Preparative and Mechanistic Studies Toward a Rational Development of Catalytic, Enantioselective Selenoetherification Reactions

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven dried (140°C) glassware. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, BHT stabilized ACS grade), and CH_2Cl_2 (Fisher, unstabilized HPLC grade) were dried by passage through two columns of neutral alumina in a solvent dispensing system. Solvents for chromatography, filtration and recrystallization were CH_2Cl_2 (Aldrich, ACS grade), ethyl acetate (Fisher, ACS grade), diethyl ether (Fisher, ACS grade), *tert*-butyl methyl ether (Aldrich, ACS grade) and hexane (Fisher, Optima) and were used as received. Triethylamine (Alfa-Aesar, 99%) and pyridine (Fisher) were freshly distilled over CaH_2. Ethanol (Fisher, ACS grade) was distilled from magnesium. Acetic acid was distilled over CrO_3 and acetic anhydride prior to use. Diphenyl diselenide (Aldrich), allyl bromide (Aldrich), triphenylphosphine oxide recrystallized from ethanol (Acros), triphenylphosphine sulfide (Strem), hexamethylphosphorous triamide (Aldrich, distilled prior to use) carbonyl diimidazole (Aldrich), 4-dimethylaminopyridine (Aldrich), trifluoroacetic acid (Aldrich), methanesulfonic acid (Aldrich), sodium borohydride (Aldrich), methanesulfonyl

chloride (Aldrich), 4-toluenesulfonylchloride (Aldrich), 1,3-bistrifluoromethylbenzene (TCI America), *N*-chlorosuccinimide recrystallized from acetic acid (Aldrich), morpholine distilled over KOH (Aldrich), phosphorous trichloride (Aldrich, distilled prior to use), and sodium hydride washed with hexane (Aldrich) were obtained from commercial sources. "Brine" refers to a saturated solution of sodium chloride.

Melting points were obtained in vacuum-sealed capillary tubes and are corrected. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254), or potassium permanganate ($KMnO_4$), or ceric ammonium molybdate (CAM). Column chromatography was performed using Merck silica 60 (40-63 μm particle size) gel purchased from Aldrich.

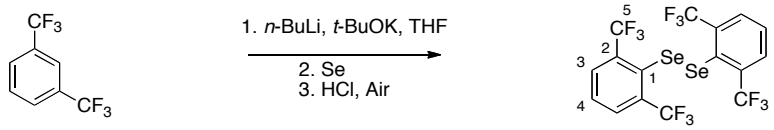
Analytical supercritical fluid chromatography was performed on a Berger Instruments SFC with spectrophotometric detector (220 nm) using Daicel Chiralpak OD, AD as well as a Regis Whelk-O1 column. Optical rotations were measured using a Jasco DIP-360 digital polarimeter in EtOH (ACS grade, distilled from magnesium) or Fischer ACS reagent grade $CHCl_3$ containing approximately 0.75% EtOH as a preservative and are reported as follows: concentration (c = g/dL), and solvent. ^{1}H NMR Spectra and ^{13}C NMR spectra were acquired in $CDCl_3$ at 500 MHz or 400 MHz and referenced to residual $CHCl_3$ at 7.26 and 77.00 ppm respectively. Assignments were obtained by reference to COSY, HMQC and HMBC correlations. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hex (hextet), hep (heptet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. EI mass spectra were performed on a 70-VSE instrument. ESI mass spectra were performed on a Waters Q-Tof Ultima instrument. Data are

reported in the form of (m/z) versus intensity. Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer in KBr pellets or NaCl cells (film). Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory and Robertson Microlit Laboratories, Inc. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus and are corrected.

Literature Preparations

(*E*)-4-Phenyl-but-3-en-1-ol, [1] (*Z*)- 4-phenyl-but-3-en-1-ol,[2] (*E*)-7-phenyl-hept-4-en-1-ol,[3] (*E*)-6-methyl-hept-4-en-1-ol, [3] *N*-phenylselenenylsuccinimide [4], tris(dimethylamino) phosphine sulfide,[5] tris(dimethylamino) phosphine selenide,[5] tricyclohexylphosphine sulfide,[6] 1,3-dimethylhexahydropyrimidine-2-thione,[7] 1,2-bis(4-methoxyphenyl)diselane,[8] 1,2-bis(4-trifluoromethylphenyl)diselane,[9] 1,2-bis(2-trifluoromethylphenyl)diselane,[9] 1,2-bis(2-nitrophenyl)diselane,[10] 1,2-bis(2,4,6-triisopropylphenyl)diselane,[11] epoxy alcohol (**23**),[12] triol (**26**, using ($(DHQ)_2PHAL$).[13] (*R*)-N^2,$N^{2'}$-dimethyl-[1,1'-binaphthalene]2,2'-diamine was synthesized via a known procedure from (*R*)-BINAM.[14]

Preparation of 1,2-Bis(2,6-bis-trifluoromethylphenyl)diselane



To an oven-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar, was added potassium *tert*-butoxide (2.72 g, 24.7 mmol, 1.30 equiv), and THF (42 mL). The mixture was stirred for 5 min at room temperature and then the white suspension was cooled to -78 °C (acetone/dry ice bath temperature). 2.31 M solution of *n*-Butyl lithium in hexanes (8.1 mL, 18.7 mmol, 1.00 equiv) was added followed by 1,3-bis-(trifluoromethyl) benzene (4.00 g, 18.7 mmol) whereupon the solution turned violet. The reaction was stirred at -78 °C for 4 h after which Se (1.77 g, 22.4 mmol, 1.20 equiv) was added in one portion. The cold bath was removed and the solution was allowed to stir at room temperature for 14 h. 10% aq H_2SO_4 (67 mL) was added slowly and then air was bubbled through the mixture for 4.5 h. The mixture was filtered through a 1-inch pad of silica and eluted with TBME (100 mL). The filtrate was transferred to a 250 mL separatory funnel and the organic and aqueous layers were separated. The organics were concentrated on the rotavap (30 °C, 30 mm Hg) and the crude was filtered through a 1-inch pad of silica, which was eluted with TBME (100 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). This procedure was repeated once more after which the crude product was recrystallized from EtOH to afford 719 mg of 1,2-bis(2,6-bis-trifluoromethylphenyl)diselane (13 %) as a yellow solid.

Data for 1,2-bis(2,6-bis-trifluoromethylphenyl)diselane:

mp: 178-179 °C

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

7.90 (d, J = 7.6 Hz, 4 H, HC(3)), 7.62 (t, J = 8.0 Hz, 2 H, HC(4)).

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

137.0 (q, J = 29.6 Hz, C(2)), 130.3 (C(4)), 130.0 (q, J = 6.1 Hz, C(3)), 126.9 (C(1)), 122.9 (q, J = 274 Hz, C(5)).

^{77}Se NMR: (114 MHz, $CDCl_3$)

503 (br s)

IR: (thin film, CH_2Cl_2)

2920 (w), 2844 (w), 1582 (w), 1424 (w), 1333 (m), 1288 (s), 1204 (m), 1176 (s), 1145 (m), 1115 (s), 1130 (s), 1064 (w), 1028 (w), 993 (w), 815 (m), 737 (m), 674 (m), 572 (w), 508 (w).

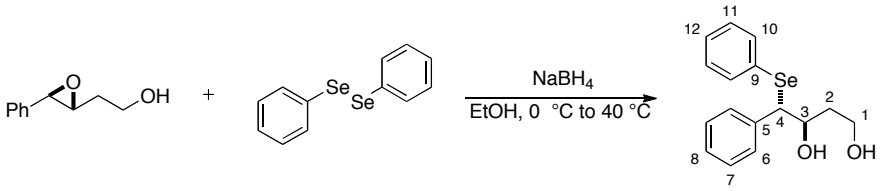
MS: (EI, 70 eV)

585.8 (23.5, M^+), 292.9 (100.0), 273.9 (90.6), 254.9 (18.2), 213.0 (30.6), 175.0 (10.0), 163.0 (20.0), 144.0 (28.2), 125.0 (23.5), 75.0 (12.3).

HRMS: calcd for $C_{16}H_6F_{12}Se_2$: 585.8608, found: 585.8608

General Procedure 1. Synthesis of Diols

Preparation of (3*R*,4*S*)-4-Phenyl-4-(phenylseleno)butane-1,3-diol (24a) (Scheme 10)



23, er = 94:6 **24a**

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (234 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then

the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. The reaction mixture was allowed to cool to room temperature and then was transferred to a 125-mL separatory funnel with an additional 10 mL of CH_2Cl_2. The mixture was extracted with a sat. aq. $NaHCO_3$ solution (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were washed with brine (1 x 25 mL) and dried over $MgSO_4$. The solution was filtered and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 250 mg of **24a** (78%) as a white solid.

Data for **24a**:

mp: 47-48 °C

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

7.46 (d, *J* = 7.5 Hz, 2 H), 7.32-7.21 (m, 8H,), 4.28 (d, *J* = 6.0 Hz, 1 H, HC(4)), 4.22-4.19 (m, 1 H, HC(3)), 3.76-3.74 (m, 2 H, H_2C(1)), 3.00 (d, *J* = 1.5 Hz, 1 H, HOC(3)), 2.57 (t, *J* = 4.5 Hz, 1 H, HOC(1)), 1.89-1.87 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)).

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

138.6, 135.0, 129.1, 128.9, 128.8, 128.5, 128.1, 127.5, 73.0 (C(3)), 61.3 (C(1)), 55.7 (C(4)), 36.3 (C(2)).

IR: (NaCl plates, CH_2Cl_2)

3383 (s, br), 3058 (m), 3027 (m), 2946 (m), 2884 (m), 1951 (w), 1880 (w), 1807 (w), 1755 (w), 1600 (w), 1578 (m), 1494 (m), 1477 (s), 1452 (m), 1437 (s), 1328

(w), 1301 (w), 1266 (w), 1181 (w), 1156 (w), 1065 (s), 1052 (s), 1022 (m), 1000 (m), 988 (w), 966 (w), 897 (w), 844 (w), 740 (s), 700 (s), 670 (m), 618 (w), 554 (w), 522 (w), 507 (w)

MS: (EI, 70 eV)

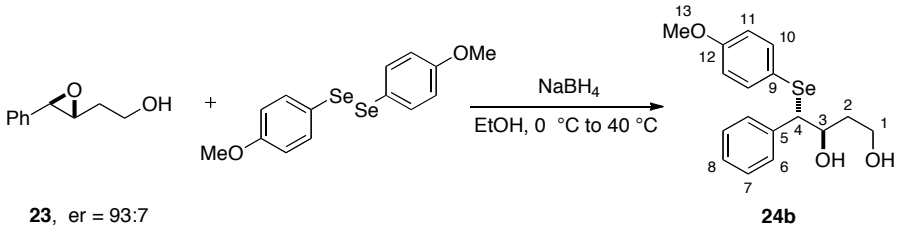
322.0 (2.7, M^+), 165.1 (44.9), 119.0 (12.5), 91.1 (100.0), 77.0 (10.3).

HRMS: calcd for $C_{16}H_{18}O_2Se$: 322.0472, found: 322.0484

TLC: R_f 0.18 (hexanes/EtOAc, 3/2) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 240.8 (c = 0.172, EtOH)

Preparation of (3*R*,4*S*)-4-[(4-Methoxyphenyl)seleno]-4-phenylbutane-1,3-diol (24b) (Scheme 10)



23, er = 93:7 **24b**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(4-methoxyphenyl)diselane (186 mg, 0.50 mmol, 0.50 equiv), and sodium borohydride (45.3 mg, 1.20 mmol, 1.20 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup, the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) to afford 175 mg of **24b** (50%) as a cream white solid.

Data for **24b**:

mp: 62-63 °C

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

7.36 (d, *J* = 8.5 Hz, 2 H, HC(10)), 7.26-7.20 (m, 5 H, HC(6,7,8)), 6.75 (d, *J* = 9.0 Hz, 2 H, HC(11)), 4.19-4.14 (m, 2 H, HC(3,4)), 3.77 (s, 3 H, H_3C(13)), 3.77-3.73 (m, 2 H, H_2C(1)), 3.06 (br s, 1 H, HOC(3)), 2.69 (br s, 1 H, HOC(1)), 1.89-1.86 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)).

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

159.8, 138.7, 137.4, 128.8, 128.4, 127.3, 118.8 (C(9), 114.6 (C(11)), 72.6 (C(3)), 61.2 (C(1)), 55.9 (C(4)), 55.1 (C(13)), 36.2 (C(2)).

IR: (NaCl plates, CH_2Cl_2)

3389 (w, br), 3060 (w), 3025 (w), 3000 (w), 2937 (w), 2836 (w), 1589 (m), 1571 (w), 1490 (s), 1461 (w), 1452 (m), 1440 (w), 1401 (w), 1285 (m), 1247 (s), 1174 (m), 1050 (m), 1029 (m), 1006 (w), 825 (m), 792 (w), 762 (w), 700 (m), 601 (w), 520 (w).

MS: (EI, 70 eV)

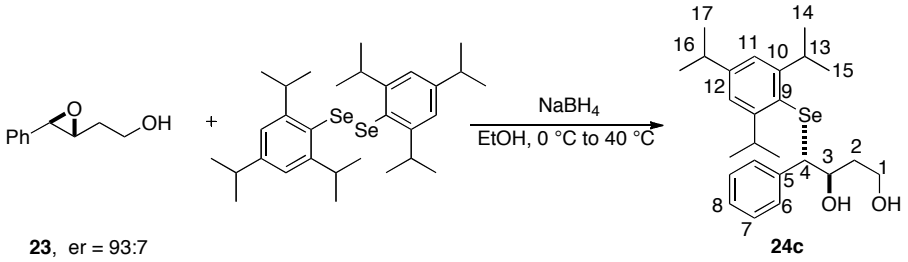
352.0 (6.6, M^+), 190.0 (10.6), 188.0 (65.6), 187.0 (14.9), 186.0 (29.9), 185.0 (15.8), 184.0 (12.9), 135.1 (18.0), 108.1 (30.0), 107.1 (16.0), 91.1 (100.0), 79.1 (14.1), 77.0 (10.7).

HRMS: calcd for $C_{17}H_{20}O_3Se$: 352.0578, found: 352.0578

TLC: R_f 0.22 (hexanes/EtOAc, 1/1) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 222.2 (c = 0.96, EtOH)..

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[2,4,6-tri(propan-2-yl)phenyl]seleno]butane-1,3-diol (24c) (Scheme 10)



23, er = 93:7 **24c**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2,4,6-triiopropylphenyl)diselane (423 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. After 5 min the ice bath was removed and the solution was stirred at 25 °C for 45 min. A solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 368 mg of **24c** (82%) as a white solid.

Data for **24c**:

mp: 120-121 °C

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

7.26-7.19 (m, 5 H, HC(6,7,8)), 6.98 (s, 2 H, HC(11)), 4.26-4.23 (m, 1 H, HC(3)), 3.87 (d, *J* = 6.0 Hz, 1 H, HC(4)), 3.78-3.71 (m, 4 H, HC(1, 13)), 2.95 (br s, 1 H, HOC(3)), 2.88 (sept, *J* = 7.0 Hz, 1 H, HC(16)), 2.66 (t, *J* = 4.5 Hz, 1 H, HOC(1)), 1.89-1.87 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)), 1.26 (d, *J* = 7.0 Hz, 6 H),

1.21 (d, J = 6.5 Hz, 6 H), 1.11 (d, J = 6.5 Hz, 6 H).

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

153.1, 149.9, 139.0, 128.5, 128.3, 127.2, 126.7, 121.7, 73.5 (C(3)), 61.4 (C(1)), 56.5 (C(4)), 36.4 (C(2)), 34.2, 34.1, 24.5, 24.4, 23.9, 23.8.

IR: (NaCl plates, CH_2Cl_2)

3353 (m, br), 3195 (w), 3060 (w), 3028 (w), 2960 (s), 2927 (m), 2868 (m), 1596 (w), 1560 (w), 1493 (w), 1461 (m), 1450 (w), 1421 (w), 1382 (w), 1361 (w), 1310 (w), 1152 (w), 1068 (m), 1054 (m), 1029 (w), 876 (w), 750 (w), 698 (m), 668 (w), 556 (w).

MS: (EI, 70 eV)

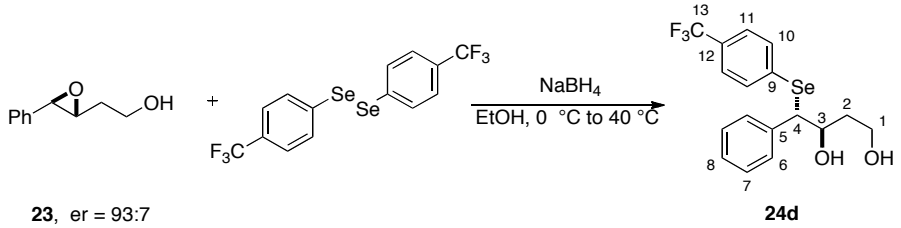
448.2 (4.6, M^+), 286.1 (13.6), 285.1 (12.1), 284.1 (75.2), 282.1 (37.7), 281.1 (14.5), 280.1 (14.2), 203.2 (31.4), 119.1 (12.1), 117.1 (10.8), 91.1 (100.0).

HRMS: calcd for $C_{25}H_{36}O_2Se$: 448.1881, found: 448.1874

TLC: R_f 0.36 (hexanes/EtOAc, 3/2) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 264.8 (c = 0.18, EtOH)

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[4-(trifluoromethyl)phenyl]seleno]butane-1,3-diol (24d) (Scheme 10)



23, er = 93:7 **24d**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(4-trifluoromethylphenyl)diselane (336 mg, 0.75 mmol, 0.75

equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup, the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 277 mg of **24d** (71%) as a white solid.

Data for **24d**:

mp: 63.5-64.5 °C

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

7.54 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.46 (d, *J* = 8.5 Hz, 2H, HC(10)), 7.37-7.25 (m, 5 H, HC(6,7,8)), 4.39 (d, *J* = 6.0 Hz, 1H, HC(4)), 4.33-4.29 (m, 1 H, HC(3)), 3.88-3.81 (m, 2H, H_2C(1)), 2.83 (d, *J* = 3.0 Hz, 1 H, HOC(3)), 2.19 (t, *J* = 5.5 Hz, 1 H, HOC(1)), 1.95-1.89 (m, 1 H, HC(2)), 1.72-1.64 (m, 1 H, HC(2)).

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

138.6, 134.6, 134.4, 129.9 (q, *J* = 32 Hz, C(12)), 129.3, 128.8, 128.0, 125.9 (q, *J* = 3.6 Hz, C(11)), 124.2 (q, *J* = 270 Hz, C(13)), 73.6 (C(3)), 61.4 (C(1)), 55.9 (C(4)), 36.7 (C(2)).

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

-63.08 (s, CF_3(13))

IR: (NaCl plates, CH_2Cl_2)

3371 (m, br), 3063 (w), 3028 (w), 2946 (w), 2886 (w), 1602 (m), 1494 (w), 1452 (w), 1397 (m), 1327 (s), 1165 (m), 1124 (s), 1102 (m), 1078 (s), 1057 (m), 1014

(m), 897 (w), 831 (w), 774 (w), 761 (w), 701 (m), 669 (w), 592 (w), 552 (w), 519 (w).

MS: (EI, 70 eV)

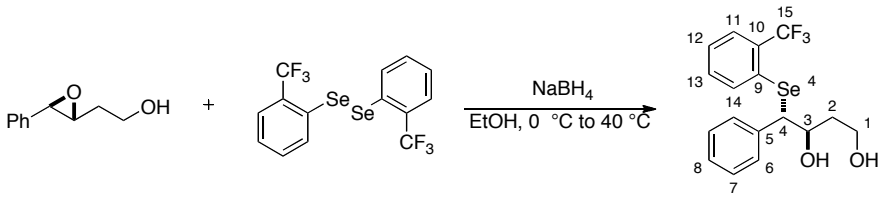
390.0 (2.0, M^+), 373.0 (13.6), 235.1 (16.9), 225.1 (14.5), 166.1 (21.3), 165.1 (86.3), 147.1 (36.7), 145.0 (12.3), 129.1 (13.3), 120.1 (13.7), 119.0 (43.6), 117.1 (21.5), 115.1 (17.1), 105.1 (18.4), 92.0 (26.9), 91.1 (100.0), 77.0 (13.9), 65.1 (14.0) .

HRMS: calcd for $C_{17}H_{17}F_3O_2Se$: 390.0346, found: 390.0340

TLC: R_f 0.19 (hexanes/EtOAc, 3/2) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 239.5 (c = 0.184, EtOH)

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[2-(trifluoromethyl)phenyl]seleno]butane-1,3-diol (24e) (Scheme 10)



23, er = 93:7 **24e**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2-trifluoromethylphenyl)diselane (336 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x

21.5 cm column, hexanes/EtOAc, 1/1) to afford 289 mg of **24e** (74%) as a clear viscous oil.

Data for **24e**:

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

7.68 (d, *J* = 7.5 Hz, 1 H), 7.55 (d, *J* = 7.0 Hz, 1 H), 7.39-7.24 (m, 7 H), 4.41 (d, *J* = 5.5 Hz, 1 H, HC(4)), 4.25-4.21 (m, 1 H, HC(3)), 3.80-3.78 (m, 2 H, HC(1)), 2.94 (d, *J* = 2.5 Hz, 1 H, HOC(3)), 2.35 (t, *J* = 4.5 Hz, 1 H, HOC(1)), 1.86-1.81 (m, 1 H, HC(2)), 1.69-1.62 (m, 1 H, HC(2)).

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

137.9, 137.5, 132.8 (q, *J* = 29 Hz, C(10)), 131.9, 129.2, 128.5, 127.9, 127.8, 127.7, 126.8 (q, *J* = 5.5 Hz, C(11)), 123.7 (q, *J* = 272 Hz, C(15)), 73.1 (C(3)), 61.2 (C(1)), 56.5 (C(4)), 36.3 (C(2)).

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

-60.32 (s, CF_3(15))

IR: (NaCl plates, CH_2Cl_2)

3371 (w, br), 3064 (w), 3028 (w), 2916 (w), 2879 (w), 1591 (w), 1571 (w), 1493 (w), 1468 (w), 1450 (w), 1434 (w), 1312 (w), 1259 (w), 1172 (m), 1127 (m), 1109 (m), 1088 (m), 1027 (m), 765 (m), 731 (w), 701 (m), 642 (w), 527 (w), 510 (w).

MS: (ESI)

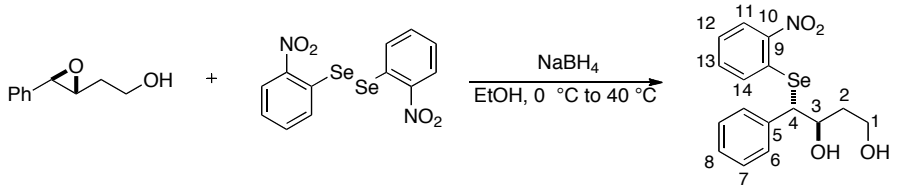
413.0 (71.4, M+Na^+), 397.1 (17.1), 373.0 (70.2), 355.0 (55.9), 282.3 (100.0), 165.1 (15.4), 147.1 (31.4), 129.1 (18.3).

HRMS: calcd for $C_{17}H_{17}F_3O_2SeNa$: 413.0247, found: 413.0244

TLC: R_f 0.32 (hexanes/EtOAc, 1/1) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 237.3 (c = 0.18, EtOH)

Preparation of (3*R*,4*S*)-4-[(2-Nitrophenyl)seleno]-4-phenylbutane-1,3-diol (24f) (Scheme 10)



23, er = 93:7 **24f**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar was added 1,2-bis(2-nitrophenyl)diselane (218 mg, 0.54 mmol, 0.62 equiv), and sodium borohydride (49.0 mg, 1.29 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.3 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (142 mg, 1.00 mmol) in EtOH (2.0 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 16 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x 28 cm column, TBME/hexanes, 7/3) to afford 268 mg of **24f** (85%) as a yellow solid.

Data for **24f**:

mp: 49-51 °C

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

8.16 (d, *J* = 8.5 Hz, 1 H, HC(11)), 7.55-7.51 (m, 3H), 7.39 (t, *J* = 7.2 Hz, 1 H), 7.33 (t, *J* = 7.0 Hz, 2 H), 7.28-7.25 (m, 2 H), 4.53 (d, *J* = 4.5 Hz, 1 H, HC(4)), 4.38 (br s, 1 H, HC(1)), 3.80 (br s, 2 H, HC(1)), 3.06 (d, *J* = 3.0 Hz, 1 H, HOC(3)), 2.41 (s br, 1 H, HOC(1)), 1.89-1.86 (m, 1 H, HC(2)), 1.69-1.62 (m, 1 H, HC(2)).

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

147.5, 137.7, 133.4, 131.7, 130.6, 129.5, 128.8, 127.9, 126.1, 126.0, 73.7 (C(3)), 61.2 (C(1)), 53.6 (C(4)), 36.5 (C(2)).

IR: (NaCl plates, CH_2Cl_2)

3340 (m, br), 2950 (w), 1589 (m), 1565 (w), 1510 (s), 1451 (m), 1329 (s), 1303 (s), 1253 (w), 1096 (w), 1053 (m), 1036 (m), 852 (w), 752 (w), 728 (m), 702 (s), 667 (w), 645 (w), 553 (w), 506 (w).

MS: (ESI)

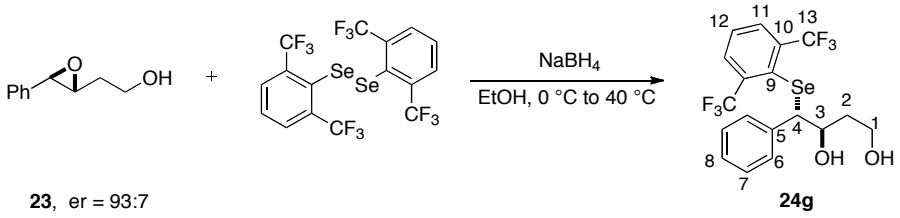
390.0 (100, M + Na^+), 201.9 (12.9).

HRMS: calcd for $C_{16}H_{17}NO_4SeNa$: 390.0220, found: 390.0224

TLC: R_f 0.14 (TBME/hexanes, 7/3) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 173.8 (c = 0.355, $CHCl_3$)

Preparation of (3*R*,4*S*)-4-[[2,6-Bis(trifluoromethyl)phenyl]seleno]-4-phenylbutane-1,3-diol (24g) (Scheme 10)



23, er = 93:7 **24g**

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2,6-bis-trifluoromethylphenyl)diselane (438 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 13 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x

26.5 cm column, hexanes/EtOAc, 3/2) to afford 380 mg of **24g** (82%) as a white solid.

Data for **24g**:

mp: 127-128 °C

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

7.91 (d, *J* = 8.0 Hz, 2 H, HC(11)), 7.58 (t, *J* = 8.0 Hz, 1 H, HC(12)), 7.28-7.20 (m, 5 H, HC(6,7,8)), 4.37 (d, *J* = 5.0 Hz, 1 H, HC(4)), 4.28-4.25 (m, 1 H, HC(3)), 3.72-3.69 (m, 2 H, HC(1)), 3.10 (s br, 1 H, HOC(3)), 2.48 (t, *J* = 5.5 Hz, 1 H, HOC(1)), 1.60-1.47 (m, 2 H, HC(2)).

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

137.4 (q, *J* = 29 Hz, C(10)), 137.3, 130.5 (q, *J* = 6.4 Hz, C(11)), 129.5, 128.9, 128.3, 127.7, 126.4, 123.2 (q, *J* = 274 Hz, C(13)), 72.9 (C(3)), 61.1 (C(1)), 58.4 (C(4)), 36.5 (C(2)).

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

-58.27 (s, CF_3(13))

IR: (NaCl plates, CH_2Cl_2)

3382 (w, br), 3030 (w), 2957 (w), 2929 (w), 2887 (w), 1580 (w), 1494 (w), 1454 (w), 1422 (w), 1332 (m), 1288 (s), 1199 (m), 1184 (m), 1159 (s), 1138 (s), 1116 (m), 1065 (m), 994 (w), 899 (w), 815 (m), 767 (w), 737 (w), 702(m), 675 (m), 654 (w).

MS: (ESI)

481.0 (100, M + Na^+), 479.0 (50), 465.0 (34), 463.0 (16), 441.0 (81), 439.0 (42), 423.0 (11), 411.0 (15), 165.1 (14), 147.1 (37), 129.1 (32).

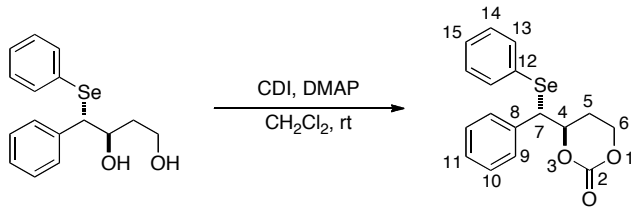
HRMS: calcd for $C_{18}H_{16}F_6O_2SeNa$: 481.0117, found: 481.0123

TLC: R_f 0.35 (hexanes/EtOAc, 3/2) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 295.4 (c = 0.186, EtOH)

General Procedure 2. Synthesis of Carbonates.

Preparation of (4*R*)-4-[(*S*)-Phenyl(phenylseleno)methyl]-1,3-dioxan-2-one (25a) (Scheme 10)



24a **25a**

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diol **24a** (149 mg, 0.465 mmol), and dry CH_2Cl_2 (2.3 mL). A solution of carbonyl diimidazole (113 mg, 0.698 mmol, 1.50 equiv) and 4-dimethylaminopyridine (14.2 mg, 0.116 mmol, 0.25 equiv) in CH_2Cl_2 (2.3 mL) was added under an atmosphere of nitrogen. The resulting solution was stirred at room temperature for 19 h. The reaction mixture was transferred to a 125-mL separatory funnel with an additional 10 mL of CH_2Cl_2. The mixture was washed with H_2O (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were washed with brine (1 x 25 mL) and dried over $MgSO_4$. The solution was filtered and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 103 mg of carbonate **25a** (64%) as a white solid.

Data for **25a**:

mp: 120.5-121.5 °C

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

7.47 (dd, *J* = 8.0, 1.0 Hz, 2 H), 7.33-7.24 (m, 8 H), 4.93 (ddd, *J* = 10.5, 6.5, 3.5 Hz, 1 H, HC(4)), 4.38.4.32 (m, 3 H, HC(6,7)), 2.31-2.26 (m, 1 H, HC(5)), 1.99-1.90 (m, 1 H, HC(5)).

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

148.2 (C(2)), 137.4, 135.3, 129.2, 128.7, 128.6, 128.5, 128.4, 127.9, 80.9 (C(4)), 66.5 (C(6)), 51.8 (C(7)), 26.2 (C(5)).

IR: (NaCl plates, CH_2Cl_2)

3057 (w), 3021 (w), 2916 (w), 2851 (w), 1744 (m), 1578 (w), 1492 (w), 1476 (w), 1450 (w), 1436 (w), 1403 (w), 1248 (w), 1227 (w), 1116 (m), 1021 (w), 996 (w), 763 (w), 742 (w), 692 (w), 560 (w), 542 (w).

MS: (EI, 70 eV)

348.0 (5.1, M^+), 304.0 (13.3), 198.0 (12.2), 156.9 (14.3), 147.1 (42.7), 146.1 (53.9), 118.1 (17.4), 117.1 (73.0), 115.0 (26.8), 105.0 (38.5), 91.1 (100.0), 78.0 (17.8), 77.0 (32.3), 51.0 (12.0).

HRMS: calcd for $C_{17}H_{16}O_3Se$: 348.0265, found: 348.0247

TLC: R_f 0.49 (hexanes/EtOAc, 1/1) [UV]

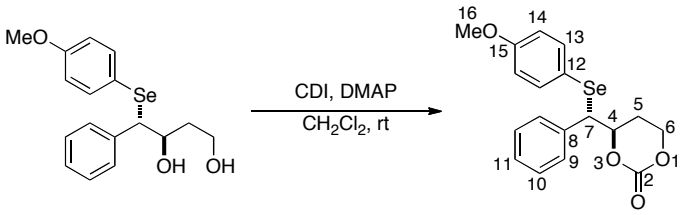
Opt. Rot.: $[\alpha]_D^{24}$ + 155.5 (c = 0.164, $CHCl_3$)

Analysis: $C_{17}H_{16}O_3Se$ (348.0265)

Calcd: C, 58.80; H, 4.64%

Found: C, 58.67; H, 4.73%

Preparation of (4*R*)-4-[(*S*)[(4-Methoxyphenyl)seleno]phenylmethyl]-1,3-dioxan-2-one (25b) (Scheme 10)



24b **25b**

Following General Procedure 2, A solution of carbonyl diimidazole (83.0 mg, 0.511 mmol, 1.50 equiv) and 4-dimethylaminopyridine (10.4 mg, 0.085 mmol, 0.25 equiv) in CH_2Cl_2 (1.7 mL) was added to a solution of diol **24b** (120 mg, 0.340 mmol) in CH_2Cl_2 (1.7 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 75.8 mg of carbonate **25b** (59%) as a light yellow solid.

