Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Straightforward access to 4-membered sulfurated heterocycles: introducing a strategy for the single and double functionalization of thietane 1-oxide

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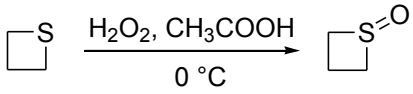
General

THF was freshly distilled under a nitrogen atmosphere over Na/benzophenone, Toluene was freshly distilled under a nitrogen atmosphere over CaH_2. Diisopropylamine (DIPA) was distilled over finely powdered CaH_2, *n*-butyllithium was purchased as hexane solution and the title established by titration method.[1] All the other chemicals were commercially available and used without further purification. Magnetic Resonance spectra were recorded using Varian 400 and 500 MHz, and Bruker 500 and 600 MHz spectrometers. For the ^{1}H, ^{13}C NMR spectra (^{1}H NMR 400, 500, 600 MHz, ^{13}C NMR 100, 125, 150 MHz), $CDCl_3$, methanol-d_4 and toluene-d_8 were used as the solvents. MS-ESI analyses were performed on AGILENT 1100 SERIES LC/MSD trap system VL. Melting points were uncorrected. GC-MS spectrometry analyses were carried out on AGILENT 6850 SERIES II NETWORK GC-Sistem (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector AGILENT 5973 operating at 70 eV (EI). Analytical thin layer chromatography (TLC) was carried out on precoated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aq. sulphuric acid and heating to 200 °C for some time until blue spots appear. Infrared spectra were recorded neat, as film or as KBr disc as indicated, by a Perkin-Elmer 283 spectrometer. For flash chromathography silica Gel 60, 0.04-0.063 mm particle size was used. CHN analyses were performed on a EuroEA 3000 analyzer. All reactions involving air-sensitive reagents were performed under argon in oven-dried glassware using syringe septum cap technique.

General procedure for synthesis of thietane 1-oxide

Thietane 1-oxide was prepared as shown in Scheme 1, following a reported procedure.[2]



Scheme1

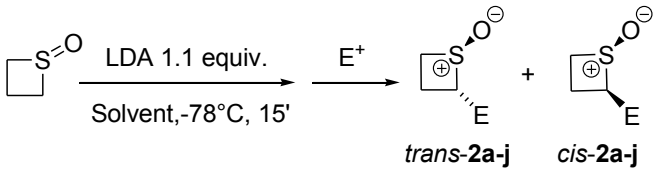
To a solution of commercially available trimethylene sulfide (26.8 mmol, 1.79 mL, 1 equiv.) in glacial acetic acid (7.2 mL, 5.4 equiv.) at 0 °C, H_2O_2 (35 wt %) (34.84 mmol, 1.05 mL, 1.3 equiv.) was added dropwise. After 3 hours at 0 °C NaOH in pellets was slowly added to neutralise the excess of CH_3COOH. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and was filtered over Na_2SO_4. The organic layer was evaporated under reduced pressure. Kugelrhor distillation (110°C, 1 x 10^{-2} torr) gave the thietane 1-oxide as colorless oil (95 % yield).

[1] Suffert, J. *J. Org. Chem.* **1989**, *54*, 509-510.

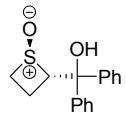
[2] Volynskii,N. P.; Shevchencko, S. E. *Petroleum Chemistry,* **2007**, *47*, 109-117.

General procedure for lithiation/electrophile trapping sequence on thietane 1-oxide

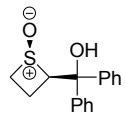
Procedure for the C2 functionalization (1 equiv of LDA)



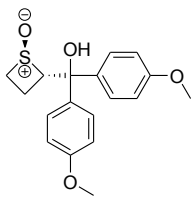
To a stirred solution of DIPA (1.1 mmol, 0.155 mL, 1.1 equiv) in 8.0 mL of THF or Toluene (depending on the solubility of the electrophile) at 0 °C, a solution of *n*-BuLi (2.5 M in hexane, 1.1 mmol, 0.440 mL, 1.1 equiv.) was added dropwise. After 20 minutes at 0 °C the solution of LDA was cooled to -78 °C and thietane 1-oxide (1.0 mmol, 90.0 mg, 1.0 equiv.) in 2.0 ml of solvent was added dropwise. After 15 minutes at -78 °C the electrophile (1.1 mmol, 1.1 equiv) neat if liquid and in 1.0 ml of solvent if solid, was added to the resulting white cloudy solution. After the reaction was complete, as determined by GC or TLC, the reaction mixture was poured in water (10 mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated in *vacuo*. Chromatography on silica gel (Hexane/AcOEt or CH_2Cl_2/MeOH) afforded the 2-substituted thietanes 1-oxide *trans*-**2a-j** and *cis*-**2a-j**.



trans-**2a** Column chromatography on silica gel (Hexane/AcOEt 70:30), white solid, 66%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.05 (q, J = 10.0 Hz, 1 H), 2.12-2.20 (m, 1 H), 2.94 (q, J = 11.0 Hz, 1 H), 3.09 (bb, 1 H), 3.36 (t, J = 9.1 Hz, 1 H), 4.36 (t, J = 11.0 Hz, 1 H), 7.23-7.25 (m, 1 H), 7.29-7.33 (m, 5 H), 7.33 (t, J = 7.7 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.1, 46.7, 75.5, 78.3, 126.0, 127.4, 127.5, 128.2, 128.4, 128.9, 143.8, 144.3. FT-IR (KBr, cm^{-1}) υ 695, 1028, 1448, 3256, 3431. ESI-MS: *m/z* (rel. int.): 295 $[M+Na]^+$ (100). Anal. Calcd. for $C_{16}H_{16}O_2S$, C 70.56, H 5.92. Found: C 70.84 %, H 5.55 %.

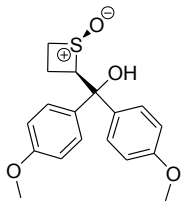


cis-**2a** Column chromatography on silica gel (Hexane/AcOEt 70:30), white solid, mp 155-158 °C, 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42-2.51(m, 1 H), 3.13-3.21 (m, 1 H), 3.29-3.39 (m, 1 H), 3.47-3.54 (m, 1 H), 4.38 (t, J = 7.6 Hz, 1 H), 5.66 (bs, 1 H), 7.10-7.32 (m, 8 H), 7.45-7.48 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.3, 47.1, 59.2, 80.2, 125.7, 125.9, 127.1, 127.6, 128.4, 128.8, 143.4, 145.4. FT-IR (KBr, cm^{-1}) υ 699, 746, 1017, 1451, 1493, 3292, 3431. ESI-MS: *m/z* (rel. int.): 295 $[M+Na]^+$ (100).

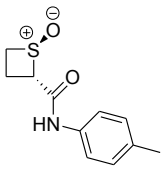


trans-**2b** Column chromatography on silica gel (Hexane/AcOEt 40:60), white solid, mp 100-102 °C, 21%. ^{1}H NMR (600 MHz, CD_3COCD_3) δ 2.05-2.15 (m, 2 H), 2.80-2.85 (m, overlapping s CH_3COCH_3, 1 H), 3.32-3.35 (m, 1 H), 3.74 (s, 6 H), 4.31-4.35 (m, 1 H), 4.94 (bs, OH, 1 H), 6.82-6.84 (m, 4 H), 7.31 (d, J = 7.3, 2 H), 7.42 (d, J = 7.4, 2 H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 13.6, 47.0, 55.5, 77.1, 77.8, 114.0$_6$, 114.0$_8$, 128.2, 129.4, 138.5, 159.6. FT-IR (KBr, cm^{-1}) υ 587, 837, 1172, 1181, 1250, 1508, 1608, 2837, 2962, 3299. ESI-MS: *m/z* (rel. int.): 355 $[M+Na]^+$ (100). Anal.Calcd. for $C_{18}H_{20}O_4S$, C

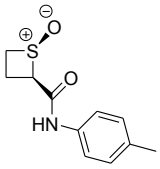
64.65, H 6.06, Found: C 64.86, H 6.14.



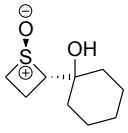
cis-**2b** Column chromatography on silica gel (Hexane/AcOEt 40:60), white solid, mp 93-95 °C, 52%. ^{1}H NMR (600 MHz, CD_3COCD_3) δ 2.55-2.61 (m, 1 H), 2.89-2.94 (m, 1 H), 3.42-3.49 (m, 1 H), 3.58-3.63 (m, 1 H), 3.71 (s, 3 H), 3.75 (s, 3 H), 4.69 (t, J = 4.7Hz, 1 H), 6.10 (bs, OH, 1 H), 6.80 (d, J = 6.8 Hz, 2 H), 6.87 (d, J = 6.9 Hz, 2 H), 7.28 (d, J = 7.3 Hz, 2 H), 7.50 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 22.1, 45.5, 55.4, 55.5, 58.7, 80.3, 114.2, 114.5, 127.5, 127.9, 137.4, 139.4, 159.4, 159.7. FT-IR (KBr, cm^{-1}) υ 540, 831, 1027, 1256, 1301, 1466, 1513, 1603, 2958, 3444. ESI-MS: *m/z* (rel. int.): 355 $[M+Na]^+$ (100). Anal.Calcd. for $C_{18}H_{20}O_2S$, C 65.04 , H 6.06; Found: C 65.03 , H 6.19.



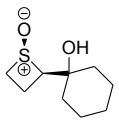
trans-**2c** Column chromatography on silica gel (AcOEt), white solid , mp 148-149 °C, 37%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3 H), 2.48-2.54 (m, 1 H), 2.61 (dq, J = 8.2, 12.9 Hz, 1 H), 3.10-3.15 (m, 1 H), 3.53 (t, J = 9.0 Hz, 1 H), 4.31 (t, J = 10.7 Hz, 1 H), 7.11 (t, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.3 Hz, 2 H), 9.00 (bs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.8, 20.8, 47.9, 69.4, 119.9, 129.4, 134.3, 135.1, 164.3. FT-IR (KBr, cm^{-1}) υ 814, 1071, 1133, 1252, 1513, 1543, 1607, 1679, 3127, 3196, 3262, 3293. ESI-MS: *m/z* (rel. int.): 246 $[M+Na]^+$ (100). Anal.Calcd. for $C_{11}H_{13}NO_2S$, C 59.17, N 6.27, H 5.87; Found: C 59.21, N 6.12, H 6.06.



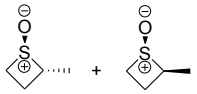
cis-**2c** Column chromatography on silica gel (AcOEt), white solid, mp 144-146 °C, 28%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.21-2.28 (m overlapping s at 2.28, 1 H), 2.28 (s, 3 H), 2.86-2.92 (m, 1 H), 2.55-3.62 (m, 2 H), 4.24-4.28 (m, 1 H), 7.05 (d, J = 8.1 Hz, 2 H), 7.45 (d, J = 8.3 Hz, 2 H), 9.19 (bs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.0, 20.8, 51.4, 59.9, 120.2, 129.3, 134.2, 135.1, 154.0. FT-IR (KBr, cm^{-1}) υ 822, 1050, 1514, 1541, 1608, 1667, 1682, 3125, 3317, 3453. ESI-MS: *m/z* (rel. int.): 246 $[M+Na]^+$ (100).



trans-**2d** Column chromatography on silica gel (Hexane/ AcOEt 20:80), white solid, mp 99 °C dec., 62%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.23-1.37 (m overlapping t, J = 7.3 Hz, at 1.35 AcOEt, 1 H), 1.51-1.64 (m, 8 H), 1.76-1.83 (m, 1 H), 2.07 (ddd, J = 8.1, 12.4, 24.6 Hz, 1 H), 2.29 (q, J = 10.7 Hz, 1 H), 2.95 (q, J = 10.7 Hz, 1 H), 3.37-3.40 (m, 2 H), 3.45-3.49 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.3, 21.6, 25.4, 34.5, 35.6, 46.8, 70.8, 77.6. FT-IR (KBr, cm^{-1}) υ 611, 1043, 1425, 1567, 2847, 2930, 3391. GC-MS (70 eV) *m/z (%)* 188 [M^+, 2], 170 (13), 137 (16), 125 (33), 112 (28), 99 (36), 97 (37), 81 (69), 74 (56), 69 (31), 55 (100), 41 (46). Anal.Calcd. for $C_9H_{16}O_2S$, C 57.41, H 8.57. Found: C 57.17 %, H 8.77 %.

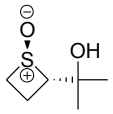


cis-**2d** Column chromatography on silica gel (Hexane/AcOEt 20:80), pale yellow oil, 18%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.07-1.12 (m, 1 H), 1.23-1.30 (m, 1 H), 1.35-1.39 (m, 1 H), 1.44-1.49 (m, 1 H), 1.54-1.77 (m, 5 H), 2.02-2.05 (m, 1 H), 2.54-2.60 (m, 1 H), 3.19-3.26 (m, 1 H), 3.31-3.39 (m, 2 H), 3.53-3.58 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.1, 21.7, 25.7, 33.9, 36.7, 47.7, 61.2, 74.5. FT-IR (film, cm^{-1}) υ 941, 1019, 1035, 1170, 1409, 1447, 1651, 1857, 2932, 3411. ESI-MS: *m/z* (rel. int.): 211 $[M+Na]^+$ (100).

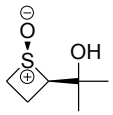


trans-**2e**, *cis*-**2e** Inseparable mixture of diastereoisomers. Column chromatography on silica gel (Methanol/AcOEt 10:90), orange oil, 76%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.44 (d, J = 6.9 Hz, 3 H, *trans*-**2e**), 1.49 (d, J = 7.3 Hz, 3 H, *cis*-**2e**), 1.58-1.66 (m, 1 H, *trans*-**2e**), 2.17-2.22 (m, 1 H, *cis*-**2e**), 2.38-2.45 (m, 1 H, *cis*-**2e**), 2.53 (q, J = 10.8 Hz, 1 H, *trans*-**2e**), 3.33-3.44 (m, 2 H, *cis*-**2e** + *trans*-**2e**), 3.49-3.52 (m, 1 H,*trans*-**2e**), 3.55-3.61 (m, 1 H, *cis*-**2e**), 3.74-3.80 (m, 1 H, *cis*-**2e**), 3.83-3.90 (m, 1 H, *trans*-**2e**). ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.0 (*cis*-**2e**), 17.2 (*trans*-**2e**), 18.5 (*trans*-**2e**), 20.9 (*cis*-**2e**), 47.9 (*trans*-**2e**), 48.3 (*cis*-**2e**), 54.1 (*cis*-**2e**), 63.2 (*trans*-**2e**). FT-IR (film, cm^{-1}) υ 1015, 1045, 1421, 1450, 1645. GC-MS (70 eV) *m/z (%)* diastereoisomer I (first

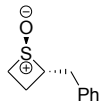
eluted) 104 [M^+, 54], 88 (9), 63 (23), 55 (100), 48 (9), 41 (30); diastereoisomer II (second eluted) 104 [M^+, 72], 63 (100), 55 (99), 45 (17), 41 (26).



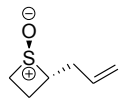
trans-**2f** Column chromatography on silica gel (AcOEt), colourless oil, 56%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25 (s, 3 H), 1.44 (s, 3 H), 1.93-2.07 (m, 1 H), 2.31-2.37 (m, 1 H), 2.92-2.97 (m, 1 H), 3.38-3.42 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 26.6, 27.6, 46.3, 69.8, 78.1. FT-IR (film, cm^{-1}) υ 736, 1046, 1134, 1195, 1266, 1379, 1464, 1633, 1721, 2927, 2970, 3370. GC-MS (70 eV) *m/z (%)* 148 [M^+, 2], 130 (7), 99 (10), 85 (24), 63 (18), 59 (35), 43 (100).



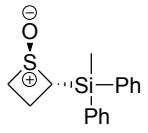
cis-**2f** Column chromatography on silica gel (AcOEt), colourless oil, 15%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.52 (s, 3 H), 2.56-2.64 (m, 1 H), 3.23-3.35 (m, 3 H), 3.55-3.60 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.4, 26.2, 28.5, 47.5, 61.9, 73.2. FT-IR (film, cm^{-1}) υ 941, 1022, 1126, 1200, 1379, 2974, 3410. GC-MS (70 eV) *m/z (%)* 148 [M^+, 2], 133 (9), 99 (12), 85 (31), 71 (46), 63 (25), 57 (33), 43 (100).



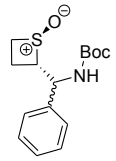
trans-**2g** Column chromatography on silica gel (Hexane/ AcOEt 70:30), orange oil, 71%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.65-1.73 (m, 1 H), 2.34-2.39 (m, 1 H), 2.95-3.02 (m, 2 H), 3.24 (dd, J = 6.3, 14.3 Hz, 1 H), 3.41-3.44 (m, 1 H), 3.61-3.67 (m, 1 H), 7.19 (d, J = 7.3 Hz, 2 H), 7.23-7.25 (m, 1 H), 7.30-7.33 (m, 2 H),^{13}C NMR (150 MHz, $CDCl_3$) δ 16.3, 37.9, 48.3, 68.8, 126.9, 128.6, 128.7, 137,0. FT-IR (film, cm^{-1}) υ 702, 752, 1054, 1454, 1495, 1638, 2942, 3027. ESI-MS: *m/z* (rel. int.): 203 $[M+Na]^+$ (100).



trans-**2h** Column chromatography on silica gel (AcOEt), yellow oil, 75%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.67 (dq, J = 7.8, 12.4 Hz, 1 H), 2.40-2.46 (m, 1 H), 2.48-2.53 (m, 1 H), 2.55-2.60 (m, 1 H), 2.99 (q, J = 10.7 Hz, 1 H), 3.42-3.50 (m, 2 H), 5.13-5.19 (m, 2 H), 5.76-5.83 (m, 1 H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.3, 36.1, 48.4, 67.6, 118.4, 132.9. FT-IR (film, cm^{-1}) υ 921, 1063, 1434, 1641, 2941, 2977. GC-MS (70 eV) *m/z (%)* 130 [M^+,2], 113 (3), 81 (100), 79 (46), 67 (30), 63 (36), 53 (27), 41 (36).



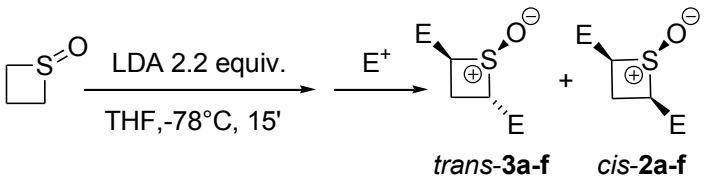
trans-**2i** Column chromatography on silica gel (Hexane/ AcOEt 90:10), colourless oil, 78%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.71(s, 3 H), 1.91-1.98 (m, 1 H), 2.42-2.48 (m, 1 H), 3.32-3.37 (m, 1 H), 3.49-3.57 (m, 2 H), 7.33-7.44 (m, 6 H), 7.52-7.56 (m, 4 H), ^{13}C NMR (150 MHz, $CDCl_3$) δ - 5.5, 13.5, 55.2, 56.5, 128.1_5, 128.1_8, 130.0_1, 130.0_6, 133.4, 133.5, 134.6_8, 134.7_0. FT-IR (film, cm^{-1}) υ 491, 700, 725, 792, 1064, 1114, 1256, 1428, 2952, 3047, 3068. ESI-MS: *m/z* (rel. int.): 309 $[M+Na]^+$ (100).



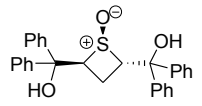
trans-**2j** minor Column chromatography on silica gel (Dichloromethane:Methanol = 95:5), white solid, 49%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.41 (s, 9 H), 1.72-1.81 (m, 1 H), 2.16-2.21 (m, 1 H), 2.98 (like q, J = 12.1 Hz, 1 H), 3.41-3.44 (m, 1 H), 3.71 (like q, J = 10.4 Hz, 1 H), 4.89-4.97 (m, 1 H), 5.75-5.76 (m, 1 H), 7.27-7.36 (m, 5 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.3, 28.3, 47.4, 56.3, 71.8, 80.1, 126.5, 128.1, 129.0, 139.0, 155.3. FT-IR (KBr, cm^{-1}) υ 703, 1055, 1174, 1252, 1365, 1543, 1704, 2979, 3241 ESI-MS: *m/z* (rel. int.): 318 $[M+Na]^+$ (100). Anal.Calcd. for $C_{15}H_{21}NO_3S$, C 60.99, H 7.17, N 4.74; Found: C 60.93, N 7.29, H 4.68. *trans*-**2k** major Column chromatography on silica gel (Dichloromethane:Methanol = 95:5), white solid, 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9 H), 1.81-1.92 (m, 1 H), 2.40-2.48 (m, 1 H), 2.90-3.03 (m, 1 H), 3.39 (like t, J = 9.8 Hz, 1 H), 3.70-3.82 (m, 1 H), 4.99-5.06 (m, 2 H), 7.28-7.41 (m, 5 H). ^{13}C NMR (150 MHz, $CDCl_3$) 14.6, 28.3, 47.7, 55.5, 72.0, 77.9, 126.4, 126.9, 128.4, 129.1, 137.7, 155.0. FT-IR (KBr, cm^{-1}) υ 701, 1051, 1170, 1367, 1540, 1701, 2981, 3238. ESI-MS: *m/z* (rel. int.): 318 $[M+Na]^+$ (100).

General procedure for lithiation-electrophile trapping sequence of thietane 1-oxide

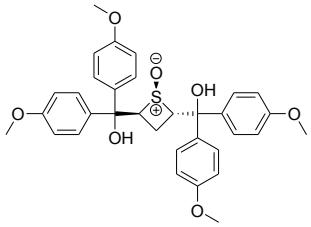
Procedure for the C2, C4 double functionalization (2 equiv of LDA).



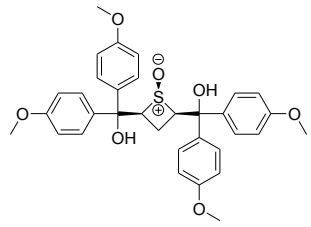
To a stirred solution of DIPA (2.2 mmol, 0.310 mL, 2.2 equiv) in 8.0 mL of THF or Toluene (depending on the solubility of the electrophile) at 0 °C, a solution of *n*-butilithium (2.5 M in hexane, 2.2 mmol, 0.880 mL, 2.2 equiv.) was added dropwise. After 20 minutes at 0 °C the solution of LDA was cooled to -78 °C and thietane 1-oxide (1.0 mmol, 90.0 mg, 1.0 equiv.) in 2.0 ml of solvent was added dropwise. After 15 minutes at -78 °C the electrophile (1.1 mmol, 1.1 equiv) neat if liquid and in 1.0 ml of solvent if solid, was added to the resulting white cloudy solution. After the reaction was complete, as determined by GC or TLC, the reaction mixture was poured in water (10 mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated in *vacuo*. Chromatography on silica gel (Hexane/AcOEt or CH_2Cl_2/MeOH) afforded the 2,4-disubstituted thietanes-1-oxide *trans*-**3a-f** and *cis*-**3a-f**.



trans-**3a** Column chromatography on silica gel (Hexane/AcOEt 70:30), white solid, mp 219-222 °C, 70%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.50 (ddd, J = 7.3, 9.8, 13.3 Hz, 1 H), 2.79 (bs, 1 H), 3.03 (ddd, J = 7.0, 11.5, 13.2 Hz, 1 H), 4.29 (2 x d, AB system, J = 7.3 Hz, 2 H), 5.72 (bb, 1 H), 7.08 (t, J = 7.3 Hz,1 H), 7.13-7.28 (m, 15 H), 7.44 (d, J = 7.6 Hz, 2 H), 7.35 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 53.7, 70.6, 78.6, 79.9, 125.5, 125.6, 125.8, 126.3, 126.9, 127.3, 127.7, 128.1, 128.5, 128.8, 128.7, 143.1, 143.5, 143.6, 145.7. FT-IR (KBr, cm^{-1}) υ 699, 753, 1031, 1065, 1448, 1493, 2955, 3059, 3368. ESI-MS: *m/z* (rel. int.): 477 $[M+Na]^+$ (100). Anal.Calcd. for $C_{29}H_{26}O_3S$, C 76.62, H 5.76; Found: C 76.58 %, H 5.79 %.

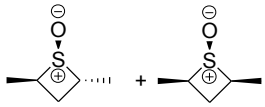


trans-**3b,** Column chromatography on silica gel (Hexane/AcOEt 60:40), white solid, 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55-2.63 (m, 1 H), 3.16-3.24 (m, 1 H), 3.71 (s, 3 H), 3.75 (s, 3 H), 3.76 (s, 6 H), 4.23-4.27 (m, 1 H), 4.41-4.46 (m, 1 H), 5.33 (bs, 1 H), 6.15 (bs, 1 H), 6.80 (d, J = 9.1 Hz, 2 H), 6.84-6.89 (m, 6 H), 7.29-7.34 (m, 4 H), 7.43 (d, J = 9.0 Hz, 2 H), 7.49 (d, J = 9.5 Hz, 2 H) . ^{13}C NMR (100 MHz, CD_3COCD_3) δ 23.0, 53.6, 55.55, 55.59, 55.62, 72.1, 78.6, 80.4, 114.3, 114.4, 114.5, 114.6, 127.7, 127.9, 128.4, 128.7, 137.7, 138.0, 140.0, 140.3, 159.5, 159.7, 159.9, 160.0. FT-IR (KBr, cm^{-1}) υ 825, 1022, 1174, 1508, 2853, 2927, 3368. ESI-MS: *m/z* (rel. int.): 597 $[M+Na]^+$ (100). Anal.Calcd. for $C_{33}H_{34}O_7S$, C 68.97, H 5.96,; Found: C 68.88 %, H 6.13 %.

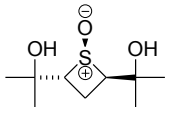


cis-**3b** Column chromatography on silica gel (Hexane/AcOEt 60:40), white solid, mp 115-118 °C, 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51-2.56 (m, 1 H), 3.72 (s, 6 H), 3.75 (s, 6 H), 3.92 (dd, J = 11.3, 7.5 Hz, 2 H), 4.69 (q, J = 11.6 Hz, 1 H), 5.42 (bs, 2 OH, 2 H), 6.76 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 7.22 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 26.1, 54.96, 55.46, 80.0, 100.9, 114.2, 114.6, 127.5, 127.9,

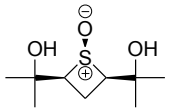
137.3, 138.6, 159.6, 159.9 . FT-IR (KBr, cm^{-1}) υ 831, 1033, 1095, 1176, 1254, 1509, 1608, 2959, 3435. ESI-MS: *m/z* (rel. int.): 597 $[M+Na]^+$ (100).



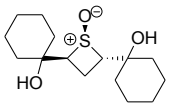
trans-**3c**, *cis*-**3c** Inseparable mixture of diastereoisomers. Column chromatography on silica gel (MeOH/AcOEt 15:85), red oil, 77%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.28 (d, J = 7.0 Hz, 6 H, *cis*), 1.45 (d, J = 6.9 Hz, 3 H, *trans*), 1.50 (d, J = 7.3 Hz, 3 H, *trans*), 1.97 (ddd, J = 8.2, 11.6, 12.8 Hz, 3 H, *trans*), 2.21-2.26 (m, 1 H, *trans*), 2.52 (td, J = 9.6, 12.3 Hz, 1 H, *cis*), 3.01 (td, J = 7.7, 12.3 Hz, 1 H, *cis*), 3.44-3.50 (m, 2 H, *cis*), 3.55-3.69 (m, 2 H, *trans*). ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.7, 12.4, 16.9, 27.0, 37.0, 48.3, 49.5, 59.6. FT-IR (film, cm^{-1}) υ 981, 1032, 1449, 1644 . GC-MS (70 eV) *m/z (%)* diastereoisomer I (first eluted) 118 [M^+, 23], 77 (100), 69 (87), 59 (53), 45 (91), 41 (60); diastereoisomer II (second eluted) 118 [M^+, 12], 77 (100), 69 (62), 59 (47), 41 (70), 43 (33).



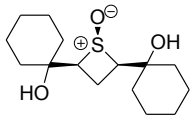
trans-**3c** Column chromatography on silica gel (AcOEt), white solid, mp 116-118 °C, 40%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.16 (s, 3 H), 1.21 (s, 3 H), 1.40 (s, 3 H), 1.52 (s, 3 H), 2.47 (dt, J = 13.9, 9.5, 7.5 Hz, 1 H), 2.87-2.92 (m, 1 H), 3.15-3.20 (m, 1 H), 3.56-3.59 (m overlapping bs at 3.59 ppm, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.7, 26.4, 28.2, 55.8, 72.7. FT-IR (KBr, cm^{-1}) υ 602, 938, 972, 1001, 1131, 1221, 1358, 1373, 1384, 1463, 2975, 3430, 3461. GC-MS (70 eV) *m/z (%)* 206 [M^+, 25], 139 (68), 97 (31), 85 (33), 72 (56), 59 (100). Anal.Calcd. for $C_9H_{18}O_3S$, C 52.40, H 8.79; Found: C 52.22, H 8.90.



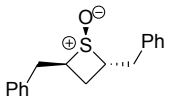
cis-**3c** Column chromatography on silica gel (Ethyl Acetate), white solid, mp 150-152 °C, 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.51 (s, 3 H), 2.90 (dt, J = 11.9, 7.5 Hz, 1 H), 3.06 (dd, J = 11.1, 7.8 Hz, 1 H), 4.44 (q, J = 11.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 26.4, 28.2, 55.8, 72.7. FT-IR (KBr, cm^{-1}) υ 602, 938, 972, 1001, 1131, 1221, 1358, 1373, 1384, 1463, 2975, 3430, 3461. GC-MS (70 eV) *m/z (%)* 206 [M^+, 0.16], 173 (13), 139 (54), 113 (19), 97 (18), 85 (31), 72 (34), 59 (100). Anal.Calcd. for $C_9H_{18}O_3S$, C 52.40, H 8.79; Found: C 52.09, H 8.68.



trans-**3e** Column chromatography on silica gel (Hexane/AcOEt 20:80), white solid, mp 194-196 °C, 57%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.13-1.17 (m, 1 H), 1.27-1.42 (m overlapping t, J = 7.3 Hz at 1.23 AcOEt, 5 H), 1.45-1.76 (m, 14 H), 1.76-1.81 (m, 1 H), 2.09-2.11 (m, 1 H), 2.47 (td, J = 9.4, 12.9 Hz, 1 H), 2.90 (td, J = 5.5, 12.7 Hz, 1 H), 3.24 (dd, J = 5.4, 9.7, 1 H), 3.66 (t, J = 10.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 21.2, 21.5, 21.6, 25.1, 25.7, 33.8, 34.0, 35.0, 37.2, 56.5, 71.0, 73.9, 74.4. FT-IR (KBr, cm^{-1}) υ 600, 962, 978, 992, 1260, 1405, 1446, 2852, 2932, 3350. ESI-MS: *m/z* (rel. int.): 309 $[M+Na]^+$ (100). Anal.Calcd. for $C_{15}H_{26}O_3S$, C 62.90, H 9.15,; Found: C 62.76 %, H 9.01 %.

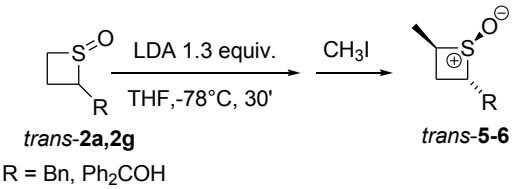


cis-**3e** Column chromatography on silica gel (Hexane/AcOEt 20:80), white solid, mp 218 °C dec., 21%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10-1.15 (m, 2 H), 1.24-1.30 (m, 3 H), 1.34-1.40 (m, 2 H), 1.45-1.68 (m, 12 H), 1.72-1.79 (m, 2 H), 1.90-1.92 (m, 2 H), 2.80-2.85 (m, 1 H), 3.11 (dd, J = 7.7, 11.3, 2 H), 4.45-4.47 (q, J = 11.5, 1 H),. ^{13}C NMR (100 MHz, $CDCl_3$) δ20.8, 21.6, 24.7, 25.4, 30.9, 34.3, 36.2, 55.6, 73.7. FT-IR (KBr, cm^{-1}) υ 531, 943, 970, 994, 1174, 1409, 1444, 2850, 2930, 3423. ESI-MS: *m/z* (rel. int.): 309 $[M+Na]^+$ (100).



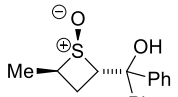
trans-**3f** Column chromatography on silica gel (Hexane/AcOEt 70:30), pale yellow solid, 70%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.88-1.93 (m, 1 H), 2.24-2.28 (m, 1 H), 2.88 (dd, J = 10.1, 14.5 Hz, 1 H), 2.93 (dd, J = 8.4, 14.3 Hz, 1 H), 3.18 (dd, J = 6.6, 14.3 Hz, 1 H), 3.33 (dd, J = 5.5, 14.5 Hz, 1 H), 3.54-3.58 (m, 1 H), 3.65-3.73 (m, 1 H), 7.12-7.26 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 31.8, 38.0, 55.0, 65.0, 126.8, 127.1, 128.8, 128.9, 129.0, 129.3, 137.3, 137.8. FT-IR (film, cm^{-1}) υ 701, 738, 1069, 1263, 1453, 1495, 2961, 3053. ESI-MS: *m/z* (rel. int.): 293 $[M+Na]^+$ (100).

General procedure for lithiation-electrophile trapping sequence of 2-substituted thietane-1-oxide with 1.3 equiv of LDA:

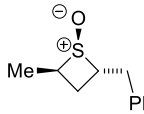


trans-**2a,2g** R = Bn, Ph_2COH *trans*-**5-6**

To a stirred solution of DIPA (2.5 mmol, 0.353 mL, 2.5 equiv for *trans*-**2a**, 1.3 mmol, 0.184 mL, 1.3 equiv for *trans*-**2g**) in 8.0 mL of THF at 0 °C, a solution of *n*-butilithium (2.5 M in hexane, 2.5 mmol, 1.0 mL, 2.5 equiv for *trans*-**2a**, 1.3 mmol, 0.520 mL, 1.3 equiv for *trans*-**2g**) was added dropwise. After 20 minutes at 0 °C the solution of LDA was cooled to -78 °C and 2-substituted thietanes-1-oxide *trans*-**2a** or *trans*-**2g** (1.0 mmol, 272.0 mg for *trans*-**2a**, 180.0 mg for *trans*-**2g,** 1.0 equiv.) in 2.0 ml of solvent was added dropwise. After 30 minutes at -78 °C the electrophile MeI (1.3 mmol, 0.081 mL, 1.3 equiv for *trans*-**2g**, 2.0 mmol, 0.125 mL, 2.0 equiv for *trans*-**2g**,) was added. After the reaction was complete, as determined by GC or TLC, the reaction mixture was poured in water (10 mL) and extracted with AcOEt (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated in *vacuo*. Chromatography on silica gel (Hexane/AcOEt) afforded the 2,4-disubstituted thietanes 1-oxide *trans*-**5** and *trans*-**6**



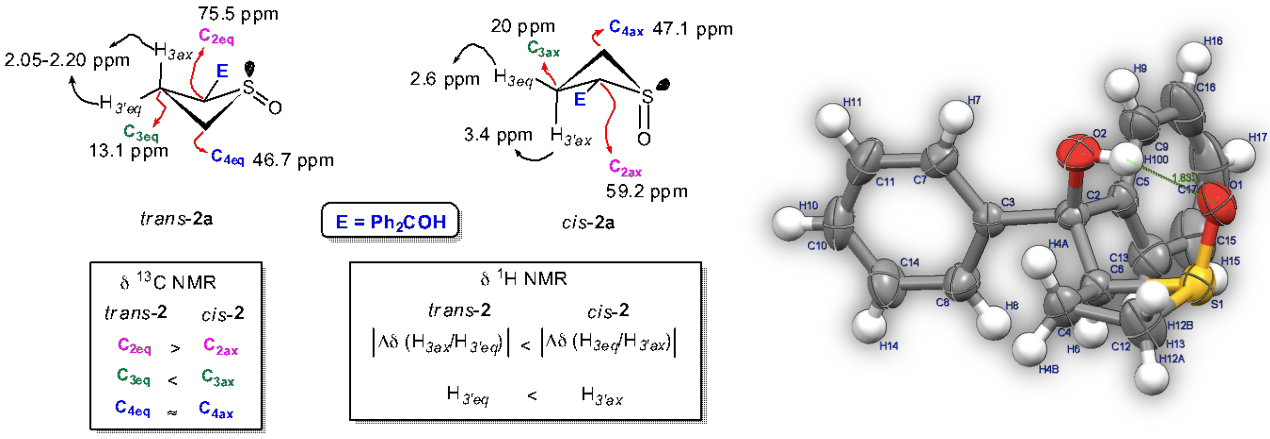
trans-**5** Column chromatography on silica gel (Hexane/AcOEt 70:30), pale yellow solid, 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.51 (d, J = 7 Hz, 3 H), 1.82 (t, J = 11 Hz, 1 H), 2.45-2.55 (m, 1 H), 2.8 (br s, OH), 3.44 (quintet, J = 7 Hz, 1 H), 4.38 (t, J = 9 Hz, 1 H), 7.20-7.25 (m, 1 H), 7.25-7.30 (m, 5 H), 7.30-7.40 (m, 2 H), 7.50-7.55 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 21.9, 47.2, 71.6, 78.4, 125.7, 127.1, 127.3, 128.0, 128.3, 128.7, 143.5, 144.3. FT-IR (film, cm^{-1}) υ 699, 747, 1002, 1035, 1170, 1447, 2953, 3317. ESI-MS: *m/z* (rel. int.): 309 $[M+Na]^+$ (100).



trans-**6** Column chromatography on silica gel (Hexane/AcOEt 70:30), pale yellow solid, 70%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.49 (d, J = 7 Hz, 3 H), 1.99-2.16 (m, 2 H), 2.98 (dd, J = 8, 14 Hz, 1 H), 3.24 (dd, J = 7, 14 Hz, 1 H), 3.52 (quintet, J = 7 Hz, 1 H), 3.69 (quintet, J = 8 Hz, 1 H), 7.10-7.37 (m, 5 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.4, 25.1, 37.9, 49.4, 64.9, 126.8, 128.6, 137.2. FT-IR (film, cm^{-1}) υ 702, 1065, 1376, 1453, 1496, 2925, 3467. ESI-MS: *m/z* (rel. int.): 195 $[M+H]^+$ (100).

Stereochemistry of C2-substituted thietane-1-oxides 2.

The stereochemistry of the mono-functionalized thietanes-1-oxides *trans*-**2** and *cis*-**2** was assigned on the basis of their ^{1}H and ^{13}C NMR data. The NMR data of *cis*-**2a**, where a crystallographic information was available, were used as reference (see Figure 1).



Ortep view of *cis*-**2a**

Figure 1

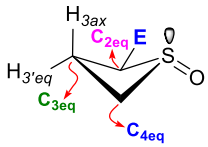
From the data available in the literature on the structure of some 3-substituted thietane-1-oxides and thiane-1-oxides,[3] and the results from our investigation, the following considerations could be made:

- The trans stereoisomer (*trans*-**eq**, Table 1) should have a pseudo-diequatorial relationship between the introduced electrophile E and the sulfinyl oxygen.
- The cis stereoisomer (*cis*-***ax***, Table 1) should have a pseudo-axial/equatorial relationship between the introduced electrophile E and the sulfinyl oxygen.
- The ^{13}C and ^{1}H NMR chemical shifts correlations reported in Table 1 fit well with that found for the reference compounds *trans*-**2a** and *cis*-**2a** (Figure 1).

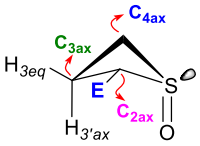
On these basis, we assigned by analogy the relative stereochemistry of derivatives *trans*-**2b-j** and *cis*-**2b-j**.

[3] a) Rasheed, K.; Warkentin, J. D. *J. Org. Chem*., **1980**, *45*, 4807. b) Rigau, J. J.; Bacon, C. C.; Johnson, C. R. *J. Org. Chem*., **1970**, *35*, 3655. c) Siegl, W. O.; Johnson, C. R. *J. Org. Chem*., **1970**, *35*, 3657. d) Buchanan, G. W. Tetrahedron Letters, **1975**, *21*, 1683.

Table 1



trans-**eq**



cis-**ax**

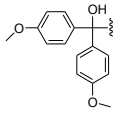
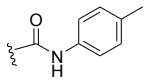
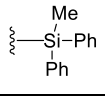
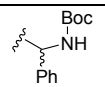
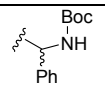
□ ^{13}C NMR

trans-**eq**		*cis*-**2**
C_{2eq}	>	C_{2ax}
C_{3eq}	<	C_{3ax}
C_{4eq}	□	C_{4ax}

□ ^{1}H NMR

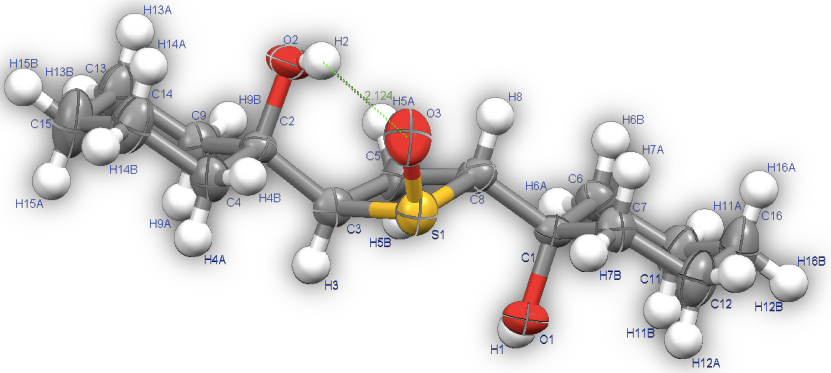
trans-**eq**		*cis*-**ax**
$\lvert$□□ ($H_{3ax}/H_{3'eq}$)$\rvert$	<	$\lvert$□□ ($H_{3eq}/H_{3'ax}$)$\rvert$

$H_{3'eq}$ < $H_{3'ax}$

E	*trans*-**eq**		*cis*-**ax**	
	C_{2eq}	75.5	C_{2ax}	59.2
	C_{4eq}	46.7	C_{4ax}	47.1
	C_{3eq}	13.1	C_{3ax}	20.3
	$H_{3ax}/H_{3'eq}$	2.0; 2.2	H_{3eq}	2.5
			$H_{3'ax}$	3.3
	C_{2eq}	77.1	C_{2ax}	55.4
	C_{4eq}	47.0	C_{4ax}	45.5
	C_{3eq}	13.6	C_{3ax}	22.1
	$H_{3ax}/H_{3'eq}$	2.0; 2.2	H_{3eq}	2.5
			$H_{3'ax}$	3.5
	C_{2eq}	69.4	C_{2ax}	59.9
	C_{4eq}	47.9	C_{4ax}	51.4
	C_{3eq}	12.8	C_{3ax}	15.0
	$H_{3ax}/H_{3'eq}$	2.4; 2.6	H_{3eq}	2.2
			$H_{3'ax}$	2.9
	C_{2eq}	70.8	C_{2ax}	61.2
	C_{4eq}	46.8	C_{4ax}	47.7
	C_{3eq}	11.3	C_{3ax}	19.1
	$H_{3ax}/H_{3'eq}$	2.1; 2.3	H_{3eq}	2.5
			$H_{3'ax}$	3.3
	C_{2eq}	63.2	C_{2ax}	54.1
	C_{4eq}	47.9	C_{4ax}	48.3
	C_{3eq}	18.5	C_{3ax}	20.9
	$H_{3ax}/H_{3'eq}$	1.6; 2.5	H_{3eq}	2.2
			$H_{3'ax}$	2.4
	C_{2eq}	69.8	C_{2ax}	61.9
	C_{4eq}	46.3	C_{4ax}	47.5
	C_{3eq}	11.9	C_{3ax}	19.4
	$H_{3ax}/H_{3'eq}$	1.9; 2.4	H_{3eq}	2. 6
			$H_{3'ax}$	3.3
	C_{2eq}	68.8		-
	C_{4eq}	48.3		
	C_{3eq}	16.3		
	$H_{3ax}/H_{3'eq}$	1.7; 2.4		
	C_{2eq}	67.6		-
	C_{4eq}	48.4		
	C_{3eq}	16.3		
	$H_{3ax}/H_{3'eq}$	1.7; 2.4		
	C_{2eq}	56.5		-
	C_{4eq}	55.2		
	C_{3eq}	13.5		
	$H_{3ax}/H_{3'eq}$	1.9; 2.5		
 minor	C_{2eq}	71.8		-
	C_{4eq}	47.4		
	C_{3eq}	15.3		
	$H_{3ax}/H_{3'eq}$	1.8; 2.2		
 major	C_{2eq}	72.3		-
	C_{4eq}	47.9		
	C_{3eq}	14.0		
	$H_{3ax}/H_{3'eq}$	1.8; 2.4		

The stereochemistry of *trans*- and *cis*- disubstituted thietanes **3** has been ascertained on the basis of the ^{1}H NMR analyisis considering that in the cis stereoisomer, for symmetry reasons, the protons at C2 and C4 are chemically equivalent while in the trans stereoisomer they are not.[4]

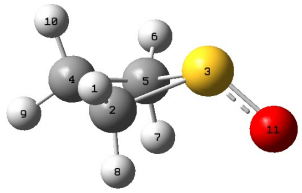
Ortep view of *trans*-**3e**



[4] Dodson, R. M.; Jancis, E. H.; Klose. G. *J. Org. Chem*., **1970**, *35*, 2520.

Thermochemical data and internal coordinates of the optimized geometries at the DFT-PCM/B3LYP/6-311++G(d,p) computational level.

