Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The Open d-Shell Enforces the Active Space in 3d Metal Catalysis: Highly Enantioselective Chromium(II) Pincer Catalysed Hydrosilylation of Ketones

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Contents

1. General Remarks

Reactions

Unless stated otherwise, all reactions were carried out under inert conditions in heat-gun dried glassware and under an atmosphere of argon using standard Schlenk techniques or inside of a Glovebox (M. Braun Unilab 2000). All chemicals were bought from commercial suppliers (Acros, Sigma-Aldrich, Alfa Aesar or ABCR) and were used without any further purification, unless mentioned otherwise. Dry solvents were taped from a solvent purification system (M. Braun SPS-800) and used immediately. Manual degassing of solvents, if needed, was done by performing three consecutive freeze-pump-thaw cycles. Dry DMF was purchased from Sigma-Aldrich. Deuterated solvents were purchased from Deutero GmbH or Sigma-Aldrich and dried over sodium (C_6D_6), distilled, degassed and stored under an atmosphere of argon. All chromium salts were purchased with a trace metal purity of 99.9 %. The PdmBox-ligands,[1] (tmeda)$CrCl_2$[2] and deuterated Silane[3] were synthesized according to reported procedures.

Analytics

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance II 400 and Bruker Avance III 600 at room temperature. Chemical shifts are reported in ppm, coupling constants in Hz. Chemical shifts were referenced to residual solvent protons and the ^{13}C isotope of deuterated solvents.[4] Multiplicities are indicated as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Atom numbering is illustrated in the respective figure shown above each procedure.

Mass spectrometry (MS) and high-resolution MS were obtained at the mass spectroscopy department of the University of Heidelberg. Electron spray ionization (ESI) was carried out on a Bruker ApexQe hybrid 9.4 T FT-IVR machine, liquid injection field desorption ionization (LIFDI) was performed on a JEOL JMS- 700 instrument.

Elemental analysis (EA) for C, H, and N was performed at a facility of the Chemistry Department at the University of Heidelberg on a vario MICRO Cube or vario EL Cube.

High Performance Liquid Chromatography (HPLC) measurements were carried out on Agilent Technologies 1260 Infinity HPLC equipped with solvent pump, auto-sampler, membrane solvent degasser and DAD detector.

Silica gel (SiO_2, pore size 60 Å) for flash column chromatography (FCC) was purchased from Sigma-Aldrich. Thin Layer chromatography (TLC) was performed with Polygram® SIL G/UV_{254} purchased from Macherey-Nagel. Components were visualized by fluorescence quenching during irradiation with UV light (254 nm) or were revealed with Hanessian's stain.

X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Table S2. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo-Kα radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 0.4°) were integrated by profile fitting.[5,6] Data were corrected for air and detector absorption, Lorentz and polarization effects[6] and scaled essentially by application of appropriate spherical harmonic functions.[6,7,8]Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling process), and augmented by a spherical correction.[7,8] The structures were solved by the charge flip procedure[9] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[10] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model.[11]

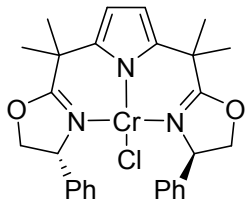
CCDC 1850233-1850234 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis of the Precatalysts ^{R}(PdmBox)Cr(CH_2SiMe_3)

2.1 Synthesis of the ^{R}(PdmBox)CrCl Complexes

The protioligand ^{R}(PdmBox)H (2.09 mmol, 1.0 eq.) was dissolved in THF (20 mL) and LiHMDS (2.30 mmol, 1.1 eq.) dissolved in THF (5 mL) was slowly added and the mixture was stirred for 30 min at rt. Subsequently, a suspension of (tmeda)$CrCl_2$ (2.09 mmol, 1.0 eq.) in THF (10 mL) was added dropwise to the reaction mixture and stirring was continued for 12 h at rt. Afterwards, the reaction was filtered, the solvent was removed, and the residue was redissovled in a mixture of toluene/pentane (1:3) and filtered over celite. The filtrate was evaporated to afford ^{R}(PdmBox)CrCl complex as dark-violet solid. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **2b** in *n*-pentane at −40 °C.

2.1.1 [$^{(R)\text{-Ph}}$(PdmBox)CrCl]



1a

Yield: dark-violet solid (582.3 mg, 62 %).

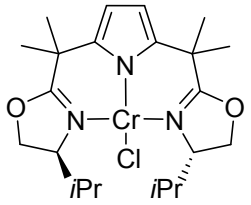
^{1}H NMR (C_6D_6, 600.13 MHz, 295 K, paramagnetic): δ [ppm] = 23.34, 18.53, 5.25, 2.41, –37.81.

Magnetic Susceptibility (Evans, C_6D_6, 295 K)[12]: μ_{eff} = 4.75 μ_b.

EA: calcd. C: 63.69 %, H: 5.72 %, N: 7.96 %; found: C: 63.09 %, H: 5.93 %, N: 7.71 %.

HR-MS (ESI^+): m/z calcd. for $[C_{28}H_{30}ClCrN_3O_2]$, $[M]^+$: 527.1422; found: 527.1421.

2.1.2 [$^{(S)\text{-}i\text{Pr}}$(PdmBox)CrCl]



1b

Yield: dark-violet solid (497.3. mg, 64 %).

^{1}H NMR (C_6D_6, 600.13 MHz, 295 K, paramagnetic): δ [ppm] = 32.03, 26.09, 19.23, 3.62, –36.95.

Magnetic Susceptibility (Evans, C_6D_6, 295 K)[12]: μ_{eff} = 4.70 μ_B.

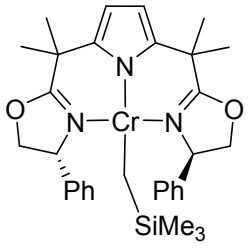
EA: calcd. C: 57.45 %, H: 7.45 %, N: 9.14 %; found: C: 57.29 %, H: 7.31 %, N: 8.91 %.

HR-MS (ESI^+): m/z calcd. for $[C_{22}H_{32}ClCrN_3O_2]^+$, $[M]^+$: 459.1817; found: 459.1818.

2.2 Syntheses of the ^{R}(PdmBox)Cr(CH_2SiMe_3) Complexes

^{R}(PdmBox)CrCl complex (1.09 mmol, 1.00 eq.) was dissolved in toluene (50 mL), a solution of $Mg(CH_2SiMe_3)_2(THF)_2$ (1.10 mmol, 1.01 eq.) in toluene (20 mL) was added and the reaction was stirred for 12 h at rt. The reaction mixture was filtered, the solvent was removed, and the residue was redissolved in a mixture of toluene/pentane (1:10) and filtered over Celite. The filtrate was evaporated to afford ^{R}(PdmBox)Cr(CH_2SiMe_3) complex as dark-red solid. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **3b** in *n*-hexane at −40 °C.

2.2.1 [$^{(R)\text{-}Ph}$(PdmBox)Cr(CH_2SiMe_3)]



2a

Yield: dark-red solid (442.7 mg, 70 %).

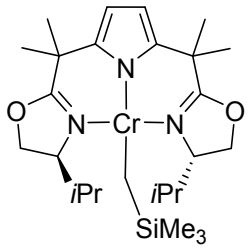
^{1}H NMR (C_6D_6, 600.13 MHz, 295 K, paramagnetic): δ [ppm] = 21.97, 20.21, 9.08 4.58, –24.46.

Magnetic Susceptibility (Evans, C_6D_6, 295 K)[12]:μ_{eff} = 4.73 μ_B.

EA: calcd. C: 66.29, H: 7.13, N: 7.25; found: C: 64.94, H: 6.90, N: 7.49.[1]

MS (LIFDI$^+$): m/z calcd. for $[C_{29}H_{31}CrN_3O_2]^+$, $[M\text{-}HSiMe_3]^+$: 505.6; found: 505.6.

2.2.2 [*(S)*-*i*Pr(PdmBox)Cr(CH_2SiMe_3)]



2b

Yield: dark-red solid (409.7 mg, 73 %).

^{1}H NMR (C_6D_6, 600.13 MHz, 295 K, paramagnetic): δ [ppm] = 31.93, 21.99, 14.72, 6.78, 4.39, –25.59.

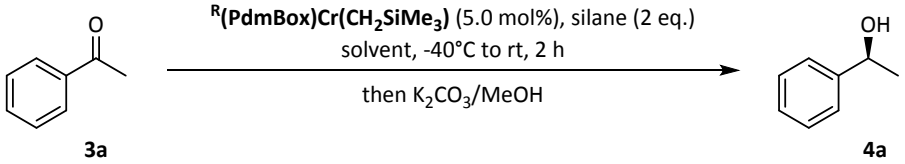
EA: calcd. C: 61.02 %, H: 8.86 %, N: 8.21 %; found: C: 59.28 %, H: 8.23 %, N: 7.93 %.[1]

MS (LIFDI+): m/z calcd. for $[C_{23}H_{35}CrN_3O_2]^+$, $[M\text{-}HSiMe_3]^+$: 437.2; found: 437.2.

[1] Systematical and analytical bias due to the high air and moist sensitivity of the alkyl complexes.

3. Catalysis

3.1 Catalytic Enantioselective Reduction



3a **4a**

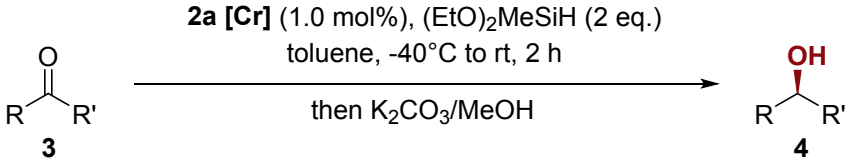
A solution of the precatalyst ^{R}(PdmBox)Cr(CH_2SiMe_3) **2a** or **2b** (6.20 µmol, 5.0 mol%; down to 0.12 µmol, 0.1 mol%) and acetophenone **3a** (15.0 mg, 0. 12 mmol, 1.0 eq.) in 1 mL solvent was cooled to −40 °C. Neat silane (0.25 mmol, 2.0 eq.) was added in one portion and the mixture was warmed to rt over a period of 2 h. The resulting silyl ether was hydrolyzed by adding a saturated solution of K_2CO_3 in MeOH (2 mL). The mixture was stirred for 1 h and filtered through a pad of silica. The residue was eluted with DCM and analyzed by chiral HPLC.

Table S1 Optimizing the reaction conditions for the hydrosilylation of ketones.

