Catalytic, Enantioselective, Intramolecular Carbosulfenocyclization of Olefins

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven (160 °C) and/or flamed-dried glassware under an atmosphere of dry argon unless otherwise noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), ether (Fisher, ACS grade, BHT stabilized), and dichloromethane (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexanes (Fisher, Optima grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, and chromatography were certified ACS grade. "Brine" refers to a saturated solution of sodium chloride in H_2O. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples. A ThermoNesLab CC-100 cryocool with an attached cryotrol was used for reactions at subambient temperatures.

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity (400 MHz, ^{1}H; 101 MHz, ^{13}C) or Inova (500 MHz, ^{1}H; 126 MHz, ^{13}C) spectrometers. ^{31}P NMR and ^{19}F spectra were recorded on Inova (202 MHz) and Inova (376 MHz) spectrometers respectively. Acquisition times were 4.096 s for ^{1}H NMR, and 1.024 s for ^{13}C NMR. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C). Chemical shifts are reported in parts per million, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants, *J*, are reported in Hertz, and integration is provided and assignments are indicated. Assignments were confirmed through 1-D, COSY, HSQC, HMQC and HMBC experiments. Elemental analysis was performed by the University of Illinois Microanalysis Laboratory or Robertson Microlit Laboratories. Mass spectrometry (MS) was performed by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnegan-MAT C5 spectrometer. Chemical Ionization (CI) spectra were performed with methane reagent gas on a Micromass 70-VSE spectrometer. Electrospray Ionization (ESI) spectra were performed on a Micromass Q-Tof Ultima spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system and peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T), w (weak, 67–100%), and br (broad). Melting points (mp) were determined on a Thomas-Hoover capillary

melting point apparatus in sealed tubes and are corrected.

Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} or Merck silica gel 60 RP-18 F_{254s} plates. Visualization was accomplished with UV light and/or potassium permanganate ($KMnO_4$) solution. R_f values reported were measured using a 10 × 2 cm TLC plate in a developing chamber containing the solvent system described. Flash chromatography was performed using Merck silica gel 60 230–400 mesh (60–63 μ, 60 Å pore size) unless otherwise stated.

Analytical supercritical fluid chromatography (SFC) was performed on an Agilent 1100 HPLC equipped with an Aurora Systems A-5 supercritical CO_2 adapter for supercritical fluid chromatography and a UV detector (220 nm or 254 nm) using Daicel Chiralcel OD, OJ, OB or Chiralpak AD, and AS columns.

Commercial reagents were purified by distillation or recrystallization prior to use unless otherwise stated. Solvents for chromatography, filtration and recrystallization were dichloromethane (Aldrich, ACS grade), ethyl acetate (Fisher, ACS grade), diethyl ether (Fisher, ACS grade), and hexane (Fisher, Optima). Methanesulfonic acid (Aldrich), Ethanesulfonic acid (Aldrich) phthalimide (Aldrich), selenium powder (Aldrich), borane-pyridine complex, iodomethane (Aldrich), sodium borohydride (Aldrich), lithium borohydride (Aldrich), cerium(III) trichloride-heptahydrate (Aldrich), potassium hydride, triphenylarsine, thallium ethoxide, cesium carbonate, potassium *tert*-butoxide, hydrogen peroxide (30% in H_2O) were used as received. Diisobutylamine (Aldrich) was purified by passage through basic alumina and triethylamine (Alfa-Aesar) was distilled from CaH_2. *N*,*N*-Dimethylformamide (Fischer) was distilled under reduced pressure from $CaSO_4$ and stored over Linde type 4Å molecular sieves prior to use.

Literature Preparations

The following compounds were prepared according to literature procedures: *N,N'*-dimethyl-1,1'-binaphthalene-2,2'-diamine **10**.[1]

Survey of Chiral Lewis Bases

General Procedure 1. Survey Of Chiral Lewis Bases to Sulfenocarbocyclization of **2a** (Table 1).

An oven-dried 5-mm NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene ((*E*)-**2a** as an *E*/*Z* mixture (1.0 equiv), *N*-phenylsulfenylphthalimide **1** (1.0 equiv), Lewis base (10 mol %) and $CDCl_3$ (0.2 M). The tube was cooled to –20 °C then methanesulfonic acid (1.0 equiv) was added and the mixture was shaken for 10 sec. The reaction was quenched after 24 h with excess of Et_3N (0.1 mL). The resultant mixture was poured into H_2O (10 mL) and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (30 mL) and then dried over $MgSO_4$, filtered through glass wool and then concentrated in vacuo (20 – 23 °C, 10 mmHg). The crude product was purified by flash column chromatography (SiO_2, 15 g, 20 mm ⌀, Hexane/Et_2O, 96:4) prior to SFC analysis. The ratio of products was measured by the appearance of the diagnostic ^{1}H NMR resonance for products *trans*-**14a** and *cis*-**14a** at 1.42 ppm and 1.33 ppm, respectively.

Table 1, Entry 1

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (62:38, *E*/*Z* mixture) (22.0 mg, 115.6 μmol), *N*-phenylsulfenylphthalimide **1** (29.6 mg, 115.6 μmol), Lewis base (*R*)-**4a** (5.8 mg, 11.2 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.5 μL, 115.6 μmol) was added at –20 °C and the tube was shaken. ^{1}H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 62:38.

SFC: (5*S*,6*S*)-**3a,** t_R 10.6 min (68%); (5*R*,6*R*)-**3a,** t_R 13.8 min (32%)

cis-**3a,** t_{R1} 10.6 min (51%); *cis*-**3a,** t_{R2} 12.4 min (49%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 2

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (96:4, *E*/*Z* mixture) (22.0 mg, 115.6 μmol), *N*-phenylsulfenylphthalimide **1** (29.6 mg, 115.6 mmol), Lewis base (*R*)-**4b** (6.0 mg, 11.2 μmol) and $CDCl_3$ (0.50 mL). MsOH (6.8 μL, 0.1 mmol) was added at –20 °C and the tube was shaken. ^{1}H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 96:4.

SFC: (5*S*,6*S*)-**3a,** t_R 10.4 min (89%); (5*R*,6*R*)-**3a,** t_R 13.2 min (11%)
cis-**3a,** t_{R1} 10.4 min (49%); *cis*-**3a,** t_{R2} 12.2 min (51%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 3

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (94:6, *E*/*Z* mixture) (23.0 mg, 120.9 μmol), *N*-phenylsulfenylphthalimide **1** (30.9 mg, 120.9 μmol), Lewis base (*S*)-**4c** (6.4 mg, 12.1 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.85 μL, 120.9 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a** /*cis*-**3a** of 94:6.
SFC: (5*S*,6*S*)-**3a,** t_R 7.6 min (14%); (5*R*,2*R*)-**3a,** t_R 9.9 min (86%)
cis-**3a,** t_{R1} 7.6 min (59%); *cis*-**3a,** t_{R2} 8.9 min (41%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 4

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (94:6, *E*/*Z* mixture) (23.0 mg, 120.9 μmol), *N*-phenylsulfenylphthalimide **1** (30.9 mg, 120.9 μmol), Lewis base (*S*)-**4d** (6.3 mg, 12.1 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.85 μL, 120.9 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 94:6.
SFC: (5*S*,6*S*)-**3a,** t_R 7.6 min (17%); (5*R*,6*R*)-**3a,** t_R 10.0 min (83%)
cis-**3a,** t_{R1} 7.6 min (61%); *cis*-**3a,** t_{R2} 8.9 min (39%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 5

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (96:4, *E*/*Z* mixture) (23.0 mg, 120.9 μmol), *N*-phenylsulfenylphthalimide **1** (30.9 mg, 120.9 μmol), Lewis base (*S*)-**4e** (6.6 mg, 12.1 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.85 μL, 120.9 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 96:4.

SFC: (5*S*,6*S*)-**3a,** t_R 7.7 min (5%); (5*R*,6*R*)-**3a,** t_R 9.9 min (95%)

cis-**3a,** t_{R1} 7.7 min (68%); *cis*-**3a,** t_{R2} 8.9 min (32%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 6

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (95:5, *E*/*Z* mixture) (22.4 mg, 117.7 μmol), *N*-phenylsulfenylphthalimide **1** (30.1 mg, 117.7 μmol), Lewis base (*S*)-**4f** (6.4 mg, 117.7 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.6 μL, 117.7 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 95:5.

SFC: (5*S*,6*S*)-**3a,** t_R 7.6 min (12%); (5*R*,6*R*)-**3a,** t_R 9.7 min (88%)

cis-**3a,** t_{R1} 7.6 min (64%); *cis*-**3a,** t_{R2} 8.9 min (36%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 7

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (62:38, *E*/*Z* mixture) (22.0 mg, 115.6 μmol), *N*-phenylsulfenylphthalimide **1** (29.6 mg, 115.6 μmol), Lewis base (*R*)-**4g** (5.7 mg, 11.6 μmol) and $CDCl_3$ (0.50 mL). MsOH (7.5 μL, 115.6 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 62:38.

SFC: (5*S*,6*S*)-**3a,** t_R 10.5 min (85%); (5*R*,2*R*)-**3a,** t_R 13.8 min (15%)

cis-**3a,** t_{R1} 10.5 min (53%); *cis*-**3a,** t_{R2} 12.3 min (47%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Table 1, Entry 8

Following General Procedure 1, an oven-dried NMR tube was charged with 5-(3′,4′-methylenedioxyphenyl)pent-2-ene (*E*)-**2a** (95:5, *E*/*Z* mixture) (24.6 mg, 129.3 μmol), *N*-phenylsulfenylphthalimide **13** (33.0 mg, 129.3 μmol), Lewis base (*S*)-**4h** (7.5 mg, 12.9 μmol) and $CDCl_3$ (0.50 mL). MsOH (8.4 μL, 129.3 μmol) was added at –20 °C and the tube was shaken. ^1H NMR spectral analysis revealed a ratio products *trans*-**3a**/*cis*-**3a** of 95:5.

SFC: (5*S*,6*S*)-**3a,** t_R 7.7 min (8%); (5*R*,6*R*)-**3a,** t_R 9.7 min (92%)
cis-**3a,** t_{R1} 7.7 min (66%); *cis*-**3a,** t_{R2} 9.0 min (34%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1, Entry 9

Following General Procedure 1, an oven-dried NMR tube was charged with (*E*)-4-(3′,4′-methylenedioxyphenyl)-1-(4-methylphenyl)but-1-ene (*E*)-**2a** (23.7 mg, 124.6 μmol, 1.0 equiv), *N*-phenylsulfenylphthalimide **1** (31.2 mg, 124.6 mmol, 1.0 equiv), Lewis base (*S*)-**4e** (6.8 mg, 12.4 μmol) and $CDCl_3$ (0.2 M). $EtSO_3H$ solution (46.7 μL, 93.4 μmol, 2 M in $CDCl_3$) was added at – 20 °C and the reaction mixture was stirred for 48 h. ^1H NMR spectral analysis revealed 100% conversion. Purification by flash column chromatography (SiO_2, 30 g, 15 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3a** (34 mg, 92%) as a white solid.
HPLC: (5*S*,6*S*)-**3a,** t_R 7.3 min (96%); (5*R*,6*R*)-**3a,** t_R 9.3 min (4%) (Chiralpak AD-H, 1% IPA in hexane, 1.25 mL/min, 220 nm)

Table 1, entry 10

Following General Procedure 1, an oven-dried NMR tube was charged with (*E*)-4-(3′,4′-methylenedioxyphenyl)-1-(4-methylphenyl)but-1-ene (*E*)-**2a** (23.7 mg, 124.6 μmol, 1.0 equiv), *N*-phenylsulfenylphthalimide **1** (31.2 mg, 124.6 mmol, 1.0 equiv), Lewis base (*S*)-**4e** (3.4 mg, 6.2 μmol) and $CDCl_3$ (0.2 M). $EtSO_3H$ solution (46.7 μL, 93.4 μmol, 2 M in $CDCl_3$) was added at – 20 °C and the reaction mixture was stirred for 48 h. ^1H NMR spectral analysis revealed 100% conversion. Purification by flash column chromatography (SiO_2, 30 g, 15 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3a** (34 mg, 92%) as a white solid.
HPLC: (5*S*,6*S*)-**3a,** t_R 7.5 min (71%); (5*R*,6*R*)-**3a,** t_R 9.8 min (29%) (Chiralpak AD-H, 1% IPA in hexane, 1.25 mL/min, 220 nm, 40 °C)

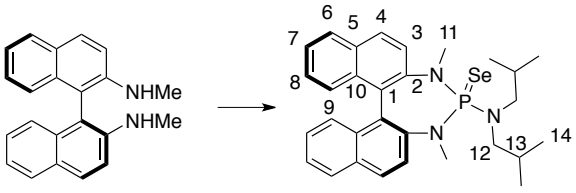
Table 1, entry 11

Following General Procedure 1, an oven-dried NMR tube was charged with (*E*)-4-(3′,4′-methylenedioxyphenyl)-1-(4-methylphenyl)but-1-ene (*E*)-**2a** (25.8 mg, 135.6 μmol, 1.0 equiv), *N*-phenylsulfenylphthalimide **1** (34.7 mg, 135.6 mmol, 1.0 equiv), Lewis base (*S*)-**4e** (1.5 mg, 2.7 μmol) and $CDCl_3$ (0.2 M). $EtSO_3H$ solution (50.8 μL, 101.7 μmol, 2 M in $CDCl_3$) was added at –

20 °C and the reaction mixture was stirred for 48 h. ^{1}H NMR spectral analysis revealed 100% conversion. Purification by flash column chromatography (SiO_2, 30 g, 15 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3a** (34 mg, 92%) as a white solid.

HPLC: (5*S*,6*S*)-**3a,** t_R 7.7 min (67%); (5*R*,6*R*)-**3a,** t_R 9.6 min (33%) (Chiralpak AD-H, 1% IPA in hexane, 1.25 mL/min, 220 nm, 40 °C)

Preparation of (*S*)-4-(Diisobutylamino)-3,5-dimethyl-4,5-dihydro-3*H*-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]diazaphosphepine-4-selenide ((*S*)-4e)



(*S*)-**10** (*S*)-**4e**

To a flame-dried, 100 mL Schlenk flask equipped with a magnetic stir bar and septum were added *N,N'*-dimethyl-1,1'-binaphthalene-2,2'-diamine **10** (2.00 g, 6.40 mmol) and Et_3N (2.23 mL, 16.0 mmol, 2.50 equiv) and THF (64.0 mL) were added via syringe. The homogeneous mixture was cooled to 0 °C. PCl_3 (1.68 mL, 19.2 mmol, 3.00 equiv) was added dropwise via syringe whereupon a colorless precipitate formed immediately. The reaction mixture was stirred at 0 °C for 1.5 h, then was allowed to warm to room temperature and was stirred for another 3 h. The volatiles were removed under high vacuum (room temperature, 0.5 mmHg) and Et_2O (20.0 mL) was added via syringe, then the mixture was stirred for 5 min. The supernatant was cannula filtered into a tared, flame-dried, argon filled, 200 mL Schlenk flask equipped with a rubber septum. The remaining precipitate in the reaction flask was washed with Et_2O (20 mL) and was filtered into the receiver Schlenk flask. The volatiles were removed under high vacuum (room temperature, 0.5 mmHg) to afford a light yellow solid. The solid was redissolved with Et_2O (20 mL) and the volatils were again removed under high vacuum (room temeraure, 1.0 mmHg) to afford a white solid. The solid was then dried for 3 h at reduced pressure (45 °C, 0.50 mmHg) to give a white foam (2.34 g). CH_2Cl_2 (60.0 mL) was added via syringe and the mixture was cooled to 0 °C. Et_3N (0.74 mL, 5.30 mmol, 1.2 equiv) and diisobutylamine (1.23 mL, 7.10 mmol, 1.1 equiv) were added via syringe and the reaction mixture was allowed to warm to room temperature and then stirred for 14 h. Powdered selenium

(1.46 g, 18.6 mmol, 2.9 equiv) was added and the mixture was stirred for 50 h, then filtered through a pad of Celite (12 g, 70 mm Ø). The pad was washed with EtOAc (100 mL) and the filtrate was concentrated in vacuo (40 °C, 10 mmHg) Purification via flash column chromatography (SiO_2, 120 g, 50 mm Ø, hexane/Et_2O 4:1) afforded (*S*)-**4e** (2.55 g, 73%) as slightly ornage solid. Recrystallization from hot pentane provided (2.35 g, 67%)

Data for (*S*)-**4e**

mp: 118-120 °C (pentane)

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

7.98 (d, *J* = 9.0 Hz, 1 H, HC(4)), 7.92 (d, *J* = 9.0 Hz, 1 H, HC(4')), 7.90 (d, *J* = 8.5 Hz, 1 H, HC(6)), 7.86 (d, *J* = 8.0 Hz, 1 H, HC(6')), 7.67 (d, *J* = 9.0 Hz, 1 H, HC(3')), 7.66 (dd, *J* = 9.0, 1.0 Hz, 1 H, HC(3)), 7.43 (dt, *J* = 7.5, 1.0 Hz, 1 H, HC(7)), 7.36 (t, *J* = 7.5 Hz, 1 H, HC(7')), 7.28 (d, *J* = 8.0 Hz, 1 H, HC(8)), 7.24 (dt, *J* = 8.5, 1.0 Hz, 1 H, HC(9)), 7.12 (dt, *J* = 8.0, 1.0 Hz, 1 H, HC(8')), 7.04 (d, *J* = 9.0 Hz, 1 H, HC(9')), 3.21 (d, *J* = 13.5 Hz, 3 H, HC(11')), 3.18 – 3.11 (m, 2 H, HC(12)), 2.96 (d, *J* = 13.5 Hz, 3 H, H_3C(11)), 2.81 (dt, *J* = 14.0, 6.0 Hz, 2 H, HC(12')), 1.96 – 1.87 (m, 2 H, HC(13, 13')), 0.86 (d, *J* = 6.5 Hz, 6 H, HC(14')), 0.84 (d, *J* = 6.5 Hz, 6 H, HC(14))

^{13}C NMR: (125 MHz, $CDCl_3$)

143.4 (d, *J* = 5.0 Hz, C(2')), 142.3 (C(2)), 132.7 (C(10)), 132.5 (C(10')), 131.5 (C(5')), 131.3 (C(5)), 129.5 (C(4)), 128.7 (C(4')), 128.3 (C(9)), 128.2 (C(6'), 128.0 (C(6)), 127.5 (C(1,1')), 127.3 (C(9')), 126.3 (C(8)), 125.9 (C(8')), 125.5 (C(7)), 124.9 (C(7')), 124.6 (C(3')), 122.6 (C(3)), 55.1 (C(12, 12')), 39.3 (d, *J* = 11.3 Hz, C(11')), 36.1 (d, *J* = 5.0 Hz, C(11)), 27.2 (C(13, 13')), 21.0 (C(14')), 20.9 (C(14'))

^{31}P NMR: (202 MHz, $CDCl_3$)

95.39

IR: (KBr)

3052 (w), 2954 (s), 2864 (s), 2801 (w), 1618 (w), 1590 (m), 1503 (s), 1465 (s), 1386 (m), 1365 (m), 1327 (s), 1271 (s), 1261 (s), 1157 (m), 1115 (s), 1087 (s), 1007 (s), 955 (m), 935 (s), 876 (m), 810 (s), 747 (s)

MS: (EI^+, 70 eV)

422.1 (5.6), 421.1 (18.7), 419.1 (9.5), 342.1 (23.5), 341.1 (100.0), 312.1 (6.4),

282.2 (5.2), 281.1 (18.4), 215.1 (6.3), 128.1 (15.5), 57.1 (7.6)

HRMS: calcd for $C_{30}H_{36}N_3PSe^+$: 549.1812, found: 549.1809

TLC: R_f 0.61 (hexanes/Et_2O, 4:1) [CAM]

Opt Rot. : $[\alpha]_D^{24}$ +187.5 (c = 1.67, EtOH)

SFC: (*S*)-**10**, t_R, 12.0 min (>99.9%); (*R*)-**10**, t_R 14.7 min (0.1%) (Chiralpak OJ, 5% MeOH in CO_2, 2 mL/min, 220 nm, 40 ˚C)[2]

Analysis: $C_{30}H_{36}N_3PSe$ (549.56)

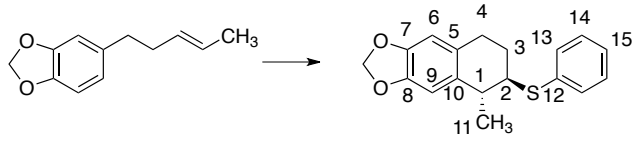
Calcd:	C, 65.68;	H, 6.61%	N, 7.66	P, 5.65	Se, 14.39%
Found:	C, 65.75;	H, 6.69%	N, 7.42	P, 5.52	Se, 14.46%

Substrate Cyclization Survey.

General Procedure 3. Cyclization with alkyl-substituted alkenes (Table 2)

An oven-dried, 10-mL, two-necked, round-bottomed flask under nitrogen was charged *N*-phenylthiophthalimide **1** (256 mg, 1.00 mmol, 1.0 equiv), (*S*)-**4e** (54.9 mg, 0.10 mmol, 0.1 eq), olefin (1.00 mmol) in CH_2Cl_2. The flask was placed into isopropyl alcohol bath and cooled at the requiste temperature via cryocool. A solution of $EtSO_3H$ (1 M in CH_2Cl_2) was added over 20 sec and the mixture was allowed to stir for the specified time. The reaction was quenched while cold by addition of Et_3N (1.6 mL). The resultant mixture was poured into H_2O (20 mL) and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered through glass wool and then concentrated in vacuo (20 – 23 °C, 10 mmHg). The thioether products were purified by flash column chromatography.

Preparation of (5*R*,6*R*)-5-Methyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3a)



trans-**3a**

Following General Procedure 9, (*E*)-**2a** (190 mg, 1.0 mmol), **1** (256 mg, 1.0 mmol,), (*S*)-**4e** (54.8 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3a** (277 mg, 93%) as a white solid. Recrystallization from hot pentane provided 273 mg (92%) of analytically pure *trans*-**3a**.

Data for *trans*-**3a**:

mp: 46-48 °C (pentane)

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

7.46 (dd, *J* = 8.0, 1.0 Hz, 2 H, HC(13)), 7.34 (t, *J* = 8.0 Hz, 2 H, HC(14)), 7.27 (tt, *J* = 8.5, 1.5 Hz, 1 H, HC(15)), 6.64 (s, 1 H, HC(6)), 6.58 (s, 1 H, HC(9)), 5.91 (s, 2 H, OCH_2O), 3.43 – 3.40 (m, 1 H, HC(2)), 2.97 – 2.91 (m, 2 H, HC(1) and HC(4)), 2.66 (ddd, *J* = 16.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.23 – 2.16 (m, 1 H, HC (3)), 1.91 – 1.85 (m, 1 H, HC(3)), 1.42 (d, *J* = 7.0 Hz, 3 H, HC(11))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.0 (C(7)), 145.9 (C(8)), 135.4 (C(12)), 132.6 (C(5)), 131.9 (C(13)), 129.0 (C(14)), 128.2 (C(10)), 126.9 (C(15)), 108.8 (C(9)), 108.6 (C(6)), 100.7 (OCH_2O), 49.9 (C(2)), 38.3 (C(1)), 26.6 (C(4)), 24.8 (C(3)), 24.1 (C(11))

IR: (KBr)

3052 (w), 2961 (m), 2926 (m), 2885 (m), 2766 (w), 1580 (m), 1500 (s), 1479 (s), 1438 (m), 1379 (m), 1233 (s), 1184 (m), 1087 (w), 1035 (s), 938 (s), 858 (m), 740 (s)

MS: (EI^+, 70 eV)

299.1 (14.2), 298.1 (69.8), 190.1 (13.2), 189.1 (100.0), 188.1 (75.1), 174.0 (18.0), 173.0 (43.8), 162.1 (26.5), 159.1 (34.4), 131.1 (22.0), 116.1 (12.2), 115.0 (26.2), 103.1 (7.3), 91.1 (10.9), 85.0 (31.7), 83.0 (48.7), 65.1 (8.1)

HRMS: calcd for $C_{18}H_{18}O_2S^+$: 298.1028, found: 298.1032

TLC: R_f 0.44 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -18.7 (c = 0.53, EtOH)

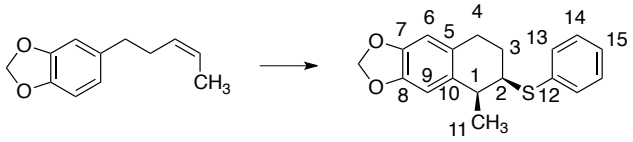
SFC: (5*S*,6*S*)-**3a,** t_R 11.7 min (3%); (5*R*,6*R*)-**3a,** t_R 15.2 min (97%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{18}H_{18}O_2S$ (298.40)

Calcd: C, 72.45; H, 6.08%

Found: C, 72.59; H, 5.90%

Preparation of *trans*-5-Methyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*cis*-3a)



cis-**3a**

Following General Procedure 9, (*Z*)-**2a** (190 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.8 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded of *cis*-**3a** (275 mg, 92%) as a white solid. Recrystallization from hot pentane provided 271 mg (91%) of analytically pure *cis*-**3a**.

Data for *cis*-**3a**:

mp: 76-78 °C (pentane)

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

7.46 (dd, *J* = 7.5 Hz, 2 H, HC(13)), 7.33 (t, *J* = 7.5 Hz, 2 H, HC(14)), 7.26 (t, *J* = 7.6 Hz, 1 H, HC(15)), 6.58 (s, 1 H, HC(6)), 6.56 (s, 1 H, HC(9)), 5.90 (s, 2 H, OCH_2O), 3.69 – 3.65 (m, 1 H, HC(2)), 3.10 – 3.04 (m, 1 H, HC(1)), 2.89 (ddd, *J* = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, *J* = 17.0, 8.5, 8.5 Hz, 1 H, HC(4)), 2.05 – 2.00 (m, 2 H, HC (3)), 1.33 (d, *J* = 7.0 Hz, 3 H, HC(11))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.1 (C(7)), 145.9 (C(8)), 135.5 (C(12)), 134.6 (C(5)), 131.5 (C(13)), 129.1 (C(14)), 127.8 (C(10)), 126.8 (C(15)), 108.5 (C(9)), 108.5 (C(6)), 100.8 (OCH_2O),

48.9 (C(2)), 36.9 (C(1)), 29.3 (C(4)), 24.9 (C(3)), 18.9 (C(11))

IR: (KBr)

2961 (m), 2898 (m), 1580 (w), 1500 (s), 1479 (s), 1434 (w), 1375 (w), 1247 (s), 1219 (s), 1087 (w), 1039 (s), 941 (m), 928 (m), 893 (w), 862 (m), 737 (m), 688 (m)

MS: (EI^+, 70 eV)

299.1 (14.4), 298.1 (68.5), 231.2 (35.6), 189.1 (100.0), 188.1 (24.8), 174.1 (11.2), 173.1 (26.7), 162.1 (34.9), 159.1 (37.9), 135.1 (20.7), 131.1 (31.6), 128.1 (10.8), 116.1 (15.2), 115.1 (30.0), 107.1 (12.6), 103.1 (12.1), 91.1 (27.6), 78.1 (12.6), 77.1 (18.8), 65.1 (14.6), 57.1 (23.6), 55.1 (12.0), 51.1 (11.6)

HRMS: calcd for $C_{18}H_{18}O_2S^+$: 298.1028, found: 298.1034

TLC: R_f 0.42 (hexanes/Et_2O, 96:4) [$KMnO_4$]

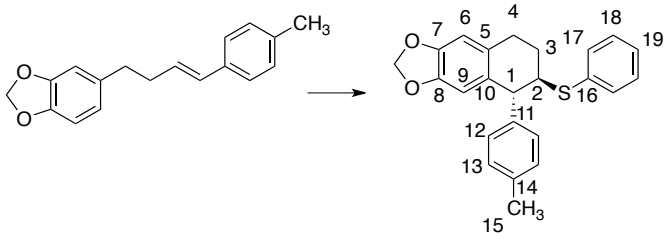
SFC: *cis*-**3a,** t_{R1} 12.6 min (52%); *cis*-**3a,** t_{R2} 14.1 min (48%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{18}H_{18}O_2S$ (298.40)

Calcd: C, 72.45; H, 6.08%

Found: C, 72.43; H, 6.03%

Preparation of ((5*R*,6*R*)-5-(4-Methylphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3b)



trans-**3b**

Following General Procedure 9, a 10-mL (*E*)-**2b** (266.3 mg, 1.0 mmol), **1** (256 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol, 0.1 equiv) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 48 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afford *trans*-**3b** (327 mg, 87%) as a white solid. Recrystallization from hot pentane provided 322 mg (86%) of analytically pure *trans*-**3b**.

Data for *trans*-**3b**:

mp: 72-74 °C (pentane)

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

7.43 (d, *J* = 7.0 Hz, 2 H, HC(17), 7.32 (t, *J* = 7.5 Hz, 2 H, HC(18)), 7.27 (t, *J* = 7.5 Hz, 1 H, HC(19)), 7.11 (d, *J* = 7.5 Hz, 2 H, HC(13)), 6.96 (d, *J* = 7.5 Hz, 2 H, HC(12)), 6.65 (s, 1 H, HC(6)), 6.33 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 4.09 (d, *J* = 4.5 Hz, 1 H, HC(1)), 3.67 – 3.64 (m, 1 H, HC(2)), 2.99 (ddd, *J* = 16.0, 8.0, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, 1H, *J* = 16.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.35 (s, 3 H, HC(15)), 2.20 – 2.14 (m, 1 H, HC(3)), 1.87 – 1.81 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.4 (C(7)), 146.1 (C(8)), 142.5 (C(14)), 136.2 (C(11)), 135.1 (C(16)), 132.3 (C(17)), 129.8 (C(5)), 129.4 (C(10)), 129.2 (C(13)), 129.0 (C(18)), 128.9 (C(12)), 127.0 (C(19)), 110.3 (C(9)), 108.2 (C(6)), 100.8 (OCH_2O), 51.4 (C(2)), 50.0 (C(1)), 26.8 (C(4)), 24.9 (C(3)), 21.2 (C(15))

IR: (KBr)

3003 (w), 2919 (m), 2885 (m), 1580 (w), 1500 (s), 1479 (s), 1434 (m), 1382 (w), 1236 (s), 1174 (w), 1035 (s), 938 (m), 869 (w), 806 (w), 740 (m), 692 (m)

MS: (EI^+, 70 eV)

375.1 (21.2), 374.1 (75.9), 326.2 (26.2), 266.1 (19.0), 265.1 (100.0), 264.1 (90.0), 249.0 (9.3), 237.0 (9.8), 224.0 (9.8), 223.0 (58.2), 191.1 (10.8), 189.0 (11.0), 179.0 (9.8), 178.0 (10.7), 173.0 (17.7), 165.0 (21.8), 159.0 (96.4), 159.0 (15.7), 143.0 (11.4), 135.0 (14.0), 115.0 (23.2), 109.0 (10.9), 105.1 (66.4)

HRMS: calcd for $C_{24}H_{22}O_2S^+$: 374.1341, found: 374.1336

TLC: R_f 0.35 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -28.4 (c = 0.59, EtOH)

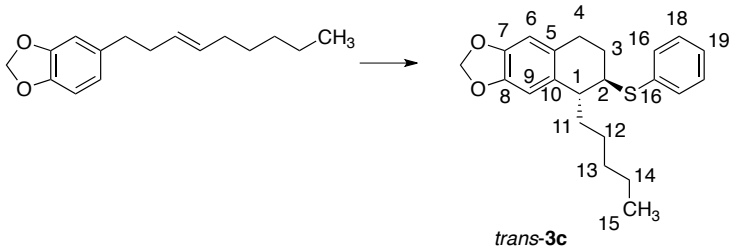
SFC: (5*S*,6*S*)-**3b,** t_R 12.7 min (6%); (5*R*,6*R*)-**3b,** t_R 14.1 min (94%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{24}H_{22}O_2S$ (374.50)

Calcd: C, 76.97; H, 5.92%

Found: C, 76.79; H, 6.03%

Preparation of ((5*R*,6*R*)-5-Pentyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3c)



trans-**3c**

Following General Procedure 9, (*E*)-**2c** (246.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded of *trans*-**3c** (266 mg, 76%) as colorless oil. Distillation provided 259 mg of analytically pure *trans*-**3c**.

