Mechanistic, Crystallographic, and Computational Studies on the Catalytic, Enantioselective Sulfenofunctionalisation of Alkenes

Scott E. Denmark,* Eduard Hartmann, David J. P. Kornfilt, Hao Wang

Department of Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois 61801

SUPPORTING INFORMATION

TABLE OF CONTENTS **PAGE**

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 (470 MHz) spectrometers respectively. Acquisition times were 4.096 s for ^{1}H NMR, and 1.024 s for ^{13}C NMR, 0.655 s for ^{31}P NMR, and 0.328 s for ^{19}F 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), pentet (pent), heptet (hept), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz, and integration is provided and assignments are indicated. Assignments were confirmed through 2-D COSY and HSQC 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 with NaCl salt plates or as neat. The 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 or ceric ammonium molybdenat (CAM) 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. Normal-Phase HPLC was performed on an Agilent 1100 HPLC using a Chiralpak AD-H or a Regis (*R*,*R*)-Whelk-O1 column. Reverse-Phase HPLC was performed on an Agilent 1100 HPLC using a Chiralpak AD-RH or a Chiralcel OJ-RH column.

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), hexane (Fisher, Optima) and methanol (Fisher, Optima). Methanesulfonic acid (Aldrich) was dried following an estblished procedure.[1] Phthalimide (Aldrich), 4-methoxythiophenol (**S14**) (Matrix Scientific), 4-(trifluoromethyl)thiophenol (**S15**) (Oakwood Products), 4-nitrobenzenesulfenyl chloride (**S16**) (Aldrich), 2-methylthiophenol (**S17**) (Aldrich), 2-ethylthiophenol (**S19**) (Oakwood Products), 2-isopropylthiophenol (**S20**) (TCI), 2,6-dimethylthiophenol (**S18**) (Oakwood Products), sulfur powder (Fisher Chemicals), selenium powder (Aldrich) *m*-Chloroperbenzoic acid (70–77%, Acros).

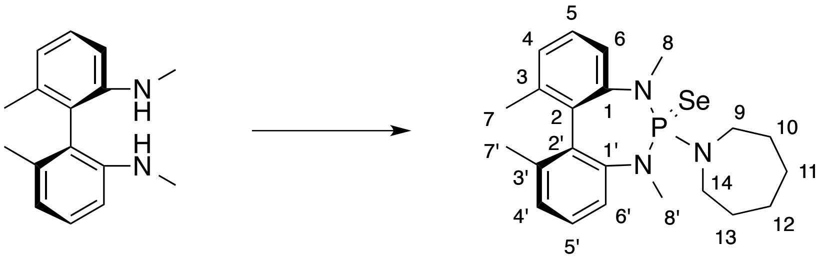
Literature Preparations

The following compounds were prepared according to literature procedures: (*R*)-6,6-dimethyl-2,2-di(methylamino)-1,1-biphenyl (**S1**)[2], (*E*)-5-(2-fluorophenyl)-pent-4-en-1-ol (**1a**)[3], (±)-*N*,*N*'-dimethyl-[1,1'-binaphthalene]-2,2'-diamine ((±)-**S2**)[4], 1,1-dichloro-*N*,*N*-diisopropyl-phosphanamine (*i*-$Pr_2N–PCl_2$)[5], 1,1-dimethyl-2-phenyldisulfan-1-ium hexachloroantimonate ($[PhS(SMe_2)]SbCl_6$)[6], benzenesulfenyl chloride (PhSCl)[7], sodium tetrakis[3,5-bis(tri-fluoromethyl)phenyl]borate ($NaBArF_{24}$)[8], 1-bromo-2,6-diethylbenzene (**S6**)[9], 1-bromo-2,6-diisopropyl-benzene (**S8**)[10], 1-bromo-3,5-diisopropylbenzene (**S10**)[11], 1,3-diisopropoxybenzene

(**S12**) [12] ,1-naphthalenethiol (**S21**) [13] , 2-naphthalenethiol (**S22**)[13], (*E*)-5-phenylpent-4-en-1-ol (**1b**)[14], catalyst (*R*)-**3c**[15], (*E*)-5-phenyl-*N*-tosylpent-4-enamide (**1f**)[15],

Experimental Procedures

Preparation of 6-(Azepan-1-yl)-1,5,7,11-tetramethyl-5,7-dihydrodibenzo[d,f][1,3,2]-diazaphosphepine 6-selenide ((*R*)-3a)



S1 (*R*)-**3a**

To a dry, 20-mL Schlenk flask under argon was added 6,6-dimethyl-2,2-di(methylamino)-1,1-biphenyl[2] (580 mg, 2.45 mmol), THF (9 mL) and Et_3N (780 µL, 5.63 mmol, 2.30 equiv). The solution was cooled to 0 °C. Neat, distilled PCl_3 (630 µL, 7.36 mmol, 3.00 equiv) was added via syringe, and the reaction was allowed to stir for 3 h at room temperature. The resulting precipitate was filtered off via cannula with the filtrate being transferred to a 100-mL Schlenk flask. The THF was removed by stirring under vacuum. Azepane (310 µL, 2.80 mmol, 1.10 equiv), CH_2Cl_2 (15 mL) and Et_3N (500 µL, 3.60 mmol, 1.48 equiv) were added and the reaction allowed to stir for 16 h. Selenium powder (580 mg, 7.36 mmol, 3.00 equiv) was added and the reaction stirred at room temperature for 24 h. The excess selenium was filtered off through a pad of Celite and the filtrate was concentrated to yield an orange foam. The material was dissolved in a minimal amount CH_2Cl_2 and purified by chromatography (SiO_2, 140 g, 20 mm ∅ × 18 cm, hexane/CH_2Cl_2, 6:1). The resulting off-white powder was filtered through a silica plug washing with hexane/Et_2O (1:1) to yield 880 mg (82%) of (*R*)-**3a** (Note: The use of ether is important to remove all traces of selenium). An analytically pure sample was obtained by recrystallization from hexane (ca. 10 mL/g).

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

mp: 105–107 °C (hexane)

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

δ 7.27 (t, J = 7.8 Hz, 1H, H(C5)), 7.22 (t, J = 7.7 Hz, 1H, H(C5')), 7.15 (dd, J = 8.1, 3.1 Hz, 2H, HC(4), HC(4')), 7.09 (d, J = 7.5 Hz, 1H, H(C6)), 7.06 (d, J = 7.6 Hz, 1H, H(C6')), 3.18 (tt, J = 9.5, 4.6 Hz, 2H, HC(9)), 3.07 (d, J = 12.5 Hz, 3H, H(C8)), 2.95 (ddd, J = 14.3, 10.3, 4.6 Hz, 2H, H(C9')), 2.75 (d, J = 13.4 Hz, 3H, H(C8')), 2.13 (s, 3H, HC(7)), 2.03 (s, 3H, H(C7')), 1.59 (s, 8H, HC(10), C(11)).

^{13}C NMR: (125 MHz, CDCl$_3$)

δ 144.6 (d, J = 5.5 Hz, C(1)), 143.6 (C(1')), 137.4 (C(3)), 136.8 (C(3')), 134.6 (C(2)), 132.5 (d, J = 2.6 Hz, C(2')), 127.8 (d, J = 2.1 Hz, C(5)), 127.4 (C(5')), 127.2 (C(6)), 126.9 (d, J = 2.5 Hz, C(6')), 122.0 (C(4)), 120.3 (d, J = 3.6 Hz, C(4')), 49.6 (d, J = 2.0 Hz, C(9)), 38.7 (d, J = 10.1 Hz, C(8)), 35.5 (d, J = 6.3 Hz, C(8')), 30.3 (d, J = 4.7 Hz, C(7)), 26.7 (C(7)), 20.0 (C(10)), 19.8 (C(11))

^{31}P NMR: (202 MHz, CDCl$_3$)

δ 89.4, $J_{\text{P–Se}}$ = 818 Hz

IR: (ATR, cm^{-1})

2934 (w), 2858 (w), 1665 (m), 1590 (w), 1510 (w), 1451 (m), 1380 (w), 1278 (s), 1239 (s), 1223 (s), 1155 (s), 1088 (m), 1055(m), 1027 (s), 1001 (m), 920 (m), 892 (w), 846 (w), 819 (s), 784 (m), 755 (m), 734 (m), 701 (s), 688 (m), 636 (s), 615 (s)

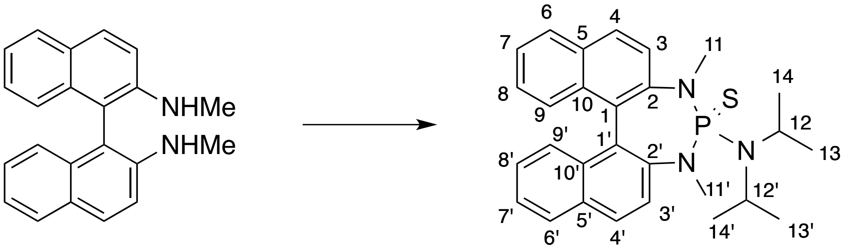
HRMS: calcd for $C_{22}H_{31}N_3PSe$: 448.1425, found: 448.1421

TLC: R_f = 0.52 (hexane/EtOAc, 4:1)

Analysis: $C_{22}H_{30}N_3PSe$ (446.44)

Calcd:	C, 59.19;	H, 6.77;	N, 9.41
Found:	C, 59.50;	H, 6.65;	N, 9.12

Preparation of 4-(Diisopropylamino)-3,5-dimethyl-3,5-dihydrodinaphtho[2,1-*d*:1',2'-*f*][1,3,2] diazaphosphepine 4-sulfide ((±)-3b)



(±)-**S2** (±)-**3b**

By analogy to a literature procedure,[15] a flame-dried Schlenk flask equipped with a magnetic stir bar and an argon inlet was evacuated and backfilled with argon (2 ×). The flask was charged with (±)-dimethyl BINAM ((±)-**S2**) (960 mg, 3.07 mmol) and THF (20.5 mL), and the solution was cooled to –72 °C (internal temperature) using a dry-ice/acetone bath. *n*-BuLi

(1.55 M solution in hexane, 4.00 mL, 6.20 mmol, 2.02 equiv) was added dropwise over 10 min yielding a yellow-black suspension. The mixture was warmed to 22 °C (internal temperature), stirred at this temperature for 30 min and cooled again to –72 °C. To the cooled mixture was added a freshly prepared solution of *i*-Pr_2N–PCl_2[5] (655 mg, 3.24 mmol, 1.06 equiv) and THF (5.2 mL) dropwise over 10 min and the mixture was warmed to 22 °C. After 45 min, sulfur powder (296 mg, 9.23 mmol, 3.00 equiv) was added at room temperature and stirring under argon was continued for 52 h. The resulting brown solution was filtered through a pad of Celite®, which was rinsed with EtOAc (100 mL). The filtrate was concentrated in vacuo (20–23 °C, 20 mmHg) yielding a brown solid. Purification by flash column chromatography (SiO_2, 140 g, 45 mm ∅, hexane/Et_2O = 60:1→30:1) afforded an off-white solid (671 mg), which was recrystallized from EtOAc/hexane to give (±)-**3b** (616 mg, 42%) as a white, crystalline compound. Traces EtOAc could not be removed from the product even when using Abderhalden's drying pistol. The product was dissolved in a minimal amount of benzene and EtOAc was removed azeotropically. Traces benzene (4%) could not be removed from the product.

Data for (±)-**3b**:

mp: 272–274 °C (benzene)

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

δ 7.99 (d, *J* = 8.9 Hz, 1H, HC(4,4')), 7.92 (d, *J* = 8.9 Hz, 1H, HC(4',4)), 7.90 (d, *J* = 8.5 Hz, 1H, HC(6)), 7.87 (d, *J* = 8.1 Hz, 1H, HC(6)), 7.70 (d, *J* = 8.8 Hz, 1H, HC(3)), 7.66 (d, *J* = 9.0 Hz, 1H, HC(3')), 7.42 (t, *J* = 7.2 Hz, 1H, HC(7)), 7.35 (t, *J* = 7.2 Hz, 1H, HC(7')), 7.29 (d, *J* = 8.5 Hz, 1H, HC(9)), 7.23 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1H, HC(8)), 7.11 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, HC(8')), 6.98 (d, *J* = 8.6 Hz, 1H, HC(9')), 3.57–3.34 (m, 2H, HC(12), HC(12')), 3.28 d, *J* = 11.7 Hz, 3H, HC(11)), 3.12 d, *J* = 13.3 Hz, 3H, HC(11')), 1.67–1.00 (br, 12H, HC(13), HC(13'), HC(14), HC(14'))

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

δ 143.7 (d, *J* = 4.4 Hz, C(2,2')), 142.3 (d, *J* = 2.0 Hz, C(2',2)), 132.7 (C(aryl)), 132.3 (C(aryl)), 131.3 (C(aryl)), 130.6 (C(aryl)), 129.1 (C(4,4')), 128.3 (C(4',4)), 128.2 (C(6,6')), 128.1 (C(6',6)), 127.73 (C(9)), 127.67 (d, *J* = 2.5 Hz, C(1,1')), 127.62 (d, *J* = 3.9 Hz, C(1',1)), 127.4 (C(9')), 125.9 (C(8)), 125.6 (C(8')), 124.9 (C(7)), 124.7

(C(7')), 122.8 (d, *J* = 2.1 Hz, C(3,3')), 122.5 (C(3',3)), 47.6 (br, C(12), C(12')), 36.8 (d, *J* = 11.1 Hz, C(11,11')), 36.3 (d, *J* = 5.3 Hz, C(11',11)), 24.7 (C(13,13')), 22.3 (br, C(14,14'))

^{31}P NMR: (202 MHz, $CDCl_3$)
δ 82.5

IR: 2975 (w), 2924 (w), 1616 (w), 1593 (w), 1505 (w), 1465 (w), 1407 (w), 1363 (w), 1326 (w), 1277 (w), 1259 (w), 1244 (w), 1177 (m), 1143 (m), 1117 (m), 1086 (m), 1025 (w), 1002 (w), 988 (s), 932 (s), 921 (s), 851 (m), 815 (s), 747 (s), 703 (s), 678 (s)

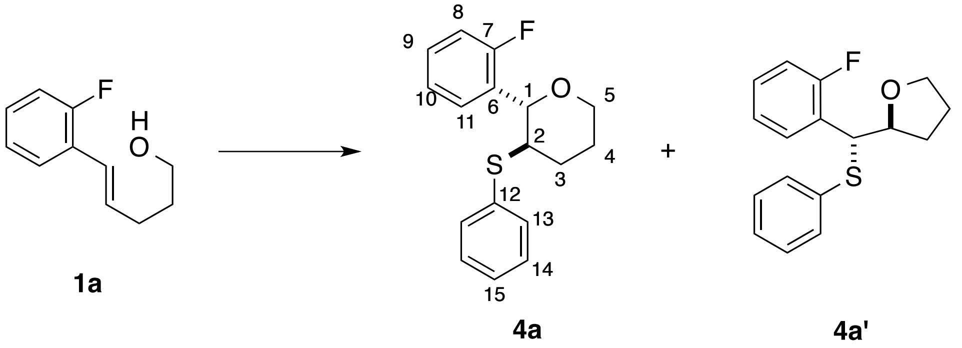
MS: (ESI)
474 (M+H)

HRMS: calcd for $C_{28}H_{33}N_3PS^+$: 474.2133, found: 474.2130

TLC: R_f 0.42 (hexanes/EtOAc, 10:1)

Analysis: $C_{28}H_{32}N_3PS$ (473.62)
Calcd: C, 71.01; H, 6.81; N, 8.87
Found: C, 71.21; H, 6.84; N, 8.62

Preparation of (2*S*,3*R*)-2-(2-Fluorophenyl)-3-(phenylthio)tetrahydro-2H-pyran (4a) and (*S*)-2-((*R*)-(2-fluorophenyl)(phenylthio)methyl)tetrahydrofuran (4a')



To a 10-mL Schlenk flask was added 5-(2-fluorophenyl)-pent-4-en-1-ol (**1a**)[3] (180 mg, 1.00 mmol), sulfenylating agent **2a** (256 mg, 1.00 mmol, 1.00 equiv), (*S*)-**3c** (52.2 mg, 0.100 mmol, 0.100 equiv). To this was added CH_2Cl_2 (7 mL) and the flask was cooled to 0 °C. Neat, dry MsOH (48 μL, 0.75 mmol, 0.75 equiv) was added via syringe. The reaction was stirred for 24 h at 0 °C and then was quenched with Et_3N (200 μL). The resulting white suspension was concentrated in vacuo (20–23 °C, 20 mmHg). The residue was taken up in a minimal amount of chloroform and the compound was purified by column chromatography (SiO_2, 140 g, 20 mm ∅ × 22 cm, hexane/EtOAc, 20:1) to afford 227 mg (79%) of a 20:1 mixture of **4a** and **4a'**. An analytically pure sample was obtained by Kugelrohr distillation.

Data for **4a**:

bp: 130 °C (ABT), 0.4 mmHg

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

δ 7.36 (td, *J* = 7.4, 1.8 Hz, 1H, HC(11)), 7.25–7.10 (m, 6H, HC(9), HC(13), HC(14), HC(15)), 7.05 (td, *J* = 7.6, 1.2 Hz, 1H, H(C(10)), 6.96 (ddd, *J* = 9.6, 8.3, 1.2 Hz, 1H, HC(8)), 4.57 (d, *J* = 10.3 Hz, 1H, HC(1)), 4.08 (ddt, *J* = 11.4, 4.8, 1.7 Hz, 1H, HC(5)), 3.57 (td, *J* = 11.8, 2.2 Hz, 1H, HC(5)), 3.33 (ddd, *J* = 12.0, 10.3, 4.0 Hz, 1H, HC(2)), 2.33 (dtd, *J* = 12.9, 4.7, 2.7 Hz, 1H, HC(3)), 1.91–1.82 (m, 1H, HC(4)), 1.75–1.71 (m, 1H, HC(4)), 1.68 (dd, *J* = 12.5, 4.1 Hz, 1H, HC(3))

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

δ 160.5 (d, *J* =247 Hz, C(7)), 133.5 (C(12)), 133.2 (C(14)), 129.6 (d, *J* = 8.7 Hz, HC(11)), 128.8 (d, *J* = 4.2 Hz, HC(10)), 128.5 (C(13)), 127.3 (d, *J* = 11.3 Hz, C(6)) 127.2 (C(15)), 124.0 (d, *J* = 3.8 Hz, C(9)), 115.3 (d, *J* = 22.5 Hz, C(8)), 78.4 (C(1)) , 68.6 (C(5)) , 50.0 (C(2)) , 32.2 (C(3)) , 27.0 (C(4))

^{19}F NMR: (476 MHz, $CDCl_3$)

δ 117.4

IR: (NaCl plate)

3059 (w), 2941 (m), 2850 (m), 1619 (w), 1584 (m), 1493 (s), 1453 (m), 1438 (m), 1371 (w), 1300 (w), 1260 (w), 1232 (s), 1190 (m), 1076 (s), 1025 (s), 970 (m), 959 (m), 829 (m), 798 (m), 757 (s)

HRMS: calcd for $C_{17}H_{18}FOS$: 289.1062, found: 289.1062

TLC: R_f = 0.46 (hexane/EtOAc, 4:1)

Opt. Rot. : $[\alpha]_D^{24}$ +14.2 (c = 0.97, $CHCl_3$)

Analysis: $C_{17}H_{17}FOS$ (288.38)

Calcd:	C, 70.80;	H, 5.94;
Found:	C, 70.56;	H, 5.96;

SFC: (2*S*,3*R*)-**4a**, t_R 5.88 min (90.4%); (2*R*,3*S*)-**4a'**, t_R 5.33 min (9.6%) (Chiralpak AD, 5% MeOH in CO_2, 2 mL/min, 200 bar, 40 °C)

Data for **4a'**:

^{1}H NMR: (500 MHz, CDCl$_3$)

Diagnostic signals: δ 4.62 (d, *J* = 6.9 Hz, 1H), 4.38 (dq, *J* = 0.8, 6.7 Hz, 1H), 3.87–3.68 (m, 2H), 2.21–2.12(m, 2H), 1.90–1.82 (m, 2H)

^{19}F NMR: (476 MHz, CDCl$_3$)

δ 118.90

Kinetic Studies (Figure 2)

General Procedure for kinetic experiments: To a dried 5-mm NMR tube, electrophile **2a** and substrate **1a** were added. To this was added 300 μL of a freshly prepared stock solution of a measured amount of catalyst **3a** and fluorobenzene standard (1.0 equiv of standard with respect to substrate) in CDCl$_3$, followed by 400 μL of neat CDCl$_3$. The sample was then inserted into a 400 MHz spectrometer that had been pre-cooled to the appropriate temperature and then allowed to equilibrate for 20 minutes. The sample was then ejected, the corresponding amount of MsOH was added, the sample was shaken for ca. 10 s, reinserted and ^{19}F data collection was begun immediately. Data acquisition parameters were as follows:

Spectral Window : –100 ppm to –130 ppm

pw = 16 μs

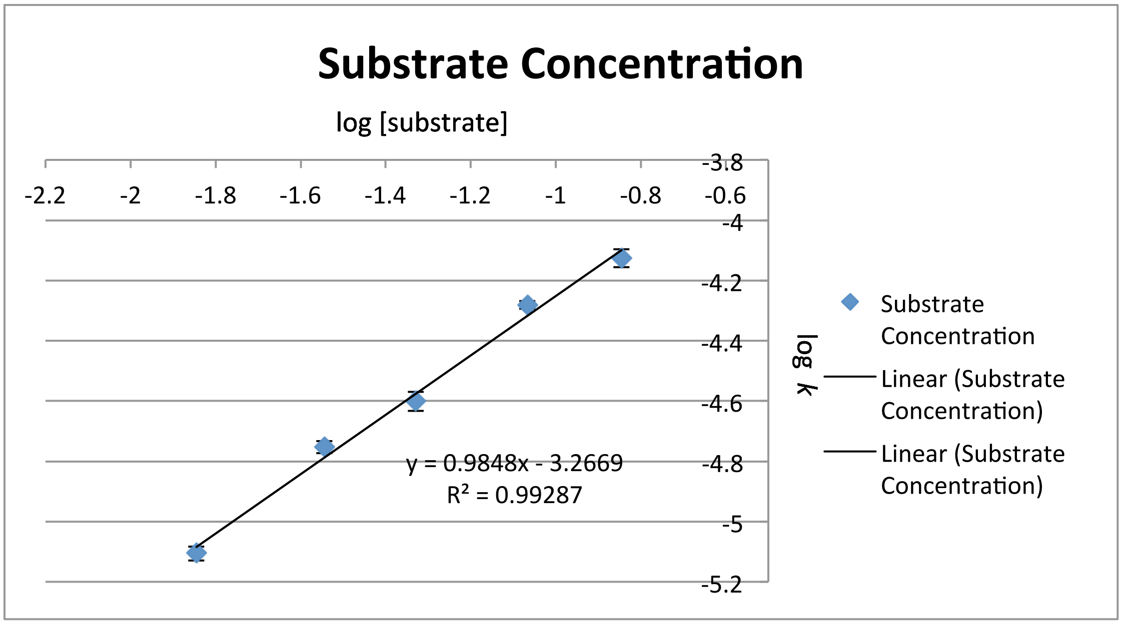
Acquisition Time: 1 s

Delay Time: 9 s

Scans per data point: 4

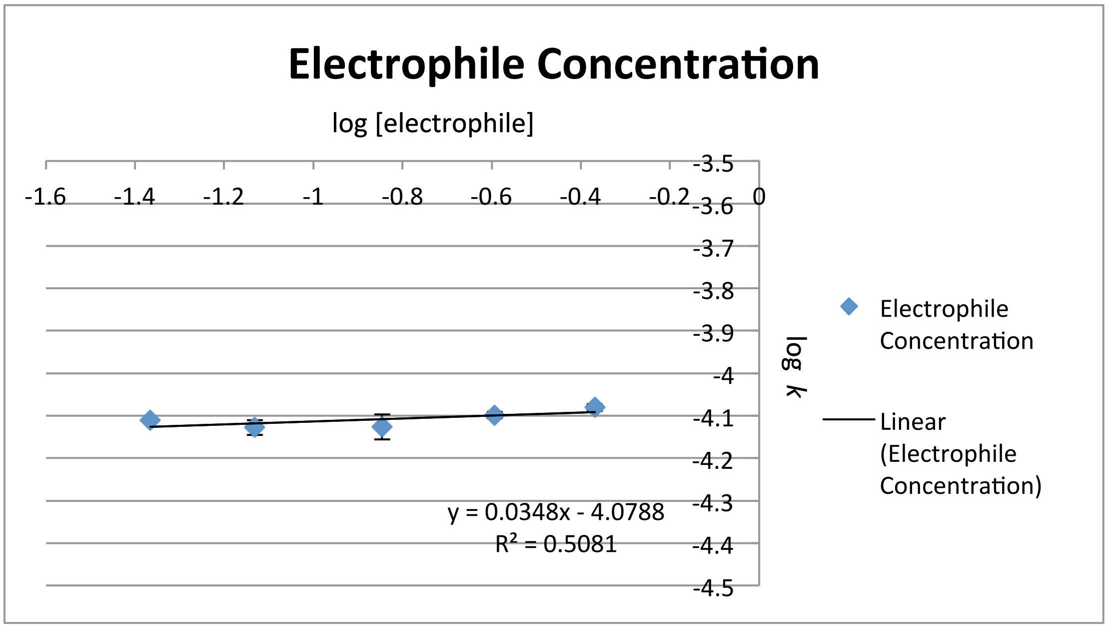
A delay parameter of 20 s was introduced after each data point such that one data point was collected every minute. The reactions were followed to a minimum of 12% conversion, of which the initial 10% was used to determine the initial rate of the reaction. Each experiment was repeated three times and the rates and standard deviations were calculated. Uncertainties are given to one standard deviation. The raw data files are attached as individual Microsoft® Excel sheets.

Dependence of Rate of Reaction on Substrate:



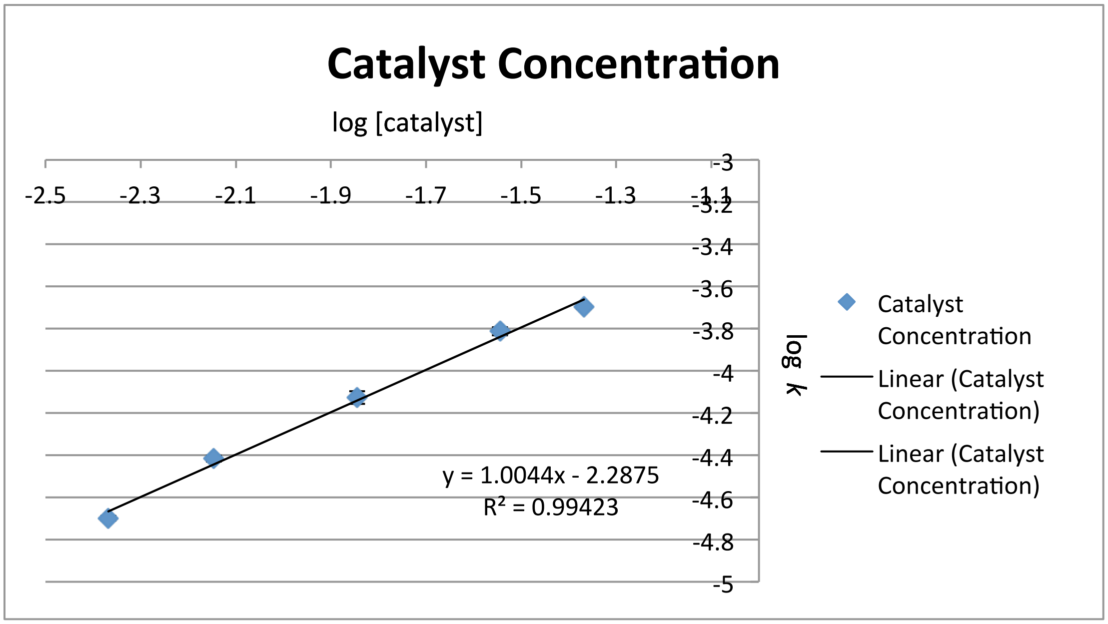
The reaction was found to be first order in substrate.

Dependence of Rate of Reaction on Electrophile:



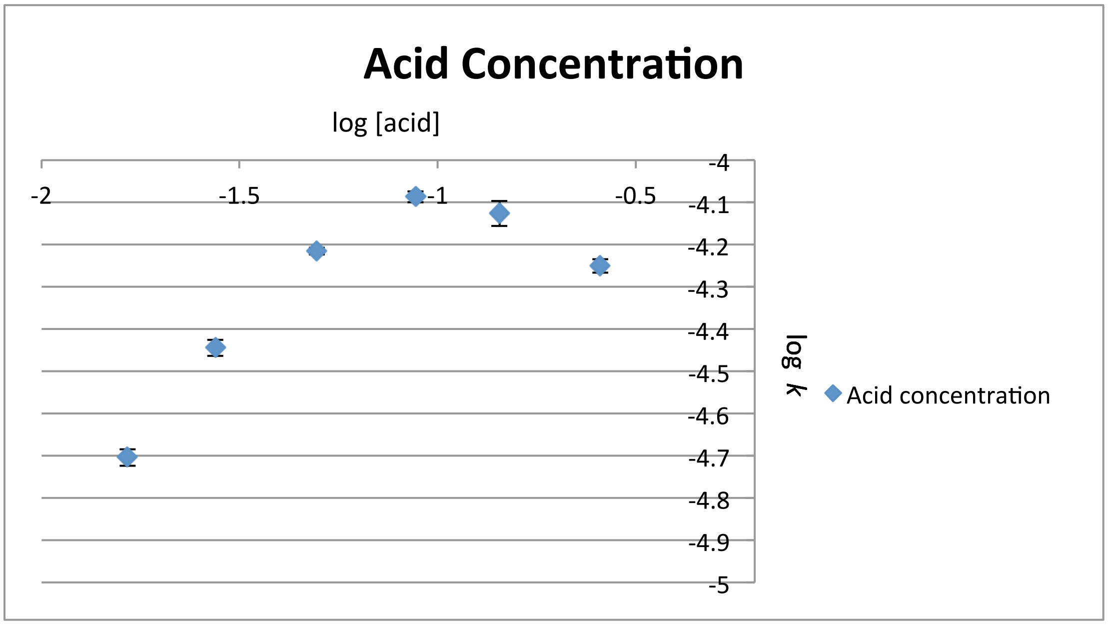
The reaction was found to be zeroth order in electrophile.

Dependence of Rate of Reaction on Catalyst:



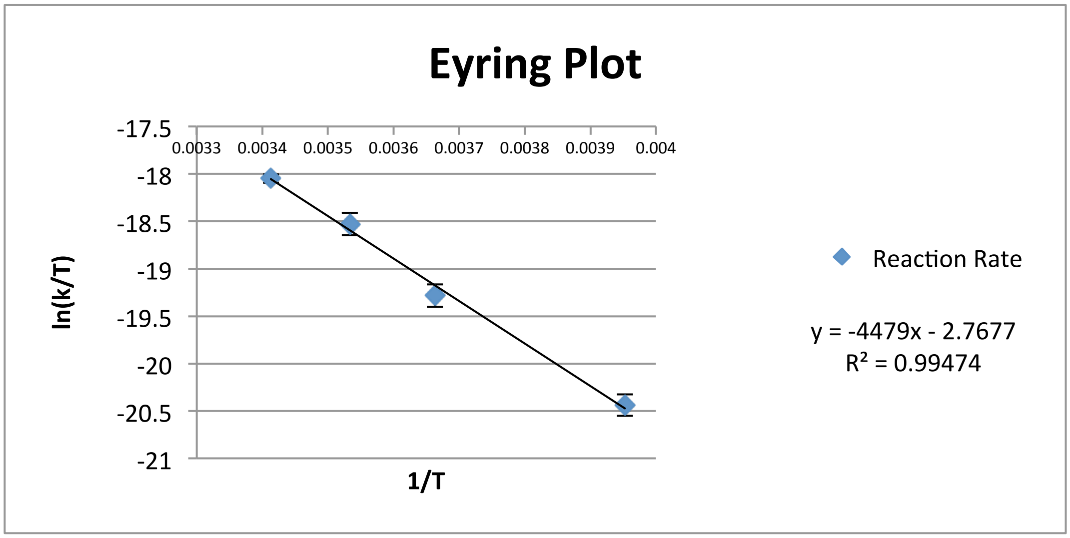
The reaction was found to be first order in catalyst.

Dependence of Rate of Reaction on Acid Concentration:



The reaction was found to have a complicated dependence on the acid concentration, possibly as result of a buffering effect of the alcoholic substrate on free MsOH.

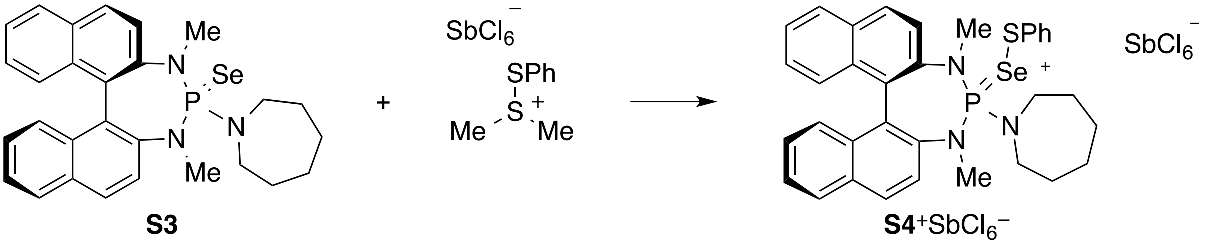
Eyring Analysis of the Activation Energy



The rates at different temperatures were graphed against ln (k/T). The enthalpy of activation was 8.9 ± 0.2 kcal/mol and the entropy was 52.7 ± 0.6 e.u.

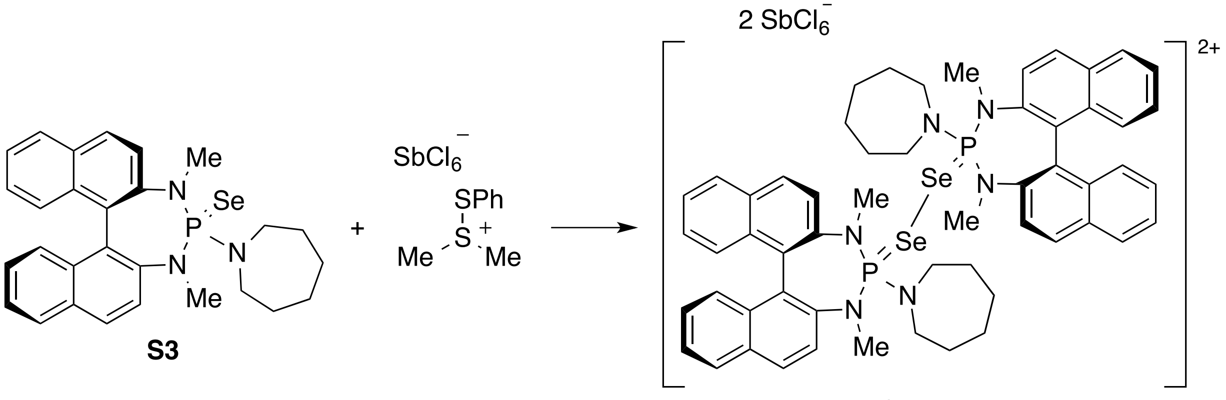
Studies of the Catalytically Active Species 5 (Equations (1)–(3))

Reaction of Selenophosphoramide S3 with [PhS(SMe$_2$)]SbCl$_6$ (Equation (1))



To a solution of **S3** (30 mg 0.06 mmol) in DME (200 µL) was added [PhS(SMe$_2$)]SbCl$_6$ (30 mg, 0.058 mmol). The solution was layered with benzene (1 mL). Precipitation was observed. The solids were partially dissolved in CDCl$_3$. A 4:1 ratio of two ^{31}P NMR resonances at 62.4 ppm and 58.3 ppm respectively was observed.

Disproportionation Upon Attempted Crystallization of Active Species S4 (Equation (2))



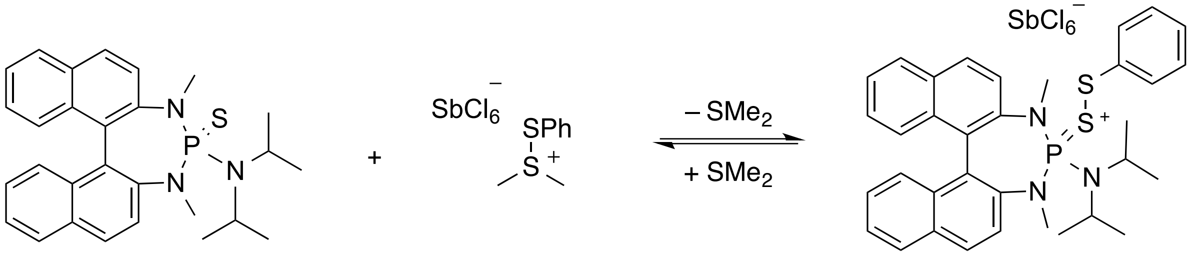
S3

S5^{2+}2SbCl$_6^-$
(X-ray crystal structure)

In a glovebox, **S3** (50 mg, 0.098 mmol) and [PhS(SMe$_2$)]SbCl$_6$ (48 mg, 0.097 mmol) were added to a 5-mm NMR tube. The material was dissolved in DME (250 μL) and layered with benzene (1 mL). Upon standing for 24 h, orange, air-stable crystals were observed. These were harvested and submitted for X-ray analysis.

Reactions of Thiophosphoramide (±)-3b with [PhS(SMe$_2$)]SbCl$_6$ (Equation (3))

With 1.0 equiv [PhS(SMe$_2$)]SbCl$_6$:



(±)-**3b** (±)-**5b**$^+$SbCl$_6^-$

(1.0 equiv) (1.0 equiv) ^{31}P NMR: 69.3 ppm

In a glove box, an oven-dried 6 dram vial was charged with (±)-**3b** (15.2 mg, 32.1 μmol) and [PhS(SMe$_2$)]SbCl$_6$ (16.4 mg, 32.4 μmol, 1.01 equiv) and capped with a septum. Outside of the glove box, the vial was connected to a Schlenk line, and CD$_3$CN (0.50 mL) as well as CDCl$_3$ (0.25 mL) were added at room temperature resulting in the formation of a yellow solution. Using a syringe, the mixture was transferred into an oven-dried, 5-mm NMR tube, which had previously been evacuated and backfilled with argon (2 ×). After 10 min ^{1}H and ^{31}P NMR spectra were recorded.

Data for the equilibrium:

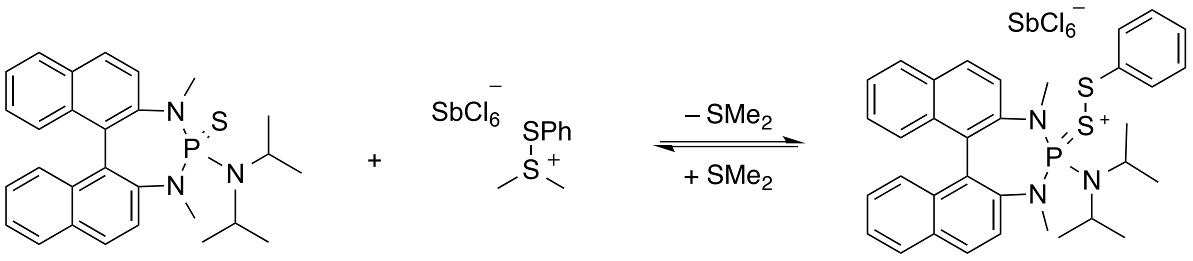
^{1}H NMR: (500 MHz, CD$_3$CN/CDCl$_3$, 2:1)

δ 8.13 (d, *J* = 9.6 Hz, 1H, HC(aryl)), 8.11 (d, *J* = 9.7 Hz, 1H, H(C-aryl)), 8.02 (d, *J* = 8.4 Hz, 1H, HC(aryl)), 8.00 (d, *J* = 8.4 Hz, 1H, HC(aryl)), 7.85 (d, *J* = 9.0 Hz, 1H, HC(aryl)), 7.72 (d, *J* = 8.9 Hz, 1H, HC(aryl)), 7.56–7.40 (m, 2H, HC(aryl)), 7.37–7.24 (m, 3H, HC(aryl)), 7.18 (t, *J* = 7.8 Hz, 2H, HC(aryl)), 7.07 (d, *J* = 8.6 Hz, 1H, HC(aryl)), 7.04 (d, *J* = 8.6 Hz, 1H, HC(aryl)), 6.94 (d, *J* = 7.8 Hz, 2H, HC(aryl)), 3.74–3.59 (m, 2H, 2 × NC*H*(CH$_3$)$_2$), 3.29 (d, *J* = 13.4 Hz, 3H, NC*H*$_3$), 2.85 (d, *J* = 12.9 Hz, 3H, NC*H*$_3$), 2.23 (s, 6H, S(C*H*$_3$)$_2$), 1.36 (d, *J* = 7.1 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.34 (d, *J* = 6.9 Hz, 6H, NCH(C*H*$_3$)$_2$))

^{31}P NMR: (202 MHz, CDCl$_3$)

δ 69.3

With 5.0 equiv [PhS(SMe$_2$)]SbCl$_6$:



(±)-**3b** (1.0 equiv) (5.0 equiv) ^{31}P NMR: 66.4 ppm (±)-**5b**$^+$SbCl$_6^-$

In a glove box, an oven-dried 6 dram vial was charged with (±)-**3b** (7.10 mg, 15.0 µmol) and [PhS(SMe$_2$)]SbCl$_6$ (37.9 mg, 74.9 µmol, 4.99 equiv) and capped with a septum. Outside of the glove box, the vial was connected to a Schlenk line, and CD$_3$CN (0.50 mL) as well as CDCl$_3$ (0.25 mL) were added at room temperature resulting in the formation of a turbid, yellow solution. Using a syringe, the mixture was transferred into an oven-dried, 5-mm NMR tube, which had previously been evacuated and backfilled with argon (2 ×). After 10 min ^{1}H and ^{31}P NMR spectra were recorded.

Data for the equilibrium:

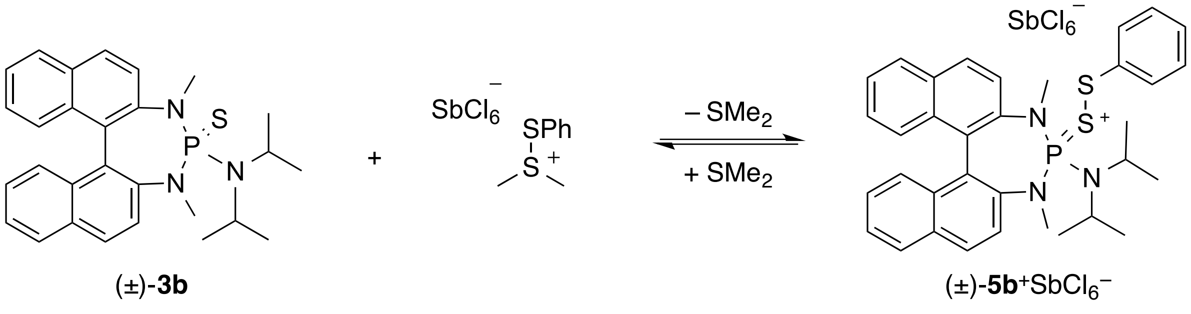
^{1}H NMR: (500 MHz, $CD_3CN/CDCl_3$, 2:1)

δ 8.18 (d, *J* = 9.5 Hz, 1H, HC(aryl)), 8.16 (d, *J* = 10.0 Hz, 1H, HC(aryl)), 7.91 (d, *J* = 8.9 Hz, 1H, HC(aryl)), 7.74 (d, *J* = 9.0 Hz, 1H, HC(aryl)), 7.71–7.48 (m, 24H, HC(aryl)), 7.37–7.26 (m, 3H, HC(aryl)), 7.07 (d, *J* = 8.4 Hz, 1H, HC(aryl)), 7.06 (d, *J* = 8.3 Hz, 1H, HC(aryl)), 3.79–3.67 (m, 2H, 2 × $NC\underline{H}(CH_3)_2$), 3.34 (d, *J* = 13.5 Hz, 3H, $NC\underline{H}_3$), 2.76 (d, *J* = 13.2 Hz, 3H, $NC\underline{H}_3$), 2.71 (s, 30H, $S(C\underline{H}_3)_2$), 1.36 (d, *J* = 6.8 Hz, 6H, $NCH(C\underline{H}_3)_2$), 1.35 (d, *J* = 6.7 Hz, 6H, $NCH(C\underline{H}_3)_2$)

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

δ 66.4

With 0.2 equiv $[PhS(SMe_2)]SbCl_6$:



(1.0 equiv) (0.2 equiv) ^{31}P NMR: 77.9 ppm

In a glove box, an oven-dried 6 dram vial was charged with (±)-**3b** (35.7 mg, 75.3 µmol) and $[PhS(SMe_2)]SbCl_6$ (7.6 mg, 15 µmol, 0.20 equiv) and capped with a septum. Outside of the glove box, the vial was connected to a Schlenk line, and CD_3CN (0.50 mL) as well as $CDCl_3$ (0.25 mL) were added at room temperature resulting in the formation of a turbid, yellow suspension. Using a syringe, the mixture was transferred into an oven-dried, 5-mm NMR tube that had previously been evacuated and backfilled with argon (2 ×). After 10 min ^{1}H and ^{31}P NMR spectra were recorded. Since (±)-**3b** did not completely dissolve under these conditions, the actual ratio of the two reactants in solution was determined to be: (±)-**3b**/$[PhS(SMe_2)]SbCl_6$ ≈ 3.5:1.

Data for the equilibrium:

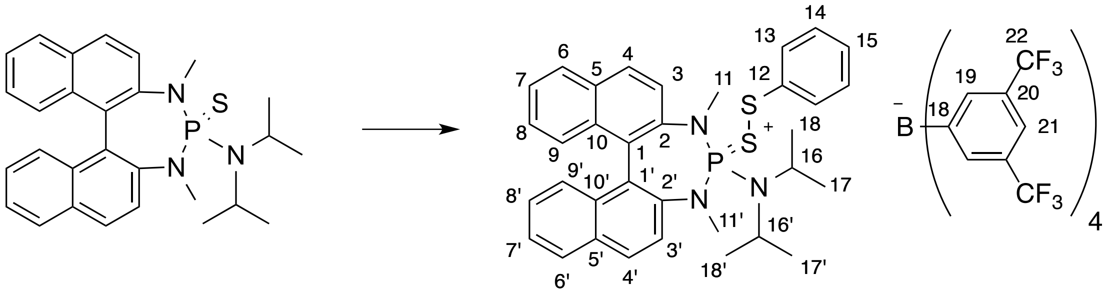
^{1}H NMR: (500 MHz, CD$_3$CN/CDCl$_3$, 2:1)

δ 8.05 (d, *J* = 8.0 Hz, 1H, HC(aryl)), 8.04 (d, *J* = 7.9 Hz, 1H, HC(aryl)), 7.96 (d, *J* = 8.0 Hz, 1H, HC(aryl)), 7.95 (d, *J* = 7.4 Hz, 1H, HC(aryl)), 7.75 (d, *J* = 8.8 Hz, 1H, HC(aryl)), 7.74 (d, *J* = 8.9 Hz, 1H, HC(aryl)), 7.48–7.37 (m, 2H, H(C-aryl)), 7.30–7.07 (m, 4H, HC(aryl)), 6.96 (d, *J* = 8.4 Hz, HC(aryl)), 6.82 (d, *J* = 7.7 Hz, HC(aryl)), 3.59–3.42 (m, 2H, 2 × NC$\underline{H}$(CH$_3$)$_2$), 3.17 (d, *J* = 13.4 Hz, 3H, NC$\underline{H}_3$), 3.09 (d, *J* = 12.2 Hz, 3H, NC$\underline{H}_3$), 2.11 (s, S(C$\underline{H}_3$)$_2$), 1.39 (br s, 6H, NCH(C$\underline{H}_3$)$_2$), 1.31 (br s, 6H, NCH(C$\underline{H}_3$)$_2$)

^{31}P NMR: (202 MHz, CDCl$_3$)

δ 77.9

Preparation of *N*,*N*-Diisopropyl-3,5-dimethyl-4-(2-phenyl-1λ^3-disulfanyl-idene)-3,5-dihydro-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]diazaphosphepin-4-amine, tetrakis(3,5-bis(trifluoromethyl) phenyl)borate salt ((±)-5b$^+$BArF$_{24}^-$) (Figure 3a)



(±)-**3b** (±)-**5b**$^+$ BArF$_{24}^-$

An oven-dried, two-necked, round-bottomed flask equipped with a magnetic stir bar was charged with (±)-**3b** (146 mg, 0.308 mmol) and NaBArF$_{24}$ (273 mg, 0.308 mmol, 1.00 equiv). The flask was evacuated, backfilled with argon (2 ×) and CH$_2$Cl$_2$ (5.0 mL) was added resulting in the formation of a white suspension. The reaction mixture was cooled to 0 °C (external temperature) using an ice/water bath, and PhSCl (35.0 μL, 0.304 mmol, 0.99 equiv) was added neat affording a brown, turbid solution. The mixture was stirred at 0 °C for 10 min and warmed to room temperature. Stirring was continued for 1 h during which the formation of a fine precipitate (NaCl) was observed. A second oven-dried, two-neck round-bottom flask was evacuated and backfilled with argon (1 ×) and used as a receiver flask for transferring the supernatant from the reaction flask. The transfer of the supernatant was accomplished using a syringe cannula. For that purpose, the end of the cannula (where usually the syringe is attached) was wrapped with a glass fiber filter (Fisher brand, G6), which was tied up with Teflon tape. This end was put into the reaction flask (without touching the suspension yet) and the sharp end was placed into the receiver flask. To moisten the glass fiber filter, CH_2Cl_2 (2.0 mL) was added to the receiver flask and transferred into the reaction flask. After this, the supernatant was transferred from the reaction flask into the receiver flask (by applying vacuum to the receiver flask). The reaction flask was rinsed with CH_2Cl_2 (2 × 3 mL) and the washings were transferred to the receiver flask. The cannula was removed from the receiver flask and the solvent was evaporated slowly (using the vacuum from the Schlenk line) to give a brown oil. Pentane (5.0 mL) was added and removed on high vacuum to give (±)-**5b**$^+$ BArF24$^-$ (399 mg, 90%) as a pale yellow, fluffy solid. Crystals suitable for single crystal X-ray diffraction were obtained by dissolving (±)-**5b**$^+$ BArF24$^-$ (120 mg) in CH_2Cl_2 (70 μL) followed by slow evaporation of the solvent at room temperature.

Data for (±)-**5b**$^+$ BArF24$^-$:

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

δ 8.13 (d, *J* = 9.0 Hz, 1H, HC(4,4')), 8.05 (d, *J* = 9.0 Hz, 1H, HC(4',4)), 8.01 (d, *J* = 8.1 Hz, 1H, HC(6,6')), 7.93 (d, *J* = 8.1 Hz, 1H, HC(6',6)), 7.74 (d, *J* = 9.2 Hz, 1H, HC(aryl)), 7.75 (br s, 8H, HC(19)), 7.61–7.48 (m, 3H, HC(aryl)), 7.55 (br s, 4H, HC(21)), 7.39 (t, *J* = 7.7 Hz, 1H, HC(aryl)), 7.32 (t, *J* = 7.6 Hz, 1H, HC(aryl)), 7.19 (t, *J* = 7.5 Hz, 1H, HC(aryl)), 7.12 (t, *J* = 8.4 Hz, 2H, HC(aryl)), 7.03 (t, *J* = 7.8 Hz, 2H, HC(aryl)), 6.71 (d, *J* = 7.8 Hz, 2H, HC(aryl)), 3.72–3.57 (m, 2H, HC(16), HC(16')), 3.33 (d, *J* = 13.4 Hz, 3H, HC(11,11')), 2.69 (d, *J* = 13.2 Hz, 3H, HC(11',11)), 1.32 (d, *J* = 6.8 Hz, 6H, HC(17,17')), 1.30 (d, *J* = 6.9 Hz, 6H, HC(18,18'))

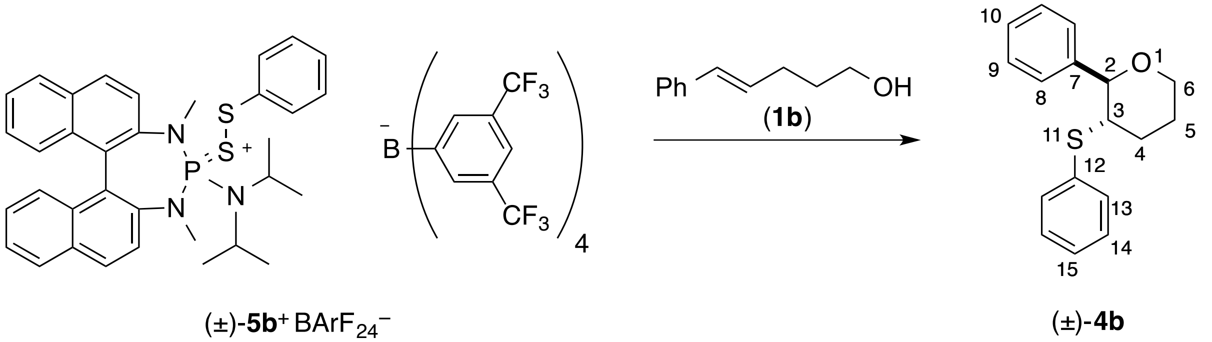
^{13}C NMR: (125 MHz, $CDCl_3$)

δ 161.8 (q, *J* = 49.9 Hz, (C(20)), 138.7 (C(aryl)), 137.4 (C(aryl)), 134.8 (C(aryl)), 134.2 (C(aryl)), 132.8 (C(aryl)), 132.6 (C(aryl)), 132.5 (C(aryl)), 132.1 (C(aryl)), 131.8 (C(aryl)), 131.6 (C(aryl)), 131.5 (C(aryl)), 131.4 (C(aryl)), 130.6 (C(aryl)), 129.7 (C(aryl)), 128.9 (qq, *J* = 32.8, 2.9 Hz, C(19)), 128.6 (C(aryl)), 128.4 (C(aryl)), 127.9 (C(aryl)), 127.6 (C(aryl)), 127.2 (C(aryl)), 125.7 (C(aryl)), 124.6 (q, *J* = 272 Hz, C(22)), 122.3 (C(aryl)), 120.4 (C(aryl)), 117.5 (C(aryl)), 50.5 (C(16), C(16')), 37.9 (br s, (C(11,11')), 37.7 (d, J = 11.0 Hz, C(11',11)), 23.8 (C(17)), 23.0 (C(18))

<u>^{31}P NMR:</u> (202 MHz, $CDCl_3$)

δ 65.8

Stoichiometric Sulfenoetherification of 1b Using Active Species (±)-5b$^+$BArF$_{24}^-$ (Figure 3a)



(±)-**5b**$^+$ BArF$_{24}^-$ (±)-**4b**

An oven-dried, 5-mm NMR tube was charged with (±)-**5b**$^+$ BArF24$^-$ (95 mg, 66 μmol, 1.1 equiv) and $CDCl_3$ (0.70 mL) affording a brown solution. At room temperature, substrate **1b** (10 mg, 62 μmol) was added neat using a syringe, and the tube was shaken well. The reaction mixture was kept at room temperature and conversion was monitored by the appearance of a diagnostic ^{1}H NMR resonance for the product at 4.14 ppm (doublet) with respect to the alkene peaks of the substrate at 6.23 and 6.43 ppm. After 17 h at room temperature, the reaction proceeded to 90% conversion, and no further consumption of substrate **1b** was observed. The reaction was quenched by addition of Et_3N (0.10 mL) and the crude product was purified by flash column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) to give 12 mg of a 5:1 mixture of (±)-**4b** and Lewis base (±)-**3b**. The spectroscopic data of (±)-**4b** match those published in the literature.[16]

<u>Data for (±)-**4b**:</u>

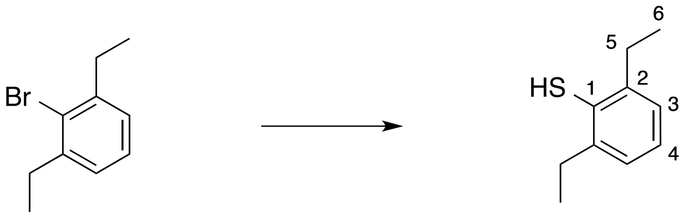
<u>^{1}H NMR:</u> (500 MHz, $CDCl_3$)

δ 7.39–7.35 (m, 2H, HC(8)), 7.31–7.23 (m, 3H, HC(9), HC(10)), 7.16–7.09 (m, 5H, HC(aryl)), 4.20 (d, J = 10.1 Hz, 1H, HC(2)), 4.12–4.06 (m, 1H, HC(6)), 3.57 (ddd, J = 12.9, 12.1, 2.1 Hz, 1H, HC(6)), 3.24 (ddd, J = 11.5, 10.1, 4.0 Hz, 1H, HC(3)), 2.33–2.26 (m, 1H, HC(4)), 1.92–1.80 (m, 1H, HC(5)), 1.76–1.63 (m, 2H, HC(4), HC(5))

Synthesis of Sulfenylating Agents

Synthesis of Thiophenols

Preparation of 2,6-Diethylthiophenol (S7)



S6 **S7**

Thiophenol **S7** was prepared by analogy to a literature procedure used for the synthesis of sterically hindered thiophenols.[17] An oven-dried, three-necked, round-bottomed flask equipped with a magnetic stir bar, a condenser, a dropping funnel and an argon inlet was charged with magnesium filings (502 mg, 20.7 mmol, 1.10 equiv). The apparatus was evacuated, backfilled with argon, and the magnesium filings were covered with THF (6.0 mL). After the addition of a chip of I_2, a solution of 1-bromo-2,6-diethylbenzene (**S6**)[9] (4.00 g, 18.8 mmol) in THF (30 mL) was added dropwise at a rate to maintain the reaction mixture warm. After complete addition, the mixture was heated to reflux for 3 h and then was cooled to room temperature. Sulfur powder (632 mg, 19.7 mmol, 1.05 equiv) was added in several portions over 10 min and the mixture was heated to reflux for another 1.5 h. Upon cooling to room temperature, a suspension of $LiAlH_4$ (358 mg, 9.38 mmol, 0.50 equiv) in THF (6.0 mL) was added dropwise to the brown-yellow reaction mixture until decoloration occurred. The mixture was heated to reflux for 30 min, then was cooled to 0 °C and quenched by *cautious* addition of H_2O. Aqueous HCl (2.0 M) was added until good phase separation was observed. The phases were separated and the aqueous phase extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated in vacuo (20–23 °C, 20 mmHg). Purification by fractional distillation afforded **S7** (2.47 g, 79%) as a colorless oil. The analytical data match those published in the literature.[18]

Data for **S7**:

bp: 79 °C (0.3 mm Hg)

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

δ 7.14–7.06 (m, 3H, HC(3), HC(4)), 3.26 (s, 1H, HS), 2.78 (q, *J* = 7.5 Hz, 4H, HC(5)), 1.28 (t, *J* = 7.5 Hz, 6H, HC(6))

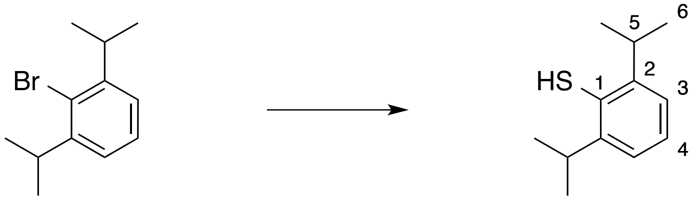
^{13}C NMR: (125 MHz, CDCl$_3$)

δ 142.6 (C(2)), 129.2 (C(1)), 126.2 (C(3)), 125.7 (C(4)), 28.5 (C(5)), 14.0 (C(6))

MS: (ES$^+$, 70 eV)

166 (100, M$^+$), 151 (69), 136 (37), 117 (17), 105 (14), 91 (11), 77 (7)

Preparation of 2,6-Diisopropylthiophenol (S9)



S8 **S9**

Following the protocol described above for the synthesis of thiophenol **S7**, the Grignard reagent was prepared from magnesium filings (1.78 g, 73.3 mmol, 1.10 equiv) in THF (21 mL) and a solution of 1-bromo-2,6-diisopropylbenzene (**S8)**[10] (16.1 g, 66.8 mmol) in THF (107 mL). After addition of sulfur powder (2.25 g, 70.2 mmol, 1.05 equiv), the mixture was heated to reflux for 2 h. Upon cooling to room temperature, a suspension of LiAlH$_4$ (1.27 g, 33.4 mmol, 0.50 equiv) in THF (21 mL) was added dropwise to the brown-yellow reaction mixture until decoloration occurred. The mixture was refluxed for another 30 min and worked up as described above (adjusting the amounts of HCl, Et$_2$O and brine proportionally to the given scale). Purification by fractional distillation afforded **S7** (10.6 g, 82%) as a colorless oil. The spectroscopic data match those published in the literature.[19]

Data for **S9**:

bp: 81 °C (0.3 mm Hg)

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.23–7.13 (m, 3H, HC(3), HC(4)), 3.49 (hept, J = 6.9 Hz, 2H, HC(5)), 3.23 (s, 1H, HS), 1.28 (d, J = 6.9 Hz, 12H, HC(6))

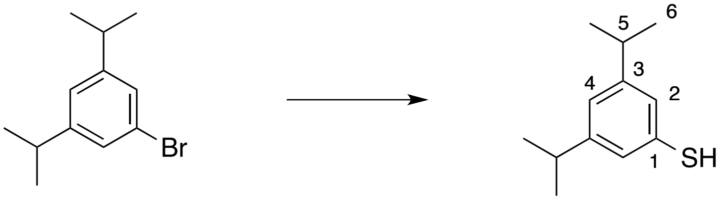
^{13}C NMR: (125 MHz, CDCl$_3$)

δ 147.8 (C(2)), 127.7(C(1)), 126.4(C(4)), 123.1(C(3)), 31.8 (C(5)), 23.1 (C(6))

MS: (ES$^+$, 70 eV)

194 (79, M$^+$), 179 (100), 151 (14), 137 (52), 115 (10), 91 (6)

Preparation of 3,5-Diisopropylthiophenol (S11)



S10 **S11**

Following the protocol described above for the synthesis of thiophenol **S7**, the Grignard reagent was prepared from magnesium filings (134 mg, 5.51 mmol, 1.10 equiv) in THF (1.6 mL) and a solution of 1-bromo-3,5-diisopropylbenzene (**S10**)[11] (1.20 g, 5.00 mmol) in THF (8.0 mL). After addition of sulfur powder (168 mg, 5.25 mmol, 1.05 equiv), the mixture was heated to reflux for 2 h. Upon cooling to room temperature, a suspension of $LiAlH_4$ (95 mg, 2.5 mmol, 0.50 equiv) in THF (1.6 mL) was added dropwise to the brown/yellow reaction mixture until decoloration occurred. The mixture was refluxed for another 30 min and worked up as described above (adjusting the amounts of HCl, Et_2O and brine proportionally to the given scale). Purification by flash column chromatography (SiO_2, 42 g, 35 mm ∅, hexane) afforded pure **S11** (628 mg, 65%) as a colorless oil.

Data for **S11**:

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

δ 6.98 (d, *J* = 1.5 Hz, 2H, HC(2)), 6.88 (d, *J* = 1.6 Hz, 1H, HC(4)), 3.41 (s, 1H, HS), 2.84 (hept, *J* = 6.9 Hz, 2H, HC(5)), 1.24 (d, *J* = 6.9 Hz, 12H, HC(6))

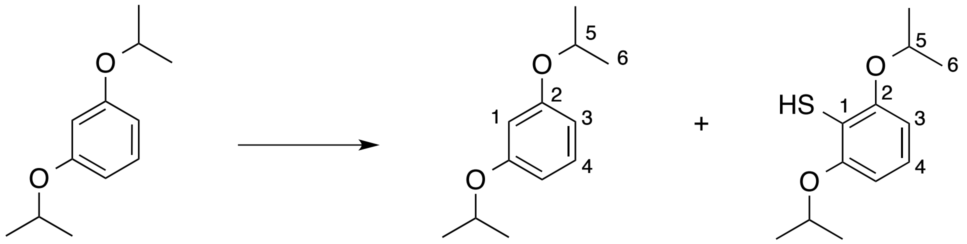
^{13}C NMR: (125 MHz, $CDCl_3$)

δ 149.9 (C(3)), 129.9 (C(1)), 125.0 (C(2)), 122.6 (C(4)), 34.1 (C(5)), 23.9 (C(6))

MS: (ES^+, 70 eV)

194 (86, M^+), 179 (100), 161 (16), 151 (19), 137 (27), 115 (8), 91 (9)

Preparation of 2,6-Diisopropoxythiophenol (S13)



S12 **S12** **S13**

An oven-dried, three-necked, round-bottomed flask equipped with a magnetic stir bar, a condenser and an argon inlet was evacuated and backfilled with argon (2 ×). The flask was charged with 1,3-diisopropoxybenzene[12] (1.00 g, 5.15 mmol, 1.10) and hexane (10 mL). At room temperature, *n*-BuLi (2.45 M solution in hexanes, 2.29 mL, 5.62 mmol, 1.20 equiv) was added dropwise, and the mixture was heated to reflux for 2.5 h. After cooling to room temperature, a suspension of sulfur powder (150 mg, 4.68 mmol, 1.00 equiv) in toluene (4 mL) was added and the mixture was heated to reflux for 16 h. Upon cooling to room temperature, H_2O (15 mL) and then aqueous HCl (2.0 M) was added, the phases were separated and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated in vacuo (20–23 °C, 20 mmHg) affording 1.00 g of a 2:1 mixture of thiophenol **S13** and starting material **S12**. Attempts to separate the mixture by flash column chromatography were unsuccessful so that the mixture was used for the synthesis of corresponding sulfenylating agent **2k**.

Data for **S13**:

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

δ 6.98 (t, *J* = 8.3 Hz, 1H, HC(4)), 6.52 (d, *J* = 8.3 Hz, 2H, HC(3)), 4.57 (hept, *J* = 6.1 Hz, 2H, HC(5)), 4.10 (s, 1H, HS), 1.37 (d, *J* = 6.1 Hz, 12H, HC(6))

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

δ 154.0 (C(2)), 126.4 (C(1)), 124.4 (C(4)), 106.5 (C(3)), 71.5 (C(5)), 22.3 (C(6))

MS: (ES^+, 70 eV)

226 (31, M^+), 184 (5), 142 (100), 113 (8)

Data for **S12**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.14 (t, *J* = 8.1 Hz, 1H, HC(4)), 6.49–6.40 (m, 3H, HC(1)), HC(3)), 4.52 (hept, *J* = 6.1 Hz, 2H, HC(5)), 1.33 (d, *J* = 6.0 Hz, 12H, HC(6))

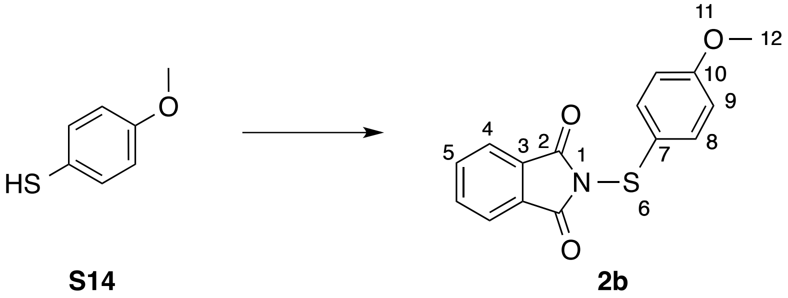
^{13}C NMR: (125 MHz, CDCl$_3$)

δ 159.1 (C(2)), 129.7 (C(4)), 107.9 (C(3)), 104.0 (C(1)), 69.8 (C(5)), 22.1 (C(6))

General Procedure 1: Synthesis of Sulfenylating Agents

The synthesis of sulfenylating agents was accomplished following a procedure from Reese[20] (conditions and yields have not been optimized for the individual sulfenylating agent). An oven-dried, three-necked, round-bottomed flask equipped with a magnetic stir bar, a dropping funnel and a gas outlet (to the rear of the hood) was charged with phthalimide and the corresponding thiophenol (1.05 equiv). MeCN (2.6 M) and pyridine (1.3 M) were added and the white suspension was heated to 80 °C (bath temperature) for 5 min resulting in a colorless solution. The mixture was cooled to 0 °C (internal temperature: 5 °C) forming a white suspension again. At this point, a solution of Br$_2$ (1.10 equiv) in MeCN (2.2 M) was added dropwise over a period of 1 h maintaining the internal temperature below 8 °C. Upon complete addition, the reaction mixture was stirred at 0 °C for the indicated time. Then, H$_2$O was added dropwise over 30 min, stirring was stopped, and the mixture was allowed to stand for 20 min at 0 °C. The resulting suspension was filtered using a glass frit and the solid product was washed with pre-cooled MeOH (0 °C, 4 ×) affording the crude product. Purification was accomplished by silica gel column chromatography and/or recrystallization.

Preparation of 2-((4-Methoxyphenyl)thio)isoindoline-1,3-dione (2b)



Following General Procedure 1, a suspension of phthalimide (999 mg, 6.79 mmol) and 4-methoxythiophenol (**S14**) (1.00 g, 7.13 mmol, 1.05 equiv) in MeCN (4.5 mL) and pyridine

(5.7 mL) was treated with a solution of Br_2 (0.40 mL, 7.8 mmol, 1.1 equiv) in MeCN (3.5 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (25 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 8 mL) yielded pure **2b** (1.76 g, 91%) as a yellow solid. Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture. The spectroscopic data match those published in the literature.[21]

Data for **2b**:

mp: 202–204 °C (hexane/CH_2Cl_2)

^{1}H NMR: (500 MHz, $CDCl_3$)
δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.76 (d, *J* = 8.8 Hz, 2H, HC(8)), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 6.84 (d, *J* = 8.8 Hz, 2H, HC(9)), 3.77 (s, 3H, HC(12))

^{13}C NMR: (125 MHz, $CDCl_3$)
δ 167.8 (C(2)), 161.4 (C(10)), 136.6 (C(8)), 134.5 (C(5)), 132.1 (C(3)), 125.4 (C(7)), 123.8 (C(4)), 114.6 (C(9)), 55.4 (C(12))

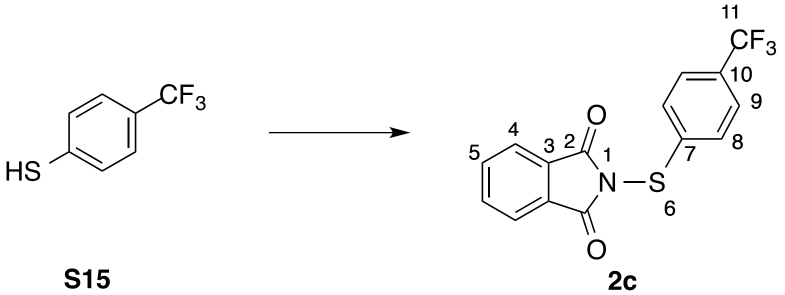
IR: (neat)
1778 (m), 1729 (s), 1704 (s), 1588 (m), 1567 (m), 1492 (m), 1466 (m), 1447 (m), 1408 (w), 1362 (w), 1345 (m), 1299 (m), 1276 (s), 1252 (s), 1171 (m), 1104 (w), 1089 (m), 1047 (s), 1025 (s), 866 (m), 831 (s), 800 (m), 711 (s)

MS: (ES^+, 70 eV)
285 (100, M^+), 270 (11), 139 (32)

HRMS: calcd for $C_{15}H_{12}NO_3S^+$: 286.0538, found: 286.0538

TLC: R_f 0.24 (hexane/EtOAc, 4:1) [CAM]

Preparation of 2-((4-(Trifluoromethyl)phenyl)thio)isoindoline-1,3-dione (2c)



Following General Procedure 1, a suspension of phthalimide (547 mg, 3.72 mmol) and 4-(trifluoromethyl)thiophenol (**S15**) (696 mg, 3.91 mmol, 1.05 equiv) in MeCN (2.5 mL) and pyridine (3.0 mL) was treated with a solution of Br_2 (0.23 mL, 4.5 mmol, 1.2 equiv) in MeCN (1.8 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and subsequently quenched by dropwise addition of H_2O (15 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 3 × 6 mL) afforded the crude product that was purified by column chromatography (SiO_2, 65 g, 45 mm ∅, hexane/EtOAc/CH_2Cl_2, 5:1:1) yielding pure **2c** (516 mg, 43%) as an off-white solid. Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

Data for **2c**:

mp: 152–154 °C (hexane/CH_2Cl_2)

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

δ 7.97 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 7.59–7.48 (m, 4H, HC(8), HC(9))

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

δ 167.3 (C(2)), 140.1 (C(7)), 135.0 (C(5)), 131.8 (C(3)), 130.3 (q, *J* = 32.8 Hz, C(10)), 127.9 (C(8)), 126.20 (q, *J* = 3.7 Hz, C(9)), 124.3 (C(4)), 123.7 (q, *J* = 272 Hz, C(11))

^{19}F NMR: (470 MHz, $CDCl_3$)

δ –63.2

IR: (neat)

1790 (m), 1744 (s), 1716 (s), 1607 (m), 1499 (w), 1468 (m), 1403 (m), 1357 (w), 1324 (s), 1274 (s), 1263 (m), 1167 (m), 1110 (s), 1090 (s), 1062 (s), 1036 (s), 1009 (m), 970 (w), 950 (w), 866 (m), 833 (m), 825 (m), 788 (m), 707 (s)

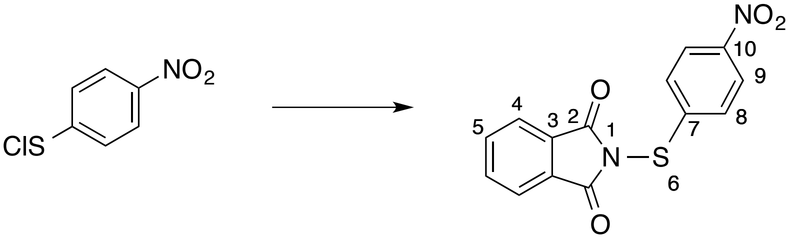
MS: (ES^+, 70 eV)

323 (58, M^+), 281 (64), 253 (13), 207 (100), 191 (15), 178 (25), 157 (11), 147 (12), 96 (20)

HRMS: calcd for $C_{15}H_9NO_2SF_3^+$: 324.0306, found: 324.0297

TLC: R_f 0.29 (hexane/EtOAc, 4:1) [$KMnO_4$]

Preparation of 2-((4-Nitrophenyl)thio)isoindoline-1,3-dione (2d)



S16 **2d**

Synthesis of title compound **2d** from 4-nitrothiophenol and phthalimide following General Procedure 1 did not provide satisfactory results with regard to yield and level of purity. Therefore, a different procedure using 4-nitrobenezenesulfenyl chloride (**S16**) as the starting material was employed: An oven-dried, three-necked, round-bottomed flask equipped with a magnetic stir bar and a gas inlet was evacuated and backfilled with argon. The flask was charged with phthalimide (234 mg, 1.58 mmol), Et_3N (0.29 mL, 2.05 mmol, 1.30 equiv) and CH_2Cl_2 (2.0 mL), and a solution of 4-nitrobenezenesulfenyl chloride (**S16**) (360 mg, 1.90 mmol, 1.20 equiv) in CH_2Cl_2 (1.5 mL) was added dropwise using a syringe. The reaction mixture was stirred for 36 h at room temperature and then was quenched with H_2O (5.0 mL). Phases were separated, the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic phases were washed with brine (10 mL) and dried over $MgSO_4$. After removal of the volatiles in vacuo (20–23 °C, 20 mmHg), the crude product was recrystallized from pentane/CH_2Cl_2 affording **2d** (247 mg, 52%) as pale red crystals. Compound **2d** has been previously synthesized.[22]

Data for **2d**:

mp: 212–214 °C (pentane/CH_2Cl_2)

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

δ 8.15 (d, *J* = 8.8 Hz, 2H, HC(9)), 8.00 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.87 (dd, *J* = 5.6, 3.1 Hz, 2H, HC(5)), 7.39 (d, *J* = 8.8 Hz, 2H, HC(8))

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

δ 167.0 (C(2)), 146.9 (C(aryl)), 144.6 (C(aryl)), 135.3 (C(5)), 131.7 (C(3)), 125.8 (C(aryl)), 124.5 (C(aryl)), 124.4 (C(aryl))

IR: (neat)

1788 (m), 1744 (s), 1716 (s), 1600 (m), 1580 (m), 1516 (m), 1469 (m), 1341 (s), 1318 (w), 1288 (m), 1273 (s), 1263 (s), 1171 (m), 1118 (w), 1087 (m), 1034 (s), 949 (w), 866 (m), 855 (m), 843 (m), 816 (w), 789 (m), 738 (s), 709 (s), 694 (m)

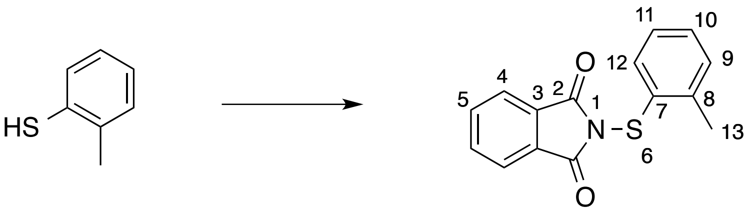
MS (ESI)

637 (11), 620 (11), 486 (18), 355 (33), 333 (48), 301 (13, M+H), 163 (100)

HRMS: calcd for $C_{14}H_9N_2O_4S^+$: 301.0283, found: 301.0281

TLC: *R*$_f$ 0.25 (hexane/EtOAc, 3:1) [$KMnO_4$]

Preparation of 2-(2-Methlylphenylthio)isoindoline-1,3-dione (2e)



S17 **2e**

Following General Procedure 1, a suspension of phthalimide (1.07 g, 7.27 mmol) and 2-methylthiophenol (**S17**) (1.00 g, 8.05 mmol, 1.11 equiv) in MeCN (4.0 mL) and pyridine (5.0 mL) was treated with a solution of Br_2 (0.45 mL, 8.8 mmol, 1.2 equiv) in MeCN (3.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (15 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 6 mL) afforded 1.72 g of crude product. Recrystallization from EtOH/CH_2Cl_2 afforded **2e** (1.54 g, 71%) as yellow needles. The analytical data match those published in the literature.[23]

Data for **2e**:

mp: 169–171 °C (EtOH/CH_2Cl_2)

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

δ 7.93 (dd, *J* = 5.5, 3.1 Hz, 1H, HC(4)), 7.78 (dd, *J* = 5.5, 3.1 Hz, 1H, HC(5)), 7.40 (d, *J* = 7.7 Hz, 1H, HC(aryl)), 7.23–7.16 (m, 2H, HC(aryl)), 7.15–7.08 (m, 1H, HC(aryl)), 2.62 (s, 3H, HC(13))

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

δ 167.7 (C(2)), 138.2 (C(8)), 134.6 (C(4)), 134.1 (C(7)), 132.0 (C(3)), 130.6 (C(aryl)), 130.4 (C(aryl)), 128.9 (C(aryl)), 126.8 (C(aryl)), 124.0 (C(5)), 20.1 (C(13))

IR: (neat)

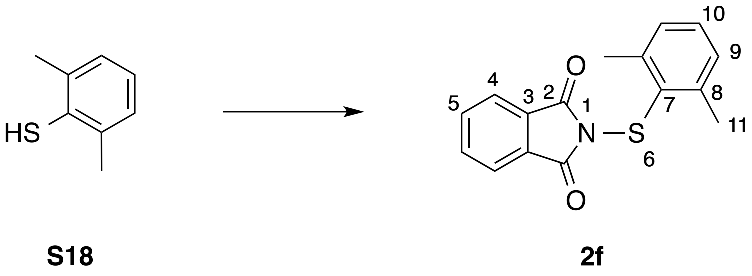
1785 (m), 1738 (s), 1712 (s), 1607 (w), 1367 (w), 1464 (m), 1367 (w), 1344 (m), 1280 (s), 1171 (w), 1041 (s), 933 (w), 864 (m), 793 (m), 738 (s), 714 (s), 686 (m), 678 (m)

MS: (ES$^+$, 70 eV)
269 (99, M$^+$), 252 (14), 236 (49), 122 (100)

HRMS: calcd for $C_{15}H_{12}NO_2S^+$: 270.0589, found: 270.0589

TLC: *R$_f$* 0.32 (hexane/EtOAc, 5:1) [CAM]

Preparation of 2-((2,6-Dimethylphenyl)thio)isoindoline-1,3-dione (2f)



Following General Procedure 1, a suspension of phthalimide (1.47 g, 10.0 mmol) and 2,6-dimethylthiophenol (**S18**) (1.45 g, 10.5 mmol, 1.05 equiv) in MeCN (3.8 mL) and pyridine (7.7 mL) was treated with a solution of Br_2 (0.56 mL, 11 mmol, 1.1 equiv) in MeCN (5.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 3 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 5 mL) afforded 2.63 g of crude product. Recrystallization from a hot MeOH/CH_2Cl_2 mixture (3:1, 107 mL) afforded **2f** (2.28 g, 80%) as pale yellow crystals. An analytically pure sample was obtained by sublimation (145°–150 °C, 0.3 mmHg).

Data for **2f**:

mp: 164–165 °C (MeOH/CH_2Cl_2)

^{1}H NMR: (500 MHz, $CDCl_3$)
δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 7.19 (t, *J* = 7.5 Hz, 1H, HC(10)), 7.10 (d, *J* = 7.5 Hz, 2H, HC(9)), 2.74 (s, 6H, HC(11))

^{13}C NMR: (125 MHz, $CDCl_3$)
δ 167.8 (C(2)), 144.1 (C(8)), 134.4 (C(5)), 132.0 (C(3)), 131.7 (C(7)), 130.7 (C(10)), 128.5 (C(9)), 123.6 (C(4)), 22.2 (C(11))

IR: (neat)

1782 (w), 1729 (s), 1704 (m), 1604 (w), 1466 (m), 1433 (w), 1362 (w), 1343 (m), 1279 (s), 1264 (m), 1147 (m), 1109 (w), 1055 (s), 895 (w), 867 (m), 798 (m), 783 (m), 722 (m)

MS: (ES^+, 70 eV)

283 (55, M^+), 250 (57), 207 (6), 136 (100), 121 (8), 91 (16), 77 (10)

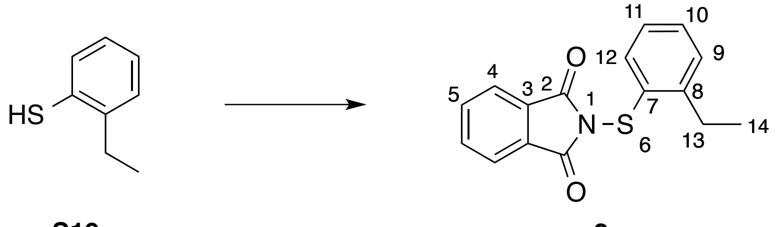
HRMS: calcd for $C_{16}H_{14}NO_2S^+$: 284.0745, found: 284.0746

TLC: R_f 0.39 (hexanes/EtOAc, 5:1) [$KMnO_4$]

Analysis: $C_{16}H_{13}NO_2S$ (283.34)

Calcd:	C, 67.82;	H, 4.62;	N, 4.94
Found:	C, 67.56;	H, 4.40;	N, 4.97

Preparation of 2-((2-Ethylphenyl)thio)isoindoline-1,3-dione (2g)



S19 **2g**

Following General Procedure 1, a suspension of phthalimide (500 mg, 3.40 mmol) and 2-ethylthiophenol (**S19**) (493 mg, 3.57 mmol, 1.05 equiv) in MeCN (2.0 mL) and pyridine (2.5 mL) was treated with a solution of Br_2 (0.21 mL, 4.1 mmol, 1.2 equiv) in MeCN (1.5 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (8.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 3 mL) afforded pure **2g** (560 mg, 58%) as a pale yellow solid. Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

Data for **2g**:

mp: 117–119 °C (hexane/CH_2Cl_2)

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

δ 7.93 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 7.43 (d, *J* = 7.8 Hz, 1H, HC(aryl)), 7.25–7.21 (m, 2H, HC(aryl)), 7.15–7.08 (m, 1H, HC(aryl)), 3.06 (q, *J* = 7.5 Hz, 2H, HC(13)), 1.31 (t, *J* = 7.5 Hz, 3H, HC(14))

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

δ 167.8 (C(2)), 144.3 (C(8)), 134.6 (C(5)), 133.8 (C(7)), 132.0 (C(3)), 130.8 (C(aryl)), 129.1 (C(aryl)), 128.9 (C(aryl)), 126.8 (C(aryl)), 124.0 (C(4)), 26.7 (C(13)), 15.5 (C(14))

IR: (neat)

2883 (w), 1784 (m), 1741 (s), 1715 (s), 1589 (w), 1467 (m), 1444 (m), 1425 (w), 1354 (m), 1338 (m), 1275 (s), 1171 (w), 1060 (w), 1038 (s), 941 (w), 865 (m), 793 (m), 744 (s), 709 (s), 695 (m), 681 (m)

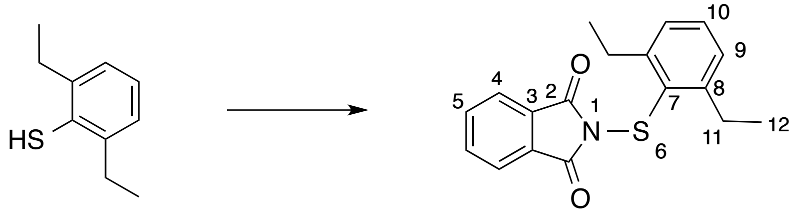
MS: (ES^+, 70 eV)

283 (26, M^+), 250 (13), 207 (6), 136 (100)

HRMS: calcd for $C_{16}H_{14}NO_2S^+$: 284.0745, found: 284.0733

TLC: R_f 0.33 (hexane/EtOAc, 5:1) [CAM]

Preparation of 2-((2,6-Diethylphenyl)thio)isoindoline-1,3-dione (2h)



S7 **2h**

Following General Procedure 1, a suspension of phthalimide (1.47 g, 10.0 mmol) and 2,6-diethylbenzenethiol (**S7**) (1.75 g, 10.5 mmol, 1.05 equiv) in MeCN (3.8 mL) and pyridine (7.7 mL) was treated with a solution of Br_2 (0.56 mL, 11 mmol, 1.1 equiv) in MeCN (5.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and 2.5 h at room temperature. Subsequently, the mixture was cooled to 0 °C and quenched by dropwise addition of H_2O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 7 mL) afforded 2.33 g of crude product. Recrystallization from a hot MeOH/CH_2Cl_2 mixture (9:1, 65 mL) afforded **2h** (2.10 g, 67%) as off-white crystals. An analytically pure sample was obtained by sublimation (100°–105 °C, 0.3 mmHg).