#	R	Solvent	Silane	Cat. load. [mol%]	Conv. [%][a]	ee [%][a]
1	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	5.0	> 99	95 *(S)*
2	(*S*)-*i*Pr	toluene	$(EtO)_2MeSiH$	5.0	> 99	75 *(R)*
3	(*R*)-Ph	toluene	$(EtO)_3SiH$	5.0	> 99	83 *(S)*
4	(*R*)-Ph	toluene	*n*$BuSiH_3$	5.0	> 99	84 *(S)*
5	(*R*)-Ph	toluene	PMHS[b]	5.0	58	84 *(S)*
6[c]	(*R*)-Ph	toluene	$PhSiH_3$	5.0	> 99	70 *(S)*
7[c]	(*R*)-Ph	toluene	Ph_2SiH_2	5.0	0	n.d.
8[c]	(*R*)-Ph	toluene	Me_2PhSiH	5.0	0	n.d.
9	(*R*)-Ph	*n*-pentane	$(EtO)_2MeSiH$	5.0	> 99	90 *(S)*
10	(*R*)-Ph	*n*-hexane	$(EtO)_2MeSiH$	5.0	> 99	90 *(S)*
11	(*R*)-Ph	Et_2O	$(EtO)_2MeSiH$	5.0	> 99	90 *(S)*
12	(*R*)-Ph	THF	$(EtO)_2MeSiH$	5.0	> 99	86 *(S)*
13	(*R*)-Ph	tmeda	$(EtO)_2MeSiH$	5.0	> 99	80 *(S)*
14	(*R*)-Ph	DCM	$(EtO)_2MeSiH$	5.0	0	n.d.
15	(*R*)-Ph	MeCN	$(EtO)_2MeSiH$	5.0	0	n.d.
16	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	2.5	> 99	95 *(S)*
17	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	1.0	> 99	95 *(S)*
18	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	0.5	> 99	95 *(S)*
19	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	0.25	53	95 *(S)*
20	(*R*)-Ph	toluene	$(EtO)_2MeSiH$	0.1	0	n.d.

[a]Determined by chiral HPLC. [b]PMHS = Poly(methylhydrosiloxane). [c]Work-up with NaOH in *i*PrOH.

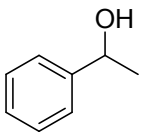
3.2 Enantioselective Hydrosilylation of Ketones



A solution of the precatalyst **2a** (0.72mg, 5.2µmol, 1.0 mol%) and the substrate **3** (0.52mmol, 1.0 eq.) in 1 mL toluene was cooled to −40 °C in a cold bath. Neat $(EtO)_2MeSiH$ (168 µl, 1.04 mmol, 2.0 eq.) was added in one portion and the mixture was allowed to warm to rt in that bath over a period of 2 h. The resulting silyl ether was hydrolyzed by adding a saturated solution of K_2CO_3 in MeOH (2 mL). The mixture was stirred for 1 h and filtered through a pad of silica. The residue was eluted with DCM. The organic layer was brined (5 mL) and the aqueous phase was washed with ethyl acetate (2 × 3 mL). The resulting alcohol **5** was purified by FCC (SiO_2, PE/EA 10:1) and analyzed by NMR spectroscopy and chiral HPLC or chiral GC. The absolute configuration was determined by comparison with reported data and commercially available samples.[13]

3.3 Characterization of Alcohols

4a **1-Phenylethanol**



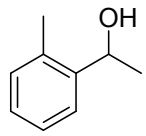
Yield: colorless liquid (56.2 mg, 89 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.36-7.32 (m, 4H), 7.26-7.23 (m, 1H), 4.87 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 1.91 (s, 1H), 1.48 (d, $^3J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 145.8, 128.5, 127.5, 125.4, 70.4, 25.1.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 15.2 min *(R)*, t_R = 19.9 min *(S)*; 95 %ee *(S)*.

4b **1-(2-Tolyl)ethanol**



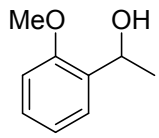
Yield: colorless liquid (61.8 mg, 87 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.50 (d, $^3J_{H,H}$= 7.5 Hz, 1H), 7.25-7.22 (m, 1H), 7.19-7.13 (m, 2H), 5.15 (q, $^3J_{H,H}$= 6.5 Hz, 1H), 2.35 (s, 3H), 1.66 (s, 1H), 1.47 (d, $^3J_{H,H}$= 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 143.8, 134.3, 130.4, 127.2, 126.4, 124.5, 66.8, 23.9, 18.9.

Chromatography: Chiralpak AD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 14.2 min *(R)*, t_R=16.4 min *(S)*; 98 %ee *(S)*.

4c **1-(2-Methoxyphenyl)ethanol**



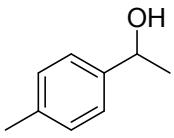
Yield: colorless solid (69.9 mg, 89 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.33-7.32 (m,1H), 7.26-7.23 (m, 1H), 6.96-6.95 (m, 1H), 6.88 (d, $^3J_{H,H}$= 8.2 Hz, 1H), 5.09 (q, $^3J_{H,H}$= 6.5 Hz, 1H), 3.87 (s, 3H), 2.55 (s, 1H), 1.50 (d, $^3J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 166.9, 150.9, 129.8, 129.3, 125.3, 70.0, 52.1, 25.3.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 99:1, 1.0 mL/min, 25 °C, λ = 210 nm); t_R = 25.6 min *(S)*, t_R = 27.9 min *(R)*; 94 %ee *(S)*.

4d **1-(4-Tolyl)ethanol**



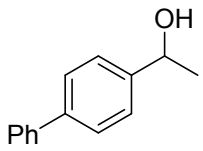
Yield: colorless liquid (63.7 mg, 91 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.24 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 7.15 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 4.85 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 2.32 (s, 3H), 1.75 (s, 1H), 1.46 (d, $^3J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 142.8, 137.2, 129.2, 125.4, 70.3, 25.1, 21.1.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 98:2, 1.0mL/min, 20 °C, λ = 210 nm); t_R = 15.1 min *(S)*, t_R = 17.8 min *(R)*; 98 %ee *(S)*.

4e 1-([1,1'-Biphenyl]-4-yl)ethanol



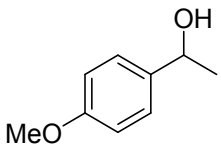
Yield: colorless solid (94.7 mg, 92 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.60-7.58 (m, 4H), 7.46-7.42 (m, 4H), 7.36-7.33 (m, 1H), 4.97 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 1.75 (s, 1H), 1.55 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 144.8, 140.9, 140.5, 128.8, 127.3, 127.1, 125.8, 70.2, 25.2.

Chromatography: Chiralpak AD-H (Hexane/*i*PrOH 95:5, 0.8 mL/min, 20 °C, λ = 230 nm); t_R = 16.1 min *(S)*, t_R = 17.6 min *(R)*; 90 %ee *(S)*.

4f 1-(4-Methoxyphenyl)ethanol



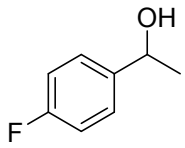
Yield: yellow liquid (73.1 mg, 91 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.27 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H), 6.89 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 4.87 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 3.81 (s, 3H), 1.72 (s, 1H), 1.50 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 158.5, 137.7, 126.4, 113.6, 69.8, 55.3, 25.1.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 10 °C, λ = 210 nm); t_R = 25.1 min *(R)*, t_R = 26.8 min *(S)*; 90 %ee *(S)*.

4g 1-(4-Fluorophenyl)ethanol



Yield: colorless liquid (64.3 mg, 87 %).

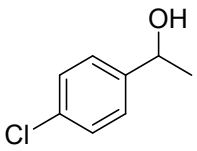
^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.36-7.32 (m, 2H), 7.05-7.00 (m, 2H), 4.90 (q, $^{3}J_{H,H}$ = 6.4 Hz, 1H), 1.82 (s, 1H), 1.48 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 162.1 (d, J = 262.0 Hz), 141.4 (d, J = 3.4 Hz) , 127.9 (d, J = 9.7 Hz), 115.3 (d, J = 23.7 Hz), 69.8, 25.3.

^{19}F NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = –115.3.

Chromatography: Chiraldex BP-M (mode: isothermal, 170 kPa, 120 °C); t_R = 16.4 min *(S)*, t_R = 16.9 min *(R)*; 90 %ee *(S)*.

4h **1-(4-Chlorophenyl)ethanol**



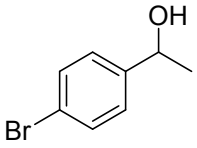
Yield: slightly yellow liquid (71.4 mg, 88 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.24-7.20 (m, 4H), 4.79 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 2.07 (s, 1H), 1.40 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 144.3, 133.0, 128.6, 126.8, 69.7, 25.3.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 95:5, 0.7 mL/min, 20 °C, λ = 210 nm); t_R = 11.3 min *(S)*, t_R = 12.1 min *(R)*; 89 %ee *(S)*.

4i **1-(4-Bromophenyl)ethanol**



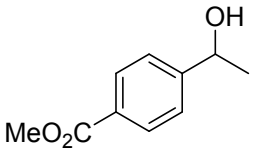
Yield: yellow liquid (97.2 mg, 92 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.47 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 7.26 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 4.87 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 1.76 (s, 1H), 1.47 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 144.7, 131.6, 127.2, 121.2, 69.8, 25.3.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 95:5, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 8.6 min *(S)*, t_R = 9.2 min *(R)*; 86 %ee *(S)*.

4j **Methyl 4-(1-Hydroxyethyl)benzoate**



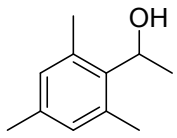
Yield: colorless liquid (29.1 mg, 31 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 8.02 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H), 7.45 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 4.96 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 3.91 (s, 3H), 1.82 (s, 1H), 1.50 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 166.9, 150.9, 129.8, 129.3, 125.3, 70.0, 52.1, 25.3.

Chromatography: Chiralpak AD-H (Hexane/*i*PrOH 95:5, 1.0 mL/min, 20 °C, λ = 215 nm); t_R = 17.2 min *(R)*, t_R = 18.4 min *(S)*; 50 %ee *(S)*.

4k **1-(2,4,6-Trimethylphenyl)ethanol**



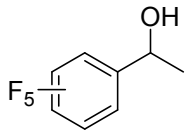
Yield: colorless solid (72.6 mg, 86 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 6.82 (s, 2H), 5.36 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 2.41 (s, 6H), 2.25 (s, 3H), 1.62 (s, 1H), 1.52 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 137.6, 136.5, 135.7, 130.2, 67.5, 52.1, 21.6, 20.7, 20.5.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 99:1, 0.8 mL/min, 20 °C, λ = 210 nm); t_R = 21.9 min *(S)*, t_R = 25.5 min *(R)*; 85 %ee *(S)*.

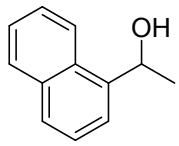
4l **1-(2,3,4,5,6-Pentafluorophenyl)ethanol**



Yield: no conv.

