Synthesis and Characterization of Enantiopure Chiral NH_2/SO Palladium Complexes

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Supporting Information

Table of contents

Experimental data

General procedures

All reactions were run under an atmosphere of dry argon using oven dried glassware and dried solvents. Toluene, THF, CH_2Cl_2 and diethyl ether were dried using molecular sieves, and highest quality solvents were used. Chemicals were obtained from commercial sources and were used without further purification. TLC was carried out on silica gel GF254 (Merck), and compounds were detected by charring with phosphomolybdic acid/EtOH. For flash chromatography, Merck 230–400 mesh silica gel was used. Chromatographic columns were eluted with a positive pressure of air, and eluents are given as volume to volume ratios (v/v). NMR spectra were recorded with Bruker Avance 300 and 500 MHz spectrometers. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Routine ^{1}H and ^{13}C spectra were referenced to the residual proton or carbon signals of the solvent, respectively. High-resolution mass spectra (HRMS) were recorded with a Kratos MS-80RFA 241-MC apparatus. Optical rotations were determined with a Perkin–Elmer 341 polarimeter. Melting points were measured with a Stuart SMP3 apparatus in open-ended capillary tubes.

Stereoselective synthesis of methylsulfoxides[1]

Methyl sulfinyl chloride, **35**

To a solution of dimethyl disulfide (8.9 mL, 0. 1 mol, 100 mol%) and glacial acetic acid (11.4 mL, 0.2 mol, 200 mol%), sulfuryl chloride (25.7 mL, 0.31 mol, 310 mol%) was added dropwise at -40 °C. The resulting mixture was stirred for 2 h at -20°C, 2 h at rt and 1h at 35°C. Then, the solvent was evaporated and the desired compound was obtained as a yellow oil with no further purification (9.1 g, 92.34 mmol, 92% yield); b.p.: 55 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 3H) ppm.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (–)-(S)-Methanesulfinate, **1(S_S)**

To a solution of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (DAGOH) (2.5 g, 9.6 mmol, 100 mol%) and diisopropylethyl amine (2.7 mL, 15.36 mmol, 160 mol%) in a mixture of dry toluene (150 mL) and dry methylene chloride (2 mL) under argon atmosphere, at -78 °C, a solution of methyl sulfinyl chloride, **35** (0.8 mL, 12.49 mmol, 130 mol%) was added dropwise with vigorous stirring. The reaction was stirred for 1 h at -78 °C, then HCl (10 % aq.) was added, and the aqueous phase was extracted with CH_2Cl_2 (3x60 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum to give sulfinate **1(S_S)** in a 98% d.e. It was purified by recrystallization in hexane to obtain diastereomerically pure sulfinate **1(S_S)** (2.8 g, 8.64 mmol, 90% yield) as a white solid; mp 92-94 °C; $[\alpha]_D^{20}$: -200 (*c* 1, acetone); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.91 (d, *J* = 3.7 Hz, 1H), 4.77 (d, *J* = 2.4 Hz, 1H), 4.61 (d, *J* = 3.6 Hz, 1H), 4.27-4.24 (m, 1H), 4.11-4.09 (m, 1H), 4.02-4.00 (m, 1H), 2.69 (s, 3H), 1.51, 1.42, 1.33, 1.30 (4s, 12H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 112.6, 109.4,

105.2, 83.9, 80.4, 78.4, 72.4, 67.0, 44.4, 26.9, 26.8, 26.4, 25.3 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{22}O_7NaS$ 345.0978; found 345.0976.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (+)-(R)-Methanesulfinate, **1(R_S)**

To a solution of DAGOH (2 g, 7.68 mmol) and pyridine (0.8 mL, 9.98 mmol) in dry THF (200 mL) at -78 °C, a solution of methyl sulfinyl chloride, **35** (0.72 mL, 9.98 mmol) was added dropwise with vigorous stirring. The reaction was stirred for 1h at -78 °C, then HCl (10 % aq.) was added, and the aqueous phase was extracted with CH_2Cl_2 (3x60 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum to give sulfinate **1(R_S)** in a 96% d.e. Purification by column chromatography (^{i}PrOH/hexane, 1:15) gave diastereomerically pure sulfinate **1(R_S)** (2.14 g, 6.69 mmol, 87 % yield) as a yellow oil. $[\alpha]_D^{20}$: +17 (*c* 4.4, acetone); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.91 (d, *J* = 3.6 Hz, 1H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 2.9 Hz, 1H), 4.17-4.09 (m, 3H), 4.02-3.98 (m, 1H), 2.70 (s, 3H), 1.50, 1.41, 1.32, 1.30 (4s, 12H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 112.6, 109.6, 105.5, 84.0, 83.1, 80.9, 72.4, 67.7, 44.9, 27.0, 26.9, 26.3, 25.4 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{22}O_7NaS$ 345.0978; found 345.0974.

Synthesis of methylsulfoxides: general procedure.

To a solution of the corresponding methanesulfinate **1** (100 mol%) in toluene or diethyl ether at 0 °C, a solution of RMgCl or ArMgBr (150 mol%) was added dropwise. After stirring for 1 h, the reaction was quenched with saturated aqueous NH_4Cl solution, and the aqueous phase was extracted with EtOAc (5 x 25 mL) and CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the reaction crude was purified by flash chromatography to obtain the desired compound.

Methyl Phenyl sulfoxide, **2(S_S)**
It was prepared following the general procedure from 5.4 g of methanesulfinate **1(S_S)** (16.76 mmol), 25 mL of 1 M PhMgBr solution (25.13 mmol) and toluene (40 mL). The residue obtained was purified by flash chromatography (EtOAc:hexane, 10:1) to obtain sulfoxide **2(S_S)** (1.9 g, 13.41 mmol, 80% yield) as a yellow oil; $[\alpha]_D^{20}$: -143 (*c* 1.0, acetone); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.55-7.48 (m, 3H), 2.73 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.0, 131.2, 129.5, 123.7, 44.2 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for C_7H_9ONaS 163.0188; found 163.0186.

Methyl Phenyl sulfoxide, **2(R_S)**
It was prepared following the general procedure from 3.2 g of methanesulfinate **1(R_S)** (10.03 mmol), 15 mL of 1.0M PhMgBr solution (15.05 mmol) and toluene (25 mL). The residue obtained was purified by flash chromatography (EtOAc: CH_2Cl_2, 1:2) to give sulfoxide **2(R_S)** (1.1 g, 7.82 mmol, 78% yield) as a yellow oil with similar physicochemical and spectroscopic characteristics than **2(S_S)**; $[\alpha]_D^{20}$: +149 (*c* 2.0, ethanol). HRMS (ESI) m/z: $[M+H]^+$ Calcd for C_7H_9OS 141.0010; found 141.0006.

Methyl Tert-butyl sulfoxide, **3(S_S)**

It was prepared following the general procedure from 3.8 g of methanesulfinate **1(S_S)** (11.76 mmol), 10.4 mL of 1.7 M ^{t}BuMgCl solution (17.63 mmol) and diethyl ether (30 mL). The residue obtained was purified by flash chromatography (EtOAc) to obtain sulfoxide **3(S_S)** (1.2 g, 9.72 mmol, 83% yield) as a colorless oil; $[\alpha]_D^{20}$: +19 (*c* 1.0, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 1.24 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 52.7, 31.7, 22.6 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_5H_{12}OSNa$ 143.0501; found 143.0501.

Methyl Tert-butyl sulfoxide, **3(R_S)**

It was prepared following the general procedure from 3.7 g of methanesulfinate **1(R_S)** (11.43 mmol), 10 mL of 1.7 M ^{t}BuMgCl solution (17.15 mmol) and diethyl ether (30 mL). The residue obtained was purified by flash chromatography (EtOAc) to obtain sulfoxide **3(R_S)** (1.1 g, 8.77 mmol, 77% yield) as a colorless oil with similar physicochemical and spectroscopic characteristics than **3(S_S)**; $[\alpha]_D^{20}$: +4.3 (*c* 1.6, acetone). HRMS (ESI) m/z: $[M]^+$ Calcd for $C_5H_{12}OS$ 120.0608; found 120.0609.

Synthesis of *N*-Sulfinylimines: general procedure.[2]

To a solution of the corresponding aldehyde (100 mol%) and the (*R*)-*tert*-butanesulfinamide (110 mol%) in dry THF, at room temperature under argon atmosphere, $Ti(OEt)_4$ (110 mol%) was added. Once the starting material was consumed (24-48h), the reaction mixture was hydrolyzed with a saturated NaCl aqueous solution. The resulting suspension was filtered through a pad of Celite. The aqueous phase was extracted with CH_2Cl_2 (3 x 40 mL) and the combined organic phases were dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the reaction crude was purified by flash chromatography to obtain the desired compound.

(R_S)-N-[(2-Naphthyl)methylidene]-2-methyl-2-propanesulfinamide, **4(R_S)**.

It was prepared following the general procedure from 5 g of (*R*)-*tert*-butanesulfinamide (41.25 mmol), 5.86 mL of 2-naphthaldehyde (37.5 mmol) and 8.7 mL of $Ti(OEt)_4$ (41.25 mmol). After 24 hours, the resulting residue was purified by flash chromatography (EtOAc:hexane, 1:10) to give **4(R_S)** (9.2 g, 35.39 mmol, 95% yield) as a white solid; mp 112-113 °C; $[\alpha]_D^{20}$: -173.7 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.21 (s, 1H), 8.04 (dd, J_1 = 1.5, J_2 = 8.6 Hz, 1H), 7.96-7.94 (m, 1H), 7.91-7.87 (m, 2H), 7.61-7.54 (m, 2H), 1.30 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 162.9, 135.6, 133.2, 132.6, 132.0, 129.3, 129.0, 128.4, 128.1, 127.1, 124.0, 58.0, 22.8 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}NOSNa$ 282.0918; found 282.0923.

(R_S)-N-Benzylidene-2-methyl-2-propanesulfinamide, **5(R_S)**.

It was prepared following the general procedure from 5 g of (*R*)-*tert*-butanesulfinamide (41.25 mmol), 3.8 mL of benzaldehyde (37.5 mmol) and 8.7 mL of $Ti(OEt)_4$ (41.25 mmol). After 24 hours, the resulting residue was purified by flash chromatography (EtOAc:hexane, 1:50) to give **5(R_S)** (6.3 g, 30.15 mmol, 80% yield) as a yellow liquid; $[\alpha]_D^{20}$: -122 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.84-7.83 (m, 2H), 7.51-7.44 (m, 3H), 1.26 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.1, 134.4, 132.7, 129.7, 129.3, 58.0, 22.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}ONS$ 210.0947; found 210.0940.

(R_S)-N-(2-methyl-1-propylidene)-2-methyl-2-propanesulfinamide, **6(R_S)**.
It was prepared following the general procedure from 5 g of (*R*)-*tert*-butanesulfinamide (41.25 mmol, 100 mol%), 5.6 mL of isopropylaldehyde (61.88 mmol, 150 mol%) and 8.7 mL of $Ti(OEt)_4$ (41.25 mmol, 100 mol%). After 24 hours, the resulting residue was purified by flash chromatography (EtOAc:hexane, 1:20) to give **6(R_S)** (7.23 g, 41.25 mmol, quant. yield) as a yellow liquid; $[\alpha]_D^{20}$: -253.2 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 4.4 Hz, 1H), 2.70-2.61 (m, 1H), 1.19 (s, 9H), 1.12 (d, *J* = 2.4 Hz, 3H), 1.10 (d, *J* =2.4 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.9, 56.7, 35.1, 22.5, 19.1, 19.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{18}ONS$ 176.1100; found 176.1104.

Synthesis of sulfinamide/sulfoxide ligands: general procedure.[2]

To a solution of the corresponding (*R*)-*tert*-butylsulfinylimine (100 mol%) and the corresponding methyl sulfoxide (100 mol%) in dry THF, at -78°C under argon atmosphere, a 1 M solution of LHMDS (300 mol%) was added dropwise. Once the starting material was consumed, the reaction mixture was hydrolyzed with a saturated NH_4Cl aqueous solution. The aqueous phase was extracted with EtOAc (3 x 40 mL) and the combined organic phases were dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash chromatography to obtain the desired compounds.

(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
7(R_S,S_C,R_S)
It was prepared following the general procedure from 454 mg of the (*R*)-*tert*-butanesulfinylimine **4(R_S)** (1.75 mmol), 245 mg of phenyl methyl sulfoxide **2(R_S)** (1.75 mmol), 5.25 mL of LHMDS (5.25 mmol) and THF (10 mL). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 2:1) to give **7(R_S,S_C,R_S)** (628 mg, 1.57 mmol, 90% yield) as a white solid; mp 176-177 °C; $[\alpha]_D^{20}$: +79.9 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.90-7.86 (m, 4H), 7.67-7.65 (m, 2H), 7.57-7.50 (m, 6H), 4.97 (td, J_1 = 3.3 Hz, J_2 = 10.1 Hz, J_3 = 10.3 Hz, 1H), 4.91 (d, *J* = 9.7 Hz, 1H), 3.24 (AB fragment of an ABX system, $\Delta\nu$ = 157 Hz, J_{AX} = 3.3 Hz, J_{BX} = 10.6 Hz, J_{AB} = 13.3 Hz, 2H), 1.26 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 145.7, 139.9, 134.2, 133.9, 132.0, 130.4, 129.4, 128.9, 128.6, 127.5, 127.3, 127.0, 126.1, 124.8, 65.8, 57.7, 57.5, 23.0 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}O_2NS_2Na$ 422.1219; found 422.1212; FTIR peaks (cm^{-1}): 1065 (ν_{SONH}), 1020 (ν_{SOPh}).

(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
7(R_S,S_C,S_S)
It was prepared following the general procedure from 454 mg of the (*R*)-*tert*-butanesulfinylimine **4(R_S)** (1.75 mmol), 245 mg of phenyl methyl sulfoxide **2(S_S)** (1.75 mmol), 5.25 mL of LHMDS (5.25 mmol) and THF (10 mL). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 2:1) to give **7(R_S,S_C,R_S)** (657 mg, 1.64 mmol, 94% yield) as a white solid; mp 178 °C; $[\alpha]_D^{20}$: -76.7 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.93-7.89 (m, 4H), 7.73-7.65 (m, 2H), 7.59-7.49 (m, 6H), 4.88 (dd, J_1 = 7.3 Hz, J_2 = 14.5 Hz, 1H), 4.79 (d, *J* = 7.0 Hz, 1H), 3.36 (AB fragment of an

ABX system, $\Delta\nu$ = 63 Hz, J_{AX} = 7.6 Hz, J_{BX} = 7.0 Hz, J_{AB} = 13.1 Hz, 2H), 1.17 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 145.6, 139.2, 134.2 (2), 132.3, 130.4, 129.5, 128.9, 128.6, 127.6, 127.5, 127.4, 126.3, 125.1, 65.3, 57.9, 57.0, 22.9 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}O_2NS_2Na$ 422.1219; found 422.1212; FTIR peaks (cm^{-1}): 1064 (ν_{SONH}), 1016 (ν_{SOPh}).

(R_S,S_C,R_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
8(*R_S*,*S_C*,*R_S*)
It was prepared following the general procedure from 419 mg of the (*R*)-*tert*-butanesulfinylimine **5(*R_S*)** (2 mmol), 280 mg of phenyl methyl sulfoxide **2(*R_S*)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (10 mL). After 10 minutes, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 1:2) to give **8(*R_S*,*S_C*,*R_S*)** (636 mg, 1.82 mmol, 91% yield) as a white solid; mp 161-162 °C; $[\alpha]_D^{20}$: +121 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.65-7.64 (m, 2H), 7.57-7.52 (m, 3H), 7.42-7.40 (m, 2H), 7.37-7.34 (m, 2H), 7.30-7.27 (m, 1H), 4.81 (m, 2H), 3.14 (AB fragment of an ABX system, $\Delta\nu$ = 150 Hz, J_{AX} = 2.9 Hz, J_{BX} = 10.8 Hz, J_{AB} = 13.3 Hz, 2H), 1.25 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 145.7, 142.5, 132.0, 130.4, 129.7, 128.9, 128.1, 124.8, 66.1, 57.7, 57.5, 23.0 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}O_2NS_2Na$ 372.1062; found 372.1056; FTIR peaks (cm^{-1}): 1054 (ν_{SONH}), 1016 (ν_{SOPh}).

(R_S,S_C,S_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
8(*R_S*,*S_C*,*S_S*)
It was prepared following the general procedure from 419 mg of the (*R*)-*tert*-butanesulfinylimine **5(*R_S*)** (2 mmol), 280 mg of phenyl methyl sulfoxide **2(*S_S*)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (10 mL). After 10 minutes, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 1:1) to give **8(*R_S*,*S_C*,*S_S*)** (625 mg, 1.79 mmol, 89% yield) as a yellow solid; mp 121-123 °C; $[\alpha]_D^{20}$: -99.7 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.66-7.64 (m, 2H), 7.59-7.55 (m, 3H), 7.45-7.38 (m, 4H), 7.35-7.32 (m, 1H), 4.70 (m, 2H), 3.26 (AB fragment of an ABX system, $\Delta\nu$ = 79 Hz, J_{AX} = 7.3 Hz, J_{BX} = 7.2 Hz, J_{AB} = 13.1 Hz, 2H), 1.16 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 145.6, 141.9, 132.3, 130.4, 129.7, 129.2, 128.5, 125.1, 65.7, 57.8, 57.0, 22.9 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}O_2NS_2Na$ 372.1062; found 372.1055; FTIR peaks (cm^{-1}): 1074 (ν_{SONH}), 1020 (ν_{SOPh}).

(R_S,S_C,R_S)-N-[1-(Phenylsulfinyl)-3-methylbut-2-yl]-2-methyl-2-propanesulfinamide,
9(*R_S*,*S_C*,*R_S*)
It was prepared following the general procedure from 351 mg of the (*R*)-*tert*-butanesulfinylimine **6(*R_S*)** (2 mmol), 280 mg of phenyl methyl sulfoxide **2(*R_S*)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (9 mL). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 1:1) to give **9(*R_S*,*S_C*,*R_S*)** (512 mg, 1.62 mmol, 81% yield) as a white solid; mp 152-153 °C; $[\alpha]_D^{20}$: +149.8 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.65-7.63 (m, 2H), 7.59-7.51 (m, 3H), 4.12 (d, *J* = 9.9 Hz, 1H), 3.63-3.57 (m, 1H), 2.80 (AB fragment of an ABX system, $\Delta\nu$ = 56 Hz, J_{AX} = 2.8 Hz, J_{BX} = 11.3 Hz, J_{AB} = 13.2 Hz, 2H), 2.11-2.02 (m, 1H), 1.26 (s, 9H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 146.5, 131.8, 130.3, 124.7, 62.4, 59.2, 57.4,

34.1, 23.2, 19.0, 17.8 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{25}O_2NS_2Na$ 338.1219; found 338.1216; FTIR peaks (cm^{-1}): 1062 (ν_{SONH}), 1017 (ν_{SOPh}).

(R_S,S_C,S_S)-N-[1-(Phenylsulfinyl)-3-methylbut-2-yl]-2-methyl-2-propanesulfinamide, **9(R_S,S_C,S_S)**

It was prepared following the general procedure from 351 mg of the (*R*)-*tert*-butanesulfinylimine **6(R_S)** (2 mmol), 280 mg of phenyl methyl sulfoxide **2(S_S)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (9 mL). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 1:2) to give **9(R_S,S_C,S_S)** (575 mg, 1.82 mmol, 91% yield) as a white solid; mp 127 °C; $[\alpha]_D^{20}$: -72.4 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.70-7.67 (m, 2H), 7.60-7.55 (m, 3H), 4.07 (d, *J* = 8.1 Hz, 1H), 3.28 (m, 1H), 2.99 (AB fragment of an ABX system, $\Delta\nu$ = 40 Hz, J_{AX} = 4.8 Hz, J_{BX} = 8.3 Hz, J_{AB} = 13.4 Hz, 2H), 2.10-2.04 (m, 1H), 1.20 (s, 9H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 145.9, 132.3, 130.4, 125.4, 61.8, 59.7, 57.1, 33.4, 23.1, 18.5, 18.0 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{25}O_2NS_2Na$ 338.1219; found 338.1217; FTIR peaks (cm^{-1}): 1066 (ν_{SONH}), 1032 (ν_{SOPh}).

(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **10(R_S,S_C,R_S)**

It was prepared following the general procedure from 454 mg of the (*R*)-*tert*-butanesulfinylimine **4(R_S)** (1.75 mmol), 210 mg of *tert*-butyl methyl sulfoxide **3(R_S)** (1.75 mmol), 5.25 mL of LHMDS (5.25 mmol) and THF (10 mL). After 1 h, the resulting residue was purified by flash chromatography (CH_2Cl_2:^{i}PrOH, 80:1) to give **10(R_S,S_C,R_S)** (516 mg, 1.36 mmol, 78% yield) as a yellow solid; mp 158-160 °C; $[\alpha]_D^{20}$: +70.5 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.94-7.87 (m, 4H), 7.59 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.55-7.50 (m, 2H), 4.93 (td, J_1 = 2.9 Hz, J_2 = 10.2 Hz, J_3 = 10.6 Hz, 1H), 4.86 (d, *J* = 10.0 Hz, 1H), 2.97 (AB fragment of an ABX system, $\Delta\nu$ = 171 Hz, J_{AX} = 3.0 Hz, J_{BX} = 10.5 Hz, J_{AB} = 12.8 Hz, 2H), 1.22 (s, 9H), 1.19 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 140.8, 134.2, 133.9, 129.2, 128.8, 128.6, 127.5, 127.2, 126.8, 126.2, 57.7, 57.4, 54.0, 53.3, 23.0 (2) ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{29}O_2NS_2Na$ 402.1532; found 402.1532; FTIR peaks (cm^{-1}): 1066 (ν_{SONH}), 1002 (ν_{SOtBu}).

(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **10(R_S,S_C,S_S)**

It was prepared following the general procedure from 454 mg of the (*R*)-*tert*-butanesulfinylimine **4(R_S)** (1.75 mmol), 210 mg of *tert*-butyl methyl sulfoxide **3(S_S)** (1.75 mmol), 5.25 mL of LHMDS (5.25 mmol) and THF (10 mL). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:MeOH, 40:1) to give **10(R_S,S_C,S_S)** (450 mg, 1.19 mmol, 68% yield) as a white solid; mp 148-160 °C; $[\alpha]_D^{20}$: -42.4 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.95-7.89 (m, 4H), 7.61 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.54-7.53 (m, 2H), 4.99 (d, *J* = 5.6 Hz, 1H), 4.92-4.88 (m, 1H), 3.06 (AB fragment of an ABX system, $\Delta\nu$ = 33 Hz, J_{AX} = 7.1 Hz, J_{BX} = 7.8 Hz, J_{AB} = 12.9 Hz, 2H), 1.18 (s, 9H), 1.17 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 139.6, 134.2, 134.1, 129.5, 128.9, 128.6, 127.8, 127.5, 127.4, 126.4, 58.4, 56.9, 54.0, 53.3, 22.8 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{29}O_2NS_2Na$ 402.1532; found 402.1525; FTIR peaks (cm^{-1}): 1071 (ν_{SONH}), 1024 (ν_{SOtBu}).

(R_S,S_C,R_S)-N-[2-(tert-butylsulfinyl)-1-phenylethyl]-2-methyl-2-propanesulfinamide,

11(*R_S*,*S_C*,*R_S*)

It was prepared following the general procedure from 136 mg of the (*R*)-*tert*-butanesulfinylimine **5(*R_S*)** (0.65 mmol), 78 mg of *tert*-butyl methyl sulfoxide **3(*R_S*)** (0.65 mmol), 1.95 mL of LHMDS (1.95 mmol) and THF (4 mL). After 1 h, the resulting residue was purified by flash chromatography (CH_2Cl_2:^{i}PrOH, 40:1) to give **11(*R_S*,*S_C*,*R_S*)** (165 mg, 0.5 mmol, 77% yield) as a yellow solid; mp 194-196 °C; $[\alpha]_D^{20}$: +77.6 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.46-7.44 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.29 (m, 1H), 4.77-4.76 (m, 2H), 3.06-2.99 (m, 1H), 2.72-2.69 (m, 1H), 1.20 (s, 9H), 1.18 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 144.0, 130.2, 129.4, 128.7, 58.3, 58.0, 54.9, 53.9, 23.6 (2) ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{27}O_2NS_2Na$ 352.1375; found 352.1372; FTIR peaks (cm^{-1}): 1067 (ν_{SONH}), 1026 (ν_{SOtBu}).

(R_S,S_C,S_S)-N-[2-(tert-butylsulfinyl)-1-phenylethyl]-2-methyl-2-propanesulfinamide,

11(*R_S*,*S_C*,*S_S*)

It was prepared following the general procedure from 419 mg of the (*R*)-*tert*-butanesulfinylimine **5(*R_S*)** (2 mmol), 240 mg of *tert*-butyl methyl sulfoxide **3(*S_S*)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (10 mL). After 1 h, the resulting residue was purified by flash chromatography (CH_2Cl_2:^{i}PrOH, 60:1) to give **11(*R_S*,*S_C*,*S_S*)** (428 mg, 1.3 mmol, 65% yield) as a yellow solid; mp 161-163 °C; $[\alpha]_D^{20}$: -68.9 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.48-7.45 (m, 2H), 7.41-7.38 (m, 2H), 7.35-7.32 (m, 1H), 4.90 (d, J = 5.4 Hz, 1H), 4.73 (dd, J_1 = 7.2 Hz, J_2 = 13.3 Hz, 1H), 2.95 (AB fragment of an ABX system, $\Delta\nu$ = 26 Hz, J_{AX} = 7.2 Hz, J_{BX} = 7.6 Hz, J_{AB} = 12.9 Hz, 2H), 1.17 (s, 9H), 1.17 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 142.2, 129.7, 129.2, 128.7, 58.4, 56.9, 54.0, 53.6, 22.9, 22.8 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{27}O_2NS_2Na$ 352.1375; found 352.1371; FTIR peaks (cm^{-1}): 1056 (ν_{SONH}), 1004 (ν_{SOtBu}).

(R_S,S_C,R_S)-N-[1-(tert-butylsulfinyl)-3-methylbutan-2-yl]-2-methyl-2-propanesulfinamide,

12(*R_S*,*S_C*,*R_S*)

It was prepared following the general procedure from 114 mg of the (*R*)-*tert*-butanesulfinylimine **6(*R_S*)** (0.65 mmol), 78 mg of *tert*-butyl methyl sulfoxide **3(*R_S*)** (0.65 mmol) 1.95 mL of LHMDS (1.95 mmol) and THF (4 mL). After 1 h, the resulting residue was purified by flash chromatography (CH_2Cl_2:^{i}PrOH, 40:1) to give **12(*R_S*,*S_C*,*R_S*)** (130 mg, 0.44 mmol, 68% yield) as a white solid; mp 177-179 °C; $[\alpha]_D^{20}$: +93 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 4.00 (d, J = 9.6 Hz, 1H), 3.53-3.48 (m, 1H), 2.53 (AB fragment of an ABX system, $\Delta\nu$ = 60 Hz, J_{AX} = 2.5 Hz, J_{BX} = 10.9 Hz, J_{AB} = 12.8 Hz, 2H), 2.11-2.05 (m, 1H), 1.19 (s, 9H), 1.18 (s, 9H), 0.98 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 59.3, 57.3, 53.1, 49.7, 34.5, 23.2, 23.0, 19.2, 18.0 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{29}O_2NS_2Na$ 318.1532; found 318.1530; FTIR peaks (cm^{-1}): 1061 (ν_{SONH}), 1026 (ν_{SOtBu}).

(R_S,S_C,S_S)-N-[1-(tert-butylsulfinyl)-3-methylbutan-2-yl)]-2-methyl-2-propanesulfinamide, **12(R_S,S_C,S_S)**

It was prepared following the general procedure from 351 mg of the (*R*)-*tert*-butanesulfinylimine **6(R_S)** (2 mmol), 240 mg of *tert*-butyl methyl sulfoxide **3(S_S)** (2 mmol), 6 mL of LHMDS (6 mmol) and THF (9 mL). After 1 hours, the resulting residue was purified by flash chromatography (EtOAc:MeOH, 40:1) to give **12(R_S,S_C,S_S)** (388 mg, 1.31 mmol, 66% yield) as a yellow solid; mp 71-72 °C; $[\alpha]_D^{20}$: -70.9 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 4.19 (d, *J* = 6.9 Hz, 1H), 3.53-3.48 (m, 1H), 2.67 (AB fragment of an ABX system, $\Delta\nu$ = 169 Hz, J_{AX} = 7.6 Hz, J_{BX} = 6.0 Hz, J_{AB} = 13.5 Hz, 2H), 2.19-2.12 (m, 1H), 1.19 (s, 9H), 1.19 (s, 9H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 60.7, 56.9, 54.0, 50.3, 32.8, 23.0, 22.9, 18.7, 18.3 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{29}O_2NS_2Na$ 318.1532; found 318.1532; FTIR peaks (cm^{-1}): 1064 (ν_{SONH}), 1025 (ν_{SOtBu}).

Synthesis of sulfinamide/sulfone ligands: general procedure.[2]

Methyl Tert-butyl sulfone, **20**

To a solution of methyl *tert*-butyl sulfide (0.6 mL, 4.8 mmol, 100 mol%) in CH_2Cl_2 (17 mL) at -78 °C, a solution of *m*CPBA (3.3 g, 14.4 mmol, 300 mol%) in CH_2Cl_2 (18 mL) was added dropwise. After 24 h, the reaction mixture was quenched with a saturated $NaHCO_3$ aqueous solution (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic phases were dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain **20** (654 mg, 4.8 mmol, quant. yield) as a colorless liquid with no further purification; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.80 (s, 3H), 1.42 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 58.8, 34.3, 23.5 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_5H_{12}O_2SNa$ 159.0450; found 159.0448.

(R_S,S_C)-N-[2-(Tert-butylsulfonyl)-1-(2-naphthyl)ethyl]-2-methyl-2-propanesulfinamide, **21(R_S,S_C)**

It was prepared following the general procedure for the synthesis of sulfonamide/sulfoxide ligands from 259 mg of (*R*)-*tert*-butanesulfinylimine **4(R_S)** (1 mmol), 136 mg of methyl *tert*-butyl sulfone **20** (1 mmol) and 3 mL of 1 M solution of LHMDS (3 mmol). After 1 h, the resulting residue was purified by flash chromatography (EtOAc:CH_2Cl_2, 1:3) to give **21(R_S,S_C)** (237 mg, 0.6 mmol, 60% yield) as a white solid; mp 196-198 °C; $[\alpha]_D^{20}$: -3.7 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, CD_3CN): δ 7.97-7.88 (m, 4H), 7.61 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.59-7.51 (m, 2H), 5.14-5.10 (m, 1H), 4.91 (d, *J* = 6.5 Hz, 1H), 3.60 (AB fragment of an ABX system, $\Delta\nu$ = 125 Hz, J_{AX} = 4.1 Hz, J_{BX} = 8.9 Hz, J_{AB} = 13.8 Hz, 2H), 1.36 (s, 9H), 1.18 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 139.3, 134.2, 134.1, 129.3, 128.9, 128.6, 127.7, 127.5, 127.4, 126.6, 60.6, 57.1, 56.4, 52.3, 23.3, 22.8 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{29}O_3NS_2Na$ 418.1485; found 418.1481; FTIR peaks (cm^{-1}): 1110 (ν_{SO_2tBu}), 1069 (ν_{SONH}).

Synthesis of Pd complexes: general procedure.

A solution of the corresponding ligand **7-12**, **19** or **21** (100 mol%) and $Pd(CNCH_3)_2Cl_2$ (100 mol%) in dry CH_2Cl_2, under argon atmosphere, is stirred at room temperature.

Once the starting material was consumed (24-48 h), the complexes are precipitated with Et_2O (8 mL) and filtered to obtain the desired compounds without further purification.

cis-Dichloro[(S_C,S_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(*S*$_C$,*S*$_S$)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **7(*R*$_S$,*S*$_C$,*R*$_S$)** (200 mg, 0.5 mmol) and $Pd(CNCH_3)_2Cl_2$ (180 mg, 0.5 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **13(*S*$_C$,*S*$_S$)** (223 mg, 0.47 mmol, 94% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.27-8.25 (m, 2H), 8.00 (bs, 1H), 7.92-7.87 (m, 3H), 7.76-7.71 (m, 3H), 7.56-7.54 (m, 3H), 5.05 (bs, 1H), 5.03-4.97 (m, 1H), 4.88-4.76 (m, 1H), 4.00 (dd, J_1 = 13.5 Hz, J_2 = 13.5 Hz, 1H), 3.86 (dt, J_1 = 2.9 Hz, J_2 = 13.8 Hz, 1H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 139.9, 135.1, 134.4, 134.0, 132.8, 130.7, 129.8, 129.0, 128.7, 128.1, 127.9 (2), 127.5, 125.6, 71.5, 59.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}ONCl_2NaPdS$ 493.9335; found 493.9323; FTIR peaks (cm^{-1}): 1133 (ν_{SOPh}).

cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(*S*$_C$,*R*$_S$)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **7(*R*$_S$,*S*$_C$,*S*$_S$)** (200 mg, 0.5 mmol) and $Pd(CNCH_3)_2Cl_2$ (180 mg, 0.5 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **13(*S*$_C$,*R*$_S$)** (236 mg, 0.5 mmol, quant. yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.53 (d, J = 7.3 Hz, 2H), 7.92-7.80 (m, 7H), 7.55-7.54 (m, 2H), 7.50-7.48 (m, 1H), 4.95 (bs, 1H), 4.82 (bs, 1H), 4.35-4.29 (m, 1H), 4.07-4.02 (m, 2H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 140.7, 135.8, 134.4, 134.1, 132.4, 131.1, 129.9, 129.0, 128.7, 128.5, 128.1, 127.9 (2), 125.4, 69.7, 56.9 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}ONCl_2NaPdS$ 493.9335; found 493.9323; FTIR peaks (cm^{-1}): 1133 (ν_{SOPh}).

cis-Dichloro[(S_C,S_S)-1-(Phenyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **14(*S*$_C$,*S*$_S$)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **8(*R*$_S$,*S*$_C$,*R*$_S$)** (200 mg, 0.57 mmol) and $Pd(CNCH_3)_2Cl_2$ (206 mg, 0.57 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **14(*S*$_C$,*S*$_S$)** (231 mg, 0.55 mmol, 96% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.26-8.24 (m, 2H), 7.77-7.70 (m, 3H), 7.48-7.46 (m, 2H), 7.42-7.37 (m, 3H), 5.0 (bs, 1H), 4.87-4.79 (m, 2H), 3.89 (dd, J_1 = 13.5 Hz, J_2 = 13.5 Hz, 1H), 3.78-3.75 (m, 1H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 139.9, 135.3, 135.1, 130.7, 130.4, 130.0, 128.3, 127.5, 71.5, 59.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{15}ONCl_2NaPdS$ 443.9178; found 443.9166; FTIR peaks (cm^{-1}): 1138 (ν_{SOPh}).

cis-Dichloro[(S_C,R_S)-1-(Phenyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **14(*S*$_C$,*R*$_S$)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **8(*R*$_S$,*S*$_C$,*S*$_S$)** (200 mg, 0.57 mmol) and $Pd(CNCH_3)_2Cl_2$ (206 mg, 0.57 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **14(*S*$_C$,*R*$_S$)** (241 mg, 0.57 mmol, quant. yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.52-8.51 (m, 2H), 7.82-7.77 (m, 3H), 7.40-7.37 (m, 5H), 4.96 (bs, 1H), 4.76 (bs, 1H), 4.25 (dd, J_1 = 12.9 Hz, J_2 = 13.2 Hz, 1H), 3.96-3.88 (m, 2H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 140.5, 135.7, 135.0, 131.1, 130.3, 130.0, 128.4,

128.3, 69.7, 56.8 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{15}ONCl_2NaPdS$ 443.9178; found 443.9167; FTIR peaks (cm^{-1}): 1125 (ν_{SOPh}).
It was also prepared following the general procedure from amine/sulfoxide ligand **24(S_C,S_S)** (20 mg, 0.08 mmol) and $Pd(CNCH_3)_2Cl_2$ (29.3 mg, 0.08 mmol) in CH_2Cl_2 (1.3 mL). After 2 h, the solvent was evaporated under reduced pressure to obtain **14(S_C,R_S)** (35 mg, 0.08 mmol, quant. yield) as a brown solid.

cis-Dichloro[(S_C,S_S)-3-methyl-1-(phenylsulfinyl)-2-butylamine]palladium (II), **15(S_C,S_S)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **9(R_S,S_C,R_S)** (200 mg, 0.63 mmol) and $Pd(CNCH_3)_2Cl_2$ (228 mg, 0.63 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **15(S_C,S_S)** (214 mg, 0.55 mmol, 88% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.19-8.17 (m, 2H), 7.77-7.69 (m, 3H), 4.52 (bs, 1H), 4.26 (bs, 1H), 3.60 (dt, J_1 = 2.8, J_2 = 13.4 Hz, 1H), 3.50-3.42 (m, 1H), 3.33 (dd, J_1 = 13.5 Hz, J_2 = 13.5 Hz, 1H), 2.04-1.97 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 140.1, 135.0, 130.6, 127.4, 70.0, 61.3, 32.1, 19.9, 19.4 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{17}ONCl_2NaPdS$ 409.9335; found 409.9325; FTIR peaks (cm^{-1}): 1141 (ν_{SOPh}).

cis-Dichloro[(S_C,R_S)-3-methyl-1-(phenylsulfinyl)-2-butylamine]palladium (II), **15(S_C,R_S)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **9(R_S,S_C,S_S)** (200 mg, 0.63 mmol) and $Pd(CNCH_3)_2Cl_2$ (228 mg, 0.63 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **15(S_C,R_S)** (235 mg, 0.6 mmol, 96% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.43-8.41 (m, 2H), 7.83-7.74 (m, 3H), 4.43 (bs, 1H), 4.22 (bs, 1H), 3.72-3.70 (m, 2H), 2.54-2.46 (m, 1H), 2.02-1.97 (m, 1H), 0.91 (d, J = 3.9 Hz, 3H), 0.89 (d, J = 3.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 140.7, 135.6, 131.0, 128.2, 68.0, 58.9, 31.7, 19.5, 19.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{17}ONCl_2NaPdS$ 409.9335; found 409.9323; FTIR peaks (cm^{-1}): 1129 (ν_{SOPh}).

cis-Dichloro[(S_C,S_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine]palladium (II), **16(S_C,S_S)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **10(R_S,S_C,R_S)** (200 mg, 0.53 mmol) and $Pd(CNCH_3)_2Cl_2$ (189 mg, 0.53 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **16(S_C,S_S)** (219 mg, 0.48 mmol, 92% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.03 (bs, 1H), 7.95-7.90 (m, 3H), 7.60-7.56 (m, 3H), 4.92-4.81 (m, 2H), 4.57 (bs, 1H), 3.72 (dd, J_1 = 13.5 Hz, J_2 = 13.5 Hz, 1H), 3.39 (dt, J_1 = 3.1 Hz, J_2 = 13.5 Hz, 1H), 1.68 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 134.4, 134.0, 133.3, 129.7, 129.0, 128.7, 128.0, 127.9, 127.9, 125.7, 67.3, 60.9, 58.5, 24.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{21}ONCl_2NaPdS$ 473.9648; found 473.9636; FTIR peaks (cm^{-1}): 1124 (ν_{SOtBu}).

cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine]palladium (II), **16(S_C,R_S)**

It was prepared following the general procedure from sulfinamide/sulfoxide ligand **10(R_S,S_C,S_S)** (200 mg, 0.53 mmol) and $Pd(CNCH_3)_2Cl_2$ (189 mg, 0.53 mmol) in CH_2Cl_2 (8 mL). After 24 h, the complex was precipitated with Et_2O and filtered to give **16(S_C,R_S)** (231 mg, 0.51 mmol, 97% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.20 (bs, 1H), 7.97-7.91 (m, 3H), 7.69-7.67 (m, 1H), 7.58-7.57 (m, 2H), 4.91 (bs, 1H), 4.77 (bs, 1H), 4.42-4.37 (m, 1H), 4.03-3.99 (m, 1H), 3.78 (dd, J_1 = 9.6 Hz, J_2 = 14.4 Hz, 1H), 1.69 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 134.3, 134.0, 133.9, 129.8, 129.0, 128.7, 128.0 (2), 127.4, 125.4, 68.8, 63.3, 58.5, 24.3 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{21}ONCl_2NaPdS$ 473.9648; found: 473.9637; FTIR peaks (cm^{-1}): 1102 (ν_{SOtBu}).

cis-Dichloro[(S_C,S_S)-2-(tert-butylsulfinyl)-1-(phenyl)ethylamine]palladium (II), **17(S_C,S_S)**

It was prepared following the general procedure from sulfinamide/sulfoxide ligand **11(R_S,S_C,R_S)** (100 mg, 0.3 mmol) and $Pd(CNCH_3)_2Cl_2$ (109 mg, 0.3 mmol) in CH_2Cl_2 (4 mL). After 24 h, the complex was precipitated with Et_2O and filtered to give **17(S_C,S_S)** (94 mg, 0.23 mmol, 78% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 7.50-7.48 (m, 2H), 7.45-7.38 (m, 3H), 4.74-4.68 (m, 2H), 4.47 (bs, 1H), 3.60 (dd, J_1 = 13.6 Hz, J_2 = 13.6 Hz, 1H), 3.30 (dt, J_1 = 3.1 Hz, J_2 = 13.3 Hz, 1H), 1.66 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 135.9, 130.3, 130.0, 128.4, 67.3, 60.9, 58.4, 24.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{19}ONCl_2NaPdS$ 423.9491; found 423.9478; FTIR peaks (cm^{-1}): 1124 (ν_{SOtBu}).

cis-Dichloro[(S_C,R_S)-2-(tert-butylsulfinyl)-1-(phenyl)ethylamine]palladium (II), **17(S_C,R_S)**

It was prepared following the general procedure from sulfinamide/sulfoxide ligand **11(R_S,S_C,S_S)** (200 mg, 0.61 mmol) and $Pd(CNCH_3)_2Cl_2$ (218 mg, 0.61 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **17(S_C,R_S)** (244 mg, 0.61 mmol, quant. yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 7.64 (d, J = 7.7 Hz, 2H), 7.48-7.45 (m, 2H), 4.42-7.39 (m, 1H), 4.81 (bs, 1H), 4.61 (bs, 1H), 4.26-4.21 (m, 1H), 3.91 (dd, J_1 = 4.8 Hz, J_2 = 14.3 Hz, 1H), 3.64 (dd, J_1 = 9.2 Hz, J_2 = 14.3 Hz, 1H), 1.66 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 136.5, 130.1, 130.0, 128.0, 68.7, 63.4, 58.4, 24.3 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{19}ONCl_2NaPdS$ 423.9491; found 423.9479; FTIR peaks (cm^{-1}): 1115 (ν_{SOtBu}).

cis-Dichloro[(S_C,S_S)-1-(tert-butylsulfinyl)-3-methyl-2-butylamine]palladium (II), **18(S_C,S_S)**

It was prepared following the general procedure from sulfinamide/sulfoxide ligand **12(R_S,S_C,R_S)** (100 mg, 0.34 mmol) and $Pd(CNCH_3)_2Cl_2$ (122 mg, 0.34 mmol) in CH_2Cl_2 (4 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **18(S_C,S_S)** (119 mg, 0.32 mmol, 95% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 4.25 (bs, 1H), 3.95 (bs, 1H), 3.38-3.31 (m, 1H), 3.10-3.08 (m, 2H), 2.03-1.99 (m, 1H), 1.62 (s, 9H), 1.01 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 67.0, 60.5, 58.8, 32.2, 23.9, 19.8, 19.3 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{21}ONCl_2NaPdS$ 389.9648; found 389.9637; FTIR peaks (cm^{-1}): 1121 (ν_{SOtBu}).

cis-Dichloro[(S_C,R_S)-1-(tert-butylsulfinyl)-3-methyl-2-butylamine]palladium (II), **18(S_C,R_S)**
It was prepared following the general procedure from sulfinamide/sulfoxide ligand **12(R_S,S_C,S_S)** (200 mg, 0.68 mmol) and $Pd(CNCH_3)_2Cl_2$ (243 mg, 0.68 mmol) in CH_2Cl_2 (8 mL). After 24 h, the complex was precipitated with Et_2O and filtered to give **18(S_C,R_S)** (199 mg, 0.54 mmol, 80% yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 4.43 (bs, 1H), 4.17 (bs, 1H), 3.47 (dd, J_1 = 4.7 Hz, J_2 = 14.4 Hz, 1H), 3.29 (ddd, J_1 = 1.4 Hz, J_2 = 6.0 Hz, J_3 = 14.4 Hz, 1H), 2.81-2.77 (m, 1H), 2.38-2.31 (m, 1H), 1.62 (s, 9H), 1.08 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 68.2, 61.4, 59.9, 32.2, 24.2, 19.6, 19.3 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{21}ONCl_2NaPdS$ 389.9648; found 389.9636; FTIR peaks (cm^{-1}): 1121 (ν_{SOtBu}).

cis-Dichloro[(S_C,R_S)/(S_C,S_S)-1-(2-Naphthyl)-2-(tert-butylsulfonyl)ethylamine]palladium (II), **22(S_C,R_S)/(S_C,S_S)**
It was prepared following the general procedure from sulfinamide/sulfone ligand **21(R_S,S_C)** (200 mg, 0.51 mmol) and $Pd(CNCH_3)_2Cl_2$ (182 mg, 0.51 mmol) in CH_2Cl_2 (8 mL). After 48 h, the complex was precipitated with Et_2O and filtered to give **22(S_C,R_S)/(S_C,S_S)** (237 mg, 0.51 mmol, quant. yield) as a brown solid; mp: decomposes before melting; ^{1}H-NMR (500 MHz, CD_3CN): δ 8.20 (bs, 1H), 8.10 (bs, 1H), 8.03-7.99 (m, 3H), 7.97-7.93 (m, 3H), 7.73 (dd, J_1 = 1.6 Hz, J_2 = 8.6 Hz, 1H), 7.69 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.61-7.57 (m, 4H), 5.26-5.25 (m, 1H), 5.06-5.01 (m, 1H), 4.18 (dd, J_1 = 9.3 Hz, J_2 = 14.1 Hz, 1H), 3.94 (dd, J_1 = 9.3 Hz, J_2 = 14.2 Hz, 1H), 3.68 (dd, J_1 = 4.0 Hz, J_2 = 14.2 Hz, 1H), 3.35 (dd, J_1 = 3.7 Hz, J_2 = 14.1 Hz, 1H), 1.42 (s, 9H), 1.37 (s, 9H) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ 137.1, 134.6, 134.3, 134.2, 133.9, 132.5, 130.1, 129.5, 129.3, 129.1, 129.0, 128.9, 128.7 (2), 128.4, 128.0, 127.8, 127.7, 126.6, 125.9, 61.3, 60.7, 54.8, 51.8, 50.8, 48.8, 23.2 (2) ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{21}O_2NCl_2NaPdS$ 489.9597; found 489.9591; FTIR peaks (cm^{-1}): 1108 (ν_{SO2tBu}).

Synthesis of amine/sulfoxide ligands.

Method A: Desulfinylation of sulfinamide/sulfoxide ligands: general procedure.
To a solution of the corresponding ligand in dry MeOH at 0°C under argon atmosphere, trifluoroacetic acid (3500 mol%) was added dropwise. The reaction mixture was slowly warmed to room temperature. Once the starting material was consumed, the solvent was evaporated under reduced pressure. The residue was dissolved in 0.3 mL dry MeOH and passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine.

Method B: Displacement of the amine/sulfoxide ligand from Pd complexes: general procedure.
To a solution of the corresponding Pd complex (100 mol%) in dry CH_2Cl_2 under argon atmosphere, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (100 mol%) was added dropwise. The reaction mixture was stirred 1 h at room temperature. Then, the reaction mixture was passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine.

(S_C,R_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine, **24(S_C,R_S)**

Method A: It was prepared following the general procedure from **10(R_S,S_C,R_S)** (100 mg, 0.26 mmol), trifluoroacetic acid (0.86 mL, 11.2 mmol) and MeOH (1 mL). After five days, the residue was passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine **24(S_S,R_C)** (44 mg, 0.16 mmol, 62% yield) as an orange oil; $[\alpha]_D^{20}$: +17.5 (*c* 1, MeOH); ^{1}H-NMR (500 MHz, MeOD): δ 7.91-7.84 (m, 4H), 7.56 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.51-7.46 (m, 2H), 4.58 (dd, J_1 = 3.1 Hz, J_2 = 10.3 Hz, 1H), 2.98 (AB fragment of an ABX system, $\Delta\nu$ = 130 Hz, J_{AX} = 10.3 Hz, J_{BX} = 3.1 Hz, J_{AB} = 13.1 Hz, 2H), 1.28 (s, 9H) ppm; ^{13}C-NMR (125 MHz, MeOD): δ 142.2, 135.0, 134.5, 129.7, 129.0, 128.7, 127.4, 127.1, 126.1, 125.6, 55.6, 54.3, 52.3, 23.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}ONS$ 276.1417; found 276.1420.

(S_C,S_S)- 1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine, **24(S_C,S_S)**

Method A: It was prepared following the general procedure from **10(R_S,S_C,S_S)** (100 mg, 0.26 mmol), trifluoroacetic acid (0.86 mL, 11.2 mmol) and MeOH (1 mL). After five days, the residue was passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine **24(S_S,S_C)** (64 mg, 0.23 mmol, 88% yield) as an orange oil; $[\alpha]_D^{20}$: -55.5 (*c* 1, MeOH); ^{1}H-NMR (500 MHz, MeOD): δ 7.92-7.85 (m, 4H), 7.59 (dd, J_1 = 1.7 Hz, J_2 = 8.5 Hz, 1H), 7.52-7.47 (m, 2H), 4.59 (dd, J_1 = 5.9 Hz, J_2 = 8.7 Hz, 1H), 3.11 (AB fragment of an ABX system, $\Delta\nu$ = 25 Hz, J_{AX} = 8.7 Hz, J_{BX} = 5.9 Hz, J_{AB} = 12.9 Hz, 2H), 1.22 (s, 9H) ppm; ^{13}C-NMR (125 MHz, MeOD): δ 140.5, 134.9, 134.7, 129.9, 129.0, 128.7, 127.4 (2), 127.3, 125.4, 54.6, 53.8, 53.7, 22.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}ONS$ 276.1417; found 276.1418.

Method B: It was prepared following the general procedure from **16(S_C,R_S)** (40 mg, 0.09 mmol), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (13 µL, 0.09 mmol) and CH_2Cl_2 (2 mL). It was obtained the corresponding amine **24(S_S,S_C)** (15 mg, 0.05 mmol, 68% yield) as an orange oil.

(S_C,S_S)-1-Phenyl-2-(phenylsulfinyl)ethylamine, **19(S_C,S_S)**

Method A: It was prepared following the general procedure from **8(R_S,S_C,S_S)** (100 mg, 0.29 mmol), trifluoroacetic acid (0.33 mL, 4.35 mmol, 1500 mol%) and MeOH (1 mL). After two days, the residue was passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine **19(S_S,S_C)** (45.1 mg, 0.18 mmol, 64% yield) as a crystalline solid; mp 93-95 °C; $[\alpha]_D^{20}$: -88.2 (*c* 1, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.52-7.48 (m, 3H), 7.39-7.33 (m, 4H), 7.29-7.28 (m, 1H), 4.57 (dd, J_1 = 5.1 Hz, J_2 = 8.3 Hz), 3.07 (AB fragment of an ABX system, $\Delta\nu$ = 135 Hz, J_{AX} = 8.4 Hz, J_{BX} = 5.0 Hz, J_{AB} = 13.1 Hz, 2H), 1.97 (bs, 2H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 144.5, 143.9, 131.3, 129.5, 129.0, 128.0, 126.5, 124.1, 66.7, 53.1 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}ONS$ 246.0947; found 246.0947.

Method B: It was prepared following the general procedure from **14(S_C,R_S)** (40 mg, 0.09 mmol), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (14 µL, 0.09 mmol) and CH_2Cl_2 (2 mL). It was obtained the corresponding amine **19(S_S,S_C)** (23 mg, 0.09 mmol, quant. yield) as a crystalline solid.

(S_C,R_S)-1-(Phenylsulfinyl)-3-methylbut-2-ylamine, **23(S_C,R_S)**

Method A: It was prepared following the general procedure from **9(R_S,S_C,R_S)** (100 mg, 0.32 mmol), trifluoroacetic acid (0.86 mL, 11.2 mmol) and MeOH (3 mL). After seven days, the residue was passed through a cation-exchange column (Isolute SPE SCX-2) to give the corresponding amine **23(S_S,R_C)** (31.4 mg, 0.15 mmol, 46% yield) as a colorless oil; $[\alpha]_D^{20}$: +169.6 (*c* 1, MeOH); ^{1}H-NMR (500 MHz, MeOD): δ 7.74-7.72 (m, 2H), 7.64-7.57 (m, 3H), 3.17 (ddd, J_1 = 2.1 Hz, J_2 = 10.0 Hz, J_3 = 5.1 Hz, 1H), 3.00 (AB fragment of an ABX system, $\Delta\nu$ = 65 Hz, J_{AX} = 10.1 Hz, J_{BX} = 2.2 Hz, J_{AB} = 13.8 Hz, 2H), 1.95 (bs, 2H), 1.83 (oct, *J* = 6.8 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, MeOD): δ 143.8, 132.6, 130.7, 125.3, 60.0, 53.1, 33.9, 18.2 (2) ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{18}ONS$ 212.1104; found 212.1101.

Method B: It was prepared following the general procedure from **15(S_C,S_S)** (40 mg, 0.10 mmol), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (16 µL, 0.10 mmol) and CH_2Cl_2 (2 mL). It was obtained the corresponding amine **23(S_S,R_C)** (22 mg, 0.10 mmol, quant. yield) as a colorless solid.

Acetylation of amine/sulfoxide ligands: general procedure.

To a solution of the corresponding ligand and triethylamine (Et_3N) (300 mol%) in dry CH_2Cl_2 at 0°C under argon atmosphere, acetyl chloride (200 mol%) was added dropwise. The reaction mixture was slowly warmed to room temperature. After stirring for 30 min, the reaction was quenched with saturated aqueous NH_4Cl solution, and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ and NaCl solution and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the reaction crude was purified by flash chromatography to obtain the desired compound.