Data for **2h**:

mp: 109–110 °C (MeOH/CH_2Cl_2)

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

δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 7.30 (t, *J* = 7.3 Hz, 1H, HC(10)), 7.15 (d, *J* = 7.6 Hz, 2H, HC(9)), 3.28 (q, *J* = 7.5 Hz, 4H, HC(11)), 1.22 (t, *J* = 7.5 Hz, 6H, HC(12))

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

δ 167.8 (C(2)), 150.1 (C(8)), 134.4 (C(5)), 132.1 (C(3)), 131.2 (C(10)), 130.8 (C(7)) 126.9 (C(9)) 123.6 (C(4)) 28.1 (C(11)), 16.4 (C(12))

IR: (neat)

2971 (w), 1779 (w), 1729 (s), 1704 (m), 1607 (w), 1463 (m), 1431 (m), 1361 (w), 1343 (m), 1274 (s), 1262 (m), 1164 (m), 1050 (s), 864 (m), 807 (m), 758 (m)

MS: (ES$^+$, 70 eV)

311 (10, M$^+$), 274 (15), 207 (10), 164 (100), 149 (42), 135 (92), 115 (11), 104 (10), 91 (12), 76 (11)

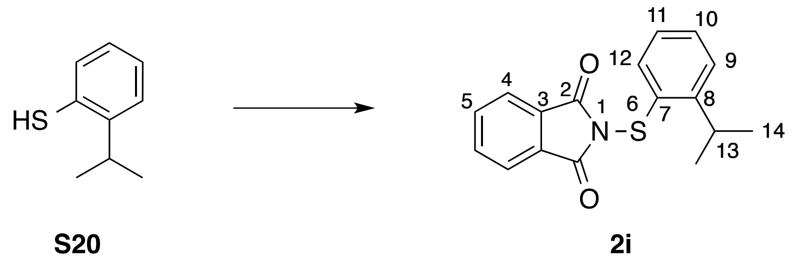
HRMS: calcd for $C_{18}H_{18}NO_2S^+$: 312.1058, found: 312.1055

TLC: R_f 0.44 (hexanes/EtOAc, 5:1) [$KMnO_4$]

Analysis: $C_{18}H_{17}NO_2S$ (311.40)

Calcd:	C, 69.43;	H, 5.50;	N, 4.50
Found:	C, 69.42;	H, 5.30;	N, 4.87

Preparation of 2-((2-Isopropylphenyl)thio)isoindoline-1,3-dione (4i)



S20 **2i**

Following General Procedure 1, a suspension of phthalimide (704 mg, 4.78 mmol) and 2-isopropylthiophenol (**S20**) (761 mg, 5.00 mmol, 1.05 equiv) in MeCN (2.5 mL) and pyridine (3.1 mL) was reacted with a solution of Br_2 (0.29 mL, 5.7 mmol, 1.2 equiv) in MeCN (1.8 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 2.5 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (10 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 6 mL) afforded pure **2i** (1.19 g, 84%) as a pale yellow solid. Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

Data for **2i**:

mp: 149–151 °C (hexane/CH_2Cl_2)

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

δ 7.92 (dd, J = 5.5, 3.1 Hz, 2H, HC(4)), 7.77 (dd, J = 5.6, 3.1 Hz, 2H, HC(5)), 7.43 (d, J = 7.9 Hz, 1H, HC(aryl)), 7.34–7.22 (m, 2H, HC(aryl)), 7.13–7.07 (m, 1H, HC(aryl)), 3.90 (hept, J = 6.8 Hz, 1H, HC(13)), 1.30 (d, J = 6.8 Hz, 6H, HC(14))

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

δ 167.8 (C(2)), 148.9 (C(8)), 134.6 (C(5)), 133.3 (C(7)), 132.0 (C(3)), 130.9 (C(aryl)), 129.3 (C(aryl)), 126.7 (C(aryl)), 126.0 (C(aryl)), 124.0 (C(4)), 30.4 (C(13)), 23.8 (C(14))

IR: (neat)

2957 (m), 1784 (m), 1738 (s), 1710 (s), 1606 (w), 1468 (m), 1433 (m), 1386 (w), 1368 (m), 1356 (m), 1337 (m), 1277 (s), 1265 (s), 1171 (w), 1041 (s), 866 (m), 794 (w), 761 (s) 751 (m), 734 (w), 710 (s), 695 (m), 688 (m)

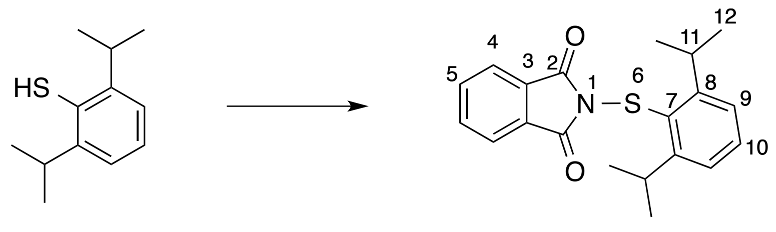
MS: (ES$^+$, 70 eV)

297 (17, M$^+$), 207 (6), 149 (100), 78 (135), 104 (8), 91 (20)

HRMS: calcd for $C_{17}H_{16}NO_2S^+$: 298.0902, found: 298.0892

TLC: R_f 0.35 (hexane/EtOAc, 5:1) [CAM]

Preparation of 2-((2,6-Diisopropylphenyl)thio)isoindoline-1,3-dione (2j)



S9 **2j**

Following General Procedure 1, a suspension of phthalimide (4.33 g, 29.4 mmol) and 2,6-diisopropylthiophenol (**S9**) (6.00 g, 30.9 mmol, 1.05 equiv) in MeCN (3.8 mL) and pyridine (7.7 mL) was treated with a solution of Br_2 (1.66 mL, 32.3 mmol, 1.10 equiv) in MeCN (5.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 2.5 h at 0 °C and 1.5 h at room temperature. Subsequently, the mixture was cooled to 0 °C and quenched by dropwise addition of H_2O (40 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 15 mL) afforded 7.40 g of crude product. Recrystallization from a hot MeOH/CH_2Cl_2 mixture (9:1, 230 mL) afforded **2j** (5.74 g). A second crop (0.46 g) was collected from the mother liquor giving a combined yield of 6.20 g (62%) of **2j** as off-white crystals. An analytically pure sample was obtained by sublimation (145°–150 °C, 0.3 mmHg).

Data for **2j**:

mp: 161–162 °C (MeOH/CH_2Cl_2)

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

δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(5)), 7.39 (t, *J* = 7.7 Hz, 1H, HC(10)), 7.21 (d, *J* = 7.7 Hz, 2H, HC(9)), 4.51 (hept, *J* = 6.8 Hz, 2H, HC(11)), 1.22 (d, *J* = 6.8 Hz, 12H, HC(12))

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

δ 167.7 (C(2)), 154.5 (C(8)), 134.4 (C(5)), 132.0 (C(3)), 131.6 (C(10)), 129.9 (C(7)) 124.0 (C(4)) 123.6 (C(9)) 31.3 (C(11)) 24.6 (C(12))

IR: (neat)

2964 (m), 2866 (m), 1781 (m), 1728 (s), 1703 (s), 1609 (w), 1575 (w), 1465 (m), 1382 (m), 1361 (m), 1340 (m), 1276 (s), 1165 (m), 1102 (w), 1046 (s), 866 (m), 802 (m), 786 (m), 752 (m), 742 (m)

MS: (ES^+, 70 eV)

339 (5, M^+), 192 (60), 177 (15), 161 (4), 149 (100), 135 (121), 115 (6), 91 (6)

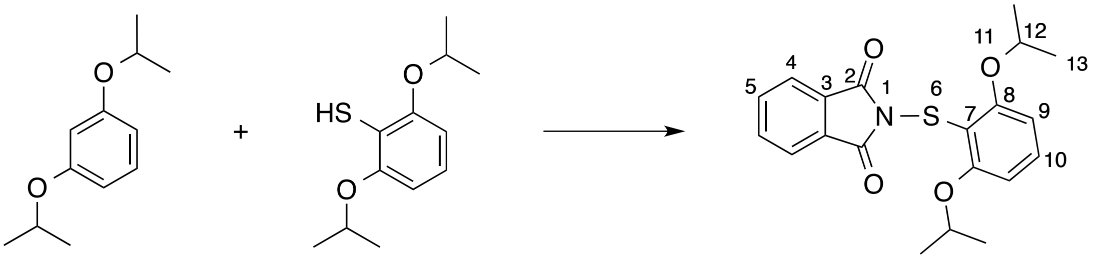
HRMS: calcd for $C_{20}H_{22}NO_2S^+$: 340.1371, found: 340.1371

TLC: R_f 0.47 (hexanes/EtOAc, 5:1) [$KMnO_4$]

Analysis: $C_{20}H_{21}NO_2S$ (339.45)

Calcd:	C, 70.77;	H, 6.24;	N, 4.13
Found:	C, 70.68;	H, 6.19;	N, 4.45

Preparation of 2-((2,6-Diisopropoxyphenyl)thio)isoindoline-1,3-dione (2k)



S12 **S13** **2k**

Following General Procedure 1, 950 mg of a 30:70 mixture of **S12** (calcd: 270 mg) and **S13** (calcd: 680 mg, 3.01 mmol, 1.10 equiv) and phthalimide (405 mg, 2.75 mmol) were suspended in MeCN (1.5 mL) and pyridine (1.9 mL). Upon complete addition of a solution of Br_2 (0.16 mL, 3.1 mmol, 1.1 equiv) in MeCN (1.1 mL), the mixture was stirred at 0 °C for 1.5 h followed by the addition of another solution of Br_2 (73 μL, 1.4 mmol, 0.52 equiv) in MeCN (0.5 mL). The reaction mixture was stirred for another 1 h at 0 °C and quenched with H_2O (7.0 mL). In contrast to the other sulfenylating agents, compound **2k** did not precipitate, and a turbid solution was obtained instead. After addition of EtOAc (10 mL) and brine (15 mL), phase separation occurred and the phases were separated. The aqueous phase was extracted with EtOAc (3 × 10 mL), dried over $MgSO_4$ and concentrated in vacuo (20–23 °C, 20 mmHg). Column chromatography (SiO_2, 35 g, 35 mm ∅, hexane/EtOAc, 10:1→5:1) afforded 653 mg of **2k** along with small impurities. Recrystallization from hexane/CH_2Cl_2 (3:1, 2.4 mL) provided pure **2k** (300 mg, 29% based on the amount of phthalimide) as yellow crystals.

Data for **2k**:

mp: 131–133 °C (hexane/CH_2Cl_2)

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

δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H, HC(5)), 7.11 (t, *J* = 8.4 Hz, 1H, HC(10)), 6.46 (d, *J* = 8.4 Hz, 2H, HC(9)), 4.56 (hept, *J* = 6.1 Hz, 2H, HC(12)), 1.23 (d, *J* = 6.1 Hz, 12H, HC(13))

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

δ 167.7 (C(2)), 157.6 (C(8)), 134.1 (C(5)), 132.6 (C(3)), 129.6 (C(10)), 123.4 (C(4)), 112.2 (C(7)), 106.3 (C(9)), 71.2 (C(12)), 21.9 (C(13))

IR: (neat)

2978 (m), 1783 (m), 1740 (a), 1715 (a), 1584 (m), 1461 (m), 1374 (m), 1344 (m), 1286 (s), 1250 (s), 1172 (w), 1139 (w), 1108 (s), 1047 (s), 900 (m), 867 (m), 798 (m), 763 (m), 718 (s), 695 (m)

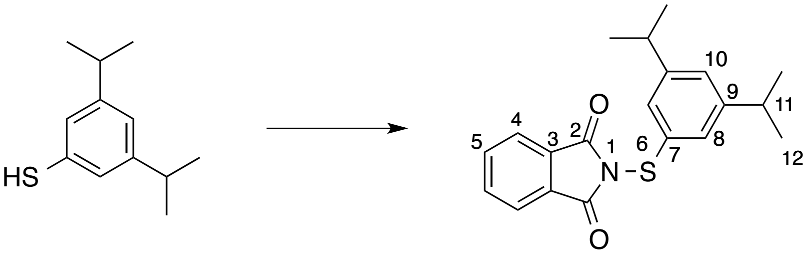
MS: (ESI)

781 (7), 760 (56), 410 (10), 389 (100), 372 (66, M+H), 225 (50), 183 (53)

HRMS: calcd for $C_{18}H_{12}NO_4S^+$: 372.1270, found: 372.1262

TLC: R_f 0.27 (hexane/EtOAc, 4:1) [CAM]

Preparation of 2-((3,5-Diisopropylphenyl)thio)isoindoline-1,3-dione (2l)



S11 **2l**

Following General Procedure 1, a suspension of phthalimide (406 mg, 2.76 mmol) and 3,5-diisopropylthiophenol (**S11**) (590 mg, 3.04 mmol, 1.10 equiv) in MeCN (1.5 mL) and pyridine (1.9 mL) was treated with a solution of Br_2 (0.16 mL, 3.1 mmol, 1.1 equiv) in MeCN (1.1 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 2 h at 0 °C and 1 h at room temperature. Subsequently, the reaction mixture was cooled to 0 °C and quenched by dropwise addition of H_2O (5.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled (0 °C) MeOH (4 × 3 mL) afforded pure **2l** (616 mg, 60%) as a pale yellow solid. Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

Data for **2l**:

mp: 116–118 °C (hexane/CH_2Cl_2)

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

δ 7.93 (dd, *J* = 5.5, 3.1 Hz, 2H, HC(4)), 7.55 (dd, *J* = 5.5, 3.0 Hz, 2H, HC(5)), 7.34 (d, *J* = 1.7 Hz, 2H, HC(8)), 7.04 (t, *J* = 1.8 Hz, 1H, HC(10)), 2.85 (hept, *J* = 6.8 Hz, 2H, HC(11)), 1.20 (d, *J* = 6.9 Hz, 12H, HC(12))

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

δ 167.9 (C(2)), 150.2 (C(9)), 134.6 (C(5)), 134.2 (C(7)), 132.0 (C(3)), 127.5 (C(8)), 126.3 (C(10)), 124.0 (C(4)), 34.0 (C(11)), 23.9 (C(12))

IR: (neat)

2958 (m), 1781 (m), 1740 (s), 1710 (s), 1594 (m), 1464 (m), 1433 (m), 1364 (m), 1347 (m), 1278 (s), 1170 (w), 1065 (m), 1045 (s), 877 (m), 865 (m), 719 (s), 701 (m), 686 (m)

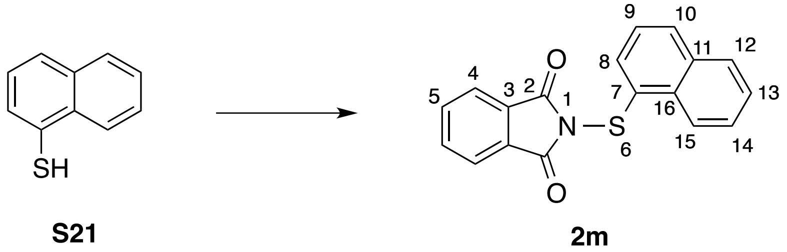
MS: (ESI)

698 (40), 637 (12), 544 (18), 528 (33), 394 (13), 372 (36), 357 (100), 340 (92, M+H), 298 (20), 219 (13), 210 (10), 163 (16)

HRMS: calcd for $C_{20}H_{22}NO_2S^+$: 340.1371, found: 340.1369

TLC: R_f 0.40 (hexane/EtOAc, 5:1) [CAM]

Preparation of 2-(1-Naphthalenylthio)isoindoline-1,3-dione (2m)



Following General Procedure 1, a suspension of phthalimide (874 mg, 5.94 mmol) and 1-naphthalenethiol (**S21**)[13] (1.00 g, 6.24 mmol, 1.05 equiv) in MeCN (4.0 mL) and pyridine (5.0 mL) was treated with a solution of Br_2 (0.35 mL, 6.8 mmol, 1.1 equiv) in MeCN (3.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (25 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 6 mL) yielded 1.55 g of crude product. Recrystallization form pentane/CH_2Cl_2 afforded **2m** (1.05 g, 55%) as orange plates.

Data for **2m**:

mp: 176–178 °C (pentane/CH_2Cl_2)

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

δ 8.97 (d, *J* = 8.5 Hz, 1H, HC(aryl)), 8.12 (d, *J* = 7.4 Hz, 1H, HC(aryl)), 7.93–7.81 (m, 4H, HC(aryl)), 7.76–7.65 (m, 3H, HC(aryl)), 7.54 (t, *J* = 7.5 Hz, 1H, HC(aryl)), 7.44 (t, *J* = 7.7 Hz, 1H, HC(aryl))

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

δ 167.9 (C(2)), 134.54 (C(aryl)), 134.49 (C(aryl)), 134.0 (C(aryl)), 133.1 (C(aryl)), 132.0 (C(aryl)), 131.4 (C(aryl)), 131.1 (C(aryl)), 128.3 (C(aryl)), 127.4 (C(aryl)), 126.6 (C(aryl)), 125.8 (C(aryl)), 125.5 (C(aryl)), 123.9 (C(aryl))

IR: neat

3060 (w), 1780 (m), 1731 (s), 1703 (m), 1586 (w), 1500 (w), 1466 (m), 1360 (m), 1343 (m), 1275 (s), 1264 (m), 1222 (w), 1198 (w), 1165 (m), 1052 (s), 1018 (w), 963 (w), 865 (s), 824 (w), 799 (m), 774 (s), 740 (m), 710 (s)

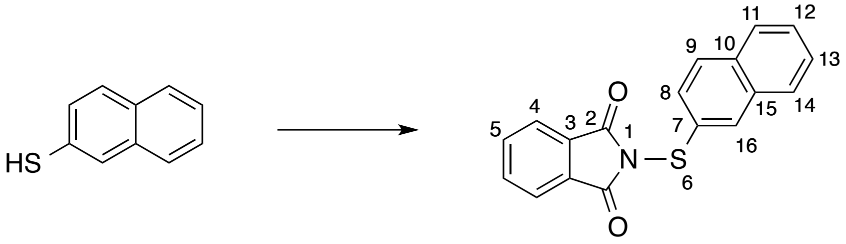
MS: (ESI)

630 (21), 477 (27), 323 (67), 306 (100, M+H), 163 (7), 159 (30)

HRMS: calcd for $C_{18}H_{12}NO_2S^+$: 306.0589, found: 306.0579

TLC: *R_f* 0.38 (hexane/EtOAc, 3:1) [CAM]

Preparation of 2-(2-Naphthalenylthio)isoindoline-1,3-dione (2n)



S22 **2n**

Following General Procedure 1, a suspension of phthalimide (874 mg, 5.94 mmol) and 2-naphthalenethiol (**S22**)[13] (1.00 g, 6.24 mmol, 1.05 equiv) in MeCN (4.0 mL) and pyridine (5.0 mL) was treated with a solution of Br_2 (0.35 mL, 6.8 mmol, 1.1 equiv) in MeCN (3.0 mL). Upon complete addition of the Br_2 solution, the mixture was stirred for 1 h at 0 °C and was subsequently quenched by dropwise addition of H_2O (25 mL). Filtration of the suspension and washing of the precipitate with pre-cooled MeOH (0 °C, 4 × 6 mL) yielded the crude product that was purified by column chromatography (SiO_2, 110 g, 60 mm ∅, hexane/ EtOAc/CH_2Cl_2, 5:1:1). Recrystallization form pentane/CH_2Cl_2 afforded **2n** (350 mg, 18%) as pale yellow crystals.

Data for **2n**:

mp: 208–210 °C (pentane/CH_2Cl_2)

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

δ 8.15 (s, 1H, HC(16)), 7.93 (dd, *J* = 5.5, 3.1 Hz, 2H, H(C(4)), 7.87–7.73 (m, 5H, HC(aryl)), 7.66 (dd, *J* = 8.6, 1.9 Hz, 1H, HC(aryl)), 7.49 (dd, *J* = 6.3, 3.2 Hz, 2H, HC(aryl))

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

δ 167.8 (C(2)), 134.7 (C(5)), 133.3 (C(aryl)), 133.2 (C(aryl)), 132.1 (C(aryl)), 132.0

(C(aryl)), 131.1 (C(aryl)), 129.2 (C(aryl)), 128.1 (C(aryl)), 127.9 (C(aryl)), 127.7 (C(aryl)), 127.2 (C(aryl)), 126.84 (C(aryl)), 124.1 (C(4))

IR: (neat)
3060 (w), 1779 (m), 1730 (s), 1703 (m), 1582 (w), 1496 (w), 1361 (m), 1342 (m), 1276 (s), 1263 (m), 1169 (w), 1149 (w), 1128 (w), 1071 (w), 1054 (s), 1009 (w), 952 (w), 897 (w), 864 (s), 822 (m), 795 (w), 765 (w), 749 (m), 711 (s)

MS: (ESI)
637 (36), 477 (26), 306 (100, M+H), 159 (9)

HRMS: calcd for $C_{18}H_{12}NO_2S^+$: 306.0589, found: 306.0586

TLC: R_f 0.37 (hexane/EtOAc, 3:1) [CAM]

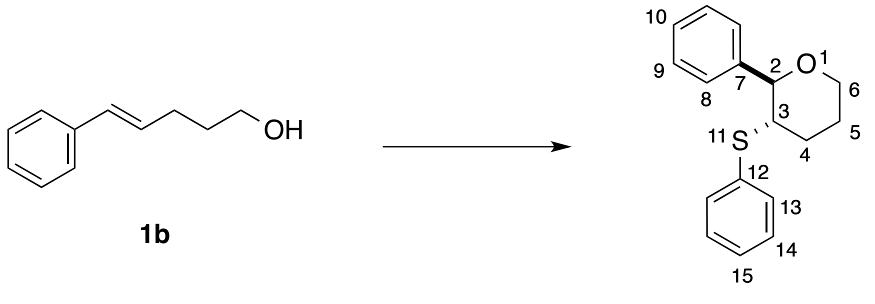
Thioetherifications (Table 1)

General Procedure 2: Sulfenylating Agent Survey

An oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 7.0 μmol, 0.10 equiv) and the corresponding sulfenylating agent (74.0 μmol, 1.05 equiv). In a 6 dram vial, (*E*)-5-phenyl-4-penten-1-ol (**1b**) (11.3 mg, 70.0 μmol) was dissolved in $CDCl_3$ (0.40 mL) and was transferred to the NMR tube washing with $CDCl_3$ (0.25 mL). The NMR tube was capped with a septum, shaken well, and placed into a dry-ice/acetone bath (–78 °C) for 2 min. Methanesulfonic acid (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe, the NMR tube was removed from the dry-ice/acetone bath and shaken again until the was homogeneous. The NMR tube was put in a freezer (–20 °C) for the indicated time. Conversion to the corresponding product was observed by the appearance of a diagnostic ^{1}H NMR resonance for the product around 4.20 ppm (doublet) with respect to the alkene peaks of the substrate at 6.23 and 6.43 ppm. Besides the formation of small quantities of the *exo*-cyclization product (< 5%), no other products were observed in the ^{1}H NMR spectra. Formation of phthalimide byproduct was visually confirmed by the precipitation out of the solution. After the indicated time the reaction was quenched with Et_3N (0.10 mL) and the crude mixture was purified by silica gel column chromatography.

Sulfenylating Agent Survey

Table 1 Entry 1: (2*R*,3*S*)-2-Phenyl-3-(phenylthio)tetrahydro-2*H*-pyran (4ba)



4ba

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.7 mg, 7.1 μmol, 0.10 equiv) and sulfenylating agent **2a** (18.9 mg, 74.1 μmol, 1.06 equiv). To this was added **1b** (11.3 mg, 69.7 μmmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 24 h. At this point, the reaction proceeded to 93% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 18 mg of **4ba** along with 10% Lewis base contaminant. The spectroscopic data match those published in the literature.[16]

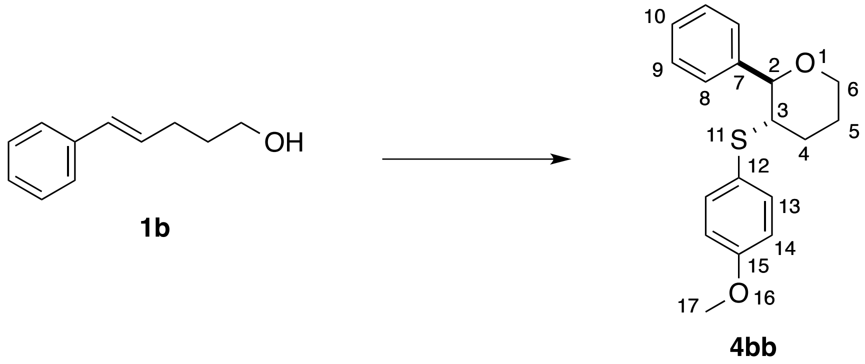
Data for **4ba**:

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

δ 7.39–7.35 (m, 2H, HC(8)), 7.31–7.23 (m, 3H, HC(9), HC(10)), 7.16–7.09 (m, 5H, HC(aryl)), 4.20 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.12–4.06 (m, 1H, HC(6)), 3.57 (ddd, *J* = 12.9, 12.1, 2.1 Hz, 1H, HC(6)), 3.24 (ddd, *J* = 11.5, 10.1, 4.0 Hz, 1H, HC(3)), 2.33–2.26 (m, 1H, HC(4)), 1.92–1.80 (m, 1H, HC(5)), 1.76–1.63 (m, 2H, HC(4), HC(5)).

SFC: (2*R*,3*S*)-**4ba**, t_R 7.06 min (95.3%); (2*S*,3*R*)-**4ba**, t_R 9.78 min (4.7%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 2: (2*R*,3*S*)-3-((4-Methoxyphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bb)



Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 6.9 µmol, 0.10 equiv) and sulfenylating agent **2b** (21.7 mg, 76.1 µmol, 1.10 equiv). To this was added **1b** (11.2 mg, 69.0 µmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 µL, 70 µmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 21 h. At this point, the reaction proceeded to full conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 17 mg of **4bb**.

Data for **4bb**:

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

δ 7.39–7.24 (m, 5H, HC(aryl)), 7.09–7.04 (m, 2H, HC(aryl)), 6.72–6.67 (m, 2H, HC(aryl)), 4.14 (d, *J* = 10.2 Hz, 1H, HC(2)), 4.09–4.02 (m, 1H, HC(6)), 3.76 (s, 3H, HC(17)), 3.53 (ddd, *J* = 12.3, 11.4, 2.3 Hz, 1H, HC(6)), 3.07 (ddd, *J* = 11.7, 10.2, 4.0 Hz, 1H, HC(3)), 2.27–2.17 (m, 1H, HC(4)), 1.88–1.77 (m, 1H, HC(5)), 1.74–1.59 (m, 2H, HC(4), HC(5))

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

δ 159.4 (C(15)), 140.1 (C(aryl)), 136.1 (C(aryl)), 128.18 (C(aryl)), 128.16 (C(aryl)) 127.8 (C(aryl)), 123.7 (C(aryl)), 114.1 (C(14)), 85.1 (C(2)), 68.5 (C(6)), 55.2 (C(17)), 51.2 (C(3)), 32.2 (C(4)), 27.1 (C(5))

MS: (ES^+, 70 eV)

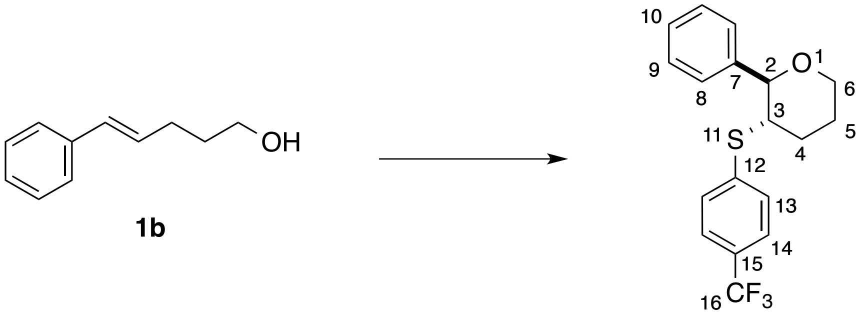
300 (100, M^+), 229 (27), 161 (46), 151 (16), 139 (20), 121 (8), 105 (23), 91 (32), 77 (10)

HRMS: calcd for $C_{18}H_{21}O_2S^+$: 301.1262, found: 301.1255

TLC: R_f 0.45 (hexane/EtOAc, 5:1) [CAM]

SFC: (2*R*,3*S*)-**4bb**, t_R 9.22 min (95.1%); (2*S*,3*R*)-**4bb**, t_R 12.62 min (4.9%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 3: (2*R*,3*S*)-2-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)tetrahydro-2*H*-pyran (4bc)



4bc

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.8 mg, 7.3 μmol, 0.10 equiv) and sulfenylating agent **2c** (23.9 mg, 73.9 μmol, 1.04 equiv). To this was added **1b** (11.5 mg, 70.9 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 0.99 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 24 h. At this point, the reaction proceeded to > 95% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 18 mg of **4bc** along with 1% Lewis base contaminant.

Data for **4bc**:

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

δ 7.33–7.28 (m, 4H, HC(aryl)), 7.23–7.18 (m, 3H, HC(9), HC(10)), 7.09 (d, *J* = 8.1 Hz, 2H, HC(aryl)), 4.21 (d, *J* = 10.0 Hz, 1H, HC(2)), 4.14–4.09 (m, 1H, HC(6)), 3.60 (ddd, *J* = 12.2, 11.9, 2.1 Hz, 1H, HC(6)), 3.23 (ddd, *J* = 12.1, 10.1, 4.0 Hz, 1H, HC(3)), 2.39–2.30 (m, 1H, HC(4)), 1.97–1.84 (m, 1H, HC(5)), 1.82–1.68 (m, 2H, HC(4), HC(5))

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

δ 139.60 (C(aryl)), 139.58 (C(aryl)), 131.1 C(aryl)), 128.32 (q, *J* = 32.4 Hz, C(15)), 128.28 C(aryl)), 128.2 C(aryl)), 127.6 C(aryl)), 125.2 (q, *J* = 3.7 Hz, C(14)), 124.0 (q, *J* = 272 Hz, C(16)), 85.4 (C(2)), 68.5 (C(6)), 50.6 (C(3)), 32.1 (C(4)), 27.0

(C(5))

MS: (ES$^+$, 70 eV)

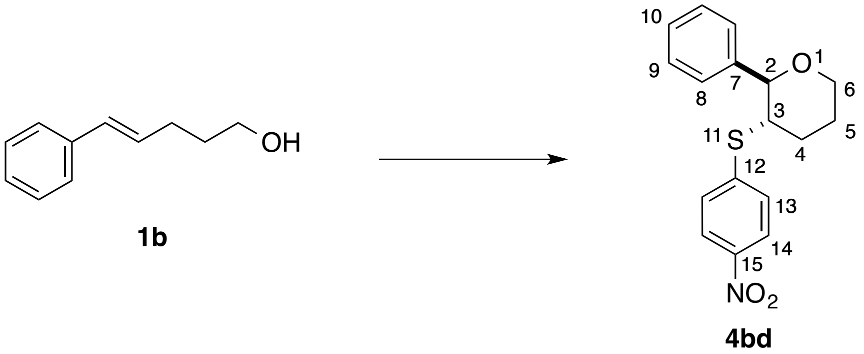
338 (83, M$^+$), 232 (10), 217 (27), 204 (100), 183 (13), 160 (38), 135 (63), 115 (8), 105 (18), 91 (30), 77 (13)

HRMS: calcd for $C_{18}H_{18}F_3OS^+$: 339.1030, found: 339.1040

TLC: R_f 0.53 (hexane/EtOAc, 4:1) [CAM]

SFC: (2*R*,3*S*)-**4bc**, t_R 4.26 min (95.6%); (2*S*,3*R*)-**4bc**, t_R 7.47 min (4.4%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 4: (2*R*,3*S*)-3-((4-Nitrophenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bd)



Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.8 mg, 7.3 μmol, 0.10 equiv) and sulfenylating agent **2c** (22.8 mg, 75.9 μmol, 1.07 equiv). To this was added **1b** (11.5 mg, 70.9 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 0.99 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 51 h. At this point, the reaction proceeded to ca. 88% conversion by ^1H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 7.0 g, 10 mm ∅, hexane/EtOAc, 20:1→10:1) afforded 16 mg of **4bd**.

Data for **4bd**:

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

δ 7.88–7.84 (m, 2H, HC(14)), 7.34–7.30 (m, 2H, HC(8)), 7.20–7.13 (m, 3H, HC(9), HC(10)), 7.04–6.99 (m, 2H, HC(13)), 4.24 (d, *J* = 9.9 Hz, 1H, HC(2)), 4.18–4.12 (m, 1H, HC(6)), 3.62 (ddd, *J* = 12.5, 12.0, 2.0 Hz, 1H, HC(6)), 3.23 (ddd, *J* = 12.0, 9.9, 4.0 Hz, 1H, HC(3)), 2.43–2.26 (m, 1H, HC(4)), 2.02–1.90 (m, 1H, HC(5)), 1.84–1.71 (m, 2H, HC(4), HC(5))

^{13}C NMR: (125 MHz, CDCl$_3$)

δ 145.3 (C(aryl)), 145.0 (C(aryl)), 139.4 (C(aryl)), 129.1 (C(aryl)), 128.3 (C(aryl)), 128.2 (C(aryl)), 127.5 (C(aryl)), 123.3 (C(aryl)), 85.2 (C(2)), 68.5 (C(6)), 50.0 (C(3)), 31.8 (C(4)), 26.9 (C(5))

MS: (ESI)

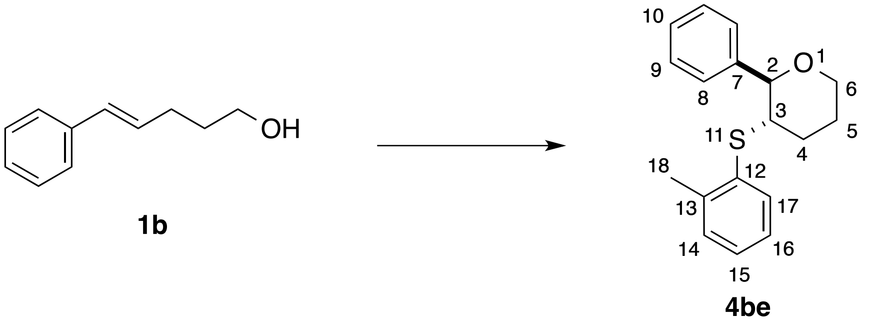
650 (15), 500 (30), 338 (11, M+Na), 333 (26), 316 (36, M+H), 282 (30) 161 (100)

HRMS: calcd for $C_{17}H_{18}NO_3S^+$: 316.1007, found: 316.1012

TLC: *R$_f$* 0.35 (hexane/EtOAc, 5:1) [CAM]

SFC: (2*R*,3*S*)-**4bd**, *t*$_R$ 9.00 min (95.7%); (2*S*,3*R*)-**4bd**, *t*$_R$ 17.44 min (4.3%) (Chiralpak AD, 10% MeOH in CO$_2$, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 5: (2*R*,3*S*)-2-Phenyl-3-((2-methylphenyl)thio)tetrahydro-2*H*-pyran (4be)



Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 6.9 μmol, 0.10 equiv) and sulfenylating agent **2e** (22.6 mg, 83.9 μmol, 1.15 equiv). To this was added **1b** (11.8 mg, 72.7 μmol) in CDCl$_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 0.96 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 21 h. At this point, the reaction proceeded to > 95% conversion by ^{1}H NMR analysis and was quenched with Et$_3$N (0.10 mL). Purification by column chromatography (SiO$_2$, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 15 mg of **4be** along with 1% Lewis base contaminant.

Data for **4be**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.39–7.33 (m, 2H, H(8)), 7.30–7.22 (m, 3H, H(9), HC(10)), 7.09–7.02 (m, 3H, HC(aryl)), 6.99–6.94 (m, 1H, HC(aryl)), 4.23 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.13–4.06 (m, 1H, HC(6)), 3.60 (td, *J* = 11.8, 2.2 Hz, 1H, HC(6)), 3.23 (ddd, *J* = 11.4, 10.1, 4.1 Hz, 1H, HC(3)), 2.27–2.20 (m, 1H, HC(4)), 2.22 (s, 3H, HC(18)), 1.89–1.77 (m, 1H, HC(5)), 1.75–1.64 (m, 2H, HC(4), HC(5))

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

δ 140.4 (C(aryl)), 139.9 (C(aryl)), 133.4 (C(aryl)), 133.1 (C(aryl)), 130.0 (C(aryl)), 128.2 (C(aryl)), 128.1 (C(aryl)), 127.6 (C(aryl)), 127.2 (C(aryl)), 126.0 (C(aryl)), 85.2 (C(2)), 68.6 (C(6)), 50.1 (C(3)), 32.3 (C(4)), 27.0 (C(5)), 20.8 (C(18))

MS: (ES^+, 70 eV)

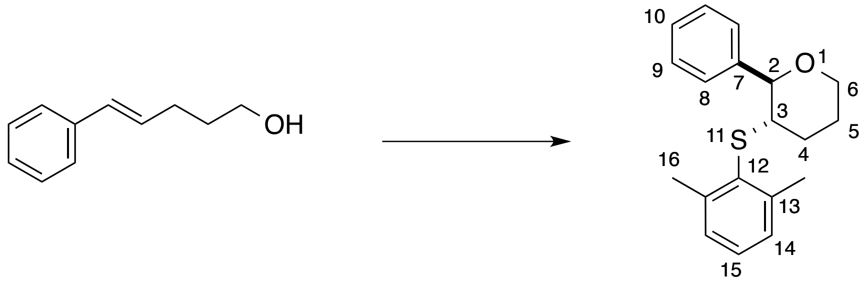
284 (100, M^+), 213 (15), 160 (57), 150 (45), 135 (88), 115 (11), 105 (27), 91 (51), 77 (17)

HRMS: calcd for $C_{18}H_{21}OS^+$: 285.1313, found: 285.1319

TLC: R_f 0.39 (hexane/EtOAc, 10:1) [CAM]

SFC: (2*R*,3*S*)-**4be**, t_R 15.01 min (97.2%); (2*S*,3*R*)-**4b3**, t_R 7.25 min (2.8%) (Chiralpak OD, 10% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 6: (2*R*,3*S*)-3-((2,6-Dimethylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bf)



4bf

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 6.9 μmol, 0.10 equiv) and sulfenylating agent **2f** (20.9 mg, 73.8 μmol, 1.06 equiv). To this was added **1b** (11.3 mg, 69.7 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 21 h. At this point, the reaction proceeded to full conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 18 mg of **4bf**.

Data for **4bf**:

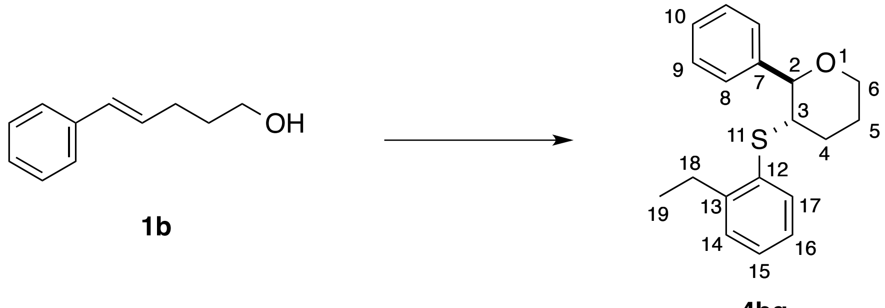
^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.41–7.36 (m, 2H, HC(8)), 7.33–7.27 (m, 3H, HC(9), HC(10)), 7.07–7.02 (m, 1H, HC(15)), 7.02–6.98 (m, 1H, HC(14)), 4.26 (d, *J* = 10.0 Hz, 1H, HC(2)), 4.10–4.04 (m, 1H, HC(6)), 3.60 (td, *J* = 11.7, 2.4 Hz, 1H, HC(6)), 3.18 (dt, *J* = 11.1, 4.3 Hz, 1H, HC(3)), 2.33 (s, 3H, HC(16)), 1.94–1.87 (m, 1H, HC(4)), 1.78–1.68 (m, 1H, HC(5)), 1.67–1.56 (m, 2H, HC(4), HC(5))

SFC: (2*R*,3*S*)-**4bf**, t_R 12.36 min (97.1%); (2*S*,3*R*)-**4bf**, t_R 5.88 min (2.9%) (Chiralpak OD, 10% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Full characterization of compound **4bf** is provided in section Table 2 Entry 2.

Table 1 Entry 7: (2*R*,3*S*)-3-((2-Ethylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bg)



4bg

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 6.9 μmol, 0.10 equiv) and sulfenylating agent **2g** (22.9 mg, 80.8 mmol, 1.18 equiv). To this was added **1b** (11.1 mg, 68.4 μmmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 42 h. At this point, the reaction proceeded to > 95% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 15 mg of **4bg**.

Data for **4bg**:

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

δ 7.39–7.35 (m, 2H, HC(8)), 7.30–7.23 (m, 3H, HC(9), HC(10)), 7.13–7.06 (m, 3H, HC(aryl)), 7.01–6.96 (m, 1H, HC(aryl)), 4.23 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.12–4.07 (m, 1H, HC(6)), 3.60 (td, *J* = 11.8, 2.1 Hz, 1H, HC(6)), 3.24 (ddd, *J* = 11.5, 10.1, 4.0 Hz, 1H, HC(3)), 2.60 (qd, *J* = 7.4, 3.3 Hz, 2H, HC(18)), 2.29–2.23 (m, 1H, HC(4)), 1.89–1.77 (m, 1H, HC(5)), 1.77–1.65 (m, 2H, HC(4), HC(5)), 1.09 (t, *J* = 7.5 Hz, 3H, HC(19))

<u>^{13}C NMR:</u> (125 MHz, CDCl$_3$)

δ 146.3 (C(13)), 139.9 (C(7)), 133.6 (C(aryl)), 132.6 (C(aryl)), 128.4 (C(aryl)), 128.1 (C(aryl)), 128.1 (C(aryl)), 127.6 (C(aryl)), 127.4 (C(aryl)), 125.9 (C(aryl)), 85.1 (C(2)), 68.6 (C(6)), 50.8 (C(3)), 32.4 (C(4)), 27.1 (C(alkyl)), 27.0 (C(alkyl)), 15.1 (C(19))

<u>MS</u>: (ES$^+$, 70 eV)

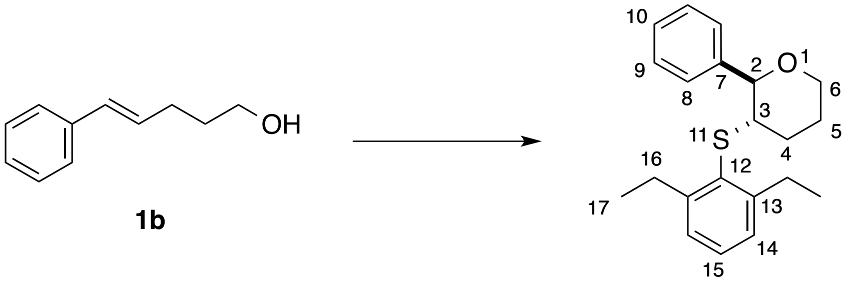
298 (100, M$^+$), 227 (13), 177 (10), 160 (52), 149 (94), 135 (35), 115 (10), 105 (24), 91 (43), 77 (23)

<u>HRMS:</u> calcd for $C_{19}H_{23}OS^+$: 299.1470, found: 299.1470

<u>TLC:</u> *R$_f$* 0.41 (hexane/EtOAc, 10:1) [CAM]

<u>SFC:</u> (2*R*,3*S*)-**4bg**, *t*$_R$ 22.30 min (97.5%); (2*S*,3*R*)-**4bg**, *t*$_R$ 8.99 min (2.5%) (Chiralpak OD, 5% MeOH in CO$_2$, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 8: (2*R*,3*S*)-3-((2,6-Diethylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bh)



4bh

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.5 mg, 6.7 μmol, 0.10 equiv) and sulfenylating agent **2h** (23.0 mg, 73.9 μmol, 1.06 equiv). To this was added **1b** (11.3 mg, 69.7 μmol) in CDCl$_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 24 h. At this point, the reaction proceeded to > 95% conversion by ^{1}H NMR analysis and was quenched with Et$_3$N (0.10 mL). Purification by column chromatography (SiO$_2$, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 19 mg of **4bh**.

<u>Data for **4bh**:</u>

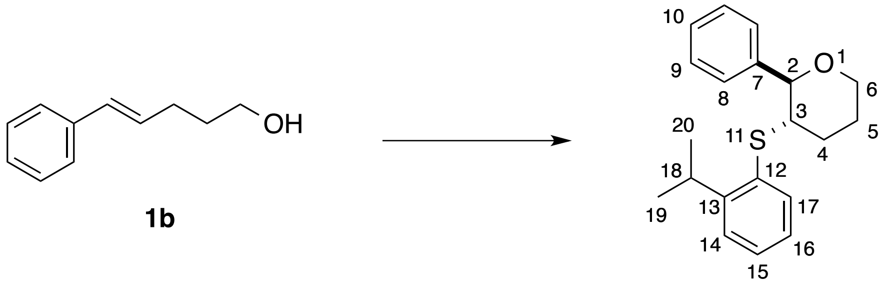
<u>^{1}H NMR:</u> (400 MHz, CDCl$_3$)

δ 7.42–7.38 (m, 2H, HC(8)), 7.36–7.28 (m, 3H, HC(9), HC(10)), 7.16 (t, *J* = 7.6 Hz, 1H, HC(15)), 7.03 (d, *J* = 7.5 Hz, 1H, HC(14)), 4.25 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.06 (ddd, *J* = 11.5, 4.1, 1.9 Hz, 1H, HC(6)), 3.59 (td, *J* = 11.3, 2.3 Hz, 1H, HC(6)), 3.10 (td, *J* = 10.6, 3.9 Hz, 1H, HC(3)), 2.83–2.63 (m, 4H, HC(16)), 1.93–1.86 (m, 1H, HC(4)), 1.76–1.56 (m, 3H, HC(4), HC(5)), 1.10 (t, *J* = 7.5 Hz, 6H, HC(17))

SFC: (2*R*,3*S*)-**4bh**, t_R 22.39 min (98.0%); (2*S*,3*R*)-**4bh**, t_R 8.01 min (2.0%) (Chiralpak OD, 5% MeOH in CO$_2$, 2.0 mL/min, 220 nm, 40 °C)

Full characterization of compound **4bh** is provided in section Table 2 Entry 3.

Table 1 Entry 9: (2*R*,3*S*)-3-((2-Isopropylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bi)



4bi

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.4 mg, 6.5 μmol, 0.09 equiv) and sulfenylating agent **2i** (22.1 mg, 74.3 μmol, 1.08 equiv). To this was added **1b** (11.2 mg, 69.0 μmol) in CDCl$_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 48 h. At this point, the reaction proceeded to ca. 67% conversion by ^{1}H NMR analysis and was quenched with Et$_3$N (0.10 mL). Purification by column chromatography (SiO$_2$, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 11 mg of **4bi**.

Data for **4bi**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.40–7.35 (m, 2H, HC(8)), 7.32–7.23 (m, 3H, HC(9), HC(10)), 7.17–7.10 (m, 3H, HC(aryl)), 7.01–6.94 (m, 1H, HC(aryl)), 4.22 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.11–4.06 (m, 1H, HC(6)), 3.60 (td, *J* = 11.8, 2.1 Hz, 1H, HC(6)), 3.33 (hept, *J* = 6.9 Hz, 1H, HC(18)), 3.19 (ddd, *J* = 11.5, 10.1, 4.0 Hz, 1H, HC(3)), 2.27–2.18 (m, 1H, HC(4)), 1.89–1.77 (m, 1H, HC(5)), 1.77–1.63 (m, 2H, HC(4), HC(5)), 1.10 (d, *J* = 6.9 Hz, 3H, HC(19)), 1.08 (d, *J* = 6.9 Hz, 3H, HC(20))

^{13}C NMR: (125 MHz, CDCl$_3$)

δ 150.9 (C(13)), 140.0 (C(7)), 134.0 (C(aryl)), 132.1 (C(aryl)), 128.2 (C(aryl)), 128.1 (C(aryl)), 127.7 (C(aryl)), 127.6 (C(aryl)), 125.7 (C(aryl)), 125.5 (C(aryl)), 85.0 (C(2)), 68.6 (C(6)), 51.3 (C(3)), 32.4 (C(4)), 30.2 (C(18)), 27.1 (C(5)), 23.8 (C(19)), 23.5 (C(20))

MS: (ES$^+$, 70eV)

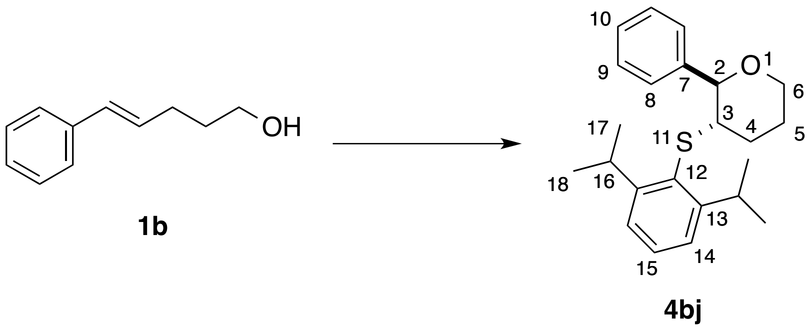
312 (100, M$^+$), 241 (12), 207 (6), 191 (6), 163 (87), 149 (40), 135 (24), 115 (14), 105 (23), 91 (50), 77 (15)

HRMS: calcd for $C_{20}H_{25}OS^+$: 313.1626, found: 313.1627

TLC: R_f 0.43 (hexane/EtOAc, 10:1) [CAM]

SFC: (2*R*,3*S*)-**4bi**, t_R 17.49 min (96.3%); (2*S*,3*R*)-**4bi**, t_R 7.49 min (3.7%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entries 10–12: (2*R*,3*S*)-3-((2,6-Diisopropylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bj)



Entry 10 (Reaction at –20 °C). Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.8 mg, 7.3 μmol, 0.11 equiv) and sulfenylating agent **2j** (25.5 mg, 75.1 μmol, 1.07 equiv). To this was added **1b** (11.3 mg, 69.7 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 65 h. At this point, the reaction proceeded to ca. 70% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 11 mg of **4bj** along with small impurities.

SFC: (2*R*,3*S*)-**4bj**, t_R 15.83 min (99.1%); (2*S*,3*R*)-**4bj**, t_R 6.54 min (0.9%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Entry 11 (Reaction at 0 °C). Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.5 mg, 6.7 µmol, 0.10 equiv) and sulfenylating agent **2j** (22.2 mg, 65.4 µmol). To this was added **1b** (10.7 mg, 66.0 µmol, 1.00 equiv) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.3 µL, 67 µmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at 0 °C for 24 h. At this point, the reaction proceeded to ca. 80% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 9.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 13 mg of **4bj** along with small impurities.

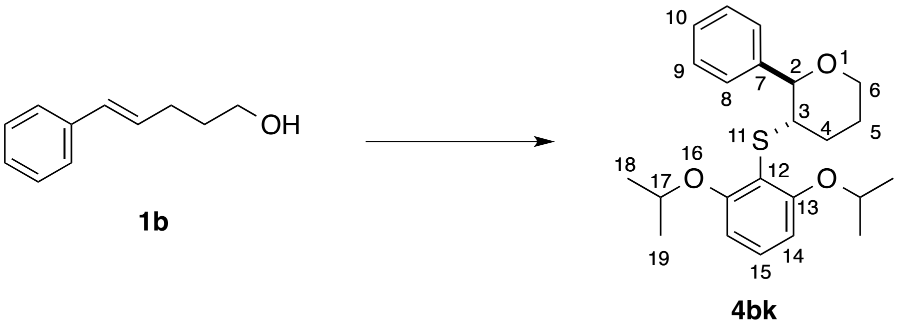
SFC: (2*R*,3*S*)-**4bj**, t_R 15.52 min (99.0%); (2*S*,3*R*)-**4bj**, t_R 6.49 min (1.0%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Entry 12 (Reaction at room temperature). Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.4 mg, 6.5 µmol, 0.10 equiv) and sulfenylating agent **2j** (22.9 mg, 67.4 µmol, 1.03 equiv). To this was added **1b** (10.6 mg, 65.3 µmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.2 µL, 65 µmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at 0 °C for 24 h. At this point, the reaction proceeded to ca. 80% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 9.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 13 mg of **4bj** along with small impurities.

SFC: (2*R*,3*S*)-**4bj**, t_R 15.38 min (98.0%); (2*S*,3*R*)-**4bj**, t_R 6.42 min (2.0%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Full characterization of compound **4bj** is provided in section Table 2 Entry 4.

Table 1 Entry 13: (2*R*,3*S*)-3-((2,6-Diisopropoxyphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bk)



1b

4bk

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.2 mg, 6.1 μmol, 0.10 equiv) and sulfenylating agent **2k** (27.1 mg, 73.0 μmol, 1.22 equiv). To this was added **1b** (9.7 mg, 60 μmol) in $CDCl_3$ (0.70 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.2 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 24 h. At this point, the reaction proceeded to ca. 80% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1→20:1) afforded 13 mg of **4bk**.

Data for **4bk**:

^{1}H NMR: (400 MHz, $CDCl_3$)
δ 7.41–7.34 (m, 2H, HC(8)), 7.24–7.15 (m, 3H, HC(9), HC(10)), 7.03 (t, *J* = 8.3 Hz, 1H, HC(15)), 6.37 (d, *J* = 8.3 Hz, 2H, HC(14)), 4.43 (hept, *J* = 6.1 Hz, 2H, HC(17)), 4.26 (d, *J* = 10.2 Hz, 1H, HC(2)), 4.08–4.02 (m, 1H, HC(6)), 3.60 (td, *J* = 11.0, 4.3 Hz, 1H, HC(6)), 3.58 (td, *J* = 11.7, 2.4 Hz, 1H, HC(3)), 2.07–1.99 (m, 1H, HC(4)), 1.83–1.53 (m, 3H, HC(4), HC(5)), 1.35 (d, *J* = 6.1 Hz, 6H, HC(18)), 1.32 (d, *J* = 6.1 Hz, 6H, HC(19))

^{13}C NMR: (125 MHz, $CDCl_3$)
δ 159.5 (C(13)), 139.9 (C(7)), 128.5 (C(aryl)), 127.9 (C(aryl)), 127.8 (C(aryl)), 127.7 (C(aryl)), 111.9 (C(12)), 106.5 (C(14)), 85.4 (C(2)), 70.9 (C(17)), 68.6 (C(6)), 46.6 (C(3)), 31.3 (C(4)), 27.1 (C(5)), 22.2 (C(18)), 22.1 (C(19))

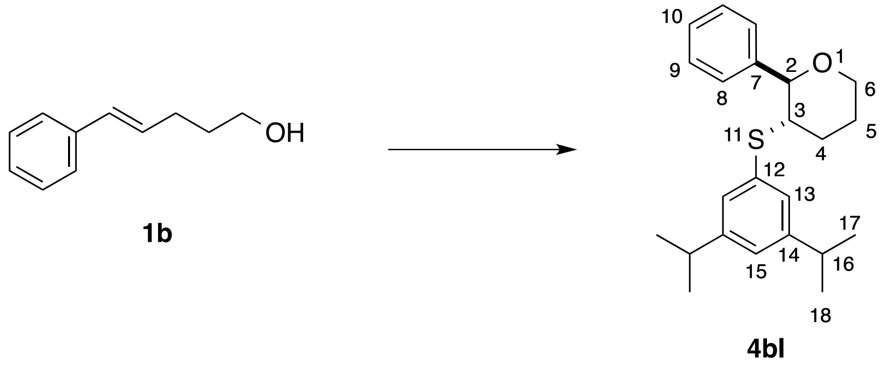
MS: (ES^+, 70 eV)
315 (29), 273 (41), 226 (50), 194 (29), 184 (26), 168 (21), 161 (84), 153 (100), 142 (66), 131 (9), 115 (9), 105 (34), 91 (87), 77 (12)

HRMS: calcd for $C_{23}H_{31}O_3S^+$: 387.1994, found: 387.1995

TLC: R_f 0.40 (hexane/EtOAc, 6:1) [CAM]

SFC: (2*R*,3*S*)-**4bk**, t_R 13.15 min (98.0%); (2*S*,3*R*)-**4bk**, t_R 7.40 min (2.0%) (Chiralpak OD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 14: (2*R*,3*S*)-3-((3,5-Diisopropylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bl)



Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.3 mg, 6.3 μmol, 0.09 equiv) and sulfenylating agent **2l** (25.3 mg, 74.5 μmol, 1.09 equiv). To this was added **1b** (11.1 mg, 68.4 μmol) in CDCl$_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 48 h. At this point, the reaction proceeded to ca. 80% conversion by ^{1}H NMR analysis and was quenched with Et$_3$N (0.10 mL). Purification by column chromatography (SiO$_2$, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 10 mg of **4bl**.

Data for **4bl**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.38–7.34 (m, 2H, HC(8)), 7.29–7.21 (m, 3H, HC(9), HC(10)), 6.84 (t, *J* = 1.6 Hz, 1H, HC(15)), 6.75 (d, *J* = 1.6 Hz, 2H, HC(13)), 4.18 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.11–4.06 (m, 1H, HC(6)), 3.56 (td, *J* = 11.7, 2.0 Hz, 1H, HC(6)), 3.58 (ddd, *J* = 11.6, 10.1, 4.0 Hz, 1H, HC(3)), 2.74 (hept, *J* = 6.8 Hz, 2H, HC(16)), 2.38–2.30 (m, 1H, HC(4)), 1.93–1.82 (m, 1H, HC(5)), 1.77–1.65 (m, 2H, HC(4), HC(5)), 1.18 (d, *J* = 6.8 Hz, 6H, HC(17)), 1.17 (d, *J* = 6.8 Hz, 6H, HC(18))

^{13}C NMR: (125 MHz, CDCl$_3$)

δ 149.1 (C(14)), 140.1 (C(7)), 133.1 (C(aryl)), 128.4 (C(aryl)), 128.1 (C(aryl)), 128.1 (C(aryl)), 127.8 (C(aryl)), 123.8 (C(aryl)), 85.4 (C(2)), 68.5 (C(6)), 50.7 (C(3)), 33.9 (C(16)), 32.5 (C(4)), 27.1 (C(5)), 23.9 (C(17)), 23.8 (C(18))

MS: (ES$^+$, 70 eV)

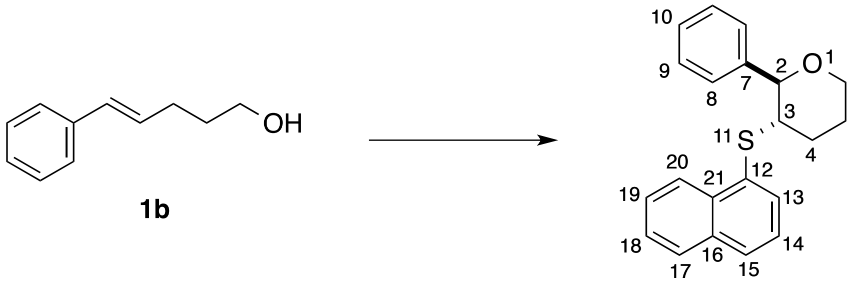
283 (53), 220 (25), 205 (20), 195 (45), 177 (21), 160 (100), 149 (17), 135 (67), 115 (15), 105 (35), 91 (53), 77 (16)

HRMS: calcd for $C_{23}H_{31}OS^+$: 355.2096, found: 355.2106

TLC: R_f 0.48 (hexane/EtOAc, 10:1) [CAM]

SFC: (2*R*,3*S*)-**4bl**, t_R 18.45 min (94.0%); (2*S*,3*R*)-**4bl**, t_R 8.76 min (6.0%) (Chiralpak OD, 3% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 15: (2*R*,3*S*)-3-(1-Naphthalenylthio)-2-phenyltetrahydro-2*H*-pyran (4bm)



4bm

Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.6 mg, 6.9 μmol, 0.10 equiv) and sulfenylating agent **2m** (22.6 mg, 74.0 μmol, 1.05 equiv). To this was added **1b** (11.3 mg, 69.7 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 21 h. At this point, the reaction proceeded to ca. 95% conversion by ^{1}H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 23 mg of **4bm** along with 10% Lewis base contaminant.

Data for **4bm**:

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

δ 8.16–8.11 (m, 1H, HC(aryl)), 7.82–7.78 (m, 1H, HC(aryl)), 7.72 (d, *J* = 8.2 Hz, 1H, HC(aryl)), 7.49–7.45 (m, 2H, HC(aryl)), 7.39–7.34 (m, 3H, HC(aryl)), 7.29–7.25 (m, 3H, HC(aryl)), 7.22 (dd, *J* = 8.2, 7.1 Hz, 1H, HC(aryl)), 4.29 (d, *J* = 10.2 Hz, 1H, HC(2)), 4.11–4.02 (m, 1H, HC(6)), 3.62–3.55 (m, 1H, HC(6)), 3.28–3.20 (m, 1H, HC(3)), 2.23–2.16 (m, 1H, HC(4)), 1.79–1.64 (m, 3H, HC(4), HC(5))

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

δ 140.0 (C(aryl)), 134.5 (C(aryl)), 134.0 (C(aryl)), 133.6 (C(aryl)), 130.8 (C(aryl)), 128.7 (C(aryl)), 128.4 (C(aryl)), 128.3 (C(aryl)), 128.2 (C(aryl)), 128.1 (C(aryl)), 127.7 (C(aryl)), 126.5 (C(aryl)), 126.0 (C(aryl)), 125.2 (C(aryl)), 85.2 (C(2)), 68.5

(C(6)), 50.9 (C(3)), 32.3 (C(4)), 27.0 (C(5))

MS: (ESI)

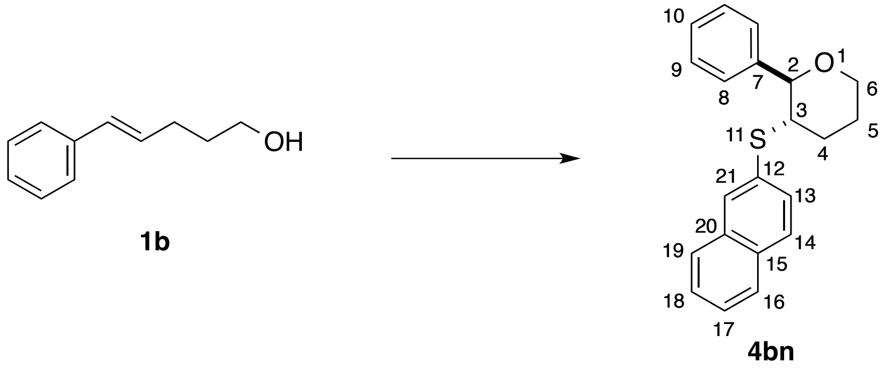
458 (100), 321 (58, M+H), 303 (69), 161 (27)

HRMS: calcd for $C_{21}H_{21}OS^+$: 321.1313, found: 321.1315

TLC: R_f 0.33 (hexane/EtOAc, 10:1) [CAM]

SFC: (2*R*,3*S*)-**4bm**, t_R 19.36 min (92.6%); (2*S*,3*R*)-**4bm**, t_R 11.89 min (7.4%) (Chiralpak OD, 15% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Table 1 Entry 16: (2*R*,3*S*)-3-(2-Naphthalenylthio)-2-phenyltetrahydro-2*H*-pyran (4bn)



Following General Procedure 2, an oven-dried, 5-mm NMR tube was charged with (*R*)-**3c** (3.5 mg, 6.7 μmol, 0.10 equiv) and sulfenylating agent **2n** (22.6 mg, 74.0 μmol, 1.05 equiv). To this was added **1b** (11.3 mg, 69.7 μmol) in $CDCl_3$ (0.65 mL) and the NMR tube was cooled in a dry-ice/acetone bath. MsOH (4.5 μL, 70 μmol, 1.0 equiv) was added via syringe and the reaction mixture was kept at –20 °C for 48 h. At this point, the reaction proceeded to ca. 90% conversion by ^1H NMR analysis and was quenched with Et_3N (0.10 mL). Purification by column chromatography (SiO_2, 8.0 g, 10 mm ∅, hexane/EtOAc, 60:1) afforded 14 mg of **4bn** along with 1% Lewis base contaminant.

Data for **4bn**:

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

δ 7.77–7.70 (m, 1H, HC(aryl)), 7.64–7.59 (m, 2H, HC(aryl)), 7.50 (s, 1H, HC(21)), 7.46–7.36 (m, 4H, HC(aryl)), 7.27–7.16 (m, 4H, HC(aryl)), 4.24 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.12–4.06 (m, 1H, HC(6)), 3.61–3.53 (m, 1H, HC(6)), 3.35–3.27 (m, 1H, HC(3)), 2.37–2.27 (m, 1H, HC(4)), 1.94–1.69 (m, 3H, HC(4), HC(5))

MS:	(ESI) 458 (100), 369 (35), 321 (58, M+H), 303 (21), 161 (94)
HRMS:	calcd for $C_{21}H_{21}OS^+$: 321.1313, found: 321.1313
TLC:	R_f 0.41 (hexane/EtOAc, 6:1) [CAM]
SFC:	(2*R*,3*S*)-**4bn**, t_R 18.70 min (91.8%); (2*S*,3*R*)-**4bn**, t_R 26.85 min (8.2%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

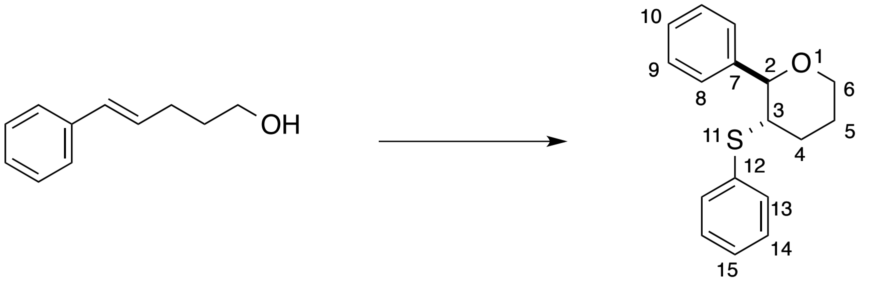
Substrate Scope Survey (Table 2)

General Procedure 3: Sulfenofunctionalisation Using Sterically Demanding Sulfenylating Agents

Following the literature procedure,[16] an oven-dried Schlenk flask was charged with the sulfenylating agent (1.05 mmol, 1.05 equiv), catalyst (*R*)-**3c** (52.0 mg, 0.100 mmol, 0.100 equiv), the corresponding alkene (1.00 mmol), nucleophile (if indicated, 1.00 mmol, 1.00 equiv) and CH_2Cl_2. The flask was capped with a septum and placed into an *i*-PrOH bath, which was cooled to the appropriate temperature using a cryocool unit. The temperature of the mixture was monitored via a thermocouple digital temperature probe. After the temperature stabilized, MsOH (65 μL, 1.0 mmol, 1.0 equiv) was added via syringe and the mixture was allowed to stir for the indicated time. Upon complete reaction (TLC monitoring) the mixture was quenched while cold by the addition of Et_3N (0.20 mL). The mixture was poured into aqueous HCl (1.0 M, 20 mL) in a separatory funnel, CH_2Cl_2 (30 mL) was added and the layers were thoroughly mixed. The organic layer was poured into aqueous NaOH (1.0 M, 20 mL), and the layers were thoroughly mixed and then separated. The acidic layer was back-extracted with CH_2Cl_2 (30 mL) which was poured into the basic layer and used to extract that layer as well. Both organic portions were combined, dried over $MgSO_4$, filtered through glass wool and concentrated in vacuo (20–23 °C, 20 mmHg). The products were purified by silica gel column chromatography using silica gel.

Sulfenofunctionalisation Using Sterically Demanding Sulfenylating Agents

Preparation of (2*R*,3*S*)-2-Phenyl-3-(phenylthio)tetrahydro-2*H*-pyran (4ba) (Table 2, Entry 1)



4ba

Since **4ba** is a known compound,[16] the thioetherification reaction was conducted on a 0.20 mmol scale. Following General Procedure 3, an oven-dried, 6 dram vial was charged with the sulfenylating agent (51 mg, 0.20 mmol, 1.0 equiv), catalyst (*R*)-**3c** (10.4 mg, 0.020 mmol, 0.100 equiv), **2a** (32 mg, 0.20 mmol) and CH_2Cl_2 (1.0 mL). The vial was capped with a polypropylene open hole cap and cooled to –20 °C in an *i*-PrOH bath. After 15 min at this temperature, MsOH (12.9 µL, 20.0 µmol, 1.00 equiv) was added and the mixture was allowed to stir for 36 h. The reaction was worked up following the general procedure (the amounts of CH_2Cl_2, HCl and NaOH were proportionally decreased for the 0.20 mmol scale). Purification by chromatography (SiO_2, 30 g, 20 mm ∅, hexane/MTBE, 60:1→30:1) afforded **4ba** (42 mg, 78%) as a yellowish oil, which solidified upon standing. The spectroscopic data match those published in the literature.[16]

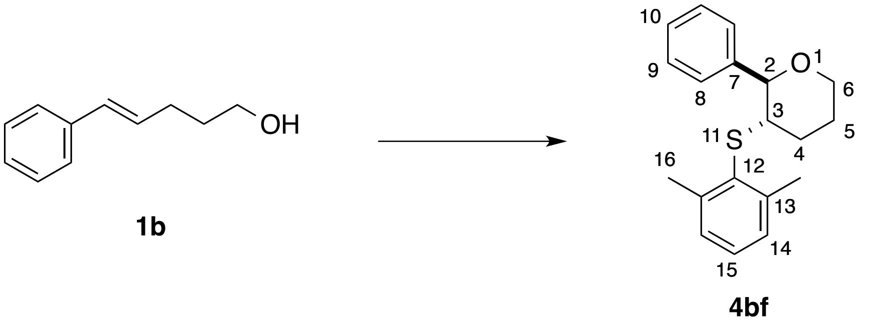
Data for **4ba**:

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

δ 7.39–7.35 (m, 2H, H(C(8)), 7.31–7.23 (m, 3H, H(C(9), HC(10)), 7.16–7.09 (m, 5H, H(C(aryl)), 4.20 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.12–4.06 (m, 1H, HC(6)), 3.57 (td, *J* = 12.1, 2.1 Hz, 1H, HC(6)), 3.24 (ddd, *J* = 11.5, 10.1, 4.0 Hz, 1H, HC(3)), 2.33–2.26 (m, 1H, HC(4)), 1.92–1.80 (m, 1H, HC(5)), 1.76–1.63 (m, 2H, HC(4), HC(5)).

SFC: (2*R*,3*S*)-**4ba**, t_R 6.03 min (95.6%); (2*S*,3*R*)-**4ba**, t_R 8.30 min (4.4%) (Chiralpak AD, 5% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Preparation of (2*R*,3*S*)-3-((2,6-Dimethylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bb) (Table 2, Entry 2)



Following General Procedure 3, an oven-dried Schlenk flask was charged with **2f** (287 mg, 1.01 mmol, 1.01 equiv), catalyst (*R*)-**3c** (51.0 mg, 0.098 mmol, 0.098 equiv), **1b** (162 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). The mixture was cooled to –20 °C in an *i*-PrOH bath. MsOH (65 µL, 1.0 mmol, 1.0 equiv) was added via syringe and the mixture was allowed to stir for 36 h at –20 °C. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 150 g, 40 mm ∅, hexane/EtOAc, 60:1→30:1) afforded 191 mg of pure **4bf** along with a mixed fraction containing **4bf** and catalyst (*R*)-**3c**. The mixed fraction was subjected to a second purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 100:1→60:1) yielding another 60 mg of pure **4bf** (combined yield: 251 mg, 84%, pale yellow oil). An analytically pure sample was obtained by Kugelrohr distillation.

Data for **4bf**:

bp: 171°C (ABT), 0.3 mmHg

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

δ 7.41–7.36 (m, 2H, HC(8)), 7.33–7.27 (m, 3H, HC(9), HC(10)), 7.07–7.02 (m, 1H, HC(15)), 7.02–6.98 (m, 2H, HC(14)), 4.26 (d, *J* = 10.0 Hz, 1H, HC(2)), 4.10–4.04 (m, 1H, HC(6)), 3.60 (td, *J* = 11.7, 2.4 Hz, 1H, HC(6)), 3.18 (dt, *J* = 11.1, 4.3 Hz, 1H, HC(3)), 2.33 (s, 6H, HC(16)), 1.94–1.87 (m, 1H, HC(4)), 1.78–1.68 (m, 1H, HC(5)), 1.67–1.56 (m, 2H, HC(4) and HC(5))

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

143.3 (C(13)), 139.8 (C(7)), 131.5 (C(12)), 128.3 (C(aryl)), 128.1 (C(aryl)), 127.9 (C(aryl)), 127.8 (C(aryl)), 127.5 (C(aryl)), 85.1 (C(2)), 68.6 (C(6)), 48.9 (C(3)), 31.6 (C(4)), 26.9 (C(5)), 22.1 (C(16))

IR: (NaCl plate)
3058 (m), 3031 (m), 2945 (s), 2848 (s), 2722 (m), 1941 (w), 1869 (w), 1801 (w), 1657 (w), 1582 (m), 1492 (m), 1459 (s), 1435 (m), 1374 (m), 1326 (m), 1286 (w), 1260 (m), 1226 (w), 1208 (w), 1178 (m), 1104 (s), 1079 (s), 1027 (s), 968 (m), 943 (m), 906 (m), 883 (m), 852 (w), 820 (m), 772 (s), 754 (s)

MS: (ES^+, 70 eV)
298 (88, M^+), 227 (21), 207 (5), 192 (5), 177 (20), 160 (69), 149 (100), 134 (15), 115 (10), 105 (35), 91 (60), 77 (25), 65 (5)

HRMS: calcd for $C_{19}H_{23}OS^+$: 299.1470, found: 299.1468

TLC: R_f 0.34 (hexane/EtOAc, 15:1) [CAM]

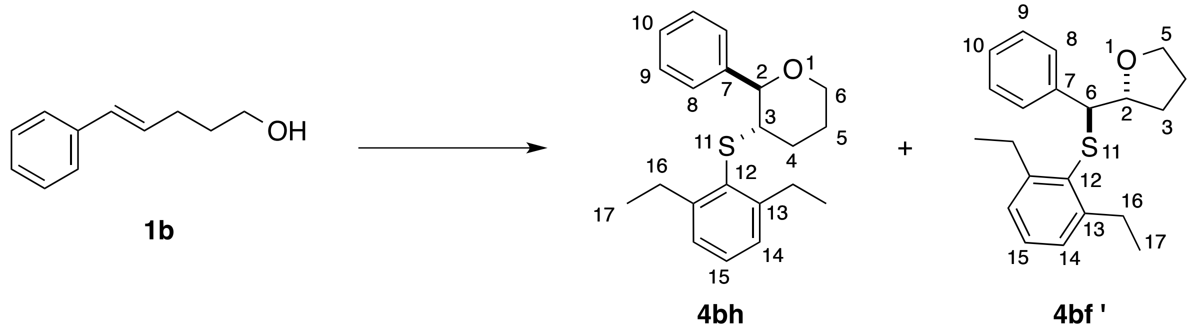
Opt. Rot. : $[\alpha]_D^{24}$ –13.8 (c = 0.57, $CHCl_3$)

SFC: (2*R*,3*S*)-**4bf**, t_R 12.36 min (97.6%); (2*S*,3*R*)-**4bf**, t_R 5.88 min (2.4%) (Chiralpak OD, 10% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{19}H_{22}OS$ (298.44)

Calcd:	C, 76.47;	H, 7.43;
Found:	C, 76.65;	H, 7.25;

Preparation of (2*R*,3*S*)-3-((2,6-Diethylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bh) and (*R*)-2-((*S*)-((2,6-Diethylphenyl)thio)(phenyl)methyl)tetrahydrofuran (4bh') (Table 2, Entry 3)



Following General Procedure 3, an oven-dried Schlenk flask was charged with **2h** (315 mg, 1.01 mmol, 1.02 equiv), catalyst (*R*)-**3c** (52.7 mg, 0.101 mmol, 0.101 equiv), **1b** (161 mg, 0.992 mmol), and CH_2Cl_2 (5.0 mL). The mixture was cooled to –20 °C in an *i*-PrOH bath. MsOH (65 μL, 1.0 mmol, 1.0 equiv) was added via syringe and the mixture was allowed to stir for 36 h at –20 °C. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 100:1) afforded 285 mg (87%) of a 97:3 mixture of **4bh** and **4bh'** as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation.

Data for isomer mixture:

bp: 171°C (ABT), 0.3 mmHg

IR: (NaCl plate)
3052 (m), 3032 (m), 2962 (s), 2850 (s), 2718 (w), 1941 (w), 1863 (w), 1797 (w), 1573 (m), 1493 (m), 1454 (s), 1433 (m), 1371 (m), 1326 (m), 1306 (m), 1260 (m), 1225 (w), 1170 (m), 1105 (s), 1079 (s), 1027 (s), 999 (w), 968 (m), 943 (m), 905 (w), 883 (m), 853 (w), 800 (m), 754 (s)

TLC: R_f 0.39 (hexanes/EtOAc, 15:1) [CAM]

HRMS: calcd for $C_{21}H_{27}OS^+$: 327.1783, found: 327.1781

Opt. Rot. : $[\alpha]_D^{24}$ –3.6 (c = 0.57, $CHCl_3$)

Analysis: $C_{21}H_{26}OS$ (326.50)
Calcd: C, 77.25; H, 8.03;
Found: C, 77.09; H, 7.98;

Data for **4bh**:

^{1}H NMR: (500 MHz, $CDCl_3$)
δ 7.42–7.38 (m, 2H, HC(8)), 7.36–7.28 (m, 3H, HC(9), HC(10)), 7.16 (t, *J* = 7.6 Hz, 1H, HC(15)), 7.03 (d, *J* = 7.5 Hz, 2H, HC(14)), 4.25 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.06 (ddd, *J* = 11.5, 4.1, 1.9 Hz, 1H, HC(6)), 3.59 (td, *J* = 11.3, 2.3 Hz, 1H, HC(6)), 3.10 (td, *J* = 10.6, 3.9 Hz, 1H, HC(3)), 2.83–2.63 (m, 4H, HC(16)), 1.93–1.86 (m, 1H, HC(4)), 1.76–1.56 (m, 3H, HC(4), HC(5)), 1.10 (t, *J* = 7.5 Hz, 6H, HC(17))

^{13}C NMR: (125 MHz, $CDCl_3$)
149.4 (C(13)), 139.9 (C(7)), 130.3 (C(12)), 128.5 (C(aryl)), 128.3 (C(aryl)), 128.1 (C(aryl)), 127.5 (C(aryl)), 126.2 (C-(aryl)), 84.8 (C(2)), 68.6 (C(6)), 50.5 (C(3)), 31.7 (C(4)), 28.1 (C(16)), 26.9 (C(5)), 15.6 (C(17))

MS: (ES^+, 70 eV)
326 (100, M^+), 225 (19), 217 (6), 205 (5), 192 (17), 177 (56), 161 (61), 149 (31), 135 (27), 115 (16), 105 (31), 91 (55), 77 (15), 55 (5)

SFC: (2*R*,3*S*)-**4bh**, t_R 13.69 min (98.4%); (2*S*,3*R*)-**4bh**, t_R 5.87 min (1.6%) (Chiralpak OD, 10% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Data for **4bh'**:

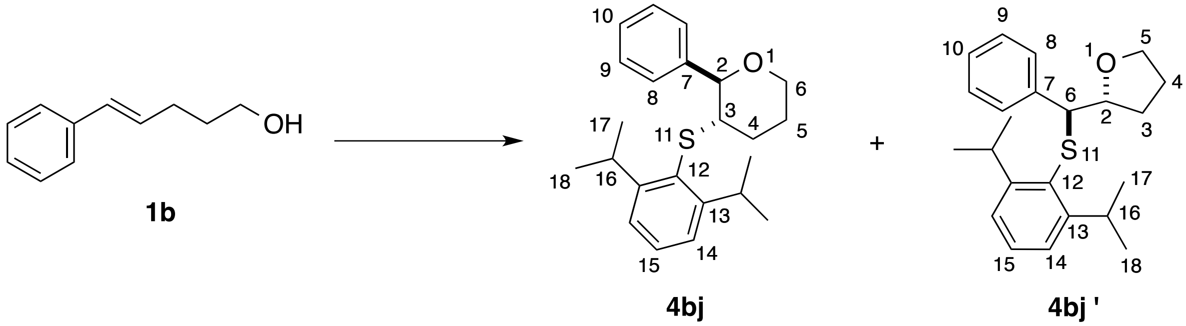
^{1}H NMR: (500 MHz, $CDCl_3$)

Diagnostic signals: δ 4.43–4.37 (m, 1H, HC(2)), 3.84–3.72 (m, 2H, HC(5))

MS: (ES^+, 70 eV)

326 (9, M^+), 281 (62), 255 (15), 207 (100), 191 (12), 161 (15), 91 (30)

Preparation of (2*R*,3*S*)-3-((2,6-Diisopropylphenyl)thio)-2-phenyltetrahydro-2*H*-pyran (4bj) and (*R*)-2-((*S*)-((2,6-Diisopropylphenyl)thio)(phenyl)methyl)tetrahydrofuran (4bj') (Table 2, Entry 4)



Following General Procedure 3, an oven-dried Schlenk flask was charged with **2j** (351 mg, 1.03 mmol, 1.03 equiv), catalyst (*R*)-**3c** (51.0 mg, 0.098 mmol, 0.098 equiv), **1b** (162 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). The mixture was cooled to 0 °C in an *i*-PrOH bath. MsOH (65 μL, 1.0 mmol, 1.0 equiv) was added via syringe and the mixture was allowed to stir for 48 h at 0 °C. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 60:1) afforded 310 mg (87%) of a 93:7 mixture of **4bj** and **4bj'** as a pale yellow oil. Partial separation of isomers was accomplished by column chromatography using high porosity silica gel (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 80:1→5:1) yielding 271 mg of a 97:3 mixture of **4bj** and **4bj'** and 30 mg of a 60:40 mixture of **4bj** and **4bj'**.

Data for isomer mixture (**4bj**:**4bj'**= 97:3):

IR: (NaCl plate)

3054 (m), 3026 (m), 2960 (s), 2864 (s), 2718 (w), 2360 (w), 2333 (w), 1941 (w), 1866 (w), 1801 (w), 1573 (m), 1493 (m), 1454 (s), 1420 (m), 1381 (m), 1360 (m), 1325 (m), 1307 (m), 1260 (m), 1226 (w), 1178 (m), 1106 (s), 1079 (s), 1053 (m), 1028 (s), 969 (m), 943 (m), 905 (w), 883 (m), 820 (m), 801 (m), 773 (m), 754 (s)

HRMS: calcd for $C_{23}H_{31}OS^+$: 355.2096, found: 355.2097

TLC: R_f 0.44 **4bj** and **4bj'** and (hexanes/EtOAc, 15:1) [CAM]

Opt. Rot. : $[\alpha]_D^{24}$ –9.7 (c = 0.27, $CHCl_3$)

Data for **4bj**:

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

δ 7.45 (d, *J* = 7.9 Hz, 2H, HC(8)), 7.38 (t, *J* = 8.0 Hz, 2H, HC(9)), 7.36–7.32 (m, 1H, HC(10)), 7.26 (t, *J* = 7.4 Hz, 1H, HC(15)), 7.09 (d, *J* = 7.6 Hz, 2H, HC(14)), 4.25 (d, *J* = 10.1 Hz, 1H, HC(2)), 4.10–4.04 (m, 1H, HC(6)), 3.71–3.45 (m, 3H, HC(6), HC(16)), 3.0–2.91 (m, 1H, HC(3)), 1.95–1.85 (m, 1H, HC(4)), 1.72–1.60 (m, 3H, HC(4), and HC(5)), 1.12 (d, *J* = 6.9 Hz, 6H, HC(17)), 1.09 (br d, *J* = 6.5 Hz, 6H, HC(18))

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

153.8 (C(13)), 140.1 (C(7)), 129.1 (C(12)), 129.0 (C(15)), 128.3 (C(10)), 128.1 (C(9)), 127.4 (C(8)), 123.4 (C(14)), 84.3 (C(2)), 68.6 (C(6)), 51.9 (C(3)), 31.8 (C(4)), 31.3 (C(16)), 27.0 (C(5)), 24.6 (C(17)), 23.8 (C(18))

MS: (ES^+, 70 eV)

311 (14), 283 (25), 263 (6), 247 (10), 205 (19), 192 (25), 177 (7), 161 (100), 149 (60), 135 (19), 115 (18), 105 (34), 91 (74), 77 (16), 55 (6)

SFC: (2*R*,3*S*)-**4bj**, t_R 10.06 min (99.3%); (2*S*,3*R*)-**4bj**, t_R 5.06 min (0.7%) (Chiralpak OD, 10% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Data for **4bj'**:

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

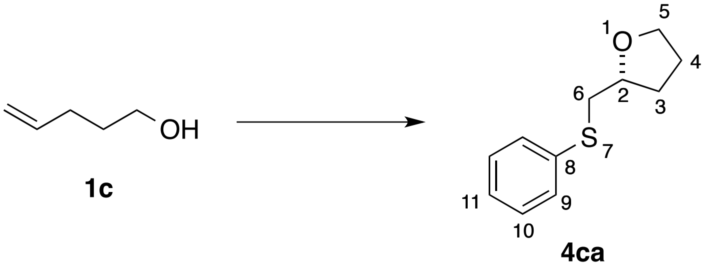
Diagnostic signals: δ 4.44–4.36 (m, 1H, HC(2)), 3.88–3.72 (m, 2H, HC(5)), 3.70 (d, *J* = 6.7 Hz, 1H, HC(6)), 2.18–2.09 (m, 1H, H(C(alkyl)), 1.19 (d, *J* = 6.9 Hz, 6H, HC(17)), 0.98 (d, *J* = 6.8 Hz, HC(18))

MS: (ES^+, 70 eV)

341 (9), 327 (7), 283 (7), 267 (9), 277 (7), 207 (100), 191 (10), 179 (10), 161 (49),

149 (13), 133 (7), 115 (18), 91 (80), 71 (13)

Preparation of (*R*)-2-((Phenylthio)methyl)tetrahydrofuran (4ca) (Table 2, Entry 5)



Since **4ca** is a known compound,[16] the thioetherification reaction was conducted on a 0.20 mmol scale: Following General Procedure 3, an oven-dried 6 dram vial was charged with the sulfenylating agent **2a** (56 mg, 0.22 mmol, 1.1 equiv), catalyst (*R*)-**3c** (11 mg, 0.021 mmol, 0.11 equiv), **1c** (17 mg, 0.20 mmol, 1.0 equiv), and CH_2Cl_2 (1.0 mL). The vial was capped with a polypropylene open hole cap and cooled to 0 °C in an *i*-PrOH bath. After 15 min at this temperature, MsOH (13 μL, 0.20 mmol, 1.0 equiv) was added and the mixture was allowed to stir for 36 h. The reaction was worked up following the general procedure (the amounts of CH_2Cl_2, HCl and NaOH were proportionally decreased for the 0.20 mmol scale). Purification by chromatography (SiO_2, 30 g, 20 mm ∅, hexane/EtOAc, 60:1) afforded **4ca** (36 mg, 83%) as a yellowish oil. The spectroscopic data match those published in the literature.[16]

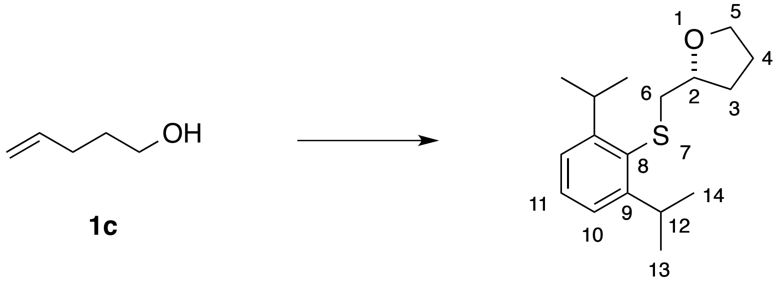
Data for **4ca**:

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

δ 7.37 (d, *J* = 8.0 Hz, 2H, HC(9)), 7.28 (t, *J* = 7.4 Hz, 2H, HC(10)), 7.17 (t, *J* = 7.3 Hz, 1H, HC(11)), 4.11–4.01 (m, 1H, HC(2)), 3.91 (dd, *J* = 15.0, 7.0 Hz, 1H, HC(5)), 3.77 (dd, *J* = 15.9, 7.3 Hz, 1H, HC(5)), 3.16 (dd, *J* = 13.0, 5.8 Hz, 1H, HC(6)), 2.97 (dd, *J* = 13.0, 6.8 Hz, 1H, HC(6)), 2.15–2.00 (m, 1H, HC(3)), 2.00–1.82 (m, 2H, HC(4)), 1.75–1.61 (m, 1H, HC(3)).

