Intermolecular Chirality Transfer from Silicon to Carbon: Interrogation of the Two-Silicon Cycle for Pd-Catalyzed Hydrosilylation by Stereoisotopochemical Cross-over

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Supporting Information

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1 General Information

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. **1**[1], **2a**[2], (phen)$PdMe_2$[3], $[H(OEt_2)_2]^+BAr_4^-$ [Ar = 3,5-bis(trifluoromethyl)phenyl][4] were prepared according to known procedures. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes or double-ended needles. Solvents were dried prior to use following standard procedures (THF, CH_2Cl_2, CD_2Cl_2, CCl_4, *n*-heptane). Technical grade solvents for extraction or chromatography (cyclohexane, *t*-butyl methyl ether) were distilled before use. Analytical thin-layer chromatography was performed on silica gel SIL G-25 glass plates by MachereyNagel/Germany and flash chromatography on silica gel 60 (4063 µm, 230-400 mesh, ASTM) by Merck/Germany using the indicated solvents. High vacuum distillations (10^{-6} mbar) were performed using standard glassware and an Edwards turbo molecular pump. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on Bruker AM300, AM 400 and DRX500, Varian Unity plus 600 or Jeol Delta 400 instruments. ^{29}Si NMR spectra were recorded on a Jeol Alpha 500 instrument. Analytical HPLC analysis were performed with Merck-Hitachi L7100 or Agilent 1200 instruments on a chiral stationary phase using a Daicel Chiralcel OD-H column (*n*-heptane as solvent) or Daicel Chiralcel OD-RH, OJ-RH (MeCN:H_2O mixtures). Mass spectra were recorded with a Finnigan MAT TSQ7000 (EI/CI-MS) or a Waters Micromass GC-TOF (EI/HRMS).

2 Experimental Procedures and Characterization Data of New Compounds

2.1 General Procedures

2.1.1 General Procedure for the Preparation of [^{2}H]-Labeled Silanes (GP 1)

A saturated solution of Cl_2 in CCl_4 (2.5 mL) was added to a solution of the silane (**2a**, **2b** or **8**) (2.00 mmol, 1.00 equiv.) in CCl_4 (4.0 mL) at 0 °C until a permanent pale yellow color appeared. After 4 min the reaction mixture was purged with argon. Evaporation of the solvent under reduced pressure provided the crude chlorosilane as a colorless oil, which then was dissolved in THF (5 mL) and added portionwise to a stirred suspension of $LiAlD_4$ (126 mg, 3.00 mmol, 1.50 equiv., 98% D) in THF (5 mL). After having refluxed this mixture for 2 h, the reaction was quenched at ambient temperature by careful addition of water (20 mL) followed by 2M HCl until pH 7 was reached. The organic layer was separated and the aqueous phase extracted with *t*-butyl methyl ether (4 × 20 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with cyclohexane as eluent, furnishing the analytically pure deuterated silanes ([^{2}H]-**2a**, [^{2}H]-**2b**, [^{2}H]-**8** (78–90%, >98% D) as colorless liquids.

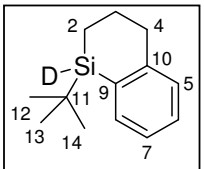
2.1.2 General Procedure for the Hydrosilylation of **1** with silanes **2a**, **2b** and **8** (GP 2)

A Schlenk tube was charged with a mixture of (phen)$PdMe_2$ (1.6 mg, 0.0050 mmol, 0.02 equiv.) and $[H(OEt_2)_2]^+BAr_4^-$ [Ar = 3,5-bis(trifluoromethyl)phenyl] (5.1 mg, 0.0050 mmol, 0.02 equiv.) under argon atmosphere. The solids were dissolved in anhydrous degassed CH_2Cl_2 (0.8 mL) at 0°C forming a pale yellow solution. At this temperature, a solution of bicyclic alkene **1** (35.6 mg, 0.250 mmol, 1.00 equiv.) and silane (**2a**, **2b** or **8**) (0.300 mmol, 1.20 equiv.) in CH_2Cl_2 (1.7 mL) was added in one portion via syringe. The resulting bright yellow solution was maintained at 0°C until complete consumption of the reactants (2 h) as monitored by ^{1}H NMR analysis. After addition of cyclohexane (10 mL) and small portion of silica gel the solvents were evaporated. Purification by flash column chromatography on silica gel (cyclohexane) afforded the analytical pure product (**4a**, **4b** or **9**) (72–88%) as a colorless, highly viscous oil (**4a**, **4b**) or as a white solid (**9**).

2.2 Experimental Details and Characterization Data for Silane Reagents 2a, 2b, 8

2.2.1 Preparation of *rac*-[^{2}H]-**2a** and *rac*-[^{13}C]-**2a**

***rac*-[1-^{2}H]-1-*tert*-Butyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene (*rac*-[^{2}H]-2a)**

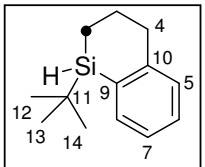


rac-[^{2}H]-**2a**
$C_{13}H_{19}DSi$
205.39 g/mol

Prepared according to GP1 from *rac*-**2a** (214 mg, 1.13 mmol, 1.00 equiv.) furnishing the analytically pure silane *rac*-[^{2}H]-**2a** (179 mg, 87%, 99% D) as a colorless liquid.

R_f (cyclohexane) = 0.74; IR ($CHCl_3$) $\tilde{\nu}$ 3055 (w), 3000 (w), 2926 (s), 2856 (s), 2105 (vw), 1591 (w), 1532 (s), 1463 (s), 1436 (s), 1406 (w), 1361 (m), 1292 (m), 1269 (m), 1141 (m), 1074 (m), 1008 (m), 974 (m), 938 (m), 917 (m), 862 (m), 822 (s), 782 (s), 742 (m), 699 (m), 674 (m), 622 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (ddd, $^2J_{2ax,2eq}$ = 14.8 Hz, $^3J_{2ax,3ax}$ = 11.5 Hz, $^3J_{2ax,3eq}$ = 5.2 Hz, 1H, H-2ax), 1.01 (s, 9H, H-12, H-13, H-14), 1.14 (dddd, $^2J_{2eq,2ax}$ = 14.9 Hz, $^3J_{2eq,3äq}$ = 5.0 Hz, $^3J_{2eq,3ax}$ = 5.0 Hz, $^4J_{2eq,4eq}$ = 1.0 Hz, 1H, H-2eq), 1.77 (ddddd, $^2J_{3ax,3eq}$ = 13.4 Hz, $^3J_{3ax,2ax}$ = 11.5 Hz, $^3J_{3ax,4ax}$ = 10.5 Hz, $^3J_{3ax,2eq}$ = 4.2 Hz, $^3J_{3ax,4eq}$ =2.9 Hz, 1H, H-3ax), 2.08 (ddddd, $^2J_{3eq,3ax}$ = 13.3 Hz, $^3J_{3eq,2äq}$ = 6.6 Hz, $^3J_{3eq,4eq}$ = 6.6 Hz, $^3J_{3eq,2ax}$ = 5.2 Hz, $^3J_{3eq,4ax}$ = 2.8 Hz, 1H, H-3eq), 2.67 (ddd, $^2J_{4ax,4eq}$ = 15.8 Hz, $^3J_{4ax,3ax}$ = 10.5 Hz, $^3J_{4ax,3eq}$ = 2.9 Hz, 1H, H-4ax), 2.76 (dddd, $^2J_{4eq,4ax}$ = 15.5 Hz, $^3J_{4eq,3eq}$ = 6.7 Hz, $^3J_{4eq,3ax}$ = 2.7 Hz, $^4J_{4eq,2eq}$ = 1.0 Hz, 1H, H-4eq), 7.12 (dd, $^3J_{5,6}$ = 7.7 Hz, 1H, H-5), 7.19 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.2 Hz, 1H, H-7), 7.28 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.5 Hz, 1H, H-6), 7.56 (dd, $^3J_{8,7}$ = 7.2 Hz, $^4J_{8,6}$ = 1.5 Hz, 1H, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.5 (C-2), 17. 2 (C-11), 23.2 (C-3), 27.2 (C-12, C-13, C-14), 35.5 (C-4), 125.2 (C-7), 128.8 (C-5), 129.2 (C-6), 130.3 (C-9), 136.2 (C-8), 150.0 (C-10) ppm. ^{29}Si NMR (99.25 MHz, $CDCl_3$) δ –13.74 (t, $^2J_{Si,D}$ = 29.5 Hz) ppm. HR-MS for $C_{13}H_{19}DSi$: 205.1397 Found: 205.1392.

rac-[2-^{13}C]-1-*tert*-Butyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene (*rac*-[^{13}C]-2a)



rac-[^{13}C]-**2a**
$C_{12}{}^{13}CH_{20}Si$
205.38 g/mol

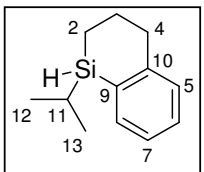
A 100-mL three-necked flask equipped with a reflux condenser, a 25-mL pressure-equalizing dropping funnel, an argon-inlet and a magnetic stirring bar was charged with magnesium turnings (811 mg, 33.3 mmol, 10.0 equiv.). The flask was subsequently flame dried *in vacuo* (3 times) with vigorous stirring, backfilled with argon and stirring was continued for 12 h. Then, the magnesium turnings were suspended in THF (10 mL) and a solution of 1,2-dibromoethane (0.29 mL, 0.63 g, 3.3 mmol, 1.00 equiv.) was added dropwise. After complete addition, the mixture was heated to reflux and a solution of 2-([3-^{13}C]-3-bromopropyl)-1-bromobenzene (930 mg, 3.33 mmol, 1.00 equiv.) – prepared analogously to the non-labeled dibromide[5] –[6] and *tert*-butyl trichlorosilane[7] (638 mg, 3.33 mmol, 1.00 equiv.) in THF (20 mL) was added slowly over a period of 2 h. The reaction mixture was maintained for further 24 h at reflux. The resulting solution was transferred to another 100-mL three-necked flask equipped with a reflux condenser, an argon-inlet and a magnetic stirring bar, containing a suspension of $LiAlH_4$ (253 mg, 6.66 mmol, 1.80 equiv.) in THF (20 mL). Heating at reflux for 12 h was followed by careful quenching of the resulting mixture by pouring it slowly on ice and, finally, adding conc. HCl (5 mL) until pH 4-5 was reached.. The organic layer was separated and the aqueous phase was extracted with *t*-butyl methyl ether (4 × 40 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with cyclohexane as eluent affording the silane *rac*-[^{13}C]-**2a** (266 mg, 39%, 5.4% overall yield based on [2-^{13}C]-acetic acid,[5,6] 99% ^{13}C) as a colorless liquid.

R_f = 0.74 (cyclohexane). IR ($CHCl_3$) $\tilde{\nu}$ 3055 (w), 3000 (w), 2926 (s), 2856 (s), 2103 (s), 1591 (w), 1466 (m), 1436 (s), 1389 (w), 1361 (w), 1290 (w), 1266 (w), 1138 (m), 1074 (m), 1009 (m), 976 (m), 939 (m), 917 (m), 886 (s), 885 (s), 821 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (ddddd, $^1J_{2ax,2C}$ = 121 Hz, $^2J_{2ax,2eq}$ = 14.8 Hz, $^3J_{2ax,3ax}$ = 11.7 Hz, $^3J_{2ax,3eq}$ = 5.0 Hz, 1H, H-2ax, $^3J_{2ax,1}$ = 3.8 Hz, 1H, H-2ax), 1.00 (s, 9H, H-12, H-13, H-14), 1.14 (dm$_c$, $^1J_{2eq,2C}$ = 121 Hz, 1H, H-2eq), 1.76 (dddddd, $^2J_{3ax,3eq}$ = 13.2 Hz, $^3J_{3ax,2ax}$ = 11.5 Hz, $^3J_{3ax,4ax}$ = 10.4 Hz, $^2J_{3ax,2C}$ = 5.7 Hz, $^3J_{3ax,2eq}$ = 4.1 Hz, $^3J_{3ax,4eq}$ = 3.0 Hz, 1H, H-3ax), 2.08 (dddddd, $^2J_{3eq,3ax}$ = 13.3 Hz, $^3J_{3eq,2eq}$ = $^3J_{3eq,4eq}$ = 6.6 Hz, $^3J_{3eq,2ax}$ = 5.1 Hz, $^2J_{3eq,2C}$ = 3.8 Hz, $^3J_{3eq,4ax}$ = 2.8 Hz, 1H, H-3eq), 2.66 (dddd, $^2J_{4ax,4eq}$ = 15.4 Hz, $^3J_{4ax,3ax}$ = 10.4 Hz, $^3J_{4ax,2C}$ = 6.3 Hz, $^3J_{4ax,3eq}$ = 2.5 Hz, 1H, H-4ax), 2.75 (dddd, $^2J_{4eq,4ax}$ = 15.1 Hz, $^3J_{4eq,3eq}$ = $^3J_{4eq,2C}$ = 6.9 Hz, $^3J_{4eq,3ax}$ = 2.5 Hz, 1H, H-4eq), 4.16 (ddd, $^2J_{1,2C}$ = 6.0 Hz, $^3J_{1,2ax}$ = $^3J_{1,2eq}$ = 3.8 Hz, 1H, H-1), 7.11 (d, $^3J_{5,6}$ = 7.5 Hz, 1H, H-5), 7.19 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.3 Hz, 1H, H-7), 7.27 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.3 Hz, $^4J_{6,8}$ = 1.6 Hz, 1H, H-6), 7.54 (dd, $^3J_{8,7}$ = 7.5 Hz, $^4J_{8,6}$ = 1.5 Hz, 1H, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.55 (^{13}C-2), 17.24 (C-11), 23.14 (d, $^2J_{3,2}$ = 31.1 Hz, C-3), 27.19 (C-12, C-13, C-14), 35.54 (C-4), 125.19 (C-7), 128.81 (C-5), 129.16 (C-6), 130.36 (d, $^2J_{9,2}$ = 2.1 Hz, C-9), 136.22 (d, $^2J_{9,2}$ = 2.1 Hz, C-8), 150.00 (C-10) ppm. ^{29}Si NMR (99.25 MHz, $CDCl_3$) δ –13.29 (d, $^2J_{Si,C}$ = 49.7 Hz) ppm. HR-MS for $C_{12}{}^{13}CH_{20}Si$: 205.1368. Found: 205.1362.

2.2.2 Preparation of (Si*R*)-**2b** and 1-[^{2}H]-(Si*S*)-**2b**

Enantiomerically enriched (Si*R*)-**2b** was prepared by analogy to a previously published procedure[2] by resolution of diastereomeric (–)-menthyl silyl ethers and subsequent stereospecific reductive cleavage.

***rac*-1-Isopropyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene (*rac*-2b)**

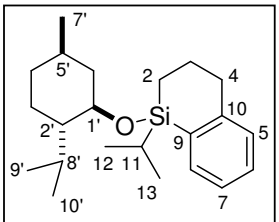


rac-**2b**
$C_{12}H_{18}Si$
190.36 g/mol

A 1-L three-necked flask equipped with a reflux condenser, a 500-mL pressure-equalizing dropping funnel, an argon-inlet and a magnetic stirring bar was charged with magnesium turnings (24.3 g, 1.00 mol, 10.0 equiv.). The flask was subsequently flame dried *in vacuo* (3 times) with vigorous stirring, backfilled with argon and stirring was continued for 12 h. Then, the magnesium turnings were suspended in THF (150 mL) and a solution of 1,2-dibromoethane (8.80 mL, 18.8 g, 100 mmol, 1.00 equiv.) in THF (50 mL) was added dropwise. After complete addition, the mixture was heated to reflux and a solution of 1-bromo-2-(3-bromopropyl)benzene[5] (27.8 g, 100 mmol, 1.00 equiv.) and isopropyltrichlorosilane[8] (17.8 g, 100 mmol, 1.00 equiv.) in THF (400 mL) was added slowly over a period of 5 h. The reaction mixture was maintained for further 14 h at reflux. The resulting solution was transferred to another 1-L three-necked flask equipped with a reflux condenser, an argon-inlet and a magnetic stirring bar, containing a suspension of $LiAlH_4$ (6.83 g, 180 mmol, 1.80 equiv.) in THF (100 mL). Heating at reflux for 3 h was followed by careful quenching of the resulting mixture by pouring it slowly on ice and, finally, adding conc. HCl (100 mL) until pH 4-5 was reached. The organic layer was separated and the aqueous phase was extracted with *t*-butyl methyl ether (4 × 150 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was distilled *in vacuo* (bp 92-93°C at 3 mbar) affording the silane *rac*-**2b** (8.30 g, 43%) as a colorless liquid.

R_f = 0.75 (cyclohexane). HPLC (Daicel Chiralcel OJ-RH column, column temperature 12°C, MeCN:H_2O = 50:50, flow rate 0.50 mL/min, λ = 230 nm): 67.3 min [(Si*R*)-**2b**)], 70.3 min [(Si*S*)-**2b**)]. IR ($CHCl_3$) 3055 (w), 2998 (w), 2923 (s), 2889 (m), 2860 (s), 2105 (s), 1591 (w), 1563 (w), 1463 (m), 1435 (m), 1408 (m), 1382 (w), 1364 (w), 1347 (w), 1292 (m), 1267 (m), 1141 (m), 1127 (m), 1074 (m), 1028 (m), 1003 (m), 978 (m), 917 (w), 879 (w), 861 (w), 819 (s), 802 (s), 772 (m), 744 (s), 702 (w), 673 (w), 645 (w) cm^{-1}, ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87–0.98 (m, 1H, H-2A), 1.00–1.20 (m, 8H, H-2B, H-11, H-12, H-13), 1.94 (m_c, 2H, H-3A, H-3B), 2.74 (m_c, 2H, H-4A, H-4B), 4.21 (ddd, $^3J_{1,2A}$ = $^3J_{1,2b}$ = $^3J_{1,11}$ = 3.0 Hz, 1H, H-1), 7.12 (d, $^3J_{5,6}$ = 7.5 Hz, 1H, H-5), 7.19 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.3 Hz, 1H, H-7), 7.27 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.5 Hz, 1H, H-6), 7.49 (dd, $^3J_{8,7}$ = 7.3 Hz, $^4J_{8,6}$ = 1.3 Hz, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.28 (C-2), 12.43 (C-11), 18.14 (C-12), 18.36 (C-13), 22.86 (C-3), 35.36 (C-4), 125.30 (C-7), 128.83 (C-5), 129.14 (C-6), 130.60 (C-9), 135.60 (C-8), 149.58 (C-10), ppm. HR-MS for $C_{12}H_{18}Si$: 190.1178. Found: 190.1172. Anal. Calcd for $C_{12}H_{18}Si$: C 75.71, H 9.53. Found: C 75.42, H 9.71.

(Si*RS*)-1-Isopropyl-1-[(1*R*,2*S*,5*R*)-1-menthyloxy]-1,2,3,4-tetrahydro-1-silanaphthalene

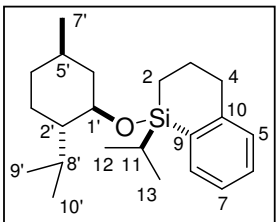


$C_{22}H_{36}OSi$
344.61 g/mol

A saturated solution of Cl_2 in CCl_4 (20 mL) was added to a solution of *rac*-**2b** (4.09 g, 20.0 mmol, 1.00 equiv.) in CCl_4 (20 mL) at 0°C until a permanent pale yellow color appeared. After 4 min the reaction mixture was purged with argon. Evaporation of the solvent under reduced pressure provided crude *rac*-1-Chloro-1-isopropyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene as a colorless oil which was used in the subsequent etherification without further purification.

A solution of (–)-menthol (4.69 g, 30.0 mmol, 1.50 equiv., >99% *ee*) in THF (40 mL) was added to a suspension of oil-free potassium hydride (1.40 g, 35.0 mmol, 1.75 equiv.) in THF (10 mL) at room temperature. To ensure complete deprotonation, the mixture was heated at reflux for for 1 h. Subsequently, the mixture was treated portionwise with a solution of freshly prepared chlorosilane in THF (50 mL) at ambient temperature. Heating at reflux for 4 h was followed by cooling to ambient temperature, quenching with water (100 mL) and then 2M HCl until pH 7 was reached. The organic layer was separated and the aqueous phase was extracted with *t*-butyl methyl ether (4 × 100 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), filtered and the volatiles were evaporated under reduced pressure. The crude product optionally was distilled under high vacuum (bp 130–140°C at 10^{-6} mbar) to remove excess (–)-menthol furnishing a diastereomeric mixture of (–)-menthyl silyl ethers (5.71 g, 83%, d.r. = 50:50) as a yellowish, viscous oil. Separation of diastereomers by repeated flash column chromatography on silica gel with cyclohexane as eluent delivered highly diastereomerically enriched (Si*S*)-1-isopropyl-1-[(1*R*,2*S*,5*R*)-1-menthyloxy]-1,2,3,4-tetrahydro-1-silanaphthalene[9] (2.24 g, 33% based on *rac*-**2b**, d.r. = 98:2) as a highly viscous oil. The opposite diastereomer was obtained by the same procedure (1.98 g, 29%, d.r. = 16:84).

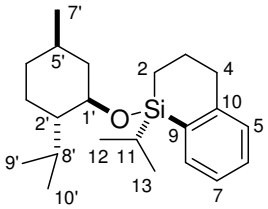
IR ($CHCl_3$): $\tilde{\nu}$ = 3054 (w), 2998 (w), 2954 (s), 2922 (s), 2865 (s), 1590 (w), 1460 (m), 1435 (m), 1370 (m), 1344 (m), 1292 (s), 1269 (s), 1236 (s), 1179 (s), 1141 (m), 1107 (s), 1181 (s) , 1081 (s), 1065 (m), 997 (w), 970 (w), 928 (w), 867 (m), 801 (m), 779 (w), 738 (s), 693 (w), 643 (w) cm^{-1}.



$C_{22}H_{36}OSi$
344.61 g/mol

Analytical data for (Si*S*): R_f (cyclohexane) = 0.21; $[\alpha]_D^{20}$ = –58.4, $[\alpha]_{578}^{20}$ = –60.9, $[\alpha]_{546}^{20}$ = –68.9, $[\alpha]_{436}^{20}$ = –115, $[\alpha]_{365}^{20}$ = –178 (*c* 1.88, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.50 (d, $^3J_{10',8'}$ = 6.9 Hz, 3H, H-10'), 0.76–1.32 (m, 8H, H-2A, H-2B, H-3'A, H-4'A, H-6'A, H-11, H-2', H-5'), 0.84 (d, $^3J_{7',5'}$ = 6.5 Hz, 3H, H-7'), 0.86 (d, $^3J_{9',8'}$ = 7.0 Hz, 3H, H-9'), 0.94 (d, $^3J_{12,11}$ = 7.0 Hz, 3H, H-12), 1.05 (d, $^3J_{13,11}$ = 6.5 Hz, 3H, H-13), 1.50–1.62 (m, 2H, H-3'B, H-4'B), 1.81 (m_c, 1H, H-6'B), 1.86–2.04 (m, 2H, H-3), 2.23 (ttd, $^3J_{8',9'}$ = $^3J_{8',10'}$ = 7.0 Hz, $^3J_{8',2'}$ = 2.4 Hz, 1H, H-8'), 2.67 (ddd, $^2J_{4A,4B}$ = 15.9 Hz, $^3J_{4A,3A}$ = 8.8 Hz, $^3J_{4A,3B}$ = 3.4 Hz, 1H, H-4A), 2.80 (ddd, $^2J_{4B,4A}$ = 16.0 Hz, $^3J_{4B,3B}$ = 7.5 Hz, $^3J_{4B,3A}$ = 3.5 Hz, 1H, H-4B), 3.39 (ddd, $^3J_{1',2'}$ = $^3J_{1',6'A}$ = 10.3 Hz, $^3J_{1',6'B}$ = 4.5 Hz, 1H, H-1'), 7.10 (d, $^3J_{5,6}$ = 7.6 Hz, 1H, H-5), 7.18 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.2 Hz, 1H, H-7), 7.26 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.5 Hz, 1H, H-6), 7.54 (dd, $^3J_{8,7}$ = 7.5 Hz, $^4J_{8,6}$ = 1.2 Hz, 1H, H-8) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.78 (C-2), 14.38 (C-11), 15.81 (C-10'), 17.12 (C-12),

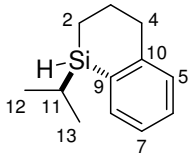
17.33 (C-13), 21.43 (C-9'), 22.42 (C-7'), 22.84 (C-3'), 23.26 (C-3), 25.21 (C-8'), 31.69 (C-5'), 34.63 (C-4'), 35.67 (C-4), 45.61 (C-6'), 50.41 (C-2'), 72.29 (C-1'), 125.13 (C-7), 128.49 (C-5), 129.29 (C-6), 132.35 (C-9), 134.82 (C-8), 149.82 (C-10) ppm. LR-MS (EI): *m/z* 344 [$(M+H)^+$], 301 [$(M–C_3H_7)^+$]. Anal. Calcd for $C_{22}H_{36}OSi$: C 76.68, H 10.53. Found: C 76.41, H 10.60.



$C_{22}H_{36}OSi$
344.61 g/mol

Analytical data for (Si*R*): R_f (cyclohexane) = 0.18; $[\alpha]_D^{20}$ = –51.1, $[\alpha]_{578}^{20}$ = –52.7, $[\alpha]_{546}^{20}$ = –60.3, $[\alpha]_{436}^{20}$ = –102, $[\alpha]_{365}^{20}$ = –160 (*c* 1.32, $CHCl_3$); ^{1}H bg NMR ($CDCl_3$, 400 MHz) δ 0.59 (d, $^3J_{10',8'}$ = 7.1 Hz, 3H, H-10'), 0.69–1.31 (m, 8H, H-2A, H-2B, H-3'A, H-4'A, H-6'A, H-11, H-2', H-5'), 0.80 (d, $^3J_{7',5'}$ = 6.4 Hz, 3H, H-7'), 0.88 (d, $^3J_{9',8'}$ = 7.1 Hz, 3H, H-9'), 0.90 (d, $^3J_{12,11}$ = 6.7 Hz, 3H, H-12), 1.07 (d, $^3J_{13,11}$ = 6.7 Hz, 3H, H-13), 1.51–1.61 (m, 2H, H-3'B, H-4'B), 1.75 (m_c, 1H, H-6'B), 1.94 (m_c, 2H, H-3A, H-3B), 2.23 (ttd, $^3J_{8',9'}$ = $^3J_{8',10'}$ = 7.2 Hz, $^3J_{8',2'}$ = 2.4 Hz, 1H, H-8'), 2.67 (ddd, $^2J_{4A,4B}$ = 15.9 Hz, $^3J_{4A,3A}$ = 8.3 Hz, $^3J_{4A,3B}$ = 3.7 Hz, 1H, H-4A), 2.79 (ddd, $^2J_{4B,4A}$ = 15.9 Hz, $^3J_{4B,3B}$ = 6.9 Hz, $^3J_{4B,3A}$ = 3.4 Hz, 1H, H-4B), 3.45 (ddd, $^3J_{1',2'}$ = $^3J_{1',6'A}$ = 10.0 Hz, $^3J_{1',6'B}$ = 4.6 Hz, 1H, H-1'), 7.10 (d, $^3J_{5,6}$ = 7.6 Hz, 1H, H-5), 7.19 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 6.6 Hz, 1H, H-7), 7.26 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.6 Hz, 1H, H-6), 7.56 (dd, $^3J_{8,7}$ = 7.1 Hz, $^4J_{8,6}$ = 1.2 Hz, 1H, H-8) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.75 (C-2), 14.41 (C-11), 15.75 (C-10'), 17.10 (C-12), 17.33 (C-13), 21.42 (C-9'), 22.36 (C-7'), 22.85 (C-3'), 23.42 (C-3), 25.22 (C-8'), 31.72 (C-5'), 34.63 (C-4'), 35.66 (C-4), 45.21 (C-6'), 50.41 (C-2'), 72.99 (C-1'), 125.13 (C-7), 128.51 (C-5), 129.27 (C-6), 133.00 (C-9), 134.77 (C-8), 149.65 (C-10) ppm. LR-MS (EI): *m/z* 344 [$(M+H)^+$], 301 [$(M–C_3H_7)^+$]. Anal. Calcd for $C_{22}H_{36}OSi$: C 76.68, H 10.53. Found: C 76.38, H 10.44.

(Si*R*)-1-Isopropyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene (Si*R*-2b)[10]

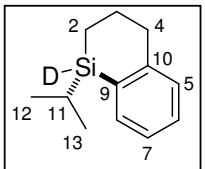


(Si*R*)-**2b**
$C_{12}H_{18}Si$
190.36 g/mol

A 25-mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with DIBAL–H (8.00 mL, 8.00 mmol, 4.00 equiv., 1.0M in CH_2Cl_2). After evaporation of dichloromethane under reduced pressure at ambient temperature, a solution of (Si*S*)-1-isopropyl-1-[(1*R*,2*S*,5*R*)-1-menthyloxy]-1,2,3,4-tetrahydro-1-silanaphthalene (689 mg, 2.00 mmol, 1.00 equiv., d.r. = 98:2) in *n*-heptane (15 mL) was added in one portion. The reaction mixture was subsequently heated to 100°C and maintained at this temperature for 20 h. The reaction was quenched at ambient temperature by careful addition of water (40 mL) followed by 2M HCl (25 mL) until pH 7 was reached. The organic layer was separated and the aqueous phase extracted with *t*-butyl methyl ether (4 × 40 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), filtered and volatiles were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with cyclohexane as eluent, furnishing the analytically pure, highly enantiomerically enriched silane (Si*R*)-**2b** (342 mg, 90%, 97% *ee*) as a colorless liquid.

R_f (cyclohexane) = 0.73; $[\alpha]_D^{20}$ = +72.5, $[\alpha]_{578}^{20}$ = +76.1, $[\alpha]_{546}^{20}$ = +86.4, $[\alpha]_{436}^{20}$ = +148, $[\alpha]_{365}^{20}$ = +237 (*c* 1.67, $CHCl_3$); HPLC (Daicel Chiralcel OJ-RH column, column temperature 12°C, MeCN:H_2O = 50:50, flow rate 0.50 mL/min, λ = 230 nm): 67.3 min [(Si*R*)-**2b**)], 70.3 min [(Si*S*)-**2b**)]

(Si*S*)-[1-^{2}H]-1-Isopropyl-1-(1,2,3,4-tetrahydro)-1-silanaphthalene (Si*S*)-[^{2}H]-2b)



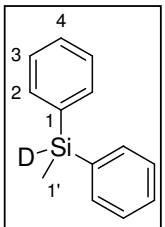
(Si*S*)-[^{2}H]-**2b**
$C_{12}H_{17}DSi$
191.36 g/mol

Prepared according to GP1 from (Si*R*)-**2b** (246 mg, 1.29 mmol, 1.00 equiv.) furnishing the analytically pure silane (Si*S*)-[^{2}H]-**2b** (205 mg, 83%, 95% *ee*, 99% D) as a colorless liquid.

R_f (cyclohexane) = 0.73; HPLC (Daicel Chiralcel OJ-RH column, column temperature 12°C, MeCN:H_2O = 50:50, flow rate 0.50 mL/min, λ = 230 nm): 67.3 min [(Si*R*)-1-[2H]-**2b**)], 70.3 min [(Si*S*)-1-[2H]-**2b**)]. IR ($CHCl_3$) $\tilde{\nu}$ 3055 (w), 2998 (w), 2923 (s), 2860 (s), 1638 (m), 1532 (s), 1463 (m), 1435 (m), 1382 (m), 1292 (w), 1269 (w), 1141 (w), 1073 (w), 1031 (w), 973 (s), 880 (m), 782 (s), 742 (w), 724 (m), 701 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (ddd, $^2J_{2A,2B}$ = 14.6 Hz, $^3J_{2A,3A}$ = 9.8 Hz, $^3J_{2A,3B}$ = 4.6 Hz, 1H, H-2A), 1.00–1.20 (m, 8H, H-2B, H-11, H-12, H-13), 1.92 (m_c, 2H, H-3A, H-3B), 2.75 (m_c, 2H, H-4A, H-4B), 7.12 (d, $^3J_{5,6}$ = 7.4 Hz, 1H, H-5), 7.19 (dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.3 Hz, 1H, H-7), 7.27 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.4 Hz, 1H, H-6), 7.49 (dd, $^3J_{8,7}$ = 7.3 Hz, $^4J_{8,6}$ = 1.2 Hz, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.19 (C-2), 12.35 (C-11), 18.13 (C-12), 18.35 (C-13), 22.86 (C-3), 35.37 (C-4), 125.29 (C-7), 128.83 (C-5), 129.14 (C-6), 130.57 (C-9), 135.60 (C-8), 149.61 (C-10), ppm. HR-MS for $C_{12}H_{18}Si$: 191.1241. Found: 190.1235.

