Supporting Information

Synthesis of Sultam Scaffolds via Intramolecular Oxa-Michael and Diastereoselective Baylis Hillman Reactions

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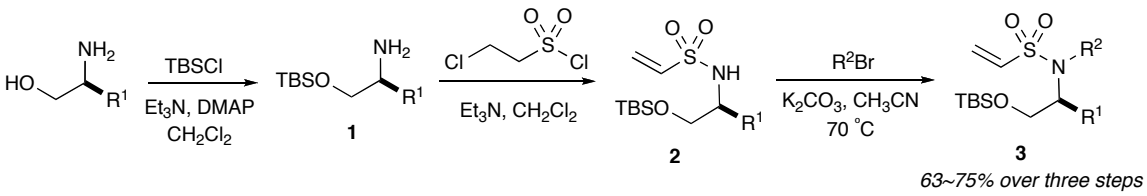
General Experimental Methods

All reactions were carried out under argon atmosphere. Stirring was achieved with oven-dried magnetic stir bars. Et_2O, toluene, THF and CH_2Cl_2 were purified by passage through the Solv-Tek purification system employing activated Al_2O_3 (Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518-1520). Et_3N was purified by passage over basic alumina and stored over KOH. Butyl lithium was purchased from Aldrich and titrated prior to use. Protected glycidol ethers were acquired from Daiso Co., Ltd., Fine Chemical Department. Flash column chromatography was performed with Sorbent Technologies silica gel (30930M-25, Silica Gel 60A, 40-63 um). Thin layer chromatography was performed on silica gel 60F254 plates (EM-5717, Merck). Deuterated solvents were purchased from Cambridge Isotope laboratories. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400 MHz, 100 MHz respectively. Observed rotations at 589 nm were measured using AUTOPOL IV Model automatic polarimeter. High-resolution mass spectrometry (HRMS) was recorded on an LCT Premier Spectrometer (Micromass UK Limited) operating on ESI (MeOH).

Experimental Data and Characterization Data

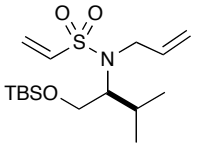
General 3-step protocol to generate vinyl sulfonamides 3a-k.



2-Chloroethanesulfonyl chloride (1.0 equiv.) was added drop wise to a stirred solution of TBS-protected amino alcohol[1] (1.0 equiv.) with Et_3N (3.5 equiv.) in CH_2Cl_2 (5 ml) at 0 °C. After addition, stirring was continued at 0 ºC for 2 hrs. The mixture then was diluted with CH_2Cl_2 (5 ml) washed with brine, dried ($MgSO_4$), concentrated under reduced pressure and carried on without further purification. The crude mixture was dissolved in CH_3CN (about 0.5 M solution), 2-bromobenzylbromide (1.05 equiv.) and K_2CO_3 (2.0 equiv.) were added and the mixture was heated to 80 °C for 2-5 hrs (reaction was monitored by TLC). The reaction was cooled to rt, filtered and concentrated under reduced pressure.

The crude products **3a-k** were purified by flash column chromatography (Hexane/EtOAc = 8:1) to yield product in a yield of 63-75% over three steps as colorless oil. The crude residues **3d-g** were directly used for next reactions to make sultams **4d-g**.

(S)-*N*-Allyl-*N*-(1-(*tert*-butyldimethylsilyloxy)-3-methylbutan-2-yl)ethenesulfonamide (3a)



2-Chloroethanesulfonyl chloride (163 mg, 1.0 equiv.) was added drop wise to a stirred solution of TBS-protected amino alcohol (217 mg, 1.0 equiv.) with Et_3N (353.5 mg, 3.5 equiv.) in CH_2Cl_2 (5 ml) at 0 °C. After addition, stirring was continued at 0 ºC for 2 hrs. The mixture then was diluted with CH_2Cl_2 (5 ml) washed with brine (2x4 ml), dried ($MgSO_4$), concentrated under reduced pressure and carried on without further purification. The crude mixture was

[1] TBS-protected amino alcohol, see Isobe, T.; Fukuda, K.; Yamaguchi, K.; Seki, H.; Tokunaga, T.; Ishikawa, T. *J. Org. Chem*. **2000**, *65,* 7779-7785.

dissolved in CH_3CN (about 0.5 M solution), 2-bromobenzylbromide (262.5 mg, 1.05 equiv.) and K_2CO_3 (276 mg, 2.0 equiv.) were added and the mixture was heated to 80 °C for 2-5 hrs (reaction was monitored by TLC). The reaction was cooled to rt, filtered and concentrated under reduced pressure. The crude products **3a** was purified by flash column chromatography (Hexane/EtOAc = 8:1) to yield product in a yield of 72% (250 mg) over three steps as colorless oil.

[α]^{23} –38.6 (c 3.80, CH_2Cl_2) Colorless oil;

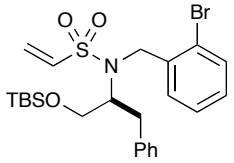
FTIR (neat): 2960, 1470, 1342, 1105, 838 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.54 (dd, *J* = 16.8, 10.0 Hz, 1H), 6.14 (d, *J* = 16.8 Hz, 1H), 5.94 (dddd, *J* = 17.2, 10.0, 8.0, 6.0 Hz, 1H), 5.79 (d, *J* = 10.0 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.87 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.83-3.70 (m, 3H), 3.44 (ddd, *J* = 10.5, 7.1, 3.6 Hz, 1H), 1.89 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.1, 135.8, 124.5, 117.3, 66.2, 62.7, 47.3, 28.0, 25.9 (3), 20.8, 20.2, 18.3, -5.5, -5.6;

HRMS m/z Calculated for $C_{16}H_{33}NO_3SiSNa$ 370.1848 $(M+Na)^+$, found 370.1820.

(S)-*N*-(2-Bromobenzyl)-*N*-(1-(*tert*-butyldimethylsilyloxy)-3-phenylpropan-2-yl)ethenesulfonamide (3b)



[α]^{23} -27.9 (c 0.90, CH_2Cl_2) Colorless oil;

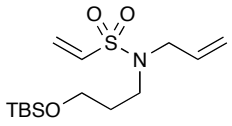
FTIR (neat): 2952, 1454, 1338, 1147, 837, 777 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.80-7.15 (aromatic H, 9H), 6.16 (overlap, 2H), 5.76 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 2H), 4.17 (m, 1H), 3.70 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.54 (d, *J* = 11.2, 5.2 Hz, 1H), 2.95 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.80 (dd, *J* = 14.0, 6.8 Hz, 1H), 0.89 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 138.2, 137.3, 135.3, 132.4, 130.3, 129.3, 128.9, 128.7, 127.6, 126.8, 126.0, 122.3, 63.4, 62.6, 48.3, 37.0, 25.9(3), 18.2, -5.5(2);

HRMS m/z Calculated for $C_{24}H_{34}NO_3SiSBrNa$ 546.1110 $(M+Na)^+$, found 546.1100.

***N*-Allyl-*N*-(3-(*tert*-butyldimethylsilyloxy)propyl)ethenesulfonamide (3c)**



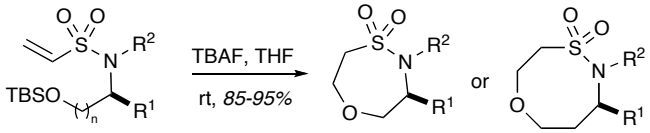
FTIR (neat): 2954, 1346, 1097, 847, 777 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.44 (dd, *J* = 16.4, 6.4 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 5.90 (d, *J* = 10.0 Hz, 1H), 5.82 (m, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 3.81 (d, *J* = 6.4 Hz, 2H), 3.64 (t, *J* = 6.0 Hz, 2H), 3.23 (t, *J* = 7.8 Hz, 2H), 1.80 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 135.4, 133.1, 126.2, 119.0, 60.1, 50.4, 44.1, 31.8, 25.9(3), 18.2, -5.4(2);

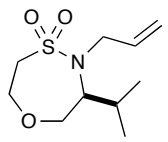
HRMS m/z Calculated for $C_{14}H_{29}NO_3SiSNa$ 342.1535 $(M+Na)^+$, found 342.1525.

Intramolecular Oxa-Michael reaction procedure:



To a stirring solution of benzylated sulfonamide **3** (1.0 equiv.) in THF was added several drops of TBAF (1.0 equiv., 1.0 M in THF) and stirring was continued for 2 hrs at rt. NH_4Cl (sat'd) was added and the organic layer was extracted with CH_2Cl_2 (2x), dried ($MgSO_4$) and the mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography (Hex: EtOAc, 2:1) to afford both 7- (**4a, 4b, 4d, 4f,** and **4g**) and 8-membered (**4c** and **4e)** ring sultams in excellent yields (85~95%).

(S)-*N*-2-Allyl-3-*iso*-prpopyl-5,1,2-oxathiazepine-1,1-dioxide (4a)



To a stirring solution of allylated sulfonamide **3a** (40 mg, 0.12 mmol) in THF (3 ml) was added TBAF (1.0 M in THF) and stirring was continued for 2 hrs at rt. NH_4Cl (2 ml, sat'd) was added and the organic layer was extracted with CH_2Cl_2 (2x4 ml), dried ($MgSO_4$) and the mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography (Hexane/EtOAc = 2:1) to afford 25 mg of **4a** (92%) in excellent yield.

[α]^{23} –15.8 (c 1.95, CH_2Cl_2) Colorless oil;

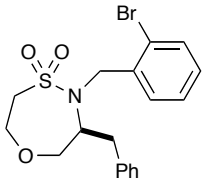
FTIR (neat) : 3468, 2966, 1740, 1298, 1203, 1145 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.95 (dddd, *J* = 16.2, 10.2, 6.7, 6.7 Hz, 1H), 5.20 (d, *J* = 16.2 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.11 (dd, *J* = 12.7, 6.4 Hz, 1H), 3.95 (m, 2H), 3.74 (m, 3H), 3.25 (overlap, 3H), 1.74 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 134.5, 118.3, 74.3, 65.5, 63.3, 54.2, 52.3, 30.8, 21.0, 19.4;

HRMS m/z Calculated for $C_{10}H_{19}NO_3SNa$ 256.0983 $(M+Na)^+$, found 256.0970.

(S)-*N*-(2-Bromobenzyl)-3-(benzyl)-5,1,2-Oxathiazepine-1,1-dioxide (4b)



[α]^{23} - 48.3 (c 2.47, CH_2Cl_2) Colorless oil;

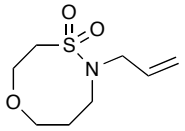
FTIR (neat): 2945, 1336, 1144, 1026, 752 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62-6.94 (aromatic H, 9H), 4.58 (d, *J* = 3.6 Hz, 2H), 4.13 (ddd, *J* = 13.4, 4.4, 4.3 Hz, 1H), 4.52 (m, 4H), 3.41 (m, 2H), 2.78 (dd, *J* = 13.5, 5.2 Hz, 1H), 2.63 (dd, *J* = 13.5, 7.8 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.2, 136.0, 132.7, 131.1, 129.3, 128.8, 128.6, 127.8, 126.6, 123.1, 75.2, 66.1, 59.5, 54.7, 52.8, 38.8;

HRMS m/z Calculated for $C_{18}H_{20}NO_3SBrNa$ 432.0245 $(M+Na)^+$, found 432.0259.

***N*-(2-Allyl)-6,1,2-Oxathiazepine-1,1-dioxide (4c)**



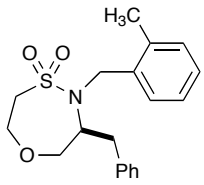
FTIR (neat): 2927, 1331, 1136, 746 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.77 (m, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.1 Hz, 1H), 4.02 (t, *J* = 5.0 Hz, 2H), 3.77 (m, 4H), 3.55 (t, *J* = 5.3 Hz, 1H), 3.08 (d, *J* = 4.9 Hz, 2H), 1.61 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 133.2, 118.8, 73.4, 69.5, 51.6, 48.2, 45.1, 26.2, 14.1;

HRMS m/z Calculated for $C_8H_{15}NO_3SNa$ 228.0670 $(M+Na)^+$, found 228.0670.

(S)-*N*-2-(*o*-Methylbenzyl)-3-benzyl-5,1,2-oxathiazepine-1,1-dioxide (4d)



$[\alpha]^{23}$ –30.1 (c 1.70, CH_2Cl_2) Colorless oil;

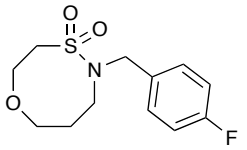
FTIR (neat): 2949, 2874, 1495, 1337, 1150, 1030, 702 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40-6.69 (aromatic H, 9H), 4.75 (d, *J* = 13.6 Hz, 1H), 4.16 (ddd, *J* = 12.0, 5.2, 2.8 Hz, 1H), 4.14 (d, *J* = 13.6 Hz, 1H), 4.06 (dd, *J* = 13.2, 6.8 Hz, 1H), 3.96 (dd, *J* = 13.2, 10.8 Hz, 1H), 3.86 (ddd, *J* = 11.6, 11.2, 2.8 Hz, 1H), 3.55 (m, 1H), 3.48 (ddd, *J* = 16.0, 11.2, 4.8 Hz, 1H), 3.31 (ddd, *J* = 14.4, 2.4, 2.4 Hz, 1H), 2.60 (dd, *J* = 8.4, 4.0 Hz, 2H), 2.42 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.9, 137.7, 133.6, 131.0, 130.6, 128.7, 128.5, 128.4, 126.4, 126.0, 76.2, 67.2, 59.0, 53.7, 39.5, 19.4;

HRMS m/z Calculated for $C_{19}H_{23}NO_3SNa$ 368.1296 $(M+Na)^+$, found 368.1282.

***N*-(2-(4-Florobenzyl))-6,1,2-Oxathiazepine-1,1-dioxide (4e)**



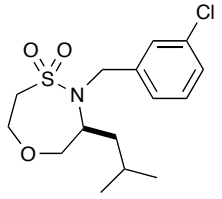
FTIR (neat): 2925, 133, 1126, 730 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40 (m, 2H), 7.05 (m, 2H), 4.38 (s, 2H), 4.16 (t, J = 5.5 Hz, 2H), 3.87 (t, J = 5.0 Hz, 2H), 3.46 (t, J = 5.0 Hz, 2H), 3.22 (t, J = 4.8 Hz, 2H), 1.61 (m, 2H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.5 (d, J_{CF} = 244 Hz), 131.2, 130.1, 130.0, 115.7, 115.5, 73.9, 69.8, 51.9, 47.9, 44.3, 25.6;

HRMS m/z Calculated for $C_{12}H_{16}FNO_3SNa$ 296.0733 $(M+Na)^+$, found 296.0721.

(S)-*N*-2-(*m*-Chlorobenzyl)-3-*iso*-butyl-5,1,2-oxathiazepine-1,1-dioxide (4f)



[α]^{23} –17.4 (c 1.52, CH_2Cl_2) Colorless oil;

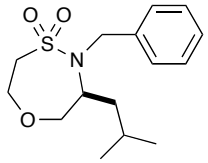
FTIR (neat): 2955, 1470, 1337, 1150, 1118, 752 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45-7.28 (aromatic H, 4H), 4.43 (d, J = 15.6 Hz, 1H), 4.26 (d, J = 15.6 Hz, 1H), 3.96 (overlap, 5H), 3.38 (m, 2H), 1.35 (m, 1H), 1.34 (ddd, J = 14.0, 7.7, 5.5 Hz, 1H), 0.96 (ddd, J = 14.1, 8.3, 4.9 Hz, 1H), 0.73 (d, J = 6.8 Hz, 3H), 0.52 (d, J = 6.8 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 139.8, 134.3, 129.8, 128.5, 127.9, 126.6, 74.2, 64.6, 55.6, 54.5, 50.9, 39.7, 24.3, 22.3, 21.9;

HRMS (ESI) m/z Calculated for $C_{15}H_{22}NO_3SClNa$ 354.0907 $(M+Na)^+$, found 354.0933.

(S)-*N*-2-Benzyl-3-*iso*-butyl-5,1,2-oxathiazepine-1,1-dioxide (4g)



[α]^{23} –26.3 (c 2.31, CH_2Cl_2) Colorless oil;

FTIR (neat): 2955, 1334, 1142, 1119, 732 cm^{-1};

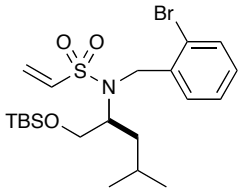
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46-7.29 (aromatic H, 5H), 4.44 (d, *J* = 5.2 Hz, 1H), 4.34 (d, *J* = 5.2 Hz, 1H), 4.02 (m, 2H), 3.93 (overlap, 3H), 3.37 (ddd, *J* = 5.9, 3.6, 3.6 Hz, 2H), 1.27 (m, 2H), 0.98 (m, 1H), 0.70 (d, *J* = 6.4 Hz, 3H), 0.48 (d, *J* = 6.4 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.4, 128.7(2), 128.5(2), 127.7, 74.6, 64.9, 55.6, 54.5, 52.0, 40.0, 24.3, 22.2, 22.0;

HRMS (ESI) m/z Calculated for $C_{15}H_{23}NO_3SNa$ 320.1296 $(M+Na)^+$, found 320.1295.

(S)-*N*-(2-Bromobenzyl)-*N*-(1-(*tert*-butyldimethylsilyloxy)-4-methylpentan-2 yl)ethenesulfonamide (3h).

In a procedure similar to the preparation of **3a**, flash chromatography (SiO_2, Hexane/EtOAc = 2:1) afforded **3i** in a yield of 71% over 3 steps as a clear liquid.



[α]^{23} –22.4 (c 2.25, CH_2Cl_2) Colorless oil;

FTIR (neat): 2955, 1470, 1342, 1111, 838 cm^{-1};

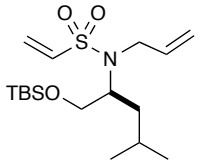
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.86-7.12 (aromatic H, 4H), 6.65 (dd, *J* = 16.8, 9.2 Hz, 1H), 6.25 (d, *J* = 16.8 Hz, 1H), 5.89 (d, *J* = 16.8, 9.6 Hz, 1H), 4.43 (s, 2H), 3.93 (m, 1H), 3.73 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.57 (dd, *J* = 10.8, 4.8 Hz, 1H), 1.64 (m, 1H), 1.14 (m, 2H), 0.92 (s, 9H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.4, 135.9, 132.3, 130.4, 128.8, 127.6, 125.8, 122.3, 63.7, 58.7, 47.4, 39.3, 26.0(3), 24.5, 22.6, 22.2, 18.4, -5.4(2);

HRMS m/z Calculated for $C_{21}H_{36}NO_3SSiNa$ 514.1266 $(M+Na)^+$, found 514.1266.

(*S*)-*N*-Allyl-*N*-(1-(*tert*-butyldimethylsilyloxy)-4-methylpentan-2-yl)ethenesulfonamide (3i)

In a procedure similar to the preparation of **3a**, flash chromatography (SiO_2, Hexane/EtOAc = 2:1) afforded **3i** in a yield of 72% over 3 steps as a clear liquid.



[α]^{23} –35.4 (c 4.12, CH_2Cl_2) Colorless oil;

FTIR (neat): 2955, 1471, 1340, 1105, 837 cm^{-1};

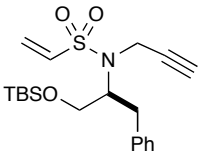
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.47 (dd, *J* = 16.4, 10.0Hz, 1H), 6.07 (d, *J* = 16.4 Hz, 1H), 5.80 (dddd, *J* = 16.4, 10.4, 6.4, 6.4 Hz, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 3.82 (m, 1H), 3.69 (d, *J* = 6.4 Hz, 2H), 3.59 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.52 (dd, *J* = 10.8, 4.8 Hz, 1H), 1.62 (m, 1H), 1.41 (ddd, *J* = 13.6, 9.6, 5.2 Hz, 1H), 1.19 (ddd, *J* = 13.6, 8.4, 5.2 Hz, 1H), 0.86 (d, *J* = 7.2 Hz, 6H), 0.85 (s, 9H), 0.01 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 136.8, 136.1, 124.6, 117.0, 64.4, 58.0, 46.4, 38.9, 25.9 (3), 24.2, 22.9, 22.0, 18.2, -5.5(2);

HRMS m/z Calculated for $C_{17}H_{35}NO_3SSiNa$ 384.2005 $(M+Na)^+$, found 384.1988.

(S)-*N*-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylpropan-2-yl)-*N*-(prop-2-ynyl)ethane-sulfonamide (3j)

In a procedure similar to the preparation of **3a**, flash chromatography (SiO_2, Hexane/EtOAc = 2:1) afforded **3j** in a yield of 68% over 3 steps as a clear liquid.



[α]^{23} –17.3 (c 5.50, CH_2Cl_2) Colorless oil;

FTIR (neat): 3282, 2953, 1456, 1340, 1149, 837, 777 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.34-7.25 (aromatic H, 5H), 6.33 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.18 (d, *J* = 16.8 Hz, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 2.4 Hz, 2H), 4.00 (m, 1H),

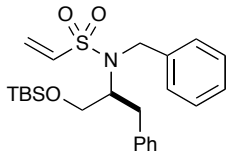
3.76 (dd, J = 5.6, 2.4 Hz, 2H), 3.12 (dd, J = 13.6, 8.4 Hz, 1H), 3.0 (dd, J = 13.6, 6.4 Hz, 1H), 2.33 (t, J = 2.4 Hz, 1H), 0.92 (s, 9H), 0.06 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 138.1, 136.3, 129.4(2), 128.5(2), 126.7, 125.5, 80.4, 72.6, 63.8, 61.3, 36.0, 33.8, 25.9(3), 18.2, -5.5(2);

HRMS m/z Calculated for $C_{20}H_{31}NO_3SSiNa$ 416.1692 $(M+Na)^+$, found 416.1700.

(S)-*N*-(Benzyl)-*N*-(1-(*tert*-butyldimethylsilyloxy)-3-phenylpropan-2-yl)ethenesulfonamide (3k)

In a procedure similar to the preparation of **3a**, flash chromatography (SiO_2, Hexane/EtOAc = 2:1) afforded **3k** in a yield of 73% over 3 steps as a clear liquid.



[α]^{23} –27.6 (c 3.44, CH_2Cl_2) Colorless oil;

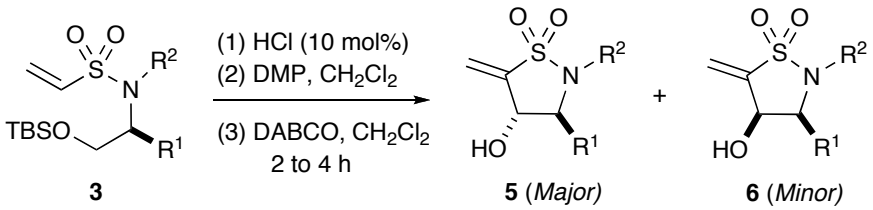
FTIR (neat): 2950, 1451, 1341, 1144, 843, 756 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.50-7.13 (aromatic H, 10H), 6.16 (d, J = 3.6 Hz, 1H), 6.15 (d, J = 6.8 Hz, 1H), 5.70 (dd, J = 6.8, 3.2 Hz, 1H), 4.17 (s, 2H), 4.08 (m, 1H), 3.75 (dd, J = 10.8, 7.6 Hz, 1H), 3.50 (dd, J = 10.8, 5.6 Hz, 1H), 2.89 (dd, J = 13.6, 6.8 Hz, 1H), 2.78 (dd, J = 14.0, 8.0 Hz, 1H), 0.90 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 138.6(2), 138.0, 136.2, 129.2(2), 128.6(2), 127.7(2), 126.6(2), 125.1(2) , 63.3, 62.7, 48.9, 37.5, 26.0(3), 18.2, -5.5(2);

HRMS m/z Calculated for $C_{24}H_{35}NO_3SiSBrNa$ 468.2005 $(M+Na)^+$, found 468.1979.

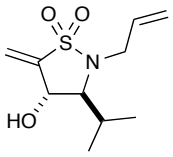
General Intramolecular Baylis-Hillman reaction procedure:



To a stirring solution of sulfonamide **3** (1 equiv.) in THF (small amount) was added 10 mol% HCl. The resulting vinyl sulfonamide alcohol was extracted with CH_2Cl_2 twice, dried ($MgSO_4$), filtered and Dess-Martin periodinane (2.0 equiv.) was added. After 2 hours, the reaction mixture was washed with $NaHCO_3$ to remove the resultant solid acid. After filtration, the organic layer was separated, dried ($MgSO_4$) and partially concentrated under reduced pressure. DABCO (0.10 equiv.) was added to the crude mixture of aldehyde vinyl sulfonamide. Stirring was continued until TLC analysis indicated that the starting material was consumed (normally 2 to 4 hrs). The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to yield an inseparable mixture of 5-membered ring sultam diastereoisomers **5a-f** and **6a-f**. The same procedure was applied to bicylic sultam and 6-membered ring sultam synthesis.

* Characterized as an inseparable mixture of major and minor diastereomers.

Major: *N*-2-Allyl-3(S)-*iso*-propyl-4(S)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5a).



To a stirring solution of sulfonamide **3a** (87 mg, 0.25 mmol) in THF (0.5 ml) was added 10 mol % HCl (5 ml). The resulting vinyl sulfonamide alcohol was extracted with CH_2Cl_2 (2x5 ml), dried ($MgSO_4$), filtered and Dess-Martin periodinane (212 mg, 2.0 equiv.) was added. After 2 hours, the reaction mixture was washed with saturated $NaHCO_3$ (10 ml) to remove the resultant solid acid. After filtration, the organic layer was separated, dried ($MgSO_4$) and partially concentrated under reduced pressure. DABCO (3.8 mg, 0.10 equiv.) was added to the crude mixture of aldehyde vinyl sulfonamide. Stirring was continued until TLC analysis indicated that the starting material was consumed (normally 2 to 4 hrs). The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography

(Hexane/EtOAc = 2:1) to yield an inseparable mixture of 5-membered ring sultam diastereoisomers (40.0 mg, 69%) **5a** (Major) and **6a** (Minor).

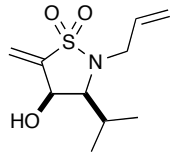
FTIR (neat): 3472, 2964, 1468, 1290, 1136, 933, 784 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.10 (s, 1H), 5.91 (s, 1H), 5.83 (m, 1H), 5.25 (overlap, 2H), 4.62 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.89 (dd, *J* = 15.6, 5.2 Hz, 1H), 3.66 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.56 (broad, 1H), 3.13 (dd, *J* = 4.4, 4.4 Hz, 1H), 2.01 (m, 1H), 1.03 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.8, 132.5, 119.8, 118.1, 68.8, 66.7, 46.8, 28.5, 18.6, 16.4;

HRMS m/z Calculated for $C_{10}H_{17}NO_3S$ 232.1007 $(M+H)^+$, found 232.0997.

Minor: *N*-2-Allyl-3(S)-*iso*-propyl-4(R)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (6a).



FTIR (neat): 3473, 2963, 1468, 1290, 1136, 932, 787 cm^{-1}. Colorless oil;

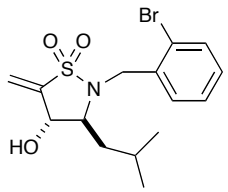
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.08 (s, 1H), 5.86 (s, 1H), 5.83 (m, 1H), 5.25 (overlap, 2H), 4.92 (d, *J* = 6.8 Hz, 1H), 3.90 (dd, *J* = 15.6, 4.4 Hz, 1H), 3.66 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.56 (broad, 1H), 3.37 (dd, *J* = 6.4, 6.0 Hz, 1H), 2.11 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 148.1, 132.4, 120.1, 117.1, 68.4, 65.9, 48.1, 28.8, 20.0, 16.4;

HRMS m/z Calculated for $C_{10}H_{17}NO_3S$ 232.1007 $(M+H)^+$, found 232.0997.

* Characterized as an inseparable mixture of major and minor diastereomers.

Major: *N*-(2-Bromobenzyl)-3(S)-*iso*-propyl-4(S)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5b)



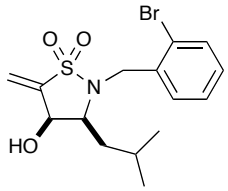
FTIR (neat): 3472, 2957, 1294, 1142, 752 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56-7.13 (aromatic H, 4H), 6.21 (s, 1H), 5.99 (s, 1H), 4.85 (d, *J* = 5.5 Hz, 1H), 4.55 (dd, *J* = 16.2, 10.5 Hz, 1H), 4.33 (dd, *J* = 16.8, 16.0 Hz, 1H), 3.60 (broad, 1H), 3.52 (ddd, *J* = 8.0, 5.6, 5.2 Hz, 1H), 1.63 (m, 2H), 1.28 (m, 1H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.8, 135.4, 133.0, 130.3, 129.4, 127.8, 123.1, 119.5, 68.1, 60.5, 46.5, 35.7, 24.6, 23.1, 22.2;

HRMS m/z Calculated for $C_{15}H_{20}NO_3SBrNa$ 396.0245 $(M+Na)^+$, found 396.0247.

Minor: *N*-(2-Bromobenzyl)-3(S)-*iso*-propyl-4(R)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (6b)



FTIR (neat): 3472, 2957, 1294, 1142, 752 cm^{-1}. Colorless oil;

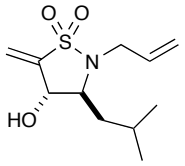
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56-7.13 (aromatic H, 4H), 6.21 (s, 1H), 5.99 (s, 1H), 4.85 (d, *J* = 5.5 Hz, 1H), 4.55 (dd, *J* = 16.2, 10.7 Hz, 1H), 4.33 (dd, *J* = 16.8, 16.0 Hz, 1H), 3.60 (broad, 1H), 3.32 (ddd, *J* = 9.0, 4.2, 3.8 Hz, 1H), 1.63 (m, 2H), 1.41 (m, 1H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.7, 135.0, 132.9, 130.4, 129.5, 127.8, 123.2, 119.5, 71.5, 63.7, 46.9, 40.6, 24.7, 23.3, 21.9;

HRMS m/z Calculated for $C_{15}H_{20}NO_3SBrNa$ 396.0245 $(M+Na)^+$, found 396.0247.

* Characterized as an inseparable mixture of major and minor diastereomers.

Major: *N*-(2-Allyl)-3(S)-*iso*-propyl-4(S)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5c)



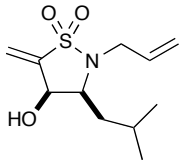
FTIR (neat): 3472, 2957, 1467, 1297, 1124, 732 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.15 (s, 1H), 5.94 (s, 1H), 5.87 (m, 1H), 5.32 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.24 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.76 (d, *J* = 4.8 Hz, 1H), 3.85 (dddd, *J* = 16.0, 4.8, 1.6, 1.6 Hz, 1H), 3.60 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.51 (ddd, *J* = 8.4, 5.6, 5.6 Hz, 1H), 3.46 (broad, 1H), 1.79 (m, 1H), 1.58 (ddd, *J* = 14.0, 8.4, 5.6 Hz, 1H), 1.38 (ddd, *J* = 14.0, 8.4, 6.0 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 148.0, 132.6, 119.7, 119.2, 67.8, 58.7, 45.4, 35.6, 24.6, 23.2, 22.1;

HRMS m/z Calculated for $C_{11}H_{19}NO_3SNa$ 268.0983 $(M+Na)^+$, found 268.0959.

Minor: *N*-(2-Allyl)-3(S)-*iso*-propyl-4(R)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (6c)



FTIR (neat): 3472, 2957, 1467, 1297, 1124, 732 cm^{-1}. Colorless oil;

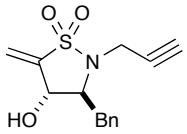
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.12 (s, 1H), 5.93 (s, 1H), 5.87 (m, 1H), 5.32 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.24 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.48 (broad, 1H), 3.85 (dddd, *J* = 16.0, 4.8, 1.6, 1.6 Hz, 1H), 3.68 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.46 (broad, 1H), 3.31 (ddd, *J* = 9.2, 4.4, 4.4 Hz, 1H), 1.79 (m, 1H), 1.53 (ddd, *J* = 13.6, 8.8, 4.8 Hz, 1H), 1.38 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.9, 132.5, 119.6, 118.7, 71.3, 62.1, 45.6, 40.6, 24.6, 23.5, 22.3;

HRMS m/z Calculated for $C_{11}H_{19}NO_3SNa$ 268.0983 $(M+Na)^+$, found 268.0959.

* Characterized as an inseparable mixture of major and minor diastereomers.

Major: *N*-(2-Propargyl)-3(*S*)-Benzyl-4(*S*)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5d)



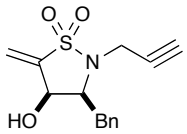
FTIR (neat): 3477, 3281, 2926, 1433, 1298, 1138, 704 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.36-7.28 (aromatic H, 5H), 6.24 (s, 1H), 5.97 (s, 1H), 4.68 (m, 1H), 4.15 (dd, *J* = 18.4, 2.0 Hz, 1H), 3.89 (ddd, *J* = 8.0, 6.4, 5.2 Hz, 1H), 3.58 (dd, *J* = 18.4, 2.4 Hz, 1H), 3.04 (dd, *J* = 13.2, 8.4 Hz, 1H), 3.07 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.83 (d, *J* = 6.8 Hz, 1H), 2.38 (dd, *J* = 2.4, 2.0 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.3, 136.2, 129.6, 128.8, 127.0, 120.1, 76.5, 74.1, 67.4, 62.0, 33.6, 32.7;

HRMS m/z Calculated for $C_{14}H_{15}NO_3SNa$ 300.0670 $(M+Na)^+$, found 300.0672.

Minor: *N*-(2-Propargyl)-3(*S*)-Benzyl-4(*R*)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (6d)



FTIR (neat): 3477, 3281, 2926, 1433, 1298, 1138, 704 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.36-7.28 (aromatic H, 5H), 6.19 (s, 1H), 5.93 (s, 1H), 4.63 (broad, 1H), 4.15 (dd, *J* = 18.4, 2.0 Hz, 1H), 3.76 (ddd, *J* = 7.2, 6.8, 4.8 Hz, 1H), 3.68 (dd, *J* = 18.4, 2.4 Hz, 1H), 3.17 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.18 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.51 (d, *J* = 6.8 Hz, 1H), 2.38 (dd, *J* = 2.4, 2.0 Hz, 1H);

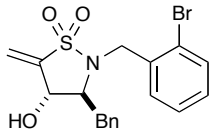
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.9, 136.0, 129.4, 129.0, 127.3, 118.5, 76.5, 74.4, 70.2, 64.9, 37.8, 33.6;

HRMS m/z Calculated for $C_{14}H_{15}NO_3SNa$ 300.0670 $(M+Na)^+$, found 300.0588.

* Characterized as an inseparable mixture of major and minor diastereomers.

The *dr* ratio is high (7.4:1), therefore the NMR of the minor product is not shown below.

Major: *N*-(2-Bromobenzyl)-3(*S*)-Benzyl-4(*S*)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5e)



FTIR (neat): 3470, 2955, 1440, 1292, 1144, 750 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56-7.08 (aromatic H, 9H), 6.26 (s, 1H), 5.99 (s, 1H), 4.77 (d, *J* = 4.7 Hz, 1H), 4.30 (dd, *J* = 16.4 Hz, 2H), 3.72 (dd, *J* = 12.8, 7.2 Hz, 1H), 3.50 (d, *J* = 6.0 Hz, 1H), 3.02 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.83 (dd, *J* = 13.6, 7.6 Hz, 1H);

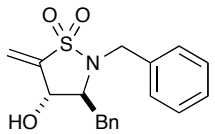
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.5, 136.8, 135.0, 132.9, 130.1, 129.7, 129.4, 128.8, 127.8, 126.9, 123.2, 119.7, 68.1, 63.6, 46.5, 33.8;

HRMS m/z Calculated for $C_{18}H_{18}NO_3SBrNa$ 430.0088 $(M+Na)^+$, found 430.0063.

* Characterized as an inseparable mixture of major and minor diastereomers.

The *dr* ratio is high (9.0:1), therefore the NMR of the minor product is not shown below.

Major: *N*-benzyl-3(S)-Benzyl-4(S)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (5f)



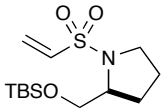
FTIR (neat): 3464, 3025, 1495, 1286, 1144, 746 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.56-7.08 (aromatic H, 10H), 6.28 (s, 1H), 5.96 (s, 1H), 4.77 (d, *J* = 4.7 Hz, 1H), 4.30 (d, *J* = 16.4 Hz, 1H), 3.55 (overlap, 2H), 2.85 (overlap, 2H), 2.70 (dd, *J* = 12.8, 9.2 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.4, 137.2, 135.2, 129.6, 128.8, 128.7(2), 128.1, 126.9, 119.0, 68.4, 61.6, 45.8, 33.9;

HRMS m/z Calculated for $C_{18}H_{18}NO_3SBrNa$ 352.0983 $(M+Na)^+$, found 352.0974.

2-((*tert*-Butyldimethylsilyloxy)methyl)-1-(vinylsulfonyl)pyrrolidine (7)



[α]^{23} –80.4 (c 2.43, CH_2Cl_2) Colorless oil;

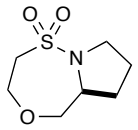
FTIR (neat): 2955, 2856, 1348, 1153, 837, 777 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.48 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.26 (d, *J* =16.4 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 3.76 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.63 (m, 1H), 3.55 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.36 (m, 1H), 3.20 (m, 1H), 2.00-1.83 (m, 4H), 0.90 (s, 9H), 0.07 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 132.1, 127.7, 65.5, 60.9, 49.2, 28.5, 25.7(3), 24.3, 18.2, -5.4(2);

HRMS m/z Calculated for $C_{13}H_{27}NO_3SiS$ 306.1559 $(M+H)^+$, found 306.1562.

(*S*)-*N*-(2-Pyrrolidine)-5,1,2-Oxathiazepine-1,1-dioxide (8)



[α]^{23} –15.4 (c 5.51, CH_2Cl_2) Colorless oil;

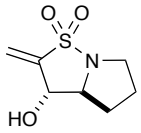
FTIR (neat): 2952, 1334, 1146, 744 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 4.11 (m, 2H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.74 (ddd, *J* = 13.2, 2.0 Hz, 1H), 3.57 (m, 2H), 3.37 (m, 1H), 3.23 (m, 1H), 3.12 (m, 1H), 2.00 (m, 4H).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 74.4, 67.0, 58.1, 52.1, 50.6, 31.3, 24.2.

HRMS m/z Calculated for $C_7H_{13}NO_3SNa$ 214.0514 (M+Na), found 214.0538 $(M+Na)^+$.

***N*-(2-Pyrroldine)-3,4(*S*,*S*)-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (10).**



[α]^{23} 31.8 (c 5.82, CH_2Cl_2) Colorless oil;

FTIR (neat): 3446, 2941, 1299, 1190, 1082 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.10 (s, 1H), 5.89 (s, 1H), 4.39 (dd, *J* = 6.4, 2.0 Hz, 1H), 3.65 (ddd, *J* = 6.8, 6.6, 3.6 Hz, 1H), 3.60 (ddd, *J* = 11.6, 8.0, 4.8 Hz, 1H), 3.1 (ddd, *J* = 14.0, 7.2, 6.4 Hz, 1H), 2.11 (m, 1H), 1.87 (m, 2H), 1.81 (m, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 149.3, 118.3, 72.1, 68.0, 46.7, 29.8, 24.8;

HRMS m/z Calculated for $C_7H_{11}NO_3SNa$ 212.0357 $(M+Na)^+$, found 212.0351.