Data for *trans*-**3c**:

bp: 140 °C @ 5.5×10^{-5} mmHg

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

7.45 (dd, *J* = 7.5, 1.0 Hz, 2 H, HC(17)), 7.33 (t, *J* = 7.5 Hz, 2 H, HC(18)), 7.26 (tt, *J* = 7.0, 1.0 Hz, 1 H, HC(19)), 6.58 (s, 2 H, HC(6) and HC(9)), 5.91 (s, 2 H, OCH_2O), 3.673 – 3.65 (m, 1 H, HC(2)), 2.97 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1 H, HC(4)), 2.80 (dt, *J* = 8.0, 4.5 Hz, 1 H, HC(1)), 2.64 (ddd, *J* = 17.0, 6.0, 3.5 Hz, 1 H, HC(4)), 2.15 (dddd, *J* = 11.0, 6.5, 3.5 Hz, 1 H, HC(3)), 1.91 – 1.85 (m, 1 H, HC(3)), 1.72 – 1.59 (m, 2 H, HC (11)), 1.41 – 1.22 (m, 6 H, HC(12) and HC(13) and HC(14)), 0.90 (t, *J* = 7.0 Hz, 3 H, HC(15))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.0 (C(7)), 145.8 (C(8)), 135.6 (C(16)), 132.0 (C(17)), 131.8 (C(5)), 129.0 (C(18)), 128.3 (C(10)), 126.9 (C(19)), 109.3 (C(6)), 108.6 (C(9)), 100.7 (OCH_2O), 46.6 (C(2)), 43.6 (C(1)), 38.1 (C(11)), 32.0 (C(13)), 27.1 (C(12)), 25.6 (C(4)), 23.4 (C(3)), 22.7 (C(14)), 14.2 (C(15))

IR: (neat)

3052 (m), 2926 (s), 2857 (m), 2766 (m), 2666 (w), 2613 (w), 1621 (w), 1583 (s), 1503 (s), 1483 (s), 1469 (s), 1451 (s), 1441 (s), 1379 (s), 1233 (s), 1118 (s), 1087 (s), 1035 (s), 938 (s), 903 (s), 858 (m)

MS: (EI^+, 70 eV)

299.1 (14.2), 298.1 (69.8), 190.1 (13.2), 189.1 (100.0), 188.1 (75.1), 174.0 (18.0), 173.0 (43.8), 162.1 (26.5), 159.1 (34.4), 131.1 (22.0), 116.1 (12.2), 115.0 (26.2), 103.1 (7.3), 91.1 (10.9), 85.0 (31.7), 83.0 (48.7), 65.1 (8.1)

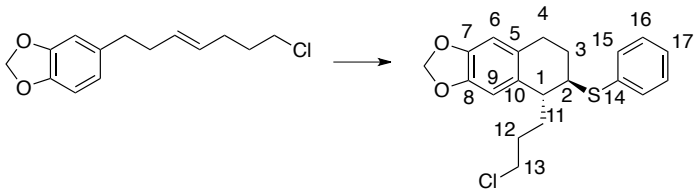
HRMS: calcd for $C_{22}H_{26}O_2S^+$: 354.1650, found: 354.1654

TLC: R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +12.8 (c = 0.76, EtOH)

SFC: (5*S*,6*S*)-**3c,** t_R 9.2 min (4%); (5*R*,6*R*)-**3c,** t_R 10.3 min (96%) (Chiralpak OD, 4% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Preparation of ((5*R*,6*R*)-5-(3-Chloropropyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3d)



trans-**3d**

Following General Procedure 9, (*E*)-**2d** (253.7 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at room temperature for 6 d. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3d** (235 mg, 65%) as colorless oil. Distillation provided 227 mg of analytically pure *trans*-**3d**.

Data for *trans*-**3d**:

bp: 135 °C @ 3.2×10^{-5} mmHg

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

7.45 (t, *J* = 7.5 Hz, 2 H, HC(15)), 7.34 (t, *J* = 7.5 Hz, 2 H, HC(16)), 7.28 (t, *J* = 7.0 Hz, 1 H, HC(17)), 6.58 (s, 2 H, HC(6) and C(9)), 5.92 (d, *J* = 2.5 Hz, 2 H, OCH_2O), 3.59 – 3.56 (m, 1 H, HC(2)), 3.55 – 3.45 (m, 2 H, HC(13)), 2.95 (ddd, *J* = 16.5, 10.5, 5.0 Hz, 1 H, HC(4)), 2.85 – 2.82 (m, 1 H, HC (1)), 2.65 (ddd, *J* = 10.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.16 (dddd, *J* = 13.5, 10.0, 5.5, 3.0 Hz, 1 H, HC(3)), 1.92 – 1.76 (m, 5 H, HC(3) and HC(11) and HC(12))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.2 (C(7)), 146.0 (C(8)), 135.1 (C(14)), 132.6 (C(16)), 130.8 (C(5)), 129.1 (C(15)), 128.6 (C(10)), 127.2 (C(17)), 109.1 (C(9)), 108.7 (C(6)), 100.8 (OCH_2O), 46.9 (C(2)), 45.0 (C(13)), 42.9 (C(1)), 34.8 (C(11)), 30.2 (C(12)), 25.9 (C(4)), 24.0 (C(3))

IR: (neat)

3044 (m), 2911 (s), 2761 (m), 1581 (s), 1501 (s), 1484 (s), 1466 (s), 1431 (s), 1378 (s), 1290 (s), 1237 (s), 1030 (s), 933 (s), 902 (s), 858 (s), 823 (s)

MS: (EI^+, 70 eV)

360.1 (63.8), 283.2 (13.6), 253.1 (30.6), 252.1 (28.7), 251.1 (92.5), 250.1 (47.2), 188.1 (19.0), 187.2 (13.8), 175.1 (18.4), 174.1 (89.9), 173.1 (100.0), 161.1 (24.9), 145.1 (17.7), 144.1 (14.8), 131.0 (18.2), 129.1 (13.0), 128.1 (13.1), 117.1 (13.1), 116.1 (23.1), 115.1 (58.9), 109.0 (13.0), 103.1 (14.6), 91.1 (10.9), 77.1 (12.8), 65.1 (11.0)

HRMS: calcd for $C_{20}H_{21}ClO_2S^+$: 360.0951, found: 360.0941

TLC: R_f 0.21 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +16.03 (c = 0.51, EtOH)

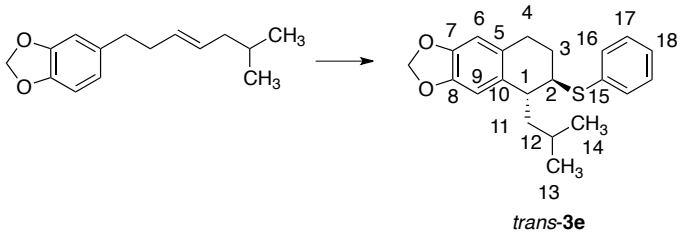
SFC: (5*S*,6*S*)-**3d,** t_R 12.1 min (6%); (5*R*,6*R*)-**3d,** t_R 14.6 min (94%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{18}H_{18}O_2S$ (360.90)

Calcd: C, 66.56; H, 5.87%

Found: C, 66.61; H, 5.90%

Preparation of ((5*R*,6*R*)-5-(2-Methylpropyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3e)



trans-**3e**

Following General Procedure 9, a 10-mL Schlenk flask was charged with (*E*)-**2e** (232.3

mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3e** (269 mg, 79%) as colorless oil. Distillation provided 262 mg (77%) of analytically pure *trans*-**3e**.

Data for *trans*-**3e**:

bp: >135 °C @1.5×10^{-5} mmHg

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

7.43 (dd, *J* = 8.0, 1.5, 2 H, HC(16)), 7.34 (t, *J* = 7.0 Hz, 2 H, HC(17)), 7.24 (tt, *J* = 7.0, 1.5 Hz, 1 H, HC(18)), 6.56 (s, 1 H, HC(6)), 6.51 (s, 1 H, C(9)), 5.88 (s, 2 H, OCH_2O), 3.64 – 3.62 (m, 1 H, HC(2)), 3.00 (ddd, *J* = 17.5, 9.5, 6.5 Hz, 1 H, HC(4)), 2.84 (dd, *J* = 9.0, 4.5 Hz, 1 H, HC(1)), 2.61 (ddd, *J* = 17.0, 6.0, 1.5 Hz, 1 H, HC(4)), 2.14 – 2.07 (m, 1 H, HC(3)), 1.90 – 1.86 (m, 1 H, HC(3)), 1.71 – 1.63 (m, 1 H, HC(12)), 1.52 (ddd, *J* = 14.0, 9.5, 5.0 Hz, 1 H, HC(11)), 1.37 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1 H, HC(11)), 0.90 (d, *J* = 6.5 Hz, 3 H, HC(14)

^{13}C NMR: (125 MHz, $CDCl_3$)

146.0 (C(7)), 145.9 (C(8)), 135.5 (C(15)), 132.3 (C(16)), 132.1 (C(5)), 129.0 (C(17)), 128.0 (C(10)), 127.1 (C(18)), 109.4 (C(9)), 108.7 (C(6)), 100.7 (OCH_2O), 48.4 (C(11)), 46.6 (C(2)), 41.2 (C(1)), 25.7 (C(12)), 24.9 (C(4)), 23.6 (C(14)), 22.3 (C(3)), 22.0 (C(13))

IR: (neat)

2917 (s), 2850 (s), 1580 (w), 1503 (s), 1483 (s), 1451 (s), 1377 (s), 1240 (s), 1216 (s), 1181 (m), 1122 (w), 1043 (s), 945 (m), 858 (m), 692 (s)

MS: (EI^+, 70 eV)

341.1 (20.6), 340.2 (83.8), 283.1 (19.1), 231.2 (63.9), 230.2 (48.2), 187.1 (12.3), 175.1 (44.3), 174.1 (100.0), 173.1 (75.0), 161.1 (50.0), 159.1 (12.6), 145.1 (15.4), 144.1 (13.8), 135.1 (13.0), 131.0 (19.2), 128.1 (10.2), 117.1 (13.5), 116.1 (23.8), 115.1 (49.3), 109.0 (13.7), 103.1 (14.4), 91.1 (12.9), 77.1 (11.6), 65.1 (10.5), 57.1 (11.2)

HRMS: calcd for $C_{21}H_{24}O_2S^+$: 340.1497, found: 340.1493

TLC: R_f 0.47 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +17.16 (c = 0.61, EtOH)

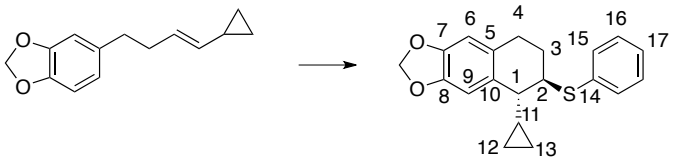
SFC: (5*R*,6*S*)-**3e,** t_R 6.4 min (96%); (5*S*,6*S*)-**3e,** t_R 6.9 min (4%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{21}H_{24}O_2S$ (340.48)

Calcd: C, 74.08; H, 7.10%

Found: C, 74.33; H, 7.31%

Preparation of ((5*R*,6*R*)-5-Cyclopropyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-2f)



trans-**3f**

Following General Procedure 9, (*E*)-**2f** (216.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 25 mm Ø, hexane/Et_2O, 96:4) to afford *trans*-**3f** (292 mg, 90%) as colorless oil. Recrystallization from hot pentane provided 285 mg (88%) of analytically pure *trans*-**3f**.

Data for *trans*-**3f**:

mp: 25 °C (pentane)

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

7.43 (dd, *J* = 7.5, 1.0, 2 H, HC(15)), 7.32 (t, *J* = 7.5 Hz, 2 H, HC(16)), 7.25 (tt, *J* = 7.5, 1.0 Hz, 1 H, HC(17)), 6.68 (s, 1 H, HC(6)), 6.61 (s, 1 H, C(9)), 5.92 (s, 2 H, OCH_2O), 3.85 (q, *J* = 2.0 Hz, 1 H, HC(2)), 3.04 (ddd, *J* = 17.5, 12.0, 6.0 Hz, 1 H HC(4)), 2.68 (ddd, *J* = 17.0, 6.0, 1.5 Hz, 1 H, HC(4)), 2.34 – 2.27 (m, 1 H, HC(3)), 2.03 (d, *J* = 9.0 Hz, 1 H, HC(1)), 2.02 – 1.97 (m, 1 H, HC(3)), 0.99 – 0.92 (m, 1 H, HC(11)), 0.65 – 0.60 (m, 1 H, HC(12)), 0.56 – 0.50 (m, 1 H, HC(13)), 0.48 – 0.44 (m, 1 H, HC(12)), 0.29 – 0.22 (m, 1 H, HC(13))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.4 (C(7)), 145.7 (C(8)), 135.6 (C(14)), 131.7 (C(15)), 139.5 (C(5)), 129.0 (C(16)), 128.1 (C(10)), 126.8 (C(17)), 109.4 (C(9)), 108.7 (C(6)), 100.8 (OCH_2O), 48.3 (C(1,2)), 25.2 (C(4)), 23.2 (C(3)), 19.9 (C(11)), 6.2 (C(12)), 4.0 (C(13))

IR: (neat)

3066 (s), 2996 (s), 2919 (s), 2766 (s), 1580 (s), 1503 (s), 1379 (s), 1344 (s), 1271 (s), 1229 (s), 1181 (s), 1125 (m), 1046 (s), 1021 (s), 983 (s), 938 (s), 737 (s)

MS: (EI^+, 70 eV)

324.9 (12.2), 324.0 (54.6), 215.0 (30.2), 214.0 (36.0), 185.0 (13.3), 175.0 (12.7), 174.0 (100.0), 173.0 (39.3), 161.0 (13.1), 160.1 (9.6), 143.0 (9.2), 128.0 (11.1), 116.0 (11.7), 115.0 (33.2), 85.9 (28.5), 83.9 (44.0)

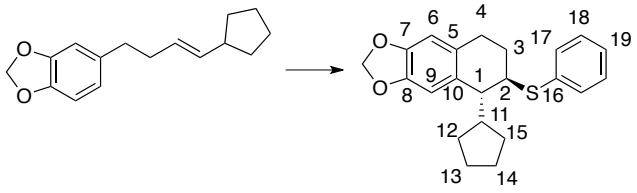
HRMS: calcd for $C_{20}H_{20}O_2S^+$: 324.1184, found: 324.1181

TLC: R_f 0.29 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -23.9 (c = 0.53, EtOH)

SFC: (5*S*,6*S*)-**3f,** t_R 9.6 min (5%); (5*R*,6*R*)-**3f,** t_R 11.3 min (95%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Preparation of ((5*R*,6*R*)-5-Cyclopentyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3g)



trans-**3g**

Following General Procedure 9, (*E*)-**2g** (244.4 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3g** (183 mg, 52%) as a white solid along with unreacted (*E*)-**2g** (37 mg, 15%). Recrystallization from hot pentane provided 180 mg (50%) of analytically pure *trans*-**3g**.

Data for *trans*-**3g**:

mp: 102-104 °C (pentane)

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

7.39 (d, *J* = 7.0 Hz, 2 H, HC(17)), 7.29 (t, *J* = 7.0 Hz, 2 H, HC(18)), 7.22 (tt, *J* = 7.0, 1.5 Hz, 1 H, HC(19)), 6.58 (s, 1 H, HC(6)), 6.55 (s, 1 H, C(9)), 5.89 (dd, *J* = 4.5, 1.5 Hz, 2 H, OCH_2O), 3.82 – 3.80 (m, 1 H, HC(2)), 2.97 (ddd, *J* = 18.0, 11.0, 7.5 Hz, 1 H, HC(4)), 2.70 (ddd, *J* = 18.0, 7.0, 2.0 Hz, 1 H, HC(4)), 2.56 (d, *J* = 9.0 Hz, 1 H, HC(1)), 2.26 – 2.19 (m, 1 H, HC(3)), 1.91 – 1.76 (m, 3 H, HC(3) and HC(11) and HC(13)), 1.68 – 1.62 (m, 3 H, HC(13) and HC(14) and HC(15)), 1.58 – 1.51 (m, 1 H, HC(12)), 1.48 – 1.37 (m, 1 H, HC(14)), 1.31 – 1.17 (m, 3 H, HC(12), and HC(15))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.2 (C(7)), 145.1 (C(8)), 136.0 (C(16)), 131.7 (C(17)), 131.1 (C(5)), 129.0 (C(18)), 128.2 (C(10)), 126.8 (C(19)), 110.4 (C(9)), 108.8 (C(6)), 100.7 (OCH_2O), 49.6 (C(1)), 47.7 (C(11)), 46.9 (C(2)), 32.9 (C(15)), 30.9 (C(12)), 25.0 (C(13)), 24.9 (C(14)), 24.4 (C(4)), 22.6 (C(3))

IR: (KBr)

2926 (m), 2864 (m), 1500 (s), 1479 (s), 1455 (m), 1434 (w), 1375 (w), 1347 (w), 1229 (s), 1181 (m), 1118 (w), 1035 (s), 935 (m), 851 (w)

MS: (EI^+, 70 eV)

325.1 (10.1), 352.1 (36.8), 284.0 (6.7), 283.0 (43.2), 243.1 (7.9), 242.1 (8.4), 175.0 (20.5), 174.0 (100.0), 173.0 (63.3), 161.0 (16.0), 145.1 (6.7), 144.0 (10.0), 143.0 (8.6), 135.0 (8.3), 119.9 (5.6), 117.0 (9.5), 116.0 (16.0), 115.0 (35.3), 110.0 (12.9), 109.0 (9.4), 103.0 (5.0)

HRMS: calcd for $C_{22}H_{24}O_2S^+$: 352.1947, found: 352.1491

TLC: R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +11.8 (c = 0.19, EtOH)

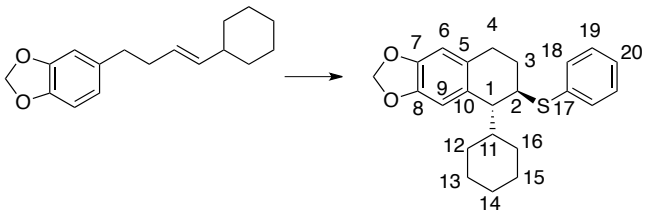
SFC: (5*S*,6*S*)-**3g,** t_R 9.6 min (18%); (5*R*,6*R*)-**3g,** t_R 11.3 min (82%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{22}H_{24}O_2S$ (352.49)

Calcd: C, 74.59; H, 6.86%

Found: C, 74.72; H, 6.50%

Preparation of ((5*R*,6*R*)-5-Cyclohexyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3h)



trans-**3h**

Following General Procedure 9, (*E*)-**2h** (258.4 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 0 °C for 72 h. Purification by flash column chromatography (SiO_2, 110 g, 50 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3h** (264 mg, 72%) as a white solid along with unreacted (*E*)-**2h** (41 mg, 16%). Recrystallization from hot pentane provided 257 mg of analytically pure *trans*-**3h**.

Data for *trans*-**3h**:

mp: 90-92 °C (pentane)

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

7.43 (dd, *J* = 8.0, 1.5 Hz, 2 H, HC(18)), 7.32 (t, *J* = 8.0 Hz, 2 H, HC(19)), 7.22 (dt, 1H, *J* = 7.0, 1.0 Hz, 1 H, HC(20)), 6.59 (s, 1 H, HC(6)), 6.55 (s, 1 H, C(9)), 5.92 (dd, *J* = 7.0, 1.5 Hz, 2 H, OCH_2O), 3.82 (dt, *J* = 7.0, 4.0 Hz, 1 H, HC(2)), 2.91 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1 H, HC(4)), 2.70 (ddd, 1H, *J* = 17.0, 10.0, 4.0 Hz, 1 H, HC(4)), 2.59 (dd, *J* = 4.0, 2.0 Hz, 1 H, HC(1)), 2.20 – 2.13 (m, 1 H, HC(3)), 1.89 – 1.84 (m, 1 H, HC(3)), 1.79 – 1.71 (m, 3 H, HC(14) and HC(15) and HC(16)), 1.67 – 1.63 (m, 1 H, HC(12)), 1.62 – 1.59 (m, 1 H, HC(13)), 1.59 – 1.43 (m, 1 H, HC(11)), 1.22 – 1.12 (m, 3 H, HC(13), and HC(14) and HC(15)), 1.08 – 1.00 (m, 2H, HC(12) and HC(16))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.1 (C(7)), 145.2 (C(8)), 136.0 (C(17)), 131.9 (C(18)), 130.1 (C(5)), 129.2 (C(10)), 129.0 (C(19)), 126.9 (C(20)), 110.6 (C(9)), 108.5 (C(6)), 100.7 (OCH_2O), 49.7 (C(1)), 45.5 (C(2)), 44.3 (C(11)), 32.2 (C(12)), 31.1 (C(16)), 27.0 (C(13)), 26.9 (C(15)), 26.6 (C(14)), 2.55 (C(4)), 24.3 (C(3))

IR: (KBr)

2919 (s), 2843 (m), 1580 (w), 1500 (m), 1479 (s), 1444 (m), 1375 (w), 1347 (w), 1236 (s), 1036 (s), 935 (m), 865 (m), 737 (m), 688 (m)

MS: (EI^+, 70 eV)

366.1 (31.9), 284.1 (10.2), 283.1 (51.0), 191.1 (8.5), 175.1 (18.5), 174.1 (100.0), 173.0 (53.4), 161.0 (9.8), 144.0 (10.2), 135.0 (10.6), 116.0 (16.2), 115.0 (28.6)

HRMS: calcd for $C_{23}H_{26}O_2S^+$: 366.1654, found: 366.1659

TLC: R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -1.29 (c = 0.21, EtOH)

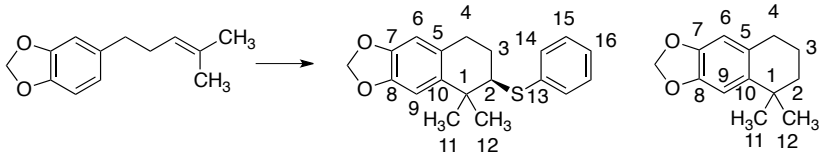
SFC: (5*S*,6*S*)-**14m,** t_R 11.0 min (15%); (5*R*,6*R*)-**14m,** t_R 12.8 min (85%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{22}H_{24}O_2S$ (366.53)

Calcd: C, 75.37; H, 7.15%

Found: C, 75.40; H, 7.11%

Preparation of (6*R*)-5,5-Dimethyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole ((*R*)-3i)



Following General Procedure 9, a 10-mL Schlenk flask was charged with **2i** (204.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.5 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.5 mL, 0.5 mmol) at –20 °C for 24 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded (*R*)-**3i** (284 mg, 91%) as a white solid along with of **10** (20 mg, 10%) as colorless oil. Distillation provided 281 mg (90%) of analytically pure (*R*)-**3i**.

Data for (*R*)-**3i**:

bp: 130 °C @ 2.2×10^{-5} mmHg

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

7.47 (t, *J* = 8.0, 1.5 Hz, 2 H, HC(14)), 7.33 (t, *J* = 7.5 Hz, 2 H, HC(15)), 7.25 (t, *J* =

7.0 Hz, 1 H, HC(16)), 6.85 (s, 1 H, HC(6)), 6.51 (s, 1 H, C(9)), 5.91 (s, 2 H, OCH_2O), 3.43 (dd, *J* = 10.5, 3.0 Hz, 1 H, HC(2)), 2.86 (ddd, *J* = 16.5, 5.5, 5.0 Hz, 1 H, HC(4)), 2.71 (ddd *J* = 16.0, 10.0, 1.0 Hz, 1 H, HC(4)), 2.21 – 2.15 (m, 1 H, HC(3)), 2.06 – 1.98 (m, 1 H, HC(3)), 1.56 (s, 3 H, HC(12)), 1.40 (m, 3 H, HC(11))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.3 (C(7)), 145.7 (C(8)), 138.1 (C(12)), 136.6 (C(5)), 131.6 (C(14)), 129.1 (C(15)), 128.0 (C(10)), 126.7 (C(16)), 108.3 (C(9)), 106.6 (C(6)), 100.8 (OCH_2O), 57.8 (C(2)), 38.9 (C(1)), 30.8 (C(11)), 29.5 (C(4)), 27.7 (C(12)), 26.6 (C(3))

IR: (neat)

3066 (m), 2961 (s), 2891 (s), 2766 (m), 1625 (w), 1580 (s), 1503 (s), 1434 (s), 1368 (s), 1333 (s), 1302 (s), 1240 (s), 1191 (s), 1160 (s), 1115 (s), 1087 (s), 1049 (s), 1021 (s), 938 (s), 914 (s), 893 (s)

MS: (EI^+, 70 eV)

313.0 (10.0), 312.0 (46.5), 204.1 (13.6), 203.1(100.0), 202.1 (13.7), 188.0 (21.3), 187.0 (29.6), 176.0 (20.6), 173.0 (23.1), 161.0 (10.4), 145.1 (10.2), 131.0 (10.4), 129.0 (9.5), 128.0 (8.3), 115.0 (11.2), 103.0 (6.5), 77.1 (6.6)

HRMS: cald for $C_{19}H_{20}O_2S^+$: 312.1184, found: 312.1190

TLC: R_f 0.42 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -10.72 (c = 0.63, EtOH)

SFC: (5*S*)-**3i,** t_R 14.7 min (20%); (*6R*)-**3i,** t_R 16.5 min (20%) (Chiralpak AD, 1-5% MeOH over 40 min in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Analysis: $C_{19}H_{20}O_2S$ (312.12)

Calcd: C, 73.04; H, 6.45%

Found: C, 73.24; H, 6.57%

Data for **10**:[3]

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

6.83 (s, 1 H, HC(6)), 6.53 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 2.69 (t, *J* = 6.5 Hz, 2 H, HC(4)), 1.82 – 1.77 (m, 2 H, HC(3)), 1.66 – 1.64 (m, 2 H, HC(2)), 1.27 (s, 6 H, HC(11) and HC(12))

^{13}C NMR: (125 MHz, $CDCl_3$)

145.9 (C(7)), 145.2 (C(8)), 139.0 (C(5)), 129.3 (C(10)), 108.6 (C(9)), 106.6 (C(6)), 100.6 (OCH_2O), 39.4 (C(2)), 34.1 (C(1)), 32.1 (C(11) and C(12)), 31.0 (C(4)), 20.0 (C(3))

IR: (neat)

2947 (s), 2926 (s), 2766 (w), 1621 (w), 1500 (s), 1483 (s), 1371 (s), 1333 (w), 1233 (s), 1191 (m), 1108 (m), 1039 (s), 1011 (w), 931 (m), 865 (m), 844 (m), 740 (w)

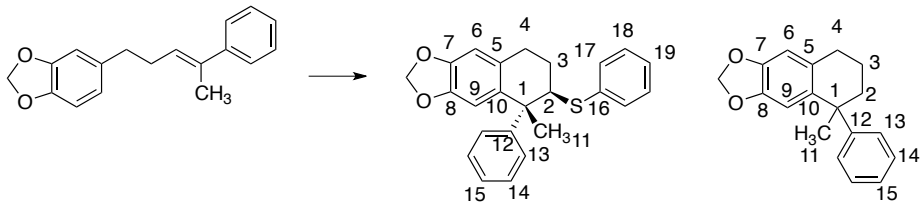
MS: (EI^+, 70 eV)

204.1 (29.0), 190.1 (12.5), 189.1 (100.0), 160.1 (29.6), 176.0 (20.6), 173.0 (23.1), 160.1 (5.7), 159.1 (23.2), 131.1 (15.0), 115.0 (9.3), 91.1 (6.8), 84.0 (6.8)

HRMS: calcd for $C_{13}H_{16}O_2^+$: 204.1150, found: 204.1154

TLC: R_f 0.52 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Preparation of ((5*R*,6*R*)-5-Methyl-5-phenyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3j)



Following General Procedure 9, a 10-mL Schlenk flask was charged with (*E*)-**2j** (266 mg, 1.0 mmol, 1.0 equiv), **1** (256 mg, 1.0 mmol, 1.0 equiv), (*S*)-**4e** (55 mg, 0.1 mmol, 0.1 equiv) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 48 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3j** (318 mg, 85%) as a white solid along with **11** (5 mg, 2%) as colorless oil. Recrystallization form hot pentane provided 310 mg of analytically pure *trans*-**3j**.

Data for *trans*-**3j**:

mp: 90-92 °C (pentane)

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

7.33 – 7.19 (m, 10 H, HC(13) and HC(14), and HC(15) and HC(17) and HC(18)

and HC(19)), 6.59 (s, 1 H, HC(6)), 6.34 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 3.68 (dd, J = 9.0, 4.5 Hz, 1 H, HC(2)), 2.97 (ddd, J = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.86 (ddd, J = 16.0, 8.0, 8.0 Hz, 1 H, HC(4)), 2.13 – 2.07 (m, 2 H, HC(3)), 1.84 (s, 3 H, HC(11))

^{13}C NMR: (125 MHz, $CDCl_3$)

148.6 (C(12)), 146.1(C(7)), 146.0 (C(8)), 137.4 (C(5)), 136.2 (C(16), 132.2 (C(17)), 128.9 (C(14)), 128.7 (C(10)), 128.0 (C(13) and C(18)), 126.8 (C(15), 126.3 (C(19)), 109.2 (C(9)), 107.9 (C(6)), 100.8 (OCH_2O), 60.2 (C(2)), 47.7 (C(1)), 29.3 (C(4)), 26.8 (C(3)), 25.7 (C(11))

IR: (KBr)

3045 (w), 2968 (m), 2933 (m), 2885 (m), 1580 (w), 1500 (m), 1483 (s), 1438 (m), 1368 (m), 1330 (w), 1229 (s), 1115 (w), 1035 (s), 935 (m), 858 (m), 752 (m), 737 (m), 699 (s)

MS: (EI^+, 70 eV)

375.1 (16.9), 374.1 (55.4), 266.1 (23.0), 265.1 (100.0), 264.1 (16.3), 249.1 (12.5), 237.1 (14.0), 224.0 (10.7), 223.0 (70.1), 205.1 (12.0), 1919.1 (17.7), 189.0 (12.5), 187.0 (11.0), 178.0 (12.7), 173.0 (107), 165.0 (24.9), 135.0 (13.0), 129.0 (10.5), 120.9 (19.6), 118.9 (22.1), 115.0 (15.7), 110.0 (12.4), 109.0 (13.8), 105.0 (32.6), 101.0 (9.5)

HRMS: calcd for $C_{24}H_{22}O_2S^+$: 374.1341, found: 374.1343

TLC: R_f 0.37 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +72.9 (c = 0.48, EtOH)

SFC: (5*R*,6*R*)-**3j,** t_R 15.5 min (71%); (5*S*,6*S*)-**3j,** t_R 21.5 min (29%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Analysis: $C_{24}H_{22}O_2S$ (374.13)

Calcd: C, 76.97; H, 5.92%

Found: C, 76.91; H, 5.85%

Data for **11**:

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

7.27 (t, J = 7.5 Hz, 2 H, HC(14)), 7.17 (t, J = 7.5 Hz, 1 H, HC(15)), 7.16 (d, J = 7.5

Hz, 2 H, HC(13)), 6.60 (s, 1 H, HC(6)), 6.46 (s, 1 H, C(9)), 5.89 (d, *J* = 10.0 Hz, 2 H, OCH_2O), 2.77 (t, *J* = 6.5 Hz, 2 H, HC(4)), 2.02 (ddd, *J* = 13.5, 8.5, 3.0 Hz, 1 H, HC(2)), 1.86 (ddd, *J* = 12.5, 9.0, 3.0 Hz, 1 H, HC(2)), 1.79 – 1.72 (m, 1 H, HC(3)), 1.70 (s, 3 H, HC(11)), 1.68 – 1.62 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

151.6 (C(12)), 145.9 (C(7)), 145.7 (C(8)), 137.4 (C(5)), 130.4 (C(10)), 127.9 (C(14), 127.5 (C(13)), 125.6 (C(15)), 108.9 (C(9)), 108.3 (C(6)), 100.7 (OCH_2O), 43.1 (C(1)), 41.6 (C(2)), 30.6 (C(4)), 30.1 (C(3)), 15.8 (C(11))

IR: (neat)

2926 (m), 1500 (m), 1479 (s), 1441 (w), 1372 (w), 1226 (s), 1163 (w), 1039 (m), 931 (w), 827 (w), 754 (w), 695 (w)

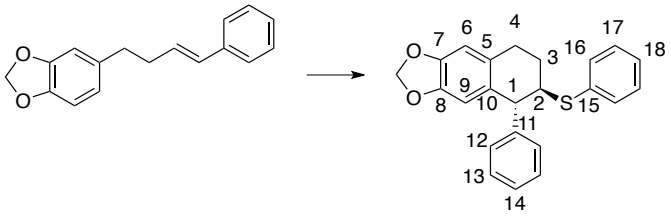
MS: (EI^+, 70 eV)

267.1 (10.8), 266.1 (56.8), 252.0 (17.8), 251.1 (100.0), 189.0 (16.9), 115.1 (7.4), 91.1 (22.7), 86.0 (15.3), 84.0 (24.0)

HRMS: calcd for $C_{18}H_{18}O_2^+$: 266.1307, found: 266.1303

TLC: R_f 0.58 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Preparation of ((5*R*,6*R*)-5-Phenyl-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3k)



trans-**3k**

Following General Procedure 9, (*E*)-**2k** (252.3 mg, 1.0 mmol), **1** (256 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 48 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3k** (328 mg, 91%) as a pale yellow solid. Recrystallization form hot pentane provided 324 mg (90%) of analytically pure *trans*-**3k**.