Data for **25b**:

mp: 125-126 °C

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

7.36 (d, *J* = 8.5 Hz, 2H, HC(13)), 7.31-7.22 (m, 5H, HC(9,10,11)), 6.78 (d, *J* = 8.5 Hz, 2H, HC(14)), 4.88 (ddd, *J* = 10.5, 6.5, 3.0 Hz, 1 H, HC(4)), 4.39-4.32 (m, 2 H, HC(6)), 4.21 (d, *J* = 6.5 Hz, 1 H, HC(7)), 3.80 (s, 3 H, HC(16)), 2.32-2.28 (m, 1 H, HC(5)), 1.99-1.91 (m, 1 H, HC(5)).

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

160.1 (C(15)), 148.3 (C(2)), 137.7, 137.4, 128.6, 128.5, 127.7, 118.4 (C(12)), 114.8 (C(14)), 80.5 (C(4)), 66.5 (C(6)), 55.2 (C(16)), 51.9 (C(7)), 26.3 (C(5)).

IR: (NaCl plates, CH_2Cl_2)

3057 (w), 3028 (w), 2936 (w), 2907 (w), 28294 (w), 1747 (s), 1588 (w), 1490 (m), 1454 (w), 1405 (m), 1286 (w), 1247 (s), 1181 (m), 1118 (s), 1026 (w), 825 (w), 791

(w), 766 (w), 700 (w), 681 (w), 603 (w), 564 (w), 553 (w), 520 (w) 509 (m).

MS: (EI, 70 eV)

378.0 (3.5, M^+), 334.0 (10.1), 226.0 (16.1), 188.0 (26.8), 187.0 (30.8), 186.0 (14.3), 185.0 (19.1), 184.0 (10.8), 171.9 (10.1), 148.1 (32.0), 147.1 (31.9), 146.1 (18.7), 145.1 (15.4), 131.1 (15.6), 130.1 (68.7), 129.1 (26.2), 118.1 (18.9), 117.1 (90.4), 116.1 (20.5), 115.1 (58.7), 108.1 (41.1), 105.0 (43.0), 93.1 (12.0), 92.0 (12.5), 91.1 (100.0), 85.9 (10.7), 84.0 (11.2), 78.1 (16.9), 77.0 (33.4), 65.1 (17.9), 63.1 (16.7), 57.1 (19.5), 55.1 (13.2), 51.0 (16.0)

HRMS: calcd for $C_{18}H_{18}O_4Se$: 378.0370, found: 378.0363

TLC: R_f 0.42 (hexanes/EtOAc, 1/1) [UV]

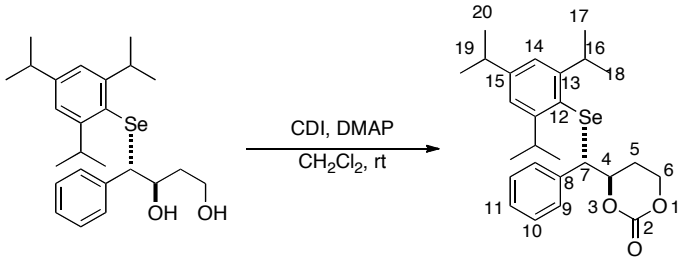
Opt. Rot.: $[\alpha]_D^{24}$ + 154.2 (c = 0.156, $CHCl_3$)

Analysis: $C_{18}H_{18}O_4Se$ (378.0370)

Calcd: C, 57.30; H, 4.81%

Found: C, 57.58; H, 4.91%

Preparation of (4*R*)-4-[(*S*)-Phenyl[[2,4,6-tri(propan-2-yl)phenyl]seleno]methyl]-1,3-dioxan-2-one (25c) (Scheme 10)



24c **25c**

Following General Procedure 2, A solution of carbonyl diimidazole (145 mg, 0.897 mmol, 1.50 equiv) and 4-dimethylaminopyridine (18.3 mg, 0.149 mmol, 0.25 equiv) in CH_2Cl_2

(3.0 mL) was added to a solution of diol **24c** (268 mg, 0.598 mmol) in CH_2Cl_2 (3.0 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 65/35) 158 mg of carbonate **25c** (56%) as a white solid.

Data for **25c**:

mp: 178-179 °C

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

7.30-7.23 (m, 5 H, HC(9,10,11)), 6.99 (s, 2 H, HC(14)), 4.85 (ddd, *J* = 11, 5.0, 1.5 Hz, 1 H, HC(4)), 4.33-4.31 (m, 2 H, HC(6)), 3.92 (d, *J* = 5.5 Hz, 1 H, HC(7)), 3.77 (sept, *J* = 7.0 Hz, 2 H, HC(16)), 2.89 (sept, *J* = 7.0 Hz, 1 H, HC(19)), 2.13-2.09 (m, 1 H, HC(5)), 1.91-1.82 (m, 1 H, HC(5)), 1.26 (d, *J* = 6.5 Hz, 6 H), 1.21 (d, *J* = 7.0 Hz, 6 H), 1.10 (d, *J* = 6.5 Hz, 6 H).

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

153.5, 150.4, 148.3, 137.2, 128.6, 128.5, 127.8, 126.5, 121.9, 80.5 (C(4)), 66.5 (C(6)), 52.0 (C(7)), 34.2, 34.1, 26.2 (C(5)), 24.6, 24.5, 23.9.

IR: (NaCl plates, CH_2Cl_2)

2960 (m), 2929 (w), 2865 (w), 1753 (s), 1595 (w), 1560 (w), 1492 (w), 1482 (w), 1461 (w), 1454 (w), 1404 (m), 1383 (w), 1362 (w), 1308 (w), 1248 (w), 1227 (w), 1181 (m), 1119 (s), 1057 (w), 940 (w), 879 (w), 766 (w), 748 (w), 700 (m), 560 (w).

MS: (EI, 70 eV)

474.2 (5.1, M^+), 282.2 (43.7), 282.1 (31.4), 281.1 (12.0), 280.1 (14.0), 242.1 (26.4), 240.1 (14.6), 239.1 (12.2), 226.0 (16.1), 204.2 (14.8), 203.2 (90.1), 199.0 (18.4), 197.0 (22.5), 195.0 (10.9), 148.1 (15.2), 147.1 (100.0), 146.1 (27.0), 145.1 (16.1),

129.1 (15.1), 128.1 (10.3), 119.1 (12.6), 117.1 (45.5), 116.1 (10.2), 115.1 (21.1), 105.1 (53.1), 91.1 (88.1), 77.1 (17.4), 57.2 (15.2).

HRMS: calcd for $C_{26}H_{34}O_3Se$: 474.1673, found: 474.1682

TLC: R_f 0.43 (hexanes/EtOAc, 65/35) [UV]

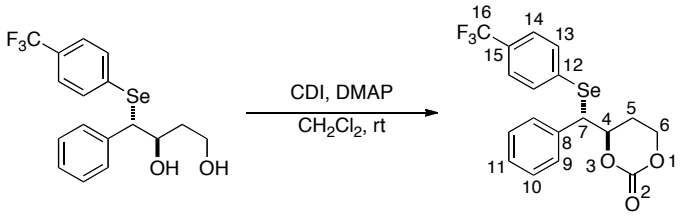
Opt. Rot.: $[\alpha]_D^{24}$ + 216.6 (c = 0.178, $CHCl_3$)

Analysis: $C_{26}H_{34}O_3Se$ (474.1673)

Calcd: C, 65.95; H, 7.24%

Found: C, 66.01; H, 7.44%

Preparation of (4*R*)-4-[(*S*)-Phenyl[[4-(trifluoromethyl)phenyl]seleno]methyl]-1,3-dioxan-2-one (25d) (Scheme 10)



24d **25d**

Following General Procedure 2, A solution of carbonyl diimidazole (109 mg, 0.674 mmol, 1.50 equiv) and 4-dimethylaminopyridine (13.7 mg, 0.112 mmol, 0.25 equiv) in CH_2Cl_2 (2.2 mL) was added to a solution of diol **24d** (175 mg, 0.449 mmol) in CH_2Cl_2 (2.2 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 130 mg of carbonate **25d** (70%) as a white solid.

Data for **25d**:

mp: 112.5-113.5 °C

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

7.55 (d, *J* = 8.0 Hz, 2 H, HC(14)), 7.47 (d, *J* = 8.0 Hz, 2 H, HC(13)), 7.34-7.28 (m,

5 H, HC(9,10,11)), 4.95 (ddd, J = 11, 5.5, 3.5 Hz, 1 H, HC(4)), 4.42 (d, J = 5.5 Hz, 1 H, HC(7)), 4.36-4.34 (m, 2 H, HC(6)), 2.22-2.18 (m, 1 H, HC(5)), 1.97-1.88 (m, 1 H, HC(5)).

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

148.1 (C(2)), 136.8, 134.6, 133.6, 130.20 (q, J = 32 Hz, C(15)), 128.9, 128.8, 128.2, 125.82 (q, J = 3.6 Hz, C(14)), 123.83 (q, J = 271 Hz, C(16)), 80.9 (C(4)), 66.5 (C(6)), 51.9 (C(7)), 25.9 (C(5))

IR: (NaCl plates, CH_2Cl_2)

3063 (w), 3031 (w), 2979 (w), 2920 (w), 1750 (s), 1601 (m), 1496 (w), 1480 (w), 1454 (w), 1398 (m), 1327 (s), 1251 (m), 1229 (w), 1166 (s), 1121 (s), 1078 (s), 1057 (m), 1014 (m), 831 (w), 766 (w), 702 (m), 692 (w), 593 (w), 563 (w), 540 (w).

MS: (EI)

415.9 (2.4, M^+), 372.0 (19.0), 265.9 (39.1), 263.9 (19.7), 225.9 (10.2), 224.9 (11.7), 197.0 (11.2), 185.0 (30.1), 148.1 (10.3), 147.1 (45.7), 146.1 (82.9), 145.0 (16.8), 127.0 (10.0), 117.0 (51.6), 116.0 (17.0), 115.0 (42.1), 105.0 (51.2), 77.0 (32.5), 65.1 (10.8), 57.1 (13.2), 51.01 (12.8)

HRMS: calcd for $C_{18}H_{15}F_3O_3Se$: 416.0139, found: 416.0124

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

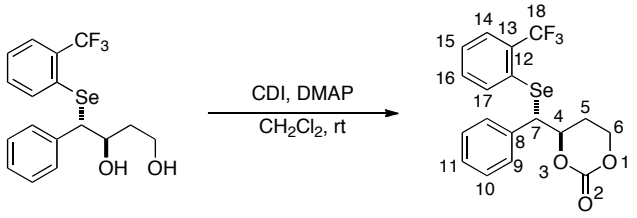
Opt. Rot.: $[\alpha]_D^{24}$ + 178.8 (c = 0.160, $CHCl_3$)

Analysis: $C_{18}H_{15}F_3O_3Se$ (416.0139)

Calcd: C, 52.06; H, 3.64%

Found: C, 52.07; H, 3.58%

Preparation of (4*R*)-4-[(*S*)-Phenyl[[2-(trifluoromethyl)phenyl]seleno]methyl]-1,3-dioxan-2-one (25e) (Scheme 10)



24e **25e**

Following General Procedure 2, A solution of carbonyl diimidazole (142 mg, 0.877 mmol, 1.50 equiv) and 4-dimethylaminopyridine (17.9 mg, 0.146 mmol, 0.25 equiv) in CH_2Cl_2 (2.9 mL) was added to a solution of diol **24e** (228 mg, 0.585 mmol) in CH_2Cl_2 (2.9 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) 148 mg of carbonate **25e** (61%) as a white solid.

Data for **25e**:

mp: 92-93 °C

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

7.69 (d, *J* = 7.5 Hz, 1 H, HC(14)), 7.48 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.32-7.23 (m, 6 H), 4.97-4.93 (m, 1 H, HC(4)), 4.41 (d, *J* = 6.0 Hz, 1 H, HC(7)), 4.35-4.33 (m, 2 H, HC(6)), 2.22-2.18 (m, 1 H, HC(5)), 1.96-1.87 (m, 1 H, HC(5)).

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

148.1 (C(2)), 138.3, 136.7, 133.0 (q, *J* = 29 Hz, C(13)), 132.0, 128.9, 128.7, 128.4, 128.1, 127.0, 126.89 (q, *J* = 5.5 Hz, C(14)), 123.65 (q, *J* = 272 Hz, C(18)), 80.9 (C(4)), 66.5 (C(6)), 52.3 (C(7)), 25.9 (C(5))

^{19}F NMR: (376 MHz, $CDCl_3$)

-60.15 (CF_3(13))

IR: (NaCl plates, CH_2Cl_2)

3057 (w), 3028 (w), 2917 (w), 2851 (w), 1751 (s), 1590 (w), 1475 (w), 1437 (w), 1405 (m), 1311 (s), 1252 (m), 1227 (w), 1173 (m), 1119 (s), 1088 (m), 1026 (m), 957 (w), 765 (m), 730 (w), 701 (m), 682 (w), 642 (w), 564 (w), 527 (w).

MS: (EI, 70 eV

416.0 (2.3, M^+), 147.1 (29.4), 146.1 (16.8), 117.1 (27.4), 115.0 (19.4), 105.0 (20.3), 91.0 (100.0), 77.0 (10.2).

HRMS: calcd for $C_{18}H_{15}F_3O_3Se$: 416.0139, found: 416.0125

TLC: R_f 0.25 (hexanes/EtOAc, 3/2) [UV]

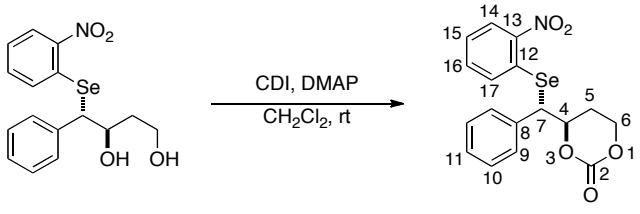
Opt. Rot.: $[\alpha]_D^{24}$ + 167.6 (c = 0.164, $CHCl_3$)

Analysis: $C_{18}H_{15}F_3O_3Se$ (416.0139)

Calcd: C, 52.06; H, 3.64%

Found: C, 51.82; H, 3.49%

Preparation of (4*R*)-4-[(*S*)[(2-Nitrophenyl)seleno]phenylmethyl]-1,3-dioxan-2-one (25f) (Scheme 10)



24f **25f**

Following General Procedure 2, A solution of carbonyl diimidazole (206 mg, 1.27 mmol, 1.50 equiv) and 4-dimethylaminopyridine (25.8 mg, 0.211 mmol, 0.25 equiv) in CH_2Cl_2 (4.2 mL)

was added to a solution of diol **24f** (310 mg, 0.850 mmol) in CH_2Cl_2 (4.2 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 185 mg of carbonate **25f** (56%) as a yellow solid. The solid was further purified by recrystallization from CH_2Cl_2/hexanes to obtain analytically pure product.

Data for **25f**:

mp: 159-160 °C

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

8.18 (d, *J* = 8.5 Hz, 1H, HC(14)), 7.56-7.51 (m, 3H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.39-7.30 (m, 4H), 5.05-5.01 (m, 1 H, HC(4)), 4.64 (d, *J* = 4.5 Hz, 1 H, HC(7)), 4.37-4.35 (m, 2 H, HC(6)), 2.21-2.16 (d, *J* = 14.5 Hz, 1 H, HC(5)), 2.04-1.96 (m, 1 H, HC(5)).

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

147.9 (C(2)), 147.7, 136.3, 133.6, 130.7, 130.5, 129.3, 129.1, 128.4, 126.6, 126.1, 81.4 (C(4)), 66.5 (C(6)), 50.2 (C(7)), 25.7 (C(5))

IR: (NaCl plates, CH_2Cl_2)

3061 (w), 3028 (w), 2979 (w), 2916 (w), 1747 (s), 1589 (m), 1566 (w), 1512 (s), 1478 (w), 1451 (w), 1432 (w), 1405 (m), 1331 (s), 1305 (m), 1250 (m), 1228 (m), 1201 (m), 1184 (m), 1143 (m), 1117 (s), 1036 (w), 956 (w), 852 (w), 783 (w), 766 (w), 730 (m), 703 (m), 681 (w), 647 (w), 564 (w), 540.0 (w), 524 (w), 509 (w).

MS: (ESI)

416.0 (100.0, M + Na^+), 414.0 (56.5), 390.0 (11.4), 372.0 (11.4).

HRMS: calcd for $C_{17}H_{15}NO_5SeNa$: 416.0013, found: 416.0013

TLC: R_f 0.18 (hexanes/EtOAc, 1/1) [UV]

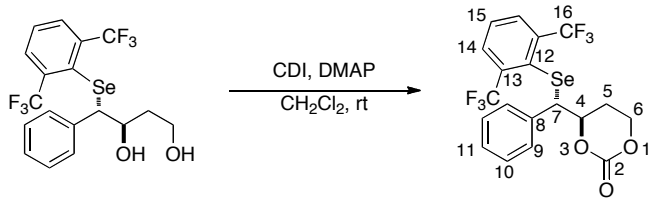
Opt. Rot.: $[\alpha]_D^{24}$ + 175.8 (c = 0.405, $CHCl_3$)

Analysis: $C_{17}H_{15}NO_5Se$ (392.26)

Calcd: C, 52.05; H, 3.85; N, 3.57%

Found: C, 52.03; H, 3.59; N, 3.66%

Preparation of (4*R*)-4-[(*S*)[[2,6-Bis(trifluoromethyl)phenyl]seleno]phenylmethyl]-1,3-dioxan-2-one (25g) (Scheme 10)



24g **25g**

Following General Procedure 2, A solution of carbonyl diimidazole (121 mg, 0.749 mmol, 1.50 equiv) and 4-dimethylaminopyridine (15.2 mg, 0.125 mmol, 0.25 equiv) in CH_2Cl_2 (2.5 mL) was added to a solution of diol **24g** (228 mg, 0.499 mmol) in CH_2Cl_2 (2.5 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 65/35) 168 mg of carbonate **25g** (69%) as a white solid.

Data for **25g**:

mp: 144-145 °C

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

7.94 (d, *J* = 8.0 Hz, 2 H, HC(14)), 7.63 (t, *J* = 8.0 Hz, 1 H, HC(15)), 7.29-7.20 (m, 5 H, HC(9,10,11)), 5.08 (ddd, *J* = 11, 4.0, 3.0 Hz, 1 H, HC(4)), 4.36-4.28 (m, 3 H, HC(6, 7)), 1.98-1.93 (m, 1 H, HC(5)), 1.88-1.80 (m, 1 H, HC(5)).

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

147.9 (C(2)), 137.4 (q, *J* = 29 Hz, C(13)), 135.9, 130.5 (q, *J* = 5.5 Hz, C(14)),

129.8, 128.8, 128.5, 128.2, 125.8, 123.1 (q, J = 273 Hz, C(16)), 81.0 (C(4)), 66.4 (C(6)), 53.9 (C(7)), 25.7 (C(5))

^{19}F NMR: (376 MHz, $CDCl_3$)

-58.34 (CF_3(16))

IR: (NaCl plates, CH_2Cl_2)

3088 (w), 3032 (w), 2980 (w), 2922 (w), 1752 (m), 1582 (w), 1496 (w), 1482 (w), 1454 (w), 1406 (w), 1333 (m), 1288 (m), 1253 (w), 1228 (w), 1202 (w), 1152 (m), 1114 (m), 1066 (w), 912 (w), 814 (w), 767 (w), 737 (m), 702 (m), 675 (m), 537 (w).

MS: (EI, 70 eV)

483.8 (1.5, M^+), 147.0 (39.5), 117.0 (11.6), 115.0 (10.0), 105.0 (12.2), 91.0 (100.0).

HRMS: calcd for $C_{19}H_{14}F_6O_3Se$: 484.0012, found: 483.9995

TLC: R_f 0.26 (hexanes/EtOAc, 65/63) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ + 203.3 (c = 0.402, $CHCl_3$)

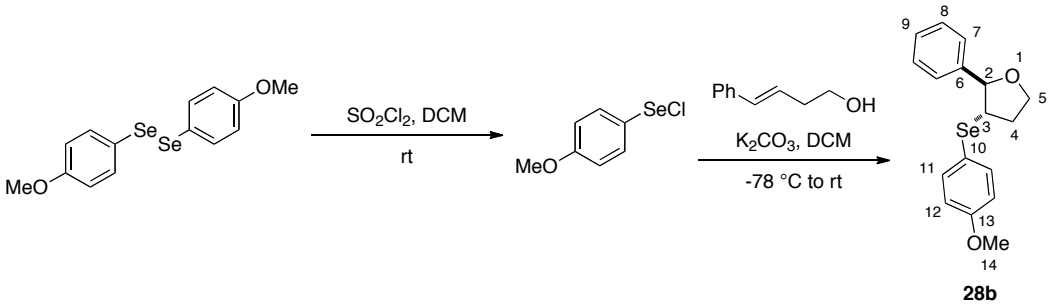
Analysis: $C_{19}H_{14}F_6O_3Se$ (484.0012)

Calcd: C, 47.22; H, 2.92%

Found: C, 47.49; H, 2.83%

General Procedure 3. Synthesis of Racemic Seleno Ethers.

Preparation of (+/-)-*trans*-3-[(4-Methoxyphenyl)seleno]-2-phenyloxolane (28b)



28b

An oven-dried, 10-mL flask equipped with a magnetic stir bar was charged with 1,2-bis(4-methoxyphenyl)diselane (94.2 mg, 0.253 mmol, 0.75 equiv). CH_2Cl_2 (0.5 mL) and SO_2Cl_2 (34.1 mg, 0.253 mmol, 0.75 equiv) were added under an atmosphere of nitrogen and the resulting solution was stirred at room temperature for 15 min. In an oven-dried, 10-mL Schlenk flask equipped with a stir bar was added olefin (*E*)-**29** (50.0 mg, 0.337 mmol) and CH_2Cl_2 (0.55 mL). The flask was cooled to -78 °C and K_2CO_3 (48.9 mg, 0.354 mmol, 1.05 equiv) was added under nitrogen. After 15 min of stirring at -78 °C, the diselenide/SO_2Cl_2 solution was added. The reaction mixture was allowed to warm to room temperature over 4 h and then was stirred for an additional 12 h. The reaction mixture was transferred to a 125-mL separatory funnel with an additional 10 mL of CH_2Cl_2. The mixture was washed with H_2O (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were washed with brine (1 x 25 mL) and dried over $MgSO_4$. The solution was filtered and concentrated on a rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 25 cm column, hexanes/EtOAc, 91/9) to afford 66.7 mg (59%) of racemic seleno ether **28b** as a clear, yellow oil.

Data for (+/-)-**28b**:

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

7.46 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.32-7.24 (m, 5 H, HC(7,8,9)), 6.79 (d, *J* = 8.5 Hz, 2 H, HC(12)), 4.80 (d, *J* = 6.5 Hz, 1 H, HC(2)), 4.15-4.11 (m, 1 H, HC(5)), 4.02-3.98 (m, 1 H, HC(5)), 3.82 (s, 3 H, H_3C(14)), 3.45 (dd, *J* = 14.0, 6.0 Hz, 1 H, HC(3)), 2.44-2.37 (m, 1 H, HC(4)), 2.11-2.04 (m, 1 H, HC(4)).

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

159.9, 141.4, 137.5, 128.3, 127.6, 125.9, 118.2 (C(10), 114.7 (C(12)), 85.9 (C(2)), 67.9 (C(5)), 55.3 (C(14)), 47.9 (C(3)), 33.9 (C(4)).

IR: (NaCl plates, CH_2Cl_2)

3085 (w), 3062 (w), 3030 (w), 2938 (m), 2869 (m), 2837 (m), 2361 (w), 2342 (w), 1590 (s), 1570 (m), 1490 (s), 1455 (m), 1441 (m), 1401 (w), 1362 (w), 1286 (s), 1247 (s), 1173 (s), 1102 (w), 1028 (s), 1006 (w), 969 (w), 928 (w), 908 (w), 825.5 (m), 793 (w), 756 (m), 700 (s), 600 (w), 521 (w).

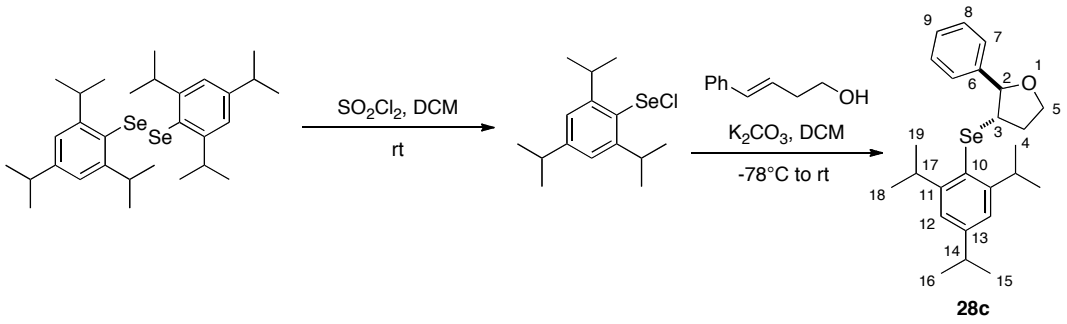
MS: (EI, 70 eV)

334.0 (5.9, M^+), 226.0 (47.0), 187.0 (52.3), 171.9 (12.3), 147.1 (85.3), 117.1 (27.0), 105.0 (100.0), 91.0 (74.7), 77.0 (39.9) .

HRMS: calcd for $C_{17}H_{18}O_2Se$: 334.0472, found: 334.0476

TLC: R_f 0.34 (hexanes/EtOAc, 91/9) [UV]

Preparation of (+/-)-*trans*-2-Phenyl-3-[[2,4,6-tri(propan-2-yl)phenyl]seleno]oxolane (28c)



Following General Procedure 3, a solution of 1,2-bis(2,4,6-triisopropylphenyl)diselane (286 mg, 0.506 mmol, 0.75 equiv) and SO_2Cl_2 (68.3 mg, 0.506 mmol, 0.75 equiv) in CH_2Cl_2 (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol,) and K_2CO_3 (112 mg, 0.810 mmol, 1.20 equiv) in CH_2Cl_2 (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 25 cm column, hexanes/EtOAc, 97/3) 218 mg (75%) of racemic seleno ether **28c** as a clear, colorless oil.

Data for (+/-)-**28c**:

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

7.29-7.22 (m, 3 H), 7.16 (d, *J* = 7.0 Hz, 2 H), 7.01 (s, 2 H, HC(11)), 4.83 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.20-4.12 (m, 2 H, H_2C(5)), 3.81 (sept, *J* = 6.5 Hz, 2 H, HC(17)), 3.35-3.31 (m, 1H, HC(3)), 2.91 (sept, *J* = 7.0 Hz, 1H, HC(14)), 2.43-2.35 (m, 1H, HC(4)), 2.14-2.08 (m, 1H, HC(4)), 1.28 (dd, *J* = 7.0, 1.0 Hz, 6H), 1.16 (d, *J* = 6.5 Hz, 12H).

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

153.2, 149.9, 141.8, 128.2, 127.4, 126.3, 125.8, 121.7, 86.2 (C(2)), 68.2 (C(5)), 48.6 (C(3)), 34.3, 34.2, 34.1, 24.4, 24.3, 23.9, 23.8.

IR: (NaCl plates, neat)

3062 (w), 3034 (w), 2960 (s), 2927 (s), 2868 (s), 1595 (m), 1562 (w), 1535 (w),

1494 (w), 1462 (s), 1422 (m), 1383 (m), 1362 (m), 1309 (w), 1247 (w), 1166 (m), 1101 (w), 1084 (m), 1067 (s), 1028 (m), 961 (w), 935 (w), 906 (w), 877 (m), 752 (m), 734 (m), 699 (s), 650 (w), 622 (w), 516 (w).

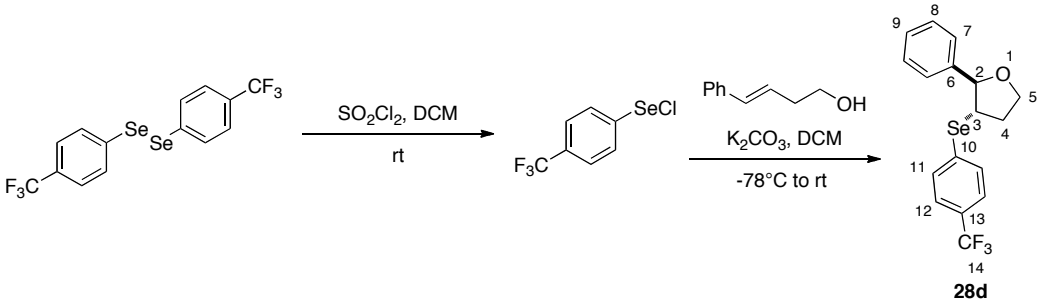
MS: (EI, 70 eV)

430.2 (9.6, M^+), 284.1 (23.8), 282.1 (15.0), 242.1 (25.8), 240.1 (13.0), 226.0 (17.0), 204.2 (12.1), 203.2 (79.6), 199.0 (10.0), 197.0 (13.9), 148.1 (10.2), 147.1 (100.0), 146.1 (26.8), 145.1 (13.2), 117.1 (13.7), 105.0 (44.6), 91.1 (40.7), 77.1 (13.7).

HRMS: calcd for $C_{25}H_{34}OSe$: 430.1775, found: 430.1767

TLC: R_f 0.41 (hexanes/EtOAc, 97/3) [UV]

Preparation of (+/-)-*trans*-2-Phenyl-3-[[4-(trifluoromethyl)phenyl]seleno]oxolane (28d)



Following General Procedure 3, a solution of 1,2-bis(4-trifluoromethylphenyl)diselane (227 mg, 0.506 mmol, 0.75 equiv) and SO_2Cl_2 (68.3 mg, 0.506 mmol, 0.75 equiv) in CH_2Cl_2 (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol) and K_2CO_3 (112 mg, 0.810 mmol, 1.20 equiv) in CH_2Cl_2 (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 24 cm column, hexanes/EtOAc, 95/5) 181 mg (72%) of racemic seleno ether **28d** as a clear colorless oil.

Data for (+/-)-**28d**:

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

7.46 (d, *J* = 8.5 Hz, 2 H, HC(12)), 7.41 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.32-7.26 (m, 5 H, HC(7, 8, 9)), 4.83 (d, *J* = 7.0 Hz, 1 H, HC(2)), 4.23-4.19 (m, 1 H, HC(5)), 4.08 (dd, *J* = 14.0, 6.5 Hz, 1 H, HC(5)), 3.66 (dd, *J* = 14.0, 6.5 Hz, 1 H, HC(3)), 2.60-2.53 (m, 1 H, HC(4)), 2.17-2.11 (m, 1H, HC(4)).

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

140.6, 134.4, 133.2, 129.3 (q, *J* = 32 Hz, C(13)), 128.4, 127.9, 125.9, 125.6 (q, *J* = 3.7 Hz, C(12)), 123.9 (q, *J* = 271 Hz, C(14)), 86.4 (C(2)), 67.8 (C(5)), 47.5 (C(3)), 34.1 (C(4)).

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

-63.1 (F_3C(14)).

IR: (NaCl plates, neat)

3065 (w), 3033 (w), 2976 (w), 2943 (w), 2872 (m), 1602 (s), 1572 (w), 1495 (m), 1454 (m), 1398 (m), 1326 (s), 1280 (w), 1165 (s), 1123 (s), 1078 (s), 1057 (s), 1028 (m), 1014 (s), 972 (w), 929 (w), 908 (w), 826 (m), 774 (w), 756 (m), 700 (s), 689 (m), 631 (w), 592 (w), 534 (w).

