Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Molecularly enlarged *S,S*-BnTsDPEN ligands for iron-catalyzed asymmetric olefin epoxidation reactions using hydrogen peroxide

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Supporting information

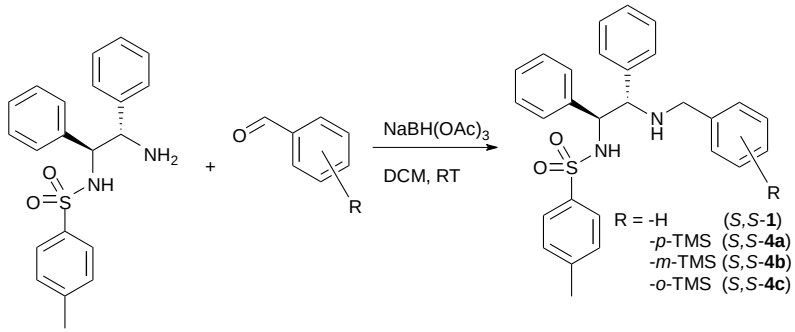
Contents

1. General remarks.

All reactions were performed under nitrogen atmosphere unless stated otherwise. Tetrahydrofuran, diethyl ether, acetonitrile and *n*-hexane were dried on a MBRAUN MB SPS-800 solvent purification system; dichloromethane was distilled over CaH_2 before use. Column chromatography was performed using Merck silica gel (230-400 mesh). Passive dialysis was performed with Sigma-Aldrich dialysis tubing consisting of a benzoylated cellulose membrane that separates compounds with molecular weights equal to or lower than 1.2 kDa from compounds with molecular weights higher than 2.0 kDa. The membrane tubing was shortly stored in methanol and pre-treated with DCM - the solvent used in the subsequent dialysis. Ultrafiltration experiments were performed in a Millipore Solvent Resistant Stirred Cell for Ultrafiltration and Filtration Applications XFUF 04701 (diameter 47 mm, volume 75 mL). ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian AS400 spectrometer at 25 °C, chemical shifts (δ) are given in ppm referenced to the residual solvent peak. GC analyses were performed on a PerkinElmer AutosystemXL Gas Chromatograph. ESI-MS measurements were carried out on a LCT PremierXE KE317 instrument in acetonitrile, dichloromethane or isopropanol as a solvent. All reagents were purchased from Sigma-Aldrich a nd were used as received. The substituted arylaldehydes and the carbosilane supports required for the ligand synthesis were prepared following previously reported general protocols.[1-6] Alkenes **2b** and **2c** were synthesized by a McMurry coupling of the corresponding alkyl-substituted benzaldehydes and obtained in high yields and purities.[7] The alkene **2d** was synthesized by a Heck reaction of 4-*tert*-butylbromobenzene with 2-vinylnaphthalene by modifying the method of Chandrasekhar et al.[8] Reference samples of racemic epoxides **3** were synthesized oxidizing **2a-d** with *meta*-chloroperbenzoic acid (MCPBA)[9,10] to give good yields of the corresponding epoxides.

2. Synthesis of DPEN ligands.

2.1. General procedure for the reductive amination reaction of substituted benzaldehydes (*S,S*-4a-d and CS-*S,S*-6).



Scheme 1. Synthesis of S,S-1 and S,S-4a-c via reductive amination reaction.

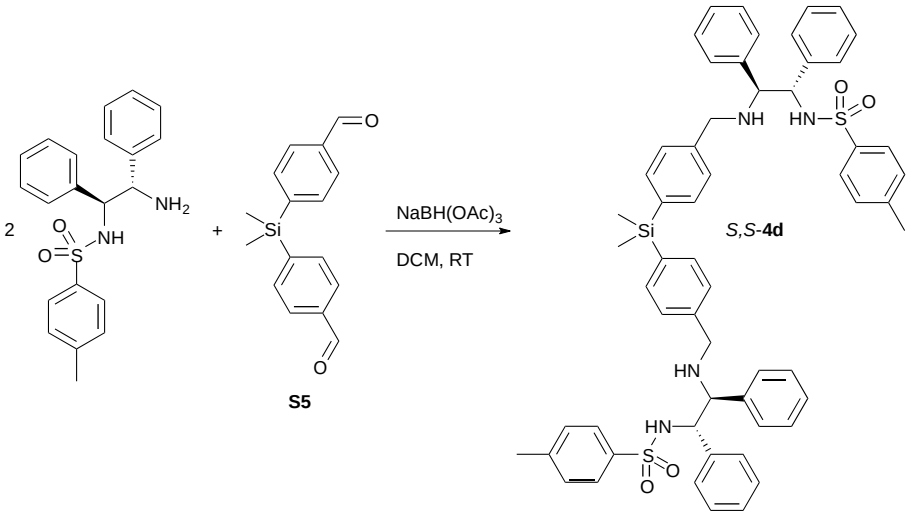
To a transparent solution of sodium triacetoxyborohydride (213 mg, 1.00 mmol) in dry DCM (10 mL) was added *N*-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-4-methylbenzenesulfonamide (*S,S*-TsDPEN) (350 mg, 0.956 mmol) and stirred for 1 h at room temperature. The formation of white suspension was observed. Subsequently, an aldehyde (0.956 mmol) was added to the mixture and it was stirred for 24 h, giving a transparent solution. The reaction mixture was poured into a saturated aqueous NaHCO3 solution (50 mL) and extracted with DCM (3 x 50 mL). The organic extracts were combined, dried over MgSO4, filtered off and concentrated under reduced pressure. The crude product was purified by column chromatography with EtOAc-hexane (1:3 to 1:5, v/v) as eluent in cases of *S,S*-**4a-c** and pure hexane was used in case of CS-*S,S*-**6**.

Ligand *S,S*-**4a**: yield 83% (white solid); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.29 (s, 9H, SiC*H*$_3$), 1.75 (bs, 1H, N*H*), 2.32 (s, 3H, Ar-C*H*$_3$), 3.42 (d, *J* = 13.3 Hz, 1H, C*H*$_2$), 3.62 (d, *J* = 13.3 Hz, 1H, C*H*$_2$), 3.73 (d, *J* = 7.7 Hz, 1H, PhC*H*N), 4.34 (d, *J* = 7.7 Hz, 1H, PhC*H*N), 6.20 (bs, 1H, N*H*), 6.88-7.21 (m, 14H, *H*Ar), 7.38 (d, *J* = 8.2 Hz, 2H, *H*Ar), 7.47 (d, *J* = 7.8 Hz, 2H, *H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -1.1 (Si*C*H$_3$), 21.4 (Ar*C*H$_3$) 50.9 (*C*H$_2$), 63.1 (PhCHN), 67.0 (PhCHN), 127.1, 127.3, 127.4, 127.51, 127.56, 127.60, 127.9, 128.4, 129.1, 133.5, 137.0, 138.3, 138.9, 139.2, 140.0, 142.7 (Ar). IR (ṽ, cm^{-1}): 3254 (br), 3029, 2954, 1599, 1495, 1454, 1396, 1323, 1155, 1091, 920, 811, 769, 696, 667. HRMS (ESI-MS) calcd. m/z for $C_{31}H_{37}N_2O_2SSi$ (M+H$^+$) 529.2345, found 529.2344. Elemental analysis calcd. (%) for $C_{31}H_{36}N_2O_2SSi.0.3H_2O$ C 69.70, H 6.91, N 5.24, found 69.74, H 7.30, N 5.12.

Ligand *S,S*-**4b**: yield 76% (white solid); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.26 (s, 9H, SiC*H*$_3$), 1.63 (bs, 1H, N*H*), 2.32 (s, 3H, Ar-C*H*$_3$), 3.43 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 3.64 (d, *J* = 13.2 Hz, 1H, C*H*$_2$), 3.68 (d, *J* = 7.7 Hz, 1H, PhC*H*N), 4.32 (d, *J* = 7.7 Hz, 1H, PhC*H*N), 6.17 (bs, 1H, N*H*), 6.89-7.08 (m, 9H, *H*Ar), 7.13-7.19 (m, 4H, *H*Ar), 7.26-7.44 (m, 5H, *H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -1.1 (Si*C*H$_3$), 21.4 (Ar*C*H$_3$) 51.0 (*C*H$_2$), 63.0 (PhCHN), 66.8 (PhCHN), 127.1, 127.3, 127.48, 127.55 (x2), 127.87 127.89, 128.4, 128.5, 129.0, 132.1, 133.0, 137.0, 138.2, 138.4, 138.9, 140.7, 142.6 (Ar). IR (ṽ, cm^{-1}): 3320, 3251 (br), 3030, 2954, 1599, 1494, 1456, 1306, 1247, 1151, 1123,

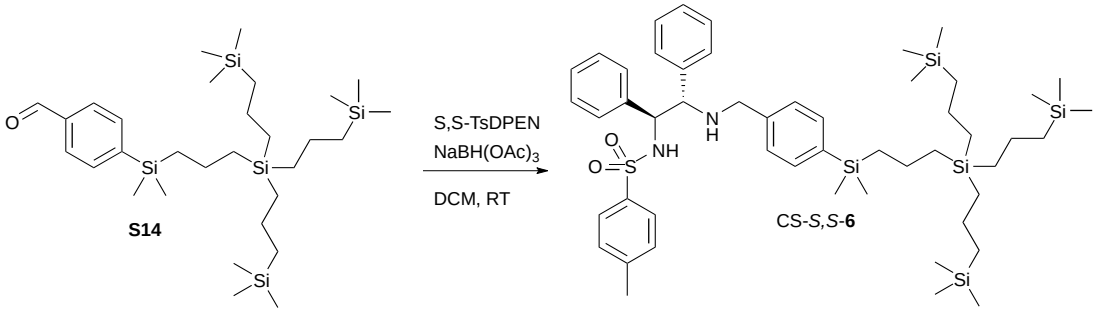
1095, 1026, 936, 861, 834, 779, 450, 699, 668. HRMS (ESI-MS) calcd. m/z for $C_{31}H_{37}N_2O_2SSi$ (M+H$^+$) 529.2345, found 529.2349.

Ligand *S,S*-**4c**: yield 77% (white solid); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.05 (s, 9H, SiC*H*$_3$), 1.66 (bs, 1H, N*H*), 2.31 (s, 3H, ArC*H*$_3$), 3.50 (d, *J* = 13.0 Hz, 1H, C*H*$_2$), 3.61 (d, *J* = 13.0 Hz, 1H, C*H*$_2$), 3.77 (d, *J* = 7.5 Hz, 1H, PhC*H*N), 4.36 (d, *J* = 7.5 Hz, 1H, PhC*H*N), 6.19 (bs, 1H, N*H*), 6.97-7.09 (m, 9H, *H*Ar), 7.13-7.24 (m, 4H, *H*Ar), 7.30-7.44 (m, 5H, *H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.06 (Si*C*H$_3$), 21.4 (Ar*C*H$_3$) 51.0 (*C*H$_2$), 62.9 (Ph*C*HN), 67.6 (Ph*C*HN), 126.4, 127.0, 127.3, 127.46, 127.54, 127.7 128.0, 128.1, 128.5, 129.1, 129.3, 134.4, 136.9, 138.27, 138.35, 138.9, 142.7, 144.7 (Ar). IR (ṽ, cm^{-1}): 3261 (br), 3031, 2955, 1600, 1495, 1455, 1326, 1249, 1154, 1091, 917, 835, 812, 745, 698, 667. HRMS (ESI-MS) calcd. m/z for $C_{31}H_{37}N_2O_2SSi$ (M+H$^+$) 529.2345, found 529.2344.



Scheme 2. Synthesis of *S,S*-**4d** via reductive amination reaction.

Ligand *S,S*-**4d**: to a transparent solution of sodium triacetoxyborohydride (607 mg, 2.87 mmol) in dry DCM (30 mL) was added *S,S*-TsDPEN (1.00 g, 2.73 mmol) and stirred for 1 h at RT. The formation of a turbid solution was observed. Subsequently, the aldehyde (356 mg, 1.33 mmol) was added to the mixture and it was stirred for 24 h, giving a transparent solution. The reaction mixture was poured into a saturated aqueous $NaHCO_3$ solution (50 mL) and extracted with DCM (3 x 50 mL). The organic extracts were combined, dried over $MgSO_4$, filtered off and concentrated under reduced pressure. The crude product was purified by column chromatography with EtOAc-hexane (1:2, v/v) as eluent. Yield: 1.24 g, 96% (white powder); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.60 (s, 6H, SiC*H*$_3$), 1.81 (bs, 2H, N*H*), 2.34 (s, 6H, Ar-C*H*$_3$), 3.46 (d, *J* = 13.3 Hz, 2H, C*H*$_2$), 3.65 (d, *J* = 13.3 Hz, 2H, C*H*$_2$), 3.76 (d, *J* = 7.7 Hz, 2H, PhC*H*N), 4.37 (d, *J* = 7.7 Hz, 2H, PhC*H*N), 6.17 (bs, 2H, N*H*), 6.91-7.23 (m, 28H, *H*Ar), 7.40 (d, *J* = 8.3 Hz, 4H, *H*Ar), 7.50 (d, *J* = 7.9 Hz, 4H, *H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.3 (Si*C*H$_3$), 21.4 (Ar*C*H$_3$), 50.8 (N*C*H$_2$), 63.1 (Ph*C*HN), 67.0 (Ph*C*HN), 127.0, 127.3 (x2), 127.4, 127.5, 127.6, 127.7, 127.9, 128.4, 129.1, 134.3, 136.9, 138.2, 138.8, 140.3, 142.7 (Ar). IR (ṽ, cm^{-1}): 3254 (br), 3030, 2954, 1599, 1495, 1455, 1396, 1323, 1155, 1091, 920, 811, 770, 696, 667. HRMS (ESI-MS) calcd. m/z for $C_{58}H_{61}N_4O_4S_2Si$ (M+H$^+$) 969.3904, found 969.3920. Elemental analysis calcd. (%) for $C_{58}H_{60}N_4O_4S_2Si.3.9H_2O$ C 67.01, H 6.57, N 5.39, found 67.08, H 6.67, N 5.00.

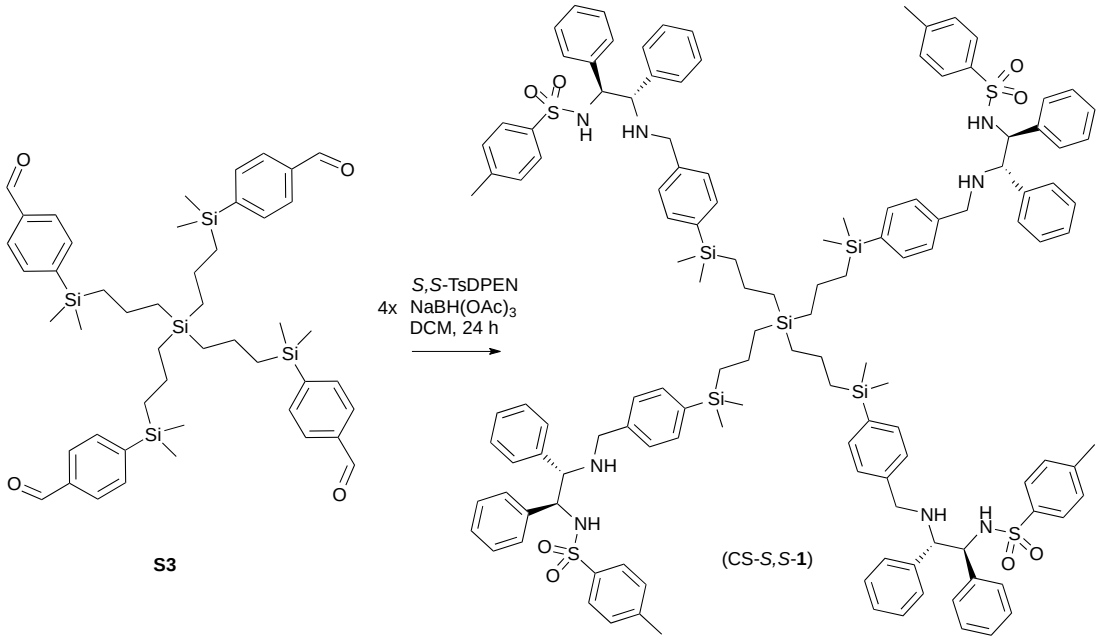


Scheme 3. Preparation of CS-S,S-6 ligand.

Ligand CS-*S,S*-**6**: yield 76% (colourless oil); GPC (THF): 9.944 min, PDI 1.02. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.00 (s, 27H, Si(C*H*$_3$)$_3$), 0.29 (s, 6H, ArSiC*H*$_3$), 0.52-0.65 (m, 14H, C*H*$_2$Si(C*H*$_2$CH$_2$C*H*$_2$TMS)$_3$), 0.86 (t, *J* = 8.2 Hz, 2H, ArSiMe$_2$C*H*$_2$), 1.29-1.46 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 1.69 (bs, 1H, N*H*), 2.36 (s, 3H, ArC*H*$_3$), 3.45 (d, *J* = 13.3 Hz, 1H, NC*H*$_2$), 3.63 (d, *J* = 13.3 Hz, 1H, NC*H*$_2$), 3.76 (d, *J* = 7.6 Hz, 1H, PhC*H*N), 4.36 (d, *J* = 7.6 Hz, 1H, PhC*H*N), 6.18 (bs, 1H, N*H*), 6.93-7.24 (m, 14H, *H*Ar), 7.40 (d, *J* = 8.3 Hz, 2H, *H*Ar), 7.47 (d, *J* = 7.8 Hz, 2H, *H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.9 (ArSi*C*H$_3$), -1.5 (Si(*C*H$_3$)$_3$), 17.4, 17.6, 18.6 (overlap), 20.6, 21.4 (Ar*C*H$_3$), 21.7, 50.9 (N*C*H$_2$), 63.1 (Ph*C*HN), 67.0 (Ph*C*HN), 127.1, 127.3 (x2), 127.49, 127.51, 127.58, 127.9, 128.4, 129.1, 133.7, 137.0, 138.3, 138.6, 138.9, 139.9, 142.7 (Ar). IR (ṽ, cm^{-1}): 3266 (br), 3065, 3031, 2952, 2911, 2874, 1601, 1495, 1455, 1412, 1331, 1246, 1160, 1093, 911, 860, 831, 768, 697, 665. HRMS (ESI-MS) calcd. m/z for $C_{51}H_{85}N_2O_2SSi_5$ (M+H$^+$) 929.5178, found 929.5161.

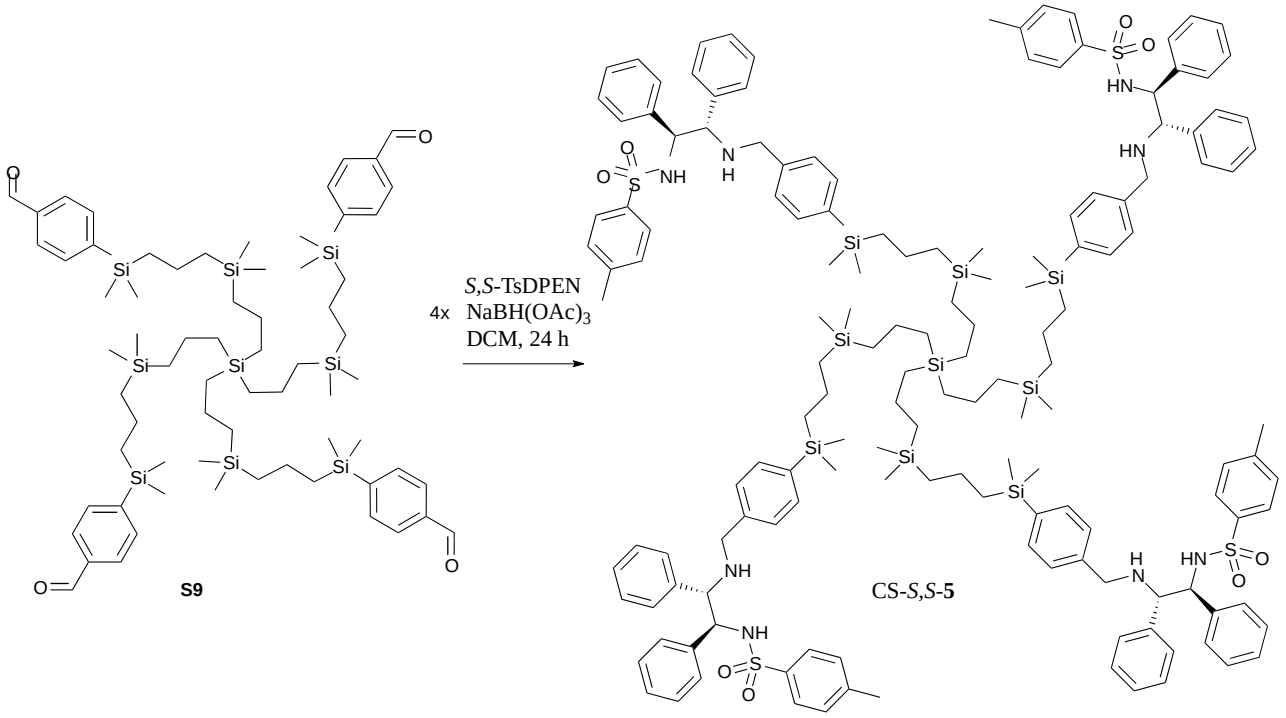
2.2 General procedure for the reductive amination reaction using carbosilane-linked benzaldehydes (CS-*S*,*S*-1 and CS-*S*,*S*-5).

To a transparent solution of sodium triacetoxyborohydride (259 mg, 1.22 mmol) in dry DCM (15 mL) was added *N*-((*1S*,*2S*)-2-amino-1,2-diphenylethyl)-4-methylbenzenesulfonamide (*S*,*S*-TsDPEN) (429 mg, 1.17 mmol) and stirred for 1 h at RT. The formation of a turbid solution was observed. Subsequently, a carbosilane-linked aldehyde (0.280 mmol) was added to the mixture and it was stirred for 24 to 48 h (the reaction progress was monitored by ^{1}H NMR), giving a transparent solution. The reaction mixture was poured into a saturated aqueous $NaHCO_3$ solution (50 mL) and extracted with DCM (3 x 50 mL). The organic extracts were combined, dried over Na_2SO_4, filtered off and concentrated under reduced pressure to give an off-white semisolid material. The crude product was purified by passive dialysis in DCM.