Chromatography: Chiralpak AD-H (Hexane/*i*PrOH 99:1, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 16.7 min *(S)*, t_R = 20.1 min *(R)*.

4m **1-(Naphthalen-1-yl)ethanol**



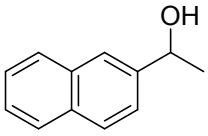
Yield: colorless solid (80.1 mg, 90 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 8.10 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 7.88 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 7.78 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 7.67 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 7.54-7.46 (m, 3H), 5.64 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 2.21 (s, 1H), 1.66 (d, $^3J_{H,H}$ = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 141.4, 133.8, 130.3, 128.9, 127.9, 127.9, 126.0, 125.6, 123.2, 122.0 67.1, 24.3.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 90:10, 0.8 mL/min, 20 °C, λ = 210 nm); t_R = 12.3 min *(R)*, t_R = 19.5 min *(S)*; 96 %ee *(S)*.

4n **1-(Naphthalen-2-yl)ethanol**



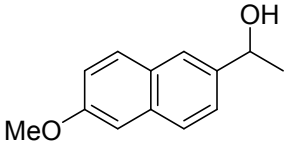
Yield: colorless solid (79.3 mg, 88 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.85-7.81 (m, 4H), 7.52-7.45 (m, 3H), 5.08 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 1.88 (s, 1H), 1.59 (d, $^3J_{H,H}$ = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 143.1, 133.2, 132.9, 128.3, 127.9, 127.7, 126.1, 125.8, 123.8, 70.6, 52.1, 25.2.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 95:5, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 16.5 min *(R)*, t_R = 17.8 min *(S)*; 90 %ee *(S)*.

4o **9-Methoxy-1-(Naphthalen-2-yl)ethanol**



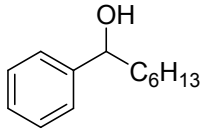
Yield: colorless solid (95.8 mg, 90 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295K): δ [ppm] = 7.74-7.71 (m, 3H), 7.48-7.46 (m, 1H), 7.16-7.12 (m, 2H), 5.04 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 3.91 (s, 3H), 1.89 (s, 1H), 1.57 (d, $^3J_{H,H}$ = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295K): δ [ppm] = 157.6, 140.9, 134.0, 129.4, 128.7, 127.2, 124.4, 123.8, 118.9, 70.5, 55.2, 20.7, 25.1.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 95:5, 0.8 mL/min, 20 °C, λ = 210 nm); t_R = 19.5 min *(S)*, t_R = 28.0 min *(R)*; 92 %ee *(S)*.

4p **1-Phenylheptanol**



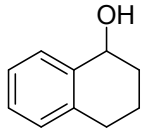
Yield: colorless liquid (89.3 mg, 90 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.35-7.26 (m, 5H), 4.66 (dd, $^3J_{H,H}$ = 7.0 Hz, 1H), 1.83-1.77 (m, 1H), 1.73-1.66 (m, 1H), 1.58 (s, 1H), 1.43-1.37 (m, 1H), 1.33-1.23 (m, 7H), 0.87 (t, $^3J_{H,H}$ = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 144.9, 128.4, 127.5, 125.9, 74.7, 39.1, 31.7, 29.2, 25.8, 22.6.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 99:1, 0.8 mL/min, 20 °C, λ = 210 nm); t_R = 18.1 min *(R)*, t_R = 22.8 min *(S)*; 86 %ee *(S)*.

4q **1,2,3,4-Tetrahydronaphthalen-1-ol**



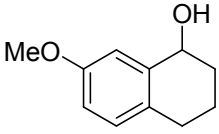
Yield: yellow liquid (72.8 mg, 93 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.46-7.44 (m, 1H), 7.25-7.22 (m, 2H), 7.15-7.12 (m, 1H) 4.82 (t, $^3J_{H,H}$ = 4.5 Hz, 1H), 2.89-2.73 (m, 2H), 2.06-1.92 (m, 3H), 1.84-1.79 (m, 1H), 1.76 (s, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 138.7, 137.1, 129.0, 128.7, 127.6, 126.2, 68.1, 32.3, 29.3, 18.8.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 99:1, 1.0 mL/min, 20 °C, λ = 215 nm); t_R = 23.9 min *(S)*, t_R = 27.5 min *(R)*; 93 %ee *(S)*.

4r **7-Methoxy-1,2,3,4-tetrahydronaphthalen-1-ol**



Yield: yellowish solid (77.2 mg, 91 %).

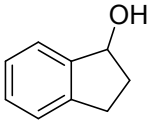
^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.02 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 6.96 (d, $^3J_{H,H}$ = 2.4 Hz, 1H), 6.78 (dd, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 2.4 Hz , 1H), 4.74

(t, $^{3}J_{H,H}$ = 5.4 Hz, 1H), 3.79 (s, 3H), 2.77-2.63 (m, 2H), 2.04-1.91 (m, 2H), 1.88-1.84 (m, 1H), 1.78-1.74 (m, 1H), 1.67 (s, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 157.6, 139.5; 129.7, 128.9, 114.2, 112.4, 68.5, 55.4, 32.5, 28.6, 19.3.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 95:5, 0.7 mL/min, 20 °C, λ = 215 nm); t_R = 42.8 min *(S)*, t_R = 50.2 min *(R)*; 87 %ee *(S)*.

4s **2,3-Dihydro-1H-inden-1-ol**



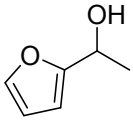
Yield: slightly yellow liquid (69.4 mg, 89 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.42 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 7.28-7.23 (m, 3H), 5.26 (t, $^{3}J_{H,H}$ = 6.2 Hz, 1H), 3.09-3.01 (m, 1H), 2.85-2.80 (m, 1H), 2.52-2.48 (m, 1H), 1.99-1.92 (m, 1H), 1.64 (s, 1H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 144.9, 143.4, 128.4, 126.7, 124.9, 124.2, 76.5, 36.0, 29.8.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 17.6 min *(S)*, t_R = 20.1 min *(R)*; 94 %ee *(S)*.

4t **1-(Furan-2-yl)ethanol**



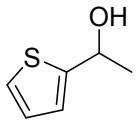
Yield: red liquid (40.7 mg, 67 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.37 (m, 1H), 6.32 (dd, $^{3}J_{H,H}$ = 6.5 Hz, $^{3}J_{H,H}$ = 3.7 Hz , 1H), 6.22 (d, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 4.88 (q, $^{3}J_{H,H}$ = 6.5 Hz, 1H), 2.56 (s, 1H), 1.54 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 149.3, 126.2, 124.4, 124.0, 123.5, 69.3, 65.3 25.2.

Chromatography: Chiralcel OJ-H (Hexane/*i*PrOH 99:1, 1.0 mL/min, 20 °C, λ = 215 nm); t_R = 30.3 min *(S)*, t_R = 33.3 min *(R)*; 90 %ee *(S)*.

4u **1-(Thiophen-2-yl)ethanol**



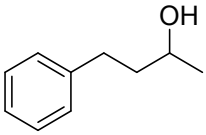
Yield: yellow liquid (59.3 mg, 90 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.24 (dd, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 3.7 Hz , 1H), 6.99-6.93 (m, 2H), 5.14 (q, $^3J_{H,H}$ = 6.4 Hz, 1H), 1.99 (s, 1H), 1.61 (d, $^3J_{H,H}$ = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 149.6, 126.7, 124.5, 124.0, 123.6, 70.3, 66.3 25.3.

Chromatography: Chiralcel OJ-H (Hexane/*i*PrOH 99:1, 1.0 mL/min, 20 °C, λ = 215 nm); t_R = 38.7 min *(S)*, t_R = 46.7 min *(R)*; 90 %ee *(S)*.

4v **4-Phenylbutan-2-ol**



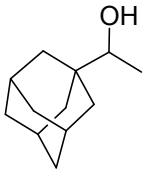
Yield: colorless liquid (63.2 mg, 84 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.32-7.30 (m, 2H), 7.23-7.20 (m, 3H), 3.86 (sext., $^3J_{H,H}$ = 6.2 Hz, 1H), 2.81-2.76 (m, 1H), 2.72-2.67 (m, 1H), 1.85-1.75 (m, 2H), 1.59 (s, 1H), 1.26 (d, $^3J_{H,H}$ = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 142.1, 128.4, 125.8, 67.5, 40.8, 32.2, 23.6.

Chromatography: Chiralpak AD-H (Hexane/*i*PrOH 96:4, 0.7 mL/min, 10 °C, λ = 215 nm); t_R = 13.8 min *(R)*, t_R = 14.6 min *(S)*; 30 %ee *(S)*.

4w **1-(Adamantan-1-yl)ethanol**



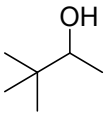
Yield: colorless liquid (76.3 mg, 81 %).

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 3.28 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 1.99 (m, 3H), 1.72-1.63 (m, 6H), 1.60-1.57 (m, 3H), 1.49-1.46 (m, 3H), 1.42 (s, 1H), 1.09 (d, $^3J_{H,H}$ = 6.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 75.8, 37.7, 37.2, 36.6, 28.3, 16.5.

Chromatography: Analysis of the benzoic ester**,** Chiralpak AD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 25 °C, λ = 230 nm); t_R = 5.0 min *(R)*, t_R = 5.7 min *(S)*; 95 %ee *(S)*.

4x **3,3-Dimethylbutan-2-ol**



Yield: colorless liquid (32.4 mg, 62 %).

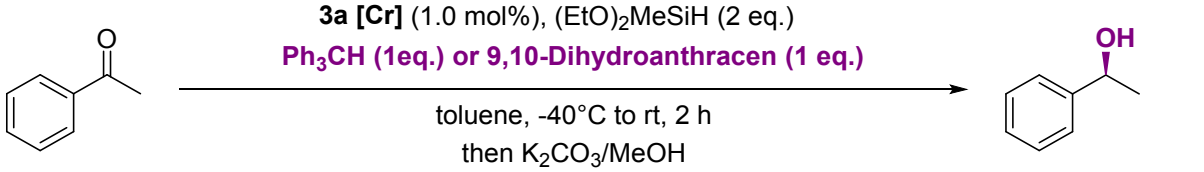
^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 3.46 (q, $^3J_{H,H}$ = 6.5 Hz, 1H), 1.62 (s, 1H), 1.17 (d, $^3J_{H,H}$ = 6.5 Hz, 3H), 0.89 (m, 9H).

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 75.6, 34.9, 25.5, 17.9.

Chromatography: Analysis of the bezoic ester Chiralcel OD-H (Hexane/*i*PrOH 100:0, 0.5 mL/min, 25 °C, λ = 230 nm); t_R = 10.0 min *(R)*, t_R = 10.7 min *(S)*; 90 %ee *(S)*.

