Mechanistic insight into copper-catalysed allylic substitutions with bis(triorganosilyl) zincs. Enantiospecific preparation of α-chiral silanes

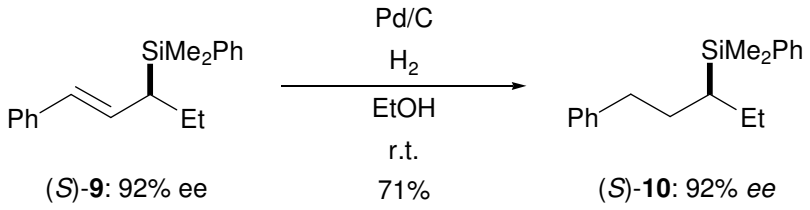
Eric S. Schmidtmann and Martin Oestreich*

Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität, Albertstrasse 21, D-79104 Freiburg im Breisgau, Germany
martin.oestreich@orgmail.chemie.uni-freiburg.de

Electronic Supplementary Information

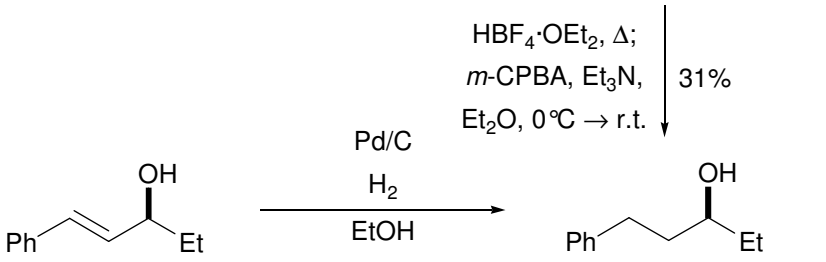
Contents

1 Chemical correlation of (*S*)-**9**



(*S*)-**9**: 92% ee

(*S*)-**10**: 92% *ee*



(*S*)-**12**: 99% ee

(*S*)-**11**: 91% ee from (*S*)-**13**
99% ee from (*S*)-**15**

The identical reaction sequence was performed with the optical antipode (*R*)-**9** producing (*R*)-**11**.

2 Characterization Data

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. 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, Et_2O, CH_2Cl_2, and toluene). Technical grade solvents for extraction or chromatography (cyclohexane and *t*-butyl methyl ether) were distilled before use. Analytical thin-layer chromatography was performed on silica gel SIL G-25 glass plates by Macherey-Nagel/Germany and flash chromatography on silica gel 60 (40-63 µm, 230-400 mesh, ASTM) by Merck/Germany using the indicated solvents. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 400 instrument. Analytical HPLC analysis on a chiral stationary phase using Daicel Chiralpak AD or Daicel Chiralcel OD-H columns (*n*-heptane:*i*-PrOH mixtures as solvent) as well as Daicel Chiralcel OJ-R and/or OD-R columns (EtOH:H_2O as well as MeCN:H_2O mixtures) provided baseline separation of enantiomers.

2-Cyclohexenyl benzoate (1a): (*S*)-**1a** (97% *ee*): HPLC (Daicel Chiralpak AD column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 20:1, flow rate 0.8 mL·min^{-1}): 12.3 min for (*R*)-**1a**, 13.9 min for (*S*)-**1a**. $[\alpha]_D^{20}$ –226, $[\alpha]_{578}^{20}$ –237, $[\alpha]_{546}^{20}$ –273, $[\alpha]_{436}^{20}$ –505, $[\alpha]_{365}^{20}$ –891 (*c* 1.23, $CHCl_3$).

2-Cyclohexenyl phenyl carbamate (1b): (*S*)-**1b** (95% *ee*): HPLC (Daicel Chiralpak AD column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 9:1, flow rate 0.8 mL·min^{-1}): 13.2 min for (*R*)-**1b**, 15.0 min for (*S*)-**1b**. $[\alpha]_D^{20}$ –200, $[\alpha]_{578}^{20}$ –212, $[\alpha]_{546}^{20}$ –244, $[\alpha]_{436}^{20}$ –451, $[\alpha]_{365}^{20}$ –792 (*c* 1.13, $CHCl_3$). *rac*-**1b**: R_f = 0.60 (cyclohexane:*t*-butyl methyl ether = 5:1). Mp 98 °C (cyclohexane–CH_2Cl_2). IR ($CHCl_3$/cuvette): 3435 (s) (NH), 1720 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.64–1.88 (m, 3H), 1.92–2.17 (m, 3H), 5.32 (m, 1H), 5.82 (m, 1H), 6.00 (dtd, *J* = 10.1, 3.7, 1.3 Hz, 1H), 6.75 (bs, 1H), 7.07 (m, 1H), 7.28–7.34 (m, 2H), 7.41 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.8, 24.9, 28.6, 68.9, 118.7, 123.3, 125.9, 129.0, 132.8, 138.1, 153.4. LRMS (EI): *m/z* = 217 [M$^+$]. Anal. Calcd for $C_{13}H_{15}NO_2$ (217.26): C, 71.87; H, 6.96; N, 6.45; Found: C, 71.58; H, 7.20; N, 6.37.

