Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Synthetic Studies toward Penitrem E: Enantiocontrolled Construction of B–E Rings

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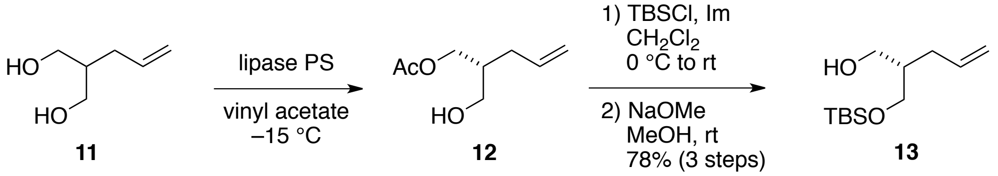
General Remarks: Materials were obtained from commercial suppliers and used without further purification unless otherwise mentioned. All reactions were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. Anhydrous THF, Et_2O, CH_2Cl_2, and MeCN were purchased from Kanto Chemical Co. Inc. Anhydrous DMF was purchased from Wako Pure Chemical Industries. Anhydrous methanol was dried and distilled according to the standard protocols. Column chromatography was performed on Silica Gel 60N (Kanto, spherical neutral, 63–210 µm) and flash column chromatography was performed on Silica Gel 60N (Kanto, spherical neutral, 40–50 µm) using the indicated eluent. Preparative and analytical TLC was performed on Merck 60 F_{254} glass plates precoated with a 0.25 mm thickness of silica gel. IR spectra were measured on a JASCO FT/IR-4100 Fourier Transform Infrared spectrometer. NMR spectra were recorded on a JNM-AL400 spectrometer, and a JEOL ECA600 spectrometer. For ^1H NMR spectra, chemical shifts are expressed in ppm downfield from internal chloroform (7.26 ppm) or tetramethylsilane (0 ppm). For ^{13}C NMR spectra, chemical shifts are expressed in ppm downfield from internal chloroform (77.0 ppm) or methanol (49.0 ppm) as an internal standard. Mass spectra were recorded on a JEOL JMS-DX-303 or a JMS-700, or a Bruker micrOTOF II spectrometers. Optical rotations were measured on a JASCO P-2200 high sensitive polarimeter.

(*S*)-(–)-2-(((*tert*-Butyldimethylsilyl)oxy)methyl)pent-4-en-1-ol (13).

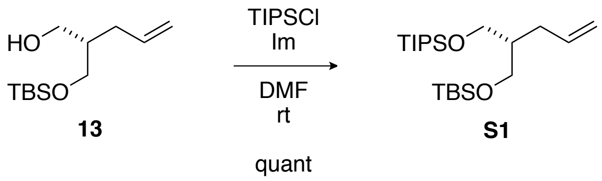


A 2-L three-necked round-bottomed flask equipped with a magnetic stirring bar was charged with diol **11**[1] (34.9 g, 300 mmol) and vinyl acetate (1.5 L). To the solution was added lipase PS (34.9 g) at –15 °C. The resulting mixture was stirred for 25 h at –15 °C before the reaction mixture was passed through a celite pad. The filtrate was concentrated under reduced pressure (0 °C, 1 mmHg) to give a crude material, which was directly used for the next reaction without further purification to minimize the decrease of enantiomeric excess.

A 3-L round-bottomed flask equipped with a magnetic stirring bar was charged with the crude acetate **12** and dry CH_2Cl_2 (1.4 L). To the solution was added imidazole (40.8 g, 600 mmol) at 0 °C. TBSCl (67.8 g, 450 mmol) in CH_2Cl_2 (100 mL) was added to the resulting mixture dropwise over 1 h at 0 °C. After additional 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 20 min, after which time TLC (ethyl acetate) indicated complete consumption of the starting alcohol **12**. The reaction was quenched with water, and the resulting mixture was extracted twice with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was used for the next reaction without further purification.

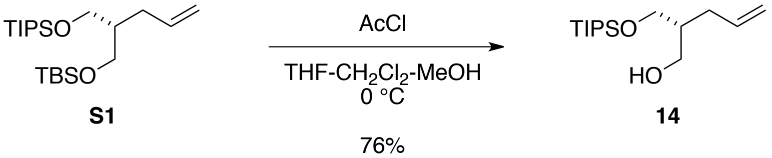
A 3-L round-bottomed flask equipped with a magnetic stirring bar was charged with the crude acetate and methanol (1.5 L). To the solution was added sodium methoxide (24.3 g, 450 mmol). The reaction mixture was stirred at room temperature for 4.5 h, after which time TLC (hexanes-ethyl acetate = 4:1) indicated complete consumption of the starting acetate. The reaction was quenched with 1 M aqueous hydrogen chloride. The mixture was concentrated under reduced pressure. The residue was partitioned twice between CH_2Cl_2/brine. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes to hexanes-ethyl acetate = 4:1, gradient) to afford TBS ether **13** (54.0 g, 234 mmol, 78% from **11** over 3 steps) as a colorless oil. Its spectral data were identical with those reported for its enantiomer[1]; $[\alpha]_D^{27}$ = –5.15 (*c* 1.76, $CHCl_3$); lit[1] $[\alpha]_D$ = +3.73 (*c* 1.76, $CHCl_3$); R_f = 0.48 (hexanes-EtOAc = 4:1); IR (neat, cm^{-1}) 3388, 2955, 2929, 2858, 1640, 1471, 1254, 1092, 1041, 836, 775; ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (dddd, 1H, *J* = 17.6, 10.0, 7.2, 7.2 Hz), 5.10–4.98 (m, 2H), 3.83–3.69 (m, 2H), 3.69–3.57 (m, 2H), 2.67 (br s, 1H), 2.08–2.01 (m, 2H), 1.87–1.77 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 116.3, 66.4, 66.1, 41.8, 32.4, 25.8, 18.1, –5.57, –5.61; HRMS-ESI (*m/z*) calcd. for $C_{12}H_{27}O_2Si$, 231.1775 ($M+H^+$); found, 231.1771.

(*S*)-(–)-6-Allyl-9,9-diisopropyl-2,2,3,3,10-pentamethyl-4,8-dioxa-3,9-disilaundecane (S1).



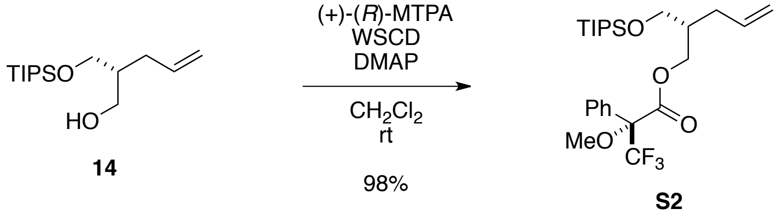
A 1-L round-bottomed flask equipped with a magnetic stirring bar was charged with **13** (10.0 g, 43.4 mmol), imidazole (8.87 g, 130 mmol), and dry DMF (217 mL). To the solution was added TIPSCl (18.4 mL, 86.8 mmol). The reaction mixture was stirred for 1.5 h, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of the alcohol **13**. The solvent was evaporated (60 °C, 1 mmHg), and the residue was partitioned between ethyl acetate and water three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 20:1) to afford bis(silyl)ether **S1** (16.9 g, 43.7 mmol, quant) as a colorless oil; $[\alpha]_D^{23}$ = –0.39 (*c* 0.62, $CHCl_3$); R_f = 0.86 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2944, 2866, 1465, 1254, 1096, 994, 912, 882, 836, 775, 681; ^1H NMR (400 MHz, $CDCl_3$): δ 5.81 (dddd, 1H, *J* = 17.2, 10.4, 7.2, 6.8 Hz), 5.06–4.94 (m, 2H), 3.72–3.55 (m, 4H), 2.14–2.06 (m, 2H), 1.76–1.64 (m, 1H) 1.14–0.95 (m, 21H), 0.89 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 115.7, 62.9, 62.5, 43.8, 32.3, 25.9, 18.3, 18.0, 12.0, –5.5; HRMS-ESI (*m/z*) calcd. for $C_{21}H_{47}O_2Si_2$, 387.3109 ($M+H^+$); found, 387.3115.

(***R***)-(+)-2-(((triisopropylsilyl)oxy)methyl)pent-4-en-1-ol (14).



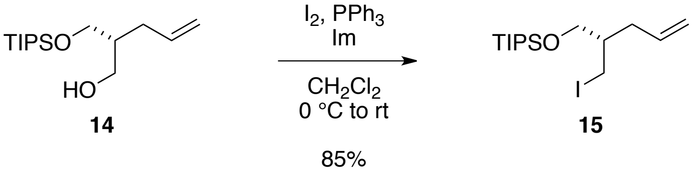
A 100-mL round-bottomed flask equipped with a magnetic stirring bar was charged with **S1** (1.21 g, 3.12 mmol) and THF-CH_2Cl_2-MeOH (5:5:1, 66 mL). To the mixture was added acetyl chloride (110 μL, 1.55 mmol) at 0 °C, and the resulting solution was stirred for 5 h at 0 °C, after which time TLC (hexanes-ethyl acetate = 9:1) indicated complete consumption of the starting **S1**. The reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was warmed to room temperature and extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 10:1) to afford the alcohol **14** (647.3 mg, 2.38 mmol, 76%) as a colorless oil. Enantiomeric excess of **14** was determined to be 90% ee by ^{1}H NMR of its Mosher ester **S2**; $[\alpha]_D^{26}$ = +2.5 (*c* 0.43, $CHCl_3$); R_f = 0.21 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 3383, 2943, 2867, 1640, 1464, 1385, 1237, 1202, 1100, 913, 882, 794, 681; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (ddt, 1H, *J* = 17.6, 10.0, 7.2 Hz), 5.08–4.98 (m, 2H), 3.88 (dd, 1H, *J* = 10.0, 4.0 Hz), 3.78–3.61 (m, 3H), 2.87 (br s, 1H) 2.04 (dd, 2H, *J* = 7.2, 7.2 Hz), 1.91–1.80 (m, 1H), 1.16–0.96 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 116.3, 67.1, 66.2, 42.0, 32.4, 17.9, 11.8; HRMS-ESI (*m/z*) calcd. for $C_{15}H_{33}O_2Si$, 273.2244 ($M+H^+$); found, 273.2242.

Determination of enantiomeric excess of compound 14.
(***R***)-(+)-2-(((Triisopropylsilyl)oxy)methyl)pent-4-en-1-yl (***R***)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S2).



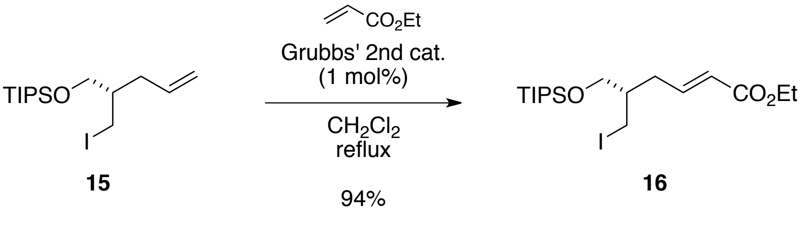
A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with **14** (13.0 mg, 47.7 μmol), (+)-(*R*)-MTPA (60.1 mg, 257 μmol), and CH_2Cl_2 (1.5 mL). To the mixture were added WSCD (70.2 mg, 366 μmol) and DMAP (5.8 mg, 47 μmol). The resulting solution was stirred for 3 h, after which time TLC (hexanes-ethyl acetate = 10:1) indicated complete consumption of alcohol **14**. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 20:1) to afford the ester **S2** (22.8 mg, 46.7 μmol, 98%, dr = 95:5) as a colorless oil; $[\alpha]_D^{29}$ = +29 (*c* 0.58, $CHCl_3$); R_f = 0.62 (hexanes-ethyl acetate = 10:1); IR (neat, cm^{-1}): 2945, 2867, 1750, 1464, 1272, 1171, 1122, 1020, 882, 719, 683; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54–7.48 (m, 2H), 7.44–7.36 (m, 3H), 5.80–5.71 (m, 1H), 5.06–5.01 (m, 2H), 4.43 (dd, 0.95H, *J* = 10.2, 5.4 Hz), 4.40–4.33 (m, 0.10H), 4.28 (dd, 0.95H, *J* = 10.2, 6.0 Hz), 3.66–3.56 (m, 2H), 3.54 (s, 3H) 2.22–2.14 (m, 1H), 2.10–2.03 (m, 1H), 2.00–1.91 (m, 1H), 1.10–0.95 (m, 21H) (a mixture of diastereomers, dr = 95:5); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5, 135.62, 135.57, 132.4, 129.5, 128.3, 127.3, 123.4 (q, $^1J_{C–F}$ = 286 Hz), 117.02, 116.99, 84.6 (q, $^2J_{C–F}$ = 28.7 Hz), 65.91, 65.87, 62.47, 62.32, 55.3, 40.41, 40.36, 32.2, 32.1, 17.9, 11.9 (a mixture of diastereomers, dr = 95:5); HRMS-ESI (*m/z*) calcd. for $C_{25}H_{40}F_3O_4Si$, 489.2642 (M+H$^+$); found, 489.2631.

(*S*)-(+)-((2-(iodomethyl)pent-4-en-1-yl)oxy)triisopropylsilane (15).



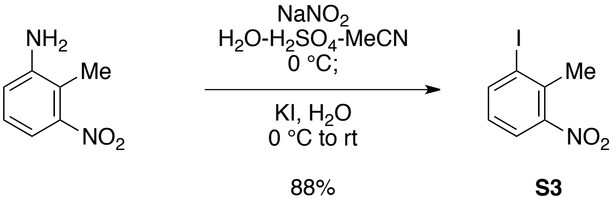
A 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar was charged with PPh_3 (246 mg, 938 µmol), imidazole (63.9 mg, 938 µmol) and CH_2Cl_2 (2.0 mL). To the mixture was added I_2 (235 mg, 926 µmol) at 0 °C. The resulting suspension was stirred for 30 min at 0 °C before alcohol **14** (183 mg, 672 µmol) in CH_2Cl_2 (2.0 mL) was added to the reaction mixture via cannula. The resulting suspension was stirred for 30 min and then warmed to room temperature. After additional 3.5 h, the reaction was quenched with saturated aqueous Na_2SO_3, and the mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes) to afford iodide **15** (219 mg, 573 µmol, 85%) as a colorless oil; $[\alpha]_D^{24}$ = +1.4 (*c* 0.18, $CHCl_3$); R_f = 0.39 (hexanes); IR (neat, cm^{-1}): 2942, 2866, 1641, 1463, 1186, 1109, 1067, 994, 917, 882, 784, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (dddd, 1H, *J* = 17.2, 10.4, 7.2, 6.8 Hz), 5.16–5.02 (m, 2H), 3.70 (dd, 1H, *J* = 9.6, 4.4 Hz), 3.58 (dd, 1H, *J* = 9.6, 6.4 Hz), 3.38 (dd, 1H, *J* = 9.6, 4.8 Hz), 3.31 (dd, 1H, *J* = 9.6, 6.0 Hz), 2.23–2.01 (m, 2H), 1.61–1.50 (m, 1H), 1.15–1.00 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 117.1, 65.1, 42.3, 35.5, 18.0, 12.0, 11.5; HRMS-ESI (*m/z*): calcd. for $C_{15}H_{32}IOSi$, 383.1262 (M+H$^+$); found, 383.1273.

(*S*,*E*)-(–)-Ethyl 6-iodo-5-(((triisopropylsilyl)oxy)methyl)hex-2-enoate (16).



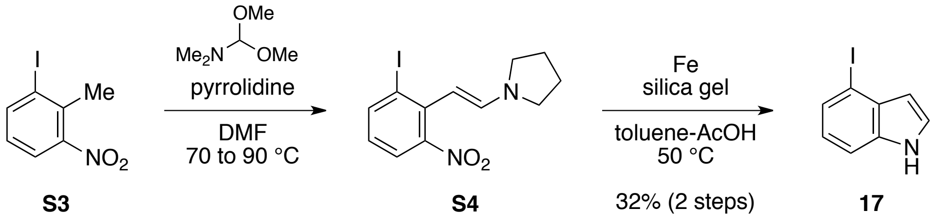
A 500-mL round-bottomed flask equipped with a magnetic stirring bar was charged with **15** (6.16 g, 16.1 mmol), 2nd-generation Grubbs catalyst (137 mg, 161 µmol), ethyl acrylate (17.5 mL, 161 mmol), and CH_2Cl_2 (161 mL). The resulting mixture was heated at reflux for 5 h, after which time TLC (hexanes) indicated complete consumption of the starting olefin **15**. The solution was cooled to room temperature, and the mixture was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 25:1) to afford unsaturated ester **16** (6.88 g, 15.1 mmol, 94%) as a colorless oil; $[\alpha]_D^{32}$ = –5.8 (*c* 0.84, $CHCl_3$); R_f = 0.51 (hexanes-ethyl acetate = 10:1); IR (neat, cm^{-1}): 2943, 2866, 1722, 1464, 1266, 1111, 882, 783, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (ddd, 1H, *J* = 15.6, 8.0, 8.0 Hz), 5.91 (ddd, 1H, *J* = 15.6, 1.6, 1.2 Hz), 4.19 (q, 2H, *J* = 7.2 Hz), 3.70 (dd, 1H, *J* = 10.4, 5.2 Hz), 3.62 (dd, 1H, *J* = 10.4, 6.0 Hz), 3.34 (dd, 1H, *J* = 10.4, 5.2 Hz), 3.27 (dd, 1H, *J* = 10.4, 6.0 Hz), 2.41–2.19 (m, 2H), 1.74–1.63 (m, 1H), 1.29 (t, 3H, *J* = 7.2 Hz), 1.17–0.95 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 145.5, 123.5, 65.0, 60.1, 41.8, 33.8, 17.9, 14.2, 11.8, 10.1; HRMS-ESI (*m/z*) calcd. for $C_{18}H_{36}IO_3Si$, 455.1473 (M+H$^+$); found, 455.1451.

1-Iodo-2-methyl-3-nitrobenzene (S3).[2]



A 1-L round-bottomed flask equipped with a magnetic stirring bar was charged with water (100 mL) and conc. H_2SO_4 (100 mL) at 0 ºC. To the solution was added 2-methyl-3-nitroaniline (12.5 g, 82.2 mmol) in MeCN (100 mL) at 0 °C. The mixture was cooled at –7 °C. To the mixture was slowly added aqueous $NaNO_2$ (10.2 g, 147 mmol in 60 mL water) over 30 min to maintain the internal temperature below –5 °C. The solution was stirred for an additional 15 min, and the solution was poured to aqueous KI (47.8 g, 288 mmol in 130 mL water) at 0 °C. The resulting mixture was stirred for 10 min and warmed to room temperature. After stirred for additional 10 min, the mixture was extracted with $CHCl_3$ three times. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, saturated aqueous Na_2SO_3, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-CH_2Cl_2 = 1:1) to afford iodide **S3** (19.1 g, 72.6 mmol, 88%) as an orange solid; R_f = 0.70 (hexanes-ethyl acetate = 4:1); IR (neat, cm^{-1}): 1523, 1444, 1351, 1002, 860, 795, 736, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, 1H, *J* = 7.6 Hz), 7.71 (d, 1H, *J* = 7.6 Hz), 7.03 (dd, 1H, *J* = 7.6, 7.6 Hz), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 143.1, 135.0, 127.9, 123.9, 103.5, 24.9; HRMS-EI (*m/z*) calcd. For 262.9443 (M$^+$); found, 262.9451.

4-Iodo-1*H*-indole (17).

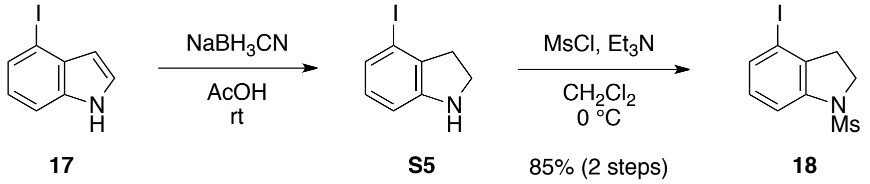


A 100-mL round-bottomed flask was charged with **S3** (1.00 g, 3.80 mmol) and DMF (19 mL). To the mixture were added *N*,*N*-dimethylformamide dimethylacetal (2.50 mL, 18.8 mmol) and pyrrolidine (650 µL, 7.81 mmol). The resulting mixture was heated at 70 °C for 1 h and then heated at 90 °C for 3 h, after which time TLC (hexanes-ethyl acetate = 4:1) indicated complete consumption of the starting material **S3**. The mixture was cooled to 0 °C and treated with 5% w/v aqueous NaCl. The mixture was warmed to room temperature and extracted with Et_2O four times. The combined organic extracts were washed twice with 5%

w/v aqueous NaCl and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give a crude enamine **S4**, which was used for the next reaction without further purification.

A 100-mL round-bottomed flask was charged with the crude enamine **S4** and toluene-AcOH (5:3, 38 mL). To the mixture were added iron powder (0.85 g, 15.2 mmol) and silica gel (1.70 g). The resulting mixture was heated at 50 °C for 1 h, after which time TLC (hexanes-ethyl acetate = 4:1) indicated complete consumption of **S4**. The mixture was cooled to room temperature and filtered through a Celite pad. The filtrate was diluted with saturated aqueous Na_2SO_3 and the mixture was extracted with ethyl acetate three times. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-CH_2Cl_2 = 2:1) and recrystallization (hexanes-CH_2Cl_2) to afford 4-iodoindole **17** (0.28 g, 1.2 mmol, 32% from **S3**) as a white solid. Its physical data were corresponding to those reported in the literature[3]; R_f = 0.44 (hexanes-CH_2Cl_2 = 1:1); IR (neat, cm^{-1}): 3402, 1557, 1425, 1412, 1331, 1176, 903, 882, 728; ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (br, 1H), 7.54 (d, 1H, J = 7.6 Hz), 7.37 (d, 1H, J = 8.4 Hz), 7.30–7.20 (m, 1H), 6.94 (dd, 1H, J = 8.4, 7.6 Hz), 6.50 (dd, 1H, J = 2.4, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 132.4, 129.4, 124.4, 123.3, 111.0, 106.3, 87.4; HRMS-EI (*m/z*) calcd. for C_8H_6NI, 242.9545 (M^+); found, 242.9548.

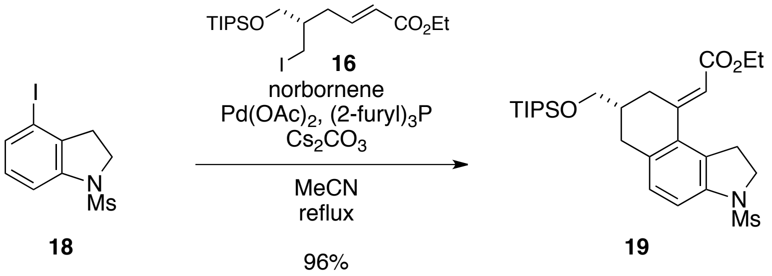
4-Iodo-1-(methylsulfonyl)indoline (18).



A 20-mL round-bottomed flask equipped with a magnetic stirring bar was charged with indole **17** (104.0 mg, 428 μmol) and AcOH (2.1 mL). To the mixture was added $NaBH_3CN$ (134.5 mg, 2.14 mmol). The resulting solution was stirred for 3 h, after which time TLC (CH_2Cl_2) indicated complete consumption of **17**. The solution was cooled to 0 °C and treated with 5 M aqueous NaOH. The mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude indoline **S5**, which was used for the next reaction without further purification.

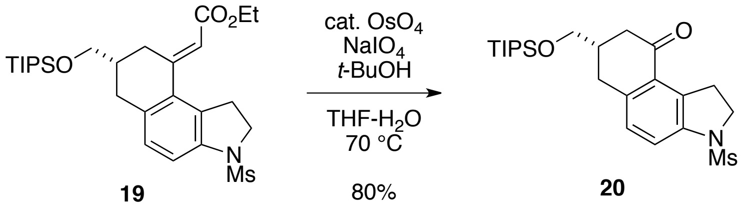
A 30-mL round-bottomed flask equipped with a magnetic stirring bar was charged with the crude indoline **S5** and CH_2Cl_2 (3.0 mL). To the solution were added Et_3N (179 µL, 1.28 mmol) and MsCl (66 µL, 86 µmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h, after which time TLC (CH_2Cl_2) indicated complete consumption of the starting unprotected indoline **S5**. The reaction was quenched with water, and the resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-CH_2Cl_2 = 1:2) to provide **18** (118 mg, 365 µmol, 85% from **17** over 2 steps) as a white solid; R_f = 0.63 (CH_2Cl_2); IR (neat, cm^{-1}): 3018, 2932, 1589, 1572, 1336, 1323, 1151, 1070, 1051, 790, 763; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 1H, J = 8.0 Hz), 7.35 (d, 1H, J = 8.4 Hz), 6.91 (dd, 1H, J = 8.4, 8.0 Hz), 3.98 (t, 2H, *J* = 8.8 Hz), 3.09 (t, 2H, *J* = 8.8 Hz), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 135.9, 132.5, 129.6, 113.0, 93.5, 48.9, 34.8, 33.1; HRMS-EI (*m/z*): calcd. for $C_9H_{10}INO_2S$, 322.9477 (M^+); found, 322.9466.

(*R*,*E*)-(+)-Ethyl 2-(3-(methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-1,2,3,6,7,8-hexahydro-9*H*-benzo[*e*]indol-9-ylidene)acetate (19).



A 10-mL round-bottomed flask equipped with a magnetic stirring bar was charged with **18** (105 mg, 326 μmol), **16** (281 mg, 619 μmol), norbornene (146 mg, 1.55 mmol), Cs_2CO_3 (302 mg, 928 μmol), (2-furyl)$_3$P (14.8 mg, 62.1 μmol), $Pd(OAc)_2$ (6.9 mg, 31 μmol), and MeCN (3.1 mL). The resulting mixture was heated at reflux for 10 h, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of the starting 4-iodoindoline **18**. The suspension was cooled to room temperature and filtered through a Celite pad. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 4:1) to afford ester **19** (163 mg, 312 μmol, 96%) as a pale yellow solid; $[\alpha]_D^{32}$ = +11.7 (*c* 0.515, $CHCl_3$); R_f = 0.46 (hexanes-ethyl acetate = 3:1); IR (neat, cm^{-1}): 2942, 2865, 1712, 1621, 1461, 1350, 1250, 1163, 1115, 1067, 881, 792, 757, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 1H, *J* = 8.0 Hz), 7.06 (d, 1H, *J* = 8.0 Hz), 5.96 (s, 1H), 4.20 (q, 2H, *J* = 7.2 Hz), 4.02–3.88 (m, 2H), 3.75 (dd, 1H, *J* = 9.6, 4.8 Hz), 3.61 (dd, 1H, *J* = 9.6, 6.8 Hz), 3.48 (dd, 1H, *J* = 16.4, 4.8 Hz), 3.38–3.21 (m, 2H), 2.90 (dd, 1H, *J* = 16.4, 4.0 Hz), 2.86 (s, 3H), 2.69–2.51 (m, 2H), 2.06–1.93 (m, 1H), 1.31 (t, 3H, *J* = 7.2 Hz), 1.15–1.00 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 153.6, 141.2, 135.8, 133.3, 128.8, 128.6, 117.2, 114.7, 67.2, 60.0, 50.8, 37.3, 34.2, 32.7, 31.3, 29.8, 18.0, 14.3, 12.0; HRMS-ESI (*m/z*) calcd. for $C_{27}H_{44}NO_5SSi$, 522.2704 ($M+H^+$); found, 522.2685. The geometry of olefin was determined using nOe correlations between the olefinic proton and the methylene protons in the indoline. For the COSY and NOE spectra, see pages S72–S73.

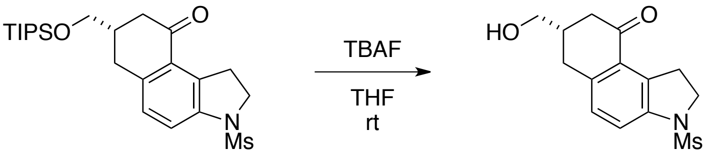
(*S*)-(+)-3-(Methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-1,2,3,6,7,8-hexahydro-9*H*-benzo[*e*]indol-9-one (20).



A 30-mL round-bottomed flask equipped with a magnetic stirring bar was charged with **19** (104 mg, 199 μmol), $NaIO_4$ (213 mg, 997 μmol), and *t*-BuOH-THF-H_2O (1:5:1, 5.0 mL). To the mixture was added OsO_4 in H_2O (1% w/w H_2O, 1.0 mL, 0.04 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 9 h, after which time TLC (hexanes-ethyl acetate = 3:2) indicated complete consumption of **19**. The mixture was cooled to room temperature and treated with saturated aqueous Na_2SO_3. The mixture was extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 3:1) to afford tetralone **20** (72.3 mg, 160 µmol, 80%) as a white solid; $[\alpha]_D^{33}$ = +23 (*c* 0.77, $CHCl_3$); R_f = 0.34 (hexanes-ethyl acetate = 3:1); IR (neat, cm^{-1}): 2942, 2865, 1682, 1466, 1351, 1256, 1163, 1112, 1066, 1009, 971, 882, 796, 759, 683; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 1H, *J* = 8.0 Hz), 7.15 (d, 1H, *J* = 8.0 Hz), 4.00 (t, 2H, *J* = 8.8 Hz), 3.78–3.67 (m, 2H), 3.54 (t, 2H, *J* = 8.8 Hz), 3.02–2.78 (m, 5H), 2.77–2.68 (m, 1H), 2.51 (dd, 1H, *J* = 16.8, 12.4 Hz), 2.43–2.30 (m, 1H), 1.16–0.95 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 141.6, 139.3, 133.2, 129.2, 129.0, 118.5, 66.6, 50.9, 42.8, 38.1, 34.5, 32.4, 29.5, 18.0, 11.9; HRMS-ESI (*m/z*) calcd. for $C_{23}H_{38}NO_4SSi$, 452.2285 ($M+H^+$); found, 452.2265.

Determination of enantiomeric excess of compound 20.

(*S*)-(+)-7-(Hydroxymethyl)-3-(methylsulfonyl)-1,2,3,6,7,8-hexahydro-9*H*-benzo[*e*]indol-9-one (S6).



20

S6

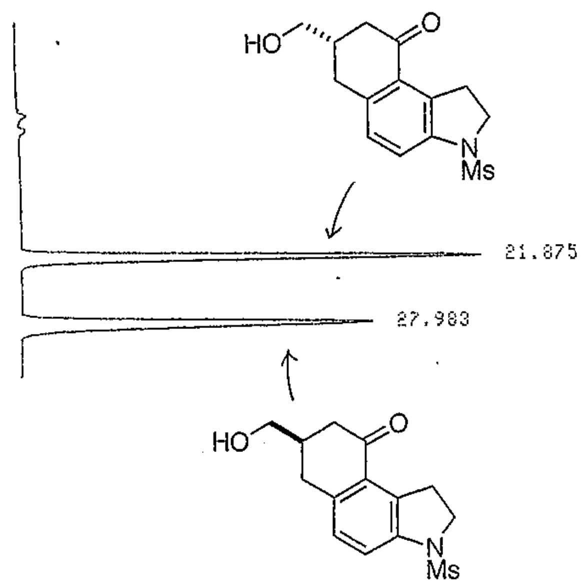
89% ee

A 30-mL round-bottomed flask equipped with a magnetic stirring bar was charged with TIPS ether **20** (62.5 mg, 138 µmol) and THF (3.0 mL). To the resulting solution was added TBAF (1.0 M in THF, 208 µL, 0.21 mmol). The mixture was stirred at room temperature for 40 min, after which time TLC (hexanes-ethyl acetate = 4:1) indicated complete consumption of **20**. The reaction was quenched with water, and the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (ethyl acetate) to afford the alcohol **S6** (35.9 mg, 122 µmol, 88%) as a white solid. The enantiomeric excess of **S6** was determined by HPLC (DAICEL-CHIRALPAK-IA, *n*-hexane-EtOH = 75:25, flow rate = 1.00 mL/min, retention time: t_S = 22 min, t_R = 28 min, 89% ee); $[\alpha]_D^{31}$ = +33 (*c* 0.83, $CHCl_3$); R_f = 0.49 (ethyl acetate); IR (neat, cm^{-1}): 3408, 2933, 2889, 1655, 1597, 1335, 1150, 1088, 828, 764; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 1H, *J* = 8.4 Hz), 7.15 (d, 1H, *J* = 8.4 Hz), 4.01 (t, 2H, *J* = 8.8 Hz), 3.75–3.61 (m, 2H), 3.54 (t, 2H, *J* = 8.8 Hz), 3.09–2.98 (m, 1H), 2.89–2.68 (m, 6H), 2.48–2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 141.8, 138.7, 133.4, 129.1, 129.0, 118.6, 66.1, 50.9, 42.5, 37.7, 34.6, 32.3, 29.5; HRMS-ESI (*m/z*) calcd. for $C_{14}H_{18}NO_4S$, 296.0951 ($M+H^+$); found, 296.0951.

Determination of enantiomeric excess of compound **S6**

DAICEL-CHIRALPAK-IA
n-hexanes-EtOH=75:25
flow rate = 1.00 mL/min

yy-12-030 (racemic)



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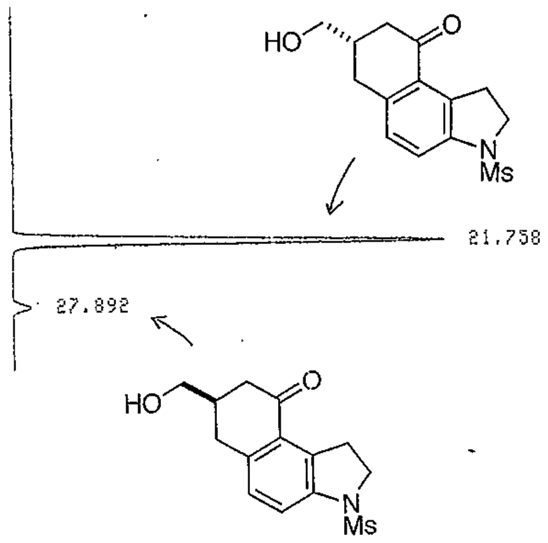
CHROMATOPAC   C-R6A                  FILE        0
SAMPLE NO   0                        METHOD        41
REPORT NO   801

PKNO      TIME      AREA  MK  IDNO      CONC        NAME

  1     21.875   6266350               49.9524
  2     27.983   6278290               50.0476
               ---------        -------------
        TOTAL   12544640              100
```

yy-12-031 (89% ee)



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CHROMATOPAC   C-R6A                  FILE        0
SAMPLE NO   0                        METHOD        41
REPORT NO   804

PKNO      TIME      AREA  MK  IDNO      CONC        NAME

  1     21.758  11558358               94.6645
  2     27.892    651458                5.3355
               ---------        -------------
        TOTAL   12209816              100
```
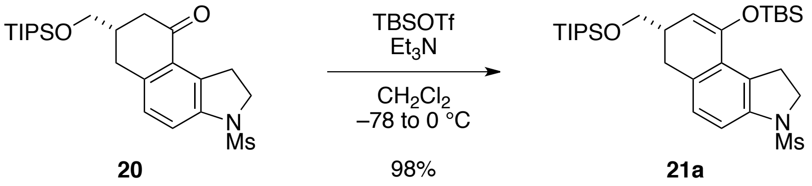
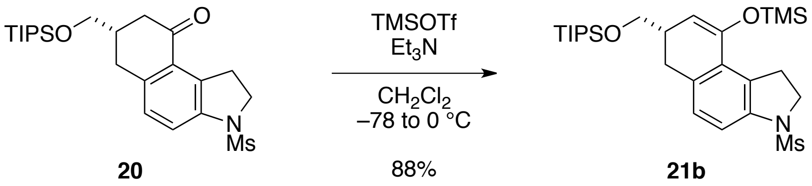

(*S*)-(–)-9-((*tert*-Butyldimethylsilyl)oxy)-3-(methylsulfonyl)-7-(((triisopropylsilyl)oxy) methyl)-2,3,6,7-tetrahydro-1*H*-benzo[*e*]indole (21a).



A 100-mL round-bottomed equipped with a magnetic stirring bar was charged with tetralone **20** (1.21 g, 2.68 mmol), Et_3N (750 µL, 5.38 mmol), and dry CH_2Cl_2 (27 mL). The solution was cooled to –78 °C. To the mixture was added TBSOTf (925 µL, 4.03 mmol) at –78 ºC. The reaction mixture was warmed to 0 °C and stirred for 1 h, after which time TLC (hexanes-ethyl acetate = 5:1) indicated complete consumption of the starting tetralone **20**. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The mixture was warmed to room temperature and extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 5:1) to afford the silyl enol ether **21a** (1.48 g, 2.62 mmol, 98%) as a pale yellow oil; $[\alpha]_D^{25}$ = –26 (*c* 0.53, $CHCl_3$); R_f = 0.50 (hexanes-ethyl acetate = 5:1); IR (neat, cm^{-1}): 2941, 2864, 1631, 1579, 1463, 1351, 1253, 1164, 1112, 840, 780, 758, 682; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, 1H, *J* = 8.0 Hz), 6.98 (d, 1H, *J* = 8.0 Hz), 5.22 (d, 1H, *J* = 3.2 Hz), 3.99–3.82 (m, 2H), 3.58 (d, 2H, *J* = 6.4 Hz), 3.46–3.26 (m, 2H), 2.83 (s, 3H), 2.74–2.53 (m, 3H), 1.16–0.84 (m, 30H), 0.25 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 141.3, 132.4, 130.5, 127.3, 126.5, 112.5, 108.9, 65.7, 50.8, 37.1, 33.9, 31.0, 29.3, 26.2, 18.7, 18.0, 11.9, –3.99, –4.03; HRMS-ESI (*m/z*) calcd. for $C_{29}H_{52}NO_4SSi_2$, 566.3150 ($M+H^+$); found, 566.3159.

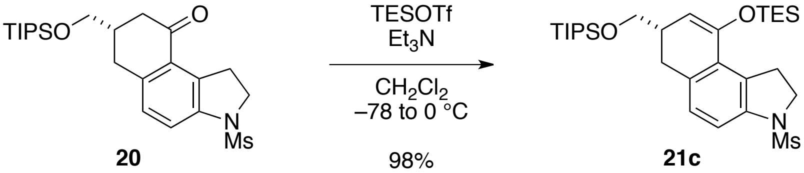
(*S*)-(–)-3-(Methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-9-((trimethylsilyl)oxy)-2,3,6,7-tetrahydro-1*H*-benzo[*e*]indole (21b).



A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with tetralone **20** (48.7 mg, 108 µmol) and dry CH_2Cl_2 (1.0 mL). The solution was cooled to –78 °C. To the mixture were added Et_3N (60.1 µL, 431 µmol) and TMSOTf (41.7 µL, 216 µmol) at –78 °C. The reaction mixture was let warm to 0 °C and stirred for 20 min, after which time TLC (hexanes-ethyl acetate = 5:1) indicated complete consumption of tetralone **20**. The reaction was then diluted with hexanes-ethyl acetate (9:1) at 0 °C. The mixture was warmed to room temperature and filtered through a pad of silica gel (hexanes-ethyl acetate = 9:1). The filtrate was concentrated under reduce pressure to afford silyl enol ether **21b** (50.0 mg, 95.4 µmol, 88%) as a pale yellow oil; $[\alpha]_D^{33}$ = –25 (*c* 0.55, $CHCl_3$); R_f = 0.16 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2943, 2865, 1464, 1350, 1253, 1163, 1111, 1067, 1014, 970, 867, 847, 683; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, 1H, *J* = 8.0 Hz), 6.97 (d, 1H, *J* = 8.0 Hz), 5.17 (d, 1H, *J* = 3.6 Hz), 3.98–3.85 (m, 2H), 3.59 (d, 2H, *J* =

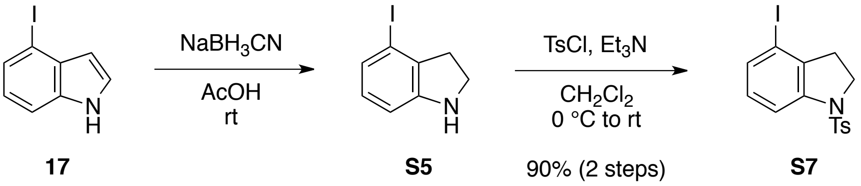
6.4 Hz), 3.45–3.27 (m, 2H), 2.83 (s, 3H), 2.76–2.57 (m, 3H), 1.15–0.95 (m, 21H) 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.1, 141.3, 132.3, 130.3, 127.4, 126.6, 112.7, 108.2, 65.8, 50.7, 37.0, 34.0, 30.9, 29.1, 18.0, 12.0, 0.2; HRMS-ESI (*m/z*) calcd. for $C_{26}H_{46}NO_4SSi_2$, 524.2681 (M+H$^+$); found, 524.2673.

(*S*)-(–)-3-(Methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-9-((triethylsilyl)oxy)-2,3,6,7-tetrahydro-1*H*-benzo[*e*]indole (21c).



A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with tetralone **20** (50.3 mg, 111 μmol) and dry CH_2Cl_2 (1.0 mL). The solution was cooled to –78 °C. To the mixture were added Et_3N (61.9 μL, 444 μmol) and TESOTf (50.4 μL, 223 μmol) at –78 ºC. The reaction mixture was let warm to 0 °C and stirred for 10 min, after which time TLC (hexanes-ethyl acetate = 5:1) indicated complete consumption of tetralone **20**. The reaction was quenched with water at 0 ºC, and the mixture was warmed to room temperature and extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1) to afford TIPS enol ether **21c** (61.1 mg, 109 µmol, 98%) as a pale yellow oil; $[\alpha]_D^{33}$ = –31 (*c* 0.34, CHCl$_3$); R$_f$ = 0.61 (hexanes-ethyl acetate = 5:1); IR (neat, cm^{-1}): 2942, 2866, 1633, 1578, 1463, 1351, 1242, 1163, 1111, 1067, 1001, 969, 882, 814, 747, 682; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22 (d, 1H, *J* = 8.4 Hz), 6.97 (d, 1H, *J* = 8.4 Hz), 5.20 (d, 1H, *J* = 3.2 Hz), 3.98–3.84 (m, 2H), 3.64–3.55 (m, 2H), 3.46–3.26 (m, 2H), 2.83 (s, 3H), 2.76–2.56 (m, 3H), 1.15–0.93 (m, 30H) 0.77 (q, 6H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.3, 141.3, 132.3, 130.4, 127.3, 126.6, 112.5, 107.7, 65.8, 50.7, 37.0, 33.9, 30.9, 29.0, 18.0, 11.9, 6.7, 4.8; HRMS-ESI (*m/z*) calcd. for $C_{29}H_{52}NO_4SSi_2$, 566.3150 (M+H$^+$); found, 566.3143.

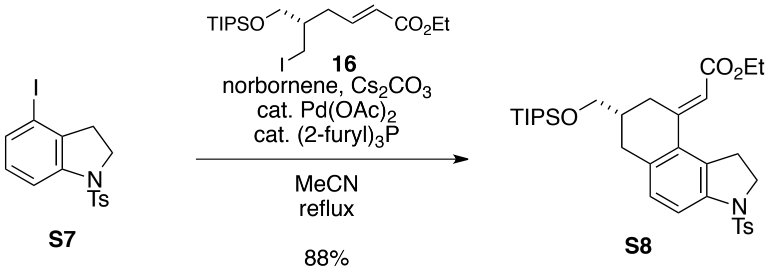
4-Iodo-1-tosylindoline (S7).



A 20-mL round-bottomed flask equipped with a magnetic stirring bar was charged with indole **17** (100 mg, 411 µmol) and AcOH (2.0 mL). To the mixture was added $NaBH_3CN$ (135 mg, 2.14 mmol) at room temperature. The resulting solution was stirred at room temperature for 7 h, after which time TLC (CH_2Cl_2) indicated complete consumption of indole **17**. The solution was cooled to 0 °C and treated with 5 M aqueous NaOH to pH 12. The mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was used for the next reaction without further purification.

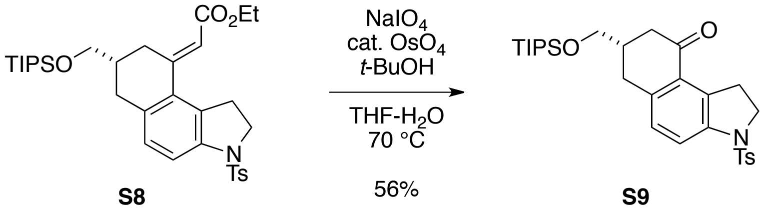
A 30-mL round-bottomed flask equipped with a magnetic stirring bar was charged with the crude indoline **S5** and CH_2Cl_2 (3.0 mL). To the mixture were added Et_3N (180 µL, 1.29 mmol) and TsCl (94.1 mg, 494 µmol) at 0 °C. The reaction mixture was let warm to room temperature and stirred for 6 h, after which time TLC (CH_2Cl_2) indicated complete consumption of the starting indoline **S5**. The reaction was quenched with water. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1) to provide *N*-tosyl-indoline **S7** (148 mg, 371 µmol, 90% from **17** over 2 steps) as a white solid; $R_f = 0.30$ (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 3028, 2920, 1589, 1445, 1350, 1243, 1173, 1049, 975, 814, 772, 665, 576; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 1H, *J* = 8.4 Hz), 7.33 (d, 1H, *J* = 8.4 Hz), 7.25 (d, 2H, *J* = 8.4 Hz), 6.90 (dd, 1H, *J* = 8.4, 8.4 Hz), 3.91 (t, 2H, *J* = 8.8 Hz), 2.86 (t, 2H, *J* = 8.8 Hz), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 141.9, 136.2, 133.8, 132.5, 129.8, 129.4, 127.3, 114.1, 93.2, 48.5, 33.0, 21.5; HRMS-EI (*m/z*) calcd. for $C_{15}H_{14}INO_2S$, 398.9790 (M^+); found, 398.9789.

(*S*,*E*)-(+)-Ethyl 2-(3-tosyl-7-((triisopropylsilyloxy)methyl)-2,3,7,8-tetrahydro-1*H*-benzo[*e*]indol-9(6*H*)-ylidene)acetate (S8).



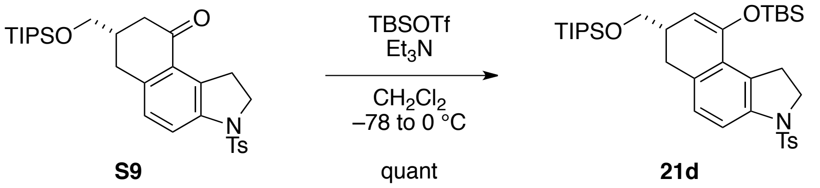
A 20-mL round-bottomed flask equipped with a magnetic stirring bar was charged with indoline **S7** (200 mg, 501 µmol), ester **16** (342 mg, 751 µmol), norbornene (236 mg, 2.50 mmol), Cs_2CO_3 (470 mg, 1.50 mmol), $(2\text{-furyl})_3P$ (23.9 mg, 100 µmol), $Pd(OAc)_2$ (11.2 mg, 49.9 µmol), and MeCN (5.0 mL). The resulting mixture was heated at reflux for 12 h, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of indoline **S7**. The suspension was cooled to room temperature and filtered through a Celite pad. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 7:1) to afford ester **S8** (264 mg, 442 µmol, 88%) as an orange oil; $[\alpha]_D^{27} = +9.1$ (*c* 0.47, $CHCl_3$); $R_f = 0.32$ (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2943, 2865, 1714, 1622, 1462, 1359, 1250, 1168, 882, 813, 758, 678, 547; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 1H, *J* = 8.4 Hz), 7.23 (d, 2H, *J* = 8.4 Hz), 7.05 (d, 1H, *J* = 8.4 Hz), 5.76 (s, 1H), 4.16 (q, 2H, *J* = 7.2 Hz), 4.00–3.81 (m, 2H), 3.71 (dd, 1H, *J* = 9.6, 4.8 Hz), 3.58 (dd, 1H, *J* = 9.6, 7.2 Hz), 3.41 (dd, 1H, *J* = 16.8, 5.2 Hz), 3.08–2.80 (m, 3H), 2.65–2.44 (m, 2H), 2.38 (s, 3H), 2.03–1.88 (m, 1H), 1.28 (t, 3H, *J* = 7.2 Hz), 1.19–0.92 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 153.7, 144.1, 141.2, 135.9, 133.9, 132.8, 129.7, 129.3, 128.5, 127.4, 116.9, 116.2, 67.2, 59.9, 50.3, 37.2, 32.7, 31.3, 29.7, 21.5, 18.0, 14.3, 11.9; HRMS-ESI (*m/z*) calcd. for $C_{33}H_{48}NO_5SSi$, 598.3017 ($M+H^+$); found, 598.2983.

(*S*)-(+)-3-Tosyl-7-((triisopropylsilyloxy)methyl)-2,3,7,8-tetrahydro-1*H*-benzo[*e*]indol-9(6*H*)-one (S9).



A 10-mL test tube equipped with a magnetic stirring bar was charged with ester **S8** (60.0 mg, 100 µmol), $NaIO_4$ (100 mg, 468 µmol), and *t*-BuOH-THF-H_2O (1:5:1, 1.0 mL). To the mixture was added OsO_4 in H_2O (1% w/w H_2O, 0.30 mL, 0.01 mmol). The reaction mixture was heated at 70 °C and stirred for 15 h, after which time TLC (CH_2Cl_2) indicated complete consumption of ester **S8**. The mixture was cooled to room temperature and treated with brine. The mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1) to afford tetralone **S9** (29.7 mg, 56.3 µmol, 56%) as a yellow amorphous; $[\alpha]_D^{24}$ = +13 (*c* 0.67, $CHCl_3$); $R_f = 0.32$ (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2943, 2865, 1682, 1465, 1446, 1357, 1256, 1169, 1110, 1092, 1066, 673, 544; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 1H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.4 Hz), 7.14 (d, 1H, *J* = 8.0 Hz), 3.93 (t, 2H, *J* = 8.4 Hz), 3.75–3.63 (m, 2H), 3.26 (t, 2H, *J* = 8.4 Hz), 2.94 (dd, 1H, *J* = 15.6, 3.2 Hz), 2.84 (dd, 1H, *J* = 15.6, 10.4 Hz), 2.70–2.61 (m, 1H), 2.44 (dd, 1H, *J* =16.4, 12.0 Hz), 2.40–2.26 (m, 4H) 1.15–0.94 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 144.1, 141.7, 139.3, 133.9, 133.8, 129.7, 128.9, 128.7, 127.3, 119.6, 66.7, 50.5, 42.8, 38.1, 32.4, 29.4, 21.5, 18.0, 11.9; HRMS-ESI (*m/z*) calcd. for $C_{29}H_{42}NO_4SSi$, 528.2598 ($M+H^+$); found, 528.2590.

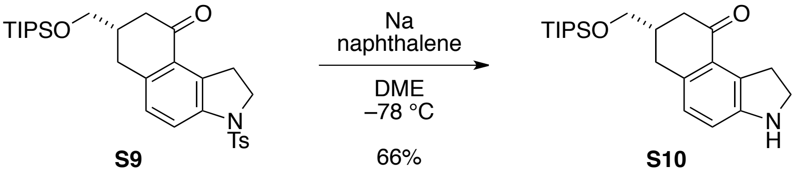
(*S*)-(–)-9-(*tert*-Butyldimethylsilyloxy)-3-tosyl-7-((triisopropylsilyloxy)methyl)-2,3,6,7-tetrahydro-1*H*-benzo[*e*]indole (21d).



A 100-mL round-bottomed flask equipped with a magnetic stirring bar was charged with tetralone **S9** (739 mg, 1.40 mmol), Et_3N (390 µL, 2.80 mmol), and CH_2Cl_2 (14 mL). The solution was cooled to –78 °C. To the mixture was added TBSOTf (420 µL, 1.83 mmol). The reaction mixture was let warm to 0 °C and stirred for 30 min, after which time TLC (hexanes-ethyl acetate = 9:1) indicated complete consumption of tetralone **S9**. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The resulting mixture was let warm to room temperature and extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1) to afford silyl enol ether **21d** (902 mg, 1.40 mmol, quant) as a pale yellow oil; $[\alpha]_D^{25}$ = –25 (*c* 0.49, $CHCl_3$); $R_f = 0.43$ (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2942, 2864, 1632, 1578, 1463, 1359, 1253, 1168, 840, 676; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64

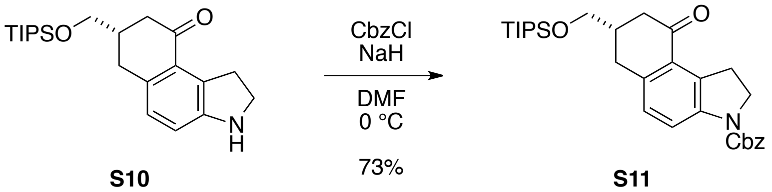
(d, 2H, *J* = 8.4 Hz), 7.46 (d, 1H, *J* = 8.4 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 6.97 (d, 1H, *J* = 8.4 Hz), 5.14 (d, 1H, *J* = 4.0 Hz), 3.95–3.78 (m, 2H), 3.54 (d, 2H, *J* = 6.8 Hz), 3.13–2.97 (m, 2H), 2.74–2.48 (m, 3H), 2.36 (s, 3H), 1.13–0.98 (m, 21H), 0.88 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 143.8, 141.3, 134.2, 132.5, 130.1, 129.5, 127.4, 127.3, 127.1, 114.2, 108.7, 65.6, 50.4, 37.0, 31.1, 29.2, 26.1, 21.5, 18.6, 18.0, 11.9. –4.08, –4.13; HRMS-ESI (*m/z*) calcd. for $C_{35}H_{56}NO_4SSi_2$, 642.3463 ($M+H^+$); found, 642.3454.

(*S*)-(+)-7-((Triisopropylsilyloxy)methyl)-2,3,7,8-tetrahydro-1*H*-benzo[*e*]indol-9(6*H*)-one (S10).