4. Mechanistic Studies

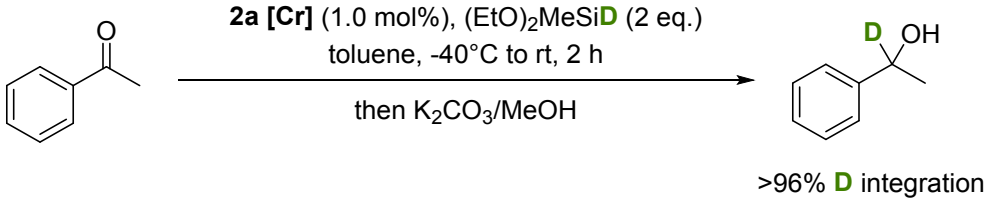
4.1 Radical Trap Experiments



The reduction of acetophenone **3a** (15.0 mg, 124 µmol, 1.0 eq.) was accomplished by the general procedure with a radical trap reagent (triphenylmethane (124 µmol, 1.0 eq.) or 9,10-dihydroanthracene (124 µmol, 1.0 eq.)). The obtained product was analyzed by chiral HPLC.

Chromatography: Chiralcel OD-H (Hexane/*i*PrOH 98:2, 1.0 mL/min, 20 °C, λ = 210 nm); t_R = 15.2 min *(R)*, t_R = 19.9 min *(S)*; 95 %ee *(S)*.

4.2 Labelling Experiments



The reduction of acetophenone **3a** (15.0 mg, 124 µmol, 1.0 eq.) was carried out analogous to the general procedure with deuterated diethoxymethylsilane (42.0 µl, 240 µmol, 2.0 eq., 2% residual H). The obtained product **4a-*d*$_1$** was characterized by NMR spectroscopy.

^{1}H NMR ($CDCl_3$, 600.24 MHz, 295 K): δ [ppm] = 7.36-7.23 (m, 5H), 4.88 (q, $^3J_{H,H}$ = 6.5 Hz, 0.037 H), 1.91 (s, 1H), 1.48 (d, $^3J_{H,H}$ = 6.5 Hz, 1H).

^{2}H NMR ($CDCl_3$, 92.12 MHz, 295 K): δ [ppm] = 4.87.

^{13}C NMR ($CDCl_3$, 150.93 MHz, 295 K): δ [ppm] = 145.8, 128.5, 127.5, 125.4, 68.9 (t, $^{2}J_{D,C}$= 22 Hz), 25.1.

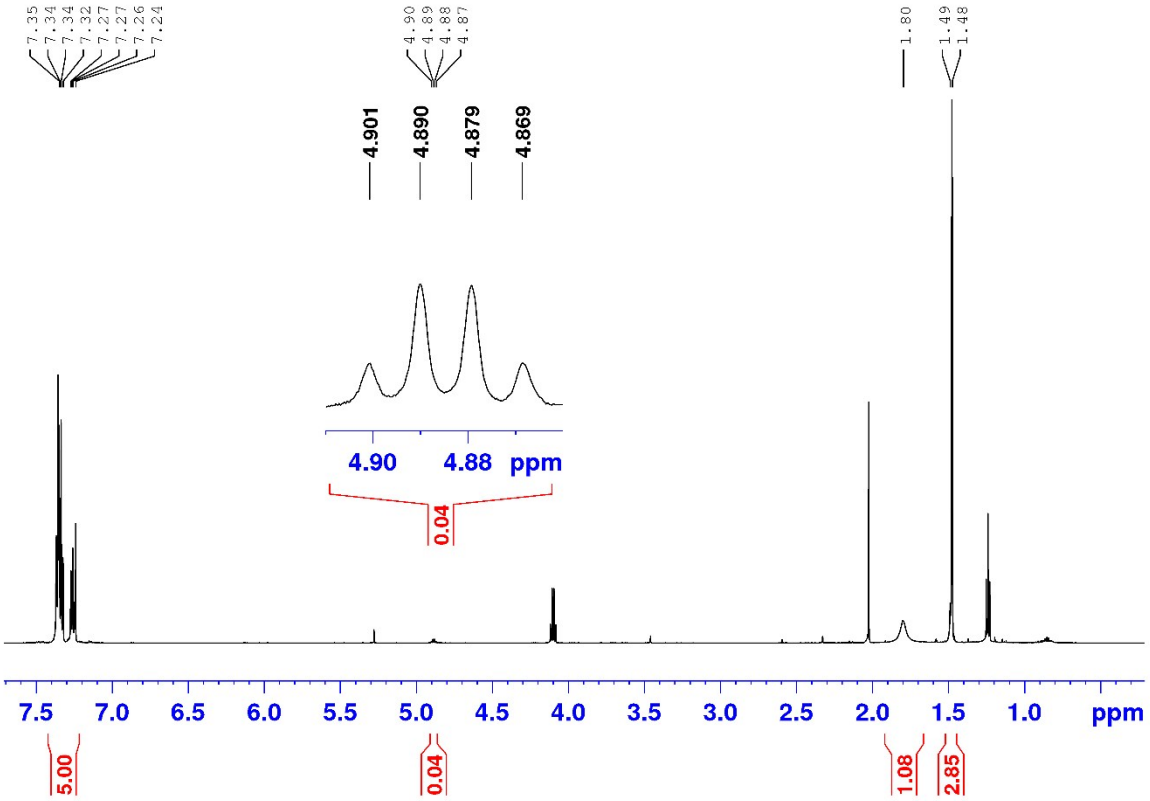
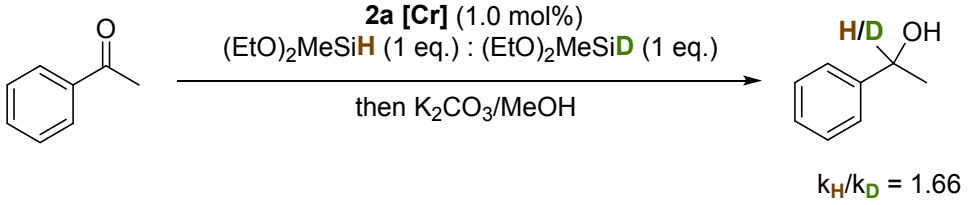


Figure S1: ^{1}H NMR spectrum of the deuterated acetophenone **4a**-d_1 with zoom at the quartet region at 4.88 ppm.

4.3 Kinetic Isotope Effect



k_H/k_D = 1.66

The reduction of acetophenone **3a** (15.0 mg, 124 µmol, 1.0 eq.) was carried out analogous to the general procedure with a mixture of equal amounts of diethoxymethylsilane (20.0 µl, 124 µmol, 1.0 eq.) and deuterated diethoxymethylsilane (20.0 µl, 124 µmol, 1.0 eq.). The ratio of deuterated to normal product was determined by ^{1}H NMR spectroscopy. The KIE was calculated using the following equation.

$$KIE = \frac{k_H}{k_D} = \frac{\ln\ (1 - F_H)}{\ln\ (1 - F_D)}$$

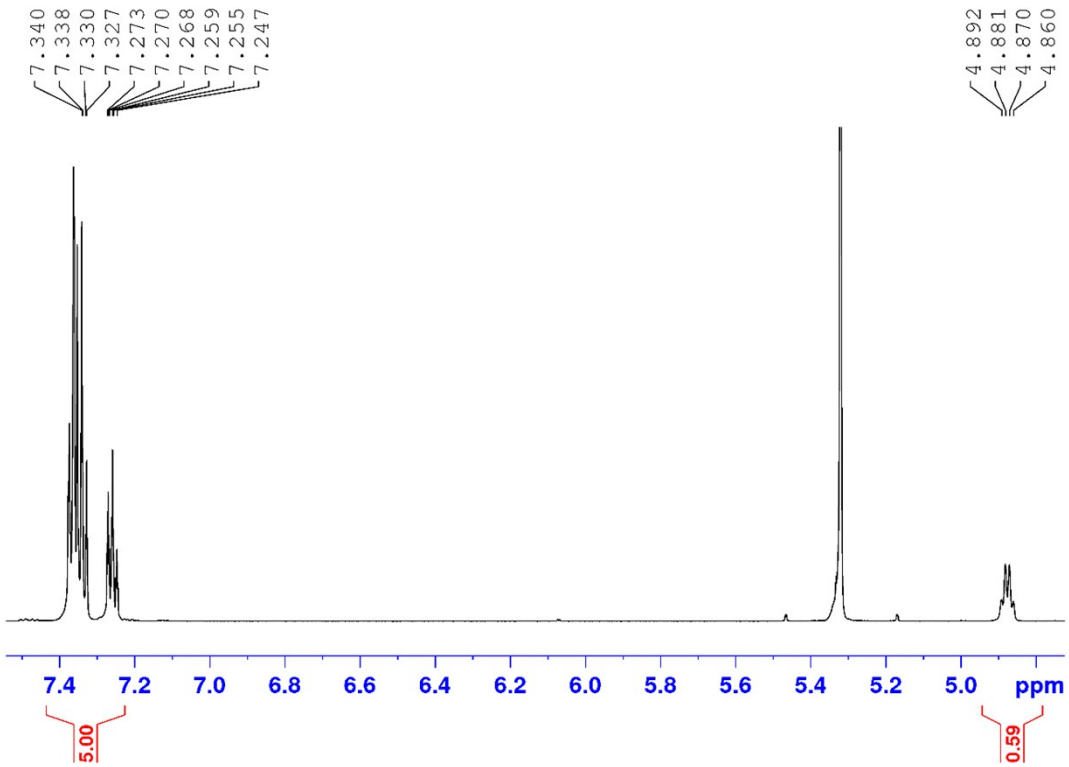


Figure S2: Extract of the ^{1}H NMR spectrum of the partially deuterated 1-phenylethanol (CD_2Cl_2, 600.24 MHz, 295 K).

KIEs of *p*-Br and *p*-OMe derivatives were calculated in analogy to the protocol outlined above.

