Supporting Information

Enantioselective Synthesis of 3,4-Disubstituted *cis*- and *trans*-1,2,5-Thiadiazolidine-1,1-dioxides as Precursors for Chiral 1,2-Diamines

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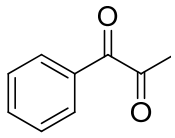
1) Experimental Section

General: ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AV-300 or at 500 MHz on a Bruker DRX 500 spectrometer. Chemical shifts are reported as δ values relative to the residual proton signal in $CDCl_3$ (δ = 7.26 ppm) or in acetone-d_6 (δ = 2.05 ppm) as internal standard. ^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker AV-300 or at 126 MHz on a Bruker DRX 500 spectrometer. Chemical shifts are reported as δ values relative to $CDCl_3$ (δ = 77.16 ppm) or acetone-d_6 (δ = 29.84 ppm). IR spectra were recorded on a Bruker Alpha-P FT-IR spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Finnigan LTQ FT spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Melting points are uncorrected. HPLC chromatograms were recorded on a JASCO instrument equipped with a JASCO MD-2010 Plus multiwavelength detector and a Daicel Chiralpak IA, IB, or IC column. Column chromatography was carried out on MN Kieselgel 60 M (Machery-Nagel, 0.040-0.063 mm). TLC analysis was carried out on pre-coated sheets (Merck DC Kieselgel 60 F_{254}). Solvents used for extraction and chromatography were of technical grade and distilled prior to use. Unless otherwise stated, all reactions were carried out under dry nitrogen in oven- and/or flame-dried glassware. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium benzophenone ketyl. CH_2Cl_2, acetonitrile and triethylamine were distilled from calcium hydride. 5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide,[1] *N*,*N*'-bis(trimethylsilyl)sulfamide,[2] RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN],[3] lithium borohydride,[4] and 3,4-dimethyl-1,2,5-thiadiazole-1,1-dioxide (**2i**)[5] were prepared as described in the literature. Racemic thiadiazoline-1,1-dioxides **4** were obtained from the respective transfer hydrogenation employing the racemic catalyst, racemic *cis*-thiadiazolidine-1,1-dioxides **5** were obtained by reduction of the respective thiadiazole-1,1-dioxides **2** with

$NaBH_4$ (8 equiv.) in EtOH following standard procedures. All other chemicals are commercially available and were used as received.

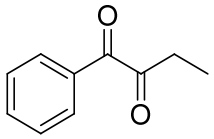
General Procedure for the Synthesis of α-Diketones 1 (GP 1):
The α-diketones were prepared via a two-step-procedure comprising an acyloin condensation of the respective aromatic and aliphatic aldehydes according to Stetter and Dämbkes (step 1)[6] and an oxidation with bismuth(III) acetate according to Rigby (step 2).[7]

1-Phenylpropane-1,2-dione (1b)[8]


1b

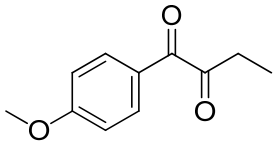
1-Phenylpropane-1,2-dione was prepared according to Wegmann and Dahn[9] from phenylacetone (5.00 g, 37.3 mmol) and selenium dioxide (6.62 g, 59.7 mmol) to yield 2.28 g (41%). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 7.50 (m_c, 2 H), 7.64 (m_c, 1 H), 8.01 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.5, 129.0, 130.5, 131.9, 134.7, 191.5, 200.7.

1-Phenylbutane-1,2-dione (1c)[10]


1c

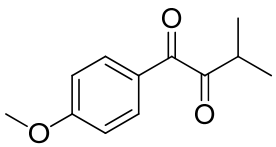
Prepared according to GP 1 from benzaldehyde (9.57 mL, 10.0 g, 94.7 mmol), propionaldehyde (20.4 mL, 16.5 g, 285 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (2.69 g, 9.43 mmol), and triethylamine (7.88 mL, 5.72 g, 56.5 mmol) in step 1 to furnish 10.3 g of the respective α-hydroxyketone. In step 2, this material was reacted with bismuth(III) oxide (8.77 g, 18.8 mmol) and acetic acid (12.0 mL, 12.6 g, 210 mmol) to yield 4.28 g of the title compound (28% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, J = 7.3 Hz, 3 H), 2.88 (q, J = 7.2 Hz, 2 H), 7.45 (m_c, 2 H), 7.60 (m_c, 1 H), 7.94 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 6.9, 32.2, 128.9, 130.2, 132.1, 134.6, 192.6, 203.8.

1-(4-Methoxyphenyl)butane-1,2-dione (1d)[11]


1d

Prepared according to GP 1 from 4-methoxybenzaldehyde (4.46 mL, 5.00 g, 36.7 mmol), propionaldehyde (7.95 mL, 6.44 g, 111 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (1.05 g, 3.67 mmol), and triethylamine (3.07 mL, 2.23 g, 22.0 mmol) in step 1 to furnish 2.64 g of the respective α-hydroxyketone. In step 2, this material was reacted with bismuth(III) oxide (1.69 g, 3.63 mmol) and acetic acid (2.80 mL, 2.94 g, 48.9 mmol) to yield 2.27 g of the title compound (32% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.3 Hz, 3 H), 2.89 (q, J = 7.3 Hz, 2 H), 3.88 (s, 3 H), 6.95 (m_c, 2 H), 7.97 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 7.0, 32.3, 55.7, 114.4, 125.2, 132.8, 165.0, 191.3, 204.5.

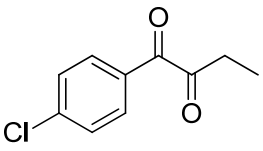
1-(4-Methoxyphenyl)-3-methylbutane-1,2-dione (1e)[11]


1e

Prepared according to GP 1 from 4-methoxybenzaldehyde (8.94 mL, 10.0 g, 73.5 mmol), isobutyraldehyde (20.1 mL, 15.9 g, 220 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (2.09 g, 7.33 mmol), and triethylamine (6.19 mL, 4.49 g, 44.4 mmol) in step 1. The crude product was reacted without further purification in step 2 with bis-

muth(III) oxide (10.27 g, 22.04 mmol) and acetic acid (4.20 mL, 4.41 g, 73.4 mmol) to yield 4.96 g of the title compound (33% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 7.0 Hz, 6 H), 3.34 (hept, *J* = 7.0 Hz, 1 H), 3.89 (s, 3 H), 6.96 (m_c, 2 H), 7.92 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.1, 36.7, 55.8, 114.4, 125.8, 132.6, 165.0, 192.8, 207.2.

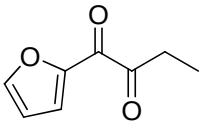
1-(4-Chlorophenyl)butane-1,2-dione (1f)[12]



1f

Prepared according to GP 1 from 4-chlorobenzaldehyde (5.68 g, 40.4 mmol), propionaldehyde (8.75 mL, 7.09 g, 122 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (1.15 g, 4.03 mmol), and triethylamine (3.41 mL, 2.48 g, 24.5 mmol) in step 1. The crude product was reacted without further purification in step 2 with bismuth(III) oxide (5.65 g, 12.1 mmol) and acetic acid (8.1 mL, 8.5 g, 0.14 mol) to yield 2.53 g of the title compound (32% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0 Hz, 3 H), 2.91 (q, *J* = 7.2 Hz, 2 H), 7.46 (m_c, 2 H), 7.94 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 6.8, 32.0, 128.6, 129.2, 131.6, 141.3, 190.6, 203.0.

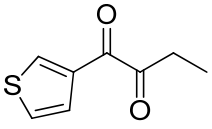
1-(Furan-2-yl)butane-1,2-dione (1g)[13]



1g

Prepared according to GP 1 from furfural (8.62 mL, 10.0 g, 104 mmol), propionaldehyde (22.5 mL, 18.2 g, 314 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (2.97 g, 10.4 mmol), and triethylamine (8.78 mL, 6.37 g, 63.0 mmol) in step 1 to furnish 7.21 g of the respective α-hydroxyketone. In step 2, this material was reacted with bismuth(III) oxide (5.87 g, 12.6 mmol) and acetic acid (9.6 mL, 10 g, 0.17 mol) to yield 5.61 g of the title compound (35% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 7.3 Hz, 3 H), 3.34 (q, *J* = 7.2 Hz, 2 H), 6.60 (dd, *J* = 3.7, 1.7 Hz, 1 H), 7.66 (dd, *J* = 3.6, 0.8 Hz, 1 H), 7.75 (dd, *J* = 1.7, 0.8 Hz, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 7.0, 31.1, 113.1, 124.8, 149.0, 149.3, 194.3, 201.0.

1-(Thiophen-3-yl)butane-1,2-dione (1h)



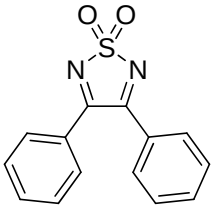
1h

Prepared according to GP 1 from thiophen-3-carbaldehyde (10.0 mL, 12.8 g, 114 mmol), propionaldehyde (24.9 mL, 19.9 g, 342 mmol), 5-(2-hydroxyethyl)-3,4-dimethylthiazolium iodide (3.25 g, 11.4 mmol), and triethylamine (9.54 mL, 6.93 g, 68.5 mmol) in step 1 to furnish 13.8 g of the respective α-hydroxyketone. In step 2, 5.00 g (29.4 mmol) of this material were reacted with bismuth(III) oxide (3.70 g, 7.94 mmol) and acetic acid (16.0 mL, 280 mmol) to yield 3.41 g of the title compound as a yellow oil (49% over 2 steps). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 7.1 Hz, 3 H), 2.93 (q, *J* = 7.1 Hz, 2 H), 7.35 (dd, *J* = 5.0, 2.6 Hz, 1 H), 7.67 (m_c, 1 H), 8.50 (m_c, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 7.1, 31.4, 126.6, 128.1, 136.8, 137.7, 183.8, 202.6. – IR (neat): ν = 3115, 2980, 2940, 2884, 1714, 1657, 1506, 1456, 1410, 1347, 1261, 1189, 1149, 1115, 1080, 995, 934, 877, 838, 796, 688, 627, 567, 420. – ESI (HR-MS) calcd. for $C_8H_8O_2SNa$: 191.0137; found 191.0139.

General Procedure for the Synthesis of 1,2,5-Thiadiazole-1,1-dioxides 2 (GP 2)

The respective 1,2-diketone (1.00 mmol) was dissolved in toluene (5 mL) and *N*,*N*'-bis(trimethylsilyl)sulfamide (842 mg, 3.50 mmol) and boron trifluoride diethyl etherate (0.19 mL, 0.22 g, 1.5 mmol) were added. The reaction mixture was stirred for 8 h at rt, poured into chloroform (10 mL) and washed with water (15 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure, and the crude product was purified by recrystallization or flash column chromatography.

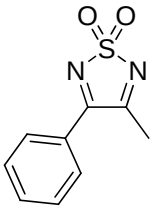
3,4-Diphenyl-1,2,5-thiadiazole-1,1-dioxide (2a)



2a

Prepared according to GP 2 from benzil (**1a**, 2.05 g, 9.75 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (8.19 g, 34.1 mmol), and boron trifluoride diethyl etherate (1.80 mL, 2.07 g, 14.6 mmol) in toluene (50 mL). Flash column chromatography (cyclohexane/EtOAc 8:1 + 5% MeOH) furnished 2.29 g (87%) of the title compound (R_f = 0.30) as a colorless solid, mp 256 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (m_c, 4 H), 7.56-7.58 (m, 4 H), 7.67 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 128.2, 128.9, 131.0, 134.1, 165.7. – IR (neat): ν = 3394, 3346, 3069, 1595, 1562, 1489, 1446, 1386, 1344, 1308, 1176, 1116, 1091, 1067, 974, 855, 802, 757, 727, 690, 649, 610, 585, 537, 502, 442, 402. – ESI (HR-MS) calcd. for $C_{14}H_{10}N_2O_2SNa$: 293.0355; found 293.0355.

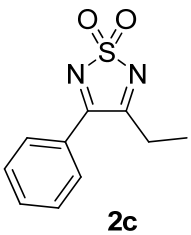
4-Methyl-3-phenyl-1,2,5-thiadiazole-1,1-dioxide (2b)



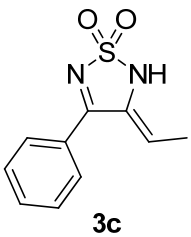
2b

Prepared according to GP 2 from 1-phenylpropane-1,2-dione (**1b**, 2.00 g, 13.5 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (11.4 g, 47.4 mmol), and boron trifluoride diethyl etherate (2.57 mL, 2.96 g, 20.8 mmol) in toluene (70 mL). Recrystallization from benzene furnished 2.19 g (78%) of the title compound as a colorless solid, mp 134 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.77 (s, 3 H), 7.59 (m_c, 2 H), 7.72 (m_c, 1 H), 7.91 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.9, 127.5, 129.6, 130.3, 134.4, 165.9, 167.9. – IR (neat): ν = 3323, 3223, 1641, 1553, 1488, 1443, 1425, 1342, 1292, 1155, 1023, 983, 927, 905, 803, 781, 754, 690, 648, 588, 553, 529, 484, 431, 410. – ESI (HR-MS) calcd. for $C_9H_7N_2O_2S$: 207.0234; found 207.0232.

4-Ethyl-3-phenyl-1,2,5-thiadiazole-1,1-dioxide (2c) and (*Z*)-4-Ethylidene-3-phenyl-1,2,5-thiadiazoline-1,1-dioxide (3c)



2c



3c

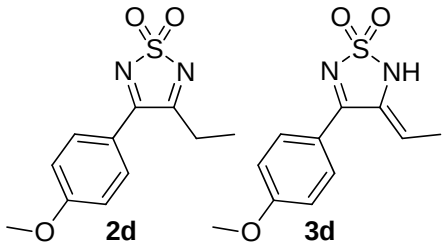
Prepared according to GP 2 from 1-phenylbutane-1,2-dione (**1c**, 1.08 g, 6.66 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (5.63 g, 23.4 mmol), and boron trifluoride diethyl etherate (1.23 mL, 1.41 g, 10.0 mmol) in toluene (33 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 1.26 g (85%) of a 1:9 mixture of the title compounds (R_f = 0.31) as a colorless solid, mp 107 °C.

2c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.0 Hz, 3 H), 3.04 (q, *J* = 7.0 Hz, 2 H), 7.60 (m_c, 2 H), 7.70 (m_c, 1 H), 7.87 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.3, 26.5, 127.7, 129.5, 130.2, 134.1, 165.3, 173.0.

3c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (d, *J* = 7.4 Hz, 3 H), 5.82 (q, *J* = 7.4 Hz, 1 H), 7.19 (bs, 1 H), 7.50 (m_c, 2 H), 7.60 (m_c, 1 H), 7.70 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.6, 119.1, 129.0, 129.3, 129.8, 132.9, 136.5, 170.8.

2c, **3c:** IR (neat): ν = 3266, 3157, 1654, 1591, 1528, 1489, 1445, 1348, 1296, 1149, 1077, 992, 934, 877, 813, 765, 698, 652, 615, 586, 531, 500, 443, 413. – ESI (HR-MS) calcd. for $C_{10}H_{10}N_2O_2SNa$: 245.0355; found 245.0353. – Anal. Calcd. (%) for $C_{10}H_{10}N_2O_2S$ (222.3): C, 54.04; H, 4.53; N 12.60. Found: C, 53.85; H, 4.81; N, 12.70.

4-Ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazole-1,1-dioxide (2d) and (*Z*)-4-Ethylidene-3-(4-methoxyphenyl)-1,2,5-thiadiazoline-1,1-dioxide (3d)



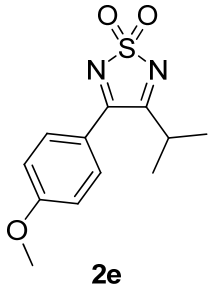
Prepared according to GP 2 from 1-(4-methoxyphenyl)-butane-1,2-dione (**1d**, 4.00 g, 20.8 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (17.5 g, 72.8 mmol), and boron trifluoride diethyl etherate (3.84 mL, 4.42 g, 31.1 mmol) in toluene (100 mL). Recrystallization from benzene furnished 4.74 g (90%) of a 1:9 mixture of the title compounds as a light yellow solid, mp 157 °C.

2d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.0 Hz, 3 H), 3.10 (q, *J* = 7.0 Hz, 2 H), 3.92 (s, 3 H), 7.04 (m_c, 2 H), 7.96 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.6, 27.1, 55.9, 115.2, 119.9, 133.2, 164.8, 165.0, 172.7.

3d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (d, *J* = 7.4 Hz, 3 H), 3.88 (s, 3 H), 5.83 (q, *J* = 7.4 Hz, 1 H), 6.88 (bs, 1 H), 7.00 (m_c, 2 H), 7.72 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.6, 55.7, 114.6, 118.1, 121.6, 132.1, 136.6, 163.8, 169.9.

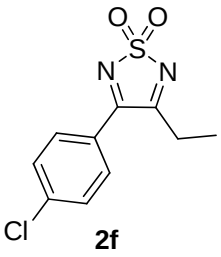
2d, **3d:** IR (neat): ν = 3232, 1651, 1601, 1493, 1423, 1383, 1307, 1256, 1148, 1016, 986, 879, 844, 818, 792, 738, 698, 637, 589, 529, 480, 443, 411. – ESI (HR-MS) calcd. for $C_{11}H_{12}N_2O_3SNa$: 275.0489; found 275.0641. – Anal. Calcd. (%) for $C_{11}H_{12}N_2O_3S$ (252.3): C, 52.37; H, 4.79; N, 11.10. Found: C, 52.02; H, 5.00; N, 10.96.

4-Isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazole-1,1-dioxide (2e)

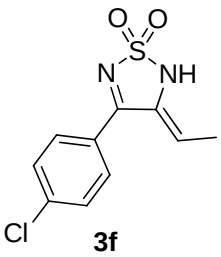


Prepared according to GP 2 from 1-(4-methoxyphenyl)-3-methylbutane-1,2-dione (**1e**, 634 mg, 3.07 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (2.59 g, 10.8 mmol), and boron trifluoride diethyl etherate (0.569 mL, 0.654 g, 4.61 mmol) in toluene (15 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 661 mg (81%) of the title compound (R_f = 0.36) as a light yellow solid, mp 149 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, *J* = 6.7 Hz, 6 H), 3.45 (hept, *J* = 6.7 Hz, 1 H), 3.92 (s, 3 H), 7.05 (m_c, 2 H), 7.90 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6, 31.1, 55.9, 115.2, 120.2, 132.6, 164.7, 164.9, 176.2. – IR (neat): ν = 3420, 3292, 2979, 1599, 1531, 1500, 1453, 1423, 1381, 1351, 1314, 1289, 1258, 1166, 1076, 1049, 1014, 978, 875, 841, 805, 764, 697, 615, 568, 534, 505, 479, 438, 407. – ESI (HR-MS) calcd. for $C_{12}H_{14}N_2O_3SNa$: 289.0617; found 289.0626.

4-Ethyl-3-(4-chlorophenyl)-1,2,5-thiadiazole-1,1-dioxide (2f) and (*Z*)-4-Ethylidene-3-(4-chlorophenyl)-1,2,5-thiadiazoline-1,1-dioxide (3f)



2f



3f

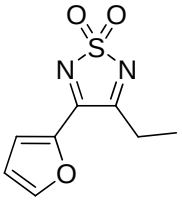
Prepared according to GP 2 from 1-(4-chlorophenyl)-butane-1,2-dione (**1f**, 527 mg, 2.68 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (2.26 g, 9.40 mmol), and boron trifluoride diethyl etherate (0.494 mL, 0.568 g, 4.00 mmol) in toluene (20 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 495 mg (72%) of a 1:15 mixture of the title compounds (R_f = 0.25) as a colorless solid, mp 119 °C.

2f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 6.9 Hz, 3 H), 3.03 (q, *J* = 7.0 Hz, 2 H), 7.56 (m_c, 2 H), 7.85 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.4, 26.6, 126.1, 130.0, 131.6, 141.2, 164.9, 172.1.

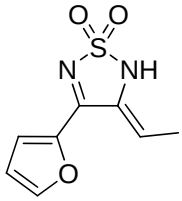
3f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (d, *J* = 7.4 Hz, 3 H), 5.79 (q, *J* = 7.4 Hz, 1 H), 7.04 (bs, 1 H), 7.50 (m_c, 2 H), 7.66 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.6, 118.9, 127.6, 129.5, 131.2, 136.3, 139.6, 169.6.

2f, **3f:** IR (neat): ν = 2984, 2937, 1627, 1593, 1570, 1547, 1487, 1454, 1405, 1345, 1281, 1181, 1148, 1092, 1000, 979, 828, 780, 727, 685, 606, 576, 535, 496, 434, 409. – ESI (HR-MS) calcd. for $C_{10}H_9{}^{35}ClN_2O_2SNa$: 278.9965, $C_{10}H_9{}^{36}ClN_2O_2SNa$: 279.9993, $C_{10}H_9{}^{37}ClN_2O_2SNa$: 280.9937; found: 278.9968, 280.0002, 280.9936. – Anal. Calcd. (%) for $C_{10}H_9ClN_2O_2S$ (256.7): C, 46.79; H, 3.53; N, 10.91. Found: C, 46.56; H, 3.82; N, 11.02.

4-Ethyl-3-(furan-2-yl)-1,2,5-thiadiazole-1,1-dioxide (2g) and (*Z*)-4-Ethylidene-3-(furan-2-yl)-1,2,5-thiadiazoline-1,1-dioxide (3g)



2g



3g

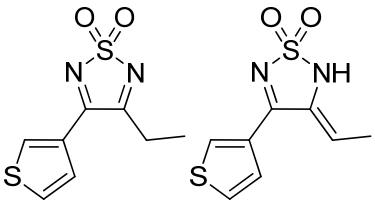
Prepared according to GP 2 from 1-(furan-2-yl)butane-1,2-dione (**1 g**, 610 mg, 4.01 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (3.37 g, 14.0 mmol), and boron trifluoride diethyl etherate (0.740 mL, 0.851 g, 6.00 mmol) in toluene (20 mL). Recrystallization from benzene furnished 0.594 g (70%) of a 1:3 mixture of the title compounds as a bright yellow solid, mp 158 °C.

2g: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.38 (t, *J* = 6.9 Hz, 3 H), 3.45 (q, *J* = 6.9 Hz, 2 H), 6.94 (dd, *J* = 3.8, 1.7 Hz, 1 H), 7.94 (dd, *J* = 3.8, 0.6 Hz, 1 H), 8.22 (dd, *J* = 1.7, 0.7 Hz, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.0, 27.1, 115.3, 125.9, 152.2, 157.1, 167.9, 174.1.

3g: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.99 (d, *J* = 7.4 Hz, 3 H), 6.58 (q, *J* = 7.4 Hz, 1 H), 6.82 (dd, *J* = 3.7, 1.8 Hz, 1 H), 7.59 (dd, *J* = 3.7, 0.8 Hz, 1 H), 8.05 (dd, *J* = 1.8, 0.7 Hz, 1 H), 9.32 (bs, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 14.4, 114.0, 117.4, 121.4, 135.7, 146.8, 150.0, 171.1.

2g, **3g:** IR (neat): ν = 3230, 1648, 1572, 1514, 1464, 1394, 1370, 1340, 1304, 1235, 1150, 1077, 1020, 902, 808, 762, 707, 628, 585, 529, 444. – ESI (HR-MS) calcd. for $C_8H_8N_2O_3SNa$: 235.0148; found 235.0142. – Anal. Calcd. (%) for $C_8H_8N_2O_3S$ (212.2): C, 45.28; H, 3.80; N, 13.20; S, 15.11. Found: C, 45.12; H, 3.90; N, 12.99; S, 15.09.

4-Ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazole-1,1-dioxide (2h) and (*Z*)-4-Ethylidene-3-(thiophen-3-yl)-1,2,5-thiadiazoline-1,1-dioxide (3h)



2h **3h**

Prepared according to GP 2 from 1-(thiophen-3-yl)butane-1,2-dione (**1h**, 740 mg, 4.40 mmol), *N*,*N*'-bis(trimethylsilyl)sulfamide (3.70 g, 15.4 mmol), and boron trifluoride diethyl etherate (0.812 mL, 0.934 g, 6.58 mmol) in toluene (25 mL). Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 752 mg (75%) of a 1:1.6 mixture of the title compounds (R_f = 0.31) as a pale yellow solid, mp 171 °C.

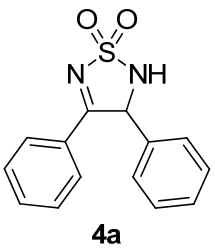
2h: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.38 (t, *J* = 6.8 Hz, 3 H), 3.45 (q, *J* = 6.9 Hz, 2 H), 7.75 (m_c, 2 H), 8.76 (dd, *J* = 2.6, 1.5 Hz, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.2, 27.1, 128.8, 130.0, 130.5, 137.6, 161.4, 174.8.

3h: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.97 (d, *J* = 7.3 Hz, 3 H), 6.10 (q, *J* = 7.3 Hz, 1 H), 7.56 (dd, *J* = 5.1, 1.3 Hz, 1 H), 7.71 (dd, *J* = 5.1, 2.9 Hz, 1 H), 8.30 (dd, *J* = 2.9, 1.3 Hz, 1 H), 9.31 (bs, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 14.3, 117.3, 128.6, 128.9, 131.6, 133.4, 137.0, 164.6.

2h, **3h:** IR (neat): ν = 3240, 3111, 2926, 1699, 1654, 1539, 1498, 1424, 1356, 1308, 1285, 1150, 1083, 1026, 1000, 899, 871, 786, 706, 631, 561, 534, 477, 442. – ESI (HR-MS) calcd. for $C_8H_8N_2O_2S_2Na$: 250.9919; found 250.9918.

General Procedure for the Ruthenium-catalyzed Asymmetric Transfer Hydrogenation of Thiadiazole-1,1-dioxides 2 (GP 3): The respective thiadiazole-1,1-dioxide **2** (1.00 mmol) and RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (32 mg, 0.050 mmol) were dissolved in acetonitrile (25 mL) and cooled to the given temperature. A 5:2 mixture of formic acid and triethylamine (0.630 mL, 0.649 g, 1.50 mmol) was added and the reaction mixture was stirred for the given time at this temperature. The reaction was quenched by addition of water (25 mL), the aqueous phase was extracted with EtOAc (3 * 25 mL), and the combined organic phases were washed with brine (50 mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography.

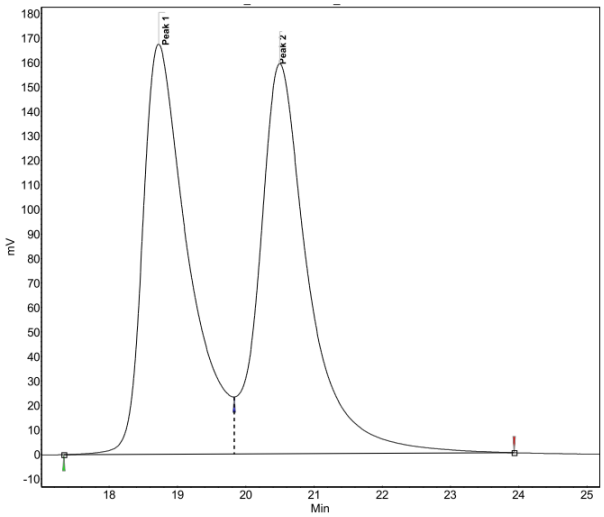
***rac*-3,4-Diphenyl-1,2,5-thiadiazoline-1,1-dioxide (4a)**



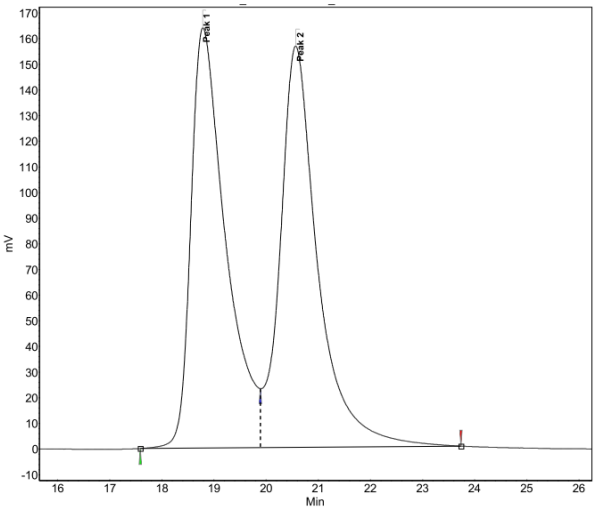
4a

Prepared according to GP 3 from 3,4-diphenyl-1,2,5-thiadiazole-1,1-dioxide (**2a**, 700 mg, 2.59 mmol), RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (82.0 mg, 0.129 mmol), and the mixture of formic acid and triethylamine (1.31 mL, 1.35 g, 3.12 mmol) in acetonitrile (65 mL) at –15 °C for 5 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 502 mg (71%) of the title compound (R_f = 0.33) as a colorless solid, mp 130-132 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.13 (d, *J* = 3.7 Hz, 1 H), 5.99 (d, *J* = 4.0 Hz, 1 H), 7.33-7.38 (m, 7 H), 7.51 (m_c, 1 H), 7.84 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 69.0, 128.1, 128.6, 129.1, 129.8, 129.9, 130.2, 134.4, 136.1, 176.9. – IR (neat): ν = 3236, 1594, 1561, 1494, 1447, 1393, 1341, 1299, 1264, 1226, 1169, 1079, 1048, 999, 920, 856, 805, 763, 689, 646, 620, 565, 526, 495, 447. – ESI (HR-MS) calcd. for $C_{14}H_{12}N_2O_2SNa$: 295.0512; found 295.0507. – The enantiomeric excess was determined by

HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate 1.5 mL/min), retention times: first enantiomer 18.8 min, second enantiomer 20.6 min, 0% ee.

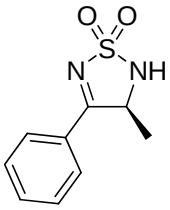


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	18.725	49.23	167.3	128.4	49.233
2	Peak 2	20.500	50.77	159.2	132.4	50.767
Total			100.00	326.5	260.8	100.000



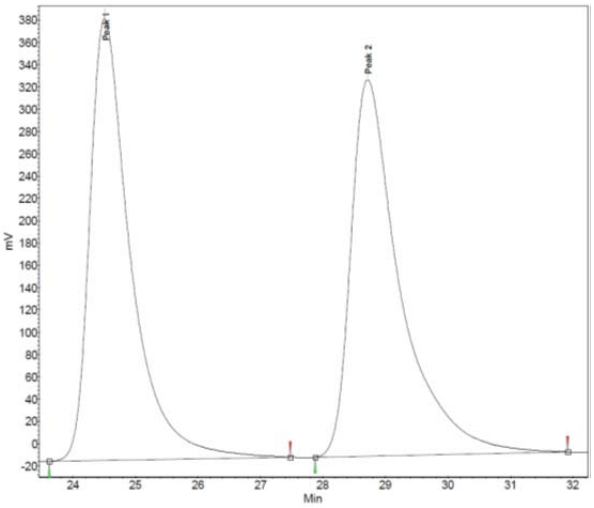
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	18.783	49.08	163.8	126.2	49.079
2	Peak 2	20.567	50.92	156.4	130.9	50.921
Total			100.00	320.3	257.1	100.000

(*S*)-4-Methyl-3-phenyl-1,2,5-thiadiazoline-1,1-dioxide (4b)

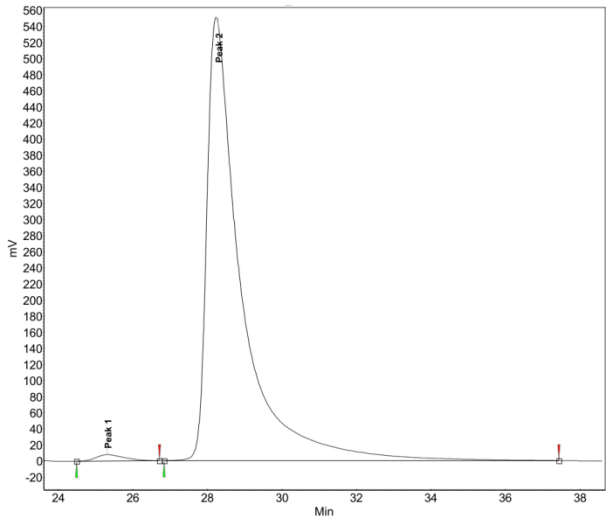


4b

Prepared according to GP 3 from 4-methyl-3-phenyl-1,2,5-thiadiazole-1,1-dioxide (**2b**, 299 mg, 1.44 mmol), RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (46.0 mg, 0.0723 mmol), and the mixture of formic acid and triethylamine (0.724 mL, 0.745 g, 1.72 mmol) in acetonitrile (35 mL) at –15 °C for 30 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 166 mg (55%) of the title compound ($R_f = 0.29$) as a slightly yellow solid, mp 123-126 °C. – $[\alpha]_D^{21} = +0.43$ (*c* 0.46, THF). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.57$ (d, $J = 7.1$ Hz, 3 H), 5.03 (m_c, 1 H), 5.13 (m_c, 1 H), 7.51 (m_c, 2 H), 7.63 (m_c, 1 H), 7.88 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.1$, 60.3, 128.5, 129.4, 129.8, 134.6, 180.7. – IR (neat): $\nu = 3266$, 3209, 1591, 1561, 1448, 1379, 1345, 1295, 1245, 1164, 1092, 1042, 994, 911, 886, 804, 778, 713, 689, 639, 524, 482, 447, 415. – ESI (HR-MS) calcd. for $C_9H_{10}N_2O_2SNa$: 233.0355; found 233.0356. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate 1.0 mL/min), retention times: (*R*)-enantiomer 25.3 min, (*S*)-enantiomer 28.2 min, 98% ee.

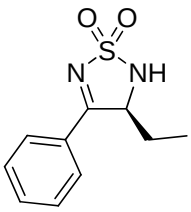


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	24,508	49,26	396,1	298,9	49,257
1	Peak 2	28,717	50,74	337,4	307,9	50,743
Total			100,00	733,5	606,7	100,000



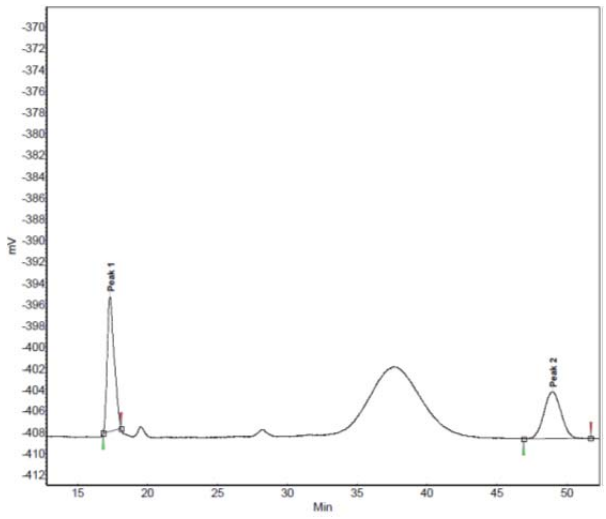
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	25,317	1,20	8,0	7,1	1,197
2	Peak 2	28,233	98,80	550,8	588,1	98,803
Total			100,00	558,7	595,2	100,000

(*S*)-4-Ethyl-3-phenyl-1,2,5-thiadiazoline-1,1-dioxide (4c)

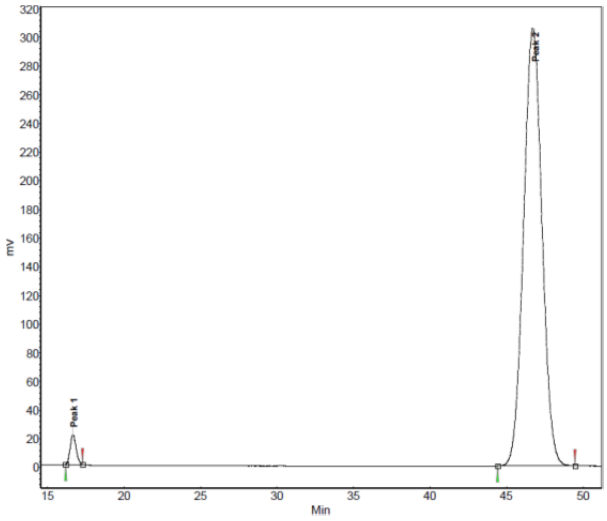


4c

Prepared according to GP 3 from the mixture of **2c** and its tautomer **3c** (530 mg, 2.38 mmol), RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (76.0 mg, 0.119 mmol), and the mixture of formic acid and triethylamine (1.50 mL, 1.55 g, 3.57 mmol) in acetonitrile (60 mL) at –15 °C for 30 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 392 mg (73%) of the title compound (R_f = 0.30) as a colorless solid, mp 89 °C. – $[\alpha]_D^{21}$ = +15.5 (*c* 0.54, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.99 (t, *J* = 7.3 Hz, 3 H), 1.68 (m_c, 1 H), 1.96 (ddq, *J* = 14.8, 7.4, 3.3 Hz, 1 H), 5.38 (ddd, *J* = 8.5, 5.6, 3.3 Hz, 1 H), 6.83 (m_c, 1 H), 7.62 (m_c, 2 H), 7.73 (m_c, 1 H), 8.07 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.3, 28.2, 66.5, 128.5, 130.1, 130.3, 134.9, 180.7. – IR (neat): ν = 3217, 2978, 2939, 2876, 1734, 1590, 1557, 1496, 1447, 1388, 1343, 1310, 1253, 1169, 1101, 1051, 1006, 979, 924, 900, 806, 765, 705, 680, 634, 609, 544, 528, 493, 451, 429. – ESI (HR-MS) calcd. for $C_{10}H_{13}N_2O_2S$: 225.0703; found 225.0700. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 3:2, flow rate 0.8 mL/min), retention times: (*R*)-enantiomer 16.7 min, (*S*)-enantiomer 46.7 min, 97% ee.

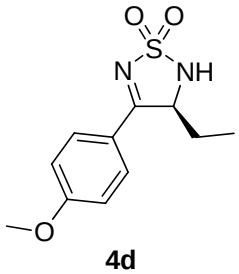


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	17,317	53,88	12,6	7,3	53,879
1	Peak 2	48,958	46,12	4,4	6,2	46,121
Total			100,00	17,0	13,5	100,000



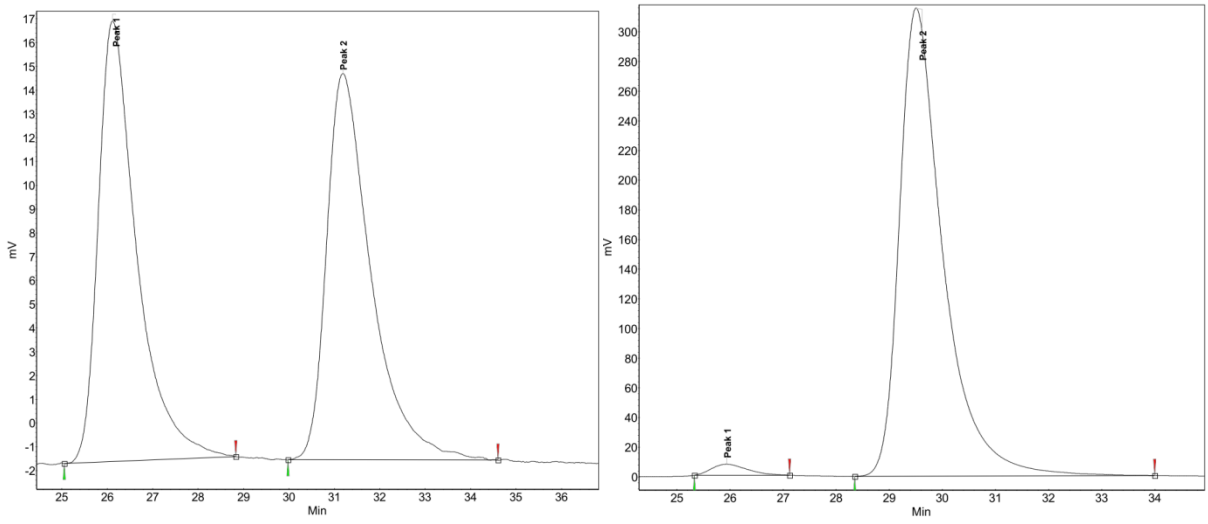
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	16,675	1,74	18,8	7,5	1,745
1	Peak 2	46,708	98,26	305,1	424,4	98,255
Total			100,00	324,0	431,9	100,000

(*S*)-4-Ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazoline-1,1-dioxide (4d)



4d

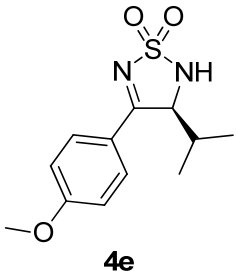
Prepared according to GP 3 from the mixture of **2d** and its tautomer **3d** (174 mg, 0.690 mmol), RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (22.0 mg, 0.0346 mmol), and the mixture of formic acid and triethylamine (0.434 mL, 0.447 g, 1.03 mmol) in acetonitrile (20 mL) at –15 °C for 40 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 171 mg (97%) of the title compound (R_f = 0.38) as a slightly yellow solid, mp 109-111 °C. – $[\alpha]_D^{21}$ = +61.8 (*c* 0.55, THF). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.4 Hz, 3 H), 1.67 (m_c, 1 H), 1.89 (ddq, *J* = 14.8, 7.4, 3.3 Hz, 1 H), 3.87 (s, 3 H), 5.00 (ddd, *J* = 8.9, 5.9, 3.3 Hz, 1 H), 5.34 (d, *J* = 5.8 Hz, 1 H), 6.89 (m_c, 2 H), 7.74 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.2, 28.2, 55.7, 66.1, 114.7, 121.0, 131.9, 164.7, 179.5. – IR (neat): ν = 3318, 2971, 2936, 2882, 2841, 1596, 1549, 1513, 1457, 1425, 1370, 1304, 1257, 1161, 1134, 1096, 1011, 982, 913, 832, 817, 782, 736, 694, 672, 643, 607, 569, 549, 516, 489, 446, 415. – ESI (HR-MS) calcd. for $C_{11}H_{14}N_2O_3SNa$: 277.0617; found 277.0614. – Anal. Calcd. (%) for $C_{11}H_{14}N_2O_3S$ (254.3): C, 51.95; H, 5.55; N, 11.02. Found: C, 52.04; H, 5.20; N, 10.54. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate: 1.5 mL/min), retention times: (*R*)-enantiomer 25.9 min, (*S*)-enantiomer 29.5 min, 96% ee.



Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	26.117	49.69	18.5	18.2	49.693
2	Peak 2	31.192	50.31	16.2	18.4	50.307
Total			100.00	34.8	36.7	100.000

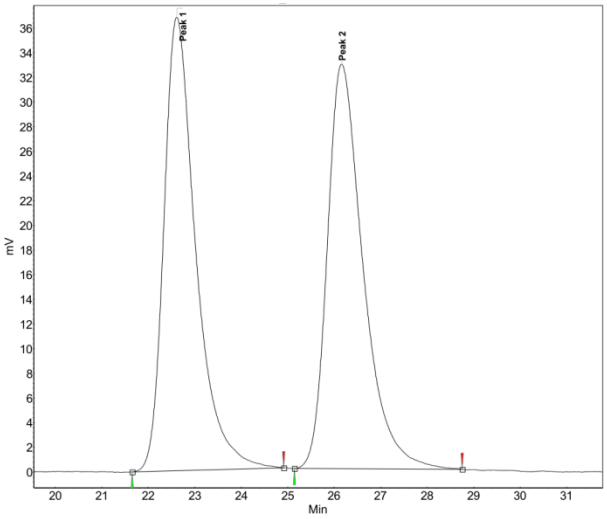
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	25.942	1.87	7.4	5.7	1.873
1	Peak 2	29.508	98.13	315.4	300.4	98.127
Total			100.00	322.8	306.1	100.000

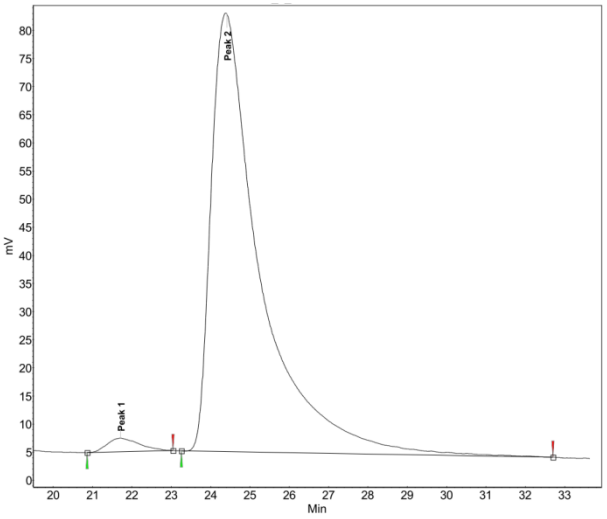
(*S*)-4-Isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazoline-1,1-dioxide (4e)



4e

Prepared according to GP 3 from 4-isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazole-1,1-dioxide (**2e**, 146 mg, 0.548 mmol), RuCl(*p*-cymene)-[(*S*,*S*)-TsDPEN] (17.0 mg, 0.0267 mmol), and the mixture of formic acid and triethylamine (0.345 mL, 0.355 g, 0.822 mmol) in acetonitrile (15 mL) at –15 °C for 48 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 139 mg (94%) of the title compound (R_f = 0.30) as a slightly yellow solid, mp 157 °C. – $[\alpha]_D^{21}$ = +79.4 (*c* 0.57, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.67 (d, *J* = 6.7 Hz, 3 H), 1.13 (d, *J* = 6.8 Hz, 3 H), 2.29 (dhept, *J* = 6.8, 2.8 Hz, 1 H), 3.93 (s, 3 H), 5.37 (dd, *J* = 6.1, 2.7 Hz, 1 H), 6.73 (d, *J* = 5.5 Hz, 1 H), 7.13 (m_c, 2 H), 8.03 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 15.2, 21.1, 32.9, 56.2, 70.5, 115.5, 122.7, 132.6, 165.3, 179.3. – IR (neat): ν = 3268, 2966, 2933, 2876, 2843, 1603, 1585, 1553, 1512, 1463, 1423, 1375, 1305, 1260, 1235, 1154, 1013, 964, 940, 841, 817, 774, 716, 616, 576, 524, 490, 441, 410. – ESI (HR-MS) calcd. for $C_{12}H_{15}N_2O_3S$: 267.0809; found 267.0809. – Anal. Calcd. (%) for $C_{12}H_{16}N_2O_3S$ (268.3): C, 53.71; H, 6.01; N, 10.44. Found: C, 53.51; H, 6.05; N, 10.24. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate: 1.5 mL/min), retention times: (*R*)-enantiomer 21.7 min, (*S*)-enantiomer 24.4 min, 96% ee.

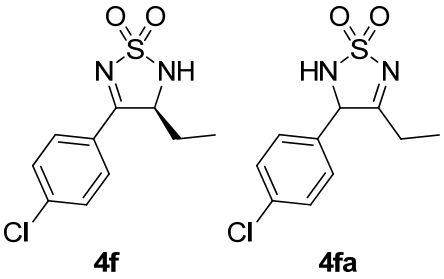




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	22,617	49,95	36,8	29,2	49,952
2	Peak 2	26,158	50,05	32,8	29,3	50,048
Total			100,00	69,6	58,5	100,000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	21,708	2,00	2,4	2,3	2,001
2	Peak 2	24,383	98,00	78,0	112,4	97,999
Total			100,00	80,4	114,7	100,000

(*S*)-4-Ethyl-3-(4-chlorophenyl)-1,2,5-thiadiazoline-1,1-dioxide (4f) and 3-Ethyl-4-(4-chlorophenyl)-1,2,5-thiadiazoline-1,1-dioxide (4fa):

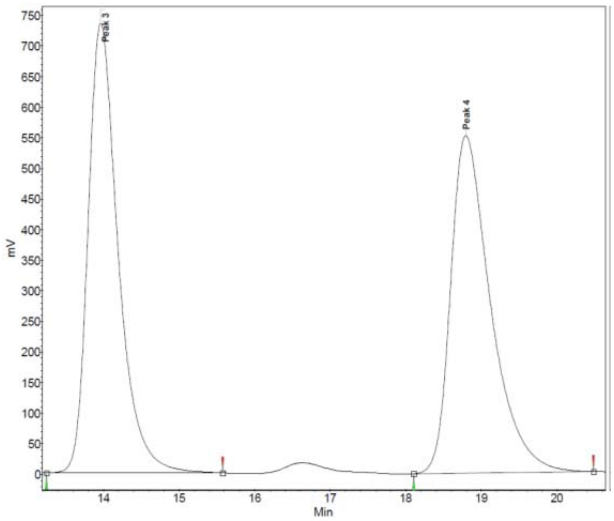


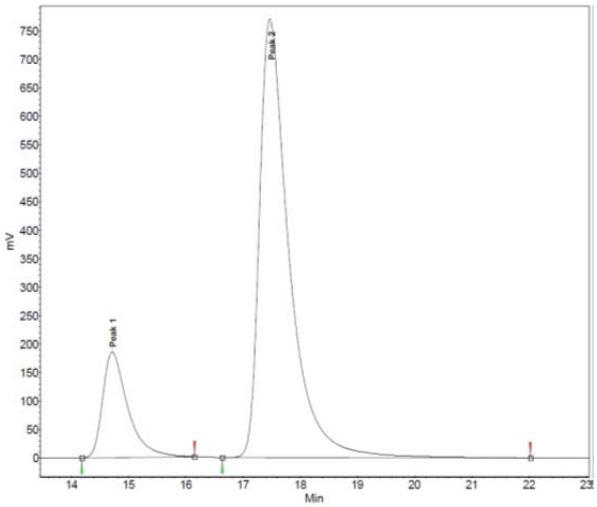
Prepared according to GP 3 from the mixture of **2f** and its tautomer **3f** (303 mg, 1.18 mmol), RuCl(*p*-cymene)-[(*S*,*S*)-TsDPEN] (38.0 mg, 0.0597 mmol), and the mixture of formic acid and triethylamine (0.743 mL, 0.765 g, 1.77 mmol) in acetonitrile (30 mL) at –15 °C for 41 h. Flash column chromatography (CH_2Cl_2/MeOH 200:1) furnished a 3.2:1 mixture (278 mg, 91%) of 4-ethyl-3-(4-chlorophenyl)-1,2,5-thiadiazoline-1,1-dioxide (**4f**) and 3-ethyl-4-(4-chlorophenyl)-1,2,5-thiadiazoline-1,1-dioxide (**4af**) (R_f = 0.15) as a colorless solid. Partial separation could be achieved by repeated column chromatography.

4f: ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.99 (t, *J* = 7.3 Hz, 3 H), 1.68 (m_c, 1 H), 1.96 (ddq, *J* = 14.7, 7.4, 3.3 Hz, 1 H), 5.37 (ddd, *J* = 8.7, 5.6, 3.3 Hz, 1 H), 6.87 (m_c, 1 H), 7.65 (m_c, 2 H), 8.09 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.3, 28.1, 66.5, 130.4, 132.0, 136.2, 140.7, 179.8.

4fa: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.11 (t, *J* = 7.3 Hz, 3 H), 2.32 (dq, *J* = 18.3, 7.2 Hz, 1 H), 2.61 (dq, *J* = 18.3, 7.3 Hz, 1 H), 5.75 (d, *J* = 5.2 Hz, 1 H), 7.30 (m_c, 1 H), 7.48 (m_c, 4 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 9.9, 25.7, 70.3, 128.9, 130.1, 130.2, 135.3, 186.8.

4f, 4fa: IR (neat): ν = 3237, 2923, 2854, 1711, 1682, 1589, 1535, 1441, 1403, 1330, 1160, 1089, 1011, 979, 938, 880, 843, 815, 757, 728, 676, 641, 575, 529, 475, 432. – ESI (HR-MS) calcd. for $C_{10}H_{11}{}^{35}ClN_2O_2SNa$: 281.0122, $C_{10}H_{11}{}^{36}ClN_2O_2SNa$: 282.0150, $C_{10}H_{11}{}^{37}ClN_2O_2SNa$: 283.0120; found: 281.0124, 282.0160, 283.0096. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate: 1.5 mL/min). Retention times (*R*)-enantiomer 14.7 min, (*S*)-enantiomer 17.5 min, 66% ee.

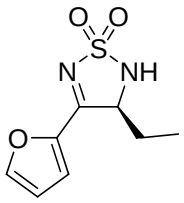




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 3	13,967	50,07	734,7	338,6	50,070
2	Peak 4	18,792	49,93	551,7	337,6	49,930
Total			100,00	1286,4	676,2	100,000

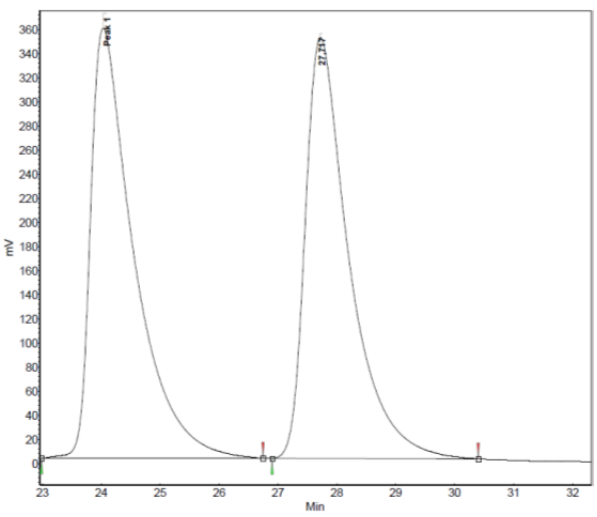
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	14,708	16,99	185,2	94,6	16,991
2	Peak 2	17,467	83,01	769,8	462,0	83,009
Total			100,00	955,1	556,6	100,000

(*S*)-4-Ethyl-3-(furan-2-yl)-1,2,5-thiadiazoline-1,1-dioxide (4g)

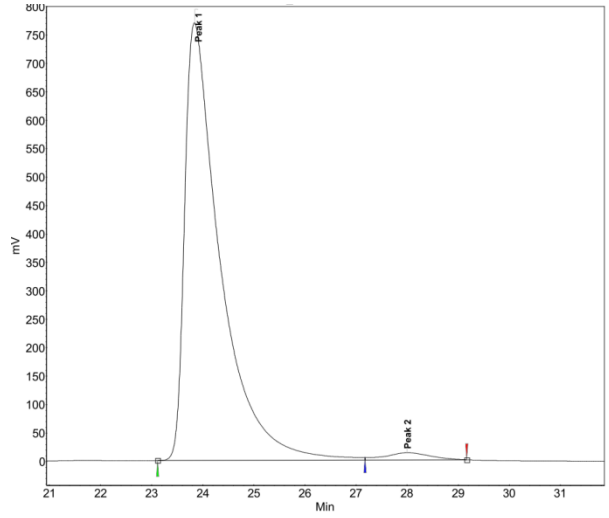


4g

Prepared according to GP 3 from the mixture of **2g** and its tautomer **3g** (312 mg, 1.47 mmol), RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN] (47.0 mg, 0.0739 mmol), and the mixture of formic acid and triethylamine (0.926 mL, 0.954 g, 2.21 mmol) in acetonitrile (35 mL) at –20 °C for 50 h. Flash column chromatography (cyclohexane/EtOAc1:1) furnished 267 mg (85%) of the title compound as a yellow solid, mp 72 °C. – $[\alpha]_D^{21}$ = +6.8 (*c* 0.62, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.02 (t, *J* = 7.3 Hz, 3 H), 1.80 (ddq, *J* = 8.7, 6.0, 3.3 Hz, 1 H), 2.05 (m_c, 1 H), 5.07 (ddd, *J* = 8.8, 5.9, 3.2 Hz, 1 H), 6.68 (m_c, 1 H), 6.84 (dd, *J* = 3.7, 1.7 Hz, 1 H), 7.64 (dd, *J* = 3.7, 0.7 Hz,1 H), 8.06 (d, *J* = 1.6 Hz, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.5, 28.4, 66.4, 114.3, 122.0, 146.6, 150.3, 169.2. – IR (neat): ν = 3241, 3139, 2979, 2939, 2877, 2362, 1594, 1536, 1460, 1381, 1339, 1309, 1256, 1169, 1104, 1084, 1033, 1008, 976, 930, 883, 769, 702, 678, 636, 589, 545, 514, 474, 451. – ESI (HR-MS) calcd. for $C_8H_{10}N_2O_3SNa$: 237.0304; found 237.0305. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IA, hexane/2-propanol 9:1, flow rate: 1.0 mL/min), retention times: (*S*)-enantiomer 23.8 min, (*R*)-enantiomer 28.0 min, 96% ee.

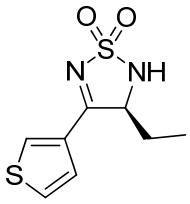


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	24.033	50.18	356.8	302.5	50.181
2	Peak 2	27.717	49.82	349.1	300.3	49.819
Total			100.00	705.9	602.9	100.000



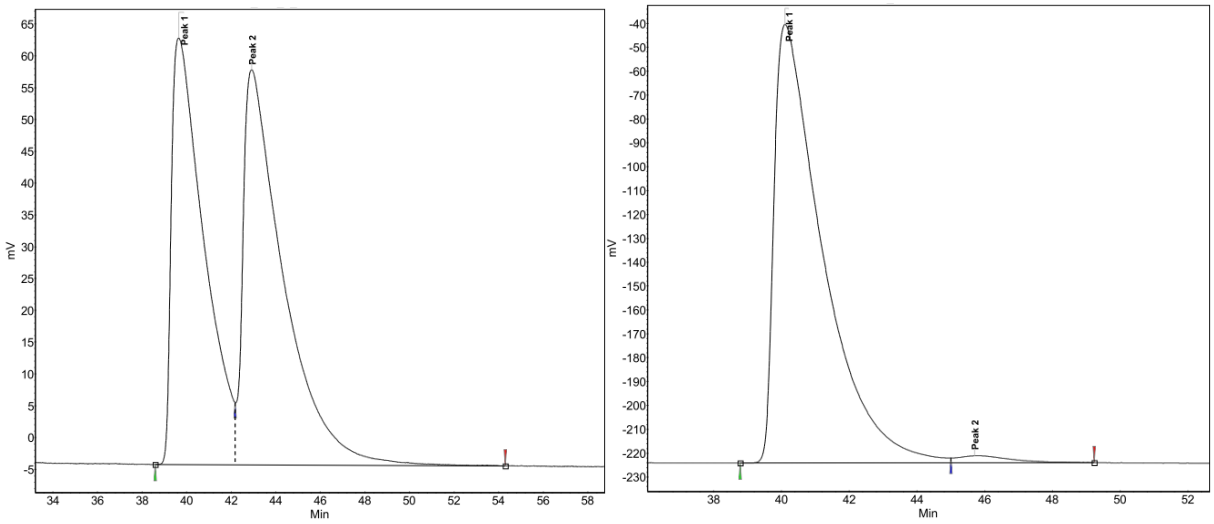
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	23.842	97.97	769.5	618.8	97.971
2	Peak 2	28.000	2.03	12.7	12.8	2.029
Total			100.00	782.2	631.6	100.000

(*S*)-4-Ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazoline-1,1-dioxide (4h)



4h

Prepared according to GP 3 from the mixture of **2h** and its tautomer **3h** (401 mg, 1.76 mmol), RuCl(*p*-cymene)[(*S*,*S*)-Ts-DPEN] (56.0 mg, 0.0880 mmol), and the mixture of formic acid and triethylamine (1.11 mL, 1.14 g, 2.64 mmol) in acetonitrile (35 mL) at –20 °C for 55 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 290 mg (72%) of the title compound as a colorless solid, mp 119 °C. – $[\alpha]_D^{21}$ = +16.1 (*c* 1.01, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.02 (t, *J* = 7.3 Hz, 3 H), 1.77 (ddq, *J* = 14.4, 8.6, 7.3 Hz, 1 H), 2.04 (m_c, 1 H), 5.22 (ddd, *J* = 8.7, 5.7, 3.2 Hz, 1 H), 6.73 (d, *J* = 5.5 Hz, 1 H), 7.73 (m_c, 2 H), 8.58 (m_c, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 10.4, 28.8, 67.1, 128.2, 129.0, 133.1, 135.5, 175.2. – IR (neat): ν = 3272, 3094, 2979, 2934, 1572, 1518, 1457, 1425, 1365, 1333, 1299, 1280, 1251, 1228, 1201, 1154, 1108, 1081, 1052, 1029, 987, 905, 875, 817, 783, 740, 692, 664, 617, 539, 507, 437, 389. – ESI (HR-MS) calcd. for $C_8H_{10}N_2O_2S_2Na$: 253.0076; found 253.0076. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IB, hexane/2-propanol 9:1, flow rate: 1.0 mL/min), retention times: (*S*)-enantiomer 40.1 min, (*R*)-enantiomer 45.7 min, 96% ee.

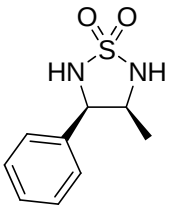


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	39,642	46,19	67,1	112,3	46,185
2	Peak 2	42,917	53,81	62,1	130,9	53,815
Total			100,00	129,2	243,2	100,000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	40,108	98,28	183,6	303,3	98,278
2	Peak 2	45,700	1,72	3,0	5,3	1,722
Total			100,00	186,6	308,6	100,000

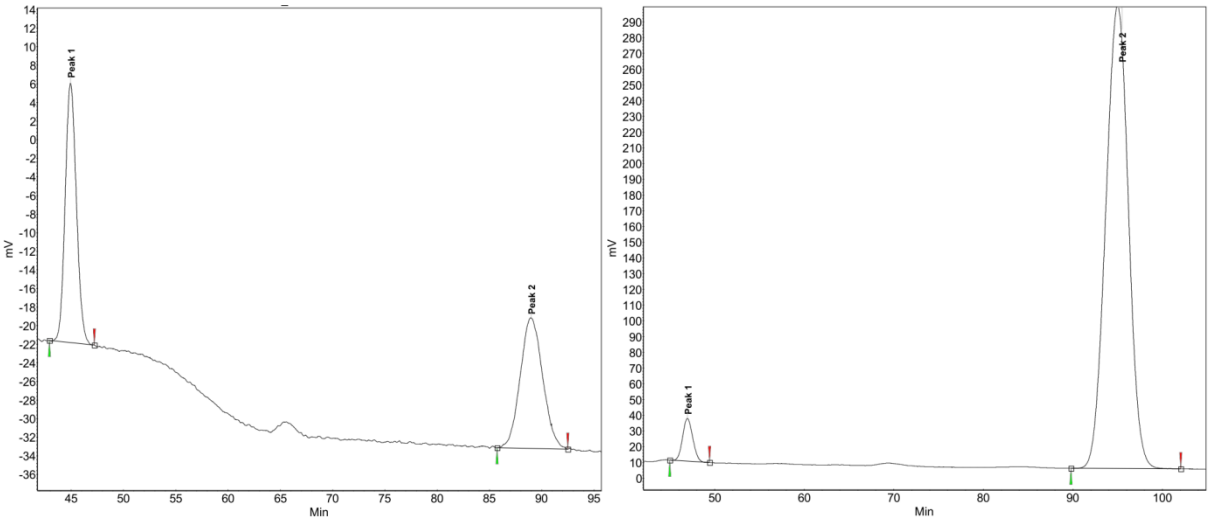
General Procedure for the Synthesis of *cis*-1,2,5-Thiadiazolidine-1,1-dioxides 5 (GP 4): A solution of the respective 1,2,5-thiadiazoline-1,1-dioxide **4** (1.00 mmol) in THF (35 mL) was cooled to 0 °C and treated with a solution of $LiBH_4$ (1.0 M in diethyl ether). The reaction mixture was gradually warmed to rt and stirred for 14 h. The pH value of the reaction mixture was adjusted to 3 by addition of HCl (1 M), water (25 mL) and EtOAc (25 mL) were added, the organic layer was separated, and the aqueous phase was re-extracted with EtOAc (25 mL). The combined organic phases were washed with brine (50 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

(3*R*,4*S*)-4-Methyl-3-phenyl-1,2,5-thiadiazolidine-1,1-dioxide (5b)



5b

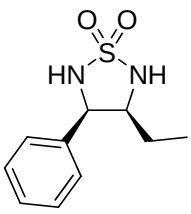
Prepared according to GP 4 from (*S*)-4-methyl-3-phenyl-1,2,5-thiadiazoline-1,1-dioxide (**4b**, 141 mg, 0.671 mmol) and $LiBH_4$ solution (2.68 mL, 2.68 mmol) in THF (25 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 129 mg (91%) of the title compound (R_f = 0.35) as a colorless solid, mp 90-91 °C. – $[\alpha]_D^{21}$ = –37.8 (*c* 0.41, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.90 (d, *J* = 6.7 Hz, 3 H), 4.19 (m_c, 1 H), 4.99 (t, *J* = 5.9 Hz, 1 H), 6.00 (d, *J* = 8.7 Hz, 1 H), 6.58 (d, *J* = 5.8 Hz, 1 H), 7.28-7.40 (m, 3 H), 7.49 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 15.9, 57.0, 65.5, 128.4, 128.5, 128.9, 138.6. – IR (neat): ν = 3335, 3227, 3059, 2975, 2930, 2875, 1694, 1604, 1495, 1452, 1403, 1373, 1345, 1273, 1229, 1145, 1074, 1004, 964, 929, 895, 862, 802, 762, 738, 697, 607, 478, 450. – ESI (HR-MS) calcd. for $C_9H_{12}N_2O_2SNa$: 235.0512; found 235.0510. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 4:1, flow rate: 1.0 mL/min), retention times: (3*S*,4*R*)-enantiomer 46.9 min, (3*R*,4*S*)-enantiomer 95.0 min, 92% ee.



Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	44.933	49.86	27.9	34.6	49.861
2	Peak 2	88.992	50.14	14.0	34.8	50.139
Total			100.00	41.9	69.4	100.000

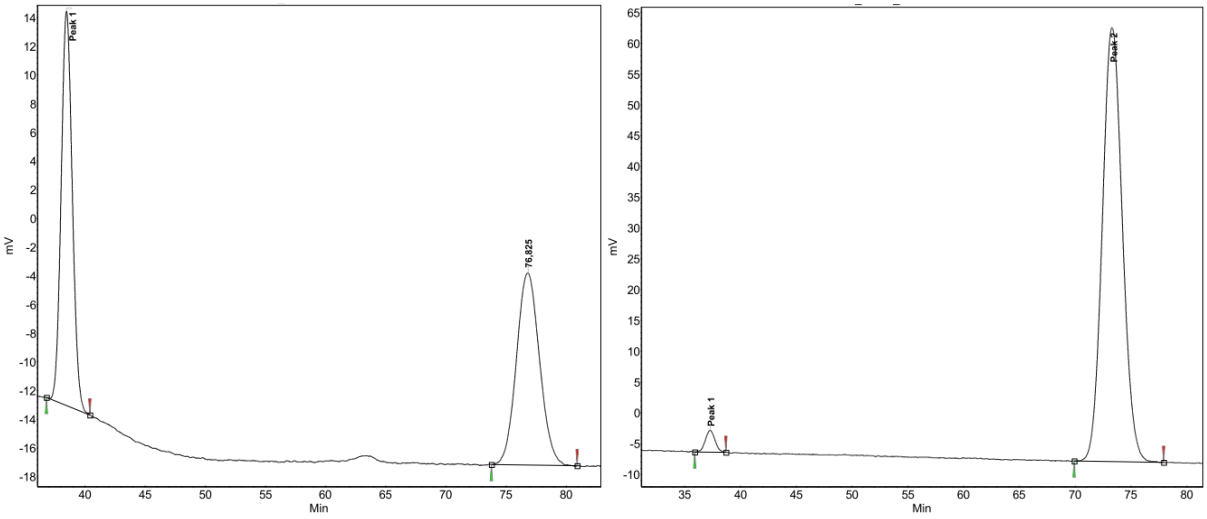
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	46.933	3.93	27.1	35.3	3.929
2	Peak 2	94.992	96.07	294.4	863.7	96.071
Total			100.00	321.5	899.0	100.000

(3*R*,4*S*)-4-Ethyl-3-phenyl-1,2,5-thiadiazolidine-1,1-dioxide (5c)



5c

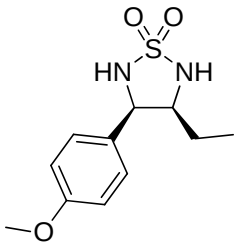
Prepared according to GP 4 from (*S*)-4-ethyl-3-phenyl-1,2,5-thiadiazoline-1,1-dioxide (**4c**, 310 mg, 1.38 mmol) and $LiBH_4$ solution (5.53 mL, 5.53 mmol) in THF (50 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 292 mg (93%) of the title compound (R_f = 0.35) as a colorless solid, mp 92 °C. – $[\alpha]_D^{21}$ = −35.7 (*c* 0.65, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.05 (ddq, *J* = 15.0, 10.9, 7.5 Hz, 1 H), 1.27 (ddq, *J* = 14.3, 7.3, 4.2 Hz, 1 H), 3.95 (ddt, *J* = 10.1, 6.2, 4.3 Hz, 1 H), 4.98 (t, *J* = 5.9 Hz, 1 H), 6.01 (m_c, 1 H), 6.59 (m_c, 1 H), 7.27-7.39 (m, 3 H), 7.49 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.6, 24.2, 63.5, 65.5, 128.50, 128.53, 128.9, 139.0. – IR (neat): ν = 3245, 2961, 2938, 1457, 1410, 1353, 1309, 1284, 1250, 1158, 1116, 1085, 1054, 1013, 973, 943, 914, 886, 807, 782, 750, 704, 637, 608, 545, 488, 459, 404. – ESI (HR-MS) calcd. for $C_{10}H_{14}N_2O_2SNa$: 249.0668; found 249.0665. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 4:1, flow rate: 1.0 mL/min), retention times: (3*S*,4*R*)-enantiomer 37.3 min, (3*R*,4*S*)-enantiomer 73.3 min, 95% ee.



Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	38,467	49,79	27,5	29,4	49,791
2	UNKNOWN	76,825	50,21	13,4	29,7	50,209
Total			100,00	40,9	59,1	100,000

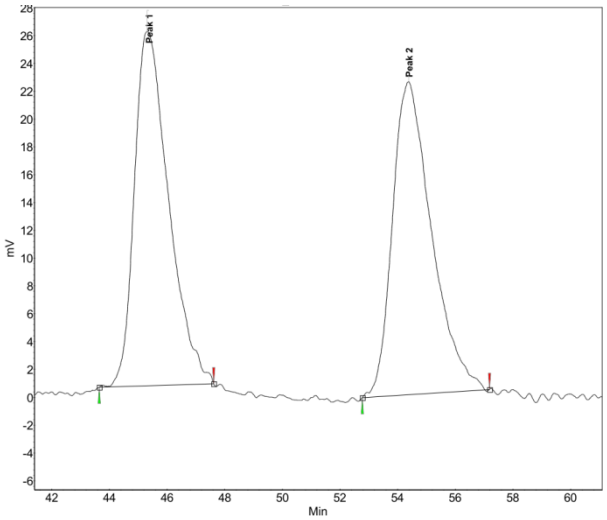
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	37,283	2,34	3,5	3,5	2,341
1	Peak 2	73,292	97,66	70,4	146,7	97,659
Total			100,00	74,0	150,2	100,000

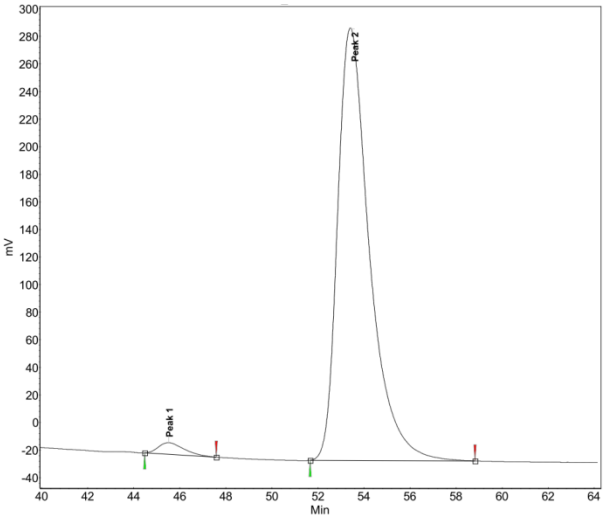
(3*R*,4*S*)-4-Ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (5d)



5d

Prepared according to GP 4 from (*S*)-4-ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazoline-1,1-dioxide (**4d**, 445 mg, 1.75 mmol) and $LiBH_4$ solution (6.99 mL, 6.99 mmol) in THF (80 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 416 mg (93%) of the title compound (R_f = 0.32) as a colorless solid, mp 134-135 °C. – $[\alpha]_D^{21}$ = −24.7 (*c* 0.63, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.10 (ddq, *J* = 13.8, 9.7, 6.9 Hz, 1 H), 1.26 (m_c, 1 H), 3.79 (s, 3 H), 3.90 (m_c, 1 H), 4.92 (t, *J* = 5.7 Hz, 1 H), 5.97 (m_c, 1 H), 6.52 (m_c, 1 H), 6.92 (m_c, 2 H), 7.41 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.6, 24.2, 55.5, 63.7, 65.0, 114.3, 129.7, 130.9, 160.3. – IR (neat): ν = 3237, 3034, 2934, 2838, 1715, 1615, 1584, 1513, 1461, 1409, 1367, 1327, 1283, 1245, 1153, 1116, 1057, 1028, 973, 934, 883, 838, 807, 767, 729, 689, 629, 601, 534, 503, 418, 394. – ESI (HR-MS) calcd. for $C_{11}H_{16}N_2O_3SNa$: 279.0774; found 279.0780. – The enantiomeric excess was determined by chiral HPLC analysis (Chiralpak IA, hexane/2-propanol 95:5, flow rate: 1.5 mL/min), retention times: (3*S*,4*R*)-enantiomer 45.5 min, (3*R*,4*S*)-enantiomer 53.4 min, 96% ee.

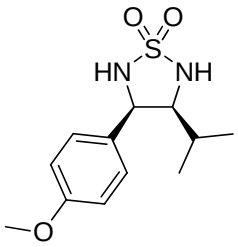




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	45.308	49.82	25.5	35.1	49.822
2	Peak 2	54.383	50.18	22.5	35.3	50.178
Total			100.00	48.0	70.4	100.000

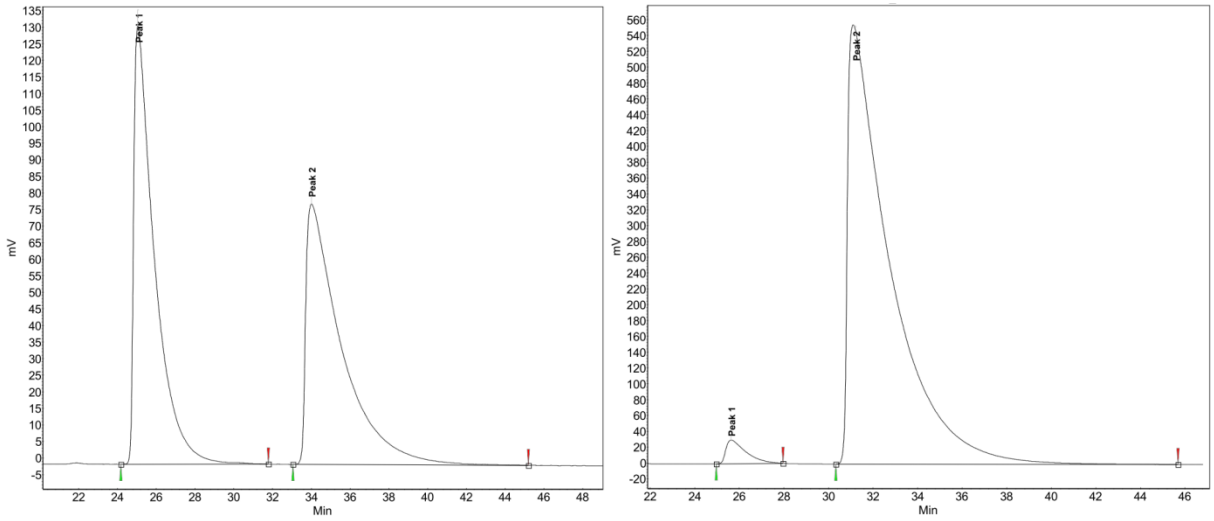
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	45.517	2.12	8.5	10.9	2.124
2	Peak 2	53.417	97.88	313.5	502.0	97.876
Total			100.00	322.0	512.9	100.000

(3*R*,4*S*)-4-Isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (5e)



5e

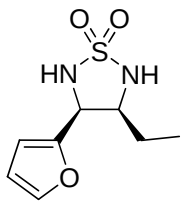
Prepared according to GP 4 from (*S*)-4-isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazoline-1,1-dioxide (**4e**, 128 mg, 0.477 mmol) and $LiBH_4$ solution (1.90 mL, 1.90 mmol) in THF (20 mL). Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 122 mg (95%) of the title compound (R_f = 0.37) as a colorless solid, mp 147 °C. – $[\alpha]_D^{21}$ = +20.1 (*c* 0.77, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.85 (d, *J* = 6.5 Hz, 3 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 1.35 (dhept, *J* = 9.8, 6.5 Hz, 1 H), 3.65 (dt, *J* = 9.6, 5.7 Hz, 1 H), 3.79 (s, 3 H), 4.87 (t, *J* = 5.3 Hz, 1 H), 6.08 (d, *J* = 9.5 Hz, 1 H), 6.50 (m_c, 1 H), 6.91 (m_c, 2 H), 7.49 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 19.5, 20.9, 28.7, 55.5, 64.6, 68.2, 114.3, 130.5, 131.3, 160.3. – IR (neat): ν = 3255, 3041, 2934, 2840, 1614, 1582, 1514, 1460, 1402, 1375, 1344, 1312, 1286, 1250, 1180, 1151, 1030, 1003, 937, 882, 834, 803, 777, 731, 706, 683, 594, 533, 505, 413. – ESI (HR-MS) calcd. for $C_{12}H_{18}N_2O_3SNa$: 293.0930; found 293.0927. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IB, hexane/2-propanol 9:1, flow rate: 1.5 mL/min), retention times: (3*S*,4*R*)-enantiomer 25.6 min, (3*R*,4*S*)-enantiomer 31.1 min, 95% ee.



Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	25.050	49.66	132.1	163.3	49.655
2	Peak 2	34.008	50.34	78.6	165.6	50.345
Total			100.00	210.7	329.0	100.000

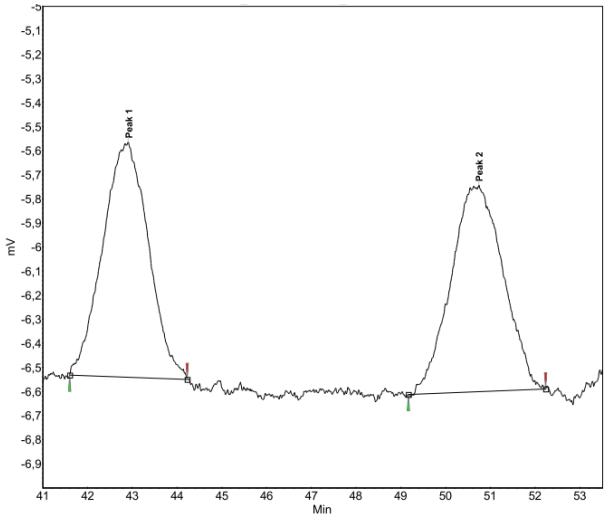
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	25.633	2.51	30.0	31.2	2.510
2	Peak 2	31.108	97.49	554.7	1213.9	97.490
Total			100.00	584.7	1245.2	100.000

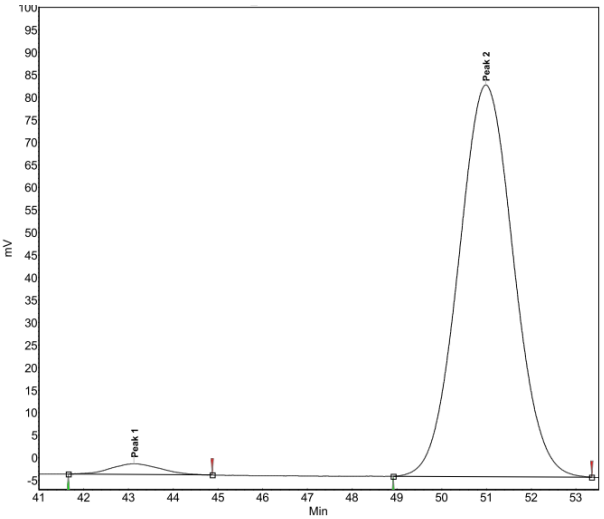
(3*R*,4*S*)-4-Ethyl-3-(furan-2-yl)-1,2,5-thiadiazolidine-1,1-dioxide (5g)



5g

Prepared according to GP 4 from (*S*)-4-ethyl-3-(furan-2-yl)-1,2,5-thiadiazolidine-1,1-dioxide (**4g**, 10.7 mg, 0.0499 mmol) and $LiBH_4$ solution (50 µL, 50 µmol) in THF (2 mL). Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 10.5 mg (97%) of the title compound (R_f = 0.48) as a colorless solid, mp: 98 °C. – $[\alpha]_D^{21} = -2.9$ (*c* 0.69, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.97 (t, *J* = 7.3 Hz, 3 H), 1.36 (m_c, 2 H), 3.87 (ddt, *J* = 10.8, 9.0, 5.5 Hz, 1 H), 4.96 (t, *J* = 5.6 Hz, 1 H), 5.89 (m_c, 1 H), 6.42 (dd, *J* = 3.3, 1.9 Hz, 1 H), 6.51 (d, *J* = 3.3 Hz, 1 H), 6.55 (m_c, 1 H), 7.52 (dd, *J* = 1.8, 0.9 Hz, 1 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.4, 23.6, 60.0, 64.1, 109.7, 111.2, 143.4, 152.9. – IR (neat): ν = 3249, 2972, 2937, 2882, 1505, 1461, 1402, 1337, 1286, 1254, 1162, 1068, 1010, 965, 911, 876, 818, 796, 735, 678, 595, 505, 466. – ESI (HR-MS) calcd. for $C_8H_{12}N_2O_3SNa$: 239.0461; found 239.0459. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 4:1, flow rate: 1.0 mL/min), retention times: (3*S*,4*R*)-enantiomer 43.1 min, (3*R*,4*S*)-enantiomer 51.0 min, 95% ee.

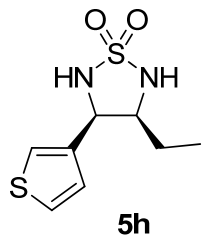




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
2	Peak 1	42,908	49,84	1,0	1,2	49,840
1	Peak 2	50,742	50,16	0,9	1,2	50,160
Total			100,00	1,8	2,3	100,000

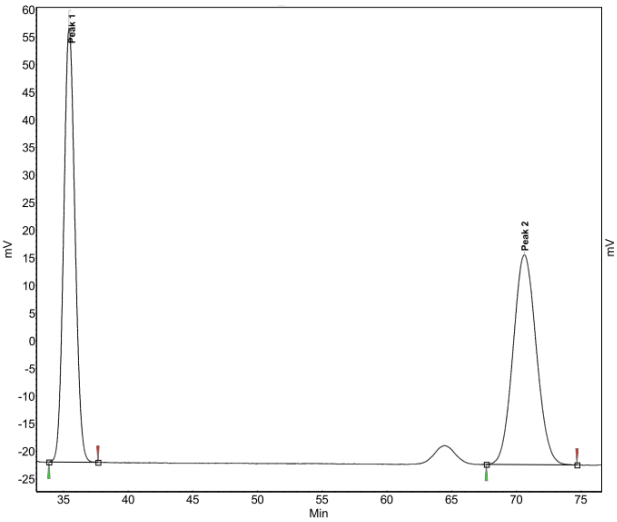
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	43,125	2,41	2,4	3,1	2,409
2	Peak 2	50,983	97,59	87,0	123,8	97,591
Total			100,00	89,3	126,8	100,000

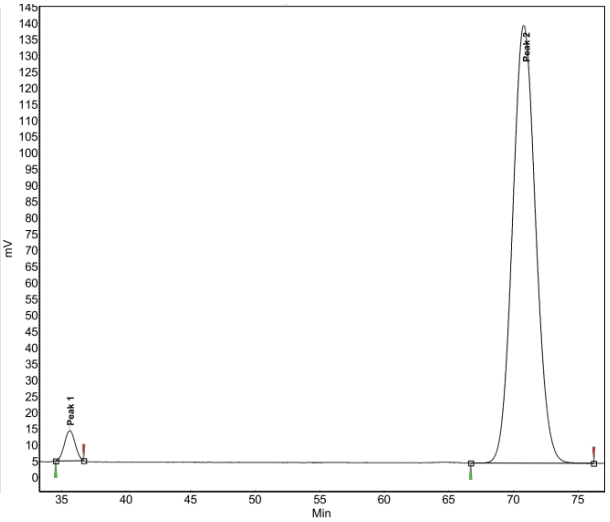
(3*R*,4*S*)-4-Ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazolidine-1,1-dioxide (5h)



5h

Prepared according to GP 4 from (*S*)-4-ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazoline-1,1-dioxide (**4h**, 38.3 mg, 0.166 mmol) and $LiBH_4$ solution (0.664 mL, 0.664 mmol) in THF (3 mL). Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 37.0 mg (96%) of the title compound (R_f = 0.38) as a colorless solid, mp 63 °C. – $[\alpha]_D^{21}$ = –5.3 (*c* 0.81, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.93 (t, *J* = 7.4 Hz, 3 H), 1.28 (m_c, 2 H), 3.88 (m_c, 1 H), 5.06 (t, *J* = 5.7 Hz, 1 H), 5.99 (d, *J* = 9.1 Hz, 1 H), 6.54 (d, *J* = 5.9 Hz, 1 H), 7.24 (dd, *J* = 4.9, 1.4 Hz, 1 H), 7.47 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.5, 23.9, 62.0, 64.1, 123.8, 126.6, 128.3, 140.1. – IR (neat): ν = 3251, 3106, 2970, 2934, 2880, 1459, 1402, 1282, 1157, 1087, 1055, 1028, 971, 915, 854, 795, 750, 689, 614, 563, 506, 460. – ESI (HR-MS) calcd. for $C_8H_{12}N_2O_2S_2Na$: 255.0243; found 255.0234. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 3:1, flow rate: 0.9 mL/min), retention times: (3*S*,4*R*)-enantiomer 35.7 min, (3*R*,4*S*)-enantiomer 70.8 min, 94% ee.





Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	35,442	50,05	78,6	79,3	50,047
2	Peak 2	70,625	49,95	38,0	79,1	49,953
Total			100,00	116,6	158,4	100,000

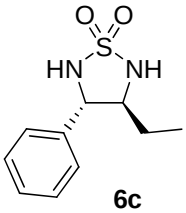
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	35,650	3,07	9,2	8,9	3,075
2	Peak 2	70,783	96,93	134,8	279,9	96,925
Total			100,00	144,1	288,8	100,000

General Procedure for the Isomerization of 1,2,5-Thiadiazolidine-1,1-dioxides 5 (GP 5)

Method A: The respective *cis*-1,2,5-thiadiazolidine-1,1-dioxide **5** (1.00 mmol) was dissolved in trifluoroacetic acid (10 mL) and stirred at rt for the given time in an open flask. The acid was removed under reduced pressure and the crude product was purified by flash column chromatography.

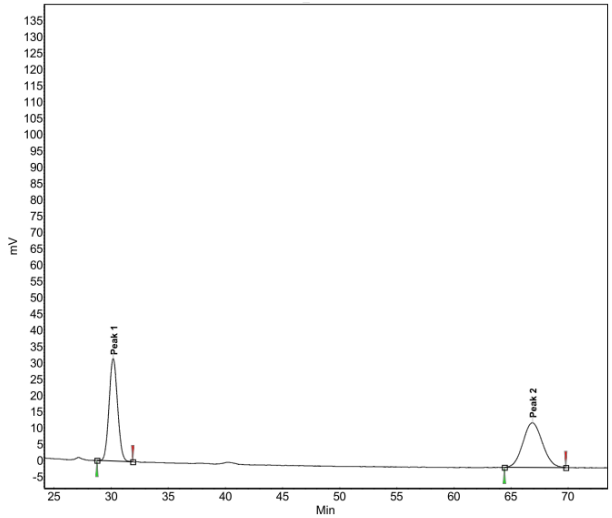
Method B: The respective *cis*-1,2,5-thiadiazolidine-1,1-dioxide **5** (1.00 mmol) was dissolved in sulfuric acid (10 mL) and stirred at rt for the given time in an open flask. The reaction mixture was poured into water (75 mL) and the aqueous phase was extracted with EtOAc (3 * 30 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography.

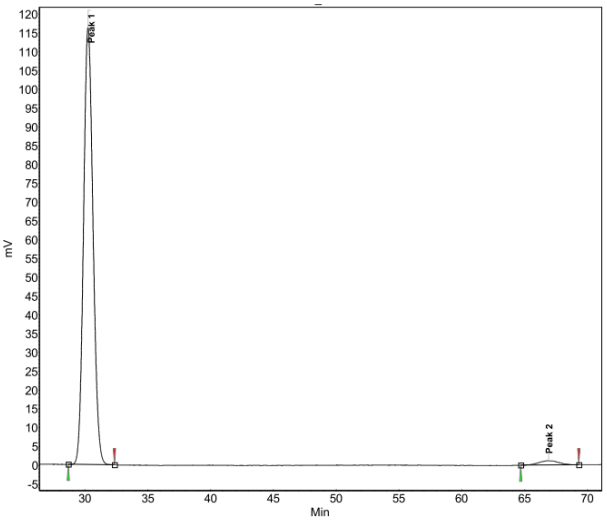
(3*S*,4*S*)-4-Ethyl-3-phenyl-1,2,5-thiadiazolidine-1,1-dioxide (6c)



6c

Prepared according to GP 5, method B from *cis*-4-ethyl-3-phenyl-1,2,5-thiadiazolidine-1,1-dioxide (**5c**, 26 mg, 0.11 mmol) with sulfuric acid (1.0 mL) for 3.5 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 25 mg (96%) of the title compound (R_f = 0.42) as a colorless solid, mp 88 °C. – $[\alpha]_D^{21}$ = +7.2 (*c* 0.43, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 1.72 (m_c, 2 H), 3.51 (ddt, *J* = 8.4, 7.4, 5.9 Hz, 1 H), 4.51 (dd, *J* = 7.5, 5.9 Hz, 1 H), 6.17 (m_c, 1 H), 6.49 (m_c, 1 H), 7.30-7.42 (m, 3 H), 7.52 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.4, 26.5, 66.9, 67.1, 128.1, 128.9, 129.4, 140.8. – IR (neat): ν = 3267, 3226, 3031, 2967, 2921, 2867, 1603, 1540, 1496, 1455, 1402, 1356, 1312, 1261, 1232, 1150, 1120, 1081, 1045, 1023, 958, 911, 868, 795, 740, 697, 629, 554, 517, 492, 462, 404. – ESI (HR-MS) calcd. for $C_{10}H_{13}N_2O_2S$: 225.0703; found 225.0703. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 4:1, flow rate: 1.0 mL/min), retention times: (3*S*,4*S*)-enantiomer 30.2 min, (3*R*,4*R*)-enantiomer 66.9 min, 96% ee.

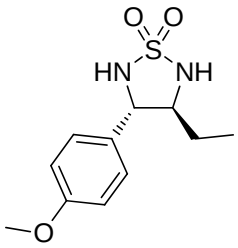




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	30,175	50,15	31,4	27,2	50,148
2	Peak 2	66,875	49,85	13,7	27,0	49,852
Total			100,00	45,1	54,2	100,000

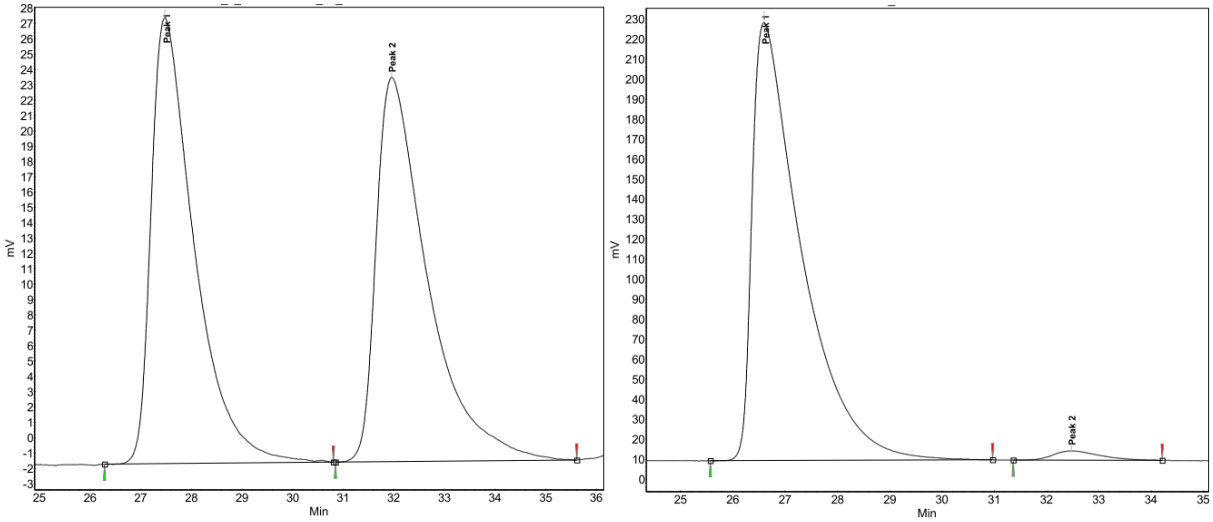
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	30,242	98,01	116,2	101,5	98,011
2	Peak 2	66,900	1,99	1,1	2,1	1,989
Total			100,00	117,3	103,5	100,000

(3*S*,4*S*)-4-Ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (6d)



6d

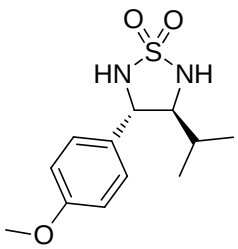
Prepared according to GP 5, method A from *cis*-4-ethyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (**5d**, 208 mg, 0.811 mmol) with trifluoroacetic acid (15 mL) for 4 h. Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 193 mg (93%) of the title compound (R_f = 0.15) as a colorless solid, mp 87 °C. – $[\alpha]_D^{21}$ = +7.9 (*c* 0.53, EtOH). – ^{1}H NMR (300 MHz, acetone-d$_6$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.69 (m$_c$, 2 H), 3.49 (m$_c$, 1 H), 3.80 (s, 3 H), 4.43 (dd, *J* = 7.4, 6.3 Hz, 1 H), 6.13 (m$_c$, 1 H), 6.38 (m$_c$, 1 H), 6.94 (m$_c$, 2 H), 7.43 (m$_c$, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d$_6$): δ = 11.5, 26.3, 55.6, 66.7, 67.0, 114.8, 129.4, 132.2, 160.6. – IR (neat): ν = 3274, 3212, 3020, 2969, 2929, 2866, 2839, 1613, 1513, 1459, 1394, 1352, 1296, 1252, 1178, 1151, 1125, 1049, 1027, 1002, 963, 912, 871, 826, 804, 772, 737, 708, 634, 572, 514, 440. – ESI (HR-MS) calcd. for $C_{11}H_{16}N_2O_3SNa$: 279.0774; found 279.0772. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IB, hexane/2-propanol 9:1, flow rate: 1.5 mL/min), retention times: (3*S*,4*S*)-enantiomer 26.6 min, (3*R*,4*R*)-enantiomer 32.5 min, 96% ee.



Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	27,475	49,32	29,0	28,6	49,322
2	Peak 2	31,958	50,68	25,0	29,4	50,678
Total			100,00	54,1	58,0	100,000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	26,600	98,05	218,7	237,7	98,052
2	Peak 2	32,475	1,95	4,6	4,7	1,948
Total			100,00	223,2	242,4	100,000

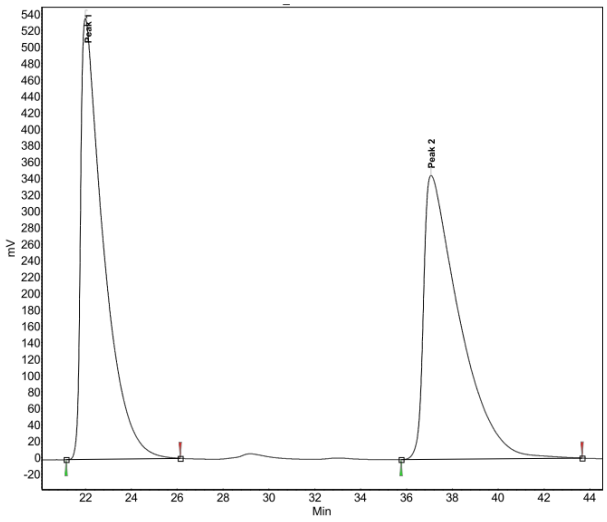
(3*S*,4*S*)-4-Isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (6e)

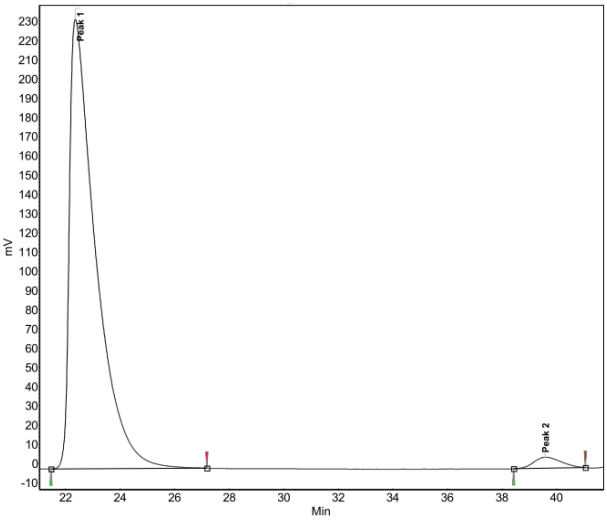


6e

Prepared according to GP 5, method A from *cis*-4-isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (**5e**, 54.2 mg, 0.200 mmol) with trifluoroacetic acid (4 mL) for 4 h. Flash column chromatography (cyclohexane/EtOAc 2:1) furnished 51.0 mg (94%) of the title compound (R_f = 0.21) as a colorless solid, mp 84 °C. – $[\alpha]_D^{20}$ = +1.1 (*c* 0.37, EtOH). – ^{1}H NMR (300 MHz, acetone-d$_6$): δ = 0.93 (d, *J* = 6.8 Hz, 3 H), 1.03 (d,

J = 6.7 Hz, 3 H), 1.91 (m_c, 1 H), 3.48 (m_c, 1 H), 3.79 (s, 3 H), 4.64 (t, J = 6.4 Hz, 1 H), 6.17 (m_c, 1 H), 6.33 (m_c, 1 H), 6.94 (m_c, 2 H), 7.45 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 18.4, 20.5, 31.3, 55.6, 63.5, 70.6, 114.7, 129.5, 133.3, 160.4. – IR (neat): ν = 3254, 2963, 2934, 2840, 1612, 1586, 1513, 1464, 1402, 1304, 1246, 1155, 1027, 959, 925, 831, 765, 740, 709, 632, 570, 528, 423. – ESI (HR-MS) calcd. for $C_{12}H_{18}N_2O_3SNa$: 293.0930; found 293.0929. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IB, hexane/2-propanol 9:1, flow rate: 1.5 mL/min), retention times: (3*S*,4*S*)-enantiomer 22.4 min, (3*R*,4*R*)-enantiomer 39.6 min, 95% ee.

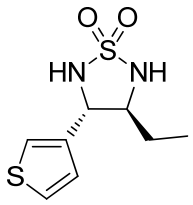




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	21.992	49.82	536.8	617.9	49.821
2	Peak 2	37.067	50.18	345.7	622.3	50.179
Total			100.00	882.6	1240.1	100.000

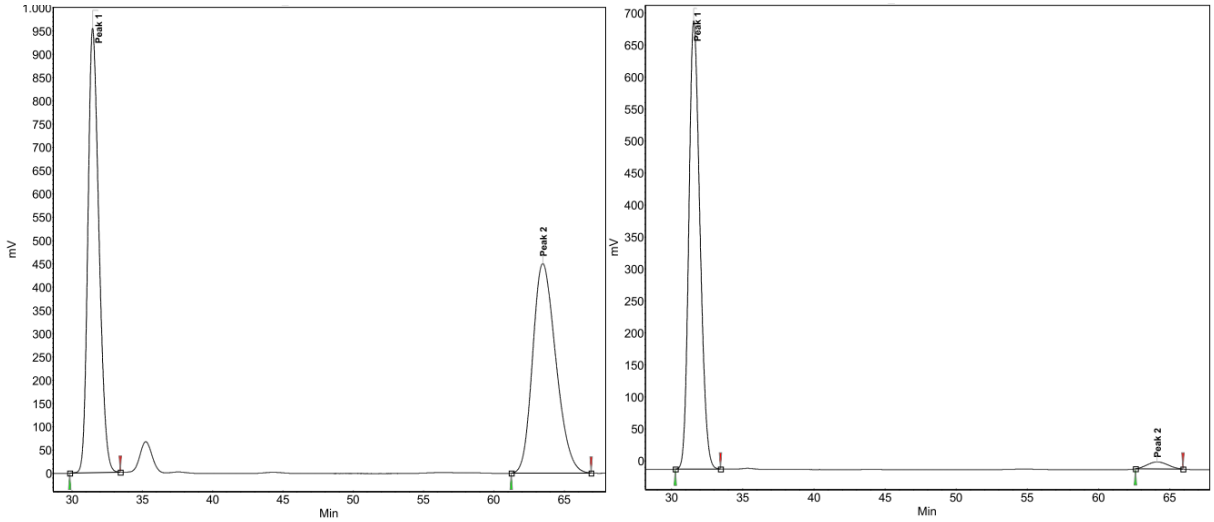
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	22.358	97.52	233.6	258.1	97.523
2	Peak 2	39.575	2.48	5.7	6.6	2.477
Total			100.00	239.3	264.7	100.000

(3*S*,4*S*)-4-Ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazolidine-1,1-dioxide (6h)



6h

Prepared according to GP 5, method A from *cis*-4-ethyl-3-(thiophen-3-yl)-1,2,5-thiadiazolidine-1,1-dioxide (**5h**, 30.8 mg, 0.133 mmol) with trifluoroacetic acid (2.5 mL) for 8 h. Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 28.9 mg (94%) of the title compound (R_f = 0.39) as a colorless solid, mp 45 °C. – $[\alpha]_D^{20}$ = –11.4 (*c* 0.29, THF). – ^{1}H NMR (300 MHz, acetone-d_6): δ = 0.98 (t, J = 7.4 Hz, 3 H), 1.73 (m_c, 2 H), 3.58 (m_c, 1 H), 4.62 (t, J = 6.7 Hz, 1 H), 6.15 (d, J = 8.1 Hz, 1 H), 6.42 (d, J = 6.5 Hz, 1 H), 7.25 (dd, J = 4.9, 1.4 Hz, 1 H), 7.50 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 11.4, 26.7, 62.9, 66.4, 123.8, 127.3, 127.5, 141.7. – IR (neat): ν = 3252, 3106, 2969, 2933, 2880, 1459, 1403, 1286, 1156, 1082, 1042, 970, 892, 859, 788, 750, 691, 641, 528, 457. – ESI (HR-MS) calcd. for $C_8H_{12}N_2O_2S_2Na$: 255.0243; found 255.0235. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol 3:1, flow rate: 0.9 mL/min), retention times: (3*S*,4*S*)-enantiomer 31.6 min, (3*R*,4*R*)-enantiomer 64.1 min, 94% ee.

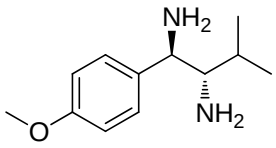


Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	31,467	50,29	954,5	868,0	50,290
2	Peak 2	63,475	49,71	449,3	858,0	49,710
Total			100,00	1403,8	1726,0	100,000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	31,558	97,17	700,6	634,0	97,171
2	Peak 2	64,100	2,83	11,0	18,5	2,829
Total			100,00	711,6	652,5	100,000

General Procedure for the Hydrazinolysis of 1,2,5-Thiadiazolidine-1,1-dioxides (GP 6):
The respective 1,2,5-thiadiazolidine-1,1-dioxide (1.00 mmol) was dissolved in hydrazine-monohydrate (10 mL) and stirred for 14 h at 110 °C under atmospheric conditions. The hydrazine was removed under reduced pressure, EtOAc (20 mL) was added to the concentrate, and the resulting suspension was filtered through celite. The filtrate was extracted with HCl (1 M, 2 * 10 mL) and the combined aqueous layers were then adjusted to pH 14 by addition of aqueous NaOH (6 M). The aqueous phase was extracted with EtOAc (2 * 15 mL) and the combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure to furnish the respective 1,2-diamine in a purity >95%.

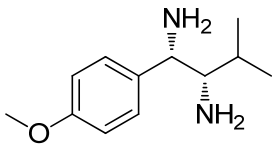
(1*R*,2*S*)-1-(4-Methoxyphenyl)-3-methylbutane-1,2-diamine (7e)



7e

Preparation according to GP 6 from (3*R*,4*S*)-4-isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (**5e**, 92.5 mg, 0.342 mmol) with hydrazine-monohydrate (4.0 mL) furnished 69.7 mg (98%) of the title compound as an ochre solid, mp 84 °C. – $[\alpha]_D^{21}$ = +2.5 (*c* 0.48, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.8 Hz, 3 H), 1.05 (d, *J* = 6.8 Hz, 3 H), 1.23 (bs, 4 H), 1.84 (m_c, 1 H), 2.65 (dd, *J* = 7.1, 5.0 Hz, 1 H), 3.81 (s, 3 H), 3.83 (m_c, 1 H), 6.88 (m_c, 2 H), 7.29 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.1, 21.0, 29.3, 55.3, 58.1, 62.2, 113.8, 128.6, 136.1, 158.9. – IR (neat): ν = 3275, 2960, 2872, 2837, 1664, 1607, 1510, 1462, 1410, 1301, 1246, 1173, 1143, 1102, 1029, 833, 759, 700, 660, 607, 545. – ESI (HR-MS) calcd. for $C_{12}H_{21}N_2O$: 209.1648; found 209.1648.

(1*S*,2*S*)-1-(4-Methoxyphenyl)-3-methylbutane-1,2-diamine (8e)



8e

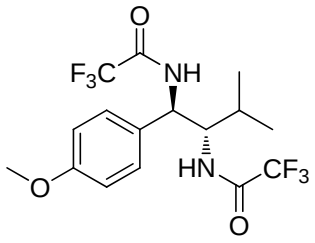
Preparation according to GP 6 from (3*S*,4*S*)-4-isopropyl-3-(4-methoxyphenyl)-1,2,5-thiadiazolidine-1,1-dioxide (**6e**, 100 mg, 0.370 mmol) with hydrazine-monohydrate (4.5 mL) furnished

71.2 mg (92%) of the title compound as an ochre oil. – $[\alpha]_D^{21}$ = +28.3 (*c* 0.61, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.7 Hz, 3 H), 0.92 (d, *J* = 6.9 Hz, 3 H), 1.39 (bs, 4 H), 1.50 (m_c, 1 H), 2.57 (dd, *J* = 7.0, 4.8 Hz, 1 H), 3.77 (d, *J* = 7.2 Hz, 1 H), 3.79 (s, 3 H), 6.86 (m_c, 2 H), 7.22 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.5, 20.9, 29.5, 55.4, 58.0, 62.9, 114.0, 127.9, 137.3, 158.7. – IR (neat): ν = 3371, 2956, 2871, 2836, 1609, 1583, 1510, 1462, 1368, 1301, 1243, 1175, 1107, 1033, 828, 752, 675, 637, 606, 557. – ESI (HR-MS) calcd. for $C_{12}H_{21}N_2O$: 209.1648; found 209.1647.

General Procedure for the Formation of Trifluoroacetamides (GP 7):

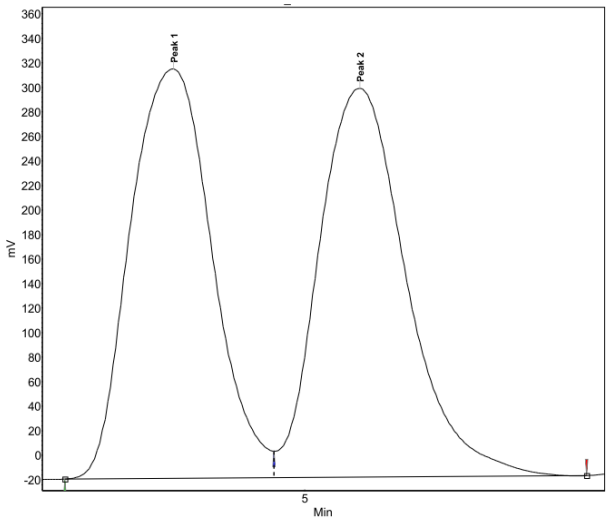
A solution of the respective 1,2-diamine (1.00 mmol) and triethylamine (6.00 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C and trifluoroacetic anhydride (2.50 mmol) was added dropwise within 15 min. The reaction mixture was stirred for 3 h and the solvent was removed under reduced pressure. The concentrate was dissolved in EtOAc (50 mL), washed with water (50 mL) and brine (50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

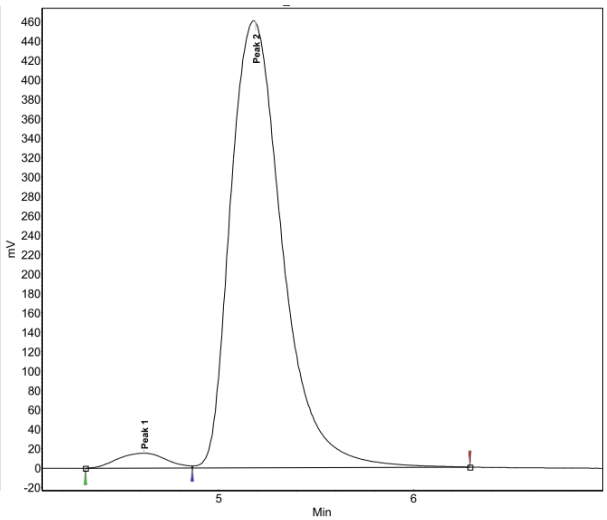
***N*,*N*'-[(1*R*,2*S*)-1-(4-Methoxyphenyl)-3-methylbutane-1,2-diyl]bis(trifluoroacetamide) (9e)**



9e

Prepared according to GP 7 from (1*R*,2*S*)-1-(4-methoxyphenyl)-3-methylbutane-1,2-diamine (**7e**, 30.0 mg, 0.144 mmol), triethylamine (0.121 mL, 0.868 mmol) and trifluoroacetic anhydride (0.050 mL, 0.074 g, 0.35 mmol). Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 50.0 mg (87%) of the title compound (R_f = 0.55) as a colorless solid, mp 158 °C. – $[\alpha]_D^{20}$ = –156.0 (*c* 0.36, EtOH). – ^{1}H NMR (500 MHz, acetone-d_6): δ = 0.96 (d, *J* = 6.9 Hz, 3 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 2.22 (m_c, 1 H), 3.76 (s, 3 H), 4.65 (dt, *J* = 10.4, 3.6 Hz, 1 H), 5.30 (m_c, 1 H), 6.87 (m_c, 2 H), 7.37 (m_c, 2 H), 8.10 (m_c, 1 H), 8.97 (m_c, 1 H). – ^{13}C NMR (126 MHz, acetone-d_6): δ = 16.0, 20.6, 29.6, 54.7, 55.5, 57.4, 114.6, 117.0 (q, *J* = 287.8 Hz), 117.1 (q, *J* = 287.5 Hz), 129.8, 131.6, 156.8 (q, *J* = 36.9 Hz), 157.9 (q, *J* = 36.3 Hz), 160.4. – IR (neat): ν = 3320, 3105, 2968, 1694, 1615, 1559, 1517, 1467, 1372, 1285, 1257, 1207, 1174, 1034, 895, 816, 770, 690, 608, 569, 547, 518, 426. – ESI (HR-MS) calcd. for $C_{16}H_{18}F_6N_2O_3Na$: 423.1114; found 423.1113. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IB, hexane/2-propanol 95:5, flow rate: 1.0 mL/min), retention times: (1*S*,2*R*)-enantiomer 4.6 min, (1*R*,2*S*)-enantiomer 5.2 min, 94% ee.

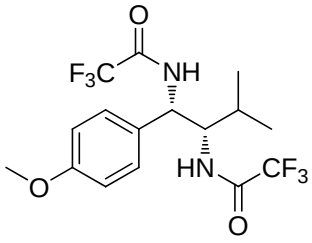




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	4,583	49,65	333,8	100,0	49,652
2	Peak 2	5,175	50,35	317,1	101,4	50,348
Total			100,00	650,9	201,3	100,000

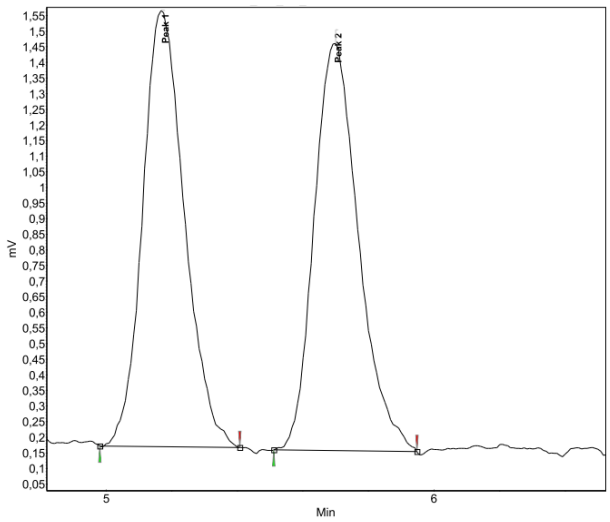
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	4,617	3,04	15,4	4,4	3,038
2	Peak 2	5,175	96,96	460,3	141,6	96,962
Total			100,00	475,7	146,0	100,000

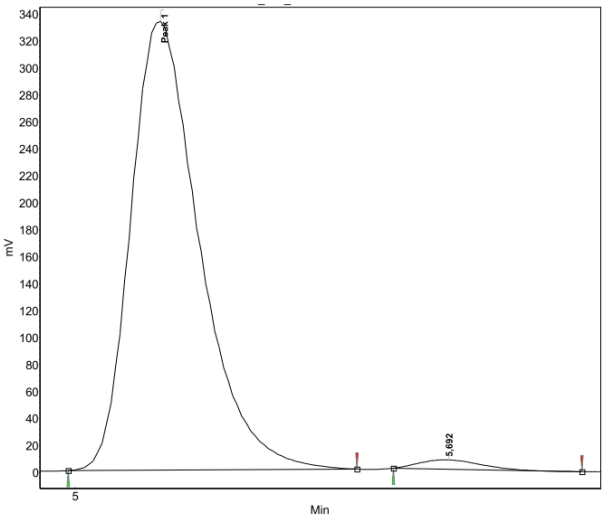
***N*,*N*'-[(1*S*,2*S*)-1-(4-Methoxyphenyl)-3-methylbutane-1,2-diyl]bis(trifluoroacetamide) (10e)**



10e

Prepared according to GP 7 from (1*S*,2*S*)-1-(4-methoxyphenyl)-3-methylbutane-1,2-diamine (**8e**, 78.6 mg, 0.377 mmol), triethylamine (0.318 mL, 2.28 mmol), and trifluoroacetic anhydride (0.131 mL, 0.927 mmol). Flash column chromatography (cyclohexane/EtOAc 1:1) furnished 135 mg (89%) of the title compound (R_f = 0.52) as a colorless solid, mp 129 °C. – $[\alpha]_D^{20}$ = +58.6 (*c* 0.67, EtOH). – ^{1}H NMR (500 MHz, acetone-d$_6$): δ = 0.95 (m$_c$, 6 H), 1.79 (m$_c$, 1 H), 3.79 (s, 3 H), 4.38 (dt, *J* = 9.3, 5.2 Hz, 1 H), 5.27 (m$_c$, 1 H), 6.95 (m$_c$, 2 H), 7.44 (m$_c$, 2 H), 8.32 (m$_c$, 1 H), 8.91 (m$_c$, 1 H). – ^{13}C NMR (126 MHz, acetone-d$_6$): δ = 16.8, 20.5, 29.7, 55.6, 55.8, 59.6, 115.0, 117.1 (q, *J* = 287.5 Hz), 117.2 (q, *J* = 287.7 Hz), 129.5, 131.1, 157.3 (q, *J* = 36.9 Hz), 158.5 (q, *J* = 36.8 Hz), 160.6. – IR (neat): ν = 3301, 3095, 2971, 1692, 1616, 1554, 1517, 1465, 1374, 1332, 1293, 1259, 1206, 1157, 1031, 962, 889, 825, 744, 719, 676, 614, 556, 518, 422. – ESI (HR-MS) calcd. for $C_{16}H_{18}F_6N_2O_3Na$: 423.1114; found 423.1112. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, chloroform, flow rate: 0.8 mL/min), retention times: (1*S*,1*S*)-enantiomer 5.2 min, (1*R*,2*R*)-enantiomer 5.7 min, 96% ee.





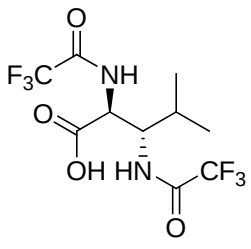
Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	5,167	50,18	1,4	0,2	50,180
2	Peak 2	5,700	49,82	1,3	0,2	49,820
Total			100,00	2,7	0,4	100,000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	5,158	98,19	332,7	48,9	98,191
2	Peak 2	5,692	1,81	6,9	0,9	1,809
Total			100,00	339,6	49,8	100,000

General Procedure for the Oxidative Cleavage of the Aromatic Ring (GP 8):

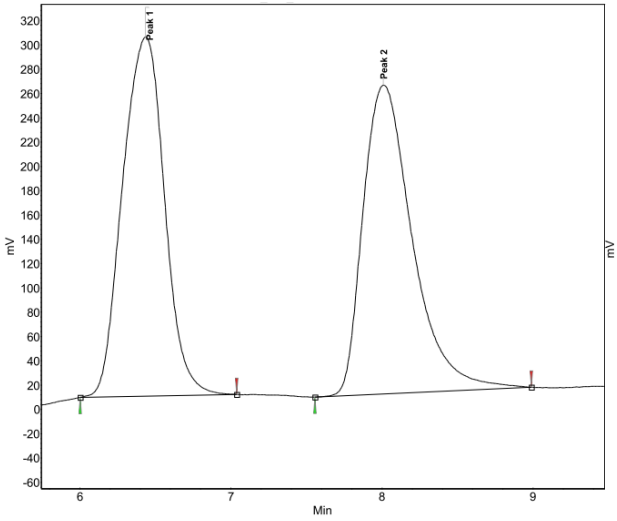
The respective trifluoroacetamide **9** or **10** (1.00 mmol) was dissolved in a 1:1 mixture of EtOAc and acetonitrile (30 mL). An aqueous solution of sodium periodate (100 mL, 10 mmol, 0.1 M) and ruthenium(III) chloride (0.050 mmol) were added. The reaction mixture was stirred for 60 h at rt, the phases were separated, and the aqueous phase was extracted with EtOAc (20 mL). The combined organic phases were extracted with aqueous NaOH (50 mL, 1 M), and the alkaline aqueous phase was adjusted to pH 2 by addition of HCl (3 M) and extracted with EtOAc (2 * 25 mL). The combined organic phases were filtered through activated charcoal, washed with brine (40 mL), and dried over $MgSO_4$, and the solvent was removed under reduced pressure to furnish the respective 2,3-diamino acid in a purity >95%.

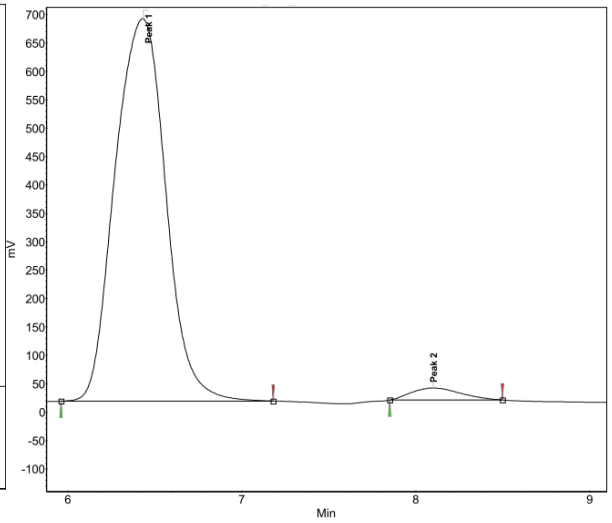
(2*S*,3*S*)-4-Methyl-2,3-bis(trifluoroacetamido)pentanoic acid (11)



11

Preparation according to GP 8 from *N*,*N*'-[(1*R*,2*S*)-1-(4-methoxyphenyl)-3-methylbutane-1,2-diyl]bis(trifluoroacetamide) (**9e**, 50.0 mg, 0.125 mmol), sodium periodate solution (13 mL, 1.3 mmol), and ruthenium(III) chloride (1.4 mg, 6.8 µmol) furnished 22.0 mg (52%) of the title compound as a colorless solid, mp 151 °C. – $[\alpha]_D^{20} = -25.4$ (*c* 0.13, EtOH). – ^{1}H NMR (500 MHz, acetone-d_6): δ = 0.96 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 2.23 (m_c, 1 H), 4.36 (dt, *J* = 9.5, 6.9 Hz, 1 H), 4.88 (dd, *J* = 8.4, 6.9 Hz, 1 H), 8.44 (m_c, 1 H), 8.83 (m_c, 1 H). – ^{13}C NMR (126 MHz, acetone-d_6): δ = 18.0, 20.1, 29.5, 54.5, 56.9, 116.9 (q, *J* = 287.1 Hz), 117.1 (q, *J* = 287.5 Hz), 157.7 (q, *J* = 37.4 Hz), 158.5 (q, *J* = 36.8 Hz), 170.2. – IR (neat): ν = 3289, 3097, 2924, 1700, 1555, 1472, 1430, 1400, 1371, 1155, 932, 893, 767, 691, 565, 518, 455. – ESI (HR-MS) calcd. for $C_{10}H_{11}F_6N_2O_4$: 337.0628; found 337.0631. – The enantiomeric excess was determined by HPLC analysis (Chiralpak IC, hexane/2-propanol/TFA 95/5/0.1, flow rate: 0.8 mL/min), retention times: (2*S*,3*S*)-enantiomer 6.4 min, (2*R*,3*R*)-enantiomer 8.1 min, 94% ee.

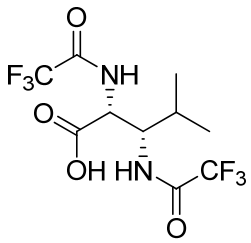




Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	6.433	49.71	295.5	95.0	49.714
2	Peak 2	8.008	50.29	254.2	96.1	50.286
Total			100.00	549.6	191.1	100.000

Index	Name	Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Peak 1	6.433	97.03	673.7	227.2	97.031
2	Peak 2	8.100	2.97	21.2	7.0	2.969
Total			100.00	694.9	234.2	100.000

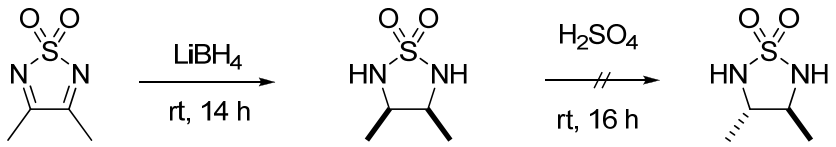
(2*R*,3*S*)-4-Methyl-2,3-bis(trifluoroacetamido)pentanoic acid (12)



12

Preparation according to GP 8 from *N*,*N*'-[(1*S*,2*S*)-1-(4-methoxyphenyl)-3-methylbutane-1,2-diyl]bis(trifluoroacetamide) (**10e**, 36.4 mg, 0.0909 mmol), sodium periodate solution (9 mL, 0.9 mmol), and ruthenium(III) chloride (1.0 mg, 4.8 µmol) furnished 10.7 mg (35%) of the title compound as a colorless solid, mp 80-82 °C. – $[\alpha]_D^{20}$ = –35.5 (*c* 0.29, EtOH). – ^{1}H NMR (500 MHz, acetone-d_6): δ = 0.99 (d, *J* = 6.6 Hz, 3 H), 1.07 (d, *J* = 6.7 Hz, 3 H), 2.00 (m_c, 1 H), 4.36 (m_c, 1 H), 5.01 (m_c, 1 H), 8.52 (d, *J* = 9.5 Hz, 1 H), 8.70 (d, *J* = 9.1 Hz, 1 H). – ^{13}C NMR (126 MHz, acetone-d_6): δ = 19.2, 20.1, 29.8, 55.0, 57.3, 117.0 (q, *J* = 287.2 Hz), 117.1 (q, *J* = 287.2 Hz), 157.896 (q, *J* = 36.3 Hz), 157.904 (q, *J* = 36.9 Hz), 171.0. – IR (neat): ν = 3286, 3088, 2974, 1707, 1553, 1472, 1396, 1371, 1151, 1059, 982, 940, 899, 843, 723, 688, 600, 518, 444. – ESI (HR-MS) calcd. for $C_{10}H_{12}F_6N_2O_4Na$: 361.0593; found 361.0591.

2) Attempted Isomerization of *cis*-3,4-Dimethyl-1,2,5-thiadiazolidine-1,1-dioxide



2i **5i** (93%) *cis*/*trans* = 1.7:1 **6i**

***cis*-3,4-Dimethyl-1,2,5-thiadiazolidine-1,1-dioxide (5i)**

A solution of 3,4-dimethyl-1,2,5-thiadiazole-1,1-dioxide **2i** (21.0 mg, 0.144 mmol) in THF (1 mL) was treated with a solution of $LiBH_4$ (1.15 mL, 1.15 mmol, 1.0 M in diethyl ether). The reaction mixture was stirred for 14 h at rt. The pH value of the reaction mixture was adjusted to 3 by addition of HCl (1 M), water (5 mL) and EtOAc (5 mL) were added, the organic layer was separated, and the aqueous phase was re-extracted with EtOAc (5 mL). The combined organic phases were washed with brine (5 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. Flash column chromatography (cyclohexane/EtOAc 7:3, 5% MeOH) furnished 20.1 mg (93%) of an inseparable 1.7:1 mixture of *cis*- and *trans*-thiadiazolidine **5i** and **6i** (R_f = 0.27) as a colorless solid, mp 59 °C.

5i: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.30 (d, J = 6.0 Hz, 6 H), 3.84 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 14.7, 58.1.

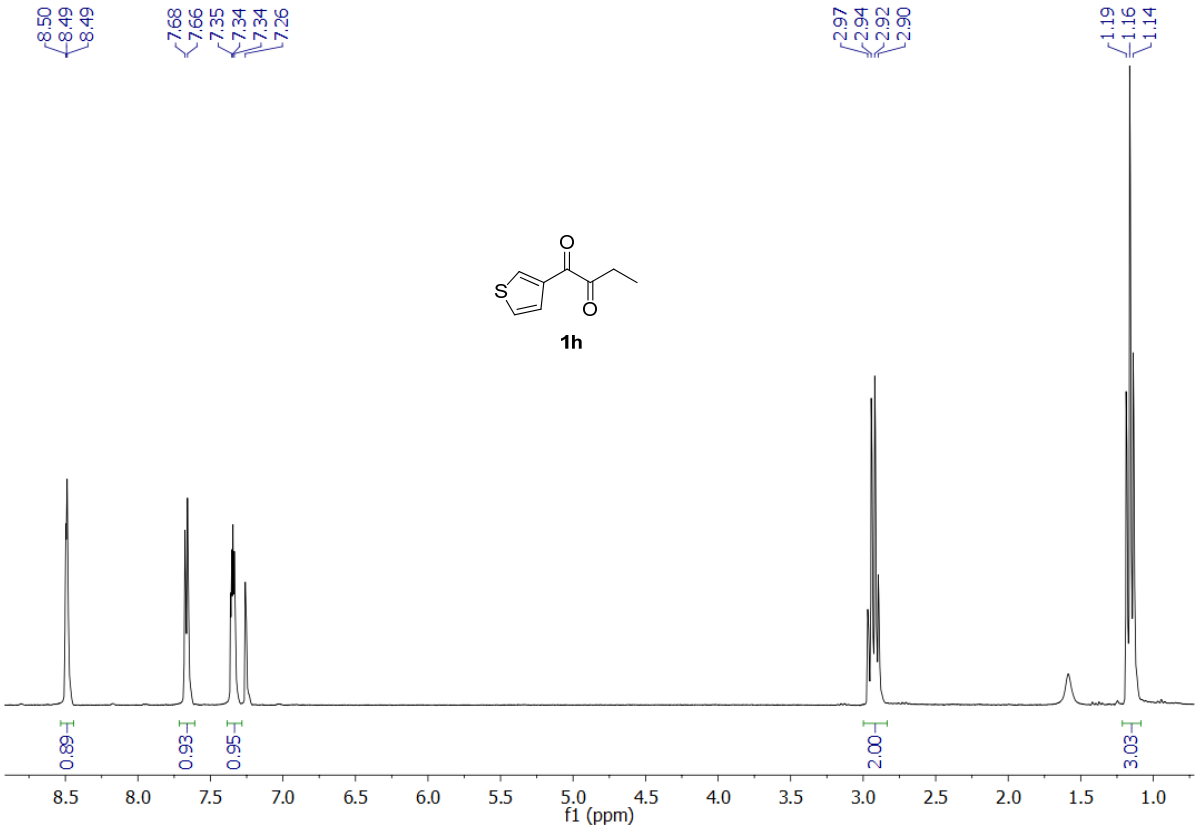
6i: ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.22 (d, J = 6.0 Hz, 6 H), 3.38 (m_c, 2 H). – ^{13}C NMR (75.5 MHz, acetone-d_6): δ = 17.5, 61.5.