Scheme 4. Preparation of CS-*S*,*S*-**1**.

Ligand CS-*S*,*S*-**1**: yield 83% (white light solid); GPC (THF): 9.612 min, PDI 1.02. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.24 (s, 24H, SiC*H*$_3$), 0.55 (t, *J* = 8.2 Hz, 8H, Si$_{core}$C*H*$_2$), 0.79 (t, *J* = 8.1 Hz, 8H, ArSiC*H*$_2$), 1.41-1.49 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 1.80 (bs, 4H, N*H*), 2.31 (s, 4H, ArC*H*$_3$), 3.42 (d, 4H, *J* = 13.2 Hz, C*H*$_2$N), 3.60 (d, 4H, *J* = 13.2 Hz, C*H*$_2$N), 3.72 (d, *J* = 7.7 Hz, 4H, PhC*H*N), 4.33 (d, *J* = 7.7 Hz, 4H, PhC*H*N), 6.21 (bs, 4H, N*H*), 6.91-7.24 (m, 56H, H$_{Ar}$), 7.39 (d, *J* = 8.3 Hz, 8H, H$_{Ar}$), 7.43 (d, *J* = 8.0 Hz, 8H, H$_{Ar}$). ^{13}C NMR (CDCl3, 100 MHz): δ -2.8 (Si*C*H$_3$), 17.5, 18.6, 20.6, 21.4 (Ar*C*H$_3$), 50.9 (N*C*H$_2$), 63.2 (Ph*C*HN), 67.1 (Ph*C*HN), 127.1, 127.26, 127.34, 127.5, 127.6, 127.9, 128.4, 129.1, 133.7, 137.0, 138.3, 138.5, 138.8, 139.0, 140.0, 142.7 (Ar). IR (ṽ, cm^{-1}): 3267 (br), 3064, 3030, 2953, 2913, 1600, 1495, 1455, 1396, 1327, 1247, 1156, 1091, 1027, 910, 8111, 769, 697, 665. HRMS (ESI-MS) calcd. *m/z* for $C_{132}H_{160}N_8O_8S_4Si_5$ (M+2H$^+$) 1126.4985, found 1126.4945. Elemental analysis calcd. (%) for $C_{132}H_{158}N_8O_8S_4Si_5$ 4H_2O C 68.24, H 7.11, N 4.82, found 68.47, H 7.27, N 4.49.



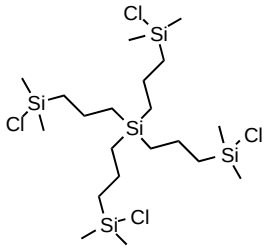
Scheme 5. Preparation of CS-*S*,*S*-**5**.

Ligand CS-*S*,*S*-**5**: yield 67% (white light solid); GPC (THF): 9.450 min, PDI 1.03. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.05 (s, 24H, $CH_2Si(CH_3)_2CH_2$), 0.26 (s, 24H, $ArSiCH_3$), 0.51-0.62 (m, 24H, Me_2SiCH_2 & $Si_{core}CH_2$), 0.82 (t, 8H, *J* = 8.2 Hz, $ArSiCH_2$), 1.25-1.43 (m, 16H, $CH_2CH_2CH_2$), 1.69 (bs, 4H, N*H*), 2.32 (s, 12H, $ArCH_3$), 3.42 (d, *J* = 13.3 Hz, 4H, NCH_2), 3.60 (d, *J* = 13.3 Hz, 4H, NCH_2), 3.72 (d, *J* = 7.7 Hz, 4H, PhC*H*N), 4.33 (d, *J* = 7.7 Hz, 4H, PhC*H*N), 6.18 (bs, 4H, N*H*), 6.90-7.20 (m, 56H, H_{Ar}), 7.37 (d, *J* = 8.2 Hz, 8H, H_{Ar}), 7.43 (d, *J* = 8.0 Hz, 8H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.1, -2.8 ($SiCH_3$), 17.6, 18.4, 18.6, 20.1, 20.3, 20.5, 21.4 ($ArCH_3$) 50.9 (NCH_2), 63.1 (PhCHN), 67.0 (PhCHN), 127.1, 127.28, 127.32, 127.49, 127.55, 127.57, 127.9, 128.4, 129.1, 133.7, 137.0, 138.3, 138.5, 138.9, 139.9, 142.7 (Ar). IR (ṽ, cm^{-1}): 3263 (br), 3065, 3031, 2953, 2912, 2874, 1600, 1495, 1455, 1396, 1329, 1265, 1247, 1159, 1092, 1026, 906, 811, 770, 735, 697, 664. HRMS (ESI-MS) *m/z* calcd. for $C_{152}H_{206}N_8O_8S_4Si_5$ ($M+2H^+$) 1326.6400, found 1326.6398. Elemental analysis calcd. (%) for $C_{152}H_{204}N_8O_8S_4Si_9{\cdot}4H_2O$ C 67.01, H 7.84, N 4.11, found 67.17, H 7.78, N 3.74.

3. Synthesis of carbosilane supports

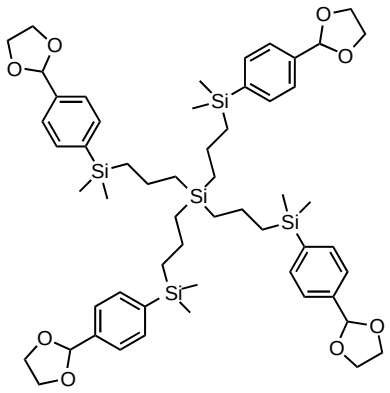
3.1. Preparation of the support for CS-*S*,*S*-1.

Tetrakis(3-(chlorodimethylsilyl)propyl)silane (S1).



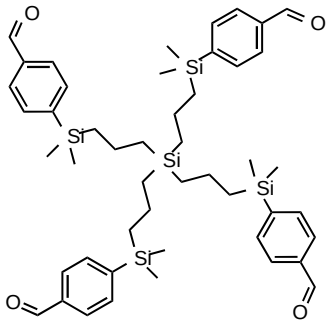
Neat tetraallylsilane (1.00 g, 5.20 mmol) and chlorodimethylsilane $HSiMe_2Cl$ (2.90 mL, 25.0 mmol) were added to a flame dried Schlenk flask. A catalyst tetrabutylamonium hexacloroplatinate (IV) (10 crystals) was dissolved in $CDCl_3$ (0.1 mL) and added to the flask by a syringe. The reaction mixture was stirred overnight at 35 ^{0}C. The product (2.23 g, 4.84 mmol, 93%) was obtained as a light yellow transparent oil after the excess of the sililating agent was removed under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.40 (s, 24H, $SiCH_3$), 0.62 (t, $^{3}J_{H-H}$ 8.4 Hz, 8H, CH_2SiCH_2), 0.89 (t, $^{3}J_{H-H}$ = 8.1 Hz, 8H, $ClSiCH_2$), 1.41-1.48 (m, 8H, $CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1.8, 16.6, 17.8, 23.6.

Tetrakis(3-((4-(1,3-dioxolan-2-yl) phenyl)dimethylsilyl)propyl)silane (S2).



A 1.6 M solution of *n*-BuLi in hexane (4.6 mL, 7.36 mmol) was added *via* a cannula to a solution of 2-(4-Bromophenyl)-1,3-dioxolane (1.83 g, 8.00 mmol) in dry THF (20 mL) at -78 ^{0}C. After 1 h of stirring at that temperature a white precipitate was formed. Then a solution of **S1** (1.00 g, 1.75 mmol) in THF (2 mL) was added dropwise. In one hour the reaction mixture was allowed to warm to RT, yielding a transparent colourless solution. The reaction mixture was quenched with MeOH (1 mL) and poured into a saturated aqueous $KHCO_3$ solution. The organic layer was separated. The aqueous layer was extracted with DCM (50 mL x 3). Combined organic fractions were dried over $MgSO_4$ and filtered off. Solvents were evaporated under reduced pressure. The crude product was purified via passive dialysis in DCM to give a colourless oil (1.44 g, 1.40 mmol, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.22 (s, 6H, SiCH_3), 0.49 (t, $^{3}J_{H-H}$ = 8.4 Hz, 2H, CH_2SiCH_2), 0.77 (t, $^{3}J_{H-H}$ = 8.4 Hz, 2H, ClSiCH_2), 1.25-1.33 (m, 2H, $CH_2CH_2CH_2$), 4.00-4.13 (m, 4H, OCH_2), 5.81 (s,1H, ArC*H*), 7.39 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H, CH_{Ar}), 7.52 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.9, 17.4, 18.5, 20.5, 65.3, 103.7, 125.6, 133.6, 138.3, 141.1. Elemental analysis calcd. (%) for $C_{56}H_{84}O_8Si_5$ C 65.58, H 8.25 found 65.21, H 8.21.

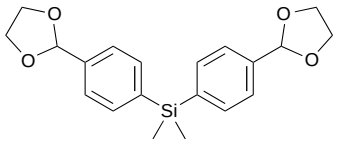
4,4',4'',4'''-((Silanetetrayltetrakis(propane-3,1diyl)) tetrakis(dimethylsilanediyl))tetrabenzaldehyde (S3).



Water (ca. 10 mL) was added to a solution of **S2** (1.44 g, 1.40 mmol) in acetone (30 mL) until a slight turbidity appeared. A catalytic amount of *p*-toluenesulfonic acid monohydrate was added to this solution and it was refluxed for 10 minutes. Finally, the reaction mixture was cooled to room temperature, diluted with a saturated aqueous $KHCO_3$ solution (20 mL) and extracted with DCM (50 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered off and evaporated under reduced pressure. The product (1.10 g, 1.29 mmol, 92%) was obtained as a colourless slightly cloudy oil. This aldehyde readily oxidizes on air and was immediately used in the next reaction step. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.24 (s, 24H, SiCH_3), 0.45 (t, $^{3}J_{H-H}$ = 8.4 Hz, 8H, CH_2SiCH_2), 0.76 (t, $^{3}J_{H-H}$ = 8.2 Hz, 8H, ArSiCH_2), 1.19-1.28 (m, 8H, $CH_2CH_2CH_2$), 7.63 (d, $^{3}J_{H-H}$ = 8.0 Hz, 8H, CH_{Ar}), 7.82 (d, $^{3}J_{H-H}$ = 7.6 Hz, 8H, CH_{Ar}), 10.00 (s, 4H, C*H*O). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.1, 17.2, 18.4, 20.2, 128.6, 134.0, 136.5, 148.5, 192.5. IR (ν̃, cm^{-1}): 2955, 2913, 2874, 1701 (CHO), 1595, 1558, 1407, 1381, 1248, 1212, 1173, 1142, 1101, 908, 836, 804, 778, 688.

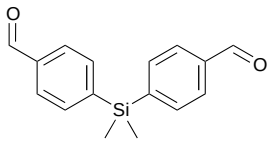
3.2. Preparation of the support for *S,S*-4d

Bis(4-(1,3-dioxolan-2-yl)phenyl)dimethylsilane (S4)



A 1.6 M solution of *n*-BuLi in hexane (5.1 mL, 8.16 mmol) was added *via* a cannula to a solution of 2-(4-Bromophenyl)-1,3-dioxolane (1.83 g, 8.00 mmol) in THF (20 mL) at -78 ^{0}C. A white precipitate was formed after an hour of stirring at that temperature. Then a solution of dichlorodimethylsilane (515 mg, 4.00 mmol) in THF (2 mL) was added dropwise to the reaction mixture and then it was allowed to warm to room temperature. After 1 h a transparent yellowish solution was formed. The reaction mixture was quenched with MeOH (ca. 1 mL) and poured into a saturated aqueous $KHCO_3$ solution. The organic layer was separated. The aqueous layer was extracted with DCM (50 mL x 3). Combined organic fractions were dried over $MgSO_4$ and filtered off. Solvents were evaporated under reduced pressure. The product (1.07 g, 3.00 mmol, 75%) was obtained as a colourless oil and was sufficiently pure to be used in the next step as it was. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.54 (s, 6H, SiCH_3), 4.01-4.14 (m, 8H, CH_2), 5.82 (s, 2H, OC*H*), 7.45 (d, $^{3}J_{H-H}$ = 8.1 Hz, 2H, Ar*H*), 7.53 (d, $^{3}J_{H-H}$ = 8.1 Hz, 4H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.4, 65.3, 103.7, 125.7, 134.3, 138.8, 139.2.

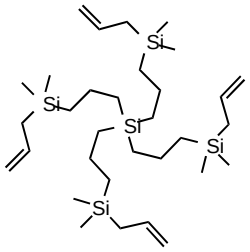
4,4'-(Dimethylsilanediyl)dibenzaldehyde (S5).



Water (ca. 10 mL) was added to a solution of **S4** (1.00 g, 2.80 mmol) in acetone (30 mL) until a slight turbidity appeared. A catalytic amount of p-toluenesulfonic acid was added to this solution and it was refluxed for 10 minutes. Finally, the reaction mixture was cooled to room temperature, diluted with saturated aqueous $KHCO_3$ solution (20 mL) and extracted with DCM (50 mL x 3), dried over $MgSO_4$, filtered off and evaporated under reduced pressure. The product (0.69 g, 2.57 mmol, 92%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.64 (s, 6H, SiCH_3), 7.67 (d, $^{3}J_{H-H}$ = 8.1 Hz, 4H, CH_{Ar}), 7.86 (d, $^{3}J_{H-H}$ = 8.1 Hz, 4H, CH_{Ar}), 10.0 (s, 2H, C*H*O). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.8, 128.8, 134.6, 137.0, 145.6, 192.4 (*C*HO).

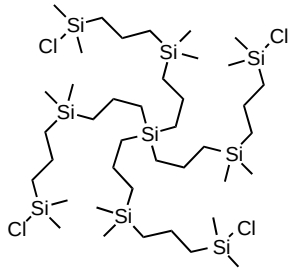
3.3. Preparation of the support for CS-*S,S*-5.

Tetrakis(3-(allyldimethylsilyl)propyl)silane (S6).



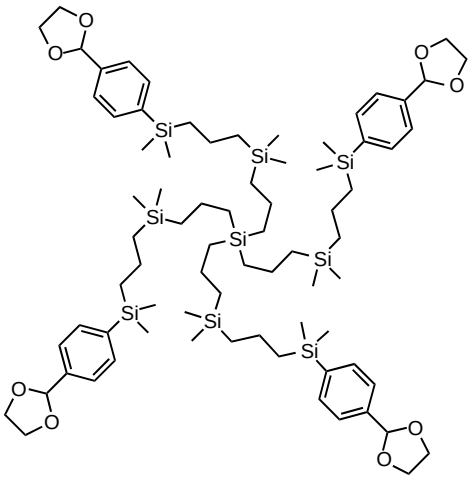
A 0.5 M diethyl ether solution of freshly prepared allylmagnesiumbromide (28.0 mL, 14 mmol) was added dropwise to a solution of tetrakis(3-(chlorodimethylsilyl)propyl)silane **(S1)** (1.60 g, 2.80 mmol) in diethylether (20 mL) at RT and the synthesis was left overnight. (If a sample of this reaction mixture gives a negative reaction with 1,10-phenantroline then some extra Grignard reagent should be added). A greyish suspension was formed. The reaction mixture was poured into a bicker with ice-cold water (150 mL) and 4 M amonium chloride solution (20 mL). The organic layer was separated and the aqueous layer was extracted with hexanes (50 mL x 3). Organic extracts were combined and dried over $MgSO_4$, filtered off. Solvents were evaporated under reduced pressure. The product (1.66 g, 2.80 mmol, quant.) was obtained as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.018 (s, 24H, SiCH_3), 0.53-0.61 (m, 16H, AllSiCH_2CH$_2$CH_2), 1.28-1.37 (m, 8H, CH$_2$CH_2CH$_2$), 1.50 (d, $^3J_{H-H}$ = 8.0 Hz, 8H, CH_2CH=CH$_2$), 4.80-4.86 (m, 8H, CH=CH_2), 5.37-5.83 (m, 4H, CH=CH$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.4, 17.7, 18.7, 20.1, 23.6, 112.7, 135.4.

2,19-Dichloro-10,10-bis(3-((3-(chlorodimethylsilyl)propyl)dimethylsilyl)propyl)-2,6,6,14,14,19-hexamethyl-2,6,10,14,19-pentasilaicosane (S7).



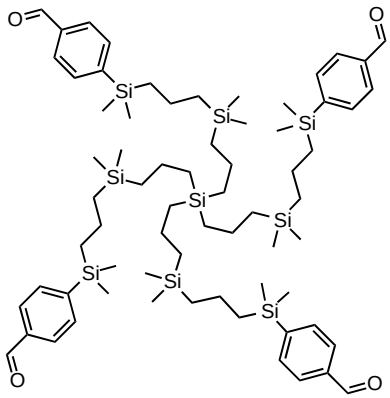
Neat **S6** (1.02 g, 1.72 mmol) and chlorodimethylsilane $HSiMe_2Cl$ (0.96 mL, 8.26 mmol) were added to a flame dried Schlenk flask. A catalyst tetrabutylamonium hexacloroplatinate (IV) (10 crystals) was dissolved in $CDCl_3$ (0.1 mL) and added to the Schlenk flask by a syringe. The reaction mixture was stirred overnight in a sealed flask at 35 ^{0}C. The product (1.65 g, 1.70 mmol, 99%) was obtained as a light yellow transparent oil after all volatiles were removed under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.03 (s, 24H, Si(CH_3)$_2$), 0.41 (s, 24H, Si(CH_3)$_2$Cl), 0.53-0.61 (m, 24H, CH_2SiCH_2), 0.83 (t, 8H, ClSiCH_2), 1.27-1.35 (m, 8H, ClSiCH$_2$CH_2), 1.40-1.48 (m, 8H, Si$_{core}$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.9, -2.1, 17.8, 17.9, 18.89, 19.7, 20.5, 23.6.

2,18-Bis(4-(1,3-dioxolan-2-yl)phenyl)-10,10-bis(3-((3-((4-(1,3-dioxolan-2-yl)phenyl)dimethylsilyl)propyl)dimethylsilyl)propyl)-2,6,6,14,14,18-hexamethyl-2,6,10,14,18-pentasilanonadecane (S8).



A 1.6 M solution of *n*-BuLi in hexane (4.40 mL, 7.04 mmol) was added *via* a cannula to a solution of 2-(4-Bromophenyl)-1,3-dioxolane (1.60 g, 7.00 mmol) in dry THF (15 mL) at -78 ^{0}C. After 1 h of stirring at that temperature a white precipitate was formed. Then a solution of **S7** (1.65 g, 1.72 mmol) in THF (2 mL) was added dropwise. In one hour the reaction mixture was allowed to warm to room temperature, yielding a yellowish solution. The reaction mixture was poured into saturated aqueous $KHCO_3$ solution. The organic layer was separated. The aqueous layer was extracted with DCM (50 mL x 3). Combined organic fractions were dried over $MgSO_4$ and filtered off. Solvents were evaporated under reduced pressure. The product (1.57 g, 1.10 mmol, 64 %) was obtained as colourless oil after purification by a passive dialysis. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.07 (s, 24H, Si(CH_3)$_2$), 0.24 (s, 24H, Si(CH_3)$_2$Ar), 0.52-0.57 (m, 24H, CH_2SiCH_2), 0.81 (t, 8H, $^3J_{H-H}$ = 8.4 Hz, ArSiCH_2), 1.26-1.40 (m, 16H, CH$_2$CH_2CH$_2$), 4.01-4.14 (m, 16H, OCH_2), 5.82 (s, 4H, OCHAr), 7.45 (d, $^3J_{H-H}$ = 7.8 Hz, 8H, CH_{Ar}), 7.53 (d, $^3J_{H-H}$ = 7.8 Hz, 8H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.2, -2.9, 17.6, 18.4, 18.6, 20.1, 20.3, 20.4, 65.3, 103.7, 125.6, 133.6, 138.3 (C$_q$), 141.1 (C$_q$). Elemental analysis calcd. (%) for $C_{76}H_{132}O_8Si_9$2H$_2$O C 62.41, H 9.37 found 62.17, H 9.61.

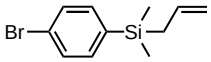
4,4'-(10,10-bis(3-((3-((4-Formylphenyl) dimethylsilyl)propyl)dimethylsilyl)propyl)-2,6,6,14,14,18-hexamethyl-2,6,10,14,18-pentasilanonadecane-2,18-diyl)dibenzaldehyde (S9).



Water (ca. 10 mL) was added to a solution of **S8** (1.57 g, 1.10 mmol) in acetone (30 mL) until a slight turbidity appeared. A catalytic amount of p-toluenesulfonic acid was added to this solution and it was refluxed for 10 minutes. Finally, the reaction mixture was cooled to room temperature and washed successively with saturated aqueous $KHCO_3$ solution, extracted with DCM (50 mL x 3), dried over $MgSO_4$, filtered off and all solvents were evaporated under reduced pressure. The product (1.26 g, 1.01 mmol, 92%) was obtained as a transparent slightly turbid oil. This aldehyde readily oxidizes on air and was immediately used in the next reaction step. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.92 (s, 24H, $CH_2Si(CH_3)_2CH_2$), 0.28 (s, 24H, $ArSiCH_3$), 0.49-0.56 (m, 24H, CH_2SiCH_2), 0.83 (t, $^3J_{H-H}$ = 8.2 Hz, 8H, $ArSiCH_2$), 1.24-1.39 (m, 16H, $CH_2CH_2CH_2$), 7.66 (d, $^3J_{H-H}$ = 9.3 Hz, 8H, $CH_{Ar,}$), 7.82 (d, $^3J_{H-H}$ = 9.3 Hz, 8H, CH_{Ar}), 10.00 (s, 4H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.8, 1.2, 17.8, 18.6, 18.8, 20.3, 20.6, 29.9, 128.8, 134.2, 136.7, 148.7, 192.8 (CHO). Elemental analysis calcd. (%) for $C_{68}H_{116}O_4Si_9$·3.3H_2O C 62.35, H 9.63 found 62.33, H 9.39. IR (ṽ, cm $^{-1}$): 2952, 2911, 2874, 1704 (CHO), 1596, 1558, 1408, 1380, 1310, 1247, 1212, 1173, 1140, 1101, 904, 802, 771, 688.