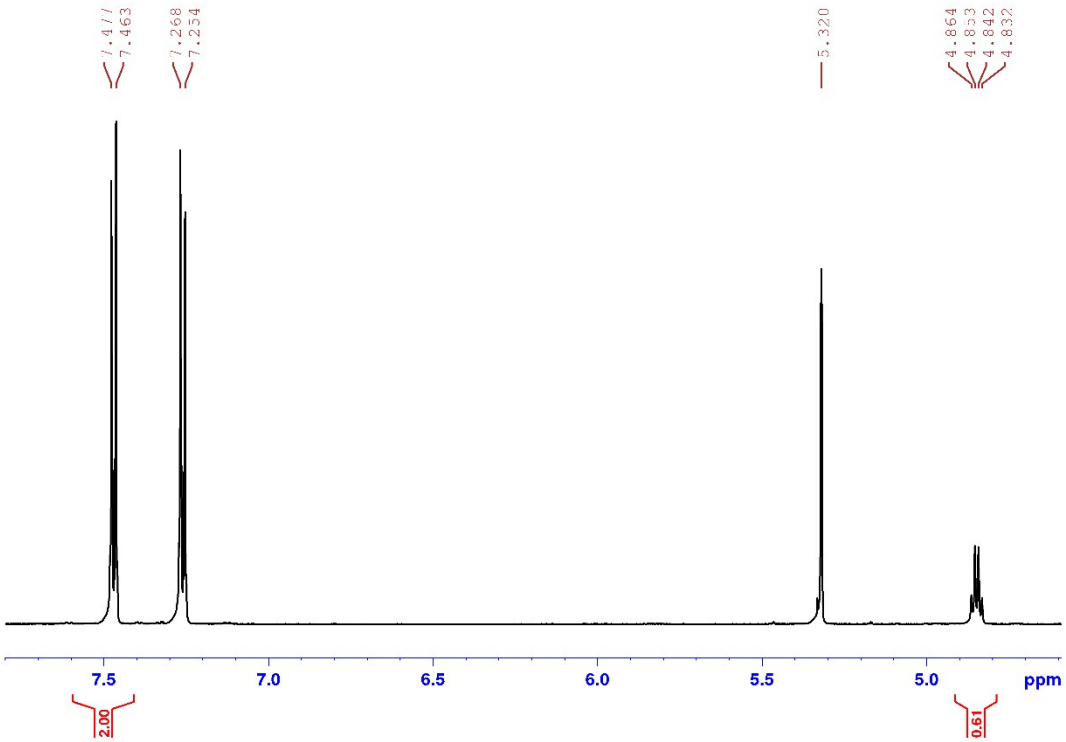


Figure S3: Extract of the ^{1}H NMR spectrum of the partially deuterated 1-(4-bromophenyl)ethanol (CD_2Cl_2, 600.24 MHz, 295 K).

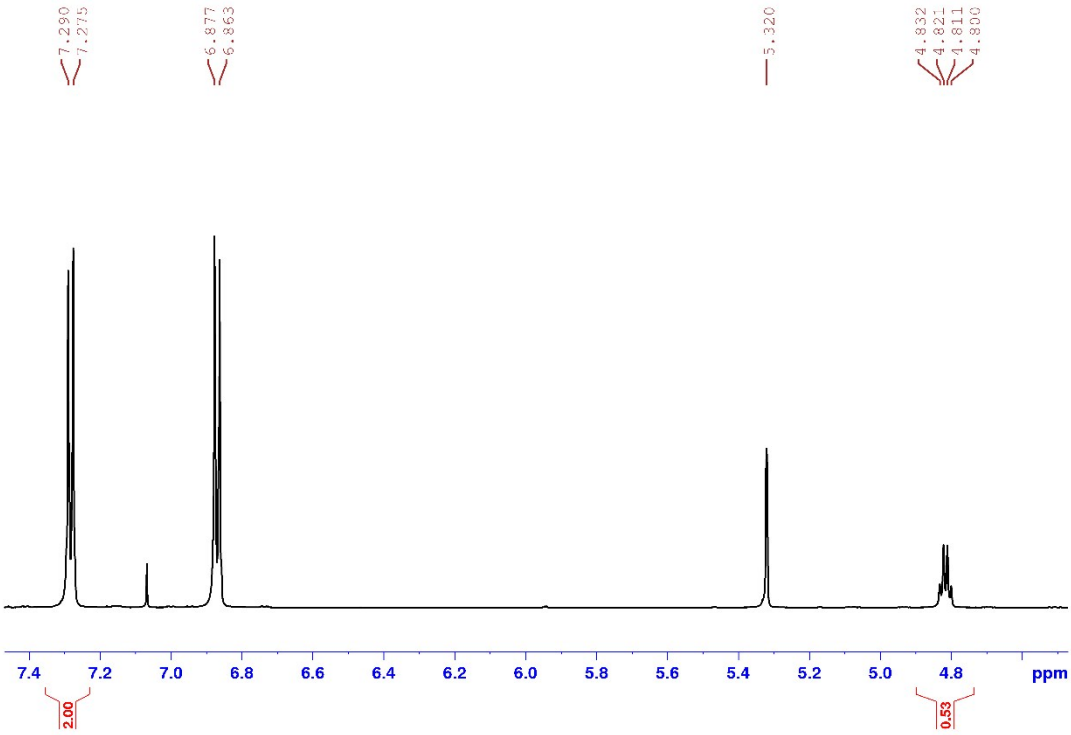


Figure S4: Extract of the ^{1}H NMR spectrum of the partially deuterated 1-(4-methoxyphenyl)ethanol (CD_2Cl_2, 600.24 MHz, 295 K).

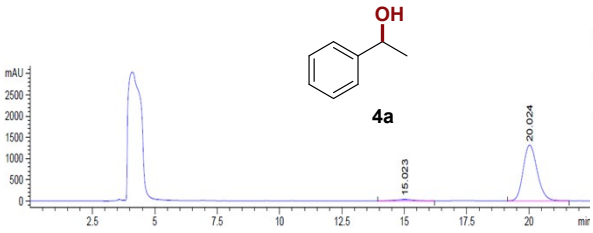
4.4 Hammett-Correlation

The precatalyst (0.72 mg, 2.6 µmol, 1.0 mol%), acetophenone 12 (15.0 mg, 124 µmol, 1.0 eq.) and one of each para substituted ketone (20mg – 35 mg each, 140 µmol – 180 µmol each, 1.0 eq. each) were dissolved in benzene-d_6 (0.5 mL). Diethoxymethylsilane (20.0 µl, 124 µmol) was added and the reaction was stirred for 2 h at rt. Afterwards, three drops of a tetrabutylammonium fluoride solution (1.0 M in THF) were added to each sample. Subsequently, all samples were analyzed by ^{13}C NMR spectroscopy (D_1-time = 5 s). The relative rate constants were determined from the NMR integral ratio of the product peaks using the following equation. The σ-values were taken from literature.[14]

$$\frac{k_R}{k_H} = \frac{\ln\left(\frac{c_{R,t}}{c_{R,t=0}}\right)}{\ln\left(\frac{c_{H,t}}{c_{H,t=0}}\right)}$$

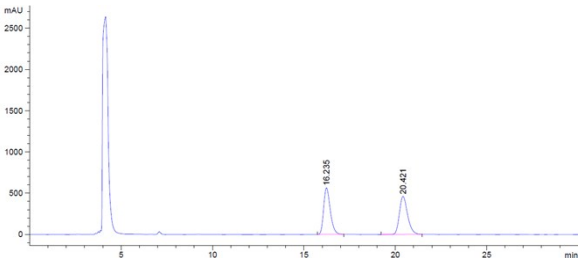
5. Chromatographic Data

4a



Signal 1: DAD1 B, Sig=215,4 Ref=360,100

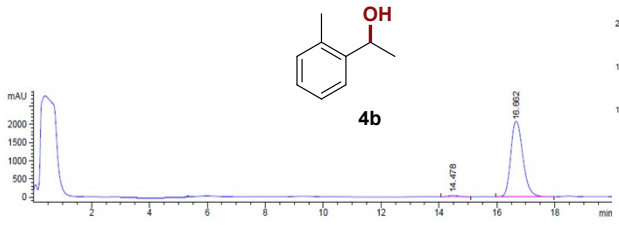
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.023	BB	0.6858	1457.72656	31.74131	2.7646
2	20.024	BB	0.6072	5.12706e4	1314.14978	97.2354
Totals :				5.27283e4	1345.89109	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

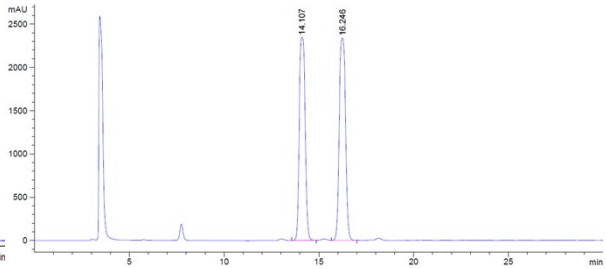
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.235	BB	0.3855	1.41906e4	564.13531	49.8150
2	20.421	BB	0.4754	1.42960e4	461.44659	50.1850
Totals :				2.84865e4	1025.58191	

4b



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

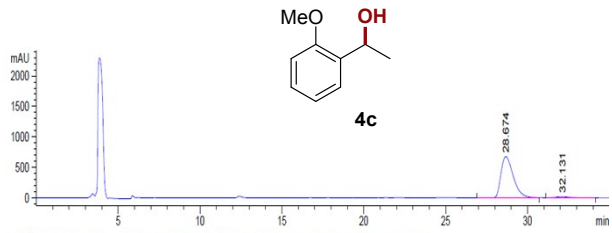
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.478	BB	0.3525	1148.20068	49.15118	1.6723
2	16.661	VB	0.4808	6.75136e4	2183.20654	98.3277
Totals :				6.86618e4	2232.35772	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

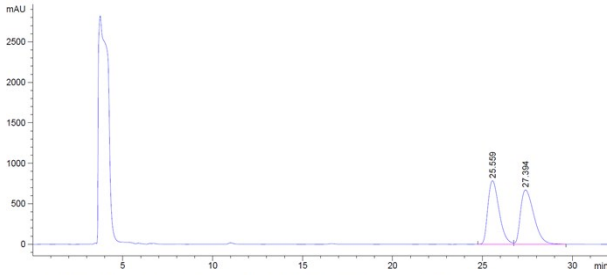
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.107	VB	0.3408	5.04860e4	2348.27759	48.4725
2	16.246	VB	0.3657	5.36680e4	2338.56616	51.5275
Totals :				1.04154e5	4686.84375	

4c



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

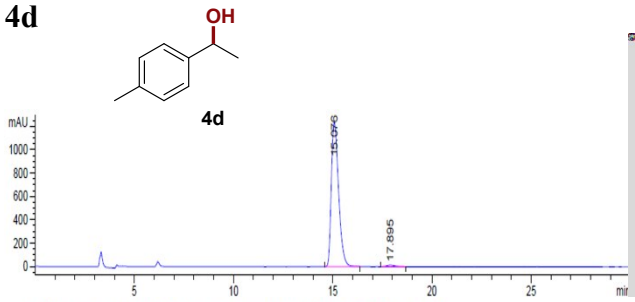
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.674	VB	0.8189	3.54312e4	676.64203	97.4371
2	32.131	BB	0.6916	931.95123	18.38011	2.5629
Totals :				3.63631e4	695.02214	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.559	BV	0.6816	3.40193e4	784.95398	49.6908
2	27.394	VB	0.8131	3.44427e4	670.69806	50.3092
Totals :				6.84621e4	1455.65204	