1eq

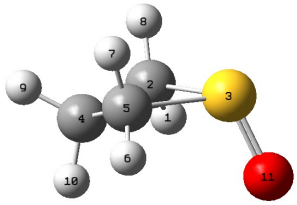



```
Sum of electronic and zero-point Energies=   -591.286311 (Hartree/Particle)
Sum of electronic and thermal Energies=       -591.281099
Sum of electronic and thermal Enthalpies=     -591.280155
Sum of electronic and thermal Free Energies= -591.314796  -371055.715861 (Kcal/mol)
```

```
                          !   Optimized Parameters   !
                          ! (Angstroms and Degrees)  !
 --------------------------                           --------------------------
 ! Name  Definition              Value          Derivative Info.                !
 ---------------------------------------------------------------------------------
 ! R1    R(1,2)                  1.089          -DE/DX =    0.0                 !
 ! R2    R(2,3)                  1.8701         -DE/DX =    0.0                 !
 ! R3    R(2,4)                  1.5408         -DE/DX =    0.0001              !
 ! R4    R(2,8)                  1.0923         -DE/DX =    0.0                 !
 ! R5    R(3,5)                  1.8701         -DE/DX =    0.0                 !
 ! R6    R(3,11)                 1.5235         -DE/DX =   -0.0001              !
 ! R7    R(4,5)                  1.5408         -DE/DX =    0.0001              !
 ! R8    R(4,9)                  1.0908         -DE/DX =    0.0                 !
 ! R9    R(4,10)                 1.092          -DE/DX =    0.0                 !
 ! R10   R(5,6)                  1.089          -DE/DX =    0.0                 !
 ! R11   R(5,7)                  1.0923         -DE/DX =    0.0                 !
 ! A1    A(1,2,3)                114.3278       -DE/DX =    0.0                 !
 ! A2    A(1,2,4)                119.3          -DE/DX =    0.0                 !
 ! A3    A(1,2,8)                111.2499       -DE/DX =    0.0                 !
 ! A4    A(3,2,4)                 89.8129       -DE/DX =    0.0                 !
 ! A5    A(3,2,8)                107.0452       -DE/DX =    0.0                 !
 ! A6    A(4,2,8)                112.8767       -DE/DX =    0.0                 !
 ! A7    A(2,3,5)                 74.999        -DE/DX =    0.0                 !
 ! A8    A(2,3,11)               112.948        -DE/DX =    0.0                 !
 ! A9    A(5,3,11)               112.948        -DE/DX =    0.0                 !
 ! A10   A(2,4,5)                 95.2683       -DE/DX =    0.0                 !
 ! A11   A(2,4,9)                115.1089       -DE/DX =    0.0                 !
 ! A12   A(2,4,10)               111.3148       -DE/DX =    0.0                 !
 ! A13   A(5,4,9)                115.1089       -DE/DX =    0.0                 !
 ! A14   A(5,4,10)               111.3148       -DE/DX =    0.0                 !
 ! A15   A(9,4,10)               108.3271       -DE/DX =    0.0                 !
 ! A16   A(3,5,4)                 89.8129       -DE/DX =    0.0                 !
 ! A17   A(3,5,6)                114.3278       -DE/DX =    0.0                 !
 ! A18   A(3,5,7)                107.0452       -DE/DX =    0.0                 !
 ! A19   A(4,5,6)                119.3          -DE/DX =    0.0                 !
 ! A20   A(4,5,7)                112.8767       -DE/DX =    0.0                 !
 ! A21   A(6,5,7)                111.2499       -DE/DX =    0.0                 !
 ! D1    D(1,2,3,5)             -144.1356       -DE/DX =    0.0                 !
 ! D2    D(1,2,3,11)             106.9059       -DE/DX =    0.0                 !
 ! D3    D(4,2,3,5)               -21.7511       -DE/DX =    0.0                 !
 ! D4    D(4,2,3,11)             -130.7096       -DE/DX =    0.0                 !
 ! D5    D(8,2,3,5)                92.1784       -DE/DX =    0.0                 !
 ! D6    D(8,2,3,11)              -16.7801       -DE/DX =    0.0                 !
 ! D7    D(1,2,4,5)               143.938        -DE/DX =    0.0                 !
```

! D8	D(1,2,4,9)	-95.1432	-DE/DX =	0.0 !
! D9	D(1,2,4,10)	28.609	-DE/DX =	0.0 !
! D10	D(3,2,4,5)	25.8674	-DE/DX =	0.0 !
! D11	D(3,2,4,9)	146.7862	-DE/DX =	0.0 !
! D12	D(3,2,4,10)	-89.4616	-DE/DX =	0.0 !
! D13	D(8,2,4,5)	-82.6007	-DE/DX =	0.0 !
! D14	D(8,2,4,9)	38.3182	-DE/DX =	0.0 !
! D15	D(8,2,4,10)	162.0703	-DE/DX =	0.0 !
! D16	D(2,3,5,4)	21.7511	-DE/DX =	0.0 !
! D17	D(2,3,5,6)	144.1356	-DE/DX =	0.0 !
! D18	D(2,3,5,7)	-92.1784	-DE/DX =	0.0 !
! D19	D(11,3,5,4)	130.7096	-DE/DX =	0.0 !
! D20	D(11,3,5,6)	-106.9059	-DE/DX =	0.0 !
! D21	D(11,3,5,7)	16.7801	-DE/DX =	0.0 !
! D22	D(2,4,5,3)	-25.8674	-DE/DX =	0.0 !
! D23	D(2,4,5,6)	-143.938	-DE/DX =	0.0 !
! D24	D(2,4,5,7)	82.6007	-DE/DX =	0.0 !
! D25	D(9,4,5,3)	-146.7862	-DE/DX =	0.0 !
! D26	D(9,4,5,6)	95.1432	-DE/DX =	0.0 !
! D27	D(9,4,5,7)	-38.3182	-DE/DX =	0.0 !
! D28	D(10,4,5,3)	89.4616	-DE/DX =	0.0 !
! D29	D(10,4,5,6)	-28.609	-DE/DX =	0.0 !
! D30	D(10,4,5,7)	-162.0703	-DE/DX =	0.0

1ax



Sum of electronic and zero-point Energies= -591.286313 (Hartree/Particle)
Sum of electronic and thermal Energies= -591.281099
Sum of electronic and thermal Enthalpies= -591.280155
Sum of electronic and thermal Free Energies= -591.314800 -371055.718371 Kcal/mol

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	
! R1	R(1,2)	1.089	-DE/DX = 0.0	!
! R2	R(2,3)	1.87	-DE/DX = 0.0	!
! R3	R(2,4)	1.5409	-DE/DX = 0.0	!
! R4	R(2,8)	1.0923	-DE/DX = 0.0	!
! R5	R(3,5)	1.87	-DE/DX = 0.0	!
! R6	R(3,11)	1.5234	-DE/DX = -0.0001	!
! R7	R(4,5)	1.5409	-DE/DX = 0.0	!
! R8	R(4,9)	1.0908	-DE/DX = 0.0	!
! R9	R(4,10)	1.092	-DE/DX = 0.0	!
! R10	R(5,6)	1.089	-DE/DX = 0.0	!
! R11	R(5,7)	1.0923	-DE/DX = 0.0	!
! A1	A(1,2,3)	114.348	-DE/DX = 0.0	!
! A2	A(1,2,4)	119.293	-DE/DX = 0.0	!
! A3	A(1,2,8)	111.2384	-DE/DX = 0.0	!
! A4	A(3,2,4)	89.838	-DE/DX = 0.0	!
! A5	A(3,2,8)	107.0315	-DE/DX = 0.0	!
! A6	A(4,2,8)	112.8706	-DE/DX = 0.0	!
! A7	A(2,3,5)	75.0289	-DE/DX = 0.0	!
! A8	A(2,3,11)	112.9653	-DE/DX = 0.0	!
! A9	A(5,3,11)	112.9653	-DE/DX = 0.0	!
! A10	A(2,4,5)	95.2921	-DE/DX = 0.0	!

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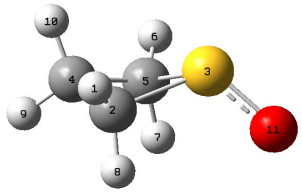
! A11   A(2,4,9)             115.1133         -DE/DX =    0.0                 !
! A12   A(2,4,10)            111.3005         -DE/DX =    0.0                 !
! A13   A(5,4,9)             115.1133         -DE/DX =    0.0                 !
! A14   A(5,4,10)            111.3005         -DE/DX =    0.0                 !
! A15   A(9,4,10)            108.3241         -DE/DX =    0.0                 !
! A16   A(3,5,4)               89.838         -DE/DX =    0.0                 !
! A17   A(3,5,6)              114.348          -DE/DX =    0.0                 !
! A18   A(3,5,7)              107.0315         -DE/DX =    0.0                 !
! A19   A(4,5,6)              119.293          -DE/DX =    0.0                 !
! A20   A(4,5,7)              112.8706         -DE/DX =    0.0                 !
! A21   A(6,5,7)              111.2384         -DE/DX =    0.0                 !
! D1    D(1,2,3,5)           -144.0391         -DE/DX =    0.0                 !
! D2    D(1,2,3,11)           106.9752         -DE/DX =    0.0                 !
! D3    D(4,2,3,5)            -21.6433         -DE/DX =    0.0                 !
! D4    D(4,2,3,11)          -130.629          -DE/DX =    0.0                 !
! D5    D(8,2,3,5)             92.2863         -DE/DX =    0.0                 !
! D6    D(8,2,3,11)           -16.6994         -DE/DX =    0.0                 !
! D7    D(1,2,4,5)            143.8456         -DE/DX =    0.0                 !
! D8    D(1,2,4,9)            -95.2144         -DE/DX =    0.0                 !
! D9    D(1,2,4,10)            28.5254         -DE/DX =    0.0                 !
! D10   D(3,2,4,5)             25.7372         -DE/DX =    0.0                 !
! D11   D(3,2,4,9)            146.6771         -DE/DX =    0.0                 !
! D12   D(3,2,4,10)           -89.5831         -DE/DX =    0.0                 !
! D13   D(8,2,4,5)            -82.7261         -DE/DX =    0.0                 !
! D14   D(8,2,4,9)             38.2138         -DE/DX =    0.0                 !
! D15   D(8,2,4,10)           161.9536         -DE/DX =    0.0                 !
! D16   D(2,3,5,4)             21.6433         -DE/DX =    0.0                 !
! D17   D(2,3,5,6)            144.0391         -DE/DX =    0.0                 !
! D18   D(2,3,5,7)            -92.2863         -DE/DX =    0.0                 !
! D19   D(11,3,5,4)           130.629          -DE/DX =    0.0                 !
! D20   D(11,3,5,6)          -106.9752         -DE/DX =    0.0                 !
! D21   D(11,3,5,7)            16.6994         -DE/DX =    0.0                 !
! D22   D(2,4,5,3)            -25.7372         -DE/DX =    0.0                 !
! D23   D(2,4,5,6)           -143.8456         -DE/DX =    0.0                 !
! D24   D(2,4,5,7)             82.7261         -DE/DX =    0.0                 !
! D25   D(9,4,5,3)           -146.6771         -DE/DX =    0.0                 !
! D26   D(9,4,5,6)             95.2144         -DE/DX =    0.0                 !
! D27   D(9,4,5,7)            -38.2138         -DE/DX =    0.0                 !
! D28   D(10,4,5,3)            89.5831         -DE/DX =    0.0                 !
! D29   D(10,4,5,6)           -28.5254         -DE/DX =    0.0                 !
! D30   D(10,4,5,7)          -161.9536         -DE/DX =    0.0                 !
```

Thermochemical data and internal coordinates of the optimized geometries at the DFT-PCM/MPW1PW91/6-311++G(d,p) computational level.

1eq




```
Sum of electronic and zero-point Energies=    -591.239157  (Hartree/Particle)
Sum of electronic and thermal Energies=        -591.234032
Sum of electronic and thermal Enthalpies=      -591.233087
Sum of electronic and thermal Free Energies=  -591.267548   -371026.0655 (Kcal/mol)
```

```
                         !   Optimized Parameters   !
                         ! (Angstroms and Degrees)  !
 --------------------------                          --------------------------
 ! Name  Definition              Value          Derivative Info.                !
 ---------------------------------------------------------------------------------
 ! R1    R(1,2)                  1.0885         -DE/DX =    0.0                 !
 ! R2    R(2,3)                  1.8458         -DE/DX =   -0.0001              !
 ! R3    R(2,4)                  1.5332         -DE/DX =    0.0002              !
 ! R4    R(2,8)                  1.0923         -DE/DX =    0.0                 !
 ! R5    R(3,5)                  1.8458         -DE/DX =   -0.0001              !
 ! R6    R(3,11)                 1.5118         -DE/DX =   -0.0001              !
 ! R7    R(4,5)                  1.5332         -DE/DX =    0.0002              !
 ! R8    R(4,9)                  1.09           -DE/DX =   -0.0001              !
 ! R9    R(4,10)                 1.0917         -DE/DX =   -0.0001              !
 ! R10   R(5,6)                  1.0885         -DE/DX =    0.0                 !
 ! R11   R(5,7)                  1.0923         -DE/DX =    0.0                 !
 ! A1    A(1,2,3)              114.7889         -DE/DX =    0.0                 !
 ! A2    A(1,2,4)              119.5823         -DE/DX =    0.0                 !
 ! A3    A(1,2,8)              111.3187         -DE/DX =   -0.0001              !
 ! A4    A(3,2,4)               89.3048         -DE/DX =   -0.0001              !
 ! A5    A(3,2,8)              107.1529         -DE/DX =    0.0001              !
 ! A6    A(4,2,8)              112.3972         -DE/DX =    0.0                 !
 ! A7    A(2,3,5)               75.3099         -DE/DX =    0.0001              !
 ! A8    A(2,3,11)             113.4481         -DE/DX =   -0.0001              !
 ! A9    A(5,3,11)             113.4481         -DE/DX =   -0.0001              !
 ! A10   A(2,4,5)               94.6869         -DE/DX =    0.0                 !
 ! A11   A(2,4,9)              115.397          -DE/DX =    0.0                 !
 ! A12   A(2,4,10)             111.2349         -DE/DX =    0.0                 !
 ! A13   A(5,4,9)              115.397          -DE/DX =    0.0                 !
 ! A14   A(5,4,10)             111.2349         -DE/DX =    0.0                 !
 ! A15   A(9,4,10)             108.4206         -DE/DX =    0.0                 !
 ! A16   A(3,5,4)               89.3048         -DE/DX =   -0.0001              !
 ! A17   A(3,5,6)              114.7889         -DE/DX =    0.0                 !
 ! A18   A(3,5,7)              107.1529         -DE/DX =    0.0001              !
 ! A19   A(4,5,6)              119.5823         -DE/DX =    0.0                 !
 ! A20   A(4,5,7)              112.3972         -DE/DX =    0.0                 !
 ! A21   A(6,5,7)              111.3187         -DE/DX =   -0.0001              !
 ! D1    D(1,2,3,5)           -145.691          -DE/DX =    0.0                 !
 ! D2    D(1,2,3,11)           104.7556         -DE/DX =    0.0001              !
 ! D3    D(4,2,3,5)            -23.129          -DE/DX =   -0.0001              !
 ! D4    D(4,2,3,11)          -132.6823         -DE/DX =    0.0                 !
 ! D5    D(8,2,3,5)             90.1398         -DE/DX =    0.0                 !
 ! D6    D(8,2,3,11)           -19.4135         -DE/DX =    0.0001              !
 ! D7    D(1,2,4,5)            145.696          -DE/DX =    0.0                 !
 ! D8    D(1,2,4,9)            -93.2874         -DE/DX =    0.0                 !
```

! D9	D(1,2,4,10)	30.7517	-DE/DX =	0.0 !
! D10	D(3,2,4,5)	27.3191	-DE/DX =	0.0 !
! D11	D(3,2,4,9)	148.3358	-DE/DX =	0.0 !
! D12	D(3,2,4,10)	-87.6251	-DE/DX =	0.0 !
! D13	D(8,2,4,5)	-80.9818	-DE/DX =	0.0 !
! D14	D(8,2,4,9)	40.0348	-DE/DX =	0.0 !
! D15	D(8,2,4,10)	164.0739	-DE/DX =	0.0 !
! D16	D(2,3,5,4)	23.129	-DE/DX =	0.0001 !
! D17	D(2,3,5,6)	145.691	-DE/DX =	0.0 !
! D18	D(2,3,5,7)	-90.1398	-DE/DX =	0.0 !
! D19	D(11,3,5,4)	132.6823	-DE/DX =	0.0 !
! D20	D(11,3,5,6)	-104.7556	-DE/DX =	-0.0001 !
! D21	D(11,3,5,7)	19.4135	-DE/DX =	-0.0001 !
! D22	D(2,4,5,3)	-27.3191	-DE/DX =	0.0 !
! D23	D(2,4,5,6)	-145.696	-DE/DX =	0.0 !
! D24	D(2,4,5,7)	80.9818	-DE/DX =	0.0 !
! D25	D(9,4,5,3)	-148.3358	-DE/DX =	0.0 !
! D26	D(9,4,5,6)	93.2874	-DE/DX =	0.0 !
! D27	D(9,4,5,7)	-40.0348	-DE/DX =	0.0 !
! D28	D(10,4,5,3)	87.6251	-DE/DX =	0.0 !
! D29	D(10,4,5,6)	-30.7517	-DE/DX =	0.0 !
! D30	D(10,4,5,7)	-164.0739	-DE/DX =	0.0

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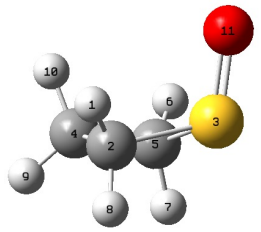


```
Sum of electronic and zero-point Energies=  -591.235365 (Hartree/Particle)
Sum of electronic and thermal Energies=     -591.230069
Sum of electronic and thermal Enthalpies=    -591.229124
Sum of electronic and thermal Free Energies= -591.264116   -371023.91367 (Kcal/mol)
```

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!
! R1	R(1,2)	1.0895	-DE/DX = 0.0	!
! R2	R(2,3)	1.8558	-DE/DX = 0.0	!
! R3	R(2,4)	1.5323	-DE/DX = 0.0	!
! R4	R(2,8)	1.0921	-DE/DX = 0.0	!
! R5	R(3,5)	1.8558	-DE/DX = 0.0	!
! R6	R(3,11)	1.5183	-DE/DX = -0.0002	!
! R7	R(4,5)	1.5323	-DE/DX = 0.0	!
! R8	R(4,9)	1.0911	-DE/DX = 0.0	!
! R9	R(4,10)	1.0902	-DE/DX = 0.0	!
! R10	R(5,6)	1.0895	-DE/DX = 0.0	!
! R11	R(5,7)	1.0921	-DE/DX = 0.0	!
! A1	A(1,2,3)	111.6808	-DE/DX = 0.0	!
! A2	A(1,2,4)	118.592	-DE/DX = 0.0	!
! A3	A(1,2,8)	110.4227	-DE/DX = 0.0	!
! A4	A(3,2,4)	92.1459	-DE/DX = 0.0	!
! A5	A(3,2,8)	108.176	-DE/DX = 0.0	!
! A6	A(4,2,8)	114.102	-DE/DX = 0.0	!
! A7	A(2,3,5)	75.1934	-DE/DX = 0.0	!

```
! A8    A(2,3,11)             108.1311         -DE/DX =    0.0001              !
! A9    A(5,3,11)             108.1311         -DE/DX =    0.0001              !
! A10   A(2,4,5)               95.2747         -DE/DX =    0.0                 !
! A11   A(2,4,9)              115.2034         -DE/DX =    0.0                 !
! A12   A(2,4,10)             111.1309         -DE/DX =    0.0                 !
! A13   A(5,4,9)              115.2034         -DE/DX =    0.0                 !
! A14   A(5,4,10)             111.1309         -DE/DX =    0.0                 !
! A15   A(9,4,10)             108.4602         -DE/DX =    0.0                 !
! A16   A(3,5,4)               92.1459         -DE/DX =    0.0                 !
! A17   A(3,5,6)              111.6808         -DE/DX =    0.0                 !
! A18   A(3,5,7)              108.176          -DE/DX =    0.0                 !
! A19   A(4,5,6)              118.592          -DE/DX =    0.0                 !
! A20   A(4,5,7)              114.102          -DE/DX =    0.0                 !
! A21   A(6,5,7)              110.4227         -DE/DX =    0.0                 !
! D1    D(1,2,3,5)           -137.8537         -DE/DX =    0.0                 !
! D2    D(1,2,3,11)           -33.2494         -DE/DX =    0.0                 !
! D3    D(4,2,3,5)            -15.8307         -DE/DX =    0.0                 !
! D4    D(4,2,3,11)            88.7736         -DE/DX =    0.0                 !
! D5    D(8,2,3,5)            100.4272         -DE/DX =    0.0                 !
! D6    D(8,2,3,11)          -154.9685         -DE/DX =    0.0                 !
! D7    D(1,2,4,5)            134.9069         -DE/DX =    0.0                 !
! D8    D(1,2,4,9)           -104.023          -DE/DX =    0.0                 !
! D9    D(1,2,4,10)            19.8314         -DE/DX =    0.0                 !
! D10   D(3,2,4,5)             18.7097         -DE/DX =    0.0                 !
! D11   D(3,2,4,9)            139.7798         -DE/DX =    0.0                 !
! D12   D(3,2,4,10)           -96.3658         -DE/DX =    0.0                 !
! D13   D(8,2,4,5)            -92.3127         -DE/DX =    0.0                 !
! D14   D(8,2,4,9)             28.7575         -DE/DX =    0.0                 !
! D15   D(8,2,4,10)           152.6118         -DE/DX =    0.0                 !
! D16   D(2,3,5,4)             15.8307         -DE/DX =    0.0                 !
! D17   D(2,3,5,6)            137.8537         -DE/DX =    0.0                 !
! D18   D(2,3,5,7)           -100.4272         -DE/DX =    0.0                 !
! D19   D(11,3,5,4)           -88.7736         -DE/DX =    0.0                 !
! D20   D(11,3,5,6)            33.2494         -DE/DX =    0.0                 !
! D21   D(11,3,5,7)           154.9685         -DE/DX =    0.0                 !
! D22   D(2,4,5,3)            -18.7097         -DE/DX =    0.0                 !
! D23   D(2,4,5,6)           -134.9069         -DE/DX =    0.0                 !
! D24   D(2,4,5,7)             92.3127         -DE/DX =    0.0                 !
! D25   D(9,4,5,3)           -139.7798         -DE/DX =    0.0                 !
! D26   D(9,4,5,6)            104.023          -DE/DX =    0.0                 !
! D27   D(9,4,5,7)            -28.7575         -DE/DX =    0.0                 !
! D28   D(10,4,5,3)            96.3658         -DE/DX =    0.0                 !
! D29   D(10,4,5,6)           -19.8314         -DE/DX =    0.0                 !
! D30   D(10,4,5,7)          -152.6118         -DE/DX =    0.0                 !
```

Thermochemical data and internal coordinates of the optimized geometries at the DFT-SMD/M06-2X/6-311++G(d,p) computational level.

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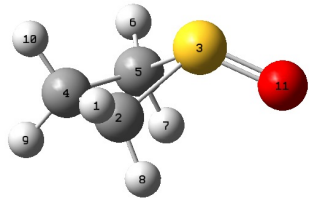


```
Sum of electronic and zero-point Energies=    -591.159134  (Hartree/Particle)
Sum of electronic and thermal Energies=         -591.154044
Sum of electronic and thermal Enthalpies=       -591.153100
Sum of electronic and thermal Free Energies=   -591.187499   -370975.83577 (Kcal/mol)
```

! Optimized Parameters !
! (Angstroms and Degrees) !

Name	Definition	Value	Derivative Info.
R1	R(1,2)	1.5115	-DE/DX = -0.0002
R2	R(1,3)	1.8409	-DE/DX = -0.0001
R3	R(1,6)	1.8409	-DE/DX = -0.0001
R4	R(3,4)	1.0918	-DE/DX = 0.0
R5	R(3,5)	1.0879	-DE/DX = 0.0
R6	R(3,9)	1.5363	-DE/DX = 0.0
R7	R(6,7)	1.0879	-DE/DX = 0.0
R8	R(6,8)	1.0918	-DE/DX = 0.0
R9	R(6,9)	1.5363	-DE/DX = 0.0
R10	R(9,10)	1.0906	-DE/DX = 0.0
R11	R(9,11)	1.0886	-DE/DX = 0.0
A1	A(2,1,3)	112.7995	-DE/DX = -0.0001
A2	A(2,1,6)	112.7995	-DE/DX = -0.0001
A3	A(3,1,6)	75.4641	-DE/DX = 0.0
A4	A(1,3,4)	106.83	-DE/DX = 0.0
A5	A(1,3,5)	115.0761	-DE/DX = 0.0
A6	A(1,3,9)	89.2926	-DE/DX = 0.0
A7	A(4,3,5)	111.5274	-DE/DX = 0.0
A8	A(4,3,9)	112.2904	-DE/DX = 0.0
A9	A(5,3,9)	119.4598	-DE/DX = 0.0
A10	A(1,6,7)	115.0761	-DE/DX = 0.0
A11	A(1,6,8)	106.83	-DE/DX = 0.0
A12	A(1,6,9)	89.2926	-DE/DX = 0.0
A13	A(7,6,8)	111.5274	-DE/DX = 0.0
A14	A(7,6,9)	119.4598	-DE/DX = 0.0
A15	A(8,6,9)	112.2904	-DE/DX = 0.0
A16	A(3,9,6)	94.3308	-DE/DX = -0.0001
A17	A(3,9,10)	111.0652	-DE/DX = 0.0
A18	A(3,9,11)	115.4293	-DE/DX = 0.0
A19	A(6,9,10)	111.0652	-DE/DX = 0.0
A20	A(6,9,11)	115.4293	-DE/DX = 0.0
A21	A(10,9,11)	108.9186	-DE/DX = 0.0
D1	D(2,1,3,4)	-19.2698	-DE/DX = 0.0
D2	D(2,1,3,5)	105.1187	-DE/DX = 0.0
D3	D(2,1,3,9)	-132.3843	-DE/DX = 0.0
D4	D(6,1,3,4)	89.7115	-DE/DX = 0.0
D5	D(6,1,3,5)	-145.8999	-DE/DX = 0.0
D6	D(6,1,3,9)	-23.4029	-DE/DX = -0.0001
D7	D(2,1,6,7)	-105.1187	-DE/DX = 0.0
D8	D(2,1,6,8)	19.2699	-DE/DX = 0.0
D9	D(2,1,6,9)	132.3843	-DE/DX = 0.0

! D10	D(3,1,6,7)	145.8999	-DE/DX =	0.0 !
! D11	D(3,1,6,8)	-89.7115	-DE/DX =	0.0 !
! D12	D(3,1,6,9)	23.4029	-DE/DX =	0.0001 !
! D13	D(1,3,9,6)	27.5188	-DE/DX =	0.0001 !
! D14	D(1,3,9,10)	-87.0283	-DE/DX =	0.0 !
! D15	D(1,3,9,11)	148.3713	-DE/DX =	0.0 !
! D16	D(4,3,9,6)	-80.4126	-DE/DX =	0.0 !
! D17	D(4,3,9,10)	165.0403	-DE/DX =	0.0 !
! D18	D(4,3,9,11)	40.4399	-DE/DX =	0.0 !
! D19	D(5,3,9,6)	146.1926	-DE/DX =	0.0 !
! D20	D(5,3,9,10)	31.6454	-DE/DX =	0.0 !
! D21	D(5,3,9,11)	-92.955	-DE/DX =	0.0 !
! D22	D(1,6,9,3)	-27.5188	-DE/DX =	-0.0001 !
! D23	D(1,6,9,10)	87.0283	-DE/DX =	0.0 !
! D24	D(1,6,9,11)	-148.3713	-DE/DX =	0.0 !
! D25	D(7,6,9,3)	-146.1926	-DE/DX =	0.0 !
! D26	D(7,6,9,10)	-31.6454	-DE/DX =	0.0 !
! D27	D(7,6,9,11)	92.955	-DE/DX =	0.0 !
! D28	D(8,6,9,3)	80.4126	-DE/DX =	0.0 !
! D29	D(8,6,9,10)	-165.0403	-DE/DX =	0.0 !
! D30	D(8,6,9,11)	-40.4399	-DE/DX =	0.0

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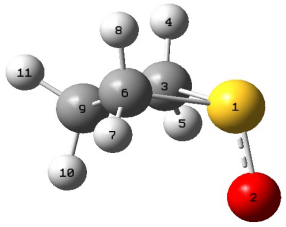


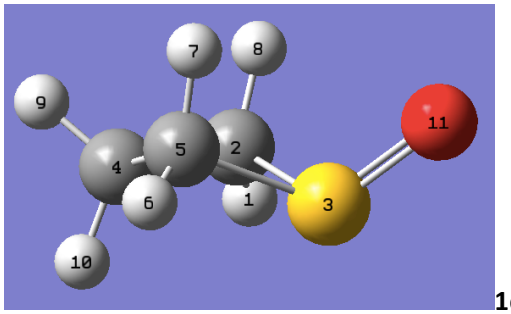
Sum of electronic and zero-point Energies= -591.155901 (Hartree/Particle)
Sum of electronic and thermal Energies= -591.150718
Sum of electronic and thermal Enthalpies= -591.149773
Sum of electronic and thermal Free Energies= -591.184395 -370973.88798 (Kcal/mol)

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!
! R1	R(1,2)	1.519	-DE/DX =	0.0001 !
! R2	R(1,3)	1.8499	-DE/DX =	0.0 !
! R3	R(1,6)	1.8499	-DE/DX =	0.0 !
! R4	R(3,4)	1.0915	-DE/DX =	0.0 !
! R5	R(3,5)	1.0889	-DE/DX =	0.0 !
! R6	R(3,9)	1.5348	-DE/DX =	0.0 !
! R7	R(6,7)	1.0889	-DE/DX =	0.0 !
! R8	R(6,8)	1.0915	-DE/DX =	0.0 !
! R9	R(6,9)	1.5348	-DE/DX =	0.0 !
! R10	R(9,10)	1.089	-DE/DX =	0.0 !
! R11	R(9,11)	1.0899	-DE/DX =	0.0 !
! A1	A(2,1,3)	106.681	-DE/DX =	0.0 !
! A2	A(2,1,6)	106.681	-DE/DX =	0.0 !
! A3	A(3,1,6)	75.0651	-DE/DX =	0.0 !
! A4	A(1,3,4)	108.4581	-DE/DX =	0.0 !
! A5	A(1,3,5)	111.8166	-DE/DX =	0.0 !
! A6	A(1,3,9)	91.4242	-DE/DX =	0.0 !