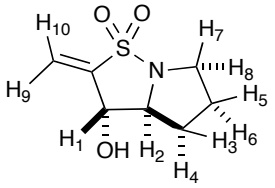
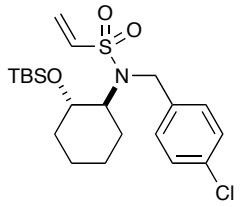


Table of data:

Assignment of ^{1}H and ^{13}C chemical shifts were based on ^{1}H, ^{13}C, DEPT, COSY, NOESY, HSQC and HMBC NMR spectra.

Protons	^{1}H chemical shift (ppm)	^{13}C chemical shift (ppm)
H1	4.89	72.0
H2	3.68	68.0
H3	1.91	29.9
H4	2.15	29.9
H5	1.81	24.8
H6	1.94	24.8
H7	3.67	46.7
H8	3.12	46.7
H9	5.90	118.3
H10	6.12	118.3

(±)-*N*-2-(*tert*-butyldimethylsilyoxy)cyclohexyl)-*N*-(4-chlorobenzyl)ethenesulfonamide



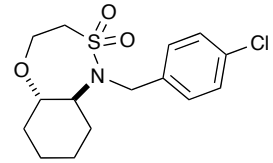
FTIR (neat): 2933, 2856, 1450, 1336, 1150, 790 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.35-7.24 (aromatic H, 4H), 6.50 (dd, *J* = 16.4, 10.0 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 4.50 (d, *J* = 16.4 Hz, 1H), 4.08 (d, *J* = 14.4 Hz, 1H), 3.73 (broad, 1H), 3.36 (broad, 1H), 2.00 (d, *J* = 12.4 Hz, 1H), 1.71 (d, *J* = 10.5 Hz, 1H), 1.60 (d, *J* = 10.9 Hz, 1H), 1.50 (d, *J* = 10.2 Hz, 1H), 1.25 (m, 1H), 1.04 (m, 3H), 0.91 (s, 9H), 0.15 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 137.3, 136.7, 133.2, 129.5, 128.5, 124.6, 71.6, 64.7, 64.6, 36.5, 33.2, 26.0(3), 25.5, 24.2, 18.0, -3.56, -3.84;

HRMS m/z Calculated for $C_{21}H_{34}NO_3SiSClNa$ 466.1615 $(M+Na)^+$, found 466.1630.

(±)-*Trans*-2-(4-chlorobenzyl)-3,4-(cyclohexyl)-5,1,2-Oxathiazepine-1,1-dioxide (13)



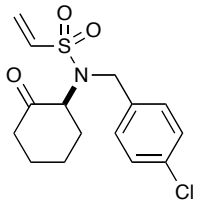
FTIR (neat): 2939, 1490, 1328, 1141, 1103 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.34-7.27 (aromatic H, 4H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.20 (d, *J* = 10.2 Hz, 1H), 4.11 (ddd, *J* = 14.2, 3.6, 3.3 Hz, 1H), 3.85 (m, 2H), 3.25 (s, 2H), 2.80 (broad, 1H), 2.01 (d, *J* = 10.8 Hz, 1H), 1.66 (d, *J* = 12.4 Hz, 1H), 1.54 (m, 2H), 1.33 (m, 2H), 1.19 (m, 1H), 0.97 (m, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 136.0, 133.5, 129.7, 128.7, 83.7, 65.2, 54.2, 53.6, 34.1, 32.7, 25.1, 24.5;

HRMS m/z Calculated for $C_{15}H_{20}NO_3SNa$ 352.0750 $(M+Na)^+$, found 352.0750.

(±)-(*S*)-*N*-(4-Chlorobenzyl)-*N*-(2-oxocyclohexyl)ethenesulfonamide (14)



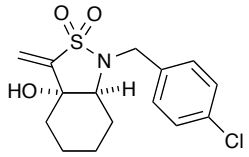
FTIR (neat): 2941, 1718, 1334, 1149, 788 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.30 (m, 4H), 6.57 (dd, *J* = 16.4, 10.0 Hz, 1H), 6.22 (d, *J* = 16.4 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 4.60 (d, *J* = 17.1 Hz, 1H), 4.55 (dd, *J* = 13.1, 5.7 Hz, 1H), 4.04 (d, *J* = 17.2 Hz, 1H), 2.53 (ddd, *J* = 14.6, 1.8, 1.8 Hz, 1H), 2.35 (ddd, *J* = 14.1, 6.2, 6.1 Hz, 1H), 2.00 (m, 2H), 1.88 (ddd, *J* = 15.7, 5.5, 2.1 Hz, 1H), 1.58 (m, 1H), 1.55 (m, 2H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 207.3, 137.2,135.2, 133.1, 128.6, 126.7, 66.4, 48.9, 41.8, 34.5, 26.4, 25.0;

HRMS m/z Calculated for $C_{15}H_{18}NO_3SClK$ 366.0333 $(M+K)^+$, found 366.0320.

(±)-*N*-(4-Chlorobenzyl)-3,4 (3*S*,4*S*) cyclohexyl-hydroxy-5-methylene-isothiazolidine-1,1-dioxide (15)



FTIR (neat): 3458, 2937, 1490, 1286, 1093, 1014 cm^{-1}. Colorless oil;

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40-7.34 (aromatic H, 4H), 6.27 (d, *J* = 2.0 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 4.30 (d, *J* = 15.2 Hz, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 3.21 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.48 (s, 1H), 2.20 (ddd, *J* = 17.6, 8.0, 4.0 Hz, 1H), 1.88 (m, 1H), 1.73 (ddd, *J* = 12.4, 8.4, 4.0 Hz, 1H), 1.60 (m, 2H), 1.37 (m, 2H), 1.22 (m, 1H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 150.9, 134.3, 133.8, 129.9, 128.9, 117.4, 72.9, 63.6, 44.9, 33.9, 25.4, 21.4, 20.9;

HRMS m/z Calculated for $C_{15}H_{18}NO_3SClNa$ 350.0594 $(M+Na)^+$, found 350.0587.

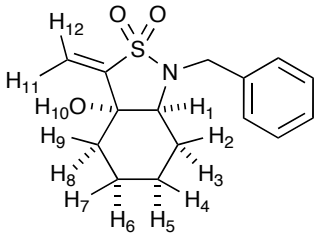
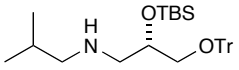


Table of data:

Assignments of ^{1}H and ^{13}C chemical shifts were based on ^{1}H, ^{13}C, DEPT, COSY, NOESY, HSQC and HMBC NMR spectra.

Protons	^{1}H chemical shift (ppm)	^{13}C chemical shift (ppm)
H1	3.21	63.6
H2	1.62	25.4
H3	1.87	25.4
H4	1.36	20.9
H5	1.21	20.9
H6	1.62	21.4
H7	1.37	21.4
H8	1.72	33.9
H9	2.20	33.9
H10	2.48	None
H11	5.90	134.3
H12	6.26	133.8

(*S*)-2-(*tert*-Butyldimethylsilyloxy)-N-isobutyl-3-(trityloxy)propan-1-amine (17)



[α]^{23} –42.3 (c 2.62, CH_2Cl_2) Colorless oil;

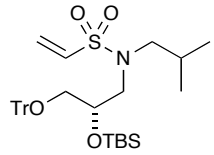
FTIR (neat): 3058, 2953, 1448, 1253, 1076, 835, 775 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.59-7.28 (aromatic H, 15H), 4.12 (m, 1H), 3.25 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.22 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.01 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.80 (dd, *J* = 11.6, 7.2 Hz, 1H), 2.56 (dd, *J* = 11.6, 6.8 Hz, 1H), 2.49 (dd, *J* = 11.2, 6.8 Hz, 1H), 1.87 (m, 1H), 1.0 (d, *J* = 6.8 Hz, 6H), 0.98 (s, 9H), 0.19 (s, 3H), 0.17 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.2(3), 128.8(6), 127.9(6), 127.1(3), 86.7, 71.2, 66.6, 58.2, 54.2, 28.4, 26.0(3), 20.8, 18.1(2), -4.3, -4.7;

HRMS m/z Calculated for $C_{32}H_{45}NO_2Si$ 504.3298 $(M+H)^+$, found 504.3245.

(*S*)-*N*-(2-(*tert*-Butyldimethylsilyloxy)-3-(trityloxy)propyl)-*N*-isobutylethenesulfonamide (18)



[α]^{23} –23.0 (c 2.25, CH_2Cl_2) Colorless oil;

FTIR (neat): 3058, 2956, 1329, 1144, 993, 788 cm^{-1};

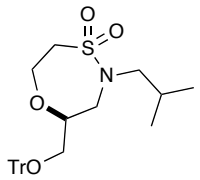
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52-7.26 (aromatic H, 15H), 6.36 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.19 (d, *J* = 16.4 Hz, 1H), 5.85 (d, *J* = 9.6 Hz, 1H), 4.18 (dddd, *J* = 23.4, 16.3, 10.3, 5.2 Hz, 1H), 3.50 (dd, *J* = 14.1, 6.0 Hz, 1H), 3.17 (overlap, 3H), 2.95 (d, *J* = 8.0 Hz, 2H), 1.94 (m, 1H), 0.95 (s, 9H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.17 (s, 3H), 0.14 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 143.9, 135.3, 128.8(3), 127.8(6), 127.1(6), 126.0(3), 86.6, 71.3, 65.6, 56.7, 51.7, 27.4, 26.0(3), 25.7, 20.0, 18.1, -3.5, -4.6;

HRMS m/z Calculated for $C_{34}H_{47}NO_4SiSNa$ 616.2893 $(M+Na)^+$, found 616.2880.

5,1,2-Oxathiazepine-2-isobutyl-4(*S*)-(trityloxymethyl)-1,1-dioxide (19)

2-Chloroethanesulfonyl chloride (120 mg, 1.05 equiv.) was slowly added to a stirred solution of (S)-2-(*tert*-butyldimethylsilyloxy)-*N*-isobutyl-3-(trityloxy)propan-1-amine **17** (350 mg, 1.0 equiv.) in CH_2Cl_2 at 0 ºC, and stirring was continued at 0 ºC for 2 hours. The mixture was diluted with 20 ml CH_2Cl_2, washed with brine (sat'd, 2x10 ml), dried ($MgSO_4$), concentrated under reduced pressure to afford crude vinyl sulfonamide **18** in a yield of 71.4% over three steps. After purification, several drops of TBAF in THF (1.0 M in THF) were added to the stirred solution of vinyl sulfonamide **18** (25 mg, 0.04 mmol) in THF (2ml). Stirring was continued for 2 hrs at room temperature, NH_4Cl (3ml, sat'd) was added and the organic layer was extracted by CH_2Cl_2 (2x4ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Hexane/EtOAc = 4:1) to yield sultam **19** (18.6 mg) in a yield of 92%.



[α]^{23} –10.37 (c = 4.92, CH_2Cl_2) Colorless oil;

FTIR (neat): 2958, 1448, 1337, 1144, 705 cm^{-1};

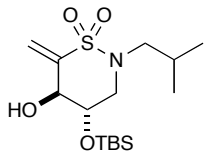
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49-7.27 (aromatic H, 15H), 4.25 (m, 2H), 3.85 (m, 1H), 3.41-3.11 (overlap, 5H), 3.07 (overlap, 3H), 1.86 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 143.6 (3), 128.6 (6), 128.0 (6), 127.2 (3), 86.8, 78.8, 64.5, 63.0, 56.2, 54.8, 46.6, 27.0, 19.9 (2);

HRMS m/z Calculated for $C_{28}H_{33}NNaO_4SNa$ 502.2028 $(M+Na)^+$, found 502.2005.

***N*-(iso-Butyl)-4-(S)-(*tert*-butyldimethylsilyloxy)-5-(R)-hydroxy-6-methylene-1,2-thiazine, tetrahedro-1,1-dioxide (22)**

To a solution of **18** (24 mg, 0.04 mmol) in CH_2Cl_2 at -10 ºC was added several drops of Me_2AlCl (1 M in CH_2Cl_2), stirring was continued until TLC analysis indicated that trityl-deprotection was complete. A brine solution (5ml) was added to the reaction mixture, the organic layer was extracted by CH_2Cl_2 (2x5 ml), dried ($MgSO_4$) and partially concentrated under reduced pressure. To the crude mixture in CH_2Cl_2, was added the Dess-Martin agent (34.3 mg, 2.0 equiv.). The reaction mixture was washed with $NaHCO_3$ (sat'd, aq.), the organic layer was dried ($MgSO_4$) and partially concentrated under reduced pressure to yield aldehyde vinyl sulfonamide **21**. To a stirred solution of **21** in CH_2Cl_2 was added DABCO (0.4 mg, 0.10 equiv.) and the reaction was monitored until TLC analysis indicated that the starting material was consumed (normally 2 to 4 hrs). The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to afford the 6-membered ring sultam **22** in a yield of 71% over three steps with *dr* ratio is more than 95:5.



[α]^{23} 19.7 (c 0.30, CH_2Cl_2) Colorless oil;

FTIR (neat): 3508, 2956, 1340, 1132, 839, 779 cm^{-1};

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.04 (s, 1H), 5.88 (s, 1H), 4.55 (dd, *J* = 6.8, 2.5 Hz, 1H), 3.70 (ddd, *J* = 16.4, 7.2, 4.5 Hz, 1H), 3.40 (m, 2H), 3.02 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.94 (d, *J* = 3.0 Hz, 1H), 2.76 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.83 (m, 1H), 0.93 (d, *J* = 8.8 Hz, 3H), 0.92 (d, *J* = 8.8 Hz, 3H), 0.92 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 143.4, 118.1, 74.9, 73.1, 57.0, 51.1, 28.2, 25.6(3), 19.9(2), 17.9, -4.7(2);

(For stereochemistry assignment, *benzene-d_6* was used as NMR solvent instead of $CDCl_3$)

HRMS m/z Calculated for $C_{15}H_{31}NO_4SiSNa$ 372.1641 $(M+Na)^+$, found 372.1625.

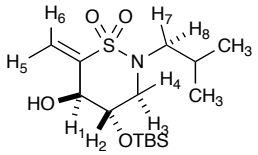


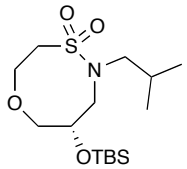
Table of data:

Assignments of ^{1}H and ^{13}C chemical shifts were based on ^{1}H, ^{13}C, DEPT, COSY, NOESY, HSQC and HMBC NMR spectra.

Protons	^{1}H chemical shift (ppm)	^{13}C chemical shift (ppm)
H1	4.51	74.9
H2	3.70	73.1
H3	3.42	51.1
H4	3.42	51.1
H5	5.88	143.4
H6	6.04	143.4
H7	2.76	57.0
H8	3.03	57.0

6,1,2-Oxathiazepine-*N*-(iso-Butyl)-4-(*S*)-(*tert*-butyldimethylsilyloxy)-1,1-dioxide (23)

To the solution of alcohol vinyl sulfonamide (30 mg, 1 equiv.) in THF was added NaH (3.4 mg, 60% dispersion in mineral oil, 1.0 equiv.), stirring was continued until TLC showed the starting material disappeared. 1N HCl was added drop wise to neutralized resulting base, then CH_2Cl_2 (2 x 3ml) was added to extract the organic layer, the organic layers were combined, dried ($MgSO_4$), concentrated under reduced pressure, and purified by flash chromatography (Hexane/EtOAc = 2:1) to afford 25.4 mg of the 8-membered-ring sultam **23** in a yield of 84%.



[α]^{23} -11.2 (c 0.56, CH_2Cl_2) Colorless oil;

FTIR (neat): 2929, 1339, 1252, 1142, 1113, 837, 777 cm^{-1};

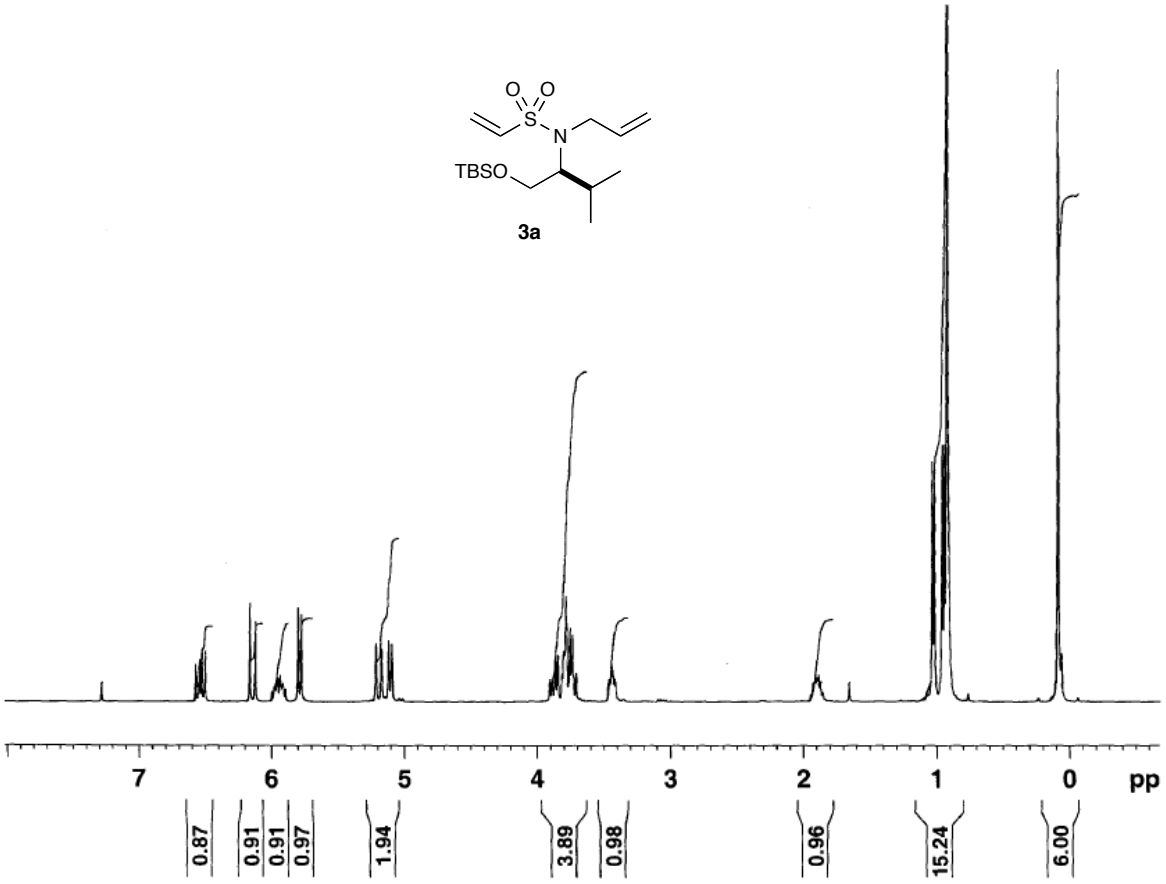
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 4.26 (ddd, *J* = 13.8, 4.9, 4.8 Hz, 1H), 4.11 (dddd, *J* = 9.8, 5.0, 4.9, 4.8 Hz, 1H), 3.83 (ddd, *J* = 16.3, 8.6, 2.7 Hz, 1H), 3.65 (d, *J* = 4.8 Hz, 2H), 3.35 (m,

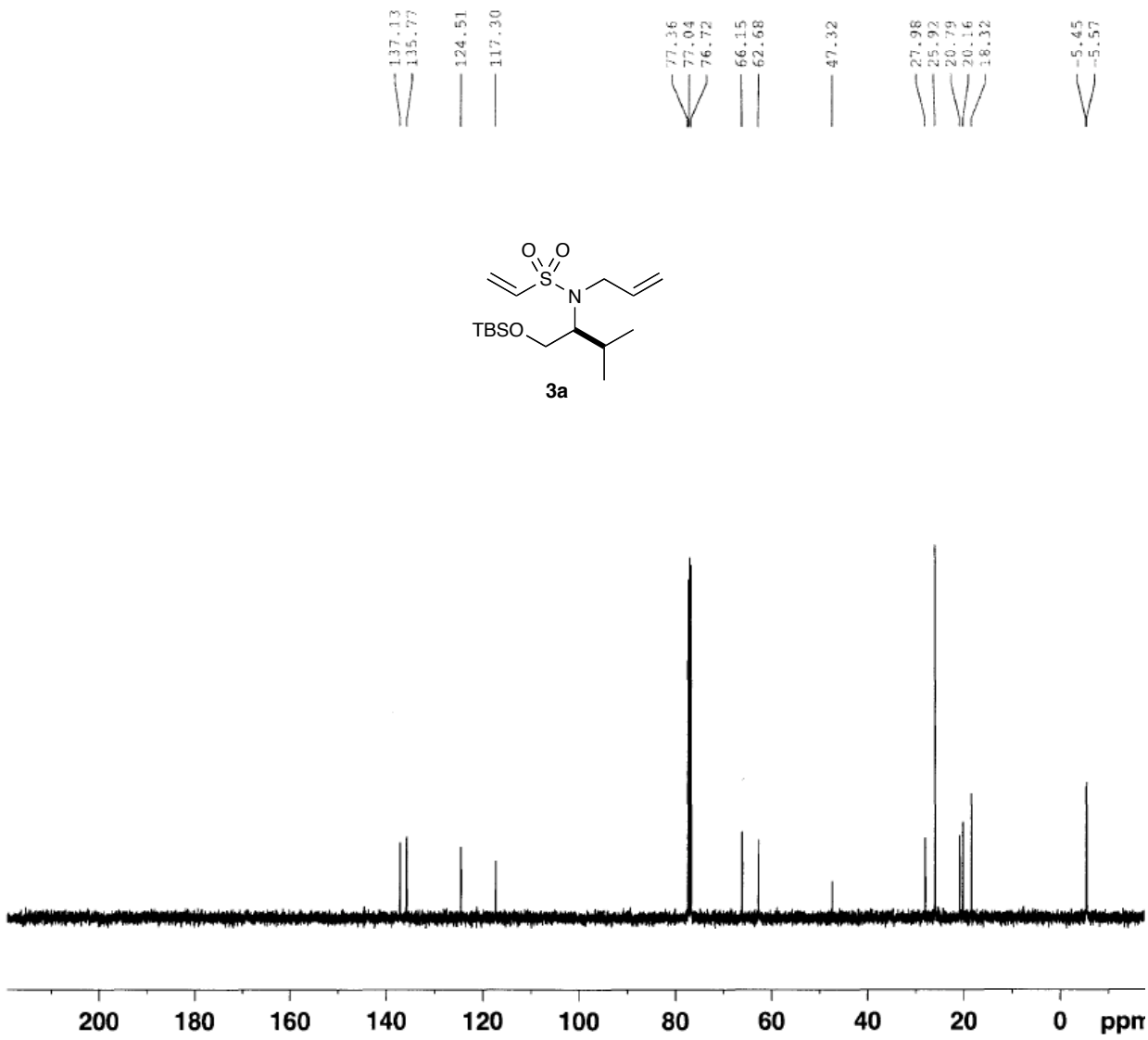
4H), 3.07 (d, J = 7.5 Hz, 2H), 1.88 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.92 (s, 9H), 0.09 (s, 6H);

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 80.1, 64.6, 63.5, 56.4, 54.9, 46.3, 27.1, 25.8(3), 19.9(2), 18.3, -5.4(2);

HRMS m/z Calculated for $C_{15}H_{33}NO_4SiSNa$ 374.1797 $(M+Na)^+$, found 374.1790.

^{1}H, ^{13}C-NMR Spectra for New Compounds

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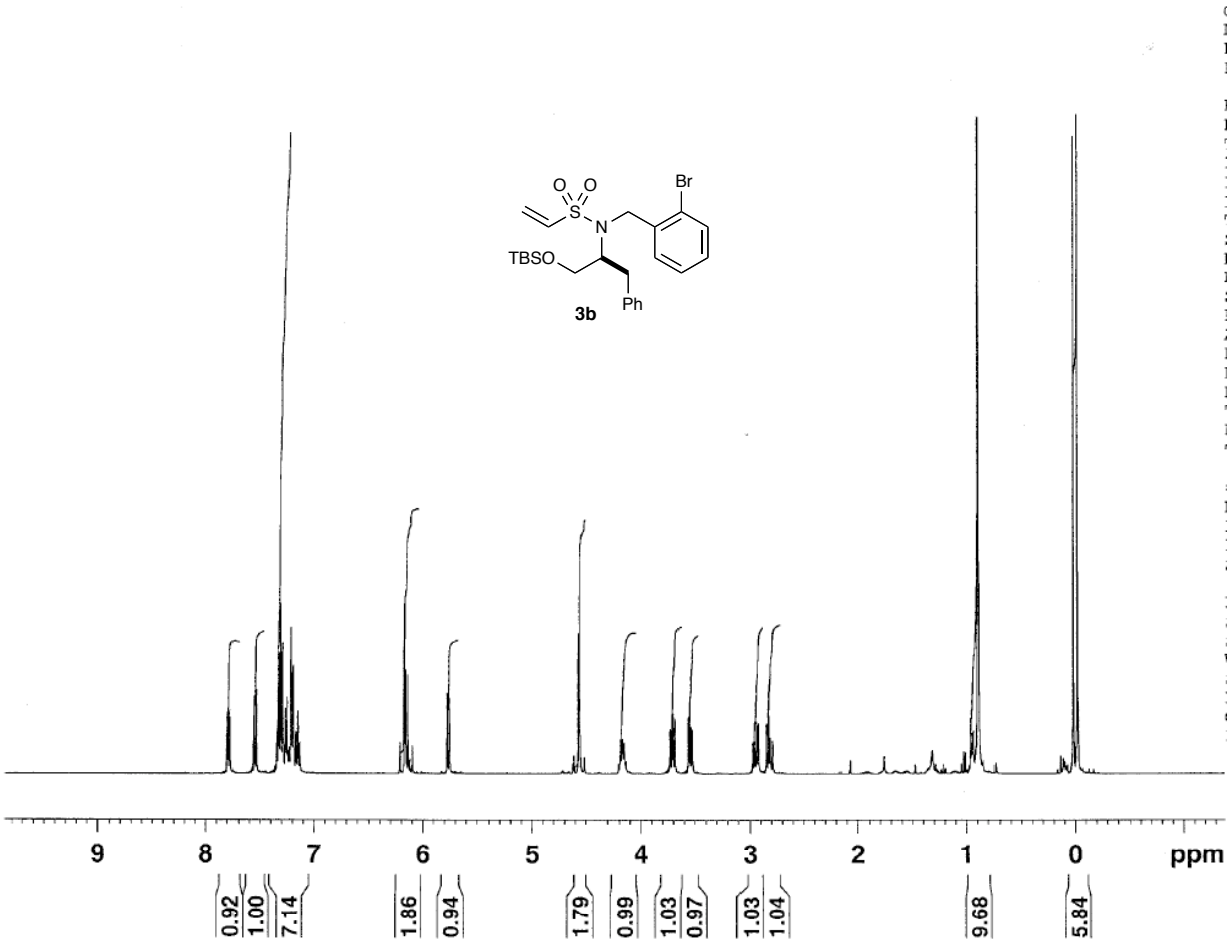
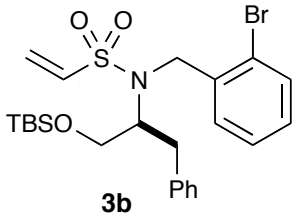
135.77
124.51
117.30
77.36
77.04
76.72
66.15
62.68
47.32
27.98
25.92
20.79
20.16
18.32
-5.45
-5.57
O
O
S
N
TBSO
200
180
160
140
120
100
80
60
40
20
0
ppm

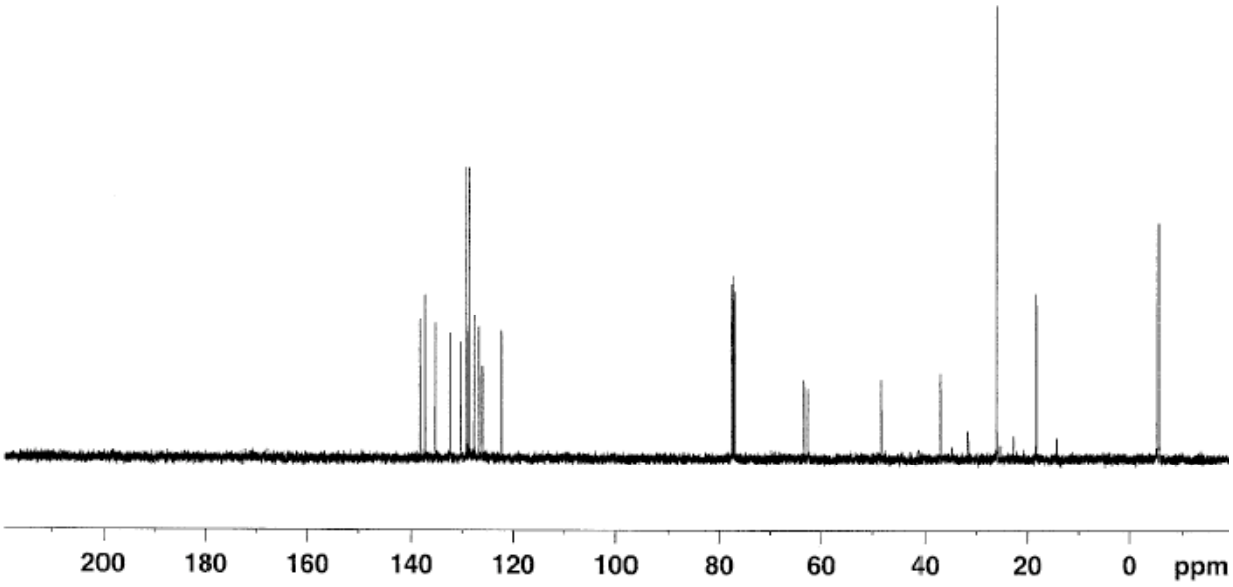
3a


O
O
S
N
Br
TBSO
Ph
3b
9
8
7
6
5
4
3
2
1
0
ppm
0.92
1.00
7.14
1.86
0.94
1.79
0.99
1.03
0.97
1.03
1.04
9.68
5.84


138.23
137.31
135.31
132.42
130.28
129.26
128.86
128.66
127.61
126.76
126.03
122.32
77.53
77.22
76.90
63.40
62.60
48.26
36.99
31.64
25.94
22.71
18.23
14.23
-5.49
-5.51


O
O
S
N
Br
TBSO
Ph

3b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180
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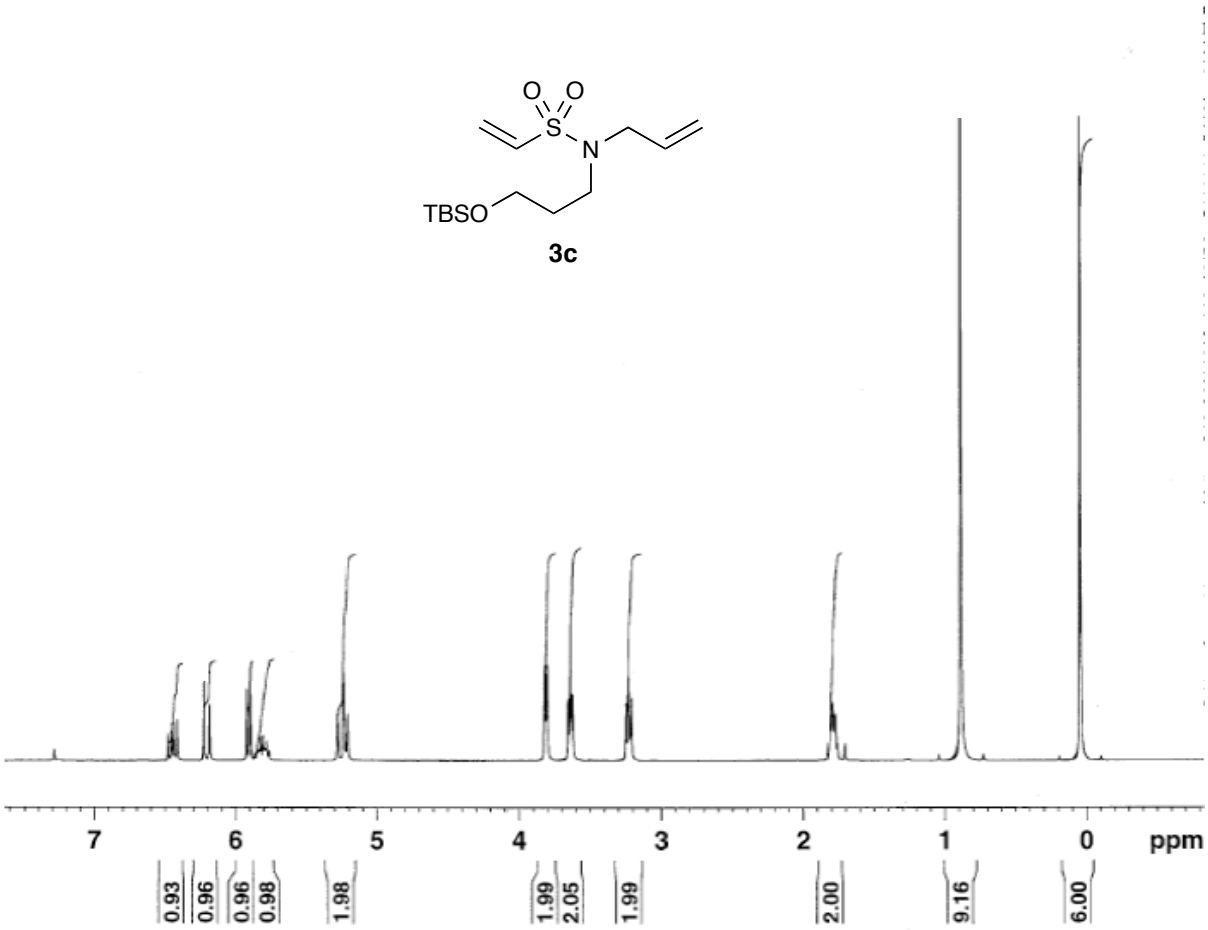
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TBSO
7
6
5
4
3
2
1
0
ppm
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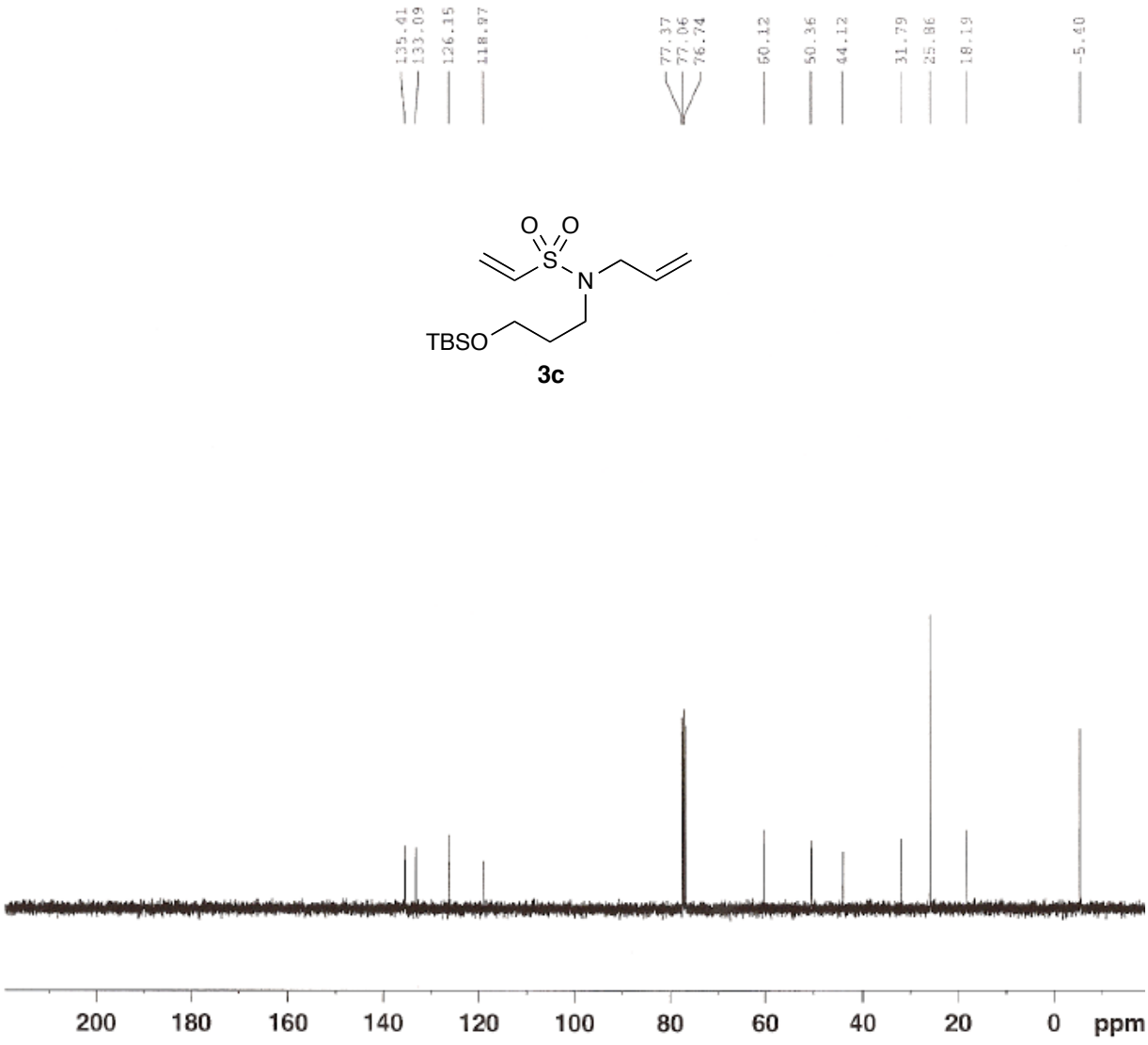
0.96
0.96
0.98
1.98
1.99
2.05
1.99
2.00
9.16
6.00