2.2.3 Preparation of [^{2}H]-**8**

[1-^{2}H]-Methyldiphenylsilane ([^{2}H]-8)



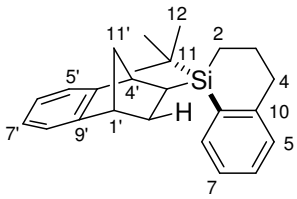
[^{2}H]-**8**
$C_{13}H_{13}DSi$
199.34 g/mol

Prepared according to GP1 from commercially available **8** (2.06 mg, 10.4 mmol, 1.00 equiv.) furnishing the analytically pure silane [^{2}H]-**8** (1.61 g, 78%, >98% D by ^{1}H NMR) as a colorless liquid.

R_f (cyclohexane) = 0.63; IR ($CHCl_3$) $\tilde{\nu}$ 3134 (w), 3068 (s), 3049 (s), 3016 (s), 2960 (m), 2902 (w), 1955 (w), 1882 (w), 1818 (w), 1765 (vw), 1588 (w), 1544 (s), 1485 (w), 1427 (s), 1328 (w), 1301 (w), 1251 (m), 1188 (w), 1115 (s), 1067 (w), 1028 (w), 997 (s), 797 (s), 725 (s), 697 (s), 670 (s), 646 (w), 584 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (s, 3H, H-1'), 7.35–7.43 (m, 6H, H-2, H-4, H-6), 7.57–7.63 (m, 4H, H-3, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.10 (C-1'), 127.95 (C-Ar), 129.50 (C-Ar), 134.82 (C-Ar), 135.32 (C-Ar_{ipso}) ppm. HR-MS for $C_{13}H_{13}DSi$: 199.0928. Found: 199.0922.

2.3 Experimental Details and Characterization Data for Hydrosilylation Products

(1*S*,2*S*,4*R*,Si*R*)-1-*tert*-Butyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)-1-sila-1,2,3,4-tetrahydronaphthalene [(Si*R*)-4a]

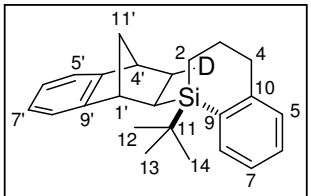


(Si*R*)-**4a**
$C_{24}H_{30}Si$
346.58 g/mol

Prepared according to GP2 from **1** (35.6 mg, 0.250 mmol, 1.00 equiv.), (Si*S*)-**2a** (61.3 mg, 0.300 mmol, 1.20 equiv., 98% *ee*) furnishing analytically pure (Si*R*)-**4a** (68 mg, 78%, 99% *ee*) as a colorless, highly viscous oil.

R_f = 0.49 (cyclohexane). $[\alpha]_D^{20}$ = –41.5, $[\alpha]_{578}^{20}$ = –43.3, $[\alpha]_{546}^{20}$ = –50.5, $[\alpha]_{436}^{20}$ = –99.0, $[\alpha]_{365}^{20}$ = –191 (*c* = 1.09 in $CHCl_3$). HPLC (Daicel Chiralcel OD-RH column, column temperature 20°C, MeCN:H_2O = 75:25, flow rate 0.50 mL/min, λ = 230 nm): 29.0 min [(Si*R*)-**4a**)], 31.8 min [(Si*S*)-**4a**)]. IR ($CHCl_3$) $\tilde{\nu}$ 3050 (s), 2922 (s), 2401 (m), 2361 (m), 2329 (w), 1943 (w), 1923 (w), 1802 (w), 1684 (w), 1654 (w), 1588 (m), 1559 (m), 1521 (m), 1471 (s), 1435 (s), 1390 (m), 1362 (m), 1294 (m), 1262 (s), 1220 (s), 1198 (s), 1114 (m), 1069 (m), 1107 (m), 981 (m), 889 (m), 821 (s), 799 (s), 674 (s), 627 (s), 627 (s), 607 (s), 519 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 0.95–1.06 (m, 2H, H-2'endo, H-2ax), 1.00 (s, 9H, H-12, H-13, H-14), 1.15 (dddd, $^2J_{2eq,2ax}$ = 14.9 Hz, $^3J_{2eq,3äq}$ = 6.8 Hz, $^3J_{2eq,3ax}$ = 4.0 Hz, $^4J_{2eq,4eq}$ = 1.2 Hz, 1H, H-2eq), 1.32 (dddd, $^2J_{3'endo,3'exo}$ = 11.8 Hz, $^3J_{3'endo,2'endo}$ = 9.7 Hz, $^3J_{3'endo,4'}$ = 2.3 Hz, $^3J_{3'endo,11'B}$ = 0.6 Hz, 1H, H-3'endo), 1.43 (ddd, $^2J_{11'A,11'B}$ = 8.9 Hz, $^3J_{11'A,4'}$ = $^3J_{11'A,1'}$ = 1.5 Hz, 1H, H-11'A), 1.60 (ddddd, $^2J_{11'B,11'A}$ = 8.9 Hz, $^3J_{11'B,4'}$ = $^3J_{11'B,1'}$ = $^4J_{11'B,3'endo}$ =$^3J_{11'B,2'endo}$ = 1.6 Hz, 1H, H-11'B), 1.78–1.87 (m, 1H, H-3ax), 1.84 (ddd, $^2J_{3'exo,3'endo}$ =11.8 Hz, $^3J_{3'exo,2'endo}$ = 6.9 Hz, $^3J_{3'exo,4'}$ = 3.8 Hz, 1H, H-3'exo), 2.13 (ddddd, $^2J_{3eq,3ax}$ = 13.4 Hz, $^3J_{3eq,2äq}$ = $^3J_{3eq,4eq}$ = 6.8 Hz, $^3J_{3eq,2ax}$ = 4.9 Hz, $^3J_{3eq,4ax}$ =2.9 Hz, 1H, H-3eq), 2.72 (ddd, $^2J_{4ax,4eq}$ = 15.7 Hz, $^3J_{4ax,3ax}$ = 10.3 Hz, $^3J_{4ax,3eq}$ = 2.9 Hz, 1H, H-4ax), 2.79 (br ddd, $^2J_{4eq,4ax}$ = 15.8 Hz, $^3J_{4eq,3eq}$ = 6.6 Hz, $^3J_{4eq,3ex}$ = 2.7 Hz, 1H, H-4eq), 3.32 (br d, $^3J_{4',3'exo}$ = 2.6 Hz, 1H, H-4'), 3.42 (br s, 1H, H-1'), 7.05–7.14 (m, 4H, H-5, H-7, H-6', H-7'), 7.16–7.19 (m, 2H, H-5', H-8'), 7.23 (m_c, 1H, H-6), 7.41 (m_c, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.73 (C-2), 18.57 (C-11), 23.92 (C-3, C-2'), 27.67 (C-12, C-13, C-14), 31.54 (C-3'), 36.03 (C-4), 44.17 (C-4'), 45.70 (C-1'), 48.39 (C-11'), 118.84 (C-8'), 121.10 (C-5'), 124.96 (C-7), 125.23 (C-6'), 125.61 (C-7'), 128.64 (C-5), 128.71 (C-6), 132.61 (C-9), 135.72 (C-8), 147.20 (C-10'), 149.93 (C-10), 151.14 (C-9') ppm. ^{29}Si NMR (99.25 MHz, $CDCl_3$) δ –5.01 (s) ppm. LRMS (CI: NH_3) m/z 347 [$(M+H)^+$], (EI) *m/z* 289 [$(M–C_4H_9)^+$]. Anal. Calcd for $C_{24}H_{30}Si$: C, 83.17; H, 8.72. Found: C, 83.16; H, 8.94.

rac-(1_R*_,2_R*_,4_S*_,Si_S*_)-[3'-^{2}H]-1-_tert_-Butyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)-1-sila-1,2,3,4-tetrahydronaphthalene (_rac_-[^{2}H]-4a])

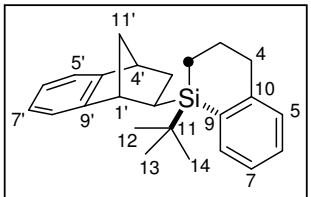


rac-[^{2}H]-**4a**
$C_{24}H_{29}DSi$
347.59 g/mol

Prepared according to GP2 from **1** (42.7 mg, 0.300 mmol, 1.00 equiv.), *rac*-[^{2}H]-**2a** (74.0 mg, 0.360 mmol, 1.20 equiv., 99% D) furnishing analytically pure *rac*-[^{2}H]-**4a** (83 mg, 80%, 97% D) as a colorless, highly viscous oil.

R_f = 0.49 (cyclohexane). IR ($CHCl_3$) $\tilde{\nu}$ 3050 (m), 3017 (m), 2998 (m), 2958 (s), 2927 (s), 2880 (s), 2854 (s), 1588 (w), 1466 (s), 1434 (m), 1407 (w), 1389 (w), 1360 (m), 1293 (m), 1266 (m), 1239 (m), 1217 (m), 1194 (m), 1155 (m), 1141 (m), 1128 (m), 1110 (m), 1072 (m), 1009 (m), 994 (m), 975 (m), 929 (m), 876 (m), 848 (m), 821 (m), 782 (s), 753 (s), 741 (s), 726 (s), 690 (m), 671 (m), 620 (m), 603 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94–1.06 (m, 2H, H-2'endo, H-2ax), 1.00 (s, 9H, H-12, H-13, H-14), 1.15 (dddd, $^2J_{2eq,2ax}$ = 14.9 Hz, $^3J_{2eq,3eq}$ = 6.8 Hz, $^3J_{2eq,3ax}$ = 4.0 Hz, $^4J_{2eq,4eq}$ = 1.2 Hz, 1H, H-2eq), 1.31 (ddd, $^3J_{3'endo,2'endo}$ = 9.7 Hz, $^3J_{3'endo,4'}$ = 1.7 Hz, $^3J_{3'endo,11'B}$ = 0.6 Hz, 1H, H-3'endo), 1.43 (ddd, $^2J_{11'A,11'B}$ = 8.9 Hz, $^3J_{11'A,4'}$ = $^3J_{11'A,1'}$ = 1.5 Hz, 1H, H-11'A), 1.60 (ddddd, $^2J_{11'B,11'A}$ = 8.9 Hz, $^3J_{11'B,4'}$ = $^3J_{11'B,1'}$ = $^4J_{11'B,3'endo}$ =$^3J_{11'B,2'endo}$ = 1.7 Hz, 1H, H-11'B), 1.82 (ddddd, $^2J_{3ax,3eq}$ = 13.2 Hz, $^3J_{3ax,2ax}$ = 11.5 Hz, $^3J_{3ax,4ax}$ = 10.3 Hz, $^3J_{3ax,2eq}$ = 4.0 Hz, $^3J_{3ax,4eq}$ = 2.9 Hz, 1H, H-3ax), 2.13 (ddddd, $^2J_{3eq,3ax}$ = 13.4 Hz, $^3J_{3eq,2äq}$ = $^3J_{3eq,4eq}$ = 6.8 Hz, $^3J_{3eq,2ax}$ = 4.9 Hz, $^3J_{3eq,4ax}$ =2.9 Hz, 1H, H-3eq), 2.73 (ddd, $^2J_{4ax,4eq}$ = 15.7 Hz, $^3J_{4ax,3ax}$ = 10.3 Hz, $^3J_{4ax,3eq}$ = 2.8 Hz, 1H, H-4ax), 2.79 (br ddd, $^2J_{4eq,4ax}$ = 15.8 Hz, $^3J_{4eq,3eq}$ = 6.4 Hz, $^3J_{4eq,3ax}$ = 2.8 Hz, 1H, H-4eq), 3.32 (br s, 1H, H-4'), 3.42 (br s, 1H, H-1'), 7.05–7.14 (m, 4H, H-5, H-7, H-6', H-7'), 7.16–7.19 (m, 2H, H-5', H-8'), 7.23 (m_c, 1H, H-6), 7.38–7.43 (m, 1H, H-8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.74 (C-2), 18.57 (C-11), 23.92 (C-3, C-2'), 27.64 (C-12, C-13, C-14), 31.22 (t, $^2J_{C,D}$ = 20 Hz, C-3'), 36.03 (C-4), 44.14 (C-4'), 45.71 (C-1'), 48.39 (C-11'), 118.84 (C-8'), 121.10 (C-5'), 124.96 (C-7), 125.23 (C-6'), 125.61 (C-7'), 128.65 (C-5), 128.71 (C-6), 132.61 (C-9), 135.72 (C-8), 147.20 (C-10'), 149.93 (C-10), 151.14 (C-9') ppm. ^{29}Si NMR (99.25 MHz, $CDCl_3$) δ –5.00 (br s) ppm. LRMS (EI) *m/z* 289 [$(M–C_4H_9)^+$]. HR-MS for $C_{24}H_{29}DSi$: 347.2180. Found: 347.2174.

rac-(1_R*_,2_R*_,4_S*_,Si_S*_)-[2-^{13}C]-1-_tert_-Butyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)-1-sila-1,2,3,4-tetrahydronaphthalene [_rac_-[^{13}C]-4a]



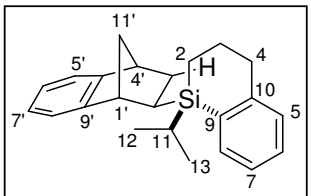
rac-[^{13}C]-**4a**
$C_{23}{}^{13}CH_{30}Si$
347.58 g/mol

Prepared according to GP2 from **1** (35.6 mg, 0.250 mmol, 1.00 equiv.), *rac*-[^{13}C]-**2a** (61.6 mg, 0.300 mmol, 1.20 equiv., 99% ^{13}C) furnishing analytically pure *rac*-[^{13}C]-**4a** (62 mg, 72%, 98% ^{13}C) as a colorless, highly viscous oil.

R_f = 0.49 (cyclohexane). IR ($CHCl_3$) $\tilde{\nu}$ 3050 (m), 2956 (s), 2926 (s), 2855 (s), 1588 (w), 1468 (s), 1434 (m), 1389 (w), 1360 (m), 1291 (m), 1262 (m), 1195 (m), 1156 (m), 1136 (m), 1072 (m), 1011 (m), 978 (m), 943 (m), 916 (m), 888 (m), 820 (m), 753 (s), 737 (s), 725 (s), 688 (m), 672 (m), 644 (m), 588 (s) cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81–1.22 (m, 3H, H-2'endo, H-2ax, H-2eq), 1.00 (s, 9H, H-12, H-13, H-14), 1.32 (ddd, $^2J_{3'endo,3'exo}$ = 11.5 Hz, $^3J_{3'endo,2'endo}$ = 9.6 Hz, $^3J_{3'endo,4'}$ =

2.5 Hz, 1H, H-3'endo), 1.42 (ddd, $^2J_{11'A,11'B}$ = 8.9 Hz, $^3J_{11'A,4'}$ = $^3J_{11'A,1'}$ = 1.4 Hz, 1H, H-11'A), 1.60 (ddddd, $^2J_{11'B,11'A}$ = 8.8 Hz, $^3J_{11'B,4'}$ = $^3J_{11'B,1'}$ = $^4J_{11'B,3'endo}$ =$^3J_{11'B,2'endo}$ = 1.8 Hz, 1H, H-11'B), 1.75–1.89 (m, 1H, H-3ax), 1.80–1.86 (ddd, $^2J_{3'exo,3'endo}$ = 11.7 Hz, $^3J_{3'exo,2'endo}$ = 6.9 Hz, $^3J_{3'exo,4'}$ = 3.7 Hz, 1H, H-3'exo), 2.12 (m_c, 1H, H-3eq), 2.76 (m_c, 2H, H-4ax, H-4eq), 3.31 (br d, $^3J_{4',3'exo}$ = 2.8 Hz, 1H, H-4'), 3.41 (br s, 1H, H-1'), 7.03–7.14 (m, 4H, H-6', H-7', H-5, H-7), 7.15–7.20 (m, 2H, H-8', H-5'), 7.23 (m_c, 1H, H-6), 7.38–7.43 (m, 1H, H-8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.78 (^{13}C-2), 18.57 (d, $^2J_{11,2}$ = 2.5 Hz, C-11), 23.92 (d, $^1J_{3,2}$ = 25 Hz, C-3), 23.98 (d, $^2J_{2',2}$ = 2.4 Hz, C-2') 27.67 (C-12, C-13, C-14), 31.55 (C-3'), 36.03 (d, $^2J_{4,2}$ = 1.0 Hz, C-4), 44.17 (C-4'), 45.70 (C-1'), 48.39 (C-11'), 118.84 (C-8'), 121.10 (C-5'), 124.96 (C-7), 125.23 (C-6'), 125.61 (C-7'), 128.65 (C-5), 128.71 (C-6), 132.61 (d, $^2J_{9,2}$ = 2.5 Hz, C-9), 135.72 (d, $^3J_{8,2}$ = 1.4 Hz, C-8), 147.20 (C-10'), 149.93 (C-10), 151.14 (C-9') ppm. ^{29}Si NMR (99.25 MHz, $CDCl_3$): –5.02 (d, $^2J_{Si,C}$ = 49.5 Hz) ppm. Anal. Calcd for $C_{23}{}^{13}CH_{30}Si$: 347.2150. Found: 347.2145.

(1*R*,2*R*,4*S*,Si*R*)-1-Isopropyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)-1-sila-1,2,3,4-tetrahydronaphthalene [(Si*R*)-4b][11]



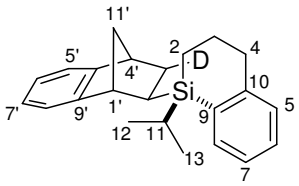
(Si*R*)-**4b**
$C_{23}H_{28}Si$
332.55 g/mol

Prepared according to GP2 from **1** (42.7 mg, 0.300 mmol, 1.00 equiv.), (Si*R*)-**2b** (62.8 mg, 0.330 mmol, 1.10 equiv., 96% *ee*) furnishing analytically pure (Si*R*)-**4b** (85 mg, 85%, 95% *ee*) as a colorless, highly viscous oil.

R_f = 0.52 (cyclohexane). $[\alpha]_D^{20}$ = –3.5, $[\alpha]_{578}^{20}$ = –3.7, $[\alpha]_{546}^{20}$ = –3.9, $[\alpha]_{436}^{20}$ = –0.8, $[\alpha]_{365}^{20}$ = +18.5 (*c* = 0.94 in $CHCl_3$). HPLC (Daicel Chiralcel OD-RH column, column temperature 12°C, MeCN:H_2O = 75:25, flow rate 0.50 mL/min, λ = 230 nm): 29.9 min [(2*S*,Si*R*)-**4b**)], 32.3 min [(2*S*,Si*S*)-**4b**)], 34.6 min [(2*R*,Si*R*)-**4b**)], 40.9 min [(2*R*,Si*S*)-**4b**)]. IR ($CHCl_3$) $\tilde{\nu}$ 3050 (m), 3017 (m), 2956 (s), 2923 (s), 2861 (s), 1589 (w), 1466 (s), 1405 (m), 1382 (w), 1292 (w), 1263 (w), 1195 (w), 1140 (m), 1073 (m), 997 (m), 978 (m), 943 (m), 916 (m), 882 (m), 820 (m), 781 (w), 753 (s), 740 (s), 726 (s), 679 (m), 636 (m), 610 (w), 587 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (ddd, $^3J_{2'endo,3'endo}$ = 9.6 Hz, $^3J_{2'endo,3'exo}$ = 6.8 Hz, $^3J_{2'endo,11'B}$ = 1.8 Hz, 1H, H-2'endo), 1.01 (d, $^3J_{12,11}$ = 7.4 Hz, 3H, H-12), 1.04 (m_c, 2H, H-2A, H-2B), 1.05 (d, $^3J_{13,12}$ = 7.4 Hz, 3H, H-13), 1.20 (tt, $^3J_{11,12}$ = $^3J_{11,13}$ = 7.4 Hz, 1H, H-11), 1.32 (m_c, 1H, H-3'endo), 1.33 (ddd, $^2J_{11'A,11'B}$ = 8.9 Hz, $^3J_{11'A,1'}$ = $^3J_{11'A,4'}$ = 1.5 Hz, 1H, H-11'A), 1.52 (ddddd, $^2J_{11'B,11'A}$ = 8.9 Hz, $^3J_{11'B,1'}$ = $^3J_{11'B,4'}$ = $^4J_{11'B,2'endo}$ =$^4J_{11'B,3'endo}$ = 1.8 Hz, 1H, H-11'B), 1.87 (ddd, $^2J_{3'exo,3'endo}$ =11.5 Hz, $^3J_{3'exo,2'endo}$ = 6.8 Hz, $^3J_{3'exo,4'}$ = 4.0 Hz, 1H, H-3'exo), 1.92 (m_c, 1H, H-3A), 2.03 (m_c, 1H, H-3B), 2.77 (m_c, 2H, H-4A, H-4B), 3.34 (br s, 2H, H-1', H-4'), 7.06 (ddd, $^3J_{6',5'}$ = $^3J_{6',7'}$ = 7.5 Hz, $^4J_{6',8'}$ = 1.4 Hz, 1H, H-6'), 7.08 (ddd, $^3J_{7',6'}$ = $^3J_{7',8'}$ = 7.5 Hz, $^4J_{7',5'}$ = 1.4 Hz, 1H, H-7'), 7.12 (br d, $^3J_{5,6}$ = 7.5 Hz, 1H, H-5), 7.14 (br dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.2 Hz, 1H, H-7), 7.16 (dd, $^3J_{8',7'}$ = 6.8 Hz, $^4J_{8',6'}$ = 1.5 Hz, 1H, H-8'), 7.17 (dd, $^3J_{5',6'}$ = 6.8 Hz, $^4J_{5',7'}$ = 1.5 Hz, 1H, H-5'), 7.24 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.5 Hz, 1H, H-6), 7.41 (dd, $^3J_{8,7}$ = 7.2 Hz, $^4J_{8,6}$ = 1.4 Hz, 1H, H-8) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.61 (C-2), 13.29 (C-11), 18.02 (C-13), 18.35 (C-12), 23.66 (C-3), 25.07 (C-2'), 30.20 (C-3'), 35.90 (C-4), 44.26 (C-4'), 45.18 (C-1'), 48.08 (C-11'), 118.84 (C-8'), 121.06 (C-5'), 125.16 (C-7, C-6'), 125.56 (C-7'), 128.67 (C-

5), 128.72 (C-6), 132.56 (C-9), 135.16 (C-8), 147.23 (C-10'), 149.82 (C-10), 151.19 (C-9') ppm. GC-MS (EI) *m/z* 332 [M^+], 289 [$(M–C_3H_7)^+$]. Anal. Calcd for $C_{23}H_{28}Si$: 332.1960. Found: 332.1955. Anal. Calcd for $C_{23}H_{28}Si$: C, 83.07; H, 8.49. Found: C, 82.63; H, 8.67.

rac-(1_R*_,2_R*_,4_S*_,Si_R*_)-3'-[2H]-1-Isopropyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)-1-sila-1,2,3,4-tetrahydronaphthalene (_rac_-3'-[^{2}H]-4b)

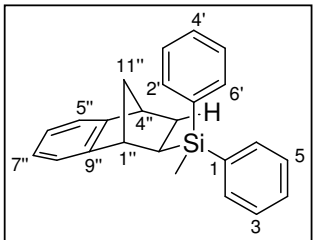


rac-[^{2}H]-**4b**
$C_{23}H_{27}DSi$
333.56 g/mol

Prepared according to GP2 from **1** (42.7 mg, 0.300 mmol, 1.00 equiv.), *rac*-[^{2}H]-**2b** (63.1 mg, 0.330 mmol, 1.10 equiv., 99% D) furnishing analytically pure *rac*-[^{2}H]-**4b** (88 mg, 88%, 99% D) as a colorless, highly viscous oil.

R_f = 0.52 (cyclohexane). IR ($CHCl_3$) $\tilde{\nu}$ 3050 (m), 3017 (m), 2957 (s), 2926 (s), 2861 (s), 1589 (w), 1463 (s), 1434 (m), 1405 (m), 1382 (w), 1363 (m), 1292 (w), 1266 (w), 1193 (w), 1155 (m), 1140 (m), 1127 (w), 1072 (m), 995 (m), 973 (m), 948 (m), 929 (m), 879 (m), 847 (m), 782 (w), 752 (s), 740 (s), 694 (w), 677 (m), 630 (m), 607 (w), 587 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (dd, $^3J_{2'endo,3'endo}$ = 9.6 Hz, $^3J_{2'endo,11'B}$ = 1.8 Hz, 1H, H-2'endo), 1.02 (d, $^3J_{12,11}$ = 7.8 Hz, 3H, H-12), 1.05 (m_c, 2H, H-2A, H-2B), 1.06 (d, $^3J_{13,12}$ = 7.5 Hz, 3H, H-13), 1.21 (tt, $^3J_{11,12}$ = $^3J_{11,13}$ = 7.4 Hz, 1H, H-11), 1.32 (m_c, 1H, H-3'endo), 1.34 (ddd, $^2J_{11'A,11'B}$ = 8.9 Hz, $^3J_{11'A,1'}$ = $^3J_{11'A,4'}$ = 1.2 Hz, 1H, H-11'A), 1.53 (ddddd, $^2J_{11'B,11'A}$ = 8.9 Hz, $^3J_{11'B,1'}$ = $^3J_{11'B,4'}$ = $^4J_{11'B,2'endo}$ = $^4J_{11'B,3'endo}$ = 1.8 Hz, 1H, H-11'B), 1.93 (m_c, 1H, H-3A), 2.03 (m_c, 1H, H-3B), 2.78 (m_c, 2H, H-4A, H-4B), 3.34 (br s, 2H, H-1', H-4'), 7.07 (ddd, $^3J_{6',5'}$ = $^3J_{6',7'}$ = 7.5 Hz, $^4J_{6',8'}$ = 1.0 Hz, 1H, H-6'), 7.09 (ddd, $^3J_{7',6'}$ = $^3J_{7',8'}$ = 7.5 Hz, $^4J_{7',5'}$ = 1.0 Hz, 1H, H-7'), 7.13 (br d, $^3J_{5,6}$ = 7.5 Hz, 1H, H-5), 7.13 (br dd, $^3J_{7,6}$ = $^3J_{7,8}$ = 7.0 Hz, 1H, H-7), 7.17 (br d, $^3J_{8',7'}$ = 7.1 Hz, 1H, H-8'), 7.18 (br d, $^3J_{5',6'}$ = 7.0 Hz, 1H, H-5'), 7.25 (ddd, $^3J_{6,5}$ = $^3J_{6,7}$ = 7.5 Hz, $^4J_{6,8}$ = 1.4 Hz, 1H, H-6), 7.42 (dd, $^3J_{8,7}$ = 7.1 Hz, $^4J_{8,6}$ = 1.0 Hz, 1H, H-8) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.61 (C-2), 13.30 (C-11), 18.02 (C-13), 18.35 (C-12), 23.65 (C-3), 24.97 (C-2'), 29.98 (t, $^2J_{C,D}$ = 20 Hz, C-3'), 35.90 (C-4), 44.14 (C-4'), 45.17 (C-1'), 48.06 (C-11'), 118.83 (C-8'), 121.07 (C-5'), 125.16 (C-7, C-6'), 125.55 (C-7'), 128.67 (C-5), 128.72 (C-6), 132.56 (C-9), 135.15 (C-8), 147.23 (C-10'), 149.81 (C-10), 151.20 (C-9') ppm. GC-MS (EI) *m/z* 333 [M^+], 290 [$(M–C_3H_7)^+$]. HR-MS $C_{23}H_{27}DSi$: 333.2023. Found: 332.2018.

rac-(1_S*_,2_R*_,4_S*_)-1-Methyl-1,1-diphenyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)silane (_rac_-9)[12]



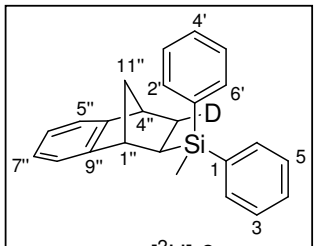
rac-**9**
$C_{24}H_{24}Si$
340.53 g/mol

Prepared according to GP2 from **1** (42.7 mg, 0.300 mmol, 1.00 equiv.), **8** (65.5 mg, 0.330 mmol, 1.10 equiv.) furnishing analytically pure *rac*-**9** (80 mg, 78%) as a white solid.

R_f = 0.32 (cyclohexane). $[\alpha]_D^{20}$ = –14.9, $[\alpha]_{578}^{20}$ = –15.4, $[\alpha]_{546}^{20}$ = –17.6, $[\alpha]_{436}^{20}$ = –31.0, $[\alpha]_{365}^{20}$ = –51.8 (*c* = 0.94 in $CHCl_3$, 34% *ee* sample of a isotopic mixture with H/D 48:52). HPLC (Daicel Chiralcel OD-H column,

column temperature 20°C, *n*-heptane, flow rate 0.80 mL/min, λ = 230 nm): 16.8 min [(1*R*,2*S*,4*R*)-**9**)], 19.6 min [(1*S*,2*R*,4*S*)-**9**)]. IR ($CHCl_3$) $\tilde{\nu}$ 3068 (m), 3047 (m), 3017 (m), 2962 (s), 2907 (m), 2865 (m), 1955 (w), 1897 (w), 1819 (w), 1588 (w), 1486 (w), 1469 (m), 1427 (s), 1306 (w), 1253 (s), 1217 (w), 1194 (m), 1156 (w), 1137 (s), 1109 (s), 1064 (w), 1013 (w), 998 (m), 976 (w), 944 (m), 915 (w), 889 (s), 846 (s), 822 (s), 784 (s), 756 (s), 737 (s), 699 (s), 673 (w), 628 (w), 587 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.56 (s, 3H, H-1'''), 1.13–1.23 (m, 2H, H-2''endo, H-11''A), 1.36–1.45 (m, 2H, H-3''endo, H-11''B), 1.88 (ddd, $^2J_{3''exo,3''endo}$ = 11.6 Hz, $^3J_{3''exo,4''}$ = 6.7 Hz, $^3J_{3''exo,2''endo}$ = 3.6 Hz, 1H, H-3''exo), 3.30 (br s, 2H, H-1'', H-4''), 6.96–7.04 (m, 2H, H-Ar), 7.05–7.14 (m, 2H, H-Ar), 7.21–7.35 (m, 6H, H-Ar), 7.43–7.55 (m, 4H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.73 (C-1'''), 25.67 (C-2''), 30.00 (C-3''), 44.43 (C-4''), 45.10 (C-1''), 47.89 (C-11''), 118.91 (C-Ar), 121.19 (C-Ar), 125.28 (C-Ar), 125.68 (C-Ar), 127.89 (C-Ar), 127.96 (C-Ar), 129.26 (C-Ar), 129.33 (C-Ar), 134.88 (C-Ar), 134.95 (C-Ar), 136.98 (*ipso*-C-Ar), 137.16 (*i*pso-C-Ar), 147.13 (*ipso*-C-Ar), 151.20 (*i*pso-C-Ar) ppm. GC-MS (EI) *m/z* 340 [M^+]. HR-MS for $C_{24}H_{24}Si$: 340.1647. Found: 340.1642. Anal. Calcd for $C_{24}H_{24}Si$: C 84.65, H 7.10. Found: C 84.52, H 7.23.

rac-(1*S**,2*R**,4*S**)-[3'-^{2}H]-1-Methyl-1,1-diphenyl-1-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-yl)silane (*rac*-[^{2}H]-9)[12]



rac-[^{2}H]-**9**
$C_{24}H_{23}DSi$
341.54 g/mol

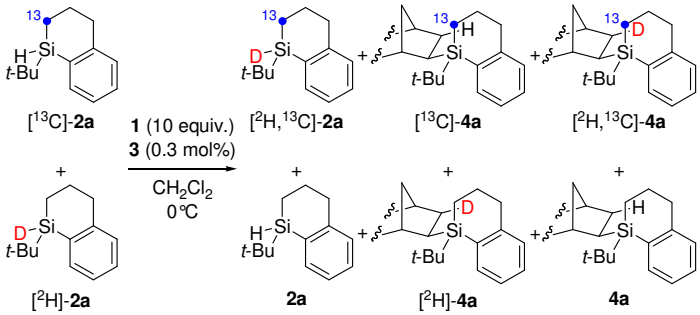
Prepared according to GP2 from **1** (42.7 mg, 0.300 mmol, 1.00 equiv.), [^{2}H]-**8** (65.8 mg, 0.330 mmol, 1.10 equiv.) furnishing analytically pure *rac*-[^{2}H]-**9** (82 mg, 81%, 98% D) as a white solid.