(S_C,S_S)-N-Acetyl-1-phenyl-2-(phenylsulfinyl)ethylamine, **25(S_C,S_S)**

It was prepared following the general procedure from **19(S_S,S_C)** (23 mg, 0.09 mmol), Et_3N (39 µL, 0.28 mmol), acetyl chloride (13 µL, 0.19 mmol) and CH_2Cl_2 (2 mL). The resulting residue was purified by flash chromatography (CH_2Cl_2:MeOH, 20:1) to give the corresponding amide **25(S_S,S_C)** (27 mg, 0.09 mmol, quant. yield) as a colorless solid; mp 172-174 °C; $[\alpha]_D^{20}$: -63.8 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.69-7.68 (m, 2H), 7.54-7.50 (m, 3H), 7.32-7.26 (m, 5H), 6.71 (d, *J* = 6.6 Hz, 1H), 5.43 (m, 1H), 3.23 (AB fragment of an ABX system, $\Delta\nu$ = 90 Hz, J_{AX} = 10.3 Hz, J_{BX} = 4.9 Hz, J_{AB} = 13.6 Hz, 2H), 2.06 (s, 3H), 1.27 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.0, 143.8, 140.3, 131.6, 129.6, 129.1, 128.2, 126.5, 124.2, 63.9, 51.1, 23.5 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{17}O_2NNaS$ 310.0872; found 310.0870.

(S_C,R_S)-N-Acetyl-1-(Phenylsulfinyl)-3-methylbut-2-ylamine, **26(S_C,R_S)**

It was prepared following the general procedure from **23(S_S,R_C)** (22 mg, 0.10 mmol), Et_3N (43 µL, 0.31 mmol), acetyl chloride (15 µL, 0.21 mmol) and CH_2Cl_2 (2 mL). The resulting residue was purified by flash chromatography (CH_2Cl_2:MeOH, 15:1) to give the corresponding amide **26(S_S,R_C)** (19 mg, 0.07 mmol, 73% yield) as a white solid; mp 158-160 °C; $[\alpha]_D^{20}$: +80.6 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.55-7.52 (m, 3H), 6.58 (d, *J* = 8.5 Hz, 1H), 4.12-4.06 (m, 1H), 3.01 (AB fragment of an ABX system, $\Delta\nu$ = 45 Hz, J_{AX} = 6.7 Hz, J_{BX} = 3.4 Hz, J_{AB} = 13.6 Hz, 2H), 2.32-2.24 (m, 1H),

2.10 (s, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.1, 143.8, 131.5, 129.6, 124.0, 59.6, 53.1, 31.5, 23.7, 19.8, 19.6 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{19}O_2NNaS$ 276.1029; found 276.1029.

(S_C,R_S)-N-Acetyl-1-(2-naphthyl)-2-(tert-butylsulfinyl)ethylamine, **27(S_C,R_S)**
It was prepared following the general procedure from **24(S_S,R_C)** (43 mg, 0.16 mmol), Et_3N (66 µL, 0.47 mmol), acetyl chloride (22 µL, 0.31 mmol) and CH_2Cl_2 (4 mL). The resulting residue was purified by flash chromatography (CH_2Cl_2:MeOH, 20:1) to give the corresponding amide **27(S_S,R_C)** (49 mg, 0.15 mmol, 98% yield) as a yellow oil; $[\alpha]_D^{20}$: +115.7 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.86-7.82 (m, 4H), 7.50-7.47 (m, 3H), 5.89-5.86 (m, 1H), 3.03 (AB fragment of an ABX system, $\Delta\nu$ = 55 Hz, J_{AX} = 3.6 Hz, J_{BX} = 5.3 Hz, J_{AB} = 13.0 Hz, 2H), 2.10 (s, 3H), 1.20 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.7, 137.0, 133.5, 133.1, 128.8, 128.3, 127.8, 126.5, 126.3, 125.5, 124.5, 53.6, 51.2, 49.5, 23.7, 22.8 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}O_2NNaS$ 340.1342; found 340.1335.

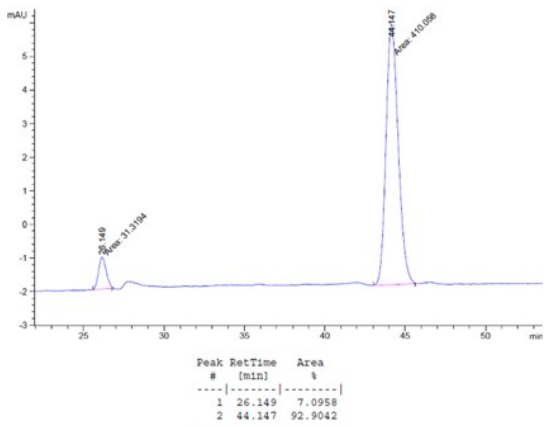
(S_C,S_S)-N-Acetyl-1-(2-naphthyl)-2-(tert-butylsulfinyl)ethylamine, **27(S_C,S_S)**
It was prepared following the general procedure from **24(S_S,S_C)** (60 mg, 0.22 mmol), Et_3N (66 µL, 0.65 mmol), acetyl chloride (34 µL, 0.44 mmol) and CH_2Cl_2 (6 mL). The resulting residue was purified by flash chromatography (CH_2Cl_2:MeOH, 20:1) to give the corresponding amide **27(S_S,S_C)** (67 mg, 0.21 mmol, 97% yield) as a yellow solid; mp 186-188 °C; $[\alpha]_D^{20}$: +36.2 (*c* 1, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.86-7.81 (m, 4H), 7.49-7.43 (m, 3H), 6.96 (d, *J* = 5.5 Hz, 1H), 5.56-5.52 (m, 1H), 2.93 (AB fragment of an ABX system, $\Delta\nu$ = 105 Hz, J_{AX} = 5.2 Hz, J_{BX} = 11.1 Hz, J_{AB} = 13.5 Hz, 2H), 2.06 (s, 3H), 1.27 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.2, 138.6, 133.5, 133.2, 129.1, 128.1, 127.8, 126.6, 126.4, 125.4, 124.1, 54.1, 52.7, 52.2, 23.5, 22.9 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{23}O_2NNaS$ 340.1342; found 340.1336.

Catalysis: Asymmetric arylation of cyclopropane:

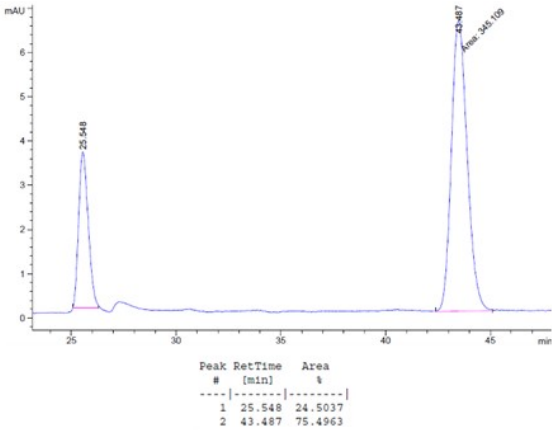
N-(2,3,4,5,6-pentafluorophenyl)-cyclopropanecarboxamide, **32**
To a solution of 2,3,4,5,6-pentafluoroaniline (2 g, 10.92 mmol, 100 mol%) in 25 mL of dried toluene, cyclopropanecarbonyl chloride (1 mL, 10.92 mmol, 100 mol%) was added dropwise under vigorous stirring. The resulting mixture was stirred 24 h at reflux. Upon cooling at 0°C, the crystallization of the compound from the reaction medium takes place to give **32** (2.4 g, 9.59 mmol, 88% yield) as a white solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.90 (bs, 1H), 1.66-1.58 (m, 1H), 1.16-1.11 (m, 2H), 0.98-0.91 (m, 2H); other data match the reported ones.[3]

(1R,2S)-N-(2,3,4,5-pentafluorophenyl)-2-(p-tolyl)cyclopropane-1-carboxamide, **34(1*R*,2*S*)**

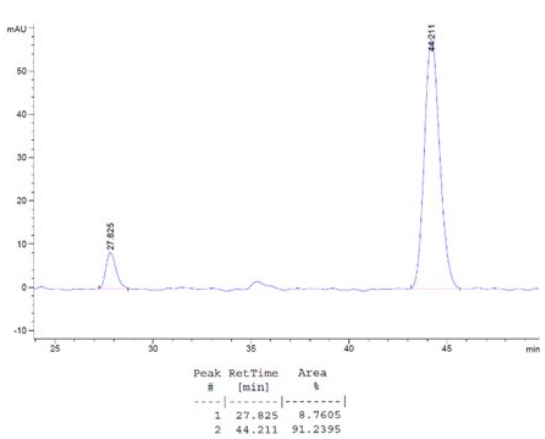
N-(2,3,4,5,6-pentafluorophenyl)-cyclopropanecarboxamide **32** (50 mg, 0.20 mmol, 100 mol%), 4-iodotoluene (87 mg, 0.40 mmol, 200 mol%), silver carbonate (110 mg, 0.40 mmol, 200 mol%), sodium trifluoroacetate (14 mg, 0.10 mmol, 50 mol%), palladium(II) trifluoroacetate (10 mg, 0.030 mmol, 15 mol%) and appropriate ligand (15 mol%) were weighted in a pressure tube. Hexane (1.3 mL) and $CHCl_3$ (0.7 mL) were added and the reaction mixture was stirred at 80 °C or 110 °C during 48 h. After cooling to room temperature, the mixture was filtered with 0.2 µm PTFE membrane, washed with chloroform and evaporated under reduced pressure. Conversion was determined by ^{1}H-NMR spectroscopy of the crude reaction mixture. The crude was purified by preparative thin layer chromatography (toluene:EtOAc, 20:1) to give **34** as a white solid; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.17 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.63 (bs, 1H), 2.64 (q, J = 8.4 Hz, 1H), 2.29 (s, 3H), 2.15-2.10 (m, 1H), 1.81 (dt, J_1 = 5.4 Hz, J_2 = 7.5 Hz, 1H), 1.44 (dt, J_1 = 8.3 Hz, J_2 = 5.3 Hz, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.4, 136.8, 132.6, 129.2, 129.0, 29.9, 25.9, 21.3, 11.5 ppm, carbons corresponding to the pentafluoroamide moiety are not reported; other data match the reported ones. Enantiomeric rate was determined by chiral HPLC using CHIRALPAK ® ADH column (n-hexane/isopropanol 95:5; 0.5 mL/min.; 23 ˚C) t_R = 25.33 min. ((1*S*,2*R*)-isomer), t_R = 43.42 min. ((1*R*,2*S*)-isomer).[4]



34(1*R*,2*S*) obtained with **25(*S*$_C$,*S*$_S$)** at 80 °C

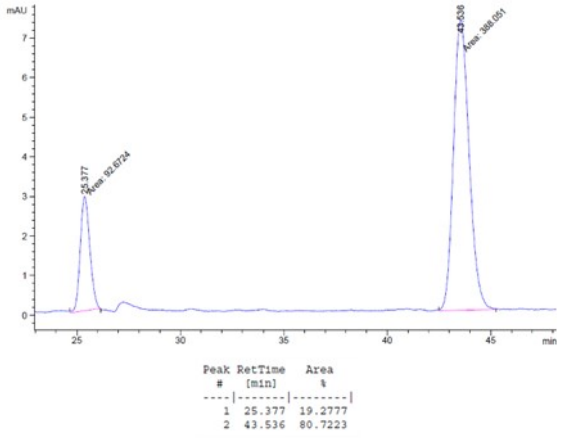


34(1*R*,2*S*) obtained with **26(*S*$_C$,*R*$_S$)** at 80 °C



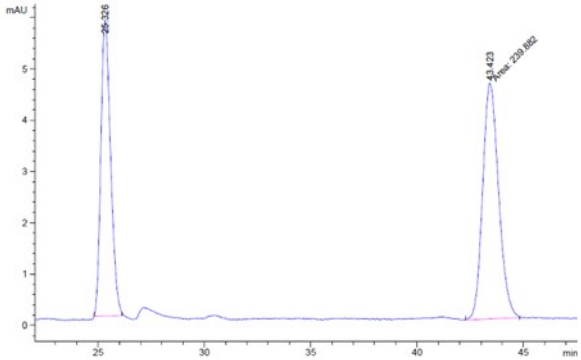
Peak #	RetTime [min]	Area %
1	27.825	8.7605
2	44.211	91.2395

34(1***R***,2***S***)** obtained with **25**(S_C,S_S) at 110 °C



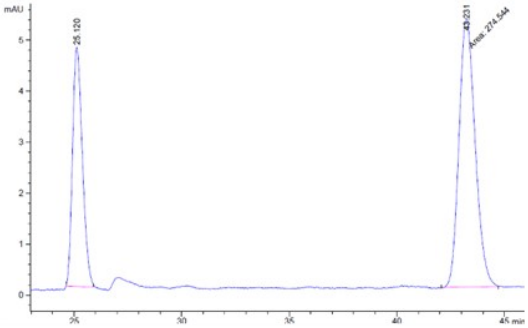
Peak #	RetTime [min]	Area %
1	25.377	19.2777
2	43.536	80.7223

34(1***R***,2***S***)** obtained with **26**(S_C,R_S) at 110 °C



Peak #	RetTime [min]	Area %
1	25.326	43.4078
2	43.423	56.5922

34(1***R***,2***S***)** obtained with **27**(S_C,R_S) at 110 °C



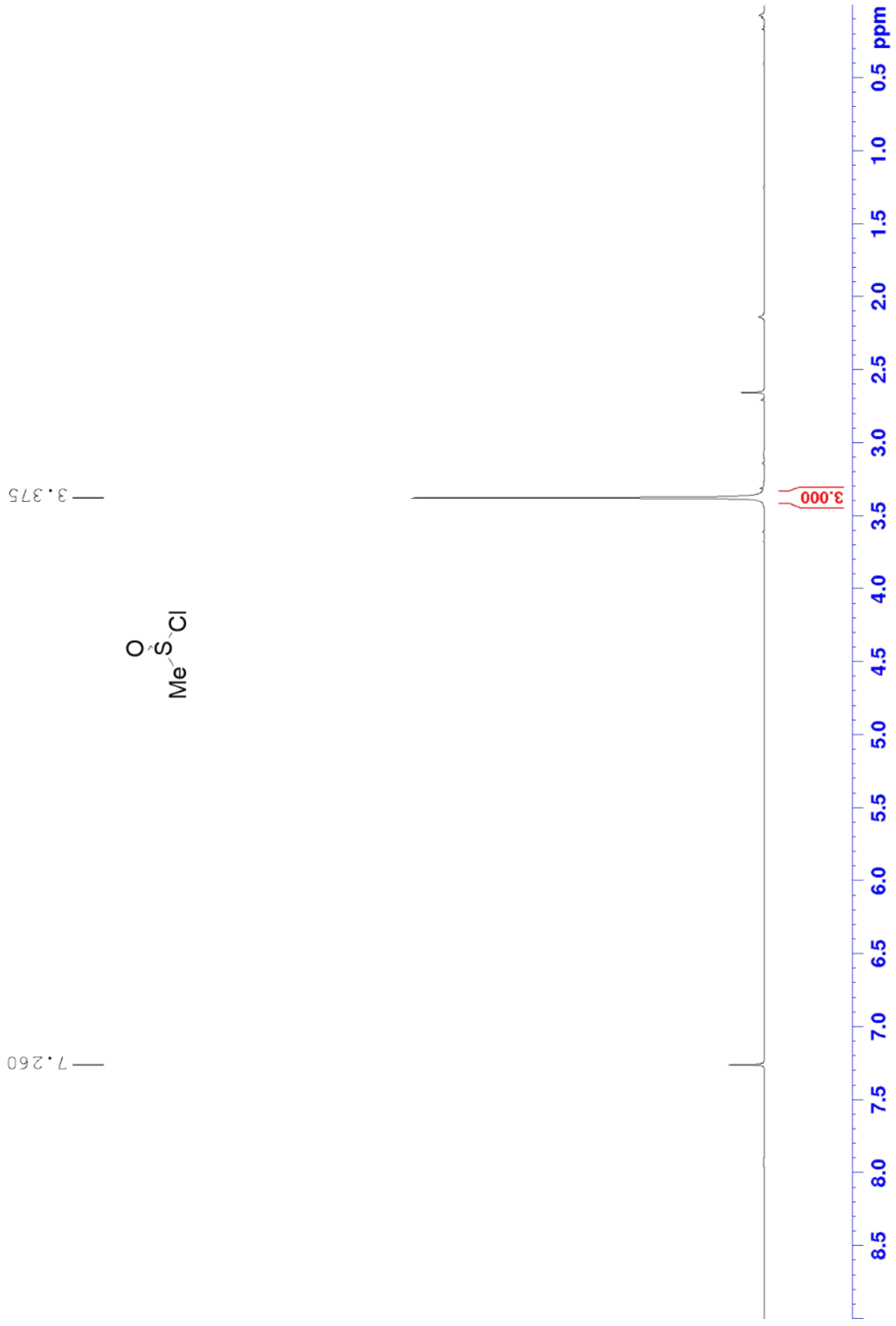
Peak #	RetTime [min]	Area %
1	25.120	35.1832
2	43.231	64.8168

34(1***R***,2***S***)** obtained with **27**(S_C,S_S) at 110 °C

^{1}H-NMR, ^{13}C-NMR of selected compounds

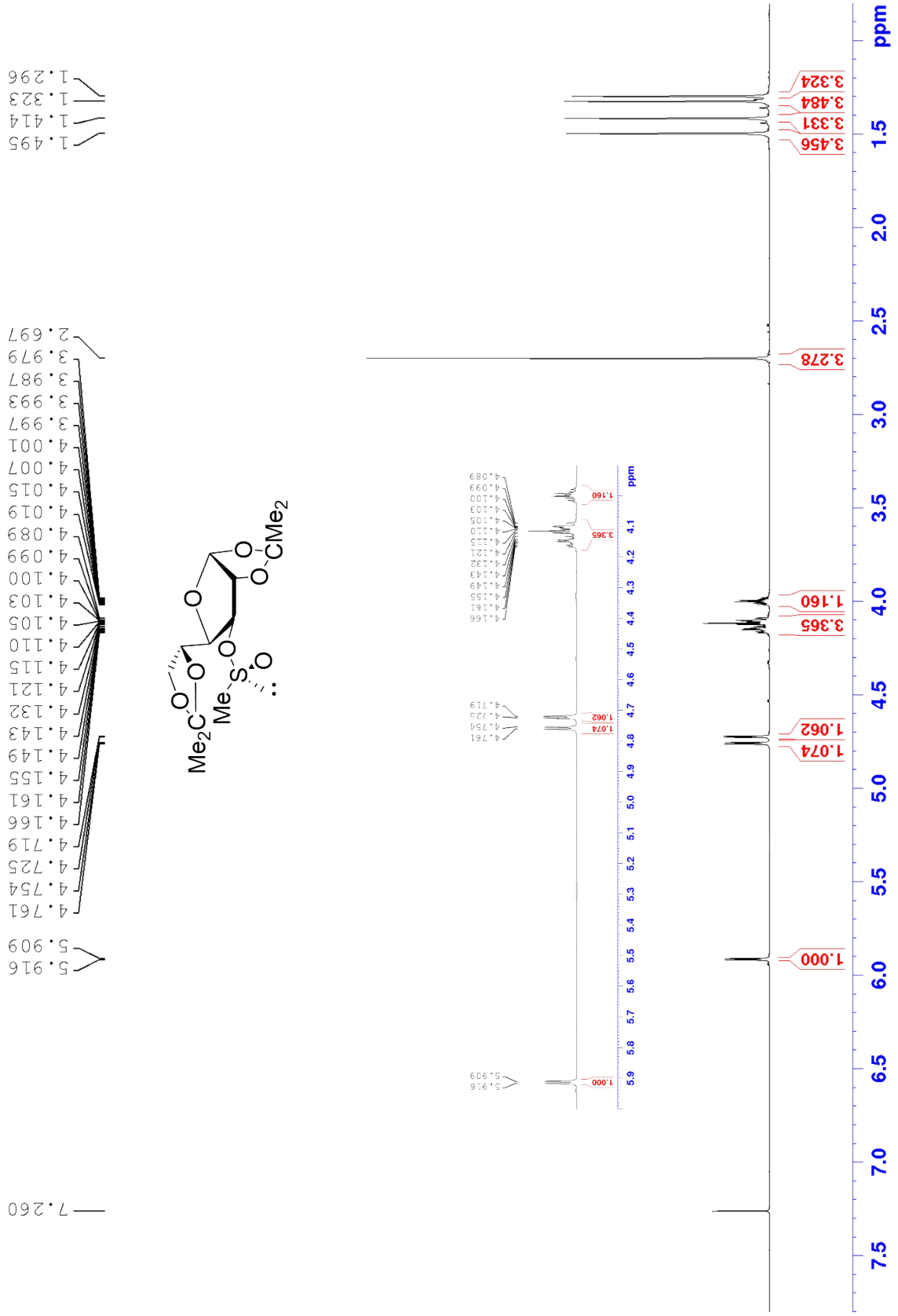
Methyl sulfinyl chloride, **35**

^{1}H-NMR (300 MHz, $CDCl_3$)

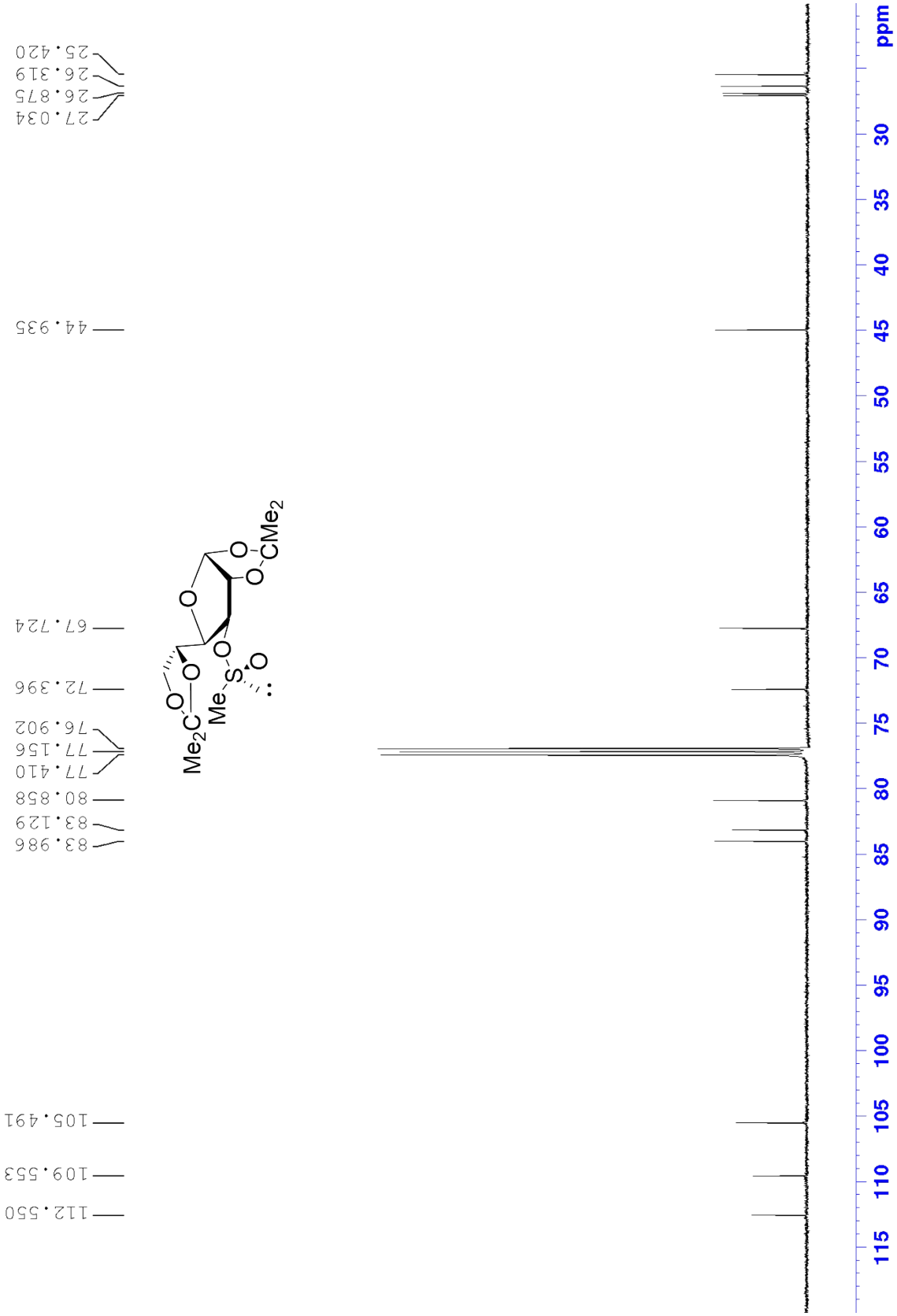


1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (+)-(R)-Methanesulfinate, **1(R_S)**

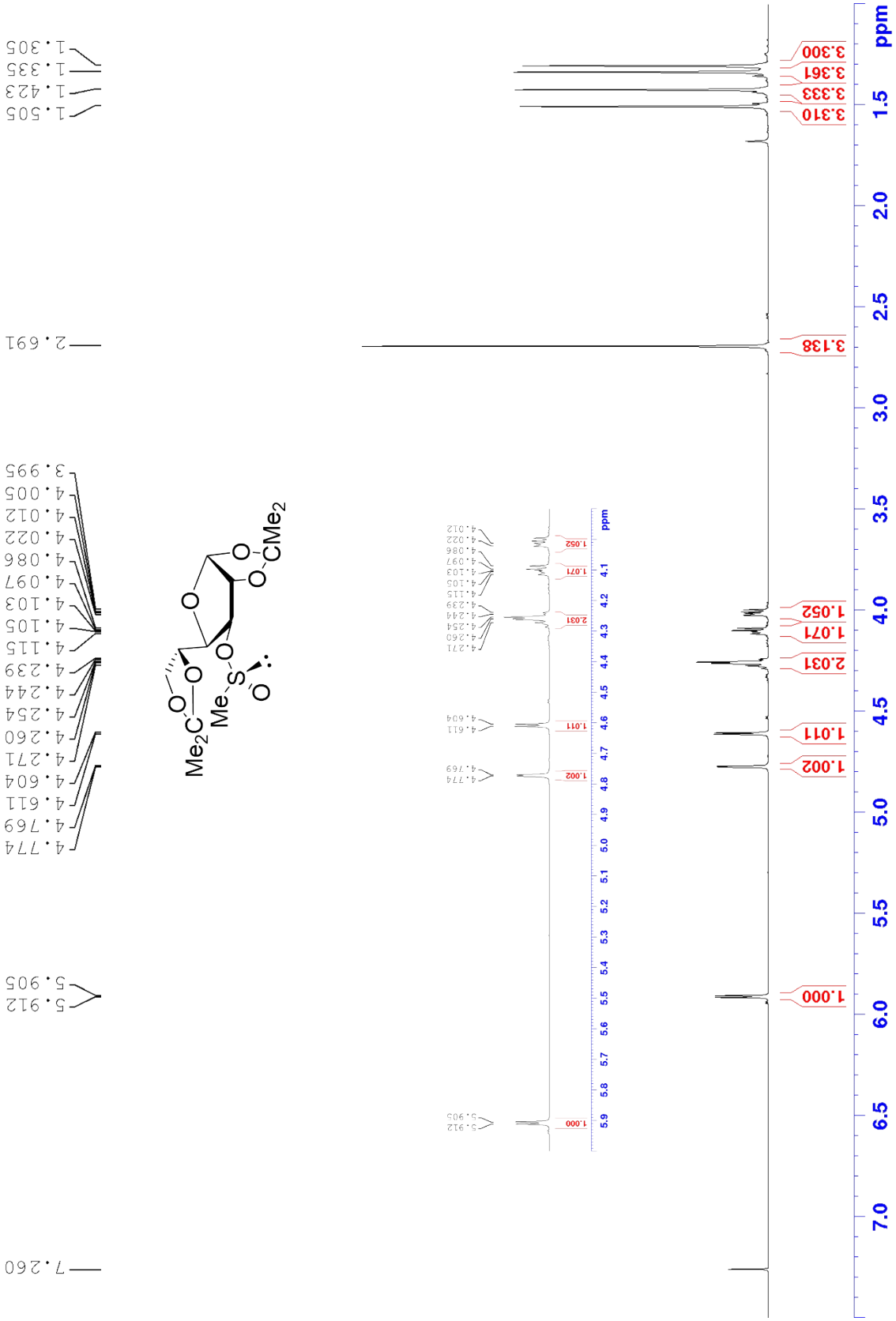
^{1}H-NMR (300 MHz, $CDCl_3$)



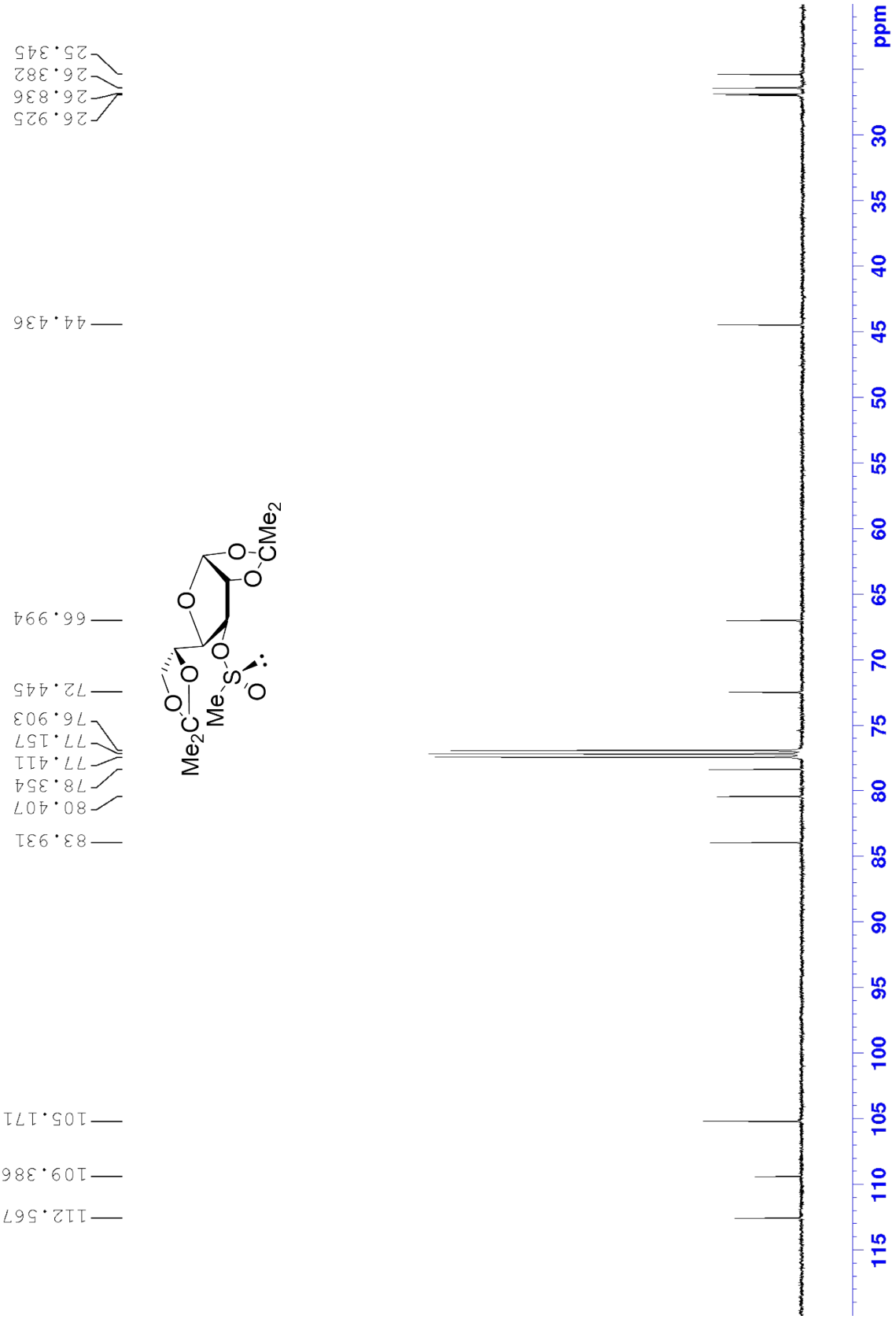
^{13}C-NMR (500 MHz, $CDCl_3$)



1,2:5,6-Di-O-isopropylidene-α-D-glucofuranosyl (–)-(S)-Methanesulfinate, **1(S_S)**

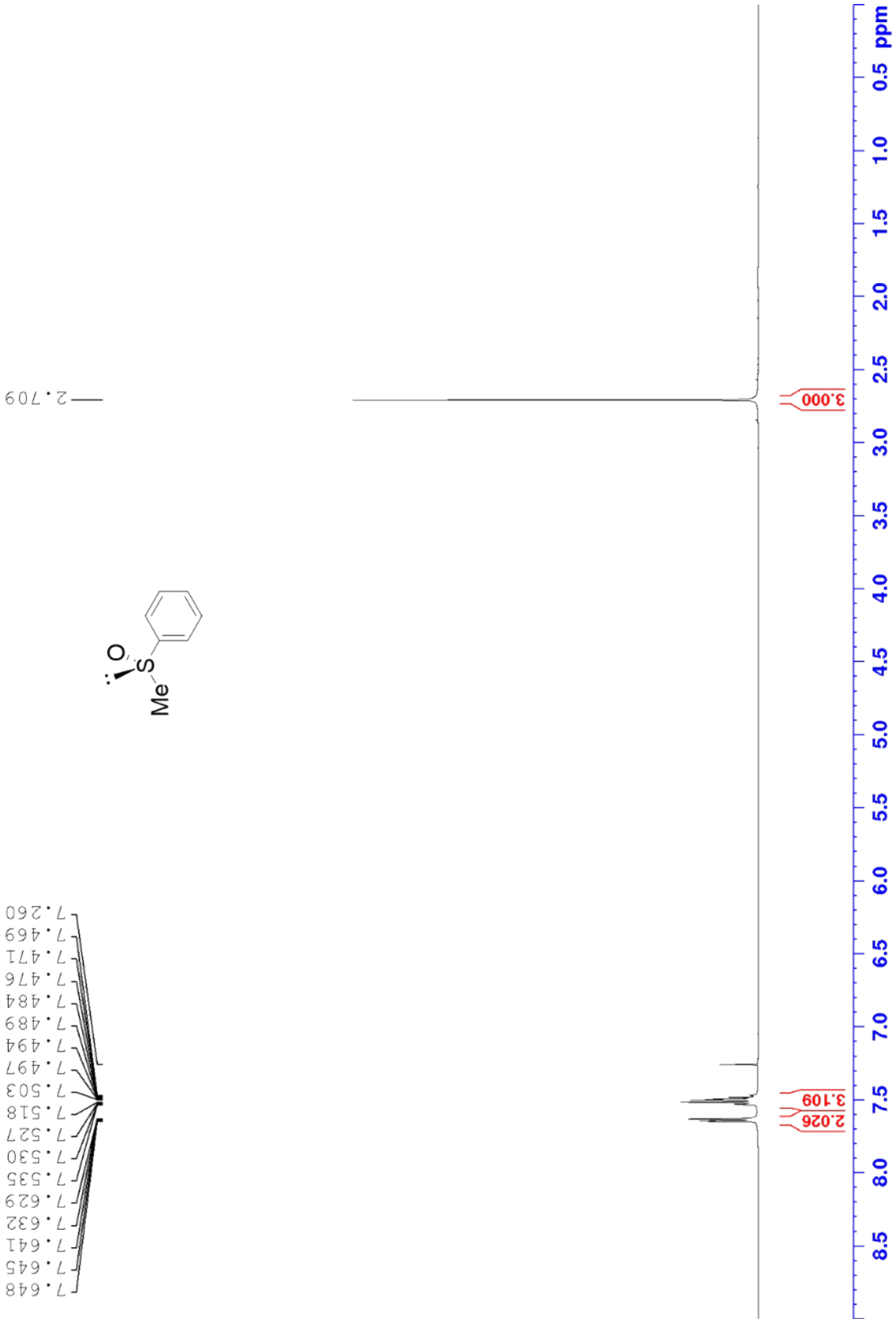


^{13}C-NMR (500 MHz, $CDCl_3$)

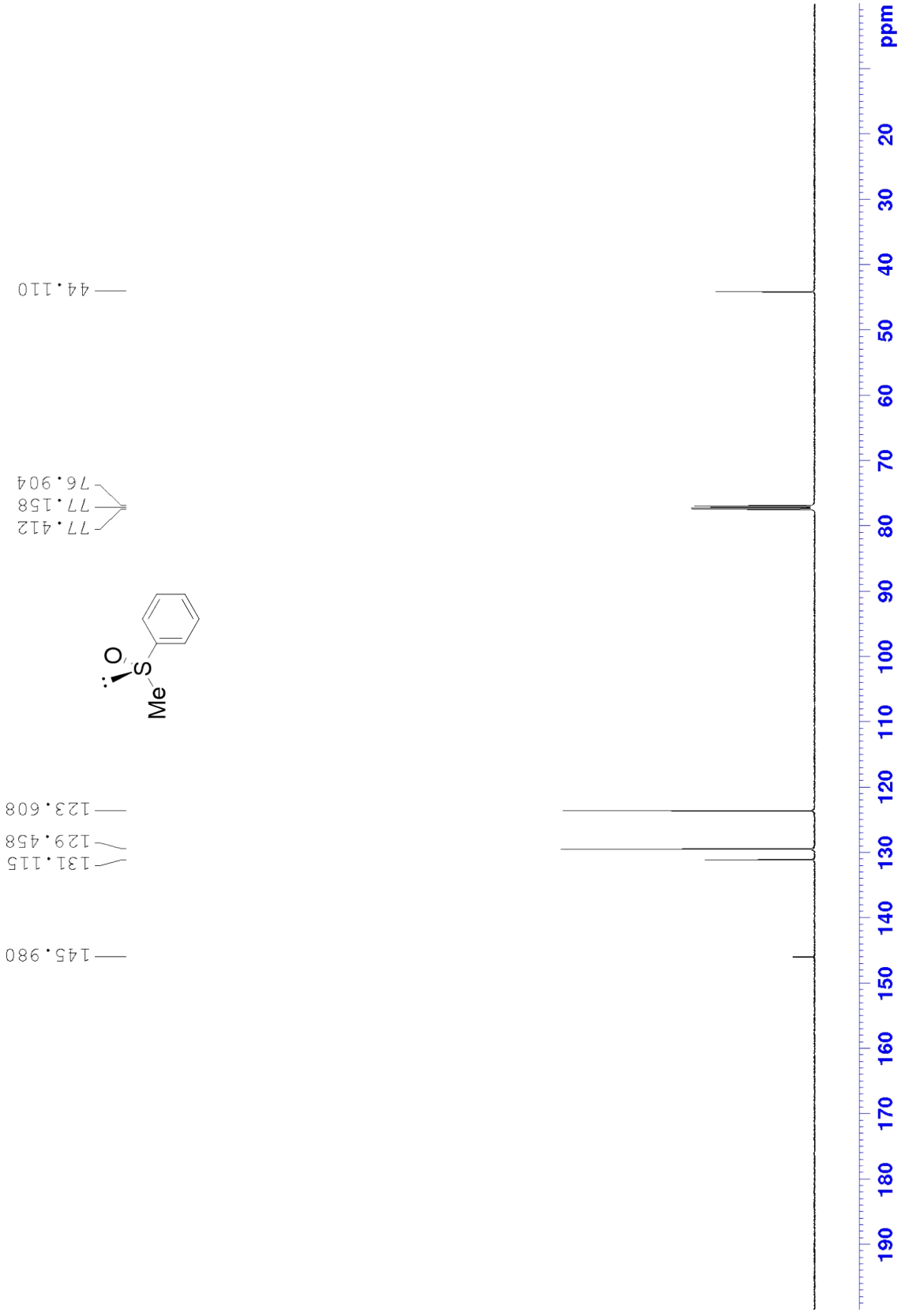


Methyl Phenyl sulfoxide, **2(S_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

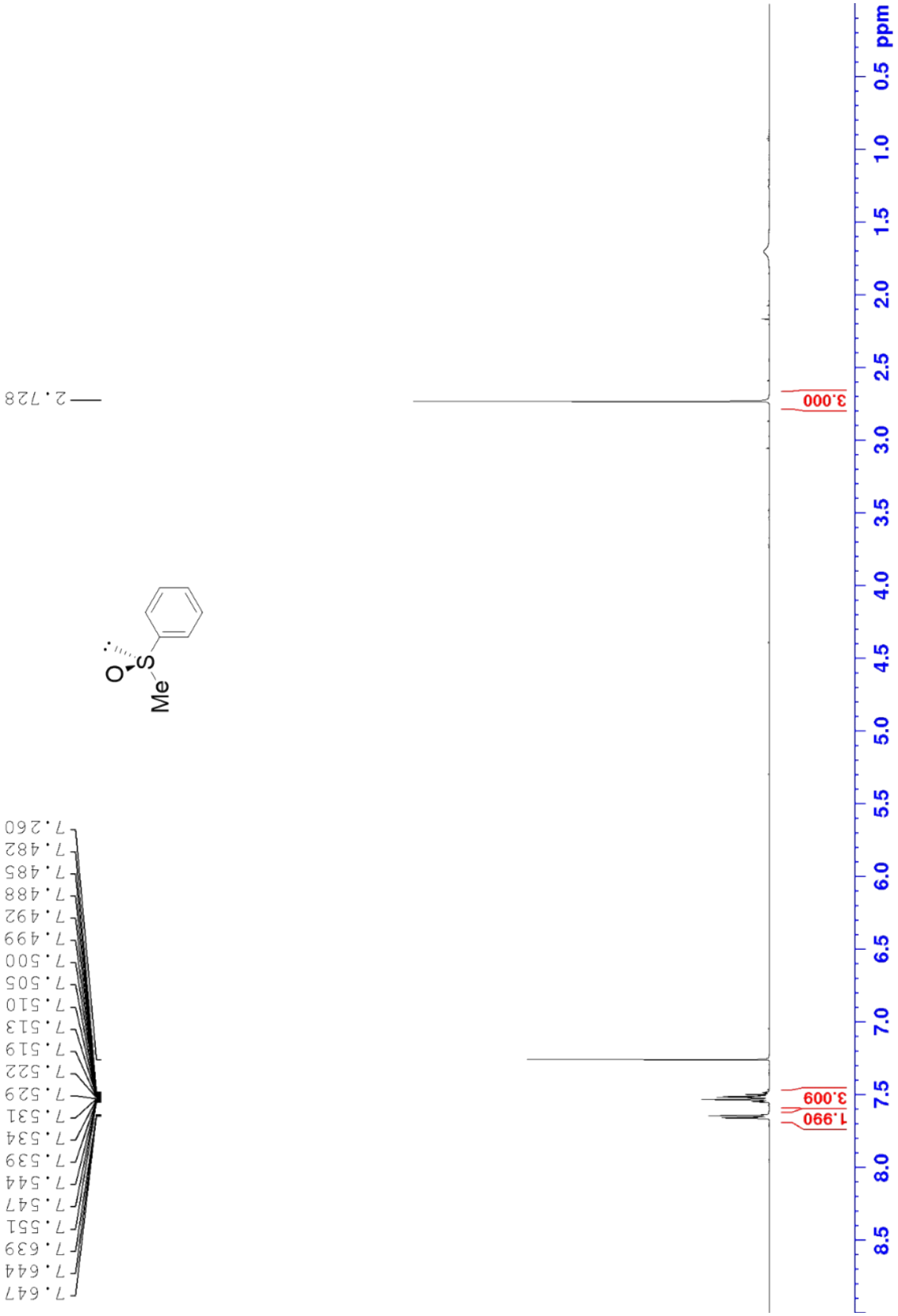


^{13}C-NMR (500 MHz, $CDCl_3$)

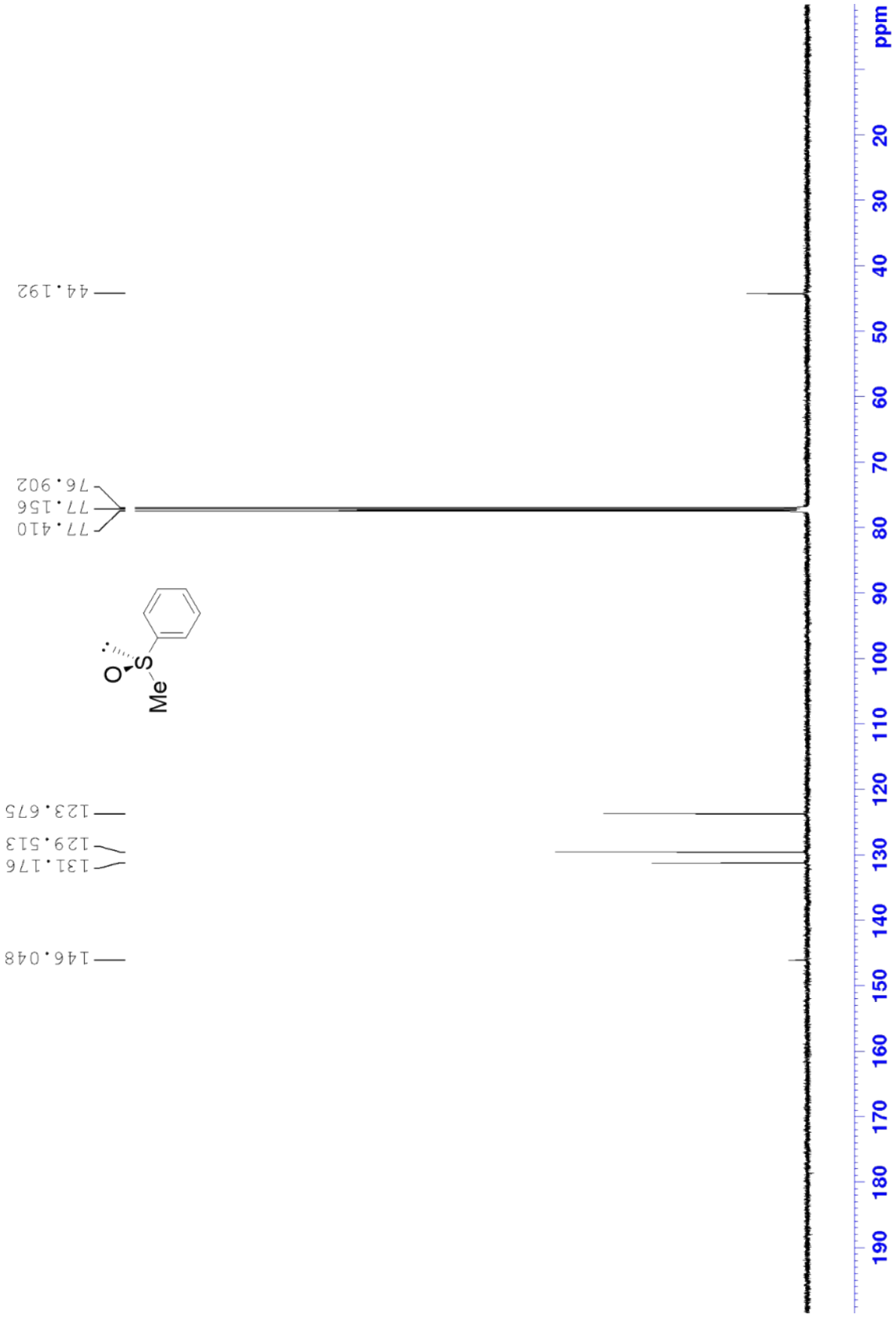


Methyl Phenyl sulfoxide, **2(R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

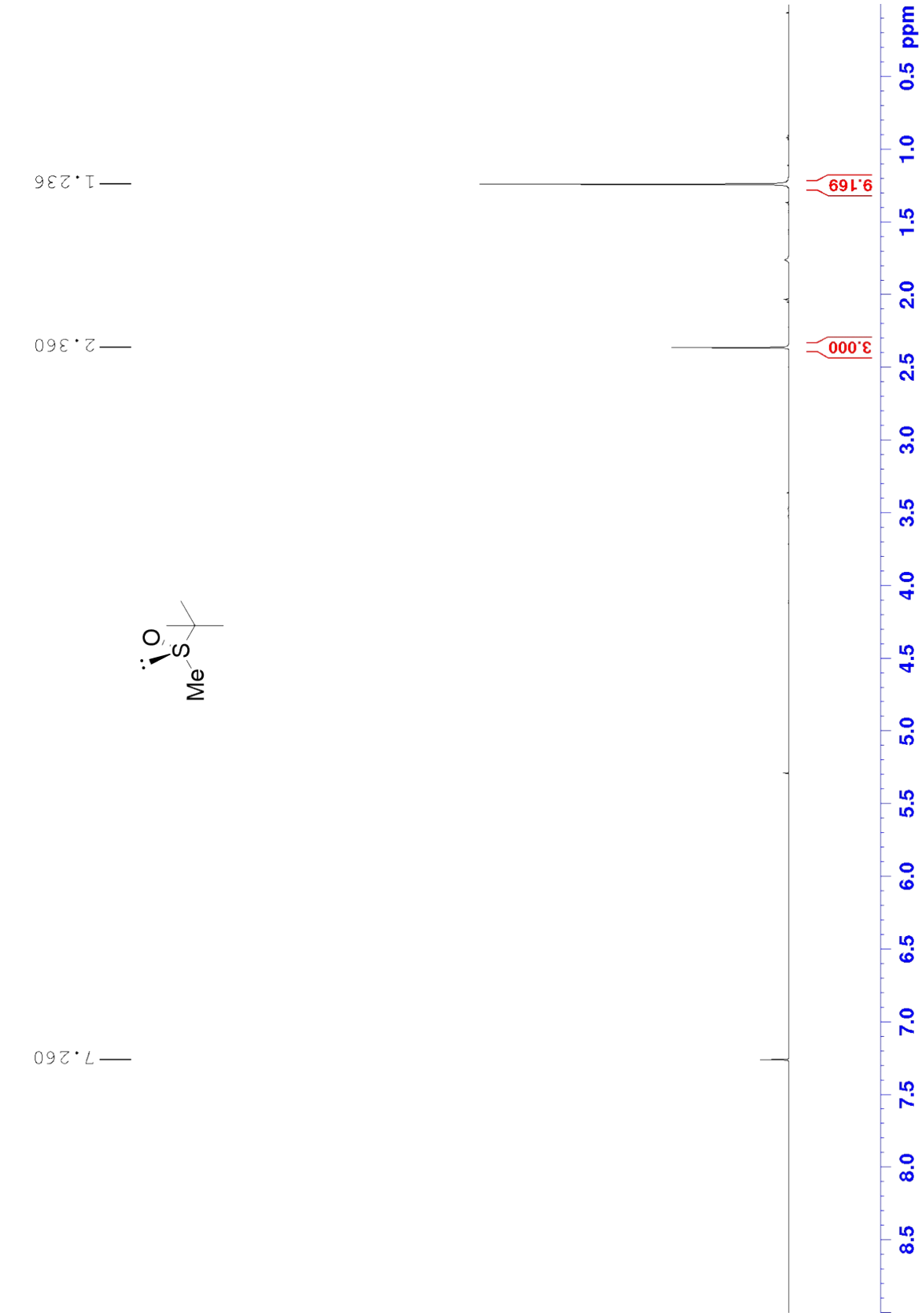


^{13}C-NMR (500 MHz, $CDCl_3$)

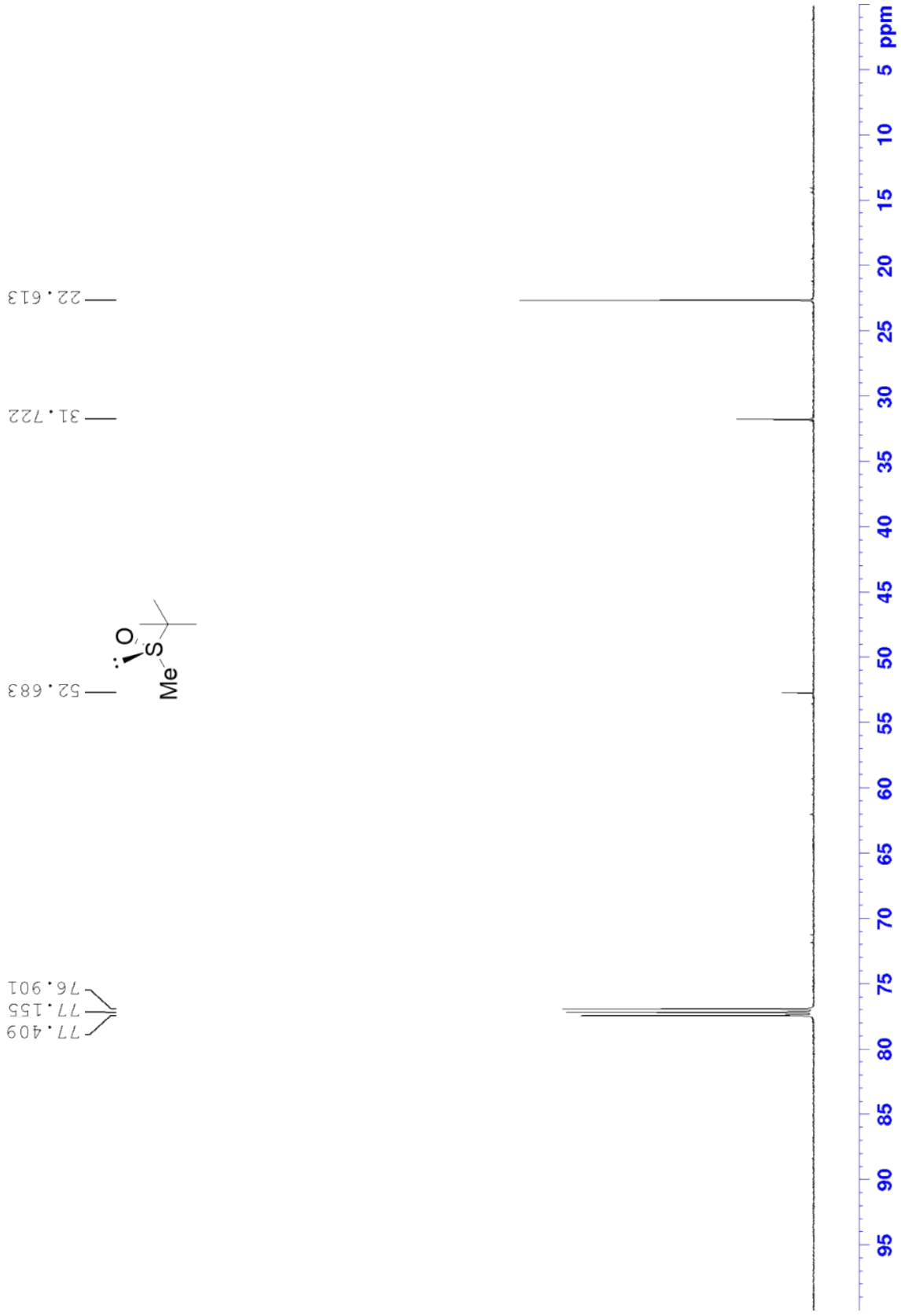


Methyl Tert-butyl sulfoxide, **3(S_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