A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with Na (50.1 mg, 2.18 mmol), naphthalene (1.01 g, 7.88 mmol), and anhydrous DME (2.5 mL). The resulting mixture was stirred for 6 h to afford a solution of Na naphthalenide in DME. A 100-mL round-bottomed flask equipped with a magnetic stirring bar was charged with *N*-tosyl-indoline **S9** (128 mg, 243 µmol) in DME (5.0 mL). The solution was cooled to –78 °C. To the reaction mixture was added the above solution of Na naphthalenide in DME (1.0 mL) dropwise. The reaction mixture was stirred at –78 °C for 15 min, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of *N*-tosyl-indoline **S9**. The reaction was quenched with saturated aqueous $NaHCO_3$ at –78 °C. The mixture was let warm to room temperature and extracted with Et_2O three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 3:1) to afford indoline **S10** (59.8 mg, 160 µmol, 66%) as a yellow oil; $[\alpha]_D^{26}$ = +36 (*c* 0.17, $CHCl_3$); R_f = 0.29 (hexanes-ethyl acetate = 3:1); IR (neat, cm^{-1}): 3375, 2942, 2865, 1675, 1598, 1468, 1281, 1108, 882, 811, 683, 648; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, 1H, *J* = 8.4 Hz), 6.75 (d, 1H, *J* = 8.4 Hz), 3.80–3.64 (m, 2H), 3.63–3.52 (m, 2H), 3.50–3.38 (m, 2H), 2.90 (dd, 1H, *J* = 15.6, 2.4 Hz), 2.80 (dd, 1H, *J* = 15.6, 10.8 Hz), 2.75–2.63 (m, 1H), 2.46 (dd, 1H, *J* = 16.8, 12.4 Hz), 2.41–2.26 (m, 1H), 1.17–0.91 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 151.3, 133.8, 131.0, 128.9, 127.8, 114.0, 66.9, 47.5, 43.0, 38.5, 32.4, 31.4, 18.0, 11.9; HRMS-ESI (*m/z*) calcd. for $C_{22}H_{36}NO_2Si$, 374.2510 ($M+H^+$); found, 374.2503.

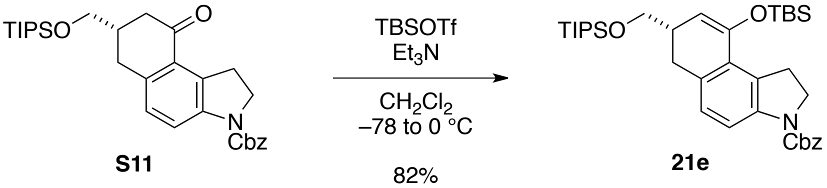
(*S*)-(+)-Benzyl 9-oxo-7-((triisopropylsilyloxy)methyl)-1,2,6,7,8,9-hexahydrobenzo[*e*] indole-3-carboxylate (S11).



A 20-mL round-bottomed flask equipped with a magnetic stirring bar was charged with indoline **S10** (31.3 mg, 83.8 µmol) and DMF (2.0 mL). To the mixture was added NaH

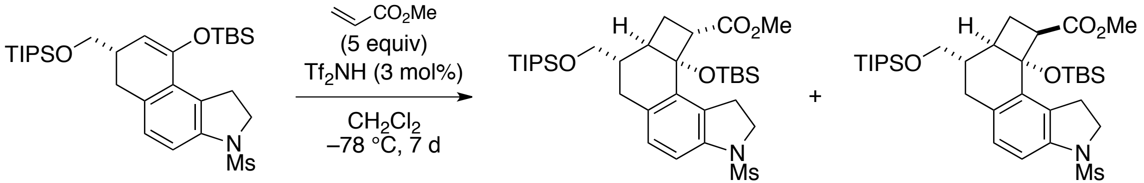
(60% in oil, 5.0 mg, 0.13 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. To the mixture was added CbzCl (16 µL, 0.11 mmol) dropwise. The reaction mixture was stirred at 0 °C for 5 min, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of indoline **S10**. The reaction was quenched with water. The mixture was let warm to room temperature and extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1) to afford Cbz carbamate **S11** (31.1 mg, 61.3 µmol, 73%) as a pale yellow solid; $[\alpha]_D^{25}$ = +20.5 (*c* 0.715, $CHCl_3$); R_f = 0.21 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2942, 2865, 1710, 1680, 1472, 1400, 1326, 1143, 1107, 882, 695, 684; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (br s, 0.84H), 7.46–7.30 (m, 5H), 7.13 (br s, 1.16H), 5.26 (br s, 2H), 4.08 (t, 2H, *J* = 8.8 Hz), 3.78–3.65 (m, 2H), 3.51 (t, 2H, *J* = 8.8 Hz), 3.01–2.78 (m, 2H), 2.76–2.64 (m, 1H), 2.49 (dd, 1H, *J* = 16.4, 12.0 Hz), 2.43–2.28 (m, 1H), 1.18–0.92 (m, 21H) (rotamer); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 153.1, 142.3, 137.9, 136.3, 133.0, 128.6, 128.4, 128.3, 128.2, 128.0, 119.3, 67.0, 66.7, 48.1, 42.9, 38.2, 32.4, 29.3, 18.0, 11.9; HRMS-ESI (*m/z*) calcd. for $C_{30}H_{42}NO_4Si$, 508.2878 (M+H$^+$); found, 508.2869.

(*S*)-(–)-9-(*tert*-Butyldimethylsilyloxy)-3-benzyloxycarbonyl-7-((triisopropylsilyloxy) methyl)-2,3,6,7-tetrahydro-1*H*-benzo[*e*]indole (21e).



A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with tetralone **S11** (14.3 mg, 28.2 µmol) and CH_2Cl_2 (1.0 mL). The solution was cooled to –78 °C. To the mixture were added Et_3N (7.9 µL, 56 µmol) and TBSOTf (9.7 µL, 42 µmol). The reaction mixture was let warm to 0 ºC and stirred for 1 h, after which time TLC (hexanes-ethyl acetate = 9:1) indicated complete consumption of tetralone **S11**. The reaction was quenched with H_2O at 0 ºC. The mixture was let warm to room temperature and extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by preparative TLC (hexanes-ethyl acetate = 9:1) to afford silyl enol ether **21e** (14.4 mg, 23.2 µmol, 82%) as a pale yellow oil; $[\alpha]_D^{25}$ = –25 (*c* 0.72, $CHCl_3$); R_f = 0.48 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2941, 2864, 1713, 1465, 1398, 1318, 1141, 840, 781, 683; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (br s, 0.73H), 7.48–7.28 (m, 5H), 6.96 (br s, 1.24H), 5.26 (br s, 2H), 5.19 (d, 1H, *J* = 3.6 Hz), 4.08–3.94 (m, 2H), 3.64–3.53 (m, 2H), 3.46–3.25 (m, 2H), 2.76–2.53 (m, 3H), 1.15–0.92 (m, 30H), 0.24 (s, 3H), 0.23 (s, 3H) (rotamer); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 149.9, 136.6, 131.1, 129.8, 128.5, 128.4, 128.1, 127.9, 126.9, 126.2, 113.4, 108.5, 66.8, 65.8, 47.9, 37.2, 31.2, 28.9, 26.2, 18.7, 18.0, 12.0, –3.96, –4.02 (rotamer) HRMS-ESI (*m/z*) calcd. for $C_{36}H_{56}NO_4Si_2$, 622.3742 (M+H$^+$); found, 622.3724.

General procedure for the (2+2)-Cycloaddition.



21a 54% (dr = 2.0:1.0) *cis*-**22a** *trans*-**22a**

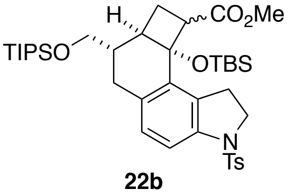
A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with **21a** (111 mg, 197 µmol) and dry CH_2Cl_2 (2.0 mL). The solution was cooled to –78 °C. To the solution were added methyl acrylate (88.6 µL, 984 µmol) and Tf_2NH (80 mM in toluene, 73.8 µL, 5.9 µmol) dropwise at –78 ºC, and the resulting mixture was stirred at –78 °C for 7 days. The reaction was then quenched with Et_3N at –78 °C. The mixture was warmed to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes-ethyl acetate = 5:1) to afford methyl ester *cis*-**22a** and *trans*-**22a** (68.7 mg, 105 µmol, 54%, dr = 2.0:1.0) as a mixture of diastereomers as a colorless oil. These diastereomers were separated by preparative TLC (hexanes-ethyl acetate = 5:1).

Structure determination of each diastereomer was performed by comparing the chemical shifts of the methyl group of the ester (*cis*-**22a**: 3.77 ppm, *trans*-**22a**: 3.37 ppm) and two methyl groups of the TBS group (*cis*-**22a**: –0.02 and –0.46 ppm, *trans*-**22a**: 0.13 and –0.13 ppm) with those of similar compounds *cis*-**S14** (confirmed by X-ray crystallographic analysis) and *trans*-**S14**; the methyl group of the ester (*cis*-**S14**: 3.72 ppm, *trans*-**S14**: 2.91 ppm): two methyl groups of the TBS group (*cis*-**S14**: –0.06 and –0.78 ppm, *trans*-**S14**: 0.12 and –0.26 ppm)

(+)-Methyl (7*S*,7a*R*,9*S*,9a*R*)-9a-((*tert*-butyldimethylsilyl)oxy)-3-(methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo [1,2-*e*]indole-9-carboxylate (*cis*-22a). $[\alpha]_D^{32}$ = +30 (*c* 0.65, $CHCl_3$); R_f = 0.51 (hexanes-ethyl acetate = 3:1); IR (neat, cm^{-1}): 2945, 2865, 1737, 1465, 1353, 1252, 1164, 1113, 1069, 836, 774, 760; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, 1H, *J* = 8.4 Hz), 6.95 (d, 1H, *J* = 8.4 Hz), 4.02 (ddd, 1H, *J* = 10.4, 10.4, 5.2 Hz), 3.87–3.70 (m, 5H), 3.67 (dd, 1H, *J* = 9.6, 5.2 Hz), 3.50–3.35 (m, 2H), 3.17 (ddd, 1H, *J* = 15.6, 9.6, 6.0 Hz), 2.88–2.76 (m, 4H), 2.70 (dd, 1H, *J* = 15.6, 4.0 Hz), 2.64–2.53 (m, 2H), 1.98–1.86 (m, 1H), 1.72–1.60 (m, 1H), 1.18–0.98 (m, 21H), 0.83 (s, 9H), –0.02 (s, 3H), –0.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 141.5, 136.6, 134.2, 130.9, 128.5, 113.6, 79.5, 65.5, 51.6, 51.0, 49.7, 45.9, 43.5, 33.9, 31.2, 27.8, 25.5, 23.9, 18.1, 18.0, 11.9, –2.8. –3.9; HRMS-ESI (*m/z*) calcd. for $C_{33}H_{57}NNaO_6SSi_2$, 674.3337 ($M+Na^+$); found, 674.3308.

(–)-Methyl (7*S*,7a*R*,9*R*,9a*R*)-9a-((*tert*-butyldimethylsilyl)oxy)-3-(methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo [1,2-*e*]indole-9-carboxylate (*trans*-22a). $[\alpha]_D^{25}$ = –24 (*c* 0.45, $CHCl_3$); R_f = 0.44 (hexanes-ethyl acetate = 3:1); IR (neat, cm^{-1}): 2946, 2864, 1732, 1470, 1352, 1163, 1110, 1069, 883, 837, 775, 681; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 1H, *J* = 8.4 Hz), 6.95 (d, 1H, *J* = 8.4 Hz), 3.94 (ddd, 1H, *J* = 10.4, 10.4, 6.4 Hz), 3.85–3.72 (m, 1H), 3.67 (dd, 1H, *J* = 9.6, 4.4 Hz), 3.61 (dd, 1H, *J* = 9.6, 6.4 Hz), 3.57–3.50 (m, 1H), 3.37 (s, 3H), 3.32–3.11 (m, 2H), 2.85–2.55 (m, 6H), 2.50–2.33 (m, 2H), 1.98 (ddd, 1H, *J* = 10.4, 5.6, 5.2 Hz), 1.14–0.94 (m, 21H), 0.88 (s, 9H), 0.13 (s, 3H), –0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 140.9, 134.3, 133.0, 130.7, 128.8, 113.8, 79.3, 64.7, 53.3, 51.4, 51.1, 43.6, 40.4, 33.6, 29.5, 28.4, 25.7, 21.4, 18.05, 18.00, 17.97, 11.9, –2.5, –3.1; HRMS-ESI (*m/z*) calcd. for $C_{33}H_{57}NNaO_6SSi_2$, 674.3337 (M+Na$^+$); found, 674.3317.

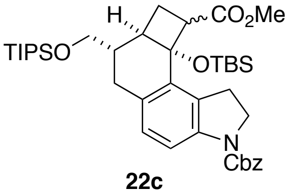
(7*S*,7a*R*,9a*R*)-(+)-Methyl 9a-((*tert*-butyldimethylsilyl)oxy)-3-tosyl-7-(((triisopropylsilyl)oxy)methyl)-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole-9-carboxylate (22b).



22b

Compound **22b** (67.3 mg, 92.4 µmol, 56%, *cis*:*trans* = 1.1:1.0) was obtained from **21d** (106 mg, 165 µmol) as a colorless oil; $[\alpha]_D^{24}$ = +11 (*c* 0.11, $CHCl_3$); R_f = 0.36 (hexanes-ethyl acetate = 5:1); IR (neat, cm^{-1}): 2946, 2865, 1733, 1465, 1359, 1253, 1112, 1069, 987, 882, 836, 776, 669; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.58 (m, 2H), 7.57–7.48 (m, 1H), 7.21–7.13 (m, 2H), 6.98–6.90 (m, 1H), 4.04–3.88 (m, 2H), 3.78–3.52 (m, 4.56H), 3.47–3.40 (m, 0.48H), 3.33 (dd, 0.52H, *J* = 8.8, 8.4 Hz), 3.17–3.05 (m, 0.52H), 3.02–2.84 (m, 2.92H), 2.81–2.63 (m, 2H), 2.62–2.45 (m, 1.52H), 2.38–2.24 (m, 3.96H), 1.97–1.82 (m, 1H), 1.67–1.54 (m, 0.52H), 1.16–0.95 (m, 21H), 0.78 (s, 4.32H), 0.71 (s, 4.68H), 0.06 (s, 1.44H), –0.13 (s, 1.56H), –0.30 (s, 1.44H), –0.82 (s, 1.56H) (mixture of diastereomers, *cis*:*trans* = 1.1:1.0); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 172.6, 171.6, 143.8, 143.7, 141.5, 140.8, 136.2, 134.2, 133.81, 133.76, 133.7, 132.7, 131.3, 131.0, 129.5, 129.4, 128.6, 128.2, 127.4, 114.92, 114.91, 79.2, 65.6, 64.7, 53.3, 51.5, 51.0, 50.6, 50.5, 49.5, 45.9, 43.5, 40.1, 31.2, 29.3, 28.4, 27.6, 25.7, 25.5, 23.8, 21.41, 21.36, 20.9, 18.02, 17.99, 17.97, 11.9, –2.5, –2.9, –3.3, –4.4 (mixture of diastereomers); HRMS-ESI (*m/z*) calcd. for $C_{39}H_{62}NO_6SSi_2$ (M+H$^+$); 728.3831, found: 728.3811.

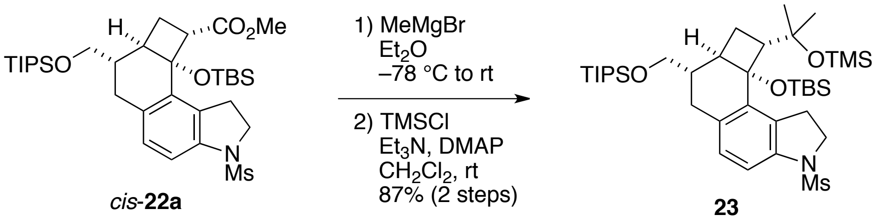
(7*S*,7a*R*,9a*R*)-(+)-3-Benzyl 9-methyl 9a-((*tert*-butyldimethylsilyl)oxy)-7-(((triisopropylsilyl)oxy)methyl)-6,7,7a,8,9,9a-hexahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole-3,9(2*H*)-dicarboxylate (22c).



22c

Compound **22c** (23.1 mg, 32.6 µmol, 46%, *cis*:*trans* = 2.4:1.0) was obtained from **21e** (44.0 mg, 70.7 µmol) as a colorless oil; $[\alpha]_D^{27}$ = +19.2 (*c* 1.09, $CHCl_3$); R_f = 0.38 (hexanes-ethyl acetate = 9:1); IR (neat, cm^{-1}): 2945, 2864, 1713, 1471, 1399, 1330, 1254, 1113, 836, 775; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (br s, 0.70H), 7.46–7.29 (m, 5H), 6.93 (br s, 1.30H), 5.26 (br s, 2H), 4.19–3.81 (m, 2H), 3.80–3.57 (m, 4.42H), 3.57–3.30 (m, 2.29H), 3.30–3.05 (m, 1.29H), 2.79–2.32 (m, 4.29H), 2.05–1.85 (m, 1H), 1.70–1.60 (m, 0.71H), 1.16–0.97 (m, 21H), 0.88 (s, 2.61H), 0.84 (s, 6.39H), 0.12 (s, 0.87H), –0.13 (s, 2.13H), –0.41 (s, 0.87H), –0.46 (s, 2.16H) (mixture of diastereomers, *cis*:*trans* = 2.4:1.0 and rotamer); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 171.8, 153.0, 142.1, 136.5, 135.8, 133.0, 131.6, 130.7, 130.5, 128.5, 128.4, 128.3, 128.1, 128.0, 114.5, 114.3, 79.6, 79.4, 66.8, 65.8, 64.9, 53.4, 51.6, 51.5, 49.6, 48.1, 46.1, 43.8, 40.5, 31.3, 29.7, 29.6, 27.3, 25.8, 25.6, 24.0, 21.6, 18.2, 18.1, 18.04, 18.02, 12.0, –2.6, –2.9, –3.1, –4.0 (mixture of diastereomers and rotamer); HRMS-ESI (*m/z*) calcd. for $C_{40}H_{62}NO_6Si_2$, 708.4110 (M+H$^+$); found, 708.4084.

(7*S*,7a*R*,9*R*,9a*R*)-(+)-9a-((*tert*-Butyldimethylsilyl)oxy)-3-(methylsulfonyl)-7-(((triisopropylsilyl)oxy)methyl)-9-(2-((trimethylsilyl)oxy)propan-2-yl)-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole (23).

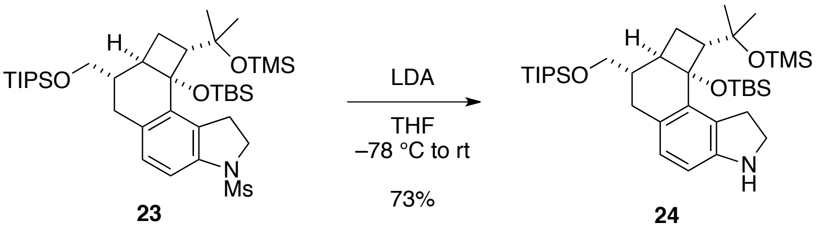


cis-**22a** **23**

A 50-mL round-bottomed flask equipped with a magnetic stirring bar was charged with *cis*-**22a** (127 mg, 195 μmol) in Et_2O (6.0 mL). To the solution was added MeMgBr (3.0 M in Et_2O, 0.60 mL, 1.8 mmol) dropwise at –78 °C. The mixture was warmed to room temperature and stirred for 4 h, after which time TLC (hexanes-ethyl acetate = 6:1) indicated complete consumption of the starting ester *cis*-**22a**. The reaction was quenched with water at 0 °C, and the mixture was extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude tertiary alcohol, which was used for the next reaction without further purification.

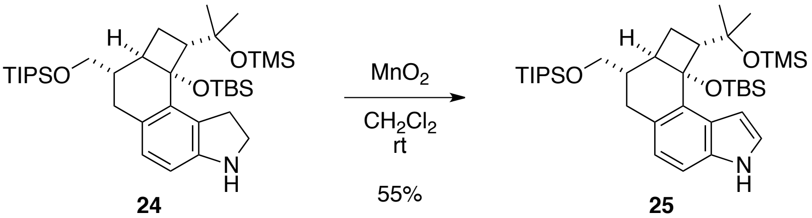
A 50-mL round-bottomed flask equipped with a magnetic stirring bar was charged with the crude alcohol and dry CH_2Cl_2 (6.0 mL). To the solution were added Et_3N (0.60 mL, 4.3 mmol), TMSCl (230 µL, 1.81 mmol), and DMAP (15.0 mg, 123 μmol) at 0 °C. The mixture was warmed to room temperature and stirred for 14.5 h, after which time TLC (hexanes-ethyl acetate = 6:1) indicated complete consumption of the alcohol. The reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 9:1 to 6:1, gradient) to afford compound **23** (123 mg, 170 μmol, 87% from *cis*-**22a**) as a colorless oil; $[\alpha]_D^{32}$ = +1.0 (*c* 0.42, $CHCl_3$); R_f = 0.56 (hexanes-ethyl acetate = 5:1); IR (neat, cm^{-1}): 2943, 2865, 1465, 1355, 1251, 1164, 1108, 1064, 1027, 881, 837, 774, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, 1H, *J* = 7.6 Hz), 6.94 (d, 1H, *J* = 7.6 Hz), 4.03–3.91 (m, 1H), 3.91–3.78 (m, 2H), 3.74 (dd, 1H, *J* = 9.6, 4.4 Hz), 3.68 (dd, 1H, *J* = 9.6, 6.0 Hz), 3.36–3.24 (m, 1H), 2.80 (s, 3H), 2.78–2.52 (m, 3H), 2.43–2.31 (m, 1H), 2.13–1.92 (m, 2H), 1.63–1.49 (m, 4H), 1.21 (s, 3H), 1.17–1.01 (m, 21H), 0.84 (s, 9H), 0.05 (s, 9H), –0.09 (s, 3H), –0.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 138.0, 133.3, 130.7, 128.4, 113.0, 82.2, 76.4, 66.0, 56.4, 50.7, 44.0, 42.1, 33.7, 31.4, 29.3, 27.8, 27.5, 26.4, 26.1, 18.6, 18,0, 12.0, 2.9, –2.6, –3.1; HRMS-ESI (*m/z*) calcd. for $C_{37}H_{69}NNaO_5SSi_3$, 746.4096 (M+Na$^+$); found, 746.4097.

(7*S*,7a*R*,9*R*,9a*R*)-(+)-9a-((*tert*-Butyldimethylsilyl)oxy)-7-(((triisopropylsilyl)oxy)methyl)-9-(2-((trimethylsilyl)oxy)propan-2-yl)-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole (24).



A 30-mL two-necked round-bottomed equipped with a magnetic stirring bar was charged with *i*-Pr_2NH (300 µL, 2.13 mmol) and dry THF (2.0 mL). To the solution was added *n*-BuLi (1.61 M in hexanes, 1.00 mL, 1.61 mmol) at –78 °C. The mixture was warmed to 0 °C and stirred for 30 min and was cooled to –78 °C. To the solution was added **23** (85.4 mg, 118 µmol) in dry THF (2.0 mL), and the resulting mixture was warmed to room temperature and stirred for 3 h, after which time TLC (hexanes-CH_2Cl_2 = 1:1) indicated complete consumption of **23**. The mixture was treated with water and extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-CH_2Cl_2 = 2:1 to CH_2Cl_2, gradient) to afford **24** (55.9 mg, 86.5 µmol, 73%) as a colorless oil; $[\alpha]_D^{23}$ = +4.3 (*c* 0.44, $CHCl_3$); R_f = 0.19 (hexanes-CH_2Cl_2 = 1:1); IR (neat, cm^{-1}): 3373, 2943, 2864, 1597, 1465, 1250, 1106, 1030, 836, 680; ^1H NMR (400 MHz, $CDCl_3$): δ 6.77 (d, 1H, *J* = 8.0 Hz), 6.54 (d, 1H, *J* = 8.0 Hz), 3.71 (dd, 1H, *J* = 9.6, 5.2 Hz), 3.64 (dd, 1H, *J* = 9.6, 6.8 Hz), 3.59–3.50 (m, 1H), 3.49–3.36 (m, 2H), 3.22–3.12 (m, 1H), 2.71–2.56 (m, 2H), 2.54–2.36 (m, 2H), 2.12–2.00 (m, 1H), 2.00–1.86 (m, 1H), 1.86–1.18 (m, 8H), 1.18–0.92 (m, 21H), 0.85 (s, 9H), 0.07 (s, 9H), –0.20 (s, 3H), –0.32 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 137.3, 129.0, 128.2, 127.4, 109.1, 79.9, 76.4, 67.1, 54.7, 47.8, 45.4, 43.9, 31.4, 30.4, 29.1, 28.5, 26.4, 26.2, 18.6, 18.1, 12.0, 2.8, –3.0, –3.3; HRMS-ESI (*m/z*) calcd. for $C_{36}H_{68}NO_3Si_3$ ($M+H^+$), 646.4502; found 646.4484.

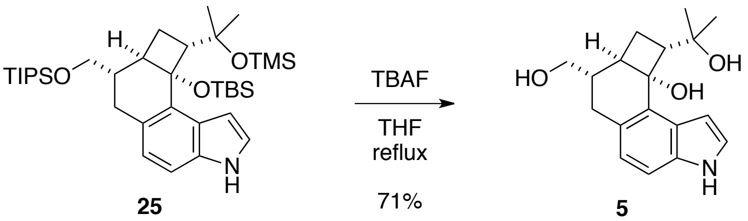
(7*S*,7a*R*,9*R*,9a*R*)-(+)-9a-((*tert*-Butyldimethylsilyl)oxy)-7-(((triisopropylsilyl)oxy)methyl)-9-(2-((trimethylsilyl)oxy)propan-2-yl)-6,7,7a,8,9,9a-hexahydro-3*H*-cyclobuta[5,6]benzo[1,2-*e*]indole (25).



A 30-mL round-bottomed equipped with a magnetic stirring bar was charged with **24** (55.9 mg, 86.5 µmol) in CH_2Cl_2 (4.0 mL). To the solution was added MnO_2 (75.2 mg, 865 µmol). The resulting mixture was stirred for 4 h, after which time TLC (CH_2Cl_2) indicated complete consumption of **24**. The reaction mixture was filtered through a celite pad. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-CH_2Cl_2 = 2:1) to afford indole **25** (30.5 mg, 47.3 µmol, 55%) as a colorless oil; $[\alpha]_D^{33}$ = +3.4 (*c* 0.27, $CHCl_3$); R_f = 0.21 (hexanes-CH_2Cl_2 = 2:1); IR (neat, cm^{-1}): 3414, 2944, 2865, 1463, 1250, 1109, 837, 680; ^1H

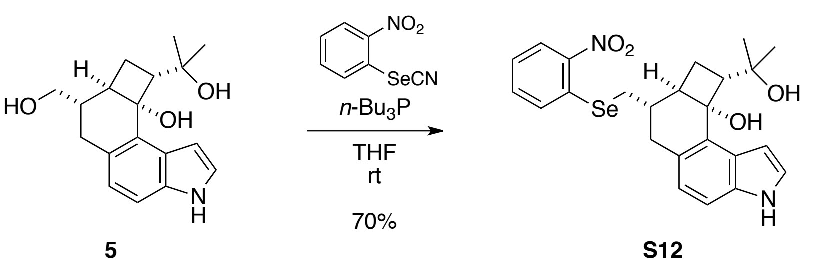
NMR (400 MHz, $CDCl_3$): δ 8.00 (br s, 1H), 7.22 (d, 1H, J = 8.4 Hz), 7.10 (dd, 1H, J = 2.8, 2.8 Hz), 6.98–6.96 (m, 1H), 6.92 (d, 1H, J = 8.4 Hz), 3.78 (dd, 1H, J = 9.6, 4.8 Hz), 3.70 (dd, 1H, J = 9.6, 6.8 Hz), 2.88–2.68 (m, 3H), 2.48 (ddd, 1H, J = 8.8, 8.8, 5.2 Hz), 2.19–2.02 (m, 2H), 1.62 (s, 3H), 1.52–1.35 (m, 4H), 1.18–1.00 (m, 21H), 0.82 (s, 9H), 0.01 (s, 9H), –0.37 (s, 3H), –0.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 132.8, 128.8, 125.6, 123.4, 122.4, 110.2, 105.9, 80.6, 76.2, 67.0, 56.0, 44.7, 43.4, 31.4, 29.3, 28.8, 26.3, 25.9, 18.6, 18.1, 12.0, 2.8, –3.2, –3.4; HRMS-ESI (m/z) calcd. for $C_{36}H_{65}NNaO_3Si_3$, 666.4164 ($M+Na^+$); found, 666.4134.

(7*S*,7a*R*,9*R*,9a*R*)-(–)-7-(Hydroxymethyl)-9-(2-hydroxypropan-2-yl)-3,6,7,7a,8,9-hexahydro-9a*H*-cyclobuta[5,6]benzo[1,2-*e*]indol-9a-ol (5).



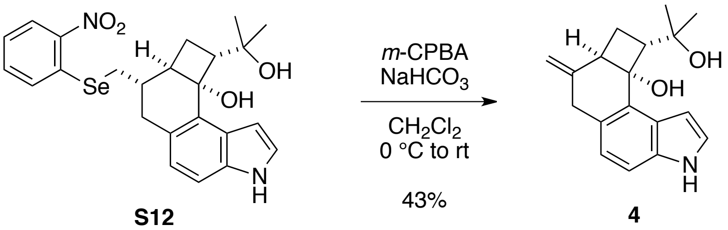
A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with **25** (15.4 mg, 23.9 µmol) and dry THF (0.50 mL). To the mixture was added TBAF (1.0 M in THF, 240 µL, 0.24 mmol). The reaction mixture was heated at 70 ºC and stirred for 4.5 h. The reaction mixture was cooled to room temperature and treated with brine. The mixture was extracted with ethyl acetate four times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by preparative TLC (ethyl acetate) to afford triol **5** (5.1 mg, 17 µmol, 71%) as a white solid; $[\alpha]_D^{29}$ = –21 (c 0.44, CH_3OH); R_f = 0.57 (ethyl acetate); IR (neat, cm^{-1}): 3401, 2925, 1725, 1588, 1450, 1332, 1260, 1038, 742; ^{1}H NMR (400 MHz, CD_3OD): δ 7.22 (d, 1H, J = 8.0 Hz), 7.15 (d, 1H, J = 3.2 Hz), 6.96–6.86 (m, 2H), 3.41–3.33 (m, 2H), 3.04 (dd, 1H, J = 16.0, 5.2 Hz), 2.98–2.85 (m, 1H), 2.74–2.66 (m, 1H), 2.30 (dd, 1H, J = 9.2, 6.0 Hz), 2.16 (ddd, 1H, J = 11.2, 11.2, 6.0 Hz), 2.02–1.93 (m, 1H), 1.68–1.57 (m, 1H), 1.43 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 137.7, 133.3, 126.1, 125.6, 124.5, 124.4, 111.5, 103.9, 76.6, 73.9, 65.1, 54.9, 46.2, 39.1, 30.1, 29.4, 27.8, 21.1; HRMS-ESI (m/z) calcd. for $C_{18}H_{23}NNaO_3$, 324.1570 ($M+Na^+$); 324.1570.

(7*S*,7a*R*,9*R*,9a*R*)-(+)-9-(2-Hydroxypropan-2-yl)-7-(((2-nitrophenyl)selanyl)methyl)-3,6,7,7a,8,9-hexahydro-9a*H*-cyclobuta[5,6]benzo[1,2-*e*]indol-9a-ol (S12).



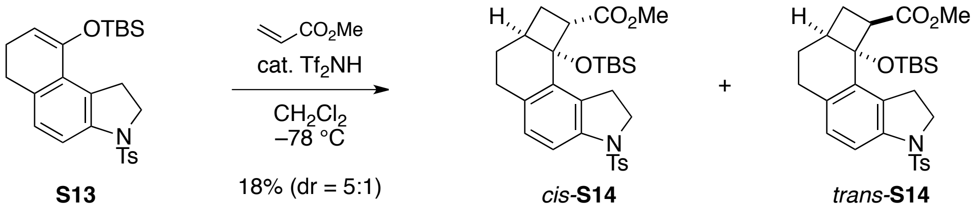
A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with **5** (6.0 mg, 20 µmol) and dry THF (750 µL). To the solution were added 2-nitrophenyl selenocyanate (15.9 mg, 70.0 µmol) and n-Bu_3P (30 µL, 0.12 mmol). The reaction mixture was stirred for 1 h, after which time TLC (hexanes-ethyl acetate = 1:1) indicated complete consumption of **5**. The reaction was quenched with MeOH (1.5 mL) at room temperature, and the mixture was stirred for 30 min. The mixture was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexanes-ethyl acetate = 1:1) and preparative TLC (hexanes-ethyl acetate = 1:1) to afford selenide **S12** (6.6 mg, 14 µmol, 70%) as a yellow oil; $[\alpha]_D^{28}$ = +59 (*c* 0.33, $CHCl_3$); R_f = 0.40 (hexanes-ethyl acetate = 1:1); IR (neat, cm^{-1}): 3409, 2971, 2925, 1589, 1508, 1331, 1303, 1038, 754, 731; ^1H NMR (600 MHz, $CDCl_3$): δ 8.27 (br s, 1H), 8.25 (d, 1H, *J* = 7.8 Hz), 7.42–7.34 (m, 2H), 7.29 (d, 1H, *J* = 8.4 Hz), 7.26–7.18 (m, 2H), 7.06–7.01 (m, 1H), 6.99 (d, 1H, *J* = 8.4 Hz), 3.62 (br s, 1H), 3.20 (dd, 1H, *J* = 16.8, 4.8 Hz), 3.10–2.95 (m, 3H), 2.90–2.80 (m, 2H), 2.38 (dd, 1H, *J* = 9.6, 4.2 Hz), 2.28–2.21 (m, 1H), 2.03 (ddd, 1H, *J* = 12.0, 10.8, 5.4 Hz), 1.68–1.55 (m, 4H), 1.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 135.9, 133.8, 133.5, 131.7, 129.4, 126.4, 125.2, 124.5, 124.4, 124.2, 123.9, 111.0, 103.0, 74.7, 73.3, 54.1, 48.9, 32.7, 31.1, 30.5, 30.4, 27.8, 19.8; HRMS-ESI (*m/z*) calcd. for $C_{24}H_{26}N_2NaO_4Se$, 509.0951 ($M+Na^+$); found, 509.0949.

(7a*R*,9*R*,9a*R*)-(–)-9-(2-Hydroxypropan-2-yl)-7-methylene-3,6,7,7a,8,9-hexahydro-9a*H*-cyclobuta[5,6]benzo[1,2-*e*]indol-9a-ol (4).



A 10-mL screw-top test tube equipped with a magnetic stirring bar was charged with selenide **S12** (6.5 mg, 13 µmol), $NaHCO_3$ (10.3 mg, 123 µmol), and dry CH_2Cl_2 (650 µL). To the mixture was added *m*-CPBA (2.3 mg, 13 µmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 10 min. The mixture was cooled to 0 °C, and *m*-CPBA (0.7 mg, 4 µmol) was added to the mixture. The reaction mixture was let warm to room temperature and stirred for 1 day, and the reaction was then quenched with saturated aqueous Na_2SO_3 (ca, 0.2 mL) and brine (1 mL). The resulting mixture was extracted with CH_2Cl_2 four times. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by preparative TLC (CH_2Cl_2 then hexanes-ethyl acetate = 1:1, multiple development with the two different solvent systems) to afford the left segment **4** (1.6 mg, 5.6 µmol, 43%) as a colorless oil; $[\alpha]_D^{28}$ = –14 (*c* 0.16, $CHCl_3$); R_f = 0.38 (hexanes-ethyl acetate = 1:1); IR (neat, cm^{-1}): 3407, 2971, 2099, 1731, 1647, 888, 801, 775, 752; ^1H NMR (600 MHz, $CDCl_3$): δ 8.22 (br s, 1H), 7.31 (d, 1H, *J* = 8.4 Hz), 7.22 (dd, 1H, *J* = 3.0, 2.4 Hz), 7.03 (dd, 1H, *J* = 2.4, 1.8 Hz), 6.97 (d, 1H, *J* = 8.4 Hz), 4.92–4.88 (m, 2H), 3.82 (d, 1H, *J* = 16.8 Hz), 3.52 (d, 1H, *J* = 19.8 Hz), 3.50 (d, 1H, *J* = 16.8 Hz), 3.26 (br s, 1H), 2.99 (br s, 1H), 2.49 (dd, 1H, *J* = 9.0, 3.6 Hz), 2.03–1.96 (m, 1H), 1.84–1.76 (m, 1H), 1.53 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.2, 135.5, 131.4, 126.9, 124.8, 123.9, 122.9, 111.3, 109.1, 103.0, 77.9, 73.1, 54.1, 51.6, 35.1, 30.6, 27.3, 21.0; HRMS-ESI (*m/z*) calcd. for $C_{18}H_{21}NNaO_2$, 306.1465 ($M+Na^+$); found, 306.1473.

Structure determination of *cis*-S14 by X-ray crystallographic analysis.
(*cis*-S14: CCDC 1026337)



A 20-mL two-necked round-bottomed flask equipped with a magnetic stirring bar was charged with **S13** (124 mg, 273 µmol) and CH_2Cl_2 (5.5 mL). The solution was cooled to –78 °C. To the solution was added methyl acrylate (246 µL, 2.73 mmol) and Tf_2NH (0.14 M in toluene, 15 µL, 2.1 µmol) dropwise, and the resulting mixture was stirred for 10 h, after which time TLC (hexanes-ethyl acetate = 3:1) indicated complete consumption of **S13**. The reaction was quenched with Et_3N (200 µL) at –78 ºC. The mixture was let warm to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes-ethyl acetate = 3:1) followed by preparative TLC (hexanes-ethyl acetate = 10:1) to afford a mixture of diastereomers **S14** (26.3 mg, 48.5 µmol, 18%, dr = 5.0:1.0) as a white solid. The diastereomers were separated by preparative TLC (hexanes-ethyl acetate = 20:1).

(±)-(7a*S,9*S**,9a*R**)-Methyl 9a-((*tert*-butyldimethylsilyl)oxy)-3-tosyl-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole-9-carboxylate (*cis*-S14):** R_f = 0.28 (hexanes-ethyl acetate = 4:1); IR (neat, cm^{-1}): 2952, 2929, 2856, 1731, 1599, 1473, 1441, 1355, 1257, 1168, 957, 836, 756, 584; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H, J = 8.0 Hz), 7.55 (d, 1H, J = 8.4 Hz), 7.18 (d, 2H, J = 8.0 Hz), 6.98 (d, 1H, J = 8.4 Hz), 3.90 (t, 2H, J = 8.8 Hz), 3.72 (s, 3H), 3.24–2.91 (m, 4H), 2.84–2.68 (m, 2H), 2.33 (s, 3H), 2.09–2.01 (m, 1H), 1.82–1.66 (m, 2H), 1.50–1.39 (m, 1H), 0.69 (s, 9H), –0.06 (s, 3H), –0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 143.8, 141.3, 136.8, 134.0, 132.1, 131.2, 129.6, 128.3, 127,4, 115.1, 72.9, 51.64, 51.58, 50.6, 41.2, 28.0, 25.8, 24.5, 21.4, 20.3, 18.0, 16.5, –2.6, –4.5; HRMS-ESI (*m/z*) calcd. for $C_{29}H_{40}NO_5SSi$, 542.2391 (M+H$^+$); found, 542.2382.

(±)-(7a*S,9*R**,9a*R**)-Methyl 9a-((*tert*-butyldimethylsilyl)oxy)-3-tosyl-2,3,6,7,7a,8,9,9a-octahydro-1*H*-cyclobuta[5,6]benzo[1,2-*e*]indole-9-carboxylate (*trans*-S14):** R_f = 0.28 (hexanes-ethyl acetate = 4:1); IR (neat, cm^{-1}): 2952, 2928, 2855, 1726, 1470, 1435, 1357, 1256, 1167, 836, 776, 586; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 2H, J = 8.4 Hz), 7.54 (d, 1H, J = 8.0 Hz), 7.19 (d, 2H, J = 8.4 Hz), 6.99 (d, 1H, J = 8.0 Hz), 4.02–3.93 (m, 1H), 3.54 (ddd, 1H, J = 10.8, 10.0, 10.0 Hz), 3.40 (t, 1H, J = 10.0 Hz), 2.98–2.79 (m, 7H), 2.75–2.65 (m, 1H), 2.32 (s, 3H), 1.96–1.60 (m, 4H), 0.82 (s, 9H), 0.12 (s, 3H), –0.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 143.7, 140.9, 134.1, 133.9, 132.6, 131.8, 129.5, 128.5, 127.5, 114.7, 77.6, 54.0, 50.8, 50.8, 41.4, 29.5, 25.9, 25.6, 21.4, 21.3, 18.2, 16.4, –2.3, –3.4; HRMS-ESI (*m/z*) calcd. for $C_{29}H_{40}NO_5SSi$, 542.2391 (M+H$^+$); found, 542.2380.

References

(1) Sells, T. B.; Nair, V. *Tetrahedron* **1994**, *50*, 117–138.
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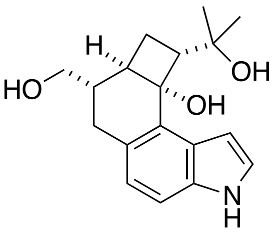
X-ray crystallographic analysis of compound 5.

(CCDC 1026313)



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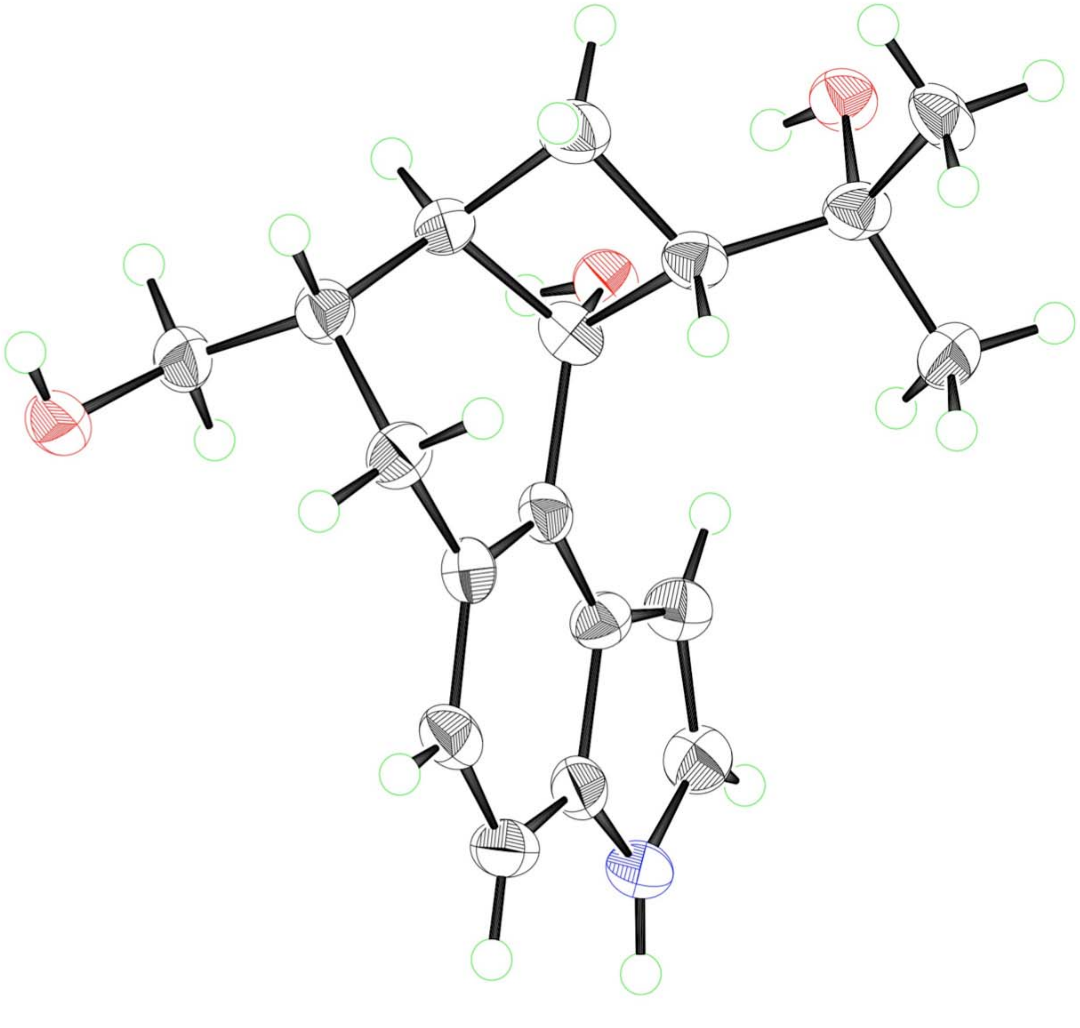


Table 1. Crystal data and structure refinement for compound **5**.

Identification code	compound **5**	
Empirical formula	$C_{18} H_{23} N O_3$	
Formula weight	301.37	
Temperature	173(2) K	
Wavelength	0.71075 Å	
Crystal system	orthorhombic	
Space group	P 212121	
Unit cell dimensions	a = 9.9760(9) Å	α= 90°.
	b = 10.5599(9) Å	β= 90°.
	c = 14.5715(15) Å	γ = 90°.
Volume	1535.0(2) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	648	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	3.14 to 27.45°.	
Index ranges	-12<=h<=12, -13<=k<=13, -18<=l<=18	
Reflections collected	14974	
Independent reflections	3479 [R(int) = 0.0670]	
Completeness to theta = 27.45°	99.4 %	
Max. and min. transmission	0.9912 and 0.9826	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3479 / 0 / 204	
Goodness-of-fit on F^2	1.200	
Final R indices [I>2sigma(I)]	R_1 = 0.0636, wR_2 = 0.1545	
R indices (all data)	R_1 = 0.1054, wR_2 = 0.2282	
Absolute structure parameter	-1(2)	
Largest diff. peak and hole	0.521 and -0.467 e.$Å^{-3}$	

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for compound **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	8100(3)	5554(3)	-1533(2)	34(1)
C(1)	7605(4)	6591(4)	-1999(3)	35(1)
C(2)	7552(4)	7611(4)	-1428(3)	34(1)
C(3)	8011(4)	7222(4)	-539(3)	28(1)
C(4)	8357(4)	5909(4)	-635(3)	31(1)
C(5)	8826(4)	5174(4)	88(3)	34(1)
C(6)	8948(4)	5777(4)	929(3)	33(1)
C(7)	8619(4)	7067(4)	1066(3)	29(1)
C(8)	8172(3)	7788(3)	329(3)	28(1)
C(9)	7917(4)	9193(3)	500(3)	28(1)
C(10)	9195(4)	10034(4)	649(3)	30(1)
C(11)	8539(4)	10600(4)	1520(3)	37(1)
C(12)	7451(4)	9558(3)	1478(3)	29(1)
C(13)	7524(4)	8525(4)	2206(3)	31(1)
C(14)	8708(4)	7644(4)	2020(3)	33(1)
C(15)	9706(4)	10913(3)	-104(3)	32(1)
C(16)	10217(4)	10147(4)	-902(3)	36(1)
C(17)	10791(4)	11787(3)	277(3)	35(1)
O(1)	8647(3)	11755(2)	-403(2)	33(1)
O(2)	7087(3)	9751(2)	-196(2)	31(1)
C(18)	6204(4)	7801(4)	2247(3)	32(1)
O(3)	6153(3)	6913(2)	2987(2)	37(1)

Table 3. Bond lengths [Å] and angles [°] for compound **5**.

N(1)-C(1)	1.379(5)
N(1)-C(4)	1.385(5)
N(1)-H(1)	0.8800
C(1)-C(2)	1.362(5)
C(1)-H(2)	0.9500
C(2)-C(3)	1.435(6)
C(2)-H(3)	0.9500
C(3)-C(8)	1.408(5)
C(3)-C(4)	1.435(5)
C(4)-C(5)	1.391(6)
C(5)-C(6)	1.387(6)
C(5)-H(4)	0.9500
C(6)-C(7)	1.415(5)
C(6)-H(5)	0.9500
C(7)-C(8)	1.389(5)
C(7)-C(14)	1.521(6)
C(8)-C(9)	1.525(5)
C(9)-O(2)	1.436(4)
C(9)-C(12)	1.548(6)
C(9)-C(10)	1.569(5)
C(10)-C(15)	1.524(6)
C(10)-C(11)	1.548(6)
C(10)-H(6)	1.0000
C(11)-C(12)	1.546(6)
C(11)-H(7)	0.9900
C(11)-H(8)	0.9900
C(12)-C(13)	1.524(5)
C(12)-H(9)	1.0000

C(13)-C(18)	1.524(5)
C(13)-C(14)	1.528(5)
C(13)-H(10)	1.0000
C(14)-H(11)	0.9900
C(14)-H(12)	0.9900
C(15)-O(1)	1.448(4)
C(15)-C(16)	1.506(6)
C(15)-C(17)	1.527(5)
C(16)-H(13)	0.9800
C(16)-H(14)	0.9800
C(16)-H(15)	0.9800
C(17)-H(16)	0.9800
C(17)-H(17)	0.9800
C(17)-H(18)	0.9800
O(1)-H(19)	0.8400
O(2)-H(20)	0.8400
C(18)-O(3)	1.431(5)
C(18)-H(21)	0.9900
C(18)-H(22)	0.9900
O(3)-H(23)	0.8400
C(1)-N(1)-C(4)	108.4(3)
C(1)-N(1)-H(1)	125.8
C(4)-N(1)-H(1)	125.8
C(2)-C(1)-N(1)	109.9(4)
C(2)-C(1)-H(2)	125.0
N(1)-C(1)-H(2)	125.0
C(1)-C(2)-C(3)	108.2(3)
C(1)-C(2)-H(3)	125.9
C(3)-C(2)-H(3)	125.9

C(8)-C(3)-C(2)	136.6(3)
C(8)-C(3)-C(4)	118.1(3)
C(2)-C(3)-C(4)	105.3(3)
N(1)-C(4)-C(5)	128.8(4)
N(1)-C(4)-C(3)	108.1(3)
C(5)-C(4)-C(3)	123.1(4)
C(6)-C(5)-C(4)	116.3(3)
C(6)-C(5)-H(4)	121.9
C(4)-C(5)-H(4)	121.9
C(5)-C(6)-C(7)	123.1(4)
C(5)-C(6)-H(5)	118.4
C(7)-C(6)-H(5)	118.4
C(8)-C(7)-C(6)	119.6(4)
C(8)-C(7)-C(14)	120.3(3)
C(6)-C(7)-C(14)	120.1(4)
C(7)-C(8)-C(3)	119.8(3)
C(7)-C(8)-C(9)	117.4(3)
C(3)-C(8)-C(9)	122.7(3)
O(2)-C(9)-C(8)	112.3(3)
O(2)-C(9)-C(12)	112.0(3)
C(8)-C(9)-C(12)	116.3(3)
O(2)-C(9)-C(10)	109.5(3)
C(8)-C(9)-C(10)	116.0(3)
C(12)-C(9)-C(10)	88.6(3)
C(15)-C(10)-C(11)	119.8(3)
C(15)-C(10)-C(9)	121.1(3)
C(11)-C(10)-C(9)	89.3(3)
C(15)-C(10)-H(6)	108.3
C(11)-C(10)-H(6)	108.3
C(9)-C(10)-H(6)	108.3

C(12)-C(11)-C(10)	89.4(3)
C(12)-C(11)-H(7)	113.7
C(10)-C(11)-H(7)	113.7
C(12)-C(11)-H(8)	113.7
C(10)-C(11)-H(8)	113.7
H(7)-C(11)-H(8)	111.0
C(13)-C(12)-C(11)	116.7(3)
C(13)-C(12)-C(9)	116.6(3)
C(11)-C(12)-C(9)	90.2(3)
C(13)-C(12)-H(9)	110.6
C(11)-C(12)-H(9)	110.6
C(9)-C(12)-H(9)	110.6
C(12)-C(13)-C(18)	110.2(3)
C(12)-C(13)-C(14)	110.4(3)
C(18)-C(13)-C(14)	111.7(3)
C(12)-C(13)-H(10)	108.1
C(18)-C(13)-H(10)	108.1
C(14)-C(13)-H(10)	108.1
C(7)-C(14)-C(13)	111.2(3)
C(7)-C(14)-H(11)	109.4
C(13)-C(14)-H(11)	109.4
C(7)-C(14)-H(12)	109.4
C(13)-C(14)-H(12)	109.4
H(11)-C(14)-H(12)	108.0
O(1)-C(15)-C(16)	110.1(3)
O(1)-C(15)-C(10)	110.3(3)
C(16)-C(15)-C(10)	110.1(3)
O(1)-C(15)-C(17)	104.8(3)
C(16)-C(15)-C(17)	111.4(3)
C(10)-C(15)-C(17)	110.1(3)

C(15)-C(16)-H(13)	109.5
C(15)-C(16)-H(14)	109.5
H(13)-C(16)-H(14)	109.5
C(15)-C(16)-H(15)	109.5
H(13)-C(16)-H(15)	109.5
H(14)-C(16)-H(15)	109.5
C(15)-C(17)-H(16)	109.5
C(15)-C(17)-H(17)	109.5
H(16)-C(17)-H(17)	109.5
C(15)-C(17)-H(18)	109.5
H(16)-C(17)-H(18)	109.5
H(17)-C(17)-H(18)	109.5
C(15)-O(1)-H(19)	109.5
C(9)-O(2)-H(20)	109.5
O(3)-C(18)-C(13)	112.9(3)
O(3)-C(18)-H(21)	109.0
C(13)-C(18)-H(21)	109.0
O(3)-C(18)-H(22)	109.0
C(13)-C(18)-H(22)	109.0
H(21)-C(18)-H(22)	107.8
C(18)-O(3)-H(23)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Torsion angles [°] for compound **5**.

