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Supporting Information

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Organocatalytic Asymmetric α-Selenenylation of Aldehydes

Marcello Tiecco[1], Armando Carlone[2], Silvia Sternativo[1], Francesca Marini[1],* Giuseppe Bartoli[2], and Paolo Melchiorre[2]*

[1]Dipartimento di Chimica e Tecnologia del Farmaco,
Sezione di Chimica Organica, Università di Perugia,
06123 Perugia, Italy
e-mail: marini@unipg.it

[2]Dipartimento di Chimica Organica "A. Mangini"
Alma Mater Studiorum - Università di Bologna
viale Risorgimento, 4 - 40136 Bologna, Italy
e-mail: pm@ms.fci.unibo.it

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General Methods. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz and 100 MHz, respectively. The chemical shifts (δ) are referenced to internal standard TMS (^{1}H NMR) and to residual signals of the solvents ($CHCl_3$ - 77.0 ppm for ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad signal. Purification of reaction products was carried out by flash chromatography (FC) on silica gel (230-400 mesh) according to the method of Still.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Mass spectra were obtained from the Department of Organic Chemistry *"A. Mangini"* Mass Spectroscopy facility. Optical rotations are reported as follows: $[\alpha]^{rt}_{D}$ (*c* in g per 100 mL, solvent). All reactions were carried out in air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted.

Materials. Commercial grade reagents and solvents were used without further purification; otherwise, where necessary, they were purified as recommended.[2] Aldehyde **1a-h** were purchased from Aldrich or Alfa Aesar and used as received. Catalysts **A**,[3] **B**,[4] and **C**[5] were prepared according to literature procedure.

N-(Phenylseleno)-phthalimide **2** was purchased from Aldrich and used as received. Note that **2** is provided in 77% of purity (Technical grade) and the stoichiometry of the reaction was adjusted accordingly.

Determination of Enantiomeric Purity. Chiral HPLC analysis was performed on an Agilent 1100-series instrumentation. Daicel Chiralpak AD-H column and Daicel Chiralcel OD-H column with *i*-PrOH/hexane as the eluent were used.

HPLC traces were compared to racemic samples prepared by carrying out the reactions with racemic Proline as the catalyst.

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[1] W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

[2] W. L. F. Armarengo, D. D. Perrin, In *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, 1996.

[3] a) K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am Chem Soc.* **2000**, *122*, 4243. b) W. S. Jen, J. J. M. Wiener, D. W. C. MacMillan, *J. Am Chem Soc.* **2000**, *122*, 9874.

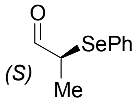
[4] M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2005**, *44*, 794.

[5] The catalyst **C** can be easily prepared by protection of the commercial available α,α -diphenylprolinol with TMSOTf. See: J. Franzén, M. Marigo, D. Fielenbach, T. C. Wabnitz, A. Kjærsgaard, K. A. Jørgensen *J. Am. Chem. Soc.* **2005**, *127*, 18296.

Determination of Absolute Configuration.

The absolute configuration of the optically active α-seleno aldehyde **3a** was determined to be (*S*) on the basis of the measured optical rotation that was compared with the literature value.[6] All other absolute configurations were assigned by analogy based on an uniform reaction mechanism.

The absolute configuration of the optically active 1,3-oxazolidinone **5** was determined to be (*R*) on the basis of the measured optical rotation that was compared with the literature value.[7]



(*S*)-**3a** (Table 1, entry 9)[6,8] **–** The reaction was carried out at −20 °C for 1 h using 10 mol% of (*S*)-5-benzyl-2,2,3,-trimethylimidazolidin-4-one dichloroacetic acid salt (**A·DCA**, 13.9 mg, 0.04 mmol) as the catalyst. To an ordinary vial equipped with a Teflon-coated stir bar and charged with catalyst **A·DCA**, 0.8 mL of CH_2Cl_2 was added. After addition of 0.6 mmol (1.5 equiv., 43 µL) of propanal **1a**, the solution was stirred for 5 minutes at −20 °C. Then *N*-(Phenylseleno)-phthalimide **2** (0.4 mmol, 157 mg) was added in one portion, the vial was capped with a rubber stopper and stirring was continued for 1 h, after which the reaction mixture was directly charged on column chromatography. The ee of the crude reaction mixture was determined by HPLC analysis to be 94%. The title compound was isolated as a yellowish oil in 99% yield (84 mg) after column chromatography (hexane/AcOEt = 92/8) with a slight racemization (80% ee).[8] The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_R = 6.2 min; τ_S = 6.7 min). $[\alpha]^{rt}_D$= - 205.6 (*c* = 1.02, CH_2Cl_2, 80% ee. Lit.[6] $[\alpha]^{20}_D$= + 265-290, (*R*)-**3a**, (*c* = 1.8, CH_2Cl_2, 95% ee). HRMS: *m/z* calcd for $C_9H_{10}OSe$: 213.98969; found: 213.9897. ^1H NMR: δ = 1.47 (d, *J* = 6.8, 3H), 3.72 (dq, *J* = 2.8, 6.8 Hz, 1H), 7.26-7.38 (m, 3H), 7.50-7.55 (m, 2H), 9.45 (d, *J* = 2.8, 1H); ^{13}C NMR: δ = 13.4 (CH_3), 45.6 (CH), 125.7 (C), 128.9 (CH), 129.3 (CH), 136.1 (C), 193.5 (C).

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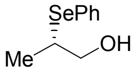
[6] a) R. G. Shea, J. N. Fitzner, J. E. Fankhauser, A. Spaltenstein, P. A. Carpino, R. M. Peevey, D. V. Pratt, B. J. Tenge, P. B. Hopkins, *J. Org. Chem*. **1986**, *51*, 5243; b) W. Wang, J. Wang, H. Lao, *Org. Lett.* **2004**, *6*, 2817.

[7] M. Feroci, A. Inesi, L. Palombi, L. Rossi, G. Sotgiu *J. Org. Chem*., **2001**, *66*, 6185.

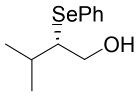
[8] The authors in reference 6 stated that the α-seleno aldehyde **3a** was prone to racemization and all the attempts to isolate the title compound following standard procedures resulted in a slight racemization.

Experimental Procedures

General Procedure for the Organocatalytic Asymmetric α-Selenenylation of Aldehydes. All the reactions were carried out in undistilled solvents without any precautions to exclude water. In an ordinary vial equipped with a Teflon-coated stir bar, catalyst **B** (0.02 mmol, 12.0 mg, 5 mol%) and *p*$NO_2C_4H_4CO_2H$ (0.02 mmol, 3.3 mg, 5 mol%) were dissolved in 0.8 mL of toluene (0.5 M). After addition of 0.6 mmol (1.5 equiv.) of the aldehyde **1**, the solution was stirred for 10 minutes at the indicated temperature (generally 0 °C). Then *N*-(Phenylseleno)-phthalimide **2** (0.4 mmol, 77% purity, 157 mg) was added in one portion, the vial was capped with a rubber stopper and stirring was continued for the indicated time (generally 40 h). Upon completion of the reaction, the mixture was cooled to 0 °C and diluted with 1.6 mL of MeOH; solid $NaBH_4$ (0.7 mmol, 1.75 equiv) was added in one portion. Frothing occurs but is readily controllable through magnetic stirring of the solution. After 30 minutes the mixture was quenched with few drops of water. Brine (5 mL) was added and the resulting mixture extracted with AcOEt (3 × 10 mL). The combined organics were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (FC) to yield the desired α-seleno alcohol derivatives **4**.

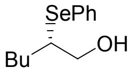


(*S*)-**4a** (Table 2, entry 1) **–** The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 95/5) in 99% yield and 95% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_S = 9.6 min; τ_R = 11.2 min). $[\alpha]^{rt}_D$= + 4.2 (c = 1.1, $CHCl_3$, 95% ee). HRMS: m/z calcd for $C_9H_{12}OSe$: 216.00534; found: 216.0053. ^1H NMR: δ = 1.41 (d, J = 7.2, 3H), 2.12 (br, OH), 3.33-3.41 (m, 1H), 3.48-3.63 (m, 2H), 7.26-7.32 (m, 3H), 7.55-7.59 (m, 2H); ^{13}C NMR: δ = 18.1 (CH_3), 43.1 (CH), 60.0 (CH_2), 127.2 (C), 128.0(CH), 129.1 (CH), 135.5 (C).



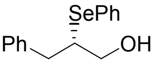
(*S*)-**4b** (Table 2, entry 2)- The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 89% yield and 99% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_{minor} = 7.5 min; τ_{major} = 8.5 min). $[\alpha]^{rt}_{D}$= - 11.6 (*c* = 1.5, $CHCl_3$, 98.5% ee). HRMS: *m/z* calcd for $C_{11}H_{16}OSe$: 244.03664; found: 244.0366. ^{1}H NMR: δ = 1.06 (d, *J* = 6.8, 3H), 1.08 (d, *J* = 6.8, 3H), 1.98-2.09 (m, 1H), 2.25 (br, OH), 3.14-3.20 (m, 1H), 3.63-3.71 (m, 1H), 3.71-3.78 (m, 1H), 7.25-7.28 (m, 3H), 7.56-7.59 (m, 2H); ^{13}C NMR: δ = 20.5 (CH_3), 21.1 (CH_3), 29.9 (CH), 60.0 (CH), 63.3 (CH_2), 127.5 (CH), 129.1 (CH), 134.5 (C).

(*S*)-**4c** (Table 2, entry 4)- The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 84% yield and 97% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_S = 8.9 min; τ_R = 9.4 min). $[\alpha]^{rt}_{D}$= - 23.5 (*c* = 1.04, $CHCl_3$, 97% ee). HRMS: *m/z* calcd for $C_{10}H_{14}OSe$: 230.02099; found: 230.0211. ^{1}H NMR: δ = 1.09 (t, *J* = 7.2, 3H), 1.56-1.78 (m, 2H), 2.17 (dd, *J* = 5.6, 7.6, OH), 3.14-3.20 (m, 1H), 3.51-3.58 (m, 1H), 3.61-3.68 (m, 1H), 7.25-7.32 (m, 3H), 7.55-7.59 (m, 2H); ^{13}C NMR: δ = 12.5 (CH_3), 24.8 (CH_2), 52.4 (CH), 64.0 (CH_2), 127.4 (C), 127.9 (CH), 129.1 (CH), 135.4 (C).

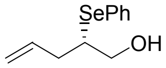


(*S*)-**4d** (Table 2, entry 5)- The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 99% yield and 98% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_S = 7.5 min; τ_R = 7.9 min). $[\alpha]^{rt}_{D}$= - 24.5 (*c* = 1.1,

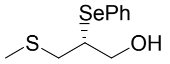
$CHCl_3$, 98% ee). HRMS: *m/z* calcd for $C_{12}H_{18}OSe$: 258.05228; found: 258.0523. ^{1}H NMR: δ = 0.90 (t, *J* = 7.2, 3H), 1.25-1.70 (m, 6H), 2.21 (br, OH), 3.20-3.26 (m, 1H), 3.49-3.56 (m, 1H), 3.59-3.65 (m, 1H), 7.25–7.31 (m, 3H), 7.55-7.58 (m, 2H); ^{13}C NMR: δ = 13.9 (CH_3), 22.5 (CH_2), 29.9 (CH_2), 31.4(CH_2), 50.6 (CH), 64.3 (CH_2), 127.4 (C), 127.4 (C), 127.9 (CH), 129.1 (CH), 135.4 (C).



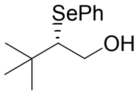
(*S*)-**4e** (Table 2, entry 6)**–** The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 81% yield and 97.2% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_R = 11.3 min; τ_S = 12.5 min). $[\alpha]^{rt}_{D}$= - 14.9 (*c* = 1.4, $CHCl_3$, 97% ee). HRMS: *m/z* calcd for $C_{15}H_{16}OSe$: 292.03664; found: 292.0365. ^{1}H NMR: δ = 2.14 (br, OH), 2.96-3.06 (m, 2H), 3.47-3.65 (m, 3H), 7.19–7.33 (m, 8H), 7.52-7.55 (m, 2H); ^{13}C NMR: δ = 38.2 (CH_2), 50.6 (CH), 63.1 (CH_2), 126.6 (CH), 127.7 (C), 128.0 (CH), 128.5 (CH), 129.1 (CH), 129.15 (CH), 135.2 (CH), 139.0 (C).



(*S*)-**4f** (Table 2, entry 7)**–** The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 91% yield and 98% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_R = 8.9 min; τ_S = 9.4 min). $[\alpha]^{rt}_{D}$= - 17.3 (*c* = 1.2, $CHCl_3$, 98% ee). HRMS: *m/z* calcd for $C_{11}H_{14}OSe$: 242.02099; found: 242.0209. ^{1}H NMR: δ = 2.11 (br, OH), 2.44-2.48 (m, 2H), 3.27-3.34 (m, 1H), 3.58 (dd, *J* = 6.0, 11.6 Hz, 1H), 3.66 (dd, *J* = 5.6, 11.6 Hz, 1H), 5.09–5.16 (m, 2H), 5.83–5.94 (m, 1H), 7.25–7.32 (m, 3H), 7.56-7.59 (m, 2H); ^{13}C NMR: δ = 36.3 (CH_2), 48.7 (CH), 63.9 (CH_2), 117.4 (CH), 127.3 (C), 128.0 (CH), 129.1 (CH), 135.4 (CH), 135.5 (C).