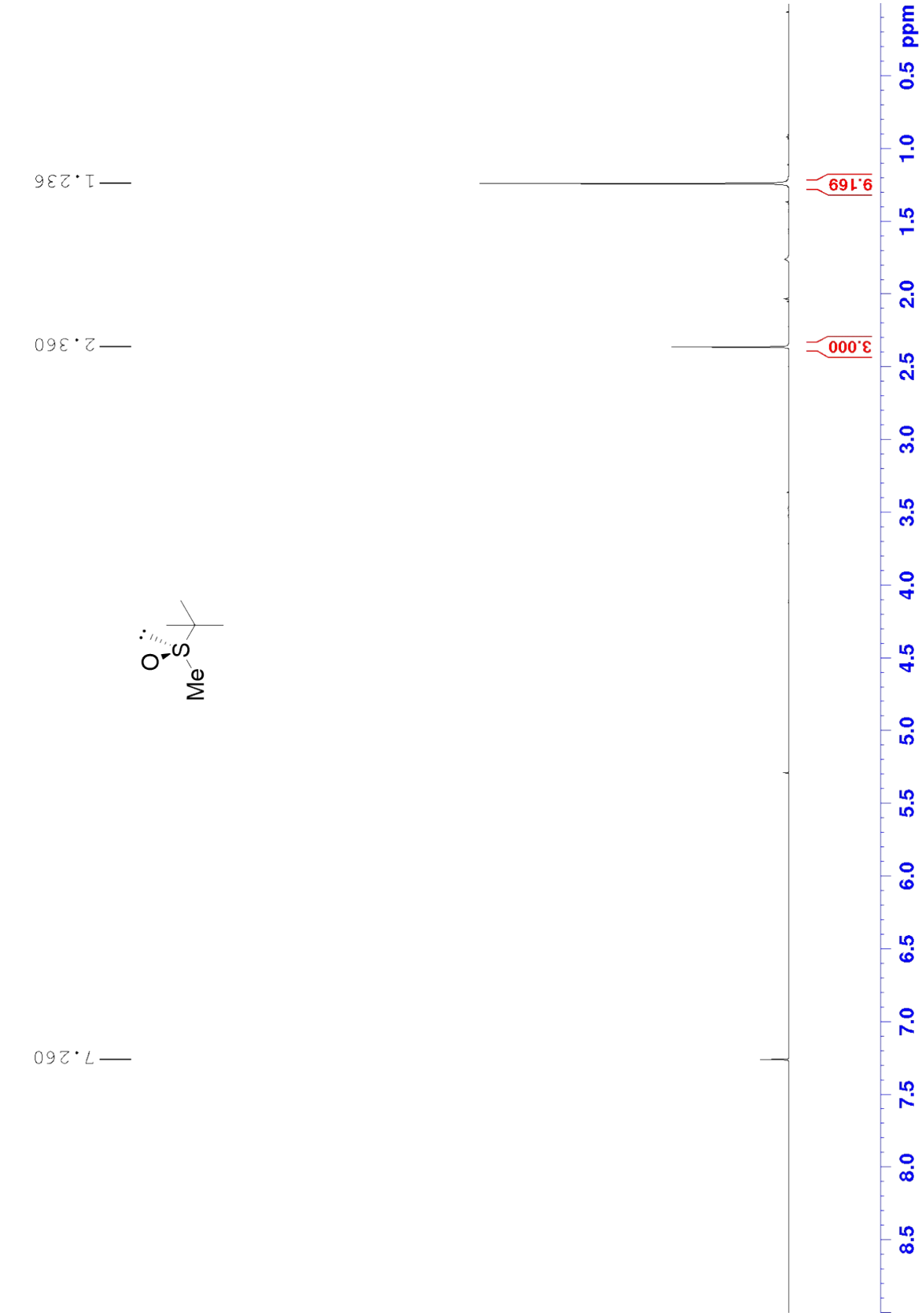


^{13}C-NMR (500 MHz, $CDCl_3$)



Methyl Tert-butyl sulfoxide, **3(R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

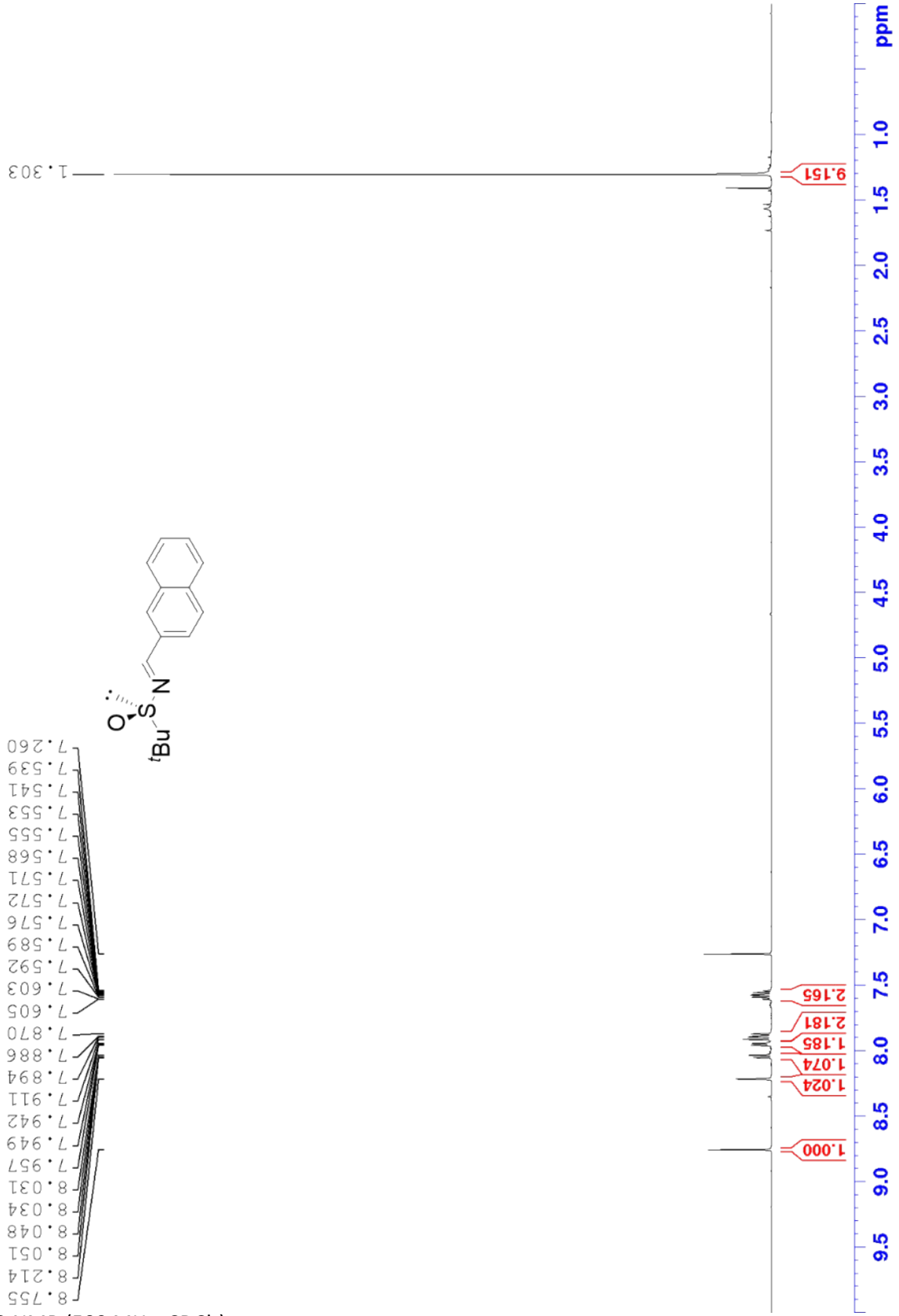


^{13}C-NMR (500 MHz, $CDCl_3$)

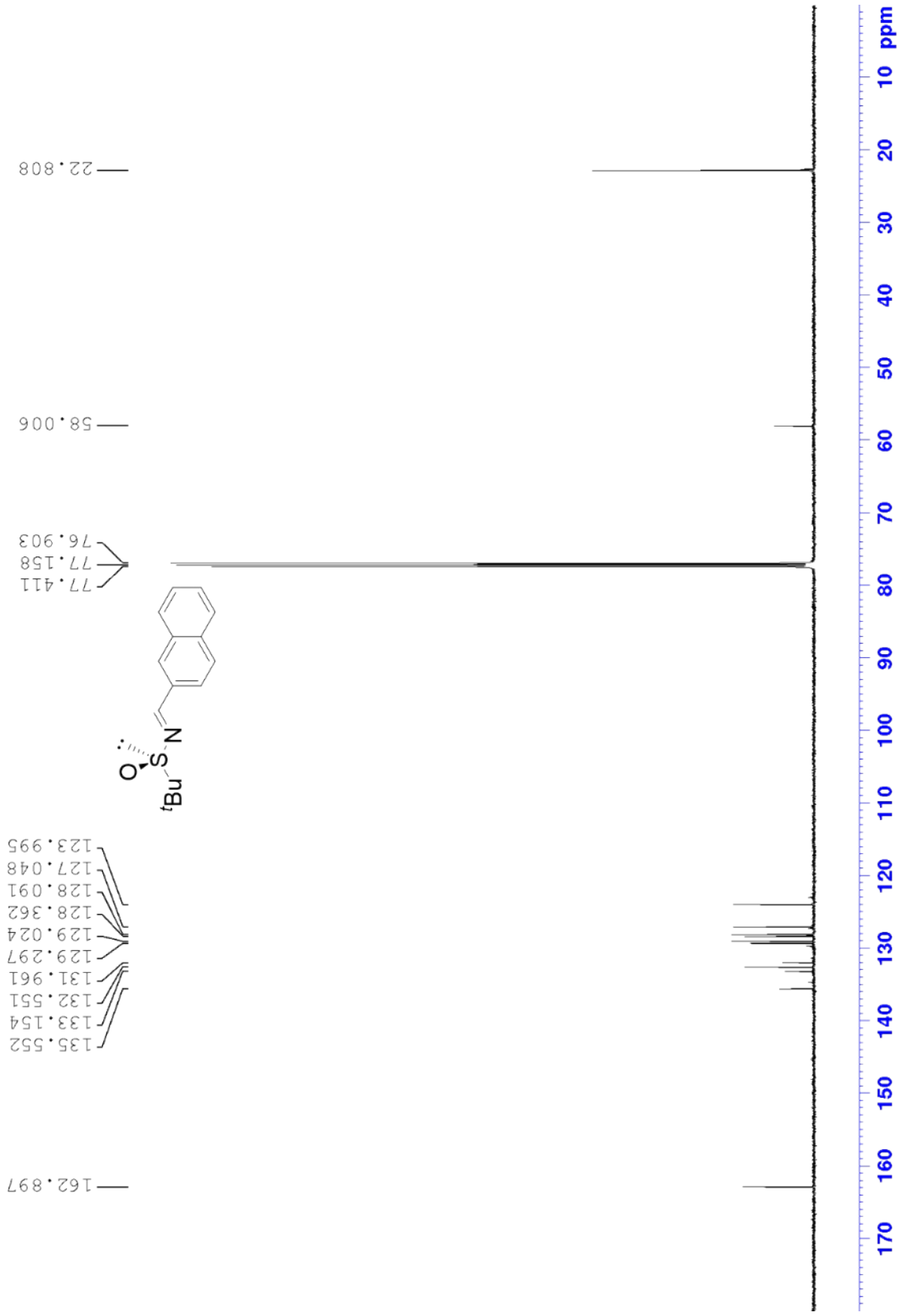
22.613
31.722
52.683
77.409
77.155
76.901
O
S
Me
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm

(R_S)-N-[(2-Naphthyl)methylidene]-2-methyl-2-propanesulfinamide, **4(R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

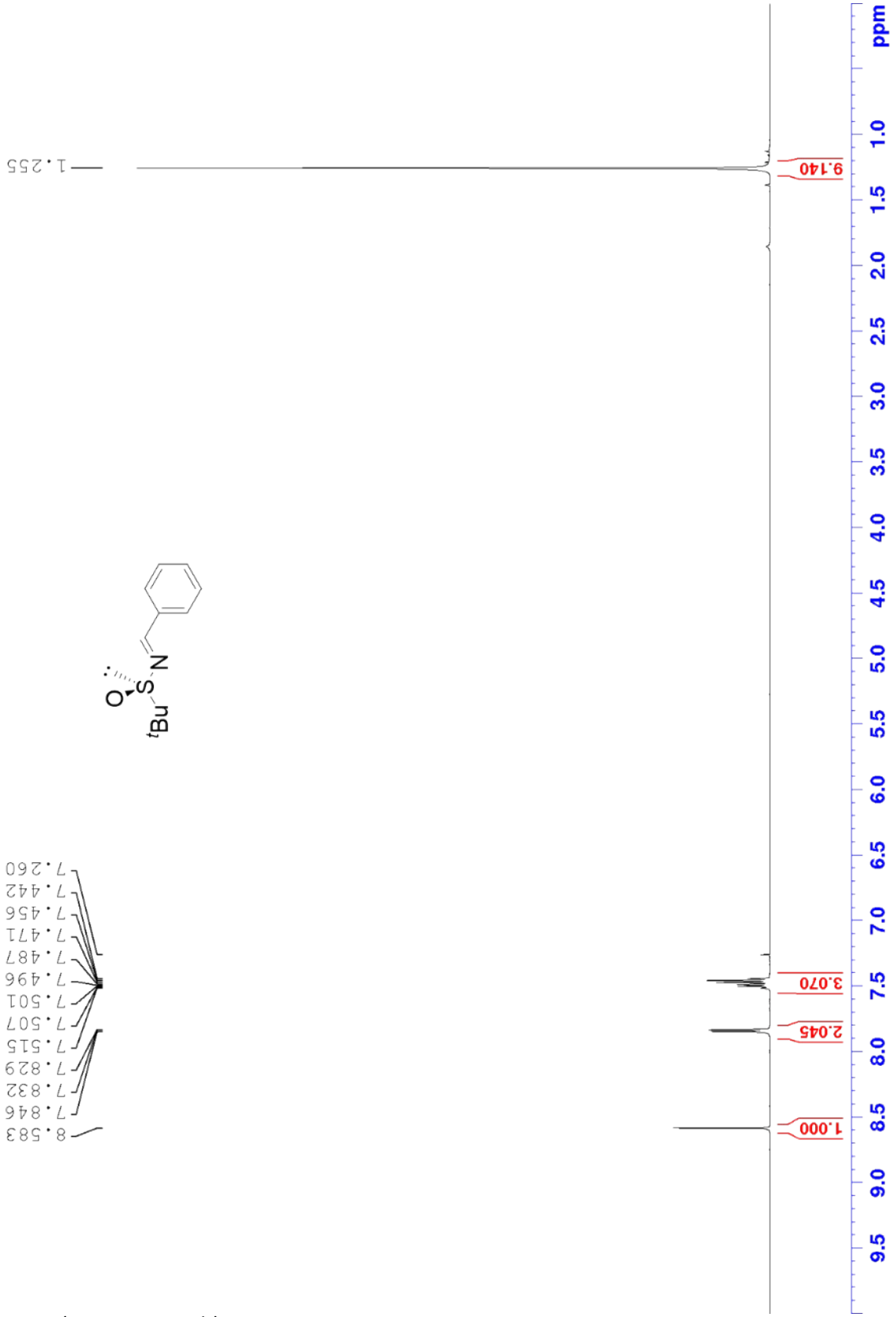


^{13}C-NMR (500 MHz, $CDCl_3$)

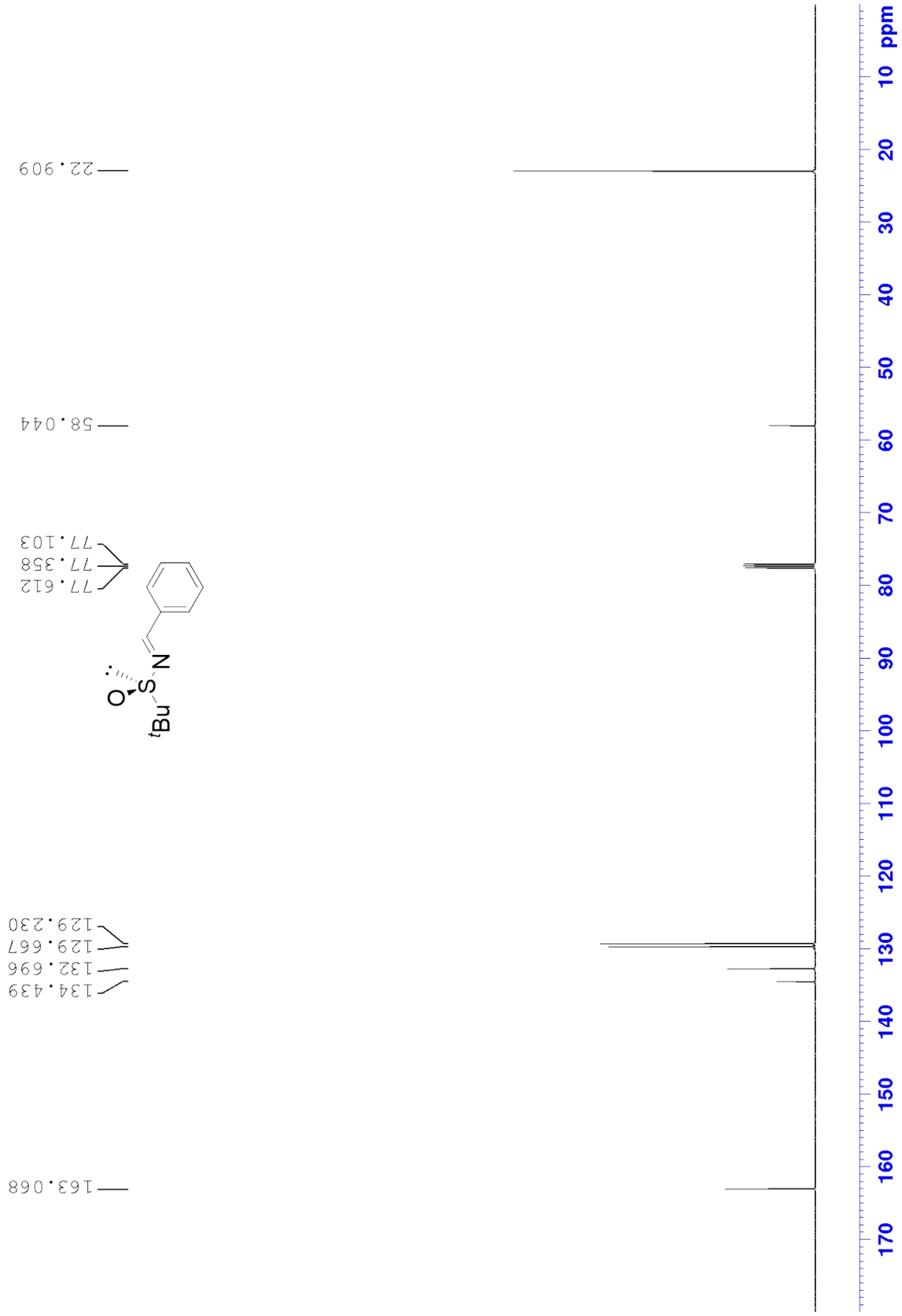


(R_S)-N-Benzylidene-2-methyl-2-propanesulfinamide, **5(R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

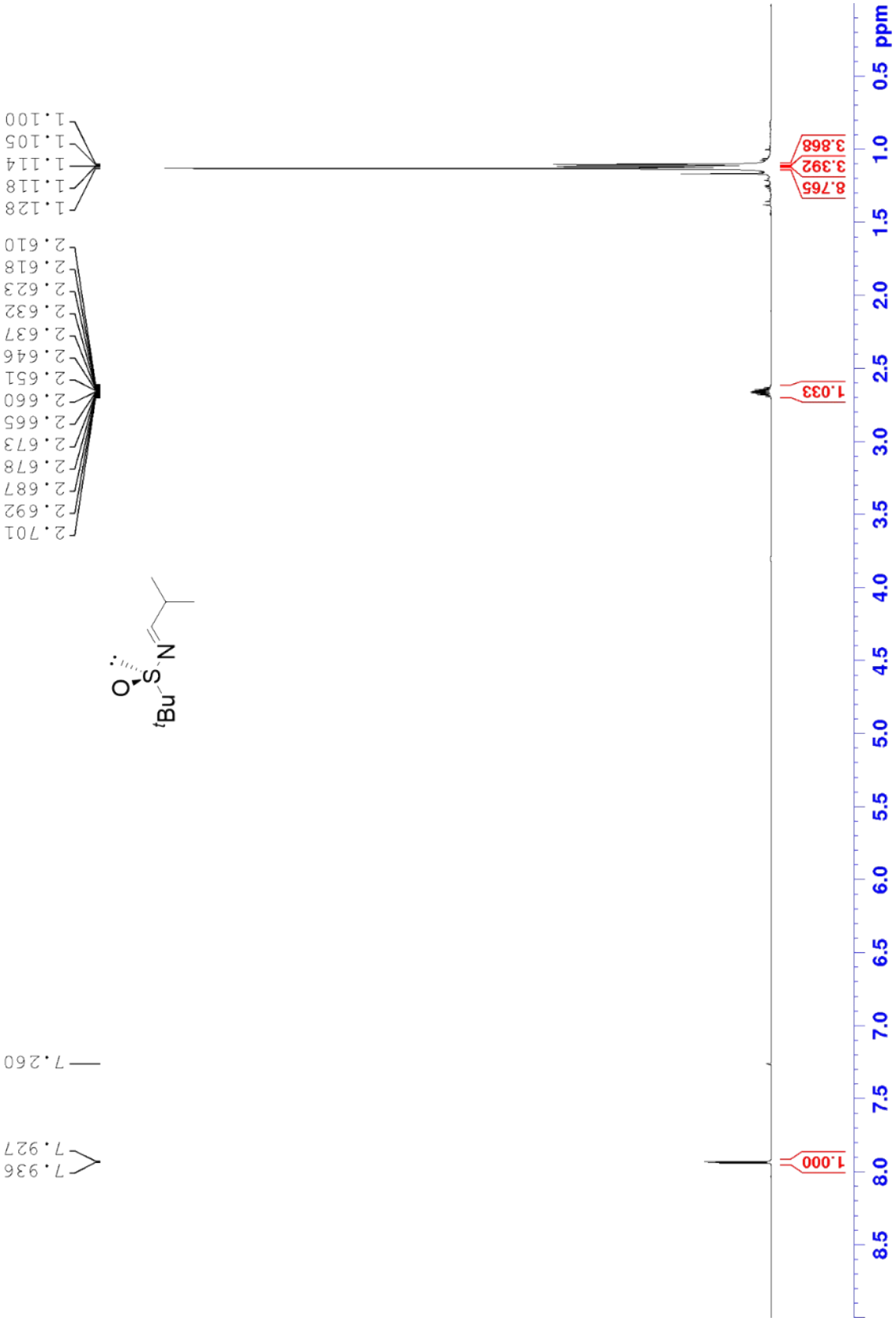


^{13}C-NMR (500 MHz, $CDCl_3$)

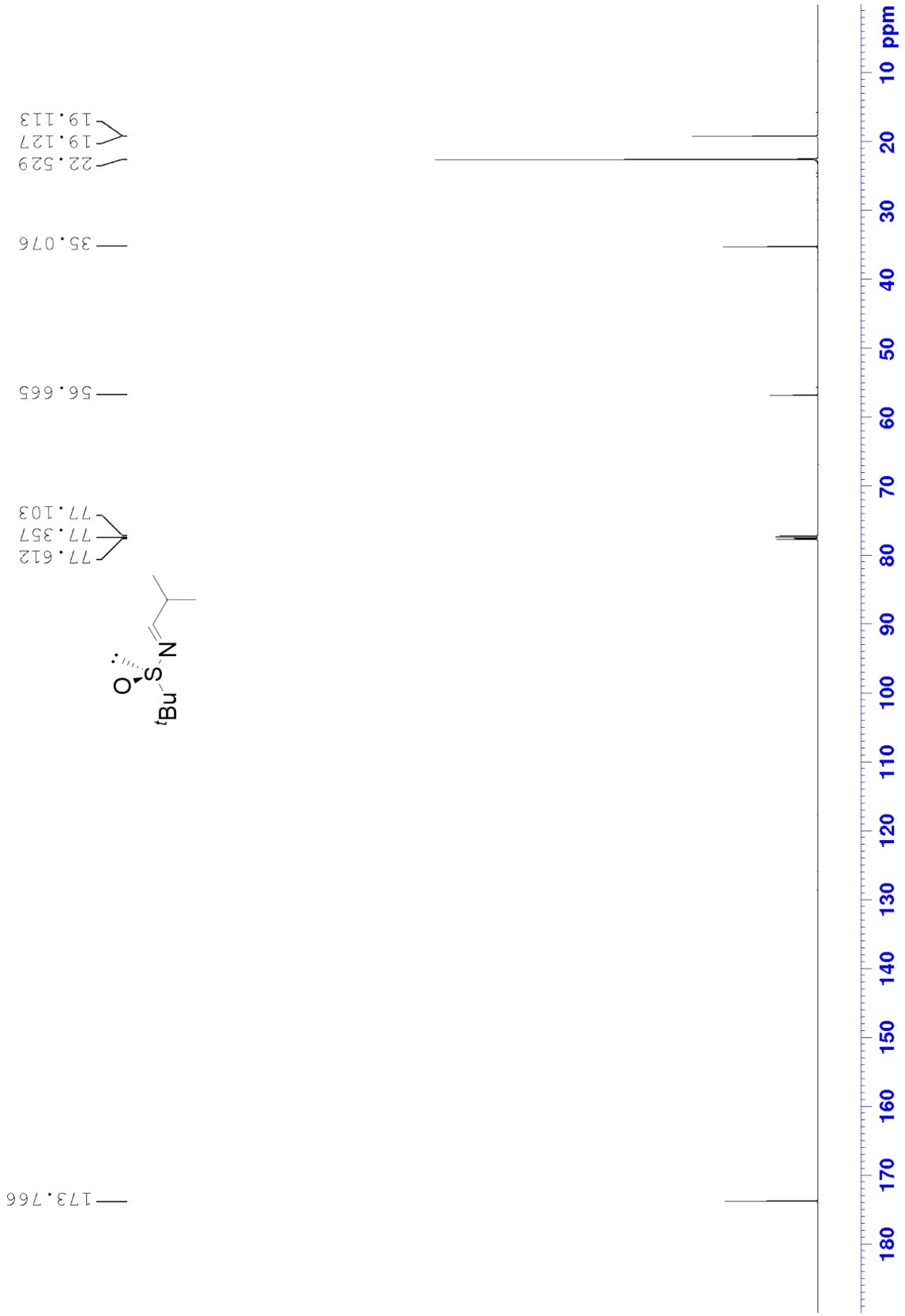


(R_S)-N-(2-methyl-1-propylidene)-2-methyl-2-propanesulfinamide, **6(R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

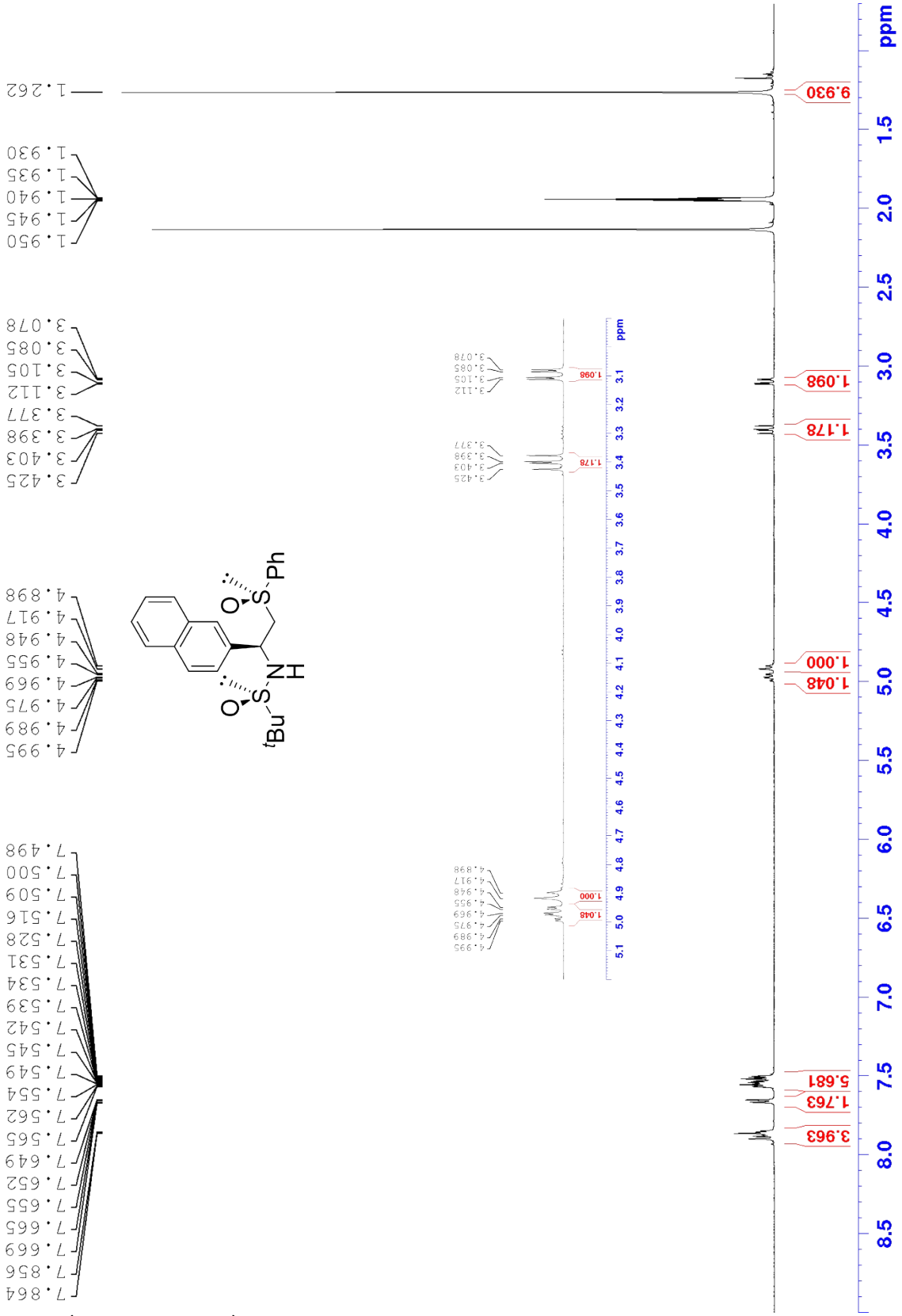


^{13}C-NMR (500 MHz, $CDCl_3$)

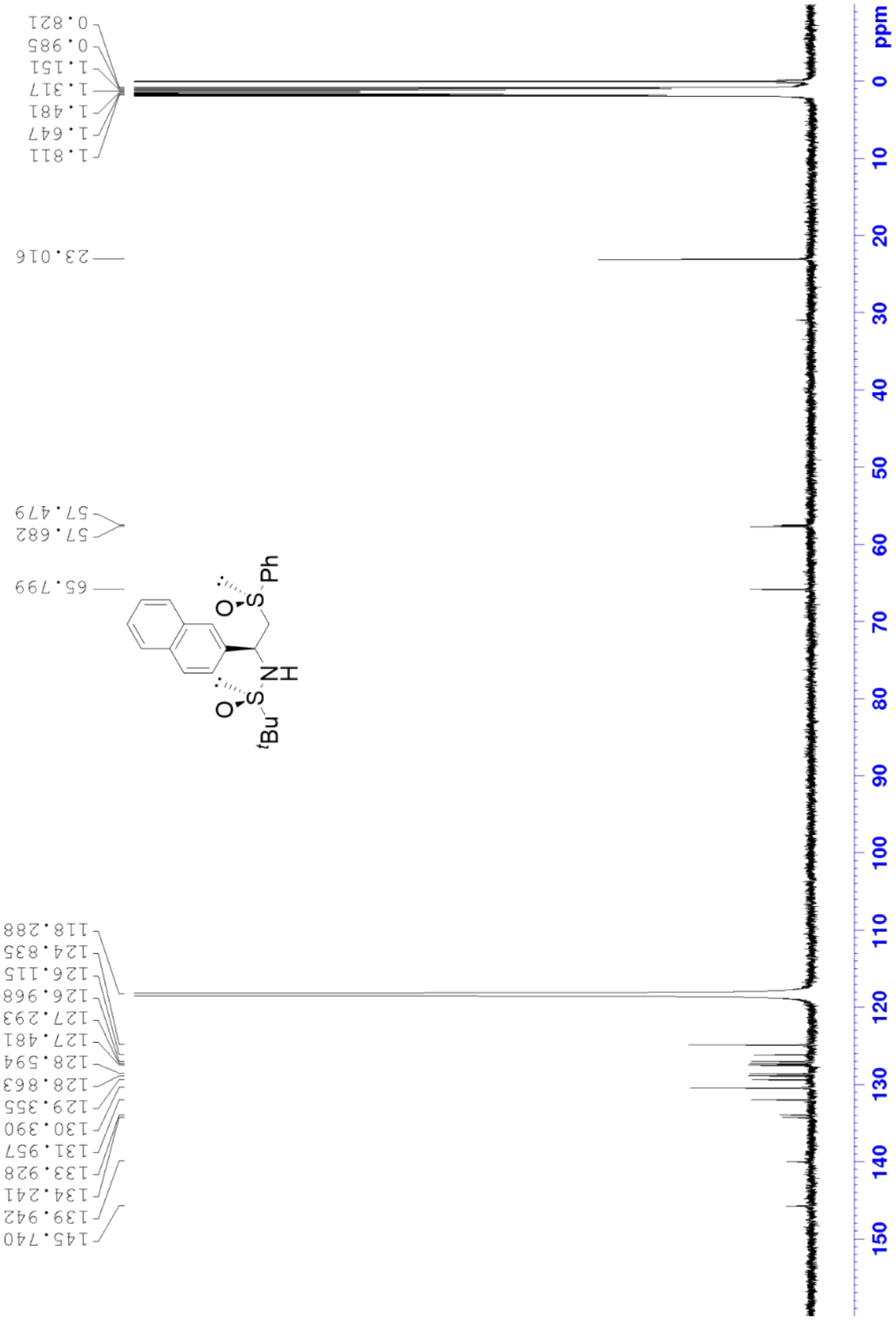


(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **7(R_S,S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

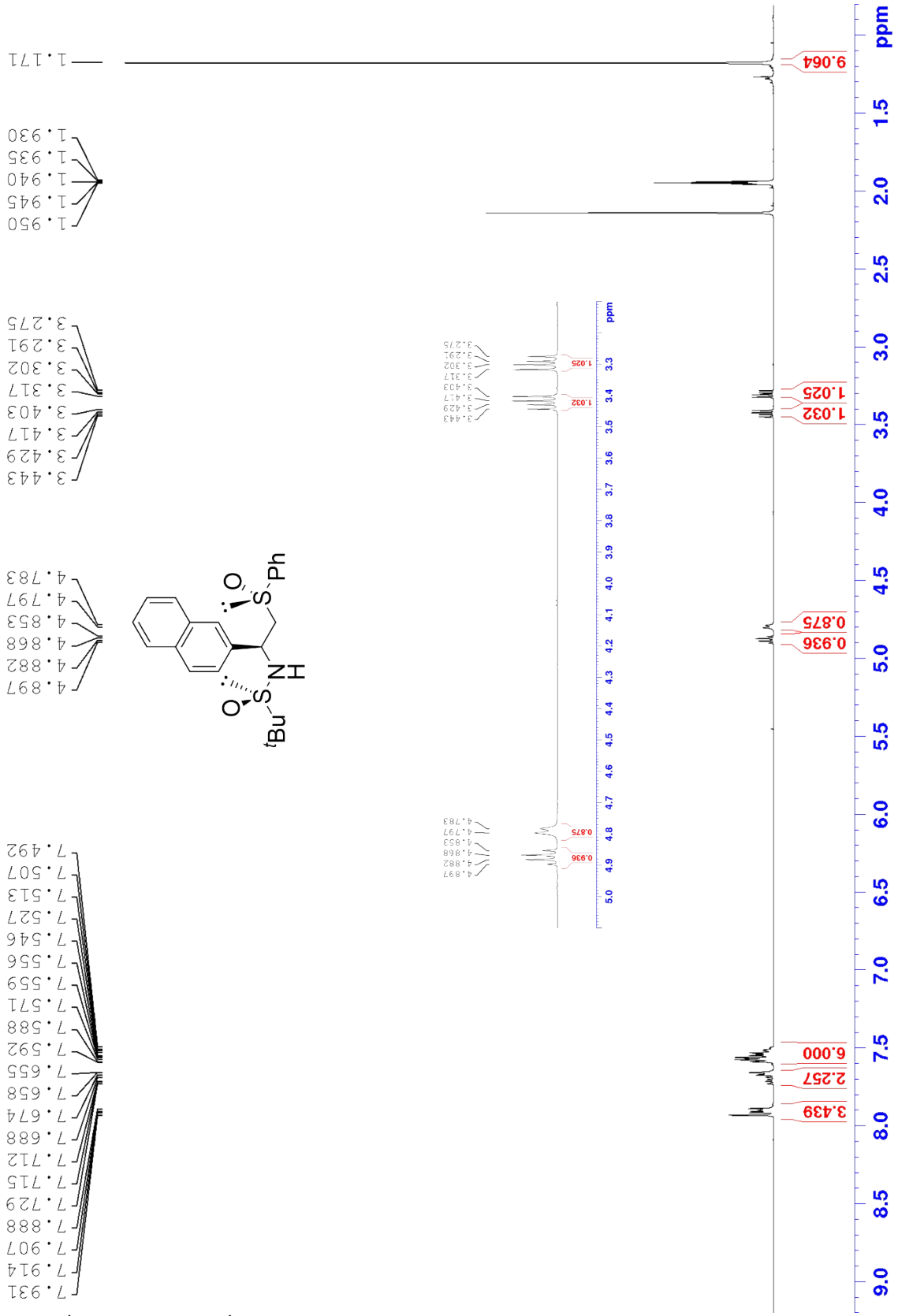


^{13}C-NMR (500 MHz, CD_3CN)

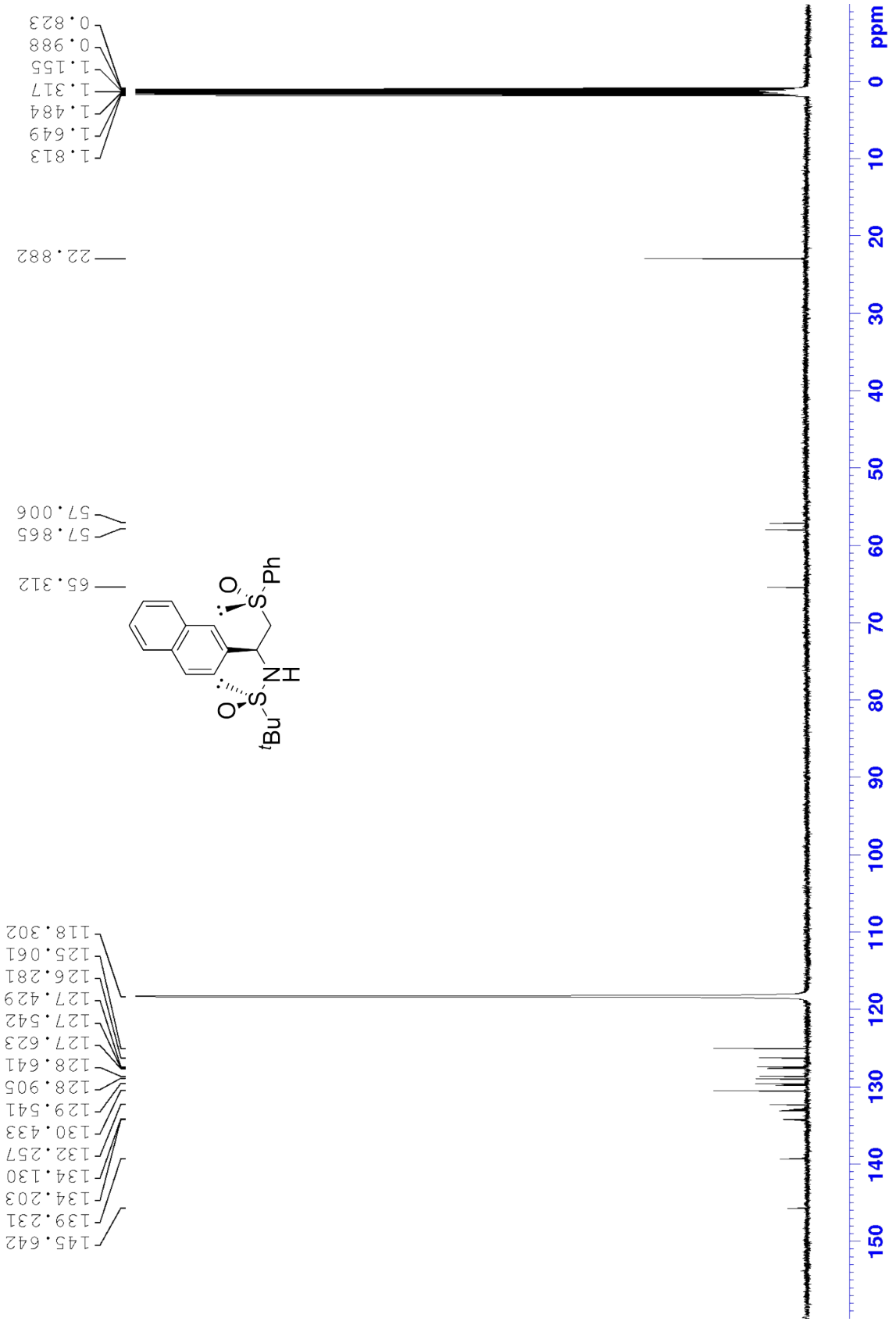

0.821
0.985
1.151
1.317
1.481
1.647
1.811
23.016
57.479
57.682
65.799
118.288
124.835
126.115
126.968
127.293
127.481
128.594
128.863
129.355
130.390
131.957
133.928
134.241
139.942
145.740
Ph
S
O
NH
S
O
tBu
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **7(R_S,S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

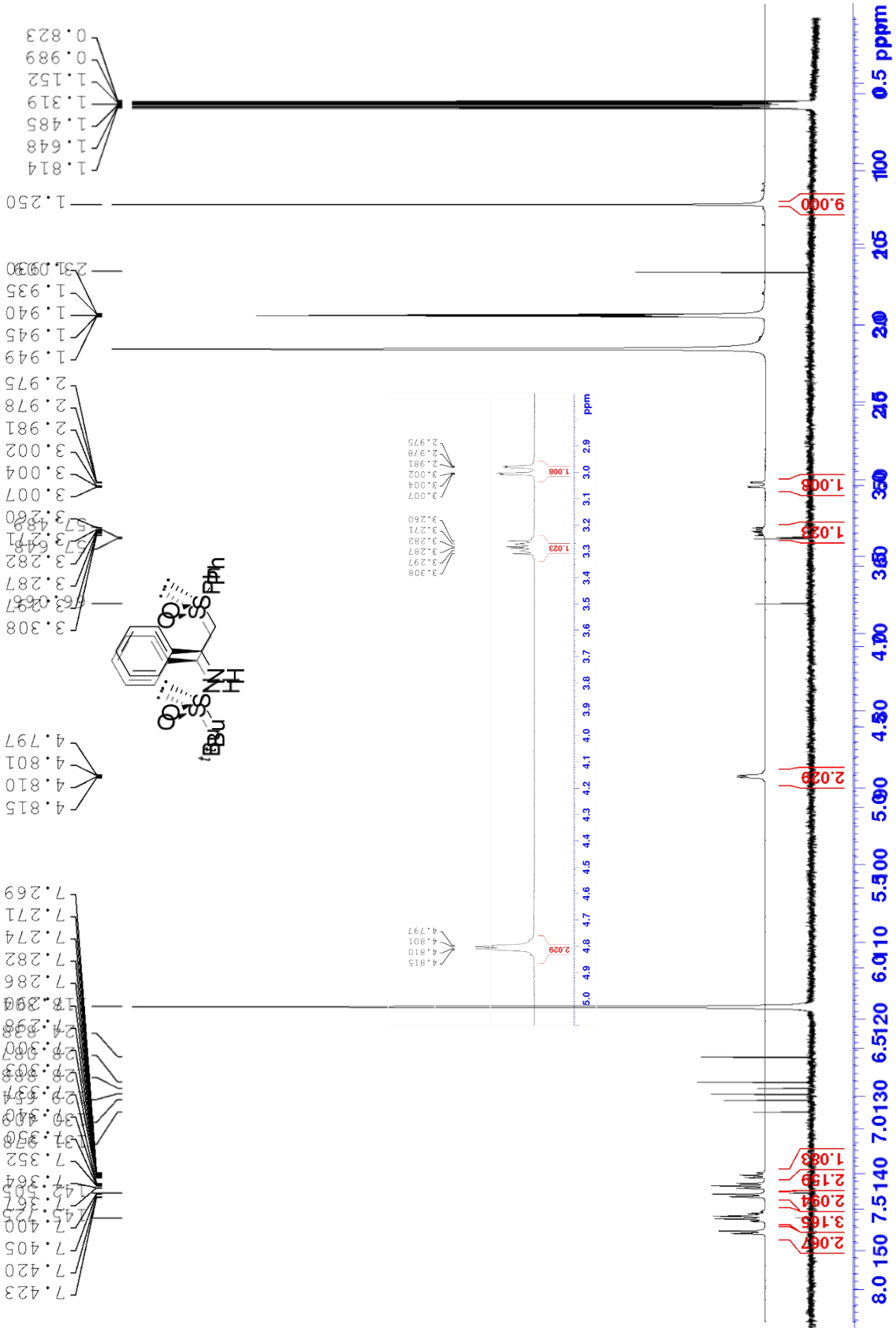


^{13}C-NMR (500 MHz, CD_3CN)



(R_S,S_C,R_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **8(R_S,S_C,R_S)**

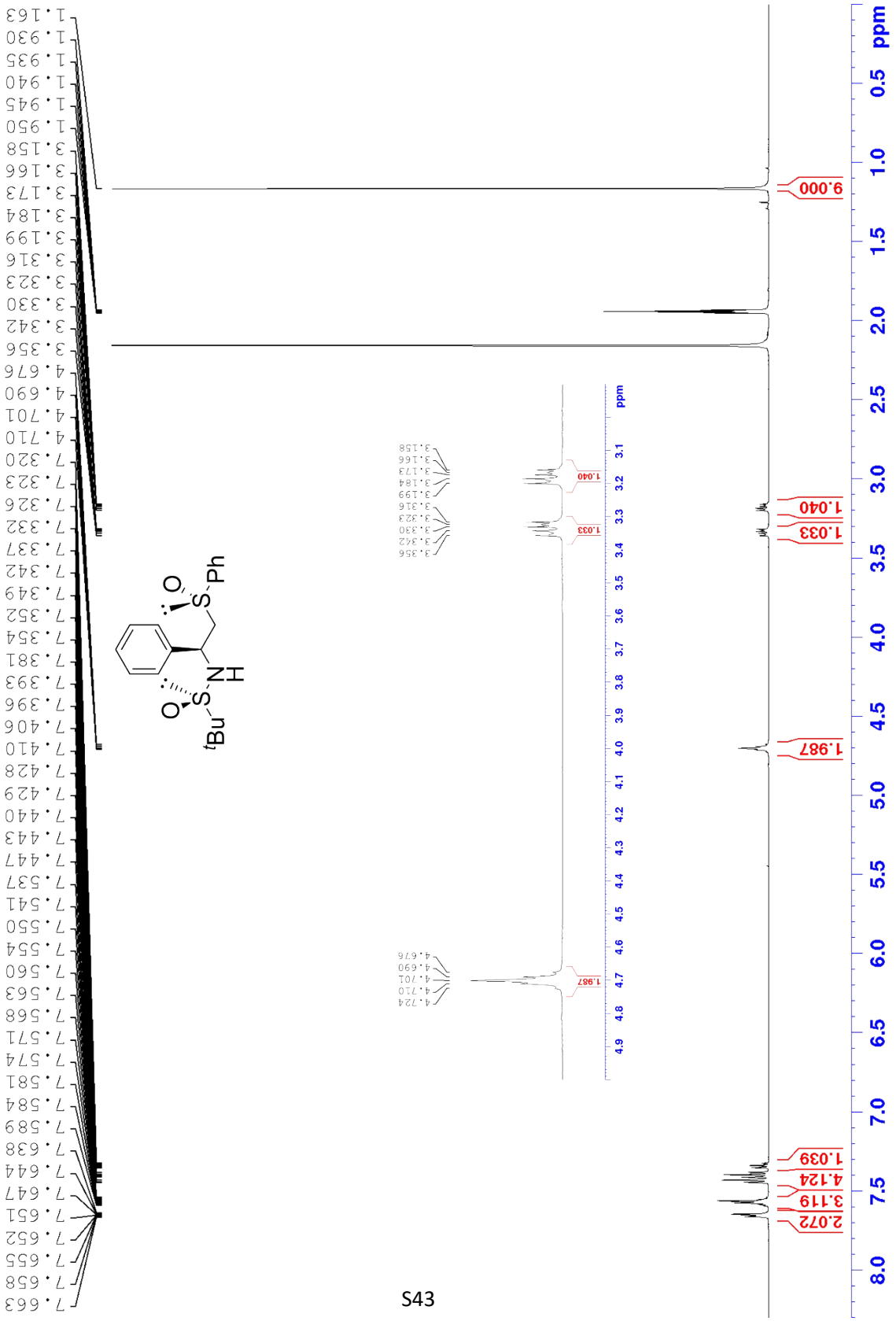
^{1}H-NMR (500 MHz, CD_3CN)



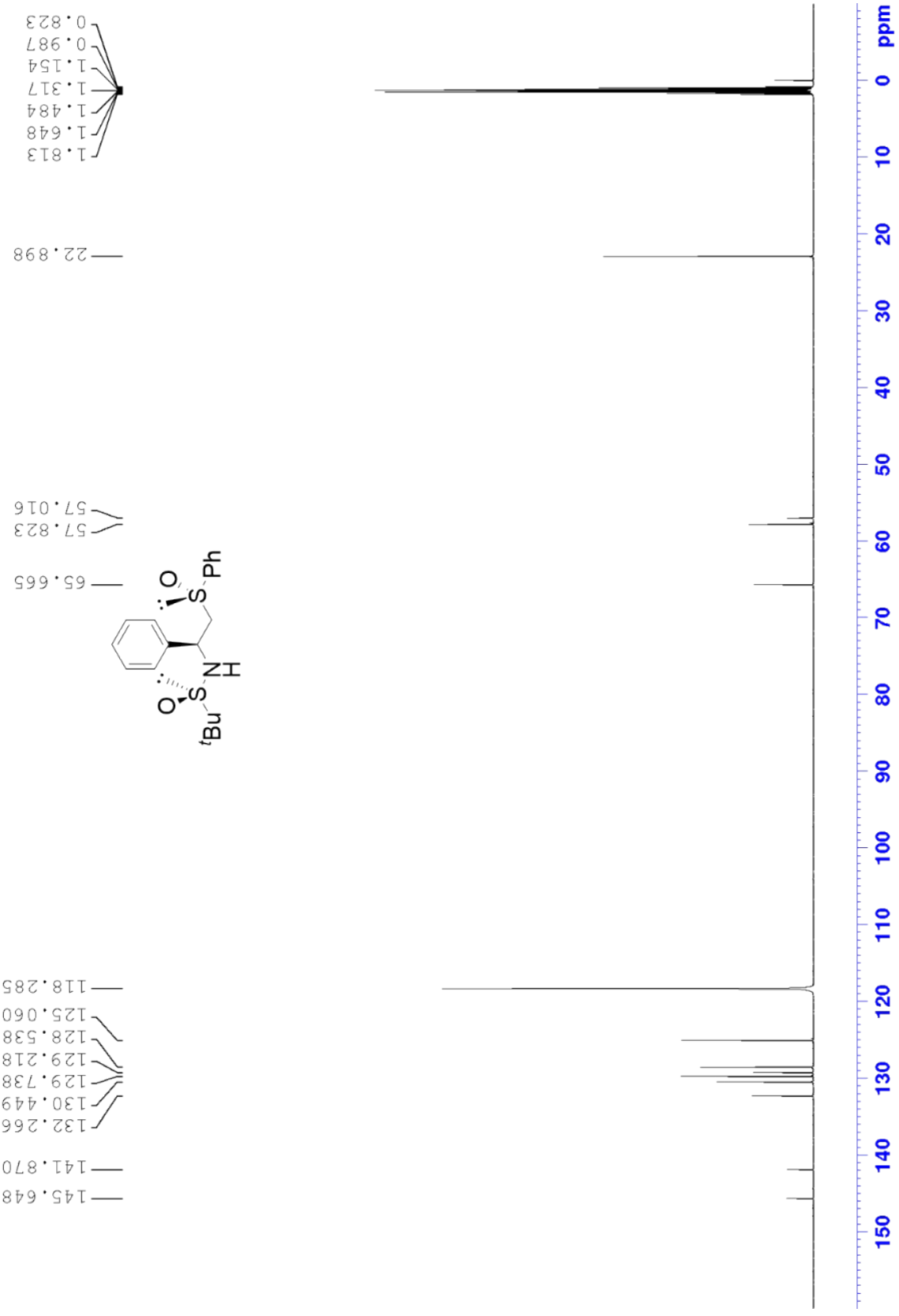
^{13}C-NMR (500 MHz, CD_3CN)

(R_S,S_C,S_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **8(R_S,S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

