-1.002641	1.820471	-1.567617
H	-4.269785	-1.590130	1.845868
H	-6.296689	-2.767305	1.084490
H	-7.005541	-2.640422	-1.299680
H	-5.652913	-1.314767	-2.922388
H	-3.617014	-0.128252	-2.167174
H	1.854235	-0.437180	-1.839499
H	0.470173	-0.365734	2.108831
H	4.157039	1.953843	-2.653415
H	3.420780	-0.969680	0.415864
H	6.578014	1.704482	-2.313482
H	5.845314	-1.252480	0.733869
H	7.458578	0.092164	-0.626065
H	2.184193	1.304472	-3.455237
H	0.617696	1.513354	-2.664055
H	1.971395	2.580833	-2.226970
H	2.311223	3.920344	-0.358645
H	0.596751	3.503326	-0.639989
H	1.020331	4.966417	0.282337
H	-0.084459	2.398953	2.876315
H	-0.440588	4.053366	2.299948
H	-0.830442	2.665820	1.267105
H	1.997338	4.714582	2.672611
H	2.309114	3.067030	3.295505
H	3.299874	3.721546	1.964551
	D(S)'		
Mn	-0.682937	1.196569	-0.295599
S	1.109587	-0.570524	1.495100
P	-1.892636	-0.590311	0.381901
O	-3.157316	2.578427	-1.040528
O	-0.405981	0.275313	-3.059857
O	1.345355	0.418378	2.674820
N	-0.829384	1.754048	1.747011
N	0.264217	2.995167	-0.354751
N	1.243369	0.171679	0.052282
C	-2.122726	-0.280764	2.192233
C	-2.016410	1.220718	2.420549
C	-0.730542	3.201843	1.830544
C	0.179836	3.735480	0.766579
C	0.834208	4.959261	0.891033
C	1.564109	5.453828	-0.184953
C	1.602276	4.710474	-1.361743
C	0.938840	3.490671	-1.401350
C	-1.395238	-2.344153	0.210841

C	-1.707477	-3.312814	1.172062
C	-1.359655	-4.646645	0.963736
C	-0.717035	-5.028718	-0.214654
C	-0.411135	-4.069193	-1.179017
C	-0.738077	-2.731437	-0.963093
C	-3.596191	-0.660398	-0.315287
C	-4.740557	-0.306192	0.406204
C	-5.994485	-0.305304	-0.207221
C	-6.119768	-0.656583	-1.548918
C	-4.981987	-1.003546	-2.279524
C	-3.731165	-0.999323	-1.669697
C	-2.194186	2.022964	-0.716769
C	-0.507433	0.664329	-1.970573
C	2.467726	0.797591	-0.447015
C	3.375846	-0.182202	-1.183489
C	4.755095	-0.267275	-0.972886
C	2.806970	-1.015302	-2.158929
C	5.537744	-1.181161	-1.684721
C	3.582000	-1.920384	-2.876037
C	4.955243	-2.015484	-2.634598
C	3.197953	1.718281	0.526916
C	2.390061	-1.901178	1.914211
C	2.497844	-2.898696	0.776388
C	3.723057	-1.302083	2.316757
C	1.720605	-2.552765	3.128042
H	-1.294347	-0.795203	2.700118
H	-3.064908	-0.684942	2.589055
H	-1.986854	1.437303	3.504528
H	-2.903813	1.732824	2.010292
H	-1.730588	3.636051	1.645574
H	-0.411667	3.549905	2.829019
H	0.762121	5.514113	1.828329
H	2.087912	6.409240	-0.109014
H	2.141762	5.060178	-2.243191
H	0.940359	2.880177	-2.306081
H	-2.224192	-3.032041	2.093154
H	-1.598130	-5.393885	1.724766
H	-0.448849	-6.075411	-0.377408
H	0.105545	-4.357684	-2.097563
H	-0.463130	-1.979214	-1.704474
H	-4.671238	-0.019551	1.457560
H	-6.878068	-0.024989	0.371715
H	-7.101715	-0.655326	-2.028284
H	-5.068144	-1.273997	-3.334775
H	-2.847498	-1.259203	-2.258677
H	2.106597	1.449477	-1.258048
H	0.021494	1.341871	2.212446
H	5.238053	0.379973	-0.238324
H	1.732591	-0.952068	-2.338165
H	6.612165	-1.237796	-1.490498
H	3.112171	-2.560578	-3.627616
H	5.566183	-2.731686	-3.189917
H	2.484677	2.409902	0.989826
H	3.966386	2.308122	0.002877
H	3.677716	1.166966	1.344468
H	1.507789	-3.265217	0.471173
H	2.995459	-2.472261	-0.102319
H	3.087392	-3.767306	1.114447
H	3.562223	-0.468348	3.016388
H	4.334885	-2.070518	2.818141
H	4.284891	-0.946154	1.444586
H	2.353036	-3.378102	3.493440
H	1.589280	-1.822006	3.938774
H	0.736069	-2.970046	2.862547