3c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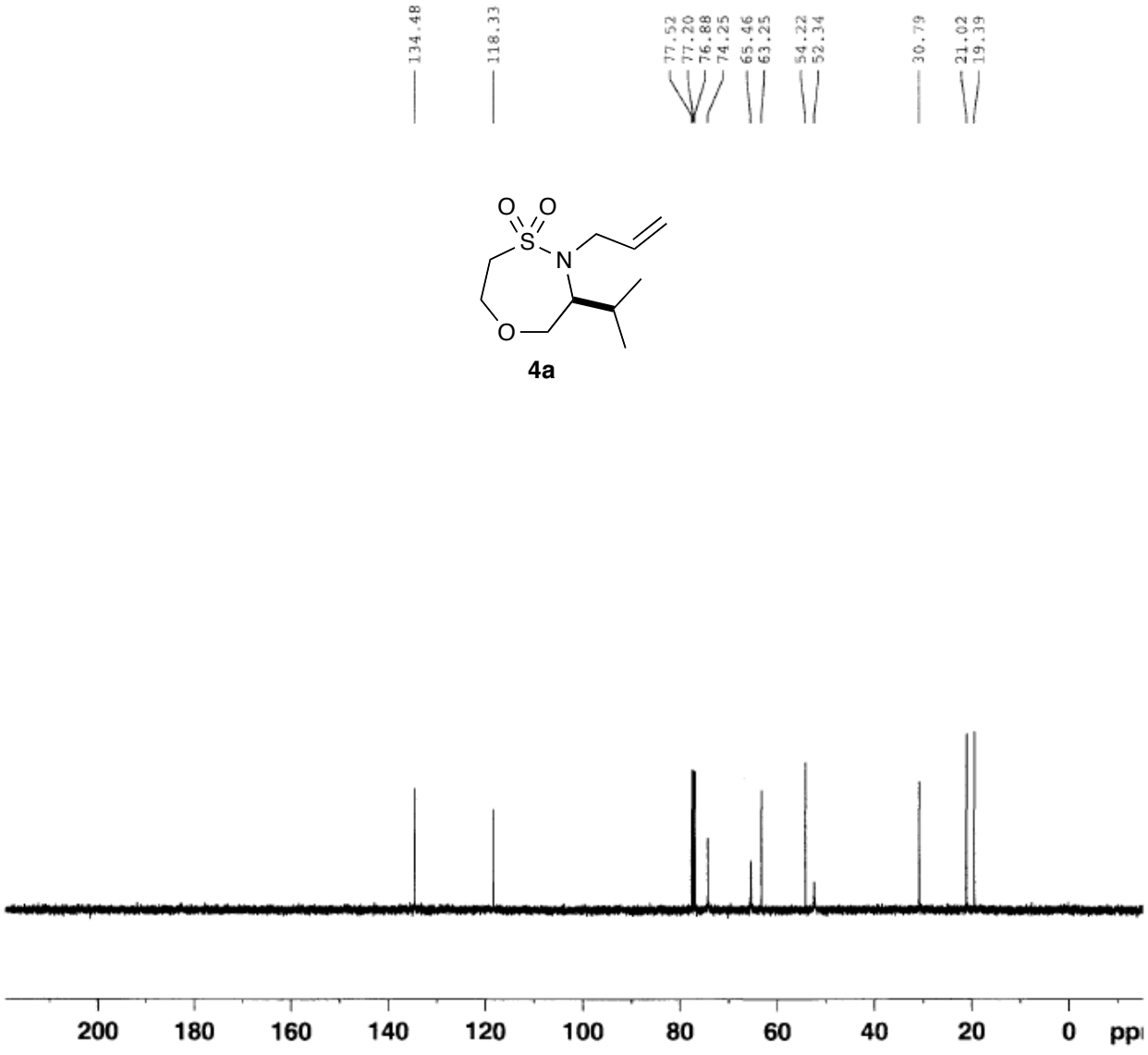
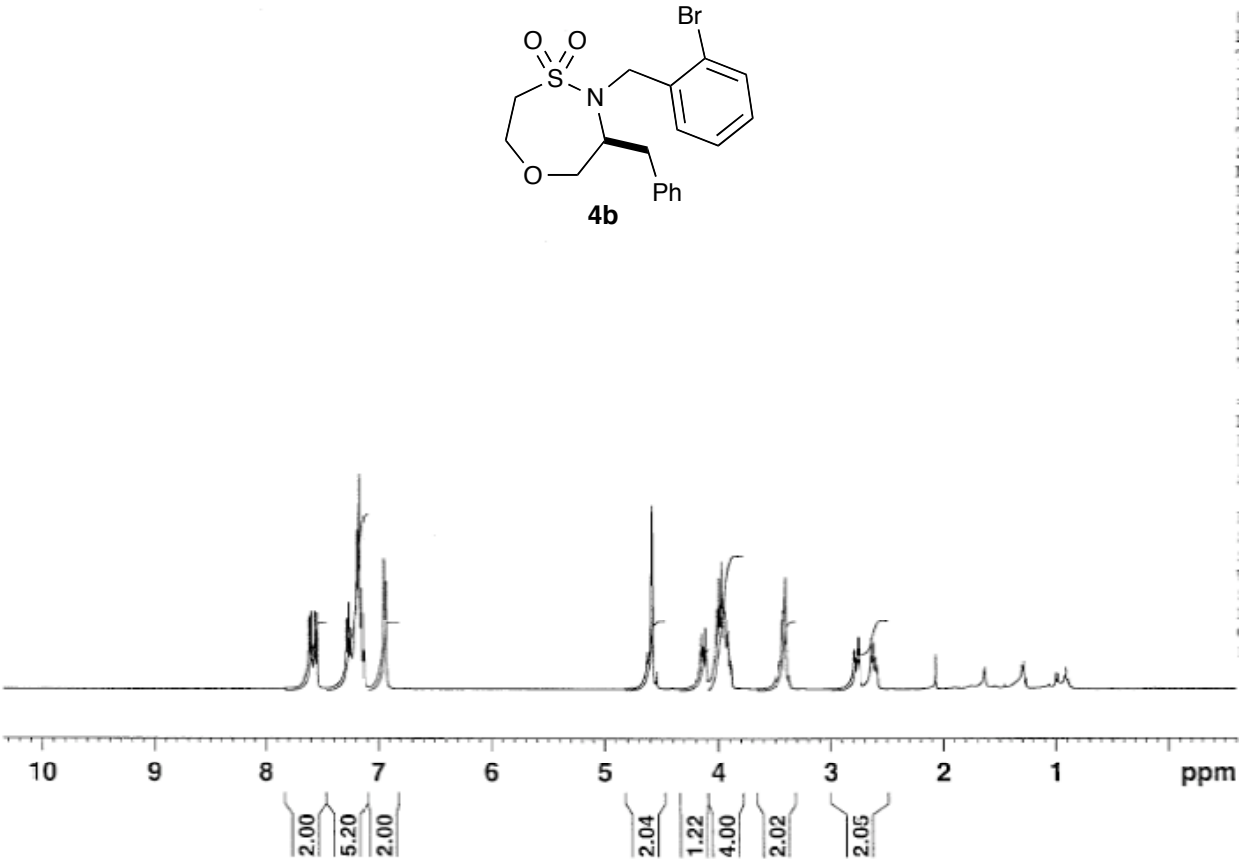
133.09
126.15
118.97
77.37
77.06
76.74
60.12
50.36
44.12
31.79
25.86
18.19
-5.40
O
O
S
N
TBSO
200
180
160
140
120
100
80
60
40
20
0
ppm

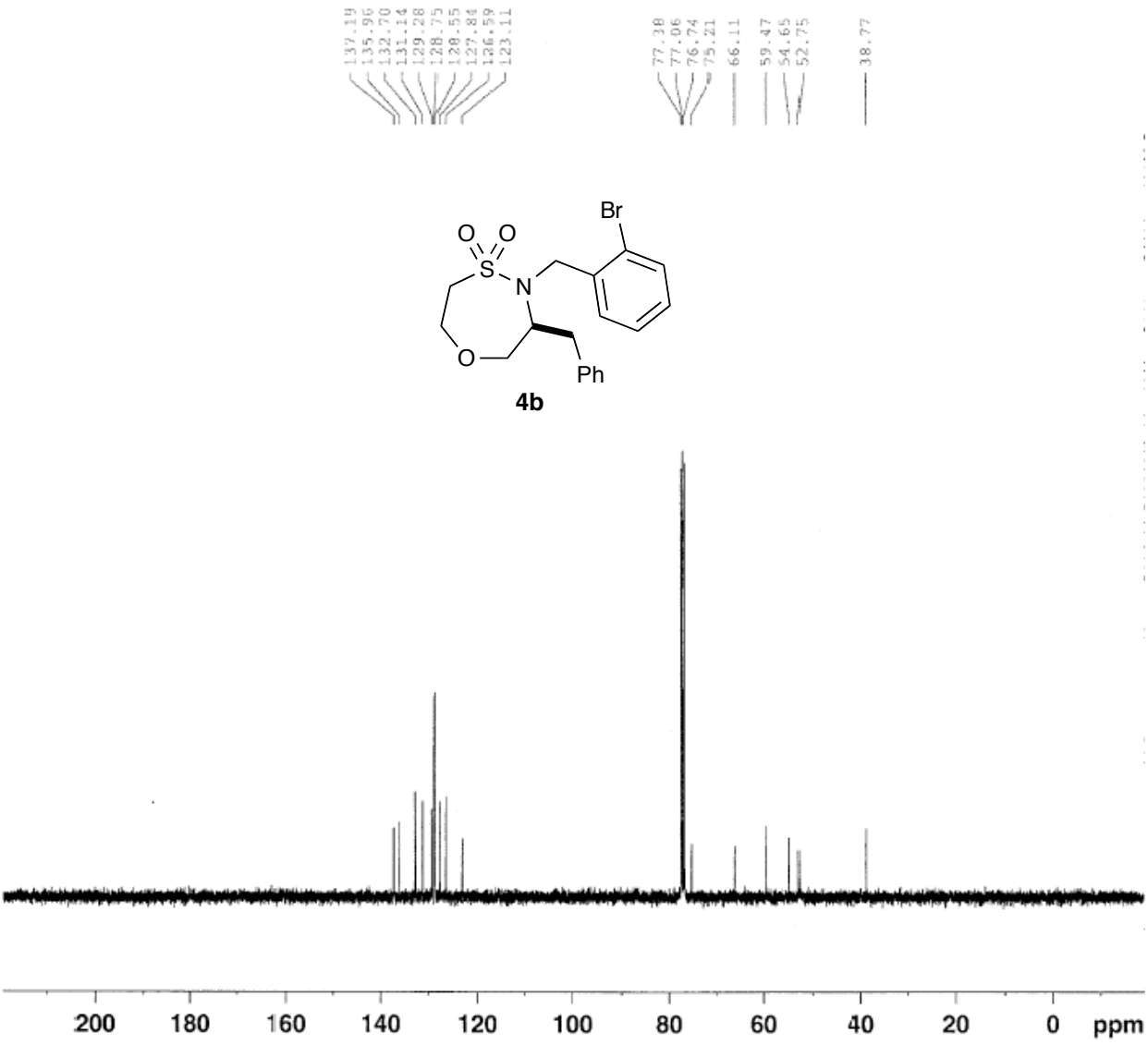
3c


134.48
118.33
77.52
77.20
76.88
74.25
65.46
63.25
54.22
52.34
30.79
21.02
19.39
O
O
S
N
O
200
180
160
140
120
100
80
60
40
20
0
ppm

4a



4b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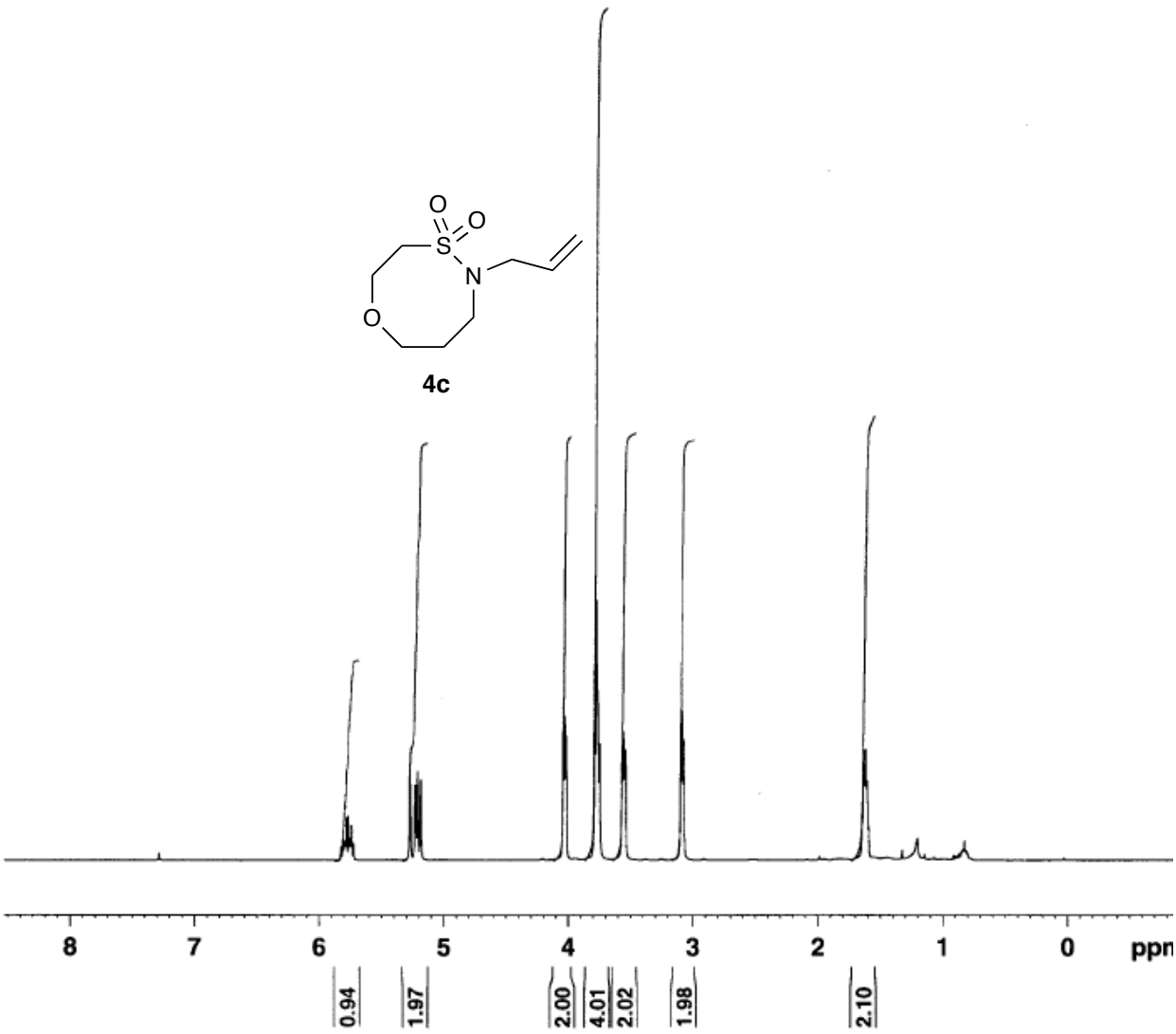
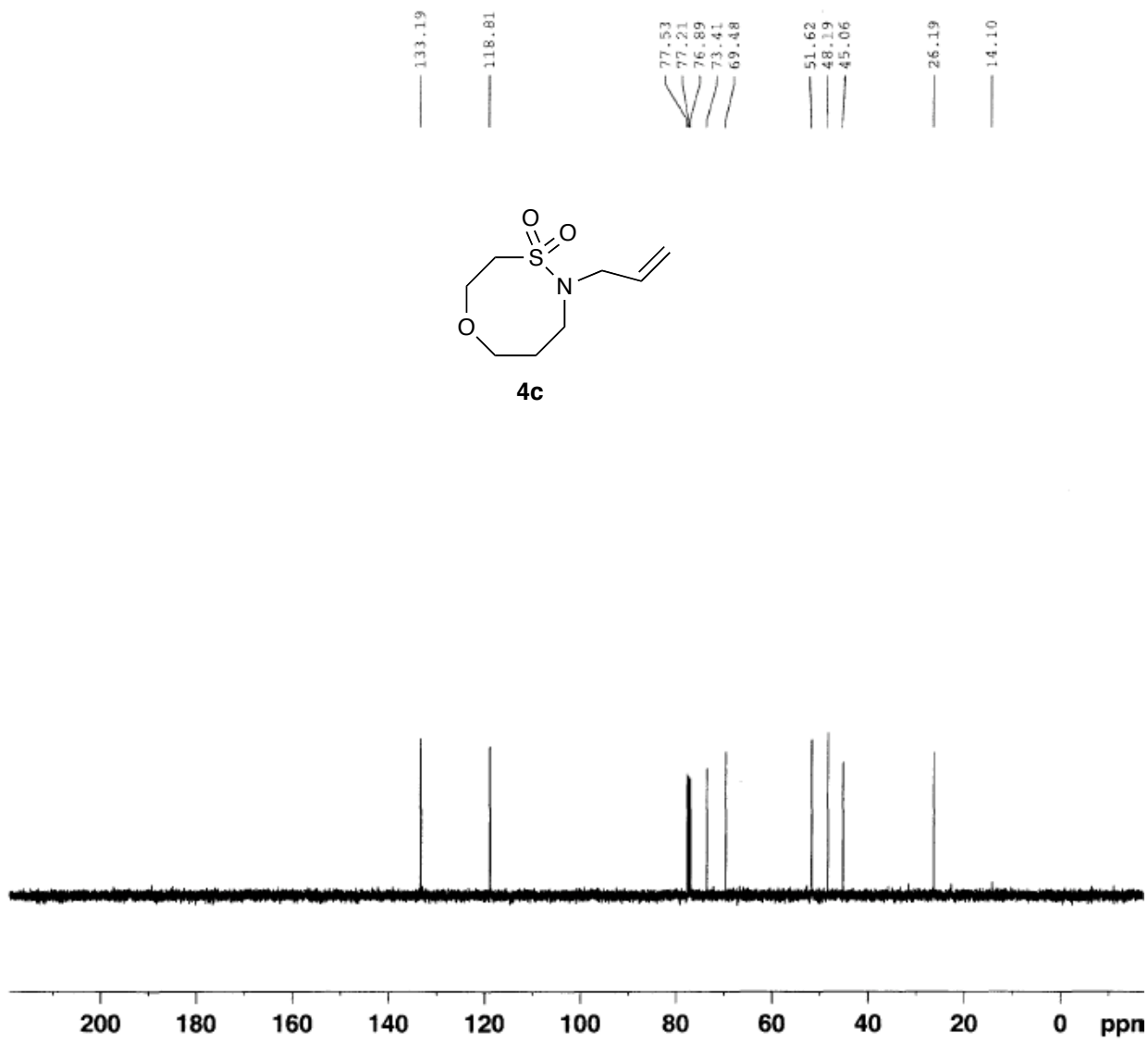
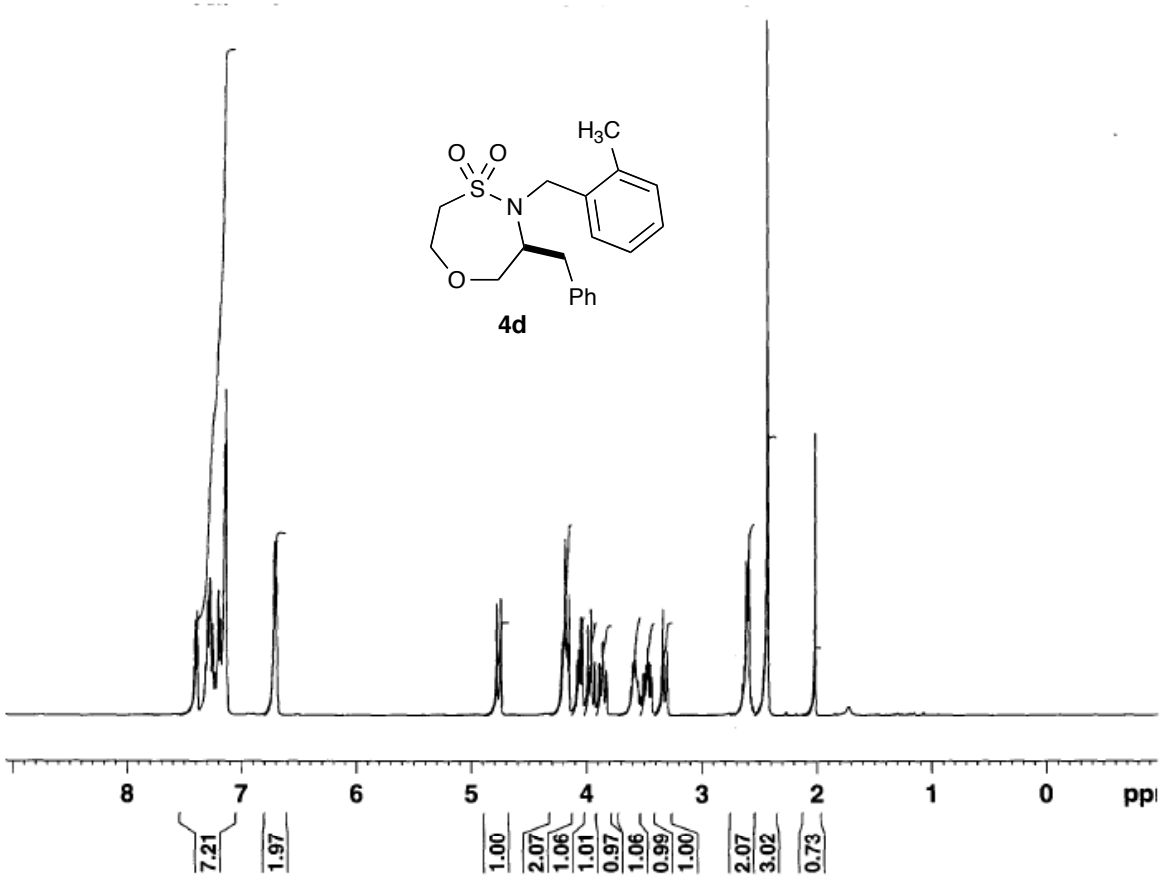
135.96
132.70
131.14
129.28
128.75
128.55
127.84
126.59
123.11
77.38
77.06
76.74
75.21
66.11
59.47
54.65
52.75
38.77
Br
O
O
S
N
O
Ph
4b
200
180
160
140
120
100
80
60
40
20
0
ppm

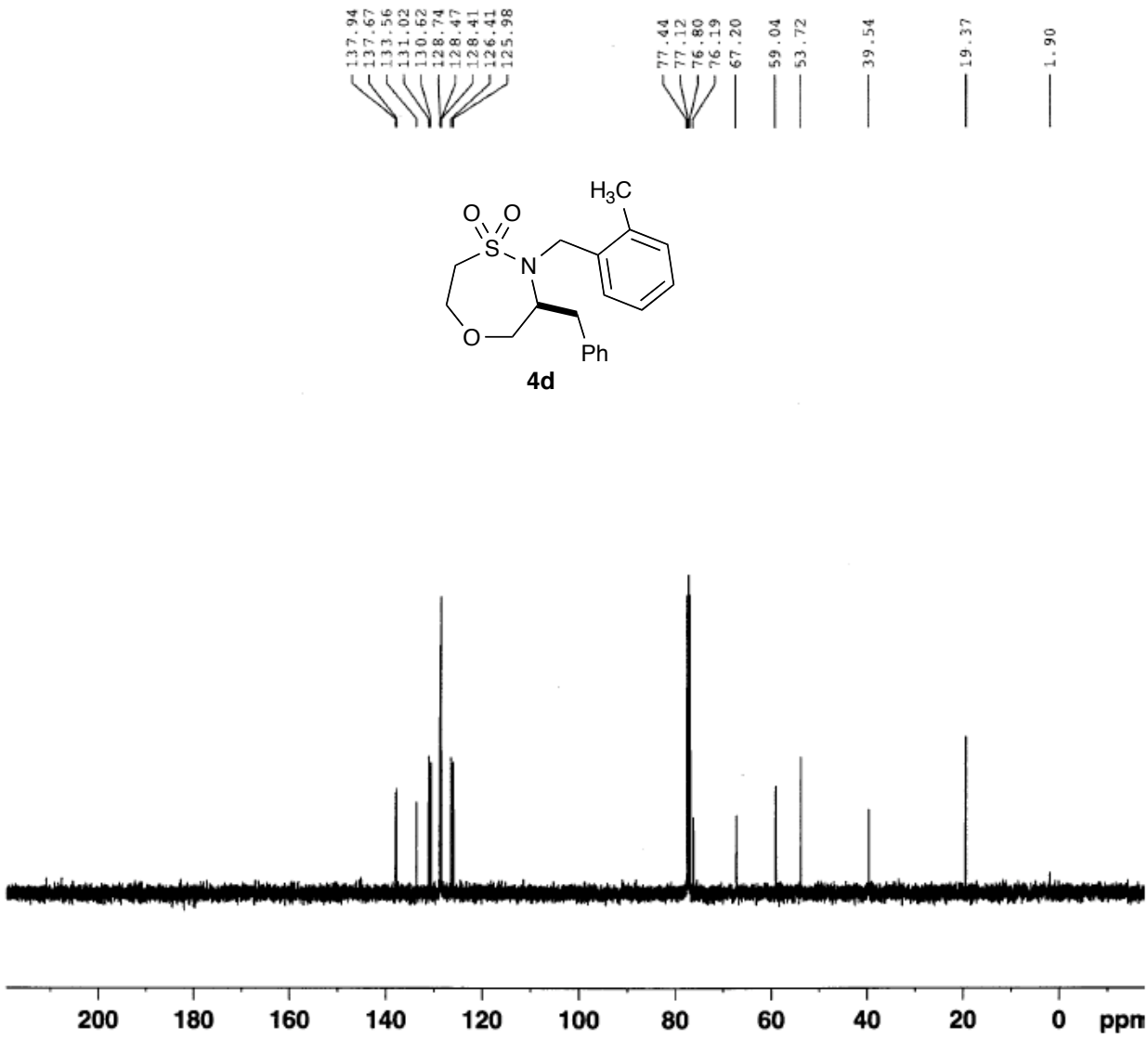


4c


133.19
118.81
77.53
77.21
76.89
73.41
69.48
51.62
48.19
45.06
26.19
14.10
O
O
S
N
O
200
180
160
140
120
100
80
60
40
20
0
ppm

4c


H3C
O
O
S
N
O
Ph
4d
8
7
6
5
4
3
2
1
0
7.21
1.97
1.00
2.07
1.06
1.01
0.97
1.06
0.99
1.00
2.07
3.02
0.73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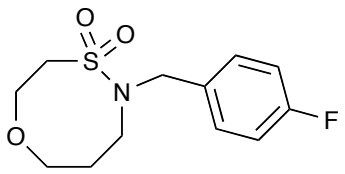
137.67
133.56
131.02
130.62
128.74
128.47
128.41
126.41
125.98
77.44
77.12
76.80
76.19
67.20
59.04
53.72
39.54
19.37
1.90
H3C
O
O
S
N
O
Ph
200
180
160
140
120
100
80
60
40
20
0
ppm

4d



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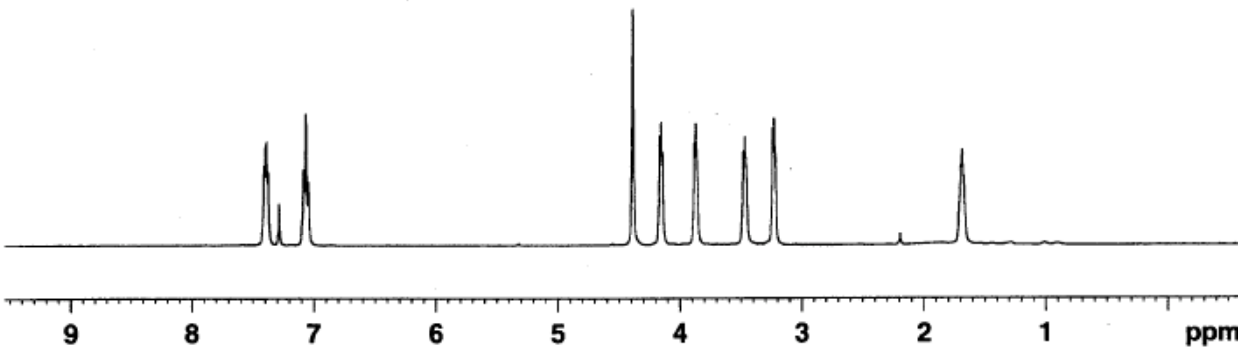

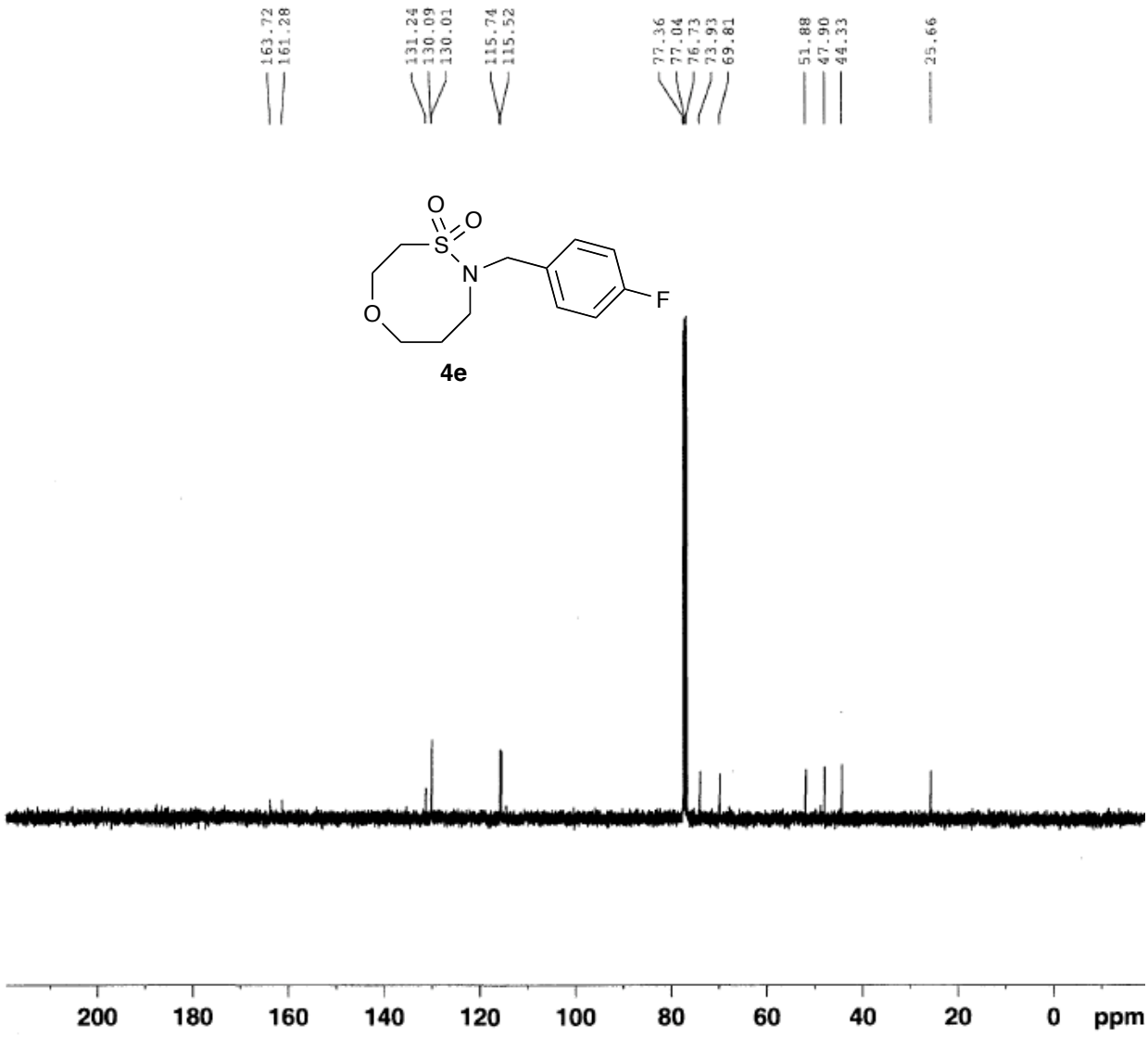
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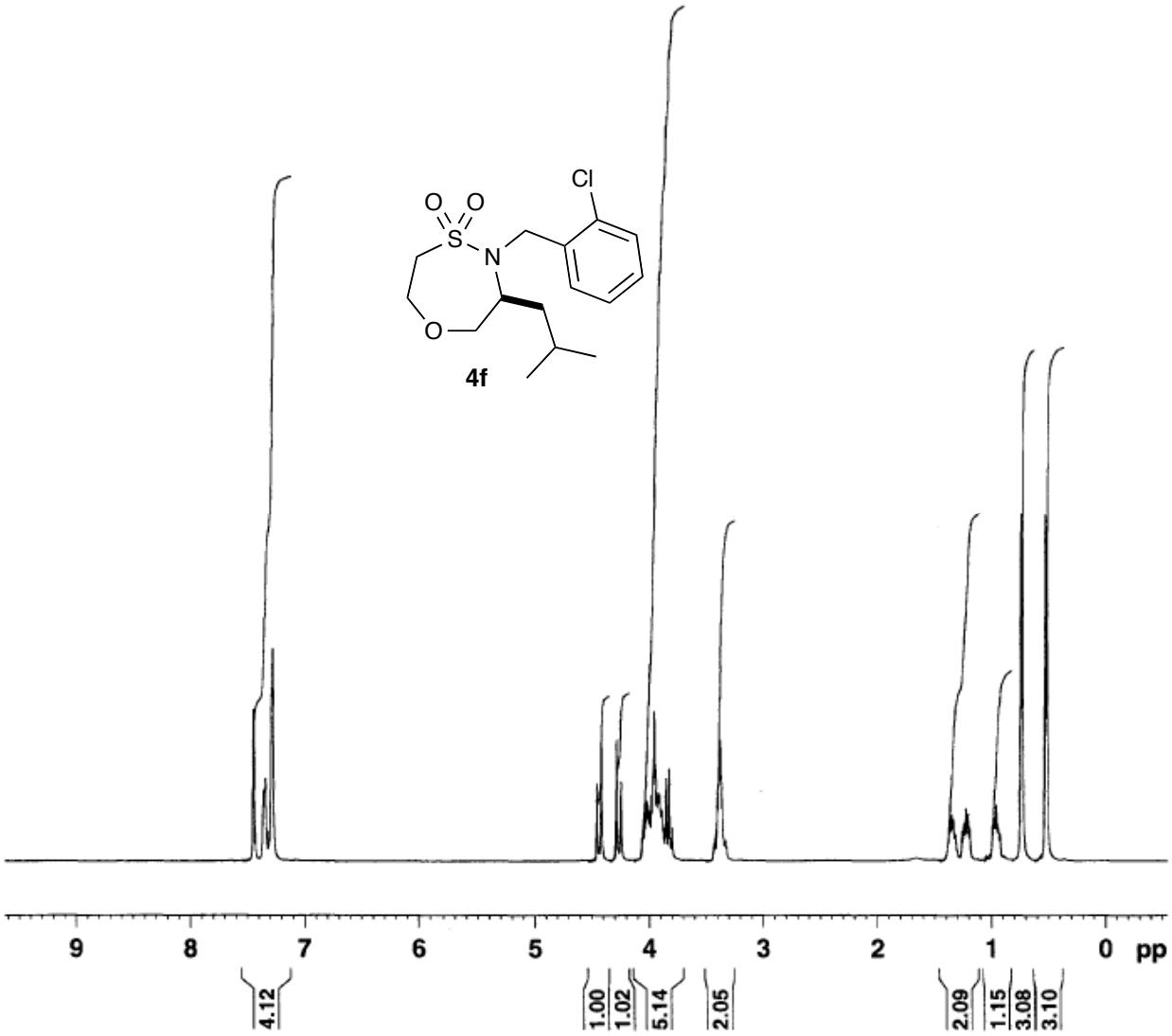
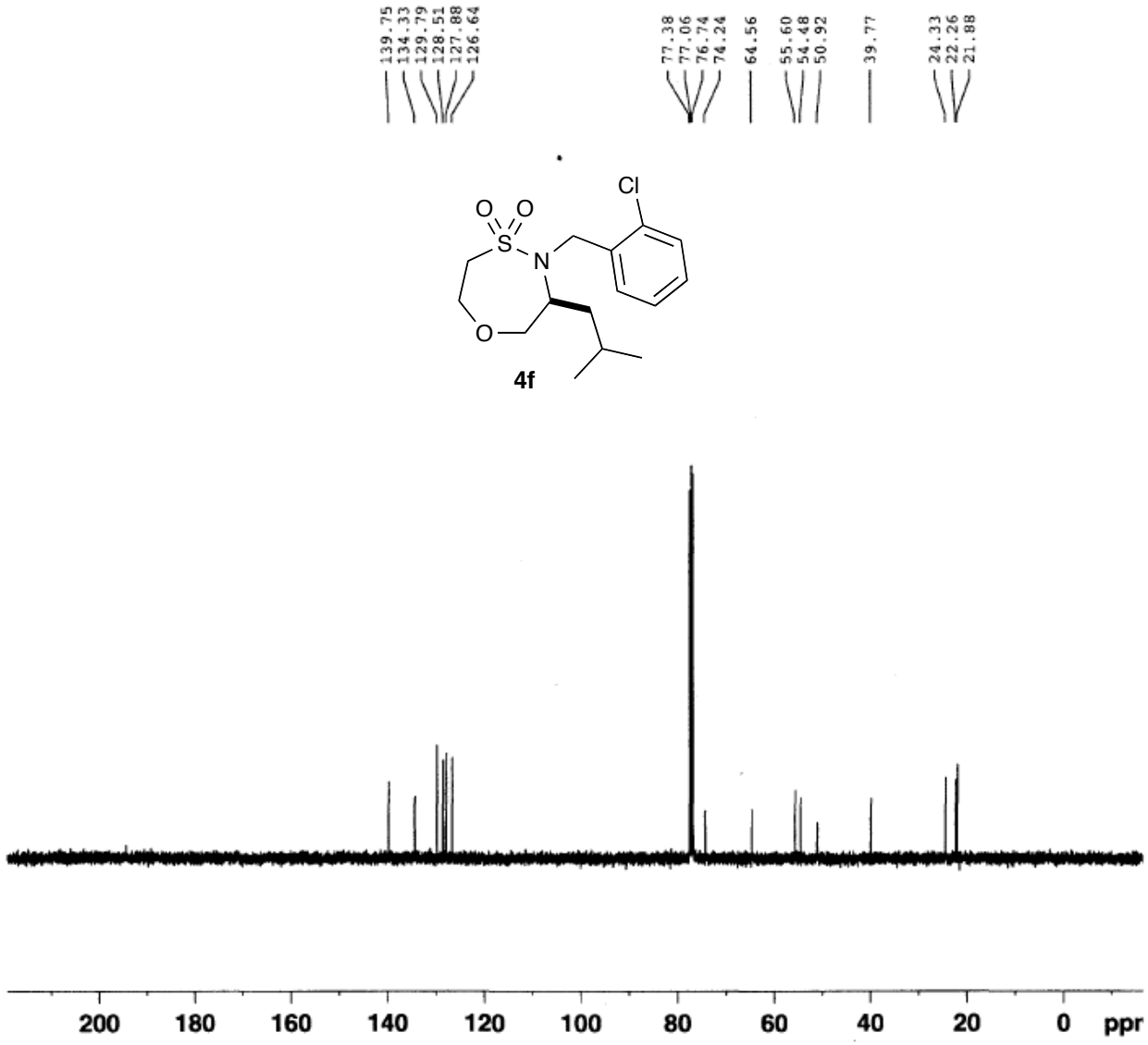
131.24
130.09
130.01
115.74
115.52
77.36
77.04
76.73
73.93
69.81
51.88
47.90
44.33
25.66
O
O
S
N
O
F
4e
200
180
160
140
120
100
80
60
40
20
0
ppm


Cl
O
O
S
N
O
4f
9
8
7
6
5
4
3
2
1
0
pp
4.12
1.00
1.02
5.14
2.05
2.09
1.15
3.08
3.10