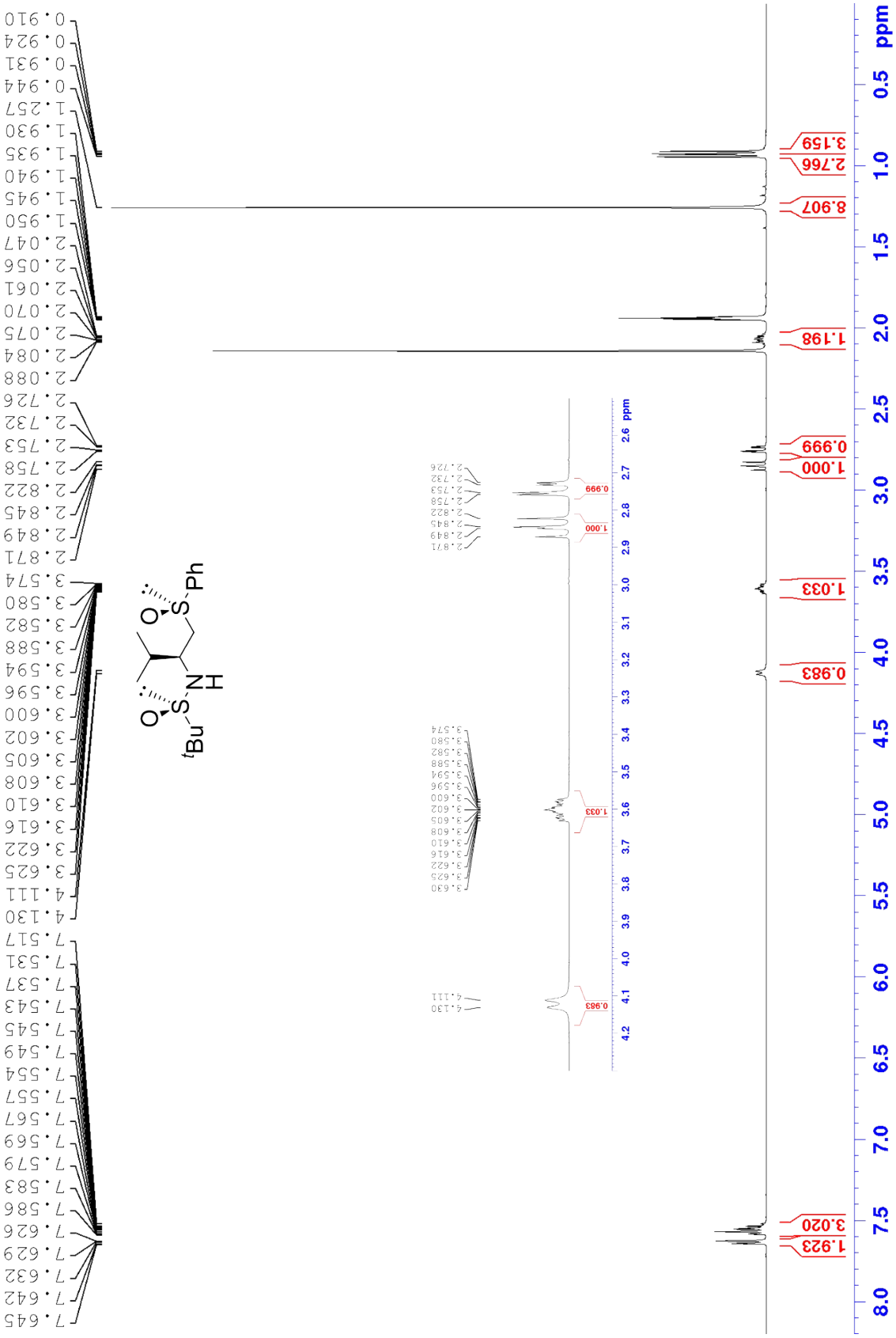


^{13}C-NMR (500 MHz, CD_3CN)

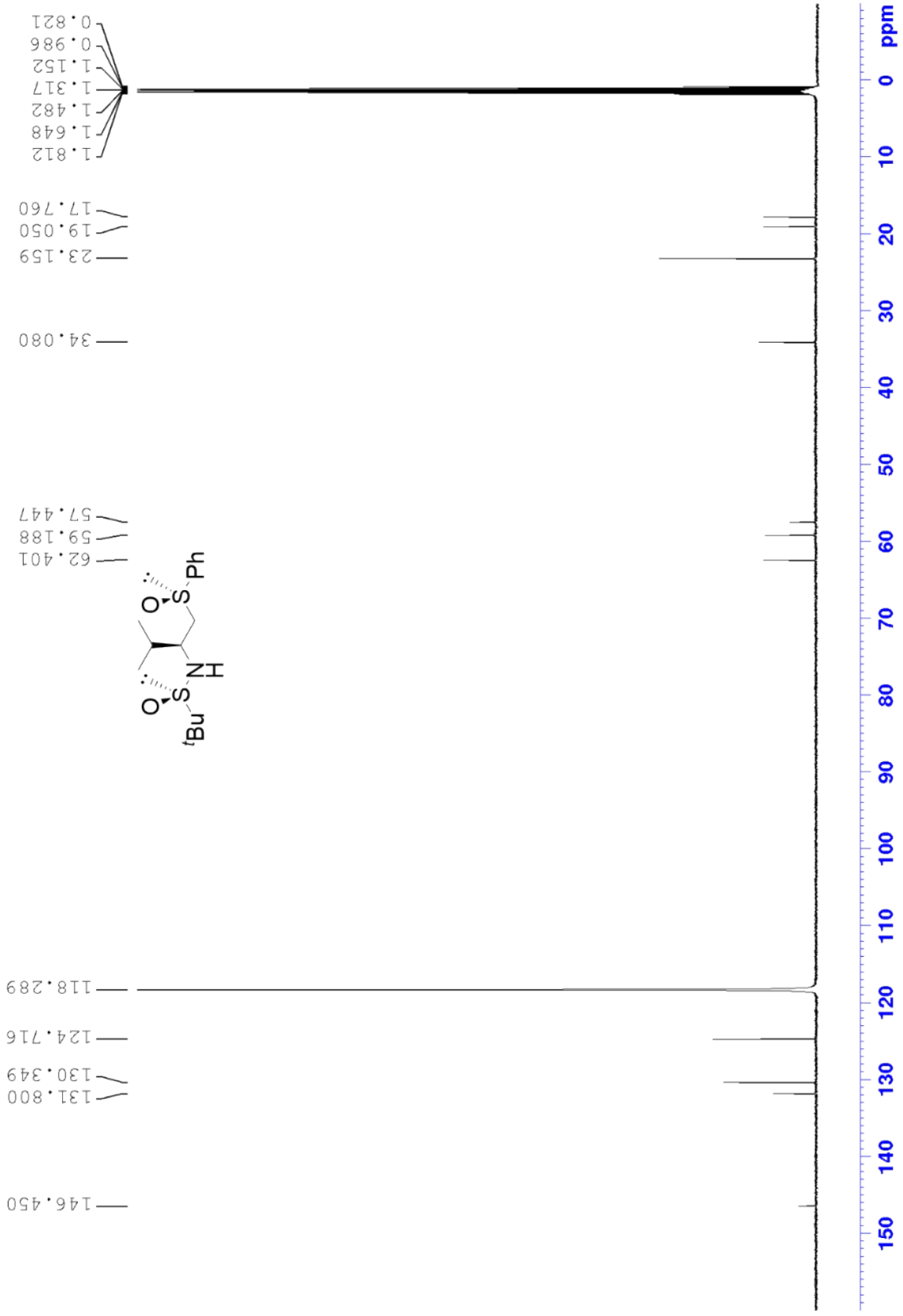


(R_S,S_C,R_S)-N-[1-(Phenylsulfinyl)-3-methylbut-2-yl]-2-methyl-2-propanesulfinamide, **9(R_S,S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

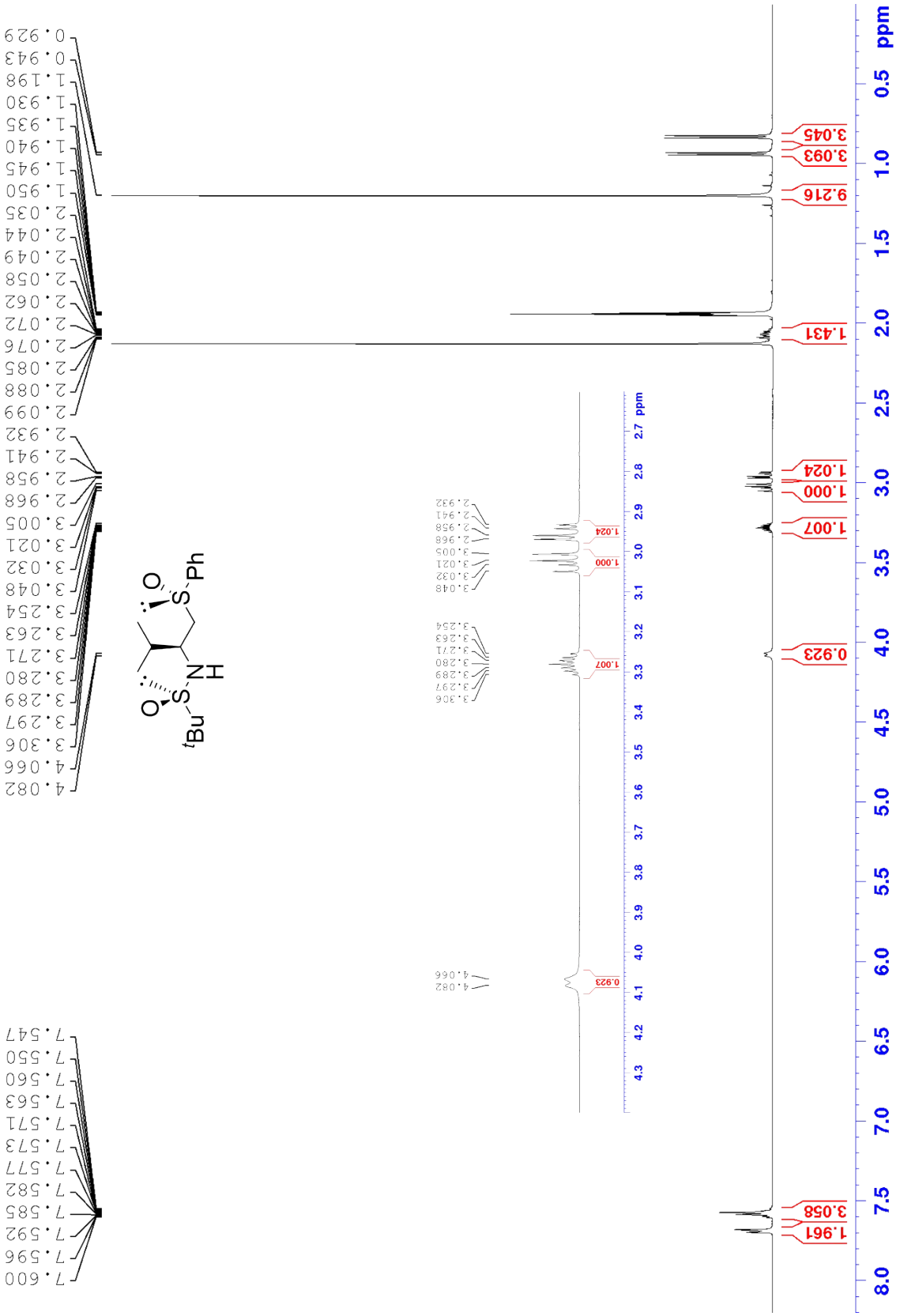


^{13}C-NMR (500 MHz, CD_3CN)

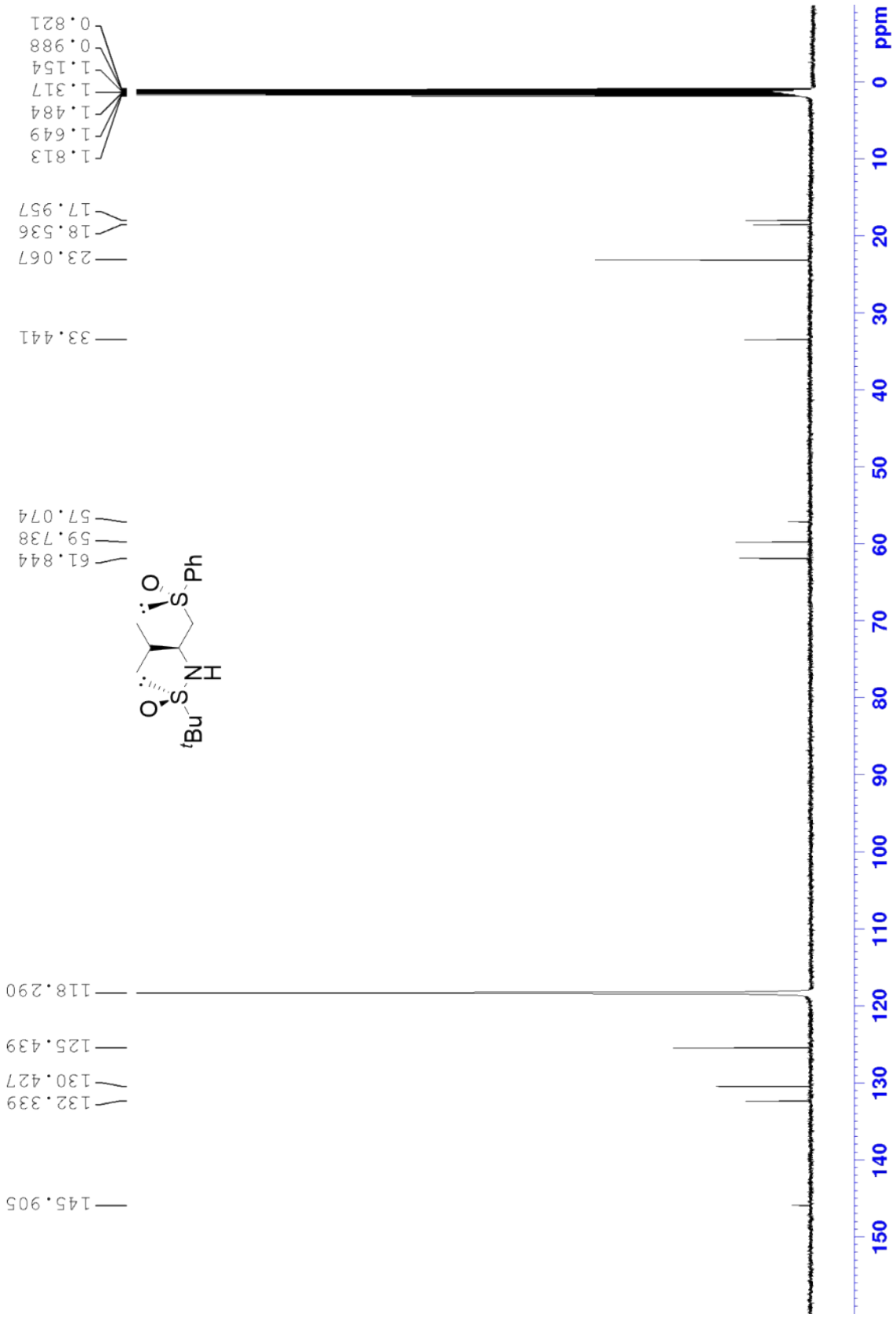


(R_S,S_C,S_S)-N-[1-(Phenylsulfinyl)-3-methylbut-2-yl]-2-methyl-2-propanesulfinamide, **9(R_S,S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

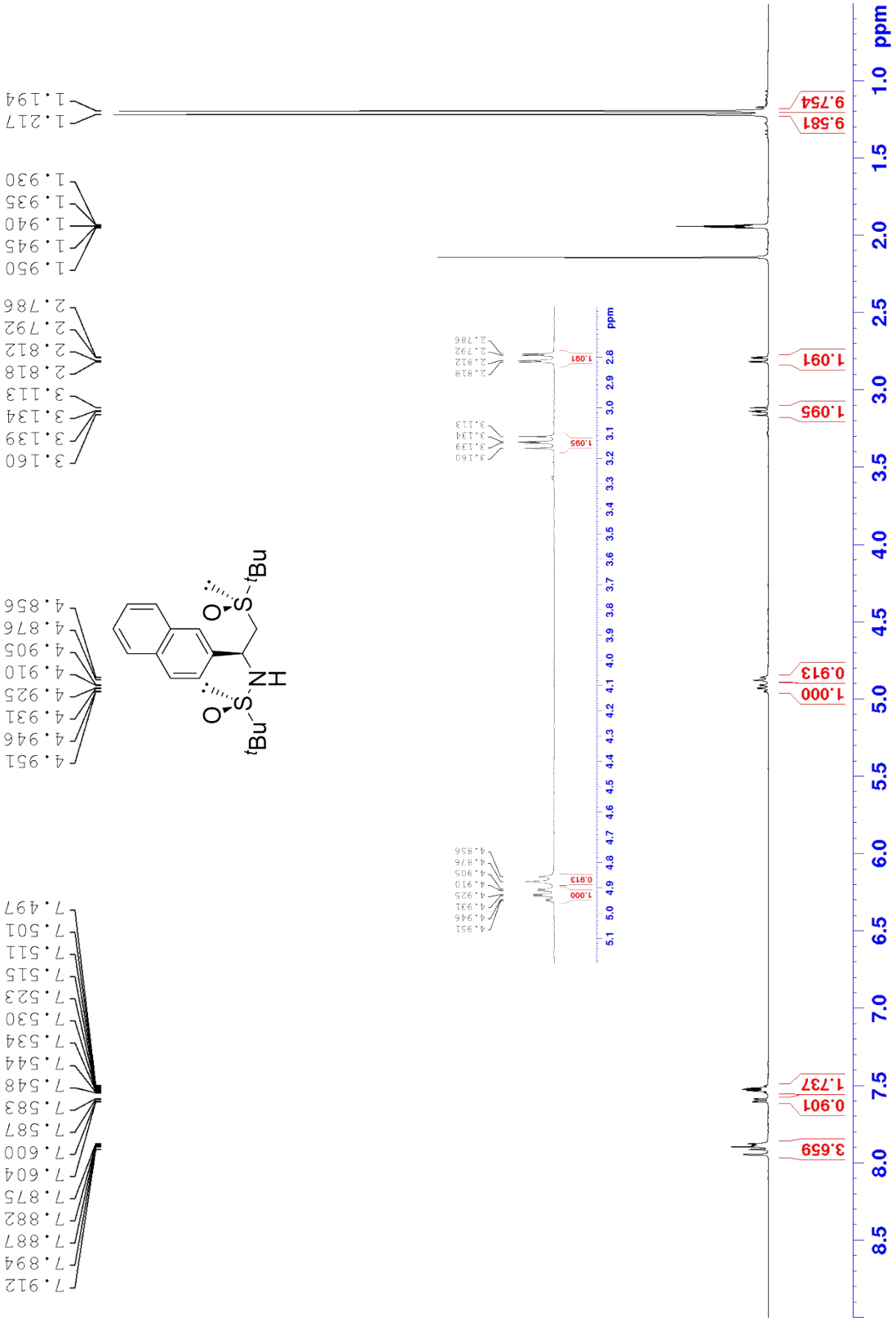


^{13}C-NMR (500 MHz, CD_3CN)

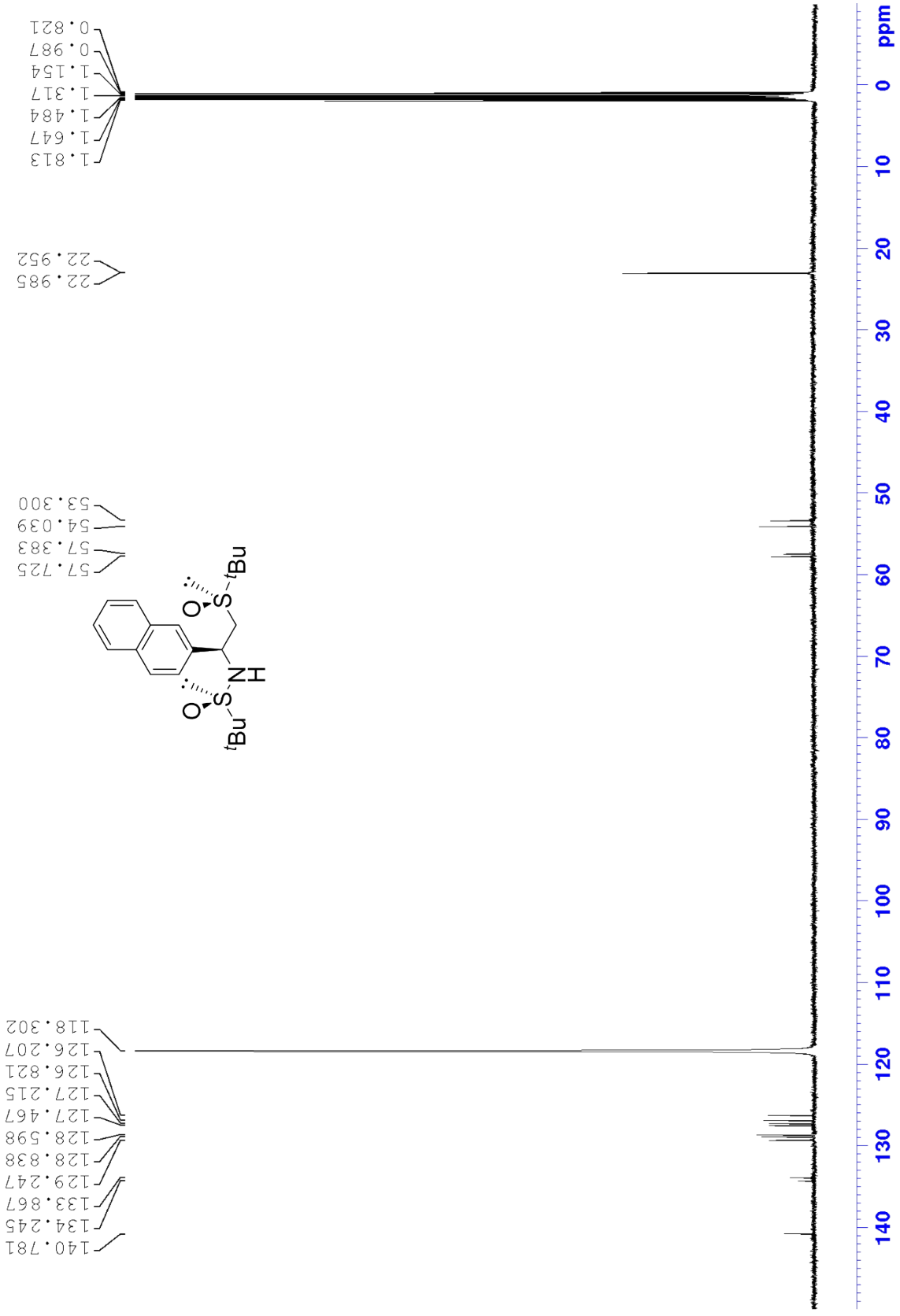


(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
10(R_S,S_C,R_S)

^{1}H-NMR (500 MHz, CD_3CN)

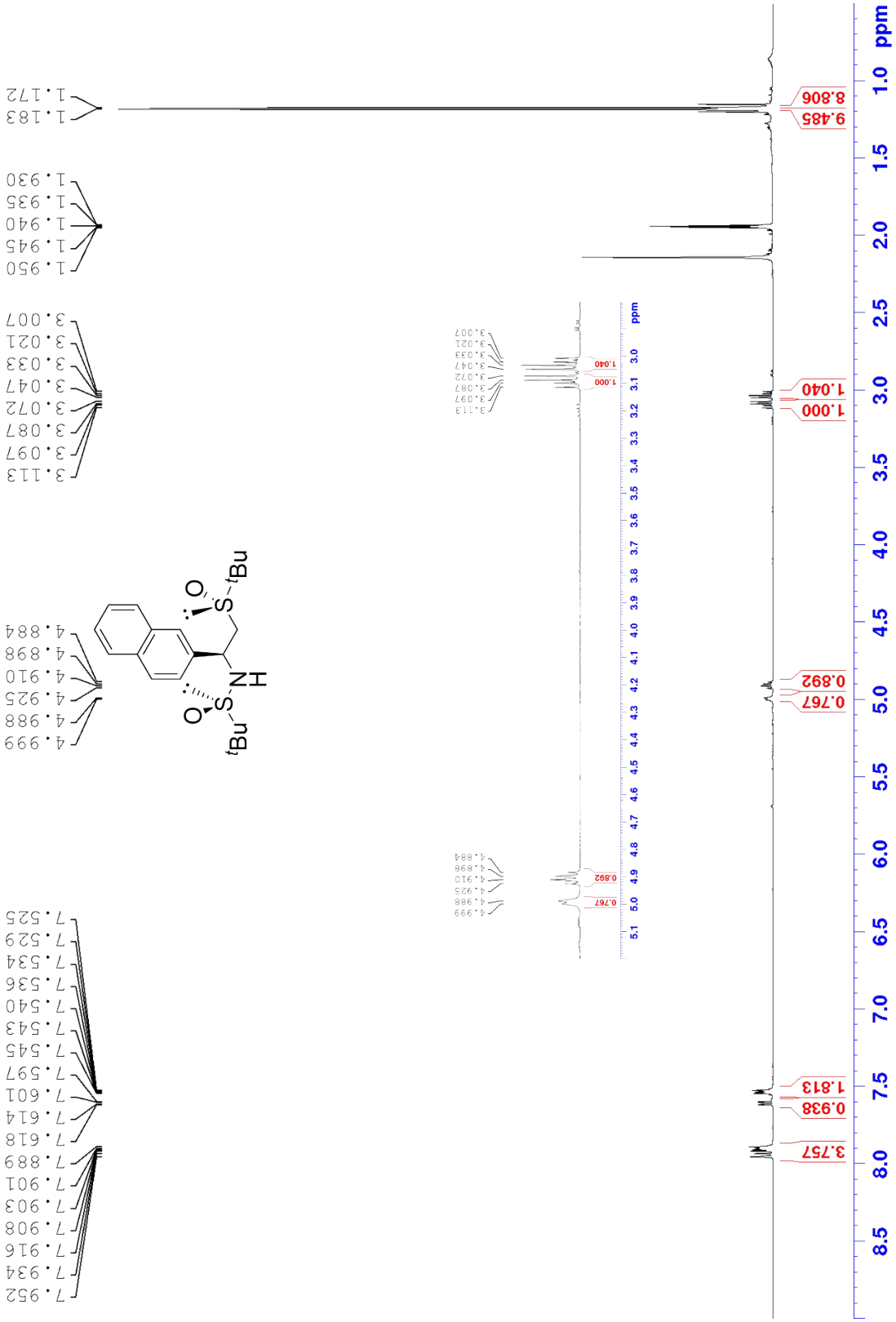


^{13}C-NMR (500 MHz, CD_3CN)

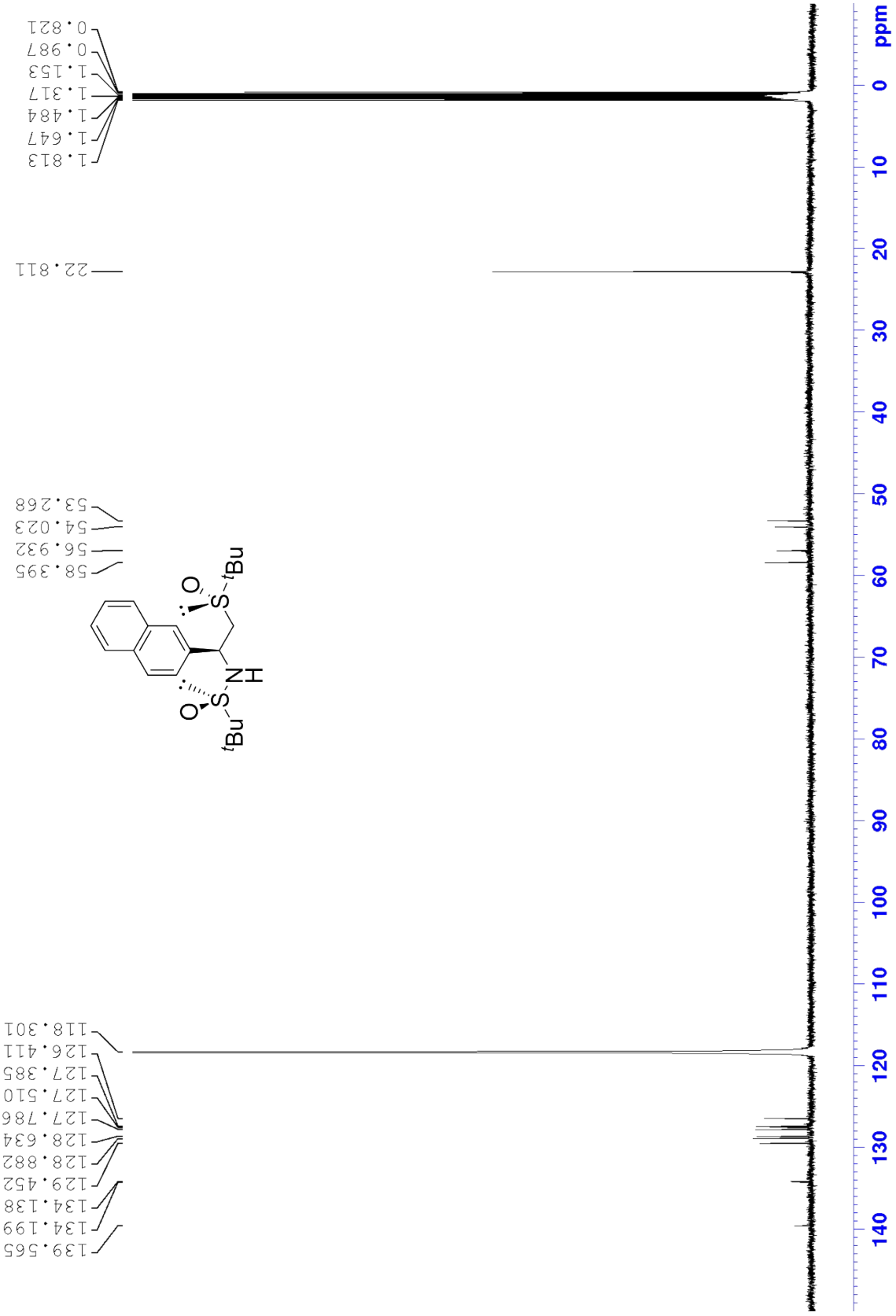


(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide,
10(R_S,S_C,S_S)

^{1}H-NMR (500 MHz, CD_3CN)

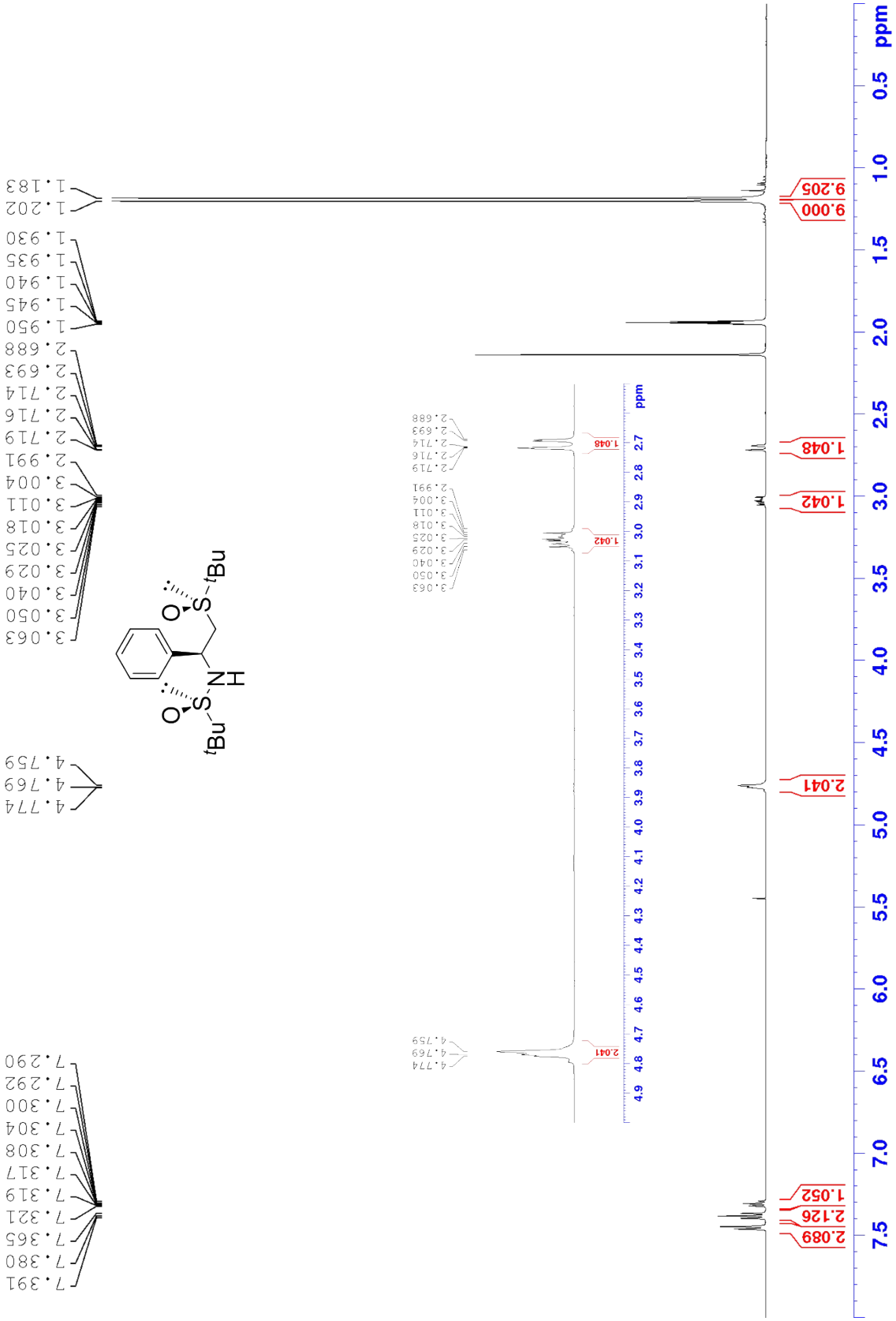


^{13}C-NMR (500 MHz, CD_3CN)

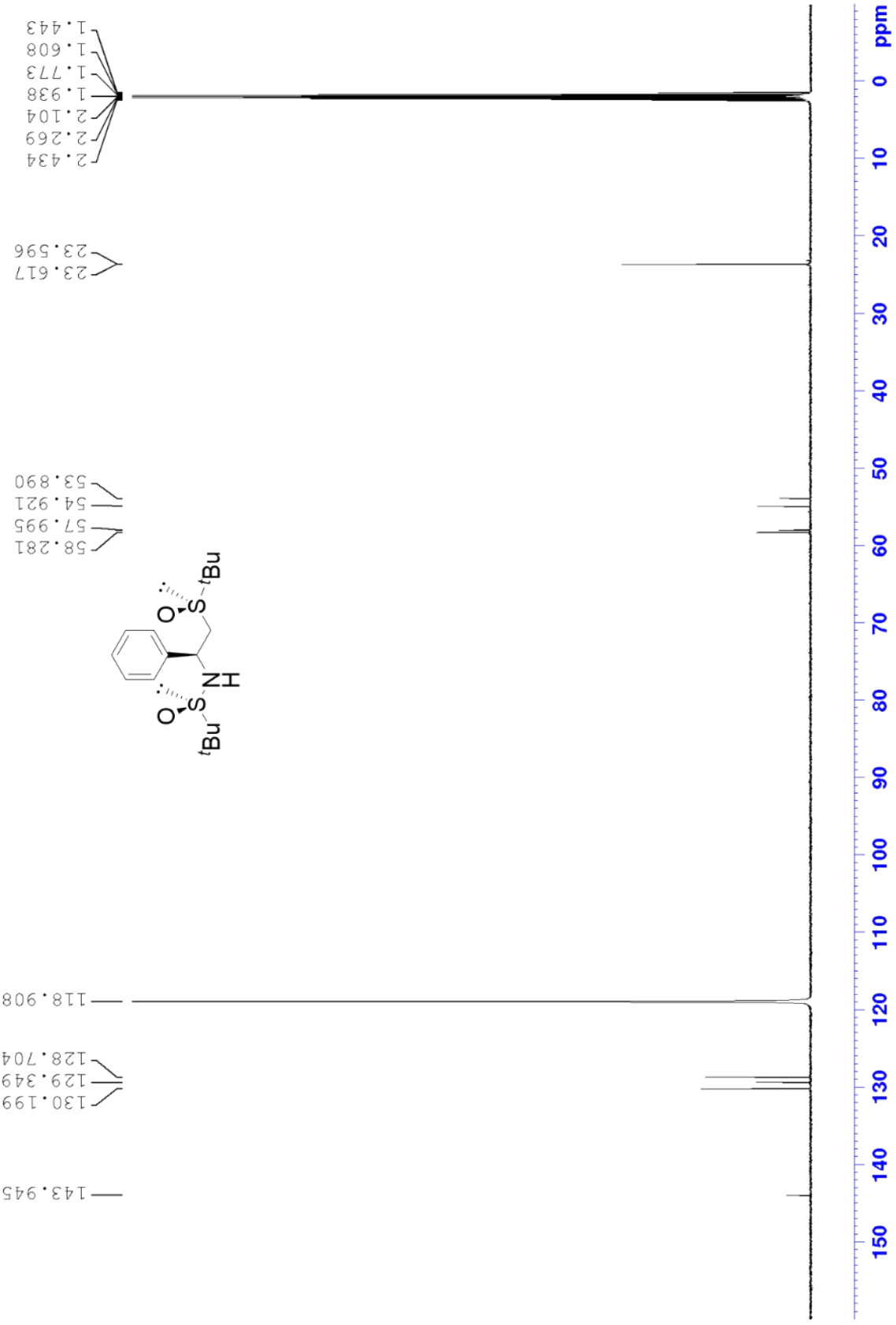


(R_S,S_C,R_S)-N-[2-(tert-butylsulfinyl)-1-phenylethyl]-2-methyl-2-propanesulfinamide, **11(R_S,S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

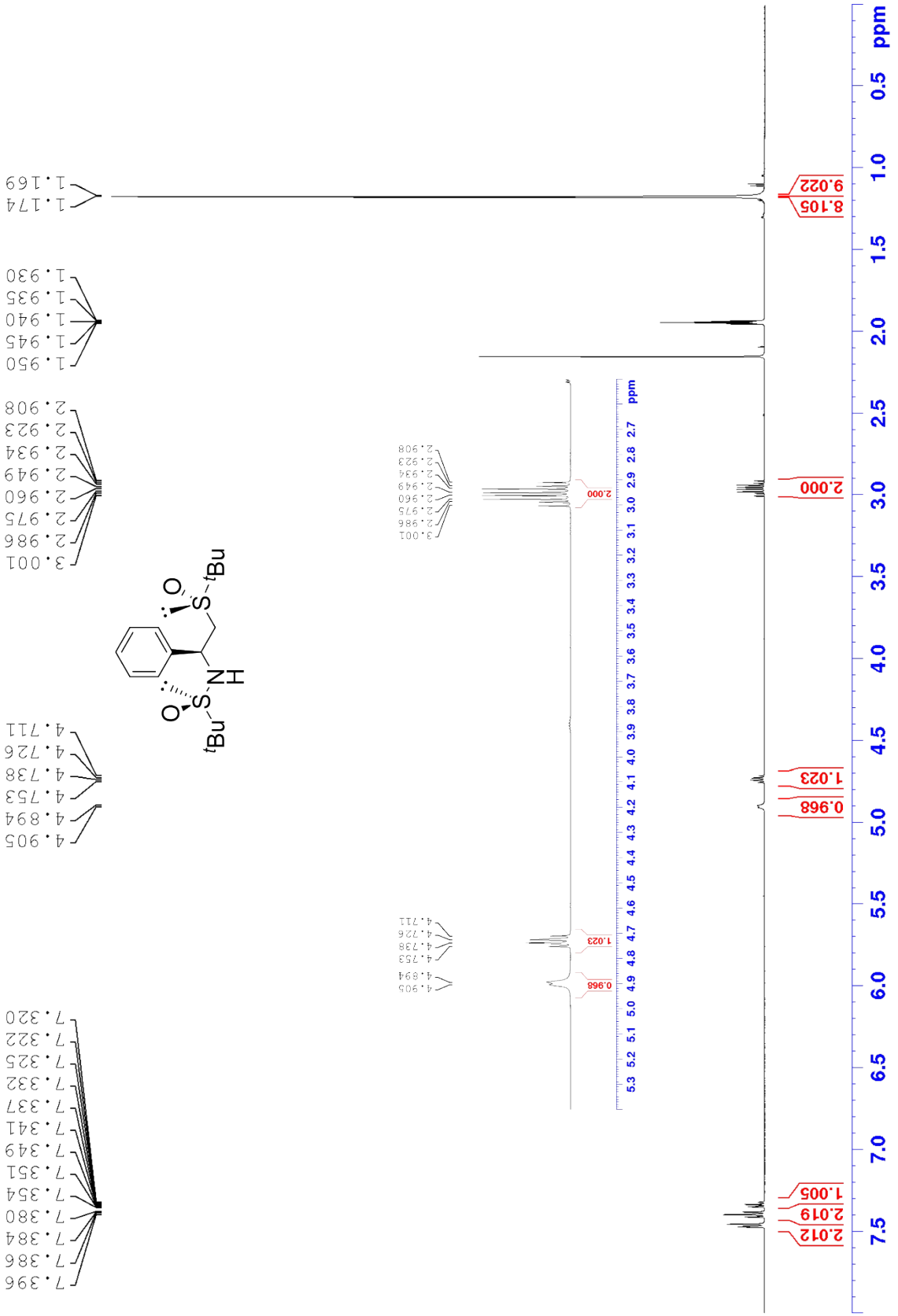


^{13}C-NMR (500 MHz, CD_3CN)

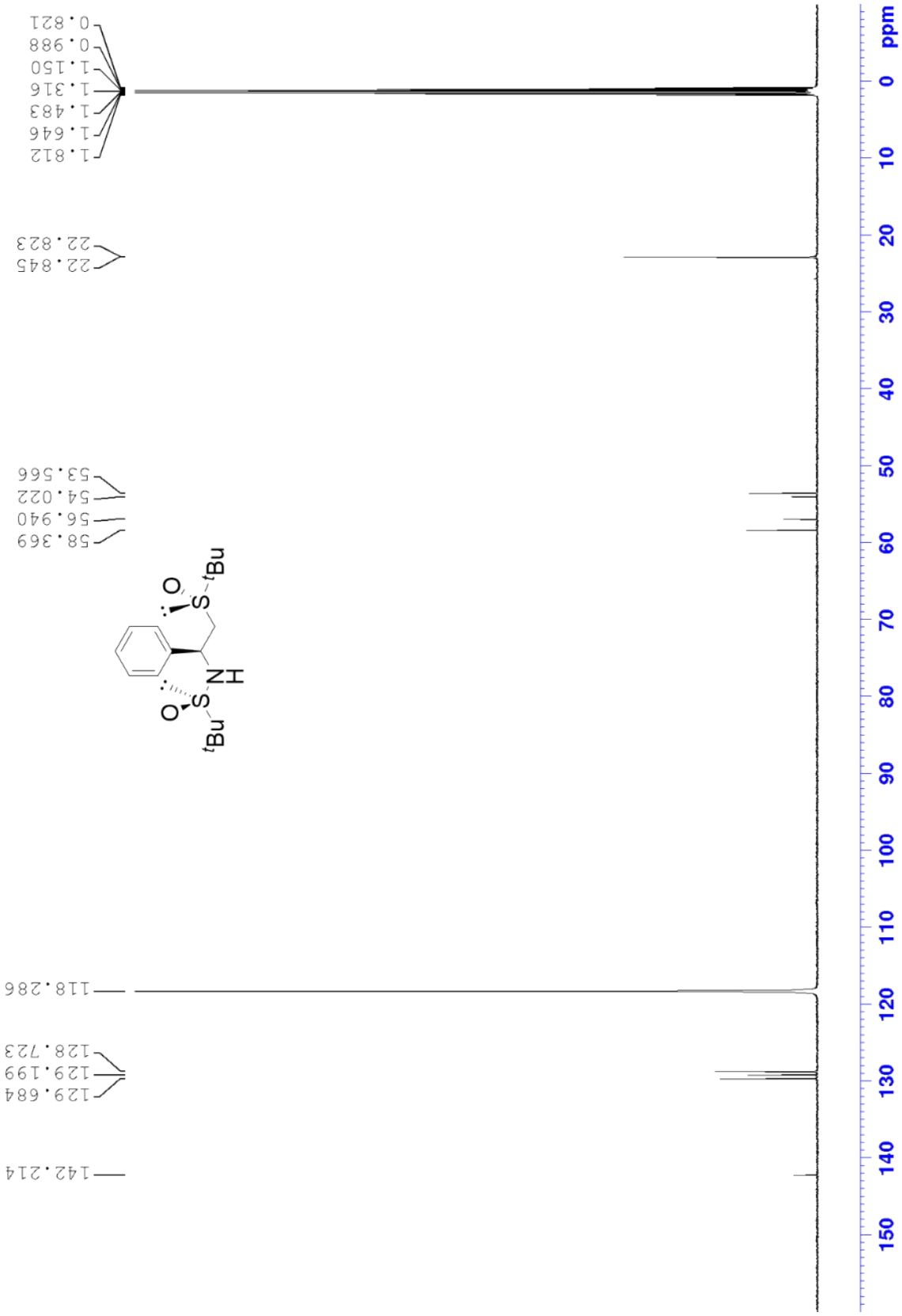


(R_S,S_C,S_S)-N-[2-(tert-butylsulfinyl)-1-phenylethyl]-2-methyl-2-propanesulfinamide, **11(R_S,S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

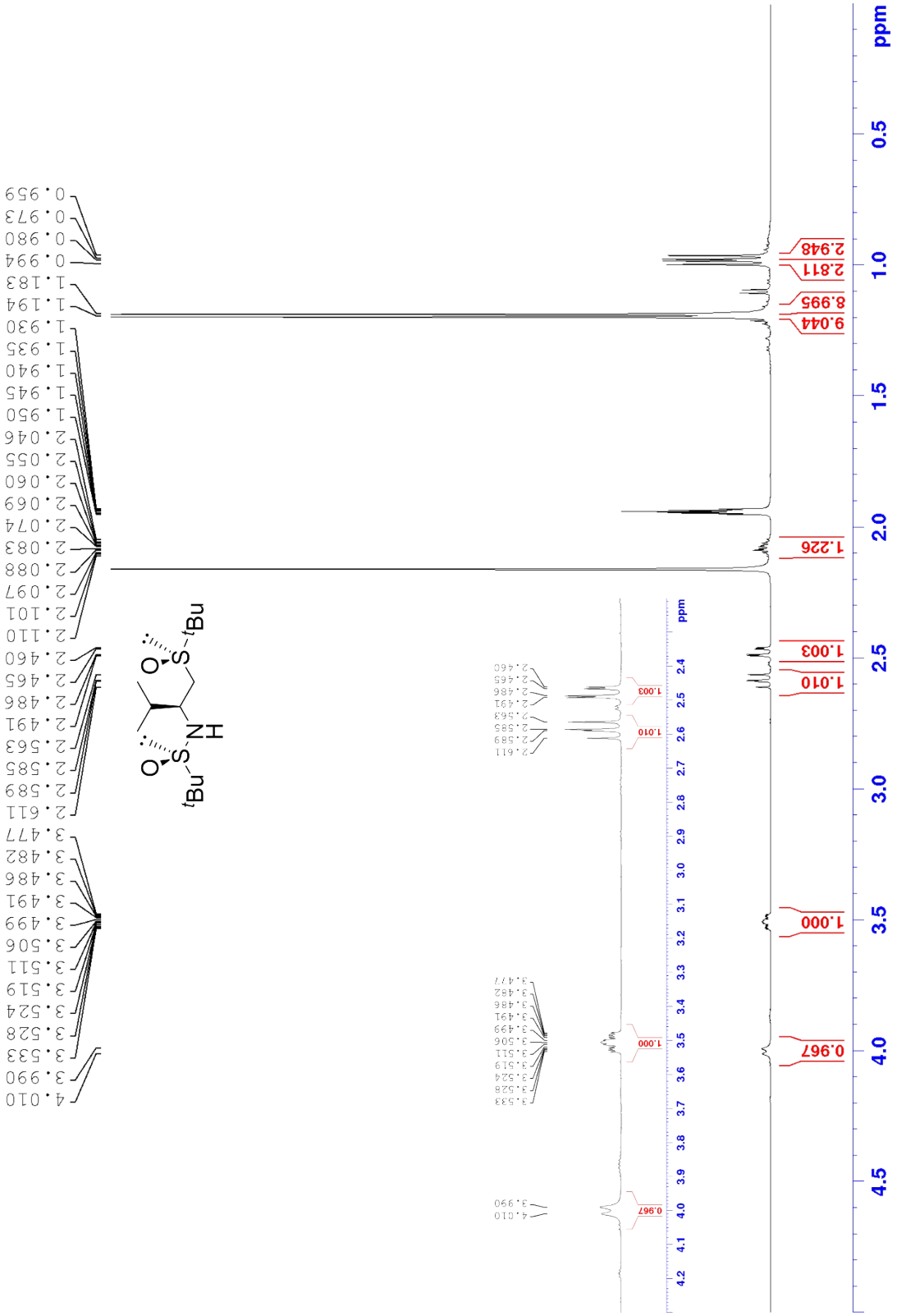


^{13}C-NMR (500 MHz, CD_3CN)

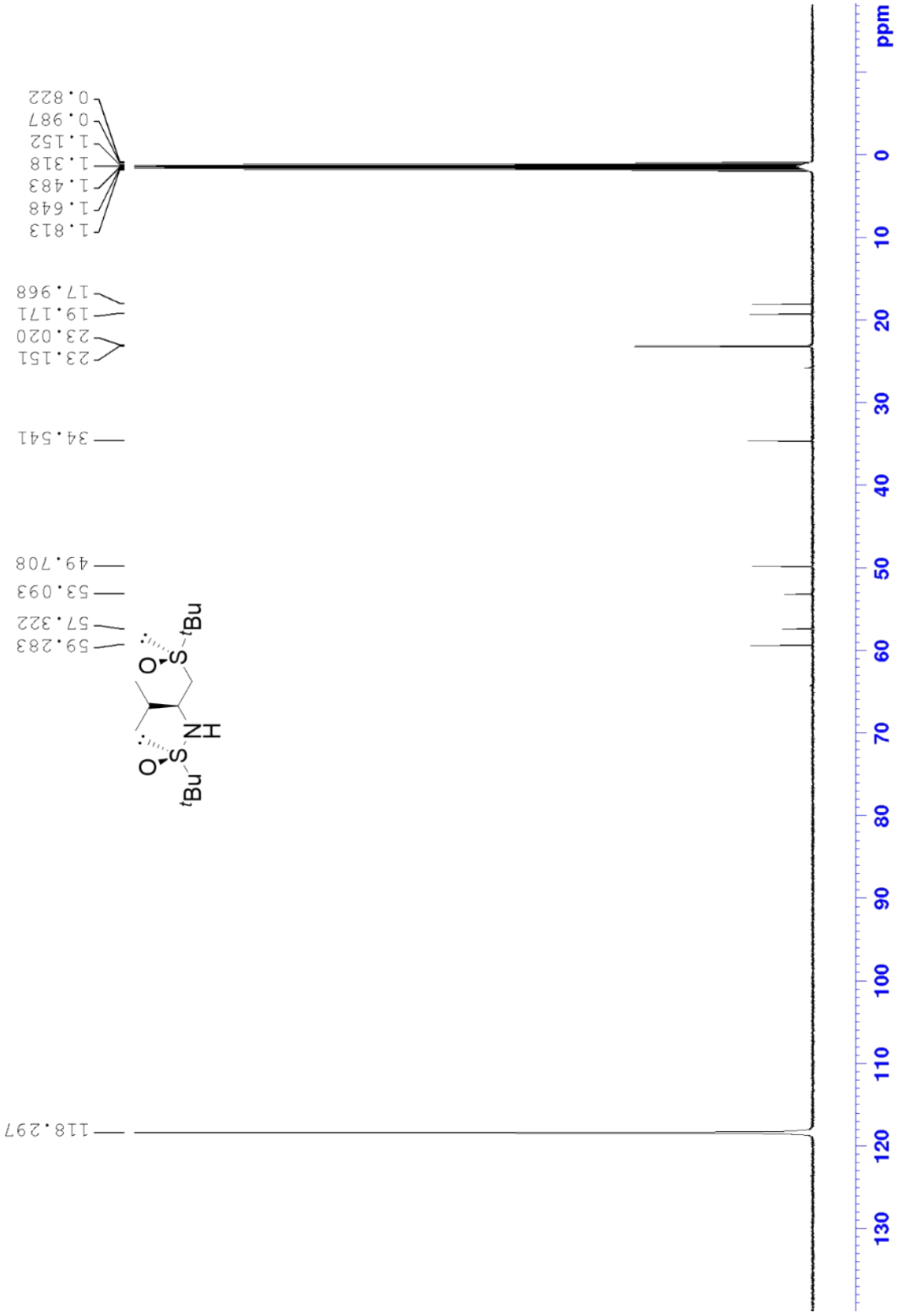


(R_S,S_C,R_S)-N-[1-(tert-butylsulfinyl)-3-methylbutan-2-yl]-2-methyl-2-propanesulfinamide,
12(R_S,S_C,R_S)

^{1}H-NMR (500 MHz, CD_3CN)

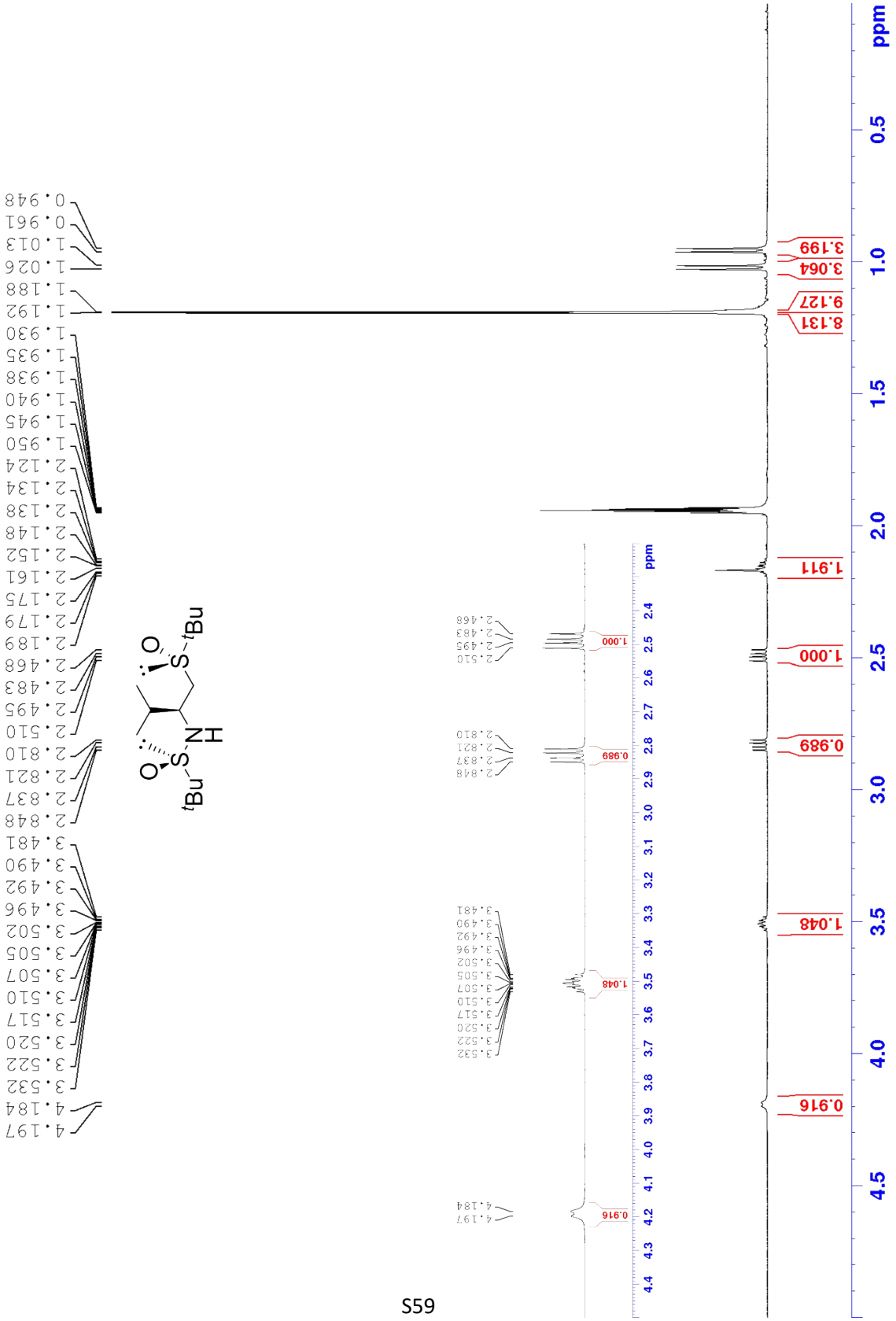


^{13}C-NMR (500 MHz, CD_3CN)