(2-Cyclohexenyl)dimethyl(phenyl)silane (2): (*R*)-**2** (9 and 11% *ee*): HPLC (Daicel Chiralcel OJ-R column, column temperature 20 °C, solvent MeCN: H_2O = 7:3, flow rate 0.8 mL·min^{-1}): 9.9 min for (*R*)-**2**, 11.1 min for (*S*)-**2**. *rac*-**2**: R_f = 0.58 (cyclohexane). IR ($CHCl_3$/cuvette): 1251 (s) (C–Si) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 3H), 0.30 (s, 3H), 1.42–1.55 (m, 2H), 1.64–1.73 (m, 1H), 1.76–1.82 (m, 2H), 1.93–2.04 (m, 2H), 5.66 (m, 2H), 7.35–7.38 (m, 3H), 7.52–7.55 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –4.7, –4.5, 22.6, 23.9, 25.1, 25.7, 126.0, 127.7, 127.8, 129.0, 134.0, 138.4. LRMS (EI): *m/z* = 216 [M$^+$]. HRMS (EI): *m/z* calcd for $C_{14}H_{20}Si$: 216.13343; Found: 216.13280.

***syn*-1-Deutero-5-methyl-2-cyclohexenyl benzoate (*syn*-3a)**: R_f = 0.54 (cyclohexane:*t*-butyl methyl ether = 8:1). IR ($CHCl_3$/cuvette): 1708 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.7 Hz, 3H), 1.42 (t, *J* = 12.2 Hz, 1H), 1.74 (m, 1H), 1.90 (m, 1H), 2.17 (m, 1H), 2.21 (m, 1H), 5.72 (m, 1H), 5.90 (ddd, *J* = 10.1, 5.0, 2.3 Hz, 1H), 7.40–7.45 (m, 2H), 7.52–7.56 (m, 1H), 8.04–8.07 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.9, 27.9, 33.6, 36.8, 71.0 (t, *J* = 22.7 Hz), 126.9, 128.4, 129.7, 130.9, 132.9, 166.4. LRMS (EI): *m/z* = 217 [M$^+$]. Anal. Calcd for $C_{14}H_{15}DO_2$ (217.28): C, 77.39; H,

7.89; Found: C, 77.12; H, 7.47. The deuterium content of 98% was determined by mass spectrometry by comparison with a non-deuterated sample.

***syn*-1-Deutero-5-methyl-2-cyclohexenyl phenyl carbamate (*syn*-3b)**: R_f = 0.37 (cyclohexane:*t*-butyl methyl ether = 8:1). IR ($CHCl_3$/cuvette): 3436 (m) (NH), 1729 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.6 Hz, 3H), 1.30 (m, 1H), 1.70 (ddt, *J* = 17.6, 10.4, 2.6 Hz, 1H), 1.85 (m, 1H), 2.09 (m, 1H), 2.15 (m, 1H), 5.67 (m, 1H), 5.86 (ddd, *J* = 10.1, 5.1, 2.2 Hz, 1H), 6.60 (bs, 1H), 7.06 (m, 1H), 7.28–7.33 (m, 2H), 7.37–7.39 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.9, 28.0, 33.6, 37.1, 71.4 (t, *J* = 22.2 Hz), 118.7, 123.4, 127.0, 129.1, 130.8, 138.1. LRMS (EI): *m/z* = 232 [M^+]. Anal. Calcd for $C_{14}H_{16}DNO_2$ (232.30): C, 72.39; H, 7.81; N, 6.03; Found: C, 72.34; H, 7.53; N, 5.96. The deuterium content of 98% was determined by mass spectrometry by comparison with a non-deuterated sample.