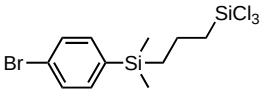
3.4. Preparation of the support for CS-*S,S*-6.

Allyl(4-bromophenyl)dimethylsilane (S10).



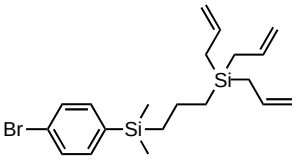
A solution of 1,4-dibromobenzene (2.98 g, 12.6 mmol) in Et_2O (25 mL) was cooled to -78 ^{0}C and a 1.6 M solution of n-BuLi (8.05 mL, 12.88 mmol) was added to it over 1-2 min period. The reaction mixture was stirred at -78 ^{0}C for additional 10 min and the cooling bath was removed for the period of 5 min and placed back again. Then allyldimethylchlorosilane (1.77 g, 12.74 mmol) solution in Et_2O (5 mL) was delivered into the reaction mixture dropwise on cooling. The reaction mixture was stirred for additional 1 h. The supernatant was removed via a cannula from LiBr and dried under vacuum to remove unreacted chlorosilane. The remaining oil was partitioned between hexanes (50 mL) and water (50 mL). The top layer was separated, dried over $MgSO_4$, filtered off and concentrated under reduced pressure to give the title compound (3.08 g, 95.6%) sufficiently pure according NMR and GC data. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.27 (s, 6H, $Si(CH_3)_2$), 1.73 (d, $^3J_{H-H}$ = 9.1 Hz, 2H, $SiCH_2$), 4.81-4.88 (m, 2H, $CHCH_2$), 5.67-5.79 (m, 1H, CH), 7.36 (d, $^3J_{H-H}$ = 8.06 Hz, 2H, CH_{Ar}), 7.49 (d, $^3J_{H-H}$ = 8.06 Hz, 2H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.6, 23.5, 113.7, 123.8, 130.9, 134.1, 135.2, 137.4.

(4-Bromophenyl)dimethyl(3-(trichlorosilyl)propyl)silane (S11).



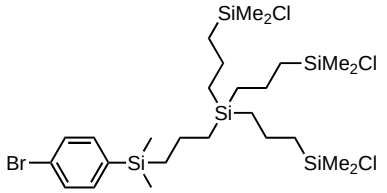
To a neat mixture of **S10** (729 mg, 2.86 mmol) and $HSiCl_3$ (1.95 g, 14.3 mmol) was added a tiny drop of the Karsted catalyst solution. The reaction mixture was stirred overnight at RT. The title product (1.11 g, quant.) was obtained as a colourless oil after all volatiles were removed under vacuum. (Dry THF (ca. 1 mL) can be added to the reaction mixture prior drying to facilitate the chlorosilane removal). This product is extremely moisture sensitive and was immediately used in the next reaction step. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.29 (s, 6H, $SiCH_3$), 0.89 (t, $^3J_{H-H}$ = 8.4 Hz, 2H, $SiCH_2$), 1.45 (t, $^3J_{H-H}$ = 8.2 Hz, 2H, $ArSiCH_2$), 1.57-1.67 (m, 2H, CH_2), 7.35 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, CH_{Ar}), 7.50 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, CH_{Ar}).

Triallyl(3-((4-bromophenyl)dimethylsilyl)propyl)silane (S12).



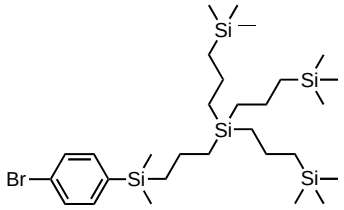
A 0.5 M diethyl ether solution of freshly prepared allylmagnesiumbromide (22.9 mL, 11.44 mmol) was added dropwise to a solution of **S11** (1.11 g, 2.86 mmol) in diethylether (30 mL) at RT and the synthesis was left overnight. (If a sample of this reaction mixture gives a negative reaction with 1,10-phenantroline then some extra Grignard reagent should be added). A off-white suspension was formed. The reaction mixture was poured into a bicker with ice-cold water (150 mL) and 4 M amonium chloride solution (20 mL). The organic layer was separated and the aqueous layer was extracted with hexanes (50 mL x 3). Organic extracts were combined and dried over $MgSO_4$, filtered off. Solvents were evaporated under reduced pressure. The product was purified by column chromatography in hexanes Rf 0.45 to give the title compound (870 mg, 74.7%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.24 (s, 6H, $SiCH_3$), 0.64 (t, 2H, $^3J_{H-H}$ = 8.4 Hz, $AllSiCH_2$), 0.79 (t, $^3J_{H-H}$ = 8.2 Hz, CH_2SiAr), 1.33-143 (m, 2H, $SiCH_2CH_2$), 1.53-1.57 (m, 6H, $SiCH_2CH$), 4.82-4.88 (m, 6H, $CH=CH_2$), 5.68-5.81 (m, 3H, $CH=CH_2$), 7.35 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, CH_{Ar}), 7.48 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.0, 16.2, 18.0, 19.7, 20.3, 113.5, 123.5, 130.8, 134.4, 135.1, 138,3. IR (ṽ, cm^{-1}): 2952, 2912, 2874, 1574, 1480, 1412, 1376, 1334, 1246, 1142, 1068. 1011, 910, 860, 832, 803, 692.

(((3-((4-Bromophenyl)dimethylsilyl)propyl)silanetriyl)tris(propane-3,1-diyl))tris(chlorodimethylsilane) (S13).



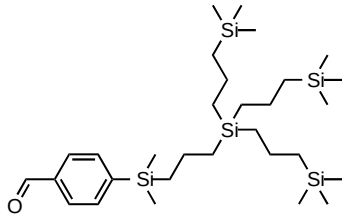
Neat **S12** (500 mg, 1.23 mmol) and $HSiMe_2Cl$ (0.96 mL, 8.26 mmol) were added to a flame dried Schlenk flask. A catalyst tetrabutylamonium hexacloroplatinate (IV) (10 crystals) was dissolved in $CDCl_3$ (0.1 mL) and added to the flask by a syringe. The reaction mixture was stirred overnight in a sealed flask at 35 ^{0}C. The product (849 mg, 1.23 mmol, quant.) was obtained as a transparent oil after all volatiles were removed under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.24 (s, 6H, ArSiC*H*$_3$), 0.39 (s, 18H, Si(C*H*$_3$)$_2$Cl), 0.53-0.60 (m, 8H, C*H*$_2$SiC*H*$_2$), 0.80 (t, $^3J_{H-H}$ = 8.2 Hz, 2H, ArSiC*H*$_2$), 0.86 (t, $^3J_{H-H}$ = 16.1 Hz, 6H, ClSiC*H*$_2$), 1.27-1.35 (m, 2H, ArSiCH$_2$C*H*$_2$), 1.35-1.45 (m, 6H, ClSiCH$_2$C*H*$_2$), 7.35 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C*H*$_{Ar}$), 7.47 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C*H*$_{Ar}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.0, 1.8, 16.6, 17.1, 17.8, 18.5, 20.4, 23.6, 123.5, 130.8, 135.1, 138,4.

(((3-((4-Bromophenyl)dimethylsilyl)propyl)silanetriyl)tris(propane-3,1-diyl))tris(trimethylsilane) (S14).



A freshly prepared 0.9 M solution of MeMgI (7.2 mL, 6.48 mmol) in Et_2O was added to a solution of **S13** (811 mg, 1.29 mmol) in Et_2O (20 mL) at 0 ^{0}C. The reaction was allowed to stir at this temperature for 1 h. Then MeOH (1 mL) was added and the reaction was poured into a bicker with ice-cold water (100 mL) and 4 M ammonium chloride solution (10 mL). The organic layer was separated and the aqueous layer was extracted with hexanes (50 mL x 3). Organic extracts were combined and dried over $MgSO_4$, filtered off. Solvents were evaporated under reduced pressure. (No dehalogenated product was observed under these conditions). The reaction product was purified by column chromatography in hexanes Rf 0.70 to give the title compound (658 mg, 1.04 mmol, 81%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.037 (s, 27H, TMS), 0.23 (s, 6H, ArSiC*H*$_3$), 0.48-0.57 (m, 14H, C*H*$_2$SiC*H*$_2$ & TMSC*H*$_2$), 0.79 (t, $^3J_{H-H}$ = 8.2 Hz, 2H, ArSiC*H*$_2$), 1.23-1.35 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 7.35 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C*H*$_{Ar}$), 7.47 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C*H*$_{Ar}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.0, -1.5, 17.38, 17.47, 18.52, 18.55, 20.5, 21.6, 123.5 (C_q), 130.8, 135.1, 138.6 (C_q).

4-(Dimethyl(3-(tris(3-(trimethylsilyl)propyl)silyl)propyl)silyl)benzaldehyde (S15).



To a solution of **S14** (658 mg, 1.04 mmol) in Et_2O (10 mL) at -100 ^{0}C a 1.6 M hexane solution of *t*BuLi (0.70 mL, 1.12 mmol) was added dropwise over ca. 1 min. The reaction mixture was stirred at -100 to -78 ^{0}C during 1 h. Then a DMF (0.10 mL, 1.30 mmol) solution in Et_2O (0.1 mL) was added all at once to the reaction mixture and the stirring was continued for additional 30 min. Subsequently, water (50 mL) was added, while the reaction solution is cold. The organic layer was separated and the aqueous layer was extracted with hexanes (20 mL x 3). Organic extracts were combined and dried over $MgSO_4$, filtered off. Solvents were evaporated under reduced pressure to give the title compound as a cloudy oil (554 mg, 91.6%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.012 (s, 27H, TMS), 0.32 (s, 6H, ArSiC*H*$_3$), 0.48-0.63 (m, 14H, C*H*$_2$SiC*H*$_2$ & TMSC*H*$_2$), 0.88 (t, $^3J_{H-H}$ = 8.2 Hz, 2H, ArSiC*H*$_2$), 1.25-1.41 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 7.70 (d, $^3J_{H-H}$ = 8.1 Hz, 2H, C*H*$_{Ar}$), 7.86 (d, $^3J_{H-H}$ = 8.1 Hz, 2H, C*H*$_{Ar}$), 10.05 (s, 1H, C*H*O). IR (ν̃, cm^{-1}): 2953, 2912, 2874, 1707 (CHO), 1596, 1559, 1412, 1335 1246, 1212, 1141, 910, 860, 832, 779. 691.

4. Catalysis.

4.1. General procedure for the Fe-catalyzed asymmetric epoxidation of alkenes 2a–d.

To a transparent solution of the ligand (0.06 mmol for *S*,*S*-**1**, *S*,*S*-**4a-c** and CS-*S*,*S*-**6**; 0.03 mmol for *S*,*S*-**4**; 0.015 mmol for CS-*S*,*S*-**1** and CS-*S*,*S*-**5**) in *tert*-amyl alcohol (4.0 mL) were sequentially added a 0.010 M solution of ferric chloride hexahydrate (2.5 mL, 0.025 mmol) in *tert*-amyl alcohol and a 0.010 M solution of pyridine-2,6-dicarboxylic acid (2.5 mL, 0.025 mmol) in *tert*-amyl alcohol and substrate (0.5 mmol). This reaction mixture was stirred at RT for about 30 min. The resulting mixture usually assumed a pale yellow colour. For the GC determination of conversions, $PhNO_2$ or PhBr was added as an internal standard. Aqueous 35% hydrogen peroxide (ca. 0.1 mL, 1 mmol) in *tert*-amyl alcohol (1 mL) was added to this mixture over 1 h using a syringe pump. [A generally accurate volume of the 35% solution can not be given in this case because the peroxide content and thus the density of this material varies considerably with time. Therefore, before each experiment the peroxide content (%) was determined by iodometric titration]. Samples for GC analysis were taken at regular intervals. For preparative purposes, excess of peroxide was eliminated by adding a saturated aqueous sodium sulfite solution (ca. 1 mL). After addition of diethyl ether (10 mL), the phases were separated, and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phases were then dried over anhydrous $MgSO_4$. After filtration and solvent removal, the crude product was purified by column chromatography on a short column (eluent: hexane/ethyl acetate 20:1, v/v, 1% Et_3N) for full characterization.

4.2. Protocol for the CS-*S,S*-5 catalyst recycling *via* precipitation.

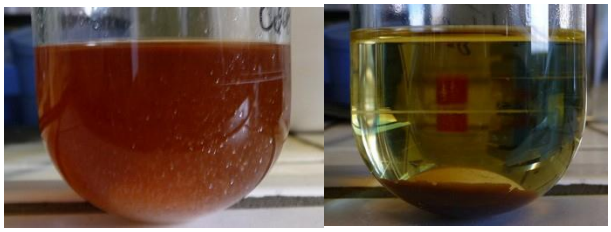


Figure 1. Oxidation of **2c** with CS-*S,S*-**5** after three runs in *tert*-amyl alcohol (left) and the same in hexanes after centrifugation (right).

Run 1: To a transparent solution of CS-S,S-**5** (79.6 mg, 0.030 mmol) in *tert*-amyl alcohol (8.0 mL) were sequentially added a 0.010 M solution of pyridine-2,6-dicarboxylic acid (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and a 0.010 M solution of ferric chloride hexahydrate (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and **2c** (293 mg, 1.0 mmol). This reaction mixture was stirred at RT for about 30 min. The resulting mixture assumed a pale yellow colour. Aqueous hydrogen peroxide ("35%", 2.0 mmol, ca. 0.2 mL) in *tert*-amyl alcohol (2 mL) was added to this mixture over 1 h using a syringe pump. Then most of the volatiles were removed under reduced pressure at RT to give a brownish slurry, which was taken up in hexanes (ca. 20 mL) and centrifuged (5 min, 2400 rpm). The yellowish transparent supernatant was decanted from the brownish precipitate. The solid residue was washed one more time with hexanes (20 mL) and centrifuged. The hexane extracts were combined and concentrated under reduced pressure. The crude product was divided onto two equal parts. The first one was purified by chromatography on a short column (eluent: hexane/ethyl acetate 20:1, v/v, 1% Et_3N) to isolated the product. The second part was mixed with PhBr and passed through a pipet silica gel column eluting with EtOAc for GC analysis of the substrate conversion. Complete substrate conversion was found. The epoxide was isolated in 92% yield (142 mg) and *ee* of 62%.
Run 2: was carried out using the catalyst residue precipitated in the previous run, *tert*-amyl alcohol (18 mL) and **2c** (293 mg, 1.0 mmol), which were mixed and stirred for 30 min prior to oxidant addition. Hydrogen peroxide solution (2.0 mmol) in *tert*-amyl alcohol (2.0 mL) was subsequently added over 1 h. The catalyst precipitation and the product isolation were performed as it was done above. Complete substrate conversion was found. The epoxide was isolated in 95% yield (146 mg) and *ee* of 42%.
Run 3: was carried out using the catalyst residue precipitated in the previous run and the same reagent quantities. Substrate conversion was 41%. The epoxide was isolated in 34% yield (52.3 mg) and *ee* of 25%.

4.3. Protocol for the CS-*S,S*-5 catalyst recycling *via* precipitation adding extra ferric chloride and H_2PDC.

Run 1: was performed according to the protocol for the catalyst recycling *via* precipitation and on the same scale. Complete substrate conversion was found. The epoxide was isolated in 91% yield (140 mg) and *ee* of 63%.
Run 2: to the catalyst residue precipitated in the previous run were sequentially added *tert*-amyl alcohol (16 mL), a 0.010 M solution of ferric chloride hexahydrate (1.0 mL, 0.010 mmol) in *tert*-amyl alcohol and a 0.010 M solution of pyridine-2,6-dicarboxylic acid (1.0 mL, 0.010 mmol) in *tert*-amyl alcohol and **2c** (293 mg, 1.0 mmol). Hydrogen peroxide (2.0 mmol) solution in *tert*-amyl alcohol (2.0 mL) was subsequently added over 1 h. The catalyst precipitation and the product isolation were performed as it was done above. Complete substrate conversion was found. The epoxide was isolated in 96% yield (148 mg) and *ee* of 51%.
Run 3: was carried out using the catalyst residue precipitated in the previous run and the same reagent and additive quantities. Substrate conversion was 78%. The epoxide was isolated in 69% yield (106 mg) and *ee* of 30%.

4.4. Protocol for the CS-*S,S*-6 catalyst recycling *via* phase separation.

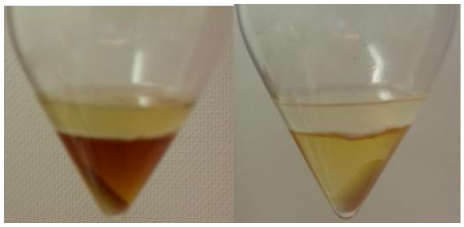


Figure 2. Reaction components partitioning between MeCN and hexanes (left picture) and the recovered ligand CS-*S,S*-**6** solution in hexanes and aqueous ethylenediamine (right picture).

Run 1: To a transparent solution of CS-S,S-**6** (111 mg, 0.12 mmol) in *tert*-amyl alcohol (8.0 mL) were sequentially added a 0.010 M solution of pyridine-2,6-dicarboxylic acid (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and a 0.010 M solution of ferric chloride hexahydrate (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and **20** (180 mg, 1.0 mmol). This reaction mixture was stirred at RT for about 30 min. The resulting mixture assumed a transparent pale yellow colour. Aqueous hydrogen peroxide ("35%", 0.60 mmol, ca. 0.12 mL) in *tert*-amyl alcohol (2 mL) was added to this mixture over 30 min using a syringe pump. Then most of the volatiles were removed under

reduced pressure at 30 °C to give a brownish slurry, which was partitioned between hexanes (ca. 8 mL) and acetonitrile (ca. 8 mL) and centrifuged (5 min, 2400 rpm). The yellowish transparent supernatant (hexanes) and a white colloid in between the organic phases were washed with acetonitrile (2 x 8 mL), centrifuging each time. The MeCN phases were combined and concentrated under reduced pressure. The crude product was divided onto two equal parts. The first one was purified by chromatography on a short column (eluent: hexane/ethyl acetate 20:1, v/v, 1% Et_3N) to isolated the **3a** product. The second part was mixed with $PhNO_2$ (0.2 mmol) and passed through a pipet silica gel column eluting with EtOAc for GC analysis of the substrate conversion. A 57% substrate conversion was found. The epoxide was isolated in 48% yield (47.1 mg) and *ee* of 40%. Water (8 mL) and ethylenediamine (0.2 mL) were added to the hexane phase and shaken thoroughly. The top layer was separated and the aqueous layer was extracted with hexanes (2x8 mL). The organic fractions were combined, dried over Na_2SO_4, filtered off and concentrated under reduced pressure to give the ligand (101 mg, >90% purity, 75% yield). This crude ligand contained below 10% (w) of **2a** and **3a** and was not further purified.

Run 2: was carried out using the ligand isolated in the previous run. The amounts of **2a**, ferric chloride, H2PDC, hydrogen peroxide and *tert*-amyl alcohol were reduced by a factor 0.78 compared to the run 1. The reaction work up was performed as it is described above. A 60% substrate conversion was found. The epoxide was isolated in 53% yield (40.5 mg) and *ee* of 37%. The ligand was recovered in ca. 80% yield (81.0 mg, 90% purity).

Run 3: was carried out using the ligand isolated in the previous run. The amounts of **2a**, ferric chloride, H_2PDC, hydrogen peroxide and *tert*-amyl alcohol were reduced by a factor 0.62 compared to the run 1. The reaction work up was performed as it is described above. A 55% substrate conversion was determined. The epoxide was isolated in 45% yield (27.3 mg) and *ee* of 38%. The ligand was recovered in ca. 83% yield (67.4 mg, 90% purity).

4.5. Protocol for the CS-*S,S*-5 catalyst separation *via* ultrafiltration.

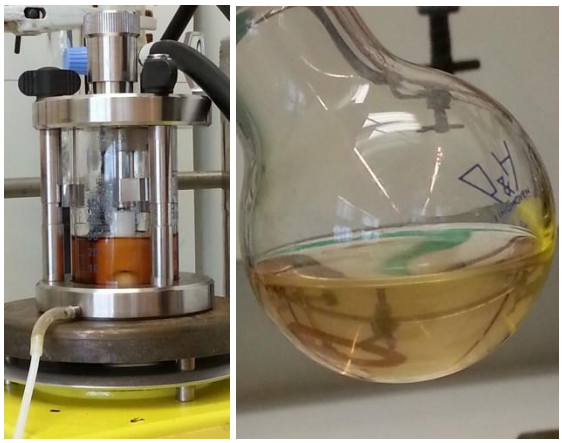


Figure 3. Oxidation of **2c** with CS-*S,S*-**5**. Catalytic retentate (left) and permeate, containing *R,R*-**3c** in DCM (right) after ultrafiltration.