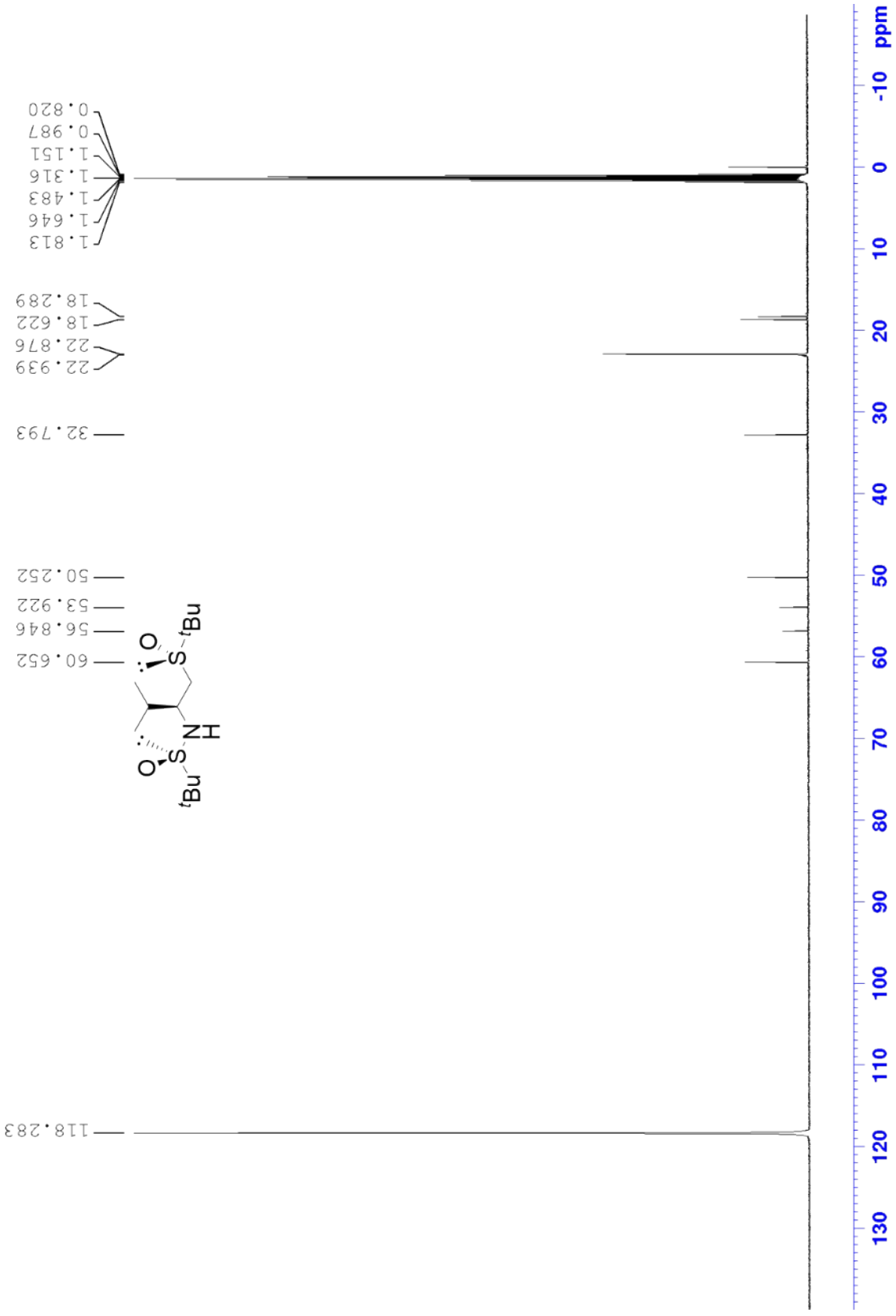


(R_S,S_C,S_S)-N-[1-(tert-butylsulfinyl)-3-methylbutan-2-yl)]-2-methyl-2-propanesulfinamide,
12(R_S,S_C,S_S)

^{1}H-NMR (500 MHz, CD_3CN)

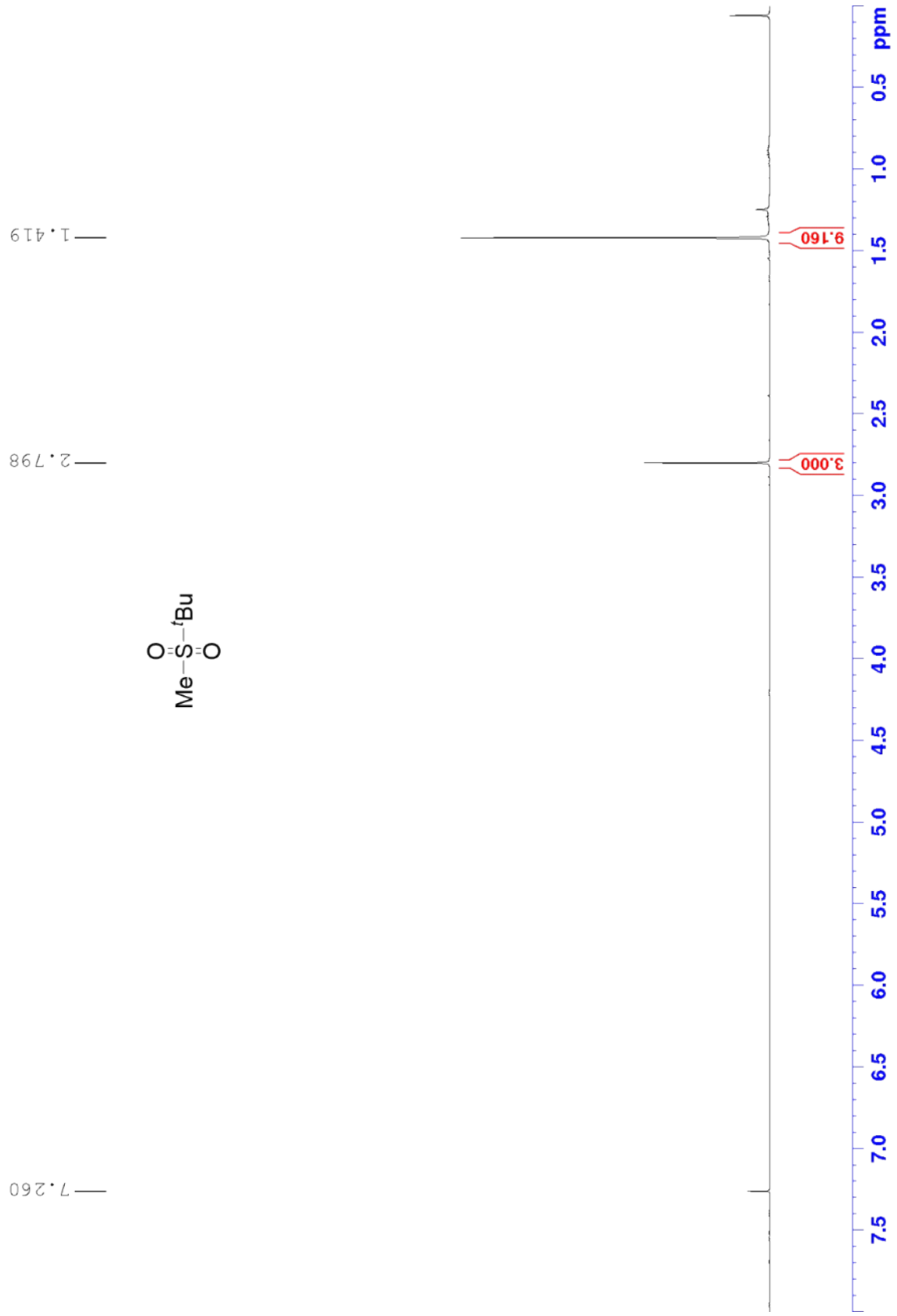


^{13}C-NMR (500 MHz, CD_3CN)

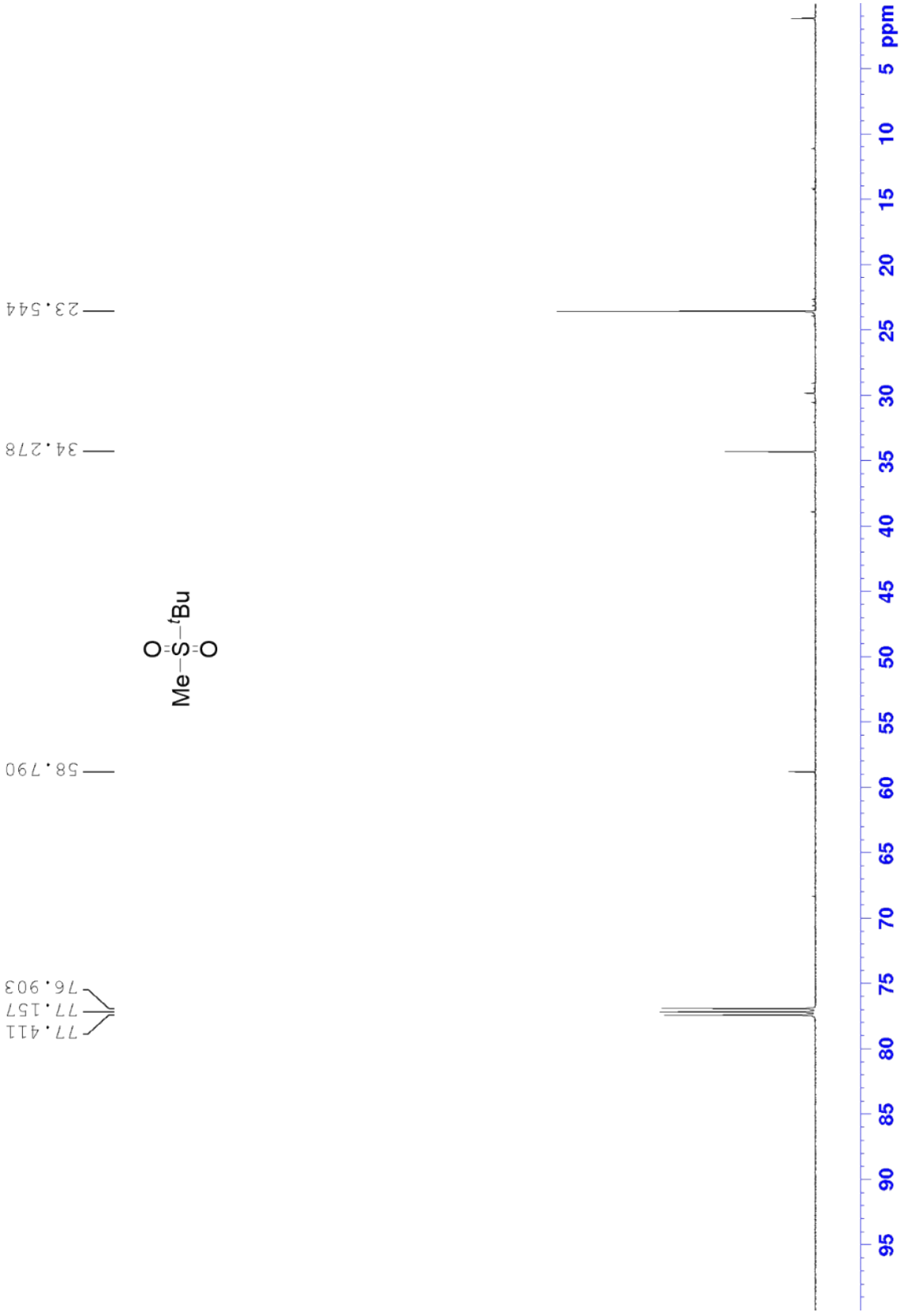


Methyl Tert-butyl sulfone, **20**

^{1}H-NMR (500 MHz, $CDCl_3$)

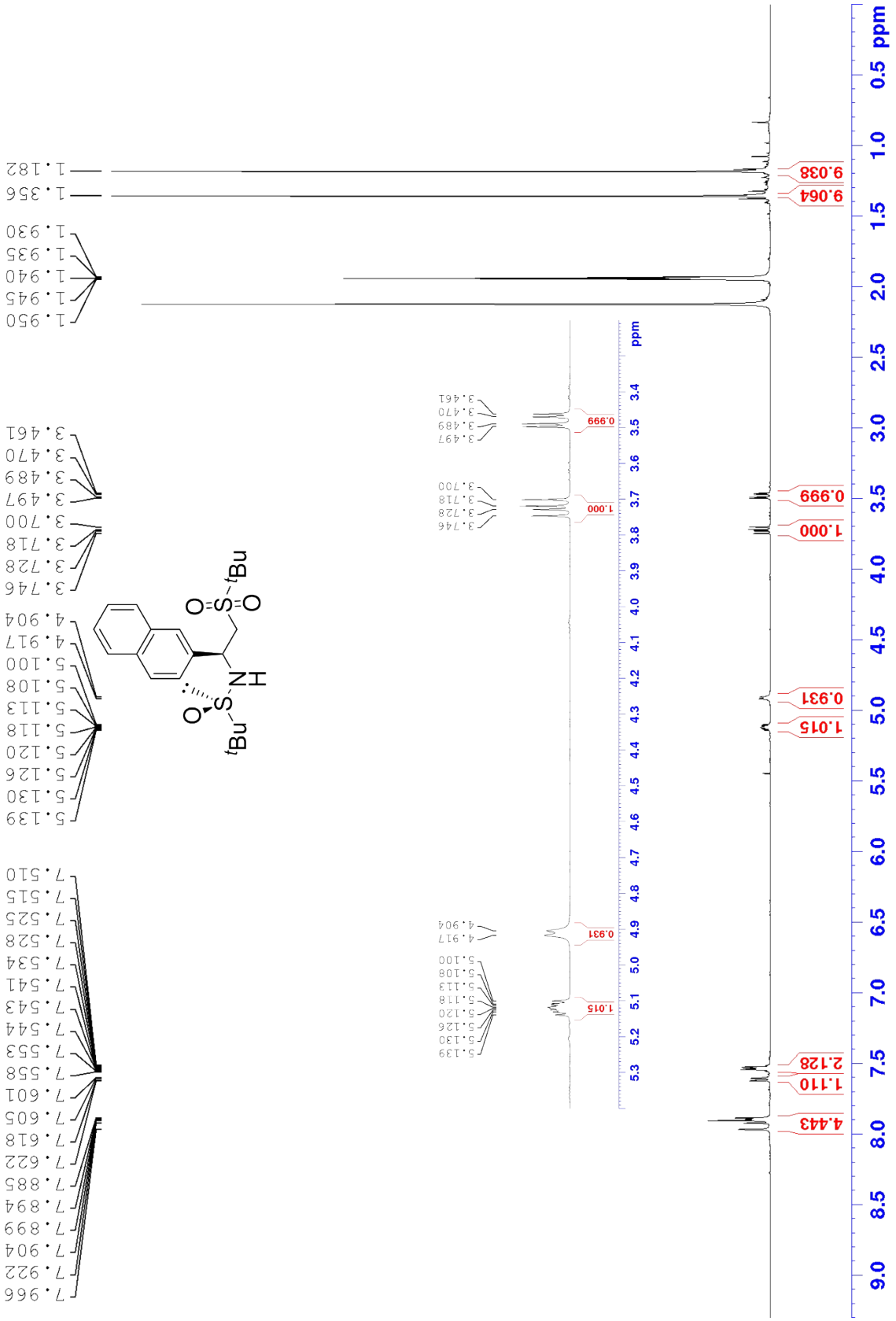


^{13}C-NMR (500 MHz, $CDCl_3$)

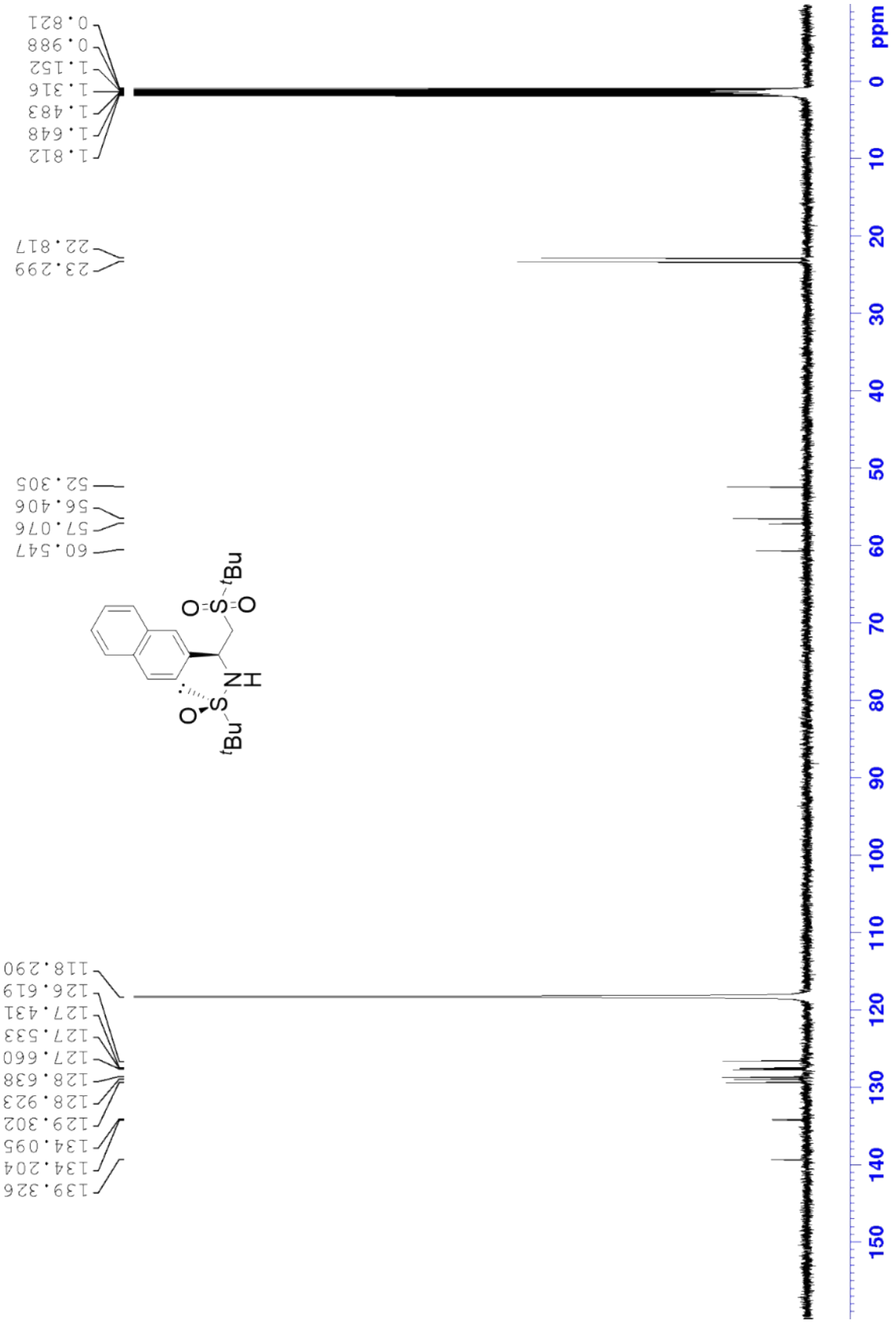


(R_S,S_C)-N-[2-(Tert-butylsulfonyl)-1-(2-naphthyl)ethyl]-2-methyl-2-propanesulfinamide, **21(R_S,S_C)**

^{1}H-NMR (500 MHz, CD_3CN)

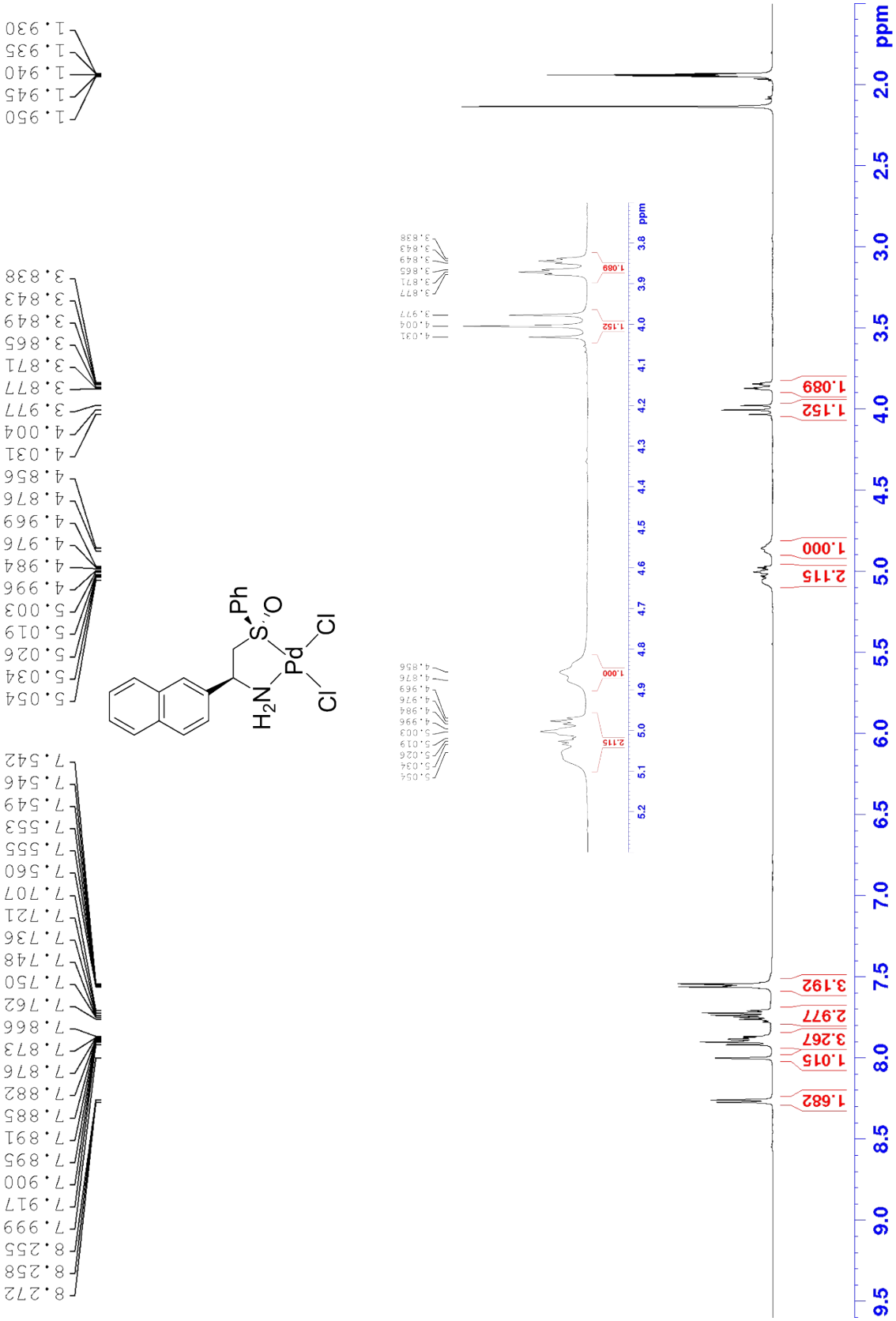


^{13}C-NMR (500 MHz, CD_3CN)

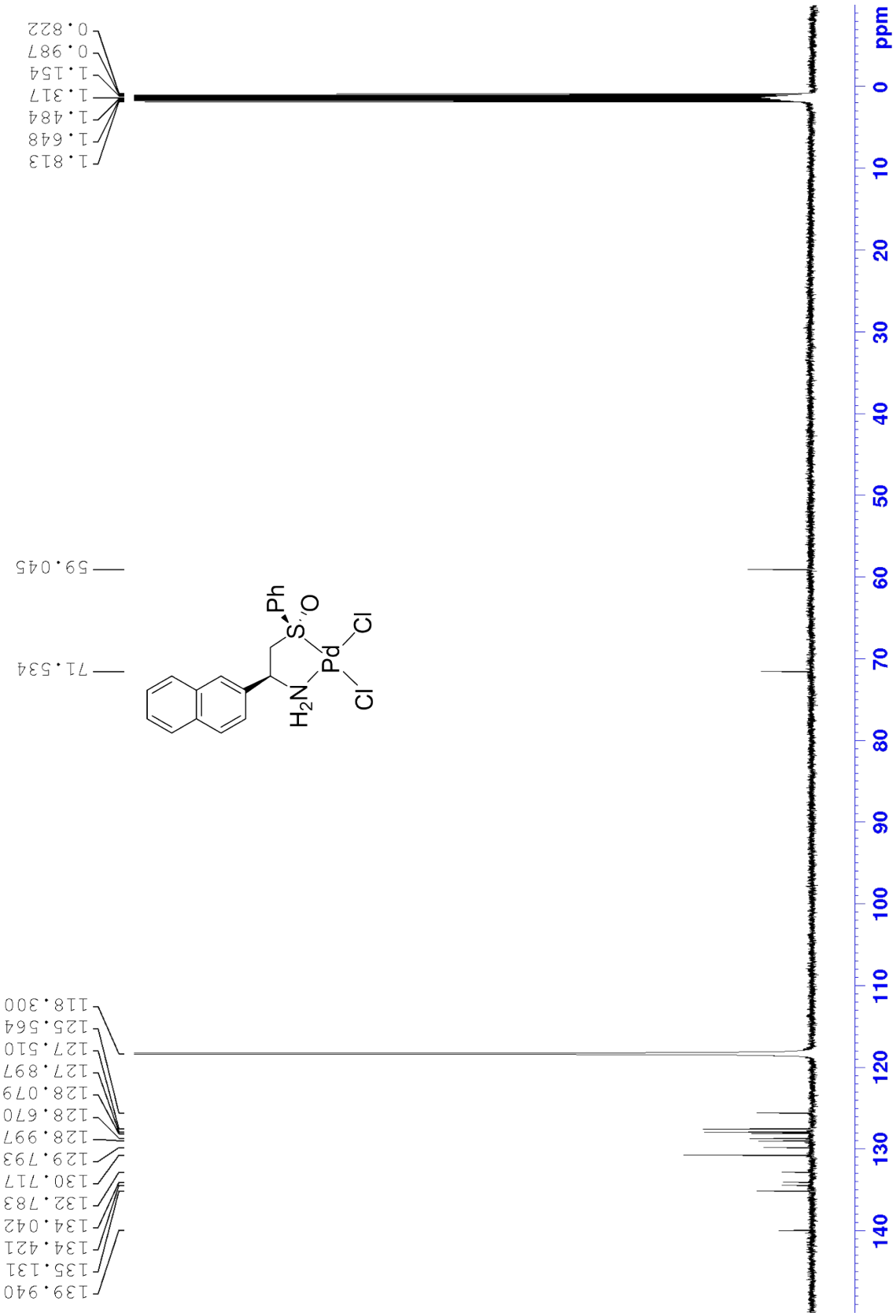


cis-Dichloro[(S_C,S_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

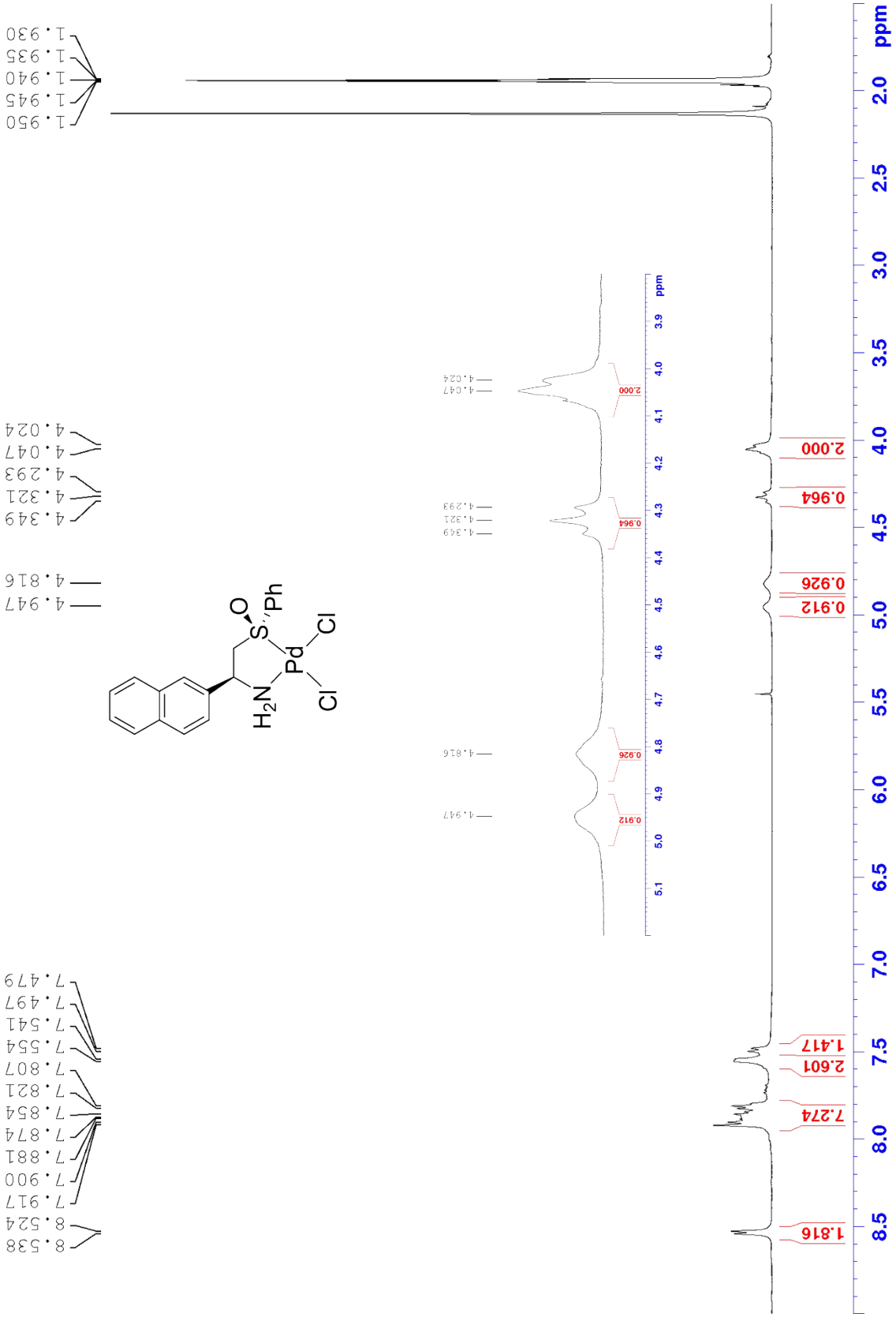


^{13}C-NMR (500 MHz, CD_3CN)

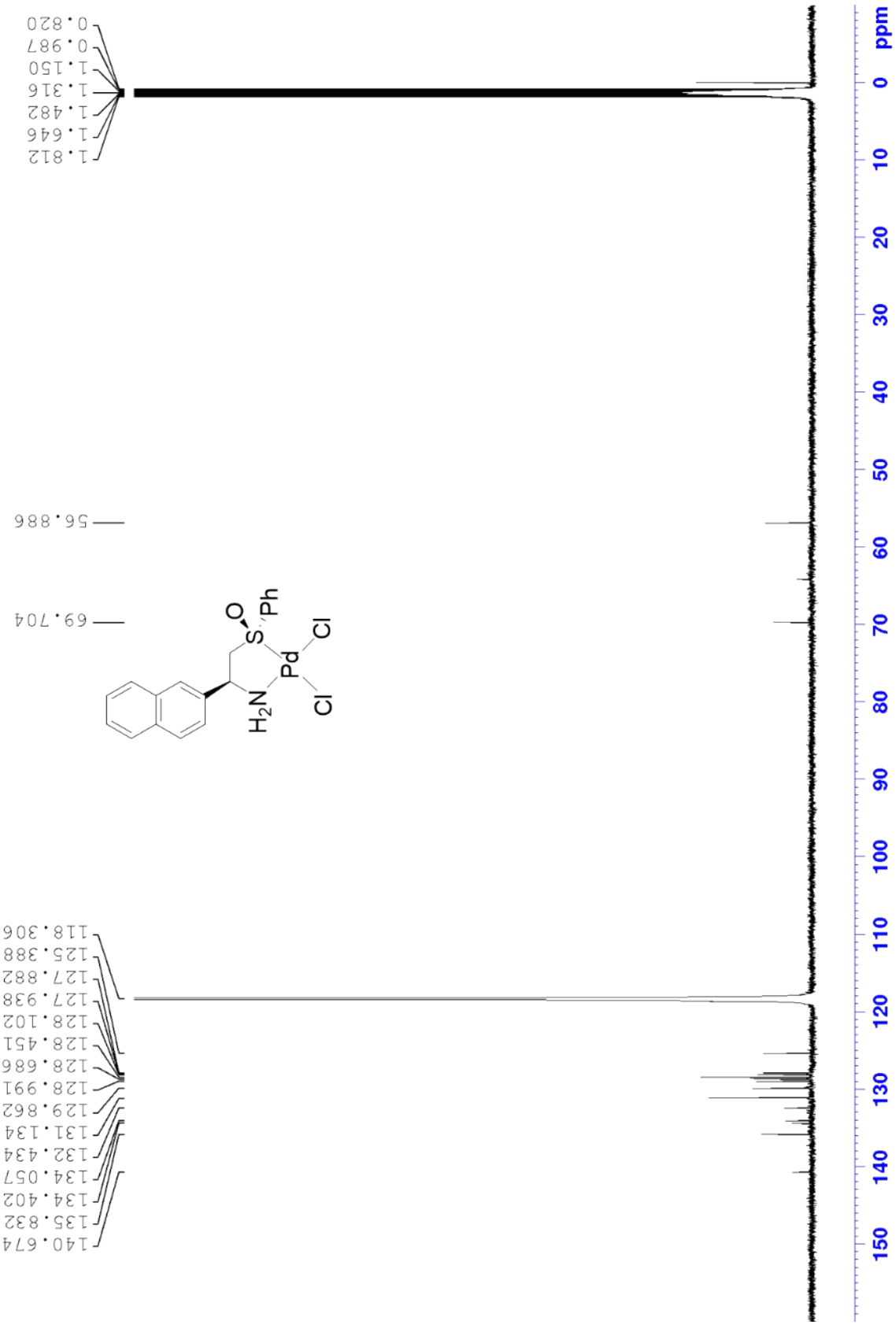


cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

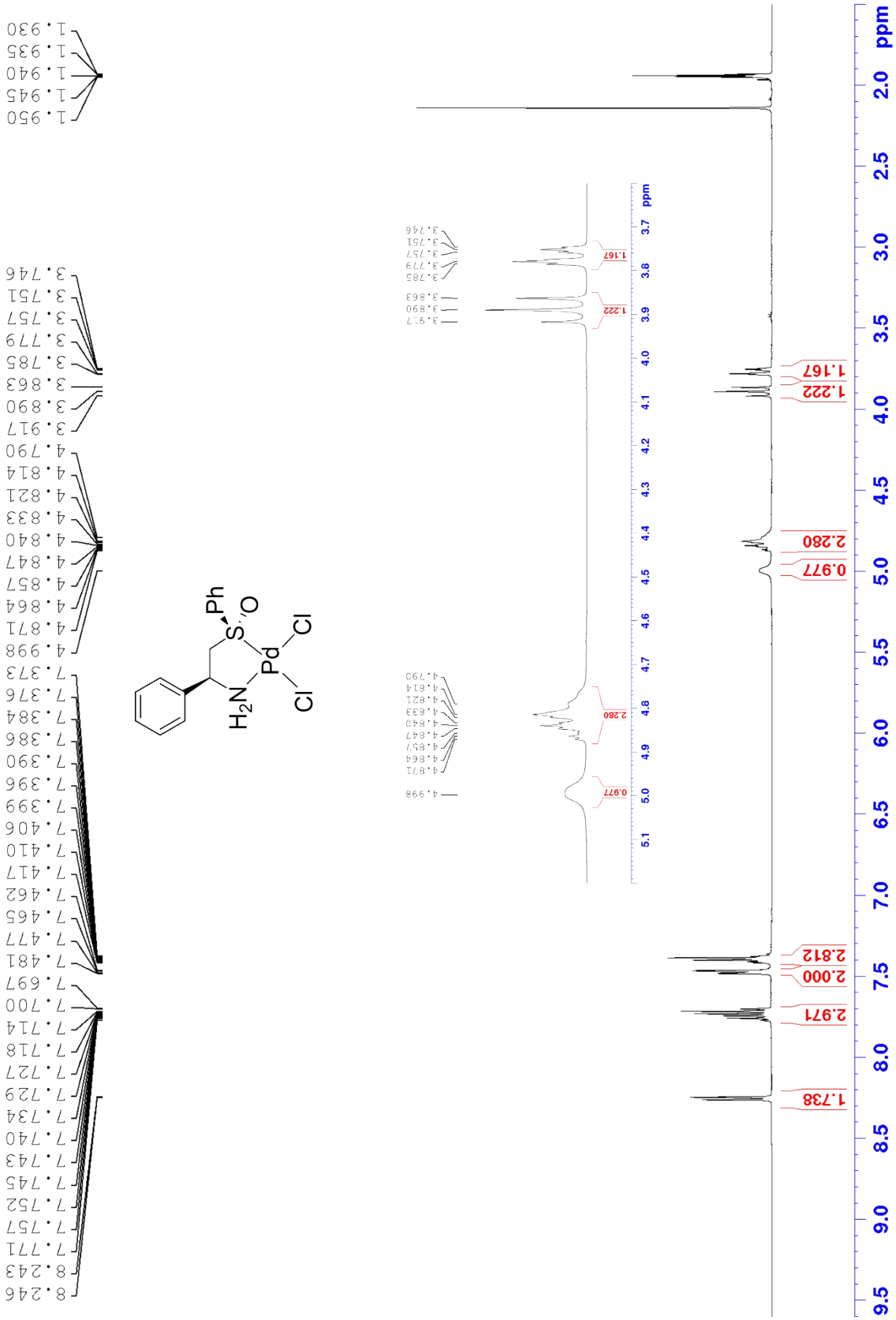


^{13}C-NMR (500 MHz, CD_3CN)

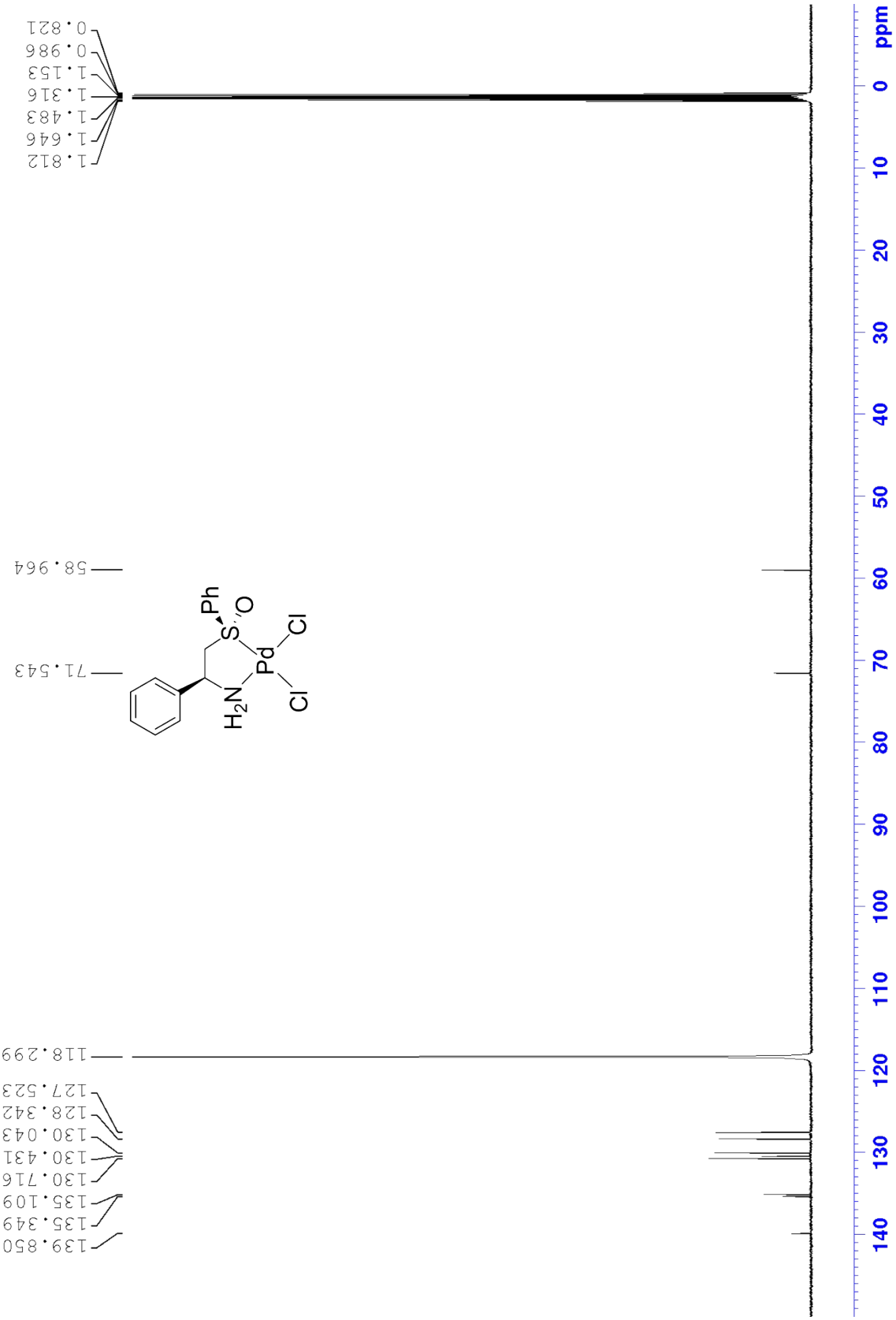


cis-Dichloro[(S_C,S_S)-1-(Phenyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **14(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

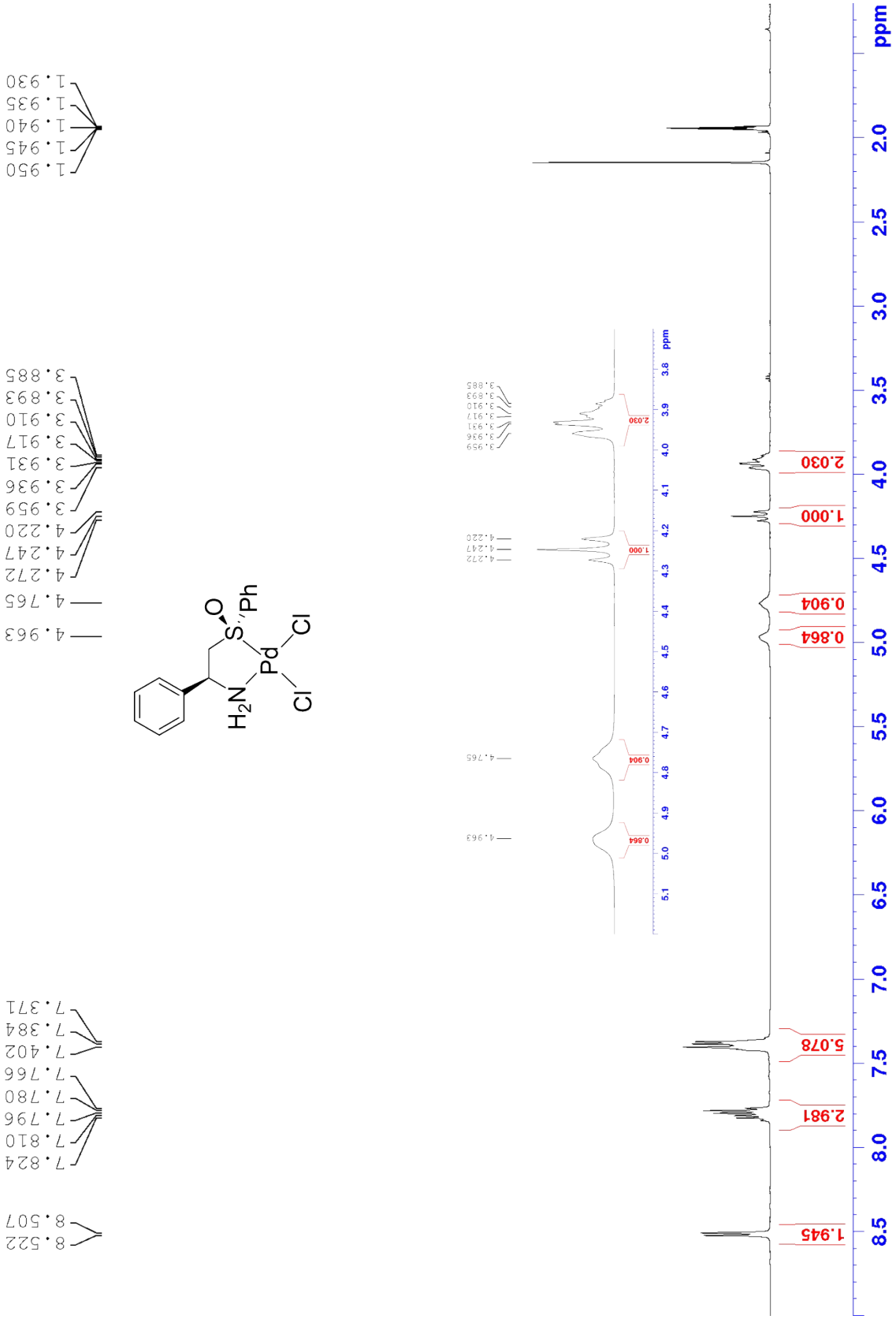


^{13}C-NMR (500 MHz, CD_3CN)

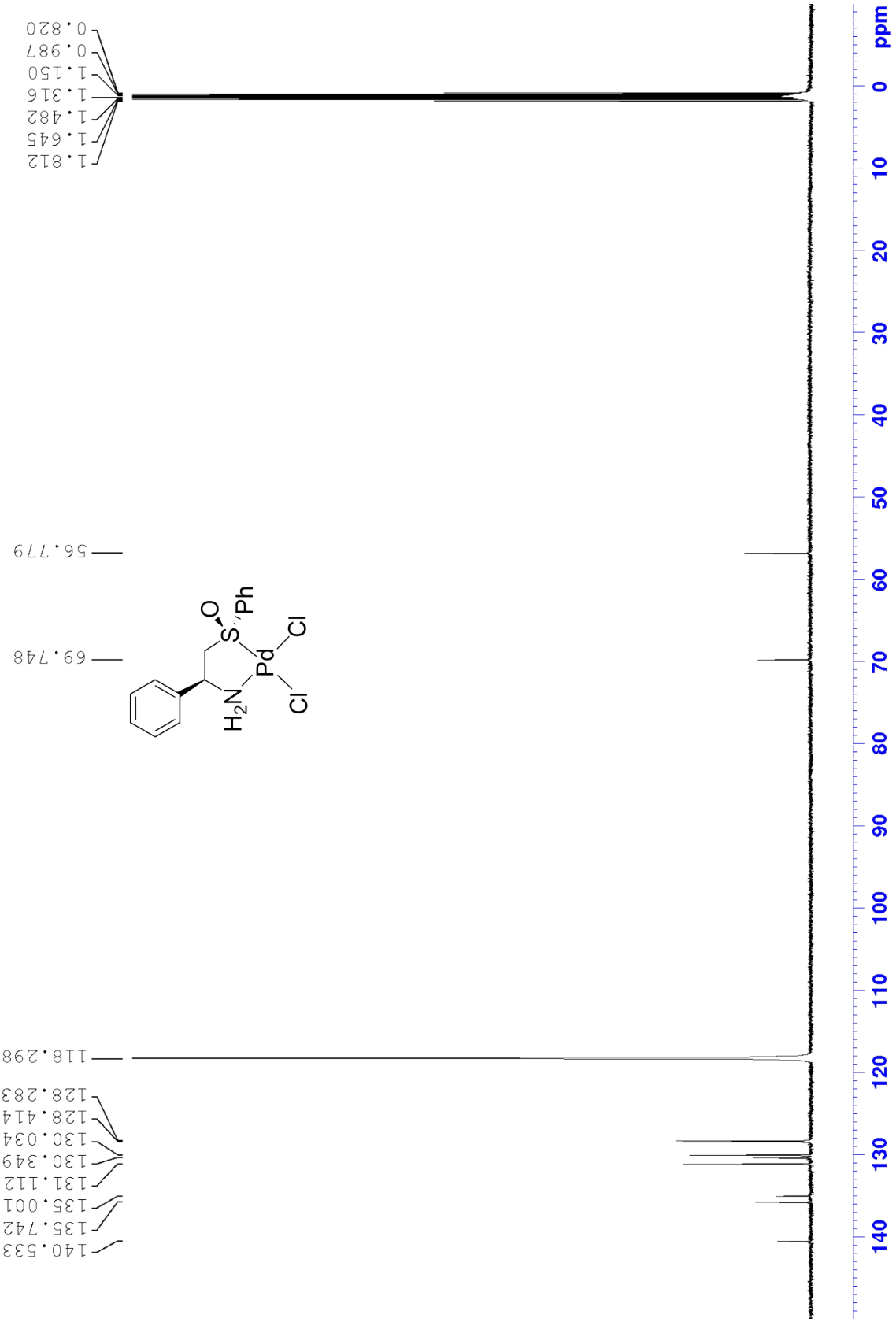


cis-Dichloro[(S_C,R_S)-1-(Phenyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **14(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

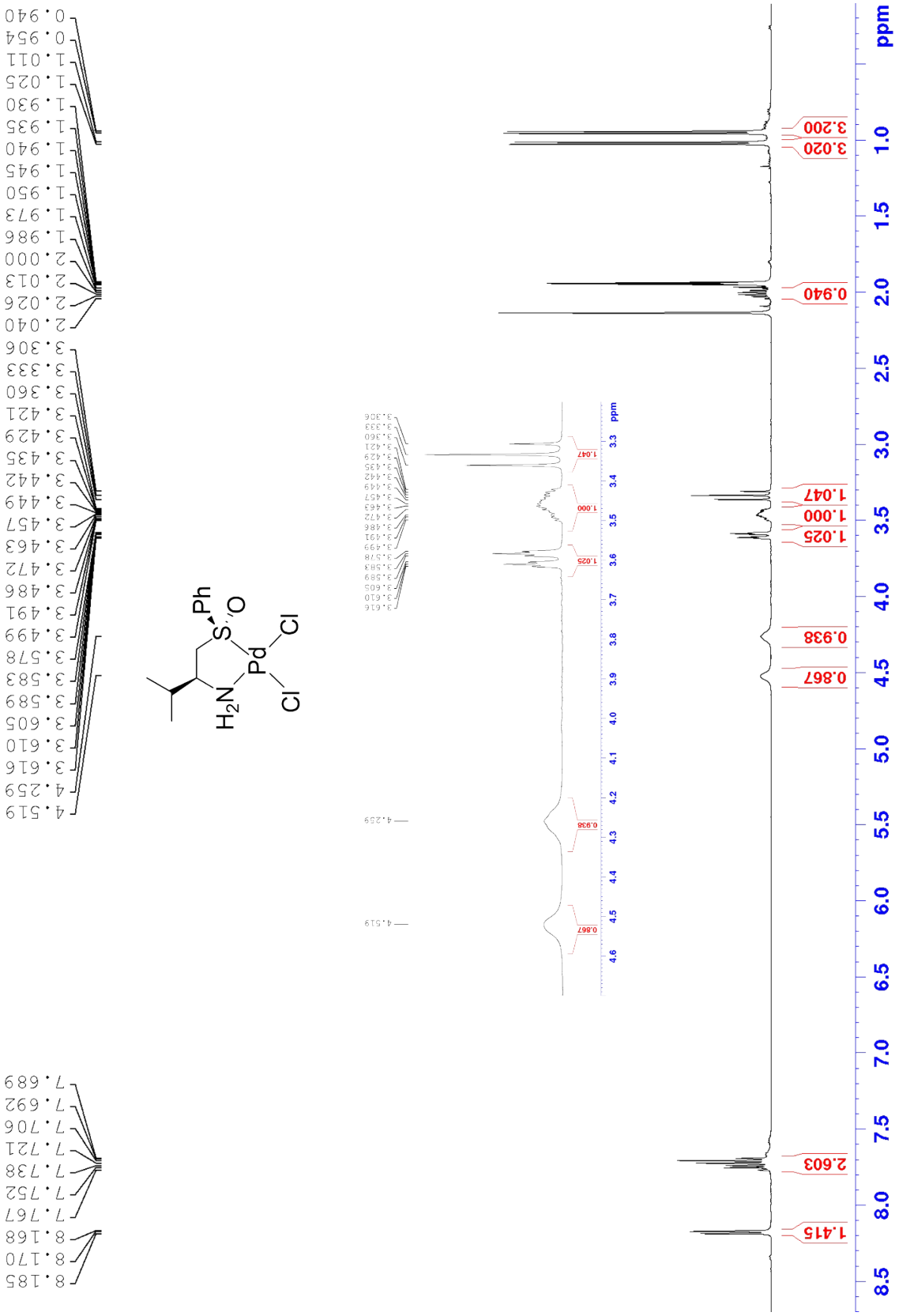


^{13}C-NMR (500 MHz, CD_3CN)