***anti*-Dimethyl(1-deutero-5-methyl-2-cyclohexenyl)(phenyl)silane (*anti*-4) and *anti*-dimethyl(3-deutero-5-methyl-2-cyclohexenyl)(phenyl)silane (*anti*-5)**: R_f = 0.58 (cyclohexane). IR ($CHCl_3$/cuvette): 1260 (m) (C–Si) cm^{-1}. *anti*-**4**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 3H), 0.32 (s, 3H), 0.90 (d, *J* = 6.3 Hz, 3H), 1.46 (m, 1H), 1.59–1.73 (m, 3H), 2.06 (m, 1H), 5.59 (m, 1H), 5.64 (m, 1H), 7.35–7.38 (m, 3H), 7.52–7.56 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –4.0, –3.9, 21.3, 24.6 (t, *J* = 18.1 Hz), 26.4, 31.2, 33.0, 124.5, 127.2, 127.8, 129.0, 134.0, 138.7. *anti*-**5**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 3H), 0.32 (s, 3H), 0.90 (d, *J* = 6.3 Hz, 3H), 1.46 (m, 1H), 1.59–1.73 (m, 3H), 1.86 (m, 1H), 2.06 (m, 1H), 5.64 (m, 1H), 7.35–7.38 (m, 3H), 7.52–7.56 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –4.0, –3.9, 21.3, 25.0, 26.4, 31.3, 33.1, 124.1 (t, *J* = 23.8 Hz), 127.3, 127.8, 129.0, 134.0, 138.7. LRMS (EI): *m/z* = 231 [M^+]. Anal. Calcd for $C_{15}H_{21}DSi$ (231.43): C, 77.85; H, 10.02; Found: C, 77.67; H, 9.75. The deuterium content of 98% was determined by mass spectrometry by comparison with a non-deuterated sample.

(*E*)-2-Deutero-3-penten-2-yl benzoate (*rac*-6a-d_1): R_f = 0.38 (cyclohexane:CH_2Cl_2 = 1:1). IR ($CDCl_3$/cuvette): 1708 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 3H), 1.72 (dd, *J* = 6.4, 0.8 Hz, 3H), 5.60 (d, *J* = 15.4 Hz, 1H), 5.82 (m_c, 1H), 7.41–7.45 (m, 2H), 7.52–7.56 (m, 1H), 8.04–8.06 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 17.8, 20.5, 71.5 (t, *J* = 22.7 Hz), 128.3, 128.4, 129.7, 130.9, 132.8, 166.0. LRMS (EI): *m/z* = 191 [M^+]. Anal. Calcd for $C_{12}H_{13}DO_2$ (191.24): C, 75.36; H, 7.90; Found: C, 74.97; H, 7.50. The deuterium content of >99% was determined by mass spectrometry by comparison with a non-deuterated sample.

(*E*)-2-Deutero-3-penten-2-yl phenyl carbamate (*rac*-6b-d_1): R_f = 0.29 (cyclohexane:CH_2Cl_2 = 1:3). IR ($CDCl_3$/cuvette): 1733 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 3H), 1.73 (dd, *J* = 6.4, 1.6 Hz, 3H), 5.55 (d, *J* = 15.3 Hz, 1H), 5.81 (dq, *J* =15.3, 6.5 Hz, 1H), 6.63 (bs, 1H), 7.05–7.09 (m, 1H), 7.28–7.36 (m, 2H), 7.39–7.41 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 17.8, 20.5, 71.9 (t, *J* = 23.4 Hz), 118.7, 123.4, 128.5, 129.1, 130.9, 138.2, 153.1. LRMS (EI): *m/z* = 206 [M^+]. Anal. Calcd for $C_{12}H_{14}DNO_2$ (206.26): C, 69.88; H, 7.82; N, 6.79; Found: C, 69.68; H, 7.58; N, 6.66. The deuterium content of >99% was determined by mass spectrometry by comparison with a non-deuterated sample.

(*E*)-3-Penten-2-yl benzoate (6a): (*R*)-**6a** (91% *ee*): HPLC (Daicel Chiralpak AD column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 200:1, flow rate 0.8 mL·min^{-1}): 7.84 min for (*R*)-**6a**, 9.75 min for (*S*)-**6a**. $[\alpha]_D^{20}$ –21.4, $[\alpha]_{578}^{20}$ –22.6, $[\alpha]_{546}^{20}$ –26.5, $[\alpha]_{436}^{20}$ –56.0, $[\alpha]_{365}^{20}$ –119 (*c* 1.33, $CHCl_3$).