139.75
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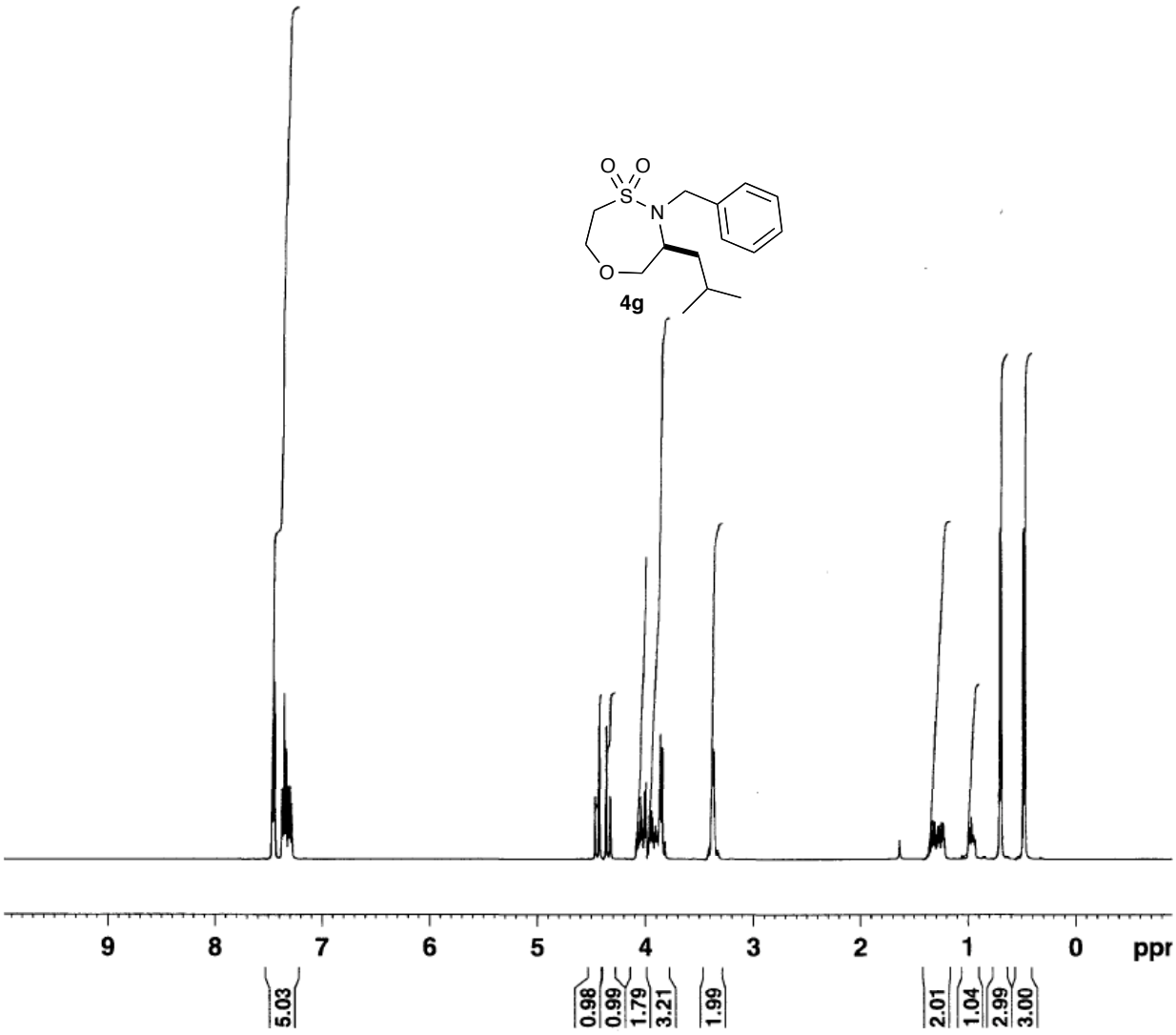
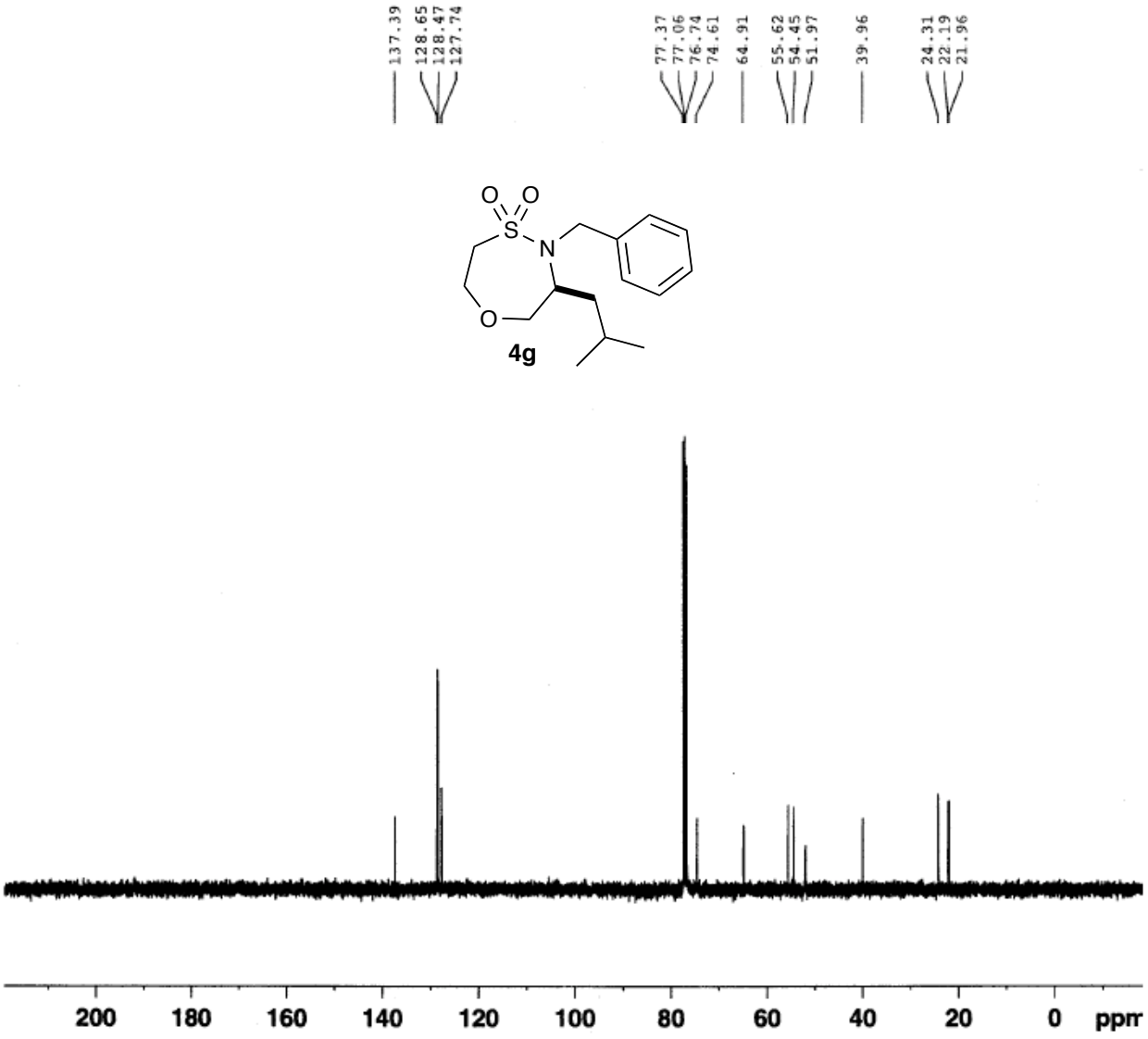
129.79
128.51
127.88
126.64
77.38
77.06
76.74
74.24
64.56
55.60
54.48
50.92
39.77
24.33
22.26
21.88
Cl
O
O
S
N
O
200
180
160
140
120
100
80
60
40
20
0
ppm

4f


O
O
S
N
O
4g
9
8
7
6
5
4
3
2
1
0
ppm
5.03
0.98
0.99
1.79
3.21
1.99
2.01
1.04
2.99
3.00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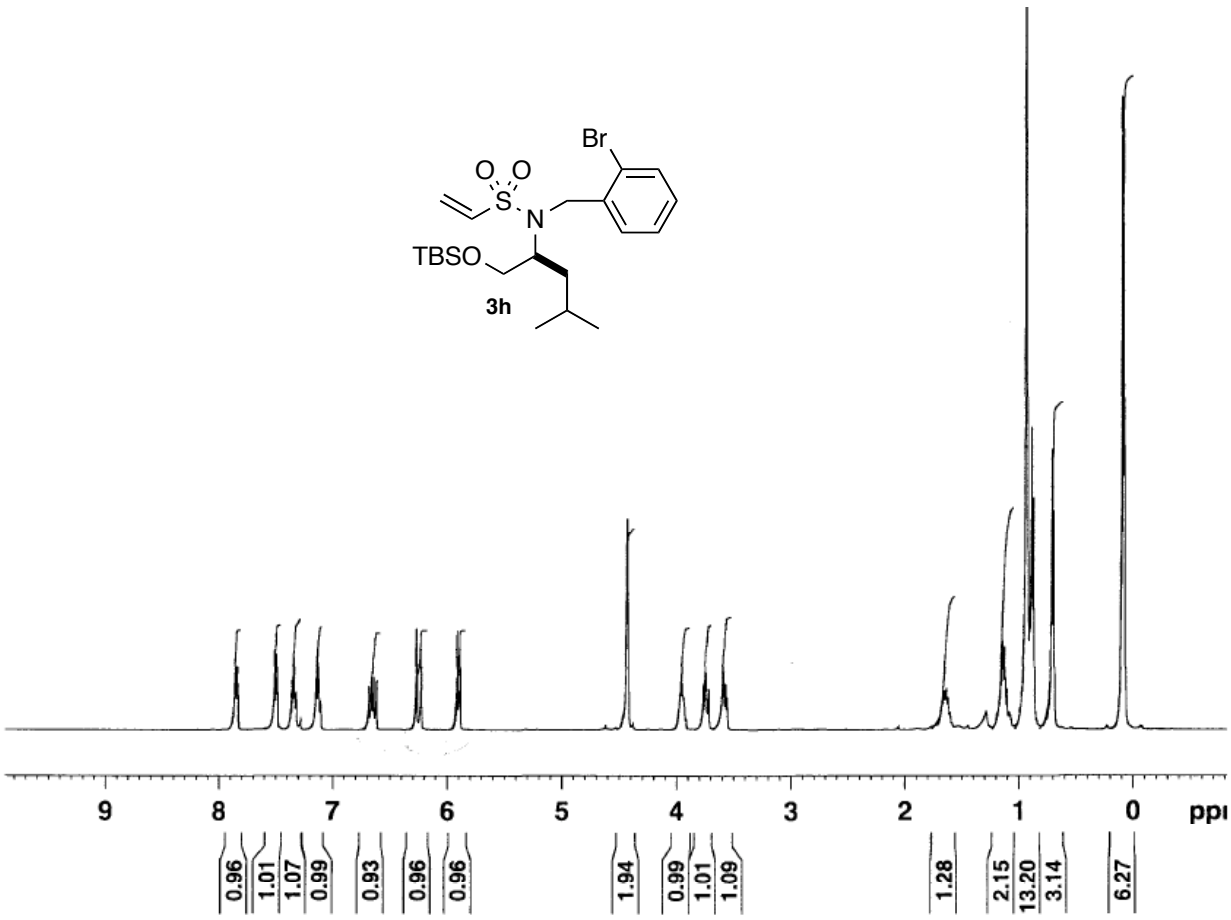
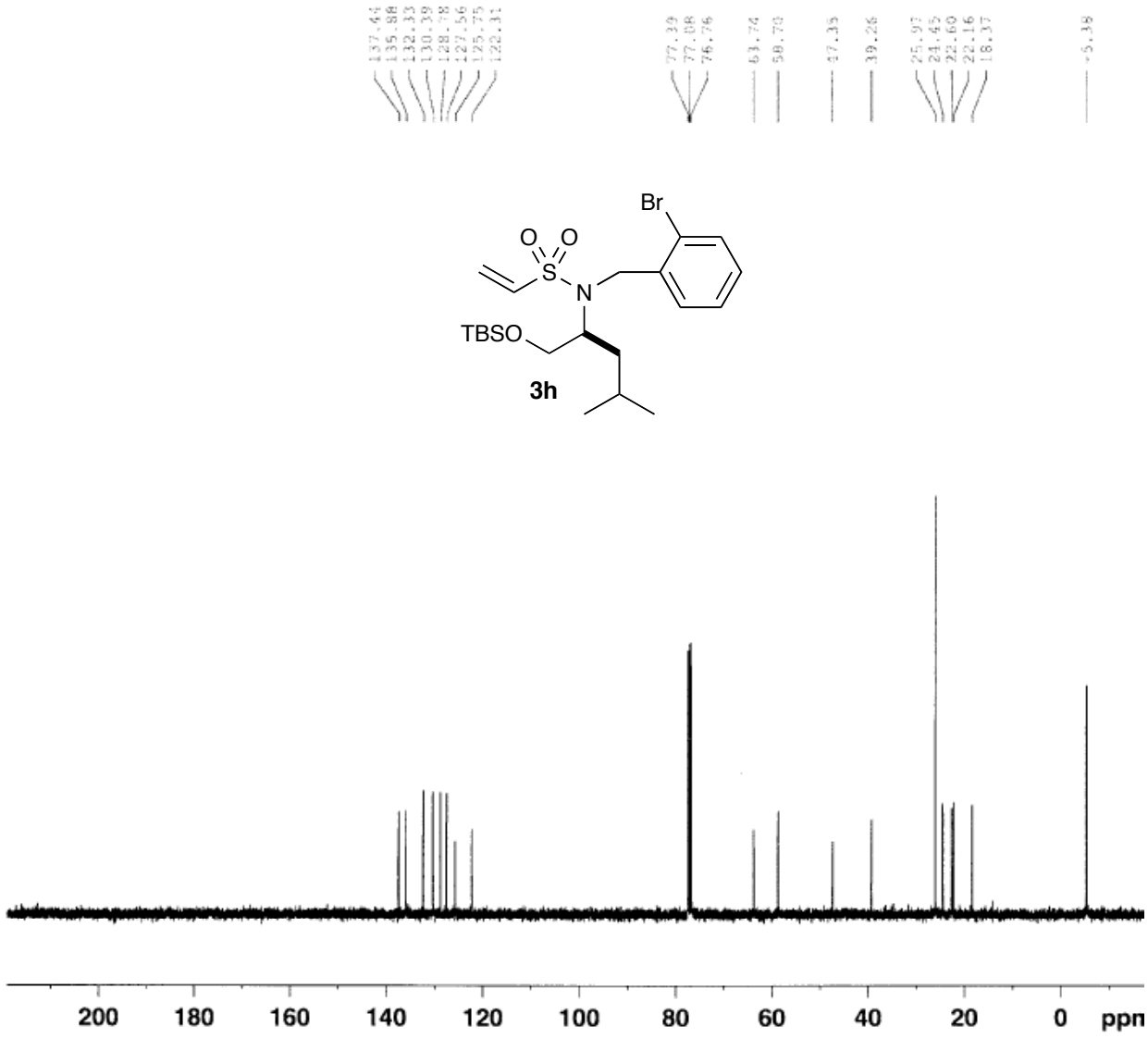
128.47
127.74
77.37
77.06
76.74
74.61
64.91
55.62
54.45
51.97
39.96
24.31
22.19
21.96
O
O
S
N
O
4g
200
180
160
140
120
100
80
60
40
20
0
ppm


Br
O
O
S
N
TBSO
3h
9
8
7
6
5
4
3
2
1
0
ppı
0.96
1.01
1.07
0.99
0.93
0.96
0.96
1.94
0.99
1.01
1.09
1.28
2.15
13.20
3.14
6.27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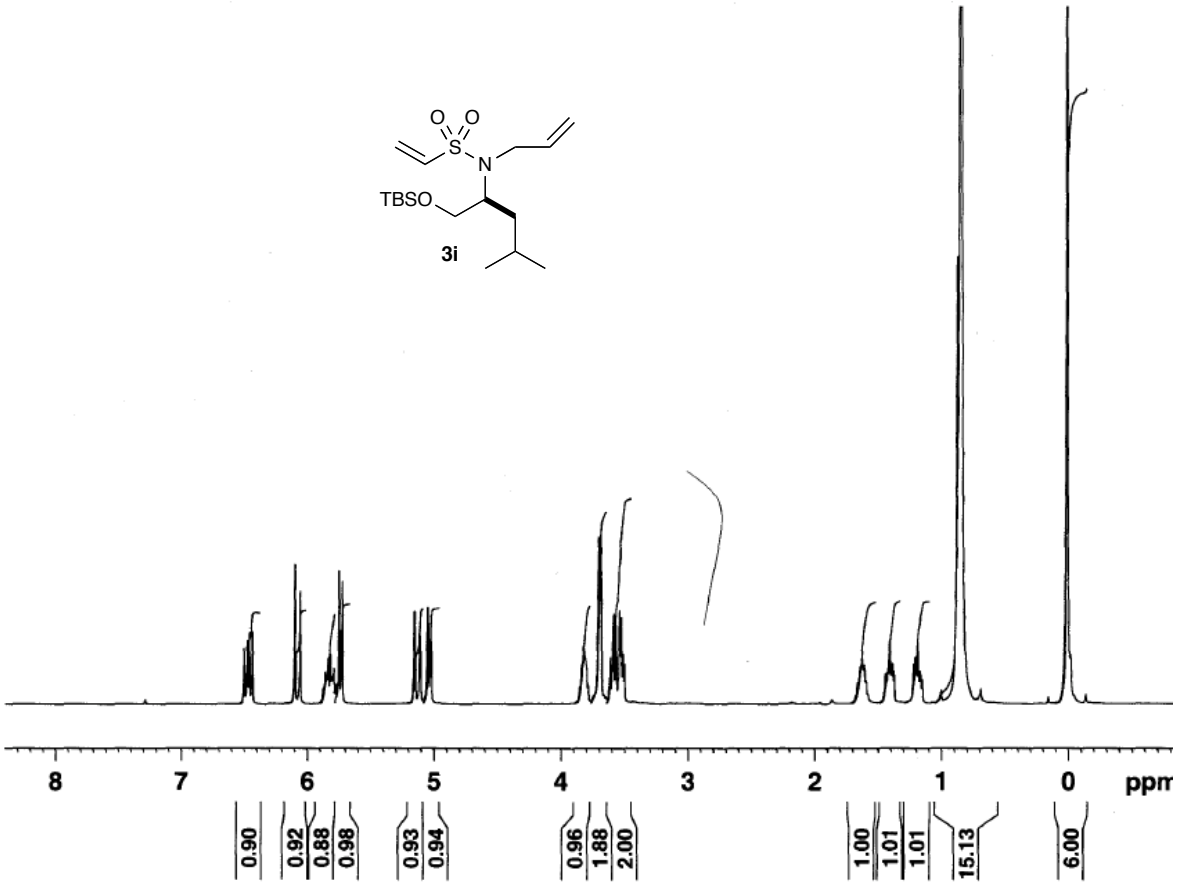
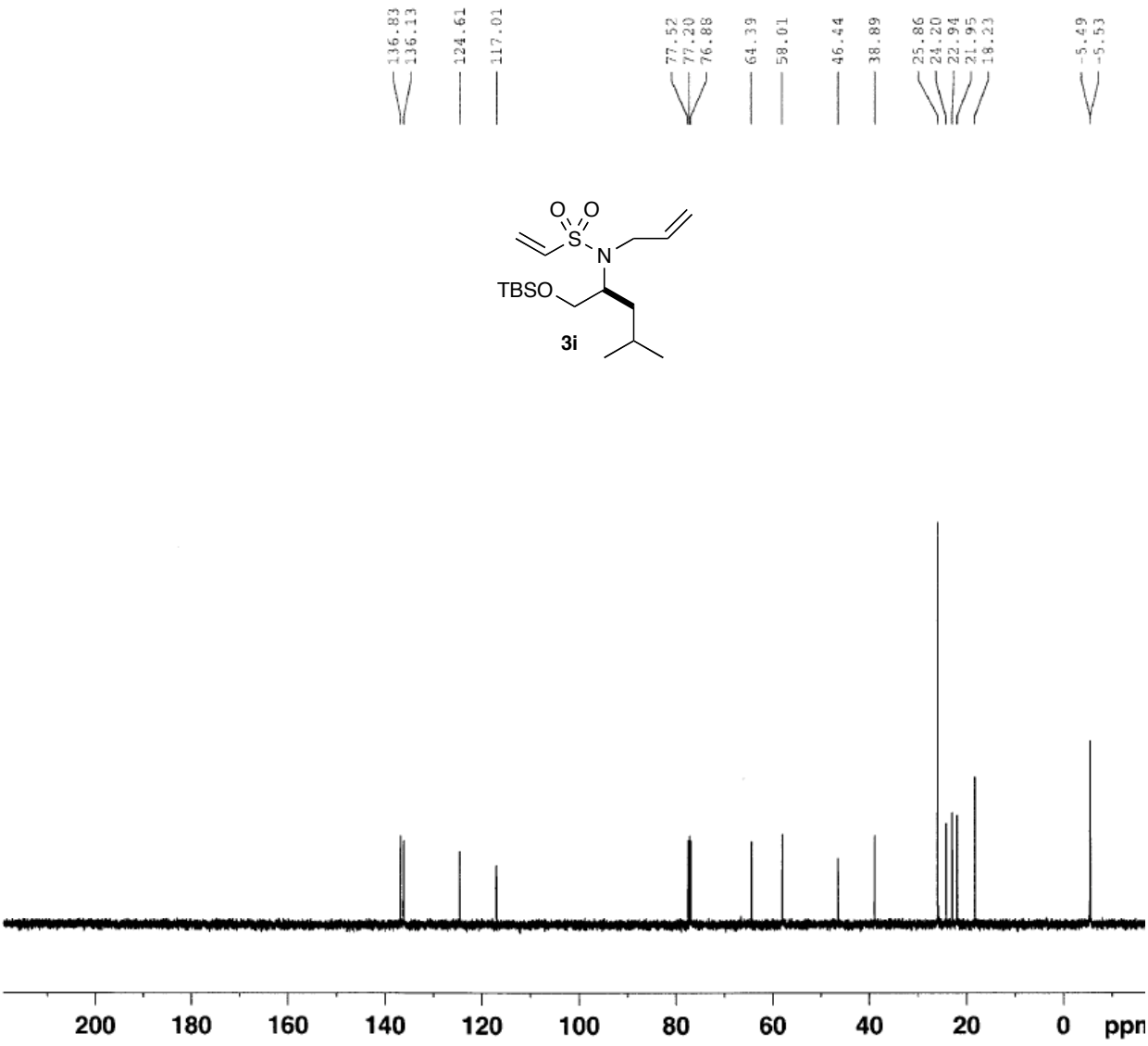
125.75
122.31
77.39
77.08
76.76
63.74
58.70
17.35
39.26
25.97
24.45
22.60
22.16
18.37
-5.38
Br
O
O
S
N
TBSO
3h
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TBSO
3i
8
7
6
5
4
3
2
1
0
ppm
0.90
0.92
0.88
0.98
0.93
0.94
0.96
1.88
2.00
1.00
1.01
1.01
15.13
6.00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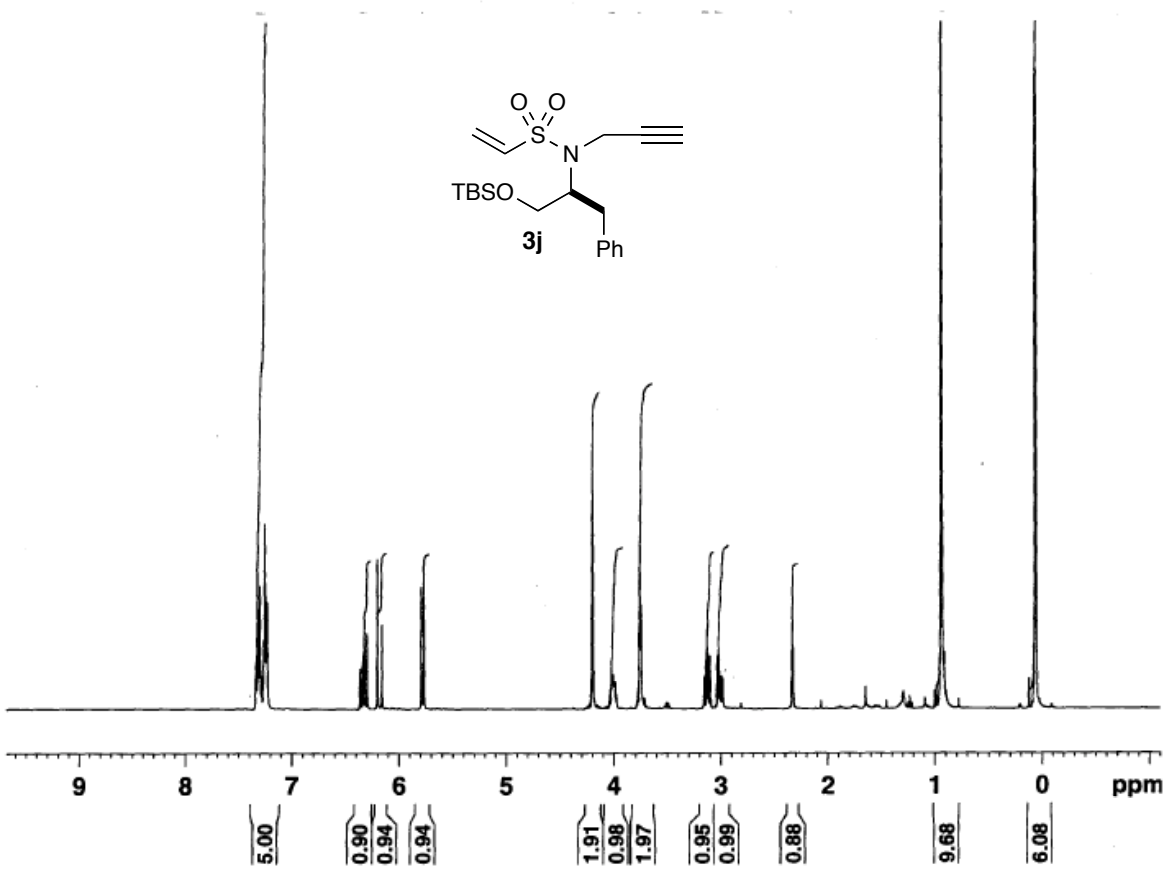
77.20
76.88
64.39
58.01
46.44
38.89
25.86
24.20
22.94
21.95
18.23
-5.49
-5.53
O
O
S
N
TBSO
3i
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TBSO
3j
Ph
9
8
7
6
5
4
3
2
1
0
ppm
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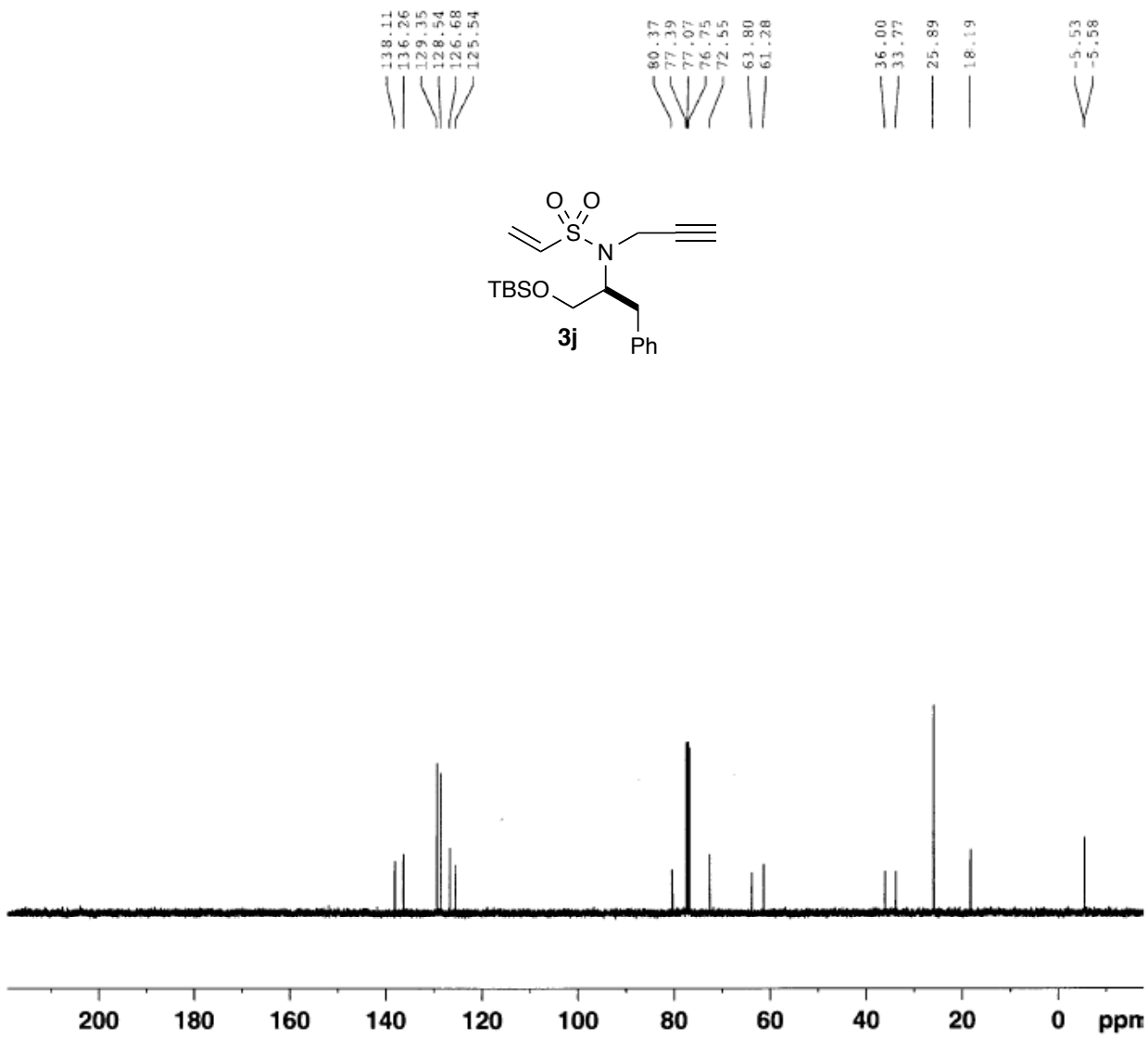
0.94
0.94
1.91
0.98
1.97
0.95
0.99
0.88
9.68
6.08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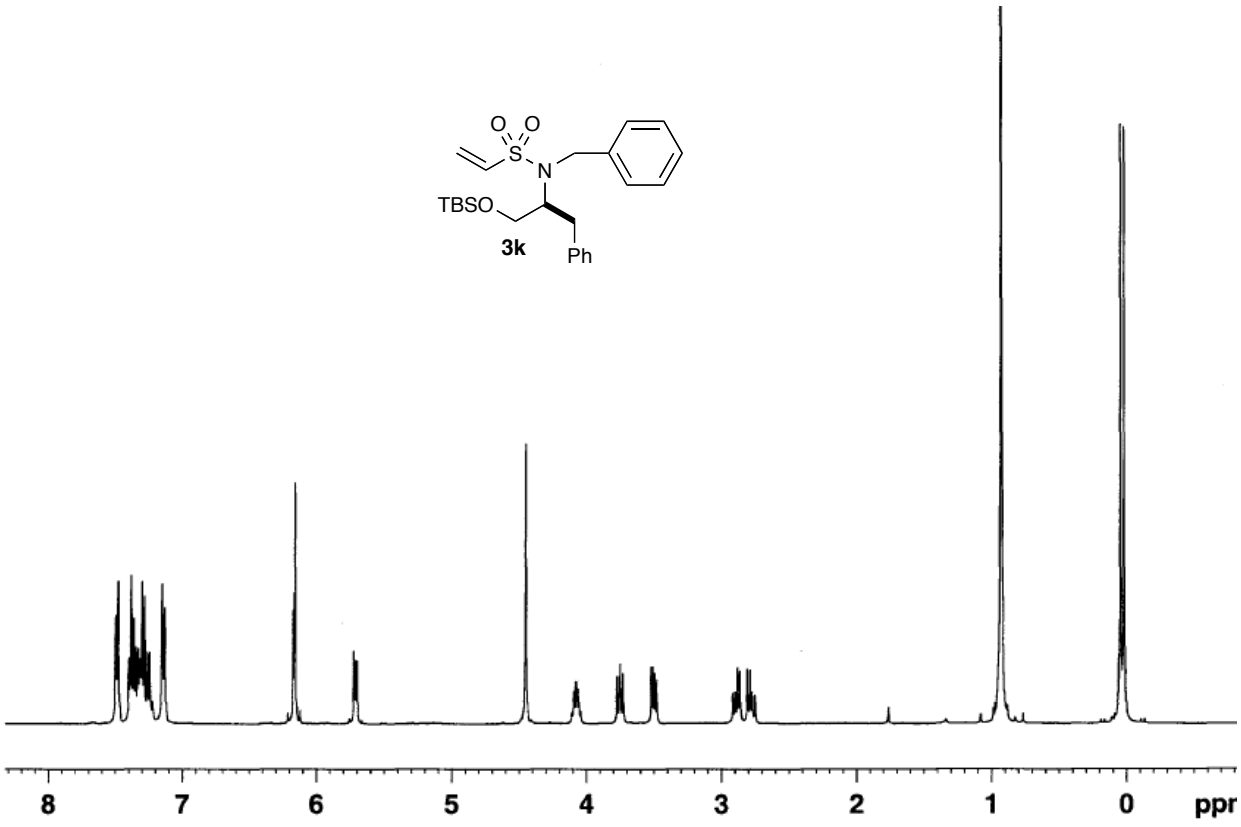
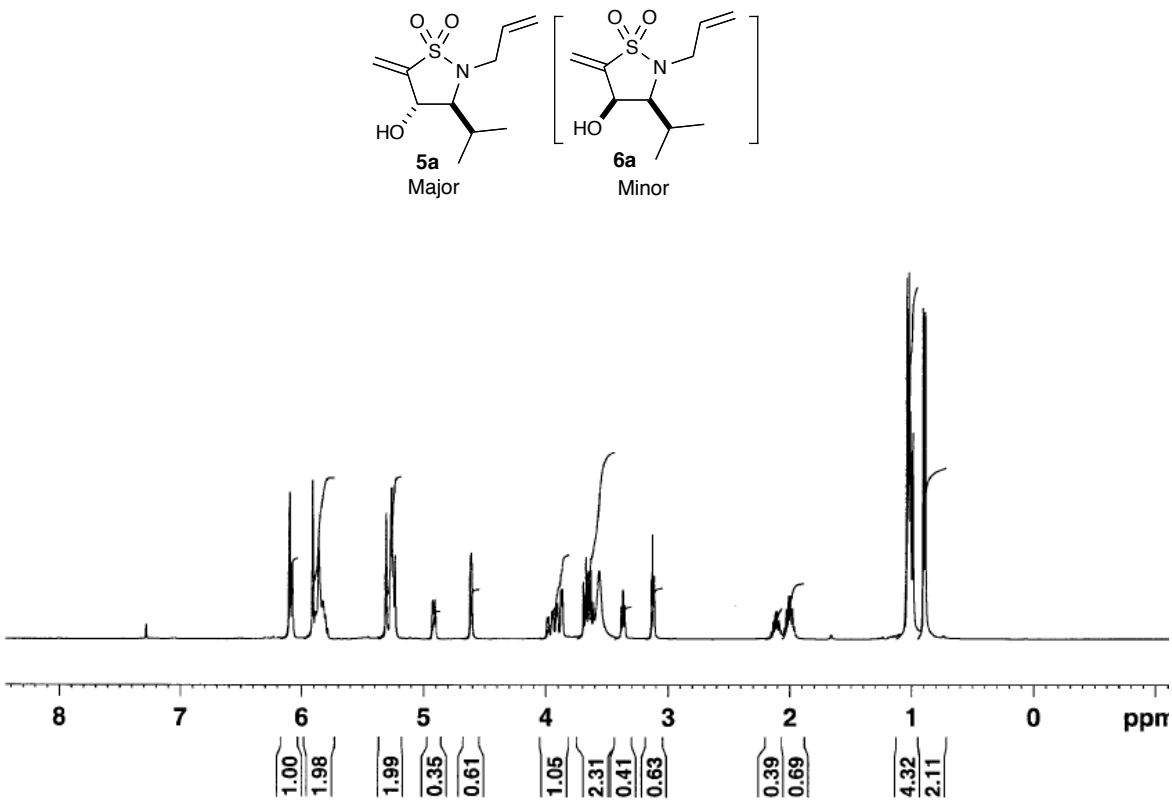
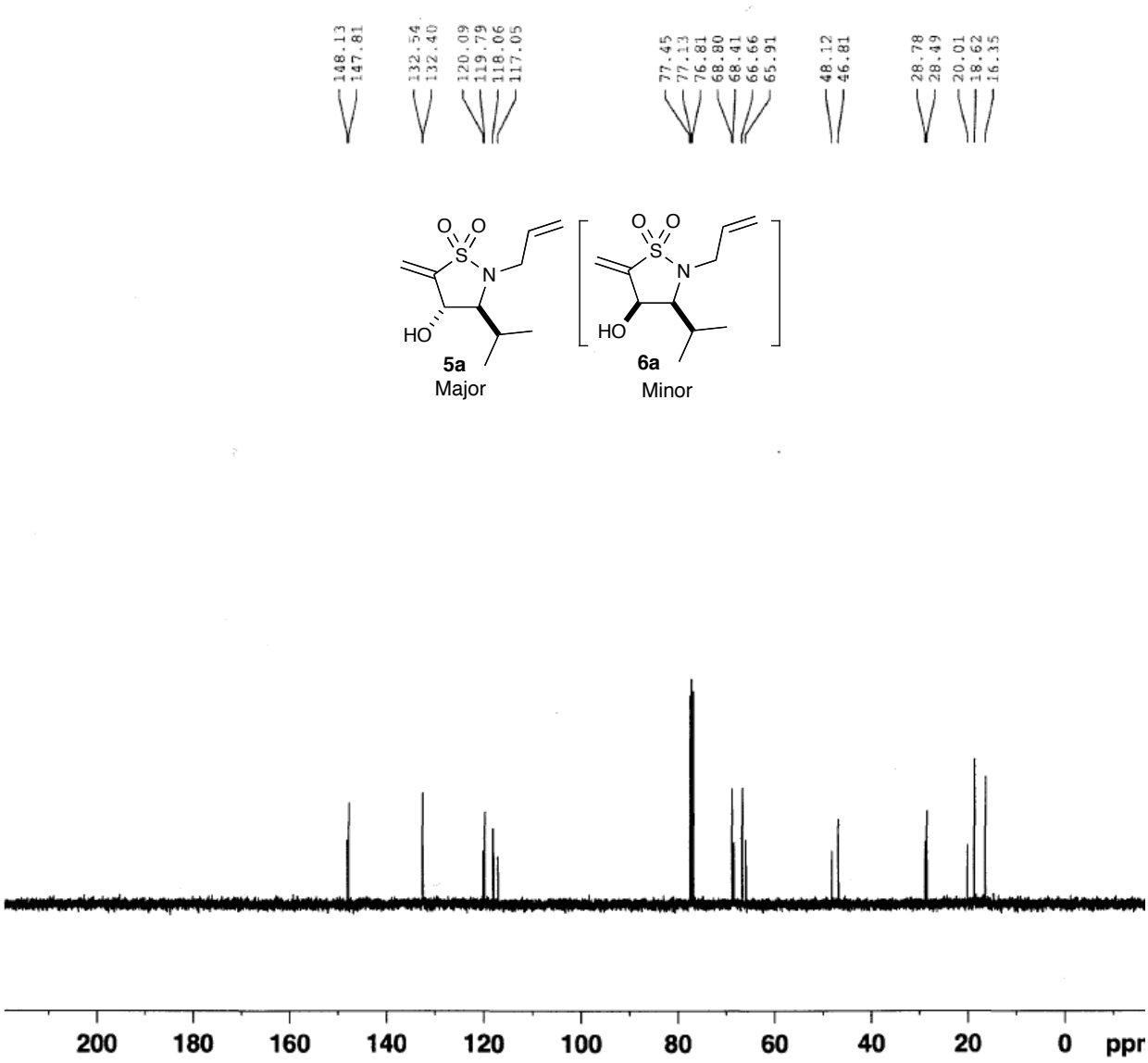
77.39
77.07
76.75
72.55
63.80
61.28
36.00
33.77
25.89
18.19
-5.53
-5.58
O
O
S
N
TBSO
Ph
3j
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TBSO
3k
Ph
8
7
6
5
4
3
2
1
0
ppr