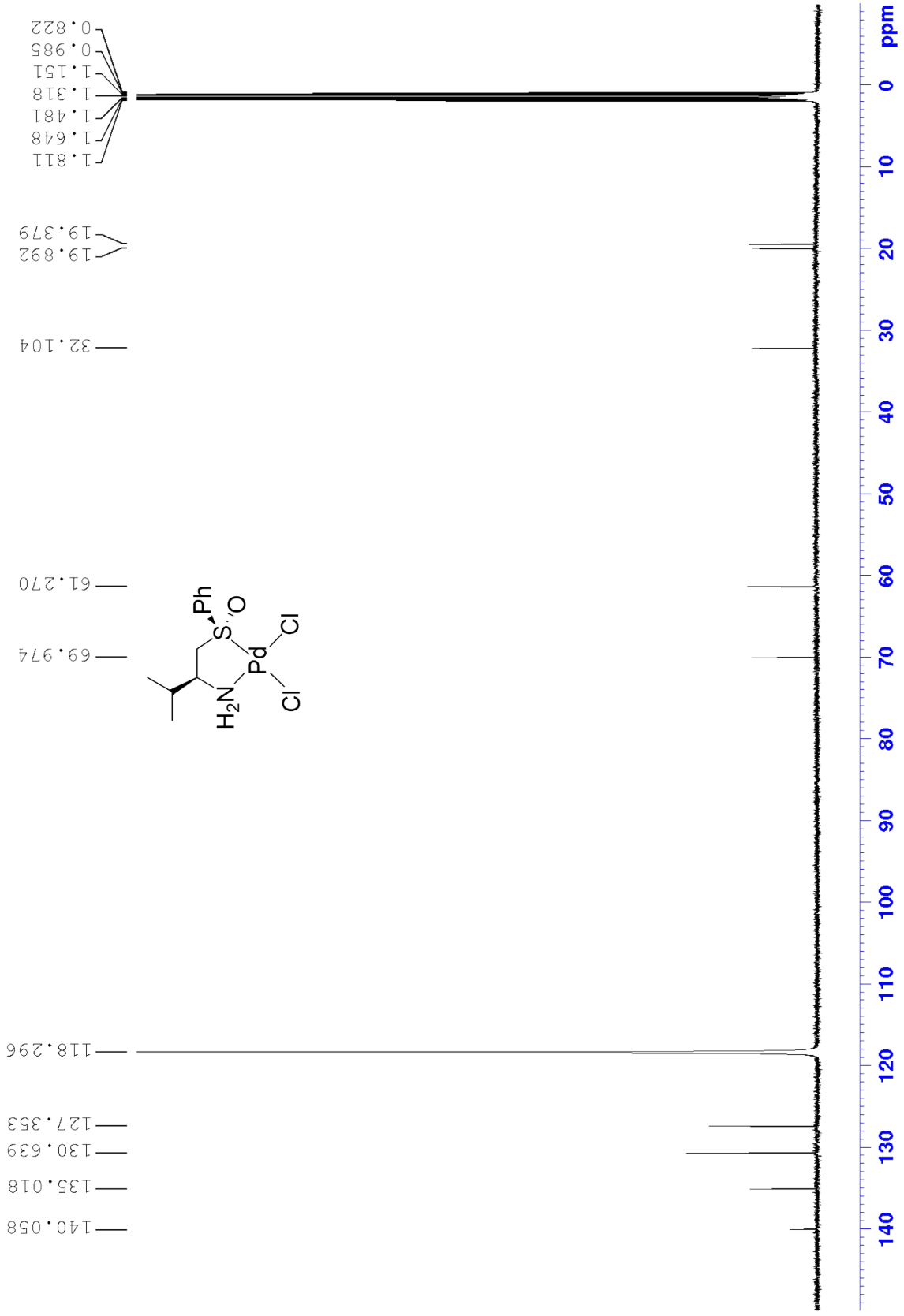


cis-Dichloro[(S_C,S_S)-3-methyl-1-(phenylsulfinyl)-2-butylamine]palladium (II), **15(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

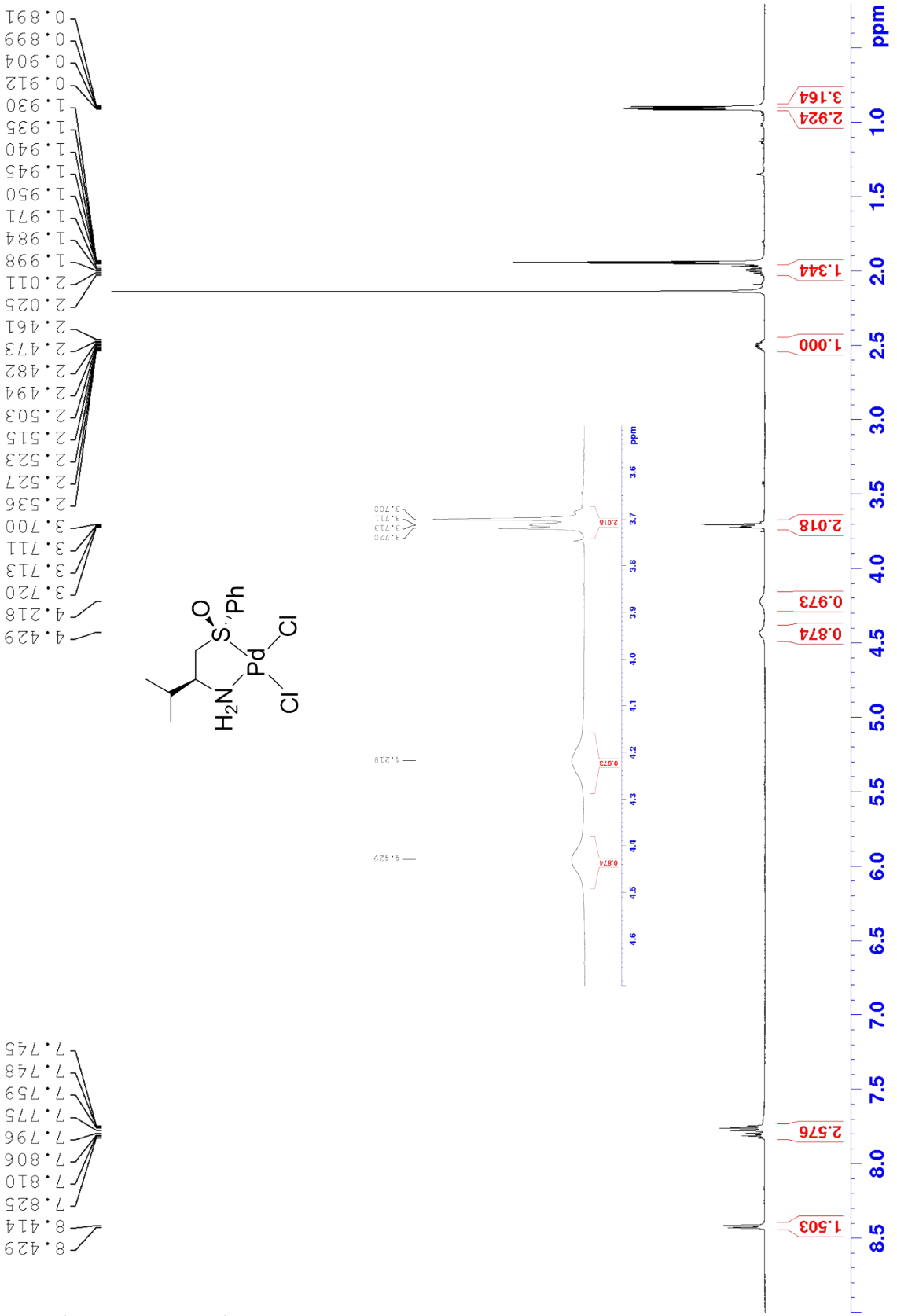


^{13}C-NMR (500 MHz, CD_3CN)

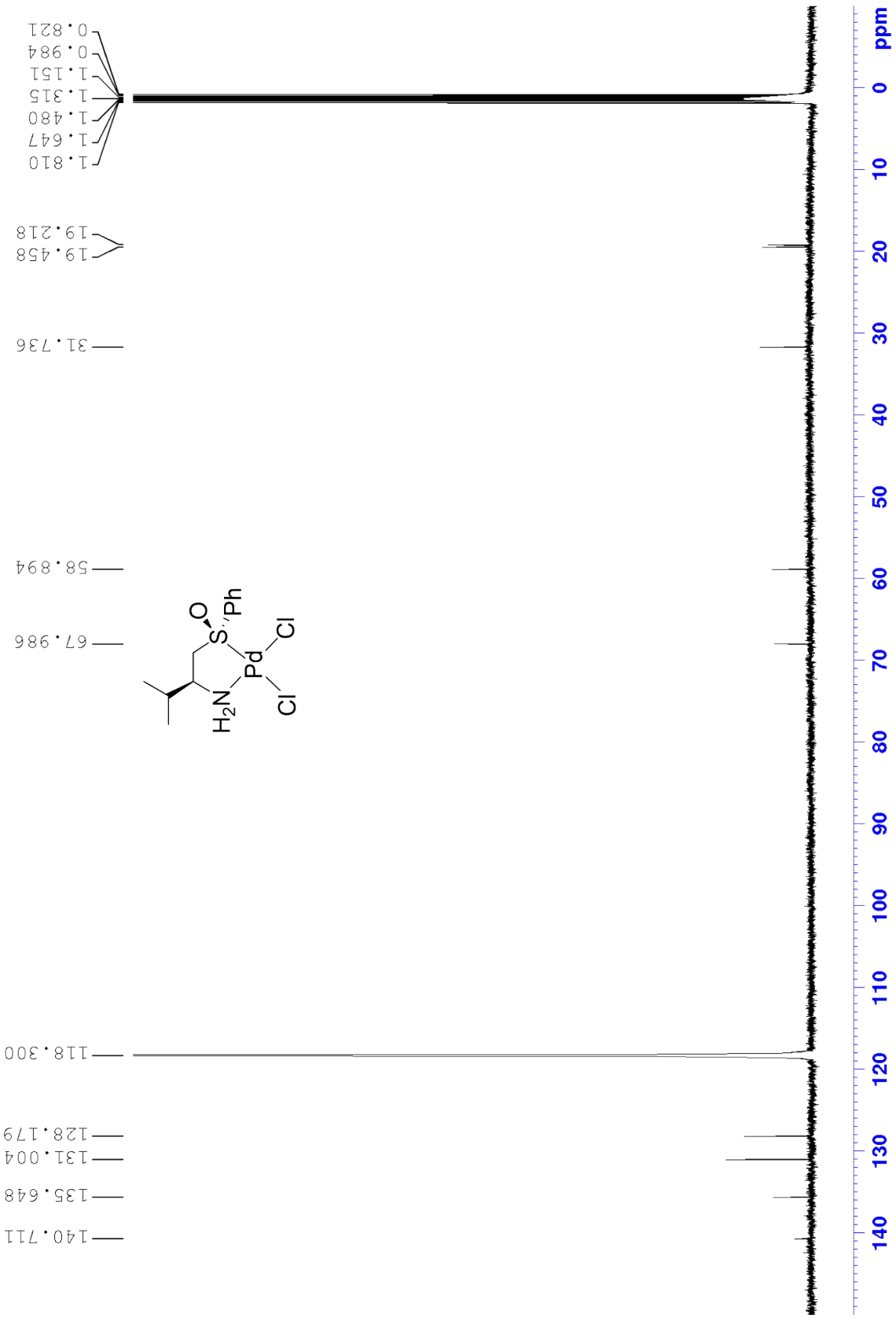


cis-Dichloro[(S_C,R_S)-3-methyl-1-(phenylsulfinyl)-2-butylamine]palladium (II), **15(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

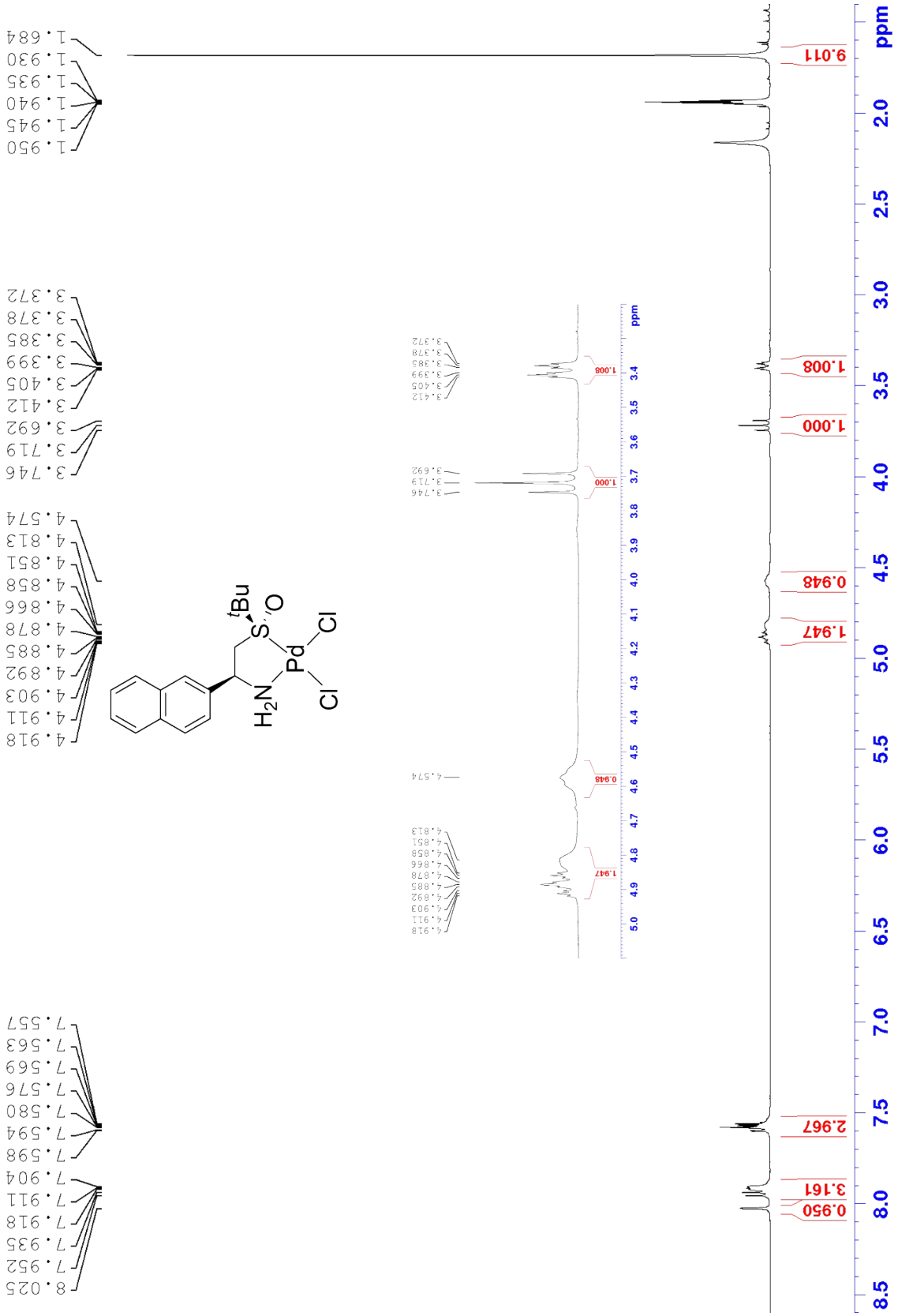


^{13}C-NMR (500 MHz, CD_3CN)

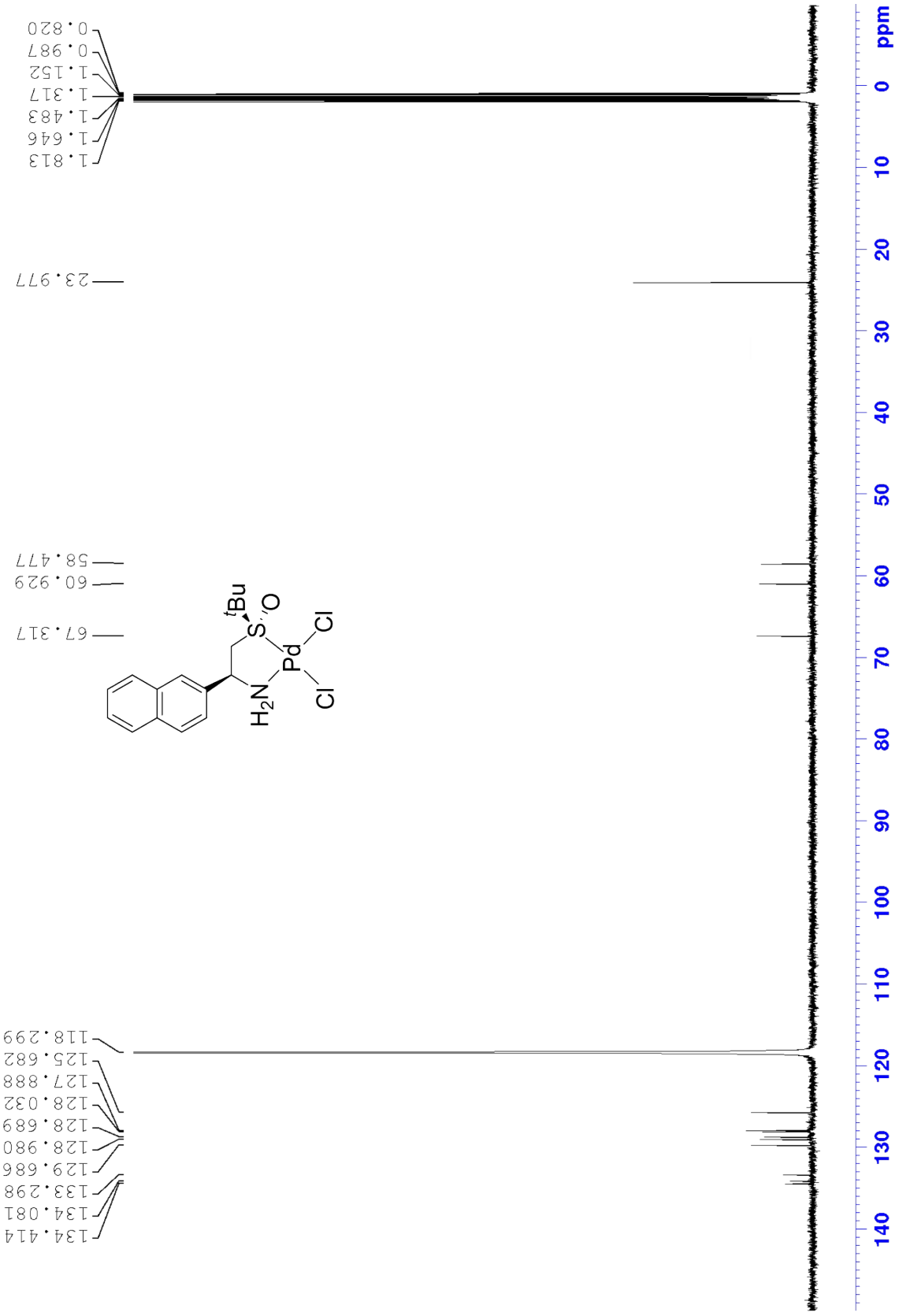

0.821
0.984
1.151
1.315
1.480
1.647
1.810
19.218
19.458
31.736
58.894
67.986
118.300
128.179
131.004
135.648
140.711
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
O
S
Ph
Pd
Cl
Cl
H2N

cis-Dichloro[(S_C,S_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine]palladium (II), **16(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

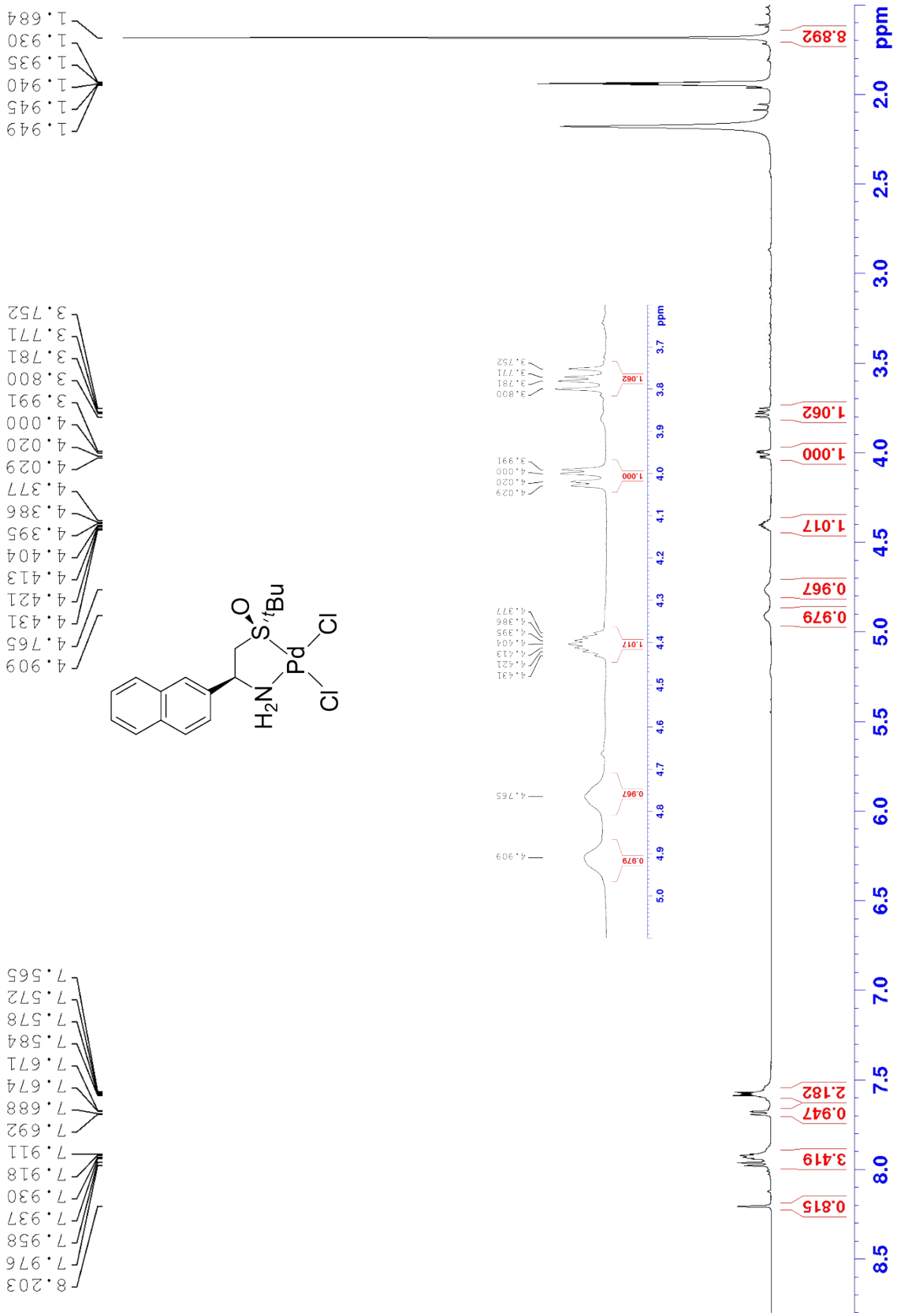


^{13}C-NMR (500 MHz, CD_3CN)

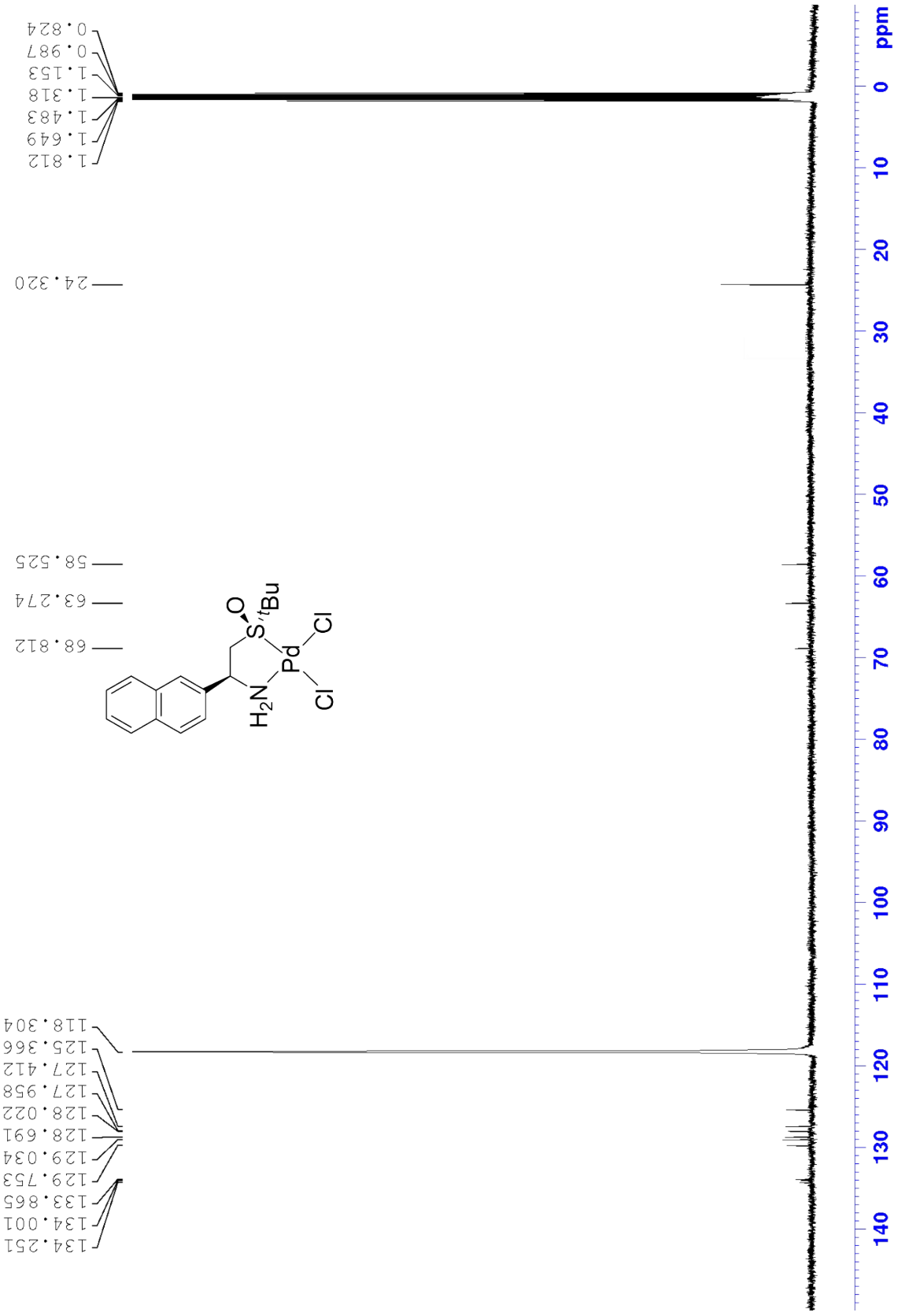

0.820
0.987
1.152
1.317
1.483
1.646
1.813
23.977
58.477
60.929
67.317
118.299
125.682
127.888
128.032
128.689
128.980
129.686
133.298
134.081
134.414
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
tBu
S
O
Pd
Cl
Cl
H2N

cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine]palladium (II), **16(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

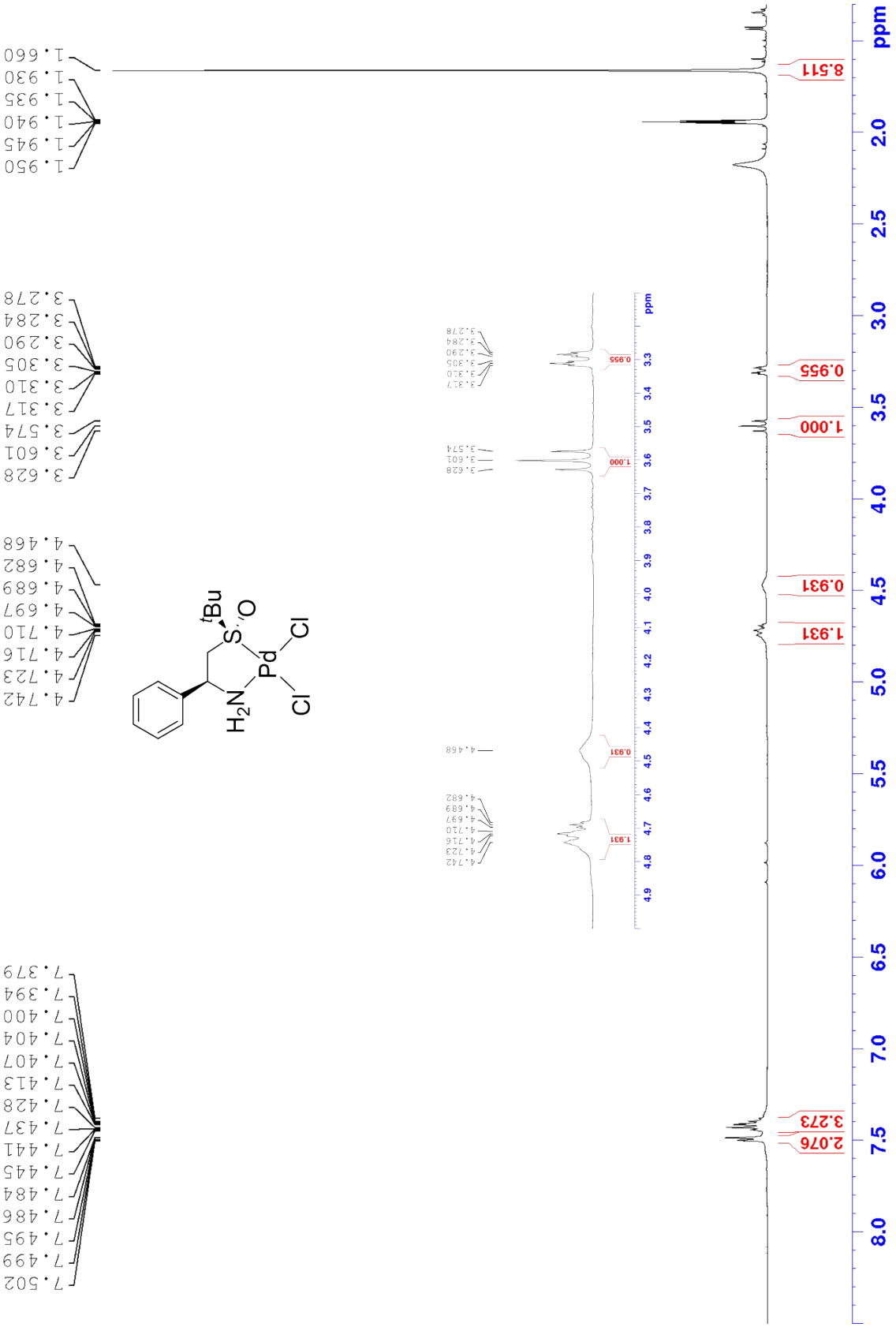


^{13}C-NMR (500 MHz, CD_3CN)

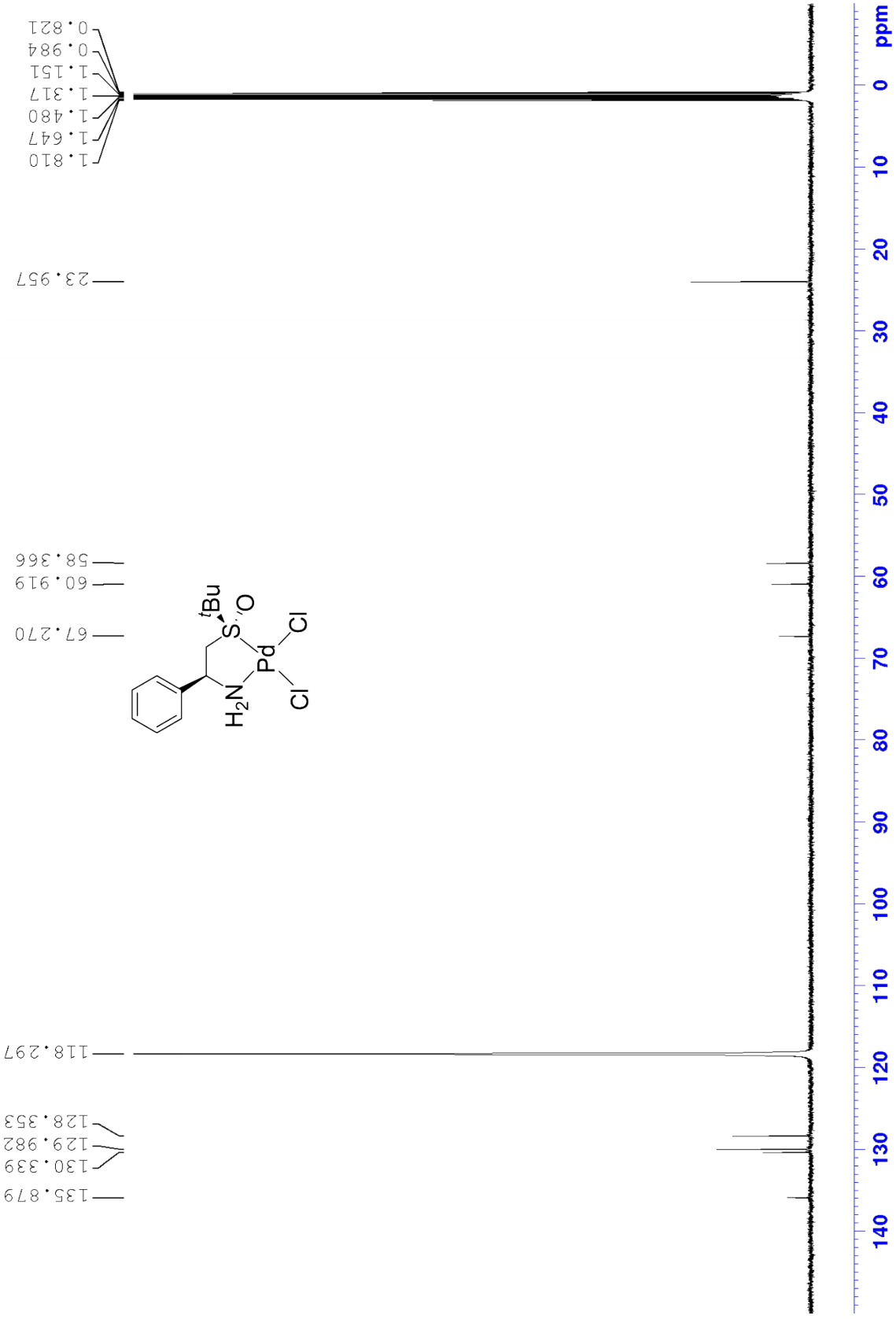


cis-Dichloro[(S_C,S_S)-2-(tert-butylsulfinyl)-1-(phenyl)ethylamine]palladium (II), **17(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

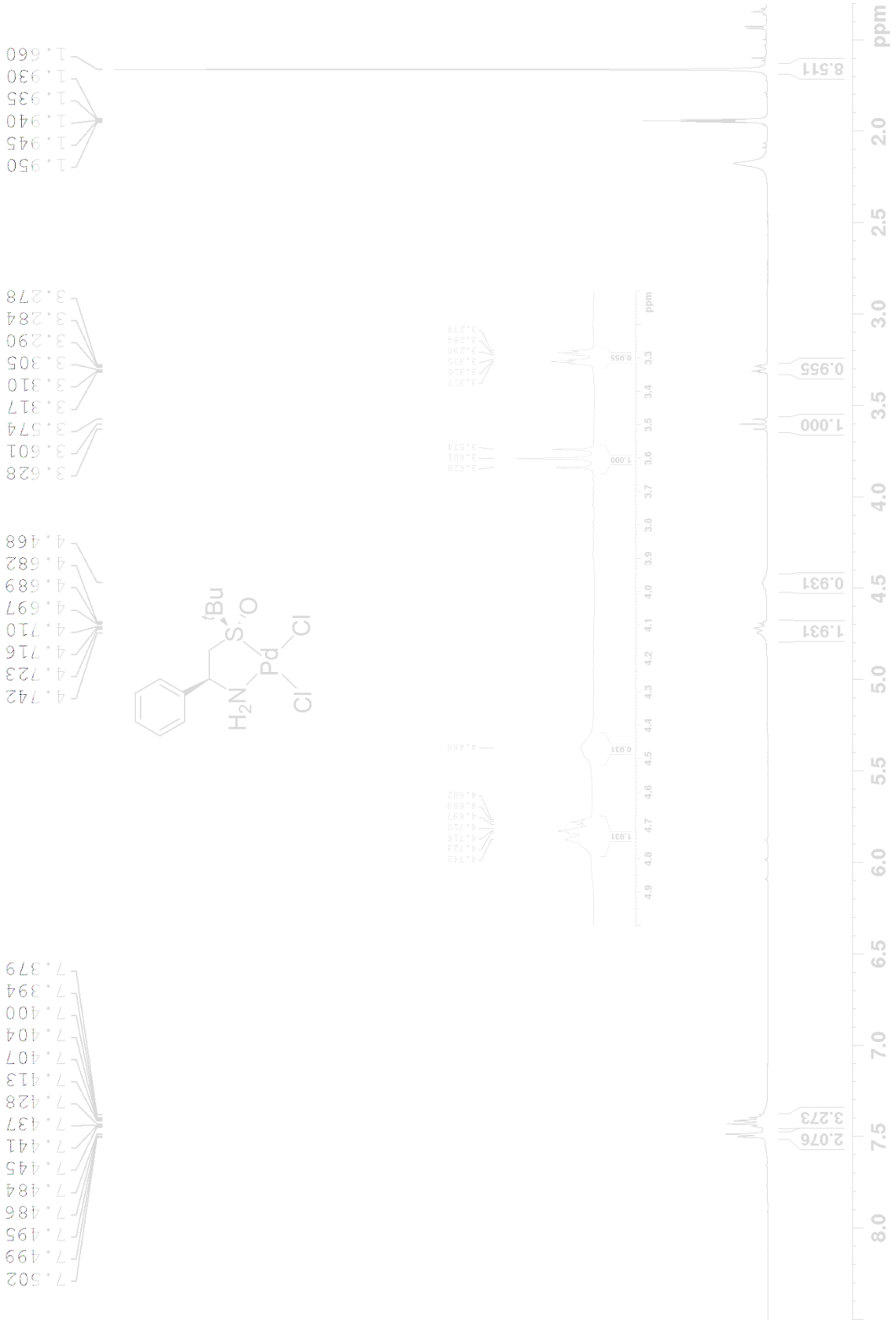


^{13}C-NMR (500 MHz, CD_3CN)

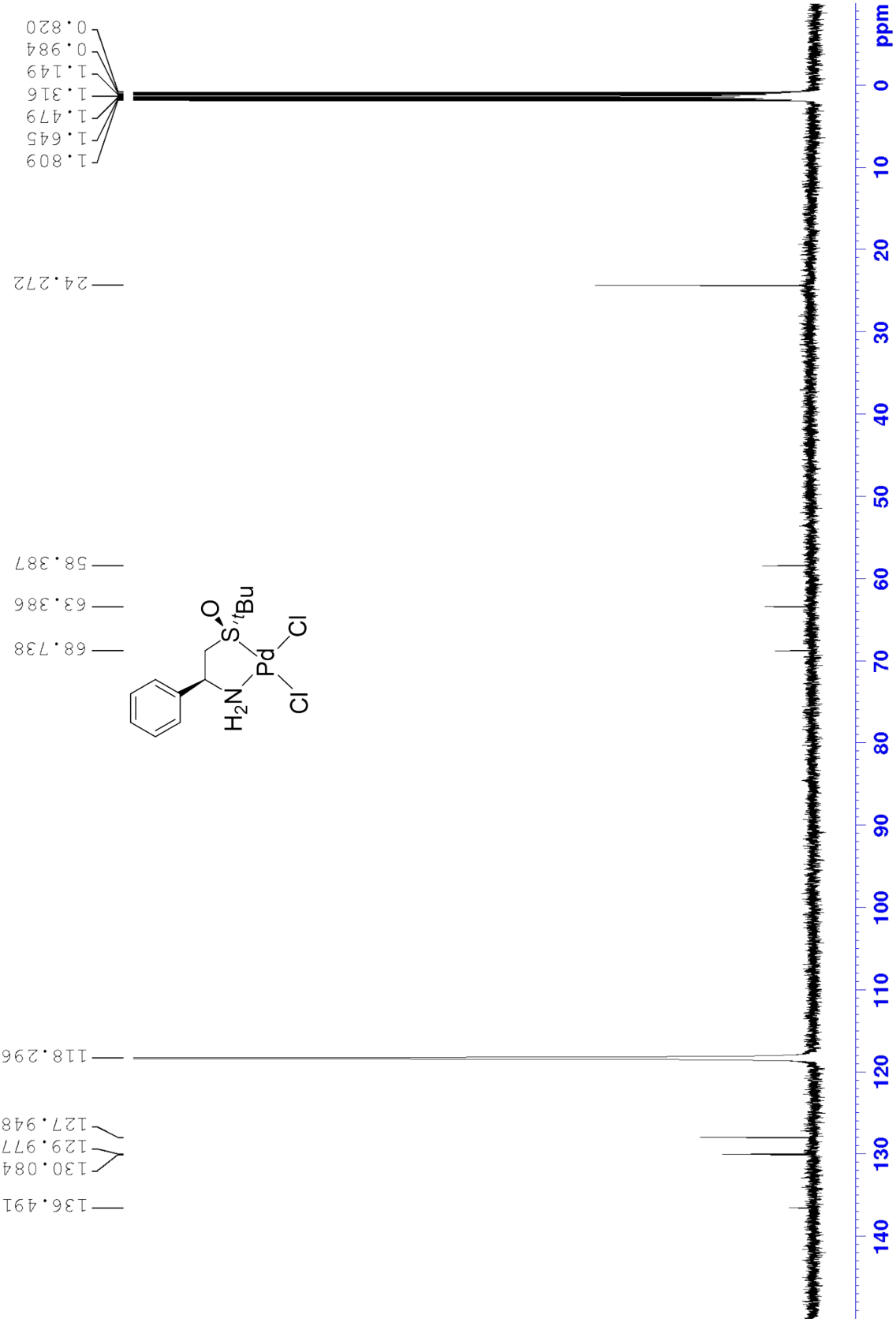


cis-Dichloro[(S_C,R_S)-2-(tert-butylsulfinyl)-1-(phenyl)ethylamine]palladium (II), **17(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

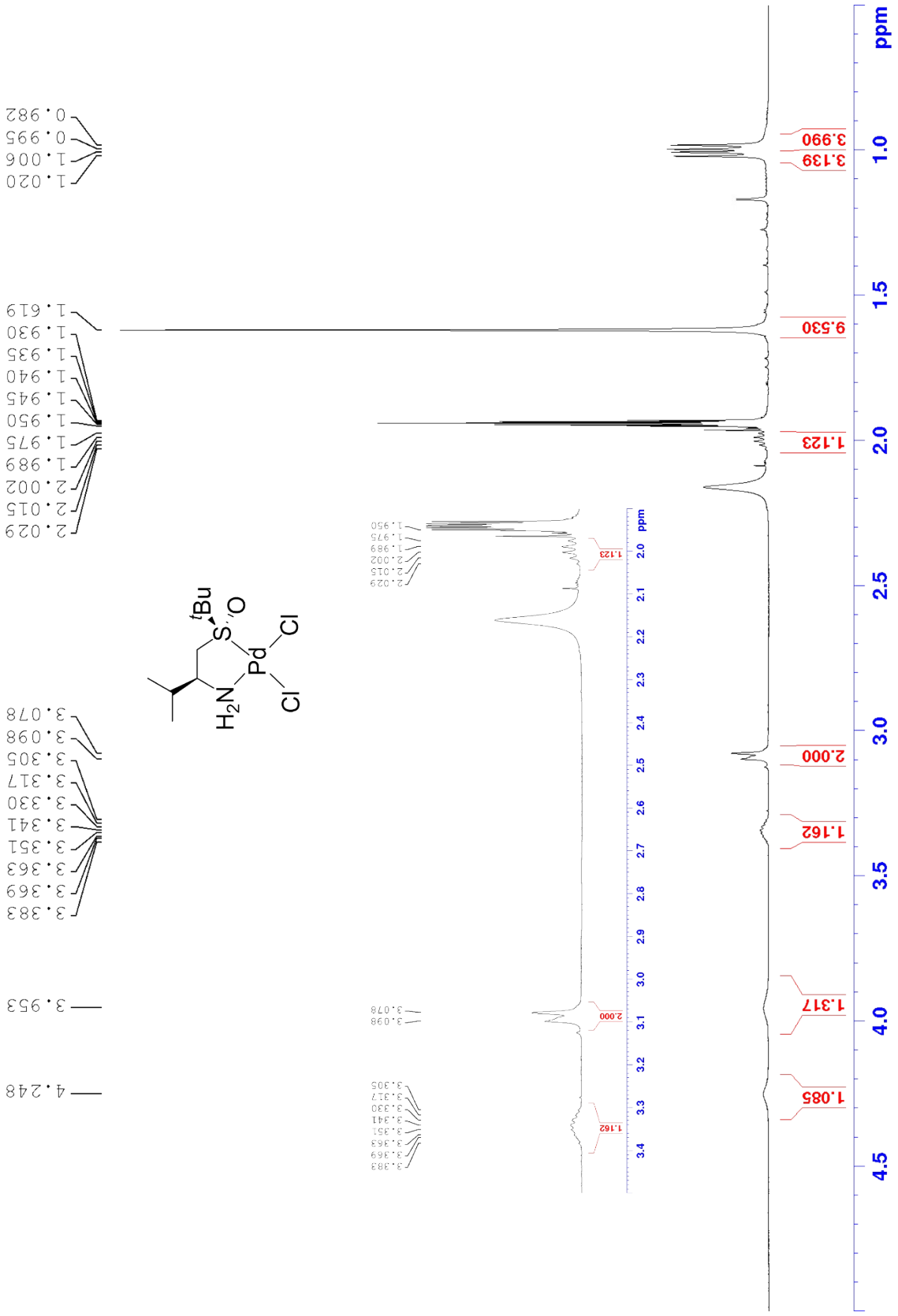


^{13}C-NMR (500 MHz, CD_3CN)

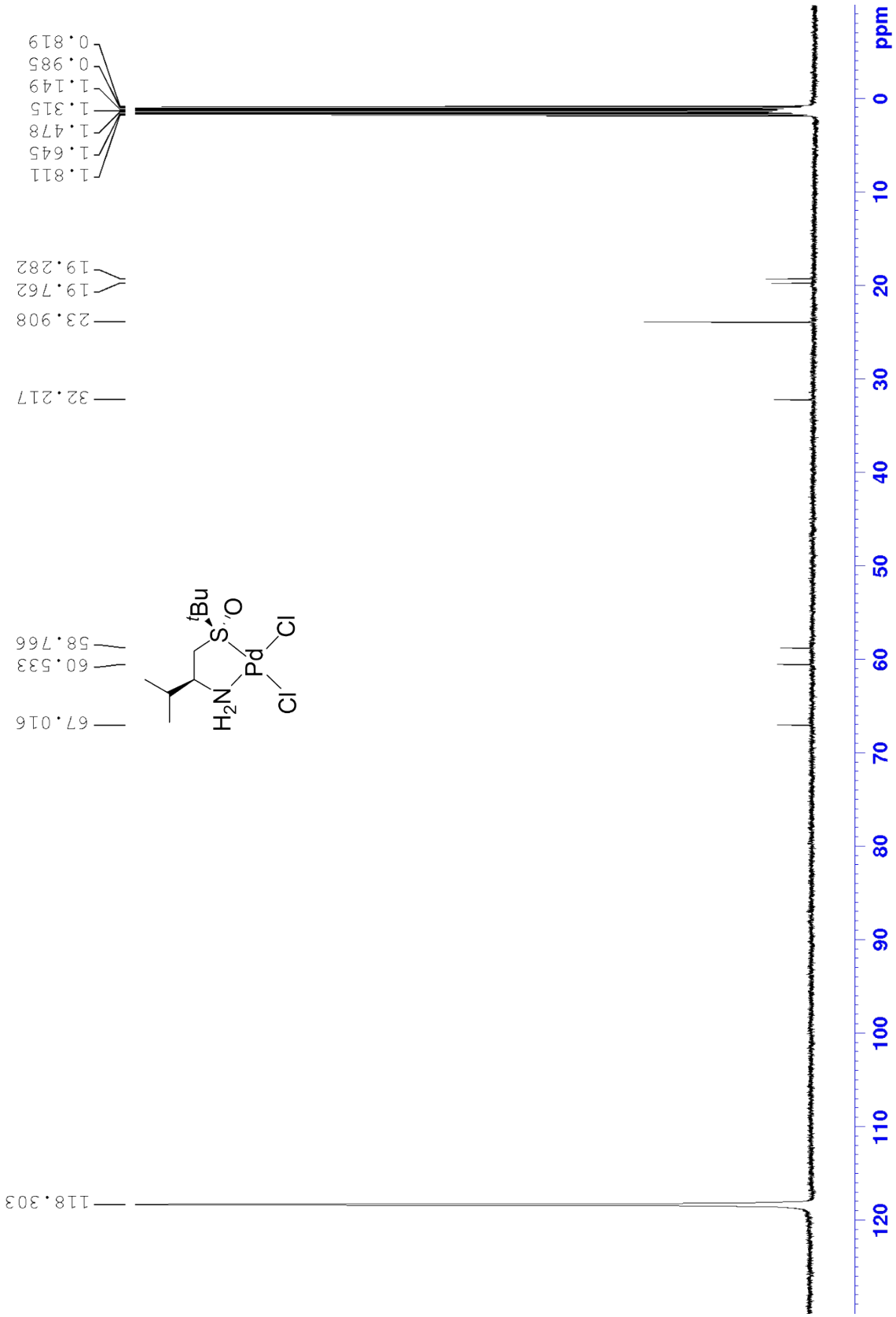


cis-Dichloro[(S_C,S_S)-1-(tert-butylsulfinyl)-3-methyl-2-butylamine]palladium (II), **18(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

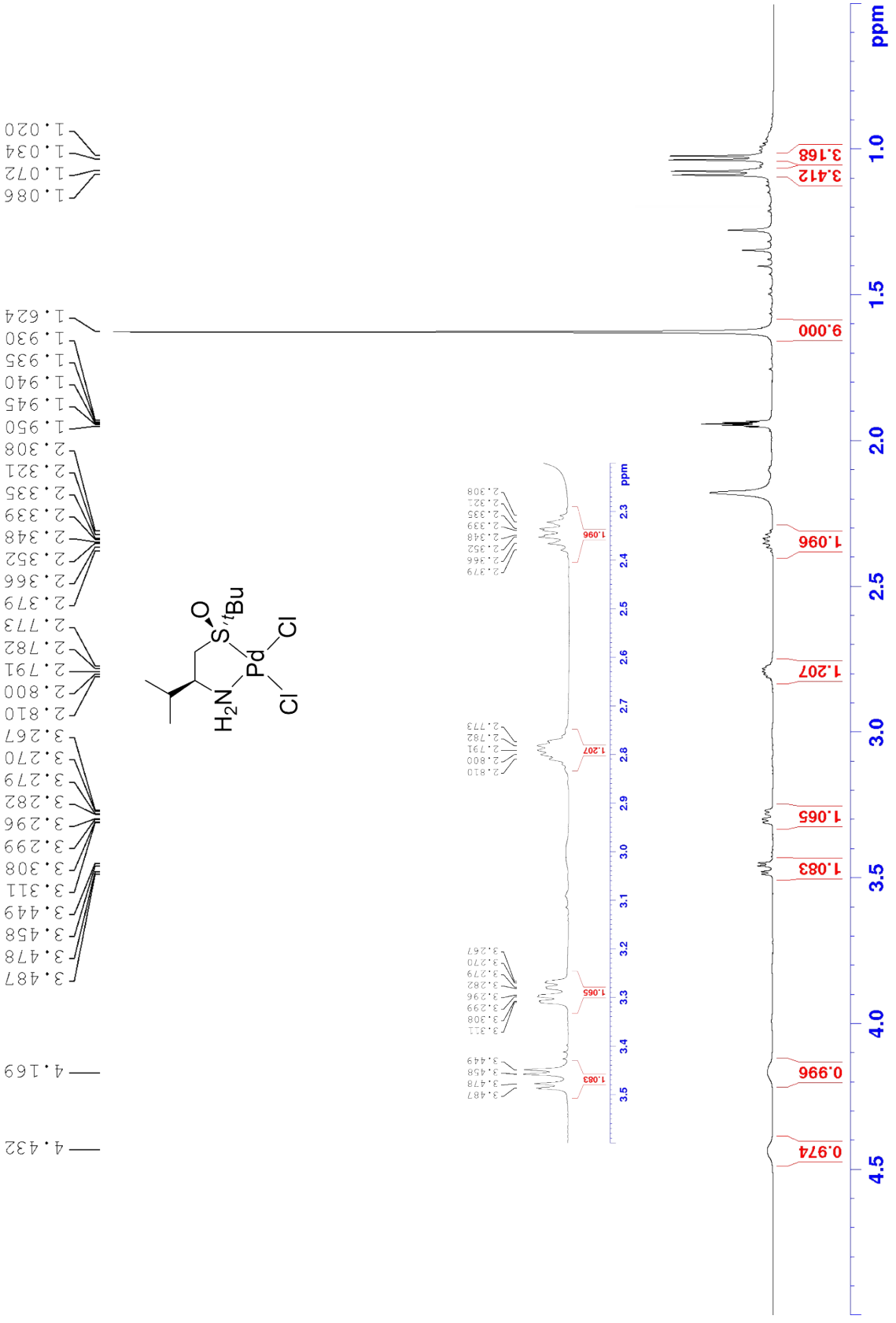


^{13}C-NMR (500 MHz, CD_3CN)

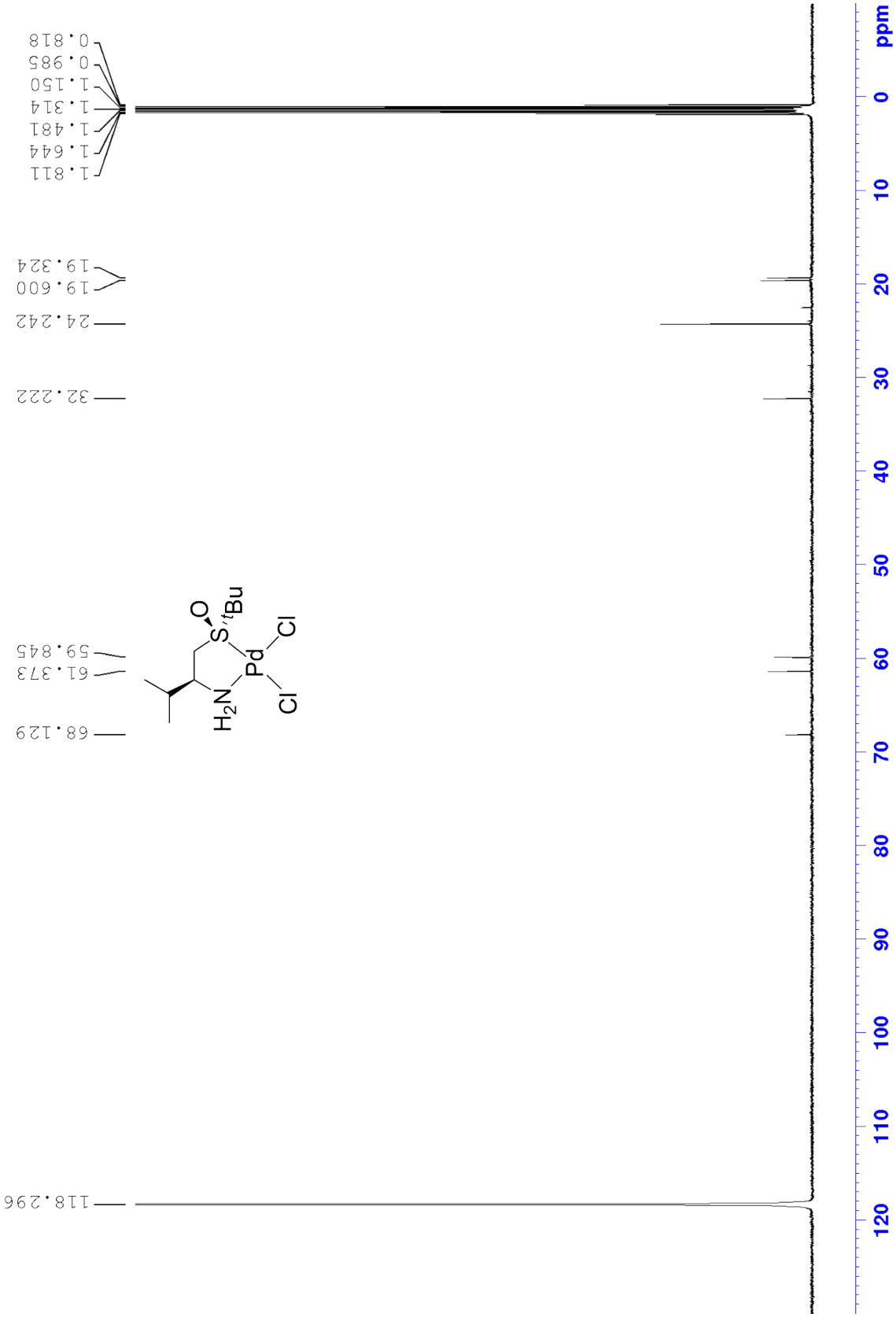


cis-Dichloro[(S_C,R_S)-1-(tert-butylsulfinyl)-3-methyl-2-butylamine]palladium (II), **18(S_C,R_S)**