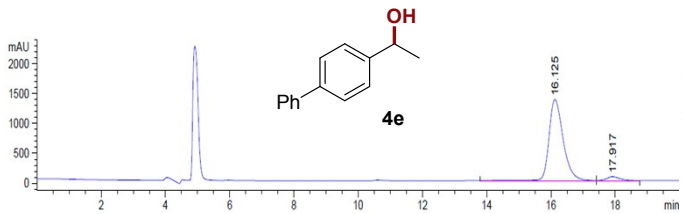
4d



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

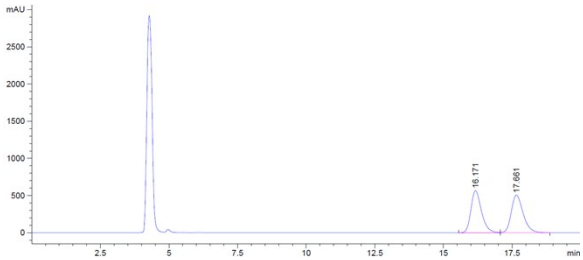
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.076	BB	0.3968	3.08068e4	1211.06824	98.3216
2	17.884	BV	0.4845	525.88599	15.71191	1.6784
Totals :				3.13327e4	1226.78015	

4e



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

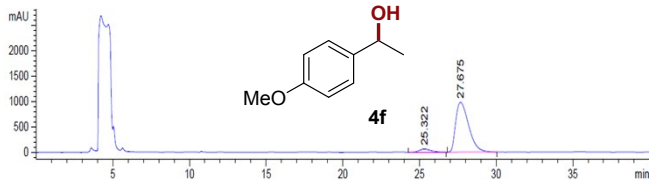
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.125	BB	0.4665	4.15811e4	1360.79980	95.7412
2	17.917	BB	0.4309	1849.61389	65.21682	4.2588
Totals :				4.34307e4	1426.01662	



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

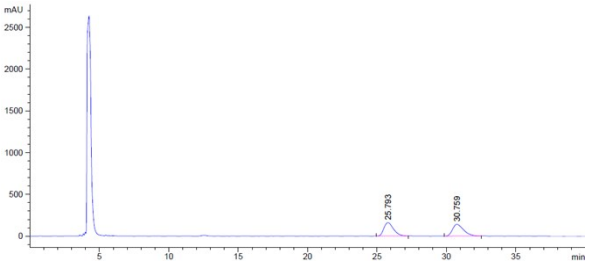
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.171	BV	0.4061	1.51945e4	568.00879	49.9848
2	17.661	VB	0.4602	1.52037e4	506.53748	50.0152
Totals :				3.03982e4	1074.54626	

4f



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

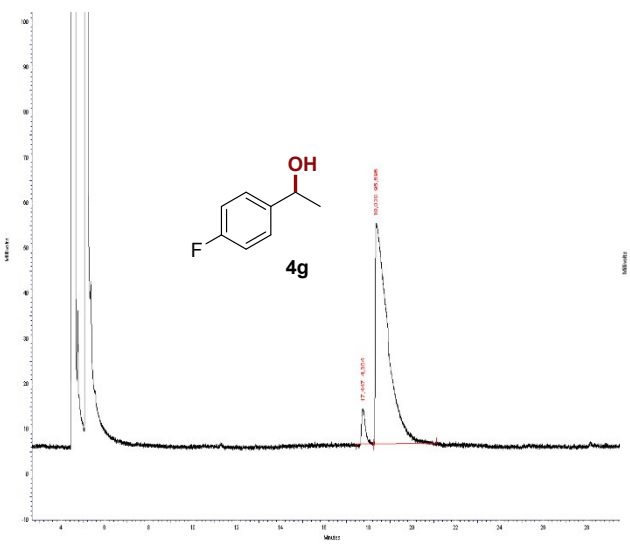
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.322	VB	0.7574	3083.91235	61.67646	5.0870
2	27.675	BB	0.9444	5.75396e4	980.84735	94.9130
Totals :				6.06235e4	1042.52382	

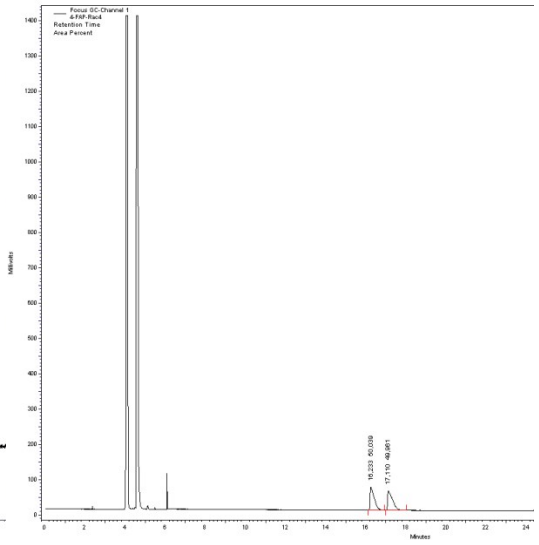


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

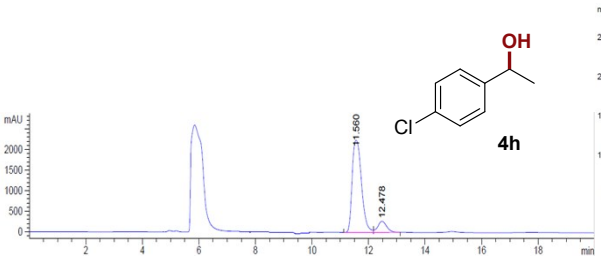
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.793	BB	0.7417	7765.30859	161.27690	49.8027
2	30.759	BB	0.8659	7826.82031	142.26196	50.1973
Totals :				1.55921e4	303.53886	

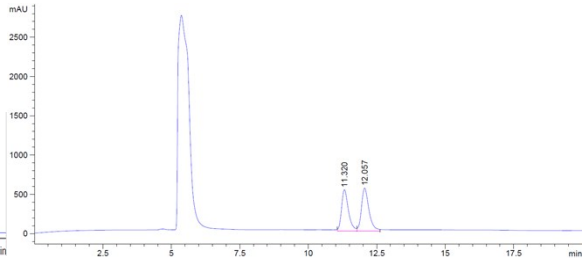
4g





4h





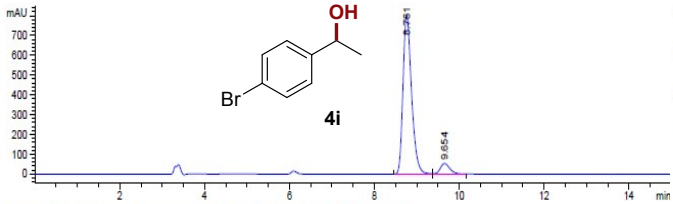
Signal 3: DAD1 C, Sig=210,8 Ref=360,100

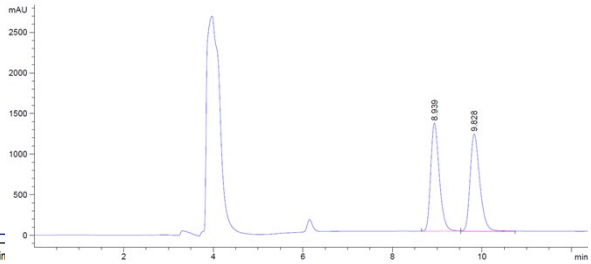
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.342	MM	0.2816	2.19660e4	1300.26270	96.9659
2	12.072	MM	0.2745	687.32568	41.72610	3.0341
Totals :				2.26533e4	1341.98880	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.320	MF	0.2907	9168.56348	525.70673	46.8626
2	12.057	FM	0.3172	1.03962e4	546.27844	53.1374
Totals :				1.95648e4	1071.98517	

4i





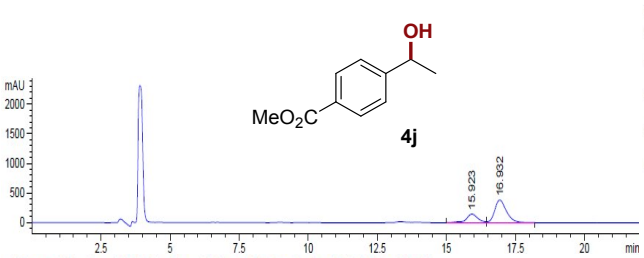
Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.761	BV	0.2154	9576.69043	683.63574	93.0471
2	9.654	VB	0.2391	715.61804	45.60443	6.9529
Totals :				1.02923e4	729.24017	

Signal 1: DAD1 C, Sig=210,8 Ref=360,100

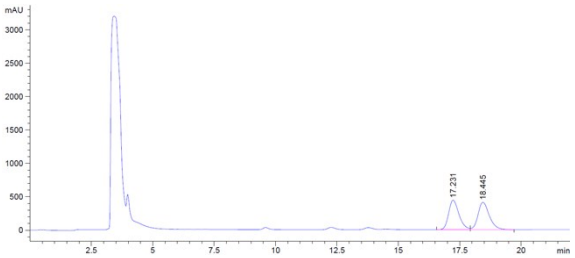
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.939	BV	0.2032	1.77246e4	1332.23499	49.8299
2	9.828	VB	0.2279	1.78456e4	1197.48718	50.1701
Totals :				3.55702e4	2529.72217	

4j



Signal 3: DAD1 D, Sig=215,4 Ref=360,100

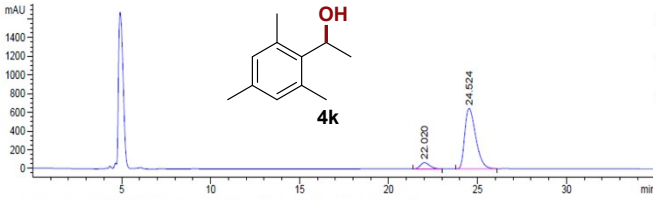
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.923	MM	0.4323	2840.11377	109.48695	24.5643
2	16.932	MM	0.4675	8721.85059	310.91879	75.4357
Totals :				1.15620e4	420.40575	



Signal 3: DAD1 D, Sig=215,4 Ref=360,100

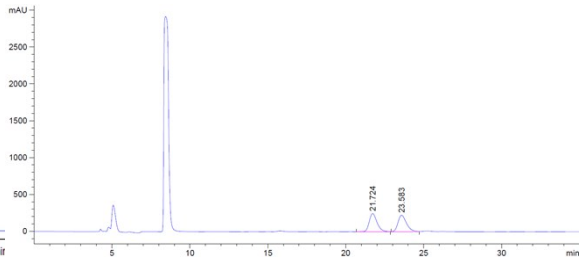
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.231	BV	0.4472	1.29377e4	442.44095	49.6298
2	18.445	VB	0.4872	1.31307e4	410.49481	50.3702
Totals :				2.60684e4	852.93576	