SFC: (2*R*)-**4ca**, t_R 7.55 min (88.9%); (2*S*)-**4ca**, t_R 6.05 min (11.1%) (Chiralpak AD, 4% MeOH in CO_2, 2.0 mL/min, 220 nm, 40 °C)

Preparation of (*R*)-2-(((2,6-Diisopropylphenyl)thio)methyl)tetrahydrofuran (4cj) (Table 2, Entry 6)



4cj

Following General Procedure 3, an oven-dried Schlenk flask was charged with **2j** (350 mg, 1.03 mmol, 1.03 equiv), catalyst (*R*)-**3c** (52.2 mg, 0.100 mmol, 0.100 equiv), **1c** (101 μL, 86.1 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). The mixture was cooled to 0 °C in an *i*-PrOH bath. MsOH (65 μL, 1.0 mmol, 1.0 equiv) was added via syringe and the mixture was allowed to stir for 36 h at 0 °C. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 60:1) afforded **4cj** (261 mg, 94%) as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation.

Data for **4cj**:

bp: 140°C (ABT), 0.3 mmHg

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

δ 7.30 (t, *J* = 7.7 Hz, 1H, HC(11)), 7.15 (d, *J* = 7.7 Hz, 2H, HC(10)), 4.03–3.93 (m, 3H, HC(12), HC(2)), 3.90 (dd, *J* = 15.6, 7.5 Hz, 1H, HC(5)), 3.75 (dd, *J* = 15.5, 7.6 Hz, 1H, HC(5)), 2.83 (dd, *J* = 12.4, 6.1 Hz, 1H, HC(6)), 2.68 (dd, *J* = 12.4, 6.7 Hz, 1H, HC(6)), 2.08–1.99 (m, 1H, HC(3)), 1.98–1.83 (m, 2H, HC(4)), 1.68–1.60 (m, 1H, HC(3)), 1.24 (d, *J* = 6.9 Hz, 6H, HC(13), 1.23 (d, *J* = 6.9 Hz, 6H, HC(14))

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

δ 153.2 (C(9)), 131.5 (C(8)), 129.1 (C(11)), 123.6 (C(10)), 77.9 (C(2)), 68.2 (C(5)), 42.9 (C(6)), 31.5 (C(12)), 31.0 (C(3)), 25.8 (C(4)), 24.43 (C(13)), 24.40 (C(14))

IR: (NaCl plate)

3054 (m), 2961 (s), 2867 (s), 1574 (m), 1461 (s), 1420 (m), 1382 (m), 1361 (m), 1307 (m), 1246 (m), 1178 (m), 1100 (m), 1054 (s), 928 (m), 800 (s), 745 (m)

MS: (ES$^+$, 70 eV)

278 (80, M$^+$), 219 (18), 192 (28), 177 (23), 161 (84), 149 (66), 135 (20), 115 (16),

105 (6), 91 (16), 71 (100)

HRMS: calcd for $C_{17}H_{27}OS^+$: 279.1783, found: 279.1779

TLC: R_f 0.25 (hexanes/EtOAc, 30:1) [CAM]

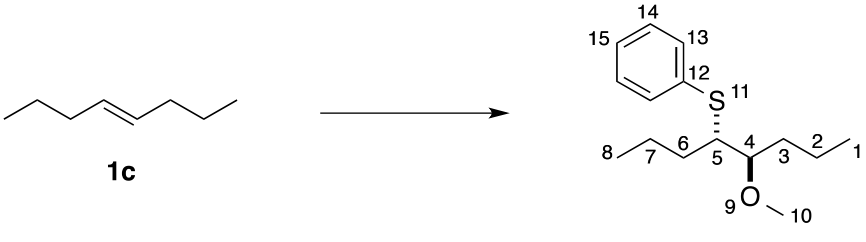
Opt. Rot. : $[\alpha]_D^{24}$ –0.7 (c = 0.66, $CHCl_3$)

HPLC: (2*R*)-**4cj**, t_R 13.47 min (98.6%); (2*S*)-**4cj**, t_R 14.97 min (1.4%) ((*R*,*R*)-Whelk-O1, hexane:*i*-PrOH = 99:1, 0.4 mL/min, 220 nm, 0 °C)

Analysis: $C_{17}H_{26}OS$ (278.45)

Calcd:	C, 73.33;	H, 9.41;
Found:	C, 73.13;	H, 9.41;

Preparation of (4*S*,5*R*)-5-(Methoxyoctan-4-yl)(phenyl)sulfane (4da) (Table 2, Entry 7)



4da

Since **4da** is a known compound,[16] the thioetherification reaction was conducted on a 0.20 mmol scale: Following General Procedure 3, an oven-dried 6 dram vial was charged with the sulfenylating agent **2a** (55.0 mg, 0.215 mmol, 1.10 equiv), catalyst (*R*)-**3c** (10.7 mg, 20.6 μmol, 0.105 equiv), **1d** (31.5 μL, 22.4 mg, 0.196 mmol), and CH_2Cl_2 (1.0 mL). MeOH (9.7 μL, 0.24 mmol, 1.2 equiv) was added, the vial was capped with a polypropylene open hole cap and cooled to –20 °C in an *i*-PrOH bath. After 15 min at this temperature, MsOH (14.5 μL, 0.22 mmol, 1.1 equiv) was added and the mixture was allowed to stir for 48 h. The reaction was worked up following the general procedure (the amounts of CH_2Cl_2, HCl and NaOH were proportionally decreased for the 0.20 mmol scale). Purification by chromatography (SiO_2, 30 g, 20 mm ∅, hexane/EtOAc, 100:1) afforded **4da** (39 mg, 77%) as a yellowish oil. The spectroscopic data match those published in the literature.[16]

Data for **4da**:

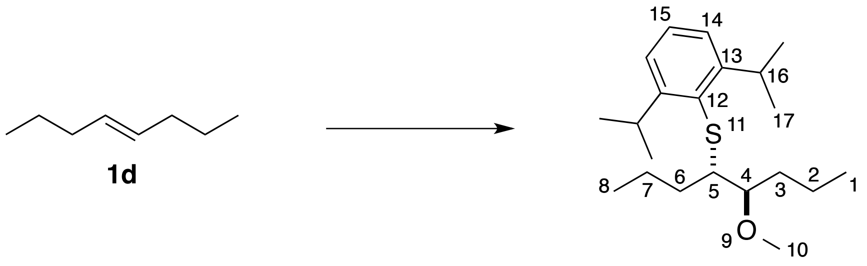
^{1}H NMR: (500 MHz, $CDCl_3$)

δ 7.42 (d *J* = 7.9 Hz, 2H, HC(13)), 7.27 (t, *J* = 7.9 Hz, 2H, HC(14)), 7.20 (t, *J* = 7.7 Hz, 1H, HC(15)), 3.37 (s, 3H, HC(10)), 3.30 (dt, *J* = 8.2, 4.2 Hz, 1H, HC(4)), 3.20

(dt, *J* = 9.3, 3.9 Hz, 1H, HC(5)), 1.74–1.24 (m, 8H, HC(2), HC(3), HC(6) and HC(7)), 0.92 (t, *J* = 7.3 Hz, 3H, HC(1,8)), 0.89 (t, *J* = 7.3 Hz, 3H, HC(8,1))

HPLC: (4*S*,5*R*)-**4da**, t_R 24.08 min (97.4%); (4*R*,5*S*)-**4da**, t_R 21.62 min (2.6%) (Chiralpak AD-RH, 50% MeCN in H_2O, 1.0 mL/min, 220 nm, 40 °C)

Preparation of (2,6-Diisopropylphenyl)((4*S*,5*R*)-5-methoxyoctan-4-yl)sulfane (4dj) (Table 2, Entry 8)



1d

4dj

Following General Procedure 3, an oven-dried Schlenk flask was charged with **2j** (351 mg, 1.03 mmol, 1.03 equiv), catalyst (*R*)-**3c** (51.9 mg, 0.100 mmol, 0.100 equiv), substrate **1d** (157 μL, 112 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). MeOH (50.0 μL, 1.23 mmol, 1.23 equiv) was added and the mixture was cooled to 0 °C in an *i*-PrOH bath. MsOH (65 μL, 1.00 mmol, 1.00 equiv) was added via syringe and the mixture was allowed to stir for 36 h at 0 °C. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 60:1) afforded pure **4dj** (285 mg, 85%) as a pale yellow oil.

Data for **4dj**:

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

δ 7.29 (t, *J* = 7.7 Hz, 1H, HC(15)), 7.14 (d, *J* = 7.7 Hz, 2H, HC(14)), 4.01 (hept, *J* = 6.9 Hz, 2H, HC(16)), 3.32 (s, 3H, HC(10)), 3.22 (ddd, *J* = 7.5, 5.4, 3.1 Hz, 1H, HC(4)), 2.93 (ddd, *J* = 7.1, 5.7, 3.1 Hz, 1H, HC(5)), 1.71–1.17 (m, 8H, HC(2), HC(3), HC(6) and HC(7)), 1.23 (d, *J* = 6.9 Hz, 6H, HC(17)), 1.22 (d, *J* = 6.9 Hz, 6H, HC(18)), 0.86 (t, *J* = 7.2 Hz, 3H, HC(1,8)), 0.83 (t, *J* = 7.5 Hz, 3H, HC(8,1))

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

δ 153.6 (C(13)), 131.4 (C(12)), 128.8 (C(14)), 123.4 (C(15)), 82.4 (C(4)), 57.3 (C(10)), 53.6 (C(5)), 32.9 (C(3,6)), 32.5 (C(6,3)), 31.3 (C(16)), 24.5 (C(17) and

C(18)), 20.9 (C(2,7)), 19.3 (C(7,2)), 14.2 (C(1,8)), 14.0 (C(8,1))

IR: 3054 (m), 2959 (s), 2870 (s), 2816 (m), 1573 (m), 1462 (s), 1420 (w), 1381 (m), 1361 (m), 1302 (w), 1244 (w), 1224 (w), 1178 (m), 1095 (s), 1053 (m), 1025 (m), 963 (w), 928 (w), 799 (m), 744 (m)

MS: (ES$^+$, 70 eV)
336 (20, M$^+$), 281 (5), 249 (100), 207 (13), 194 (5), 151 (16), 87 (5)

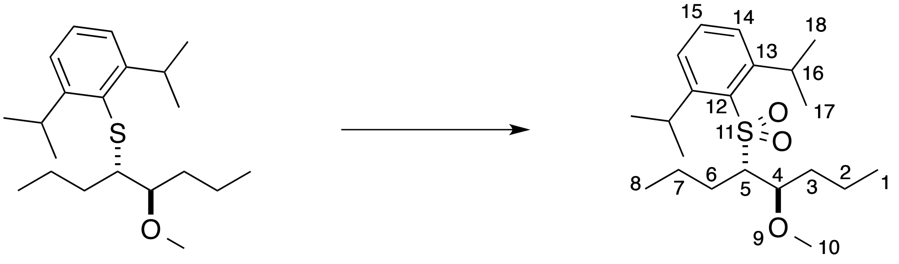
HRMS: calcd for $C_{21}H_{37}OS^+$: 337.2565, found: 337.2567

TLC: *R*$_f$ 0.53 (hexanes/EtOAc, 30:1) [CAM]

Opt. Rot. : $[\alpha]_D^{24}$ –7.4 (c = 0.36, CHCl$_3$)

The enantiomeric purity of product **4dj** was determined after its oxidation to the sulfone (see below)

Preparation of ((4*S*,5*R*)-5-Methoxyoctan-4-yl)(2,6-diisopropylphenyl)sulfone (S23)



4dj **S23**

A round-bottom flask equipped with a magnetic stir bar was charged with **4dj** (36 mg, 0.11 mmol) and CH$_2$Cl$_2$ (2.5 mL). At room temperature, *m*-Chloroperbenzoic acid (70–75%, 74 mg, 2.8–3.0 equiv) was added in three portions and the reaction mixture was stirred at room temperature for 3 h. TLC monitoring indicated full conversion and the reaction was quenched by the addition of a mixture of saturated aqueous Na$_2$S$_2$O$_3$ and H$_2$O (4:1, 5.0 mL). The quenched mixture was poured into a separatory funnel, the flask was rinsed with CH$_2$Cl$_2$ (5.0 mL) and the layers were separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (5.0 mL) and the combined organic layers were washed with aqueous NaOH (1.0 M, 2 × 5.0 mL). After phase separation, the alkaline layer was extracted with CH$_2$Cl$_2$ (2 × 5.0 mL) and the combined organic layers were dried over MgSO$_4$. The solvent was removed in vacuo (20–23 °C, 20 mmHg) and the crude product was purified by column chromatography (SiO$_2$, 6 g, 10 mm ∅, hexane/EtOAc, 20:1) affording 33 mg (84%) of pure **S23** as an off-white solid.

Data for **S23**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.49 (t, *J* = 7.8 Hz, 1H, HC(15)), 7.35 (d, *J* = 7.8 Hz, 2H, HC(14)), 4.18 (m, 2H, HC(16)), 4.02 (ddd, *J* = 7.7, 5.7, 1.9 Hz, 1H, HC(5)), 3.47 (s, 3H, HC(10)), 3.04 (ddd, *J* = 6.7, 5.0, 1.9 Hz, 1H, HC(4)), 2.00–1.71 (m, 3H, H(C-alkyl)), 1.47–1.21 (m, 4H, H(C-alkyl)), 1.29 (d, *J* = 7.4 Hz, 6H, HC(17)), 1.27 (d, *J* = 7.4 Hz, 6H, HC(18)), 1.19–1.05 (m, 1H, H(C-alkyl)), 0.93 (t, *J* = 7.1 Hz, 3H, HC(1)), 0.78 (t, *J* = 7.3 Hz, 3H, HC(8))

^{13}C NMR: (125 MHz, CDCl$_3$)

151.1 (C(13)), 135.3 (C(12)), 132.8 (C(15)), 126.1 (C(14)), 77.1 (C(4)), 68.7 (C(5)), 58.7 (C(10)), 36.6 (C(alkyl)), 29.6 (C(alkyl)), 26.2 (C(alkyl)), 25.3 (br, C(17)), 24.7 (br, C(18)), 21.9 (C(2,7)), 19.2 (C(7,2)), 14.0 (C(1,8)), 13.9 (C(8,1))

MS: (ES$^+$, 70 eV)

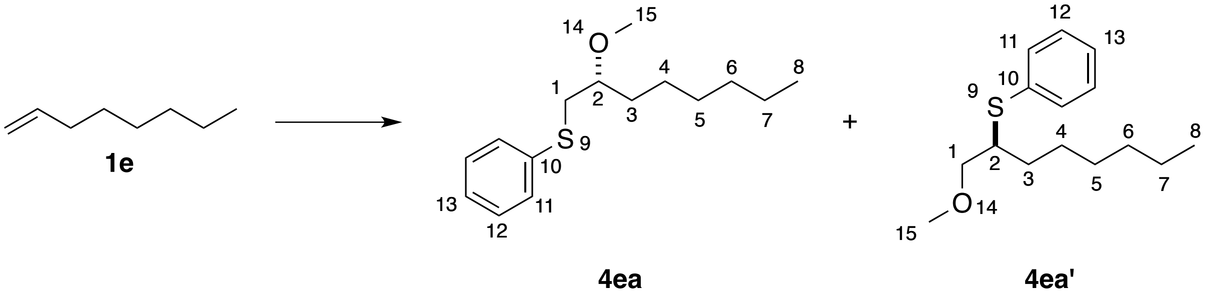
336 (6), 319 (70), 293 (7), 281 (17), 271 (15), 225 (100), 209 (28), 193 (34), 160 (17), 145 (42), 131 (10), 111 (11), 87 (36), 69 (34), 55 (15)

HRMS: calcd for $C_{21}H_{37}O_3S^+$: 369.2463, found: 369.2460

TLC: R_f 0.43 (hexanes/EtOAc, 15:1) [CAM]

HPLC: (4*S*,5*R*)-**S21**, t_R 33.36 min (99.2%); (4*R*,5*S*)-**S21**, t_R 28.64 min (0.8%) (Chiralpak AD-RH, 50% MeCN in H$_2$O, 0.5 mL/min, 220 nm, 40 °C)

Preparation of (*R*)-(2-Methoxyoctyl)(phenyl)sulfane (4ea) and (*S*)-(1-methoxyoctan-2yl)-(phenyl)sulfane (4ea') (Table 2, Entry 9)



Since **4ea** is a known compound,[16] the thioetherification reaction was conducted on a 0.20 mmol scale: Following General Procedure 3, an oven-dried 6 dram vial was charged with the sulfenylating agent **2a** (53.6 mg, 0.210 mmol, 1.05 equiv), catalyst (*R*)-**3c** (10.8 mg, 20.7 μmol, 0.106 equiv), **1e** (31.5 μL, 22.4 mg, 0.196 mmol), and CH$_2$Cl$_2$ (1.0 mL). MeOH

(9.7 μL, 0.24 mmol, 1.2 equiv) was added, the vial was capped with a polypropylene open hole cap and MsOH (14.5 μL, 0.22 mmol, 1.1 equiv) was added at room temperature. The reaction was stirred at room temperature for 24 h and worked up following the general procedure (the amounts of CH_2Cl_2, HCl and NaOH were proportionally decreased for the 0.20 mmol scale). Purification by chromatography (SiO_2, 30 g, 20 mm ∅, hexane/EtOAc, 100:1) afforded 38 mg (75%) of an inseparable 82:18 mixture of **4ea** and **4ea'** as a yellowish oil. The spectroscopic data match those published in the literature.[16]

Data for **4ea**:

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

δ 7.37 (d, *J* = 8.2 Hz, 2H, HC(11)), 7.28 (t, *J* = 8.0 Hz, 2H, HC(12)), 7.18 (t, *J* = 7.6 Hz, 1H, HC(13)), 3.36 (s, 3H, HC(15)), 3.37–3.32 (m, 1H, HC(2)), 3.11 (dd, *J* = 13.1, 5.6 Hz, 1H, HC(1)), 2.99 (dd, *J* = 13.1, 6.1 Hz, 1H, HC(1)), 1.69–1.52 (m, 2H, HC(3)), 1.49–1.16 (m, 8H, HC(4), HC(5), HC(6), HC(7)), 0.88 (t, *J* = 7.1 Hz, 3H, HC(8))

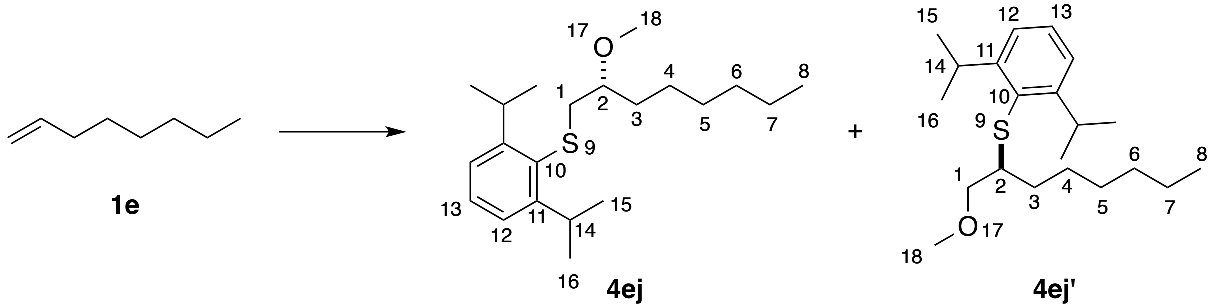
HPLC: (*R*)-**4ea**, t_R 5.02 min (87.8%); (*S*)-**4ea'**, t_R 5.36 min (12.2%) (Chiralpak AD-H, hexane:*i*-PrOH = 99:1, 0.8 mL/min, 220 nm, 25 °C)

Data for **4ea'**:

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

δ 7.42 (d, *J* = 8.1 Hz, 2H, HC(11)), 7.33–7.25 (2H, HC(12)), 7.22 (t, *J* = 7.3 Hz, 1H, HC(13)), 3.48 (dd, *J* = 9.8, 5.1 Hz, 1H, HC(1)), 3.40 (dd, *J* = 9.8, 7.3 Hz, 1H, HC(1)), 3.33 (s, 3H, HC(15)), 3.25–3.18 (m, 1H, HC(2)), 1.88–1.72 (m, 1H, HC(3)), 1.68–1.52 (m, 1H, HC(3)), 1.52–1.14 (m, 8H, HC(4), HC(5), HC(6), HC(7)), 0.88 (t, *J* = 7.1 Hz, 3H, HC(8))

Preparation of (*R*)-(2,6-Diisopropylphenyl)(2-methoxyoctyl)sulfane (4ej) and (*S*)-(2,6-Diisopropylphenyl)(1-methoxyoctan-2-yl)sulfane (4ej') (Table 2, Entry 10)



Following General Procedure 3, an oven-dried Schlenk flask was charged with **2j** (344 mg, 1.01 mmol, 1.01 equiv), catalyst (*R*)-**3c** (51.3 mg, 0.099 mmol, 0.099 equiv), substrate **1e** (157 μL, 112 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). MeOH (50.0 μL, 1.23 mmol, 1.23 equiv) was added, followed by the addition of MsOH (48 μL, 0.75 mmol, 0.75 equiv) and the mixture was allowed to stir for 24 h at room temperature. The reaction was worked up following the general procedure. Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/MTBE, 60:1) afforded 284 mg (84%) of an inseparable 79:21 mixture of **4ej'** and **4ej'** as yellowish oil.

<u>Data for isomer mixture</u>:

<u>bp:</u> 140 °C (ABT), 0.3 mmHg

<u>IR:</u> 3055 (m), 2960 (s), 2926 (s), 2862 (s), 2821 (m), 1574 (m), 1461 (s), 1420 (m), 1381 (m), 1361 (m), 1338 (w), 1307 (w), 1246 (w), 1178 (m), 1097 (s), 1053 (m), 929 (w), 800 (m), 744 (m)

<u>HRMS:</u> calcd for $C_{21}H_{37}OS^+$: 337.2565, found: 337.2565

<u>TLC:</u> R_f 0.44, **4ej'**; 0.47, **4ej** (hexanes/EtOAc, 30:1) [CAM]

<u>Opt. Rot. :</u> $[\alpha]_D^{24}$ 11.0 (c = 0.80, $CHCl_3$)

<u>Data for **4ej**</u>:

<u>^{1}H NMR:</u> (500 MHz, $CDCl_3$)

δ 7.32 (t, *J* = 7.7 Hz, 1H, HC(13)), 7.18 (d, *J* = 7.6 Hz, 2H, HC(12)), 3.99 (hept, *J* = 7.0 Hz, 2H, HC(14)), 3.36–3.31 (m, 1H, HC(2)), 3.35 (s, 3H, HC(18)), 2.82 (dd, *J* = 12.5, 5.5 Hz, 1H, HC(1)), 2.73 (dd, *J* = 12.4, 6.0 Hz, 1H, HC(1)), 1.71–1.46 (m, 2H, HC(3)), 1.42–1.17 (m, 8H, HC(4), HC(5), HC(6), HC(7)), 1.27 (d, *J* = 6.8 Hz, 12H, HC(15), HC(16)), 0.91 (t, *J* = 7.2 Hz, 3H, HC(8))

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

δ 153.1 (C(11)), 132.1 (C(10)), 129.0 (C(13)), 123.6 (C(12)), 80.4 (C(2)), 56.8 (C(18)), 41.6 (C(1)), 33.4 (C(alkyl)), 31.8 (C(alkyl)), 31.5 (C(14)), 29.3 (C(alkyl)), 25.2 (C(alkyl),) 24.5 (C(15)), 24.4 (C(16)), 22.6 (C(alkyl)), 14.1 (C(8))

MS: (ES^+, 70 eV)

336 (83, M^+), 208 (31), 192 (31), 177 (18), 161 (30), 149 (55), 129 (100), 115 (9), 97 (90), 69 (12), 55 (31)

HPLC: (2*R*)-**4ej**, t_R 61.45 min (98.6%); (2*S*)-**4ej**, t_R 56.39 min (1.4%) (Chiralpak AD-RH, 50% MeCN in H_2O, 0.5 mL/min, 220 nm, 40 °C)

Data for **4ej'**:

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

δ 7.33 (t, *J* = 7.8 Hz, 1H, HC(13)), 7.18 (d, *J* = 7.6 Hz, 2H, HC(12)), 3.99 (hept, *J* = 7.0 Hz, 2H, HC(14)), 3.38 (dd, *J* = 9.6, 7.1 Hz, 1H, HC(1)), 3.36–3.29 (m,1H, HC(1)), 3.29 (s, 3H, HC(18)), 2.92–2.86 (m, 1H, HC(2)), 1.86–1.78 (m, 1H, HC(3)), 1.70–1.48 (m, 1H, HC(3)), 1.42–1.21 (m, 8H, HC(4), HC(5), HC(6), HC(7)), 1.23 (d, *J* = 7.0 Hz, 12H, HC(15), HC(16)), 0.91 (t, *J* = 7.2 Hz, 3H, HC(8))

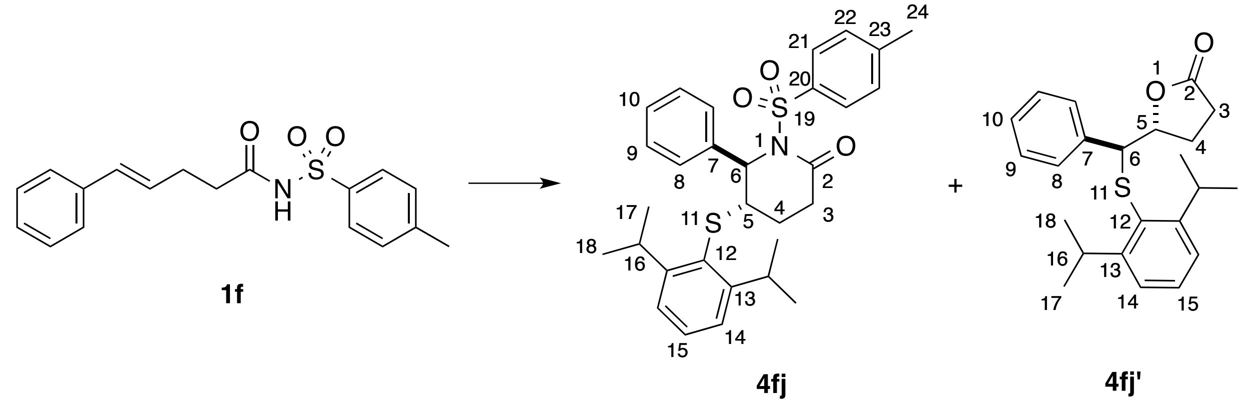
^{13}C NMR: (125 MHz, $CDCl_3$)

δ 153.7 (C(11)), 130.5 (C(10)), 129.0 (C(13)), 123.5 (C(12)), 74.5 (C(1)), 58.7 (C(18)), 50.2 (C(2)), 31.9 (C(alkyl)), 31.7 (C(alkyl)), 31.4 (C(alkyl)), 26.8 (C(alkyl)), 24.7 (C(alkyl)), 24.1 (C(alkyl)), 22.6 (C(alkyl)), 14.1 (C(8))

MS: (ES^+, 70 eV)

336 (42, M^+), 291 (100), 207 (16), 194 (14), 179 (8), 161 (14), 151 (20), 135 (5), 123 (5), 69 (7), 55 (4)

Preparation of (5*S*,6*R*)-5-((2,6-Diisopropylphenyl)thio)-6-phenyl-1-tosylpiperidin-2-one (4fj) and (*R*)-5-((*S*)-((2,6-Diisopropylphenyl)thio)(phenyl)methyl)dihydrofuran-2(3*H*)-one (4fj') (Table 2, Entry 12)



Following General Procedure 3, an oven-dried Schlenk flask was charged with **2j** (352 mg, 1.04 mmol, 1.04 equiv), catalyst (*R*)-**3c** (54.3 mg, 0.104 mmol, 0.104 equiv), **1f**[15] (329 mg, 1.00 mmol), and CH_2Cl_2 (5.0 mL). MsOH (32 μL, 0.50 mmol, 0.50 equiv)[15] was added via syringe and the mixture was allowed to stir for 24 h at room temperature. The mixture was quenched by the addition of Et_3N (0.20 mL) and was poured into saturated aqueous $NaHCO_3$ (10 mL) in a separatory funnel. CH_2Cl_2 (20 mL) was added and the layers were thoroughly mixed. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered through glass wool and concentrated in vacuo (20–23 °C, 20 mmHg). Purification by column chromatography (SiO_2, 65 g, 35 mm ∅, hexane/EtOAc, 30:1→5:1) afforded 441 mg of a 89:11 mixture of **4fj** and **4fj'** as a white solid. Separation of the mixture was accomplished by column chromatography using C-18 reversed phase silica gel (C-18 reversed-phase silica gel, 30 × 160 mm ∅, MeOH/water, 80:20→93:7) yielding 375 mg (72%) of **4fj** as a white solid and 33 mg (9%) of **4fj'** as a white solid, respectively. Analytically pure **4fj** was obtained by recrystallization from hexane/Et_2O.

Data for **4fj**:

mp: 128–131°C (hexane/Et_2O)

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

δ 7.77 (d, *J* = 8.1 Hz, 2H, HC(21)), 7.36 (t, *J* = 7.7 Hz, 1H, HC(aryl)), 7.33–7.26 (m, 3H, HC(aryl)), 7.25–7.19 (m, 4H, HC(aryl)), 7.05 (d, *J* = 7.5 Hz, 2H, HC(14), 5.85 (br s, 1H, HC(6)), 3.85 (hept, *J* = 7.0 Hz, 2H, HC(16)), 3.22 (m, 1H, HC(5)), 2.84 (ddd, *J* = 18.6, 11.0, 7.6 Hz, 1H, HC(3)), 2.52 (ddd, *J* = 18.6, 6.9, 2.3 Hz, 1H, HC(3)), 2.41 (s, 3H, HC(24)), 1.91 (dddd, *J* = 14.5, 10.7, 6.9, 3.5 Hz, 1H, HC(4)), 1.71–1.64 (m, 1H, HC(4)), 1.26 (d, *J* = 6.9 Hz, 6H, HC(17)), 1.23 (d, *J* = 6.9 Hz, 6H, HC(18))

^{13}C NMR: (125 MHz, CDCl$_3$)

δ 169.6 (C(2)), 153.5 (C(13)), 144.7 (C(20)), 139.9 (C(7)), 135.7 (C(23)), 129.8 (C(15)), 129.6 (C(18)), 129.4 (C(12)), 128.8 (2 ×, C(9), C(22)), 128.0 (C(10)), 126.1 (C(8)), 124.1 (C(14)), 65.1 (C(6)), 52.4 (C(5)), 31.8 (C(16)), 30.1 (C(3)), 24.6 (C(18)), 24.5 (C(17)), 21.7 (C(24)), 20.8 (C(4))

IR: (neat)

2960 (m), 2928 (w), 1695 (s), 1596 (w), 1495 (m), 1449 (m), 1351 (s), 1283 (m), 1253 (m), 1166 (s), 1149 (s), 1125 (s), 1089 (s), 1026 (m), 966 (m), 893 (w), 823 (m), 810 (s), 780 (m), 748 (m)

MS: (ESI)

544 (15, M+Na), 522.2 (100, M+H), 328 (70)

HRMS: calcd for $C_{30}H_{36}NO_3S^+$: 522.2137, found: 522.2132

TLC: normal phase: R_f 0.25 (hexanes/EtOAc, 5:1) [CAM]

reversed phase: R_f 0.23 (MeOH/H$_2$O, 9:1) [CAM]

Opt. Rot. : $[\alpha]_D^{24}$ –16.5 (c = 0.39, CHCl$_3$)

HPLC: Prior to recrystallization: (5*S*,6*R*)-**4fj**, t_R 18.24 min (94.3%); (5*R*,6*S*)-**4fj**, t_R 31.53 min (5.7%) (Chiralcel AD-H, hexane:*i*-PrOH, 95:5, 0.8 mL/min, 220 nm, 25 °C)

Analysis: $C_{30}H_{35}NO_3S$ (521.73)

Calcd: C, 69.06; H, 6.76; N, 2.68;

Found: C, 69.13; H, 6.89; N, 2.67

Data for **4fj'**:

^{1}H NMR: (500 MHz, CDCl$_3$)

δ 7.32–7.21 (m, 6H, HC(aryl)), 7.13 (d, *J* = 7.7 Hz, 2H, HC(14)), 4.85 (m, 1H, HC(5)), 3.89–3.75 (m, 2H, HC(16)), 3.79 (d, *J* = 5.0 Hz, 1H, HC(6)), 2.44–2.29 (m, 2H, HC(alkyl)), 2.20–2.09 (m, 1H, HC(alkyl)), 2.05–1.98 (m, 1H, HC(alkyl)), 1.20 (d, *J* = 6.9 Hz, 6H, HC(17)), 1.05 (d, *J* = 6.9 Hz, 6H, HC(18))

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

δ 176.4 (C(2)), 153.9 (C(13)), 136.9 (C(7)), 129.7 (C(aryl)), 129.4 (C(12)), 128.8 (C(aryl)), 128.5 (C(aryl)), 128.0 (C(aryl)), 123.8 (C(14)), 80.9 (C(5)), 59.4 (C(6)), 31.5 (C(16)), 28.4 (C(alkyl)), 25.9 (C(alkyl)), 24.3 (br, C(alkyl))

MS: (ESI)

391 (44, M+Na), 386 (50), 369 (100, M+H), 351 (6), 327 (6), 309 (12), 204 (15), 177 (15)

HRMS: calcd for $C_{23}H_{29}O_2S^+$: 369.1888, found: 369.1884

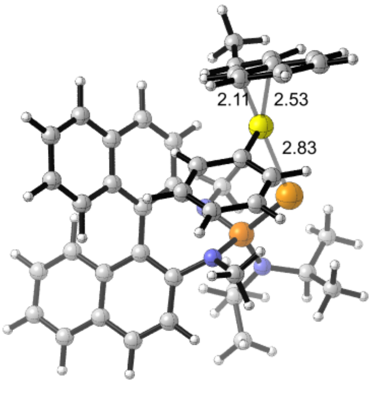
TLC: normal phase: R_f 0.25 (hexanes/EtOAc, 5:1) [CAM]

reversed phase: R_f 0.35 ($MeOH/H_2O$, 9:1) [CAM]

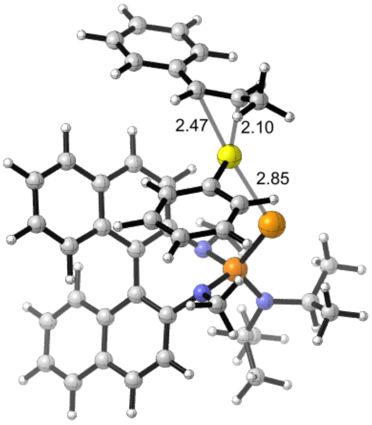
Calculations of the Transition States (Figure 5)

All geometry optimizations and frequency calculations were performed in Gaussian 09[24] at the B3LYP/6-31G* level in gas phase. The transition states were characterized by one imaginary frequency. Figures for the transition state structures are prepared with CYLview. The Cartesian coordinates (Å), total SCF energies, enthalpies at 253.15K (-20^{o}C), and Gibbs free energies at 253.15K (-20^{o}C) for the optimized structures are given below. Donor-acceptor orbital interactions and the corresponding second order perturbation stabilization energies were calculated using Natural Bond Orbital (NBO)[25] method at B3LYP/6-31G* level of theory. Data given in parentheses have been computed using CPCM solvent model (UFF radii, CH_2Cl_2). Solvation free energy corrections were computed by singlet point CPCM[26,27] calculations on gas-phase optimized geometries, UFF atomic radii were used and dichloromethane was specified as the solvent.

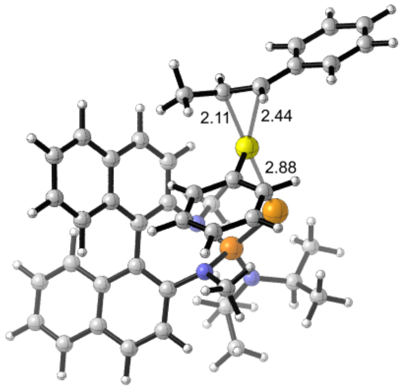
Optimized Structures and Energies for Transition States with the Phenylsulfenyl Group (R = H) H-TS-major1, H-TS-major2, H-TS-minor1, H-TS-minor-2



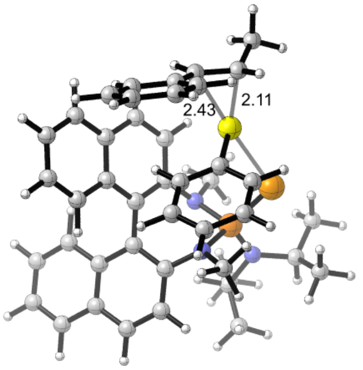
H-TS-major1
ΔΔG (253K) = 0.0 (0.0) kcal/mol



H-TS-major2
ΔΔG (253K) = 1.5 (1.1) kcal/mol



H-TS-minor1
ΔΔG (253K) = 1.7 (1.4) kcal/mol



H-TS-minor2
ΔΔG (253K) = 3.0 (2.3) kcal/mol

Data given in parentheses have been computed using CPCM solvent model (UFF radii, CH_2Cl_2)

Cartesian Coordinates of H-TS-major2, H-TS-major1, H-TS-minor2, H-TS-minor1

H-TS-major1

S	0.47445255	0.48905109	0.00000000
N	4.59084455	0.68854909	-2.06317900
N	5.01284355	0.59938209	0.55870800
N	5.75780055	-1.58937591	-0.81348100
C	0.49361455	1.25219109	-1.61405800
C	1.06543755	2.52082409	-1.78757700
H	1.50251955	3.04199809	-0.94166500
C	1.08851755	3.10015609	-3.05655800
H	1.53500555	4.08177609	-3.18674500
C	0.55602055	2.41294109	-4.15115600
H	0.57731155	2.86567709	-5.13849300
C	0.00053155	1.14186909	-3.97895300
H	-0.40850345	0.60546809	-4.83026000
C	-0.03380545	0.55841009	-2.71326600
H	-0.46101545	-0.42928591	-2.57260600
C	5.66750455	1.62622809	-2.21605100
C	5.83364055	2.64570809	-1.28508800
C	7.01175755	3.47194009	-1.35632500
C	7.89804255	3.33954509	-2.47496700
C	7.60347355	2.37521109	-3.47347900
H	8.25569755	2.29626709	-4.33944900
C	6.53543955	1.52531509	-3.33792000
H	6.34929655	0.77143609	-4.09383500
C	4.42620955	1.90759109	0.65212000
C	4.79186755	2.89733909	-0.25398400
C	4.12952655	4.17630809	-0.19926800
C	3.23530355	4.46518509	0.88377000
C	2.98081355	3.45463709	1.84565400
H	2.32854455	3.67959009	2.68630000
C	3.52644655	2.20242209	1.71394700
H	3.28288855	1.43759109	2.44113400
C	5.15134355	-0.13075191	1.83664000
H	5.57849355	0.54647409	2.57912600
H	5.82577055	-0.97231891	1.69657000
H	4.18976155	-0.51950191	2.19537400
C	3.86515555	0.29893809	-3.28824900
H	3.60428755	1.20622209	-3.83743200
H	2.95214255	-0.22084691	-2.99887200
H	4.45119755	-0.36243991	-3.93878400
C	5.53209055	-3.07681791	-0.89044800
H	6.54337255	-3.47272791	-1.00477400
C	7.18420155	-1.14457691	-1.00629000
H	7.17161155	-0.05367391	-0.96638000
C	-0.86689545	1.78747109	0.99106400
C	-1.94643945	1.07010909	0.42618400
Se	2.59963055	-1.29089491	-0.57868300
P	4.57394955	-0.39909391	-0.75455100
C	7.73982955	-1.56092091	-2.37687900
H	8.70788255	-1.07579691	-2.54100700
H	7.90019255	-2.64225191	-2.44517100
H	7.07194055	-1.26271991	-3.18865700
C	8.10845655	-1.62421191	0.12396700
H	8.15794655	-2.71660391	0.18382700
H	9.12497255	-1.26303791	-0.06639200

H	7.79893855	-1.23887091	1.09857700
C	4.98195555	-3.67722691	0.41085600
H	5.62559555	-3.42498191	1.26006000
H	3.96984855	-3.32576291	0.62285800
H	4.95367855	-4.76919891	0.32410100
C	4.75523055	-3.52502091	-2.13739800
H	5.22314955	-3.13868891	-3.04889800
H	4.75565755	-4.61921491	-2.19449000
H	3.71695355	-3.18667691	-2.10796300
C	2.60956555	5.73888709	0.96191100
C	4.30792455	5.18038509	-1.19393500
C	3.67039055	6.39848009	-1.10174800
C	2.82230955	6.69105709	-0.00752800
C	7.35432955	4.41100009	-0.34402200
C	9.05168555	4.16320409	-2.55925500
C	9.34409355	5.07078609	-1.56755300
H	10.23250355	5.69158309	-1.63683100
C	8.48967355	5.18462509	-0.44618500
H	9.70692455	4.05361809	-3.41979300
H	8.73443555	5.88645909	0.34601600
H	6.71848755	4.50639809	0.52866300
H	3.82399755	7.14432409	-1.87660800
H	4.95321055	4.97916809	-2.04069900
H	2.33880255	7.66131809	0.05952300
H	1.95257455	5.94429209	1.80381000
H	-0.64212045	2.76901509	0.57992500
C	-0.54950345	1.62533809	2.46136200
H	-1.23605445	2.24296609	3.05320100
H	-0.66743645	0.58654409	2.78736800
H	0.47270755	1.94567309	2.67462200
C	-2.74863445	1.40905409	-0.71652400
C	-3.72072145	0.47528009	-1.15041100
C	-2.64636445	2.64519209	-1.39855400
C	-4.55421945	0.76273109	-2.22276300
H	-3.81134245	-0.47480691	-0.63023300
C	-3.48163045	2.92638809	-2.47049900
H	-1.91839145	3.38432209	-1.08251200
C	-4.43578845	1.98910709	-2.88527500
H	-5.29775145	0.03914209	-2.54231000
H	-3.39908745	3.87967809	-2.98335700
H	-5.09103845	2.21834209	-3.72060800
H	-2.22179745	0.14984709	0.93923600

Sum of electronic and zero-point Energies= -4969.096617
Sum of electronic and thermal Energies= -4969.049364
Sum of electronic and thermal Enthalpies= -4969.048420
Sum of electronic and thermal Free Energies= -4969.179411
Imaginary frequency: -110.65 cm^{-1}

H-TS-major2

S	-0.40145985	0.03649635	0.00000000
N	-4.94036885	0.84301235	0.66045500
N	-4.46309085	1.15908035	-1.92033600
N	-5.94402785	-0.99585365	-1.25839800
C	-0.82544785	0.41812135	1.69901200
C	-1.01932185	1.75299035	2.07864000
H	-0.90803185	2.54752135	1.34782900

C	-1.36991485	2.05163435	3.39673300
H	-1.51934985	3.08689735	3.68885200
C	-1.53461585	1.02500935	4.32876700
H	-1.80437585	1.26055635	5.35424500
C	-1.36156085	-0.30788565	3.94206700
H	-1.50200885	-1.10771265	4.66339400
C	-1.01370085	-0.61640565	2.62839300
H	-0.90910085	-1.65028065	2.31589100
C	-5.80171085	1.99242935	0.63334600
C	-5.42658285	3.12421435	-0.08158900
C	-6.36962285	4.20326735	-0.22699500
C	-7.60670085	4.15943235	0.49548400
C	-7.88226585	3.03667335	1.31862700
H	-8.80619585	3.01636735	1.89089600
C	-7.01832185	1.97258735	1.36892900
H	-7.26431985	1.10776135	1.97397800
C	-3.61548585	2.27080435	-1.57864100
C	-4.06152885	3.21743935	-0.66402700
C	-3.16728785	4.27070635	-0.25726100
C	-1.89793985	4.40964635	-0.90955700
C	-1.53083985	3.46971835	-1.90637000
H	-0.57327985	3.57892335	-2.40842200
C	-2.34912185	2.41108335	-2.20806000
H	-2.02826185	1.67947235	-2.93965800
C	-4.33592285	0.66508535	-3.30700800
H	-4.33870285	1.52519535	-3.97980100
H	-5.18681785	0.02982335	-3.54252800
H	-3.41869985	0.08142135	-3.45860600
C	-4.74909485	0.17927435	1.96356200
H	-4.50909685	0.94099735	2.70904700
H	-3.91183885	-0.51303065	1.87722900
H	-5.63373685	-0.38078765	2.29142300
C	-5.96799085	-2.49175965	-1.42893600
H	-7.00365485	-2.69037465	-1.71390300
C	-7.28226785	-0.31217665	-1.36023700
H	-7.09877785	0.74762635	-1.17302700
C	1.83175815	1.09326435	0.07019600
C	1.65872615	-0.31034365	0.15847500
H	1.80022315	1.63801535	1.01217000
H	1.81276015	-0.87633265	-0.75905000
Se	-2.87424285	-1.30000765	-0.46166000
P	-4.64442385	-0.06299565	-0.74641500
C	2.12821415	1.87925735	-1.10244800
C	2.34465815	3.26634535	-0.93654200
C	2.25744115	1.32620335	-2.39741200
C	2.68896115	4.06805435	-2.01899400
H	2.25061715	3.70312435	0.05418300
C	2.58618615	2.13383935	-3.47796600
H	2.10173015	0.26405035	-2.55832300
C	2.80637115	3.50477335	-3.29331600
H	2.86996515	5.12871035	-1.87271700
H	2.68314215	1.69763535	-4.46751200
H	3.07524315	4.12892135	-4.14040600
C	2.04499115	-1.06441965	1.40743800
H	1.80846615	-0.50680465	2.31683100
H	1.55196315	-2.03951965	1.45018200
H	3.12840015	-1.23794865	1.38662000
C	-8.26814685	-0.81558265	-0.29509900

H	-9.16284885	-0.18398965	-0.29561900
H	-8.59249985	-1.84360465	-0.48882400
H	-7.82956885	-0.78044465	0.70572300
C	-7.89358085	-0.41822565	-2.76589300
H	-8.08171485	-1.45599565	-3.06068400
H	-8.85702885	0.10288735	-2.77816400
H	-7.25853185	0.04599235	-3.52439500
C	-5.72146385	-3.26904565	-0.12693300
H	-5.88014385	-4.33880765	-0.30319300
H	-4.69959985	-3.13108765	0.23413700
H	-6.41496785	-2.94911765	0.65745000
C	-5.10239585	-2.98591765	-2.59627800
H	-5.37790785	-2.48158065	-3.52827800
H	-4.03888385	-2.82017165	-2.40978700
H	-5.26109785	-4.06104265	-2.73620600
C	-1.02509885	5.46572135	-0.53050700
C	-3.47582785	5.18163735	0.79308600
C	-2.60042085	6.18361035	1.15007100
C	-1.36616585	6.33933235	0.47591500
C	-6.13826985	5.31458935	-1.08440400
C	-8.53365385	5.22739235	0.36624800
C	-8.27027985	6.29350835	-0.46245700
C	-7.06414485	6.32822735	-1.20030200
H	-0.07644385	5.56398135	-1.05252200
H	-0.69230085	7.14309135	0.75871400
H	-2.86133185	6.86253235	1.95705200
H	-4.41408885	5.07830435	1.32485200
H	-5.22447685	5.35437535	-1.66613800
H	-6.86830785	7.16091835	-1.86991800
H	-8.98839685	7.10235635	-0.56041500
H	-9.46322485	5.18024035	0.92798600

Sum of electronic and zero-point Energies= -4969.094035

Sum of electronic and thermal Energies= -4969.046748

Sum of electronic and thermal Enthalpies= -4969.045804

Sum of electronic and thermal Free Energies= -4969.177083

Imaginary frequency: -114.73 cm^{-1}

H-TS-minor1

S	-0.15328467	0.73722627	0.00000000
N	4.21187033	1.94341027	1.01207000
N	3.98761633	2.04069027	-1.62933000
N	4.31103733	4.41141827	-0.39511700
C	0.39231033	0.19213627	1.61615400
C	1.46137833	-0.70750473	1.73533200
H	1.96720633	-1.07412673	0.84929500
C	1.87879533	-1.11931973	3.00146700
H	2.70207433	-1.82245673	3.08873300
C	1.24470033	-0.62850073	4.14528200
H	1.57115633	-0.95305273	5.12910500
C	0.19300633	0.28470327	4.02568800
H	-0.29446167	0.67480227	4.91442200
C	-0.23436467	0.69875827	2.76490600
H	-1.04356667	1.41586027	2.66746700
C	5.50737133	1.33986227	0.87645900
C	5.72373833	0.36338027	-0.09061600
C	7.06622633	-0.10689573	-0.32052900

C	8.11937533	0.31017727	0.55740500
C	7.81544033	1.20322327	1.61747000
H	8.60605233	1.49669127	2.30333000
C	6.55468833	1.72450827	1.75843500
H	6.35295033	2.43638027	2.55017000
C	3.76277933	0.62145127	-1.62263300
C	4.58100933	-0.20140673	-0.85706700
C	4.29322733	-1.61258773	-0.79694900
C	3.27649033	-2.16372773	-1.64556000
C	2.53309633	-1.28974773	-2.47964500
H	1.77631833	-1.70767573	-3.13944600
C	2.74163133	0.06559627	-2.44170100
H	2.13332633	0.71664727	-3.05733800
C	3.65299033	2.72872527	-2.89408100
H	4.07467333	2.15422627	-3.72158100
H	4.09656933	3.72164227	-2.89154500
H	2.56960733	2.83698427	-3.03314400
C	3.72173733	2.18502527	2.38366500
H	3.86841133	1.27533627	2.96975400
H	2.65645233	2.41165727	2.33179800
H	4.23265733	3.02012527	2.87944800
C	3.65831633	5.76234927	-0.26395400
H	4.49700533	6.45257827	-0.37948700
C	5.81379733	4.42650227	-0.48154500
H	6.12693333	3.38204827	-0.53024600
C	-1.25572167	-0.94824973	-0.63851000
C	-2.34456967	-0.34170273	0.03552000
Se	1.42911233	3.14096227	0.07305500
P	3.56322433	2.91632727	-0.22642100
H	-2.44529367	-0.58913273	1.09126800
H	-1.20171267	-0.79711273	-1.71527400
C	-3.37397667	0.50566727	-0.51315200
C	-4.35931967	1.01237627	0.36474800
C	-3.46058367	0.82842127	-1.88695900
C	-5.39191967	1.81112427	-0.11003200
H	-4.30525167	0.76677427	1.42225800
C	-4.49067267	1.63207127	-2.35551400
H	-2.72514467	0.44582427	-2.58766000
C	-5.45785367	2.12511727	-1.47069800
H	-6.14436367	2.18979527	0.57472600
H	-4.54931467	1.87348627	-3.41237300
H	-6.26402967	2.74947927	-1.84440100
C	-0.69662267	-2.27069173	-0.17542500
H	0.32237833	-2.42347373	-0.53950000
H	-0.70110967	-2.36201673	0.91324800
H	-1.32440067	-3.07269473	-0.58545700
C	6.45617533	5.05397827	0.76474200
H	7.53873633	4.89010727	0.74190100
H	6.28915533	6.13524927	0.81293000
H	6.06546433	4.60795327	1.68297700
C	6.32546033	5.10437727	-1.76226500
H	6.02647333	6.15610027	-1.82526400
H	7.42052833	5.07707927	-1.76998700
H	5.97714133	4.59207227	-2.66249300
C	2.68349433	6.07958927	-1.40607800
H	3.17561333	5.97941727	-2.37908800
H	1.81122633	5.42264027	-1.38524000
H	2.33536733	7.11412427	-1.31012800

C	3.06346233	6.03569627	1.12595400
H	3.80933133	5.87025527	1.91006900
H	2.73727333	7.08014627	1.18468200
H	2.19996033	5.39727027	1.32618600
C	3.01921133	-3.56166373	-1.61960300
C	4.96760033	-2.50053973	0.08970700
C	4.67979233	-3.84788573	0.10720300
C	3.70663533	-4.39124173	-0.76421500
C	7.40603933	-0.95812073	-1.40868100
C	9.44104733	-0.16351973	0.34484200
C	9.73015333	-0.99792273	-0.71012100
H	10.74536733	-1.34915673	-0.86958800
C	8.70123633	-1.38733473	-1.59889600
H	10.22430233	0.15723027	1.02713400
H	8.93599133	-2.02788273	-2.44430400
H	6.63442633	-1.25952473	-2.10780300
H	5.20843133	-4.50091573	0.79580800
H	5.71766933	-2.10523673	0.76419000
H	3.50190033	-5.45779873	-0.75067700
H	2.26352133	-3.96355473	-2.29071000

Sum of electronic and zero-point Energies= -4969.093795
Sum of electronic and thermal Energies= -4969.046656
Sum of electronic and thermal Enthalpies= -4969.045712
Sum of electronic and thermal Free Energies= -4969.176641
Imaginary frequency: -107.68 cm^{-1}

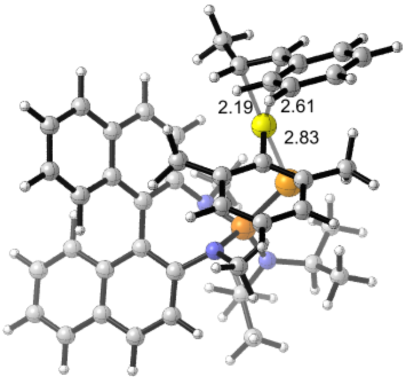
H-TS-minor2

S	0.53284671	0.67883211	0.00000000
N	-3.42014929	2.04874911	1.74552800
N	-3.85623829	2.00875011	-0.87169200
N	-5.32007829	0.28620511	0.59950800
C	0.63197771	1.20809011	1.70522800
C	0.45730071	2.56351511	2.01041000
H	0.29906771	3.28353111	1.21395700
C	0.48447371	2.97504111	3.34413000
H	0.35393171	4.02607011	3.58479600
C	0.67779371	2.04067311	4.36286000
H	0.69579671	2.36407211	5.39954500
C	0.84242971	0.68670611	4.05341000
H	0.98085971	-0.04152189	4.84703600
C	0.81644371	0.26436111	2.72598900
H	0.91719171	-0.78976489	2.48496600
C	-4.02050629	3.34851011	1.81492100
C	-3.74133129	4.29853811	0.83740800
C	-4.47540529	5.53890711	0.83861800
C	-5.34741429	5.84081811	1.93529400
C	-5.48990429	4.89150011	2.98020200
H	-6.12783529	5.13111511	3.82710900
C	-4.86733429	3.67153211	2.91132200
H	-5.01994529	2.94487411	3.70051000
C	-2.77679129	2.94238711	-1.03049900
C	-2.68920529	4.04151811	-0.18251400
C	-1.56034629	4.92884611	-0.30244400
C	-0.64308629	4.76558511	-1.39239600
C	-0.83074129	3.68056411	-2.28610400
H	-0.15225229	3.56594511	-3.12873200
C	-1.84172729	2.77352911	-2.08934100

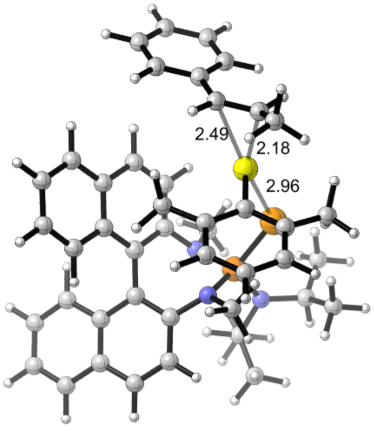
H	-1.94233429	1.93390911	-2.76636600
C	-4.30887229	1.35003311	-2.11419100
H	-4.43084129	2.11329911	-2.88582300
H	-5.26910129	0.87141011	-1.93675300
H	-3.60262929	0.58399911	-2.45988400
C	-2.94947429	1.45710311	3.01181600
H	-2.39827929	2.21878811	3.56821100
H	-2.28134129	0.62892911	2.77359900
H	-3.76608929	1.07777311	3.63959800
C	-5.64560829	-1.18066189	0.69698600
H	-6.73150629	-1.18523289	0.81717800
C	-6.47360229	1.22297811	0.82820300
H	-6.06541729	2.23282211	0.75462500
C	2.69417271	1.61748711	-0.61363500
C	2.45619471	0.20409911	-0.72626400
Se	-2.24723129	-0.54090289	0.34957400
P	-3.78514229	0.96035911	0.48079600
C	-7.07819929	1.05951911	2.23102000
H	-7.79990429	1.86200711	2.41719000
H	-7.60932029	0.10791311	2.34002900
H	-6.30831529	1.10924811	3.00541400
C	-7.56065729	1.10176211	-0.25157400
H	-8.01939429	0.10745311	-0.26990100
H	-8.35783229	1.82329211	-0.04172600
H	-7.17255029	1.32050611	-1.24942900
C	-5.06934329	-1.86573289	1.94559700
H	-5.44672629	-2.89284189	2.00544400
H	-3.97846529	-1.90205589	1.91078000
H	-5.37432529	-1.34092189	2.85694000
C	-5.35390729	-1.95394789	-0.59666500
H	-5.86664429	-1.49694689	-1.44957600
H	-4.28317029	-1.99123389	-0.80968800
H	-5.71960929	-2.98202989	-0.49630600
C	0.43104671	5.68409711	-1.55004200
C	-1.30486629	5.97856911	0.62595800
C	-0.24006029	6.83679111	0.46150900
C	0.62952271	6.70380211	-0.64668100
C	-4.39450229	6.48146011	-0.22404500
C	-6.05832229	7.06999511	1.95093300
C	-5.94243129	7.96542711	0.91298300
C	-5.11001829	7.65824411	-0.18831900
H	1.09000471	5.57538811	-2.40882600
H	1.44658171	7.40696911	-0.78279200
H	-0.07151129	7.62880211	1.18574900
H	-1.96265929	6.10162911	1.47819200
H	-3.77167029	6.25954211	-1.08281500
H	-5.03874729	8.35544011	-1.01838000
H	-6.49608229	8.89961311	0.92982600
H	-6.70779629	7.28397711	2.79615200
C	2.33880671	-0.42833789	-2.09834200
H	1.76665471	0.20258711	-2.78621900
H	3.34196071	-0.56460089	-2.51891500
H	1.85275871	-1.40553089	-2.03660700
H	2.93495871	-0.43022289	0.01753800
C	3.43858471	2.32352011	0.39500100
C	3.43054471	3.73794511	0.34791800
C	4.20586271	1.67844711	1.39237200
C	4.16394871	4.48102911	1.26227500

```
 H                 2.82890171    4.22819411   -0.41267000
 C                 4.94137471    2.42810111    2.30090000
 H                 4.23711871    0.59522811    1.44663100
 C                 4.92248871    3.82670511    2.23923700
 H                 4.14946371    5.56552811    1.21690500
 H                 5.53731771    1.92644911    3.05704200
 H                 5.50323971    4.40582911    2.95130000
 H                 2.32722071    2.22036011   -1.44166500
Sum of electronic and zero-point Energies=          -4969.091537
Sum of electronic and thermal Energies=             -4969.044074
Sum of electronic and thermal Enthalpies=           -4969.043129
Sum of electronic and thermal Free Energies=        -4969.174739
Imaginary frequency: -103.60 cm-1
```

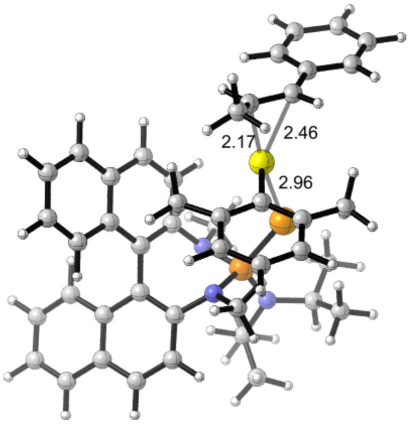
Transitions State Structures with the 2,6-Dimethylphenylsulfenyl Group (R = Me)



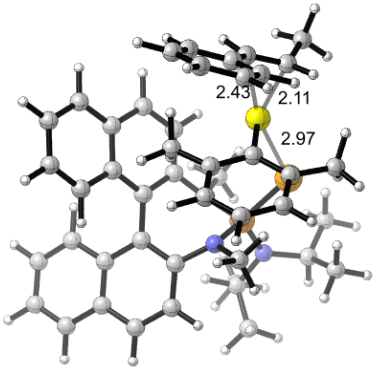
Me-TS-major1
ΔΔG (253K) = 0.0 (0.0) kcal/mol



Me-TS-major2
ΔΔG (253K) = 1.8 (1.0) kcal/mol



Me-TS-minor1
ΔΔG (253K) = 3.5 (2.2) kcal/mol



Me-TS-minor2
ΔΔG (253K) = 5.4 (4.6) kcal/mol

Cartesian Coordinates of Me-TS-major1, Me-TS-major2, Me-TS-minor1, Me-TS-minor2

Me-TS-major1

S	0.19708029	0.10948905	0.00000000
N	4.25665729	-0.54020195	-1.86434600
N	5.01232129	-0.53334395	0.67122600
N	5.11039129	-2.92447995	-0.56858400
C	-0.02710071	0.22006005	-1.76581500
C	0.47001929	1.34357805	-2.47808100
C	0.26169129	1.39285305	-3.86187400
H	0.63284529	2.24922005	-4.41888000
C	-0.39293371	0.36193105	-4.53088100
H	-0.53862771	0.41925405	-5.60609800
C	-0.84508071	-0.75194195	-3.82578500
H	-1.33713871	-1.56324695	-4.35480200
C	-0.67579871	-0.84949095	-2.44184100
C	5.44117429	0.20018705	-2.20563200
C	5.87876329	1.23855505	-1.38764500
C	7.15567629	1.84809805	-1.65777400
C	7.86893129	1.49531705	-2.84976000
C	7.30805029	0.52828405	-3.72315100
H	7.83090529	0.28190105	-4.64372200
C	6.14337229	-0.12019995	-3.39991100
H	5.75367629	-0.88385495	-4.06256800
C	4.61364329	0.84840605	0.72967800
C	5.02374529	1.72119005	-0.27044700
C	4.57446129	3.08990505	-0.22938800
C	3.83202429	3.55411605	0.90646000
C	3.49626429	2.63296705	1.93173000
H	2.94310429	2.98728805	2.79830200
C	3.83963029	1.30847805	1.82831500
H	3.53589429	0.61106805	2.59947700
C	5.24634029	-1.17997895	1.97962900
H	5.84325929	-0.50315495	2.59423900
H	5.80066729	-2.10413295	1.83175200
H	4.31004629	-1.41899295	2.50020600
C	3.35304229	-0.92419695	-2.96555300
H	3.15268929	-0.04341795	-3.57926600
H	2.41943429	-1.27650795	-2.52737400
H	3.76321429	-1.71942295	-3.60080700
C	4.59414929	-4.33307695	-0.44083900
H	5.48105529	-4.94002495	-0.63599300
C	6.53747829	-2.79903895	-1.03514500
H	6.74207529	-1.72917695	-1.10708100
C	-1.07509871	1.75202605	0.70090000
C	-2.20947771	0.93303805	0.58680400
Se	2.13682829	-1.94593295	0.07110600
P	4.21031929	-1.51013695	-0.46762500
C	6.74110929	-3.41375895	-2.42793400
H	7.73801329	-3.15524795	-2.80030400
H	6.67123929	-4.50658795	-2.40859800
H	6.00452129	-3.03787895	-3.14277300
C	7.54293529	-3.37999495	-0.02896200
H	7.40071529	-4.45430495	0.12874300

H	8.55803429	-3.24044595	-0.41632000
H	7.48898429	-2.87897095	0.94061900
C	4.13706829	-4.68455095	0.98117200
H	4.92983229	-4.48398295	1.70905300
H	3.24660729	-4.12059095	1.27013700
H	3.89417929	-5.75175295	1.03236200
C	3.56126929	-4.71426995	-1.51105700
H	3.94826929	-4.52233295	-2.51702800
H	3.32974629	-5.78243995	-1.43436200
H	2.63550229	-4.15129095	-1.37789200
C	3.42201329	4.91302805	0.97186100
C	4.81761929	4.01564305	-1.28397400
C	4.39013429	5.32254905	-1.19946300
C	3.69734429	5.78476605	-0.05565200
C	7.76294629	2.78009705	-0.77066800
C	9.12011129	2.10688405	-3.12760300
C	9.66975729	3.01619905	-2.25381600
H	10.63043729	3.47384905	-2.47094100
C	8.98574229	3.34462305	-1.06001900
H	9.64136329	1.83268705	-4.04137100
H	9.43252729	4.04582405	-0.36091400
H	7.25947529	3.03697905	0.15425400
H	4.58905329	6.00644805	-2.01981200
H	5.34489629	3.68332805	-2.17005300
H	3.37869429	6.82148505	0.00301400
H	2.87791329	5.24942405	1.85126600
H	-0.92763471	2.52078505	-0.05223600
C	-0.49259571	2.06667305	2.05874200
H	-1.05374471	2.89317805	2.51289200
H	-0.55690971	1.20680505	2.73377800
H	0.55455929	2.36734205	1.97508800
C	-3.17388871	0.88118505	-0.47965000
C	-4.23814071	-0.04616995	-0.37060500
C	-3.13697771	1.73553205	-1.60726200
C	-5.22392571	-0.11792395	-1.34561800
H	-4.28133971	-0.70307595	0.49442500
C	-4.12238571	1.65597605	-2.58183900
H	-2.33902271	2.46180005	-1.71551100
C	-5.16685571	0.73252005	-2.45476000
H	-6.03701771	-0.83017895	-1.24493200
H	-4.08509871	2.31782105	-3.44160500
H	-5.93863771	0.68081905	-3.21721300
H	-2.40200071	0.26622605	1.42650100
C	1.22054029	2.47814405	-1.82215300
H	0.54313629	3.25670505	-1.44525500
H	1.82748329	2.14025905	-0.98048800
H	1.88154529	2.96699105	-2.54318700
C	-1.13190271	-2.09883395	-1.72953600
H	-0.27593171	-2.60822895	-1.27386300
H	-1.84142371	-1.87856795	-0.92619700
H	-1.61103771	-2.78849095	-2.42951900

Sum of electronic and zero-point Energies= -5047.674461

Sum of electronic and thermal Energies= -5047.625032

Sum of electronic and thermal Enthalpies= -5047.624087

Sum of electronic and thermal Free Energies= -5047.757211

Imaginary frequency: -153.55 cm^{-1}

Me-TS-major2

S	-0.10948905	0.22627737	0.00000000
N	-4.71375705	0.33720337	0.40097500
N	-4.66836405	0.98261437	-2.14957000
N	-5.58617705	-1.49031663	-1.58548200
C	-0.54382405	0.00437037	1.71462700
C	-0.92994205	1.12490537	2.49423200
C	-1.24518405	0.91212537	3.84164900
H	-1.53192105	1.76177437	4.45519400
C	-1.20224305	-0.36279463	4.39983400
H	-1.45005505	-0.50459263	5.44806000
C	-0.85845505	-1.46080163	3.61239600
H	-0.85348705	-2.45654863	4.04674200
C	-0.52425505	-1.30791763	2.26414800
C	-5.73635305	1.32705237	0.60133100
C	-5.64421505	2.57300537	-0.01462700
C	-6.75798005	3.48113937	0.07819900
C	-7.86295705	3.15978537	0.93229600
C	-7.84482705	1.93274137	1.64409900
H	-8.66842405	1.69882437	2.31384200
C	-6.82651705	1.03128437	1.46526400
H	-6.85257005	0.08215237	1.98754400
C	-3.93529505	2.16463937	-1.78060000
C	-4.40125505	2.95339037	-0.73696100
C	-3.63091605	4.10238637	-0.33514900
C	-2.46746005	4.46747137	-1.09064800
C	-2.06132905	3.64778337	-2.17514000
H	-1.17058005	3.91818137	-2.73584500
C	-2.75451305	2.50740137	-2.49040300
H	-2.40425005	1.86380537	-3.28851100
C	-4.69929005	0.68554937	-3.59534200
H	-4.93029105	1.61068537	-4.12766700
H	-5.48164505	-0.04260263	-3.79774100
H	-3.74905105	0.28042237	-3.96622100
C	-4.27625405	-0.43676963	1.57658600
H	-4.07872505	0.25336437	2.39989800
H	-3.35248605	-0.95318763	1.31525400
H	-5.01380905	-1.18149663	1.90132500
C	-5.34048205	-2.92647463	-1.96041300
H	-6.34748305	-3.31360863	-2.13123600
C	-7.02980705	-1.10145563	-1.41584500
H	-7.03022505	-0.04513963	-1.13982700
C	1.91058395	1.66931537	-0.11739800
C	2.06401095	0.29230537	0.15059000
H	1.83316895	2.32224237	0.74927800
H	2.32900595	-0.35554063	-0.68140900
Se	-2.41494205	-1.16363563	-1.24073400
P	-4.43331105	-0.35729363	-1.12711500
C	1.93746295	2.32426737	-1.40170300
C	1.89225195	3.73670537	-1.43296400
C	2.04978195	1.62225637	-2.62399200
C	1.97921395	4.42346637	-2.63804100
H	1.80027995	4.28609737	-0.49988300
C	2.11758795	2.31287137	-3.82679300
H	2.08290295	0.53745037	-2.63226100
C	2.08910995	3.71288737	-3.83783300
H	1.96502495	5.50917737	-2.64676700

H	2.20364495	1.76444037	-4.75978900
H	2.15763295	4.24787637	-4.78051400
C	2.58369895	-0.15513763	1.49317900
H	2.22991195	0.48534737	2.30518200
H	2.31315995	-1.18809363	1.71814300
H	3.68018995	-0.10005263	1.46974600
C	-7.70276605	-1.88781163	-0.28109500
H	-8.69540305	-1.47076363	-0.08036700
H	-7.83553805	-2.94418163	-0.53825600
H	-7.11832005	-1.83368063	0.64133500
C	-7.83895605	-1.21972463	-2.71722600
H	-7.89471405	-2.25028663	-3.08358900
H	-8.86562405	-0.88659863	-2.53013900
H	-7.42994005	-0.59308663	-3.51362600
C	-4.73295705	-3.76814663	-0.82959300
H	-4.70591305	-4.82185963	-1.12888400
H	-3.71397605	-3.44319863	-0.61324600
H	-5.33024205	-3.68973363	0.08452400
C	-4.58450905	-3.08300663	-3.28653600
H	-5.08863505	-2.53946063	-4.09225800
H	-3.55676305	-2.71907763	-3.20692300
H	-4.54930005	-4.14236863	-3.56432800
C	-1.72362805	5.62026537	-0.72006700
C	-3.95486105	4.89265837	0.80481900
C	-3.20315705	5.99511837	1.14777600
C	-2.08228805	6.37514037	0.37237600
C	-6.82514505	4.68944337	-0.67014100
C	-8.95464505	4.06187037	1.03857900
C	-8.97795805	5.22959937	0.31172700
C	-7.90544205	5.53683737	-0.55783400
H	-0.85802105	5.89148637	-1.31972500
H	-1.50764805	7.25555237	0.64592700
H	-3.47536305	6.57999437	2.02192500
H	-4.80726005	4.61938637	1.41512600
H	-6.01773505	4.93720237	-1.34970000
H	-7.93697305	6.44837137	-1.14796700
H	-9.82046705	5.91002337	0.39390500
H	-9.77954205	3.80467137	1.69837700
C	-1.01098305	2.52656937	1.94089400
H	-0.02399405	3.00621537	1.90569000
H	-1.41615005	2.54619537	0.92719500
H	-1.64515405	3.15230337	2.57434000
C	-0.24022005	-2.53457963	1.43131800
H	-0.98695405	-2.62520563	0.63461000
H	0.73809495	-2.49926663	0.94060300
H	-0.27565805	-3.43653863	2.04787700

Sum of electronic and zero-point Energies= -5047.669752
Sum of electronic and thermal Energies= -5047.619390
Sum of electronic and thermal Enthalpies= -5047.618446
Sum of electronic and thermal Free Energies= -5047.754750
Imaginary frequency: -137.17 cm^{-1}

Me-TS-minor1

S	-0.29927007	-0.67883211	0.00000000
N	4.20525093	0.73381389	0.50755300

N	4.12804493	0.90133989	-2.11821200
N	4.16157593	3.25365489	-0.79641900
C	0.15231193	-0.79985311	1.71604700
C	1.06163393	-1.81772411	2.11029200
C	1.37667893	-1.92338211	3.46889300
H	2.06580193	-2.69907311	3.79127700
C	0.83212593	-1.04637711	4.40525900
H	1.08489493	-1.15164911	5.45660700
C	-0.01729507	-0.01962211	3.99546600
H	-0.41029107	0.68113189	4.72672500
C	-0.36614207	0.13443589	2.65059800
C	5.53595493	0.20151589	0.40850700
C	5.84712293	-0.73893711	-0.57136600
C	7.22102193	-1.12923611	-0.75168300
C	8.21238093	-0.67779811	0.17959500
C	7.81605493	0.17145089	1.24480400
H	8.56022393	0.49110789	1.96984300
C	6.52327293	0.61972989	1.34247300
H	6.24988993	1.30161789	2.13918200
C	3.91989193	-0.52291811	-2.13575700
C	4.76081593	-1.33975411	-1.39110300
C	4.51696293	-2.76007311	-1.37287000
C	3.48119493	-3.30625211	-2.20284100
C	2.67745393	-2.42709911	-2.97304200
H	1.88897693	-2.84458511	-3.59477300
C	2.86719593	-1.06988011	-2.91672800
H	2.21724493	-0.40700011	-3.47520000
C	3.86927093	1.59151389	-3.39730500
H	4.35130493	1.02285889	-4.19540000
H	4.30229493	2.58901789	-3.36310900
H	2.79794993	1.68986189	-3.61580900
C	3.63332993	0.89815789	1.85619000
H	3.80858093	-0.01675611	2.42656000
H	2.55931293	1.05377089	1.74751100
H	4.05790193	1.74879489	2.40470900
C	3.38327693	4.53578889	-0.67945100
H	4.16070993	5.30272789	-0.70656000
C	5.65835093	3.39825089	-0.76330200
H	6.06388193	2.38783589	-0.84575100
C	-1.76190507	-2.28156511	-0.12502900
C	-2.67738507	-1.21733111	-0.30127400
Se	1.37106993	1.68620489	-0.61711200
P	3.53799493	1.69446489	-0.73149500
H	-3.14680707	-0.83684111	0.60411400
H	-1.41497807	-2.80262711	-1.01362600
C	-3.11193007	-0.61760811	-1.53594200
C	-4.04067207	0.44721489	-1.47426300
C	-2.66895207	-1.06063611	-2.80413600
C	-4.51344507	1.04427389	-2.63518500
H	-4.38650207	0.79507489	-0.50440800
C	-3.13976307	-0.45564511	-3.96120200
H	-1.96272807	-1.88097311	-2.88123300
C	-4.06199907	0.59510789	-3.88038700
H	-5.22992907	1.85748589	-2.57528300
H	-2.79687907	-0.80283311	-4.93095900
H	-4.43097507	1.06056089	-4.78961400
C	-1.85839407	-3.13003811	1.11908300
H	-0.92741407	-3.65423411	1.33855800

H	-2.14166907	-2.54025311	1.99486000
H	-2.63423607	-3.88997111	0.95569000
C	6.14548593	4.00018089	0.56341200
H	7.23755593	3.93813689	0.61850800
H	5.87139593	5.05641189	0.65875100
H	5.73114893	3.46273189	1.42053600
C	6.20752093	4.19398889	-1.95794100
H	5.84470393	5.22705489	-1.97368800
H	7.30002693	4.23494889	-1.88836900
H	5.95549893	3.72598789	-2.91276300
C	2.47357793	4.80233789	-1.88604200
H	3.04241693	4.76552889	-2.82084000
H	1.65965193	4.07540089	-1.94184000
H	2.03351693	5.80209489	-1.79787300
C	2.65446893	4.69804289	0.66231000
H	3.34620293	4.58030989	1.50292900
H	2.21432493	5.69974689	0.72321400
H	1.85447193	3.96176789	0.75941200
C	3.25586193	-4.70911411	-2.21346100
C	5.24273293	-3.66088611	-0.54215000
C	4.98996593	-5.01495811	-0.56473200
C	3.99624593	-5.55135811	-1.41716400
C	7.65053193	-1.93456011	-1.84325800
C	9.56549993	-1.07532811	0.01274400
C	9.94207793	-1.86804111	-1.04671200
H	10.98047893	-2.16138711	-1.17018700
C	8.97343593	-2.29054811	-1.98708400
H	10.30168793	-0.73007911	0.73443900
H	9.27749393	-2.89800911	-2.83483700
H	6.92379993	-2.25918811	-2.57924400
H	5.56077493	-5.67826111	0.07909500
H	6.00543693	-3.27242811	0.12160300
H	3.81631993	-6.62246711	-1.43330600
H	2.47929693	-5.10474511	-2.86394800
C	1.74617193	-2.72778011	1.11830600
H	1.04245393	-3.34249011	0.54772100
H	2.31735793	-2.15274511	0.38210800
H	2.43859493	-3.40225911	1.62834600
C	-1.21908207	1.30660089	2.23217600
H	-0.68922507	1.90244289	1.48070700
H	-2.17188907	0.99931189	1.78691400
H	-1.44178907	1.94645889	3.08999800

Sum of electronic and zero-point Energies= -5047.668186
Sum of electronic and thermal Energies= -5047.618544
Sum of electronic and thermal Enthalpies= -5047.617599
Sum of electronic and thermal Free Energies= -5047.751810
Imaginary frequency: -140.01 cm^{-1}

Me-TS-minor2

S	-0.27007299	-0.29927007	0.00000000
N	-4.36741499	0.20850993	1.85182300
N	-5.00880799	0.22683893	-0.71185400
N	-5.88288599	-1.90068107	0.70415900
C	-0.11194399	0.03461493	1.73870300
C	-0.39585499	1.35991693	2.14897600

C	-0.29755699	1.64711293	3.51778600
H	-0.49880399	2.65996493	3.85567100
C	0.04277001	0.66513693	4.44284800
H	0.11143401	0.91456093	5.49841200
C	0.27139301	-0.64384407	4.02088100
H	0.50498501	-1.41251707	4.75231800
C	0.19170301	-0.99774407	2.66905800
C	-5.27833999	1.29602893	2.07382400
C	-5.36338399	2.34577293	1.16349900
C	-6.41926499	3.31639093	1.31864200
C	-7.23627999	3.28797893	2.49656700
C	-7.00638199	2.28007593	3.46772200
H	-7.60493299	2.27422393	4.37516500
C	-6.07644599	1.29644193	3.25088900
H	-5.94968599	0.50738993	3.98306400
C	-4.21747999	1.41792693	-0.85303100
C	-4.36798799	2.45679693	0.06223400
C	-3.55058499	3.63905693	-0.08134200
C	-2.74519199	3.79735593	-1.25870400
C	-2.66823199	2.72708893	-2.18471300
H	-2.05287099	2.84131593	-3.07354400
C	-3.35237399	1.55783993	-1.97130200
H	-3.26005899	0.74570393	-2.68191400
C	-5.38839299	-0.43612607	-1.97904000
H	-5.75841899	0.32545293	-2.66853700
H	-6.18405599	-1.15259607	-1.78665900
H	-4.54883799	-0.97191807	-2.43984700
C	-3.64439099	-0.32516307	3.02274200
H	-3.24205299	0.51237593	3.59614100
H	-2.81994099	-0.94018207	2.65954600
H	-4.27766799	-0.93906207	3.67648300
C	-5.83552099	-3.40639607	0.70052000
H	-6.87307499	-3.68502007	0.89764300
C	-7.20867699	-1.30094507	1.08596400
H	-7.07014399	-0.21822207	1.07318500
C	1.92454001	0.59959693	-0.55196400
C	1.68039001	-0.78915107	-0.63860200
Se	-2.74133099	-1.94851407	0.14539400
P	-4.57794399	-0.85498407	0.53703300
C	-7.63798299	-1.70678407	2.50393100
H	-8.51771099	-1.12653807	2.80170400
H	-7.90908899	-2.76641607	2.56360000
H	-6.84432299	-1.51710207	3.23111000
C	-8.31419099	-1.61858607	0.06703200
H	-8.51411699	-2.69252607	-0.01041700
H	-9.24499499	-1.13739007	0.38634500
H	-8.07238699	-1.23992907	-0.92943200
C	-5.00046399	-4.00187807	1.84369500
H	-5.11154299	-5.09205107	1.84966000
H	-3.94137399	-3.76526107	1.72249900
H	-5.33721599	-3.62189607	2.81380500
C	-5.48590099	-4.00632207	-0.66798500
H	-6.16724199	-3.64008507	-1.44263100
H	-4.46102399	-3.76964807	-0.96185900
H	-5.58435899	-5.09662507	-0.62219300
C	-2.02517099	5.00329193	-1.46404600
C	-3.56661999	4.70982593	0.85509700
C	-2.84278099	5.86097893	0.63560800

```
 C                 -2.07221499    6.01958793   -0.54076400
 C                 -6.71303599    4.30086193    0.33381200
 C                 -8.26453599    4.25270193    2.66525500
 C                 -8.50753099    5.20083093    1.69905700
 C                 -7.72898699    5.21290793    0.51841200
 H                 -1.43834699    5.10802493   -2.37345700
 H                 -1.52347499    6.94132993   -0.71044100
 H                 -2.86919399    6.65967093    1.37158900
 H                 -4.15305599    4.61167093    1.76010800
 H                 -6.13717599    4.32175793   -0.58385300
 H                 -7.93828899    5.94640993   -0.25510500
 H                 -9.30104299    5.93022093    1.83271300
 H                 -8.86594099    4.21844693    3.57022000
 C                  1.47584501   -1.44288907   -1.98162300
 H                  0.91193701   -0.80181407   -2.66690800
 H                  2.46271001   -1.62889207   -2.42265000
 H                  0.95558601   -2.40044307   -1.89067400
 H                  2.11330501   -1.43884507    0.11501800
 C                  2.65963801    1.31453693    0.46531000
 C                  2.78323101    2.71647793    0.33614800
 C                  3.31547501    0.68293193    1.54875700
 C                  3.52426901    3.45699393    1.24783800
 H                  2.29358701    3.21921693   -0.49490300
 C                  4.05538401    1.42652093    2.45863400
 H                  3.25924001   -0.39231807    1.67514100
 C                  4.16166801    2.81418093    2.31330100
 H                  3.61085301    4.53270993    1.12931500
 H                  4.55901101    0.92649993    3.28029400
 H                  4.74618701    3.39075493    3.02416800
 H                  1.61527901    1.19172293   -1.41091000
 C                 -0.81656599    2.43529993    1.19689400
 H                 -0.07478299    2.59438093    0.39323500
 H                 -1.77739899    2.21205493    0.69264000
 H                 -0.95226799    3.39511793    1.72349800
 C                  0.36959301   -2.43660507    2.27983800
 H                 -0.55611199   -2.81928507    1.81292200
 H                  1.18491101   -2.60871407    1.55889400
 H                  0.58655801   -3.05457207    3.16385100
Sum of electronic and zero-point Energies=         -5047.666985
Sum of electronic and thermal Energies=            -5047.618220
Sum of electronic and thermal Enthalpies=          -5047.617276
Sum of electronic and thermal Free Energies=       -5047.748274
```

Imaginary frequency: -123.25 cm^{-1}

	ΔE_{dist}_**A**[a]	ΔE_{dist}_**B**[b]	ΔE_{d}	ΔE_{i}	ΔE_{act}[c]	ΔH	ΔG	π(C=C)-σ*(S-Se)[d]
H-TS-major1	**9.6**	**26.1**	**35.7**	**-24.8**	**10.9 (0.0)**	**11.9 (0.0)**	**23.9 (0.0)**	**63.3 (6.7)**
H-TS-major2	10.7	27.4	38.1	-25.6	12.5 (1.6)	13.5 (1.6)	25.4 (1.5)	57.5 (0.9)
H-TS-minor1	**10.4**	**28.1**	**38.5**	**-25.9**	**12.6 (1.7)**	**13.6 (1.7)**	**25.6 (1.7)**	**64.2 (7.6)**
H-TS-minor2	13.3	33.5	46.8	-32.2	14.6 (3.7)	15.2 (3.3)	26.9 (3.0)	56.6 (0.0)
Me-TS-major1	**7.8**	**22.8**	**30.7**	**-19.9**	**10.8 (0.0)**	**11.2 (0.0)**	**25.0 (0.0)**	**61.7 (7.3)**
Me-TS-major2	9.0	27.2	36.1	-22.4	13.7 (2.9)	14.7 (3.5)	26.8 (1.8)	55.9 (1.5)
Me-TS-minor1	**9.4**	**28.6**	**38.0**	**-23.0**	**15.0 (4.2)**	**15.3 (4.1)**	**28.5 (3.5)**	**62.1 (7.7)**
Me-TS-minor2	9.1	29.9	39.0	-23.6	15.4 (4.6)	15.5 (4.3)	30.4 (5.4)	54.4 (0.0)

[a] **A** = β-methylstyrene. [b] **B** = **5c** (H = C_6H_5; Me = 2,6-$Me_2C_6H_3$) [c] $\Delta E_{\mathrm{act}} = \Delta E_{\mathrm{d}} + \Delta E_{\mathrm{i}}$; $\Delta E_{\mathrm{d}} = \Delta E_{\mathrm{dist}}$_**A** + ΔE_{dist}_**B.** [d] π(C=C)-σ*(S-Se) orbital interaction energy is calculated by NBO analysis.

Crystallographic Data for S5^{2+}

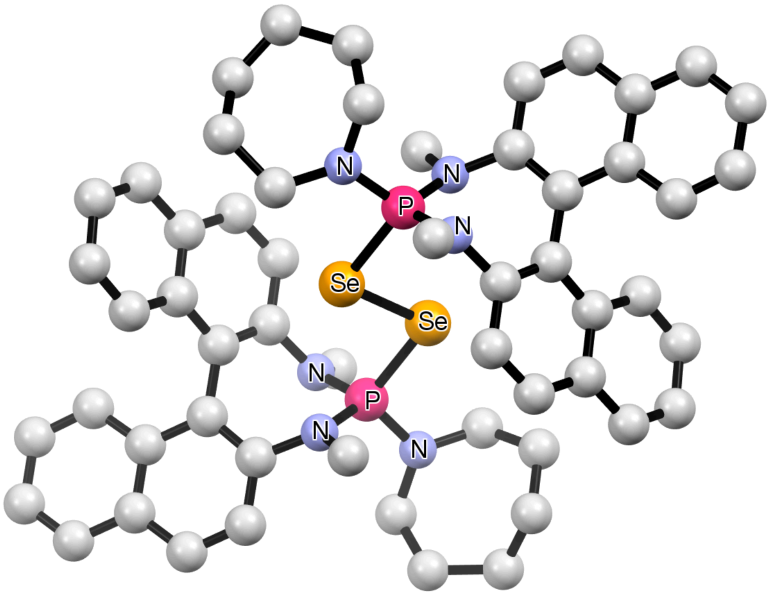


Figure S1. ORTEP image of the X-ray crystal structure of **S5^{2+}** (Hydrogens and $SbCl_6^-$ counteranions omitted for clarity).

The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 1006824. 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 S1. Crystal data and structure refinement for bc11tasq

Identification code	bc11tasq	
Empirical formula	$C_{66}H_{76}Cl_{12}N_6O_2P_2Sb_2Se_2$	
Formula weight	1874.09	
Temperature	193(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0050(6) Å	a= 67.081(2)°.
	b = 12.2783(6) Å	b= 73.258(2)°.
	c = 14.5779(7) Å	g = 88.706(2)°.