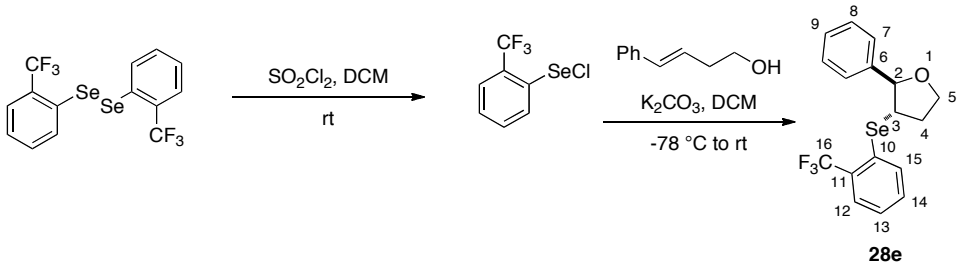
MS: (EI, 70 eV)

372.0 (29.8, M^+), 370.0 (14.8), 266.0 (56.4), 264.0 (26.9), 263.0 (10.1), 262.0 (10.1), 197.0 (12.9), 185.1 (37.4), 147.1 (33.8), 146.1 (100.0), 145.0 (11.6), 135.1 (10.3), 117.1 (21.1), 116.1 (10.6), 115.1 (25.1), 105.0 (46.4), 91.1 (38.0), 77.1 (27.3), 62.1 (32.6).

HRMS: calcd for $C_{17}H_{15}F_3OSe$: 372.0240, found: 372.0228

TLC: R_f 0.33 (hexanes/EtOAc, 95/5) [UV]

Preparation of (+/-)-*trans*-2-Phenyl-3-[[2-(trifluoromethyl)phenyl]seleno]oxolane (28e)



28e

Following General Procedure 3, a solution of 1,2-bis(4-trifluoromethylphenyl)diselane (227 mg, 0.506 mmol, 0.75 equiv) and SO_2Cl_2 (68.3 mg, 0.506 mmol, 0.75 equiv) in CH_2Cl_2 (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol) and K_2CO_3 (112 mg, 0.810 mmol, 1.20 equiv) in CH_2Cl_2 (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 24 cm column, hexanes/EtOAc, 95/5) 163 mg (65%) of racemic seleno ether **28e** as a clear oil.

Data for (+/-)-**28e**:

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

7.65 (d, *J* = 8.0 Hz, 1 H, HC(12)), 7.44 (d, *J* = 7.5 Hz, 1 H), 7.32-7.24 (m, 7 H), 4.88 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.24-4.20 (m, 1 H, HC(5)), 4.14-4.09 (m, 1 H, HC(5)), 3.71 (dd, *J* = 13.5, 6.0 Hz, 1 H, HC(3)), 2.56-2.49 (m, 1 H, HC(4)), 2.16-2.10 (m, 1 H, HC(4)).

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

140.9, 135.8, 132.0 (q, *J* = 29 Hz, C(11)), 131.8, 128.5, 128.3, 127.8, 127.2, 126.7 (q, *J* = 5.5 Hz, C(12)), 125.9, 123.7 (q, *J* = 272 Hz, C(16)), 86.2 (C(2)), 67.8 (C(5)), 48.1 (C(3)), 33.8 (C(4)).

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

-60.7 (F_3C(16)).

IR: (NaCl plates, neat)

3064 (w), 3032 (w), 2977 (w), 2943 (w), 2872 (m), 1592 (m), 1571 (w), 1494 (w), 1469 (w), 1444 (m), 1312 (s), 1259 (s), 1171 (s), 1128 (s), 1110 (s), 1088 (s), 1067 (m), 1039 (m), 1027 (s), 972 (w), 929 (w), 908 (w), 761 (s), 729 (m), 699 (s), 683 (m), 642 (m), 596 (w), 571 (w).

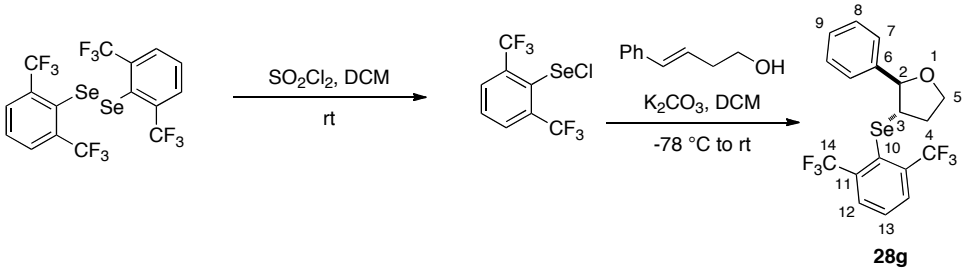
MS: (EI, 70 eV)

372.0 (24.6, M^+), 370.0 (12.3), 268.0 (10.7), 266.0 (62.1), 264.0 (29.4), 263.0 (10.8), 262.0 (11.2), 185.1 (26.0), 147.1 (47.9), 146.1 (100.0), 145.0 (11.9), 117.1 (19.3), 115.1 (24.5), 105.0 (48.9), 91.1 (40.8), 77.0 (27.3), 62.1 (54.5), 61.1 (12.6).

HRMS: calcd for $C_{17}H_{15}F_3OSe$: 372.0240, found: 372.0242

TLC: R_f 0.27 (hexanes/EtOAc, 95/5) [UV]

Preparation of (+/-)-*trans*-2-Phenyl-3-[[2-(trifluoromethyl)phenyl]seleno]oxolane (28g)



28g

Following General Procedure 3, a solution of 1,2-bis(2,6-di-trifluoromethylphenyl)diselane (148 mg, 0.253 mmol, 0.75 equiv) and SO_2Cl_2 (1.02 g, 7.59 mmol, 22.5 equiv) in CH_2Cl_2 (0.5 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (50.0 mg, 0.337 mmol, 1.00 equiv) and K_2CO_3 (46.8 mg, 0.354 mmol, 1.05 equiv) in CH_2Cl_2 (0.26 mL) to yield after column chromatography (hexanes/EtOAc, 90/10) 40 mg (27%) of racemic

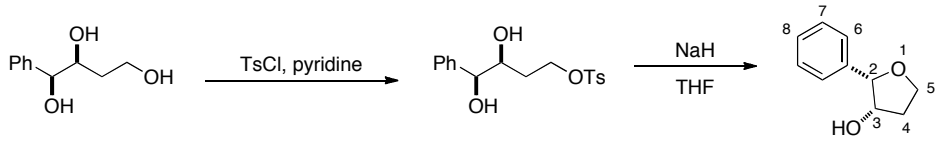
seleno ether **28g** as a clear yellow oil.

Data for (+/-)-**28g**:

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

7.91 (d, *J* = 8.0 Hz, 2 H, HC(12)), 7.58 (t, *J* = 8.0 Hz, 1 H, HC(13)), 7.26-7.15 (m, 5 H), 4.94 (d, *J* = 5.4 Hz, 1 H, HC(2)), 4.17-4.13 (m, 1 H), 4.08 (dd, *J* = 15.5, 8.0 Hz, 1 H), 3.78 (dd, *J* = 12.5, 6.0 Hz, 1H), 2.28-2.20 (m, 1 H), 2.04-1.98 (m, 1 H).

Preparation of (2*S*,3*S*)-Tetrahydro-2-phenyl-2-furanol (27) (Scheme 11)



26 **26-I** **27**

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added triol **26** (177 mg, 0.97 mmol), and pyridine (1.0 mL). The solution was cooled to -10 °C (NaCl/ice bath temperature) and a solution of *p*-toluenesulfonyl chloride (185 mg, 0.97 mmol, 1.00 equiv) in pyridine (1.71 mL) was added slowly over 45 min. The reaction mixture was stirred at -10 °C for 3h 15 min. The reaction mixture was poured onto ice and 2 N HCl (10 mL) was added. The solution was then transferred to a 125-mL separatory funnel and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered concentrated on the rotavap (30 °C, 30 mm Hg), and dried under high vacuum. ^{1}H NMR spectroscopic analysis of the crude product showed complete conversion of **26** to **26-I**. The crude product was used for the next step without further purification.

To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added sodium hydride (58.2 mg, 2.43 mmol, 2.50 equiv) in the glove box. The flask was attached to the

manifold and THF (6 mL) was added to it. The suspension was cooled to 0 °C and a solution of **26-I** in THF (6 mL) was added to it dropwise. The resulting solution was stirred at 0 °C for 1.5 h and then stirred at room temperature for 13 h. Satd. aq. NH_4Cl (10 mL) was added and then the reaction mixture was transferred to a 125-mL separatory funnel and extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 24 cm column, hexanes/TBME, 3/2) to afford 63.2 mg of **27** (40% over two steps) as a clear oil.

Data for **27**:

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

7.38-7.26 (m, 5 H, HC(6, 7, 8)), 4.86 (d, J = 3.5 Hz, 1H, HC(2)), 4.37 (br s, 1 H), 4.24 (dd, J = 16.5, 8.5 Hz, 1 H, HC(5)), 4.03-3.99 (m, 1 H, HC(5)), 2.29-2.22 (m, 1 H, HC(4)), 2.14-2.09 (m, 1 H, HC(4)), 1.34 (br s, 1H, HOC).

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

136.9, 128.4, 127.8, 126.7, 84.9 (C(2)), 73.5 (C(3)), 66.9 (C(5)), 34.7 (C(4)).

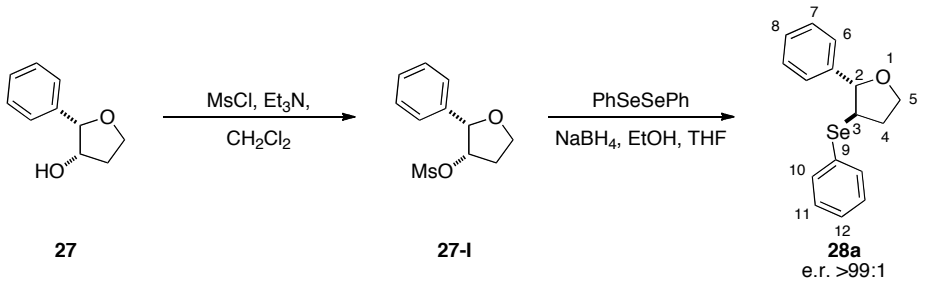
MS: (EI, 70 eV)

164.1 (17.7, M^+), 120.1 (18.4), 108.1 (12.2), 107.1 (100.0), 105.0 (15.0), 91.1 (17.1), 79.1 (45.5), 77.0 (26.3), 58.1 (12.2), 57.1 (24.9), 51.1 (11.0).

HRMS: calcd for $C_{10}H_{12}O_2$: 164.0837, found: 164.0844

TLC: R_f 0.25 (hexanes/TBME, 3/2) [UV, $KMnO_4$]

Preparation of (2*S*, 3*R*)-Preparation of 2-phenyl-3-(phenylseleno)oxolane (28a) (Scheme 11)



To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added a solution of **27** (63.2 mg, 0.38 mmol) in CH_2Cl_2 (3.8 mL), Et_3N (0.16 mL, 1.15 mmol, 3.00 equiv), and methanesulfonyl chloride (89 μL, 1.15 mmol, 3.00 equiv). The solution was stirred at room temperature for 1h 15 min, and concentrated on the rotavap (30 °C, 30 mm Hg). ^{1}H NMR spectroscopic analysis of the crude product showed complete conversion of **27** to **27-I**. The crude product was used for the next step without further purification.

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (96.1 mg, 0.31 mmol, 0.80 equiv), sodium borohydride (23.3 mg, 0.61 mmol, 1.60 equiv), and EtOH (0.5 mL) and the mixture was stirred at room temperature for 15 min. A solution of **27-I** in THF (2 mL) was added and the resulting mixture was concentrated under high vacuum. EtOH (0.1 mL) and THF (0.1 mL) were added to it and the solution was stirred at 40 °C (oil bath temperature) for 14.5 h. THF (0.1 mL) was added and the reaction was stirred at 40 °C for another 24 h. ^{1}H NMR spectroscopic analysis of the reaction aliquot showed 50% conversion of **27-I** to **28a**. The reaction mixture was cooled to room temperature, quenched with H_2O (10 mL), and transferred to a 125-mL separatory funnel with additional CH_2Cl_2 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was re-subjected to the reaction conditions as follows. To an

oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (60.0 mg, 0.19 mmol, 0.50 equiv), sodium borohydride (21.8 mg, 0.58 mmol, 1.50 equiv), and EtOH (0.5 mL) and the mixture was stirred at room temperature for 15 min. A solution of the crude mixture of **27-I** and **28a** in THF (0.5 mL) was added and the resulting mixture was concentrated under high vacuum. EtOH (0.1 mL) and THF (0.1 mL) were added to it and the solution was stirred at 40 °C (oil bath temperature) for 42 h. The reaction mixture was cooled to room temperature, quenched with H_2O (15 mL), and transferred to a 125-mL separatory funnel with additional CH_2Cl_2 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). ^{1}H NMR spectroscopic analysis of the crude product showed complete consumption of **27-I**. The crude product was purified by column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 96/4) to afford 48.0 mg of **28a** (41% over two steps) as a clear yellow oil.

Data for **28a**:

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

7.51 (d, *J* = 7.0 Hz, 2 H), 7.34-7.24 (m, 8 H), 4.87 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.18 (dd, *J* = 13.7, 7.2 Hz, 1 H, HC(5)), 4.07 (dd, *J* = 15.5, 7.5 Hz, 1 H, HC(5)), 3.60 (dd, *J* = 13.5, 6.0 Hz, 1 H, HC(3)), 2.53-2.46 (m, 1 H, HC(4)), 2.18-2.12 (m, 1 H, HC(4)).

MS: (EI, 70 eV)

303.9 (26.3, M^+), 301.9 (12.9), 197.9 (23.3), 195.9 (11.3), 182.9 (17.1), 156.9 (18.8), 154.9 (10.2), 147.0 (56.9), 146.0 (100.0), 145.0 (11.4), 118.0 (22.5), 117.0 (94.1), 116.0 (13.8), 115.0 (34.6), 105.0 (67.1), 104.0 (13.3), 91.0 (68.8), 78.0

(24.4), 77.0 (55.0).

HRMS: calcd for $C_{16}H_{16}OSe$: 304.0366, found: 304.0376

SFC: (2*R*,3*S*)-31a, t_R 6.8 min (<1%); (2*S*,3*R*)-31a, t_R 8.4 min (>99%), (Chiralpak AD, 125 bar, 3% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28a toward Brønsted Acids

Table 1, entry 1

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH_2Cl_2 (0.9 mL). Triflic acid (0.076 μl, 0.001 mmol, 0.1 equiv) in CH_2Cl_2 (10 μL) was added over 1 min. After 30 minutes an aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

HPLC: t_R 6.1 min (50.0%); t_R 6.7 min (50.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1, entries 2 and 3

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH_2Cl_2 (0.9 mL). Methanesulfonic acid (0.058 μL, 0.001 mmol, 0.1 equiv) in CH_2Cl_2 (10 μL) was added over 1 min. An aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

HPLC (0.5 h): t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

HPLC (3.0 h): t_R 6.1 min (87.0%); t_R 6.7 min (13.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1, entry 4

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH_2Cl_2 (0.9 mL). Trifluoroacetic acid (0.067 μl, 0.001 mmol, 0.1 equiv) in CH_2Cl_2 (10 μL) was added over 1 min. After 30 min and 24 h an aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

HPLC (0.5 h): t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

HPLC (24 h): t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1 entry 5

To an oven-dried NMR tube was added trifluoroacetic acid (0.20 μL, 0.002 mmol, 0.12 equiv), and $CDCl_3$ (0.1 mL). A solution of seleno ether **28a** (e.r. = >99:1) (6.80 mg, 0.022 mmol) in $CDCl_3$ (0.12 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28a**, t_R 6.8 min (<1%); (2*S*,3*R*)-**28a**, t_R 8.4 min (>99%), (Chiralpak AD, 125 bar, 3% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Table 1 entry 6

To an oven-dried NMR tube was added trifluoroacetic acid (1.70 μL, 0.022 mmol, 1.00 equiv), and $CDCl_3$ (0.1 mL). A solution of seleno ether **28a** (e.r. = >99:1) (6.80 mg, 0.022 mmol) in $CDCl_3$ (0.12 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28a**, t_R 6.8 min (50%); (2*S*,3*R*)-**28a**, t_R 8.4 min (50%), (Chiralpak AD, 125 bar, 3% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

General Procedure 4. Configurational Stability of Seleno Ethers 28d-f

Configurational Stability of Seleno Ether 28d

To an oven-dried NMR tube was added trifluoroacetic acid (2.70 μL, 0.036 mmol, 1.00 equiv), and $CDCl_3$ (0.1 mL). A solution of seleno ether **28d** (e.r. = 63.2:36.8) (13.3 mg, 0.036 mmol) in $CDCl_3$ (0.25 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 6 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc,

(9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28d** as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product. Note: The reaction of carbonate **25d** afforded the product with very similar enantiomeric ratios when conducted for 6 h (62.1:37.9) or 24 h (61.8:38.2) suggesting that seleno ether **28d** does not racemize to a significant extent even over 24 h.

SFC: (2*R*,3*S*)-**28d**, t_R 5.92 min (62.5%); (2*S*,3*R*)-**28d**, t_R 7.30 min (37.5%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28e

Following General Procedure 4, to an oven-dried NMR tube was added trifluoroacetic acid (2.80 μL, 0.037 mmol, 1.00 equiv), and $CDCl_3$ (0.1 mL). A solution of seleno ether **28e** (e.r. = 64.5:35.5) (13.6 mg, 0.037 mmol) in $CDCl_3$ (0.27 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 8 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then purified to obtain **28e** as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product. Note: The reaction of carbonate **25e** afforded the product with very similar enantiomeric ratios when conducted for 8 h (64.5:35.5) or 24 h (67.2:32.8) suggesting that seleno ether **28e** does not racemize to a significant extent even over 24 h.

SFC: (2*R*,3*S*)-**28e**, t_R 8.07 min (64.2%); (2*S*,3*R*)-**28e**, t_R 8.98 min (35.8%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28f toward TFA

To an oven-dried NMR tube was added trifluoroacetic acid (3.70 μL, 0.047 mmol, 1.00

equiv), and $CDCl_3$ (0.1 mL). A solution of seleno ether **28f** (e.r. = 61:39) (16.6 mg, 0.047 mmol) in $CDCl_3$ (0.37 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product **28f** was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28f**, t_R 8.26 min (61.0%); (2*S*,3*R*)-**28f**, t_R 11.56 min (39.0%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

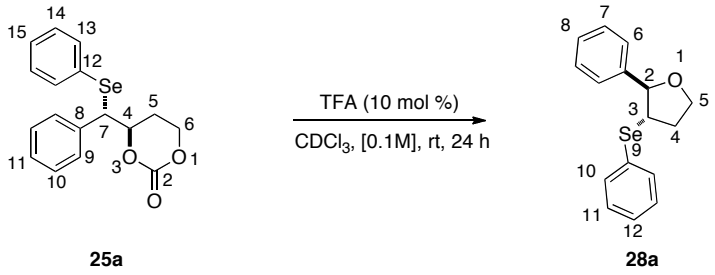
Configurational Stability of Seleno Ether 28f toward MsOH

To an oven-dried NMR tube was added a solution of seleno ether **28f** (e.r. = 90.4:9.6) (5.00 mg, 0.014 mmol) in $CDCl_3$ (0.14 mL). Methanesulfonic acid (0.95 μL, 0.014 mmol, 1.00 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The mixture was quenched with 25 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of product **28f** was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28f**, t_R 8.26 min (90.8%); (2*S*,3*R*)-**28f**, t_R 11.56 min (9.2%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

General Procedure 5. Carbonate Opening Experiments.

Table 2, entry 1

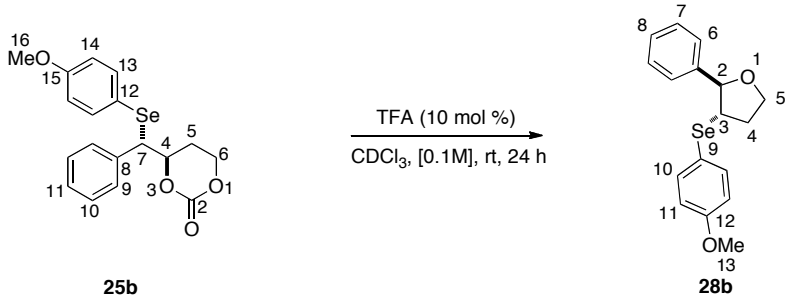


25a **28a**

To an oven-dried NMR tube was added trifluoroacetic acid (0.45 μL, 0.006 mmol, 0.1 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25a** (20.3 mg, 0.058 mmol) in $CDCl_3$ (0.48 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 19% conversion to product by comparison of the integration of protons HC(4) of the carbonate **25a** and HC(2) of ether **28a**. The mixture was quenched with 10 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28a**, t_R 6.8 min (57.4%); (*2S,3R*)-**28a**, t_R 8.4 min (42.6%), (Chiralpak AD, 125 bar, 3% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Table 2, entry 2

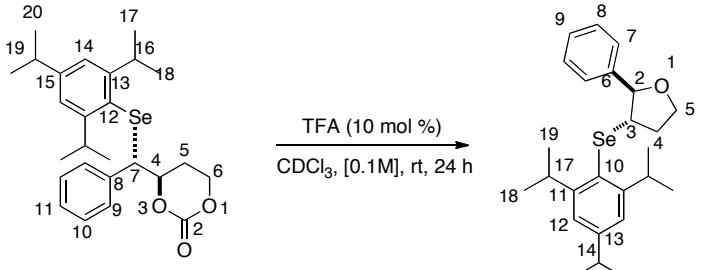


25b **28b**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (0.40 μL, 0.005 mmol, 0.1 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25b** (20.0 mg, 0.053 mmol) in $CDCl_3$ (0.43 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 46% conversion to product by integration of HC(5) of **25b** and **28b**. After purification, **28b** was obtained as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28b**, t_R 11.33 min (52.5%); (*2S,3R*)-**28b**, t_R 12.82 min (47.5%), (Chiralpak AD, 125 bar, 4% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 3



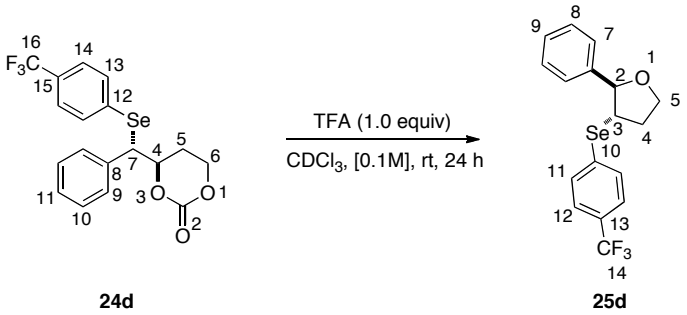
25c **28c**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (0.38 μL, 0.005 mmol, 0.1 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25c** (23.4

mg, 0.049 mmol) in $CDCl_3$ (0.39 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 44% conversion to product by comparison of the integrations of HC(5) in the carbonate and the ether. After purification, **28c** was obtained as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2S,3R*)-**28c**, t_R 11.81 min (37.2%); (*2R,3S*)-**28c**, t_R 14.90 min (62.8%), (Chiralpak OD, 125 bar, 2.5% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 4



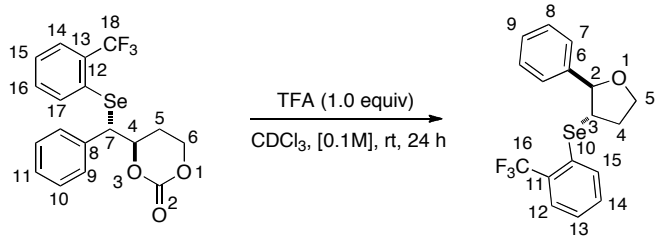
24d **25d**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.7 μL, 0.z48 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25d** (20.0 mg, 0.048 mmol) in $CDCl_3$ (0.38 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 100% conversion to product. After purification, **28d** was obtained as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28d**, t_R 5.92 min (61.8%); (*2S,3R*)-**28d**, t_R 7.30 min (38.2%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Opt. Rot.: $[\alpha]_D^{24}$ + 5.60 (c = 1.0, $CHCl_3$)

Table 2, entry 5



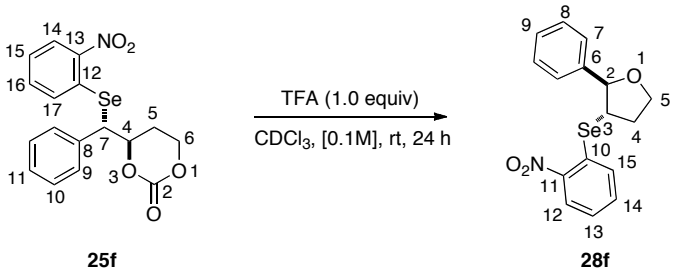
25e **28e**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μL, 0.051 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25e** (20.0 mg, 0.051 mmol) in $CDCl_3$ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 100% conversion to product. After purification, **28e** was obtained as a clear oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28e**, t_R 8.07 min (67.2%); (*2S,3R*)-**28e**, t_R 8.98 min (32.8%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Opt. Rot.: $[\alpha]_D^{24}$ + 0.28 (c = 0.97, $CHCl_3$)

Table 2, entry 6



25f **28f**

Following General Procedure 4, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μL, 0.051 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25f** (21.3 mg, 0.051 mmol) in $CDCl_3$ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 36% conversion to product by comparison of the integration of protons HC(4) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28f**, t_R 8.26 min (93.6%); (*2S,3R*)-**28f**, t_R 11.56 min (6.4%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 7

25g **28g**

To an oven-dried Schlenk flask was added methanesulfonic acid (6.7 μL, 0.103 mmol, 1.0 equiv), and $CDCl_3$ (0.5 mL). A solution of carbonate **25g** (50.0 mg, 0.103 mmol) in $CDCl_3$ (0.53 mL) was added and the flask was secured with a septum. The resulting solution was stirred for 2 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 100% conversion of **25g** to **28g**. The mixture was quenched with 14 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9.5 cm column, hexanes/EtOAc, 95/5) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

Data for **28g**:

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

7.91 (d, J = 8.0 Hz, 2 H, HC(12)), 7.58 (t, J = 8.0 Hz, 1 H, HC(13)), 7.26-7.15 (m, 5 H), 4.94 (d, J = 5.4 Hz, 1 H, HC(2)), 4.17-4.13 (m, 1 H), 4.08 (dd, J = 15.5, 8.0 Hz, 1 H), 3.78 (dd, J = 12.5, 6.0 Hz, 1H), 2.28-2.20 (m, 1 H), 2.04-1.98 (m, 1 H).

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

140.8, 137.9 (q, J = 29 Hz, C(11)), 130.3 (q, J = 5.9 Hz, C(12)), 129.5, 128.3, 127.7, 125.8, 125.5, 123.19 (q, J = 273 Hz, C(14)), 86.2 (C(2)), 67.6 (C(5)), 49.9 (C(3)), 32.9 (C(4)).

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

-58.3 (F_3C(14)).

IR: (NaCl plates, CH_2Cl_2)

3035 (w), 2917 (w), 2872 (w), 1582 (w), 1493 (w), 1454 (w), 1423 (w), 1332 (m), 1288 (s), 1201 (m), 1142 (s), 1114 (m), 1066 (m), 1028 (w), 813 (w), 759 (w), 736 (w), 700 (w), 675 (m).

MS: (EI, 70 eV)

440.1 (15.7, M^+), 336.0 (17.0), 335.0 (11.0), 334.0 (100.0), 332.0 (48.0), 331.0 (16.1), 330.0 (17.1), 293.0 (21.0), 291.0 (10.3), 274.0 (16.8), 147.1 (94.8), 146.1 (80.5), 121.0 (18.7), 117.1 (32.7), 116.1 (14.4), 115.1 (44.2), 105.0 (93.2), 91.1 (84.4), 86.0 (41.5), 84.0 (65.3), 77.1 (56.9), 65.0 (10.2).

HRMS: calcd for $C_{18}H_{14}F_6OSe$: 440.0114, found: 440.0122

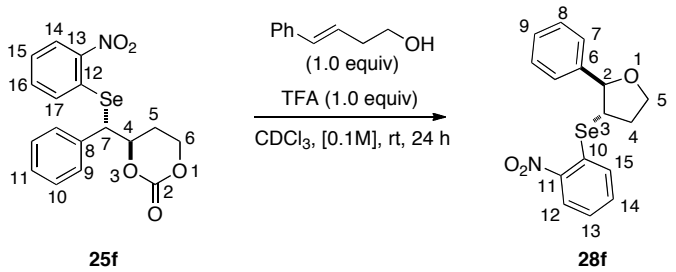
TLC: R_f 0.30 (hexanes/EtOAc, 95/5) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 19.9 (c = 0.45, $CHCl_3$)

SFC: (*2R,3S*)-**28g**, t_R 17.06 min (93.7%); (*2S,3R*)-**28g**, t_R 19.57 min (6.3%), (Chiralpak Regis WhelkO1, 125 bar, 1% MeOH in CO_2, 1.5 mL/min, 220 nm, 40 °C)

Olefin Transfer Experiments

Scheme 12a

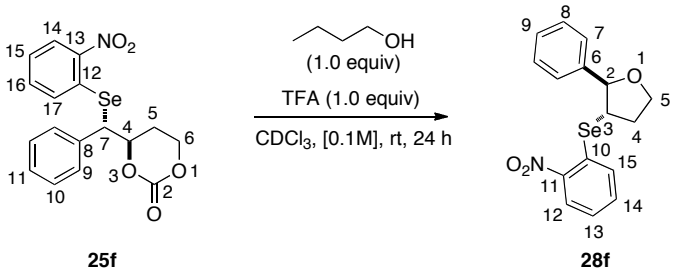


25f **28f**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μL, 0.051 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) and olefin (*E*)-**29** (7.50 mg, 0.051 mmol, 1.0 equiv) in $CDCl_3$ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed 21% conversion to product by comparison of the integration of protons HC(5) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28f**, t_R 8.26 min (87.9%); (*2S,3R*)-**28f**, t_R 11.56 min (12.1%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

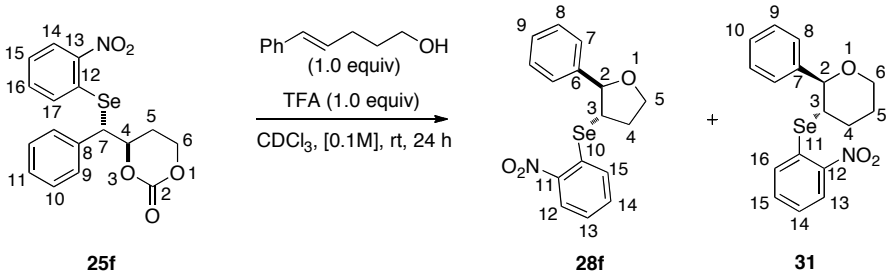
Scheme 12b



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μL, 0.051 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) in $CDCl_3$ (0.41 mL) followed by 1-butanol were added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed trace conversion to product by comparison of the integration of protons HC(4) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μL of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28f**, t_R 8.26 min (94.8%); (*2S,3R*)-**28f**, t_R 11.56 min (5.2%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Scheme 12c



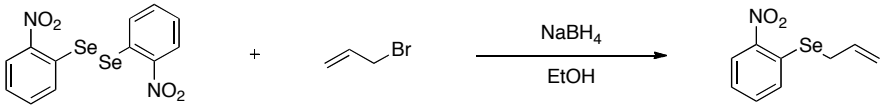
25f **28f** **31**

Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μL, 0.051 mmol, 1.0 equiv), and $CDCl_3$ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) and olefin (*E*)-**30** (8.30 mg, 0.051 mmol, 1.0 equiv) in $CDCl_3$ (0.41 mL) and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ^{1}H NMR spectroscopy analysis of the reaction mixture showed trace conversion to products **28f** and **31**. The mixture was quenched with 10 μL of triethylamine and then was concentrated on the rotavap. The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the product was isolated as a 2:1 mixture of **28f** to **31**. The enantiomeric composition of the products **28f** and **31** were determined by CSP-SFC analysis of the product.