C(4)-N(1)-C(1)-C(2)	0.8(5)
N(1)-C(1)-C(2)-C(3)	-1.1(5)
C(1)-C(2)-C(3)-C(8)	-178.4(4)
C(1)-C(2)-C(3)-C(4)	0.9(4)
C(1)-N(1)-C(4)-C(5)	178.0(4)
C(1)-N(1)-C(4)-C(3)	-0.2(4)
C(8)-C(3)-C(4)-N(1)	179.1(3)
C(2)-C(3)-C(4)-N(1)	-0.4(4)
C(8)-C(3)-C(4)-C(5)	0.8(6)
C(2)-C(3)-C(4)-C(5)	-178.8(4)
N(1)-C(4)-C(5)-C(6)	-177.9(4)
C(3)-C(4)-C(5)-C(6)	0.1(6)
C(4)-C(5)-C(6)-C(7)	0.1(6)
C(5)-C(6)-C(7)-C(8)	-1.1(6)
C(5)-C(6)-C(7)-C(14)	176.7(4)
C(6)-C(7)-C(8)-C(3)	1.9(5)
C(14)-C(7)-C(8)-C(3)	-175.9(3)
C(6)-C(7)-C(8)-C(9)	-176.2(3)
C(14)-C(7)-C(8)-C(9)	6.0(5)
C(2)-C(3)-C(8)-C(7)	177.6(4)
C(4)-C(3)-C(8)-C(7)	-1.7(5)
C(2)-C(3)-C(8)-C(9)	-4.4(7)
C(4)-C(3)-C(8)-C(9)	176.3(3)
C(7)-C(8)-C(9)-O(2)	-161.9(3)
C(3)-C(8)-C(9)-O(2)	20.0(5)
C(7)-C(8)-C(9)-C(12)	-31.1(5)
C(3)-C(8)-C(9)-C(12)	150.9(3)
C(7)-C(8)-C(9)-C(10)	71.1(4)

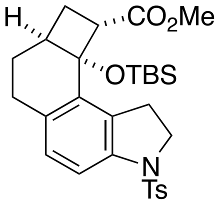
C(3)-C(8)-C(9)-C(10)	-107.0(4)
O(2)-C(9)-C(10)-C(15)	-23.9(5)
C(8)-C(9)-C(10)-C(15)	104.5(4)
C(12)-C(9)-C(10)-C(15)	-136.8(3)
O(2)-C(9)-C(10)-C(11)	101.0(3)
C(8)-C(9)-C(10)-C(11)	-130.6(3)
C(12)-C(9)-C(10)-C(11)	-11.8(3)
C(15)-C(10)-C(11)-C(12)	137.9(3)
C(9)-C(10)-C(11)-C(12)	11.8(3)
C(10)-C(11)-C(12)-C(13)	108.1(4)
C(10)-C(11)-C(12)-C(9)	-12.0(3)
O(2)-C(9)-C(12)-C(13)	141.1(3)
C(8)-C(9)-C(12)-C(13)	10.1(5)
C(10)-C(9)-C(12)-C(13)	-108.4(3)
O(2)-C(9)-C(12)-C(11)	-98.6(3)
C(8)-C(9)-C(12)-C(11)	130.3(3)
C(10)-C(9)-C(12)-C(11)	11.8(3)
C(11)-C(12)-C(13)-C(18)	164.1(3)
C(9)-C(12)-C(13)-C(18)	-91.1(4)
C(11)-C(12)-C(13)-C(14)	-72.0(4)
C(9)-C(12)-C(13)-C(14)	32.8(4)
C(8)-C(7)-C(14)-C(13)	38.9(5)
C(6)-C(7)-C(14)-C(13)	-139.0(4)
C(12)-C(13)-C(14)-C(7)	-56.8(4)
C(18)-C(13)-C(14)-C(7)	66.2(4)
C(11)-C(10)-C(15)-O(1)	-54.6(5)
C(9)-C(10)-C(15)-O(1)	54.6(5)
C(11)-C(10)-C(15)-C(16)	-176.3(3)
C(9)-C(10)-C(15)-C(16)	-67.1(4)
C(11)-C(10)-C(15)-C(17)	60.5(4)

C(9)-C(10)-C(15)-C(17)	169.7(3)
C(12)-C(13)-C(18)-O(3)	-173.3(3)
C(14)-C(13)-C(18)-O(3)	63.6(4)

Symmetry transformations used to generate equivalent atoms:

X-ray crystallographic analysis of compound *cis*-S14.

(CCDC 1026337)



cis-**S14**

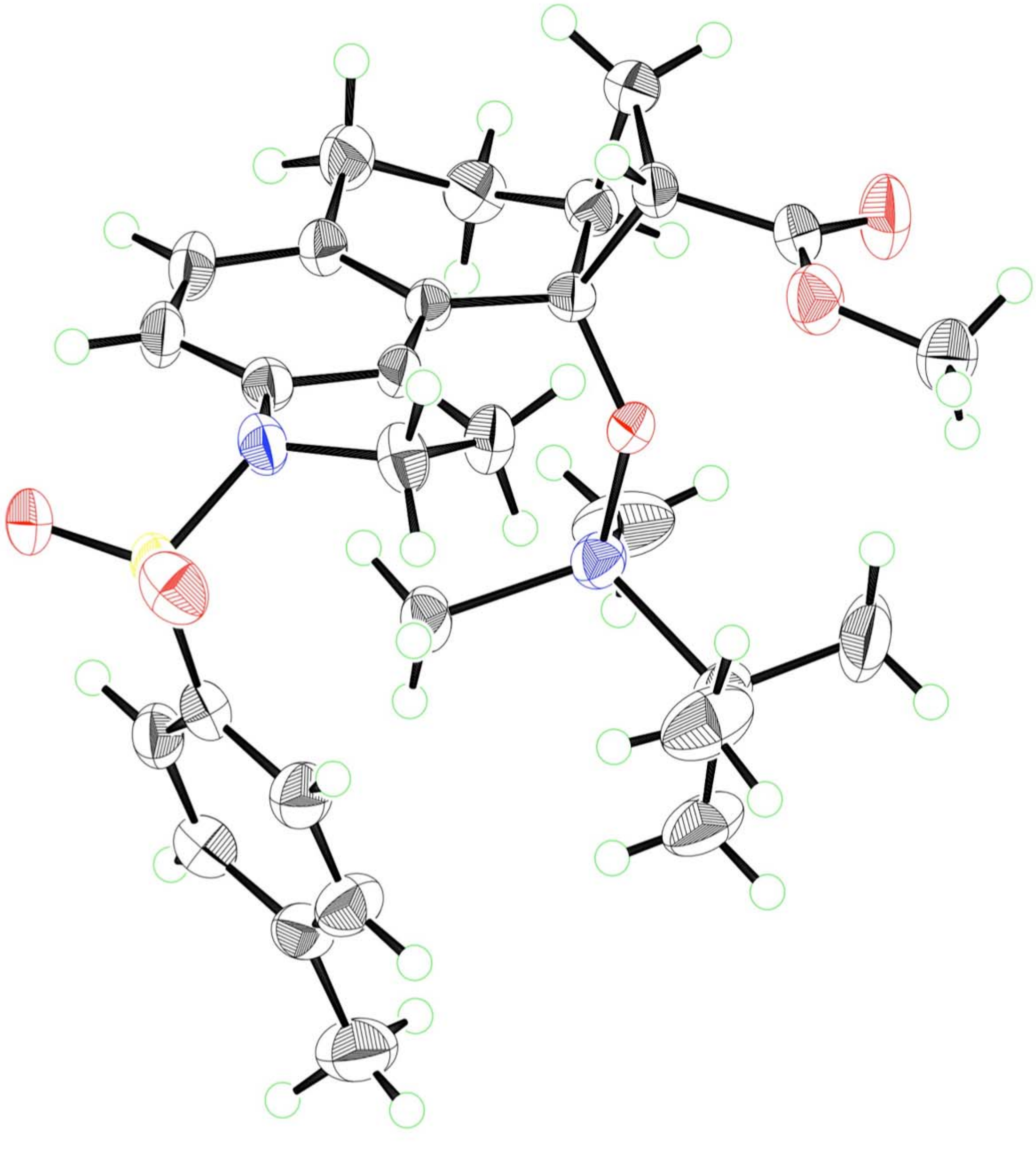


Table 5. Crystal data and structure refinement for compound *cis*-**S14**.

Identification code	compound *cis*-**S14**	
Empirical formula	$C_{29} H_{39} N O_5 S Si$	
Formula weight	541.76	
Temperature	173(2) K	
Wavelength	0.71075 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.8640(2) Å	α= 90°.
	b = 21.4218(6) Å	β= 100.8814(8)°.
	c = 15.2662(4) Å	γ = 90°.
Volume	2846.67(13) Å^3	
Z	4	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	1160	
Crystal size	0.35 x 0.15 x 0.15 mm^3	
Theta range for data collection	3.02 to 27.43°.	
Index ranges	-11<=h<=10, -27<=k<=27, -19<=l<=19	
Reflections collected	27316	
Independent reflections	6440 [R(int) = 0.0498]	
Completeness to theta = 27.43°	99.3 %	
Max. and min. transmission	0.9715 and 0.9351	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6440 / 0 / 341	
Goodness-of-fit on F^2	1.153	
Final R indices [I>2sigma(I)]	R_1 = 0.0687, wR_2 = 0.1805	
R indices (all data)	R_1 = 0.1026, wR_2 = 0.2307	
Largest diff. peak and hole	2.159 and -0.581 e.Å^{-3}	

Table 6. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for compound *cis*-**S14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9200(3)	10313(1)	7920(2)	35(1)
C(1)	9497(4)	10978(2)	7708(2)	39(1)
C(2)	8594(4)	11362(2)	8276(2)	38(1)
C(3)	8299(3)	10916(1)	8979(2)	29(1)
C(4)	7801(3)	11029(1)	9782(2)	27(1)
C(5)	7464(3)	11690(1)	10029(2)	27(1)
C(6)	8971(3)	12081(1)	10357(2)	31(1)
C(7)	8789(4)	11943(2)	11328(2)	36(1)
C(8)	7096(4)	11757(2)	10974(2)	32(1)
C(9)	6418(4)	11195(2)	11370(2)	40(1)
C(10)	7316(4)	10603(2)	11262(2)	41(1)
C(11)	7636(4)	10518(1)	10327(2)	32(1)
C(12)	7869(4)	9916(2)	10031(2)	39(1)
C(13)	8323(4)	9798(2)	9229(2)	38(1)
C(14)	8561(3)	10309(1)	8715(2)	30(1)
S(1)	8605(1)	9834(1)	7082(1)	37(1)
C(15)	6737(4)	10075(2)	6596(2)	33(1)
C(16)	6557(4)	10540(2)	5949(2)	44(1)
C(17)	5092(4)	10769(2)	5614(2)	47(1)
C(18)	3815(4)	10539(2)	5908(2)	42(1)
C(19)	4018(4)	10063(2)	6544(2)	41(1)
C(20)	5478(4)	9837(2)	6890(2)	39(1)
C(21)	2234(5)	10795(2)	5546(3)	61(1)
O(1)	9604(3)	9940(1)	6459(2)	47(1)

O(2)	8514(3)	9228(1)	7465(2)	44(1)
O(3)	6417(2)	11987(1)	9331(1)	29(1)
Si(1)	4565(1)	11838(1)	8935(1)	34(1)
C(22)	3996(4)	12444(2)	8051(3)	43(1)
C(23)	2305(4)	12358(2)	7595(3)	61(1)
C(24)	4173(6)	13100(2)	8492(4)	75(2)
C(25)	5014(5)	12395(3)	7343(3)	68(1)
C(26)	3321(5)	11926(3)	9780(3)	67(1)
C(27)	4346(4)	11044(2)	8463(3)	47(1)
C(28)	8757(4)	12755(2)	10091(2)	35(1)
O(4)	9238(3)	12863(1)	9323(2)	44(1)
C(29)	8988(5)	13490(2)	8964(3)	57(1)
O(5)	8215(3)	13151(1)	10499(2)	53(1)

Table 7. Bond lengths [Å] and angles [°] for compound *cis*-**S14**.

N(1)-C(14)	1.432(4)
N(1)-C(1)	1.495(4)
N(1)-S(1)	1.647(3)
C(1)-C(2)	1.527(5)
C(1)-H(1)	0.9900
C(1)-H(2)	0.9900
C(2)-C(3)	1.497(4)
C(2)-H(3)	0.9900
C(2)-H(4)	0.9900
C(3)-C(14)	1.392(4)
C(3)-C(4)	1.400(4)
C(4)-C(11)	1.400(4)
C(4)-C(5)	1.511(4)
C(5)-O(3)	1.423(3)
C(5)-C(8)	1.546(4)
C(5)-C(6)	1.576(4)
C(6)-C(28)	1.503(4)
C(6)-C(7)	1.549(5)
C(6)-H(5)	1.0000
C(7)-C(8)	1.548(4)
C(7)-H(6)	0.9900
C(7)-H(7)	0.9900
C(8)-C(9)	1.520(5)
C(8)-H(8)	1.0000
C(9)-C(10)	1.522(5)
C(9)-H(9)	0.9900
C(9)-H(10)	0.9900
C(10)-C(11)	1.517(5)

C(10)-H(11)	0.9900
C(10)-H(12)	0.9900
C(11)-C(12)	1.395(4)
C(12)-C(13)	1.382(5)
C(12)-H(13)	0.9500
C(13)-C(14)	1.386(4)
C(13)-H(14)	0.9500
S(1)-O(2)	1.431(3)
S(1)-O(1)	1.436(3)
S(1)-C(15)	1.759(3)
C(15)-C(20)	1.377(5)
C(15)-C(16)	1.391(5)
C(16)-C(17)	1.392(5)
C(16)-H(15)	0.9500
C(17)-C(18)	1.384(5)
C(17)-H(16)	0.9500
C(18)-C(19)	1.396(5)
C(18)-C(21)	1.510(5)
C(19)-C(20)	1.389(5)
C(19)-H(17)	0.9500
C(20)-H(18)	0.9500
C(21)-H(19)	0.9800
C(21)-H(20)	0.9800
C(21)-H(21)	0.9800
O(3)-Si(1)	1.669(2)
Si(1)-C(27)	1.844(4)
Si(1)-C(26)	1.858(4)
Si(1)-C(22)	1.872(4)
C(22)-C(25)	1.537(6)
C(22)-C(23)	1.540(5)

C(22)-C(24)	1.553(6)
C(23)-H(22)	0.9800
C(23)-H(23)	0.9800
C(23)-H(24)	0.9800
C(24)-H(25)	0.9800
C(24)-H(26)	0.9800
C(24)-H(27)	0.9800
C(25)-H(28)	0.9800
C(25)-H(29)	0.9800
C(25)-H(30)	0.9800
C(26)-H(31)	0.9800
C(26)-H(32)	0.9800
C(26)-H(33)	0.9800
C(27)-H(34)	0.9800
C(27)-H(35)	0.9800
C(27)-H(36)	0.9800
C(28)-O(5)	1.204(4)
C(28)-O(4)	1.340(4)
O(4)-C(29)	1.453(4)
C(29)-H(37)	0.9800
C(29)-H(38)	0.9800
C(29)-H(39)	0.9800

C(14)-N(1)-C(1)	107.6(2)
C(14)-N(1)-S(1)	122.3(2)
C(1)-N(1)-S(1)	118.0(2)
N(1)-C(1)-C(2)	105.0(3)
N(1)-C(1)-H(1)	110.8
C(2)-C(1)-H(1)	110.8
N(1)-C(1)-H(2)	110.8

C(2)-C(1)-H(2)	110.8
H(1)-C(1)-H(2)	108.8
C(3)-C(2)-C(1)	104.1(3)
C(3)-C(2)-H(3)	110.9
C(1)-C(2)-H(3)	110.9
C(3)-C(2)-H(4)	110.9
C(1)-C(2)-H(4)	110.9
H(3)-C(2)-H(4)	109.0
C(14)-C(3)-C(4)	120.8(3)
C(14)-C(3)-C(2)	109.1(3)
C(4)-C(3)-C(2)	130.0(3)
C(11)-C(4)-C(3)	118.1(3)
C(11)-C(4)-C(5)	122.5(3)
C(3)-C(4)-C(5)	119.4(3)
O(3)-C(5)-C(4)	111.3(2)
O(3)-C(5)-C(8)	115.8(2)
C(4)-C(5)-C(8)	114.0(2)
O(3)-C(5)-C(6)	113.3(2)
C(4)-C(5)-C(6)	112.4(2)
C(8)-C(5)-C(6)	88.2(2)
C(28)-C(6)-C(7)	114.3(3)
C(28)-C(6)-C(5)	111.6(2)
C(7)-C(6)-C(5)	88.2(2)
C(28)-C(6)-H(5)	113.5
C(7)-C(6)-H(5)	113.5
C(5)-C(6)-H(5)	113.5
C(8)-C(7)-C(6)	89.2(2)
C(8)-C(7)-H(6)	113.8
C(6)-C(7)-H(6)	113.8
C(8)-C(7)-H(7)	113.8

C(6)-C(7)-H(7)	113.8
H(6)-C(7)-H(7)	111.0
C(9)-C(8)-C(5)	117.8(3)
C(9)-C(8)-C(7)	119.7(3)
C(5)-C(8)-C(7)	89.3(2)
C(9)-C(8)-H(8)	109.5
C(5)-C(8)-H(8)	109.5
C(7)-C(8)-H(8)	109.5
C(8)-C(9)-C(10)	111.2(3)
C(8)-C(9)-H(9)	109.4
C(10)-C(9)-H(9)	109.4
C(8)-C(9)-H(10)	109.4
C(10)-C(9)-H(10)	109.4
H(9)-C(9)-H(10)	108.0
C(11)-C(10)-C(9)	113.4(3)
C(11)-C(10)-H(11)	108.9
C(9)-C(10)-H(11)	108.9
C(11)-C(10)-H(12)	108.9
C(9)-C(10)-H(12)	108.9
H(11)-C(10)-H(12)	107.7
C(12)-C(11)-C(4)	119.4(3)
C(12)-C(11)-C(10)	118.8(3)
C(4)-C(11)-C(10)	121.6(3)
C(13)-C(12)-C(11)	122.8(3)
C(13)-C(12)-H(13)	118.6
C(11)-C(12)-H(13)	118.6
C(12)-C(13)-C(14)	117.3(3)
C(12)-C(13)-H(14)	121.3
C(14)-C(13)-H(14)	121.3
C(13)-C(14)-C(3)	121.4(3)

C(13)-C(14)-N(1)	127.7(3)
C(3)-C(14)-N(1)	110.7(3)
O(2)-S(1)-O(1)	120.32(16)
O(2)-S(1)-N(1)	106.39(15)
O(1)-S(1)-N(1)	105.60(15)
O(2)-S(1)-C(15)	108.48(15)
O(1)-S(1)-C(15)	108.81(16)
N(1)-S(1)-C(15)	106.40(14)
C(20)-C(15)-C(16)	120.4(3)
C(20)-C(15)-S(1)	120.7(3)
C(16)-C(15)-S(1)	118.8(3)
C(15)-C(16)-C(17)	119.1(3)
C(15)-C(16)-H(15)	120.5
C(17)-C(16)-H(15)	120.5
C(18)-C(17)-C(16)	121.3(3)
C(18)-C(17)-H(16)	119.3
C(16)-C(17)-H(16)	119.3
C(17)-C(18)-C(19)	118.6(3)
C(17)-C(18)-C(21)	120.8(4)
C(19)-C(18)-C(21)	120.6(4)
C(20)-C(19)-C(18)	120.5(3)
C(20)-C(19)-H(17)	119.7
C(18)-C(19)-H(17)	119.7
C(15)-C(20)-C(19)	120.1(3)
C(15)-C(20)-H(18)	120.0
C(19)-C(20)-H(18)	120.0
C(18)-C(21)-H(19)	109.5
C(18)-C(21)-H(20)	109.5
H(19)-C(21)-H(20)	109.5
C(18)-C(21)-H(21)	109.5

H(19)-C(21)-H(21)	109.5
H(20)-C(21)-H(21)	109.5
C(5)-O(3)-Si(1)	130.07(19)
O(3)-Si(1)-C(27)	109.94(14)
O(3)-Si(1)-C(26)	113.67(16)
C(27)-Si(1)-C(26)	109.4(2)
O(3)-Si(1)-C(22)	104.00(13)
C(27)-Si(1)-C(22)	111.32(18)
C(26)-Si(1)-C(22)	108.4(2)
C(25)-C(22)-C(23)	109.0(3)
C(25)-C(22)-C(24)	110.0(4)
C(23)-C(22)-C(24)	108.3(3)
C(25)-C(22)-Si(1)	110.2(3)
C(23)-C(22)-Si(1)	110.5(3)
C(24)-C(22)-Si(1)	108.8(3)
C(22)-C(23)-H(22)	109.5
C(22)-C(23)-H(23)	109.5
H(22)-C(23)-H(23)	109.5
C(22)-C(23)-H(24)	109.5
H(22)-C(23)-H(24)	109.5
H(23)-C(23)-H(24)	109.5
C(22)-C(24)-H(25)	109.5
C(22)-C(24)-H(26)	109.5
H(25)-C(24)-H(26)	109.5
C(22)-C(24)-H(27)	109.5
H(25)-C(24)-H(27)	109.5
H(26)-C(24)-H(27)	109.5
C(22)-C(25)-H(28)	109.5
C(22)-C(25)-H(29)	109.5
H(28)-C(25)-H(29)	109.5

C(22)-C(25)-H(30)	109.5
H(28)-C(25)-H(30)	109.5
H(29)-C(25)-H(30)	109.5
Si(1)-C(26)-H(31)	109.5
Si(1)-C(26)-H(32)	109.5
H(31)-C(26)-H(32)	109.5
Si(1)-C(26)-H(33)	109.5
H(31)-C(26)-H(33)	109.5
H(32)-C(26)-H(33)	109.5
Si(1)-C(27)-H(34)	109.5
Si(1)-C(27)-H(35)	109.5
H(34)-C(27)-H(35)	109.5
Si(1)-C(27)-H(36)	109.5
H(34)-C(27)-H(36)	109.5
H(35)-C(27)-H(36)	109.5
O(5)-C(28)-O(4)	123.7(3)
O(5)-C(28)-C(6)	125.4(3)
O(4)-C(28)-C(6)	110.9(3)
C(28)-O(4)-C(29)	116.0(3)
O(4)-C(29)-H(37)	109.5
O(4)-C(29)-H(38)	109.5
H(37)-C(29)-H(38)	109.5
O(4)-C(29)-H(39)	109.5
H(37)-C(29)-H(39)	109.5
H(38)-C(29)-H(39)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [°] for compound *cis*-**S14**.

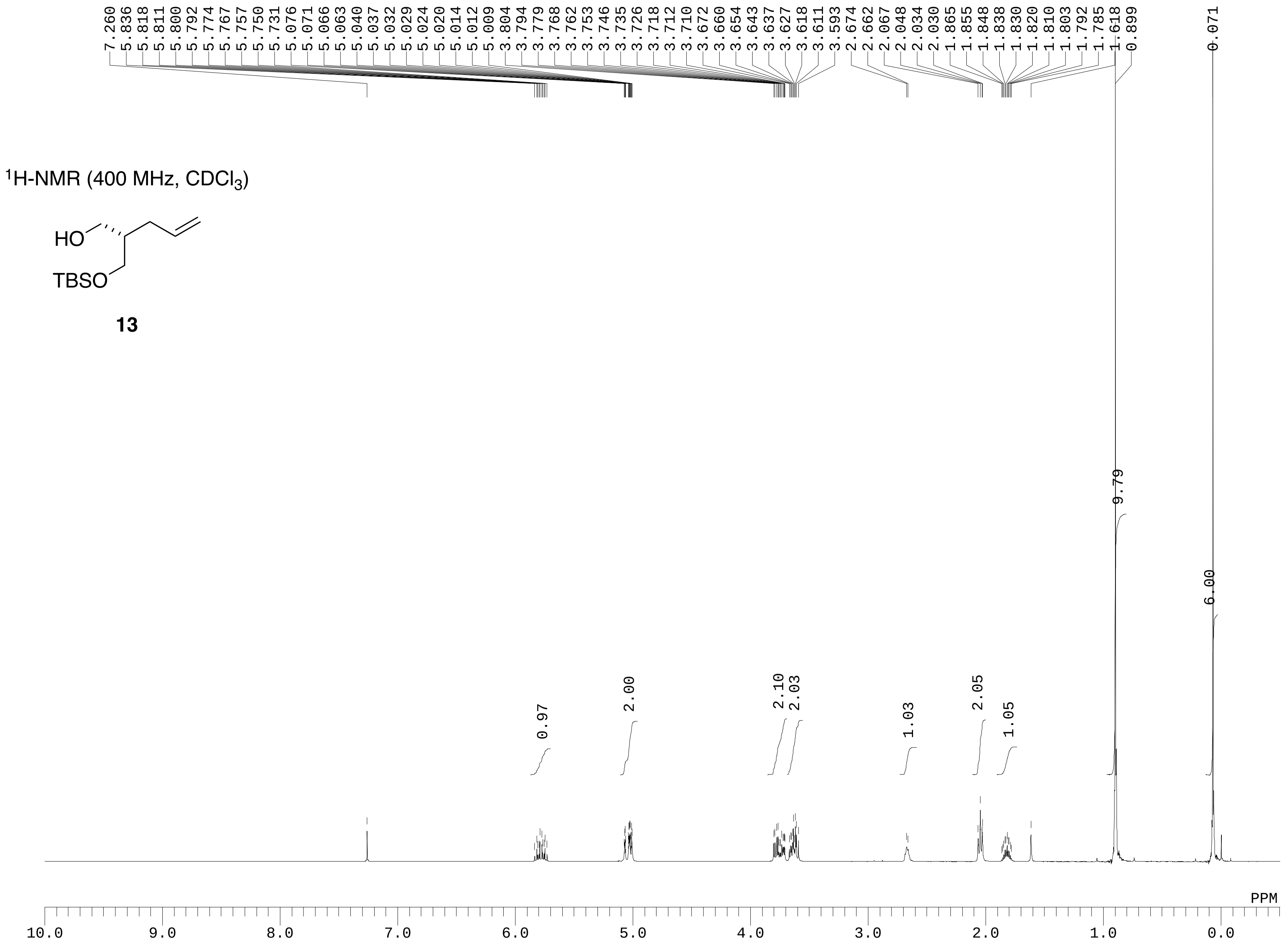
C(14)-N(1)-C(1)-C(2)	-15.1(3)
S(1)-N(1)-C(1)-C(2)	128.4(2)
N(1)-C(1)-C(2)-C(3)	18.5(3)
C(1)-C(2)-C(3)-C(14)	-16.0(3)
C(1)-C(2)-C(3)-C(4)	165.6(3)
C(14)-C(3)-C(4)-C(11)	2.5(4)
C(2)-C(3)-C(4)-C(11)	-179.2(3)
C(14)-C(3)-C(4)-C(5)	-177.4(3)
C(2)-C(3)-C(4)-C(5)	0.8(5)
C(11)-C(4)-C(5)-O(3)	-126.9(3)
C(3)-C(4)-C(5)-O(3)	53.1(3)
C(11)-C(4)-C(5)-C(8)	6.3(4)
C(3)-C(4)-C(5)-C(8)	-173.7(2)
C(11)-C(4)-C(5)-C(6)	104.7(3)
C(3)-C(4)-C(5)-C(6)	-75.3(3)
O(3)-C(5)-C(6)-C(28)	18.9(4)
C(4)-C(5)-C(6)-C(28)	146.2(3)
C(8)-C(5)-C(6)-C(28)	-98.5(3)
O(3)-C(5)-C(6)-C(7)	134.4(3)
C(4)-C(5)-C(6)-C(7)	-98.3(3)
C(8)-C(5)-C(6)-C(7)	17.0(2)
C(28)-C(6)-C(7)-C(8)	96.0(3)
C(5)-C(6)-C(7)-C(8)	-16.9(2)
O(3)-C(5)-C(8)-C(9)	104.3(3)
C(4)-C(5)-C(8)-C(9)	-26.8(4)
C(6)-C(5)-C(8)-C(9)	-140.6(3)
O(3)-C(5)-C(8)-C(7)	-132.1(3)
C(4)-C(5)-C(8)-C(7)	96.9(3)

C(6)-C(5)-C(8)-C(7)	-17.0(2)
C(6)-C(7)-C(8)-C(9)	139.3(3)
C(6)-C(7)-C(8)-C(5)	17.3(2)
C(5)-C(8)-C(9)-C(10)	47.8(4)
C(7)-C(8)-C(9)-C(10)	-58.8(4)
C(8)-C(9)-C(10)-C(11)	-47.4(4)
C(3)-C(4)-C(11)-C(12)	-4.3(4)
C(5)-C(4)-C(11)-C(12)	175.7(3)
C(3)-C(4)-C(11)-C(10)	171.5(3)
C(5)-C(4)-C(11)-C(10)	-8.5(4)
C(9)-C(10)-C(11)-C(12)	-154.5(3)
C(9)-C(10)-C(11)-C(4)	29.7(4)
C(4)-C(11)-C(12)-C(13)	2.8(5)
C(10)-C(11)-C(12)-C(13)	-173.1(3)
C(11)-C(12)-C(13)-C(14)	0.5(5)
C(12)-C(13)-C(14)-C(3)	-2.3(5)
C(12)-C(13)-C(14)-N(1)	172.1(3)
C(4)-C(3)-C(14)-C(13)	0.8(4)
C(2)-C(3)-C(14)-C(13)	-177.8(3)
C(4)-C(3)-C(14)-N(1)	-174.5(2)
C(2)-C(3)-C(14)-N(1)	6.9(3)
C(1)-N(1)-C(14)-C(13)	-169.5(3)
S(1)-N(1)-C(14)-C(13)	48.9(4)
C(1)-N(1)-C(14)-C(3)	5.4(3)
S(1)-N(1)-C(14)-C(3)	-136.2(2)
C(14)-N(1)-S(1)-O(2)	-45.9(3)
C(1)-N(1)-S(1)-O(2)	176.2(2)
C(14)-N(1)-S(1)-O(1)	-174.9(2)
C(1)-N(1)-S(1)-O(1)	47.2(3)
C(14)-N(1)-S(1)-C(15)	69.6(3)

C(1)-N(1)-S(1)-C(15)	-68.3(3)
O(2)-S(1)-C(15)-C(20)	24.6(3)
O(1)-S(1)-C(15)-C(20)	157.1(3)
N(1)-S(1)-C(15)-C(20)	-89.5(3)
O(2)-S(1)-C(15)-C(16)	-159.6(3)
O(1)-S(1)-C(15)-C(16)	-27.1(3)
N(1)-S(1)-C(15)-C(16)	86.3(3)
C(20)-C(15)-C(16)-C(17)	1.0(5)
S(1)-C(15)-C(16)-C(17)	-174.8(3)
C(15)-C(16)-C(17)-C(18)	-0.5(6)
C(16)-C(17)-C(18)-C(19)	-0.8(6)
C(16)-C(17)-C(18)-C(21)	179.4(4)
C(17)-C(18)-C(19)-C(20)	1.6(5)
C(21)-C(18)-C(19)-C(20)	-178.6(3)
C(16)-C(15)-C(20)-C(19)	-0.3(5)
S(1)-C(15)-C(20)-C(19)	175.5(3)
C(18)-C(19)-C(20)-C(15)	-1.1(5)
C(4)-C(5)-O(3)-Si(1)	67.3(3)
C(8)-C(5)-O(3)-Si(1)	-65.1(3)
C(6)-C(5)-O(3)-Si(1)	-164.9(2)
C(5)-O(3)-Si(1)-C(27)	-62.4(3)
C(5)-O(3)-Si(1)-C(26)	60.6(3)
C(5)-O(3)-Si(1)-C(22)	178.3(3)
O(3)-Si(1)-C(22)-C(25)	57.9(3)
C(27)-Si(1)-C(22)-C(25)	-60.4(3)
C(26)-Si(1)-C(22)-C(25)	179.2(3)
O(3)-Si(1)-C(22)-C(23)	178.4(3)
C(27)-Si(1)-C(22)-C(23)	60.0(3)
C(26)-Si(1)-C(22)-C(23)	-60.3(4)
O(3)-Si(1)-C(22)-C(24)	-62.8(3)

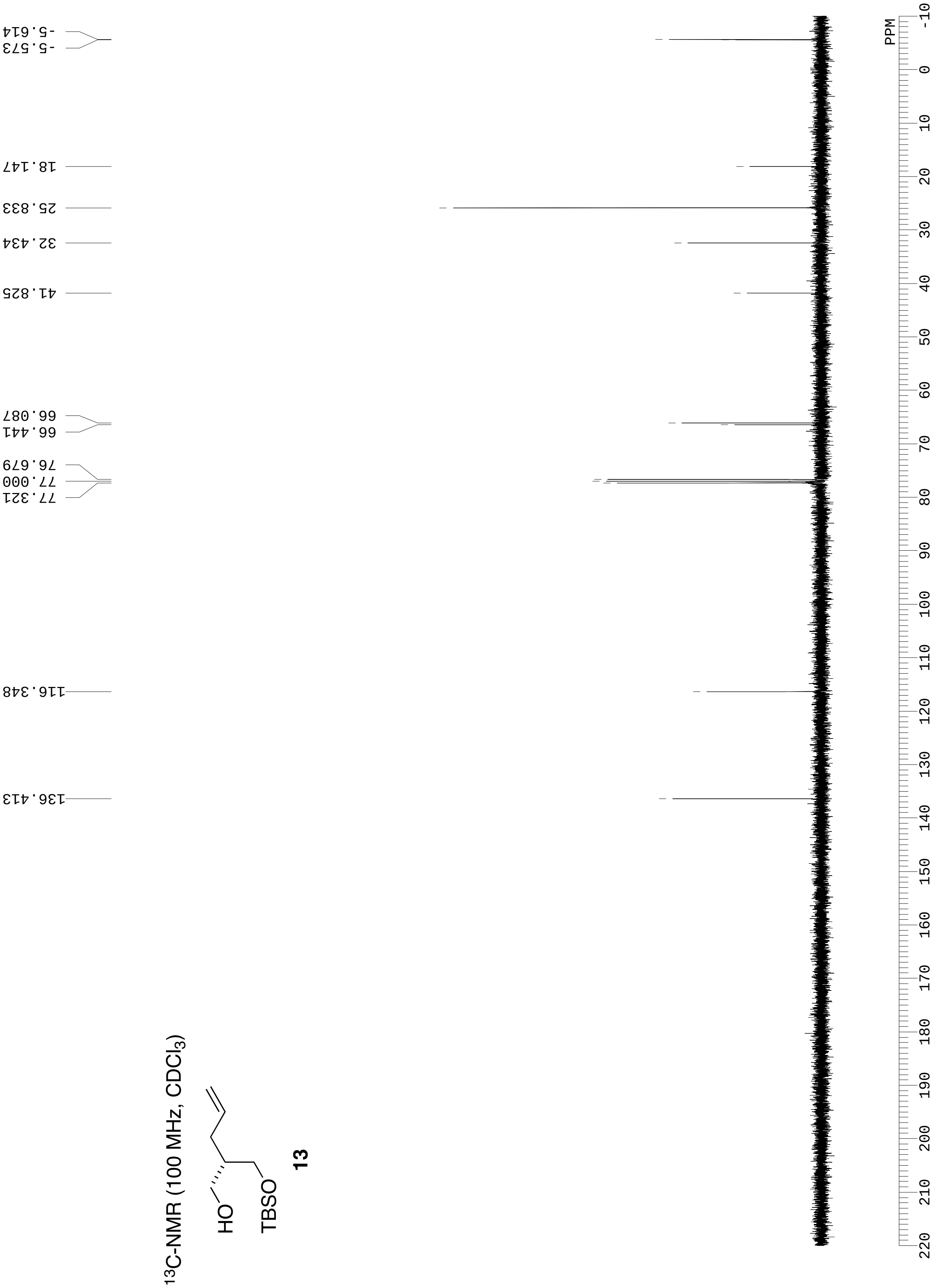
C(27)-Si(1)-C(22)-C(24)	178.8(3)
C(26)-Si(1)-C(22)-C(24)	58.4(3)
C(7)-C(6)-C(28)-O(5)	-13.6(5)
C(5)-C(6)-C(28)-O(5)	84.5(4)
C(7)-C(6)-C(28)-O(4)	167.2(3)
C(5)-C(6)-C(28)-O(4)	-94.7(3)
O(5)-C(28)-O(4)-C(29)	-3.5(5)
C(6)-C(28)-O(4)-C(29)	175.8(3)

Symmetry transformations used to generate equivalent atoms:



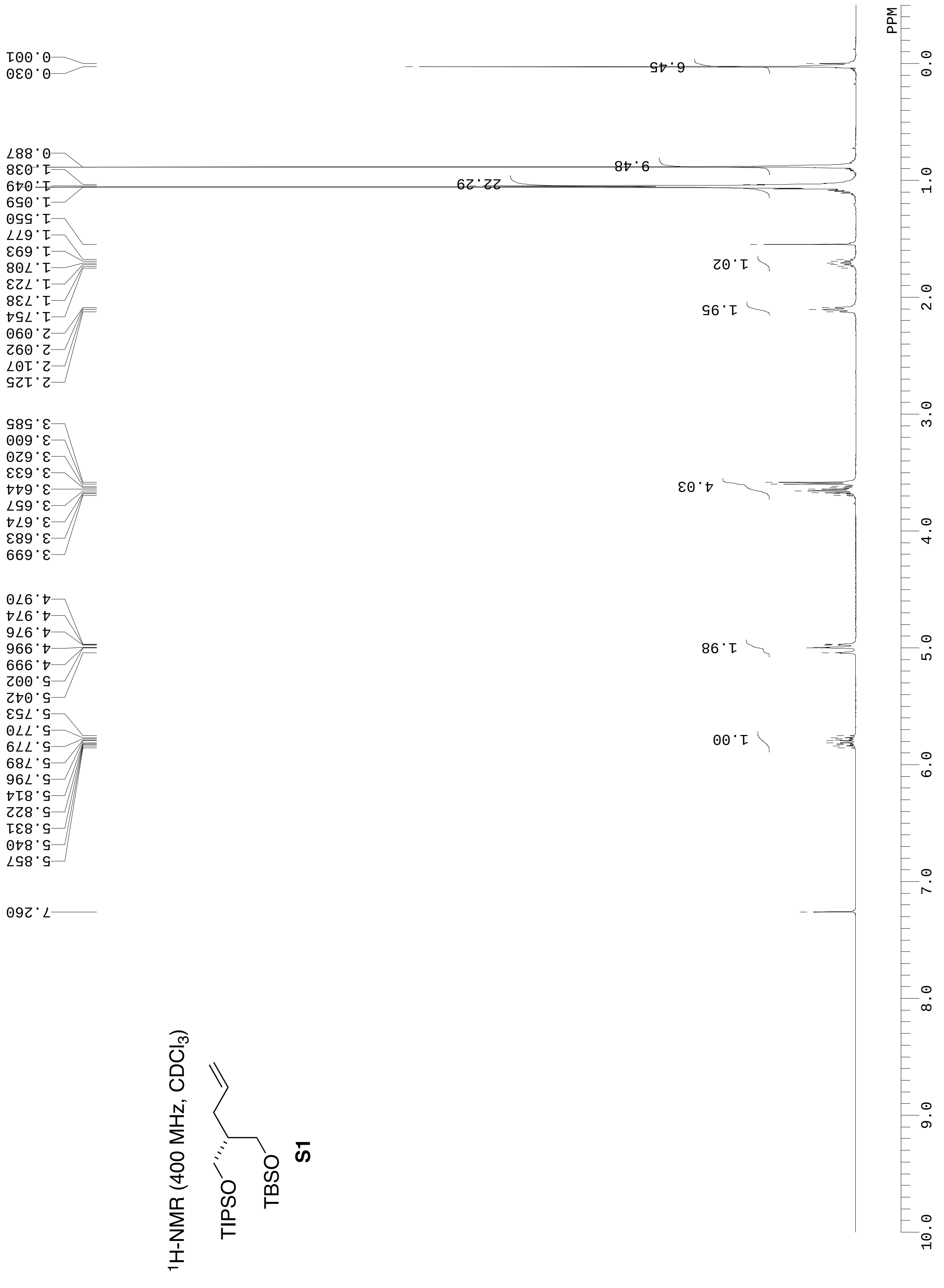
^{1}H-NMR (400 MHz, $CDCl_3$)

13



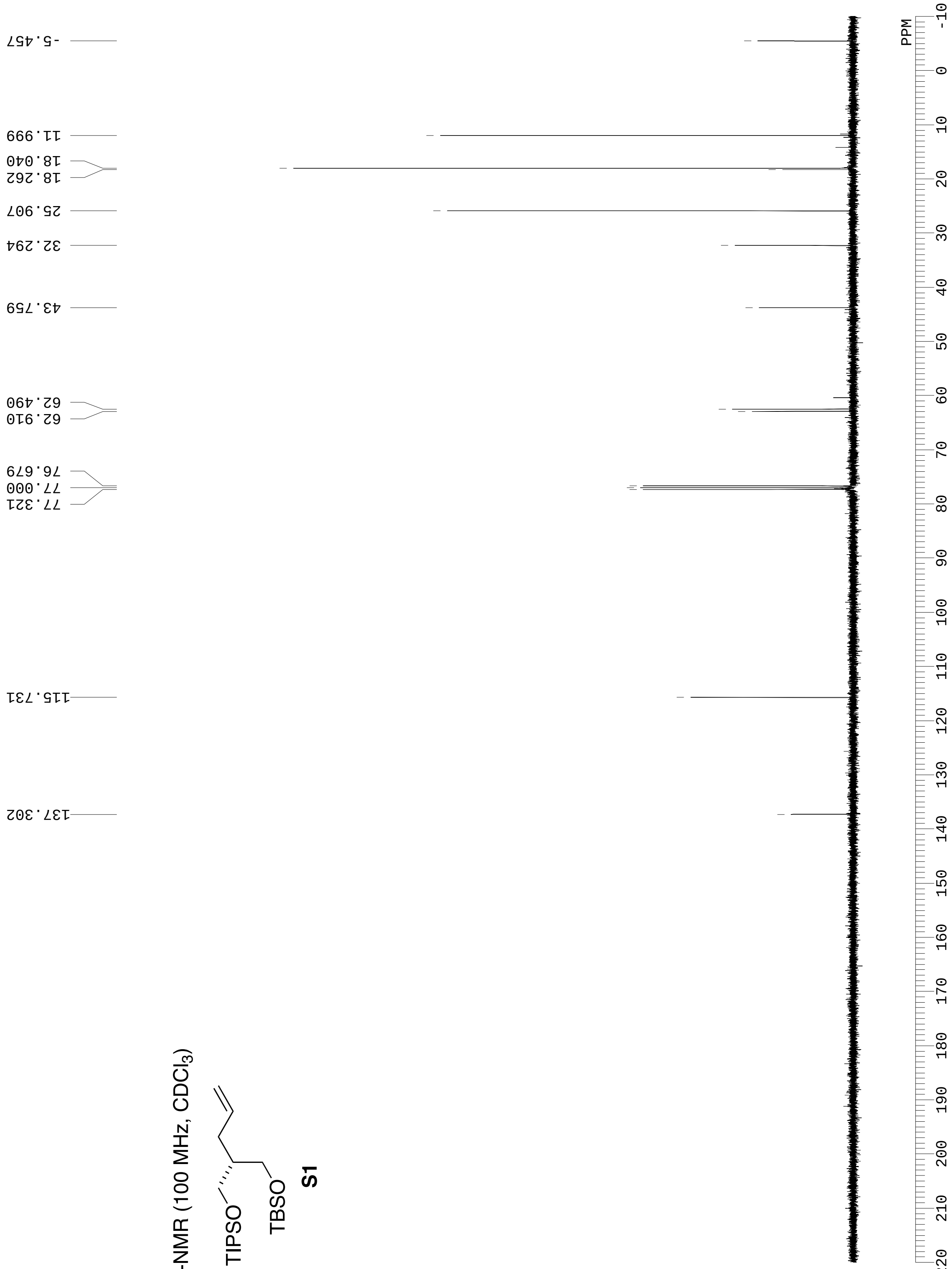
^{13}C-NMR (100 MHz, CDCl$_3$)

13



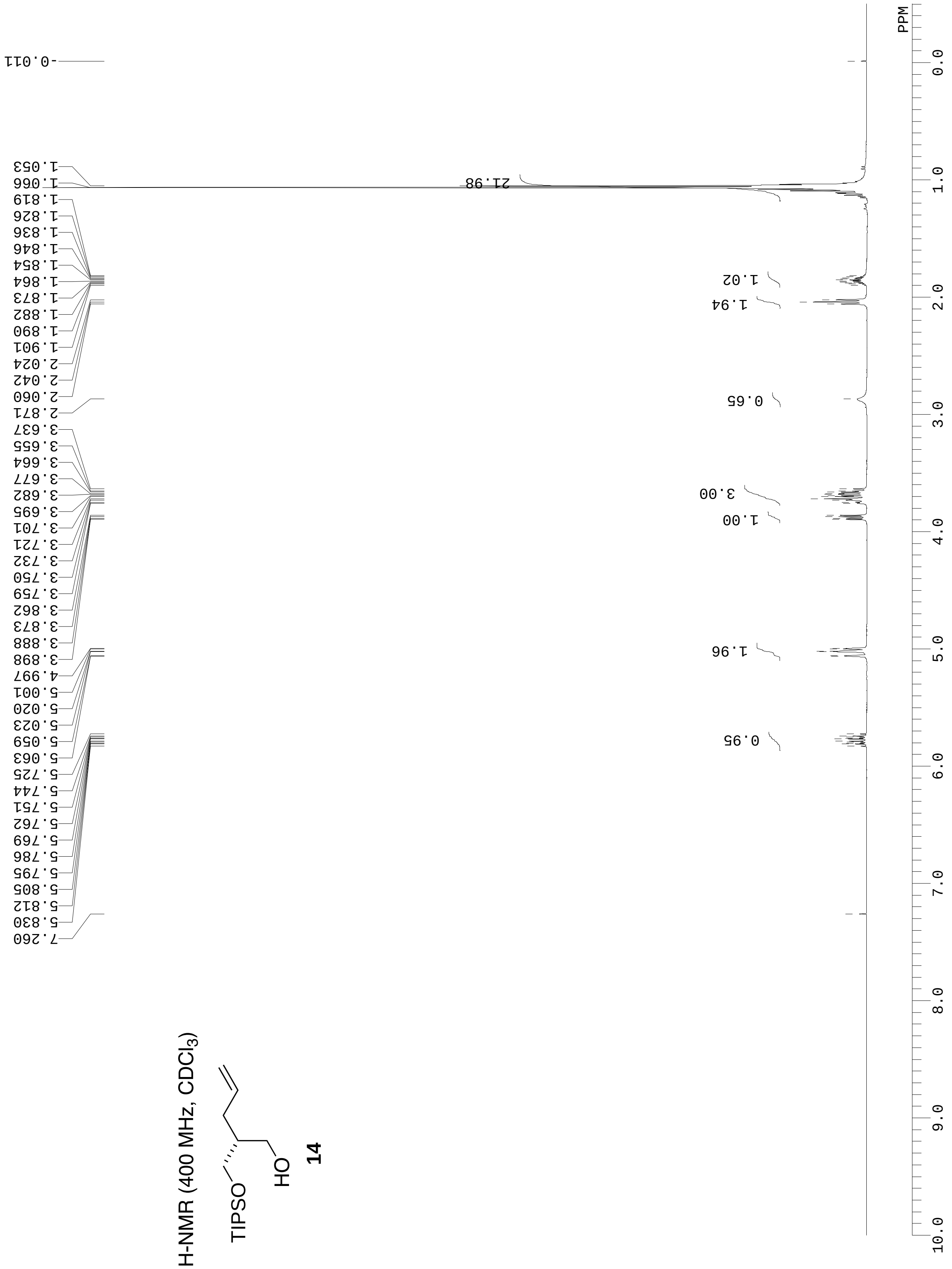
^{1}H-NMR (400 MHz, $CDCl_3$)

S1



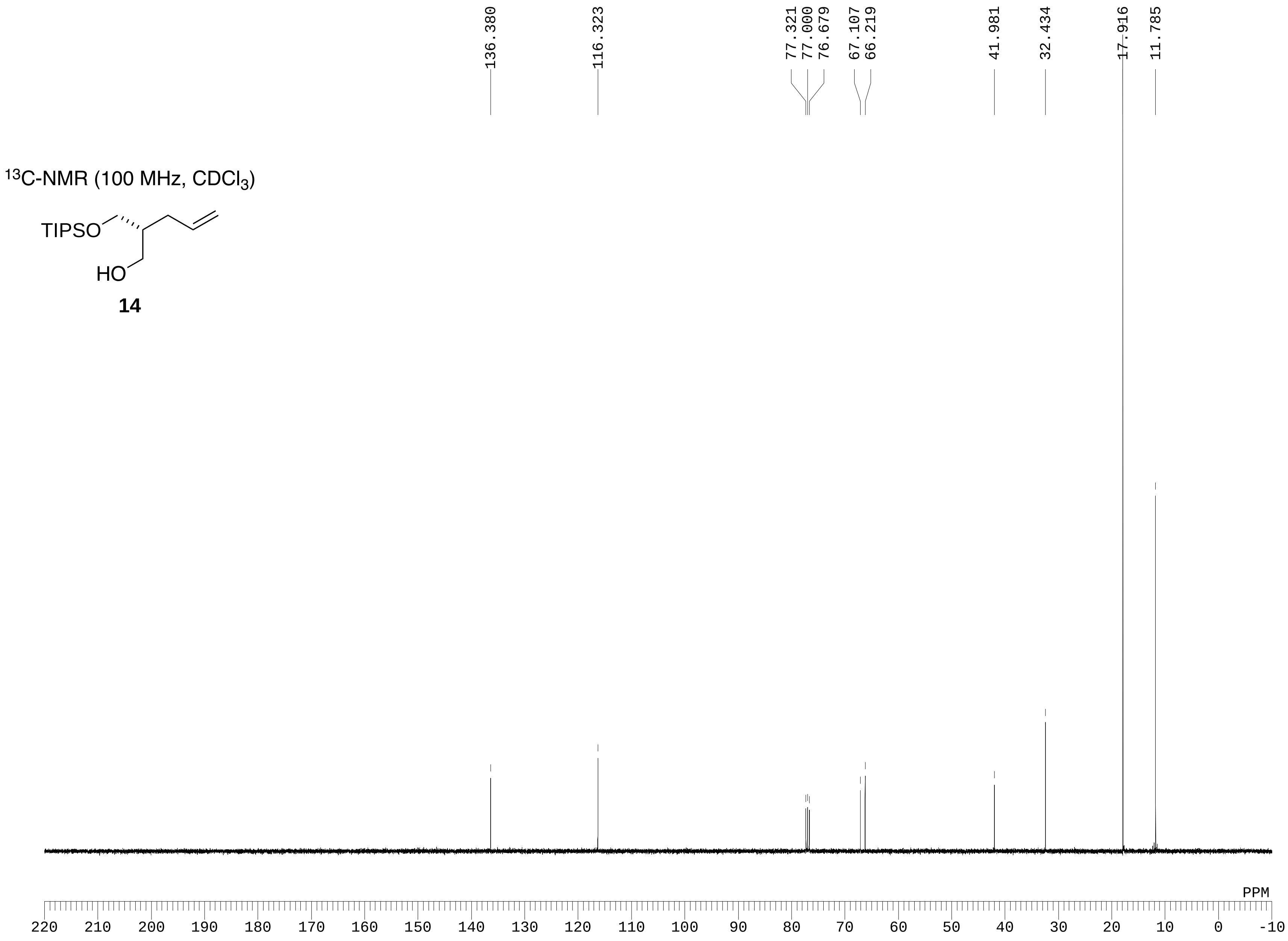
^{13}C-NMR (100 MHz, CDCl$_3$)

S1



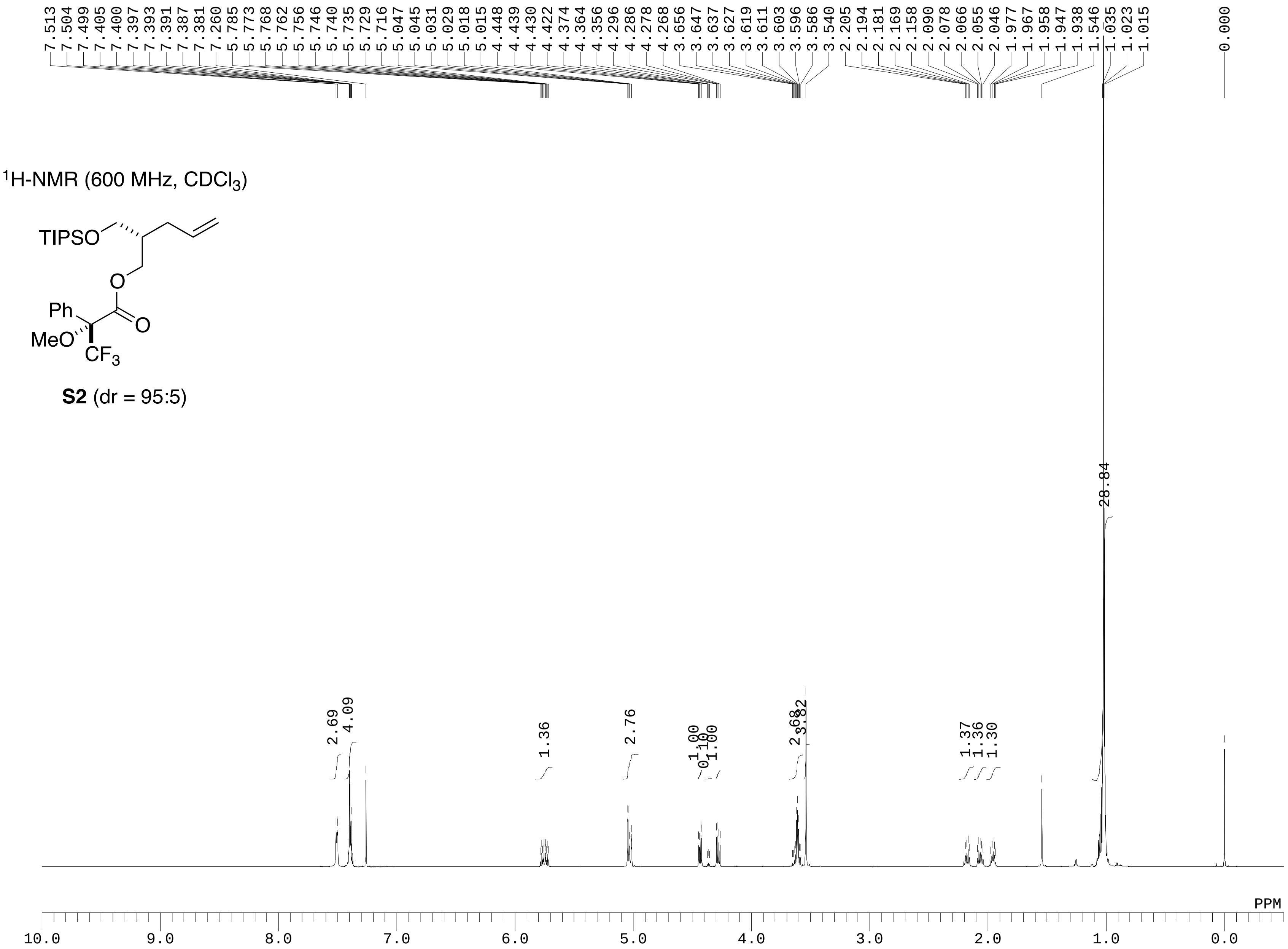
^{1}H-NMR (400 MHz, CDCl$_3$)