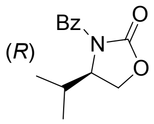


(*R*)-**4g** (Table 2, entry 8)**-** The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 94% yield and 98% ee. The ee was determined by HPLC analysis using a Chiralcel OD-H column (90/10 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_S = 9.6 min; τ_R = 11.0 min). $[\alpha]^{rt}_{D}$= + 0.7 (*c* = 2.1, $CHCl_3$, 98% ee). HRMS: *m/z* calcd for $C_{10}H_{14}OSSe$: 261.99306; found: 261.9933. ^{1}H NMR: δ = 2.12 (s, 3H), 2.29 (t, *J* = 6.4, OH), 2.81 (dd, *J* = 9.6, 13.6 Hz, 1H), 2.94 (dd, *J* = 9.6, 13.6 Hz, 1H), 3.41-3.47 (m, 1H), 3.74-3.88 (m, 2H), 7.27-7.33 (m, 3H), 7.58-7.62 (m, 2H); ^{13}C NMR: δ = 16.1 (CH_3), 36.9 (CH_2), 47.4 (CH), 63.5 (CH_2), 127.1 (C), 128.3 (CH), 129.3 (CH), 135.5 (CH).



(*S*)-**4h** (Table 2, entry 9)**-** The reaction was carried out at 0 °C for 40 h using 5 mol% of catalyst **B**·*p*NO_2PhCO_2H following the general procedure. The title compound was isolated as a colourless oil by column chromatography (DCM/Et_2O = 97/3) in 99% yield and 99% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 214, 254 nm; τ_R = 5.7 min; τ_S = 6.4 min). $[\alpha]^{rt}_{D}$= + 3.7 (*c* = 1.0, $CHCl_3$, 99% ee). HRMS: *m/z* calcd for $C_{12}H_{18}OSe$: 258.05228; found: 258.0523. ^{1}H NMR: δ = 1.09 (s, 9H), 2.42 (br, OH), 3.13 (dd, *J* = 4.4, 8.8 Hz, 1H), 3.65 (dd, *J* = 8.8, 12.0 Hz, 1H), 3.83-3.92 (m, 1H), 7.23-7.28 (m, 3H), 7.58-7.62 (m, 2H); ^{13}C NMR: δ = 28.8 (CH_3), 34.9 (C), 61.1 (CH_2), 67.6 (CH), 127.4 (CH), 129.2 (CH), 134.1 (CH).

Synthesis of the 1,3-oxazolidinone 5



(*R*)-**5** (Scheme 1)[7] **-** In a 10 mL vial equipped with a Teflon-coated stir bar compound **4b** (0.4 mmol, 98 mg) was dissolved in CH_2Cl_2 (2 mL) and treated with benzoyl isocyanate (90% of purity, 0.44 mmol, 72 mg). The vial was capped with a rubber septum and the reaction was stirred under nitrogen at room temperature overnight. Then, the mixture was diluted with 5.0 mL of CH_2Cl_2 and K_2HPO_4 (2 mmol, 0.35 g) and MCPBA, (77% of purity, 1.6 mmol, 0.36 g) were added. After 15 minutes KOH (2.8 mmol, 0.16 g) was added and the mixture was stirred for 2 h, then quenched with water (10 mL) and extracted with diethyl ether (3 x 10 mL). The organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (light petroleum/Et_2O = 60/40) to yield the (4*R*)-3-benzoyl-4-isopropyl-1,3-oxazolidin-2-one **5** in 84% yield and 96% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (85/15 hexane/*i*-PrOH; flow rate 0.8 mL/min; λ = 230 nm; τ_S = 14.3 min; τ_R = 15.6 min). $[\alpha]^{rt}_D$= - 105.0 (*c* = 0.3, AcOEt, 96% ee). Lit.[7] $[\alpha]^{20}_D$= + 155, (*S*)-**5**, (*c* = 1.0, AcOEt, 99% ee). ^{1}H NMR: δ = 1.0 (d, *J* = 6.9, 3H), 1.01 (d, *J* = 6.9, 3H), 2.51 (dsept, *J = 4.4, 7.0*, 1H), 4.28 (dd, *J* = 5.5, 9.0, 1H), 4.42 (t, *J* = 9.0, 1H), 4.71 (ddd, *J = 4.4,* 5.5, 9.0, 1H),7.43-7.49 (m, 2H), 7.54-7.59 (m, 1H), 7.71-7.66 (m, 2H); ^{13}C NMR: δ = 15.1 (CH_3), 17.9 (CH_3), 28.3 (CH), 58.6 (CH), 63.4 (CH_2), 127.9 (CH), 129.1 (CH), 132.4 (CH), 133 2 (C), 153.8 (C), 169.8 (C).

Synthesis of the N-benzyl seleno amine 6

(*S*)-**6** (Scheme 1) **-** In a 10 mL vial equipped with a Teflon-coated stir bar catalyst **B** (0.04 mmol, 24.0 mg) and *p*NO_2PhCO_2H (0.04 mmol, 6.7 mg) were dissolved in 0.8 mL of CH_2Cl_2. After addition of the aldehyde **1b** (0.6 mmol, 64.4 µL), the solution was stirred for 5 minutes at -10 °C. Then, N-(Phenylseleno)-phthalimide **2** (0.4 mmol, 157 mg) was added and the vial was capped with a rubber stopper. Stirring was continued for 2.5 h then the reaction was diluted with CH_2Cl_2 (3 mL) and $MgSO_4$ (0.24 g) was added.

The ee of the aldehyde intermediate **3b** was determined to be 98% by HPLC analysis of the crude reaction mixture (Chiralpak AS-H column, 85/15 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 230 nm; τ_{minor} = 6.2 min; τ_{major} = 6.7 min). The mixture was stirred for ten minutes and benzylamine (1 mmol, 109.0 µL) was added. After 4h vigorous stirring at room temperature EtOH (5 mL), $NaCNBH_3$ (0.25 mmol, 16 mg) and acetic acid (0.4 mmol, 23 µL) were added successively at -78 °C under nitrogen. The temperature was allowed to rise to room temperature in one hour and then the reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (light petroleum/Et_2O = 80/20) to yield **6**[9] in 60% overall yield and 98% ee. The ee was determined by HPLC analysis using a Chiralpak AD-H column (99.3/0.7 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 230 nm; τ_S = 6.7 min; τ_R = 7.5 min). $[\alpha]^{rt}_D$= - 18.0 (*c* = 3.2, $CHCl_3$, 98% ee), ^1H NMR: δ = 1.03 (d, J = 6.8, 3H), 1.07 (d, J = 6.8, 3H), 1.82 (br s, 1H), 1.99-2.09 (m, 1H), 2.83 (dd, J = 8.5, 12.6, 1H), 2.92 (dd, J = *5.1,* 12.6, 1H), 3.29 (dt, J = 5.1, 8.5, 1H), 3.77 (d, J = *13.3*, 1H), 3.82 (d, J = 13.3, 1H), 7.25-7.38 (m, 8H), 7.50-7.55 (m, 2H); ^{13}C NMR: δ = 20.1 (CH_3), 21.0 (CH_3), 31.3 (CH), 51.7 (CH_2), 53.6 (CH_2), 56.7 (CH), 126.9 (CH), 127.2 (CH), 128.0 (CH), 128.4 (CH), 129.0 (CH), 130.1 (C), 134 4 (CH), 140.2 (C).

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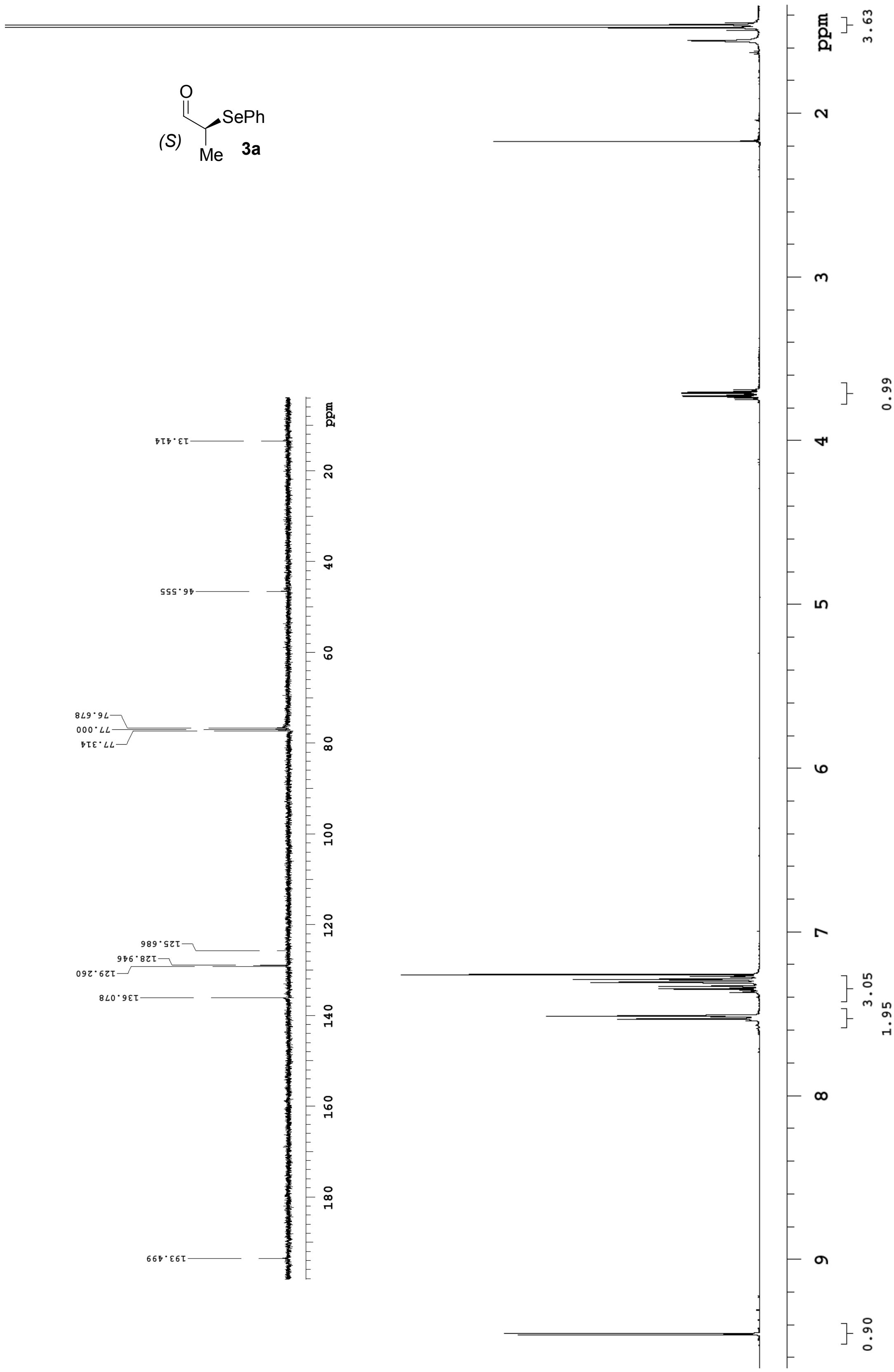
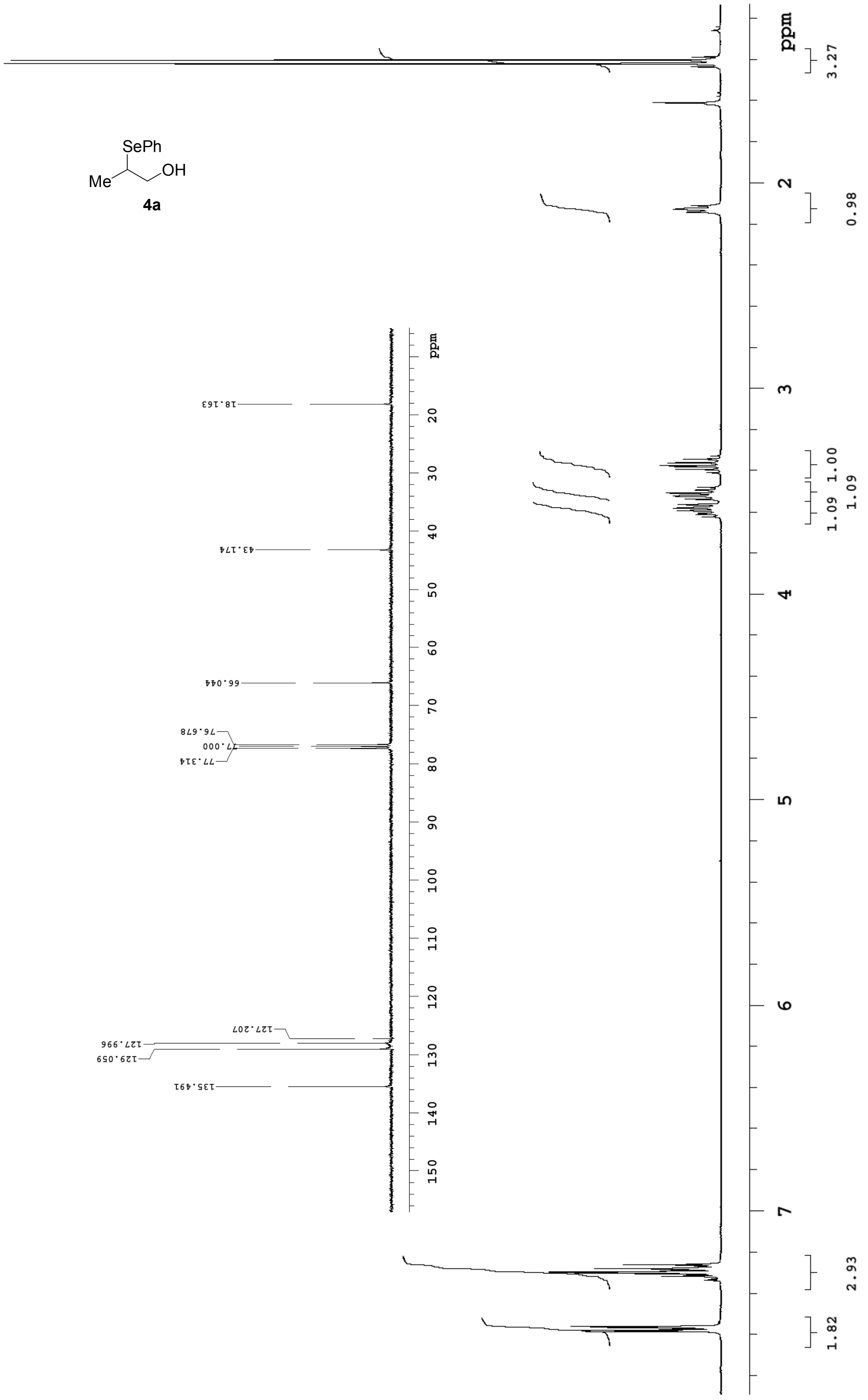
[9] C. Miniejew, F. Outurquin, X. Pannecoucke *Tetrahedron*, **2005**, *61*, 447.