To a transparent solution of CS-S,S-**5** (80.0 mg, 0.03 mmol) in *tert*-amyl alcohol (8.0 mL) were sequentially added a 0.010 M solution of pyridine-2,6-dicarboxylic acid (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and a 0.010 M solution of ferric chloride hexahydrate (5.0 mL, 0.050 mmol) in *tert*-amyl alcohol and **2c** (293 mg, 1.0 mmol). This reaction mixture was stirred at RT for about 30 min. Aqueous hydrogen peroxide ("35%", 1.5 mmol) in *tert*-amyl alcohol (1.5 mL) was added to this mixture over 45 min using a syringe pump and the reaction mixture was stirred over extra 45 min. Then most of the volatiles were removed under reduced pressure at RT to give a brownish slurry, which was dissolved in DCM (30 mL) and transferred to an ultrafiltration membrane setup (with 1 kDa MWCO membrane). The vessel was closed and pressurized with air (3-4 bars). The filtration was paused when only ca. 5 mL of retentate left. At this point the permeate contained 143 mg (out of 308 mg in theory) of pure product. Subsequently, the retentate was diluted with DCM (30 mL) and repetitively filtered. The obtained permeate contained 113 mg of the epoxide **3c**. The last retentate dilution with DCM followed by ultrafiltration provided extra 40 mg of the product. In total in this experiment 296 mg (yield 96%, *ee* 64%) of the epoxide was obtained. Evaporation of the retentate afforded 132 mg of dark-brown solids, containing the initial ligand according to ESI-MS as well previously not observed species.

5. References

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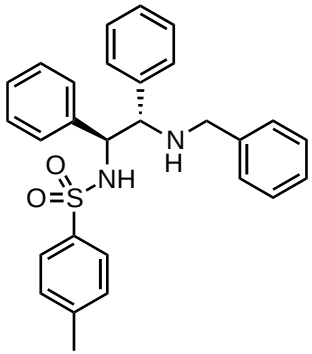
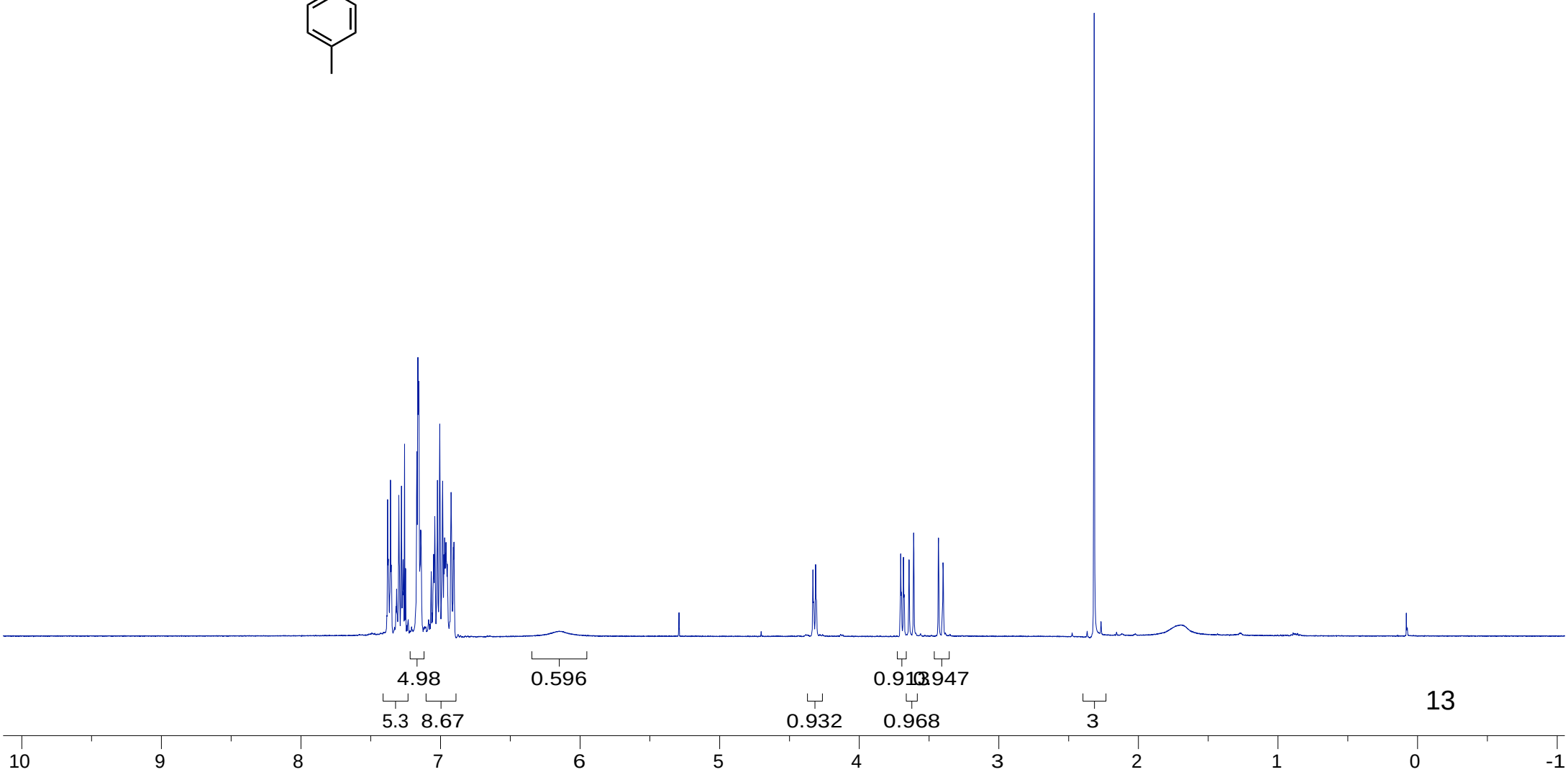
^{1}H-NMR SPECTRUM OF *S,S*-1





^{13}C-NMR SPECTRUM OF *S,S*-1

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127.911
127.574
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127.270
127.129
127.067

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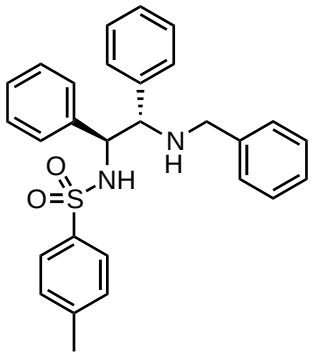

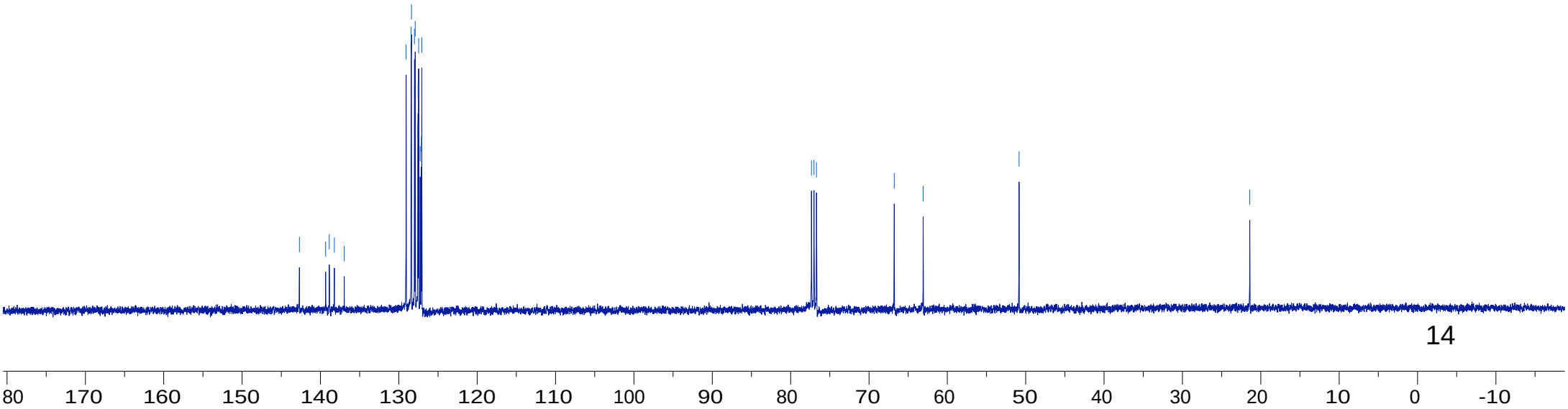

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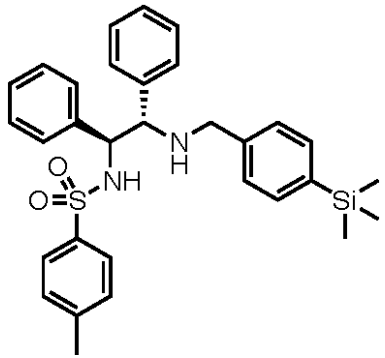

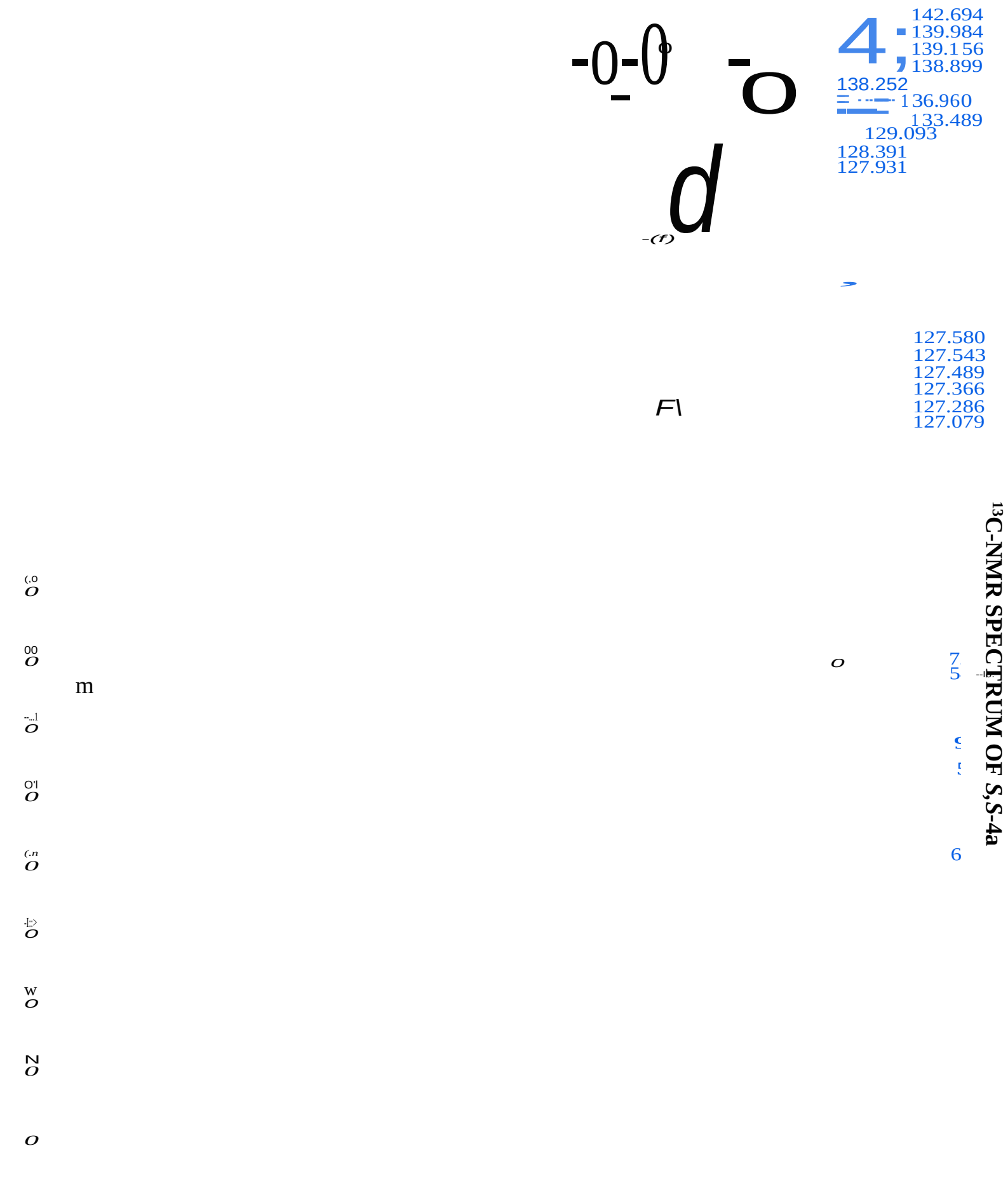

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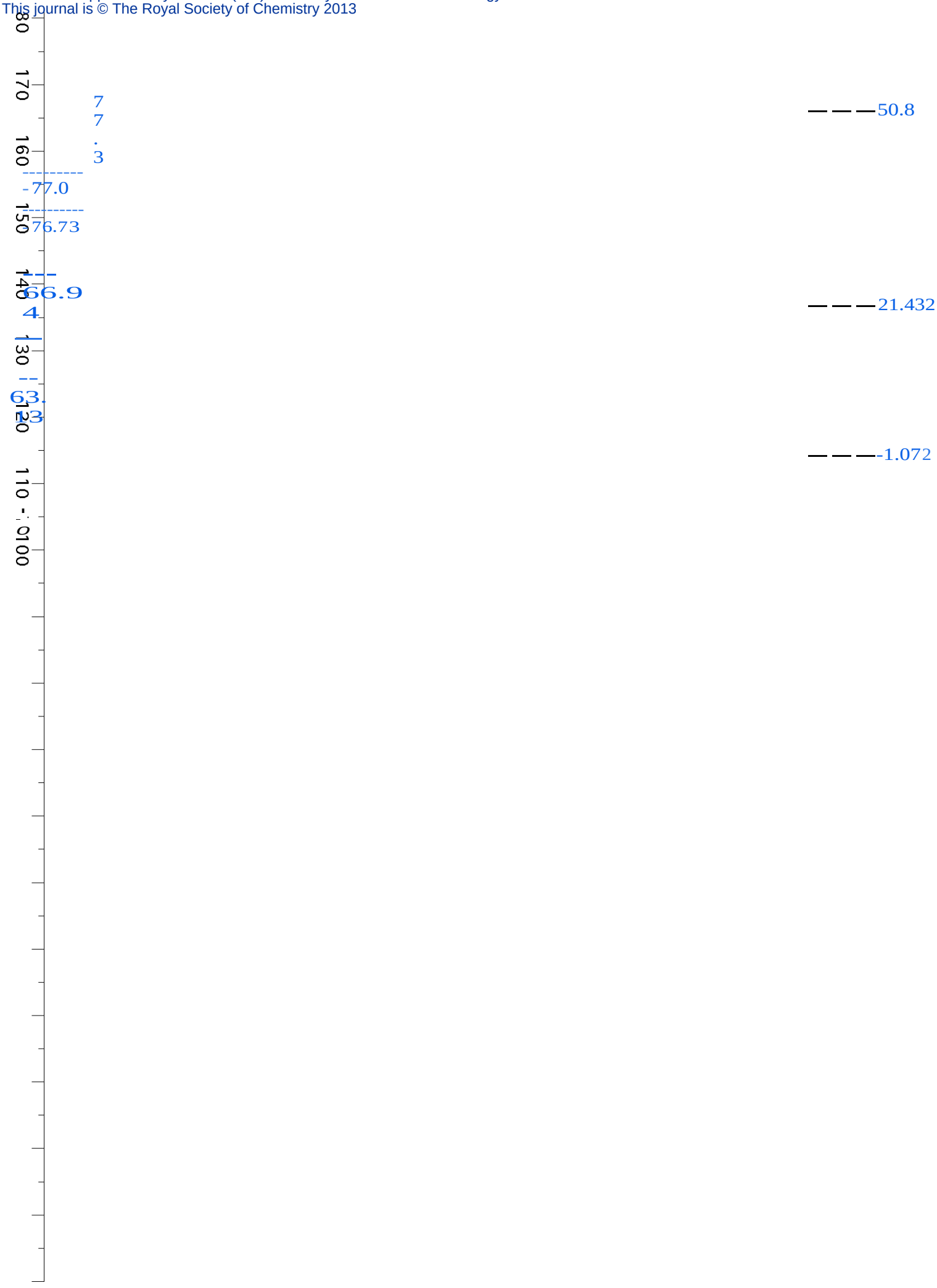

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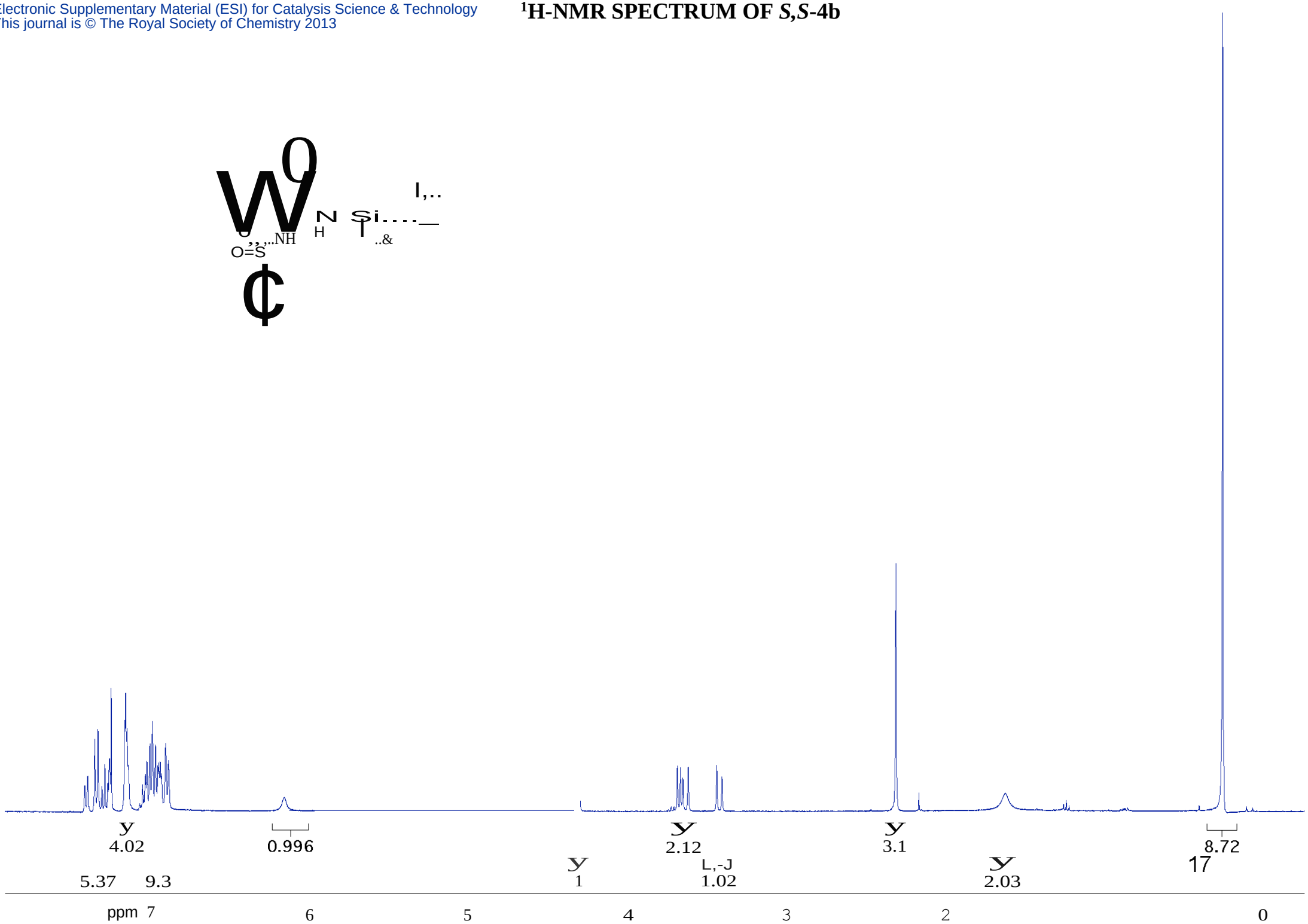

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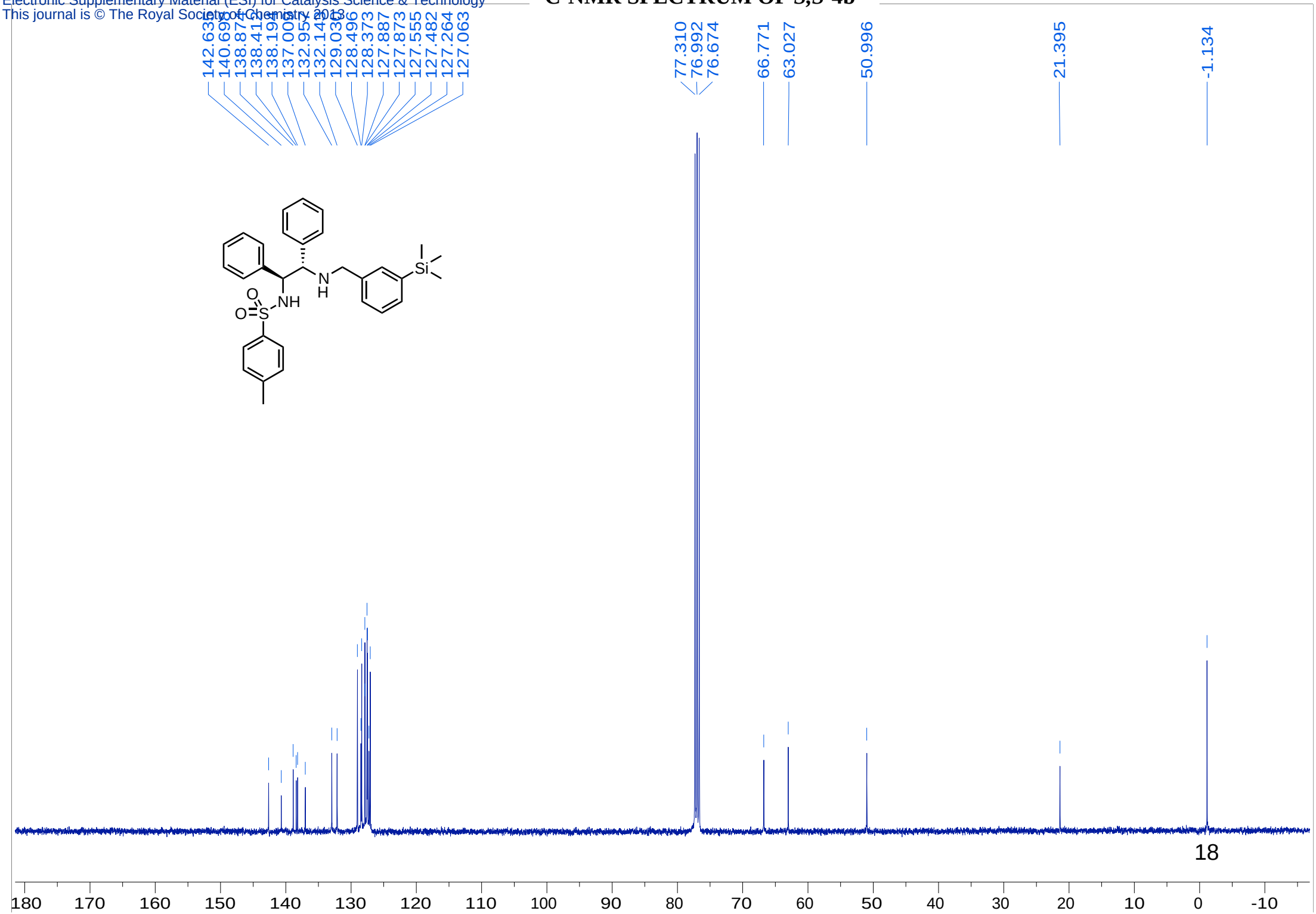