4k



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

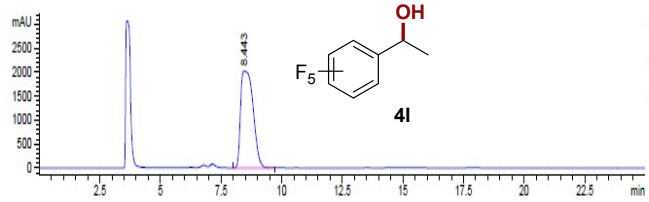
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.020	BB	0.5500	2358.32593	66.13913	7.8811
2	24.524	BB	0.6703	2.75654e4	645.44666	92.1189
Totals :				2.99237e4	711.58578	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

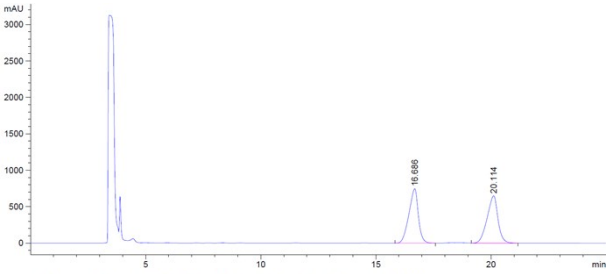
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.724	BB	0.5333	8574.23926	246.83929	50.4017
2	23.583	BB	0.5754	8437.55762	224.03615	49.5983
Totals :				1.70118e4	470.87544	

4l



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

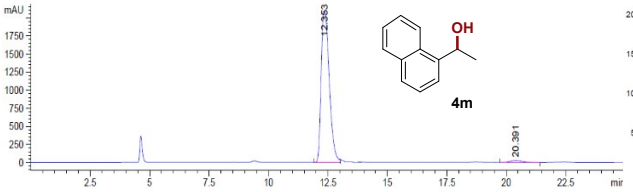
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.443	BB	0.4769	7.27329e4	2025.50549	100.0000
Totals :				7.27329e4	2025.50549	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

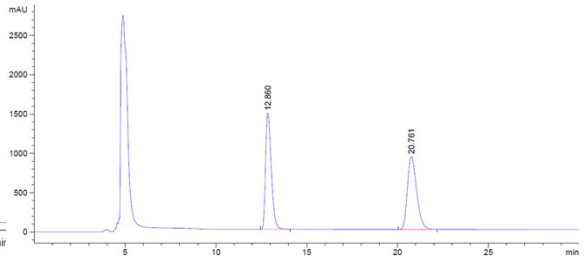
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.686	BB	0.4208	2.11732e4	746.75647	50.0781
2	20.114	VB	0.4893	2.11071e4	649.14795	49.9219
Totals :				4.22803e4	1395.90442	

4m



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

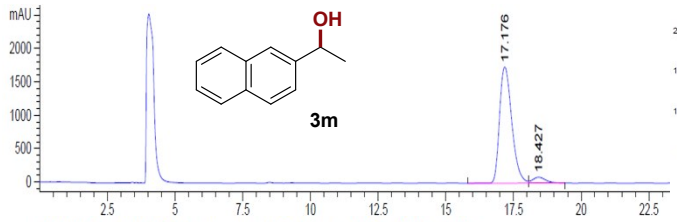
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.353	VV	0.3749	4.95475e4	2087.61694	98.0758
2	20.391	BB	0.5471	972.09729	27.45671	1.9242
Totals :				5.05196e4	2115.07365	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

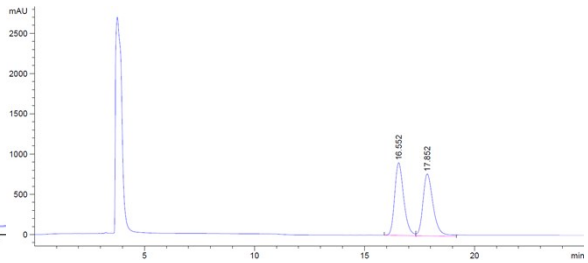
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.860	BB	0.3381	3.22216e4	1479.54590	49.6469
2	20.761	BB	0.5437	3.26799e4	930.60547	50.3531
Totals :				6.49015e4	2410.15137	

4n



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

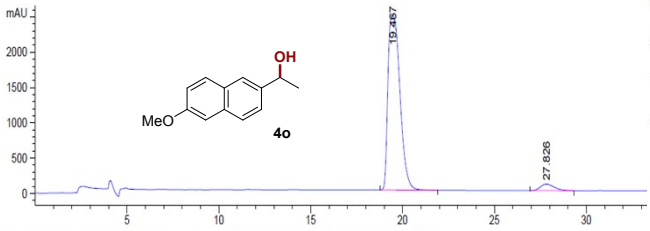
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.176	VV	0.4905	5.46712e4	1740.51355	94.7478
2	18.427	VB	0.5125	3030.59155	89.61423	5.2522
Totals :				5.77018e4	1830.12778	



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

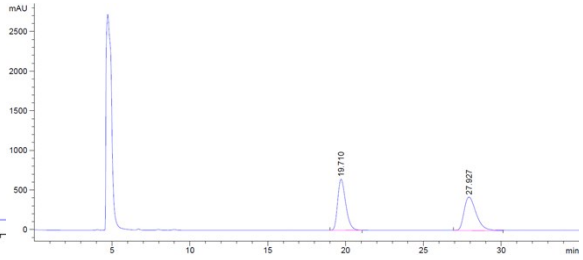
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.552	MF	0.4751	2.57487e4	903.32465	50.7427
2	17.852	FM	0.5411	2.49950e4	769.85748	49.2573
Totals :				5.07437e4	1673.18213	

4o



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

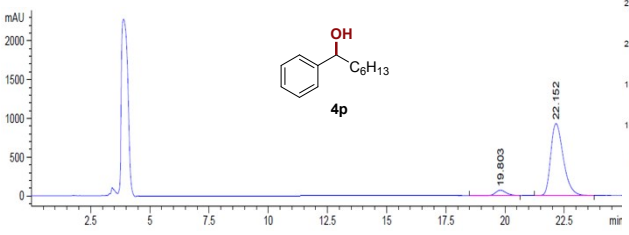
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.467	BB	0.5611	1.12585e5	2482.47021	95.9548
2	27.826	BB	0.8060	4746.30420	91.68262	4.0452
Totals :				1.17332e5	2574.15284	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

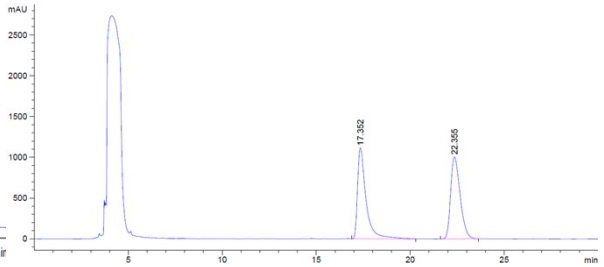
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.710	BB	0.5546	2.31084e4	644.08221	50.1815
2	27.927	MM	0.9048	2.29412e4	422.57077	49.8185
Totals :				4.60496e4	1066.65298	

4p



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

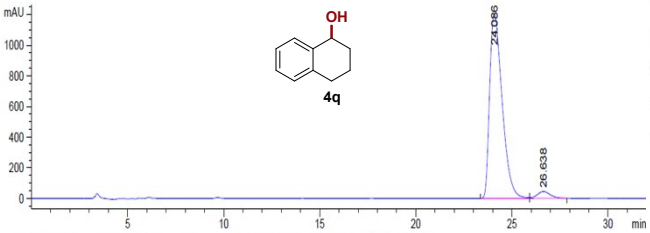
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.803	VV	0.5275	2552.06299	72.35876	6.8131
2	22.152	VB	0.5804	3.49060e4	933.17627	93.1869
Totals :				3.74580e4	1005.53503	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

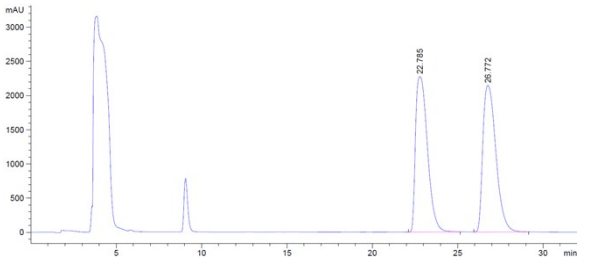
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.352	VB	0.4614	3.49421e4	1115.57532	49.9325
2	22.355	BB	0.5395	3.50366e4	1003.04236	50.0675
Totals :				6.99787e4	2118.61768	

4q



Signal 2: DAD1 D, Sig=215,8 Ref=360,100

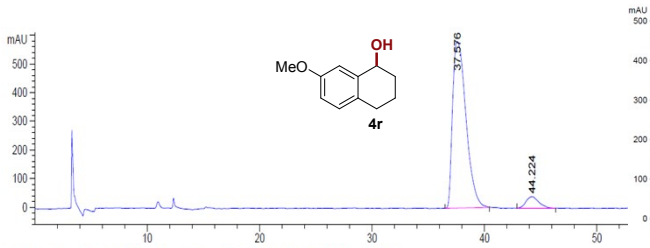
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.086	BB	0.6986	5.43163e4	1203.36731	96.2823
2	26.638	BB	0.7222	2097.27734	44.63340	3.7177
Totals :				5.64136e4	1248.00071	



Signal 2: DAD1 D, Sig=215,8 Ref=360,100

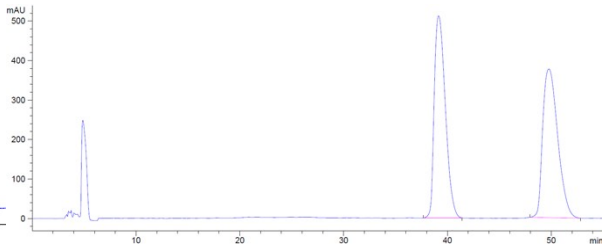
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.785	BB	0.7643	1.10023e5	2274.66260	49.1366
2	26.772	BB	0.8443	1.13890e5	2142.21973	50.8634
Totals :				2.23912e5	4416.88232	

4r



Signal 2: DAD1 D, Sig=215,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.575	BB	1.2945	3.04791e4	371.74728	94.0274
2	44.218	BB	1.0766	1936.01990	24.53619	5.9726
Totals :				3.24151e4	396.28348	