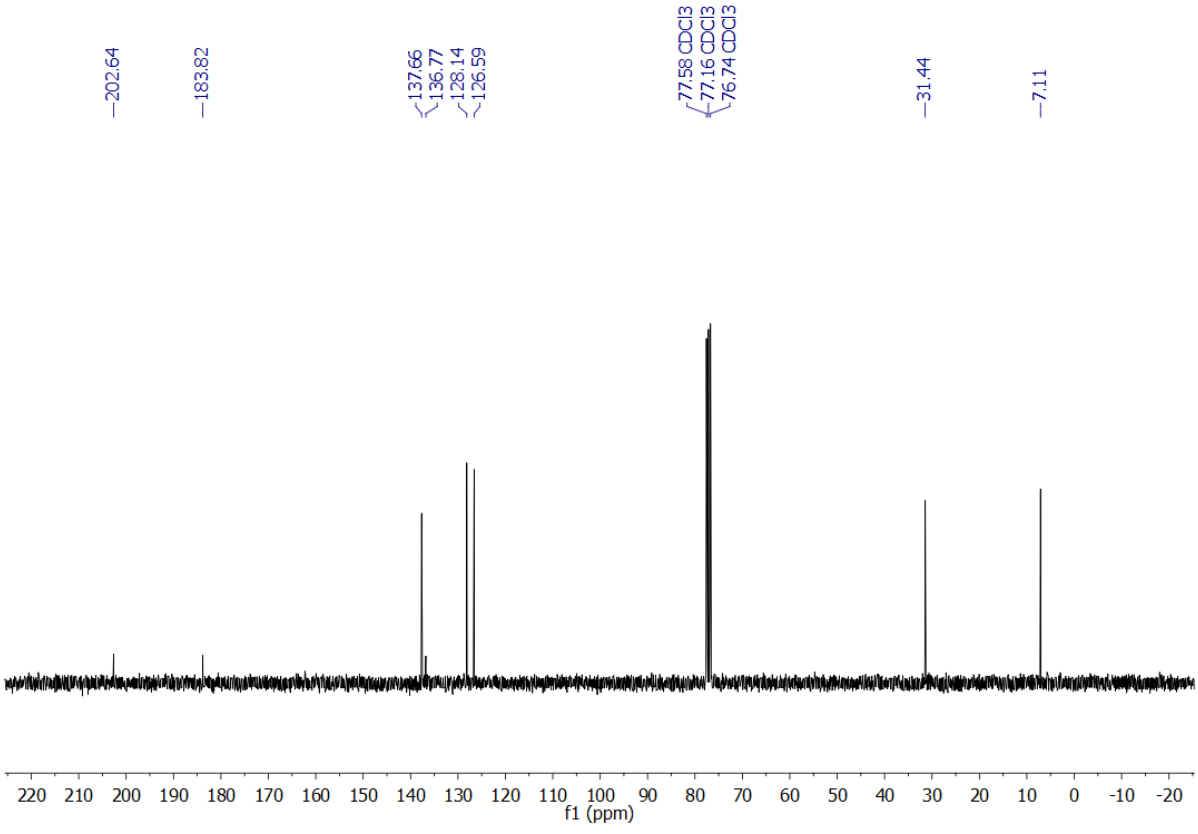
5i, **6i**: IR (neat): ν = 3247, 2922, 2853, 1710, 1657, 1514, 1456, 1404, 1288, 1261, 1157, 1102, 1172, 1031, 932, 888, 799, 675, 620, 487, 420, 389. – ESI (HR-MS) calcd. for $C_4H_{10}N_2O_2SNa$: 173.0355; found 173.0356.

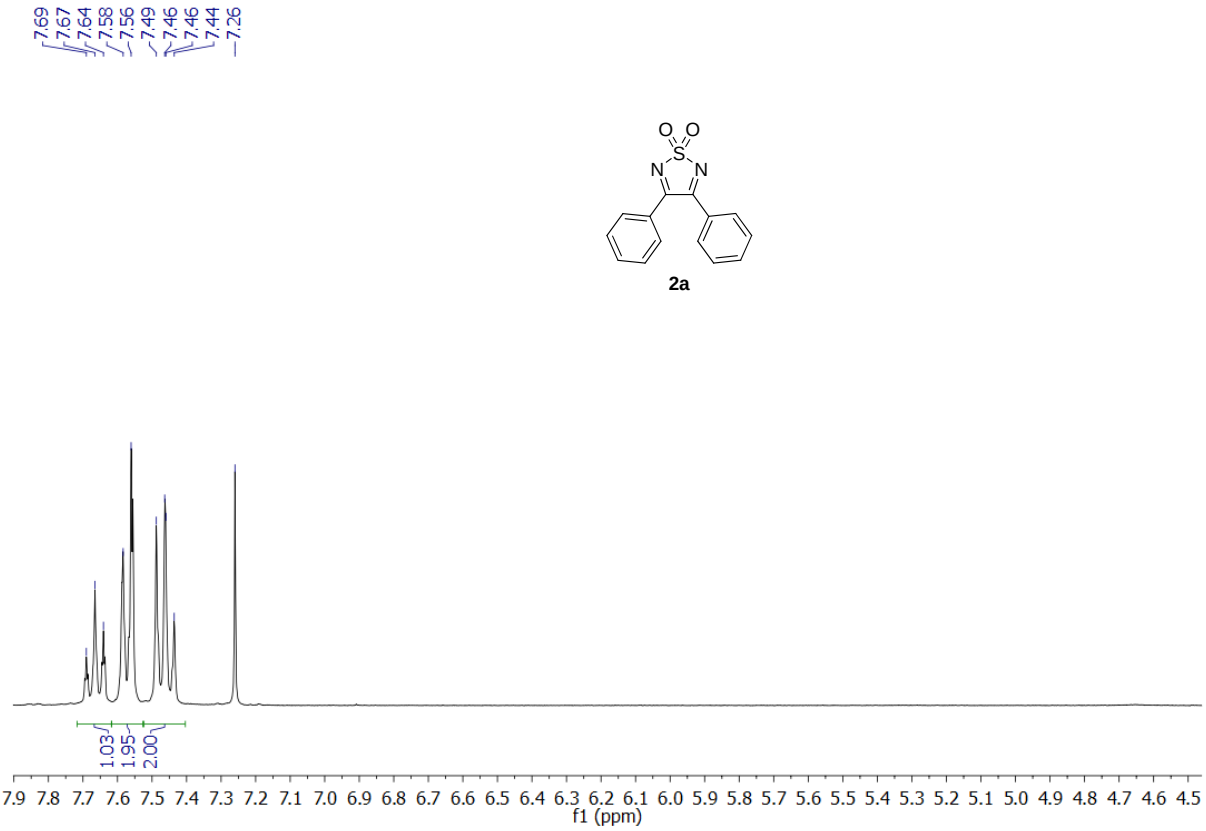
Attempted Isomerization of *cis*-Thiadiazolidine 5i

A 1.7:1 mixture of *cis*- and *trans*-3,4-dimethyl-1,2,5-thiadiazolidine-1,1-dioxide (**5i** + **6i**, 20.1 mg, 0.134 mmol) was treated with sulfuric acid (1.0 mL, 18.8 mmol) and stirred for 16 h at rt. The reaction mixture was poored into water (5 mL) and the aqueous phase was extracted with EtOAc (2 * 5 mL). The combined organic phases were washed with brine (5 mL) and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure furnishing 19.7 mg (98%) of an unchanged 1.7:1 mixture of the starting materials. Thus, no isomerization took place.

3) ^{1}H and ^{13}C NMR Spectra



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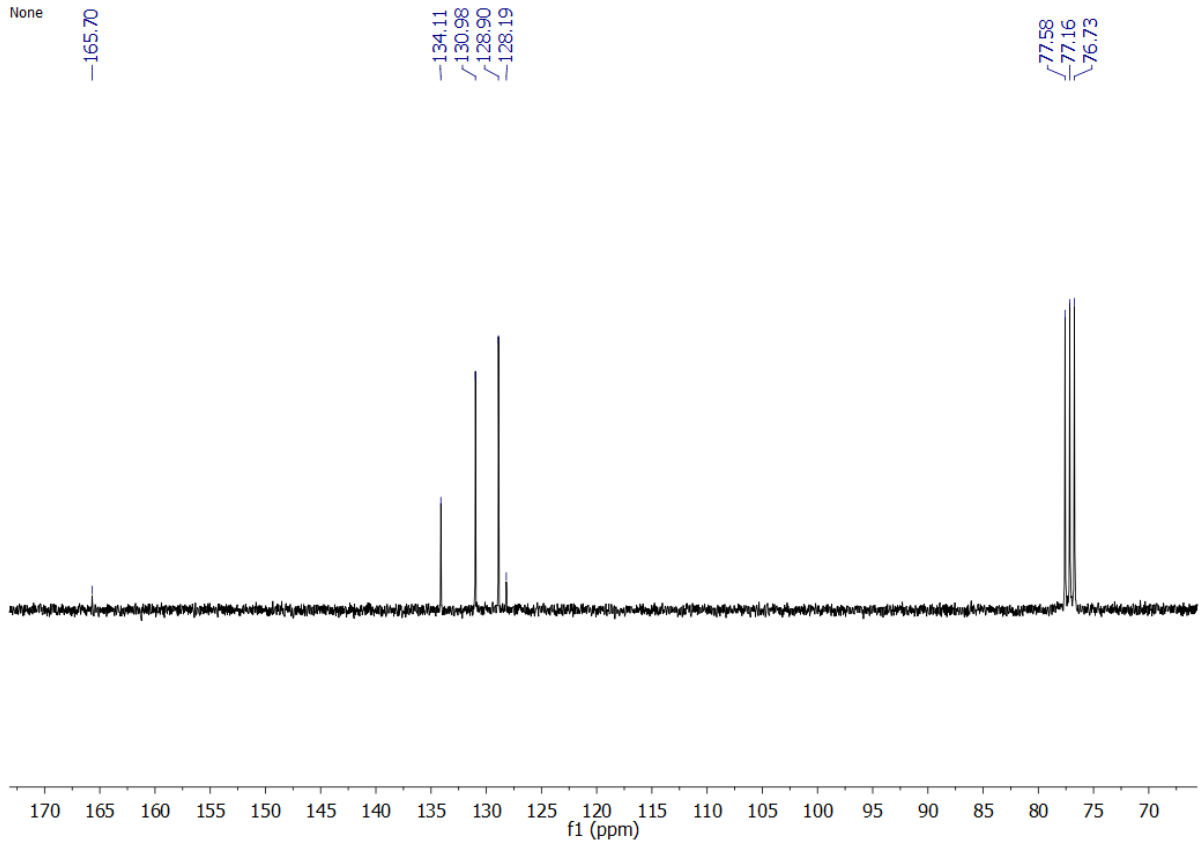
7.58
7.56
7.49
7.46
7.46
7.44
7.26
O
O
S
N
N
1.03
1.95
2.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)

2a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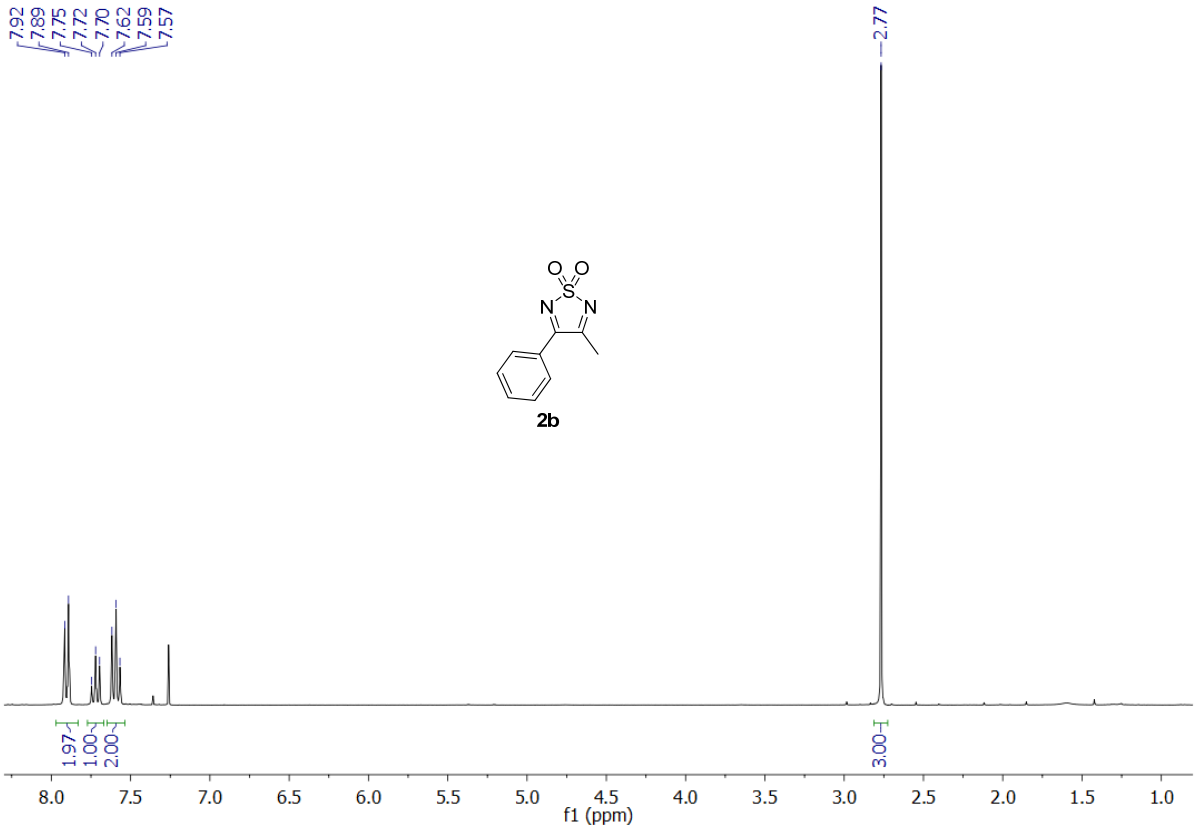
128.90
128.19
77.58
77.16
76.73
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70
f1 (ppm)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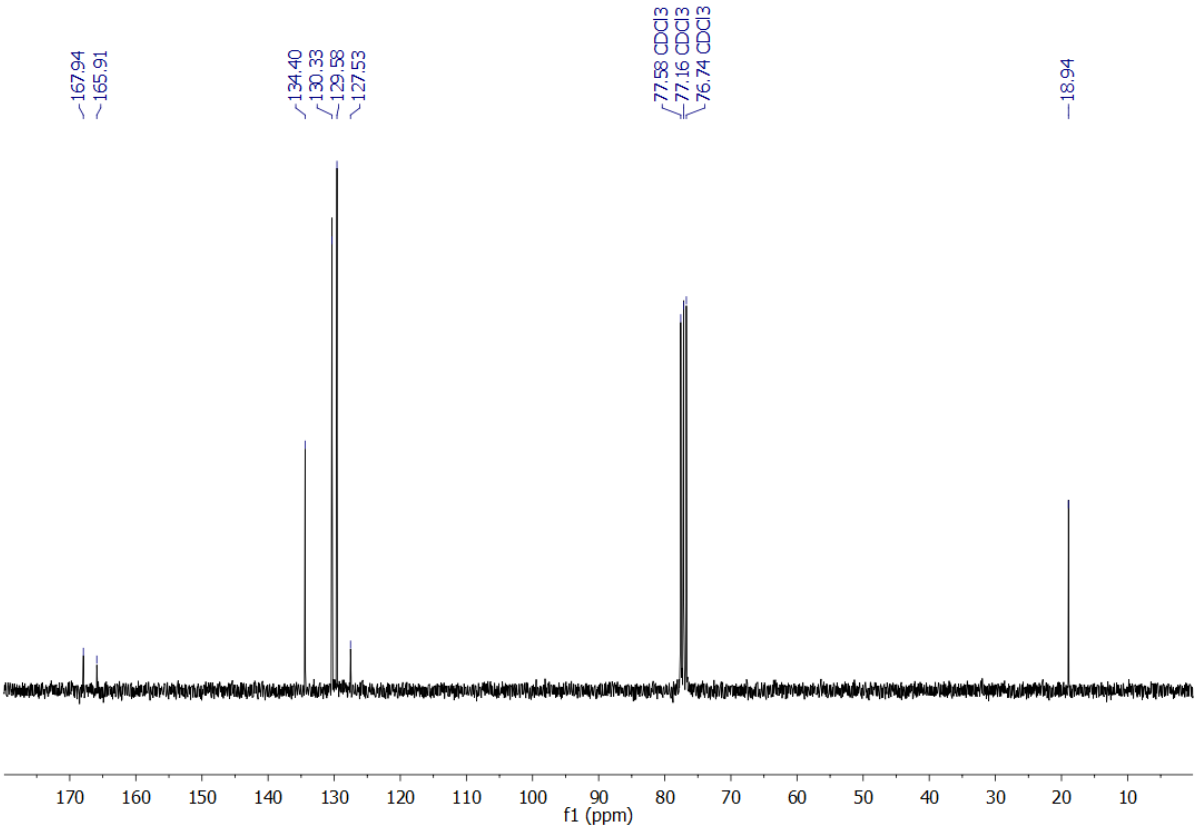
7.57
2.77
2b
1.97
1.00
2.00
3.00
f1 (ppm)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127.53
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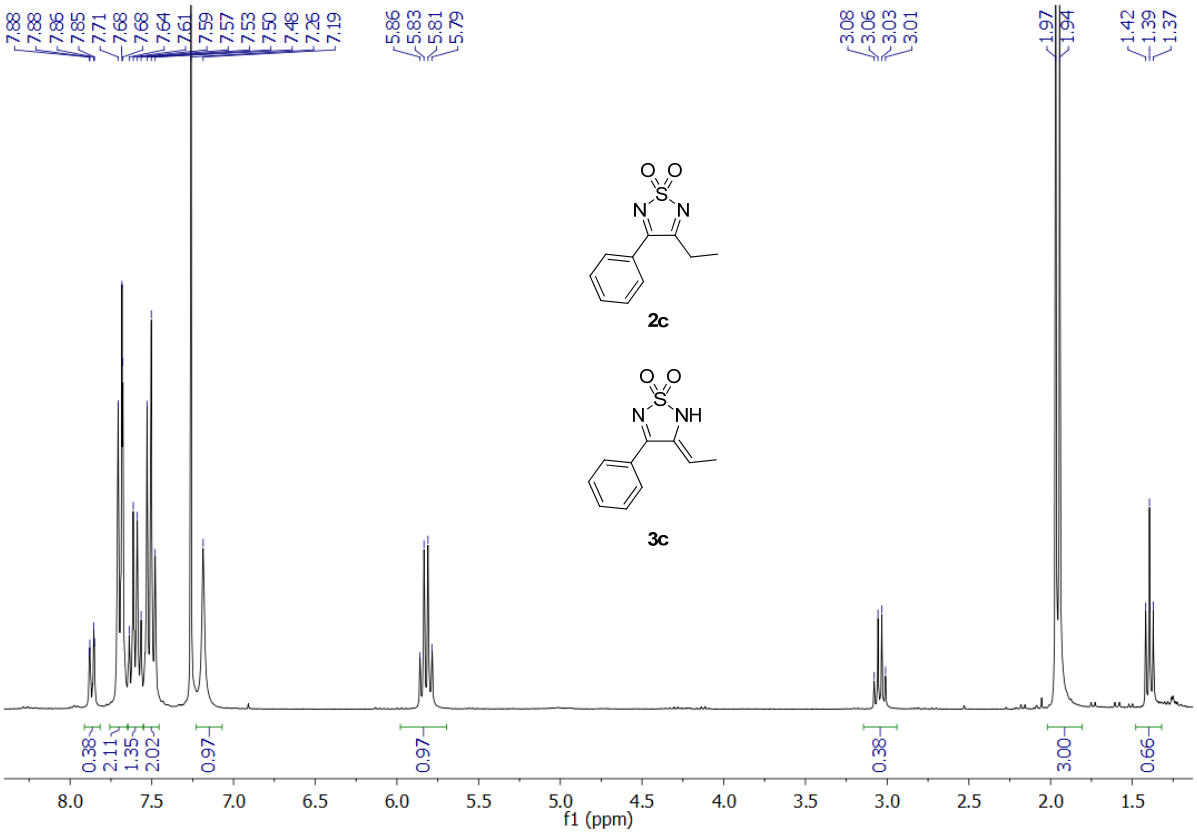
77.16 CDCl3
76.74 CDCl3
18.94
f1 (ppm)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7.68
7.68
7.64
7.61
7.59
7.57
7.53
7.50
7.48
7.26
7.19
5.86
5.83
5.81
5.79
3.08
3.06
3.03
3.01
1.97
1.94
1.42
1.39
1.37
0.38
2.11
1.35
2.02
0.97
0.97
0.38
3.00
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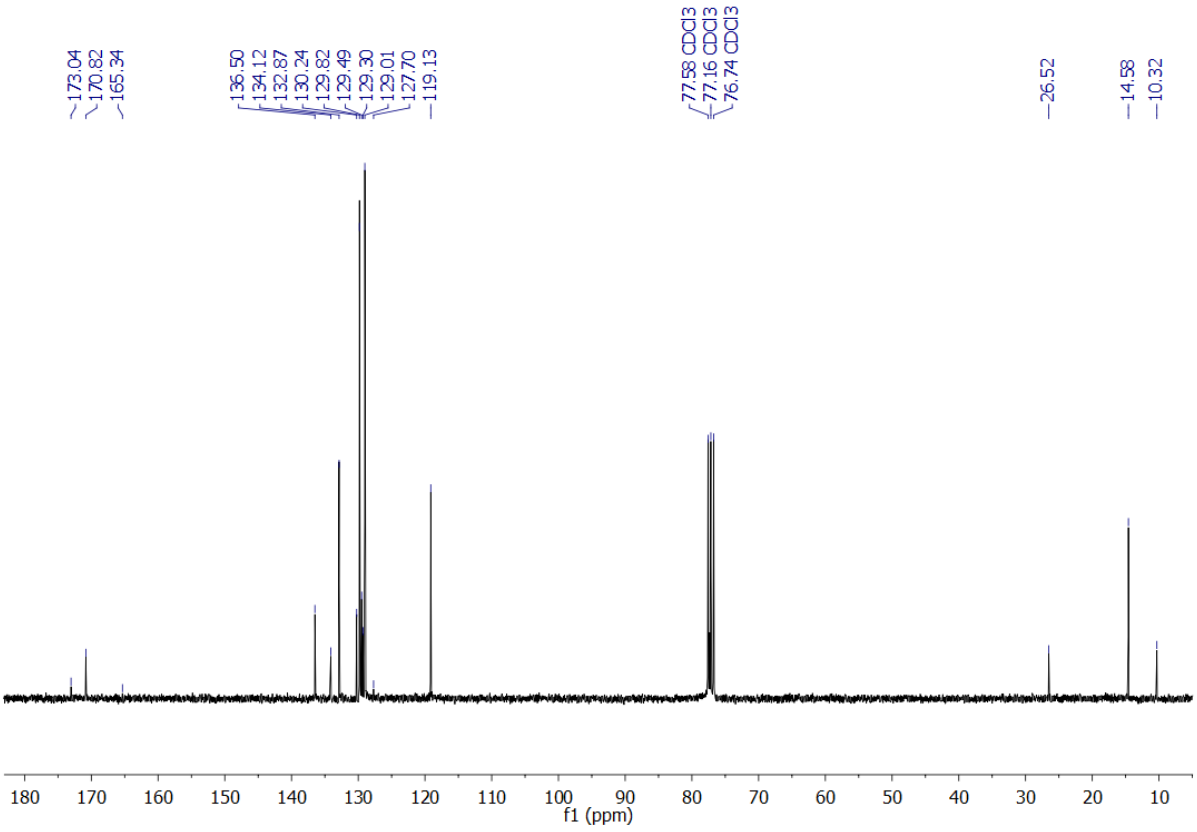
f1 (ppm)