Volume	1885.47(16) Å^3
Z	1
Density (calculated)	1.651 Mg/m^3
Absorption coefficient	11.470 mm^{-1}
F(000)	934
Crystal size	0.374 x 0.215 x 0.172 mm^3
Theta range for data collection	3.45 to 67.82°.
Index ranges	-14<=h<=14, -14<=k<=14, -16<=l<=17
Reflections collected	23671
Independent reflections	6453 [R(int) = 0.0376]
Completeness to theta = 67.82°	94.4 %
Absorption correction	Integration
Max. and min. transmission	0.3726 and 0.1241
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6453 / 499 / 556
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0805
R indices (all data)	R1 = 0.0315, wR2 = 0.0816
Largest diff. peak and hole	0.511 and -0.432 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for bc11tasq. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	-127(5)	4413(4)	2512(3)	38(1)
Cl(1)	1698(7)	3617(9)	2293(6)	101(2)
Cl(2)	-476(8)	3773(6)	1285(4)	56(2)
Cl(3)	-1950(6)	5195(6)	2703(6)	69(1)
Cl(4)	221(7)	5042(8)	3744(5)	74(2)
Cl(5)	-1008(8)	2579(4)	3876(4)	57(2)
Cl(6)	771(8)	6246(6)	1151(5)	66(1)
Sb(1B)	56(8)	4348(7)	2492(7)	42(2)
Cl(1B)	1247(10)	2788(10)	2581(8)	82(3)
Cl(2B)	-635(15)	4023(14)	1258(11)	64(5)
Cl(3B)	-1114(14)	5917(11)	2404(10)	104(4)

Cl(4B)	701(14)	4684(13)	3747(11)	85(5)
Cl(5B)	-1467(9)	2969(11)	3835(8)	80(3)
Cl(6B)	1589(11)	5721(12)	1136(9)	115(4)
Sb(1C)	158(5)	4446(4)	2521(3)	37(1)
Cl(1C)	2013(5)	3720(6)	2244(6)	70(1)
Cl(2C)	-203(6)	3843(7)	1287(5)	53(1)
Cl(3C)	-1657(7)	5240(9)	2754(7)	82(2)
Cl(4C)	545(8)	5059(7)	3742(5)	69(2)
Cl(5C)	-684(6)	2591(5)	3866(5)	62(2)
Cl(6C)	1016(9)	6304(6)	1156(6)	78(2)
Se(1)	137(1)	9337(1)	797(1)	41(1)
P(1)	2029(1)	9990(1)	333(1)	33(1)
N(2)	2168(2)	11434(2)	-286(2)	37(1)
N(3)	2920(2)	9529(2)	-496(2)	34(1)
N(1)	2366(6)	9525(7)	1411(3)	40(1)
C(1)	1801(5)	8404(5)	2307(3)	47(1)
C(2)	926(5)	8600(5)	3210(4)	59(1)
C(3)	1201(5)	9687(6)	3379(5)	65(2)
C(4)	2446(6)	9969(7)	3293(4)	69(2)
C(5)	3234(8)	10677(7)	2164(5)	59(1)
C(6)	3449(5)	10026(6)	1444(5)	49(1)
N(1B)	2160(20)	9400(20)	1498(9)	40(3)
C(1B)	1409(18)	8415(16)	2428(12)	47(3)
C(2B)	1381(17)	8417(12)	3474(10)	57(3)
C(3B)	1474(18)	9579(15)	3562(15)	63(3)
C(4B)	2600(20)	10350(20)	3123(16)	64(3)
C(5B)	3220(30)	10740(20)	1950(16)	59(4)
C(6B)	3290(18)	9770(20)	1544(17)	50(3)
C(7)	1380(2)	12156(3)	179(2)	46(1)
C(8)	3238(2)	12050(2)	-1095(2)	37(1)
C(9)	3883(3)	12852(2)	-916(2)	46(1)
C(10)	4881(3)	13476(2)	-1644(2)	49(1)
C(11)	5311(2)	13330(2)	-2599(2)	45(1)
C(12)	6366(3)	13967(3)	-3357(3)	57(1)
C(13)	6795(3)	13801(3)	-4257(3)	64(1)
C(14)	6197(3)	12964(3)	-4425(3)	58(1)

C(15)	5182(2)	12320(3)	-3708(2)	48(1)
C(16)	4681(2)	12501(2)	-2773(2)	40(1)
C(17)	3595(2)	11872(2)	-2011(2)	36(1)
C(18)	2926(2)	11009(2)	-2191(2)	33(1)
C(19)	2558(2)	11330(2)	-3104(2)	35(1)
C(20)	2624(3)	12522(2)	-3821(2)	45(1)
C(21)	2298(3)	12791(3)	-4697(2)	55(1)
C(22)	1900(3)	11872(3)	-4921(2)	56(1)
C(23)	1797(3)	10730(3)	-4245(2)	50(1)
C(24)	2092(2)	10422(2)	-3307(2)	40(1)
C(25)	1916(2)	9237(2)	-2565(2)	42(1)
C(26)	2173(2)	8948(2)	-1655(2)	39(1)
C(27)	2680(2)	9845(2)	-1476(2)	33(1)
C(28)	3479(2)	8429(2)	-109(2)	42(1)

Table S3. Bond lengths [Å] and angles [°] for bc11tasq.

Sb(1)-Cl(4)	2.350(4)
Sb(1)-Cl(2)	2.352(4)
Sb(1)-Cl(5)	2.356(4)
Sb(1)-Cl(3)	2.357(4)
Sb(1)-Cl(6)	2.358(4)
Sb(1)-Cl(1)	2.366(5)
Sb(1B)-Cl(3B)	2.342(7)
Sb(1B)-Cl(2B)	2.348(7)
Sb(1B)-Cl(1B)	2.350(7)
Sb(1B)-Cl(4B)	2.353(7)
Sb(1B)-Cl(5B)	2.354(7)
Sb(1B)-Cl(6B)	2.363(7)
Sb(1C)-Cl(2C)	2.340(5)
Sb(1C)-Cl(4C)	2.341(5)
Sb(1C)-Cl(5C)	2.354(5)
Sb(1C)-Cl(3C)	2.356(5)
Sb(1C)-Cl(1C)	2.364(4)
Sb(1C)-Cl(6C)	2.369(5)

Se(1)-P(1)	2.2441(6)
Se(1)-Se(1)#1	2.3728(5)
P(1)-N(1)	1.619(3)
P(1)-N(1B)	1.621(8)
P(1)-N(2)	1.633(2)
P(1)-N(3)	1.638(2)
N(2)-C(8)	1.445(3)
N(2)-C(7)	1.483(3)
N(3)-C(27)	1.440(3)
N(3)-C(28)	1.475(3)
N(1)-C(6)	1.472(5)
N(1)-C(1)	1.480(5)
C(1)-C(2)	1.527(6)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.507(7)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.500(8)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.544(6)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.515(6)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
N(1B)-C(6B)	1.466(10)
N(1B)-C(1B)	1.477(9)
C(1B)-C(2B)	1.517(10)
C(1B)-H(1C)	0.9900
C(1B)-H(1D)	0.9900
C(2B)-C(3B)	1.491(10)
C(2B)-H(2C)	0.9900

C(2B)-H(2D)	0.9900
C(3B)-C(4B)	1.487(11)
C(3B)-H(3C)	0.9900
C(3B)-H(3D)	0.9900
C(4B)-C(5B)	1.535(10)
C(4B)-H(4C)	0.9900
C(4B)-H(4D)	0.9900
C(5B)-C(6B)	1.517(10)
C(5B)-H(5C)	0.9900
C(5B)-H(5D)	0.9900
C(6B)-H(6C)	0.9900
C(6B)-H(6D)	0.9900
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(17)	1.381(4)
C(8)-C(9)	1.411(4)
C(9)-C(10)	1.350(4)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.419(4)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.415(4)
C(11)-C(16)	1.421(4)
C(12)-C(13)	1.358(5)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.400(5)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.367(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.423(4)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.439(4)
C(17)-C(18)	1.488(3)
C(18)-C(27)	1.377(3)
C(18)-C(19)	1.431(4)
C(19)-C(20)	1.417(4)

C(19)-C(24)	1.423(4)
C(20)-C(21)	1.360(4)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.417(5)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.347(5)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.417(4)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.409(4)
C(25)-C(26)	1.358(4)
C(25)-H(25A)	0.9500
C(26)-C(27)	1.414(4)
C(26)-H(26A)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800

Cl(4)-Sb(1)-Cl(2)	179.7(3)
Cl(4)-Sb(1)-Cl(5)	89.3(2)
Cl(2)-Sb(1)-Cl(5)	90.4(2)
Cl(4)-Sb(1)-Cl(3)	90.4(2)
Cl(2)-Sb(1)-Cl(3)	89.7(2)
Cl(5)-Sb(1)-Cl(3)	90.4(2)
Cl(4)-Sb(1)-Cl(6)	90.4(3)
Cl(2)-Sb(1)-Cl(6)	89.8(2)
Cl(5)-Sb(1)-Cl(6)	179.5(3)
Cl(3)-Sb(1)-Cl(6)	90.0(3)
Cl(4)-Sb(1)-Cl(1)	90.7(3)
Cl(2)-Sb(1)-Cl(1)	89.2(3)
Cl(5)-Sb(1)-Cl(1)	89.6(3)
Cl(3)-Sb(1)-Cl(1)	178.8(3)
Cl(6)-Sb(1)-Cl(1)	89.9(3)
Cl(3B)-Sb(1B)-Cl(2B)	89.7(5)
Cl(3B)-Sb(1B)-Cl(1B)	179.3(5)
Cl(2B)-Sb(1B)-Cl(1B)	90.8(5)

Cl(3B)-Sb(1B)-Cl(4B)	89.2(5)
Cl(2B)-Sb(1B)-Cl(4B)	178.6(6)
Cl(1B)-Sb(1B)-Cl(4B)	90.3(4)
Cl(3B)-Sb(1B)-Cl(5B)	91.5(5)
Cl(2B)-Sb(1B)-Cl(5B)	89.2(5)
Cl(1B)-Sb(1B)-Cl(5B)	89.0(4)
Cl(4B)-Sb(1B)-Cl(5B)	89.9(5)
Cl(3B)-Sb(1B)-Cl(6B)	88.9(5)
Cl(2B)-Sb(1B)-Cl(6B)	90.5(5)
Cl(1B)-Sb(1B)-Cl(6B)	90.7(5)
Cl(4B)-Sb(1B)-Cl(6B)	90.4(5)
Cl(5B)-Sb(1B)-Cl(6B)	179.5(5)
Cl(2C)-Sb(1C)-Cl(4C)	179.3(3)
Cl(2C)-Sb(1C)-Cl(5C)	90.5(3)
Cl(4C)-Sb(1C)-Cl(5C)	89.9(3)
Cl(2C)-Sb(1C)-Cl(3C)	90.6(2)
Cl(4C)-Sb(1C)-Cl(3C)	90.0(3)
Cl(5C)-Sb(1C)-Cl(3C)	91.5(3)
Cl(2C)-Sb(1C)-Cl(1C)	89.7(2)
Cl(4C)-Sb(1C)-Cl(1C)	89.8(2)
Cl(5C)-Sb(1C)-Cl(1C)	90.6(2)
Cl(3C)-Sb(1C)-Cl(1C)	177.9(3)
Cl(2C)-Sb(1C)-Cl(6C)	89.1(3)
Cl(4C)-Sb(1C)-Cl(6C)	90.5(3)
Cl(5C)-Sb(1C)-Cl(6C)	179.4(3)
Cl(3C)-Sb(1C)-Cl(6C)	88.9(3)
Cl(1C)-Sb(1C)-Cl(6C)	89.1(3)
P(1)-Se(1)-Se(1)#1	94.31(2)
N(1)-P(1)-N(2)	114.4(3)
N(1B)-P(1)-N(2)	119.9(10)
N(1)-P(1)-N(3)	109.8(3)
N(1B)-P(1)-N(3)	113.4(12)
N(2)-P(1)-N(3)	104.41(10)
N(1)-P(1)-Se(1)	105.4(2)
N(1B)-P(1)-Se(1)	96.3(8)
N(2)-P(1)-Se(1)	108.04(8)

N(3)-P(1)-Se(1)	115.08(8)
C(8)-N(2)-C(7)	116.9(2)
C(8)-N(2)-P(1)	120.66(17)
C(7)-N(2)-P(1)	119.75(18)
C(27)-N(3)-C(28)	117.9(2)
C(27)-N(3)-P(1)	115.13(16)
C(28)-N(3)-P(1)	120.11(17)
C(6)-N(1)-C(1)	115.8(4)
C(6)-N(1)-P(1)	120.2(4)
C(1)-N(1)-P(1)	122.1(4)
N(1)-C(1)-C(2)	113.3(5)
N(1)-C(1)-H(1A)	108.9
C(2)-C(1)-H(1A)	108.9
N(1)-C(1)-H(1B)	108.9
C(2)-C(1)-H(1B)	108.9
H(1A)-C(1)-H(1B)	107.7
C(3)-C(2)-C(1)	116.4(4)
C(3)-C(2)-H(2A)	108.2
C(1)-C(2)-H(2A)	108.2
C(3)-C(2)-H(2B)	108.2
C(1)-C(2)-H(2B)	108.2
H(2A)-C(2)-H(2B)	107.3
C(4)-C(3)-C(2)	117.3(5)
C(4)-C(3)-H(3A)	108.0
C(2)-C(3)-H(3A)	108.0
C(4)-C(3)-H(3B)	108.0
C(2)-C(3)-H(3B)	108.0
H(3A)-C(3)-H(3B)	107.2
C(3)-C(4)-C(5)	114.2(5)
C(3)-C(4)-H(4A)	108.7
C(5)-C(4)-H(4A)	108.7
C(3)-C(4)-H(4B)	108.7
C(5)-C(4)-H(4B)	108.7
H(4A)-C(4)-H(4B)	107.6
C(6)-C(5)-C(4)	115.7(5)
C(6)-C(5)-H(5A)	108.4

C(4)-C(5)-H(5A)	108.4
C(6)-C(5)-H(5B)	108.4
C(4)-C(5)-H(5B)	108.4
H(5A)-C(5)-H(5B)	107.4
N(1)-C(6)-C(5)	113.3(4)
N(1)-C(6)-H(6A)	108.9
C(5)-C(6)-H(6A)	108.9
N(1)-C(6)-H(6B)	108.9
C(5)-C(6)-H(6B)	108.9
H(6A)-C(6)-H(6B)	107.7
C(6B)-N(1B)-C(1B)	117.8(10)
C(6B)-N(1B)-P(1)	113.0(15)
C(1B)-N(1B)-P(1)	128.2(13)
N(1B)-C(1B)-C(2B)	115.6(10)
N(1B)-C(1B)-H(1C)	108.4
C(2B)-C(1B)-H(1C)	108.4
N(1B)-C(1B)-H(1D)	108.4
C(2B)-C(1B)-H(1D)	108.4
H(1C)-C(1B)-H(1D)	107.4
C(3B)-C(2B)-C(1B)	118.8(11)
C(3B)-C(2B)-H(2C)	107.6
C(1B)-C(2B)-H(2C)	107.6
C(3B)-C(2B)-H(2D)	107.6
C(1B)-C(2B)-H(2D)	107.6
H(2C)-C(2B)-H(2D)	107.0
C(4B)-C(3B)-C(2B)	122.3(13)
C(4B)-C(3B)-H(3C)	106.8
C(2B)-C(3B)-H(3C)	106.8
C(4B)-C(3B)-H(3D)	106.8
C(2B)-C(3B)-H(3D)	106.8
H(3C)-C(3B)-H(3D)	106.6
C(3B)-C(4B)-C(5B)	117.2(12)
C(3B)-C(4B)-H(4C)	108.0
C(5B)-C(4B)-H(4C)	108.0
C(3B)-C(4B)-H(4D)	108.0
C(5B)-C(4B)-H(4D)	108.0

H(4C)-C(4B)-H(4D)	107.2
C(6B)-C(5B)-C(4B)	115.2(13)
C(6B)-C(5B)-H(5C)	108.5
C(4B)-C(5B)-H(5C)	108.5
C(6B)-C(5B)-H(5D)	108.5
C(4B)-C(5B)-H(5D)	108.5
H(5C)-C(5B)-H(5D)	107.5
N(1B)-C(6B)-C(5B)	113.3(13)
N(1B)-C(6B)-H(6C)	108.9
C(5B)-C(6B)-H(6C)	108.9
N(1B)-C(6B)-H(6D)	108.9
C(5B)-C(6B)-H(6D)	108.9
H(6C)-C(6B)-H(6D)	107.7
N(2)-C(7)-H(7A)	109.5
N(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
N(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(17)-C(8)-C(9)	121.7(2)
C(17)-C(8)-N(2)	121.0(2)
C(9)-C(8)-N(2)	117.2(2)
C(10)-C(9)-C(8)	120.6(3)
C(10)-C(9)-H(9A)	119.7
C(8)-C(9)-H(9A)	119.7
C(9)-C(10)-C(11)	120.8(3)
C(9)-C(10)-H(10A)	119.6
C(11)-C(10)-H(10A)	119.6
C(12)-C(11)-C(10)	121.0(3)
C(12)-C(11)-C(16)	120.1(3)
C(10)-C(11)-C(16)	118.9(2)
C(13)-C(12)-C(11)	121.1(3)
C(13)-C(12)-H(12A)	119.5
C(11)-C(12)-H(12A)	119.5
C(12)-C(13)-C(14)	119.4(3)
C(12)-C(13)-H(13A)	120.3

C(14)-C(13)-H(13A)	120.3
C(15)-C(14)-C(13)	121.4(3)
C(15)-C(14)-H(14A)	119.3
C(13)-C(14)-H(14A)	119.3
C(14)-C(15)-C(16)	120.9(3)
C(14)-C(15)-H(15A)	119.6
C(16)-C(15)-H(15A)	119.6
C(11)-C(16)-C(15)	117.1(2)
C(11)-C(16)-C(17)	119.9(2)
C(15)-C(16)-C(17)	123.0(2)
C(8)-C(17)-C(16)	117.9(2)
C(8)-C(17)-C(18)	121.7(2)
C(16)-C(17)-C(18)	120.2(2)
C(27)-C(18)-C(19)	118.1(2)
C(27)-C(18)-C(17)	119.5(2)
C(19)-C(18)-C(17)	122.4(2)
C(20)-C(19)-C(24)	117.9(2)
C(20)-C(19)-C(18)	123.0(2)
C(24)-C(19)-C(18)	119.1(2)
C(21)-C(20)-C(19)	121.3(3)
C(21)-C(20)-H(20A)	119.4
C(19)-C(20)-H(20A)	119.4
C(20)-C(21)-C(22)	120.2(3)
C(20)-C(21)-H(21A)	119.9
C(22)-C(21)-H(21A)	119.9
C(23)-C(22)-C(21)	120.1(3)
C(23)-C(22)-H(22A)	119.9
C(21)-C(22)-H(22A)	119.9
C(22)-C(23)-C(24)	121.1(3)
C(22)-C(23)-H(23A)	119.5
C(24)-C(23)-H(23A)	119.5
C(25)-C(24)-C(23)	121.3(2)
C(25)-C(24)-C(19)	119.5(2)
C(23)-C(24)-C(19)	119.2(3)
C(26)-C(25)-C(24)	121.3(2)
C(26)-C(25)-H(25A)	119.4

C(24)-C(25)-H(25A)	119.4
C(25)-C(26)-C(27)	119.1(2)
C(25)-C(26)-H(26A)	120.4
C(27)-C(26)-H(26A)	120.4
C(18)-C(27)-C(26)	122.5(2)
C(18)-C(27)-N(3)	119.1(2)
C(26)-C(27)-N(3)	118.4(2)
N(3)-C(28)-H(28A)	109.5
N(3)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
N(3)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for bc11tasq. 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}
Sb(1)	48(1)	36(1)	27(1)	-13(1)	-9(1)	7(1)
Cl(1)	65(3)	137(5)	66(2)	-15(3)	-7(2)	49(3)
Cl(2)	99(4)	33(2)	32(2)	-14(1)	-13(2)	-2(2)
Cl(3)	65(2)	87(2)	72(2)	-47(2)	-24(2)	36(2)
Cl(4)	85(3)	99(3)	52(2)	-41(1)	-24(2)	-16(2)
Cl(5)	80(4)	48(2)	29(1)	-12(1)	-1(2)	-13(2)
Cl(6)	95(3)	40(2)	49(2)	1(1)	-29(2)	-21(1)
Sb(1B)	46(4)	33(2)	38(3)	-14(2)	3(2)	-20(2)
Cl(1B)	94(5)	98(6)	73(5)	-58(4)	-22(4)	38(5)
Cl(2B)	98(8)	59(8)	43(5)	-20(4)	-30(5)	-3(6)
Cl(3B)	122(7)	95(6)	102(6)	-36(5)	-50(5)	57(5)
Cl(4B)	90(7)	87(8)	104(7)	-56(5)	-43(5)	3(5)
Cl(5B)	72(5)	97(7)	55(4)	-28(5)	1(4)	-2(5)
Cl(6B)	123(7)	81(6)	101(6)	-26(5)	11(5)	-27(5)

Sb(1C)	45(1)	34(1)	31(1)	-13(1)	-10(1)	3(1)
Cl(1C)	45(2)	82(2)	62(2)	-16(1)	-5(2)	12(2)
Cl(2C)	61(2)	67(3)	41(2)	-36(2)	-11(1)	13(2)
Cl(3C)	74(3)	129(4)	73(2)	-65(2)	-33(2)	59(3)
Cl(4C)	82(4)	76(3)	63(2)	-33(1)	-36(2)	-6(2)
Cl(5C)	67(3)	58(2)	39(1)	0(1)	-10(1)	-21(1)
Cl(6C)	109(4)	46(2)	61(2)	-10(2)	-12(2)	-19(2)
Se(1)	38(1)	44(1)	33(1)	-7(1)	-8(1)	-1(1)
P(1)	36(1)	35(1)	30(1)	-15(1)	-9(1)	4(1)
N(2)	41(1)	36(1)	36(1)	-20(1)	-8(1)	6(1)
N(3)	39(1)	31(1)	33(1)	-13(1)	-9(1)	5(1)
N(1)	40(3)	47(2)	32(2)	-15(2)	-12(1)	2(2)
C(1)	49(3)	53(2)	35(2)	-12(2)	-15(2)	4(2)
C(2)	57(2)	77(3)	34(2)	-17(2)	-6(2)	-7(2)
C(3)	57(3)	89(3)	47(3)	-34(2)	-3(2)	-1(2)
C(4)	72(3)	92(4)	50(3)	-38(3)	-15(2)	-5(3)
C(5)	65(2)	74(3)	45(3)	-31(2)	-15(2)	-14(2)
C(6)	41(2)	65(3)	47(2)	-23(2)	-18(2)	-1(2)
N(1B)	39(5)	49(5)	38(4)	-22(4)	-18(4)	0(4)
C(1B)	51(6)	54(5)	35(4)	-12(4)	-21(4)	-4(5)
C(2B)	56(5)	70(4)	40(4)	-17(4)	-14(4)	-2(4)
C(3B)	66(5)	84(5)	42(4)	-31(4)	-10(4)	-9(4)
C(4B)	64(5)	79(5)	52(5)	-36(5)	-9(4)	-13(5)
C(5B)	56(5)	75(5)	46(5)	-26(5)	-12(5)	-11(4)
C(6B)	50(5)	59(5)	42(4)	-23(4)	-11(4)	0(4)
C(7)	52(1)	46(2)	47(2)	-30(1)	-10(1)	12(1)
C(8)	42(1)	30(1)	38(1)	-15(1)	-11(1)	4(1)
C(9)	58(2)	38(1)	47(2)	-24(1)	-16(1)	3(1)
C(10)	57(2)	37(1)	58(2)	-25(1)	-18(1)	-4(1)
C(11)	50(1)	34(1)	50(2)	-16(1)	-12(1)	-1(1)
C(12)	56(2)	42(2)	60(2)	-15(1)	-7(1)	-13(1)
C(13)	58(2)	55(2)	59(2)	-17(2)	2(1)	-16(1)
C(14)	56(2)	59(2)	49(2)	-22(1)	2(1)	-9(1)
C(15)	51(1)	45(2)	43(2)	-21(1)	-5(1)	-3(1)
C(16)	44(1)	32(1)	41(1)	-14(1)	-10(1)	1(1)
C(17)	42(1)	30(1)	37(1)	-16(1)	-12(1)	4(1)

C(18)	35(1)	32(1)	31(1)	-17(1)	-4(1)	2(1)
C(19)	38(1)	35(1)	32(1)	-16(1)	-6(1)	4(1)
C(20)	58(2)	37(1)	40(1)	-15(1)	-13(1)	4(1)
C(21)	71(2)	46(2)	43(2)	-9(1)	-21(1)	6(1)
C(22)	71(2)	61(2)	35(1)	-17(1)	-19(1)	5(2)
C(23)	58(2)	56(2)	39(1)	-25(1)	-13(1)	-2(1)
C(24)	42(1)	43(1)	35(1)	-20(1)	-5(1)	0(1)
C(25)	52(1)	38(1)	39(1)	-22(1)	-9(1)	-4(1)
C(26)	46(1)	31(1)	37(1)	-14(1)	-7(1)	-1(1)
C(27)	35(1)	32(1)	32(1)	-16(1)	-6(1)	5(1)
C(28)	42(1)	36(1)	45(1)	-14(1)	-10(1)	10(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for bc11tasq.

	x	y	z	U(eq)
H(1A)	2413	7939	2565	56
H(1B)	1393	7929	2065	56
H(2A)	151	8648	3091	71
H(2B)	858	7892	3862	71
H(3A)	967	10381	2865	78
H(3B)	706	9592	4083	78
H(4A)	2781	9215	3596	83
H(4B)	2455	10432	3715	83
H(5A)	2875	11410	1854	71
H(5B)	3999	10920	2194	71
H(6A)	3893	10583	729	59
H(6B)	3937	9375	1678	59
H(1C)	1678	7655	2406	56
H(1D)	601	8442	2383	56
H(2C)	642	7962	3993	68
H(2D)	2027	7974	3684	68
H(3C)	910	10065	3242	76

H(3D)	1190	9414	4317	76
H(4C)	3140	9921	3508	76
H(4D)	2447	11072	3268	76
H(5C)	2816	11387	1559	71
H(5D)	4029	11082	1798	71
H(6C)	3859	10060	835	60
H(6D)	3583	9075	2002	60
H(7A)	1248	12863	-381	69
H(7B)	1740	12399	602	69
H(7C)	631	11682	621	69
H(9A)	3614	12955	-278	55
H(10A)	5301	14019	-1515	58
H(12A)	6781	14519	-3233	68
H(13A)	7493	14249	-4769	76
H(14A)	6503	12842	-5052	70
H(15A)	4807	11744	-3835	57
H(20A)	2902	13146	-3687	55
H(21A)	2336	13598	-5161	66
H(22A)	1706	12062	-5550	67
H(23A)	1522	10122	-4399	60
H(25A)	1612	8630	-2704	50
H(26A)	2015	8153	-1146	47
H(28A)	4019	8311	-703	63
H(28B)	2877	7751	285	63
H(28C)	3912	8493	347	63

Table S6. Torsion angles [°] for bc11tasq.

Se(1)#1-Se(1)-P(1)-N(1)	162.8(3)
Se(1)#1-Se(1)-P(1)-N(1B)	164.4(12)
Se(1)#1-Se(1)-P(1)-N(2)	40.12(8)
Se(1)#1-Se(1)-P(1)-N(3)	-76.06(8)
N(1)-P(1)-N(2)-C(8)	93.6(3)
N(1B)-P(1)-N(2)-C(8)	102.0(12)
N(3)-P(1)-N(2)-C(8)	-26.4(2)

Se(1)-P(1)-N(2)-C(8)	-149.36(17)
N(1)-P(1)-N(2)-C(7)	-67.3(4)
N(1B)-P(1)-N(2)-C(7)	-58.9(12)
N(3)-P(1)-N(2)-C(7)	172.7(2)
Se(1)-P(1)-N(2)-C(7)	49.7(2)
N(1)-P(1)-N(3)-C(27)	177.5(3)
N(1B)-P(1)-N(3)-C(27)	168.4(8)
N(2)-P(1)-N(3)-C(27)	-59.39(18)
Se(1)-P(1)-N(3)-C(27)	58.85(17)
N(1)-P(1)-N(3)-C(28)	27.2(3)
N(1B)-P(1)-N(3)-C(28)	18.1(8)
N(2)-P(1)-N(3)-C(28)	150.26(18)
Se(1)-P(1)-N(3)-C(28)	-91.49(18)
N(1B)-P(1)-N(1)-C(6)	-175(10)
N(2)-P(1)-N(1)-C(6)	-46.5(7)
N(3)-P(1)-N(1)-C(6)	70.4(7)
Se(1)-P(1)-N(1)-C(6)	-165.1(5)
N(1B)-P(1)-N(1)-C(1)	21(9)
N(2)-P(1)-N(1)-C(1)	149.6(5)
N(3)-P(1)-N(1)-C(1)	-93.4(6)
Se(1)-P(1)-N(1)-C(1)	31.1(7)
C(6)-N(1)-C(1)-C(2)	89.3(7)
P(1)-N(1)-C(1)-C(2)	-106.2(8)
N(1)-C(1)-C(2)-C(3)	-33.0(8)
C(1)-C(2)-C(3)-C(4)	-42.3(7)
C(2)-C(3)-C(4)-C(5)	84.0(8)
C(3)-C(4)-C(5)-C(6)	-66.2(9)
C(1)-N(1)-C(6)-C(5)	-78.5(7)
P(1)-N(1)-C(6)-C(5)	116.7(8)
C(4)-C(5)-C(6)-N(1)	52.9(8)
N(1)-P(1)-N(1B)-C(6B)	-2(8)
N(2)-P(1)-N(1B)-C(6B)	-57(2)
N(3)-P(1)-N(1B)-C(6B)	66.9(19)
Se(1)-P(1)-N(1B)-C(6B)	-172.2(17)
N(1)-P(1)-N(1B)-C(1B)	-170(12)
N(2)-P(1)-N(1B)-C(1B)	135(2)

N(3)-P(1)-N(1B)-C(1B)	-101(3)
Se(1)-P(1)-N(1B)-C(1B)	20(3)
C(6B)-N(1B)-C(1B)-C(2B)	39(3)
P(1)-N(1B)-C(1B)-C(2B)	-153(2)
N(1B)-C(1B)-C(2B)-C(3B)	34(3)
C(1B)-C(2B)-C(3B)-C(4B)	-75(2)
C(2B)-C(3B)-C(4B)-C(5B)	57(3)
C(3B)-C(4B)-C(5B)-C(6B)	-45(3)
C(1B)-N(1B)-C(6B)-C(5B)	-90(2)
P(1)-N(1B)-C(6B)-C(5B)	100(3)
C(4B)-C(5B)-C(6B)-N(1B)	72(3)
C(7)-N(2)-C(8)-C(17)	-133.8(3)
P(1)-N(2)-C(8)-C(17)	64.8(3)
C(7)-N(2)-C(8)-C(9)	45.0(3)
P(1)-N(2)-C(8)-C(9)	-116.4(2)
C(17)-C(8)-C(9)-C(10)	0.0(4)
N(2)-C(8)-C(9)-C(10)	-178.8(3)
C(8)-C(9)-C(10)-C(11)	-0.7(5)
C(9)-C(10)-C(11)-C(12)	-178.9(3)
C(9)-C(10)-C(11)-C(16)	-0.9(4)
C(10)-C(11)-C(12)-C(13)	178.1(3)
C(16)-C(11)-C(12)-C(13)	0.0(5)
C(11)-C(12)-C(13)-C(14)	-1.6(6)
C(12)-C(13)-C(14)-C(15)	0.8(6)
C(13)-C(14)-C(15)-C(16)	1.6(5)
C(12)-C(11)-C(16)-C(15)	2.3(4)
C(10)-C(11)-C(16)-C(15)	-175.8(3)
C(12)-C(11)-C(16)-C(17)	-178.7(3)
C(10)-C(11)-C(16)-C(17)	3.2(4)
C(14)-C(15)-C(16)-C(11)	-3.1(4)
C(14)-C(15)-C(16)-C(17)	177.9(3)
C(9)-C(8)-C(17)-C(16)	2.3(4)
N(2)-C(8)-C(17)-C(16)	-178.9(2)
C(9)-C(8)-C(17)-C(18)	178.8(2)
N(2)-C(8)-C(17)-C(18)	-2.4(4)
C(11)-C(16)-C(17)-C(8)	-3.9(4)

C(15)-C(16)-C(17)-C(8)	175.0(3)
C(11)-C(16)-C(17)-C(18)	179.6(2)
C(15)-C(16)-C(17)-C(18)	-1.5(4)
C(8)-C(17)-C(18)-C(27)	-54.7(3)
C(16)-C(17)-C(18)-C(27)	121.7(3)
C(8)-C(17)-C(18)-C(19)	127.5(3)
C(16)-C(17)-C(18)-C(19)	-56.1(3)
C(27)-C(18)-C(19)-C(20)	171.4(2)
C(17)-C(18)-C(19)-C(20)	-10.7(4)
C(27)-C(18)-C(19)-C(24)	-8.0(3)
C(17)-C(18)-C(19)-C(24)	169.8(2)
C(24)-C(19)-C(20)-C(21)	-2.6(4)
C(18)-C(19)-C(20)-C(21)	178.0(3)
C(19)-C(20)-C(21)-C(22)	-1.1(5)
C(20)-C(21)-C(22)-C(23)	2.8(5)
C(21)-C(22)-C(23)-C(24)	-0.6(5)
C(22)-C(23)-C(24)-C(25)	175.9(3)
C(22)-C(23)-C(24)-C(19)	-3.1(4)
C(20)-C(19)-C(24)-C(25)	-174.4(2)
C(18)-C(19)-C(24)-C(25)	5.1(3)
C(20)-C(19)-C(24)-C(23)	4.6(4)
C(18)-C(19)-C(24)-C(23)	-176.0(2)
C(23)-C(24)-C(25)-C(26)	-178.4(3)
C(19)-C(24)-C(25)-C(26)	0.6(4)
C(24)-C(25)-C(26)-C(27)	-3.1(4)
C(19)-C(18)-C(27)-C(26)	5.6(3)
C(17)-C(18)-C(27)-C(26)	-172.3(2)
C(19)-C(18)-C(27)-N(3)	-172.90(19)
C(17)-C(18)-C(27)-N(3)	9.2(3)
C(25)-C(26)-C(27)-C(18)	-0.1(4)
C(25)-C(26)-C(27)-N(3)	178.5(2)
C(28)-N(3)-C(27)-C(18)	-136.4(2)
P(1)-N(3)-C(27)-C(18)	72.6(2)
C(28)-N(3)-C(27)-C(26)	45.0(3)
P(1)-N(3)-C(27)-C(26)	-106.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z

Crystallographic Data for (±)-**5b**$^+$

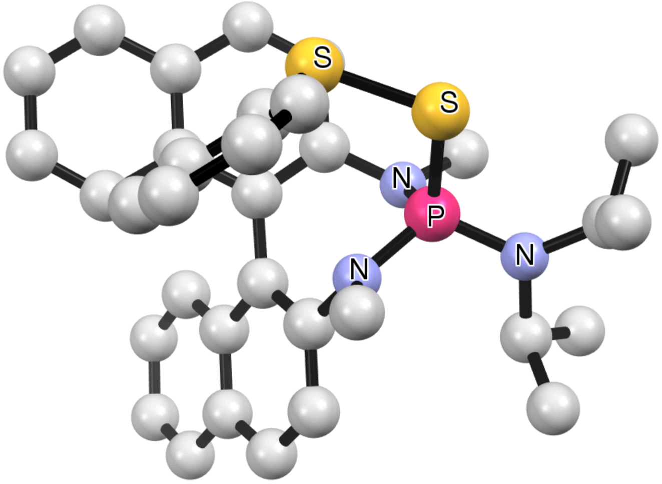


Figure S2. ORTEP image of the X-ray crystal structure of (±)-**5b**$^+$ (Hydrogens and BArF$_{24}^-$ counteranion omitted for clarity).

Crystals suitable for single crystal X-ray diffraction were obtained by dissolving (±)-**5b**$^+$ BArF$_{24}^-$ (120 mg) in CH_2Cl_2 (70 μL) followed by slow evaporation of the solvent at room temperature. The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 1006831. 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 S7. Crystal data and structure refinement for bm32zas:

Identification code	bm32zas	
Empirical formula	$C_{68}H_{53}BCl_4F_{24}N_3PS_2$	
Formula weight	1615.83	
Temperature	167(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.370(2) Å	a= 76.883(2)°.
	b = 15.135(2) Å	b= 70.416(2)°.
	c = 19.376(3) Å	g = 65.366(2)°.

Volume	3590.2(9) Å^3
Z	2
Density (calculated)	1.495 Mg/m^3
Absorption coefficient	0.351 mm^{-1}
F(000)	1636
Crystal size	0.542 x 0.41 x 0.396 mm^3
Theta range for data collection	1.12 to 26.39°.
Index ranges	-17<=h<=17, -18<=k<=18, -24<=l<=24
Reflections collected	42822
Independent reflections	14547 [R(int) = 0.0441]
Completeness to theta = 26.39°	99.0 %
Absorption correction	Integration
Max. and min. transmission	0.9985 and 0.9152
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14547 / 1164 / 1132
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0746, wR2 = 0.2062
R indices (all data)	R1 = 0.1075, wR2 = 0.2315
Largest diff. peak and hole	0.889 and -0.729 e.Å^{-3}

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for bm32zas. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	4052(1)	3634(1)	1854(1)	27(1)
S(1)	3965(1)	2429(1)	2627(1)	35(1)
S(2)	4384(1)	2638(1)	3480(1)	38(1)
N(1)	3343(3)	4628(3)	2272(2)	28(1)
N(2)	5262(3)	3662(3)	1531(2)	32(1)
N(3)	3629(3)	3572(3)	1191(2)	33(1)
C(1)	3143(4)	3229(4)	4108(3)	36(1)
C(2)	2982(5)	4107(4)	4328(3)	45(1)
C(3)	2067(5)	4563(5)	4852(3)	58(2)
C(4)	1306(5)	4142(5)	5151(3)	62(2)
C(5)	1456(5)	3276(6)	4932(3)	62(2)
C(6)	2385(5)	2807(4)	4411(3)	46(1)
C(7)	3605(4)	5494(3)	2053(2)	29(1)
C(8)	4553(4)	5470(3)	2105(2)	28(1)
C(9)	4800(4)	6343(3)	1842(2)	32(1)
C(10)	5798(4)	6364(4)	1798(3)	41(1)
C(11)	5998(5)	7205(4)	1545(3)	53(2)
C(12)	5230(5)	8062(4)	1328(4)	59(2)
C(13)	4268(5)	8069(4)	1354(3)	52(2)
C(14)	4027(4)	7214(3)	1601(3)	36(1)
C(15)	3059(4)	7192(4)	1594(3)	40(1)
C(16)	2853(4)	6358(3)	1801(3)	36(1)
C(17)	5718(4)	3715(3)	2077(3)	31(1)
C(18)	5324(4)	4568(3)	2390(2)	30(1)
C(19)	5666(4)	4569(4)	3013(3)	34(1)
C(20)	5208(4)	5372(4)	3428(3)	43(1)
C(21)	5547(5)	5339(5)	4018(3)	57(2)
C(22)	6359(5)	4507(6)	4218(4)	66(2)
C(23)	6805(5)	3715(5)	3838(3)	55(2)
C(24)	6476(4)	3713(4)	3229(3)	41(1)
C(25)	6916(4)	2886(4)	2835(3)	42(1)
C(26)	6539(4)	2874(4)	2290(3)	40(1)
C(27)	6028(4)	3083(4)	910(3)	43(1)

C(28)	2232(4)	4765(4)	2707(3)	34(1)
C(29)	3476(4)	2718(4)	1032(3)	39(1)
C(30)	2525(5)	2513(5)	1583(3)	52(1)
C(31)	4470(5)	1819(4)	895(3)	50(1)
C(32)	3430(20)	4479(10)	648(9)	35(3)
C(33)	2250(20)	4927(13)	693(11)	44(4)
C(34)	4120(20)	4270(20)	-137(9)	47(4)
C(32B)	3140(30)	4515(11)	743(13)	33(4)
C(33B)	1970(20)	4800(20)	794(16)	51(5)
C(34B)	3810(30)	4500(20)	-58(15)	44(5)
B(1)	273(4)	396(4)	2330(3)	27(1)
C(35)	787(3)	77(3)	1490(2)	27(1)
C(36)	643(3)	-639(3)	1232(2)	28(1)
C(37)	1157(4)	-897(3)	512(3)	31(1)
C(38)	1866(4)	-487(4)	32(3)	35(1)
C(39)	2051(4)	200(4)	285(3)	35(1)
C(40)	1519(4)	469(3)	993(2)	30(1)
C(41)	966(4)	-1657(4)	264(3)	37(1)
F(1)	-35(3)	-1591(3)	507(2)	68(1)
F(2)	1555(3)	-2564(2)	478(2)	63(1)
F(3)	1221(3)	-1624(3)	-474(2)	65(1)
C(42)	2813(4)	657(4)	-199(3)	51(1)
F(4)	3302(9)	392(8)	-851(4)	68(3)
F(5)	3667(6)	369(7)	104(4)	69(3)
F(6)	2499(7)	1586(5)	-164(6)	79(3)
F(4B)	3598(7)	78(6)	-673(5)	58(3)
F(5B)	3144(9)	1078(9)	114(5)	80(3)
F(6B)	2323(6)	1400(6)	-671(5)	82(3)
C(43)	-855(4)	253(3)	2778(2)	28(1)
C(44)	-1579(4)	244(3)	2447(3)	29(1)
C(45)	-2541(4)	143(3)	2863(3)	32(1)
C(46)	-2821(4)	61(4)	3619(3)	42(1)
C(47)	-2138(4)	92(4)	3962(3)	42(1)
C(48)	-1185(4)	188(4)	3551(3)	35(1)
C(49)	-3246(4)	72(4)	2473(3)	39(1)
F(7)	-4229(3)	220(3)	2898(2)	64(1)
F(8)	-2869(3)	-811(3)	2238(2)	69(1)
F(9)	-3334(3)	713(2)	1873(2)	50(1)

C(50)	-2376(6)	-35(6)	4788(3)	64(2)
F(10)	-2357(4)	674(4)	5043(2)	101(2)
F(11)	-3299(3)	-148(4)	5118(2)	83(1)
F(12)	-1631(4)	-840(4)	5036(2)	94(1)
C(51)	1197(4)	-288(3)	2750(2)	27(1)
C(52)	1204(4)	-1184(3)	3156(2)	28(1)
C(53)	2013(4)	-1791(3)	3488(2)	31(1)
C(54)	2867(4)	-1530(3)	3412(3)	33(1)
C(55)	2889(4)	-659(3)	3002(3)	32(1)
C(56)	2070(4)	-51(3)	2681(2)	30(1)
C(57)	1959(4)	-2723(3)	3928(3)	40(1)
F(13)	2434(5)	-3471(3)	3526(2)	75(2)
F(14)	987(3)	-2683(4)	4263(3)	77(2)
F(15)	2465(4)	-3006(3)	4450(3)	70(2)
F(13B)	2877(11)	-3463(14)	3854(15)	79(7)
F(14B)	1341(17)	-3043(16)	3760(13)	60(6)
F(15B)	1580(20)	-2640(20)	4639(6)	86(7)
C(58)	3780(4)	-335(4)	2912(3)	42(1)
F(16)	4595(3)	-1034(3)	3114(3)	85(1)
F(17)	3459(3)	404(3)	3320(2)	68(1)
F(18)	4148(3)	12(3)	2227(2)	52(1)
C(59)	0(3)	1573(3)	2313(2)	28(1)
C(60)	55(4)	1974(4)	2871(3)	32(1)
C(61)	-231(4)	2976(4)	2864(3)	38(1)
C(62)	-589(4)	3622(4)	2291(3)	38(1)
C(63)	-659(4)	3242(3)	1731(3)	35(1)
C(64)	-379(4)	2246(3)	1747(3)	30(1)
C(65)	-107(4)	3352(4)	3459(3)	50(1)
F(19)	-631(6)	3132(6)	4111(3)	70(2)
F(20)	908(5)	3052(7)	3447(4)	84(2)
F(21)	-394(9)	4327(4)	3375(5)	102(3)
F(19B)	-1015(7)	3959(10)	3849(8)	87(4)
F(20B)	213(13)	2657(7)	3998(6)	91(4)
F(21B)	521(10)	3821(10)	3248(6)	71(3)
C(66)	-1032(4)	3909(3)	1101(3)	47(1)
F(22)	-1034(11)	4790(5)	1022(6)	83(3)
F(23)	-463(8)	3568(6)	446(3)	79(3)
F(24)	-2001(6)	4013(8)	1111(5)	81(3)

F(22B)	-1718(9)	4786(6)	1300(5)	80(3)
F(23B)	-243(7)	4092(10)	597(6)	96(4)
F(24B)	-1502(10)	3596(7)	798(6)	74(3)
C(68)	8915(15)	6921(15)	2729(13)	120(5)
Cl(1)	9762(10)	7293(9)	2878(7)	114(3)
Cl(2)	9287(14)	6366(10)	1988(8)	173(4)
C(68B)	9010(20)	7203(18)	2220(20)	121(6)
Cl(1B)	9816(15)	7183(15)	2667(12)	135(5)
Cl(2B)	9448(12)	6271(8)	1736(9)	130(4)
C(69)	5459(9)	8361(11)	4576(7)	81(4)
Cl(3)	4702(3)	7627(3)	5032(2)	60(1)
Cl(4)	6589(4)	7646(5)	3941(3)	115(3)
C(69B)	5851(17)	7905(16)	4289(10)	103(5)
Cl(3B)	4816(15)	7567(15)	4917(10)	282(8)
Cl(4B)	6490(8)	7133(7)	3561(6)	168(4)

Table S9. Bond lengths [Å] and angles [°] for bm32zas.

P(1)-N(3)	1.629(4)
P(1)-N(1)	1.638(4)
P(1)-N(2)	1.655(4)
P(1)-S(1)	2.0993(16)
S(1)-S(2)	2.0625(17)
S(2)-C(1)	1.781(5)
N(1)-C(7)	1.446(6)
N(1)-C(28)	1.485(6)
N(2)-C(17)	1.449(6)
N(2)-C(27)	1.487(6)
N(3)-C(29)	1.508(6)
N(3)-C(32)	1.515(9)
N(3)-C(32B)	1.516(10)
C(1)-C(6)	1.385(7)
C(1)-C(2)	1.392(7)
C(2)-C(3)	1.380(8)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.387(10)
C(3)-H(3A)	0.9500

C(4)-C(5)	1.380(10)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.392(9)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500
C(7)-C(8)	1.385(6)
C(7)-C(16)	1.415(6)
C(8)-C(9)	1.448(6)
C(8)-C(18)	1.484(6)
C(9)-C(10)	1.422(7)
C(9)-C(14)	1.427(7)
C(10)-C(11)	1.367(7)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.396(9)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.362(9)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.415(7)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.410(7)
C(15)-C(16)	1.358(7)
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500
C(17)-C(18)	1.368(7)
C(17)-C(26)	1.421(7)
C(18)-C(19)	1.447(6)
C(19)-C(20)	1.406(7)
C(19)-C(24)	1.426(7)
C(20)-C(21)	1.370(8)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.398(10)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.354(10)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.412(8)
C(23)-H(23)	0.9500
C(24)-C(25)	1.414(8)
C(25)-C(26)	1.345(8)

C(25)-H(25A)	0.9500
C(26)-H(26A)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(31)	1.501(8)
C(29)-C(30)	1.525(8)
C(29)-H(29A)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(34)	1.530(12)
C(32)-C(33)	1.533(13)
C(32)-H(32A)	1.0000
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(32B)-C(33B)	1.529(14)
C(32B)-C(34B)	1.529(13)
C(32B)-H(32B)	1.0000
C(33B)-H(33D)	0.9800
C(33B)-H(33E)	0.9800
C(33B)-H(33F)	0.9800
C(34B)-H(34D)	0.9800
C(34B)-H(34E)	0.9800
C(34B)-H(34F)	0.9800
B(1)-C(35)	1.637(7)
B(1)-C(43)	1.641(7)
B(1)-C(51)	1.642(6)

B(1)-C(59)	1.652(7)
C(35)-C(40)	1.403(6)
C(35)-C(36)	1.403(6)
C(36)-C(37)	1.400(6)
C(36)-H(36A)	0.9500
C(37)-C(38)	1.384(7)
C(37)-C(41)	1.494(6)
C(38)-C(39)	1.393(7)
C(38)-H(38A)	0.9500
C(39)-C(40)	1.387(7)
C(39)-C(42)	1.485(7)
C(40)-H(40A)	0.9500
C(41)-F(1)	1.322(6)
C(41)-F(2)	1.336(6)
C(41)-F(3)	1.346(6)
C(42)-F(5B)	1.275(7)
C(42)-F(4)	1.284(7)
C(42)-F(6)	1.297(7)
C(42)-F(4B)	1.315(7)
C(42)-F(6B)	1.379(7)
C(42)-F(5)	1.400(7)
C(43)-C(44)	1.399(6)
C(43)-C(48)	1.405(6)
C(44)-C(45)	1.400(6)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.374(7)
C(45)-C(49)	1.500(7)
C(46)-C(47)	1.377(8)
C(46)-H(46A)	0.9500
C(47)-C(48)	1.384(7)
C(47)-C(50)	1.504(8)
C(48)-H(48A)	0.9500
C(49)-F(7)	1.328(6)
C(49)-F(9)	1.338(6)
C(49)-F(8)	1.340(6)
C(50)-F(10)	1.293(8)
C(50)-F(11)	1.331(7)
C(50)-F(12)	1.361(9)

C(51)-C(56)	1.401(6)
C(51)-C(52)	1.403(6)
C(52)-C(53)	1.397(6)
C(52)-H(52A)	0.9500
C(53)-C(54)	1.394(7)
C(53)-C(57)	1.491(6)
C(54)-C(55)	1.383(7)
C(54)-H(54A)	0.9500
C(55)-C(56)	1.395(6)
C(55)-C(58)	1.497(7)
C(56)-H(56A)	0.9500
C(57)-F(14)	1.309(5)
C(57)-F(13B)	1.315(9)
C(57)-F(15B)	1.316(9)
C(57)-F(14B)	1.324(9)
C(57)-F(13)	1.324(5)
C(57)-F(15)	1.332(5)
C(58)-F(16)	1.315(6)
C(58)-F(18)	1.328(6)
C(58)-F(17)	1.349(7)
C(59)-C(60)	1.392(6)
C(59)-C(64)	1.402(6)
C(60)-C(61)	1.394(7)
C(60)-H(60A)	0.9500
C(61)-C(62)	1.388(7)
C(61)-C(65)	1.485(7)
C(62)-C(63)	1.386(7)
C(62)-H(62A)	0.9500
C(63)-C(64)	1.384(7)
C(63)-C(66)	1.492(7)
C(64)-H(64A)	0.9500
C(65)-F(21B)	1.282(7)
C(65)-F(19)	1.285(6)
C(65)-F(20)	1.328(6)
C(65)-F(19B)	1.330(8)
C(65)-F(21)	1.342(6)
C(65)-F(20B)	1.353(8)
C(66)-F(24B)	1.297(7)

C(66)-F(22)	1.306(6)
C(66)-F(23B)	1.308(7)
C(66)-F(24)	1.328(7)
C(66)-F(22B)	1.330(7)
C(66)-F(23)	1.339(7)
C(68)-Cl(2)	1.646(11)
C(68)-Cl(1)	1.662(11)
C(68)-H(68A)	0.9900
C(68)-H(68B)	0.9900
C(68B)-Cl(2B)	1.652(12)
C(68B)-Cl(1B)	1.654(12)
C(68B)-H(68C)	0.9900
C(68B)-H(68D)	0.9900
C(69)-Cl(3)	1.765(11)
C(69)-Cl(4)	1.767(12)
C(69)-H(69A)	0.9900
C(69)-H(69B)	0.9900
C(69B)-Cl(3B)	1.759(12)
C(69B)-Cl(4B)	1.785(13)
C(69B)-H(69C)	0.9900
C(69B)-H(69D)	0.9900

N(3)-P(1)-N(1)	114.1(2)
N(3)-P(1)-N(2)	110.8(2)
N(1)-P(1)-N(2)	104.11(19)
N(3)-P(1)-S(1)	106.36(15)
N(1)-P(1)-S(1)	108.19(14)
N(2)-P(1)-S(1)	113.44(15)
S(2)-S(1)-P(1)	103.49(7)
C(1)-S(2)-S(1)	104.07(16)
C(7)-N(1)-C(28)	116.6(4)
C(7)-N(1)-P(1)	122.4(3)
C(28)-N(1)-P(1)	117.9(3)
C(17)-N(2)-C(27)	115.6(4)
C(17)-N(2)-P(1)	115.4(3)
C(27)-N(2)-P(1)	119.0(3)
C(29)-N(3)-C(32)	117.3(9)
C(29)-N(3)-C(32B)	112.7(10)

C(29)-N(3)-P(1)	128.4(3)
C(32)-N(3)-P(1)	114.2(9)
C(32B)-N(3)-P(1)	118.0(9)
C(6)-C(1)-C(2)	120.4(5)
C(6)-C(1)-S(2)	121.8(4)
C(2)-C(1)-S(2)	117.6(4)
C(3)-C(2)-C(1)	120.1(6)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	119.4(6)
C(2)-C(3)-H(3A)	120.3
C(4)-C(3)-H(3A)	120.3
C(5)-C(4)-C(3)	120.8(6)
C(5)-C(4)-H(4A)	119.6
C(3)-C(4)-H(4A)	119.6
C(4)-C(5)-C(6)	119.9(6)
C(4)-C(5)-H(5A)	120.0
C(6)-C(5)-H(5A)	120.0
C(1)-C(6)-C(5)	119.3(6)
C(1)-C(6)-H(6A)	120.3
C(5)-C(6)-H(6A)	120.3
C(8)-C(7)-C(16)	121.9(4)
C(8)-C(7)-N(1)	120.3(4)
C(16)-C(7)-N(1)	117.7(4)
C(7)-C(8)-C(9)	118.0(4)
C(7)-C(8)-C(18)	121.6(4)
C(9)-C(8)-C(18)	120.3(4)
C(10)-C(9)-C(14)	118.2(4)
C(10)-C(9)-C(8)	122.5(4)
C(14)-C(9)-C(8)	119.3(4)
C(11)-C(10)-C(9)	120.5(5)
C(11)-C(10)-H(10A)	119.7
C(9)-C(10)-H(10A)	119.7
C(10)-C(11)-C(12)	121.0(6)
C(10)-C(11)-H(11A)	119.5
C(12)-C(11)-H(11A)	119.5
C(13)-C(12)-C(11)	120.2(5)
C(13)-C(12)-H(12A)	119.9

C(11)-C(12)-H(12A)	119.9
C(12)-C(13)-C(14)	120.9(6)
C(12)-C(13)-H(13A)	119.5
C(14)-C(13)-H(13A)	119.5
C(15)-C(14)-C(13)	121.8(5)
C(15)-C(14)-C(9)	119.1(4)
C(13)-C(14)-C(9)	119.1(5)
C(16)-C(15)-C(14)	121.5(4)
C(16)-C(15)-H(15A)	119.2
C(14)-C(15)-H(15A)	119.2
C(15)-C(16)-C(7)	119.9(5)
C(15)-C(16)-H(16A)	120.1
C(7)-C(16)-H(16A)	120.1
C(18)-C(17)-C(26)	121.6(4)
C(18)-C(17)-N(2)	119.0(4)
C(26)-C(17)-N(2)	119.4(4)
C(17)-C(18)-C(19)	118.5(4)
C(17)-C(18)-C(8)	120.9(4)
C(19)-C(18)-C(8)	120.6(4)
C(20)-C(19)-C(24)	118.5(4)
C(20)-C(19)-C(18)	122.6(4)
C(24)-C(19)-C(18)	118.8(5)
C(21)-C(20)-C(19)	120.7(5)
C(21)-C(20)-H(20A)	119.6
C(19)-C(20)-H(20A)	119.6
C(20)-C(21)-C(22)	120.6(6)
C(20)-C(21)-H(21A)	119.7
C(22)-C(21)-H(21A)	119.7
C(23)-C(22)-C(21)	120.2(5)
C(23)-C(22)-H(22A)	119.9
C(21)-C(22)-H(22A)	119.9
C(22)-C(23)-C(24)	121.2(6)
C(22)-C(23)-H(23)	119.4
C(24)-C(23)-H(23)	119.4
C(23)-C(24)-C(25)	122.0(5)
C(23)-C(24)-C(19)	118.7(5)
C(25)-C(24)-C(19)	119.3(4)
C(26)-C(25)-C(24)	121.1(5)

C(26)-C(25)-H(25A)	119.5
C(24)-C(25)-H(25A)	119.5
C(25)-C(26)-C(17)	120.3(5)
C(25)-C(26)-H(26A)	119.9
C(17)-C(26)-H(26A)	119.9
N(2)-C(27)-H(27A)	109.5
N(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(1)-C(28)-H(28A)	109.5
N(1)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
N(1)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(31)-C(29)-N(3)	114.2(4)
C(31)-C(29)-C(30)	113.2(5)
N(3)-C(29)-C(30)	113.2(4)
C(31)-C(29)-H(29A)	105.0
N(3)-C(29)-H(29A)	105.0
C(30)-C(29)-H(29A)	105.0
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
N(3)-C(32)-C(34)	112.7(12)
N(3)-C(32)-C(33)	108.0(12)
C(34)-C(32)-C(33)	112.0(9)

N(3)-C(32)-H(32A)	108.0
C(34)-C(32)-H(32A)	108.0
C(33)-C(32)-H(32A)	108.0
N(3)-C(32B)-C(33B)	115.5(17)
N(3)-C(32B)-C(34B)	110.1(15)
C(33B)-C(32B)-C(34B)	111.4(11)
N(3)-C(32B)-H(32B)	106.4
C(33B)-C(32B)-H(32B)	106.4
C(34B)-C(32B)-H(32B)	106.4
C(32B)-C(33B)-H(33D)	109.5
C(32B)-C(33B)-H(33E)	109.5
H(33D)-C(33B)-H(33E)	109.5
C(32B)-C(33B)-H(33F)	109.5
H(33D)-C(33B)-H(33F)	109.5
H(33E)-C(33B)-H(33F)	109.5
C(32B)-C(34B)-H(34D)	109.5
C(32B)-C(34B)-H(34E)	109.5
H(34D)-C(34B)-H(34E)	109.5
C(32B)-C(34B)-H(34F)	109.5
H(34D)-C(34B)-H(34F)	109.5
H(34E)-C(34B)-H(34F)	109.5
C(35)-B(1)-C(43)	115.6(4)
C(35)-B(1)-C(51)	104.2(4)
C(43)-B(1)-C(51)	110.4(4)
C(35)-B(1)-C(59)	109.8(4)
C(43)-B(1)-C(59)	104.8(4)
C(51)-B(1)-C(59)	112.2(3)
C(40)-C(35)-C(36)	115.4(4)
C(40)-C(35)-B(1)	118.7(4)
C(36)-C(35)-B(1)	125.6(4)
C(37)-C(36)-C(35)	121.5(4)
C(37)-C(36)-H(36A)	119.2
C(35)-C(36)-H(36A)	119.2
C(38)-C(37)-C(36)	121.5(4)
C(38)-C(37)-C(41)	119.3(4)
C(36)-C(37)-C(41)	119.2(4)
C(37)-C(38)-C(39)	118.0(4)
C(37)-C(38)-H(38A)	121.0

C(39)-C(38)-H(38A)	121.0
C(40)-C(39)-C(38)	120.2(4)
C(40)-C(39)-C(42)	119.2(4)
C(38)-C(39)-C(42)	120.6(4)
C(39)-C(40)-C(35)	123.3(4)
C(39)-C(40)-H(40A)	118.3
C(35)-C(40)-H(40A)	118.3
F(1)-C(41)-F(2)	106.6(4)
F(1)-C(41)-F(3)	105.9(4)
F(2)-C(41)-F(3)	104.4(4)
F(1)-C(41)-C(37)	113.6(4)
F(2)-C(41)-C(37)	112.6(4)
F(3)-C(41)-C(37)	113.0(4)
F(5B)-C(42)-F(4)	122.3(8)
F(5B)-C(42)-F(6)	52.5(6)
F(4)-C(42)-F(6)	114.1(7)
F(5B)-C(42)-F(4B)	111.8(7)
F(6)-C(42)-F(4B)	131.0(7)
F(5B)-C(42)-F(6B)	103.3(7)
F(4)-C(42)-F(6B)	73.6(7)
F(6)-C(42)-F(6B)	53.6(6)
F(4B)-C(42)-F(6B)	100.6(6)
F(4)-C(42)-F(5)	101.1(7)
F(6)-C(42)-F(5)	96.5(6)
F(4B)-C(42)-F(5)	77.7(6)
F(6B)-C(42)-F(5)	139.2(6)
F(5B)-C(42)-C(39)	116.8(6)
F(4)-C(42)-C(39)	118.2(6)
F(6)-C(42)-C(39)	114.7(5)
F(4B)-C(42)-C(39)	113.2(6)
F(6B)-C(42)-C(39)	109.3(5)
F(5)-C(42)-C(39)	108.6(5)
C(44)-C(43)-C(48)	115.0(4)
C(44)-C(43)-B(1)	124.8(4)
C(48)-C(43)-B(1)	120.1(4)
C(43)-C(44)-C(45)	121.9(4)
C(43)-C(44)-H(44A)	119.0
C(45)-C(44)-H(44A)	119.0

C(46)-C(45)-C(44)	121.0(4)
C(46)-C(45)-C(49)	119.9(4)
C(44)-C(45)-C(49)	119.0(4)
C(45)-C(46)-C(47)	118.5(5)
C(45)-C(46)-H(46A)	120.7
C(47)-C(46)-H(46A)	120.7
C(46)-C(47)-C(48)	120.4(5)
C(46)-C(47)-C(50)	121.2(5)
C(48)-C(47)-C(50)	118.3(5)
C(47)-C(48)-C(43)	123.0(4)
C(47)-C(48)-H(48A)	118.5
C(43)-C(48)-H(48A)	118.5
F(7)-C(49)-F(9)	106.6(4)
F(7)-C(49)-F(8)	106.6(4)
F(9)-C(49)-F(8)	105.7(4)
F(7)-C(49)-C(45)	112.8(4)
F(9)-C(49)-C(45)	113.1(4)
F(8)-C(49)-C(45)	111.4(4)
F(10)-C(50)-F(11)	109.6(6)
F(10)-C(50)-F(12)	103.6(6)
F(11)-C(50)-F(12)	105.6(6)
F(10)-C(50)-C(47)	112.6(6)
F(11)-C(50)-C(47)	112.4(6)
F(12)-C(50)-C(47)	112.4(6)
C(56)-C(51)-C(52)	115.7(4)
C(56)-C(51)-B(1)	122.1(4)
C(52)-C(51)-B(1)	122.0(4)
C(53)-C(52)-C(51)	122.4(4)
C(53)-C(52)-H(52A)	118.8
C(51)-C(52)-H(52A)	118.8
C(54)-C(53)-C(52)	120.4(4)
C(54)-C(53)-C(57)	119.9(4)
C(52)-C(53)-C(57)	119.7(4)
C(55)-C(54)-C(53)	118.3(4)
C(55)-C(54)-H(54A)	120.8
C(53)-C(54)-H(54A)	120.8
C(54)-C(55)-C(56)	120.9(4)
C(54)-C(55)-C(58)	120.5(4)

C(56)-C(55)-C(58)	118.6(4)
C(55)-C(56)-C(51)	122.3(4)
C(55)-C(56)-H(56A)	118.8
C(51)-C(56)-H(56A)	118.8
F(14)-C(57)-F(13B)	131.0(12)
F(14)-C(57)-F(15B)	60.2(12)
F(13B)-C(57)-F(15B)	105.3(12)
F(14)-C(57)-F(14B)	48.8(10)
F(13B)-C(57)-F(14B)	104.6(11)
F(15B)-C(57)-F(14B)	105.5(12)
F(14)-C(57)-F(13)	107.3(5)
F(13B)-C(57)-F(13)	46.6(12)
F(15B)-C(57)-F(13)	134.1(12)
F(14B)-C(57)-F(13)	62.8(11)
F(14)-C(57)-F(15)	106.0(4)
F(13B)-C(57)-F(15)	59.5(12)
F(15B)-C(57)-F(15)	50.2(12)
F(14B)-C(57)-F(15)	133.7(10)
F(13)-C(57)-F(15)	103.6(4)
F(14)-C(57)-C(53)	113.7(4)
F(13B)-C(57)-C(53)	114.9(12)
F(15B)-C(57)-C(53)	112.5(12)
F(14B)-C(57)-C(53)	113.2(10)
F(13)-C(57)-C(53)	112.6(4)
F(15)-C(57)-C(53)	112.8(4)
F(16)-C(58)-F(18)	107.3(5)
F(16)-C(58)-F(17)	106.5(4)
F(18)-C(58)-F(17)	104.7(4)
F(16)-C(58)-C(55)	113.1(4)
F(18)-C(58)-C(55)	113.3(4)
F(17)-C(58)-C(55)	111.4(5)
C(60)-C(59)-C(64)	115.6(4)
C(60)-C(59)-B(1)	123.3(4)
C(64)-C(59)-B(1)	121.0(4)
C(59)-C(60)-C(61)	122.4(4)
C(59)-C(60)-H(60A)	118.8
C(61)-C(60)-H(60A)	118.8
C(62)-C(61)-C(60)	120.6(4)

C(62)-C(61)-C(65)	119.6(4)
C(60)-C(61)-C(65)	119.7(5)
C(63)-C(62)-C(61)	118.1(4)
C(63)-C(62)-H(62A)	121.0
C(61)-C(62)-H(62A)	121.0
C(64)-C(63)-C(62)	120.7(4)
C(64)-C(63)-C(66)	119.4(4)
C(62)-C(63)-C(66)	119.9(4)
C(63)-C(64)-C(59)	122.6(4)
C(63)-C(64)-H(64A)	118.7
C(59)-C(64)-H(64A)	118.7
F(21B)-C(65)-F(19)	130.1(7)
F(21B)-C(65)-F(20)	49.9(6)
F(19)-C(65)-F(20)	108.5(6)
F(21B)-C(65)-F(19B)	104.6(8)
F(19)-C(65)-F(19B)	54.8(7)
F(20)-C(65)-F(19B)	134.3(7)
F(21B)-C(65)-F(21)	53.7(7)
F(19)-C(65)-F(21)	106.5(6)
F(20)-C(65)-F(21)	101.6(6)
F(19B)-C(65)-F(21)	56.2(7)
F(21B)-C(65)-F(20B)	106.7(8)
F(19)-C(65)-F(20B)	49.0(6)
F(20)-C(65)-F(20B)	63.4(7)
F(19B)-C(65)-F(20B)	100.6(8)
F(21)-C(65)-F(20B)	132.6(7)
F(21B)-C(65)-C(61)	115.5(6)
F(19)-C(65)-C(61)	114.4(5)
F(20)-C(65)-C(61)	111.6(5)
F(19B)-C(65)-C(61)	113.9(6)
F(21)-C(65)-C(61)	113.3(5)
F(20B)-C(65)-C(61)	114.0(6)
F(24B)-C(66)-F(22)	127.9(7)
F(24B)-C(66)-F(23B)	109.3(8)
F(22)-C(66)-F(23B)	62.7(7)
F(22)-C(66)-F(24)	106.4(7)
F(23B)-C(66)-F(24)	134.2(7)
F(24B)-C(66)-F(22B)	106.1(7)

F(23B)-C(66)-F(22B)	103.8(7)
F(24)-C(66)-F(22B)	70.6(7)
F(24B)-C(66)-F(23)	64.4(6)
F(22)-C(66)-F(23)	104.8(7)
F(23B)-C(66)-F(23)	48.6(6)
F(24)-C(66)-F(23)	101.1(7)
F(22B)-C(66)-F(23)	133.1(6)
F(24B)-C(66)-C(63)	114.5(5)
F(22)-C(66)-C(63)	116.1(5)
F(23B)-C(66)-C(63)	110.6(6)
F(24)-C(66)-C(63)	113.5(5)
F(22B)-C(66)-C(63)	111.9(5)
F(23)-C(66)-C(63)	113.4(5)
Cl(2)-C(68)-Cl(1)	118.6(12)
Cl(2)-C(68)-H(68A)	107.7
Cl(1)-C(68)-H(68A)	107.7
Cl(2)-C(68)-H(68B)	107.7
Cl(1)-C(68)-H(68B)	107.7
H(68A)-C(68)-H(68B)	107.1
Cl(2B)-C(68B)-Cl(1B)	115.5(15)
Cl(2B)-C(68B)-H(68C)	108.4
Cl(1B)-C(68B)-H(68C)	108.4
Cl(2B)-C(68B)-H(68D)	108.4
Cl(1B)-C(68B)-H(68D)	108.4
H(68C)-C(68B)-H(68D)	107.5
Cl(3)-C(69)-Cl(4)	106.6(8)
Cl(3)-C(69)-H(69A)	110.4
Cl(4)-C(69)-H(69A)	110.4
Cl(3)-C(69)-H(69B)	110.4
Cl(4)-C(69)-H(69B)	110.4
H(69A)-C(69)-H(69B)	108.6
Cl(3B)-C(69B)-Cl(4B)	109.3(12)
Cl(3B)-C(69B)-H(69C)	109.8
Cl(4B)-C(69B)-H(69C)	109.8
Cl(3B)-C(69B)-H(69D)	109.8
Cl(4B)-C(69B)-H(69D)	109.8
H(69C)-C(69B)-H(69D)	108.3

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$x 10^3) for bm32zas. 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}
P(1)	29(1)	28(1)	25(1)	-2(1)	-8(1)	-11(1)
S(1)	44(1)	31(1)	30(1)	0(1)	-11(1)	-16(1)
S(2)	36(1)	46(1)	31(1)	0(1)	-12(1)	-14(1)
N(1)	26(2)	30(2)	28(2)	-4(2)	-7(2)	-10(2)
N(2)	27(2)	29(2)	36(2)	-8(2)	-5(2)	-8(2)
N(3)	43(2)	31(2)	30(2)	-2(2)	-13(2)	-16(2)
C(1)	41(3)	41(3)	27(2)	1(2)	-13(2)	-17(2)
C(2)	55(3)	42(3)	40(3)	-3(2)	-15(3)	-20(3)
C(3)	66(4)	54(4)	52(4)	-16(3)	-18(3)	-12(3)
C(4)	52(4)	77(5)	45(3)	-23(3)	-10(3)	-7(3)
C(5)	45(4)	100(5)	48(4)	-9(3)	-5(3)	-40(4)
C(6)	49(3)	60(3)	39(3)	-5(3)	-11(3)	-29(3)
C(7)	30(2)	31(2)	26(2)	-4(2)	-7(2)	-12(2)
C(8)	30(2)	30(2)	24(2)	-4(2)	-6(2)	-10(2)
C(9)	37(3)	34(2)	28(2)	-6(2)	-4(2)	-18(2)
C(10)	45(3)	45(3)	37(3)	-7(2)	-5(2)	-25(2)
C(11)	52(4)	57(4)	55(4)	-12(3)	4(3)	-37(3)
C(12)	68(4)	41(3)	63(4)	-6(3)	7(3)	-34(3)
C(13)	60(4)	31(3)	51(3)	-3(2)	1(3)	-16(3)
C(14)	40(3)	31(2)	31(2)	-2(2)	-3(2)	-12(2)
C(15)	42(3)	29(2)	40(3)	1(2)	-14(2)	-5(2)
C(16)	31(3)	36(3)	38(3)	-3(2)	-14(2)	-8(2)
C(17)	25(2)	33(2)	33(2)	-1(2)	-6(2)	-12(2)
C(18)	24(2)	35(2)	32(2)	1(2)	-8(2)	-15(2)
C(19)	30(2)	46(3)	31(2)	0(2)	-8(2)	-20(2)
C(20)	42(3)	57(3)	36(3)	-9(2)	-12(2)	-20(3)
C(21)	58(4)	75(4)	44(3)	-18(3)	-16(3)	-23(3)
C(22)	57(4)	108(6)	47(4)	-8(4)	-26(3)	-34(4)
C(23)	39(3)	77(4)	49(3)	8(3)	-22(3)	-22(3)
C(24)	29(3)	56(3)	40(3)	6(2)	-16(2)	-19(2)
C(25)	25(2)	44(3)	49(3)	4(2)	-11(2)	-7(2)

C(26)	32(3)	33(3)	47(3)	-4(2)	-7(2)	-8(2)
C(27)	36(3)	47(3)	41(3)	-14(2)	3(2)	-15(2)
C(28)	23(2)	37(3)	38(3)	-4(2)	-5(2)	-9(2)
C(29)	50(3)	39(3)	38(3)	-8(2)	-13(2)	-21(2)
C(30)	55(4)	64(4)	55(3)	-1(3)	-19(3)	-38(3)
C(31)	66(4)	40(3)	46(3)	-11(2)	-13(3)	-21(3)
C(32)	43(7)	35(4)	29(5)	4(4)	-11(5)	-18(4)
C(33)	44(7)	48(6)	36(6)	5(5)	-15(6)	-15(5)
C(34)	54(8)	50(8)	29(5)	-4(5)	-9(5)	-15(7)
C(32B)	44(8)	35(5)	30(6)	-3(4)	-16(6)	-19(5)
C(33B)	45(9)	56(8)	47(8)	6(7)	-18(7)	-16(7)
C(34B)	45(9)	40(8)	39(8)	8(6)	-12(6)	-13(7)
B(1)	26(3)	31(3)	28(3)	-1(2)	-9(2)	-12(2)
C(35)	24(2)	27(2)	30(2)	-2(2)	-12(2)	-6(2)
C(36)	26(2)	27(2)	30(2)	2(2)	-13(2)	-8(2)
C(37)	28(2)	30(2)	36(3)	-6(2)	-14(2)	-6(2)
C(38)	38(3)	40(3)	29(2)	-8(2)	-9(2)	-14(2)
C(39)	35(3)	40(3)	30(2)	-3(2)	-8(2)	-15(2)
C(40)	28(2)	36(2)	30(2)	-6(2)	-8(2)	-15(2)
C(41)	38(3)	36(3)	42(3)	-9(2)	-16(2)	-12(2)
F(1)	50(2)	75(2)	97(3)	-39(2)	-13(2)	-32(2)
F(2)	84(2)	35(2)	86(2)	-7(2)	-50(2)	-15(2)
F(3)	97(3)	70(2)	48(2)	-14(2)	-27(2)	-42(2)
C(42)	58(4)	65(4)	36(3)	-17(3)	5(3)	-37(3)
F(4)	81(5)	86(5)	49(4)	-13(4)	-4(4)	-49(4)
F(5)	59(4)	82(5)	79(4)	6(4)	-15(3)	-49(4)
F(6)	72(5)	49(4)	93(5)	2(3)	15(4)	-35(3)
F(4B)	40(4)	54(4)	59(4)	-1(3)	8(3)	-17(3)
F(5B)	95(5)	101(6)	72(5)	-25(4)	-7(4)	-67(4)
F(6B)	72(5)	79(5)	84(5)	28(4)	-10(4)	-44(4)
C(43)	28(2)	30(2)	29(2)	-2(2)	-9(2)	-12(2)
C(44)	28(2)	30(2)	29(2)	-3(2)	-8(2)	-10(2)
C(45)	28(2)	32(2)	38(3)	-4(2)	-8(2)	-11(2)
C(46)	34(3)	50(3)	44(3)	-5(2)	-2(2)	-22(2)
C(47)	38(3)	53(3)	34(3)	-4(2)	-3(2)	-22(3)
C(48)	33(3)	44(3)	31(2)	-4(2)	-8(2)	-17(2)
C(49)	33(3)	36(3)	51(3)	-7(2)	-13(2)	-14(2)
F(7)	39(2)	92(3)	71(2)	-3(2)	-16(2)	-36(2)

F(8)	76(2)	48(2)	103(3)	-21(2)	-53(2)	-13(2)
F(9)	50(2)	57(2)	55(2)	4(2)	-29(2)	-25(2)
C(50)	63(4)	97(5)	39(3)	-12(3)	4(3)	-46(4)
F(10)	128(4)	133(4)	57(2)	-34(2)	-5(2)	-67(3)
F(11)	71(3)	128(3)	47(2)	0(2)	3(2)	-53(2)
F(12)	89(3)	125(3)	56(2)	21(2)	-28(2)	-38(3)
C(51)	28(2)	31(2)	24(2)	-2(2)	-8(2)	-12(2)
C(52)	28(2)	34(2)	26(2)	-4(2)	-7(2)	-14(2)
C(53)	34(3)	31(2)	28(2)	-1(2)	-11(2)	-11(2)
C(54)	31(2)	36(3)	31(2)	2(2)	-13(2)	-9(2)
C(55)	29(2)	40(3)	31(2)	2(2)	-13(2)	-16(2)
C(56)	33(2)	31(2)	29(2)	5(2)	-13(2)	-14(2)
C(57)	40(3)	38(3)	37(3)	4(2)	-14(2)	-13(2)
F(13)	116(4)	42(2)	58(3)	-5(2)	-7(3)	-34(2)
F(14)	43(2)	66(3)	90(3)	39(2)	-7(2)	-24(2)
F(15)	98(3)	65(3)	67(3)	33(2)	-55(3)	-45(2)
F(13B)	78(8)	71(8)	81(8)	2(6)	-17(6)	-29(6)
F(14B)	66(8)	53(7)	66(8)	5(5)	-21(5)	-32(5)
F(15B)	91(9)	79(8)	80(8)	2(6)	-16(6)	-34(6)
C(58)	41(3)	49(3)	46(3)	10(2)	-24(3)	-23(3)
F(16)	57(2)	83(3)	130(3)	43(2)	-62(2)	-39(2)
F(17)	77(2)	95(3)	61(2)	-16(2)	-15(2)	-60(2)
F(18)	47(2)	70(2)	50(2)	3(2)	-11(2)	-38(2)
C(59)	25(2)	35(2)	27(2)	-2(2)	-8(2)	-13(2)
C(60)	27(2)	42(3)	30(2)	-7(2)	-7(2)	-14(2)
C(61)	37(3)	44(3)	36(3)	-16(2)	-5(2)	-17(2)
C(62)	36(3)	35(3)	47(3)	-10(2)	-8(2)	-14(2)
C(63)	32(3)	32(2)	40(3)	-3(2)	-11(2)	-11(2)
C(64)	31(2)	32(2)	31(2)	-4(2)	-11(2)	-12(2)
C(65)	56(4)	51(3)	49(3)	-20(3)	-12(3)	-20(3)
F(19)	82(4)	109(5)	39(3)	-22(3)	-4(3)	-58(4)
F(20)	69(4)	125(5)	87(4)	-54(4)	-28(3)	-36(3)
F(21)	158(6)	75(4)	95(4)	-30(3)	-51(4)	-40(4)
F(19B)	82(6)	106(6)	90(6)	-56(5)	-20(5)	-30(5)
F(20B)	121(7)	89(6)	80(6)	-23(4)	-44(5)	-34(5)
F(21B)	79(6)	92(6)	76(5)	-22(4)	-14(4)	-61(5)
C(66)	49(3)	32(3)	56(4)	3(2)	-19(3)	-12(2)
F(22)	120(6)	54(4)	87(5)	17(3)	-46(4)	-40(4)

F(23)	92(5)	65(4)	42(3)	8(3)	-21(3)	3(3)
F(24)	57(4)	99(5)	73(5)	26(4)	-33(3)	-21(4)
F(22B)	80(5)	56(4)	68(5)	0(3)	-26(4)	9(4)
F(23B)	79(5)	108(6)	75(5)	40(4)	-21(4)	-35(4)
F(24B)	101(6)	67(5)	77(5)	4(4)	-56(4)	-34(4)
C(68)	123(8)	106(8)	121(8)	-15(7)	-27(7)	-35(6)
Cl(1)	124(5)	96(4)	139(6)	-30(4)	-24(4)	-57(4)
Cl(2)	221(8)	146(6)	166(7)	-53(5)	-56(6)	-60(5)
C(68B)	129(8)	104(8)	126(9)	-26(8)	-29(8)	-35(7)
Cl(1B)	103(6)	117(7)	154(9)	-20(6)	-20(6)	-18(5)
Cl(2B)	152(6)	66(4)	135(8)	-14(4)	13(6)	-43(4)
C(69)	80(6)	82(6)	75(6)	-4(5)	-23(5)	-26(5)
Cl(3)	67(2)	59(2)	67(2)	6(1)	-38(2)	-27(2)
Cl(4)	90(3)	120(4)	89(3)	11(3)	-17(2)	-12(3)
C(69B)	99(7)	107(7)	97(7)	-6(5)	-30(5)	-31(5)
Cl(3B)	278(10)	275(10)	278(10)	-21(6)	-74(6)	-93(6)
Cl(4B)	168(6)	156(6)	171(6)	8(4)	-30(4)	-76(4)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for bm32zas.

	x	y	z	U(eq)
H(2A)	3504	4394	4116	54
H(3A)	1959	5158	5008	70
H(4A)	674	4455	5511	74
H(5A)	925	2999	5137	74
H(6A)	2499	2204	4265	56
H(10A)	6331	5790	1945	49
H(11A)	6670	7206	1517	63
H(12A)	5378	8642	1161	70
H(13A)	3751	8656	1204	62
H(15A)	2540	7773	1440	48
H(16A)	2204	6355	1777	43
H(20A)	4657	5944	3297	52
H(21A)	5228	5887	4294	68

H(22A)	6599	4497	4622	79
H(23)	7349	3150	3984	66
H(25A)	7487	2329	2958	51
H(26A)	6823	2301	2047	48
H(27A)	6686	3213	757	65
H(27B)	5716	3269	496	65
H(27C)	6188	2385	1070	65
H(28A)	2023	5160	3109	51
H(28B)	2183	4126	2912	51
H(28C)	1756	5098	2387	51
H(29A)	3286	2931	554	47
H(30A)	1917	3131	1679	78
H(30B)	2707	2187	2044	78
H(30C)	2339	2091	1380	78
H(31A)	5027	1981	496	75
H(31B)	4323	1317	755	75
H(31C)	4709	1572	1344	75
H(32A)	3615	4959	807	42
H(33A)	2083	5564	400	66
H(33B)	1831	5011	1208	66
H(33C)	2062	4492	502	66
H(34A)	3854	4835	-483	70
H(34B)	4102	3691	-259	70
H(34C)	4861	4165	-173	70
H(32B)	3177	5048	943	40
H(33D)	1704	5439	523	76
H(33E)	1551	4817	1311	76
H(33F)	1891	4309	579	76
H(34D)	3555	5145	-325	66
H(34E)	3760	4014	-289	66
H(34F)	4557	4323	-73	66
H(36A)	187	-957	1553	33
H(38A)	2215	-668	-455	42
H(40A)	1657	942	1149	36
H(44A)	-1412	310	1925	35
H(46A)	-3472	-15	3899	51
H(48A)	-732	211	3804	42
H(52A)	638	-1385	3208	34

H(54A)	3420	-1939	3636	40
H(56A)	2106	545	2406	37
H(60A)	297	1549	3271	39
H(62A)	-780	4305	2282	46
H(64A)	-446	2009	1359	37
H(68A)	8725	6473	3162	144
H(68B)	8257	7499	2711	144
H(68C)	8323	7226	2582	145
H(68D)	8862	7813	1882	145
H(69A)	5676	8557	4933	97
H(69B)	5038	8959	4315	97
H(69C)	6373	7842	4543	124
H(69D)	5560	8595	4085	124

Table S12. Torsion angles [°] for bm32zas.