NMR Spectra



3a

SePh
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5
6
7
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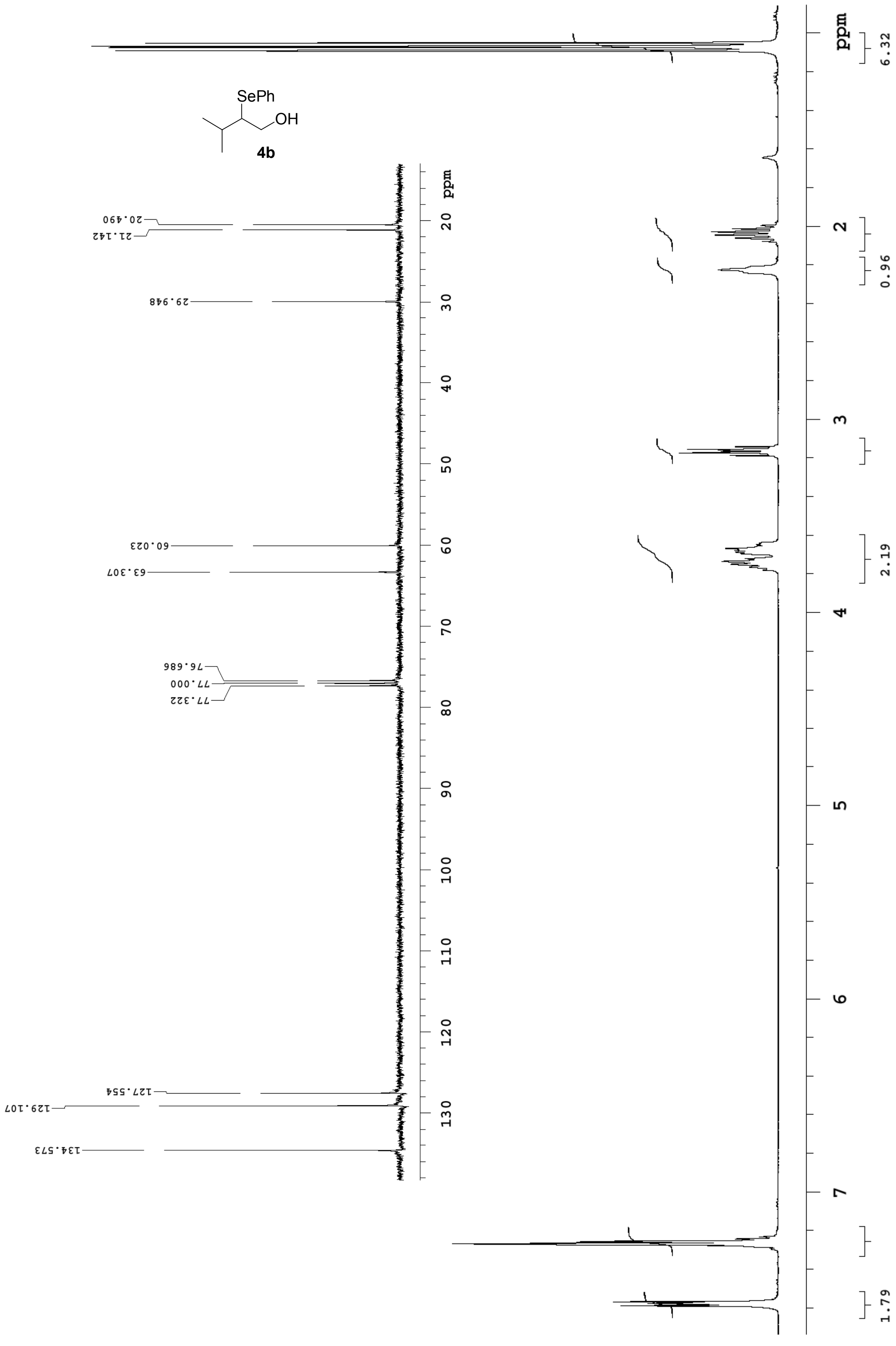
1.09
1.09
2.93
1.82
18.163
43.174
66.044
76.678
77.000
77.314
127.207
127.996
129.059
135.491
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150

4a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134.573
20
30
40
50
60
70
80
90
100
110
120
130
ppm
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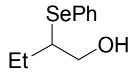
5
6
7
6.32
1.06
0.96
1.00
2.19
2.81
1.79

4b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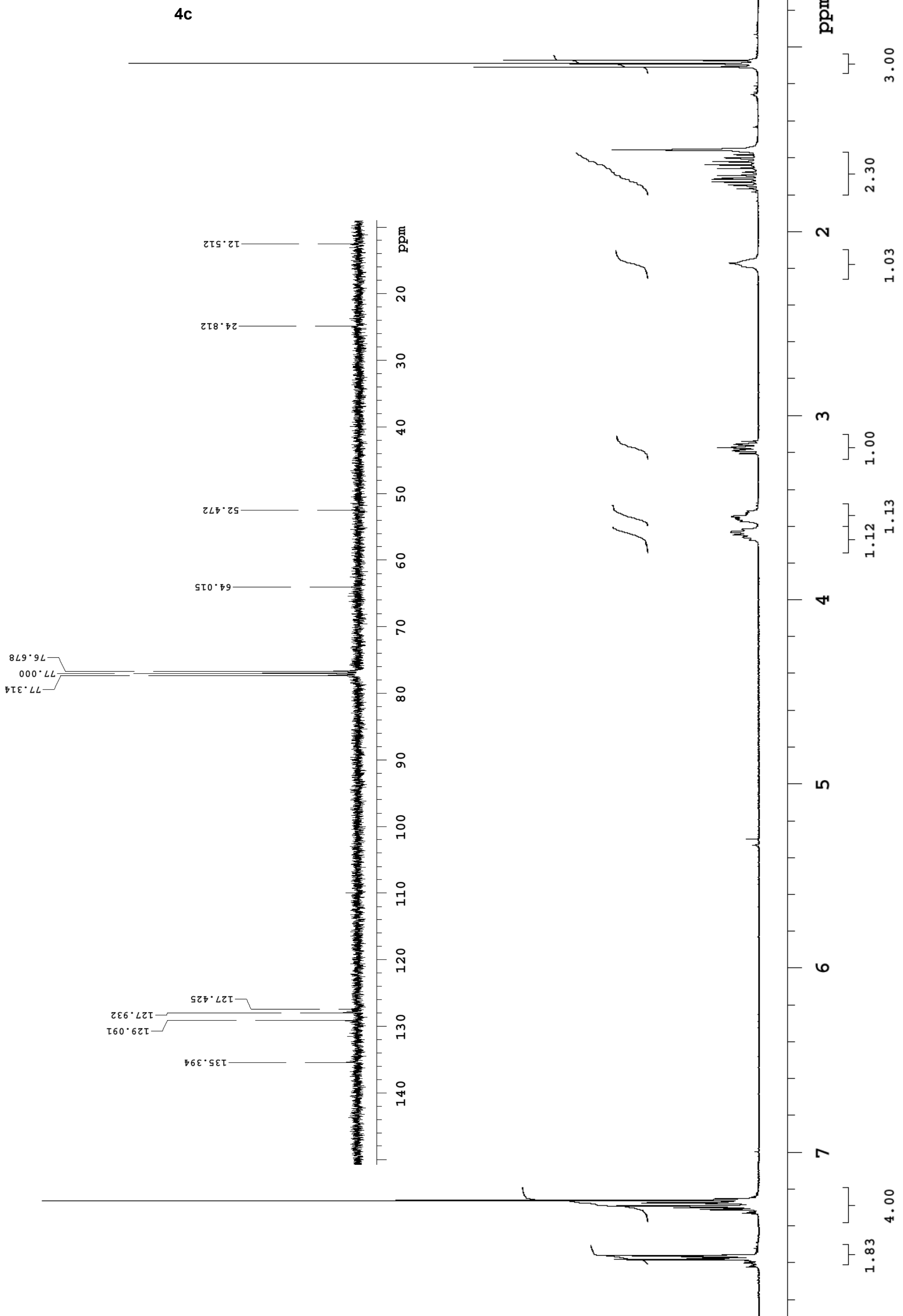
OH
Et