1-phenylethan-1-ol

O	-2.198410	1.074717	-0.544287
C	-1.652336	-0.205827	-0.336981
C	-2.263404	-0.870403	0.893030
C	-0.151874	-0.077408	-0.196719
C	0.438981	1.140953	0.148276
C	0.665411	-1.199497	-0.375341
C	1.820938	1.233087	0.317551
C	2.045009	-1.109556	-0.203675
C	2.628263	0.109641	0.145101
H	-1.848440	-0.853670	-1.216812

H -3.157508 0.995879 -0.520651
H -1.835325 -1.869293 1.062130
H -2.072203 -0.253668 1.784352
H -3.353309 -0.986267 0.771347
H -0.198604 2.017811 0.272483
H 0.215649 -2.156566 -0.657828
H 2.270515 2.193234 0.584453
H 2.669818 -1.994601 -0.349069
H 3.710752 0.183467 0.276436

acetophenone

O 2.206508 -1.304907 -0.000067
C 1.698623 -0.202444 -0.000003
C 2.547624 1.043250 0.000056
C 0.207839 -0.052184 0.000004
C -0.571017 -1.217817 0.000029
C -0.429938 1.195708 -0.000023
C -1.959013 -1.139669 0.000030
C -1.821397 1.274394 -0.000030
C -2.586703 0.108362 0.108362
H 2.336504 1.660972 -0.886537
H 2.336266 1.661113 0.886490
H 3.604804 0.752738 0.000205
H -0.054184 -2.179964 0.000045
H 0.155424 2.117394 -0.000047
H -2.558087 -2.053562 0.000054
H -2.311082 2.251109 -0.000057
H -3.677820 0.171854 -0.000001

(R)-2-methylpropane-2-sulfinamide

S -0.918389 -0.187890 -0.519368
O -1.372483 -1.397271 0.239393
N -1.706799 1.143971 0.155103
C 0.858182 0.060655 0.037951
C 1.358308 1.365933 -0.558658
C 0.888373 0.046080 1.555601
C 1.595328 -1.144611 -0.536771
H -1.711940 1.955871 -0.457374
H -1.444695 1.373714 1.113303
H 1.257094 1.373424 -1.656134
H 0.814898 2.232616 -0.152514
H 2.425738 1.500128 -0.321358
H 0.345974 -0.833326 1.934495
H 1.929487 -0.001255 1.911977
H 0.440158 0.954677 1.989101
H 2.659622 -1.101771 -0.255883
H 1.167620 -2.080061 -0.148286
H 1.536578 -1.165750 -1.637037