N(3)-P(1)-S(1)-S(2)	-175.10(17)
N(1)-P(1)-S(1)-S(2)	-52.17(16)
N(2)-P(1)-S(1)-S(2)	62.80(17)
P(1)-S(1)-S(2)-C(1)	95.99(18)
N(3)-P(1)-N(1)-C(7)	-92.7(4)
N(2)-P(1)-N(1)-C(7)	28.2(4)
S(1)-P(1)-N(1)-C(7)	149.2(3)
N(3)-P(1)-N(1)-C(28)	66.5(4)
N(2)-P(1)-N(1)-C(28)	-172.6(3)
S(1)-P(1)-N(1)-C(28)	-51.6(3)
N(3)-P(1)-N(2)-C(17)	-179.9(3)
N(1)-P(1)-N(2)-C(17)	57.1(3)
S(1)-P(1)-N(2)-C(17)	-60.3(3)
N(3)-P(1)-N(2)-C(27)	-35.8(4)
N(1)-P(1)-N(2)-C(27)	-158.8(4)
S(1)-P(1)-N(2)-C(27)	83.8(4)
N(1)-P(1)-N(3)-C(29)	-134.2(4)
N(2)-P(1)-N(3)-C(29)	108.7(4)
S(1)-P(1)-N(3)-C(29)	-15.0(5)
N(1)-P(1)-N(3)-C(32)	49.9(11)
N(2)-P(1)-N(3)-C(32)	-67.2(11)

S(1)-P(1)-N(3)-C(32)	169.1(11)
N(1)-P(1)-N(3)-C(32B)	34.0(15)
N(2)-P(1)-N(3)-C(32B)	-83.1(15)
S(1)-P(1)-N(3)-C(32B)	153.1(15)
S(1)-S(2)-C(1)-C(6)	58.3(4)
S(1)-S(2)-C(1)-C(2)	-126.0(4)
C(6)-C(1)-C(2)-C(3)	0.3(8)
S(2)-C(1)-C(2)-C(3)	-175.5(4)
C(1)-C(2)-C(3)-C(4)	-0.8(8)
C(2)-C(3)-C(4)-C(5)	0.2(9)
C(3)-C(4)-C(5)-C(6)	0.7(10)
C(2)-C(1)-C(6)-C(5)	0.6(8)
S(2)-C(1)-C(6)-C(5)	176.3(4)
C(4)-C(5)-C(6)-C(1)	-1.1(9)
C(28)-N(1)-C(7)-C(8)	137.1(4)
P(1)-N(1)-C(7)-C(8)	-63.5(5)
C(28)-N(1)-C(7)-C(16)	-41.6(6)
P(1)-N(1)-C(7)-C(16)	117.9(4)
C(16)-C(7)-C(8)-C(9)	-4.5(7)
N(1)-C(7)-C(8)-C(9)	176.8(4)
C(16)-C(7)-C(8)-C(18)	178.2(4)
N(1)-C(7)-C(8)-C(18)	-0.4(6)
C(7)-C(8)-C(9)-C(10)	-173.1(4)
C(18)-C(8)-C(9)-C(10)	4.2(7)
C(7)-C(8)-C(9)-C(14)	5.5(6)
C(18)-C(8)-C(9)-C(14)	-177.2(4)
C(14)-C(9)-C(10)-C(11)	1.3(7)
C(8)-C(9)-C(10)-C(11)	180.0(5)
C(9)-C(10)-C(11)-C(12)	0.2(8)
C(10)-C(11)-C(12)-C(13)	-1.0(9)
C(11)-C(12)-C(13)-C(14)	0.1(9)
C(12)-C(13)-C(14)-C(15)	-176.4(5)
C(12)-C(13)-C(14)-C(9)	1.5(8)
C(10)-C(9)-C(14)-C(15)	175.8(5)
C(8)-C(9)-C(14)-C(15)	-2.9(7)
C(10)-C(9)-C(14)-C(13)	-2.2(7)
C(8)-C(9)-C(14)-C(13)	179.2(5)
C(13)-C(14)-C(15)-C(16)	177.0(5)

C(9)-C(14)-C(15)-C(16)	-0.9(7)
C(14)-C(15)-C(16)-C(7)	2.0(8)
C(8)-C(7)-C(16)-C(15)	0.8(7)
N(1)-C(7)-C(16)-C(15)	179.5(4)
C(27)-N(2)-C(17)-C(18)	142.9(4)
P(1)-N(2)-C(17)-C(18)	-71.8(5)
C(27)-N(2)-C(17)-C(26)	-39.0(6)
P(1)-N(2)-C(17)-C(26)	106.4(4)
C(26)-C(17)-C(18)-C(19)	-7.6(7)
N(2)-C(17)-C(18)-C(19)	170.5(4)
C(26)-C(17)-C(18)-C(8)	173.2(4)
N(2)-C(17)-C(18)-C(8)	-8.7(6)
C(7)-C(8)-C(18)-C(17)	55.8(6)
C(9)-C(8)-C(18)-C(17)	-121.4(5)
C(7)-C(8)-C(18)-C(19)	-123.4(5)
C(9)-C(8)-C(18)-C(19)	59.4(6)
C(17)-C(18)-C(19)-C(20)	-171.9(5)
C(8)-C(18)-C(19)-C(20)	7.4(7)
C(17)-C(18)-C(19)-C(24)	6.2(6)
C(8)-C(18)-C(19)-C(24)	-174.6(4)
C(24)-C(19)-C(20)-C(21)	1.3(8)
C(18)-C(19)-C(20)-C(21)	179.3(5)
C(19)-C(20)-C(21)-C(22)	0.2(9)
C(20)-C(21)-C(22)-C(23)	-1.4(10)
C(21)-C(22)-C(23)-C(24)	0.9(10)
C(22)-C(23)-C(24)-C(25)	-178.6(6)
C(22)-C(23)-C(24)-C(19)	0.6(9)
C(20)-C(19)-C(24)-C(23)	-1.7(7)
C(18)-C(19)-C(24)-C(23)	-179.8(5)
C(20)-C(19)-C(24)-C(25)	177.6(5)
C(18)-C(19)-C(24)-C(25)	-0.5(7)
C(23)-C(24)-C(25)-C(26)	175.2(5)
C(19)-C(24)-C(25)-C(26)	-4.0(8)
C(24)-C(25)-C(26)-C(17)	2.8(8)
C(18)-C(17)-C(26)-C(25)	3.2(7)
N(2)-C(17)-C(26)-C(25)	-174.9(4)
C(32)-N(3)-C(29)-C(31)	116.4(12)
C(32B)-N(3)-C(29)-C(31)	132.0(14)

P(1)-N(3)-C(29)-C(31)	-59.4(6)
C(32)-N(3)-C(29)-C(30)	-112.0(12)
C(32B)-N(3)-C(29)-C(30)	-96.5(15)
P(1)-N(3)-C(29)-C(30)	72.2(6)
C(29)-N(3)-C(32)-C(34)	-56.9(17)
C(32B)-N(3)-C(32)-C(34)	-132(7)
P(1)-N(3)-C(32)-C(34)	119.5(11)
C(29)-N(3)-C(32)-C(33)	67.3(14)
C(32B)-N(3)-C(32)-C(33)	-8(5)
P(1)-N(3)-C(32)-C(33)	-116.3(11)
C(29)-N(3)-C(32B)-C(33B)	53(2)
C(32)-N(3)-C(32B)-C(33B)	165(7)
P(1)-N(3)-C(32B)-C(33B)	-116.7(15)
C(29)-N(3)-C(32B)-C(34B)	-74(2)
C(32)-N(3)-C(32B)-C(34B)	37(6)
P(1)-N(3)-C(32B)-C(34B)	116.1(14)
C(43)-B(1)-C(35)-C(40)	158.6(4)
C(51)-B(1)-C(35)-C(40)	-80.0(5)
C(59)-B(1)-C(35)-C(40)	40.3(5)
C(43)-B(1)-C(35)-C(36)	-28.2(6)
C(51)-B(1)-C(35)-C(36)	93.2(5)
C(59)-B(1)-C(35)-C(36)	-146.5(4)
C(40)-C(35)-C(36)-C(37)	-3.4(6)
B(1)-C(35)-C(36)-C(37)	-176.8(4)
C(35)-C(36)-C(37)-C(38)	2.8(7)
C(35)-C(36)-C(37)-C(41)	-179.3(4)
C(36)-C(37)-C(38)-C(39)	-0.4(7)
C(41)-C(37)-C(38)-C(39)	-178.2(4)
C(37)-C(38)-C(39)-C(40)	-1.2(7)
C(37)-C(38)-C(39)-C(42)	179.1(4)
C(38)-C(39)-C(40)-C(35)	0.4(7)
C(42)-C(39)-C(40)-C(35)	-179.9(4)
C(36)-C(35)-C(40)-C(39)	1.8(6)
B(1)-C(35)-C(40)-C(39)	175.8(4)
C(38)-C(37)-C(41)-F(1)	-142.3(5)
C(36)-C(37)-C(41)-F(1)	39.8(6)
C(38)-C(37)-C(41)-F(2)	96.4(5)
C(36)-C(37)-C(41)-F(2)	-81.5(6)

C(38)-C(37)-C(41)-F(3)	-21.6(6)
C(36)-C(37)-C(41)-F(3)	160.5(4)
C(40)-C(39)-C(42)-F(5B)	17.5(10)
C(38)-C(39)-C(42)-F(5B)	-162.8(8)
C(40)-C(39)-C(42)-F(4)	179.5(7)
C(38)-C(39)-C(42)-F(4)	-0.8(10)
C(40)-C(39)-C(42)-F(6)	-41.2(9)
C(38)-C(39)-C(42)-F(6)	138.4(7)
C(40)-C(39)-C(42)-F(4B)	149.5(7)
C(38)-C(39)-C(42)-F(4B)	-30.8(8)
C(40)-C(39)-C(42)-F(6B)	-99.2(7)
C(38)-C(39)-C(42)-F(6B)	80.5(7)
C(40)-C(39)-C(42)-F(5)	65.3(7)
C(38)-C(39)-C(42)-F(5)	-115.0(6)
C(35)-B(1)-C(43)-C(44)	-25.1(6)
C(51)-B(1)-C(43)-C(44)	-143.0(4)
C(59)-B(1)-C(43)-C(44)	96.0(5)
C(35)-B(1)-C(43)-C(48)	158.9(4)
C(51)-B(1)-C(43)-C(48)	41.0(6)
C(59)-B(1)-C(43)-C(48)	-80.0(5)
C(48)-C(43)-C(44)-C(45)	-2.2(7)
B(1)-C(43)-C(44)-C(45)	-178.4(4)
C(43)-C(44)-C(45)-C(46)	1.0(7)
C(43)-C(44)-C(45)-C(49)	-176.0(4)
C(44)-C(45)-C(46)-C(47)	0.7(8)
C(49)-C(45)-C(46)-C(47)	177.6(5)
C(45)-C(46)-C(47)-C(48)	-0.9(8)
C(45)-C(46)-C(47)-C(50)	-177.5(6)
C(46)-C(47)-C(48)-C(43)	-0.4(8)
C(50)-C(47)-C(48)-C(43)	176.2(5)
C(44)-C(43)-C(48)-C(47)	1.9(7)
B(1)-C(43)-C(48)-C(47)	178.3(5)
C(46)-C(45)-C(49)-F(7)	18.6(7)
C(44)-C(45)-C(49)-F(7)	-164.4(4)
C(46)-C(45)-C(49)-F(9)	139.7(5)
C(44)-C(45)-C(49)-F(9)	-43.3(6)
C(46)-C(45)-C(49)-F(8)	-101.3(6)
C(44)-C(45)-C(49)-F(8)	75.7(6)

C(46)-C(47)-C(50)-F(10)	-126.0(7)
C(48)-C(47)-C(50)-F(10)	57.4(8)
C(46)-C(47)-C(50)-F(11)	-1.6(9)
C(48)-C(47)-C(50)-F(11)	-178.1(6)
C(46)-C(47)-C(50)-F(12)	117.4(6)
C(48)-C(47)-C(50)-F(12)	-59.2(8)
C(35)-B(1)-C(51)-C(56)	81.1(5)
C(43)-B(1)-C(51)-C(56)	-154.1(4)
C(59)-B(1)-C(51)-C(56)	-37.6(6)
C(35)-B(1)-C(51)-C(52)	-94.2(5)
C(43)-B(1)-C(51)-C(52)	30.6(6)
C(59)-B(1)-C(51)-C(52)	147.1(4)
C(56)-C(51)-C(52)-C(53)	1.5(7)
B(1)-C(51)-C(52)-C(53)	177.1(4)
C(51)-C(52)-C(53)-C(54)	-1.3(7)
C(51)-C(52)-C(53)-C(57)	178.6(4)
C(52)-C(53)-C(54)-C(55)	0.0(7)
C(57)-C(53)-C(54)-C(55)	-179.8(4)
C(53)-C(54)-C(55)-C(56)	0.8(7)
C(53)-C(54)-C(55)-C(58)	179.0(5)
C(54)-C(55)-C(56)-C(51)	-0.5(7)
C(58)-C(55)-C(56)-C(51)	-178.7(5)
C(52)-C(51)-C(56)-C(55)	-0.7(7)
B(1)-C(51)-C(56)-C(55)	-176.2(4)
C(54)-C(53)-C(57)-F(14)	147.9(5)
C(52)-C(53)-C(57)-F(14)	-31.9(7)
C(54)-C(53)-C(57)-F(13B)	-38.5(15)
C(52)-C(53)-C(57)-F(13B)	141.6(14)
C(54)-C(53)-C(57)-F(15B)	81.9(15)
C(52)-C(53)-C(57)-F(15B)	-97.9(15)
C(54)-C(53)-C(57)-F(14B)	-158.6(13)
C(52)-C(53)-C(57)-F(14B)	21.6(14)
C(54)-C(53)-C(57)-F(13)	-89.7(6)
C(52)-C(53)-C(57)-F(13)	90.5(6)
C(54)-C(53)-C(57)-F(15)	27.2(7)
C(52)-C(53)-C(57)-F(15)	-152.7(5)
C(54)-C(55)-C(58)-F(16)	13.8(7)
C(56)-C(55)-C(58)-F(16)	-168.0(5)

C(54)-C(55)-C(58)-F(18)	136.1(5)
C(56)-C(55)-C(58)-F(18)	-45.7(7)
C(54)-C(55)-C(58)-F(17)	-106.2(5)
C(56)-C(55)-C(58)-F(17)	72.1(6)
C(35)-B(1)-C(59)-C(60)	-147.8(4)
C(43)-B(1)-C(59)-C(60)	87.4(5)
C(51)-B(1)-C(59)-C(60)	-32.5(6)
C(35)-B(1)-C(59)-C(64)	36.7(6)
C(43)-B(1)-C(59)-C(64)	-88.1(5)
C(51)-B(1)-C(59)-C(64)	152.1(4)
C(64)-C(59)-C(60)-C(61)	-0.9(7)
B(1)-C(59)-C(60)-C(61)	-176.6(4)
C(59)-C(60)-C(61)-C(62)	0.0(8)
C(59)-C(60)-C(61)-C(65)	-177.2(4)
C(60)-C(61)-C(62)-C(63)	0.4(7)
C(65)-C(61)-C(62)-C(63)	177.7(5)
C(61)-C(62)-C(63)-C(64)	0.0(7)
C(61)-C(62)-C(63)-C(66)	-179.6(5)
C(62)-C(63)-C(64)-C(59)	-1.0(8)
C(66)-C(63)-C(64)-C(59)	178.6(4)
C(60)-C(59)-C(64)-C(63)	1.4(7)
B(1)-C(59)-C(64)-C(63)	177.2(4)
C(62)-C(61)-C(65)-F(21B)	-57.9(10)
C(60)-C(61)-C(65)-F(21B)	119.4(9)
C(62)-C(61)-C(65)-F(19)	123.8(6)
C(60)-C(61)-C(65)-F(19)	-58.9(7)
C(62)-C(61)-C(65)-F(20)	-112.5(7)
C(60)-C(61)-C(65)-F(20)	64.8(7)
C(62)-C(61)-C(65)-F(19B)	63.2(10)
C(60)-C(61)-C(65)-F(19B)	-119.4(9)
C(62)-C(61)-C(65)-F(21)	1.4(8)
C(60)-C(61)-C(65)-F(21)	178.8(7)
C(62)-C(61)-C(65)-F(20B)	177.9(9)
C(60)-C(61)-C(65)-F(20B)	-4.8(10)
C(64)-C(63)-C(66)-F(24B)	29.0(9)
C(62)-C(63)-C(66)-F(24B)	-151.4(8)
C(64)-C(63)-C(66)-F(22)	-163.8(8)
C(62)-C(63)-C(66)-F(22)	15.8(9)

C(64)-C(63)-C(66)-F(23B)	-95.0(9)
C(62)-C(63)-C(66)-F(23B)	84.6(9)
C(64)-C(63)-C(66)-F(24)	72.3(8)
C(62)-C(63)-C(66)-F(24)	-108.0(8)
C(64)-C(63)-C(66)-F(22B)	149.9(8)
C(62)-C(63)-C(66)-F(22B)	-30.5(9)
C(64)-C(63)-C(66)-F(23)	-42.3(8)
C(62)-C(63)-C(66)-F(23)	137.3(7)

Symmetry transformations used to generate equivalent atoms:

Table S13. Hydrogen bonds for bm32zas [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

References

(1) Armarego, W. L. F. & Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th Ed.; p. 159 (Elsevier: Oxford, 2009)

(2) Denmark, S. E. & Wilson T. W. Construction of quaternary stereogenic carbon centers by the Lewis base catalyzed conjugate addition of silyl ketene imines to α,β-unsaturated aldehydes and ketones. *Synlett*, 1723– 1728 (2010).

(3) Logan, A. W. J., Parker, J. S., Hallside, M. S. & Burton, J. W. Manganese(III) acetate mediated oxidative radical cyclizations. toward vicinal all-carbon quaternary stereocenters. *Org. Lett* **14**, 2940–2943 (2012).

(4) Mimmi, M. C., Gullotti, M., Santagostini, L., Pagliarin, R., De Gioia, L., Monzani, E. & Casella, L. Synthesis and conformational studies of a chiral octadentate ligand derived from (*R*)-1,1′-binaphthyl-2,2′-diamine and its dinuclear zinc(II) and nickel(II) complexes. *Eur. J. Inorg. Chem.,* 3934–3934 (2003).

(5) Nurminen, E. J., Mattinen, J. K. & Lönnberg, H. Kinetics and mechanism of tetrazole-catalyzed phosphoramidite alcoholysis. *J. Chem. Soc., Perkin Trans. 2*, 1621–1628 (1998).

(6) Kal'yan, Y. B., Krimer, M. Z., Cherepanova, E. G., Bogdanov, V. S. & Smit, V. A. Arylthiosulfonium salts as transfer agents of the S-aryl group to double bonds. *Russ. Chem. Bull.* **31**, 342–349 (1982).

(7) Smith, C. R., Zhang, A., Mans, D. J. & RajanBabu, T. V. (*R*)-3-Methyl-3-phenyl-1-pentene via catalytic asymmetric hydrovinylation. *Org. Synth.* **85**, 248–266 (2008).

(8) Barrett, A. G. M., Dhanak, D., Graboski, G. G. & Taylor, S. J. (Phenylthio)nitromethane. *Org. Synth.* **68**, 8–11 (1990).

(9) 1-bromo-2,6-diethylbenzene was prepared following a procedure described for the synthesis of 1-bromo-2,6- diisopropylbenzene.[10]

(10) Wallasch, M. W., Weismann, D., Riehn, C., Ambrus, S., Wolmershäuser, G., Lagutschenkov, A., Niedner-Schatteburg, G. & Sitzmann, H. Reactive sigma-aryliron complexes or iron-promoted coupling of two phenyl anions to one bis(cyclohexadien-ylidene) ligand: synthesis, structure, mass spectrometry, and DFT calculations. *Organometallics* **29***,* 806–813 (2010).

(11) Diemer, V., Chaumeil, H., Defoin, A., Fort, A., Boeglin, A. & Carré, C. Syntheses of sterically hindered pyridinium phenoxides as model compounds in nonlinear optics. *Eur. J. Org. Chem.*, 2727–2738 (2006).

(12) Milne, J. E. & Buchwald, S. L. An extremely active catalyst for the Negishi cross-coupling reaction. *J. Am. Chem. Soc.* **126**, 13028–13023 (2004).

(13) Nakayama, J., Duan, S. & Hoshino, M. Reaction of 1,8-dehydronaphthalene with carbon disulphide. *J. Chem. Soc., Perkin Trans. 1*, 413–414 (1981).

(14) The ester precursor was prepared using the method of Johnson: Johnson, W. S., Werthemann, L., Bartlett, W. R., Brocksom, T. J., Li, T., Faulkner, D. J. & Petersen, M. R. Simple stereoselective version of the Claisen rearrangement leading to trans-trisubstituted olefinic bonds. Synthesis of squalene. *J. Am. Chem. Soc.* **92**, 741–743 (1970). Reduction to the alcohol was carried out following a literature procedure: Hashem, A. & Weyerstahl, P. Reactivity of 1-cyclopropene-1-lactones dependent on the substitution degree. *Tetrahedron* **40**, 2003–2009 (1984). However, in contrast to the original procedure, the reduction was conducted at room temperature, not at reflux.

(15) Denmark, S. E. & Chi, H. M. Catalytic, Enantioselective Intramolecular Sulfenoamination of Olefins. *J. Am. Chem. Soc.* **136**, dx.doi.org/10.1021/ja5046296 |(2014).

(16) Denmark, S. E., Kornfilt, D. J. P. & Vogler, T. Catalytic asymmetric thiofunctionalization of unactivated alkenes. *J. Am. Chem. Soc.* **133**, 15308–15311 (2011).

(17) Rundel, W. Notiz über die Darstellung tert.-butylierter Thiophenole, Diphenylsulfide und Thianthrene. *Chem. Ber* **101**, 2956–2962 (1968).

(18) Kessler, H. & Rundel, W. Nachweis innermolekularer Beweglichkeit durch NMR-Spektroskopie, VI. Konformationen und gehinderte Rotation in Disulfiden und Diseleniden. *Chem. Ber.* **101**, 3350–3357 (1968).

(19) Novakova, V., Miletin, M., Filandrova, T., Lenco, J., Ruzicka, A. & Zimcik, P. Role of Steric Hindrance in the Newman-Kwart Rearrangement and in the Synthesis and Photophysical Properties of Arylsulfanyl Tetrapyrazinoporphyrazines. *J. Org. Chem.* **79**, 2082–2093 (2014).

(20) Klose, J., Reese, C. B .& Song, Q. Preparation of 2-(2-cyanoethyl)sulfanyl-1*H*-isoindole-1,3-(2*H*)-dione and related sulfur transfer agents. *Tetrahedron* **53**, 14411–14416 (1997).

(21) Gillis, H. M.; Greene, L.; Thompson A. Preparation of sulfenyl pyrrols. *Synlett*, 112–116 (2009).

(22) Bozkurt, Y. S. & Kutuk, H. The synthesis of sulfinylphthalimides and their reactions with some nucleophiles in dioxane. *Phosphorus, Sulfur and Silicon and the Related Elements* **186**, 2250–2257 (2011).

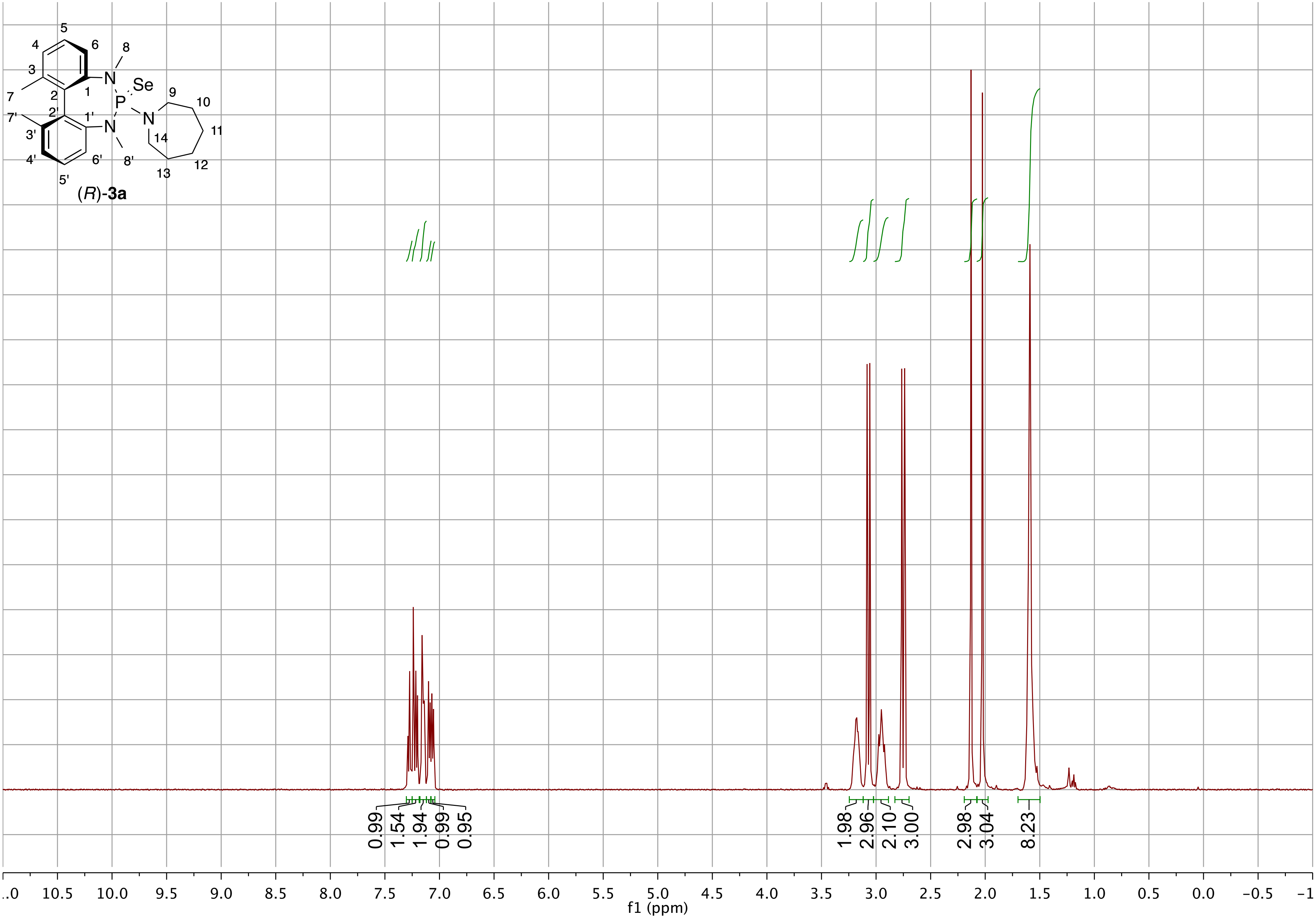
(23) Büchel, K. H. & Conte, A. Über die Reaktion von *N*-Brom-Imiden mit Disulfiden zu Sulfenimiden. *Chem. Ber.* **100**, 1248–1251 (1967).

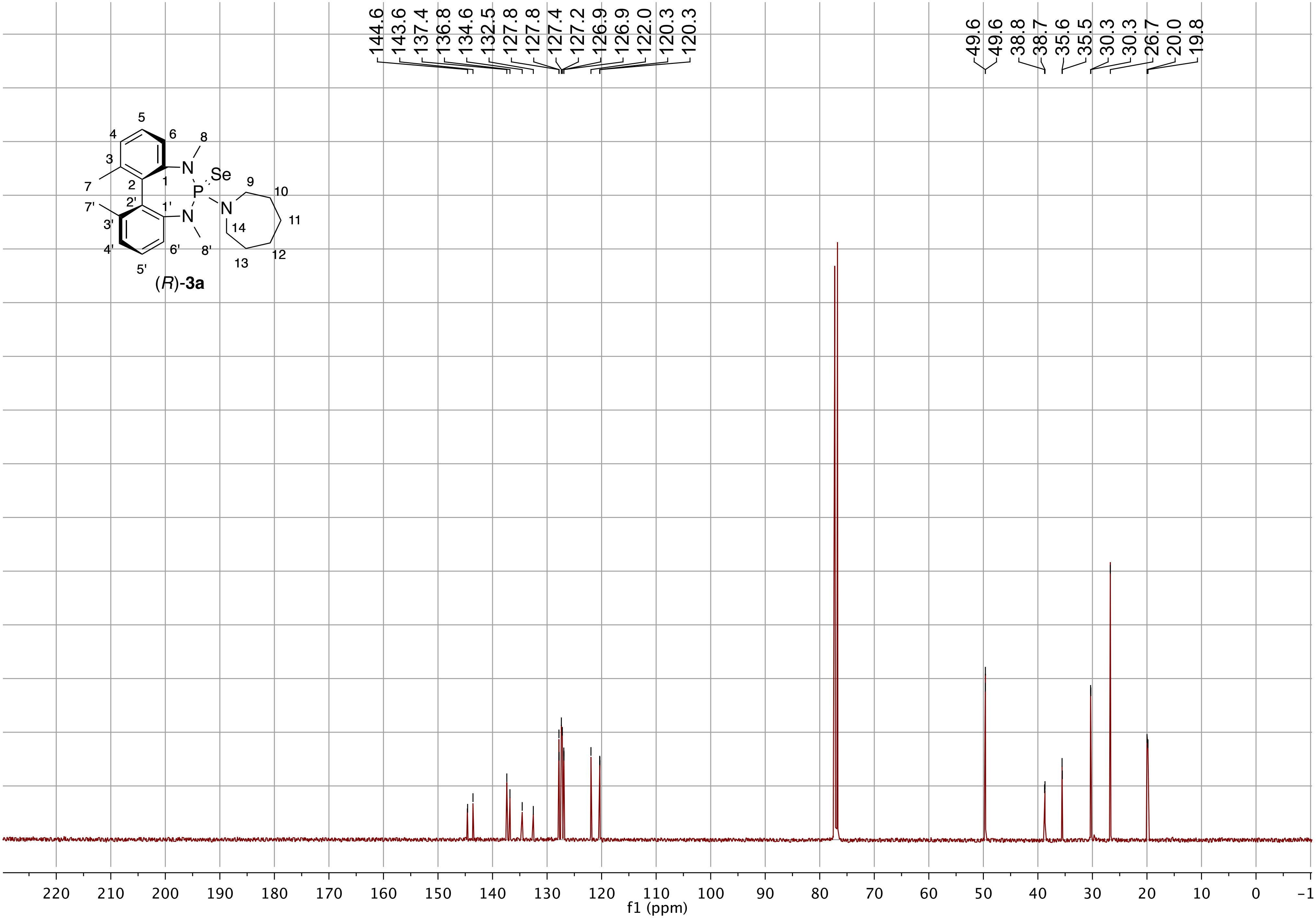
(24) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

(25) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **88**, 899-926 (1988). (b) Glendening, E. D.; Reed, A. E.; Carpenter J. E.; Weinhold, F. NBO Version 3.1. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2001**).

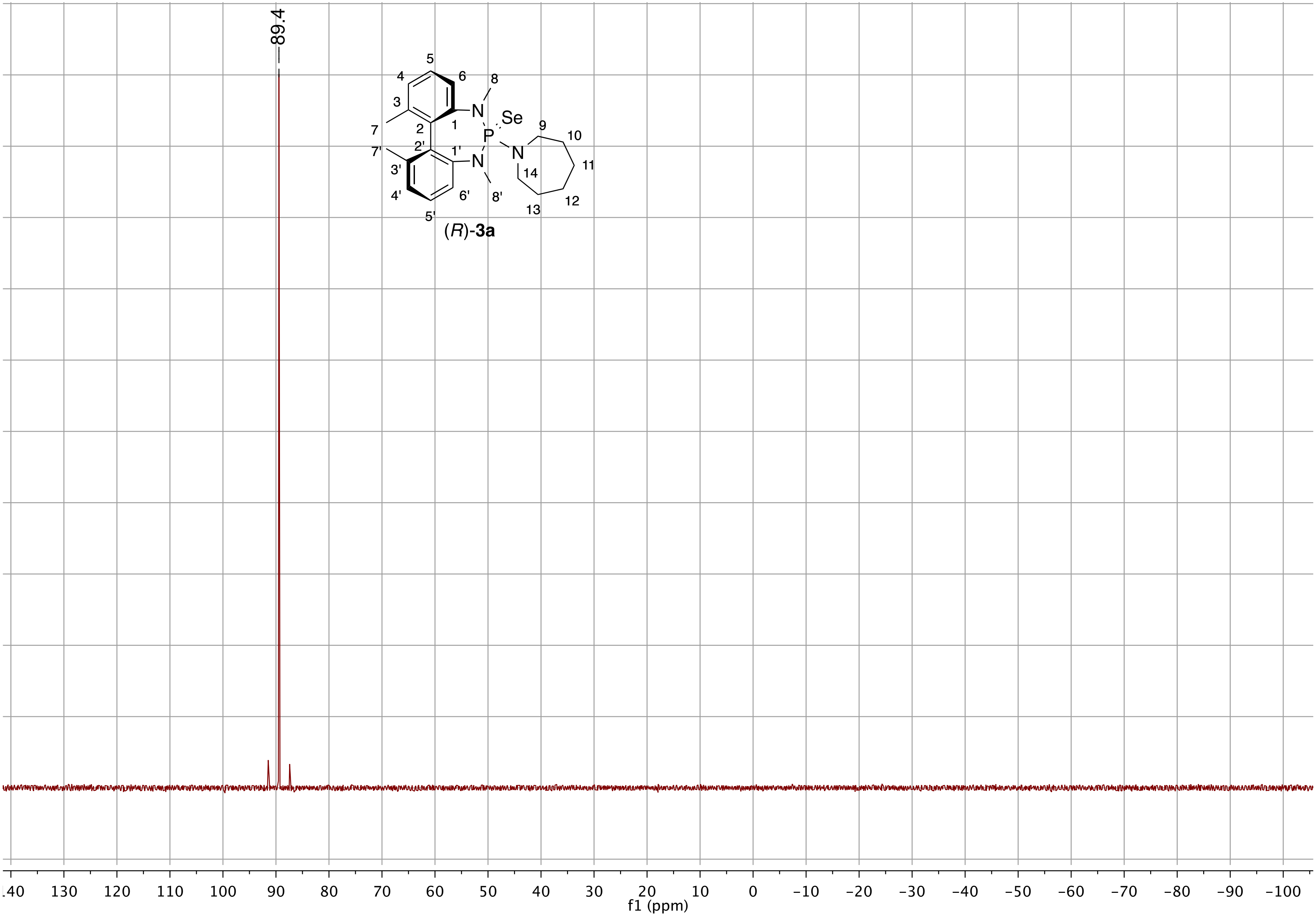
(26) Barone, V.; Cossi, M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A* **102**, 1995–2001 (1998).

(27) Cossi, M., Rega, N., Scalmani, G. & Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.*, **24**, 669–681 (2003).

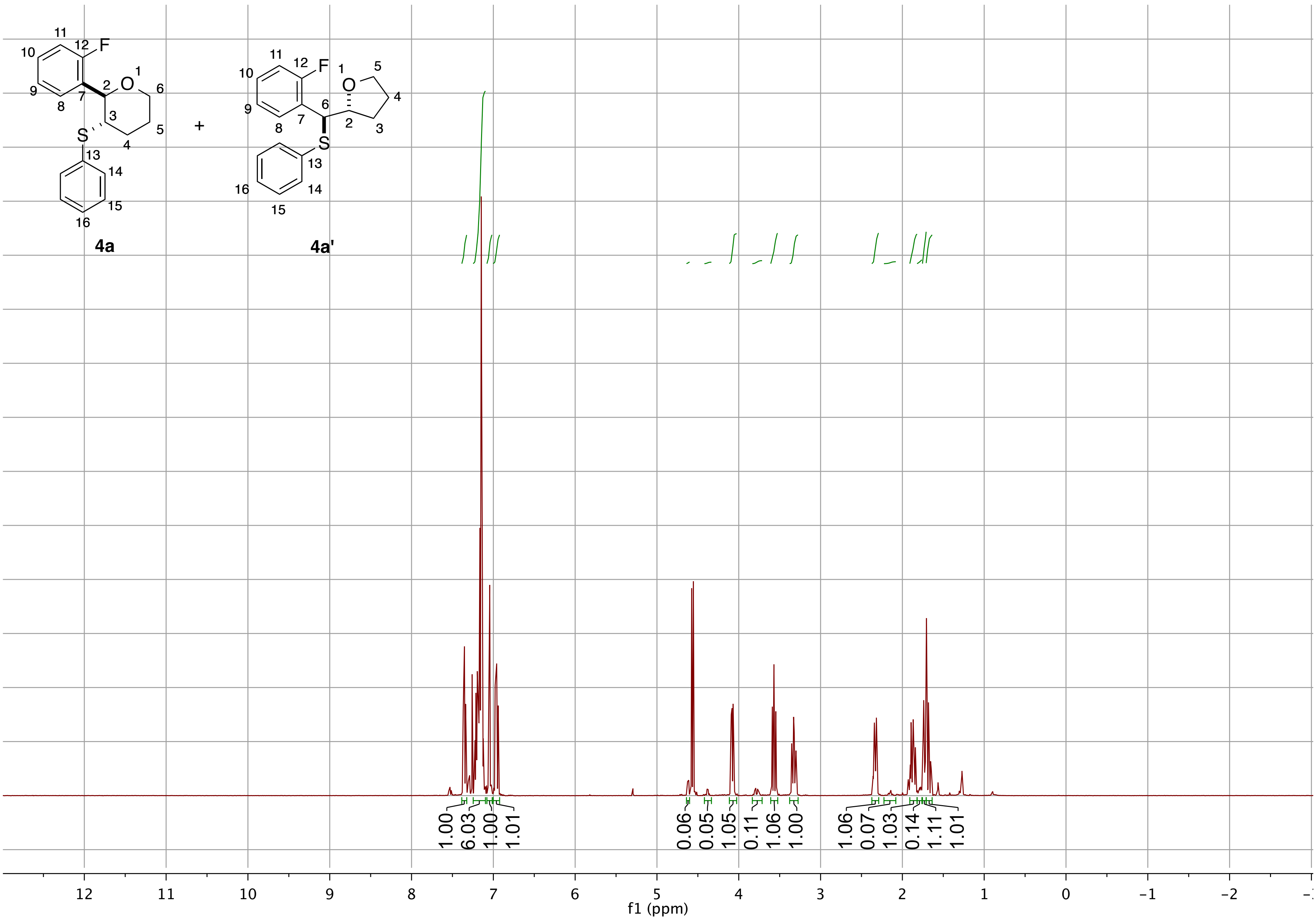

5
4
6
8
3
N
Se
7
2
1
9
P
10
7'
2'
1'
N
3'
N
14
11
4'
6'
8'
5'
13
12
(R)-3a
0.99
1.54
1.94
0.99
0.95
1.98
2.96
2.10
3.00
2.98
3.04
8.23
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
–1
f1 (ppm)


(*R*)-**3a**

144.6
143.6
137.4
136.8
134.6
132.5
127.8
127.8
127.4
127.2
126.9
126.9
122.0
120.3
120.3
49.6
49.6
38.8
38.7
35.6
35.5
30.3
30.3
26.7
20.0
19.8
Se
P
N
N
N
1
2
3
4
5
6
7
8
1'
2'
3'
4'
5'
6'
7'
8'
9
10
11
12
13
14
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)

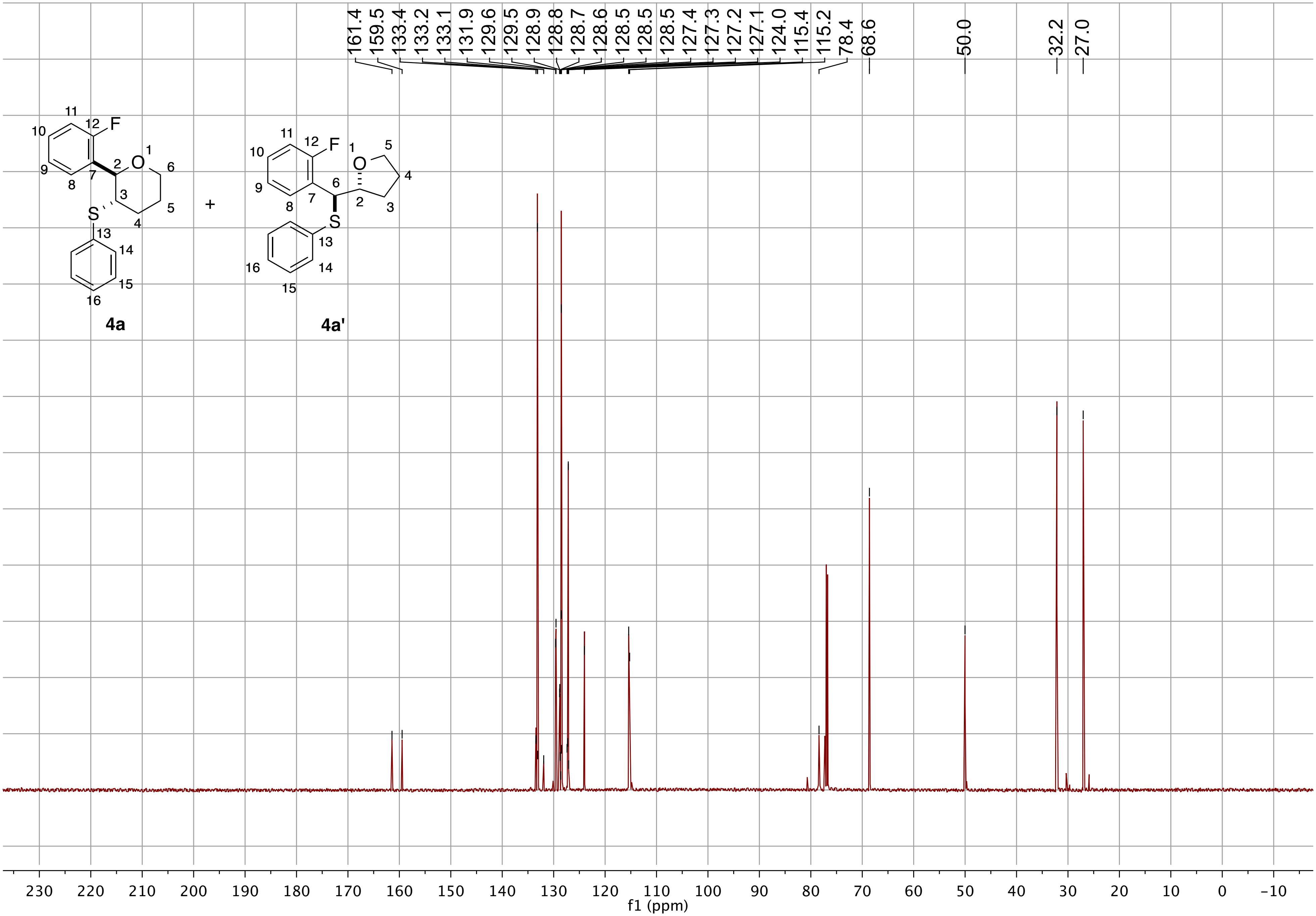

89.4
5
4
6
8
3
N
Se
7
2
1
9
P
10
7'
2'
1'
N
N
11
3'
14
4'
6'
8'
12
13
5'
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
f1 (ppm)

(*R*)-**3a**



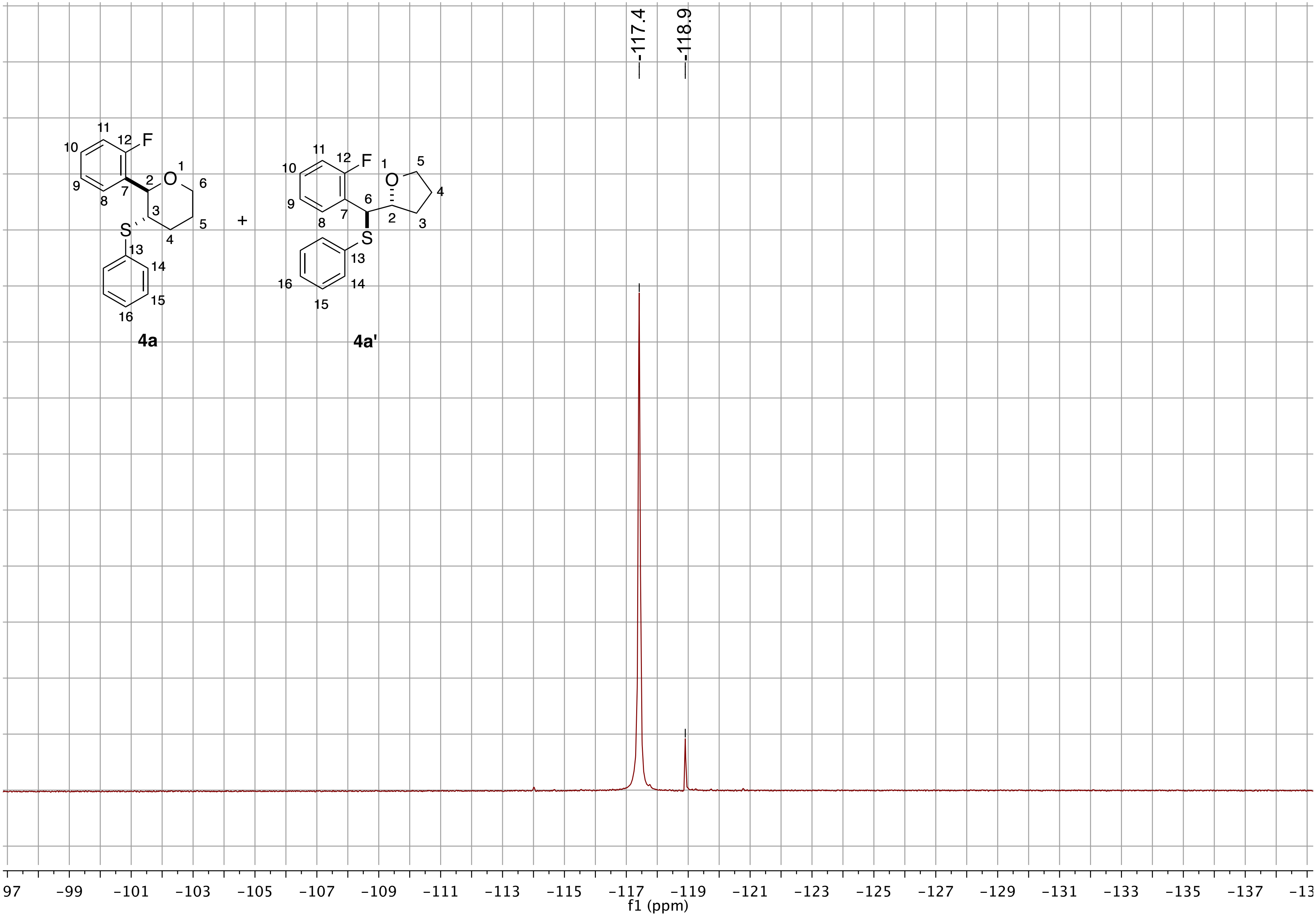
11
10
12
F
1
O
2
6
9
7
8
3
5
S
4
13
14
15
16
+
11
12
F
1
5
10
O
4
9
6
7
2
8
3
S
13
16
14
15
1.00
6.03
1.00
1.01
0.06
0.05
1.05
0.11
1.06
1.00
1.06
0.07
1.03
0.14
1.11
1.01
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

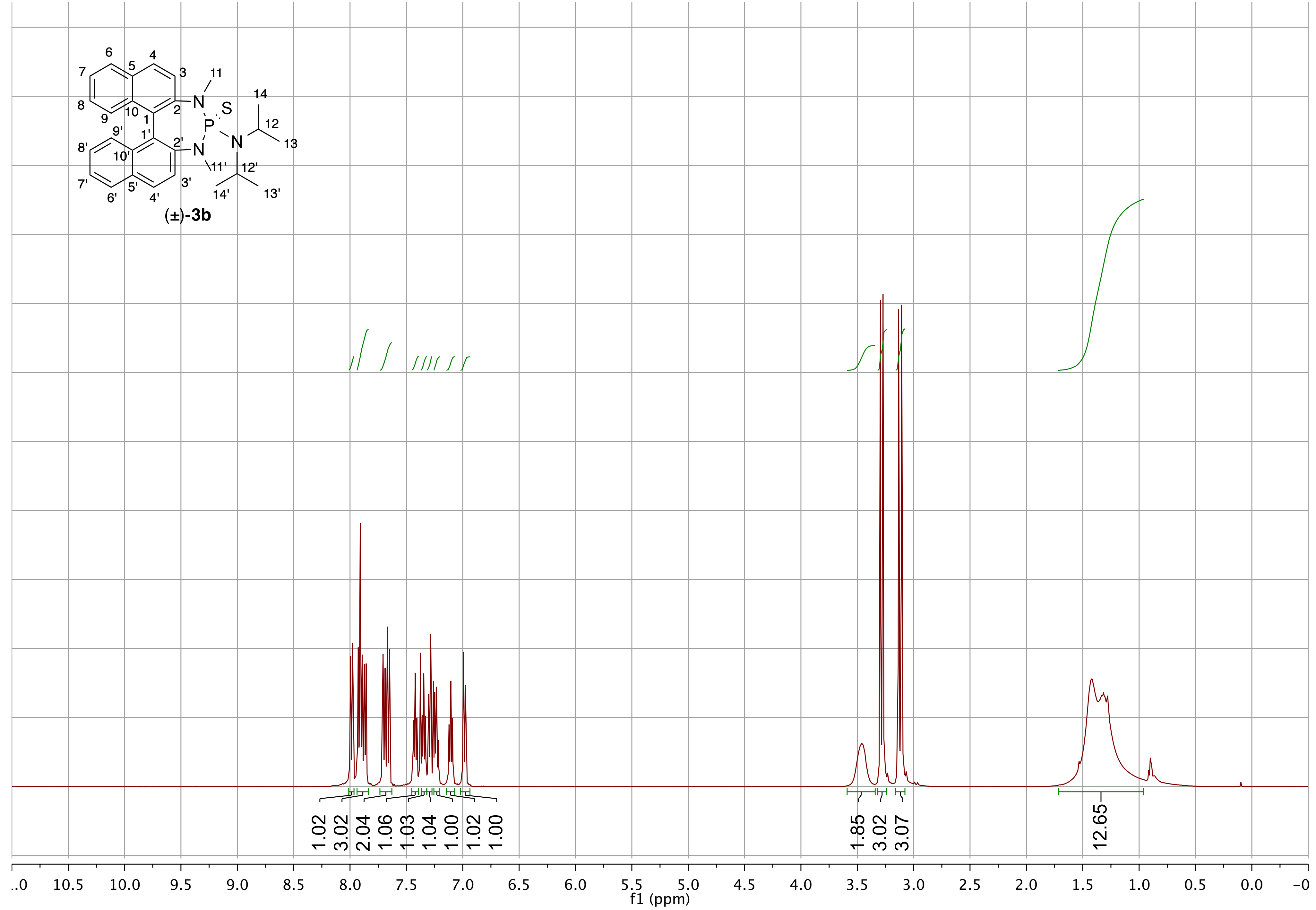
4a + **4a'**


161.4
159.5
133.4
133.2
133.1
131.9
129.6
129.5
128.9
128.8
128.7
128.6
128.5
128.5
128.5
127.4
127.3
127.2
127.1
124.0
115.4
115.2
78.4
68.6
50.0
32.2
27.0
F
O
S
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
+
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

4a

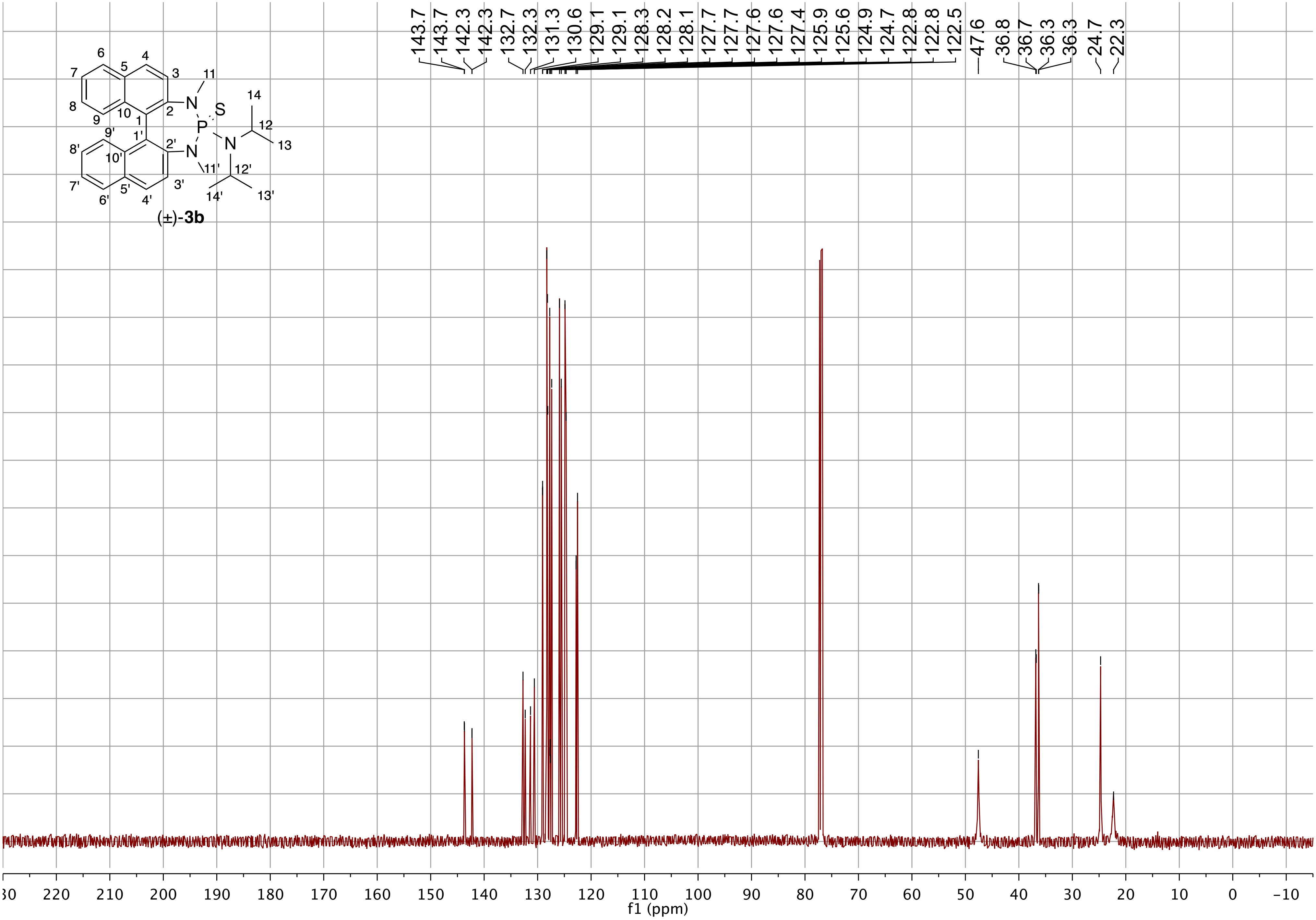
4a'

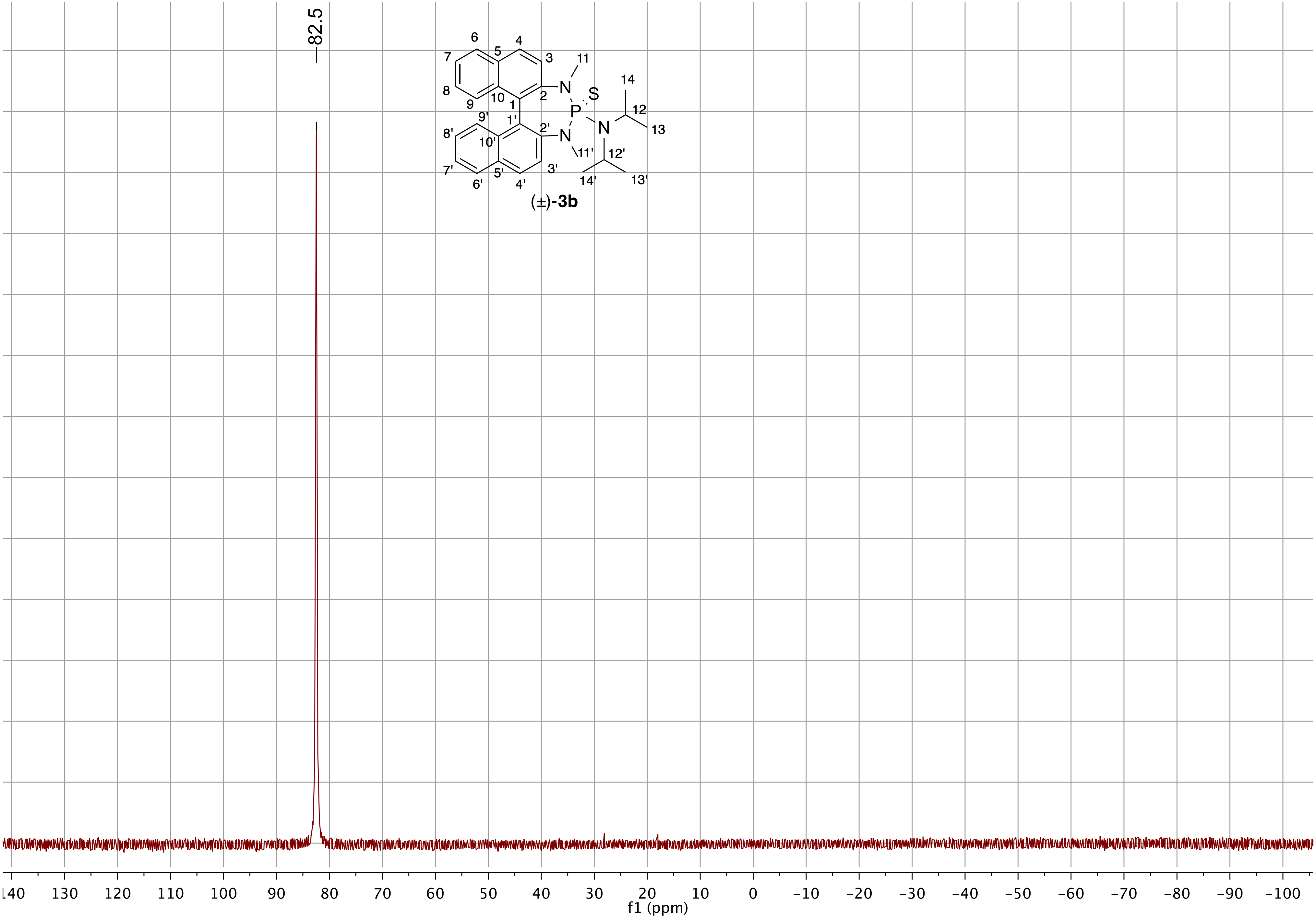

-117.4
-118.9
F
O
S
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
+
4a
4a'
97
−99
−101
−103
−105
−107
−109
−111
−113
−115
−117
−119
−121
−123
−125
−127
−129
−131
−133
−135
−137
f1 (ppm)



(±)-**3b**

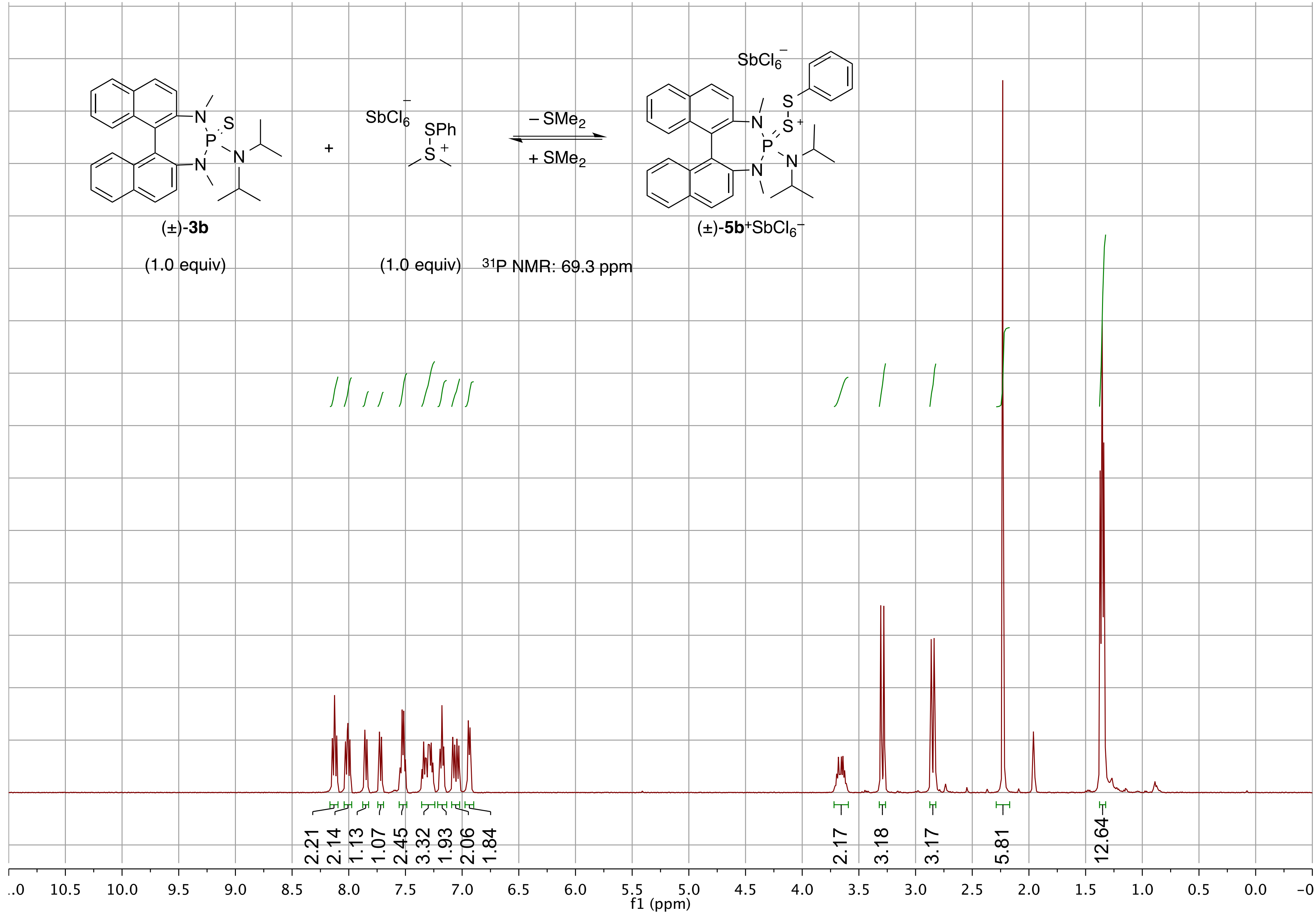
6
7
5
4
3
11
8
9
10
1
2
N
S
P
14
12
N
13
9'
1'
2'
8'
10'
N
11'
12'
7'
5'
3'
6'
4'
14'
13'
1.02
3.02
2.04
1.06
1.03
1.04
1.00
1.02
1.00
1.85
3.02
3.07
12.65
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

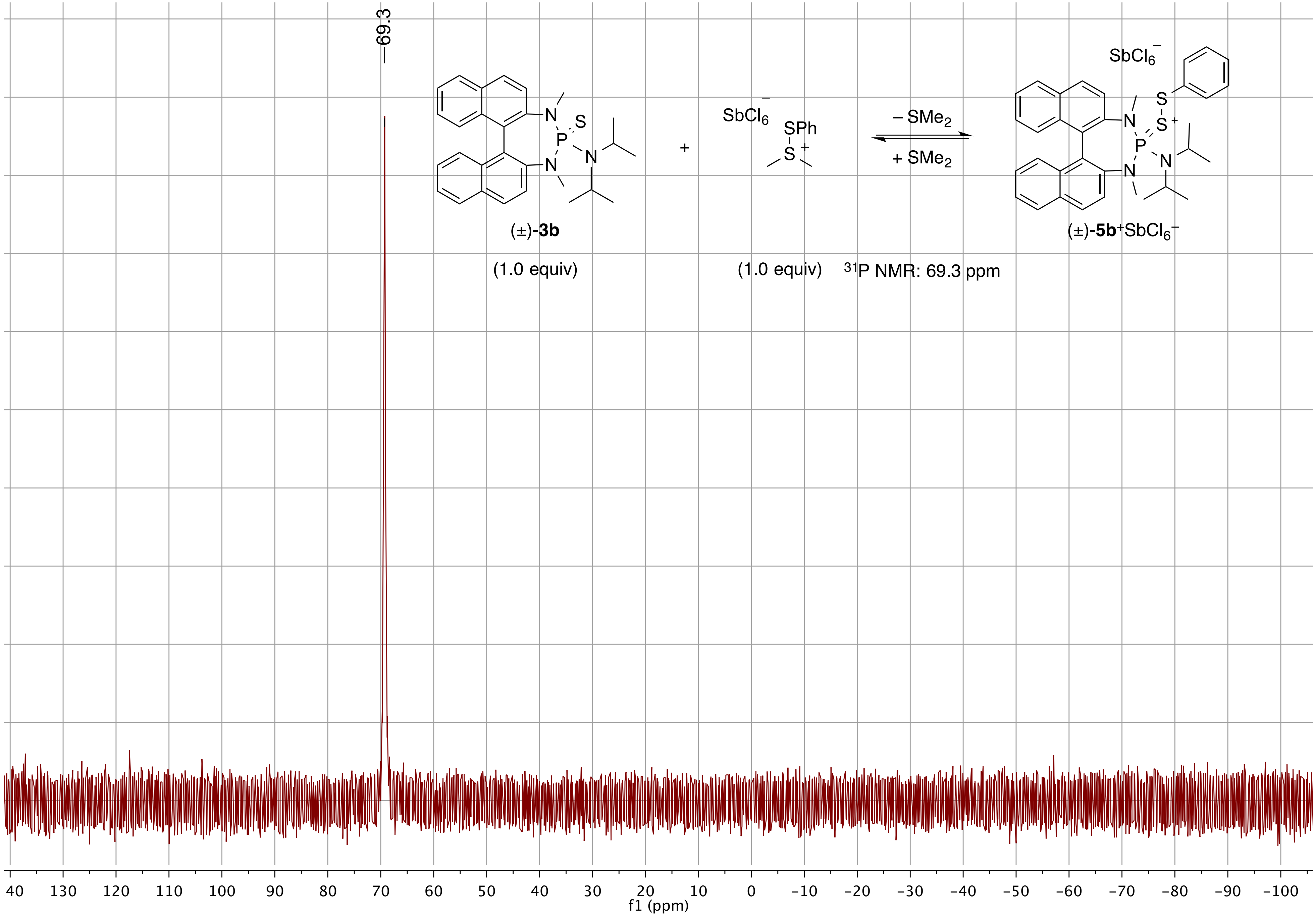

143.7
143.7
142.3
142.3
132.7
132.3
131.3
130.6
129.1
129.1
128.3
128.2
128.1
127.7
127.7
127.6
127.6
127.4
125.9
125.6
124.9
124.7
122.8
122.8
122.5
47.6
36.8
36.7
36.3
36.3
24.7
22.3
(±)-3b
N
P
S
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
1'
2'
3'
4'
5'
6'
7'
8'
9'
10'
11'
12'
13'
14'
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)



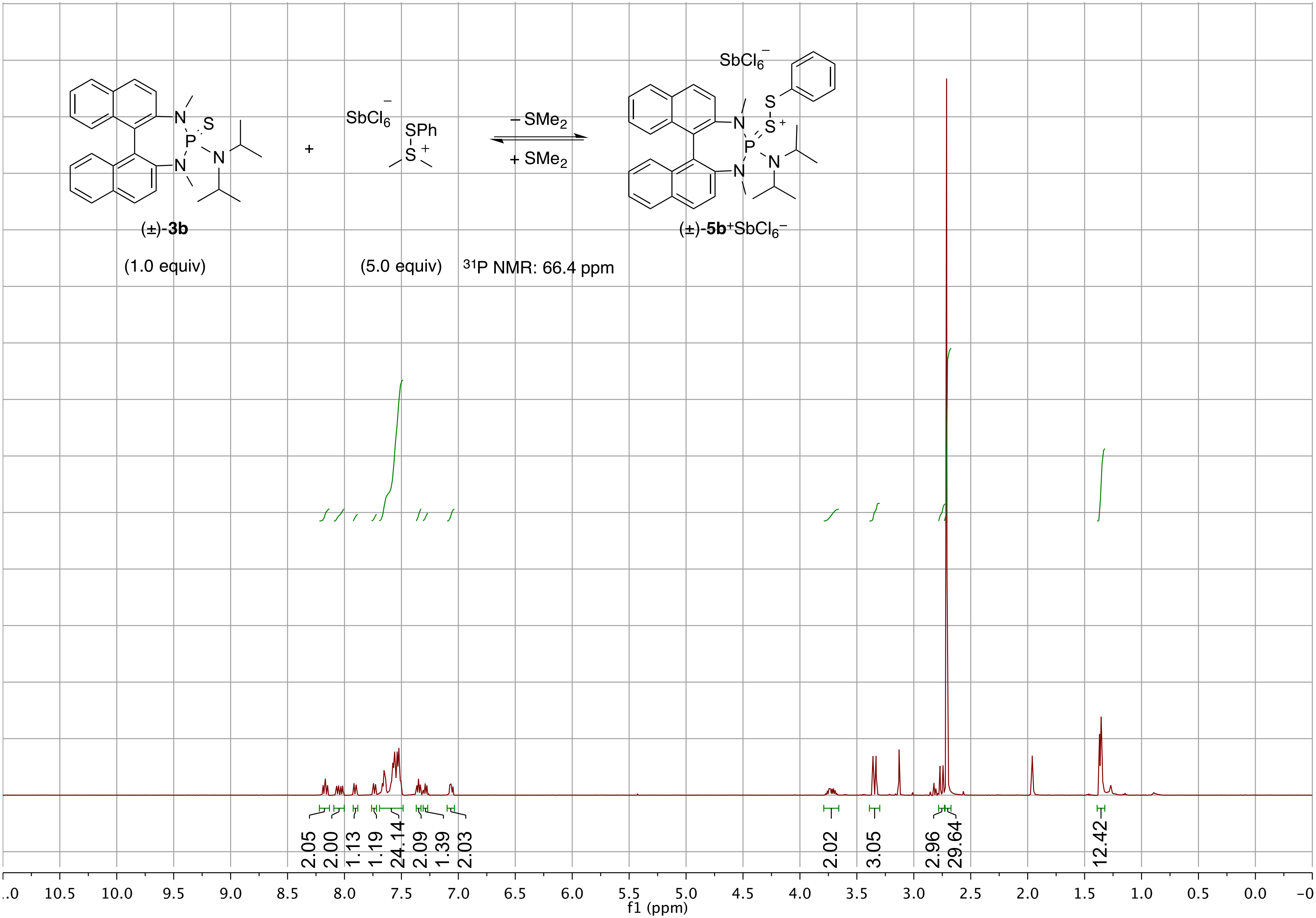
82.5
6
4
5
7
3
11
N
S
14
8
9
10
1
2
P
12
N
13
9'
1'
2'
8'
10'
N
11'
12'
7'
5'
3'
6'
4'
14'
13'
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
f1 (ppm)

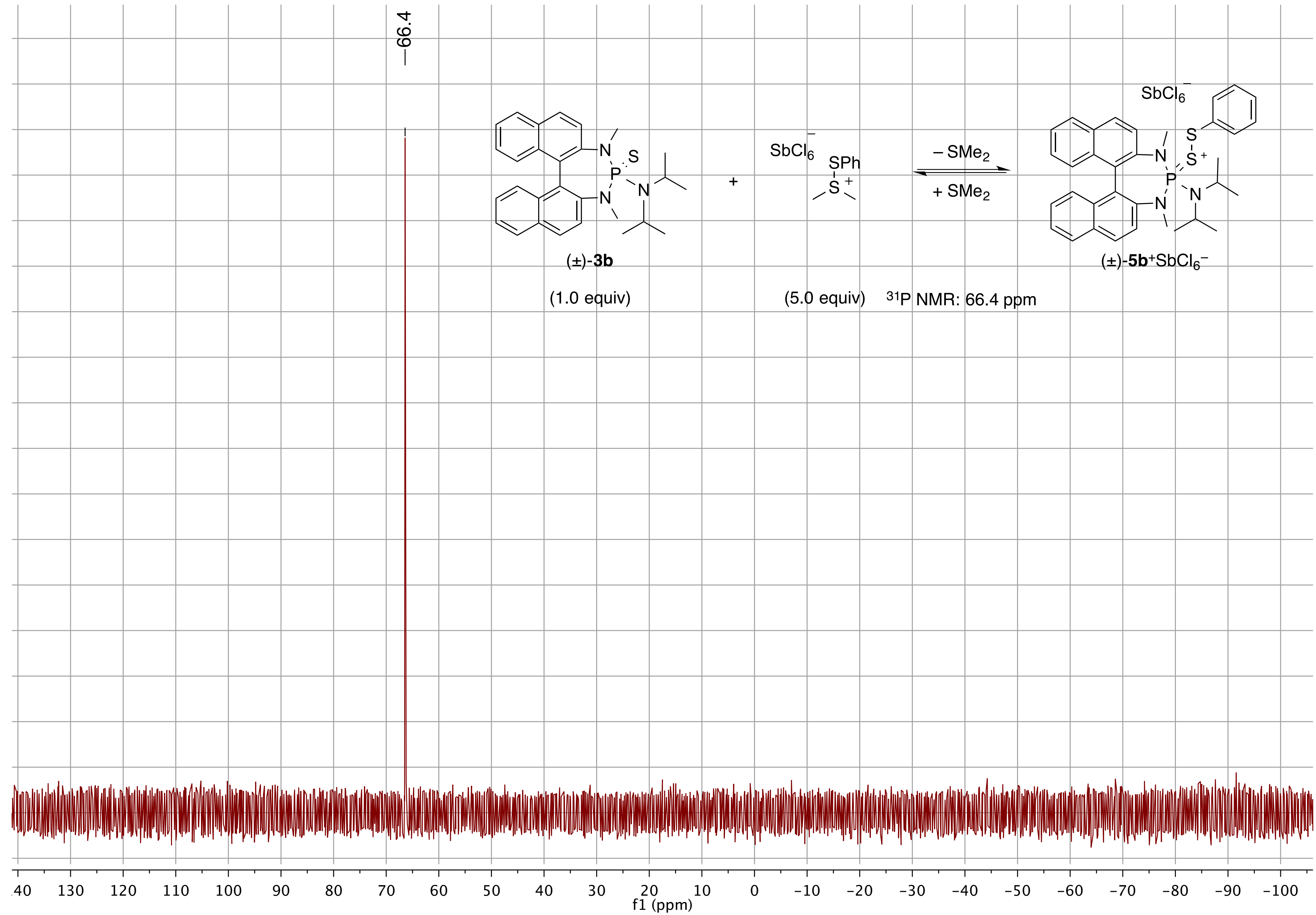
(±)-**3b**

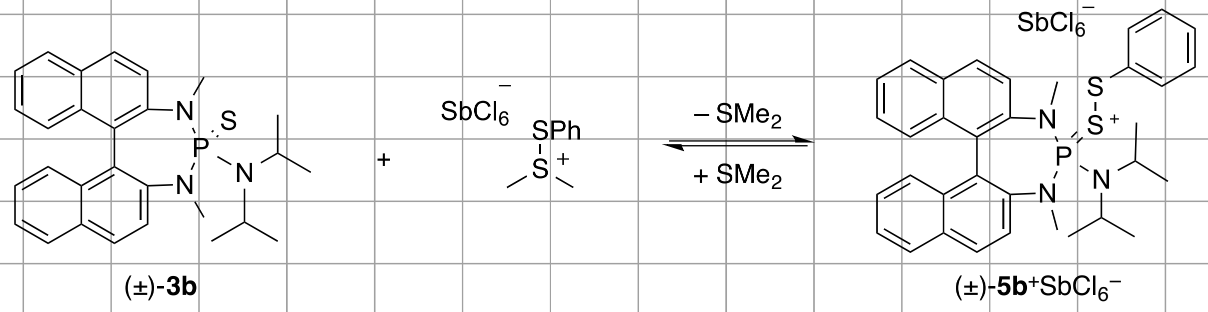

(±)-3b
(1.0 equiv)
SbCl6−
SPh
S+
+
(1.0 equiv)
− SMe2
+ SMe2
SbCl6−
(±)-5b+SbCl6−
31P NMR: 69.3 ppm
2.21
2.14
1.13
1.07
2.45
3.32
1.93
2.06
1.84
2.17
3.18
3.17
5.81
12.64
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)



^{31}P NMR: 69.3 ppm


SbCl$_6^-$
(±)-**3b**
(1.0 equiv)
+
SbCl$_6^-$
SPh
S+
(5.0 equiv)
− SMe$_2$
+ SMe$_2$
^{31}P NMR: 66.4 ppm
(±)-**5b**$^+$SbCl$_6^-$
N
S
P
2.05
2.00
1.13
1.19
24.14
2.09
1.39
2.03
2.02
3.05
2.96
29.64
12.42
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

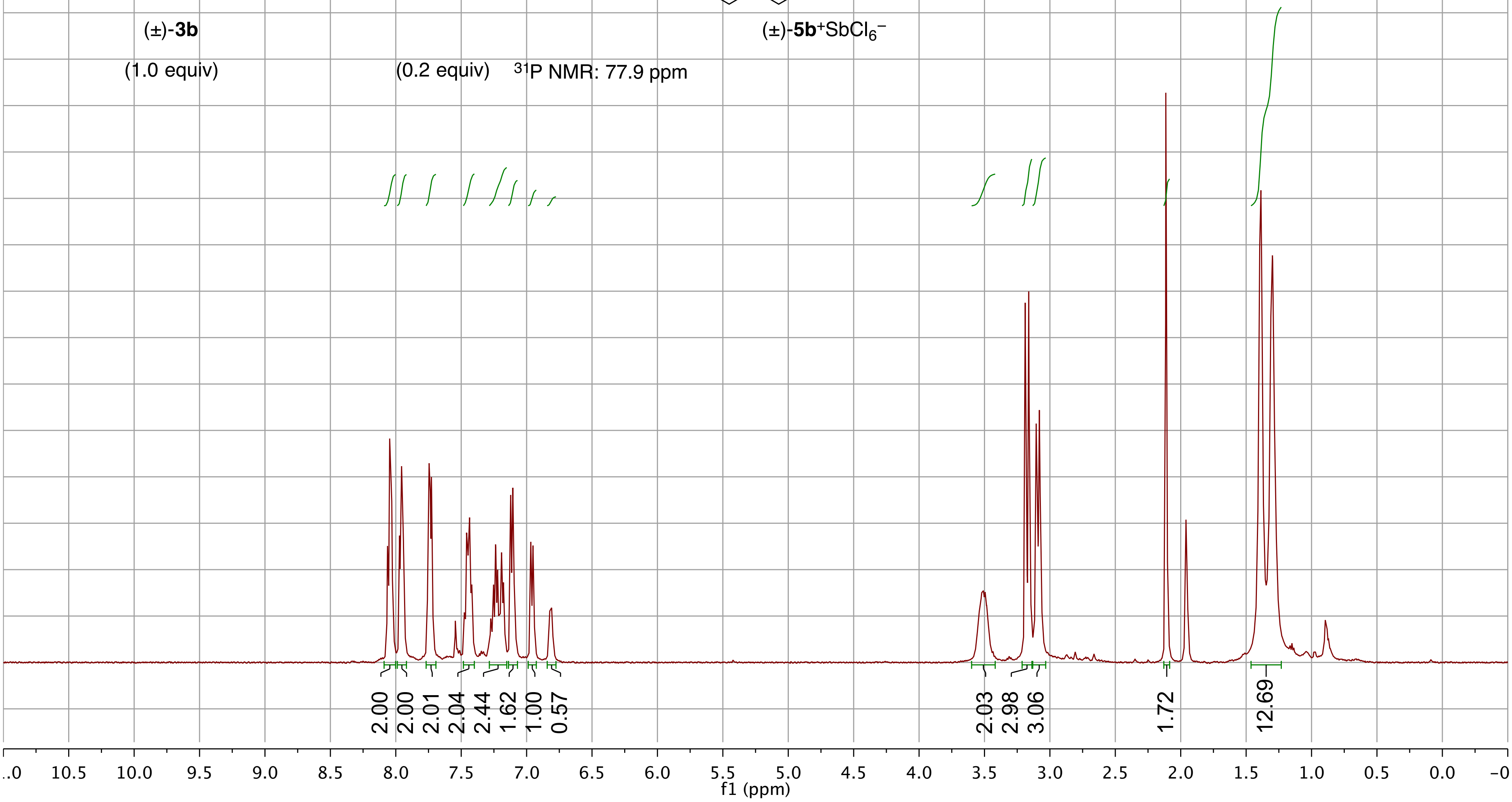

66.4
SbCl$_6^-$
SPh
S$^+$
+
– SMe$_2$
+ SMe$_2$
(±)-**3b**
(1.0 equiv)
(5.0 equiv)
^{31}P NMR: 66.4 ppm
(±)-**5b**$^+$SbCl$_6^-$
N
P
S
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
f1 (ppm)

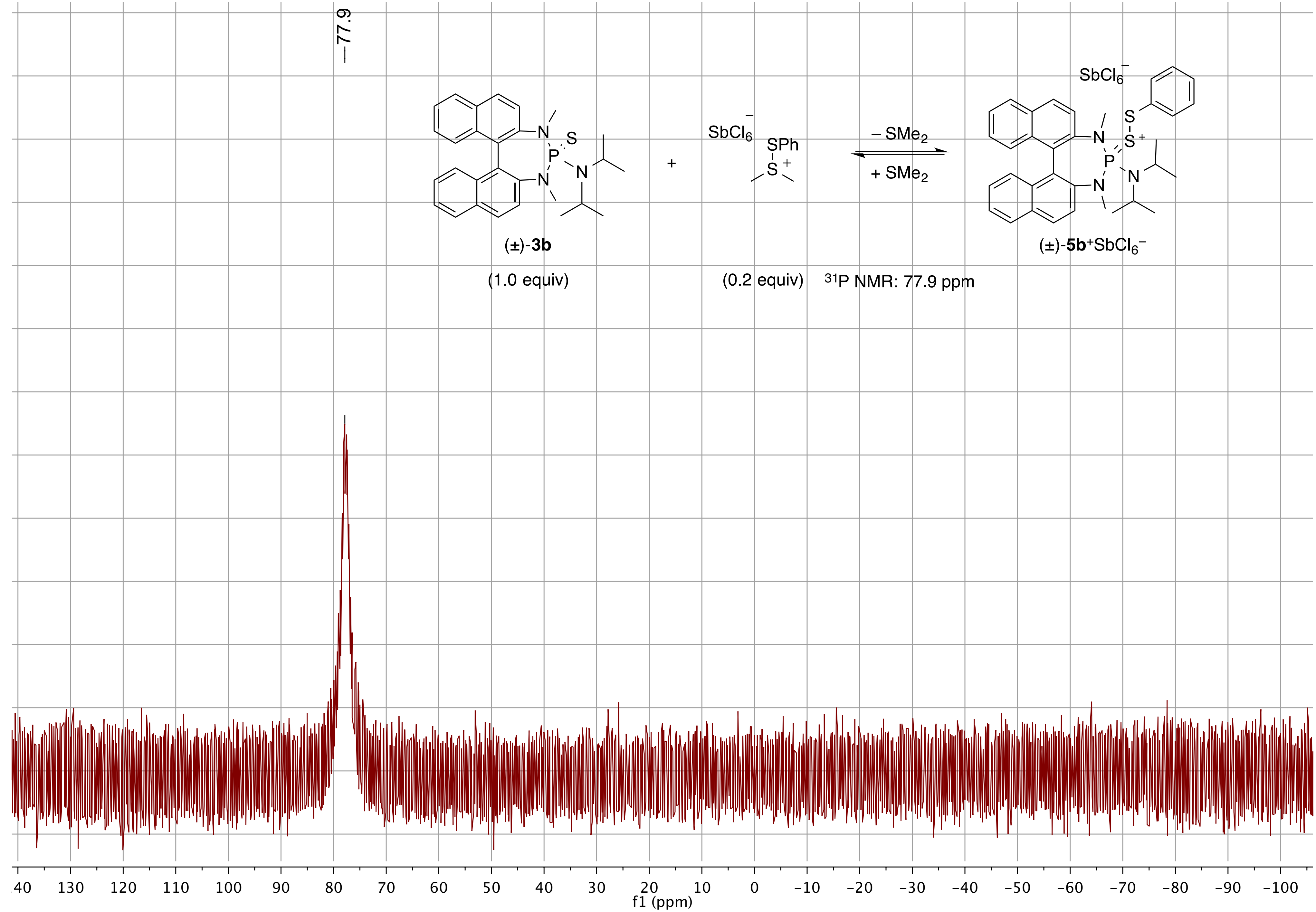


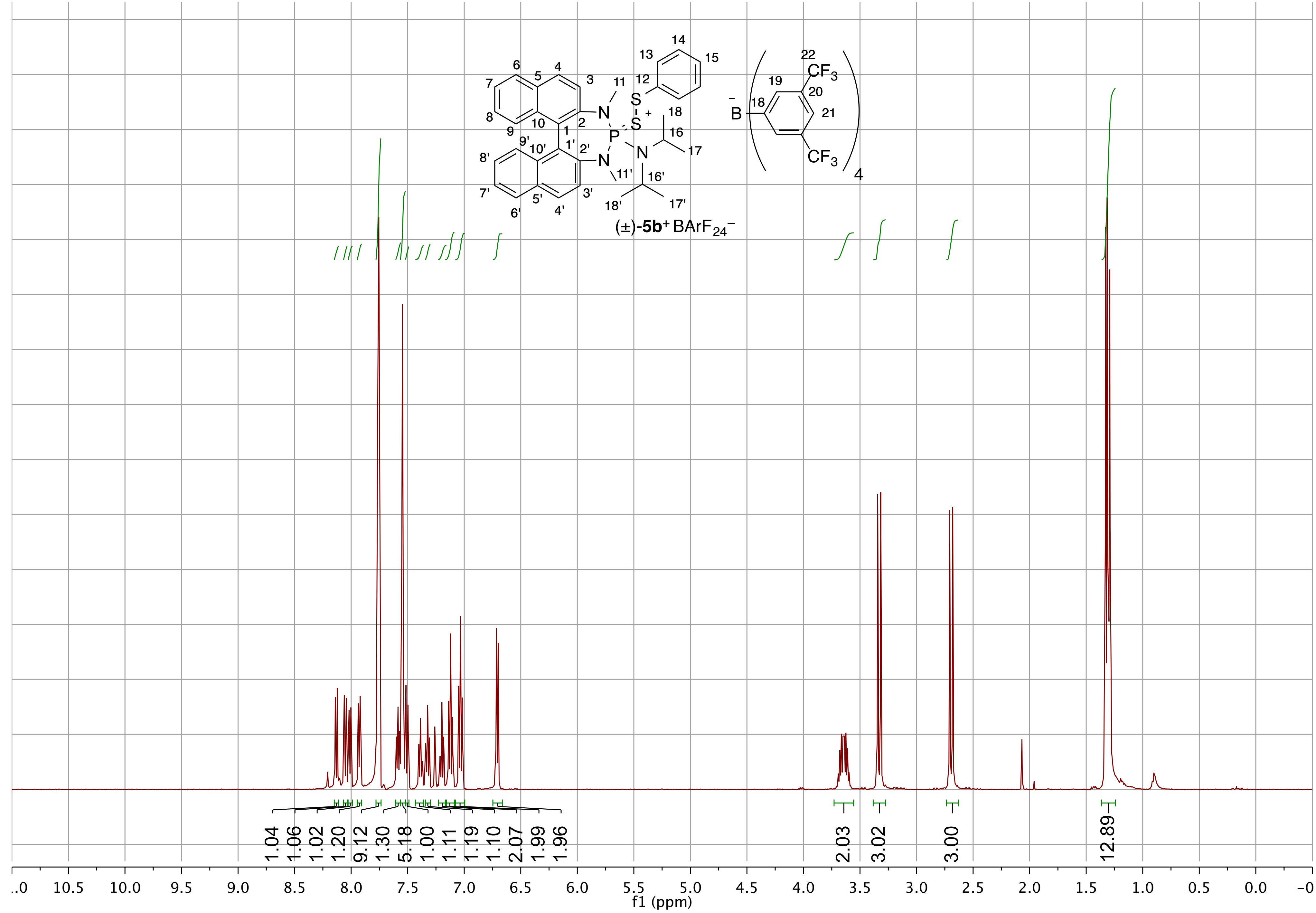
(1.0 equiv)

(0.2 equiv)

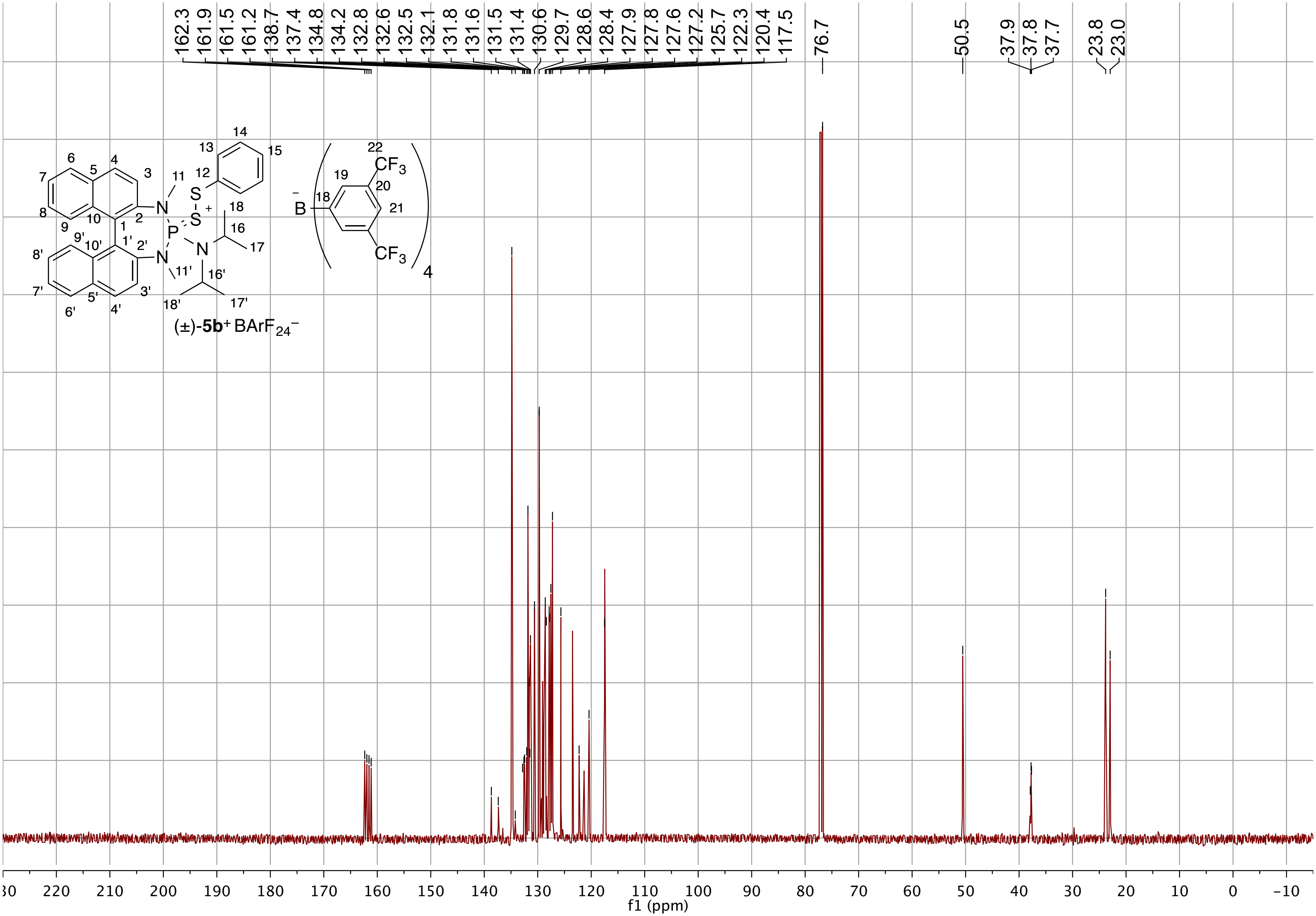
^{31}P NMR: 77.9 ppm



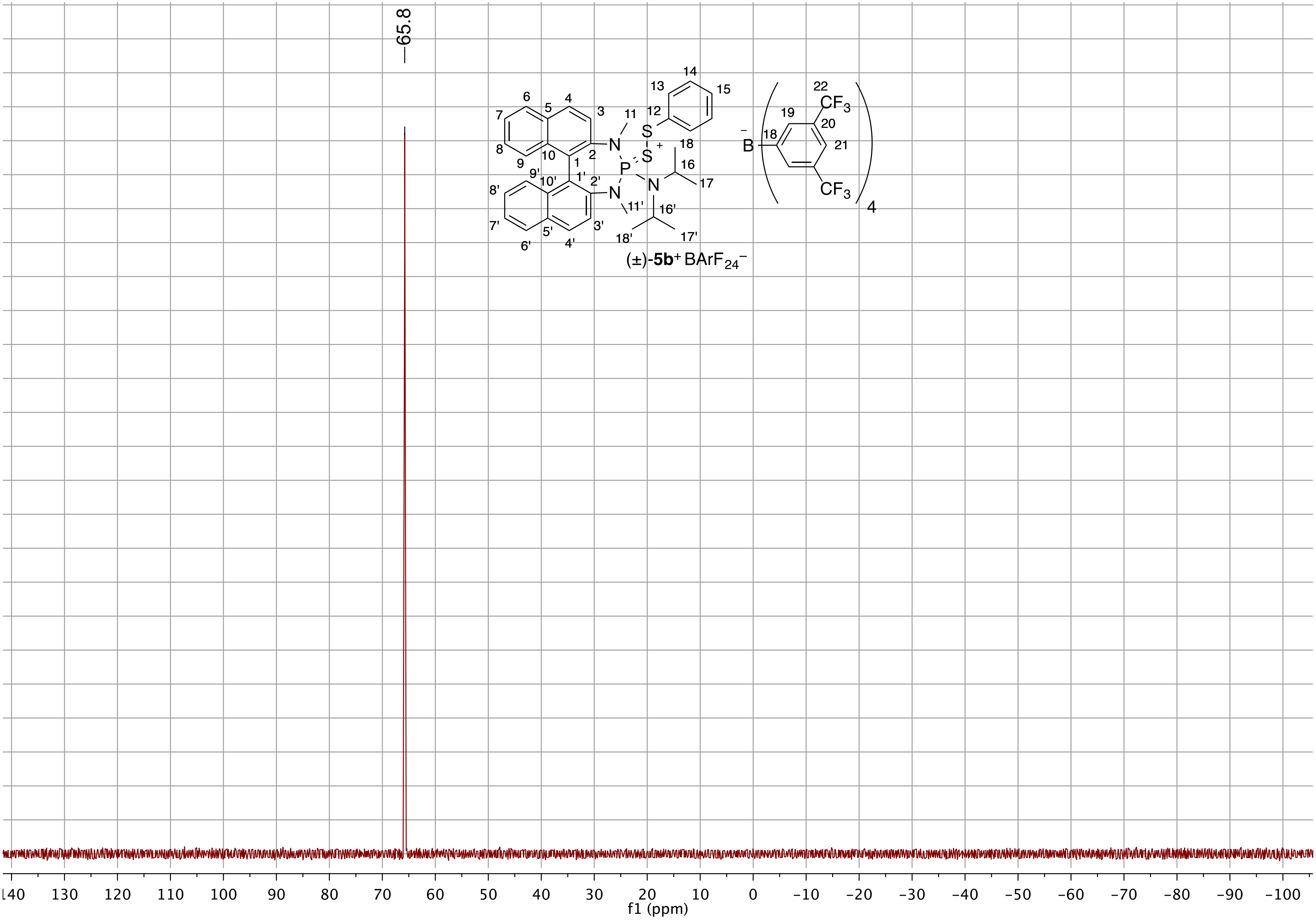

—77.9
(±)-**3b**
(1.0 equiv)
+
$SbCl_6^-$
SPh
S^+
(0.2 equiv)
– SMe_2
+ SMe_2
$SbCl_6^-$
S
S^+
P
N
(±)-**5b**$^+$$SbCl_6^-$
^{31}P NMR: 77.9 ppm
40
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
–20
–30
–40
–50
–60
–70
–80
–90
–100
f1 (ppm)