R_f = 0.32 (cyclohexane). IR ($CHCl_3$) $\tilde{\nu}$ 3068 (m), 3047 (m), 3017 (m), 2962 (s), 2875 (m), 1955 (w), 1897 (w), 1588 (w), 1486 (w), 1463 (m), 1427 (s), 1304 (w), 1251 (s), 1218 (w), 1192 (m), 1156 (w), 1110 (s), 1068 (w), 1013 (w), 995 (m), 950 (w), 929 (m), 879 (s), 850 (s), 827 (s), 791 (s), 755 (s), 736 (s), 699 (s), 672 (w), 618 (w), 586 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.54 (s, 3H, H-1'''), 1.12–1.20 (m, 2H, H-2''endo, H-11''A), 1.35–1.45 (m, 2H, H-3''endo, H-11''B), 3.26–3.30 (m, 2H, H-1'', H-4''), 6.95–7.03 (m, 2H, H-Ar), 7.04–7.08 (m, 1H, H-Ar), 7.09–7.13 (m, 1H, H-Ar), 7.21–7.35 (m, 6H, H-Ar), 7.42–7.47 (m, 2H, H-Ar), 7.47–7.54 (m, 2H, H-Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.72 (C-1'''), 25.58 (C-2''), 29.65 (C-3'', $^2J_{C,D}$ = 20 Hz), 44.35 (C-4''), 45.09 (C-1''), 47.88 (C-11''), 118.90 (C-Ar), 121.89 (C-Ar), 125.28 (C-Ar), 125.68 (C-Ar), 127.89 (C-Ar), 127.96 (C-Ar), 129.26 (C-Ar), 129.33 (C-Ar), 134.88 (C-Ar), 134.95 (C-Ar), 136.99 (*ipso*-C-Ar), 137.06 (*i*pso-C-Ar), 147.13 (*ipso*-C-Ar), 151.22 (*i*pso-C-Ar) ppm. GC-MS (EI) *m/z* 341 [M^+]. HR-MS for $C_{24}H_{23}DSi$: 341.1710. Found: 341.1705.

3 Cross-over Experiments involving [^{2}H]-2a and [^{13}C]-2a

3.1 Experimental Details

Representative Procedure for the Hydrosilylation of **1** with mixtures of *rac*-[^{2}H]-**2a** and *rac*-[^{13}C]-**2a**



A Schlenk tube was charged with a solution of *rac*-[^{2}H]-**2a** (30.8 mg, 0.150 mmol, 0.500 equiv.), *rac*-[^{13}C]-**2a** (30.8 mg, 0.150 mmol, 0.500 equiv.), and bicyclic alkene **1** (427 mg, 10.0 equiv.) in anhydrous degassed CH_2Cl_2 (2.5 mL) under argon atmosphere. An aliquot (0.50 mL) was taken via syringe to determine the exact composition of the unreacted mixture by ^{1}H NMR. After cooling to 0 °C, a solution of (phen)PdMe(OEt$_2$)$^+$ BAr$_4^-$ (**3**) [Ar = 3,5-bis(trifluoromethyl)phenyl] (100 µL, 0.00075 mmol, 0.003 equiv., 0.0075M in CH_2Cl_2) – prepared in situ from (phen)PdMe$_2$ (2.4 mg, 0.0075 mmol, 0.03 equiv.) and [H(OEt$_2$)$_2$]$^+$BAr$_4^-$ (7.6 mg, 0.0075 mmol, 0.03 equiv.) in CH_2Cl_2 (1.0 mL) at 0 °C – was added via a microliter syringe. The resulting solution was maintained at 0 °C for the 20 h and monitored by ^{1}H NMR. After removal of the catalyst by filtration through a plug of silica gel, the solvent was evaporated. The remaining mixture was dissolved in $CDCl_3$ together with a drop of TMS for subsequent NMR analysis (see Table S1 for results).

^{29}Si NMR Spectra were measured on a JEOL Alpha500 spectrometer with a tuneable multinuclear TH5 probe. The data were obtained using a ^{29}Si-^{1}H DEPT sequence with a ^{29}Si-^{1}H coupling constant of 21 Hz. Spectral width was 4 kHz (~40 ppm) and the FID contained 32 k points which were zero-filled to 128 k for processing. Standard processing employed a single exponential window function (typically 2 Hz) prior to Fourier transform, although where elucidation of isotope shifts was required, sequential Gaussian (0.15 Hz) and single exponential (–0.32 Hz) window functions were applied, prior to Fourier transform.

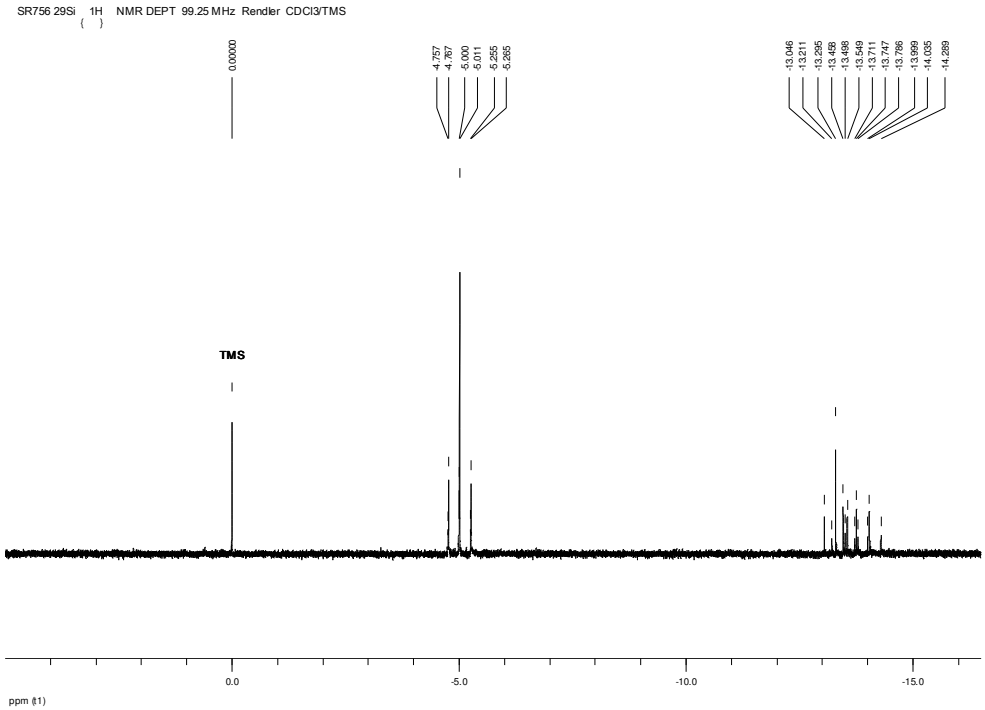
Table S1. Cross-over experiments of *rac*-[^{2}H]-**2a** and *rac*-[^{13}C]-**2a**

	Run				
	1	**2**	**3**	**4**	**5**
	Initial Composition[a]				
1 [equiv.]	400	113	400	1000	1000
rac-[^{2}H]-**2a** [equiv.]	0.48	0.51	0.48	0.48	0.48
rac-[^{13}C]-**2a** [equiv.]	0.52	0.49	0.52	0.52	0.52
3 [equiv.]	0.003	0.003	0.003	0.003	0.003
Conversion [%][b]	18	26	38	11	38
Reaction time [h]	30	20	78	20	40
Temperature [°C]	0	0	0	0	0
	Final Composition[b,c]				
rac-[^{2}H]-**2a** [%]	43.05	32.78	32.84	44.37	33.25
rac-[^{13}C]-**2a** [%]	3.28	6.14	3.78	0.00	1.80
rac-**2a** [%]	2.46	6.81	2.53	1.15	1.52
rac-[^{2}H,^{13}C]-**2a** [%]	33.21	28.34	22.84	43.48	25.42
Total silanes [%][b]	82.00	74.07	61.99	89.00	61.99
rac-[^{2}H]-**4a** [%]	1.94	5.43	5.97	0.92	3.80
rac-[^{13}C]-**4a** [%.]	7.67	8.11	13.98	4.66	17.18
rac-**4a** [%]	5.26	8.84	9.54	3.63	9.83
rac-[^{13}C,^{2}H]-**4a** [%]	3.13	3.61	8.47	1.79	7.19
Total Products [%][b]	18.00	25.99	37.96	11.00	38.00
Total [%]	100.00	100.06	99.95	100.00	99.99

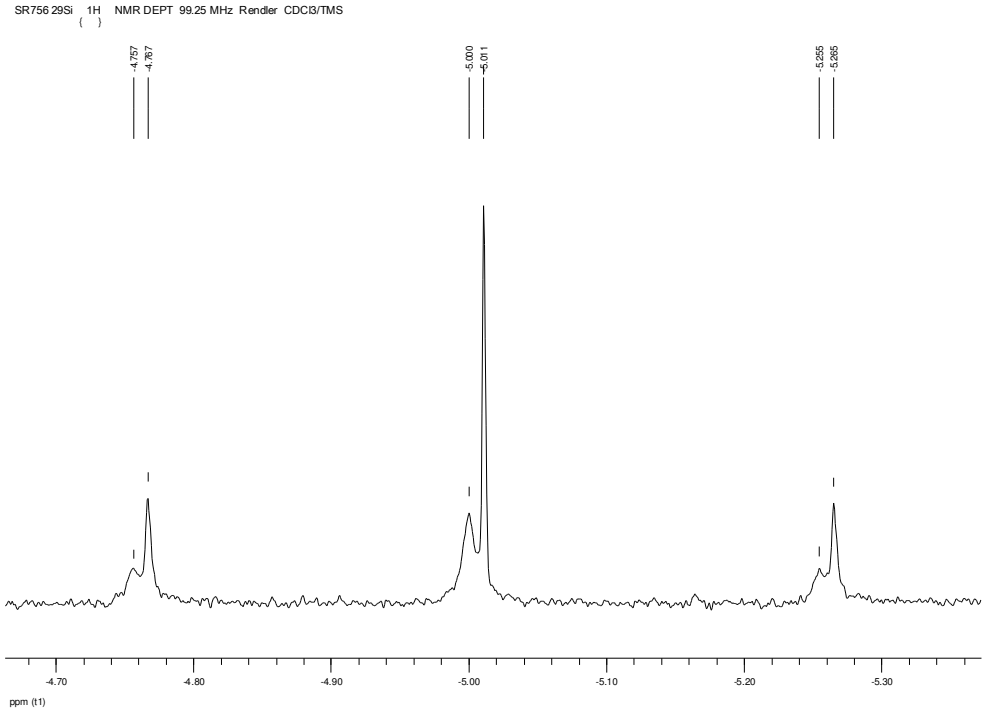
[a] The composition of the mixture of alkene and silanes was determined by integration of the ^{1}H NMR signals at 3.82 ppm (alkene **1**, 2H), 2.56–2.79 ppm (silanes *rac*-[^{2}H]-**2a** and *rac*-[^{13}C]-**2a**, 2H), and 4.17 ppm (silane *rac*-[^{13}C]-**2a**, 1H). [b] The conversion was calculated by comparison of the ^{1}H NMR integrals at 2.56–2.79 ppm (silanes *rac*-[^{2}H]-**2a** and *rac*-[^{13}C]-**2a**, $2H_{silanes}$, and all isotopomers of **4a**, $2H_{products}$) versus 3.38 ppm (all isotopomers of **4a**, $1H_{products}$) by the equation: *conversion (%) = 100 {integral (3.38 ppm) /[(integral (2.56–2.79 ppm)/2]}*. [c] According to ^{29}Si{^{1}H} NMR; only integrals of the same moieties were compared (isotopomers of **2a** *or* isotopomers of **4a**); for partially overlapping integrals of *rac*-[^{2}H]-**4a** and *rac*-**4a** and, analogously *rac*-[^{2}H,^{13}C]-**4a** and *rac*-[^{13}C]-**4a**, results were obtained by integration from baseline to maximum for downfield shifted *rac*-[^{2}H]-**4a**/*rac*-[^{2}H,^{13}C]-**4a** and by integration from maximum to baseline for upfield shifted signals *rac*-**4a**/*rac*-^{13}C]-**4a**, being consistent with preliminary integration results of samples with known H/D ratios.

3.2 Copies of $^{29}Si\{^{1}H\}$ NMR Spectra

- **Reference Sample (0.6 mol% 3, 2.5 h, 0 °C, 60% conversion)**



Product Region



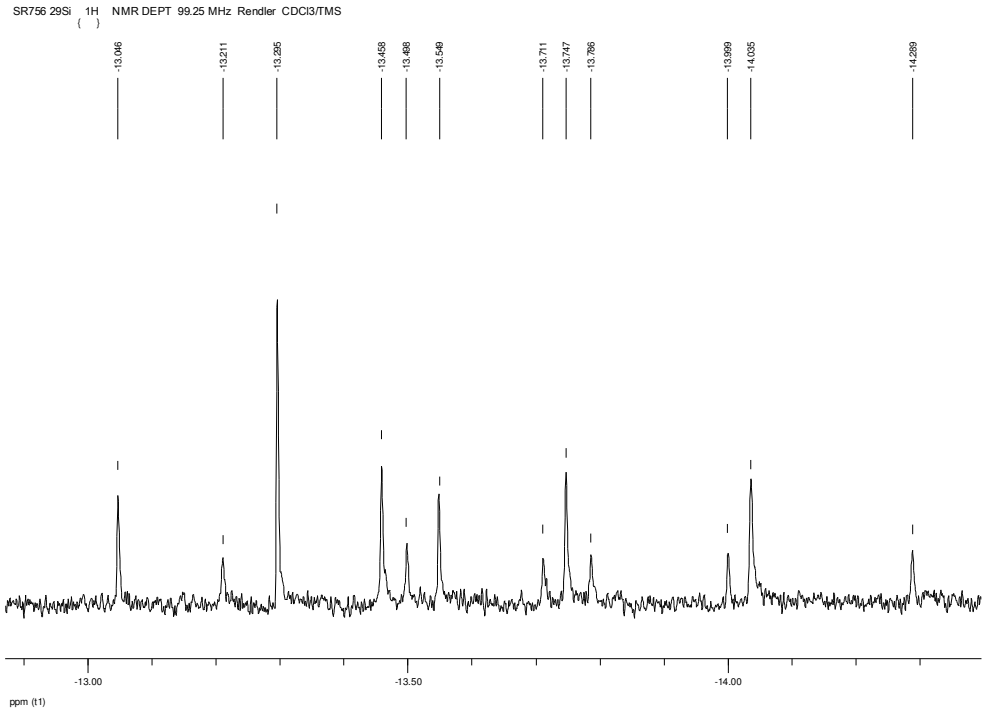
E [^{2}H]-**4a** δ = –5.00 [br s, $\Delta\delta(\gamma\text{-}^{2}H)$ = +1.0 Hz] ppm.

F [^{13}C]-**4a** δ = –5.02 [d, $^{1}J_{Si,C}$ = 49.5 Hz, $\Delta\delta(\alpha\text{-}^{13}C)$ = –1.0 Hz] ppm.

G **4a** δ = –5.01 [s] ppm.

H [^{13}C,^{2}H]-**4a** δ = –5.01 [br d, $^{1}J_{Si,C}$ = 49.5 Hz, $\Delta\delta(\gamma\text{-}^{2}H)$ = +1.0 Hz, $\Delta\delta(\alpha\text{-}^{13}C)$ = –1.0 Hz] ppm.

Silane Region



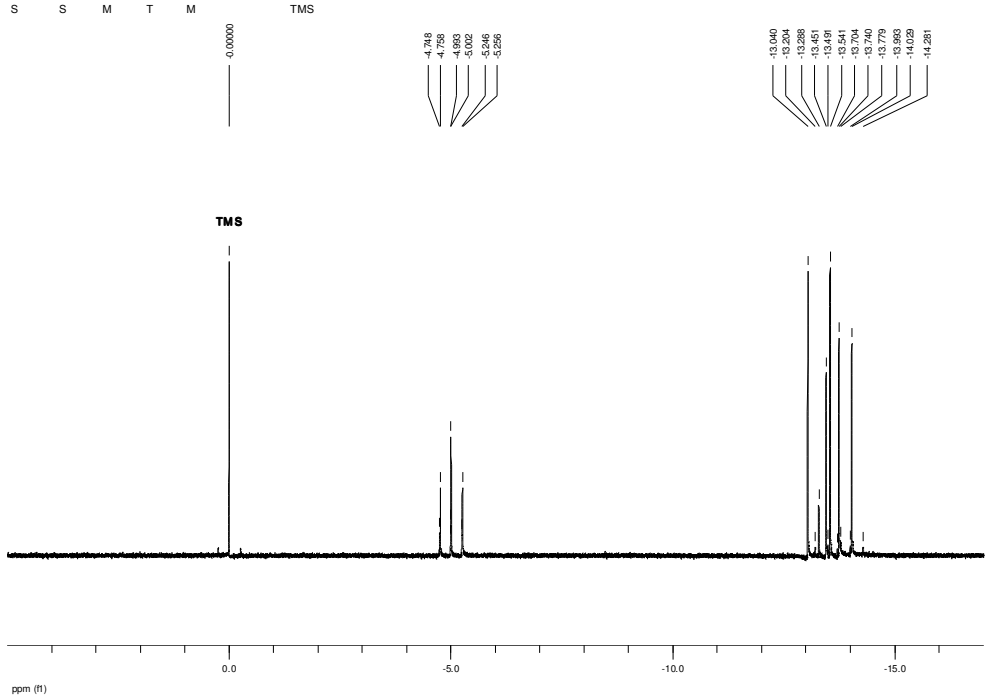
A [^{13}C]-**2a** δ = –13.30 [d, $^{1}J_{Si,C}$ = 50.0 Hz , $\Delta\delta(\alpha\text{-}^{13}C)$ = –1.0 Hz] ppm.

B [^{2}H]-**2a** δ = –13.75 [t, $^{1}J_{Si,D}$ = 29.0 Hz, $\Delta\delta(\alpha\text{-}^{2}H)$ = –548 Hz] ppm.

C **2a** δ = –13.29 [s] ppm.

D [^{13}C,^{2}H]-**2a** δ = –13.75 [dt, $^{1}J_{Si,C}$ = 50.0 Hz, $^{1}J_{Si,D}$ = 29.0 Hz, $\Delta\delta(\alpha\text{-}^{2}H)$ = –548 Hz, $\Delta\delta(\alpha\text{-}^{13}C)$ = –1.0 Hz] ppm.

Run 1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-13.288
-13.451
-13.491
-13.541
-13.704
-13.740
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-14.029
-14.281
TMS
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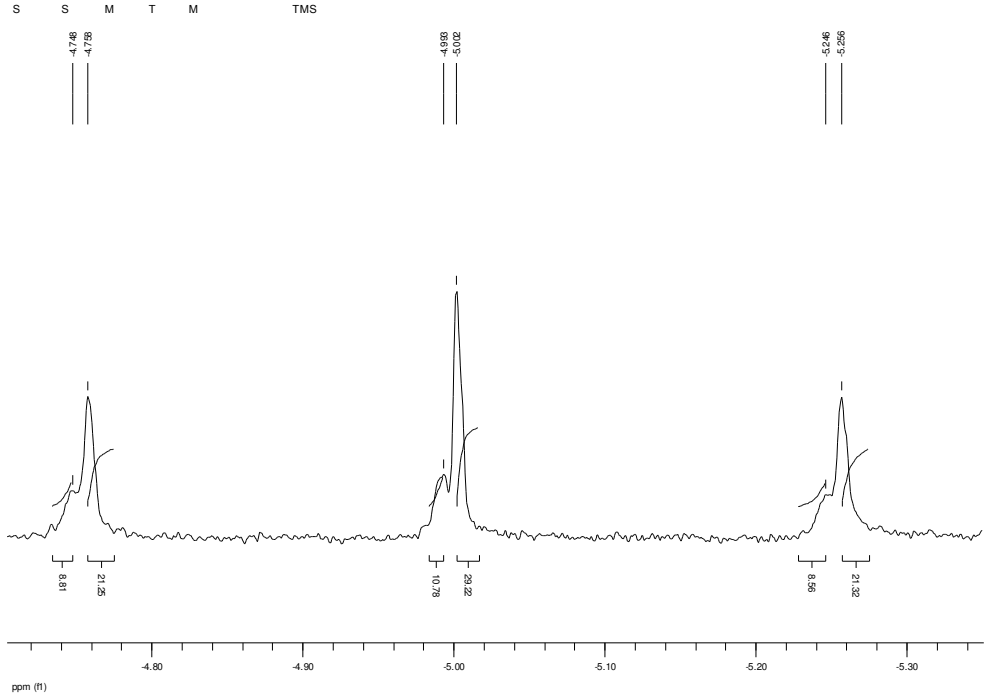
-10.0
-15.0
ppm (f1)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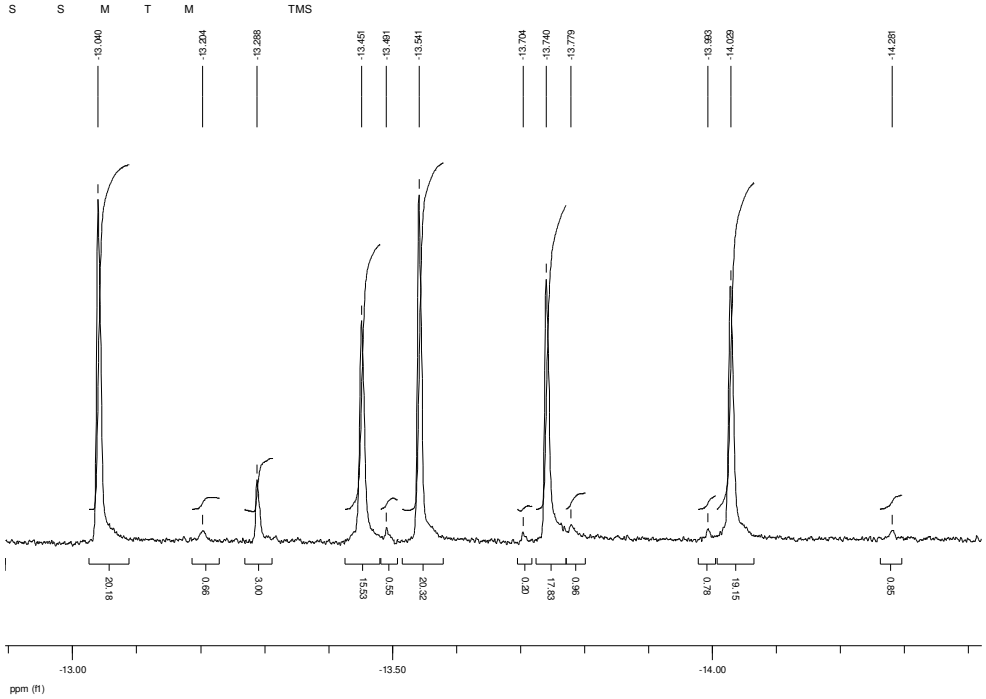
-5.20
-5.30
ppm (f1)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-13.451
-13.491
-13.541
-13.704
-13.740
-13.779
-13.993
-14.029
-14.281
20.18
0.69
3.00
15.53
0.55
20.32
0.20
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0.78
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0.86
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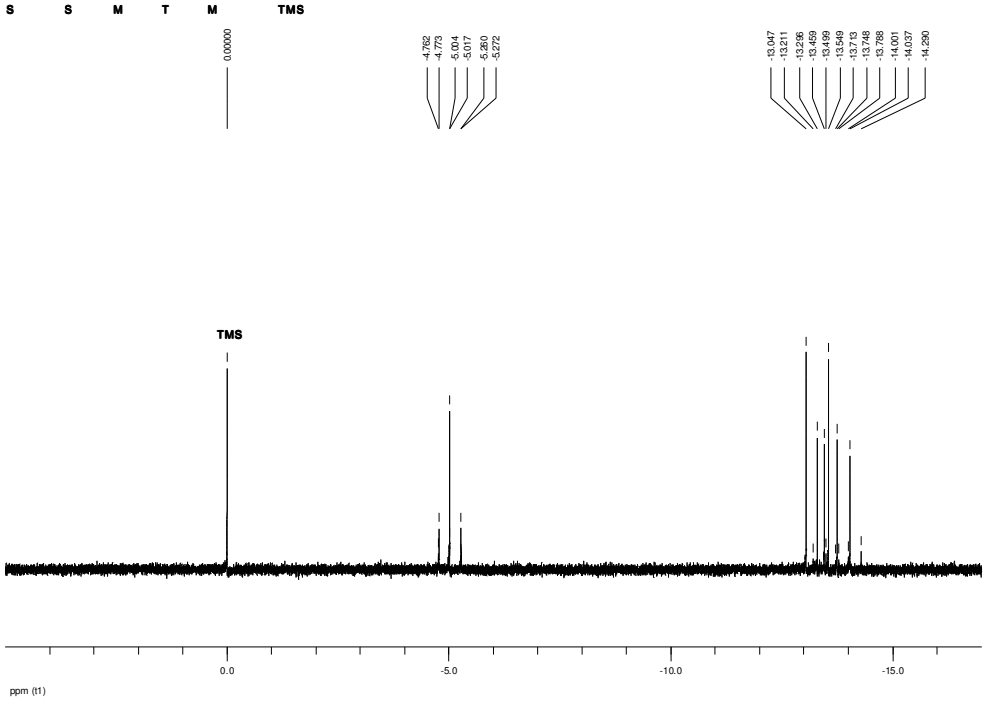
ppm (f1)

- **Run 2**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-13.459
-13.499
-13.549
-13.713
-13.748
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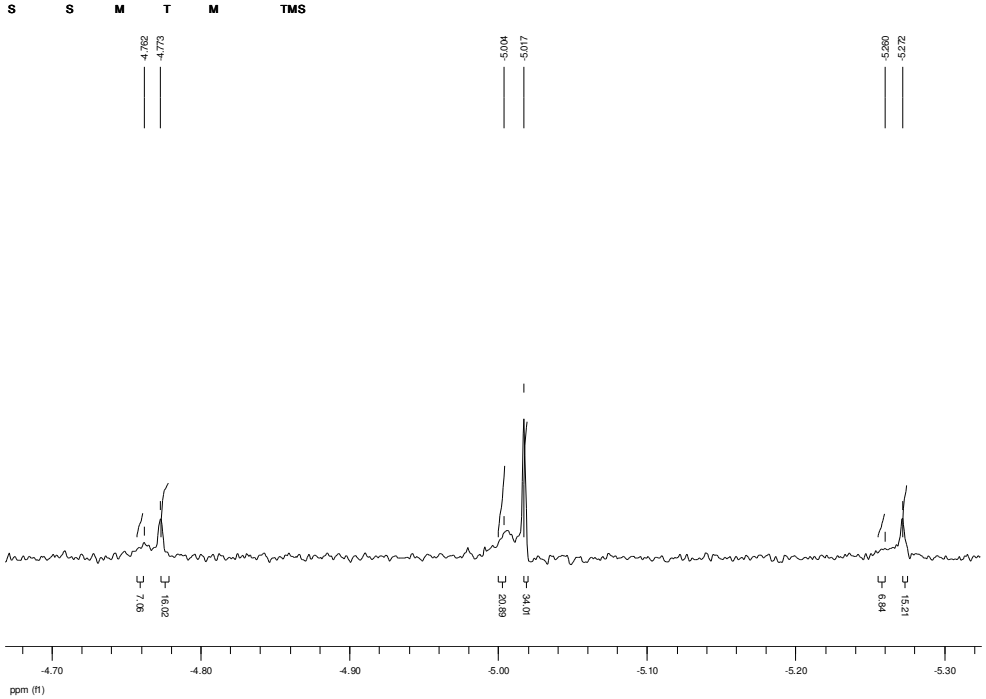
ppm (f1)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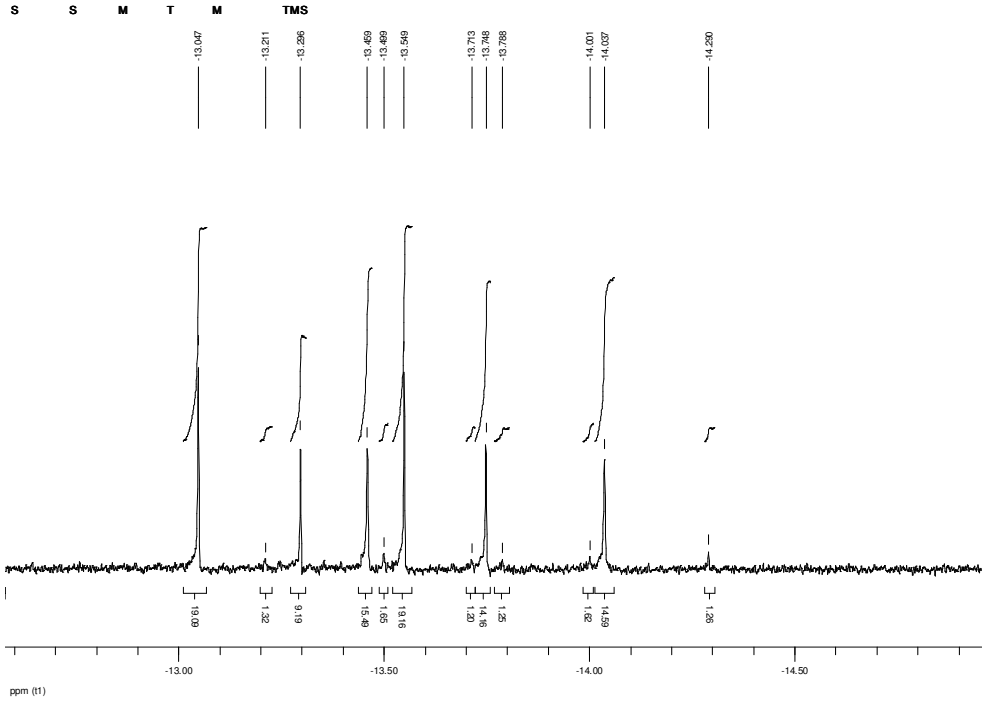
ppm (f1)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-14.001
-14.037
-14.230
19.09
1.32
9.19
15.49
1.85
19.16
1.20
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1.25
1.62
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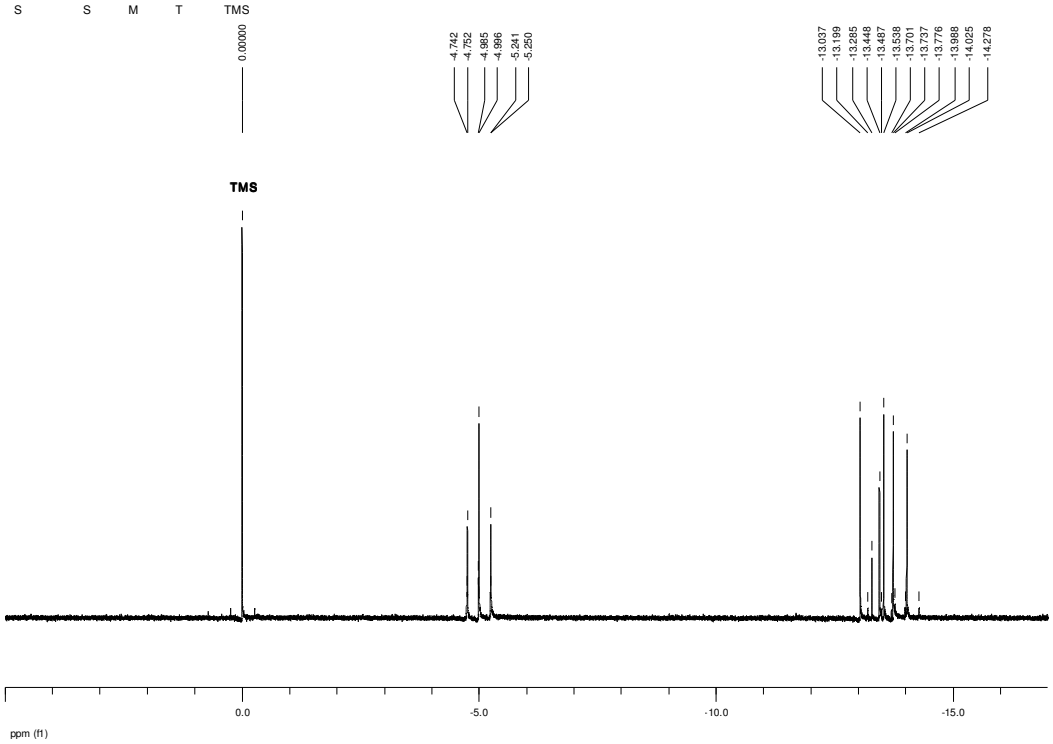
ppm (f1)