5a
Major
6a
Minor
8
7
6
5
4
3
2
1
0
ppm
1.00
1.98
1.99
0.35
0.61
1.05
2.31
0.41
0.63
0.39
0.69
4.32
2.11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120.09
119.79
118.06
117.05
77.45
77.13
76.81
68.80
68.41
66.66
65.91
48.12
46.81
28.78
28.49
20.01
18.62
16.35
HO
5a
Major
HO
6a
Minor
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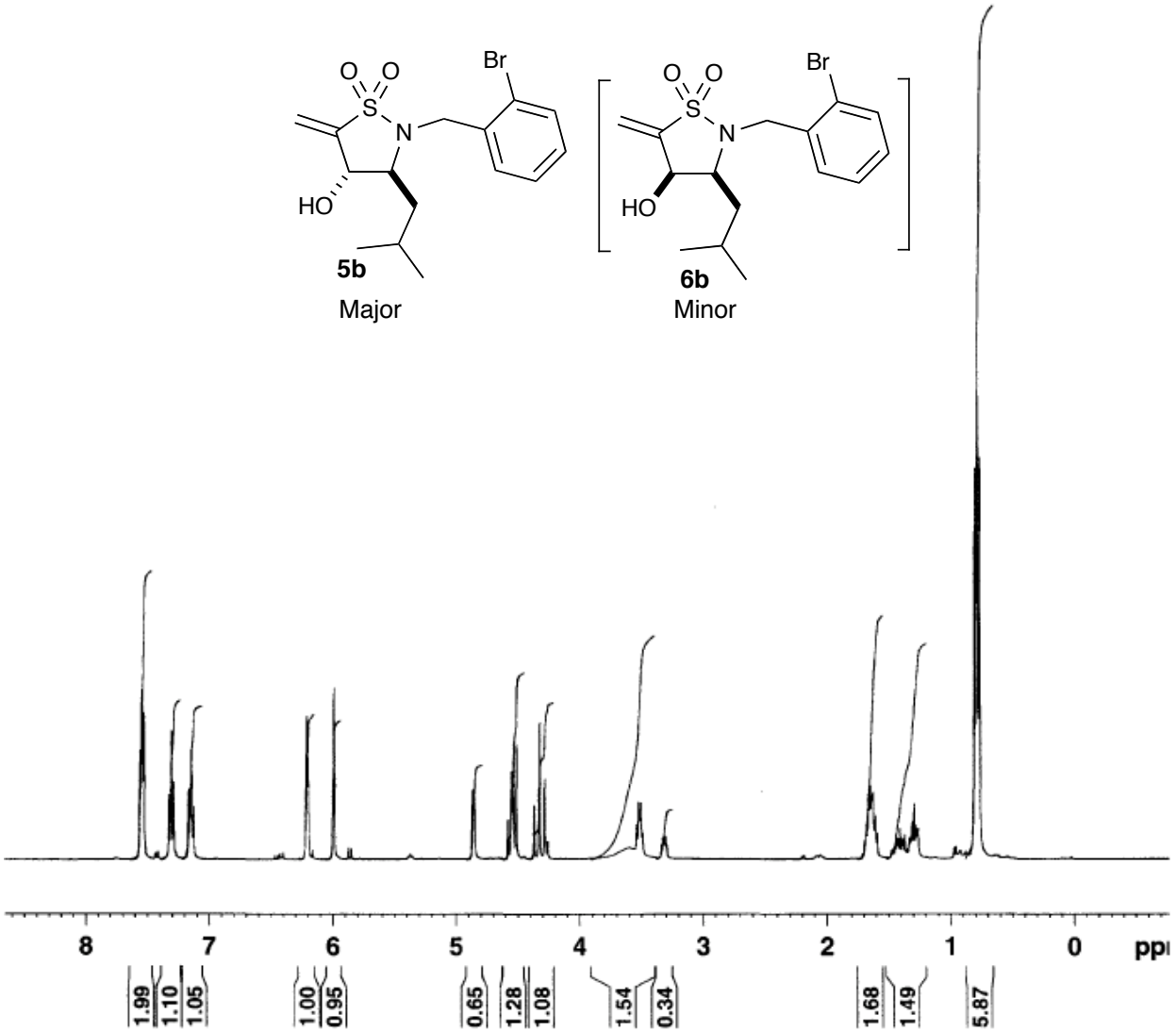
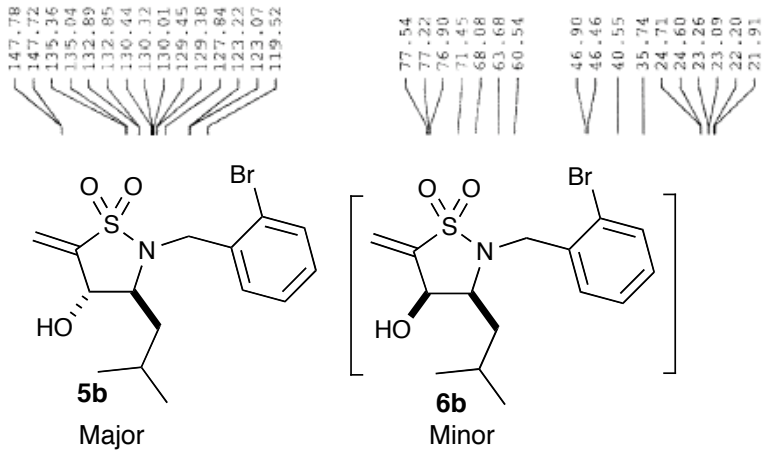
180
160
140
120
100
80
60
40
20
0
ppm


Br
O
O
S
N
HO
5b
Major
Br
O
O
S
N
HO
6b
Minor
8
7
6
5
4
3
2
1
0
ppm
1.99
1.10
1.05
1.00
0.95
0.65
1.28
1.08
1.54
0.34
1.68
1.49
5.87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147.72
135.36
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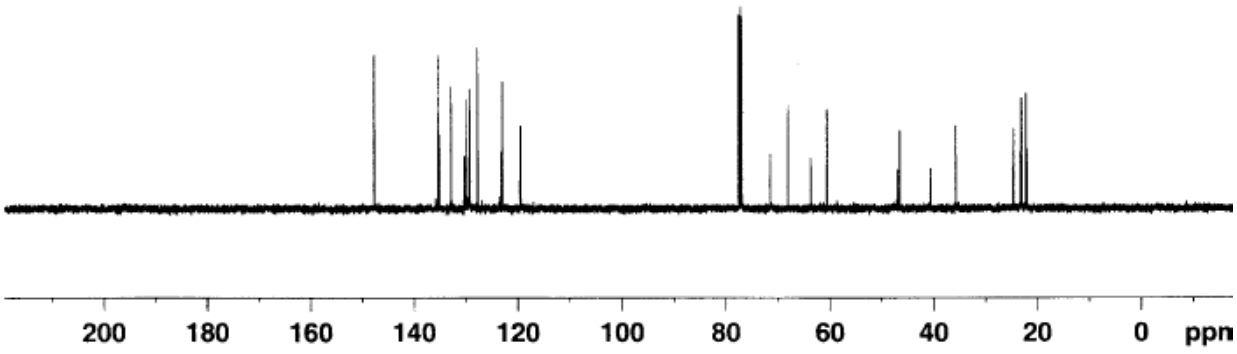
132.85
130.44
130.32
130.01
129.45
129.38
127.84
123.22
123.07
119.52
77.54
77.22
76.90
71.45
68.08
63.68
60.54
46.90
46.46
40.55
35.74
24.71
24.60
23.26
23.09
22.20
21.91
Br
O
O
S
N
HO
5b
Major
Br
O
O
S
N
HO
6b
Minor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140
120
100
80
60
40
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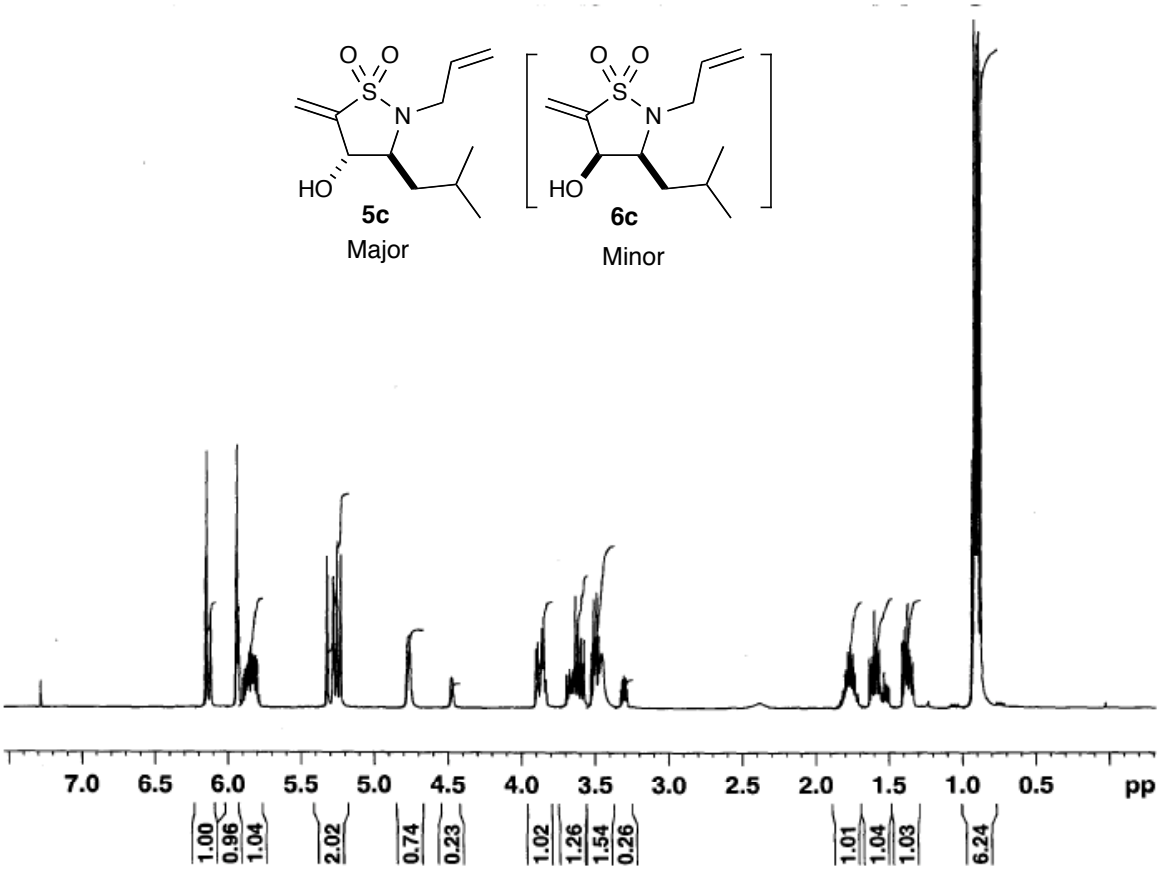
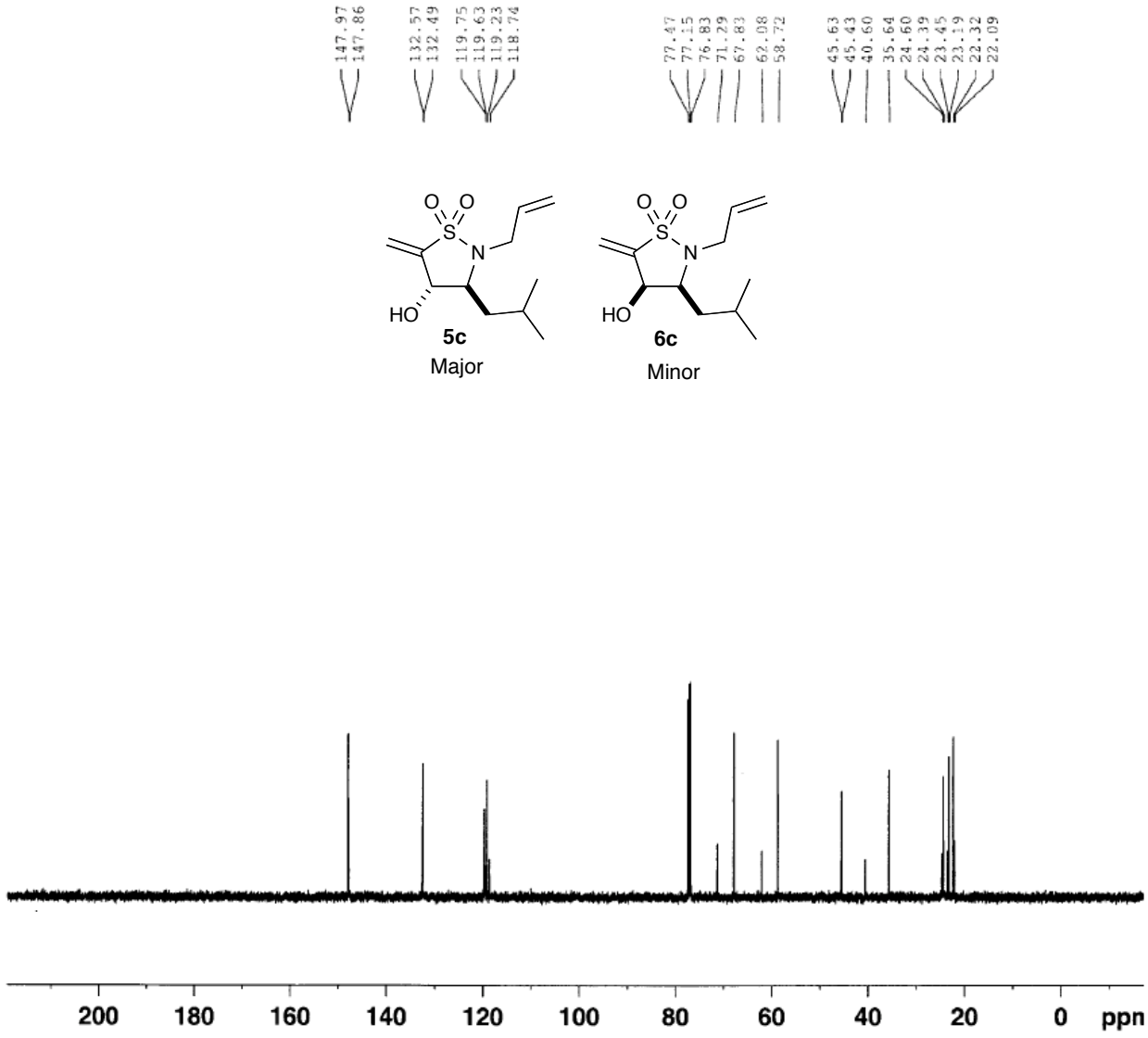
ppm


5c
Major
6c
Minor
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
pp
1.00
0.96
1.04
2.02
0.74
0.23
1.02
1.26
1.54
0.26
1.01
1.04
1.03
6.24


147.97
147.86
132.57
132.49
119.75
119.63
119.23
118.74
77.47
77.15
76.83
71.29
67.83
62.08
58.72
45.63
45.43
40.60
35.64
24.60
24.39
23.45
23.19
22.32
22.09
O
O
S
N
HO
5c
Major
6c
Minor
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180
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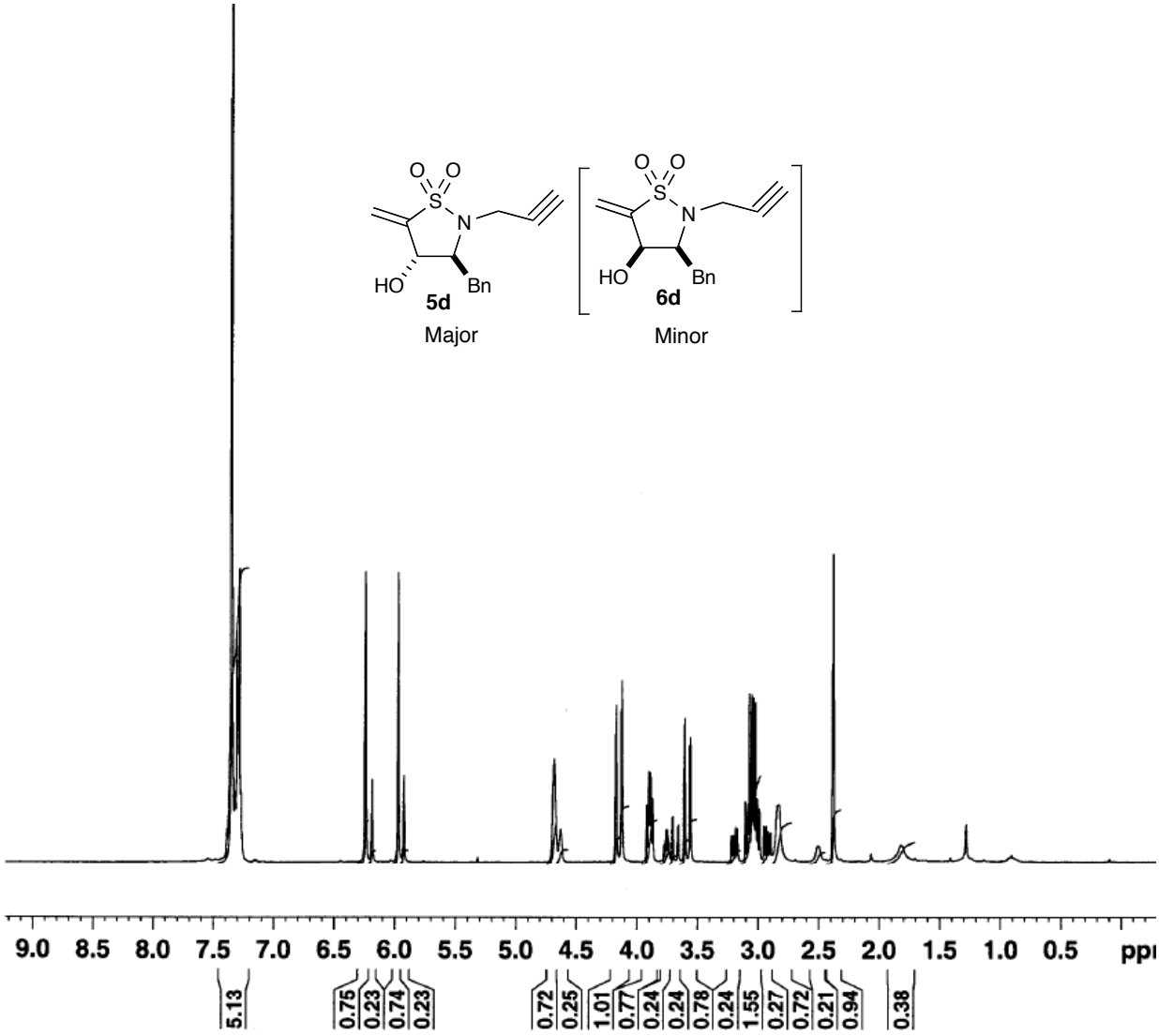
140
120
100
80
60
40
20
0
ppm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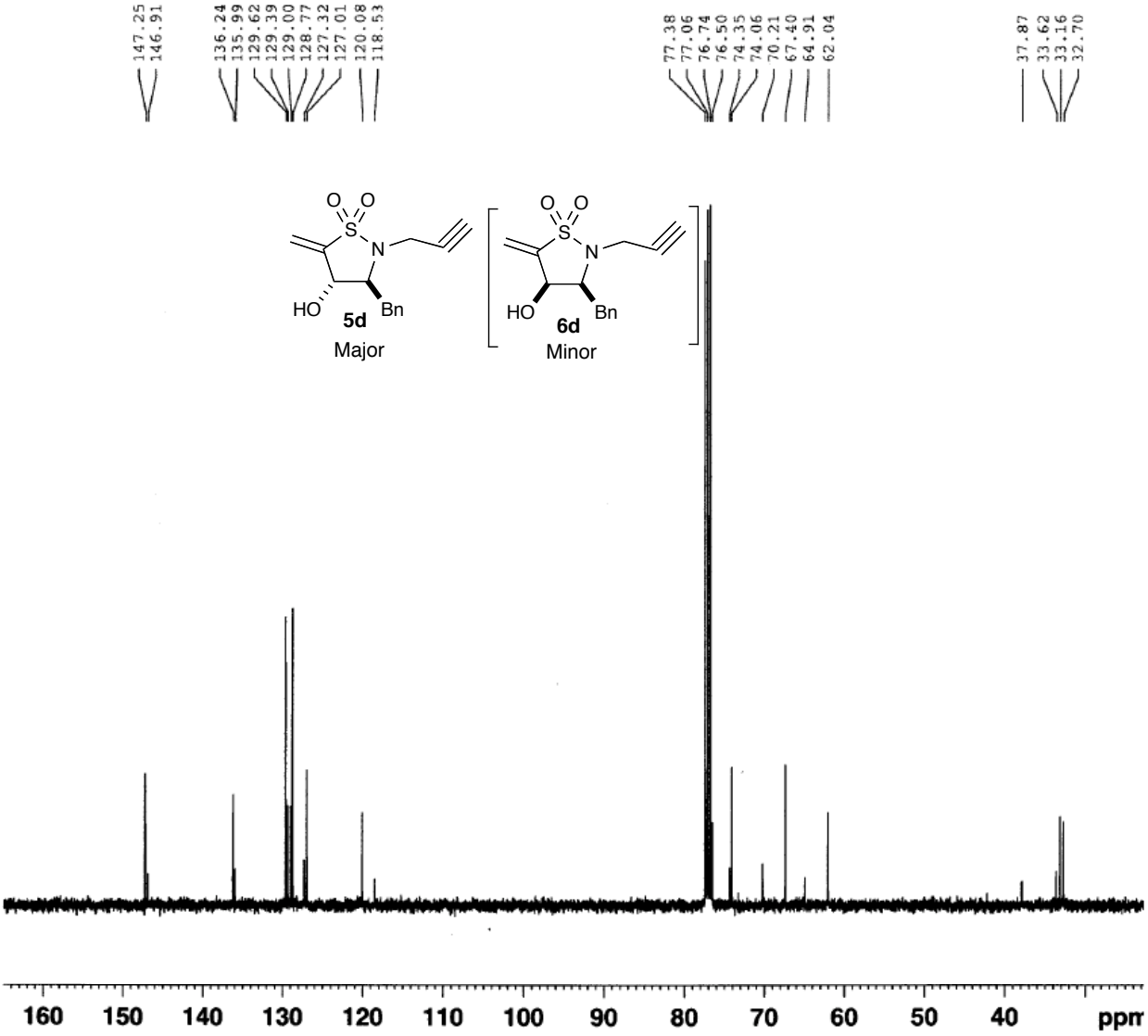
Major
6d
Minor
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
5.13
0.76
0.23
0.74
0.23
0.72
0.25
1.01
0.77
0.24
0.24
0.78
0.24
1.55
0.27
0.72
0.21
0.94
0.38


147.25
146.91
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129.39
129.00
128.77
127.32
127.01
120.08
118.53
77.38
77.06
76.74
76.50
74.35
74.06
70.21
67.40
64.91
62.04
37.87
33.62
33.16
32.70
HO
Bn
5d
Major
HO
Bn
6d
Minor
160
150
140
130
120
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100
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60
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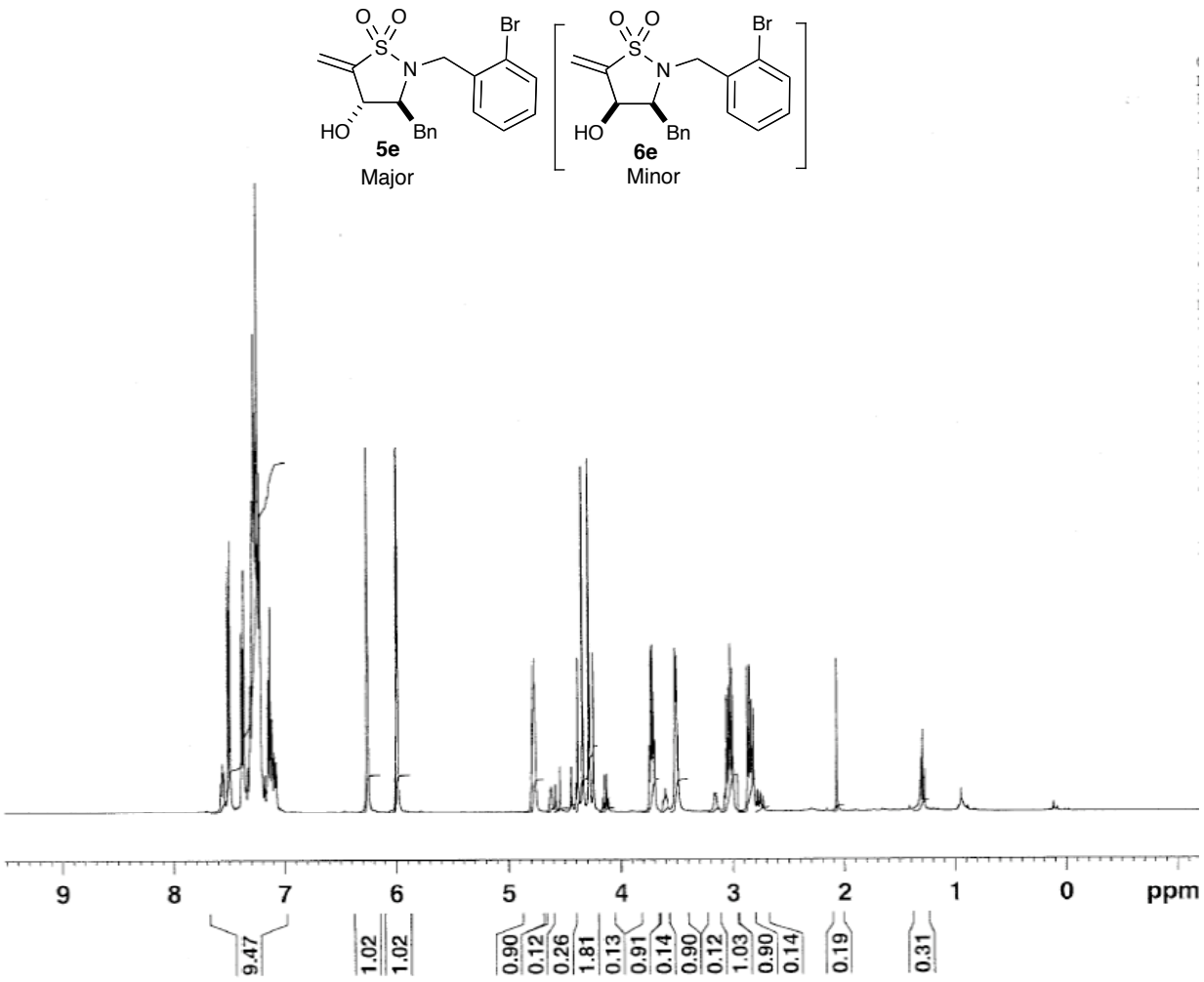
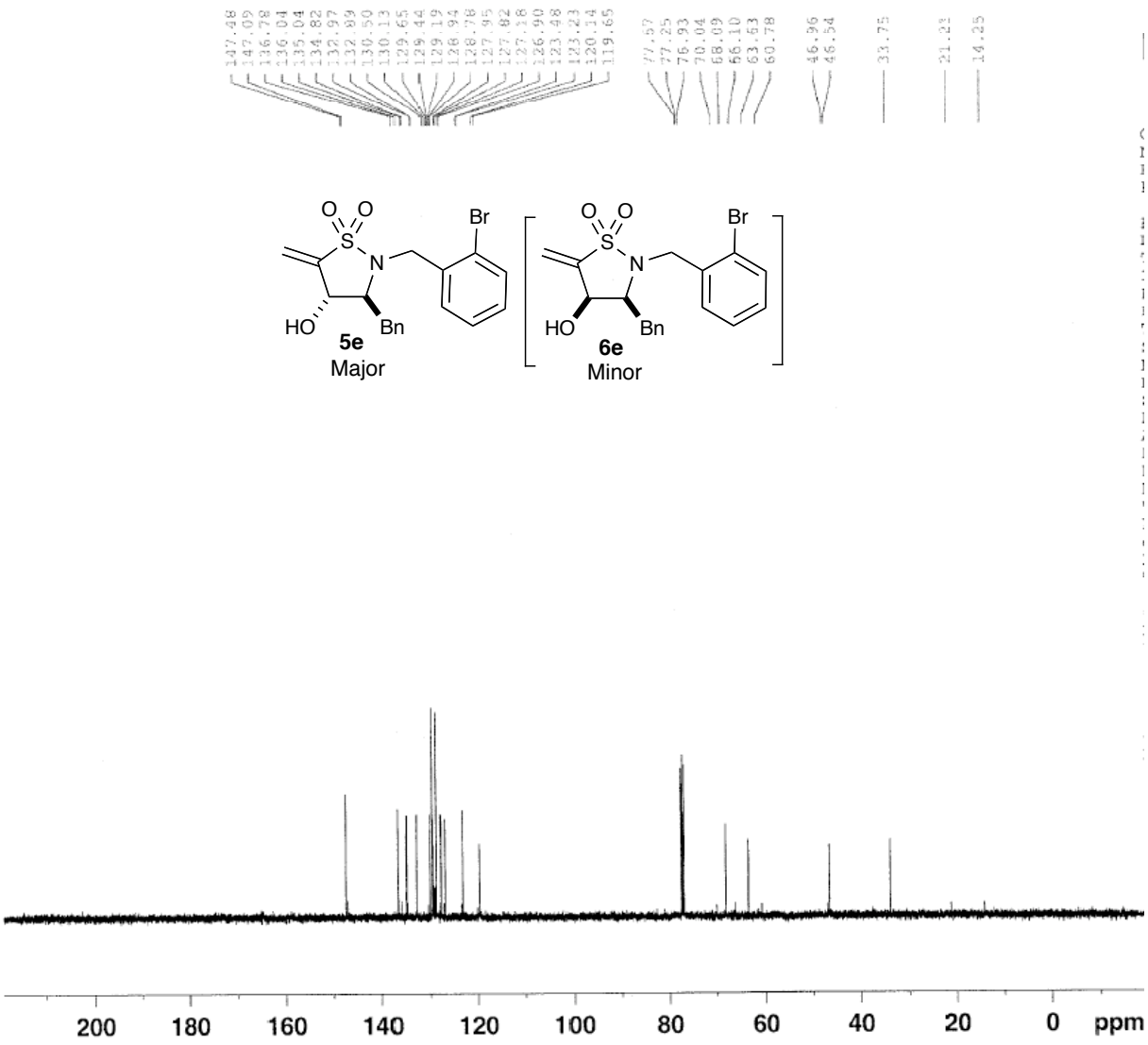
40
ppm


O
O
S
N
Br
HO
Bn
5e
Major
6e
Minor
9
8
7
6
5
4
3
2
1
0
ppm
9.47
1.02
1.02
0.90
0.12
0.26
1.81
0.13
0.91
0.14
0.90
0.12
1.03
0.90
0.14
0.19
0.31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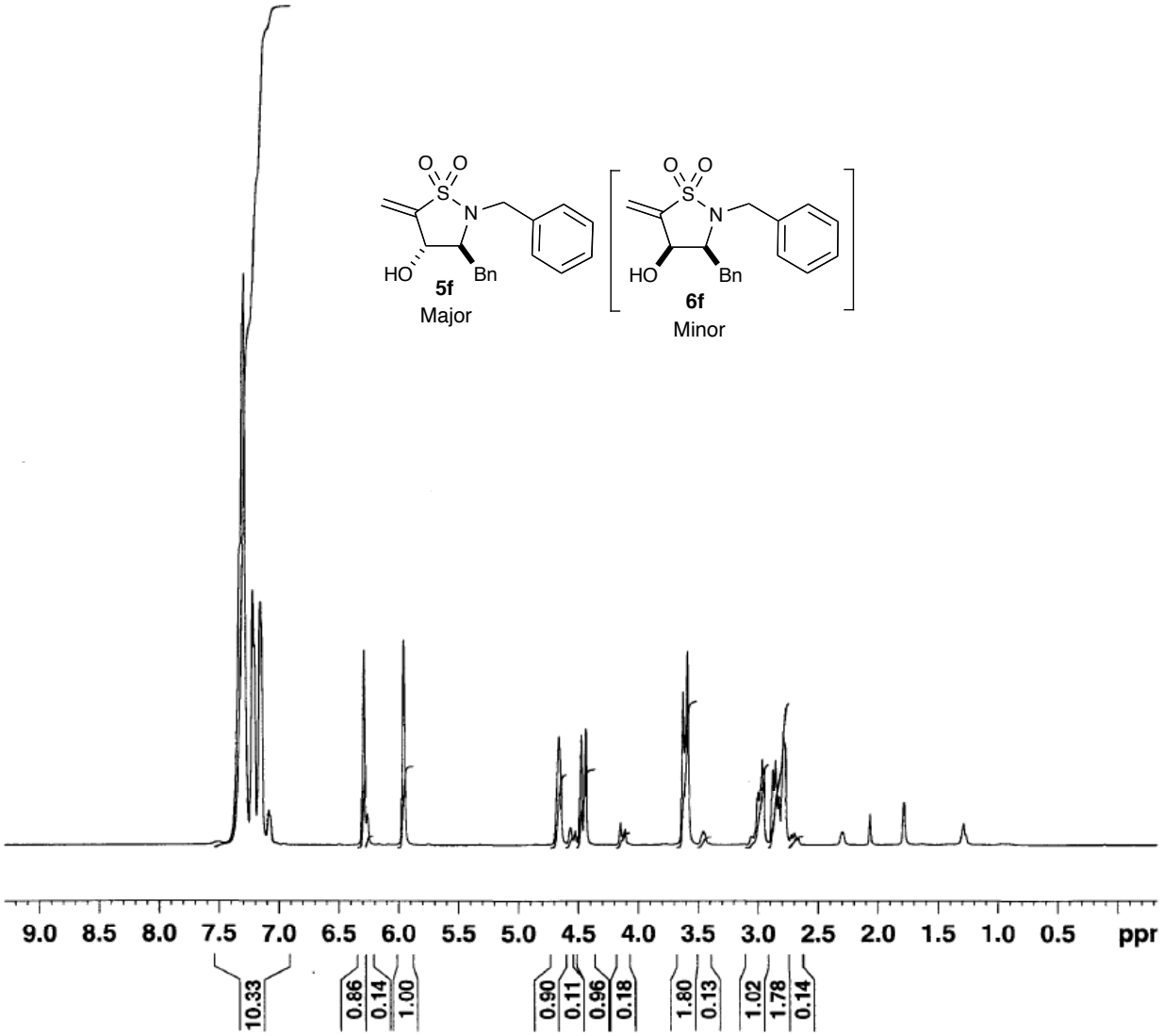
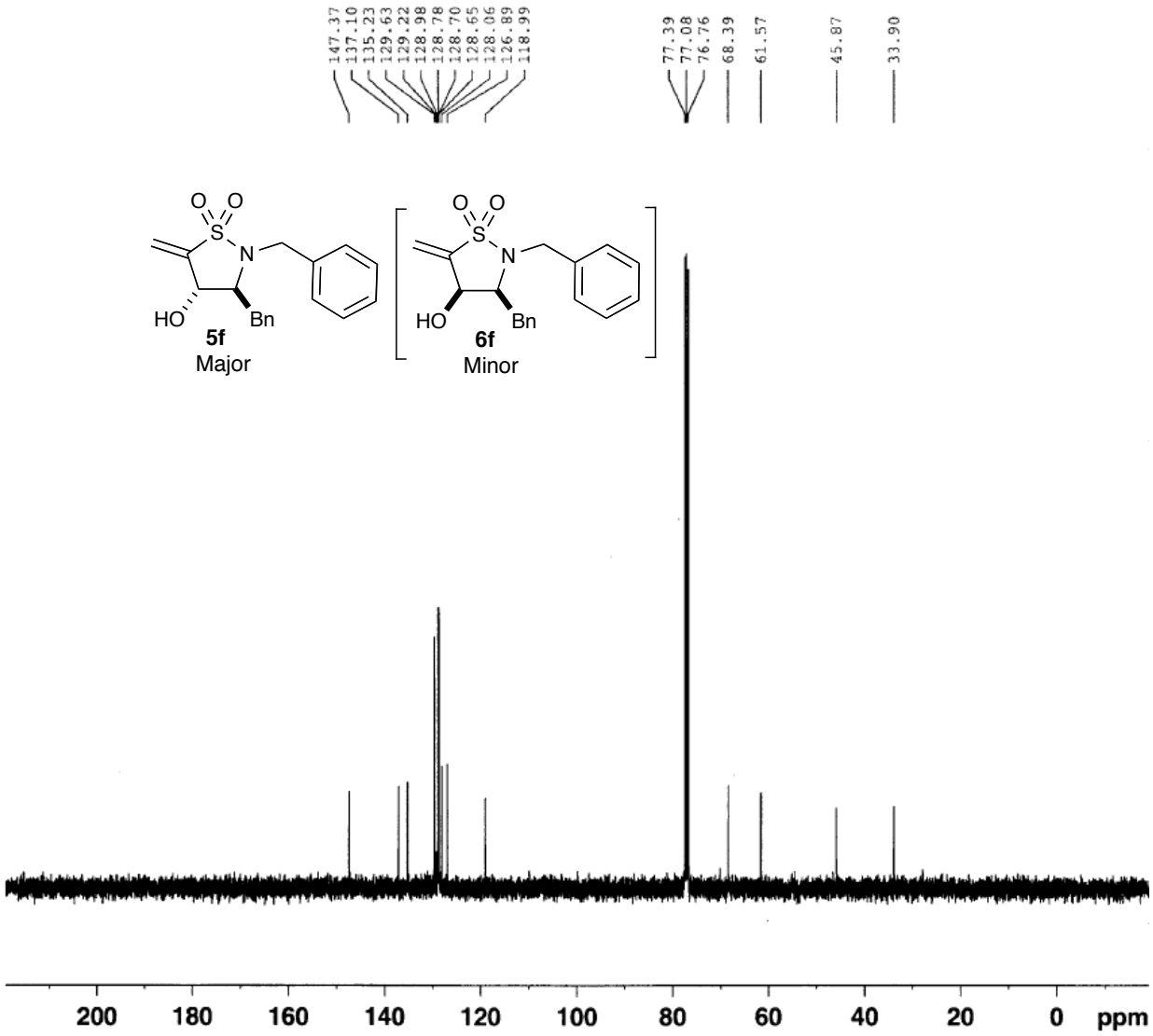
147.09
136.78
136.04
135.04
134.82
132.97
132.99
130.50
130.13
129.65
129.44
129.19
128.94
128.78
127.95
127.82
127.18
126.90
123.48
123.23
120.14
119.65
77.57
77.25
76.93
70.04
68.09
66.10
63.63
60.78
46.96
46.54
33.75
21.23
14.25
O
O
S
N
Br
HO
Bn
5e
Major
6e
Minor
200
180
160
140
120
100
80
60
40
20
0
ppm