6
4
5
3
7
11
12
13
14
15
8
10
2
1
9
9'
10'
1'
2'
8'
7'
6'
5'
4'
3'
11'
16
16'
17
17'
18
18'
S
S
+
P
N
N
N
N
B
−
CF$_3$
CF$_3$
19
20
21
22
18
4
1.04
1.06
1.02
1.20
9.12
1.30
5.18
1.00
1.11
1.19
1.10
2.07
1.99
1.96
2.03
3.02
3.00
12.89
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

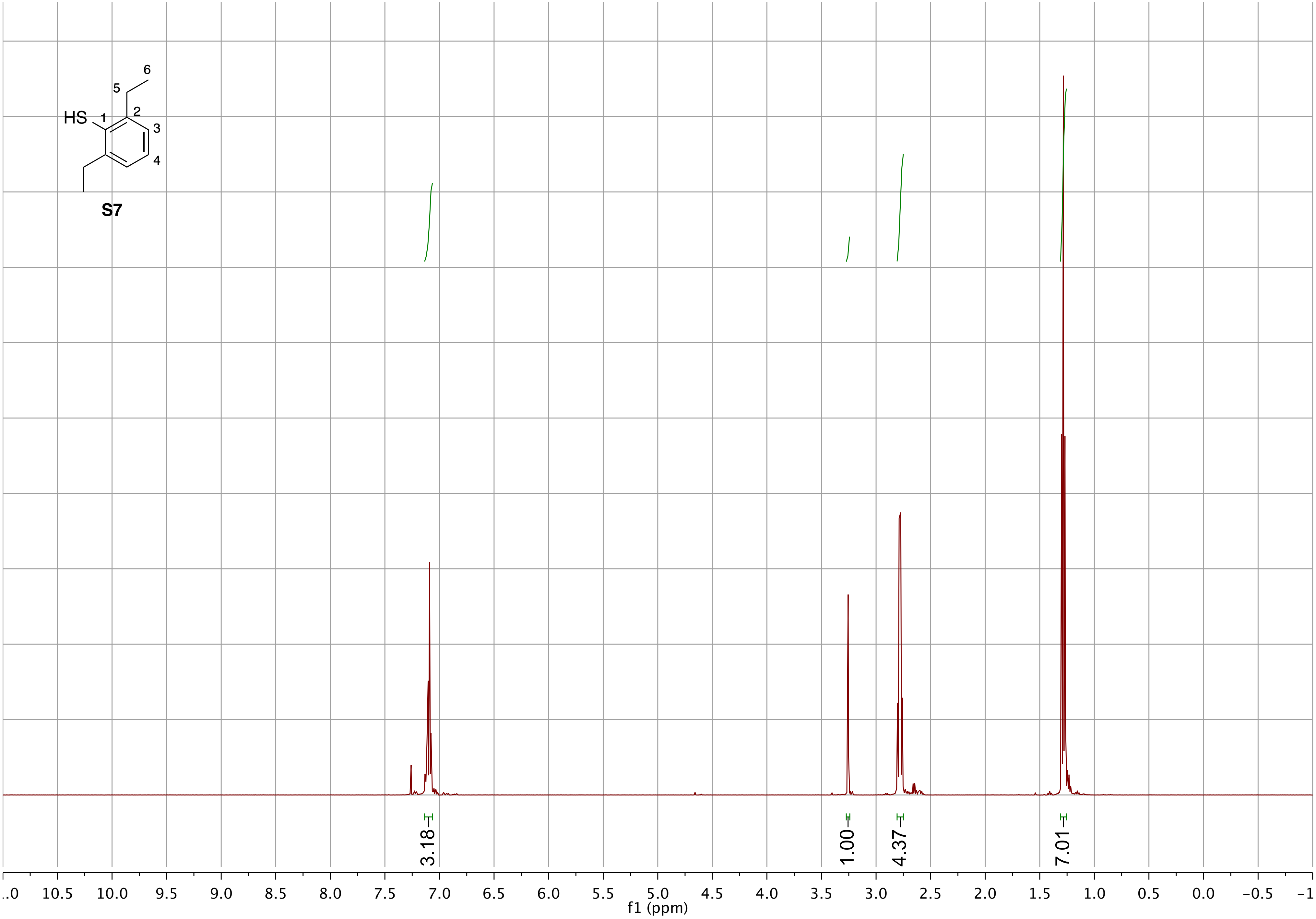
$(\pm)$-**5b**$^+$ BArF$_{24}^-$


162.3
161.9
161.5
161.2
138.7
137.4
134.8
134.2
132.8
132.6
132.5
132.1
131.8
131.6
131.5
131.4
130.6
129.7
128.6
128.4
127.9
127.8
127.6
127.2
125.7
122.3
120.4
117.5
76.7
50.5
37.9
37.8
37.7
23.8
23.0
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
S
S
P
N
N
N
B
CF3
CF3
4

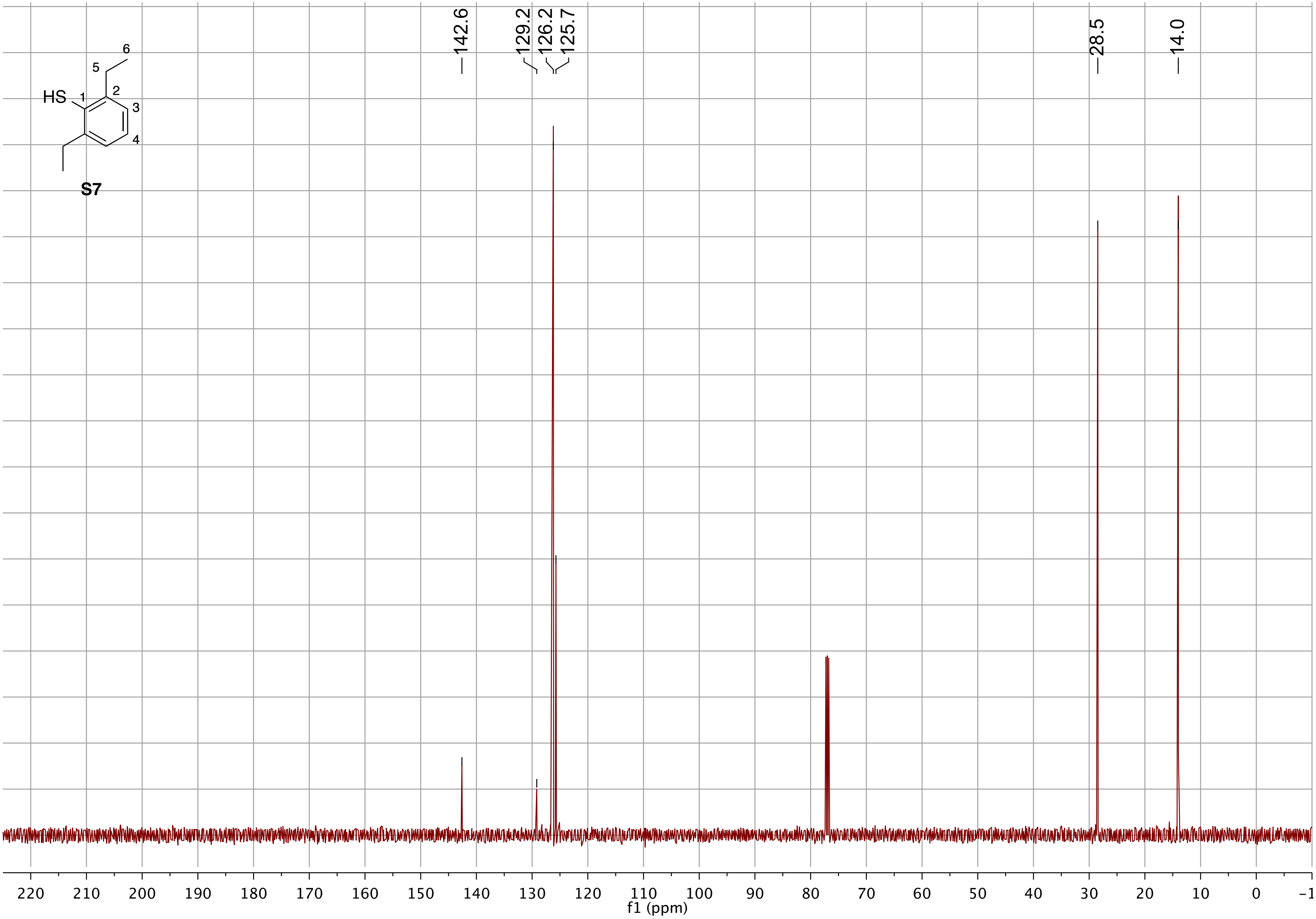
(±)-**5b**+ BArF24−



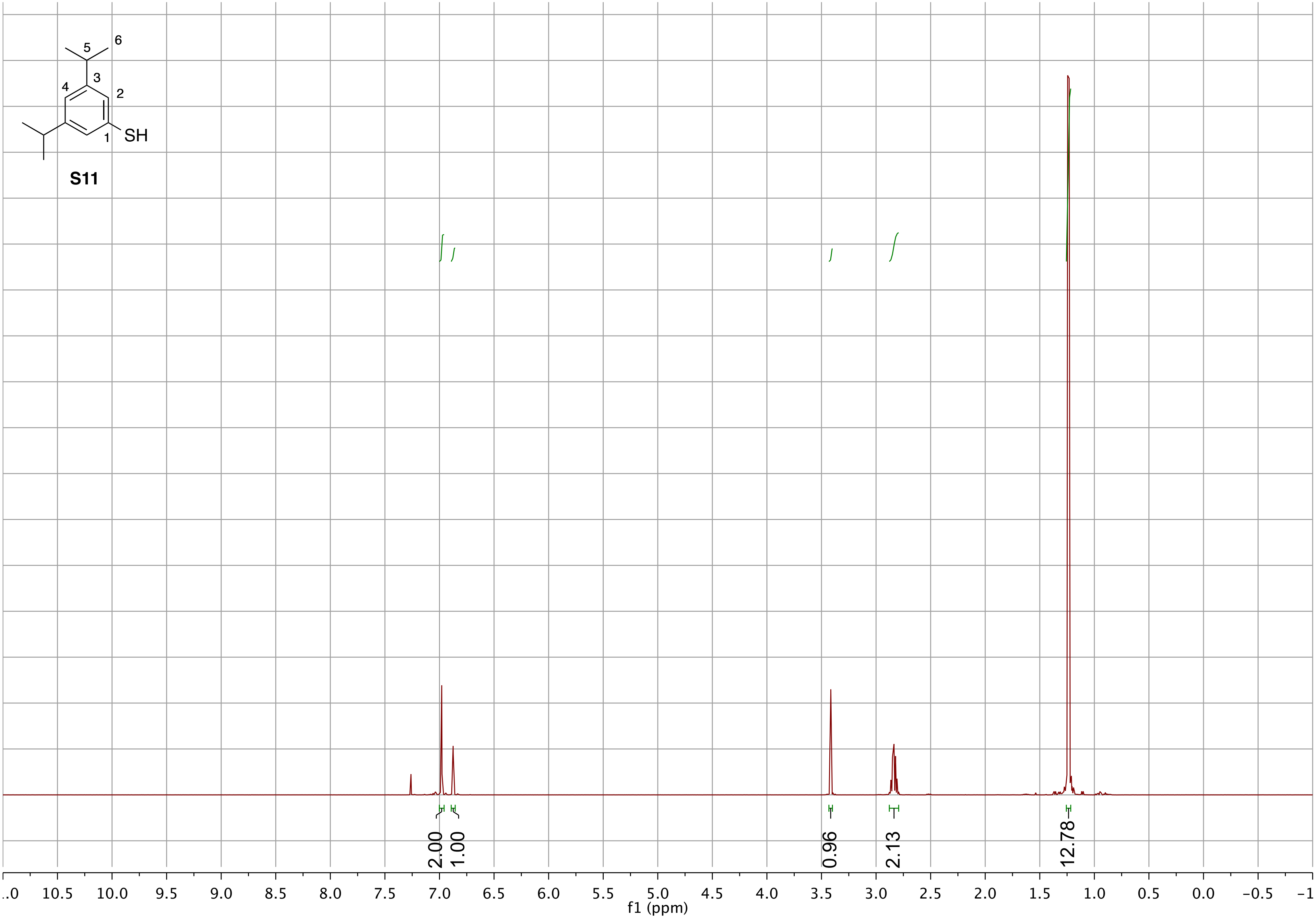
—65.8
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
f1 (ppm)
(±)-5b+ BArF24−



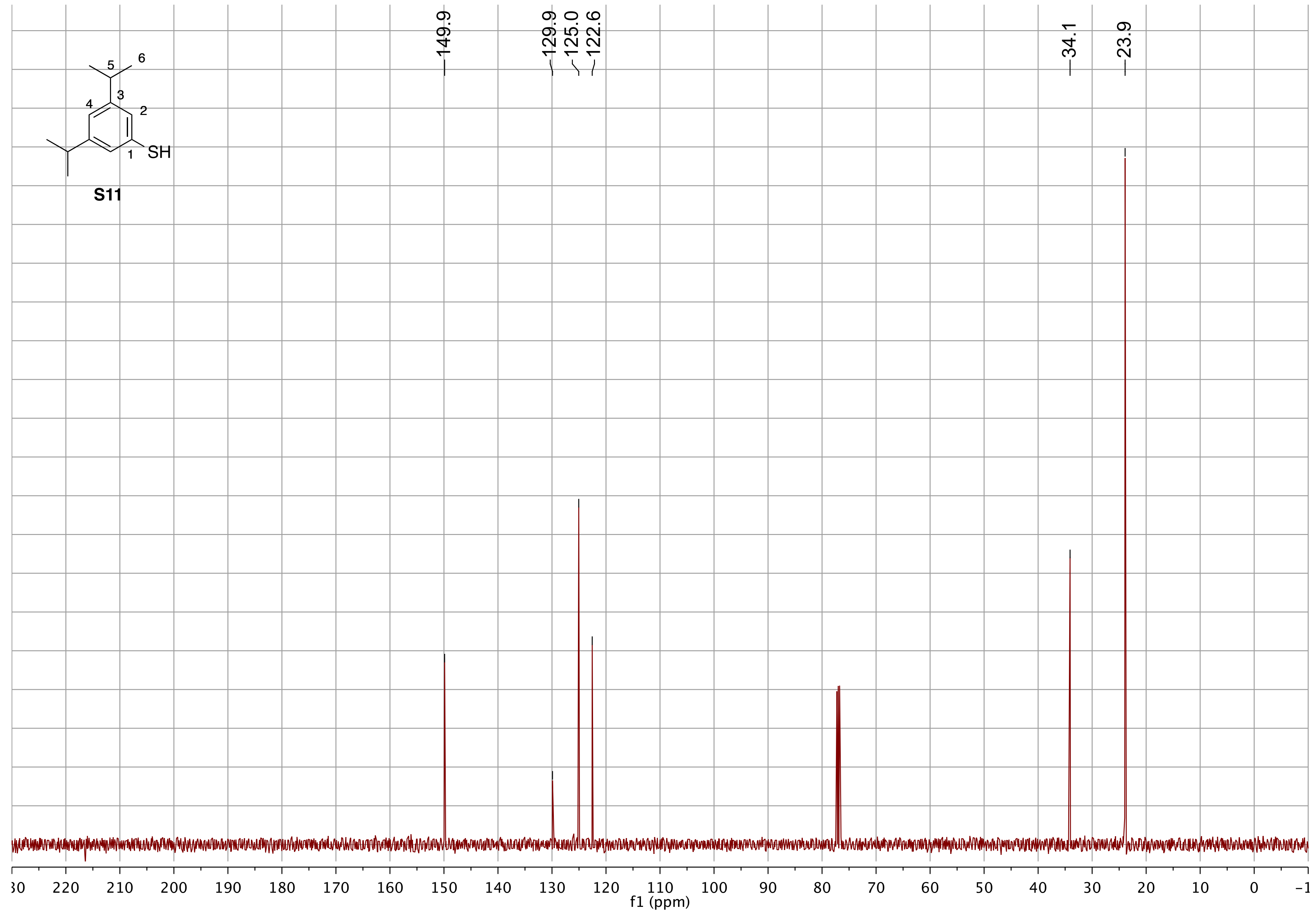
HS
1
2
3
4
5
6
S7
3.18
1.00
4.37
7.01
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

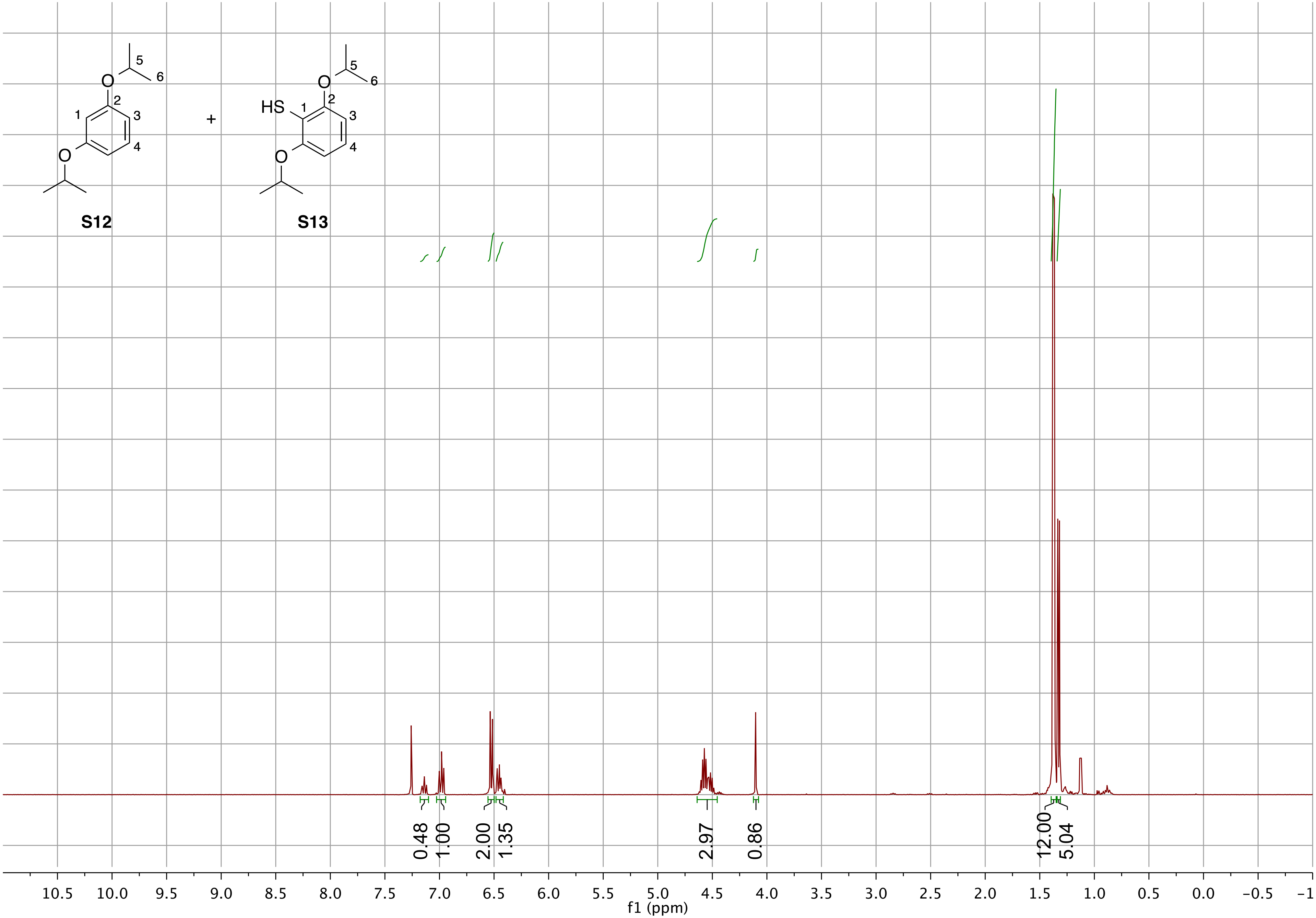


142.6
129.2
126.2
125.7
28.5
14.0
HS
1
2
3
4
5
6
S7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)

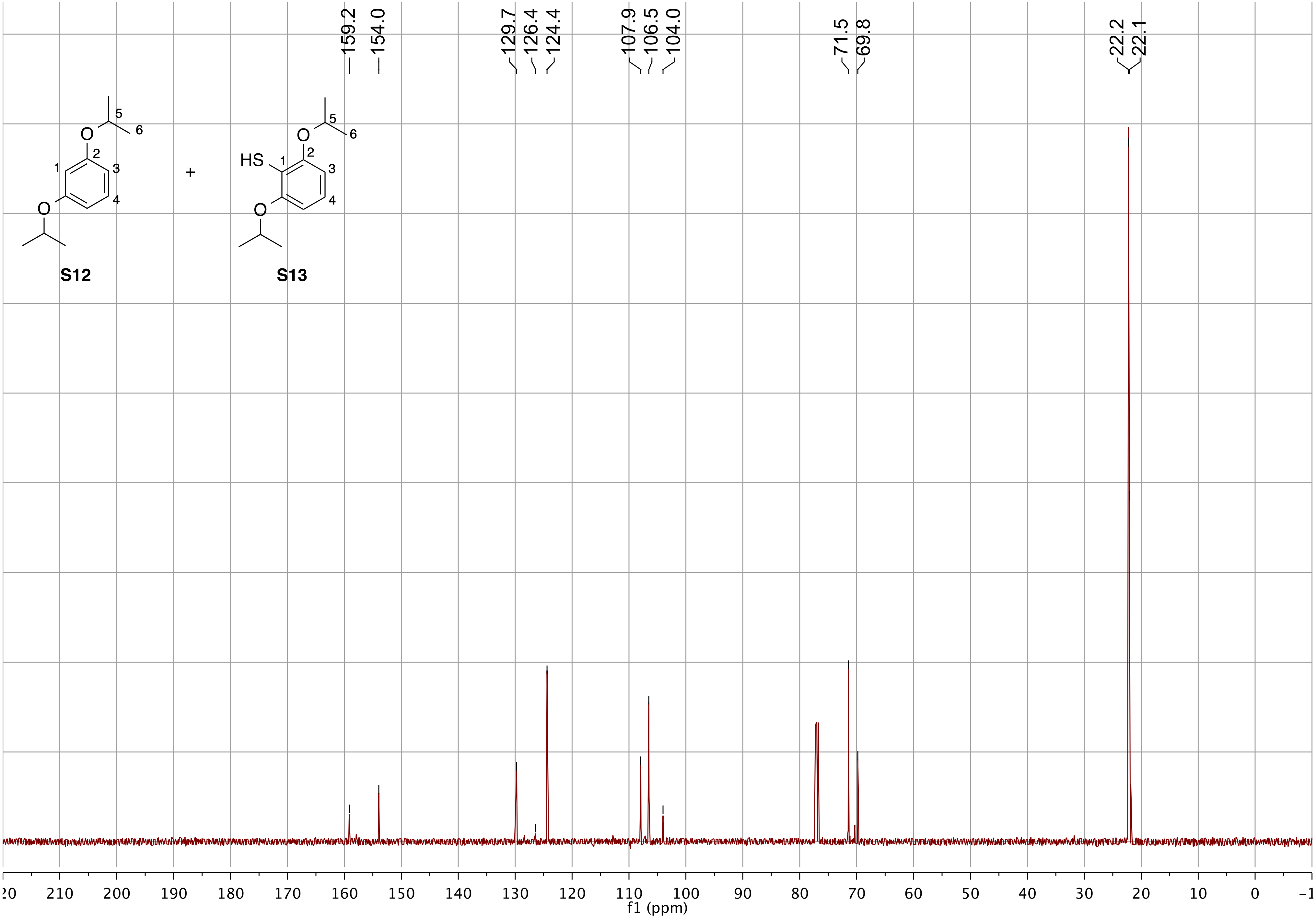


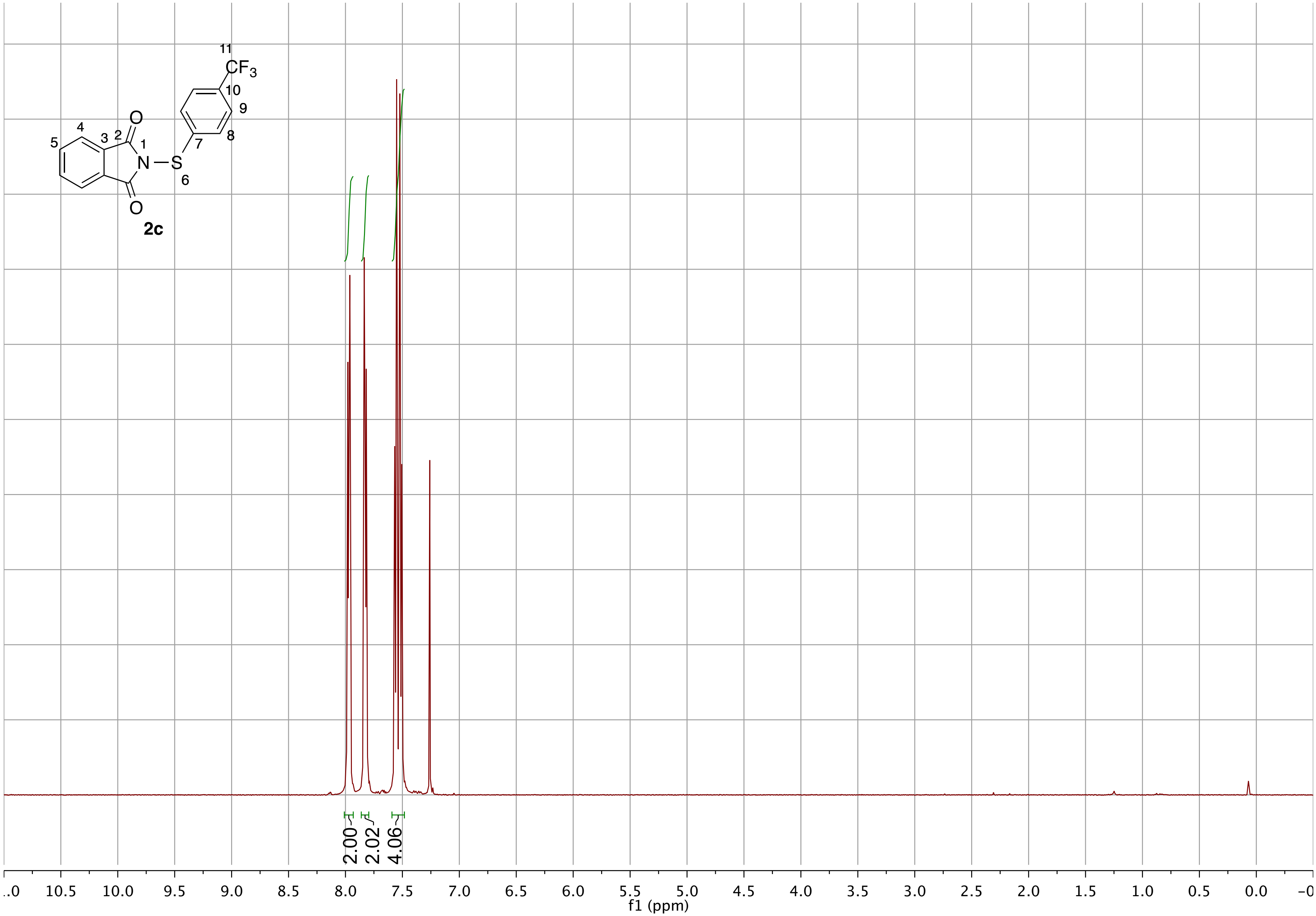
6
5
3
4
2
1
SH
S11
2.00
1.00
0.96
2.13
12.78
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
–1
f1 (ppm)


149.9
129.9
125.0
122.6
34.1
23.9
5
6
3
4
2
1
SH
S11
30
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)

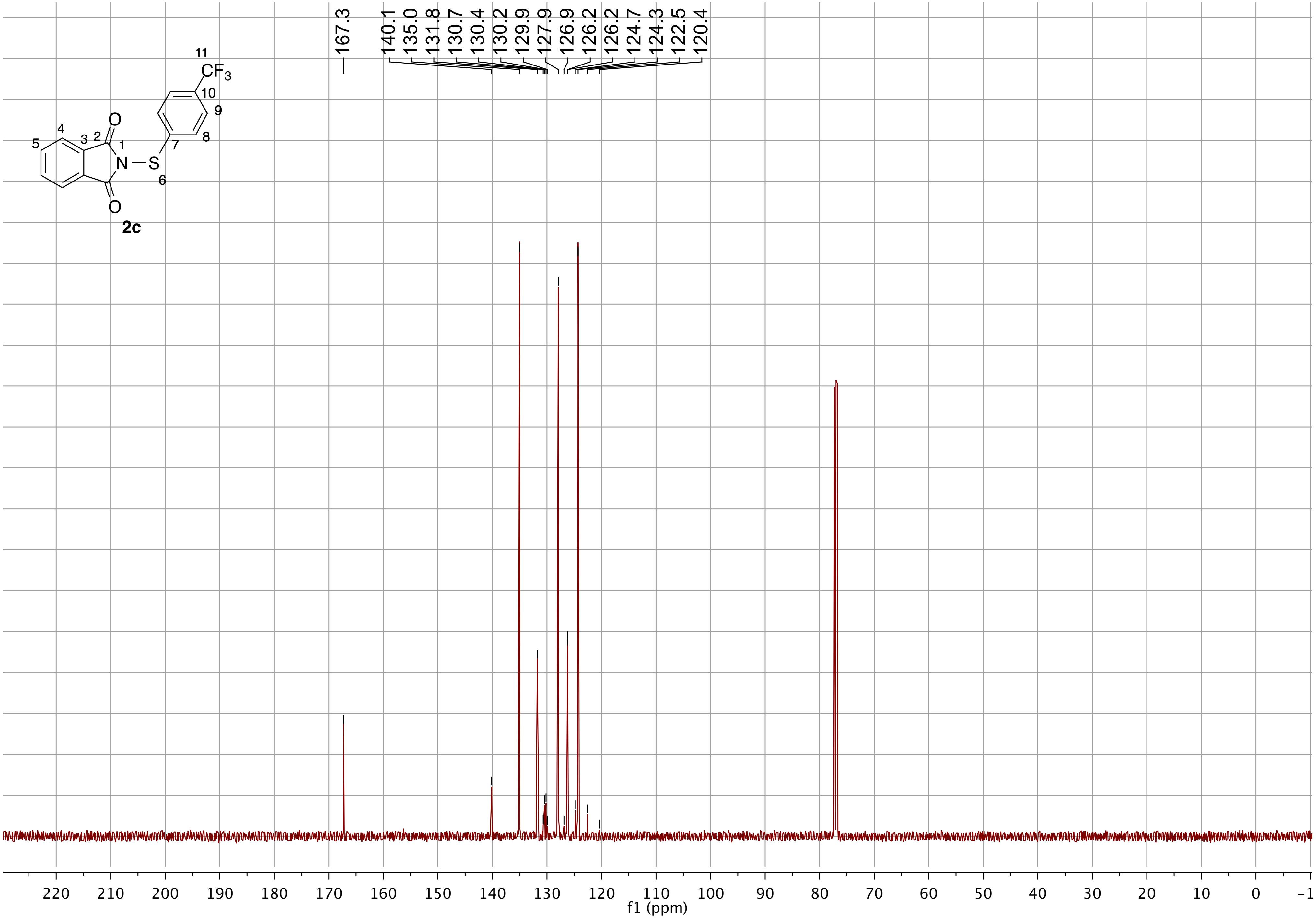


S12
S13
HS
O
1
2
3
4
5
6
+
0.48
1.00
2.00
1.35
2.97
0.86
12.00
5.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

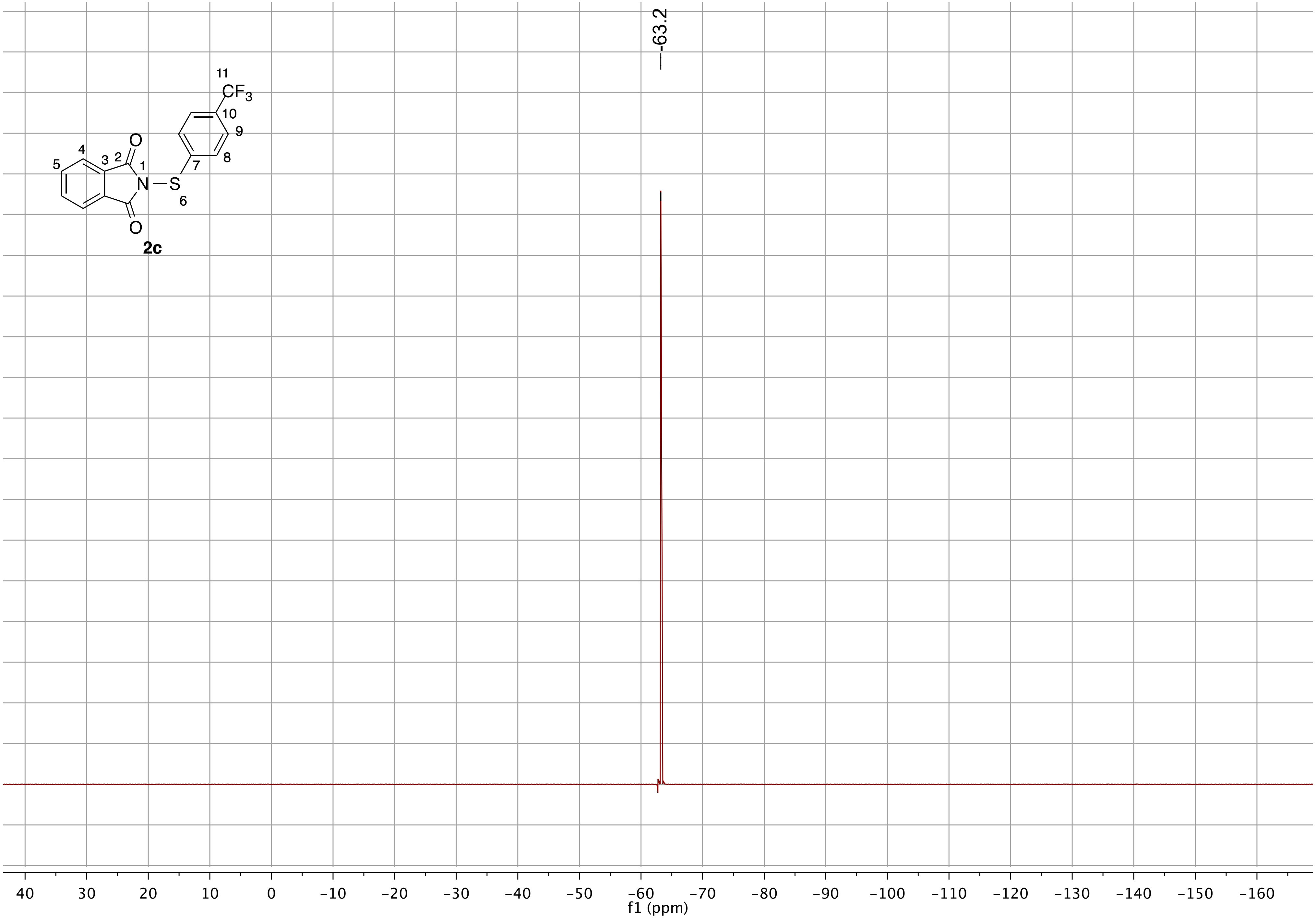

S12
S13
HS
O
1
2
3
4
5
6
+
159.2
154.0
129.7
126.4
124.4
107.9
106.5
104.0
71.5
69.8
22.2
22.1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

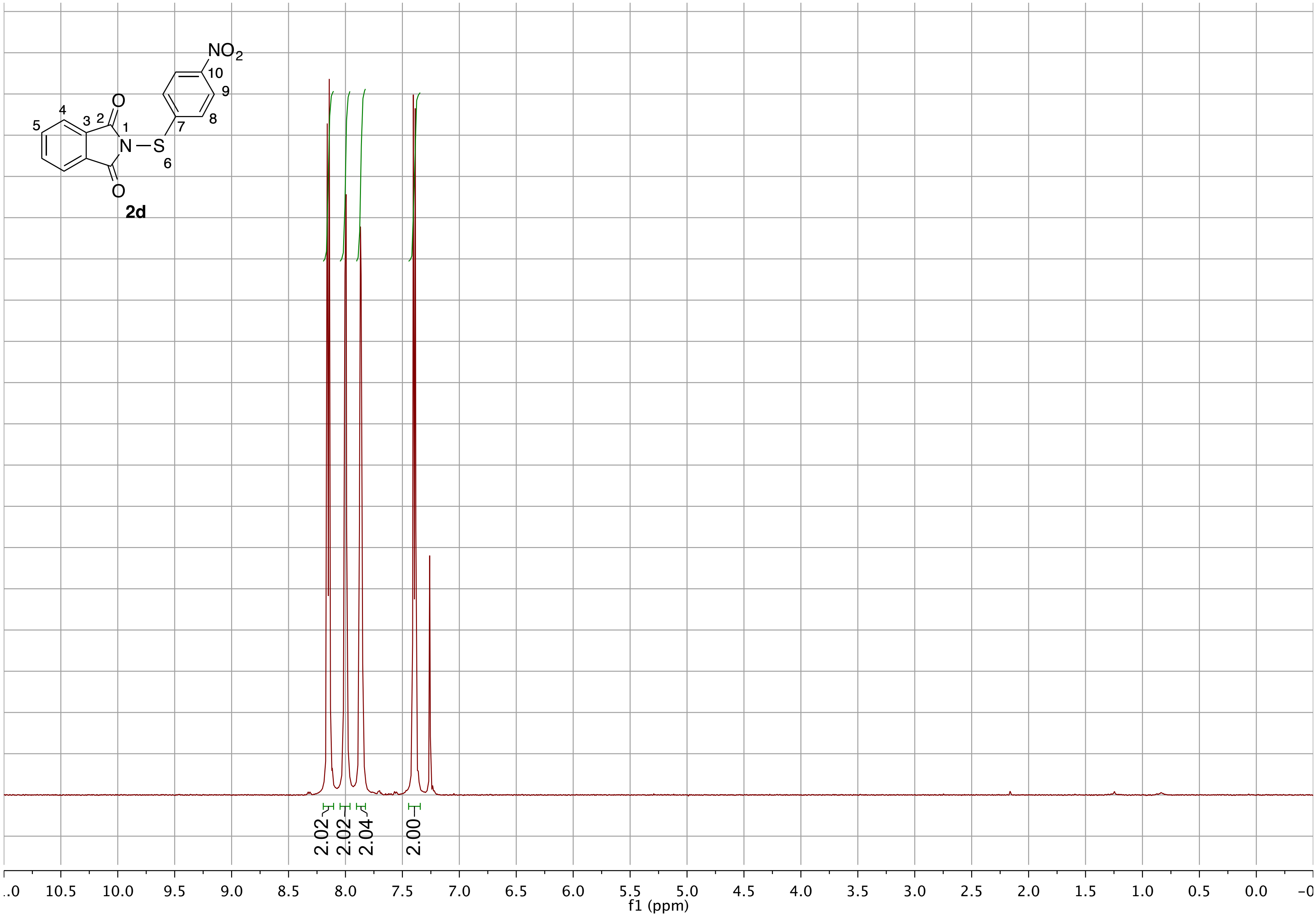


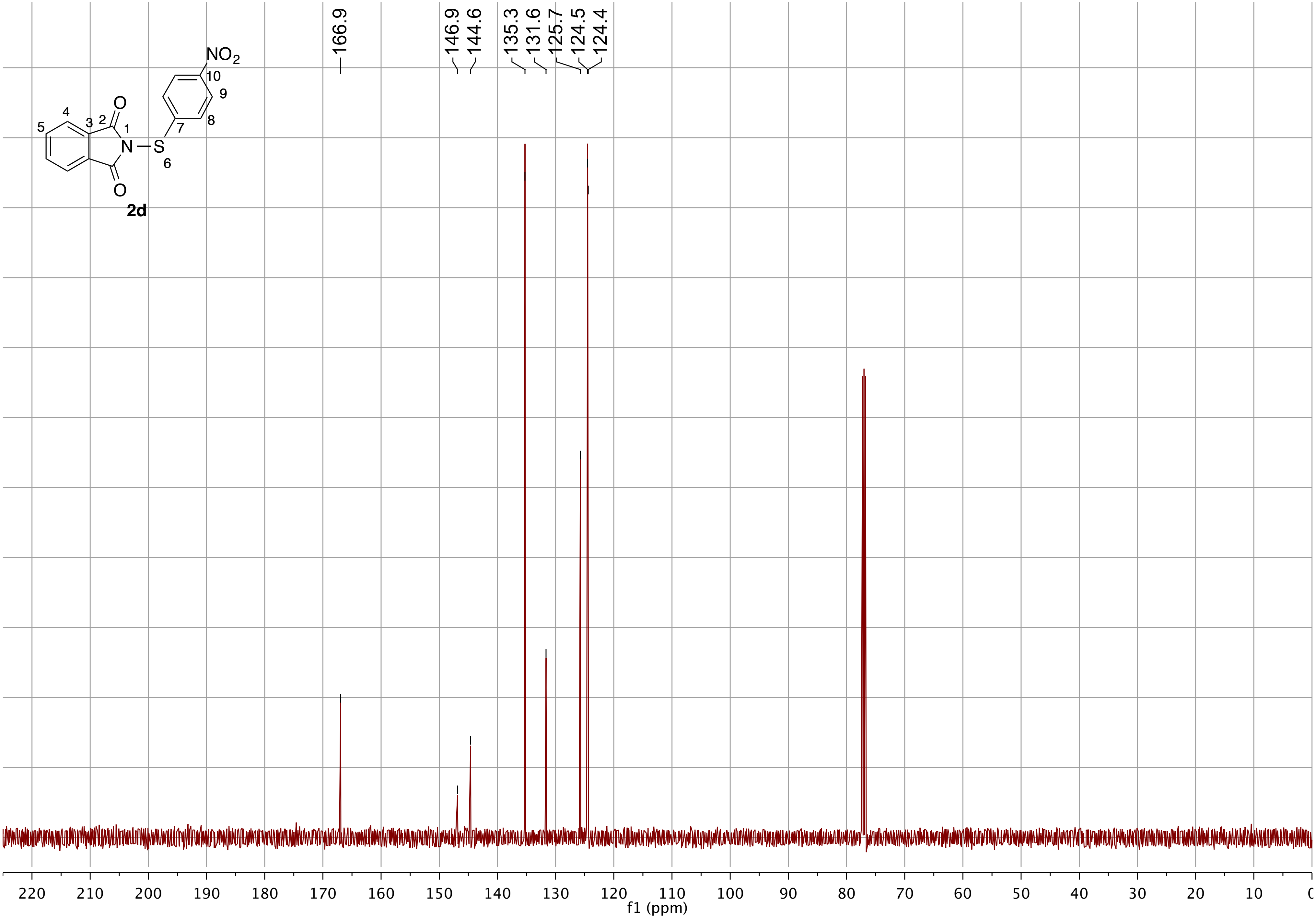
11
CF3
10
9
8
7
O
O
N
S
6
1
2
3
4
5
2c
2.00
2.02
4.06
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)


167.3
140.1
135.0
131.8
130.7
130.4
130.2
129.9
127.9
126.9
126.2
126.2
124.7
124.3
122.5
120.4
11
CF_3
10
9
8
7
O
O
N
S
6
1
2
3
4
5
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)

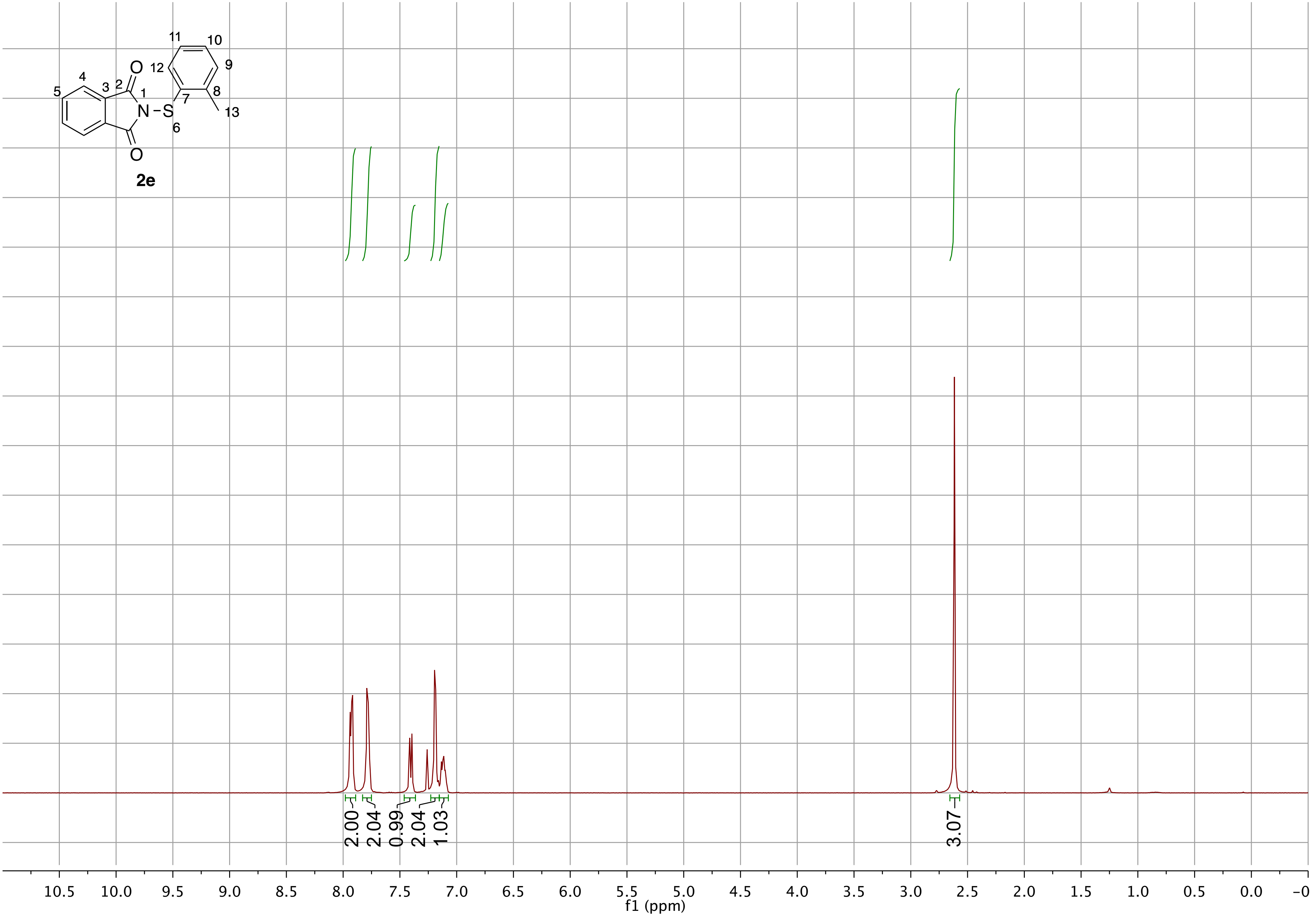
2c


-63.2
2c
11
CF3
10
9
8
7
6
S
N
1
2
3
4
5
O
O
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)

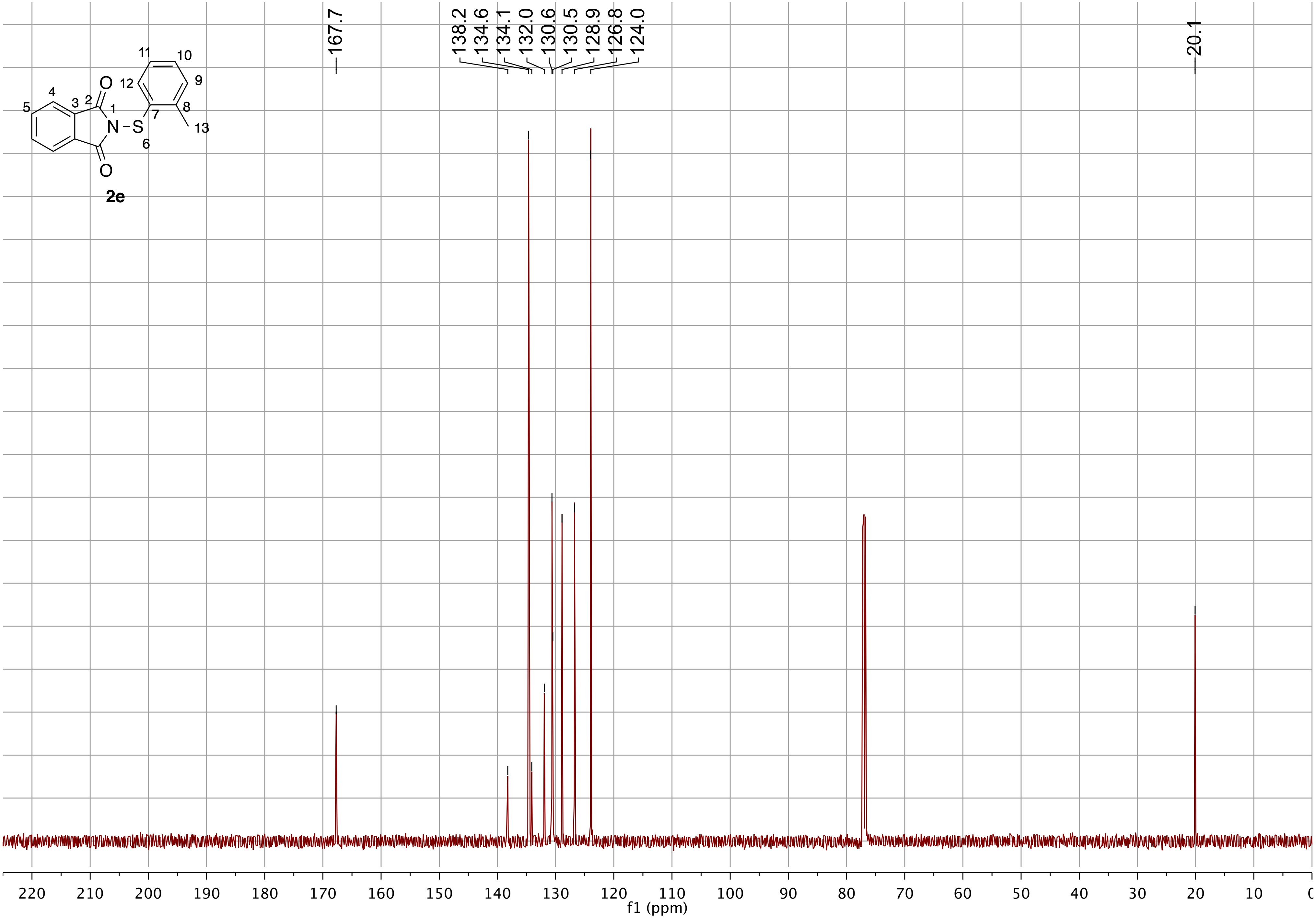

NO2
10
9
8
7
O
4
5
3
2
1
N
S
6
O
2d
2.02
2.02
2.04
2.00
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)



NO2
10
9
8
7
6
S
N
1
2
3
4
5
O
O
2d
166.9
146.9
144.6
135.3
131.6
125.7
124.5
124.4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

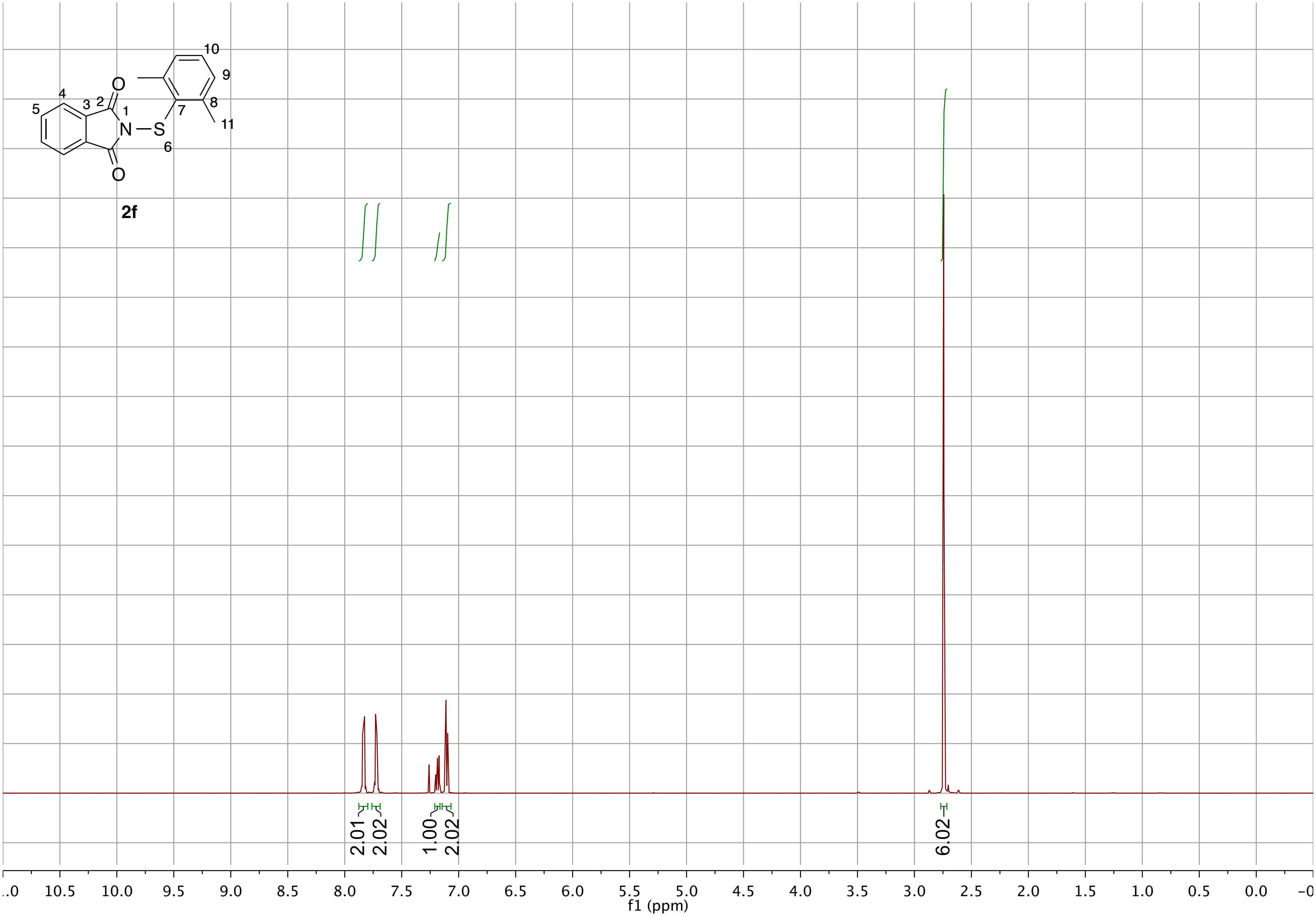


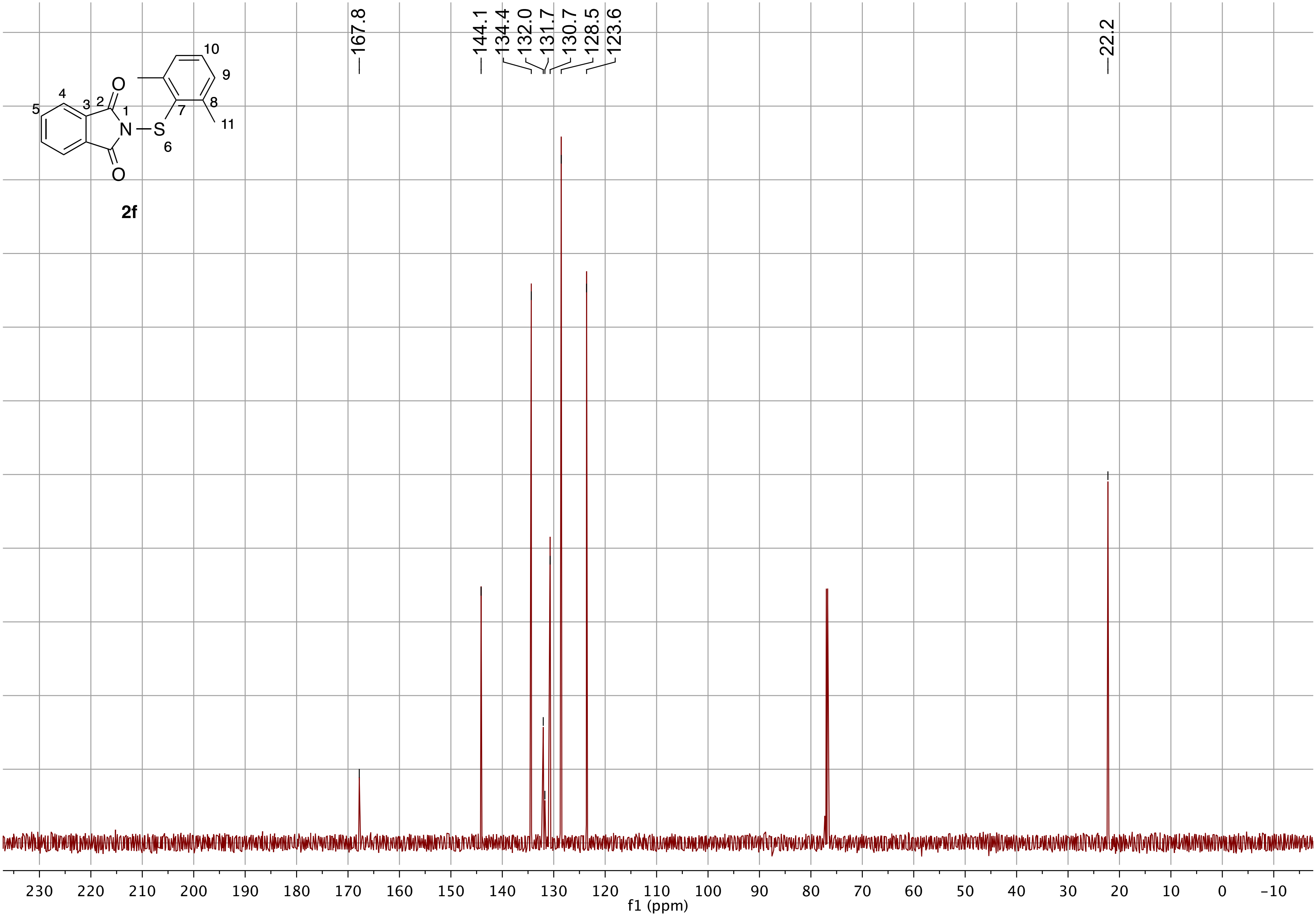
2e
2.00
2.04
0.99
2.04
1.03
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)



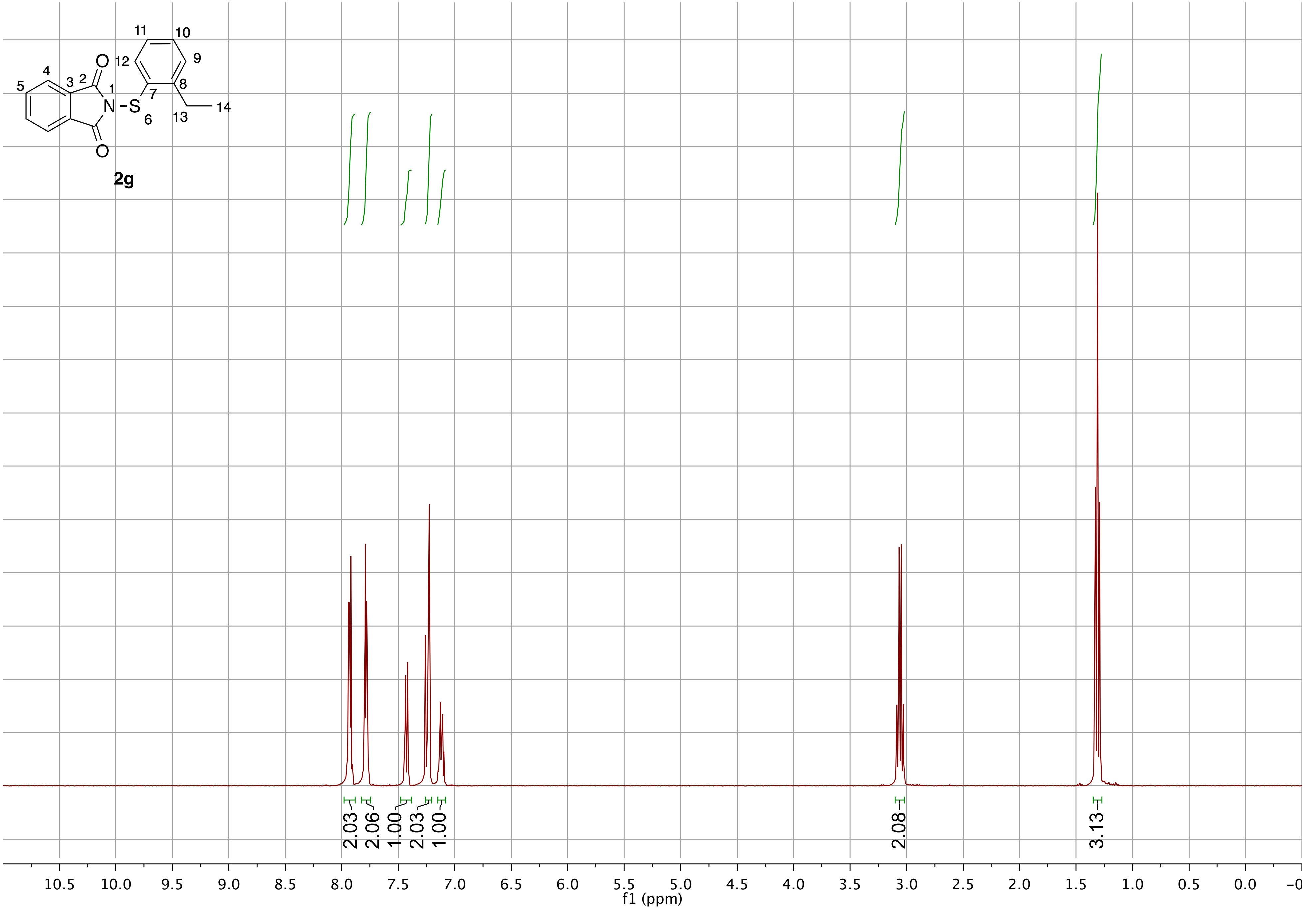
167.7
138.2
134.6
134.1
132.0
130.6
130.5
128.9
126.8
124.0
20.1
O
O
N
S
1
2
3
4
5
6
7
8
9
10
11
12
13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2e


10
9
4
5
3
2
1
8
7
11
6
O
O
N
S
2f
2.01
2.02
1.00
2.02
6.02
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

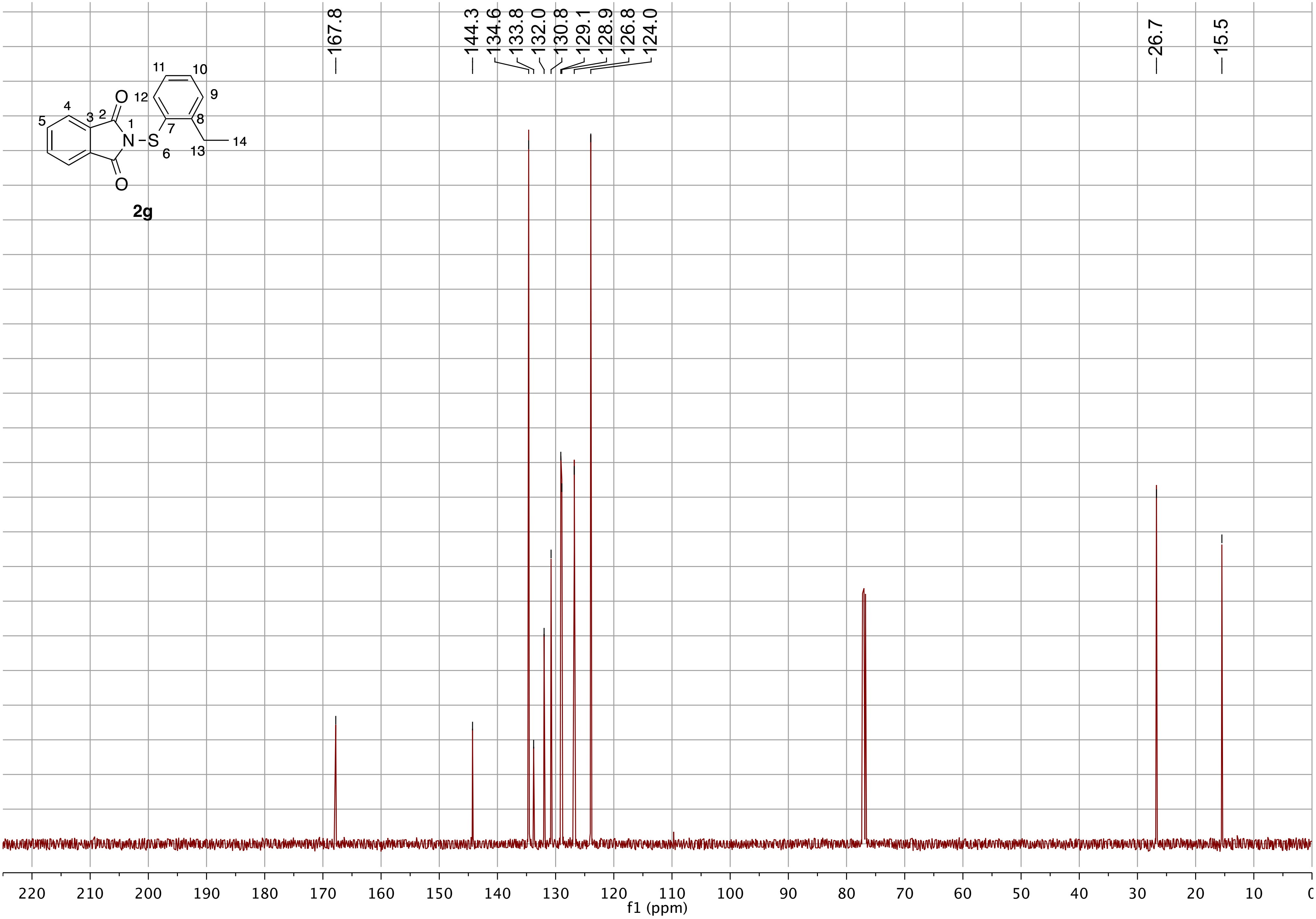


10
9
8
11
7
6
5
4
3
2
1
O
N
S
O
2f
167.8
144.1
134.4
132.0
131.7
130.7
128.5
123.6
22.2
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



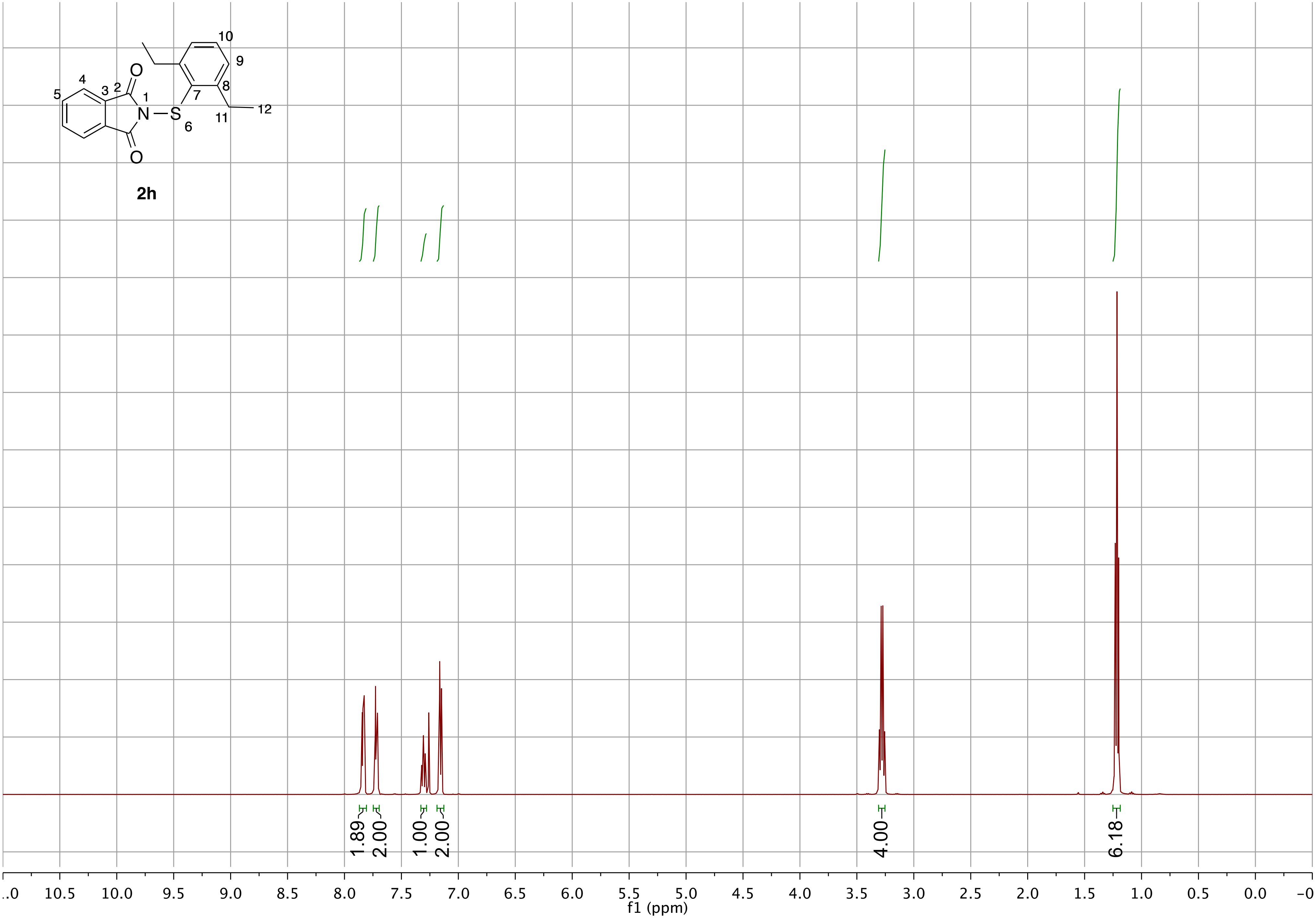
2g

1
2
3
4
5
6
7
8
9
10
11
12
13
14
O
O
N
S
2.03
2.06
1.00
2.03
1.00
2.08
3.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



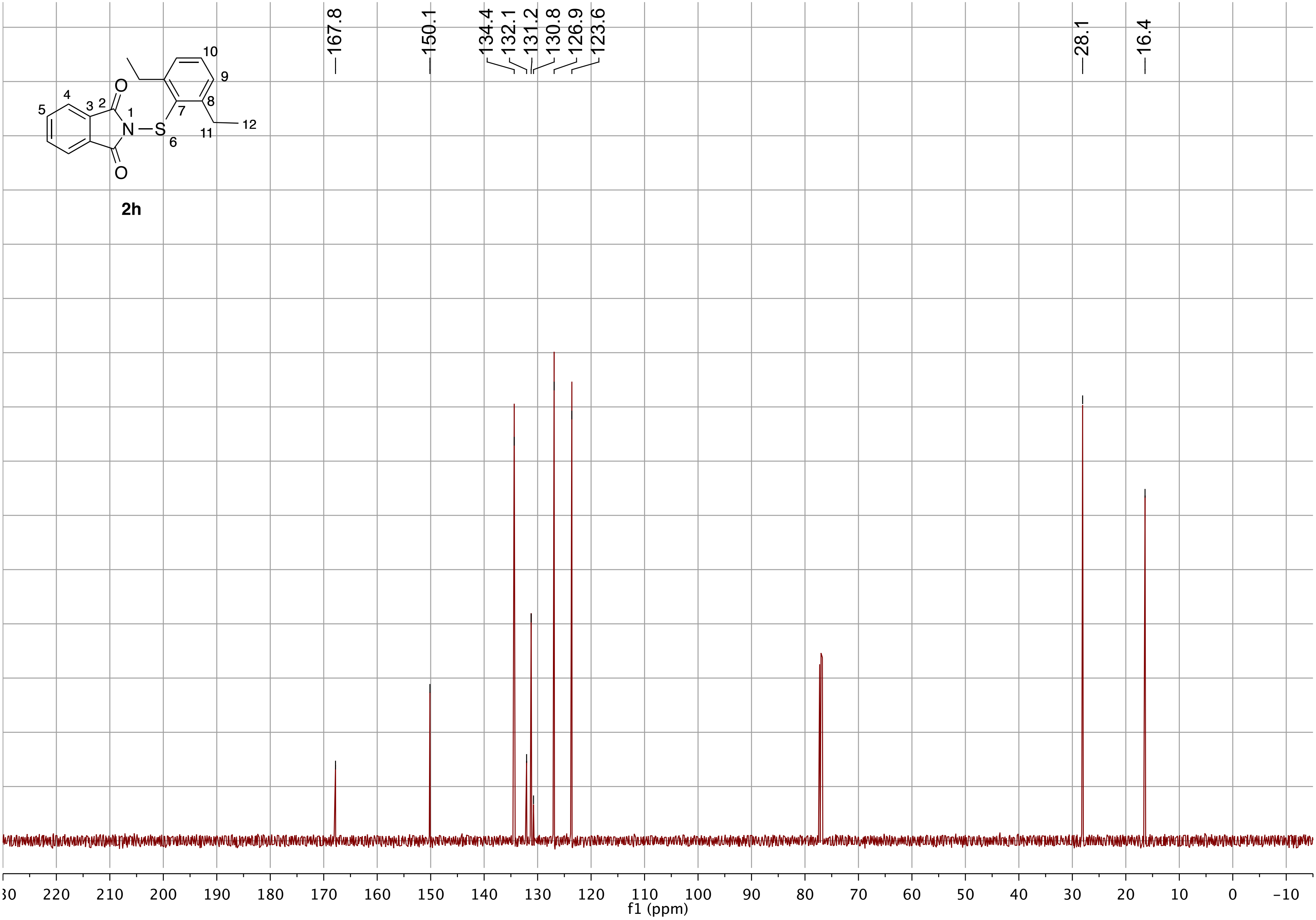
2g

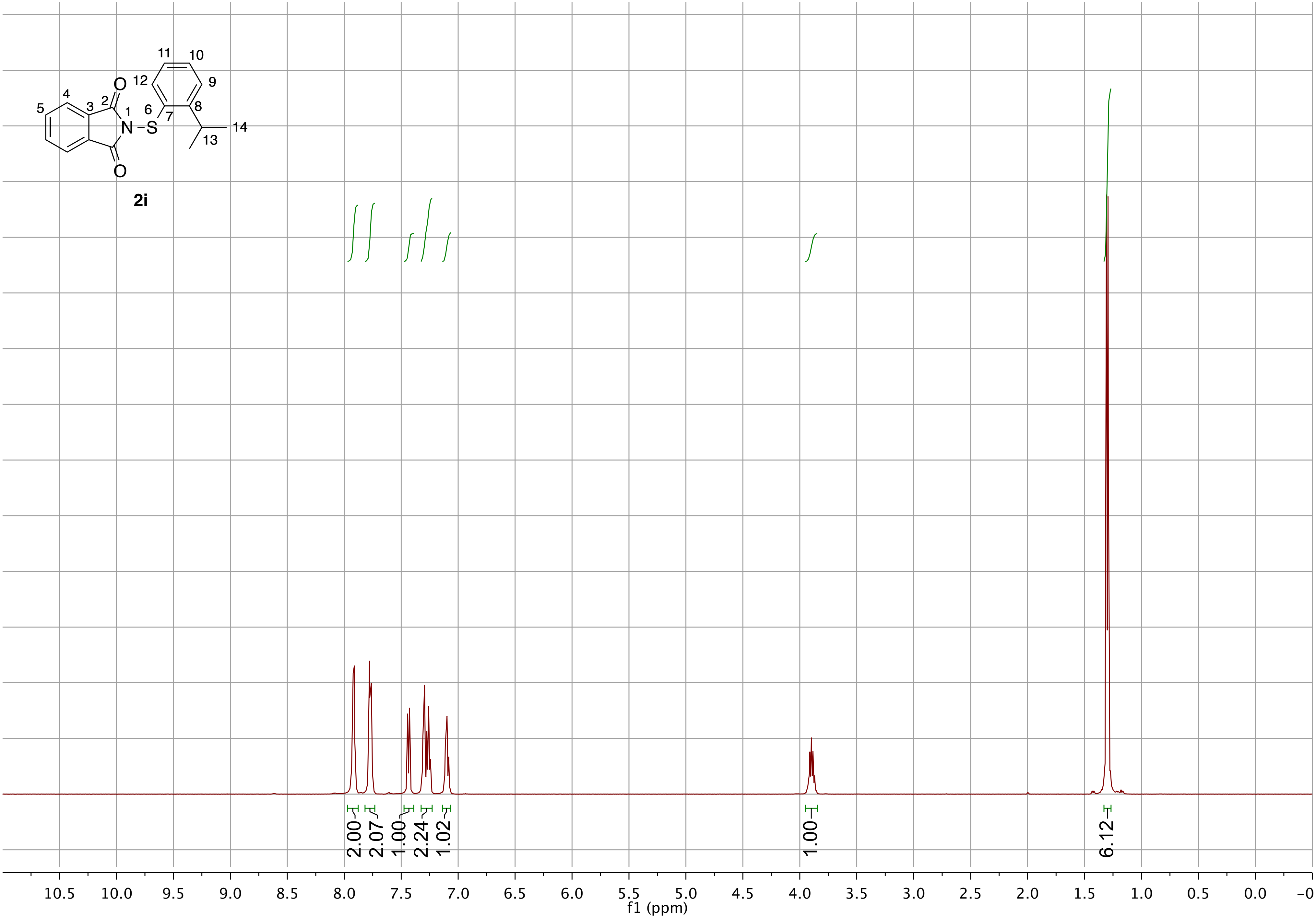
167.8
144.3
134.6
133.8
132.0
130.8
129.1
128.9
126.8
124.0
26.7
15.5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


2h
1
2
3
4
5
6
7
8
9
10
11
12
N
S
O
O
1.89
2.00
1.00
2.00
4.00
6.18
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

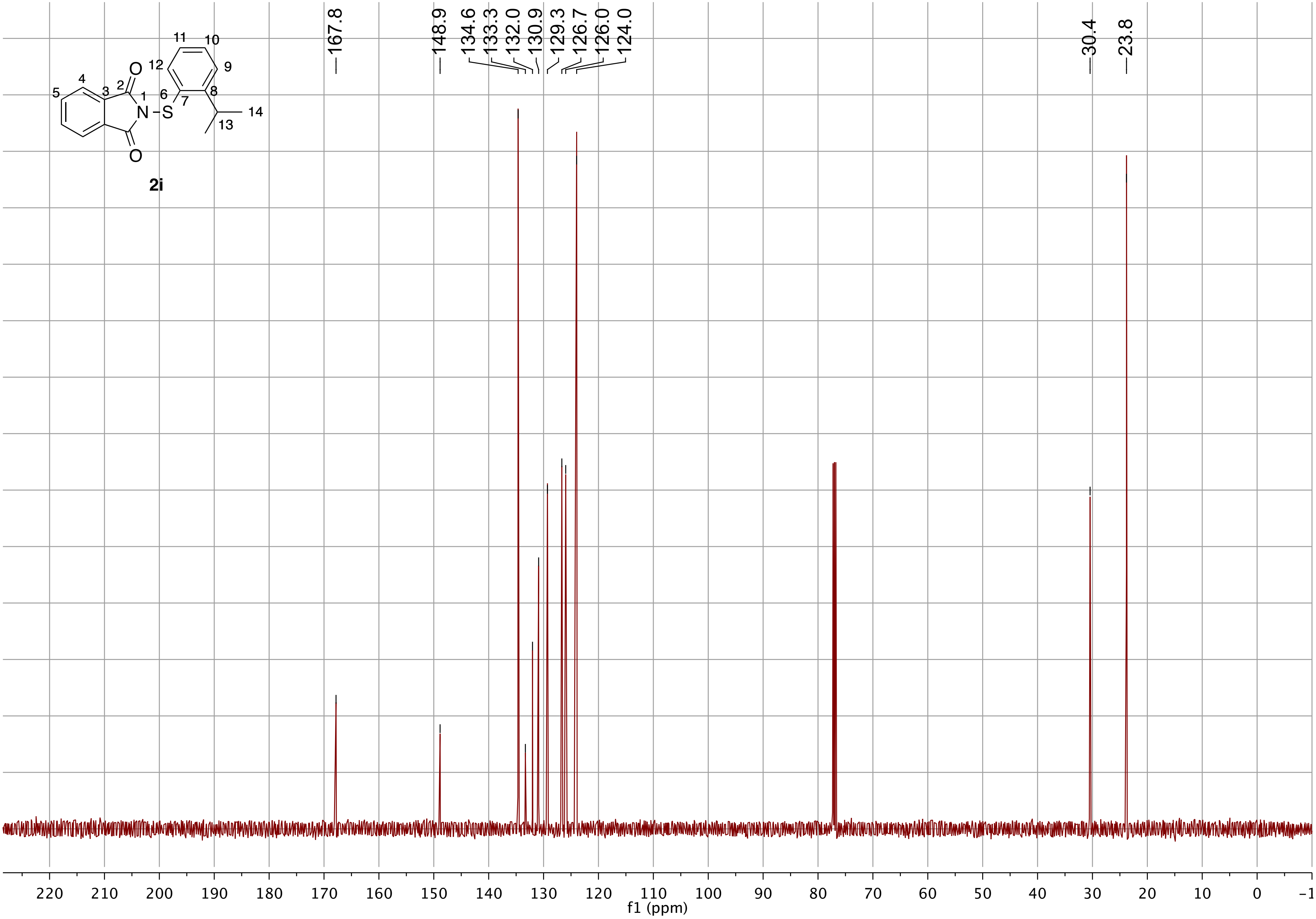
1
2
3
4
5
6
7
8
9
10
11
12
O
O
N
S

2h


167.8
150.1
134.4
132.1
131.2
130.8
126.9
123.6
28.1
16.4
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