14



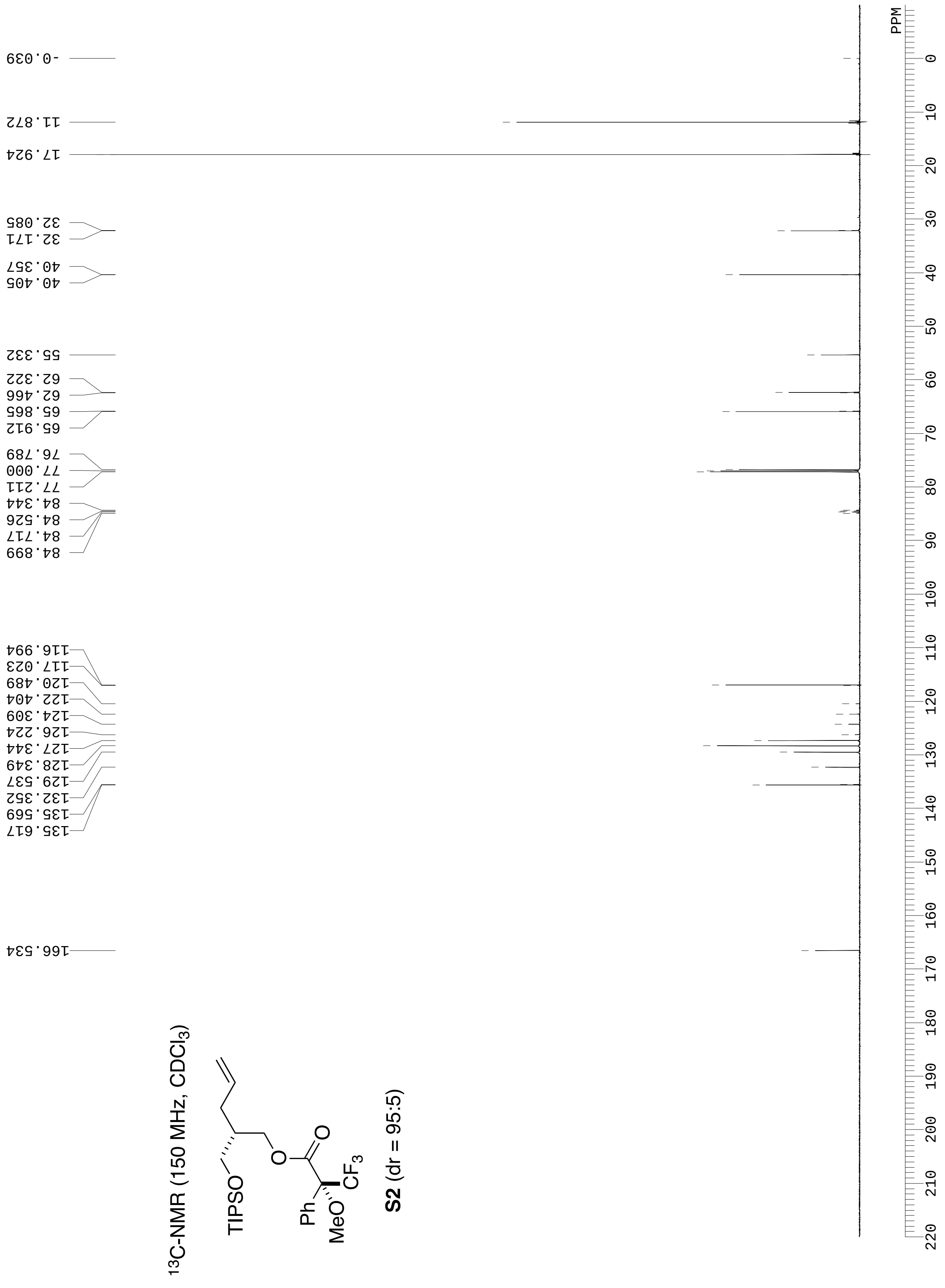
^{13}C-NMR (100 MHz, CDCl$_3$)

14



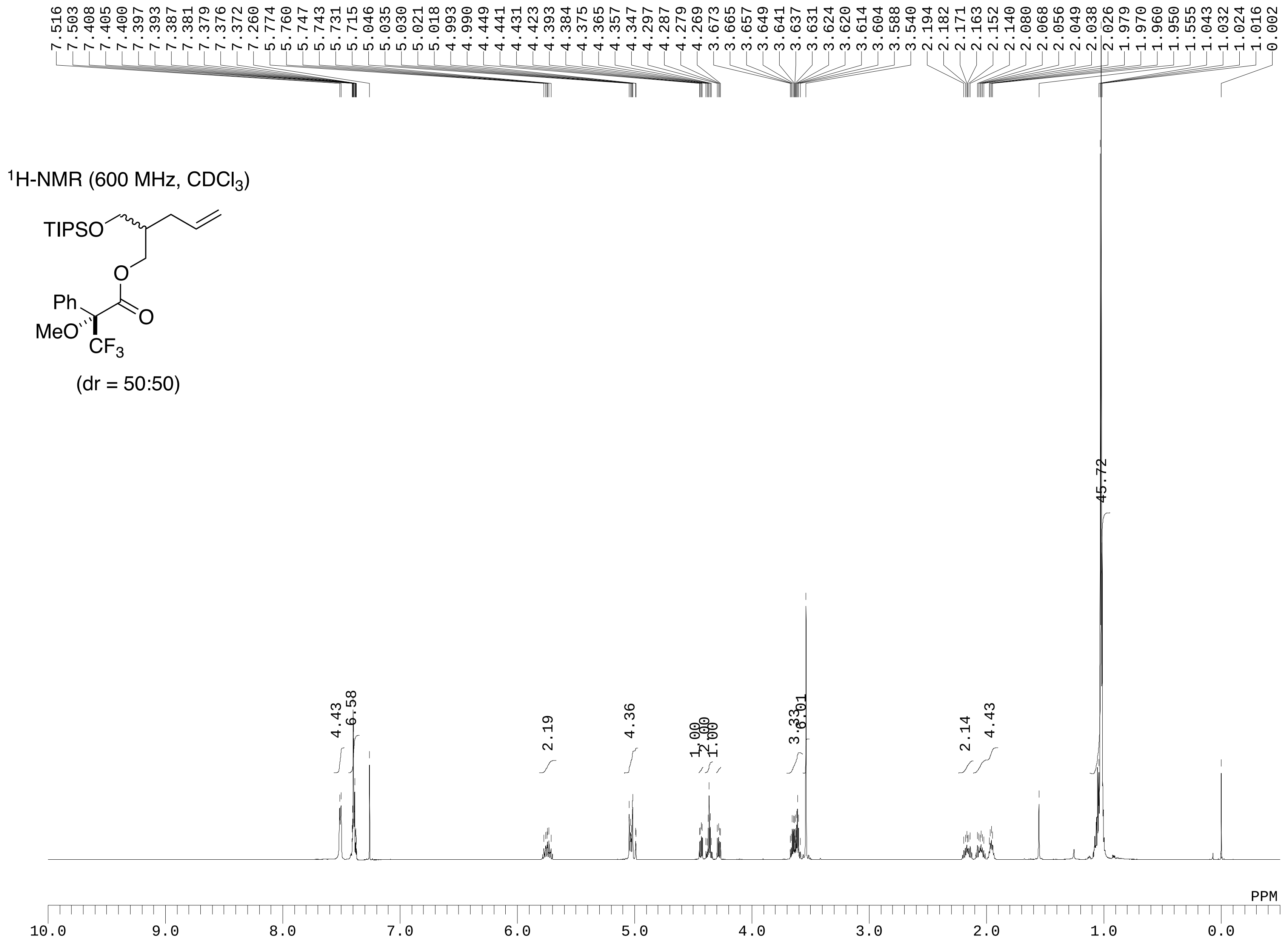
^{1}H-NMR (600 MHz, $CDCl_3$)

S2 (dr = 95:5)



^{13}C-NMR (150 MHz, $CDCl_3$)

S2 (dr = 95:5)


1H-NMR (600 MHz, CDCl3)
TIPSO
O
O
Ph
MeO
CF3
(dr = 50:50)
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7.503
7.408
7.405
7.400
7.397
7.393
7.387
7.381
7.379
7.376
7.372
7.260
5.774
5.760
5.747
5.743
5.731
5.715
5.046
5.035
5.030
5.021
5.018
4.993
4.990
4.449
4.441
4.431
4.423
4.393
4.384
4.375
4.365
4.357
4.347
4.297
4.287
4.279
4.269
3.673
3.665
3.657
3.649
3.641
3.637
3.631
3.624
3.620
3.614
3.604
3.588
3.540
2.194
2.182
2.171
2.163
2.152
2.140
2.080
2.068
2.056
2.049
2.038
2.026
1.979
1.970
1.960
1.950
1.555
1.043
1.032
1.024
1.016
0.002
4.43
6.58
2.19
4.36
1.00
2.00
1.00
3.33
6.01
2.14
4.43
45.72
PPM
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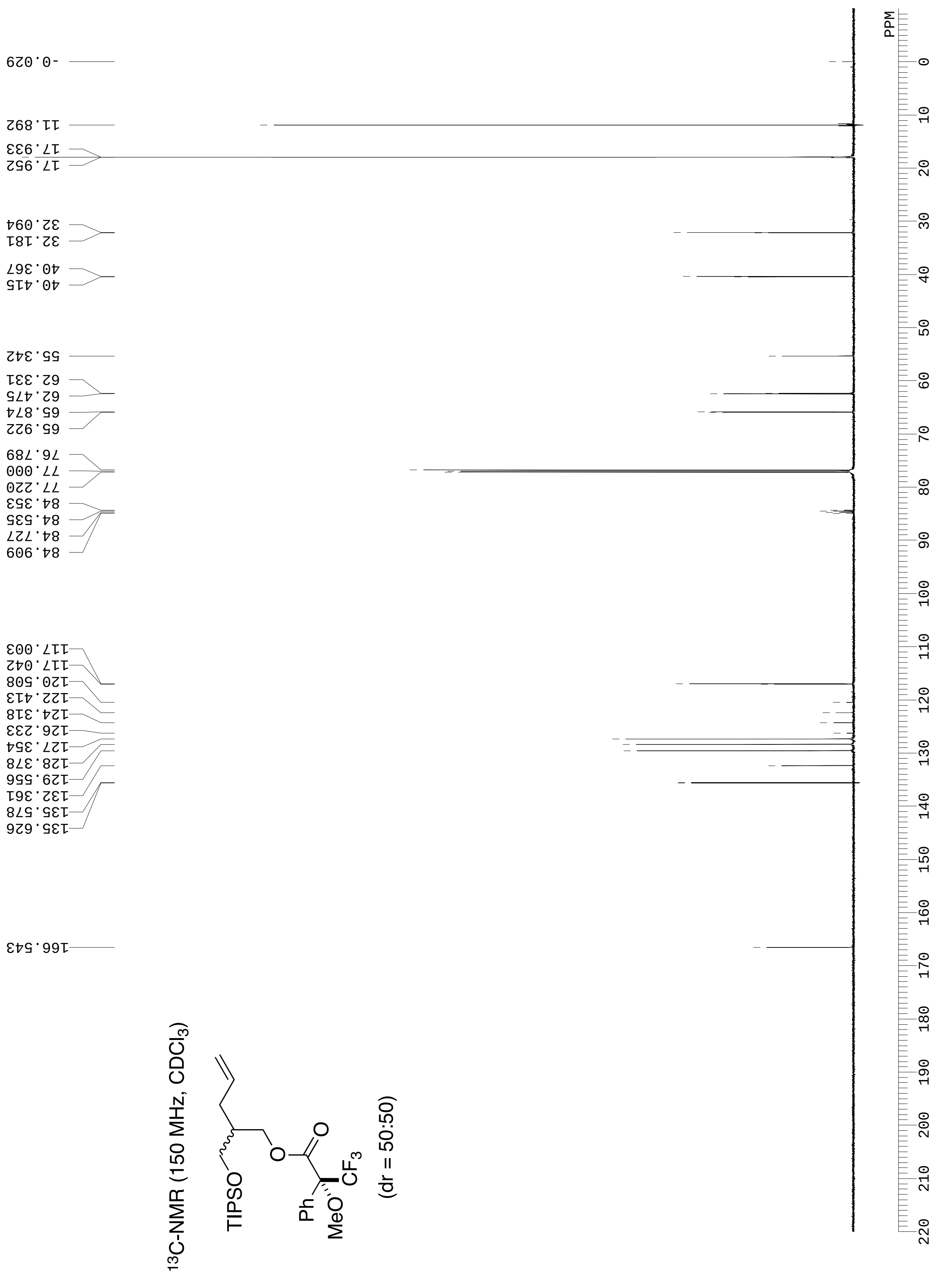
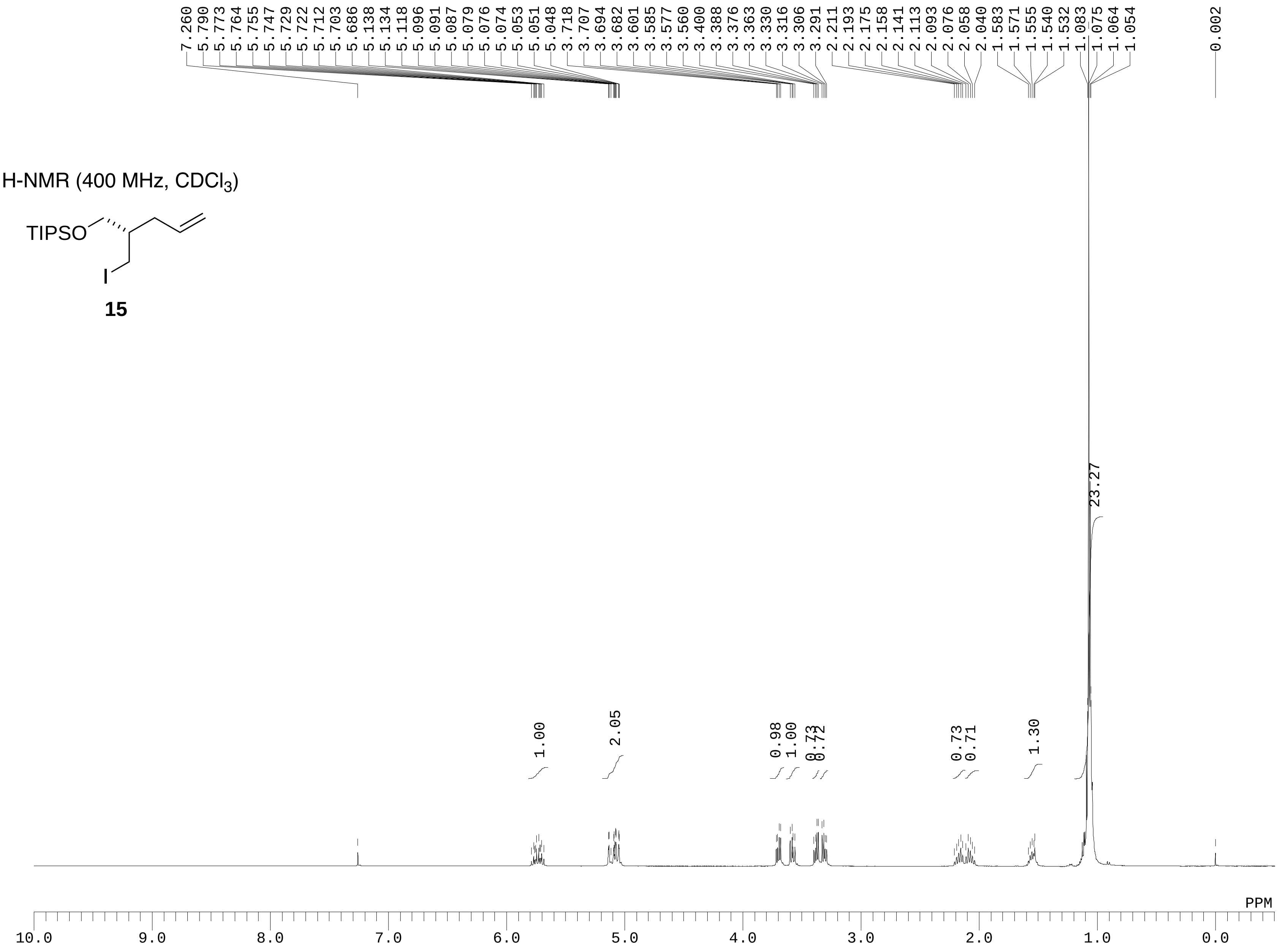
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



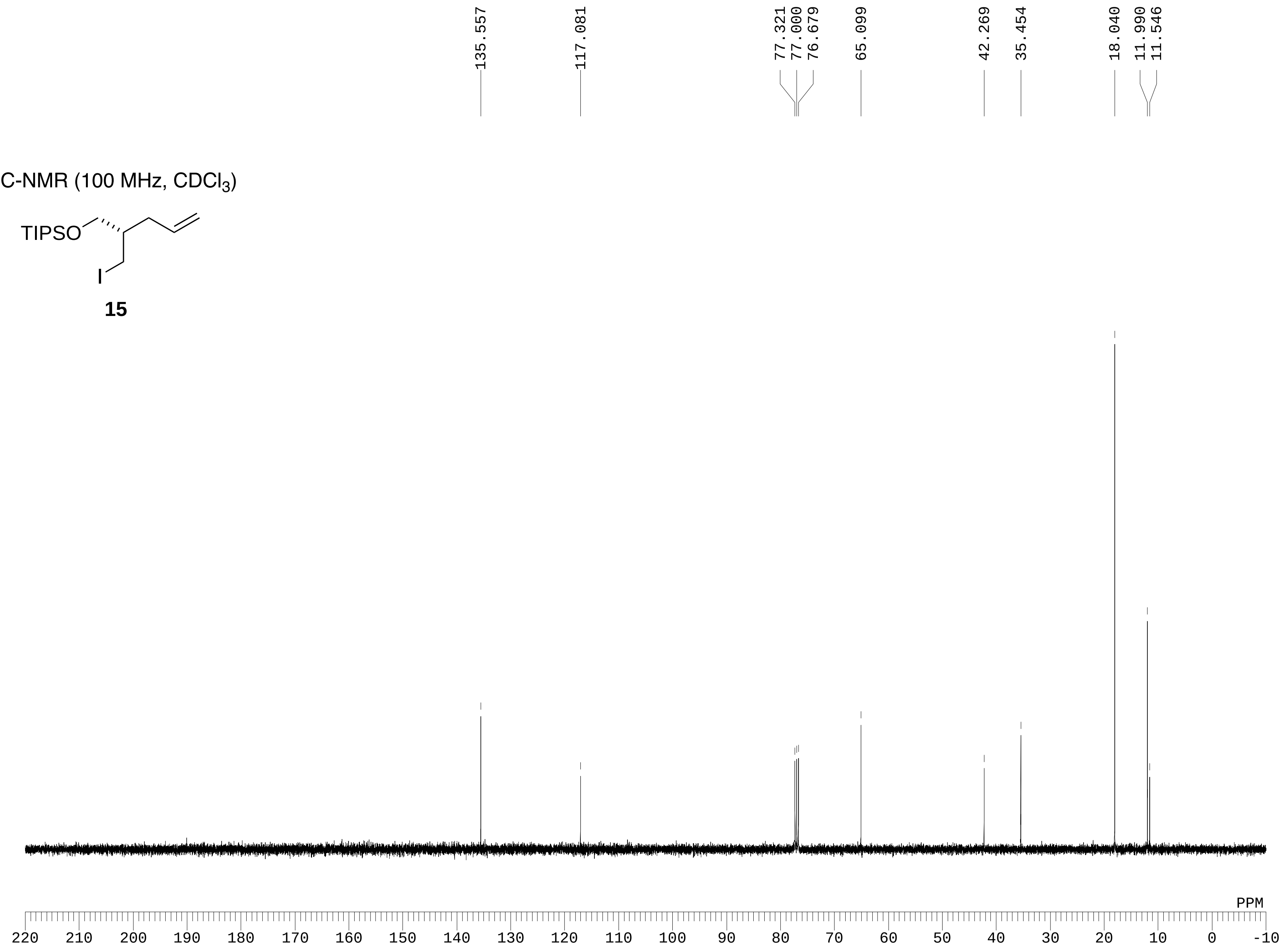
^{13}C-NMR (150 MHz, $CDCl_3$)

(dr = 50:50)



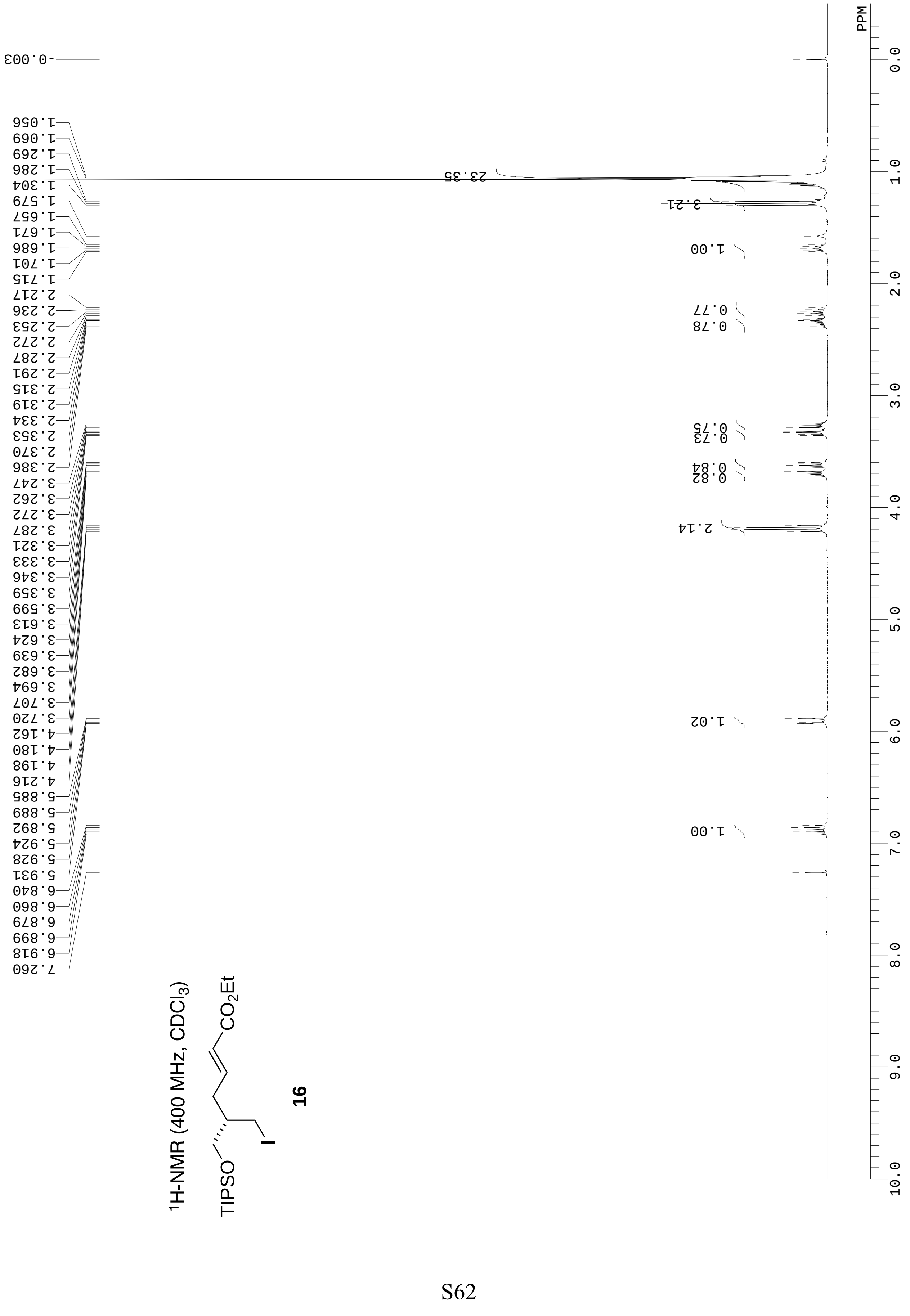
^{1}H-NMR (400 MHz, CDCl$_3$)

15



^{13}C-NMR (100 MHz, $CDCl_3$)

15


1H-NMR (400 MHz, CDCl3)
TIPSO
I
CO2Et
-0.003
1.056
1.069
1.269
1.286
1.304
1.579
1.657
1.671
1.686
1.701
1.715
2.217
2.236
2.253
2.272
2.287
2.291
2.315
2.319
2.334
2.353
2.370
2.386
3.247
3.262
3.272
3.287
3.321
3.333
3.346
3.359
3.599
3.613
3.624
3.639
3.682
3.694
3.707
3.720
4.162
4.180
4.198
4.216
5.885
5.889
5.892
5.924
5.928
5.931
6.840
6.860
6.879
6.899
6.918
7.260
23.35
3.21
1.00
0.77
0.78
0.75
0.73
0.84
0.82
2.14
1.02
1.00
PPM
0.0
1.0
2.0
3.0
4.0
5.0
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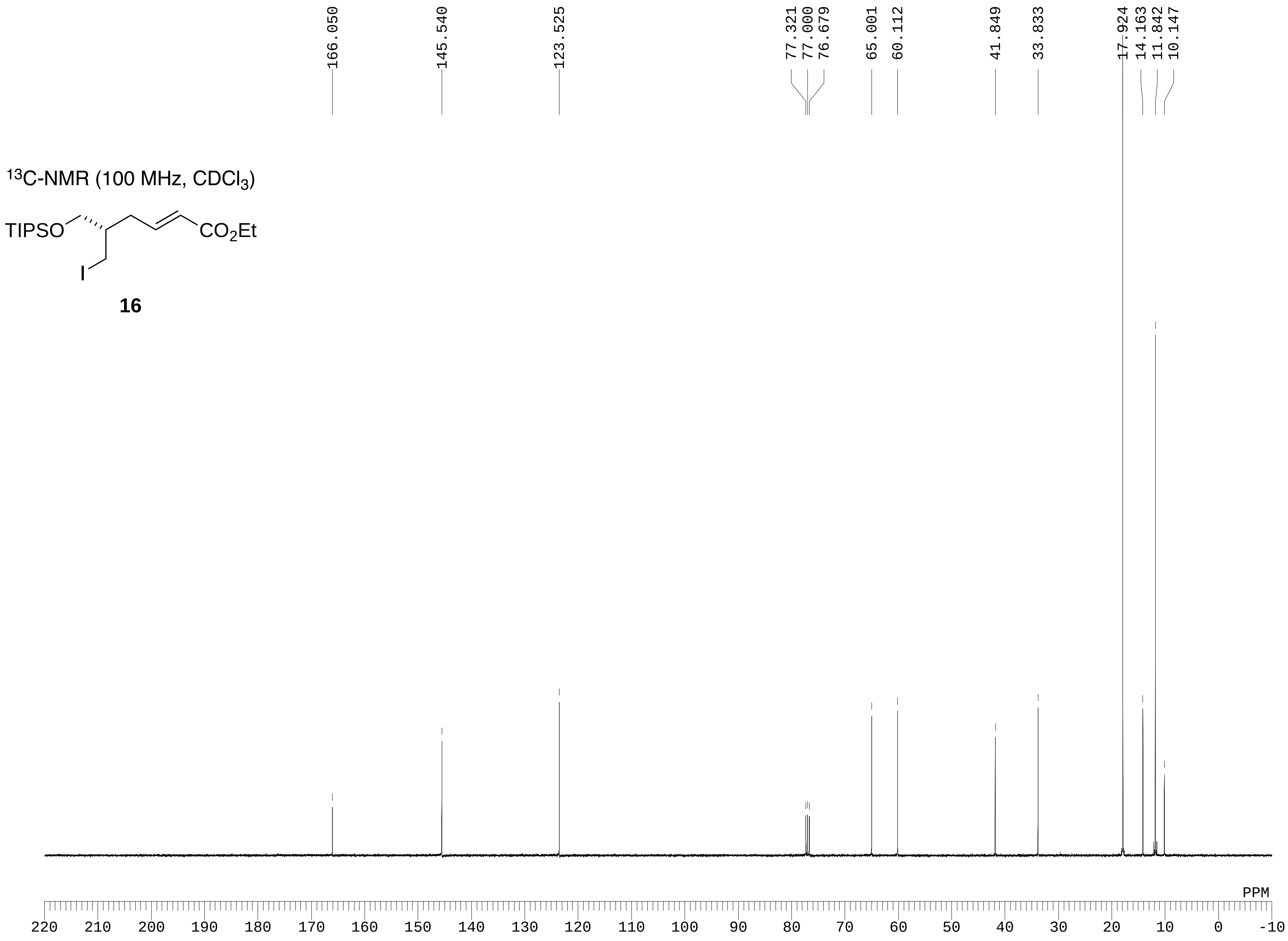
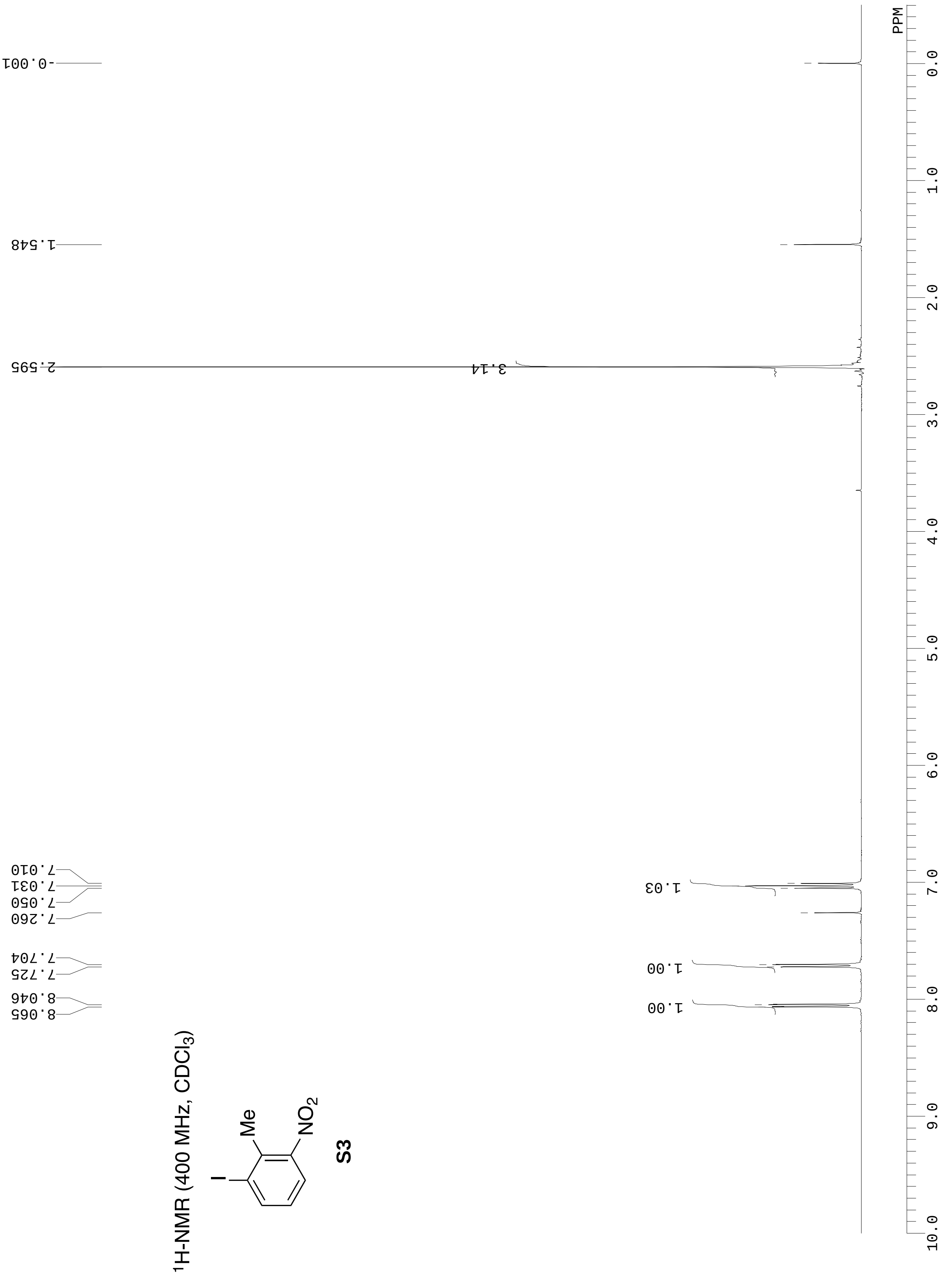
7.0
8.0
9.0
10.0

16



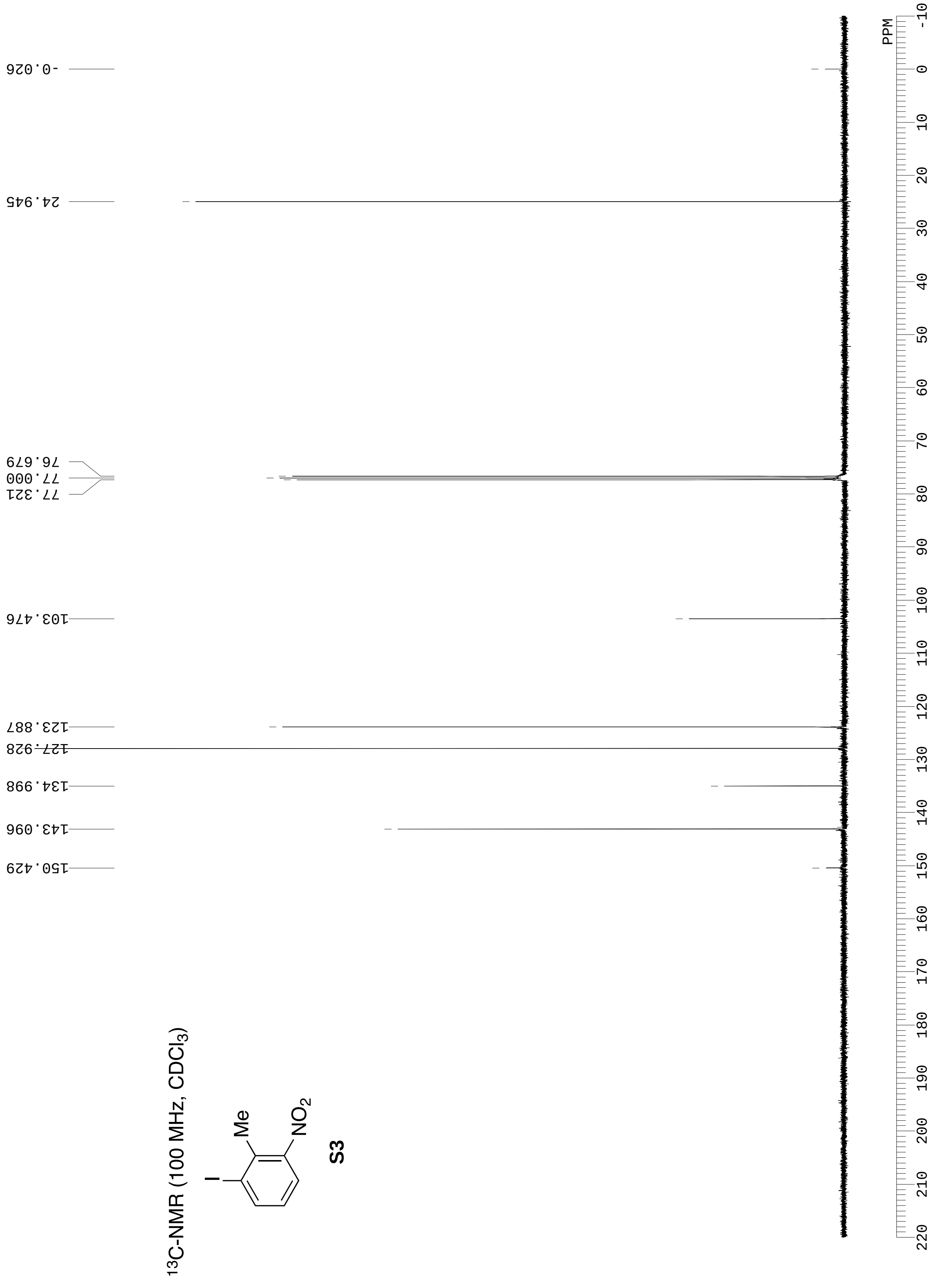
^{13}C-NMR (100 MHz, CDCl$_3$)

16

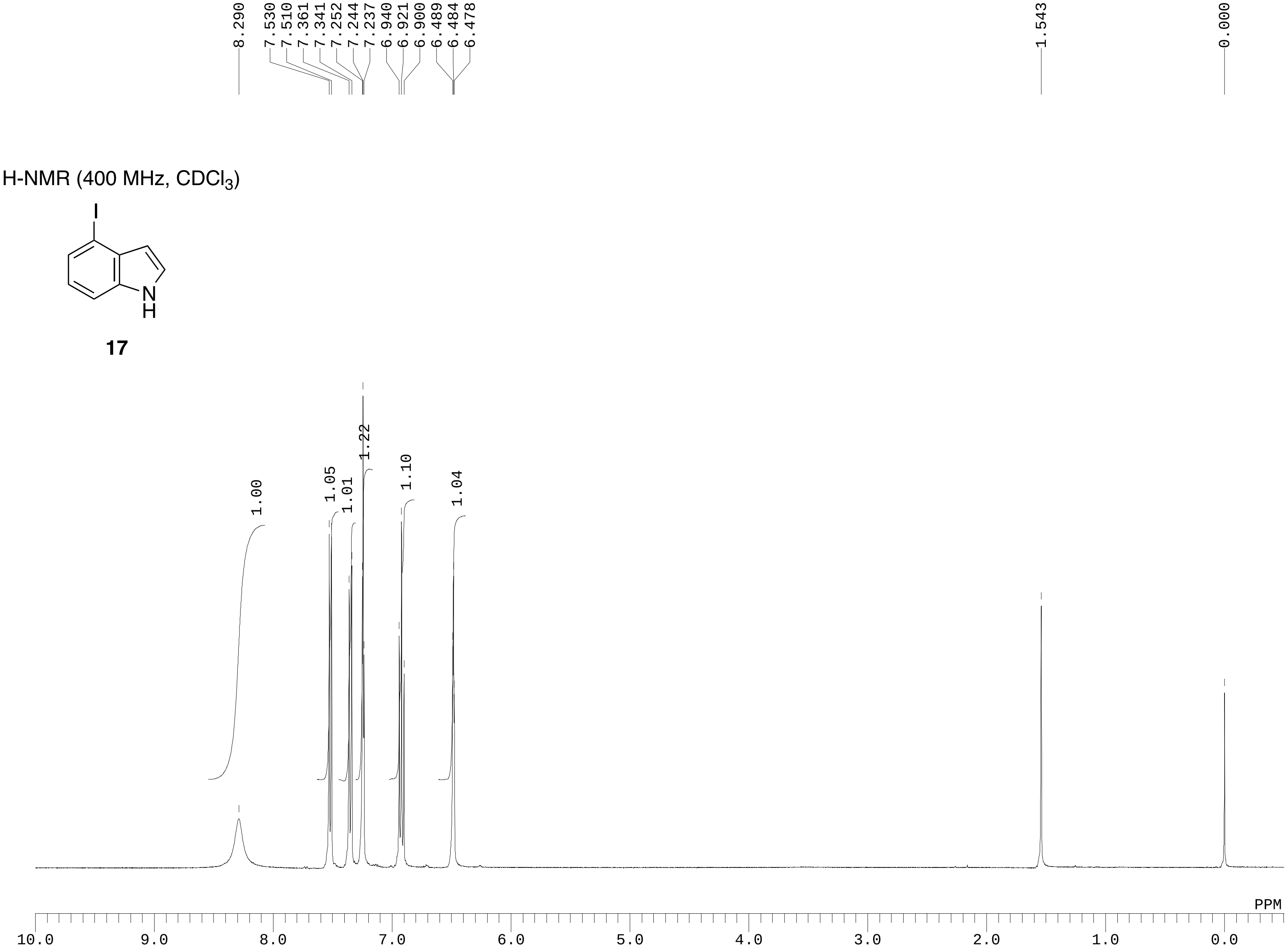


^{1}H-NMR (400 MHz, CDCl$_3$)

S3



13C-NMR (100 MHz, CDCl3)
I
Me
NO2
S3
-0.026
24.945
76.679
77.000
77.321
103.476
123.887
127.928
134.998
143.096
150.429
PPM
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

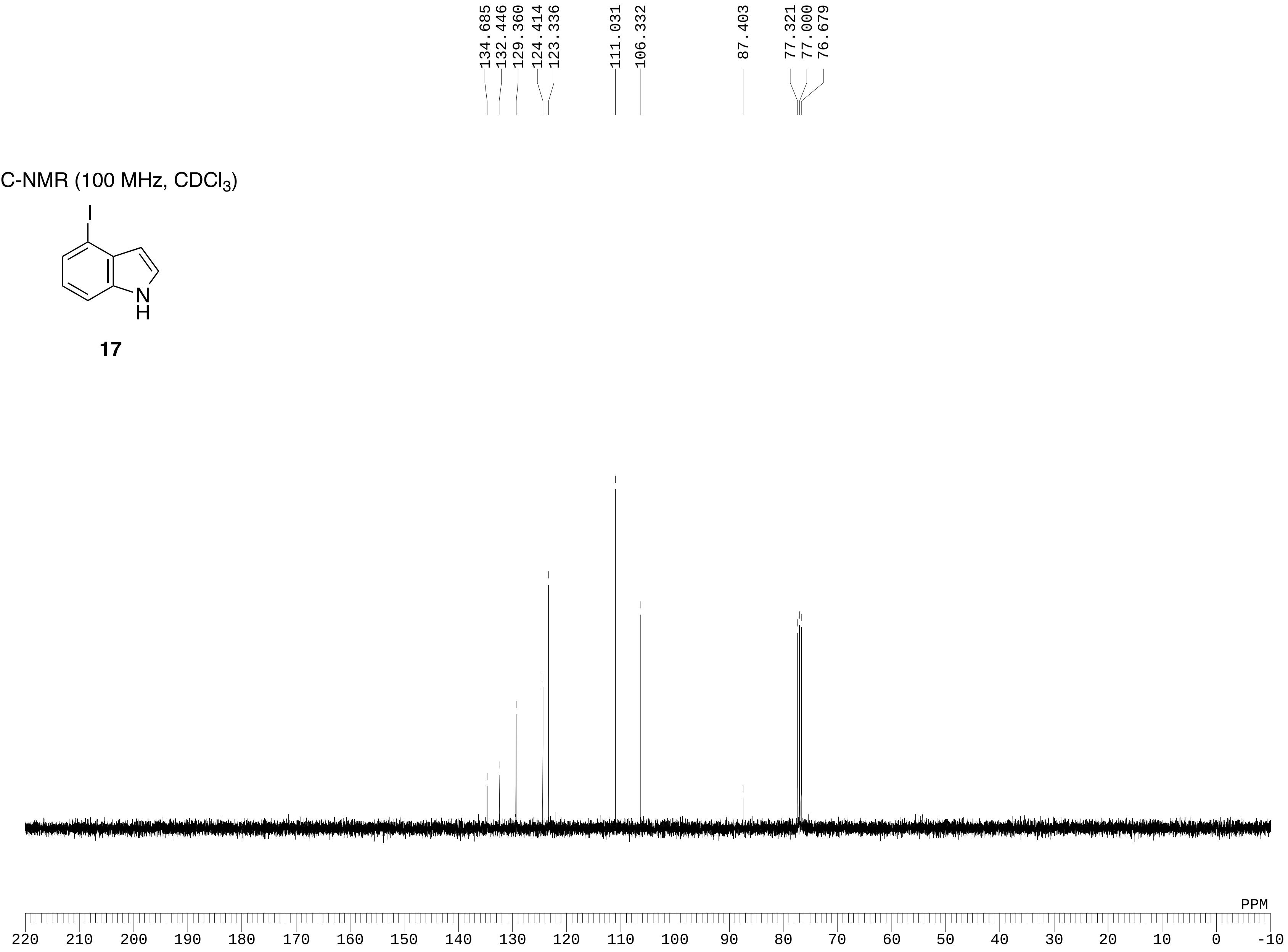


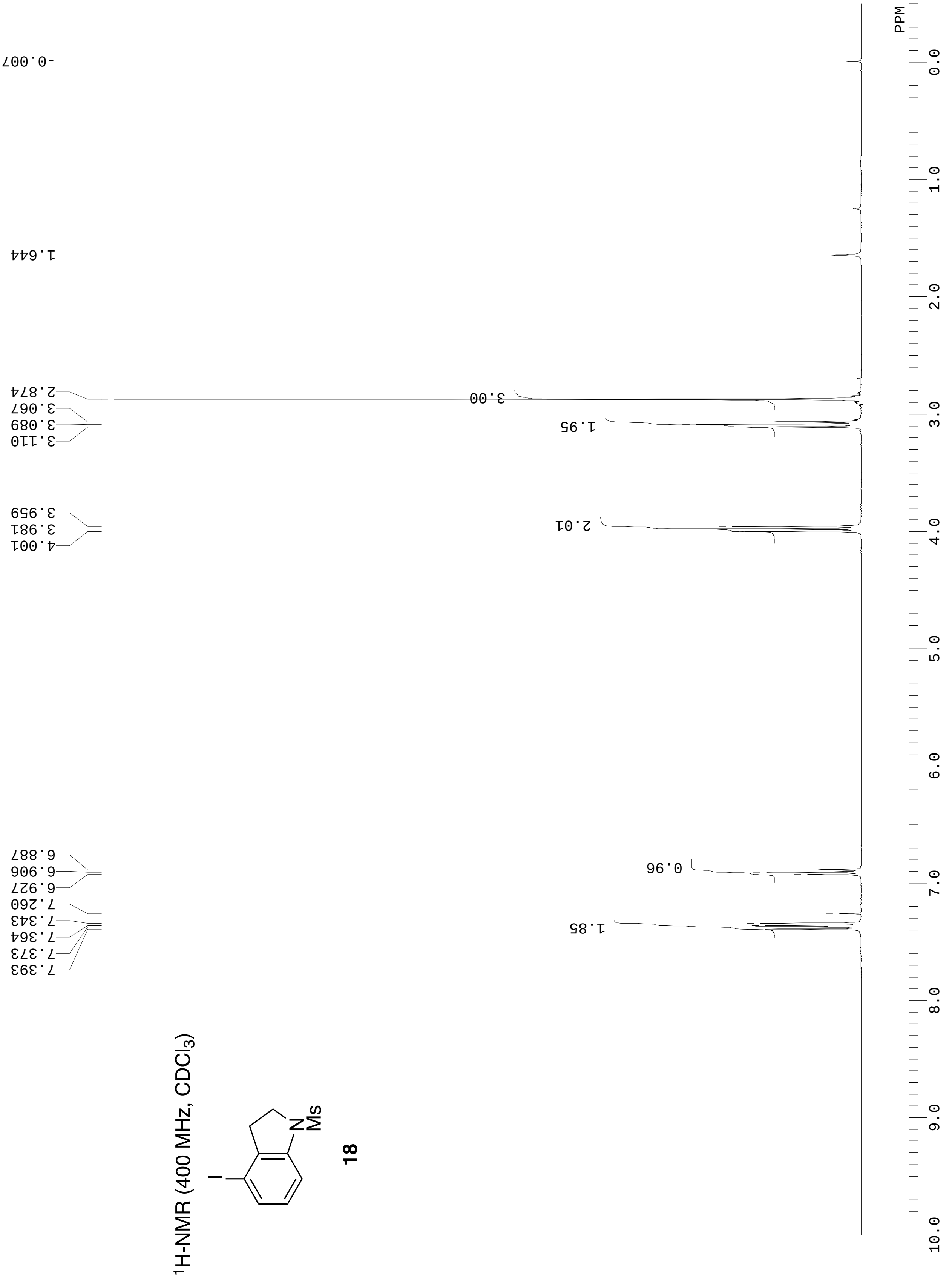
^{1}H-NMR (400 MHz, $CDCl_3$)

17

^{13}C-NMR (100 MHz, $CDCl_3$)

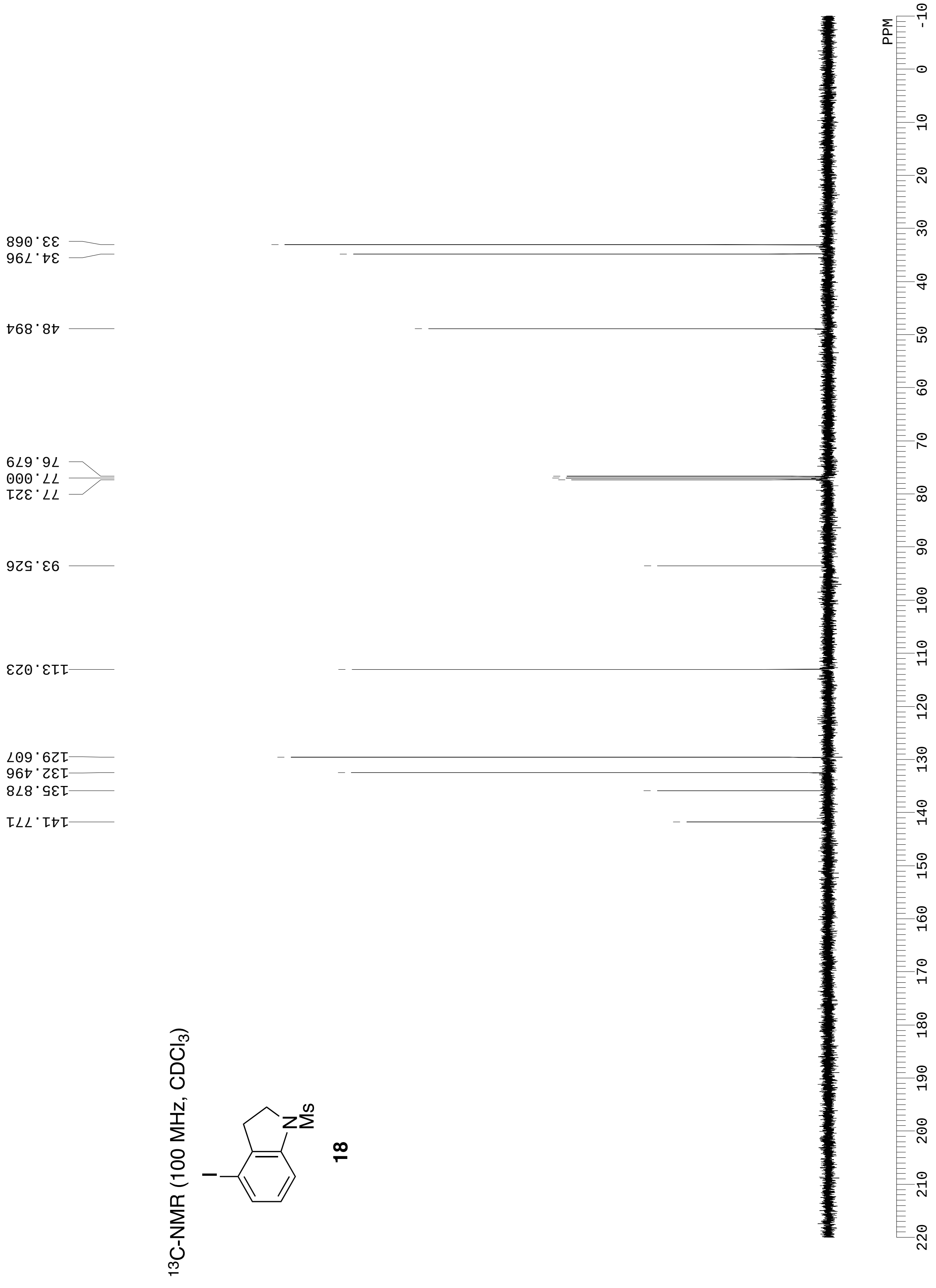
17





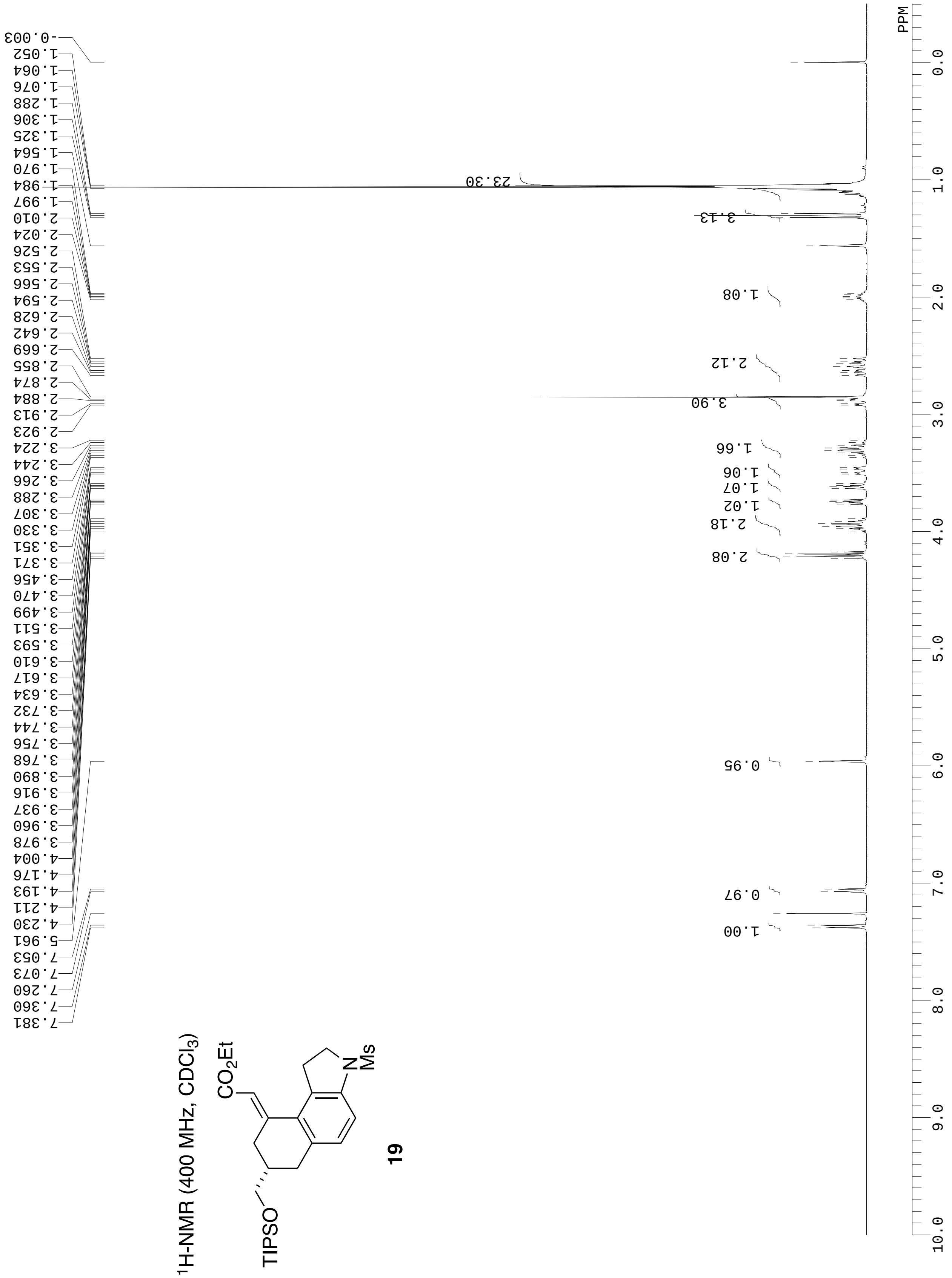
^{1}H-NMR (400 MHz, $CDCl_3$)