SFC: (*2R,3S*)-**28f**, t_R 15.5 min (96.3%); (*2S,3R*)-**28f**, t_R 18.2 min (3.7%), (Chiralpak Regis WhelkO1, 125 bar, 10% MeOH in CO_2, 1.5 mL/min, 220 nm, 40 °C)

(*2R,3S*)-**31**, t_R 13.7 min (50.9%); (*2S,3R*)-**31**, t_R 14.6 min (49.1%), (Chiralpak Regis WhelkO1, 125 bar, 10% MeOH in CO_2, 1.5 mL/min, 220 nm, 40 °C)

Preparation of Allyl-2-nitrophenylselenide (33) (Scheme 13)



33

To an oven-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2-nitrophenyl)diselane (3.71 g, 9.20 mmol) and EtOH (46 mL). The flask was cooled to 0 °C (the ice bath temperature) and sodium borohydride (869 mg, 22.9 mmol, 2.5 equiv) was added to the yellow suspension. Within 5 min the mixture turned dark brown. The solution was stirred at 0 °C for 2 h and then allyl bromide (1.7 mL, 19.3 mmol, 2.1 equiv) was added dropwise at 0 °C whereupon the reaction turned yellow. After stirring at 0 °C for 2.5 h, the ice bath was removed and the solution stirred at room temperature for 2.5 h. The reaction mixture was transferred to a 500-mL separatory funnel with hexanes 100 mL and H_2O (100 mL). The organic and the aqueous layers were separated and the aqueous layer was extracted with hexanes (3 x 150 mL). The combined organic extracts were dried over $MgSO_4$ filtered, concentrated on the rotavap (30 °C, 30 mm Hg) and dried under high vacuum to afford 3.0 g of **33** (67%) as a yellow solid.

Data for **33**:

mp: 52-53 °C

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

8.28 (d, *J* = 8.0 Hz, 1 H), 7.54-7.50 (m, 2 H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.02-5.93 (m, 1H)), 5.33 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 3.61 (d, *J* = 7.50 Hz, 2H)

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

146.6, 133.5, 133.4, 132.3, 129.2, 126.3, 125.5, 119.1, 29.1.

^{77}SeNMR: (114 MHz, $CDCl_3$)

377.0

IR: (NaCl plates, CH_2Cl_2)

3078 (w), 2978 (w), 2929 (w), 1632 (w), 1588 (m), 1564 (m), 1503 (s), 1450 (m), 1432 (m), 1404 (w), 1328 (s), 1303 (s), 1250 (m), 1195 (w), 1167 (w), 1149 (w), 1096 (m), 1036 (m), 985 (w), 917 (w), 851 (m), 780 (m), 727 (s), 702 (w), 677 (w), 646 (w), 532 (w), 521 (w), 507 (w)

MS: (EI, 70 eV)

242.9 (31.8, M^+), 240.9 (15.0), 203.9 (11.2), 201.9 (68.9), 199.9 (31.4), 198.9 (10.1) 197.9 (11.7), 185.9 (34.6), 183.9 (17.3), 155.9 (24.6), 153.9 (11.9), 143.9 (12.1), 115.0 (10.4), 106.0 (100.0), 78.0 (33.5), 63.1 (14.6)

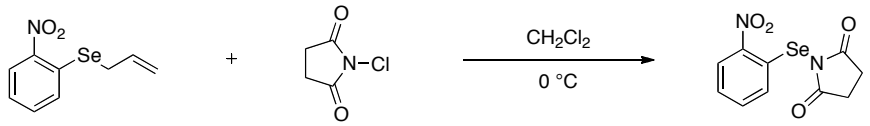
HRMS: calcd for $C_9H_9NO_2Se$: 242.9815, found: 242.9798

Analysis: $C_9H_9NO_2Se$ (242.981)

Calcd: C, 44.64; H, 3.75; N, 5.78%

Found: C, 44.83; H, 3.60; N, 5.78%

Preparation of *N*-(2-Nitrophenylselenenyl)succinimide (34) (Scheme 13)



33 **34**

To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added *N*-chlorosuccinimide (689 mg, 5.20 mmol) and CH_2Cl_2 (3.4 mL) and the flask was cooled to 0 °C (the ice bath temperature). A solution of **33** (1.50 g, 6.20 mmol, 1.2 equiv) in CH_2Cl_2 (9.4 mL) was added and the solution was stirred at 0 °C for 2 h. The ice bath was removed and the

solution stirred at room temperature for 1 h. The reaction mixture was concentrated on the rotavap (30 °C, 30 mm Hg) to afford a greenish brown solid. The crude product was dissolved in 25 mL of hexanes and collected on a frit. The solid was washed with hexanes (100 mL) and anhydrous Et_2O (75 mL) to afford a yellow solid. The product was further purified by recrystallization (CH_2Cl_2/hexanes) to afford 1.25 g (81%) of analytically pure **34** as a yellow solid.

Data for **34**:

mp: 212-214 °C (d)

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

8.37 (d, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 3.04 (s, 4 H)

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

178.6, 143.5, 135.7, 135.3, 127.3, 126.2, 125.5, 29.7.

IR: (NaCl plates, CH_2Cl_2)

3302 (w), 2943 (w), 1759 (w), 1706 (s), 1590 (w), 1568 (w), 1512 (m), 1452 (w), 1423 (w), 1325 (m), 1298 (s), 1240 (m), 1151 (s), 1106 (w), 1034 (w), 1006 (w), 850 (w), 819 (w), 787 (w), 732 (m), 702 (w), 670 (w), 660 (w), 642 (w), 599 (w), 568 (w), 532 (w)

MS: (EI, 70 eV)

299.9 (29.0, M^+), 297.9 (14.0), 253.9 (24.5), 251.9 (11.8), 201.9 (40.1), 199.9 (19.5) 185.9 (14.2), 155.9 (15.2), 143.9 (13.8), 106.0 (100.0), 78.0 (36.8), 63.1 (21.3), 56.1 (10.9), 55.1 (15.1)

HRMS: calcd for $C_{10}H_8N_2O_4Se$: 299.9649, found: 299.9638

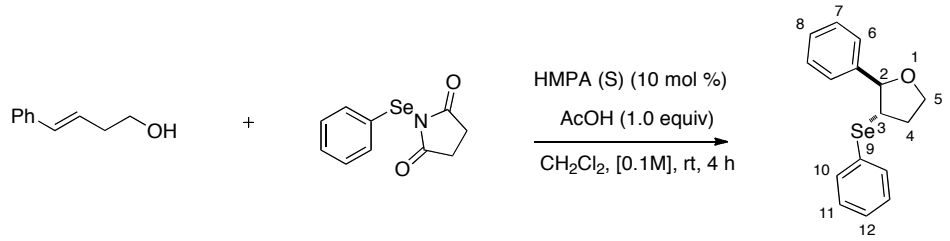
Analysis: $C_{10}H_8N_2O_4Se$ (299.965)

Calcd: C, 40.15; H, 2.70; N, 9.36; Se, 26.40%

Found: C, 40.20; H, 2.46; N, 9.12; Se, 24.75%

Catalytic Selenoetherification with *N*-Phenylselenenylsuccinimide (6)

Preparation of (+/-)-2-Phenyl-3-(phenylseleno)oxolane (28a)



(*E*)-**29** **6** **28a**

An oven-dried, 10-mL Schlenk flask equipped with a magnetic stir bar was charged with HMPA(S) (19.5 mg, 0.100 mmol, 0.1 equiv) and (*E*)-**29** (148 mg, 1.00 mmol). *N*-Phenylselenenylsuccinimide (**6**) (279 mg, 1.10 mmol, 1.1 equiv) was added in the glove box. The flask was attached to the manifold and CH_2Cl_2 (10 mL) was added to it. AcOH (57.0 μL, 1.00 mmol, 1.0 equiv) was added to the reaction using a syringe and the solution was stirred at room temperature for 4 h. Then the reaction mixture was quenched with Et_3N (140 μL, 1.00 mmol, 1.0 equiv) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in EtOAc (20 mL) and filtered through a 1.5-inch pad of silica gel which was further eluted with EtOAc (150 mL). The filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). The crude product was purified by column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 96/4) to afford 263 mg (87%) of seleno ether **28a** as a colorless clear oil.

Data for **28a**:

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

7.51 (d, *J* = 7.0 Hz, 2 H), 7.34-7.24 (m, 8 H), 4.87 (d, *J* = 6.0 Hz, 1H, HC(2)), 4.18 (dd, *J* = 13.7, 7.2 Hz, 1 H, HC(5)), 4.07 (dd, *J* = 15.5, 7.5 Hz, 1 H, HC(5)), 3.60 (dd, *J* = 13.5, 6.0 Hz, 1H, HC(3)), 2.53-2.46 (m, 1 H, HC(4)), 2.18-2.12 (m, 1 H, HC(4)).

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

141.2, 134.6, 129.0, 128.6, 128.3, 127.7, 127.6, 125.9, 86.0 (C(2)), 67.9 (C(5)), 47.6 (C(3)), 34.1 (C(4)).

IR: (NaCl plates, neat)

3059 (s), 3031 (s), 2973 (s), 2940 (s), 2869 (s), 1951 (w), 1880 (w), 1808 (w), 1738 (w), 1603 (m), 1579 (s), 1494 (s), 1477 (s), 1453 (s), 1438 (s), 1362 (m), 1348 (m), 1327 (m), 1302 (s), 1247 (m), 1209 (m), 1175 (s), 1064 (s), 1042 (s), 1024 (s), 1000 (m), 970 (s), 909 (s), 874 (w), 844 (w), 734 (s), 691 (s), 670 (s), 624 (m), 574 (w), 531 (w).

MS: (EI, 70 eV)

304.0 (34.7, M^+), 302.0 (16.6), 198.0 (27.5), 196.0 (13.1), 183.0 (18.5), 157.0 (20.0), 155.0 (10.0), 147.1 (60.1), 146.1 (100.0), 145.1 (11.3), 118.1 (21.6), 117.1 (84.7), 116.1 (13.2), 115.1 (31.5), 105.0 (69.1), 104.1 (13.3), 91.1 (69.5), 78.1 (18.4), 77.0 (55.2), 51.0 (17.7).

HRMS: calcd for $C_{16}H_{16}OSe$: 304.0366, found: 304.0362

TLC: R_f 0.25 (hexanes/EtOAc, 96/4) [UV]

General Procedure 6. Catalytic Selenoetherification with 34 and Achiral Lewis Bases. Table 3

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (if indicated) (0.006 mmol, 0.10 equiv) in $CDCl_3$ (0.67 mL) under an ambient atmosphere. Acid (TFA or MsOH as indicated) (0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ^1H NMR spectroscopy over 24 h. Note: For entries 7 and 6 in Table 3, HMPT and HMPA were added neat and not as a solution with olefin (*E*)-**29**. Additionally, the HMPT reaction was set up under an argon atmosphere. For entry 2, solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (0.006 mmol, 0.10 equiv) in $CDCl_3$ (0.57 mL) was used and 100 μL of a stock solution (39 μL in 1 mL $CDCl_3$) of AcOH was added

General Procedure 7. Catalytic Selenoetherification with 34 and Chiral Lewis Bases. Figure 2 and Figure S1

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (0.013 mmol, 0.20 equiv) in $CDCl_3$ (0.67 mL) under an ambient atmosphere. TFA (5.2 μL, 0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ^1H NMR spectroscopy over 24 h. After the time indicated in the Figure for a particular Lewis base, the reaction was quenched with Et_3N (10 μL) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric

composition of the product was determined by CSP-SFC analysis of the product.

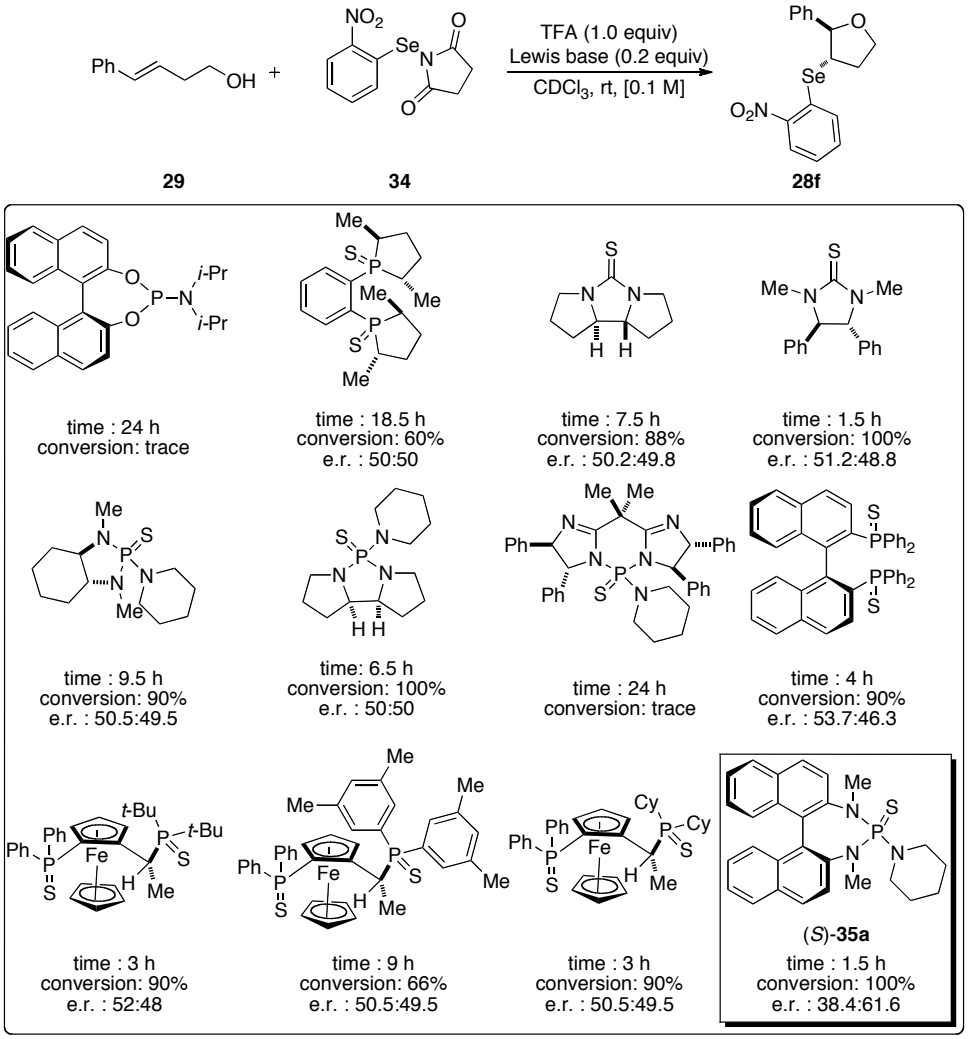


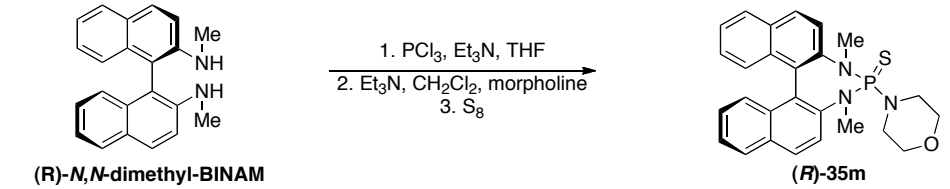
Figure S1 Chiral Lewis base survey with *N*-(2-nitrophenylselenenyl)succinimide**.**

Catalytic Selenoetherification with NPSS (6) and Chiral Lewis Base (*R*)-35a.

To an oven-dried NMR tube containing NPSS (18.8 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and thiophosphoramide **(*R*)-35a** (6.20 mg, 0.013 mmol, 0.20 equiv) in $CDCl_3$ (0.57 mL) under an argon atmosphere. 100 μL of a stock solution (39 μL in 1 mL $CDCl_3$) of AcOH was added. The resulting solution was shaken and monitored periodically by ^1H NMR spectroscopy, which showed 60% conversion to product over 3 h. The reaction was quenched with Et_3N (10 μL) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 96/4). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

HPLC: t_R 8.7 min (45.4%); t_R 10.4 min (54.6%), (Chiralpak Regis WhelkO1, 95:5, hexanes/*i*-PrOH, 1.0 mL/min, 220 nm, 25 °C)

Preparation of (*R*)-2,4-Dimethyl-3,4-dihydro-3-morpholino-dinaphthol[2,1-d:1'2'-f]-1H-[1,3,2]diazaphosphepine 3-Sulfide ((*R*)-35m)



(R)-*N,N*-dimethyl-BINAM (*R*)-35m

To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added (*R*)-*N,N*-dimethyl-BINAM (469 mg, 1.50 mmol), dry THF (15 mL), and Et_3N (0.52 mL, 3.75 mmol, 2.50 equiv) under an atmosphere of nitrogen and the homogeneous mixture was cooled to 0 °C (ice bath temperature). PCl_3 (0.39 mL, 4.50 mmol, 3.00 equiv) was added dropwise whereupon a colorless precipitate formed immediately. After the addition of PCl_3, the ice bath was removed and the reaction was stirred at room temperature for 3h. The volatiles were removed under high vacuum on the manifold and anhydrous Et_2O (15 mL) was added to it and the solution stirred for a minute. The supernatant was cannula filtered into another 50-mL, oven-dried Schlenk flask under nitrogen. The remaining precipitate in the reaction flask was washed with anhydrous Et_2O (6.0 mL) and was also cannula filtered into the receiver Schlenk flask. The combined filtrate was concentrated under high vacuum to afford a light yellow solid. The solid was redissolved in anhydrous Et_2O (5.0 mL) and the volatiles were again removed under high vacuum to remove any trace HCl and the light yellow foam was dried for 2.5 h. Anhydrous CH_2Cl_2 (12.5 mL) was added to it and the mixture was cooled to 0 °C (ice bath temperature). Et_3N (0.25 mL, 1.80 mmol, 1.20 equiv) and morpholine (0.14 mL, 1.65 mmol, 1.1 equiv) were added sequentially after which the ice bath was removed and the reaction mixture stirred at room temperature for 17 h. S_8 (154 mg, 4.80 mmol, 3.2 equiv) was added and the reaction was stirred at room temperature for 21 h. The solution was concentrated on the rotavap (30 °C, 30 mm Hg).

The crude residue was purified by column chromatography (silica gel, 25 mm x 22 cm column, hexanes/EtOAc, 85/15) to afford 588 mg of thiophosphoramide (*R*)-**35m** (85%) as a white solid. The e.r. (>99:1) of the (*R*)-**35m** is assumed to be the same as that of its precursor, namely the carbamate of (*R*)-BINAM precursor.

Data for (*R*)-**35m**:

mp: 255-256 °C (d)

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

7.99 (d, *J* = 9.0 Hz, 1 H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 9.0 Hz, 1 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30-7.24 (m, 2 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 8.5 Hz, 1H), 3.55 (br s, 4H), 3.14 (d, *J* = 12 Hz, 3H), 3.11 (br s, 4H), 3.01 (d, *J* = 12.5 Hz, 3H).

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

142.6 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz), 141.4, 132.5, 132.3, 131.4, 131.3, 129.6, 129.5, 129.1, 128.1, 128.0, 127.8, 127.1 (two overlapping peaks), 126.3, 126.0, 125.5, 124.9, 123.5, 122.0 (d, $^{2}J_{C\text{-}P}$ = 2.8 Hz), 67.4 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz), 46.4, 37.9 (d, $^{2}J_{C\text{-}P}$ = 9.1 Hz), 35.4 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz).

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

87.7

IR: (NaCl plates, CH_2Cl_2)

3049 (w), 2960 (w), 2894 (w), 2850 (w), 1618 (w), 1593 (w), 1506 (m), 1467 (w), 1447 (w), 1429 (w), 1360 (w), 1329 (m), 1294 (w), 1273 (m), 1255 (m), 1158 (w), 1145 (w), 1129 (m), 1114 (m), 1084 (m), 1024 (w), 964 (s), 933 (s), 866 (w), 820

(s), 751 (m), 736 (m), 720 (s), 701 (m), 687 (w), 667 (w), 652 (w), 560 (w), 536 (w).

MS: (EI, 70 eV)

460.2 (18.3), 459.2 (63.2, M^+), 375.1 (10.0), 374.1 (40.8), 373.1 (19.9), 342.1 (25.3), 341.1 (100.0), 311.2 (12.2), 281.1 (33.3), 280.1 (10.8), 84.0 (12.5).

HRMS: calcd for $C_{26}H_{26}N_3OPS$: 459.1534, found: 459.1547

TLC: R_f 0.23 (hexanes/EtOAc, 85/15) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ –358.6 (c = 1.15, $CHCl_3$)

Analysis: $C_{26}H_{26}N_3OPS$ (459.1534)

Calcd: C, 67.95; H, 5.70 N, 9.14%

Found: C, 67.91; H, 5.77 N, 8.94%

Optimization of Catalytic Selenoetherification with (*R*)-35m.

Table 4, entry 1

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of (*E*)-**29** (10.0 mg, 0.067 mmol), and (*R*)-**35m** (3.1 mg, 0.006 mmol, 0.10 equiv) in $CDCl_3$ (0.67 mL) under an ambient atmosphere. MsOH (4.4 μL, 0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ^{1}H NMR spectroscopy which showed complete conversion of (*E*)-**29** to **28f** in 20 min. The reaction was quenched with Et_3N (10 μL) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28f**, t_R 8.26 min (68%); (2*S*,3*R*)-**28f**, t_R 11.56 min (32%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C

Table 4, entry 2

To an oven-dried, 10 mL, Schlenk flask was added electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv), olefin (*E*)-**29** (10.0 mg, 0.067 mmol), thiophosphoramide (*R*)-**35m** (3.10 mg, 0.006 mmol, 0.10 equiv) and $CDCl_3$ (0.67 mL). The flask was cooled to -12 °C using a Cryocool, MsOH (4.4 μL, 0.067 mmol, 1 equiv) was added and solution was stirred at -12 °C for 24 h. The reaction was quenched with Et_3N (10 μL) at -12 °C and analyzed by ^1H NMR spectroscopy, which showed 50% conversion of (*E*)-**29** to **28f**. The reaction mixture was concentrated on the rotavap and the crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28f**, t_R 8.26 min (73%); (2*S*,3*R*)-**28f**, t_R 11.56 min (27%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C

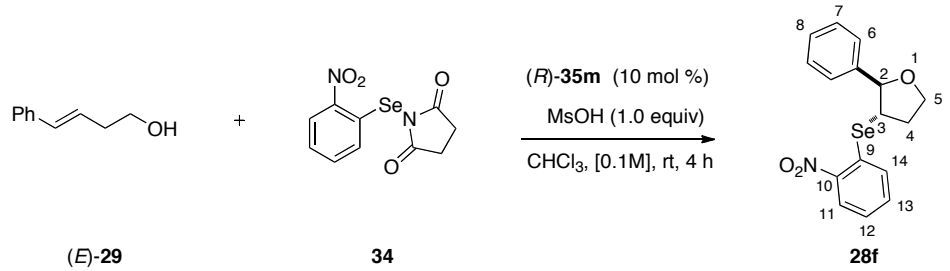
Table 4, entry 3

To an oven-dried, 10 mL, Schlenk flask was added electrophile **34** (44.4 mg, 0.15 mmol, 1.10 equiv), thiophosphoramide (*R*)-**35m** (12.4 mg, 0.03 mmol, 0.20 equiv) and $CDCl_3$ (1.34 mL). MsOH (8.8 μL, 0.13 mmol, 1.00 equiv) was added and then a solution of olefin (*E*)-**29** (20.0 mg, 0.13 mmol) in $CDCl_3$ (0.67 mL) was added over 14 h using a syringe pump. The reaction was quenched with Et_3N (10 μL), concentrated on the rotavap and the crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The

enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2*R*,3*S*)-**28f**, t_R 8.26 min (69%); (2*S*,3*R*)-**28f**, t_R 11.56 min (31%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C

General Procedure 8. Catalytic Asymmetric Selenoetherification with (*R*)-35m and 34. (2*R*,3*S*)-[3-(2-Nitrophenyl)selenenyl]-2-phenyloxolane (28f) (Table 5, entry 1)



(*E*)-**29** **34** **28f**

An oven-dried, 10-mL Schlenk flask equipped with a magnetic stir bar was charged with *N*-2-nitrophenylselenenyl succinimide **34** (329 mg, 1.10 mmol, 1.1 equiv), thiophosphoramide (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv) and $CHCl_3$ (5 mL). A solution of olefin (*E*)-**29** (148 mg, 1.00 mmol) in $CHCl_3$ (5 mL) was added under an atmosphere of nitrogen. Finally MsOH (65 μL, 1.00 mmol, 1.0 equiv) was added to the reaction using a syringe and the yellow solution was stirred at room temperature for 4 h. Then the reaction mixture was quenched with Et_3N (140 μL, 1.00 mmol, 1.0 equiv) and was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in EtOAc (20 mL) and filtered through a 1.5-inch pad of silica gel which was further eluted with EtOAc (150 mL). The filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). The crude product was purified by column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 92/8) to afford 338 mg (97%) of seleno ether **28f** as a yellow oil. Note: The racemate of **28f** was prepared following General Procedure 6 with $Ph_3P(S)$ as the catalyst and TFA as the Brønsted acid.

Data for **28f**:

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

8.24 (dd, *J* = 8.2, 2.0 Hz, 1 H, HC(11)), 7.41 (d, *J* = 7.0 Hz, 2 H), 7.35-7.25 (m, 6 H), 4.86 (d, *J* = 6.5 Hz, 1 H, HC(2)), 4.31-4.27 (m, 1 H, HC(5)), 4.09 (dd, *J* = 16.0, 7.5 Hz, 1 H, HC(5)), 3.72 (dd, *J* = 14.5, 6.5 Hz, 1 H, HC(3)), 2.79-2.72 (m, 1 H, HC(4)), 2.23-2.17 (m, 1 H, HC(4)).

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

146.9, 140.8, 133.4, 132.8, 130.0, 128.6, 128.0, 126.3, 125.9, 125.7, 85.4 (C(2)), 67.9 (C(5)), 45.8 (C(3)), 34.0 (C(4)).

^{77}Se NMR: (114 MHz, $CDCl_3$)

423.9

IR: (NaCl plates, CH_2Cl_2)

3085 (w), 3064 (w), 3028 (w), 2972 (w), 2936 (w), 2867 (w), 1590 (m), 1566 (m), 1513 (s), 1451 (m), 1331 (s), 1304 (s), 1252 (m), 1098 (m), 1085 (w), 1067 (m), 1038 (m), 973 (w), 909 (w), 852 (w), 759 (m), 730 (s), 701 (s), 646 (w).

MS: (EI, 70 eV)

349.0 (12.9, M^+), 243.0 (11.6), 201.9 (12.3), 186.0 (55.3), 184.0 (27.4), 182.0 (11.7), 163.1 (22.8), 156.0 (12.5), 147.1 (69.6), 146.1 (100.0), 117.1 (19.8), 116.1 (10.1), 115.1 (29.1), 106.0 (36.0), 105.0 (59.6), 91.1 (71.0), 78.0 (15.5), 77.1 (36.0).

HRMS: calcd for $C_{16}H_{15}NO_3Se$: 349.0217, found: 349.0223

TLC: R_f 0.12 (hexanes/EtOAc, 92/8) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 51.64 (c = 1.02, $CHCl_3$)

SFC: (*2R,3S*)-**28f**, t_R 8.41 min (68.9%); (*2S,3R*)-**28f**, t_R 11.60 min (31.1%), (Chiralpak

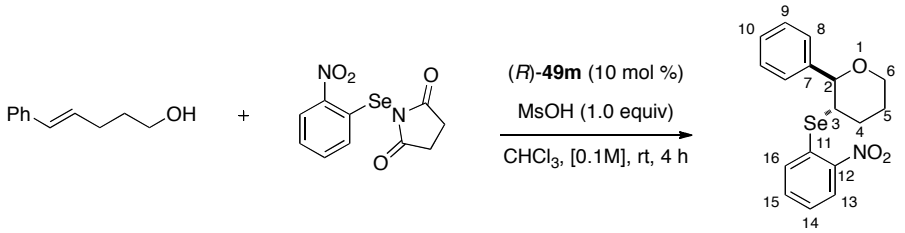
AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Analysis: $C_{16}H_{15}NO_3Se$ (349.0217)

Calcd: C, 55.18; H, 4.34; N, 4.02%

Found: C, 55.09; H, 4.32; N, 3.95%

Preparation of (2*R*,3*S*)-3-(2-Nitrophenyl)selenenyl-2-phenyloxane (31) (Table 5, entry 2)



(*E*)-**30** **34** **31**

Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**30** (162 mg, 1.00 mmol), MsOH (65.0 μL, 1.10 mmol, 1.0 equiv), and $CHCl_3$ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 92/8) 312 mg (86%) of seleno ether **31** as a yellow solid. Note: The racemate of **31** was prepared following General Procedure 6 with $Ph_3P(S)$ as the catalyst and TFA as the Brønsted acid.

Data for **31**:

mp: 75-76 °C

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

7.94 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 7.0 Hz, 2 H), 7.18-7.08 (m, 6 H), 4.37 (d, *J* = 10.5 Hz, 1 H, HC(2)), 4.17 (dd, *J* = 11.5, 4.5 Hz, 1 H, HC(6)), 3.65 (td, *J* = 11.5, 2.0 Hz, 1 H, HC(6)), 3.58-3.52 (m, 1 H, HC(3)), 2.45-2.42 (m, 1 H, HC(4)), 2.01-1.93 (m, 1H), 1.86 (ddd, *J* = 25, 12.5, 3.5 Hz, 1 H), 1.77 (d, *J* = 13.0 Hz, 1 H).

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

148.2, 139.6, 132.5, 131.5, 130.1, 128.1, 128.0, 127.2, 125.7, 125.4, 85.2 (C(2)), 68.6 (C(6)), 45.7 (C(3)), 31.4 (C(4)), 27.6 (C(5)).

IR: (KBr pellets)

3092 (w), 3057 (w), 3034 (w), 2934 (m), 2851 (m), 1589 (s), 1565 (s), 1515 (s), 1452 (s), 1434 (m), 1330 (s), 1304 (s), 1248 (s), 1182 (m), 1141 (m), 1098 (s), 1076 (s), 1036 (s), 1024 (s), 962 (m), 938 (s), 910 (w), 881 (w), 852 (m), 781 (m), 758 (s), 728 (s), 701 (s), 646 (m), 533 (m).

MS: (EI, 70 eV)

363.0 (8.2, M^+), 322.3 (13.5), 162.1 (11.3), 161.1 (100.0), 105.0 (24.5), 91.1 (61.6), 77.1 (10.4), 71.1 (29.3), .

HRMS: calcd for $C_{17}H_{17}NO_3Se$: 363.0374, found: 363.0360

TLC: R_f 0.17 (hexanes/EtOAc, 91/9) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 62.04 (c = 1.95, $CHCl_3$)

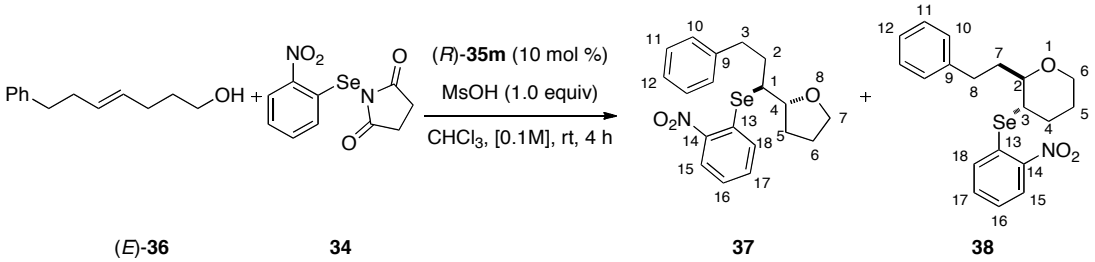
SFC: (*2S,3R*)-**31**, t_R 24.86 min (25.1%); (*2R,3S*)-**31**, t_R 26.09 min (74.9%), (Chiralpak AD, 125 bar, 10% MeOH in CO_2, 1.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{17}H_{17}NO_3Se$ (363.0374)

Calcd: C, 56.36; H, 4.73; N, 3.87%

Found: C, 56.04; H, 4.60; N, 3.92%

Preparation of (1*S*,2*R*)-[1-[(2-Nitrophenyl)seleno]-3-phenylpropyl]oxolane (37) and (2*R*,3*S*)-3-(2-Nitrophenyl)selenenyl-2-(2-phenylethyl)oxane (38) (Table 5, entry 3)



(*E*)-**36** **34** **37** **38**

Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**36** (190 mg, 1.00 mmol), MsOH (65.0 μL, 1.10 mmol, 1.0 equiv), and $CHCl_3$ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 30 cm column, hexanes/EtOAc, 92.5/7.5) and three sets of fractions were collected. These fractions contained pure **37** (199 mg, yellow oil), mixture of **37** and **38** (99.2 mg, yellow oil), and pure **38** (69.7 mg, yellow oil). The combined yield of the **37** and **38** was 94% (368 mg). Note: The racemates of **37** and **38** were prepared following General Procedure 6 with $Ph_3P(S)$ as the catalyst and TFA as the Brønsted acid.