5f
Major
6f
Minor
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 ppr
10.33
0.86
0.14
1.00
0.90
0.11
0.96
0.18
1.80
0.13
1.02
1.78
0.14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137.10
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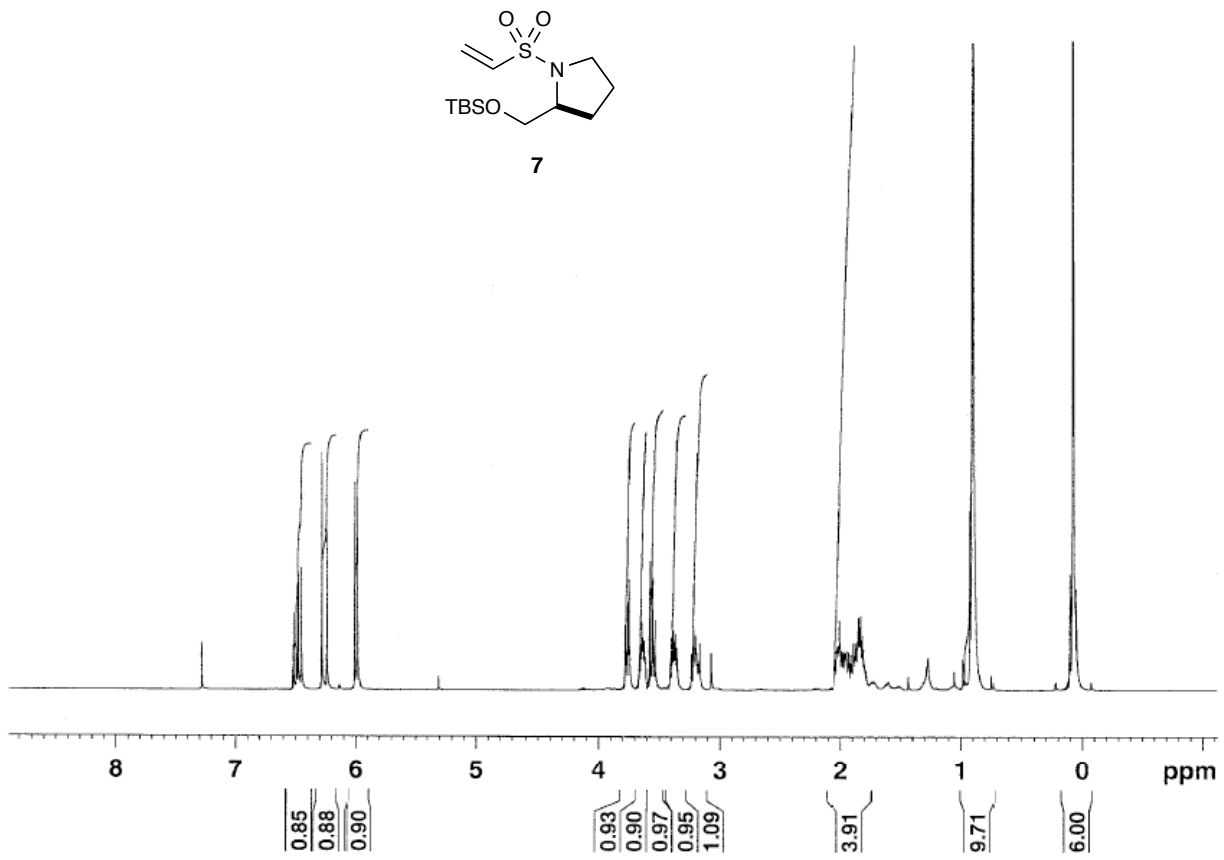
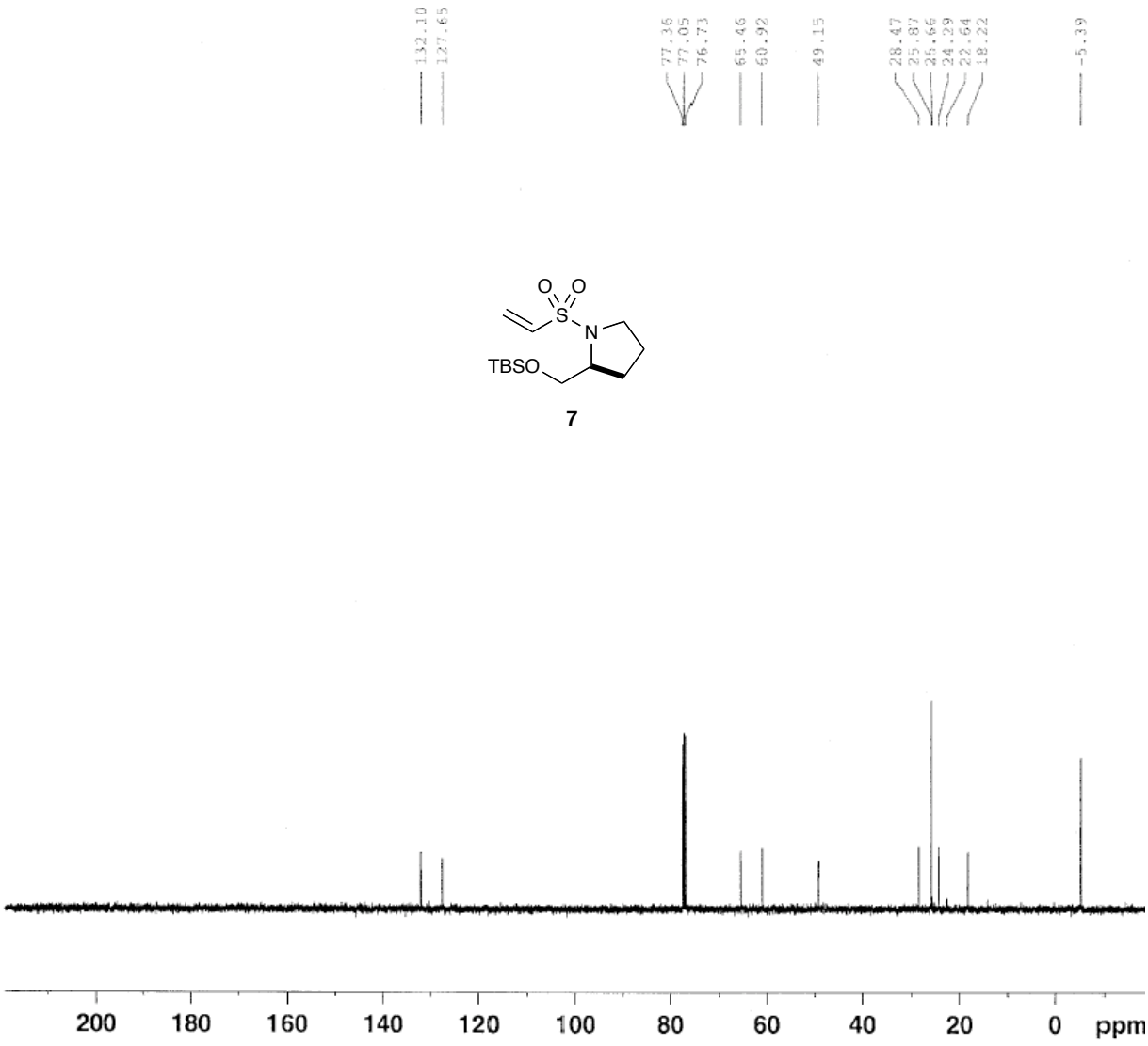
129.63
129.22
128.98
128.78
128.70
128.65
128.06
126.89
118.99
77.39
77.08
76.76
68.39
61.57
45.87
33.90
O
O
S
N
HO
Bn
5f
Major
6f
Minor
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TBSO
8
7
6
5
4
3
2
1
0
ppm
0.85
0.88
0.90
0.93
0.90
0.97
0.95
1.09
3.91
9.71
6.00

7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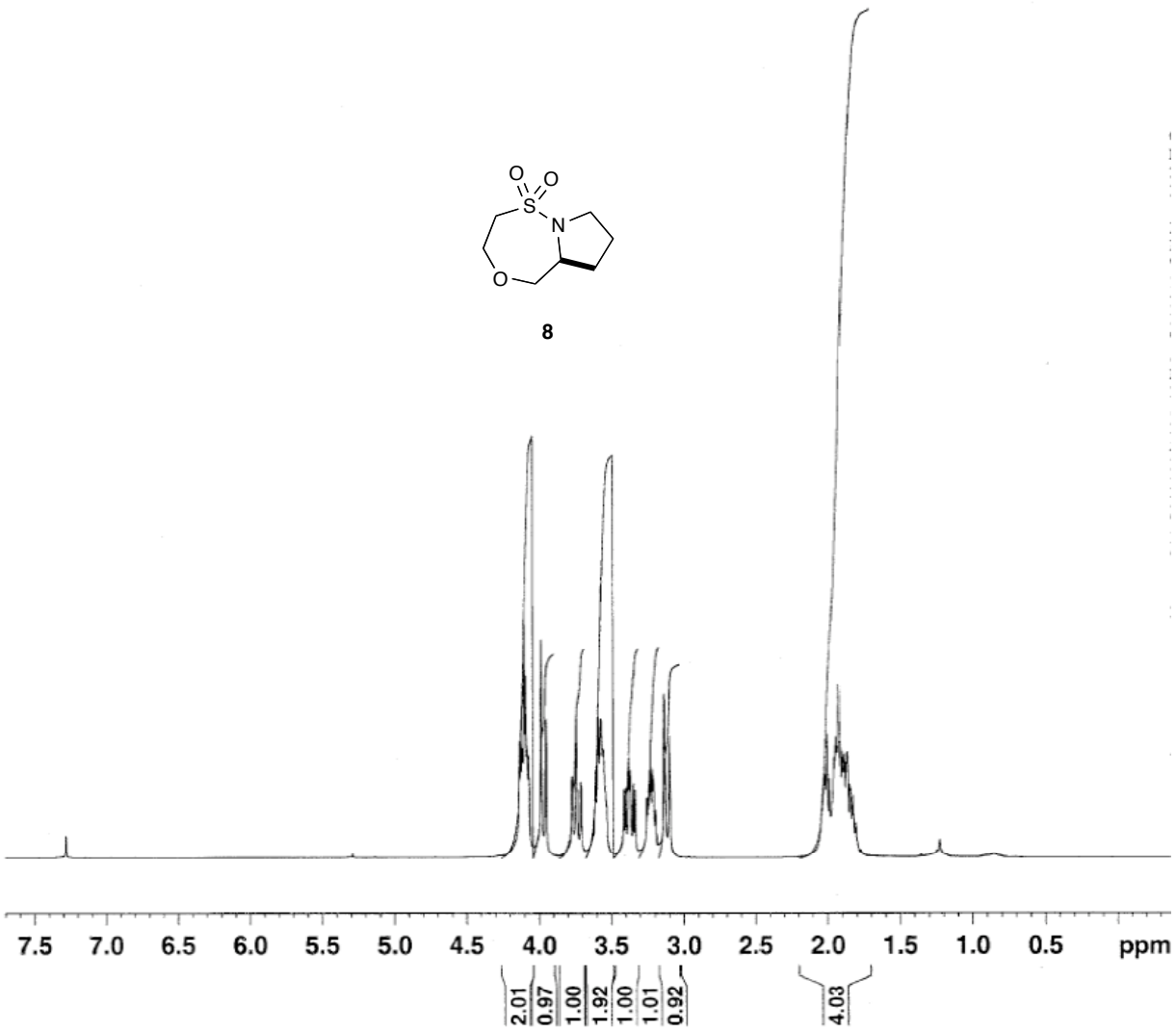
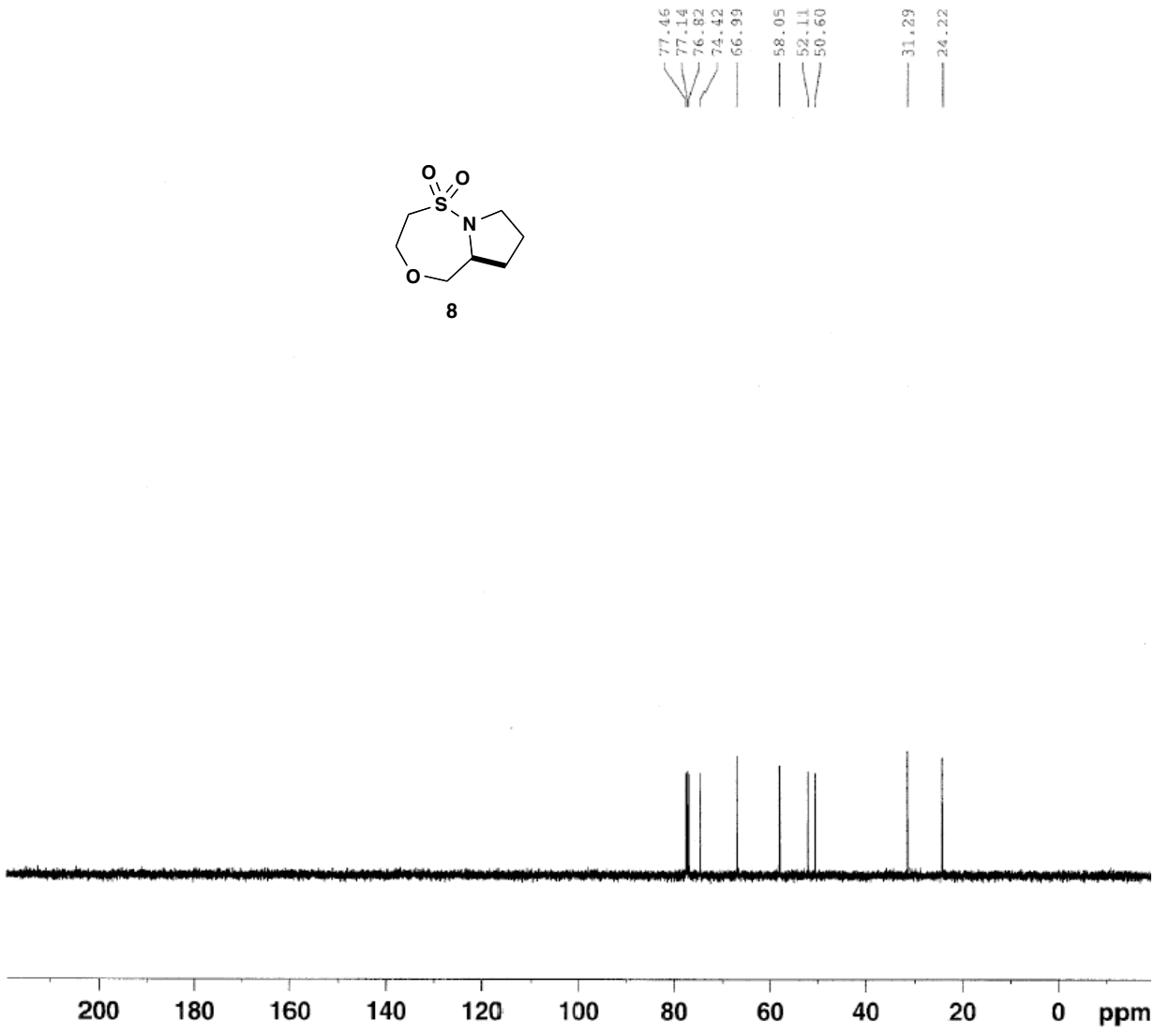
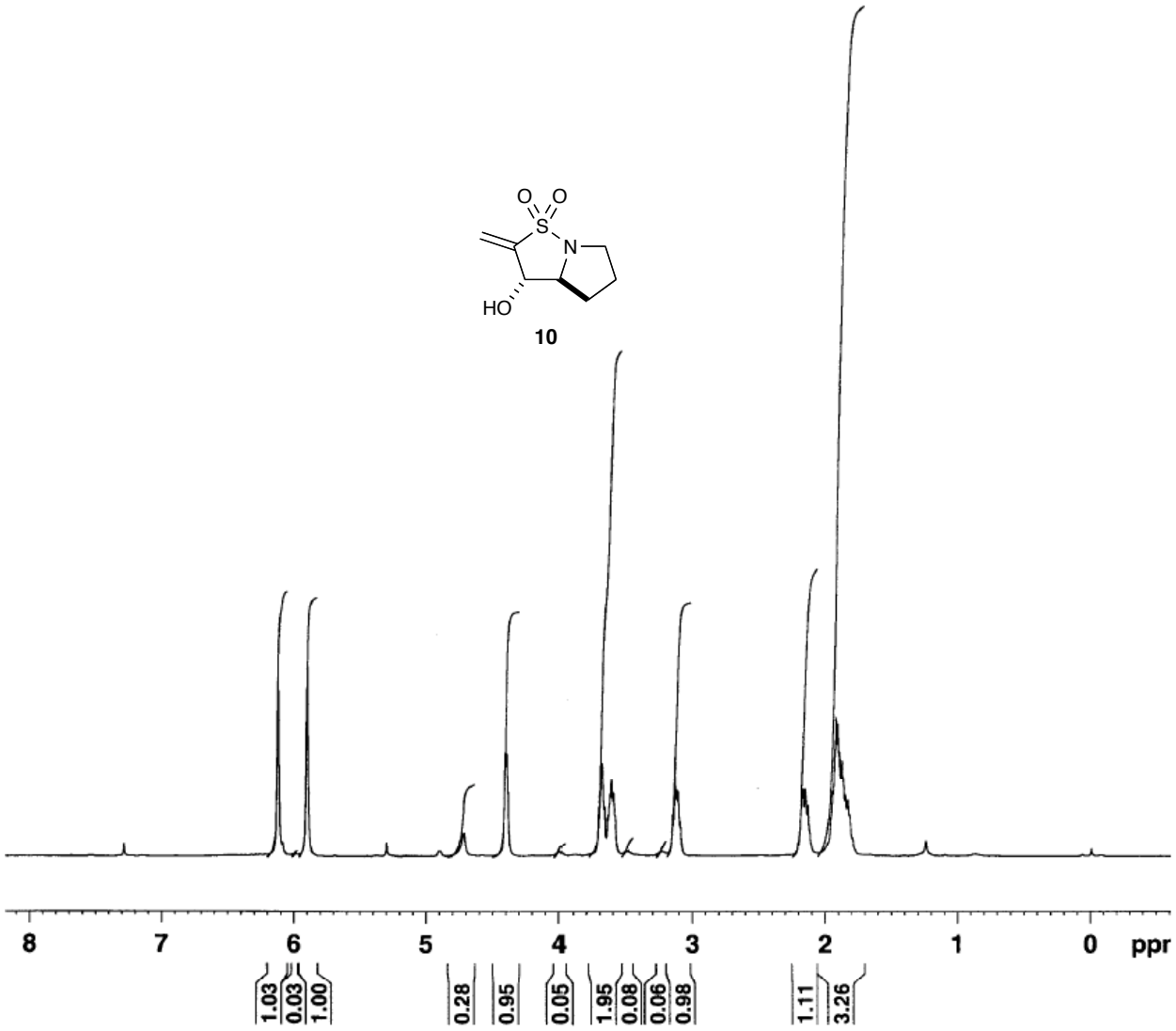
127.65
77.36
77.05
76.73
65.46
60.92
49.15
28.47
25.87
25.66
24.29
22.64
18.22
-5.39
O
O
S
N
TBSO
200
180
160
140
120
100
80
60
40
20
0
ppm

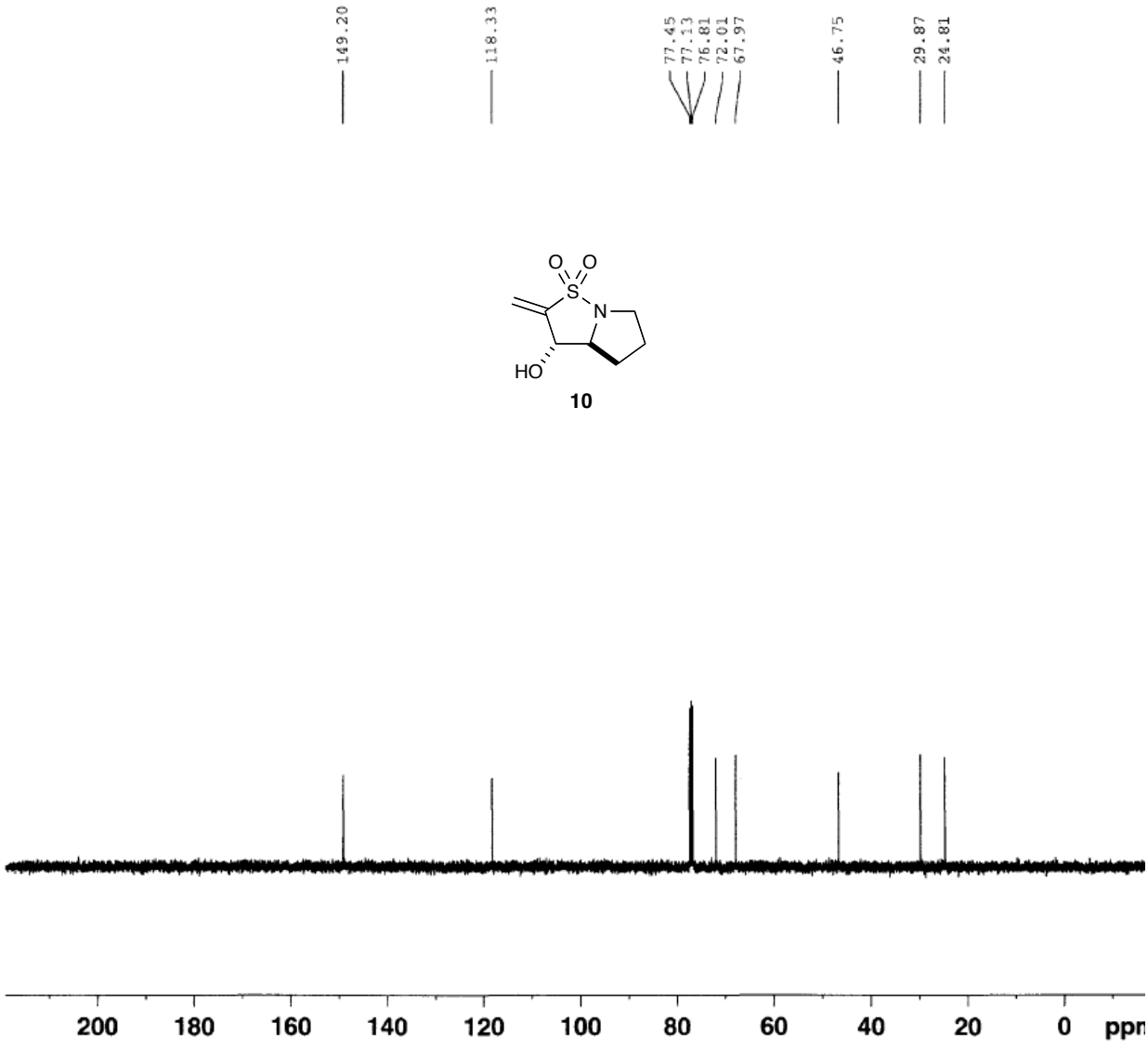
7


O
O
S
N
O
8
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
ppm
2.01
0.97
1.00
1.92
1.00
1.01
0.92
4.03

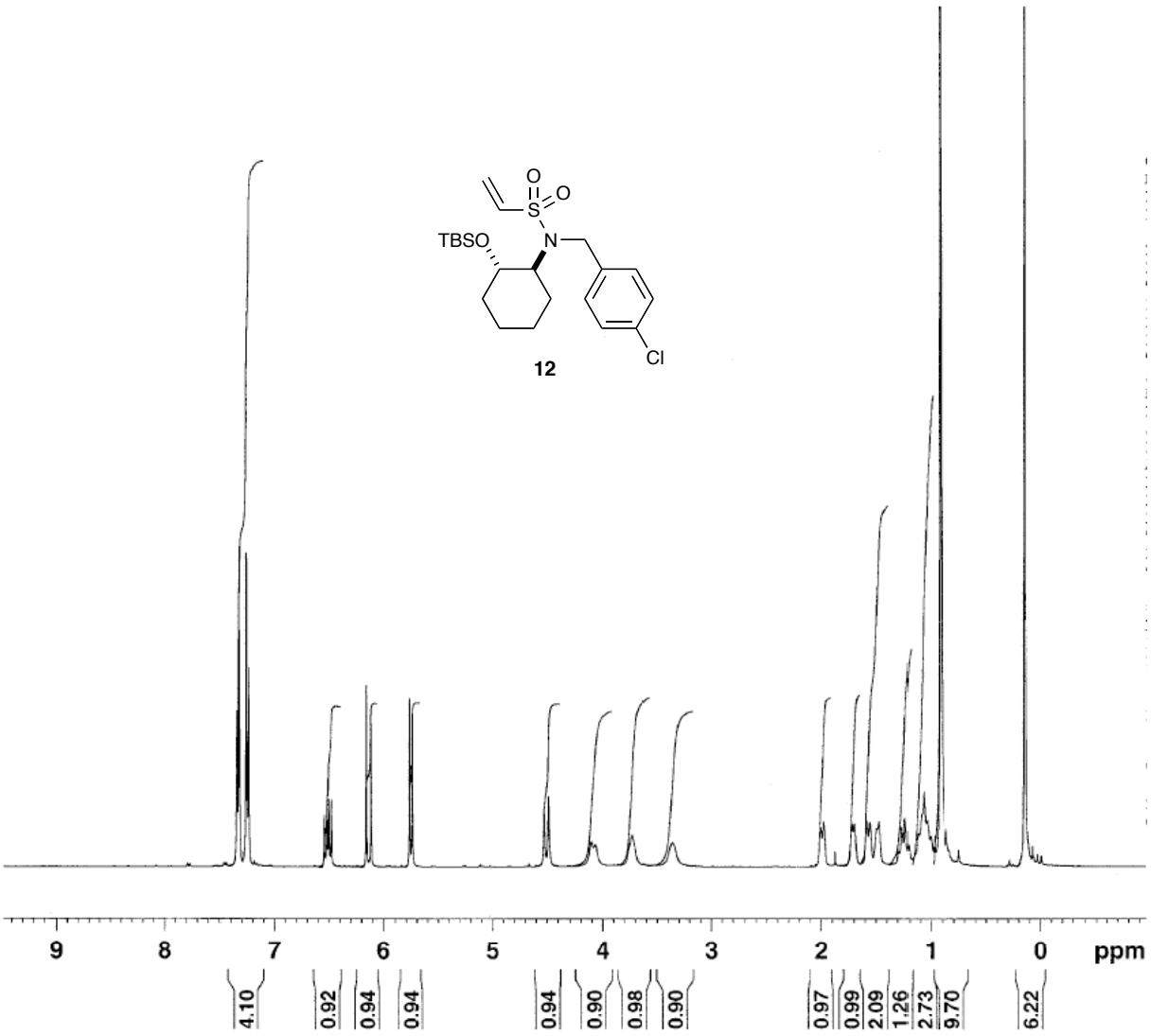

77.46
77.14
76.82
74.42
66.99
58.05
52.11
50.60
31.29
24.22
O
O
S
N
O
200
180
160
140
120
100
80
60
40
20
0
ppm

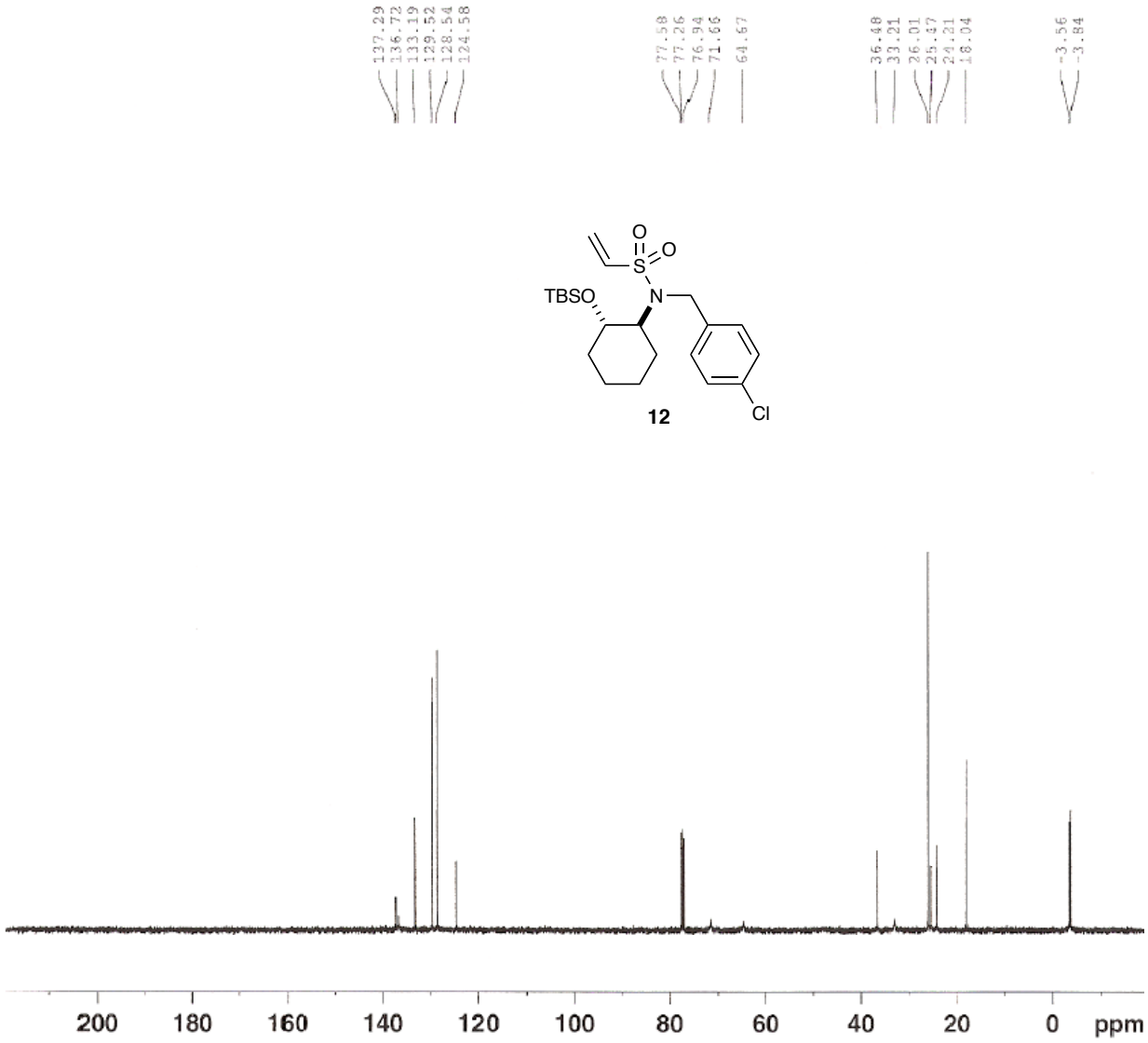
8


O
O
S
N
HO
10
8
7
6
5
4
3
2
1
0
ppr
1.03
0.03
1.00
0.28
0.95
0.05
1.95
0.08
0.06
0.98
1.11
3.26


149.20
118.33
77.45
77.13
76.81
72.01
67.97
46.75
29.87
24.81
O
O
S
N
HO
200
180
160
140
120
100
80
60
40
20
0
ppm

10


O
O
S
N
TBSO
Cl
12
9
8
7
6
5
4
3
2
1
0
ppm
4.10
0.92
0.94
0.94
0.94
0.90
0.98
0.90
0.97
0.99
2.09
1.26
2.73
9.70
6.22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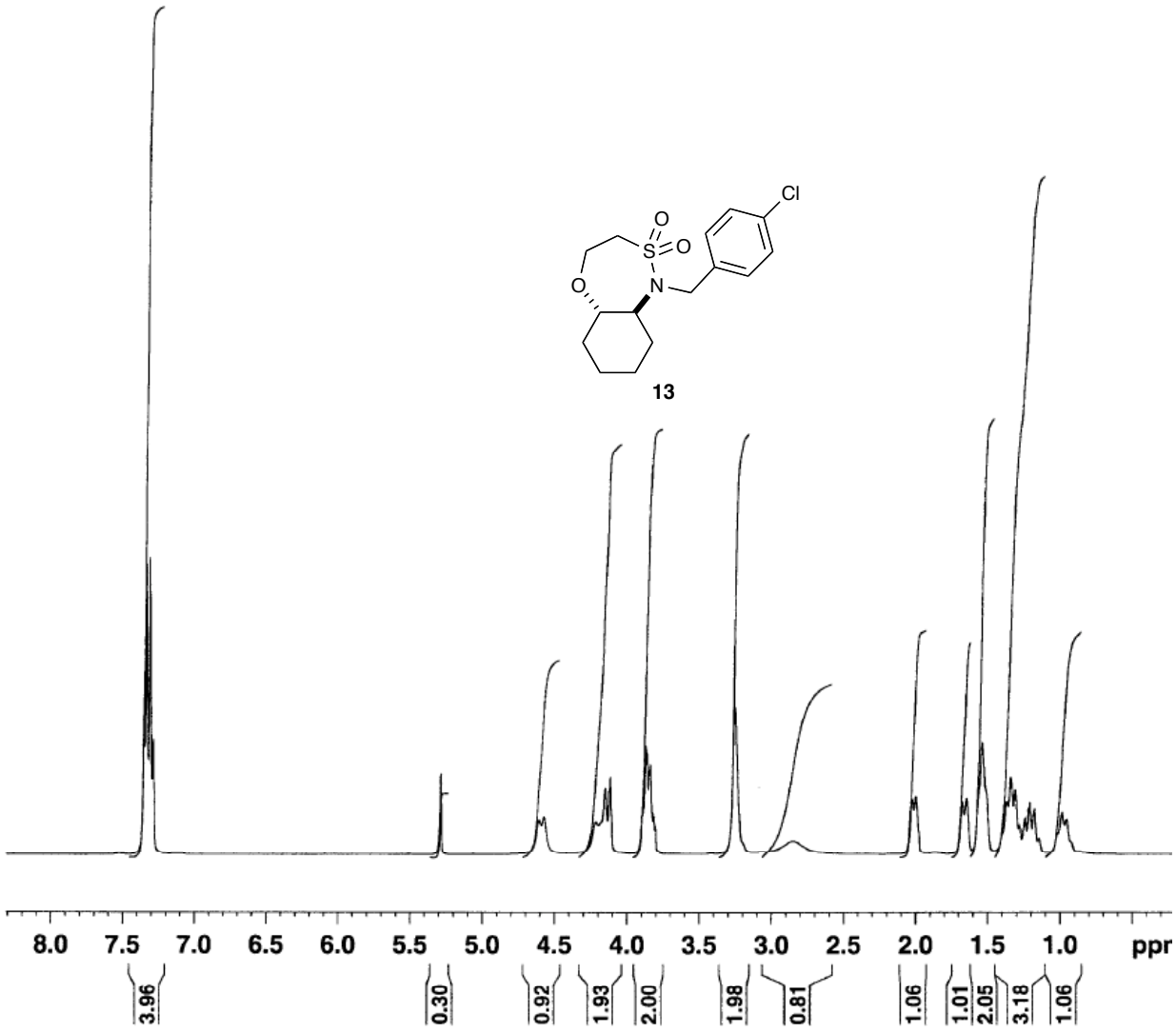
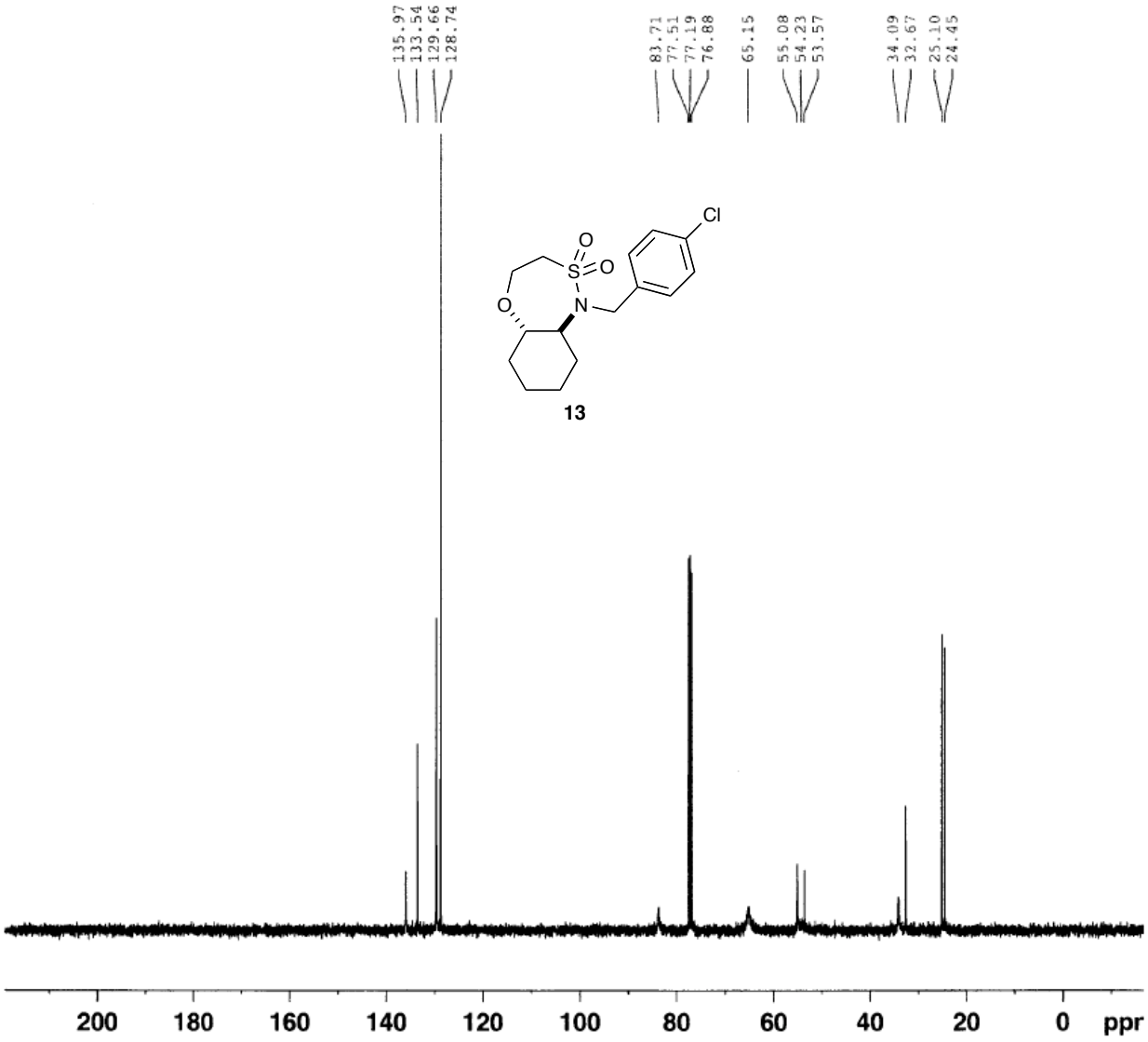
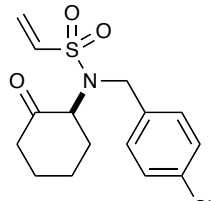
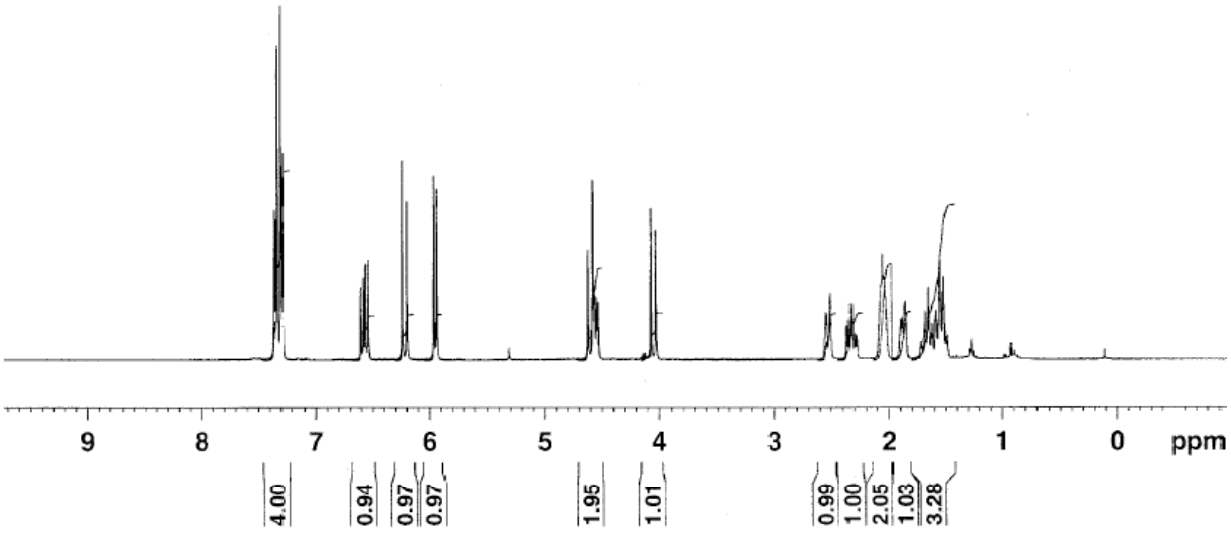
136.72
133.19
129.52
128.54
124.58
77.58
77.26
76.94
71.66
64.67
36.48
33.21
26.01
25.47
24.21
18.04
-3.56
-3.84
O
O
S
N
TBSO
Cl
12
200
180
160
140
120
100
80
60
40
20
0
ppm