Data for *trans*-**3k**:

mp: 54-56 °C (pentane)

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

7.42 (d, *J* = 7.5 Hz, 2 H, HC(16)), 7.34 – 7.22 (m, 6 H, HC(13) and HC(14) and HC(17) and HC(18)), 7.07 (d, *J* = 7.5 Hz, 2 H, HC(12)), 6.66 (s, 1 H, HC(6)), 6.32 (s, 1 H, C(9)), 5.90 (d, *J* = 2.5 Hz, 2 H, OCH_2O), 4.13 (d, *J* = 5.0 Hz, 1 H, HC(1)), 3.68 – 3.65 (m, 1 H, HC(2)), 3.00 (ddd, *J* = 16.0, 8.0, 5.5 Hz, 1 H, HC(4)), 2.81 (ddd, *J* = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.20 – 2.14 (m, 1 H, HC(3)), 2.19 – 2.12 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.4 (C(7)), 146.2 (C(8)), 145.5 (C(11)), 135.1 (C(15)), 132.4 (C(16)), 129.5 (C(5)), 129.4 (C(10)), 129.1 (C(12)), 129.0 (C(13)), 128.5 (C(17)), 127.2 (C(18)), 126.7 (C(14)), 110.4 (C(9)), 108.3 (C(6)), 100.8 (OCH_2O), 51.5 (C(2)), 50.4 (C(1)), 26.8 (C(4)), 24.9 (C(3))

IR: (KBr)

3052 (w), 3017 (w), 2919 (m), 2885 (m), 1580 (w), 1500 (m), 1479 (s), 1448 (m), 1434 (m), 1382 (w), 1236 (s), 1170 (w), 1039 (s), 938 (m), 869 (m), 740 (m), 699 (m)

MS: (EI^+, 70 eV)

361.1 (18.7), 360.0 (71.7), 252.1 (16.6), 251.1 (91.6), 250.0 (100.0), 224.0 (20.2), 223.0 (29.6), 205.1 (19.0), 194.0 (15.6), 193.1 (10.4), 191.1 (19.0), 189.0 (13.2), 178.0 (13.9), 173.0 (13.6), 166.1 (17.0), 165.0 (35.2), 160.0 (9.5), 159.0 (15.7), 152.0 (8.4), 143.0 (7.3), 135.0 (18.3), 115.0 (28.6), 109.0 (11.8)

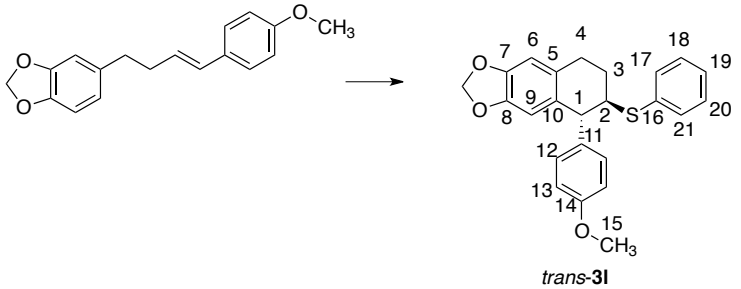
HRMS: calcd for $C_{23}H_{20}O_2S^+$: 360.1164, found: 360.1178

TLC: R_f 0.40 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -33.0 (c = 0.65, EtOH)

SFC: (5*R*,6*R*)-**3k,** t_R 14.0 min (94%); (5*S*,6*S*)-**3k,** t_R 17.2 min (6%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Preparation of ((5*R*,6*R*)-5-(4-Methoxyphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3l)



trans-**3l**

Following General Procedure 9, a 10-mL Schlenk flask was charged with (*E*)-**2l** (282.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 24 h. Purification by flash column chromatography (SiO_2, 95 g, 30 mm Ø, hexane/Et_2O, 90:10) afforded *trans*-**3l** (340 mg, 87%) as a white solid. Recrystallization from hot pentane provided 336 mg (86%) of analytically pure *trans*-**3l**.

Data for *trans*-**3l**:

mp: 104-106 °C (pentane)

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

7.42 – 7.41 (m, 2 H, HC(17) and HC(21)), 7.33 – 7.28 (m, 2 H, HC(18) and HC(20)), 7.26 (tt, *J* = 7.0, 2.0 Hz, 1 H, HC(19)), 6.97 (d, *J* = 7.5 Hz, 2 H, HC(13)), 6.84 (d, *J* = 7.5 Hz, 2 H, HC(12)), 6.64 (s, 1 H, HC(6)), 6.32 (s, 1 H, C(9)), 5.86 (s, 2 H, OCH_2O), 4.06 (d, *J* = 5.0 Hz, 1 H, HC(1)), 3.81 (s, 3 H, HC(15)), 3.63 – 3.60 (m, 1 H, HC(2)), 2.98 (ddd, *J* = 16.0, 9.0, 6.0 Hz, 1 H, HC(4)), 2.79 (ddd, *J* = 17.0, 5.5, 5.5 Hz, 1 H, HC(4)), 2.19 – 2.13 (m, 1 H, HC(3)), 1.88 – 1.81 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

158.4 (C(14)), 146.4 (C(7)), 146.2 (C(8)), 137.7 (C(11)), 135.3 (C(16)), 132.4 (C(17,20)), 130.1 (C(13)), 130.0 (C(5)), 129.4 (C(10)), 129.1 (C(18,20)), 127.2 (C(19)), 113.9 (C(12)), 110.4 (C(9)), 108.3 (C(6)), 100.9 (OCH_2O), 55.5 (C(15)), 51.7 (C(2)), 49.7 (C(1)), 27.0 (C(4)), 25.0 (C(3))

IR: (KBr)

2919 (m), 2829 (m), 1608 (m), 1580 (m), 1507 (s), 1479 (s), 1434 (m), 1389 (w), 1299 (w), 1240 (s), 1039 (m), 941 (w), 869 (w), 817 (m), 740 (m)

MS: (EI^+, 70 eV)

390.2 (17.0), 381.5 (16.5), 340.3 (20.3), 326.2 (26.2), 325.2 (100.0), 295.4 (12.0), 281.2 (23.0), 280.2 (20.2), 269.3 (15.0), 231.2 (43.9), 223.1 (16.0), 191.2 (58.7), 175.2 (14.2), 159.1 (14.1), 149.2 (16.1), 143.1 (11.5), 141.1 (20.0), 135.1 (40.6), 133.1 (12.1), 128.1 (14.8), 127.1 (13.6), 121.1 (32.2), 115.1 (28.0), 57.0 (60.0)

HRMS: calcd for $C_{24}H_{22}O_3S^+$: 390.1290, found: 390.1297

TLC: R_f 0.36 (hexanes/Et_2O, 90:10) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -25.9 (c = 0.54, EtOH)

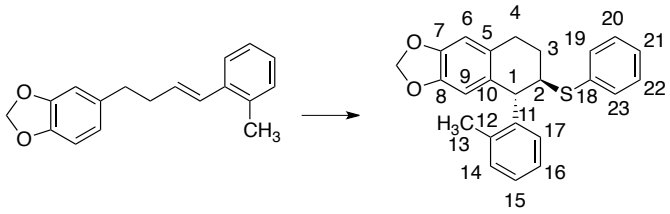
SFC: (5*R*,6*R*)-**3l,** t_R 23.7 min (92%); (5*S*,6*S*)-**3l,** t_R 42.7 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{24}H_{22}O_3S$ (390.13)

Calcd: C, 73.82; H, 5.68%

Found: C, 73.89; H, 5.60%

Preparation of ((5*R*,6*R*)-5-(2-Methylphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3m)



trans-**3m**

Following General Procedure 9, (*E*)-**2m** (266.3 mg, 1.00 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 86 h. Purification by flash column chromatography (SiO_2, 95 g, 40 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**14i** (323 mg, 86%) as a white solid along unreacted (*E*)-**2m** (10 mg, 4%). Recrystallization of *trans*-**3m** from hot pentane provided 308 mg (82%) of analytically pure *trans*-**3m**.

Data for *trans*-**3m**:

mp: 56-58 °C (pentane)

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

7.45 – 7.43 (m, 2 H, HC(19) and HC(23)), 7.32 – 7.25 (m, 3 H, HC(20) and HC(21)

and HC(22)), 7.18 (d, *J* = 6.5 Hz, 1 H, HC(14)), 7.12 (d, *J* = 7.5 Hz, 1.5 H, HC(15)), 7.08 (dt, *J* = 7.5, 1.5 Hz, 1 H, HC(16)), 6.76 (d, *J* = 7.5 Hz, 1 H, HC(17)), 6.66 (s, 1 H, HC(6)), 6.28 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 4.36 (d, *J* = 4.5 Hz, 1 H, HC(1)), 3.58 – 3.55 (m, 1 H, HC(2)), 3.06 (ddd, *J* = 16.5, 11.5, 5.5 Hz, 1 H, HC(4)), 2.80 (ddd, *J* = 16.5, 5.5, 5.5 Hz, 1 H, HC(4)), 2.31 (s, 3 H, HC(13)), 2.18 – 2.11 (m, 1 H, HC(3)), 1.87 – 1.80 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.4 (C(7)), 146.3 (C(8)), 143.6 (C(14)), 136.2 (C(18)), 135.1 (C(12)), 133.2 (C(19,23)), 130.5 (C(14)), 130.0 (C(5)), 129.6 (C(17)), 129.5 (C(10)), 129.0 (C(20, 22)), 127.4 (C(21)), 126.5 (C(15)), 126.0 (C(16)), 110.1 (C(9)), 108.2 (C(6)), 100.8 (OCH_2O), 50.4 (C(2)), 46.6 (C(1)), 26.5 (C(4)), 24.5 (C(3)), 19.6 (C(13))

IR: (KBr)

3059 (m), 3015 (m), 2924 (s), 2770 (w), 1583 (m), 1504 (s), 1485 (s), 1454 (s), 1385 (s), 1348 (m), 1305 (w), 1283 (w), 1236 (s), 1176 (m), 1088 (w), 1038 (s), 941 (s), 907 (m), 868 (m), 823 (m), 741 (s)

MS: (EI^+, 70 eV)

374.1 (32.2), 325.2 (25.5), 265.1 (41.9), 264.1 (33.9), 239.1 (14.8), 223.1 (28.9), 220.2 (28.9), 206.2 (21.1), 205.2 (71.9), 192.1 (15.5), 191.1 (100.0), 175.1 (16.6), 165.1 (17.3), 149.0 (43.8), 145.1 (16.6), 135.1 (86.3), 131.1 (16.1), 129.1 (17.1), 128.1 (15.4), 121.1 (27.4), 115.1 (28.3), 111.1 (13.1), 109.1 (12.2), 107.1 (36.4), 105.1 (44.9)

HRMS: calcd for $C_{24}H_{22}O_2S^+$: 374.1341, found: 374.1334

TLC: R_f 0.37 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -40.1 (c = 0.43, EtOH)

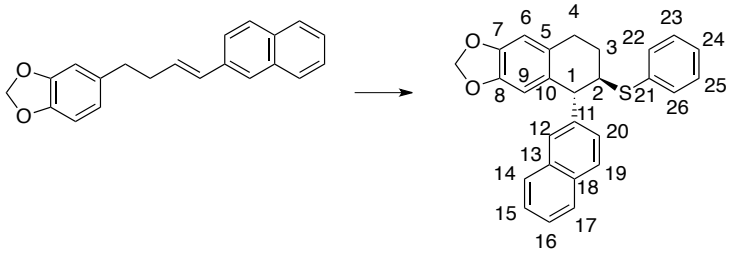
SFC: (5*S*,6*S*)-**3m,** t_R 10.2 min (8%); (5*R*,26*R*)-**3m,** t_R 11.5 min (92%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Analysis: $C_{24}H_{22}O_2S$ (374.13)

Calcd: C, 76.97; H, 5.92%

Found: C, 77.26; H, 5.77%

Preparation of ((5*R*,6*R*)-5-(2-Naphthyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3n)



trans-**3n**

Following General Procedure 9, (*E*)-**2n** (302 mg, 1.0 mmol, 1.0 equiv), **1** (256 mg, 1.0 mmol, 1.0 equiv), (*S*)-**4e** (55 mg, 0.1 mmol, 0.1 equiv) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 48 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**3n** (254 mg, 62%) as a white solid along with unreacted (*E*)-**2n** (109 mg, 36%). Recrystallization from hot pentane provided 250 mg (61%) of analytically pure *trans*-**3n**.

Data for trans-**3n**:

mp: 92-94 °C (pentane)

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

7.83 – 7.77 (m, 2 H, H(C-aryl)), 7.50 – 7.42 (m, 5 H, HC(22) and HC(26) and H(C-aryl)), 7.32 – 7.20 (m, 5 H, HC(23) and HC(24) and HC(25) and H(C-aryl)), 6.69 (s, 1 H, HC(6)), 6.33 (s, 1 H, C(9)), 5.89 (s, 2 H, OCH_2O), 4.27 (d, J = 5.5 Hz, 1 H, HC(1)), 3.78 – 3.73 (m, 1 H, HC(2)), 3.03 (ddd, J = 18.0, 8.0, 6.5 Hz, 1 H, HC(4)), 2.86 (ddd, J = 17.0, 6.0, 5.5 Hz, 1 H, HC(4)), 2.25 – 2.18 (m, 1 H, HC(3)), 1.91 – 1.85 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.6 (C(7)), 146.3 (C(8)), 142.9 (C(11)), 135.1 (C(21)), 133.5 (C-aryl), 132.6 (C(22,26)), 132.5 (C-aryl), 129.7 (C(5)), 129.5 (C(10)), 129.1 (C(23,25)), 128.4 (C(aryl)), 128.3 (C(aryl)), 128.0 (C(aryl)), 127.8 (C(aryl)), 127.3 (C(aryl), 127.0 (C(24)), 126.3 (C(aryl)), 125.9 (C(aryl)), 110.5 (C(9)), 108.4 (C(6)), 101.0 (OCH_2O), 51.5 (C(2)), 50.8 (C(1)), 27.2 (C(4)), 25.5 (C(3))

IR: (KBr)

3045 (w), 2968 (w), 2919 (m), 2885 (m), 1597 (w), 1580 (w), 1500 (s), 1479 (s),

1438 (m), 1382 (w), 1236 (s), 1170 (w), 1115 (m), 1035 (s), 938 (m), 855 (w), 817 (m), 796 (w), 744 (s), 692 (m)

MS: (EI^+, 70 eV)

446.2 (66.5), 325.2 (58.7), 310.4 (12.6), 295.3 (34.6), 279.3 (30.9), 259.3 (18.2), 247.2 (17.8), 239.2 (54.4), 231.2 (100.0), 227.2 (21.0), 215.2 (17.1), 205.2 (15.7), 191.2 (93.0), 175.2 (28.9), 159.1 (24.4), 149.1 (27.1), 143.1 (25.5), 141.1 (33.5), 133.1 (21.2), 128.1 (25.7), 121.1 (32.4), 115.1 (38.3), 109.1 (30.5), 107.1 (44.4), 105.1 (46.2)

HRMS: calcd for $C_{27}H_{22}O_2S^+$: 410.1341, found: 410.1343

TLC: R_f 0.36 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -19.2 (c = 0.54, EtOH)

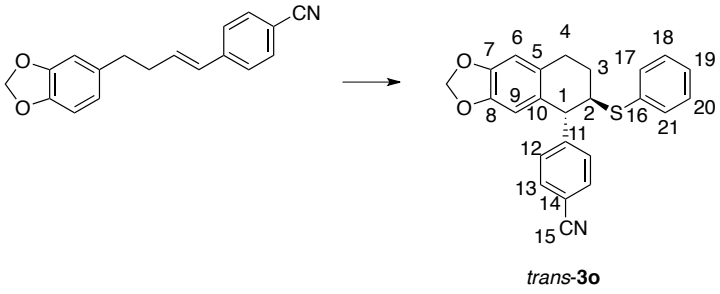
SFC: (5*S*,6*S*)-**3n,** t_R 23.4 min (11%); (5*R*,6*R*)-**3n,** t_R 23.5 min (89%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{27}H_{22}O_2S$ (410.13)

Calcd: C, 78.99; H, 5.40%

Found: C, 78.98; H, 5.48%

Preparation of ((5*R*,6*R*)-5-(4-Cyanophenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3o)



trans-**3o**

Following General Procedure 9, (*E*)-**2o** (277.3 mg, 1.0 mmol, 1.0 equiv), **1** (256 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at room temperature for 96 h. Purification by flash column chromatography (SiO_2, 90 g, 30 mm Ø, hexane/Et_2O, 80:20) afford *trans*-**3o** (324 mg, 84%) as a white solid. Recrystallization from hot pentane provided 320 mg (83%) of analytically pure *trans*-**3o**.

Data for *trans*-**3o**:

mp: 64-66 °C (pentane)

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

7.55 (d, J = 8.0 Hz, 2 H, HC(13)), 7.37 – 7.35 (m, 2 H, HC(17) and HC(23)), 7.41 – 7.25 (m, 3 H, HC(18) and HC(19) and HC(20)), 7.13 (d, J = 8.0 Hz, 2 H, HC(12)), 6.63 (s, 1 H, HC(6)), 6.17 (s, 1 H, C(9)), 5.88 (s, 2 H, OCH_2O), 4.11 (d, J = 5.5 Hz, 1 H, HC(1)), 3.52 – 3.49 (m, 1 H, HC(2)), 2.97 (ddd, J = 17.0, 14.0, 6.0 Hz, 1 H, HC(4)), 2.79 (ddd, 1H, J = 17.0, 6.5, 6.5 Hz, 1 H, HC(4)), 2.13 – 2.07 (m, 1 H, HC(3)), 1.88 – 1.82 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

151.0 (C(7)), 146.9 (C(8)), 146.5 (C(16)), 134.5 (C(17,21)), 132.9 (C(13)), 132.4 (C(12), 129.7 (C(10)), 129.3 (C(18,20)), 128.4 (C(5)), 127.7 (C(19)), 119.1 (C(15)), 110.7 (C(14)), 110.0 (C(9)), 108.6 (C(6)), 101.1 (OCH_2O), 51.8 (C(2)), 50.9 (C(1)), 27.3 (C(4)), 25.8 (C(3))

IR: (KBr)

3059 (w), 2968 (w), 2926 (w), 2885 (w), 2216 (m), 1604 (w), 1580 (w), 1500 (s), 1476 (s), 1434 (m), 1382 (m), 1236 (s), 1035 (s), 938 (m), 820 (m), 740 (m)

MS: (EI^+, 70 eV)

385.2 (22.9), 381.3 (18.4), 340.3 (17.6), 326.2 (24.7), 325.2 (100), 276.2 (30.4), 275.1 (33.4), 269.2 (14.2), 239.2 (14.6), 231.2 (34.4), 191.2 (48.8), 190.1 (16.6), 175.1 (12.8), 160.1 (14.1), 141.1 (12.4), 135.1 (29.8), 121.0 (12.8), 115.1 (22.3), 107.1 (18.8), 91.1 (22.0), 77.1 (19.2), 69.1 (14.0), 57.1 (48.1), 55.1 (22.0)

HRMS: calcd for $C_{24}H_{19}NO_2S^+$: 385.1137, found: 385.1129

TLC: R_f 0.38 (hexanes/Et_2O, 80:20) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -19.9 (c = 0.58, EtOH)

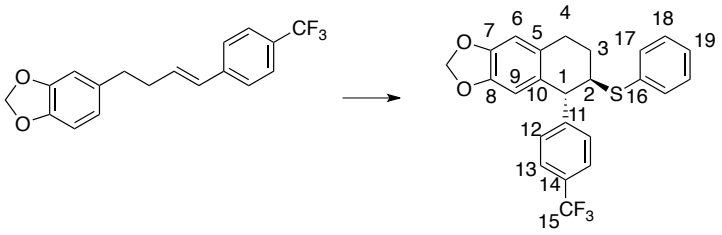
SFC: (5*S*,6*S*)-**3o,** t_R 23.9 min (89%); (5*R*,6*R*)-**3o,** t_R 27.6 min (11%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{27}H_{22}NO_2S$ (385.48)

Calcd: C, 74.78; H, 4.97%; N, 3.63%

Found: C, 74.50; H, 4.69%; N, 3.60%

Preparation of ((5*R*,6*R*)-5-(4-Trifluoromethylphenyl)-6-(phenylthio)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-3p)



trans-**3p**

Following General Procedure 9, (*E*)-**2p** (320.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at 22 °C for 72 h. Purification by flash column chromatography (SiO_2, 90 g, 32 mm Ø, hexane/Et_2O, 96:4) afford *trans*-**3p** (368 mg, 86%) as a white solid. Recrystallization from hot pentane provided 364 mg (85%) of analytically pure *trans*-**3p**.

Data for *trans*-**3p**:

mp: 98-100 °C (pentane)

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

7.54 (d, *J* = 8.0 Hz, 2 H, HC(13)), 7.39 (t, *J* = 7.0 Hz, 2 H, HC(17), 7.31 (t, *J* = 6.5 Hz, 2 H, HC(18)), 7.23 (t, *J* = 7.5 Hz, 1 H, HC(19)), 7.16 (d, *J* = 8.0 Hz, 2 H, HC(12)), 6.66 (s, 1 H, HC(6)), 6.23 (s, 1 H, C(9)), 5.90 (s, 2 H, OCH_2O), 4.16 (d, *J* = 5.5 Hz, 1 H, HC(1)), 3.60 – 3.57 (m, 1 H, HC(2)), 3.00 (ddd, *J* = 16.5, 8.0, 6.0 Hz, 1 H, HC(4)), 2.82 (ddd, 1H, *J* = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.18 – 2.11 (m, 1 H, HC(3)), 1.90 – 1.84 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

149.5 (C(11)), 146.7 (C(7)), 146.3 (C(8)), 134.6 (C(16)), 132.6 (C(18)), 129.6 (C(10)), 129.5 (C(12)), 129.1 (C(17)), 129.0 (q, *J* = 32.0 Hz, (C(14)), 128.8 (C(5)), 127.5 (C(19)), 125.4 (q, *J* = 3.9 Hz, C(13)), 124.3 (q, *J* = 272.0 Hz, C(15)), 110.1 (C(9)), 108.4 (C(6)), 101.0 (OCH_2O), 51.6 (C(2)), 50.6 (C(1)), 27.1 (C(4)), 25.5 (C(3))

IR: (KBr)

2927 (w), 2891 (w), 1608 (w), 1580 (w), 1503 (s), 1479 (s), 1437 (m), 1381 (w), 1301 (w), 1238 (s), 1171 (m), 1032 (s), 937 (m), 906 (w), 818 (m)

MS: (EI^+, 70 eV)

429.2 (22.9), 428.2 (84.1), 325.2 (17.9), 319.1 (17.2), 318.1 (100.0), 291.1 (9.2), 289.2 (9.5), 260.1 (9.2), 233.1 (12.0), 223.1 (47.5), 191.1 (10.3), 189.1 (11.4), 165.0 (20.0), 161.1 (11.6), 160.1 (36.1), 159.1 (30.9), 115.1 (16.3)

HRMS: calcd for $C_{24}H_{19}F_3O_2S^+$: 428.1058, found: 428.1050

TLC: R_f 0.29 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -18.5 (c = 0.55, EtOH)

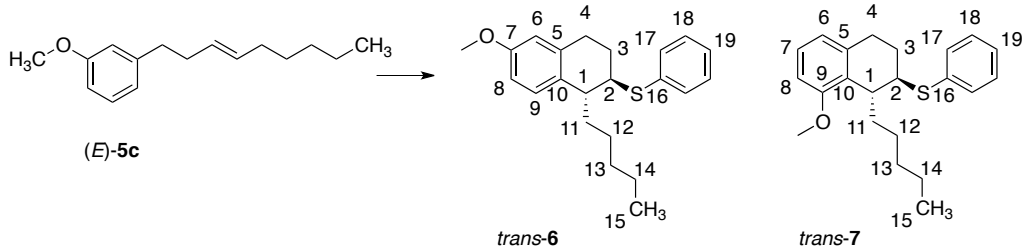
SFC: (5*R*,6*R*)-**3p,** t_R 6.4 min (92%); (5*S*,6*S*)-**3p,** t_R 9.8 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{24}H_{22}F_3O_2S$ (428.11)

Calcd: C, 67.28; H, 4.47%

Found: C, 67.92; H, 4.35%

Preparation of (1*R*,2*R*)-6-Methoxy-1-pentyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*trans*-6) and (1*R*,2*R*)-8-Methoxy-1-pentyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*trans*-7)



Following General Procedure 9, (*E*)-**5c** (232.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at –20 °C for 72 h. Purification by flash column chromatography (SiO_2, 95 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**6** (210 mg, 62%) as colorless oil along with *trans*-**7** (73 mg, 21%) as a white solid. Distillation provided 204 mg (60%) of analytically pure *trans*-**6**. Recrystallization of *trans*-**7** from hot pentane provided 68 mg (20%) of analytically pure *trans*-**7**.

Data for *trans*-**6**:

bp: 140 °C @ 1.5×10^{-5} mmHg

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

7.46 (dd, *J* = 7.5, 1.5 Hz, 2 H, HC(17)), 7.33 (tt, *J* = 7.5, 1.5 Hz, 2 H, HC(18)), 7.27 (tt, *J* = 7.0, 1.0 Hz, 1 H, HC(19)), 7.04 (d, *J* = 8.5 Hz, 1 H, HC(9)), 6.76 (dd, *J* = 8.5, 2.5 Hz, 1 H, HC(8)), 6.66 (d, *J* = 2.5 Hz, 1 H, HC(6)), 3.81 (s, 3 H, OCH_3), 3.71 – 3.69 (m, 1 H, HC(2)), 3.06 (ddd, *J* = 17.0, 11.0, 5.5 Hz, 1 H, HC(4)), 2.89 – 2.86 (m, 1 H, HC(1)), 2.72 (ddd, *J* = 17.5, 6.0, 4.0 Hz, 1H, HC(4)), 2.19 (dddd, *J* = 14.0, 9.0, 6.0, 3.0 Hz, 1 H, HC(3)), 1.94 – 1.88 (m, 1 H, HC(3)), 1.74 – 1.62 (m, 2 H, HC(11)), 1.42 – 1.24 (m, 6 H, H(12) and HC(13), and HC(14)), 0.90 (t, J = 7.0 Hz, 3 H, HC(15))

^{13}C NMR: (125 MHz, $CDCl_3$)

157.7 (C(7)), 136.5 (C(5)), 135.6 (C(16)), 132.0 (C(17)), 131.1 (C(10)), 130.7 (C(9)), 129.0 (C(18)), 126.9 (C(19)), 113.2 (C(6)), 112.4 (C(8)), 55.2 (OCH_3), 46.8 (C(2)), 42.7 (C(1)), 38.0 (C(11)), 32.00 (C(13)), 27.0 (C(12)), 25.8 (C(4)), 23.4 (C(3)), 22.7 (C(14)), 14.2 (C(15))

IR: (neat)

3052 (s), 2919 (s), 2843 (s), 1608 (s), 1580 (s), 1500 (s), 1455 (s), 1434 (s), 1375 (m), 1320 (m), 1254 (s), 1233 (s), 1157 (m), 1125 (s), 1087 (m), 1039 (s), 896 (m), 844 (m), 813 (m), 740 (s)

MS: (EI^+, 70 eV)

340.1 (20.5), 269.2 (23.0), 231.1 (100.0), 191.2 (47.8), 161.1 (24.5), 160.1 (36.1), 159.1 (30.2), 147.1 (31.4), 135.1 (48.5), 121.1 (24.7), 115.1 (19.2), 107.1 (26.8), 91.1 (25.00), 77.1 (19.5), 57.1 (37.7), 55.1 (22.8)

HRMS: calcd for $C_{22}H_{28}OS^+$: 340.1801, found: 340.1856

TLC: R_f 0.38 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +14.5 (c = 0.54, EtOH)

SFC: (1*R*,2*R*)-**6,** t_R 8.8 min (96%); (1*S*,2*S*)-**6,** t_R 13.7 min (4%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^{o}C)

Analysis: $C_{22}H_{28}OS$ (340.19)

Calcd: C, 77.60; H, 8.29%

Found: C, 77.89; H, 8.42%

Data for *trans*-**7**:

mp: 72-74 °C (pentane)

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

7.45 (dd, *J* = 7.5 Hz, 2 H, HC(17)), 7.32 (t, *J* = 7.5 Hz, 2 H, HC(18), 7.25 (t, *J* = 7.0, 1.0 Hz, 1 H, HC(19)), 7.13 (t, *J* = 8.0 Hz, 1 H, HC(7)), 6.74 (d, *J* = 8.5, 1 H, HC(6)), 6.71 (d, *J* = 8.5 Hz, 1 H, HC(8)), 3.82 (s, 3 H, OCH_3), 3.79 (s, 1 H, HC(2)), 3.22 (d, *J* = 6.0 Hz, 1 H, HC(1)), 3.10 (ddd, *J* = 17.5, 11.5, 6.0 Hz, 1 H, HC(4)), 2.72 (dd, *J* = 17.5, 4.5 Hz, 1 H, HC(4)), 2.20 – 2.13 (m, 1 H, HC(3)), 1.90 – 1.87 (m, 1 H, HC(3)), 1.79 – 1.68 (m, 1 H, HC(11)), 1.50 – 1.23 (m, 7 H, HC(11) and (HC(12) and HC(13), and HC(14)), 0.91 (t, *J* = 7.0 Hz, 3 H, HC(15))

^{13}C NMR: (125 MHz, $CDCl_3$)

157.6 (C(9)), 136.4 (C(16)), 136.1 (C(5)), 131.8 (C(17)), 128.9 (C(18)), 128.1 (C(10)), 126.70 (C(19)), 126.4 (C(7)), 121.66 (C(6)), 107.7 (C(8)), 55.3 (OCH_3), 45.6 (C(2)), 37.6 (C(1)), 35.6 (C(11)), 31.7 (C(13)), 27.6 (C(12)), 24.9 (C(4)), 22.7 (C(14)), 22.0 (C(3)), 14.2 (C(15))

IR: (KBr)

2940 (m), 2912 (s), 2843 (m), 1580 (s), 1465 (s), 1451 (s), 1438 (m), 1337 (m), 1250 (s), 1084 (s), 1066 (s), 765 (m), 737 (m)

MS: (EI^+, 70 eV)

341.1 (12.6), 340.2 (47.4), 269.1 (34.7), 231.2 (42.7), 230.2 (11.9), 174.1 (13.9), 161.1 (50.4), 160.1 (31.8), 159.1 (69.0), 148.0 (12.1), 147.1 (100.0), 145.1 (13.3), 144.0 (17.2), 135.1 (11.6), 129.1 (14.2), 128.1 (14.9), 127.0 (10.3), 121.1 (10.3), 115.1 (24.0), 109.0 (10.8), 91.1 (14.7), 85.9 (52.3), 84.0 (79.4), 58.1 (9.6)

HRMS: calcd for $C_{22}H_{28}OS^+$: 340.1801, found: 340.1865

TLC: R_f 0.54 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ +13.6 (c = 0.61, EtOH)

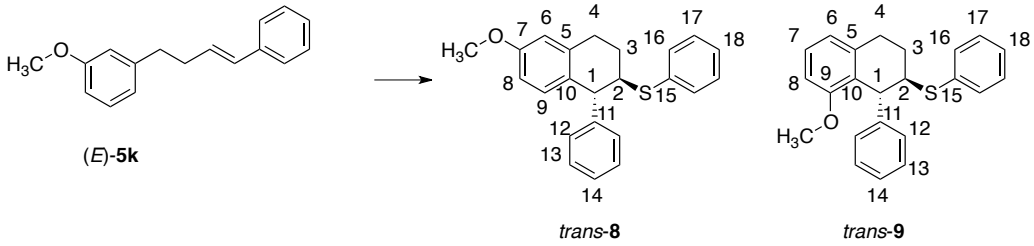
SFC: (1*R*,2*R*)-**7,** t_R 5.8 min (91%); (1*S*,2*S*)-**7,** t_R 8.9 min (9%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{22}H_{28}OS$ (340.19)

Calcd: C, 77.60; H, 8.29%

Found: C, 77.43; H, 8.22%

Preparation of (1*R*,2*R*)-6-Methoxy-1-phenyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*trans*-8) and (1*R*,2*R*)-8-Methoxy-1-phenyl-2-(phenylthio)-1,2,3,4-tetrahydronaphthalene (*trans*-9)



Following General Procedure 9, (*E*)-**2k** (238.3 mg, 1.0 mmol), **1** (256.0 mg, 1.0 mmol), (*S*)-**4e** (54.9 mg, 0.1 mmol) and CH_2Cl_2 (4.25 mL) were reacted with a solution of $EtSO_3H$ (1 M in CH_2Cl_2, 0.75 mL, 0.75 mmol) at −20 °C for 72 h. Purification by flash column chromatography (SiO_2, 95 g, 30 mm Ø, hexane/Et_2O, 96:4) afforded *trans*-**8** (160 mg, 46%) as colorless oil along with *trans*-**9** (161 mg, 46%) as a white solid. Distillation provided 156 mg (45%) of analytically pure *trans*-**8**. Recrystallization of *trans*-**9** from hot pentane provided 156 mg (45%) of analytically pure *trans*-**9**.