```
! A7    A(4,3,5)              110.9455         -DE/DX =    0.0                 !
! A8    A(4,3,9)              113.49           -DE/DX =    0.0                 !
! A9    A(5,3,9)              118.8229         -DE/DX =    0.0                 !
! A10   A(1,6,7)              111.8166         -DE/DX =    0.0                 !
! A11   A(1,6,8)              108.4581         -DE/DX =    0.0                 !
! A12   A(1,6,9)               91.4242         -DE/DX =    0.0                 !
! A13   A(7,6,8)              110.9455         -DE/DX =    0.0                 !
! A14   A(7,6,9)              118.8229         -DE/DX =    0.0                 !
! A15   A(8,6,9)              113.49           -DE/DX =    0.0                 !
! A16   A(3,9,6)               94.4954         -DE/DX =    0.0                 !
! A17   A(3,9,10)             110.7587         -DE/DX =    0.0                 !
! A18   A(3,9,11)             115.4902         -DE/DX =    0.0                 !
! A19   A(6,9,10)             110.7587         -DE/DX =    0.0                 !
! A20   A(6,9,11)             115.4902         -DE/DX =    0.0                 !
! A21   A(10,9,11)            109.1817         -DE/DX =    0.0                 !
! D1    D(2,1,3,4)           -160.3401         -DE/DX =    0.0                 !
! D2    D(2,1,3,5)            -37.6866         -DE/DX =    0.0                 !
! D3    D(2,1,3,9)             84.279          -DE/DX =    0.0                 !
! D4    D(6,1,3,4)             96.351          -DE/DX =    0.0                 !
! D5    D(6,1,3,5)           -140.9955         -DE/DX =    0.0                 !
! D6    D(6,1,3,9)            -19.03           -DE/DX =    0.0                 !
! D7    D(2,1,6,7)             37.6866         -DE/DX =    0.0                 !
! D8    D(2,1,6,8)            160.3401         -DE/DX =    0.0                 !
! D9    D(2,1,6,9)            -84.279          -DE/DX =    0.0                 !
! D10   D(3,1,6,7)            140.9955         -DE/DX =    0.0                 !
! D11   D(3,1,6,8)            -96.351          -DE/DX =    0.0                 !
! D12   D(3,1,6,9)             19.03           -DE/DX =    0.0                 !
! D13   D(1,3,9,6)             22.3898         -DE/DX =    0.0                 !
! D14   D(1,3,9,10)           -91.8157         -DE/DX =    0.0                 !
! D15   D(1,3,9,11)           143.4354         -DE/DX =    0.0                 !
! D16   D(4,3,9,6)            -88.473          -DE/DX =    0.0                 !
! D17   D(4,3,9,10)           157.3215         -DE/DX =    0.0                 !
! D18   D(4,3,9,11)            32.5726         -DE/DX =    0.0                 !
! D19   D(5,3,9,6)            138.3661         -DE/DX =    0.0                 !
! D20   D(5,3,9,10)            24.1606         -DE/DX =    0.0                 !
! D21   D(5,3,9,11)          -100.5883         -DE/DX =    0.0                 !
! D22   D(1,6,9,3)            -22.3898         -DE/DX =    0.0                 !
! D23   D(1,6,9,10)            91.8157         -DE/DX =    0.0                 !
! D24   D(1,6,9,11)          -143.4354         -DE/DX =    0.0                 !
! D25   D(7,6,9,3)           -138.3661         -DE/DX =    0.0                 !
! D26   D(7,6,9,10)           -24.1606         -DE/DX =    0.0                 !
! D27   D(7,6,9,11)           100.5883         -DE/DX =    0.0                 !
! D28   D(8,6,9,3)             88.473          -DE/DX =    0.0                 !