Run 3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-13.037
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-13.285
-13.448
-13.487
-13.538
-13.701
-13.737
-13.776
-13.988
-14.025
-14.278
TMS
0.0
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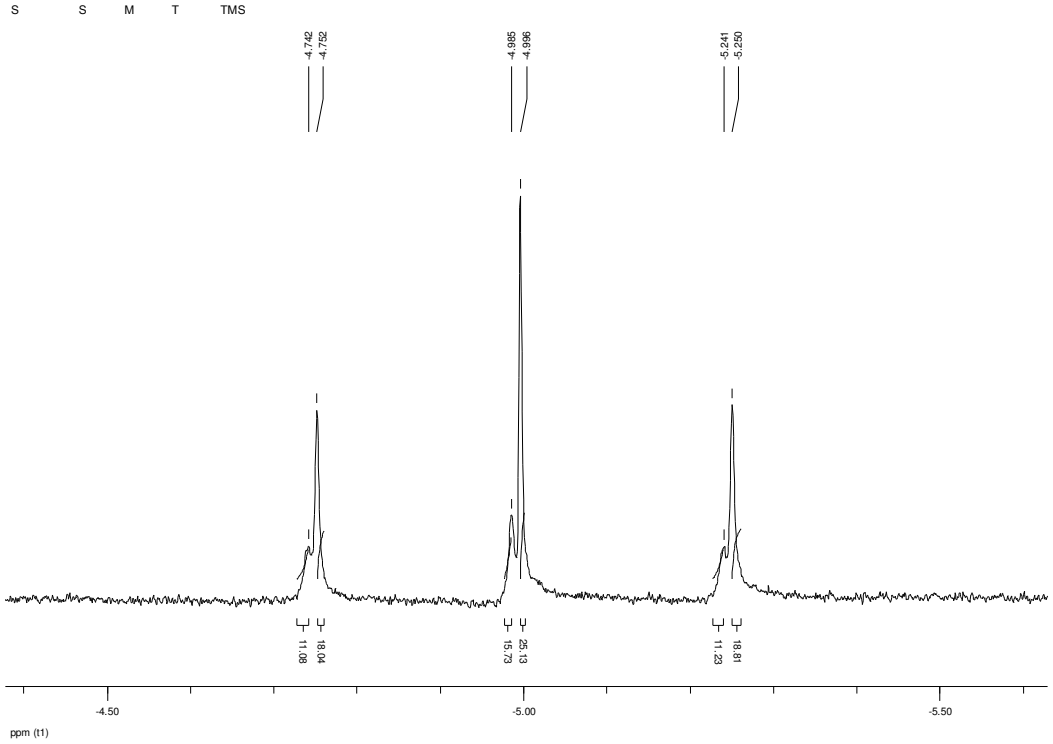
-10.0
-15.0
ppm (f1)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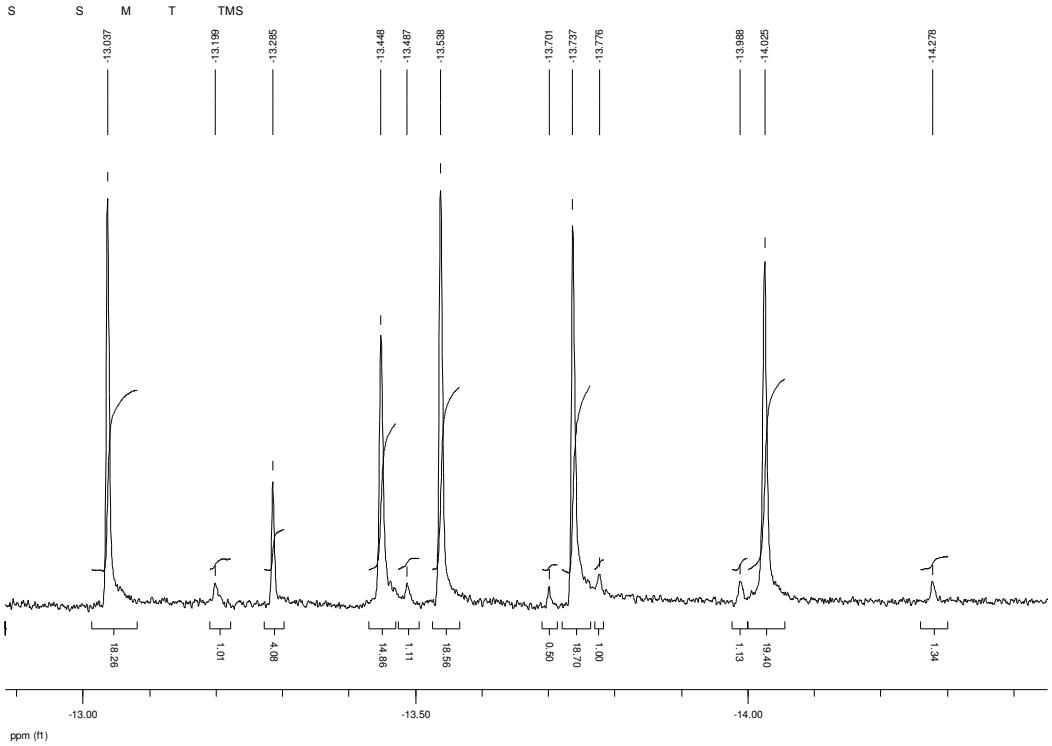
11.23
18.81
-4.50
-5.00
-5.50
ppm (t1)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-13.199
-13.285
-13.448
-13.487
-13.538
-13.701
-13.737
-13.776
-13.988
-14.025
-14.278
18.26
1.01
4.08
14.86
1.11
18.56
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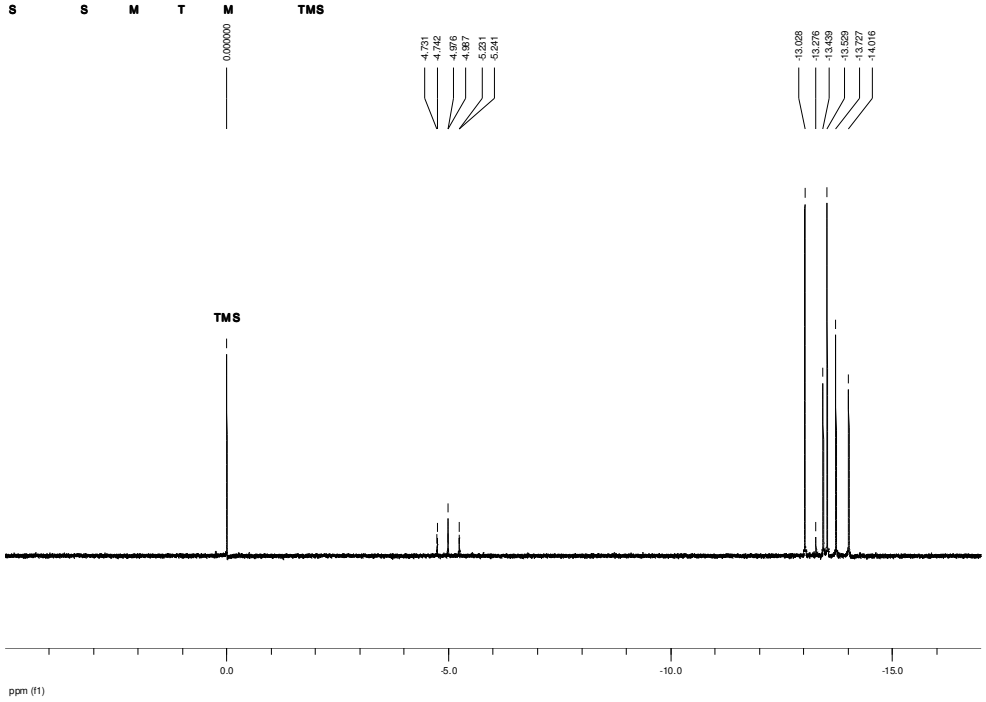
ppm (f1)

- **Run 4**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-5.241
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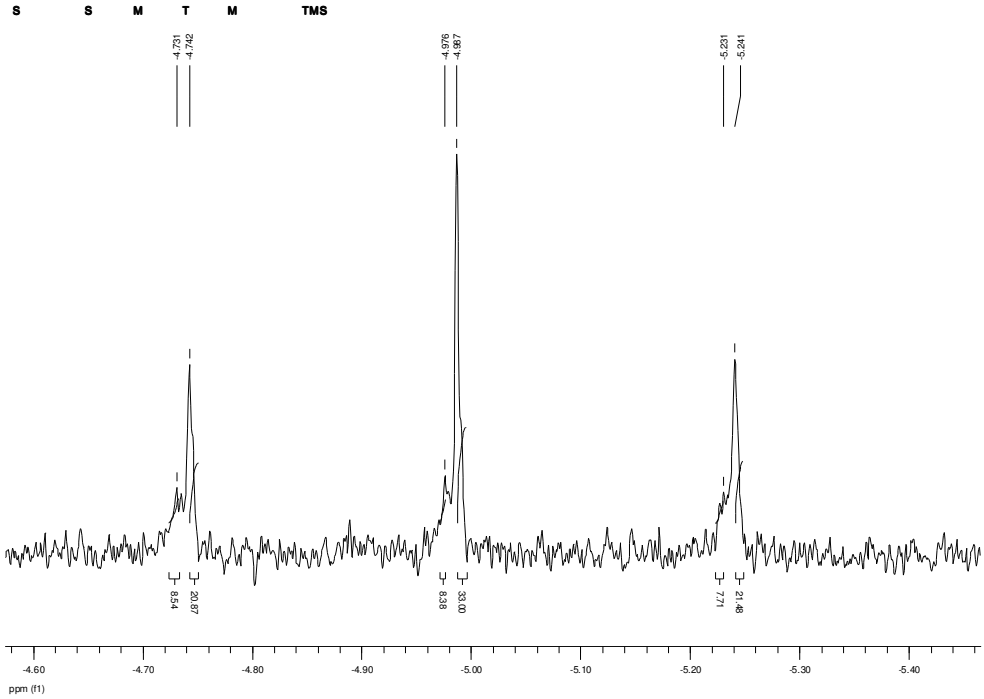
-13.276
-13.439
-13.529
-13.727
-14.016
TMS
0.0
-5.0
-10.0
-15.0
ppm (f1)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8.38
33.00
7.71
21.48
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-4.80
-4.90
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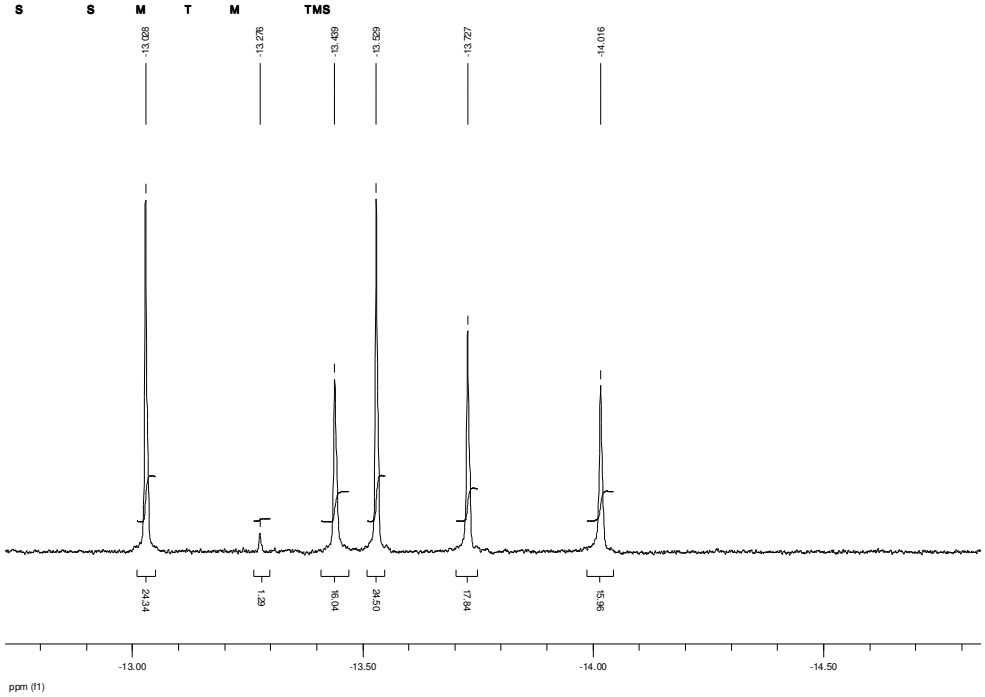
ppm (f1)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-13.529
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-14.016
24.34
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24.50
17.64
15.56
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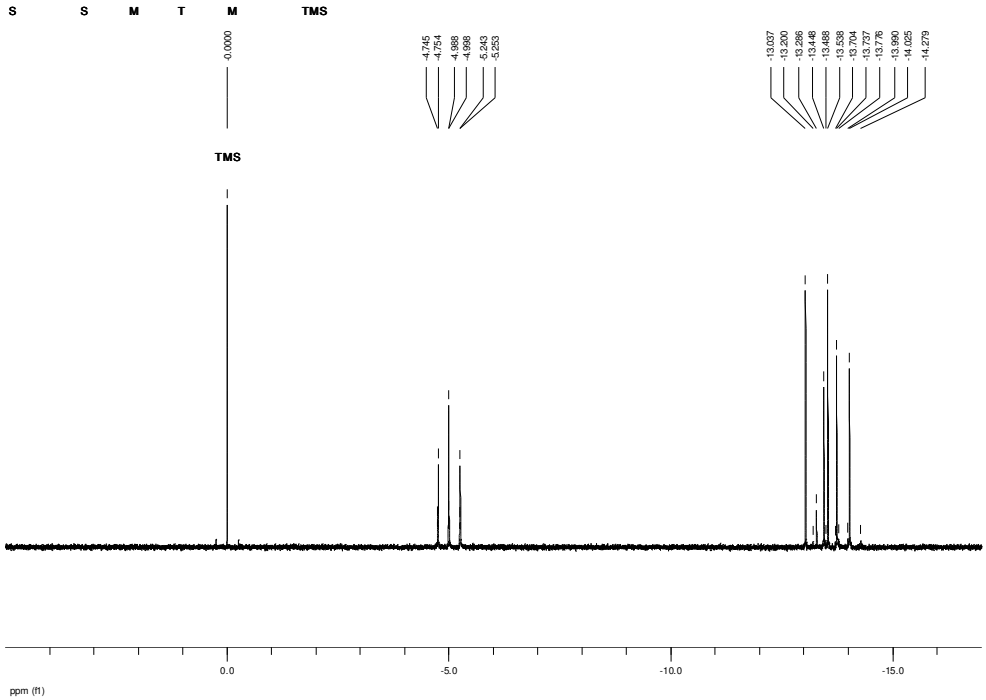
-14.00
-14.50
ppm (f1)

Run 5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-4.988
-4.998
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-13.037
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-13.286
-13.448
-13.488
-13.538
-13.704
-13.737
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-13.990
-14.025
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-10.0
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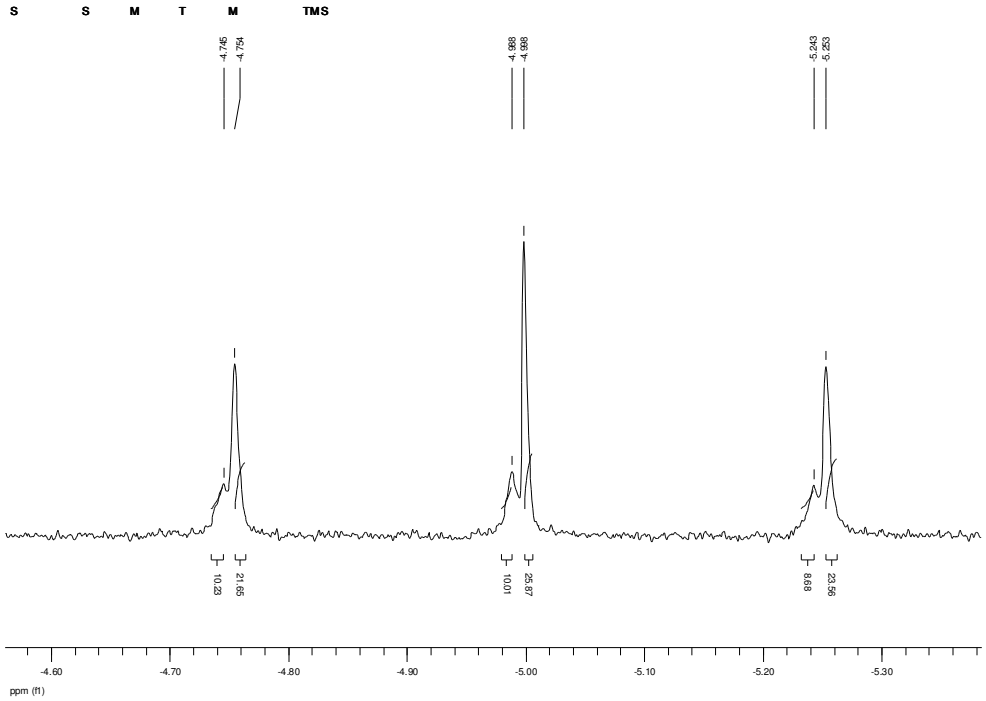
ppm (f1)


S S M T M TMS
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-4.988
-4.998
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21.65
10.01
25.67
8.69
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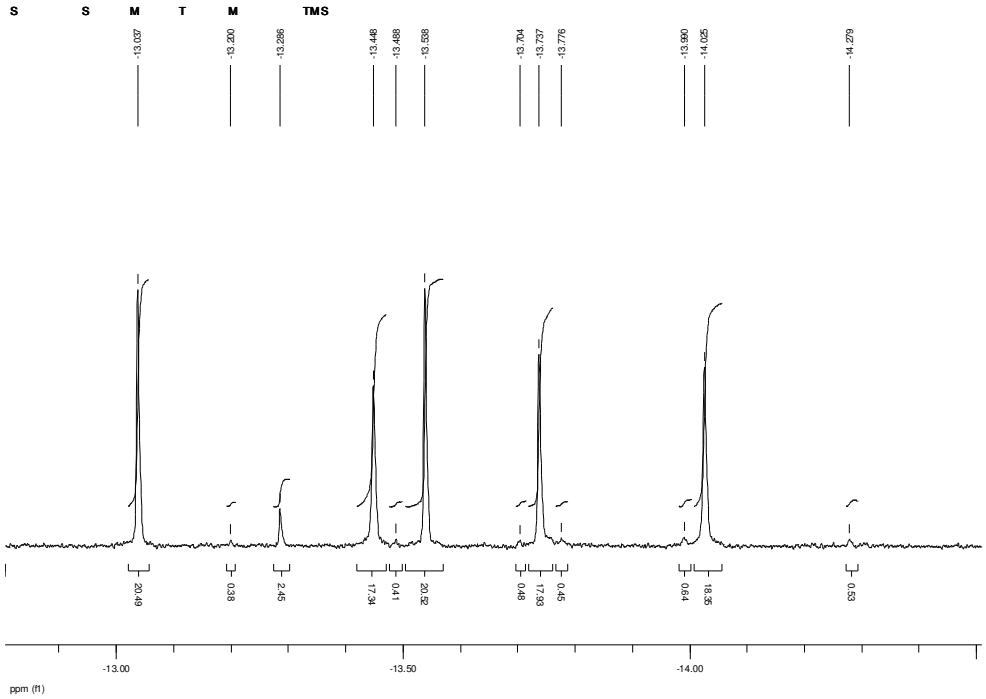
ppm (f1)

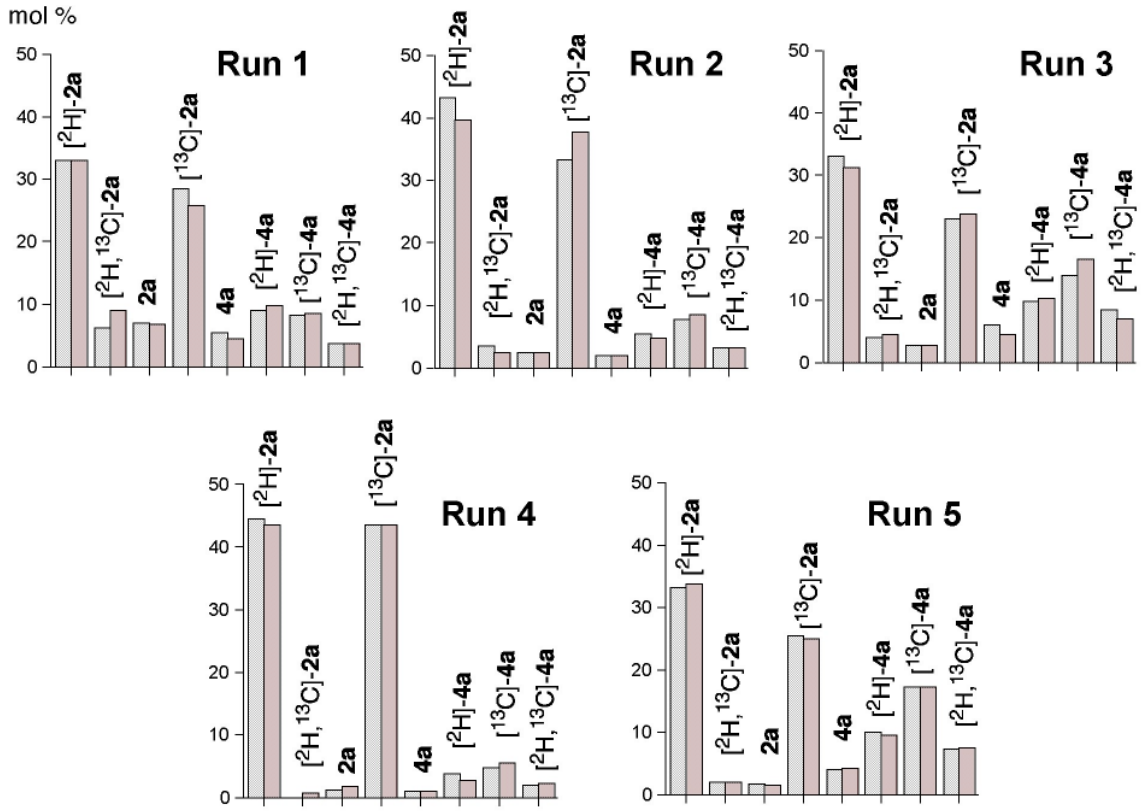


3.3 Product Distribution Analysis / Modeling

The product distributions from all five runs were modelled by computer-based application of the Gear integration method.[13] Models were simplified such that steps (i), (ii) and (iii) shown in Scheme 2 were telescoped into one step: **7a** + **2a** → **4a** + **7a** + **X**, with an associated rate constant k_1, where '**X**' was used as a marker of total number of turnovers, where intermediates **7a** were denoted as '12C' or '13C' as appropriate, and where silane **2a** was denoted as '[^{2}H]', '[^{13}C]', '[^{2}H,^{13}C]' or unlabeled as appropriate. When reactions involved **2a** or [^{13}C]-**2a**, the value of k_1 was multiplied by k_{KIE} (to reflect the net PKIE which was found to give the best fit). Absolute rate constants have no meaning outside of the framework of the model. The units of concentration of all species were arbitrarily based on % mol fractions. The starting concentrations were such that **7a** and [^{13}C]-**7a** were equal (0.15 mol %) and the concentrations of [^{2}H]-**2a** and [^{13}C]-**2a** reflected the isotopic purities (98% ^{2}H, 99% ^{13}C) of the reagent as well as their initial ratios (e.g. for runs 1, 3, 4 and 5, [[^{13}C]-**2a**]$_0$ = 51.48; [[^{2}H]-**2a**]$_0$ = 47.04; [**2a**]$_0$ = 1.48). The models included a scrambling mechanism to generate [^{2}H,^{13}C]-**2a** and **2a** from the initial state. As the catalyst loading was invariant between all five runs, there was no need for this to occur via a chemically meaningful model involving **5a** (or **7a**) and a simple bimolecular exchange proces between species **2a** was employed with a rate constant k_2. To account for the effect of [**1**] on K_1 in Scheme 2, and an associated redcution in silane exchange via **5a**, the magnitude of k_2 was inversely linked to the alkene concentration such that k_2 [**1a**]$_0$ = k_{ex} (where [**1a**] is in mol%) and all of the four non-degenerate interactions were given the same relative rate (no KIE). Relative rates were varied, and best fits obtained through manual iteration. A satisfactory fit for all five runs was found when k_{KIE} =

2.5 × k_1 and k_{ex} = 325 × k_1. A comparison of observed (grey) with model (pink) data is given in Figure S1.

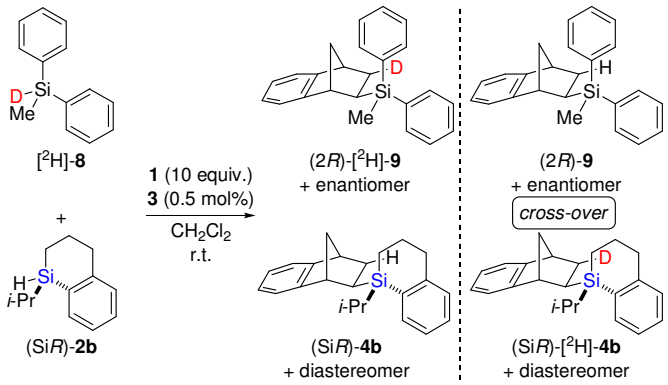
Figure S1. Comparison of observed (grey shaded bars, data from Table 1) versus predicted (pink shaded bars, using model outlined in section 3.3) product **4a** and silane **2a** distributions for cross-over experiments involving [^{2}H]-**2a** and [^{13}C]-**2a**.



4 Cross-over Experiments of 2b and 8

4.1 Experimental Details

Representative Procedure for the Hydrosilylation of **1** with mixtures of (Si*R*/Si*S*)-[^{1}H/^{2}H]-**2b** and [^{1}H/^{2}H]-**8**



A Schlenk tube was charged with a solution of (Si*R*)-**2b** (28.7 mg, 0.150 mmol, 0.500 equiv., 97% *ee*), [^{2}H]-**8** (29.9 mg, 0.150 mmol, 0.500 equiv., >98% D), and bicyclic alkene **1** (427 mg, 3.00 mmol, 10.0 equiv.) in anhydrous degassed CH_2Cl_2 (2.5 mL) under argon atmosphere. An aliquot (0.50 mL) was taken via syringe to determine the exact composition of the mixture by ^{1}H NMR. Subsequently, a freshly prepared solution of (phen)PdMe(OEt$_2$)$^+$ BAr$_4^-$ (**3**) [Ar = 3,5-bis(trifluoromethyl)phenyl] (0.50 mL, 0.00125 mmol, 0.005 equiv., 0.0025M in CH_2Cl_2) – prepared in situ from (phen)PdMe$_2$ (0.8 mg, 0.0025 mmol, 0.010 equiv.) and [H(OEt$_2$)$_2$]$^+$BAr$_4^-$ (2.5 mg, 0.0025 mmol, 0.010 equiv.) in CH_2Cl_2 (1.0 mL) at 0°C – was added via a microliter syringe. The resulting solution was stirred at room temperature for 48 h. ^{1}H NMR analysis indicated complete conversion of silanes. After removal of the catalyst by filtration through a plug of silica gel using cyclohexane as eluent, the solvents were evaporated. The excess alkene was removed by Kugelrohr distillation in vacuo. Subsequent flash column chromatography on silica gel with cylcohexane as eluent delivered (Si*R*)-[^{1}H/^{2}H]-**4b** (36 mg, 87%, 97% *ee*) and (2*R*)-[^{1}H/^{2}H]-**9** (28 mg, 66%, 34% *ee*) as separated products. Mass spectrometric analysis revealed a golbal ^{1}H/^{2}H ratio of 52:48 for (Si*R*)-**4b** and 48:52 for (2*R*)-**9**.

Both products were subjected to analytical HPLC analysis using chiral stationary phases. Identical stereoisomeric fractions of several runs were collected, concentrated and analyzed by mass spectrometry (see Table S2 for results).

Analogously, mixtures of (Si*S*)-[^{2}H]-**4b** (95% *ee*, 99% D) and **8**, or (Si*S*)-[^{2}H]-**4b** (95% *ee*, 99% D) and **8**, or (Si*R*)-**4b** (97% *ee*) and [^{2}H]-**8** (>98% D) were co-reacted and analyzed (see Table S2 for results).

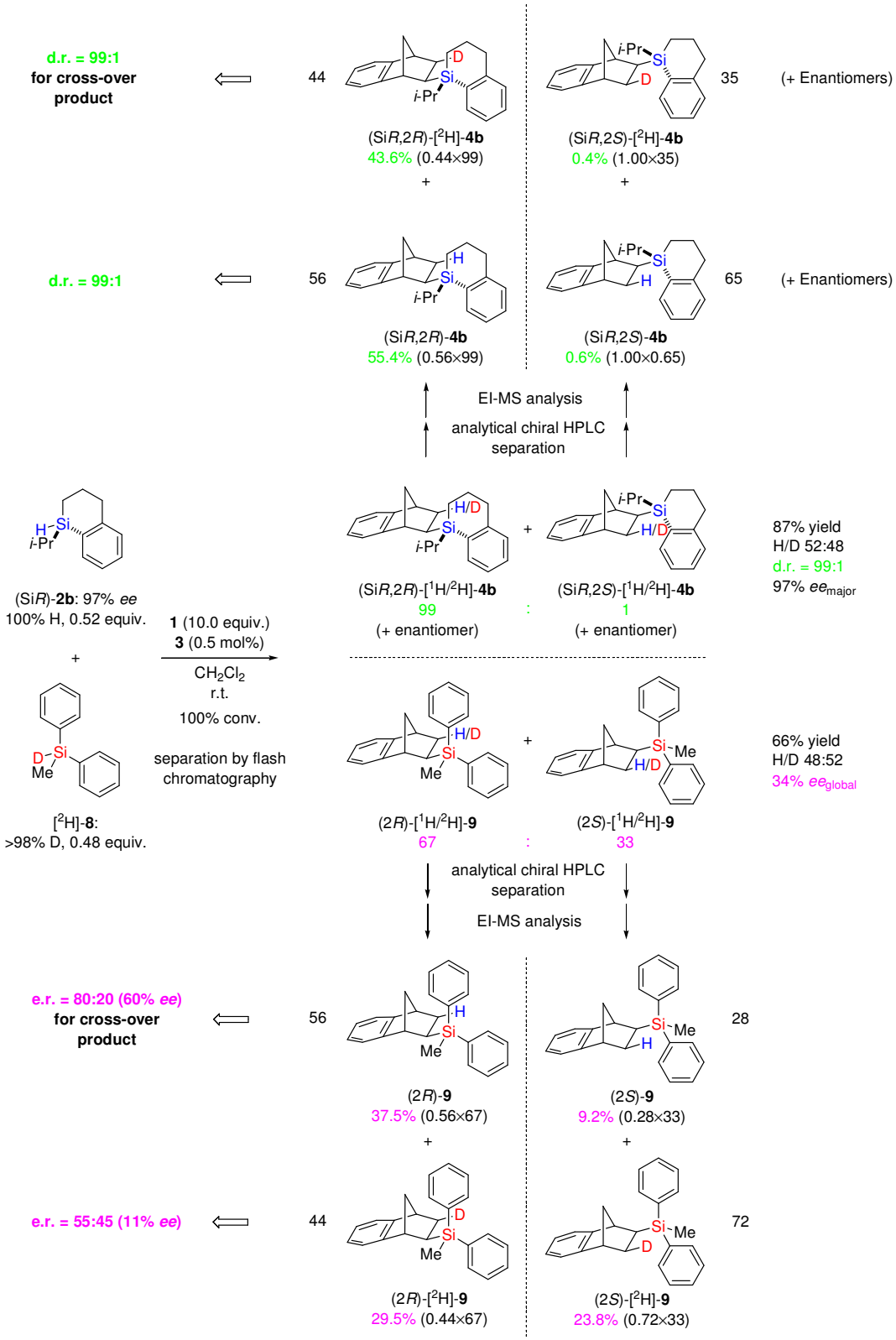
Table S2. Co-reactions of **2b** and **8**.