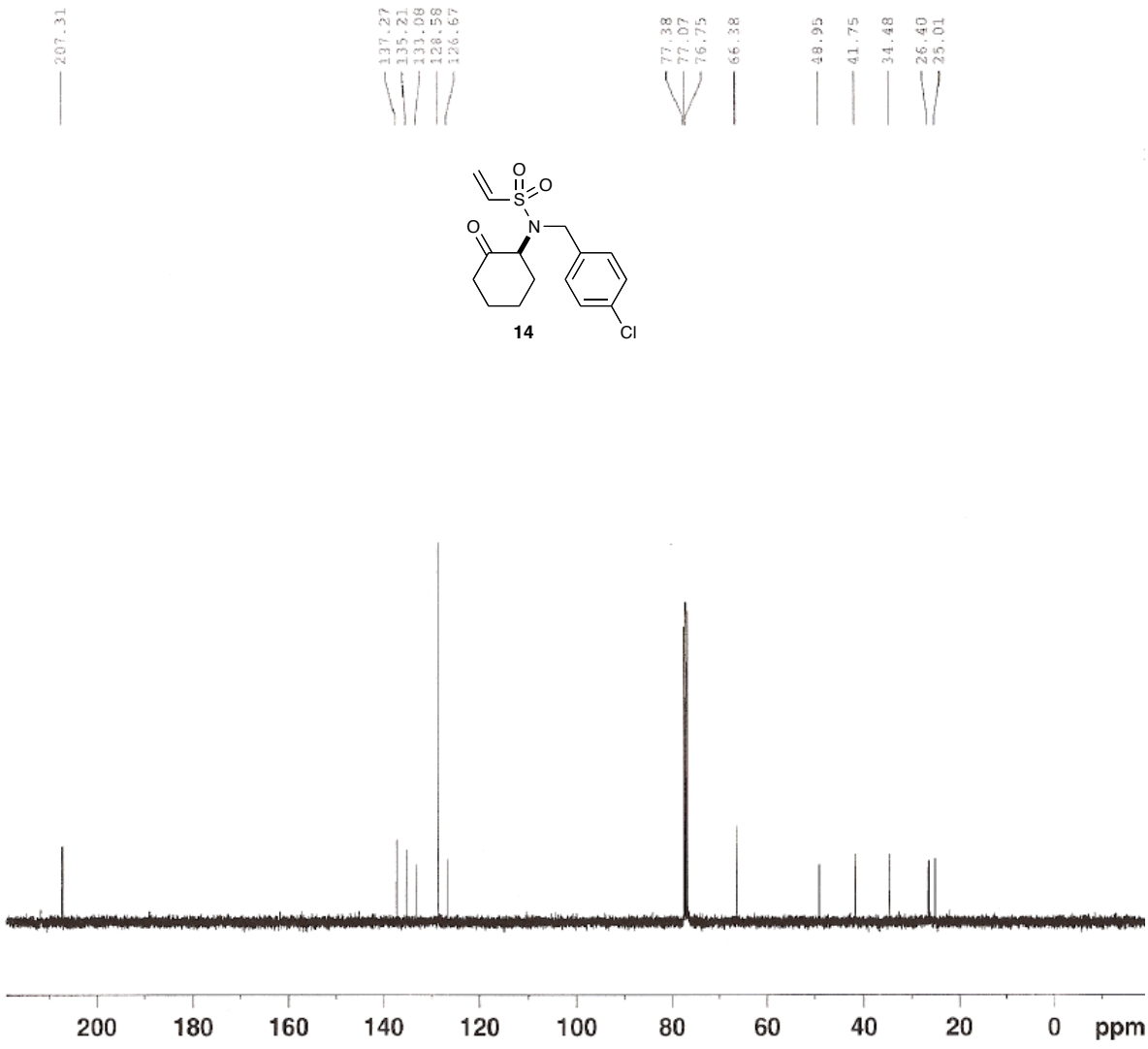

Cl
O
S
O
O
N
13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppr
3.96
0.30
0.92
1.93
2.00
1.98
0.81
1.06
1.01
2.05
3.18
1.06

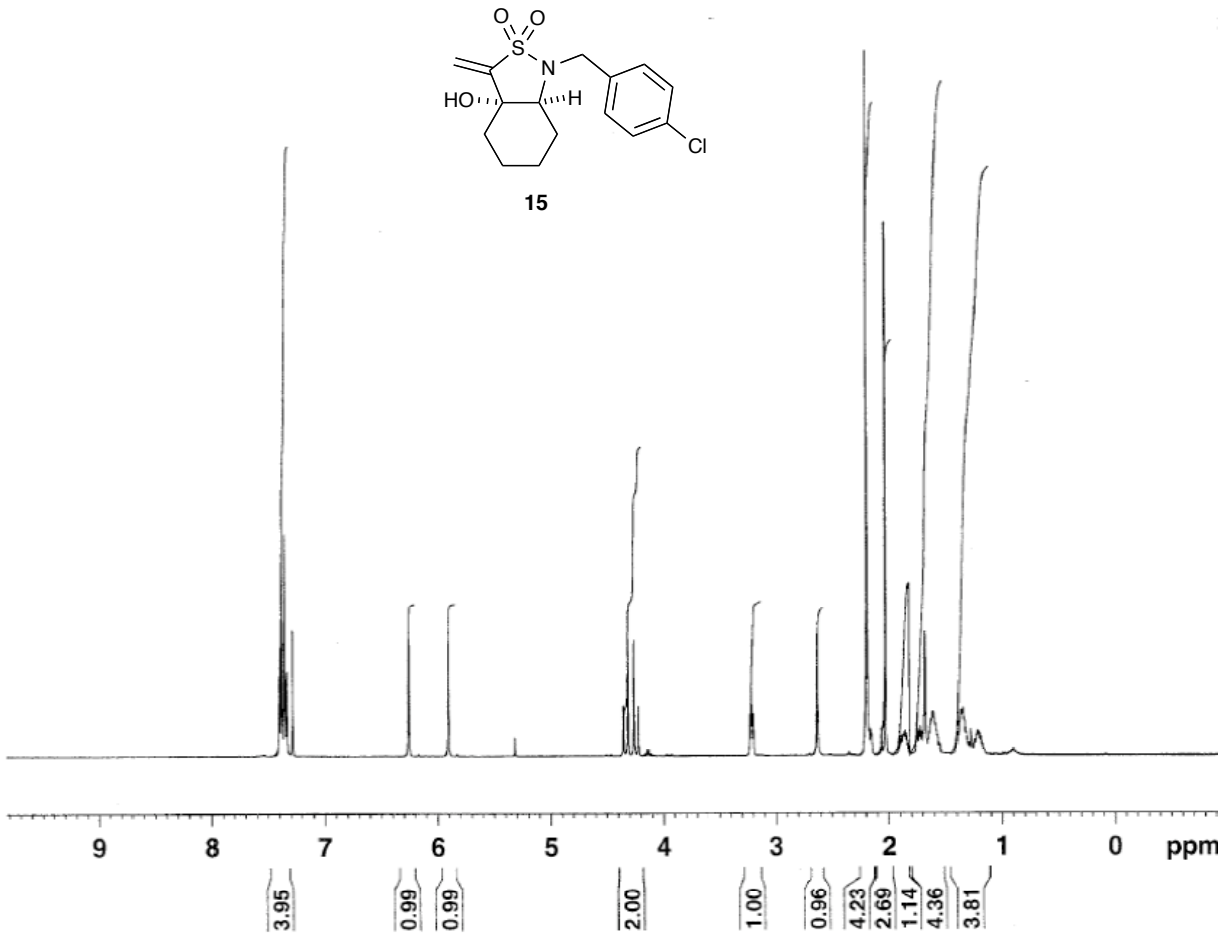

135.97
133.54
129.66
128.74
83.71
77.51
77.19
76.88
65.15
55.08
54.23
53.57
34.09
32.67
25.10
24.45
Cl
O
S
O
O
N
13
200
180
160
140
120
100
80
60
40
20
0
ppr


O
S
O
O
N
Cl

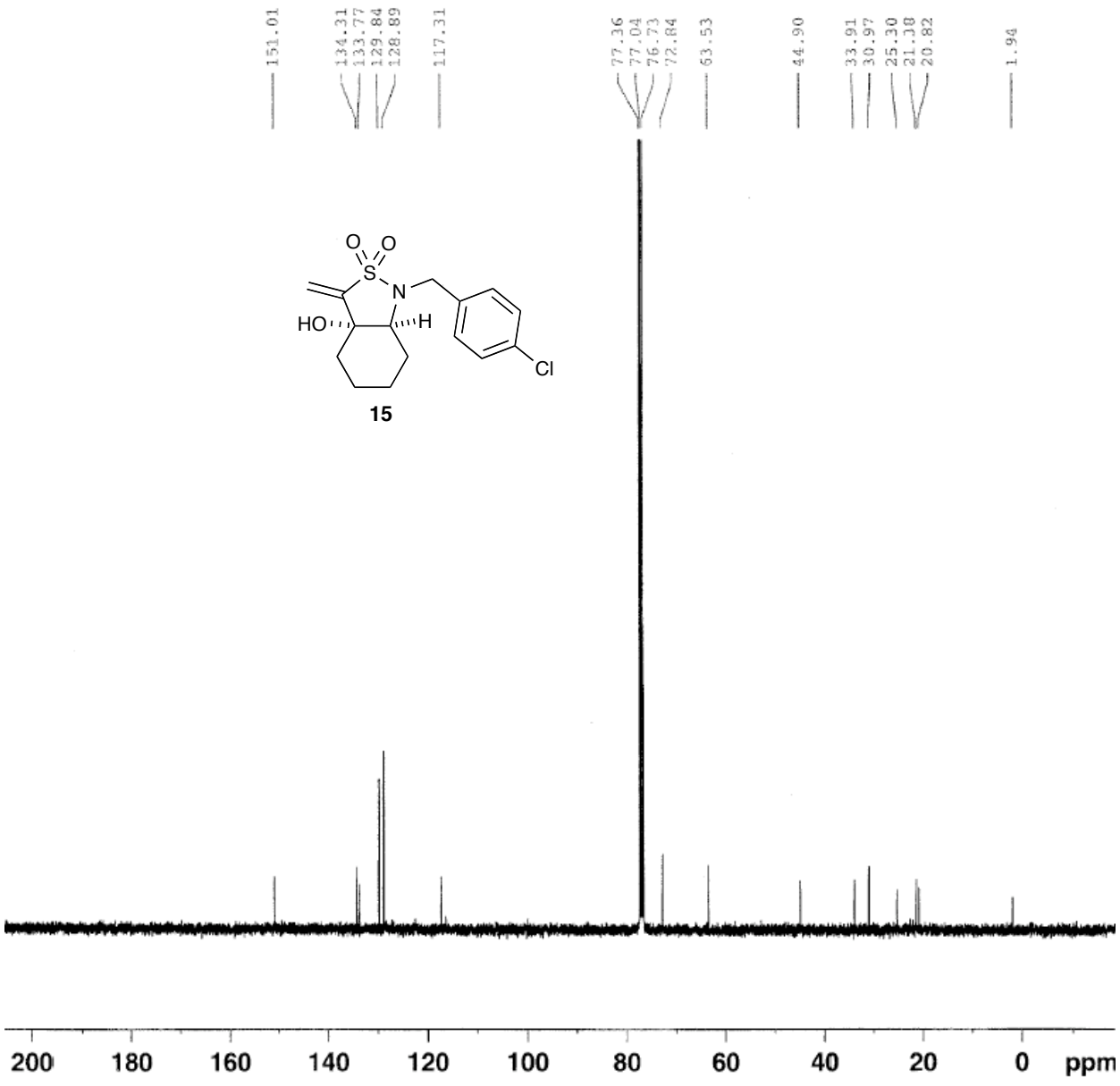
14

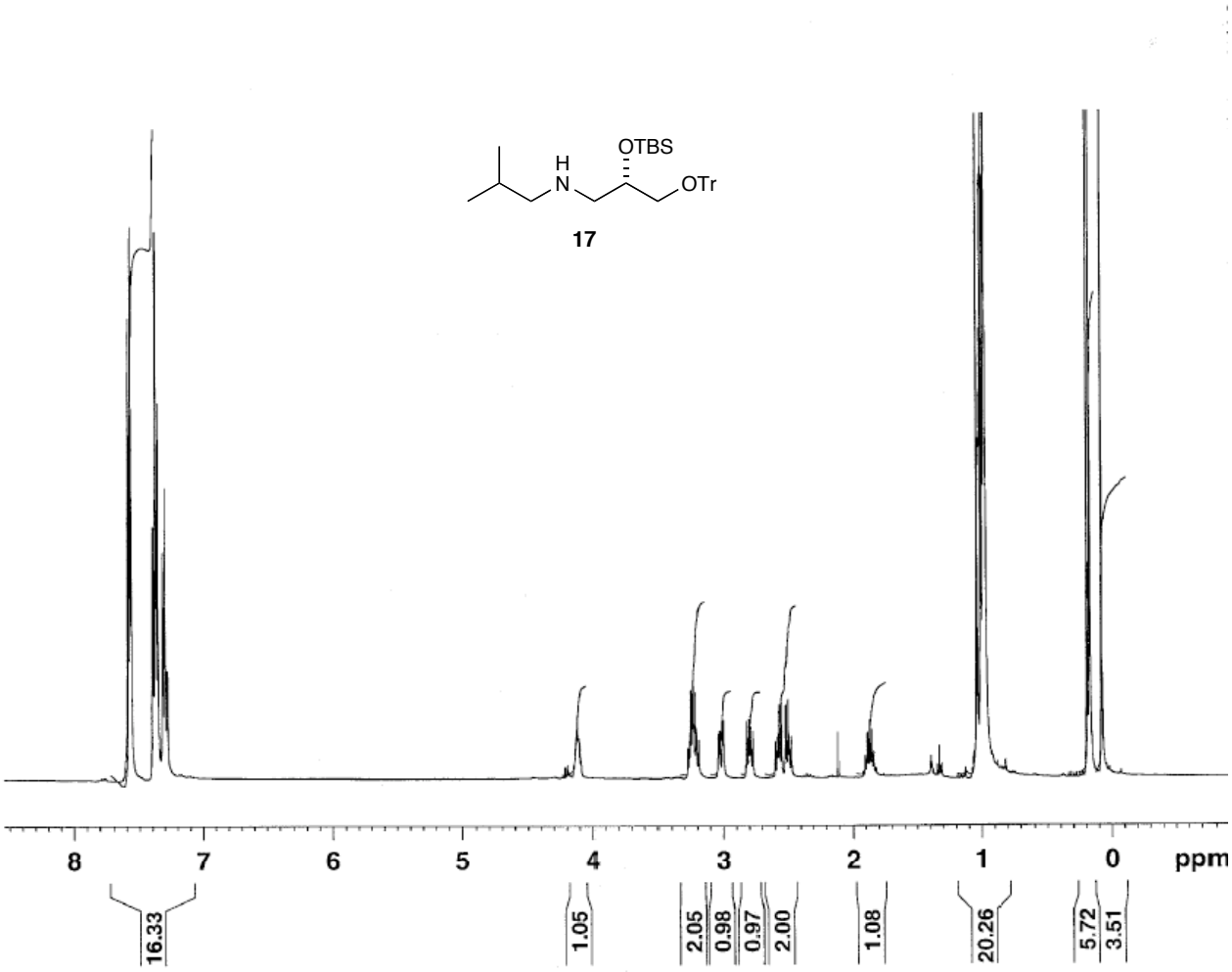

9
8
7
6
5
4
3
2
1
0
ppm
4.00
0.94
0.97
0.97
1.95
1.01
0.99
1.00
2.05
1.03
3.28

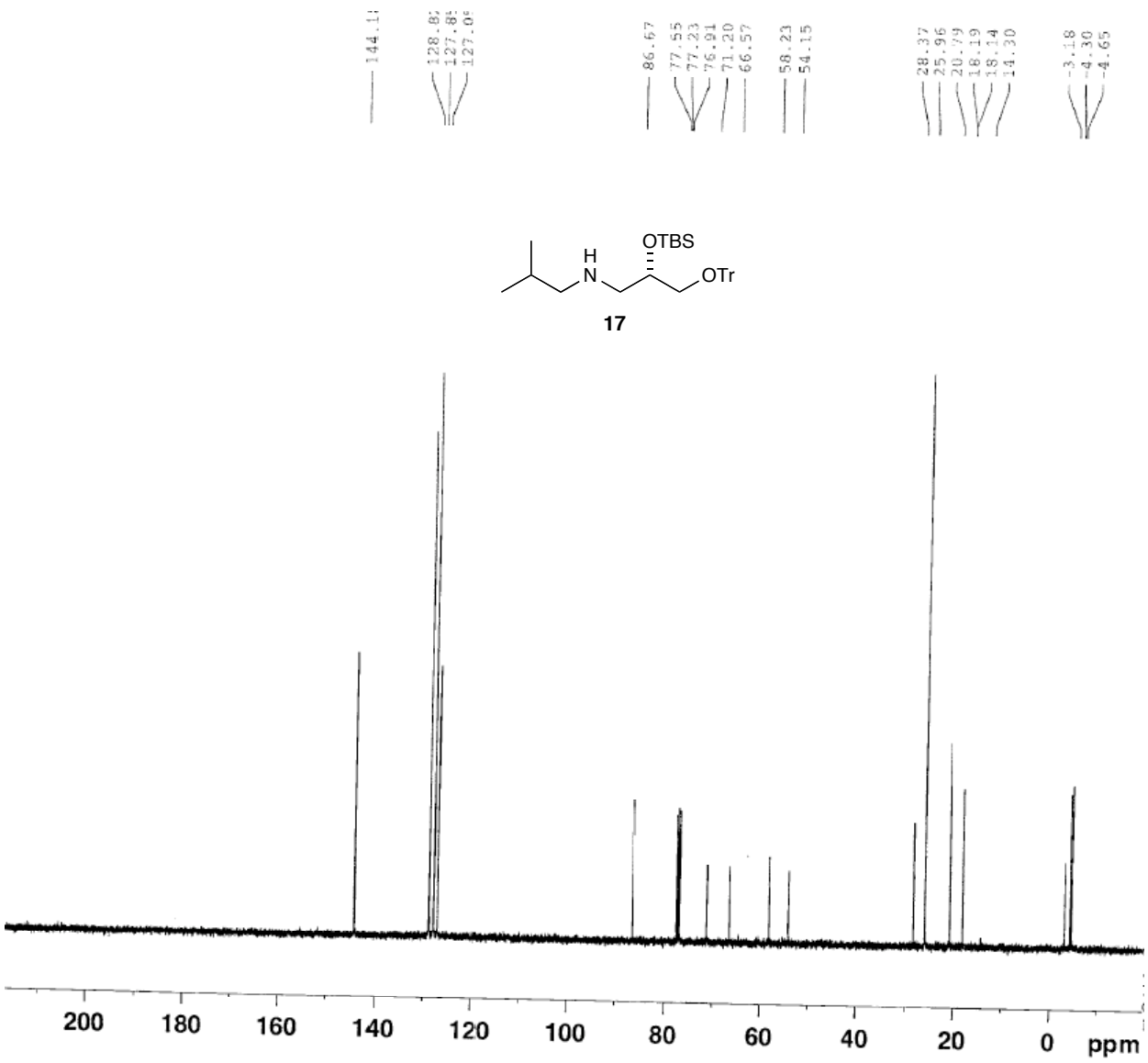

207.31
137.27
135.21
133.08
128.58
126.67
77.38
77.07
76.75
66.38
48.95
41.75
34.48
26.40
25.01
O
O
S
O
N
O
Cl
14
200
180
160
140
120
100
80
60
40
20
0
ppm

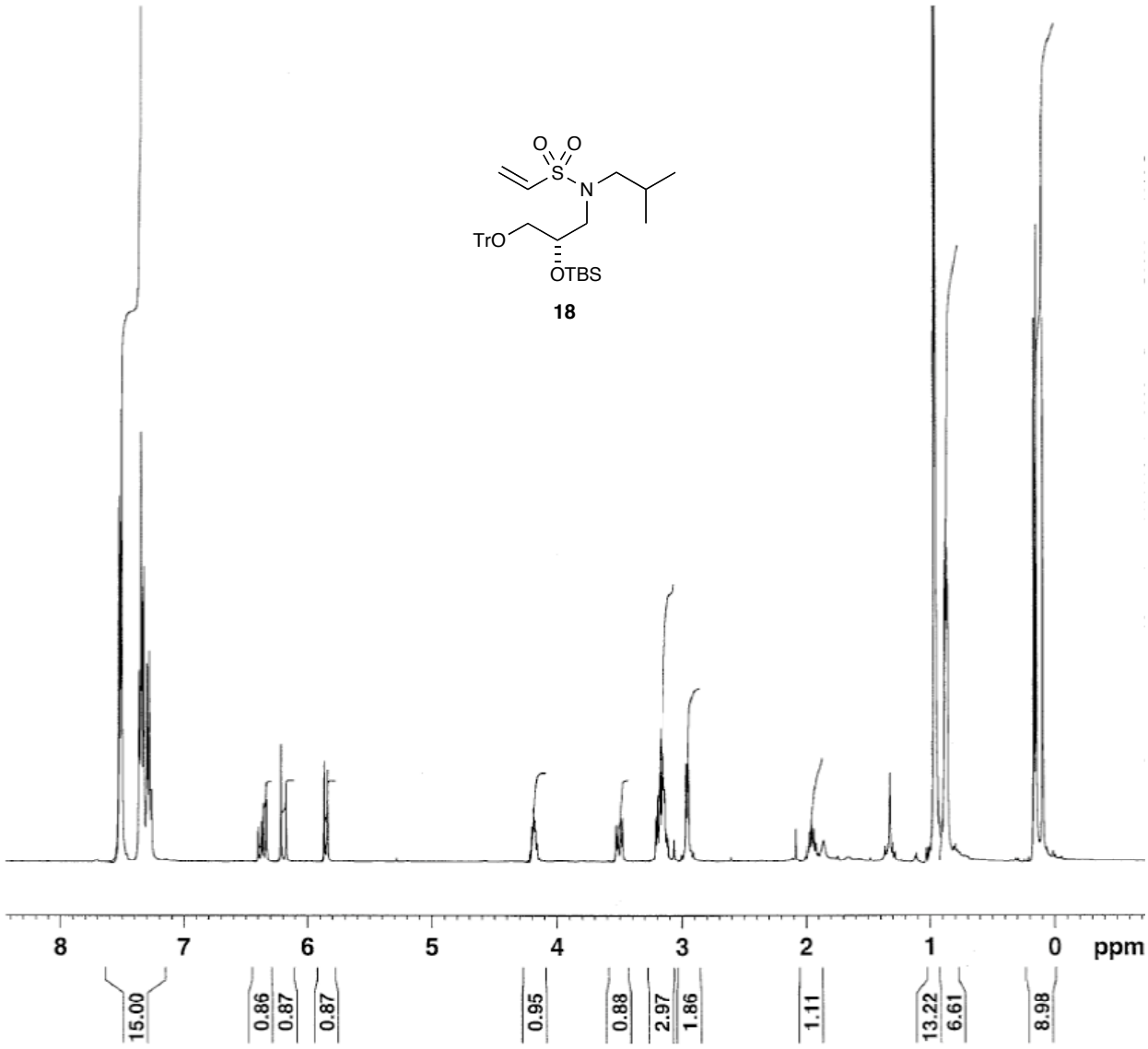

O
O
S
N
HO
H
Cl
9
8
7
6
5
4
3
2
1
0
ppm
3.95
0.99
0.99
2.00
1.00
0.96
4.23
2.69
1.14
4.36
3.81

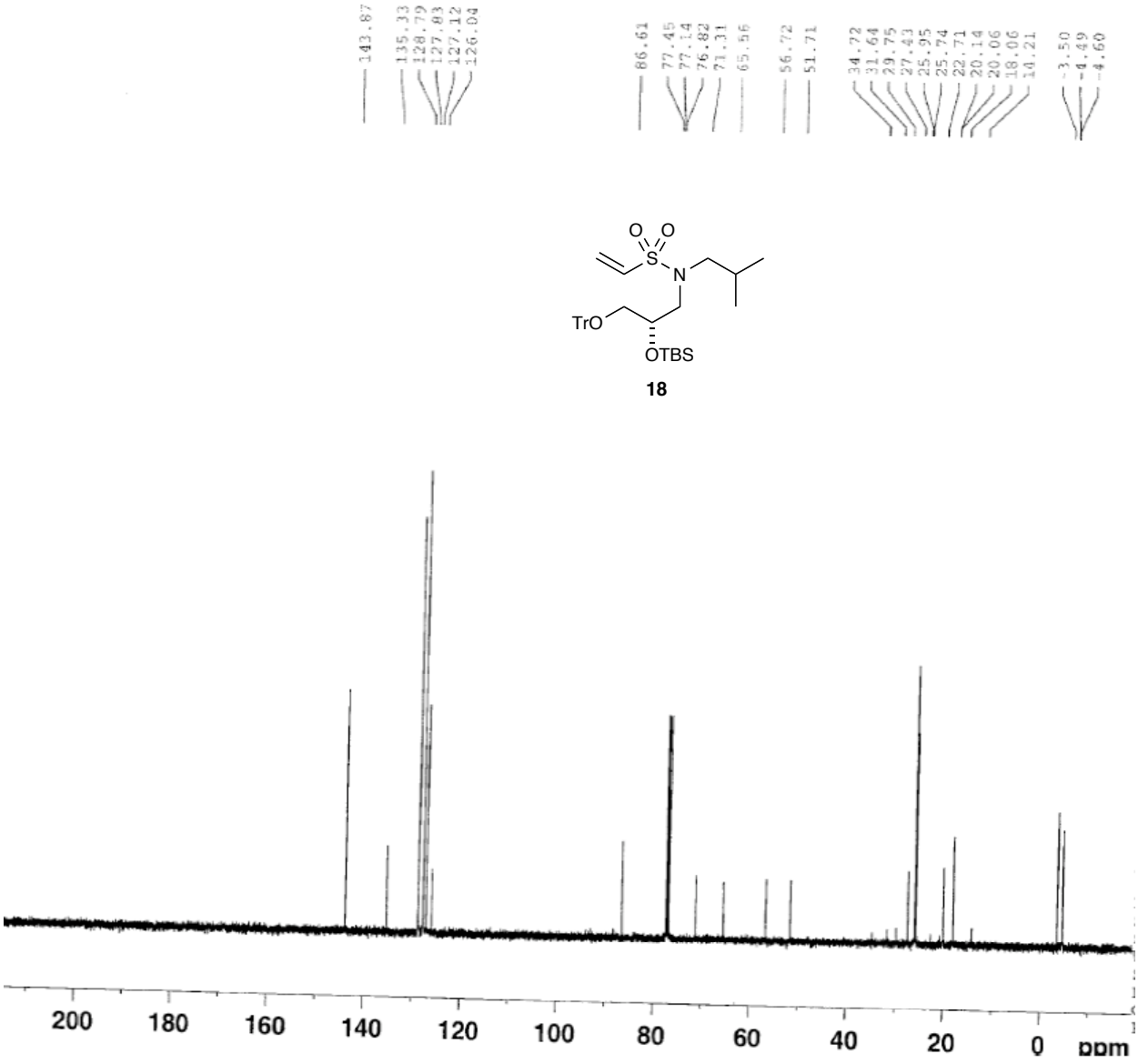
15

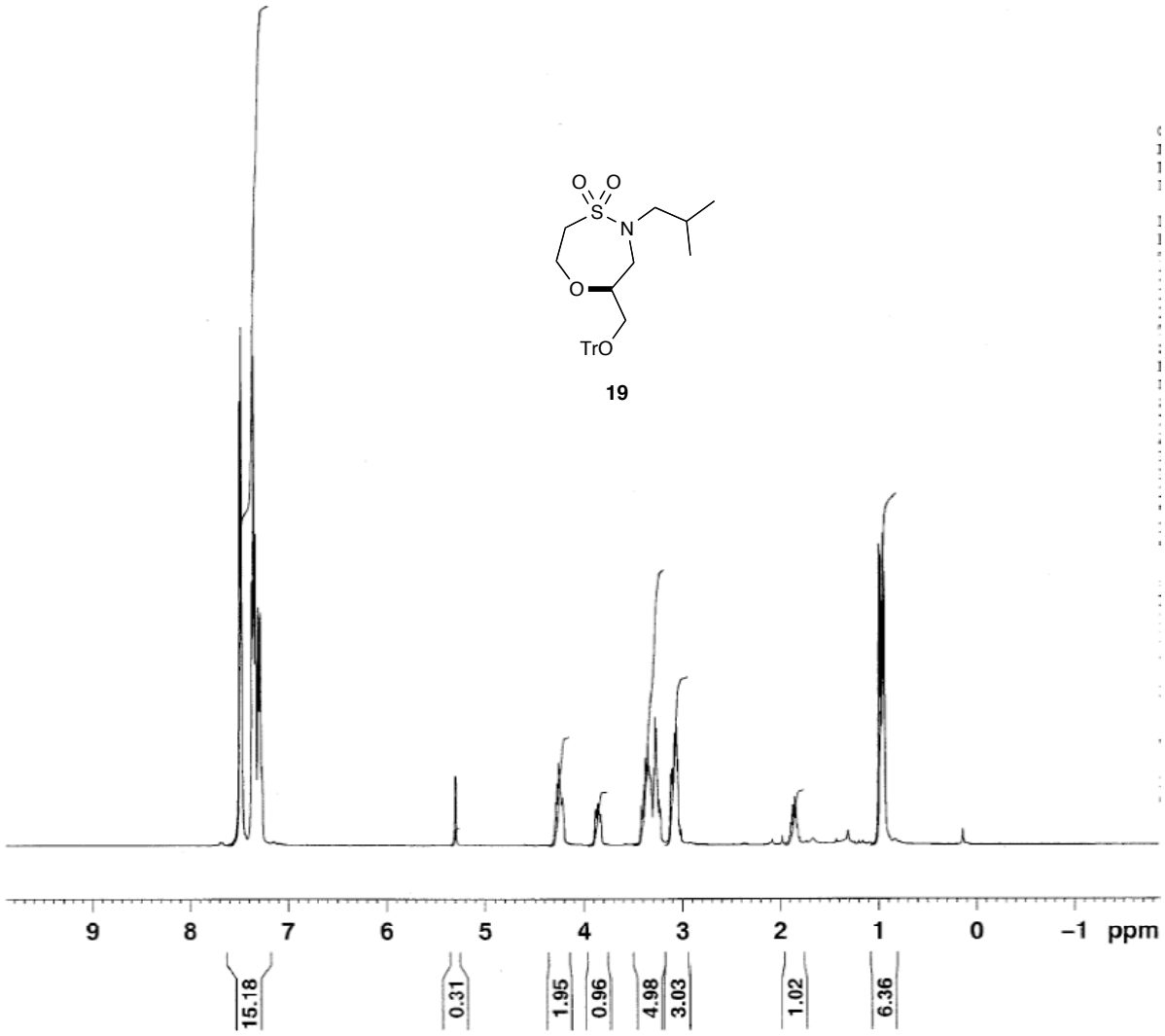

151.01
134.31
133.77
129.84
128.89
117.31
77.36
77.04
76.73
72.84
63.53
44.90
33.91
30.97
25.30
21.38
20.82
1.94
O
O
S
N
HO
H
Cl
15
200
180
160
140
120
100
80
60
40
20
0
ppm


OTBS
H
N
OTr
17
8
7
6
5
4
3
2
1
0
ppm
16.33
1.05
2.05
0.98
0.97
2.00
1.08
20.26
5.72
3.51

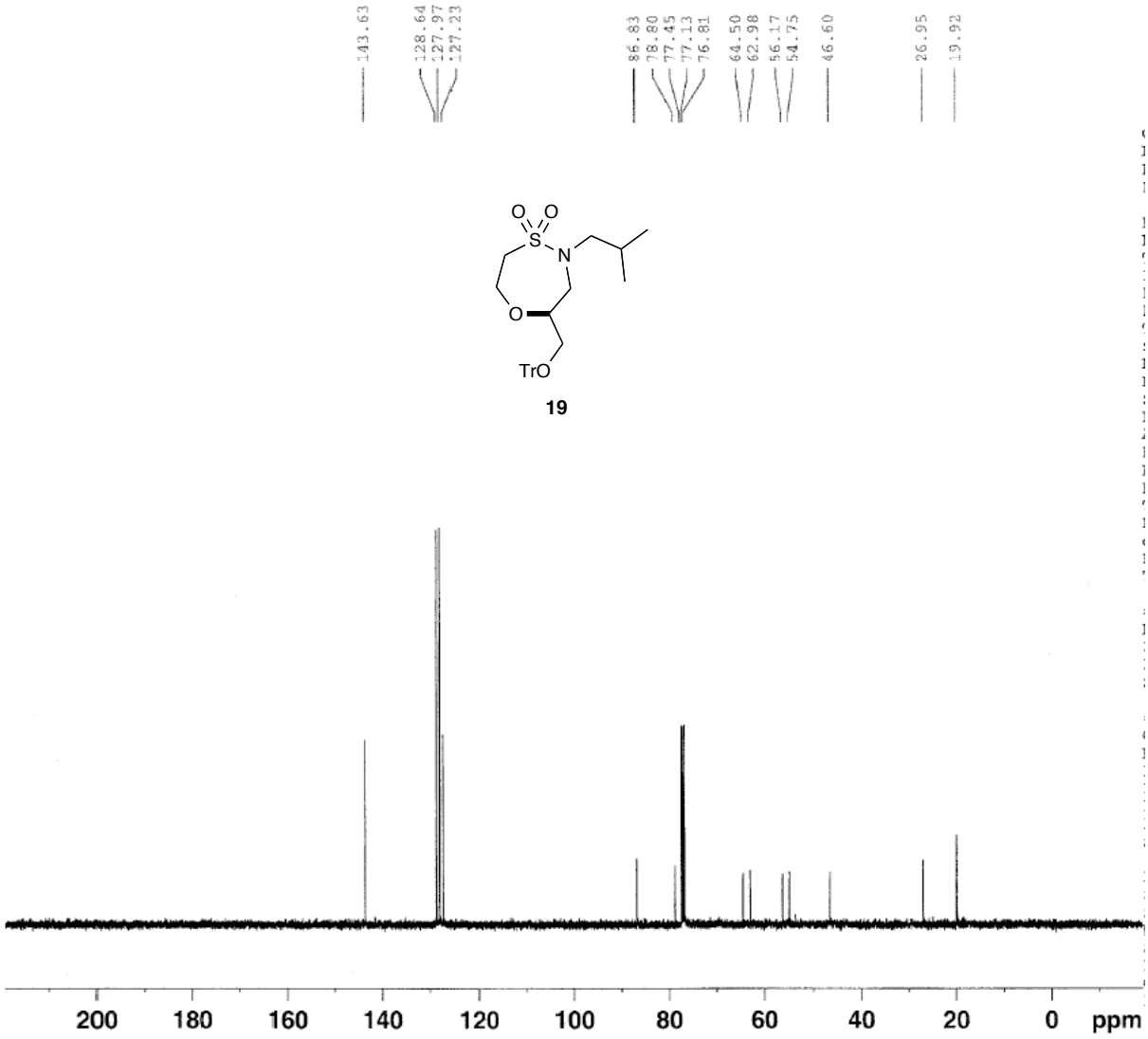

144.11
128.82
127.84
127.05
86.67
77.55
77.23
76.91
71.20
66.57
58.23
54.15
28.37
25.96
20.79
18.19
18.14
14.30
-3.18
-4.30
-4.65
OTBS
H
N
OTr
17
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
S
N
TrO
OTBS
18
8
7
6
5
4
3
2
1
0
ppm
15.00
0.86
0.87
0.87
0.95
0.88
2.97
1.86
1.11
13.22
6.61
8.98

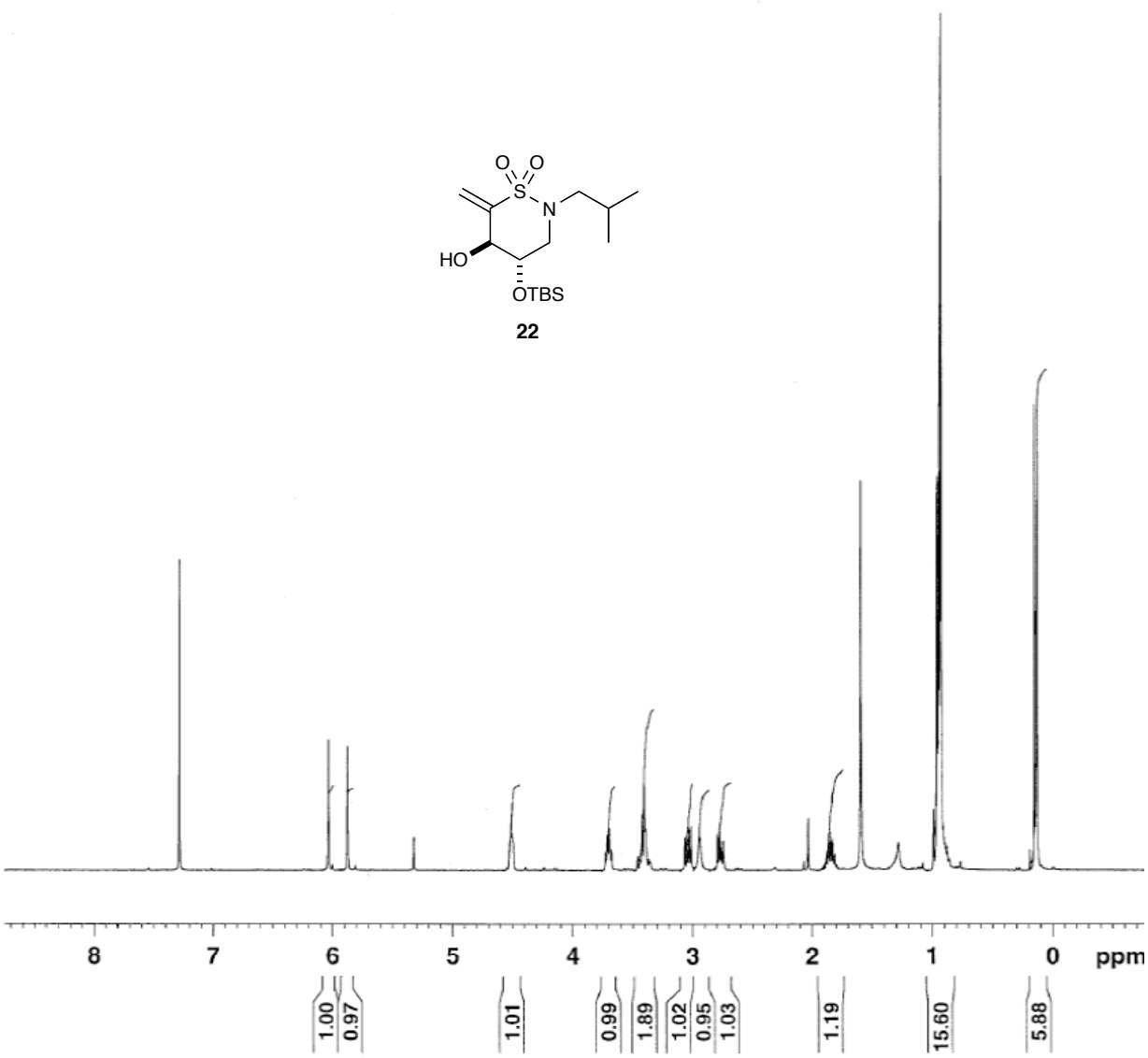

143.87
135.33
128.79
127.83
127.12
126.04
86.61
77.45
77.14
76.82
71.31
65.56
56.72
51.71
34.72
31.64
29.75
27.43
25.95
25.74
22.71
20.14
20.06
18.06
14.21
-3.50
-4.49
-4.60
O
O
S
N
TrO
OTBS
18
200
180
160
140
120
100
80
60
40
20
0
ppm