(R)-2-methyl-N-(1-phenylethylidene)propane-2-sulfinamide

S 1.906424 0.154620 -0.953555
O 2.376750 -0.997509 -1.781535
N 0.283474 -0.239210 -0.527424
C -0.621703 0.668907 -0.448675
C -2.005918 0.201085 -0.159779
C -3.032550 1.096495 0.174072
C -2.295999 -1.172140 -0.209525
C -4.316096 0.630045 0.453942
C -3.577832 -1.634559 0.061367
C -4.592836 -0.734524 0.396176
C -0.399570 2.148237 -0.602305
C 2.645371 -0.112715 0.751569
C 2.083052 0.934894 1.698118
C 2.334939 -1.536013 1.181090
C 4.140014 0.083047 0.515496
H -2.838296 2.169147 0.228205
H -1.488814 -1.859434 -0.469912
H -5.104226 1.339229 0.717887
H -3.790424 -2.705227 0.011118
H -5.600438 -1.098916 0.611354
H 0.596601 2.364212 -1.007512
H -1.161070 2.590010 -1.260482
H -0.483238 2.643600 0.378030
H 2.246469 1.957150 1.320066
H 1.007404 0.787978 1.876403
H 2.593903 0.857249 2.671234
H 2.608024 -2.238044 0.378924
H 2.917901 -1.786061 2.082073

```
H                          1.266686   -1.663880    1.403550
H                          4.687377   -0.099438    1.453709
H                          4.507745   -0.621590   -0.244700
H                          4.368073    1.108095    0.181899
                           water
O                          0.000000    0.000000    0.120138
H                          0.000000    0.753396   -0.480551
H                          0.000000   -0.753396   -0.480551
 (R)-2-methyl-N-((R)-1-phenylethyl)propane-2-sulfinamide
S                         -1.840587   -0.860580    0.028729
O                         -2.035145   -1.532350   -1.302945
N                         -0.310028   -0.111355    0.076201
C                          0.804566   -1.021531    0.381533
C                          2.105843   -0.310945    0.079784
C                          3.128821   -0.968605   -0.609551
C                          2.320285    1.002656    0.515962
C                          4.345568   -0.332065   -0.854381
C                          3.533321    1.641967    0.268029
C                          4.550862    0.975570   -0.416400
C                          0.741161   -1.467826    1.838549
C                         -2.870439    0.698295   -0.042269
C                         -2.656360    1.469676    1.250113
C                         -2.485408    1.485914   -1.283896
C                         -4.298628    0.171194   -0.156714
H                          0.759311   -1.918392   -0.266034
H                         -0.148918    0.354632   -0.819837
H                          2.967388   -1.991278   -0.962578
H                          1.521981    1.525120    1.049382
H                          5.134761   -0.859324   -1.396269
H                          3.686606    2.668114    0.611990
H                          5.502000    1.477279   -0.611198
H                         -0.202571   -1.991769    2.052319
H                          1.572986   -2.150923    2.062218
H                          0.813124   -0.596191    2.506396
H                         -2.880380    0.846572    2.130740
H                         -1.621087    1.827573    1.334446
H                         -3.332760    2.339219    1.274023
H                         -2.469354    0.822889   -2.162817
H                         -3.226126    2.280794   -1.464140
H                         -1.503411    1.971471   -1.176383
H                         -4.998905    1.018457   -0.221517
H                         -4.414364   -0.449888   -1.056703
H                         -4.577076   -0.432575    0.721893
 (R)-2-methyl-N-((S)-1-phenylethyl)propane-2-sulfinamide
S                          1.476907    0.004762   -0.705515
O                          1.124141   -1.420366   -1.055066
N                          0.425552    0.644163    0.445430
C                         -0.807921    1.331864    0.059305
C                         -2.039965    0.446791    0.138477
C                         -2.010233   -0.885926   -0.289654
C                         -3.244979    0.981626    0.607315
C                         -3.168847   -1.661507   -0.250584
C                         -4.403220    0.206532    0.643570
C                         -4.367768   -1.119872    0.213428
C                         -0.693593    1.983726   -1.314756
C                          2.983282   -0.147278    0.394685
C                          3.382966    1.245724    0.852971
C                          2.664007   -1.090100    1.543651
C                          4.034015   -0.759515   -0.528492
H                         -0.943216    2.144897    0.794803
H                          0.297250    0.028092    1.247847
H                         -1.070595   -1.318367   -0.648836
H                         -3.275881    2.020054    0.952344
H                         -3.131870   -2.701192   -0.586182
H                         -5.335810    0.638490    1.015747
H                         -5.272731   -1.731921    0.244922
H                         -1.589835    2.591554   -1.501228
H                          0.193126    2.632477   -1.375564
H                         -0.631489    1.226460   -2.111571
H                          3.543499    1.918381   -0.004783
H                          2.614756    1.690003    1.500781
H                          4.328257    1.189612    1.416367
H                          2.193675   -2.008662    1.160553
H                          3.593640   -1.367775    2.064864
H                          2.000797   -0.626106    2.290037
```

H	4.973937	-0.900279	0.027659
H	3.699385	-1.735792	-0.907145
H	4.244137	-0.104732	-1.389355

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