(*E*)-3-Penten-2-yl phenyl carbamate (6b): (*R*)-**6b** (90% *ee*): HPLC (Daicel Chiralpak AD column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 9:1, flow rate 0.8 mL·min^{-1}): 9.63 min for (*R*)-**6b**, 11.7 min for (*S*)-**6b**. $[\alpha]_D^{20}$ +30.0, $[\alpha]_{578}^{20}$ +31.5, $[\alpha]_{546}^{20}$ +36.5, $[\alpha]_{436}^{20}$ +65.3, $[\alpha]_{365}^{20}$ +110 (*c* 1.08, $CHCl_3$).

(*E*)-Dimethyl(2-deutero-3-penten-2-yl)(phenyl)silane (*rac*-7-d_1) and (*E*)-Dimethyl(4-deutero-3-penten-2-yl)(phenyl)silane (regio-*rac*-7-d_1): R_f = 0.58 (cyclohexane). IR ($CDCl_3$/cuvette): 1249 (m) (C–Si) cm^{-1}. ***rac*-7-d_1**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 6H), 1.01 (s, 3H), 1.66 (dd, *J* = 6.3, 1.5 Hz, 3 H), 5.22 (dq, *J* = 15.2, 6.4 Hz, 1H), 5.43 (d, *J* = 15.2 Hz, 1H), 7.33–7.37 (m, 3H), 7.48–7.51 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –5.3, –4.6, 14.0, 18.3, 25.2 (t, *J* = 18.4 Hz), 121.4, 127.7, 129.0, 133.6, 134.2, 138.3. **regio-*rac*-7-d_1**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 6H), 1.01 (s, 3H), 1.66 (dd, *J* = 6.3, 1.5 Hz, 3 H), 1.75 (m, 1H), 5.43 (m, 1H), 7.33–7.37 (m, 3H), 7.48–7.51 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –5.3, –4.6, 14.0, 18.3, 25.6, 121.1 (t, *J* = 23.2 Hz), 127.7, 129.0, 133.6, 134.2, 138.3. LRMS (EI): *m/z* = 205 [M$^+$]. Anal. Calcd for $C_{13}H_{19}DSi$ (205.39): C, 76.02; H, 10.30; Found: C, 75.59; H, 9.89. The deuterium content of >99% was determined by mass spectrometry by comparison with a non-deuterated sample.

(*E*)-Dimethyl(phenyl)(3-penten-2-yl)silane (7): (*S*)-**7** (70% *ee*): HPLC (Daicel Chiralcel OJ-R column, column temperature 40 °C, solvent MeOH:H_2O = 7:3, flow rate 0.8 mL·min^{-1}): 58.6 min for (*R*)-**7**, 60.6 min for (*S*)-**7**. Peaks were not completely baseline-separated.

(*E*)-1-Phenyl-1-penten-3-yl benzoate (8a): (*S*)-**8a** (98% *ee*): HPLC (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 100:1, flow rate 0.8 mL·min^{-1}): 8.70 min for (*S*)-**8a**, 9.59 min for (*R*)-**8a**. $[\alpha]_D^{20}$ +9.23, $[\alpha]_{578}^{20}$ +9.92, $[\alpha]_{546}^{20}$ +12.2, $[\alpha]_{436}^{20}$ +27.2, $[\alpha]_{365}^{20}$ +62.8 (*c* 1.30, $CHCl_3$). *rac*-**8a**: R_f = 0.59 (cyclohexane:*t*-butyl methyl ether = 6:1). IR ($CHCl_3$/cuvette): 3064 (m) (C=C), 1713 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.5 Hz, 3H), 1.92 (m, 2H), 5.64 (m, 1H), 6.28 (dd, *J* = 16.0, 7.1 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 7.24–7.28 (m, 1H), 7.31–7.35 (m, 2H), 7.41–7.49 (m, 4H), 7.56–7.60 (m, 1H), 8.11–8.13 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 9.7, 27.9, 76.6, 126.7, 127.6, 128.0, 128.4, 128.6, 129.7, 130.8, 132.7, 132.9, 136.5, 166.0. LRMS (EI): *m/z* = 266 [M$^+$]. Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81; Found: C, 80.98; H, 6.94.