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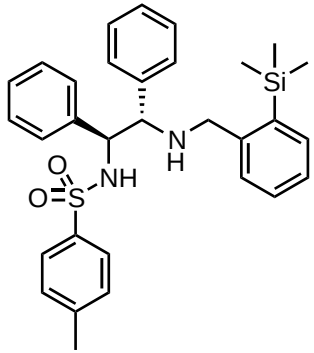

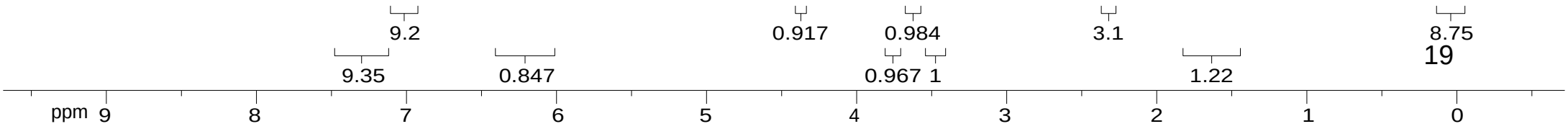

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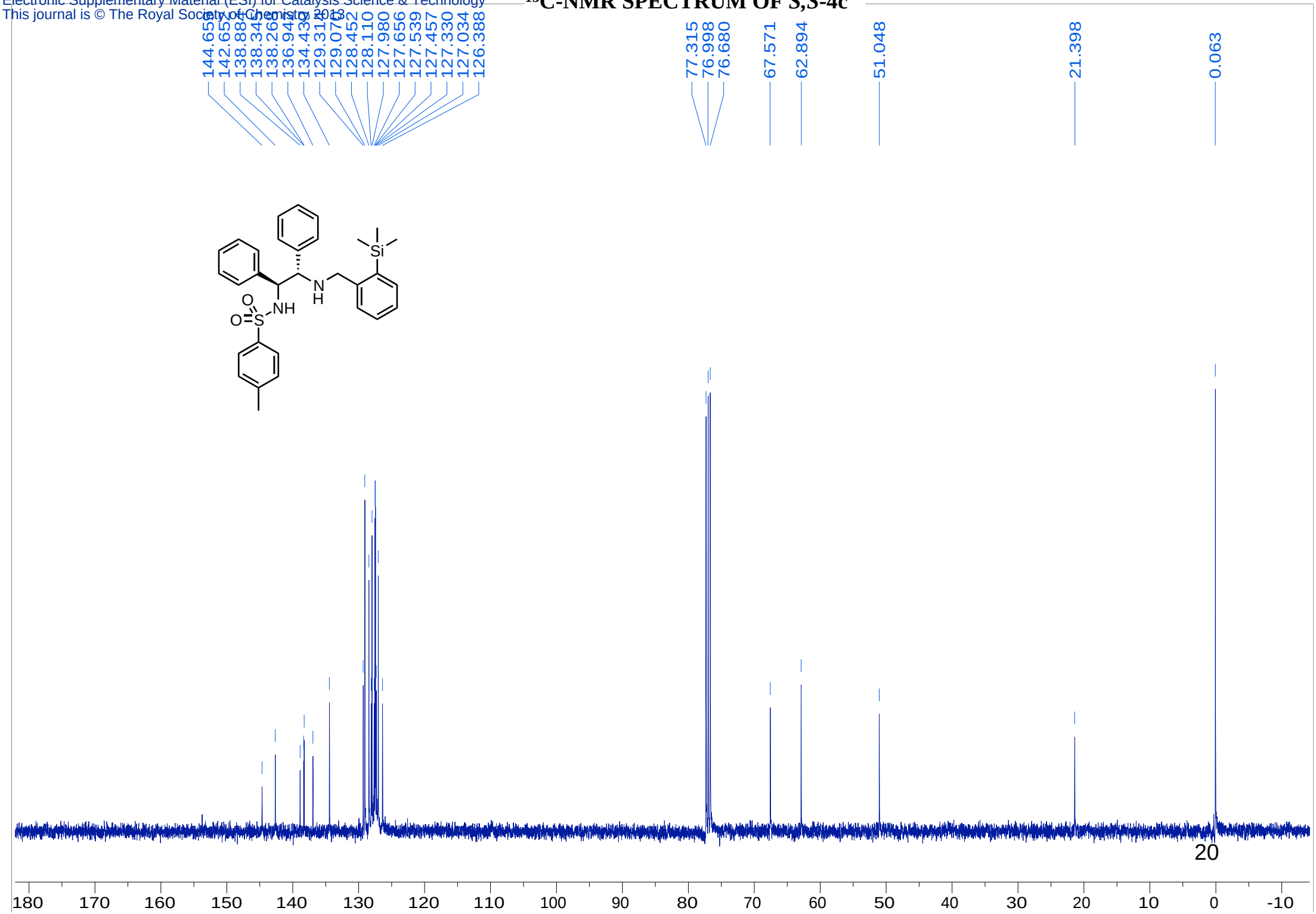

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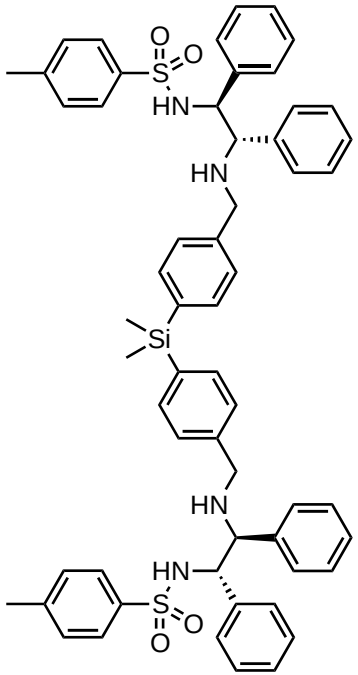

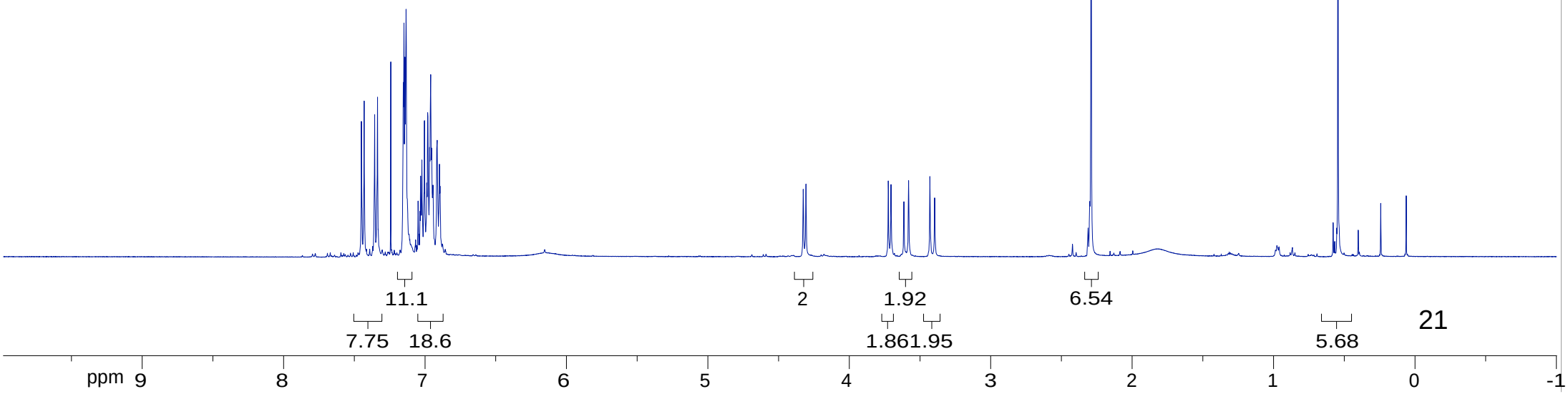

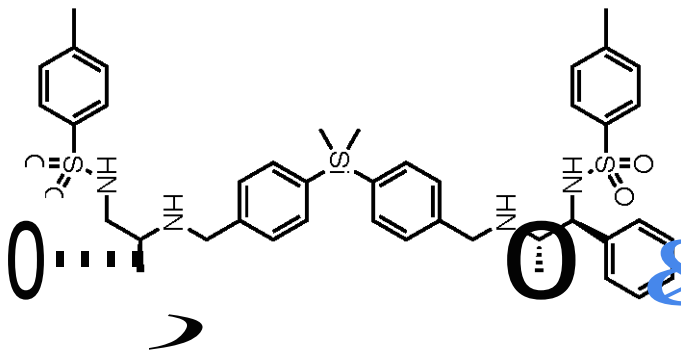

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127.517
127.442
127.274
127.043

77.3
76.9
76.6

66.9
63.0

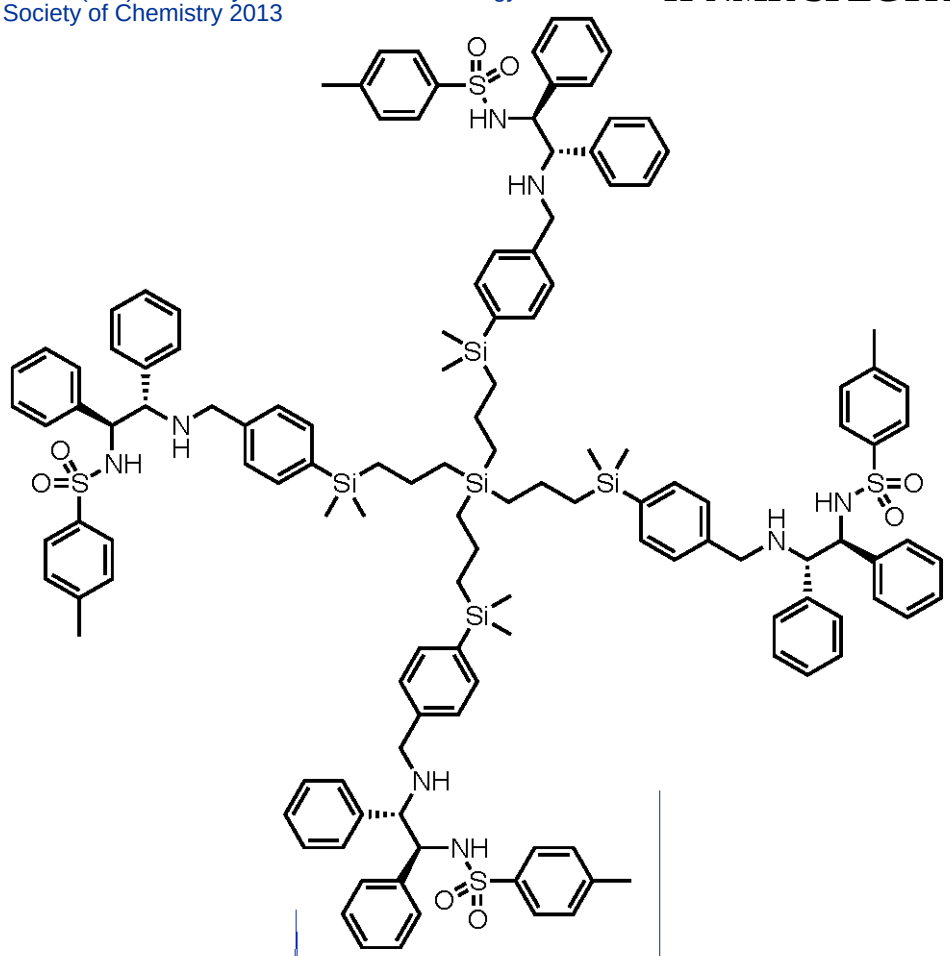
50.846

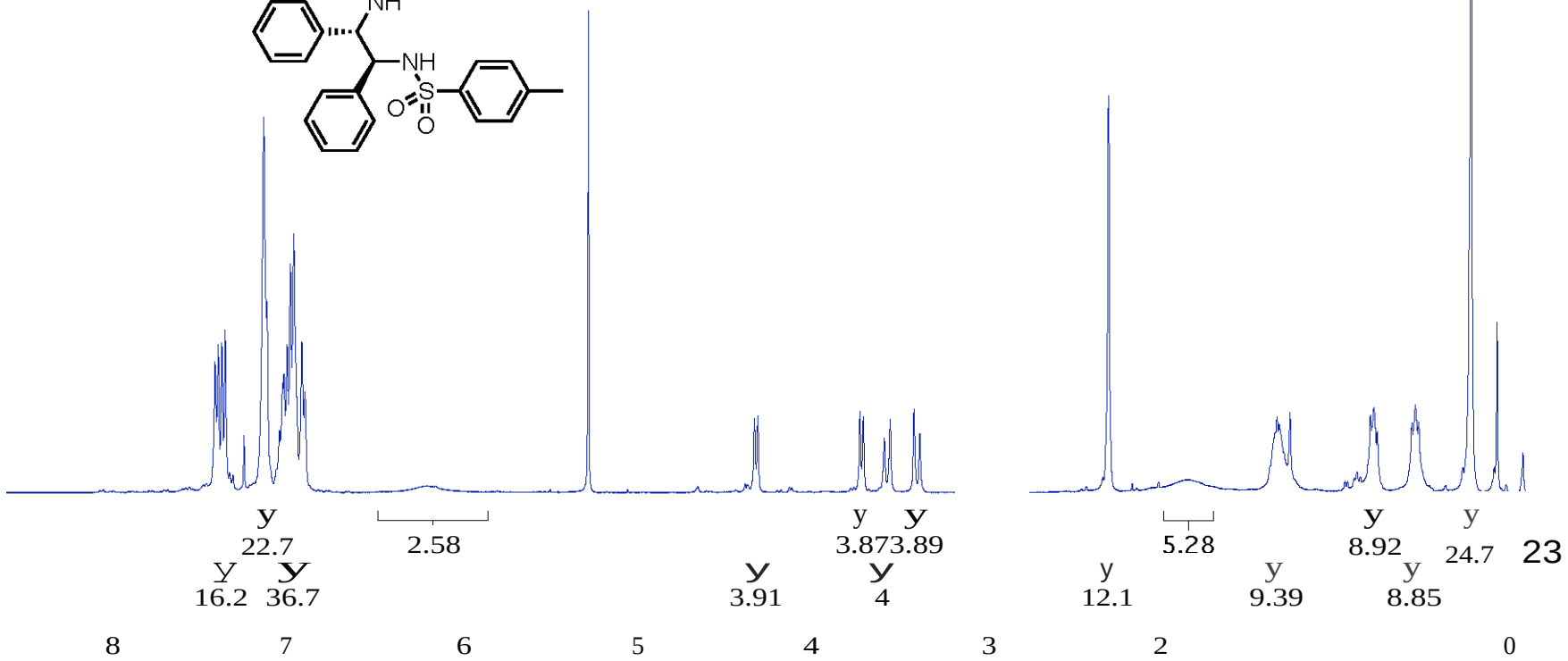
21.389

-2.347

^{13}C-NMR SPECTRUM OF S,S-4d

^{1}H-NMR SPECTRUM OF CS-*S*,*S*-1





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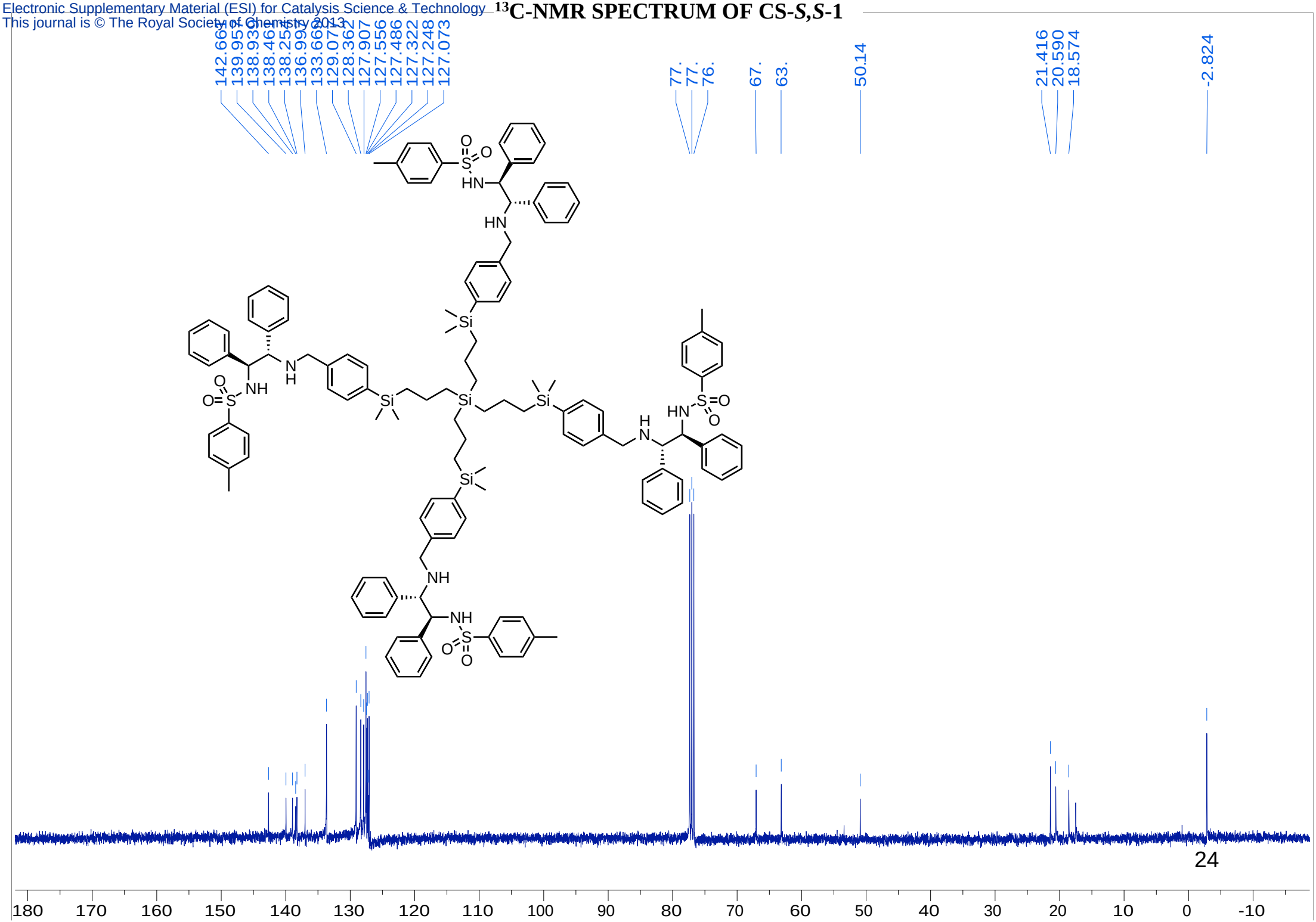