4c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52.472
64.015
76.678
77.000
77.314
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ppm
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130
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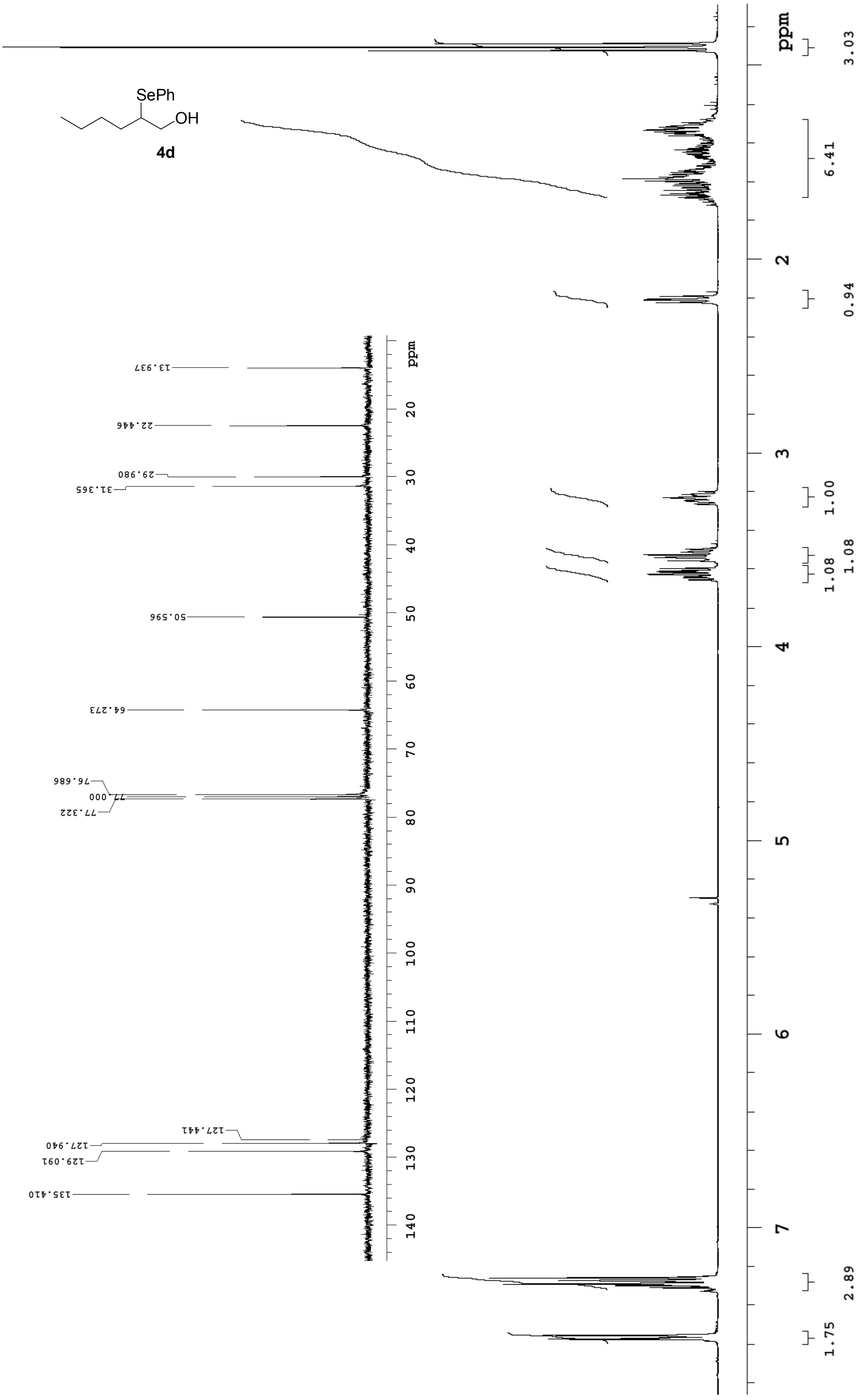
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OH
4d
ppm
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4
5
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22.446
29.980
31.365
50.596
64.273
76.686
77.000
77.322
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129.091
135.410
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30
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50
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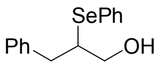
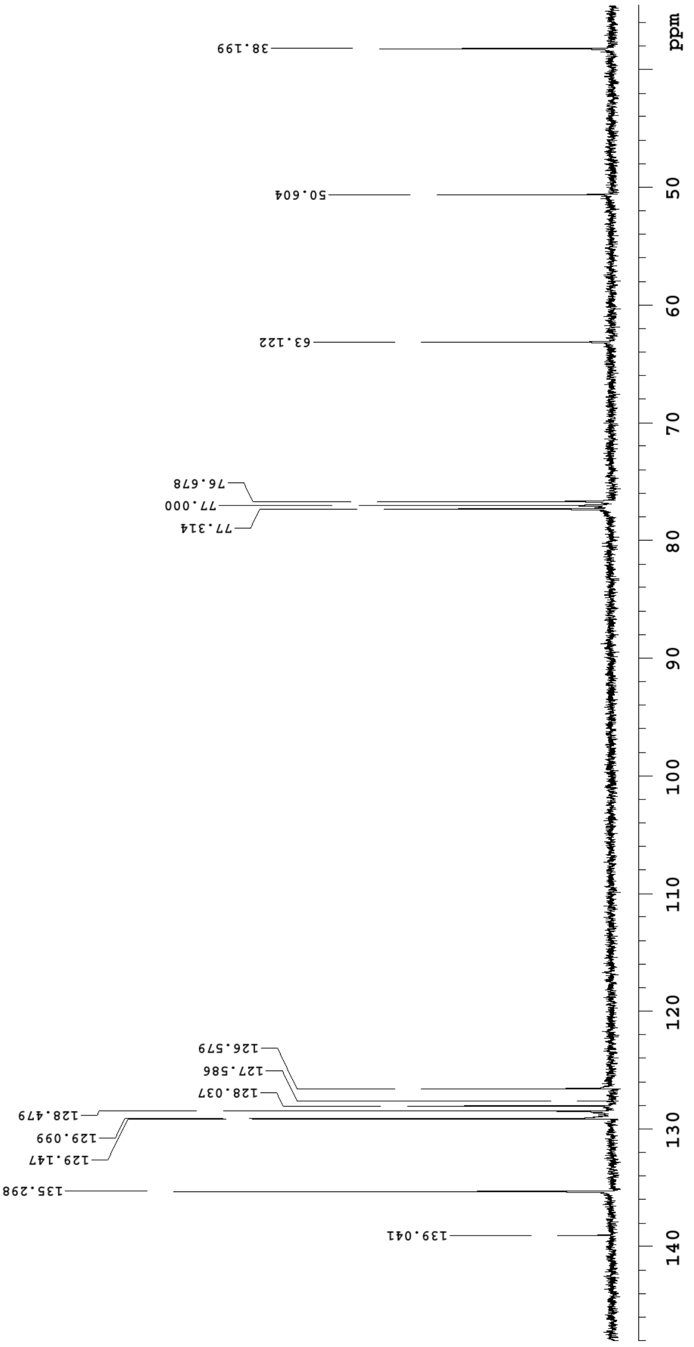
110
120
130
140


SePh
Ph
OH

4e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77.000
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139.041
ppm
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70
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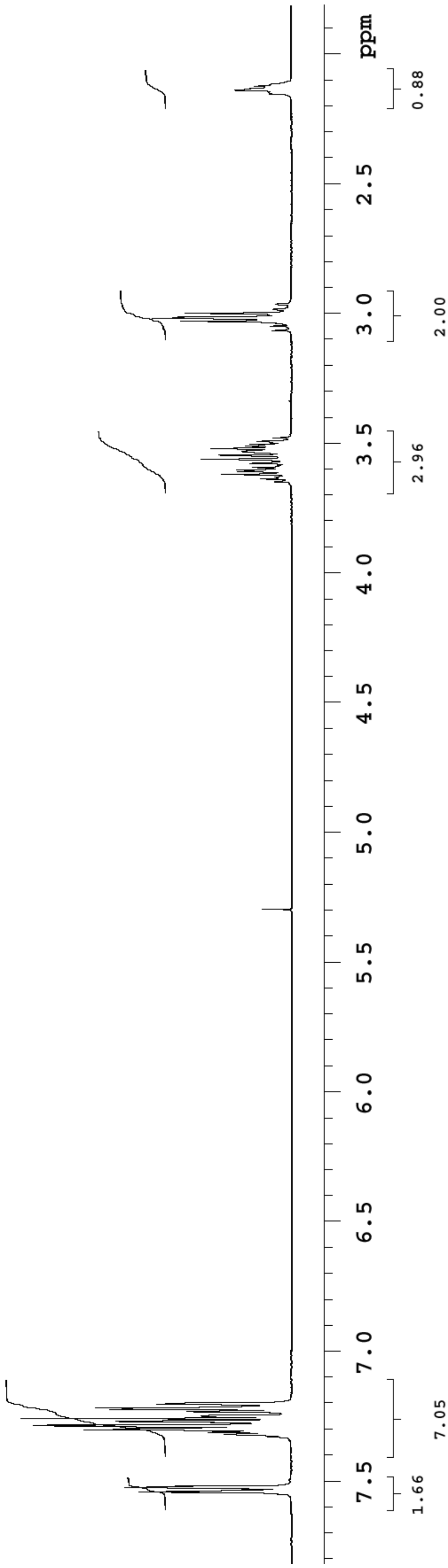
130
140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7.0
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0.88
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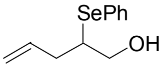
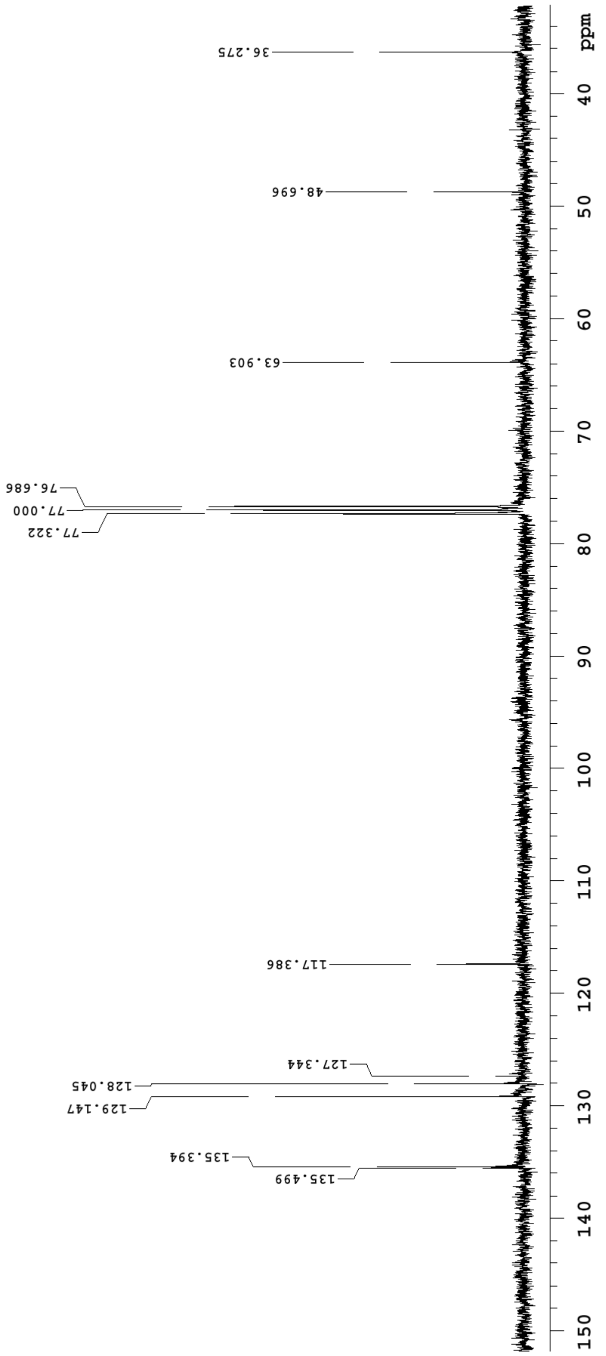
2.96
7.05
1.66