2c

3c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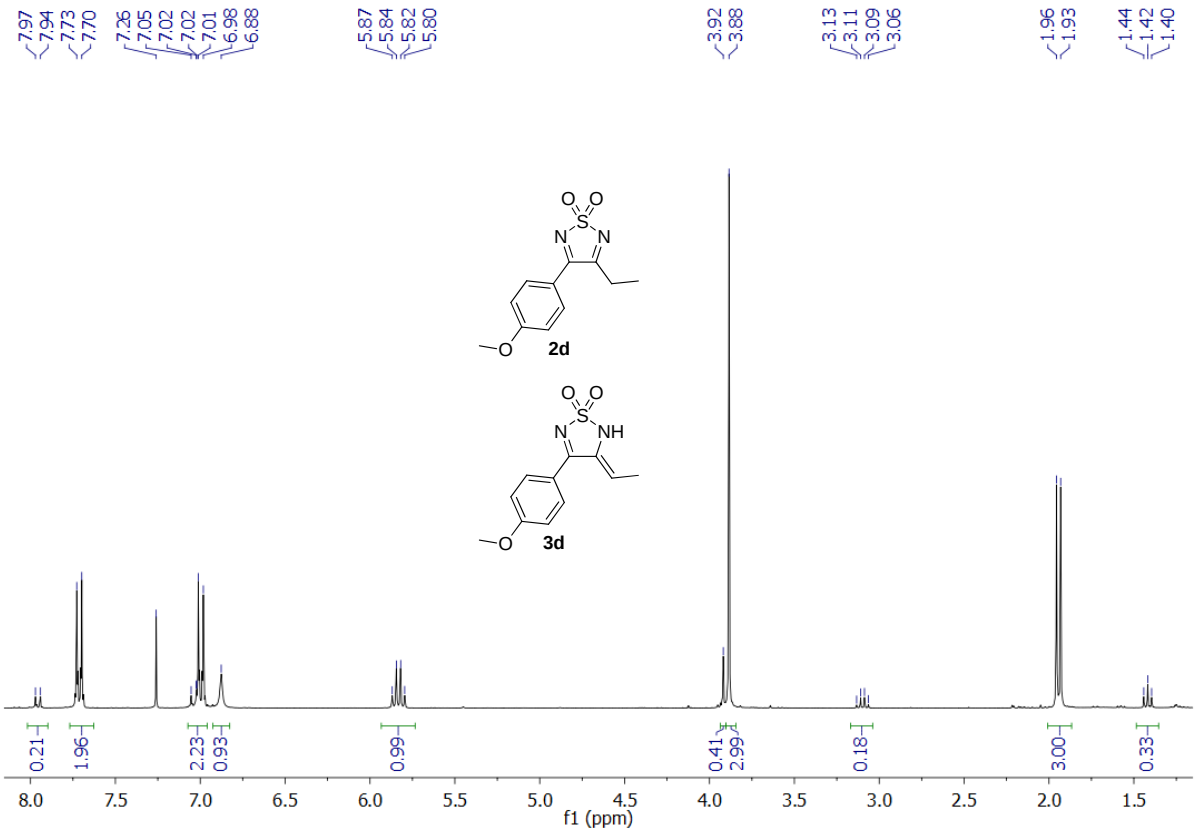
165.34
136.50
134.12
132.87
130.24
129.82
129.49
129.30
129.01
127.70
119.13
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
26.52
14.58
10.32
f1 (ppm)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7.05
7.02
7.02
7.01
6.98
6.88
5.87
5.84
5.82
5.80
3.92
3.88
3.13
3.11
3.09
3.06
1.96
1.93
1.44
1.42
1.40
2d
3d
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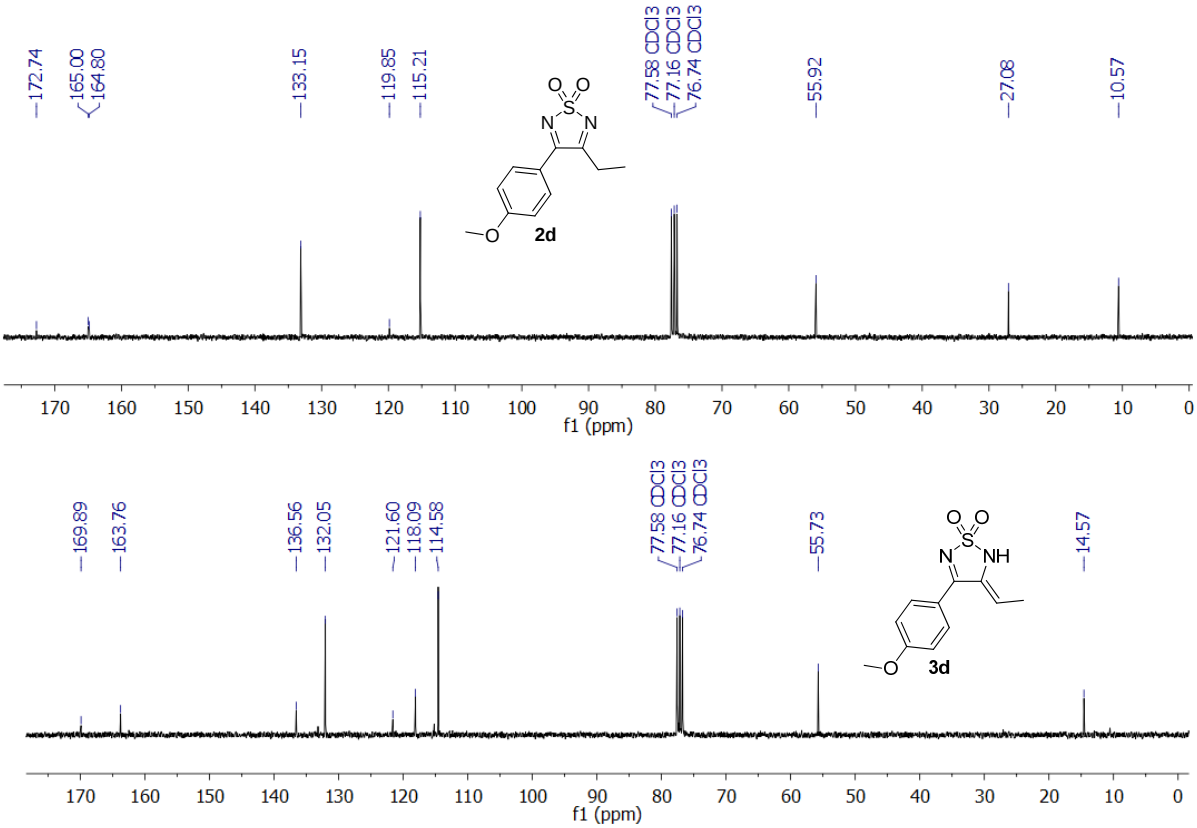
2.23
0.93
0.99
0.41
2.99
0.18
3.00
0.33
f1 (ppm)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115.21
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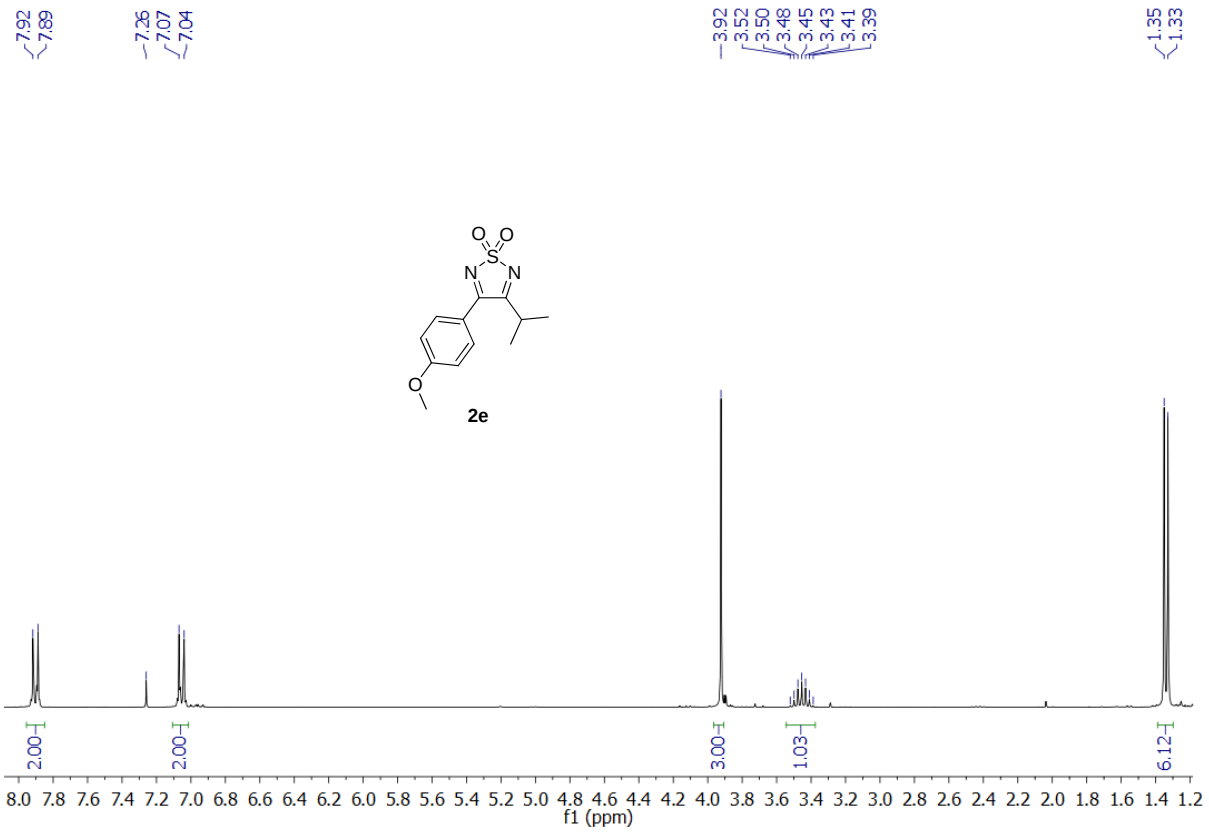
77.16 CDCl3
76.74 CDCl3
55.92
27.08
10.57
2d
f1 (ppm)
169.89
163.76
136.56
132.05
121.60
118.09
114.58
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.73
14.57
3d
f1 (ppm)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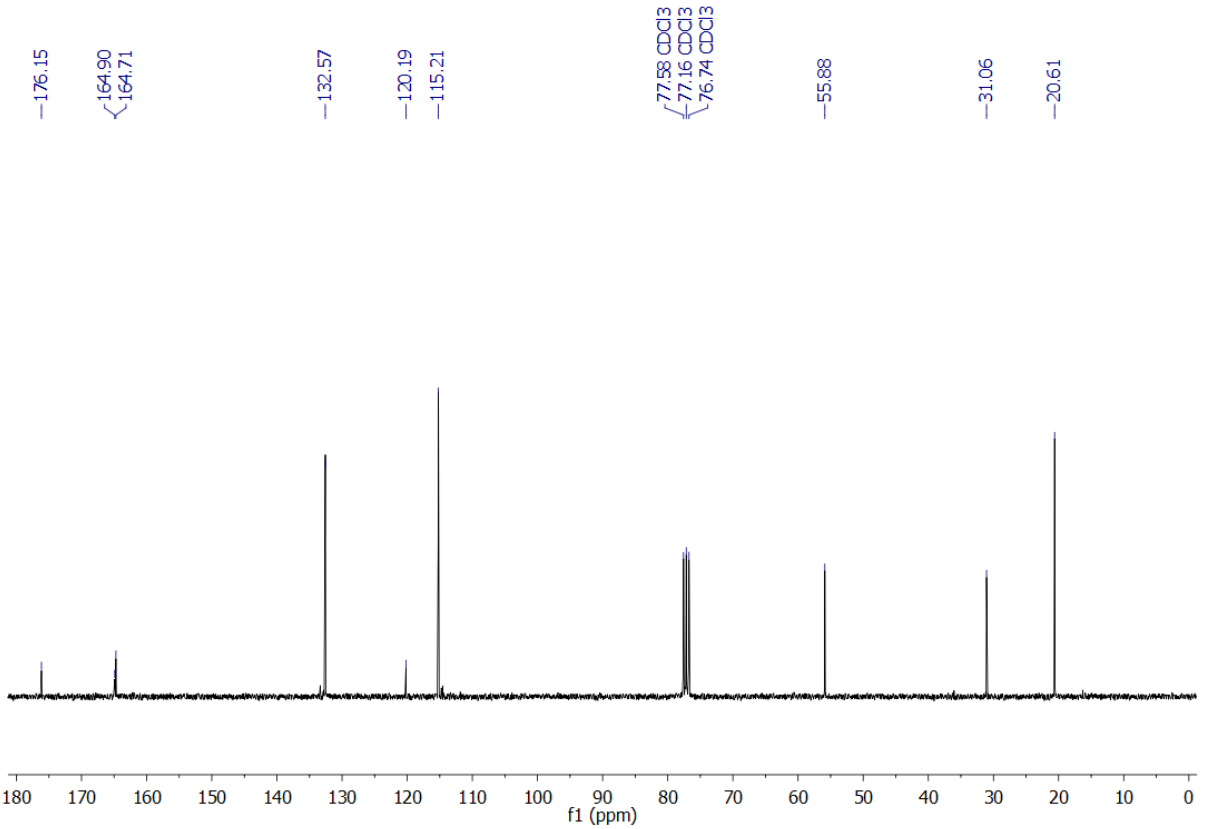
2.00
3.00
1.03
6.12
f1 (ppm)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115.21
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77.16 CDCl3
76.74 CDCl3
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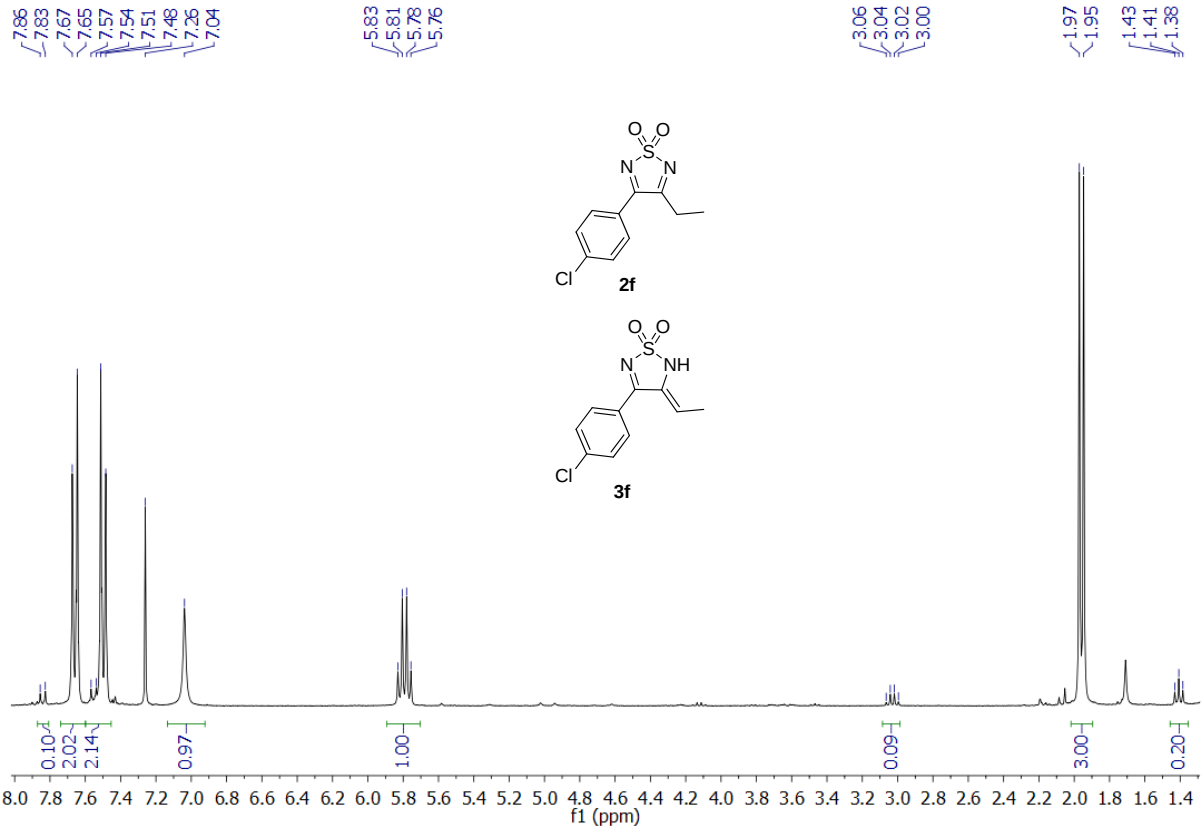
31.06
20.61
f1 (ppm)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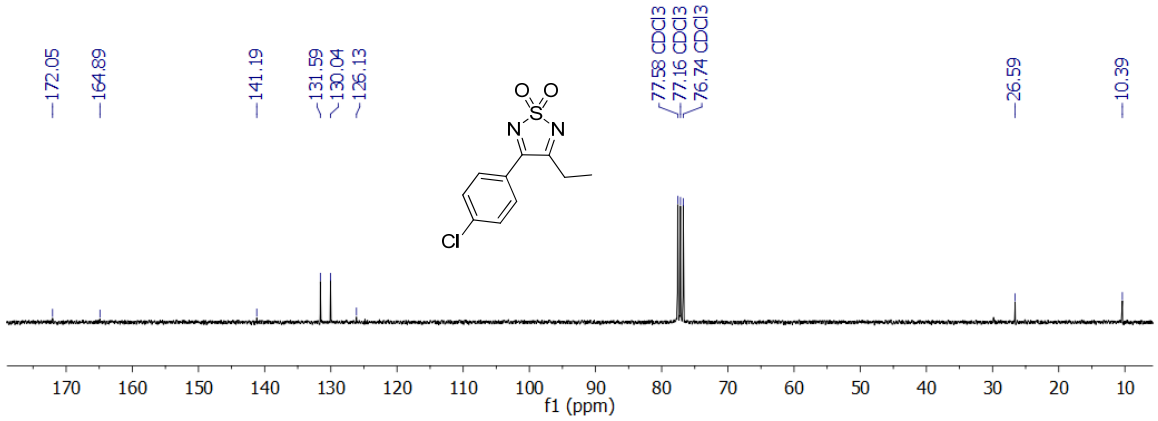
7.54
7.51
7.48
7.26
7.04
5.83
5.81
5.78
5.76
3.06
3.04
3.02
3.00
1.97
1.95
1.43
1.41
1.38
2f
3f
0.10
2.02
2.14
0.97
1.00
0.09
3.00
0.20
f1 (ppm)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130.04
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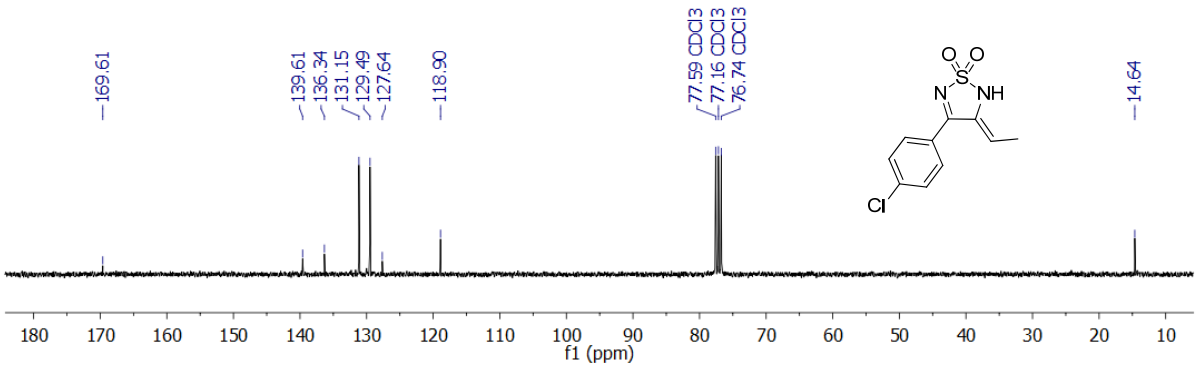
77.16 CDCl3
76.74 CDCl3
26.59
10.39
f1 (ppm)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77.16 CDCl3
76.74 CDCl3
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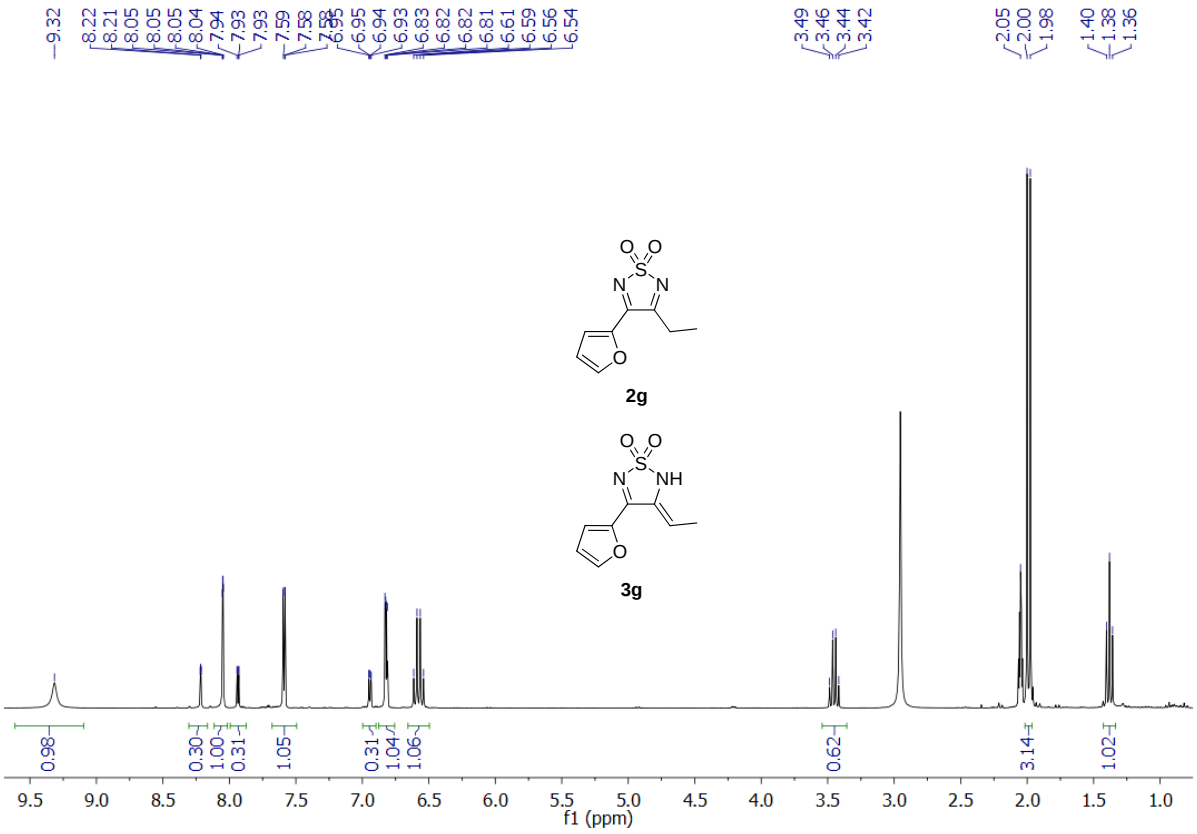
f1 (ppm)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3.49
3.46
3.44
3.42
2.05
2.00
1.98
1.40
1.38
1.36
2g
3g
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1.06
0.62
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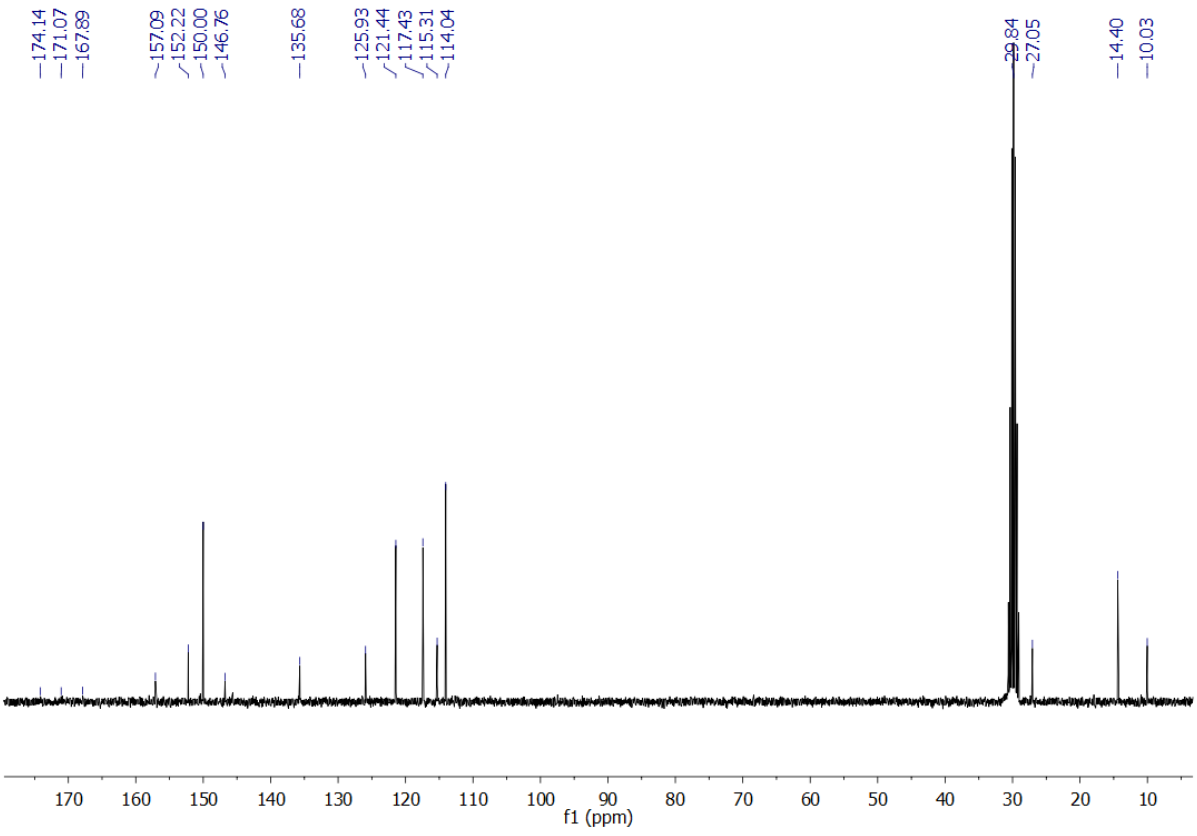
f1 (ppm)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10.03
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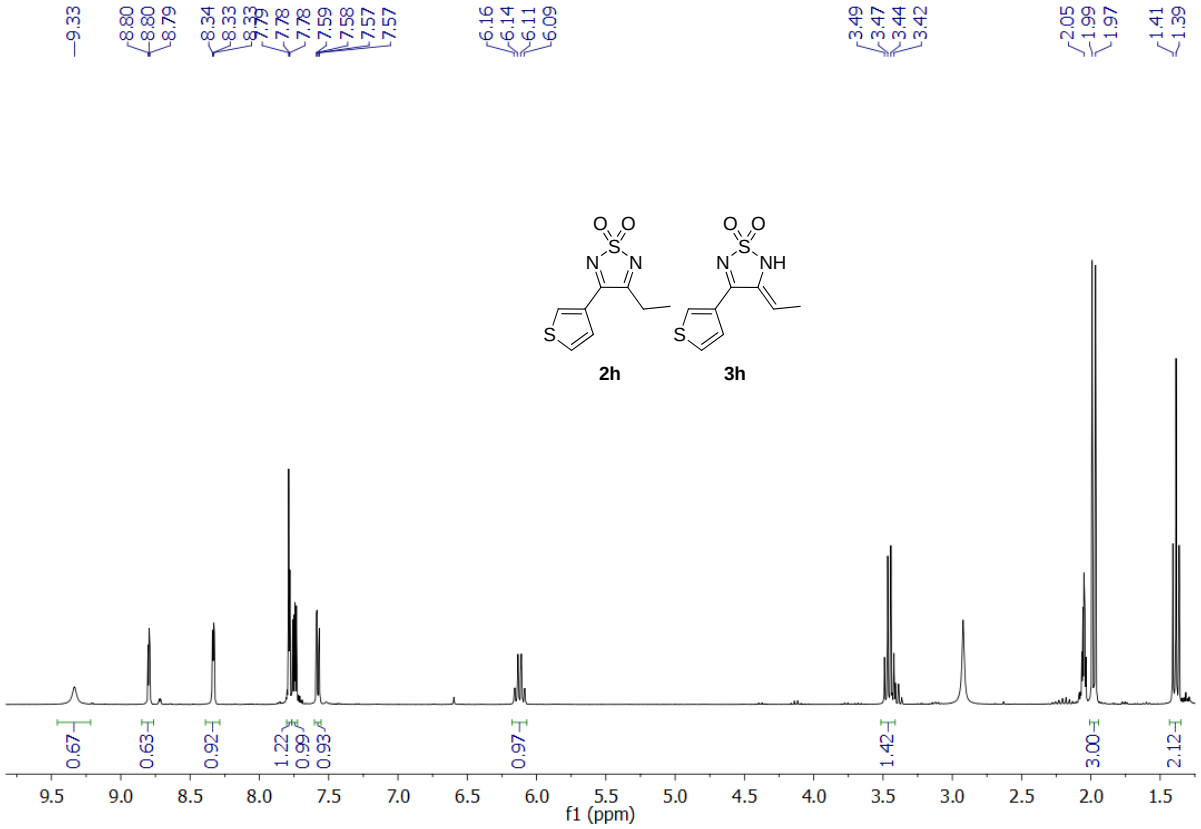
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3.42
2.05
1.99
1.97
1.41
1.39
2h
3h
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0.92
1.22
0.99
0.93
0.97
1.42
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2.12
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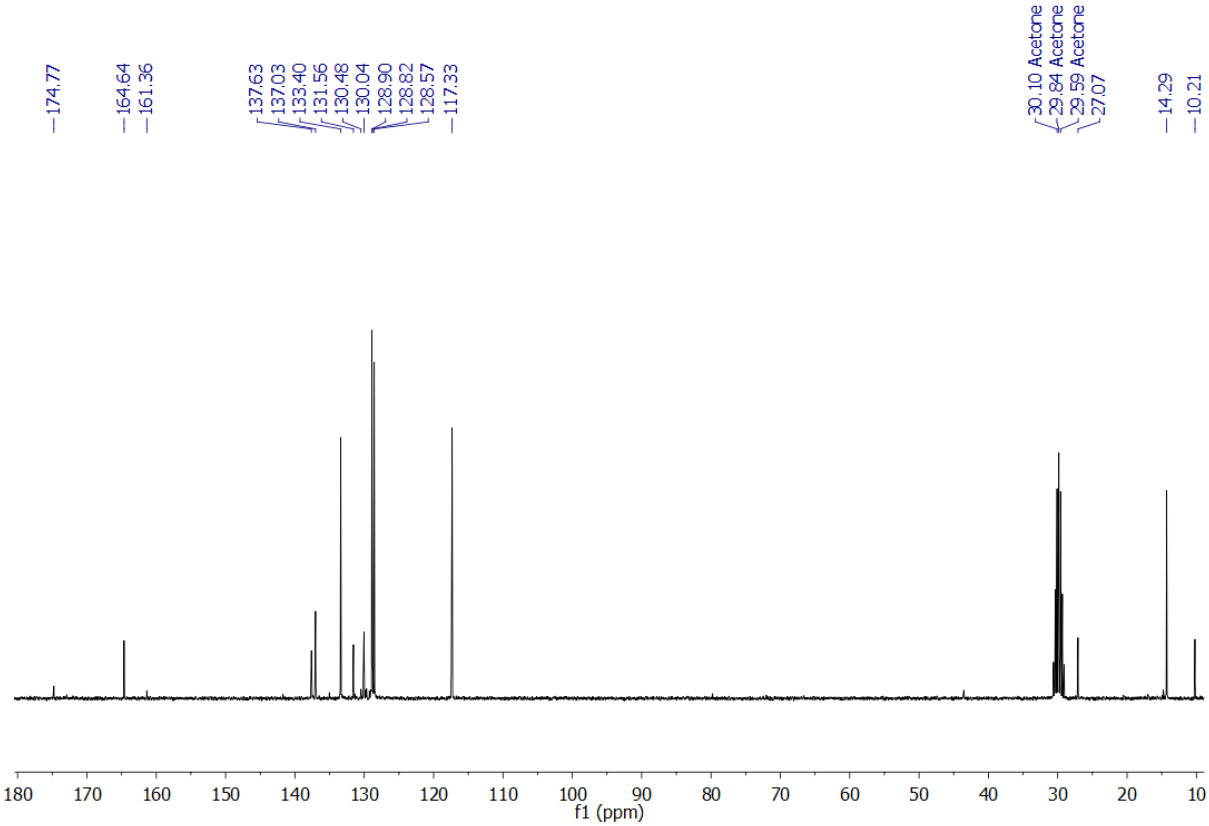
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30.10 Acetone
29.84 Acetone
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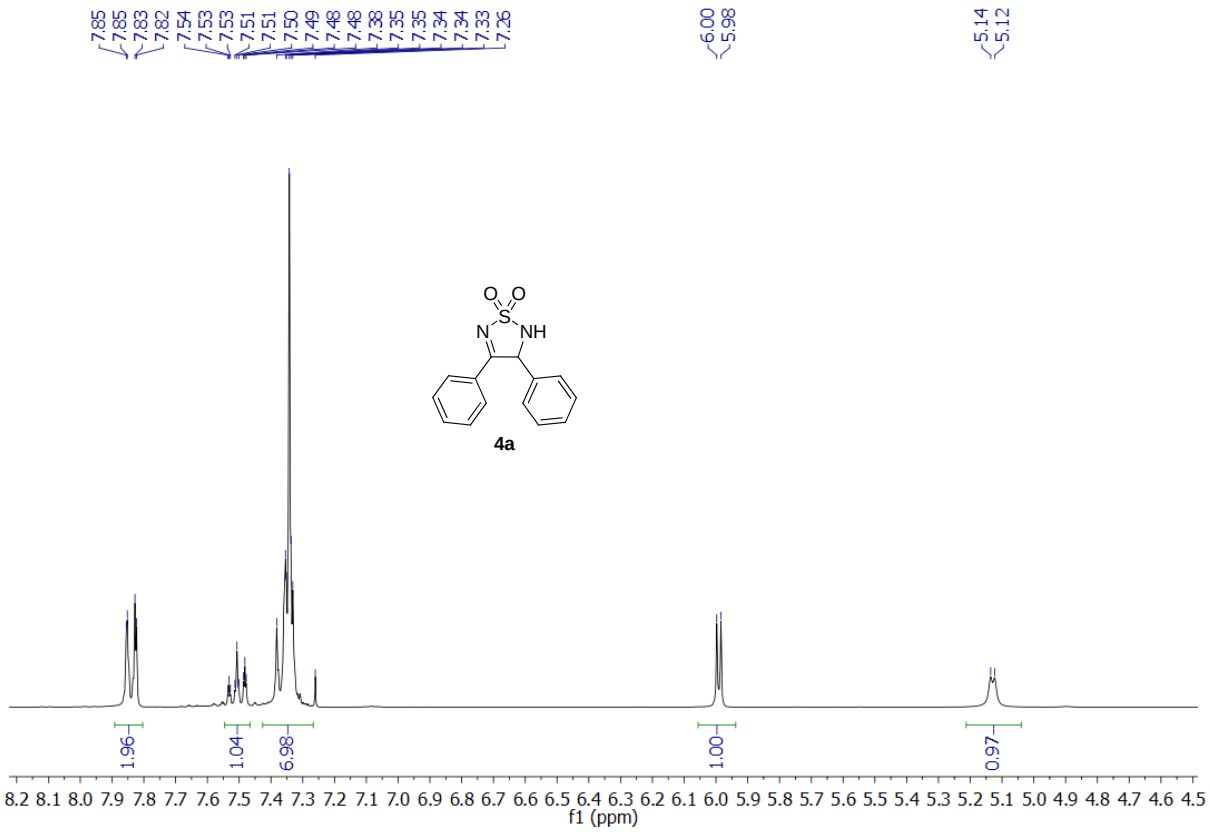
27.07
14.29
10.21
f1 (ppm)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6.00
5.98
5.14
5.12
O
O
S
N
NH
4a
1.96
1.04
6.98
1.00
0.97
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
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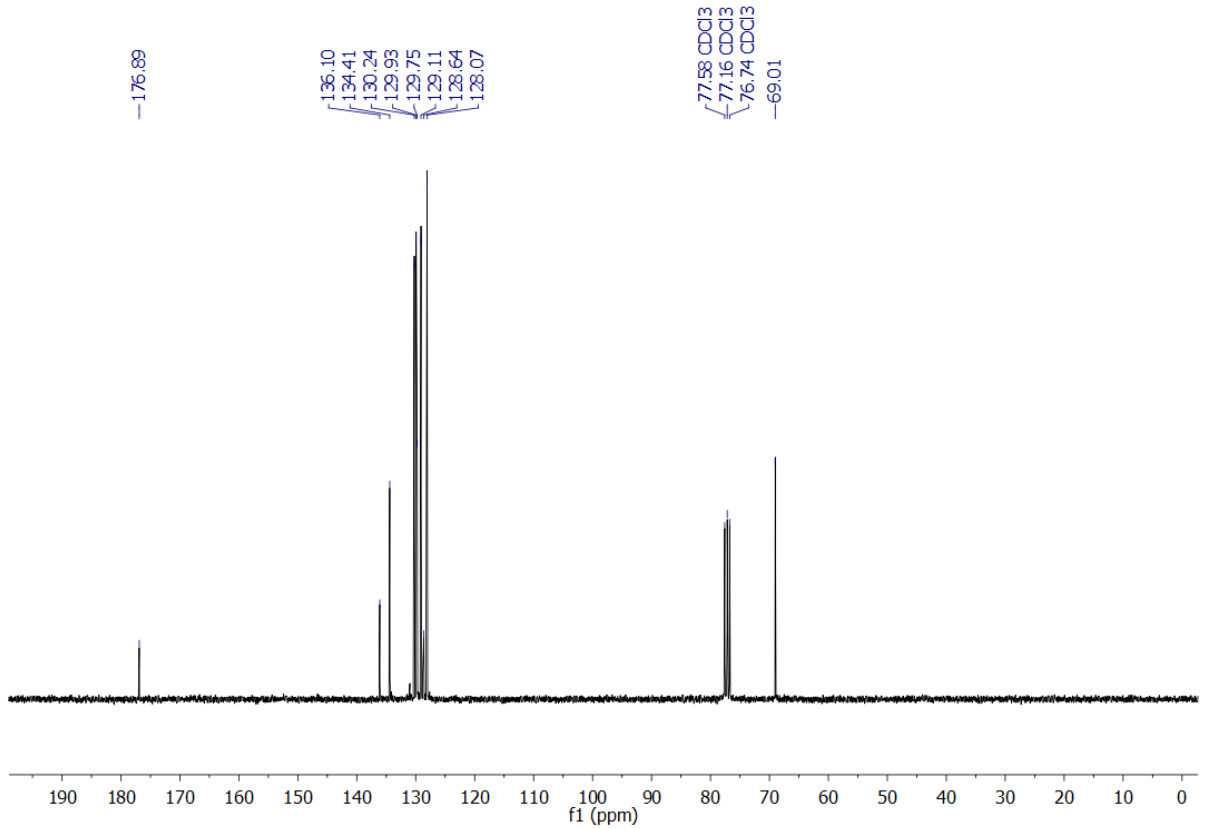
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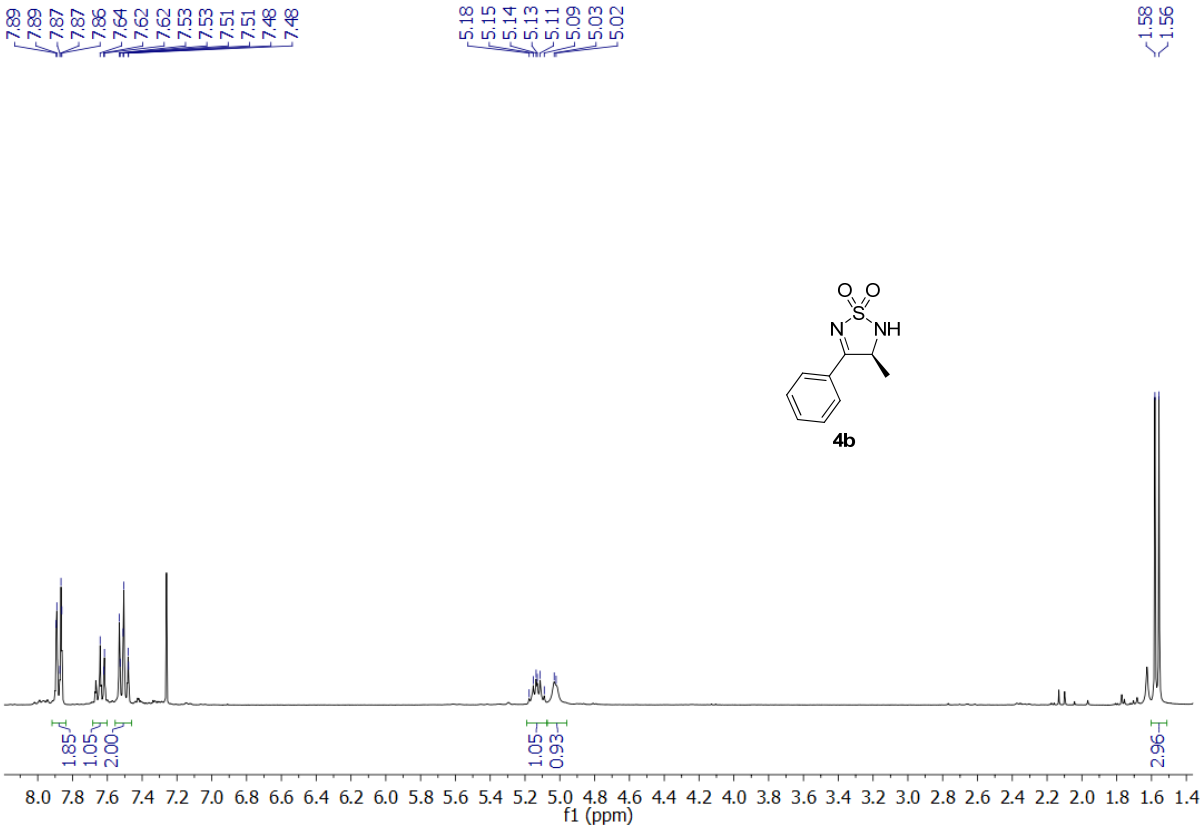
f1 (ppm)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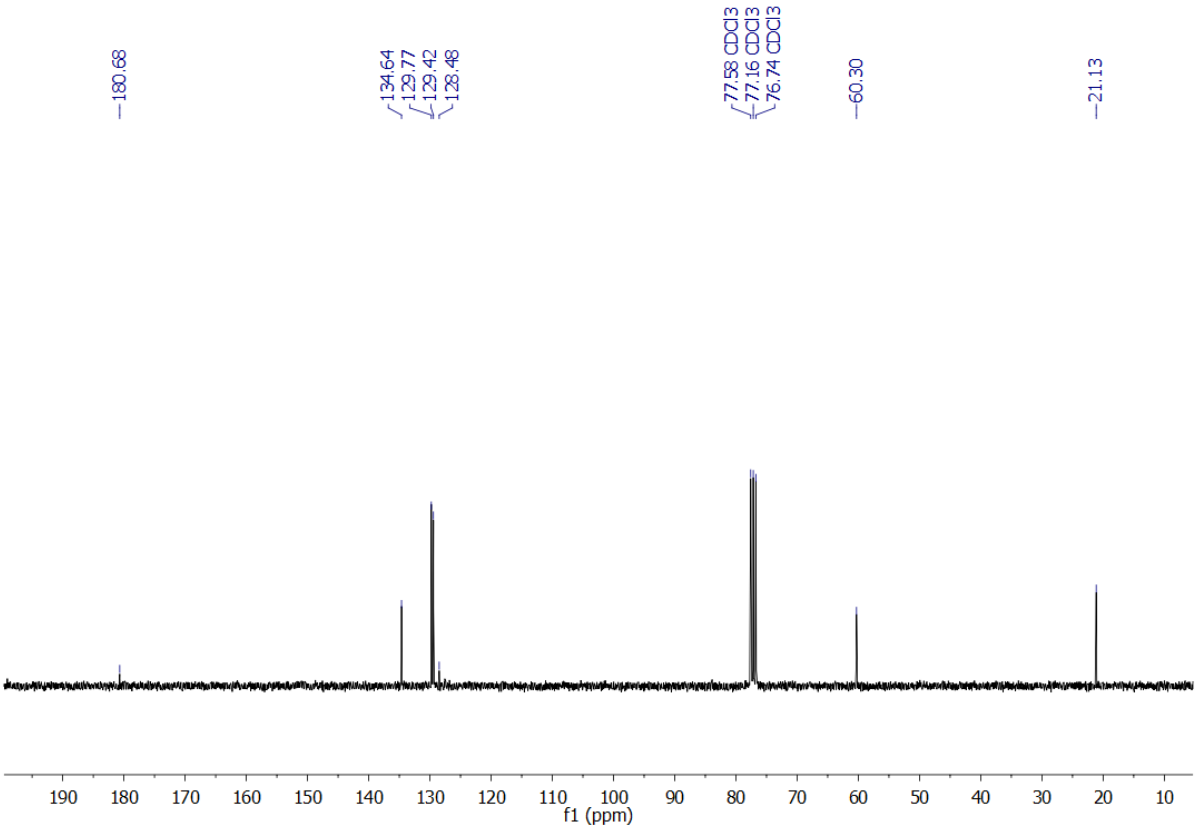
5.03
5.02
1.58
1.56
O
O
S
N
NH
4b
1.85
1.05
2.00
1.05
0.93
2.96
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)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60.30
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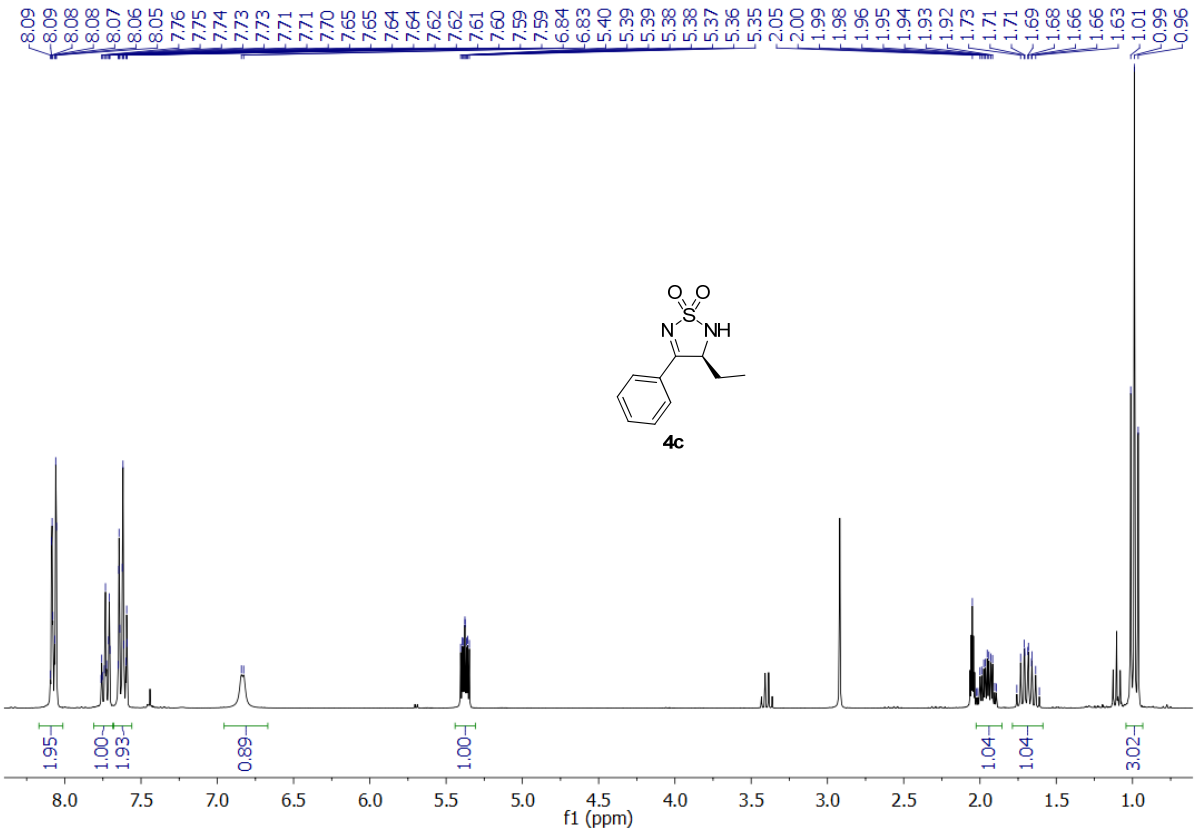
f1 (ppm)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O O S N NH
4c
1.95 1.00 1.93 0.89 1.00 1.04 1.04 3.02
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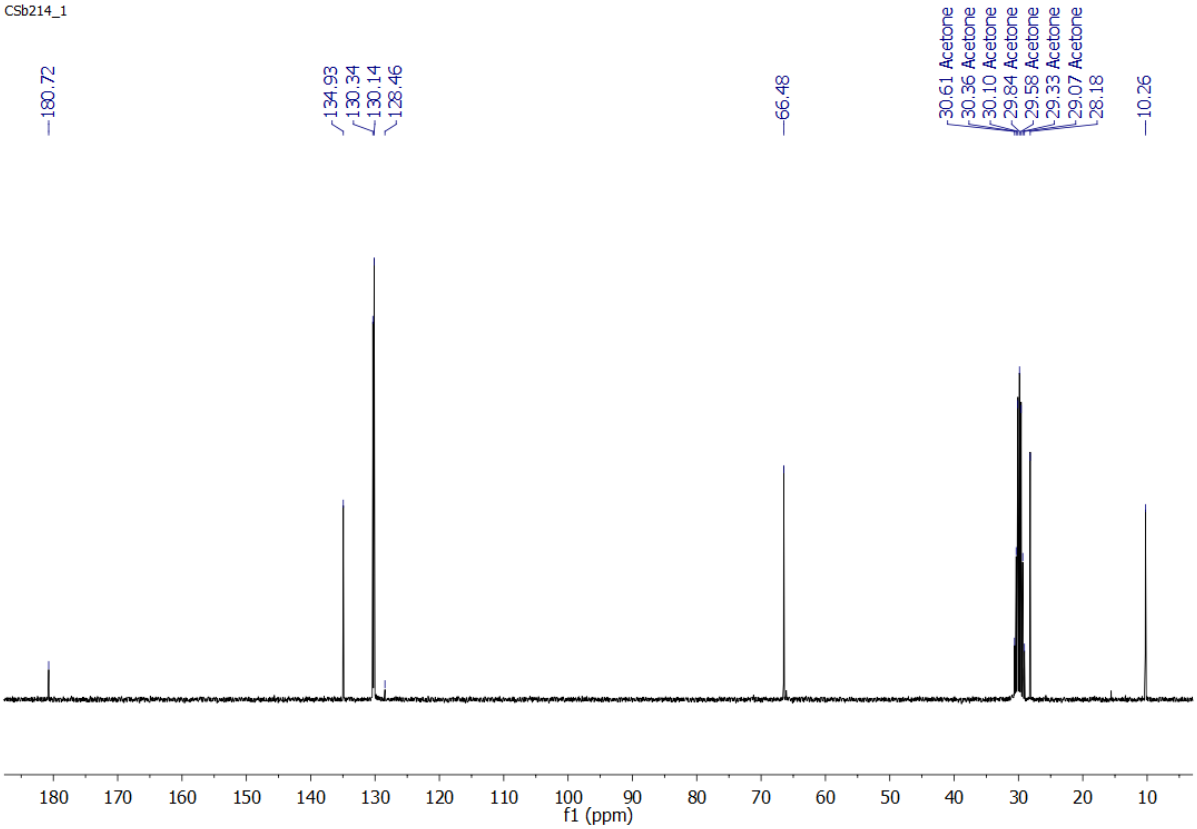
f1 (ppm)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180.72
134.93 130.34 130.14 128.46
66.48
30.61 Acetone 30.36 Acetone 30.10 Acetone 29.84 Acetone 29.58 Acetone 29.33 Acetone 29.07 Acetone 28.18
10.26
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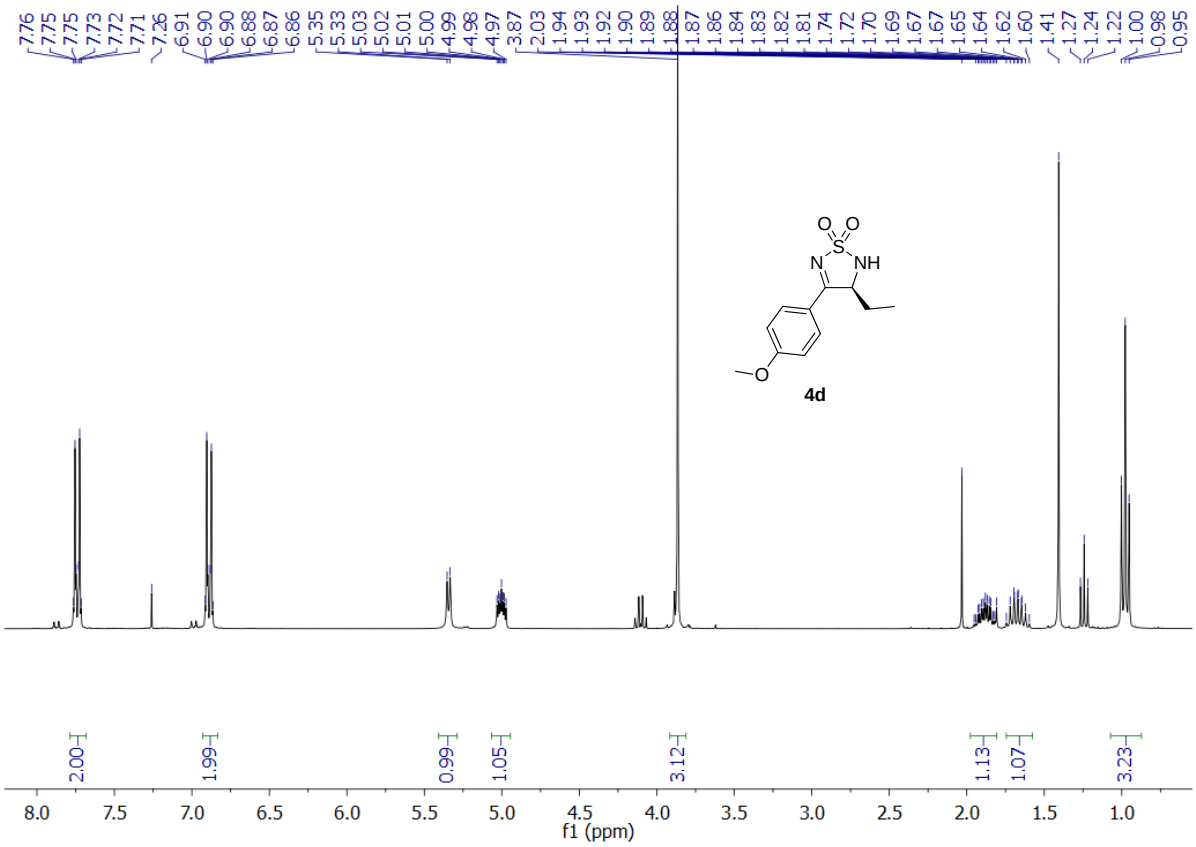
f1 (ppm)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7.75
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6.90
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6.87
6.86
5.35
5.33
5.03
5.02
5.01
5.00
4.99
4.98
4.97
3.87
2.03
1.94
1.93
1.92
1.90
1.89
1.88
1.87
1.86
1.84
1.83
1.82
1.81
1.74
1.72
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1.69
1.67
1.67
1.65
1.64
1.62
1.60
1.41
1.27
1.24
1.22
1.00
0.98
0.95
O
O
S
N
NH
O
4d
2.00
1.99
0.99
1.05
3.12
1.13
1.07
3.23
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7.5
7.0
6.5
6.0
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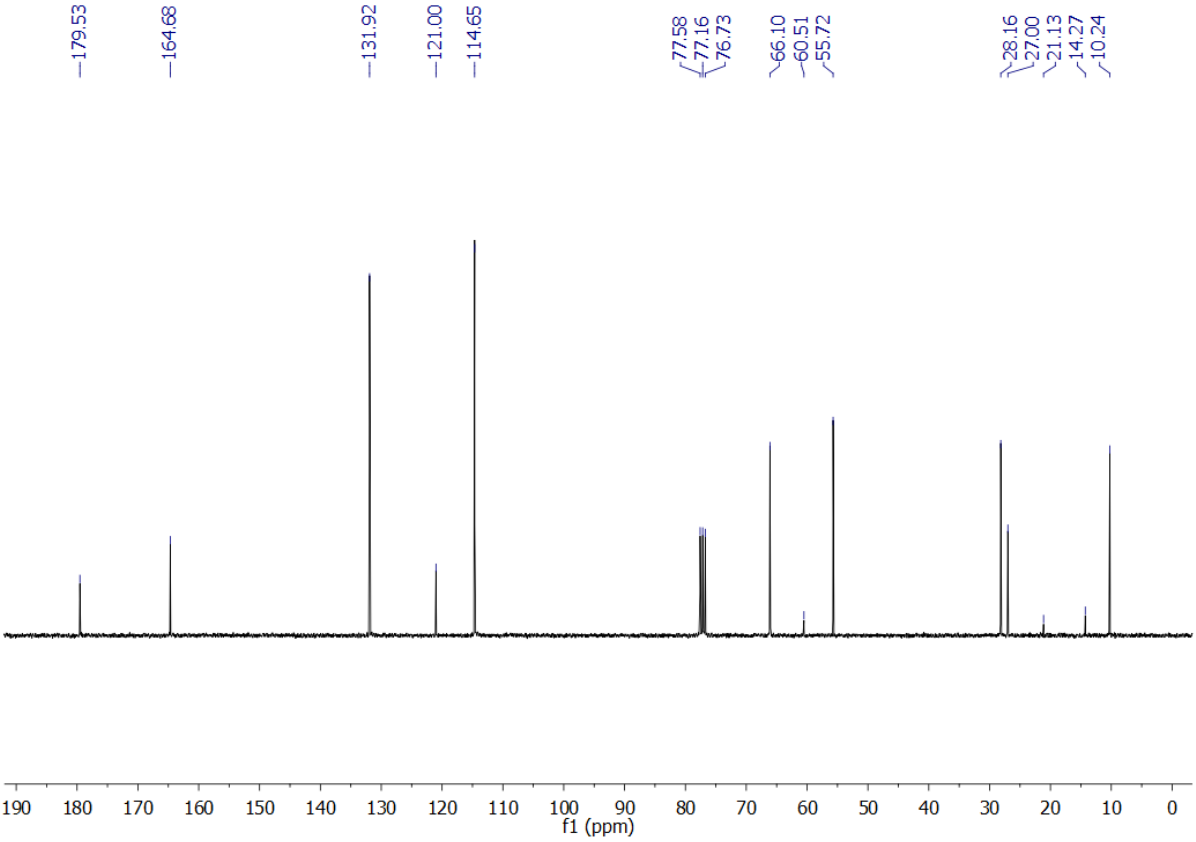
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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131.92
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77.58
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76.73
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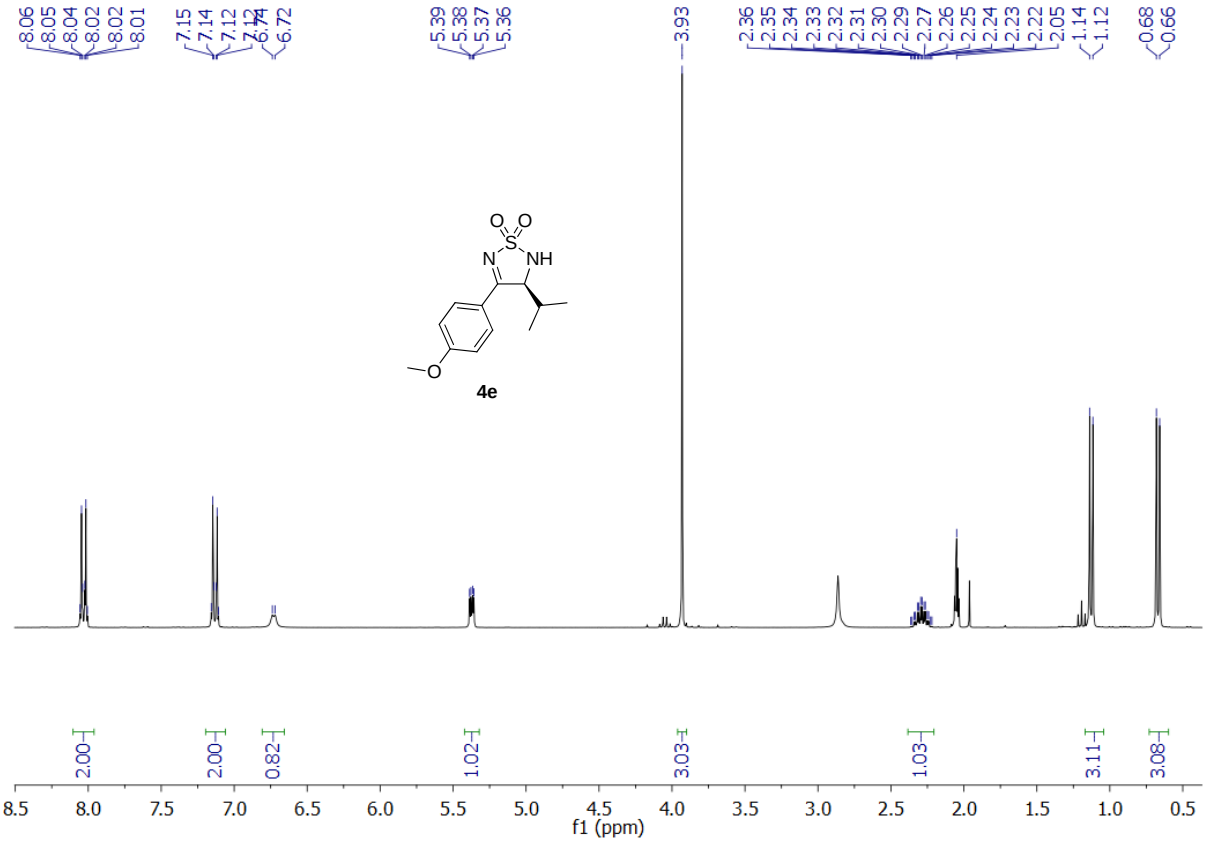
60.51
55.72
28.16
27.00
21.13
14.27
10.24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.02
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7.14
7.12
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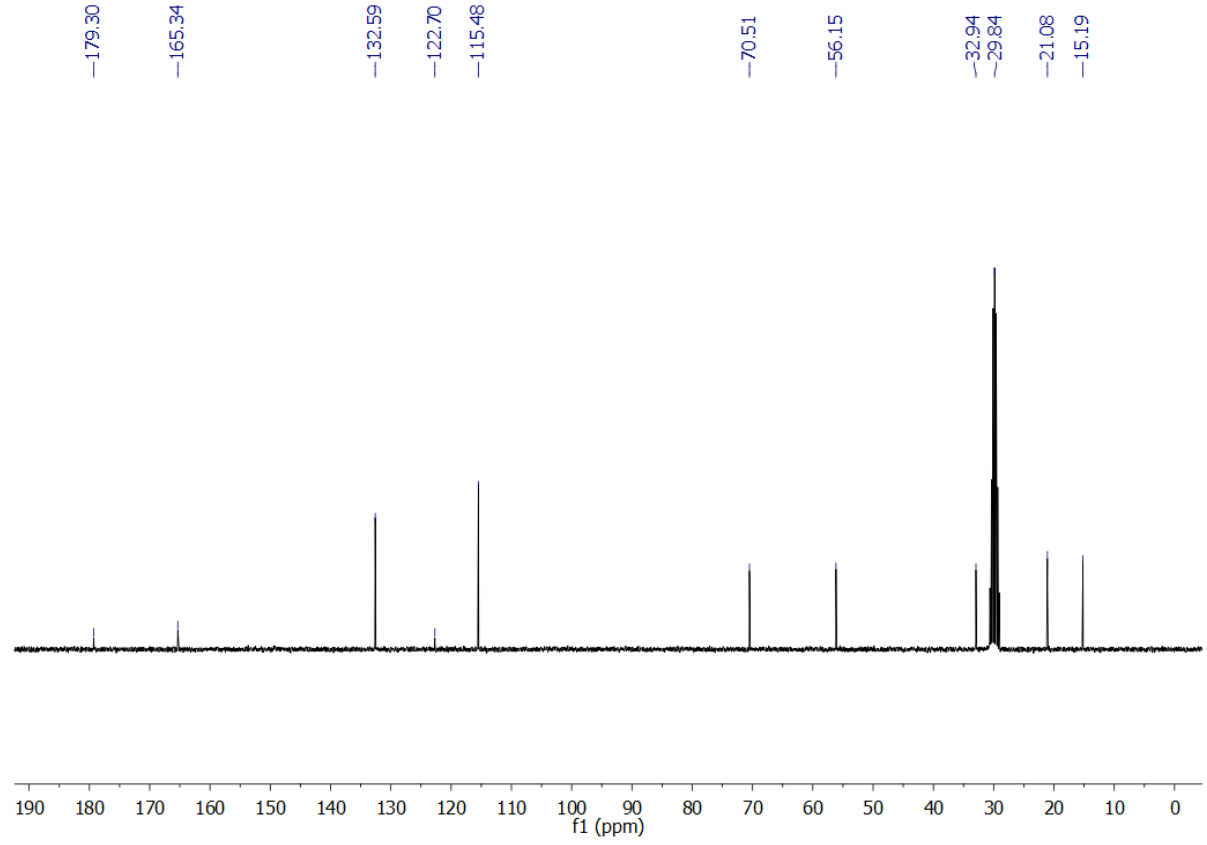
6.72
5.39
5.38
5.37
5.36
3.93
2.36
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.27
2.26
2.25
2.24
2.23
2.22
2.05
1.14
1.12
0.68
0.66
O
O
S
N
NH
O
4e
2.00
2.00
0.82
1.02
3.03
1.03
3.11
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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70.51
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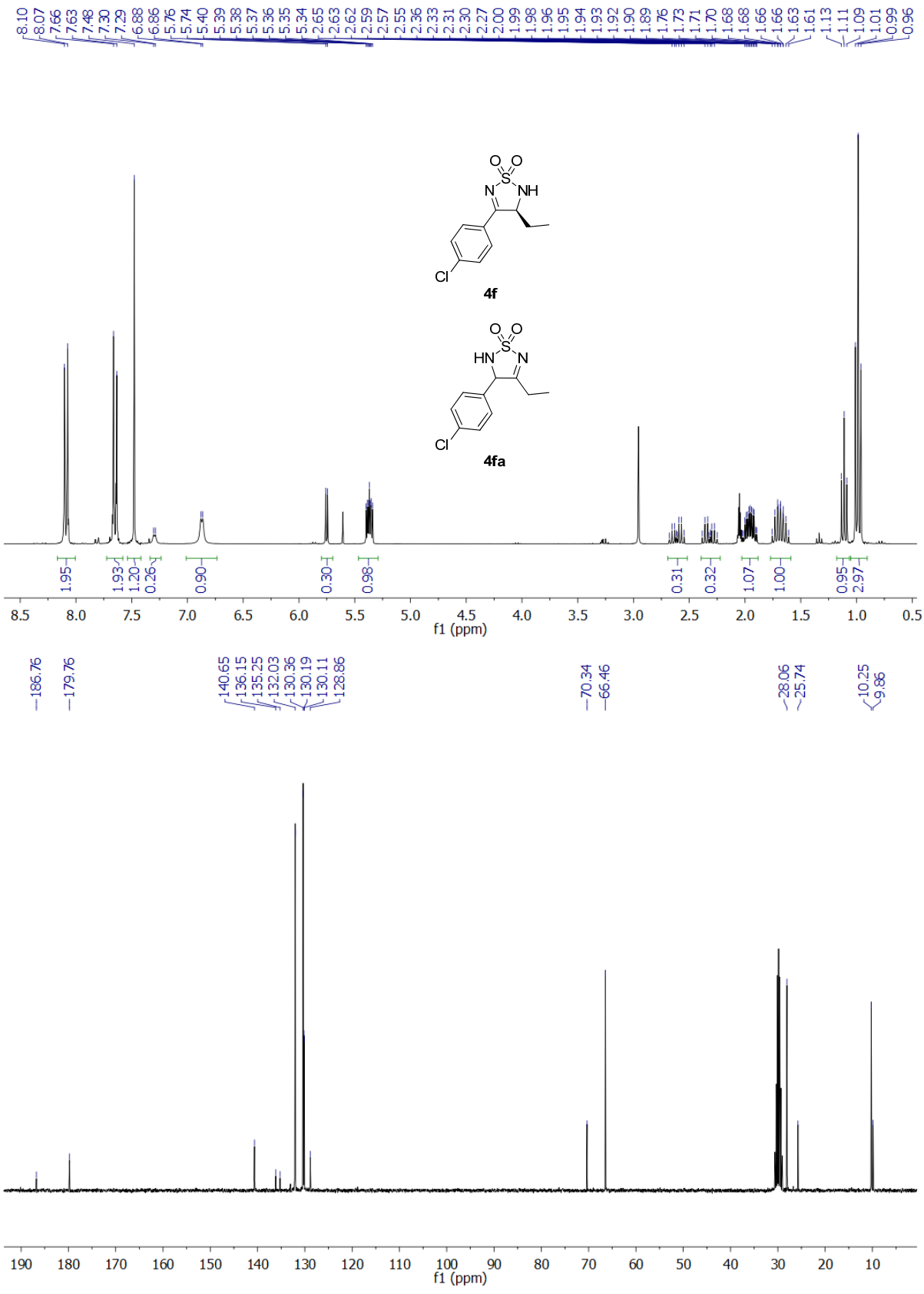
32.94
29.84
21.08
15.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.30
7.29
6.88
6.86
5.76
5.74
5.40
5.39
5.38
5.37
5.36
5.35
5.34
2.65
2.63
2.62
2.59
2.57
2.55
2.36
2.33
2.31
2.30
2.27
2.00
1.99
1.98
1.96
1.95
1.94
1.93
1.92
1.90
1.89
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1.71
1.70
1.68
1.68
1.66
1.66
1.63
1.61
1.13
1.11
1.09
1.01
0.99
0.96
O
O
S
N
NH
Cl
4f
HN
4fa
1.95
1.93
1.20
0.26
0.90
0.30
0.98
0.31
0.32
1.07
1.00
0.95
2.97
f1 (ppm)
186.76
179.76
140.65
136.15
135.25
132.03
130.36
130.19
130.11
128.86
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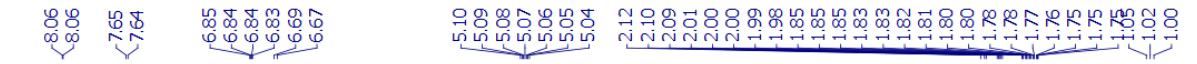
28.06
25.74
10.25
9.86
f1 (ppm)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8.06
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7.64
6.85
6.84
6.84
6.83
6.69
6.67
5.10
5.09
5.08
5.07
5.06
5.05
5.04
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2.09
2.01
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1.85
1.85
1.85
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1.83
1.82
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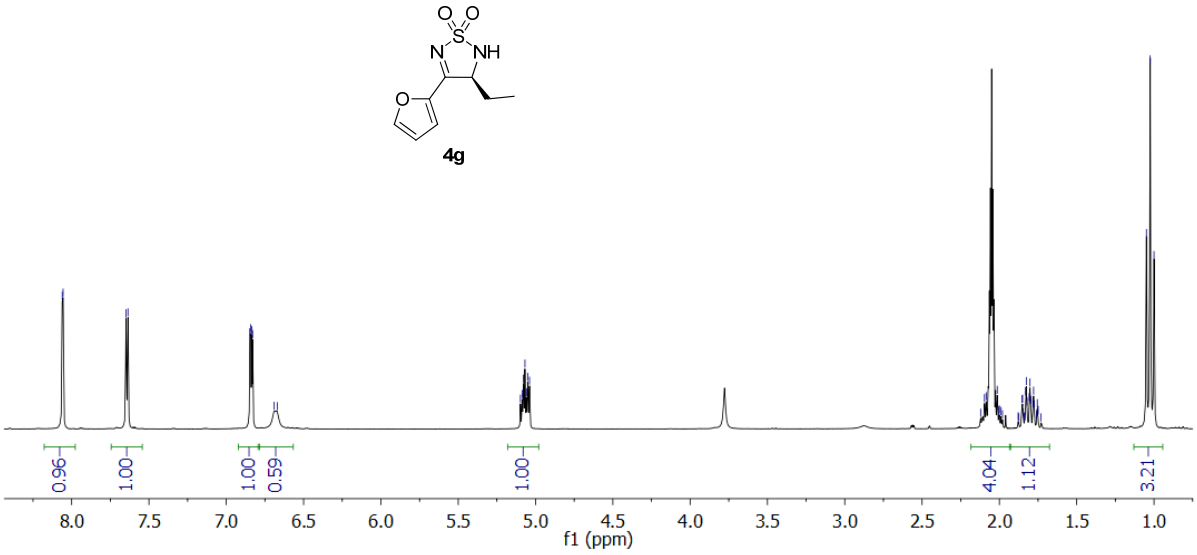
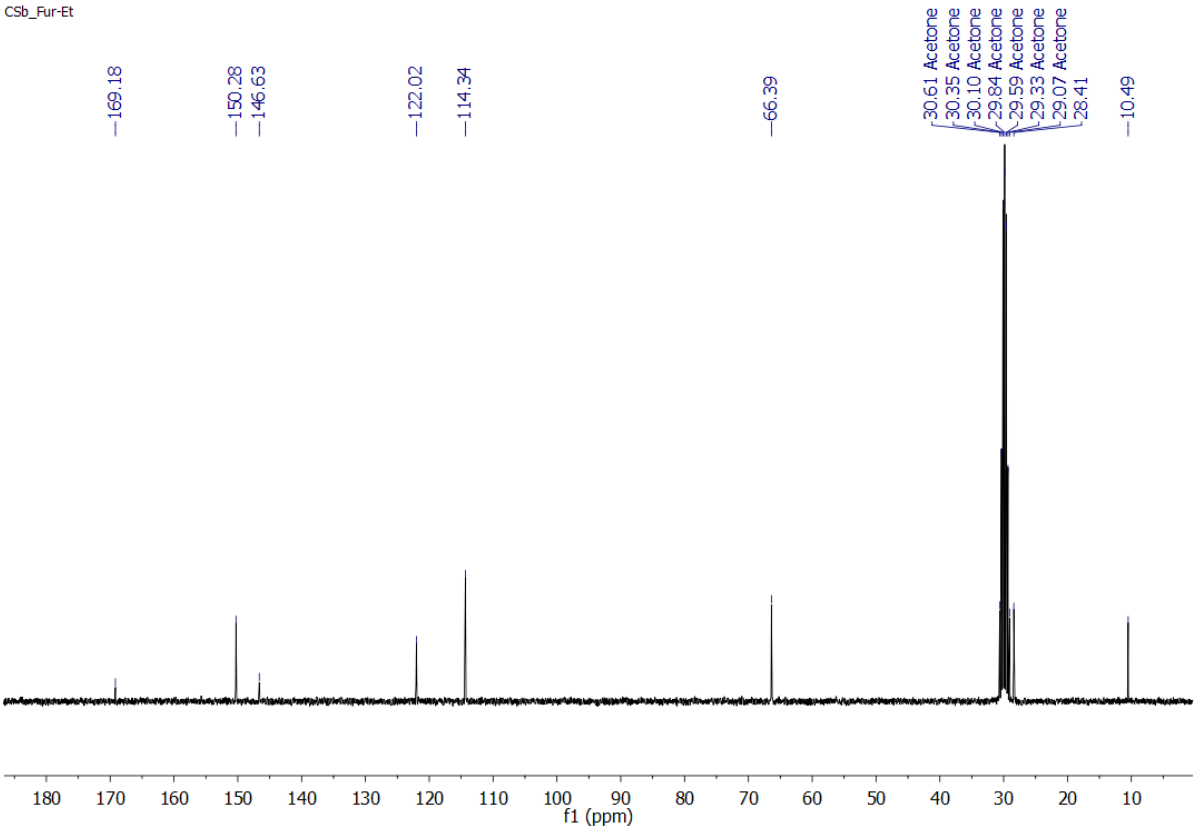
1.75
1.75
1.75
1.05
1.02
1.00