		Run[a]			
		1	**2**	**3**	**4**
Silane **2b**	equiv.[b]	0.52	0.48	0.47	0.46
	ee [%][c]	97 (Si*R*)	95 (Si*S*)	97 (Si*R*)	95 (Si*S*)
	H/D[d]	100:0	1:99	100:0	1:99
Silane **8**	equiv.[b]	0.48	0.52	0.53	0.54
	H/D[e]	<2:98	100:0	100:0	<2:98
Product **4b**	yield [%][f]	87	72	77	70
	d.r. [(Si*R*)-[^{1}H/^{2}H]-**4b**][g]	99:1	--	99:1	--
	d.r. [(Si*S*)-[^{1}H/^{2}H]-**4b**][g]	--	99:1	--	99:1
	ee (major) [%][h]	97 (Si*R*)	94 (Si*S*)	91 (Si*R*)	93 (Si*S*)
	H/D (global)[d]	52:48	38:62	100:0	2:98
	H/D (major)[i]	56:44	39:61		
	H/D (minor)[i]	65:35	22:78		
	d.r. [(Si*R*)-**4b**][j]	99:1	--		
	d.r. [(Si*R*)-[^{2}H]-**4b**][j]	99:1	--		
	d.r. [(Si*S*)-**4b**][j]	--	99:1		
	d.r. [(Si*S*)-[^{2}H]-**4b**][j]	--	99:1		
Product **9**	yield [%][f]	66	87	70	66
	ee (global) [%][k]	34 (2*R*)	10 (2*S*)	19 (2*R*)	11(2*S*)
	H/D (global)[d]	48:52	69:31	100:0	1:99
	H/D [(2*R*)-**9**][l]	56:44	80:20		
	H/D [(2*S*)-**9**][l]	28:72	58:42		
	ee (**9**) [%][m]	62 (2*R*)	6 (2*R*)		
	ee ([^{2}H]-**9**) [%][m]	10 (2*R*)	44 (2*S*)		

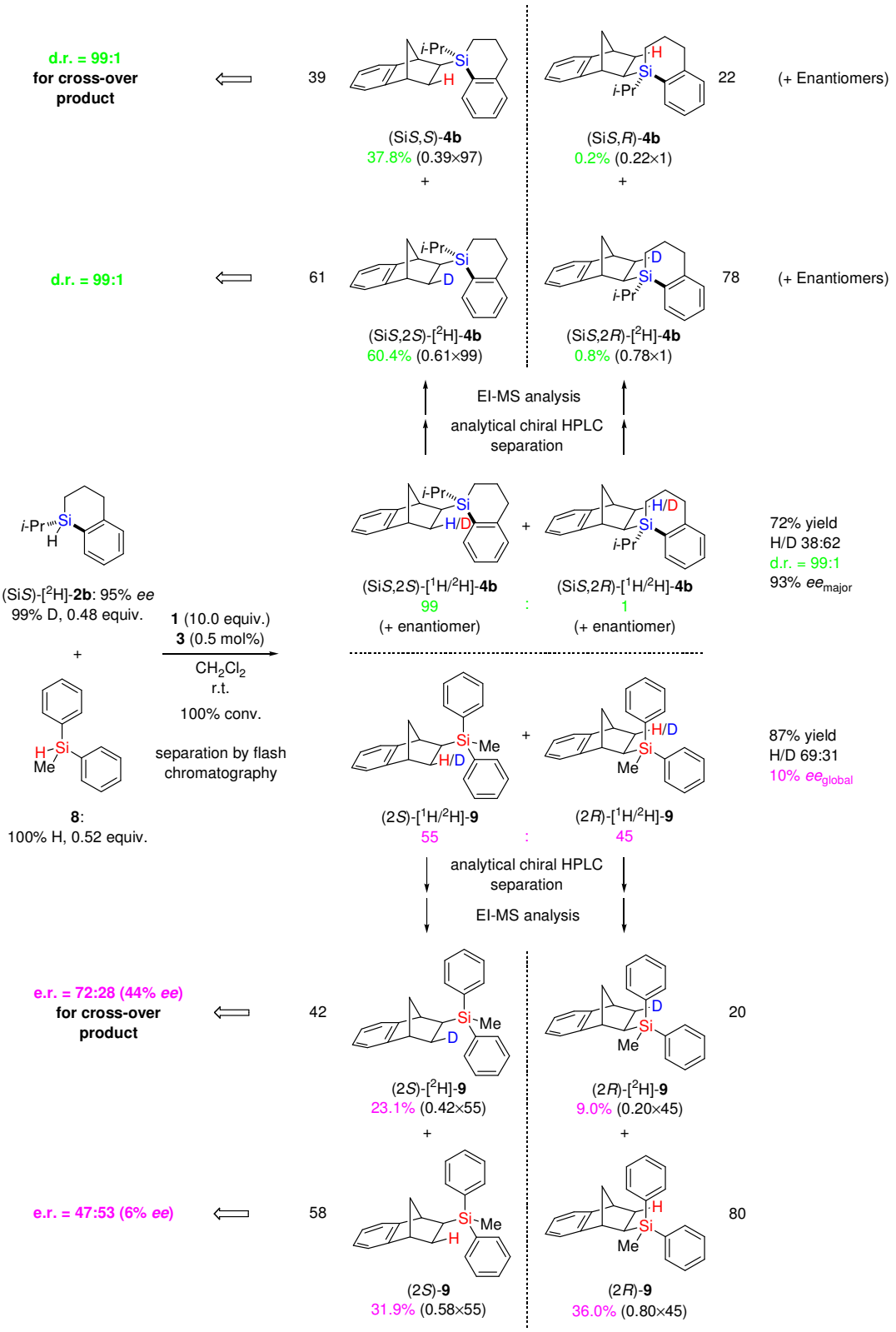
[a] See representative procedure for experimental details. [b] Determined by integration of ^{1}H NMR signals at 0.65 (d, 3H for **8** or s, 3H, for [^{2}H]-**8**) and 0.87–1.20 ppm (m, 9H, [^{1}H/^{2}H]-**2b**. [c] HPLC analysis using a Daicel Chiralcel OJ-RH column (MeCN/H_2O 50:50 at 12°C) provided sufficient separation of enantiomers. [d] Determined by EI-MS. [e] Determined by ^{1}H NMR. [f] Yields of isolated product based on employed amount of corresponding silane. [g] HPLC analysis using a Daicel Chiralcel OD-RH column (MeCN/H_2O 75:25 at 12°C) provided baseline separation of all four stereoisomers; only major enantiomer included. [h] HPLC analysis using a Daicel Chiralcel OD-RH column (MeCN/H_2O 75:25 at 12°C) provided baseline separation of all four stereoisomers; only major diastereomer included. [i] Determined by EI-MS of concentrated samples of stereoisomerically pure fractions obtained from three analytical HPLC runs; major = major diastereomer, major enantiomer; minor = minor diastereomer, major enantiomer. [j] Values calculated by comparison of H/D ratios of each stereoisomer (see correlation scheme for details). [k] HPLC analysis using a Daicel Chiralcel OD-H column (*n*-heptane at 20°C) provided baseline separation of enantiomers. [l] Determined by EI-MS of concentrated samples of enantiopure fractions obtained from three analytical HPLC runs. [m] Calculated from H/D ratio and ee_{global}; e.g. run 1 with $e.r._{global}$ = 67:33: e.r. (**9**) = (67·0.56):(33·0.28) = 37.5:9.2 (62% *ee*) [*cf.* Correlation Schemes].

4.2 Correlation Schemes

Scheme S1. Results for co-reaction of (Si*R*)-**2b** and [^{2}H]-**8** (Run 1).



Scheme S2. Results for co-reaction of (Si*S*)-[^{2}H]-**2b** and **8** (Run 2).

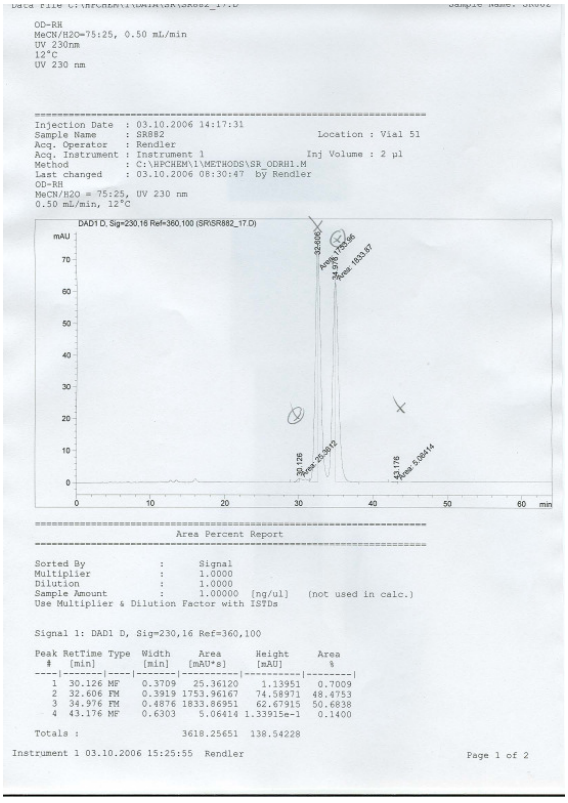


4.3 Copies of HPLC and MS analyses

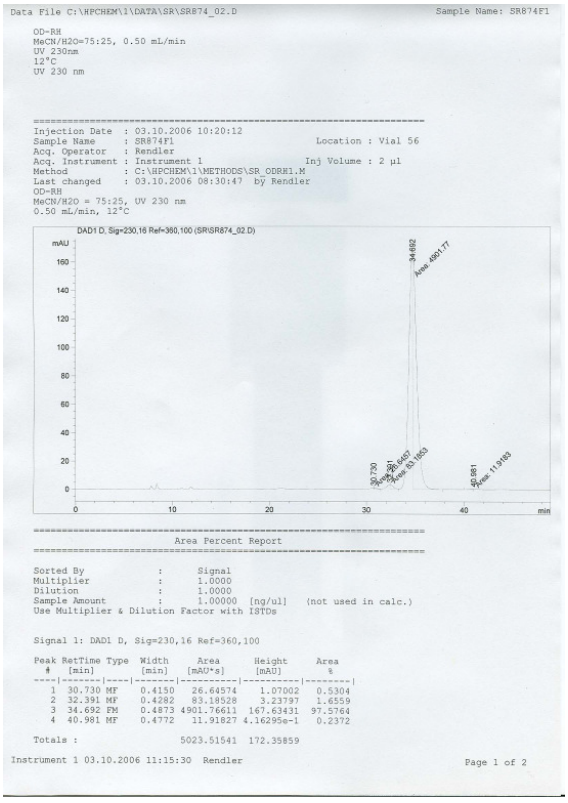
- **Complete Characterization Data for Pure Compounds can be found in a separate file.** This is consisting of NMR files, copies of HPLC data for racemic **2b** and **4b**, **9** as well as MS analyses of deuterated and non-deuterated compounds thereof and of **8**. In addition, data for enantioenriched **2b** and **4b** are included.

- **Run 1: Products**

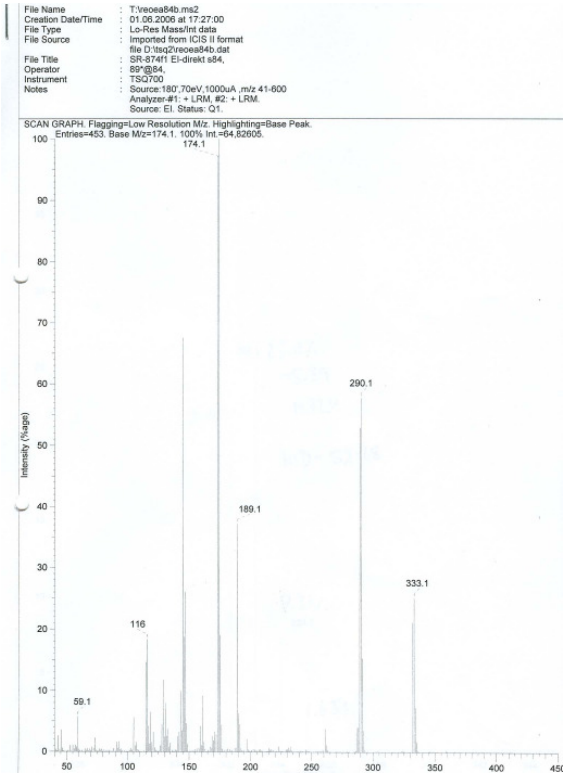
rac-**4b** (HPLC)



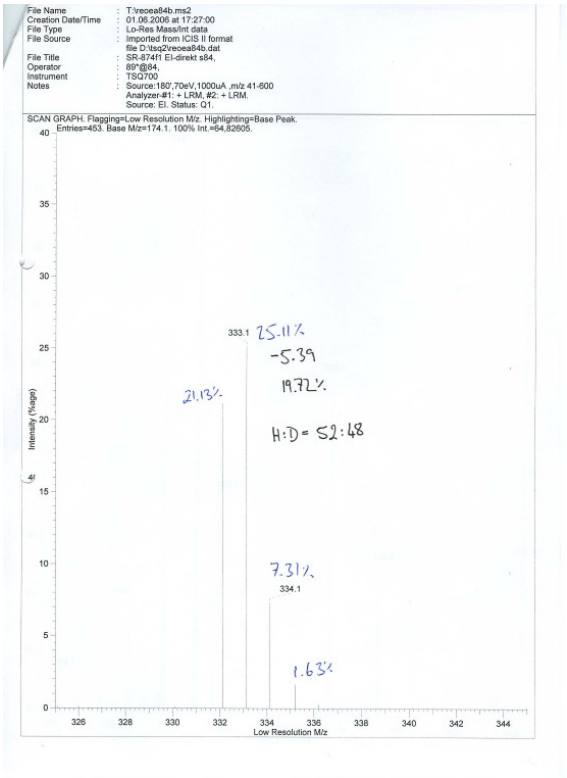
4b (HPLC, run 1)



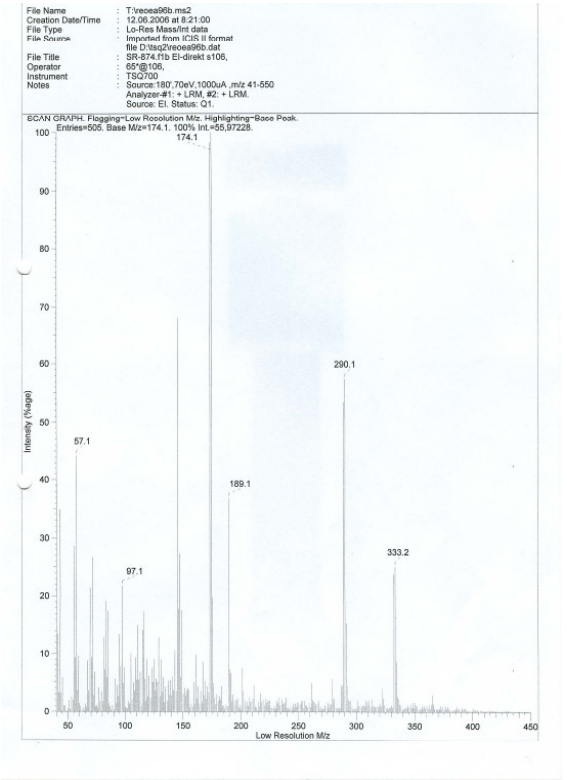
H/D$_{global}$ (before separation) **4b** (EI-MS)



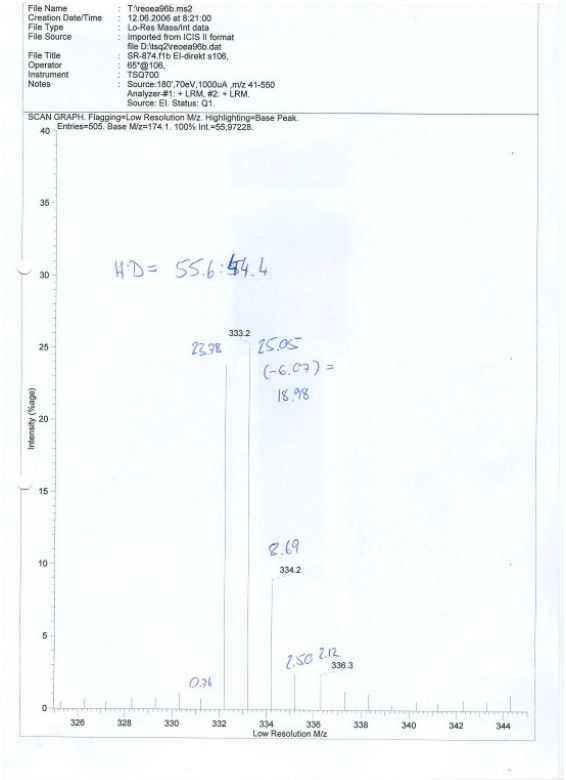
H/D$_{global}$ (before separation) **4b** (EI-MS) [enlargement]



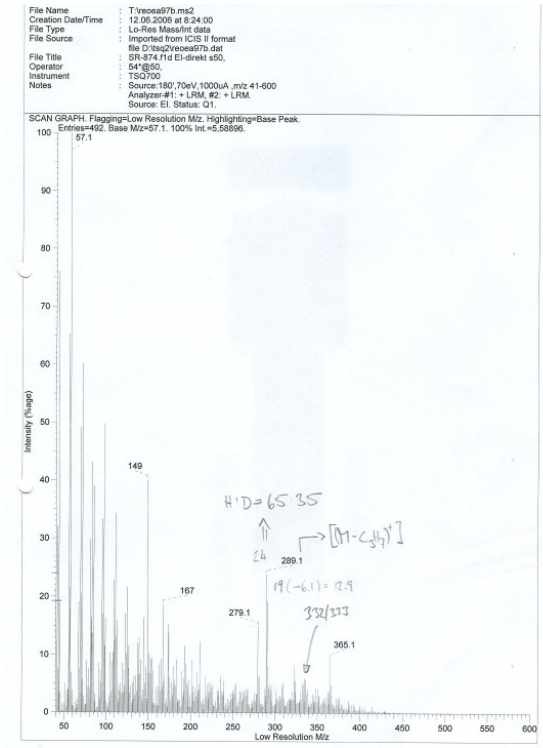
H/D (Si*R*,2*R*) **4b** (EI-MS) (t_R = 34.7 min)



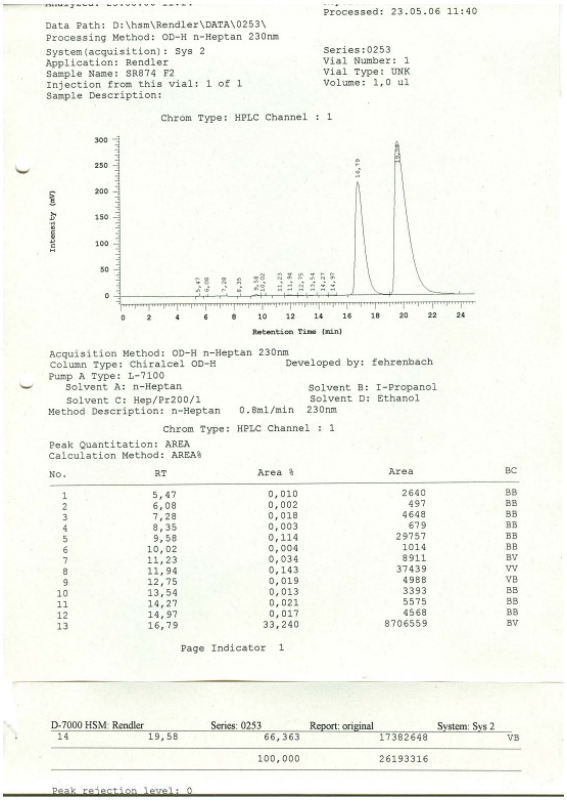
H/D (Si*R*,2*R*) **4b** (EI-MS) [enlargement]



H/D (Si*R*,2*S*) **4b** (EI-MS) (t_R = 30.7 min)

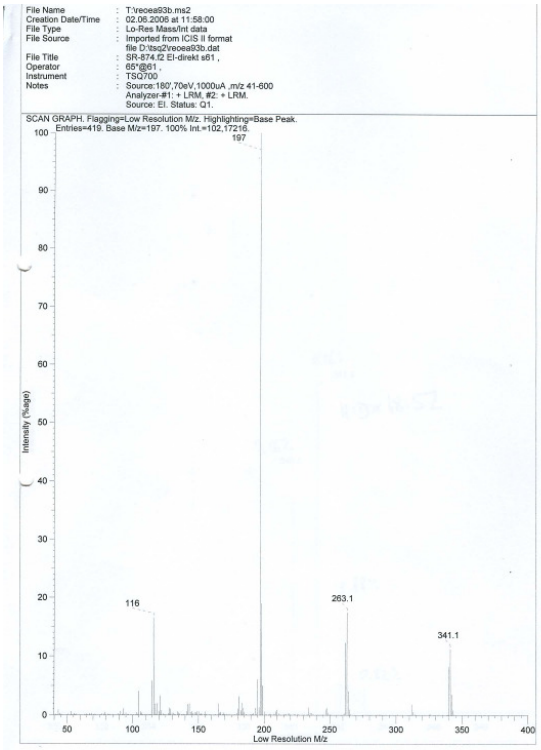


9 (run 1)

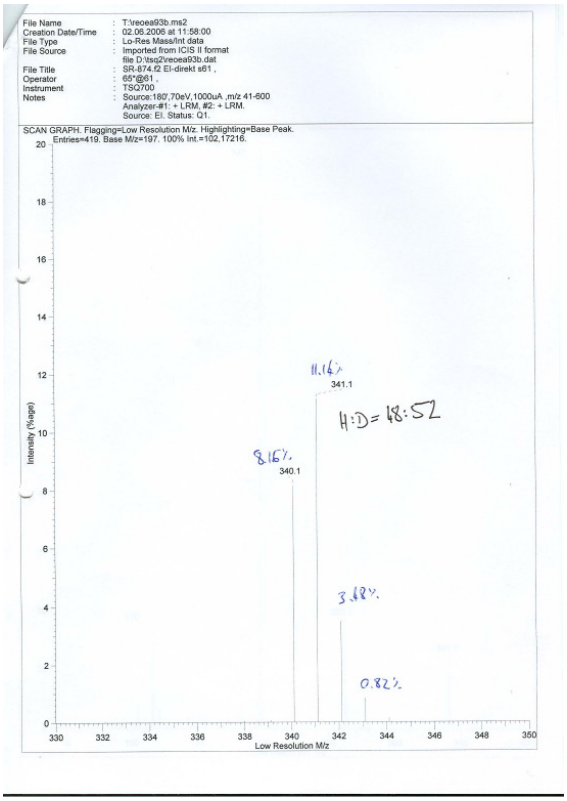


No.	RT	Area %	Area	BC
1	5,47	0,010	2640	BB
2	6,08	0,002	497	BB
3	7,28	0,018	4648	BB
4	8,35	0,003	679	BB
5	9,58	0,114	29757	BB
6	10,02	0,004	1014	BB
7	11,23	0,034	8911	BV
8	11,94	0,143	37439	VV
9	12,75	0,019	4988	VB
10	13,54	0,013	3393	BB
11	14,27	0,021	5575	BB
12	14,97	0,017	4568	BB
13	16,79	33,240	8706559	BV

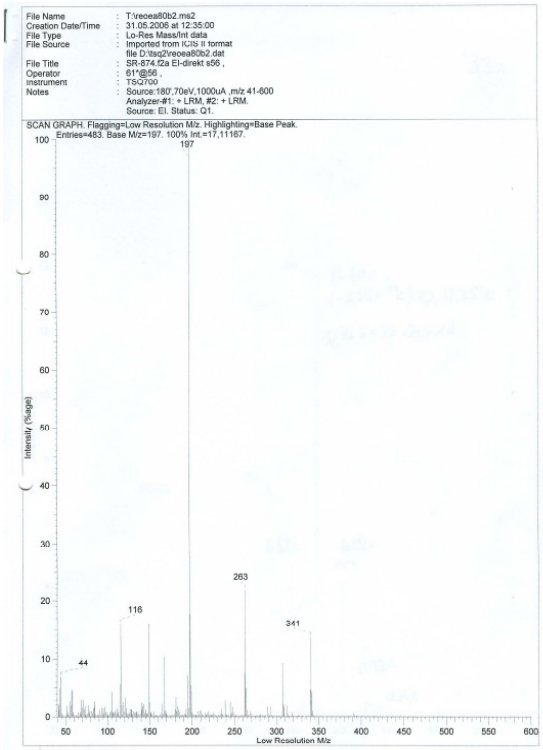
H/D$_{global}$ (before separation) **9** (EI-MS)



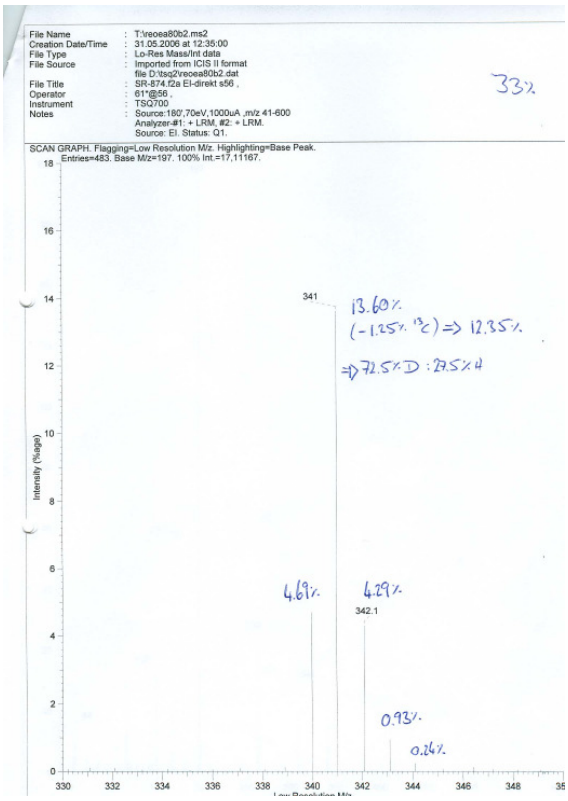
H/D$_{global}$ (before separation) **9** (EI-MS) [enlarged]



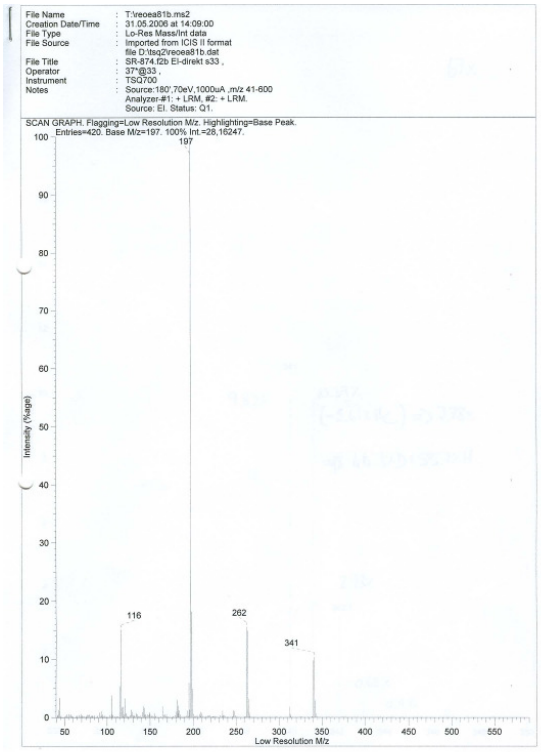
H/D (2*S*)-**9** (EI-MS) t_R = 16.8 min



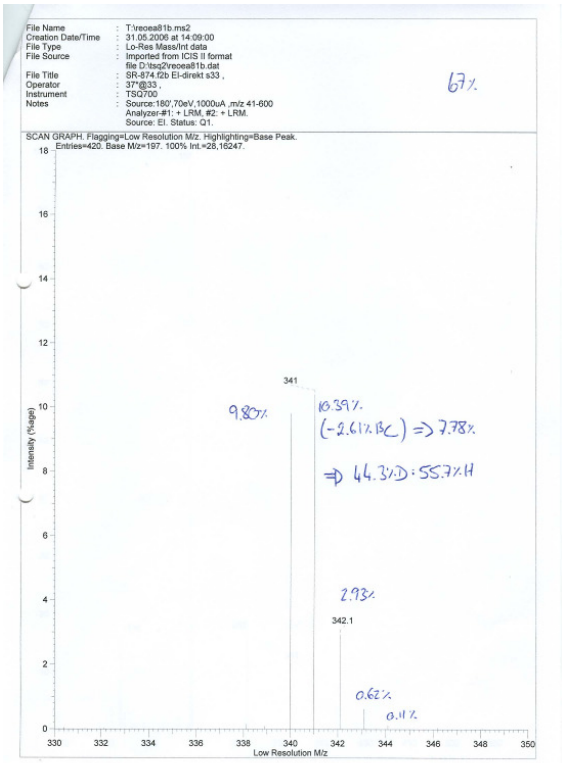
H/D (2*S*)-**9** (EI-MS) [enlarged]



H/D (2*R*)-**9** (EI-MS) t_R = 19.5 min

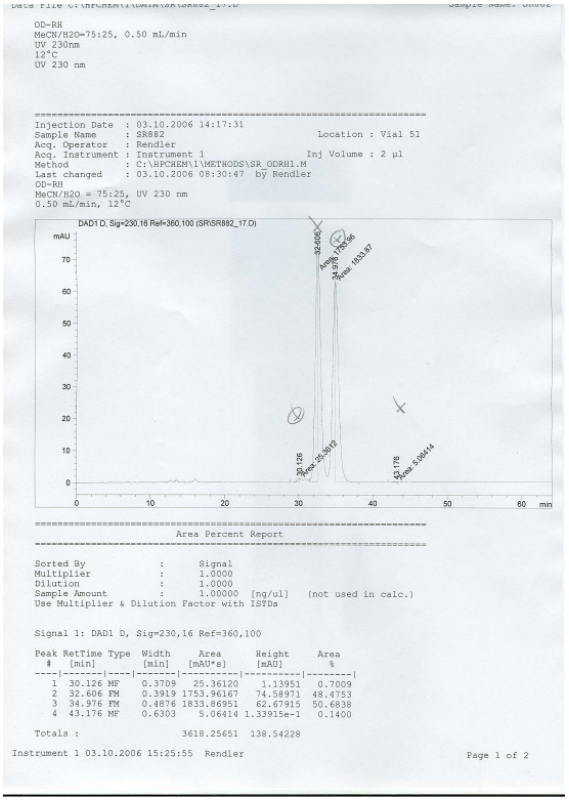


H/D (2*R*)-**9** (EI-MS) [enlarged]