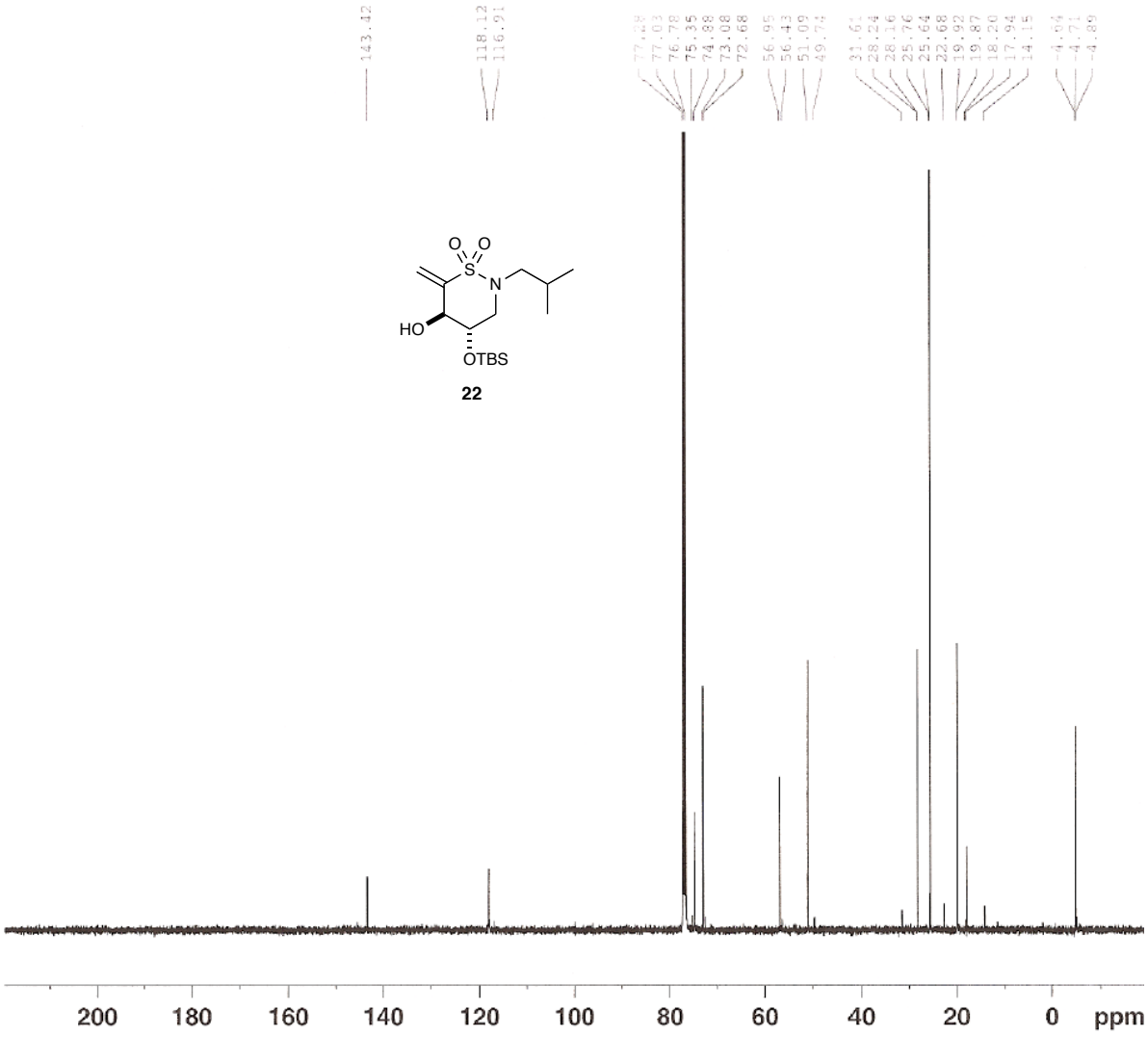
19

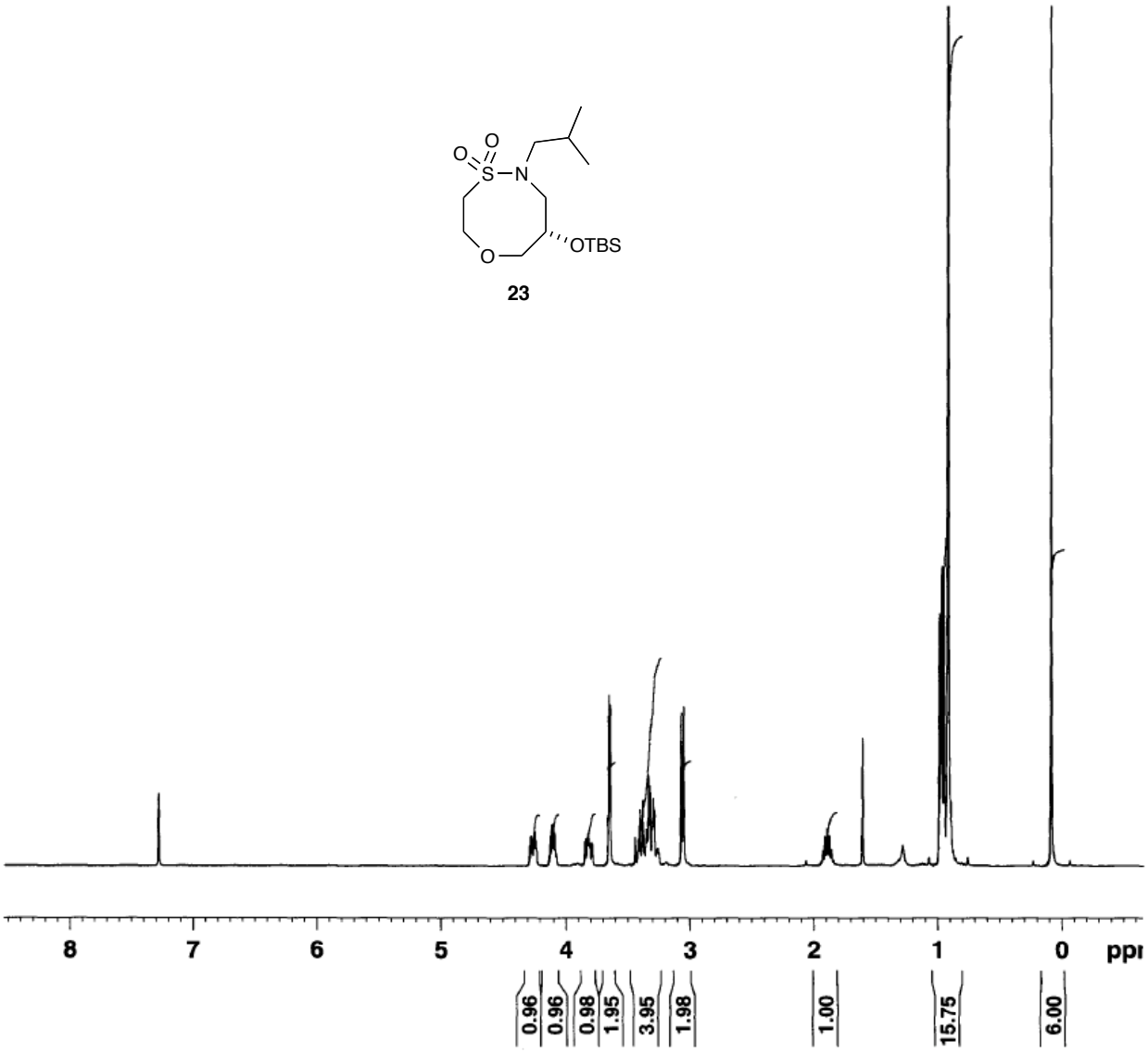

143.63
128.64
127.97
127.23
86.83
78.80
77.45
77.13
76.81
64.50
62.98
56.17
54.75
46.60
26.95
19.92
O
O
S
N
O
TrO
200
180
160
140
120
100
80
60
40
20
0
ppm

19

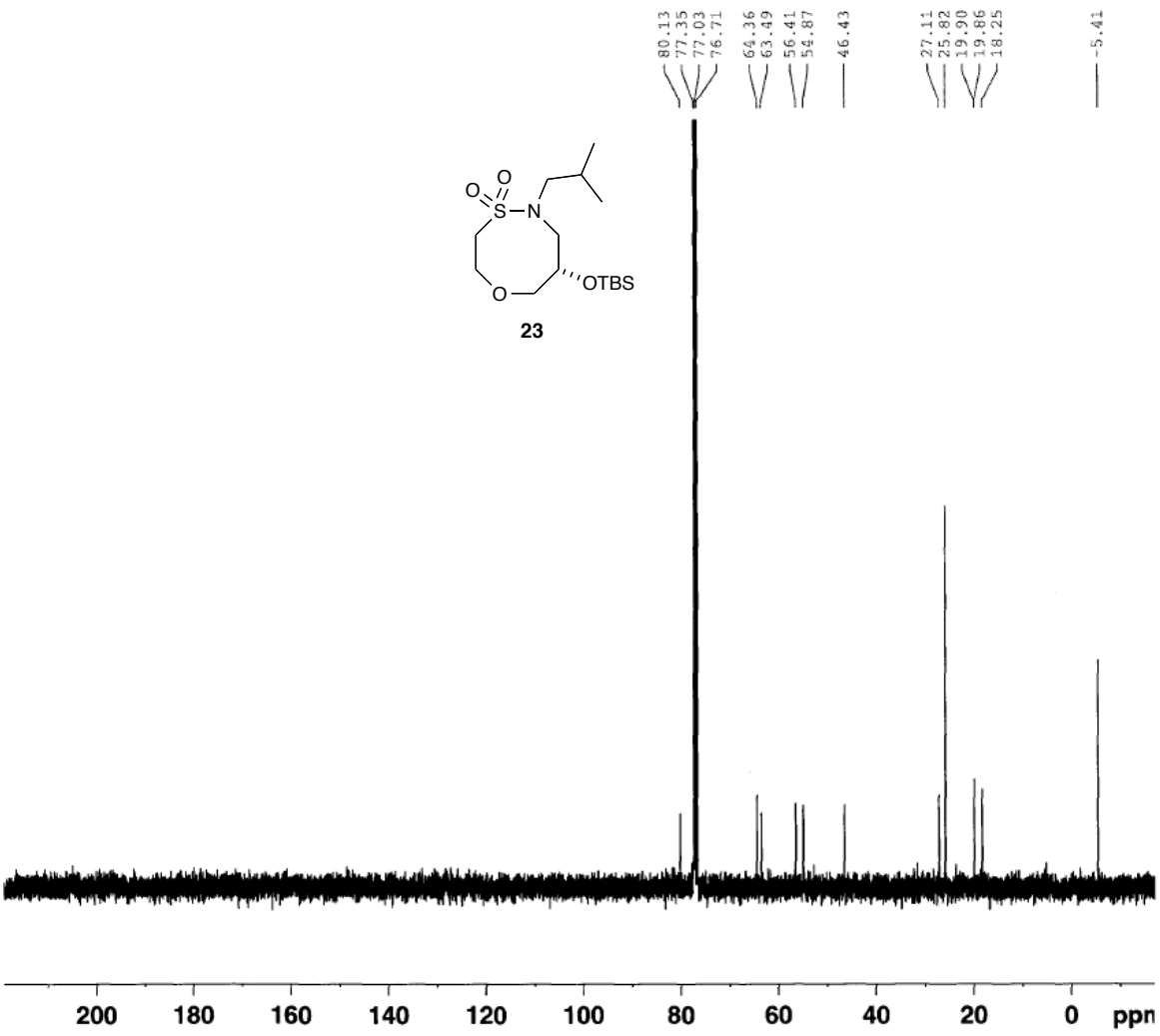

O
O
S
N
HO
OTBS
8
7
6
5
4
3
2
1
0
ppm
1.00
0.97
1.01
0.99
1.89
1.02
0.95
1.03
1.19
15.60
5.88

22

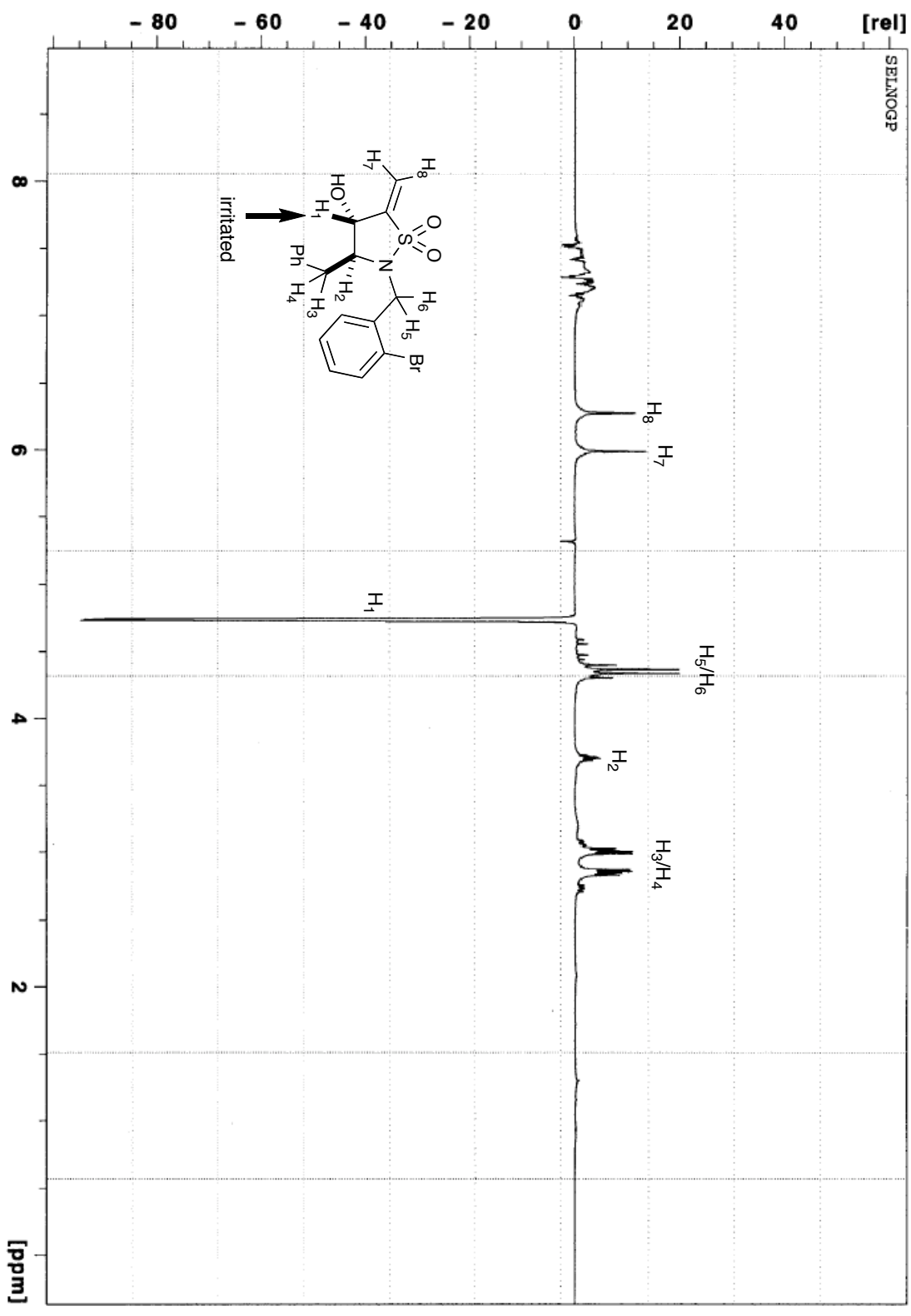

143.42
118.12
116.91
77.28
77.03
76.78
75.35
74.88
73.08
72.68
56.95
56.43
51.09
49.74
31.61
28.24
28.16
25.76
25.64
22.68
19.92
19.87
18.20
17.94
14.15
-4.64
-4.71
-4.89
O
O
S
N
HO
OTBS
22
200
180
160
140
120
100
80
60
40
20
0
ppm



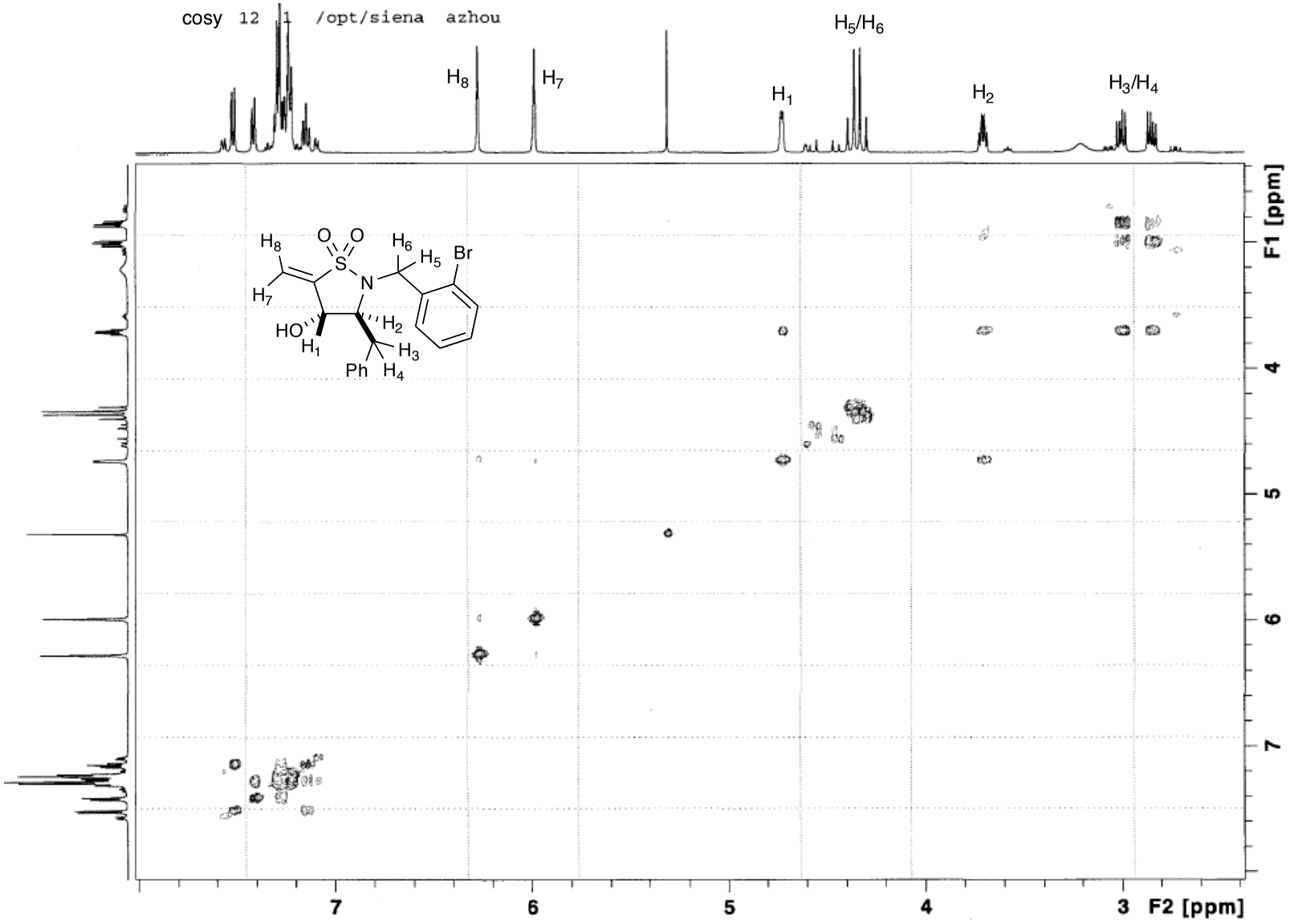
23


80.13
77.35
77.03
76.71
64.36
63.49
56.41
54.87
46.43
27.11
25.82
19.90
19.86
18.25
-5.41
O
O
S
N
O
OTBS
23
200
180
160
140
120
100
80
60
40
20
0
ppm

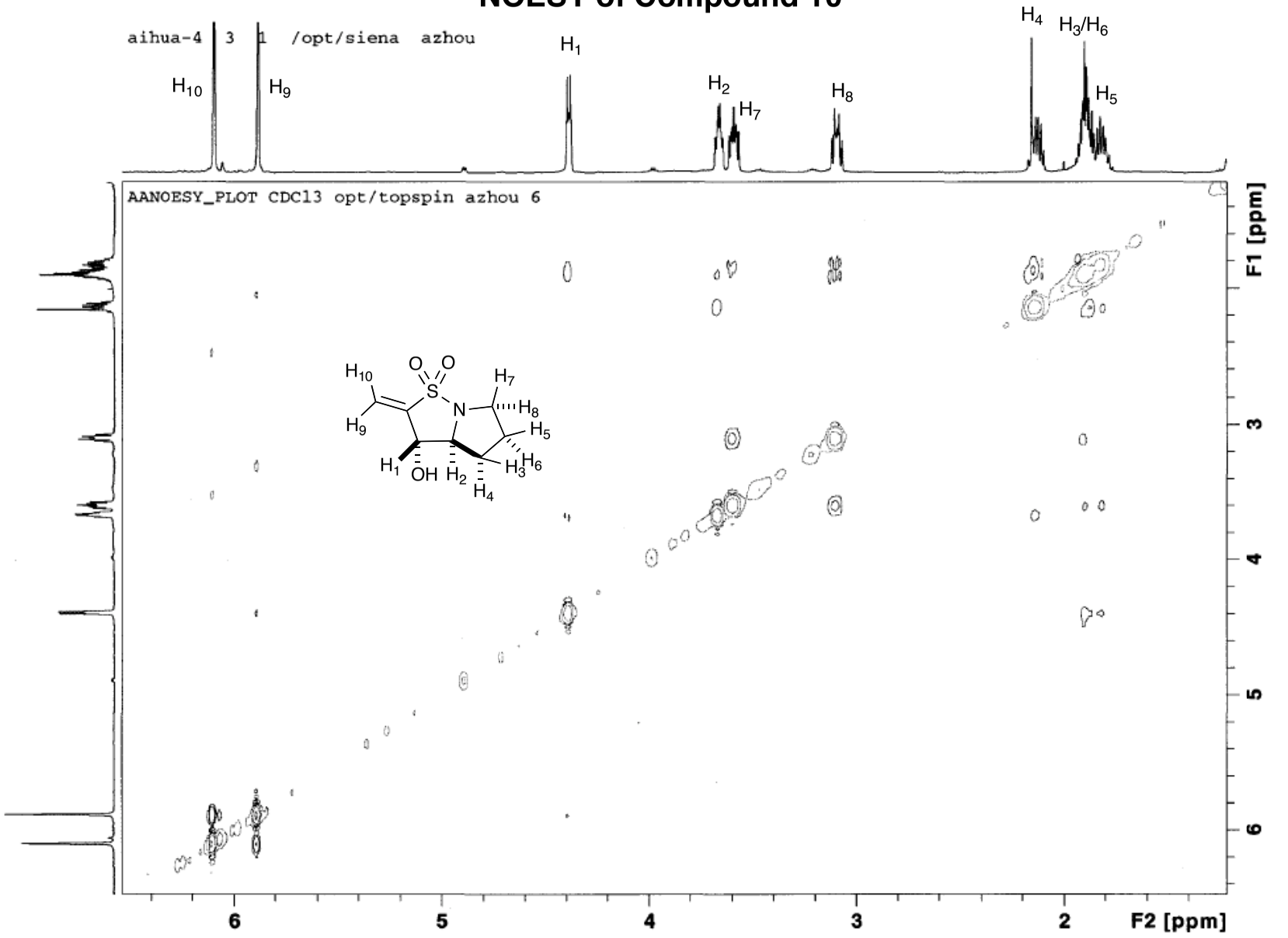
1D-NOE-difference of Compound 5b



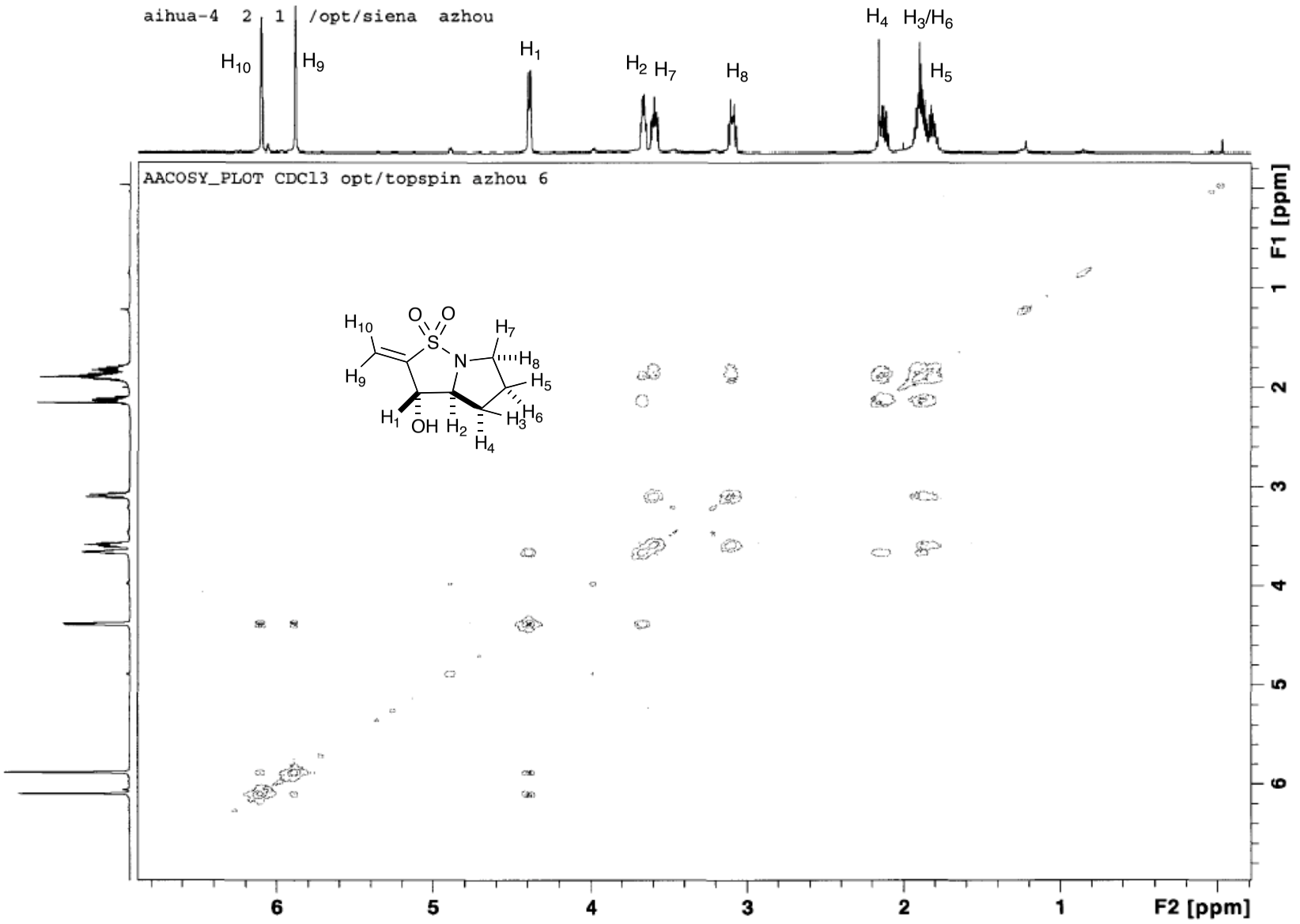
COSY of Compound 5b



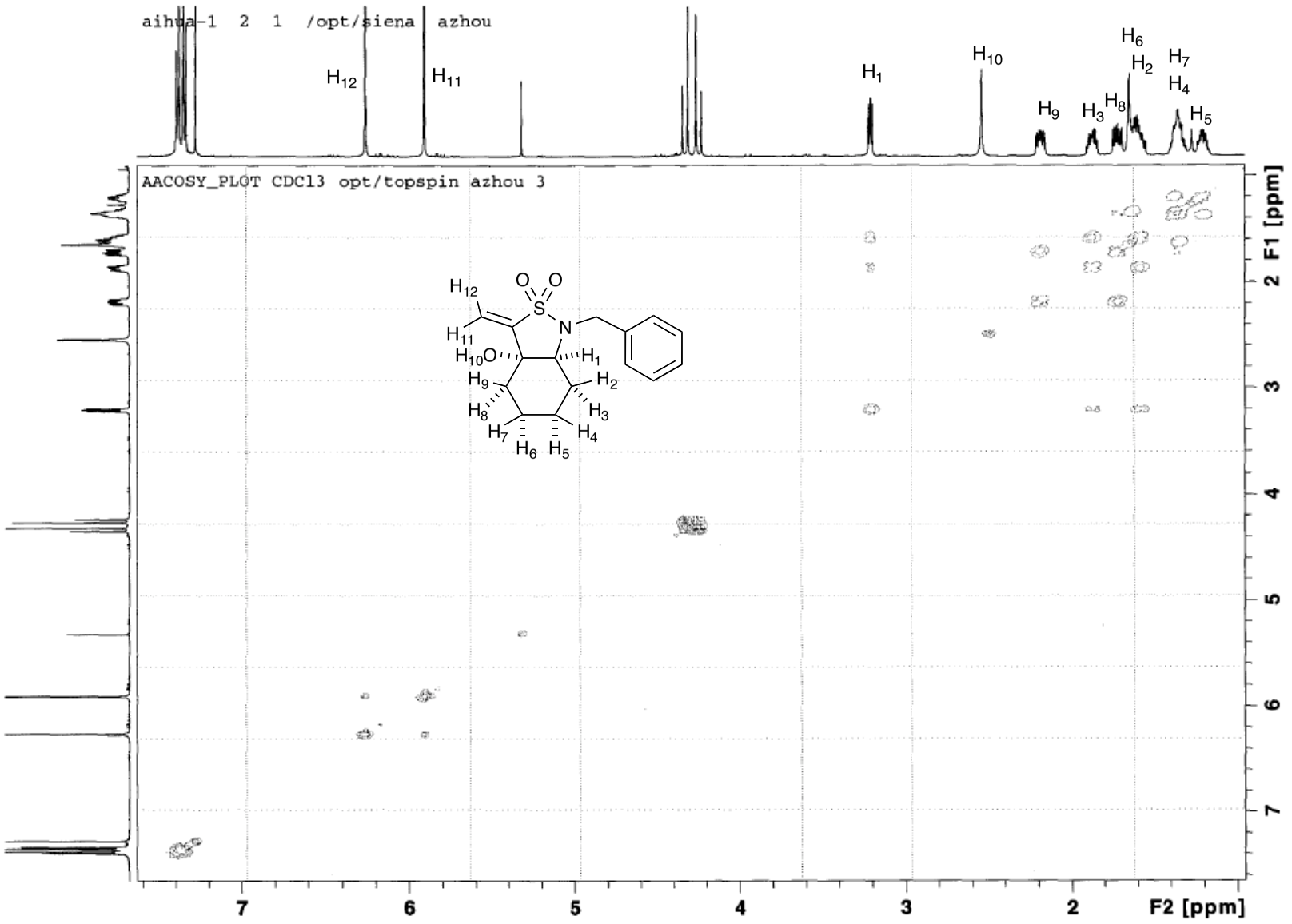
NOESY of Compound 10

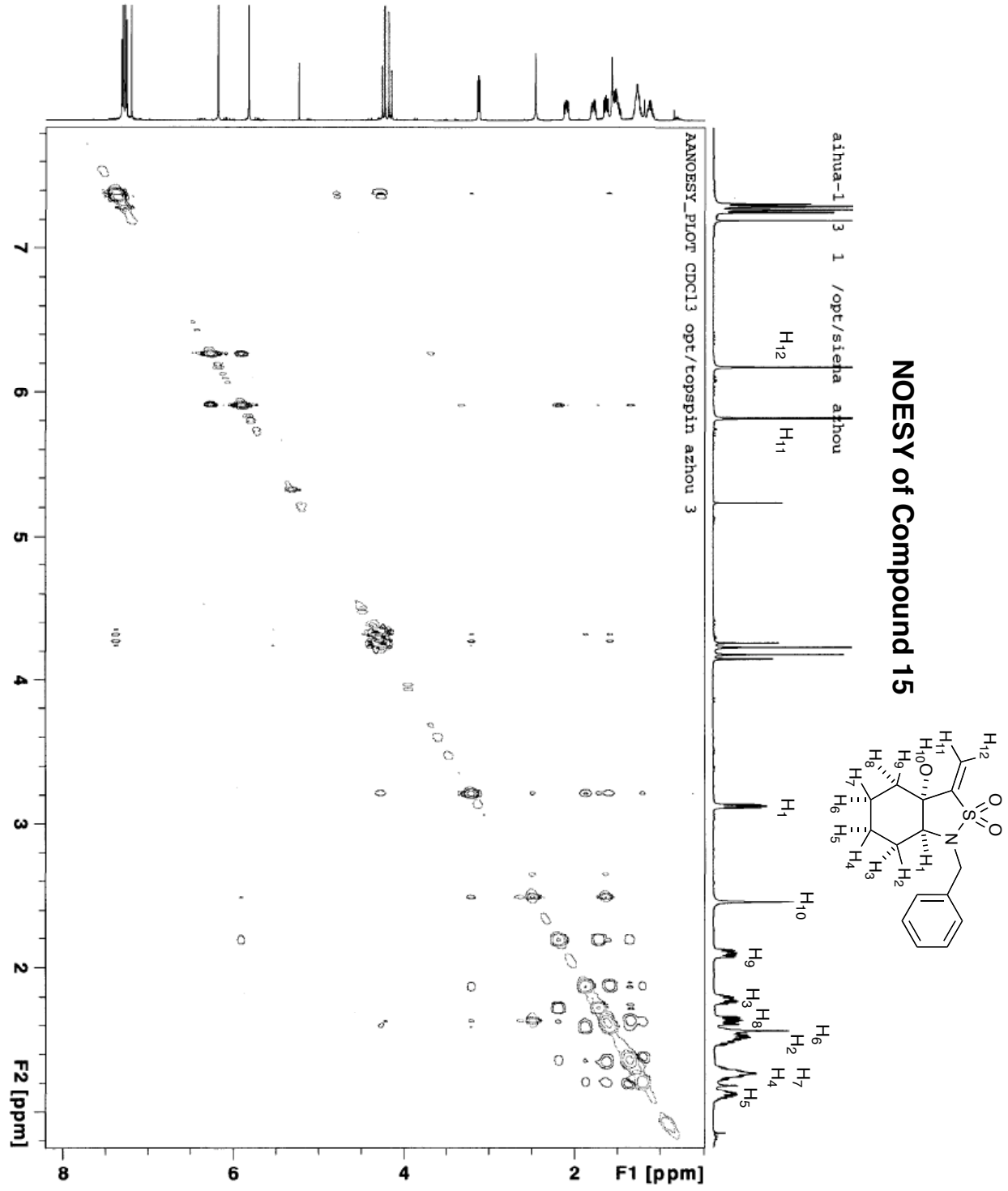


COSY of Compound 10

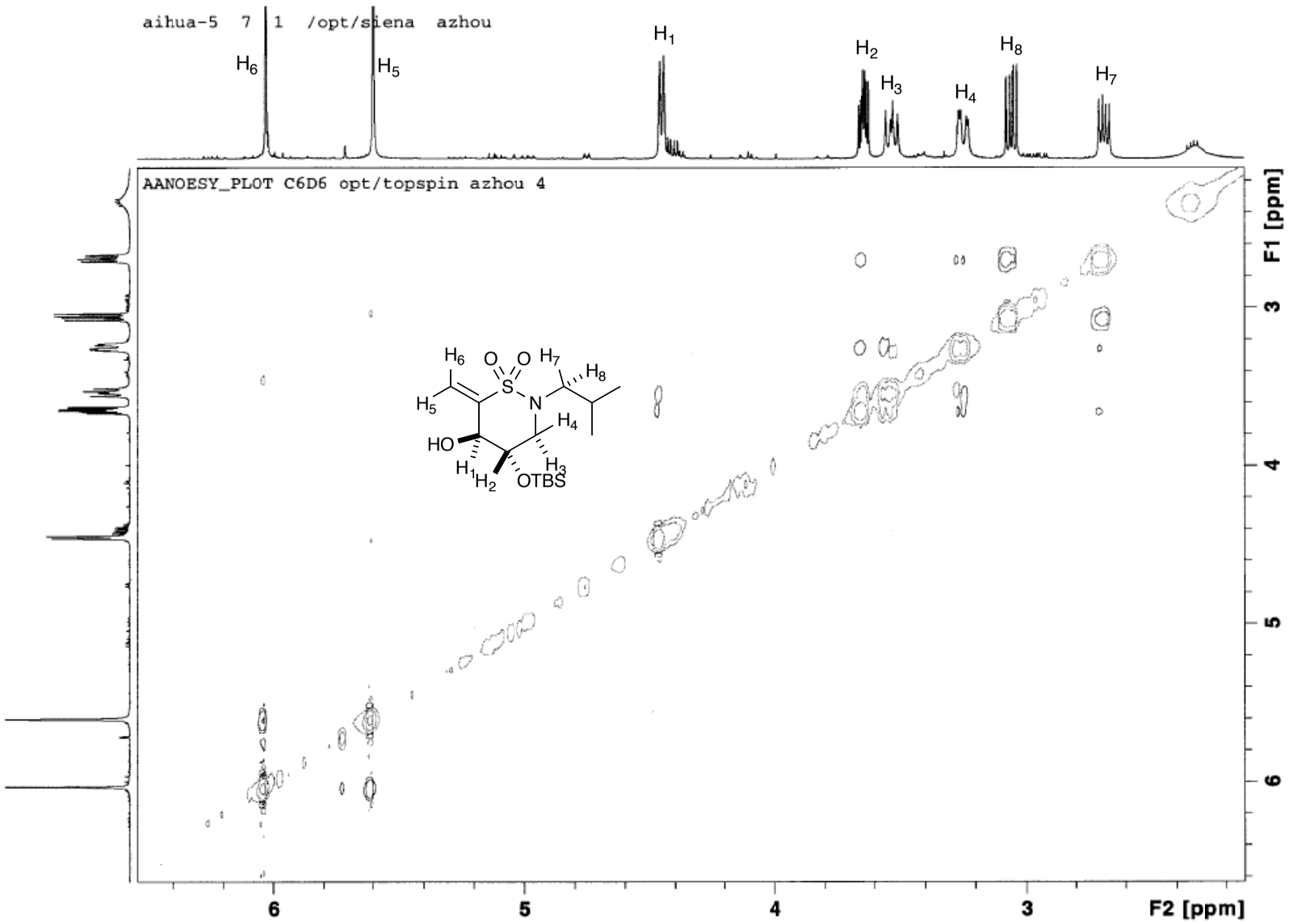


COSY of Compound 15




NOESY of Compound 15
aihua-1 3 1 /opt/siena azhou
AANOESY_PLOT CDCl3 opt/topspin azhou 3
F1 [ppm]
F2 [ppm]
H12
H11
H1
H10
H9
H3
H8
H6
H2
H7
H4
H5

NOESY of Compound 22 (Benzene-d_6 was used as a solvent)



COSY of Compound 22 (benzene-d_6 was used as a solvent)