O
O
S
N
NH
O
4g
0.96
1.00
1.00
0.59
1.00
4.04
1.12
3.21
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
f1 (ppm)


CSb_Fur-Et
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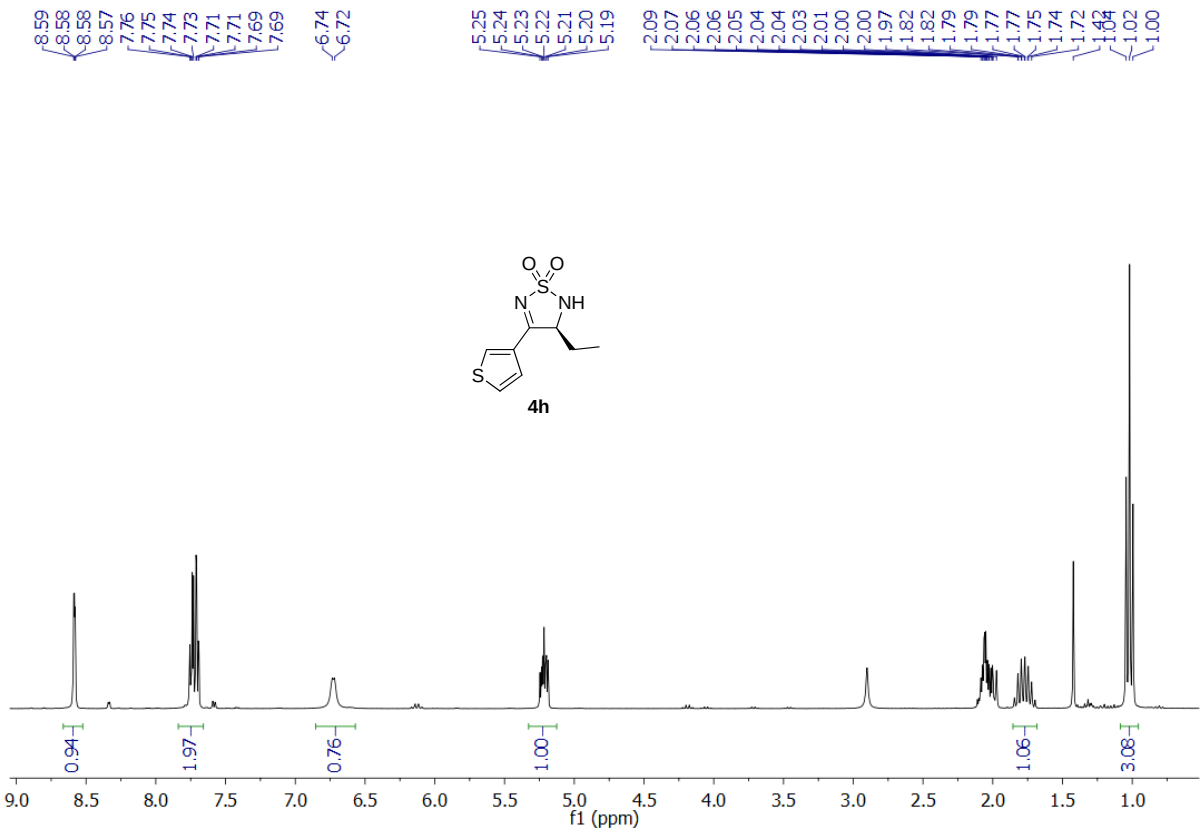
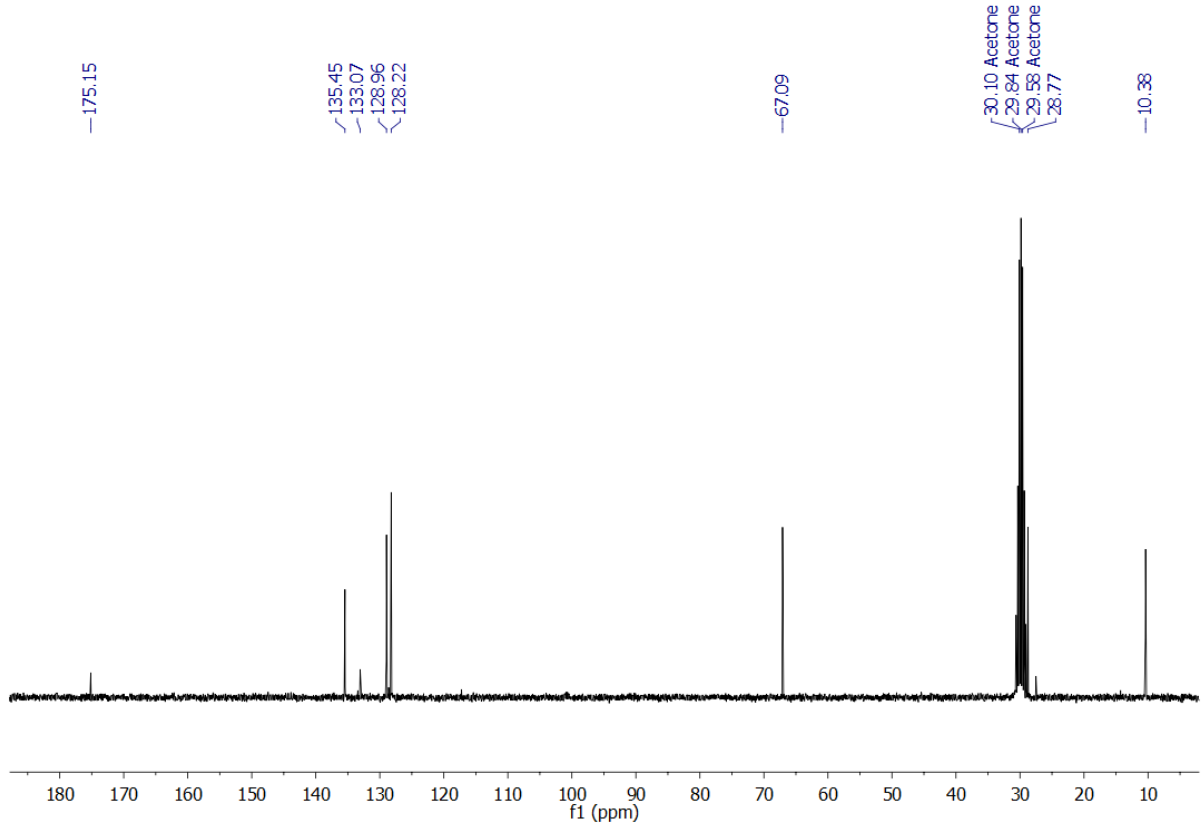
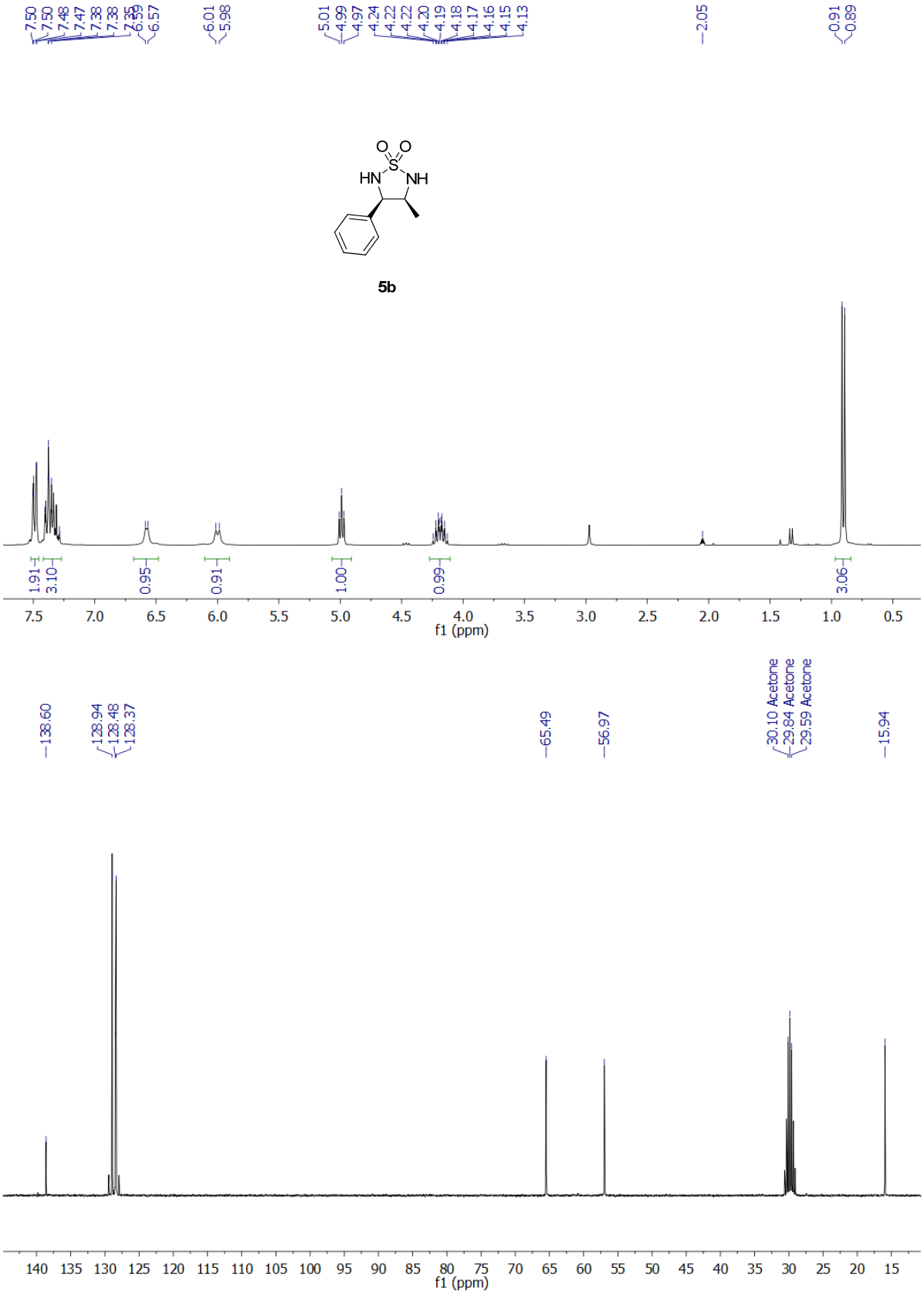
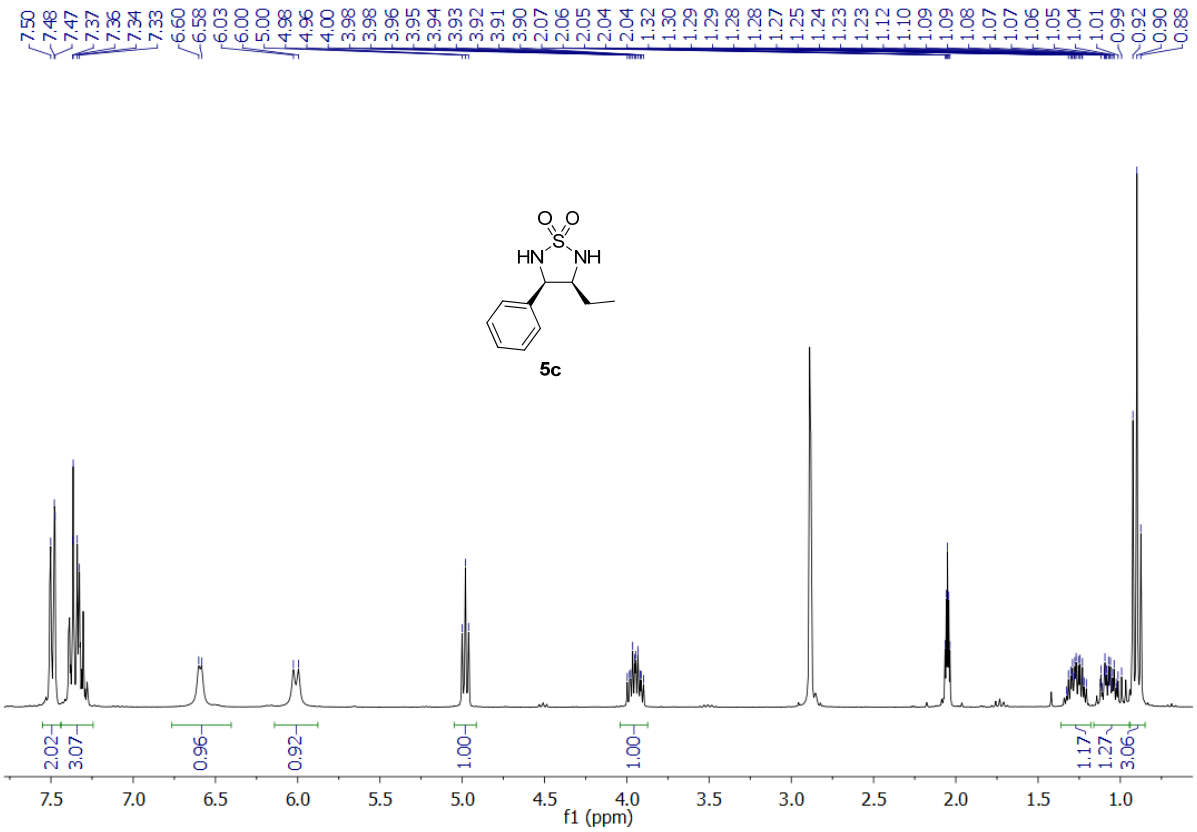
150.28
146.63
122.02
114.34
66.39
30.61 Acetone
30.35 Acetone
30.10 Acetone
29.84 Acetone
29.59 Acetone
29.33 Acetone
29.07 Acetone
28.41
10.49
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.59
8.58
8.58
8.57
7.76
7.75
7.74
7.73
7.71
7.71
7.69
7.69
6.74
6.72
5.25
5.24
5.23
5.22
5.21
5.20
5.19
2.09
2.07
2.06
2.06
2.05
2.04
2.04
2.03
2.01
2.00
2.00
1.97
1.82
1.82
1.79
1.79
1.77
1.77
1.75
1.74
1.72
1.02
1.00
O
O
N
S
NH
S
4h
0.94
1.97
0.76
1.00
1.06
3.08
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
f1 (ppm)