SePh
OH

4f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77.322
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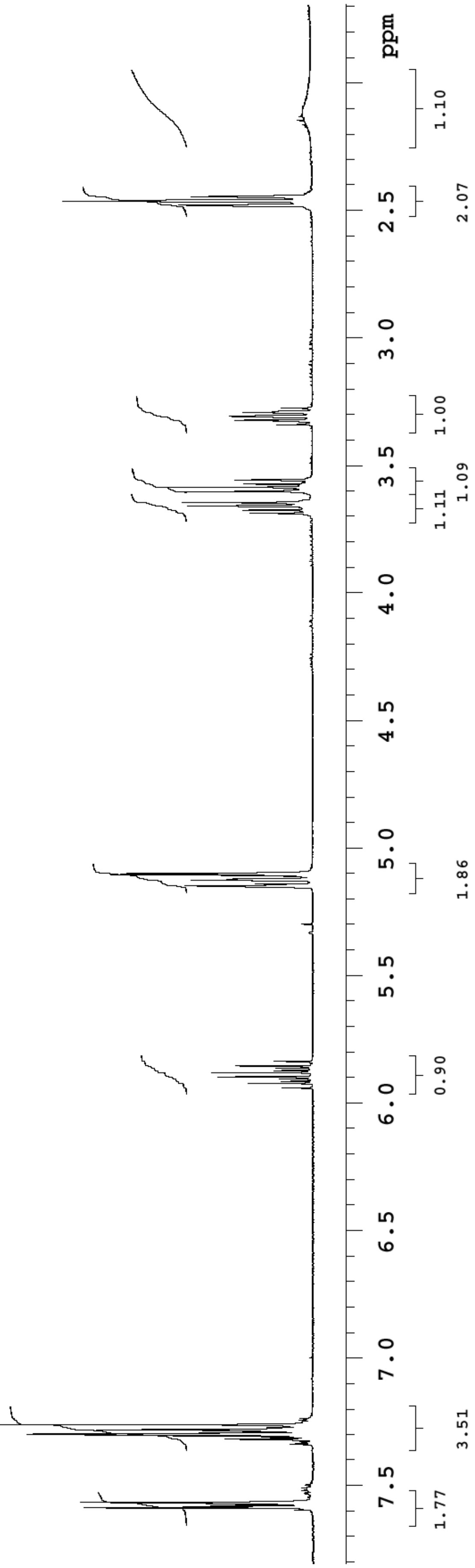
100
110
120
130
140
150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7.0
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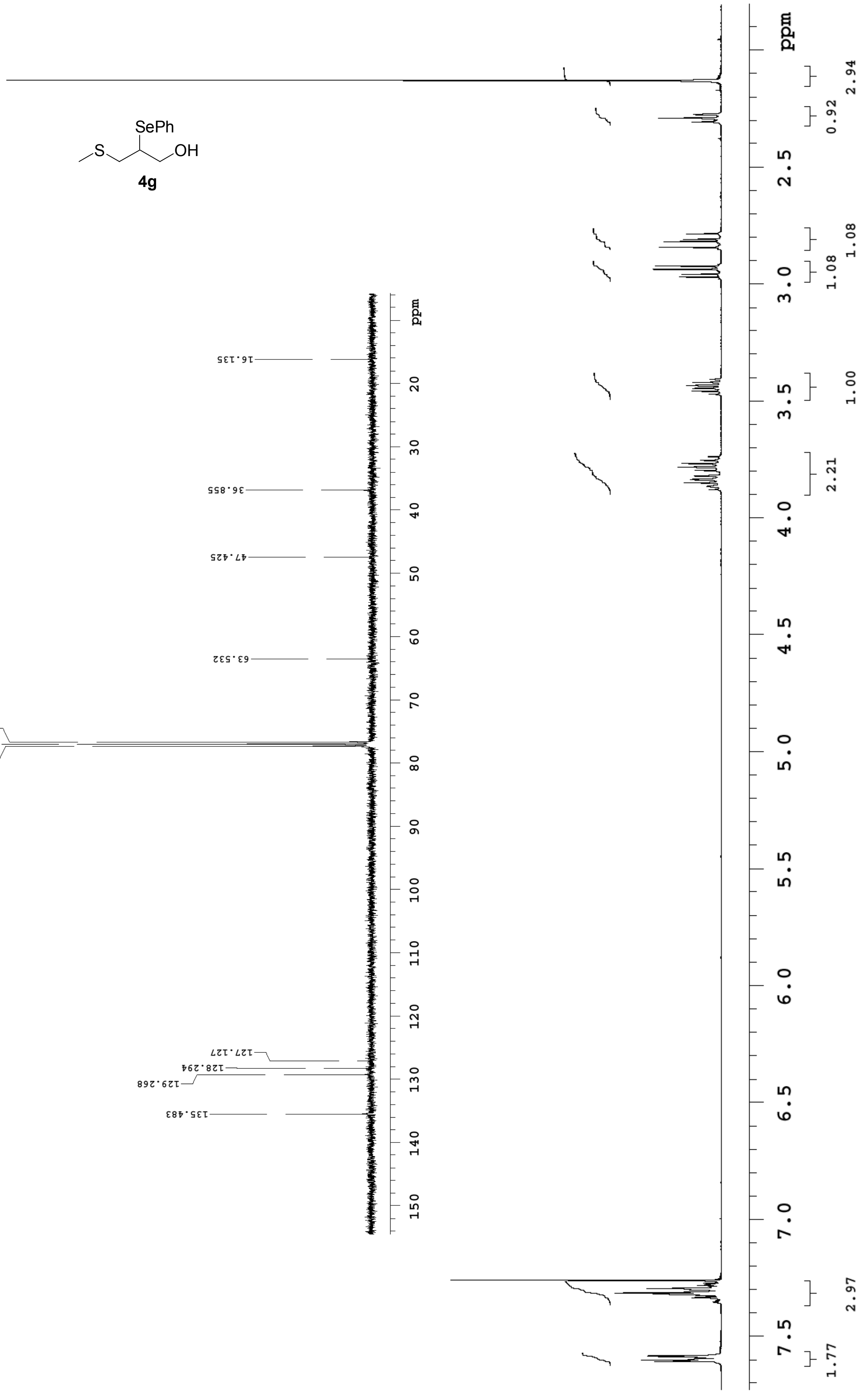
1.10
2.07
1.00
1.11
1.09
1.86
0.90
3.51
1.77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129.268
135.483
ppm
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30
40
50
60
70
80
90
100
110
120
130
140
150
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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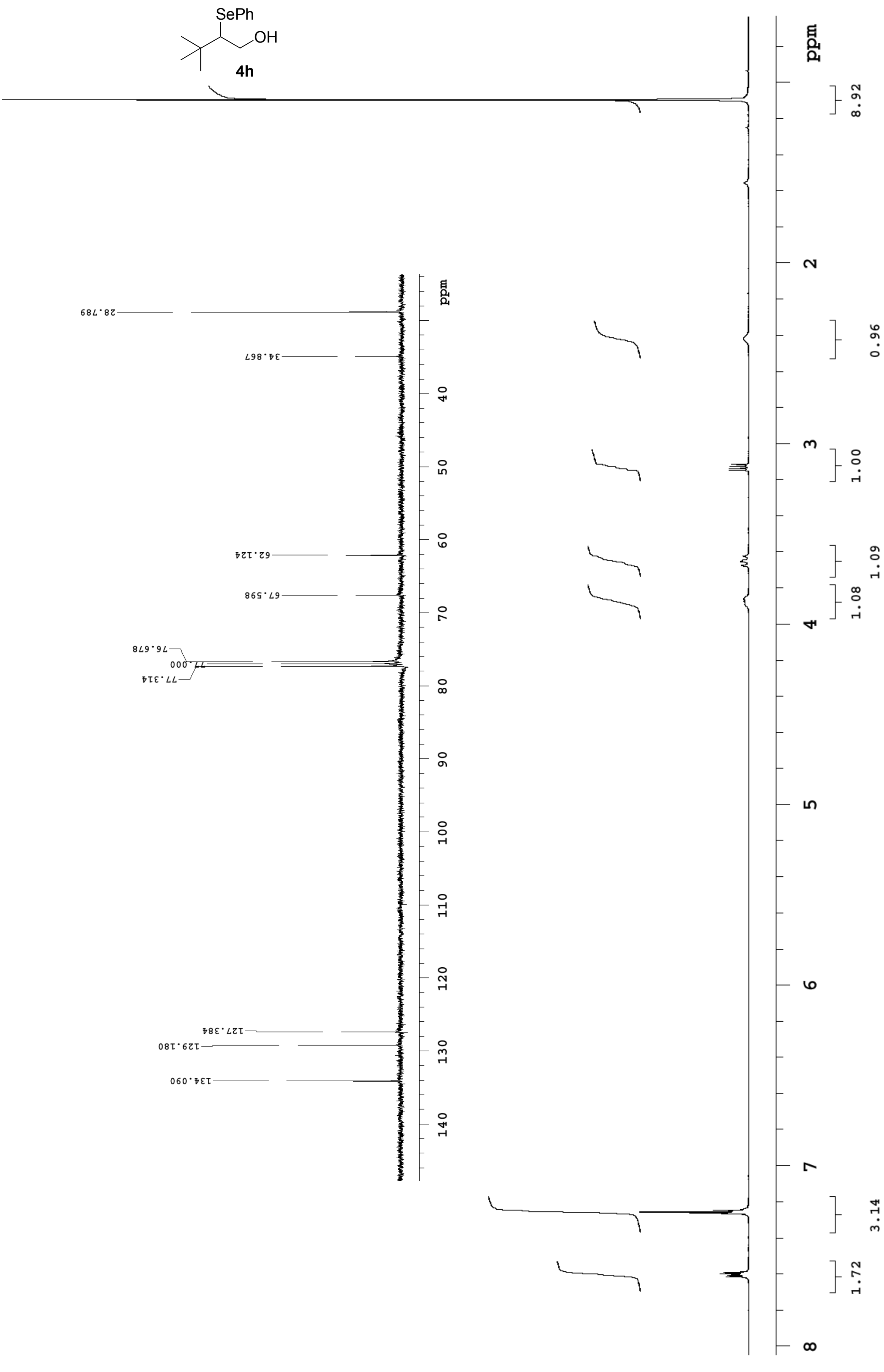
0.92
1.08
1.08
1.00
2.21
2.97
1.77


4h

SePh
OH
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62.124
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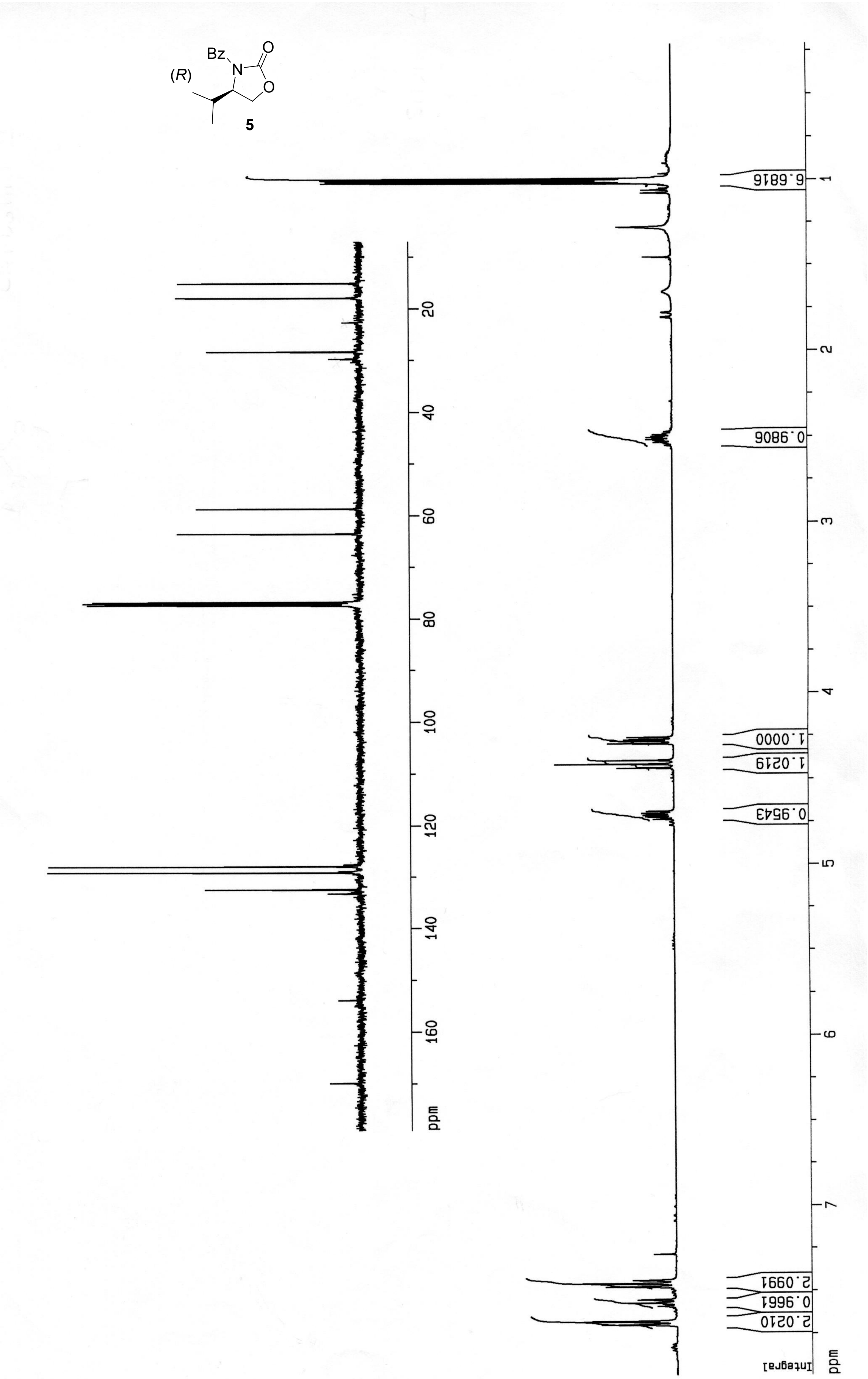
76.678
77.000
77.314
127.384
129.180
134.090
ppm
40
50
60
70
80
90
100
110
120
130
140
ppm
2
3
4
5
6
7
8
8.92
0.96
1.00
1.09
1.08
3.14
1.72


Bz
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O
O
(R)
ppm
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40
60
80
100
120
140
160
ppm
Integral
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2
3
4
5
6
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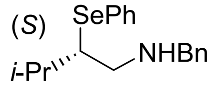
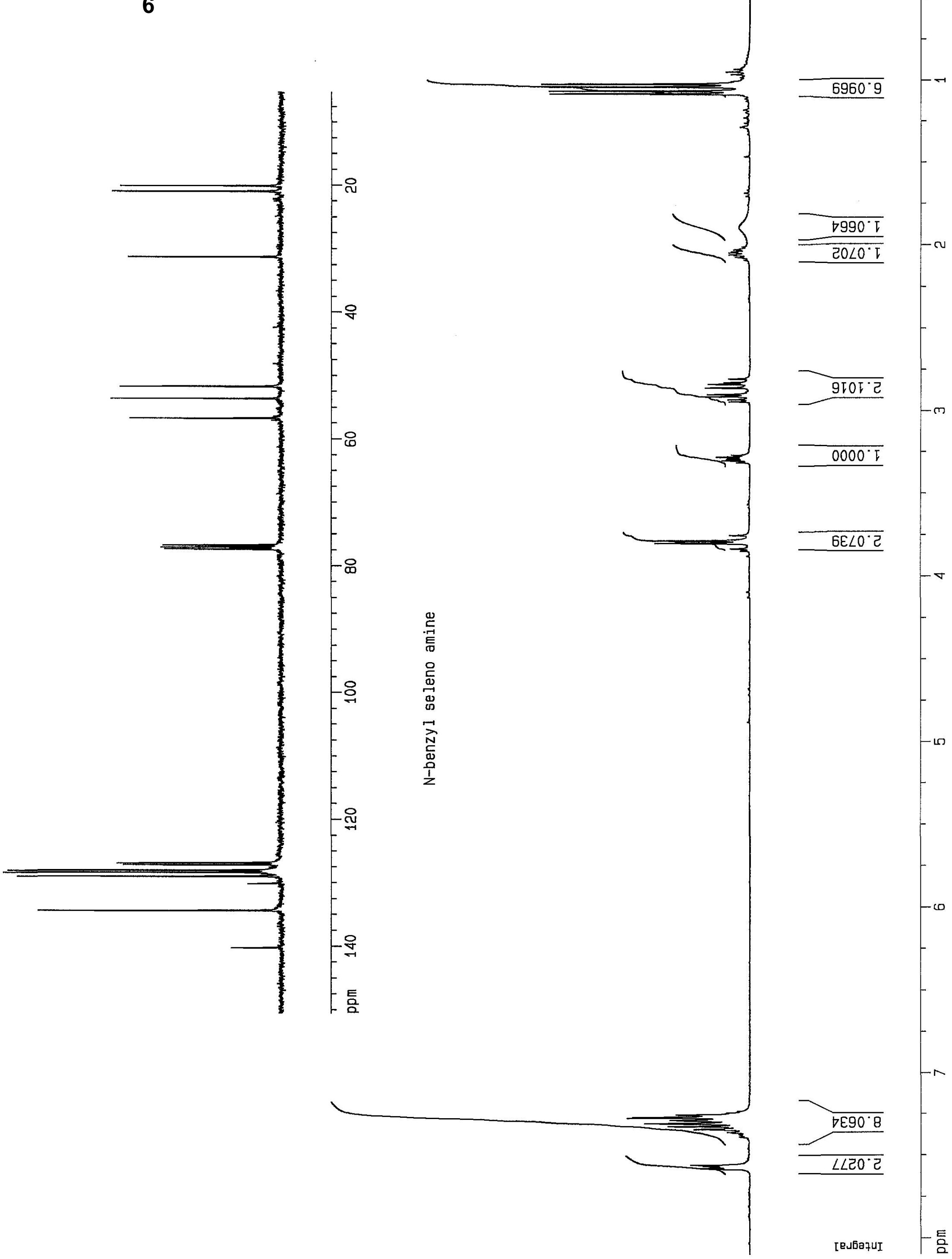
0.9806
1.0000
1.0219
0.9543
2.0991
0.9661
2.0210