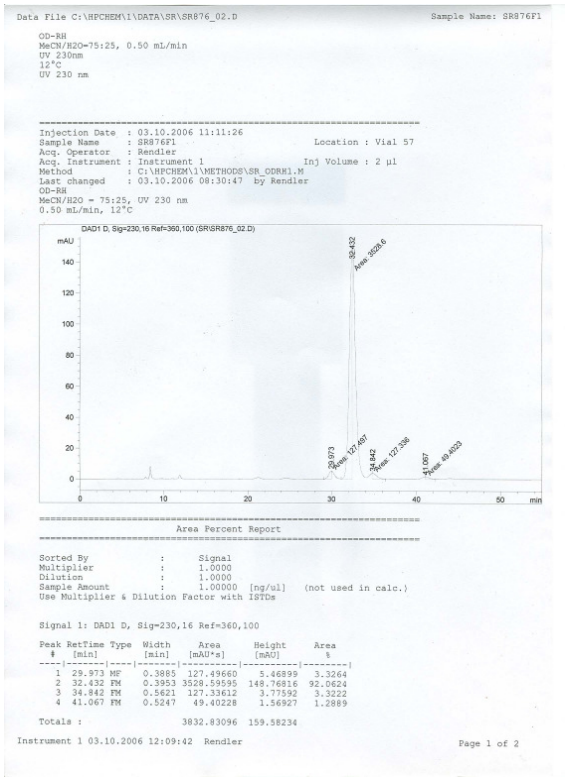


- **Run 2: Products**

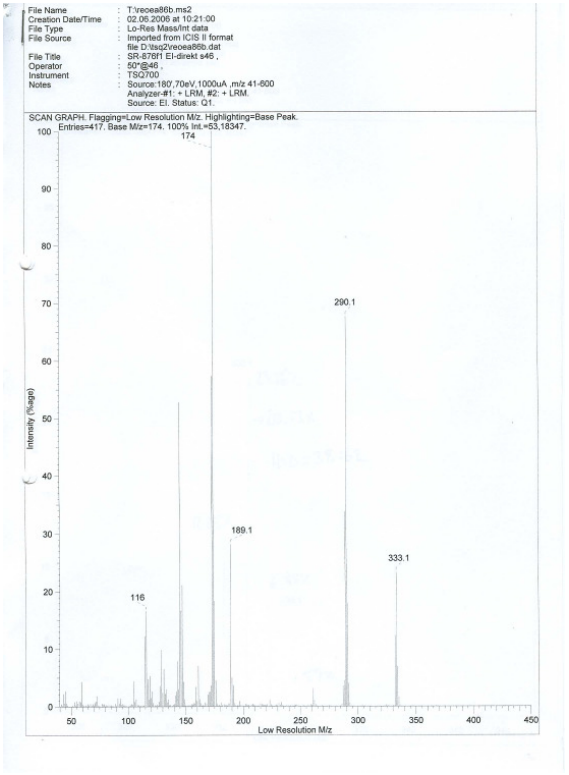
rac-**4b** (HPLC)



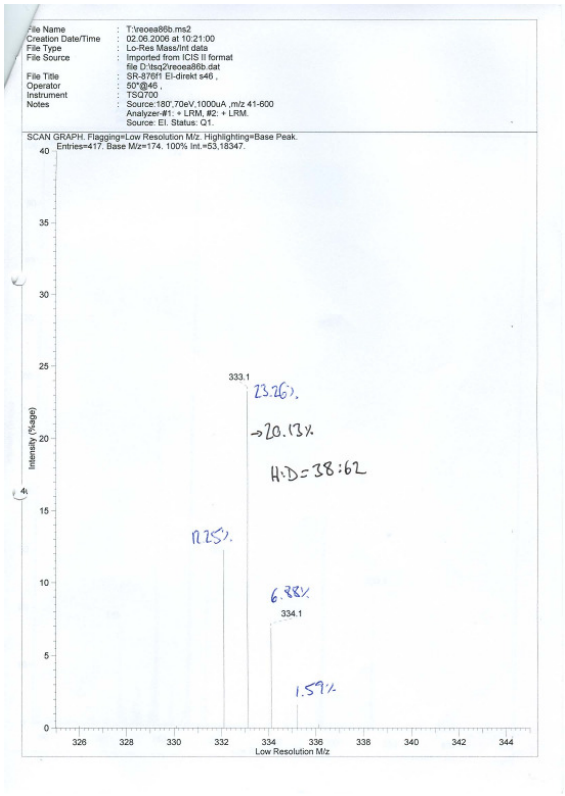
4b (HPLC, run 2)



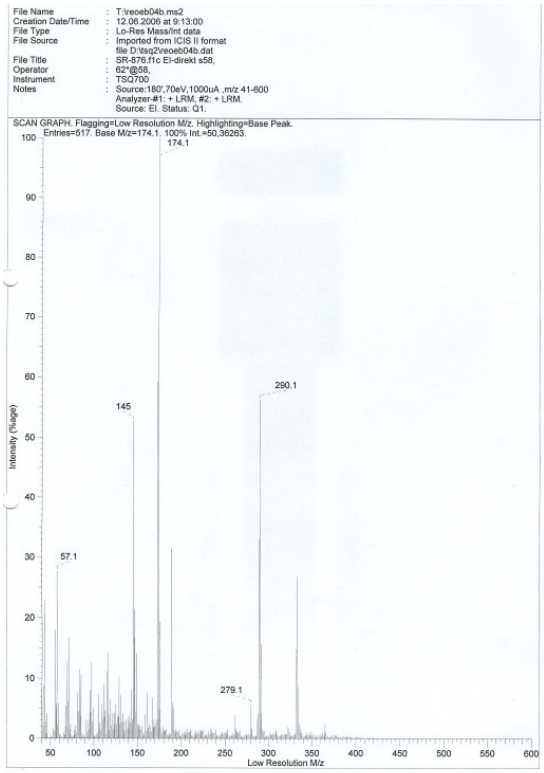
H/D_{global} (before separation) **4b** (EI-MS)



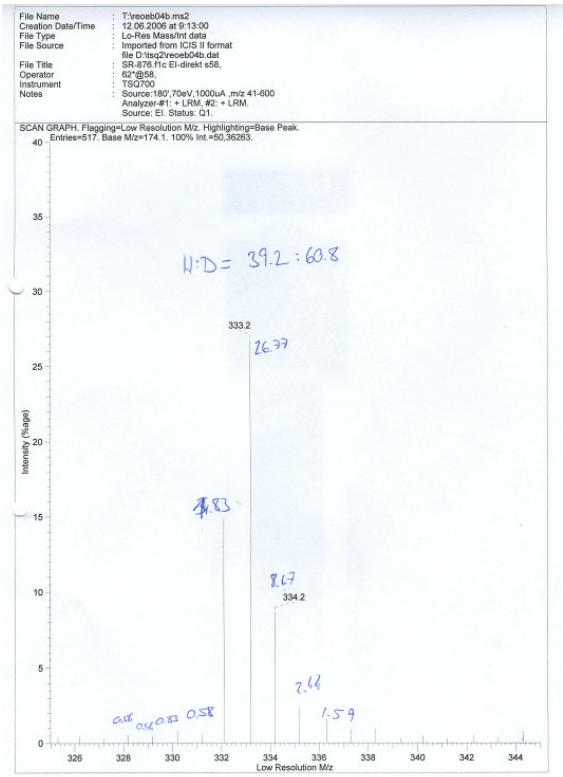
H/D_{global} (before separation) **4b** (EI-MS) [enlargement]



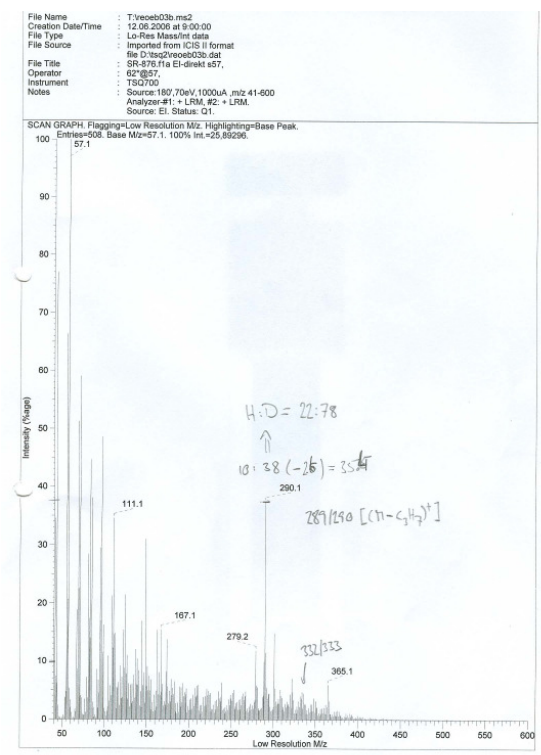
H/D (Si*S*,2*S*) **4b** (EI-MS) (t_R = 32.4 min)



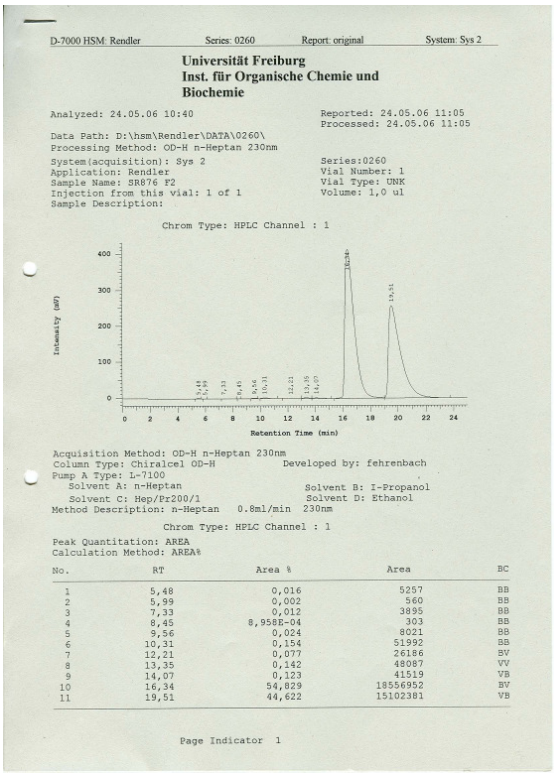
H/D (Si*S*,2*S*) **4b** (EI-MS) [enlargement]



H/D (Si*S*,2*R*) **4b** (EI-MS) (t_R = 41.1 min)



9 (run 2)



D-7000 HSM: Rendler Series: 0260 Report: original System: Sys 2

Universität Freiburg
Inst. für Organische Chemie und Biochemie

Analyzed: 24.05.06 10:40
Reported: 24.05.06 11:05
Processed: 24.05.06 11:05

Data Path: D:\hsm\Rendler\DATA\0260\
Processing Method: OD-H n-Heptan 230nm
System(acquisition): Sys 2
Application: Rendler
Sample Name: SR876 F2
Injection from this vial: 1 of 1
Sample Description:
Series:0260
Vial Number: 1
Vial Type: UNK
Volume: 1,0 ul

Chrom Type: HPLC Channel : 1

Acquisition Method: OD-H n-Heptan 230nm
Column Type: Chiralcel OD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: n-Heptan Solvent B: I-Propanol
Solvent C: Hep/Pr200/1 Solvent D: Ethanol
Method Description: n-Heptan 0.8ml/min 230nm

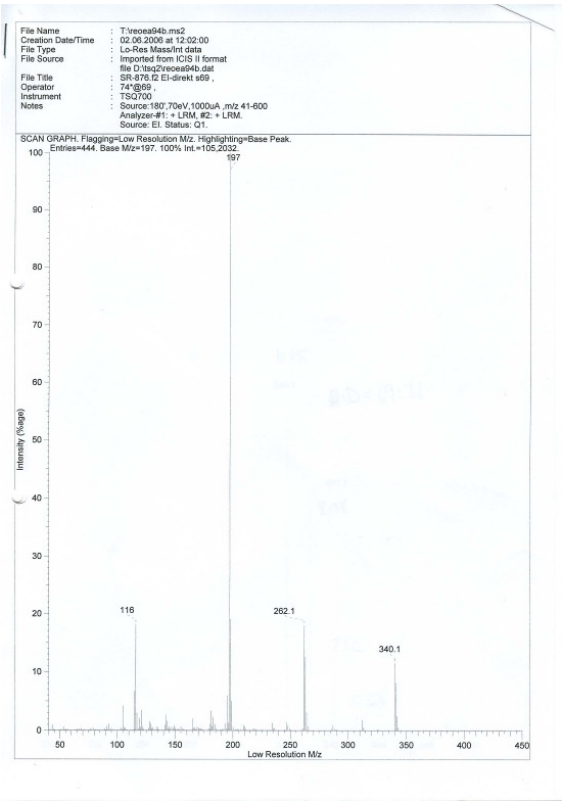
Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

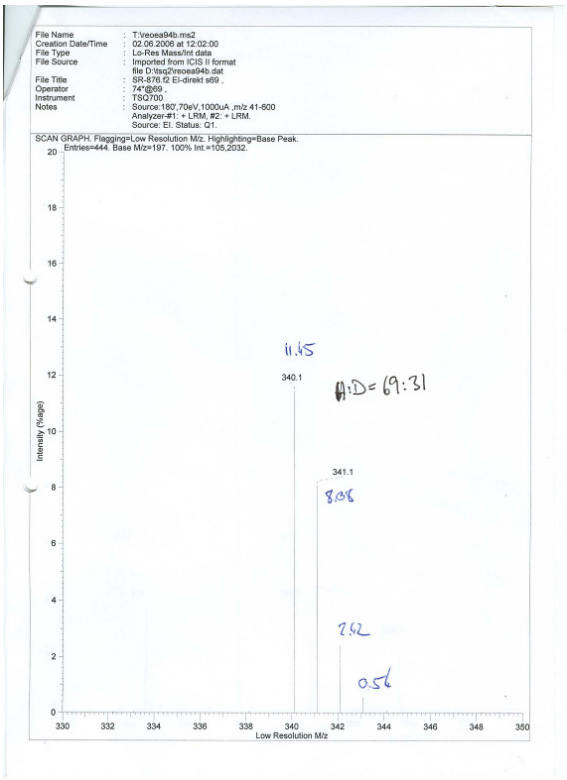
No.	RT	Area %	Area	BC
1	5,48	0,016	5257	BB
2	5,99	0,002	560	BB
3	7,33	0,012	3895	BB
4	8,45	8,958E-04	303	BB
5	9,56	0,024	8021	BB
6	10,31	0,154	51992	BB
7	12,21	0,077	26186	BV
8	13,35	0,142	48087	VV
9	14,07	0,123	41519	VB
10	16,34	54,829	18556952	BV
11	19,51	44,622	15102381	VB

Page Indicator 1

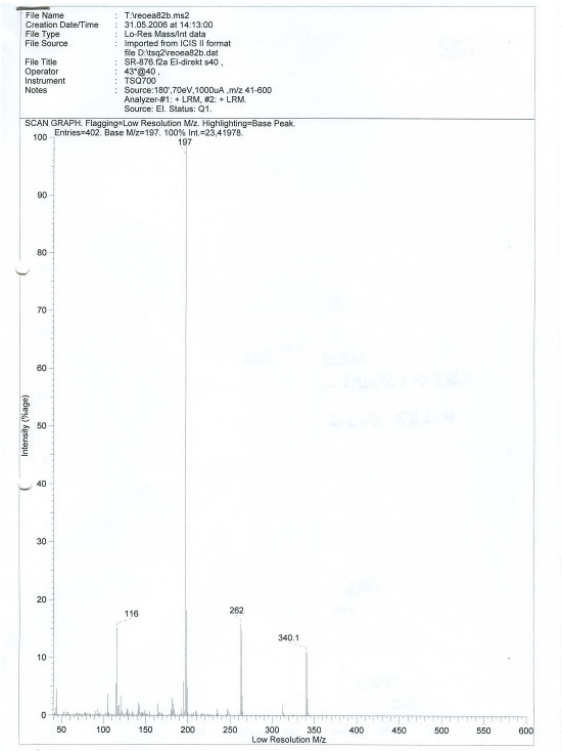
H/D$_{global}$ (before separation) **9** (EI-MS)



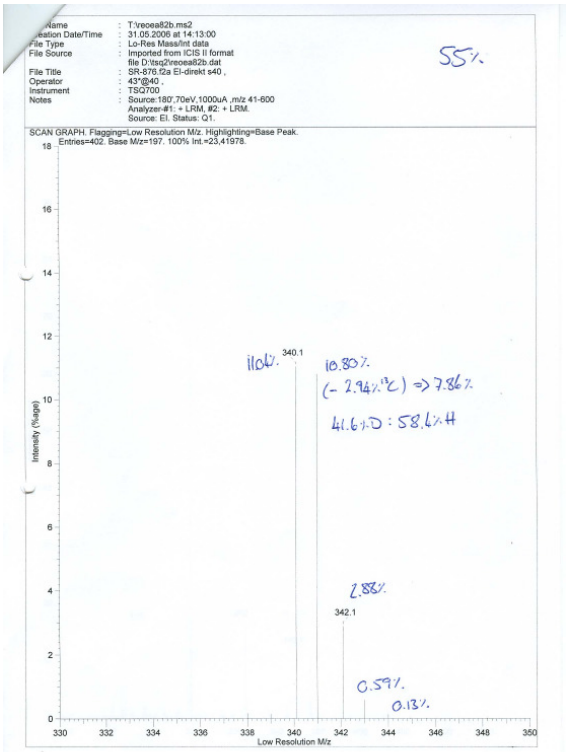
H/D$_{global}$ (before separation) **9** (EI-MS) [enlarged]



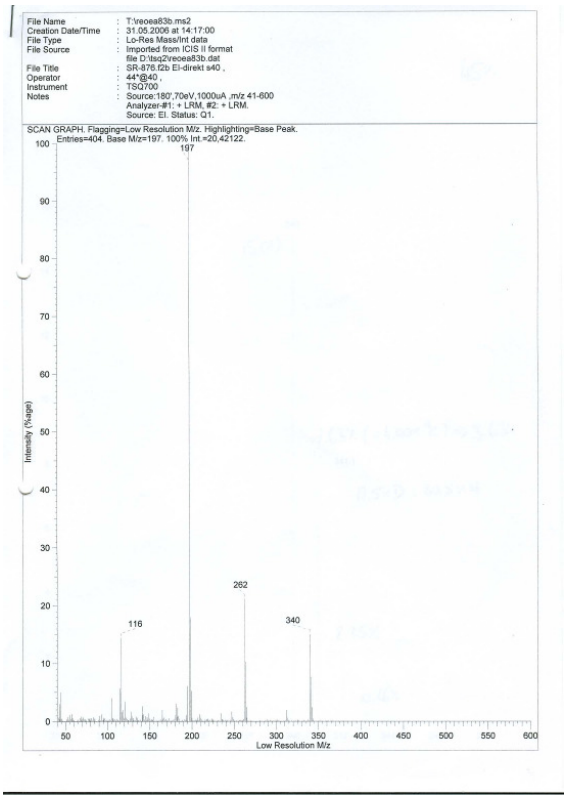
H/D (2*S*)-**9** (EI-MS) t_R = 16.3 min



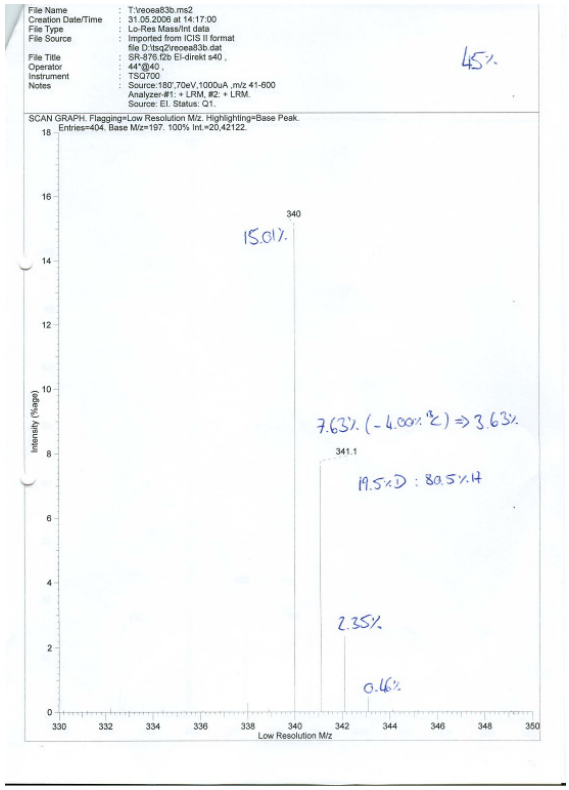
H/D (2*S*)-**9** (EI-MS) [enlarged]



H/D (2*R*) **9** (EI-MS) (t_R = 19.5 min)

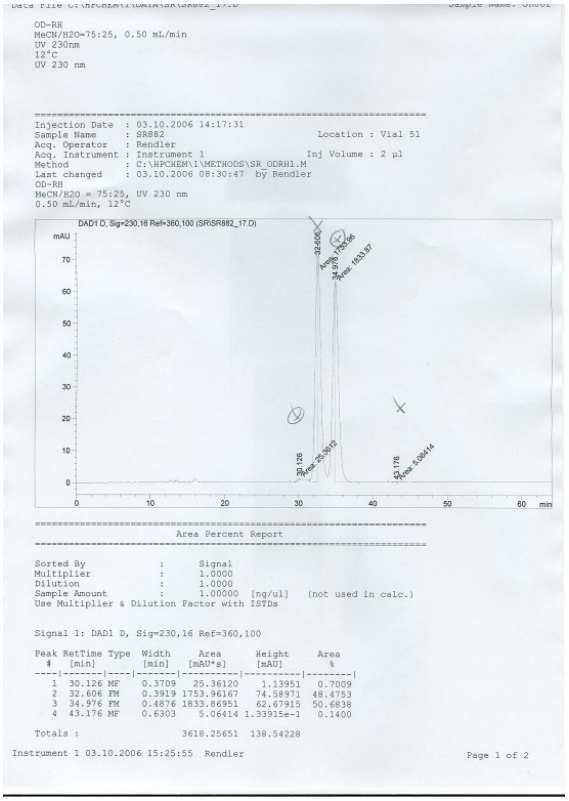


H/D (2*R*)-**9** (EI-MS) [enlarged]



- **Run 3: Products**

rac-**4b** (HPLC, run 3)



OD-RH
MeCN/H2O=75:25, 0.50 mL/min
UV 230nm
12°C
UV 230 nm

Injection Date : 03.10.2006 14:17:31
Sample Name : SR882 Location : Vial 51
Acq. Operator : Rendler
Acq. Instrument : Instrument 1 Inj Volume : 2 µl
Method : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed : 03.10.2006 08:30:47 by Rendler
OD-RH
MeCN/H2O = 75:25, UV 230 nm
0.50 mL/min, 12°C

DAD1 D, Sig=230,16 Ref=360,100 (SR\SR882_17.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

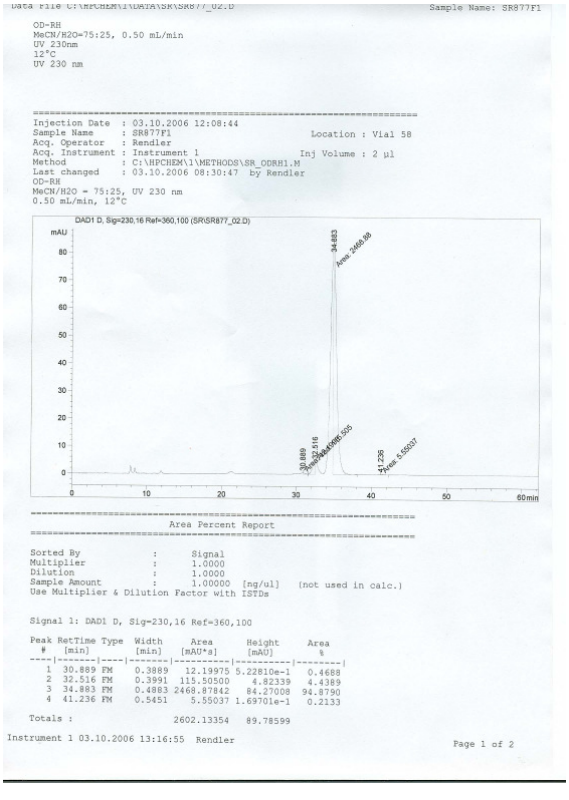
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.126	MF	0.3709	25.36120	1.13951	0.7009
2	32.606	FM	0.3919	1753.96167	74.58971	48.4753
3	34.976	FM	0.4876	1833.86951	62.67915	50.6838
4	43.176	MF	0.6303	5.06414	1.33915e-1	0.1400

Totals : 3618.25651 138.54228

Instrument 1 03.10.2006 15:25:55 Rendler Page 1 of 2

4b (HPLC, run 3)



Sample Name: SR877F1

OD-RH
MeCN/H2O=75:25, 0.50 mL/min
UV 230nm
12°C
UV 230 nm

Injection Date : 03.10.2006 12:08:44
Sample Name : SR877F1 Location : Vial 58
Acq. Operator : Rendler
Acq. Instrument : Instrument 1 Inj Volume : 2 µl
Method : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed : 03.10.2006 08:30:47 by Rendler
OD-RH
MeCN/H2O = 75:25, UV 230 nm
0.50 mL/min, 12°C

DAD1 D, Sig=230,16 Ref=360,100 (SR\SR877_02.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

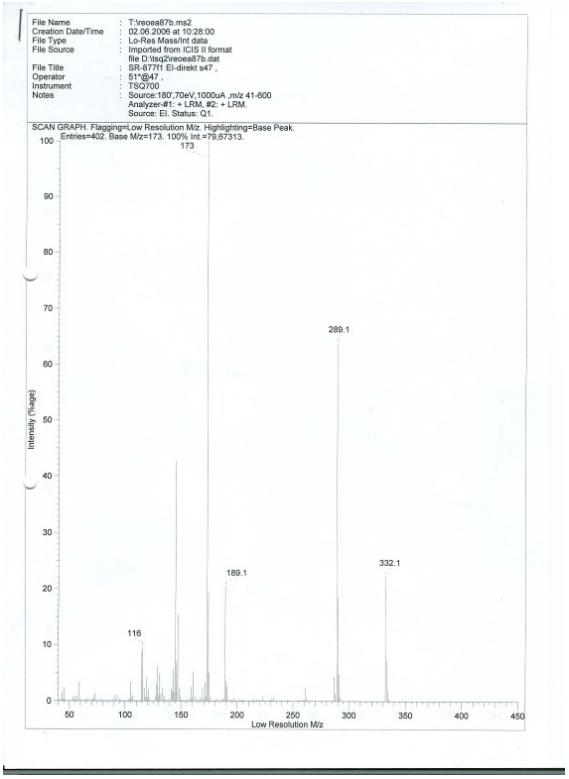
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.889	FM	0.3889	12.19975	5.22810e-1	0.4688
2	32.516	FM	0.3991	115.50500	4.82339	4.4389
3	34.883	FM	0.4883	2468.87842	84.27008	94.8790
4	41.236	FM	0.5451	5.55037	1.69701e-1	0.2133

Totals : 2602.13354 89.78599

Instrument 1 03.10.2006 13:16:55 Rendler Page 1 of 2

H/D$_{global}$ (H only) **4b** (EI-MS)

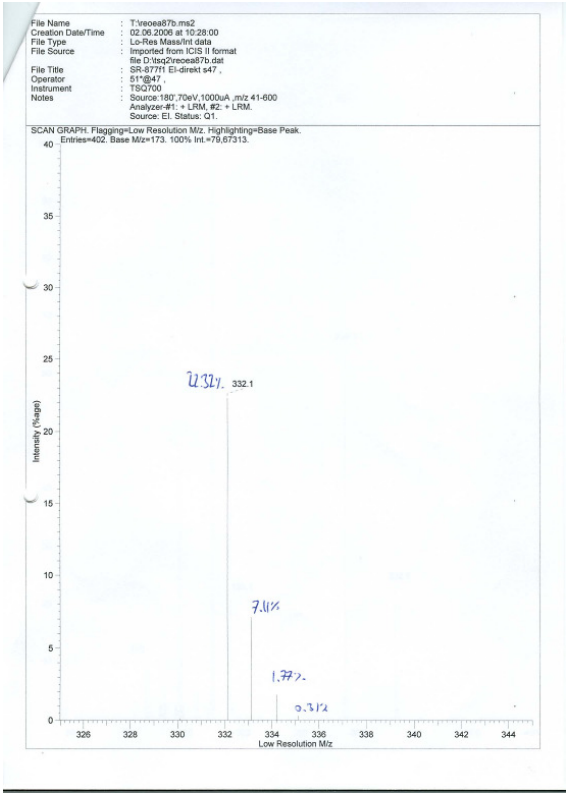


File Name : T:\reoea87b.ms2
Creation Date/Time : 02.06.2006 at 10:28:00
File Type : Lo-Res Mass/Int data
File Source : Imported from ICIS II format file D:\tsq2\reoea87b.dat
File Title : SR-877f1 El-direkt s47 ,
Operator : 51*@47 ,
Instrument : TSQ700
Notes : Source:180',70eV,1000uA ,m/z 41-600 Analyzer-#1: + LRM, #2: + LRM. Source: EI. Status: Q1.

SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak. Entries=402. Base M/z=173. 100% Int.=79,67313.

Intensity (%age)
Low Resolution M/z

H/D$_{global}$ **4b** (EI-MS) [enlarged]



File Name : T:\reoea87b.ms2
Creation Date/Time : 02.06.2006 at 10:28:00
File Type : Lo-Res Mass/Int data
File Source : Imported from ICIS II format file D:\tsq2\reoea87b.dat
File Title : SR-877f1 El-direkt s47 ,
Operator : 51*@47 ,
Instrument : TSQ700
Notes : Source:180',70eV,1000uA ,m/z 41-600 Analyzer-#1: + LRM, #2: + LRM. Source: EI. Status: Q1.

SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak. Entries=402. Base M/z=173. 100% Int.=79,67313.