175.15
135.45
133.07
128.96
128.22
67.09
30.10 Acetone
29.84 Acetone
29.58 Acetone
28.77
10.38
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.50
7.50
7.48
7.47
7.38
7.38
7.35
6.59
6.57
6.01
5.98
5.01
4.99
4.97
4.24
4.22
4.22
4.20
4.19
4.18
4.17
4.16
4.15
4.13
2.05
0.91
0.89
O
O
HN
S
NH
5b
1.91
3.10
0.95
0.91
1.00
0.99
3.06
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)
138.60
128.94
128.48
128.37
65.49
56.97
30.10 Acetone
29.84 Acetone
29.59 Acetone
15.94
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
f1 (ppm)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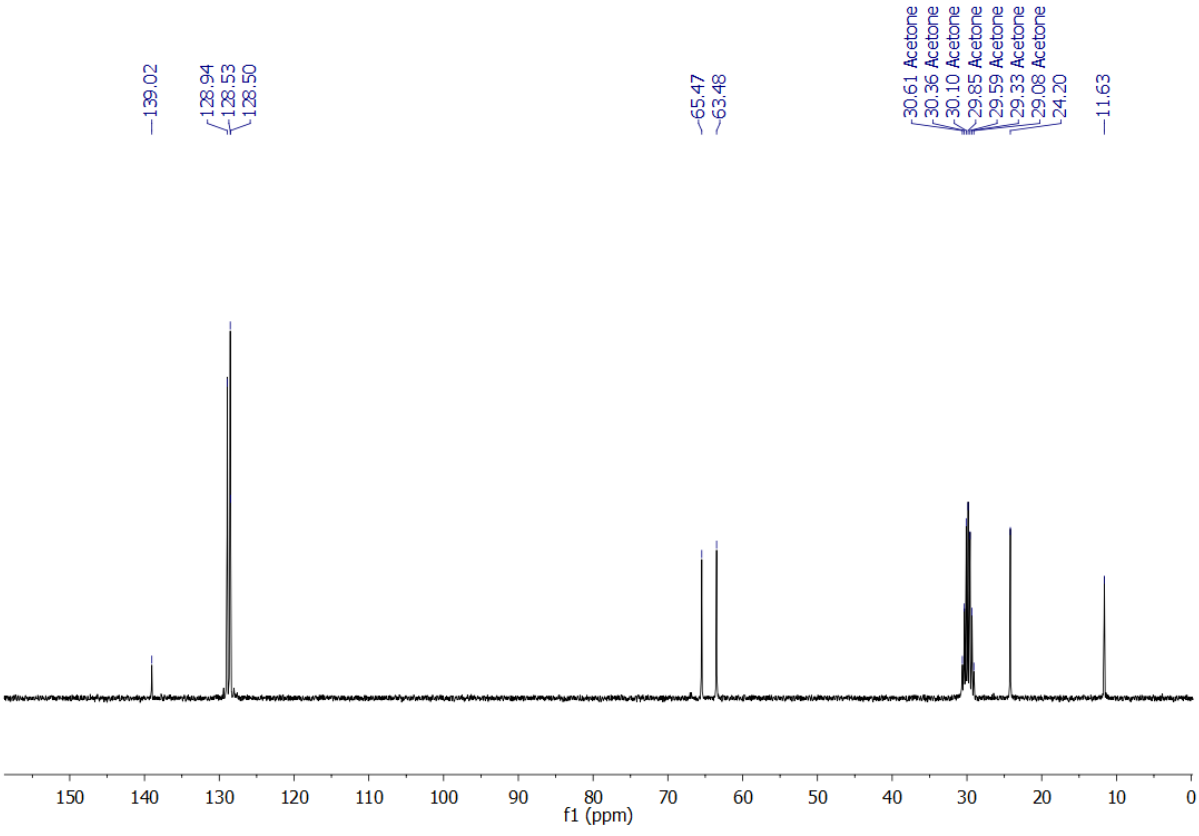
O O
S
HN NH
5c
2.02 3.07 0.96 0.92 1.00 1.00 1.17 1.27 3.06
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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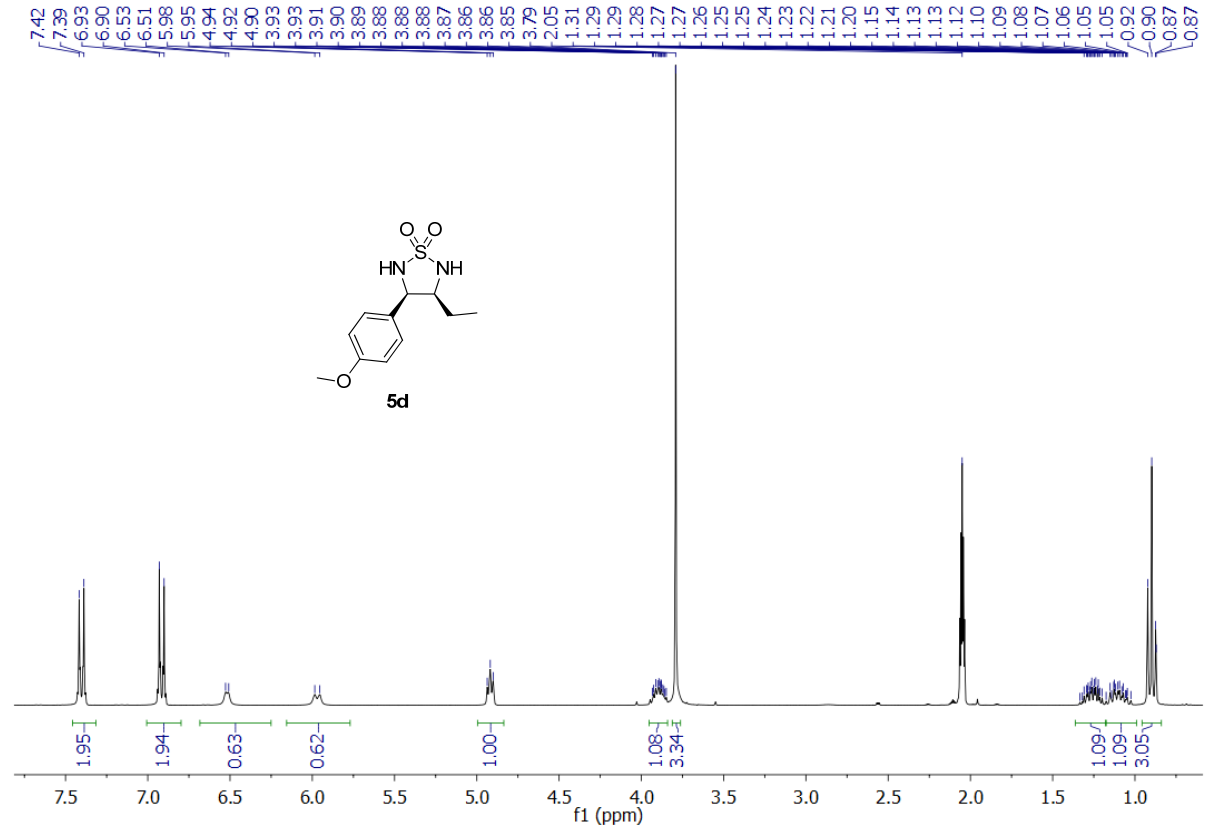
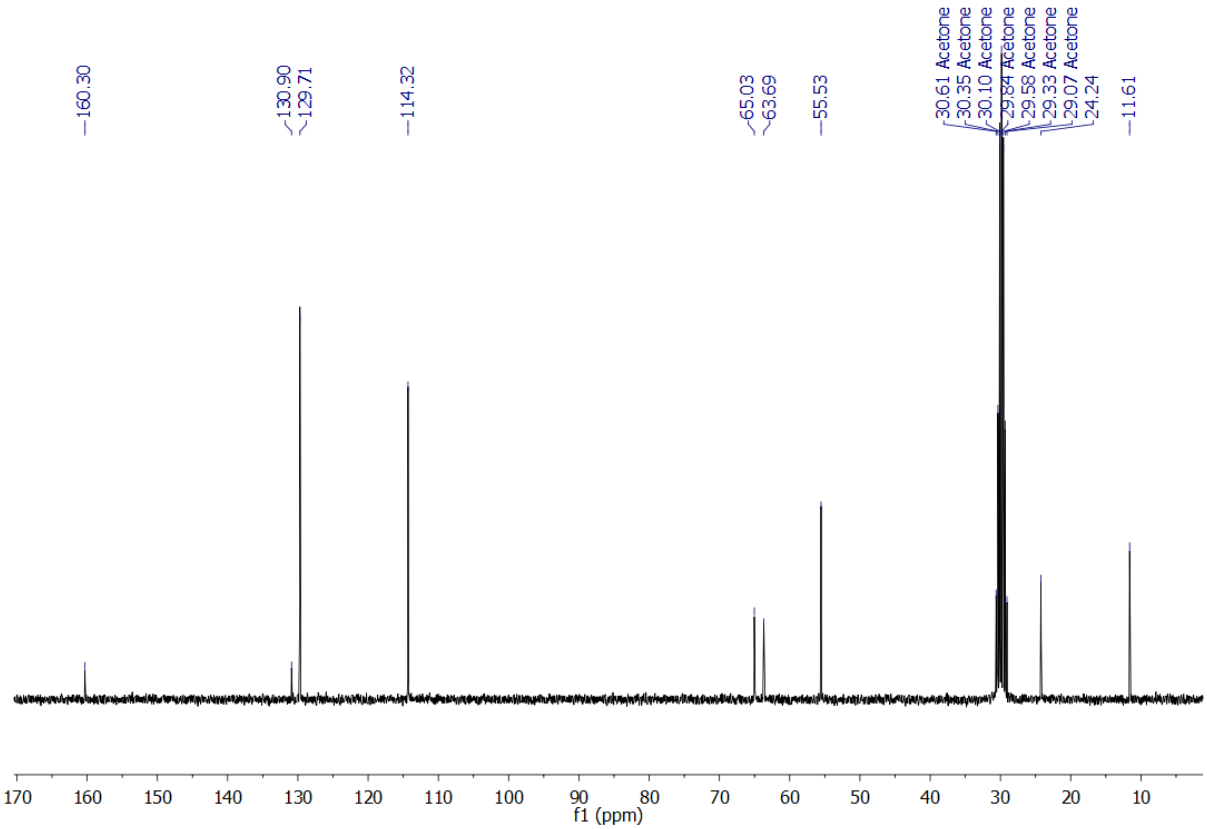
128.94 128.53 128.50
65.47 63.48
30.61 Acetone 30.36 Acetone 30.10 Acetone 29.85 Acetone 29.59 Acetone 29.33 Acetone 29.08 Acetone 24.20
11.63
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42 7.39 6.93 6.90 6.53 6.51 5.98 5.95 4.94 4.92 4.90 3.93 3.93 3.91 3.90 3.89 3.88 3.88 3.88 3.87 3.86 3.86 3.85 3.79 2.05 1.31 1.29 1.29 1.28 1.27 1.27 1.26 1.25 1.25 1.24 1.23 1.22 1.21 1.20 1.15 1.14 1.13 1.13 1.12 1.10 1.09 1.08 1.07 1.06 1.05 1.05 0.92 0.90 0.87 0.87
O O
HN S NH
O
5d
1.95 1.94 0.63 0.62 1.00 1.08 3.34 1.09 1.09 3.05
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
f1 (ppm)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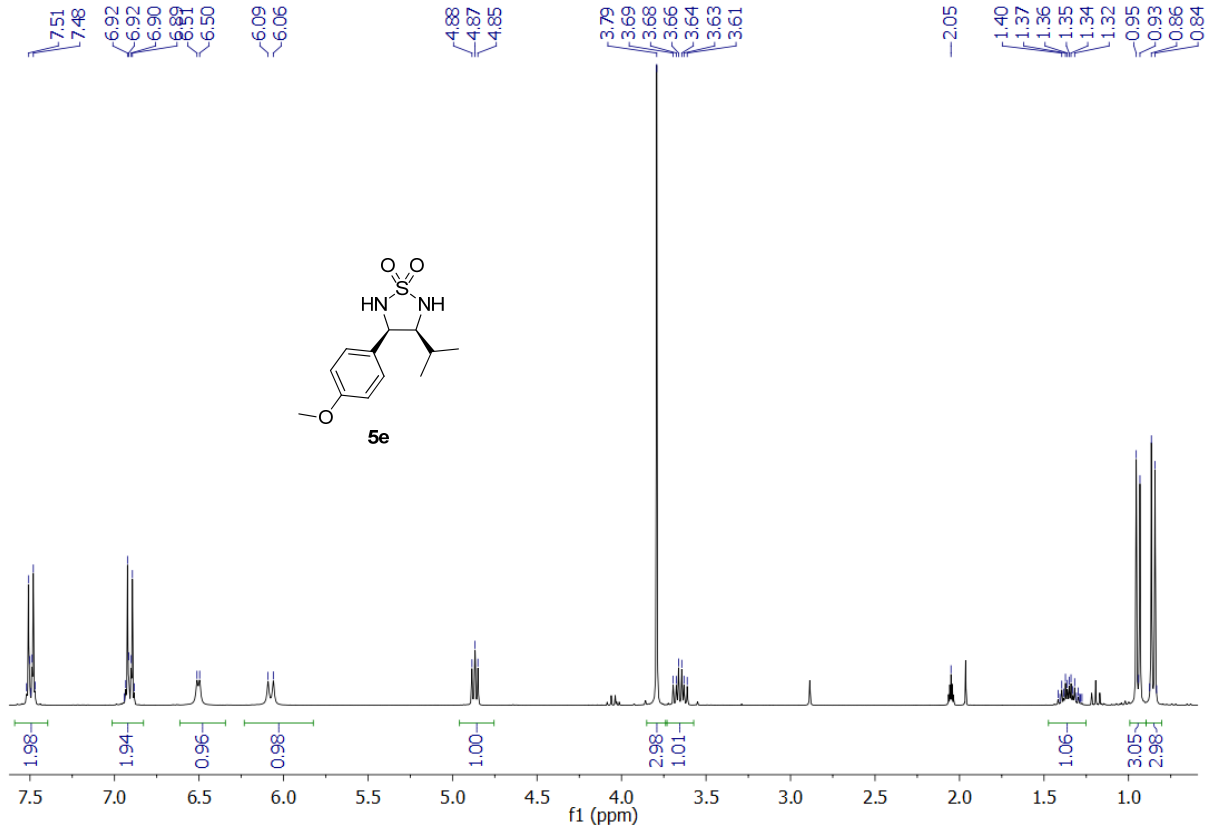
114.32
65.03
63.69
55.53
30.61 Acetone
30.35 Acetone
30.10 Acetone
29.84 Acetone
29.58 Acetone
29.33 Acetone
29.07 Acetone
24.24
11.61
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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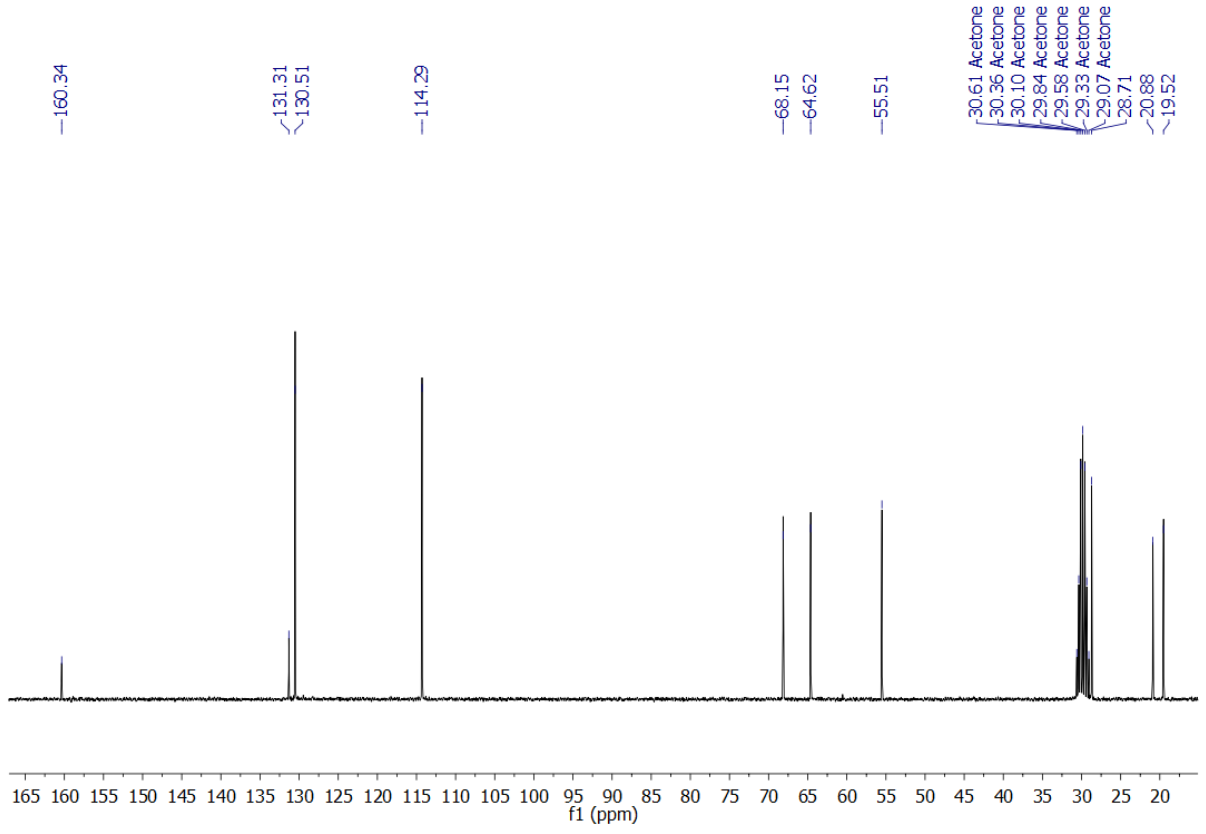
6.51
6.50
6.09
6.06
4.88
4.87
4.85
3.79
3.69
3.68
3.66
3.64
3.63
3.61
2.05
1.40
1.37
1.36
1.35
1.34
1.32
0.95
0.93
0.86
0.84
HN
NH
O
O
O
5e
1.98
1.94
0.96
0.98
1.00
2.98
1.01
1.06
3.05
2.98
f1 (ppm)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131.31
130.51
114.29
68.15
64.62
55.51
30.61 Acetone
30.36 Acetone
30.10 Acetone
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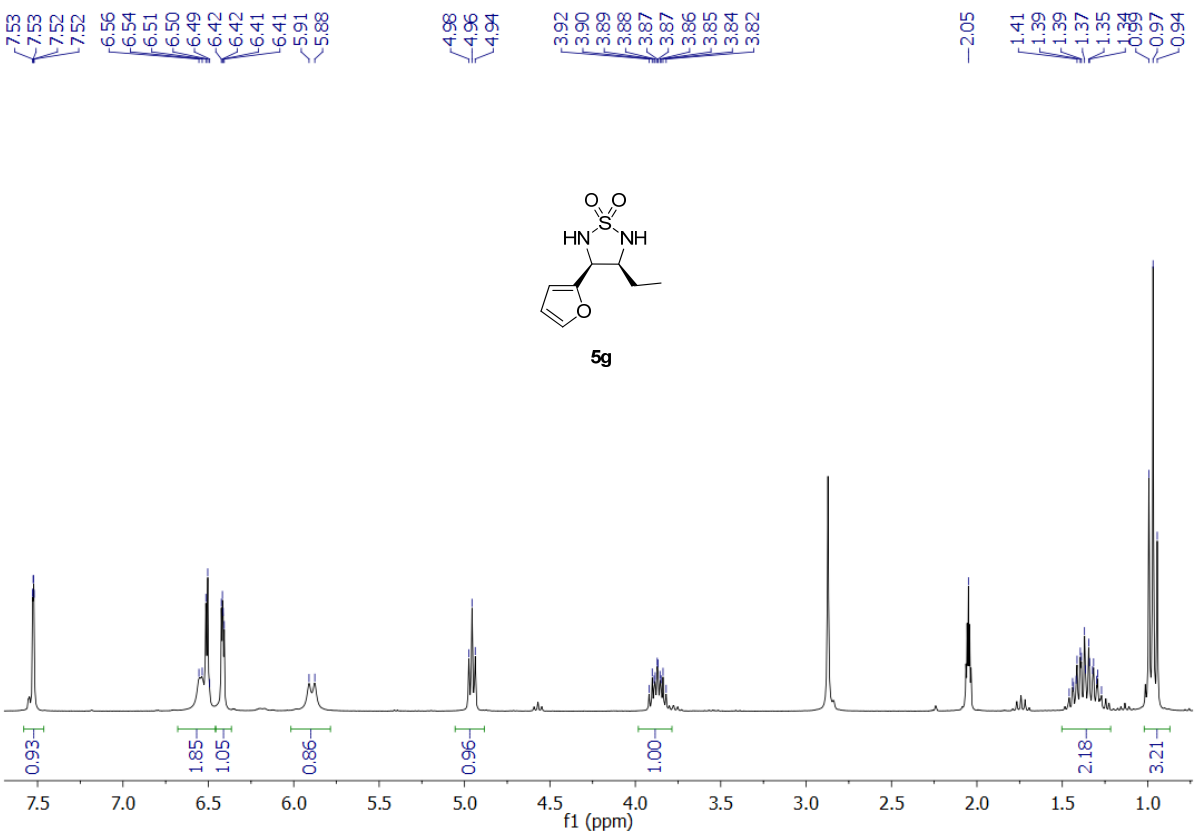
29.07 Acetone
28.71
20.88
19.52
f1 (ppm)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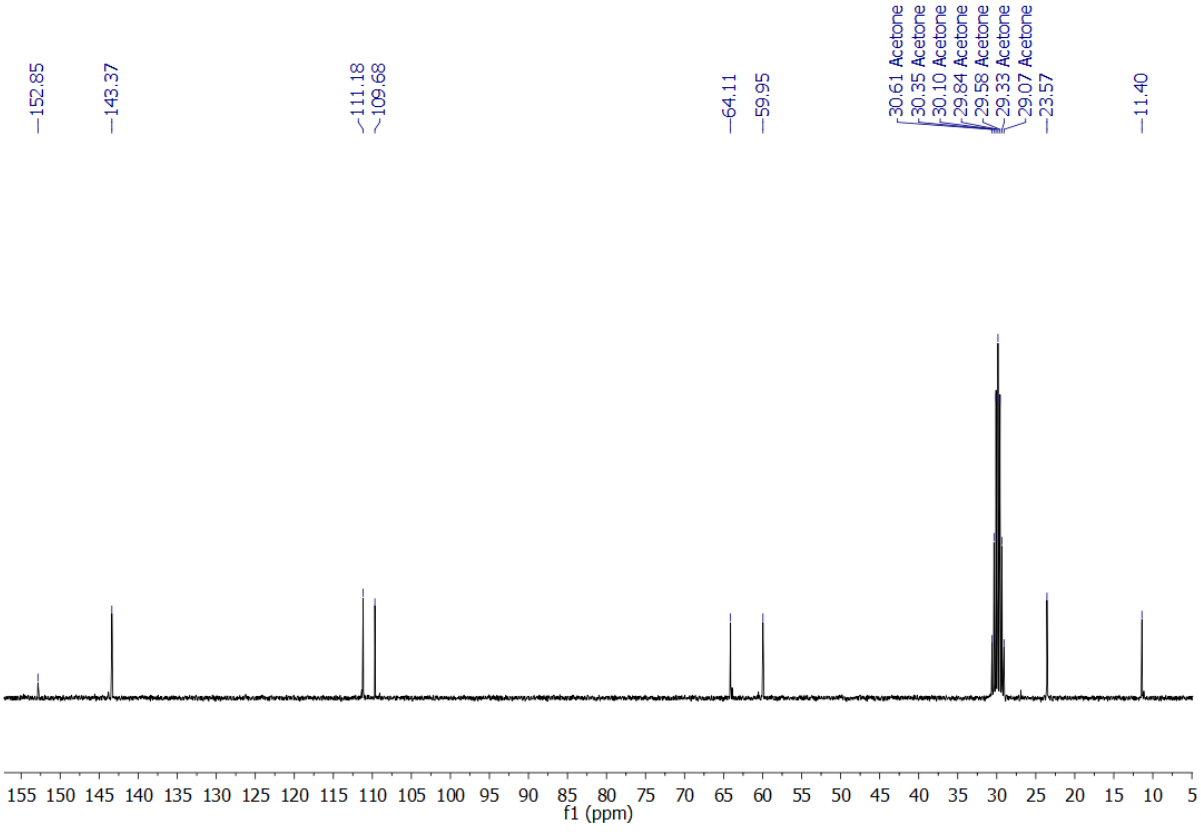
4.98
4.96
4.94
3.92
3.90
3.89
3.88
3.87
3.87
3.86
3.85
3.84
3.82
2.05
1.41
1.39
1.39
1.37
1.35
1.34
0.99
0.97
0.94
HN
NH
O
O
O
5g
0.93
1.85
1.05
0.86
0.96
1.00
2.18
3.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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64.11
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30.10 Acetone
29.84 Acetone
29.58 Acetone
29.33 Acetone
29.07 Acetone
23.57
11.40
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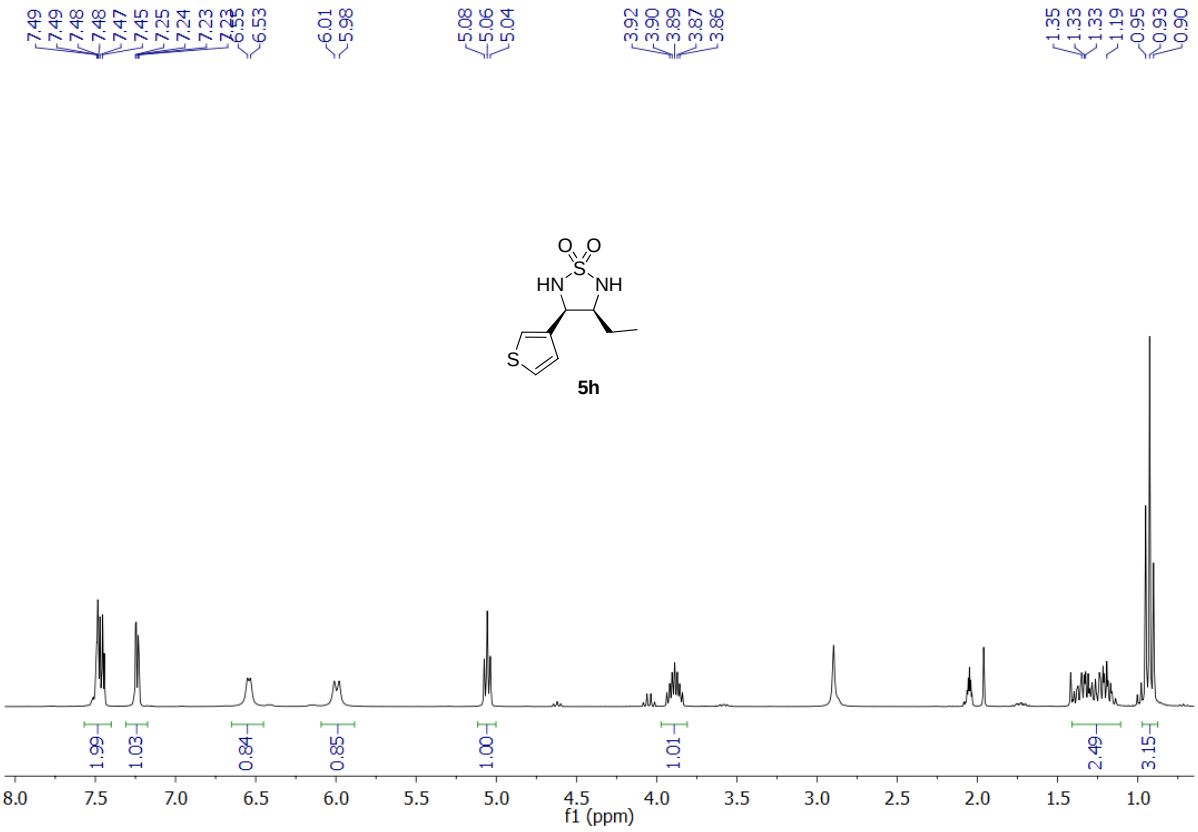
f1 (ppm)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6.53
6.01
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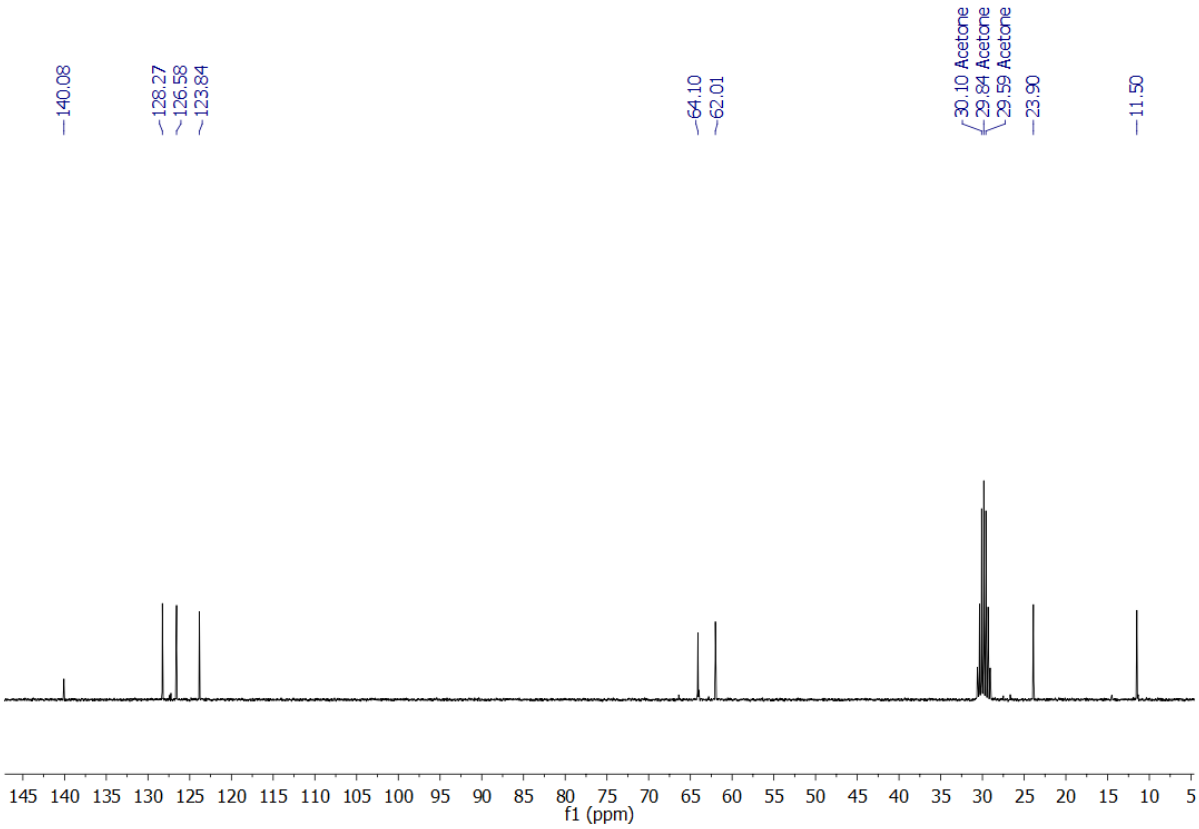
5.08
5.06
5.04
3.92
3.90
3.89
3.87
3.86
1.35
1.33
1.33
1.19
0.95
0.93
0.90
O
O
S
HN
NH
S
5h
1.99
1.03
0.84
0.85
1.00
1.01
2.49
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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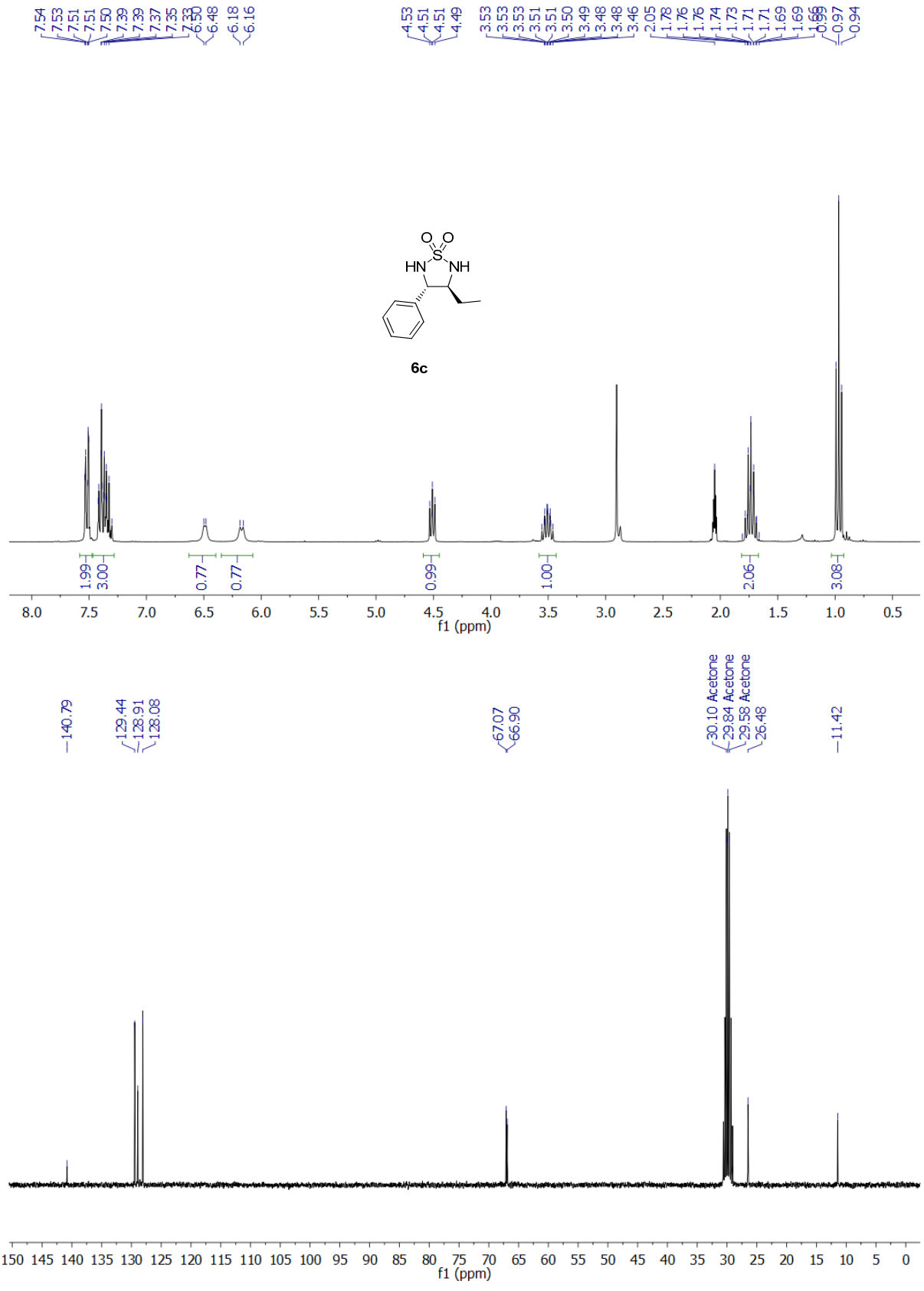
126.58
123.84
64.10
62.01
30.10 Acetone
29.84 Acetone
29.59 Acetone
23.90
11.50
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)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7.37
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6.50
6.48
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6.16
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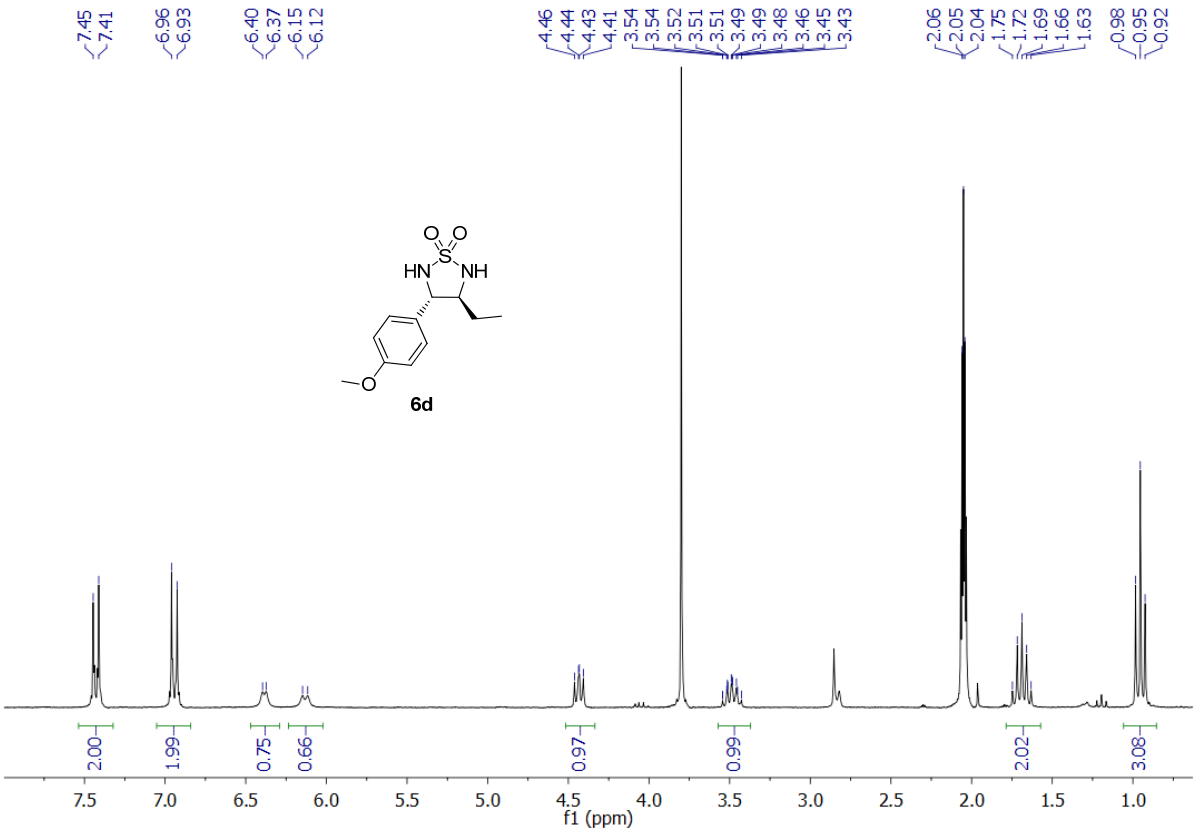
3.48
3.46
2.05
1.78
1.76
1.76
1.74
1.73
1.71
1.71
1.69
1.69
0.97
0.94
HN
S
NH
6c
1.99
3.00
0.77
0.77
0.99
1.00
2.06
3.08
f1 (ppm)
140.79
129.44
128.91
128.08
67.07
66.90
30.10 Acetone
29.84 Acetone
29.58 Acetone
26.48
11.42
f1 (ppm)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6.37
6.15
6.12
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4.44
4.43
4.41
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3.54
3.52
3.51
3.51
3.49
3.49
3.48
3.46
3.45
3.43
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2.05
2.04
1.75
1.72
1.69
1.66
1.63
0.98
0.95
0.92
HN
S
NH
O
O
O
6d
2.00
1.99
0.75
0.66
0.97
0.99
2.02
3.08
7.5
7.0
6.5
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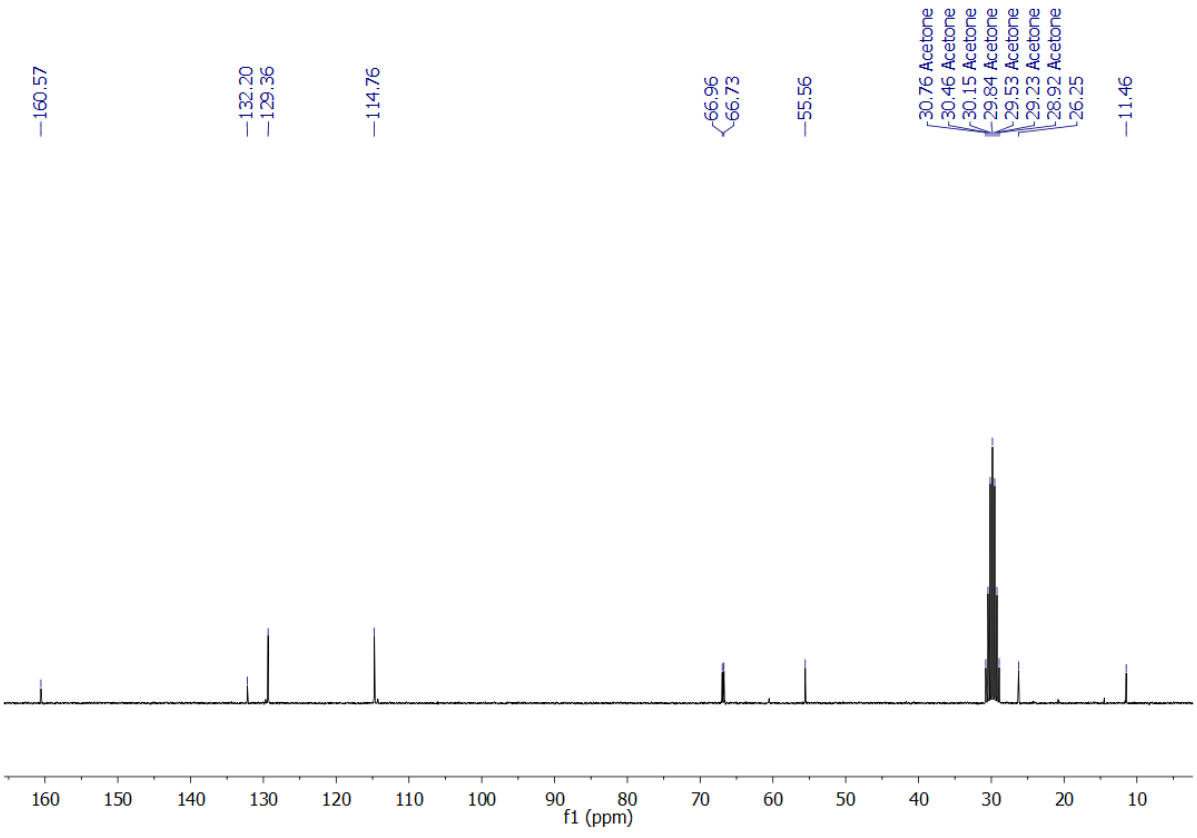
f1 (ppm)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66.96
66.73
55.56
30.76 Acetone
30.46 Acetone
30.15 Acetone
29.84 Acetone
29.53 Acetone
29.23 Acetone
28.92 Acetone
26.25
11.46
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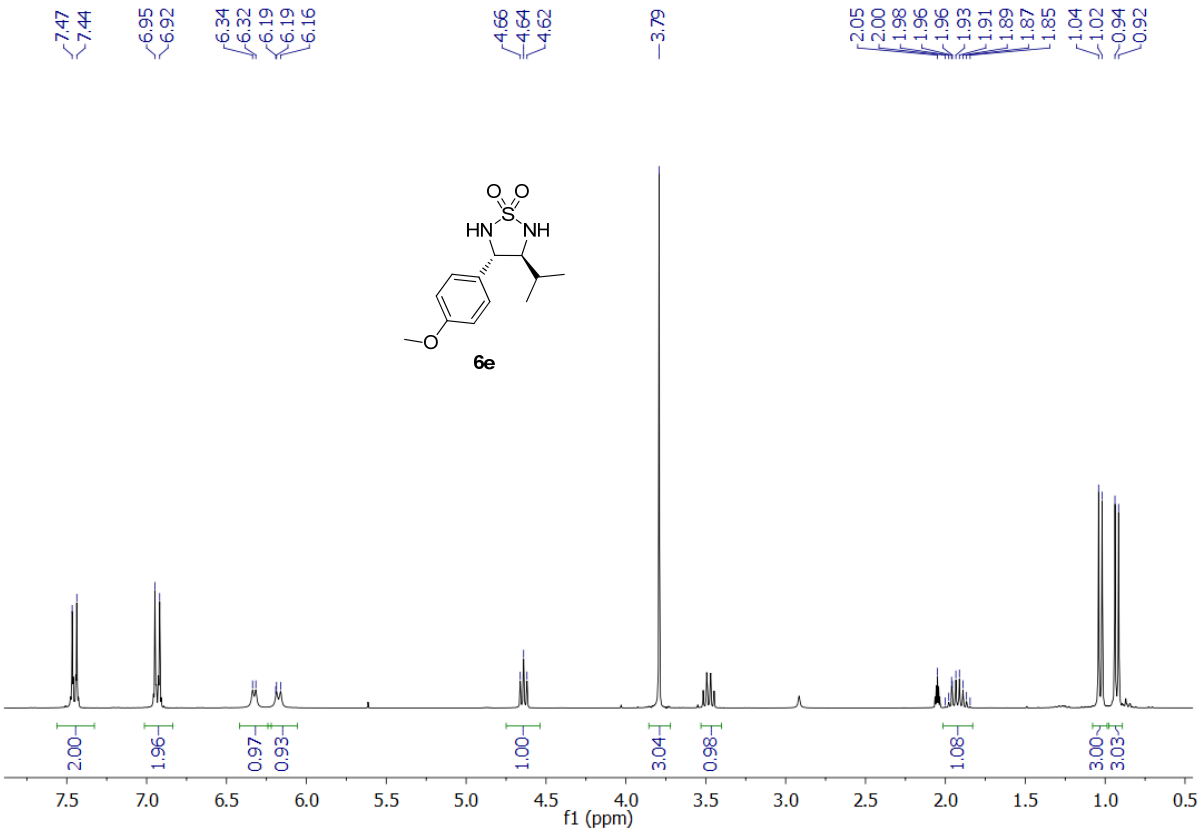
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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6.19
6.16
4.66
4.64
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3.79
2.05
2.00
1.98
1.96
1.96
1.93
1.91
1.89
1.87
1.85
1.04
1.02
0.94
0.92
HN
S
NH
O
O
O
6e
2.00
1.96
0.97
0.93
1.00
3.04
0.98
1.08
3.00
3.03
7.5
7.0
6.5
6.0
5.5
5.0
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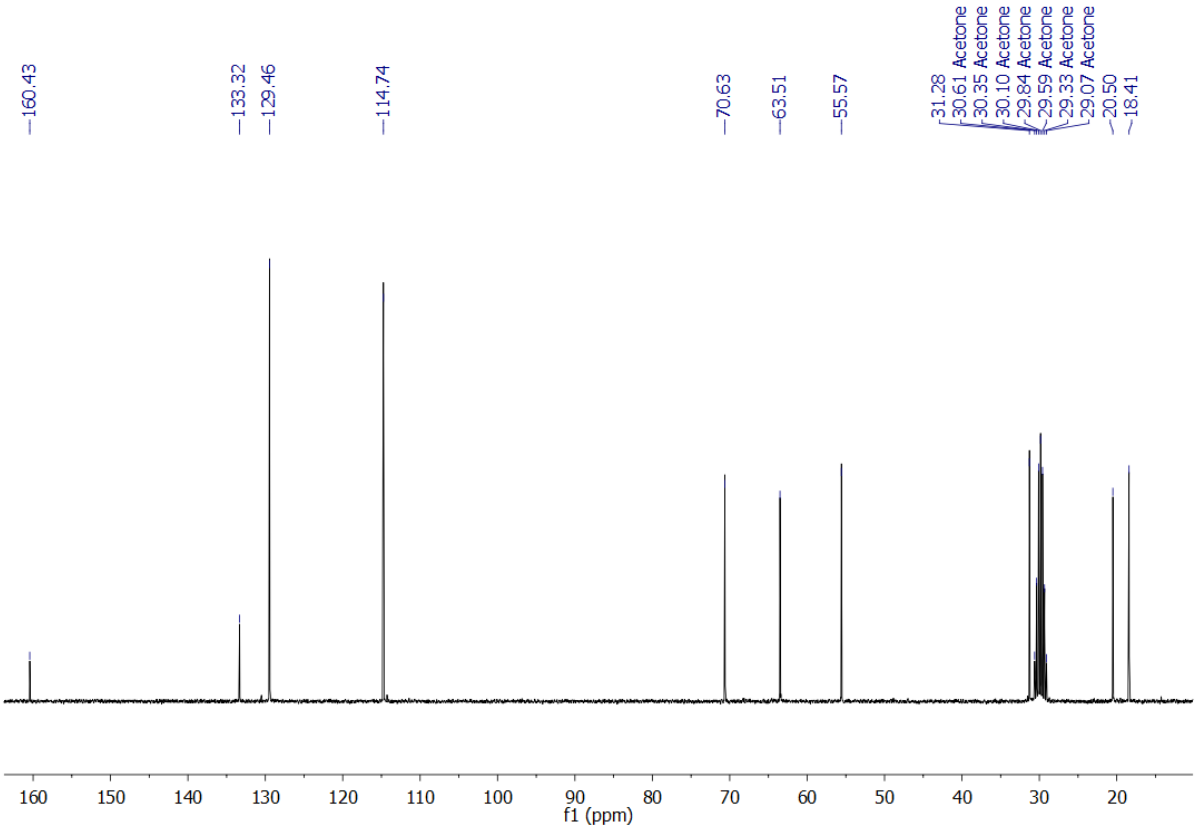
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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133.32
129.46
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63.51
55.57
31.28
30.61 Acetone
30.35 Acetone
30.10 Acetone
29.84 Acetone
29.59 Acetone
29.33 Acetone
29.07 Acetone
20.50
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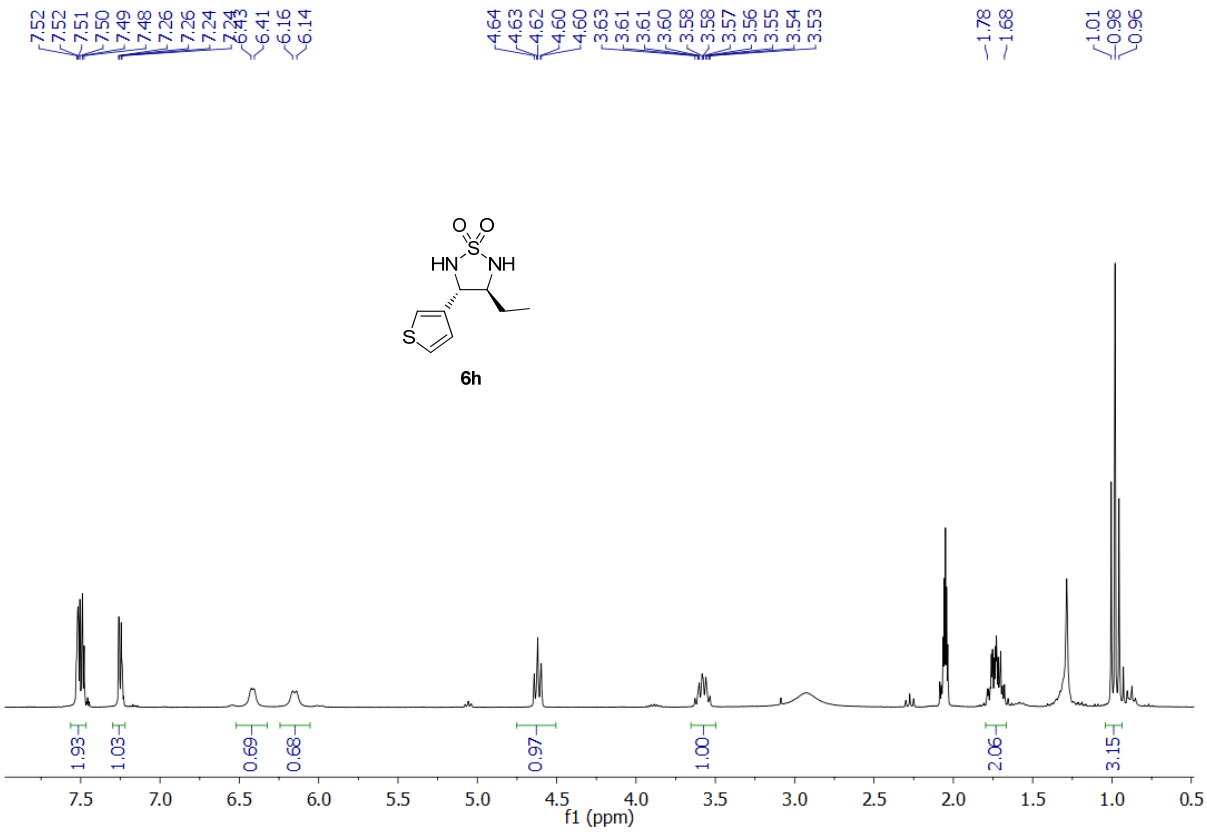
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.51
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7.26
7.24
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6.41
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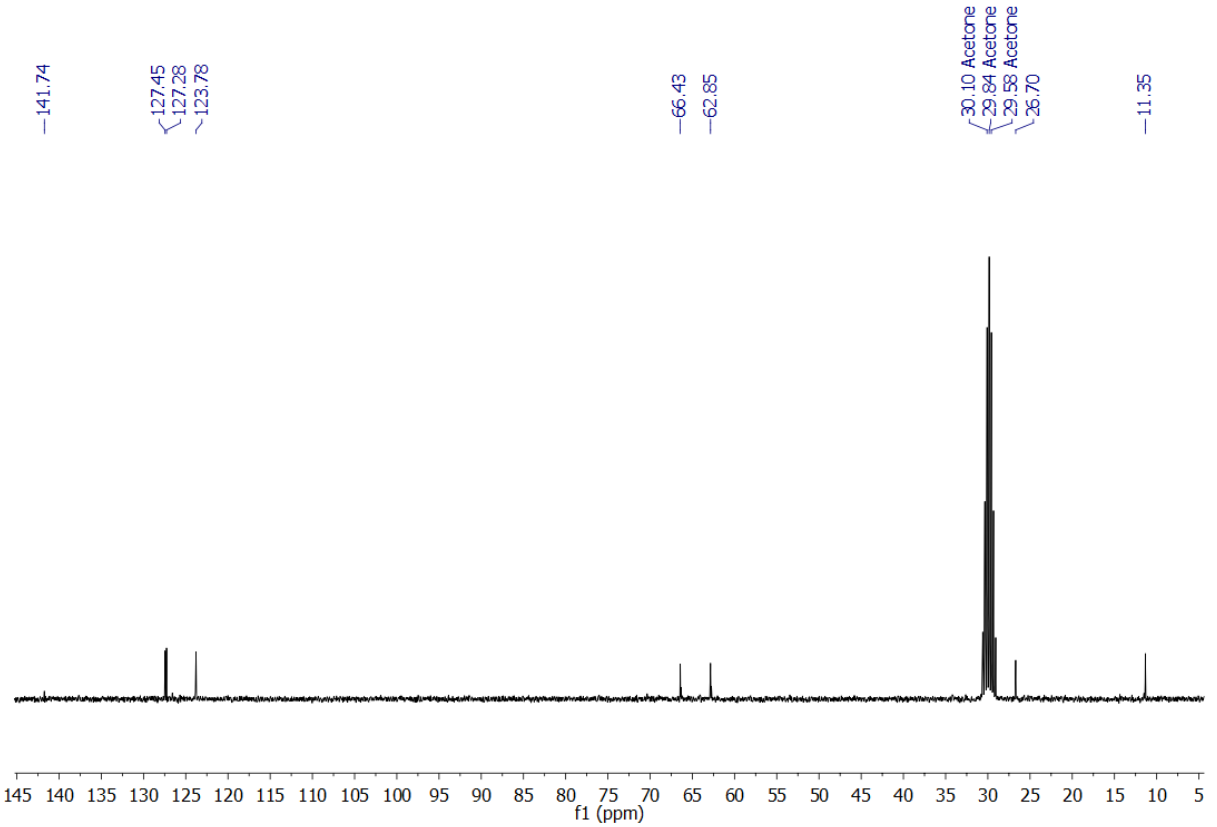
6.14
4.64
4.63
4.62
4.60
4.60
3.63
3.61
3.61
3.60
3.58
3.58
3.57
3.56
3.55
3.54
3.53
1.78
1.68
1.01
0.98
0.96
6h
1.93
1.03
0.69
0.68
0.97
1.00
2.06
3.15
f1 (ppm)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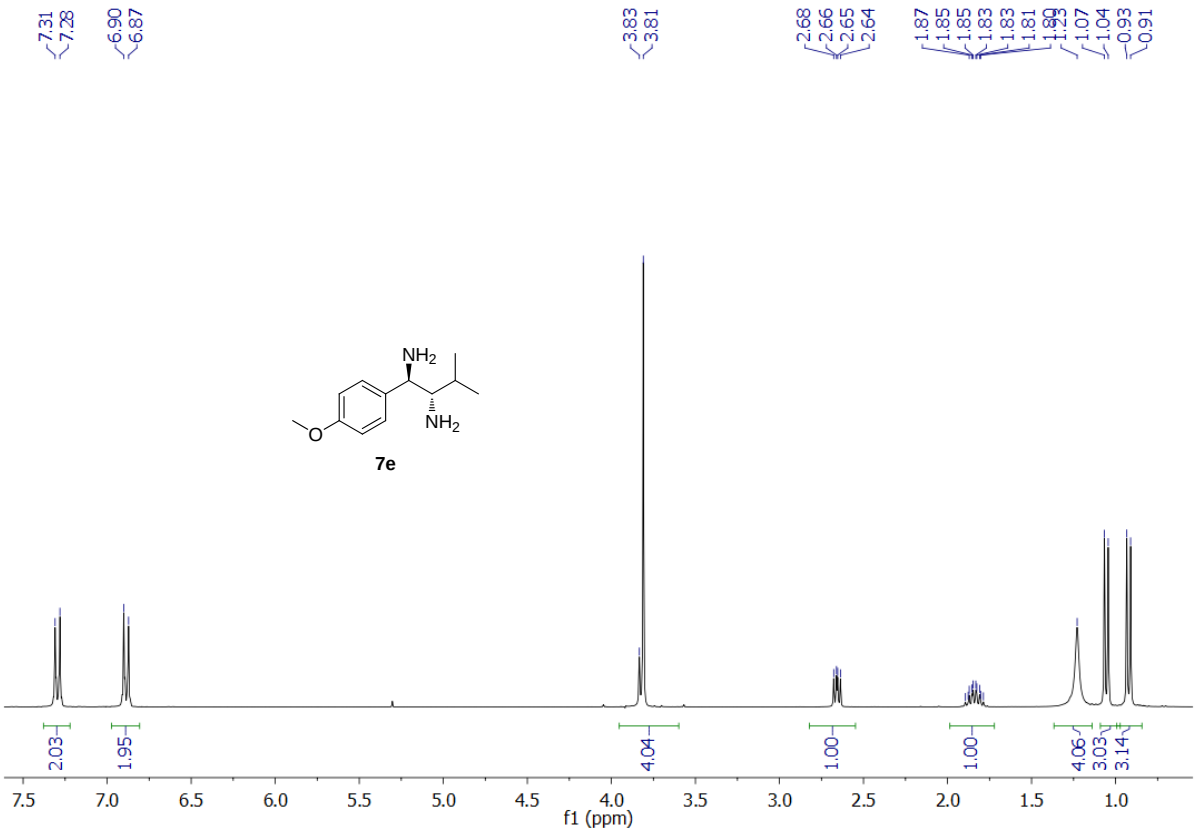
127.45
127.28
123.78
66.43
62.85
30.10 Acetone
29.84 Acetone
29.58 Acetone
26.70
11.35
f1 (ppm)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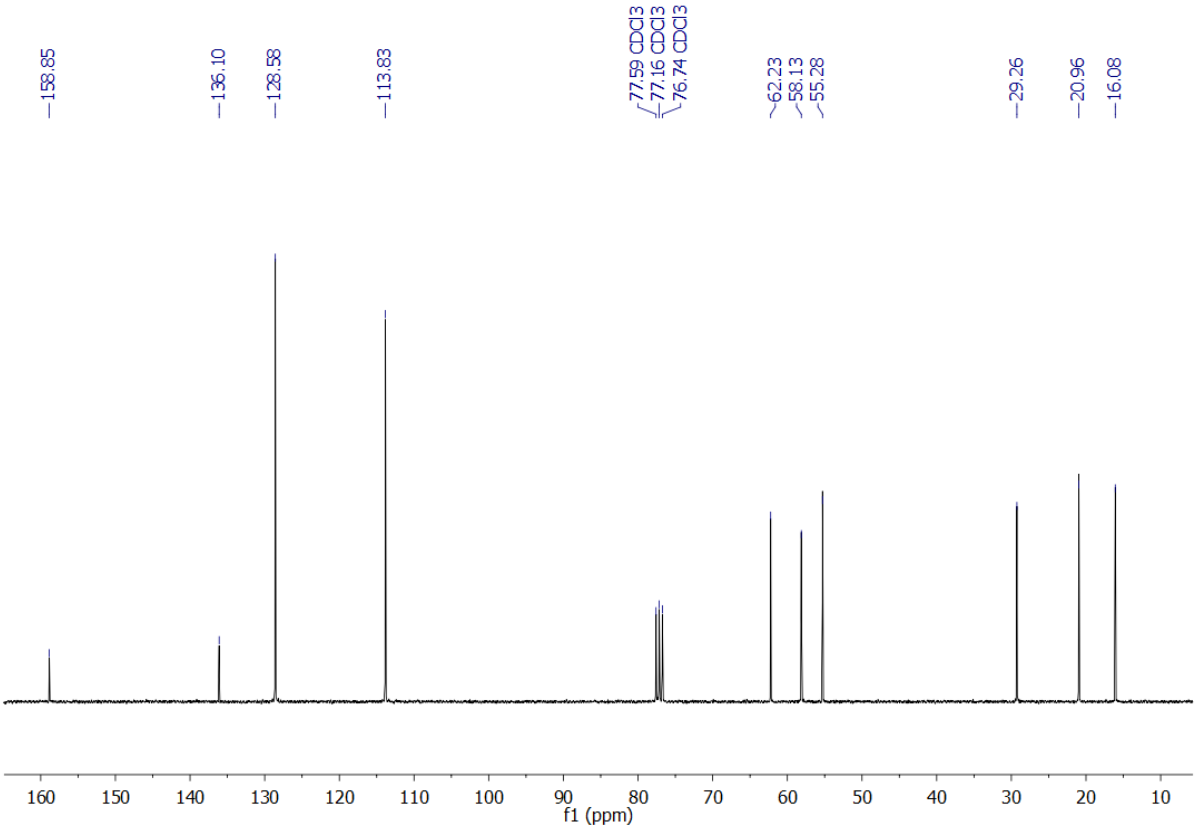
7.28
6.90
6.87
3.83
3.81
2.68
2.66
2.65
2.64
1.87
1.85
1.85
1.83
1.83
1.81
1.23
1.07
1.04
0.93
0.91
NH2
NH2
O
7e
2.03
1.95
4.04
1.00
1.00
4.06
3.03
3.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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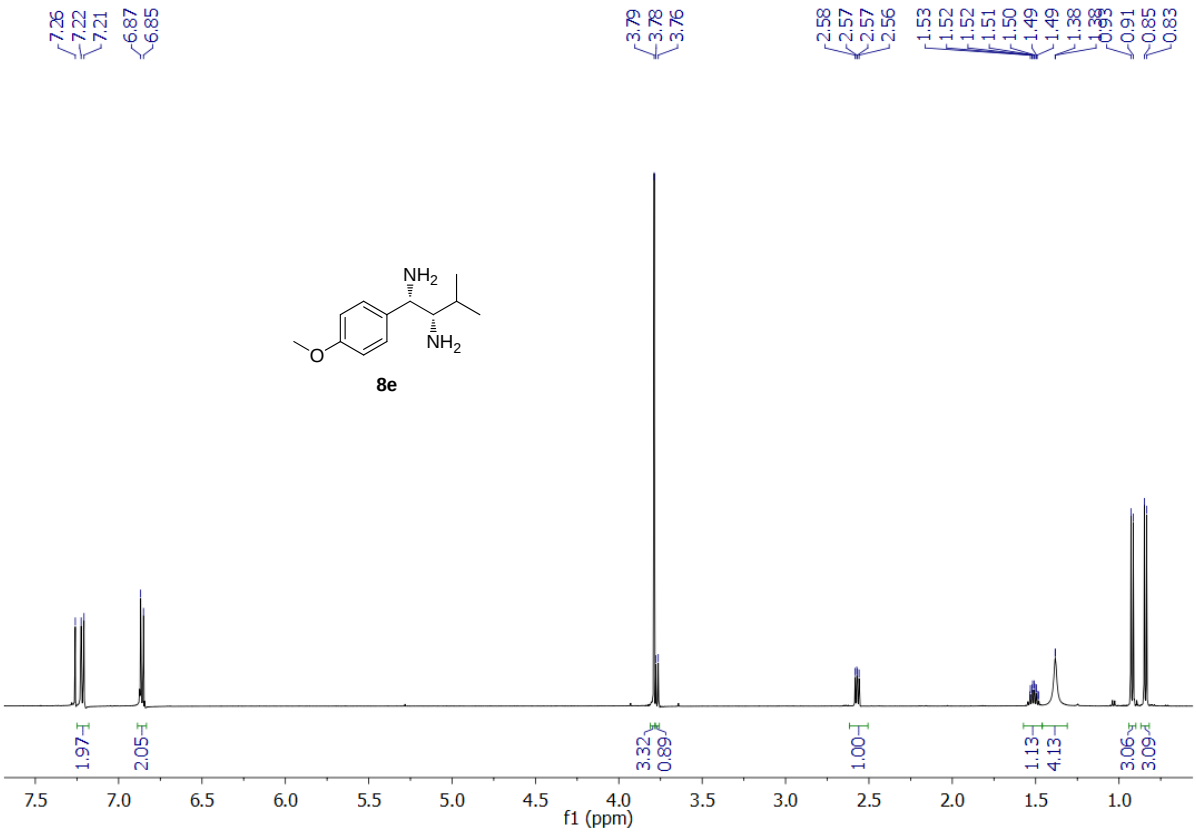
136.10
128.58
113.83
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
62.23
58.13
55.28
29.26
20.96
16.08
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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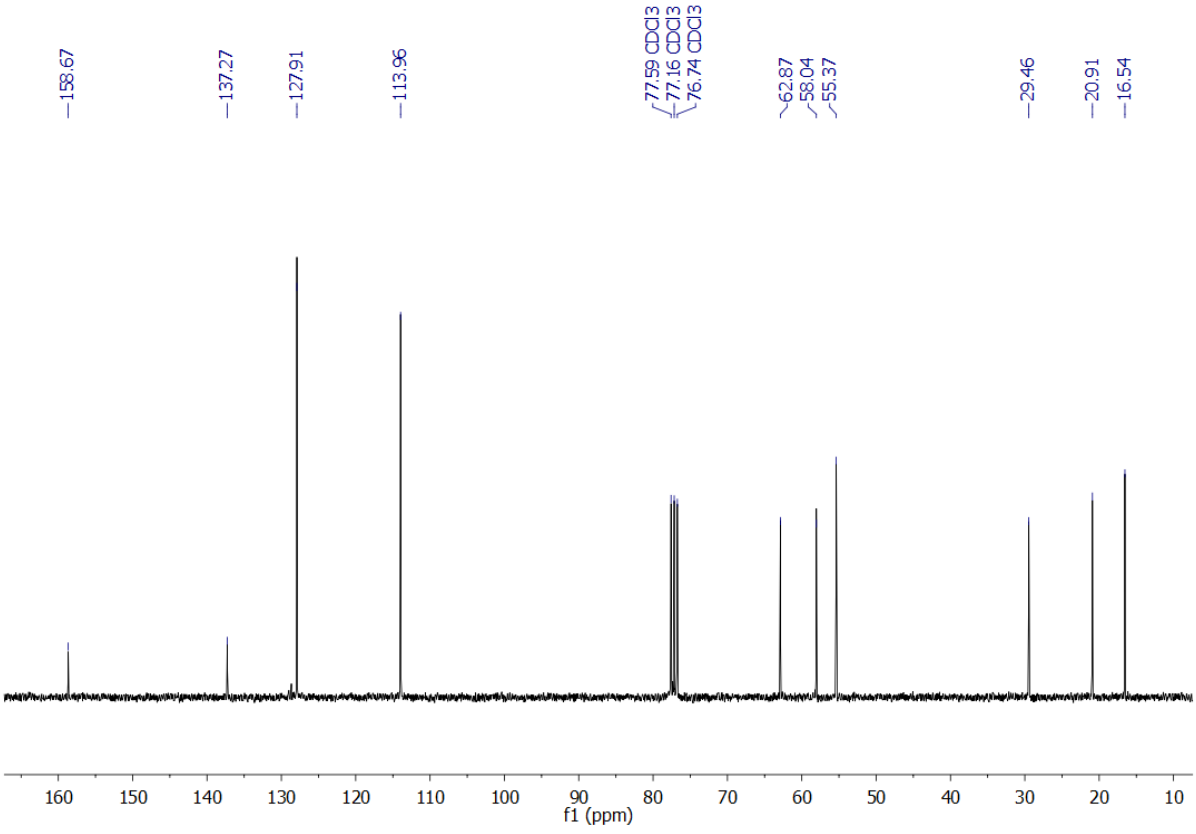
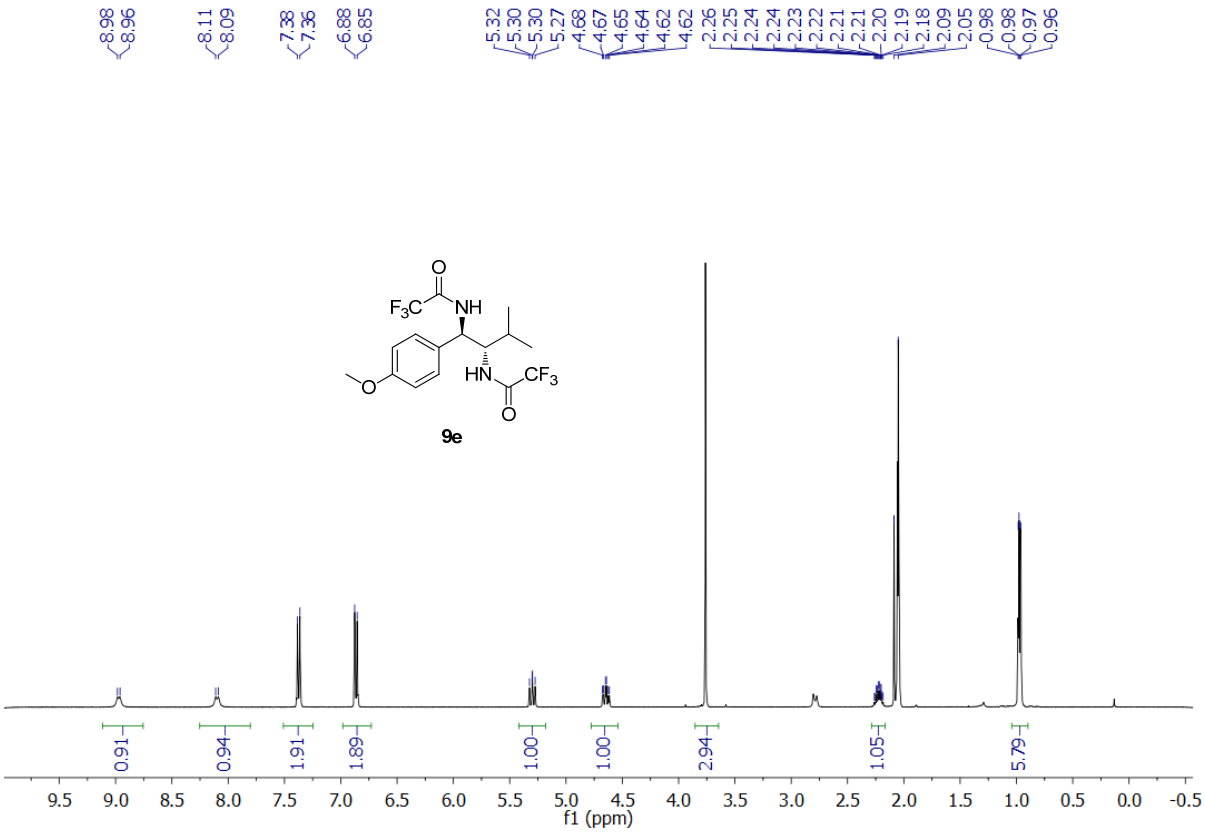
7.22
7.21
6.87
6.85
3.79
3.78
3.76
2.58
2.57
2.57
2.56
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.38
0.93
0.91
0.85
0.83
NH2
NH2
O
8e
1.97
2.05
3.32
0.89
1.00
1.13
4.13
3.06
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