Data for *trans*-**8**:

bp: 135 °C @ 1.6×10^{-5} mmHg

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

7.49 (dd, J = 8.5, 1.5 Hz, 2 H, HC(16)), 7.35 (t, J = 9.0 Hz, 2 H HC(17), 7.30 – 7.22 (m, 4 H, HC(7) and HC(13) and HC(18)), 7.18 (tt, J = 7.0, 1.0 Hz, 1 H, HC(14)), 6.99 (d, J = 7.0 Hz, 2 H, HC(12)), 6.88 (d, J = 7.5 Hz, 1 H, HC(6)), 6.70 (d, J = 8.0 Hz, 1 H, HC(8)), 4.55 (s, 1 H, HC(1)), 3.81 – 3.79 (m, 1 H, HC(2)), 3.57 (s, 3 H, OCH_3), 3.19 (ddd, J = 17.5, 12.5, 6.0 Hz, 1 H, HC(4)), 2.85 (ddd, J = 17.0, 5.5, 2.0 Hz, 1H, HC(4)), 2.11 – 2.03 (m, 1 H, HC(3)), 1.83 – 1.77 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

158.1 (C(9)), 146.0 (C(11), 137.7 (C(10)), 135.8 (C(15)), 132.1 (C(16)), 129.2 (C(12), 128.3 (C(17)), 128.2 (C(13)), 127.4 (C(7)), 127.1 (C(18)), 126.2 (C(14)), 125.7 (C(5)), 121.3 (C(6)), 108.3 (C(7)), 55.7 (OCH_3), 50.8 (C(2)), 44.0 (C(1)), 25.1 (C(4)), 21.6 (C(3))

IR: (neat)

3052 (w), 3017 (w), 2926 (m), 2829 (w), 1583 (s), 1465 (s), 1434 (m), 1337 (w),

1254 (s), 1222 (w), 1091 (s), 1066 (m), 1021 (w), 955 (w), 817 (w), 768 (m), 737 (s), 699 (s)

MS: (EI^+, 70 eV)

346.0 (12.4), 346.0 (43.1), 238.0 (18.9), 237.1 (98.4), 236.0 (29.3), 179.0 (12.1), 178.0 (13.6), 165.0 (13.7), 159.0 (27.4), 145.0 (21.7), 144.0 (11.0); 129.0 (11.8), 121 (16.5), 115.0 (19.4), 109.0 (10.8), 91.0 (100.0), 65.1 (10.3)

HRMS: calcd for $C_{23}H_{22}OS^+$: 346.1391, found: 346.1384

TLC: R_f 0.38 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -84.3 (c = 0.55, EtOH)

SFC: (1*R*,2*R*)-**8,** t_R 12.3 min (90%); (1*S*,2*S*)-**8,** t_R 13.8 min (10%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 ^oC)

Data for *trans*-**9**:

mp: 77-79 °C (pentane)

^1H NMR: (500 MHz, $CDCl_3$)

7.41 (d, *J* = 7.5 Hz, 2 H, HC(16)), 7.32 – 7.19 (m, 6 H, HC(13) and HC(14) and HC(17) and HC(18)), 7.03 (d, *J* = 7.5 Hz, 1 H, HC(12)), 6.76 (d, *J* = 8.5 Hz, 1 H, HC(9)), 6.71 (d, *J* = 2.5 Hz, 1 H, HC(6)), 6.66 (dd, *J* = 8.5, 2.5 Hz, 1 H, HC(8)), 4.16 (d, *J* = 5.5 Hz, 1 H, HC(1)), 3.77 (s, 3 H, OCH_3), 3.67 (ddd, *J* = 8.5, 5.5, 3.0 Hz, 1 H, HC(2)), 3.05 (ddd, *J* = 16.5, 8.5, 5.5 Hz, 1 H, HC(4)), 2.86 (ddd, *J* = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.21 – 2.15 (m, 1 H, HC(3)), 1.89 – 1.83 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

158.2 (C(7)), 145.9 (C(11), 137.5 (C(10)), 135.2 (C(15)), 132.5 (C(16)), 132.1 (C(9), 129.2 (C(5,12)), 129.1 (C(17)), 128.5 (C(13)), 127.2 (C(18)), 125.7 (C(14)), 113.1 (C(6)), 113.0 (C(8)), 55.4 (OCH_3), 51.8 (C(2)), 49.9 (C(1)), 27.3 (C(4)), 25.3 (C(3))

IR: (KBr)

3052 (m), 3017 (m), 2926 (s), 2829 (m), 1608 (s), 1583 (s), 1503 (s), 1451 (s), 1434 (s), 1323 (s), 1250 (s), 1236 (s), 1219 (s), 1153 (s), 1122 (s), 1108 (m), 1087 (m), 1035 (s), 928 (m), 893 (m), 858 (m), 820 (m), 792 (s), 696 (s)

MS: (EI^+, 70 eV)

246.3 (15.0), 243.5 (14.5), 237.2 (26.8), 231.12 (100.0), 191.2 (86.0), 175.2 (17.7), 159.1 (17.2), 149.1 (42.0), 145.1 (14.8), 135.1(99.9), 129.1 (13.3), 121.0 (43.0), 115.1 (19.3), 111.1 (12.4), 107.1 (53.5), 105.1 (22.2), 95.1 (20.9), 91.1 (37.8), 81.1 (16.2), 77.1 (23.8), 69.1 (20.8), 67.1 (14.7), 65.1 (11.7), 57.1 (65.4), 55.1 (38.4)

HRMS: calcd for $C_{23}H_{22}OS^+$: 346.1391, found: 346.1383

TLC: R_f 0.32 (hexanes/Et_2O, 96:4) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ -55.0 (c = 0.48, EtOH)

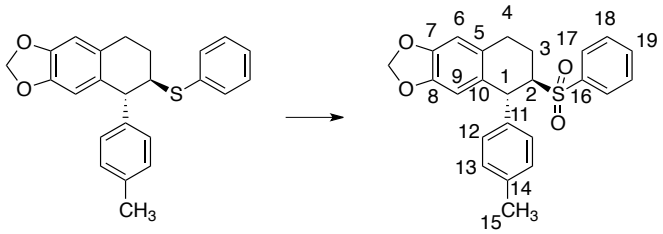
SFC: (1*R*,2*R*)-**9,** t_R 13.6 min (94%); (1*S*,2*S*)-**9,** t_R 16.1 min (6%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{23}H_{22}OS$ (346.14)

Calcd: C, 79.73; H, 6.40%

Found: C, 80.01; H, 6.03%

Preparation of ((5*R*,6*R*)-5-(4-Methylphenyl)-6-(phenylsulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-*d*]-1,3-dioxole (*trans*-12)



trans-**12**

To a solution of *trans*-**3b** (128.0 mg, 0.34 mmol) in CH_2Cl_2 (6 mL) was added *m*-CPBA (177 mg, 1.02 mmol) at room temperature After being stirred for 2 h, the contents of the flask were poured in H_2O (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were successively washed with satd aq. Na_2SO_3 (10 mL), brine (40 mL) then dried over $MgSO_4$ and filtered through glass wool and then concentrated in vacuo (20 – 23 °C, 10 mmHg). Purification by flash column chromatography (SiO_2, 40 g, 25 mm Ø, hexane/Et_2O, 1:1) afforded *trans*-**12** (135 mg, 98%) as white solid. Recrystallization from pentane/CH_2Cl_2 (60:10) (v/v) (14 mL) provided 130 mg (94%) of analytically pure *trans*-**12**.

Data for *trans*-**12**:

mp: 138-140 °C (pentane/CH_2Cl_2)

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

7.82 (d, J = 7.5 Hz, 2 H, HC(17)), 7.62 (t, *J* = 7.5 Hz, 1 H, HC(19)), 7.49 (t, *J* = 8.0, 2 H, HC(18)), 6.98 (d, *J* = 8.0 Hz, 2 H, HC(13)), 6.77 (d, *J* = 8.0 Hz, 2 H, HC(12)), 6.58 (s, 1 H, HC(6)), 6.31 (s, 1 H, HC(9)), 5.87 (d, *J* = 2.5 Hz, 2 H, OCH_2O), 4.54 (d, *J* = 4.5 Hz, 1 H, HC(1)), 3.57 – 3.54 (m, 1 H, HC(2)), 3.03 (ddd, *J* = 16.0, 8.0, 5.5, 1 H, HC(4)), 2.81 (ddd, J = 17.0, 6.0, 6.0 Hz, 1 H, HC(4)), 2.28 (s, 3 H, HC(14)), 2.29 – 2.23 (m, 1 H, HC(3)), 2.19 – 2.12 (m, 1 H, HC(3))

^{13}C NMR: (125 MHz, $CDCl_3$)

146.4 (C(7,8)), 141.6 (C(11)), 138.7 (C(16)), 136.5 (C(14)), 133.5 (C(19)), 129.4 (C(13)), 129.1 (C(10,18)), 128.9 (C(5)), 128.7 (C(17)), 128.5 (C(12)), 109.8 (C(9)), 108.0 (C(6)), 100.9 (OCH_2O), 67.1 (C(2)), 43.6 (C(1)), 26.7 (C(4)), 21.1 (C(15)), 20.5 (C(3))

IR: (KBr)

3445 (bm), 2968 (m), 2912 (m), 2878 (m), 1698 (s), 1573 (w), 1503 (m), 1483 (s), 1444 (m), 1302 (s), 1261 (s), 1240 (s), 1143 (s), 1084 (m), 1035 (m), 938 (w), 848 (w), 810 (w), 747 (s)

MS: (EI^+, 70 eV)

325.5 (21.7), 265.1 (21.1), 264.1 (1000), 231.1 (37.6), 191.1 (60.5), 158.0 (21.0), 156.0 (63.3), 141.0 (21.6), 139.0 (64.1), 135.1 (37.3), 115.0 (19.7), 11.0 (35.6), 107.0 (24.4), 105.1 (30.6)

HRMS: calcd $C_{24}H_{23}O_4S^+$: 407.1317, found: 407.1316

TLC: R_f 0.37 (hexanes/Et_2O, 50:50) [$KMnO_4$]

Opt Rot. : $[\alpha]_D^{25}$ –30.3 (c = 0.52, EtOH)

SFC: (1*R*,2*R*)-**12,** t_R 14.0 min (92%); (1*S*,2*S*)-**12,** t_R 17.7 min (8%) (Chiralpak OJ, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{24}H_{22}O_4S$ (406.12)

Calcd: C, 70.91; H, 5.46%

Found: C, 70.85; H, 5.38%

X-Ray Crystal Structure of *trans*-12

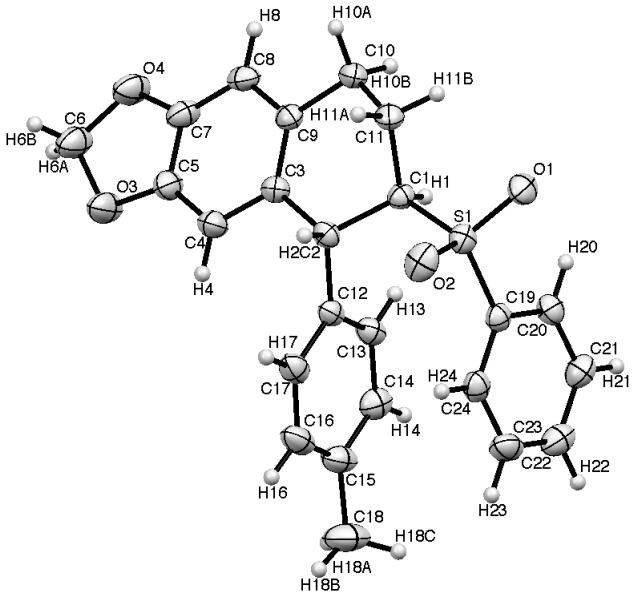


Figure 1: ORTEP image of X-ray crystal structure of *trans*-**12**.

Recrystallization of *trans*-**12** was carried out from refluxing hot CH_2Cl_2 (1 mL) followed by slow addition of pentane (4 mL). Slow evaporation of the mixture at room temperature resulted in the formation of cylindrical crystals.

The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 913987. These data can be obtained free of charge via from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; via www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.cam.ac.uk)

Table 1. Crystal data and structure refinement for bm53uas.

Identification code	bm53uas
Empirical formula	C24 H22 O4 S
Formula weight	406.48
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)	
Unit cell dimensions	a = 5.7172(12) Å	a= 90°.
	b = 10.941(2) Å	b= 92.598(3)°.
	c = 15.717(3) Å	g = 90°.
Volume	982.1(4) $Å^3$	
Z	2	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	428	
Crystal size	0.322 x 0.225 x 0.136 mm^3	
Theta range for data collection	2.27 to 26.44°.	
Index ranges	-7<=h<=7, -13<=k<=13, -19<=l<=19	
Reflections collected	11732	
Independent reflections	4038 [R(int) = 0.0389]	
Completeness to theta = 26.44°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.9829 and 0.9603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4038 / 1 / 263	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0798	
R indices (all data)	R1 = 0.0434, wR2 = 0.0847	
Absolute structure parameter	0.03(6)	
Largest diff. peak and hole	0.146 and -0.226 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)

for bm53uas. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5169(1)	6816(1)	684(1)	29(1)
O(1)	5921(3)	6957(1)	-172(1)	37(1)
O(2)	2796(3)	6434(1)	809(1)	40(1)
O(3)	9741(3)	2673(2)	4428(1)	50(1)
O(4)	12412(3)	1737(2)	3588(1)	48(1)
C(1)	7162(3)	5742(2)	1208(1)	25(1)
C(2)	6361(4)	5285(2)	2074(1)	26(1)
C(3)	8014(4)	4276(2)	2416(1)	26(1)
C(4)	7959(4)	3979(2)	3286(1)	36(1)
C(5)	9447(4)	3101(2)	3599(1)	36(1)
C(6)	11222(5)	1632(2)	4362(1)	50(1)
C(7)	11043(4)	2530(2)	3099(2)	35(1)
C(8)	11142(4)	2794(2)	2246(1)	34(1)
C(9)	9543(4)	3665(2)	1901(1)	28(1)
C(10)	9554(4)	3894(2)	948(1)	32(1)
C(11)	7474(4)	4647(2)	619(1)	32(1)
C(12)	6144(3)	6295(2)	2734(1)	26(1)
C(13)	7941(4)	7127(2)	2904(1)	30(1)
C(14)	7711(4)	8057(2)	3499(1)	35(1)
C(15)	5685(4)	8156(2)	3958(1)	40(1)
C(16)	3939(4)	7298(2)	3806(1)	40(1)
C(17)	4139(4)	6386(2)	3199(1)	34(1)
C(18)	5421(5)	9190(3)	4580(2)	58(1)
C(19)	5613(3)	8241(2)	1197(1)	26(1)

C(20)	7610(4)	8910(2)	1049(1)	31(1)
C(21)	7920(4)	10041(2)	1430(1)	36(1)
C(22)	6266(4)	10493(2)	1958(2)	40(1)
C(23)	4268(4)	9829(2)	2100(1)	39(1)
C(24)	3919(4)	8696(2)	1717(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for bm53uas.

S(1)-O(1)	1.4391(14)
S(1)-O(2)	1.4417(15)
S(1)-C(19)	1.768(2)
S(1)-C(1)	1.809(2)
O(3)-C(5)	1.388(3)
O(3)-C(6)	1.425(3)
O(4)-C(7)	1.379(3)
O(4)-C(6)	1.425(3)
C(1)-C(11)	1.530(3)
C(1)-C(2)	1.539(3)
C(1)-H(1)	1.0000
C(2)-C(12)	1.524(3)
C(2)-C(3)	1.535(3)
C(2)-H(2)	1.0000
C(3)-C(9)	1.389(3)
C(3)-C(4)	1.408(3)
C(4)-C(5)	1.360(3)
C(4)-H(4)	0.9500
C(5)-C(7)	1.380(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.375(3)
C(8)-C(9)	1.412(3)

C(8)-H(8)	0.9500
C(9)-C(10)	1.518(3)
C(10)-C(11)	1.518(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.389(3)
C(12)-C(17)	1.391(3)
C(13)-C(14)	1.392(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.396(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.383(3)
C(15)-C(18)	1.508(3)
C(16)-C(17)	1.389(3)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.385(3)
C(19)-C(24)	1.388(3)
C(20)-C(21)	1.382(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.379(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.380(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.388(3)
C(23)-H(23)	0.9500

C(24)-H(24)	0.9500

O(1)-S(1)-O(2)	118.80(9)
O(1)-S(1)-C(19)	106.81(9)
O(2)-S(1)-C(19)	108.03(10)
O(1)-S(1)-C(1)	106.69(9)
O(2)-S(1)-C(1)	109.08(9)
C(19)-S(1)-C(1)	106.85(9)
C(5)-O(3)-C(6)	104.35(17)
C(7)-O(4)-C(6)	104.18(16)
C(11)-C(1)-C(2)	109.18(16)
C(11)-C(1)-S(1)	108.71(14)
C(2)-C(1)-S(1)	114.06(13)
C(11)-C(1)-H(1)	108.2
C(2)-C(1)-H(1)	108.2
S(1)-C(1)-H(1)	108.2
C(12)-C(2)-C(3)	110.60(16)
C(12)-C(2)-C(1)	113.74(16)
C(3)-C(2)-C(1)	109.88(16)
C(12)-C(2)-H(2)	107.5
C(3)-C(2)-H(2)	107.5
C(1)-C(2)-H(2)	107.5
C(9)-C(3)-C(4)	119.82(19)
C(9)-C(3)-C(2)	122.44(18)
C(4)-C(3)-C(2)	117.74(18)
C(5)-C(4)-C(3)	118.2(2)
C(5)-C(4)-H(4)	120.9
C(3)-C(4)-H(4)	120.9
C(4)-C(5)-C(7)	122.2(2)
C(4)-C(5)-O(3)	128.6(2)
C(7)-C(5)-O(3)	109.1(2)

O(4)-C(6)-O(3)	107.85(18)
O(4)-C(6)-H(6A)	110.1
O(3)-C(6)-H(6A)	110.1
O(4)-C(6)-H(6B)	110.1
O(3)-C(6)-H(6B)	110.1
H(6A)-C(6)-H(6B)	108.5
C(8)-C(7)-O(4)	128.90(19)
C(8)-C(7)-C(5)	121.1(2)
O(4)-C(7)-C(5)	109.94(19)
C(7)-C(8)-C(9)	117.51(19)
C(7)-C(8)-H(8)	121.2
C(9)-C(8)-H(8)	121.2
C(3)-C(9)-C(8)	120.97(18)
C(3)-C(9)-C(10)	121.72(18)
C(8)-C(9)-C(10)	117.31(18)
C(9)-C(10)-C(11)	112.80(17)
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10B)	109.0
C(11)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
C(10)-C(11)-C(1)	109.27(17)
C(10)-C(11)-H(11A)	109.8
C(1)-C(11)-H(11A)	109.8
C(10)-C(11)-H(11B)	109.8
C(1)-C(11)-H(11B)	109.8
H(11A)-C(11)-H(11B)	108.3
C(13)-C(12)-C(17)	118.17(19)
C(13)-C(12)-C(2)	121.58(17)
C(17)-C(12)-C(2)	120.23(19)
C(12)-C(13)-C(14)	121.1(2)

C(12)-C(13)-H(13)	119.4
C(14)-C(13)-H(13)	119.4
C(13)-C(14)-C(15)	120.6(2)
C(13)-C(14)-H(14)	119.7
C(15)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	117.9(2)
C(16)-C(15)-C(18)	121.9(2)
C(14)-C(15)-C(18)	120.2(2)
C(15)-C(16)-C(17)	121.7(2)
C(15)-C(16)-H(16)	119.2
C(17)-C(16)-H(16)	119.2
C(16)-C(17)-C(12)	120.5(2)
C(16)-C(17)-H(17)	119.8
C(12)-C(17)-H(17)	119.8
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(24)	120.8(2)
C(20)-C(19)-S(1)	119.45(16)
C(24)-C(19)-S(1)	119.71(16)
C(21)-C(20)-C(19)	119.4(2)
C(21)-C(20)-H(20)	120.3
C(19)-C(20)-H(20)	120.3
C(22)-C(21)-C(20)	120.3(2)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(21)-C(22)-C(23)	120.2(2)
C(21)-C(22)-H(22)	119.9

C(23)-C(22)-H(22)	119.9
C(22)-C(23)-C(24)	120.3(2)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
C(19)-C(24)-C(23)	119.0(2)
C(19)-C(24)-H(24)	120.5
C(23)-C(24)-H(24)	120.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for bm53uas. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	30(1)	28(1)	28(1)	1(1)	-3(1)	-2(1)
O(1)	53(1)	34(1)	24(1)	0(1)	-3(1)	2(1)
O(2)	28(1)	38(1)	54(1)	3(1)	-7(1)	-6(1)
O(3)	73(1)	48(1)	31(1)	5(1)	2(1)	30(1)
O(4)	62(1)	43(1)	39(1)	0(1)	-4(1)	25(1)
C(1)	25(1)	24(1)	25(1)	-1(1)	-1(1)	1(1)
C(2)	24(1)	29(1)	25(1)	0(1)	2(1)	-1(1)
C(3)	26(1)	27(1)	26(1)	-2(1)	2(1)	1(1)
C(4)	42(1)	36(1)	29(1)	-1(1)	7(1)	9(1)
C(5)	48(1)	33(1)	26(1)	1(1)	0(1)	7(1)
C(6)	75(2)	40(1)	35(1)	1(1)	-5(1)	22(1)
C(7)	39(1)	29(1)	37(1)	-4(1)	-5(1)	9(1)
C(8)	38(1)	27(1)	36(1)	-9(1)	5(1)	3(1)
C(9)	31(1)	24(1)	28(1)	-4(1)	3(1)	-3(1)
C(10)	41(1)	27(1)	28(1)	-3(1)	9(1)	1(1)
C(11)	42(1)	27(1)	27(1)	-4(1)	3(1)	-2(1)

C(12)	26(1)	30(1)	21(1)	3(1)	0(1)	8(1)
C(13)	28(1)	35(1)	25(1)	-1(1)	1(1)	6(1)
C(14)	36(1)	35(1)	33(1)	-1(1)	-7(1)	6(1)
C(15)	48(2)	45(1)	26(1)	-4(1)	-1(1)	19(1)
C(16)	38(1)	51(1)	30(1)	2(1)	8(1)	16(1)
C(17)	30(1)	41(1)	30(1)	6(1)	5(1)	9(1)
C(18)	68(2)	57(2)	48(2)	-20(1)	1(1)	22(2)
C(19)	28(1)	26(1)	25(1)	4(1)	-2(1)	3(1)
C(20)	30(1)	34(1)	27(1)	1(1)	1(1)	-1(1)
C(21)	38(1)	29(1)	42(1)	0(1)	-3(1)	-2(1)
C(22)	48(1)	31(1)	39(1)	-4(1)	-10(1)	6(1)
C(23)	43(1)	38(1)	36(1)	0(1)	4(1)	16(1)
C(24)	30(1)	32(1)	33(1)	7(1)	2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for bm53uas.

	x	y	z	U(eq)
H(1)	8715	6152	1302	29
H(2)	4775	4912	1976	31
H(4)	6911	4381	3646	43
H(6A)	12366	1601	4853	60
H(6B)	10277	874	4358	60
H(8)	12245	2405	1902	40
H(10A)	9542	3099	647	38
H(10B)	11016	4324	817	38
H(11A)	6041	4138	600	38
H(11B)	7739	4936	34	38

H(13)	9350	7060	2609	35
H(14)	8945	8629	3594	42
H(16)	2568	7335	4124	48
H(17)	2897	5819	3101	41
H(18A)	6655	9134	5032	87
H(18B)	3886	9136	4831	87
H(18C)	5551	9972	4282	87
H(20)	8756	8595	688	37
H(21)	9279	10508	1327	44
H(22)	6503	11264	2227	47
H(23)	3127	10149	2460	47
H(24)	2540	8239	1810	38

Table 6. Torsion angles [°] for bm53uas.

O(1)-S(1)-C(1)-C(11)	-46.70(16)
O(2)-S(1)-C(1)-C(11)	82.78(16)
C(19)-S(1)-C(1)-C(11)	-160.67(14)
O(1)-S(1)-C(1)-C(2)	-168.79(14)
O(2)-S(1)-C(1)-C(2)	-39.31(17)
C(19)-S(1)-C(1)-C(2)	77.24(16)
C(11)-C(1)-C(2)-C(12)	176.28(17)
S(1)-C(1)-C(2)-C(12)	-61.9(2)
C(11)-C(1)-C(2)-C(3)	51.7(2)
S(1)-C(1)-C(2)-C(3)	173.52(13)
C(12)-C(2)-C(3)-C(9)	-142.79(19)
C(1)-C(2)-C(3)-C(9)	-16.4(3)
C(12)-C(2)-C(3)-C(4)	36.8(3)
C(1)-C(2)-C(3)-C(4)	163.18(18)
C(9)-C(3)-C(4)-C(5)	0.8(3)

C(2)-C(3)-C(4)-C(5)	-178.8(2)
C(3)-C(4)-C(5)-C(7)	2.2(3)
C(3)-C(4)-C(5)-O(3)	178.7(2)
C(6)-O(3)-C(5)-C(4)	170.8(2)
C(6)-O(3)-C(5)-C(7)	-12.4(3)
C(7)-O(4)-C(6)-O(3)	-21.1(2)
C(5)-O(3)-C(6)-O(4)	20.8(3)
C(6)-O(4)-C(7)-C(8)	-167.8(2)
C(6)-O(4)-C(7)-C(5)	13.4(2)
C(4)-C(5)-C(7)-C(8)	-2.5(4)
O(3)-C(5)-C(7)-C(8)	-179.6(2)
C(4)-C(5)-C(7)-O(4)	176.4(2)
O(3)-C(5)-C(7)-O(4)	-0.7(3)
O(4)-C(7)-C(8)-C(9)	-179.0(2)
C(5)-C(7)-C(8)-C(9)	-0.3(3)
C(4)-C(3)-C(9)-C(8)	-3.5(3)
C(2)-C(3)-C(9)-C(8)	176.05(18)
C(4)-C(3)-C(9)-C(10)	175.9(2)
C(2)-C(3)-C(9)-C(10)	-4.5(3)
C(7)-C(8)-C(9)-C(3)	3.3(3)
C(7)-C(8)-C(9)-C(10)	-176.18(19)
C(3)-C(9)-C(10)-C(11)	-10.8(3)
C(8)-C(9)-C(10)-C(11)	168.65(19)
C(9)-C(10)-C(11)-C(1)	46.3(2)
C(2)-C(1)-C(11)-C(10)	-68.5(2)
S(1)-C(1)-C(11)-C(10)	166.49(14)
C(3)-C(2)-C(12)-C(13)	74.1(2)
C(1)-C(2)-C(12)-C(13)	-50.1(2)
C(3)-C(2)-C(12)-C(17)	-104.3(2)
C(1)-C(2)-C(12)-C(17)	131.52(19)
C(17)-C(12)-C(13)-C(14)	-2.5(3)

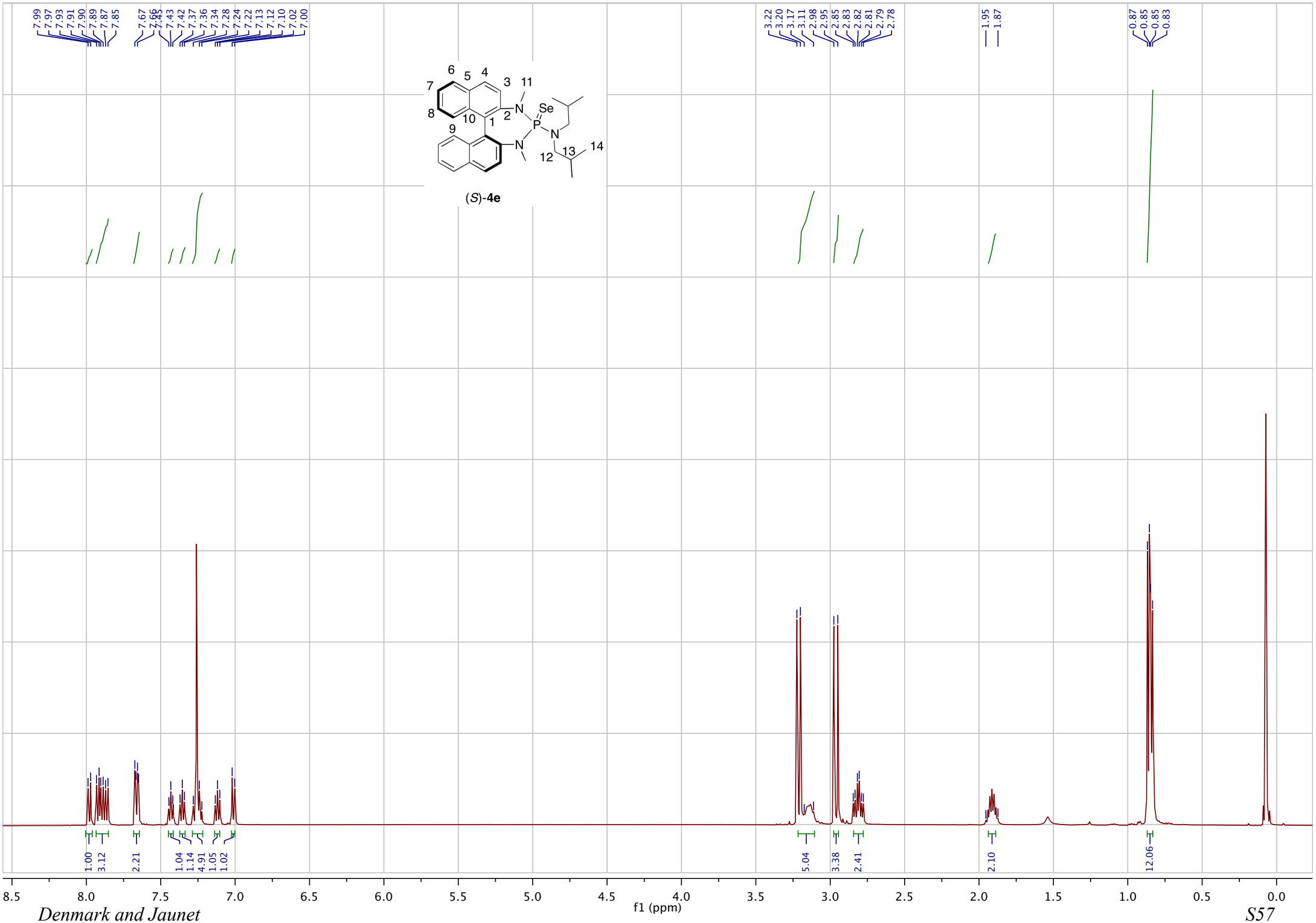
C(2)-C(12)-C(13)-C(14)	179.09(18)
C(12)-C(13)-C(14)-C(15)	1.7(3)
C(13)-C(14)-C(15)-C(16)	0.5(3)
C(13)-C(14)-C(15)-C(18)	-178.0(2)
C(14)-C(15)-C(16)-C(17)	-2.0(3)
C(18)-C(15)-C(16)-C(17)	176.5(2)
C(15)-C(16)-C(17)-C(12)	1.2(3)
C(13)-C(12)-C(17)-C(16)	1.0(3)
C(2)-C(12)-C(17)-C(16)	179.49(19)
O(1)-S(1)-C(19)-C(20)	-39.85(18)
O(2)-S(1)-C(19)-C(20)	-168.72(16)
C(1)-S(1)-C(19)-C(20)	74.04(17)
O(1)-S(1)-C(19)-C(24)	137.66(16)
O(2)-S(1)-C(19)-C(24)	8.79(19)
C(1)-S(1)-C(19)-C(24)	-108.45(17)
C(24)-C(19)-C(20)-C(21)	0.5(3)
S(1)-C(19)-C(20)-C(21)	178.01(16)
C(19)-C(20)-C(21)-C(22)	0.5(3)
C(20)-C(21)-C(22)-C(23)	-1.1(3)
C(21)-C(22)-C(23)-C(24)	0.7(3)
C(20)-C(19)-C(24)-C(23)	-1.0(3)
S(1)-C(19)-C(24)-C(23)	-178.47(16)
C(22)-C(23)-C(24)-C(19)	0.4(3)

References

(1) Miyano, S.; Nawa, M.; Mori A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171-2176.

(2) The CSP-SFC analysis was performed on the diamine (*S*)-**10** because the racemic catalyst **4e** was not available. The enantiomeric purity of the catalyst is assumed to be no lower than that of the diamine.