Intensity (%age)
Low Resolution M/z

9 (run 3, HPLC)

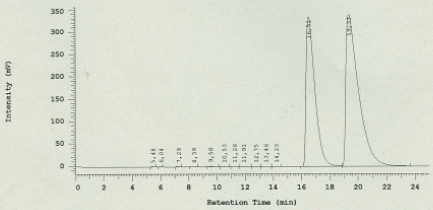
D-7000 HSM: Rendler Series: 0255 Report: original System: Sys 2

Universität Freiburg
Inst. für Organische Chemie und Biochemie

Analyzed: 23.05.06 13:10
Reported: 23.05.06 13:36
Processed: 23.05.06 13:36

Data Path: D:\hsm\Rendler\DATA\0255\
Processing Method: OD-H n-Heptan 230nm
System(acquisition): Sys 2
Series:0255
Application: Rendler
Vial Number: 1
Sample Name: SR877 P2
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1



Acquisition Method: OD-H n-Heptan 230nm
Column Type: Chiralcel OD-H
Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: n-Heptan
Solvent B: I-Propanol
Solvent C: Hep/Pr200/1
Solvent D: Ethanol
Method Description: n-Heptan 0.8ml/min 230nm

Chrom Type: HPLC Channel : 1

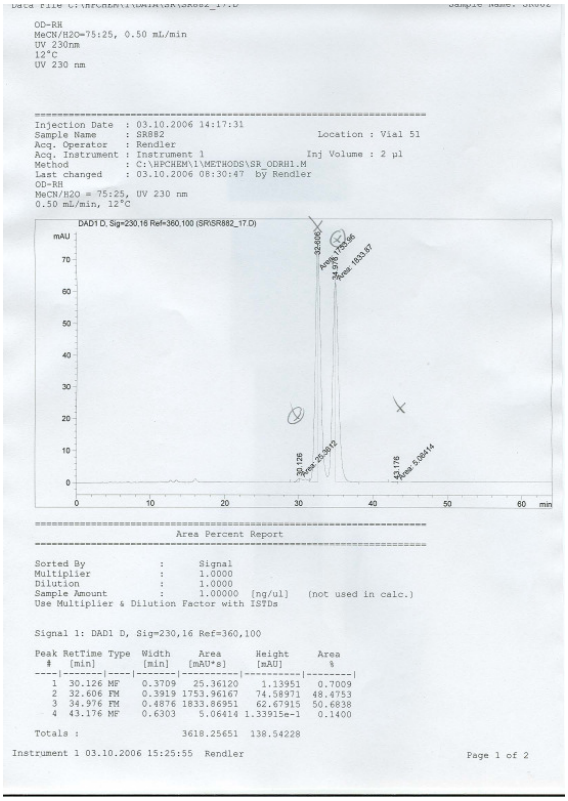
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area %	Area	BC
1	5,48	0,012	4306	BB
2	6,04	0,002	596	BB
3	7,29	0,014	4979	BB
4	8,39	0,014	4779	BB
5	9,58	0,079	27472	BB
6	10,53	0,005	1637	BB
7	11,26	0,003	1133	BB
8	11,91	0,043	14817	BB
9	12,75	0,011	3649	BB
10	13,46	0,018	6255	BB
11	14,23	0,020	7000	BB
12	16,51	40,371	13962606	BV
13	19,33	59,407	20546333	VB

Page Indicator 1

- **Run 4: Products**

rac-**4b** (HPLC, run 4)



OD-RH
MeCN/H2O=75:25, 0.50 mL/min
UV 230nm
12°C
UV 230 nm

Injection Date : 03.10.2006 14:17:31
Sample Name : SR882 Location : Vial 51
Acq. Operator : Rendler
Acq. Instrument : Instrument 1 Inj Volume : 2 µl
Method : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed : 03.10.2006 08:30:47 by Rendler
OD-RH
MeCN/H2O = 75:25, UV 230 nm
0.50 mL/min, 12°C

DAD1 D, Sig=230,16 Ref=360,100 (SR\SR882_17.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

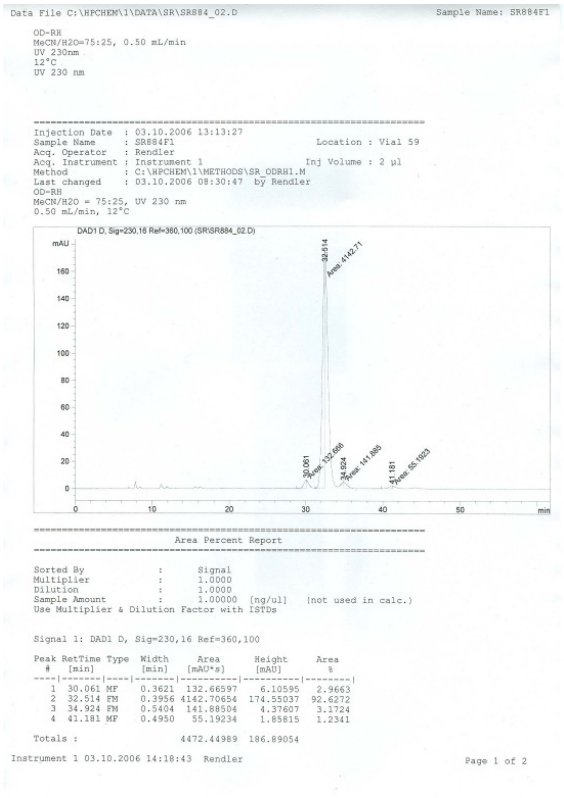
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.126	MF	0.3709	25.36120	1.13951	0.7009
2	32.606	FM	0.3919	1753.96167	74.58971	48.4753
3	34.976	FM	0.4876	1833.86951	62.67915	50.6838
4	43.176	MF	0.6303	5.06414	1.33915e-1	0.1400

Totals : 3618.25651 138.54228

Instrument 1 03.10.2006 15:25:55 Rendler Page 1 of 2

4b (HPLC, run 4)



Data File C:\HPCHEM\1\DATA\SR\SR884_02.D Sample Name: SR884F1

OD-RH
MeCN/H2O=75:25, 0.50 mL/min
UV 230nm
12°C
UV 230 nm

Injection Date : 03.10.2006 13:13:27
Sample Name : SR884F1 Location : Vial 59
Acq. Operator : Rendler
Acq. Instrument : Instrument 1 Inj Volume : 2 µl
Method : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed : 03.10.2006 08:30:47 by Rendler
OD-RH
MeCN/H2O = 75:25, UV 230 nm
0.50 mL/min, 12°C

DAD1 D, Sig=230,16 Ref=360,100 (SR\SR884_02.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

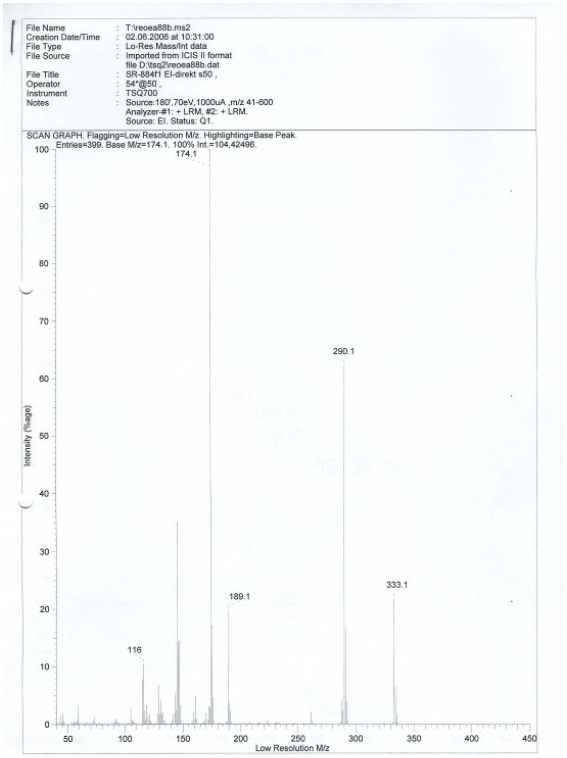
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.061	MF	0.3621	132.66597	6.10595	2.9663
2	32.514	FM	0.3956	4142.70654	174.55037	92.6272
3	34.924	FM	0.5404	141.88504	4.37607	3.1724
4	41.181	MF	0.4950	55.19234	1.85815	1.2341

Totals : 4472.44989 186.89054

Instrument 1 03.10.2006 14:18:43 Rendler Page 1 of 2

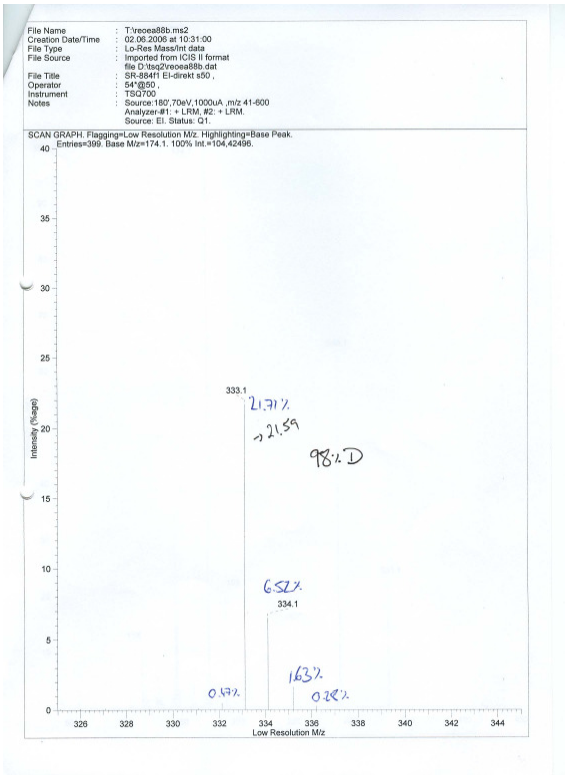
H/D$_{global}$ (H only) **4b** (EI-MS)



File Name : T:\reoea88b.ms2
Creation Date/Time : 02.06.2006 at 10:31:00
File Type : Lo-Res Mass/Int data
File Source : Imported from ICIS II format file D:\tsq2\reoea88b.dat
File Title : SR-884f1 EI-direkt s50 ,
Operator : 54*@50 ,
Instrument : TSQ700
Notes : Source:180',70eV,1000uA ,m/z 41-600 Analyzer-#1: + LRM, #2: + LRM. Source: EI. Status: Q1.

SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak. Entries=399. Base M/z=174.1. 100% Int.=104,42496.

H/D$_{global}$ **4b** (EI-MS) [enlarged]



File Name : T:\reoea88b.ms2
Creation Date/Time : 02.06.2006 at 10:31:00
File Type : Lo-Res Mass/Int data
File Source : Imported from ICIS II format file D:\tsq2\reoea88b.dat
File Title : SR-884f1 EI-direkt s50 ,
Operator : 54*@50 ,
Instrument : TSQ700
Notes : Source:180',70eV,1000uA ,m/z 41-600 Analyzer-#1: + LRM, #2: + LRM. Source: EI. Status: Q1.

SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak. Entries=399. Base M/z=174.1. 100% Int.=104,42496.

9 (run 4, HPLC)

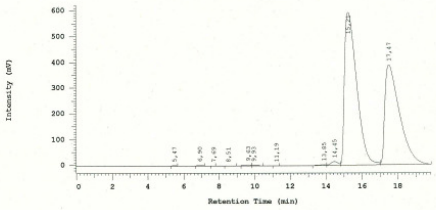
D-7000 HSM: Rendler Series: 0261 Report: modified System: Sys 2

Universität Freiburg
Inst. für Organische Chemie und Biochemie

Analyzed: 29.05.06 10:21 Reported: 29.05.06 14:36
Processed: 29.05.06 14:36

Data Path: D:\hsm\Rendler\DATA\0261\
Processing Method: OD-H ~~Hep/IPA 100/1 253nm~~
System(acquisition): Sys 2 Series:0261
Application: Rendler Vial Number: 1
Sample Name: SR884 F2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 1,0 ul
Sample Description:

Chrom Type: HPLC Channel : 1



Acquisition Method: OD-H n-Heptan 230nm
Column Type: Chiralcel OD-H Developed by: fehrenbach
Pump A Type: L-7100
Solvent A: n-Heptan Solvent B: I-Propanol
Solvent C: Hep/Pr200/1 Solvent D: Ethanol
Method Description: n-Heptan 0.8ml/min 230nm

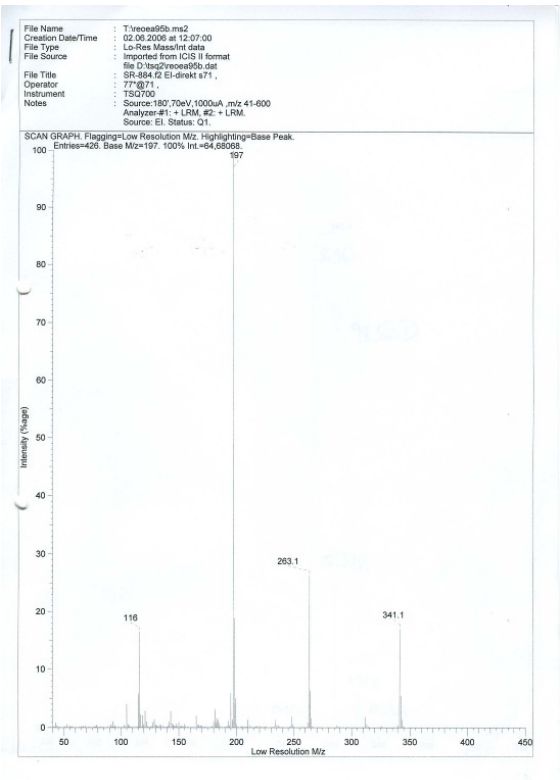
Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

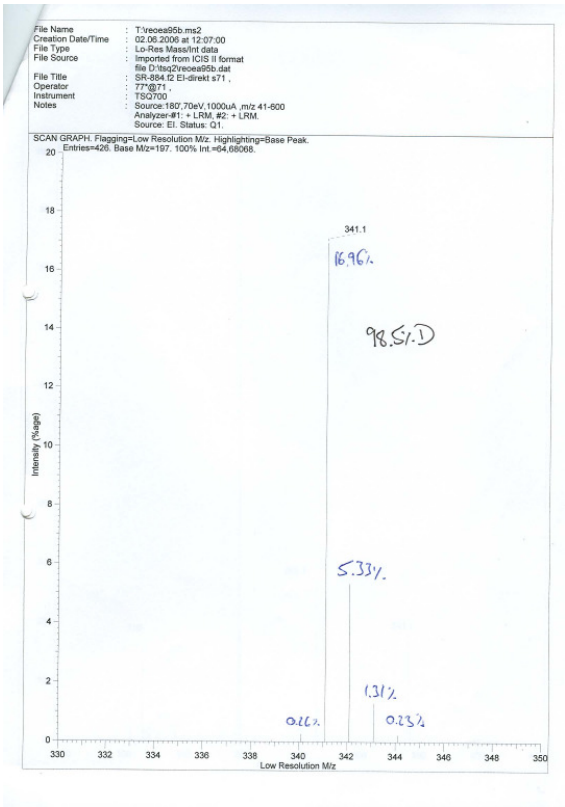
No.	RT	Area %	Area	BC
1	5,47	0,011	5548	BB
2	6,90	0,038	18688	BB
3	7,69	7,220E-04	353	BB
4	8,51	0,004	2161	BB
5	9,63	0,082	40319	BV
6	9,93	0,061	29869	VB
7	11,19	0,002	1073	BB
8	13,85	0,116	56837	BV
9	14,45	0,789	386332	VV
10	15,21	55,107	26995853	VV
11	17,47	43,788	21450680	VB

Page Indicator 1 / 4

H/D$_{global}$ **9** (EI-MS)



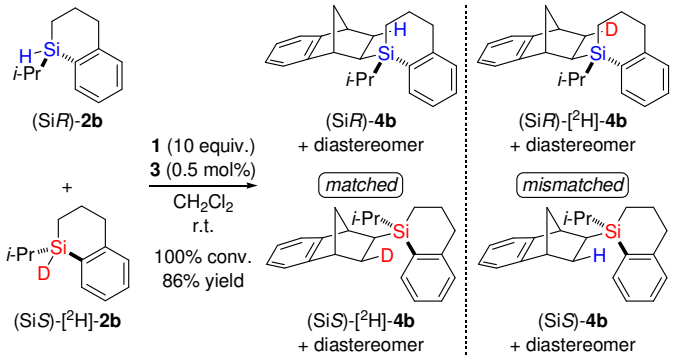
H/D$_{global}$ **9** (EI-MS)



5 Cross-over Experiments of (Si*S*)-[^{2}H]-2b and (Si*R*)-2b

5.1 Experimental Details

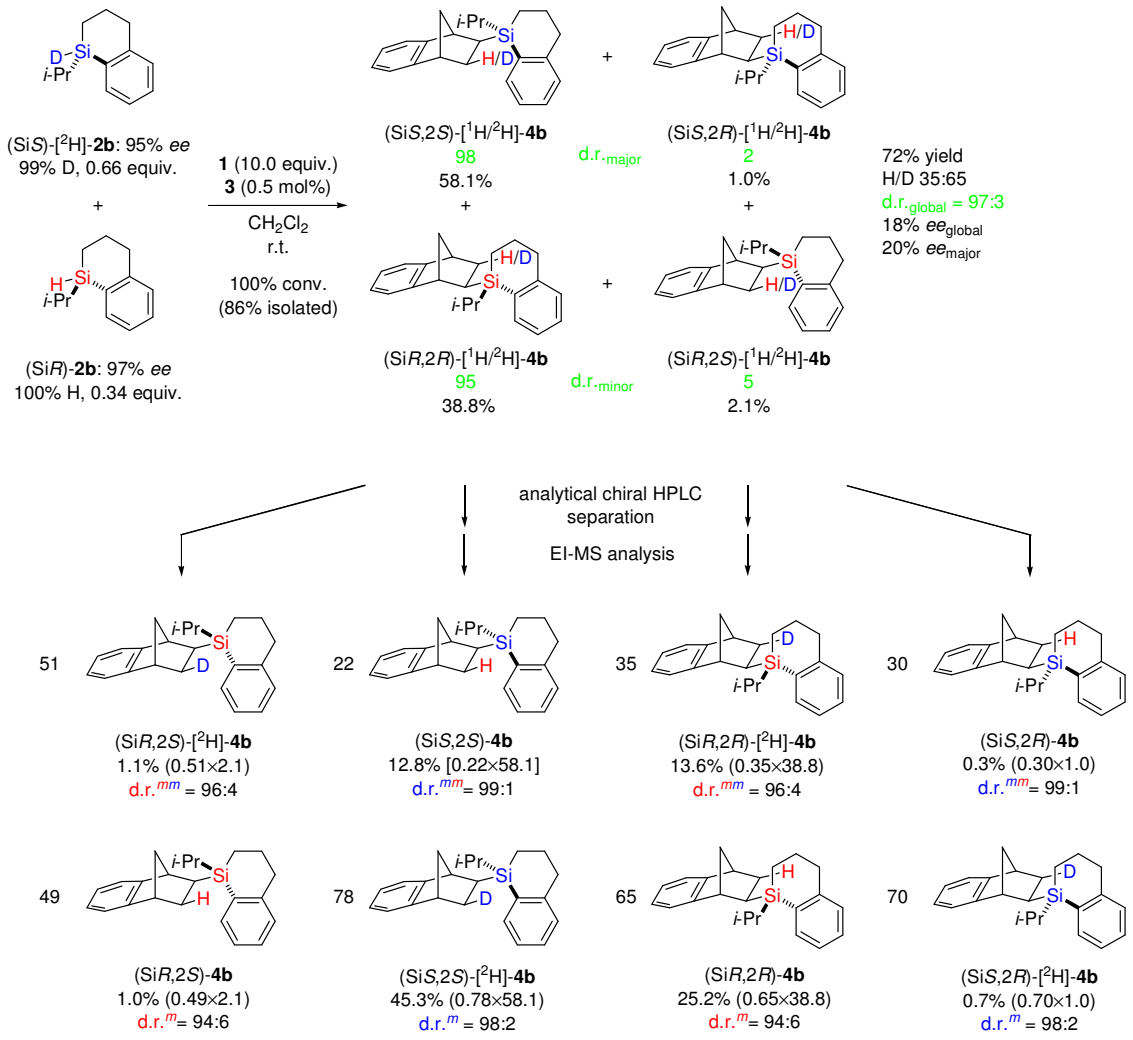
Hydrosilylation of **1** with a mixture of (Si*R*)-**2b** and (Si*S*)-[^{2}H]-**2b**



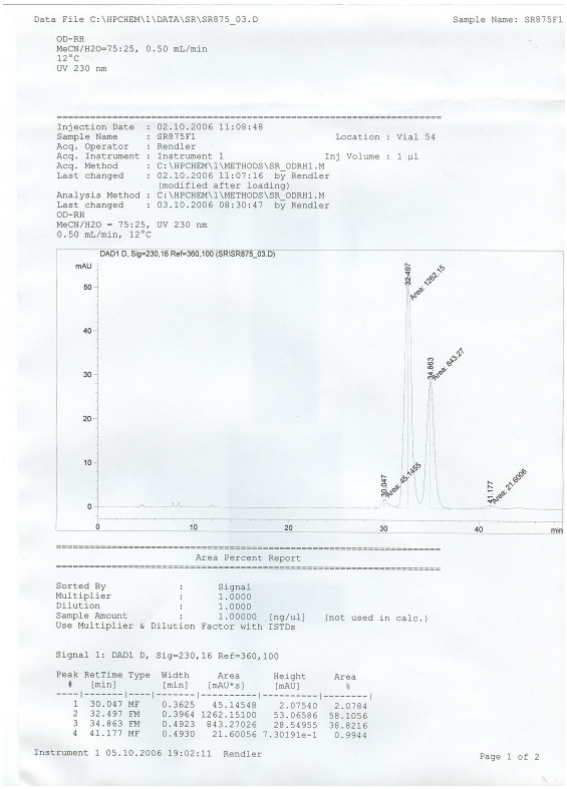
A Schlenk tube was charged with a solution of (Si*R*)-**2b** (19.0 mg, 0.100 mmol, 0.333 equiv., 97% *ee*), (Si*S*)-[^{2}H]-**2b** (38.3 mg, 0.200 mmol, 0.667 equiv., 95% *ee*), and bicyclic alkene **1** (427 mg, 3.00 mmol, 10.0 equiv.) in anhydrous degassed CH_2Cl_2 (2.0 mL) under argon atmosphere. An aliquot (0.50 mL) was taken via syringe to determine the exact composition of the mixture by ^{1}H NMR. Subsequently, a freshly prepared solution of (phen)PdMe(OEt$_2$)$^+$ BAr$_4^-$ (**3**) [Ar = 3,5-bis(trifluoromethyl)phenyl] (0.50 mL, 0.00125 mmol, 0.005 equiv., 0.0025M in CH_2Cl_2) – prepared in situ from (phen)PdMe$_2$ (0.8 mg, 0.0025 mmol, 0.010 equiv.) and [H(OEt$_2$)$_2$]$^+$BAr$_4^-$ (2.5 mg, 0.0025 mmol, 0.010 equiv.) in CH_2Cl_2 (1.0 mL) at 0°C – was added via a microliter syringe. The resulting solution was stirred at room temperature for 48 h. ^{1}H NMR analysis indicated complete conversion of silanes. After removal of the catalyst by filtration through a plug of silica gel using cyclohexane as eluent, the solvents were evaporated. The excess alkene was removed by Kugelrohr distillation in vacuo. Subsequent flash column chromatography on silica gel with cylcohexane as eluent delivered a mixture of enantio- and isotopomers of **4b** (72 mg, 86%). Mass spectrometric analysis revealed a H/D ratio of 35:65.

Analytical HPLC using chiral stationary phases. provided sufficient separation of all four stereoisomers. Identical fractions of several runs were collected, concentrated and analyzed by mass spectrometry (see Scheme S3 for results).

Scheme S3. Results for co-reaction of (Si*R*)-**2b** and (Si*S*)-[^{2}H]-**2b**



5.2 Copies of HPLC and MS data



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Data File C:\HPCHEM\1\DATA\SR\SR875_03.D                    Sample Name: SR875F1

OD-RH
MeCN/H2O=75:25, 0.50 mL/min
12°C
UV 230 nm

==================================================================
Injection Date  : 02.10.2006 11:08:48
Sample Name     : SR875F1                          Location : Vial 54
Acq. Operator   : Rendler
Acq. Instrument : Instrument 1                   Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed    : 02.10.2006 11:07:16  by Rendler
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\SR_ODRH1.M
Last changed    : 03.10.2006 08:30:47  by Rendler
OD-RH
MeCN/H2O = 75:25, UV 230 nm
0.50 mL/min, 12°C
```

DAD1 D, Sig=230,16 Ref=360,100 (SR\SR875_03.D)


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


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

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  30.047 MF    0.3625   45.14548    2.07540   2.0784
   2  32.497 FM    0.3964 1262.15100   53.06586  58.1056
   3  34.863 FM    0.4923  843.27026   28.54955  38.8216
   4  41.177 MF    0.4930   21.60056 7.30191e-1   0.9944

Instrument 1 05.10.2006 19:02:11  Rendler                    Page 1 of 2
```

HPLC of isolated (Si*RS*,2*RS*)-[^{1}H/^{2}H]-**4b**

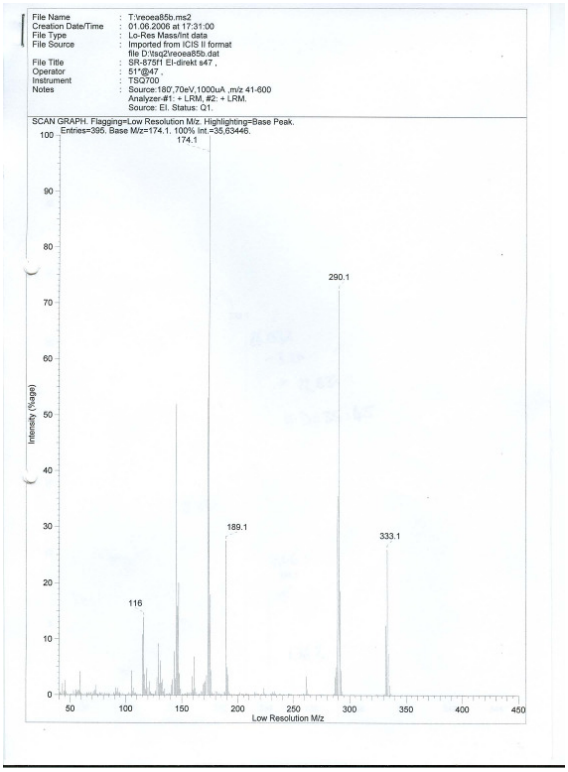
t_R = 30.0 min [(Si*R*,2*S*)-[^{1}H/^{2}H]-**4b**]

t_R = 32.5 min [(Si*S*,2*S*)-[^{1}H/^{2}H]-**4b**]

t_R = 34.9 min [(Si*R*,2*R*)-[^{1}H/^{2}H]-**4b**]

t_R = 41.2 min [(Si*S*,2*R*)-[^{1}H/^{2}H]-**4b**]

H/D$_{global}$ of (Si*RS*,2*RS*)-[^{1}H/^{2}H]-**4b**



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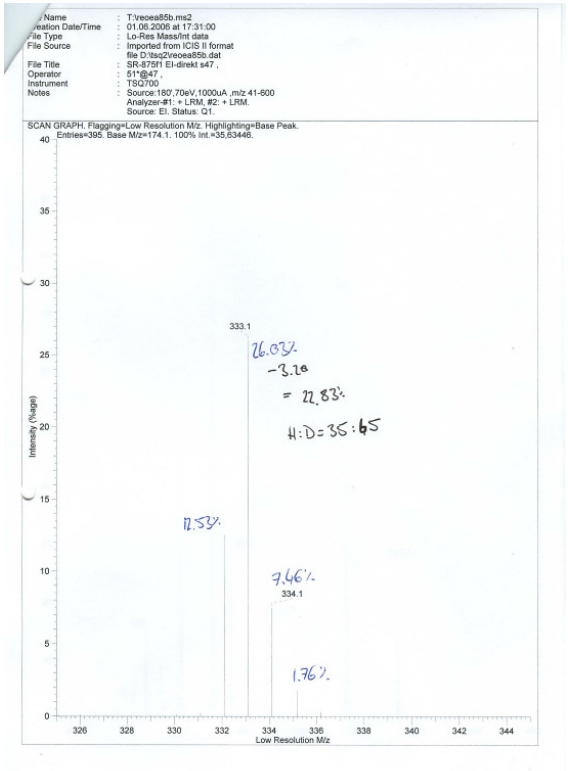
                     file D:\tsq2\eoea85b.dat
File Title         : SR-875f1 EI-direkt s47 ,
Operator           : 51*@47 ,
Instrument         : TSQ700
Notes              : Source:180',70eV,1000uA ,m/z 41-600
                     Analyzer-#1: + LRM, #2: + LRM.
                     Source: EI. Status: Q1.
SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak.
Entries=395. Base M/z=174.1. 100% Int.=35,63446.
```


H/D$_{global}$ of (Si*RS*,2*RS*)-[^{1}H/^{2}H]-**4b** [enlarged]



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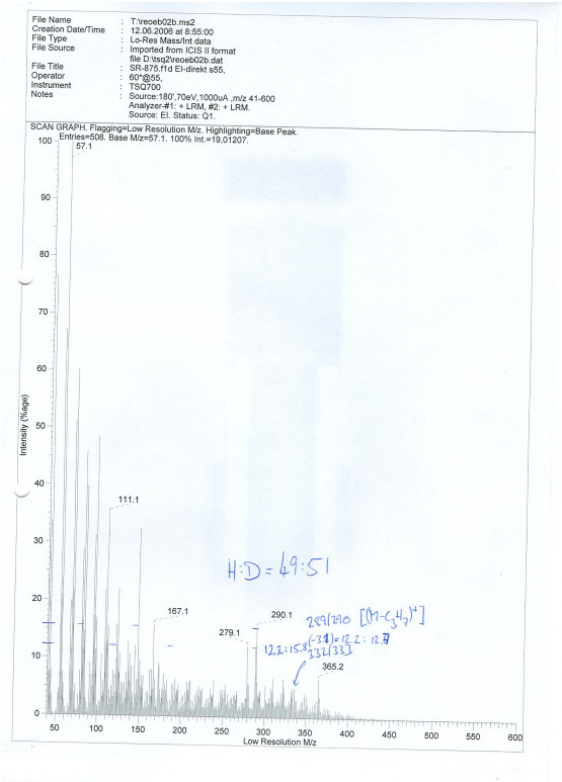
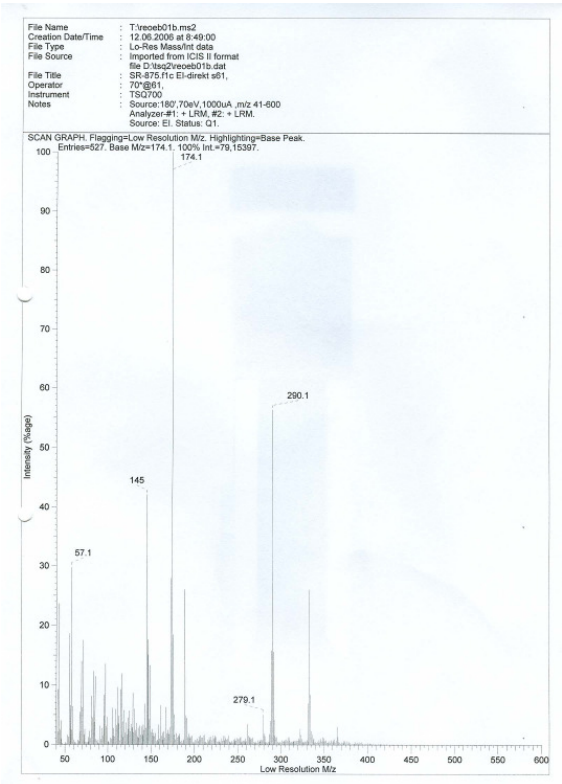
Creation Date/Time : 01.06.2006 at 17:31:00
File Type          : Lo-Res Mass/Int data
File Source        : Imported from ICIS II format
                     file D:\tsq2\eoea85b.dat
File Title         : SR-875f1 EI-direkt s47 ,
Operator           : 51*@47 ,
Instrument         : TSQ700
Notes              : Source:180',70eV,1000uA ,m/z 41-600
                     Analyzer-#1: + LRM, #2: + LRM.
                     Source: EI. Status: Q1.
SCAN GRAPH. Flagging=Low Resolution M/z. Highlighting=Base Peak.
Entries=395. Base M/z=174.1. 100% Int.=35,63446.
```

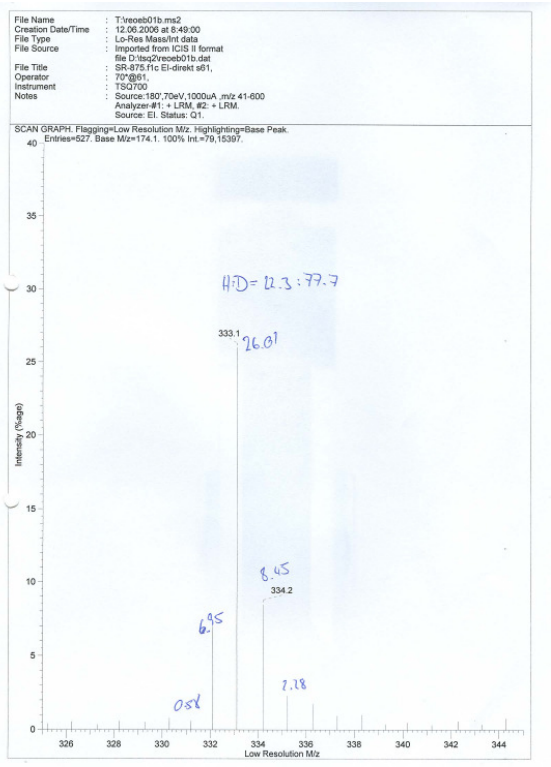
H/D for (Si*R*,2*S*)-[^{1}H/^{2}H]-**4b** (EI-MS)



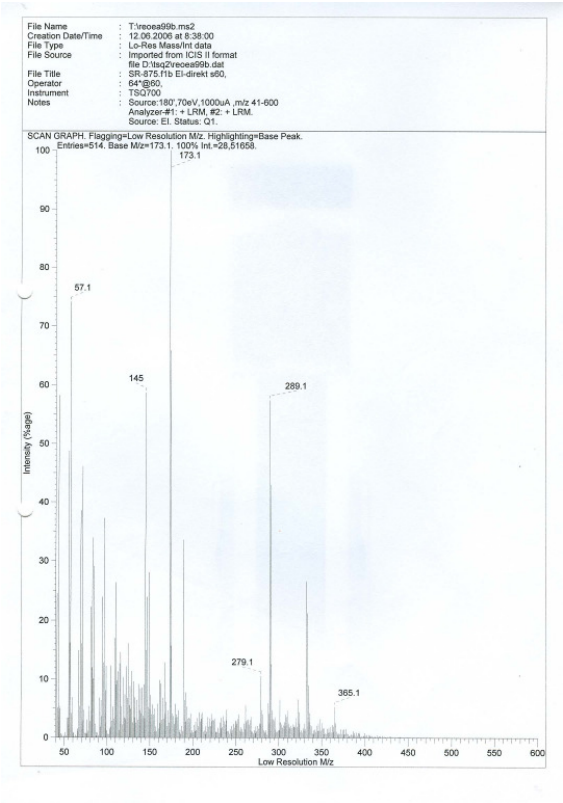
H/D for (Si*S*,2*S*)-[^{1}H/^{2}H]-**4b** (EI-MS)