158.67
137.27
127.91
113.96
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
62.87
58.04
55.37
29.46
20.91
16.54
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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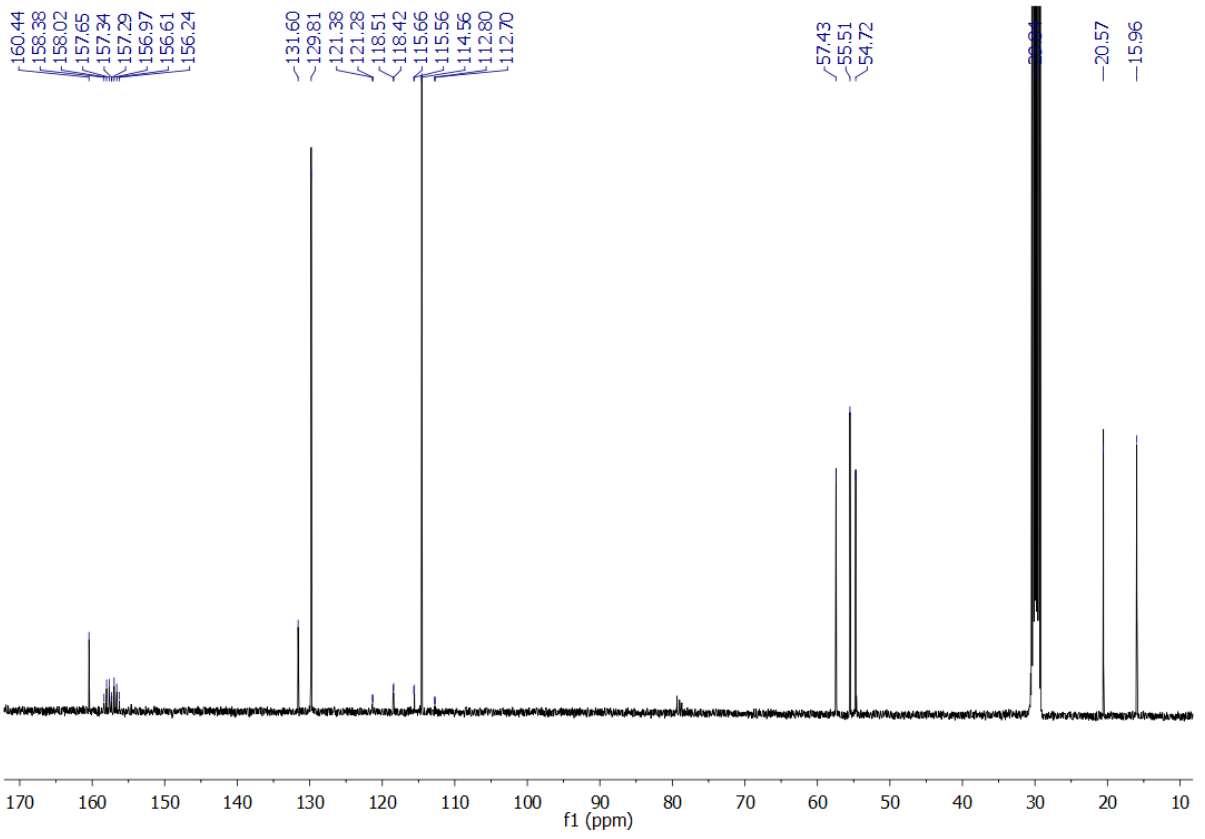
8.96
8.11
8.09
7.38
7.36
6.88
6.85
5.32
5.30
5.30
5.27
4.68
4.67
4.65
4.64
4.62
4.62
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.21
2.20
2.19
2.18
2.09
2.05
0.98
0.98
0.97
0.96
O
F3C
NH
HN
CF3
O
O
9e
0.91
0.94
1.91
1.89
1.00
1.00
2.94
1.05
5.79
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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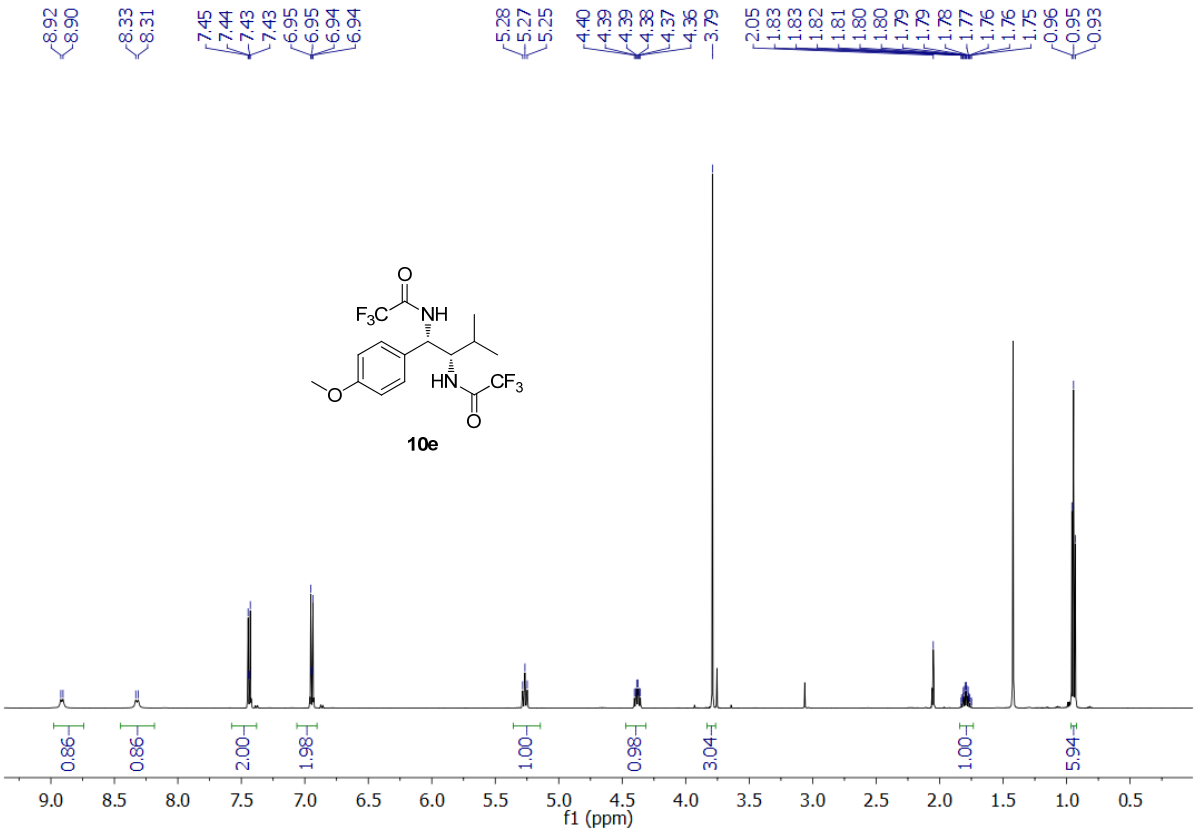
156.97
156.61
156.24
131.60
129.81
121.38
121.28
118.51
118.42
115.66
115.56
114.56
112.80
112.70
57.43
55.51
54.72
20.57
15.96
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.90
8.33
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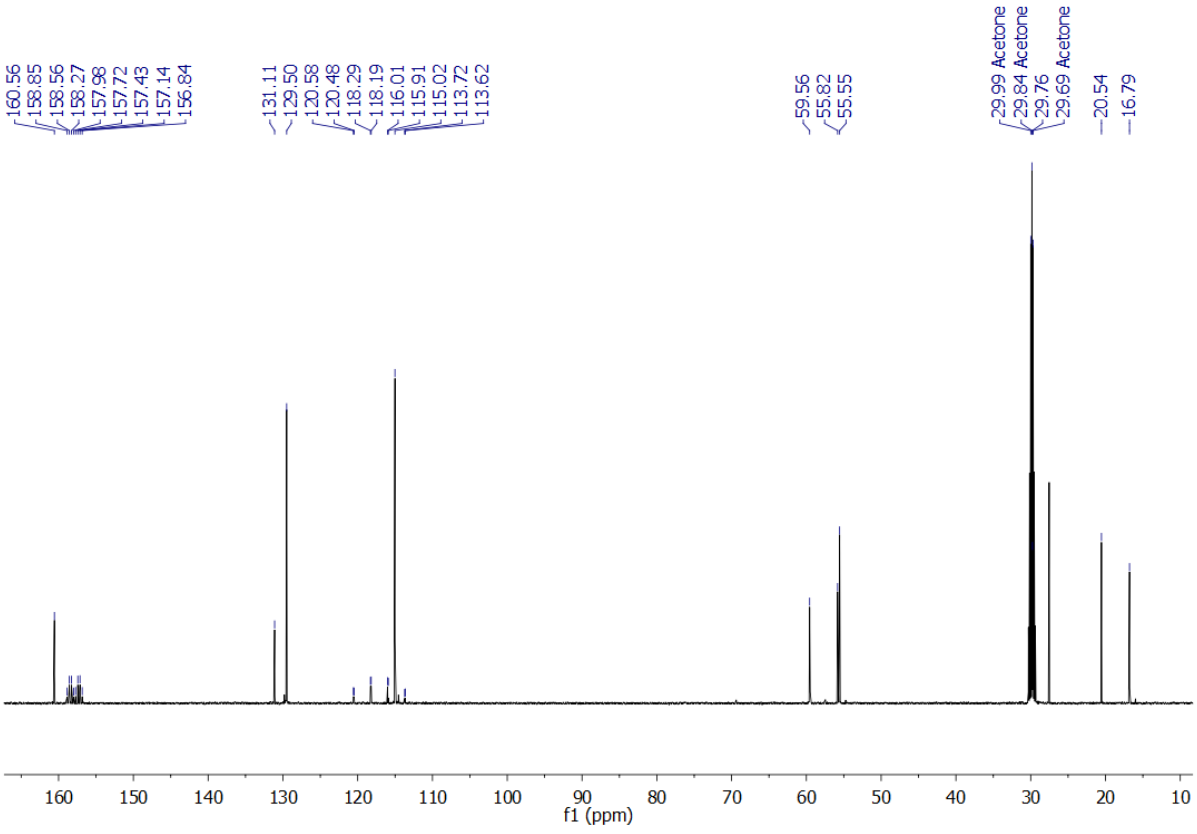
7.44
7.43
7.43
6.95
6.94
6.94
5.28
5.27
5.25
4.40
4.39
4.39
4.38
4.37
4.36
3.79
2.05
1.83
1.83
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.77
1.76
1.76
1.75
0.96
0.95
0.93
O
F3C
NH
HN
CF3
O
O
10e
0.86
0.86
2.00
1.98
1.00
0.98
3.04
1.00
5.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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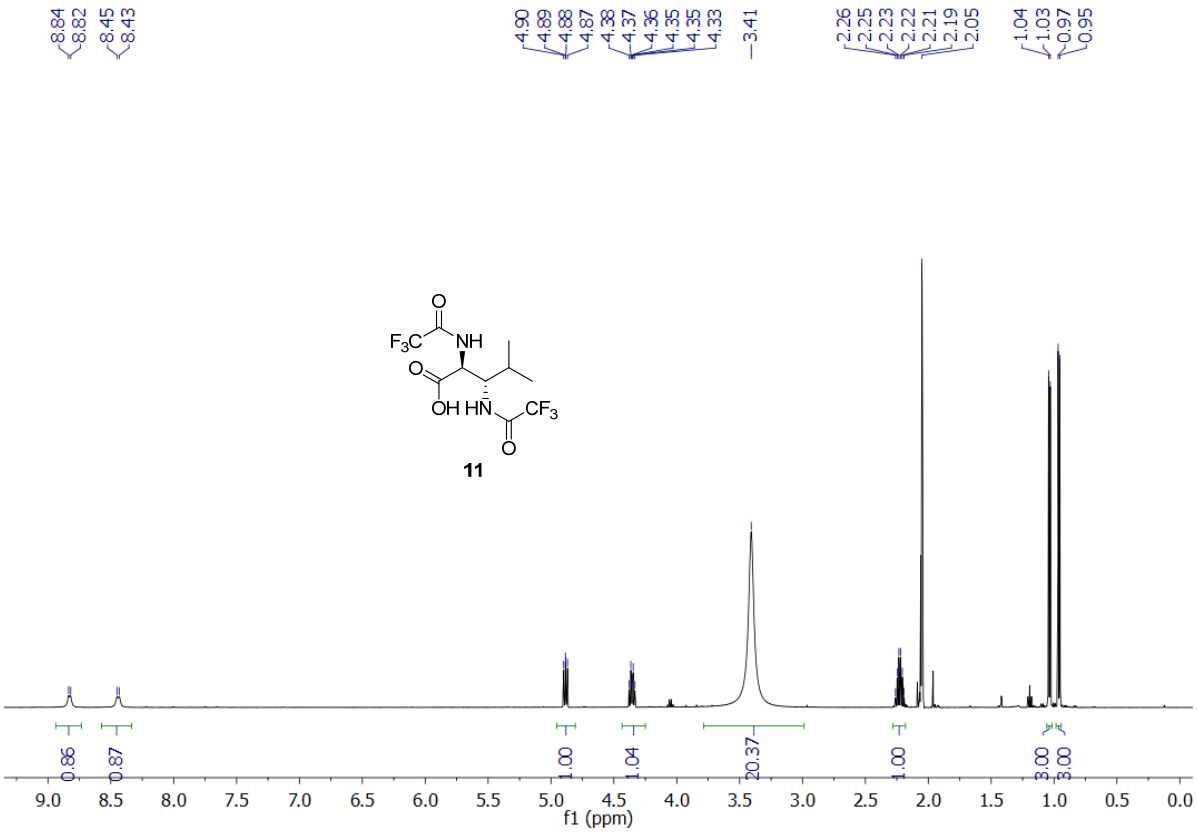
158.56
158.27
157.98
157.72
157.43
157.14
156.84
131.11
129.50
120.58
120.48
118.29
118.19
116.01
115.91
115.02
113.72
113.62
59.56
55.82
55.55
29.99 Acetone
29.84 Acetone
29.76
29.69 Acetone
20.54
16.79
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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4.87
4.38
4.37
4.36
4.35
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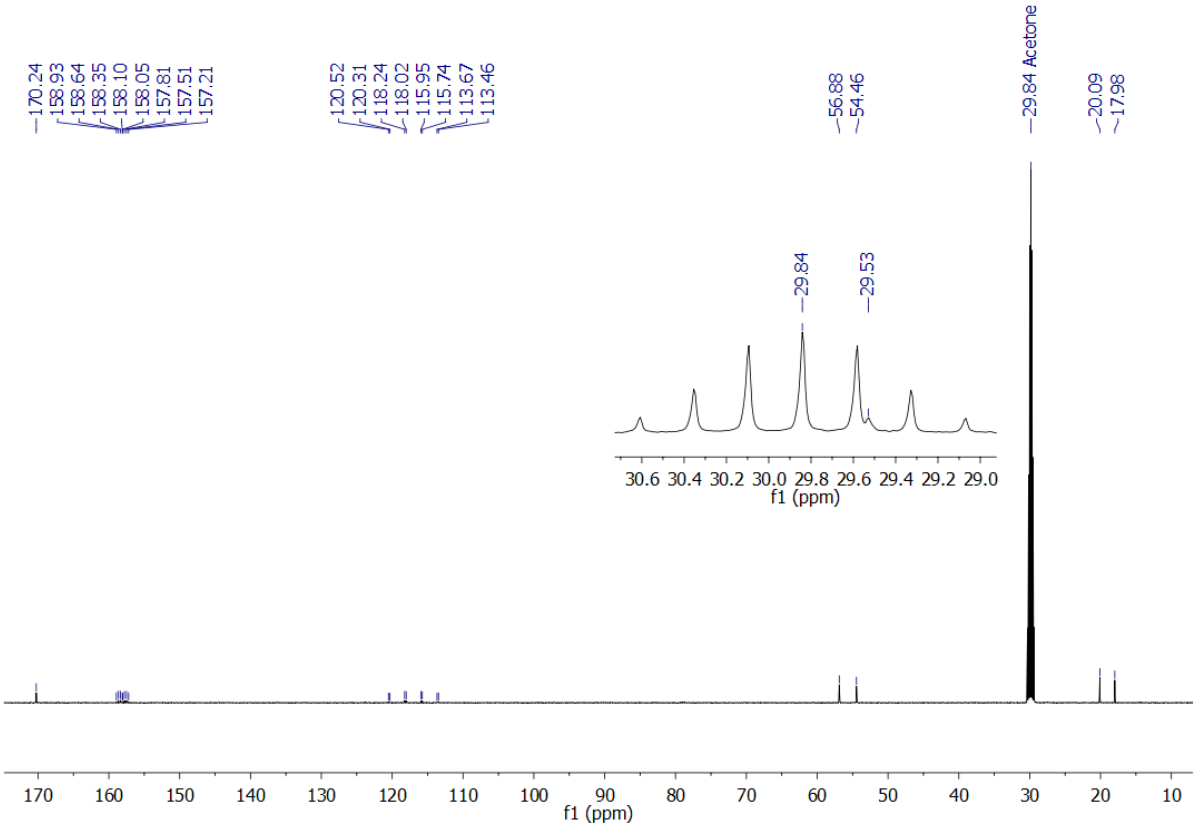
4.33
3.41
2.26
2.25
2.23
2.22
2.21
2.19
2.05
1.04
1.03
0.97
0.95
O
F3C
NH
O
OH HN
CF3
O
11
0.86
0.87
1.00
1.04
20.37
1.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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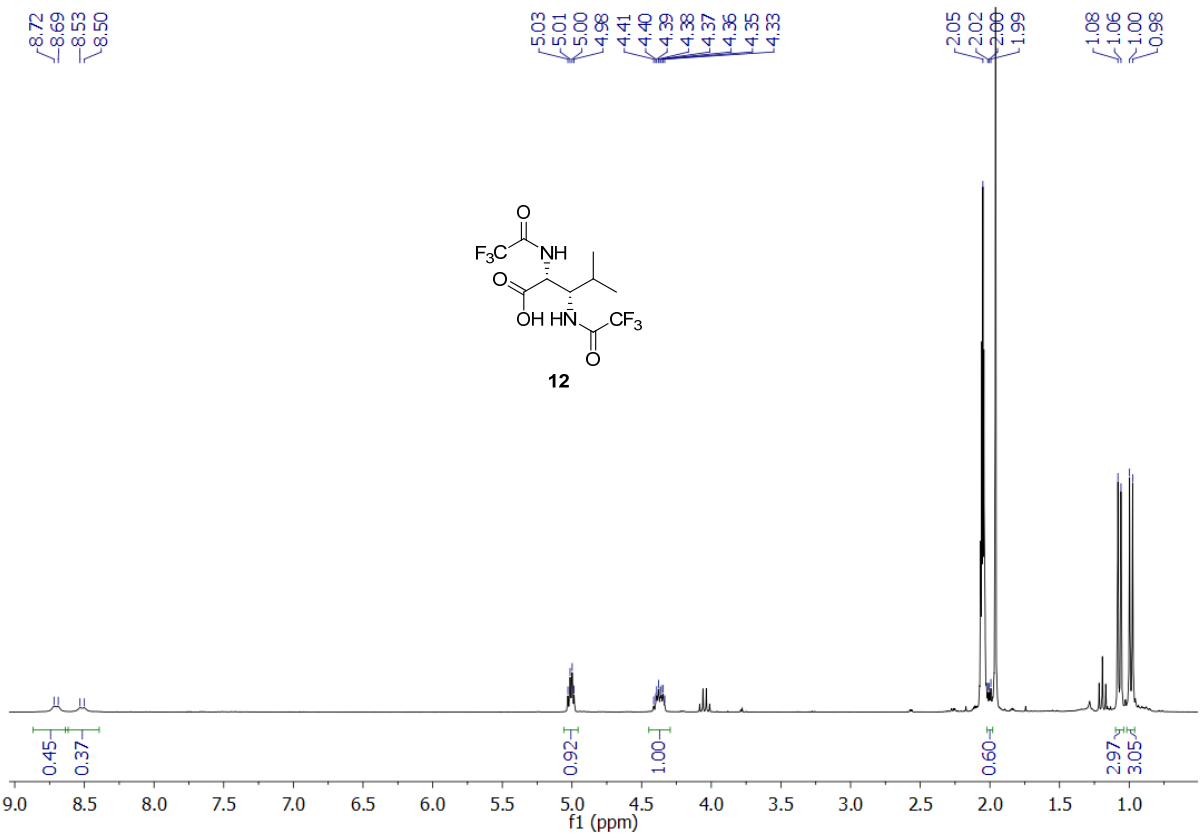
158.05
157.81
157.51
157.21
120.52
120.31
118.24
118.02
115.95
115.74
113.67
113.46
56.88
54.46
29.84 Acetone
20.09
17.98
29.84
29.53
30.6 30.4 30.2 30.0 29.8 29.6 29.4 29.2 29.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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4.98
4.41
4.40
4.39
4.38
4.37
4.36
4.35
4.33
2.05
2.02
2.00
1.99
1.08
1.06
1.00
0.98
O
F3C
NH
O
OH HN
CF3
O
12
0.45
0.37
0.92
1.00
0.60
2.97
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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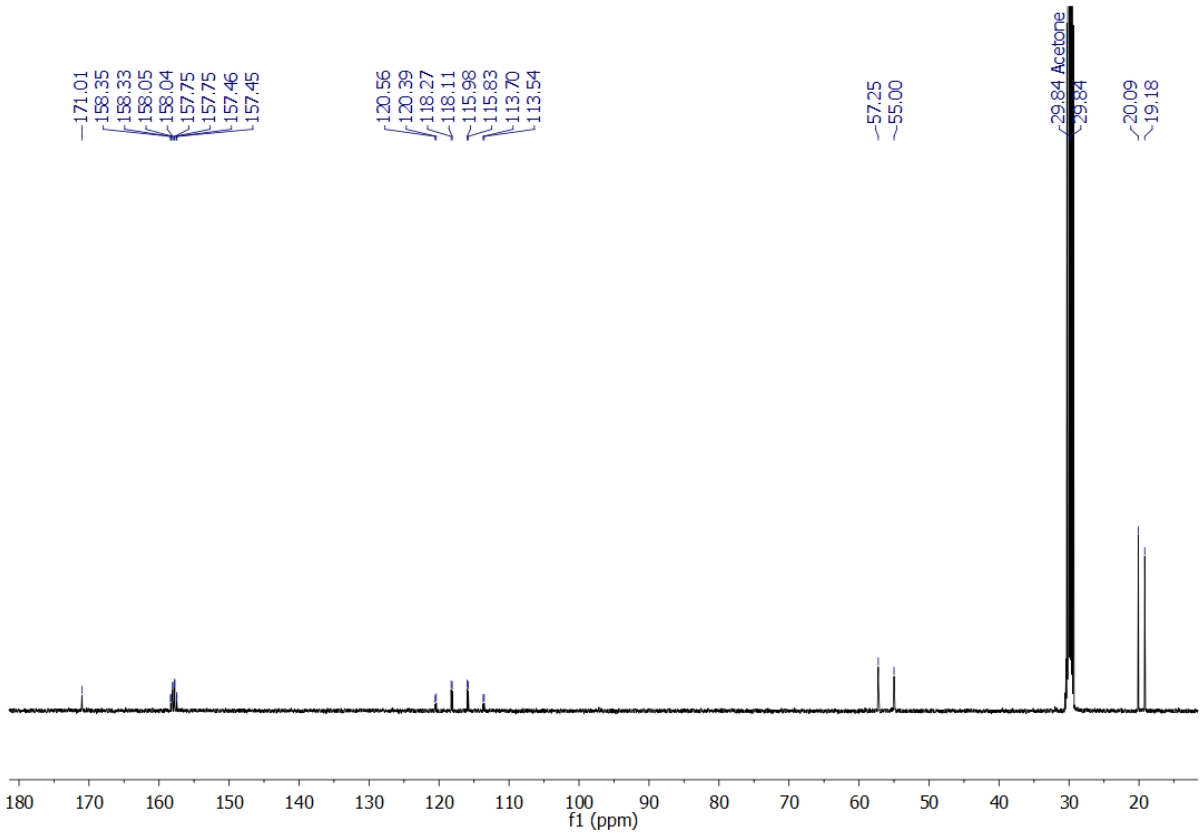
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


171.01
158.35
158.33
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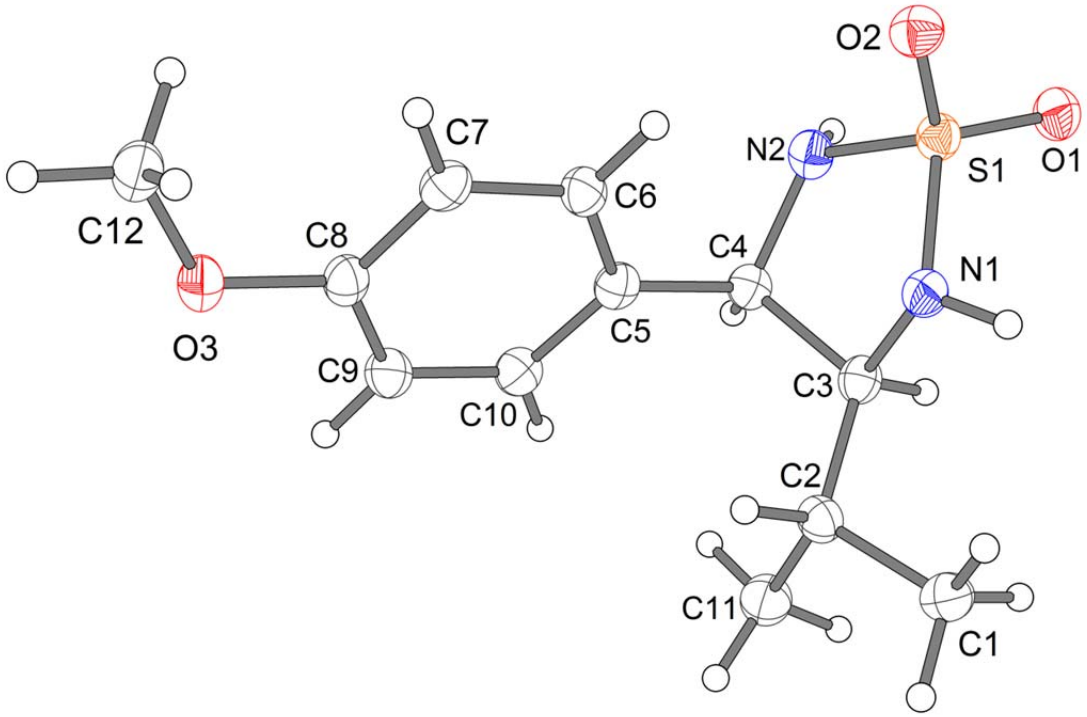
157.46
157.45
120.56
120.39
118.27
118.11
115.98
115.83
113.70
113.54
57.25
55.00
29.84 Acetone
29.84
20.09
19.18
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

4) ORTEP Drawing of Compound 5e



Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as CCDC 920509.

5) References

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