Data for **37**:

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

8.18 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.39 (td, *J* = 8.5, 1.5 Hz, 1 H), 7.30-7.25 (m, 3 H), 7.18 (t, *J* = 7.0 Hz, 1 H), 7.13 (d, *J* = 7.0 Hz, 2 H), 4.15 (dd, *J* = 13.5, 7.0 Hz, 1 H), 3.85 (dd, *J* = 15.5, 7.0 Hz, 1 H), 3.76 (dd, *J* = 13.5, 7.5 Hz, 1 H), 3.57-3.53 (m, 1 H), 2.95 (ddd, *J* = 14.0, 9.0, 5.5 Hz, 1 H), 2.82-2.77 (m, 1 H), 2.15-2.08 (m, 1 H), 2.05-1.84 (m, 4 H), 1.78-1.70 (m, 1 H).

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

148.1, 141.1, 133.2, 132.6, 131.4, 128.5, 128.4, 126.0, 125.9, 125.6, 81.5, 68.5, 48.7, 33.8, 33.7, 29.6, 26.0.

IR: (NaCl plates, CH_2Cl_2)

3085 (w), 3057 (w), 3028 (w), 2972 (w), 2943 (w), 2859 (w), 1589 (m), 1566 (m), 1514 (s), 1454 (m), 1332 (s), 1303 (m), 1252 (w), 1096 (w), 1057 (m), 1035 (m), 852 (w), 783 (w), 748 (w), 730 (m), 700 (m), 645 (w).

MS: (EI, 70 eV)

391.1 (6.9, M^+), 189.1 (39.5), 171.1 (12.7), 129.1 (21.2), 117.1 (13.3), 105.1 (11.6), 97.1 (15.8), 91.1 (74.2), 71.1 (100.0) .

HRMS: calcd for $C_{19}H_{21}NO_3Se$: 391.0687, found: 391.0699

TLC: R_f 0.15 (hexanes/EtOAc, 92.5/7.5) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ – 85.9 (c = 2.01, $CHCl_3$)

SFC: (*2R,3S*)-**37**, t_R 19.56 min (78.8%); (*2S,3R*)-**37**, t_R 20.70 min (21.2%), (Chiralpak AD, 125 bar, 10% MeOH in CO_2, 1.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{19}H_{21}NO_3Se$ (391.0687)

Calcd: C, 58.46; H, 5.42; N, 3.59%

Found: C, 58.55; H, 5.38; N, 3.64%

Data for **38**:

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

8.19 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.27-7.24 (m, 2 H), 7.18-7.14 (m, 3 H), 4.09-4.07 (m,

1 H, HC(6)), 3.49 (td, *J* = 11.5, 2.5 Hz, 1 H, HC(6)), 3.38 (td, *J* = 8.0, 2.0 Hz, 1 H, HC(2)), 3.35-3.30 (m, 1 H, HC(3)), 2.84 (ddd, *J* = 14.0, 10.0, 4.5 Hz, 1 H, HC(8)), 2.66 (ddd, *J* = 16.5, 9.5, 7.0 Hz, 1 H, HC(8)), 2.31-2.29 (m, 1 H), 2.24-2.17 (m, 1 H), 1.85-1.66 (m, 4 H).

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

148.2, 141.7, 133.2, 130.8, 130.7, 128.5, 128.3, 126.3, 126.1, 125.7, 80.2 (C(2)), 68.1 (C(6)), 44.1 (C(3)), 36.0, 32.0, 31.6, 27.8.

IR: (NaCl plates, CH_2Cl_2)

3085 (w), 3057 (w), 3021 (w), 2947 (m), 2848 (w), 2859 (w), 1590 (m), 1566 (m), 1515 (s), 1452 (m), 1331 (s), 1303 (m), 1248 (w), 1117 (w), 1098 (m), 1085 (m), 1060 (w), 1037 (m), 852 (w), 783 (w), 730 (s), 700 (m), 645 (w).

MS: (EI, 70 eV)

391.1 (7.5, M^+), 189.1 (72.3), 171.1 (30.1), 143.1 (13.8), 135.1 (18.0), 129.1 (31.1), 117.1 (12.8), 105.1 (23.7), 91.1 (100.0), 71.1 (41.7), 57.2 (10.9), 55.1 (19.8).

HRMS: calcd for $C_{19}H_{21}NO_3Se$: 391.0687, found: 391.0682

TLC: R_f 0.12 (hexanes/EtOAc, 92.5/7.5) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 23.6 (c = 0.33, $CHCl_3$)

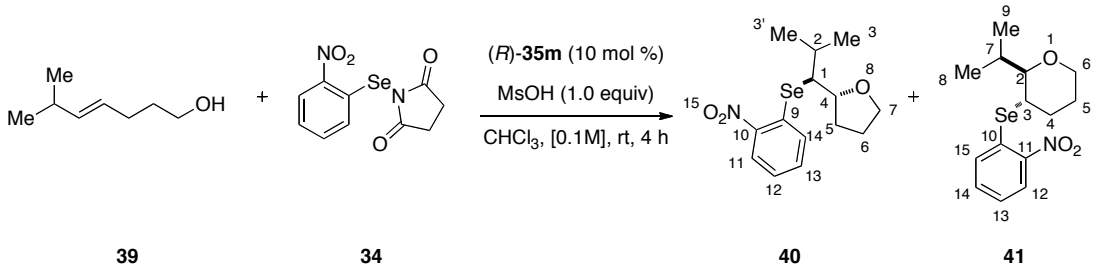
SFC: (*2S,3R*)-**38**, t_R 11.48 min (14.9%); (*2R,3S*)-**38**, t_R 18.66 min (85.1%), (Chiralpak OD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Analysis: $C_{19}H_{21}NO_3Se$ (391.0687)

Calcd: C, 58.46; H, 5.42; N, 3.59%

Found: C, 58.35; H, 5.13; N, 3.62%

Preparation of (1*S*,2*R*)-2-[2-Methyl-1-[(2-nitrophenyl)selenenyl]propyl]oxolane (40) and (2*R*,3*S*)-3-(2-Nitrophenyl)selenenyl-2-(1-methylethyl)oxane (41) (Table 5, entry 4)



39 **34** **40** **41**

Following General Procedure 9, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**39** (128 mg, 1.00 mmol), MsOH (65.0 μL, 1.10 mmol, 1.0 equiv), and $CHCl_3$ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 91/9) three sets of fractions. These fractions contained pure **41** (26.4 mg, yellow oil), mixture of **40** and **41** (110 mg, yellow oil), and pure **40** (147 mg, yellow oil). The combined yield of the **40** and **41** was 86% (283 mg). Note: The racemates of **40** and **41** were prepared following General Procedure 6 with $Ph_3P(S)$ as the catalyst and TFA as the Brønsted acid.

Data for **40**:

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

8.12 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.47 (td, *J* = 8.5, 1.5 Hz, 1 H), 7.29 (td, *J* = 8.0, 1.0 Hz, 1 H), 4.16 (dd, *J* = 14.5, 7.5 Hz, 1 H), 3.85 (dd, *J* = 15.0, 7.0 Hz, 1 H), 3.75 (dd, *J* = 7.5, 6.0 Hz, 1 H), 3.43 (dd, *J* = 7.5, 4.5 Hz, 1 H), 2.28-2.22 (m, 1 H), 2.12-2.05 (m, 1 H), 1.90-1.83 (m, 2 H), 1.65-1.57 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 3 H), 1.06 (d, *J* = 7.0 Hz, 3 H).

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

148.8, 133.0, 132.2, 131.8, 125.8, 125.7, 80.3, 68.2, 58.6, 30.9, 30.3, 25.9, 21.5, 19.6.

IR: (NaCl plates, CH_2Cl_2)

3085 (w), 3057 (w), 2959 (s), 2872 (s), 1589 (s), 1566 (m), 1512 (s), 1450 (m), 1383 (w), 1331 (s), 1298 (s), 1252 (m), 1181 (w), 1149 (w), 1096 (m), 1055 (s), 1053 (s), 925 (w), 851 (m), 784 (m), 729 (s), 698 (m), 645 (m).

MS: (EI, 70 eV)

329.1 (4.2, M^+), 127.1 (15.8), 71.1 (100.0), 57.2 (11.0).

HRMS: calcd for $C_{14}H_{19}NO_3Se$: 329.0530, found: 329.0528

TLC: R_f 0.26 (hexanes/EtOAc, 91/9) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 11.70 (c = 1.80, $CHCl_3$)

SFC: (*2S,3R*)-**40**, t_R 10.47 min (17.4%); (*2R,3S*)-**40**, t_R 11.35 min (82.6%), (Chiralpak OD, 125 bar, 10% MeOH in CO_2, 1.0 mL/min, 220 nm, 40 °C)

Analysis: $C_{14}H_{19}NO_3Se$ (329.0530)

Calcd: C, 51.22; H, 5.83; N, 4.27%

Found: C, 51.24; H, 5.77; N, 4.28%

Data for **41**:

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

8.18 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(12)), 7.64 (d, *J* = 7.5 Hz, 1 H, HC(15)), 7.52 (td, *J* = 8.0, 1.0 Hz, 1 H, , HC(14)), 7.34 (td, *J* = 8.0, 1.0 Hz, 1 H, HC(13)), 4.04-4.02 (m, 1 H, HC(6)), 3.49-3.41 (m, 2 H), 3.31 (dd, *J* = 10.0, 2.5 Hz, 1 H), 2.32-2.28 (m,

1 H), 2.17 (septd, J = 6.5, 2.0 Hz, 1 H, HC(2)), 1.84-1.62 (m, 3H), 1.00 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H).

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

148.6, 133.2, 130.9, 130.5, 126.2, 126.1, 84.5 (C(2)), 68.3 (C(6)), 41.9 (C(3)), 32.2, 29.9, 27.8, 20.4, 14.7.

IR: (NaCl plates, CH_2Cl_2)

3071 (w), 2960 (s), 2872 (m), 2851 (m), 1590 (m), 1567 (m), 1515 (s), 1464 (m), 1450 (m), 1379 (w), 1331 (s), 1302 (m), 1262 (m), 1252 (m), 1102 (s), 1081 (m), 1067 (m), 1026 (m), 999 (m), 922 (m), 872 (w), 852 (m), 805 (w), 783 (m), 730 (s), 702 (m), 645 (w).

MS: (EI, 70 eV)

329.1 (5.5, M^+), 201.9 (22.9), 199.9 (11.1), 127.1 (32.2), 106.0 (14.2), 71.1 (100.0), 55.1 (18.6).

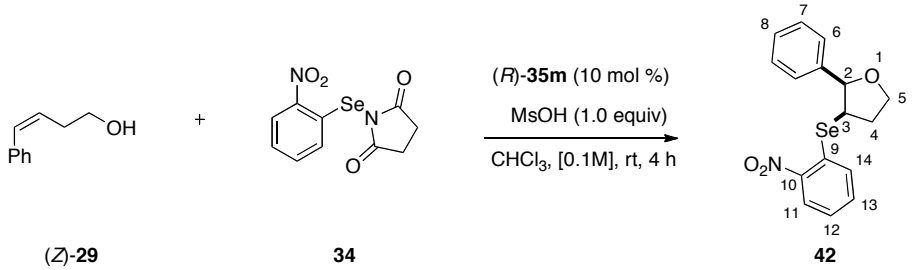
HRMS: calcd for $C_{14}H_{19}NO_3Se$: 329.0530, found: 329.0525

TLC: R_f 0.32 (hexanes/EtOAc, 91/9) [UV]

Opt. Rot.: $[\alpha]_D^{24}$ 14.3 (c = 0.80, $CHCl_3$)

SFC: (*2R,3S*)-**41**, t_R 3.27 min (83.8%); (*2S,3R*)-**41**, t_R 3.85 min (16.2%), (Chiralpak OD, 125 bar, 10% MeOH in CO_2, 3.0 mL/min, 220 nm, 40 °C)

Preparation of *rel* (2*R*,3*R*)-3-(2-Nitrophenyl)selenenyl-2-phenyloxolane (42) (Table 5, entry 5)



(*Z*)-**29** **34** **42**

Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*Z*)-**29** (148 mg, 1.00 mmol), MsOH (65.0 μL, 1.10 mmol, 1.0 equiv), and $CHCl_3$ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, 91/9 then 88/12 hexanes/EtOAc) 278 mg (80%) of seleno ether **42** as a yellow solid. The product was further purified by recrystallization (EtOAc/hexanes) to obtain analytically pure material. Note: The racemate of **42** was prepared following General Procedure 6 with $Ph_3P(S)$ as the catalyst and TFA as the Brønsted acid.

Data for **42**:

mp: 109-110 °C

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

8.13 (d, *J* = 8.0 Hz, 1 H, HC(11)), 7.55 (d, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.34-7.23 (m, 6 H), 5.30 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.35 (dd, *J* = 14.0, 7.5 Hz, 1 H, HC(5)), 4.25 (dd, *J* = 11.0, 5.5 Hz, 1 H, HC(3)), 4.05 (dd, *J* = 14.0, 8.0 Hz, 1 H, HC(5)), 2.79-2.72 (m, 1 H, HC(4)), 2.30-2.23 (m, 1 H, HC(4)).

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

147.5, 138.6, 133.2, 132.5, 130.3, 128.0, 127.9, 126.3, 126.1, 125.5, 82.7 (C(2)), 67.3 (C(5)), 44.7 (C(3)), 33.8 (C(4)).

IR: (KBr pellets)

3078 (s), 3035 (s), 2979 (m), 2950 (s), 2922 (m), 2876 (s), 1975 (w), 1948 (m), 1819 (w), 1741 (w), 1589 (s), 1563 (s), 1513 (s), 1496 (s), 1457 (s), 1369 (s), 1332 (s), 1305 (s), 1252 (s), 1223 (s), 1213 (s), 1174 (s), 1149 (s), 1099 (s), 1092 (s), 940 (s), 1055 (s), 1021 (s), 961 (s), 940 (s), 903 (s), 852 (s), 808 (m), 786 (s), 752 (s), 733 (s), 700 (s), 681 (s), 644 (s), 620 (s), 546 (m).

MS: (EI, 70 eV)

349.1 (17.8, M^+), 243.0 (12.5), 202.0 (13.1), 188.0 (10.3), 186.0 (61.5), 184.0 (29.7), 183.0 (10.3), 182.0 (12.4), 163.1 (21.0), 156.0 (11.0), 147.1 (73.0), 146.1 (100.0), 117.1 (12.2), 115.1 (19.2), 106.0 (32.8), 105.1 (73.6), 91.1 (40.1), 78.1 (12.1), 77.1 (40.2).

HRMS: calcd for $C_{16}H_{15}NO_3Se$: 349.0217, found: 349.0201

TLC: R_f 0.06 (hexanes/EtOAc, 88/12) [UV]

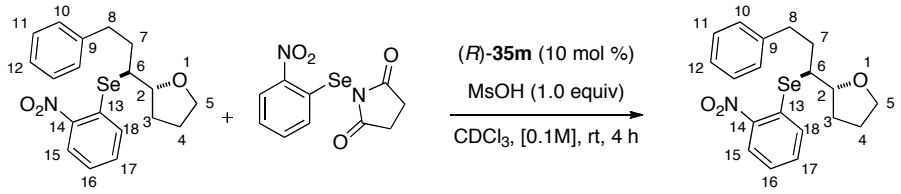
SFC: (*2R,3R*)-**42**, t_R 12.57 min (50.9%); (*2S,3S*)-**42**, t_R 13.48 min (49.1%), (Chiralpak AD, 125 bar, 12% MeOH in CO_2, 2.5 mL/min, 220 nm, 40 °C)

Analysis: $C_{16}H_{15}NO_3Se$ (349.0217)

Calcd: C, 55.18; H, 4.34; N, 4.02%

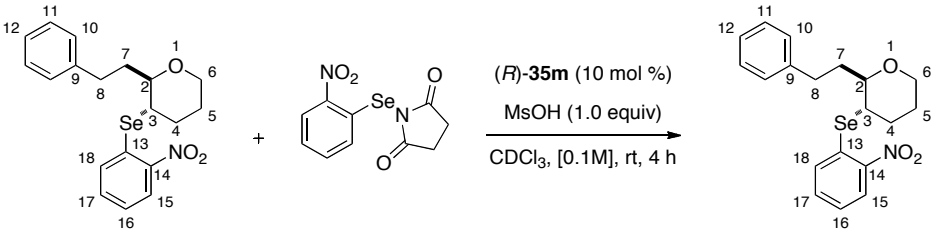
Found: C, 55.10; H, 4.34; N, 3.99%

General Procedure 9. Isomerization Procedure for Seleno Ethers 37, 38, 40 and 41



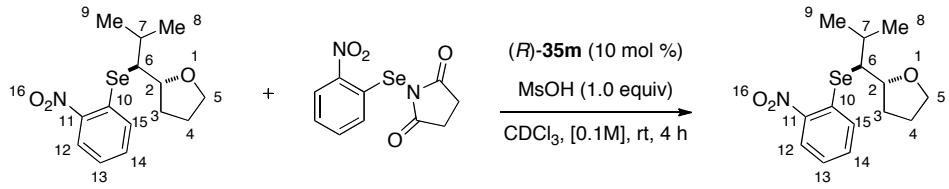
37 **37**

To an oven-dried NMR tube containing **34** (14.9 mg, 0.049 mmol, 1.0 equiv) was added a solution of seleno ether **37** (19.5 mg, 0.049 mmol), and (*R*)-**35m** (2.3 mg, 0.005 mmol, 0.10 equiv) in $CDCl_3$ (0.50 mL) under an ambient atmosphere. MsOH (3.2 μL, 0.049 mmol, 1.0 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ^1H NMR spectroscopy which showed no isomerization of **37** to **38** over 4 h.



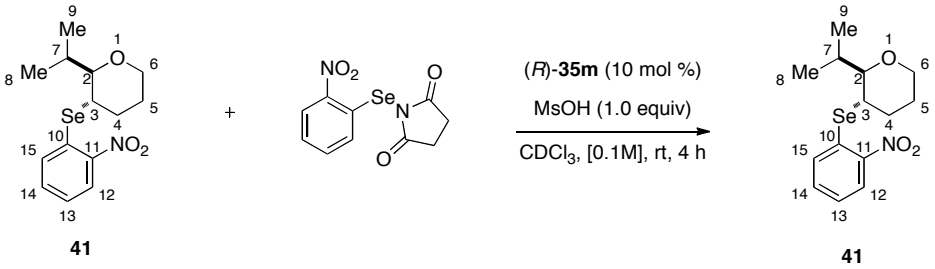
38 **38**

Following General Procedure 9, **34** (2.4 mg, 0.008 mmol, 1. 0 equiv), seleno ether **38** (3.1 mg, 0.008 mmol), (*R*)-**35m** (0.4 mg, 0.001 mmol, 0.10 equiv) and MsOH (0.51 μL, 0.008 mmol, 1 equiv) were combined in $CDCl_3$ (0.1 mL) under an ambient atmosphere. ^1H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **38** to **37** over 4 h.



40 **40**

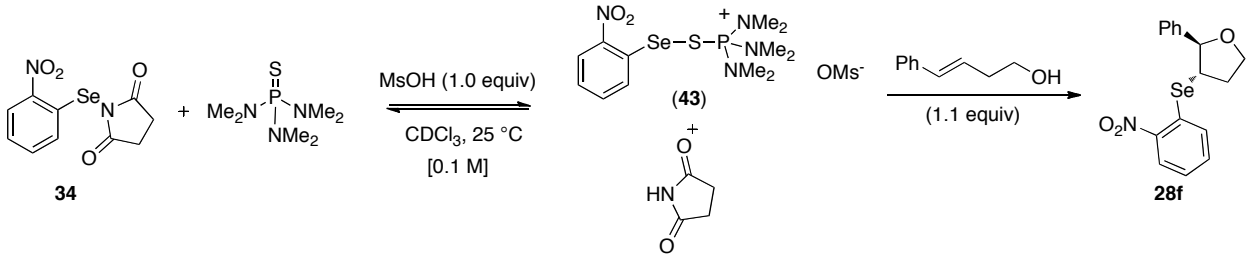
Following General Procedure 9, **34** (17.7 mg, 0.059 mmol, 1.0 equiv), seleno ether **40** (19.5 mg, 0.059 mmol), (*R*)-**35m** (2.7 mg, 0.006 mmol, 0.10 equiv) and MsOH (3.8 μL, 0.059 mmol, 1.0 equiv) were combined in $CDCl_3$ (0.59 mL) under an ambient atmosphere. ^{1}H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **40** to **41** over 4 h.



Following General Procedure 9, **34** (6.8 mg, 0.023 mmol, 1.0 equiv), seleno ether **41** (7.5 mg, 0.023 mmol), (*R*)-**35m** (1.0 mg, 0.002 mmol, 0.10 equiv) and MsOH (1.5 μL, 0.023 mmol, 1.0 equiv) were combined in $CDCl_3$ (0.23 mL) under an ambient atmosphere. ^{1}H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **41** to **40** over 4 h.

Mechanistic Studies. Formation of Complexes 43-45.

Formation of complex 43. Scheme 14



To an oven-dried, NMR tube containing **34** (25.0 mg, 0.083 mmol) was added a solution of HMPA(S) (16.3 mg, 0.083 mmol, 1.00 equiv) in $CDCl_3$ (0.83 mL). Methanesulfonic acid (5.4 μL, 0.083 mmol, 1.00 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ^{1}H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **43**. The ratio of **43** to **34** equilibrated to 2:1 favoring **43** within 3 h. At room temperature ^{31}P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to **43** and HMPA(S) at -50 °C. The ^{77}Se NMR also showed two sharp peaks corresponding to **43** and **34** at room temperature. This mixture was stable in solution for 48 h after which olefin (*E*)-**29** (13.6 mg, 0.092 mmol, 1.10 equiv) was added. ^{1}H NMR spectroscopic analysis revealed complete conversion of the electrophile to the seleno ether after 1 h.

Data for **43**:

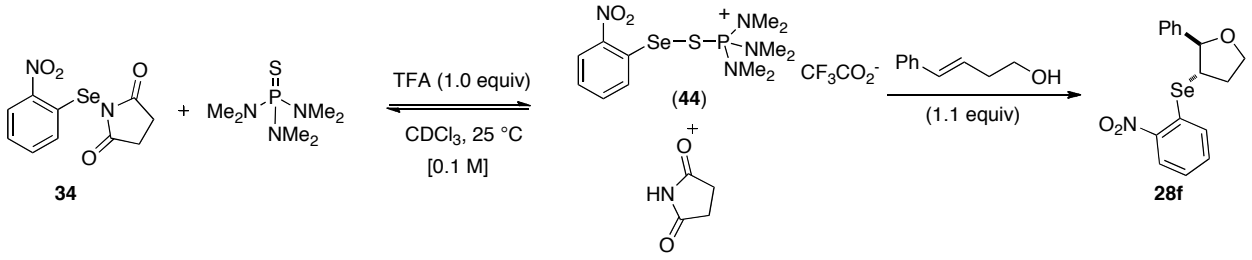
^{31}P NMR: (162 MHz, $CDCl_3$)

62.4

^{77}Se NMR: (114 MHz, $CDCl_3$)

582

Formation of Complex 44. Scheme 15



To an oven-dried, NMR tube containing **34** (25.0 mg, 0.083 mmol) was added a solution of HMPA(S) (16.35 mg, 0.083 mmol, 1.00 equiv) in $CDCl_3$ (0.83 mL). Trifluoroacetic acid (6.4 μL, 0.083 mmol, 1.0 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ^{1}H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **44**. The ratio of **44** to **34** equilibrated to 0.9:1 within 3 h. At room temperature ^{31}P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to HMPA(S) and **44** at -50 °C. The ^{77}Se NMR also showed two sharp peaks corresponding to **34** and **44** at room temperature. This mixture was stable in solution for 48 h after which olefin (*E*)-**29** (13.6 mg, 0.092 mmol, 1.10 equiv) was added. ^{1}H NMR spectroscopic analysis revealed 77% conversion of the electrophile to the seleno ether after 1 h.

Data for **44**:

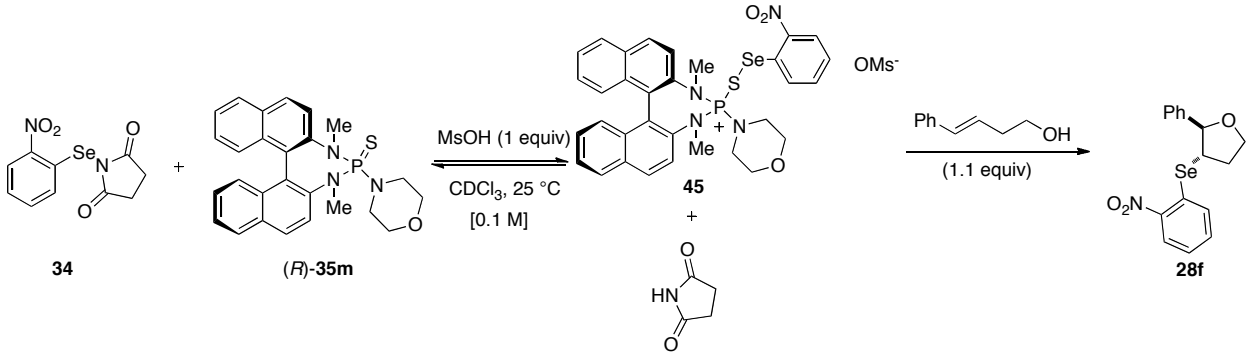
^{31}P NMR: (162 MHz, $CDCl_3$)

63.4

^{77}Se NMR: (114 MHz, $CDCl_3$)

587

Formation of Complex 45. Scheme 16



To an oven-dried, NMR tube containing **34** (16.3 mg, 0.054 mmol) was added a solution of (*R*)-**35m** (25.0 mg, 0.054 mmol, 1.00 equiv) in $CDCl_3$ (0.54 mL). Methanesulfonic acid (3.5 μL, 0.054 mmol, 1.00 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ^{1}H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **45**. The ratio of (*R*)-**35m** to **45** equilibrated to 0.28:1 within 3 h. At room temperature ^{31}P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to (*R*)-**35m** and **45** at -50 °C. The ^{77}Se NMR also showed two sharp peaks corresponding to **34** and (*R*)-**35m** at room temperature. This mixture was stable in solution for 24 h after which olefin (*E*)-**29** (8.86 mg, 0.060 mmol, 1.1 equiv) was added. ^{1}H NMR spectroscopic analysis revealed 100% conversion of the electrophile to the seleno ether after 1 h.

Data for **45**:

^{31}P NMR: (500 MHz, $CDCl_3$)

65.1

^{77}Se NMR: (500 MHz, $CDCl_3$)