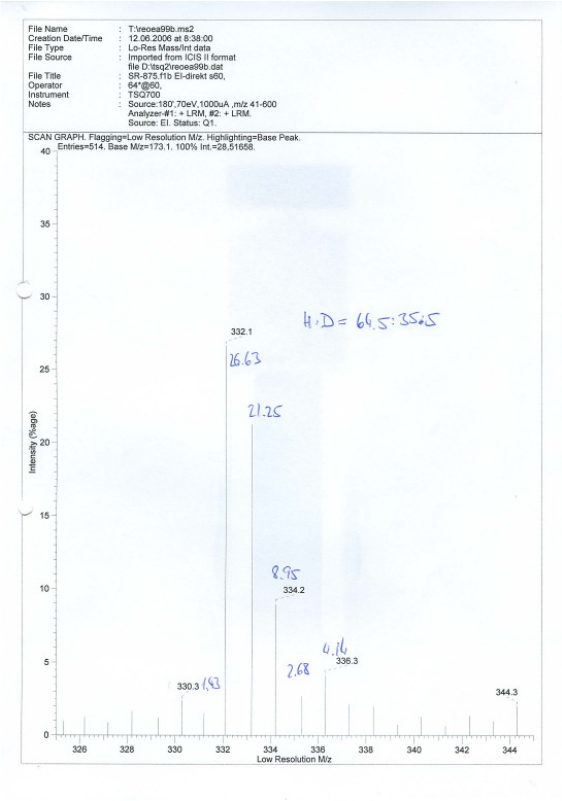
H/D for (Si*S*,2*S*)-[^{1}H/^{2}H]-**4b** (EI-MS) [enlarged]



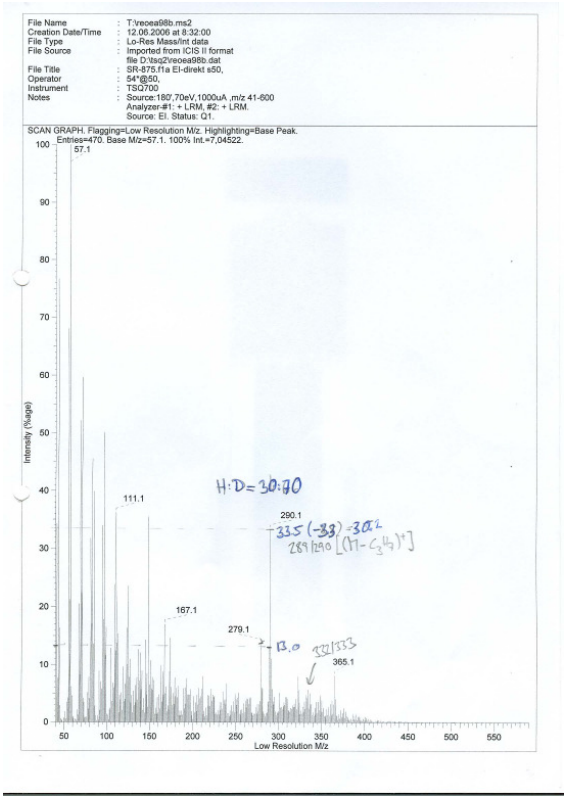
H/D for (Si*R*,2*R*)-[^{1}H/^{2}H]-**4b** (EI-MS)



H/D for (Si*R*,2*R*)-[^{1}H/^{2}H]-**4b** (EI-MS) [enlarged]



H/D for (Si*S*,2*R*)-[^{1}H/^{2}H]-**4b** (EI-MS)

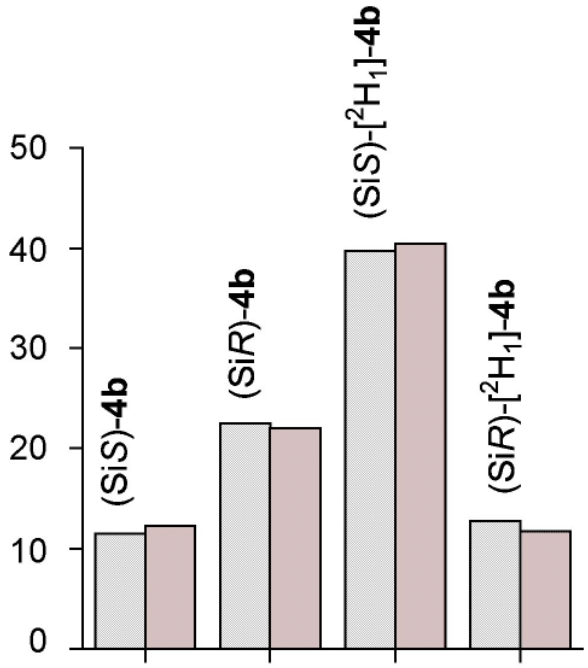


5.3 Product Distribution Analysis / Modeling

The relative proportions (mol fraction %) of (Si*R*)-**4b**, (Si*R*)-[^{2}H]-**4b**, (Si*S*)-**4b** and (Si*S*)-[^{2}H]-**4b** as a function of conversion of total **2b** were modeled by computer-based application of the Gear integration method.[13] The model was simplified such that steps (i), (ii) and (iii) shown in Scheme 2 were telescoped into one step: **7b** + **2b** → **4b** + **7b + X**, with an associated rate constant k_1. Stereochemical / labeling descriptors were applied such that intermediate **7** has two forms: (Si*R*)-**7b** and (Si*S*)-**7b** and silane **2b** has four forms (Si*R*)-**2b**, (Si*R*)-[^{2}H]-**2b**, (Si*S*)-**2b**, (Si*S*)-[^{2}H]-**2b**. Eight possible combinations of **2b** and **7b** emerge. For those combinations involving [^{2}H]-**2b**, the rate constant k_1 was reduced to reflect the PKIE. For those combinations involving opposite stereoisomers of **2b** and **7b** the rate constant was reduced by a mismatching factor (k^m/k^{mm}). For combinations involving both [^{2}H]-**2b** and opposite stereoisomers of **2b** and **7b** the rate constant was reduced by both factor (PKIE × k^m/k^{mm}). The absolute rate constants have no meaning outside of the framework of the model. The concentration of all species were based on mol fraction % as defined by the initial charging of the reagents to the reaction vessel (see above for details) and also take into account the enantiomeric and isotopic purities of the reagents ([(Si*R*)-**2b**]$_0$ = 33.49 mol%; [(Si*R*)-[^{2}H]-**2b**]$_0$ = 1.6 mol%; [(Si*S*)-**2b**]$_0$ = 1.81 mol%; [(Si*S*)-[^{2}H]-**2b**]$_0$ = 63.10 mol%). The output for (Si*R*)-**4b**, (Si*R*)-[^{2}H]-**4b**, (Si*S*)-**4b** and (Si*S*)-[^{2}H]-**4b** at **X** = 86% [total-**2b**]$_0$ was compared with the observed data (see Figure S2) and a best-fit of PKIE = 2.5 and k^m/k^{mm} = 2.5 obtained through manual iteration and comparing the sum square errors for all four components. The distributions and sum square error (%) values obtained, together with a comparison of observed versus best fit is given in Figure S2.

Figure S2. Upper section: predicted and observed distributions of (Si*S*)-**4b**, (Si*R*)-**4b**, (Si*S*)-[^{2}H]-**4b** and (Si*R*)-[^{2}H]-**4b** at **X** = 84.5% [total-**2**]$_0$ using model outlined in section 5.3 at various values of KIE and k^m/k^{mm}. Lower section: graphical comparison of observed (grey shaded bars, data from Scheme 5) versus predicted (pink shaded bars) for best fit when PKIE = k^m/k^{mm} = 2.5.

			(Si*S*)-**4b**	(Si*R*)-**4b**	(Si*S*)-[^{2}H]-**4b**	(Si*R*)-[^{2}H]-**4b**	**SSE** (%)
OBSERVED (mol fraction %)			**13.1**	**26.2**	**46.0**	**14.7**	**0.0**
MODELS	PKIE	k^m/k^{mm}					
	2.5	2.4	14.4	25.0	46.4	13.7	155.4
	2.5	**2.5**	**14.1**	**25.3**	**47.0**	**13.5**	**126.9**
	2.5	2.6	13.8	25.7	47.6	13.1	148.6
	2.4	2.5	14.2	25.1	47.3	13.6	138.2
	2.6	2.5	14.1	25.6	47.1	13.4	136.4
	2.4	2.4	14.5	24.9	46.7	13.8	169.8
	2.6	2.6	13.7	25.8	47.7	13.1	140.3



5.4 Modeling of Asymmetric Amplification

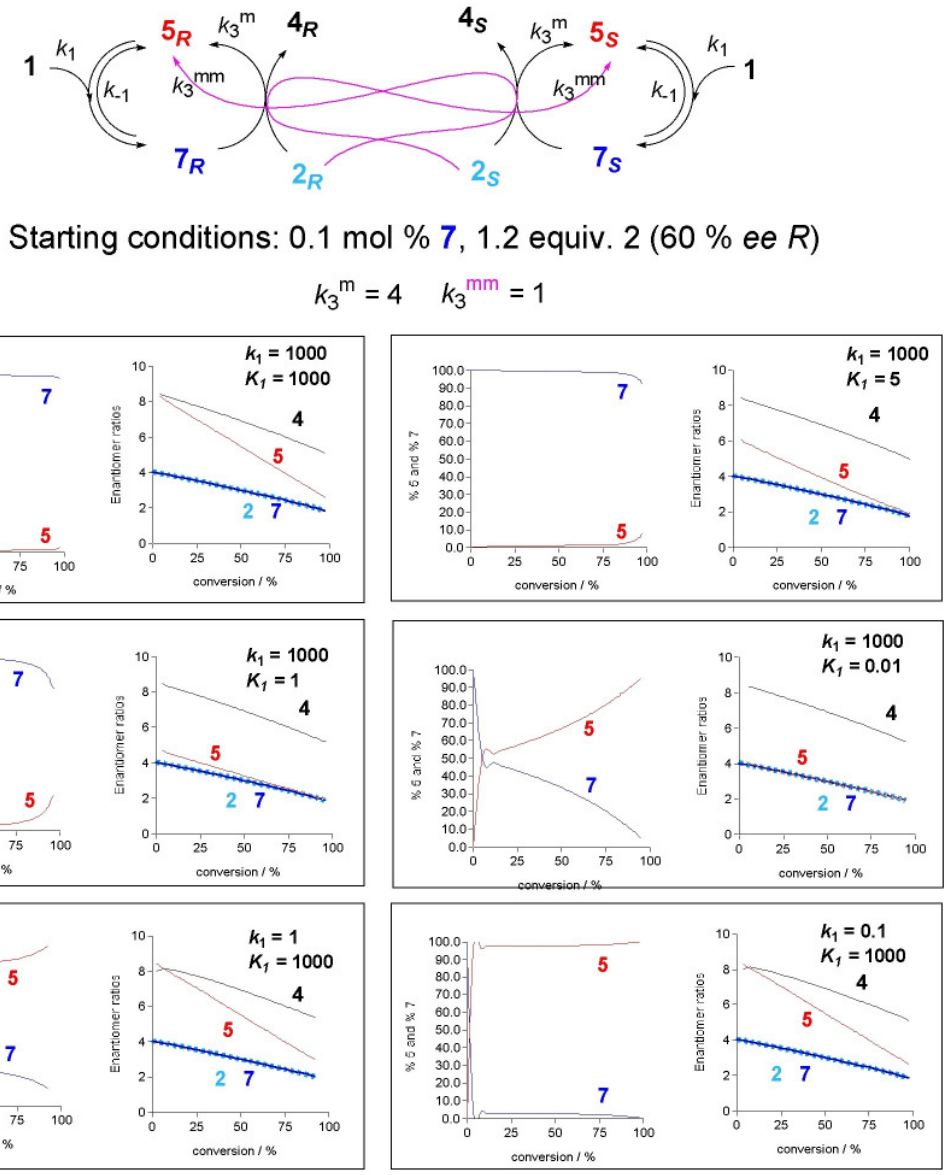
The relative proportions of (Si*R*)-**2**, (Si*S*)-**2**, (Si*R*)-**4**, (Si*S*)-**4**, (Si*R*)-**5**, (Si*S*)-**5** and (Si*R*)-**7**, (Si*S*)-**7** as a function of conversion of **1** (%), according to Scheme 2 (two-silicon cycle) were modeled by computer-based application of the Gear integration method.[13] The model was simplified such that steps (i) and (ii) shown in Scheme 2 were telescoped into one step, giving a two-step cycle: step one is alkene coordination / insertion via **1** + **5** → **7**, k_1 (and an associated equilibrium constant K_1, to allow reversibility) and step 2 is σ-bond metathesis via **2** + **7** → **4** + **5**, k_3 (irreversible). The value of k_3 was set as 4 for matched combinations and as 1 for mismatched combinations of stereoisomers of **2** and **7** (thus k_3^{m}/k_3^{mm} = 4). The absolute rate constants have no meaning outside of the framework of the model. The concentration of all species were based on mol fraction %. The initial *ee* of **2** = 60% (thus (Si*R*)-**2**:(Si*S*)-**2** = 80:20) and the stoichiometry of **2** was set at 20% excess over **1**. The catalyst loading was set at 0.1 mol% **7** (starting with **5**, and/or with different enantiomer ratios of **7** or **5** was found to have little or no effect after 5 or less % reaction). A schematic of the model is outlined at the top of Figure S3. Various values of k_1, and K_1 were explored such that the 'resting state' (= bulk catalyst concentration) was **5** or **7** or both. As shown graphically in Figure S3, it is found that the asymmetric amplification is independent of relative values of k_1 and K_1 and depends only on the enantiomer ratio of **2** which sets the enantiomer ratio of **7**. At any point, the *nascent* enantiomer ratio of **4** is given by:

$$er\ \mathbf{4}_{nascent} =$$

$$\{k_3^{m}[(\mathrm{Si}R)\text{-}\mathbf{2}][(\mathrm{Si}R)\text{-}\mathbf{7}] + k_3^{mm}[(\mathrm{Si}S)\text{-}\mathbf{2}][(\mathrm{Si}S)\text{-}\mathbf{7}]\} / \{k_3^{m}[(\mathrm{Si}S)\text{-}\mathbf{2}][(\mathrm{Si}S)\text{-}\mathbf{7}] + k_3^{mm}[(\mathrm{Si}R)\text{-}\mathbf{2}][(\mathrm{Si}R)\text{-}\mathbf{7}]\}$$

A key point for the discussion of the attenuation (masking) of asymmetric amplification below is that when K_1 is small, the *er* of **5** becomes predominantly determined by the *er* of **7** (and thus **2**). As K_1 increases, the *er* becomes predominantly determined by *er* $\mathbf{4}_{nascent}$ (and thus *er* $\mathbf{5}_{nascent}$).

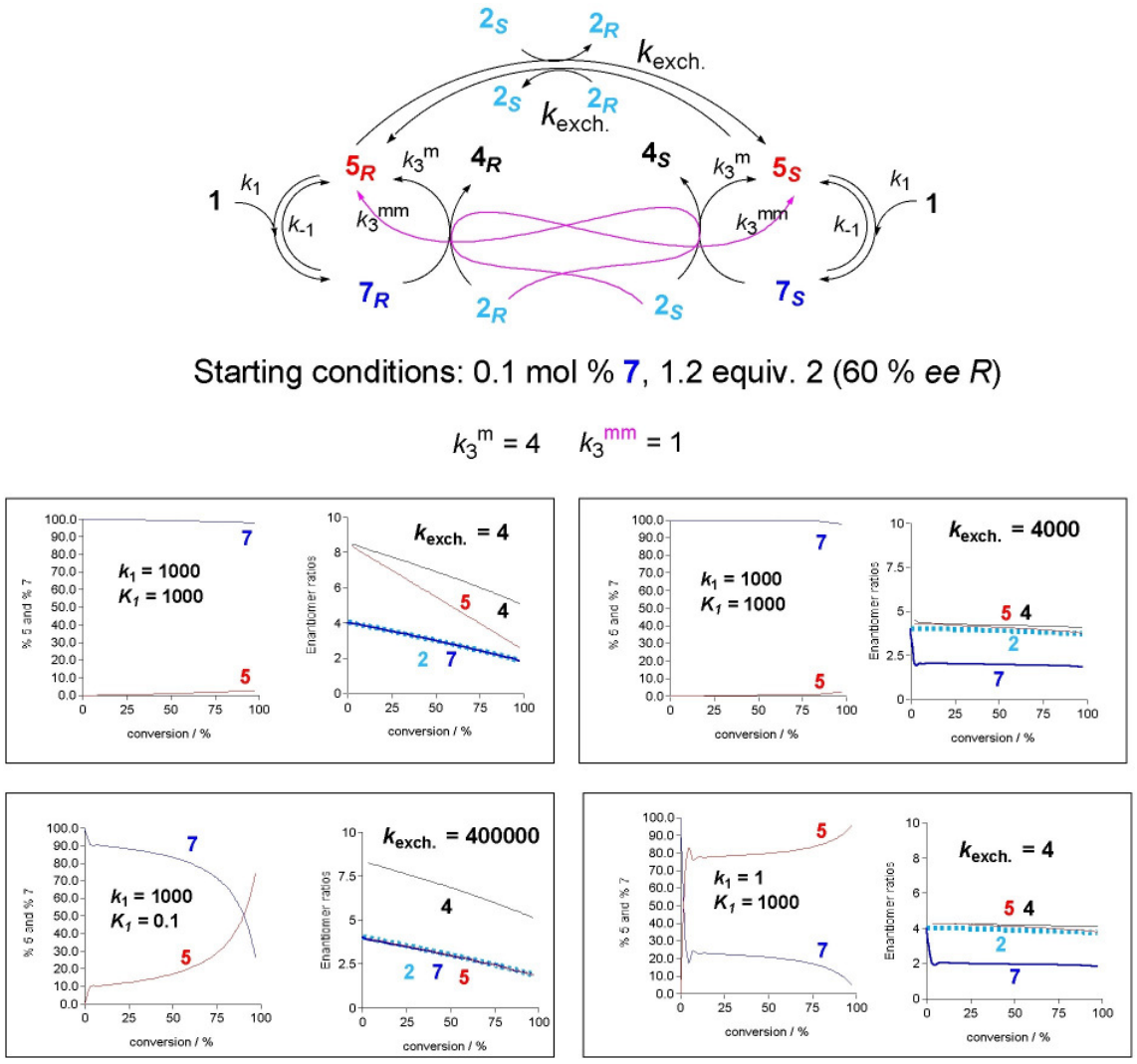
Figure S3. A selection of graphical analyses of asymmetric amplification according to the simplified model shown at the top of the figure. In the lower section, plots of relative % **5** and **7** and of enantiomer ratios of **2**, **4**, **5** and **7** as functions of conversion (%) of **1** are given. See text above for full discussion.



A second model was explored in which exchange of silane **2** with **5** was faciliated *via* the process [(Si*S*)-**2**] + [(Si*R*)-**5**] → [(Si*R*)-**2**] + [(Si*S*)-**5**], with associated rate constant k_{exch} as well as the reverse process (K_{exch} = 1). A schematic of the model is outlined at the top of Figure S4. Various values of k_1, and K_1 were again explored such that the 'resting state' was **5** or **7** or both. It was found that under the conditions that would normally generate **5** in higher *er* than that of **2** (see Figure S3) relatively low values of k_{exch} faciliate the equilibration of the *er* of **5** with that of **2**. Due to the requirement for equal flux around all stages of the cycle at 'steady state', the reduction in the *er* of **5** causes a reduction in the *er* of **7** and thus attenuates the *er* of nascent **4**. With high values of k_{exch} the *er* of **4** becomes equal

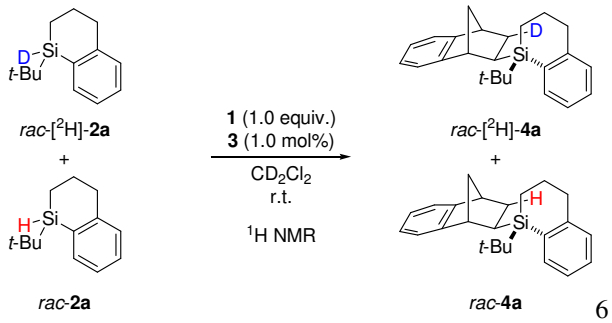
to that of **2** (not net amplification) eventhough the value of k_3^{m}/k_3^{mm} = 4 and the *match*/*mismatch* is just as efficient as in Figure S3. Increasing the reactivity of **1** (k_1) or its concentration ([**1**]) supresses the attenuation (i.e. restores amplification). Analogously, it was also found that under the conditions that would normally generate **5** in equal *er* to that of **2** and **7** (see Figure S3) extrememely high values of k_{exch} were required to have any effect on the *er* of **4**. Thus as the *er* of **5** approaches that of **7** the system becomes increasingly immune to supression of amplification (as is logical since equilibration of **5** with **2**will have no effect on the *er* of **5** or **7**).

Figure S4. A selection of graphical analyses of attenuation of asymmetric amplification according to the simplified model shown at the top of the figure which has in addition to that shown in Figure S3, a mechanism for silane exchange with **5**. In the lower section, plots of relative % **5** and **7** and of enantiomer ratios of **2**, **4**, **5** and **7** as functions of conversion (%) of **1** are given (See text above for full discussion).



6 Estimation of the Kinetic Isotope Effect (PKIE)

Hydrosilylation of **1** with a mixture of *rac*-**2a** and *rac*-[^{2}H]-**2a**



A NMR tube was charged with a solution of *rac*-**2a** (20.4 mg, 0.100 mmol, 1.00 equiv.), *rac*-[^{2}H]-**2a** (20.5 mg, 0.100 mmol, 1.00 equiv.), and bicyclic alkene **1** (14.2 mg, 0.100 mmol, 1.00 equiv.) in anhydrous degassed CD_2Cl_2 (0.80 mL) under argon atmosphere. After the exact composition had been determined by ^{1}H NMR, a freshly prepared solution of (phen)PdMe(OEt$_2$)$^+$ BAr$_4^-$ (**3**) [Ar = 3,5-bis(trifluoromethyl)phenyl] (200 µL, 0.00100 mmol, 0.001 equiv., 0.0005M in CD_2Cl_2) – prepared in situ from (phen)PdMe$_2$ (1.0 mg, 0.0030 mmol, 0.030 equiv.) and [H(OEt$_2$)$_2$]$^+$BAr$_4^-$ (3.0 mg, 0.0010 mmol, 0.010 equiv.) in CD_2Cl_2 (600 µL) at 0°C – was added via a microliter syringe. The reaction was monitored by ^{1}H NMR analysis at 25°C over a period of 48h. The results are obtained by integration are shown in Table S3 (see Figure S6 for exemplified NMR spectra).

Table S3. Concentrations as determined by ^{1}H NMR

			Concentration [mmol/mL] [a]				
Entry	time [h]	conversion [%][b]	**1**	*rac*-**2a**	*rac*-[^{2}H]-**2a**	*rac*-**4a**	*rac*-[^{2}H]-**4a**
1	0.00	0.00	0.1000	0.0898	0.1352	0.0000	0.0000
2	0.17	13.73	0.1179	0.0650	0.1291	0.0145	0.0164
3	0.22	15.46	0.1047	0.0658	0.1244	0.0141	0.0207
4	0.28	15.19	0.1048	0.0653	0.1255	0.0151	0.0190
5	0.35	16.65	0.0956	0.0659	0.1217	0.0137	0.0238
6	0.43	15.79	0.0918	0.0603	0.1292	0.0045	0.0311
7	0.48	16.70	0.0935	0.0650	0.1225	0.0253	0.0123
8	0.53	16.58	0.0938	0.0655	0.1222	0.0235	0.0138
9	0.58	17.33	0.0887	0.0649	0.1211	0.0337	0.0052
10	0.62	16.42	0.0902	0.0630	0.1251	0.0074	0.0296
11	0.67	17.69	0.0835	0.0630	0.1222	0.0146	0.0252
12	1.07	17.65	0.0854	0.0643	0.1210	0.0259	0.0139
13	1.33	19.16	0.0787	0.0652	0.1167	0.0282	0.0150
14	1.38	19.02	0.0788	0.0652	0.1170	0.0201	0.0227

15	1.42	19.55	0.0764	0.0644	0.1166	0.0346	0.0093
16	1.47	23.32	0.0571	0.0577	0.1148	0.0332	0.0193
17	4.10	22.97	0.0528	0.0570	0.1164	0.0279	0.0237
18	4.18	23.42	0.0526	0.0579	0.1144	0.0394	0.0133
19	4.23	22.20	0.0544	0.0572	0.1179	0.0292	0.0208
20	7.43	26.07	0.0384	0.0531	0.1132	0.0384	0.0203
21	7.47	26.79	0.0374	0.0533	0.1114	0.0399	0.0204
22	24.23	38.80	0.0082	0.0347	0.1031	0.0506	0.0367
23	26.23	39.53	0.0078	0.0382	0.0979	0.0493	0.0397
24	26.30	38.83	0.0070	0.0337	0.1039	0.0521	0.0353
25	26.35	41.03	0.0068	0.0348	0.0979	0.0705	0.0218
26	43.17	44.80	0.0003	0.0310	0.0931	0.0705	0.0303
27	43.22	44.54	0.0003	0.0322	0.0926	0.0623	0.0379
28	43.25	44.09	0.0003	0.0313	0.0945	0.0584	0.0408

[a] Reaction performed in 0.1M solution in CD_2Cl_2. Initial concentrations calculated by weight of used **1** (giving a 0.1M solution) and comparison of ^{1}H NMR signals at 4.12 (*rac*-**2a**, 1H), 3.78 (**1**, 2H), 2.70 (*rac*-**2a**, 2H; *rac*-[^{2}H]-**2a**, 2H; *rac*-**4a**, 2H; *rac*-[^{2}H]-**2a**, 2H), 2.08 (*rac*-**2a**, 1H; *rac*-[^{2}H]-**2a**, 1H; *rac*-**4a**, 1H); and 1.30 (*rac*-**4a**, 1H; *rac*-[^{2}H]-**4a**, 1H). [b] based on consumed silane *rac*-**2a** and *rac*-[^{2}H]-**2a**.

The concentrations of **2a** and [^{2}H]-**2a** as a function of conversion were modeled by computer-based application of the Gear integration method.[13] The model was simplified to a pair of bimolecular non-catalysed competitions: **1** + **2a** → **X**, with an associated rate constant k_1 and **1** + [^{2}H]-**2a** → **X** with an associated rate constant k_2. In both processes, '**X**' was used as a marker for conversion of **1**. The absolute rate constants have no meaning outside of the framework of the model. The concentration of all species were based on molarity as defined by the initial charging of the reagents to the NMR tube (see above for details). The relative rate k_1/k_2 (= PKIE) was varied manually and compared with the observed data as a function of concentration of **2a** and [^{2}H]-**2a** with conversion of **1**, see Figure S5. A best-fit of $k_1 / k_2 = 3.0$ (green line) ± 0.5 (black and red lines) was obtained.

Figure S5. Graphical analysis of predicted and observed concentrations of silane **2a** and deuterated silane [^{2}H]-**2a** as determined by ^{1}H NMR analysis. Circles: NMR derived data; solid lines passing through data: predictions based on simple first-order bimolecular competition model: red PKIE = 2.5, green PKIE = 3.0; black PKIE = 3.5. .

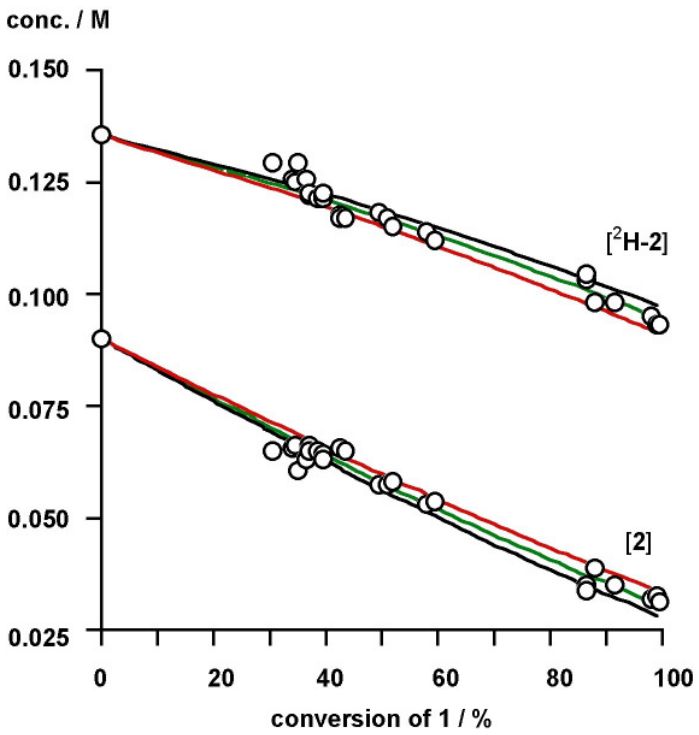
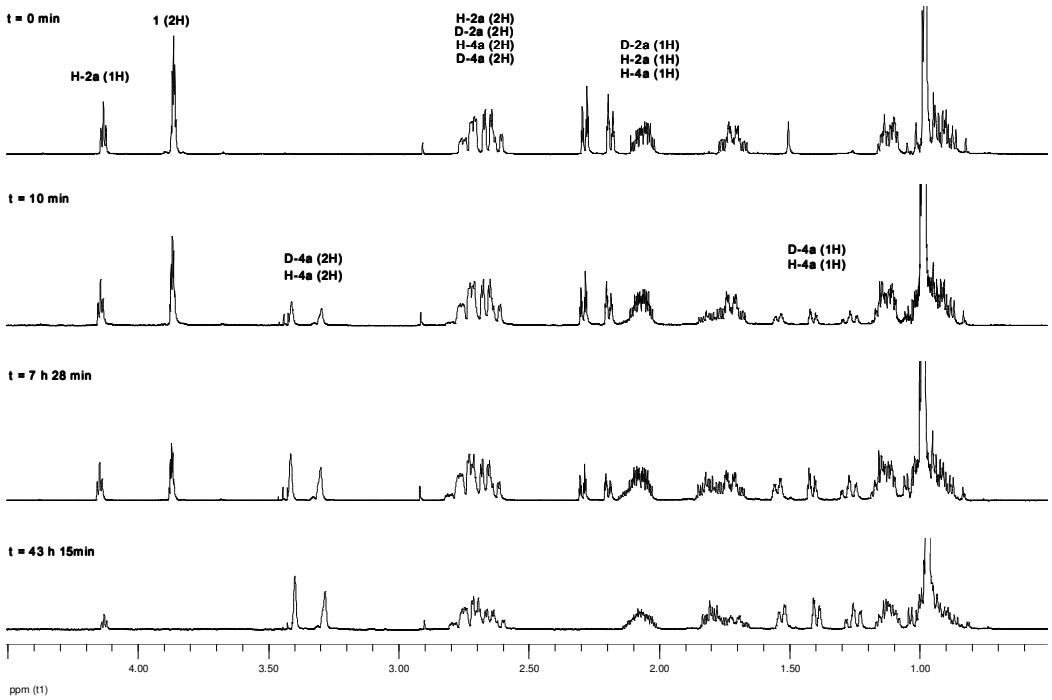


Figure S6. Characteristic ^{1}H NMR signals for analysis of a PKIE.



7 References and Footnotes

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‡ University of Bristol

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[9] Absolute configuration deducted in from polarity in comparison to the known properties and absolute configuration of the **2a** derived (–)-menthyl ether.[2] The assignment is in agreemnent with comparable chiral HPLC properties of silanes **2b** *versus* **2a** after stereospecific reductive cleavage.

[10] Absolute configuration deducted from similar HPLC properties as (Si*R*)-**2a** using the same chiral stationary phase.

[11] Relative stereochemistry assigend by analogy to **4a**; absolute stereochemistry assigned by a stereoretentive process being operative.

[12] Stereochemistry assigned by comparison of the stereoinduction being operative in the formation of **4b**.

[13] a) Weigert, F. J. *Computers and Chemistry* **1987**, *II*, 273; b) Stabler, R. N.; Cheswick, J. *Int. J. Kinet.* **1978**, *10*, 461; c) McKinney, R. J.; Weigert, F. J. *Quantum Chemistry, Program Exchange, program No. QCMP022*. Commercially available software (MacKinetics, Leipold Associates, USA) was employed for the simulations described herein.