5


(S)
SePh
i-Pr
NHBn

6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80
100
120
140
ppm
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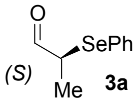
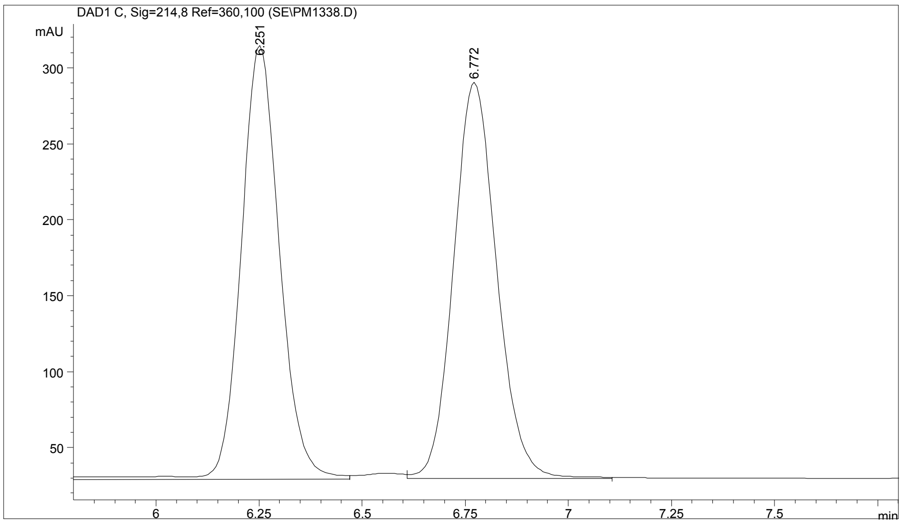
1.0702
2.1016
1.0000
2.0739
8.0634
2.0277
Integral
1
2
3
4
5
6
7
ppm

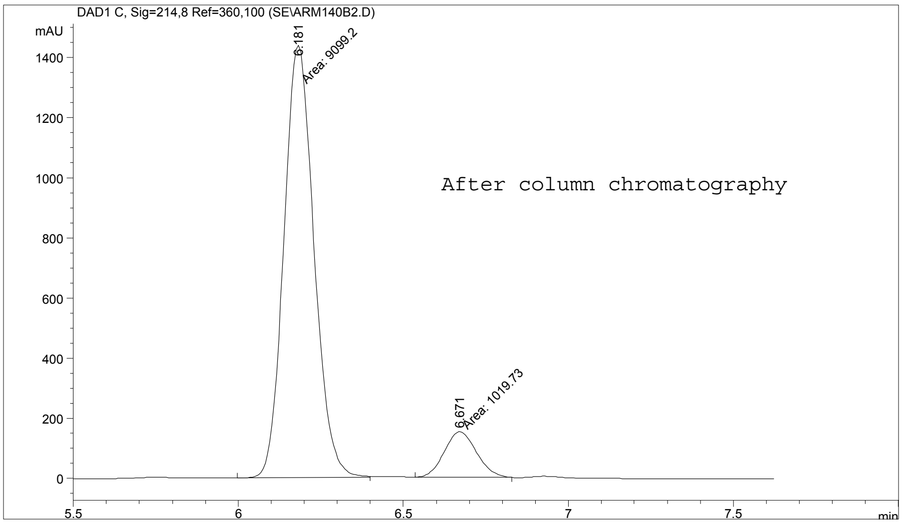
Representative HPLC Traces



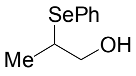
3a

Chiralpak AD-H column (8/2 hexane/*i*PrOH – flow rate: 0.75 mL/min)



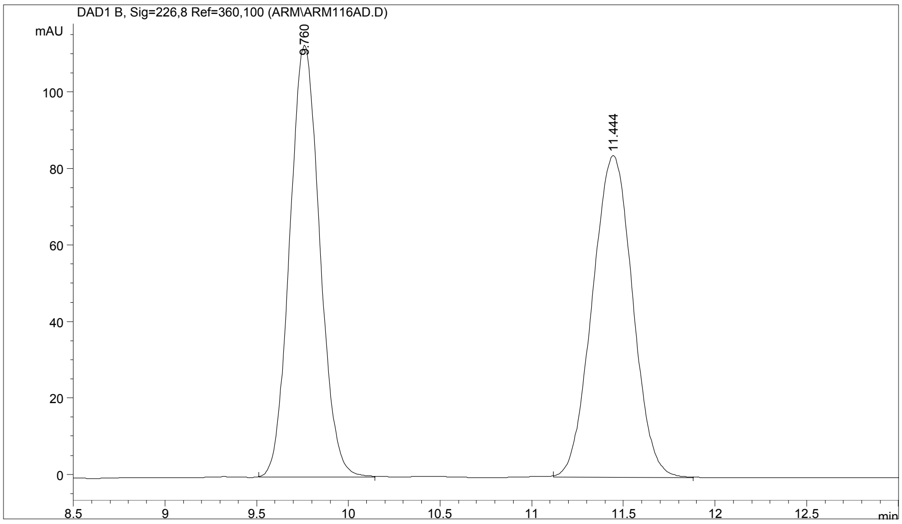


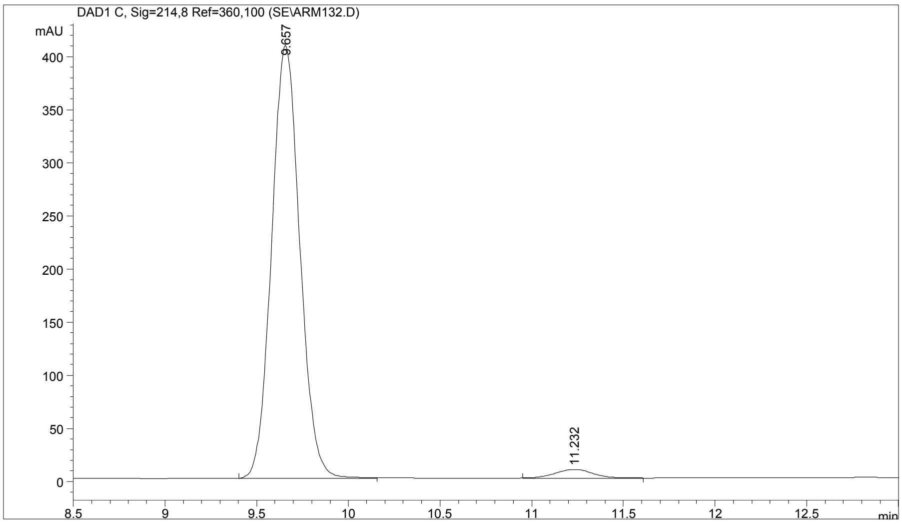
```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   6.181 MM    0.1054 9099.20117 1438.42383  89.9225
   2   6.671 MM    0.1126 1019.73090  150.90479  10.0775
```



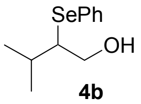
4a

Chiralpak AD-H column (9/1 hexane/*i*PrOH - flow rate: 0.75 mL/min)



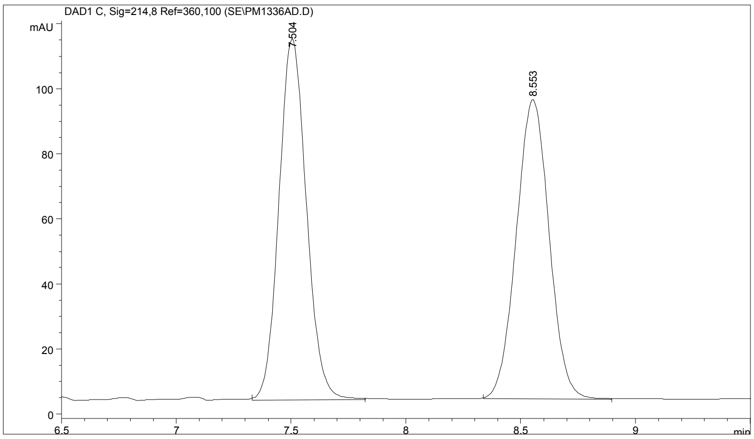


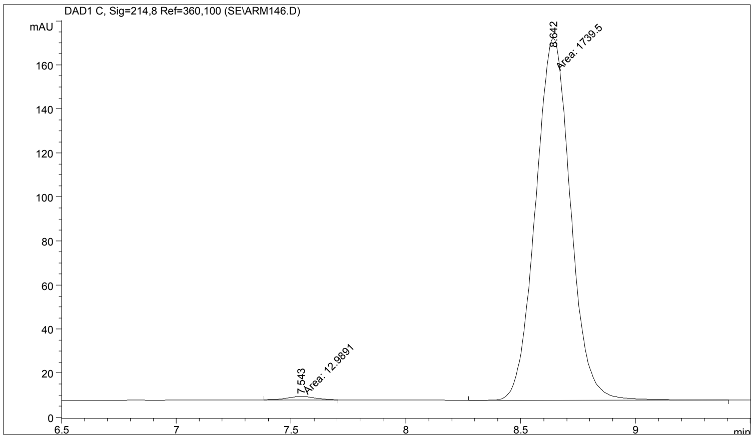
```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.657 BB    0.1666 4353.00830  407.56747 97.4676
   2  11.232 BP    0.2154  113.10140    8.17477  2.5324
```



4b

Chiralpak AD-H column (9/1 hexane/*i*PrOH - flow rate: 0.75 mL/min)





```
 Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1   7.543 MM    0.1412   12.98906    1.53269   0.7412
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```

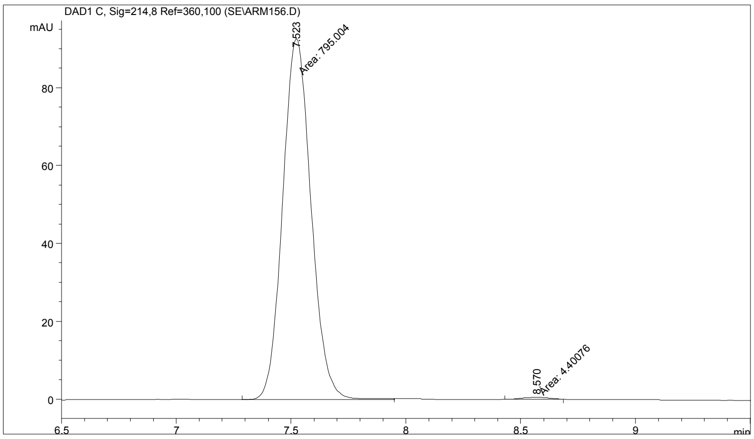