(*E*)-1-Phenyl-1-penten-3-yl phenyl carbamate (8b): (*S*)-**8b** (91% *ee*): HPLC (Daicel Chiralpak AD column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 9:1, flow rate 0.8 mL·min^{-1}): 16.7 min for (*R*)-**8b**, 21.2 min for (*S*)-**8b**. $[\alpha]_D^{20}$ –1.23, $[\alpha]_{578}^{20}$ –1.29, $[\alpha]_{546}^{20}$ –1.52, $[\alpha]_{436}^{20}$ –3.18, $[\alpha]_{365}^{20}$ –6.83 (*c* 1.28, $CHCl_3$). *rac*-**8b**: R_f = 0.59 (cyclohexane:*t*-butyl methyl ether = 4:1). Mp 91–92 °C (cyclohexane–*t*-butyl methyl ether). IR ($CHCl_3$/cuvette): 3437 (s) (NH), 1731 (s) (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.5 Hz, 3H), 1.74 (m, 2H), 5.29 (m, 1H), 6.11 (dd, *J* = 16.0, 7.3 Hz,

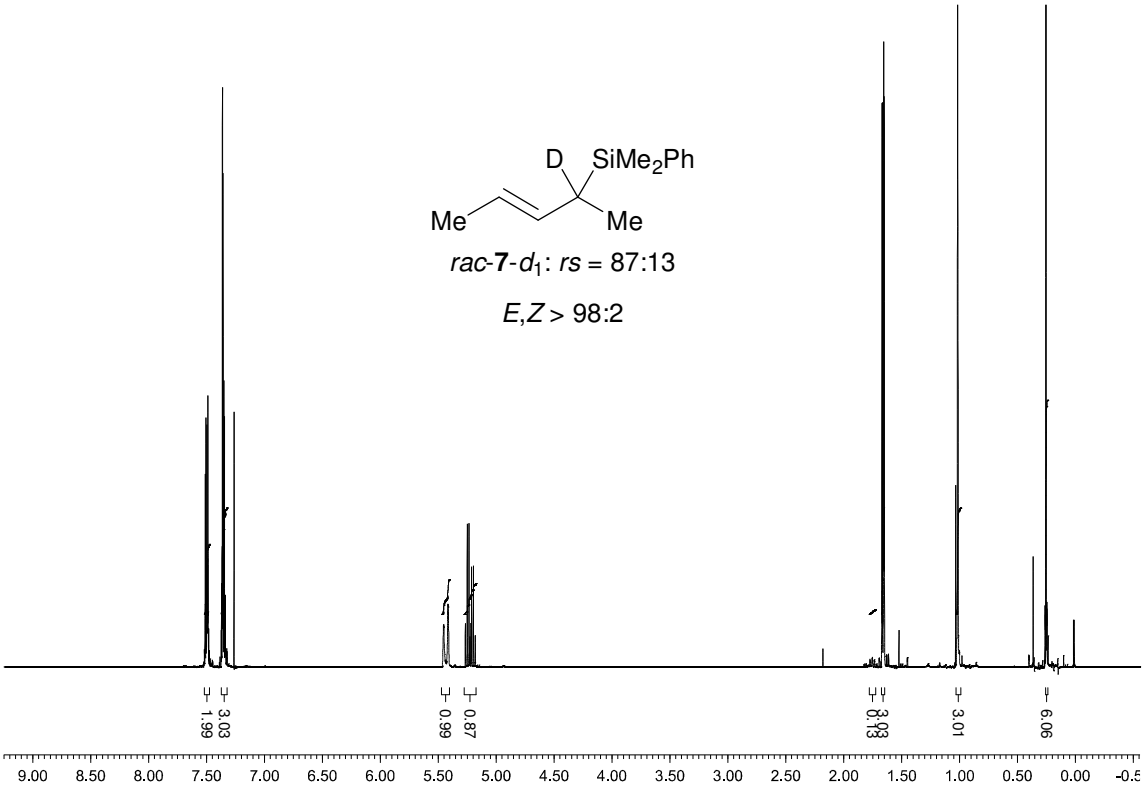
1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.65 (bs, 1H), 6.99 (m, 1H), 7.16–7.27 (m, 5H), 7.31–7.36 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 9.6, 27.9, 77.1, 118.7, 123.4, 126.6, 127.6, 127.9, 128.6, 129.1, 132.7, 136.4, 138.0, 153.1. LRMS (CI/NH_3): *m/z* = 280 [(M – H)$^-$]. Anal. Calcd for $C_{18}H_{19}NO_2$ (281.35): C, 76.84; H, 6.81; N, 4.98; Found: C, 76.67; H, 6.83; N, 4.96.