18



^{13}C-NMR (100 MHz, CDCl$_3$)

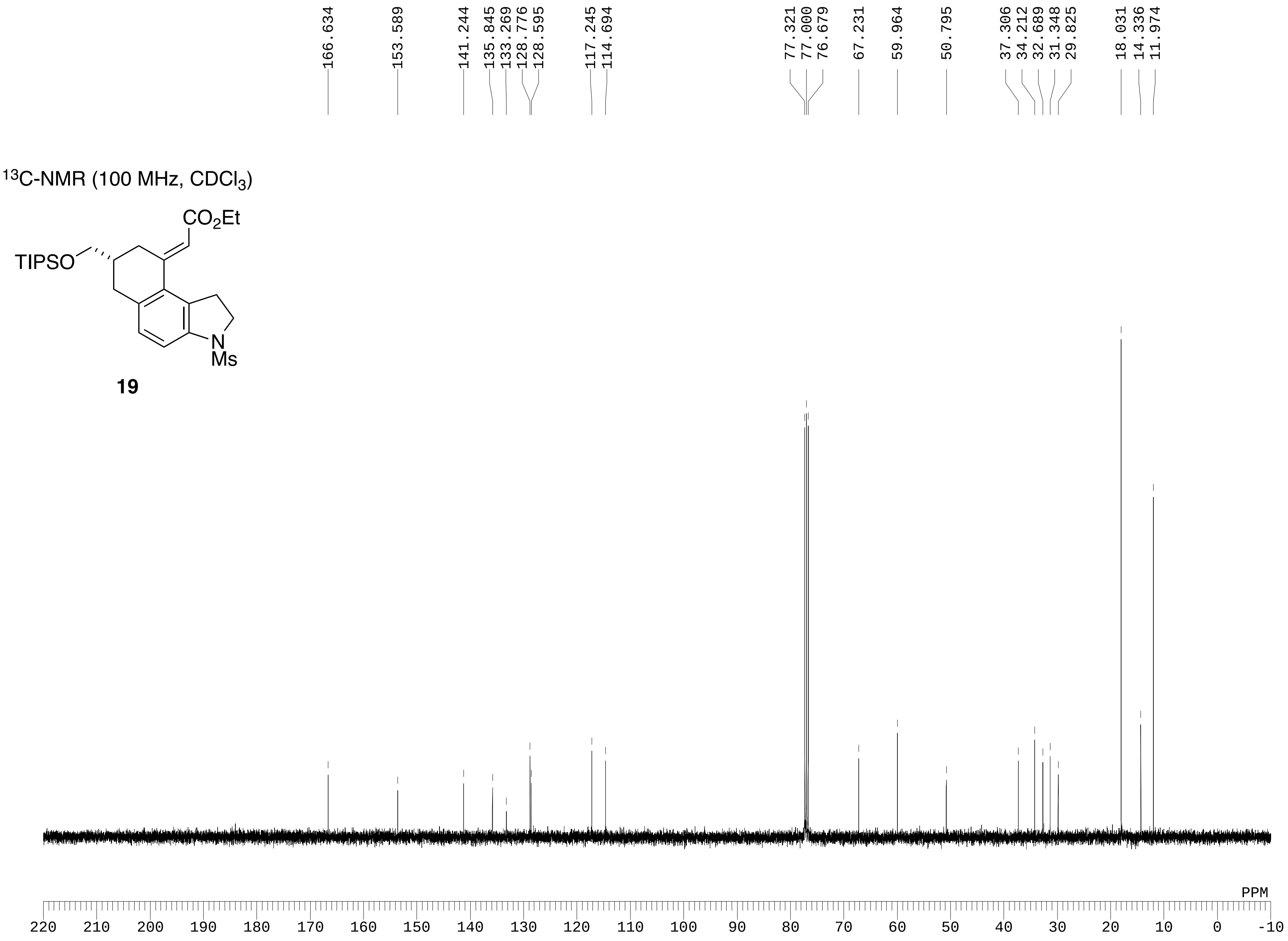
18



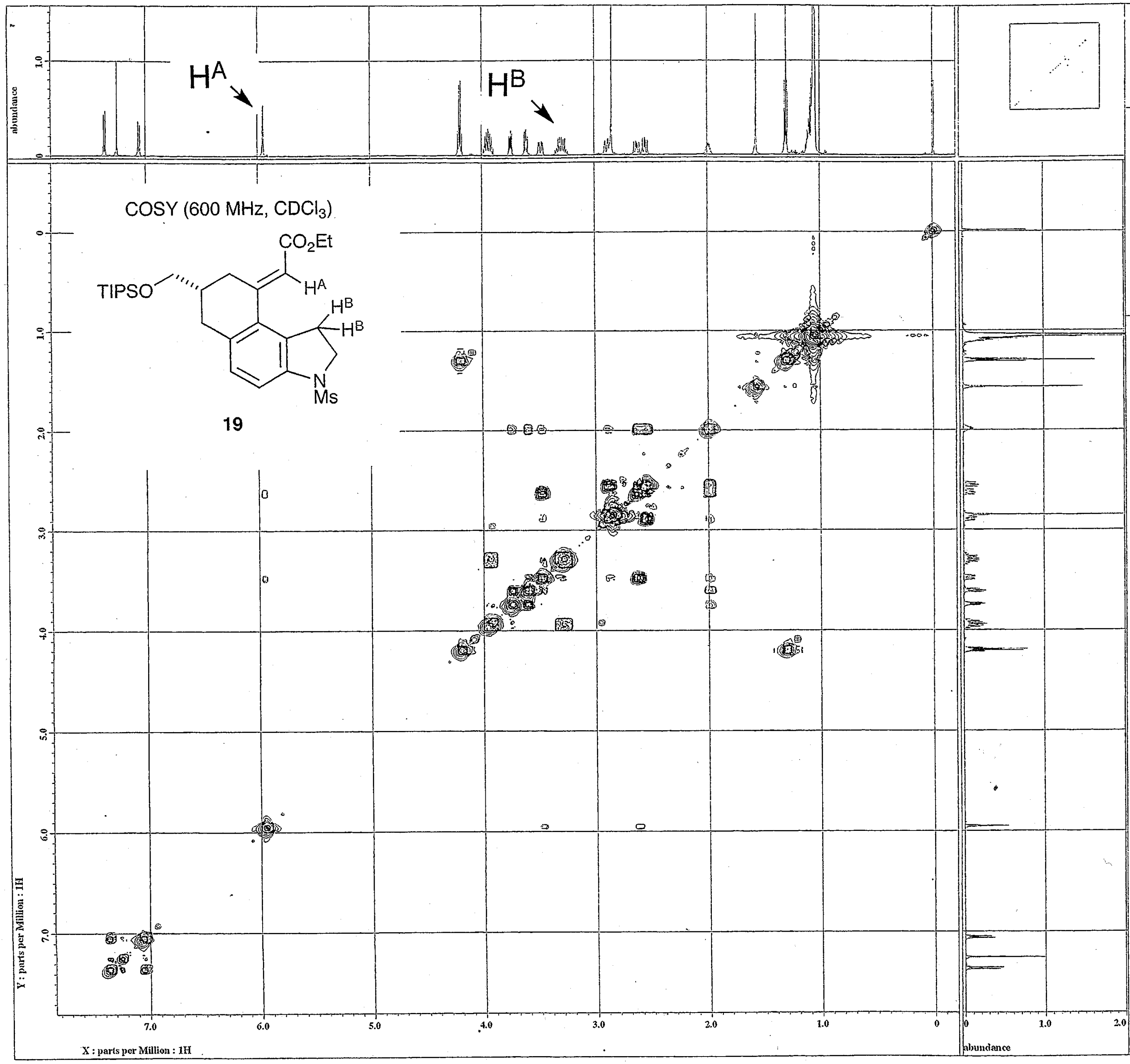
^{1}H-NMR (400 MHz, CDCl$_3$)

19

^{13}C-NMR (100 MHz, CDCl$_3$)



19



COSY (600 MHz, $CDCl_3$)

19

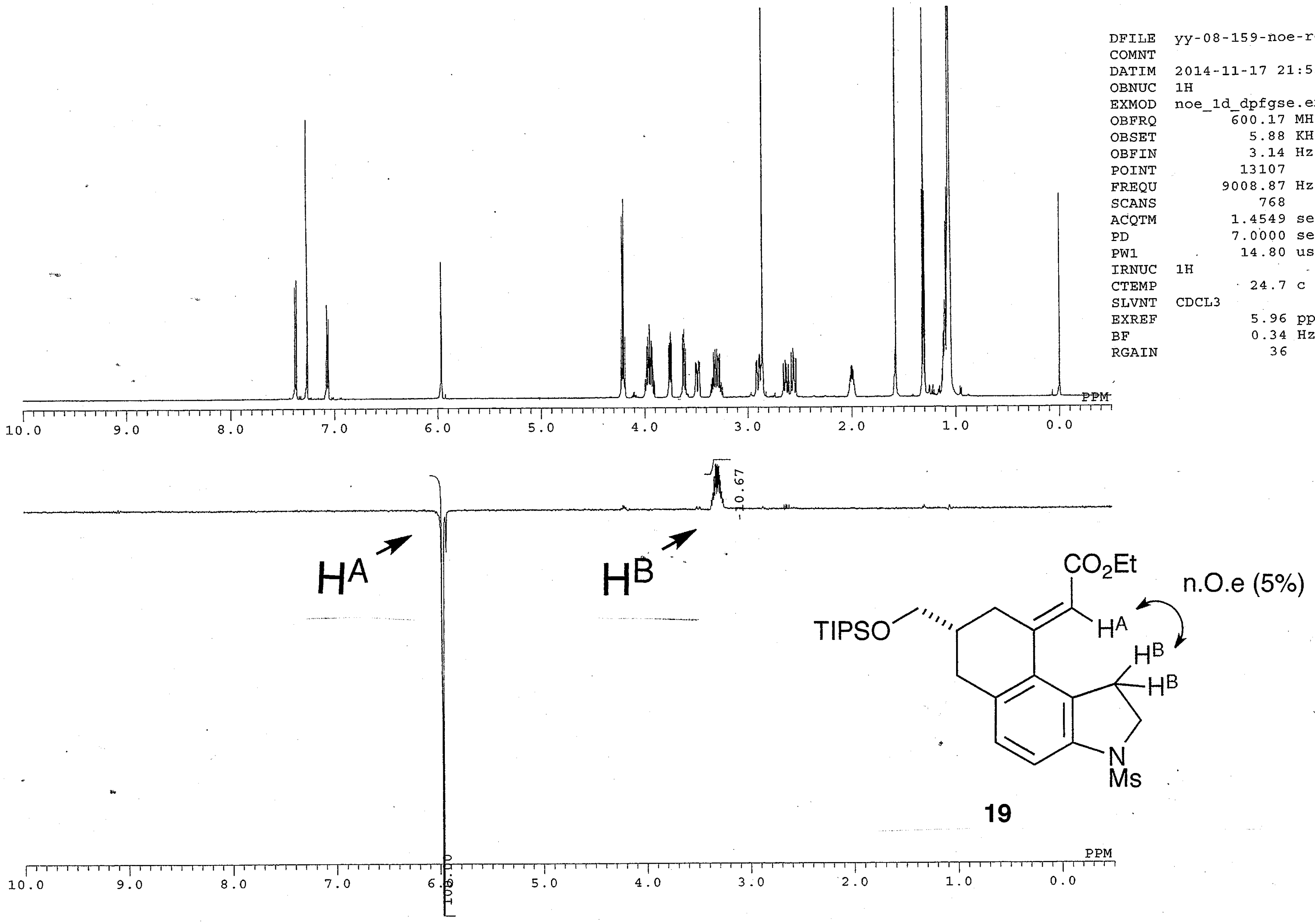
```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE : TRUE
ppm
abs
thresh : 2[%] : 1
symmetrize : Cosy : 24
[transpose]
```

```
Filename            = yy-08-159-last-cosy-2
Author              = yakkou
Experiment          = cosy.ex2
Sample_id           = S#40922
Solvent             = CHLOROFORM-D
Creation_time       = 18-NOV-2014 07:40:32
Revision_time       = 18-NOV-2014 08:33:00
Current_time        = 18-NOV-2014 08:37:44

Comment             = absolute value COSY
Data_format         = 2D REAL REAL
Dim_size            = 1024, 1024
Dim_title           = 1H 1H
Dim_units           = [ppm] [ppm]
Dimensions          = X Y
Site                = ECA600
Spectrometer        = JNM-ECA600

Field_strength      = 14.09636928[T] (600[M
X_acq_duration      = 0.113664[s]
X_domain            = 1H
X_freq              = 600.1723046[MHz]
X_offset            = 5[ppm]
X_points            = 1280
X_prescans          = 4
X_resolution        = 8.79786036[Hz]
X_sweep             = 11.26126126[kHz]
Y_domain            = 1H
Y_freq              = 600.1723046[MHz]
Y_offset            = 5[ppm]
Y_points            = 256
Y_prescans          = 0
Y_resolution        = 35.17242932[Hz]
Y_sweep             = 9.00414191[kHz]
Irr_domain          = 1H
Irr_freq            = 600.1723046[MHz]
Irr_offset          = 5[ppm]
Tri_domain          = 1H
Tri_freq            = 600.1723046[MHz]
Tri_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 64
Total_scans         = 16384

X_90_width          = 14.8[us]
X_acq_time          = 0.113664[s]
X_atn               = 3.5[dB]
X_pulse             = 14.8[us]
Y_acq_time          = 28.43136[ms]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Delta               = 0[ms]
Initial_wait        = 1[s]
Pulse_1             = 14.8[us]
Pulse_2             = 14.8[us]
Pulse_angle_1       = 90[deg]
Pulse_angle_2       = 90[deg]
Recvr_gain          = 36
Relaxation_delay    = 1.5[s]
Repetition_time     = 1.613664[s]
T1                  = 1[us]
Temp_get            = 24.7[dC]
```

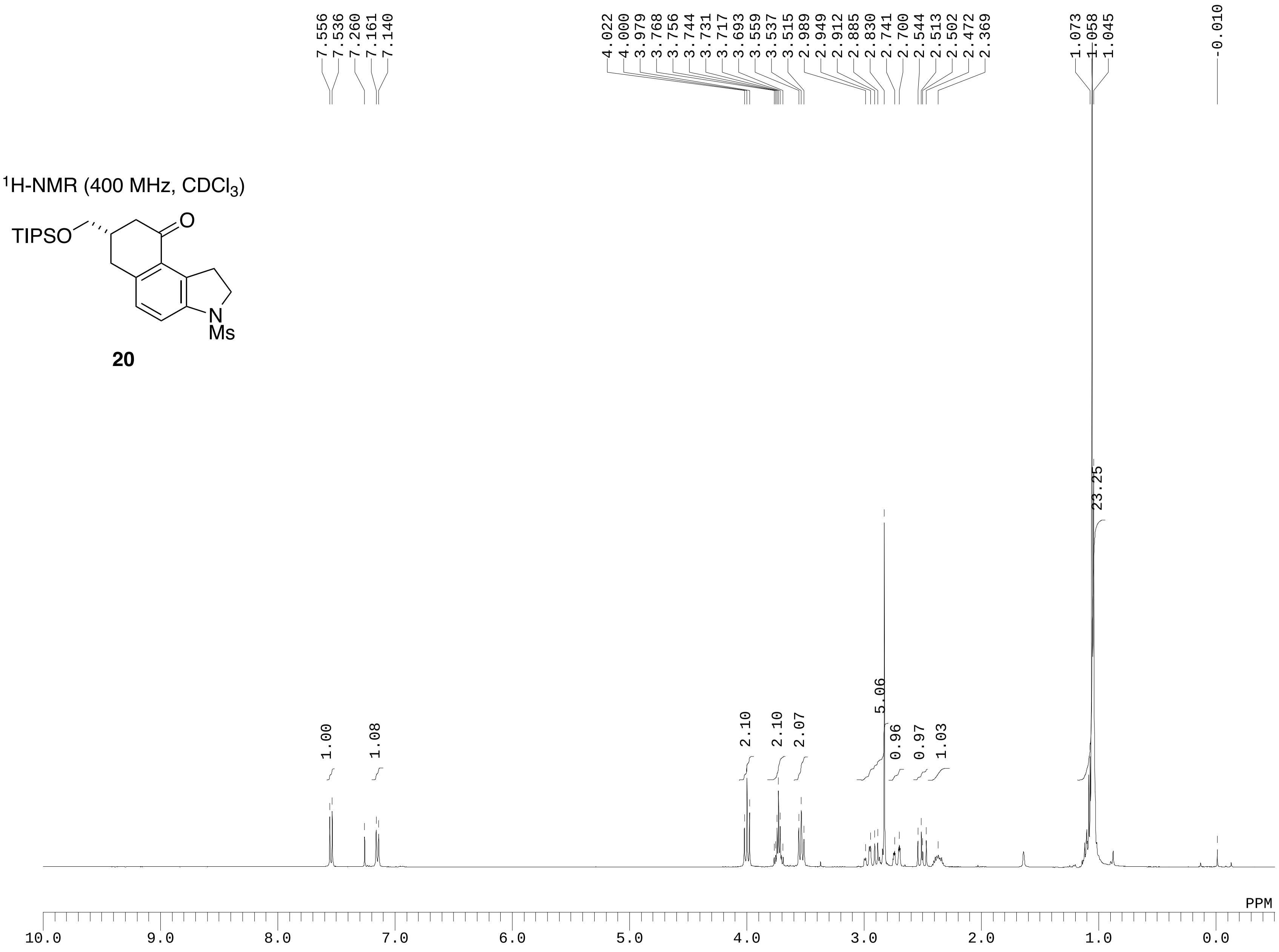


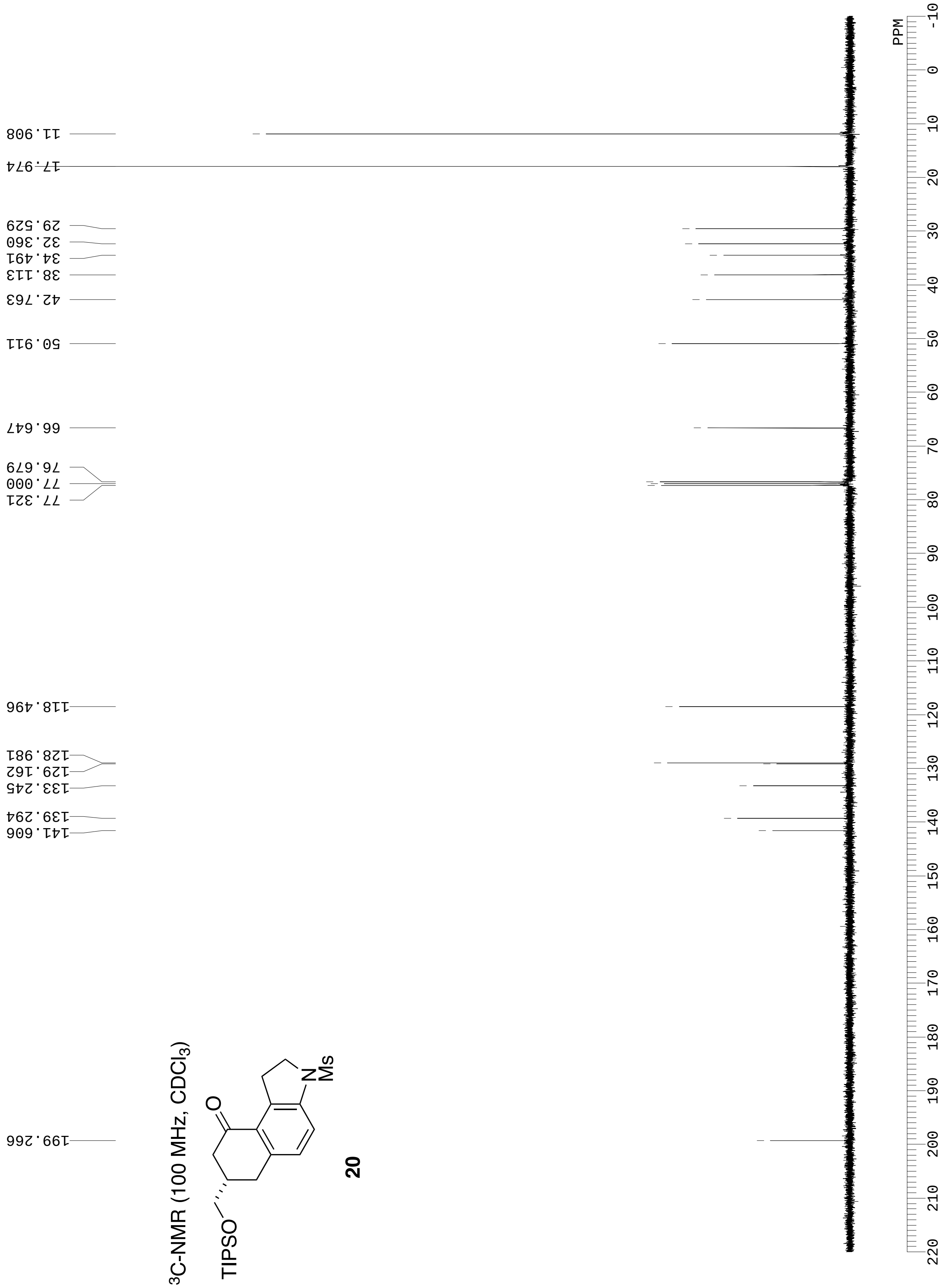
```
DFILE   yy-08-159-noe-revised.als
COMNT
DATIM   2014-11-17 21:55:12
OBNUC   1H
EXMOD   noe_1d_dpfgse.ex
OBFRQ         600.17 MHz
OBSET           5.88 KHz
OBFIN           3.14 Hz
POINT          13107
FREQU        9008.87 Hz
SCANS            768
ACQTM         1.4549 sec
PD            7.0000 sec
PW1            14.80 usec
IRNUC   1H
CTEMP           24.7 c
SLVNT   CDCL3
EXREF           5.96 ppm
BF              0.34 Hz
RGAIN             36
```

19

^{1}H-NMR (400 MHz, $CDCl_3$)

20

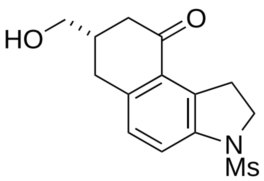




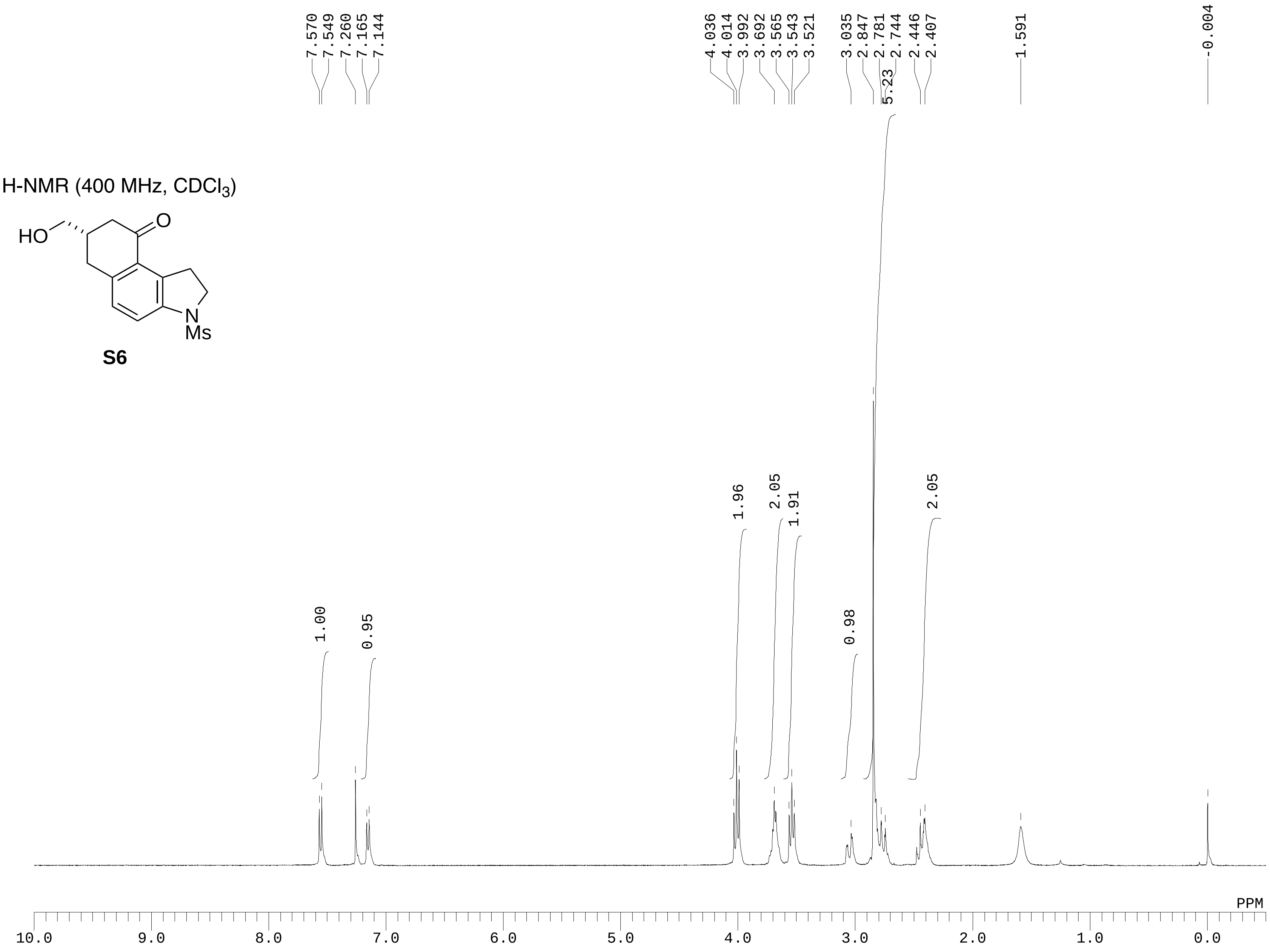
^{13}C-NMR (100 MHz, $CDCl_3$)

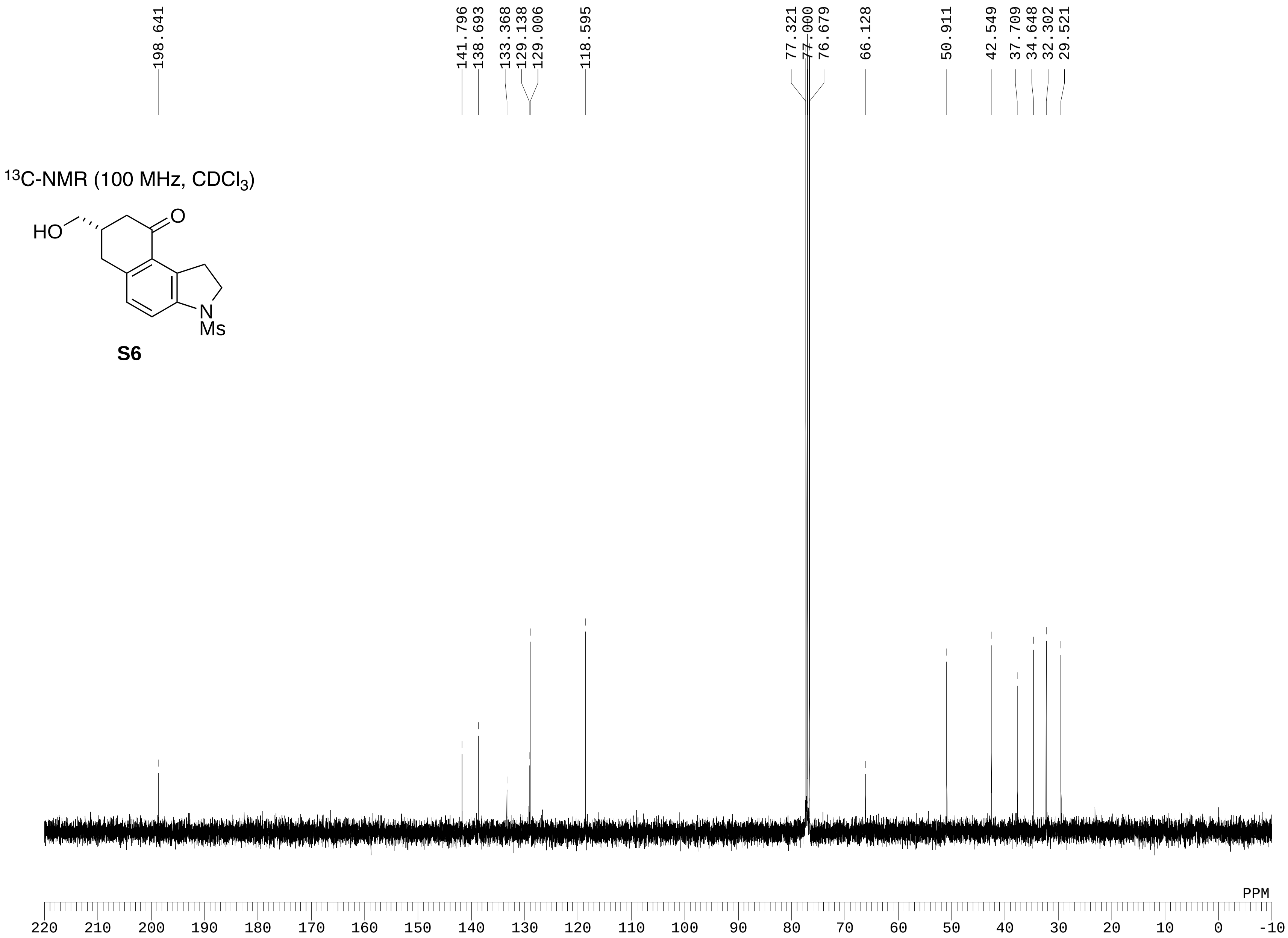
20

^{1}H-NMR (400 MHz, $CDCl_3$)



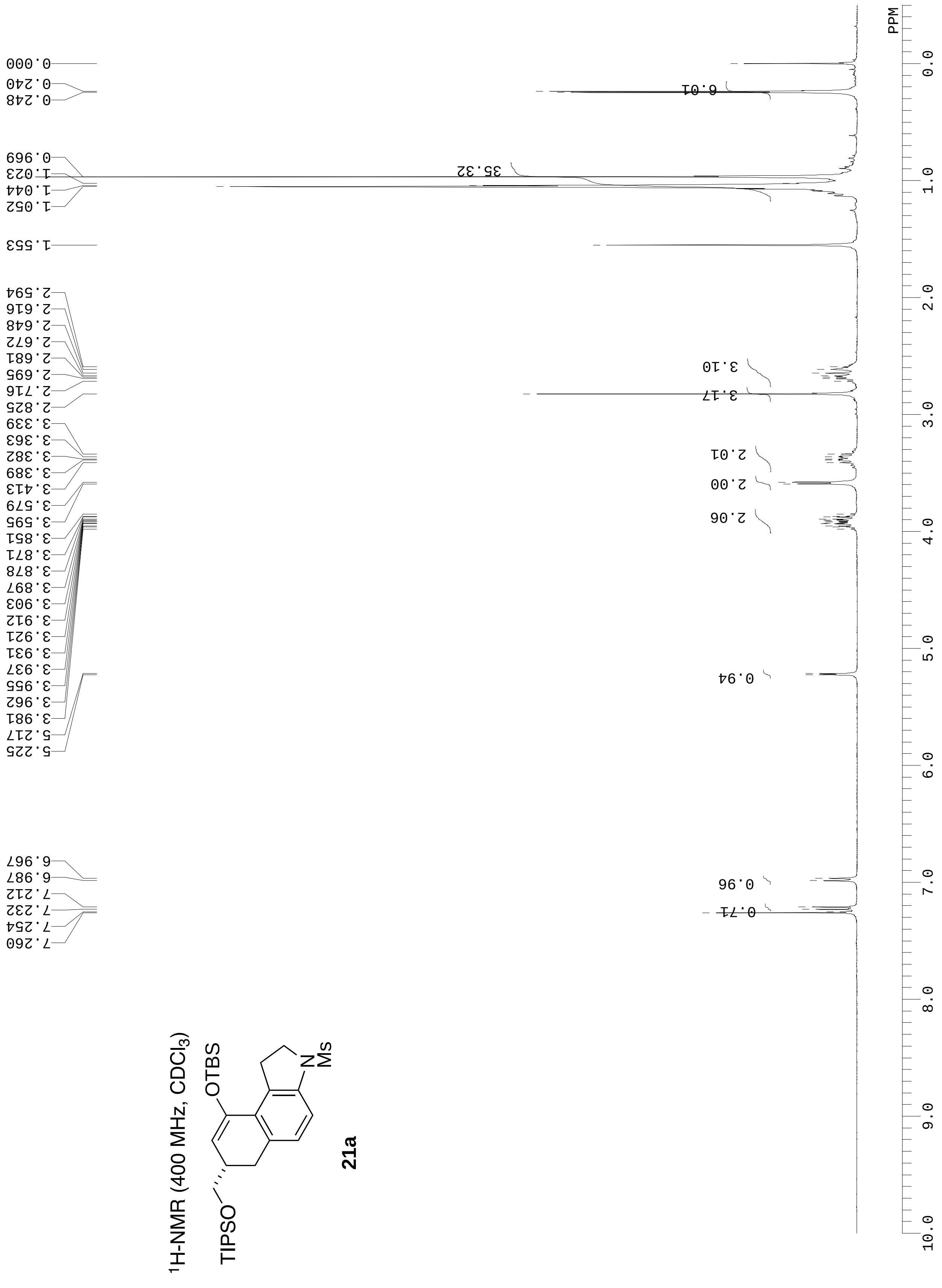
S6





^{13}C-NMR (100 MHz, CDCl$_3$)

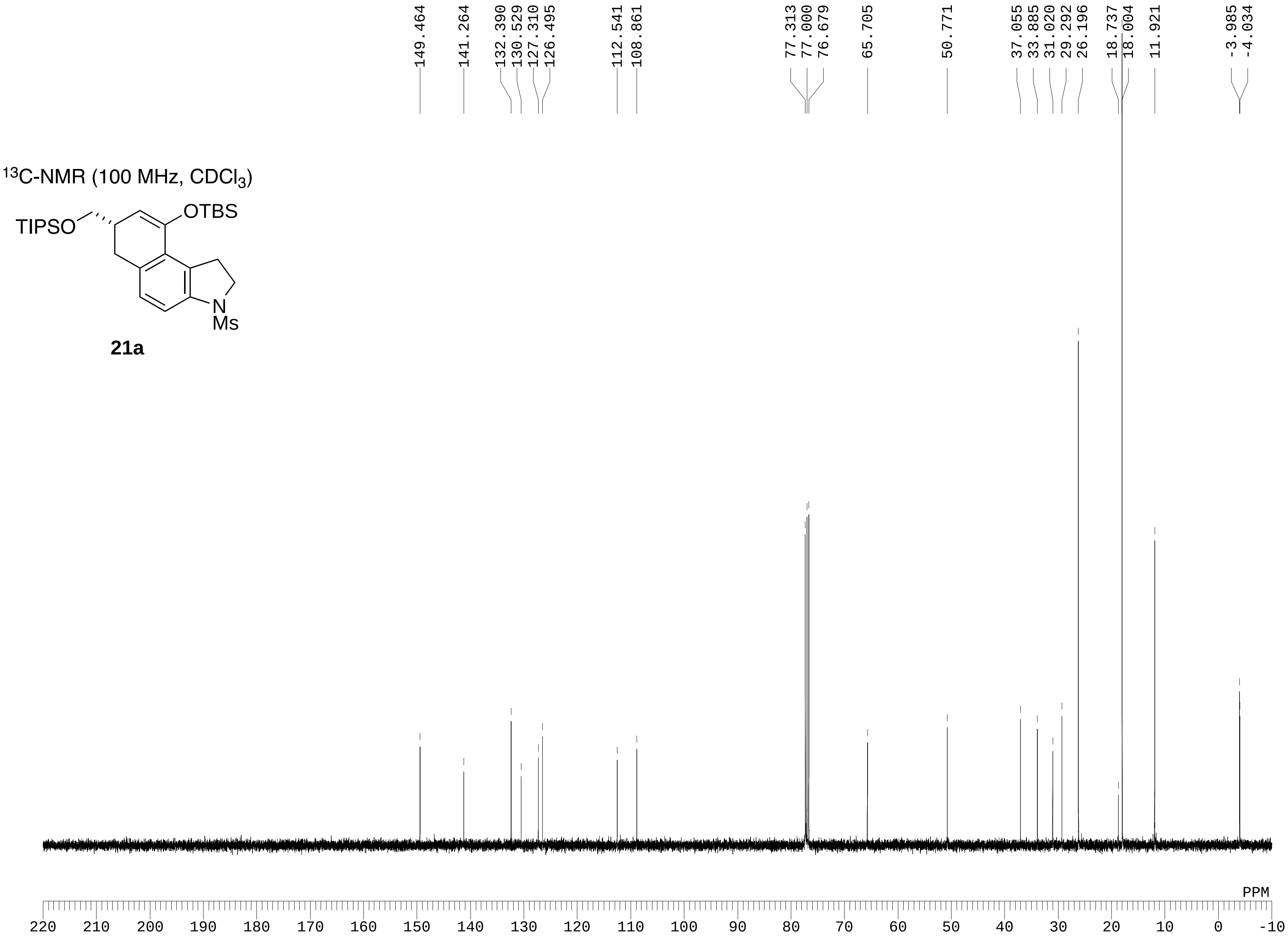
S6



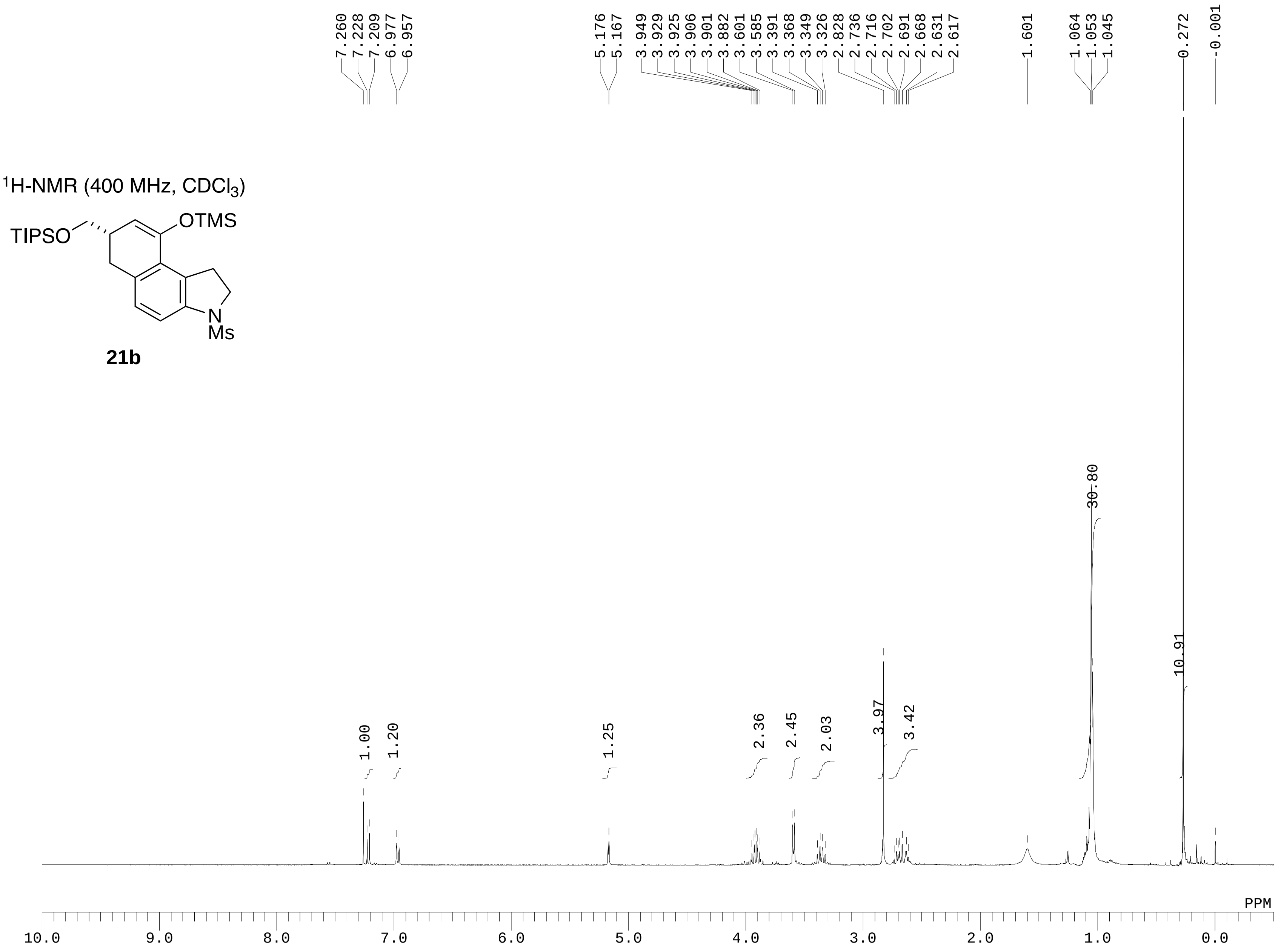
^{1}H-NMR (400 MHz, CDCl$_3$)

21a

^{13}C-NMR (100 MHz, CDCl$_3$)

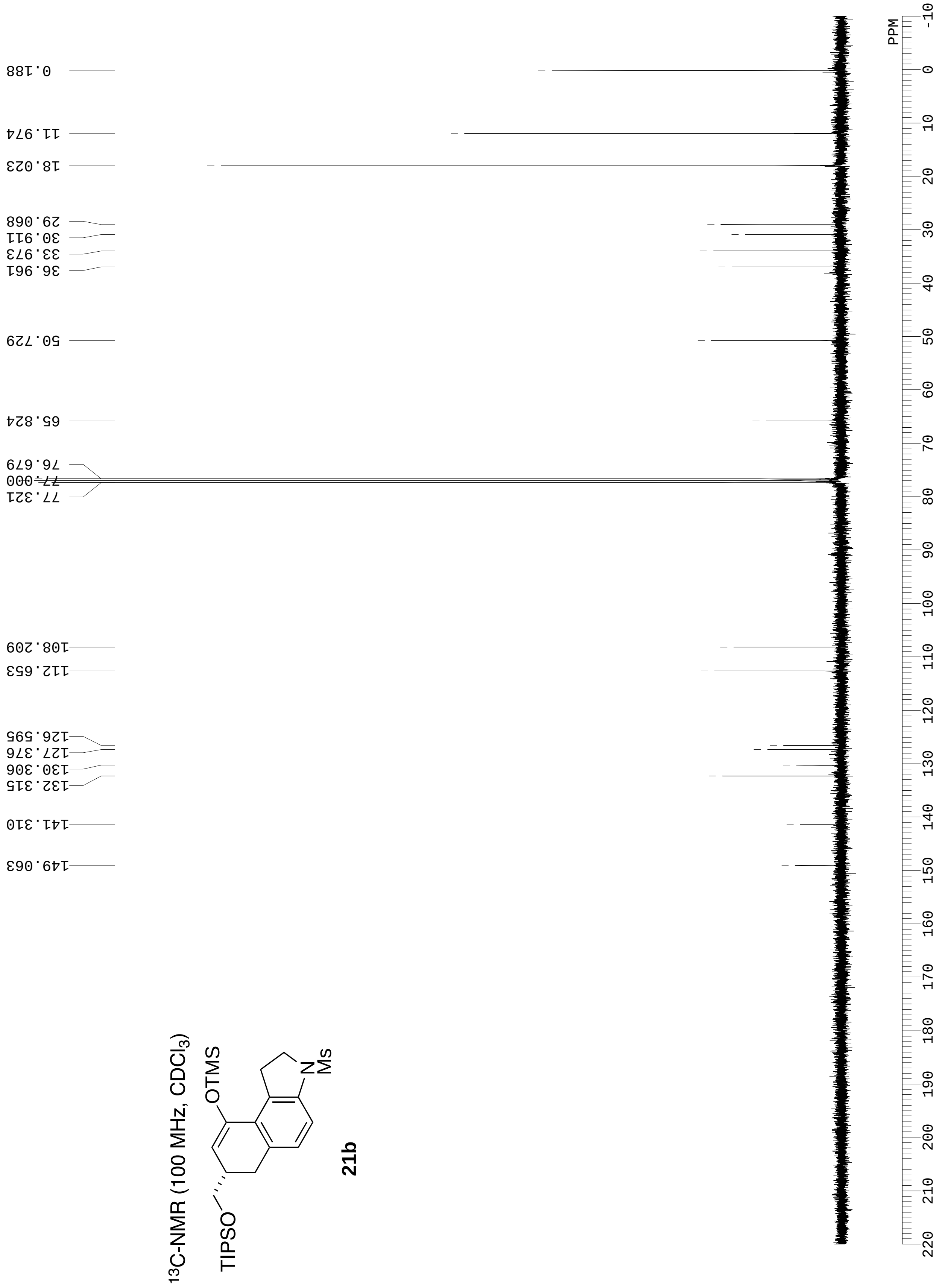


21a



^{1}H-NMR (400 MHz, CDCl$_3$)

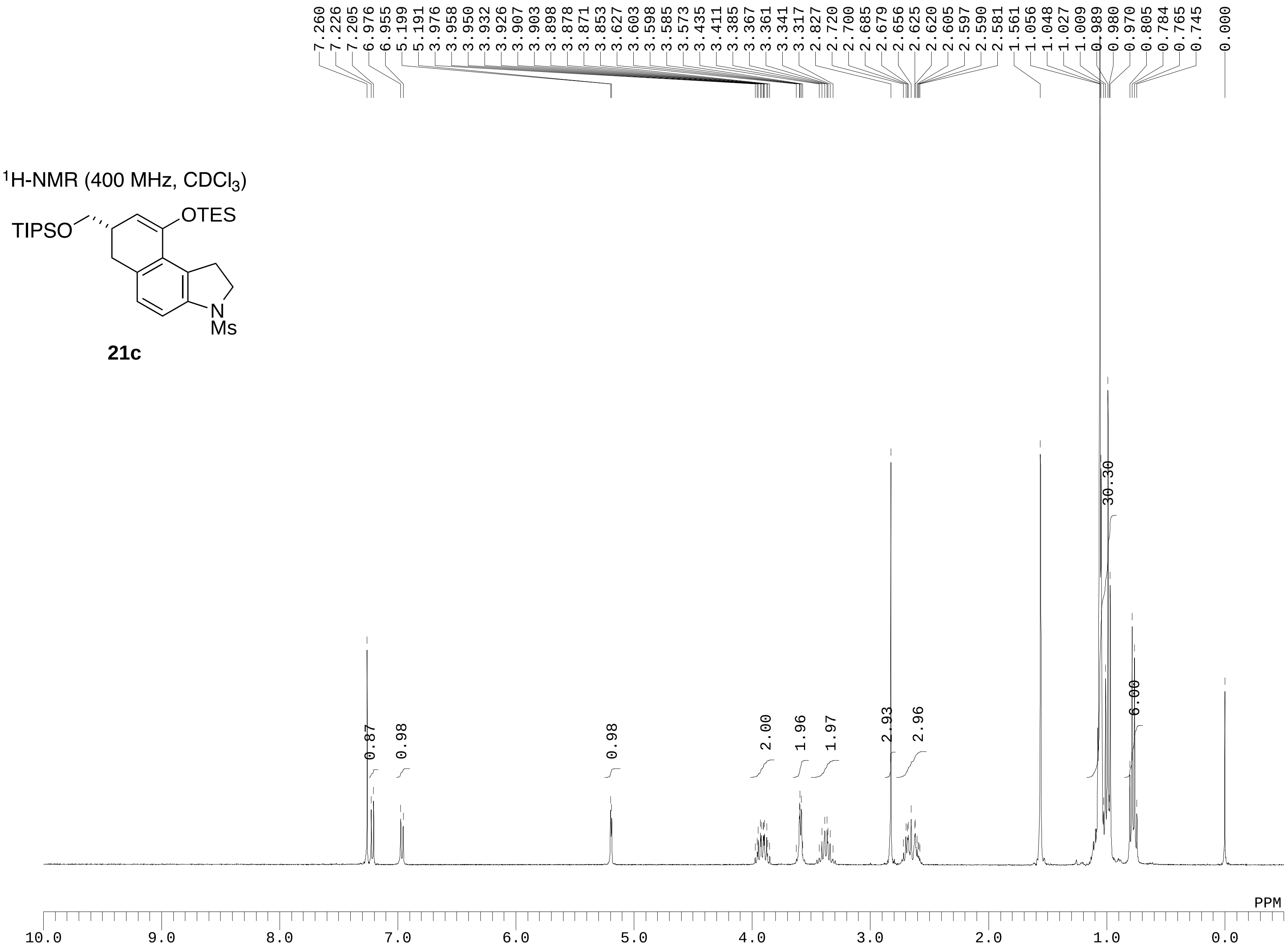
21b



^{13}C-NMR (100 MHz, $CDCl_3$)

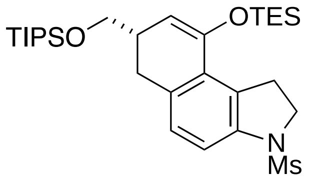
21b

^{1}H-NMR (400 MHz, $CDCl_3$)

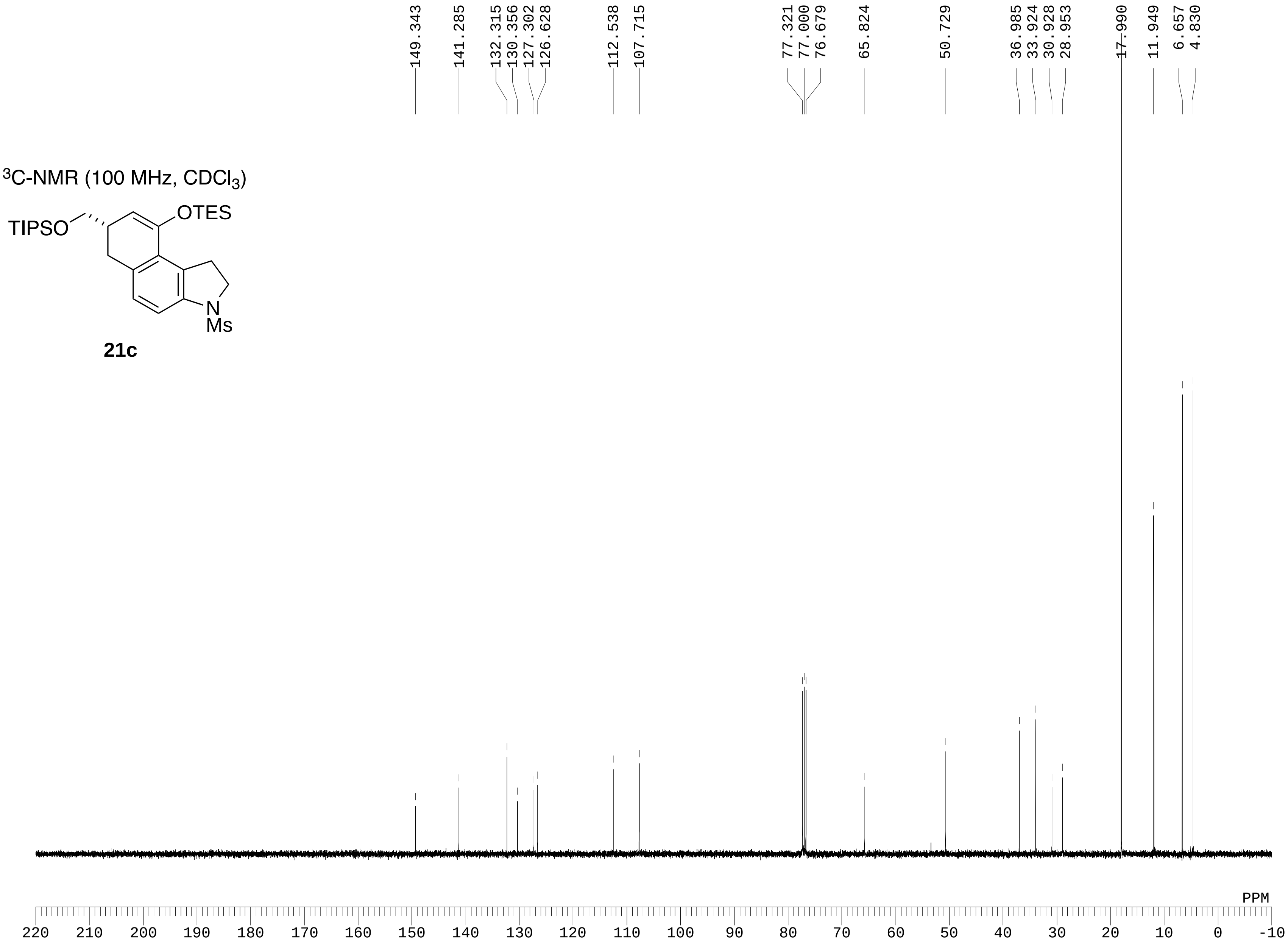


21c

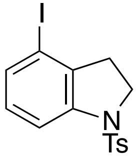
^{13}C-NMR (100 MHz, $CDCl_3$)