```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]         [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.523 MM    0.1429  795.00409   92.74030  99.4495
   2   8.570 MM    0.1416    4.40076 5.17930e-1   0.5505
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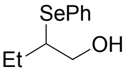
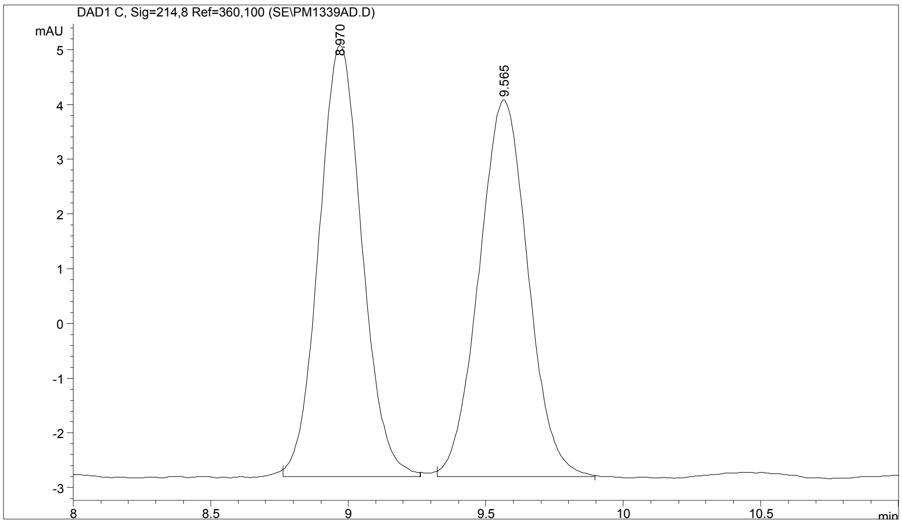
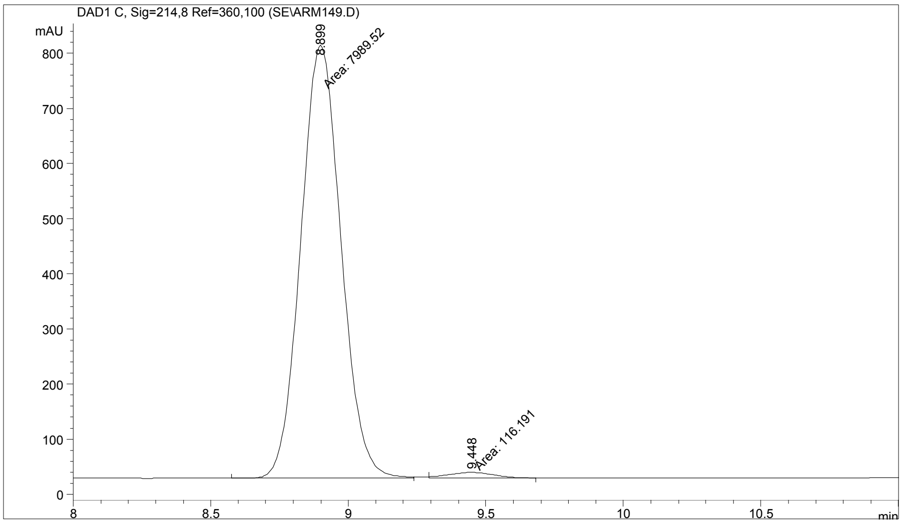


4c

Chiralpak AD-H column (9/1 hexane/*i*PrOH - flow rate: 0.75 mL/min)





```
Peak RetTime Type  Width     Area      Height     Area
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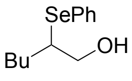
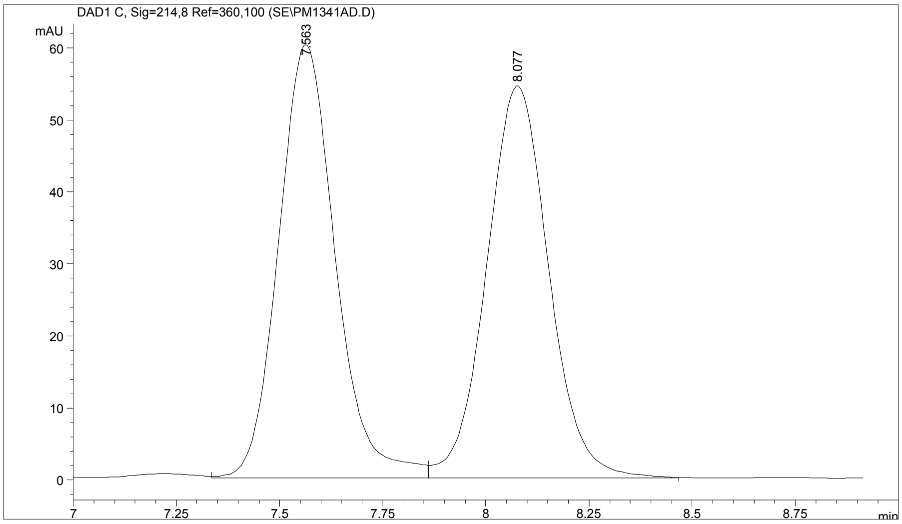
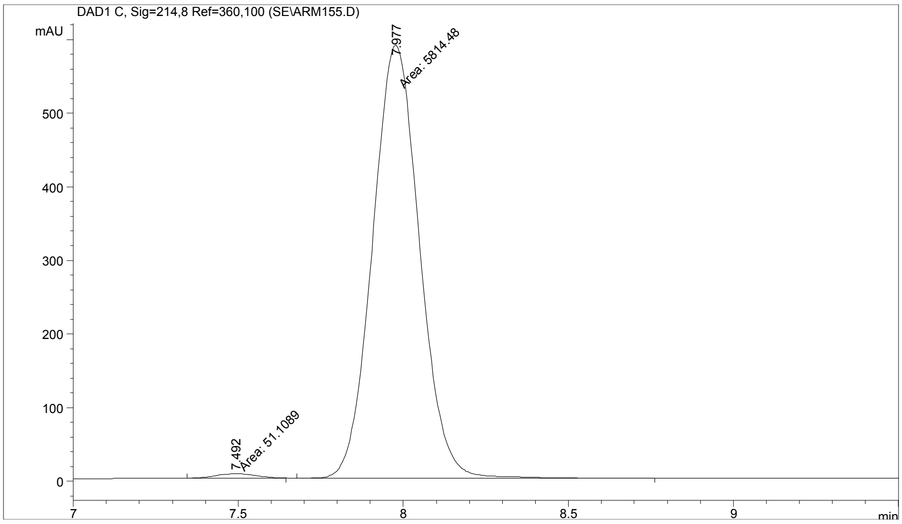
----|-------|----|-------|----------|----------|--------|
   1   8.899 MM    0.1694 7989.51709  785.98401 98.5666
   2   9.448 MM    0.1934  116.19065   10.01442  1.4334
```



4d

Chiralpak AD-H column (9/1 hexane/*i*PrOH - flow rate: 0.75 mL/min)





```
Peak RetTime Type  Width     Area      Height     Area
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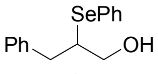
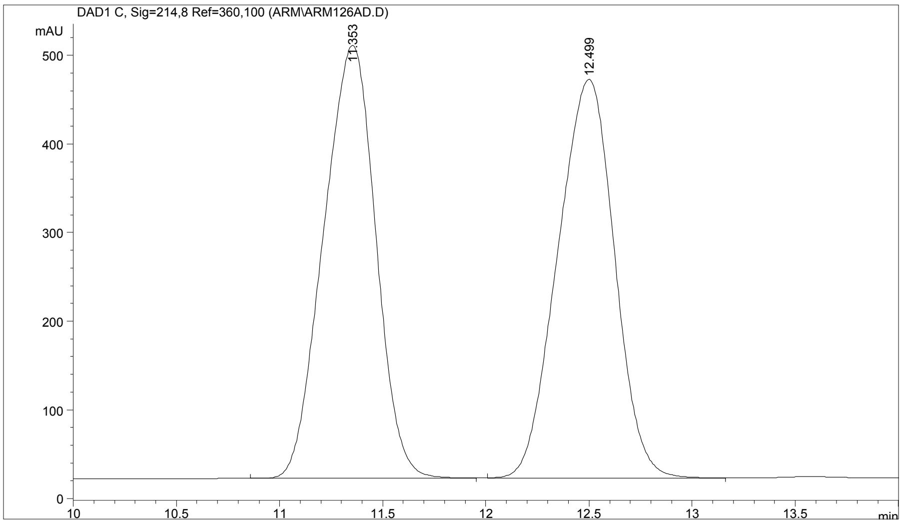
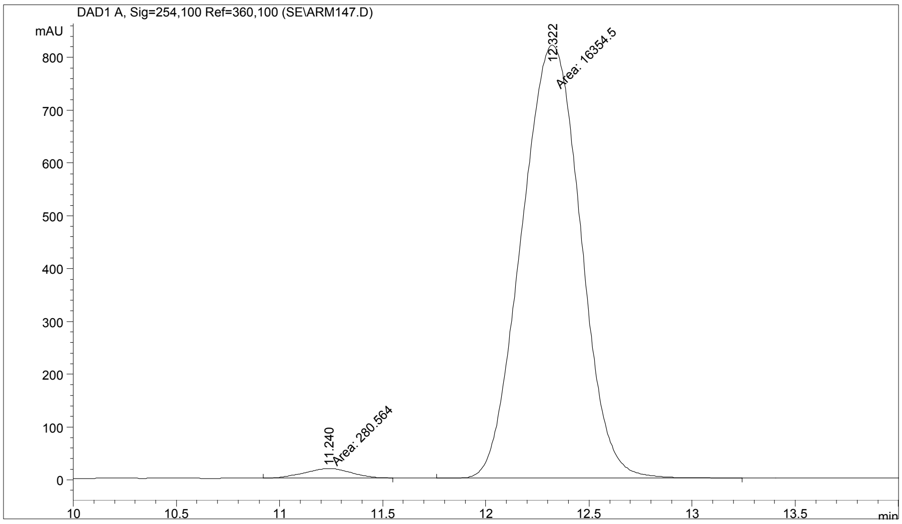
----|-------|----|-------|----------|----------|--------|
   1   7.492 MM    0.1408   51.10894    6.05022   0.8713
   2   7.977 MM    0.1646 5814.48437  588.77167  99.1287
```