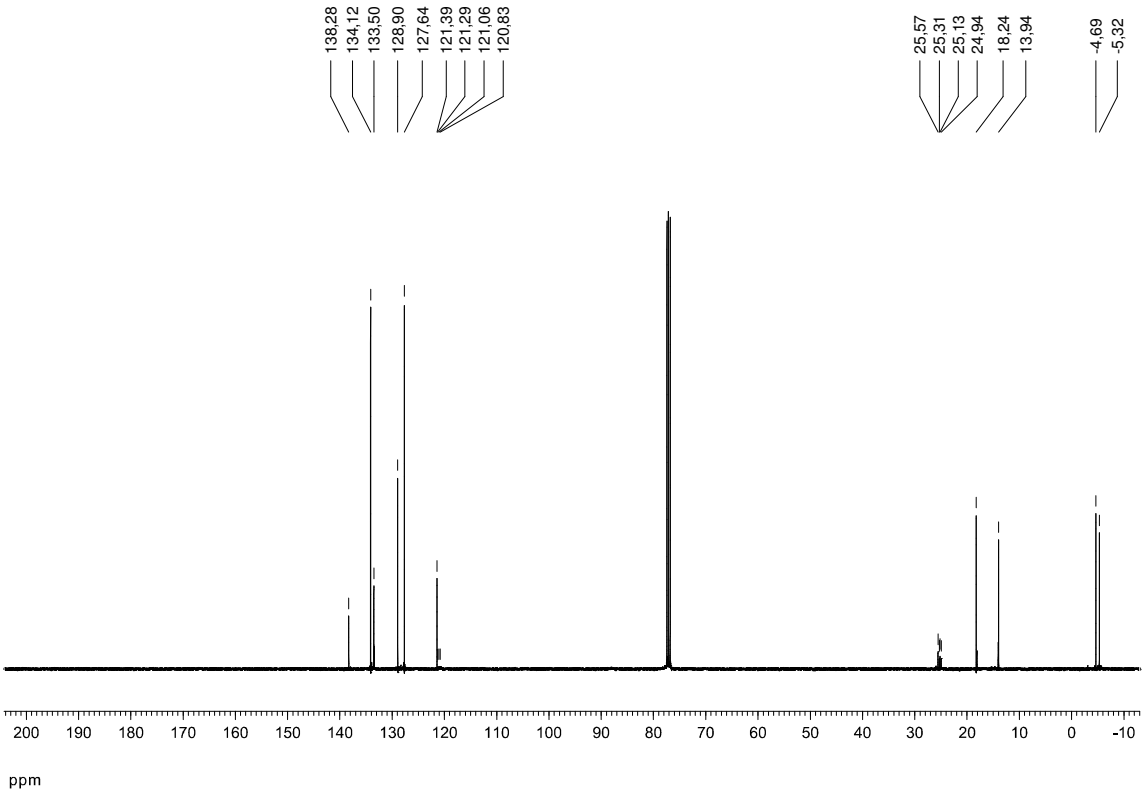
(*E*)-Dimethyl(phenyl)(1-phenyl-1-penten-3-yl)silane (9): HPLC (Daicel Chiralcel OD-R column coupled with Daicel Chiralcel OJ-R column, column temperature 30 °C, solvent MeCN:H_2O = 7:3, flow rate 0.8 mL·min^{-1}): 37.3 min for (*S*)-**9**, 39.3 min for (*R*)-**9**. (*R*)-**9** (88 and 91% *ee*): $[\alpha]_D^{20}$ +30.5, $[\alpha]_{578}^{20}$ +32.3, $[\alpha]_{546}^{20}$ +38.6, $[\alpha]_{436}^{20}$ +90.5, $[\alpha]_{365}^{20}$ +226 (*c* 1.05, $CHCl_3$). (*S*)-**9** (92 and 97% *ee*): $[\alpha]_D^{20}$ –39.8, $[\alpha]_{578}^{20}$ –42.2, $[\alpha]_{546}^{20}$ –50.3, $[\alpha]_{436}^{20}$ –117, $[\alpha]_{365}^{20}$ –292 (*c* 1.02, $CHCl_3$). *rac*-**9**: R_f = 0.41 (cyclohexane). IR ($CHCl_3$/cuvette): 1250 (s) (C–Si) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 3H), 0.28 (s, 3H), 0.86 (t, *J* = 7.3 Hz, 3H), 1.40 (m, 1H), 1.58 (m, 1H), 1.76 (m, 1H), 5.99 (dd, *J* = 15.8, 9.6 Hz, 1H), 6.17 (d, *J* = 16.3 Hz, 1H), 7.10–7.16 (m, 1H), 7.21–7.36 (m, 7H), 7.46–7.48 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –4.8, –4.1, 14.6, 22.4, 36.3, 125.7, 126.4, 127.8, 128.3, 128.6, 129.1, 132.7, 134.2, 137.9, 138.6. LRMS (EI): *m/z* = 280 [M$^+$]. HRMS (EI): *m/z* calcd for $C_{19}H_{24}Si$: 280.16473; Found: 280.16430.