(3) Orcutt, R. M.; Bogert, M. T. *J. Am. Chem. Soc.* **1936**, *58*, 2055-2056.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7.37
7.36
7.34
7.28
7.24
7.22
7.13
7.12
7.10
7.02
7.00
3.22
3.20
3.17
3.11
2.98
2.95
2.85
2.83
2.82
2.81
2.79
2.78
1.95
1.87
0.87
0.85
0.85
0.83
(S)-4e
1.00
3.12
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1.02
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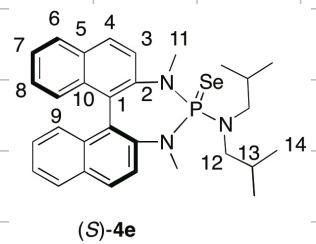

(*S*)-**4e**

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131.45
131.34
129.47
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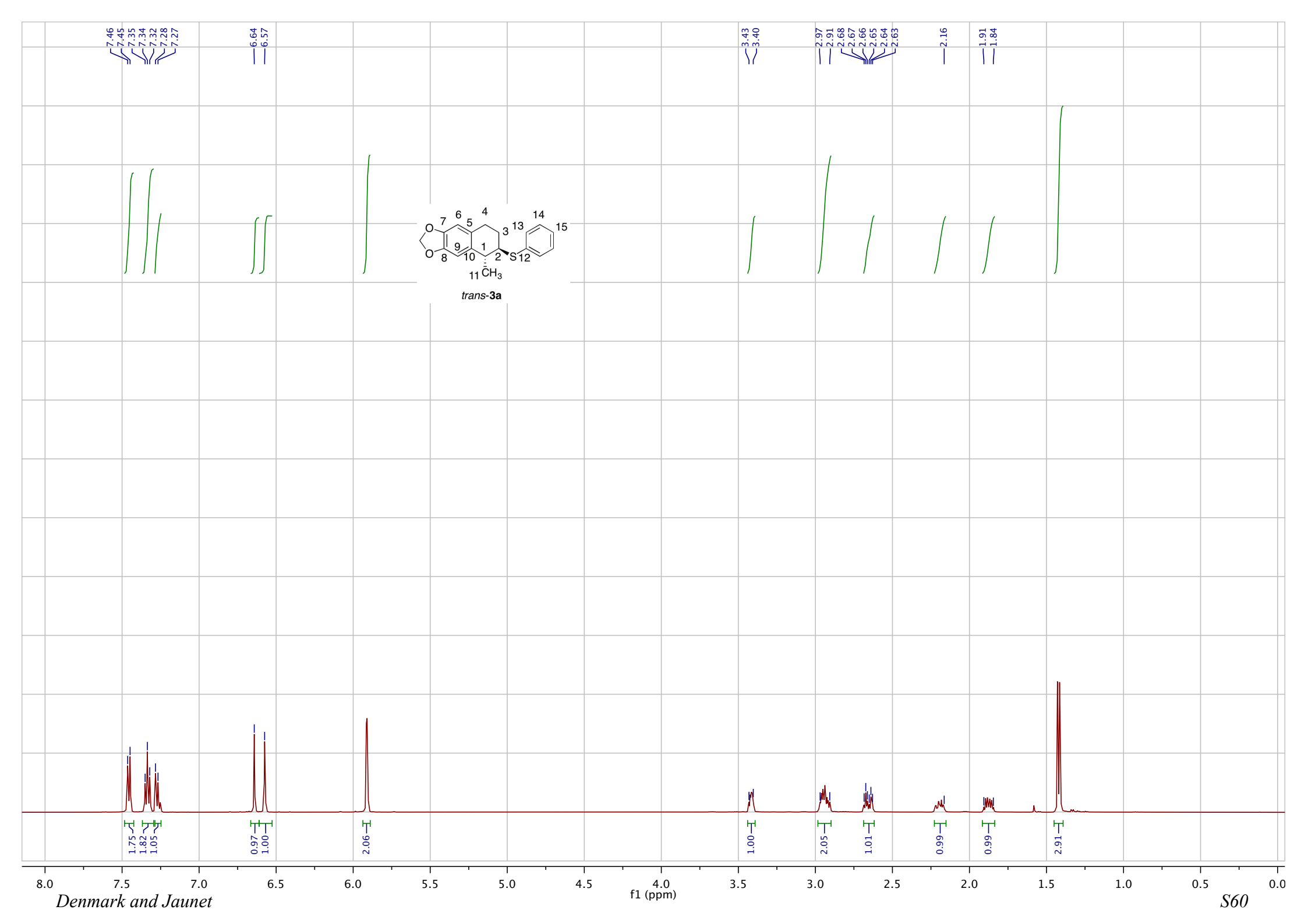
128.70
128.32
128.19
127.99
127.32
126.27
125.91
125.46
124.94
124.56
122.57
55.01
39.34
39.25
36.15
36.11
27.36
27.34
21.01
20.88

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)


95.39
6
5
4
3
11
7
8
10
1
2
9
N
Se
P
N
N
12
13
14
(S)-4e
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
f1 (ppm)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7.45
7.35
7.34
7.32
7.28
7.27
6.64
6.57
3.43
3.40
2.97
2.91
2.68
2.67
2.66
2.65
2.64
2.63
2.16
1.91
1.84
O
O
S
CH3
trans-3a
1.75
1.82
1.05
0.97
1.00
2.06
1.00
2.05
1.01
0.99
0.99
2.91
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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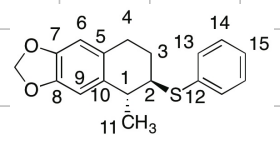
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

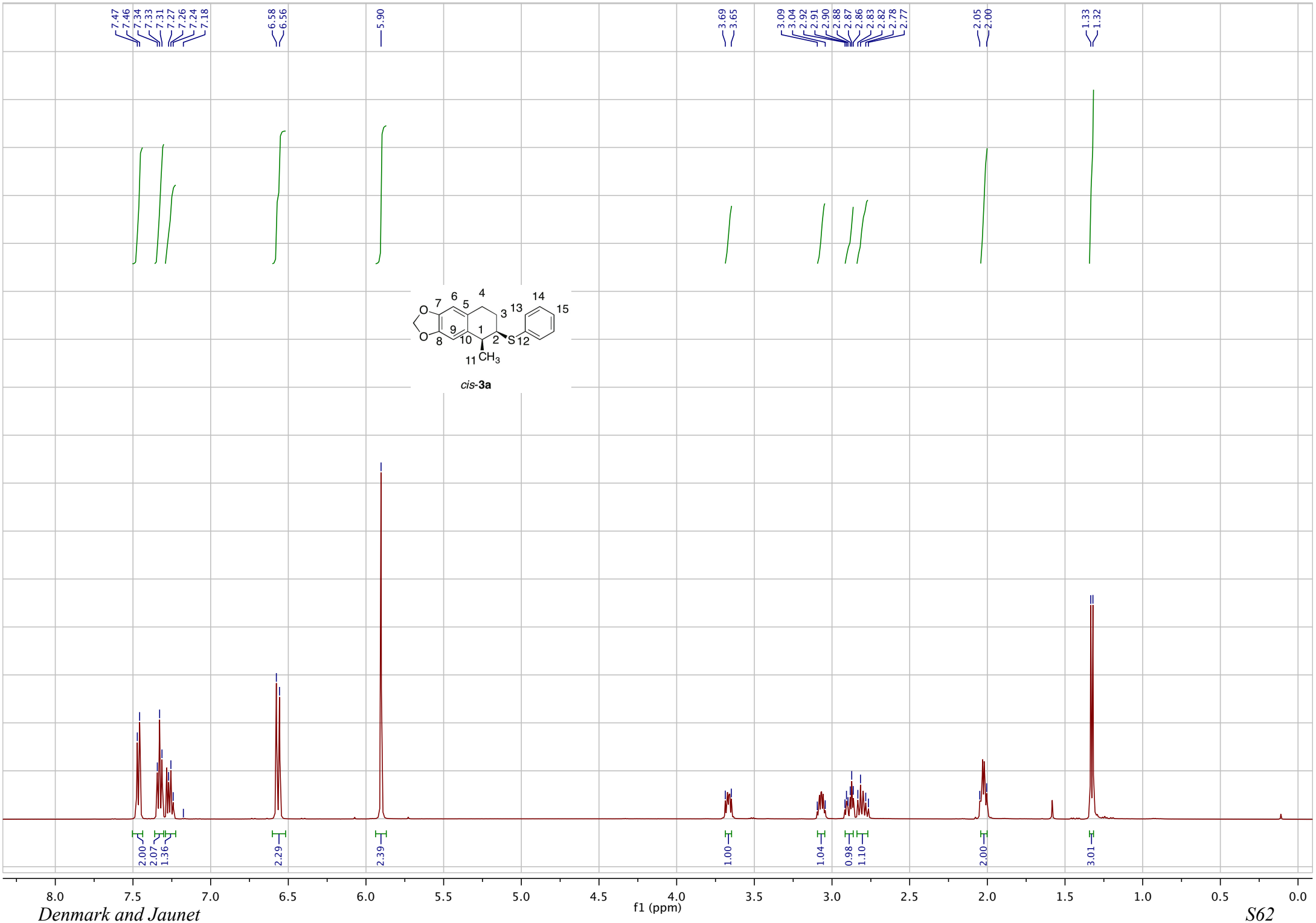


trans-**3a**

146.03
145.90
135.37
132.58
131.86
129.02
128.24
126.87
108.79
108.55
100.74
49.90
38.32
26.60
24.83
24.07

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)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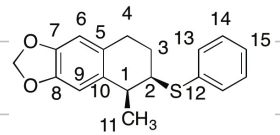
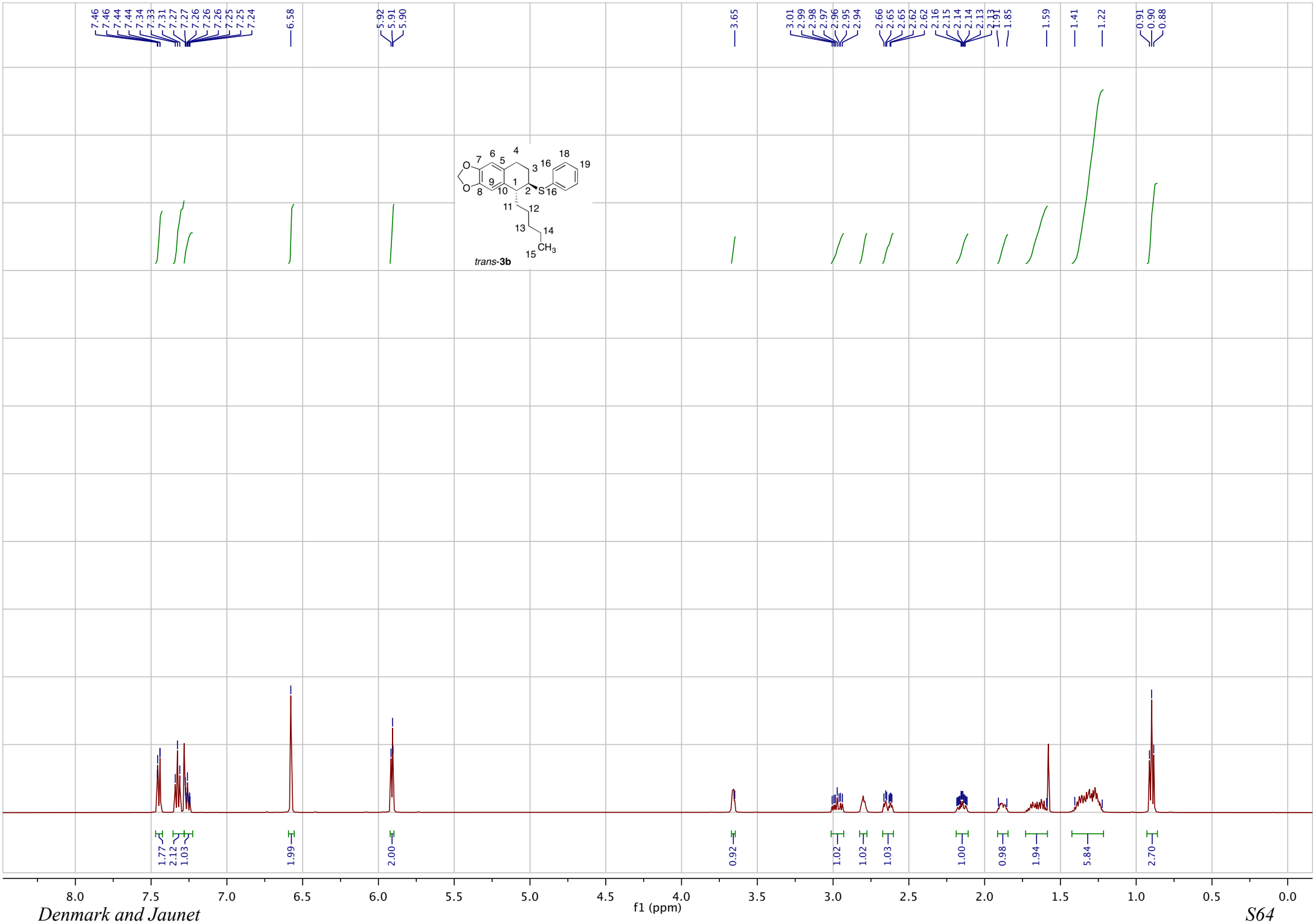
7.31
7.27
7.26
7.24
7.18
6.58
6.56
5.90
3.69
3.65
3.09
3.04
2.92
2.91
2.90
2.88
2.87
2.86
2.83
2.82
2.78
2.77
2.05
2.00
1.33
1.32
cis-3a
2.00
2.07
1.36
2.29
2.39
1.00
1.04
0.98
1.10
2.00
3.01
f1 (ppm)


4
6
5
7
3
13
14
15
O
9
1
O
8
10
2
S
12
11
CH3

cis-**3a**

146.10
145.86
135.47
134.65
131.49
129.08
127.78
126.77
108.52
108.47
100.78
48.94
36.94
29.30
24.59
18.75
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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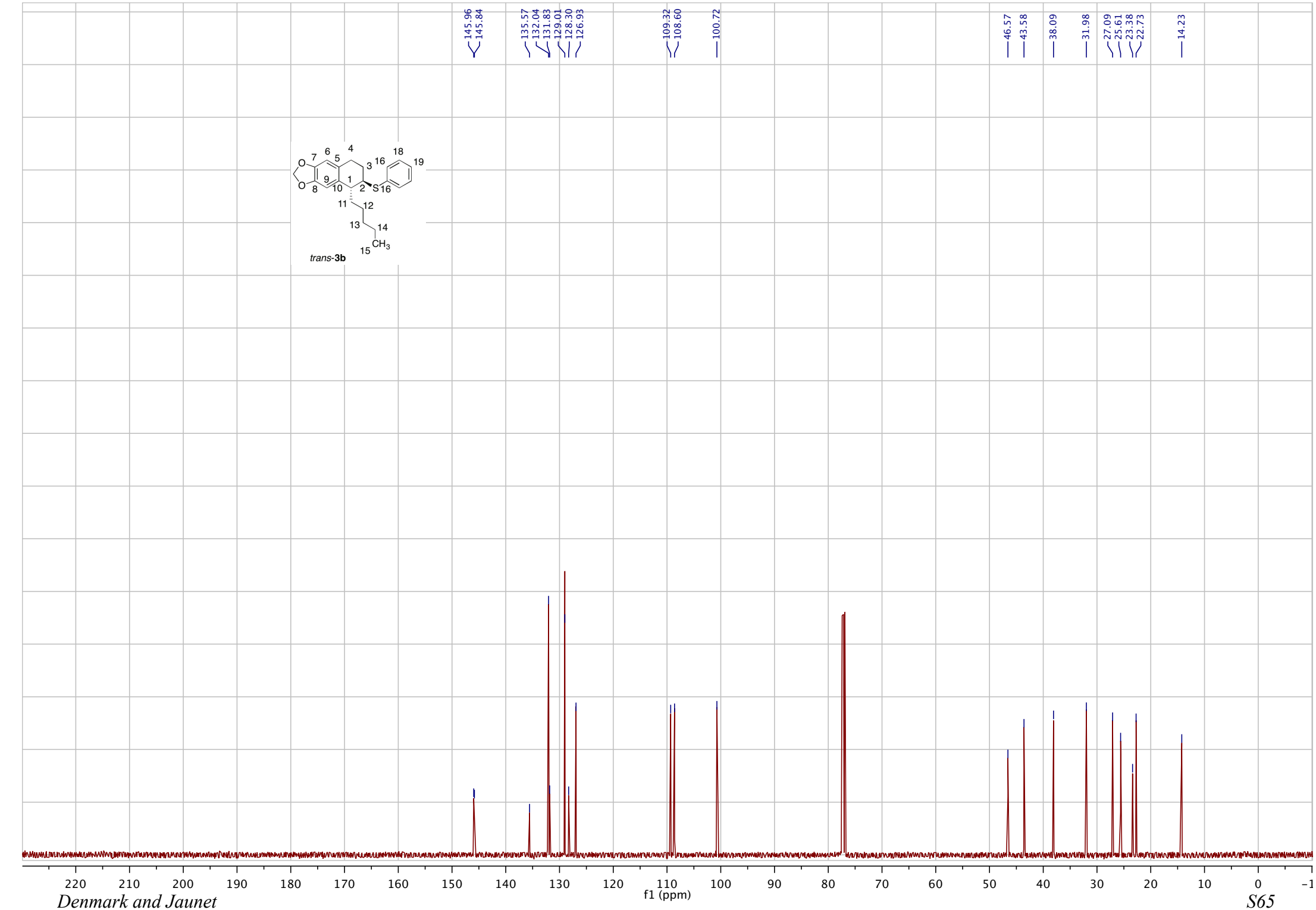
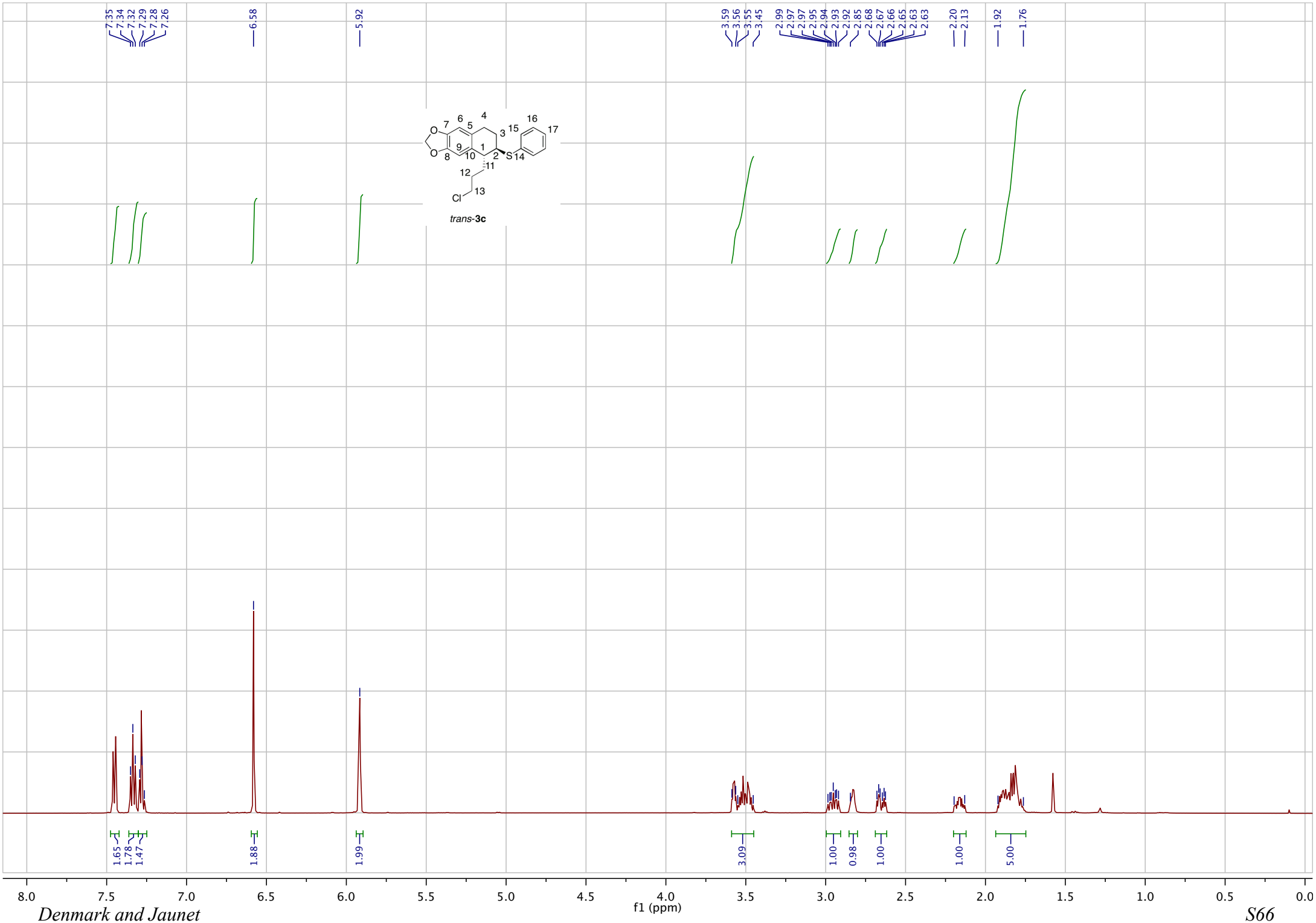
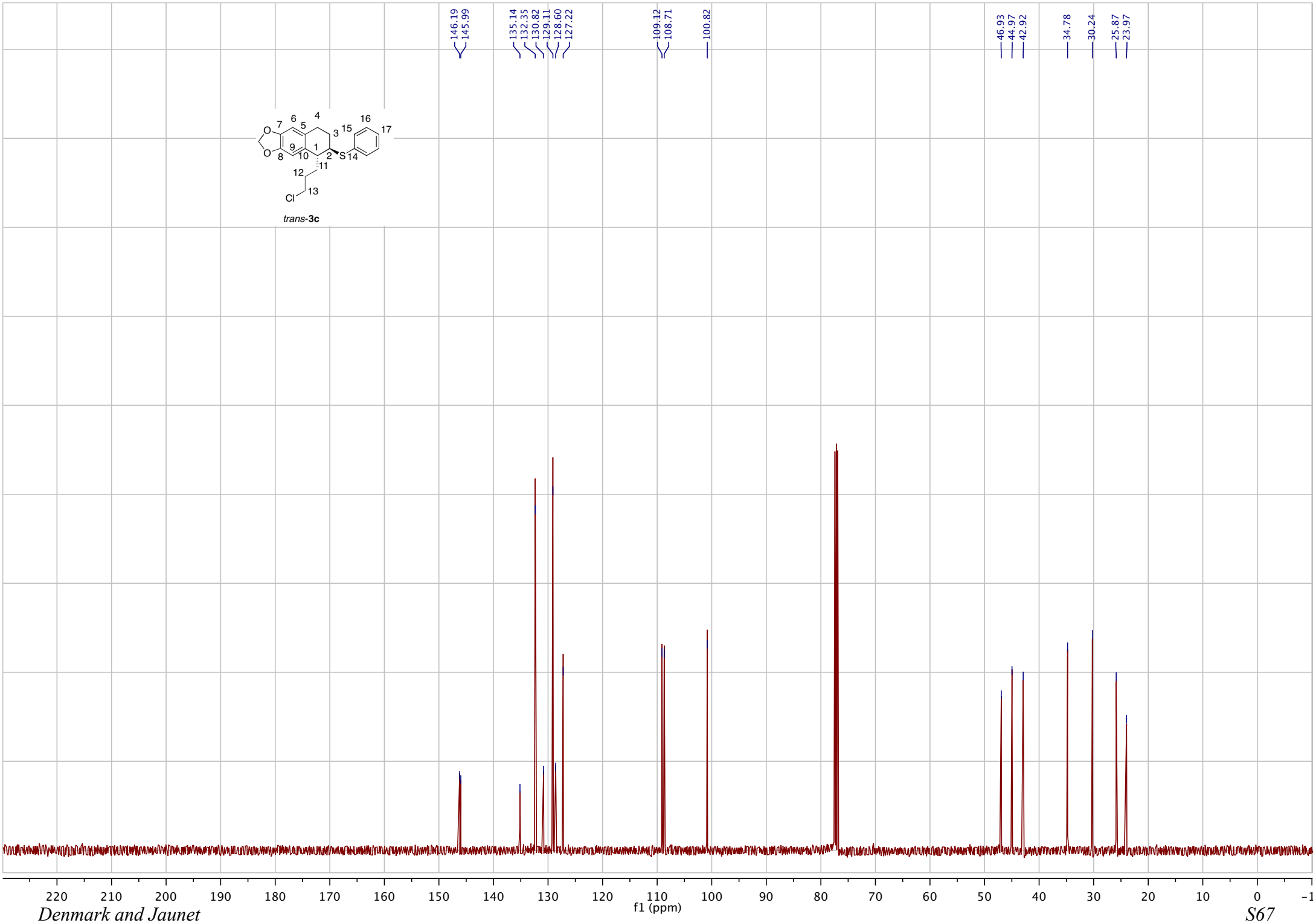
7.44
7.44
7.34
7.33
7.31
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
6.58
5.92
5.91
5.90
3.65
3.01
2.99
2.98
2.97
2.96
2.95
2.94
2.66
2.65
2.65
2.62
2.62
2.16
2.15
2.14
2.14
2.13
1.91
1.85
1.59
1.41
1.22
0.91
0.90
0.88
trans-3b
1.77
2.12
1.03
1.99
2.00
0.92
1.02
1.02
1.03
1.00
0.98
1.94
5.84
2.70
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.96
145.84
135.57
132.04
131.83
129.01
128.30
126.93
109.32
108.60
100.72
46.57
43.58
38.09
31.98
27.09
25.61
23.38
22.73
14.23
trans-3b
f1 (ppm)


7.35
7.34
7.32
7.29
7.28
7.26
6.58
5.92
3.59
3.56
3.55
3.45
2.99
2.97
2.97
2.95
2.94
2.93
2.92
2.85
2.68
2.67
2.66
2.65
2.63
2.63
2.20
2.13
1.92
1.76
trans-3c
1.65
1.78
1.47
1.88
1.99
3.09
1.00
0.98
1.00
1.00
5.00
f1 (ppm)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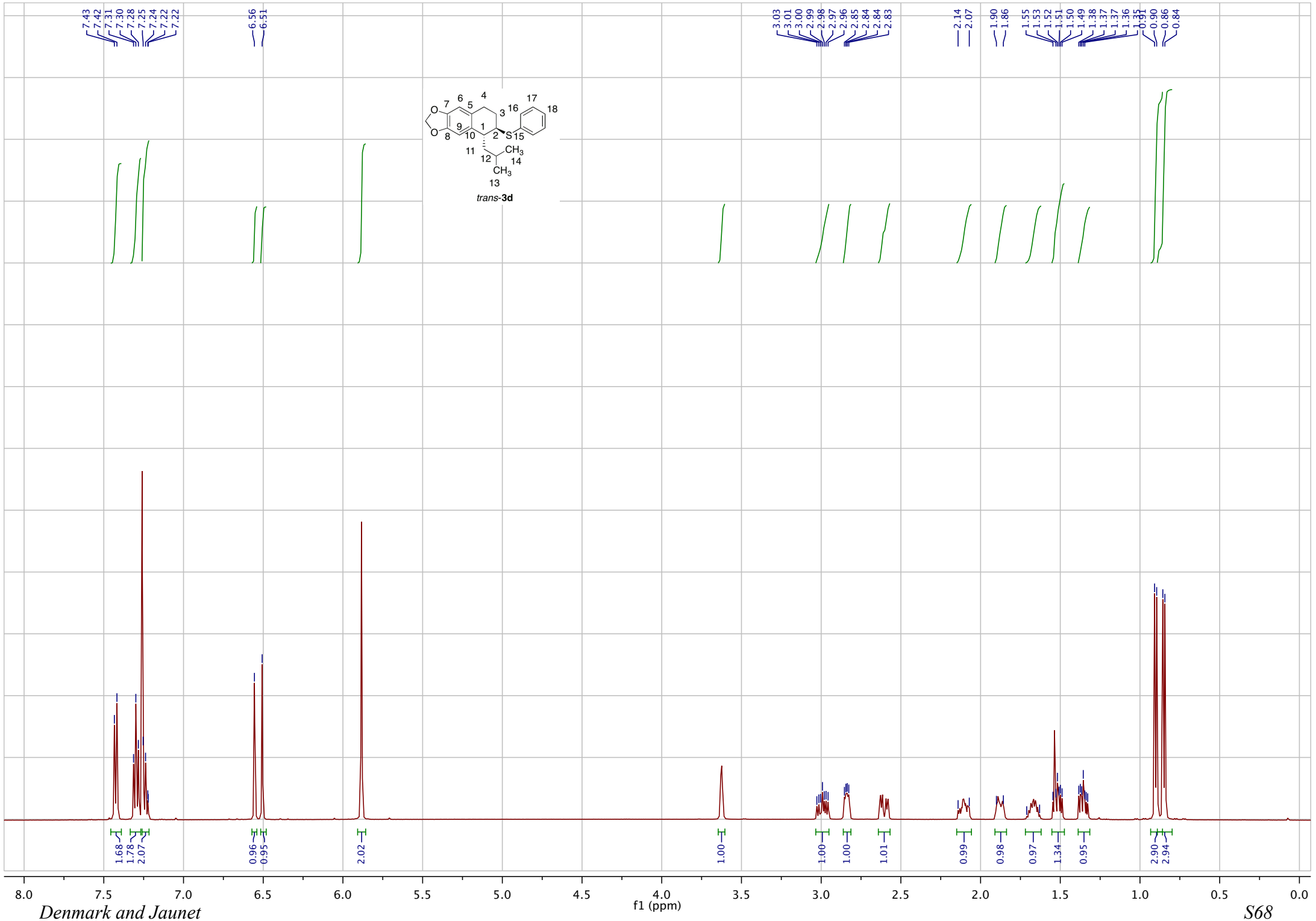
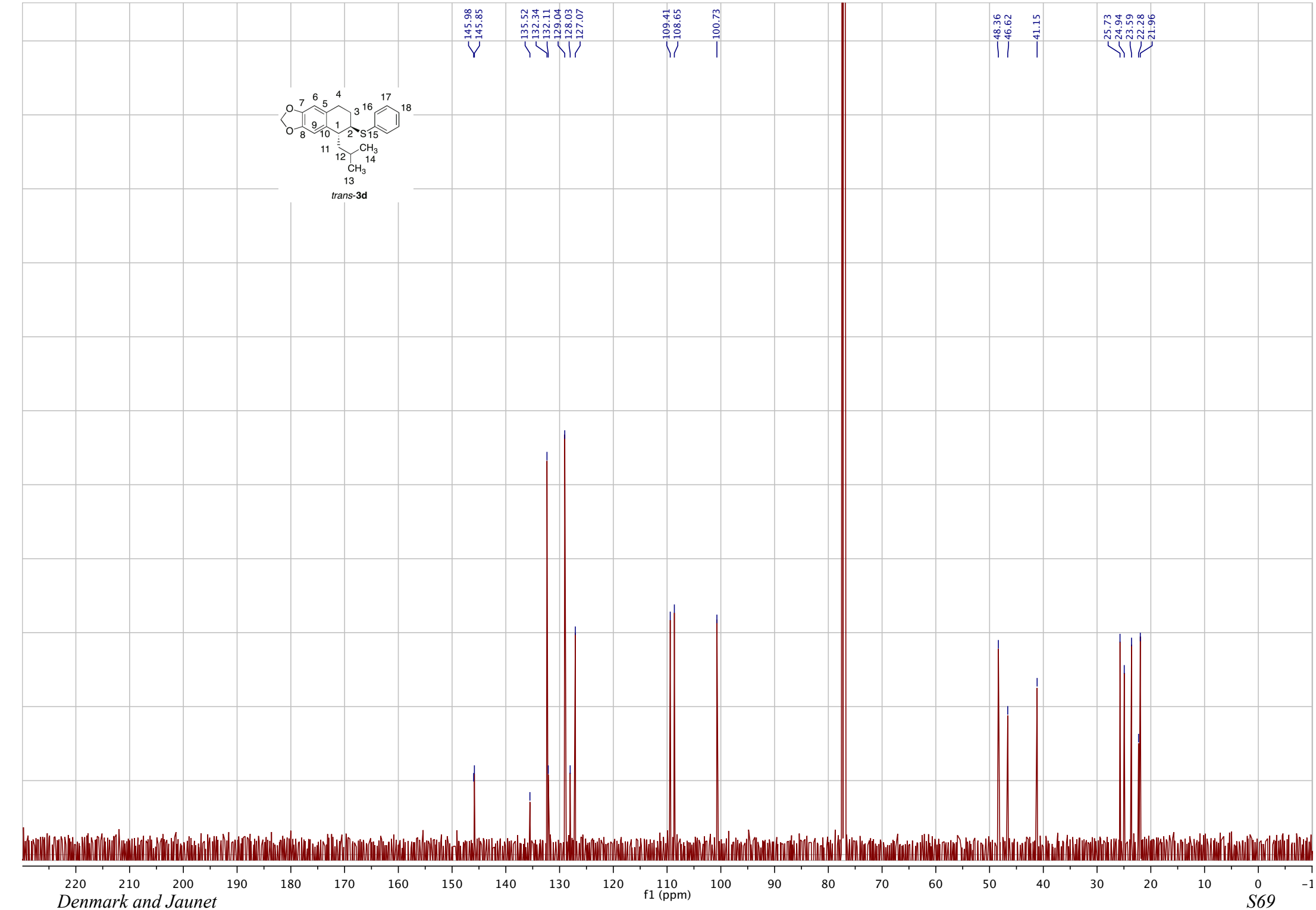
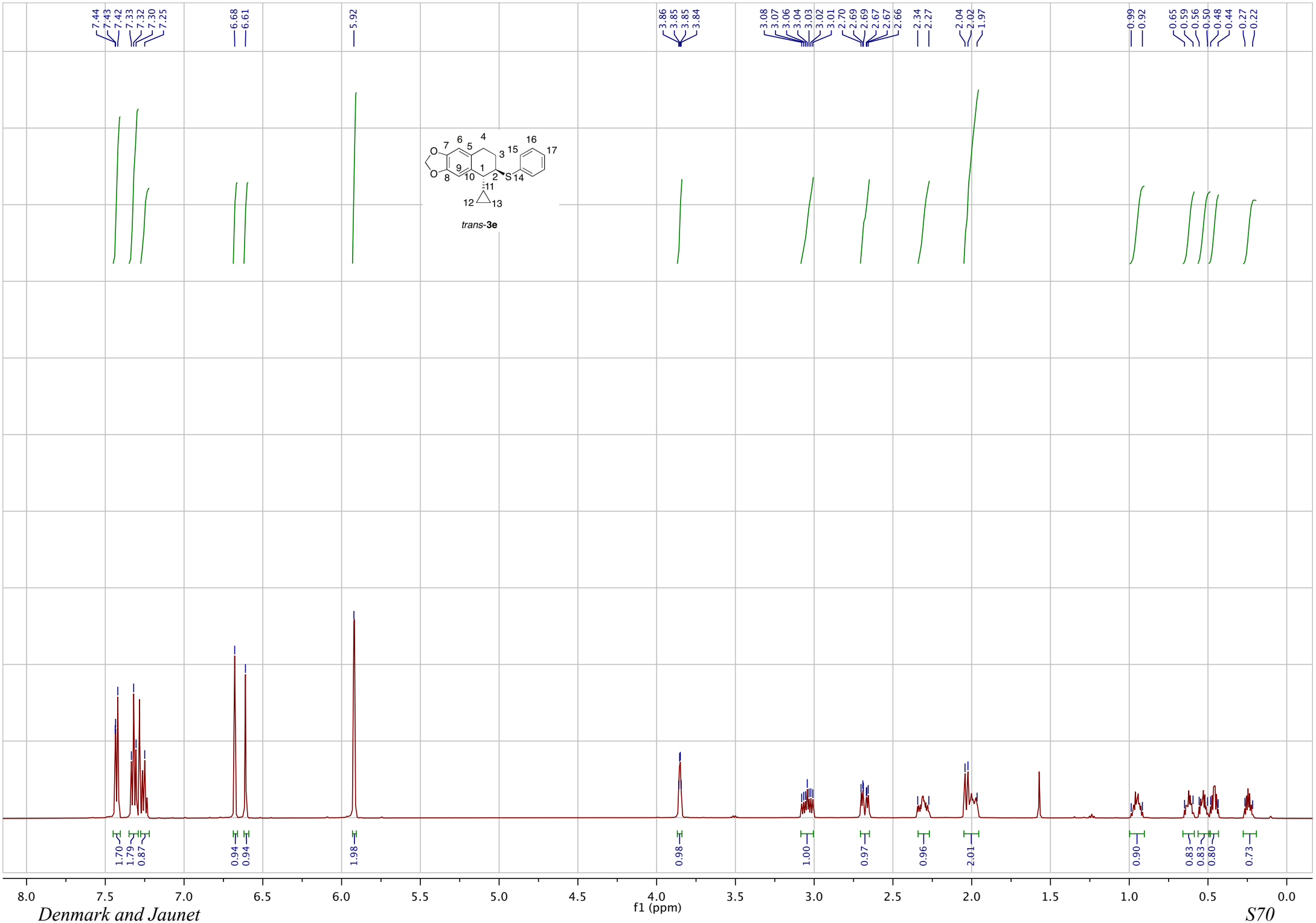
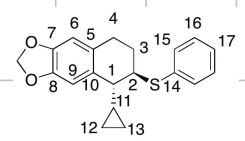
145.99
135.14
132.35
130.82
129.11
128.60
127.22
109.12
108.71
100.82
46.93
44.97
42.92
34.78
30.24
25.87
23.97
trans-3c
f1 (ppm)