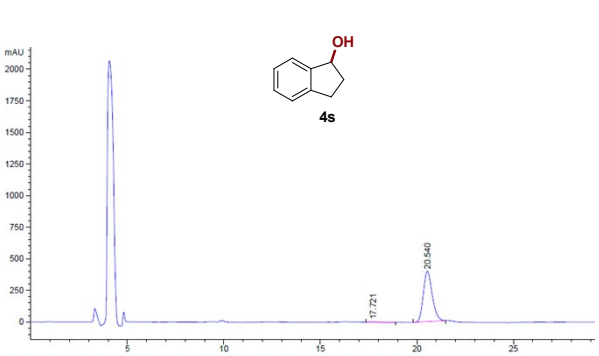


Signal 2: DAD1 D, Sig=215,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.575	BB	1.1827	3.80335e4	511.95123	50.1507
2	44.218	BB	1.6273	3.78050e4	376.56360	49.8493
Totals :				7.58385e4	888.51483	

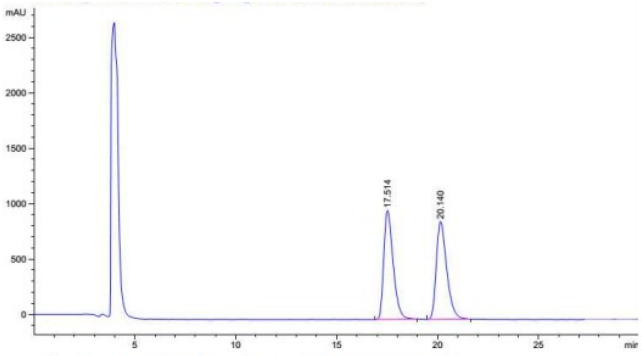
Data agree with reported racemate.[13a]

4s



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

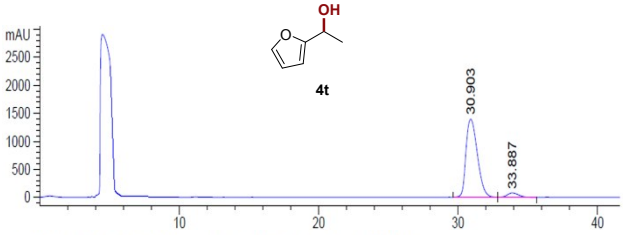
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.721	VB	0.4191	156.59662	5.20371	1.2124
2	20.540	BB	0.4924	1.27602e4	399.72852	98.7876
Totals :				1.29168e4	404.93223	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

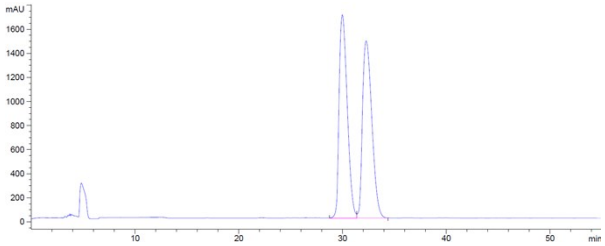
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.514	BB	0.4903	3.15029e4	981.91467	49.9212
2	20.140	BB	0.5502	3.16023e4	881.56042	50.0788

4t



Signal 1: DAD1 B, Sig=215,4 Ref=360,100

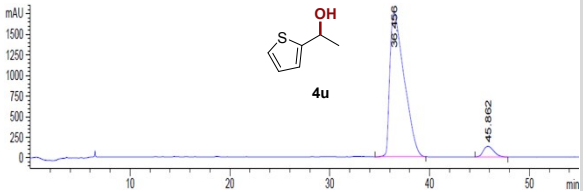
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.903	BB	0.9097	7.79231e4	1369.66309	94.6282
2	33.885	BB	0.8887	4423.52637	77.41204	5.3718
Totals :				8.23466e4	1447.07513	



Signal 1: DAD1 B, Sig=215,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.977	BV	0.8781	9.20907e4	1689.02271	49.8811
2	32.274	VB	1.0035	9.25296e4	1471.79517	50.1189
Totals :				1.84620e5	3160.81787	

4u



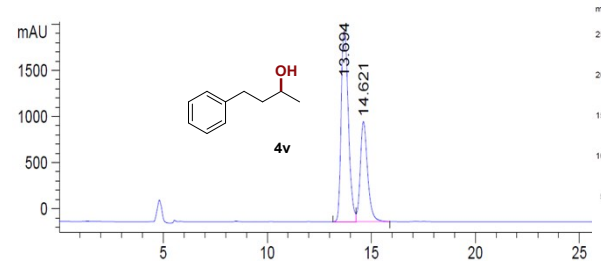
Signal 1: DAD1 B, Sig=215,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.456	VB	1.4150	1.76906e5	1768.56421	94.8289
2	45.864	BB	1.1162	9646.81250	132.05803	5.1711
Totals :				1.86553e5	1900.62224	

Signal 1: DAD1 B, Sig=215,4 Ref=360,100

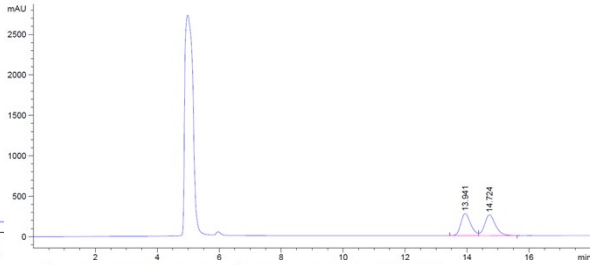
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.151	BB	1.1827	3.80335e4	511.95123	50.1507
2	49.775	BB	1.6273	3.78050e4	376.56360	49.8493
Totals :				7.58385e4	888.51483	

4v



Signal 3: DAD1 D, Sig=215,4 Ref=360,100

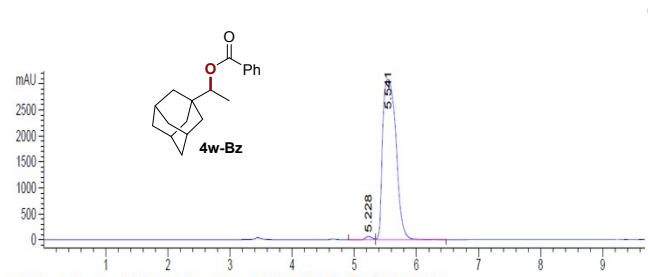
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.694	BV	0.3813	5.01619e4	2065.83276	65.3926
2	14.621	VB	0.3710	2.65469e4	1086.53491	34.6074
Totals :				7.67088e4	3152.36768	



Signal 3: DAD1 D, Sig=215,4 Ref=360,100

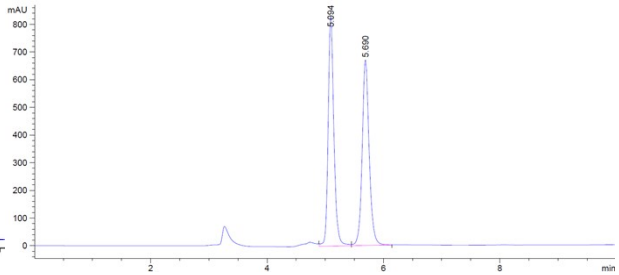
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.941	BV	0.3382	6033.42822	272.59311	49.2202
2	14.724	VB	0.3663	6224.60791	257.23038	50.7798
Totals :				1.22580e4	529.82349	

4w



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

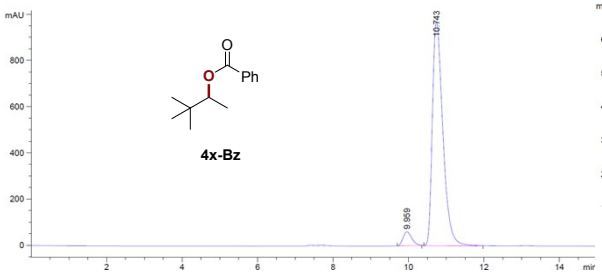
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.382	VB	0.1296	2562.64771	306.47476	97.5699
2	5.929	BB	0.1381	63.82467	7.02082	2.4301
Totals :				2626.47237	313.49558	



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

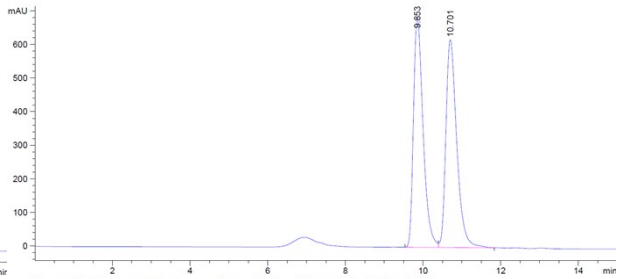
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.094	VV	0.1018	5676.69824	829.47650	50.3031
2	5.690	VB	0.1256	5608.28369	670.55634	49.6969
Totals :				1.12850e4	1500.03284	

4x



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.959	MM	0.2712	980.92780	60.29387	4.9686
2	10.743	VB	0.2956	1.87614e4	970.42322	95.0314
Totals :				1.97424e4	1030.71708	



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.853	BV	0.2648	1.17669e4	683.75092	49.4732
2	10.701	VB	0.2966	1.20175e4	618.83972	50.5268
Totals :				2.37844e4	1302.59064	

6. Crystal Structure Data

Table S2. Details of the crystal structure determinations of **1b** and **2b**.

	1b	**2b**
formula	$C_{22}H_{34}ClCrN_3O_2$	$C_{26}H_{45}CrN_3O_2Si$
crystal system	orthorhombic	orthorhombic
space group	$P\,2_12_12_1$	$P\,2_12_12_1$
a /Å	9.01882(13)	11.7996(7)
b /Å	13.64803(16)	14.2516(10)
c /Å	19.2371(2)	17.9837(12)
V /Å^3	2367.88(5)	3024.2(3)
Z	4	4
M_r	459.97	511.74
F_{000}	976	1104
δ_c /Mg·m^{-3}	1.290	1.124
m /mm^{-1}	0.618	0.442
max., min. transmission factors	1.116, 0.911	1.000, 0.411
X-radiation, λ /Å	Mo-K_α, 0.71073	
data collect. temperat. /K	120(1)	220(1)
θ range /°	2.1 to 32.4	2.2 to 25.2 °
index ranges h,k,l	-13 ... 13, -20 ... 20, -28 ... 28	-14 ... 14, -17 ... 17, -21 ... 21
reflections measured	193770	38247
unique [R_{int}]	8348 [0.0691]	5422 [0.1452]
observed [$I \geq 2\sigma(I)$]	7583	3677
data / restraints /parameters	8348 / 0 / 270	5422 / 0 / 309
GooF o*n* F^2	1.041	1.056
R indices [$F>4\sigma(F)$] R(F), wR(F^2)	0.0378, 0.0912	0.0645, 0.1553
R indices (all data) R(F), wR(F^2)	0.0449, 0.0946	0.1000, 0.1794
absolute structure parameter	-0.019(5)	0.02(3)
largest residual peaks /e·Å^{-3}	0.502, -0.232	0.577, -0.452
CCDC deposition number	1850233	1850234

7. Literature

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