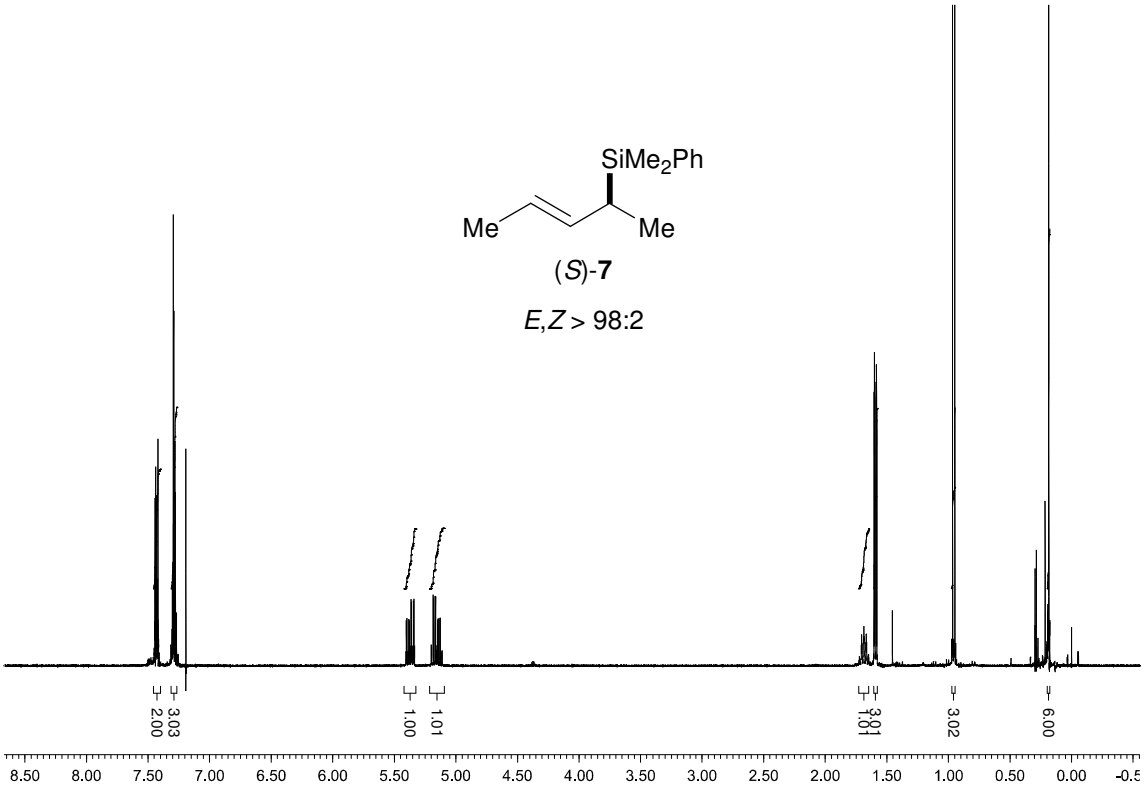
Dimethyl(phenyl)(1-phenyl-3-pentanyl)silane (10): HPLC (Daicel Chiralcel OJ-R column, column temperature 35 °C, solvent (EtOH:H_2O = 8:2):(MeCN:H_2O = 8:2) = 9:1, flow rate 0.8 mL·min^{-1}): 19.5 min for (*R*)-**10**, 21.9 min for (*S*)-**10**. (*S*)-**10** (92% *ee*): $[\alpha]_D^{20}$ –9.53, $[\alpha]_{578}^{20}$ –12.3, $[\alpha]_{546}^{20}$ –14.2, $[\alpha]_{436}^{20}$ –24.4, $[\alpha]_{365}^{20}$ –45.9 (*c* 1.07, $CHCl_3$). *rac*-**10**: R_f = 0.43 (cyclohexane). IR ($CHCl_3$/cuvette): 1256 (s) (C–Si) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 3H), 0.21 (s, 3H), 0.76 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H), 1.35 (tt, *J* = 14.3, 7.2 Hz, 1H), 1.52 (m, 2H), 1.67 (dddd, *J* = 13.8, 10.8, 6.0, 4.8 Hz, 1H), 2.38 (ddd, *J* = 13.4, 10.7, 6.1 Hz, 1H), 2.53 (ddd, *J* = 13.5, 10.8, 5.3 Hz, 1H), 6.98–7.47 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = –3.6, –3.4, 13.8, 22.4, 26.8, 31.5, 35.6, 125.7, 127.8, 128.4, 128.5, 128.9, 134.0, 139.4, 143.1. LRMS (CI/NH_3): *m/z* = 300 [(M + NH_4)$^+$]. Anal. Calcd for $C_{19}H_{26}Si$ (282.50): C, 80.78; H, 9.28; Found: C, 80.45; H, 9.19.