7.43
7.42
7.31
7.30
7.28
7.25
7.24
7.22
7.22
6.56
6.51
3.03
3.01
3.00
2.99
2.98
2.97
2.96
2.85
2.84
2.84
2.83
2.14
2.07
1.90
1.86
1.55
1.53
1.52
1.51
1.50
1.49
1.38
1.37
1.37
1.36
1.35
0.91
0.90
0.86
0.84
trans-3d
1.68
1.78
2.07
0.96
0.95
2.02
1.00
1.00
1.00
1.01
0.99
0.98
0.97
1.34
0.95
2.90
2.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

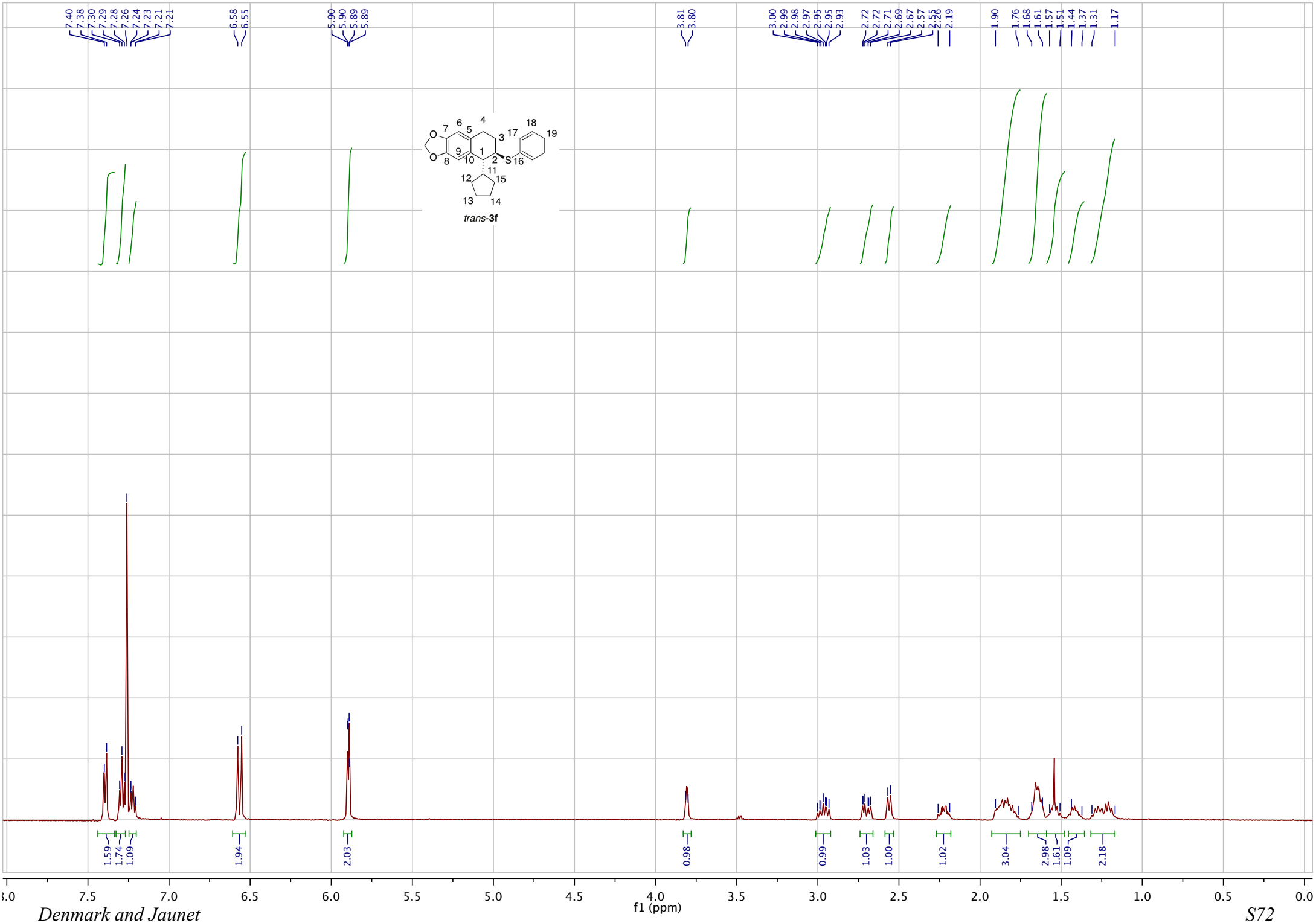

145.98
145.85
135.52
132.34
132.11
129.04
128.03
127.07
109.41
108.65
100.73
48.36
46.62
41.15
25.73
24.94
23.59
22.28
21.96
trans-3d
f1 (ppm)


7.44
7.43
7.42
7.33
7.32
7.30
7.25
6.68
6.61
5.92
3.86
3.85
3.85
3.84
3.08
3.07
3.06
3.04
3.03
3.02
3.01
2.70
2.69
2.69
2.67
2.67
2.66
2.34
2.27
2.04
2.02
1.97
0.99
0.92
0.65
0.59
0.56
0.50
0.48
0.44
0.27
0.22
trans-3e
1.70
1.79
0.87
0.94
0.94
1.98
0.98
1.00
0.97
0.96
2.01
0.90
0.83
0.83
0.80
0.73
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



trans-**3e**

146.36
145.74
135.59
131.71
130.45
129.02
128.14
126.84
109.41
108.66
100.75
48.32
25.20
23.19
19.94
6.23
4.04
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.40
7.38
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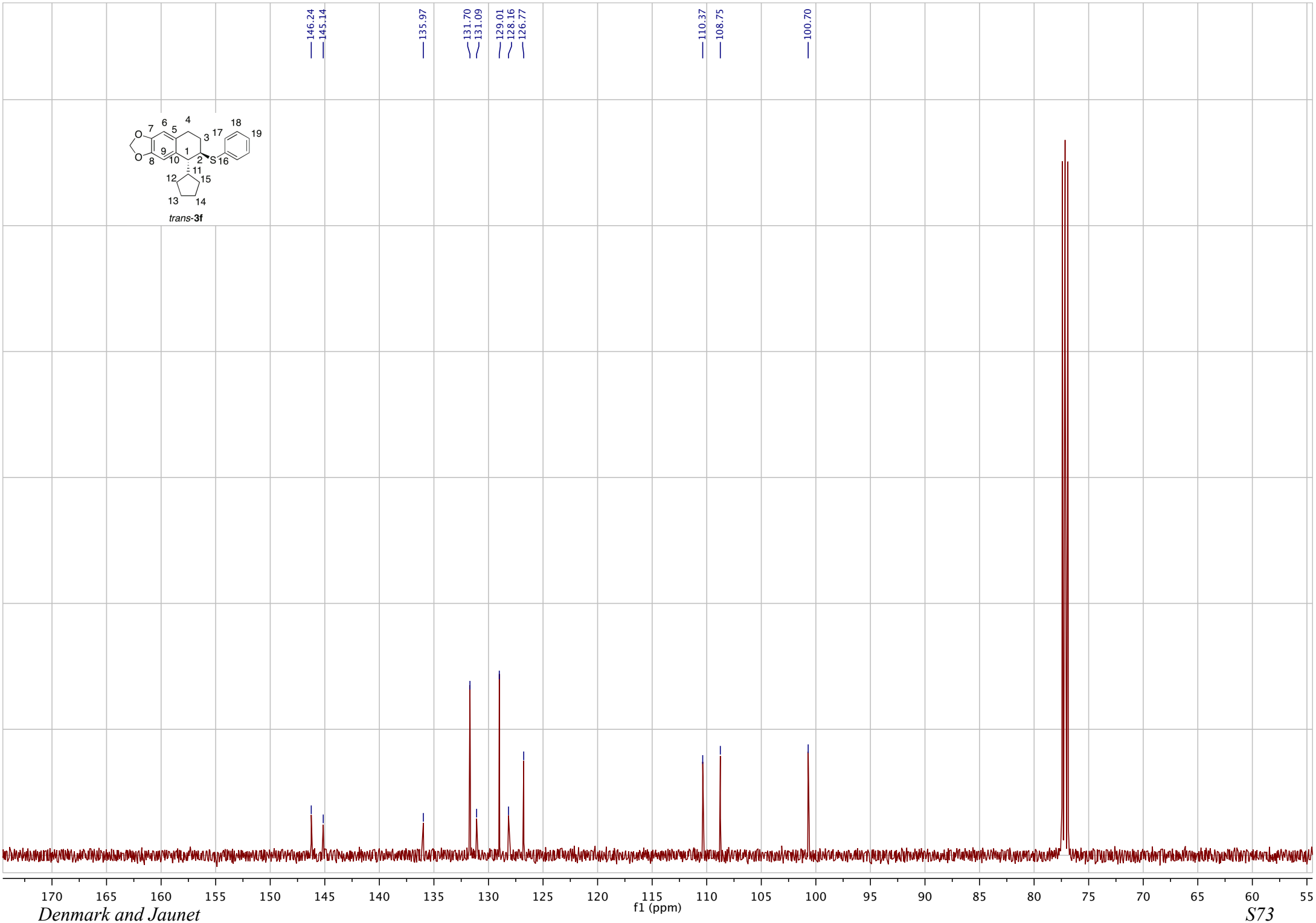
7.26
7.24
7.23
7.21
7.21
6.58
6.55
5.90
5.90
5.89
5.89
3.81
3.80
3.00
2.99
2.98
2.97
2.95
2.95
2.93
2.72
2.72
2.71
2.69
2.67
2.57
2.55
2.19
1.90
1.76
1.68
1.61
1.57
1.51
1.44
1.37
1.31
1.17
trans-3f
1.59
1.74
1.09
1.94
2.03
0.98
0.99
1.03
1.00
1.02
3.04
2.98
1.61
1.09
2.18
f1 (ppm)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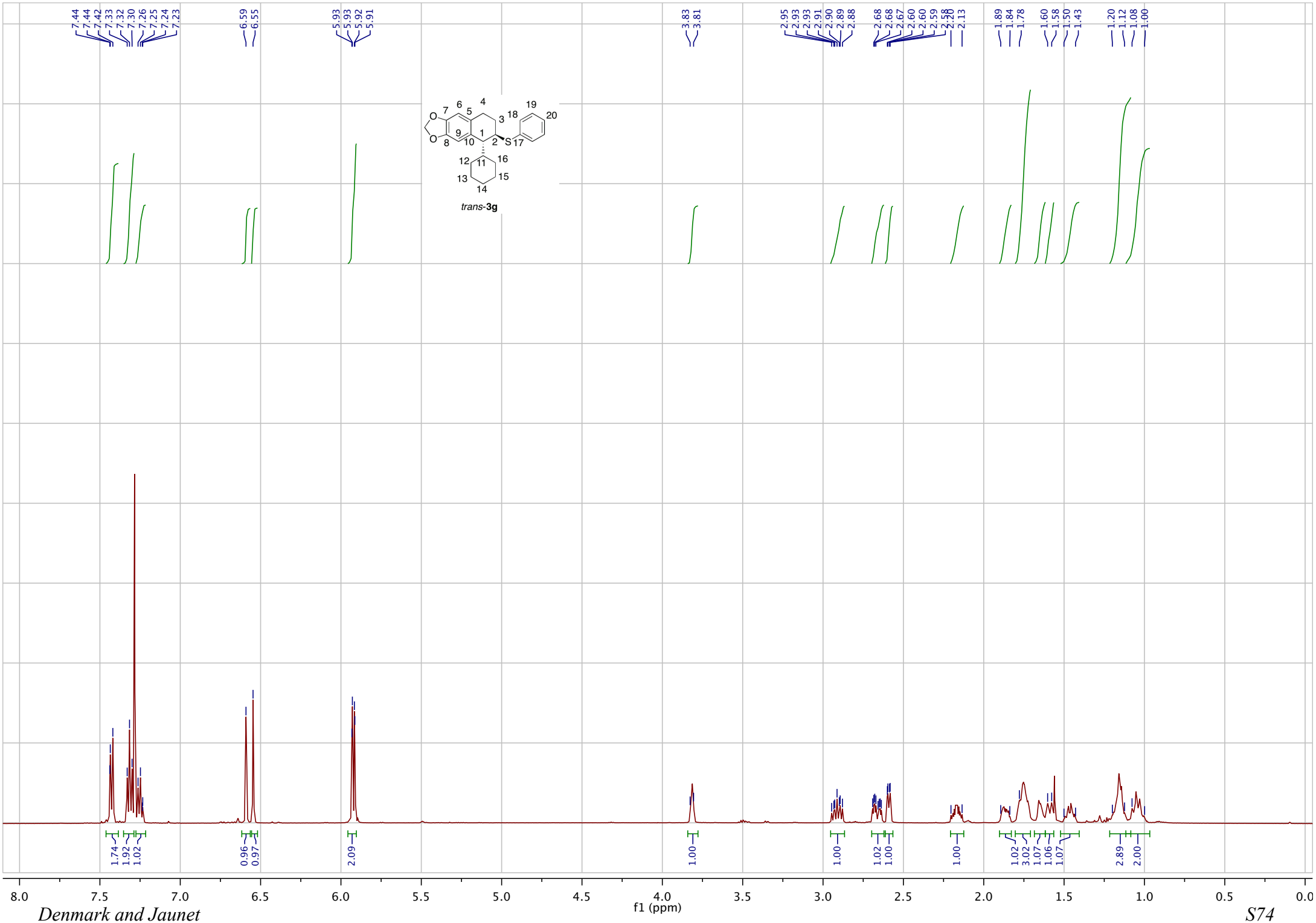
131.70
131.09
129.01
128.16
126.77
110.37
108.75
100.70
trans-3f
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)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7.23
6.59
6.55
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5.93
5.92
5.91
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2.93
2.93
2.91
2.90
2.89
2.88
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2.59
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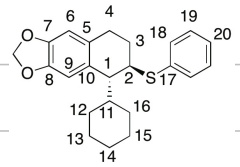
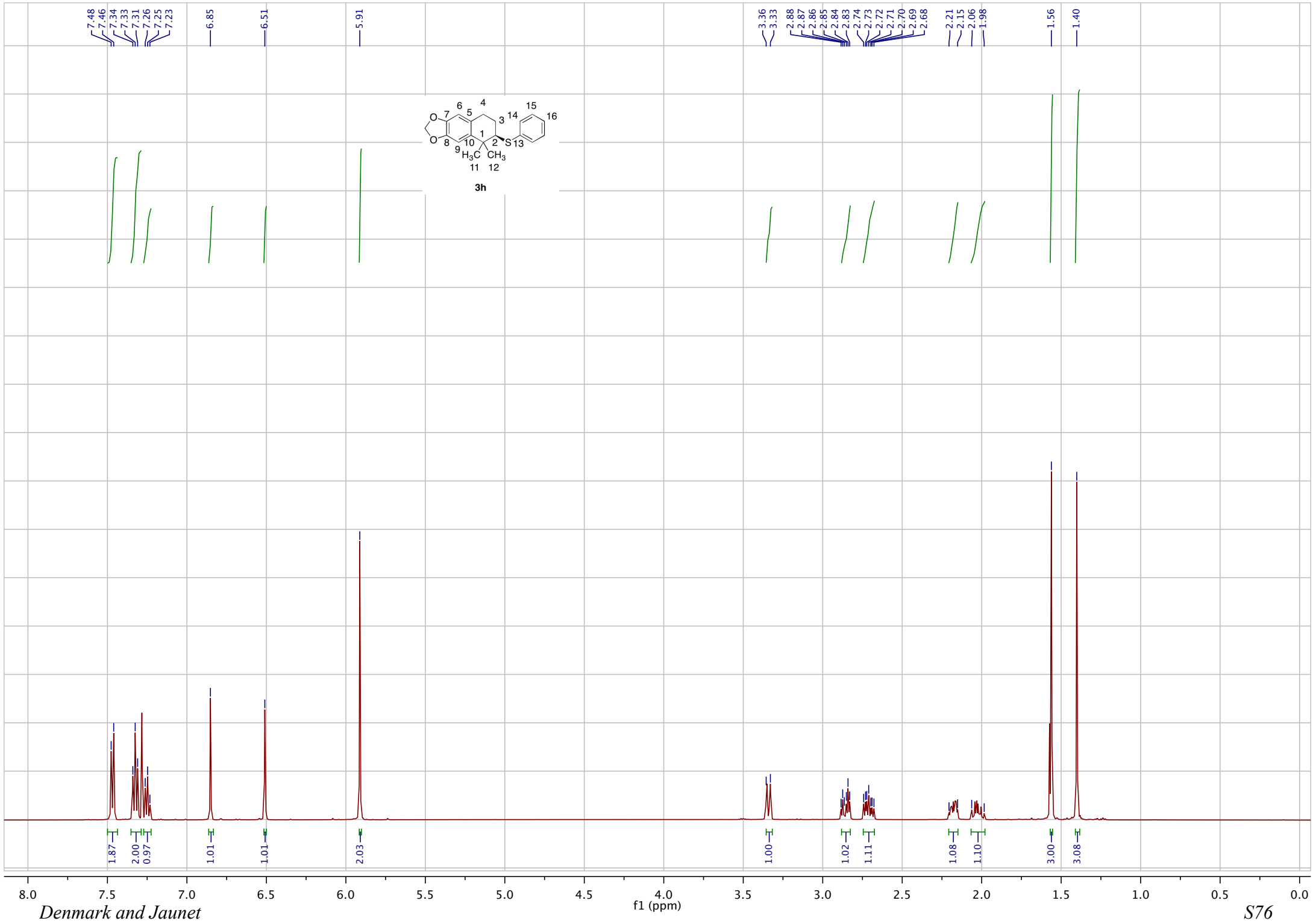
1.89
1.84
1.78
1.60
1.58
1.50
1.43
1.20
1.12
1.08
1.00
trans-3g
1.74
1.92
1.02
0.96
0.97
2.09
1.00
1.00
1.02
1.00
1.00
1.02
3.02
1.07
1.06
1.07
2.89
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


trans-3g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7.25
7.23
6.85
6.51
5.91
3.36
3.33
2.88
2.87
2.86
2.85
2.84
2.83
2.74
2.73
2.72
2.71
2.70
2.69
2.68
2.21
2.15
2.06
1.98
1.56
1.40
3h
1.87
2.00
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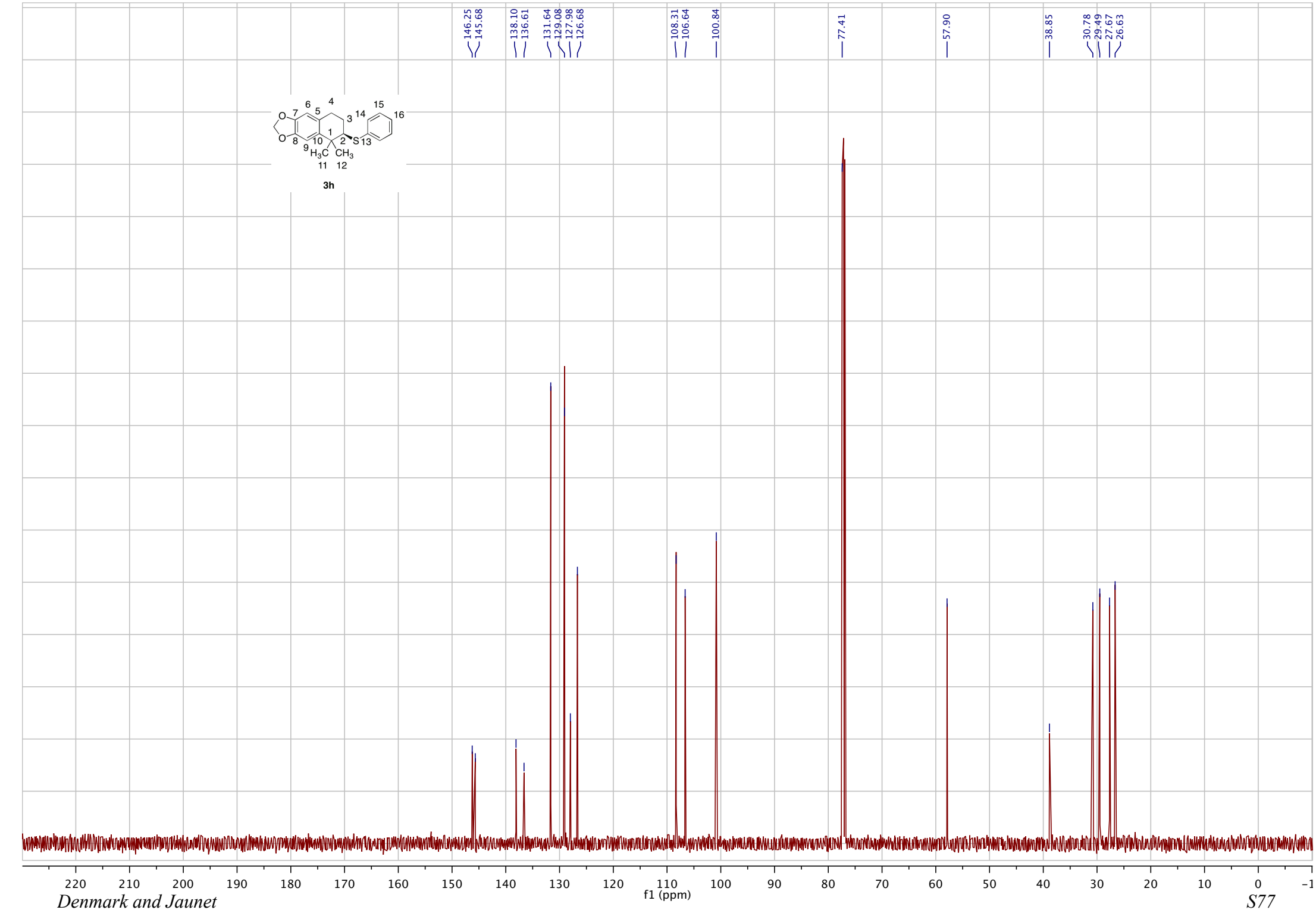
2.03
1.00
1.02
1.11
1.08
1.10
3.00
3.08
f1 (ppm)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131.64
129.08
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126.68
108.31
106.64
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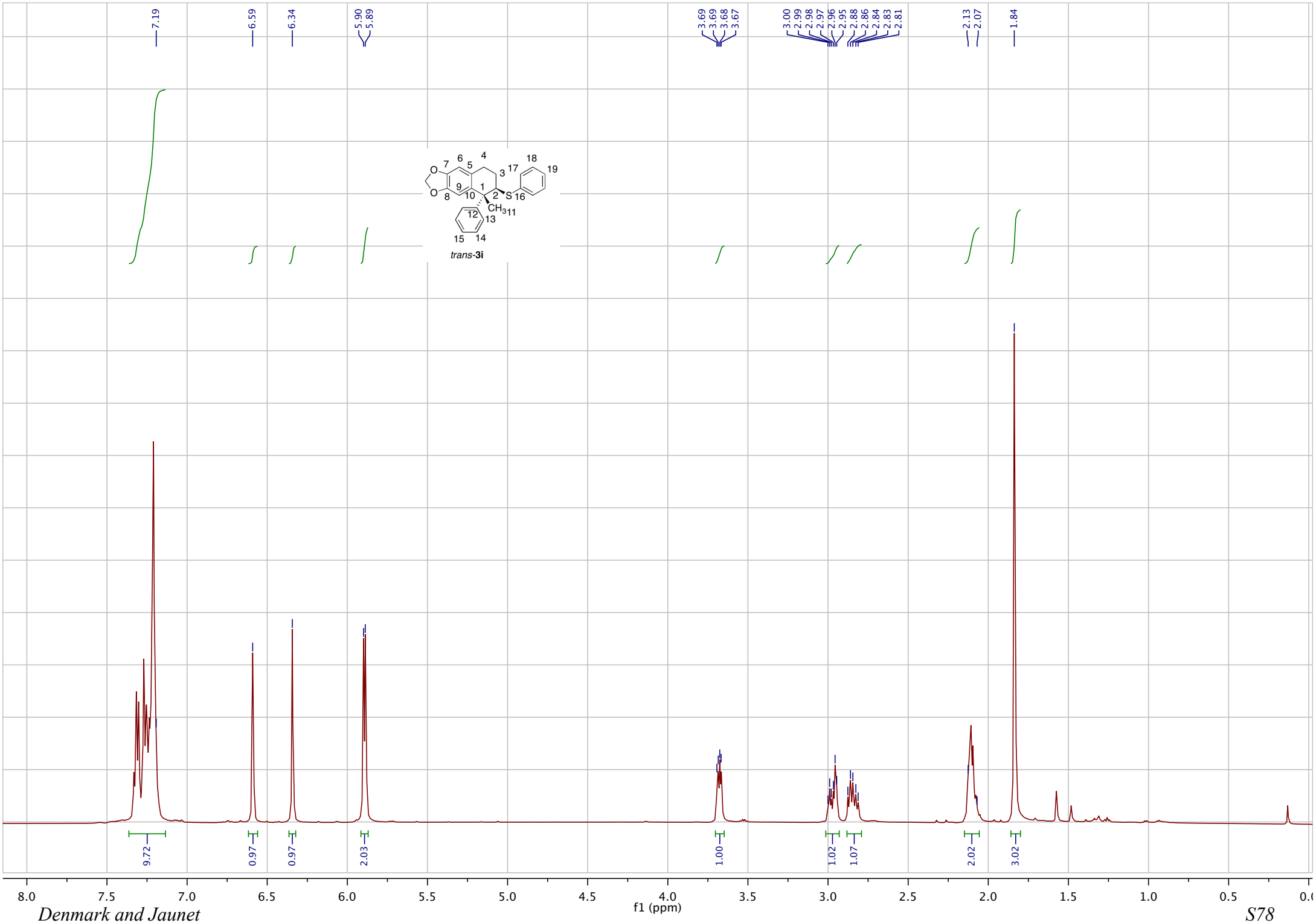
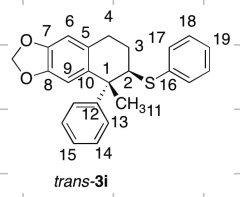
77.41
57.90
38.85
30.78
29.49
27.67
26.63
3h
f1 (ppm)

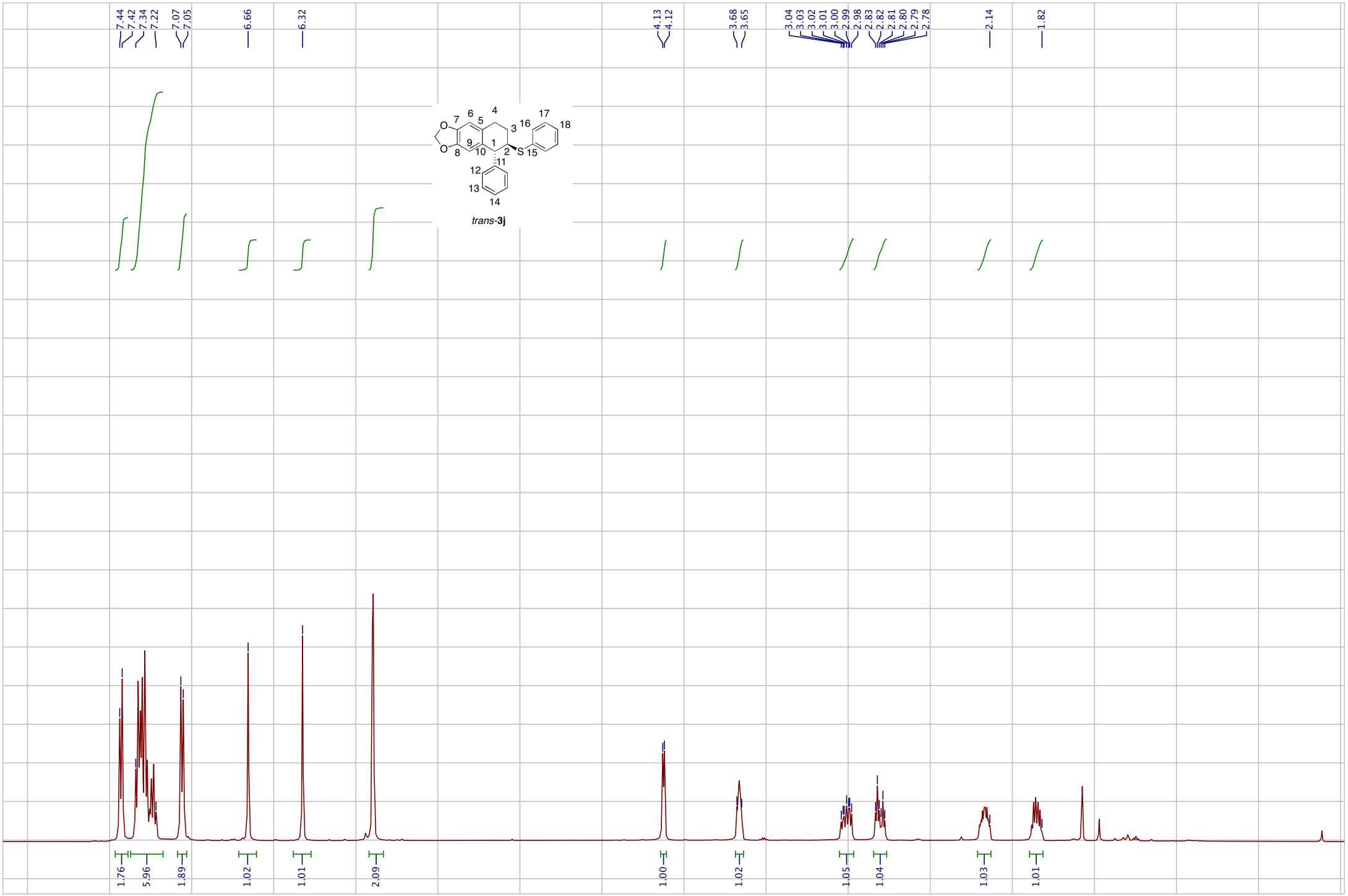

7.19
6.59
6.34
5.90
5.89
3.69
3.69
3.68
3.67
3.00
2.99
2.98
2.97
2.96
2.95
2.88
2.86
2.84
2.83
2.81
2.13
2.07
1.84
trans-3i
9.72
0.97
0.97
2.03
1.00
1.02
1.07
2.02
3.02
f1 (ppm)