620

References

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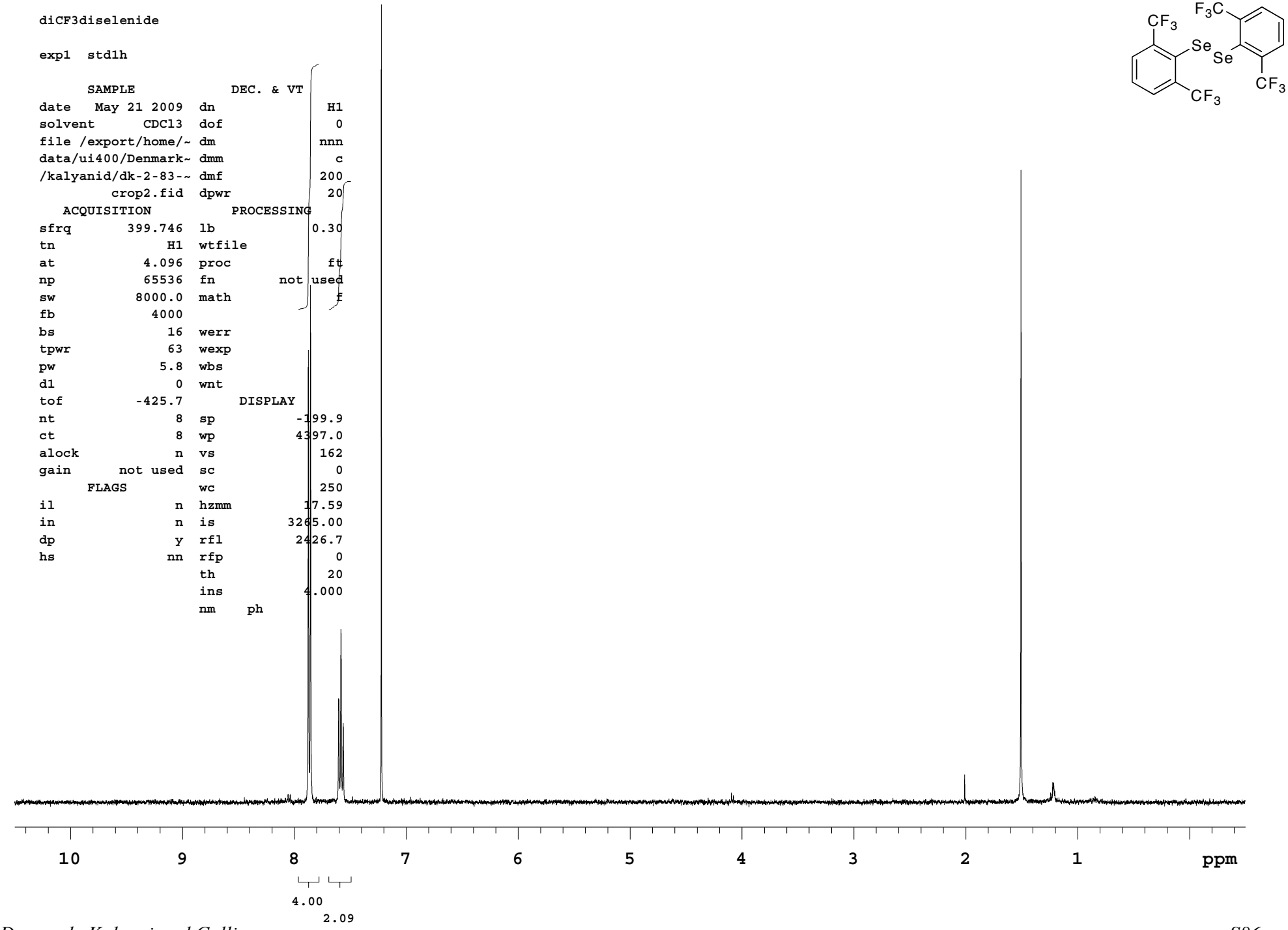
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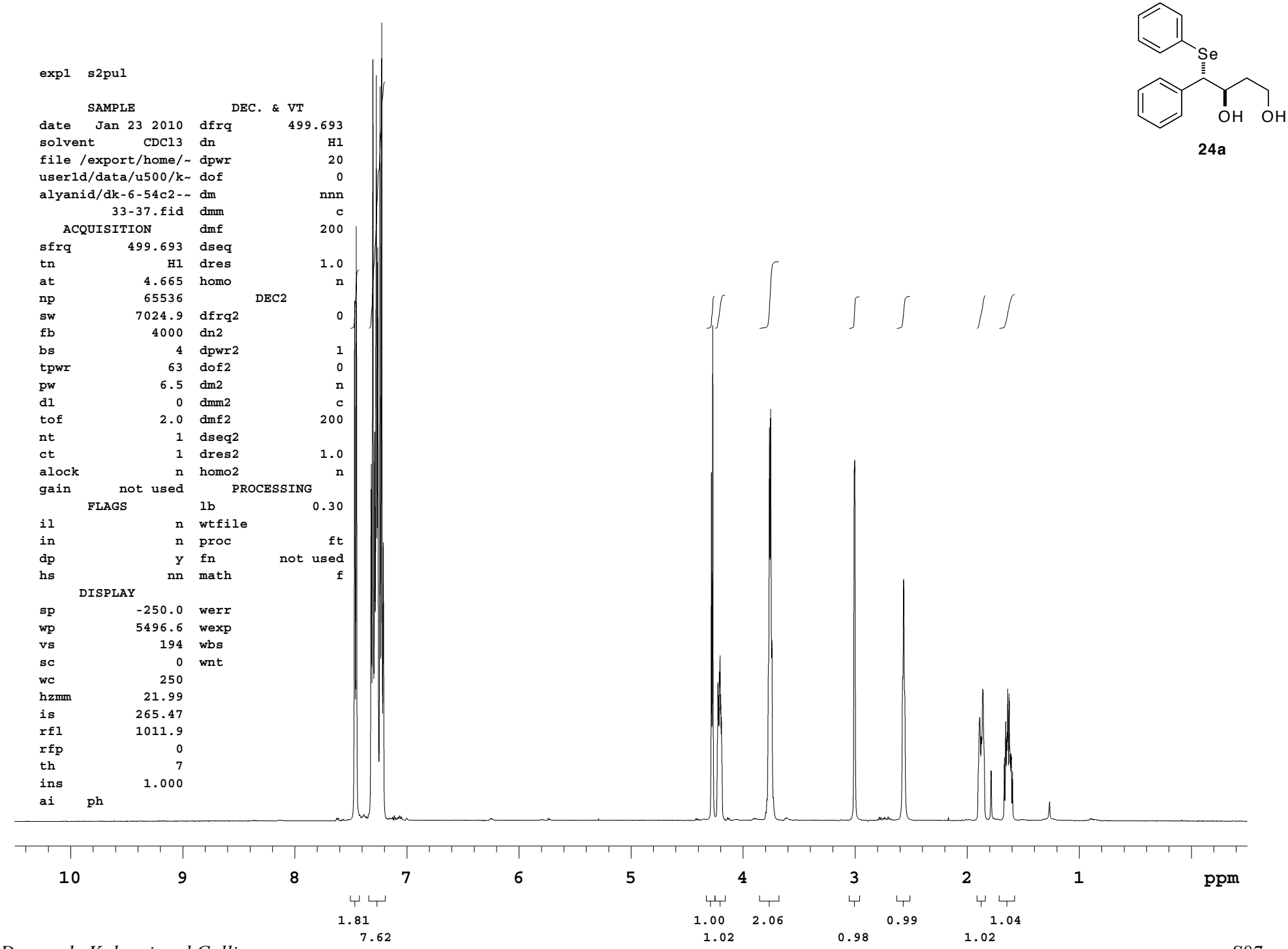
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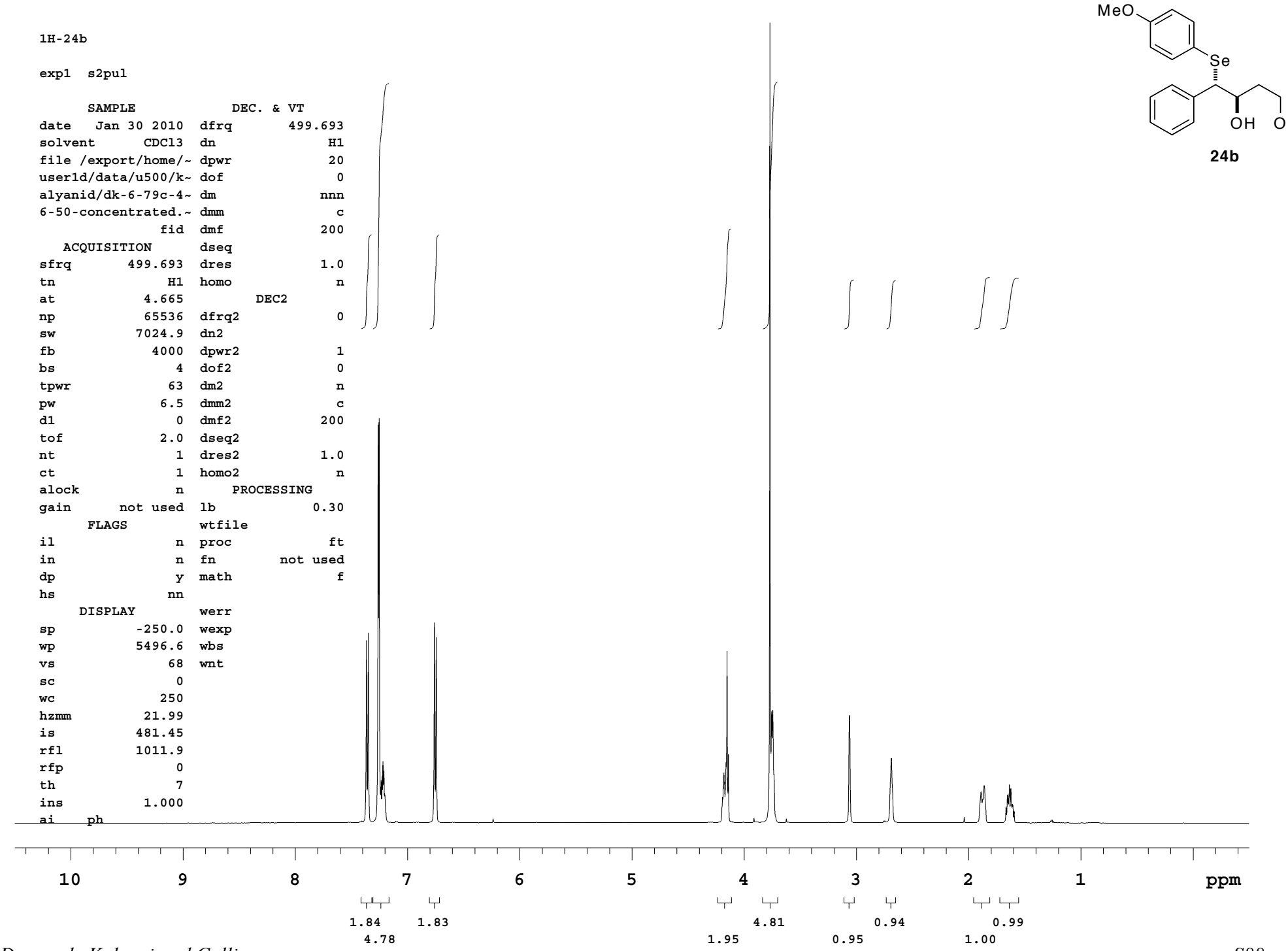
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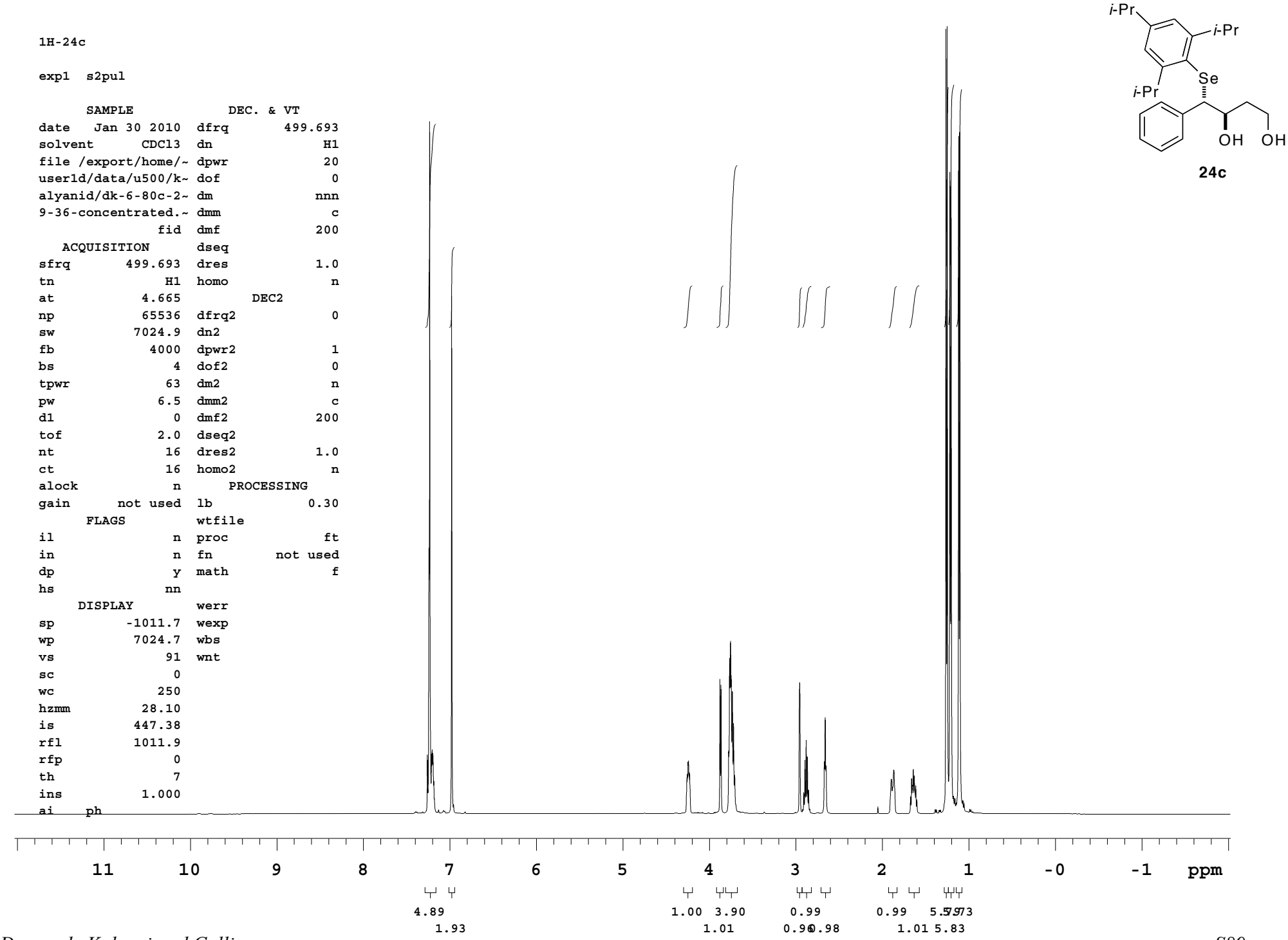
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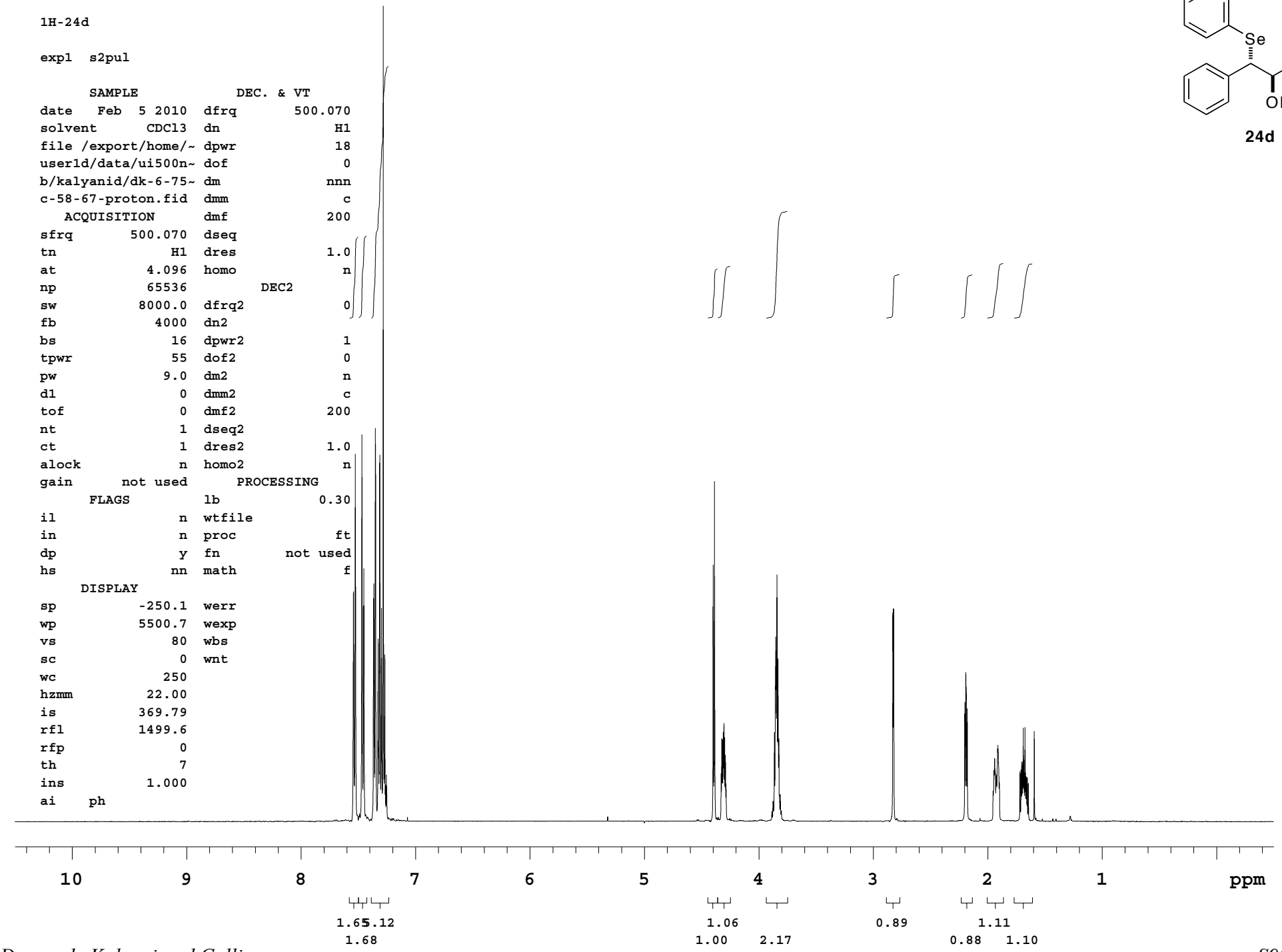
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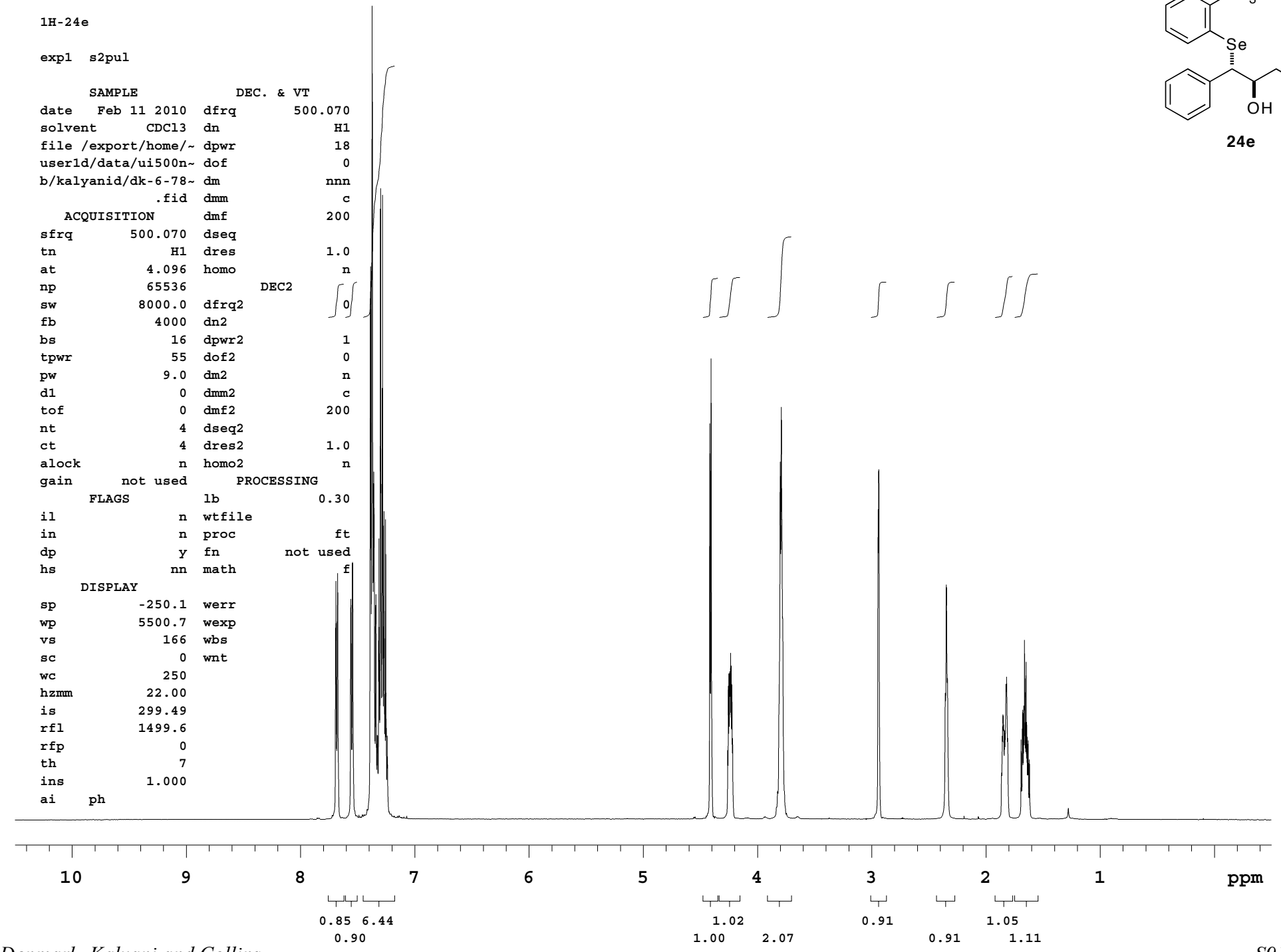
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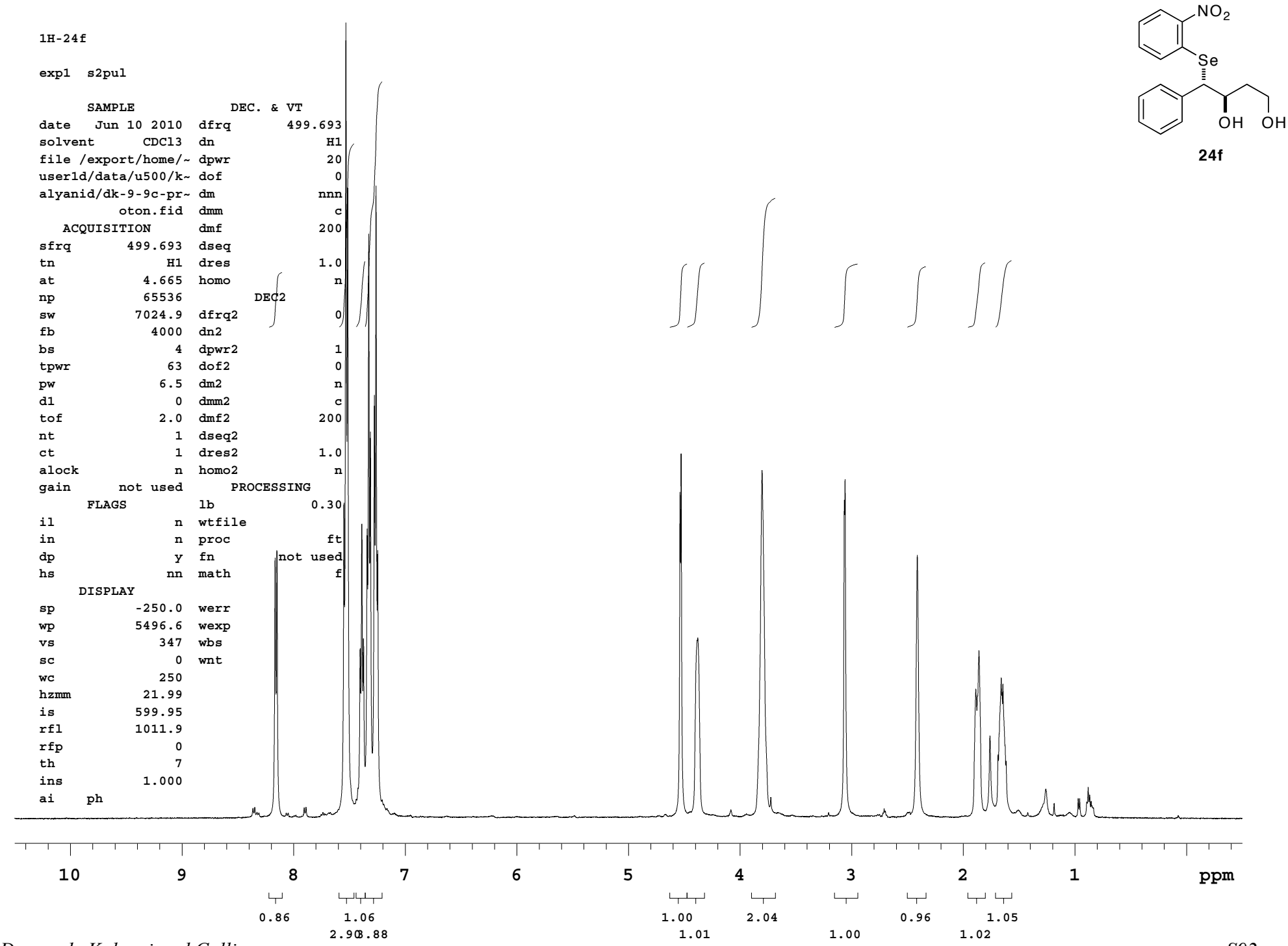
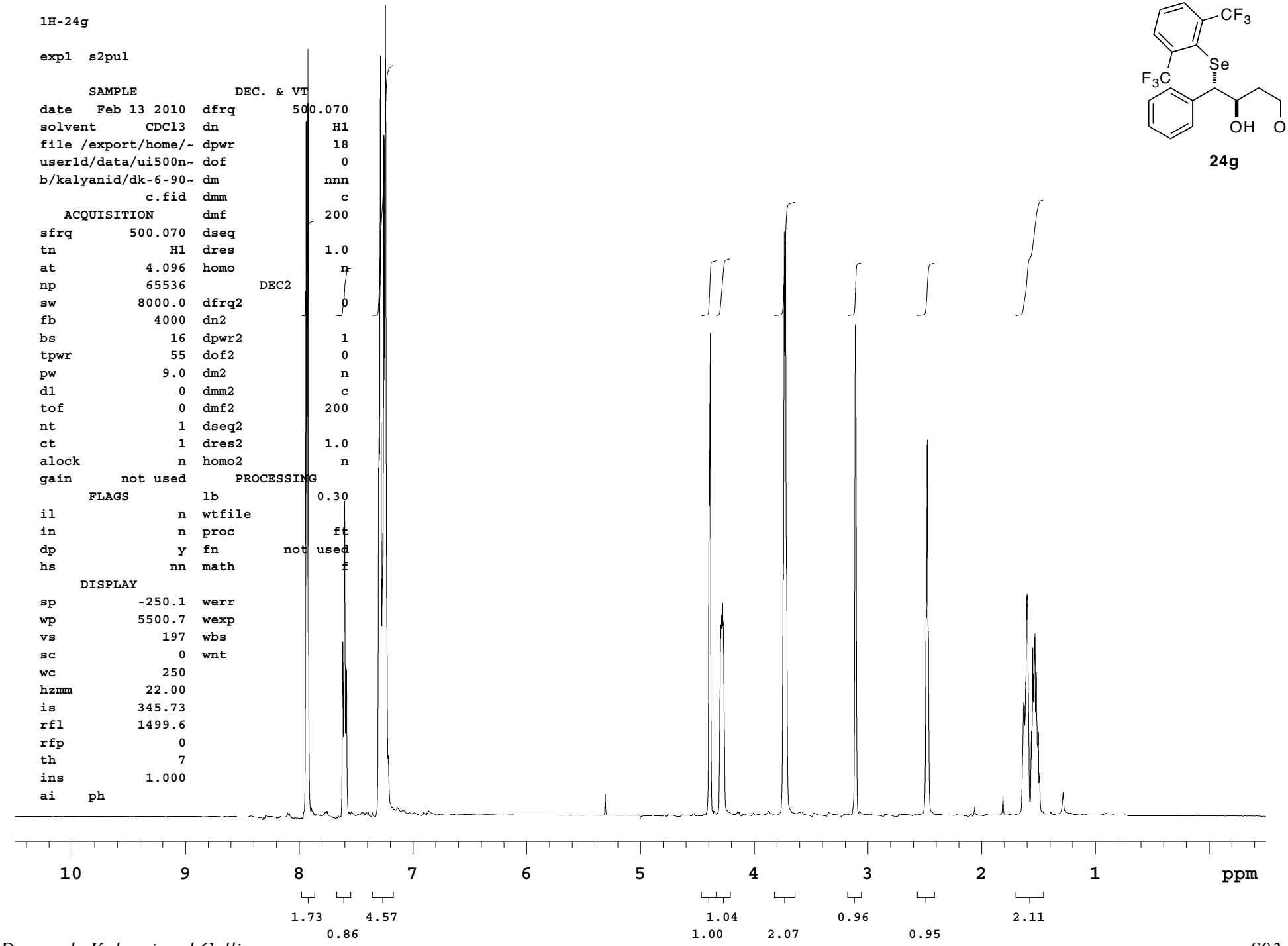
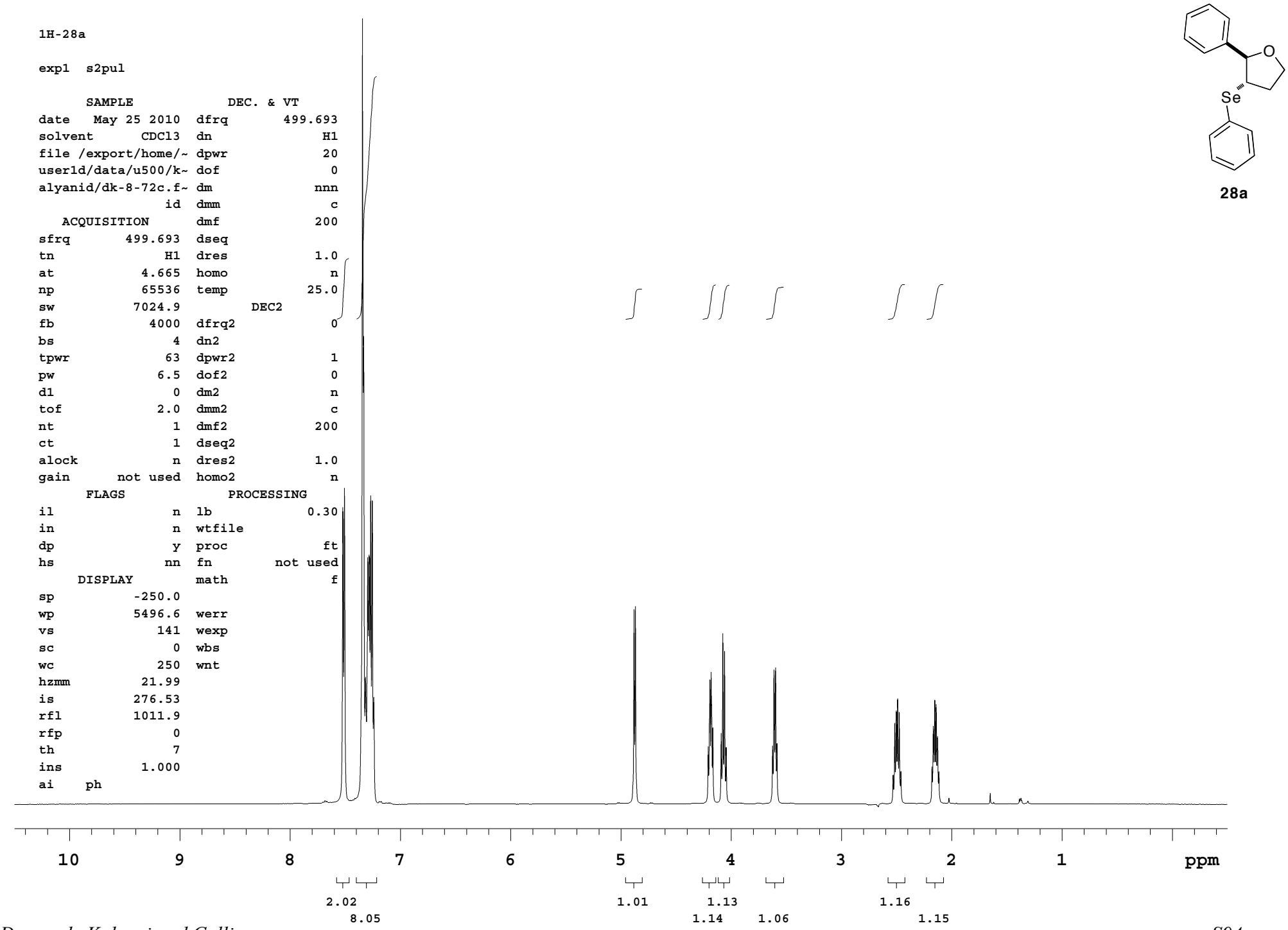
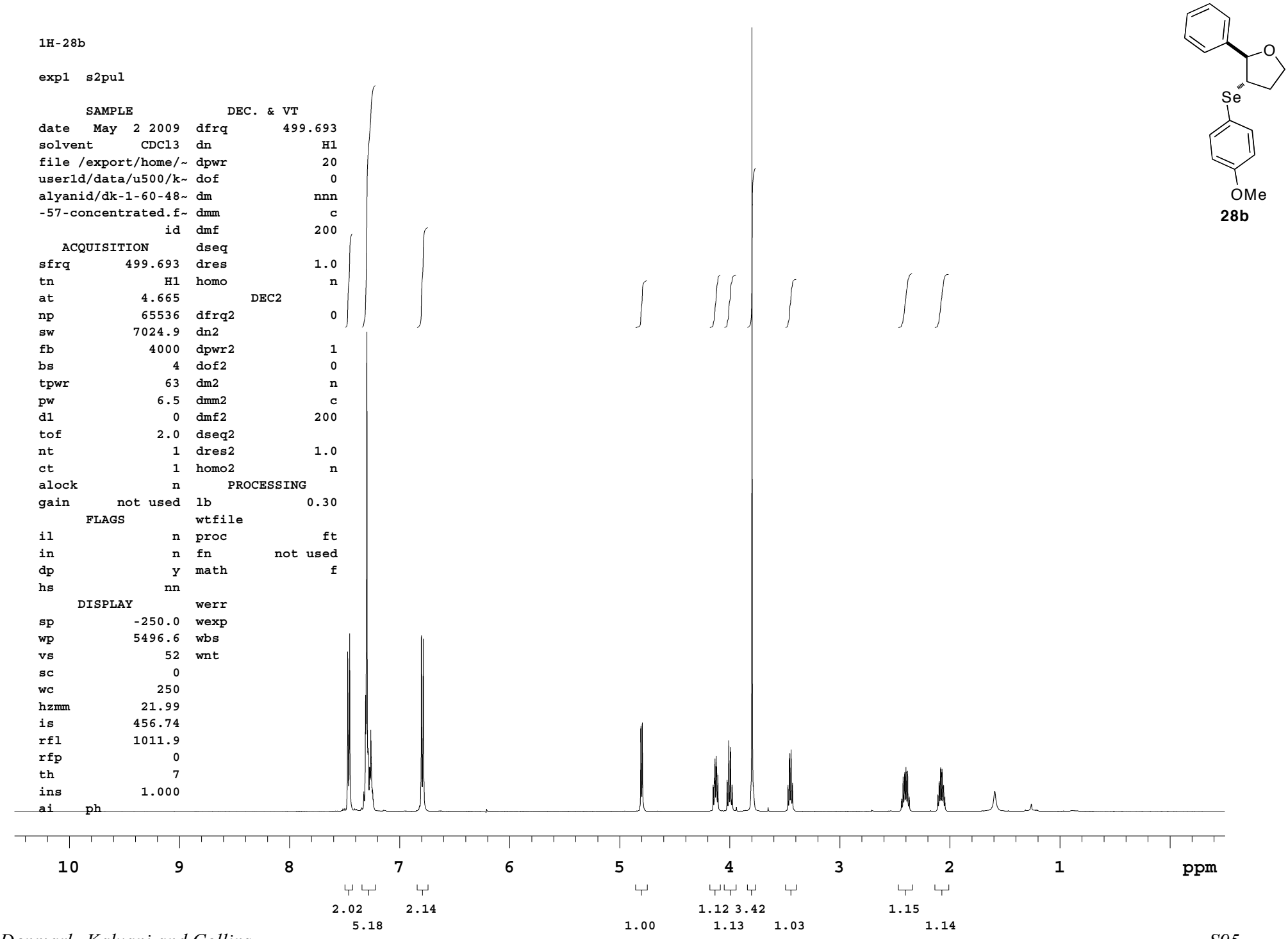
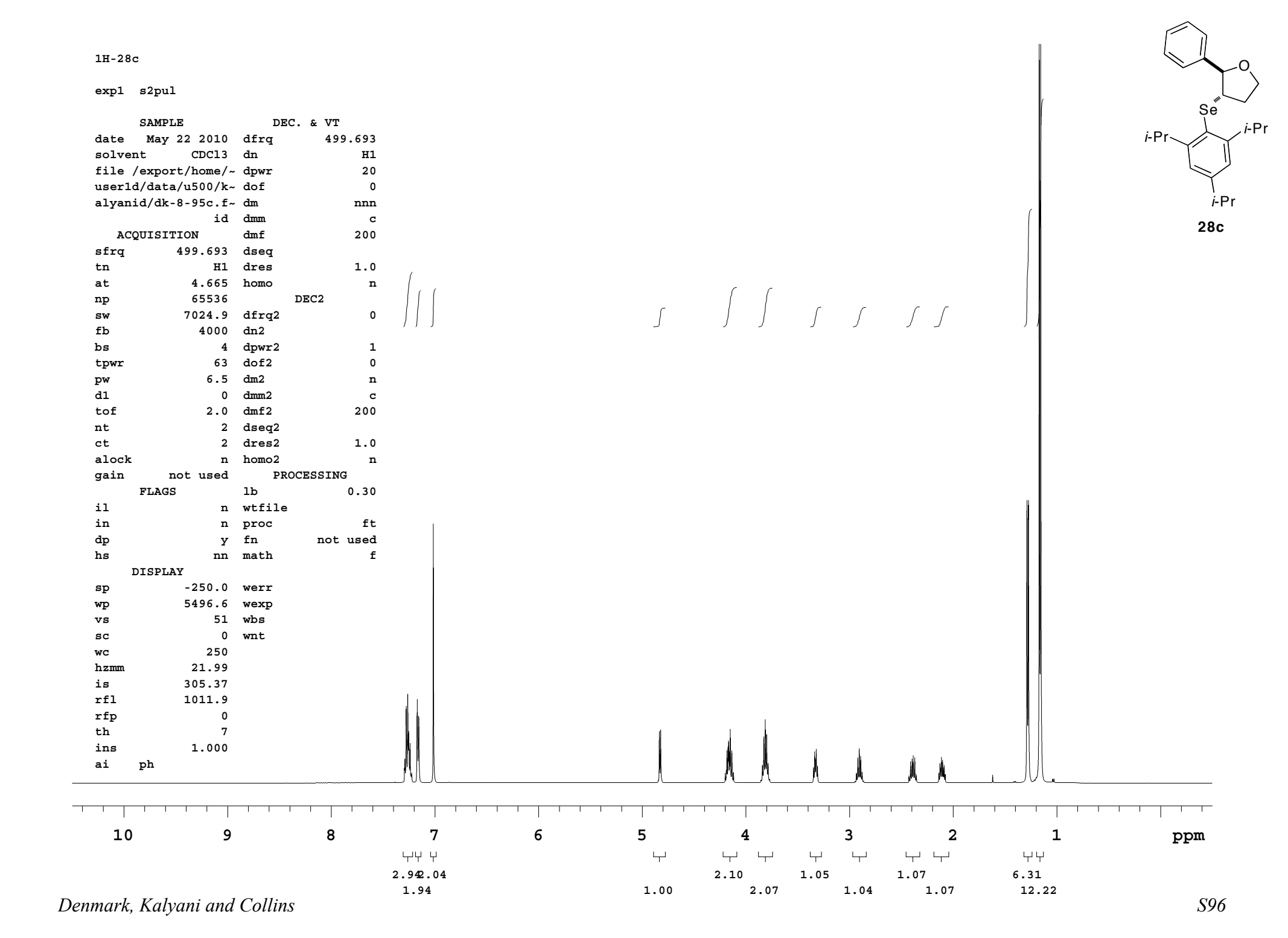
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
CF3
Se
OH
OH
24e
10
9
8
7
6
5
4
3
2
1
ppm
0.85
6.44
0.90
1.02
1.00
2.07
0.91
0.91
1.05
1.11