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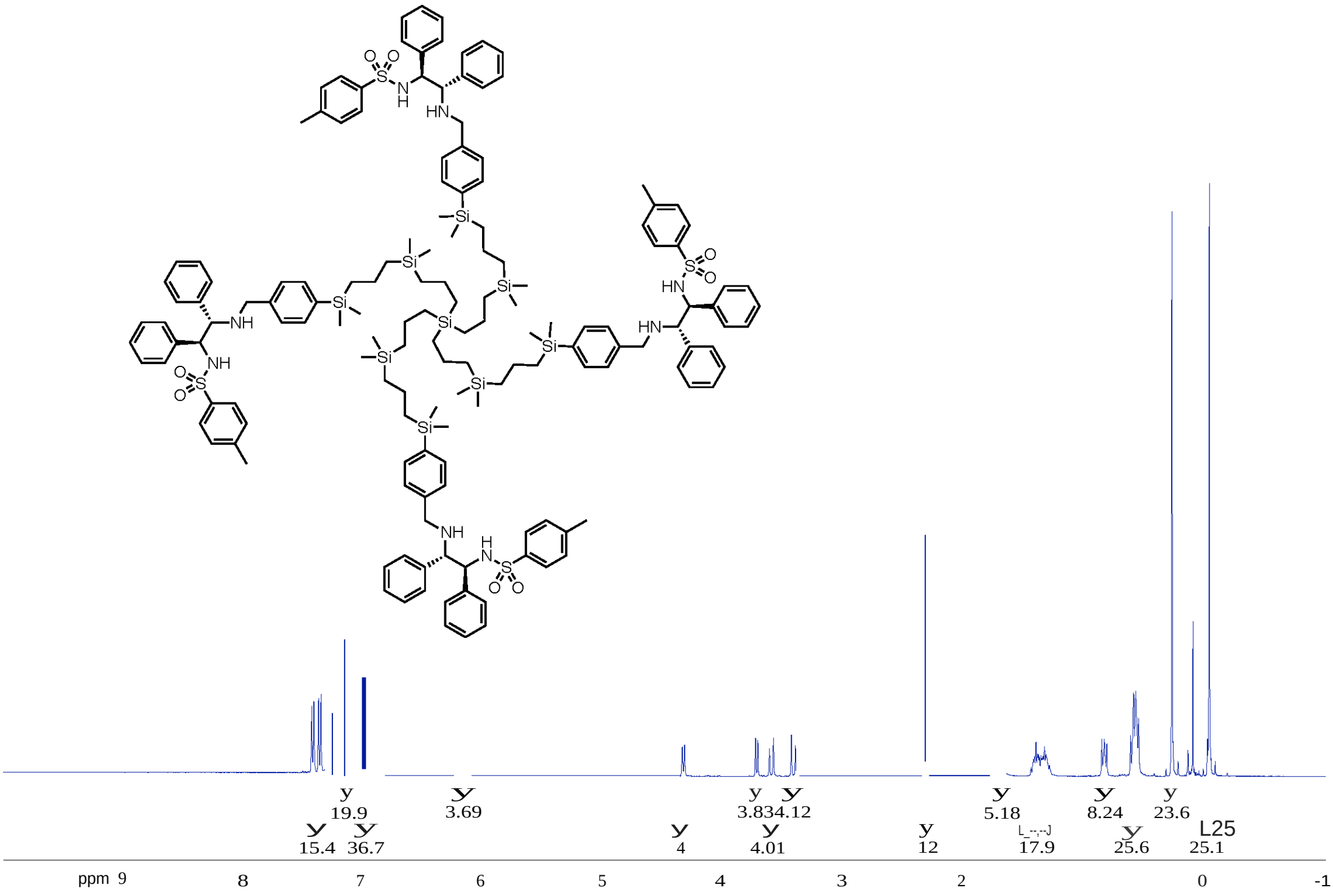
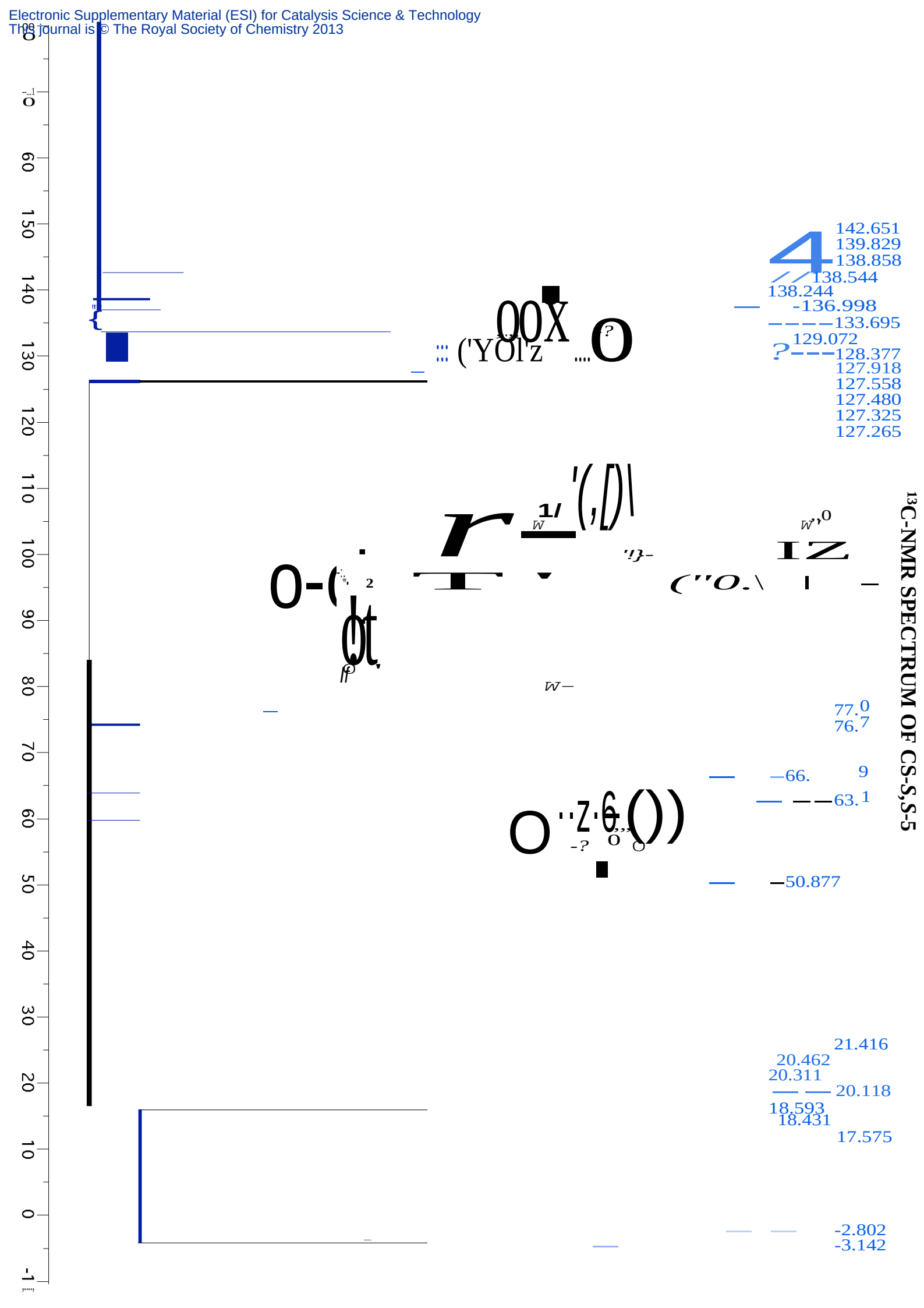
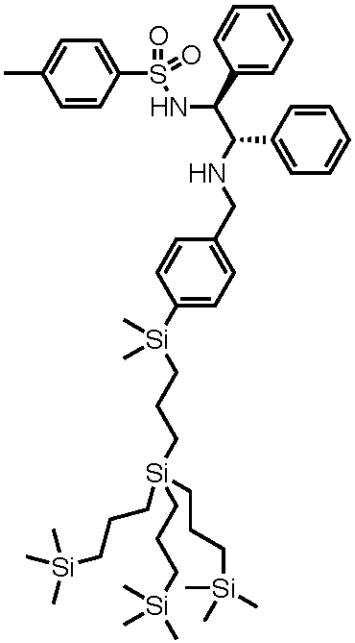
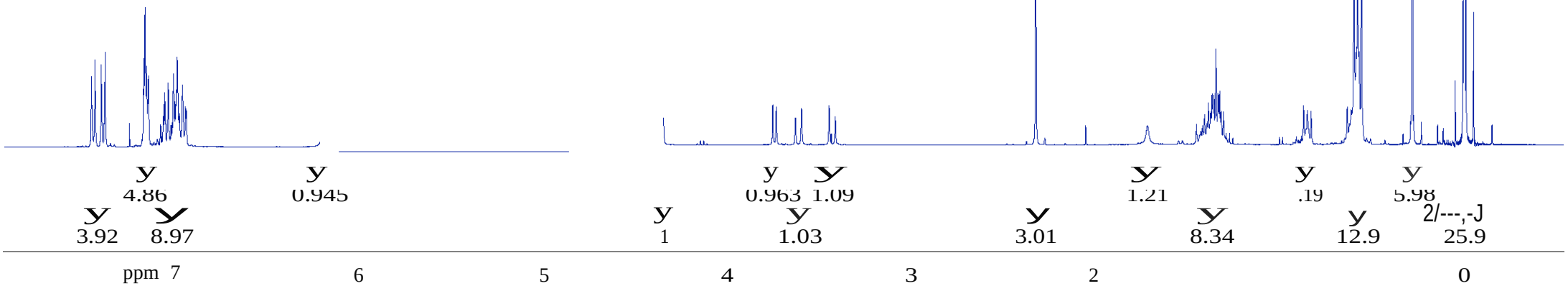


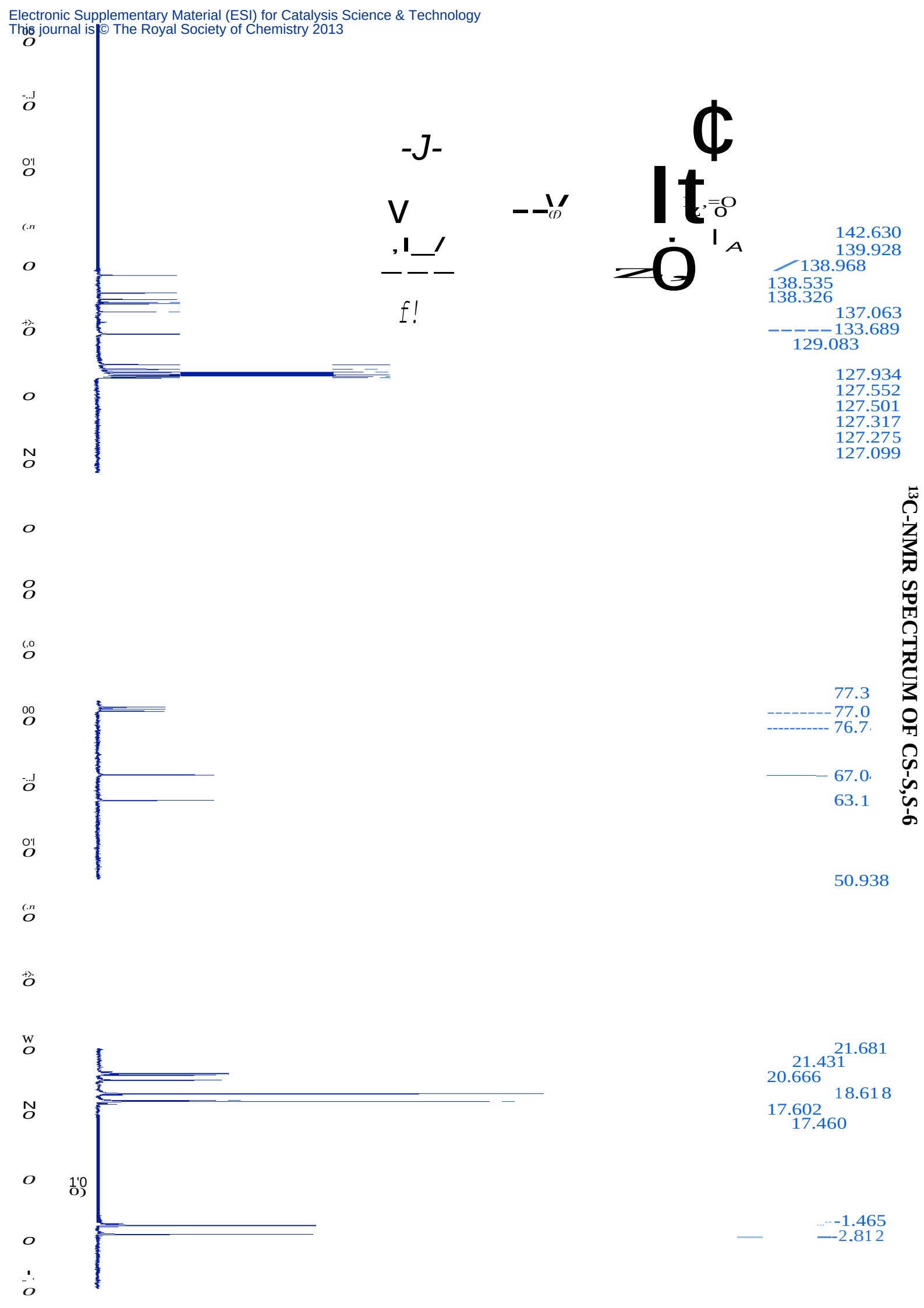


^{13}C-NMR SPECTRUM OF CS-S,S-5

^{1}H-NMR SPECTRUM OF CS-*S,S*-6







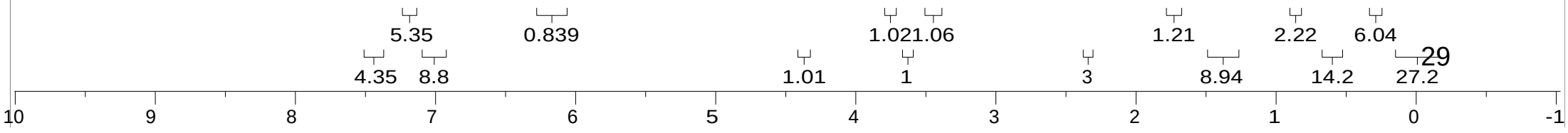
^{13}C-NMR SPECTRUM OF CS-S,S-6

^{1}H-NMR SPECTRA OVERLAY OF CS-*S,S*-6 BEFORE (BOTTOM) AND AFTER (MIDDLE) CATALYSIS AND *TRANS*-STILBENE OXIDE (TOP)

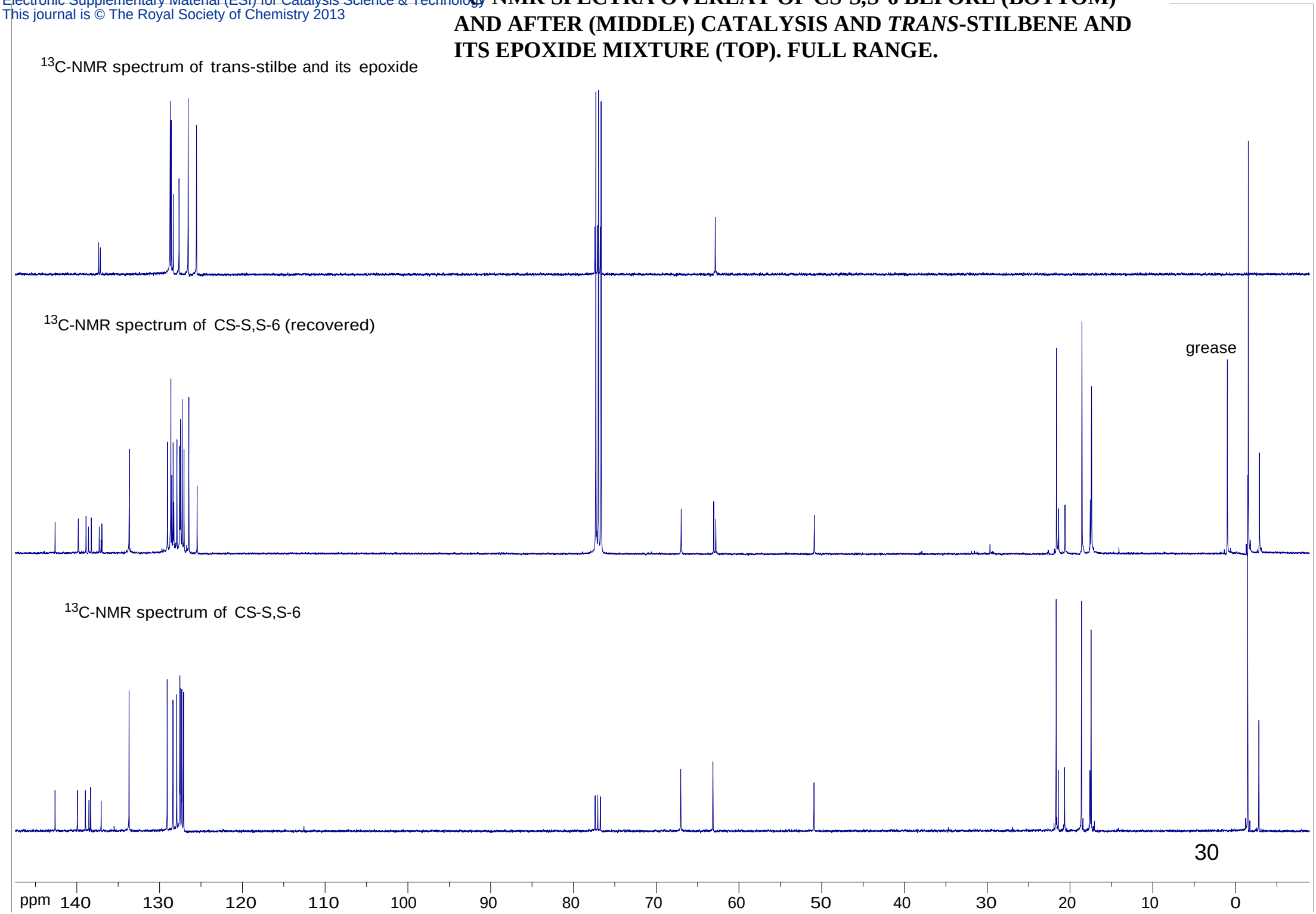
^{1}H-NMR spectrum of trans-stilbene oxide

^{1}H-NMR spectrum of CS-S,S-6 (recovered)

^{1}H-NMR spectrum of CS-S,S-6 (pure)

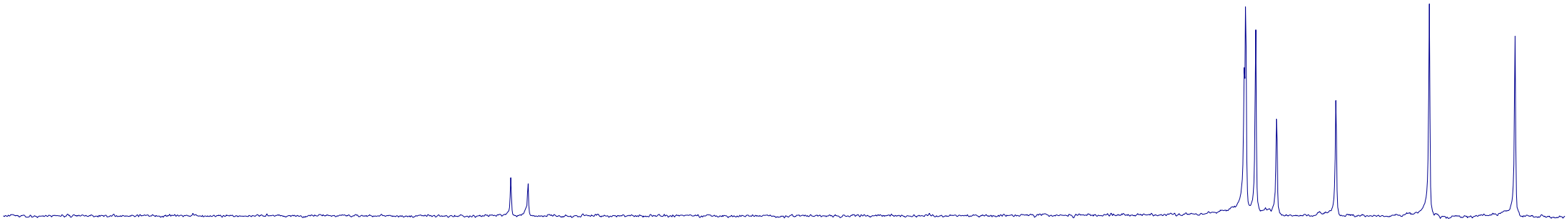


^{13}C-NMR SPECTRA OVERLAY OF CS-*S,S*-6 BEFORE (BOTTOM) AND AFTER (MIDDLE) CATALYSIS AND *TRANS*-STILBENE AND ITS EPOXIDE MIXTURE (TOP). FULL RANGE.

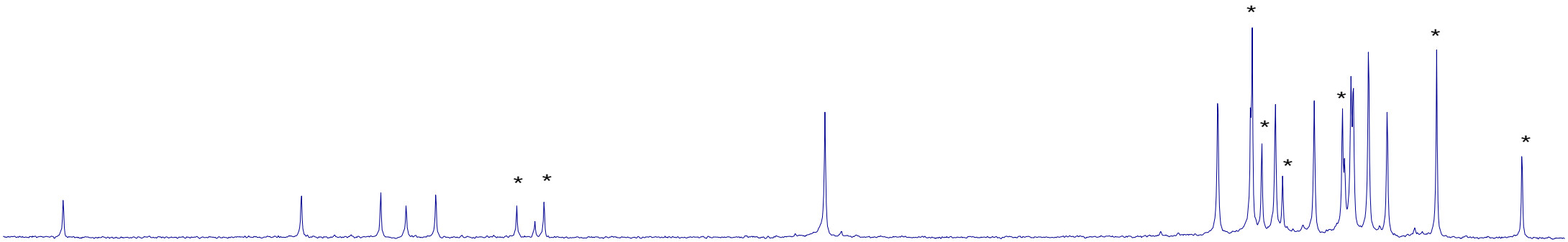


^{13}C-NMR SPECTRA OVERLAY OF CS-*S,S*-6 BEFORE (BOTTOM) AND AFTER (MIDDLE) CATALYSIS AND *TRANS*-STILBENE AND ITS EPOXIDE MIXTURE (TOP). MAGNIFICATION 125-145 PPM

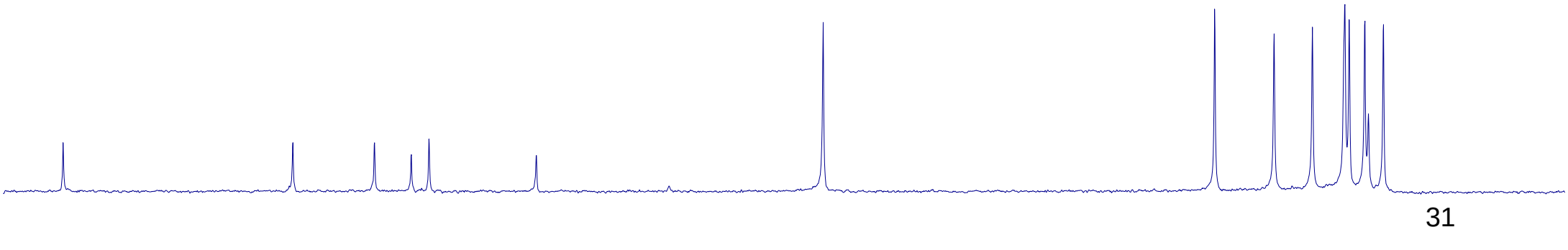
^{13}C-NMR spectrum of trans-stilbe and its epoxide (ca. 1:1)