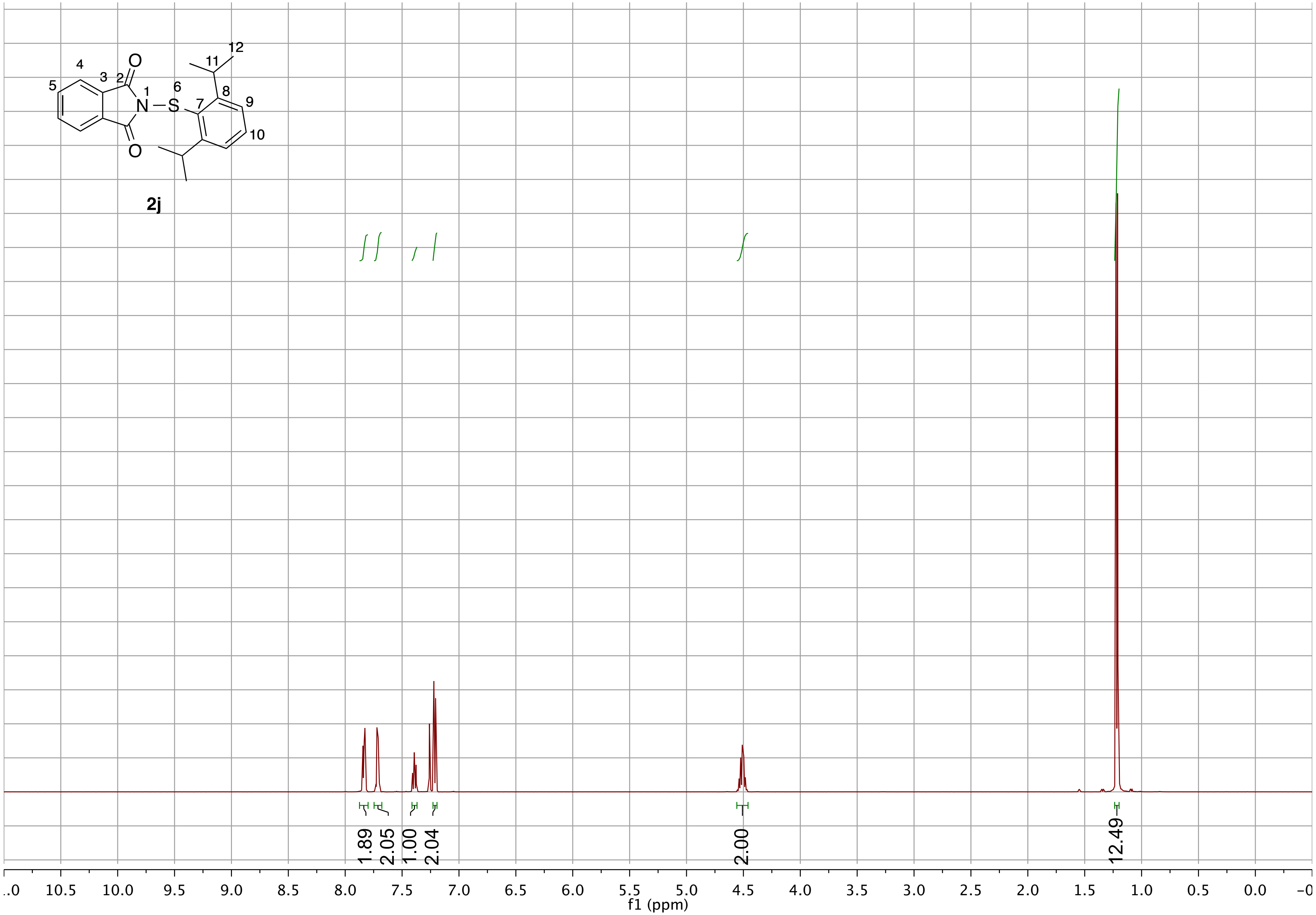


4
5
3
2
O
1
N
S
6
7
O
12
11
10
9
8
13
14
2i
2.00
2.07
1.00
2.24
1.02
1.00
6.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

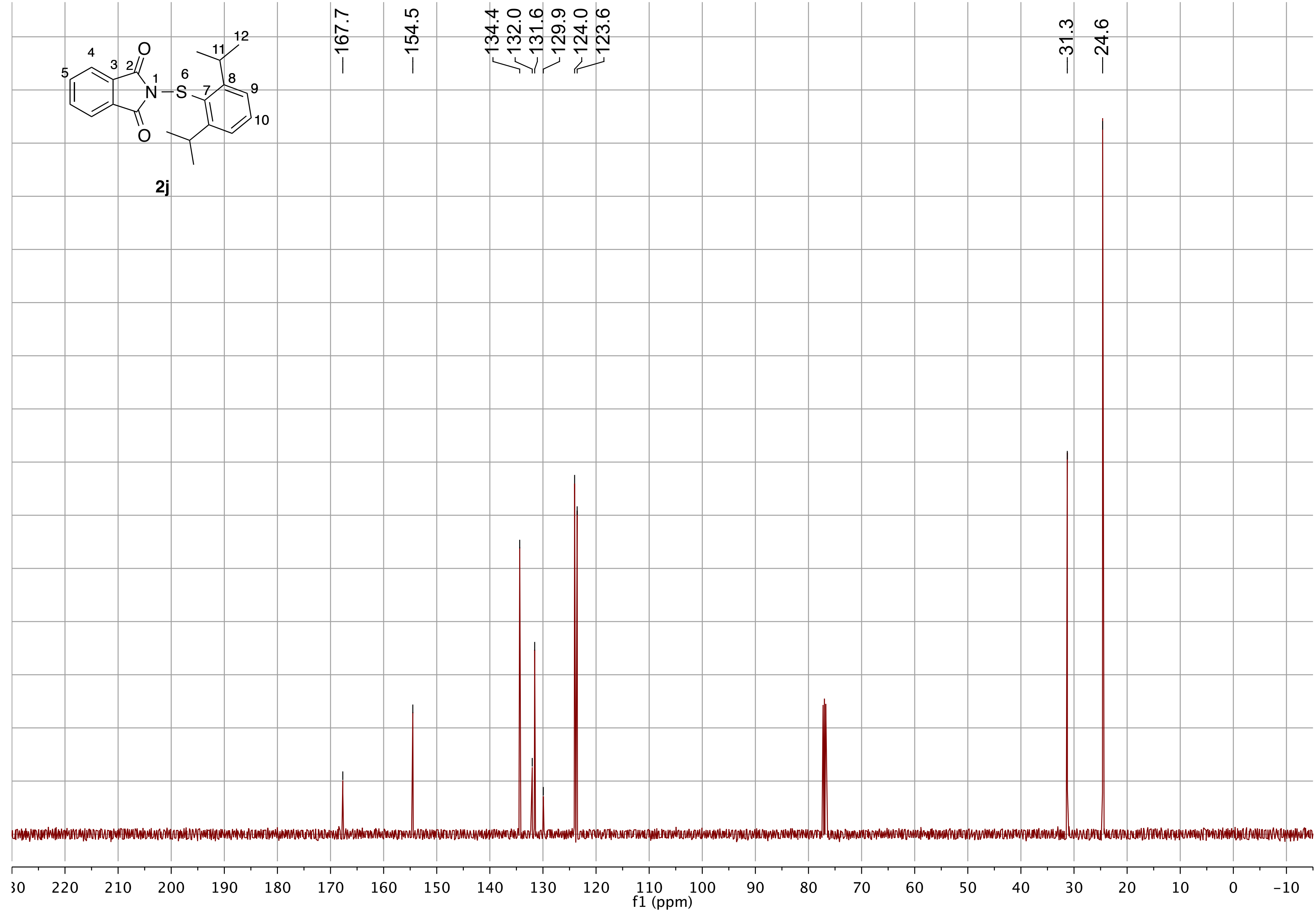


2i

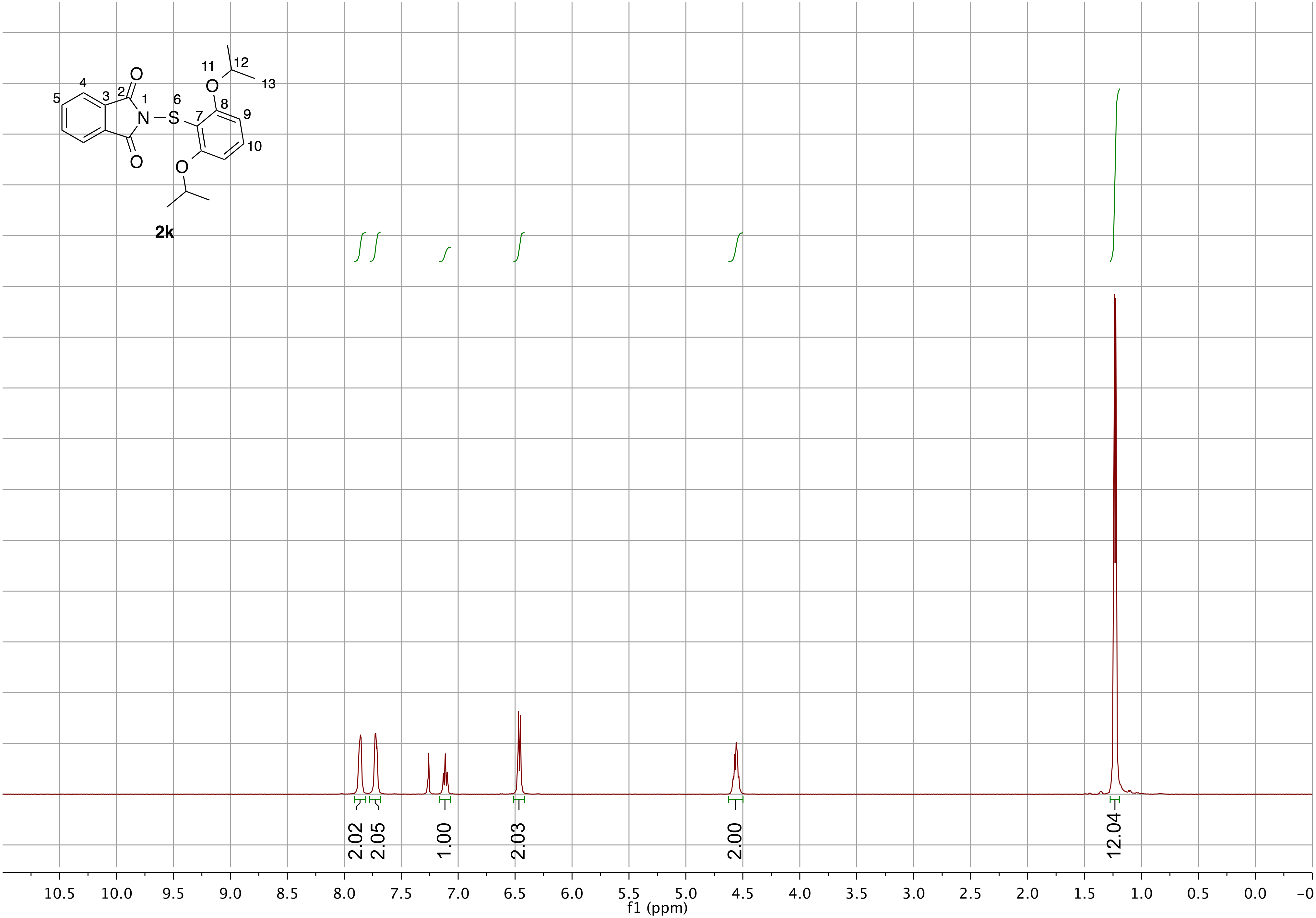
167.8
148.9
134.6
133.3
132.0
130.9
129.3
126.7
126.0
124.0
30.4
23.8
O
O
N
S
1
2
3
4
5
6
7
8
9
10
11
12
13
14
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)



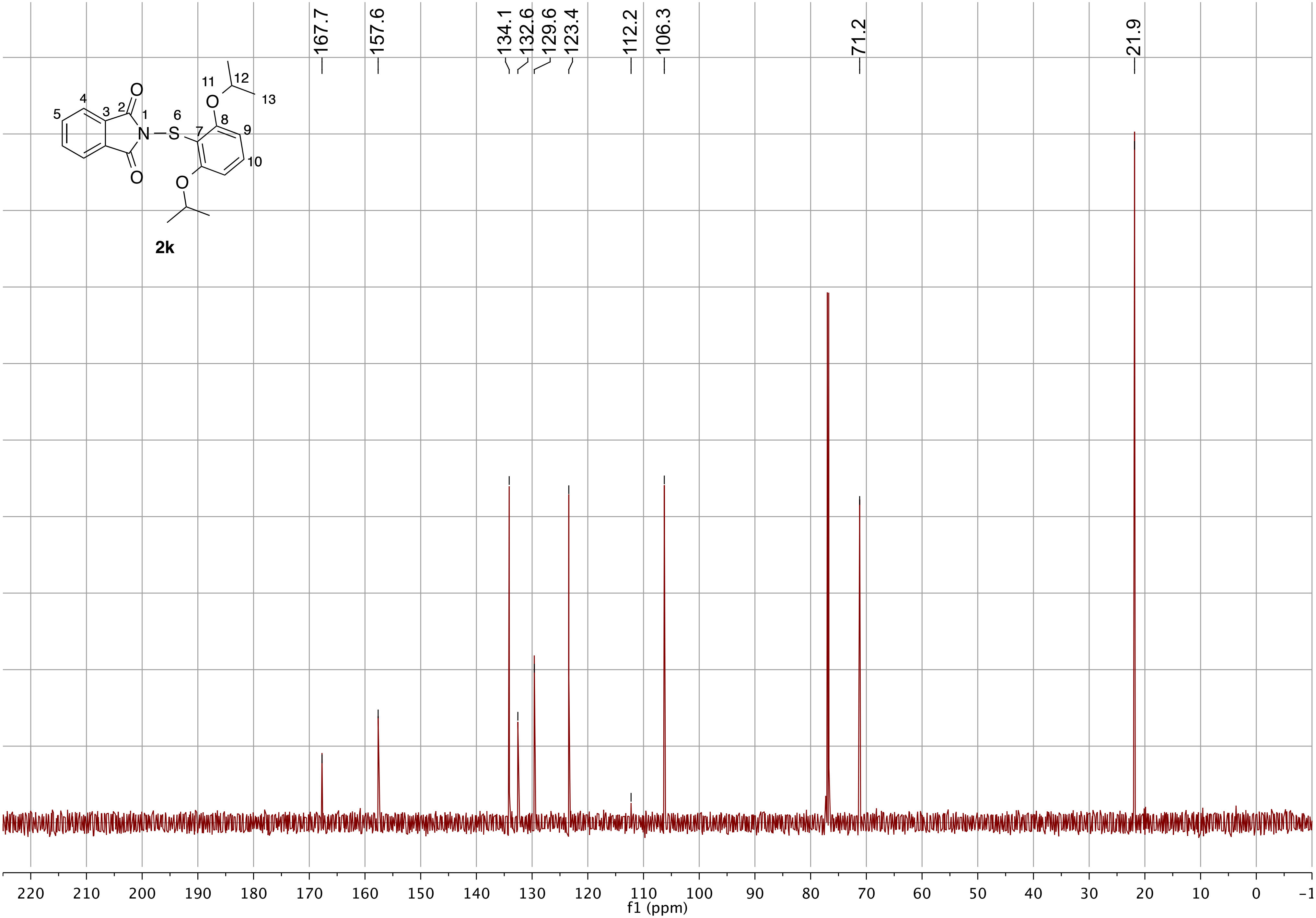
4
5
3
2
O
1
N
6
S
7
8
11
12
9
10
O
2j
1.89
2.05
1.00
2.04
2.00
12.49
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

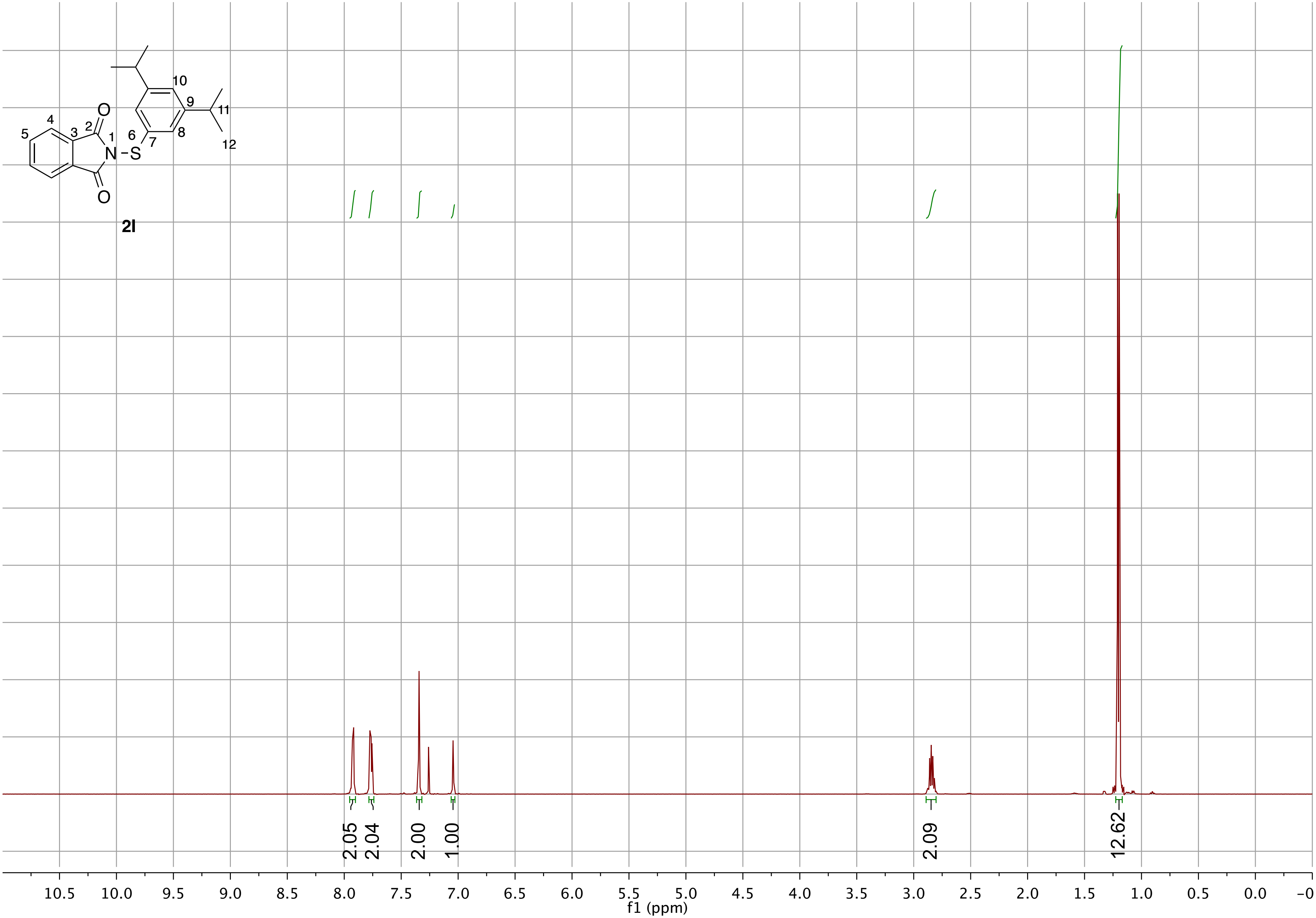


167.7
154.5
134.4
132.0
131.6
129.9
124.0
123.6
31.3
24.6
O
O
N
S
1
2
3
4
5
6
7
8
9
10
11
12
2j
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

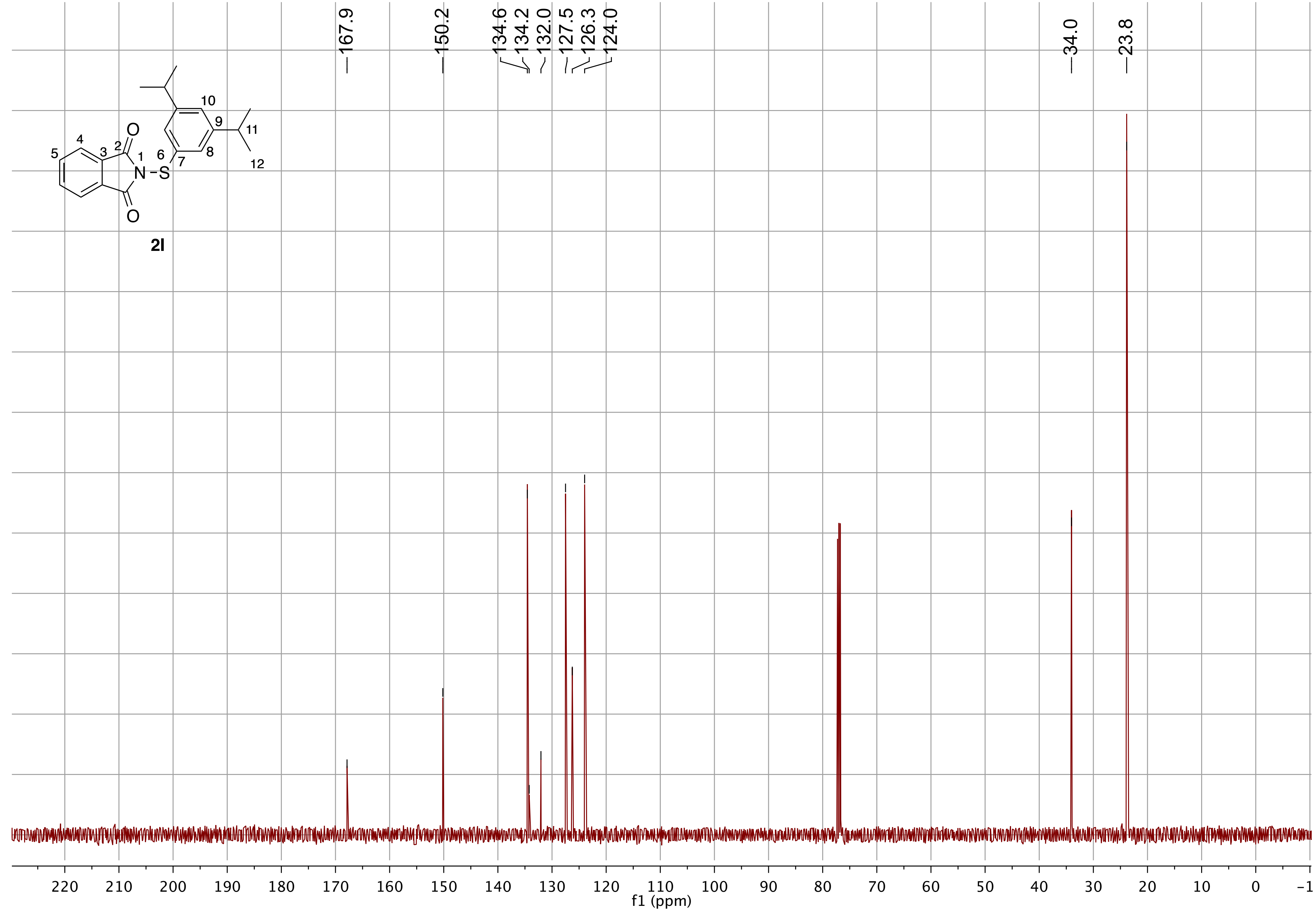


2k
1
2
3
4
5
6
7
8
9
10
11
12
13
O
N
S
2.02
2.05
1.00
2.03
2.00
12.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

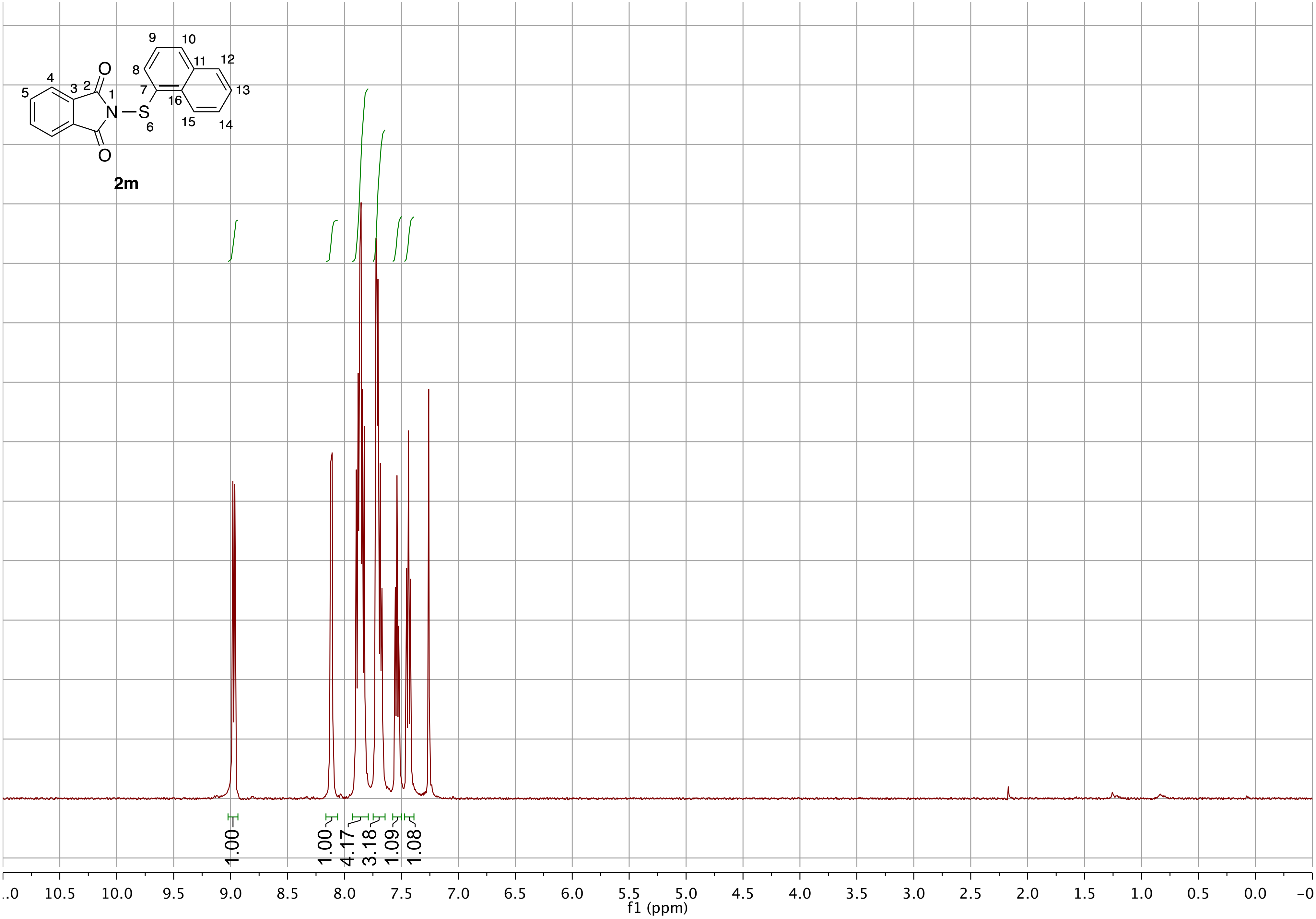

167.7
157.6
134.1
132.6
129.6
123.4
112.2
106.3
71.2
21.9
2k
1
2
3
4
5
6
7
8
9
10
11
12
13
N
S
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)



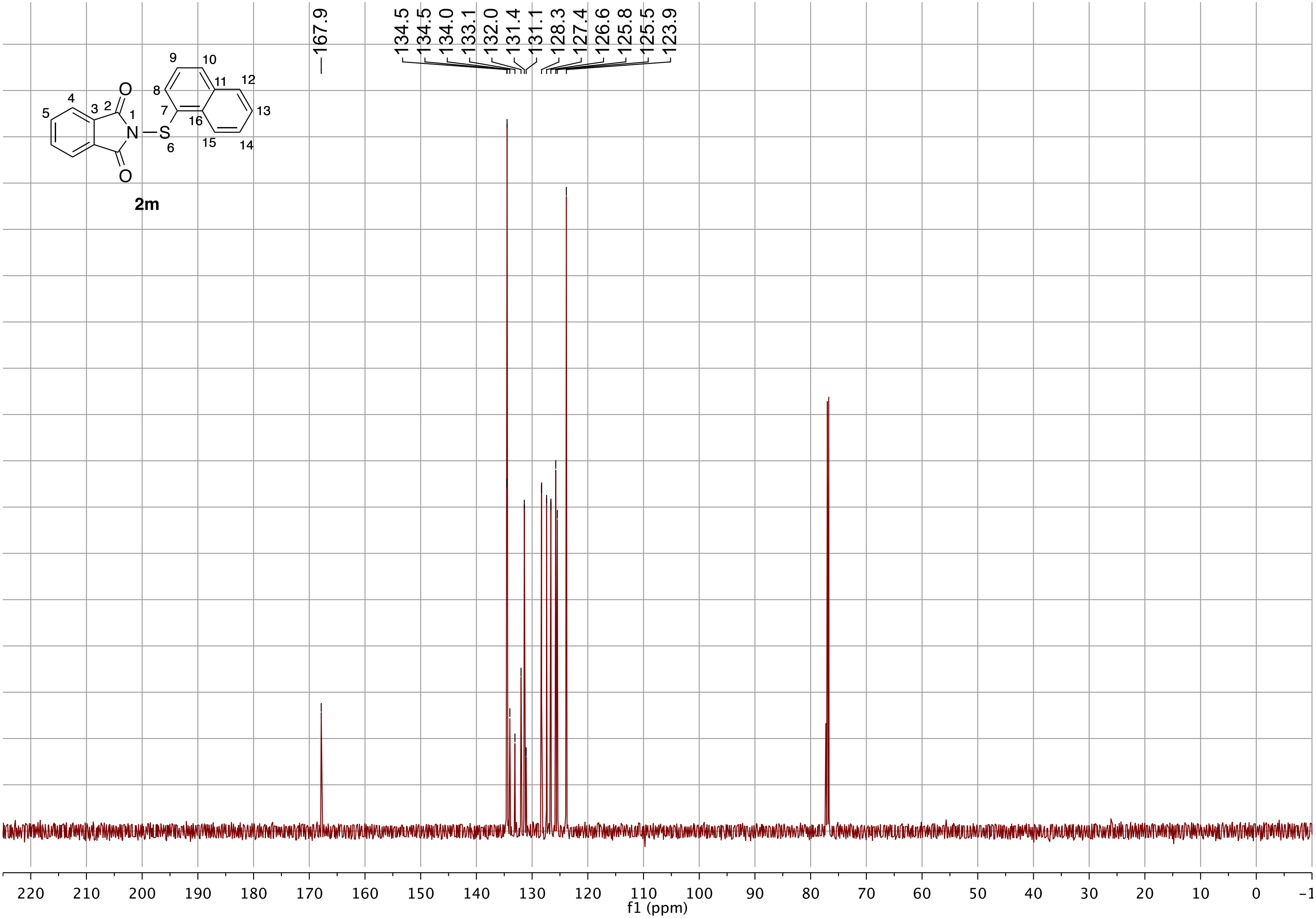
2l
1
2
3
4
5
6
7
8
9
10
11
12
O
O
N
S
2.05
2.04
2.00
1.00
2.09
12.62
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)



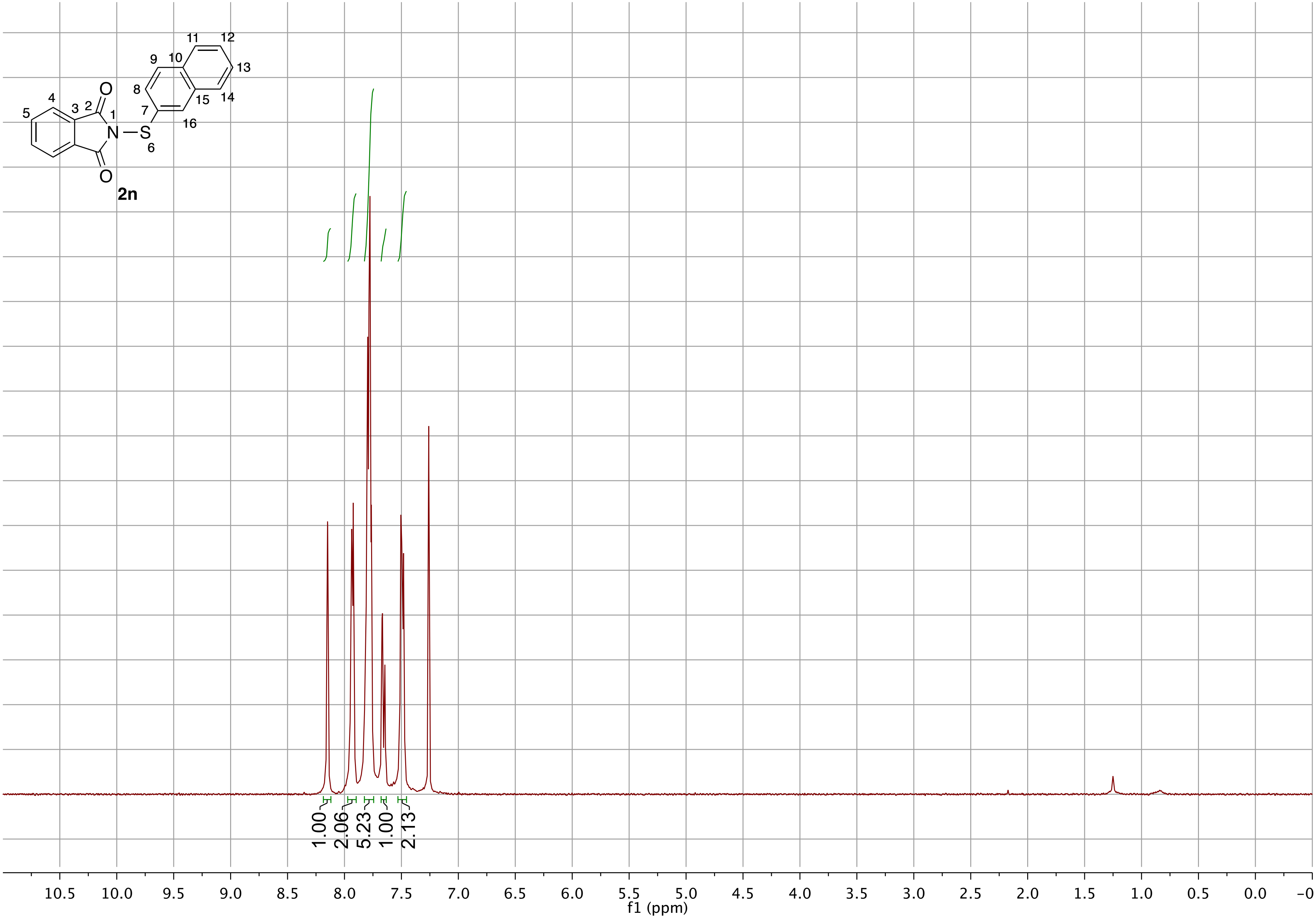
167.9
150.2
134.6
134.2
132.0
127.5
126.3
124.0
34.0
23.8
2l
1
2
3
4
5
6
7
8
9
10
11
12
O
N
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)



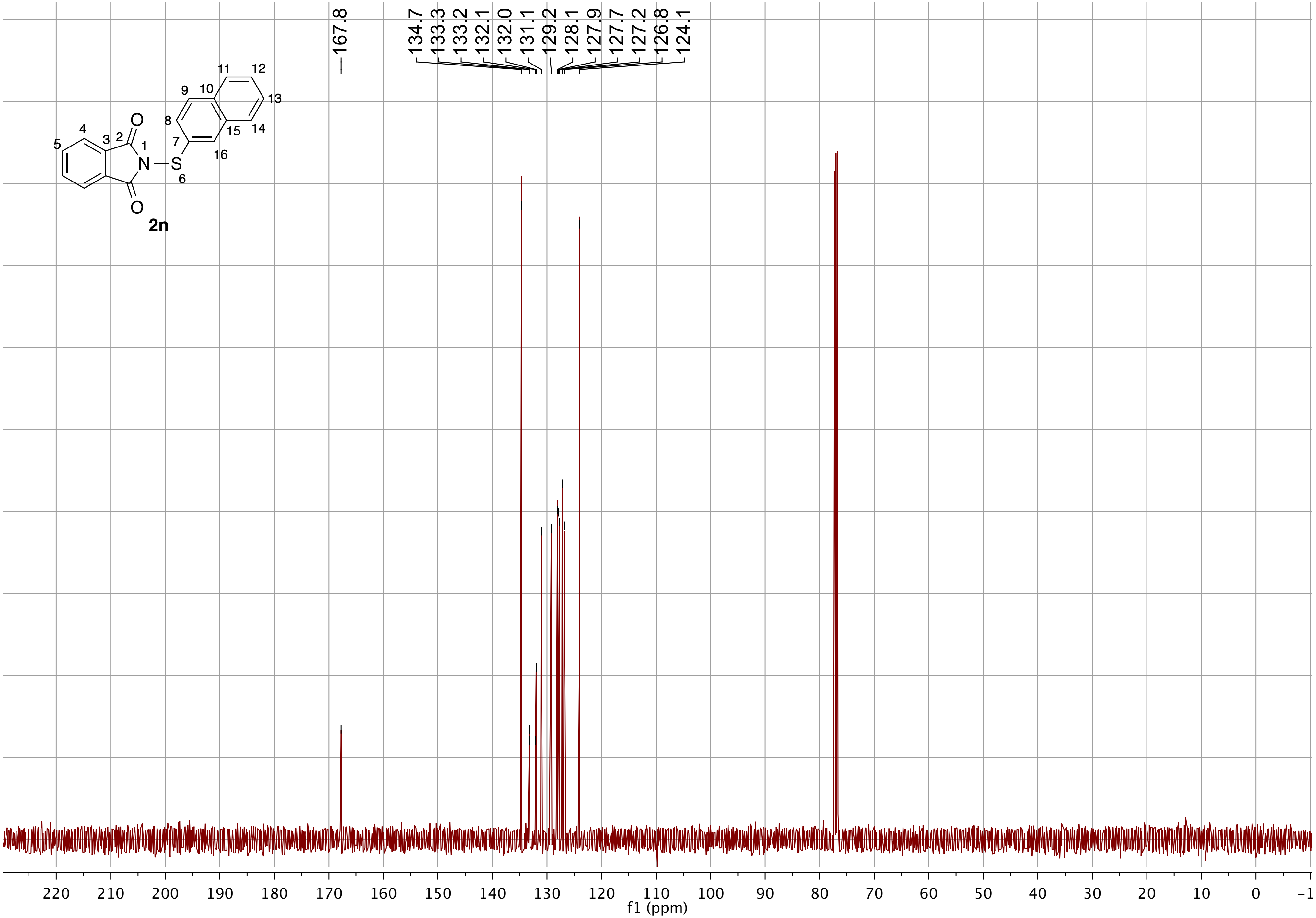
2m
1.00
1.00
4.17
3.18
1.09
1.08
f1 (ppm)

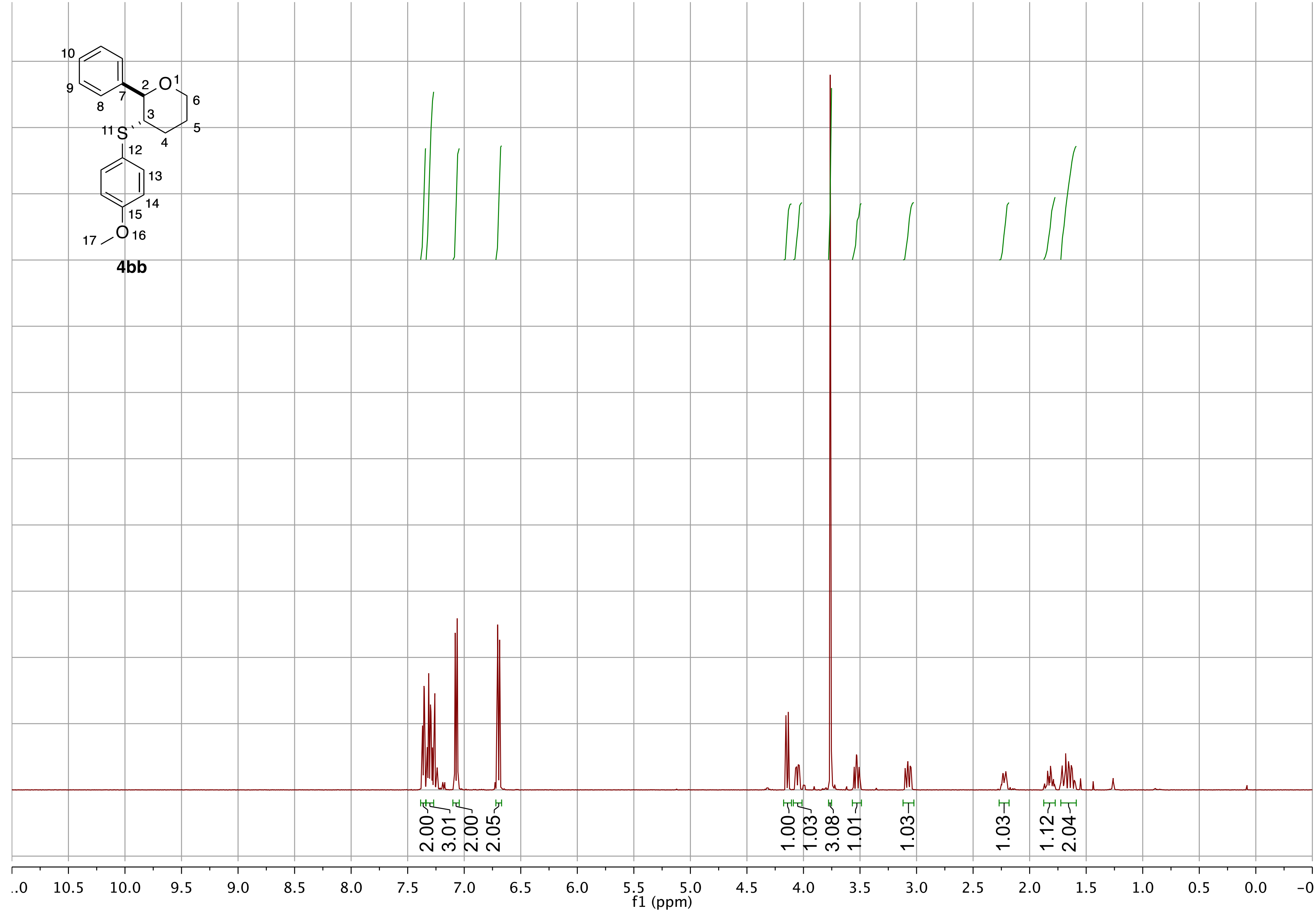


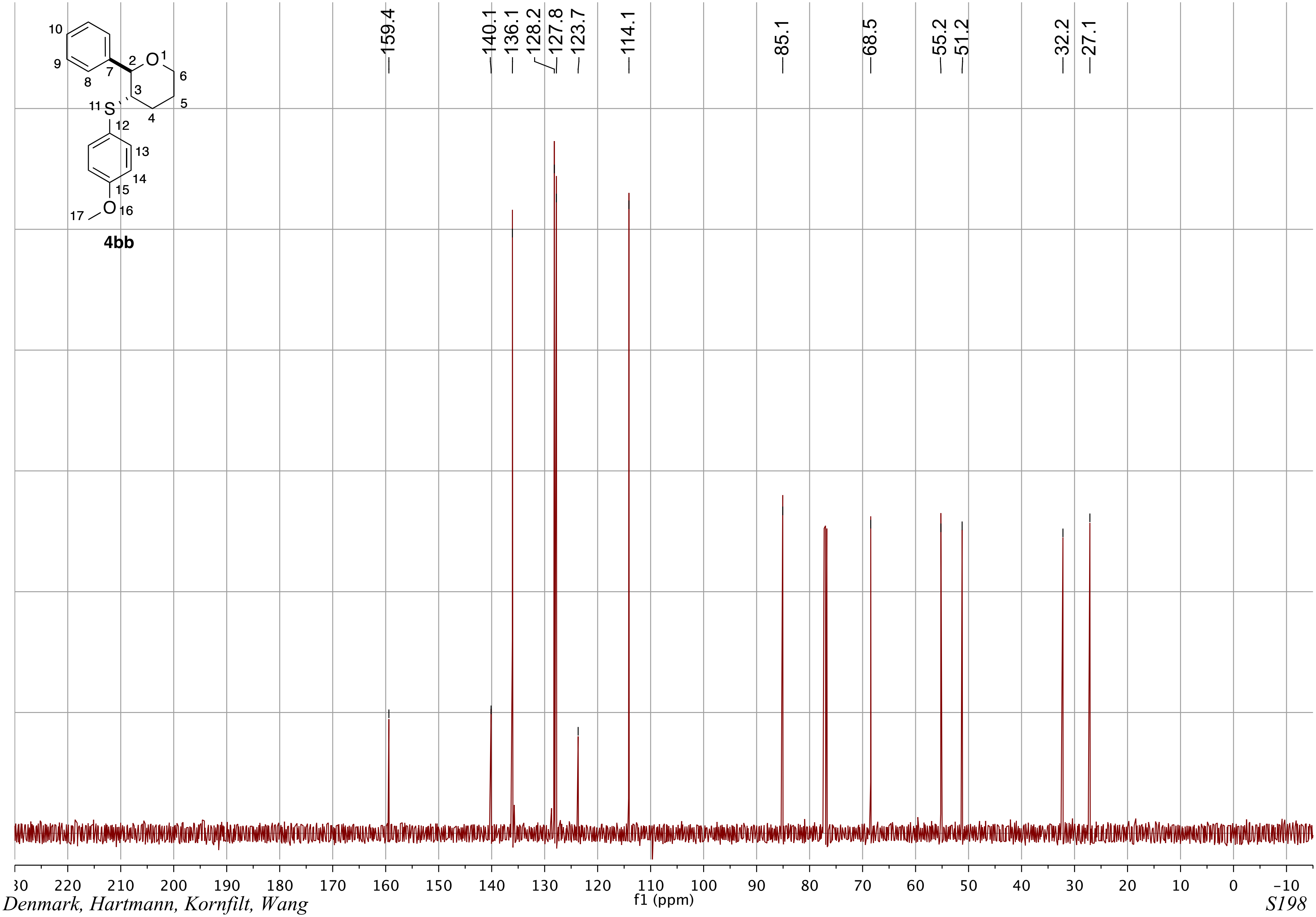
2m
O
N
S
O
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
167.9
134.5
134.5
134.0
133.1
132.0
131.4
131.1
128.3
127.4
126.6
125.8
125.5
123.9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)

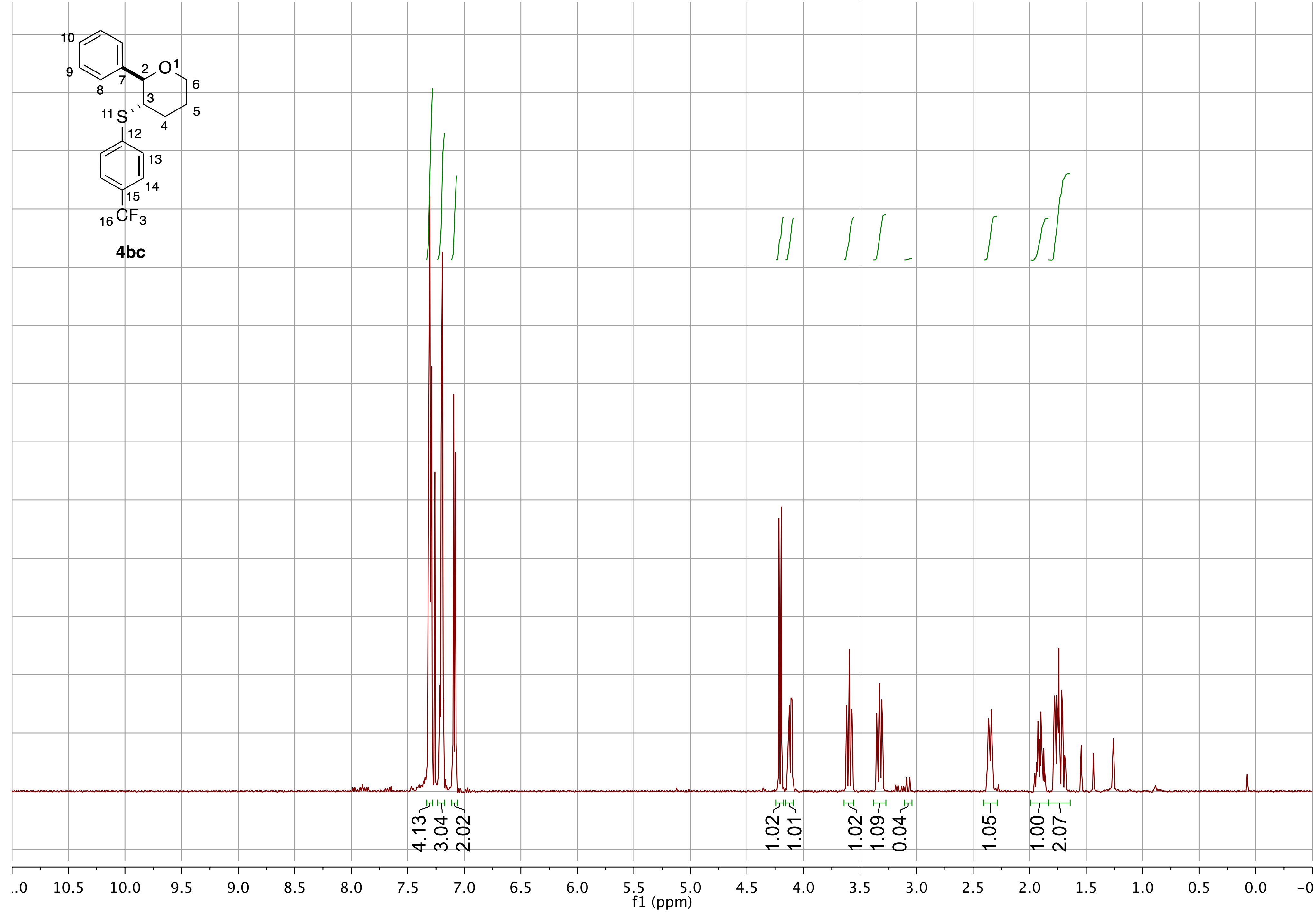


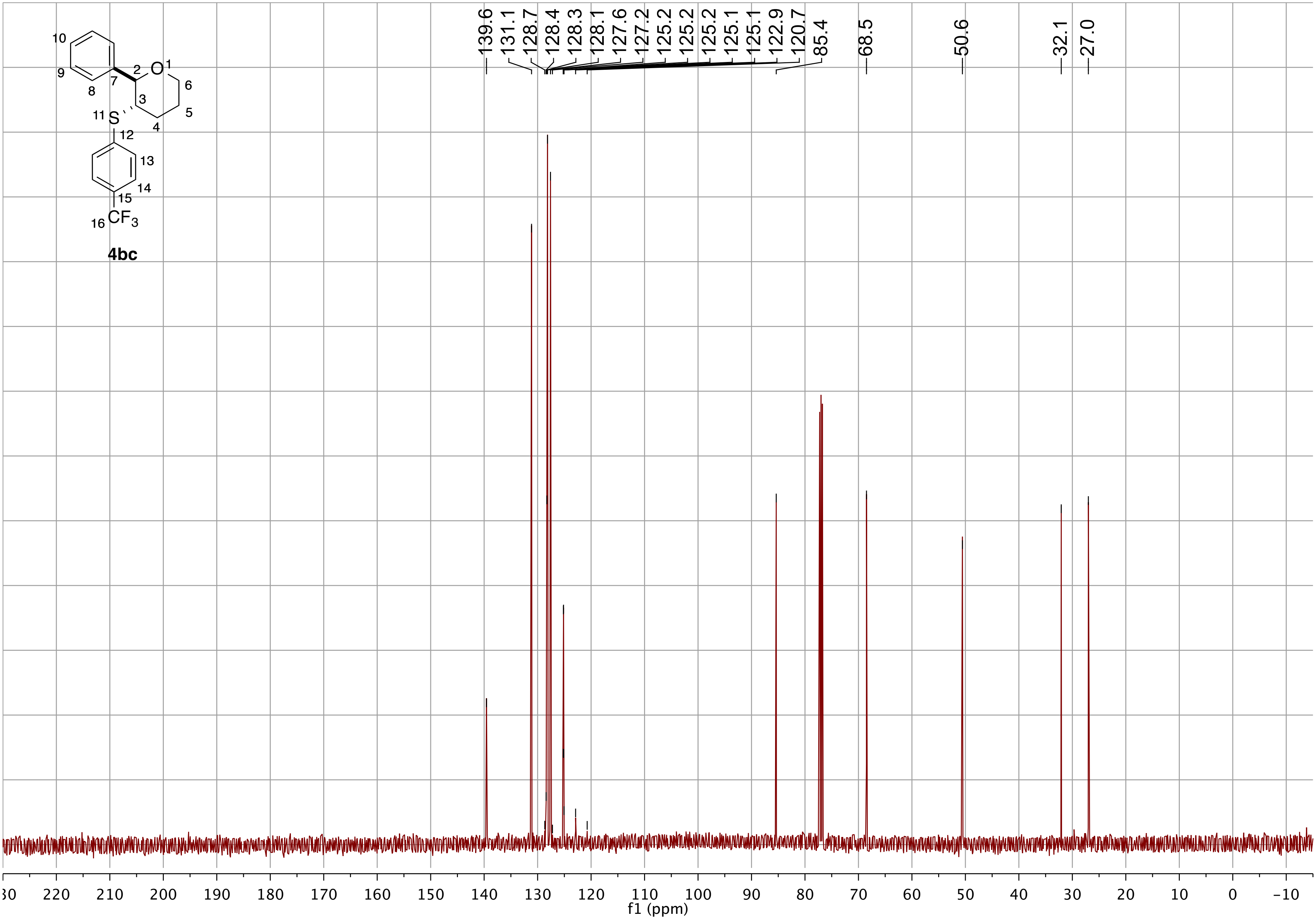
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
O
O
N
S
2n
1.00
2.06
5.23
1.00
2.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

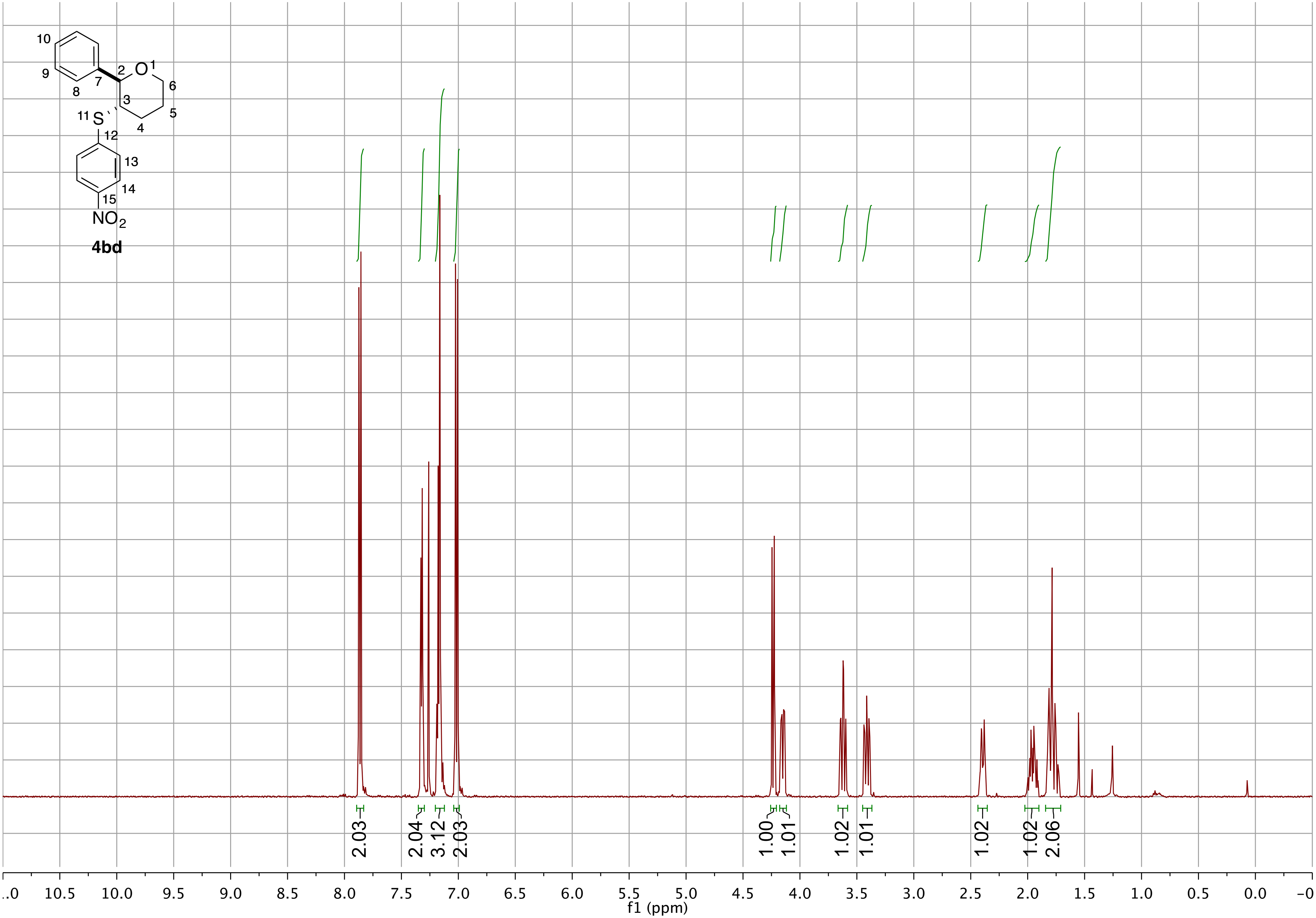

167.8
134.7
133.3
133.2
132.1
132.0
131.1
129.2
128.1
127.9
127.7
127.2
126.8
124.1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
O
O
N
S
2n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)


10
9
8
7
2
O
1
6
3
5
4
11
S
12
13
14
15
17
O
16
4bb
2.00
3.01
2.00
2.05
1.00
1.03
3.08
1.01
1.03
1.03
1.12
2.04
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

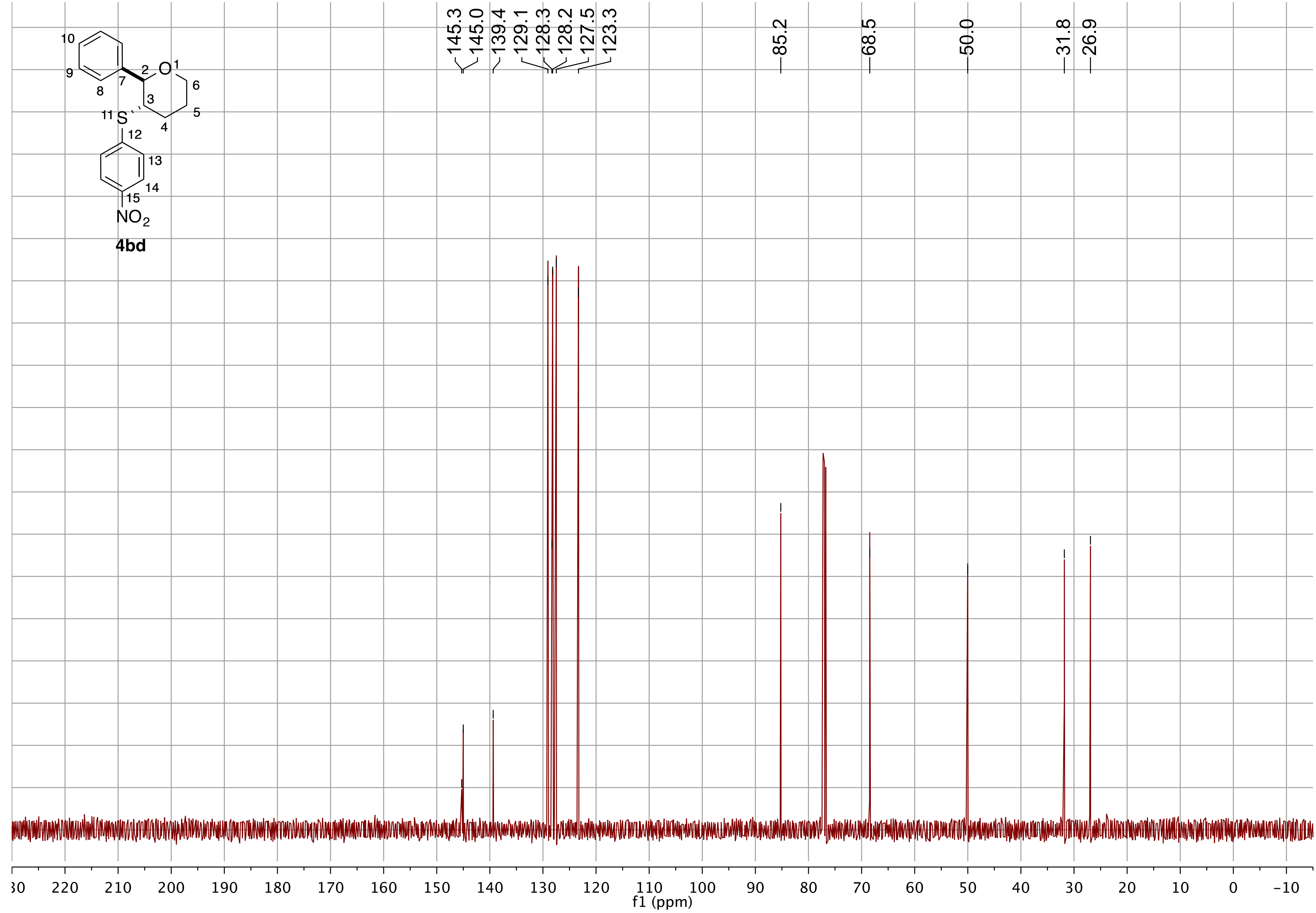

4bb
10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
O
16
17
159.4
140.1
136.1
128.2
127.8
123.7
114.1
85.1
68.5
55.2
51.2
32.2
27.1
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

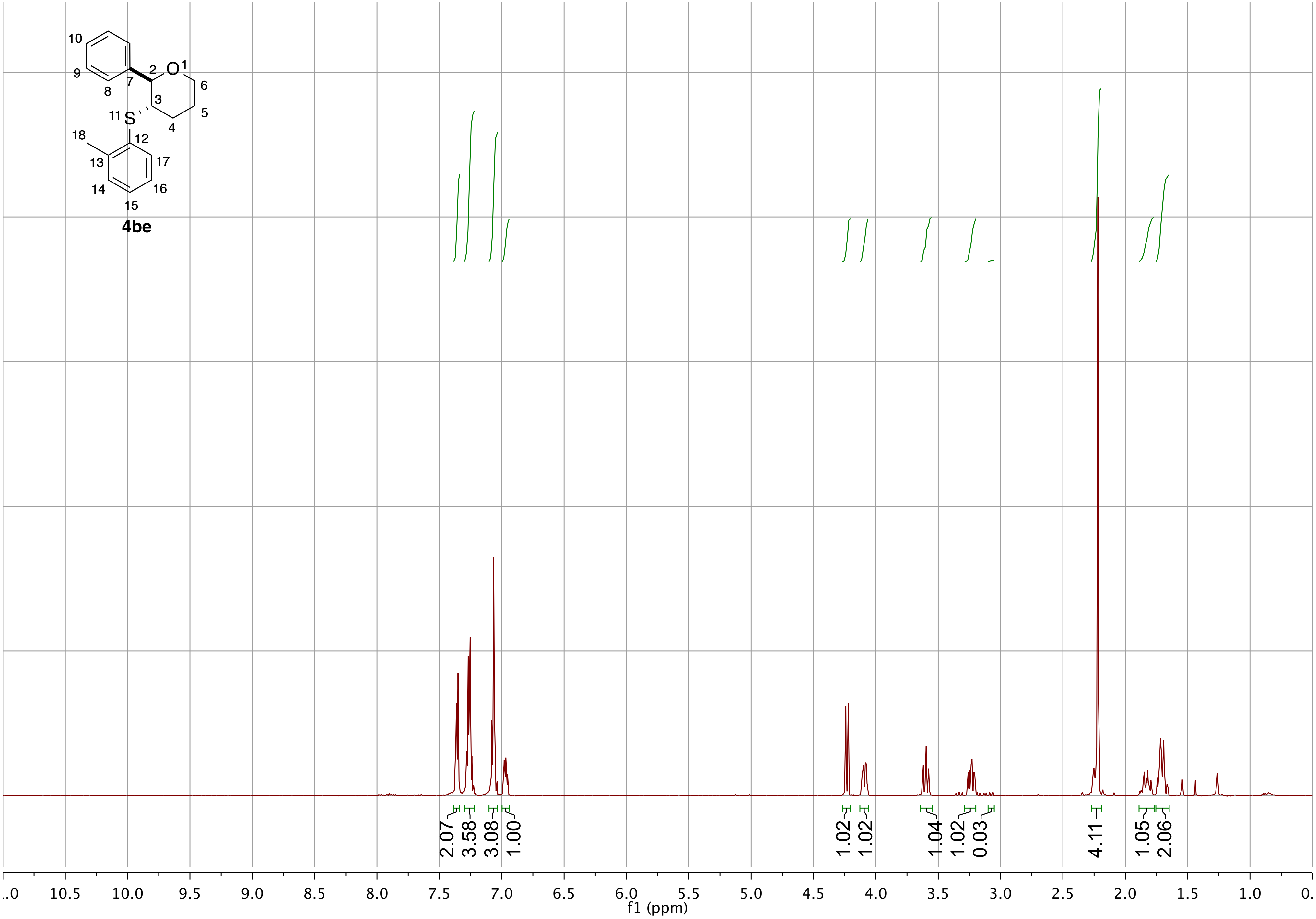

10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
16
CF3
4bc
4.13
3.04
2.02
1.02
1.01
1.02
1.09
0.04
1.05
1.00
2.07
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

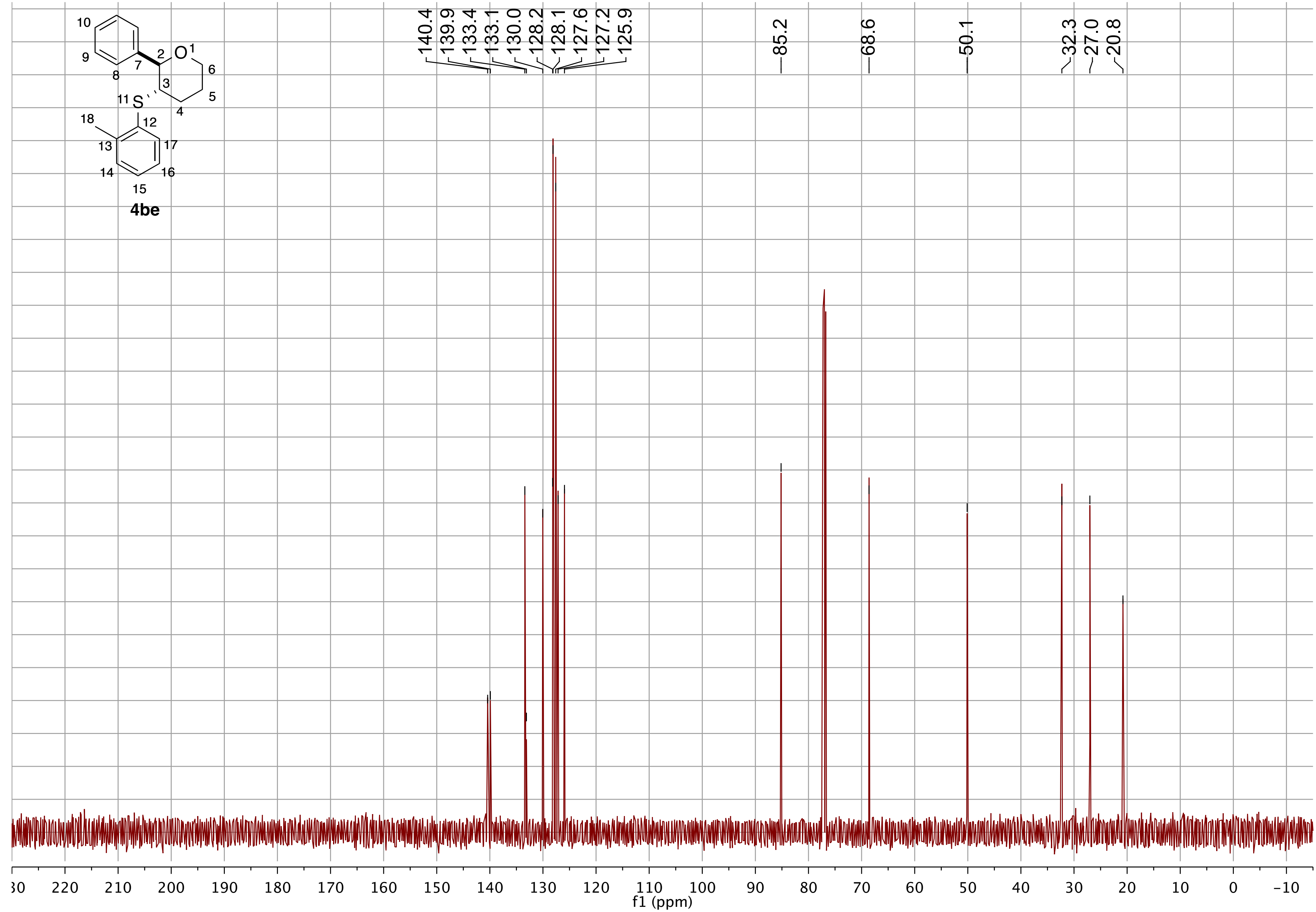

139.6
131.1
128.7
128.4
128.3
128.1
127.6
127.2
125.2
125.2
125.2
125.1
125.1
122.9
120.7
85.4
68.5
50.6
32.1
27.0
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
S
CF3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
4bc

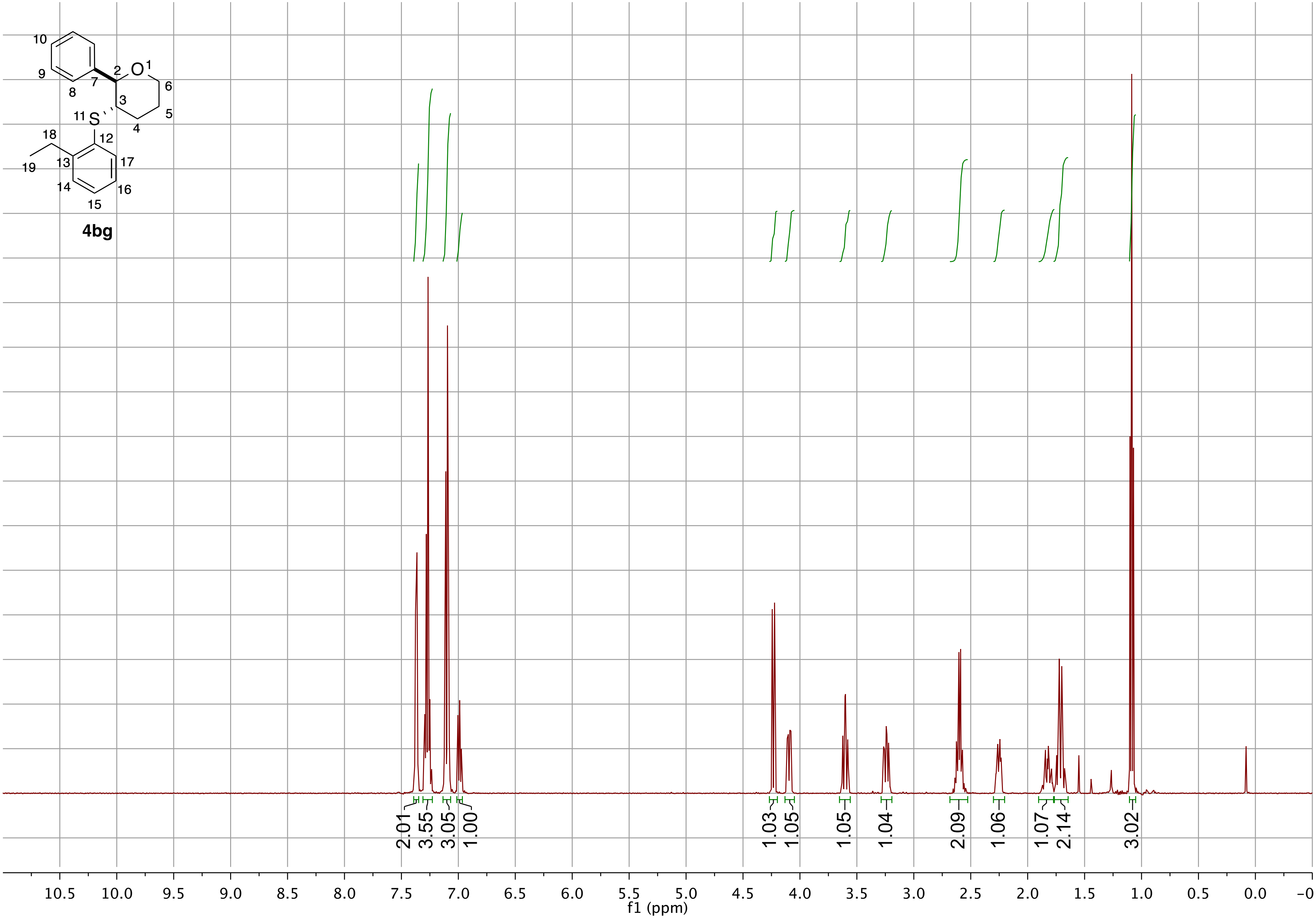

10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
NO2
2.03
2.04
3.12
2.03
1.00
1.01
1.02
1.01
1.02
1.02
2.06
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

4bd

145.3
145.0
139.4
129.1
128.3
128.2
127.5
123.3
85.2
68.5
50.0
31.8
26.9
10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
NO2
4bd
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

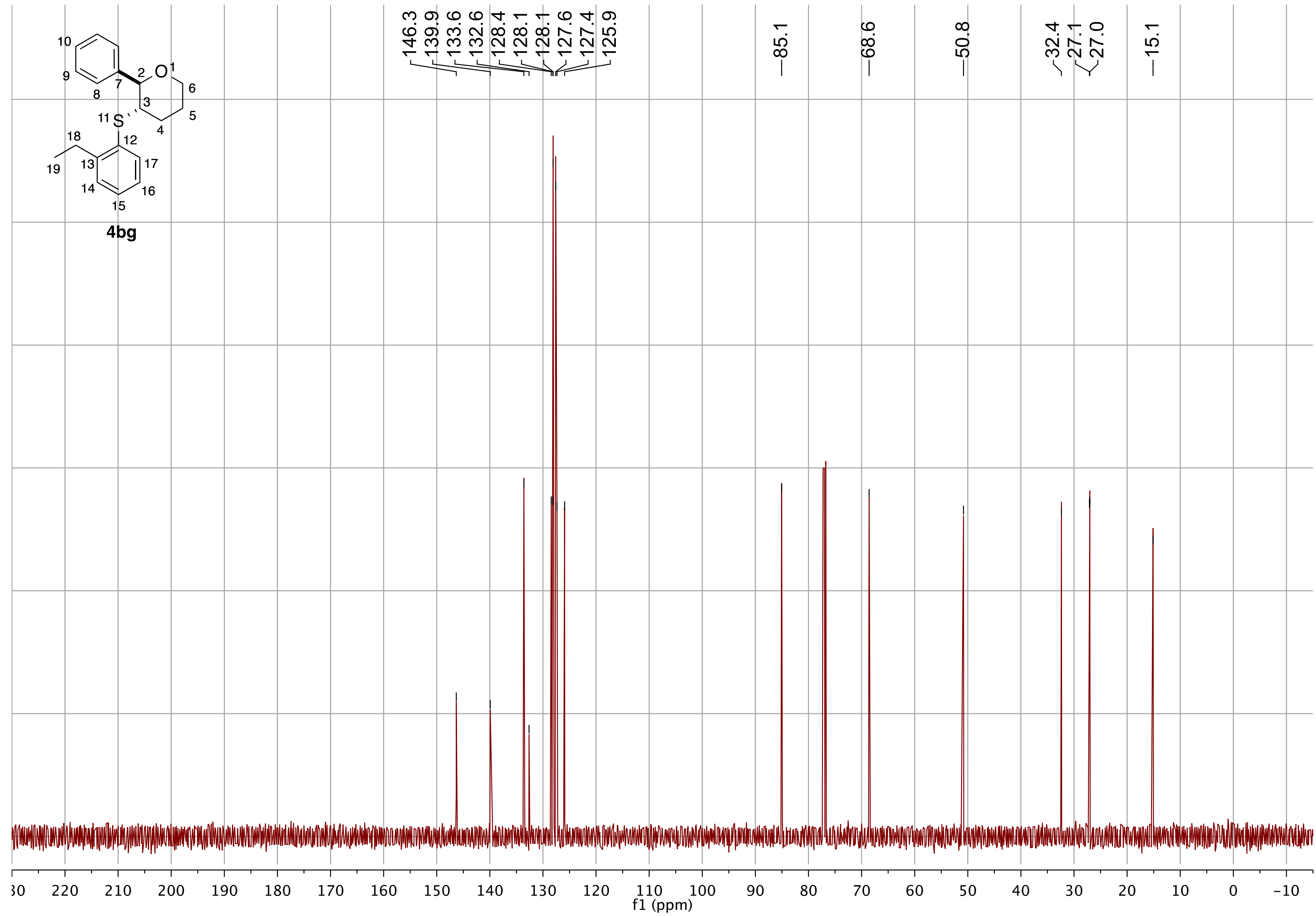

10
9
8
7
2
O
1
6
5
4
3
11
S
12
18
13
17
14
16
15
4be
2.07
3.58
3.08
1.00
1.02
1.02
1.04
1.02
0.03
4.11
1.05
2.06
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)


10
9
8
7
2
O
1
6
3
5
4
11
S
18
12
13
17
14
16
15
4be
140.4
139.9
133.4
133.1
130.0
128.2
128.1
127.6
127.2
125.9
85.2
68.6
50.1
32.3
27.0
20.8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

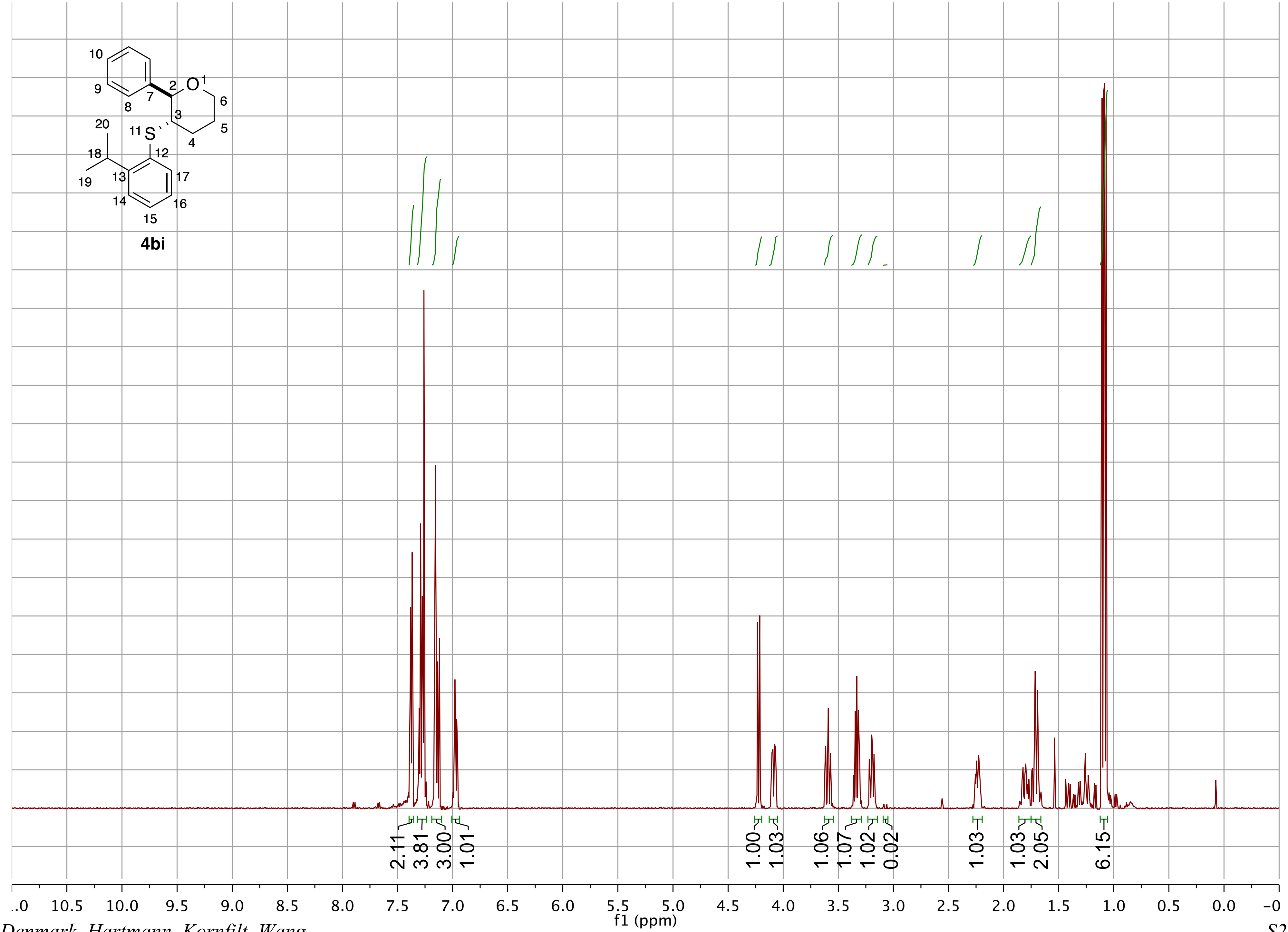


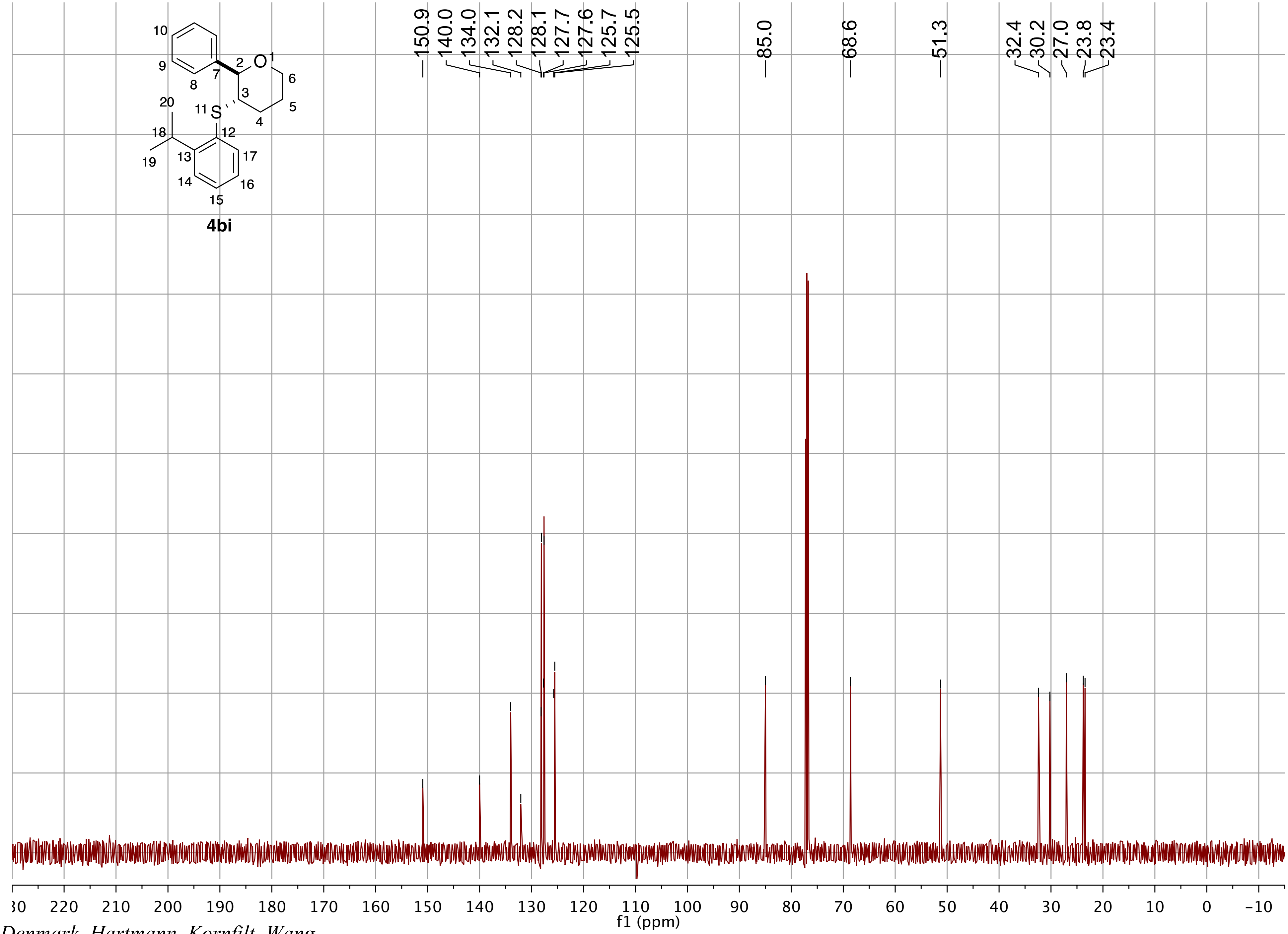
10
9
8
7
2
O
1
6
5
4
3
11
S
18
12
17
19
13
14
16
15
2.01
3.55
3.05
1.00
1.03
1.05
1.05
1.04
2.09
1.06
1.07
2.14
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

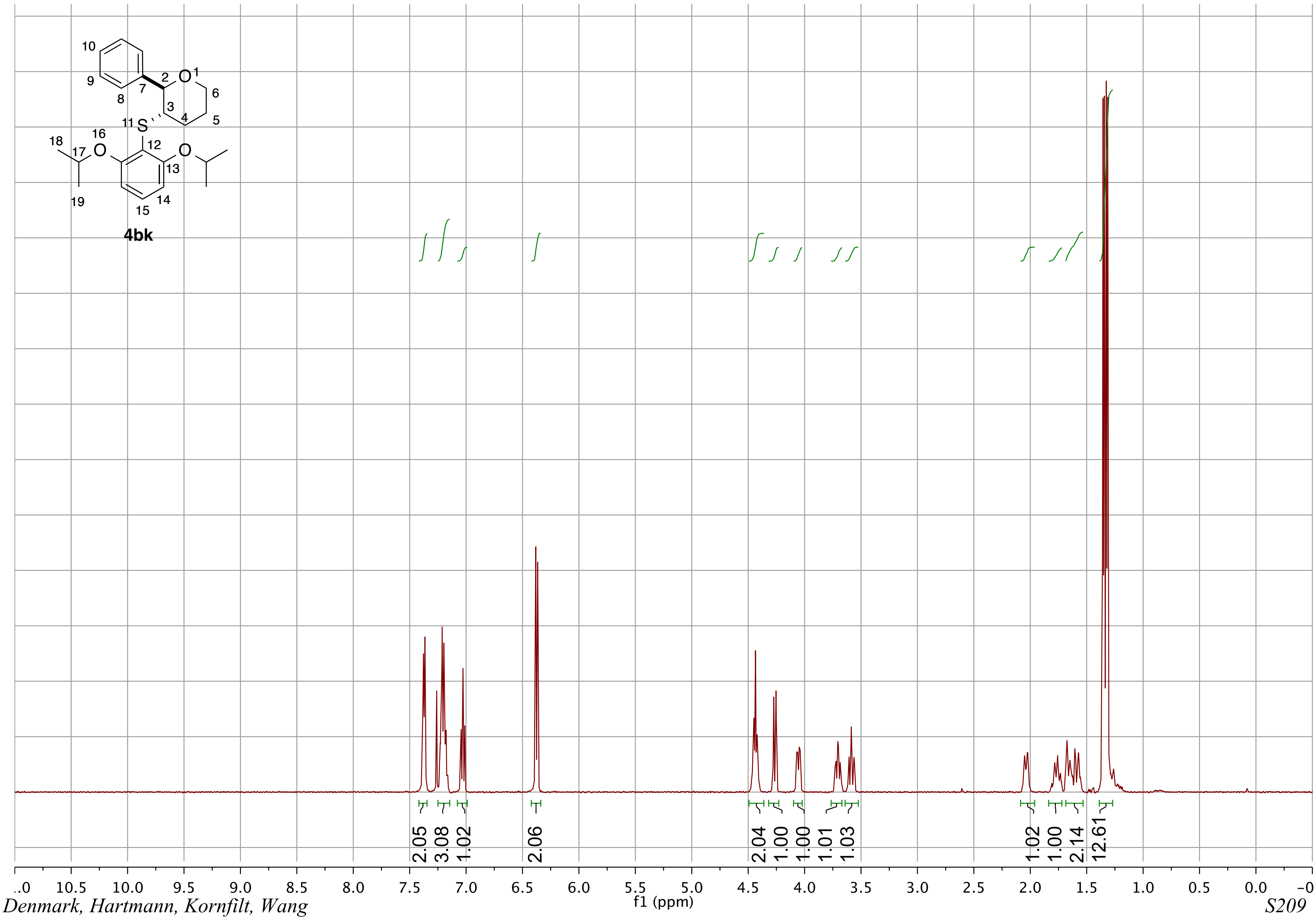
4bg



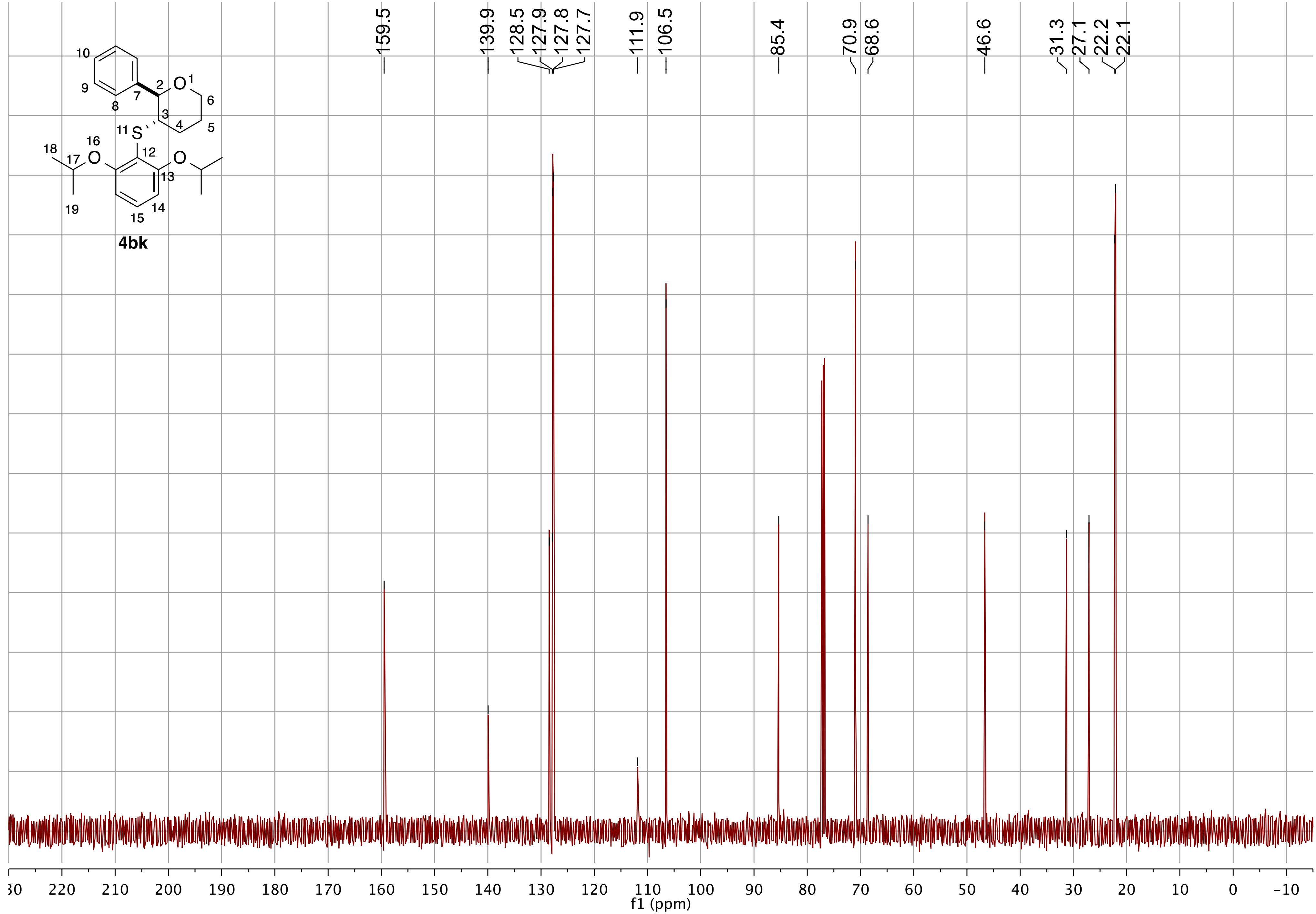
4bg
146.3
139.9
133.6
132.6
128.4
128.1
128.1
127.6
127.4
125.9
85.1
68.6
50.8
32.4
27.1
27.0
15.1
f1 (ppm)