! D29   D(8,6,9,10)          -157.3215         -DE/DX =    0.0                 !
! D30   D(8,6,9,11)           -32.5726         -DE/DX =    0.0
```

Experimental and theoretical SCF-GIAO chemical shifts δ (ppm)



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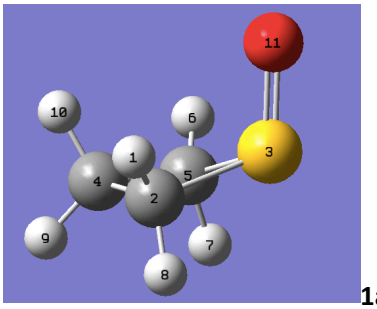

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Atom	δ_{exp} [a]	$\delta_{MPW1PW91}$ [b]	δ_{B3LYP} [c]	δ_{M06-2x} [d]	$\delta_{MPW1PW91}$ [b]	δ_{B3LYP} [c]	δ_{M06-2x} [d]
C_2 =C_5	52.30	58.77	67.79	61.61	52.88	62.60	55.75
C_4	9.90	12.86	19.86	11.75	26.36	31.95	26.82
H_1=H_6	3.44	3.39	3.44	3.39	2.68	2.62	3.40
H_7=H_8	3.14	3.16	3.11	3.10	3.49	3.48	2.61
H_9	2.27	2.08	2.11	2.01	2.74	2.73	4.16
H_{10}	1.92	1.91	2.04	1.80	4.01	3.90	2.69

[a] Experimental values in $CDCl_3$ at 298 K [b] Theoretical PCM/MPW1PW91/6-311++g(d,p) SCF-GIAO chemical shifts, σ_H^{TMS} (ppm)=31.8802; σ_C^{TMS} (ppm)=188.9116, implicit solvent $CHCl_3$; [c] theoretical PCM/B3LYP/6-311++g(d,p) SCF-GIAO chemical shifts, σ_H^{TMS}(ppm)=31.8832; σ_C^{TMS}(ppm)=184.4860, implicit solvent $CHCl_3$; [d] theoretical SMD/M06-2X/6-311++g(d,p) SCF-GIAO chemical shifts, σ_H^{TMS}(ppm)=32.0060; σ_C^{TMS}(ppm)=189.9264, , implicit solvent $CHCl_3$.

Experimental and theoretical spin spin coupling contants J_{HH} (Hz)

J_{HH}	exp[a]	$J_{MPW1PW91}$[b]	J_{B3LYP}[c]	J_{M062X}[d]
$J_{1-8}= J_{6-7}=J_{4-5}$	8.5	9.7 (10.0)	8.7 (9.35)	8.8(9.57)
$J_{9-10}=J_{10-11}$	12.7	12.6 (13.05)	11.6 (12.5)	11.5(12.57)
$J_{1-9}= J_{6-9}=J_{5-11}$	1.9	1.1 (1.0)	1.3(1.37)	0.8(0.66)
$J_{8-10}= J_{7-10}=J_{4-10}$	12.7	11.4 (11.8)	11.2(12.04)	10.4(11.35)
$J_{1-10}= J_{6-10}=J_{5-10}$	7.6	7.1 (7.3)	7.4(7.95)	6.5(7.0)
$J_{7-9}= J_{8-9}=J_{8-11}$	10.6	9.8 (10.1)	9.9(10.64)	8.8(9.57)
$J_{1-6}=J_{5-7}$	3.18	4.5 (4.6)	4.2(4.5)	4.0(4.23)
$J_{1-7}=J_{5-8}$	1.93	1.3 (1.2)	1.3(1.37)	1.1(1)
$J_{6-8}=J_{7-4}$	1.93	1.3 (1.2)	1.3(1.37)	1.1(1)
$J_{7-8}=J_{8-4}$	-	0.34	0.27	0.28
MAE		0.751	0.673	0.992
CMAE		0.712	0.563	0.925

[a]Values in Hz. [b]At DFT-PCM/MPW1PW91/6-311++G(d,p) level of theory, scaled values in parentheses. [c]At DFT-PCM/ B3LYP/6-311++G(d,p) level of theory, scaled values in parentheses. [d]At DFT-SMD/M062X/6-311++G(d,p) level of theory, scaled values in parentheses.

The scaled values and the statistical parameters MAE (Mean Absolute Error) and CMAE (Corrected Mean Absolute Error) are calculated according to the equations:

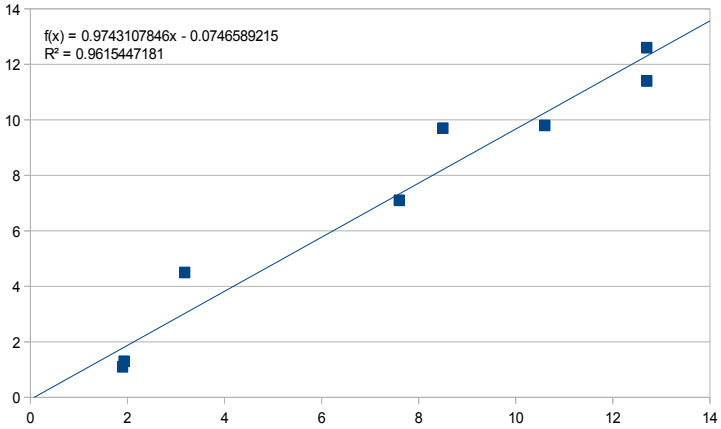
$$MAE = \frac{1}{N} + \sum_{j=1}^{j=N} x_j - x_{sper}$$

$$CMAE = \frac{1}{N} + \sum_{j=1}^{j=N} x_{corr} - x_{sper}$$

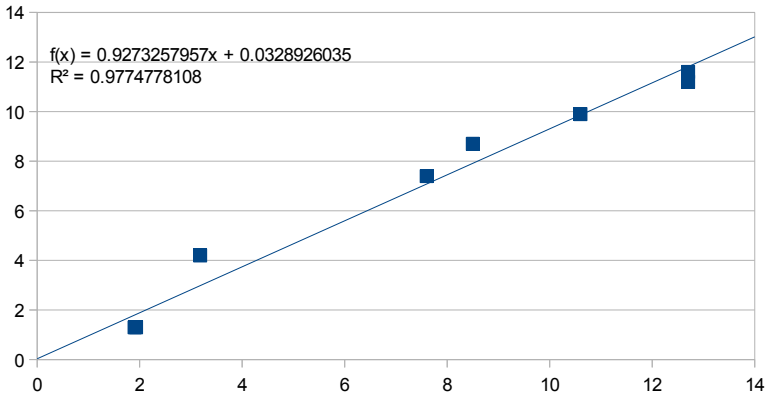
$$x_{corr} = \frac{x - intercept}{slope}$$

Linear fitting correlation coefficient index R^2 of the spin spin coupling contants J_{HH} experimental and calculated (PCM/B3LYP/6-311++g(d,p), PCM/MPW1PW91/6-311++g(d,p) and SMD/M06-2X/6-311++g(d,p) level of theory) for the conformer 1eq and simulation with the more accurate magnetic parameters

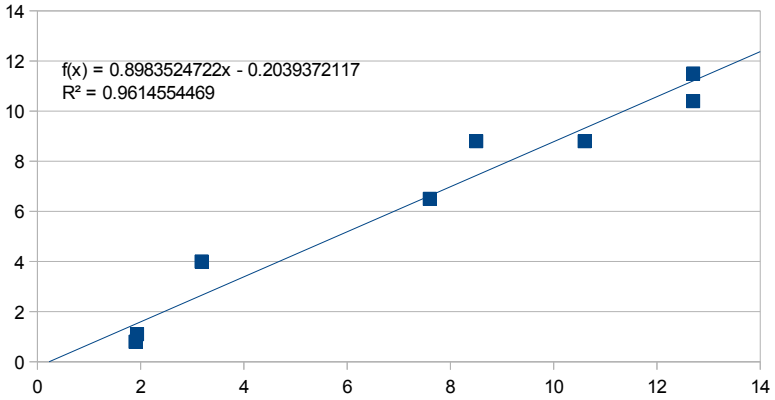
MPW1PW91

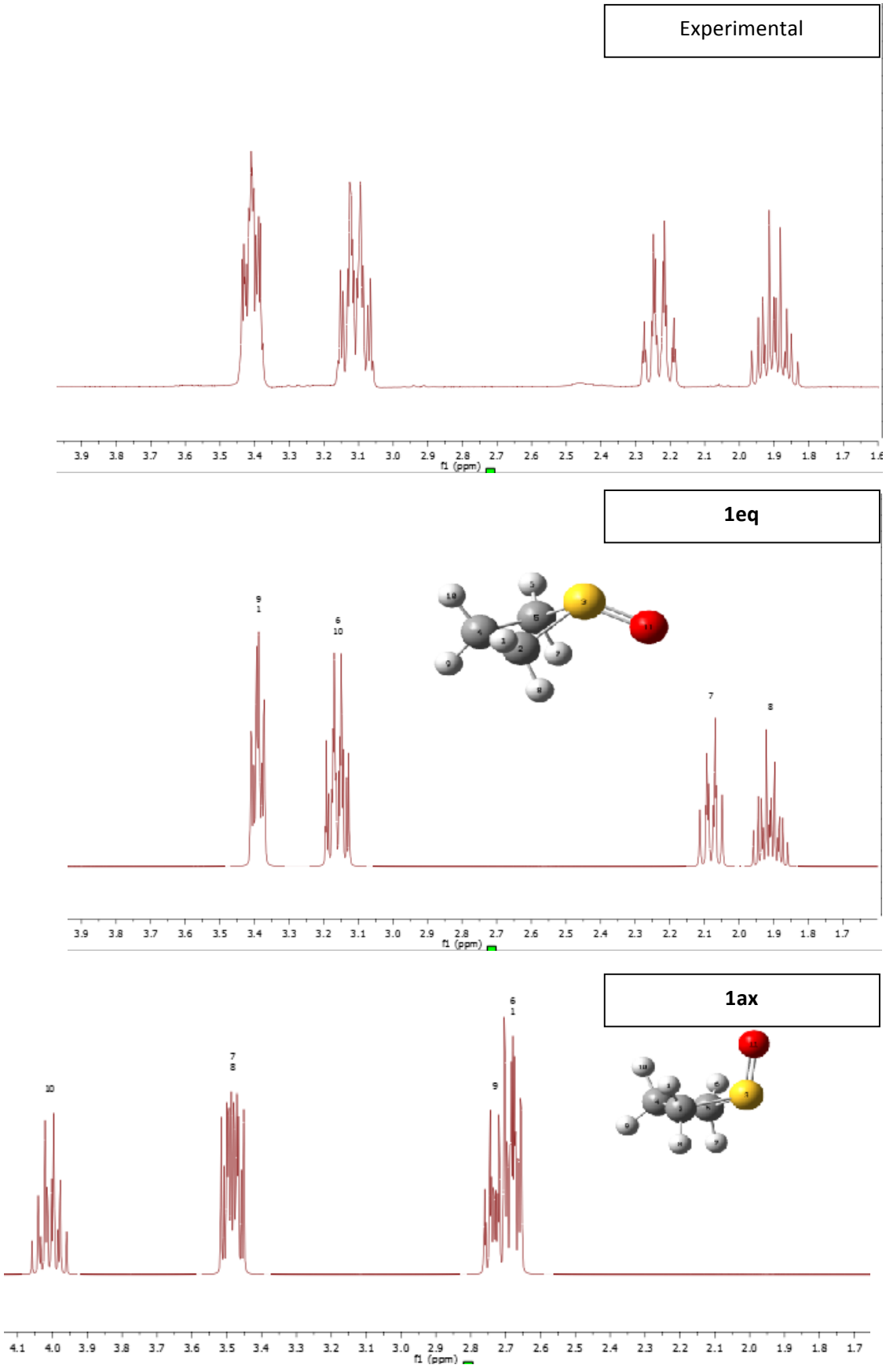


B3LYP

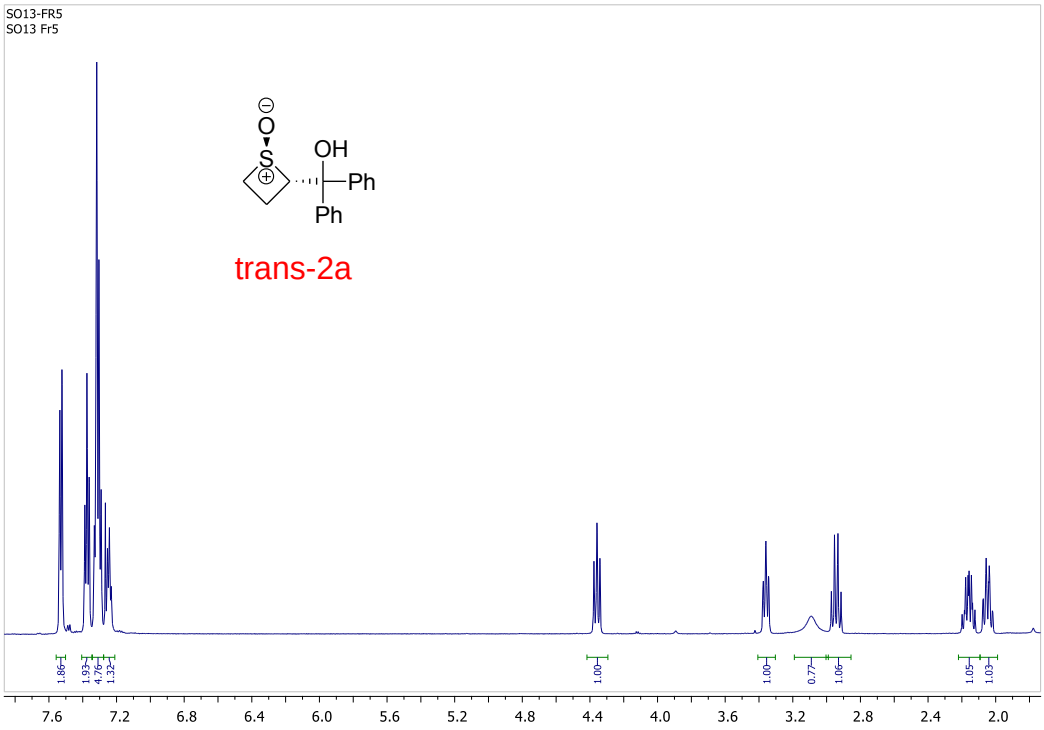


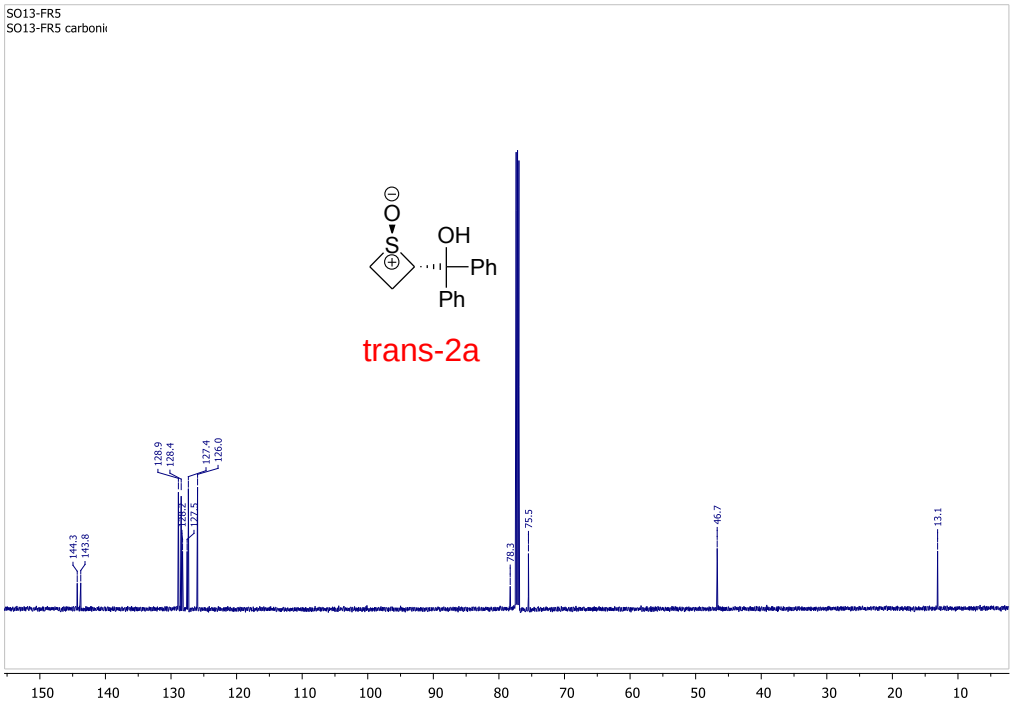
M06-2X

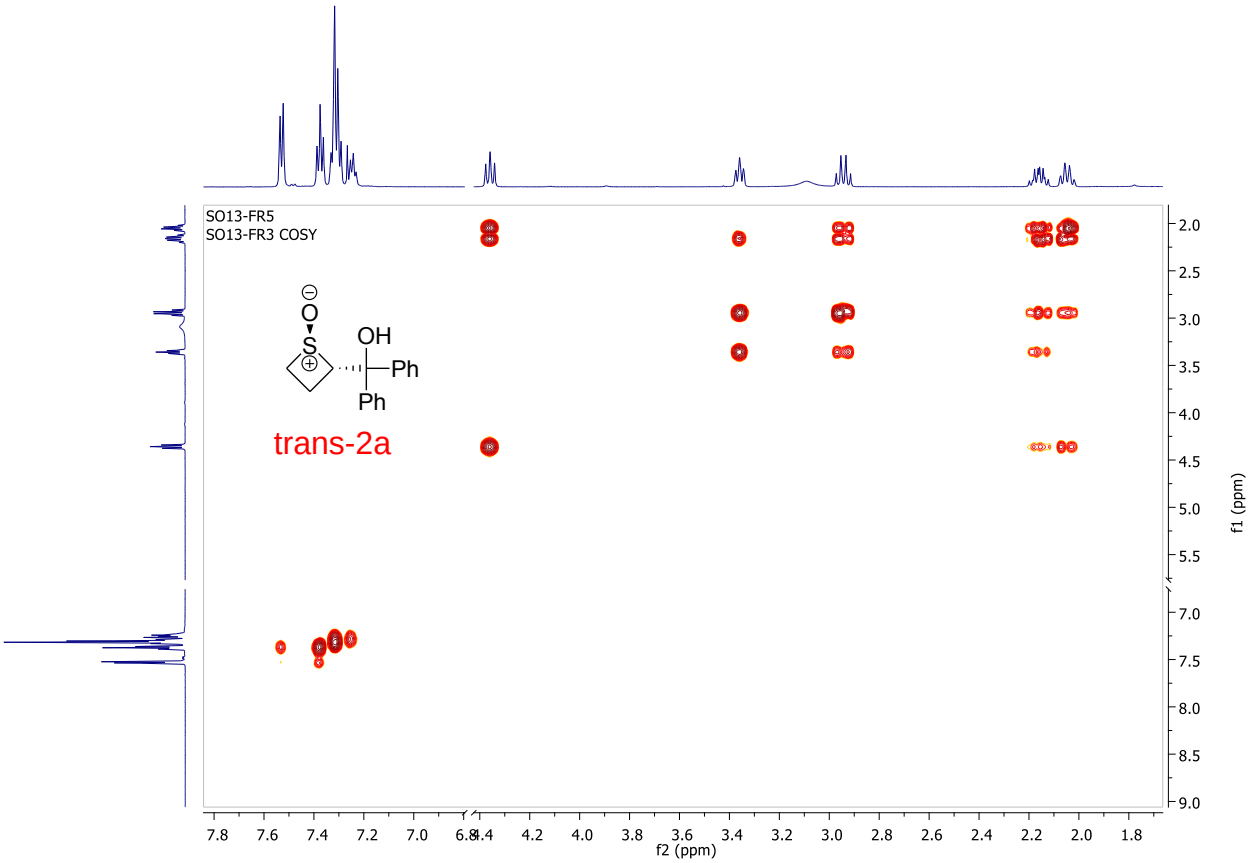


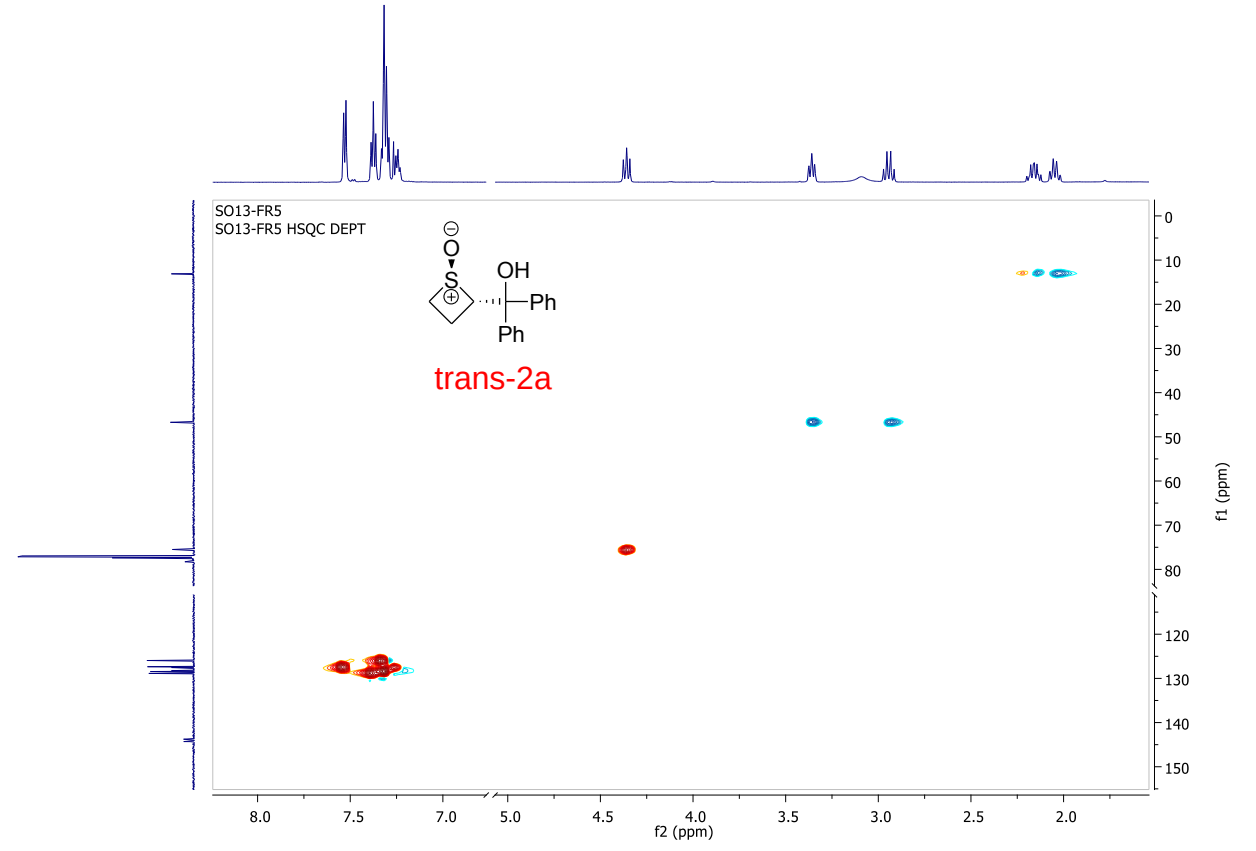


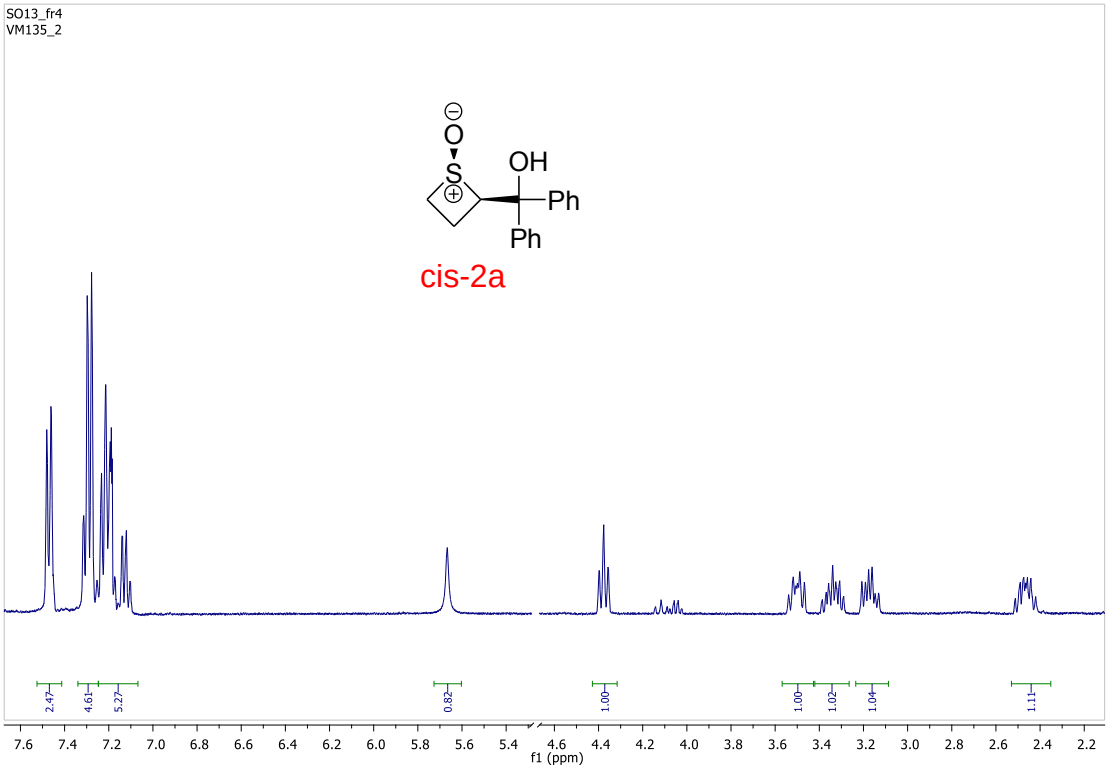
Experimental and simulated ^{1}H-NMR spectra by using the MPW1PW91 NMR parameters

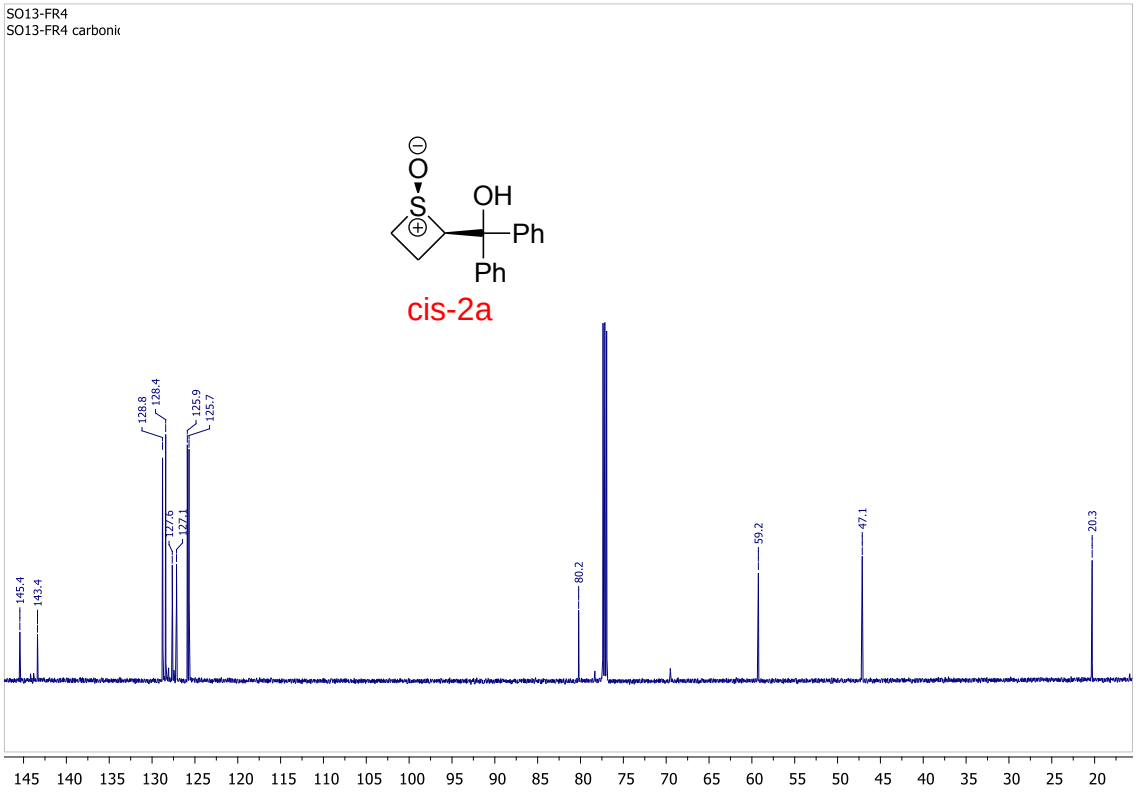

SO13-FR5
SO13 Fr5
OH
Ph
Ph
trans-2a
1.86
1.93
4.76
1.32
1.00