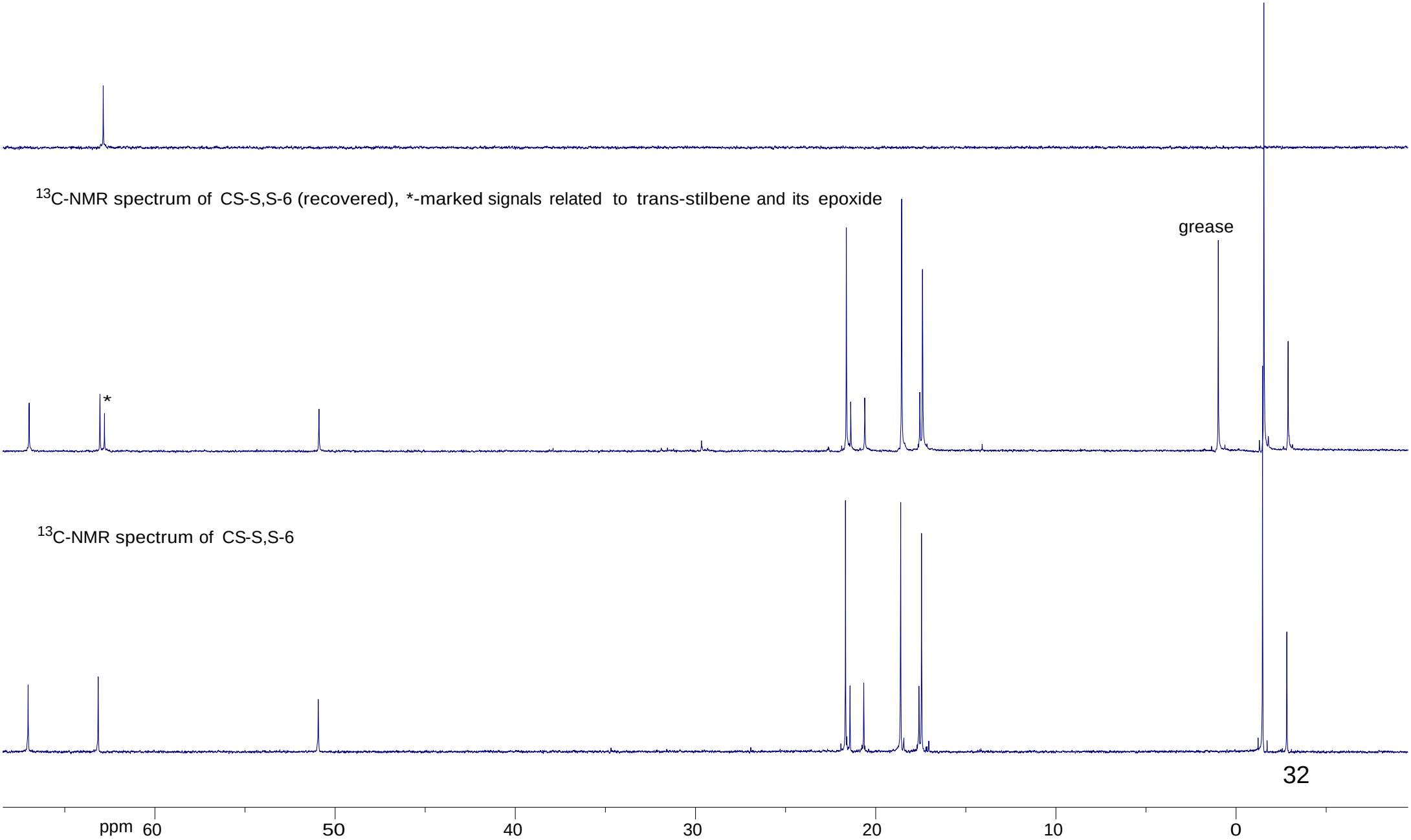
^{13}C-NMR spectrum of CS-S,S-6 (recovered), *-marked signals related to trans-stilbene and its epoxide



^{13}C-NMR spectrum of CS-S,S-6



^{13}C-NMR SPECTRA OVERLAY OF CS-*S,S*-6 BEFORE (BOTTOM) AND AFTER (MIDDLE) CATALYSIS AND *TRANS*-STILBENE AND ITS EPOXIDE MIXTURE (TOP). MAGNIFICATION -10-70 PPM



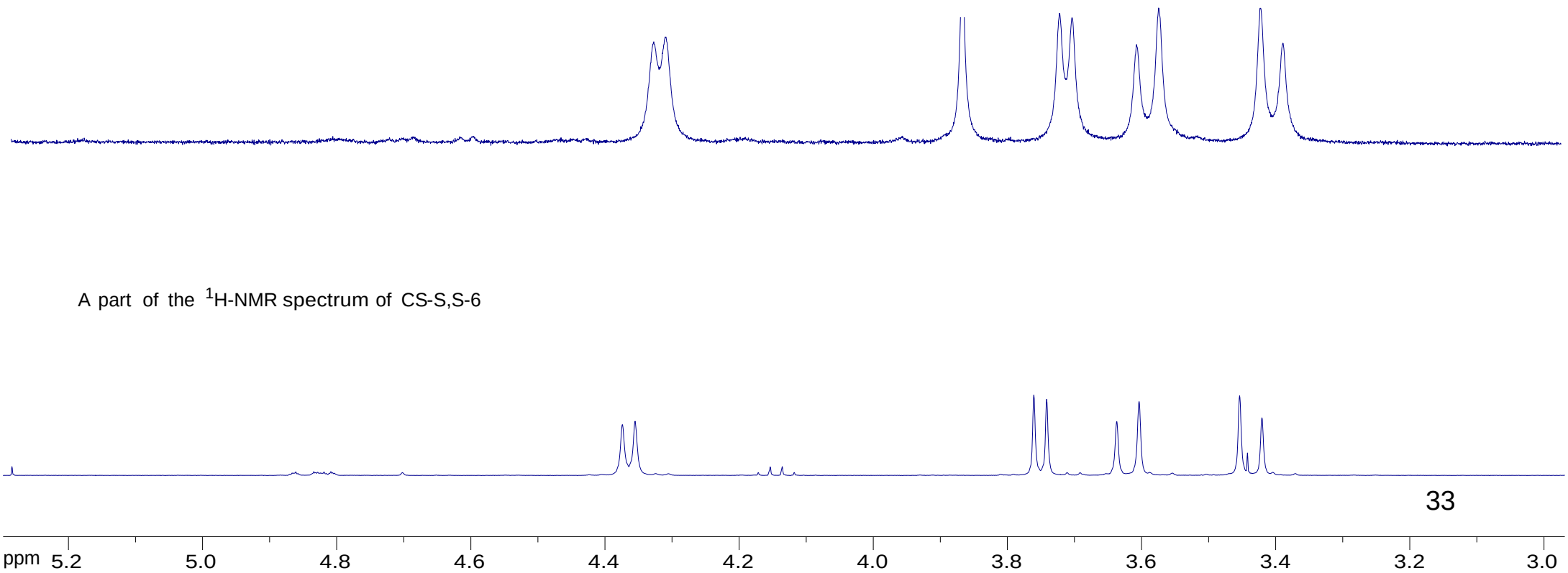
^{1}H-NMR SPECTRA OVERLAY OF CS-S,S-6 BEFORE (BOTTOM) AND RECOVERED AFTER CATALYSIS USING 0.6 EQ. H2O2 (MIDDLE) AND 2.0 EQ. H2O2 (TOP). MAGNIFICATION 3.0-5.3 PPM

***- marked signals related to trans-stilbene oxide**

A part of the ^{1}H-NMR spectrum of CS-S,S-6 isolated after catalysis using 2.0 eq. H_2O_2

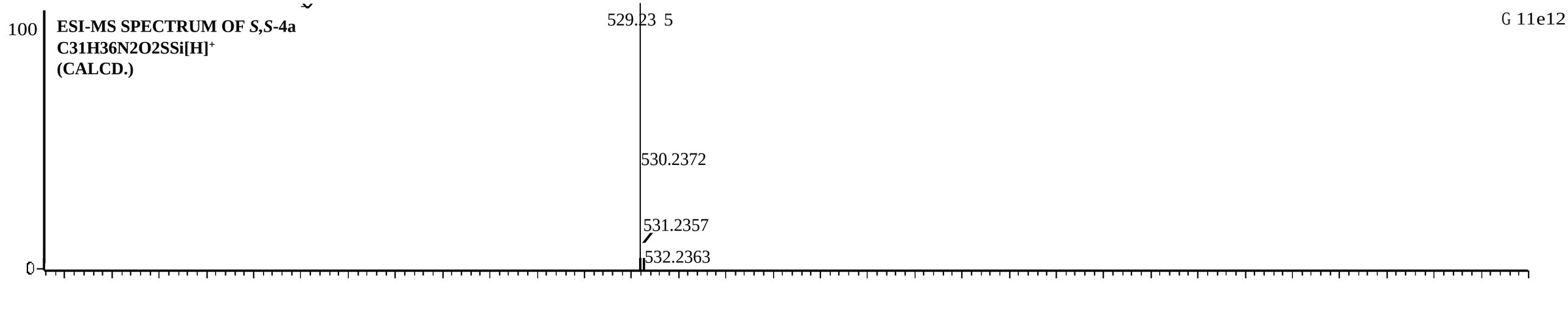
A part of the ^{1}H-NMR spectrum of CS-S,S-6 isolated after catalysis using 0.6 eq. H_2O_2

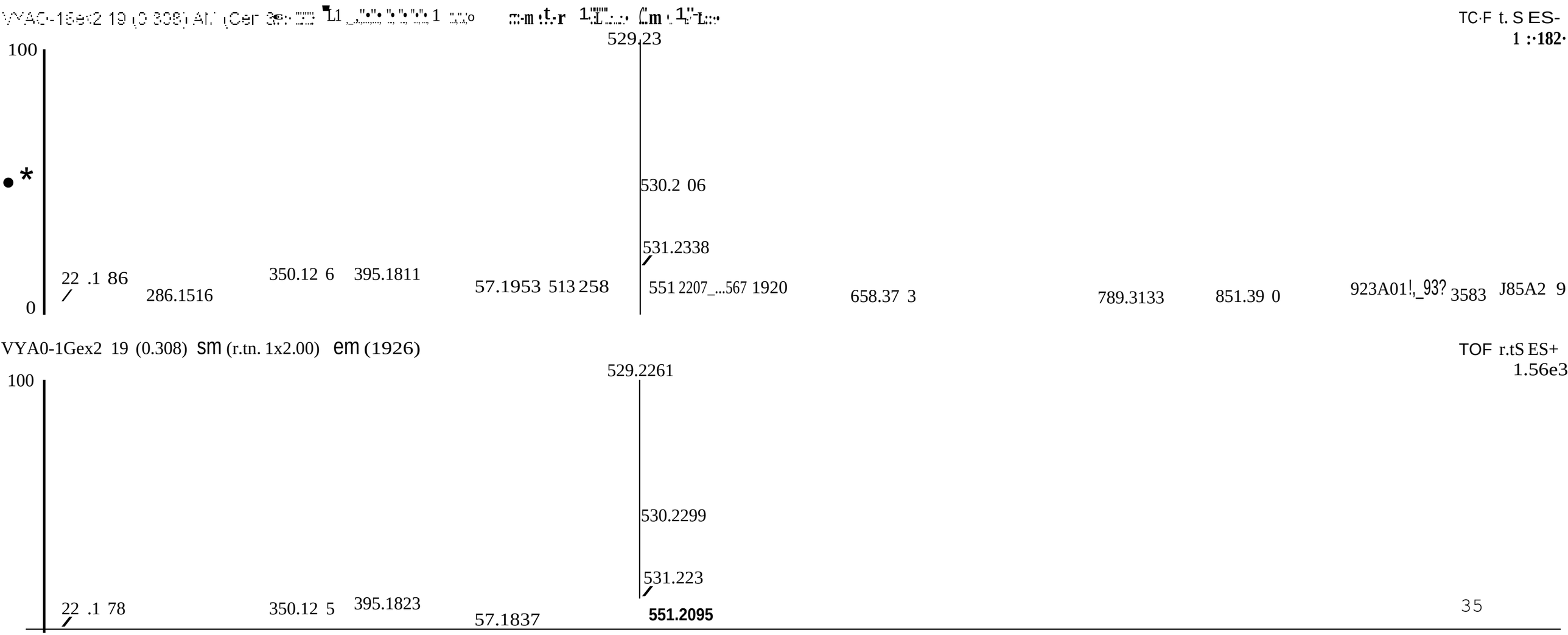
A part of the ^{1}H-NMR spectrum of CS-S,S-6



Acetonitril

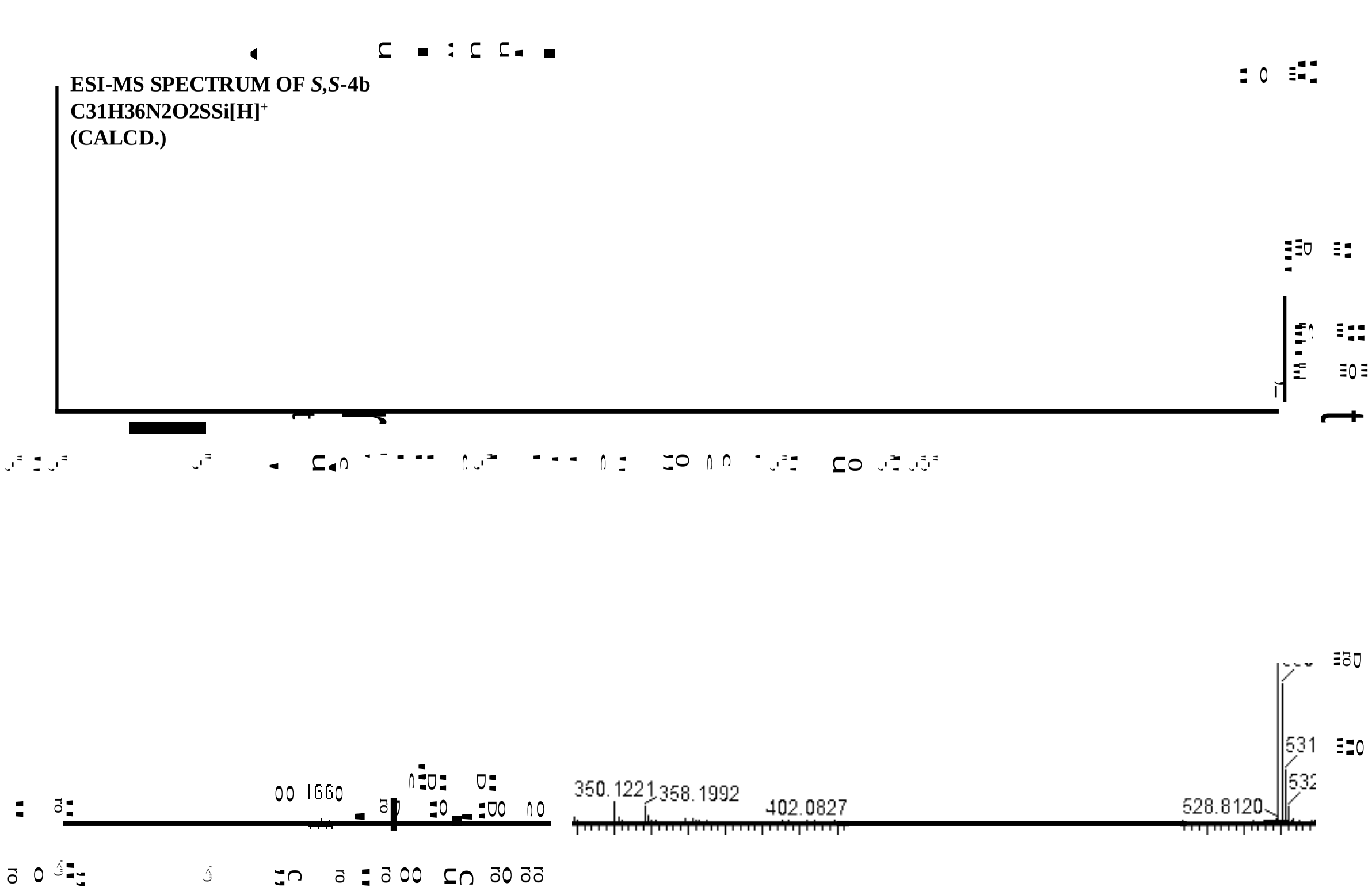
19-Feb-2013- 13:30:07



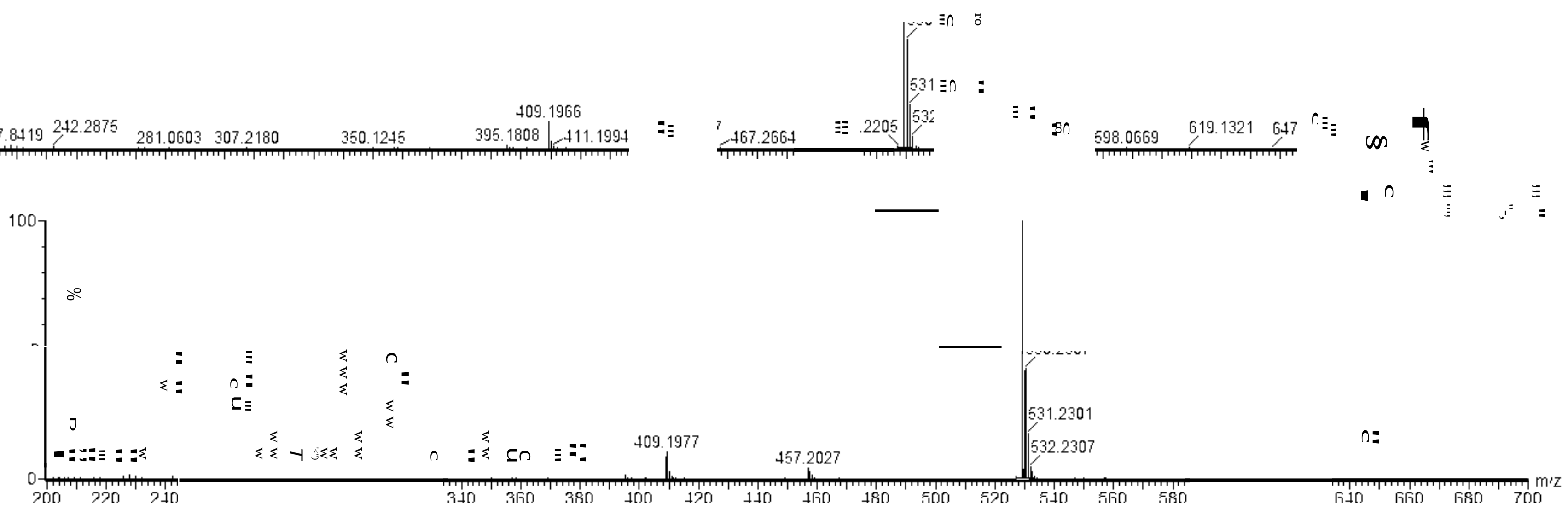


VYA0-1Gex2 19 (0.308) sm (r.tn. 1x2.00) em (1926)

ESI-MS SPECTRUM OF *S,S*-4b
$C_{31}H_{36}N_2O_2SSi[H]^+$
(CALCD.)



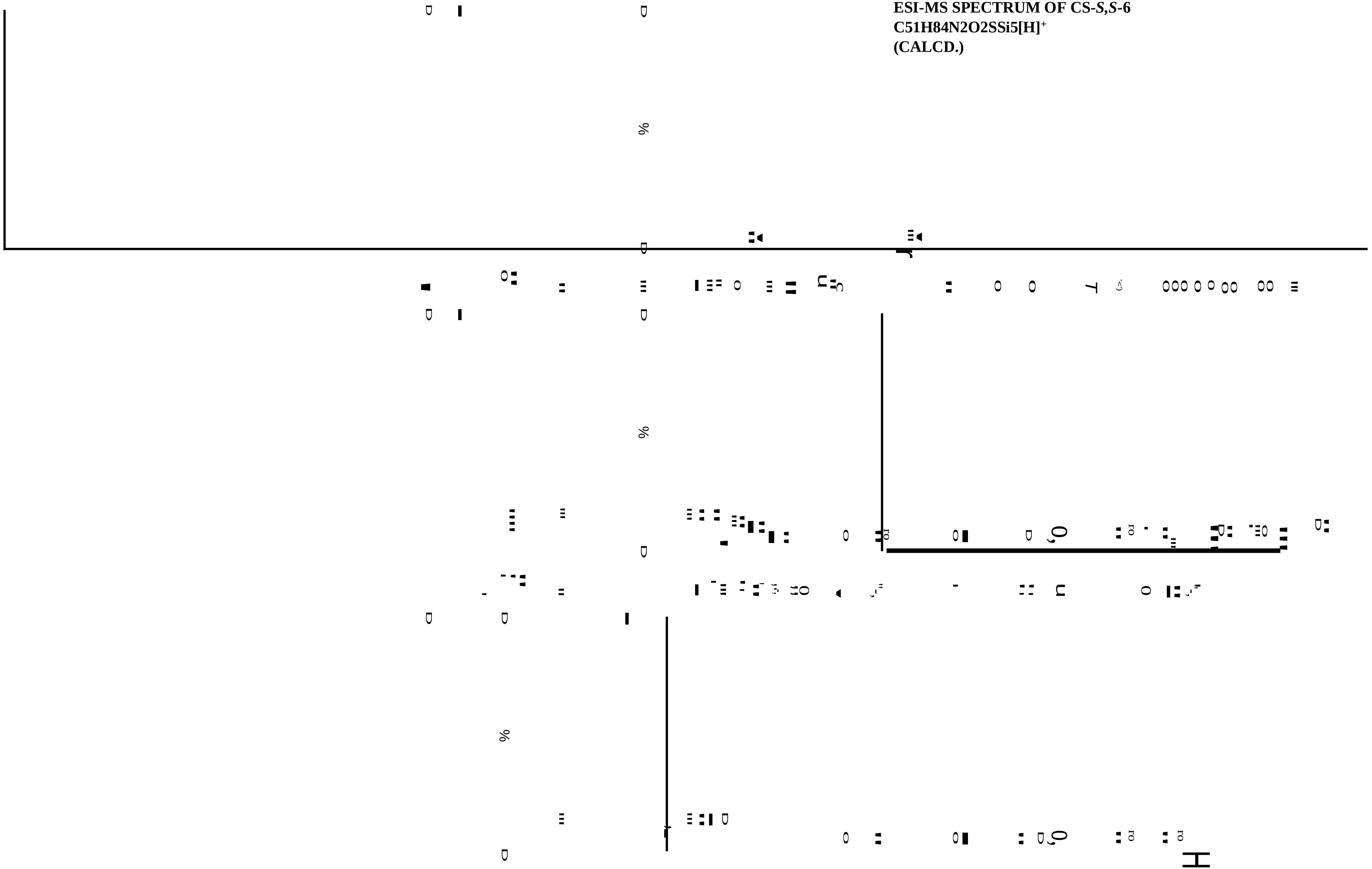
SPECTRUM OF *S,S*-4c
$_{5}N_{2}O_{2}SSi[H]^{+}$
D.)