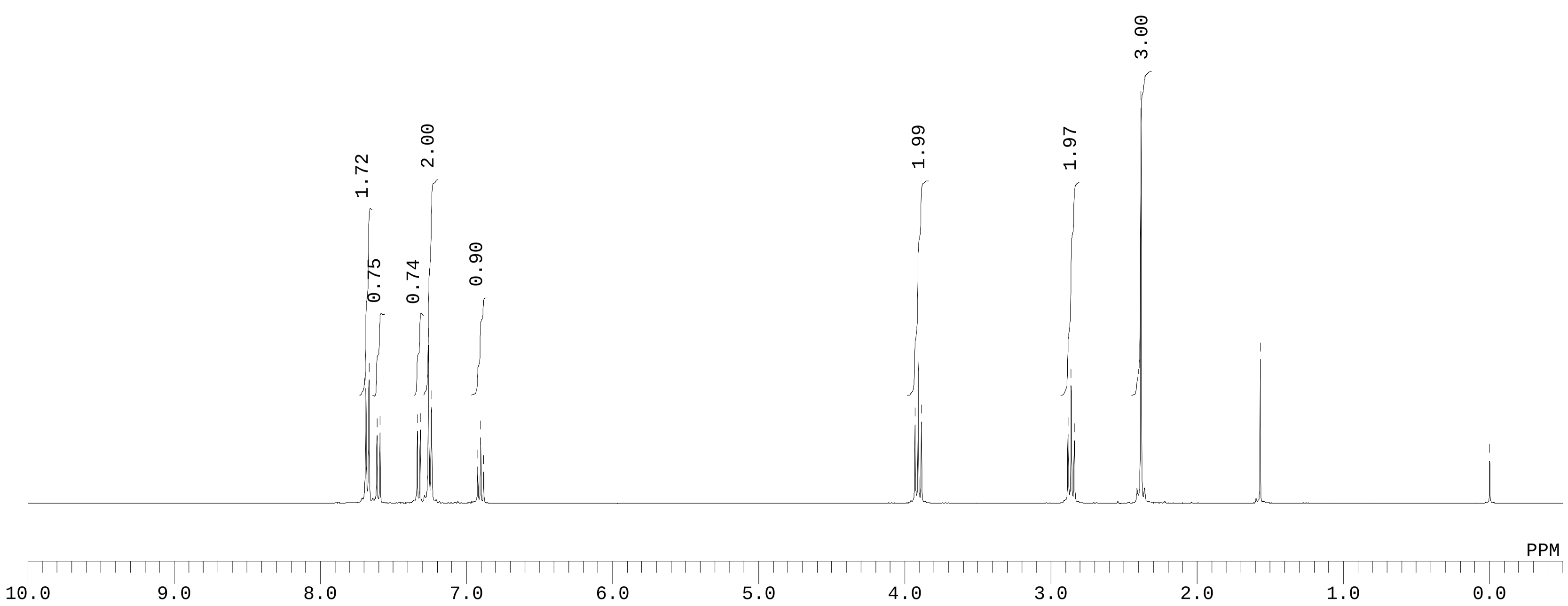
21c

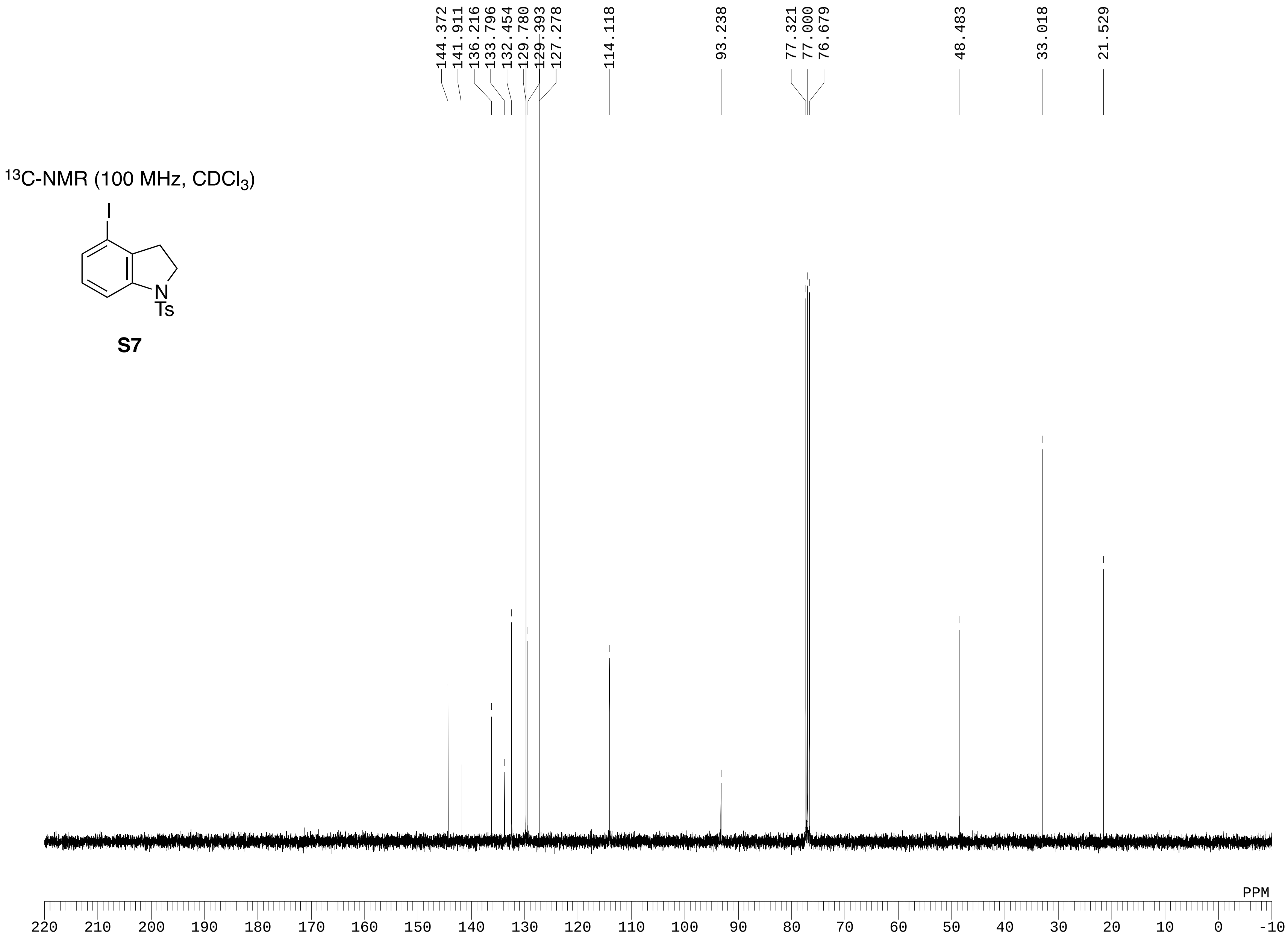


^{1}H-NMR (400 MHz, $CDCl_3$)

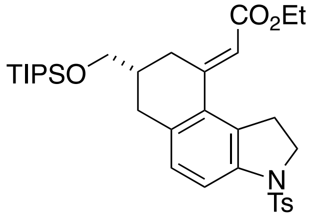


S7

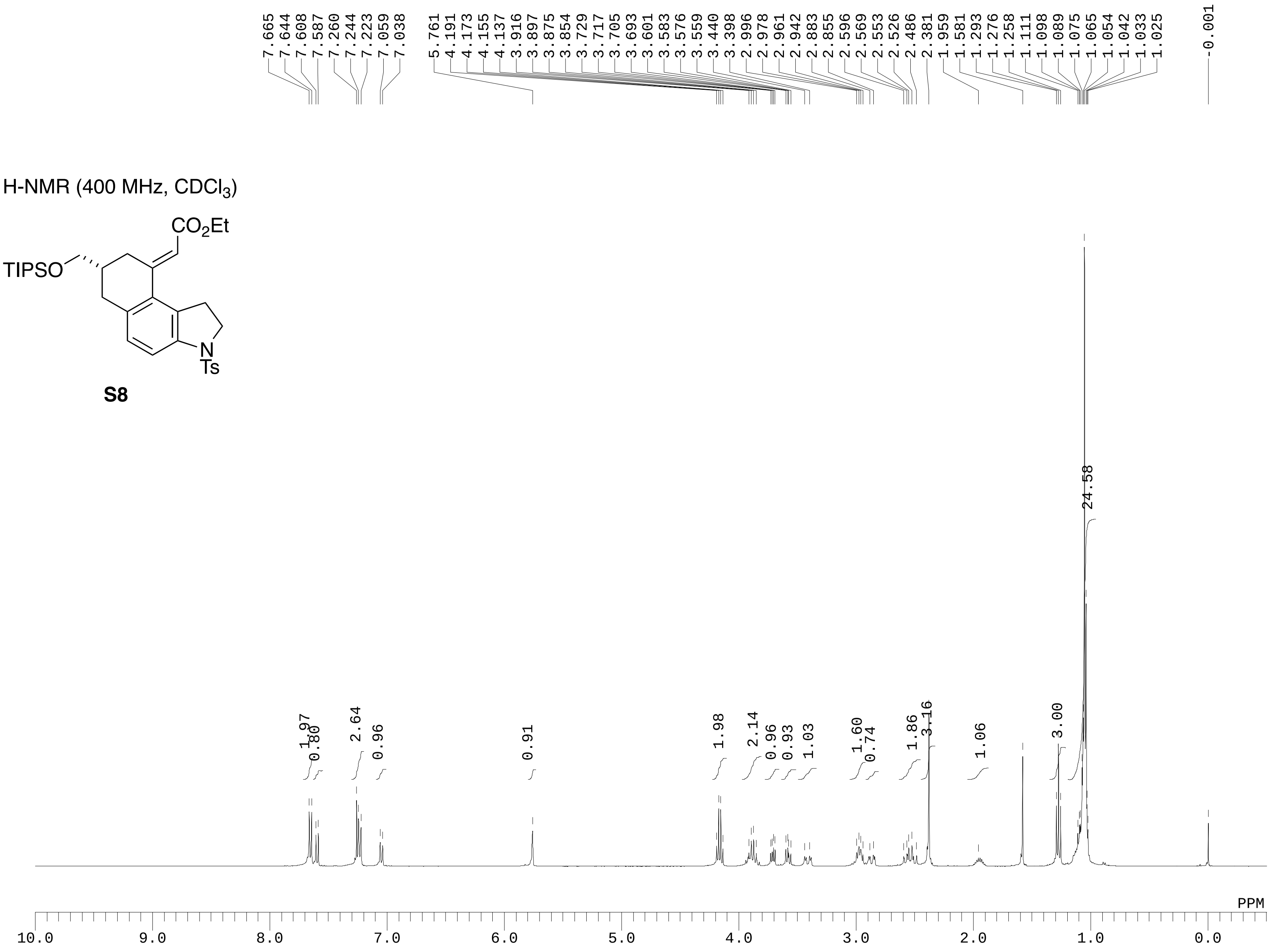


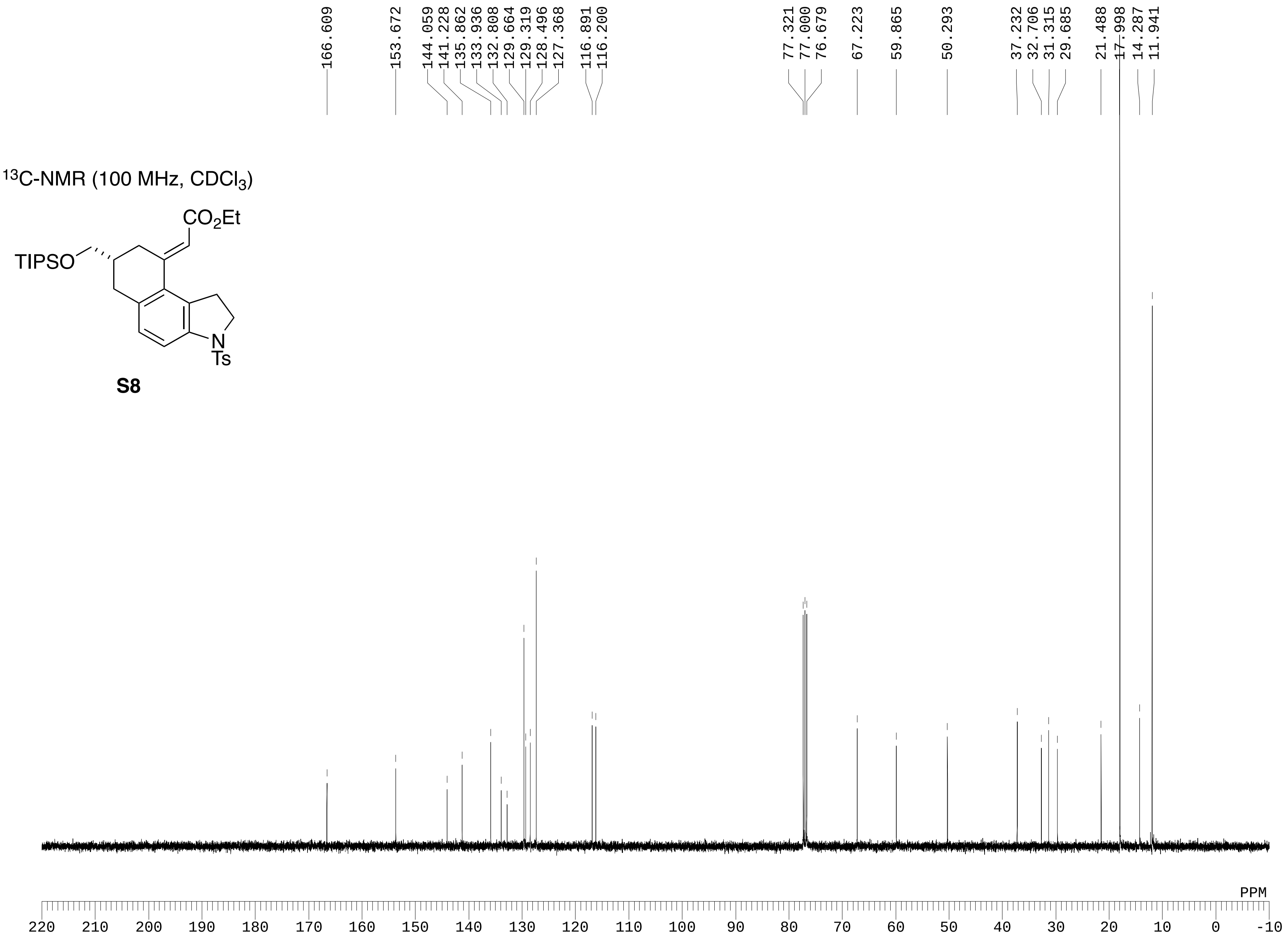

^{13}C-NMR (100 MHz, CDCl$_3$)
I
N
Ts
S7
144.372
141.911
136.216
133.796
132.454
129.780
129.393
127.278
114.118
93.238
77.321
77.000
76.679
48.483
33.018
21.529
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H-NMR (400 MHz, CDCl$_3$)



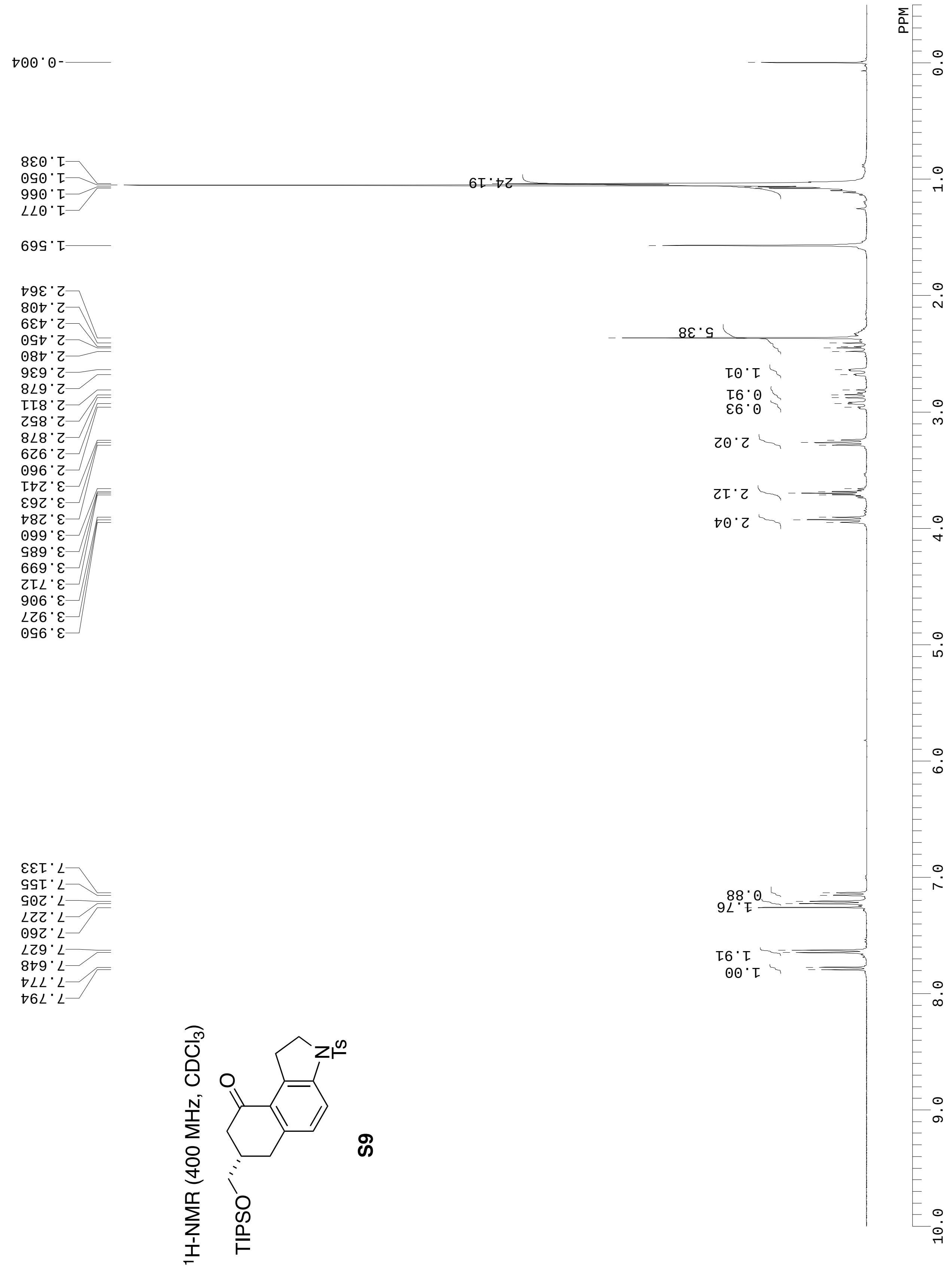
S8





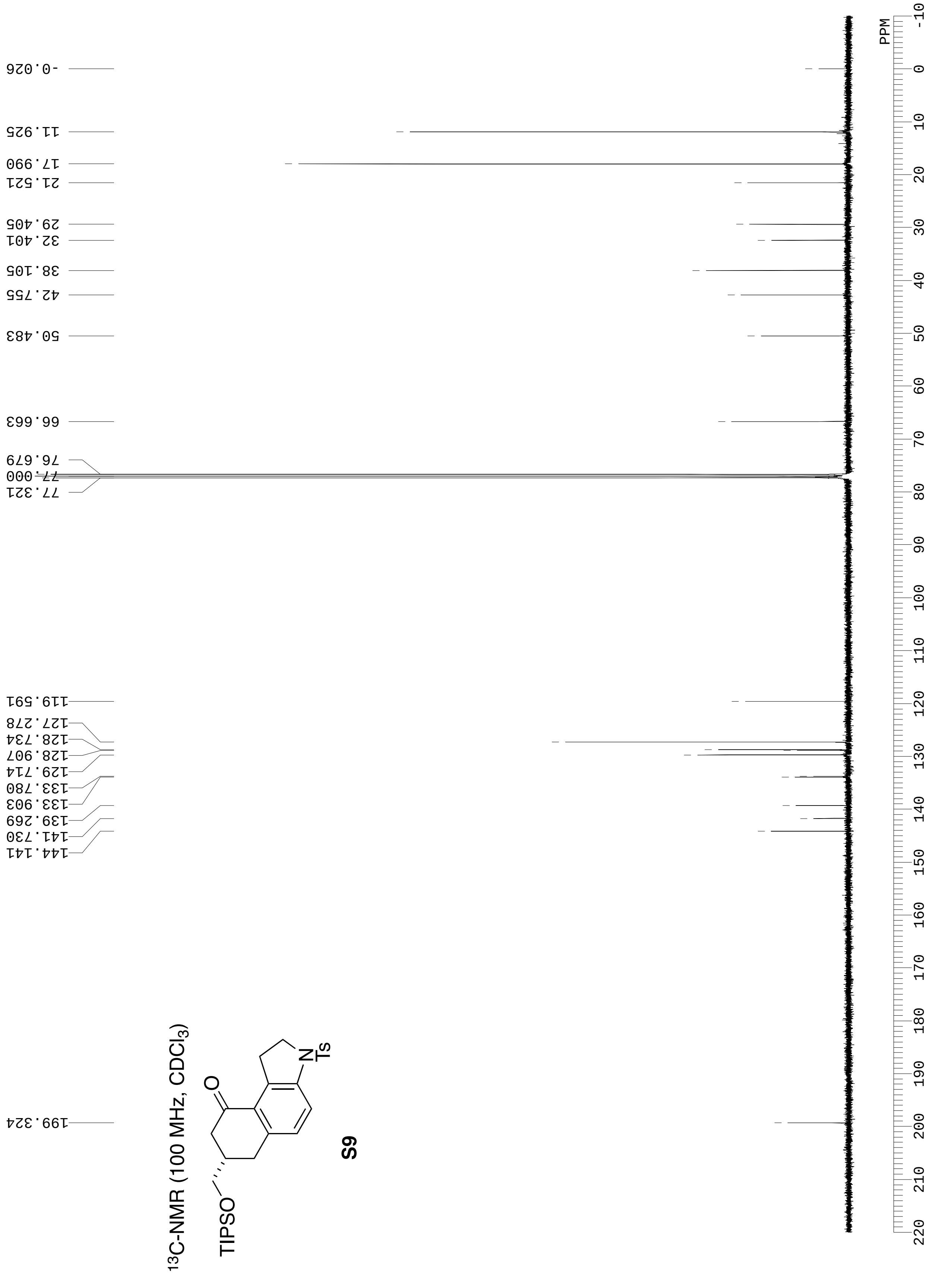
^{13}C-NMR (100 MHz, $CDCl_3$)

S8



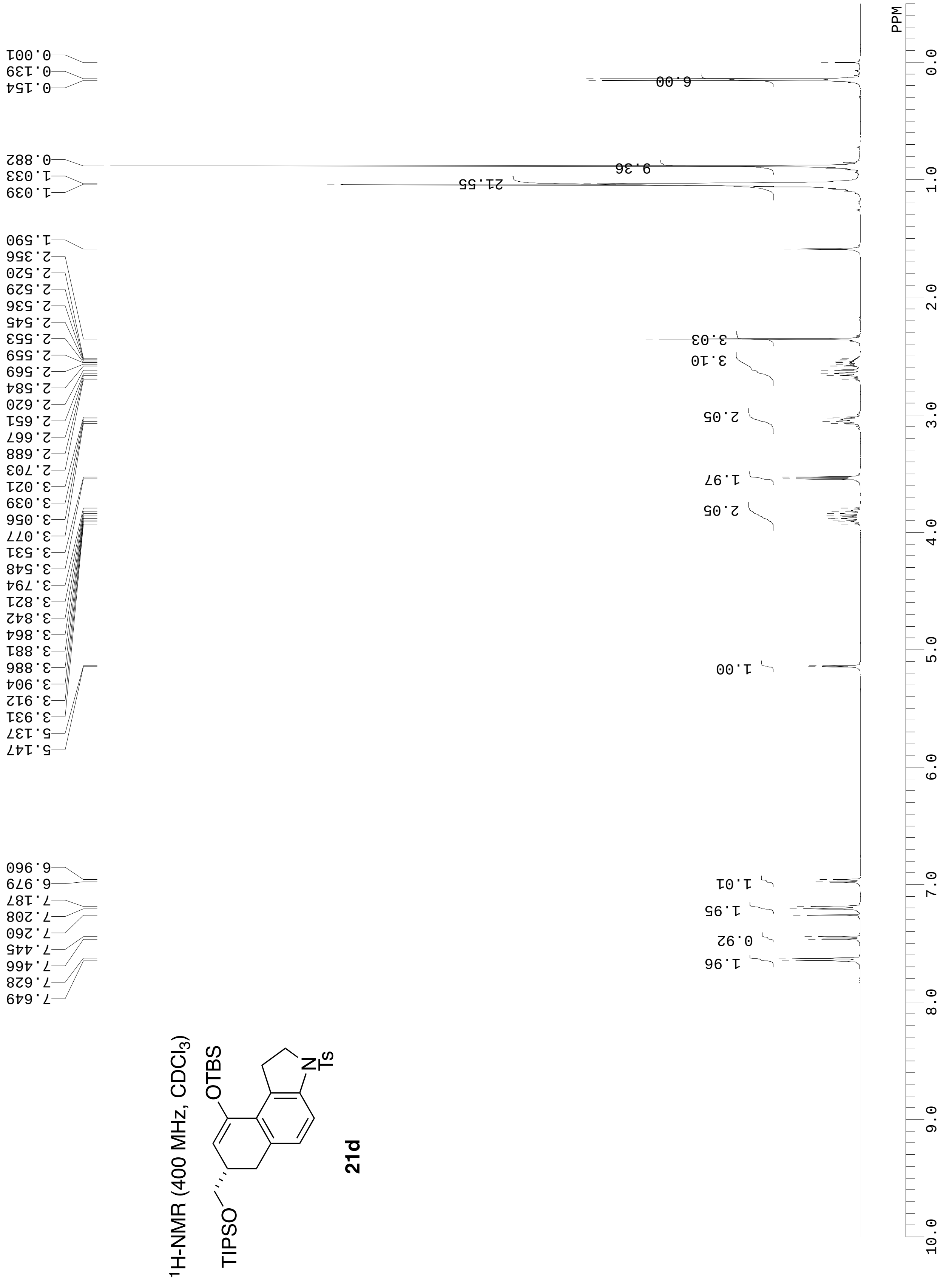
^{1}H-NMR (400 MHz, $CDCl_3$)

S9



^{13}C-NMR (100 MHz, CDCl$_3$)

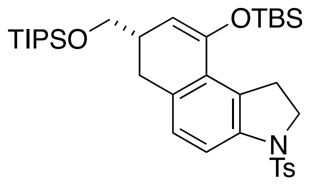
S9



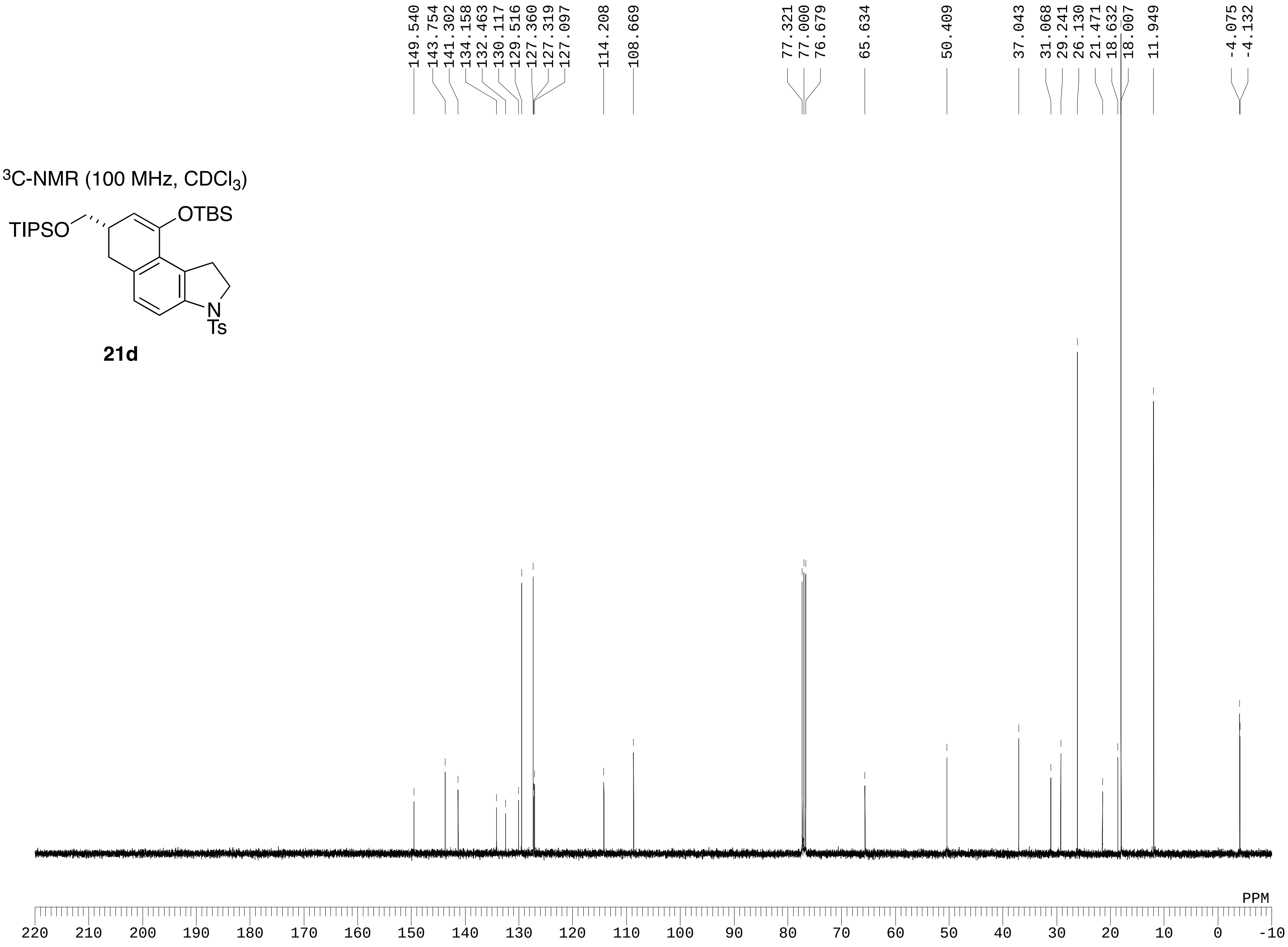
^{1}H-NMR (400 MHz, CDCl$_3$)

21d

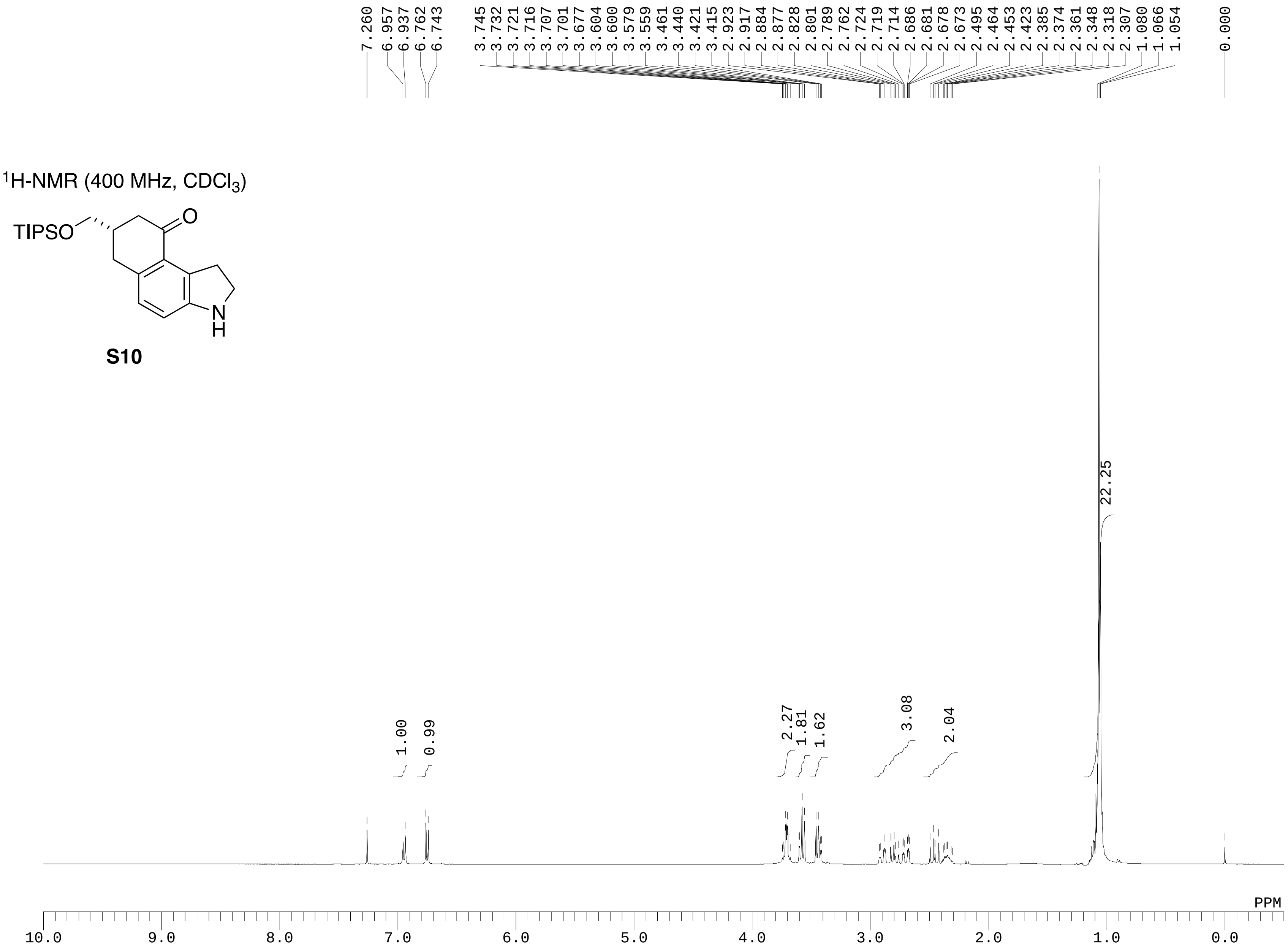
^{13}C-NMR (100 MHz, $CDCl_3$)



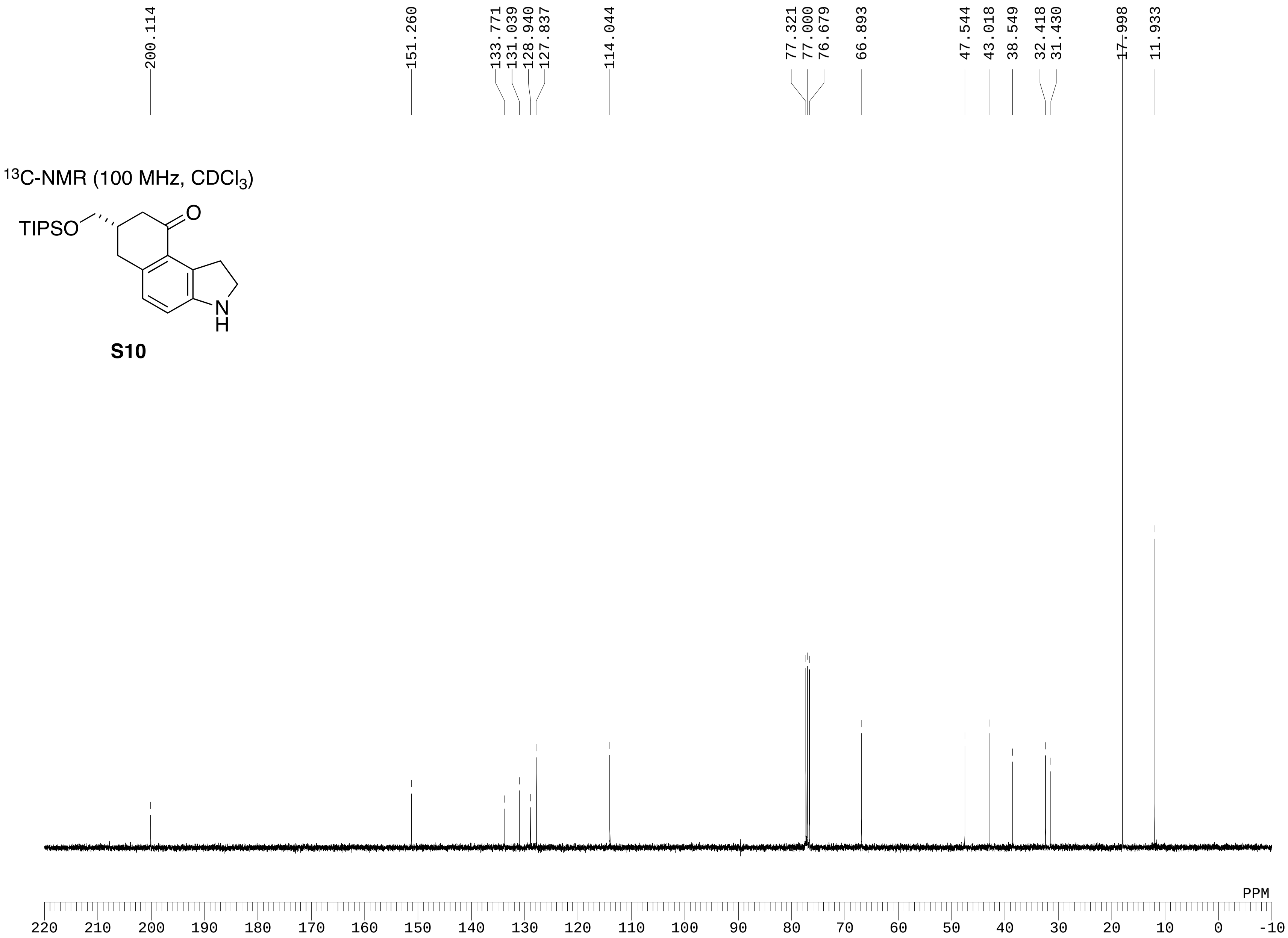
21d



^{1}H-NMR (400 MHz, $CDCl_3$)



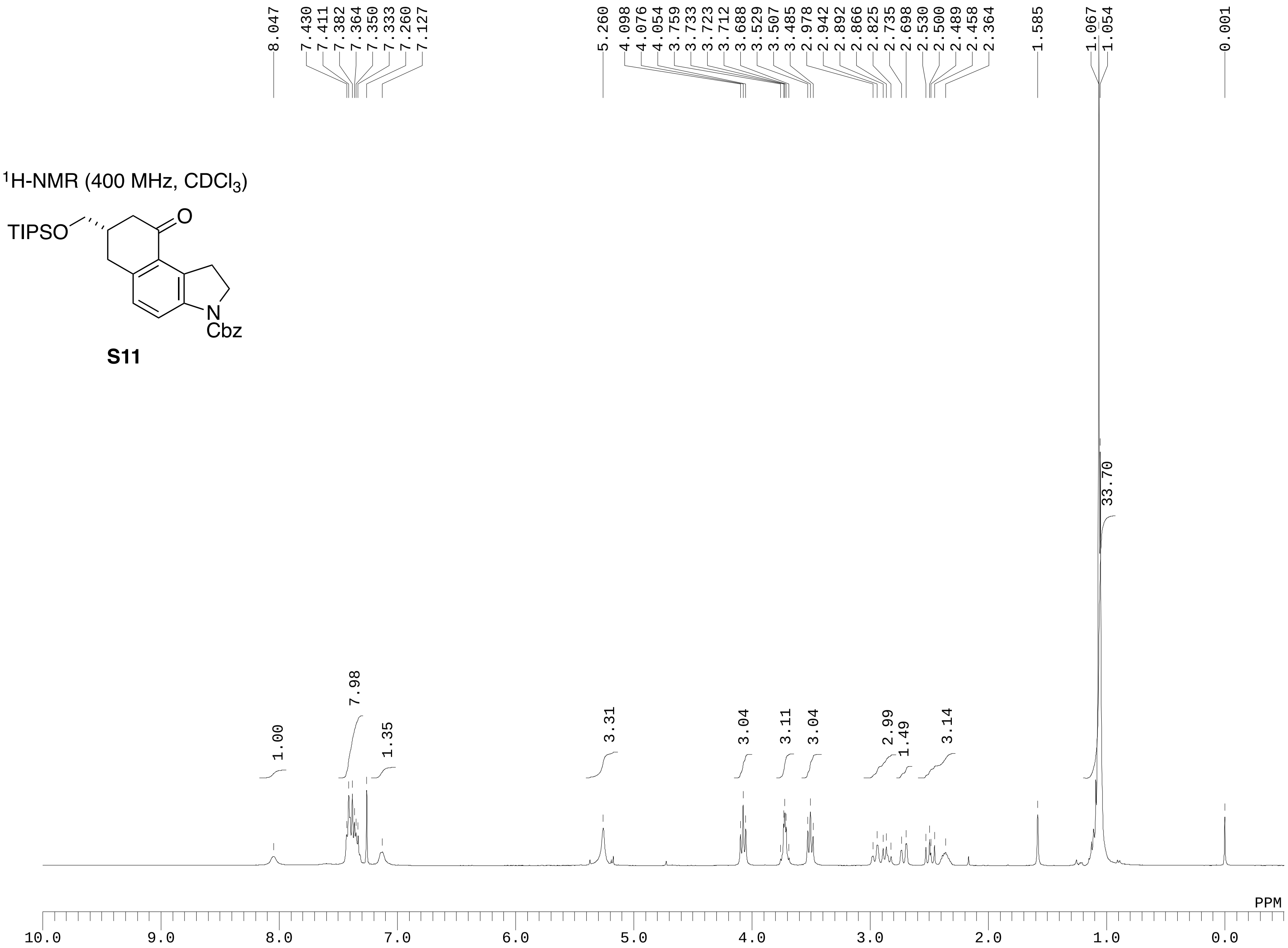
S10



^{13}C-NMR (100 MHz, $CDCl_3$)

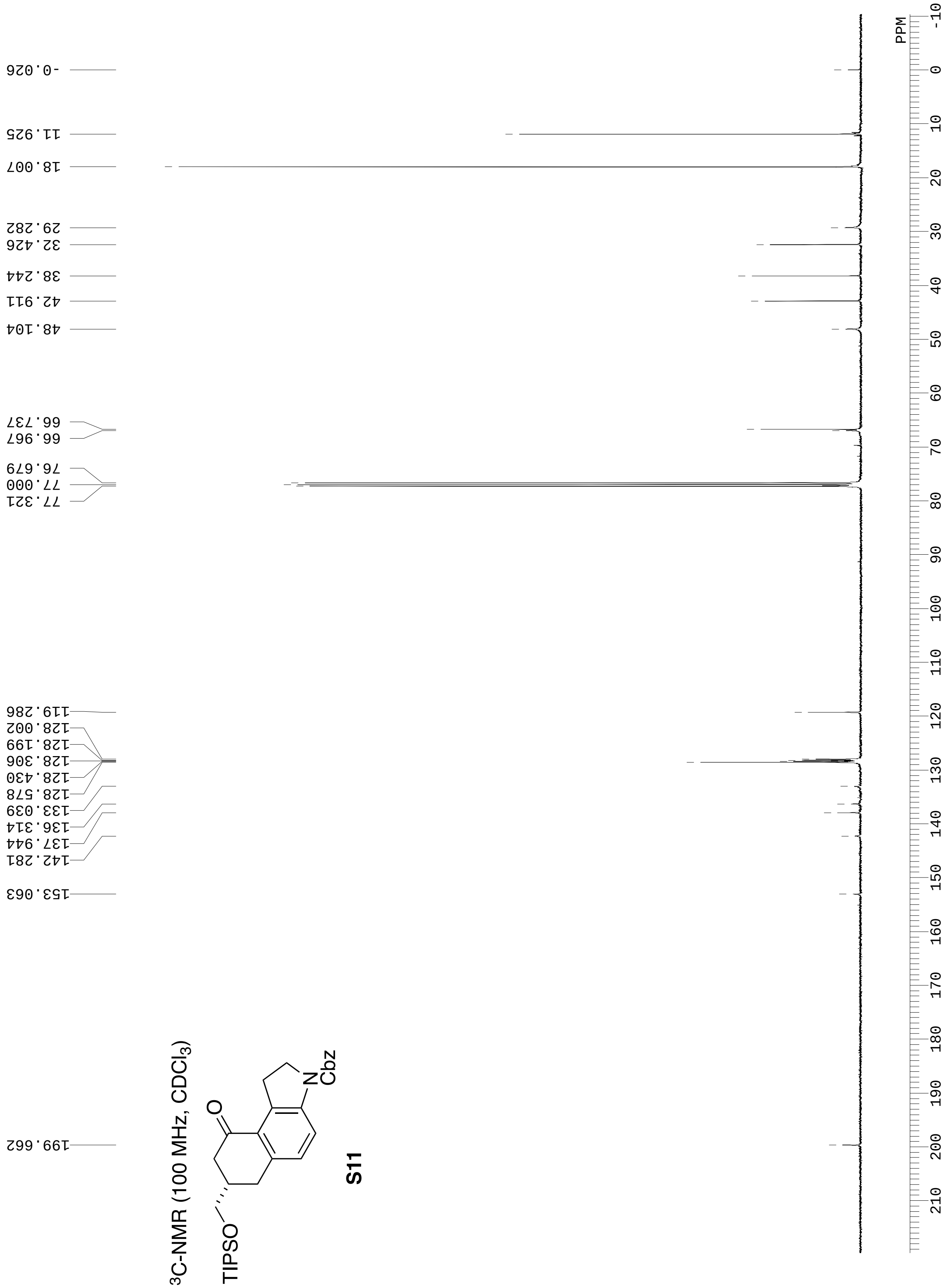
S10

^{1}H-NMR (400 MHz, $CDCl_3$)



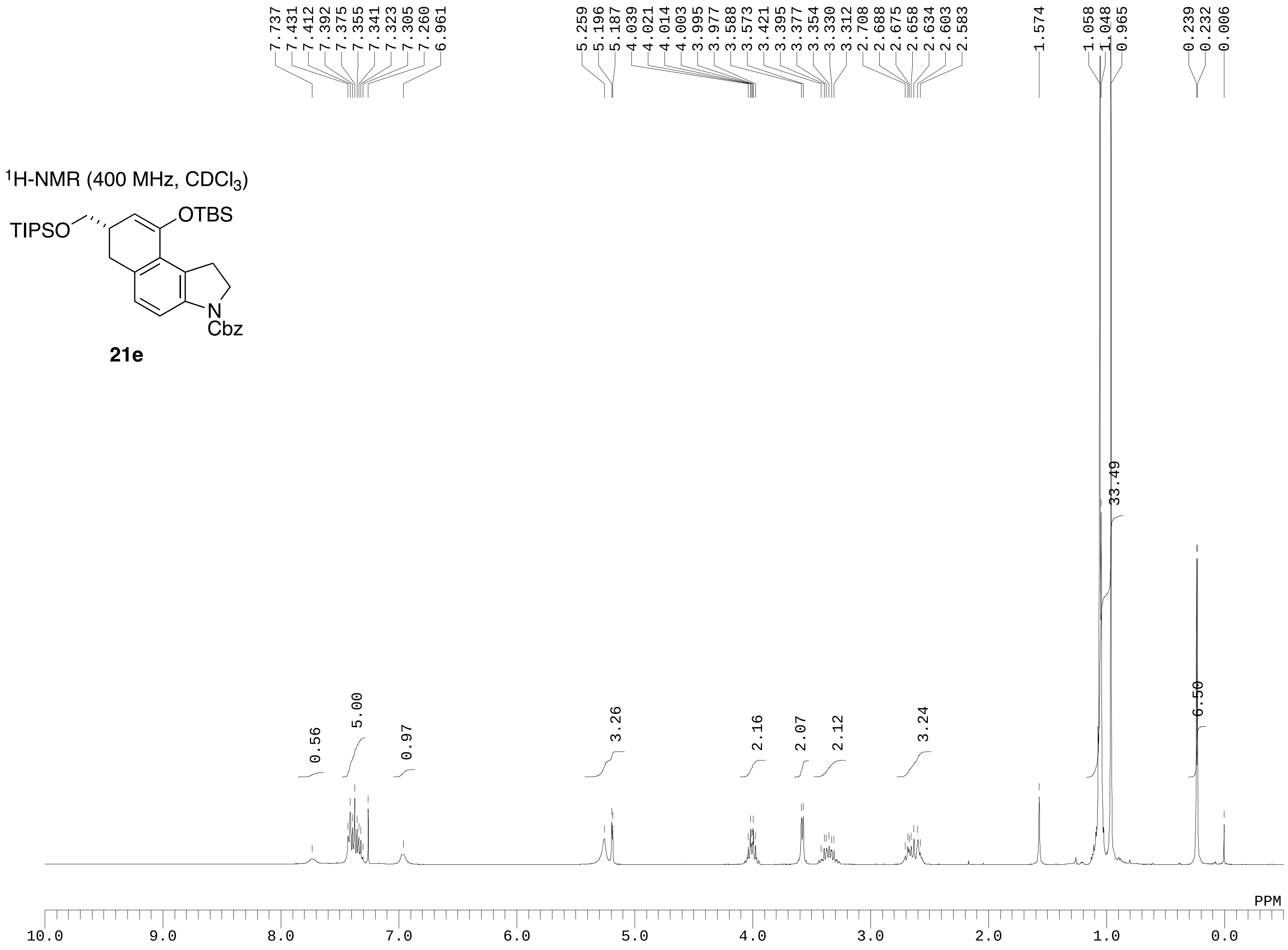
S11

^{13}C-NMR (100 MHz, CDCl$_3$)



S11

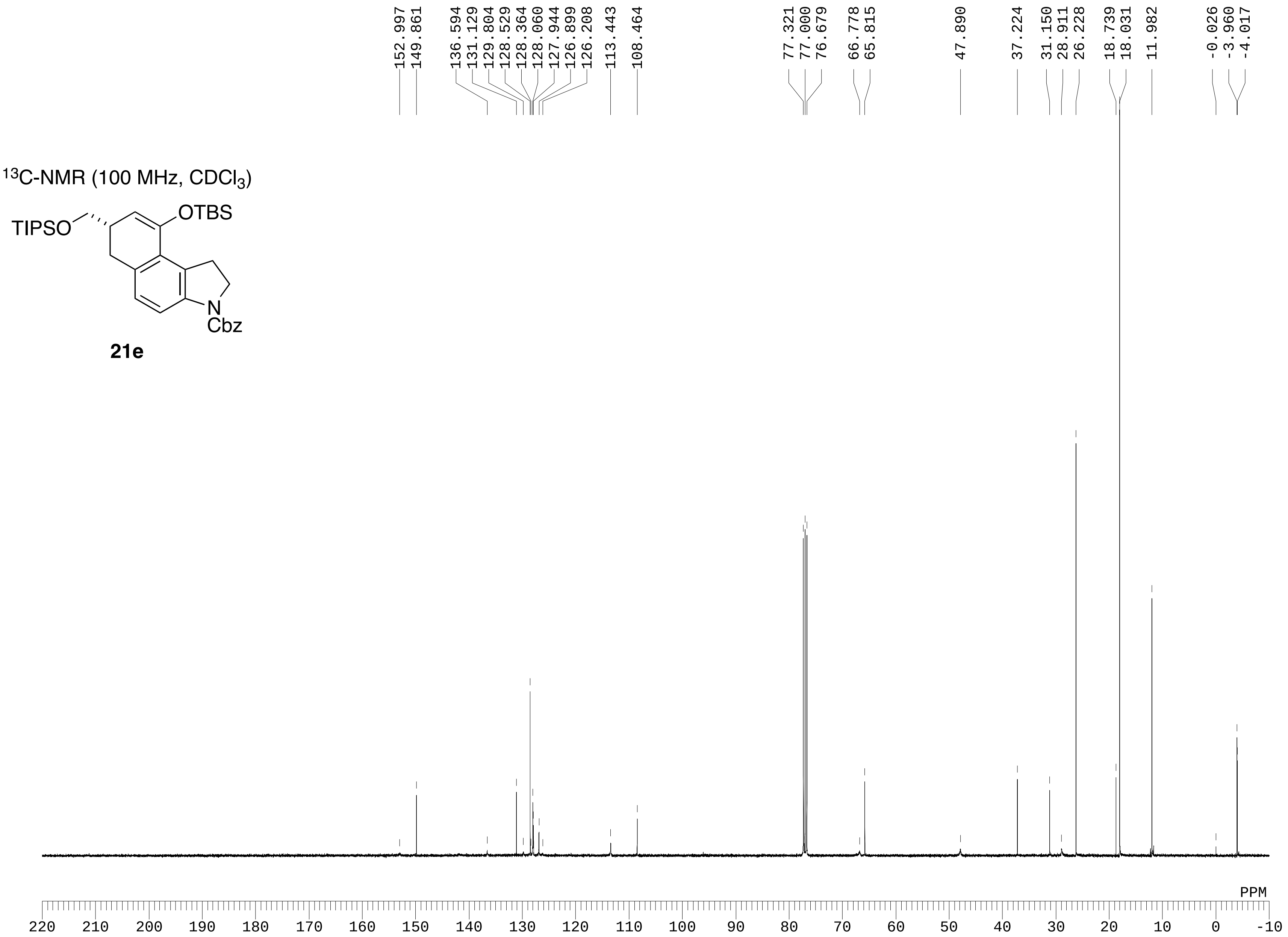
^{1}H-NMR (400 MHz, CDCl$_3$)