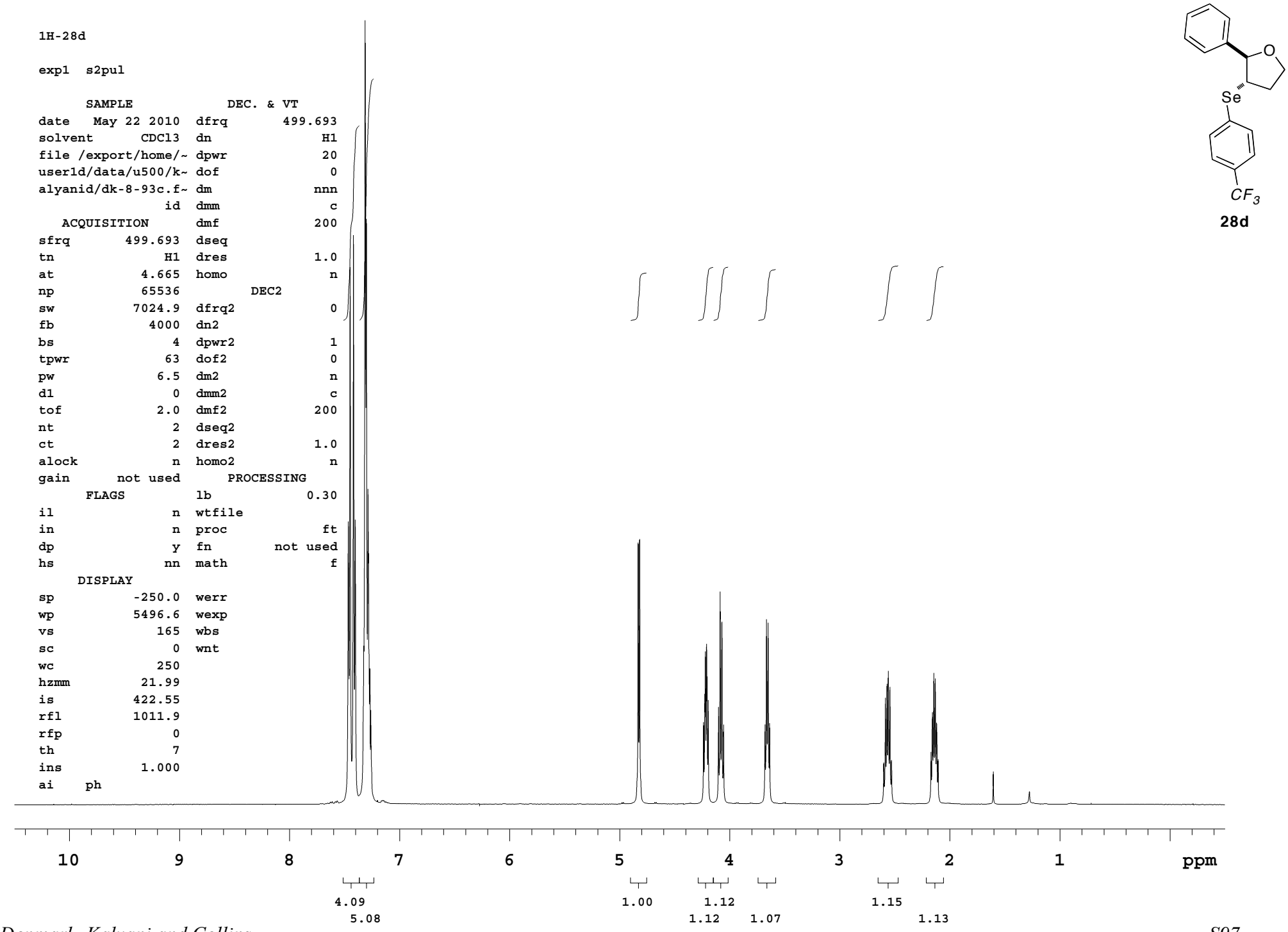

1H-24f
exp1 s2pul
SAMPLE
date Jun 10 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-9-9c-pr~
oton.fid
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 347
sc 0
wc 250
hzmm 21.99
is 599.95
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
0.86
1.06
2.90
3.88
1.00
1.01
2.04
1.00
0.96
1.02
1.05
NO2
Se
OH
OH
24f

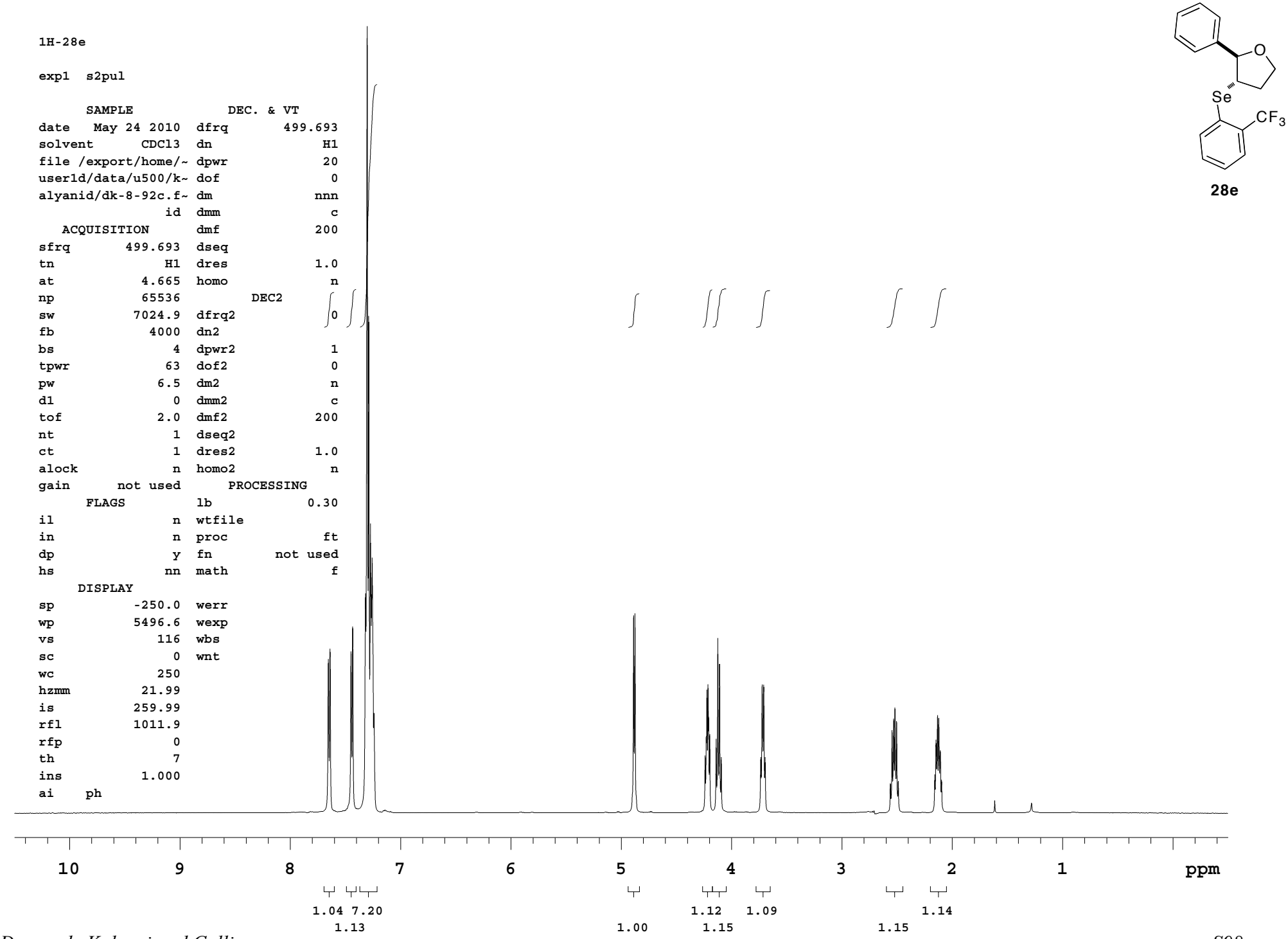

1H-24g
exp1 s2pul
SAMPLE
date Feb 13 2010
solvent CDCl3
file /export/home/~
user1d/data/ui500n~
b/kalyanid/dk-6-90~
c.fid
ACQUISITION
sfrq 500.070
tn H1
at 4.096
np 65536
sw 8000.0
fb 4000
bs 16
tpwr 55
pw 9.0
d1 0
tof 0
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5500.7
vs 197
sc 0
wc 250
hzmm 22.00
is 345.73
rfl 1499.6
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 500.070
dn H1
dpwr 18
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
CF3
F3C
Se
OH
OH
24g
10
9
8
7
6
5
4
3
2
1
ppm
1.73
0.86
4.57
1.04
1.00
2.07
0.96
0.95
2.11

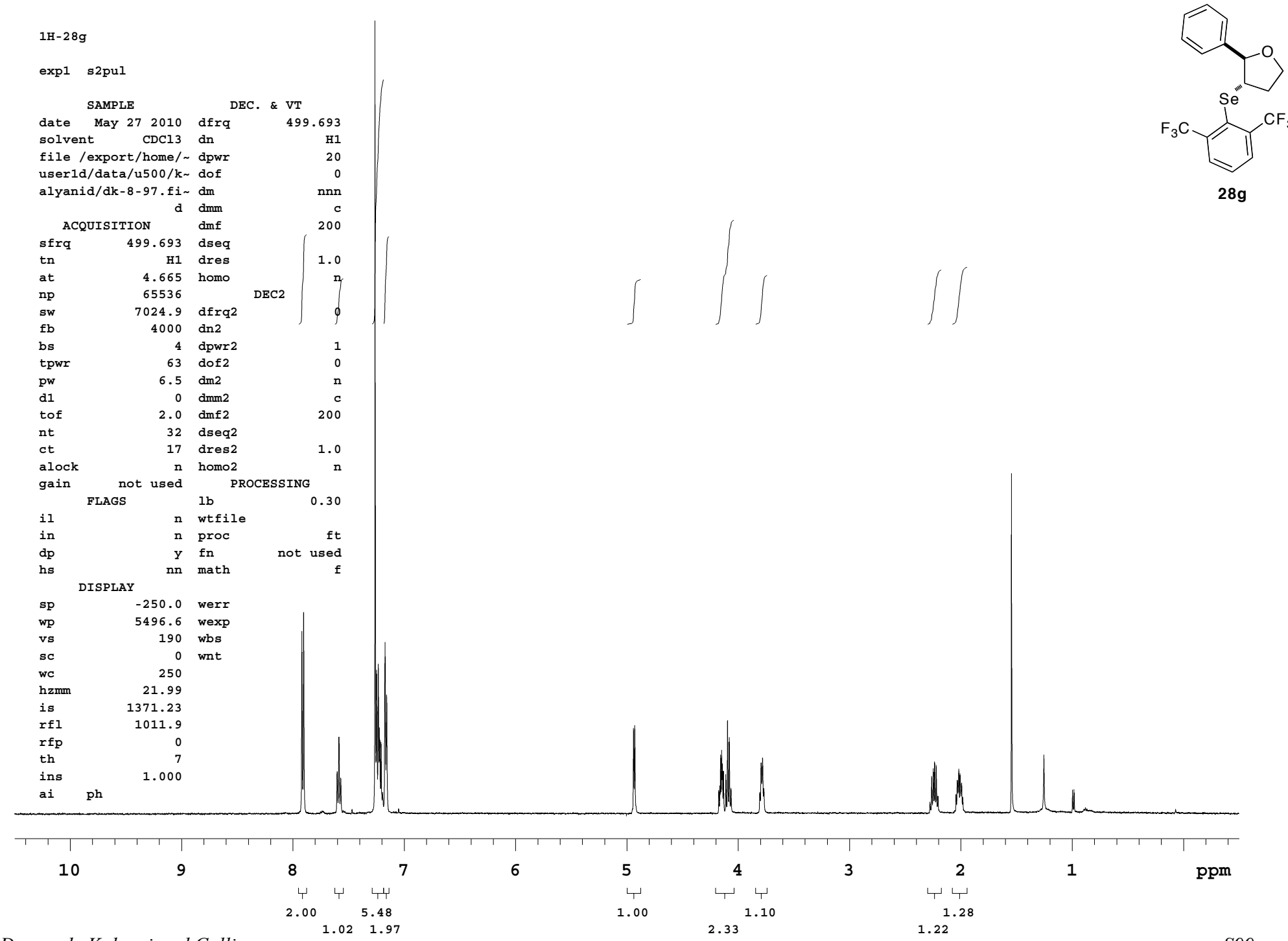

1H-28a
exp1 s2pul
SAMPLE
date May 25 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-72c.f~
id
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 141
sc 0
wc 250
hzmm 21.99
is 276.53
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
2.02
8.05
1.01
1.13
1.14
1.06
1.16
1.15
O
Se
28a

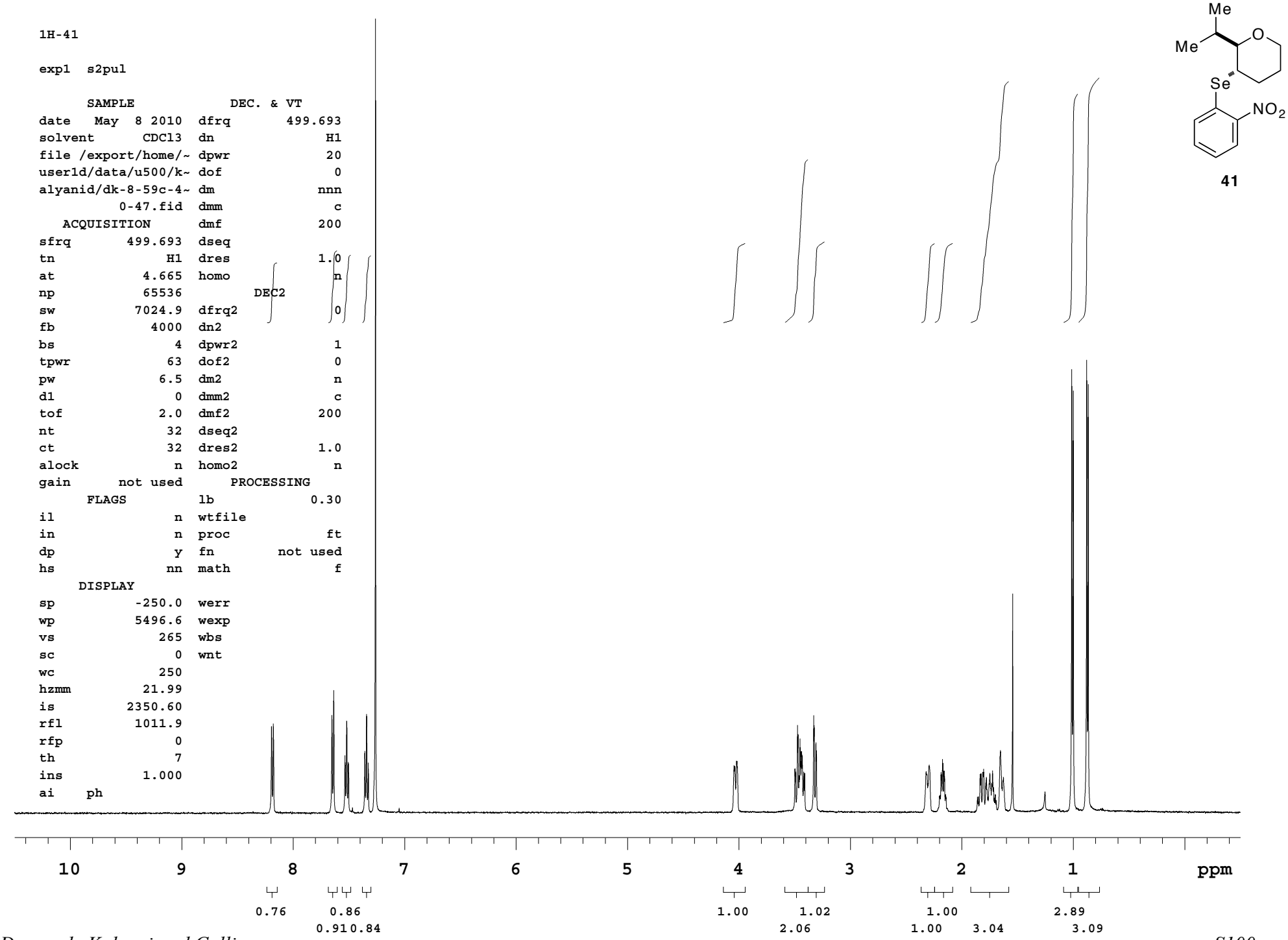

1H-28b
exp1 s2pul
SAMPLE
date May 2 2009
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-1-60-48~
-57-concentrated.f~
id
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 52
sc 0
wc 250
hzmm 21.99
is 456.74
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
2.02
5.18
2.14
1.00
1.12
1.13
3.42
1.03
1.15
1.14
Se
O
OMe
28b


1H-28c
exp1 s2pul
SAMPLE
date May 22 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-95c.f~
id
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 2
ct 2
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 51
sc 0
wc 250
hzmm 21.99
is 305.37
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Se
O
i-Pr
i-Pr
i-Pr
28c
10
9
8
7
6
5
4
3
2
1
ppm
2.94
2.04
1.94
1.00
2.10
2.07
1.05
1.04
1.07
1.07
6.31
12.22


1H-28d
exp1 s2pul
SAMPLE
date May 22 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-93c.f~
id
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 2
ct 2
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 165
sc 0
wc 250
hzmm 21.99
is 422.55
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
4.09
5.08
1.00
1.12
1.12
1.07
1.15
1.13
O
Se
CF3
28d


1H-28e
exp1 s2pul
SAMPLE
date May 24 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-92c.f~
id
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 116
sc 0
wc 250
hzmm 21.99
is 259.99
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
1.04
7.20
1.13
1.00
1.12
1.09
1.15
1.15
1.14
O
Se
CF3
28e

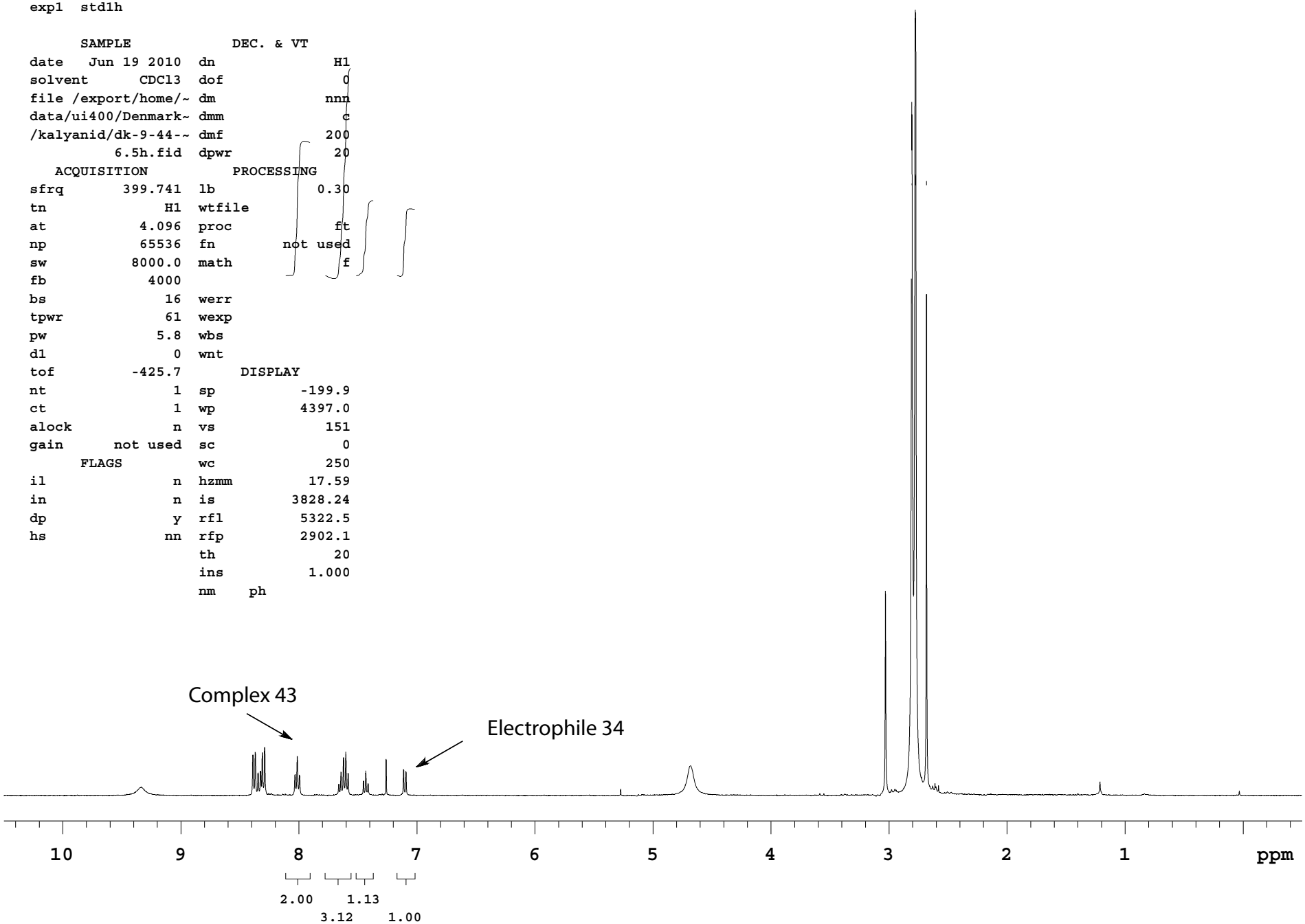

1H-28g
exp1 s2pul
SAMPLE
date May 27 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-97.fi~
d
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 32
ct 17
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 190
sc 0
wc 250
hzmm 21.99
is 1371.23
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.02
5.48
1.97
1.00
2.33
1.10
1.22
1.28
O
Se
F3C
CF3
28g

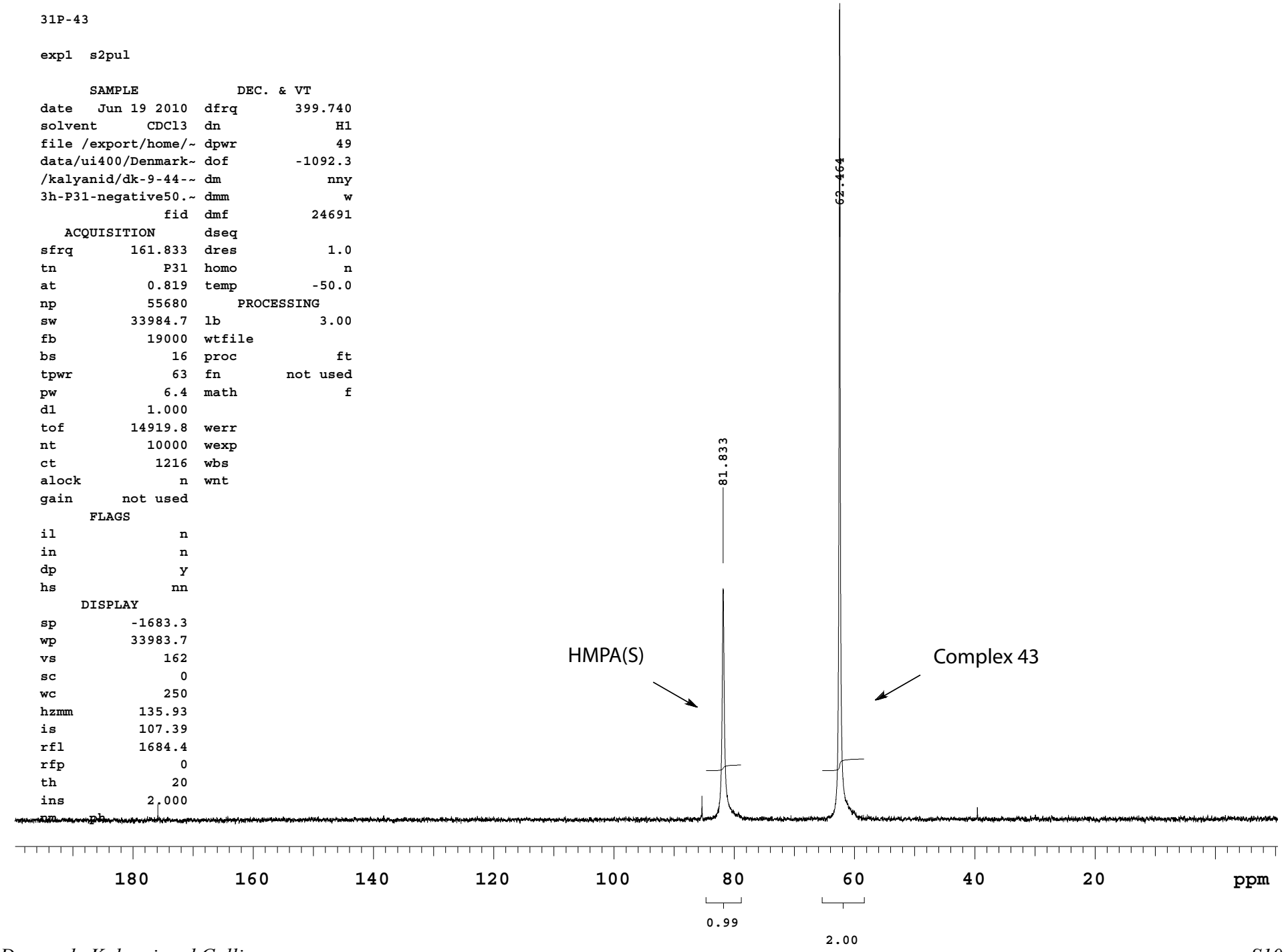

1H-41
exp1 s2pul
SAMPLE
date May 8 2010
solvent CDCl3
file /export/home/~
user1d/data/u500/k~
alyanid/dk-8-59c-4~
0-47.fid
ACQUISITION
sfrq 499.693
tn H1
at 4.665
np 65536
sw 7024.9
fb 4000
bs 4
tpwr 63
pw 6.5
d1 0
tof 2.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5496.6
vs 265
sc 0
wc 250
hzmm 21.99
is 2350.60
rfl 1011.9
rfp 0
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 499.693
dn H1
dpwr 20
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Me
Me
O
Se
NO2
41
10
9
8
7
6
5
4
3
2
1
ppm
0.76
0.86
0.91
0.84
1.00
1.02
2.06
1.00
1.00
3.04
2.89
3.09