1.00
0.77
1.06
1.05
1.03
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0

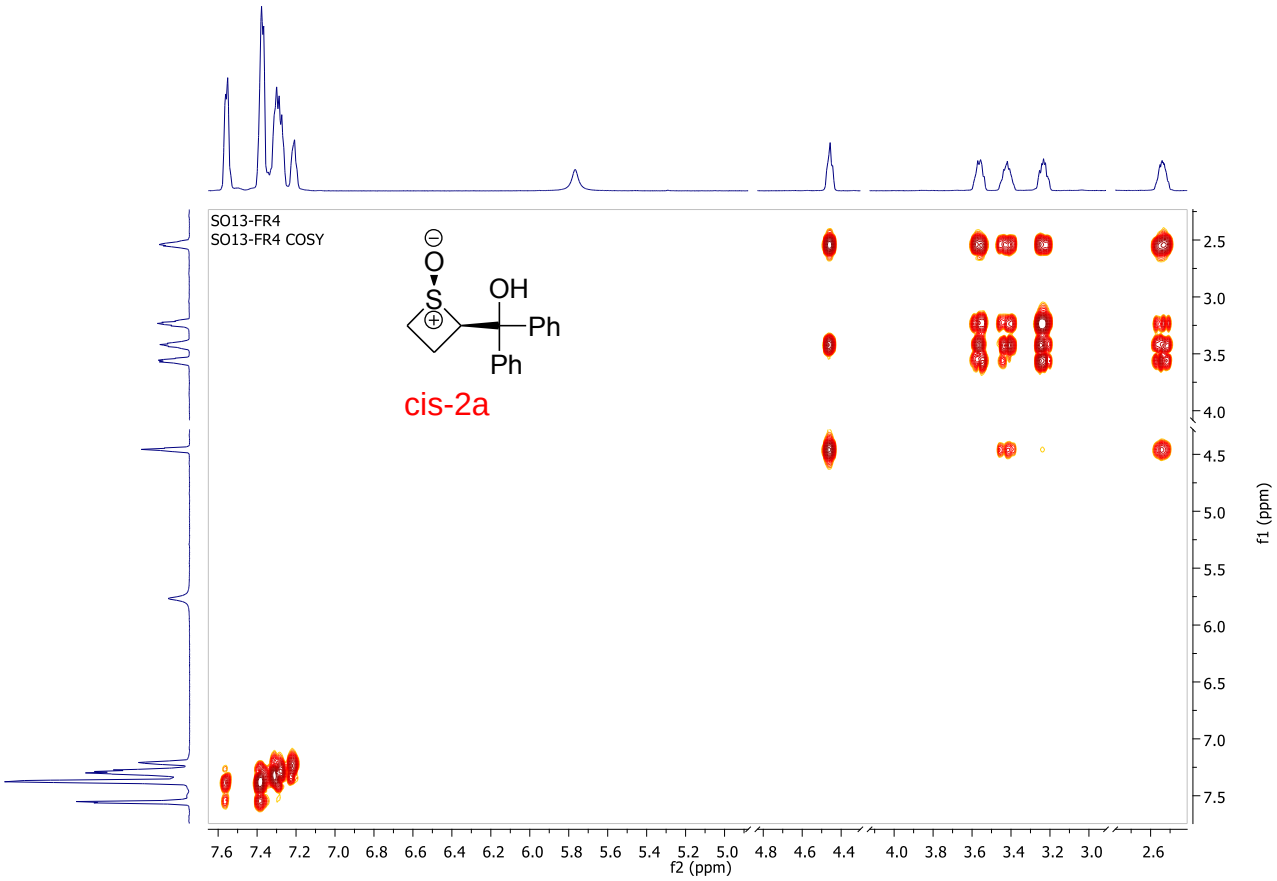

SO13-FR5
SO13-FR5 carboni
OH
Ph
Ph
trans-2a
144.3
143.8
128.9
128.4
127.4
126.0
79.3
75.5
46.7
13.1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

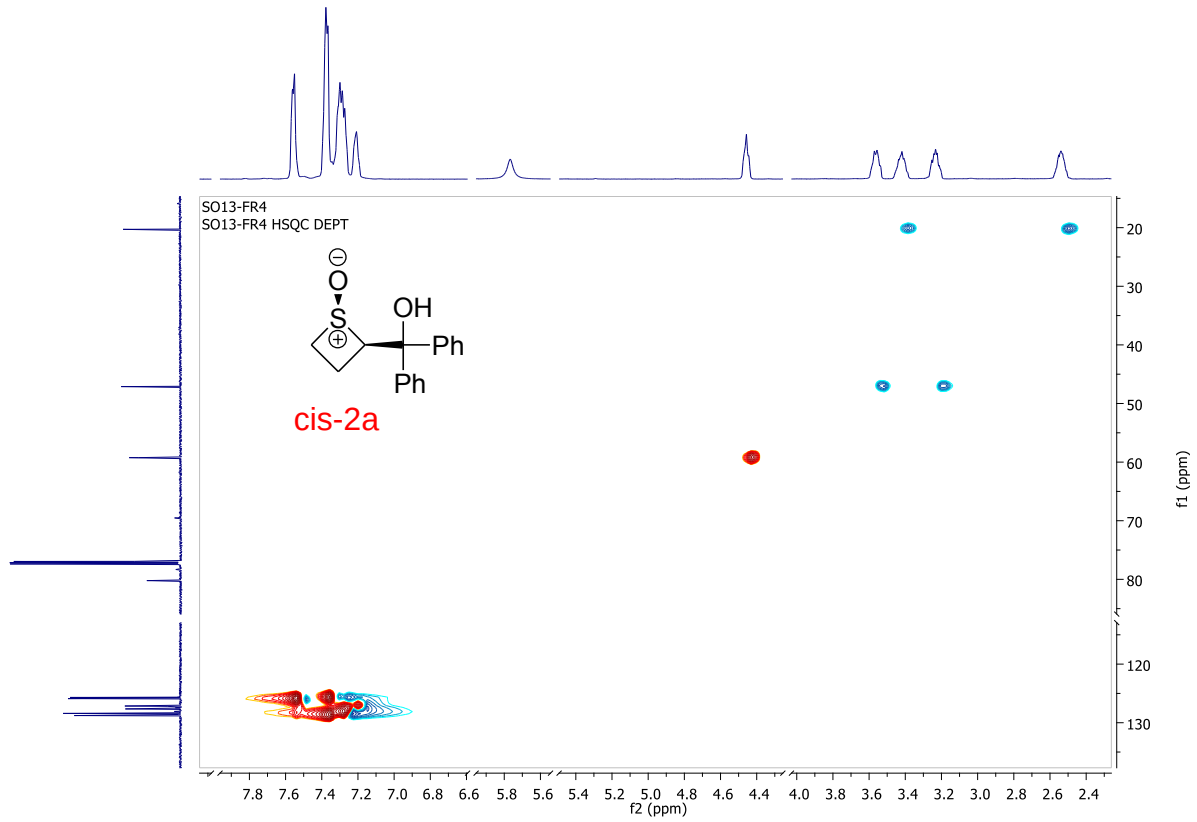

SO13-FR5
SO13-FR3 COSY
OH
Ph
Ph
trans-2a
f2 (ppm)
f1 (ppm)

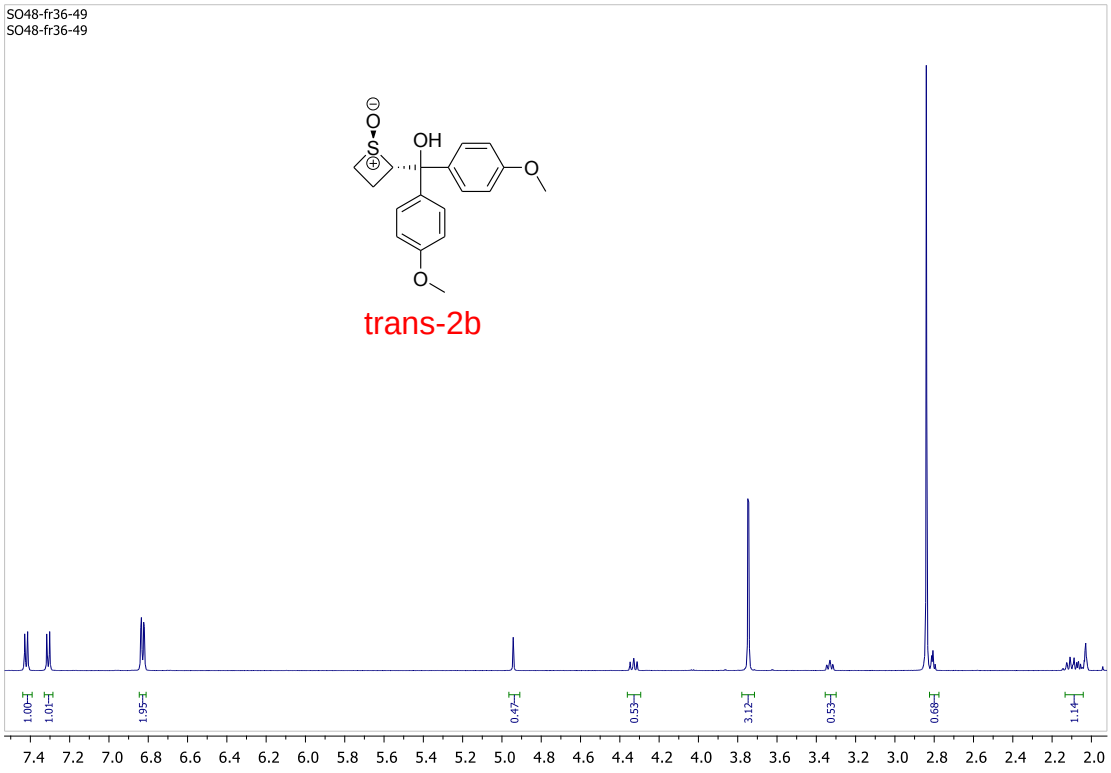

SO13-FR5
SO13-FR5 HSQC DEPT
OH
Ph
Ph
trans-2a
f2 (ppm)
f1 (ppm)

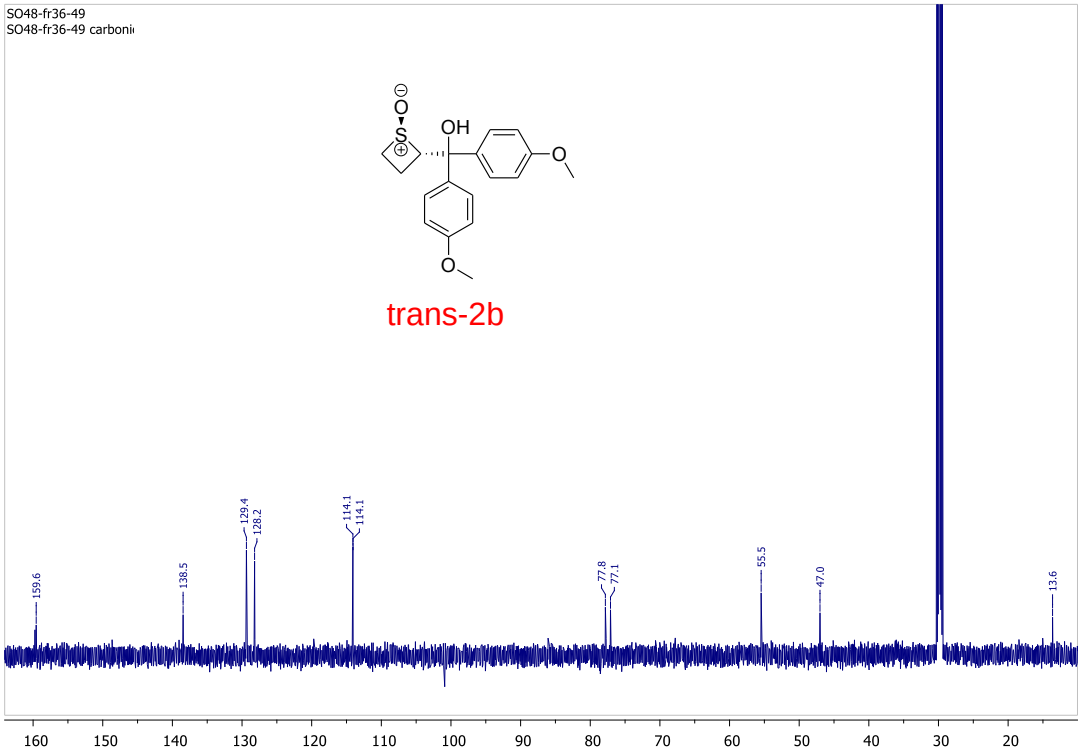

SO13_fr4
VM135_2
O
S
OH
Ph
Ph
cis-2a
2.47
4.61
5.27
0.82
1.00
1.00
1.02
1.04
1.11
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f1 (ppm)

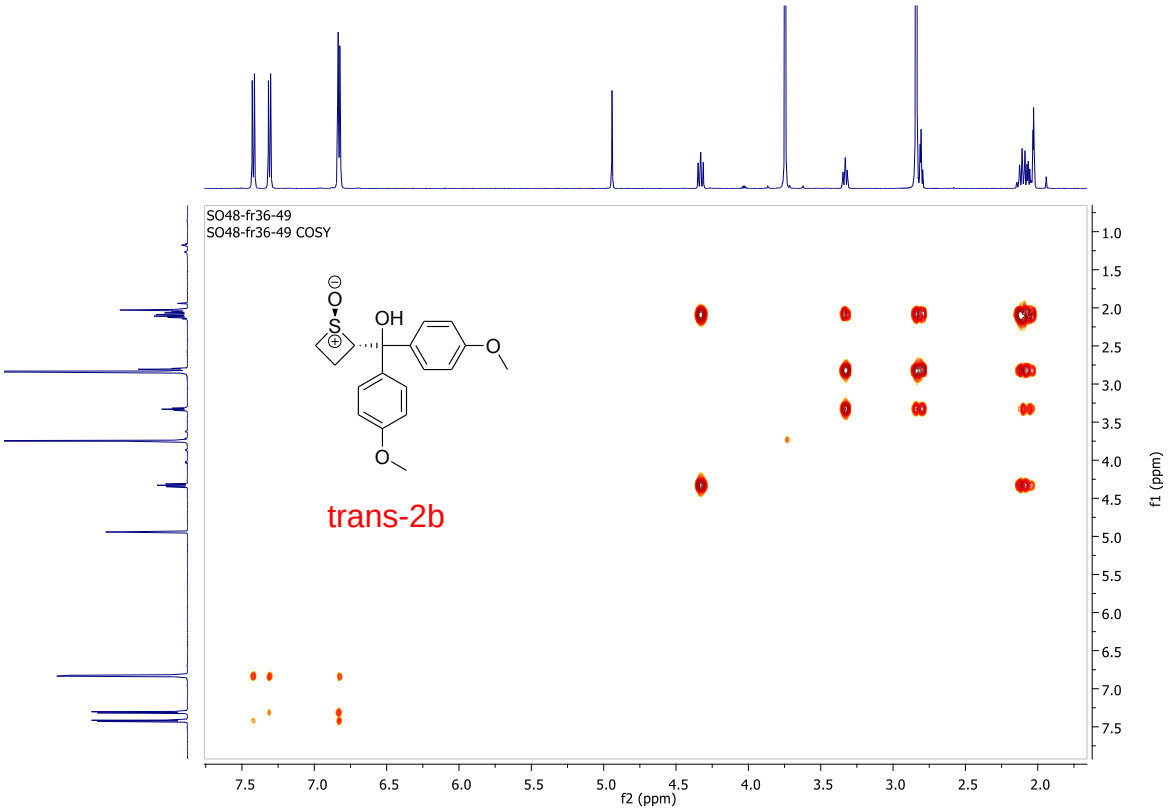

SO13-FR4
SO13-FR4 carbonic
O
S
OH
Ph
Ph
cis-2a
145.4
143.4
128.8
128.4
127.6
127.1
125.9
125.7
80.2
59.2
47.1
20.3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

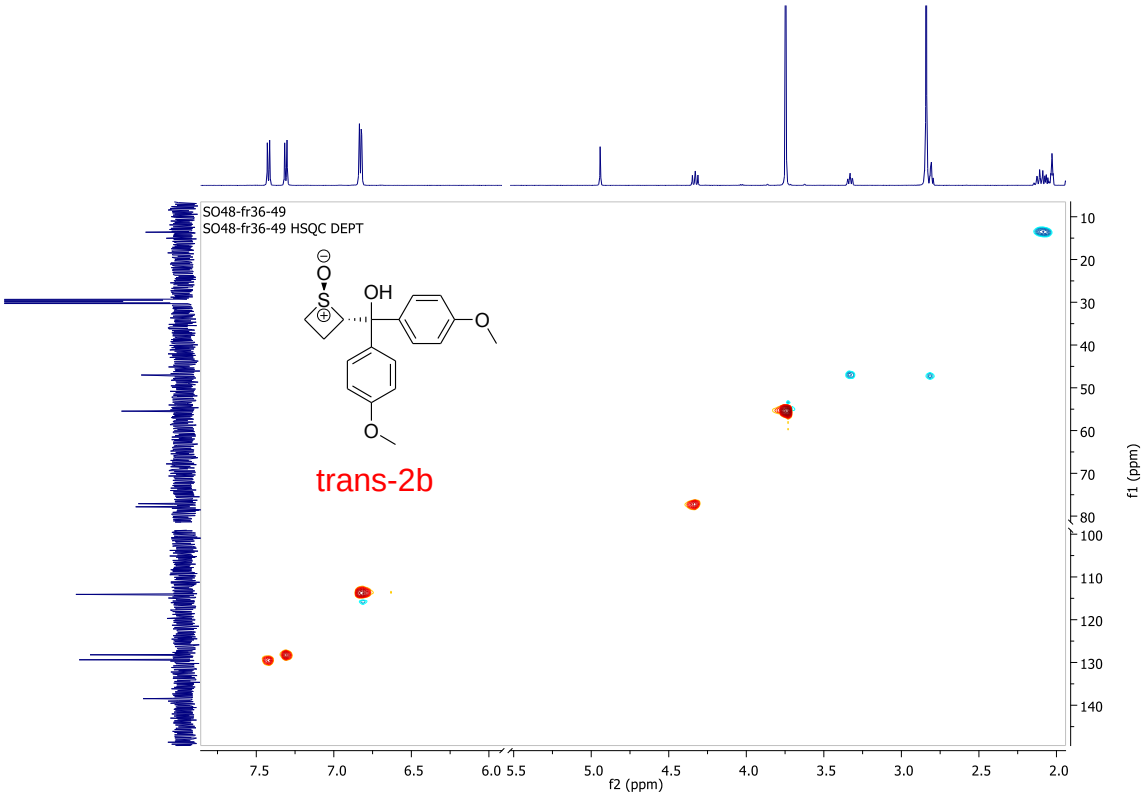

SO13-FR4
SO13-FR4 COSY
OH
Ph
Ph
cis-2a
f2 (ppm)
f1 (ppm)

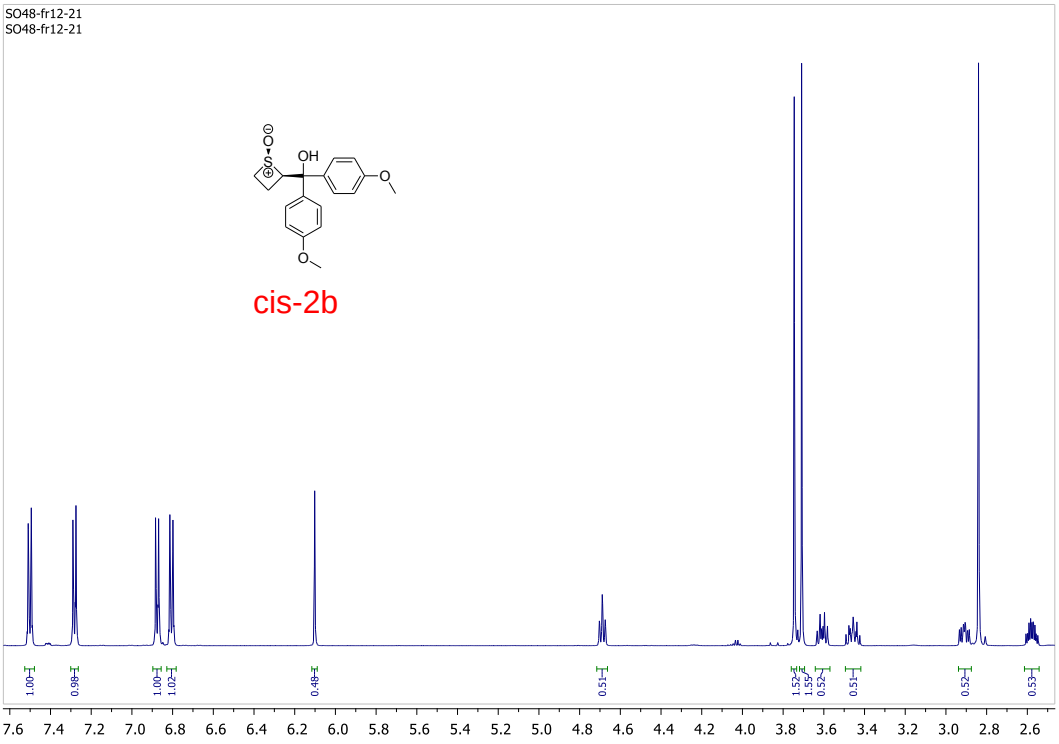

SO13-FR4
SO13-FR4 HSQC DEPT
OH
Ph
Ph
cis-2a
f2 (ppm)
f1 (ppm)

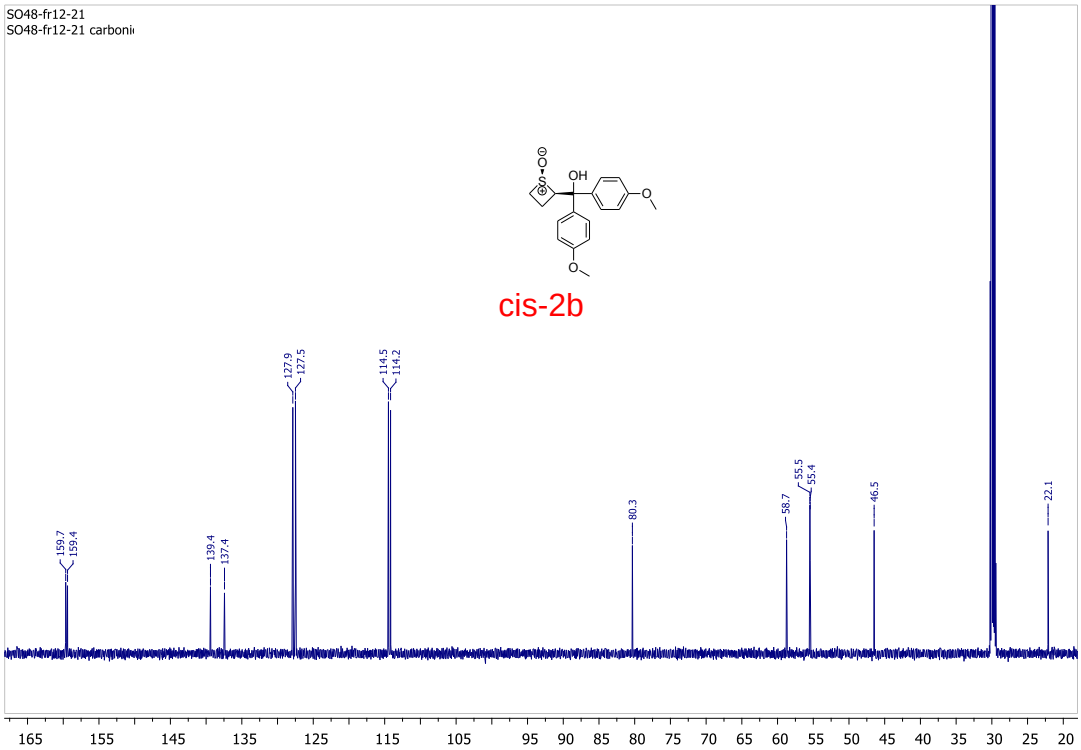

SO48-fr36-49
SO48-fr36-49
OH
O
O
O
trans-2b
1.00
1.01
1.95
0.47
0.53
3.12
0.53
0.68
1.14
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0

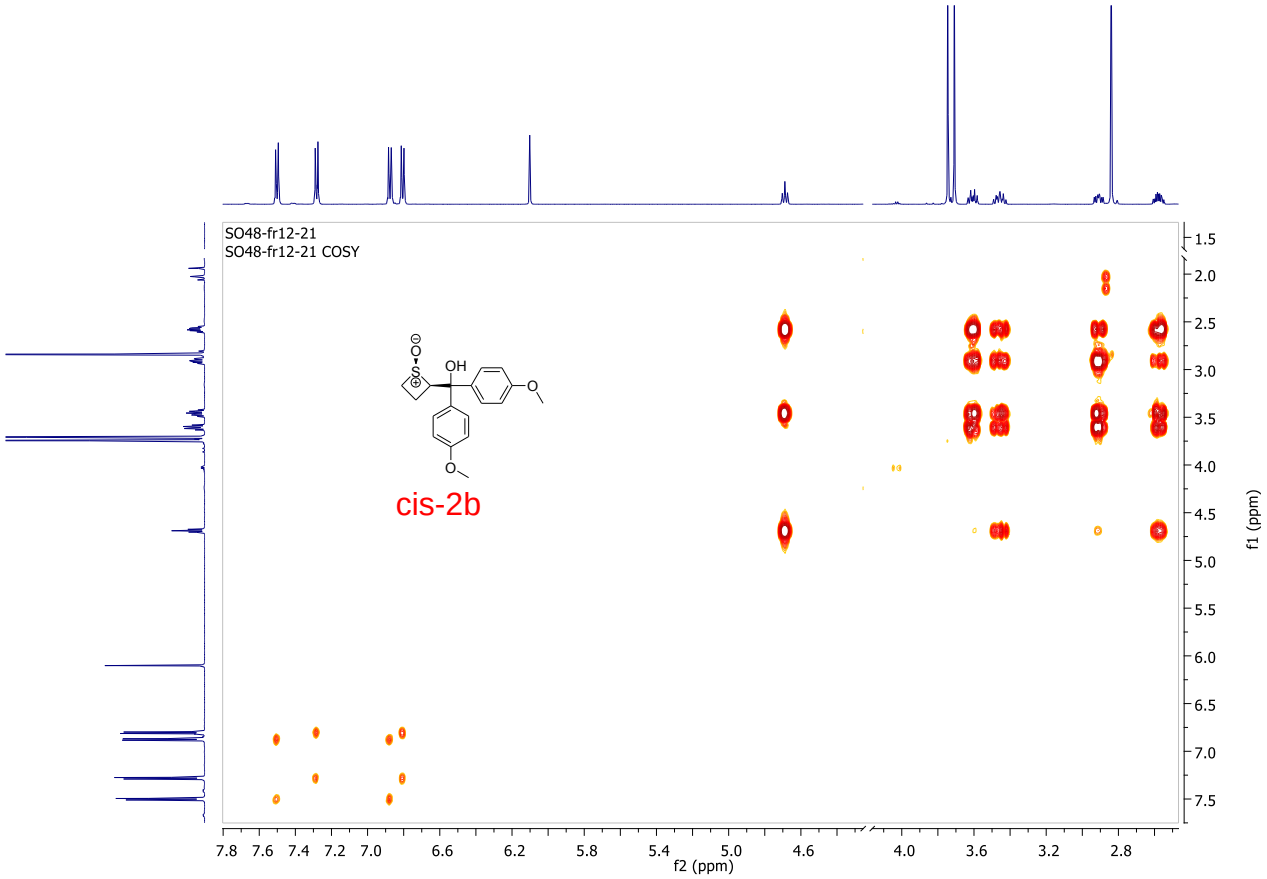

SO48-fr36-49
SO48-fr36-49 carboni
OH
O
O
O
trans-2b
159.6
138.5
129.4
128.2
114.1
114.1
77.8
77.1
55.5
47.0
13.6
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

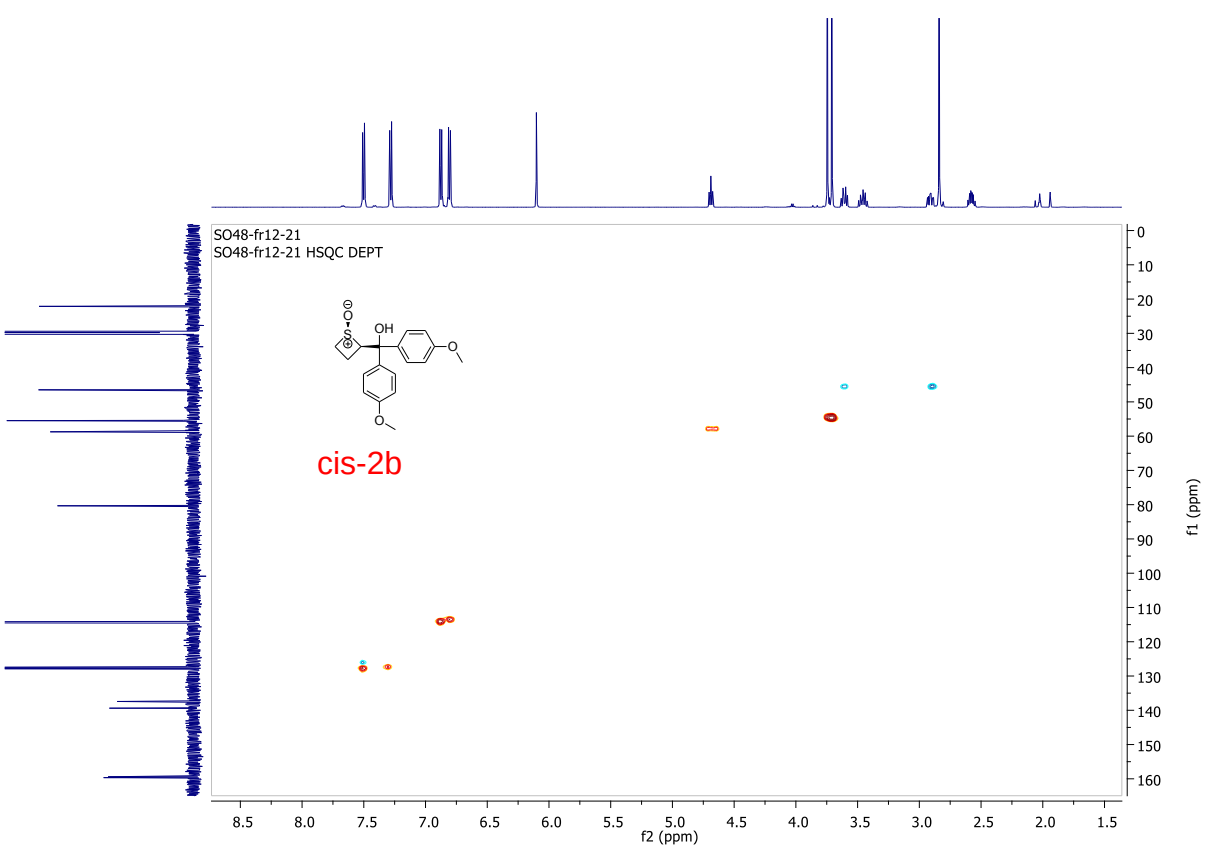

SO48-fr36-49
SO48-fr36-49 COSY
OH
O
O
trans-2b
f2 (ppm)
f1 (ppm)

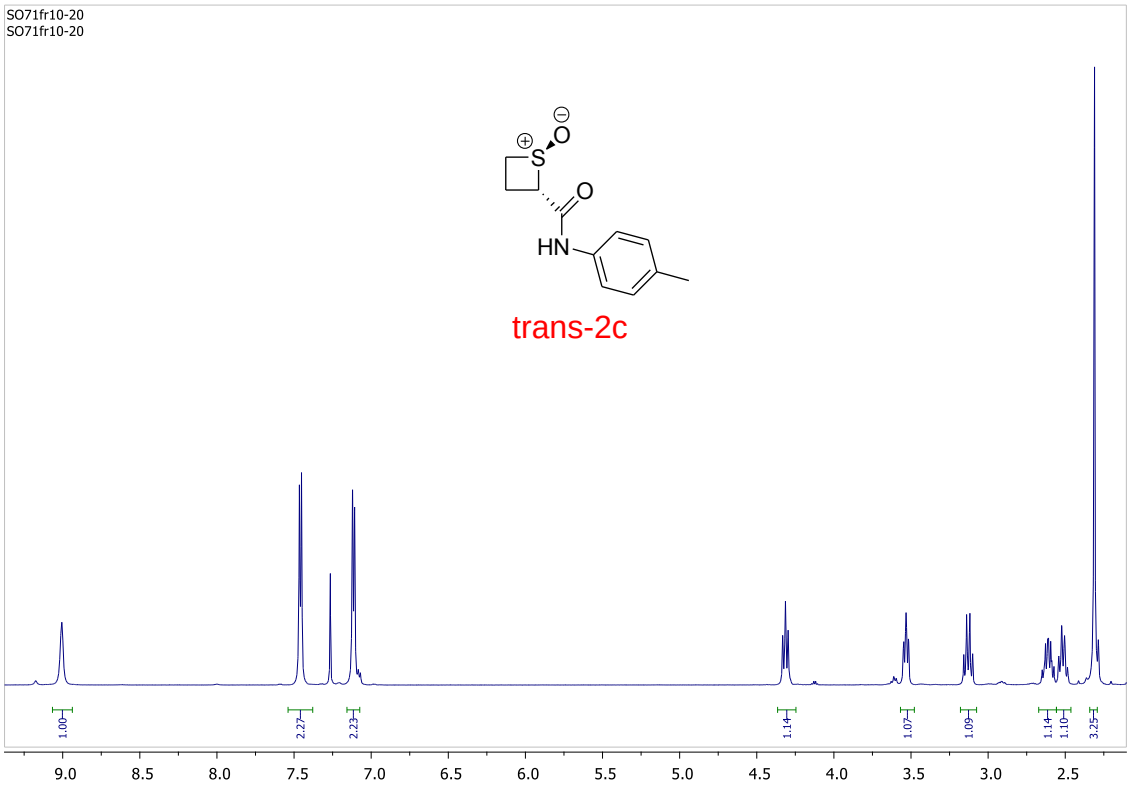

SO48-fr36-49
SO48-fr36-49 HSQC DEPT
OH
O
O
trans-2b
f2 (ppm)
f1 (ppm)

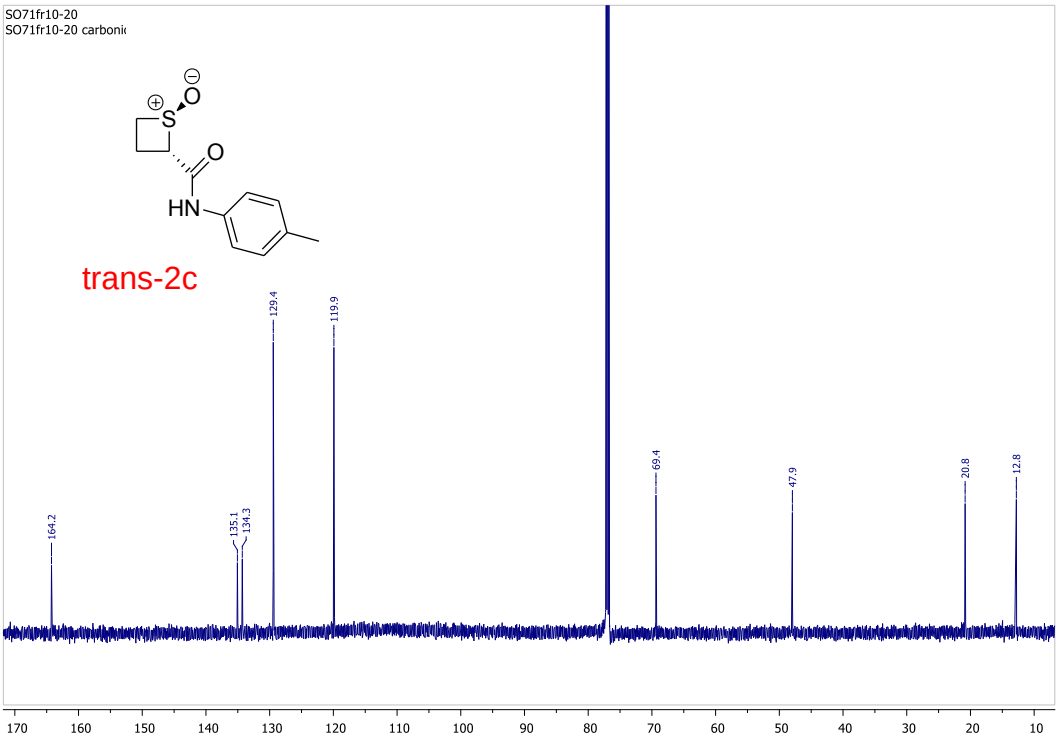

SO48-fr12-21
SO48-fr12-21
OH
O
O
cis-2b
1.00
0.98
1.00
1.02
0.48
0.51
1.52
1.52
0.52
0.51
0.52
0.53
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6

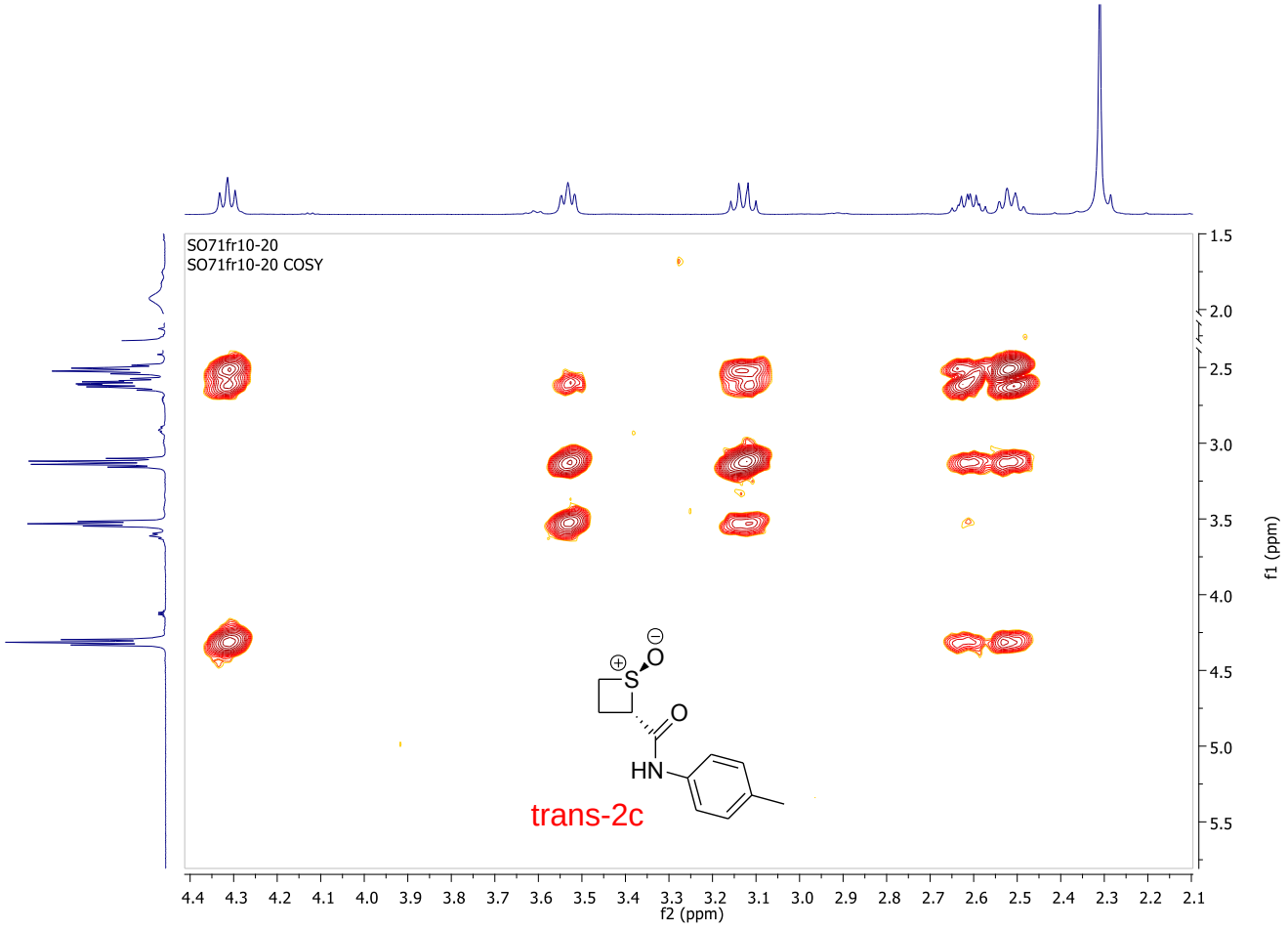

SO48-fr12-21
SO48-fr12-21 carboni
OH
O
O
cis-2b
159.7
159.4
139.4
137.4
127.9
127.5
114.5
114.2
80.3
58.7
55.5
55.4
46.5
22.1
165 155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

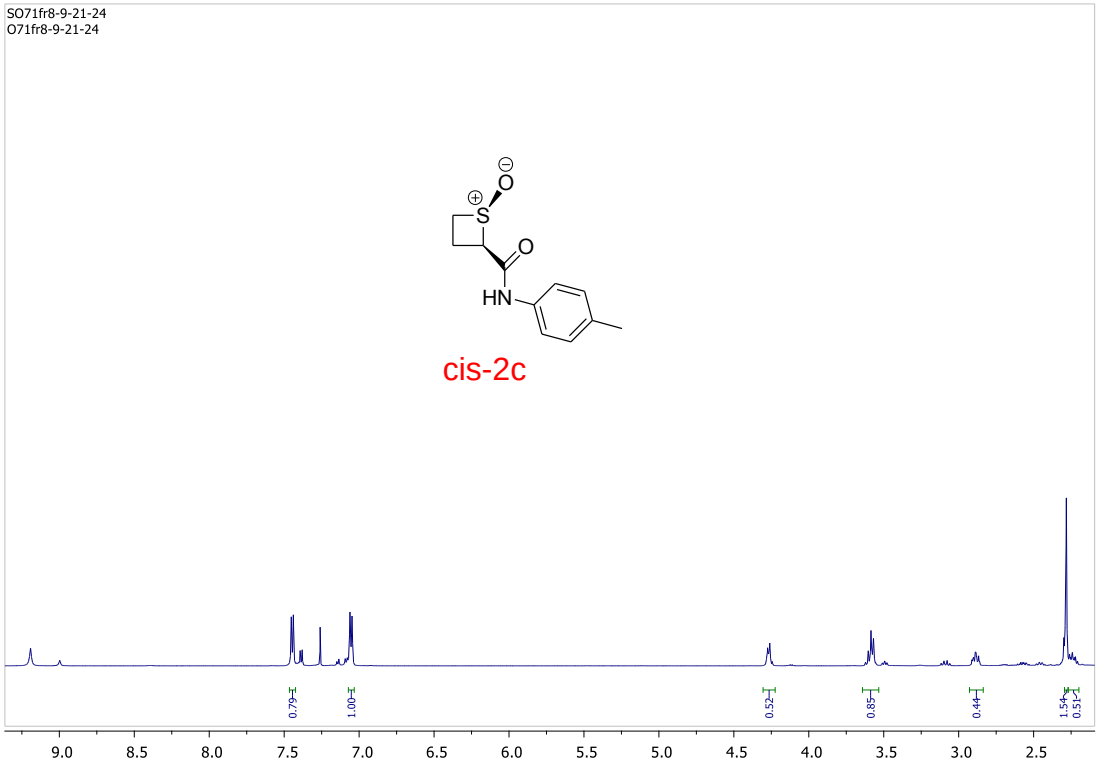

SO48-fr12-21
SO48-fr12-21 COSY
OH
O
cis-2b
f1 (ppm)
f2 (ppm)

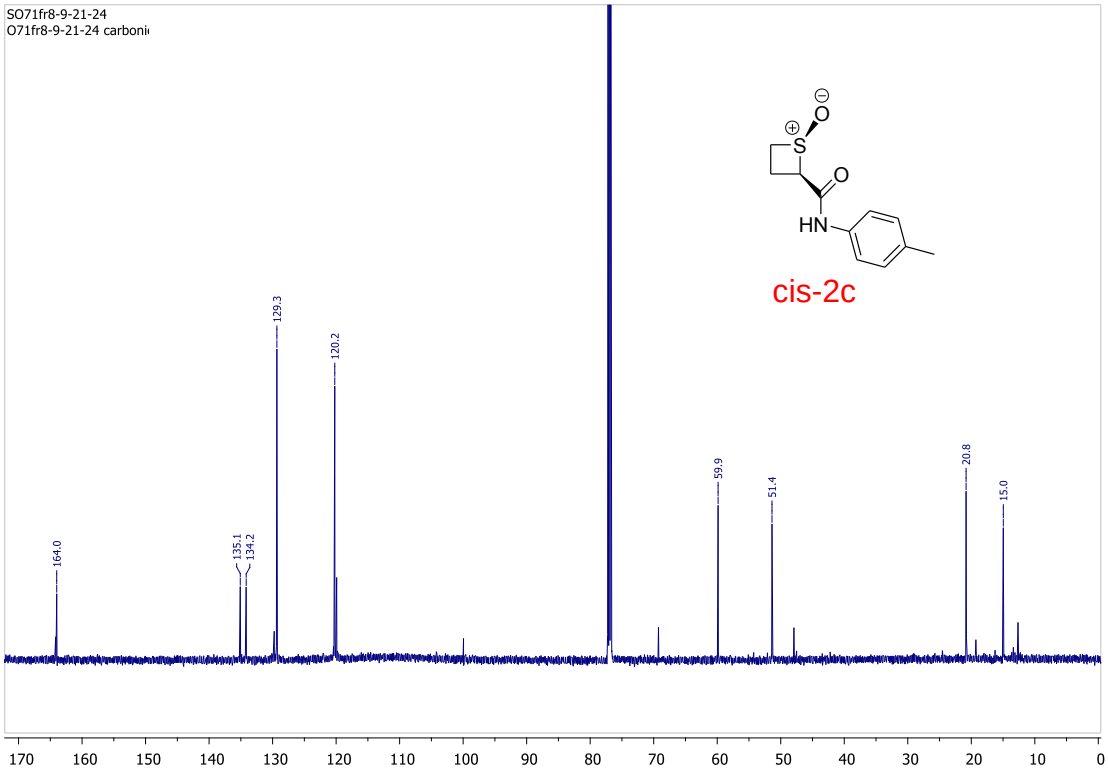

SO48-fr12-21
SO48-fr12-21 HSQC DEPT
OH
O
cis-2b
f1 (ppm)
f2 (ppm)

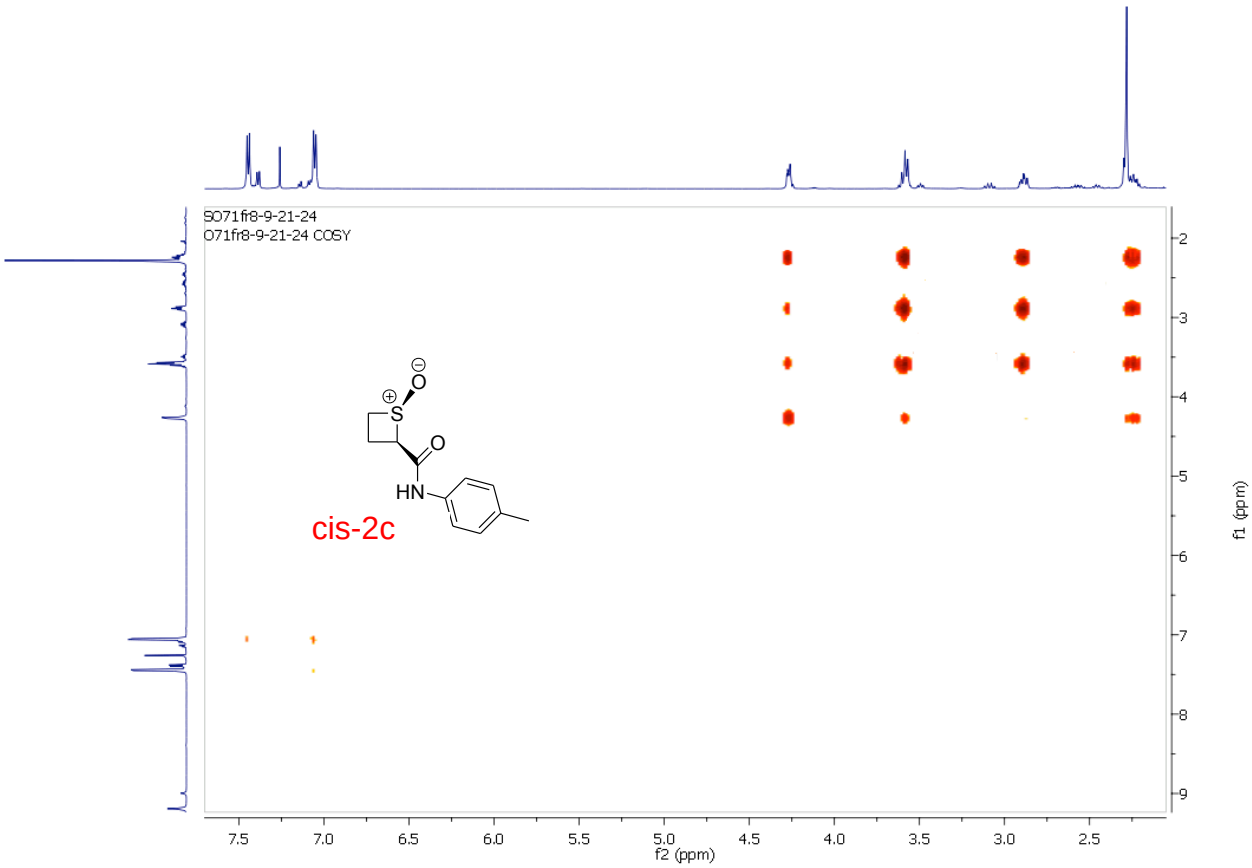

SO71fr10-20
SO71fr10-20
trans-2c
1.00
2.27
2.23
1.14
1.07
1.09
1.14
1.10
3.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

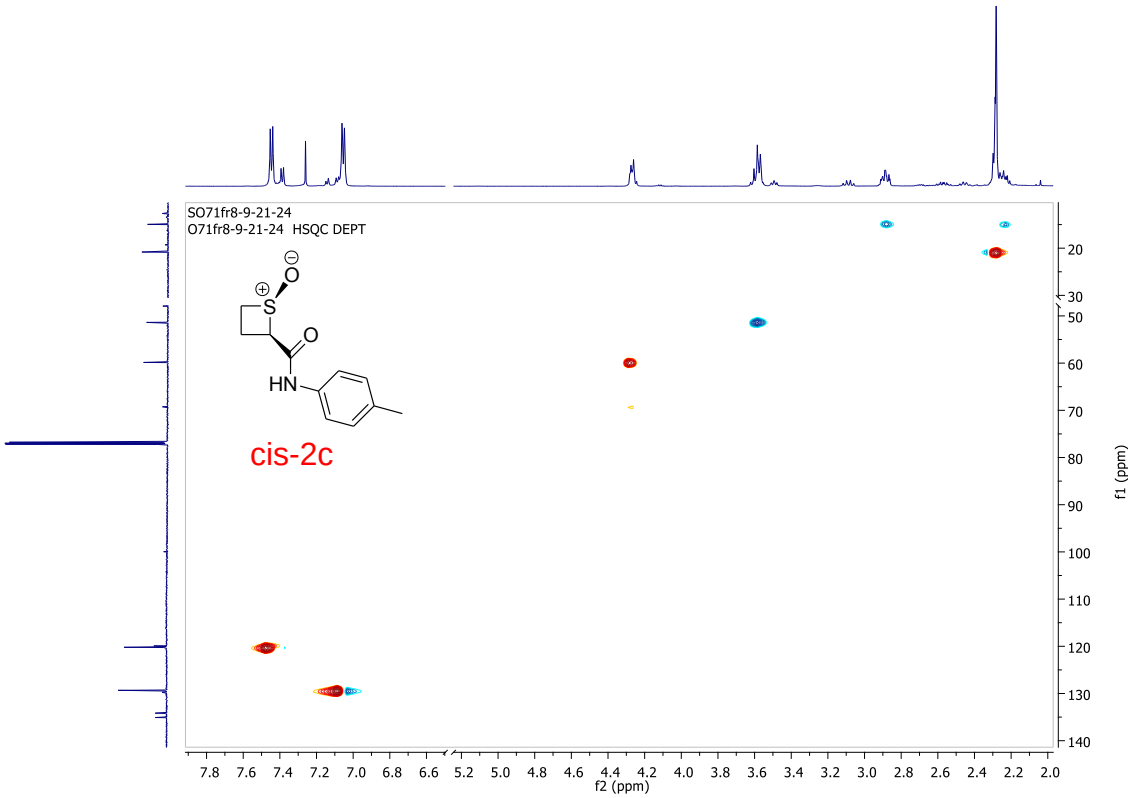

SO71fr10-20
SO71fr10-20 carboni
trans-2c
164.2
135.1
134.3
129.4
119.9
69.4
47.9
20.8
12.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

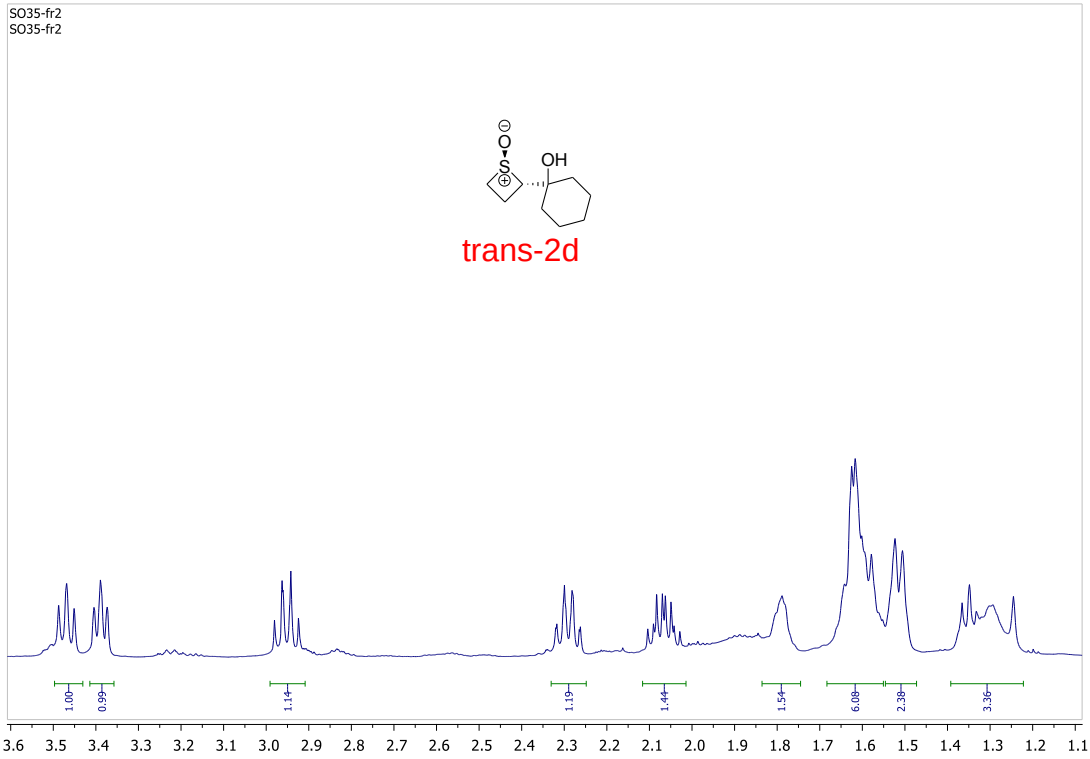

SO71fr10-20
SO71fr10-20 COSY
trans-2c
f1 (ppm)
f2 (ppm)

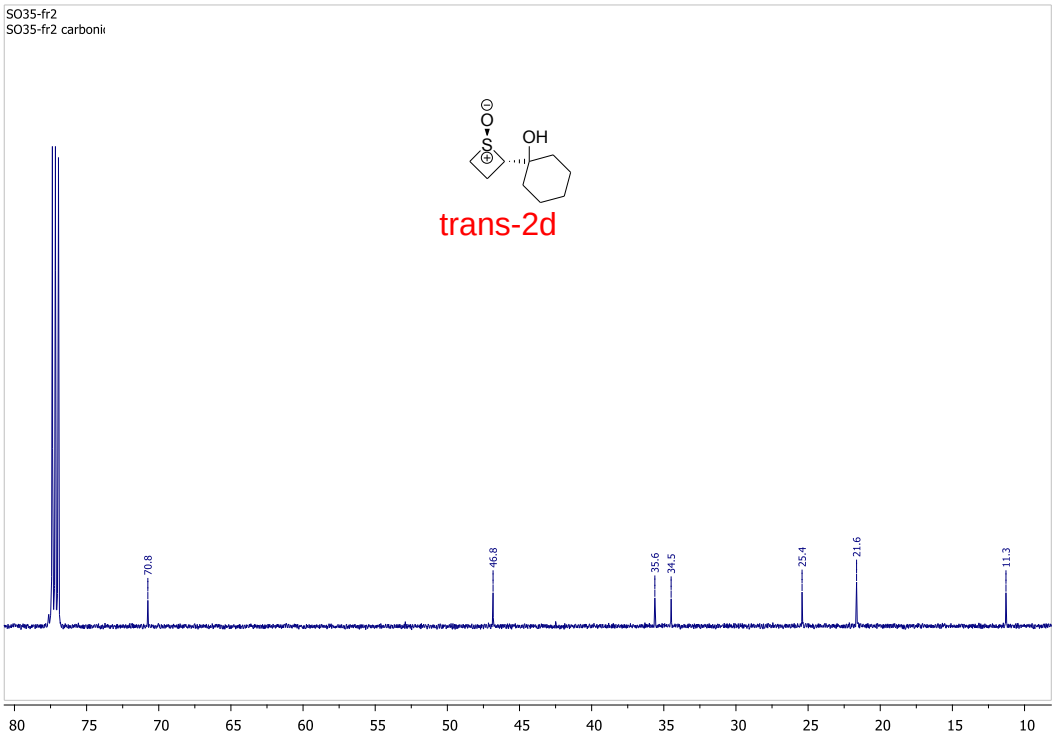

SO71fr8-9-21-24
O71fr8-9-21-24
cis-2c
0.79
1.00
0.52
0.85
0.44
1.54
0.51
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

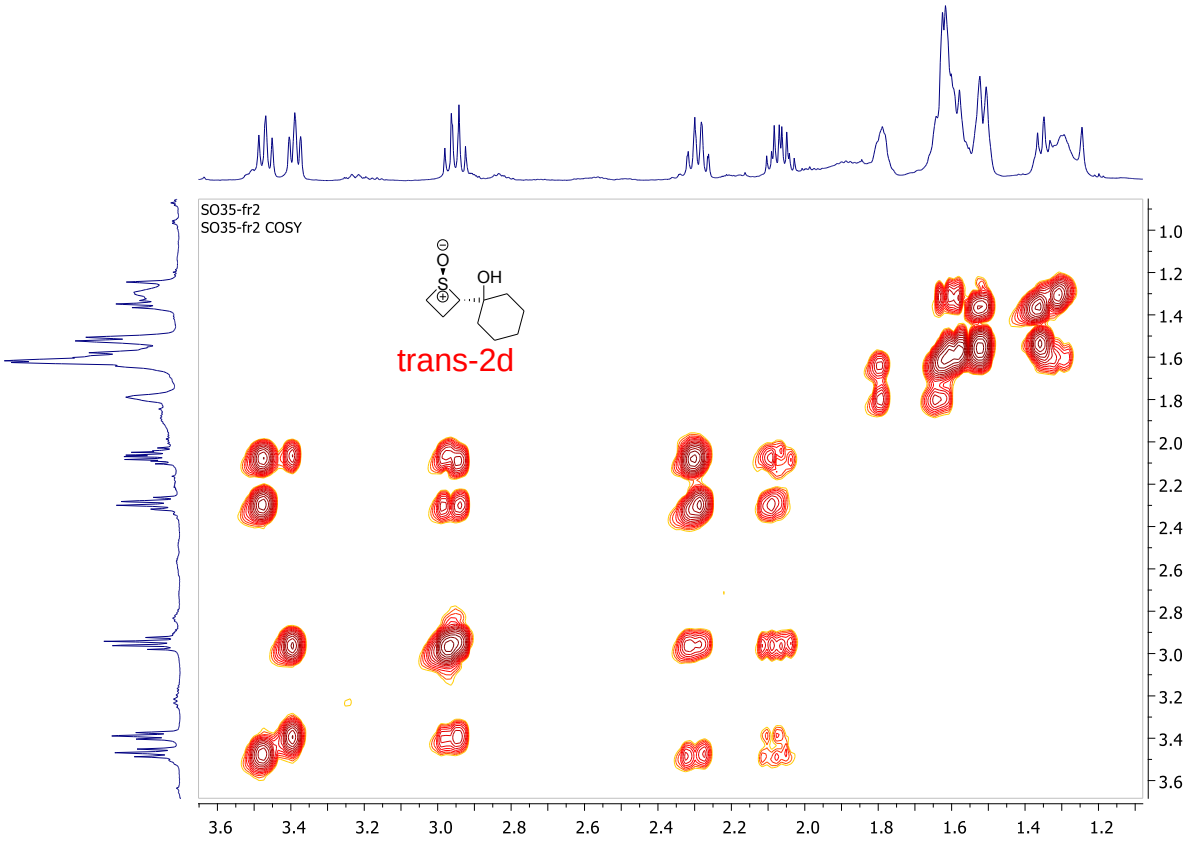

SO71fr8-9-21-24
O71fr8-9-21-24 carboni
cis-2c
164.0
135.1
134.2
129.3
120.2
59.9
51.4
20.8
15.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

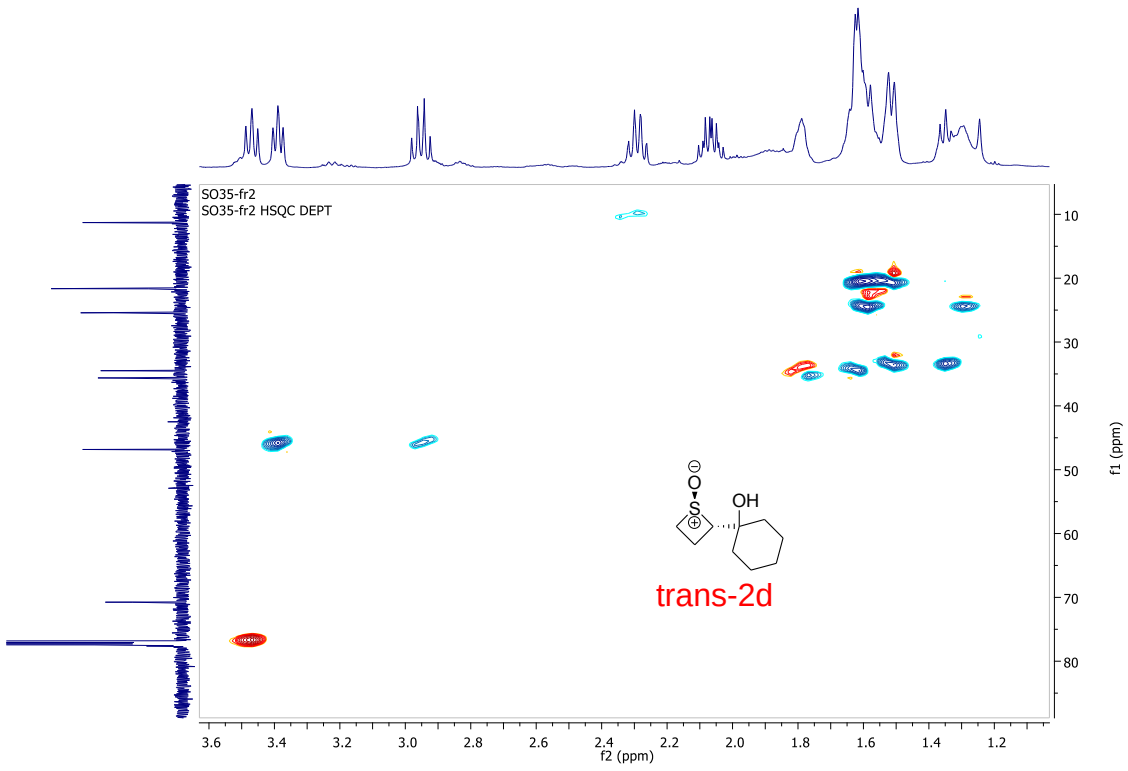

SO71fr8-9-21-24
O71fr8-9-21-24 COSY
cis-2c
f2 (ppm)
f1 (ppm)

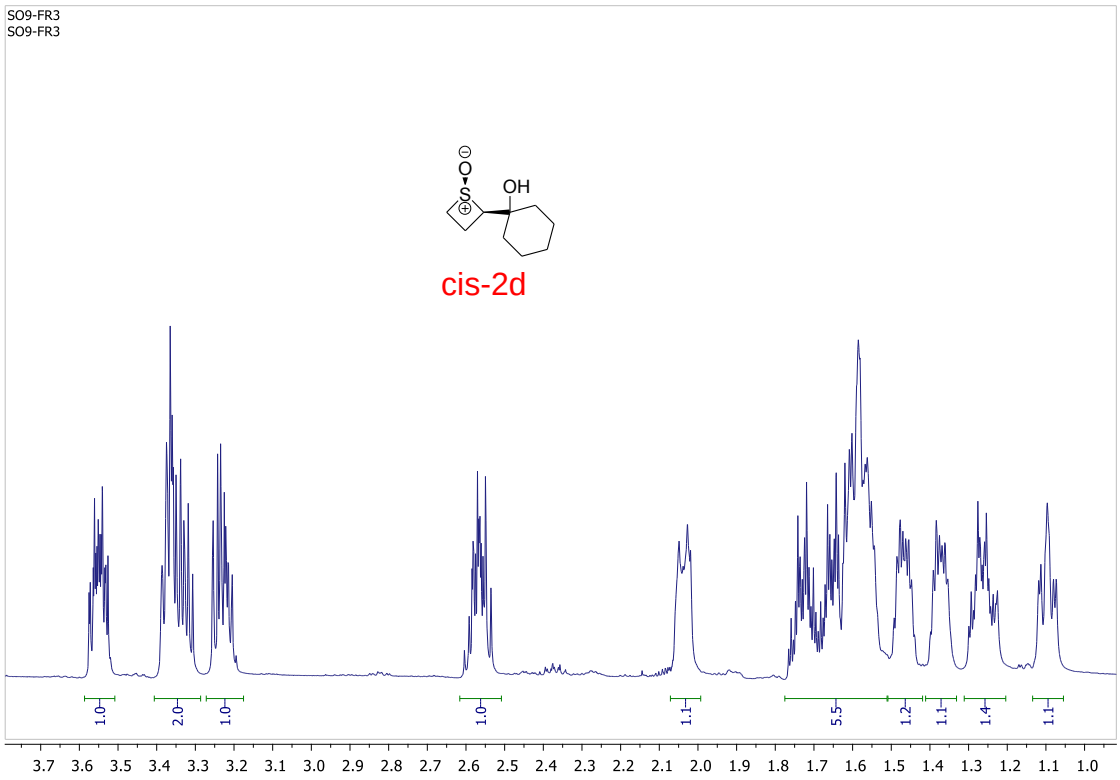

SO71fr8-9-21-24
O71fr8-9-21-24 HSQC DEPT
cis-2c
f2 (ppm)
f1 (ppm)

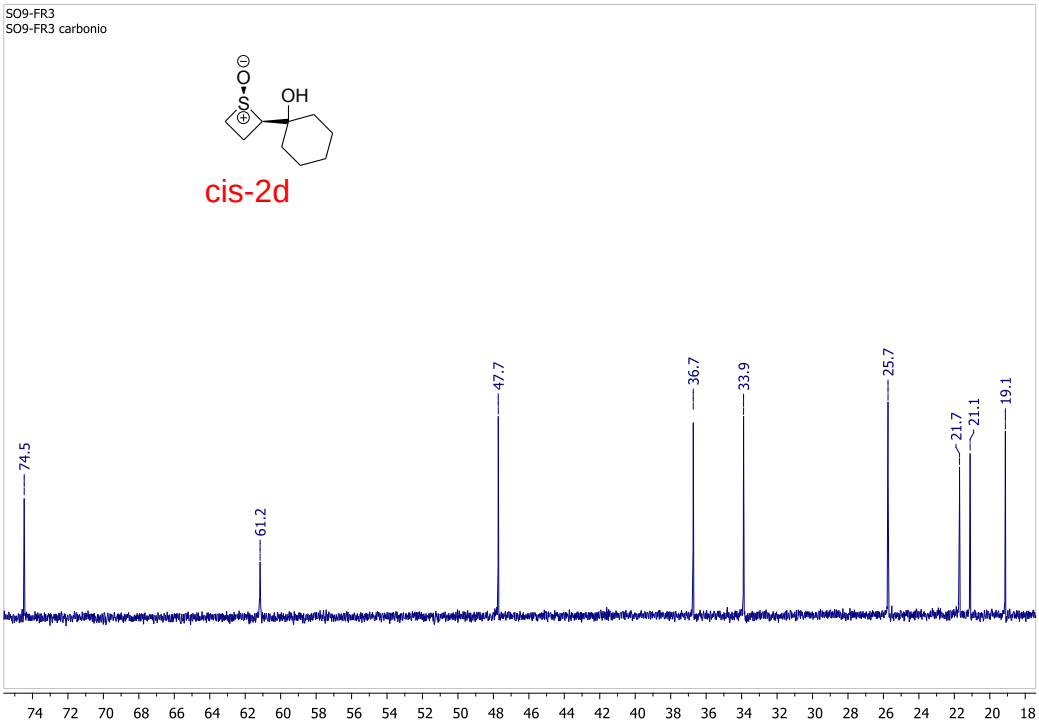

SO35-fr2
SO35-fr2
OH
trans-2d
1.00
0.99
1.14