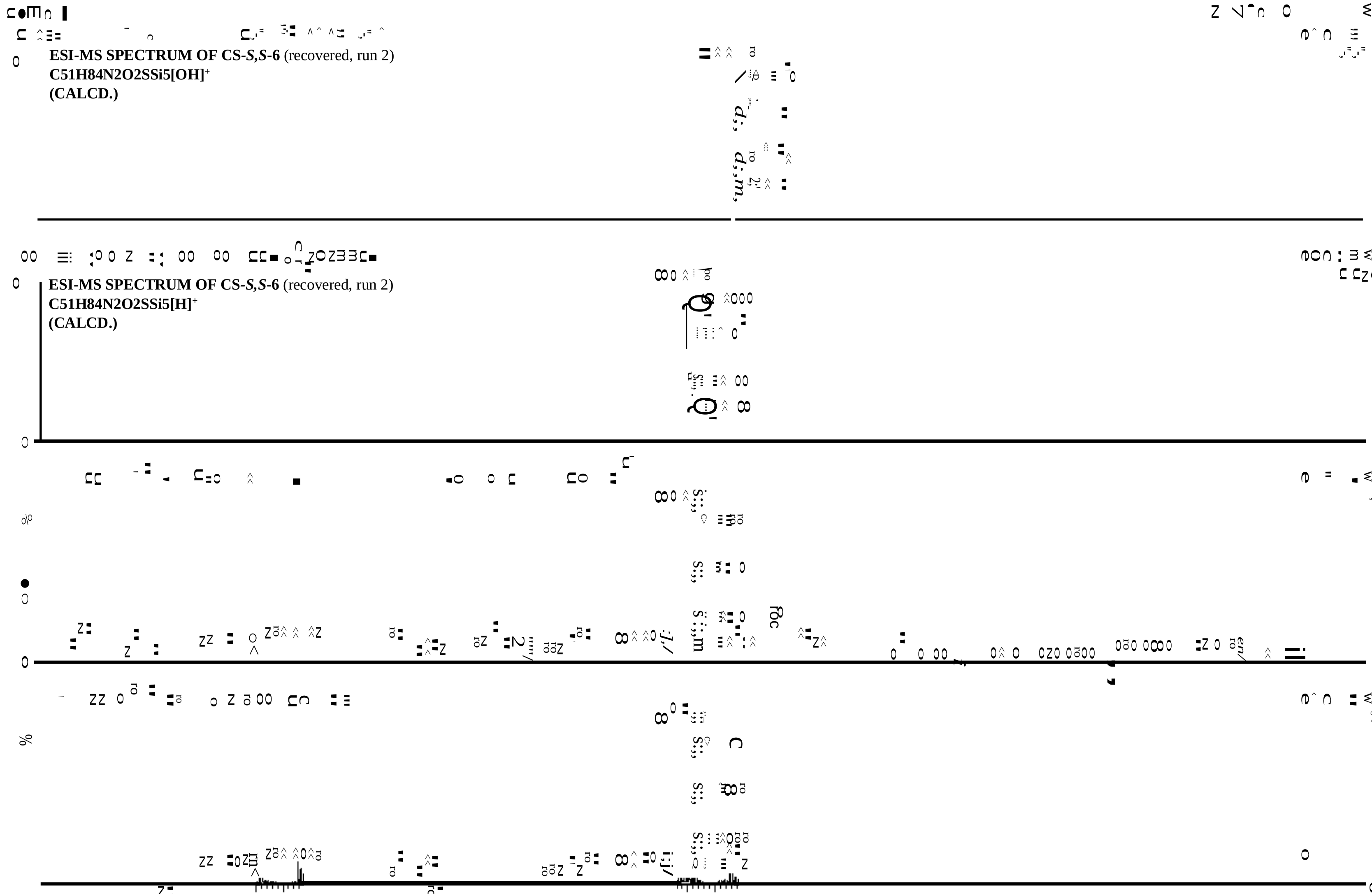
ESI-MS SPECTRUM OF *S,S*-4d
$C_{58}H_{60}N_4O_4S_2Si[H]^+$
(CALCD.)

-MS SPECTRUM OF *S,S*-4d
$H_{60}N_4O_4S_2Si[Na]^+$
LCD.)

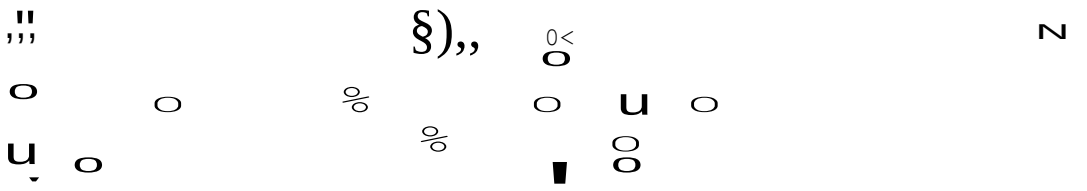
MS SPECTRUM OF *S,S*-4d
$H_{60}N_4O_4S_2Si[K]^+$
LCD.)



ESI-MS SPECTRUM OF CS-*S,S*-6 (recovered, run 2)
C51H84N2O2SSi5[OH]$^+$
(CALCD.)



ESI-MS SPECTRUM OF CS-*S,S*-6 (recovered, run 2)
C51H84N2O2SSi5[H]$^+$
(CALCD.)



ESI-MS SPECTRUM OF CS-*S,S*-6 (recovered, run 3)
C51H84N2O2SSi5[H]$^+$
(CALCD.)

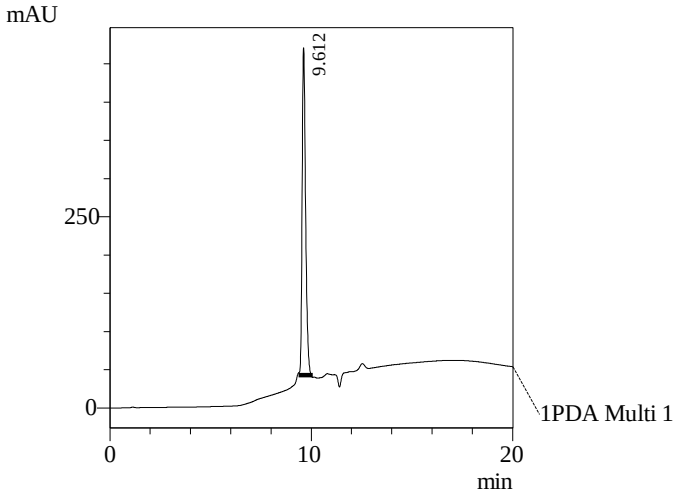
GPC data for CS-*S*,*S*-1

==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by	: student
Sample Name	: VY140
Sample ID	: 240nm
Injection Volume	: 20 uL
Data Filename	: vera12102501.lcd
Method Filename	: gpc methode pda 2012.lcm
Report Filename	: report_landscape_4ch.lcr
Date Acquired	: 10/25/2012 5:34:08 PM
Data Processed	: 10/25/2012 5:55:17 PM

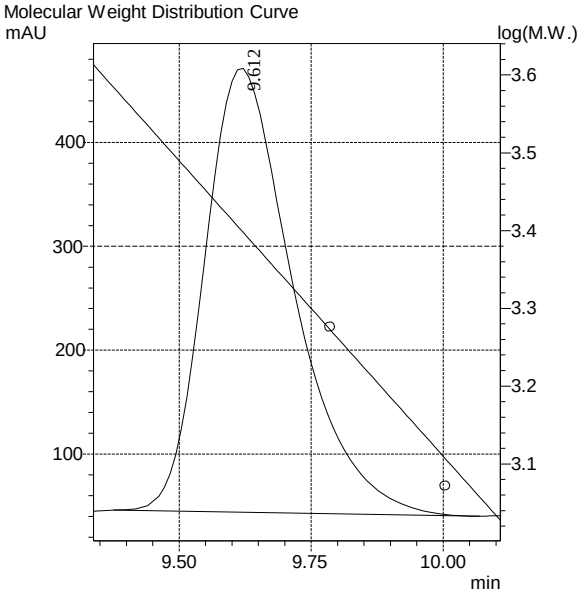
Chromatogram

VY140 D:\GPC HPLC DATA\2012-2013\vera12102501.lcd



1 PDA Multi 1 / 254nm 4nm

Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (PDA Ch1)

[Peak Information]

	Time(min)	Molecular Weight	Height
Start	9.376	3837	46035
End	10.069	1141	40274

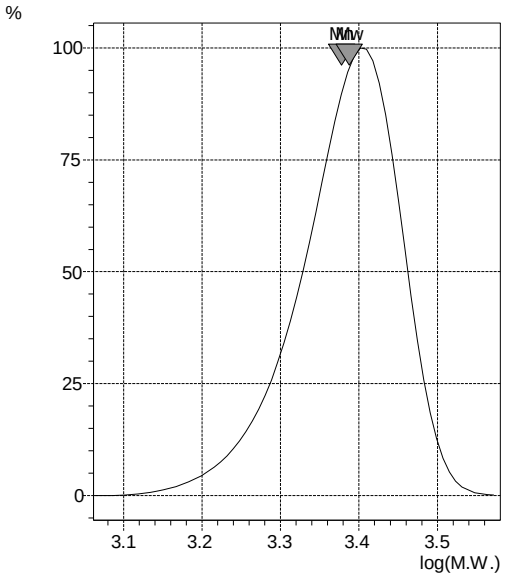
[Average Molecular Weight]

Weight Average Molecular Weight(Mw)	2441
Number Average Molecular Weight(Mn)	2387
Mw/Mn	1.02263

PDA Ch1

[Average Molecular Weight(Total)]

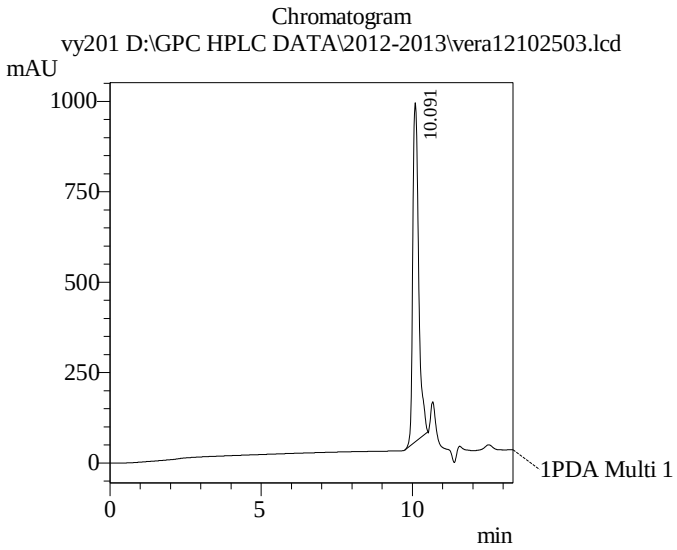
Weight Average Molecular Weight(Mw)	2441
Number Average Molecular Weight(Mn)	2387
Mw/Mn	1.02263



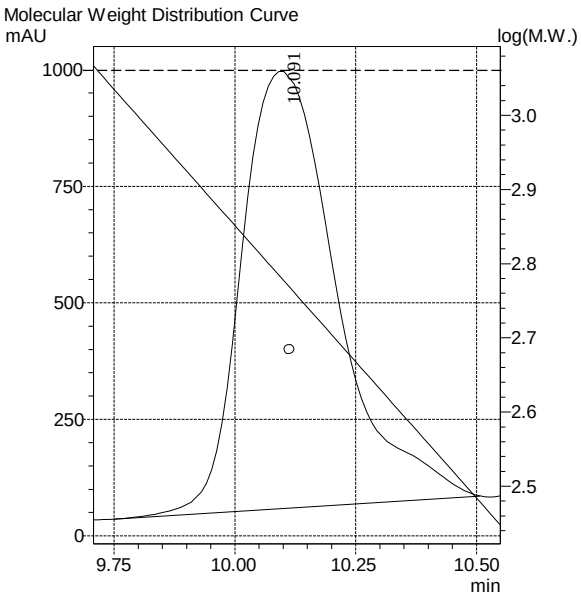
GPC data for *S,S*-4d

==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by	: student
Sample Name	: vy201
Sample ID	: 240nm
Injection Volume	: 20 uL
Data Filename	: vera12102503.lcd
Method Filename	: gpc methode pda 2012.lcm
Report Filename	: report_landscape_4ch.lcr
Date Acquired	: 10/26/2012 5:13:18 PM
Data Processed	: 10/26/2012 5:29:32 PM



1 PDA Multi 1 / 240nm 4nm



GPC Calculation Results

Peak#:1 (PDA Ch1)
[Peak Information]

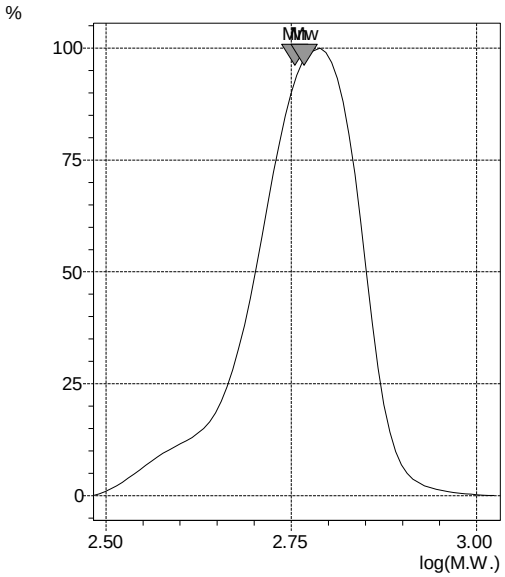
	Time(min)	Molecular Weight	Height
Start	9.749	1085	36033
Top	10.091	609	937697
End	10.507	301	85477

[Average Molecular Weight]

Weight Average Molecular Weight(Mw)	585
Number Average Molecular Weight(Mn)	568
Mw/Mn	1.02915

PDA Ch1
[Average Molecular Weight(Total)]

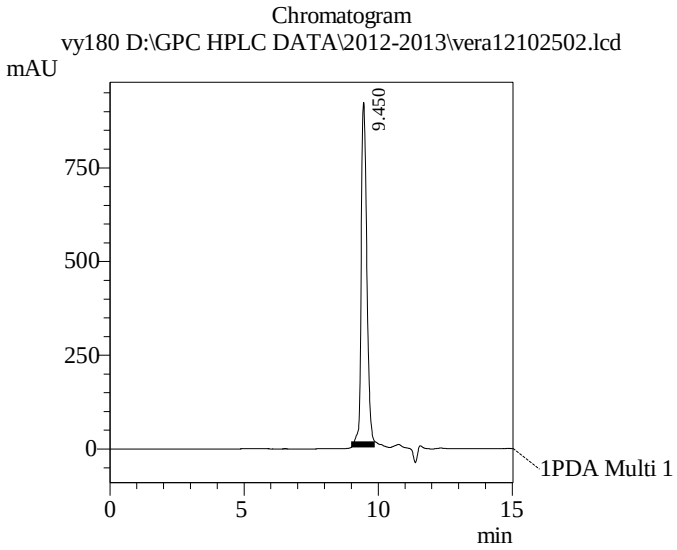
Weight Average Molecular Weight(Mw)	585
Number Average Molecular Weight(Mn)	568
Mw/Mn	1.02915



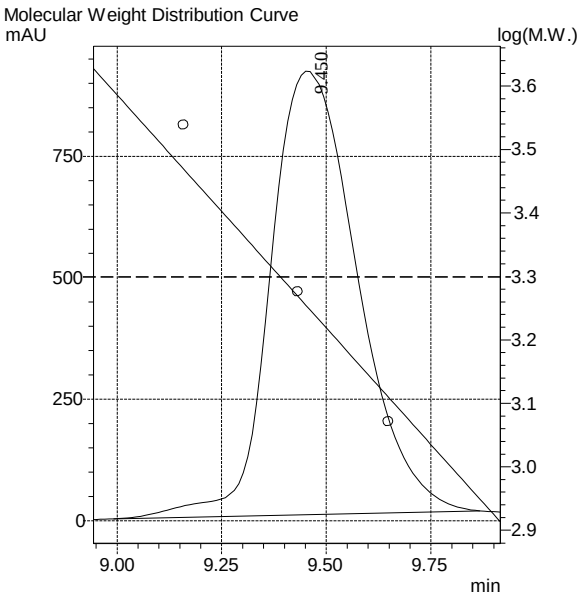
GPC data for CS-*S*,*S*-5

==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by	: student
Sample Name	: vy180
Sample ID	: 240nm
Injection Volume	: 20 uL
Data Filename	: vera12102502.lcd
Method Filename	: gpc methode pda 2012.lcm
Report Filename	: report_landscape_4ch.lcr
Date Acquired	: 10/26/2012 4:54:15 PM
Data Processed	: 10/26/2012 5:16:15 PM



1 PDA Multi 1 / 240nm 4nm



GPC Calculation Results

Peak#:1 (PDA Ch1)
[Peak Information]

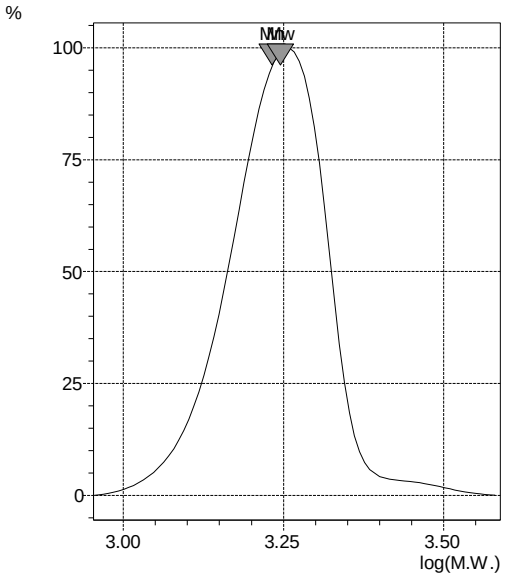
	Time(min)	Molecular Weight	Height
Start	8.992	3908	4199
Top	9.450	1801	911846
End	9.867	890	20654

[Average Molecular Weight]

Weight Average Molecular Weight(Mw)	1759
Number Average Molecular Weight(Mn)	1707
Mw/Mn	1.03077

PDA Ch1
[Average Molecular Weight(Total)]

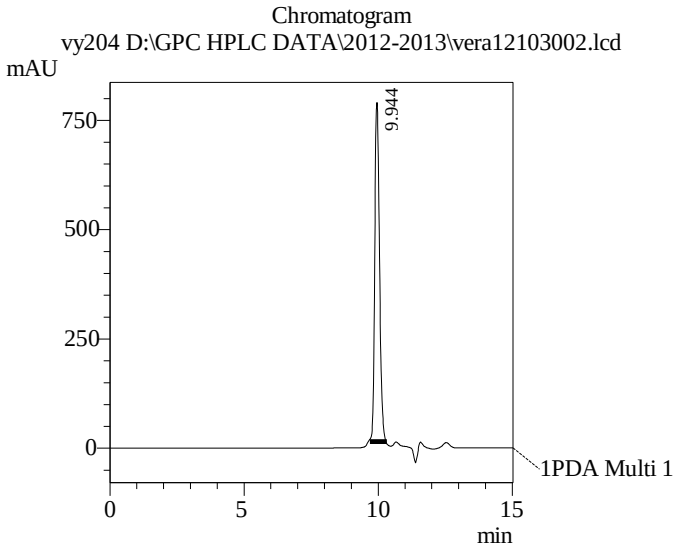
Weight Average Molecular Weight(Mw)	1759
Number Average Molecular Weight(Mn)	1707
Mw/Mn	1.03077



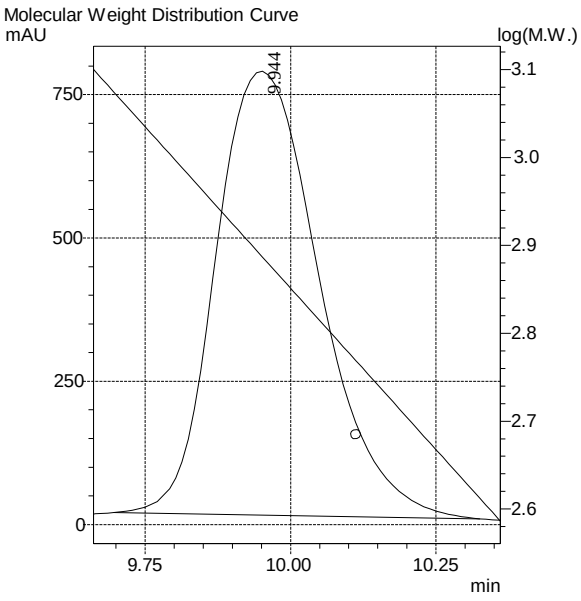
GPC data for CS-*S*,*S*-6

==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by	: student
Sample Name	: vy204
Sample ID	: 240nm
Injection Volume	: 20 uL
Data Filename	: vera12103002.lcd
Method Filename	: gpc methode pda 2012.lcm
Report Filename	: report_landscape_4ch.lcr
Date Acquired	: 10/30/2012 11:01:06 AM
Data Processed	: 10/30/2012 11:18:46 AM



1 PDA Multi 1 / 240nm 4nm



GPC Calculation Results

Peak#:1 (PDA Ch1)
[Peak Information]

	Time(min)	Molecular Weight	Height
Start	9.696	1188	20936
End	10.325	410	9987

[Average Molecular Weight]

Weight Average Molecular Weight(Mw)	761
Number Average Molecular Weight(Mn)	746
Mw/Mn	1.02014

PDA Ch1
[Average Molecular Weight(Total)]

Weight Average Molecular Weight(Mw)	761
Number Average Molecular Weight(Mn)	746
Mw/Mn	1.02014