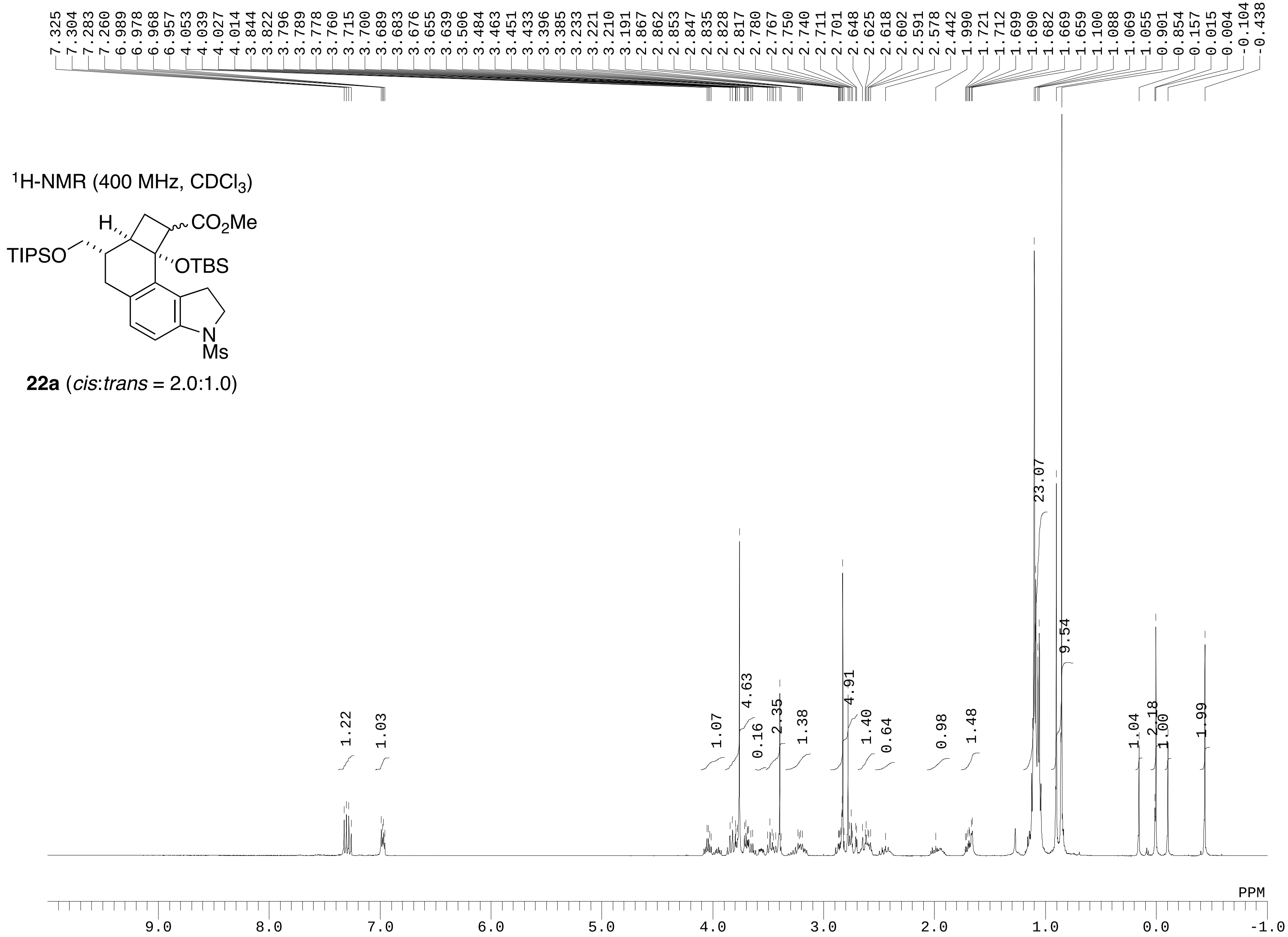


21e

^{13}C-NMR (100 MHz, CDCl$_3$)

21e

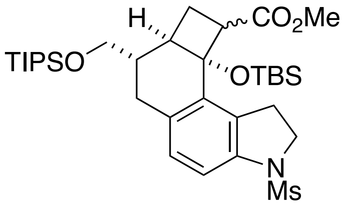




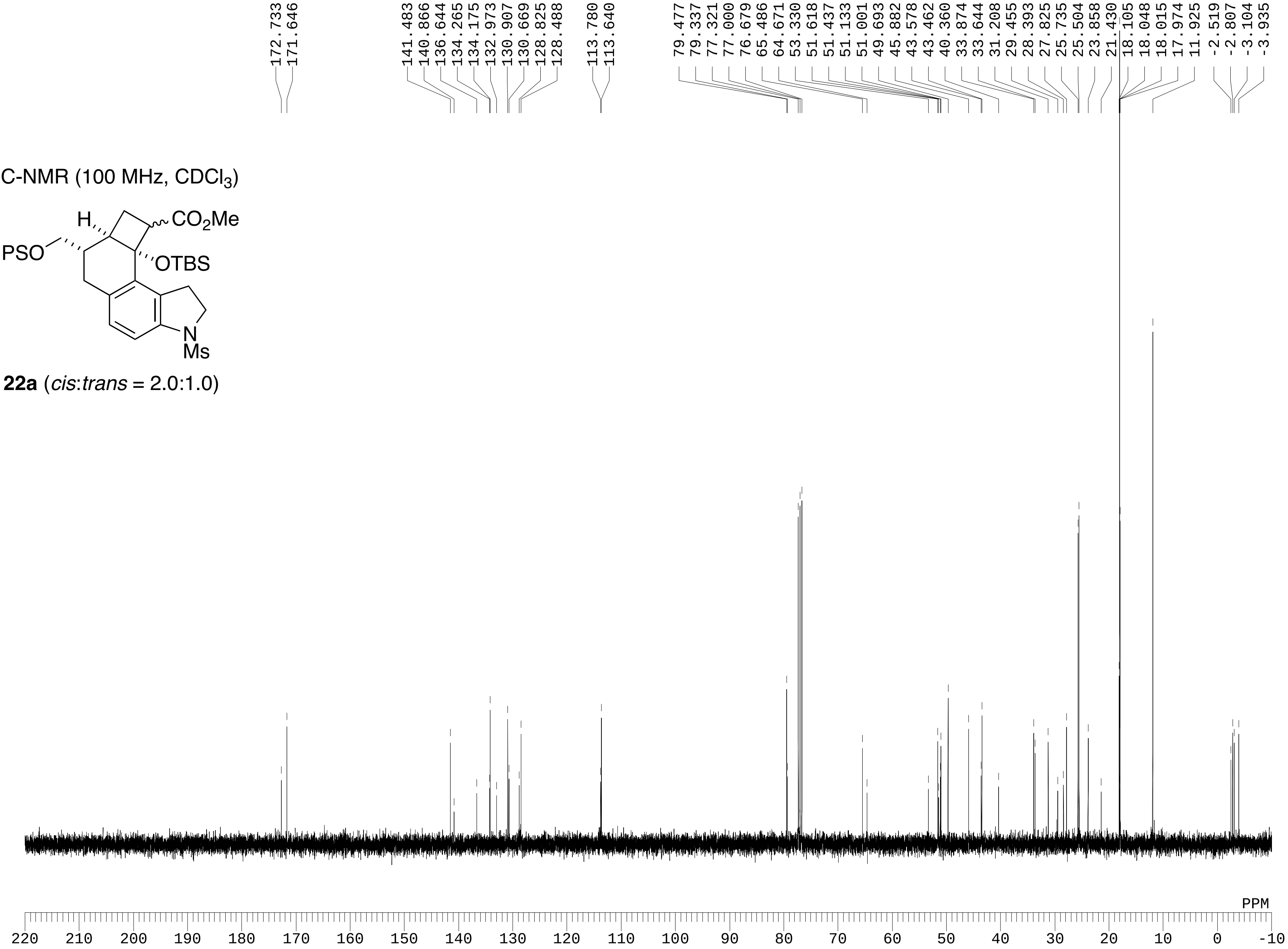
^{1}H-NMR (400 MHz, $CDCl_3$)

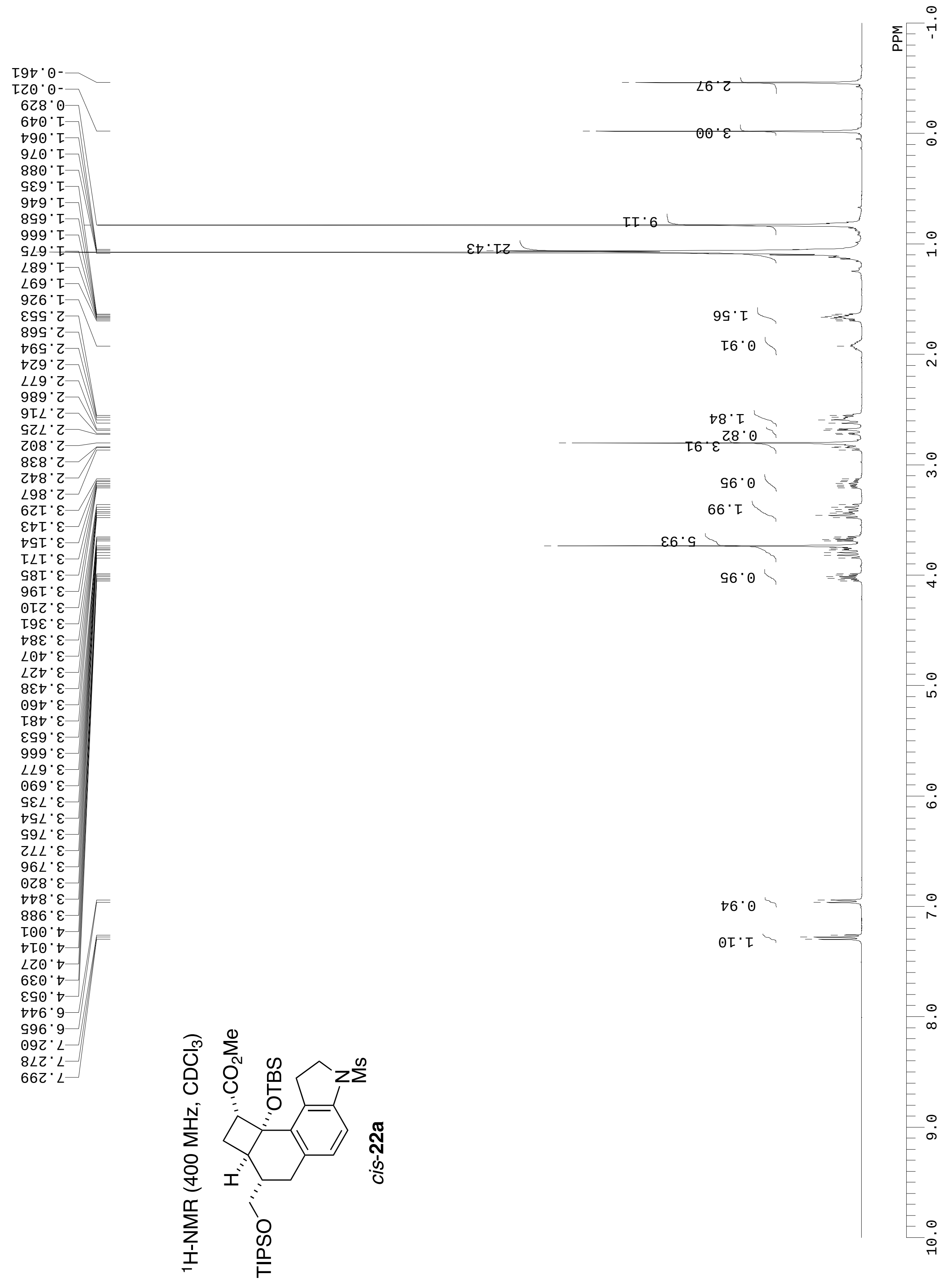
22a (*cis*:*trans* = 2.0:1.0)

^{13}C-NMR (100 MHz, $CDCl_3$)

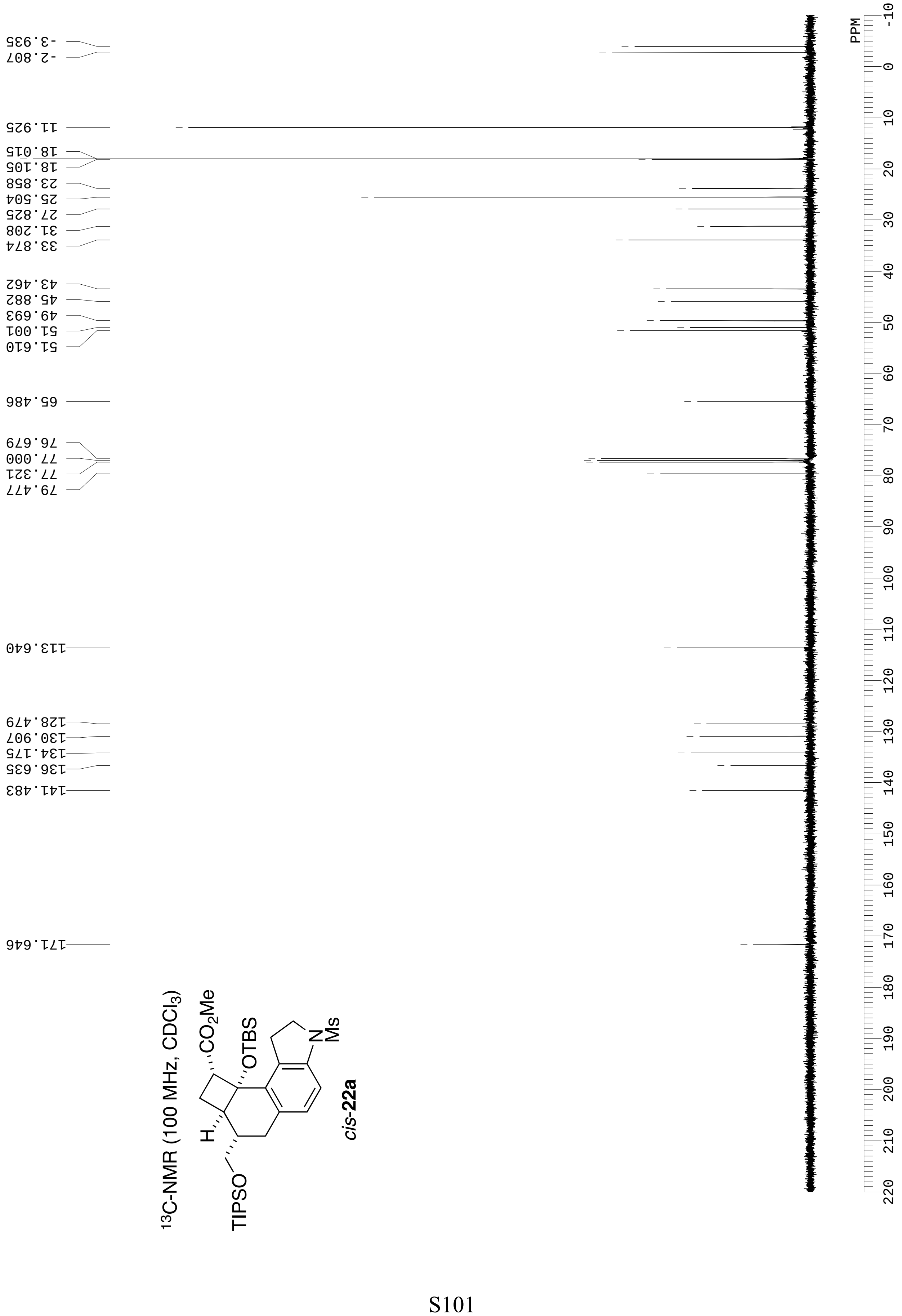


22a (*cis*:*trans* = 2.0:1.0)

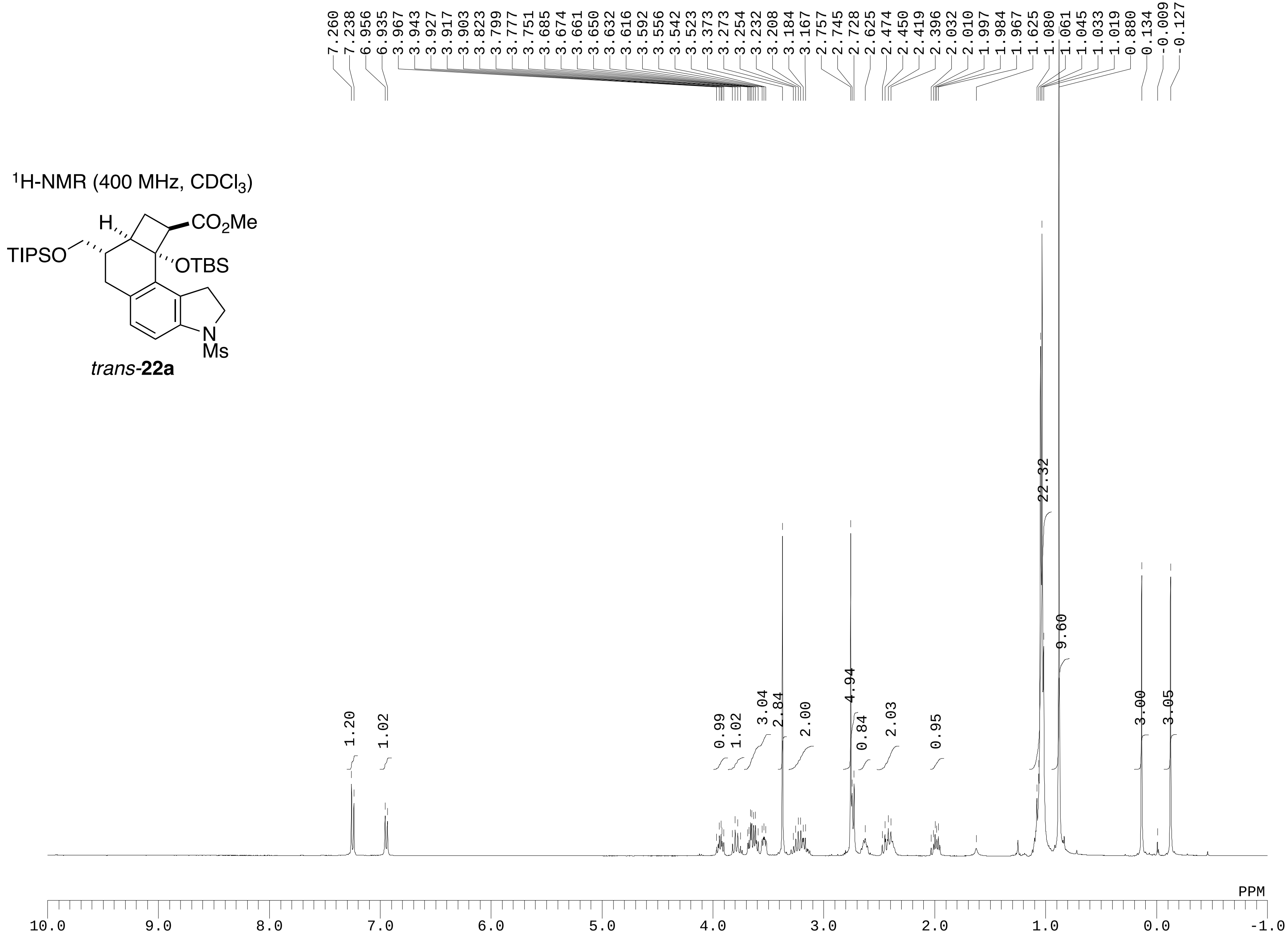




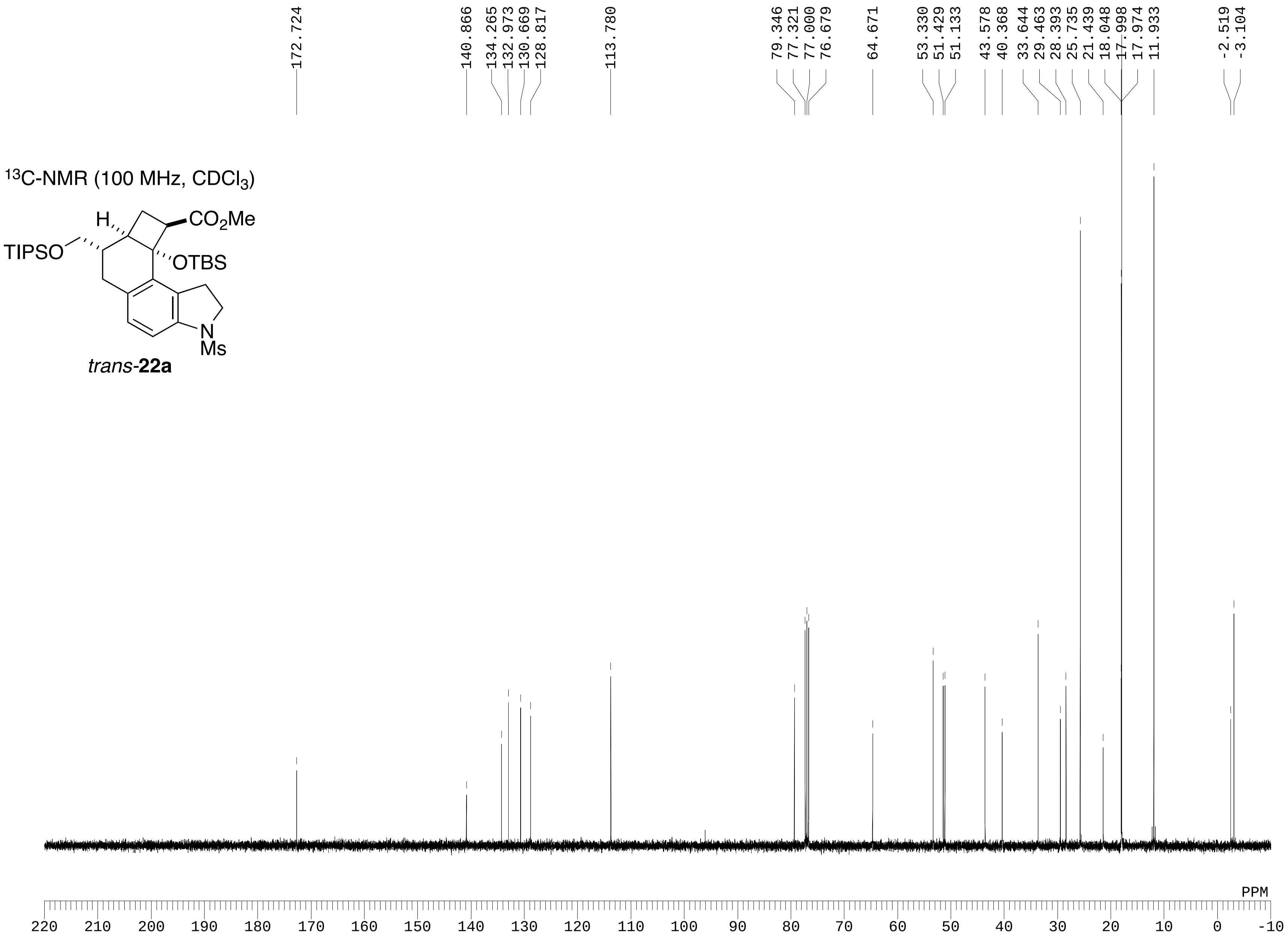
1H-NMR (400 MHz, CDCl3)
TIPSO
H
CO2Me
OTBS
N
Ms
cis-22a
-0.461
-0.021
0.829
1.049
1.064
1.076
1.088
1.635
1.646
1.658
1.666
1.675
1.687
1.697
1.926
2.553
2.568
2.594
2.624
2.677
2.686
2.716
2.725
2.802
2.838
2.842
2.867
3.129
3.143
3.154
3.171
3.185
3.196
3.210
3.361
3.384
3.407
3.427
3.438
3.460
3.481
3.653
3.666
3.677
3.690
3.735
3.754
3.765
3.772
3.796
3.820
3.844
3.988
4.001
4.014
4.027
4.039
4.053
6.944
6.965
7.260
7.278
7.299
2.97
3.00
9.11
21.43
1.56
0.91
1.84
0.82
3.91
0.95
1.99
5.93
0.95
0.94
1.10
PPM
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0


13C-NMR (100 MHz, CDCl3)
TIPSO
H
CO2Me
OTBS
N
Ms
cis-22a
-3.935
-2.807
11.925
18.015
18.105
23.858
25.504
27.825
31.208
33.874
43.462
45.882
49.693
51.001
51.610
65.486
76.679
77.000
77.321
79.477
113.640
128.479
130.907
134.175
136.635
141.483
171.646
PPM
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

^{1}H-NMR (400 MHz, CDCl$_3$)

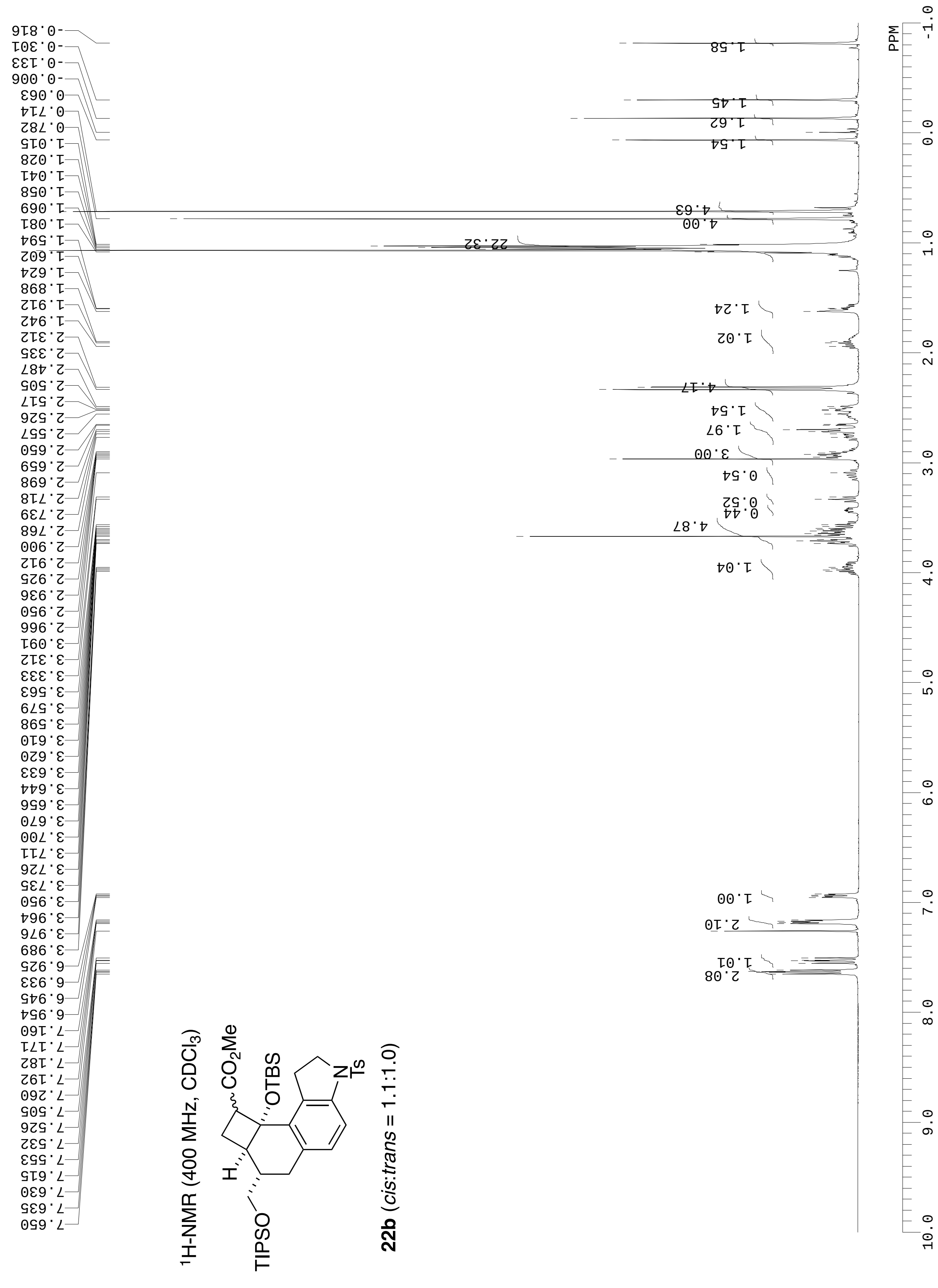


trans-**22a**



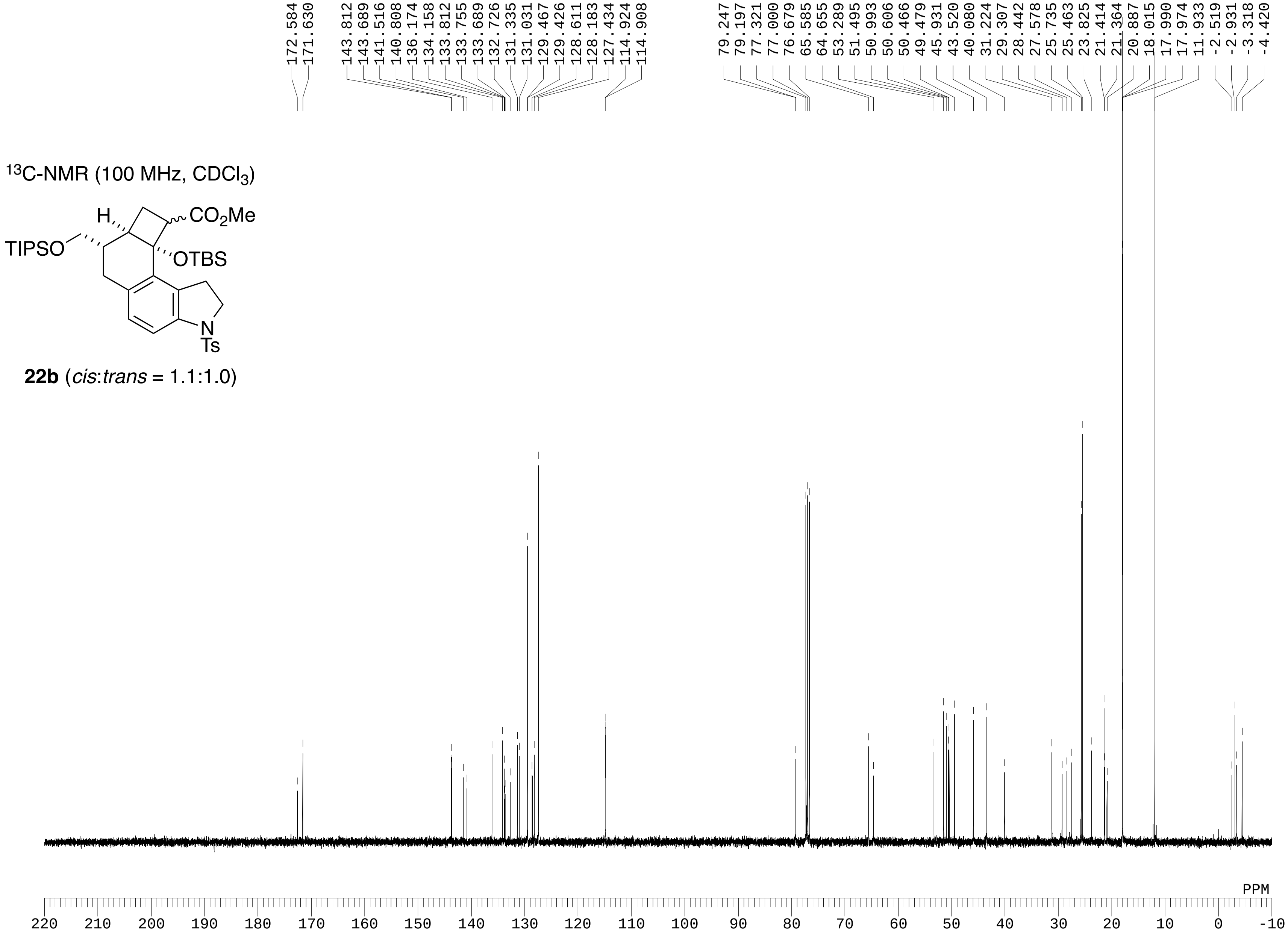
^{13}C-NMR (100 MHz, $CDCl_3$)

trans-**22a**



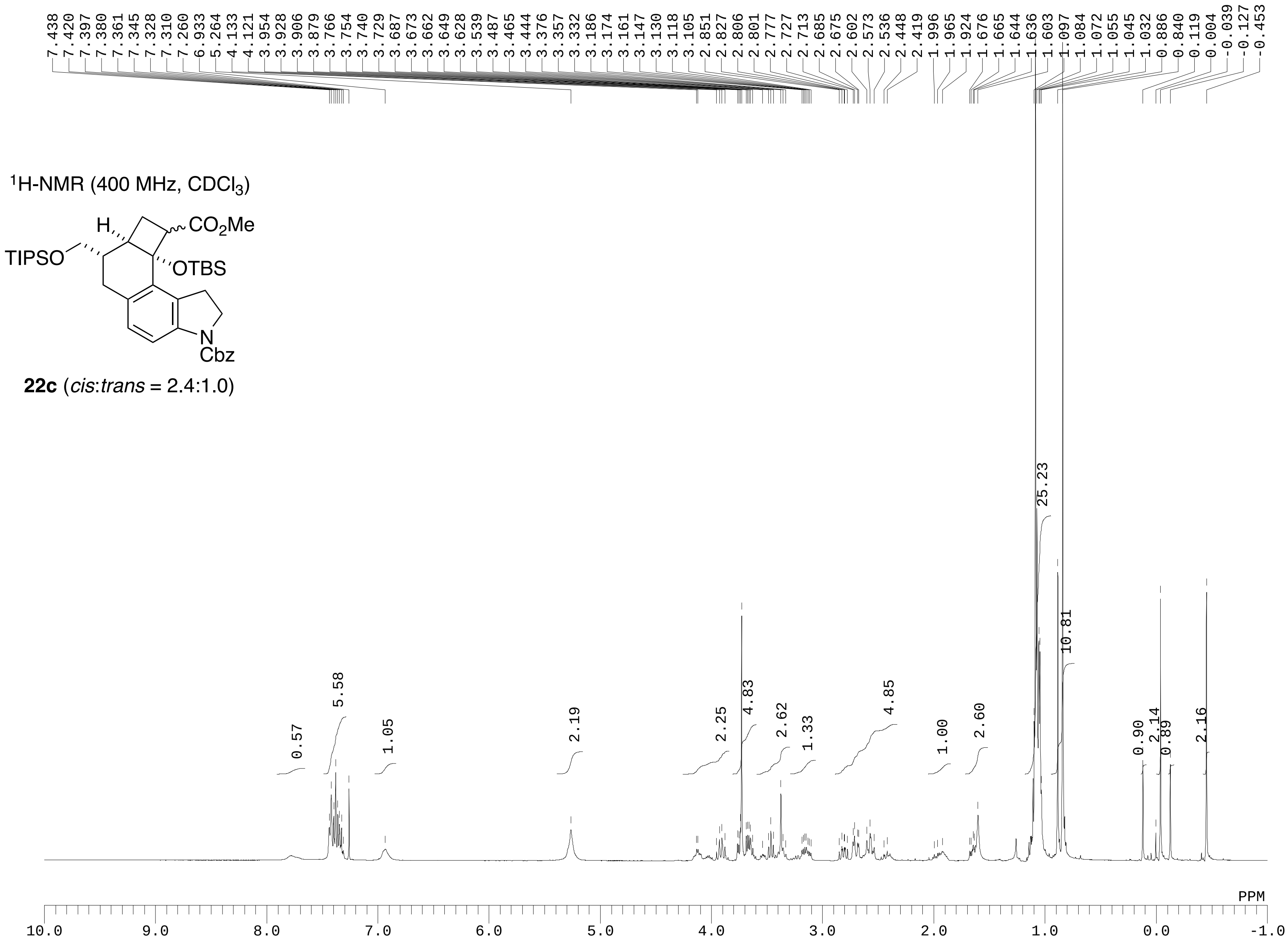
^{1}H-NMR (400 MHz, $CDCl_3$)

22b (*cis*:*trans* = 1.1:1.0)



^{13}C-NMR (100 MHz, CDCl$_3$)

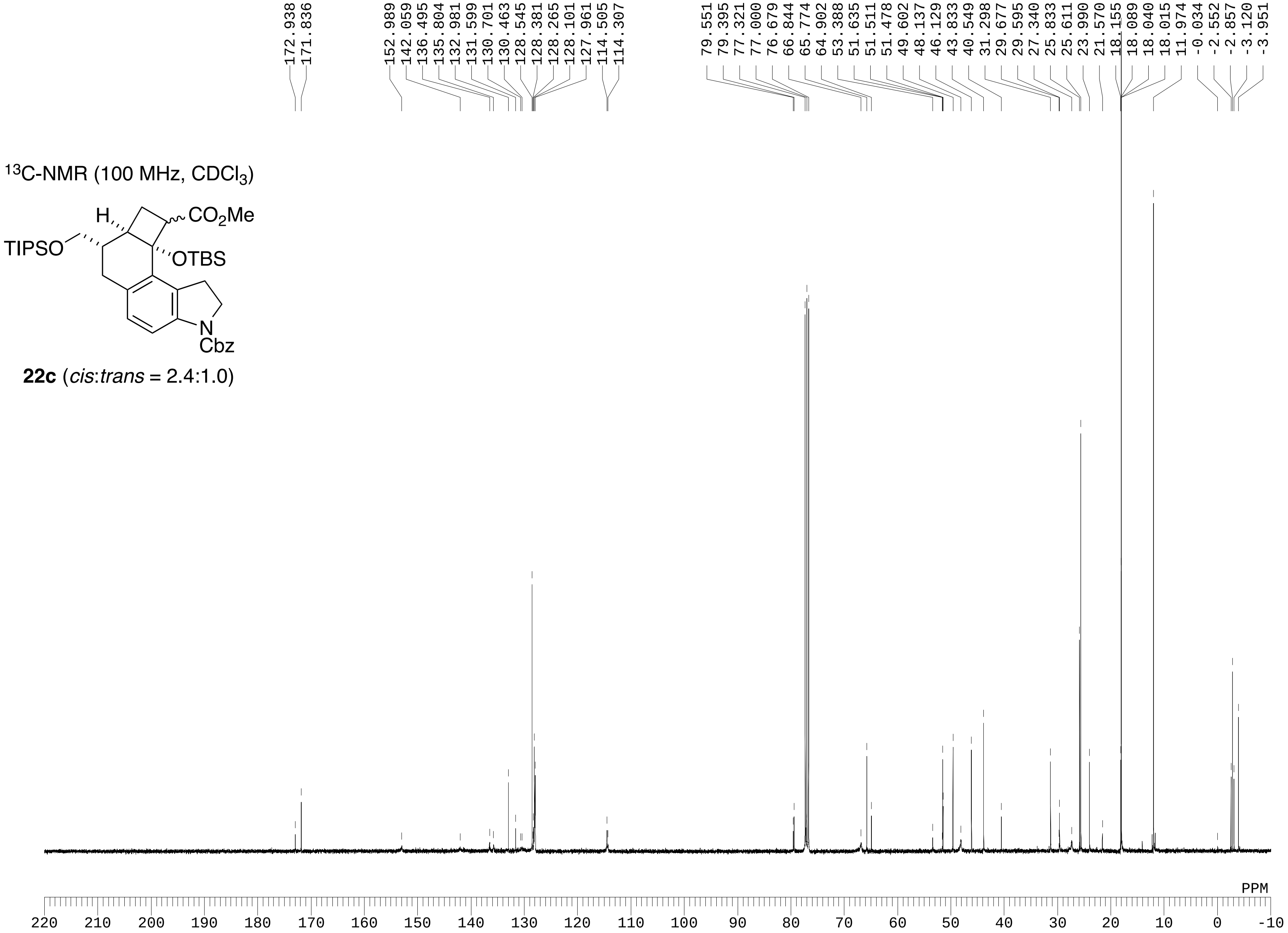
22b (*cis*:*trans* = 1.1:1.0)



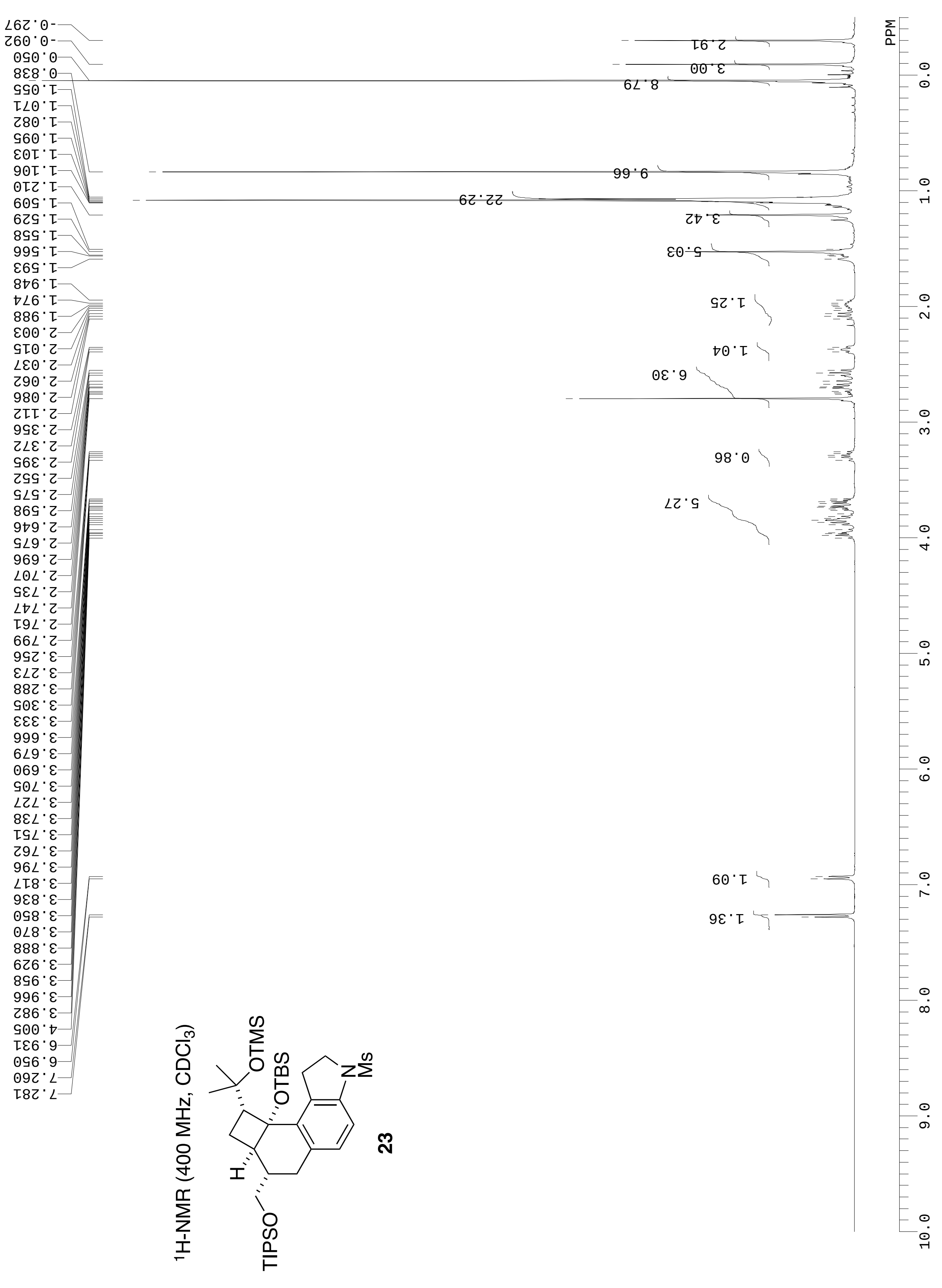
^{1}H-NMR (400 MHz, $CDCl_3$)

22c (*cis*:*trans* = 2.4:1.0)

^{13}C-NMR (100 MHz, $CDCl_3$)

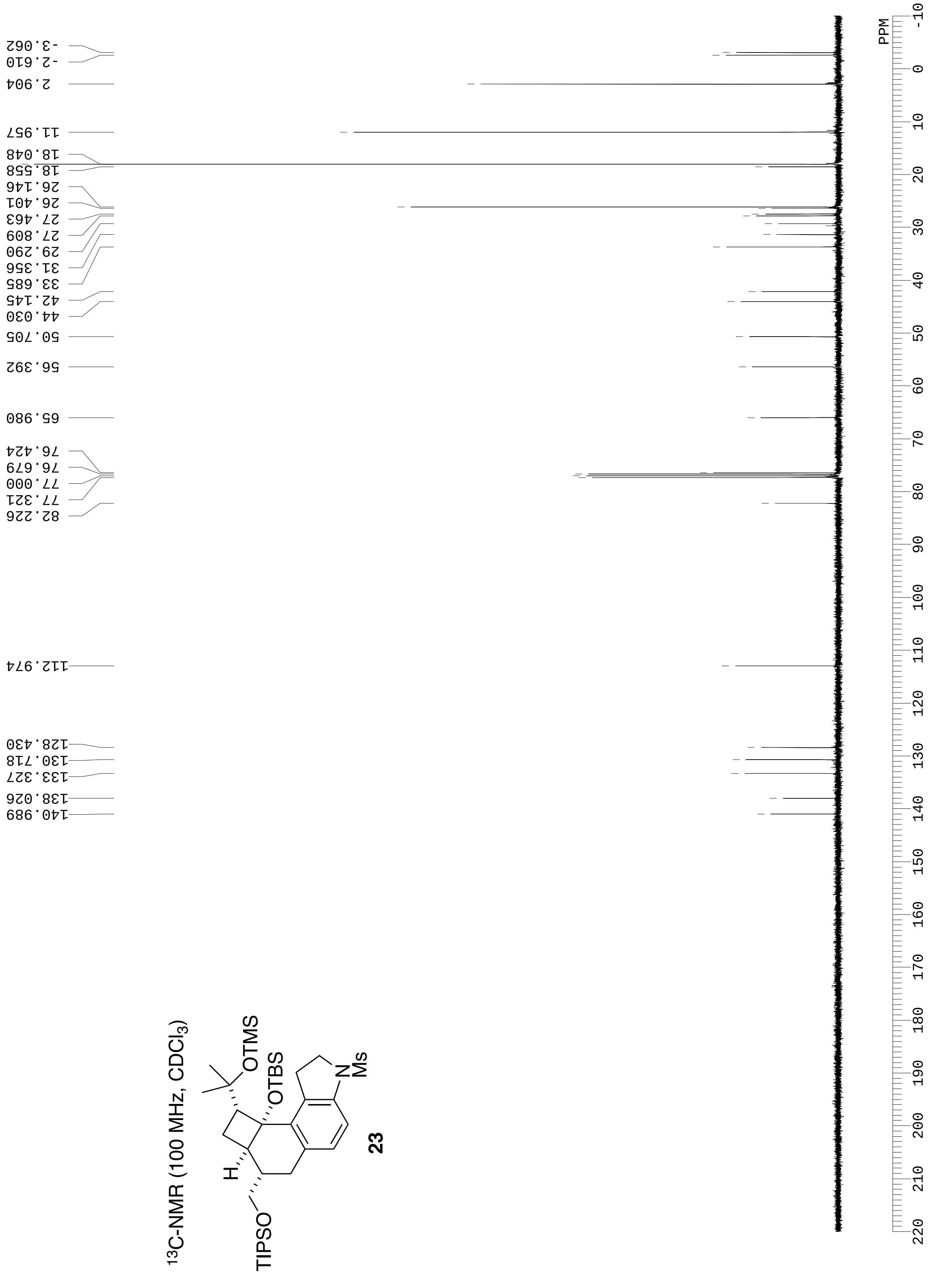


22c (*cis*:*trans* = 2.4:1.0)



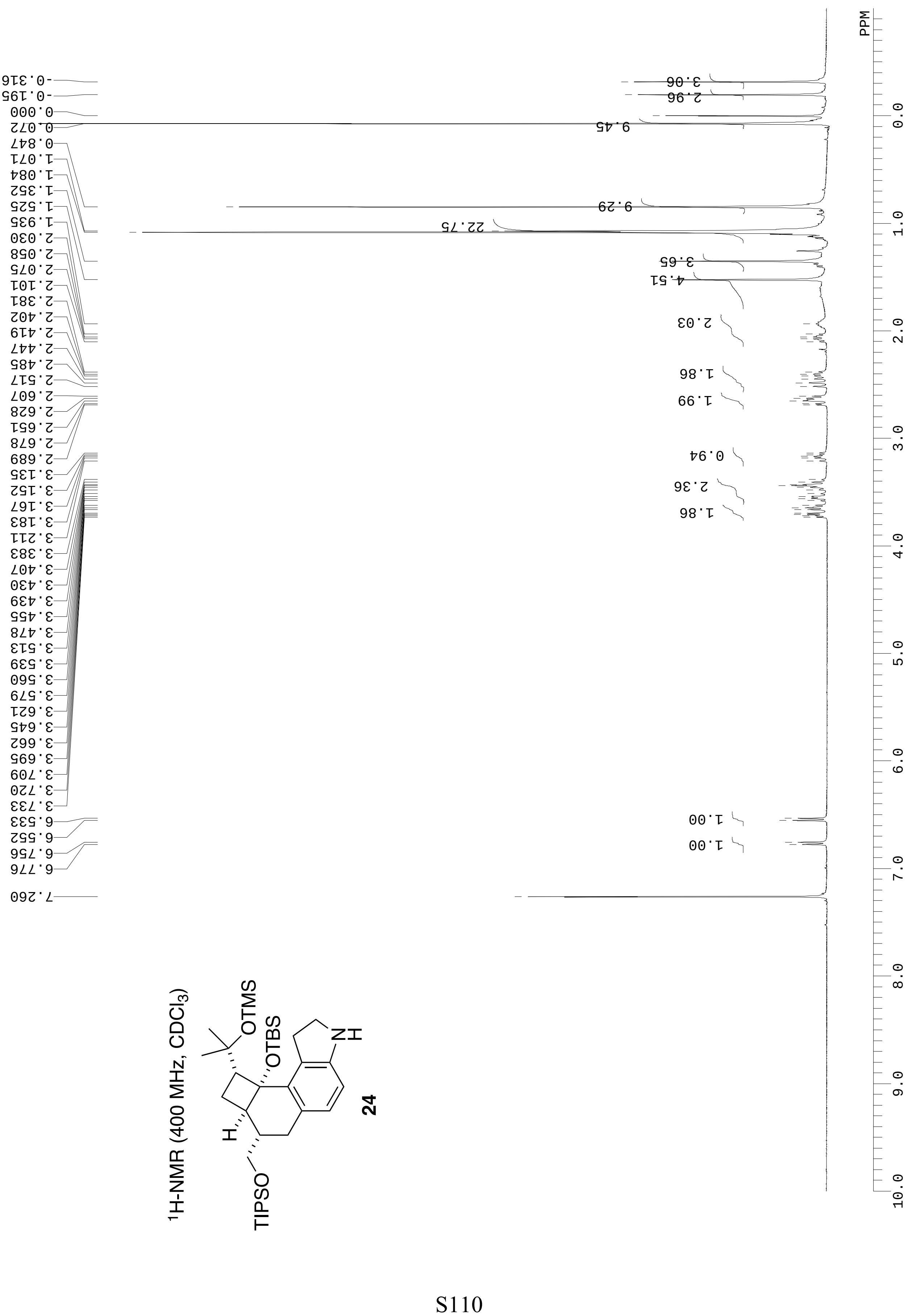
^{1}H-NMR (400 MHz, CDCl$_3$)

23



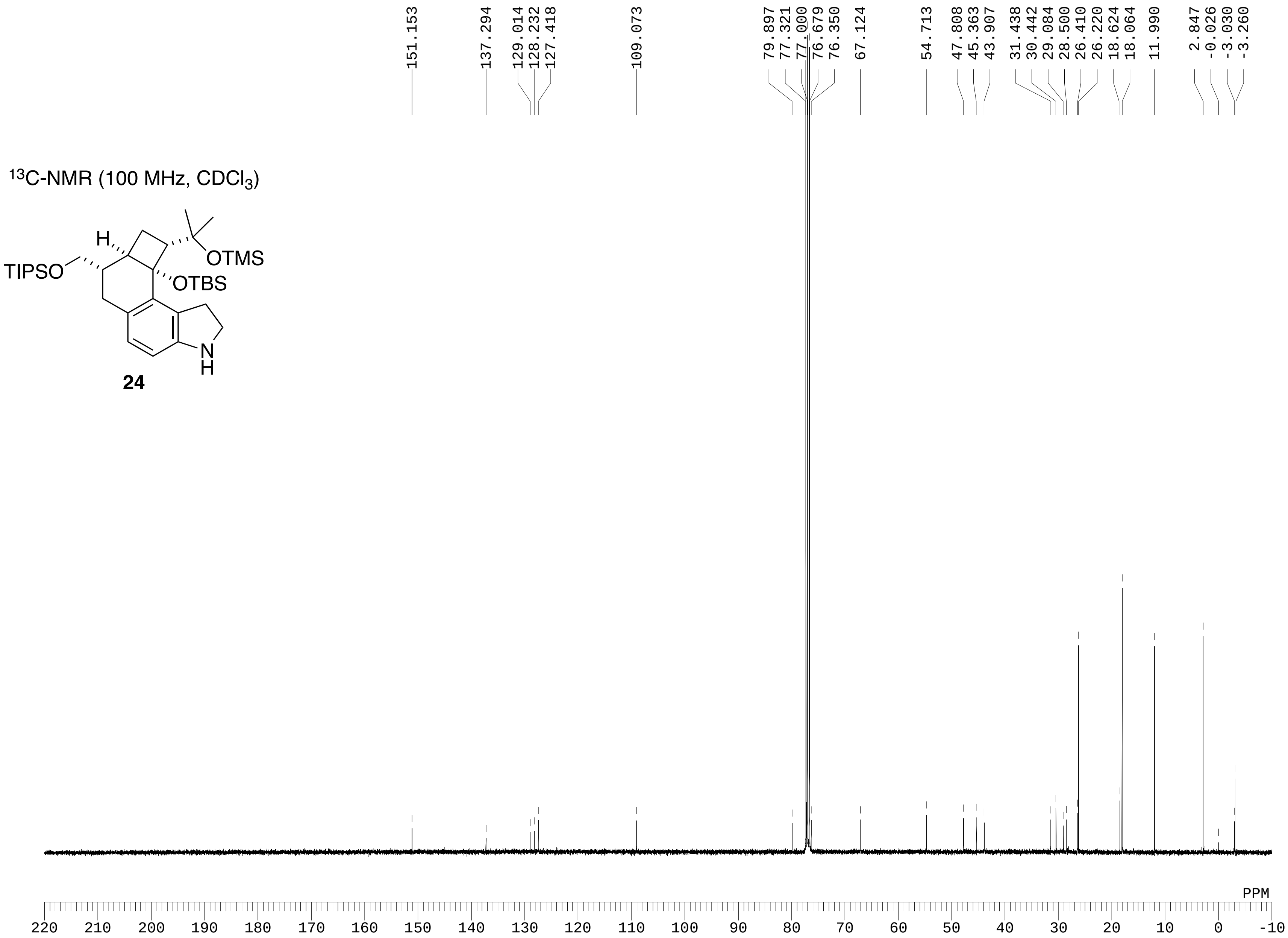
^{13}C-NMR (100 MHz, $CDCl_3$)

23


^{1}H-NMR (400 MHz, CDCl$_3$)