149.56
146.07
146.01
137.42
136.19
132.18
128.87
128.74
127.99
126.83
126.25
109.22
107.90
100.83
60.15
47.73
29.29
26.84
25.72

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)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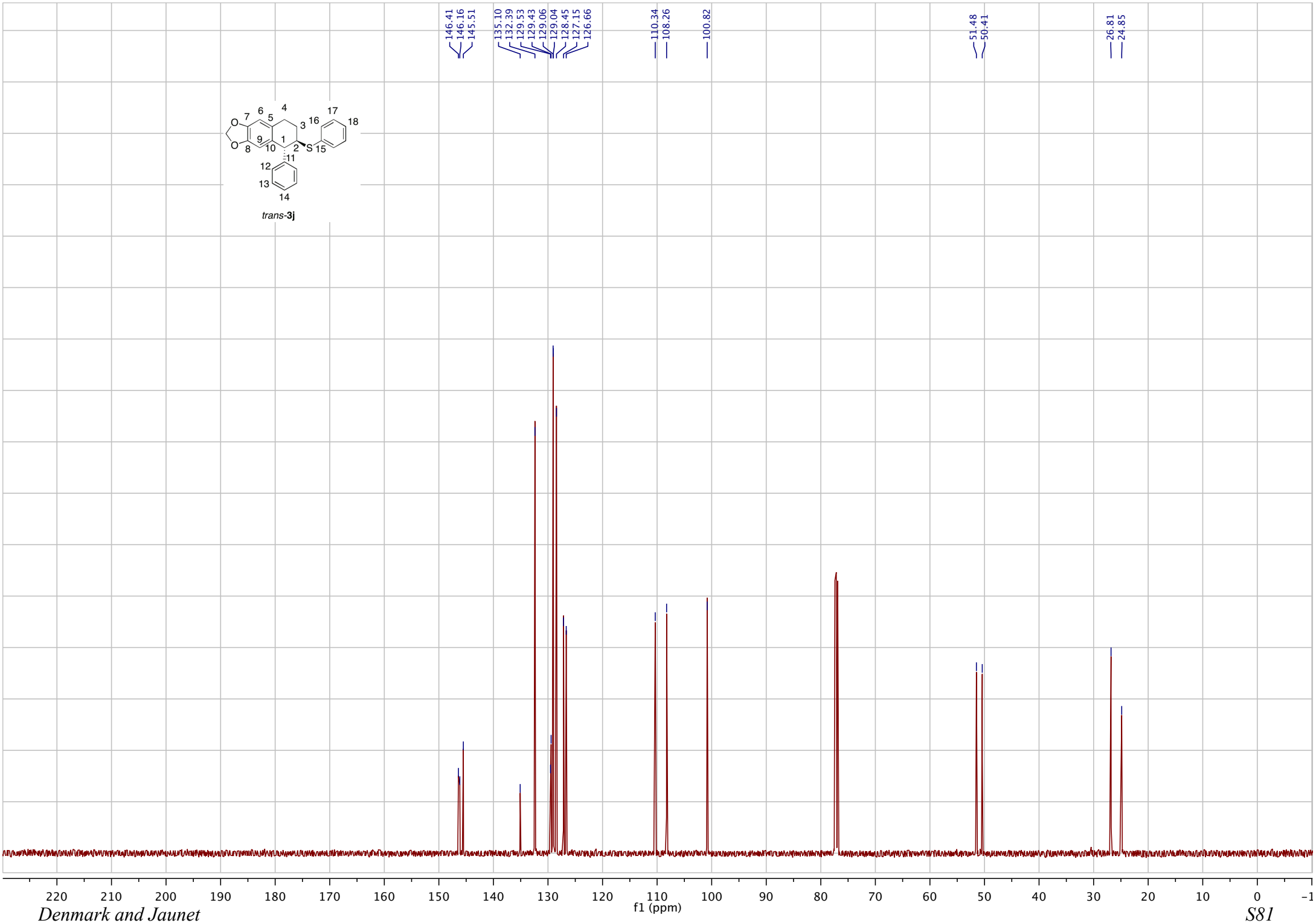
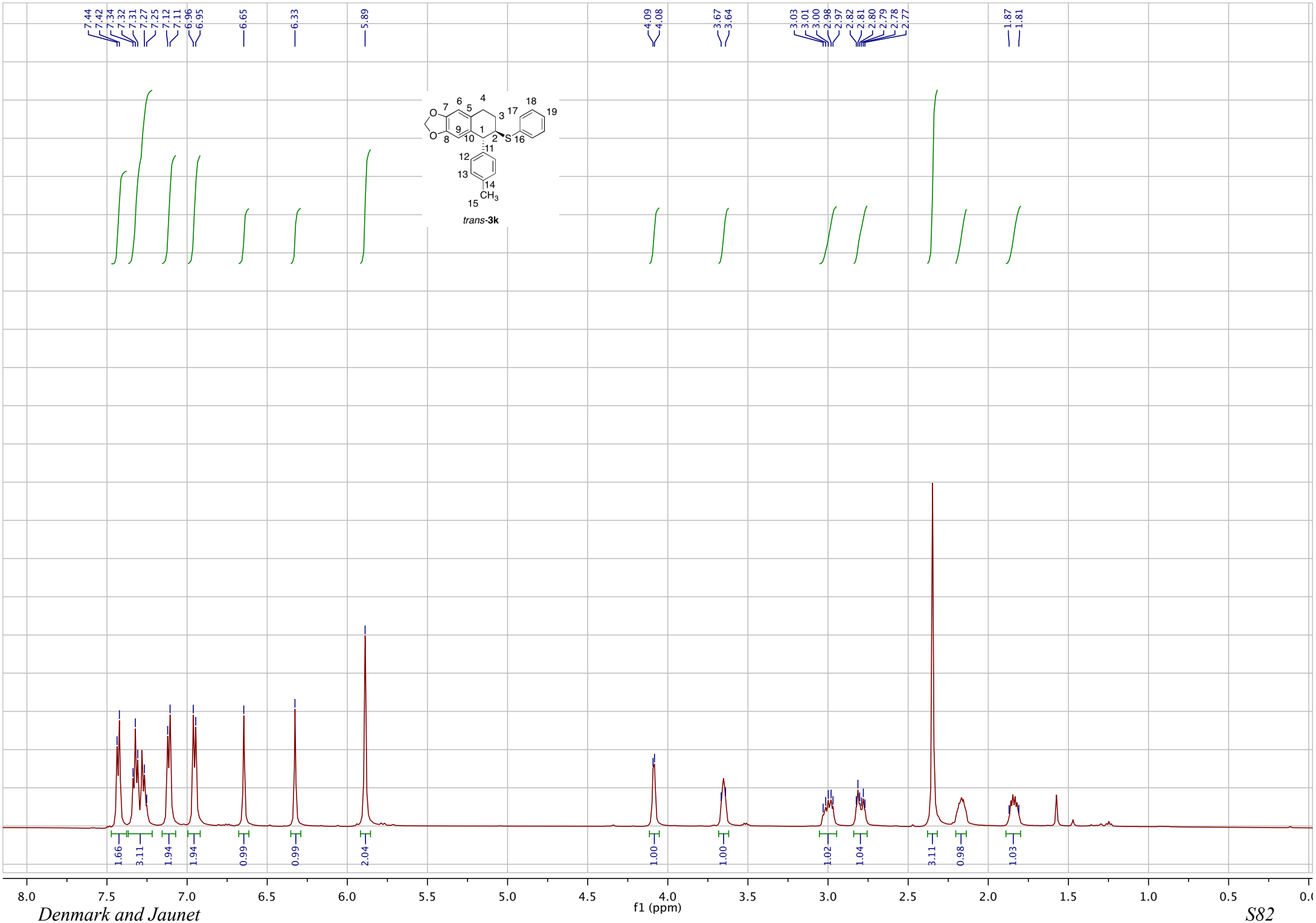
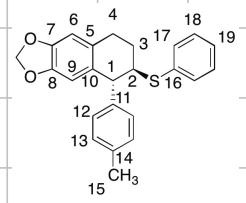
7.22
7.07
7.05
6.66
6.32
4.13
4.12
3.68
3.65
3.04
3.03
3.02
3.01
3.00
2.99
2.98
2.83
2.82
2.81
2.80
2.79
2.78
2.14
1.82
trans-3j
1.76
5.96
1.89
1.02
1.01
2.09
1.00
1.02
1.05
1.04
1.03
1.01
f1 (ppm)


146.41
146.16
145.51
135.10
132.39
129.53
129.43
129.06
129.04
128.45
127.15
126.66
110.34
108.26
100.82
51.48
50.41
26.81
24.85
trans-3j
f1 (ppm)


7.44
7.42
7.34
7.32
7.31
7.27
7.25
7.12
7.11
6.96
6.95
6.65
6.33
5.89
4.09
4.08
3.67
3.64
3.03
3.01
3.00
2.98
2.97
2.82
2.81
2.80
2.79
2.78
2.77
1.87
1.81
trans-3k
1.66
3.11
1.94
1.94
0.99
0.99
2.04
1.00
1.00
1.02
1.04
3.11
0.98
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

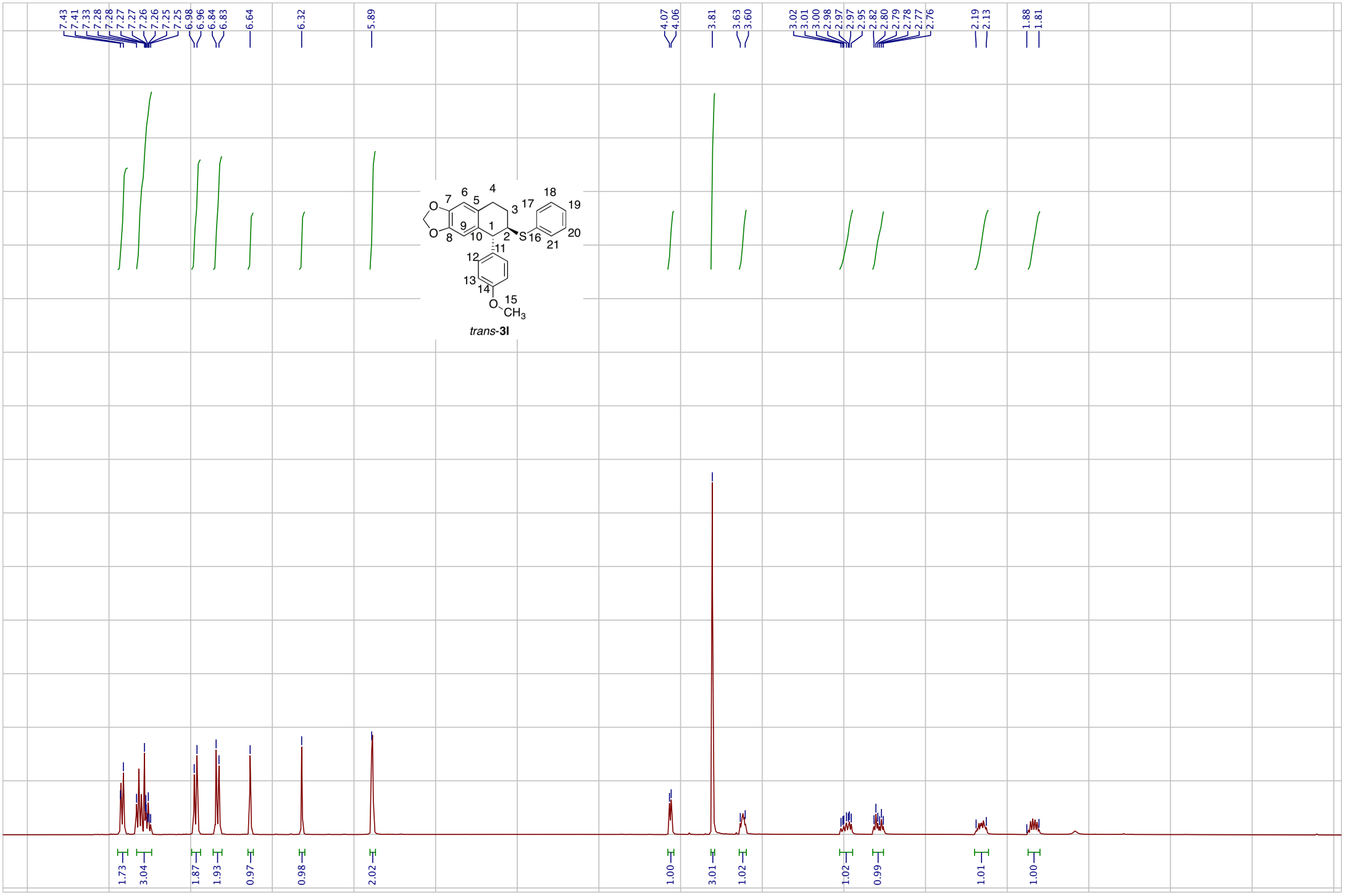


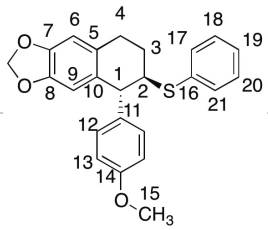
trans-**3k**

146.35
146.13
142.53
136.23
135.15
132.30
129.79
129.35
129.16
129.01
128.91
127.06
123.20
110.32
108.22
100.79
51.41
50.02
26.83
24.88
21.18

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)


7.43
7.41
7.33
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
6.98
6.96
6.84
6.83
6.64
6.32
5.89
4.07
4.06
3.81
3.63
3.60
3.02
3.01
3.00
2.98
2.97
2.97
2.95
2.82
2.80
2.79
2.78
2.77
2.76
2.19
2.13
1.88
1.81
trans-3l
1.73
3.04
1.87
1.93
0.97
0.98
2.02
1.00
3.01
1.02
1.02
0.99
1.01
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

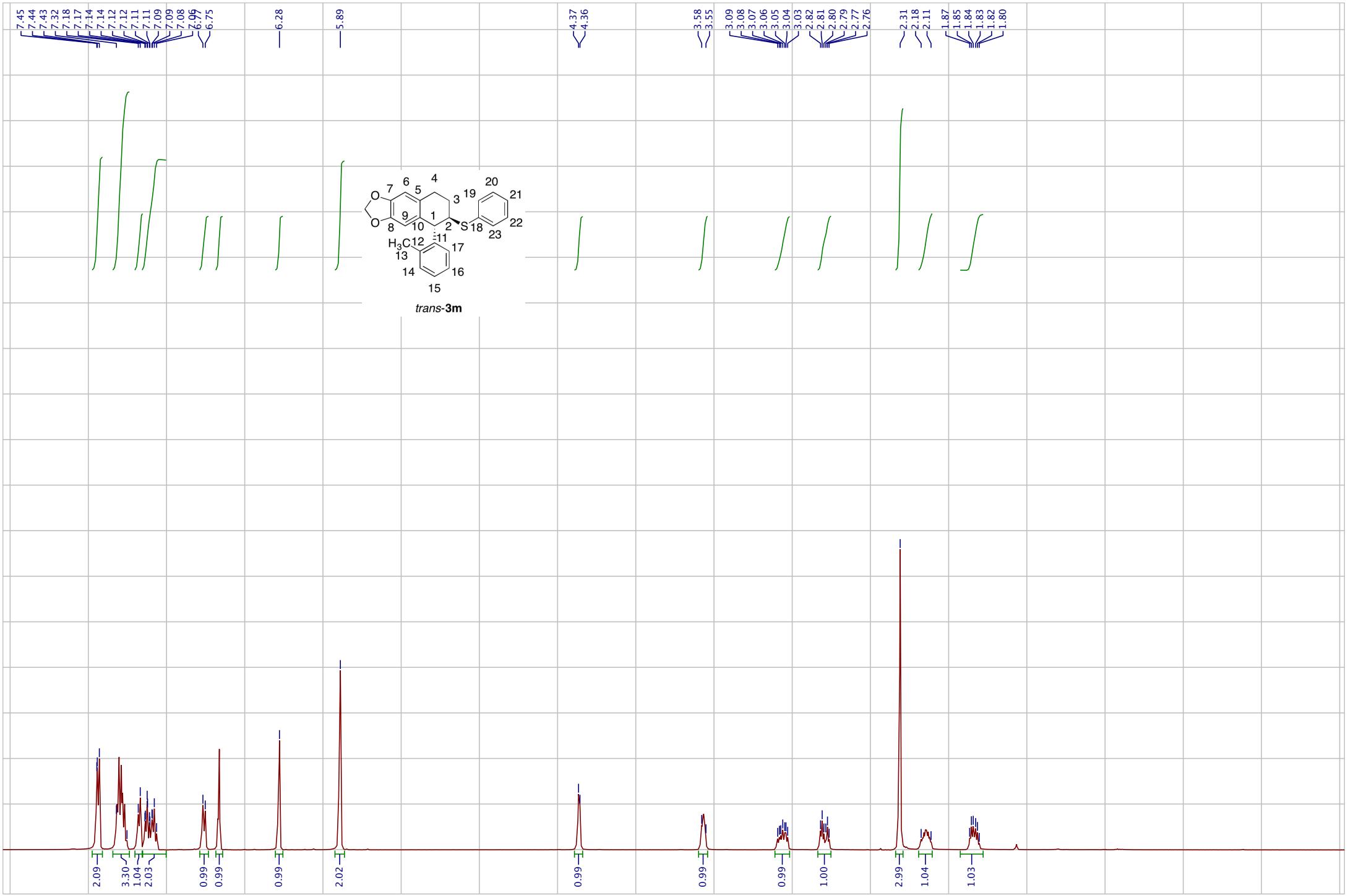


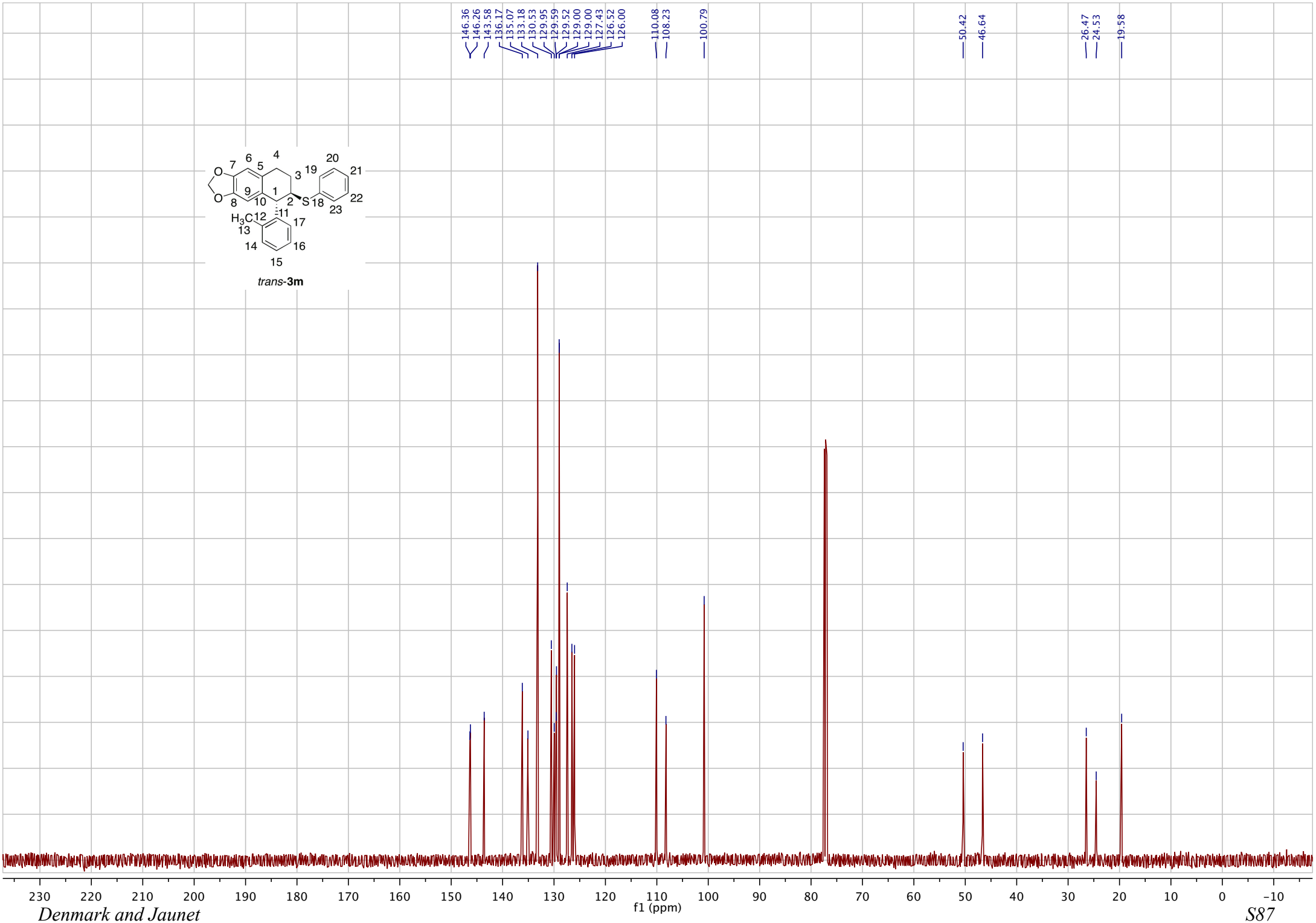
trans-**3l**

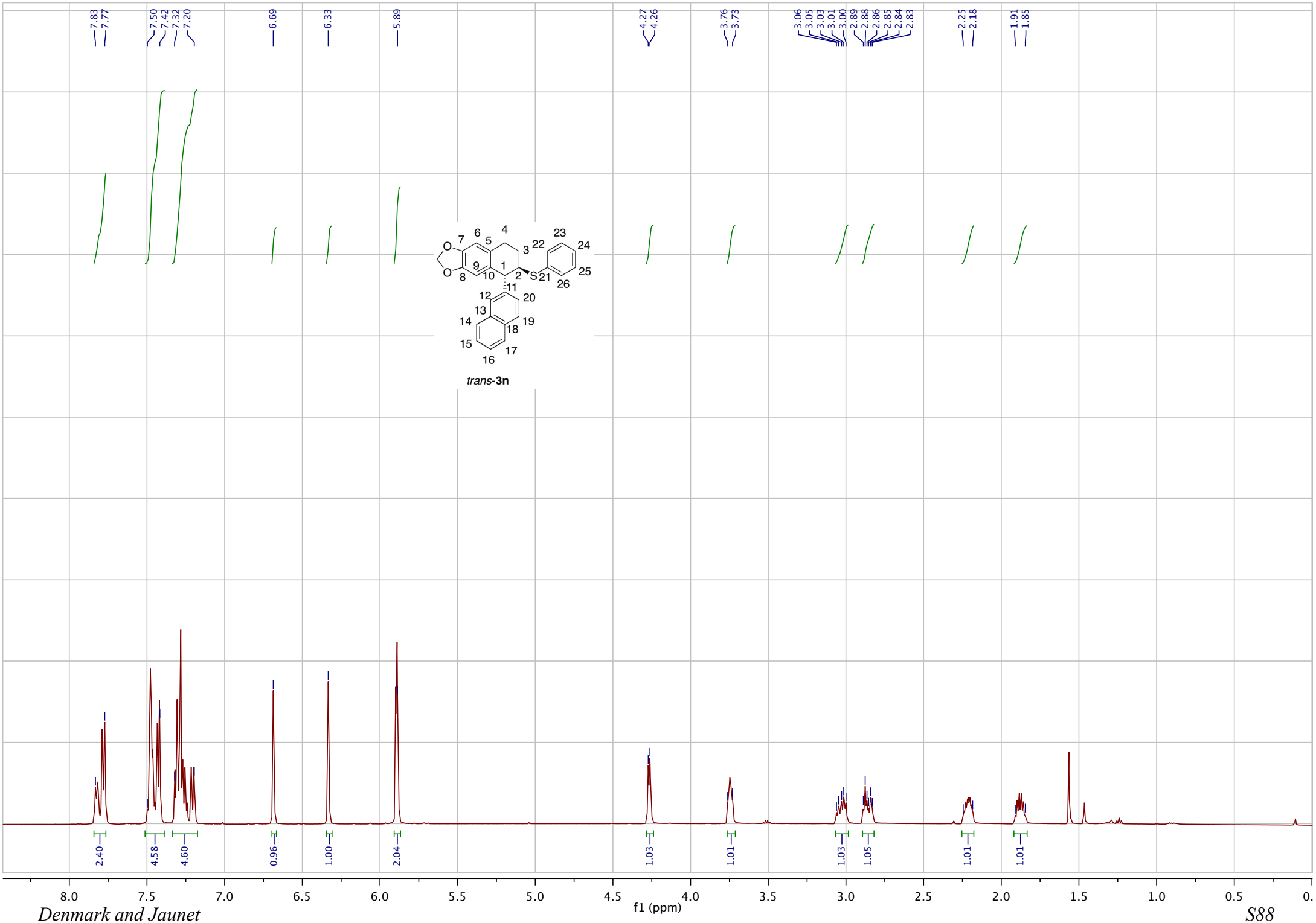
158.40
146.44
146.23
137.76
135.26
132.40
130.07
130.04
129.42
129.13
127.17
113.91
110.40
108.32
100.90
55.47
51.67
49.73
26.97
25.04

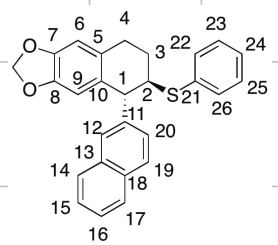
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

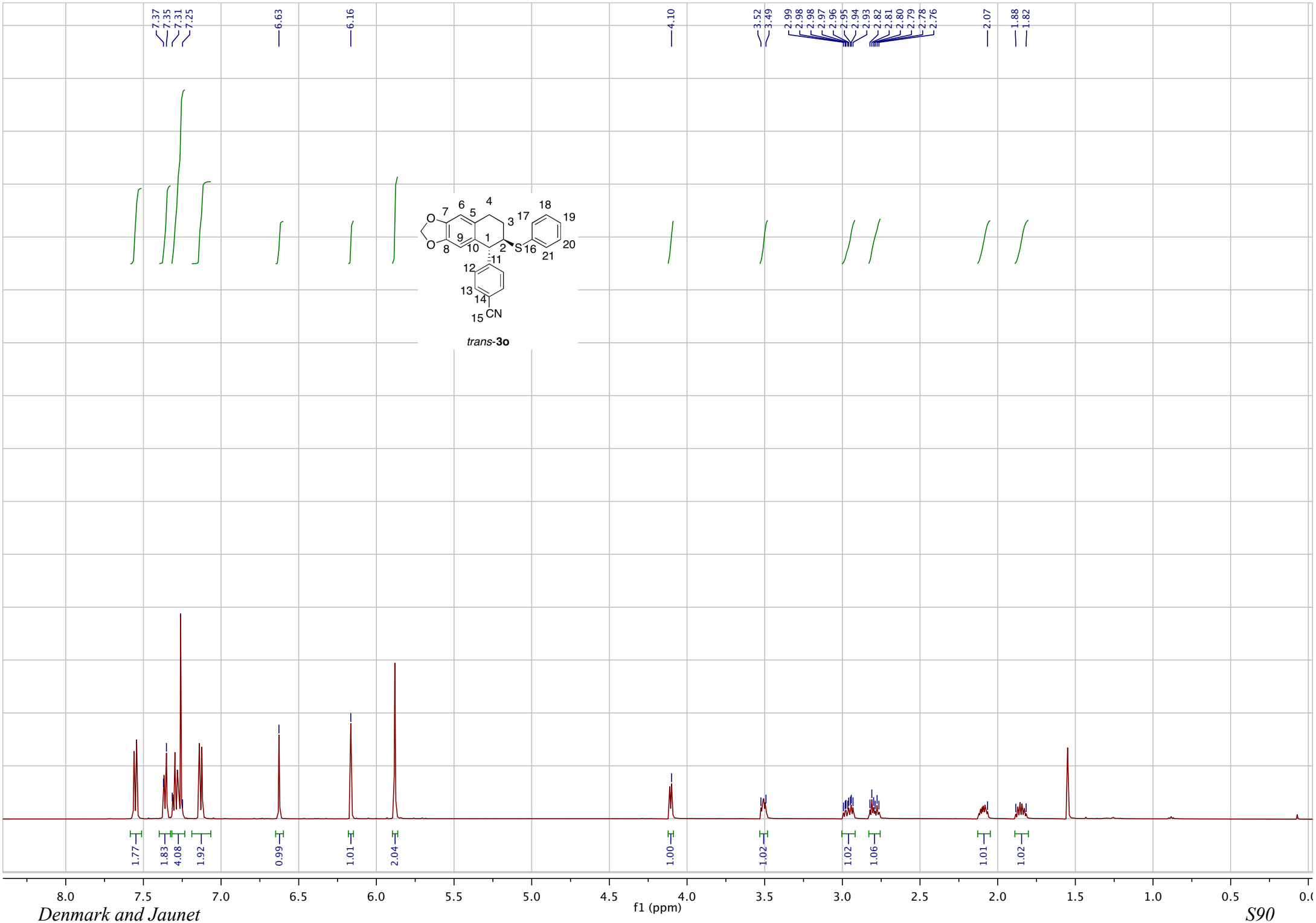

7.45
7.44
7.43
7.32
7.18
7.17
7.14
7.14
7.12
7.12
7.11
7.11
7.09
7.09
7.08
7.06
7.06
6.77
6.75
6.28
5.89
4.37
4.36
3.58
3.55
3.09
3.08
3.07
3.06
3.05
3.04
3.03
2.82
2.81
2.80
2.79
2.77
2.76
2.31
2.18
2.11
1.87
1.85
1.84
1.83
1.82
1.80
trans-3m
2.09
3.30
1.04
2.03
0.99
0.99
0.99
2.02
0.99
0.99
0.99
1.00
2.99
1.04
1.03
f1 (ppm)