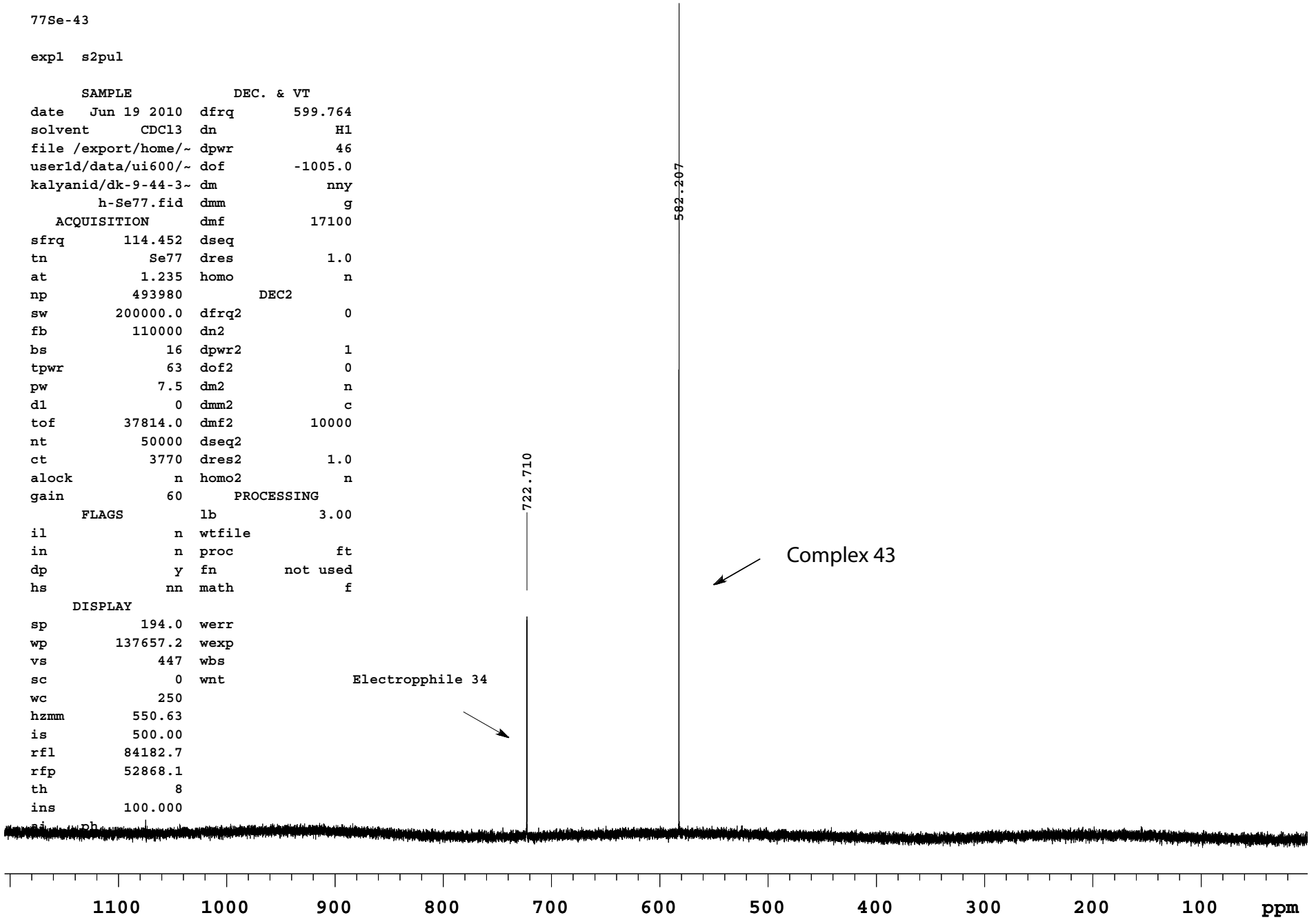
1H-43

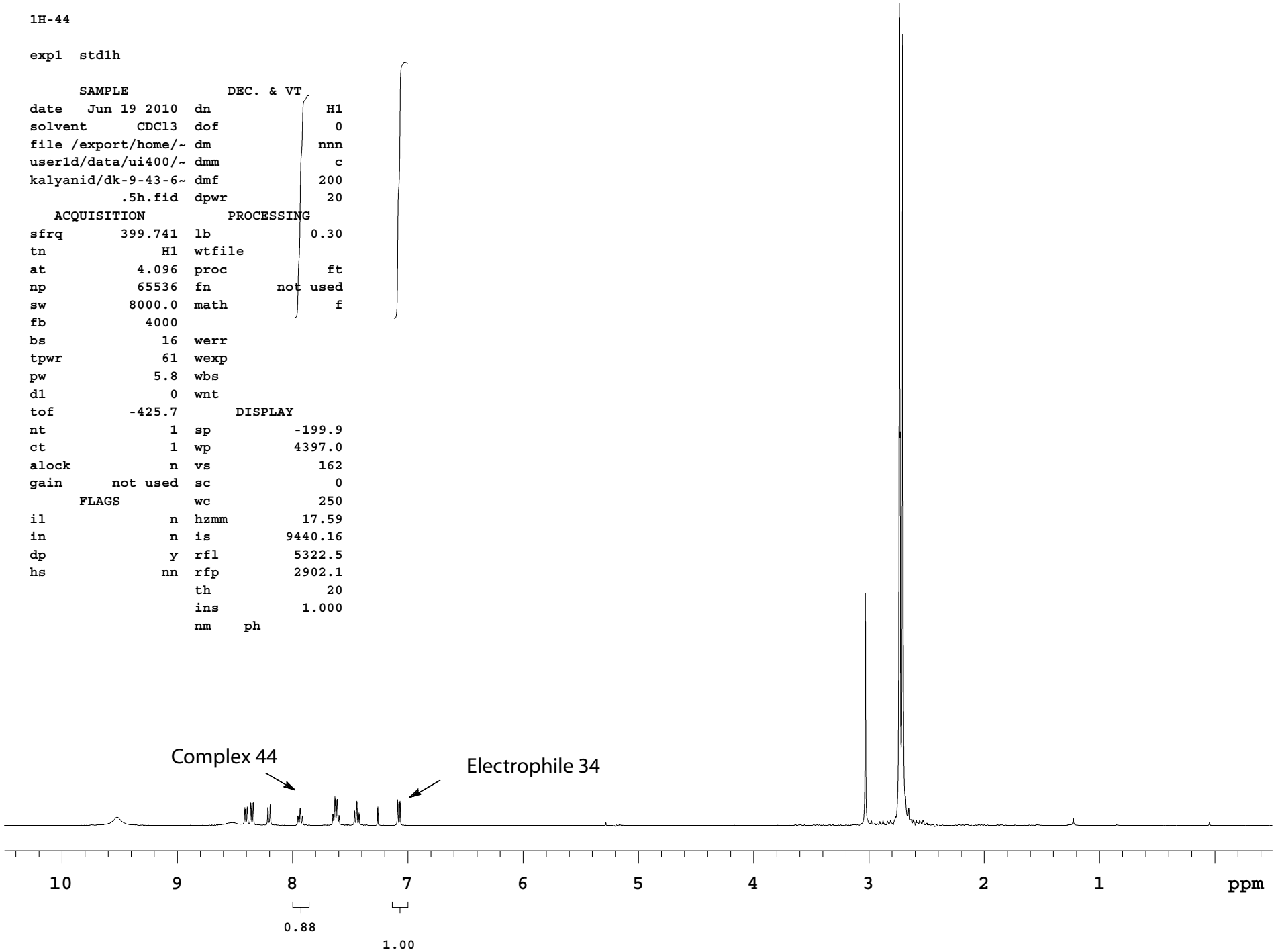
exp1 std1h

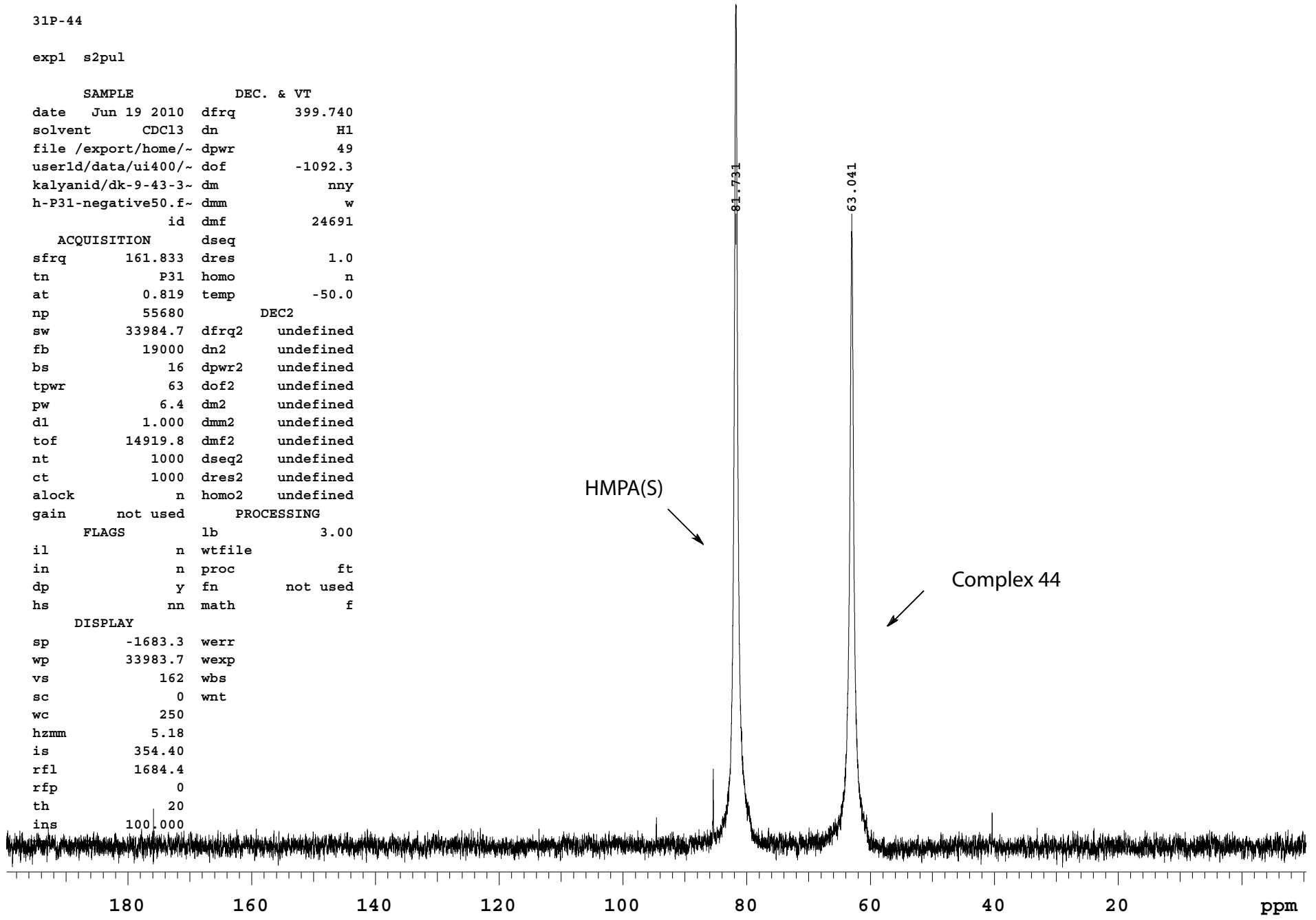
SAMPLE		DEC. & VT	
date	Jun 19 2010	dn	H1
solvent	CDCl3	dof	0
file	/export/home/~	dm	nnn
data/ui400/Denmark~		dmm	c
/kalyanid/dk-9-44--~		dmf	200
	6.5h.fid	dpwr	20
ACQUISITION		PROCESSING	
sfrq	399.741	lb	0.30
tn	H1	wtfile	
at	4.096	proc	ft
np	65536	fn	not used
sw	8000.0	math	f
fb	4000		
bs	16	werr	
tpwr	61	wexp	
pw	5.8	wbs	
d1	0	wnt	
tof	-425.7	DISPLAY	
nt	1	sp	-199.9
ct	1	wp	4397.0
alock	n	vs	151
gain	not used	sc	0
FLAGS		wc	250
il	n	hzmm	17.59
in	n	is	3828.24
dp	y	rfl	5322.5
hs	nn	rfp	2902.1
		th	20
		ins	1.000
		nm	ph




31P-43
exp1 s2pul
SAMPLE
date Jun 19 2010
solvent CDCl3
file /export/home/~
data/ui400/Denmark~
/kalyanid/dk-9-44-~
3h-P31-negative50.~
fid
ACQUISITION
sfrq 161.833
tn P31
at 0.819
np 55680
sw 33984.7
fb 19000
bs 16
tpwr 63
pw 6.4
d1 1.000
tof 14919.8
nt 10000
ct 1216
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1683.3
wp 33983.7
vs 162
sc 0
wc 250
hzmm 135.93
is 107.39
rfl 1684.4
rfp 0
th 20
ins 2.000
DEC. & VT
dfrq 399.740
dn H1
dpwr 49
dof -1092.3
dm nny
dmm w
dmf 24691
dseq
dres 1.0
homo n
temp -50.0
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
81.833
62.464
HMPA(S)
Complex 43
180
160
140
120
100
80
60
40
20
ppm
0.99
2.00


77Se-43
exp1 s2pul
SAMPLE
date Jun 19 2010
solvent CDCl3
file /export/home/~
user1d/data/ui600/~
kalyanid/dk-9-44-3~
h-Se77.fid
ACQUISITION
sfrq 114.452
tn Se77
at 1.235
np 493980
sw 200000.0
fb 110000
bs 16
tpwr 63
pw 7.5
d1 0
tof 37814.0
nt 50000
ct 3770
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 194.0
wp 137657.2
vs 447
sc 0
wc 250
hzmm 550.63
is 500.00
rfl 84182.7
rfp 52868.1
th 8
ins 100.000
DEC. & VT
dfrq 599.764
dn H1
dpwr 46
dof -1005.0
dm nny
dmm g
dmf 17100
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
582.207
722.710
Complex 43
Electropphile 34
1100
1000
900
800
700
600
500
400
300
200
100
ppm

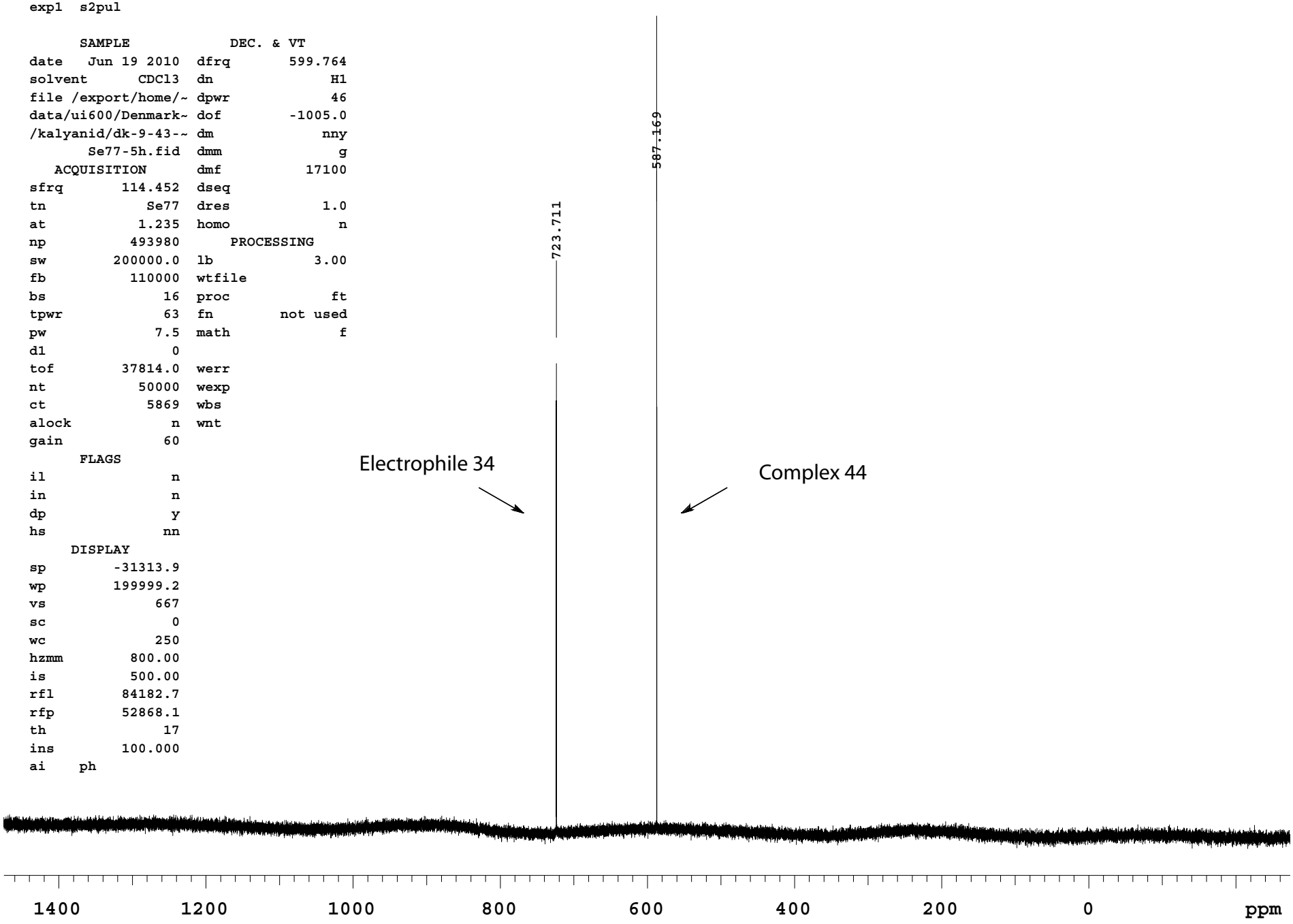

1H-44
exp1 std1h
SAMPLE
date Jun 19 2010
solvent CDCl3
file /export/home/~
user1d/data/ui400/~
kalyanid/dk-9-43-6~
.5h.fid
ACQUISITION
sfrq 399.741
tn H1
at 4.096
np 65536
sw 8000.0
fb 4000
bs 16
tpwr 61
pw 5.8
d1 0
tof -425.7
nt 1
ct 1
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 20
PROCESSING
lb 0.30
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp -199.9
wp 4397.0
vs 162
sc 0
wc 250
hzmm 17.59
is 9440.16
rfl 5322.5
rfp 2902.1
th 20
ins 1.000
nm ph
Complex 44
Electrophile 34
10
9
8
7
6
5
4
3
2
1
ppm
0.88
1.00


31P-44
exp1 s2pul
SAMPLE
date Jun 19 2010
solvent CDCl3
file /export/home/~
user1d/data/ui400/~
kalyanid/dk-9-43-3~
h-P31-negative50.f~
id
ACQUISITION
sfrq 161.833
tn P31
at 0.819
np 55680
sw 33984.7
fb 19000
bs 16
tpwr 63
pw 6.4
d1 1.000
tof 14919.8
nt 1000
ct 1000
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1683.3
wp 33983.7
vs 162
sc 0
wc 250
hzmm 5.18
is 354.40
rfl 1684.4
rfp 0
th 20
ins 100.000
DEC. & VT
dfrq 399.740
dn H1
dpwr 49
dof -1092.3
dm nny
dmm w
dmf 24691
dseq
dres 1.0
homo n
temp -50.0
DEC2
dfrq2 undefined
dn2 undefined
dpwr2 undefined
dof2 undefined
dm2 undefined
dmm2 undefined
dmf2 undefined
dseq2 undefined
dres2 undefined
homo2 undefined
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
81.731
63.041
HMPA(S)
Complex 44
180
160
140
120
100
80
60
40
20
ppm

77Se-44

exp1 s2pul

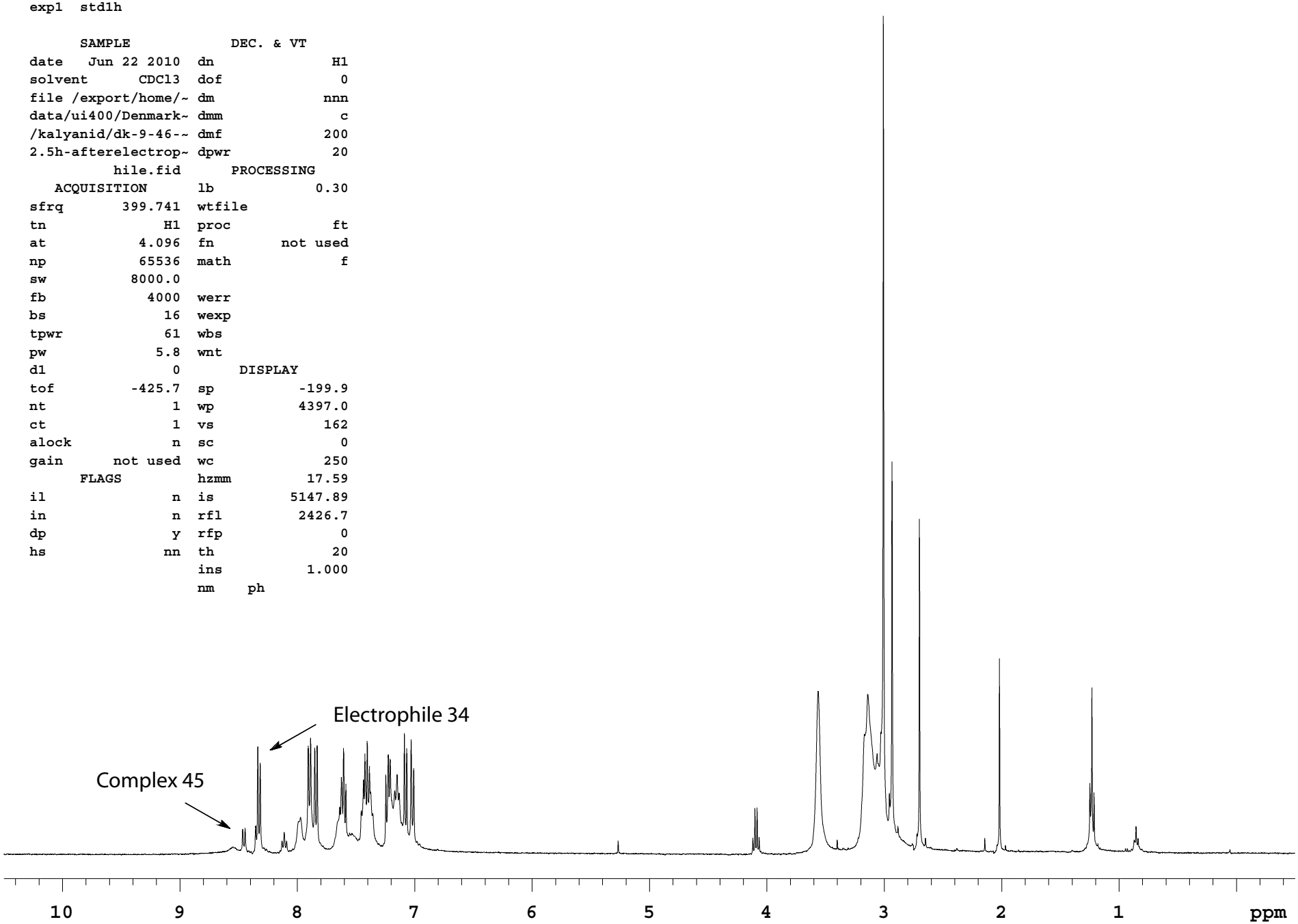
SAMPLE		DEC. & VT	
date	Jun 19 2010	dfrq	599.764
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	46
data/ui600/Denmark~		dof	-1005.0
/kalyanid/dk-9-43--~		dm	nny
	Se77-5h.fid	dmm	g
ACQUISITION		dmf	17100
sfrq	114.452	dseq	
tn	Se77	dres	1.0
at	1.235	homo	n
np	493980	PROCESSING	
sw	200000.0	lb	3.00
fb	110000	wtfile	
bs	16	proc	ft
tpwr	63	fn	not used
pw	7.5	math	f
d1	0		
tof	37814.0	werr	
nt	50000	wexp	
ct	5869	wbs	
alock	n	wnt	
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-31313.9		
wp	199999.2		
vs	667		
sc	0		
wc	250		
hzmm	800.00		
is	500.00		
rfl	84182.7		
rfp	52868.1		
th	17		
ins	100.000		
ai	ph		

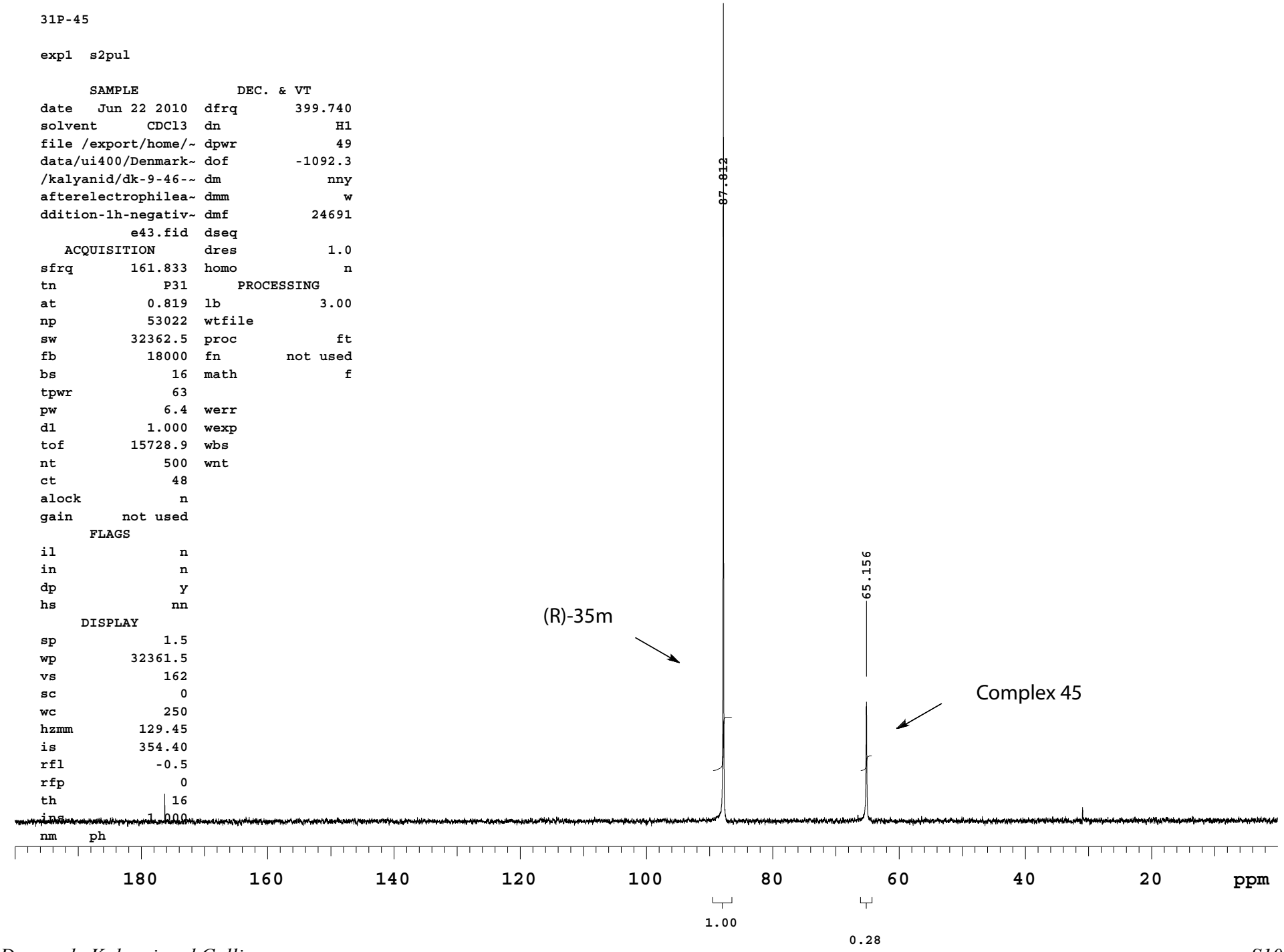


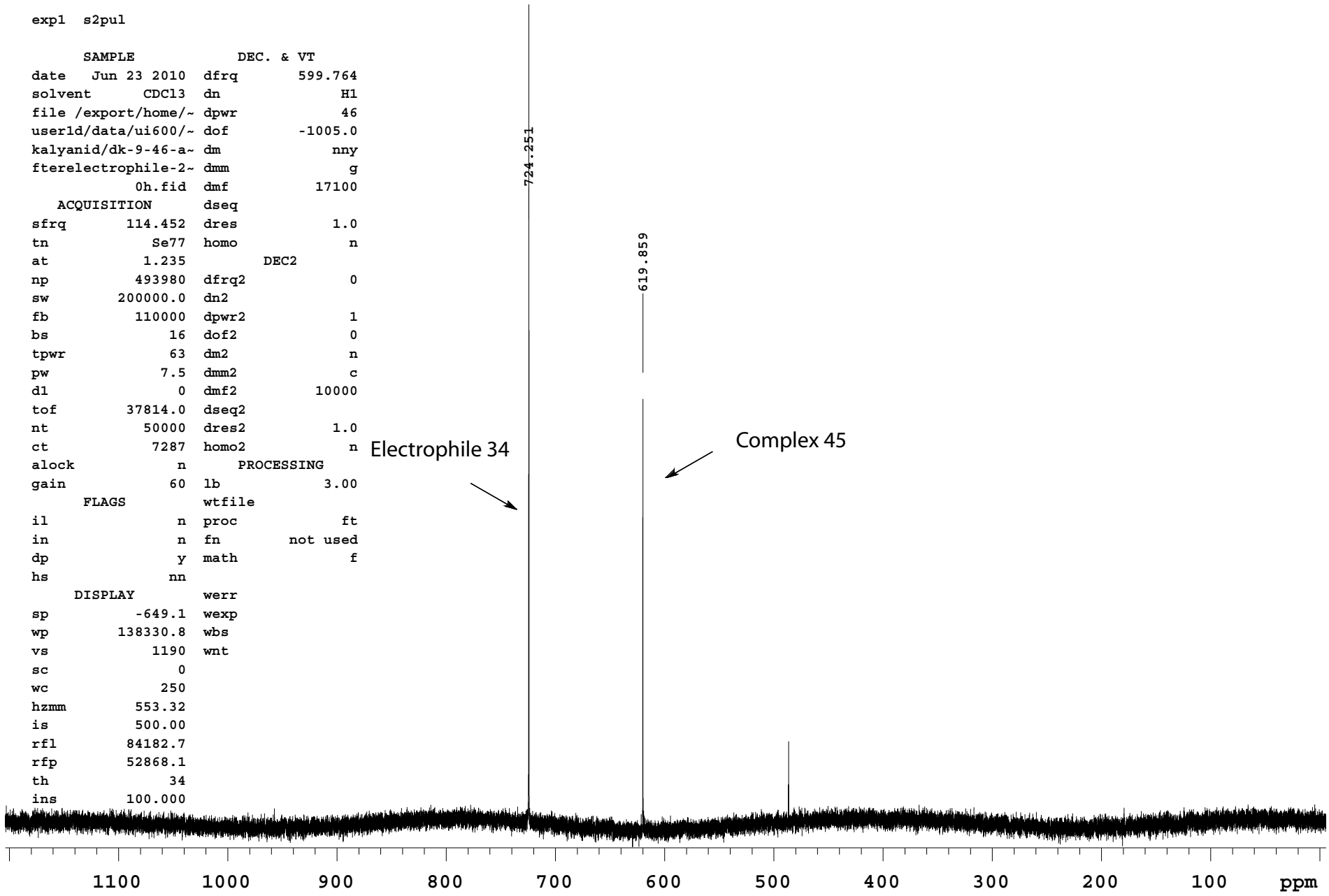
1H-45

exp1 std1h

SAMPLE		DEC. & VT	
date	Jun 22 2010	dn	H1
solvent	CDCl3	dof	0
file	/export/home/~	dm	nnn
data/ui400/Denmark~		dmm	c
/kalyanid/dk-9-46-~		dmf	200
2.5h-afterelectrop~		dpwr	20
hile.fid		PROCESSING	
ACQUISITION		lb	0.30
sfrq	399.741	wtfile	
tn	H1	proc	ft
at	4.096	fn	not used
np	65536	math	f
sw	8000.0		
fb	4000	werr	
bs	16	wexp	
tpwr	61	wbs	
pw	5.8	wnt	
d1	0	DISPLAY	
tof	-425.7	sp	-199.9
nt	1	wp	4397.0
ct	1	vs	162
alock	n	sc	0
gain	not used	wc	250
FLAGS		hzmm	17.59
il	n	is	5147.89
in	n	rfl	2426.7
dp	y	rfp	0
hs	nn	th	20
		ins	1.000
		nm	ph




31P-45
exp1 s2pul
SAMPLE
date Jun 22 2010
solvent CDCl3
file /export/home/~
data/ui400/Denmark~
/kalyanid/dk-9-46--~
afterelectrophilea~
ddition-1h-negativ~
e43.fid
ACQUISITION
sfrq 161.833
tn P31
at 0.819
np 53022
sw 32362.5
fb 18000
bs 16
tpwr 63
pw 6.4
d1 1.000
tof 15728.9
nt 500
ct 48
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 1.5
wp 32361.5
vs 162
sc 0
wc 250
hzmm 129.45
is 354.40
rfl -0.5
rfp 0
th 16
ins 1.000
nm ph
DEC. & VT
dfrq 399.740
dn H1
dpwr 49
dof -1092.3
dm nny
dmm w
dmf 24691
dseq
dres 1.0
homo n
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
87.812
65.156
(R)-35m
Complex 45
180
160
140
120
100
80
60
40
20
ppm
1.00
0.28


77Se-45.ps
exp1 s2pul
SAMPLE
date Jun 23 2010
solvent CDCl3
file /export/home/~
user1d/data/ui600/~
kalyanid/dk-9-46-a~
fterelectrophile-2~
0h.fid
ACQUISITION
sfrq 114.452
tn Se77
at 1.235
np 493980
sw 200000.0
fb 110000
bs 16
tpwr 63
pw 7.5
d1 0
tof 37814.0
nt 50000
ct 7287
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -649.1
wp 138330.8
vs 1190
sc 0
wc 250
hzmm 553.32
is 500.00
rfl 84182.7
rfp 52868.1
th 34
ins 100.000
DEC. & VT
dfrq 599.764
dn H1
dpwr 46
dof -1005.0
dm nny
dmm g
dmf 17100
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
724.251
619.859
Electrophile 34
Complex 45
1100
1000
900
800
700
600
500
400
300
200
100
ppm