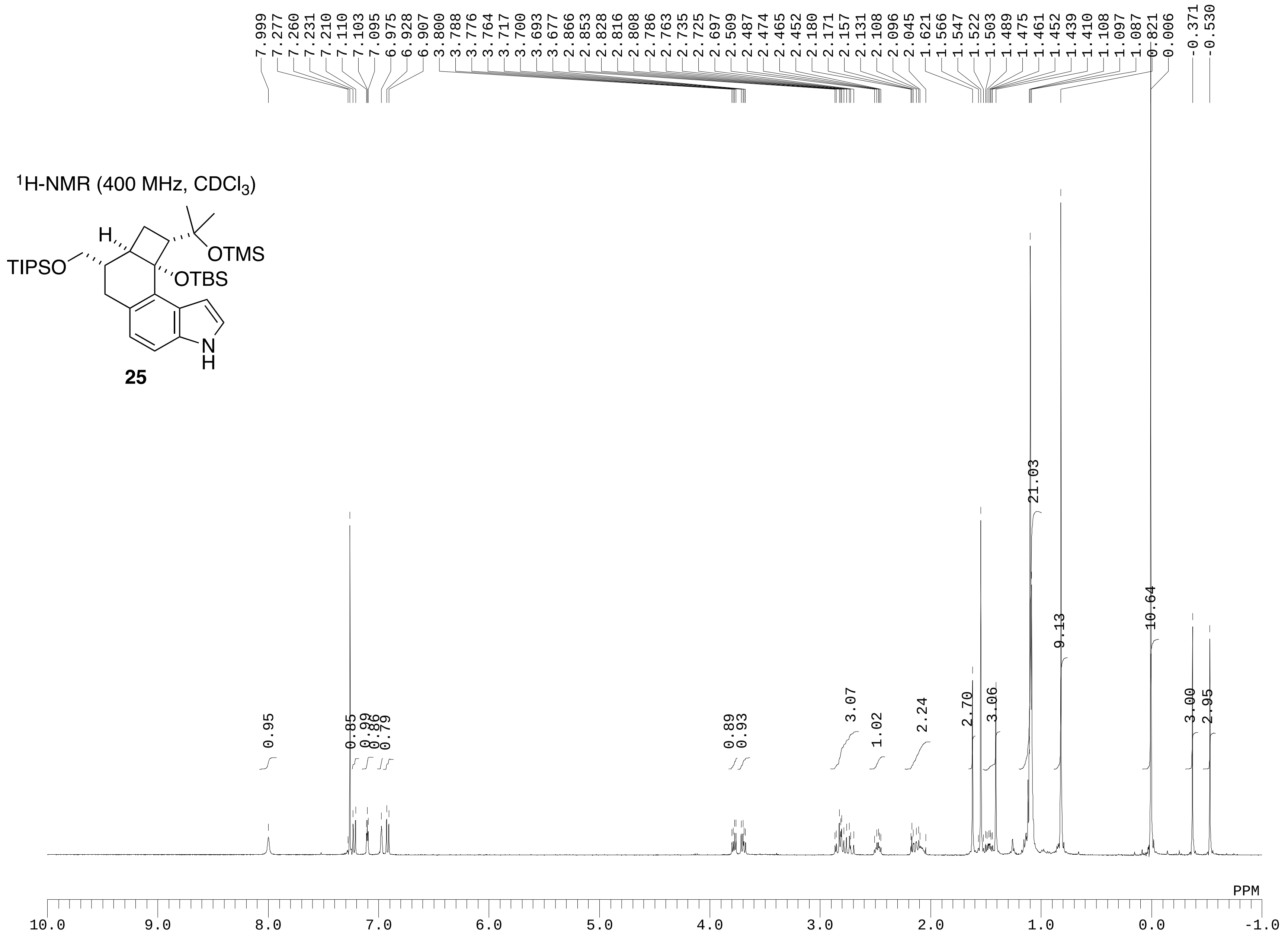
24

^{13}C-NMR (100 MHz, CDCl$_3$)



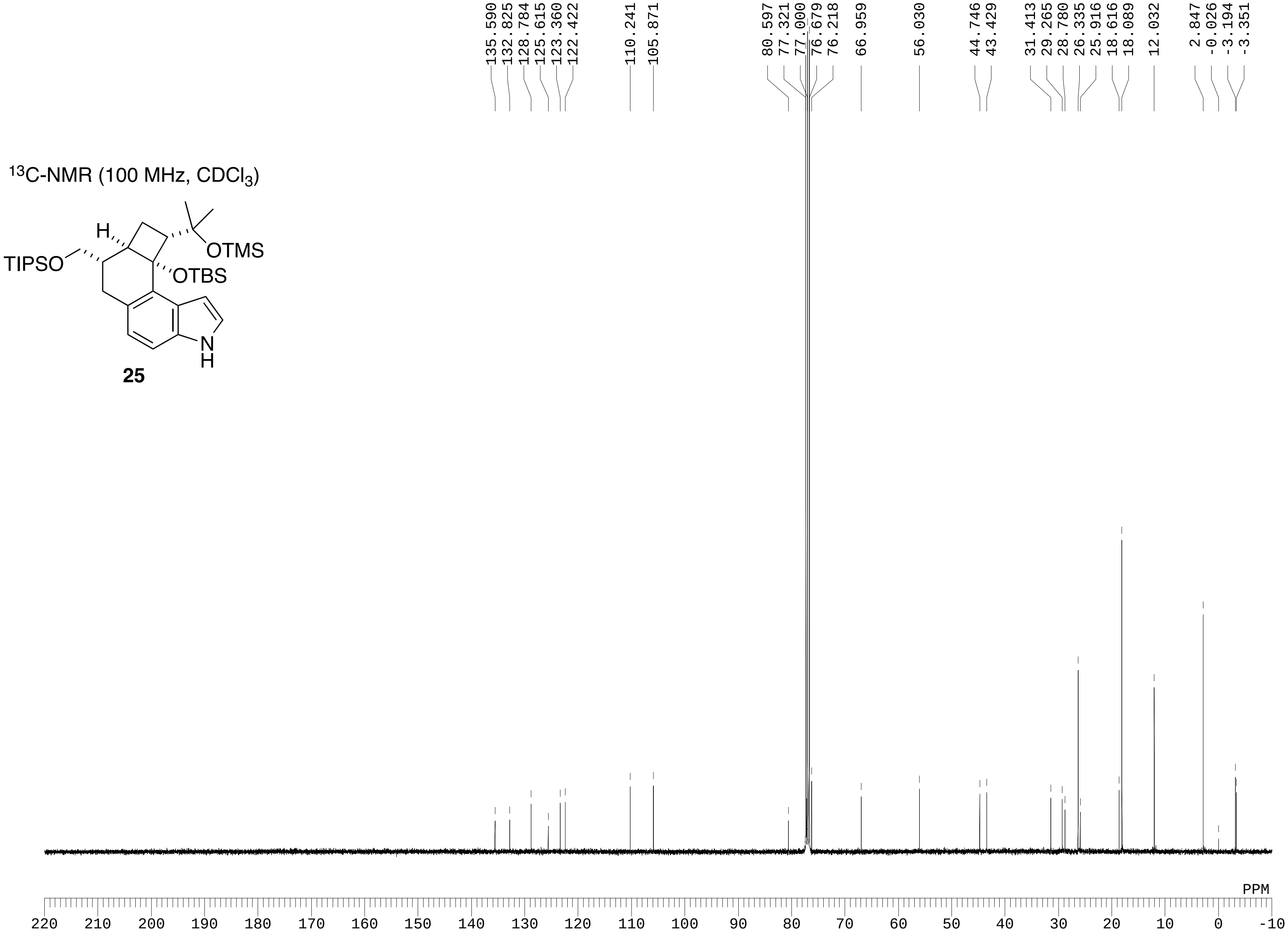
24

^{1}H-NMR (400 MHz, CDCl$_3$)

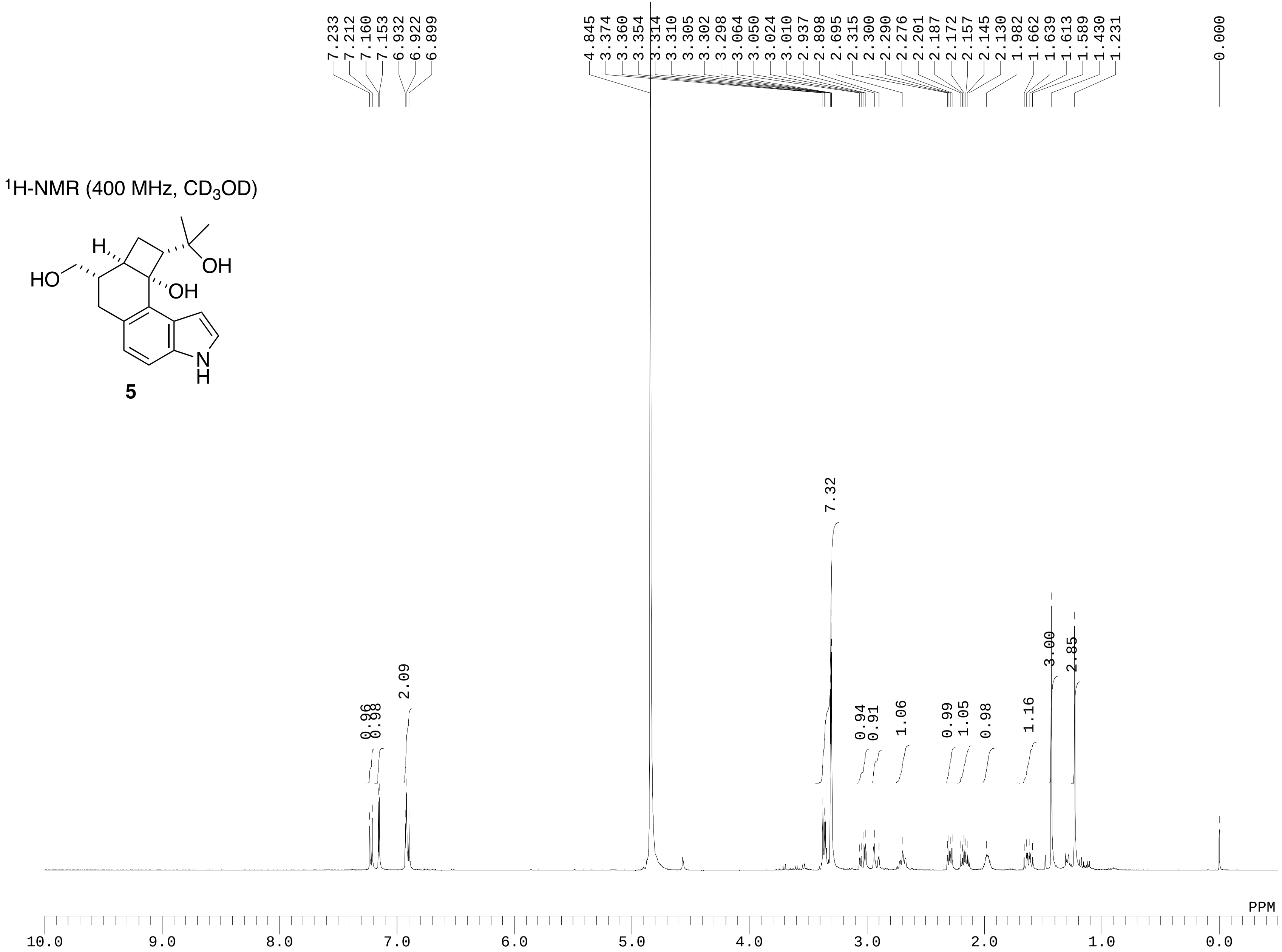


25

¹³C-NMR (100 MHz, CDCl$_3$)

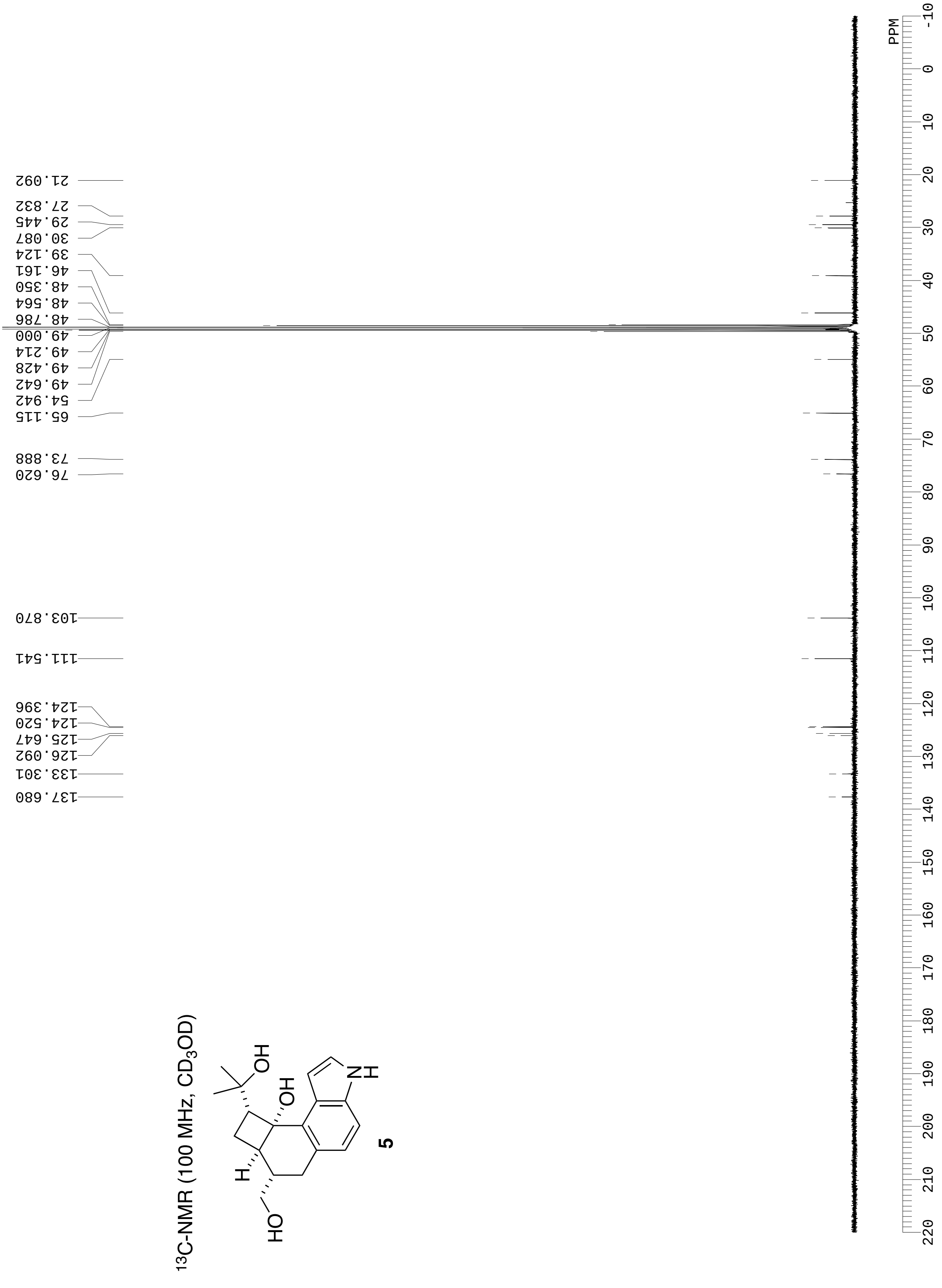


25



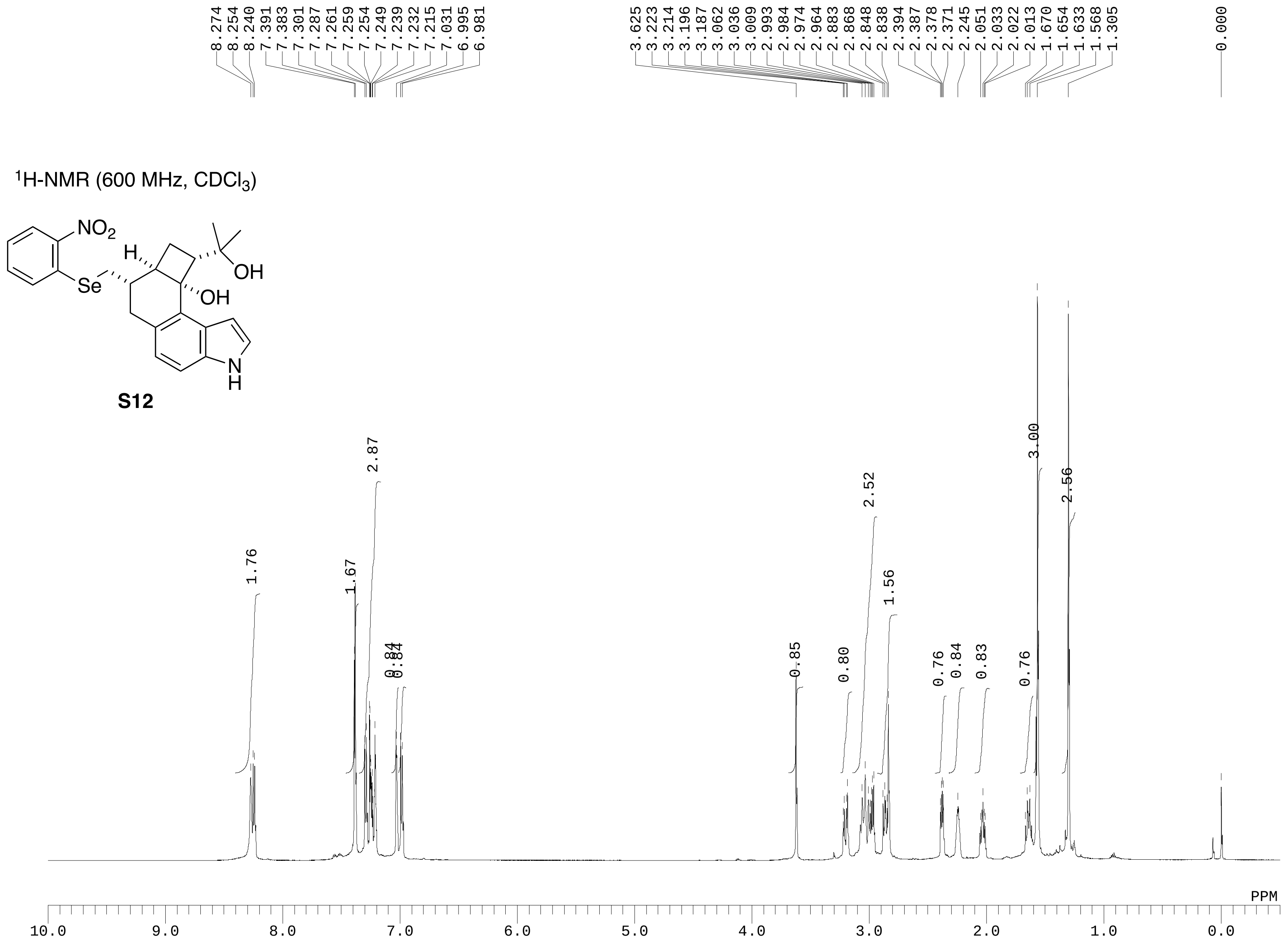
^{1}H-NMR (400 MHz, CD_3OD)

5



^{13}C-NMR (100 MHz, CD$_3$OD)

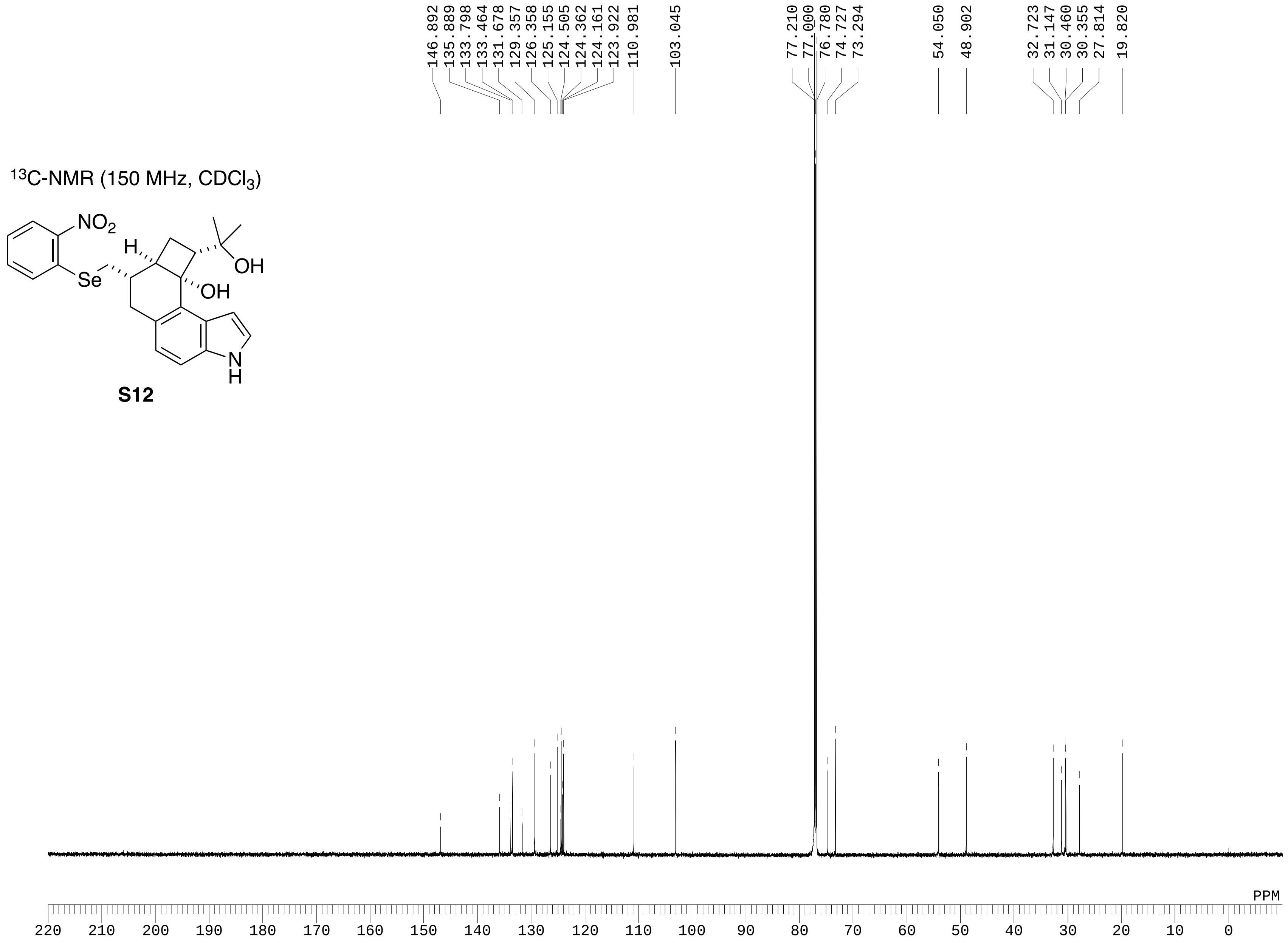
5



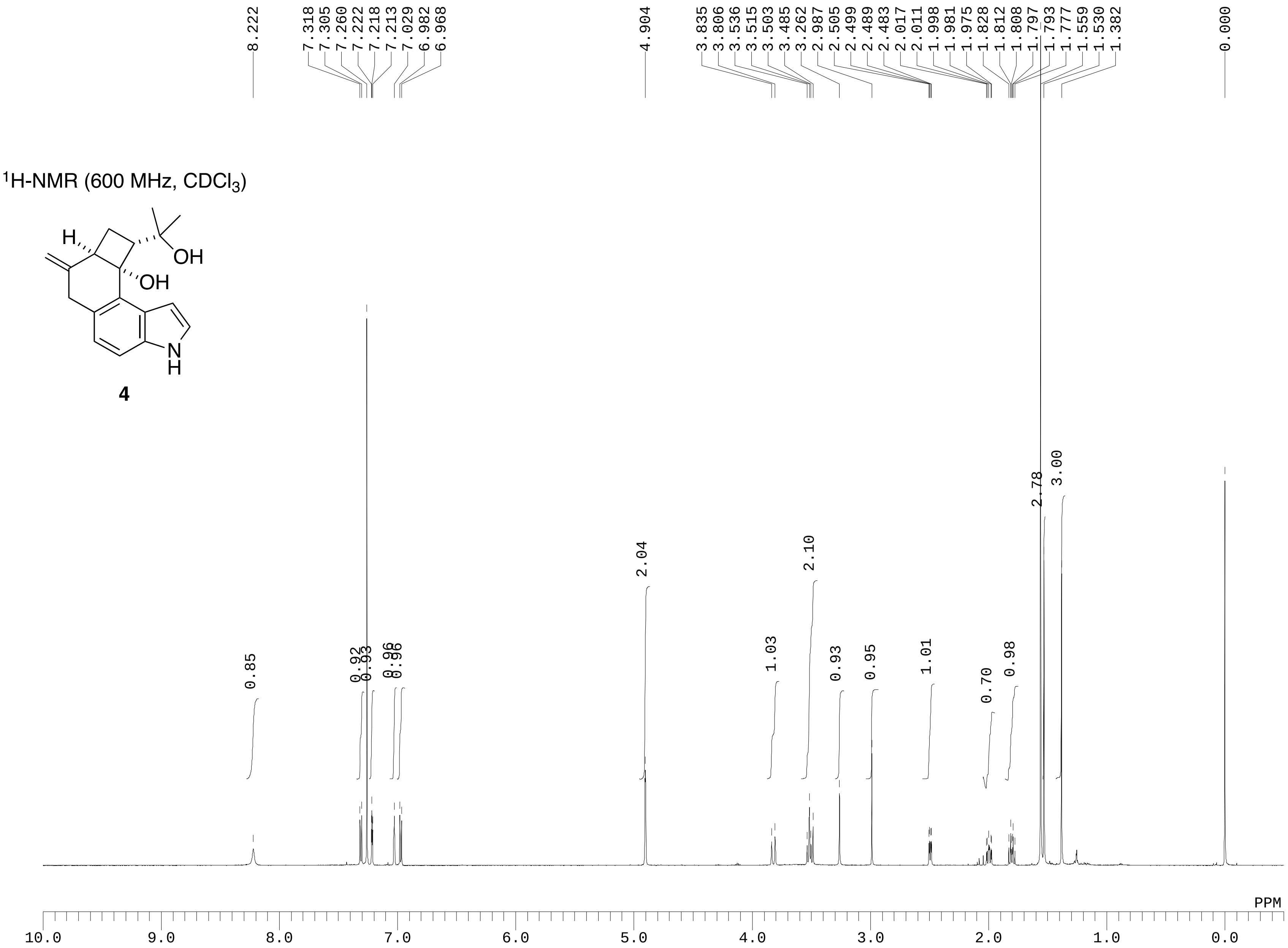
^{1}H-NMR (600 MHz, $CDCl_3$)

S12

^{13}C-NMR (150 MHz, CDCl$_3$)



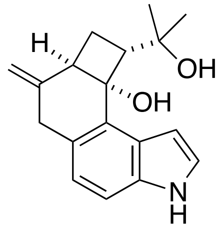
S12



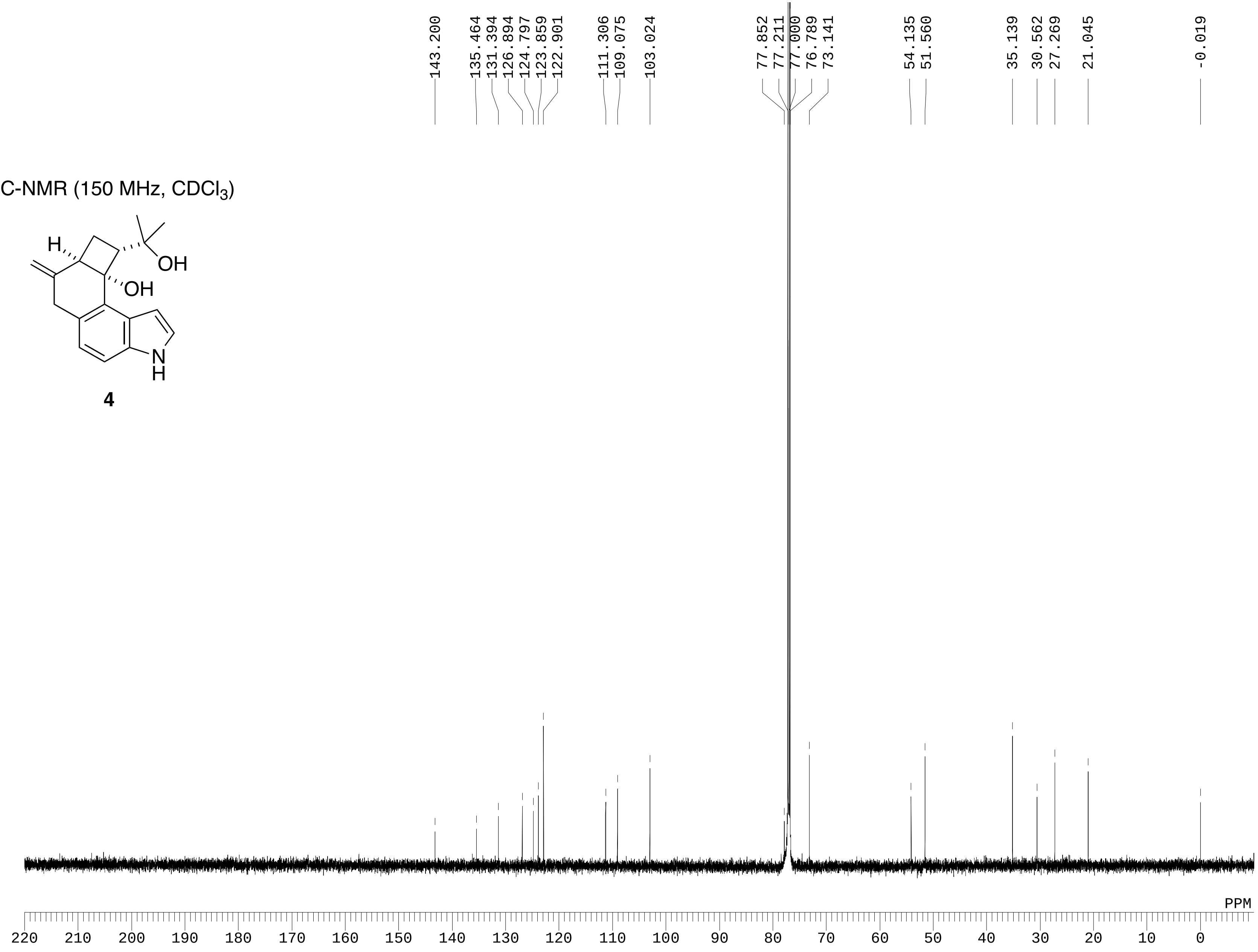
^{1}H-NMR (600 MHz, CDCl$_3$)

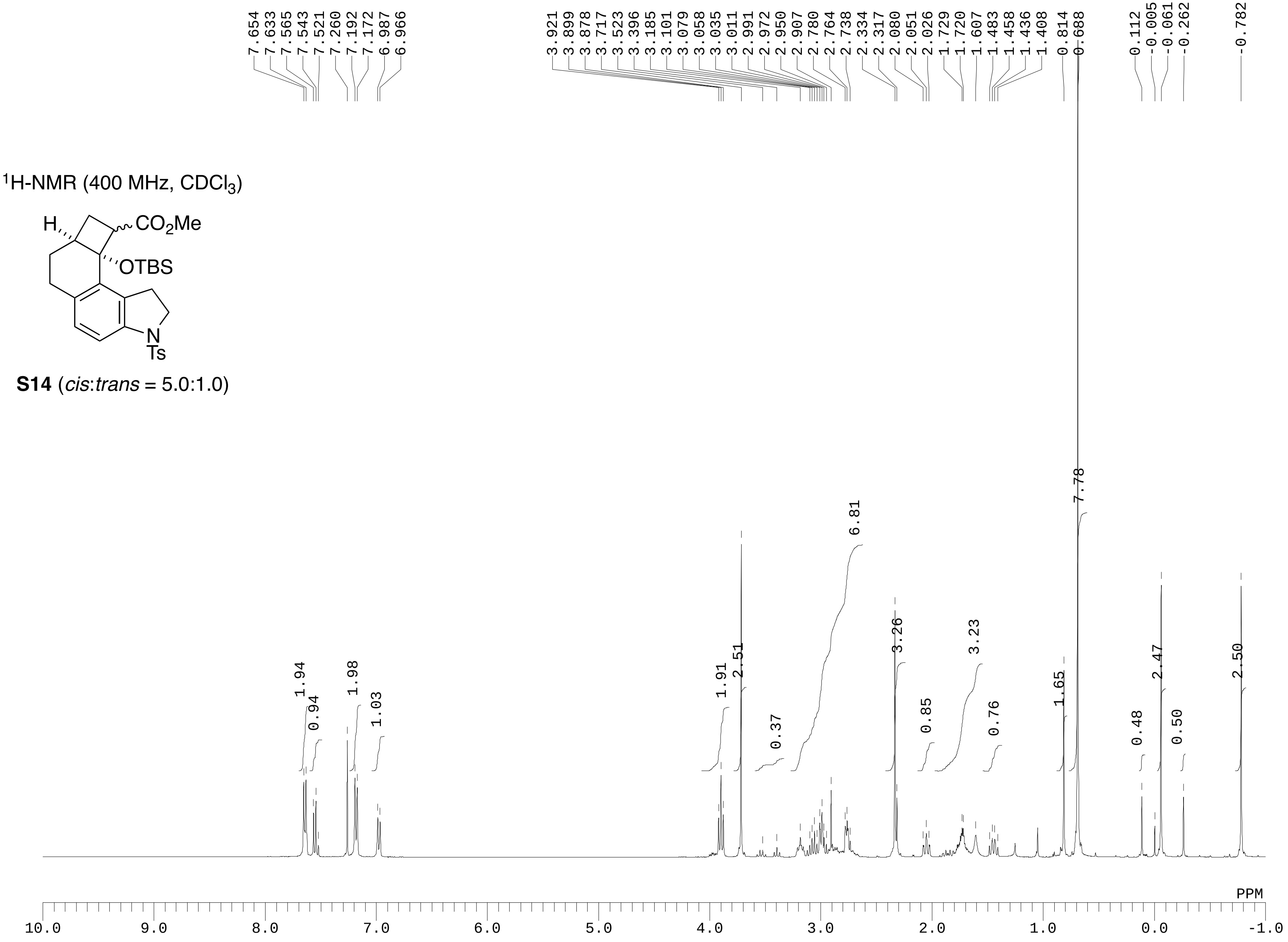
4

^{13}C-NMR (150 MHz, CDCl$_3$)



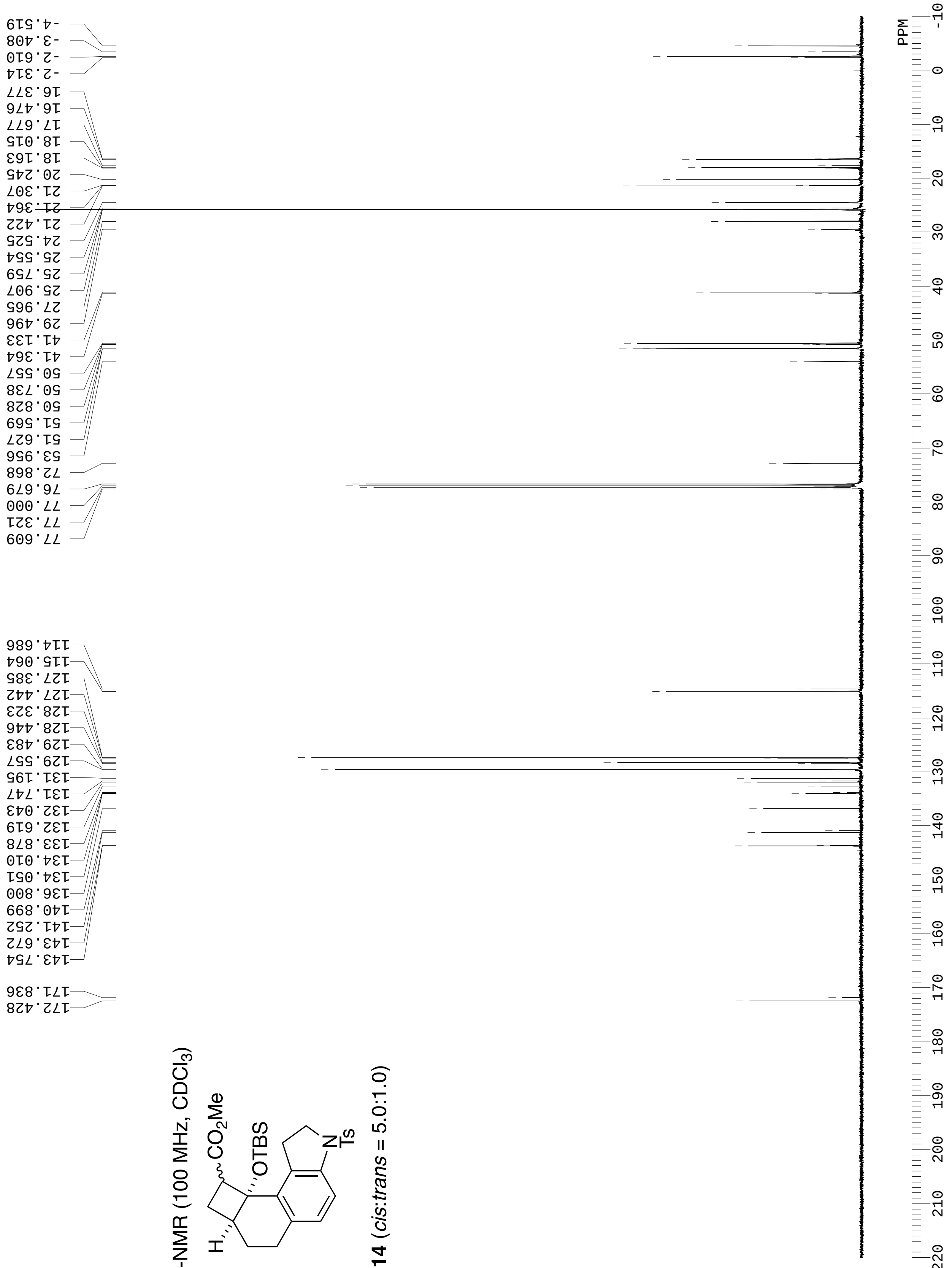
4





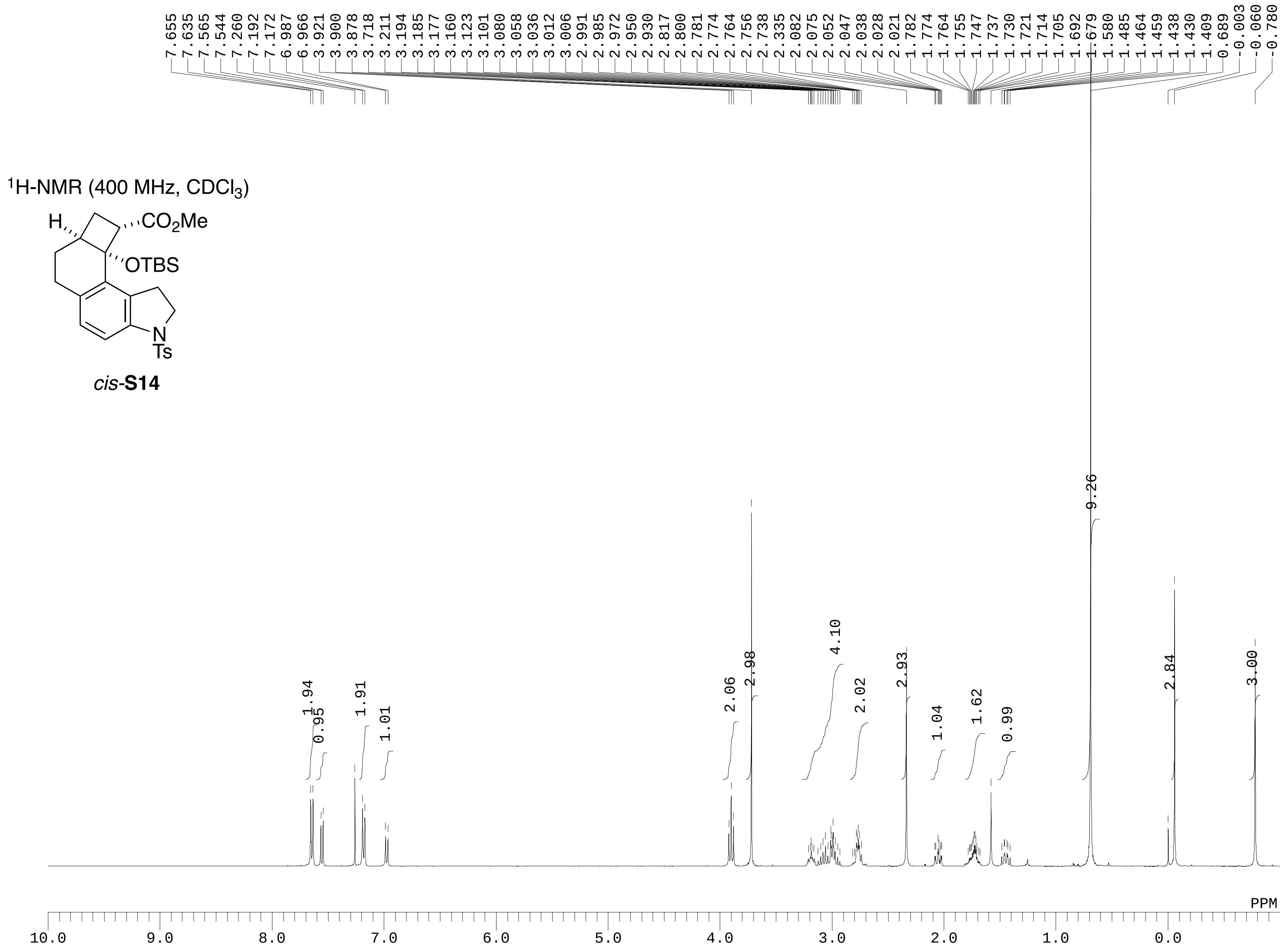
^{1}H-NMR (400 MHz, CDCl$_3$)

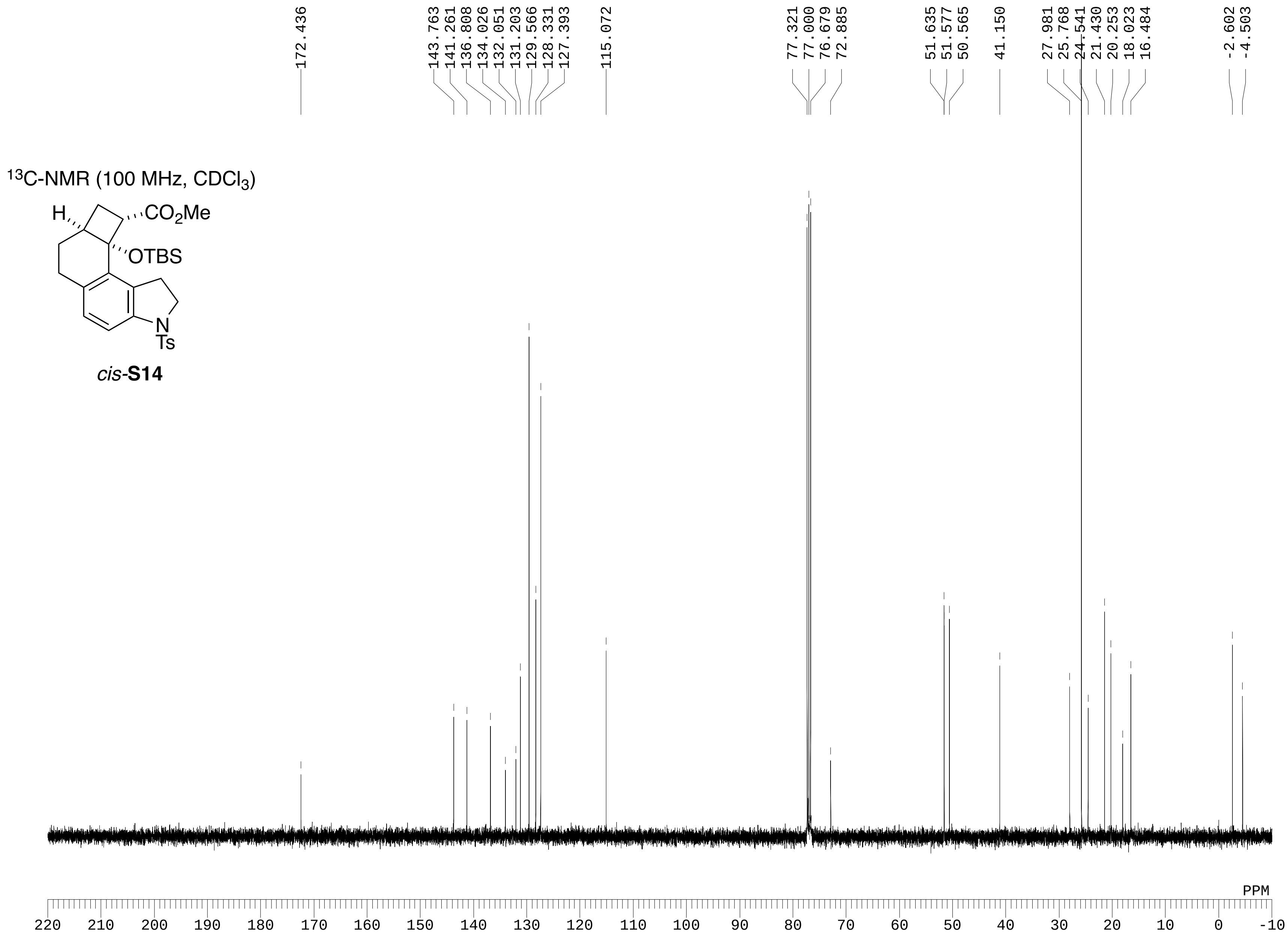
S14 (*cis*:*trans* = 5.0:1.0)



^{13}C-NMR (100 MHz, $CDCl_3$)

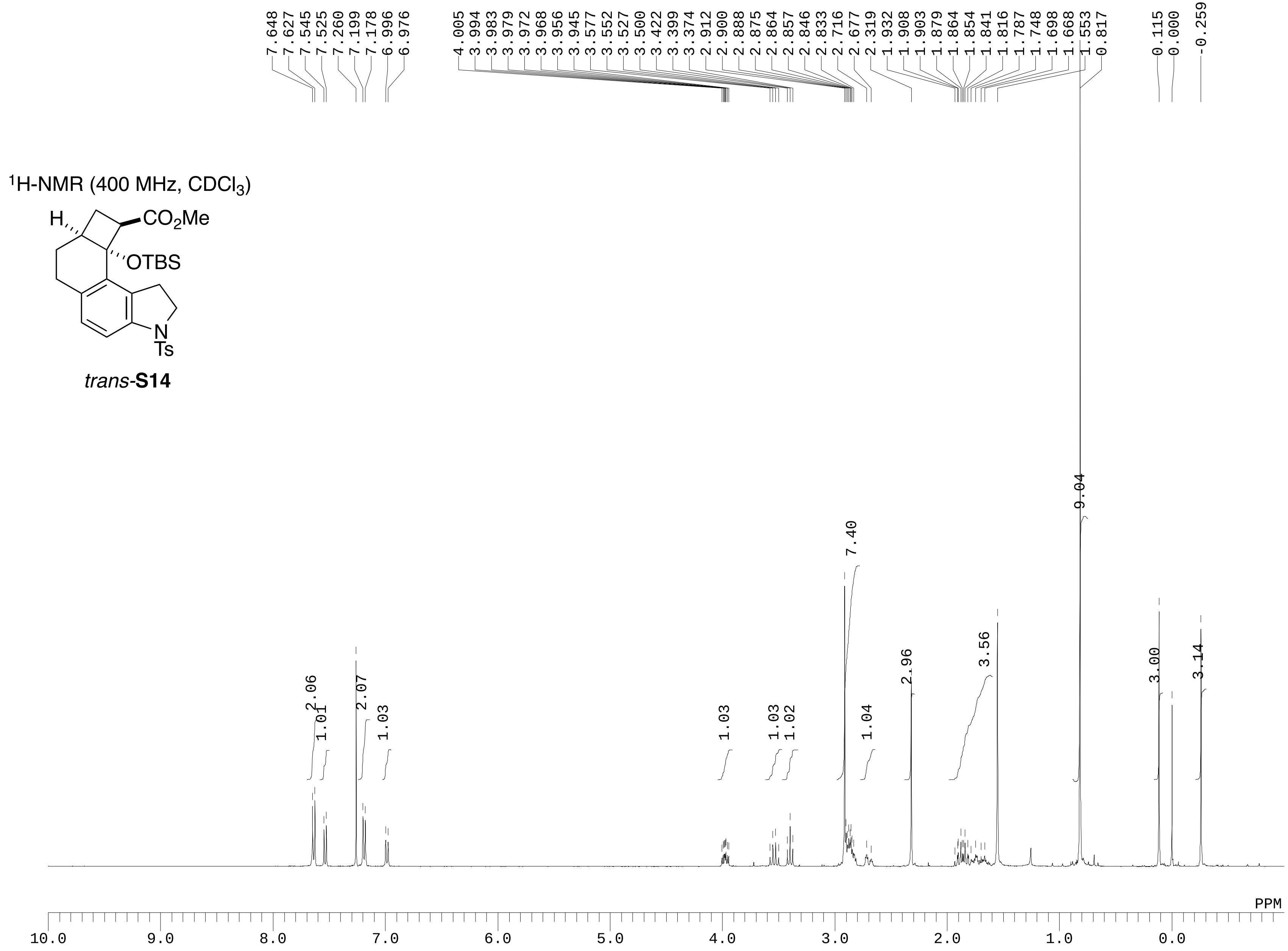
S14 (*cis*:*trans* = 5.0:1.0)


1H-NMR (400 MHz, CDCl3)
H
CO2Me
OTBS
N
Ts
cis-S14
7.655
7.635
7.565
7.544
7.260
7.192
7.172
6.987
6.966
3.921
3.900
3.878
3.718
3.211
3.194
3.185
3.177
3.160
3.123
3.101
3.080
3.058
3.036
3.012
3.006
2.991
2.985
2.972
2.950
2.930
2.817
2.800
2.781
2.774
2.764
2.756
2.738
2.335
2.082
2.075
2.052
2.047
2.038
2.028
2.021
1.782
1.774
1.764
1.755
1.747
1.737
1.730
1.721
1.714
1.705
1.692
1.679
1.580
1.485
1.464
1.459
1.438
1.430
1.409
0.689
-0.003
-0.060
-0.780
1.94
0.95
1.91
1.01
2.06
2.98
4.10
2.02
2.93
1.04
1.62
0.99
9.26
2.84
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



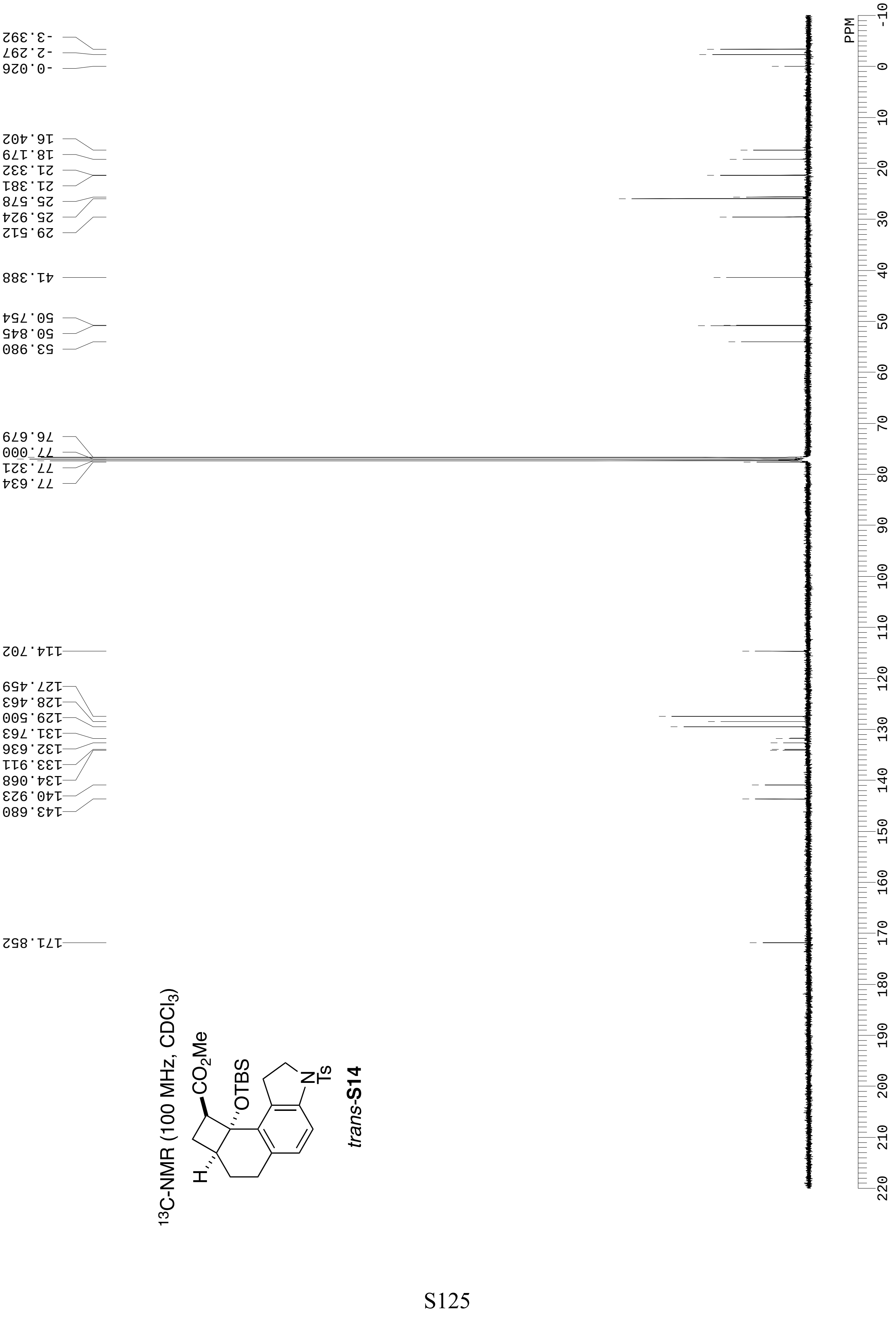
^{13}C-NMR (100 MHz, CDCl$_3$)

cis-**S14**



^{1}H-NMR (400 MHz, CDCl$_3$)

trans-**S14**


^{13}C-NMR (100 MHz, CDCl$_3$)

trans-**S14**