^{1}H-NMR (500 MHz, CD_3CN)

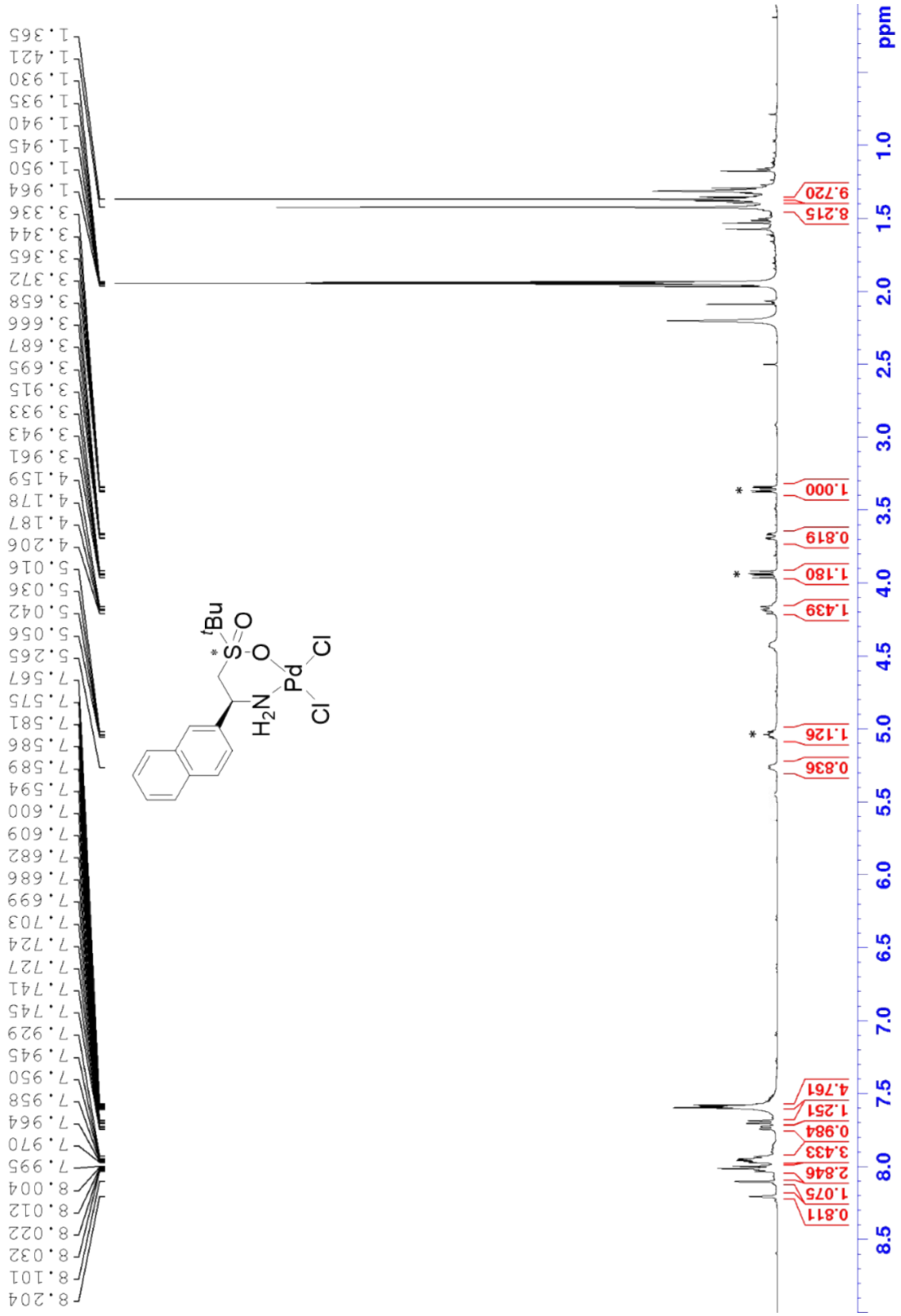


^{13}C-NMR (500 MHz, CD_3CN)

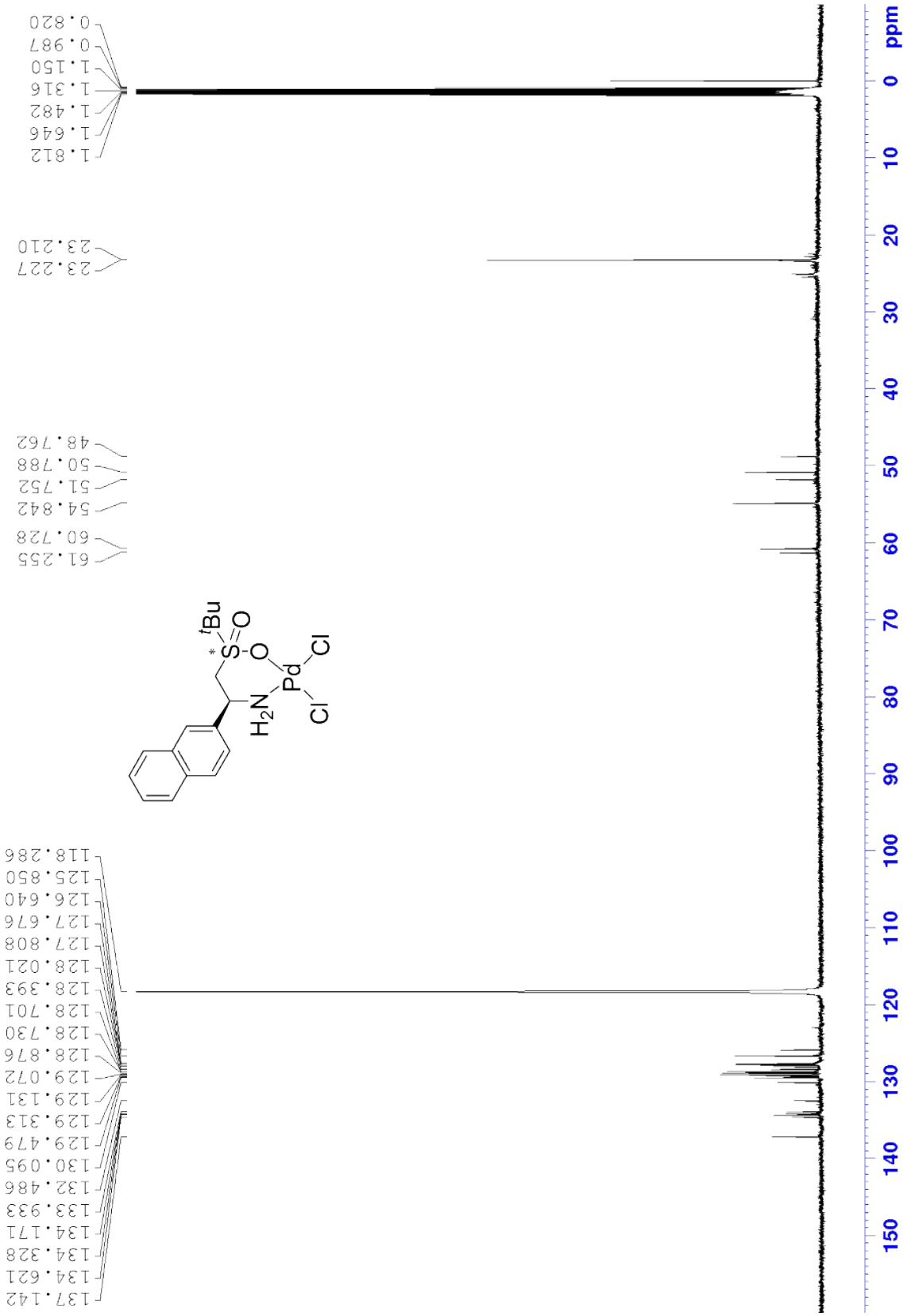


cis-Dichloro[(S_C,R_S)/(S_C,S_S)-1-(2-Naphthyl)-2-(tert-butylsulfonyl)ethylamine]palladium (II), **22(S_C,R_S)/(S_C,S_S)**

^{1}H-NMR (500 MHz, CD_3CN)

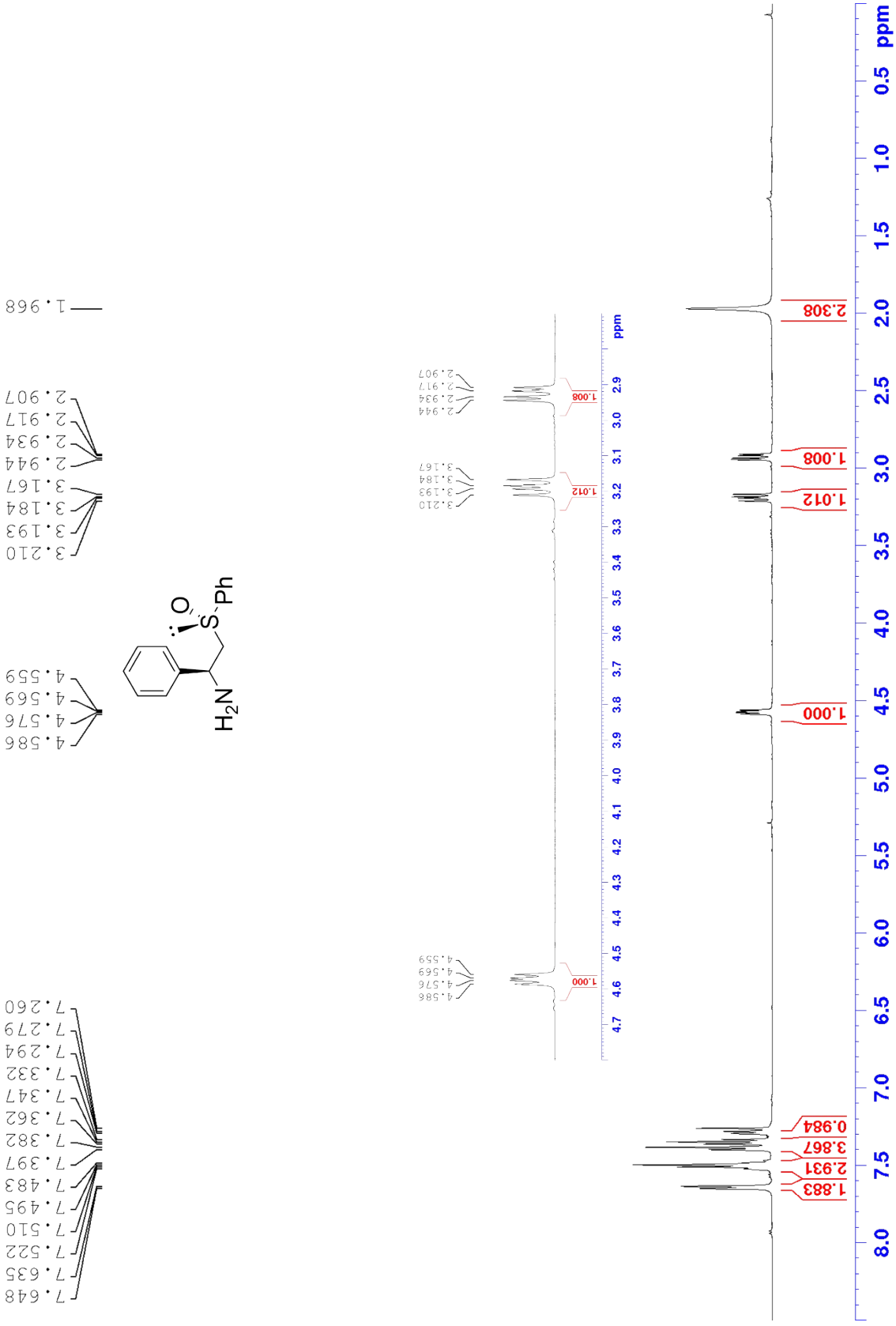


^{13}C-NMR (500 MHz, CD_3CN)

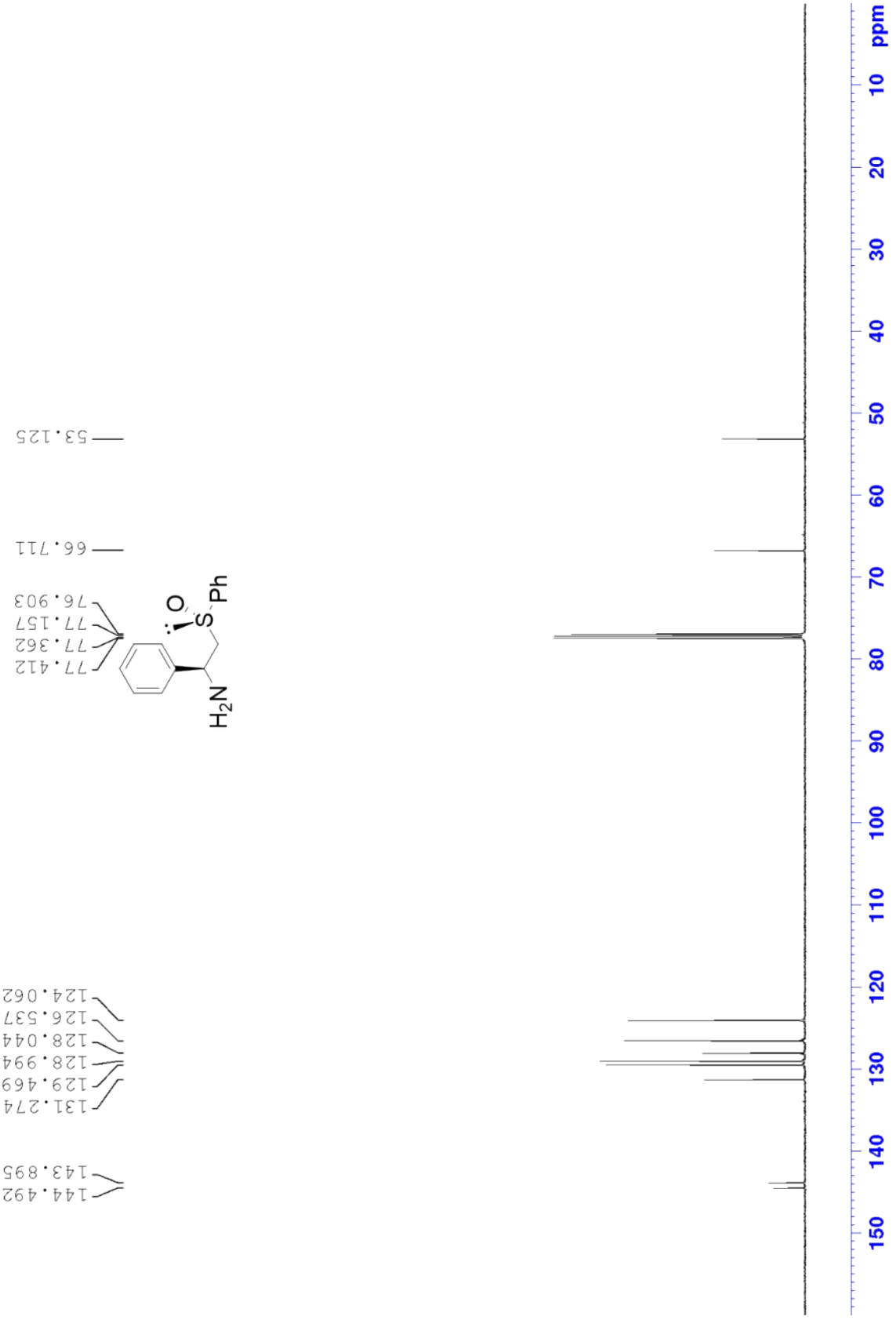


(S_C,S_S)-1-Phenyl-2-(phenylsulfinyl)ethylamine, **19(S_C,S_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

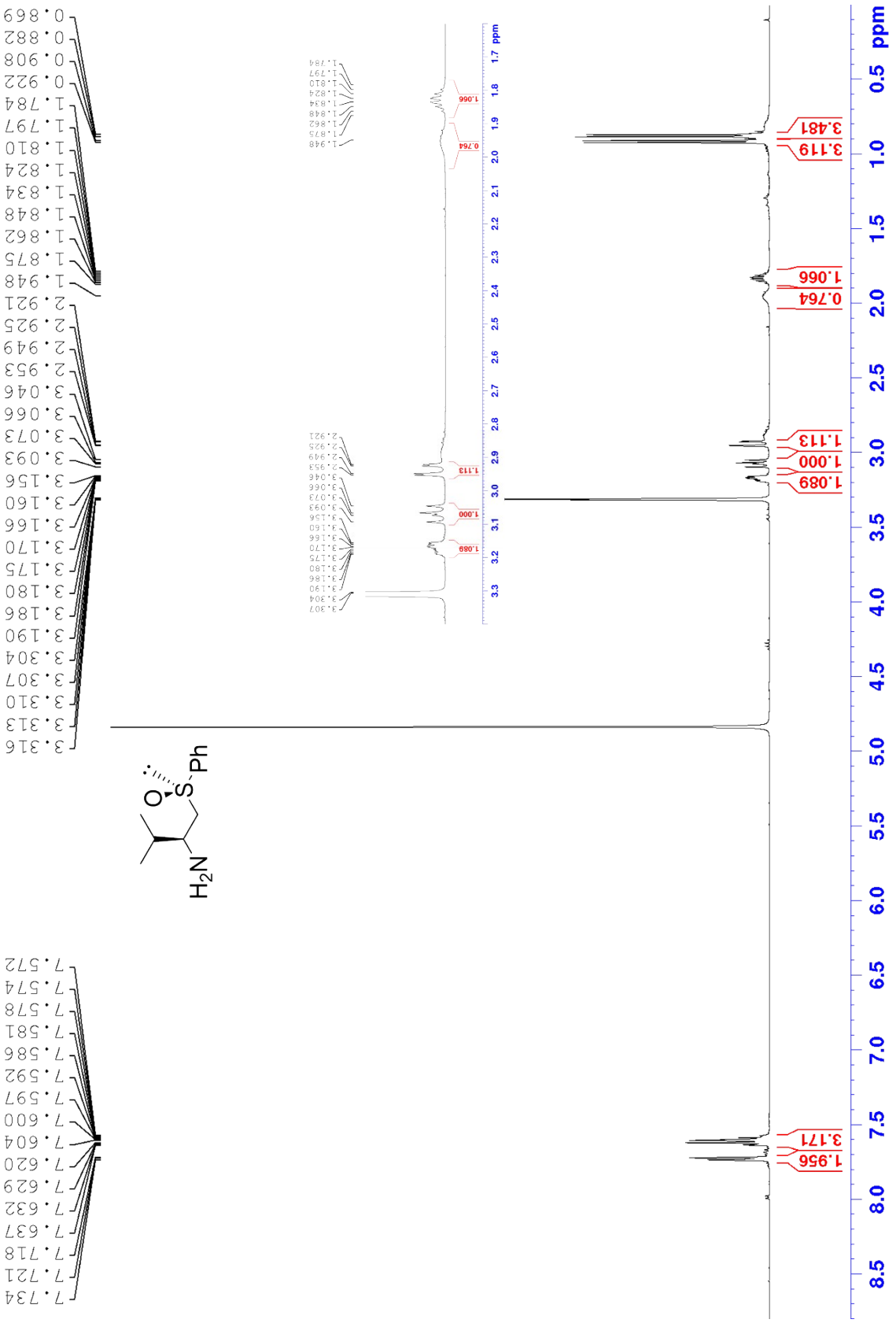


^{13}C-NMR (500 MHz, $CDCl_3$)

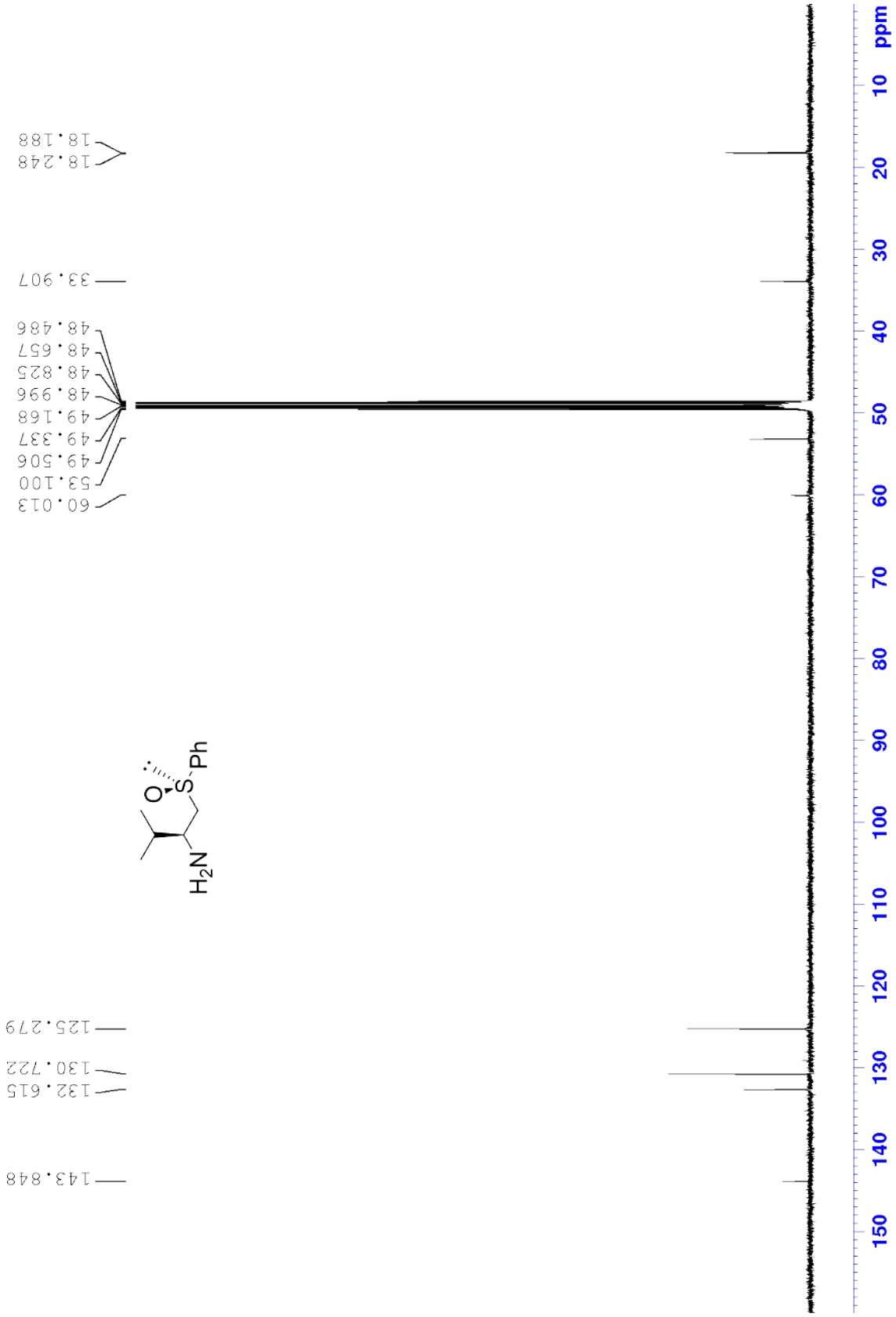


(S_C,R_S)-1-(Phenylsulfinyl)-3-methylbut-2-ylamine, **23(S_C,R_S)**

^{1}H-NMR (500 MHz, MeOD)

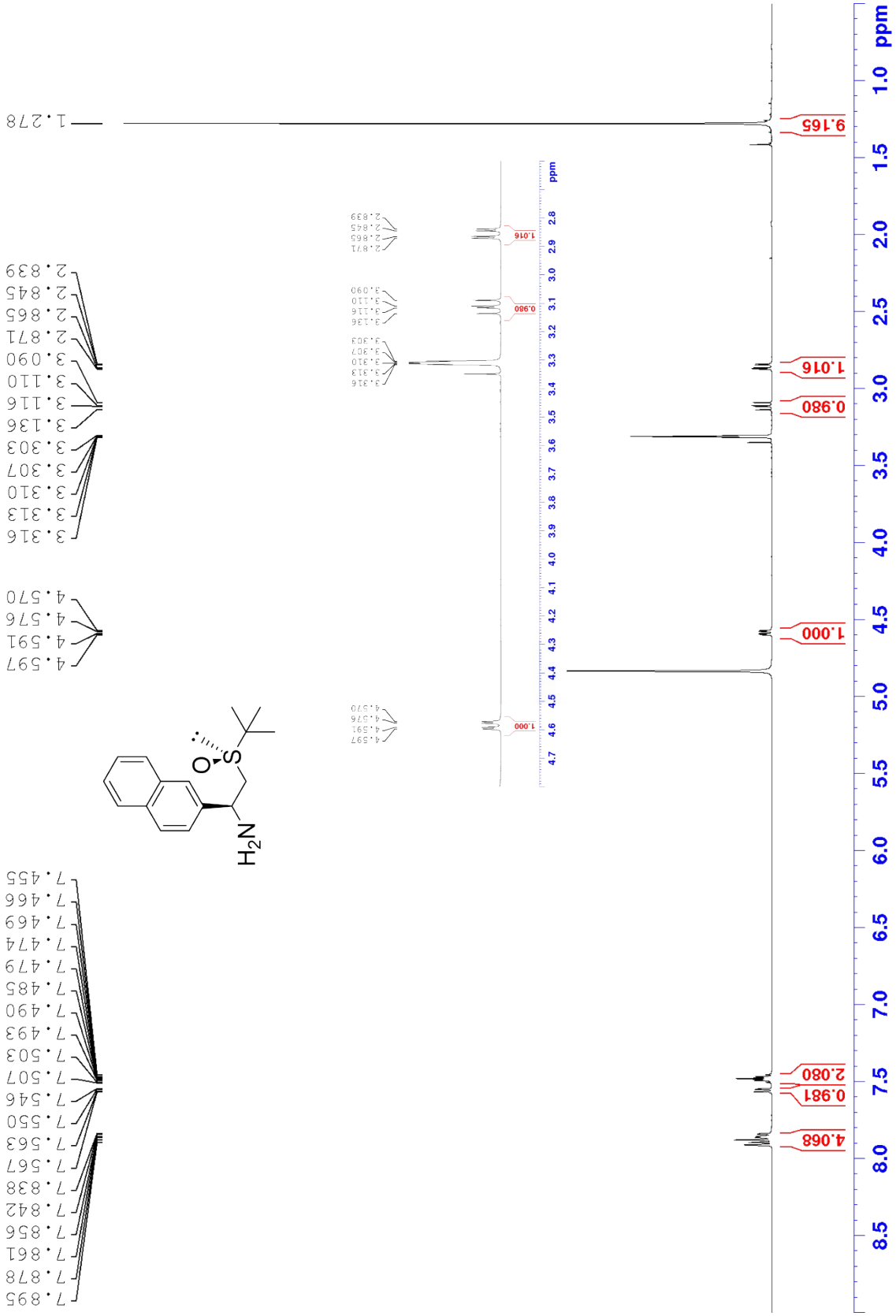


^{13}C-NMR (500 MHz, MeOD)

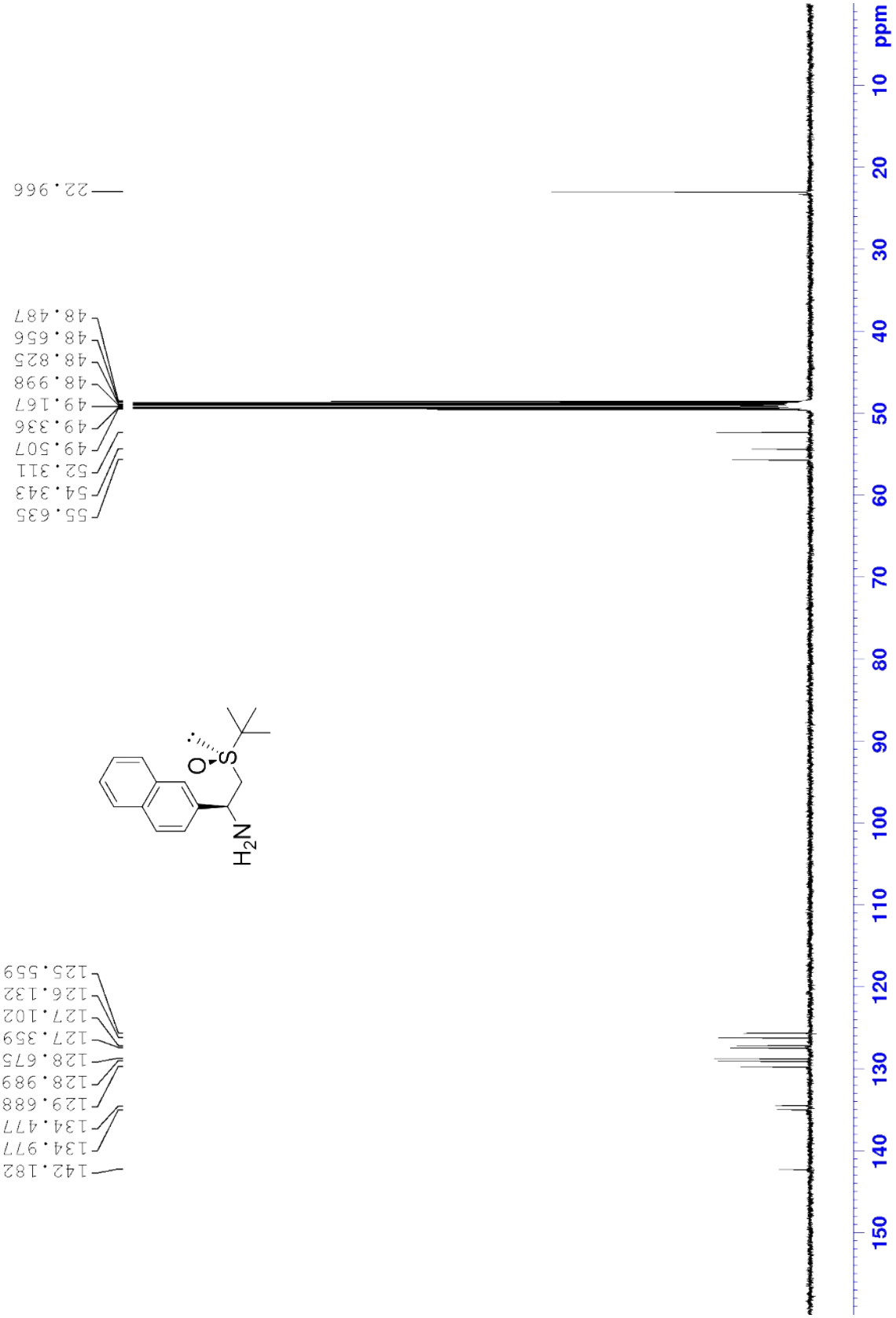


(S_C,R_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine, **24(S_C,R_S)**

^{1}H-NMR (500 MHz, MeOD)

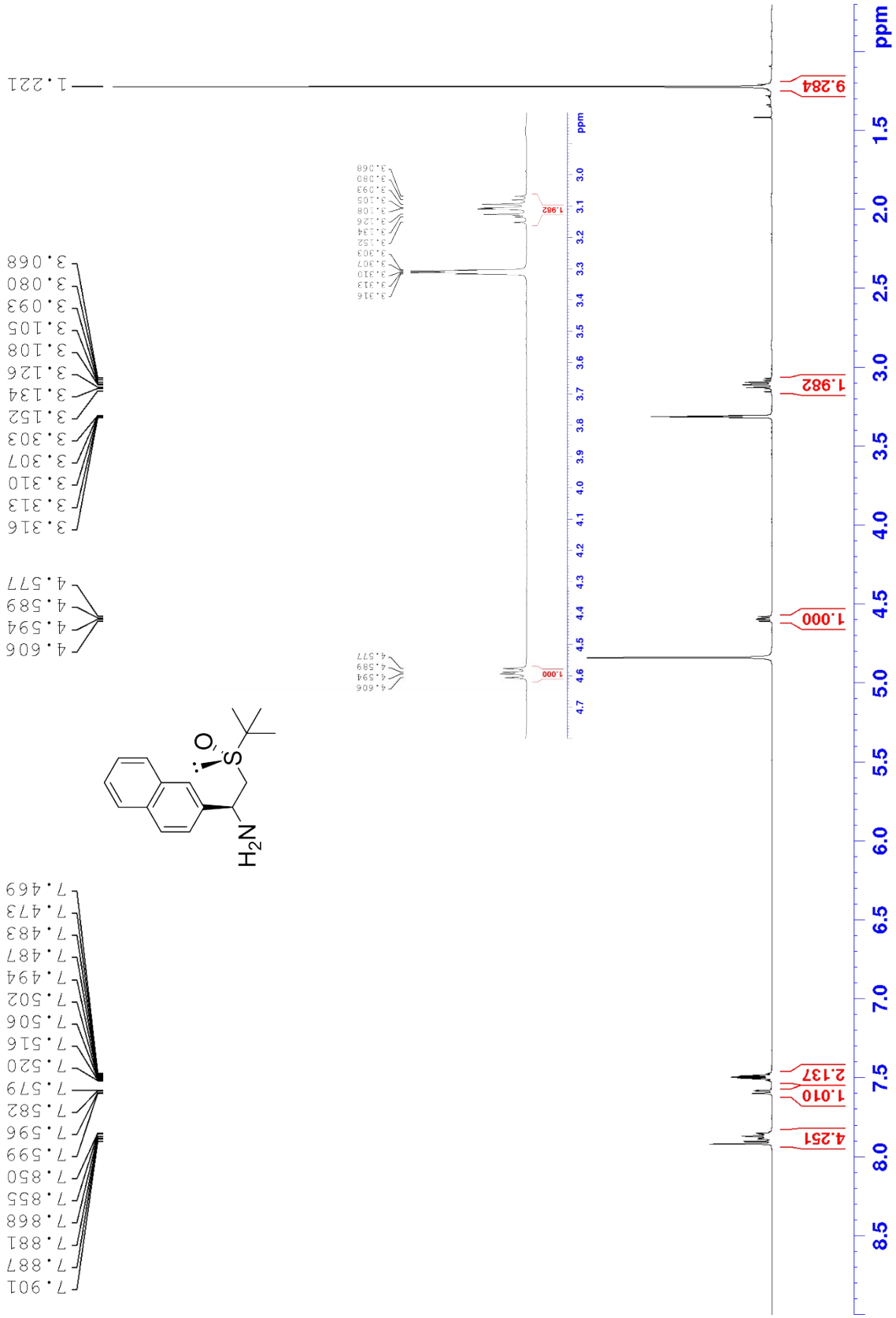


^{13}C-NMR (500 MHz, MeOD)

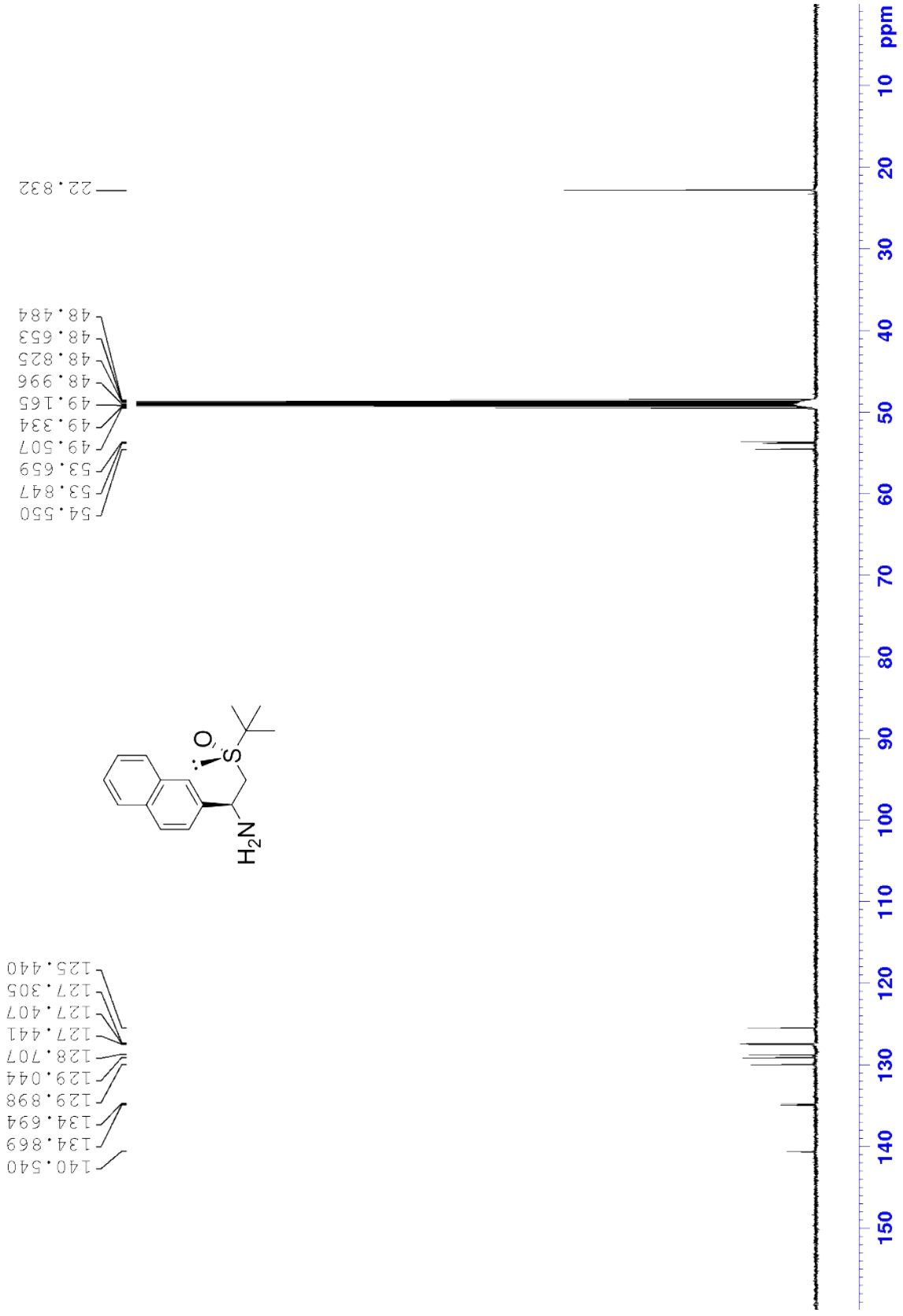


(S_C,S_S)- 1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine, **24(S_C,S_S)**

^{1}H-NMR (500 MHz, MeOD)

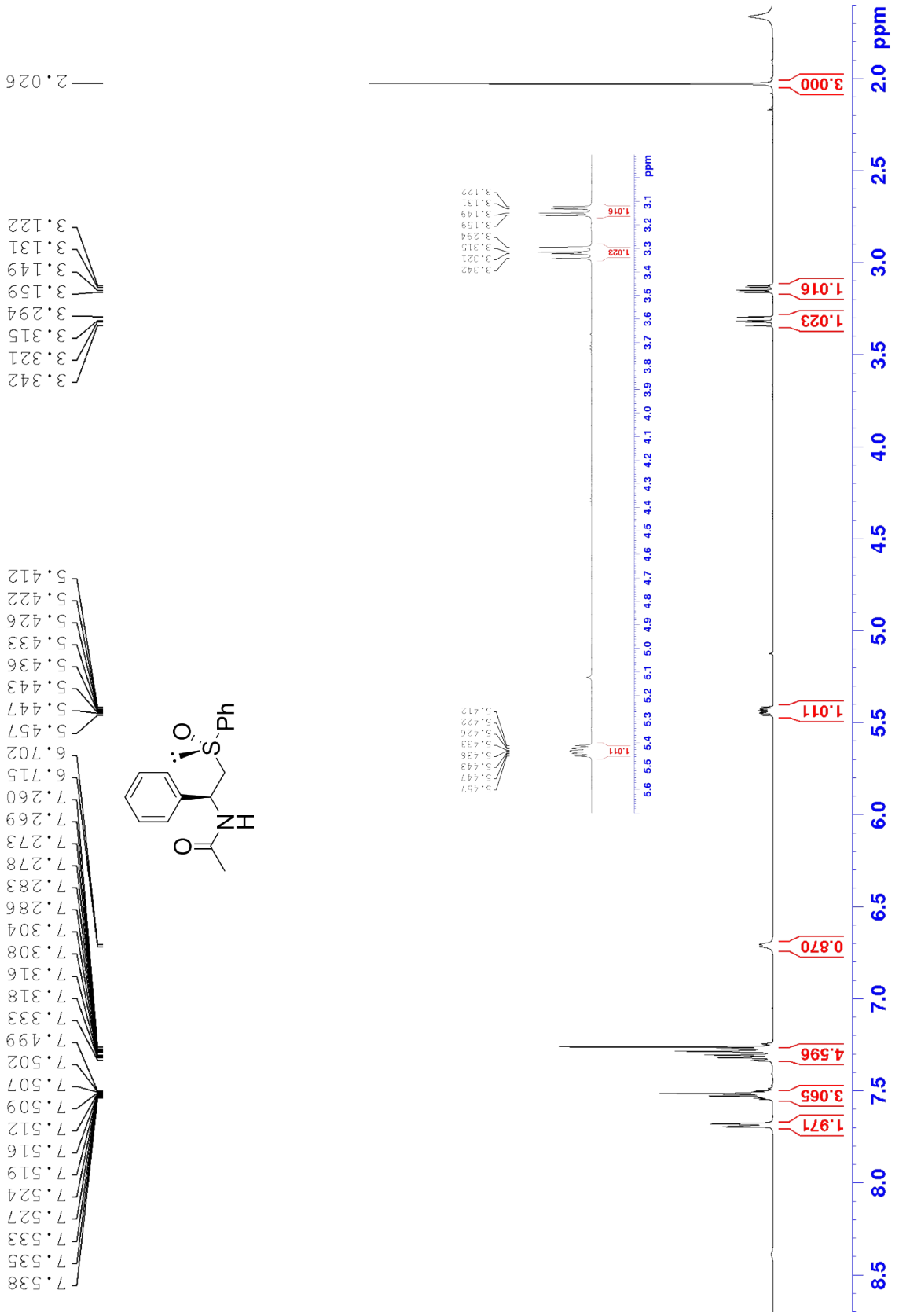


^{13}C-NMR (500 MHz, MeOD)

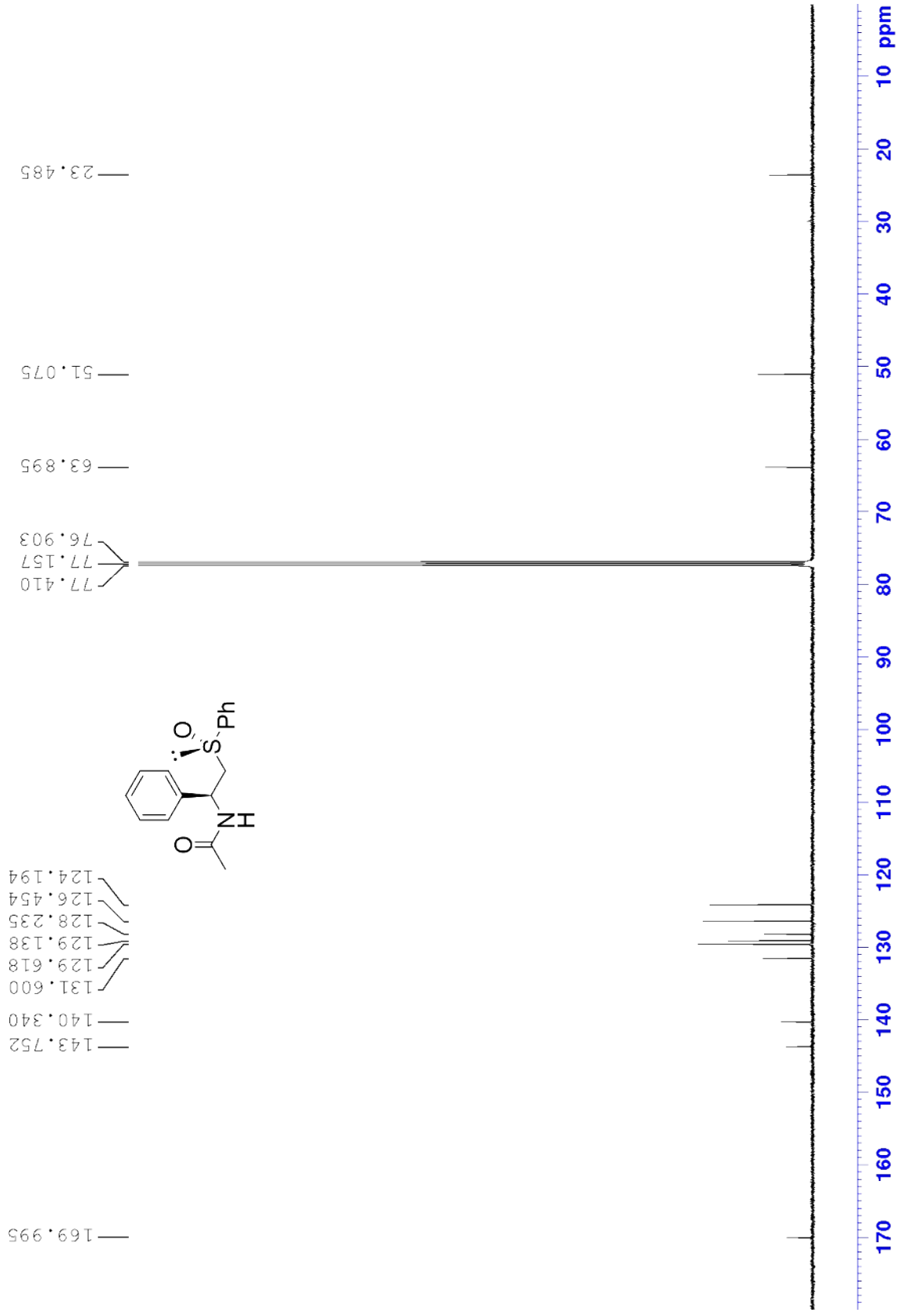


(S_C,S_S)-N-Acetyl-1-phenyl-2-(phenylsulfinyl)ethylamine, **25(S_C,S_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

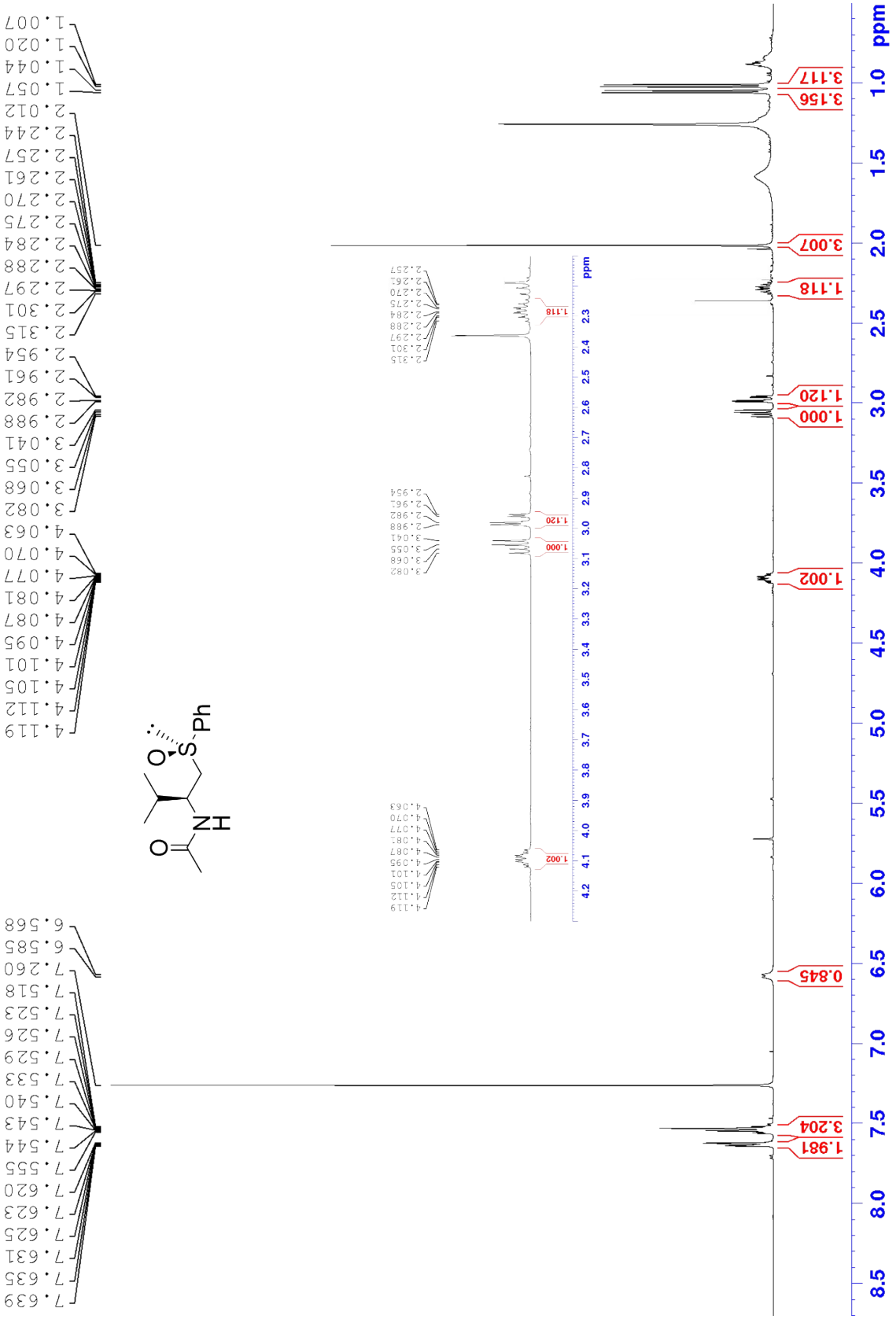


^{13}C-NMR (500 MHz, $CDCl_3$)

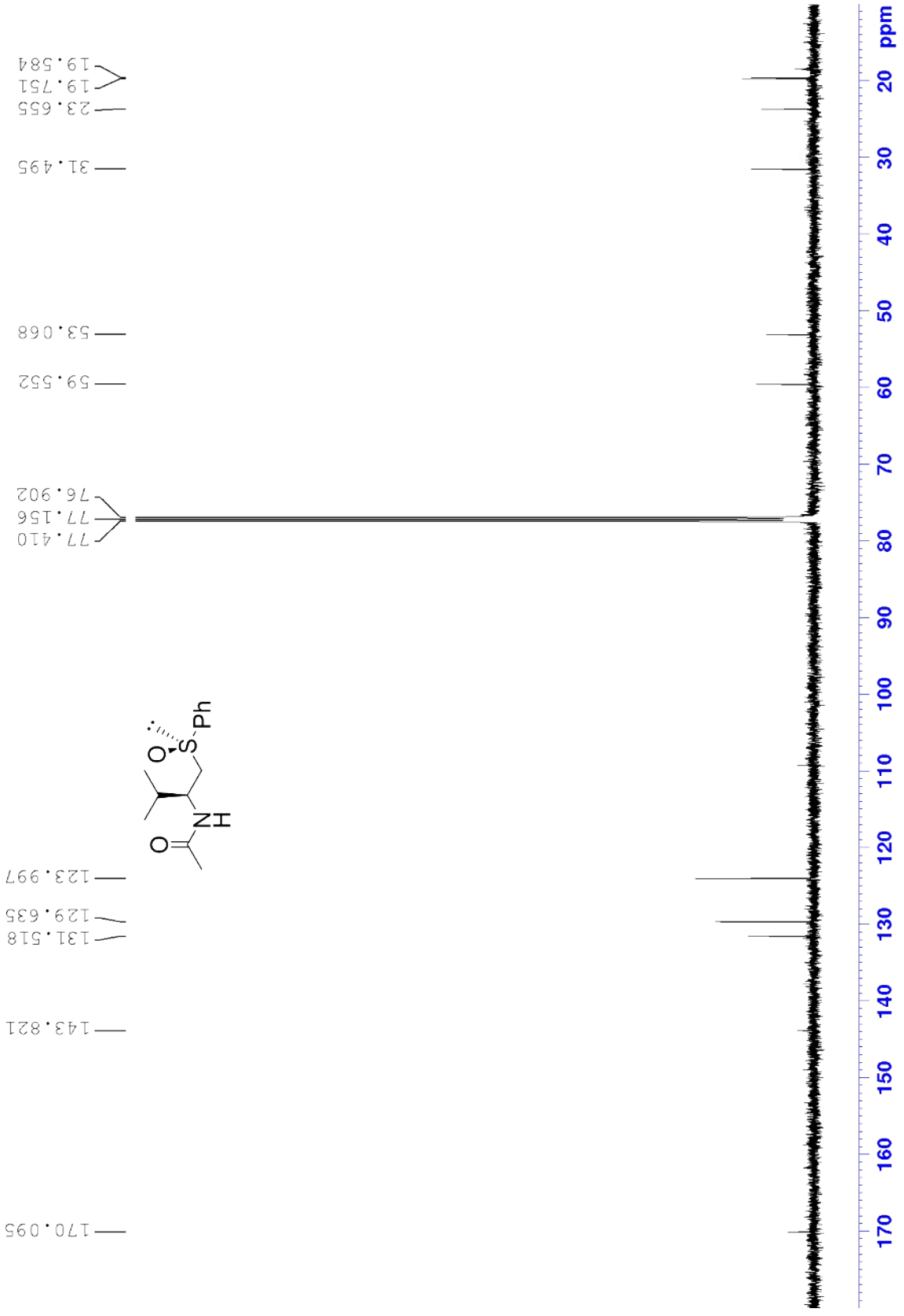


(S_C,R_S)-N-Acetyl-1-(Phenylsulfinyl)-3-methylbut-2-ylamine, **26(S_C,R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