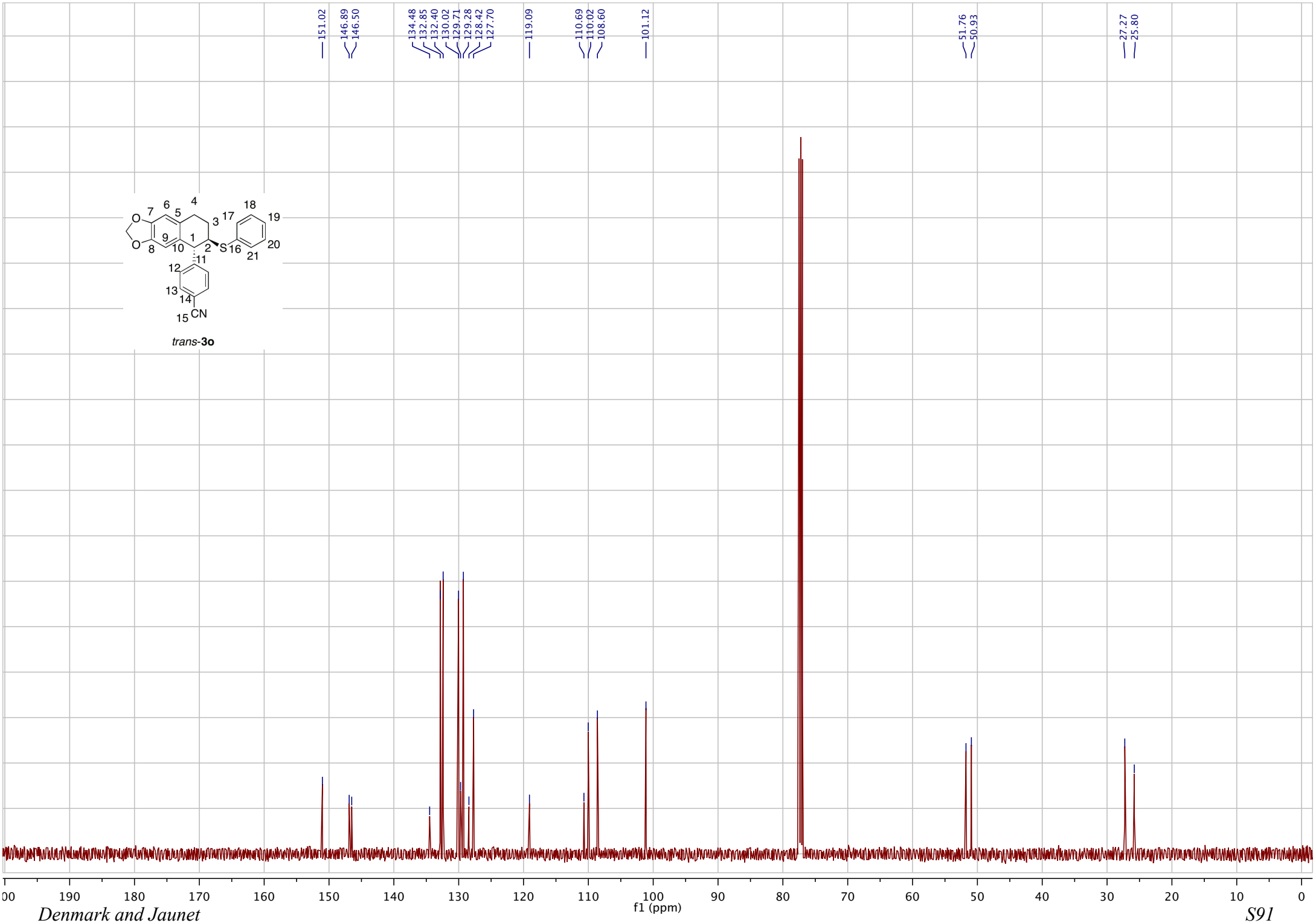

146.36
146.26
143.58
136.17
135.07
133.18
130.53
129.95
129.59
129.52
129.00
129.00
127.43
126.52
126.00
110.08
108.23
100.79
50.42
46.64
26.47
24.53
19.58
trans-3m
f1 (ppm)


7.83
7.77
7.50
7.42
7.32
7.20
6.69
6.33
5.89
4.27
4.26
3.76
3.73
3.06
3.05
3.03
3.01
3.00
2.89
2.88
2.86
2.85
2.84
2.83
2.25
2.18
1.91
1.85
trans-3n
2.40
4.58
4.60
0.96
1.00
2.04
1.03
1.01
1.03
1.05
1.01
1.01
f1 (ppm)

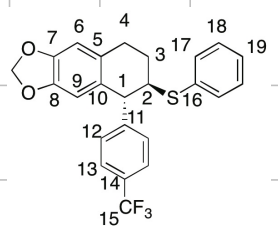


trans-**3n**


7.37
7.35
7.31
7.25
6.63
6.16
4.10
3.52
3.49
2.99
2.98
2.98
2.97
2.96
2.95
2.94
2.93
2.82
2.81
2.80
2.79
2.78
2.76
2.07
1.88
1.82
trans-3o
1.77
1.83
4.08
1.92
0.99
1.01
2.04
1.00
1.02
1.02
1.06
1.01
1.02
f1 (ppm)


151.02
146.89
146.50
134.48
132.85
132.40
130.02
129.71
129.28
128.42
127.70
119.09
110.69
110.02
108.60
101.12
51.76
50.93
27.27
25.80
trans-3o
f1 (ppm)


7.54
7.53
7.40
7.38
7.33
7.31
7.30
7.29
7.27
7.26
7.17
7.15
6.65
6.23
5.90
4.16
4.15
3.60
3.57
3.03
3.02
3.01
2.99
2.98
2.98
2.97
2.85
2.84
2.83
2.82
2.81
2.79
2.17
2.11
1.90
1.84
trans-3p
1.78
1.81
4.04
1.89
1.00
1.03
2.06
1.04
1.03
1.03
1.01
1.03
1.04
f1 (ppm)

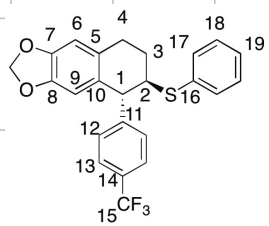


trans-**3p**

149.48
146.67
143.25
134.64
132.64
129.56
129.46
129.36
129.10
128.58
127.55
125.46
125.43
125.37
123.23
121.06
108.43
100.97
76.91
51.63
50.58
27.11
25.50

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

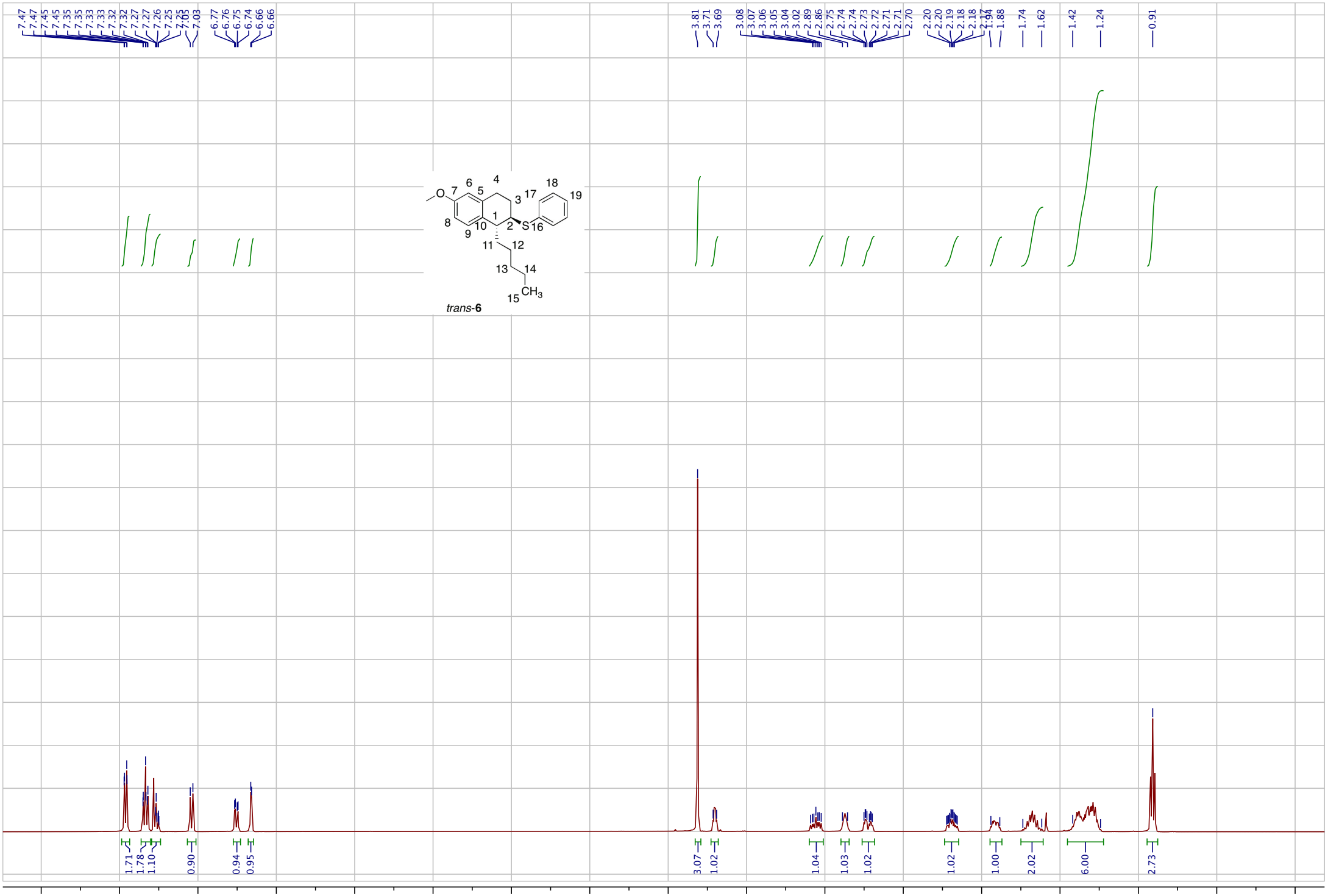


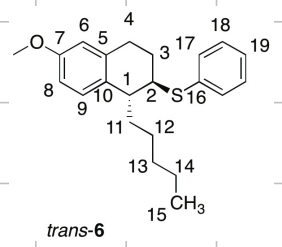
trans-**3p**

-62.78

100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100

f1 (ppm)


7.47
7.47
7.45
7.45
7.35
7.35
7.33
7.33
7.32
7.32
7.27
7.27
7.26
7.25
7.25
7.03
6.77
6.76
6.75
6.74
6.66
6.66
3.81
3.71
3.69
3.08
3.07
3.06
3.05
3.04
3.02
2.89
2.86
2.75
2.74
2.74
2.73
2.72
2.71
2.71
2.70
2.20
2.20
2.19
2.18
2.18
2.17
1.94
1.88
1.74
1.62
1.42
1.24
0.91
trans-6
1.71
1.78
1.10
0.90
0.94
0.95
3.07
1.02
1.04
1.03
1.02
1.02
1.00
2.02
6.00
2.73
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

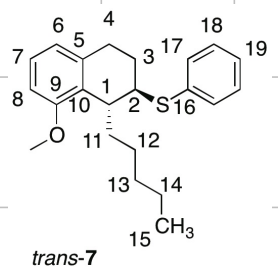


trans-**6**

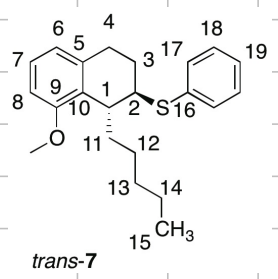
157.70
136.51
135.64
131.98
131.07
130.67
128.98
126.86
113.24
112.43
55.24
46.82
42.71
38.04
31.99
27.04
25.84
23.39
22.73
14.23

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)



trans-**7**

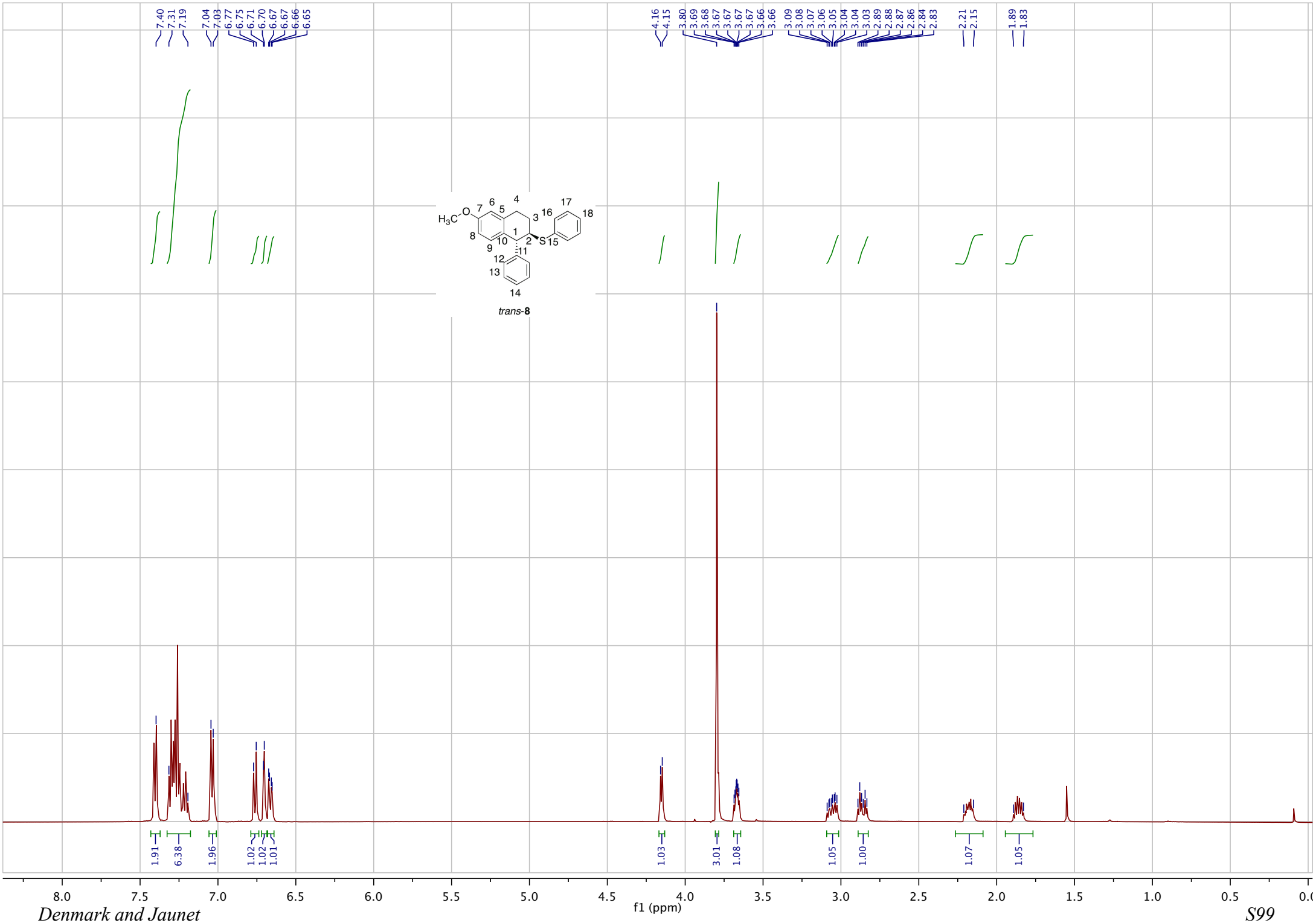


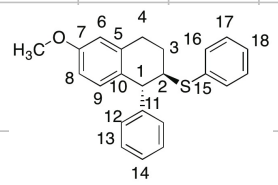
trans-**7**

157.64
136.36
136.07
131.82
128.93
128.11
126.69
126.40
121.29
107.66
55.32
45.57
37.58
35.58
31.73
27.56
24.86
22.71
22.01
14.24

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)

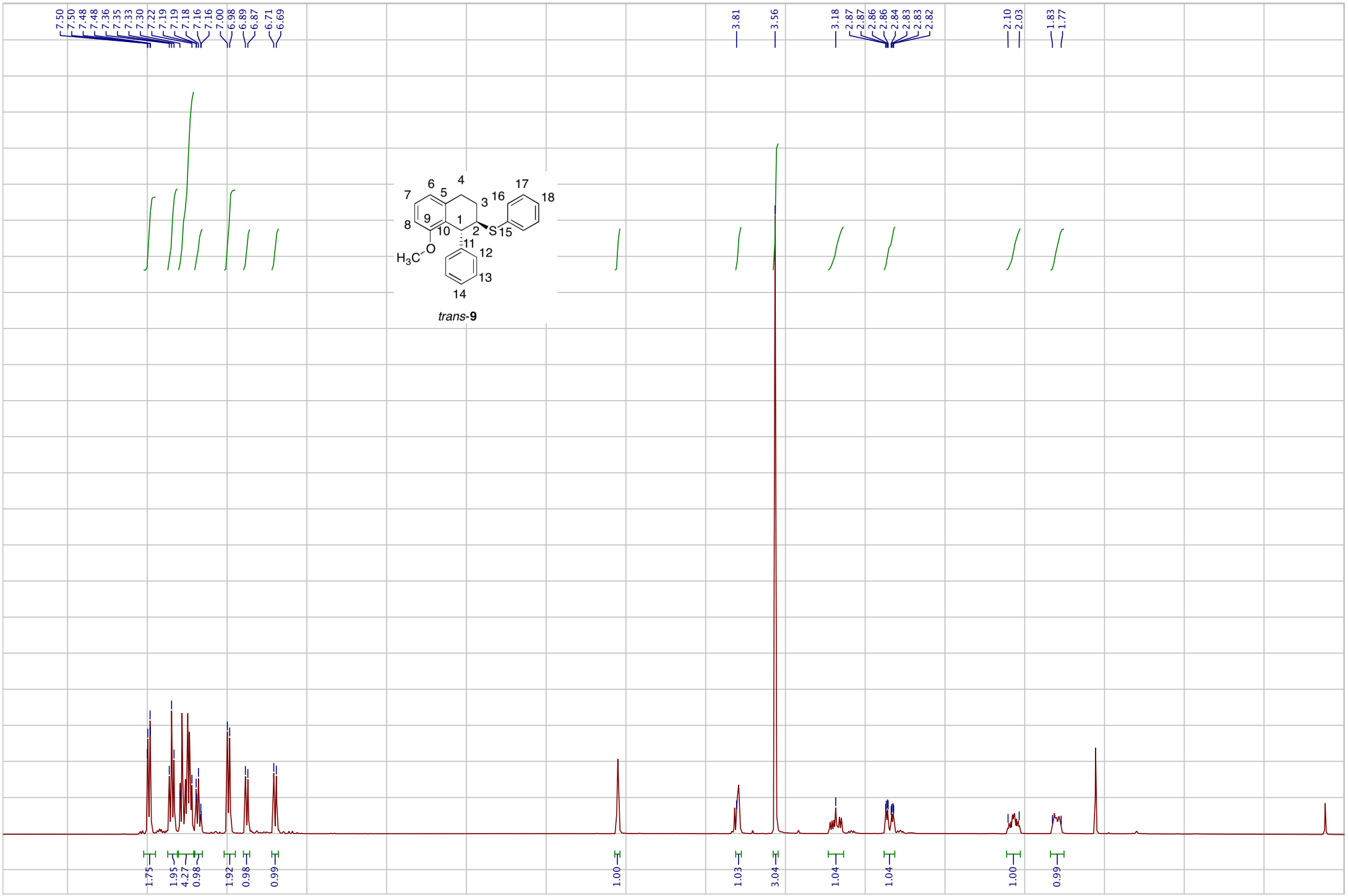

7.40
7.31
7.19
7.04
7.03
6.77
6.75
6.71
6.70
6.67
6.67
6.66
6.65
4.16
4.15
3.80
3.69
3.68
3.67
3.67
3.67
3.67
3.66
3.66
3.09
3.08
3.07
3.06
3.05
3.04
3.04
3.03
2.89
2.88
2.87
2.86
2.84
2.83
2.21
2.15
1.89
1.83
H3C
O
trans-8
1.91
6.38
1.96
1.02
1.02
1.01
1.03
3.01
1.08
1.05
1.00
1.07
1.05
f1 (ppm)

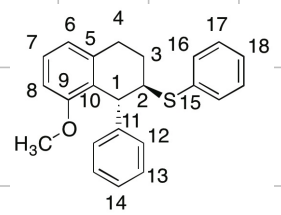


trans-**8**

158.15
145.92
137.53
135.24
132.49
132.06
129.24
129.21
129.13
128.51
127.21
126.67
113.11
112.96
55.40
51.81
49.86
27.30
25.26

f1 (ppm)

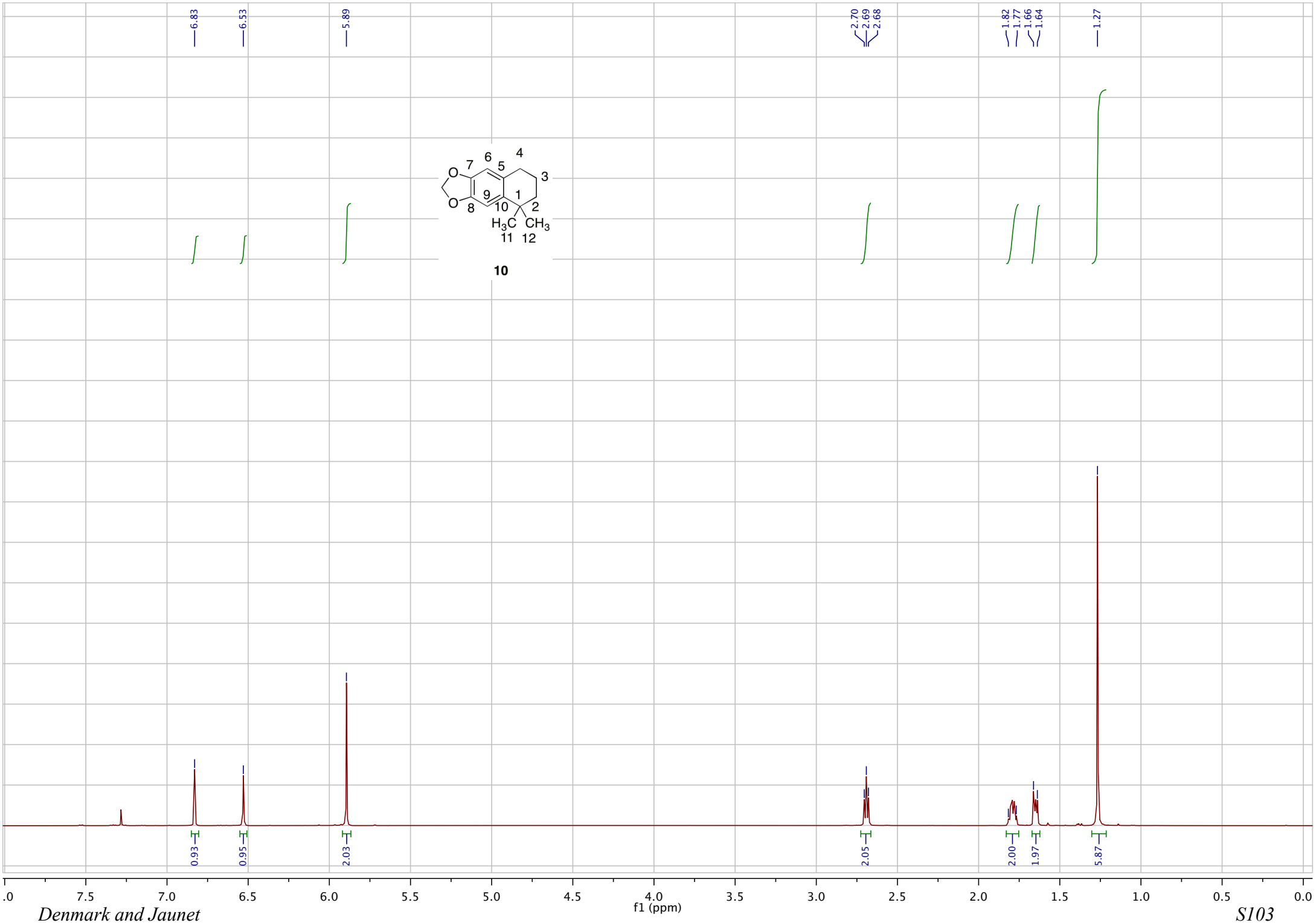

7.50
7.50
7.48
7.48
7.36
7.35
7.33
7.30
7.22
7.19
7.19
7.18
7.16
7.16
7.00
6.98
6.89
6.87
6.71
6.69
3.81
3.56
3.18
2.87
2.87
2.86
2.86
2.84
2.83
2.83
2.82
2.10
2.03
1.83
1.77
trans-9
1.75
1.95
4.27
0.98
1.92
0.98
0.99
1.00
1.03
3.04
1.04
1.04
1.00
0.99
f1 (ppm)



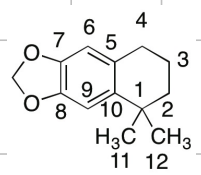
trans-**9**

158.14
145.97
137.74
135.76
132.12
129.15
128.33
128.22
127.40
127.06
126.16
124.69
121.30
108.31
55.66
50.77
43.99
25.13
21.64

f1 (ppm)

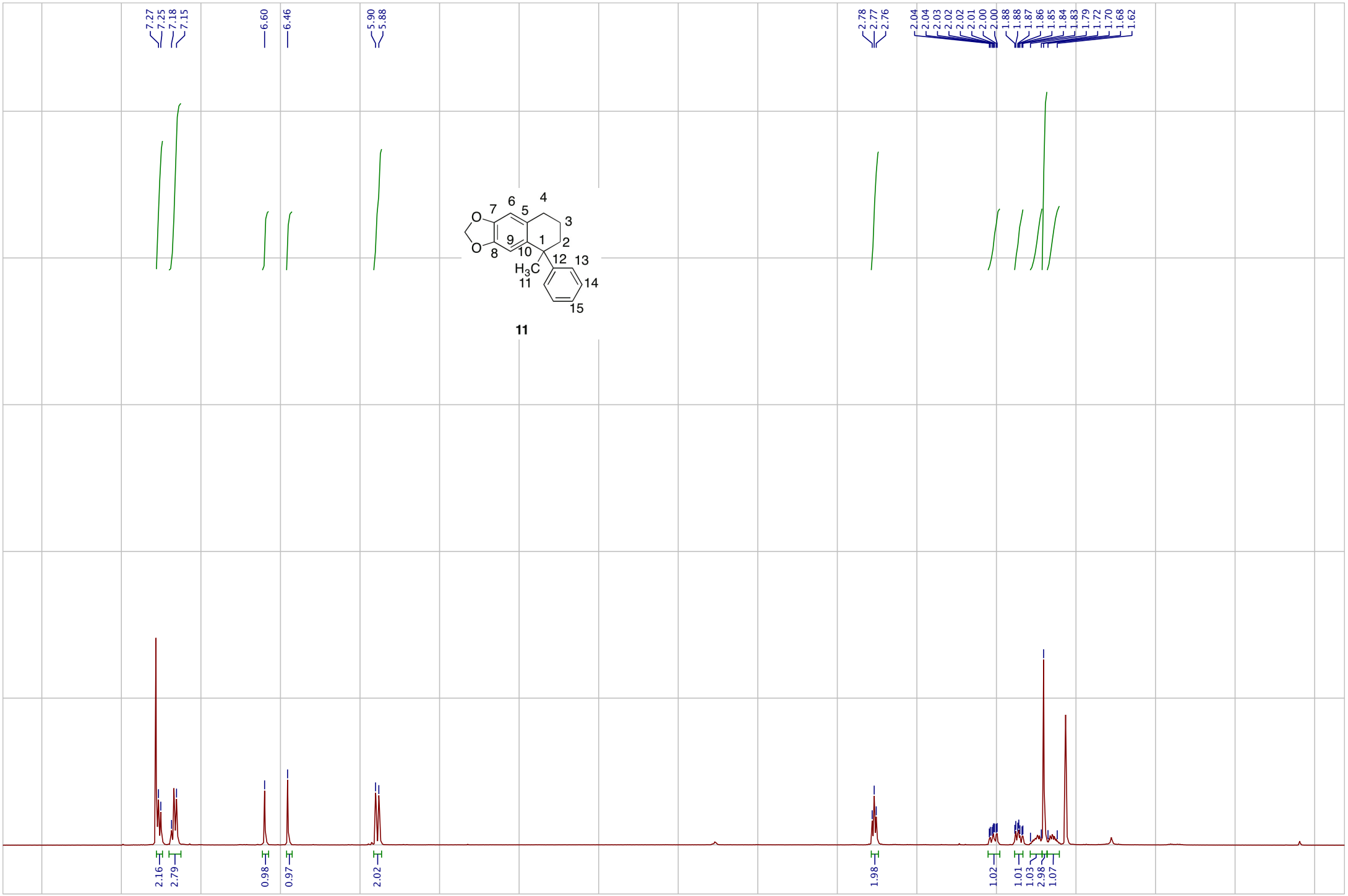

6.83
6.53
5.89
2.70
2.69
2.68
1.82
1.77
1.66
1.64
1.27
0.93
0.95
2.03
2.05
2.00
1.97
5.87
f1 (ppm)

10

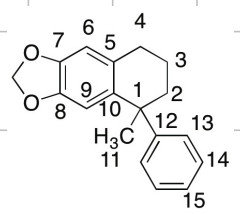

7
6
5
4
3
O
O
9
1
8
10
2
H3C
CH3
11
12

10

145.88
145.21
138.97
129.28
108.59
106.59
100.62
39.37
34.11
32.10
31.02
19.98
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


7.27
7.25
7.18
7.15
6.60
6.46
5.90
5.88
2.78
2.77
2.76
2.04
2.04
2.03
2.02
2.02
2.01
2.00
2.00
1.88
1.88
1.87
1.86
1.85
1.84
1.83
1.79
1.72
1.70
1.68
1.62
O
O
H3C
11
12
13
14
15
1
2
3
4
5
6
7
8
9
10
2.16
2.79
0.98
0.97
2.02
1.98
1.02
1.01
1.03
2.98
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

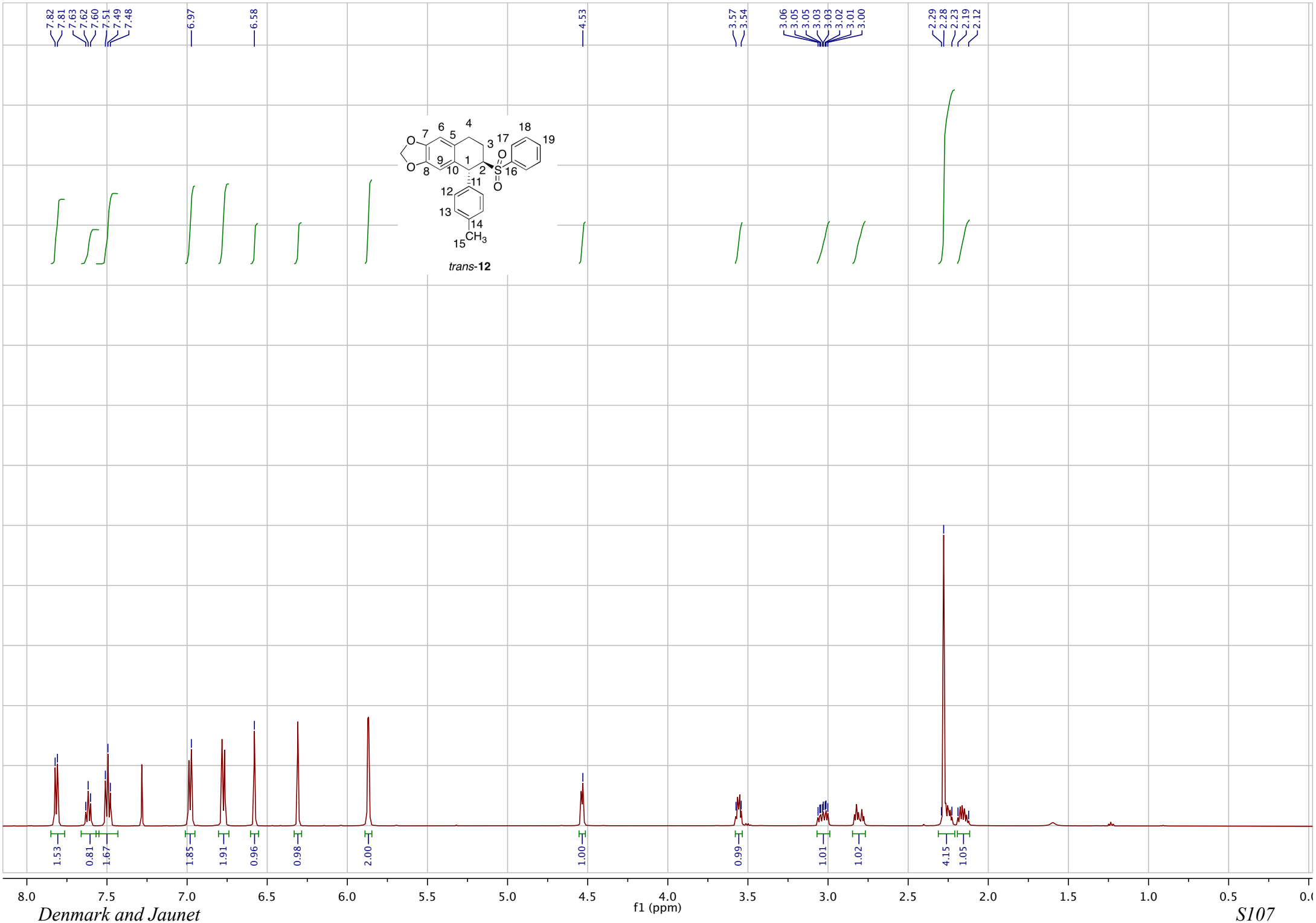
11

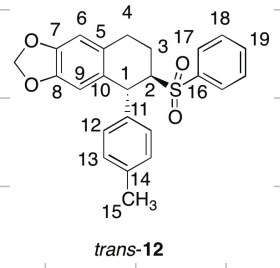


11

151.60
145.87
145.67
137.41
130.35
127.93
127.53
125.60
108.89
108.34
100.69
43.11
41.63
30.57
30.19
19.75

f1 (ppm)


7.82
7.81
7.63
7.62
7.60
7.51
7.49
7.48
6.97
6.58
4.53
3.57
3.54
3.06
3.05
3.05
3.03
3.03
3.02
3.01
3.00
2.29
2.28
2.23
2.19
2.12
trans-12
1.53
0.81
1.67
1.85
1.91
0.96
0.98
2.00
1.00
0.99
1.01
1.02
4.15
1.05
f1 (ppm)



trans-**12**

146.41
146.40
141.59
138.71
136.49
133.46
129.38
129.14
129.11
128.94
128.72
128.49
109.84
108.04
100.90
67.14
43.56
26.76
21.08
20.54

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)