1.19
1.44
1.54
6.08
2.38
3.36
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1

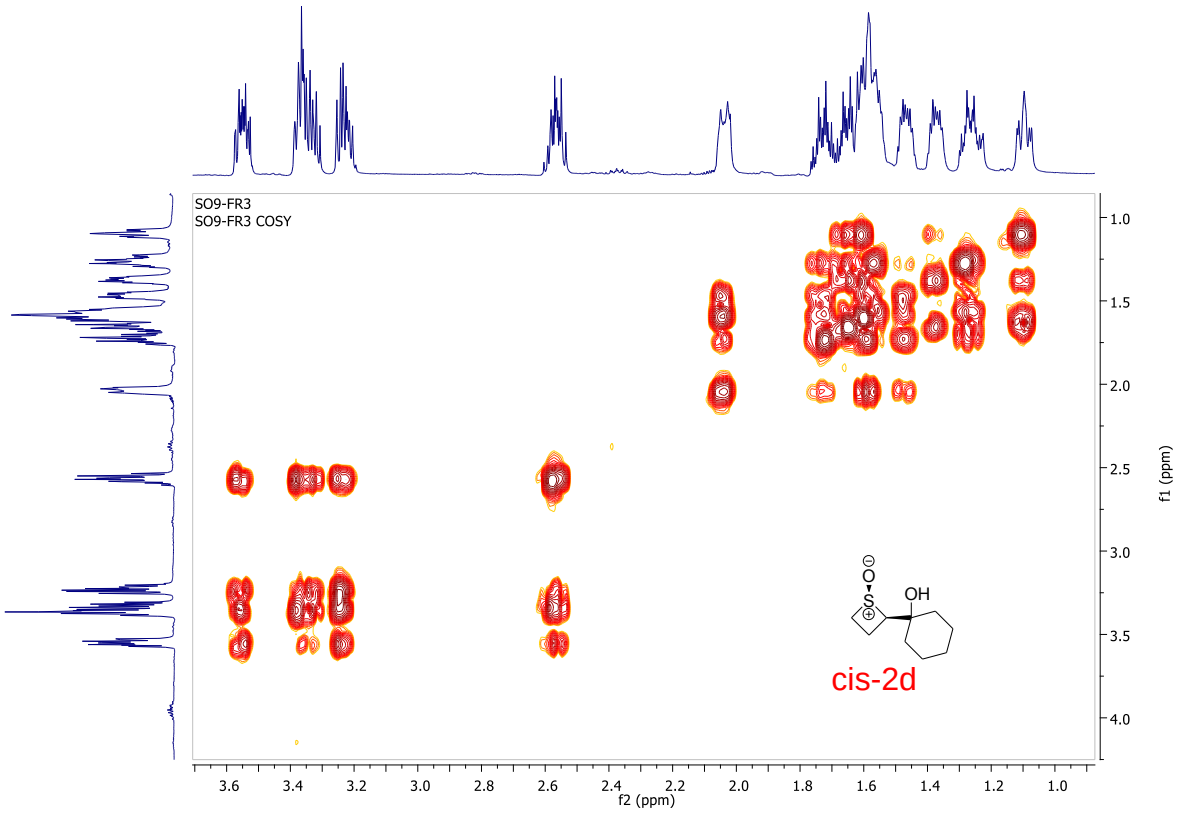

SO35-fr2
SO35-fr2 carboni
OH
trans-2d
70.8
46.8
35.6
34.5
25.4
21.6
11.3
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10

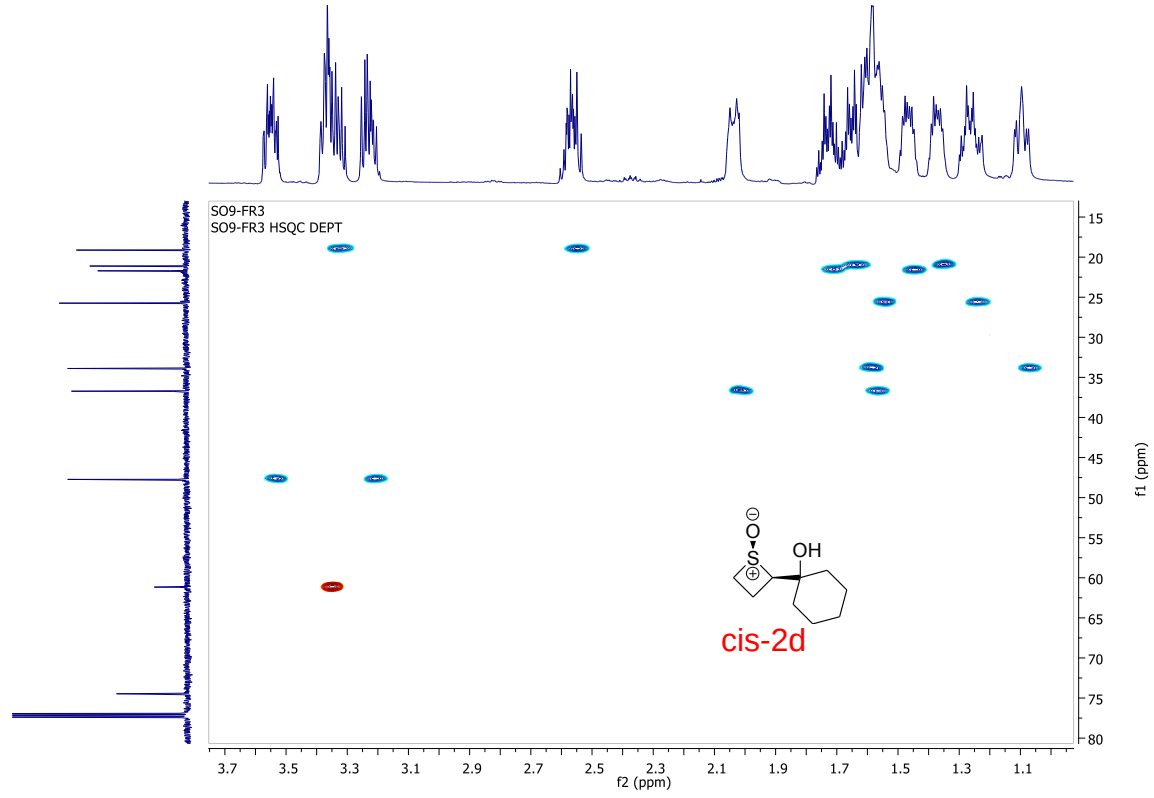

SO35-fr2
SO35-fr2 COSY
OH
trans-2d
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0

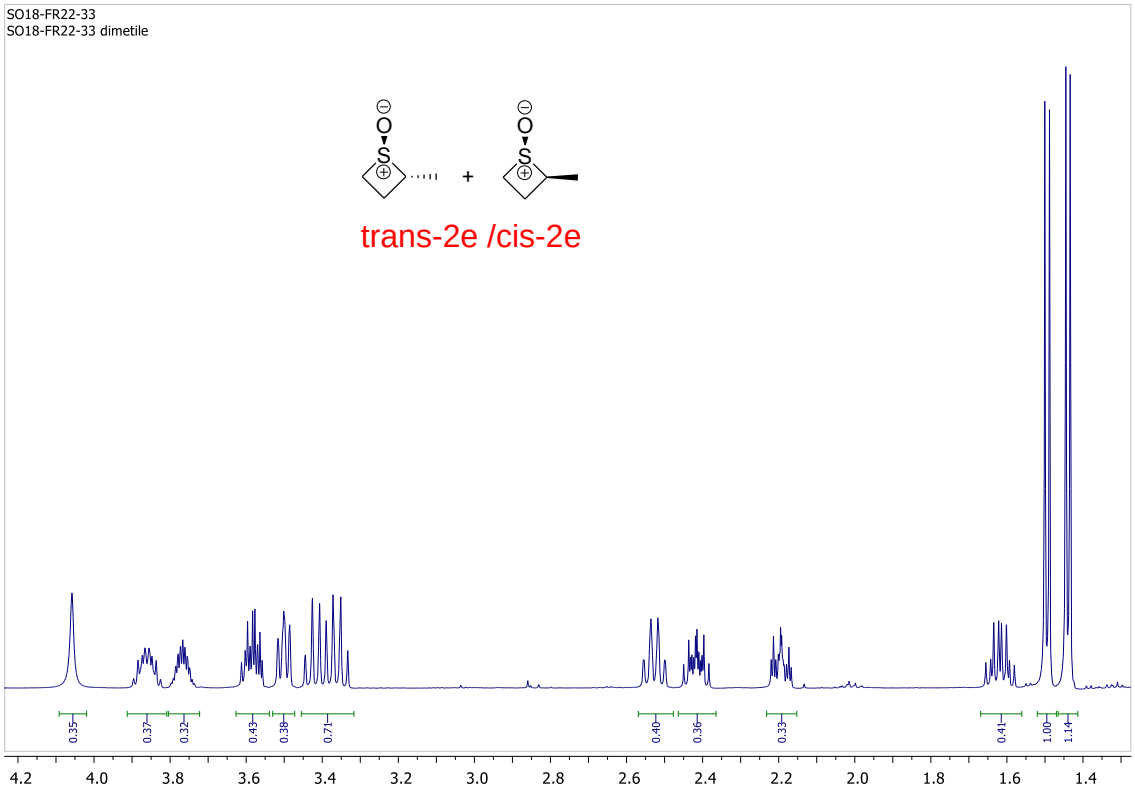

SO35-fr2
SO35-fr2 HSQC DEPT
OH
trans-2d
f2 (ppm)
f1 (ppm)
10
20
30
40
50
60
70
80

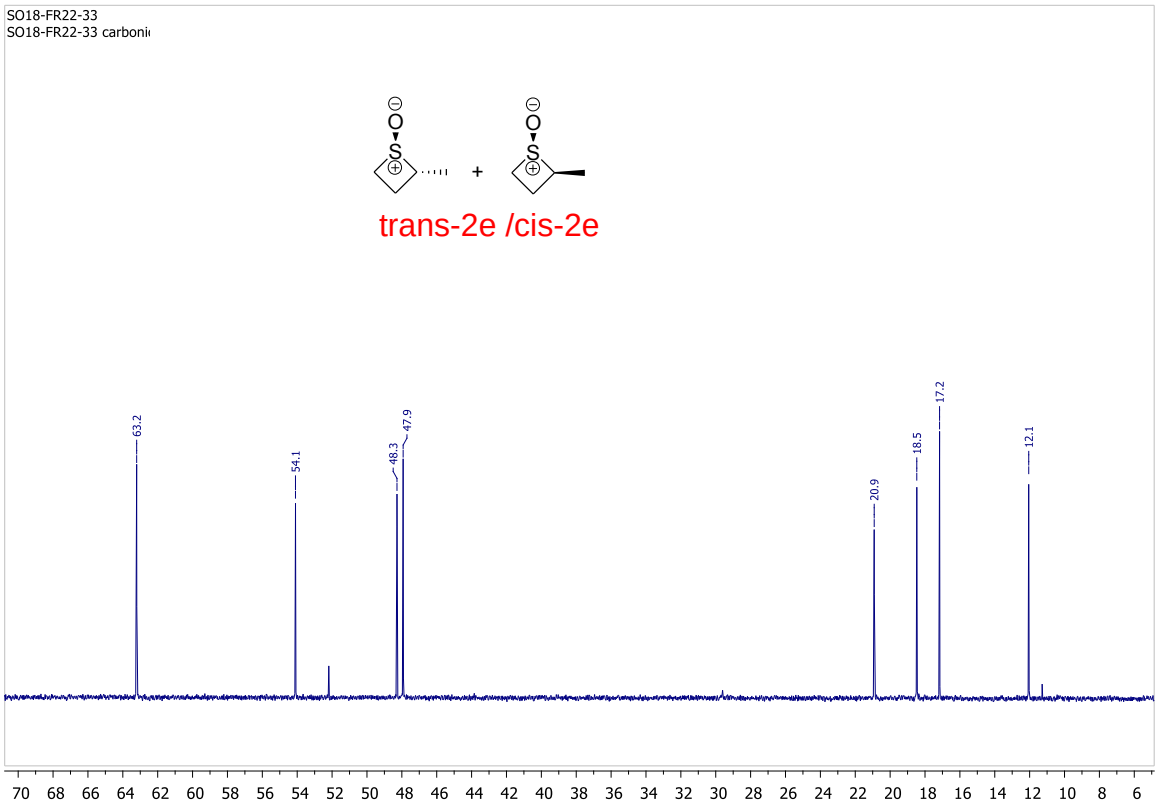

SO9-FR3
SO9-FR3
OH
cis-2d
1.0
2.0
1.0
1.0
1.1
5.5
1.2
1.1
1.4
1.1
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0

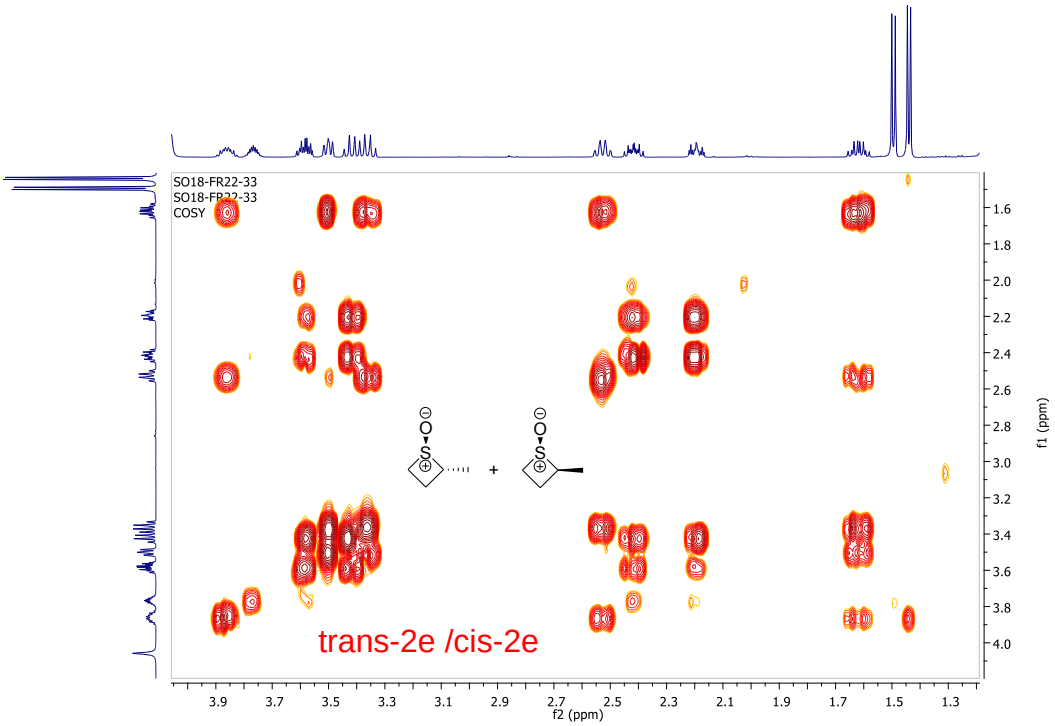

SO9-FR3
SO9-FR3 carbonio
OH
cis-2d
74.5
61.2
47.7
36.7
33.9
25.7
21.7
21.1
19.1
74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18

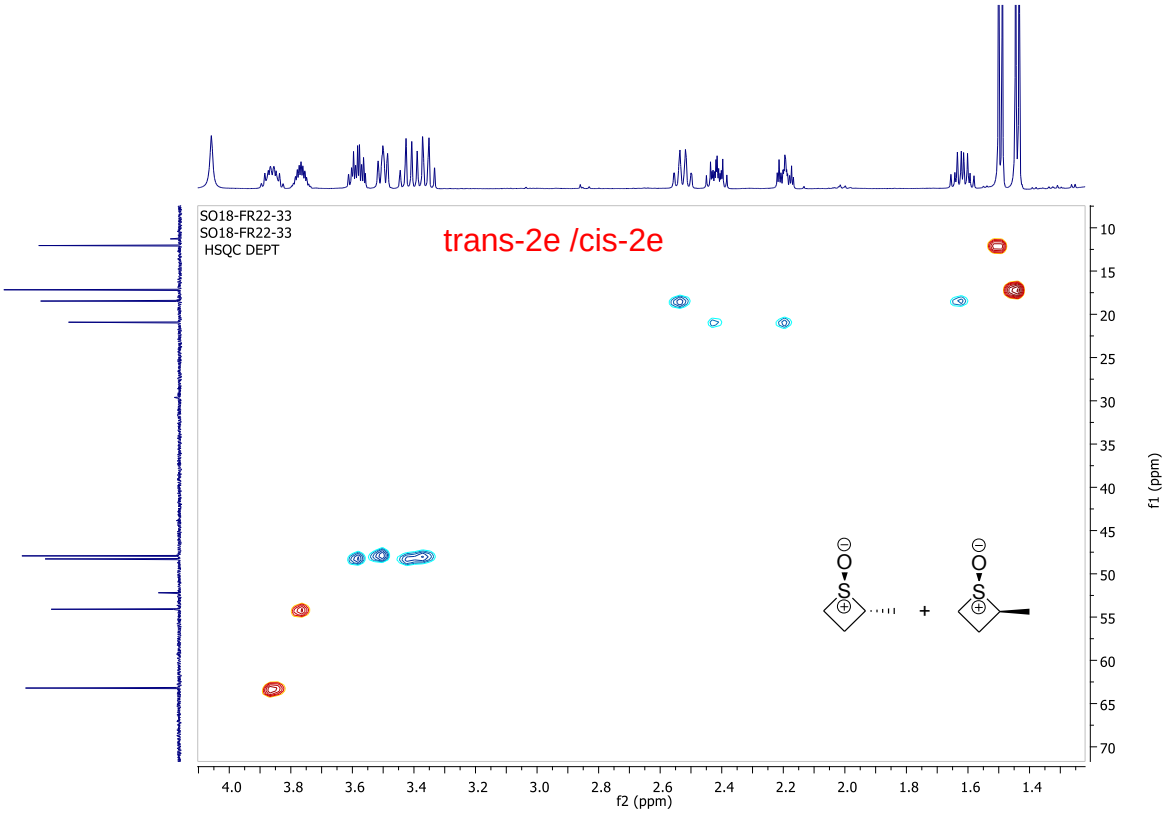

SO9-FR3
SO9-FR3 COSY
OH
cis-2d
f1 (ppm)
f2 (ppm)

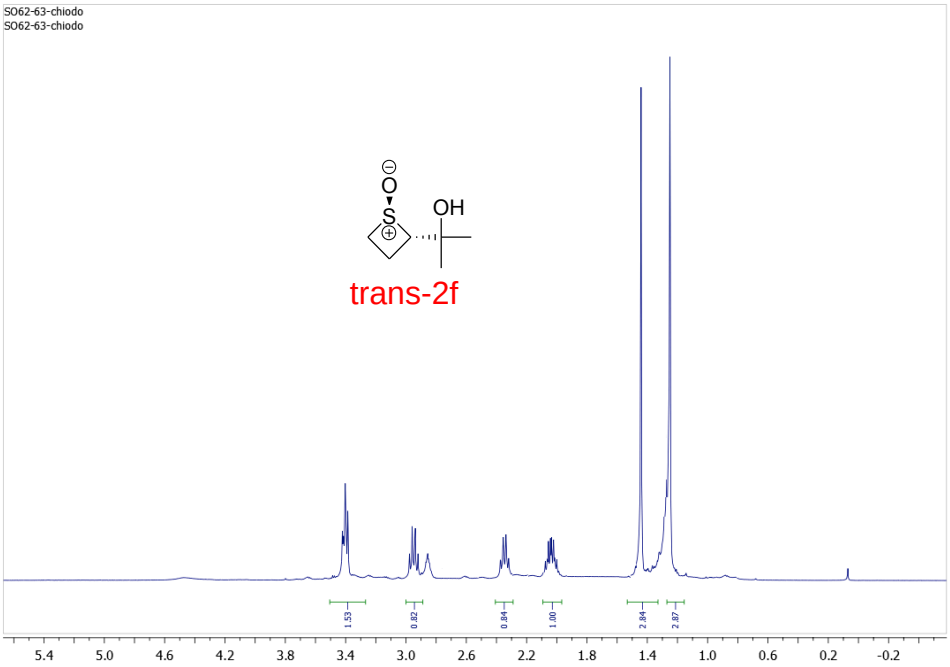

SO9-FR3
SO9-FR3 HSQC DEPT
OH
cis-2d
f1 (ppm)
f2 (ppm)

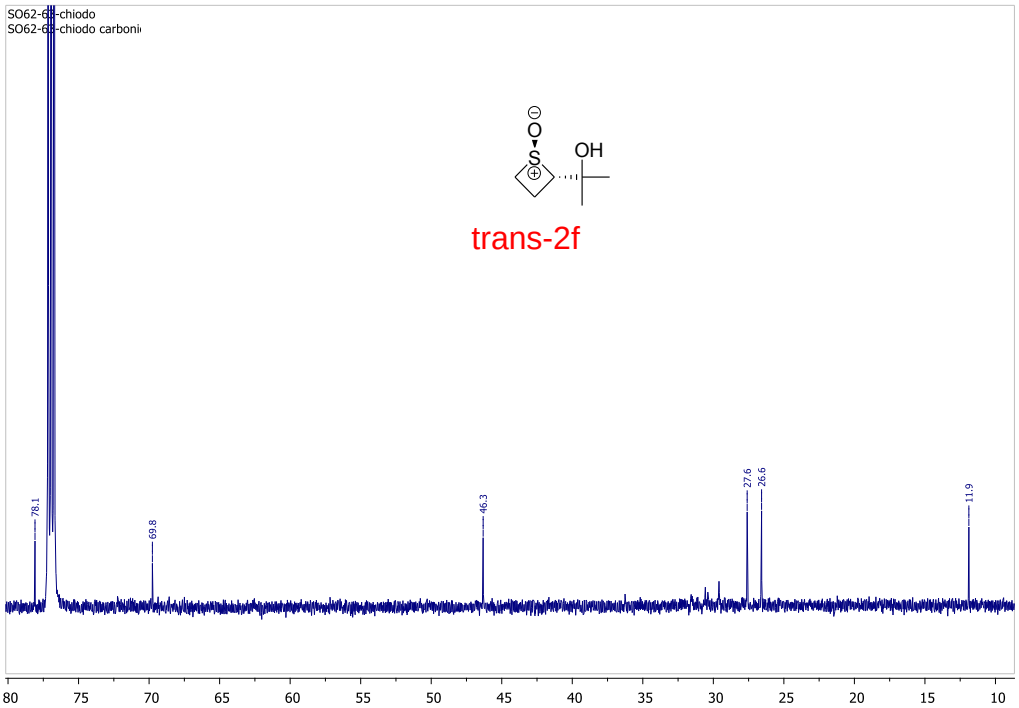

SO18-FR22-33
SO18-FR22-33 dimetile
trans-2e /cis-2e
0.35
0.37
0.32
0.43
0.38
0.71
0.40
0.36
0.33
0.41
1.00
1.14
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4

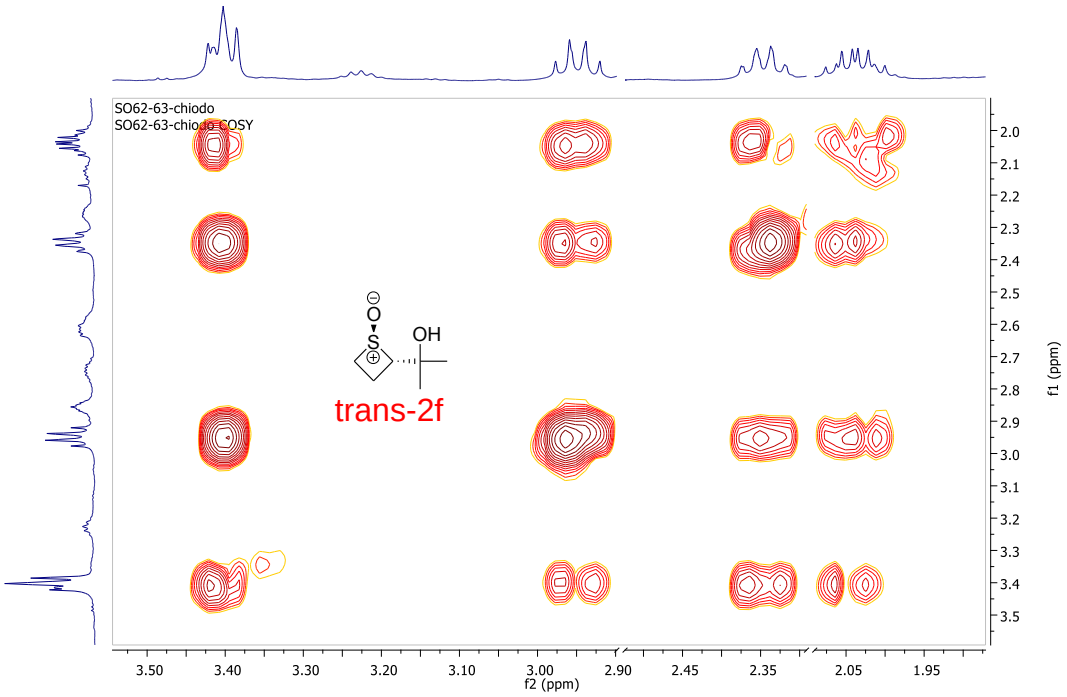

SO18-FR22-33
SO18-FR22-33 carboni
trans-2e /cis-2e
63.2
54.1
48.3
47.9
20.9
18.5
17.2
12.1
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6

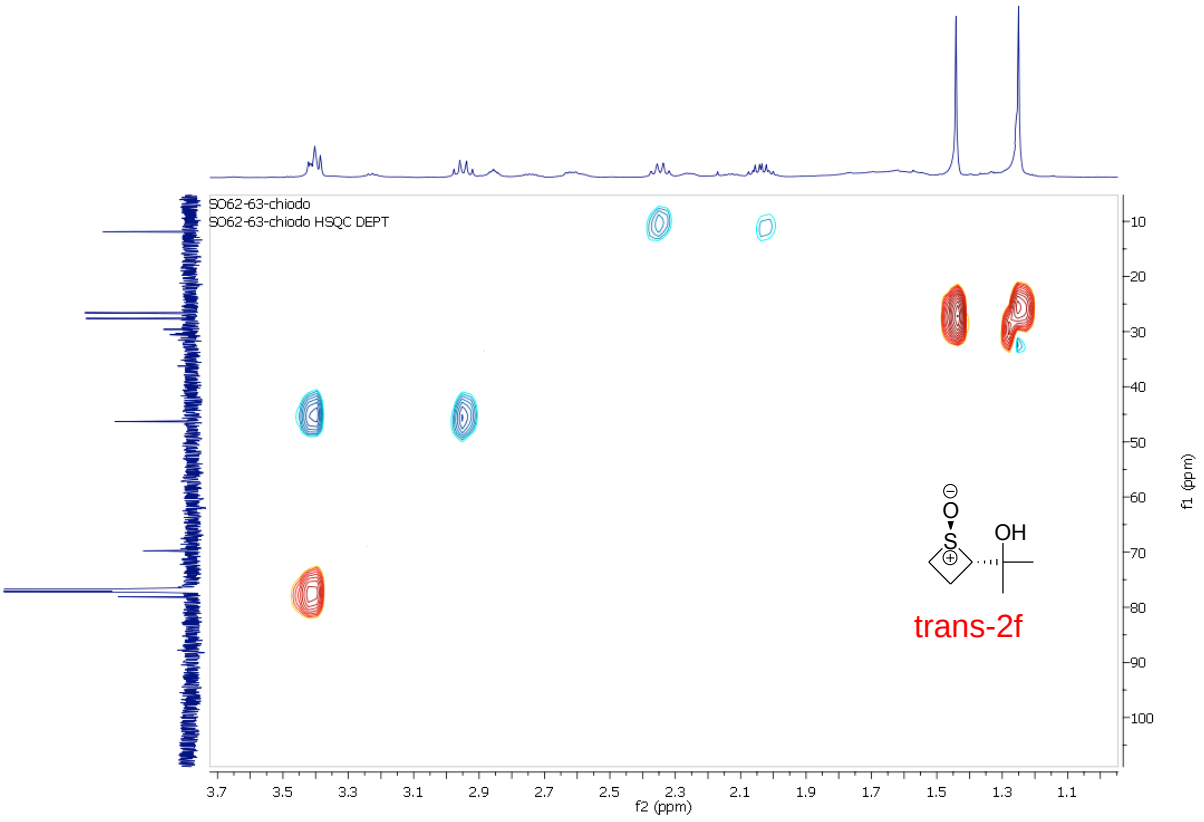

SO18-FR22-33
SO18-FR22-33
COSY
trans-2e /cis-2e
f2 (ppm)
f1 (ppm)

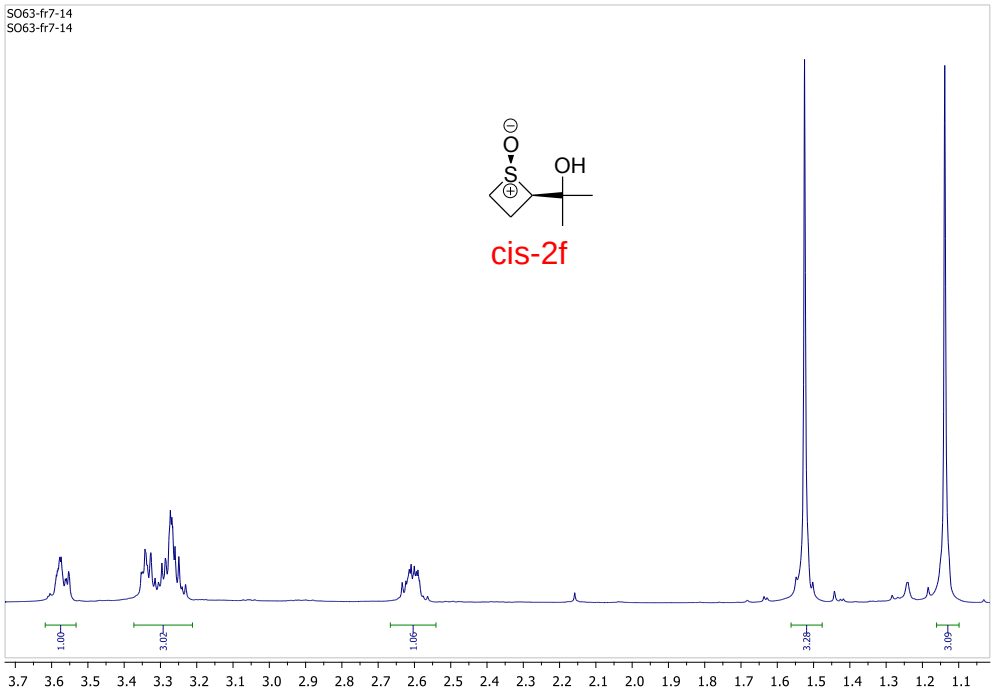

SO18-FR22-33
SO18-FR22-33
HSQC DEPT
trans-2e /cis-2e
f2 (ppm)
f1 (ppm)

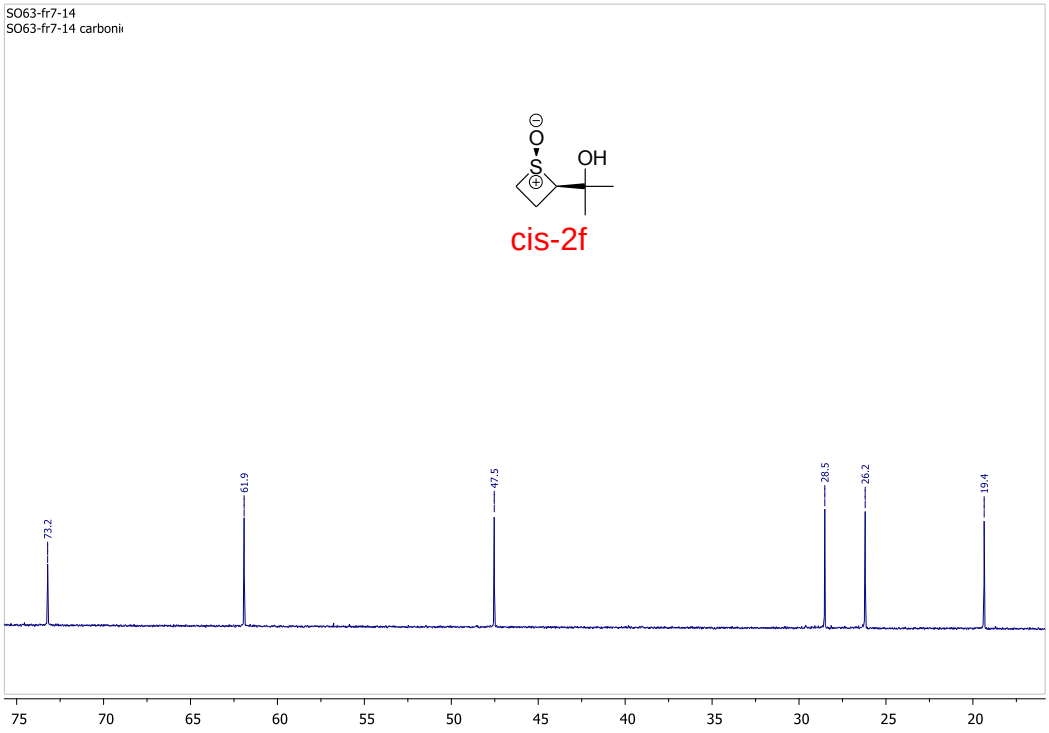

SO62-63-chiodo
SO62-63-chiodo
OH
trans-2f
1.53
0.82
0.84
1.00
2.84
2.87
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2

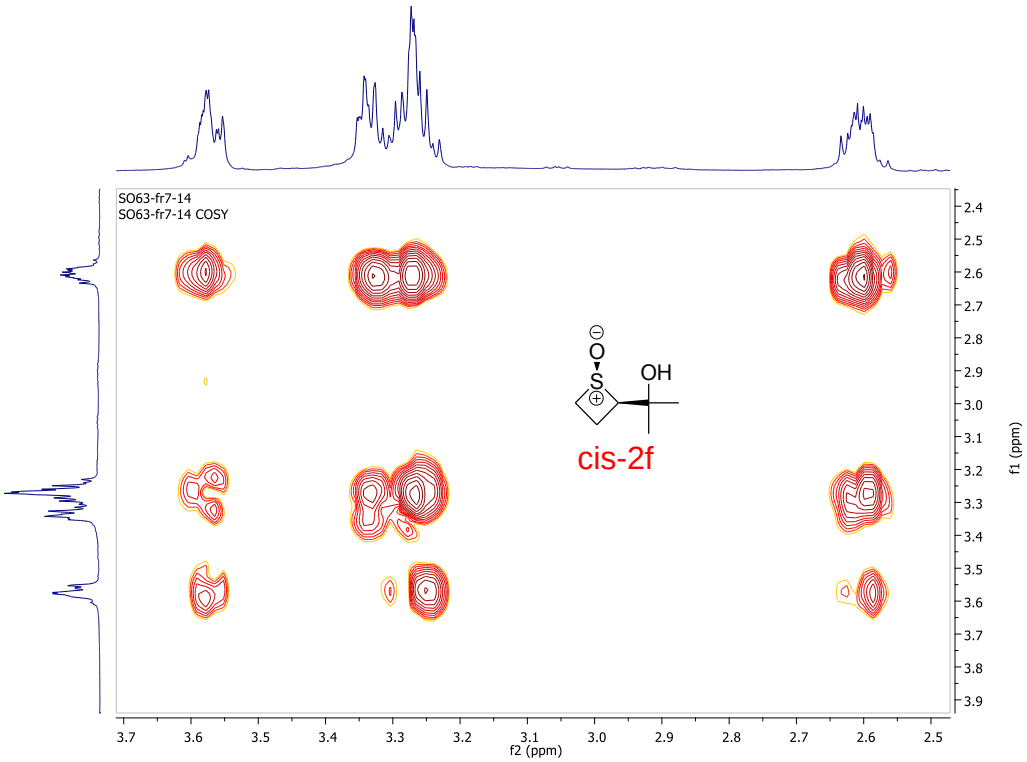

SO62-63-chiodo
SO62-63-chiodo carboni
OH
trans-2f
78.1
69.8
46.3
27.6
26.6
11.9
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10

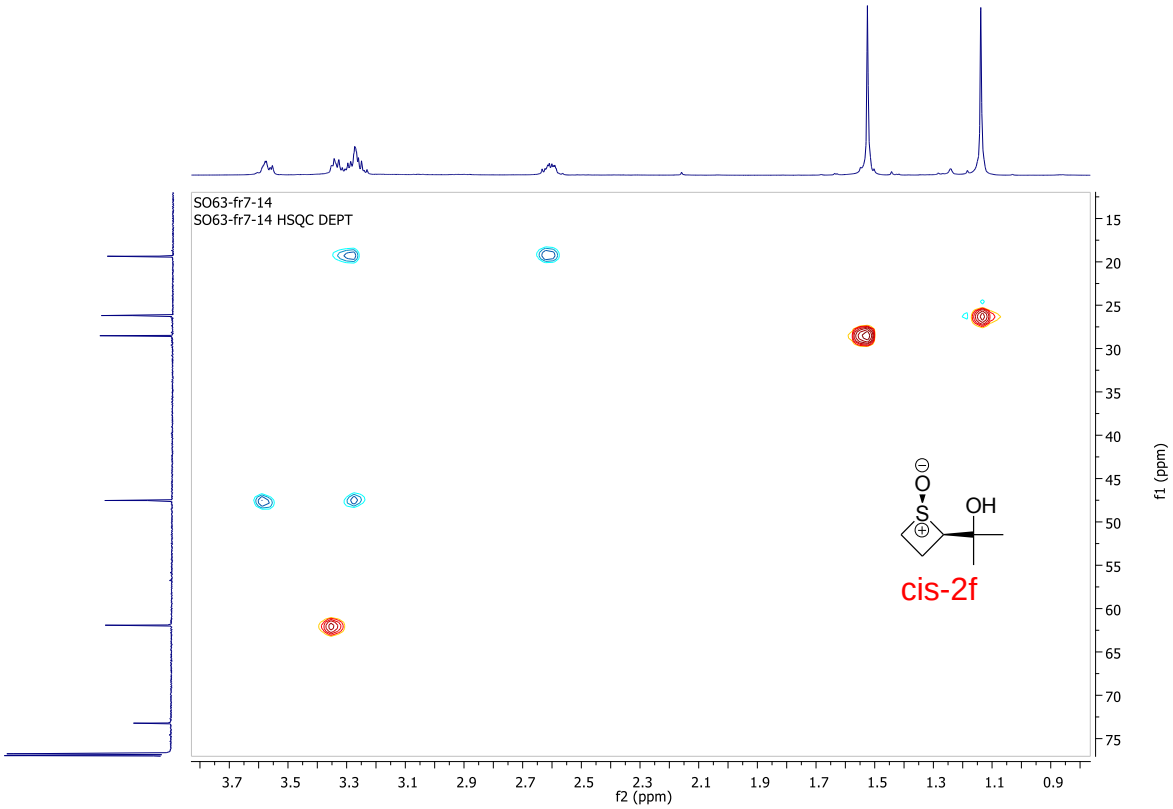

SO62-63-chiodo
SO62-63-chiodo COSY
OH
trans-2f
f1 (ppm)
f2 (ppm)

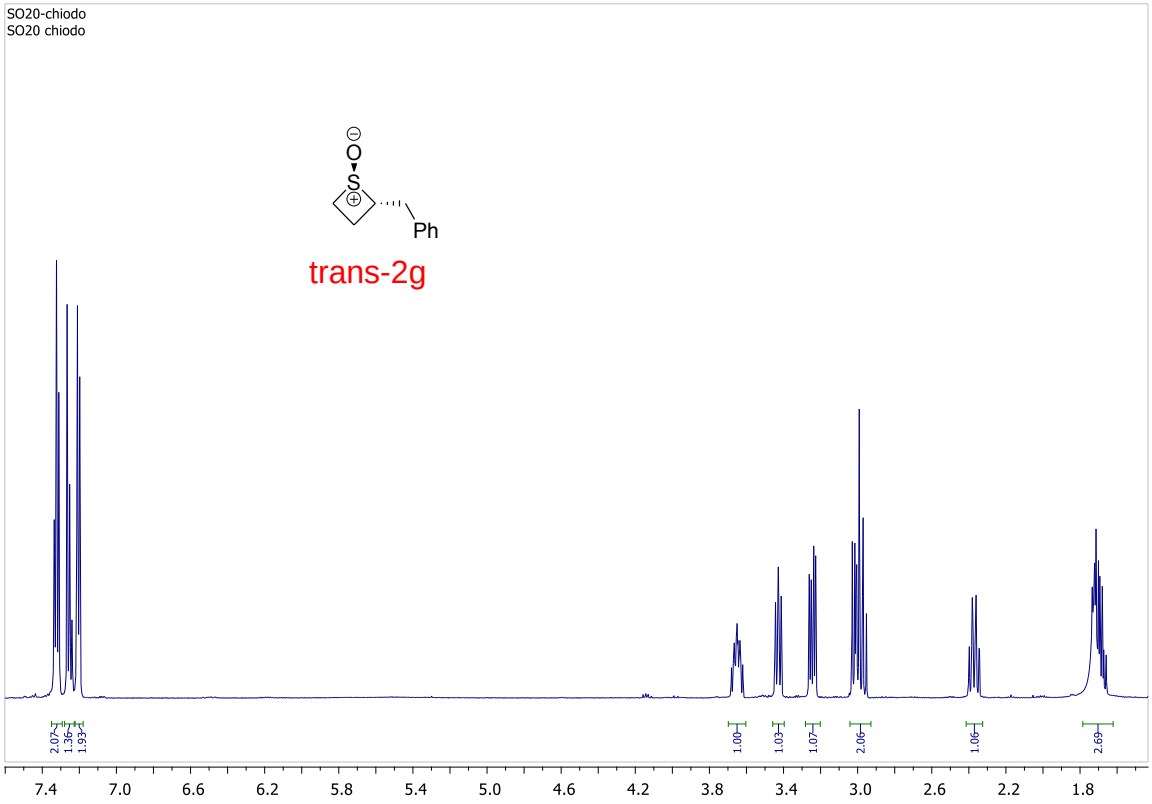

SO62-63-chiodo
SO62-63-chiodo HSQC DEPT
OH
trans-2f
f1 (ppm)
f2 (ppm)

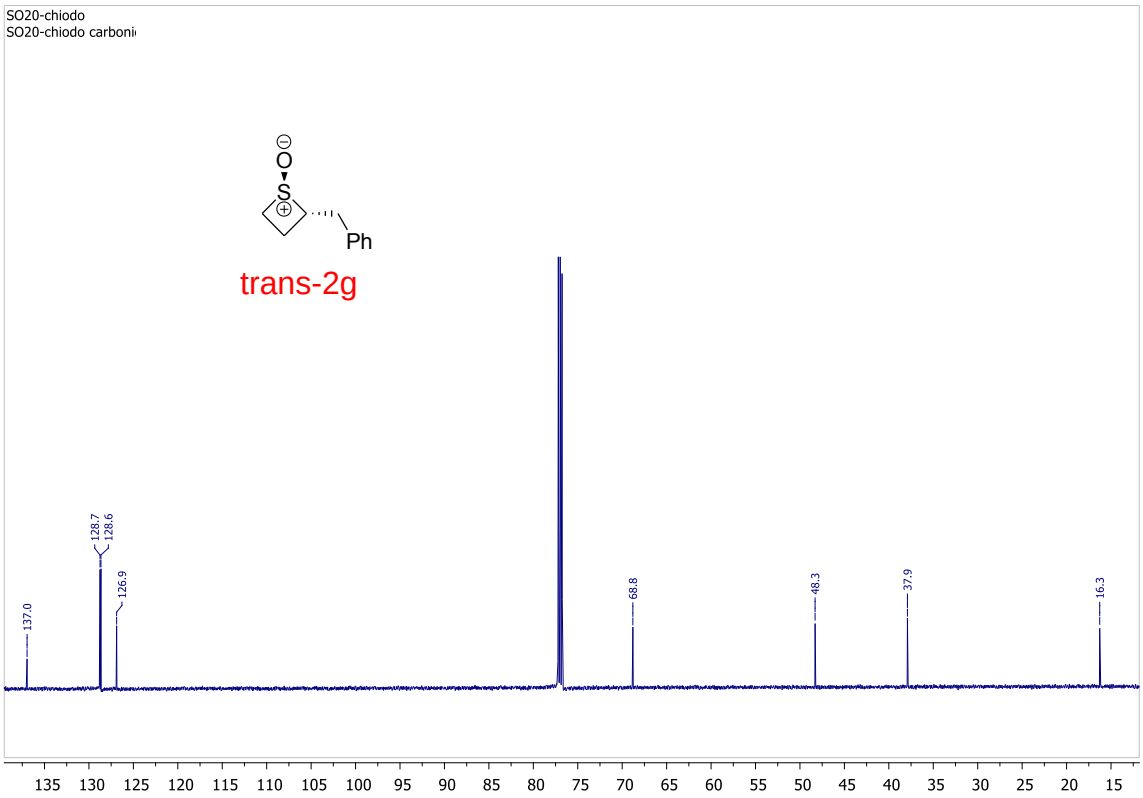

SO63-fr7-14
SO63-fr7-14
OH
cis-2f
1.00
3.02
1.06
3.28
3.09
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1

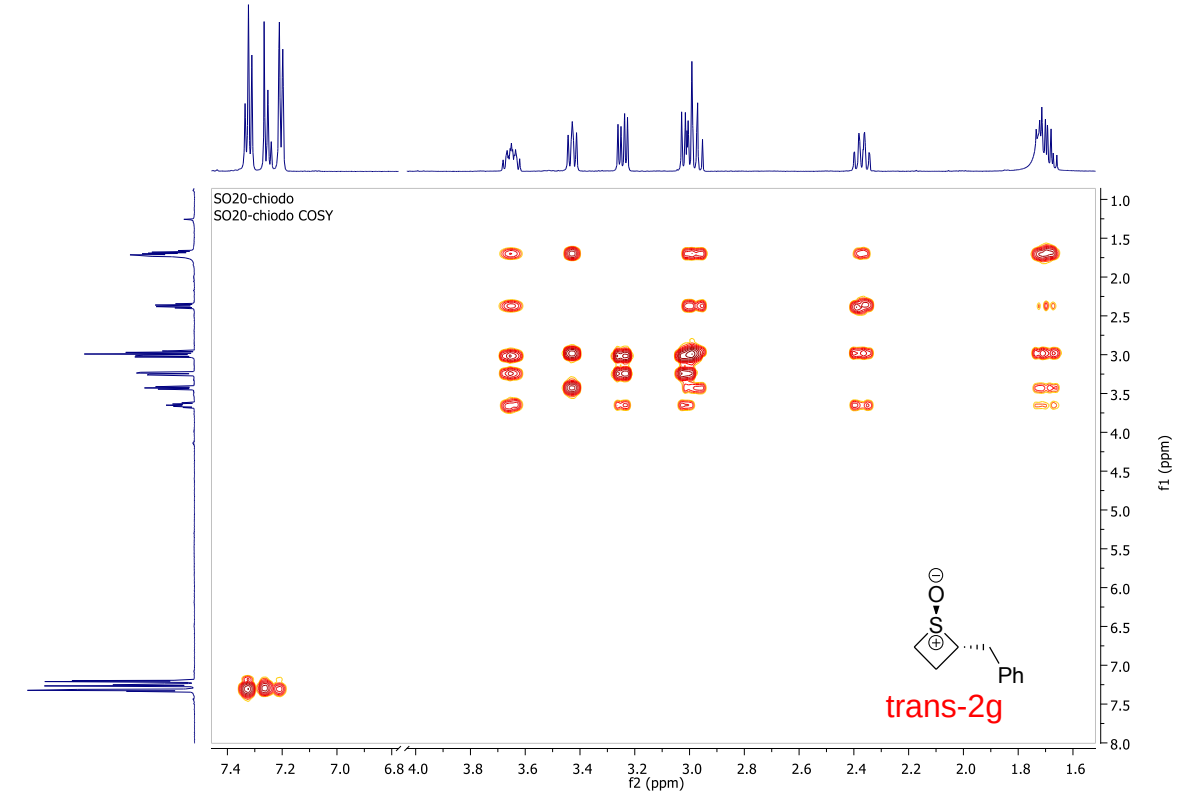

SO63-fr7-14
SO63-fr7-14 carboni
OH
cis-2f
73.2
61.9
47.5
28.5
26.2
19.4
75 70 65 60 55 50 45 40 35 30 25 20

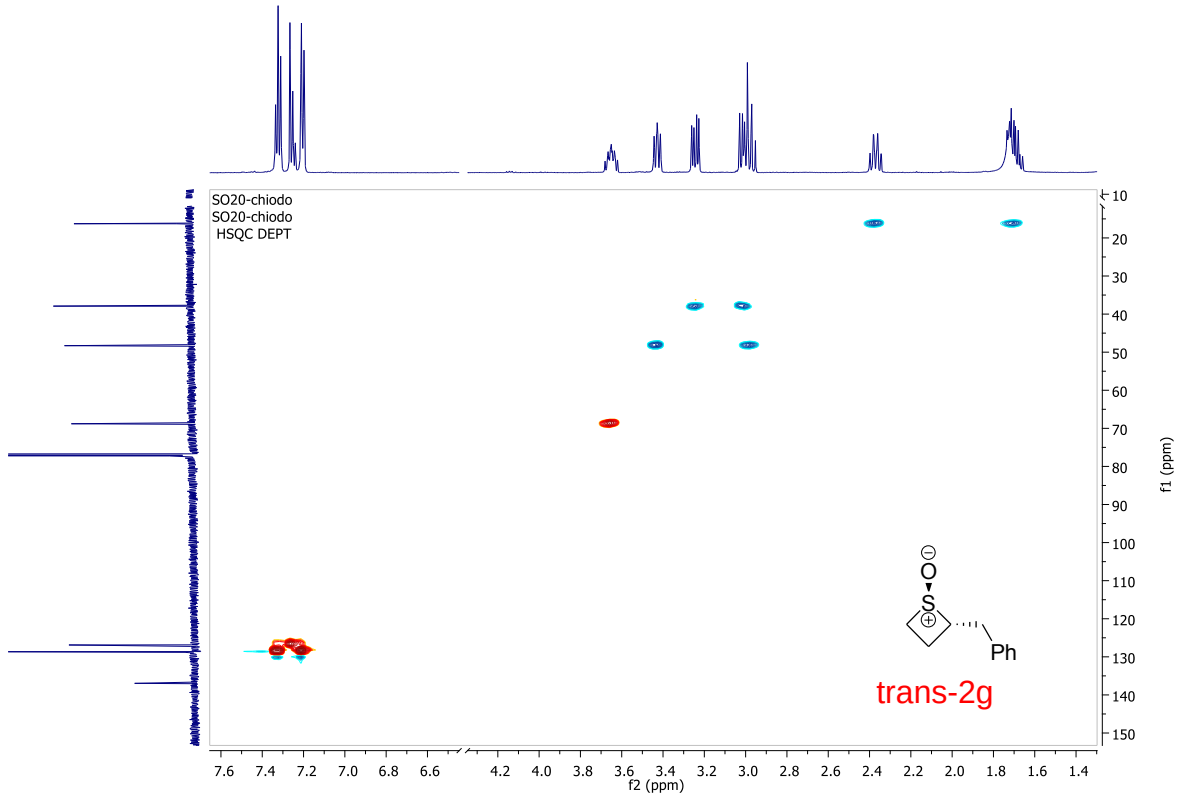

SO63-fr7-14
SO63-fr7-14 COSY
OH
cis-2f
f1 (ppm)
f2 (ppm)

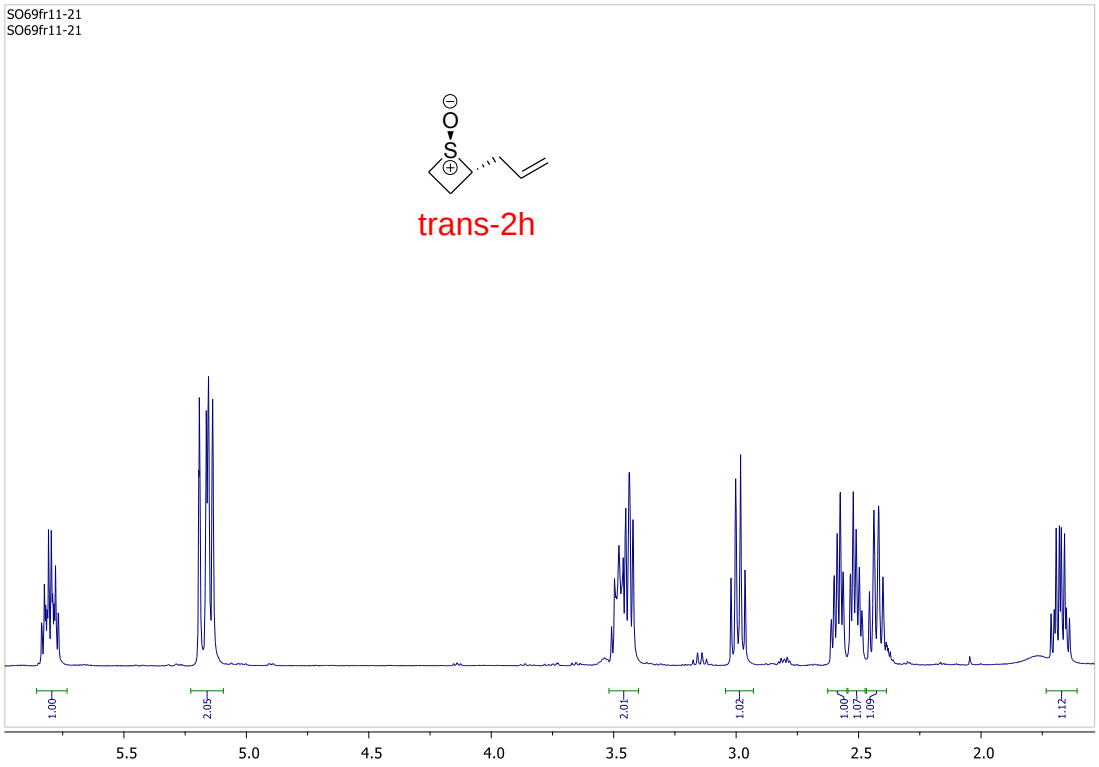

SO63-fr7-14
SO63-fr7-14 HSQC DEPT
OH
cis-2f
f1 (ppm)
f2 (ppm)

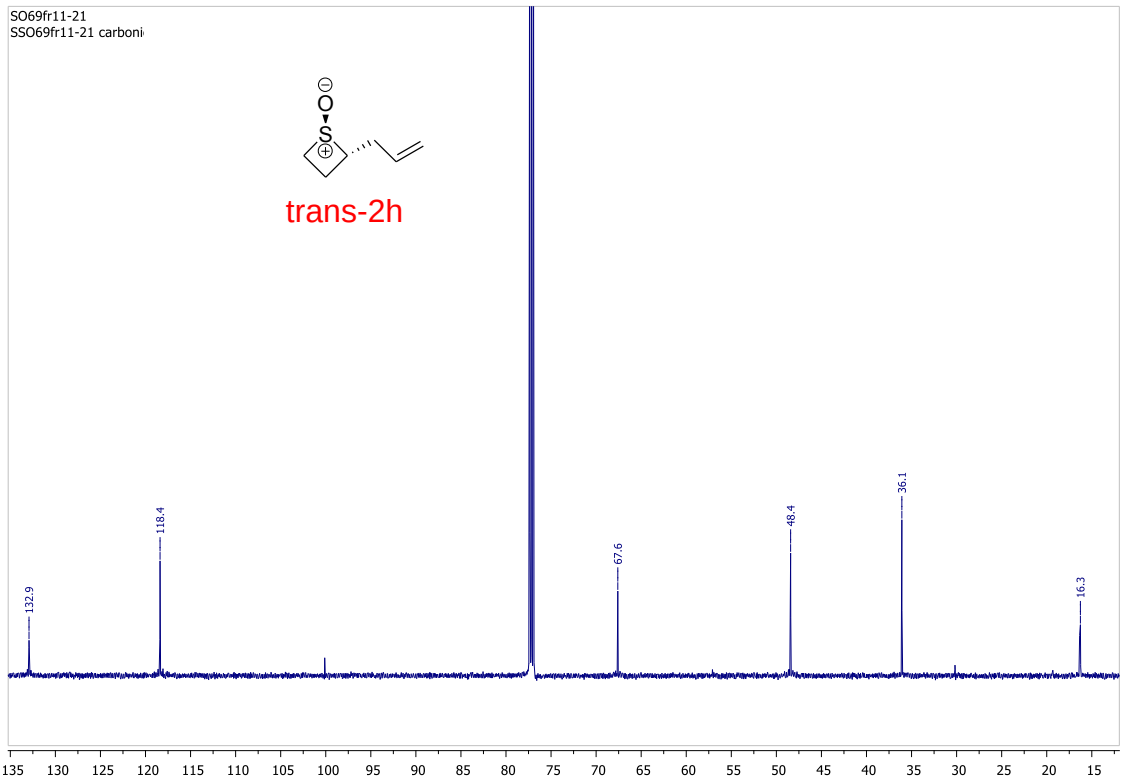

SO20-chiodo
SO20 chiodo
Ph
trans-2g
2.07
1.36
1.93
1.00
1.03
1.07
2.06
1.06
2.69
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8

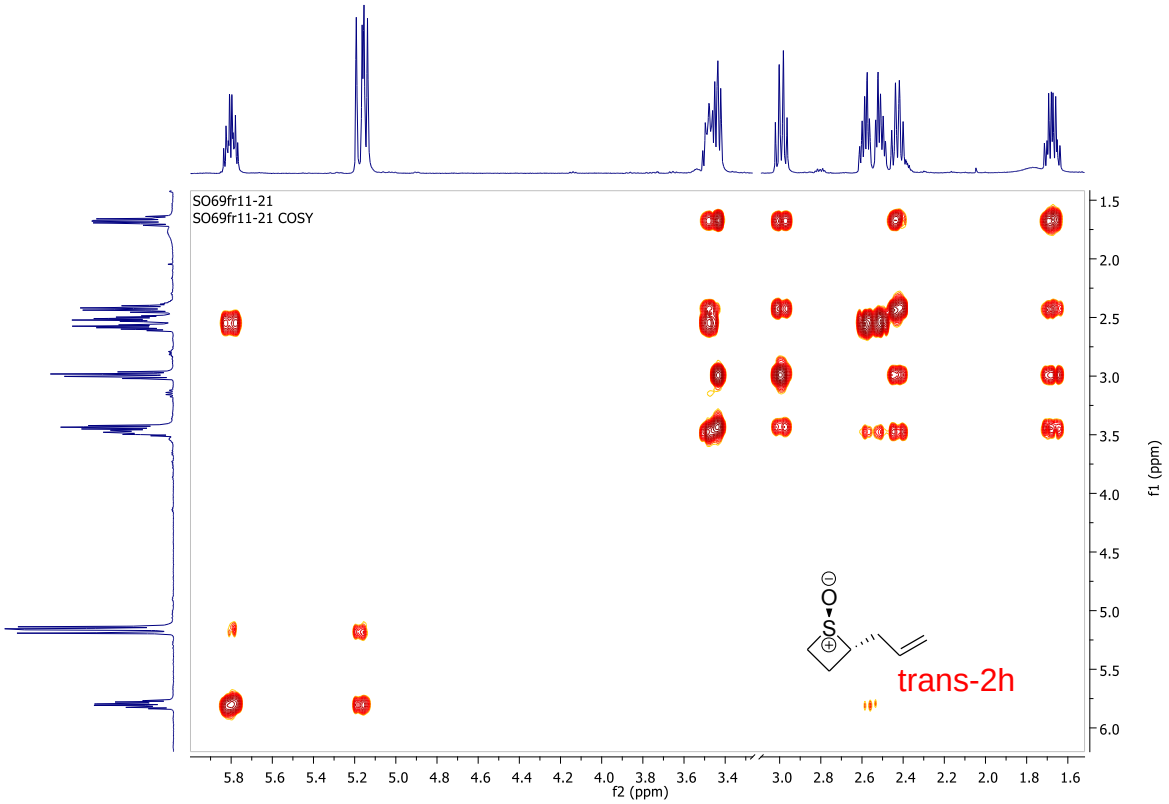

SO20-chiodo
SO20-chiodo carboni
Ph
trans-2g
137.0
128.7
128.6
126.9
68.8
48.3
37.9
16.3
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

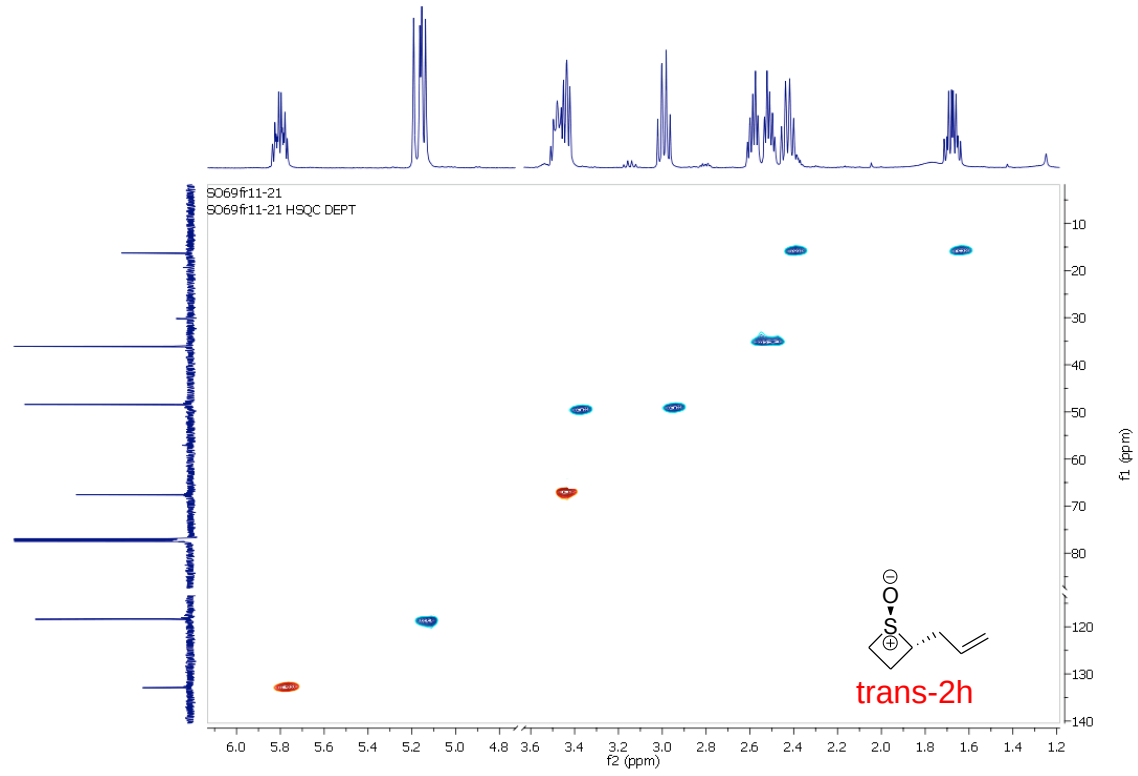

SO20-chiodo
SO20-chiodo COSY
trans-2g
f1 (ppm)
f2 (ppm)

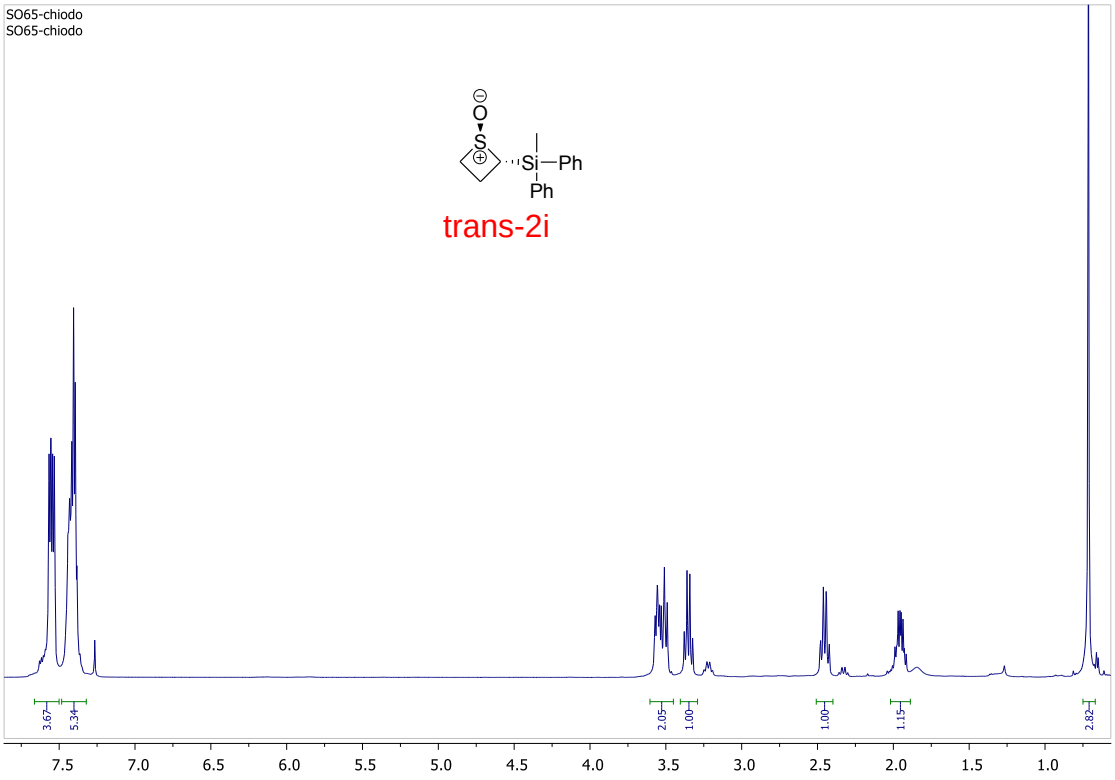

SO20-chiodo
SO20-chiodo
HSQC DEPT
trans-2g
f1 (ppm)
f2 (ppm)

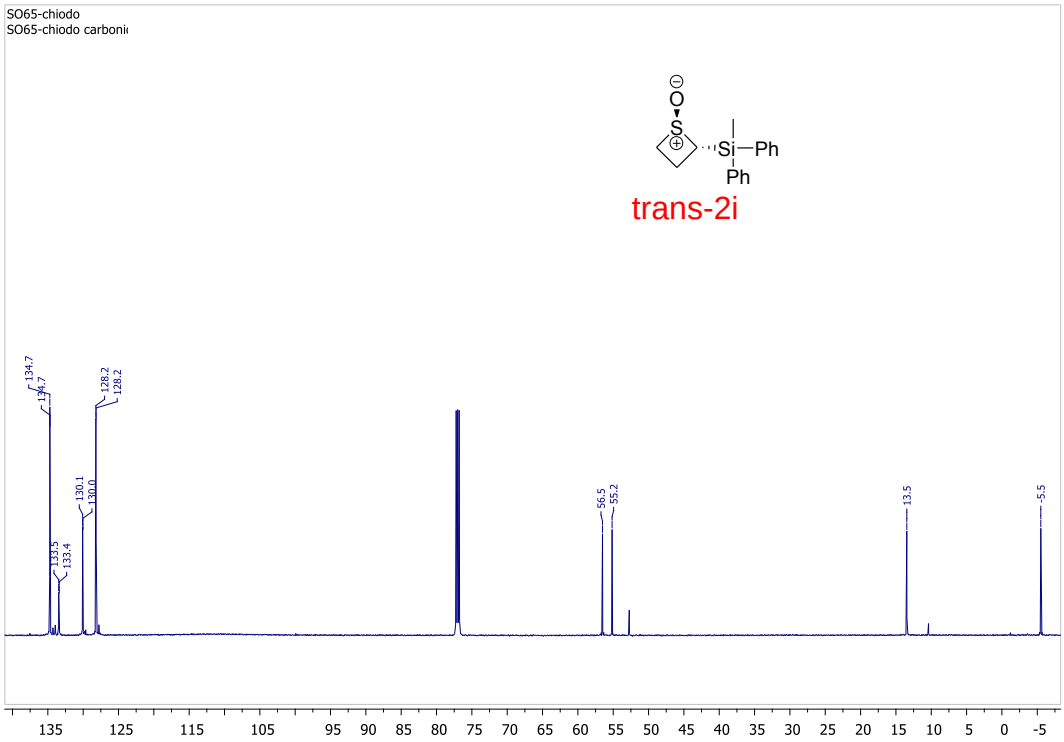

SO69fr11-21
SO69fr11-21
trans-2h
1.00
2.05
2.01
1.02
1.00
1.07
1.09
1.12
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