4e

Chiralpak AD-H column (9/1 hexane/*i*PrOH – flow rate: 0.75 mL/min)





```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]  [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.240 MM    0.2625  280.56375   17.81289   1.6866
   2  12.322 MM    0.3322 1.63545e4   820.43994  98.3134
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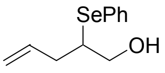
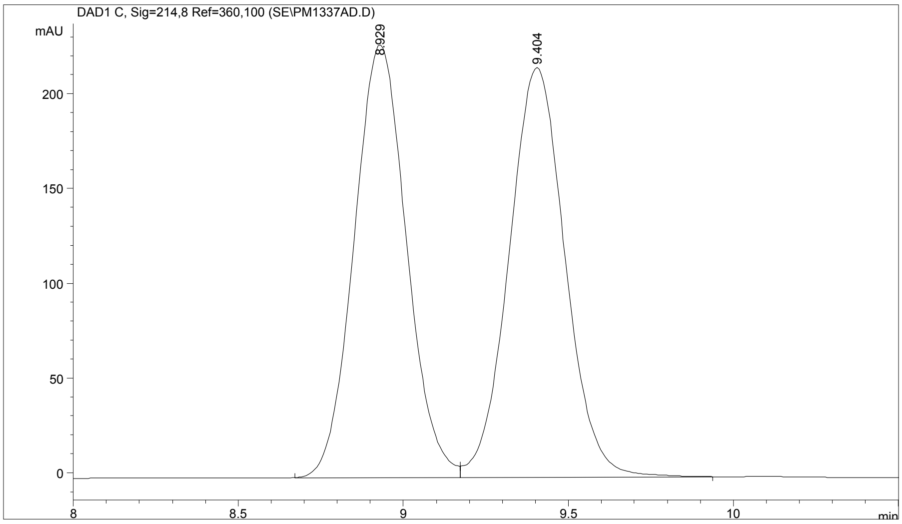
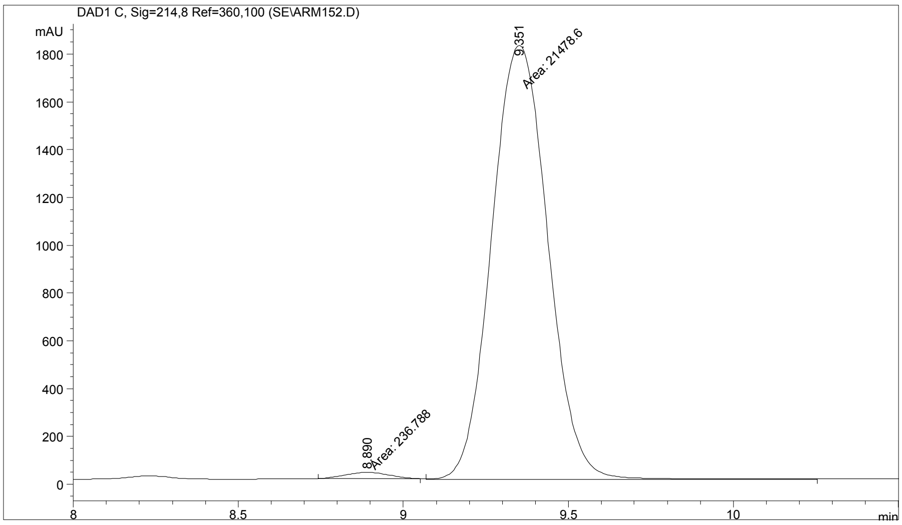


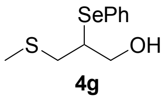
4f

Chiralpak AD-H column (9/1 hexane/*i*PrOH – flow rate: 0.75 mL/min)



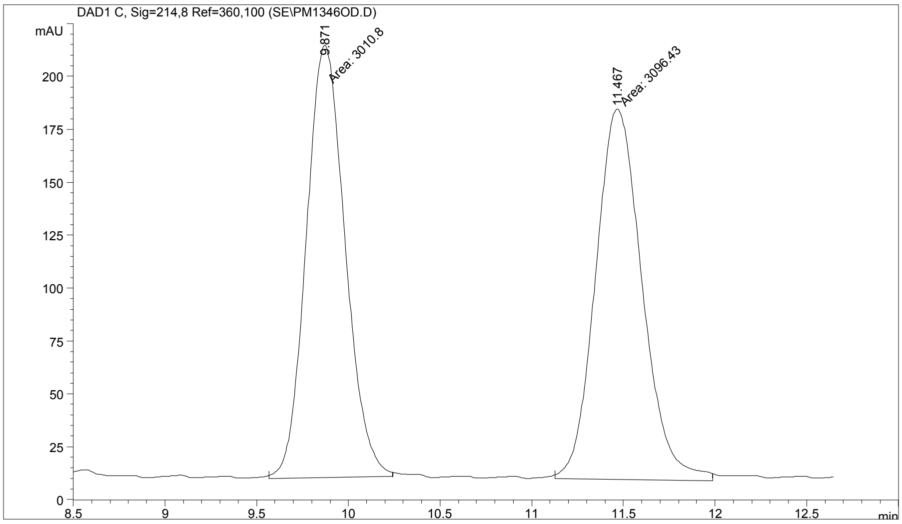


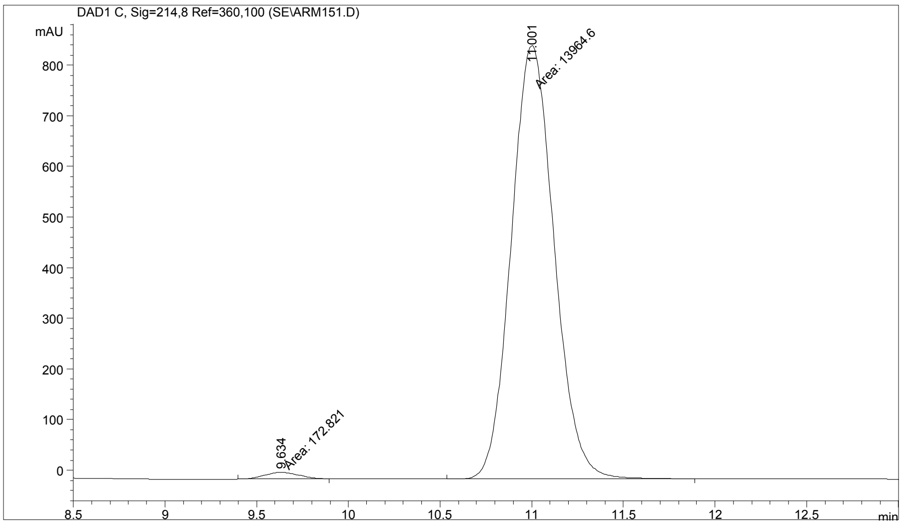
```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.890 MM    0.1540  236.78754   25.62654   1.0904
   2   9.351 MM    0.1971 2.14786e4 1816.24890  98.9096
```



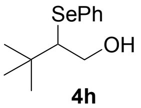
4g

Chiralcel OD-H column (9/1 hexane/*i*PrOH - flow rate: 0.75 mL/min)



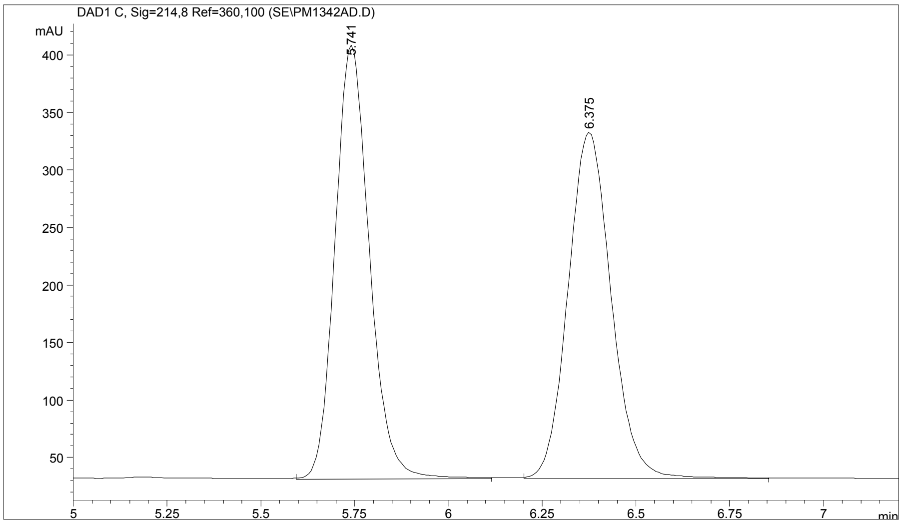


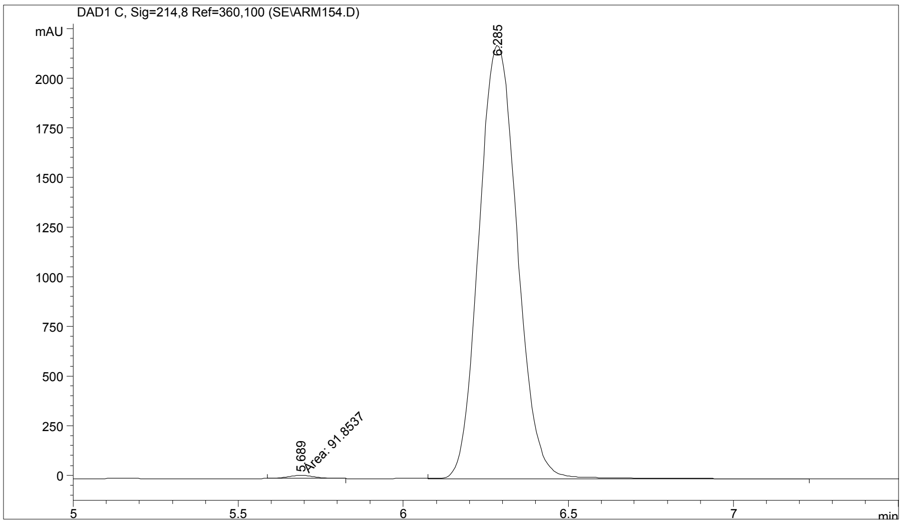
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.634 MM    0.2234  172.82126   12.89050   1.2224
   2  11.001 MM    0.2716 1.39646e4   856.99030  98.7776
```



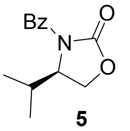
4h

Chiralpak AD-H column (8/2 hexane/*i*PrOH - flow rate: 0.75 mL/min)



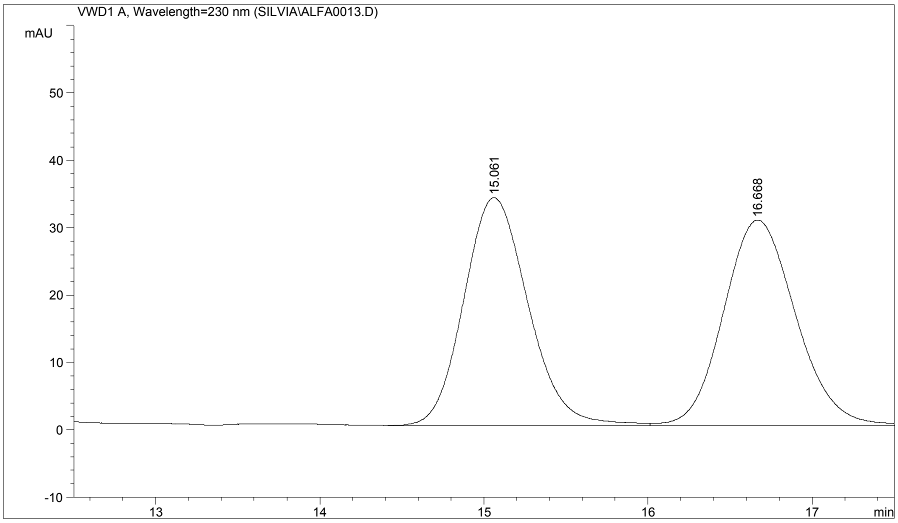


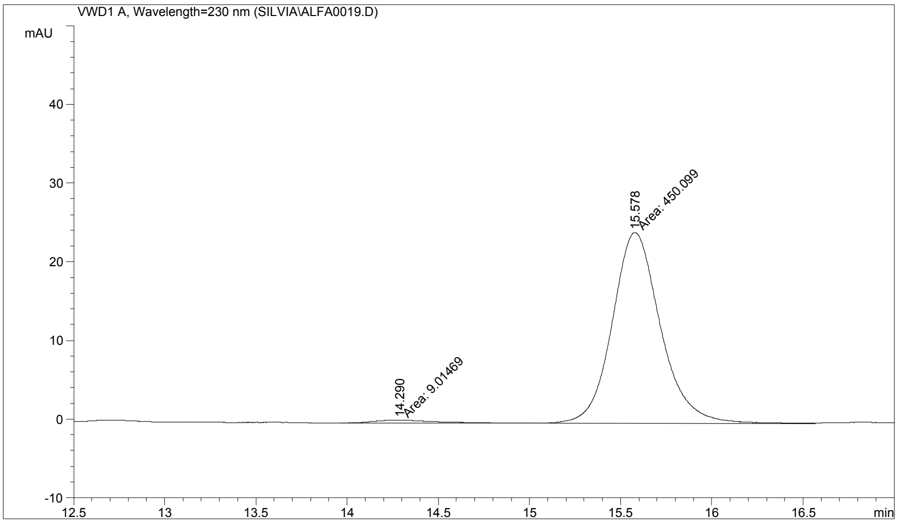
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.689 MM    0.0985   91.85374   15.53846   0.5180
   2   6.285 VB    0.1283 1.76393e4  2183.11938  99.4820
```



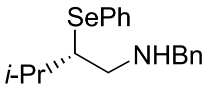
5

HPLC conditions: Chiralpak AD-H, hexane/i-PrOH 85/15, Flow 0.8 mL/min



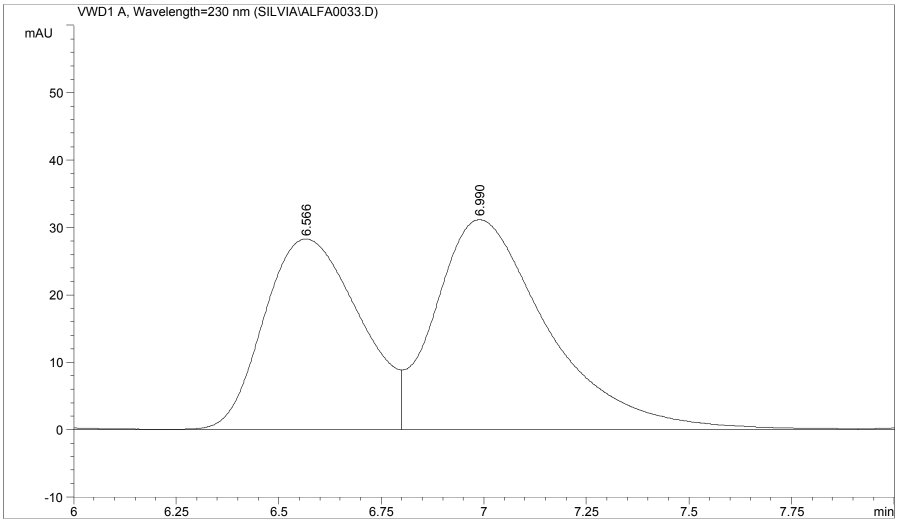


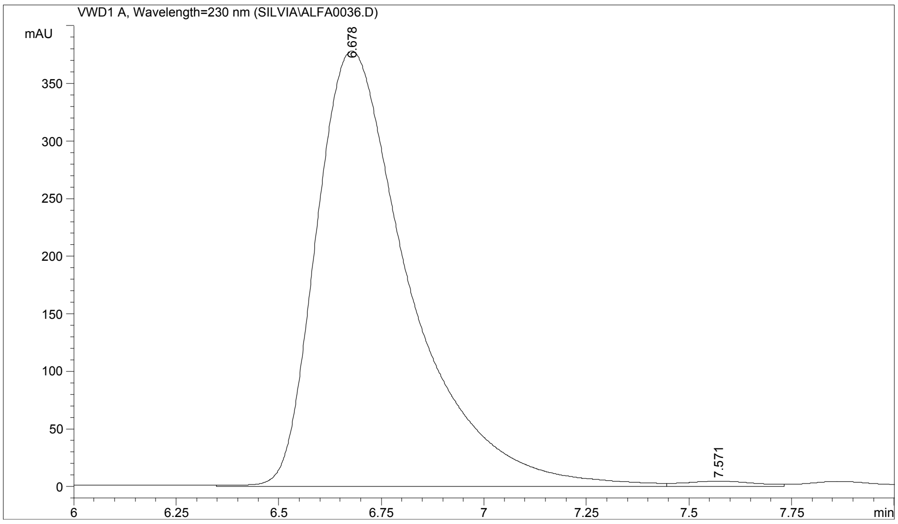
```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.290 MF    0.3932    9.01469 3.82093e-1   1.9635
   2  15.578 FM    0.3089  450.09885   24.28397  98.0365
      Totals :                459.11354   24.66606
```



6

HPLC conditions: Chiralpak AD-H, hexane/i-PrOH 99.3/0.7, Flow 1.0 mL/min





```
 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.678 BV    0.2381 5960.44482  377.36426  99.3136
   2   7.570 VV    0.1612   41.19590    3.67972   0.6864
     Totals :                6001.64072  381.04398
```