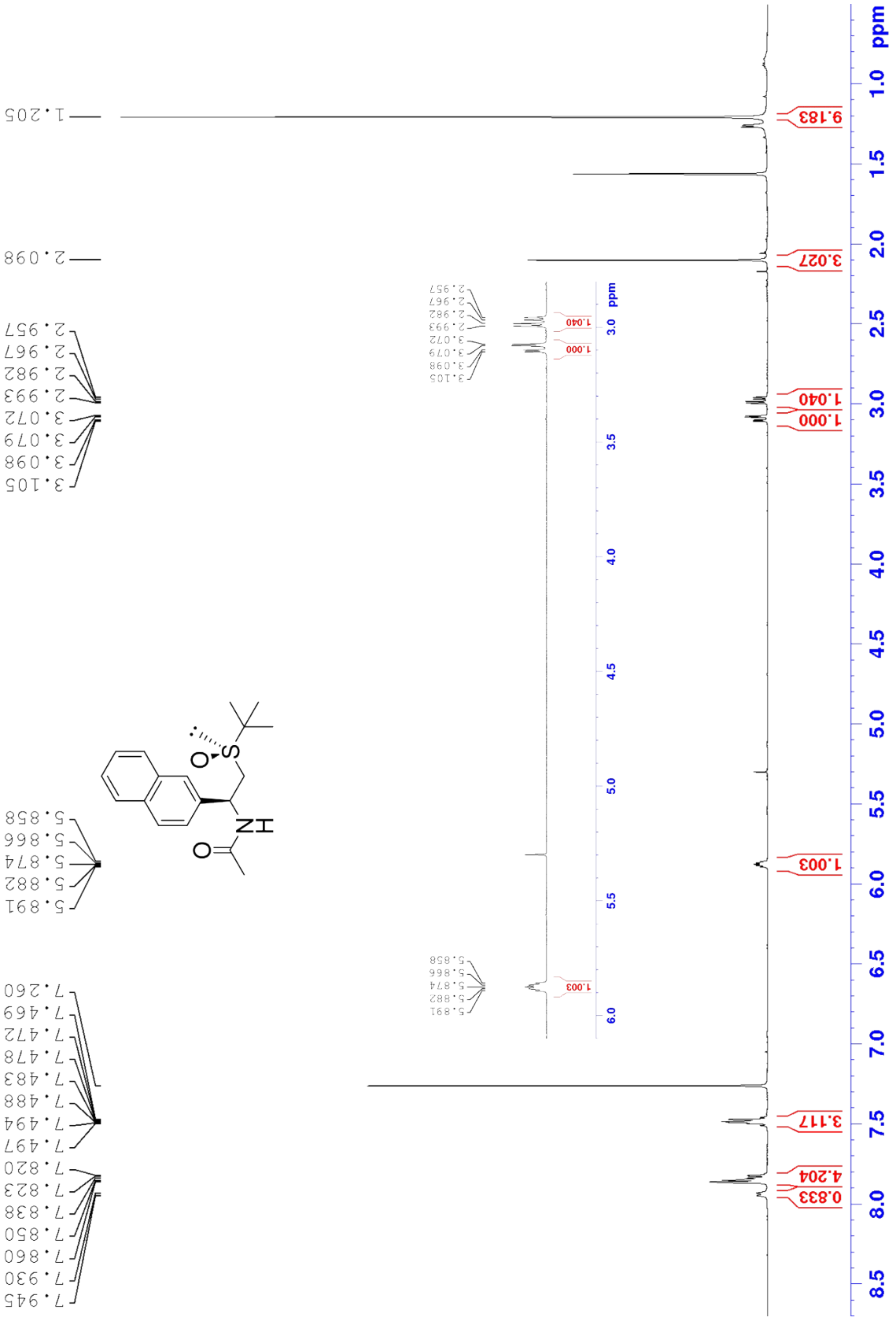


^{13}C-NMR (500 MHz, $CDCl_3$)

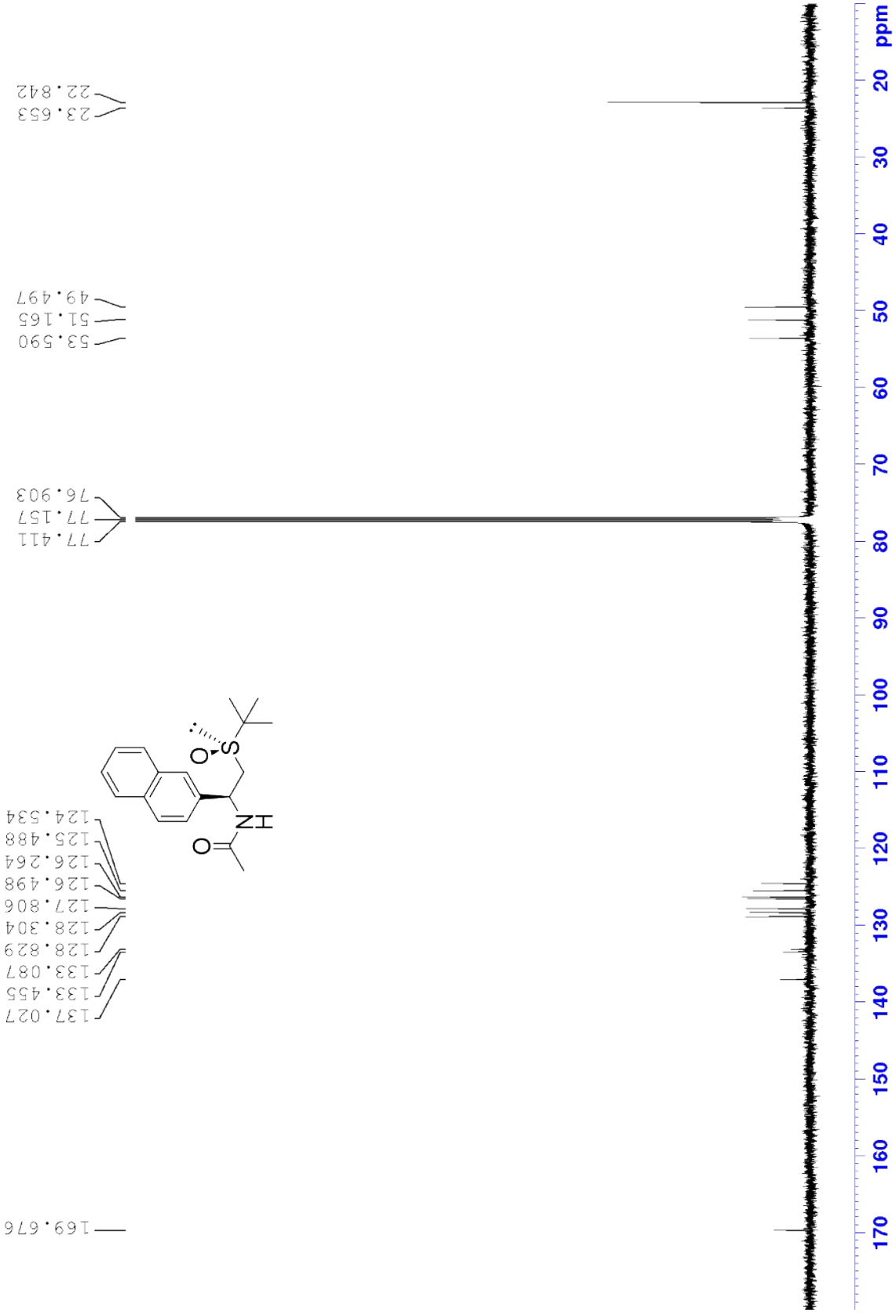


(S_C,R_S)-N-Acetyl-1-(2-naphthyl)-2-(tert-butylsulfinyl)ethylamine, **27(S_C,R_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

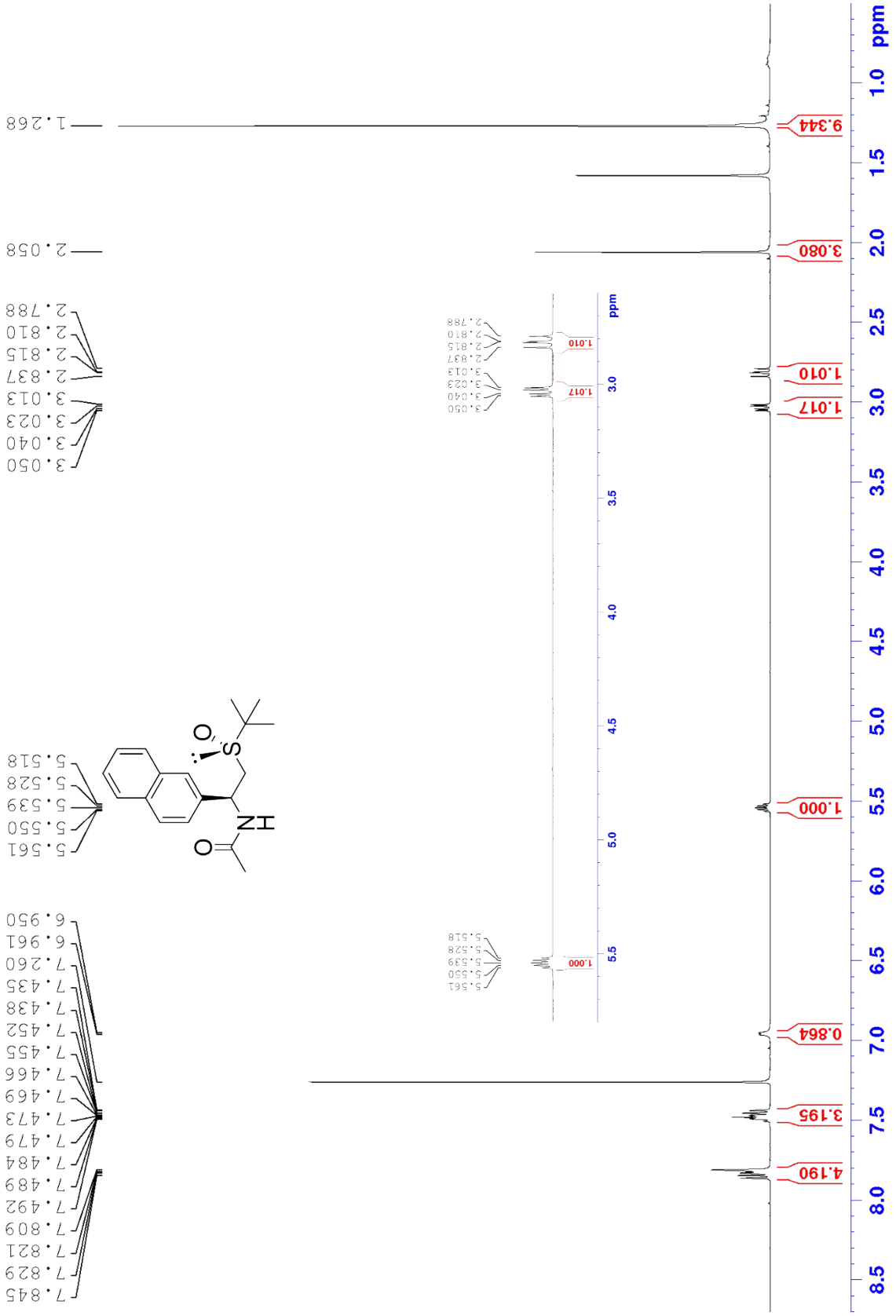


^{13}C-NMR (500 MHz, $CDCl_3$)

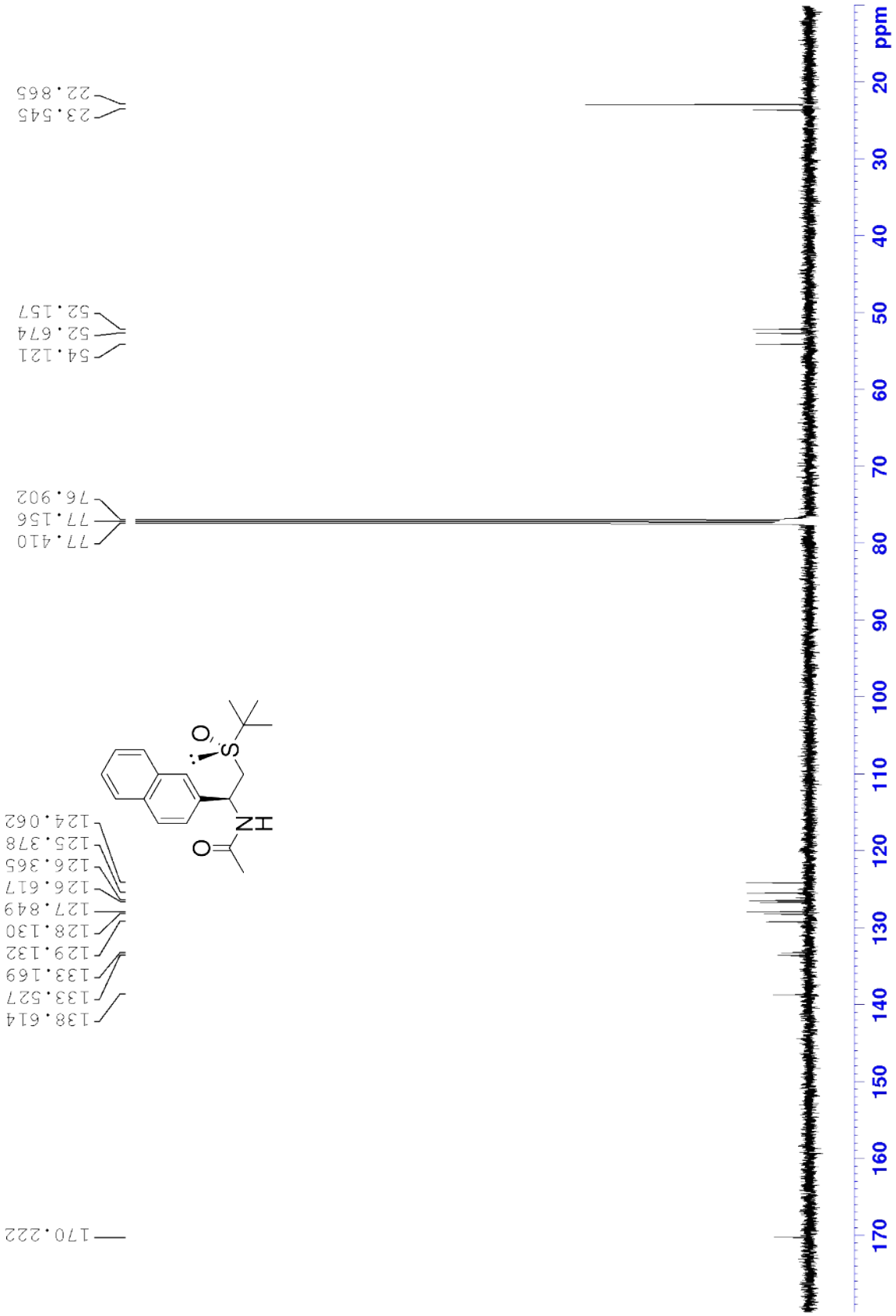


(S_C,S_S)-N-Acetyl-1-(2-naphthyl)-2-(tert-butylsulfinyl)ethylamine, **27(S_C,S_S)**

^{1}H-NMR (500 MHz, $CDCl_3$)

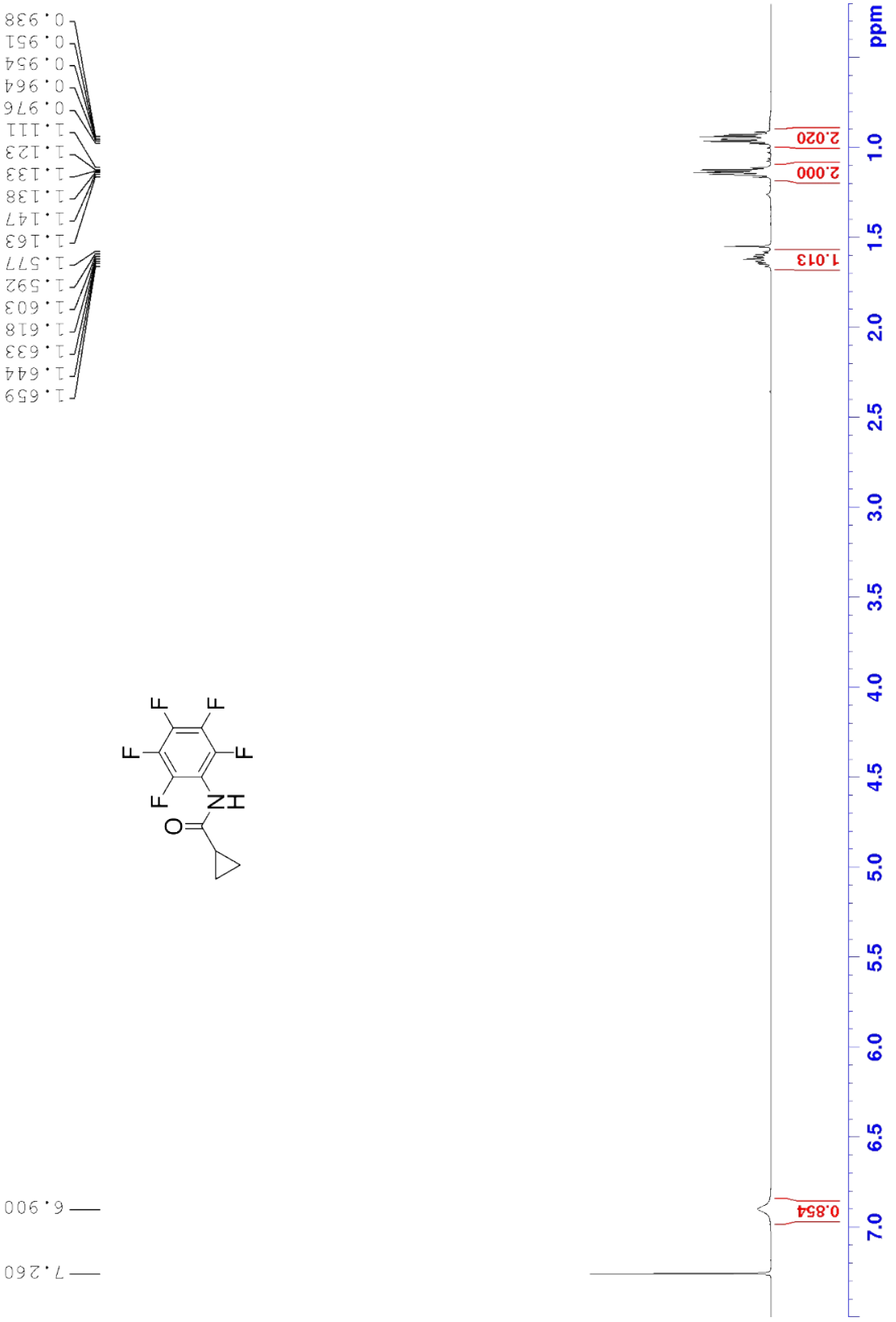


^{13}C-NMR (500 MHz, $CDCl_3$)



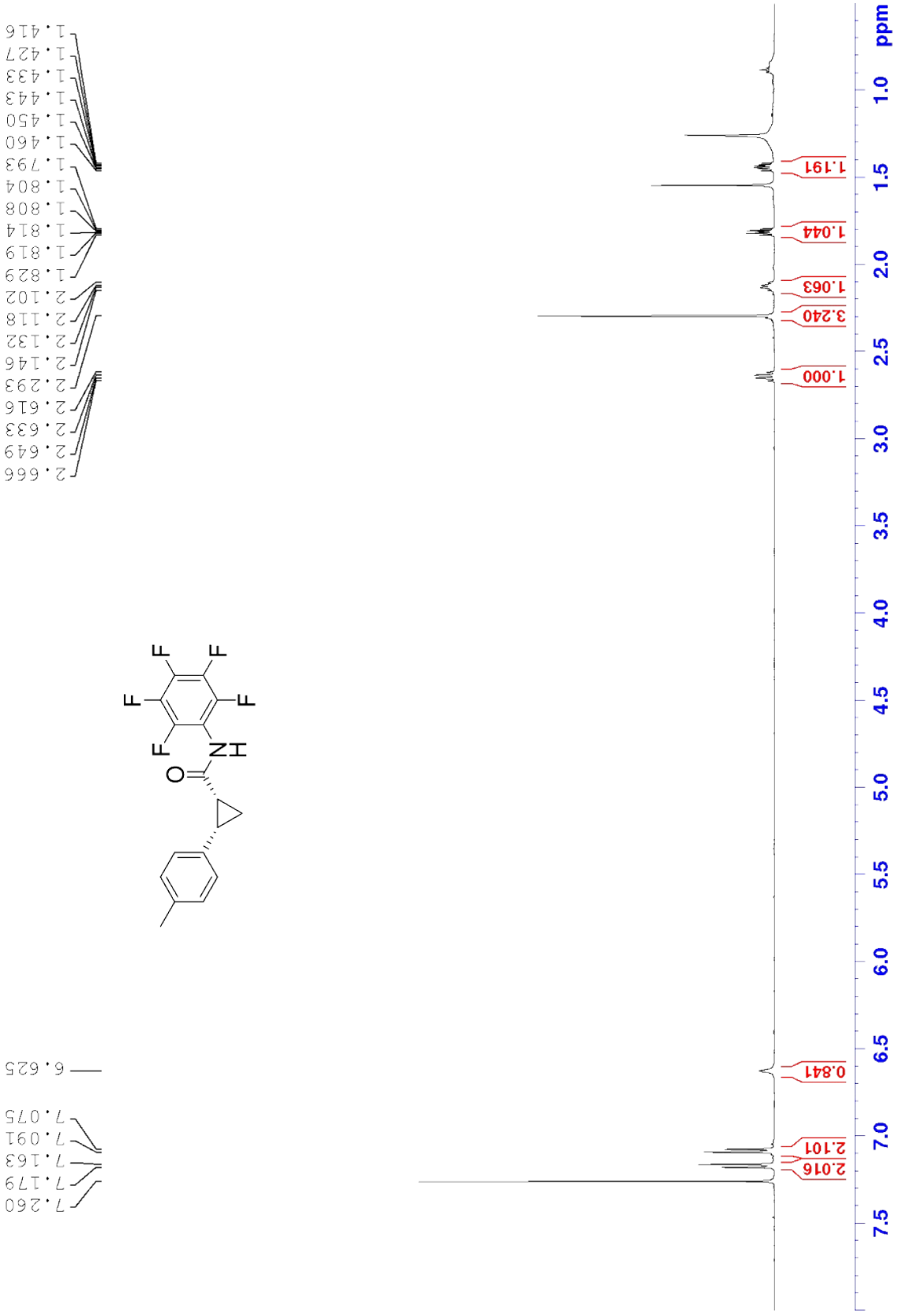
N-(2,3,4,5,6-pentafluorophenyl)-cyclopropanecarboxamide, **32**

^{1}H-NMR (300 MHz, $CDCl_3$)

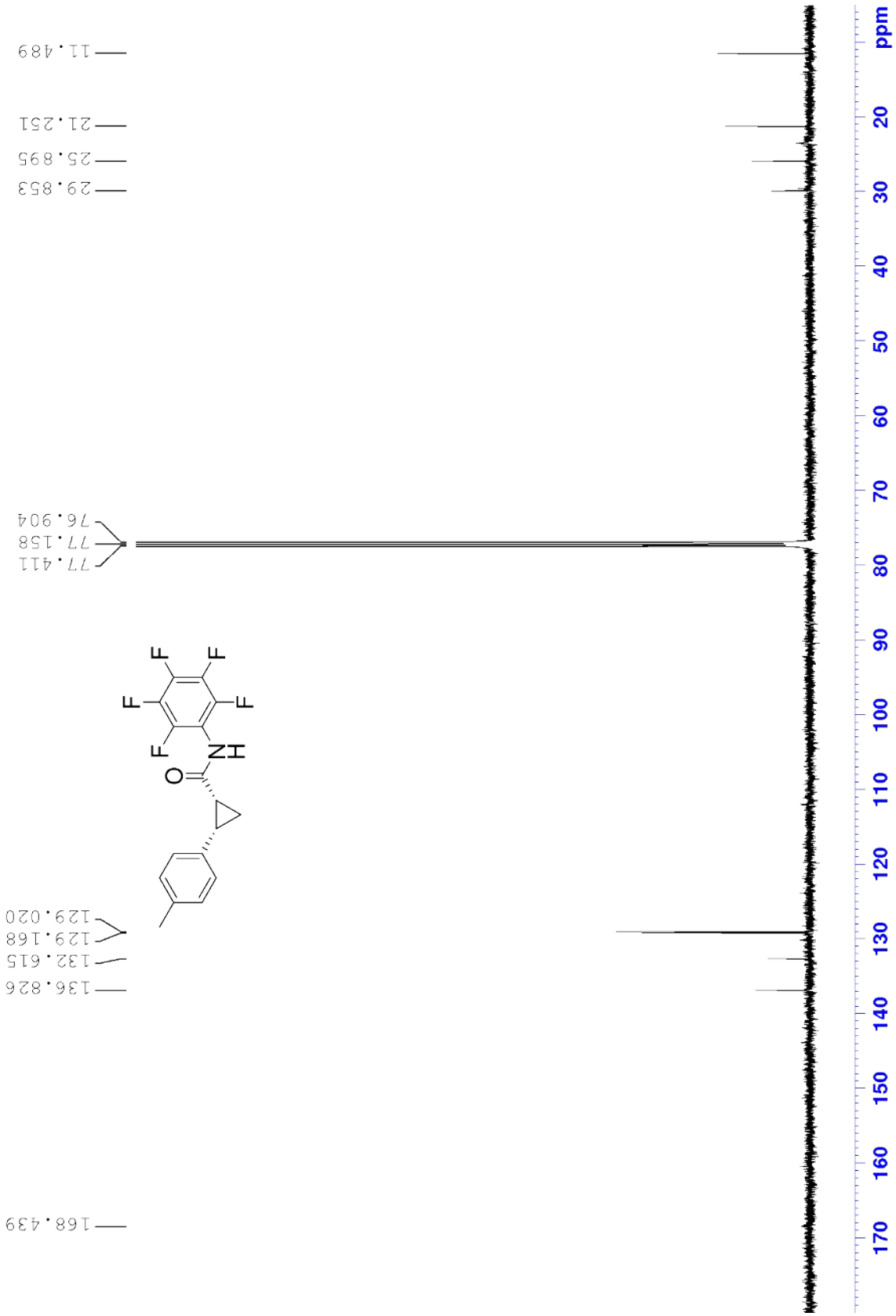


(1R,2S)-N-(2,3,4,5-pentafluorophenyl)-2-(p-tolyl)cyclopropane-1-carboxamide, **34(1*R*,2*S*)**

^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (500 MHz, $CDCl_3$)



X-ray Structural Analysis for the compounds of this work.

A summary of the crystallographic data and the structure refinement results for compounds **7(R_S,S_C,R_S)**, **7(R_S,S_C,S_S)**, **8(R_S,S_C,R_S)**, **8(R_S,S_C,S_S)**, **9(R_S,S_C,R_S)**, **10(R_S,S_C,R_S)**, **10(R_S,S_C,S_S)**, **11(R_S,S_C,R_S)**, **12(R_S,S_C,R_S)**, **13(S_C,R_S)**, **13(S_C,S_S)**, **14(S_C,R_S)**, **15(S_C,R_S)**, **16(S_C,R_S)**, **17(S_C,S_S)**, **18(S_C,S_S)** and **21(R_S,S_C)** are given in **Tables S1-S17**. Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 213 K) to the goniometer head. Data collection was carried out on a Bruker-Nonius X8kappa APEX II CCD area detector or a Bruker-AXS, D8 QUEST ECO, PHOTON II area detector diffractometer, using monochromatic radiation λ(Mo Kα) = 0.71073 Å, by means of ω and ϕ scans with a width of 0.50 degrees. The data were reduced (SAINT)[5] and corrected for absorption effects by the multi-scan method (SADABS)[5,6]. The structures were solved by direct methods (SIR-2002)[7] and refined against all F2 data by full-matrix least-squares techniques (SHELXTL-2016/16 or 2018/3)[8,9] minimizing w[Fo2-Fc2]2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. A search for solvent accessible voids for the crystal structures **7(R_S,S_C,R_S)**, **8(R_S,S_C,R_S)** and **10(R_S,S_C,R_S)** using SQUEEZE[10] showed four small volumes of potential solvents whose solvent content could not be identified or refined with the most severe restraints. The corresponding CIF data represent SQUEEZE treated structures with the solvent molecules handling as a diffuse contribution to the overall scattering, without specific atom position and excluded from the structural model. The SQUEEZE results were appended to the CIF. CCDC 1912692 [**7(R_S,S_C,R_S)**], 2261905 [**7(R_S,S_C,S_S))**], 1912693 [**8(R_S,S_C,R_S)**], 2261906 [**8(R_S,S_C,S_S)**], 1912694 [**9(R_S,S_C,R_S)**], 1912695 [**10(R_S,S_C,R_S)**], 2261907 [**10(R_S,S_C,S_S)**], 2261908 [**11(R_S,S_C,R_S)**], 2261909 [**12(R_S,S_C,R_S)**], 2261910 [**13(S_C,R_S)**], 2261911 [**13(S_C,S_S)**], 2261912 [**14(S_C,R_S)**], 2261913 [**15(S_C,R_S)**], 2261914 [**16(S_C,R_S)**], 2261915 [**17(S_C,S_S)**], 2261916 [**18(S_C,S_S)**] and 2261917 [**21(R_S,S_C)**] contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via: https://www.ccdc.cam.ac.uk/structures/.

X-ray structure determination of selected ligands

(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **7(R_S,S_C,R_S)**

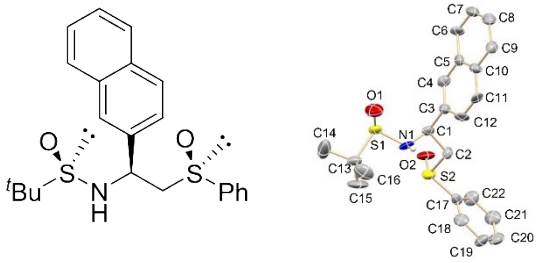
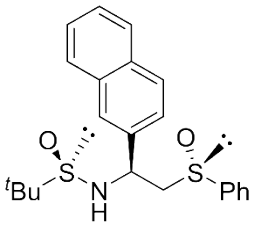


Table S1. Crystal data and structure refinement for 7(R_S,S_C,R_S).

Empirical formula	$C_{22}H_{25}NO_2S_2$	
Formula weight	399.55	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8957(8) Å	α= 90°.
	b = 19.877(3) Å	β= 90°.
	c = 20.288(3) Å	γ = 90°.
Volume	2377.6(6) $Å^3$	
Z	4	
Density (calculated)	1.116 Mg/m^3	
Absorption coefficient	0.238 mm^{-1}	
F(000)	848	
Crystal size	0.500 x 0.300 x 0.050 mm^3	
Theta range for data collection	2.008 to 25.249°.	
Index ranges	-7<=h<=3, -23<=k<=22, -24<=l<=22	
Reflections collected	49397	
Independent reflections	4150 [R(int) = 0.1003]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9882 and 0.8901	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4150 / 0 / 247
Goodness-of-fit on F^2	1.136
Final R indices [I>2sigma(I)]	R1 = 0.1133, wR2 = 0.2653
R indices (all data)	R1 = 0.1253, wR2 = 0.2722
Absolute structure parameter	0.02(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.537 and -0.574 e.Å^{-3}

(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **7(R_S,S_C,S_S)**



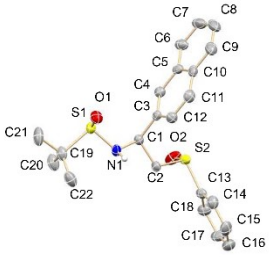
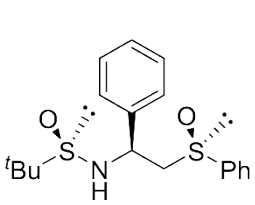


Table S2. Crystal data and structure refinement for 7(R_S,S_C,S_S).

Empirical formula	$C_{22}H_{25}NO_2S_2$	
Formula weight	399.55	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.8356(4) Å	α= 90°.
	b = 19.1473(11) Å	β= 98.968(4)°.
	c = 9.4506(7) Å	γ = 90°.
Volume	1043.06(12) Å^3	
Z	2	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.272 mm^{-1}	
F(000)	424	
Crystal size	0.500 x 0.150 x 0.100 mm^3	

Theta range for data collection	2.127 to 30.805°.
Index ranges	-8<=h<=8, -27<=k<=27, -13<=l<=13
Reflections collected	21111
Independent reflections	5592 [R(int) = 0.1048]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5196
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5592 / 1 / 247
Goodness-of-fit on F^2	1.149
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.1251
R indices (all data)	R1 = 0.1072, wR2 = 0.1377
Absolute structure parameter	0.01(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.393 and -0.432 e.Å^{-3}

(R_S,S_C,R_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **8(R_S,S_C,R_S)**



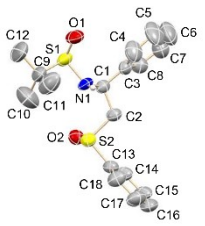
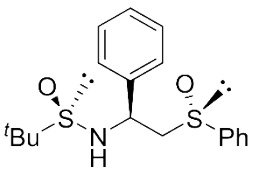


Table S3. Crystal data and structure refinement for 8(R_S,S_C,R_S).

Empirical formula	$C_{18}H_{25}NO_3S_2$	
Formula weight	367.51	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_1$	
Unit cell dimensions	a = 14.1201(3) Å	α= 90°.
	b = 14.1201(3) Å	β= 90°.
	c = 19.4225(6) Å	γ = 120°.
Volume	3353.60(18) Å^3	

Z	6
Density (calculated)	1.092 Mg/m^3
Absorption coefficient	0.251 mm^{-1}
F(000)	1176
Crystal size	0.500 x 0.200 x 0.150 mm^3
Theta range for data collection	1.665 to 25.248°.
Index ranges	-16<=h<=16, -14<=k<=16, -14<=l<=23
Reflections collected	29542
Independent reflections	3288 [R(int) = 0.0773]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9633 and 0.8847
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3288 / 122 / 229
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0631, wR2 = 0.1643
R indices (all data)	R1 = 0.0754, wR2 = 0.1736
Absolute structure parameter	0.10(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.255 and -0.215 $e.Å^{-3}$

(R_S,S_C,S_S)-N-[1-Phenyl-2-(phenylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **8(R_S,S_C,S_S)**



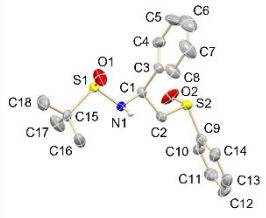
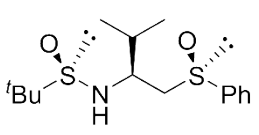


Table S4. Crystal data and structure refinement for 8(R_S,S_C,S_S).

Empirical formula	$C_{18}H_{23}NO_2S_2$
Formula weight	349.49
Temperature	193(2) K
Wavelength	0.71073 Å

Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.2150(12) Å	α= 90°.
	b = 29.247(3) Å	β= 90°.
	c = 5.8198(7) Å	γ= 90°.
Volume	1908.9(4) $Å^3$	
Z	4	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.287 mm^{-1}	
F(000)	744	
Crystal size	0.400 x 0.100 x 0.050 mm^3	
Theta range for data collection	1.945 to 25.245°.	
Index ranges	-13<=h<=12, -35<=k<=35, -6<=l<=6	
Reflections collected	20320	
Independent reflections	3435 [R(int) = 0.1131]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5990	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3435 / 0 / 211	
Goodness-of-fit on F^2	1.172	
Final R indices [I>2sigma(I)]	R1 = 0.0788, wR2 = 0.1756	
R indices (all data)	R1 = 0.0857, wR2 = 0.1787	
Absolute structure parameter	0.13(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.538 and -0.462 $e.Å^{-3}$	

(R_S,S_C,R_S)-N-[1-(Phenylsulfinyl)-3-methylbut-2-yl]-2-methyl-2-propanesulfinamide, **9(R_S,S_C,R_S)**



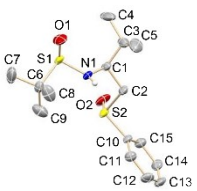


Table S5. Crystal data and structure refinement for 9(R_S,S_C,R_S).

Empirical formula	$C_{15}H_{25}NO_2S_2$	
Formula weight	315.48	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.7979(3) Å	α= 90°.
	b = 11.3878(6) Å	β= 99.733(2)°.
	c = 13.2360(7) Å	γ = 90°.
Volume	861.33(8) Å^3	
Z	2	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.310 mm^{-1}	
F(000)	340	
Crystal size	0.400 x 0.250 x 0.200 mm^3	
Theta range for data collection	3.565 to 25.248°.	
Index ranges	-6<=h<=6, -13<=k<=11, -14<=l<=15	
Reflections collected	7790	
Independent reflections	2369 [R(int) = 0.0198]	
Completeness to theta = 25.242°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9405 and 0.8859	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2369 / 2 / 189	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0728	
R indices (all data)	R1 = 0.0315, wR2 = 0.0743	
Absolute structure parameter	0.05(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.253 and -0.174 e.Å^{-3}	

(R_S,S_C,R_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **10(R_S,S_C,R_S)**

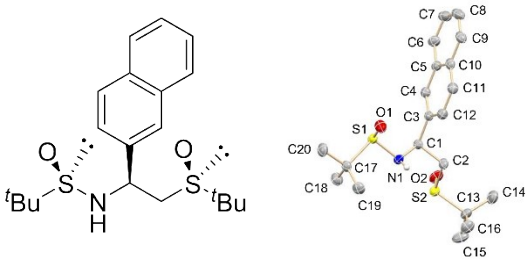
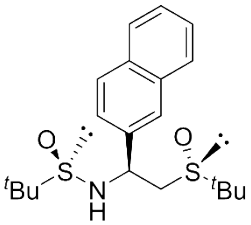


Table S6. Crystal data and structure refinement for 10(R_S,S_C,R_S).

Empirical formula	$C_{20}H_{29}NO_2S_2$	
Formula weight	379.56	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.8277(6) Å	α= 71.359(3)°.
	b = 9.3792(9) Å	β= 74.525(3)°.
	c = 10.3043(10) Å	γ= 75.502(3)°.
Volume	505.86(9) $Å^3$	
Z	1	
Density (calculated)	1.246 Mg/m^3	
Absorption coefficient	0.276 mm^{-1}	
F(000)	204	
Crystal size	0.300 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.130 to 30.647°.	
Index ranges	-8<=h<=8, -13<=k<=13, -14<=l<=14	
Reflections collected	26033	
Independent reflections	6101 [R(int) = 0.0401]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6101 / 3 / 232	

Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0859
R indices (all data)	R1 = 0.0420, wR2 = 0.0916
Absolute structure parameter	0.00(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.460 and -0.346 e.Å^{-3}

(R_S,S_C,S_S)-N-[1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethyl]-2-methyl-2-propanesulfinamide, **10(R_S,S_C,S_S)**



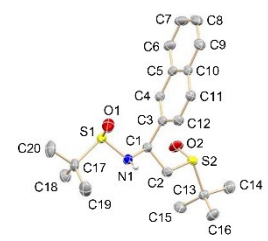


Table S7. Crystal data and structure refinement for 10(R_S,S_C,S_S).

Empirical formula	$C_{20}H_{29}NO_2S_2$	
Formula weight	379.56	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.0206(4) Å	α= 90°.
	b = 18.0652(12) Å	β= 100.221(3)°.
	c = 9.4916(7) Å	γ= 90°.
Volume	1015.96(12) Å^3	
Z	2	
Density (calculated)	1.241 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	408	
Crystal size	0.500 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.180 to 30.568°.	
Index ranges	-8<=h<=8, -25<=k<=25, -13<=l<=13	
Reflections collected	26489	

Independent reflections	6205 [R(int) = 0.0556]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6051
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6205 / 1 / 232
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0769
R indices (all data)	R1 = 0.0355, wR2 = 0.0804
Absolute structure parameter	0.05(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.245 and -0.290 e.$Å^{-3}$

(R_S,S_C,R_S)-N-[2-(tert-butylsulfinyl)-1-phenylethyl]-2-methyl-2-propanesulfinamide, **11(R_S,S_C,R_S)**

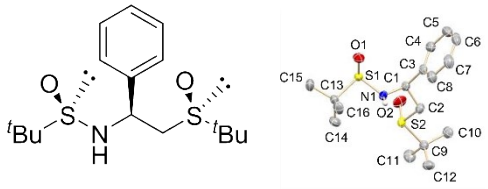


Table S8. Crystal data and structure refinement for 11(R_S,S_C,R_S).

Empirical formula	$C_{16}H_{27}NO_2S_2$	
Formula weight	329.50	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.0077(3) Å	α= 90°.
	b = 15.1960(7) Å	β= 90°.
	c = 19.9670(12) Å	γ= 90°.
Volume	1822.85(17) $Å^3$	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.296 mm^{-1}	

F(000)	712
Crystal size	0.500 x 0.300 x 0.200 mm^3
Theta range for data collection	2.441 to 30.528°.
Index ranges	-8<=h<=8, -21<=k<=21, -28<=l<=28
Reflections collected	43624
Independent reflections	5572 [R(int) = 0.0823]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5574
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5572 / 0 / 196
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0772
R indices (all data)	R1 = 0.0494, wR2 = 0.0865
Absolute structure parameter	-0.07(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.295 and -0.303 e.$Å^{-3}$

(R_S,S_C,R_S)-N-[1-(tert-butylsulfinyl)-3-methylbutan-2-yl]-2-methyl-2-propanesulfinamide, **12(R_S,S_C,R_S)**

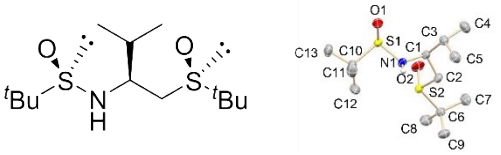
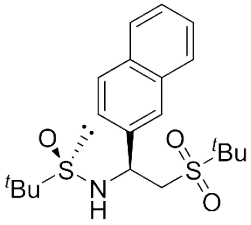


Table S9. Crystal data and structure refinement for 12(R_S,S_C,R_S).

Empirical formula	$C_{13}H_{29}NO_2S_2$	
Formula weight	295.49	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.0101(3) Å	α= 90°.
	b = 14.6331(6) Å	β= 90°.
	c = 19.1993(8) Å	γ = 90°.

Volume	1688.51(13) Å^3
Z	4
Density (calculated)	1.162 Mg/m^3
Absorption coefficient	0.312 mm^{-1}
F(000)	648
Crystal size	0.300 x 0.200 x 0.100 mm^3
Theta range for data collection	2.121 to 30.539°.
Index ranges	-8<=h<=8, -20<=k<=19, -27<=l<=27
Reflections collected	39152
Independent reflections	5146 [R(int) = 0.0784]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6466
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5146 / 1 / 174
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0726
R indices (all data)	R1 = 0.0489, wR2 = 0.0804
Absolute structure parameter	0.02(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.435 and -0.371 e.Å^{-3}

(R_S,S_C)-N-[2-(Tert-butylsulfonyl)-1-(2-naphthyl)ethyl]-2-methyl-2-propanesulfinamide, **21(R_S,S_C)**



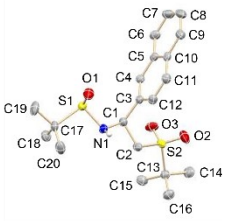


Table S10. Crystal data and structure refinement for 21(R_S,S_C).

Empirical formula	$C_{20}H_{29}NO_3S2$
Formula weight	395.56
Temperature	193(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.0258(4) Å	α= 90°.
	b = 17.9919(12) Å	β= 99.556(2)°.
	c = 9.5010(6) Å	γ= 90°.
Volume	1015.76(12) $Å^3$	
Z	2	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	0.281 mm^{-1}	
F(000)	424	
Crystal size	0.500 x 0.200 x 0.150 mm^3	
Theta range for data collection	2.174 to 30.518°.	
Index ranges	-8<=h<=6, -25<=k<=25, -13<=l<=13	
Reflections collected	23525	
Independent reflections	6169 [R(int) = 0.0612]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5659	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6169 / 2 / 241	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0818	
R indices (all data)	R1 = 0.0617, wR2 = 0.0907	
Absolute structure parameter	0.03(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.453 and -0.408 $e.Å^{-3}$	

X-ray structure determination of selected complexes

cis-Dichloro[(S_C,S_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(S_C,S_S)**

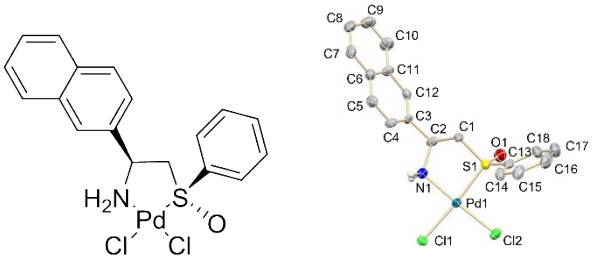


Table S11. Crystal data and structure refinement for 13(S_C,S_S).

Empirical formula	$C_{18}H_{17}Cl_2NOPdS$	
Formula weight	472.68	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 13.1185(13) Å	α= 90°.
	b = 6.3138(9) Å	β= 114.291(7)°.
	c = 13.7978(13) Å	γ= 90°.
Volume	1041.7(2) $Å^3$	
Z	2	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	1.251 mm^{-1}	
F(000)	472	
Crystal size	0.400 x 0.050 x 0.030 mm^3	
Theta range for data collection	2.976 to 25.247°.	
Index ranges	-15<=h<=15, -7<=k<=2, -16<=l<=16	
Reflections collected	5328	
Independent reflections	2071 [R(int) = 0.0320]	
Completeness to theta = 25.242°	91.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5483	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2071 / 1 / 217	

Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0852
R indices (all data)	R1 = 0.0440, wR2 = 0.0884
Absolute structure parameter	-0.02(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.672 and -0.488 e.$Å^{-3}$

cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **13(S_C,R_S)**

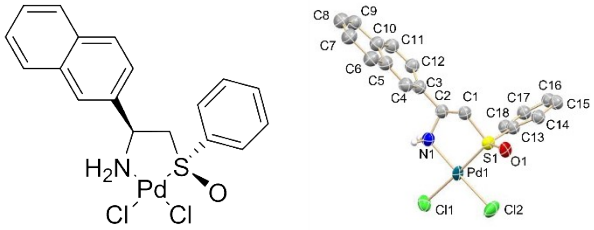


Table S12. Crystal data and structure refinement for 13(S_C,R_S).

Empirical formula	$C_{18}H_{17}Cl_2NOPdS$	
Formula weight	472.68	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 12.6204(8) Å	α= 90°.
	b = 6.6213(3) Å	β= 95.562(3)°.
	c = 22.7235(14) Å	γ= 90°.
Volume	1889.91(19) $Å^3$	
Z	4	
Density (calculated)	1.661 Mg/m^3	
Absorption coefficient	1.379 mm^{-1}	
F(000)	944	
Crystal size	0.400 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.538 to 25.243°.	
Index ranges	-14<=h<=12, -7<=k<=7, -27<=l<=26	
Reflections collected	17292	
Independent reflections	4598 [R(int) = 0.0354]	

Completeness to theta = 25.242°	79.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5483
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4598 / 553 / 433
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1306
R indices (all data)	R1 = 0.0713, wR2 = 0.1350
Absolute structure parameter	0.09(3)
Extinction coefficient	n/a
Largest diff. peak and hole	1.077 and -1.851 e.Å^{-3}

cis-Dichloro[(S_C,R_S)-1-(Phenyl)-2-(phenylsulfinyl)ethylamine]palladium (II), **14(S_C,R_S)**

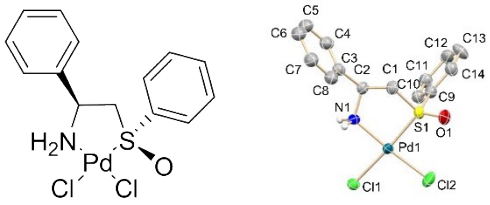
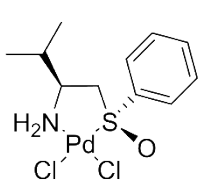


Table S13. Crystal data and structure refinement for 14(S_C,R_S).

Empirical formula	$C_{14}H_{15}Cl_2NOPdS$	
Formula weight	422.63	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.148(2) Å	α= 90°.
	b = 13.389(4) Å	β= 90°.
	c = 20.420(6) Å	γ= 90°.
Volume	1680.9(9) Å^3	
Z	4	
Density (calculated)	1.670 Mg/m^3	
Absorption coefficient	1.540 mm^{-1}	
F(000)	840	

Crystal size	0.200 x 0.050 x 0.020 mm^3
Theta range for data collection	1.995 to 25.248°.
Index ranges	-7<=h<=7, -15<=k<=15, -24<=l<=22
Reflections collected	8066
Independent reflections	3004 [R(int) = 0.0639]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6030
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3004 / 131 / 181
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1222
R indices (all data)	R1 = 0.0836, wR2 = 0.1292
Absolute structure parameter	0.06(4)
Extinction coefficient	n/a
Largest diff. peak and hole	1.183 and -1.218 e.$Å^{-3}$

cis-Dichloro[(S_C,R_S)-3-methyl-1-(phenylsulfinyl)-2-butylamine]palladium (II), **15(S_C,R_S)**



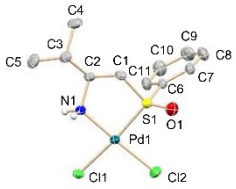


Table S14. Crystal data and structure refinement for 15(S_C,R_S).

Empirical formula	$C_{11}H_{17}Cl_2NOPdS$	
Formula weight	388.61	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.1116(5) Å	α= 90°.
	b = 12.0151(7) Å	β= 90°.
	c = 14.6744(7) Å	γ= 90°.
Volume	1430.19(14) $Å^3$	

Z	4
Density (calculated)	1.805 Mg/m^3
Absorption coefficient	1.800 mm^{-1}
F(000)	776
Crystal size	0.200 x 0.050 x 0.030 mm^3
Theta range for data collection	2.191 to 30.539°.
Index ranges	-11<=h<=11, -17<=k<=17, -20<=l<=20
Reflections collected	27751
Independent reflections	4379 [R(int) = 0.0497]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4379 / 0 / 156
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0472
R indices (all data)	R1 = 0.0301, wR2 = 0.0484
Absolute structure parameter	-0.003(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.368 and -0.780 e.Å^{-3}

cis-Dichloro[(S_C,R_S)-1-(2-Naphthyl)-2-(tert-butylsulfinyl)ethylamine]palladium (II), **16(S_C,R_S)**

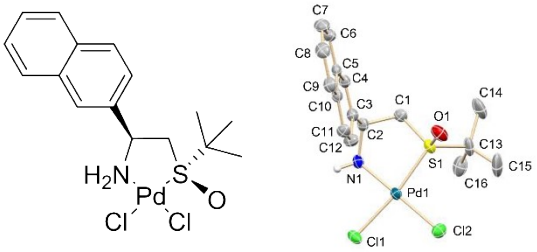


Table S15. Crystal data and structure refinement for 16(S_C,R_S).

Empirical formula	$C_{16}H_{21}Cl_2NOPdS$
Formula weight	452.70
Temperature	193(2) K

Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8774(5) Å	α= 90°.
	b = 12.2061(9) Å	β= 90°.
	c = 24.8164(16) Å	γ= 90°.
Volume	1780.3(2) $Å^3$	
Z	4	
Density (calculated)	1.689 Mg/m^3	
Absorption coefficient	1.460 mm^{-1}	
F(000)	912	
Crystal size	0.500 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.341 to 30.555°.	
Index ranges	-8<=h<=8, -17<=k<=17, -35<=l<=34	
Reflections collected	29285	
Independent reflections	5447 [R(int) = 0.0930]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5061	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5447 / 0 / 202	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.0951	
R indices (all data)	R1 = 0.0482, wR2 = 0.1009	
Absolute structure parameter	0.04(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.931 and -1.630 $e.Å^{-3}$	

cis-Dichloro[(S_C,S_S)-2-(tert-butylsulfinyl)-1-(phenyl)ethylamine]palladium (II), **17(S_C,S_S)**

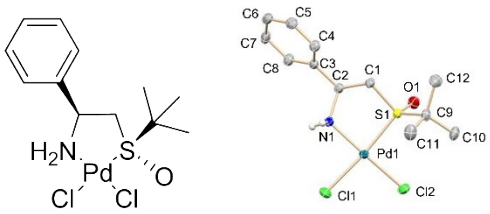


Table S16. Crystal data and structure refinement for 17(S_C,S_S).

Empirical formula	$C_{12}H_{19}Cl_2NOPdS$	
Formula weight	402.64	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.7251(3) Å	α= 90°.
	b = 11.3374(3) Å	β= 90°.
	c = 14.2512(4) Å	γ= 90°.
Volume	1571.30(8) $Å^3$	
Z	4	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	1.642 mm^{-1}	
F(000)	808	
Crystal size	0.300 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.296 to 30.503°.	
Index ranges	-13<=h<=13, -16<=k<=16, -20<=l<=20	
Reflections collected	33427	
Independent reflections	4798 [R(int) = 0.0315]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6387	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4798 / 0 / 166	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0169, wR2 = 0.0392	

R indices (all data)	R1 = 0.0184, wR2 = 0.0403
Absolute structure parameter	0.006(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.385 and -0.580 e.Å^{-3}

cis-Dichloro[(S_C,S_S)-1-(tert-butylsulfinyl)-3-methyl-2-butylamine]palladium (II), **18(S_C,S_S)**

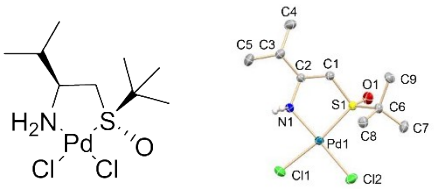


Table 17. Crystal data and structure refinement for 18(S_C,S_S).

Empirical formula	$C_9H_{21}Cl_2NOPdS$	
Formula weight	368.63	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.5540(4) Å	α= 90°.
	b = 10.1169(4) Å	β= 90°.
	c = 16.2154(7) Å	γ= 90°.
Volume	1403.28(11) Å^3	
Z	4	
Density (calculated)	1.745 Mg/m^3	
Absorption coefficient	1.829 mm^{-1}	
F(000)	744	
Crystal size	0.500 x 0.300 x 0.200 mm^3	
Theta range for data collection	2.512 to 30.538°.	
Index ranges	-11<=h<=12, -14<=k<=14, -23<=l<=22	
Reflections collected	30895	
Independent reflections	4283 [R(int) = 0.0329]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5458	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4283 / 0 / 141
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0151, wR2 = 0.0357
R indices (all data)	R1 = 0.0160, wR2 = 0.0362
Absolute structure parameter	-0.008(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.240 and -0.496 e.$Å^{-3}$

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