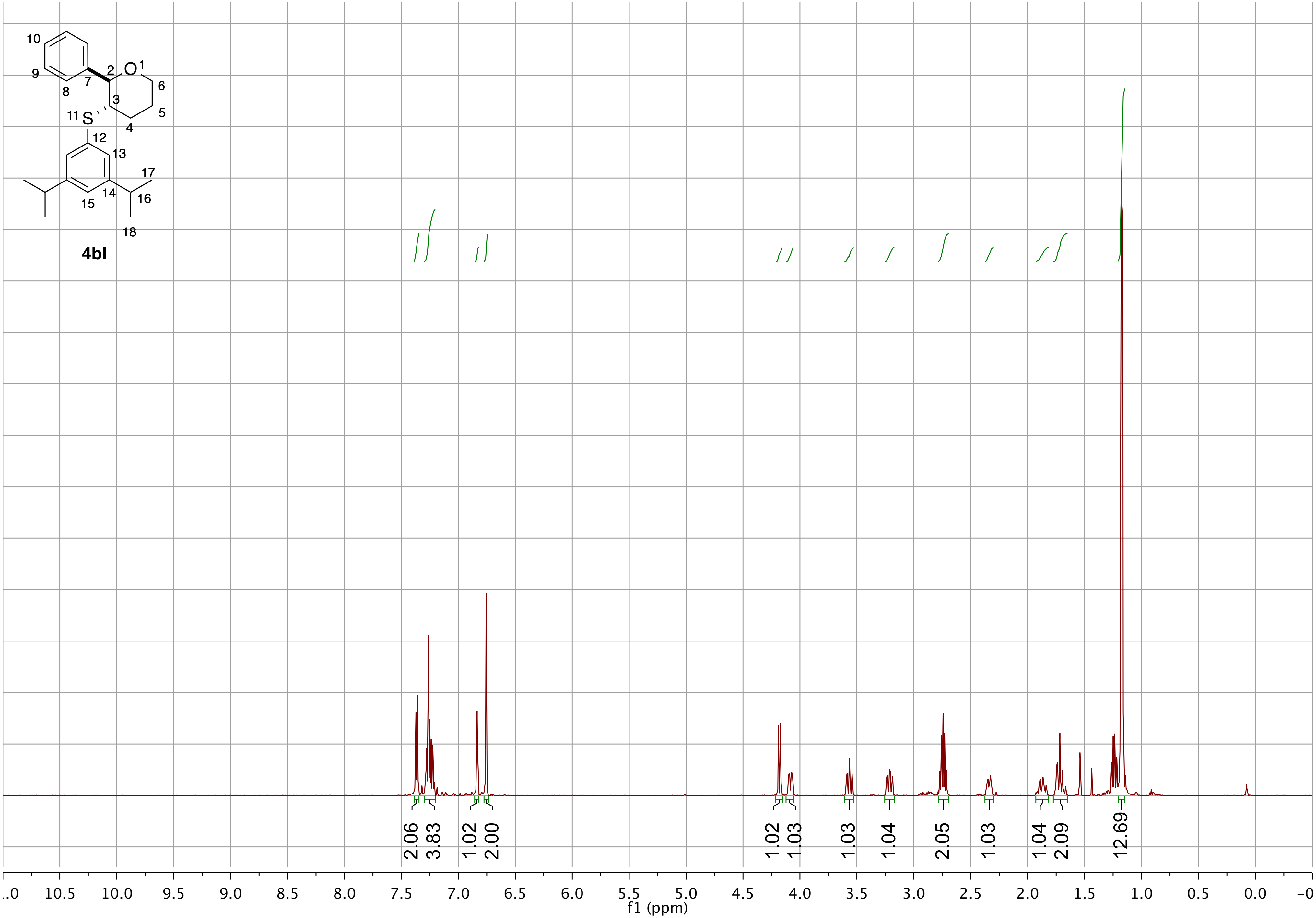

10
9
8
7
2
O
1
6
5
4
3
11
S
20
18
12
17
19
13
14
16
15
4bi
2.11
3.81
3.00
1.01
1.00
1.03
1.06
1.07
1.02
0.02
1.03
1.03
2.05
6.15
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)


150.9
140.0
134.0
132.1
128.2
128.1
127.7
127.6
125.7
125.5
85.0
68.6
51.3
32.4
30.2
27.0
23.8
23.4
10
9
8
7
2
O
1
6
5
4
3
S
11
20
18
19
13
12
17
16
15
14
4bi
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

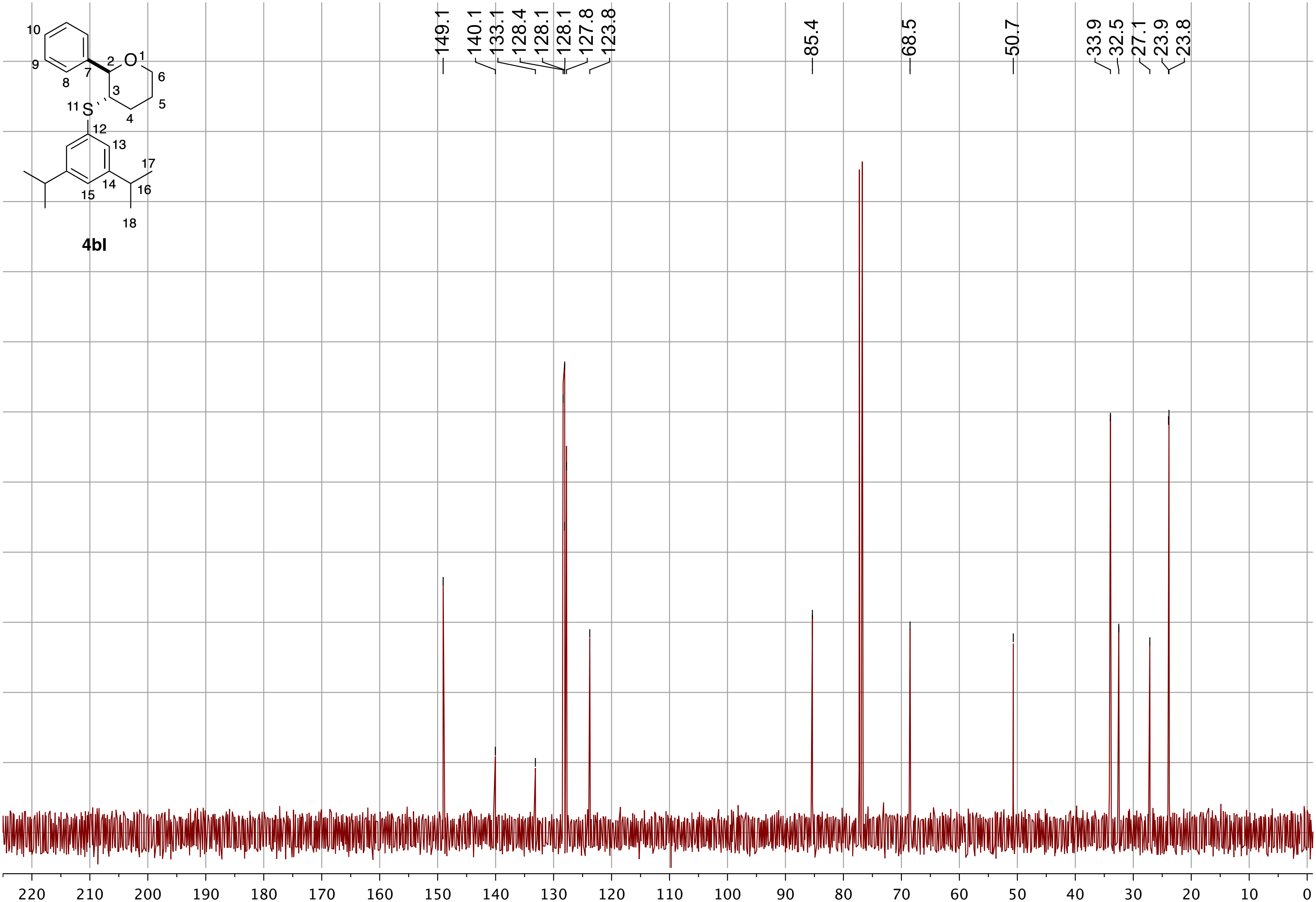

10
9
8
7
2
O
1
6
3
4
5
11
S
16
18
17
O
12
O
13
19
15
14
2.05
3.08
1.02
2.06
2.04
1.00
1.00
1.01
1.03
1.02
1.00
2.14
12.61
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

4bk

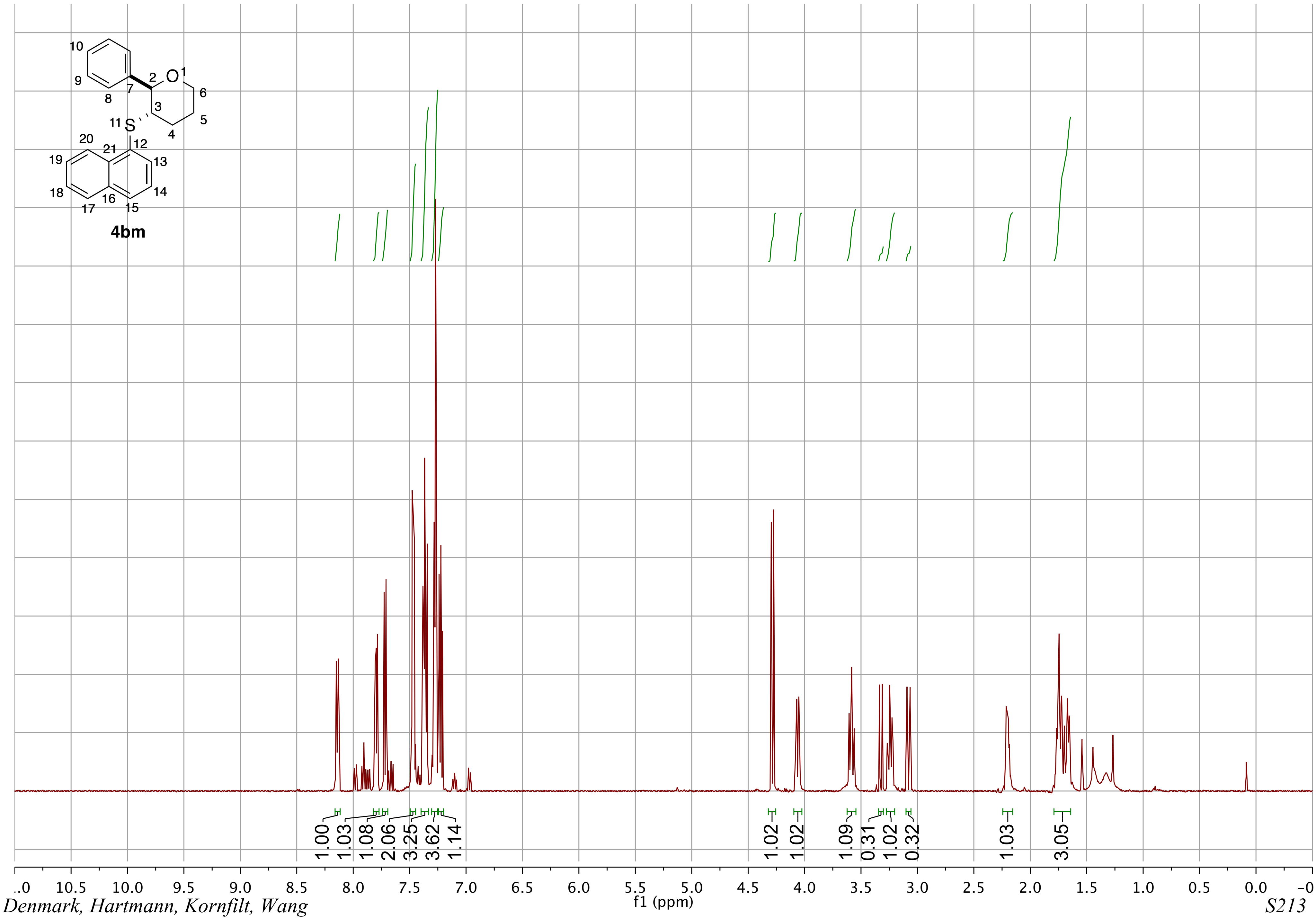

159.5
139.9
128.5
127.9
127.8
127.7
111.9
106.5
85.4
70.9
68.6
46.6
31.3
27.1
22.2
22.1
4bk
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
O
S
O
O
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)


10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
17
14
16
15
18
4bl
2.06
3.83
1.02
2.00
1.02
1.03
1.03
1.04
2.05
1.03
1.04
2.09
12.69
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

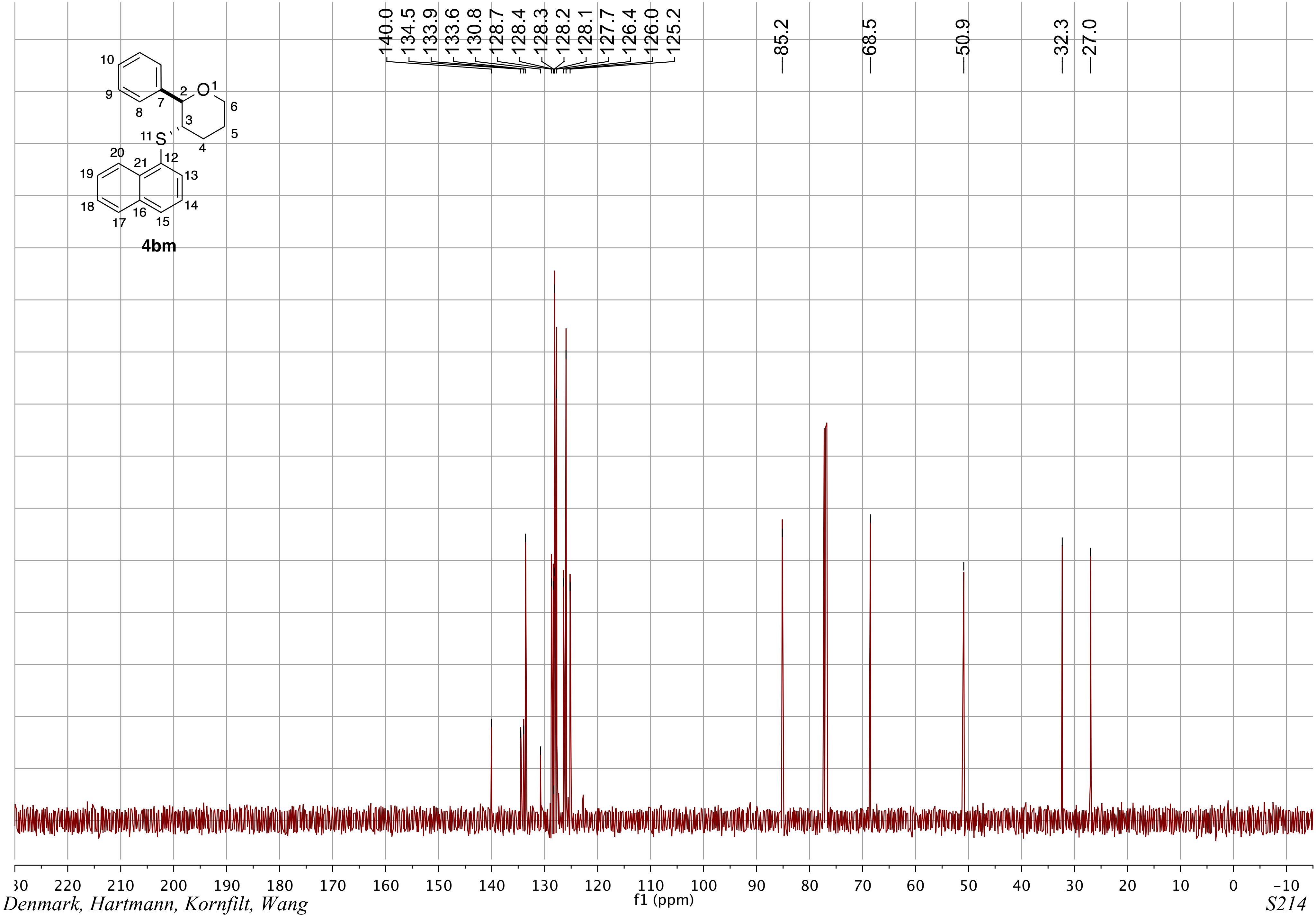
4bl



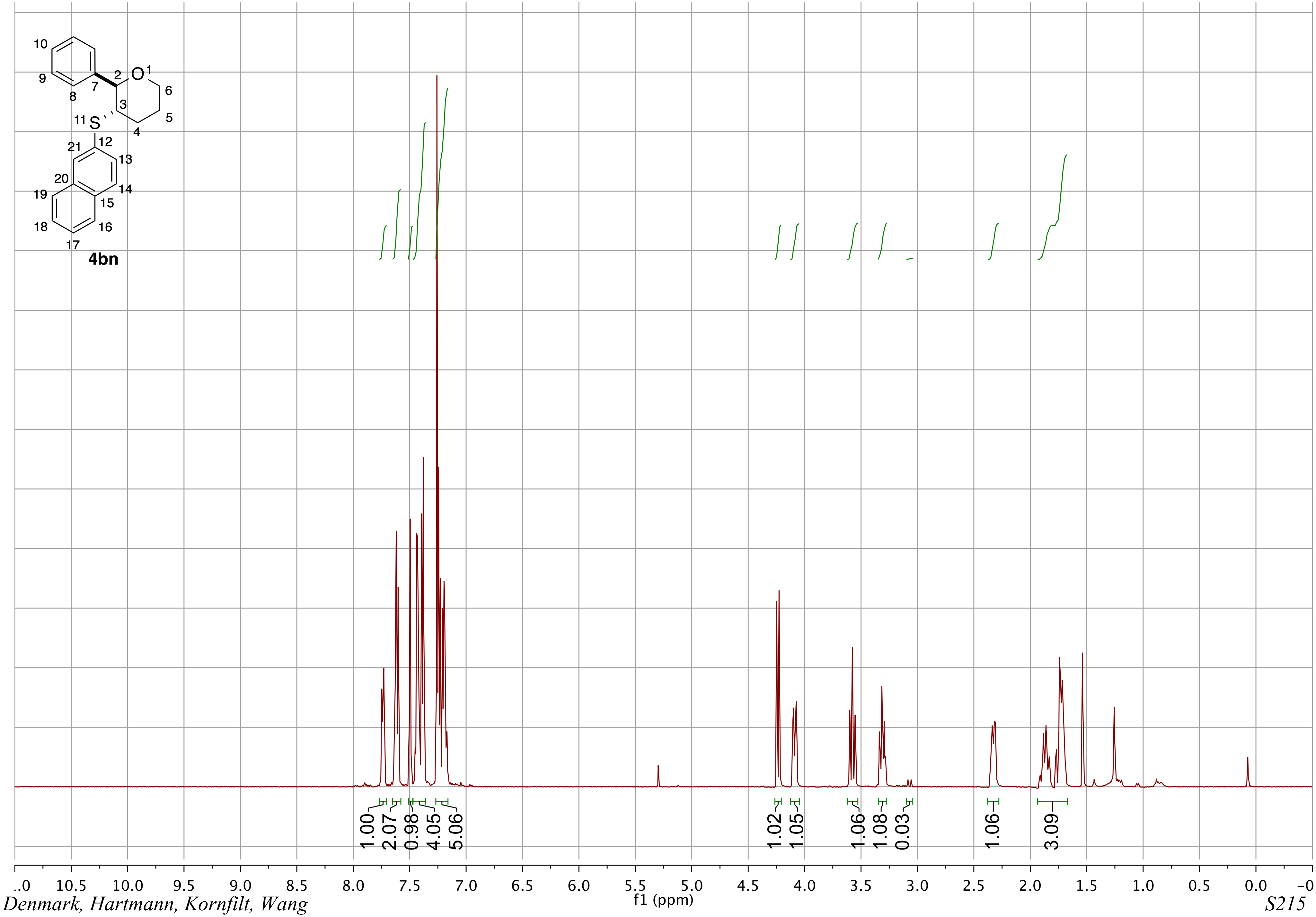
149.1
140.1
133.1
128.4
128.1
128.1
127.8
123.8
85.4
68.5
50.7
33.9
32.5
27.1
23.9
23.8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
16
17
18
19
20
21
1.00
1.03
1.08
2.06
3.25
3.62
1.14
1.02
1.02
1.09
0.31
1.02
0.32
1.03
3.05
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

4bm



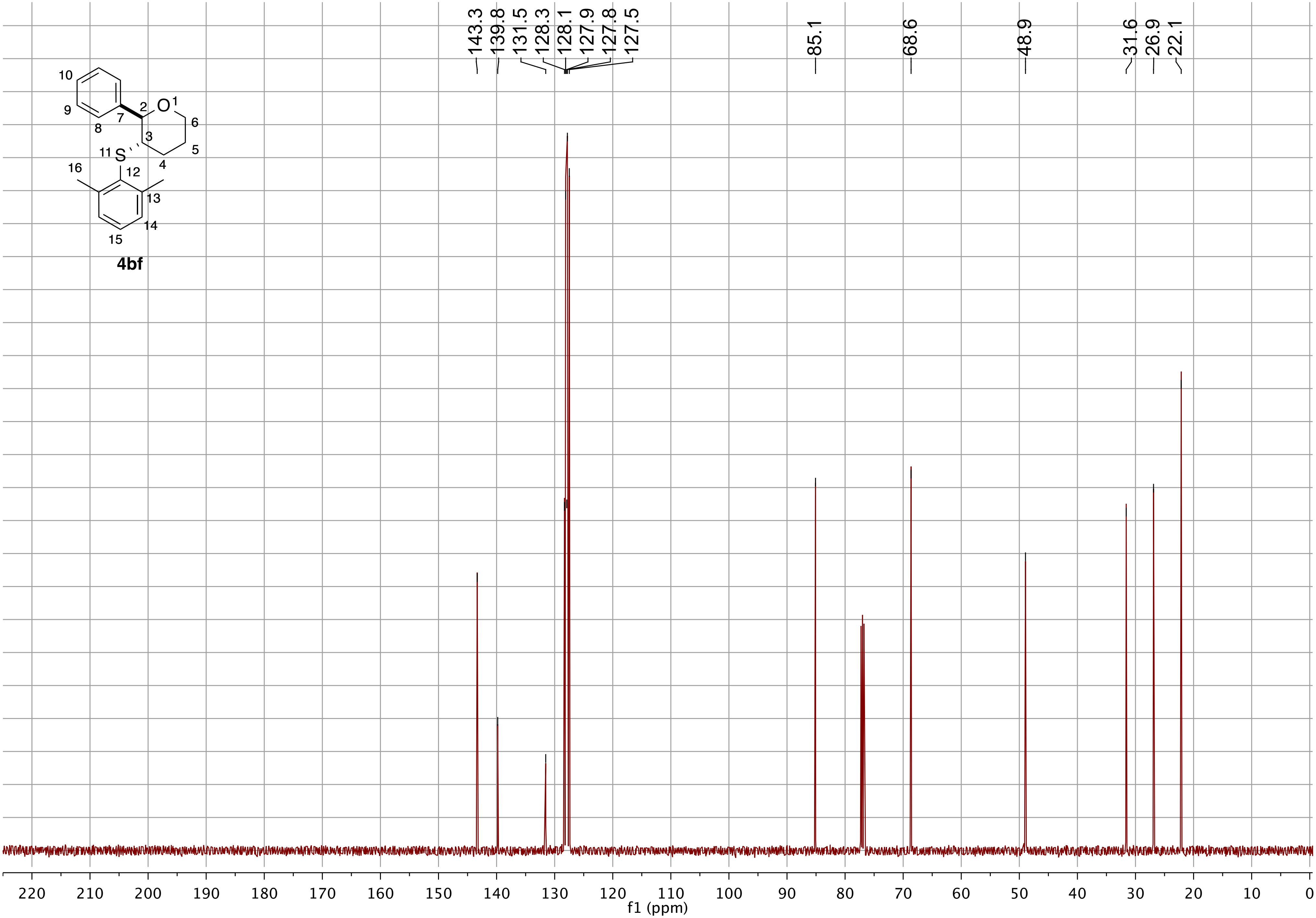
140.0
134.5
133.9
133.6
130.8
128.7
128.4
128.3
128.2
128.1
127.7
126.4
126.0
125.2
85.2
68.5
50.9
32.3
27.0
4bm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
O
S
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)

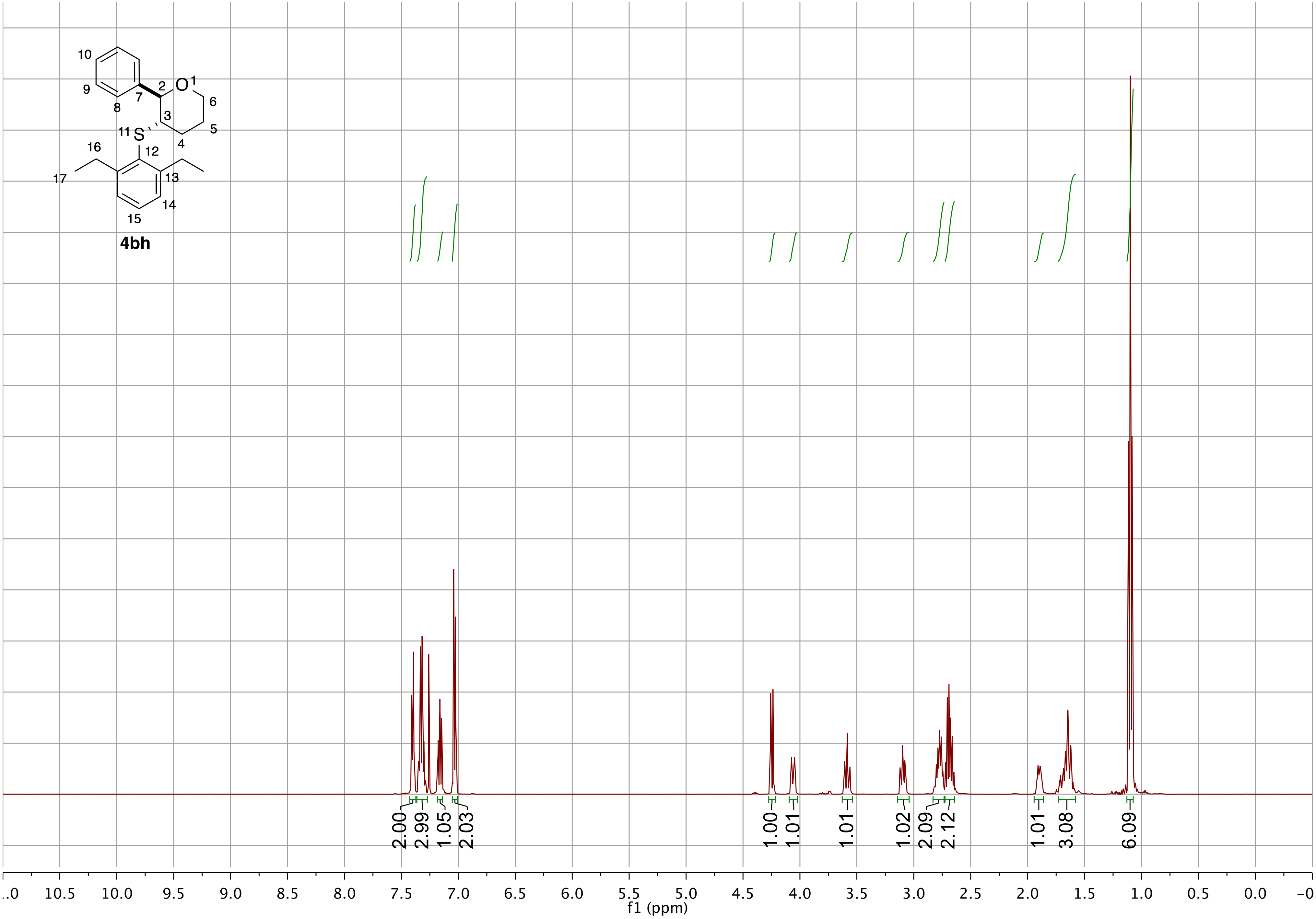


10
9
8
7
2
O
1
6
5
4
3
11
S
12
21
13
20
14
19
15
18
16
17
4bn
1.00
2.07
0.98
4.05
5.06
1.02
1.05
1.06
1.08
0.03
1.06
3.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

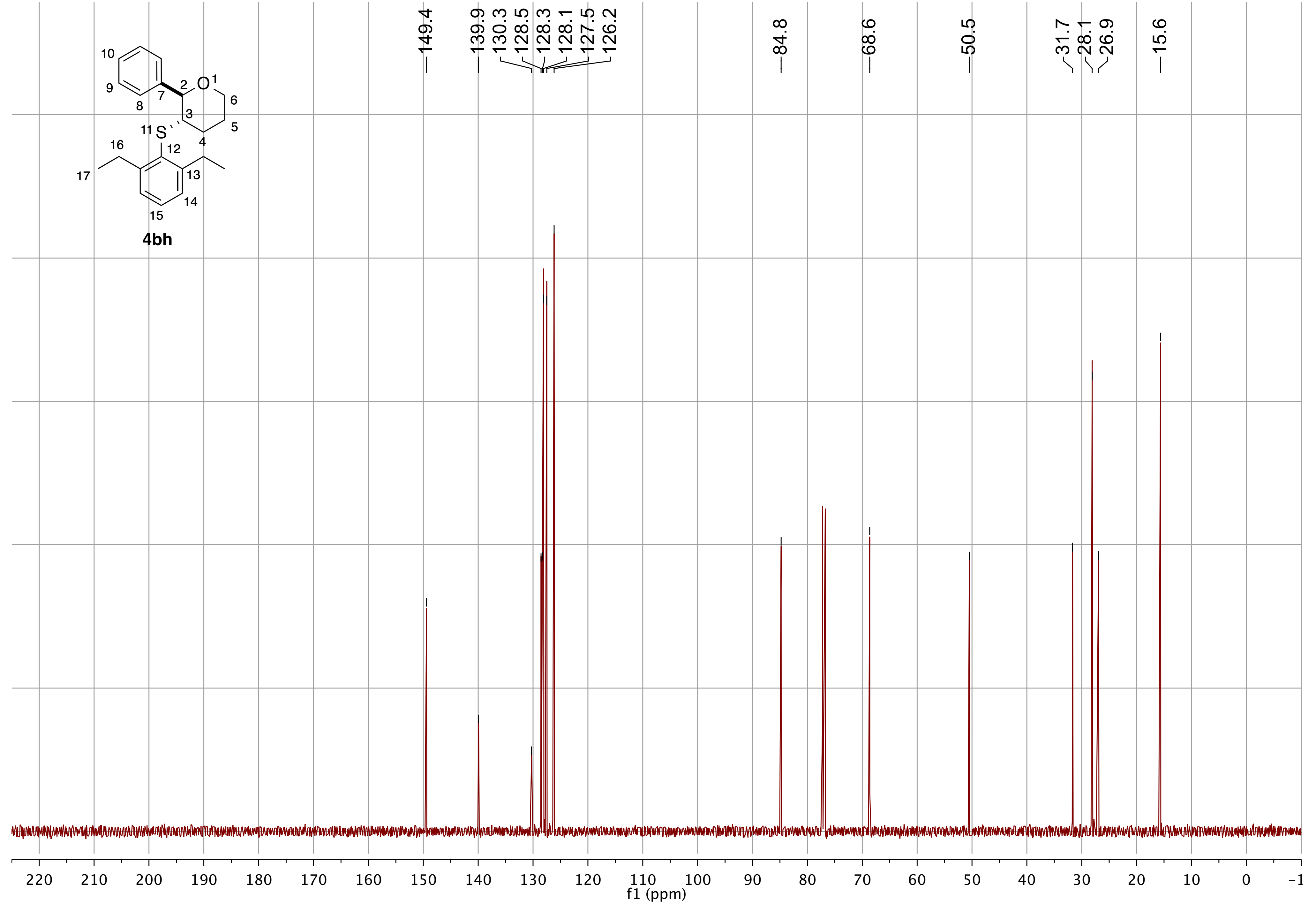

10
9
8
7
2
O
1
6
5
4
3
11
S
16
12
13
14
15
2.03
3.04
1.05
2.00
1.05
1.06
1.06
1.06
6.14
1.05
1.02
2.14
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

4bf


143.3
139.8
131.5
128.3
128.1
127.9
127.8
127.5
85.1
68.6
48.9
31.6
26.9
22.1
10
9
8
7
2
O
1
6
5
4
3
11
S
16
12
13
14
15
4bf
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

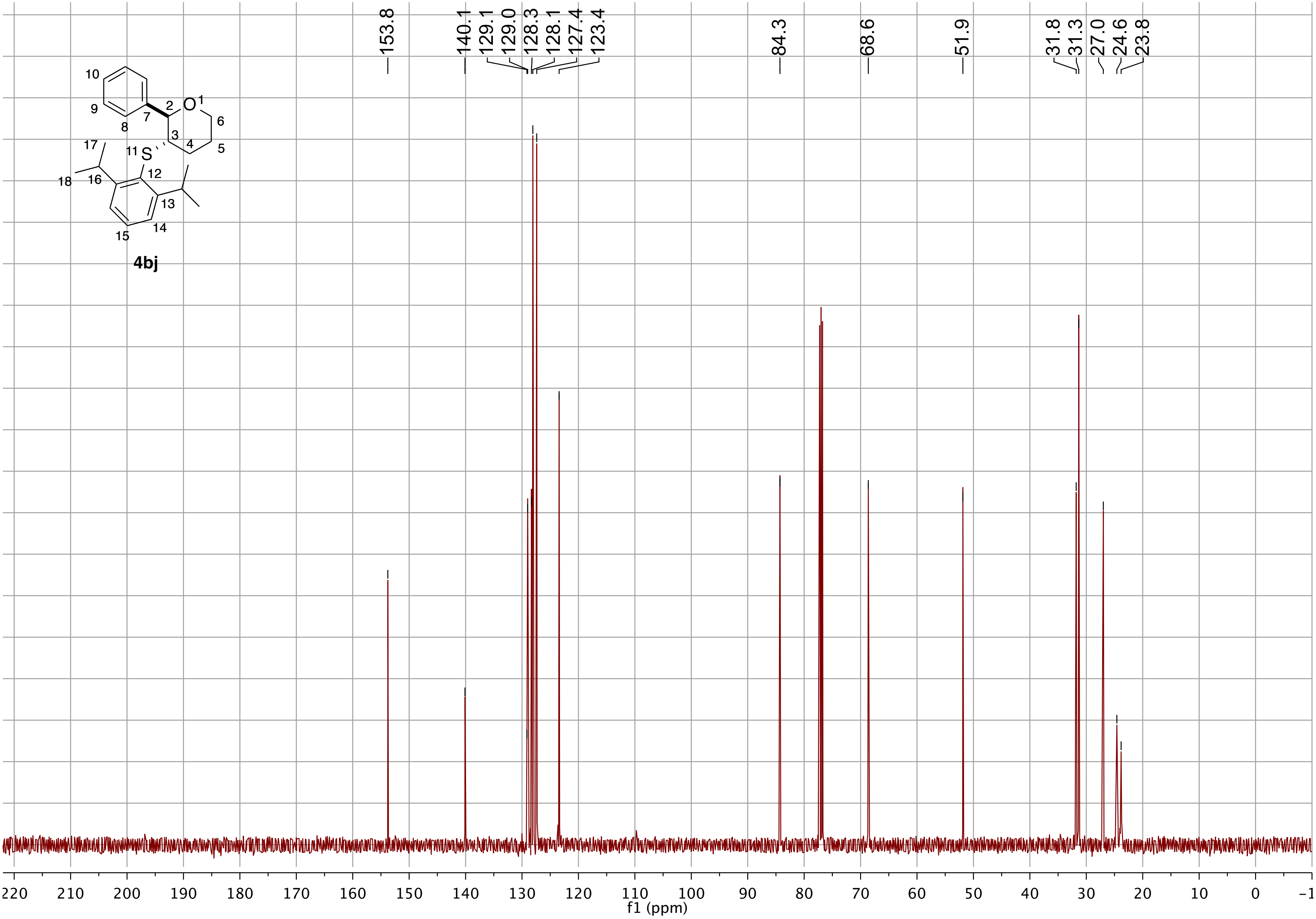


10
9
8
7
2
O
1
6
5
4
3
11
S
12
16
17
13
14
15
4bh
2.00
2.99
1.05
2.03
1.00
1.01
1.01
1.02
2.09
2.12
1.01
3.08
6.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)


149.4
139.9
130.3
128.5
128.3
128.1
127.5
126.2
84.8
68.6
50.5
31.7
28.1
26.9
15.6
10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
16
17
4bh
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)

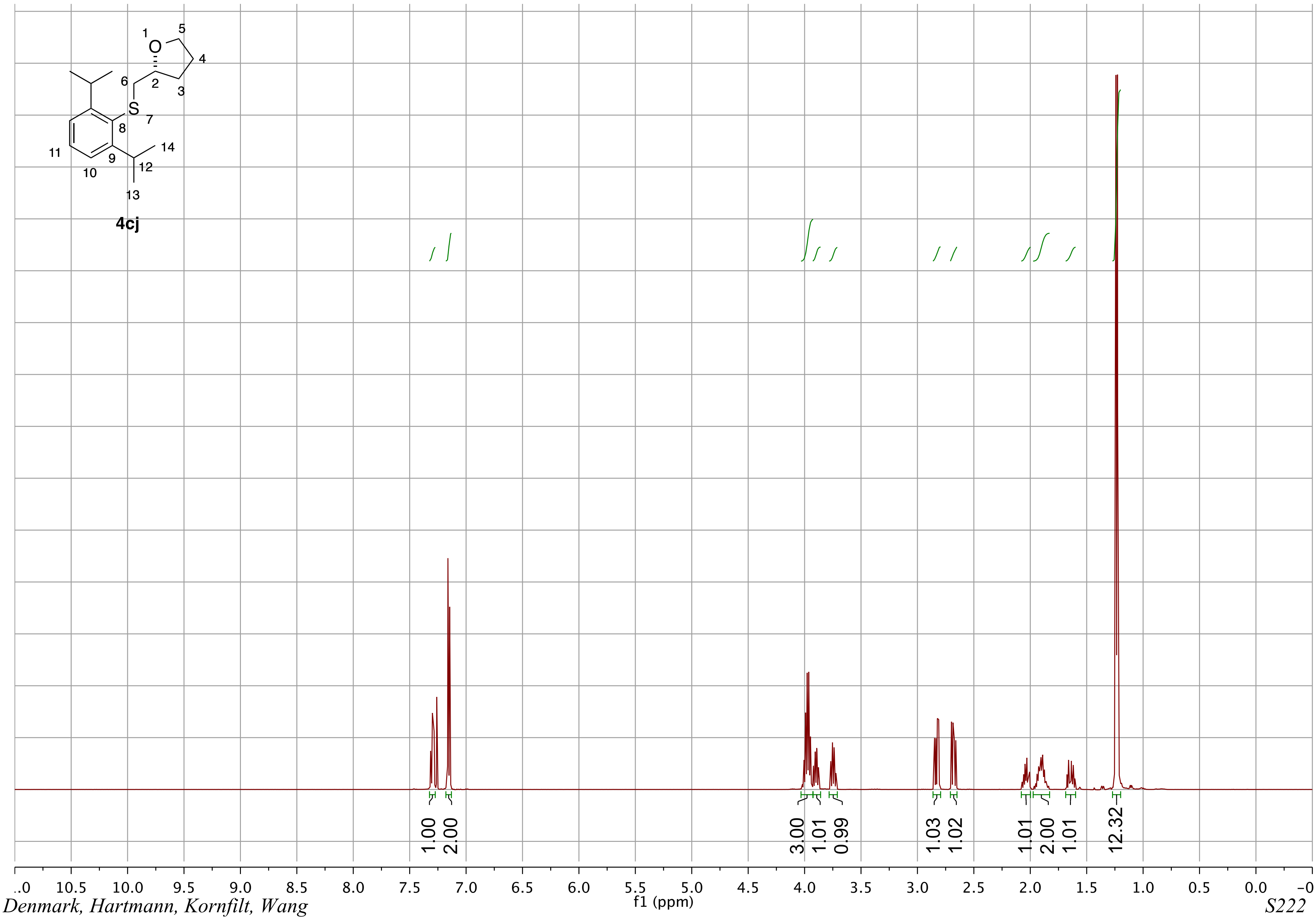

4bj

10
9
8
7
2
O
1
6
5
4
3
11
S
12
13
14
15
16
17
18
2.00
1.94
0.96
1.36
2.08
0.03
1.00
1.01
2.96
1.02
1.05
3.04
12.46
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

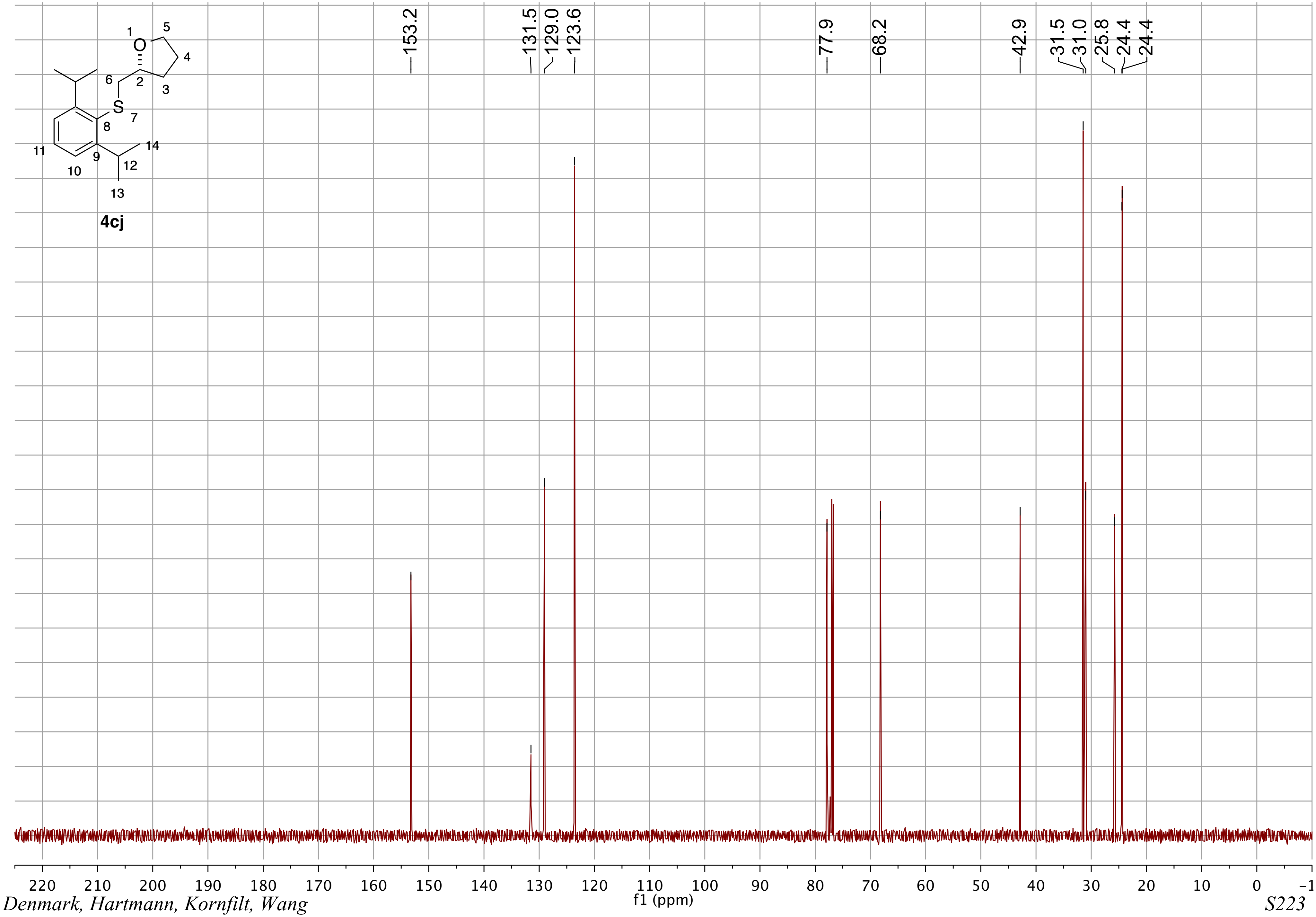


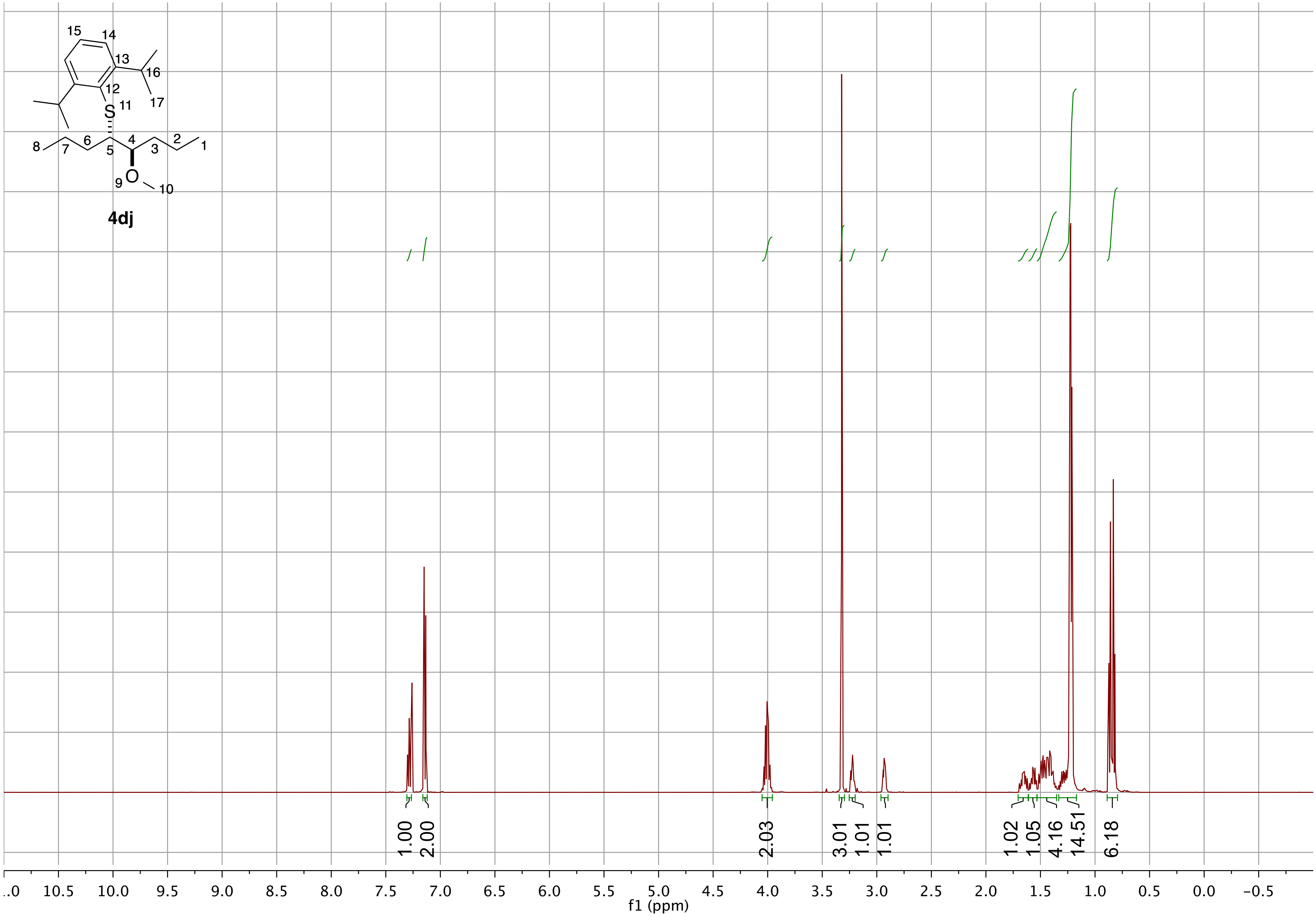
4bj

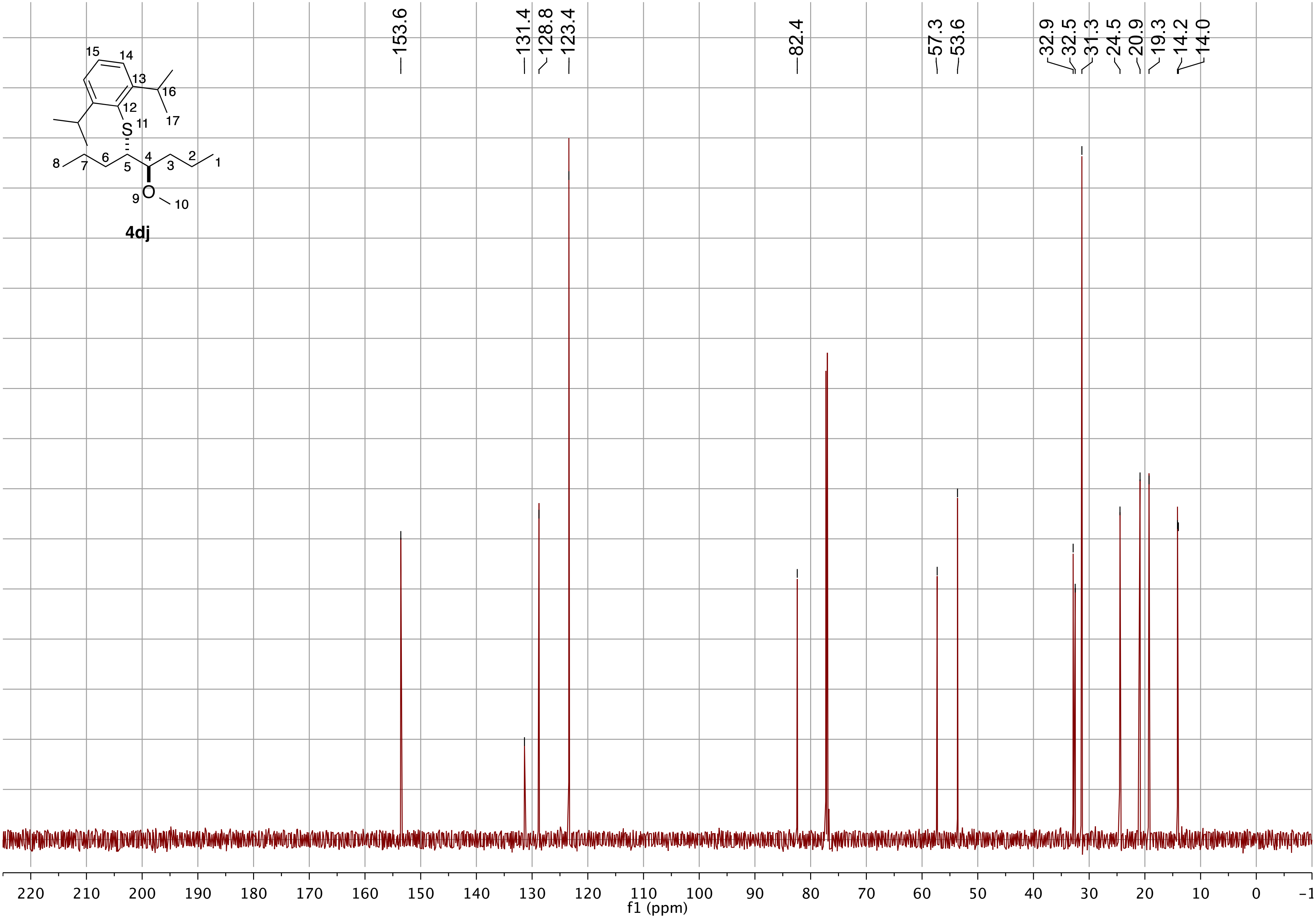
153.8
140.1
129.1
129.0
128.3
128.1
127.4
123.4
84.3
68.6
51.9
31.8
31.3
27.0
24.6
23.8
O
S
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



1
5
O
4
6
2
3
S
7
8
11
14
9
12
10
13
4cj
1.00
2.00
3.00
1.01
0.99
1.03
1.02
1.01
2.00
1.01
12.32
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

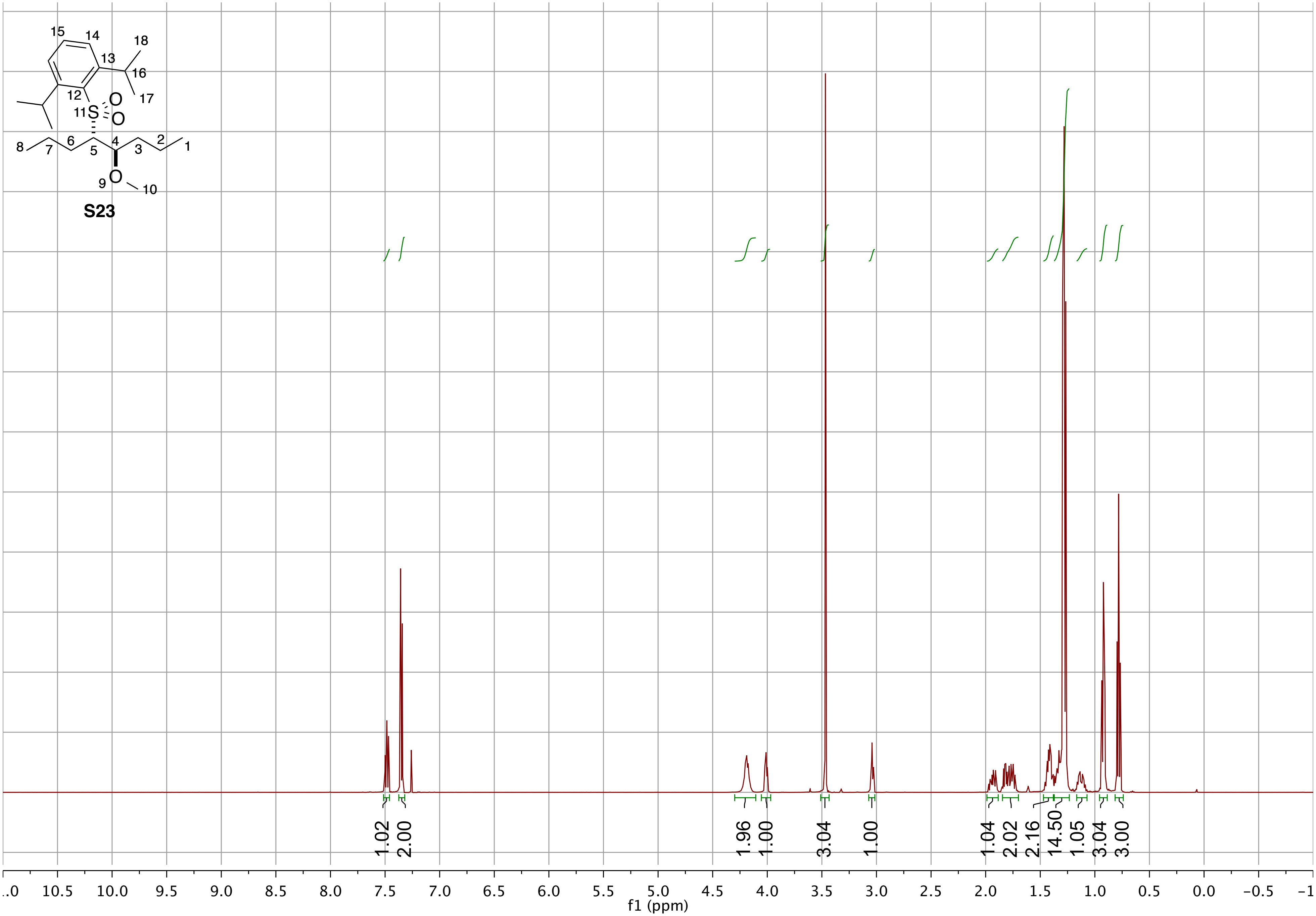

153.2
131.5
129.0
123.6
77.9
68.2
42.9
31.5
31.0
25.8
24.4
24.4
1
O
5
4
6
2
3
S
7
8
11
9
14
12
10
13
4cj
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

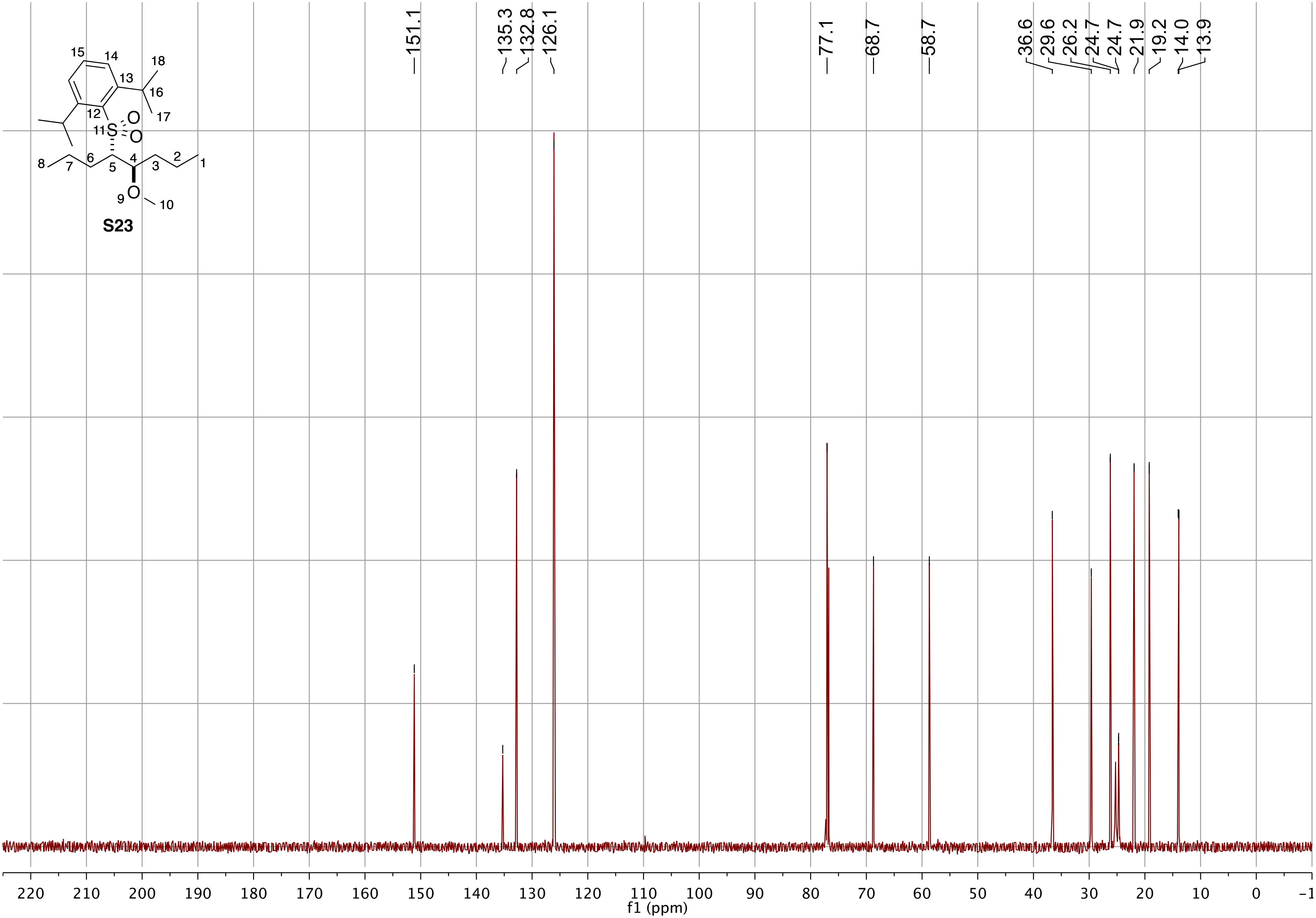

15
14
13
16
12
17
S
11
8
7
6
5
4
3
2
1
9
O
10
4dj
1.00
2.00
2.03
3.01
1.01
1.01
1.02
1.05
4.16
14.51
6.18
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)



4dj

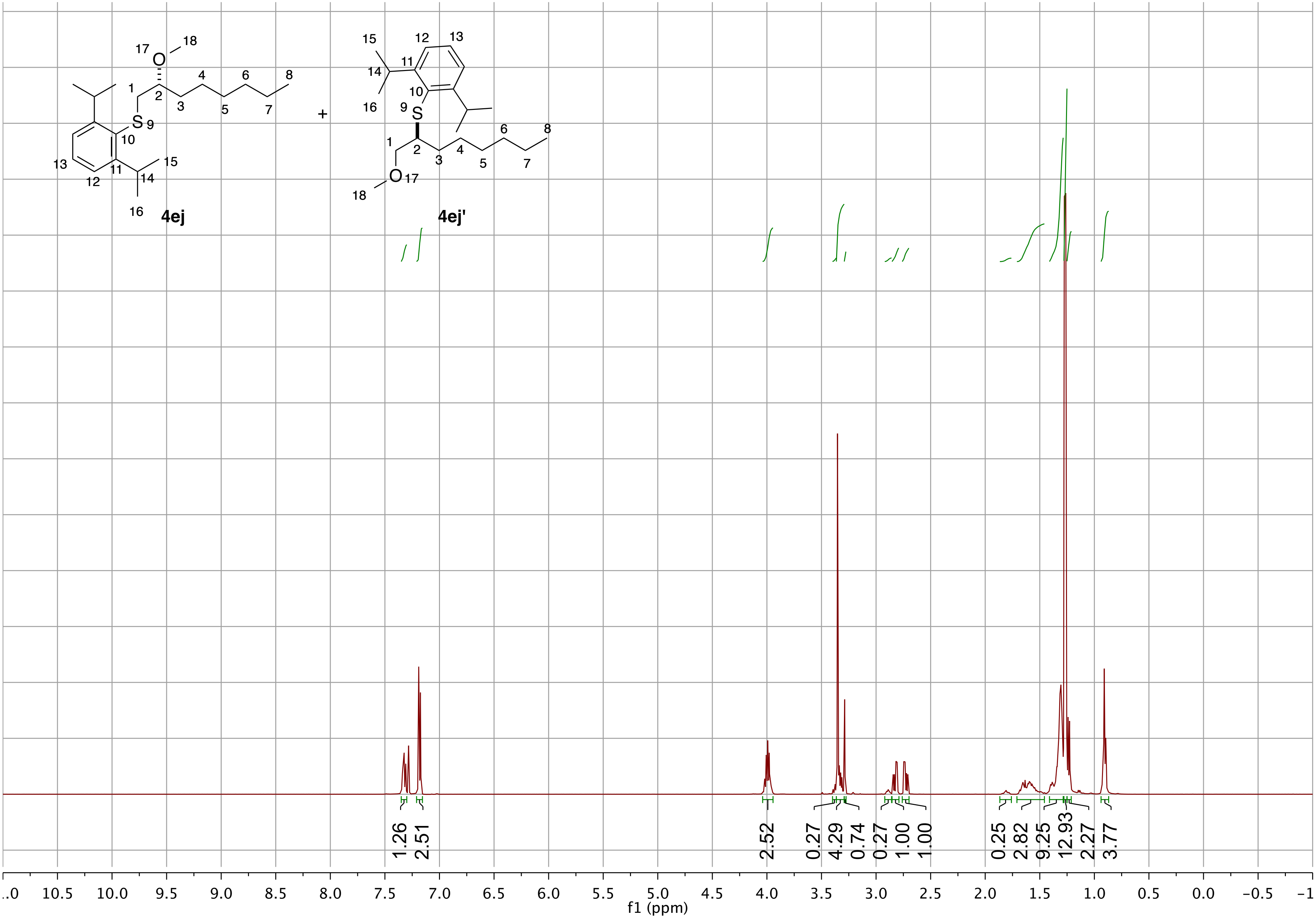
153.6
131.4
128.8
123.4
82.4
57.3
53.6
32.9
32.5
31.3
24.5
20.9
19.3
14.2
14.0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)

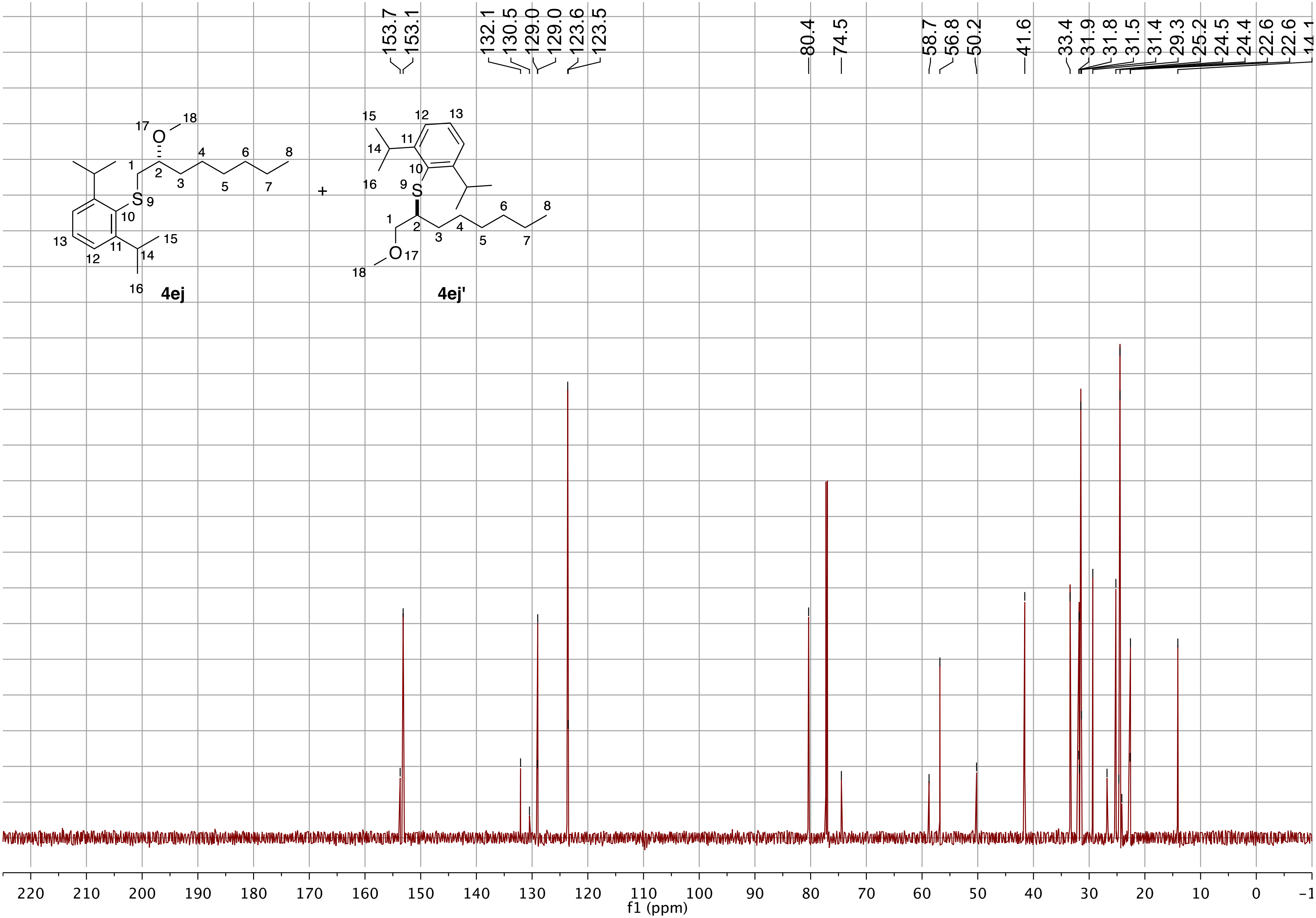

S23
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1.02
2.00
1.96
1.00
3.04
1.00
1.04
2.02
2.16
14.50
1.05
3.04
3.00
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1

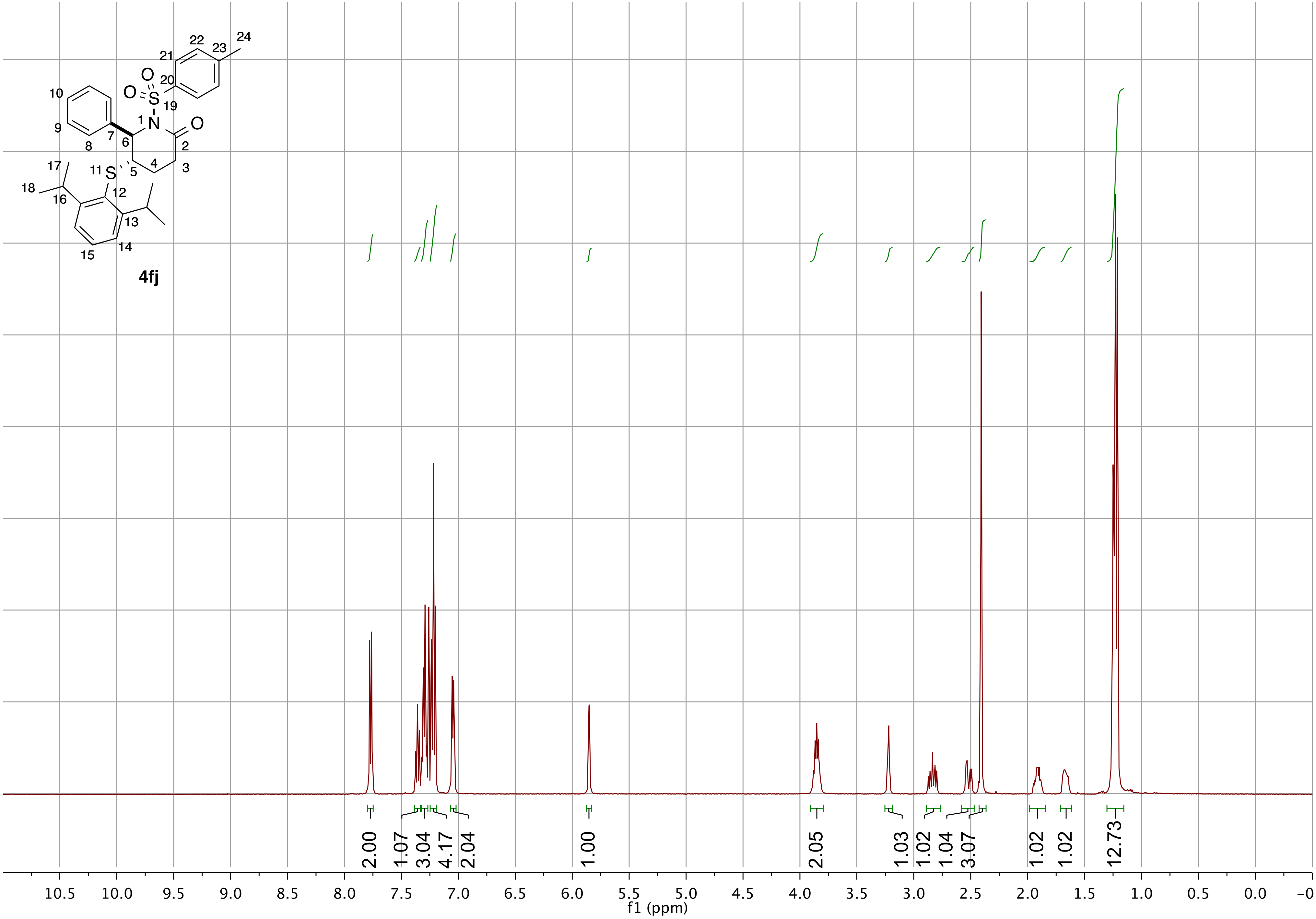


S23

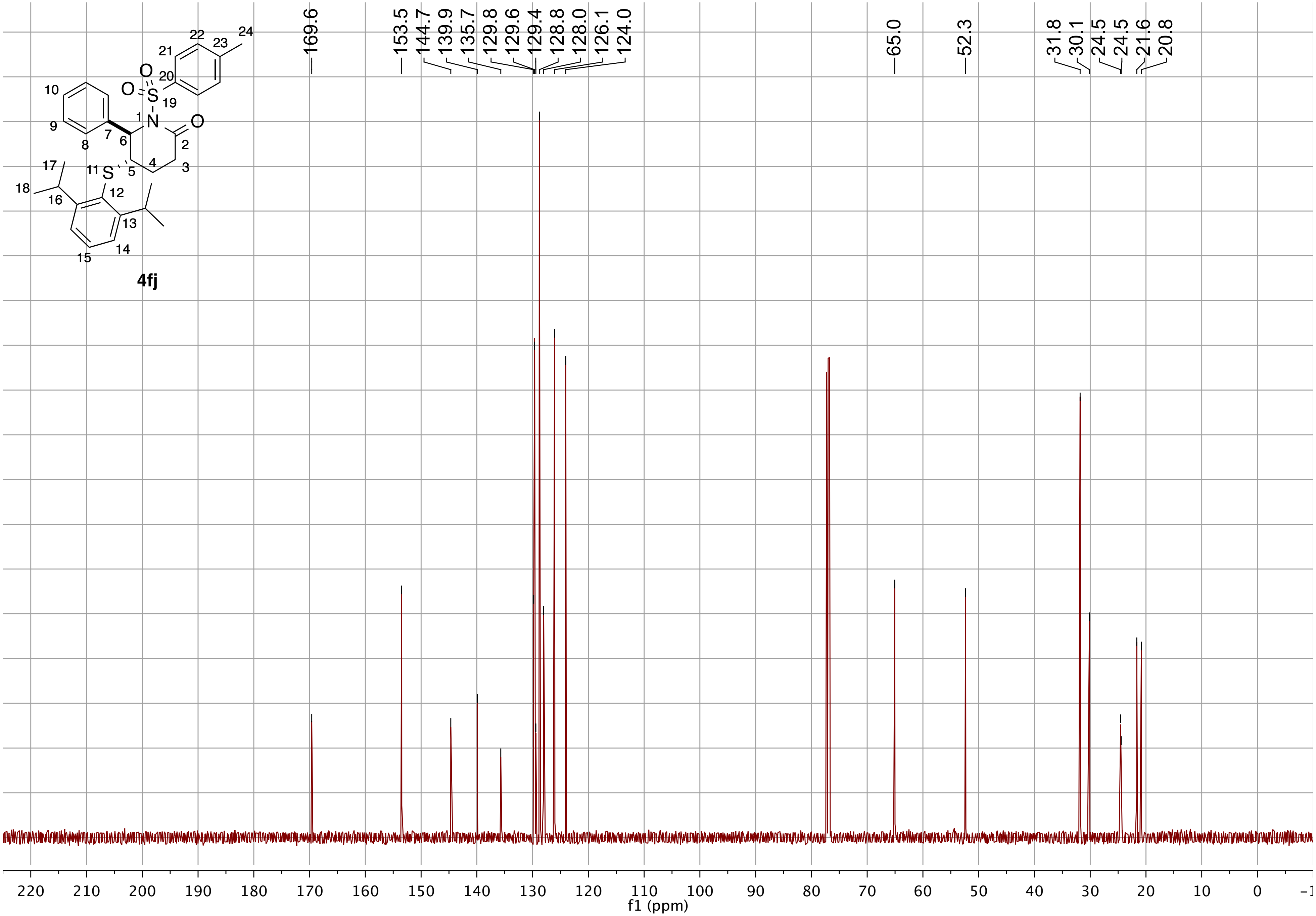
151.1
135.3
132.8
126.1
77.1
68.7
58.7
36.6
29.6
26.2
24.7
24.7
21.9
19.2
14.0
13.9
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
S
O
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

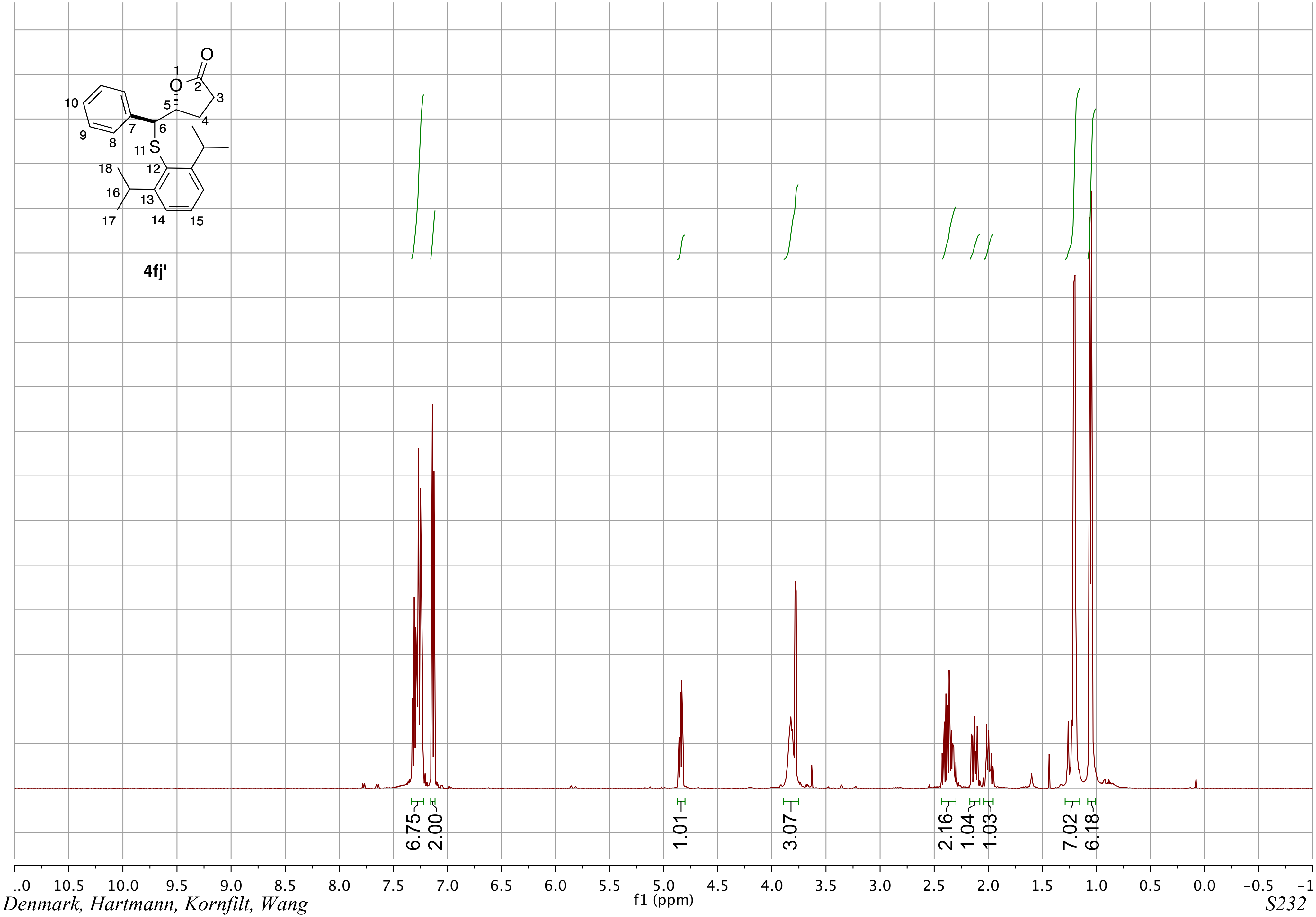

4ej
4ej'
+
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
O
S
1.26
2.51
2.52
0.27
4.29
0.74
0.27
1.00
1.00
0.25
2.82
9.25
12.93
2.27
3.77
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)


153.7
153.1
132.1
130.5
129.0
129.0
123.6
123.5
80.4
74.5
58.7
56.8
50.2
41.6
33.4
31.9
31.8
31.5
31.4
29.3
25.2
24.5
24.4
22.6
22.6
14.1
17
18
O
1
2
3
4
5
6
7
8
S
9
10
11
12
13
14
15
16
4ej
+
15
12
13
11
14
10
16
9
S
1
2
3
4
5
6
7
8
O
17
18
4ej'
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)

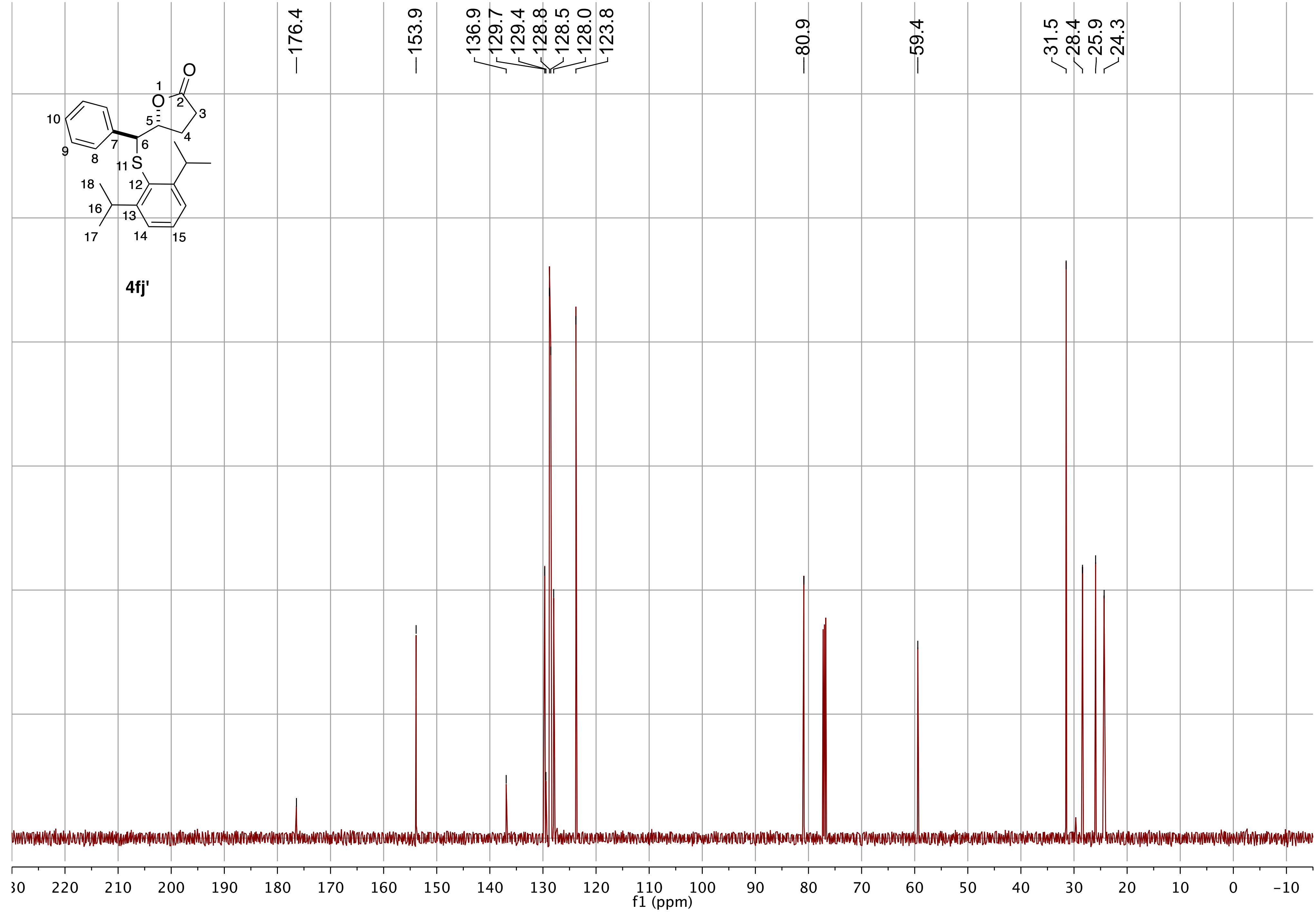


4fj
2.00
1.07
3.04
4.17
2.04
1.00
2.05
1.03
1.02
1.04
3.07
1.02
1.02
12.73
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)


4fj
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
N
O
S
169.6
153.5
144.7
139.9
135.7
129.8
129.6
129.4
128.8
128.0
126.1
124.0
65.0
52.3
31.8
30.1
24.5
24.5
21.6
20.8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4fj'
O
1
2
3
4
5
6
7
8
9
10
11 S
12
13
14
15
16
17
18
6.75
2.00
1.01
3.07
2.16
1.04
1.03
7.02
6.18
..0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)


176.4
153.9
136.9
129.7
129.4
128.8
128.5
128.0
123.8
80.9
59.4
31.5
28.4
25.9
24.3
O
1
O
2
3
4
5
6
7
8
9
10
11 S
12
13
14
15
16
17
18
4fj'
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)