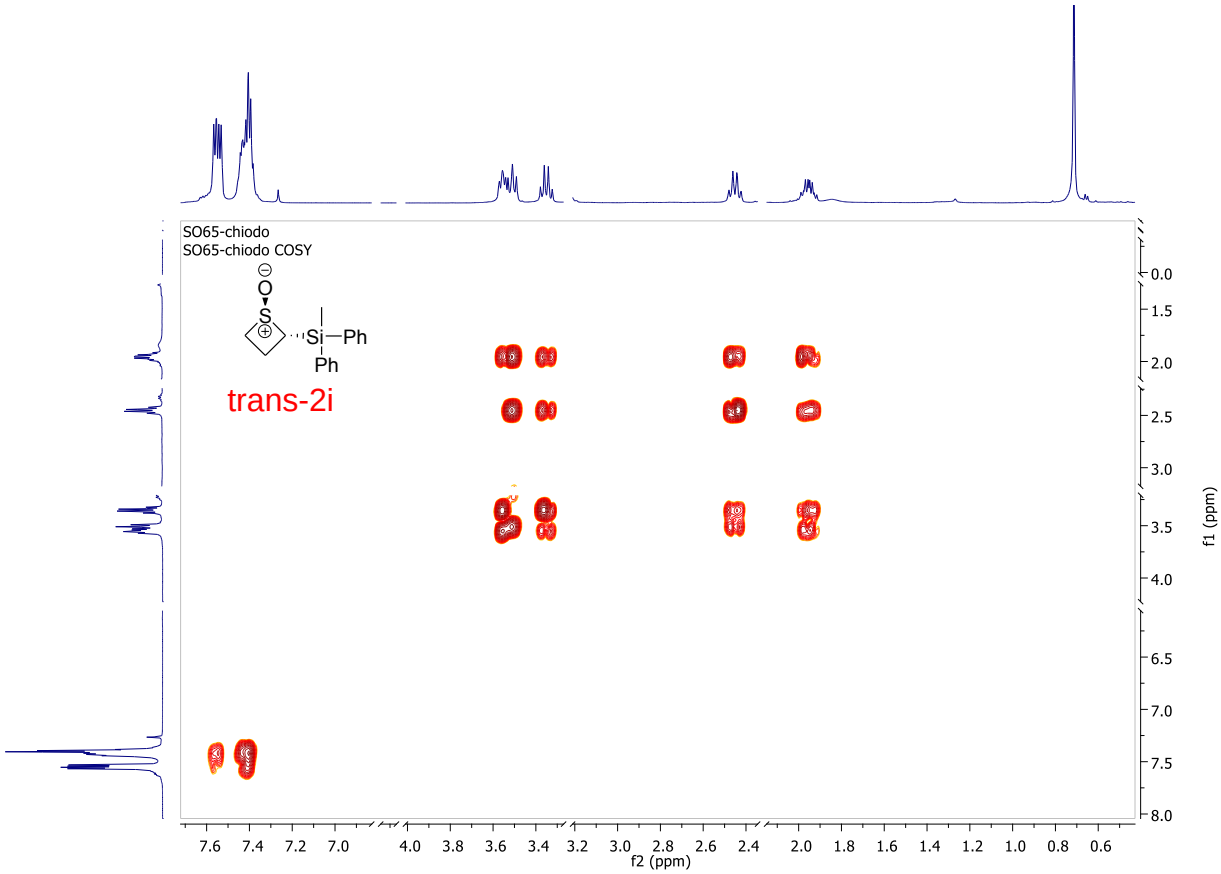

SO69fr11-21
SSO69fr11-21 carboni
trans-2h
132.9
118.4
67.6
48.4
36.1
16.3
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

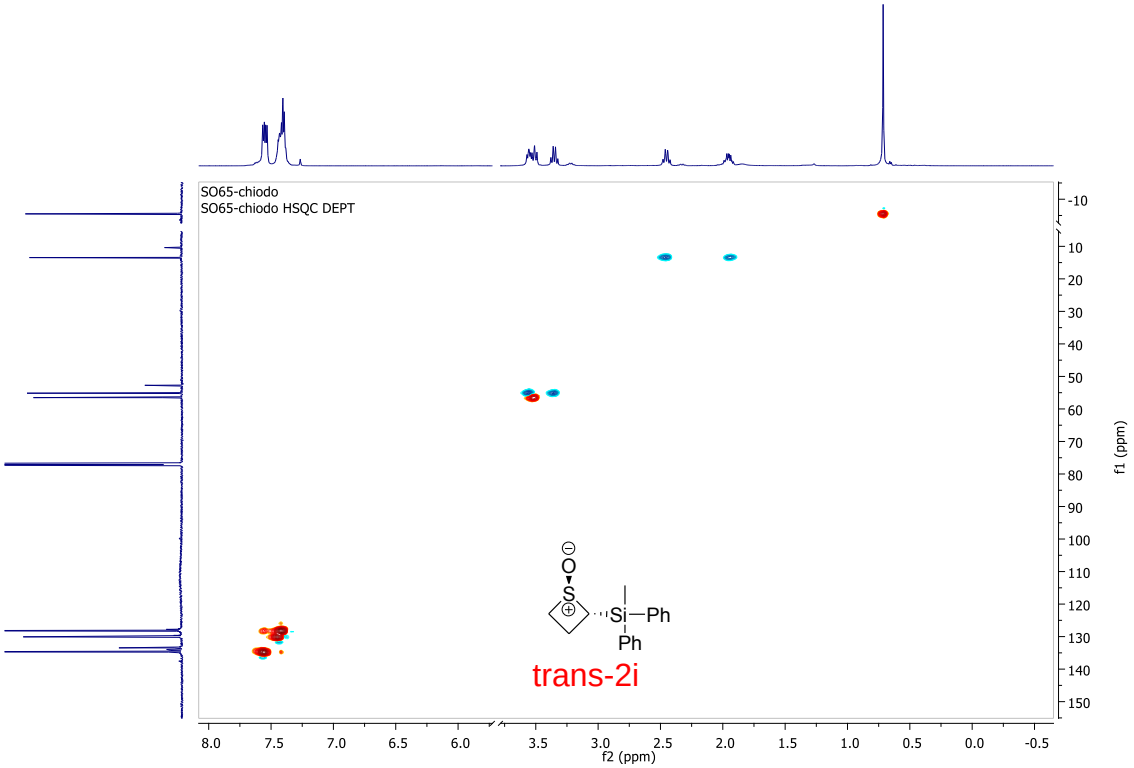

SO69fr11-21
SO69fr11-21 COSY
f2 (ppm)
f1 (ppm)
trans-2h

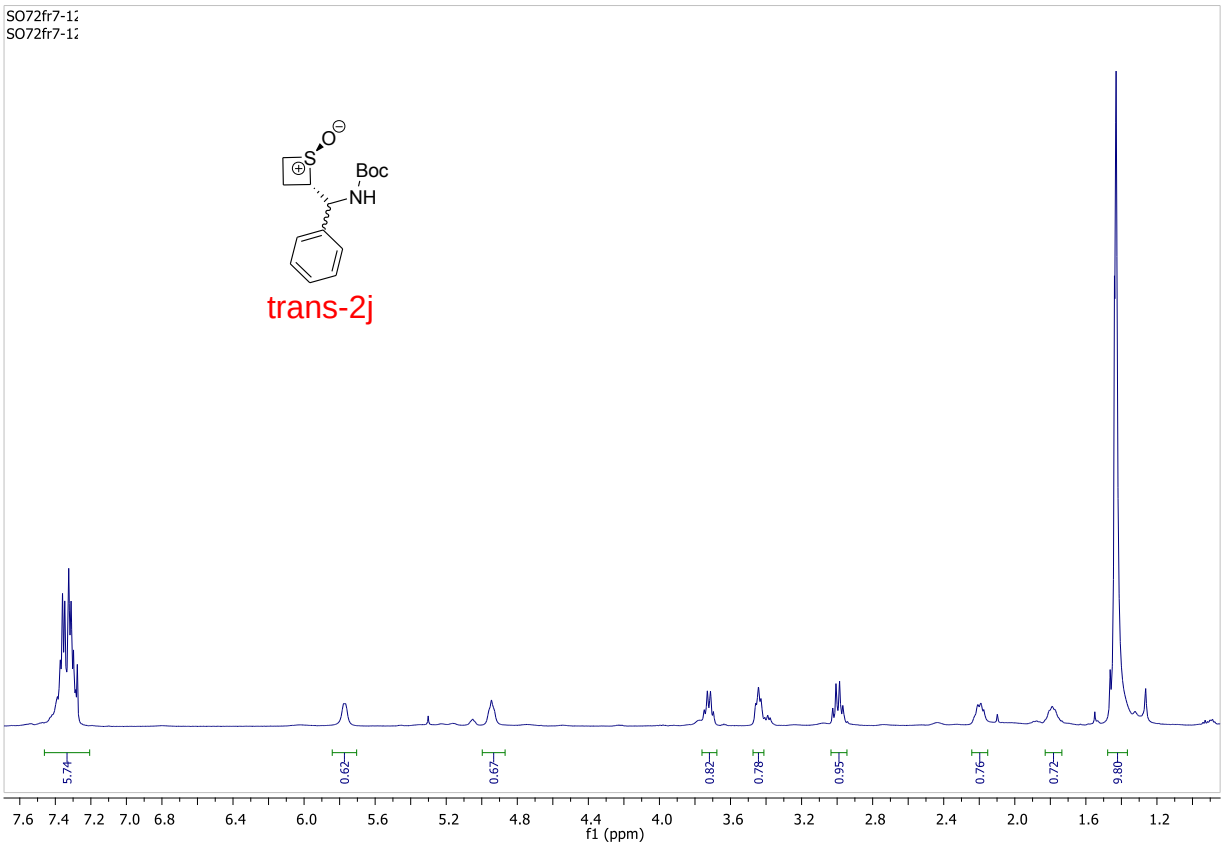

SO69fr11-21
SO69fr11-21 HSQC DEPT
f2 (ppm)
f1 (ppm)
trans-2h

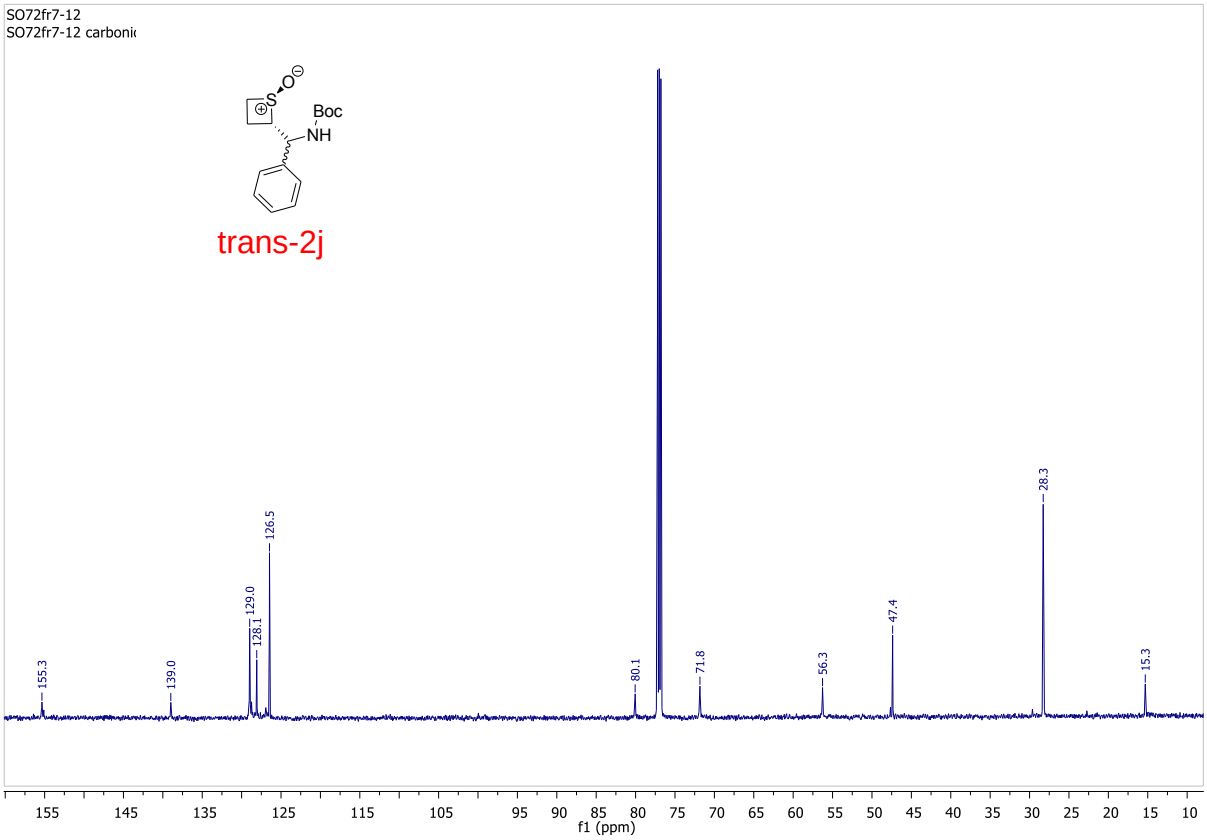

SO65-chiodo
SO65-chiodo
trans-2i
3.67
5.34
2.05
1.00
1.00
1.15
2.82
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

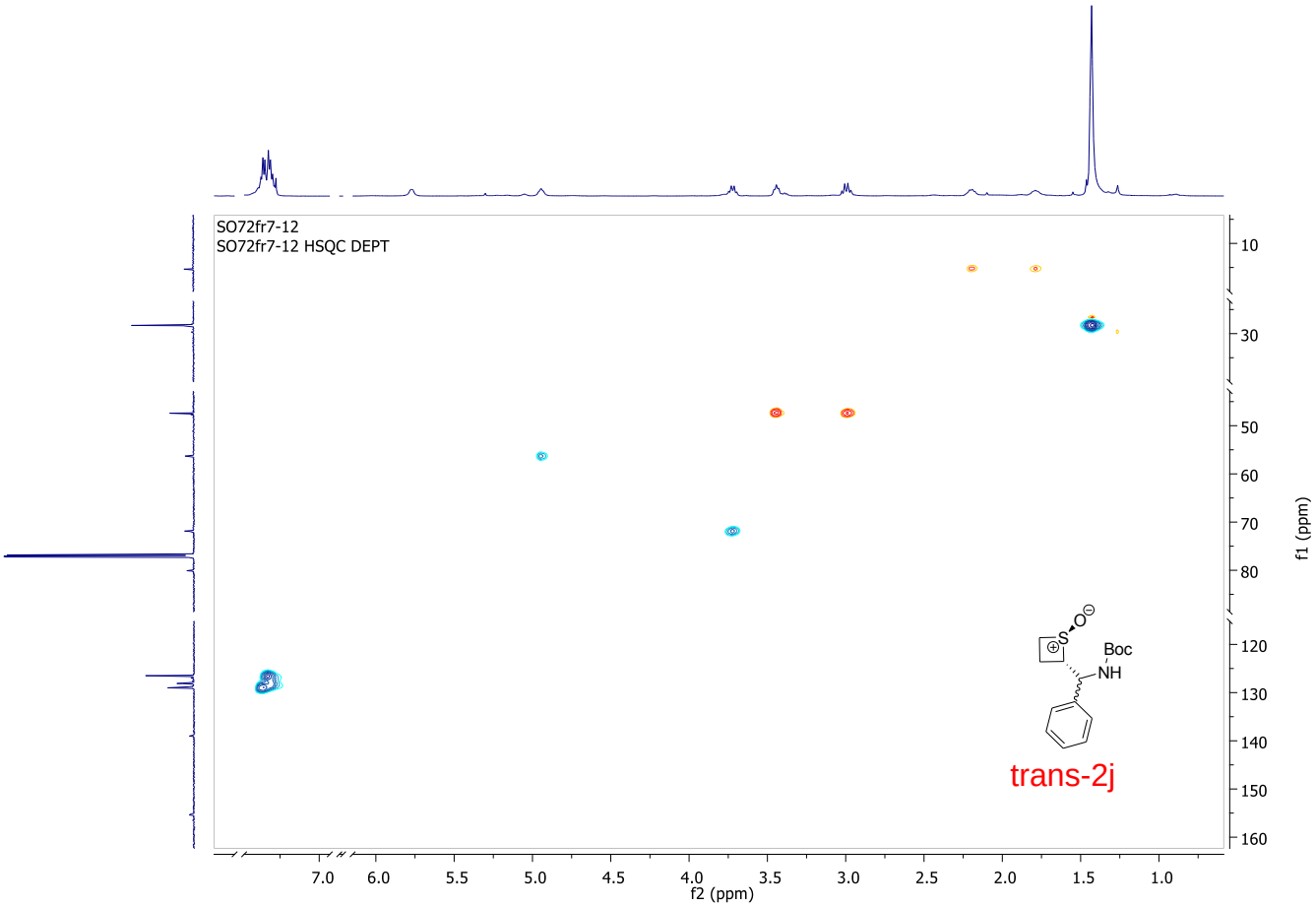

SO65-chiodo
SO65-chiodo carboni
trans-2i
134.7
134.7
133.5
133.4
130.1
130.0
128.2
128.2
56.5
55.2
13.5
-5.5
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

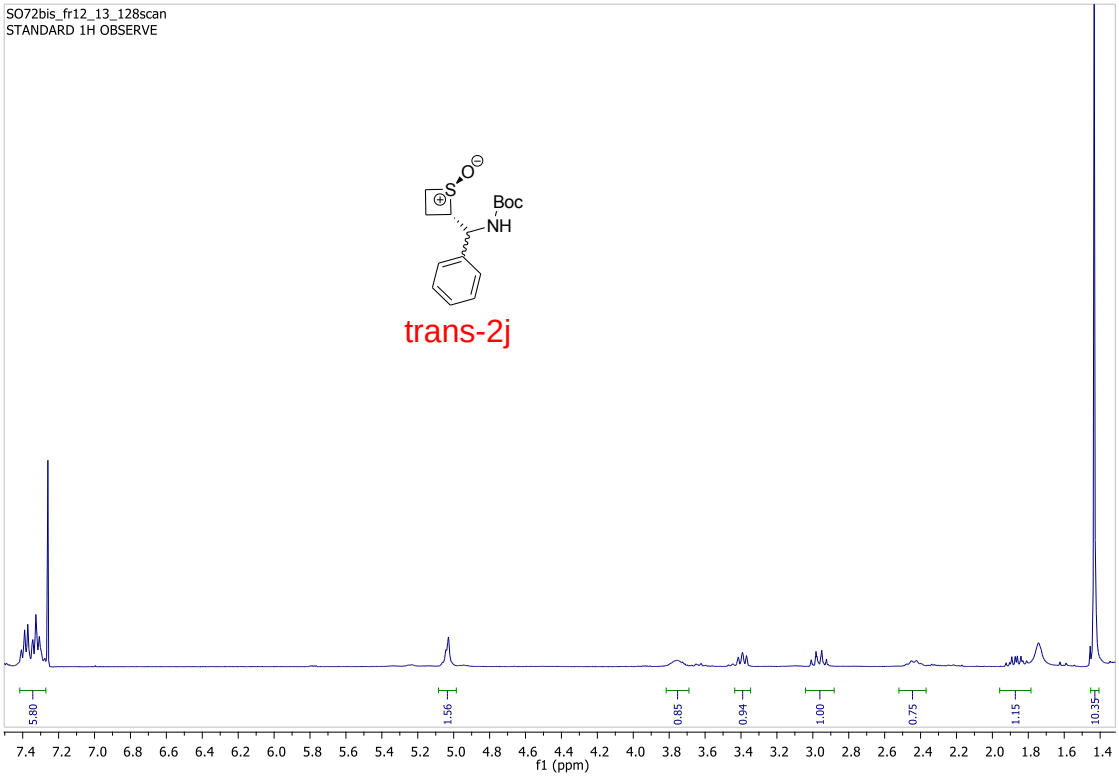

SO65-chiodo
SO65-chiodo COSY
trans-2i
f2 (ppm)
f1 (ppm)

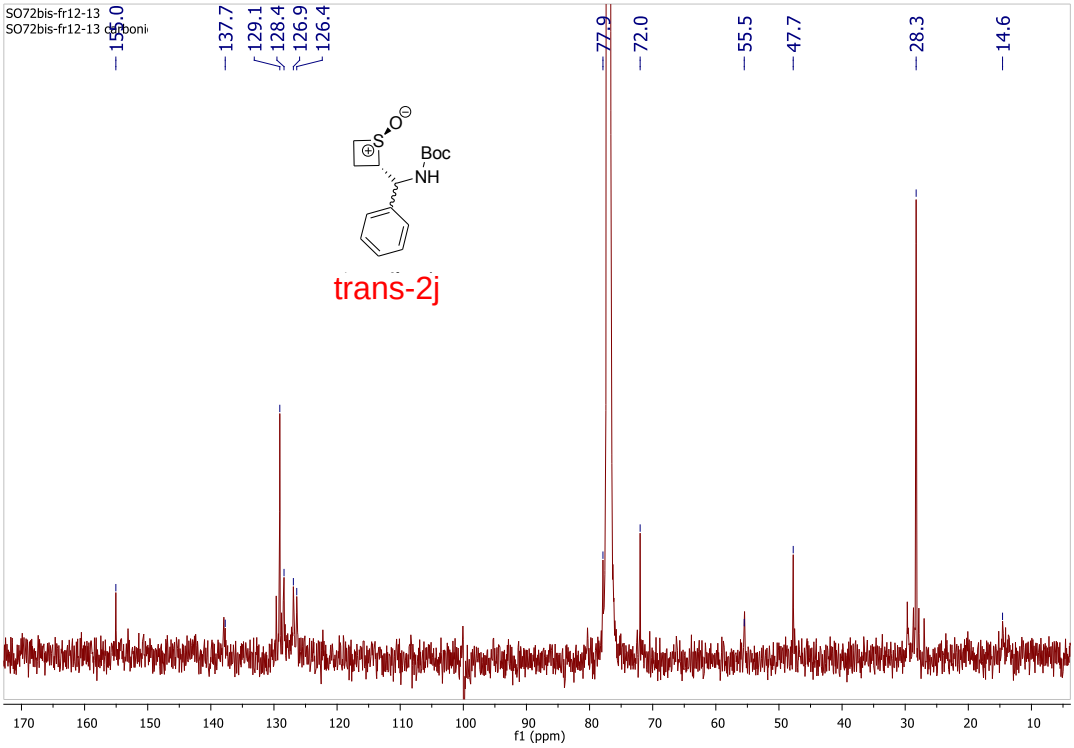

SO65-chiodo
SO65-chiodo HSQC DEPT
trans-2i
f2 (ppm)
f1 (ppm)

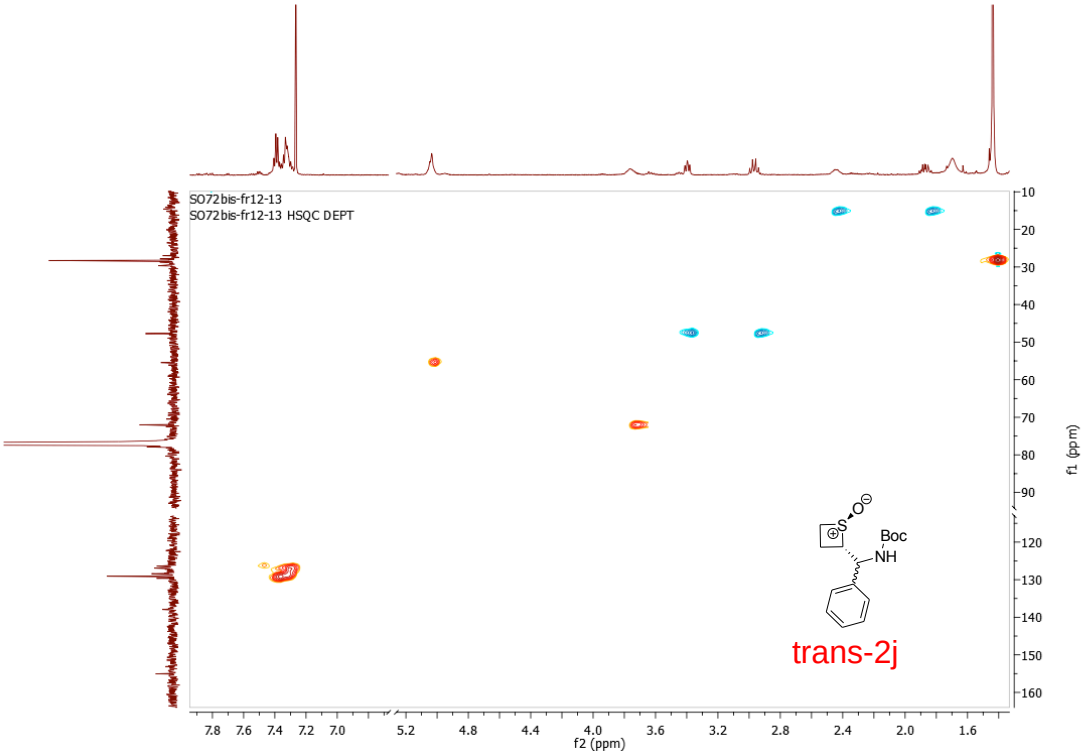

SO72fr7-12
SO72fr7-12
Boc
NH
trans-2j
5.74
0.62
0.67
0.82
0.78
0.95
0.76
0.72
9.80
f1 (ppm)

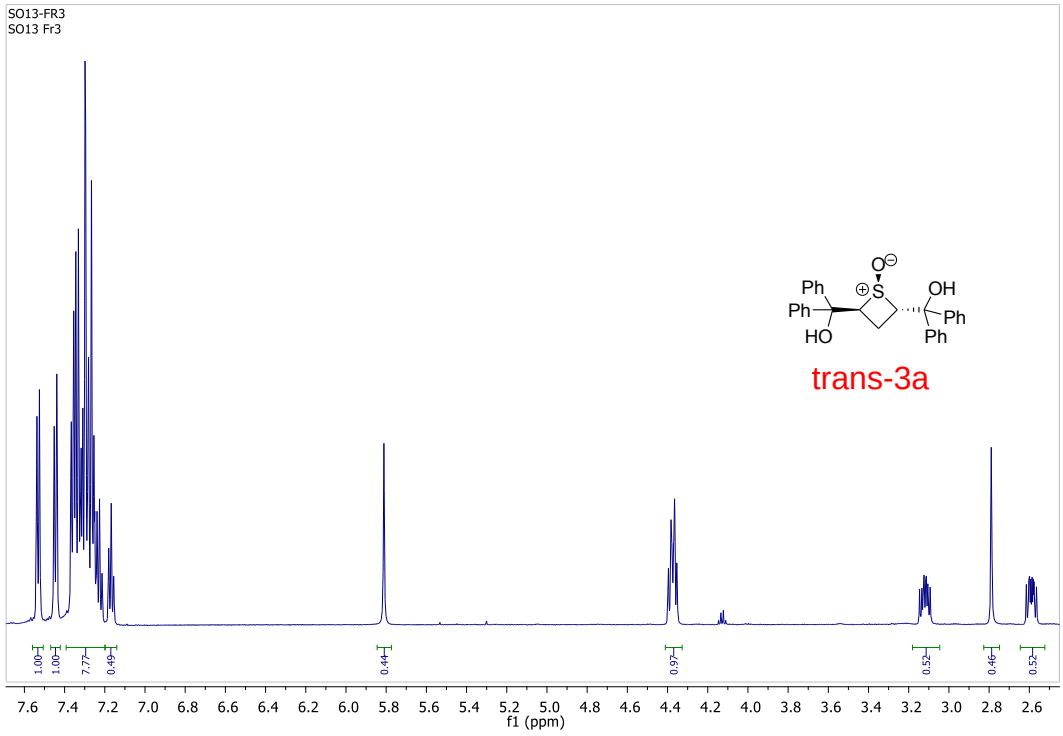

SO72fr7-12
SO72fr7-12 carbonic
Boc
NH
trans-2j
155.3
139.0
128.1
129.0
126.5
80.1
71.8
56.3
47.4
28.3
15.3
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

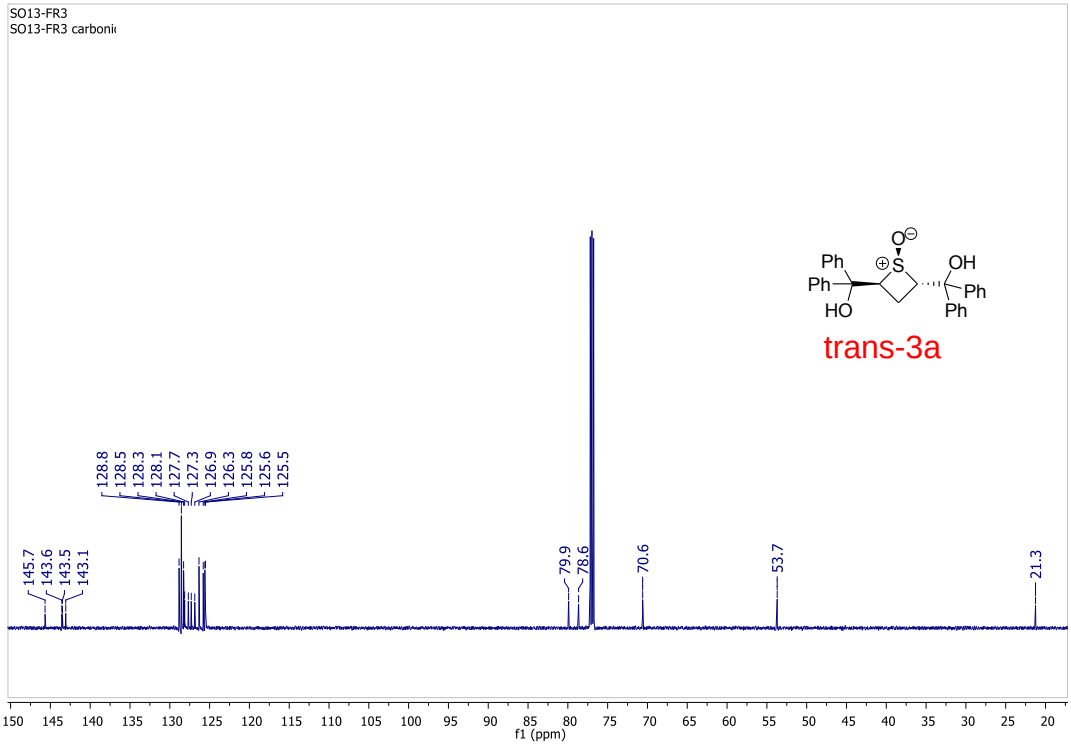

SO72fr7-12
SO72fr7-12 HSQC DEPT
Boc
NH
trans-2j
f2 (ppm)
f1 (ppm)

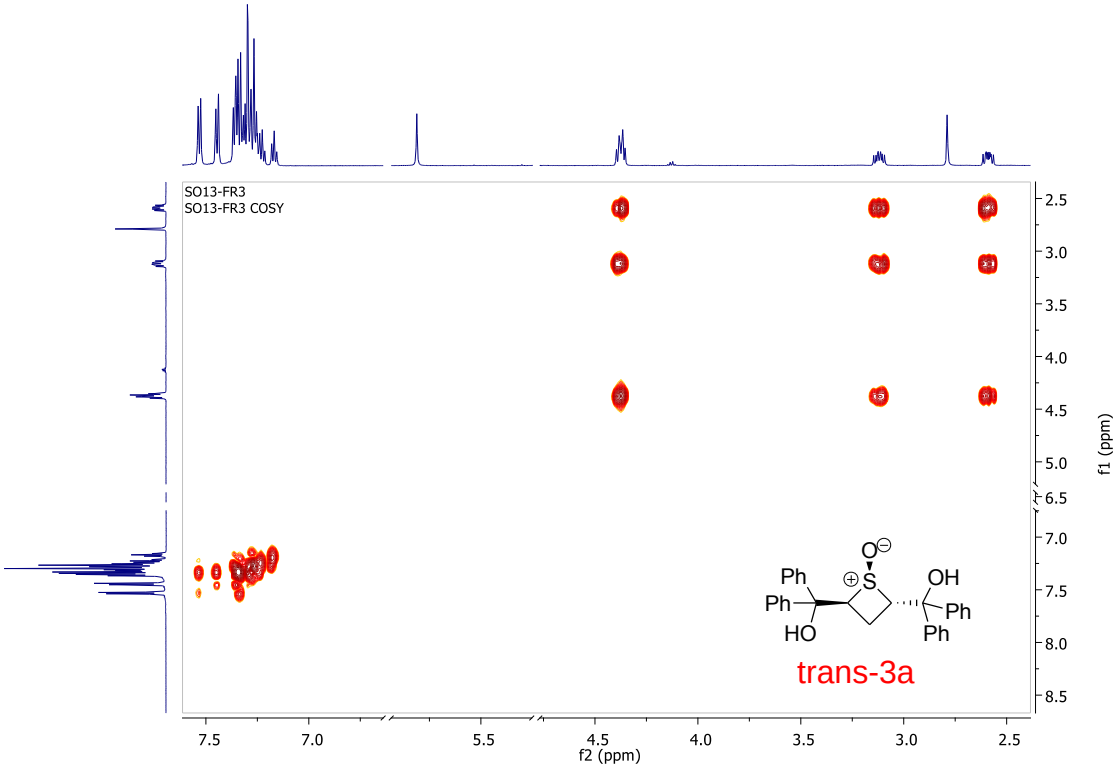

SO72bis_fr12_13_128scan
STANDARD 1H OBSERVE
Boc
NH
trans-2j
5.80
1.56
0.85
0.94
1.00
0.75
1.15
10.35
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)

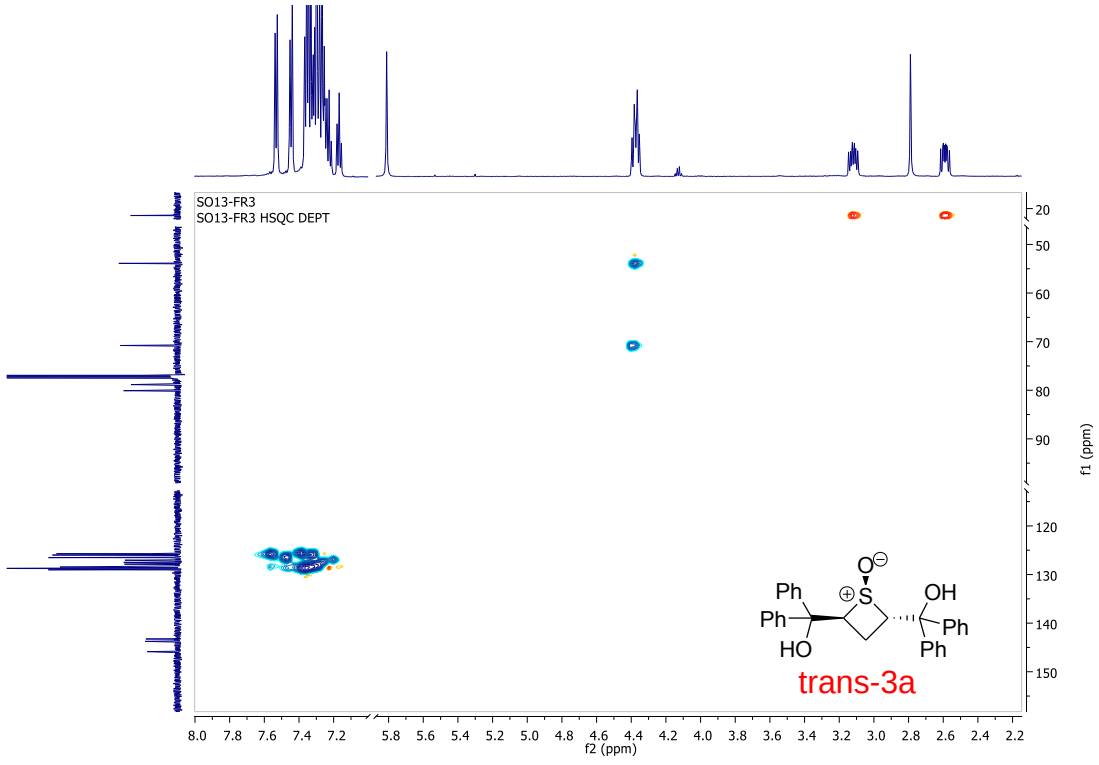

SO72bis-fr12-13
SO72bis-fr12-13 carboni
151.0
137.7
129.1
128.4
126.9
126.4
77.9
72.0
55.5
47.7
28.3
14.6
Boc
NH
trans-2j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

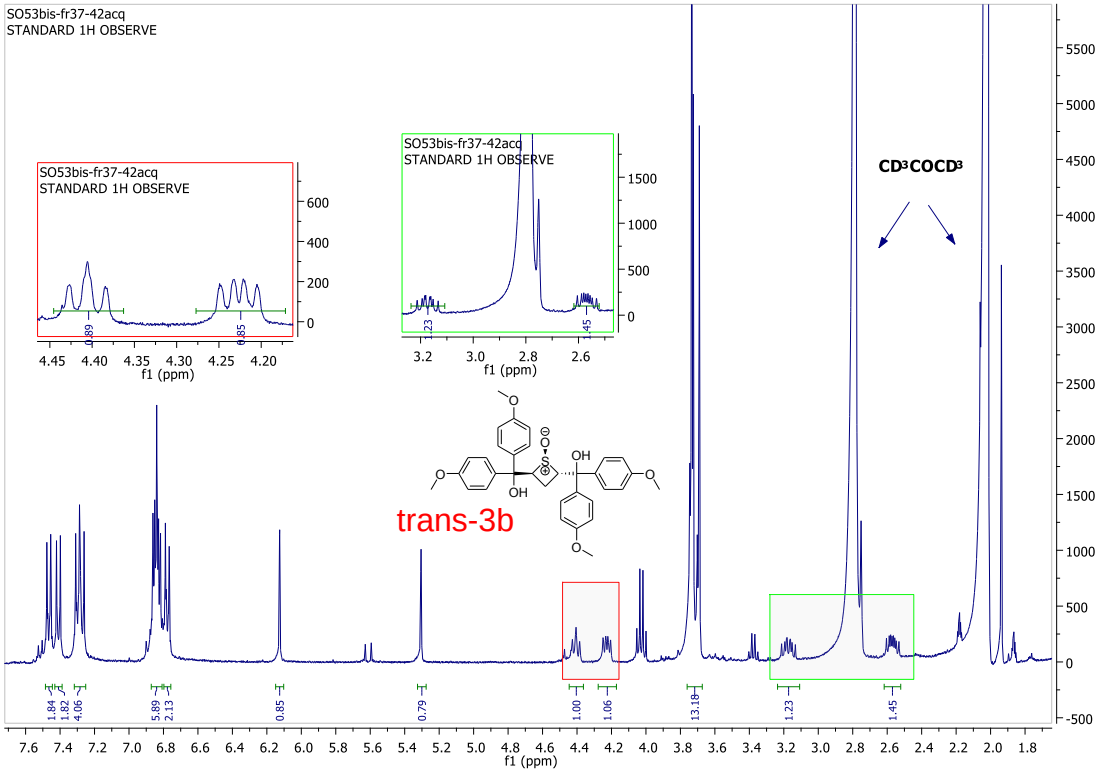

SO72bis-fr12-13
SO72bis-fr12-13 HSQC DEPT
Boc
NH
trans-2j
f2 (ppm)
f1 (ppm)

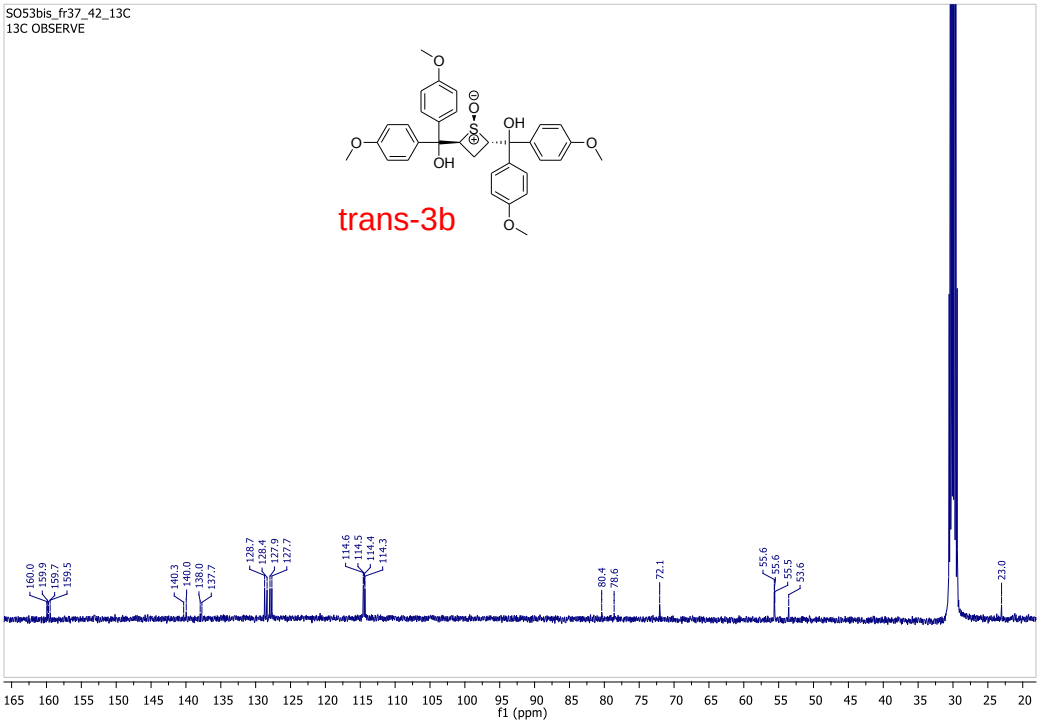

SO13-FR3
SO13 Fr3
trans-3a
1.00
1.00
7.77
0.49
0.44
0.97
0.52
0.46
0.52
f1 (ppm)

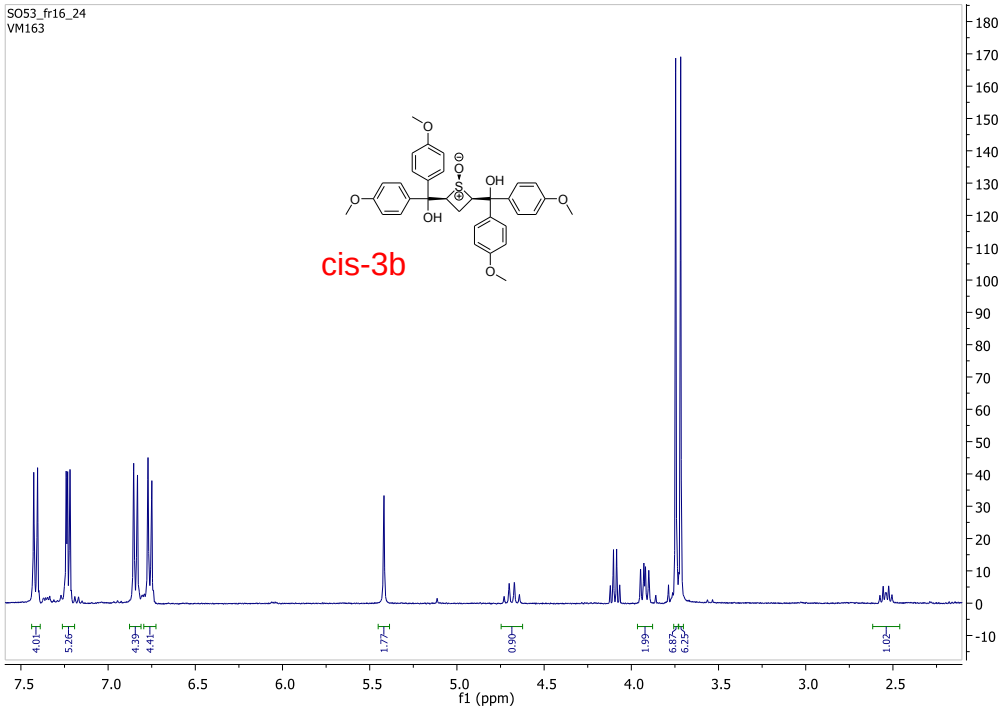

SO13-FR3
SO13-FR3 carboni
trans-3a
128.8
128.5
128.3
128.1
127.7
127.3
126.9
126.3
125.8
125.6
125.5
145.7
143.6
143.5
143.1
79.9
78.6
70.6
53.7
21.3
f1 (ppm)

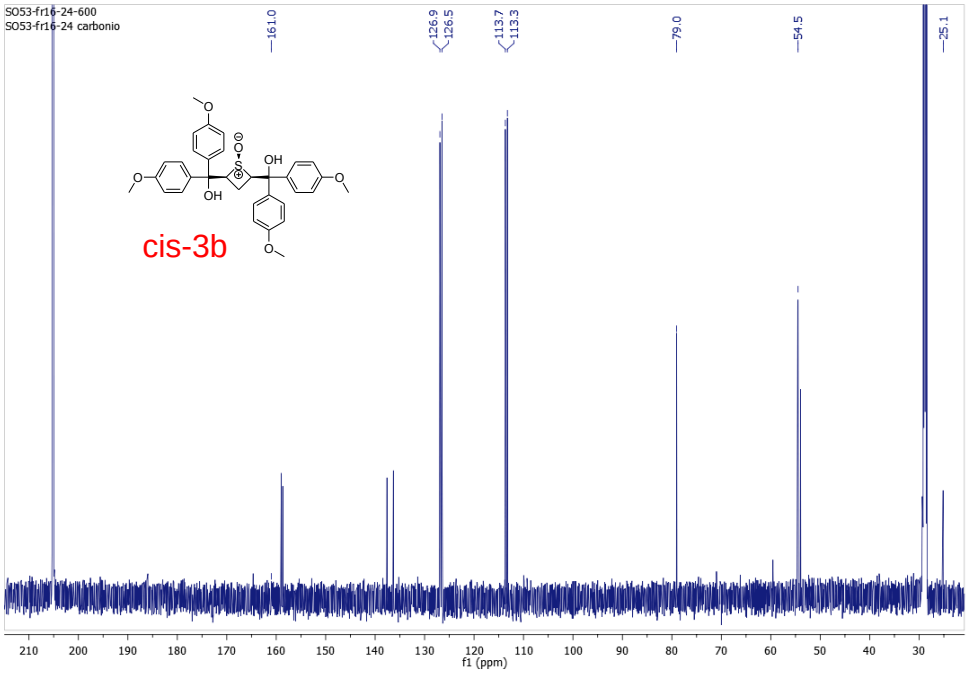

SO13-FR3
SO13-FR3 COSY
f2 (ppm)
f1 (ppm)
trans-3a

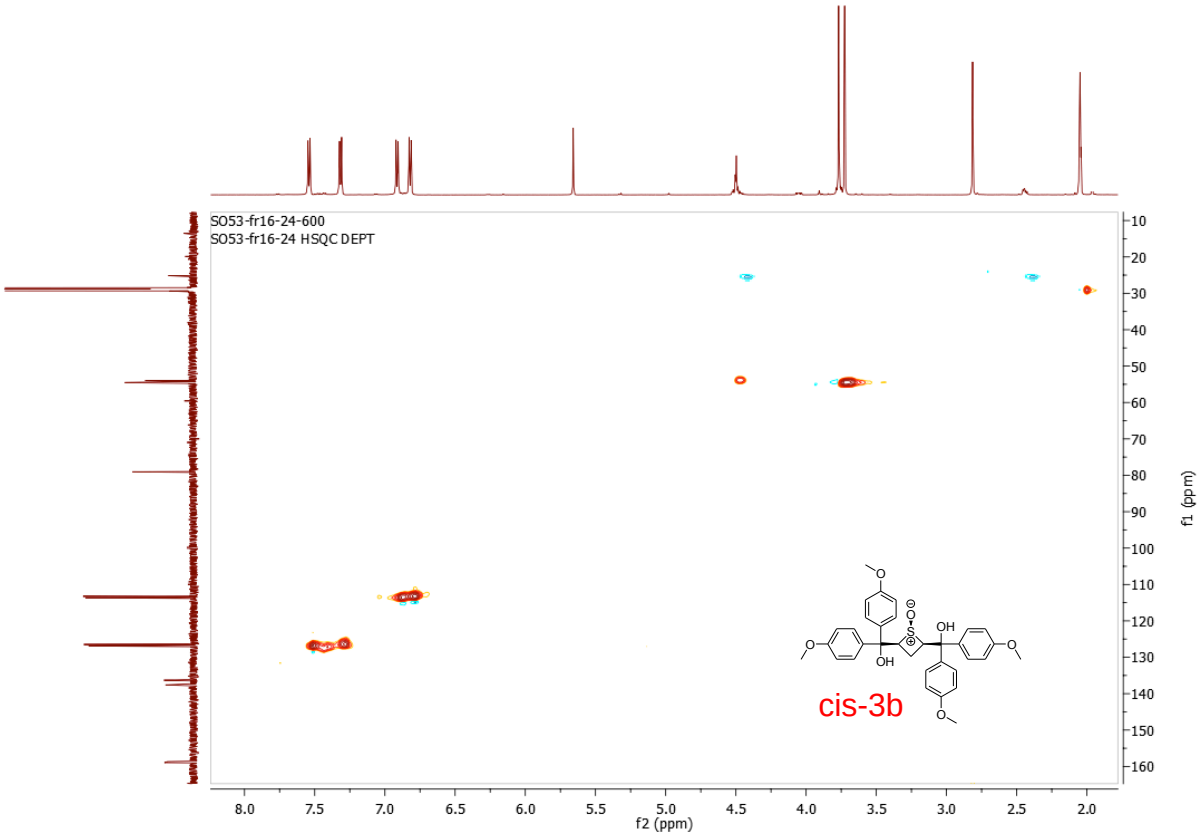

SO13-FR3
SO13-FR3 HSQC DEPT
f2 (ppm)
f1 (ppm)
trans-3a

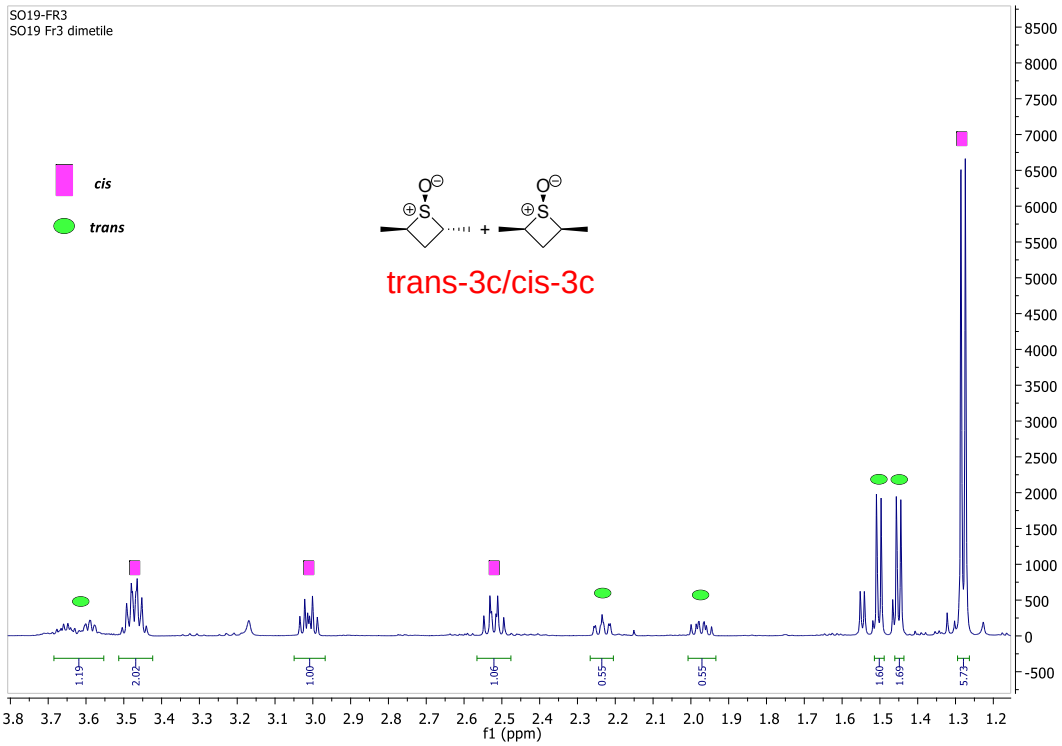

SO53bis-fr37-42acq
STANDARD 1H OBSERVE
CD3COCD3
trans-3b
f1 (ppm)

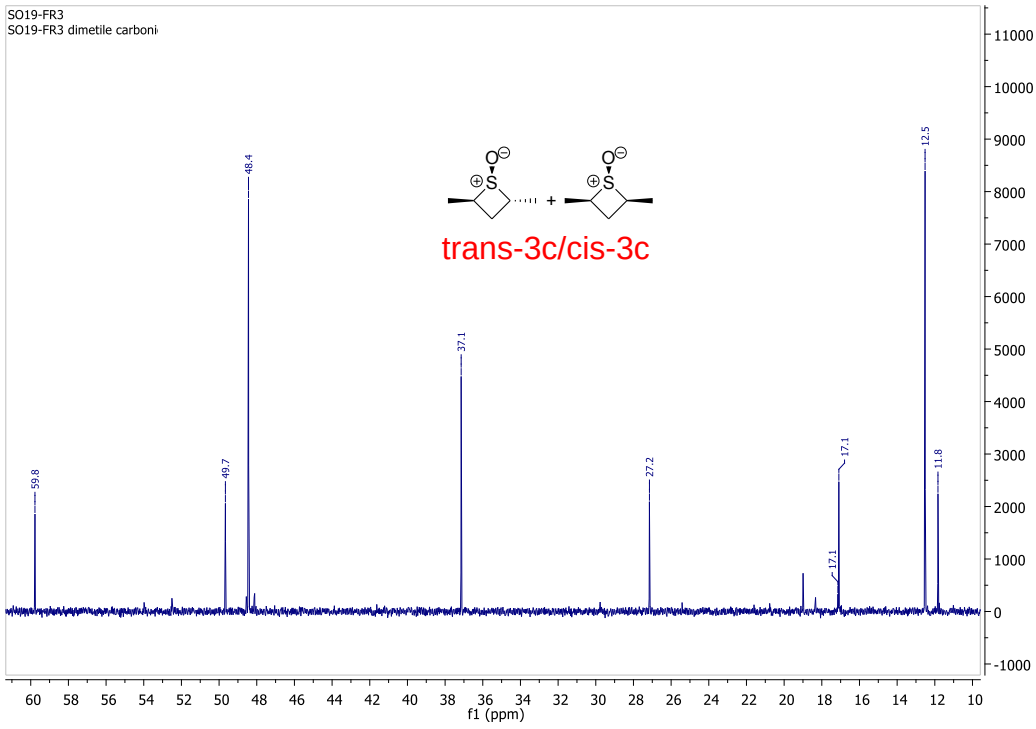

SO53bis_fr37_42_13C
13C OBSERVE
trans-3b
f1 (ppm)

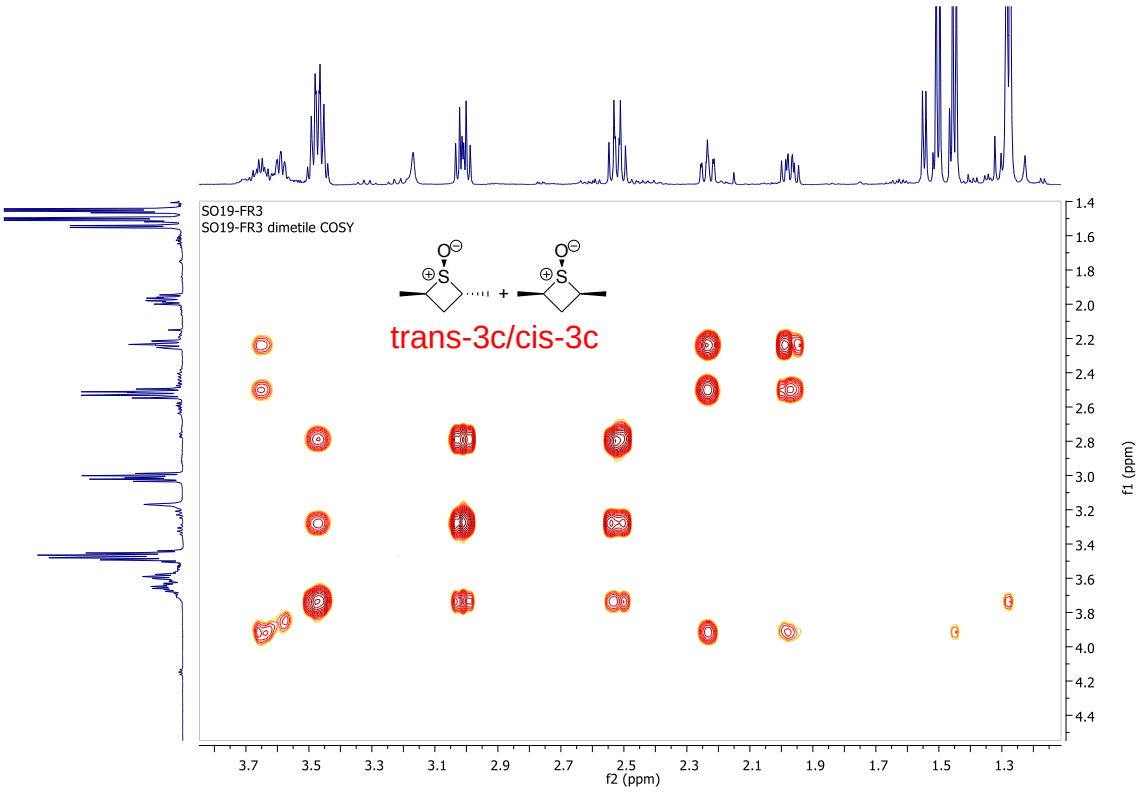

SO53_fr16_24
VM163
cis-3b
4.01
5.26
4.39
4.41
1.77
0.90
1.99
6.87
6.25
1.02
f1 (ppm)

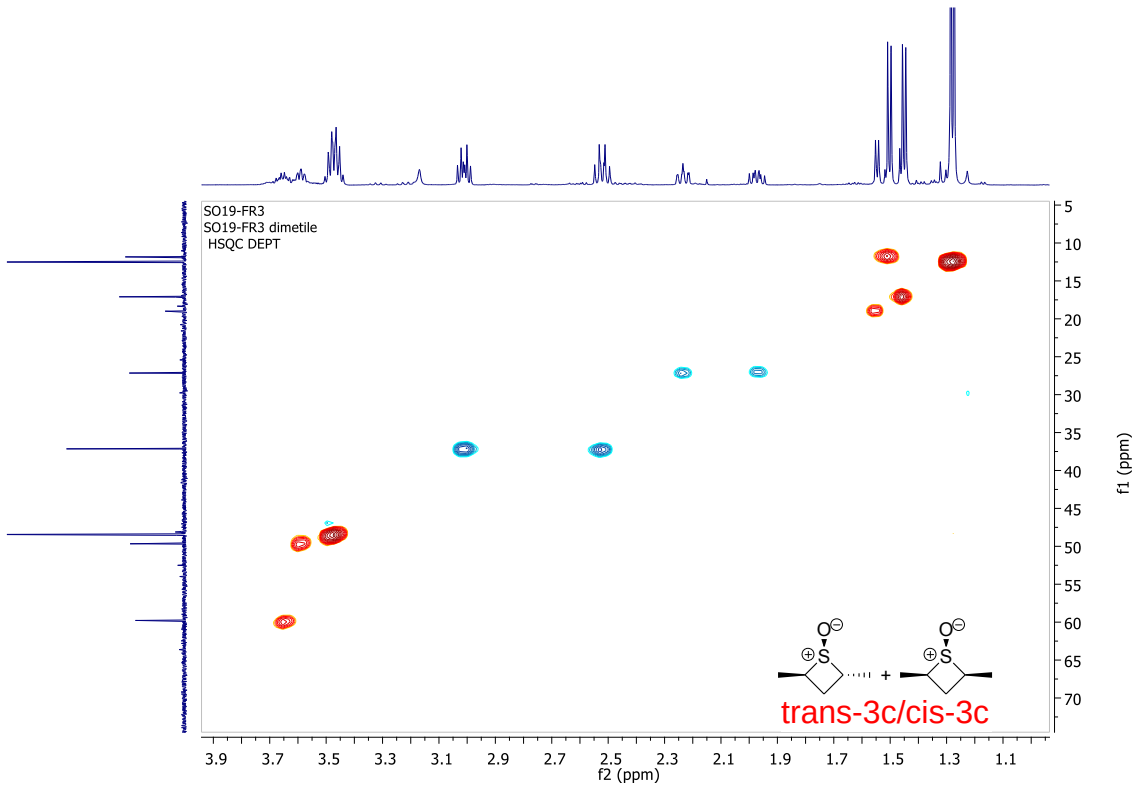

SO53-fr16-24-600
SO53-fr16-24 carbonio
161.0
126.9
126.5
113.7
113.3
79.0
54.5
25.1
cis-3b
f1 (ppm)

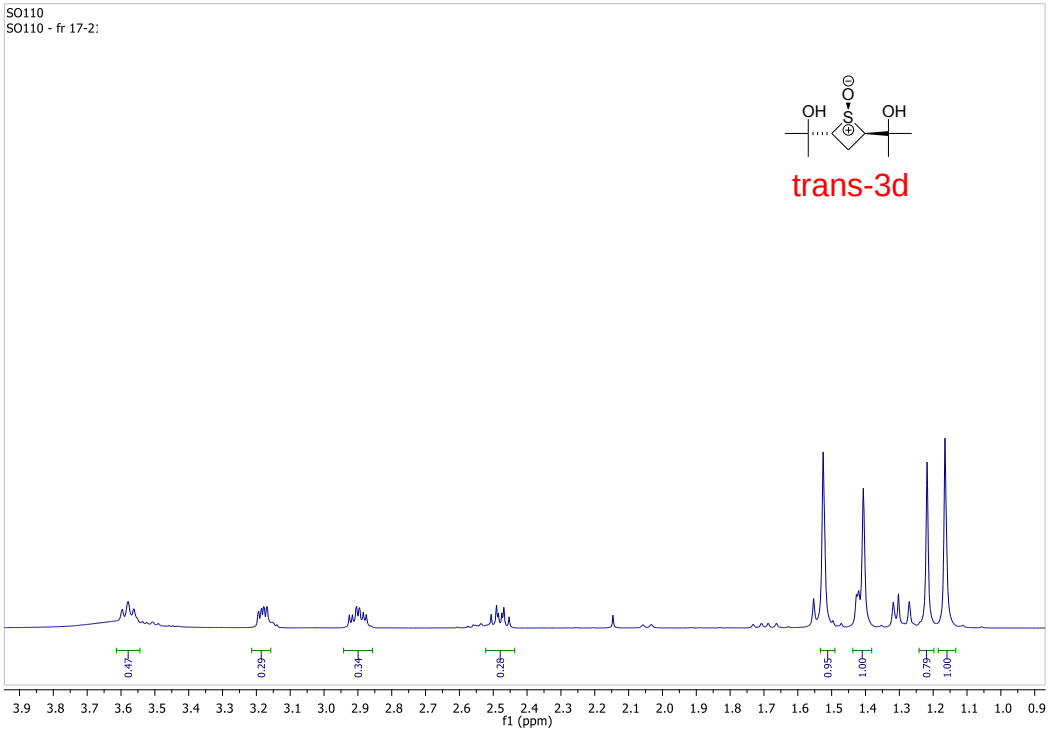

SO53-fr16-24-600
SO53-fr16-24 HSQC DEPT
f2 (ppm)
f1 (ppm)
cis-3b

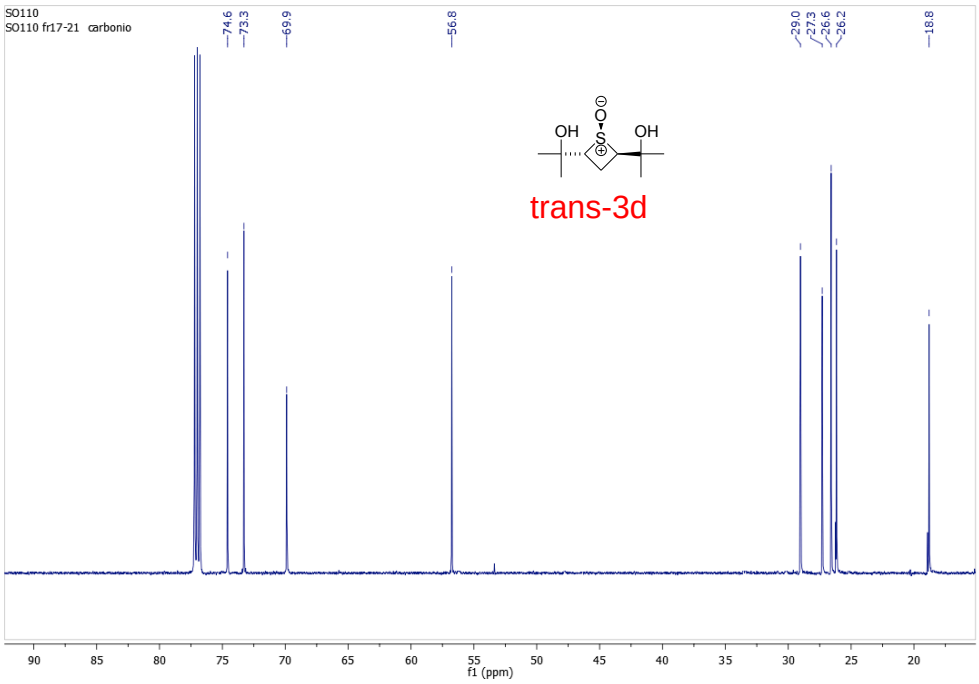

SO19-FR3
SO19 Fr3 dimetile
cis
trans
trans-3c/cis-3c
f1 (ppm)

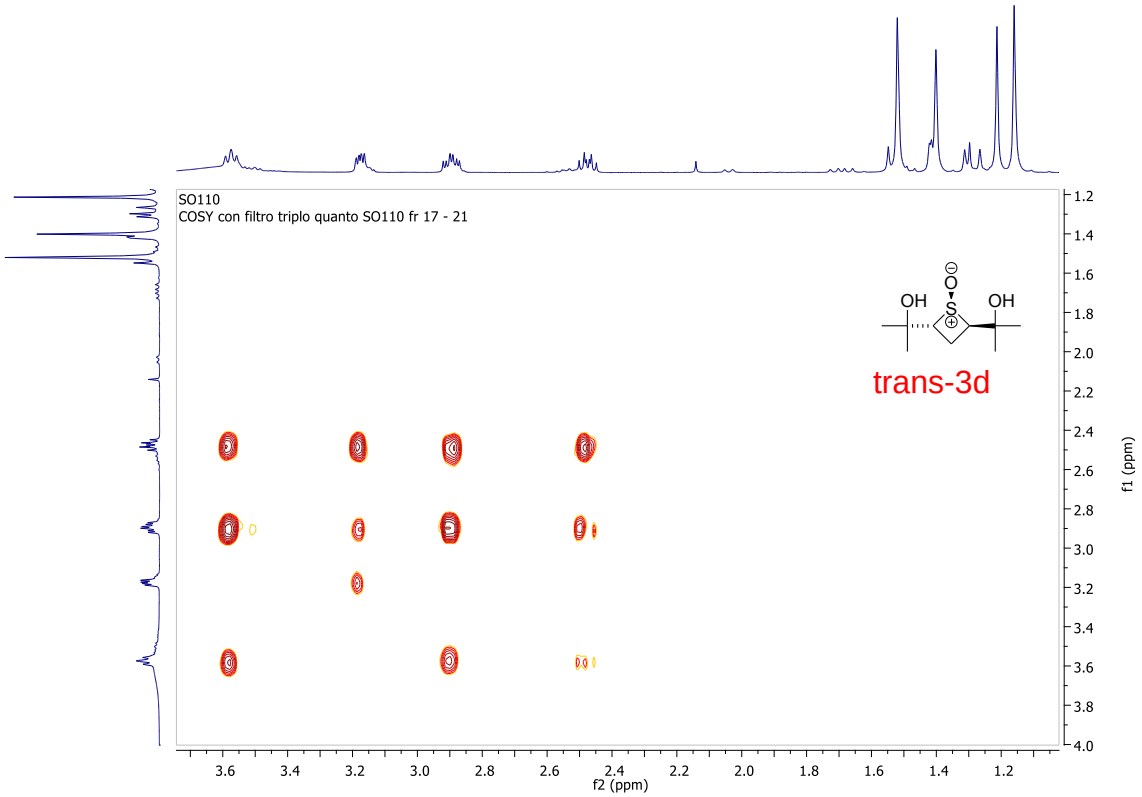

SO19-FR3
SO19-FR3 dimetile carboni
trans-3c/cis-3c
59.8
49.7
48.4
37.1
27.2
17.1
17.1
12.5
11.8
f1 (ppm)

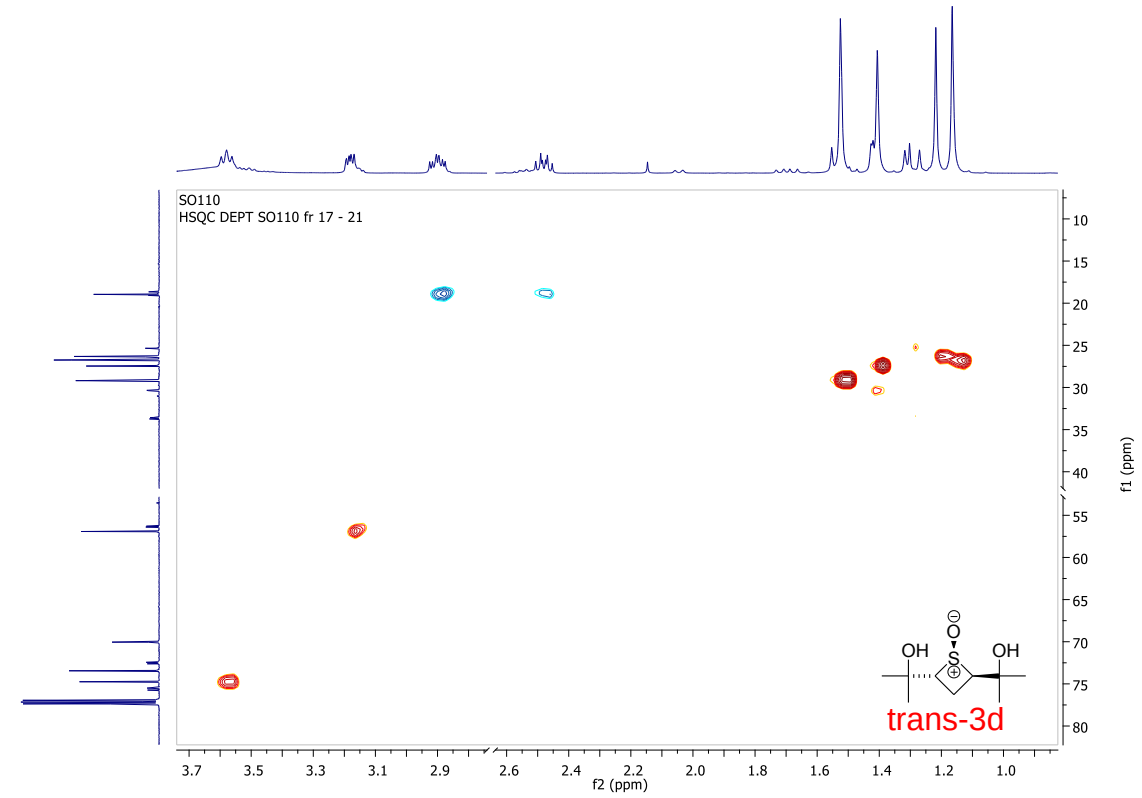

SO19-FR3
SO19-FR3 dimetile COSY
trans-3c/cis-3c
f1 (ppm)
f2 (ppm)

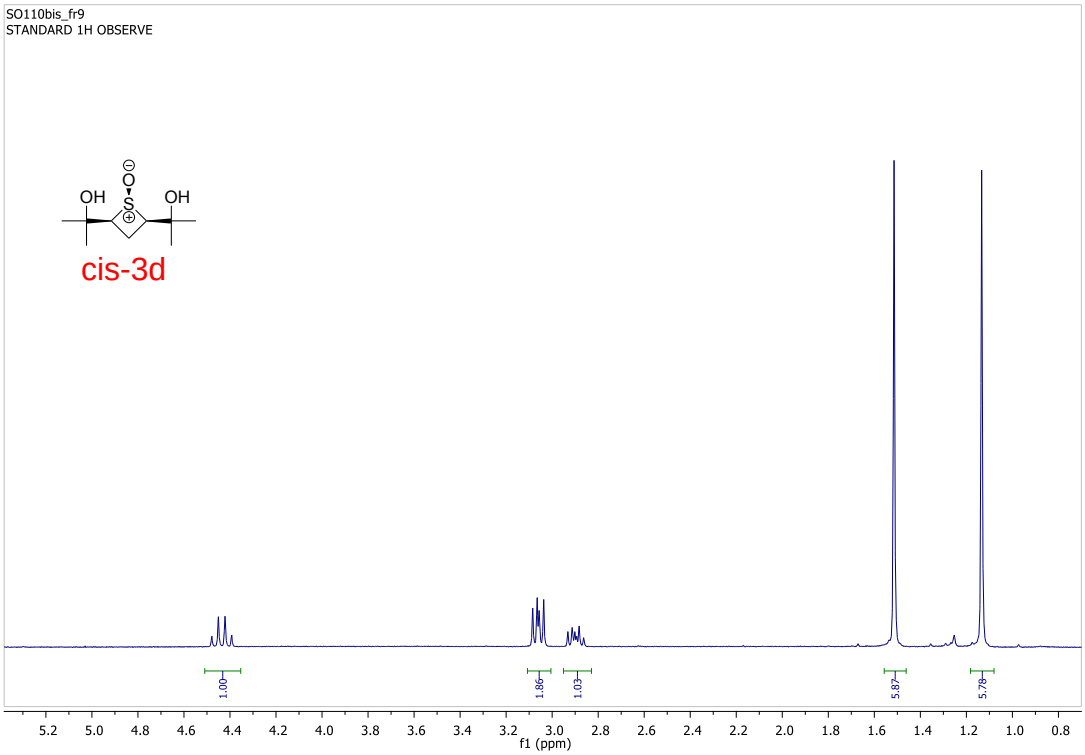

SO19-FR3
SO19-FR3 dimetile
HSQC DEPT
trans-3c/cis-3c
f1 (ppm)
f2 (ppm)

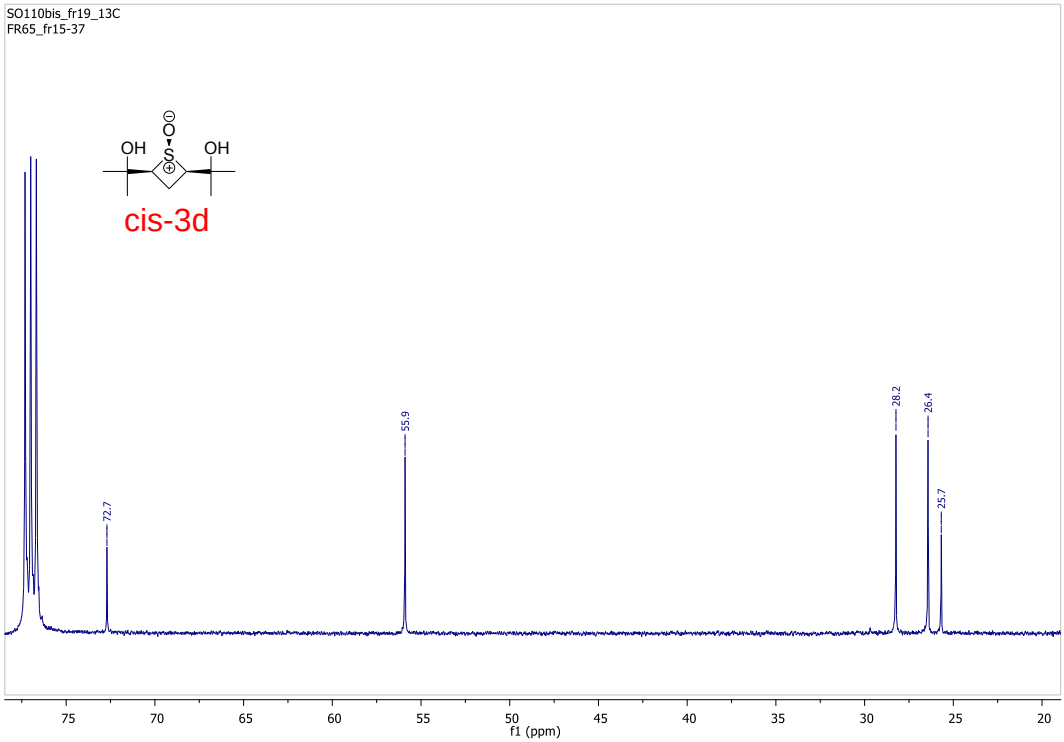

SO110
SO110 - fr 17-2
OH
OH
trans-3d
0.47
0.29
0.34
0.28
0.95
1.00
0.79
1.00
3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
f1 (ppm)

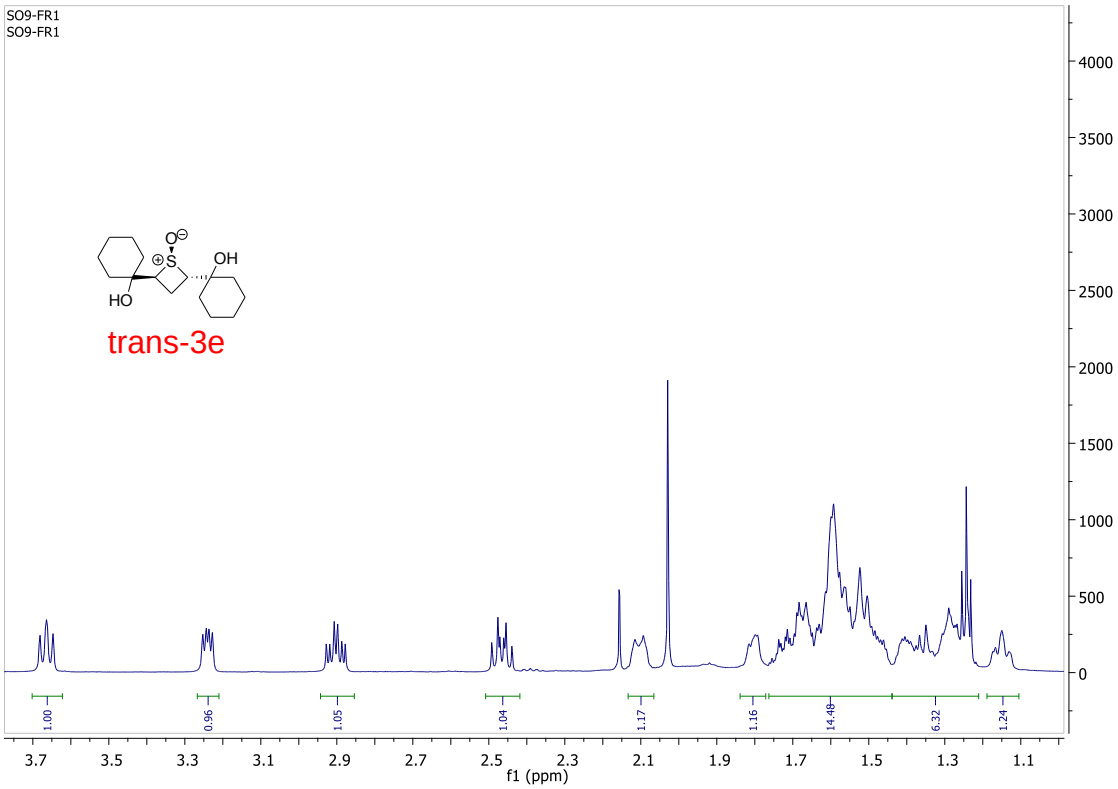

SO110
SO110 fr17-21 carbonio
74.6
73.3
69.9
56.8
29.0
27.3
26.6
26.2
18.8
OH
OH
trans-3d
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

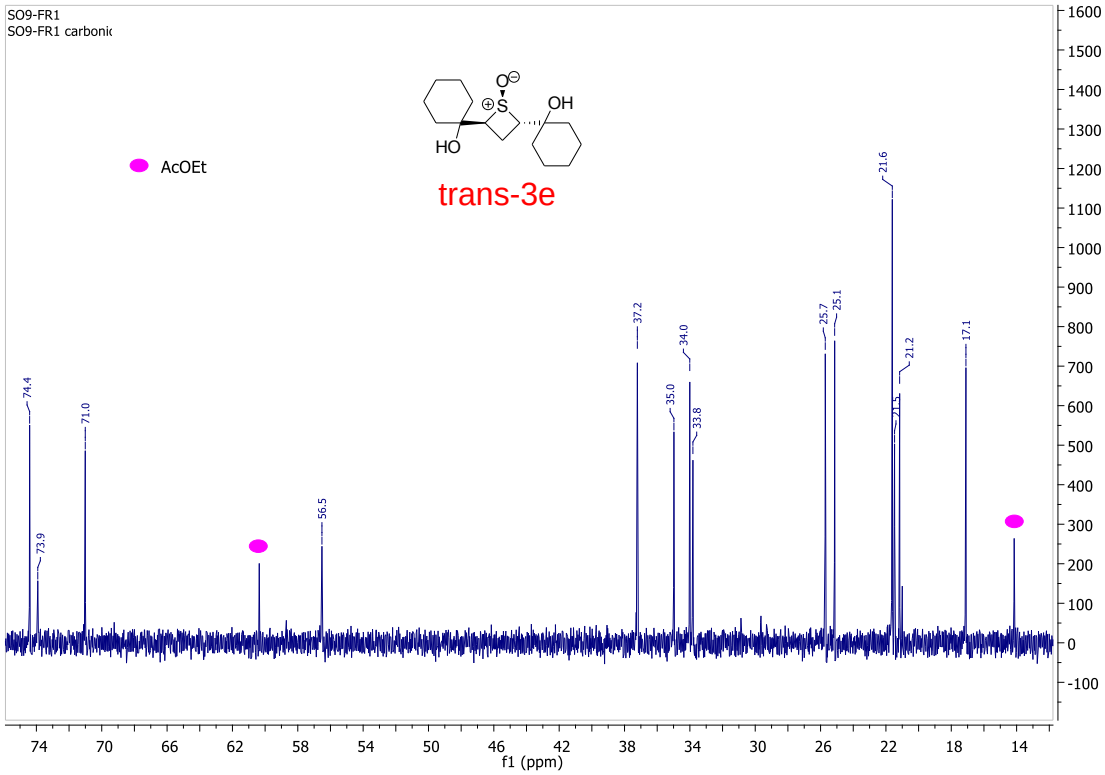

SO110
COSY con filtro triplo quanto SO110 fr 17 - 21
OH
OH
trans-3d
f1 (ppm)
f2 (ppm)

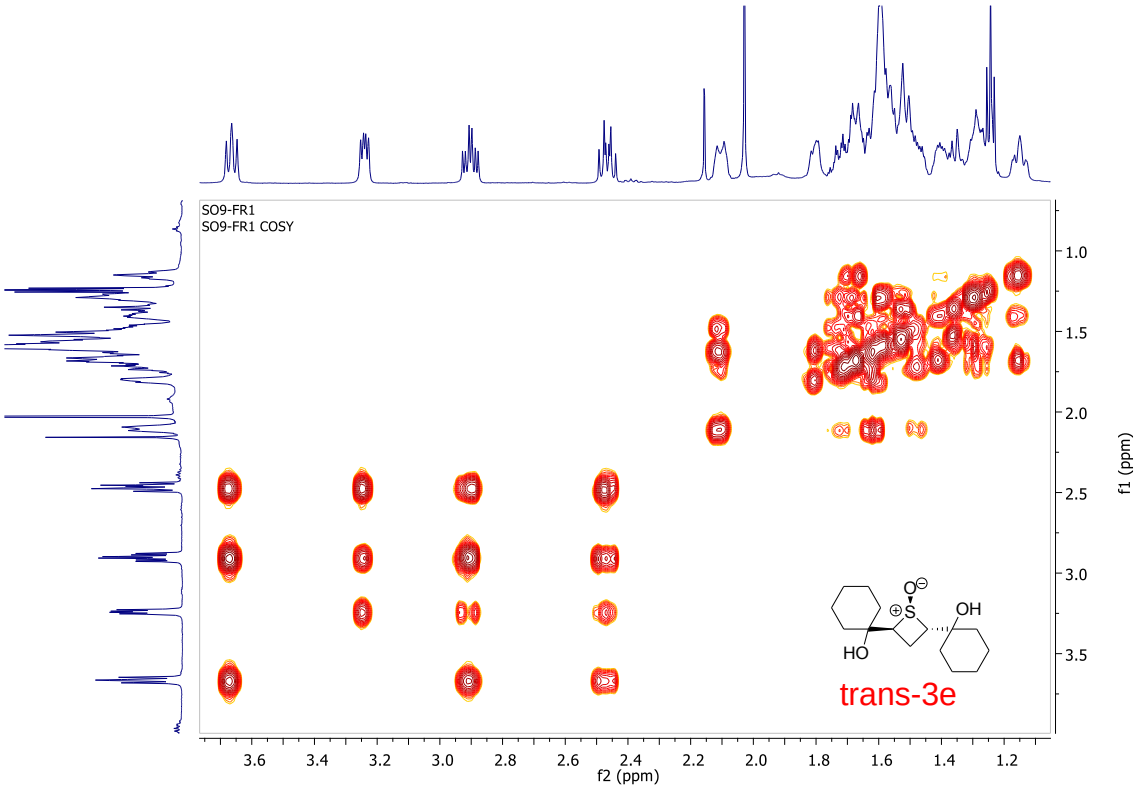

SO110
HSQC DEPT SO110 fr 17 - 21
OH
OH
trans-3d
f1 (ppm)
f2 (ppm)

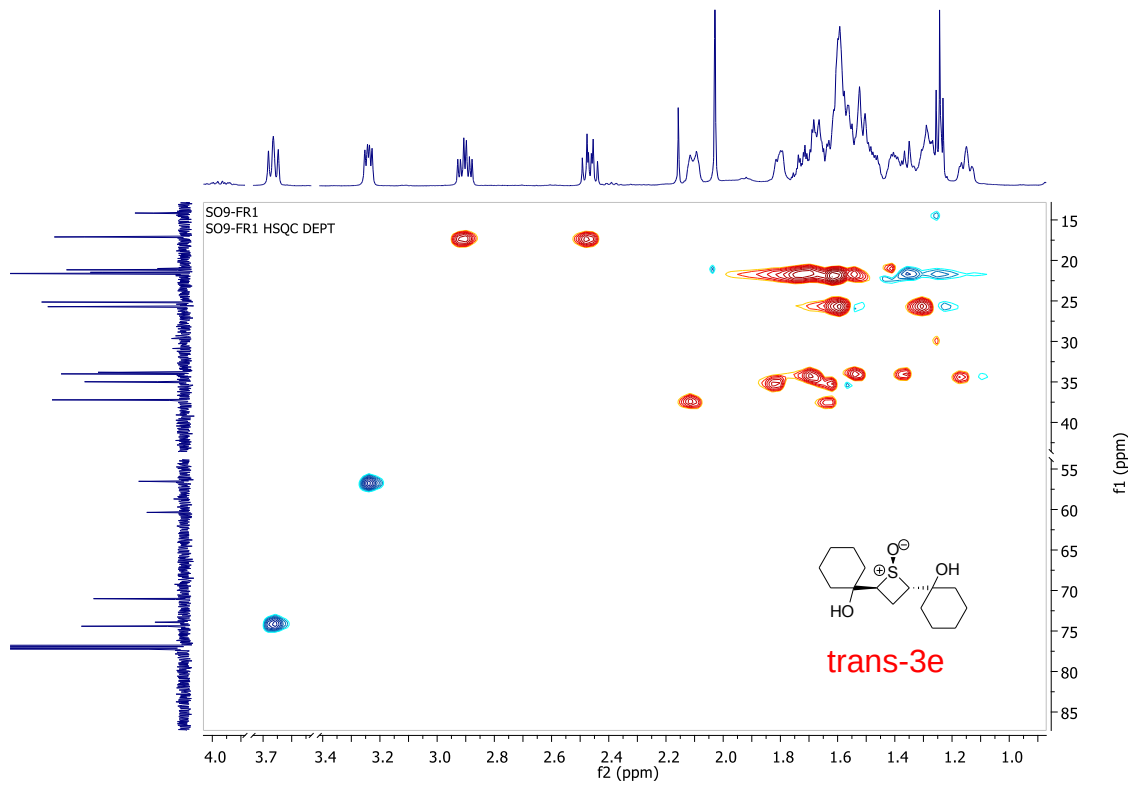

SO110bis_fr9
STANDARD 1H OBSERVE
OH
OH
cis-3d
1.00
1.86
1.03
5.87
5.78
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

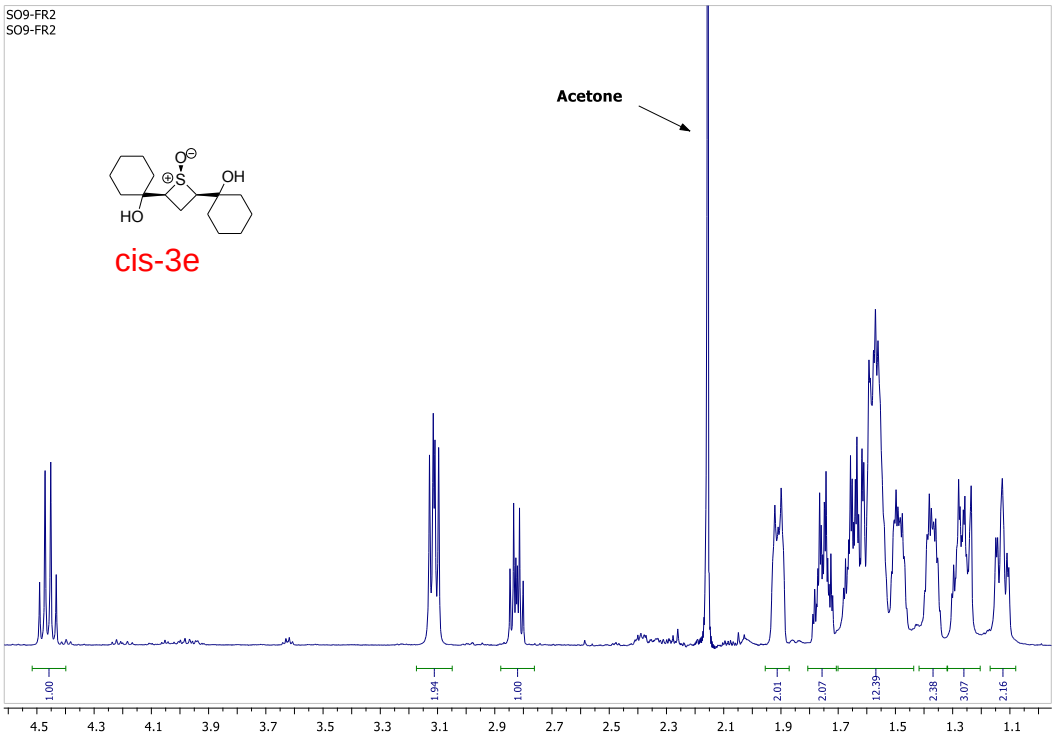

SO110bis_fr19_13C
FR65_fr15-37
OH
OH
cis-3d
72.7
55.9
28.2
26.4
25.7
75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

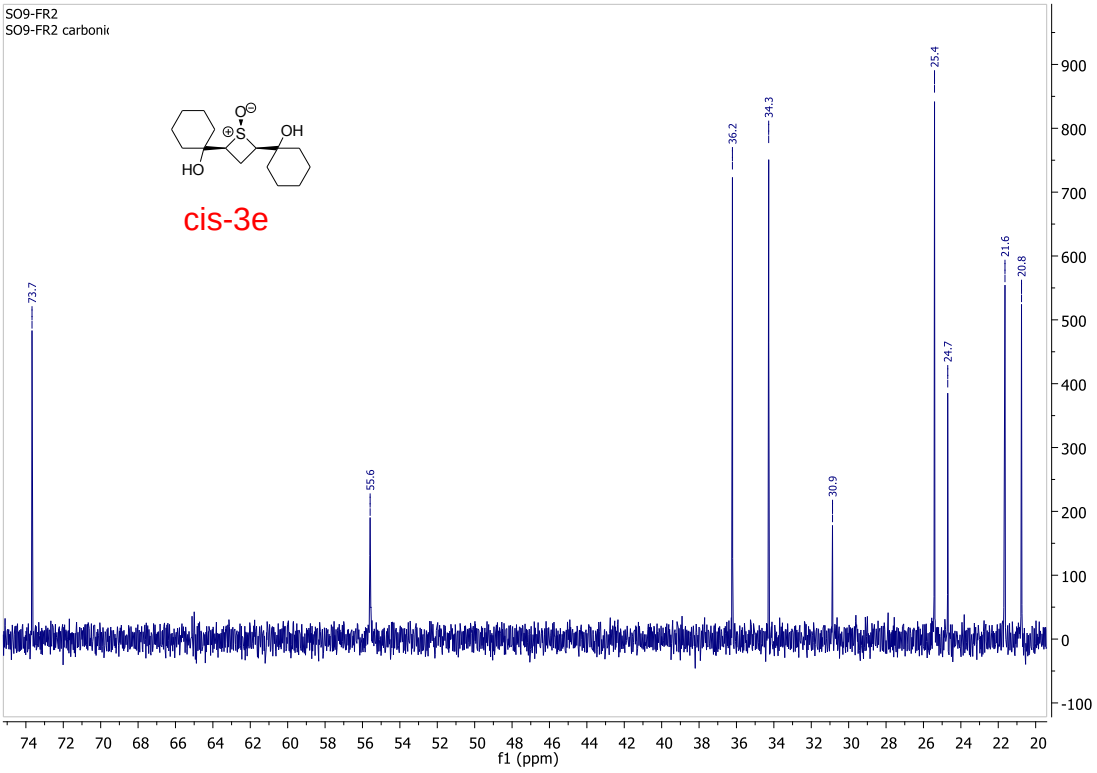

SO9-FR1
SO9-FR1
OH
HO
trans-3e
1.00
0.96
1.05
1.04
1.17
1.16
14.48
6.32
1.24
f1 (ppm)

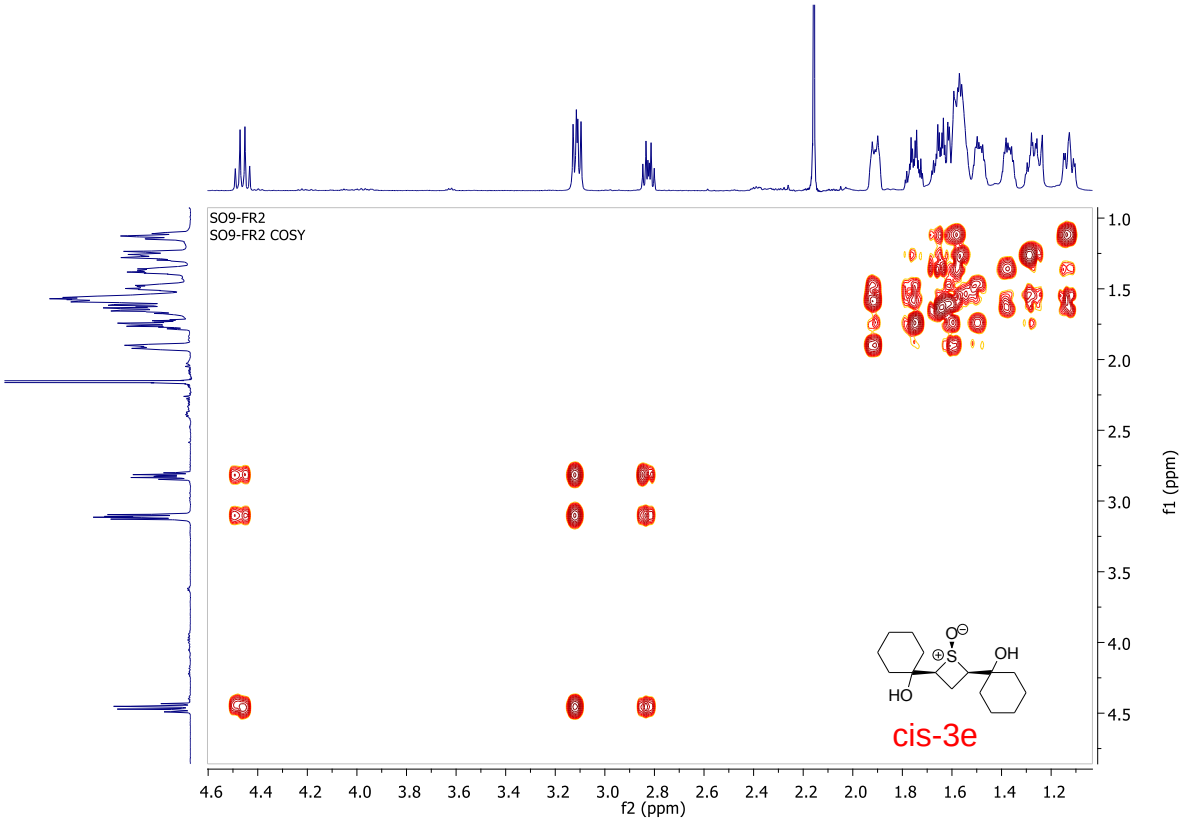

SO9-FR1
SO9-FR1 carbonic
AcOEt
OH
HO
trans-3e
74.4
73.9
71.0
56.5
37.2
35.0
34.0
33.8
25.7
25.1
21.6
21.2
17.1
f1 (ppm)

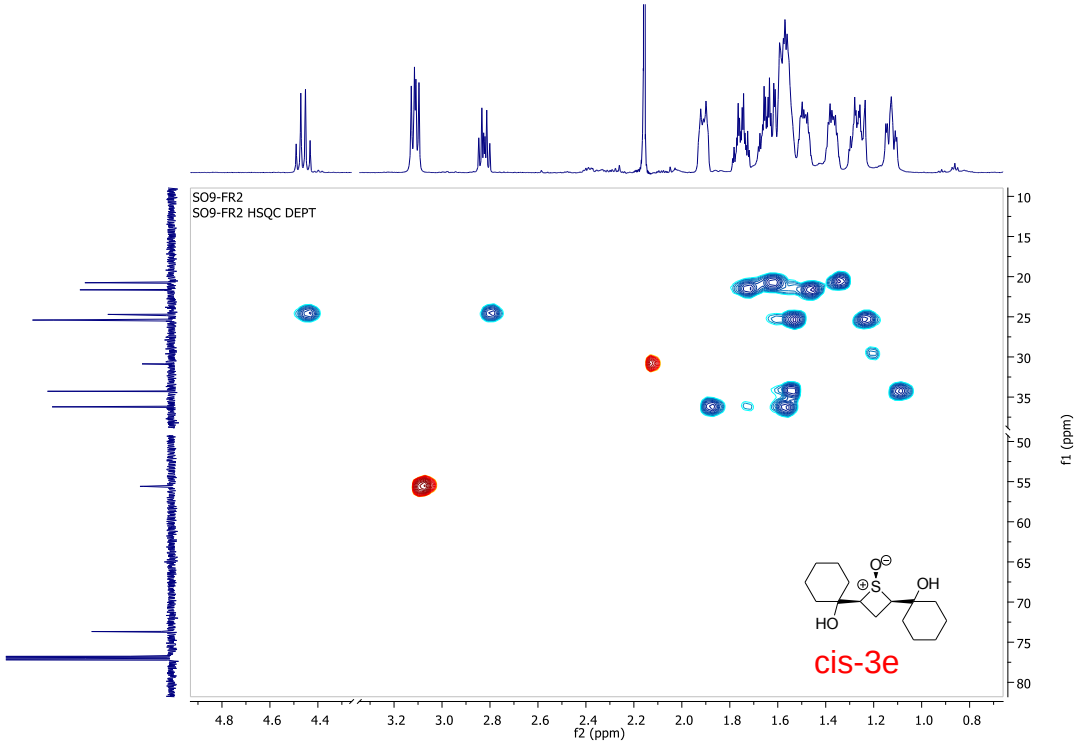

SO9-FR1
SO9-FR1 COSY
f2 (ppm)
f1 (ppm)
trans-3e

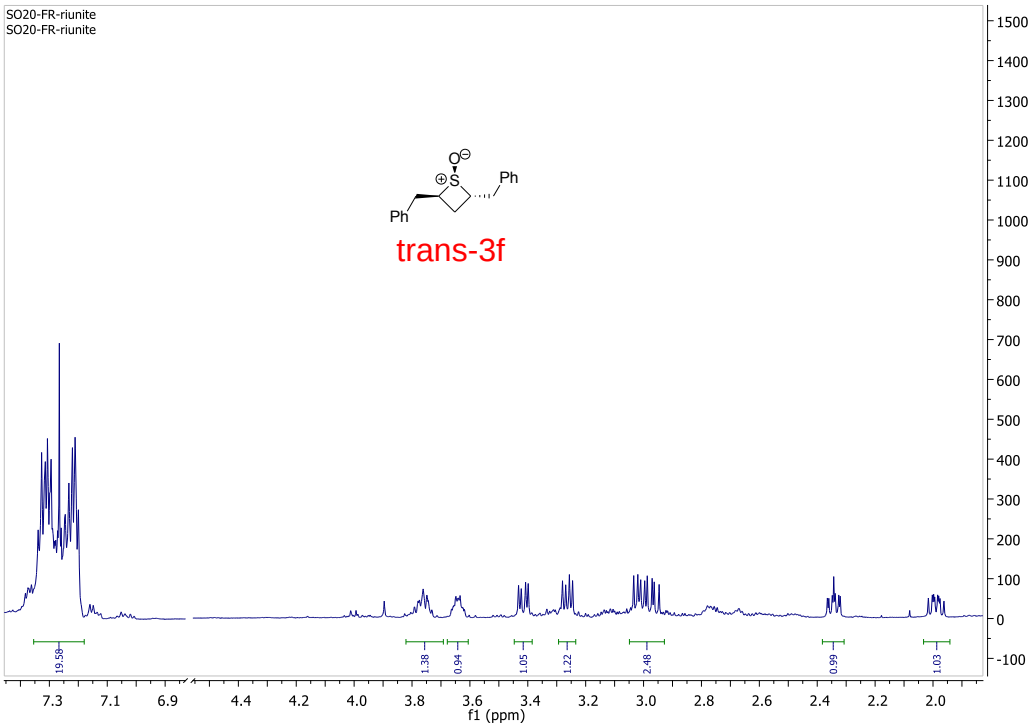

SO9-FR1
SO9-FR1 HSQC DEPT
f2 (ppm)
f1 (ppm)
trans-3e

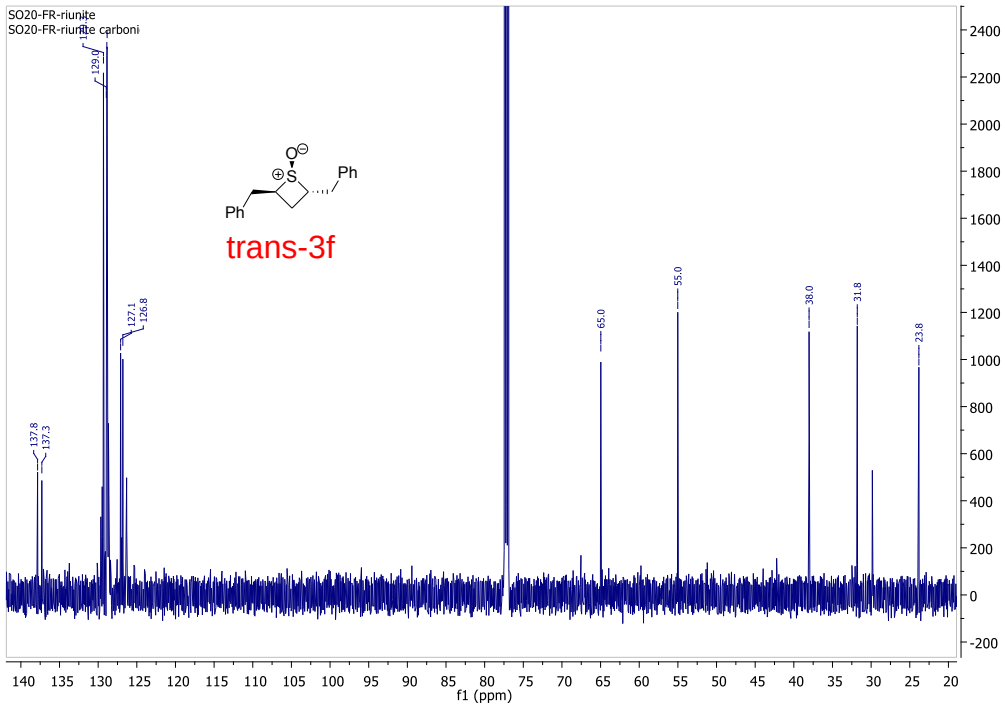

SO9-FR2
SO9-FR2
Acetone
cis-3e
1.00
1.94
1.00
2.01
2.07
12.39
2.38
3.07
2.16
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1

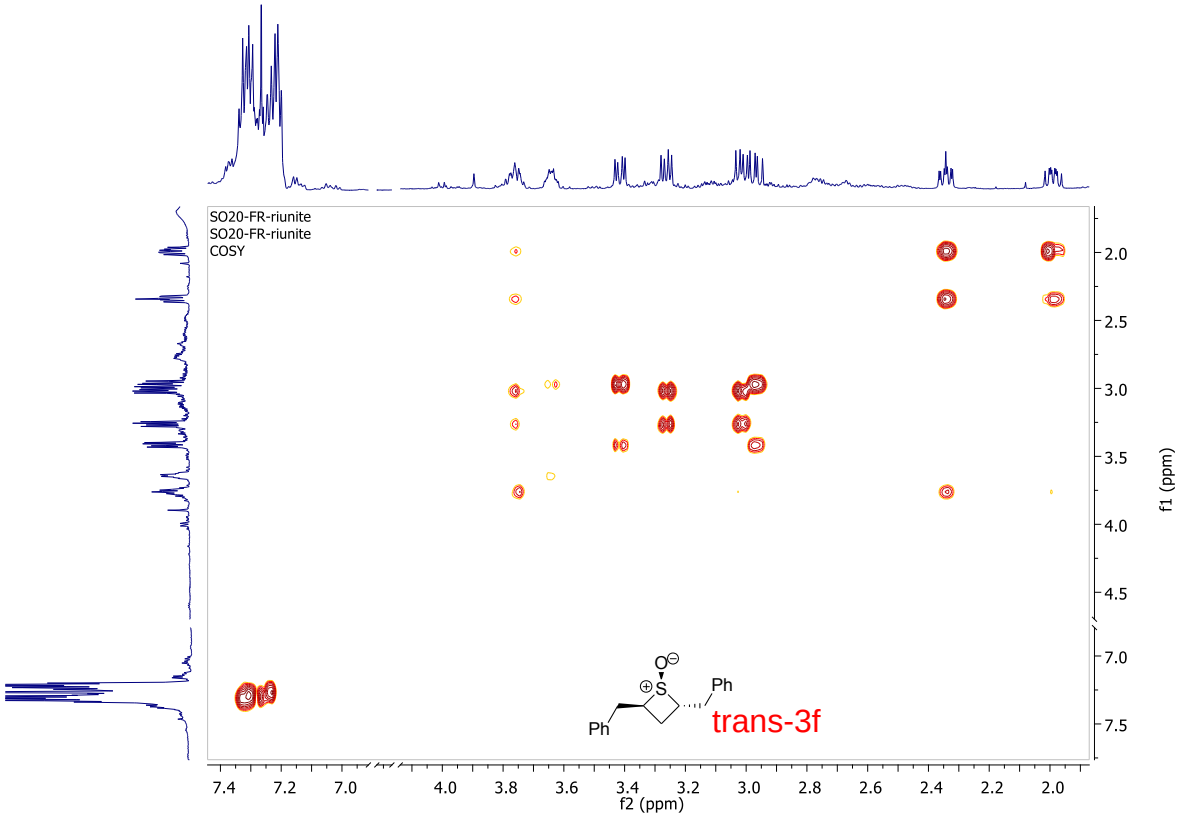

SO9-FR2
SO9-FR2 carbonic
cis-3e
73.7
55.6
36.2
34.3
30.9
25.4
24.7
21.6
20.8
900
800
700
600
500
400
300
200
100
0
-100
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
f1 (ppm)

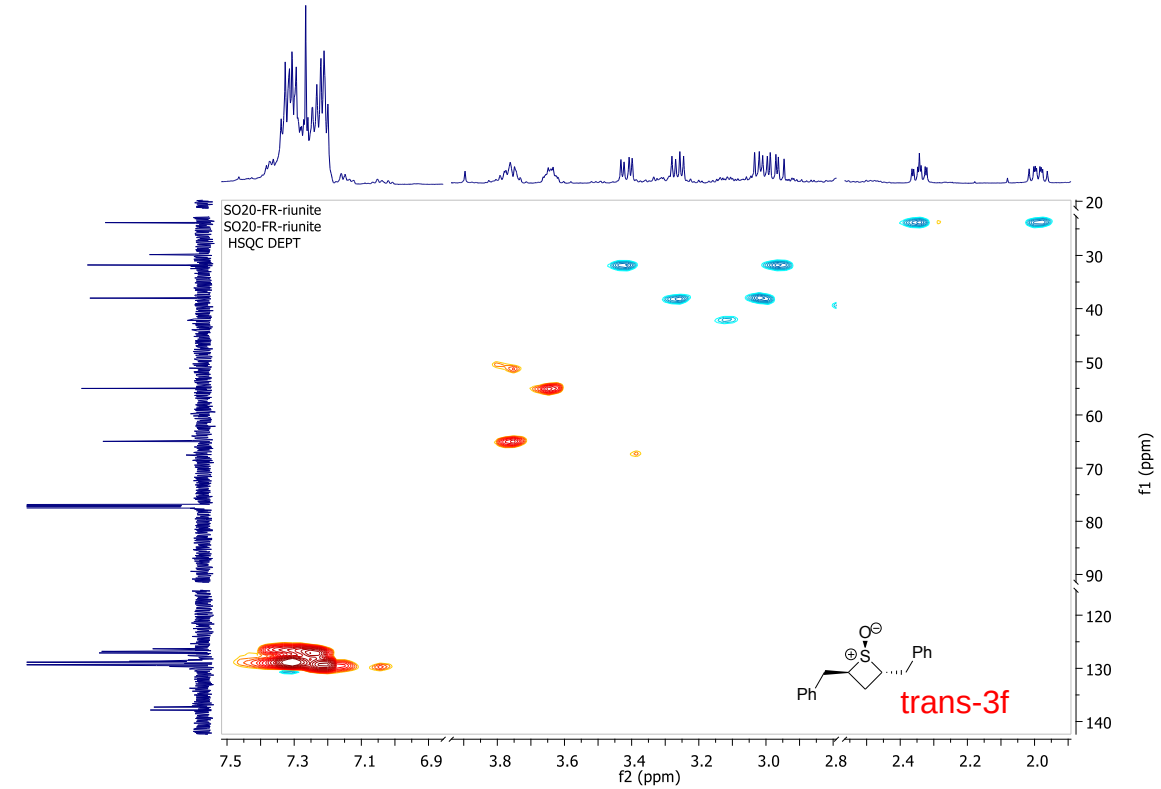

SO9-FR2
SO9-FR2 COSY
f2 (ppm)
f1 (ppm)
OH
HO
cis-3e

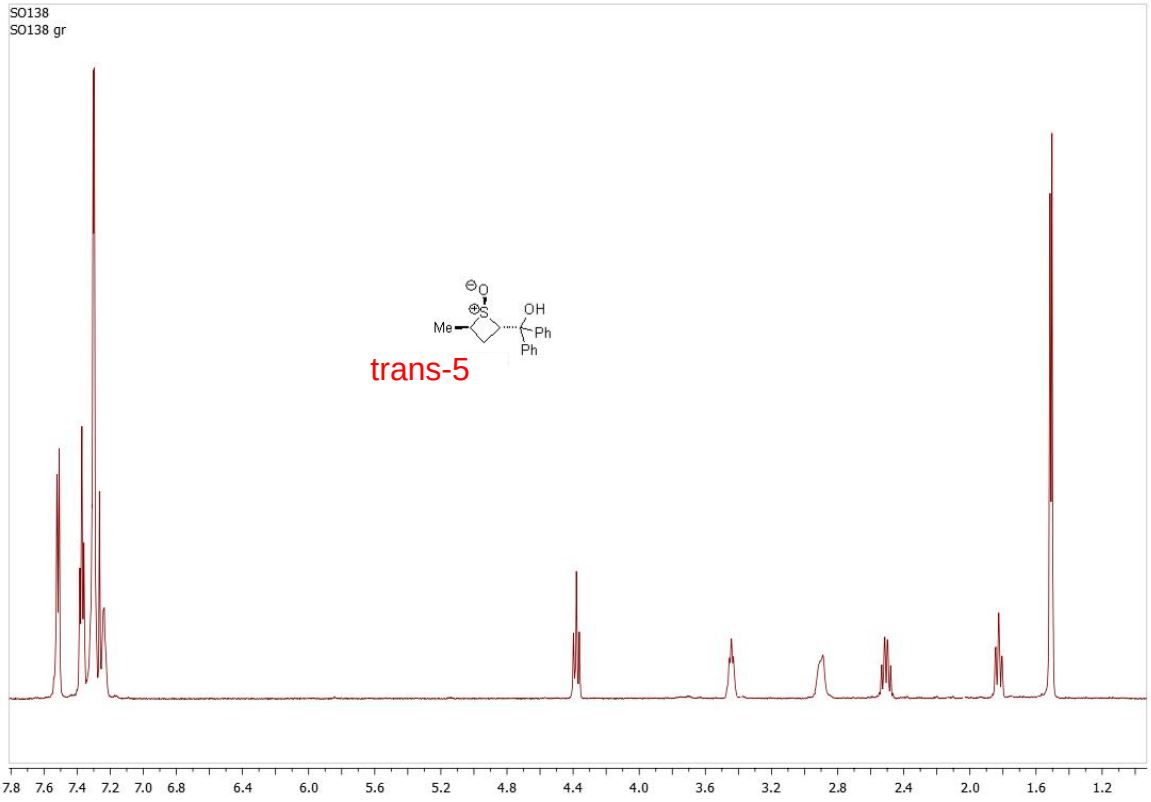

SO9-FR2
SO9-FR2 HSQC DEPT
f2 (ppm)
f1 (ppm)
OH
HO
cis-3e

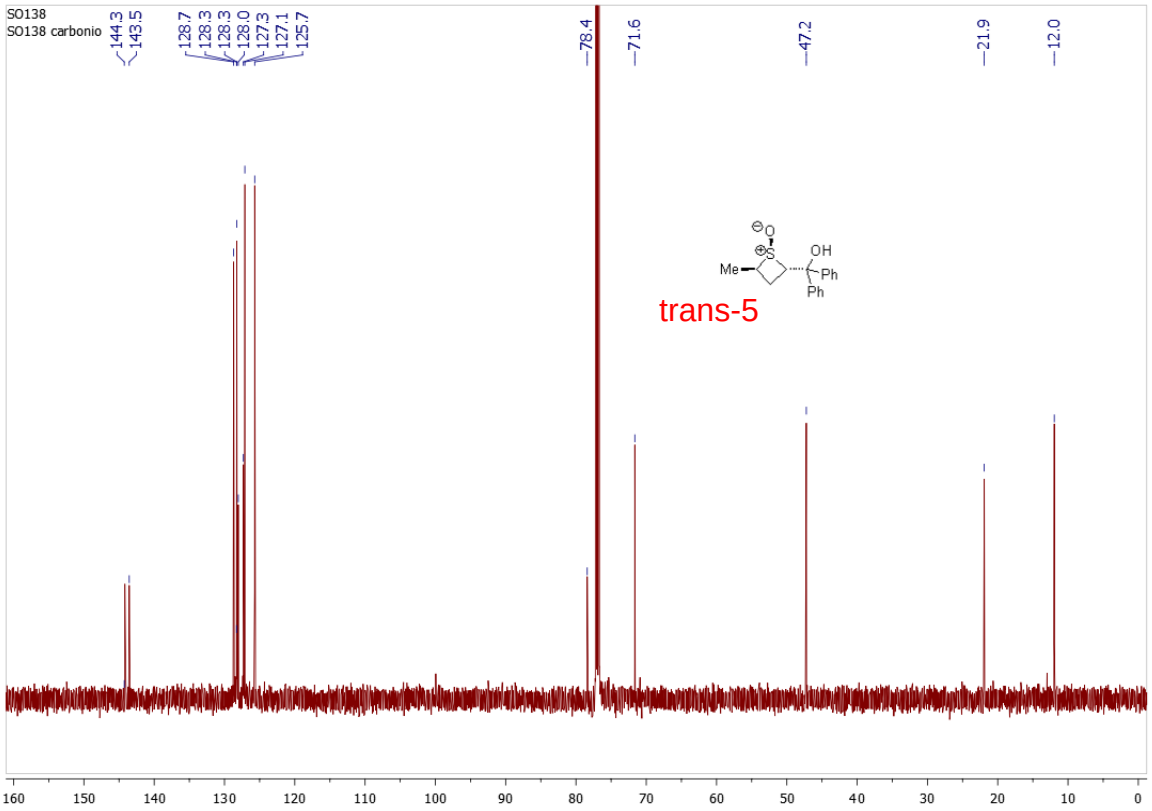

SO20-FR-riunite
SO20-FR-riunite
Ph
Ph
trans-3f
19.58
1.38
0.94
1.05
1.22
2.48
0.99
1.03
f1 (ppm)

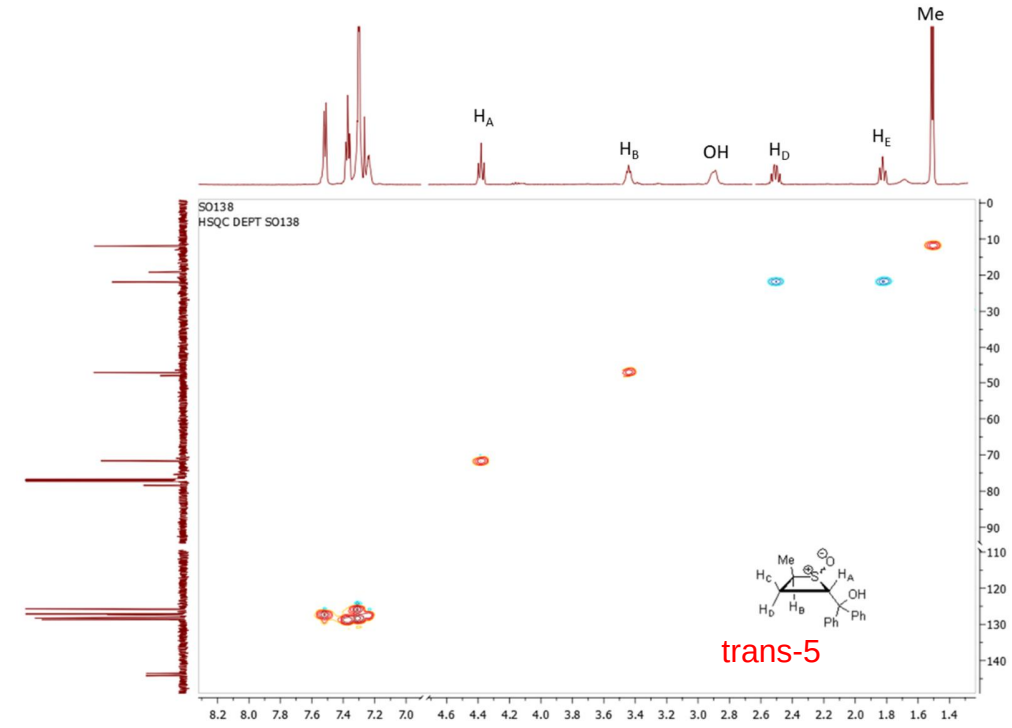

SO20-FR-riunite
SO20-FR-riunite carboni
Ph
Ph
trans-3f
137.8
137.3
129.0
127.1
126.8
65.0
55.0
38.0
31.8
23.8
f1 (ppm)

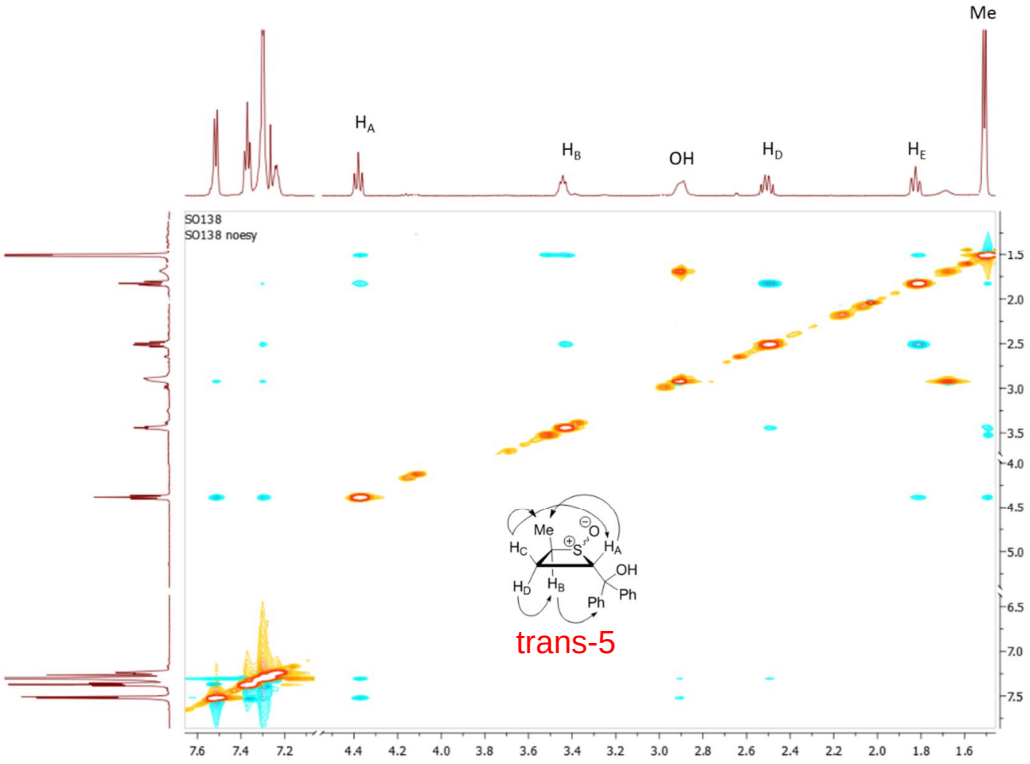

SO20-FR-riunite
SO20-FR-riunite
COSY
Ph
Ph
trans-3f
f2 (ppm)
f1 (ppm)

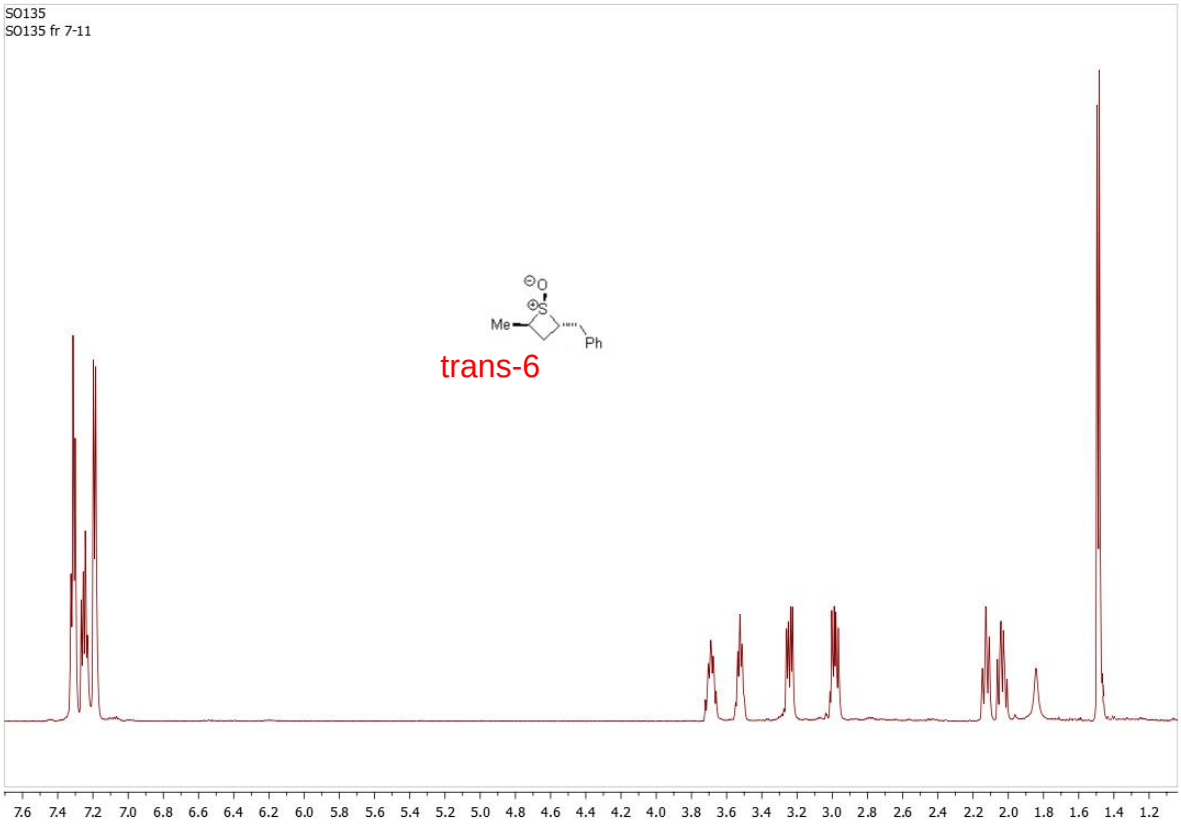

SO20-FR-riunite
SO20-FR-riunite
HSQC DEPT
Ph
Ph
trans-3f
f2 (ppm)
f1 (ppm)

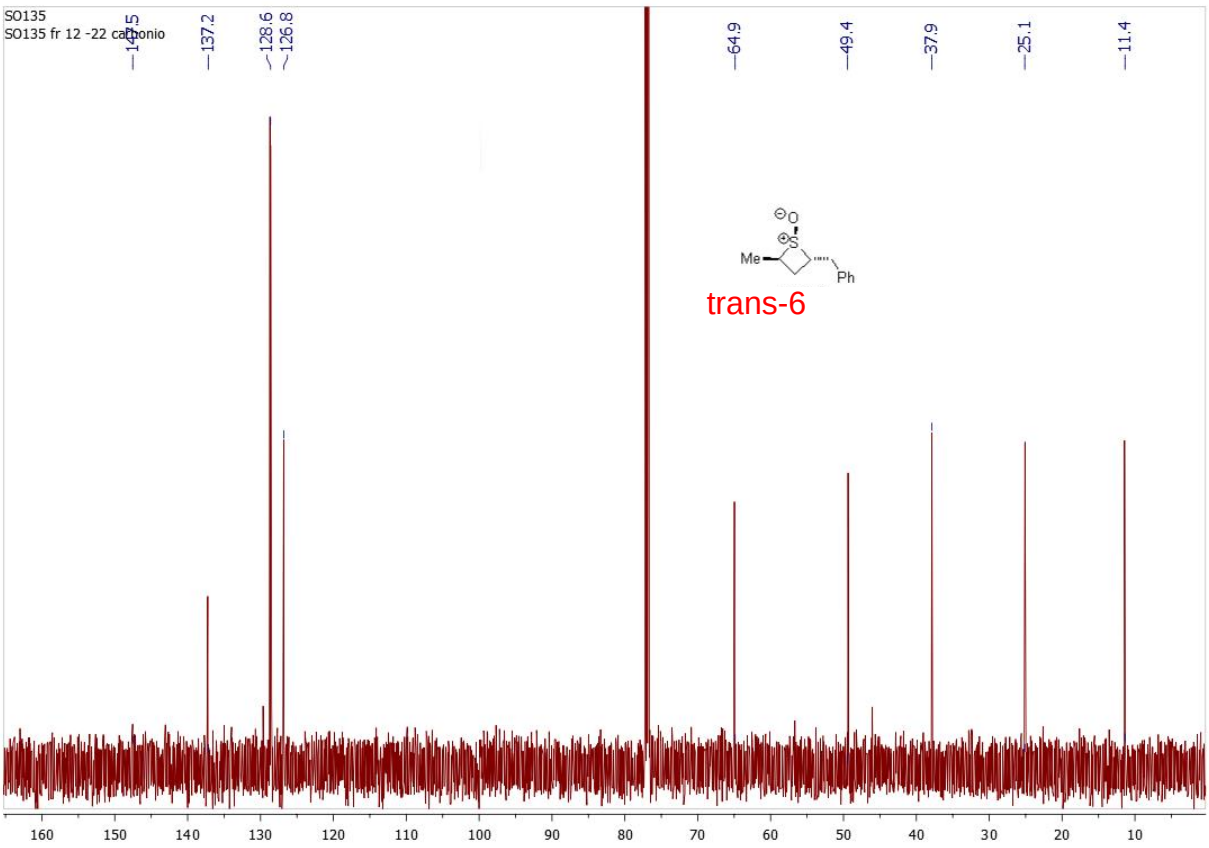

SO138
SO138 gr
trans-5
7.8 7.6 7.4 7.2 7.0 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2

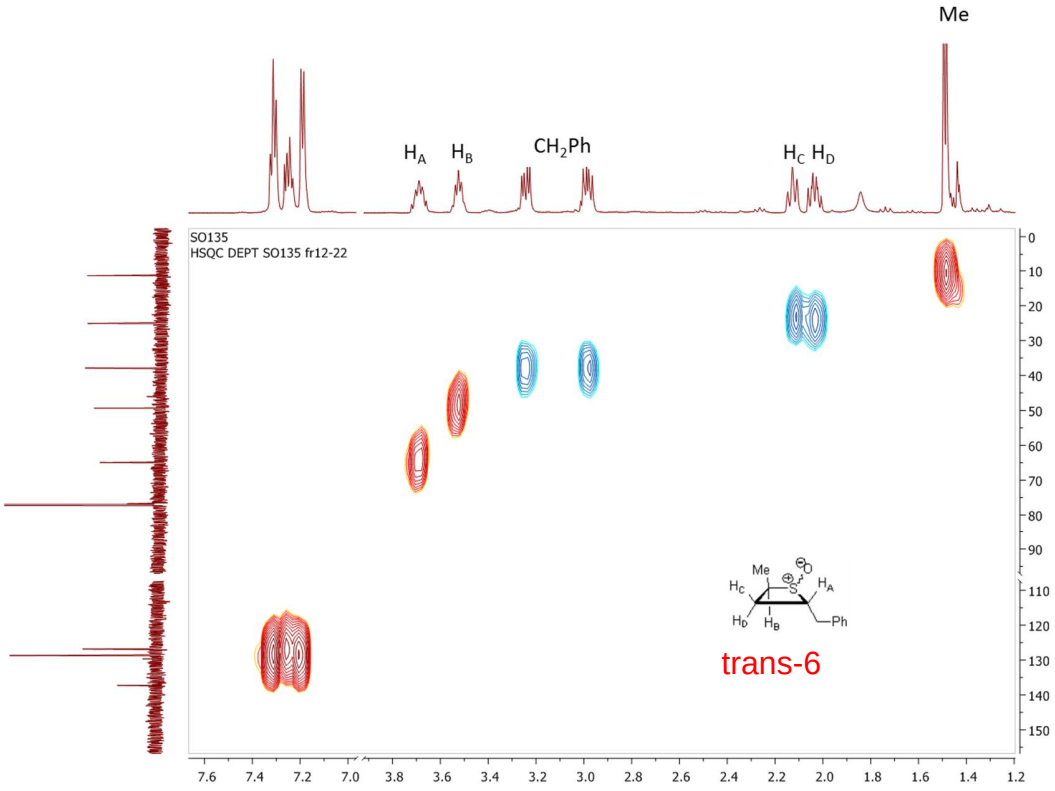

SO138
SO138 carbonio
144.3
143.5
128.7
128.3
128.3
128.0
127.3
127.1
125.7
78.4
71.6
47.2
21.9
12.0
trans-5
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

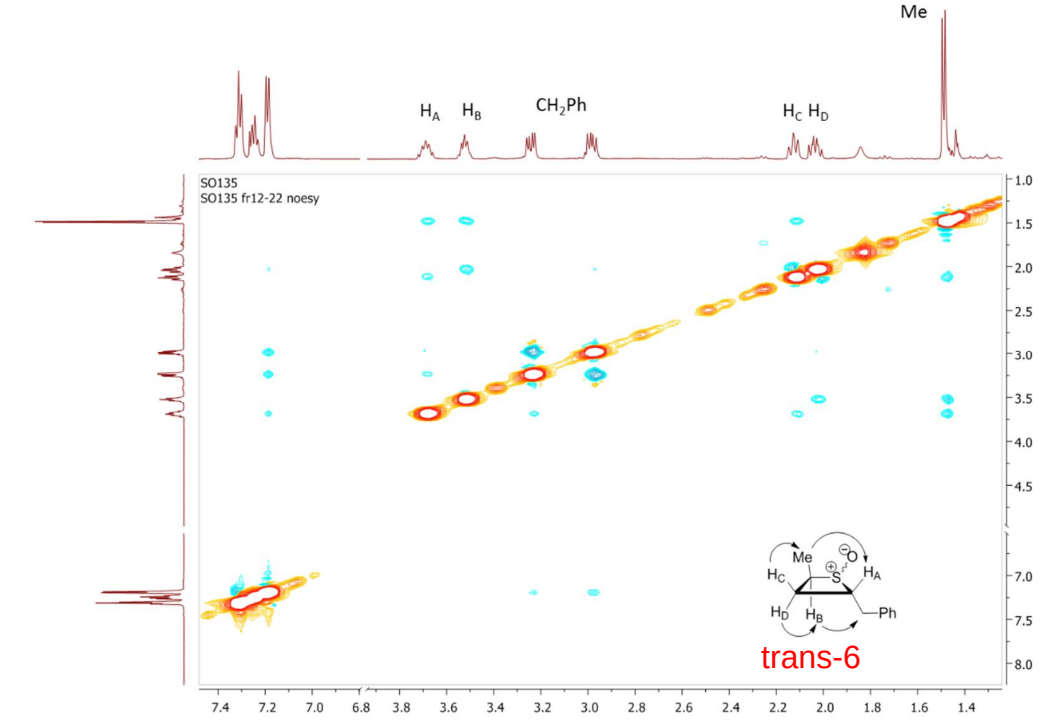

Me
H_A
H_B
OH
H_D
H_E
SO138
HSQC DEPT SO138
trans-5


Me
H_A
H_B
OH
H_D
H_E
SO138
SO138 noesy
trans-5


SO135
SO135 fr 7-11
Me
Ph
trans-6
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 1.2


SO135
SO135 fr 12 -22 cationio
145.5
137.2
128.6
126.8
64.9
49.4
37.9
25.1
11.4
Me
Ph
trans-6
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


Me
H_A H_B
CH_2Ph
H_C H_D
SO135
HSQC DEPT SO135 fr12-22
trans-6


Me
H_A H_B
CH_2Ph
H_C H_D
SO135
SO135 fr12-22 noesy
trans-6