1-Phenyl-3-pentanol (11): HPLC (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent *n*-heptane:*i*-PrOH = 9:1, flow rate 0.8 mL·min^{-1}): 8.9 min for (*R*)-**11**, 11.4 min for (*S*)-**11**. (*S*)-**11** (91 and 99% *ee*): $[\alpha]_D^{20}$ +23.5, $[\alpha]_{578}^{20}$ +24.8, $[\alpha]_{546}^{20}$ +27.9, $[\alpha]_{436}^{20}$ +48.9, $[\alpha]_{365}^{20}$ +79.9 (*c* 1.78, $CHCl_3$).

3 Copies of NMR spectra for compounds *rac*-**7**-d_1, (*S*)-**7**, and (*R*)-**9**



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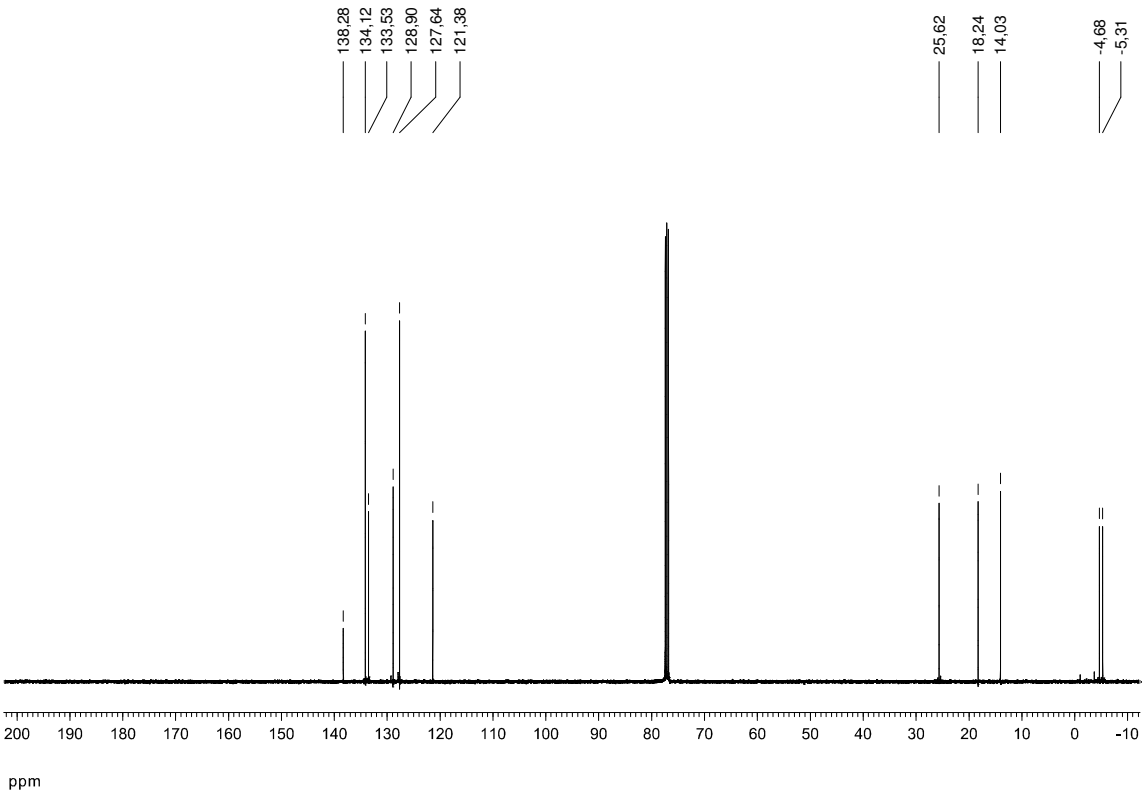
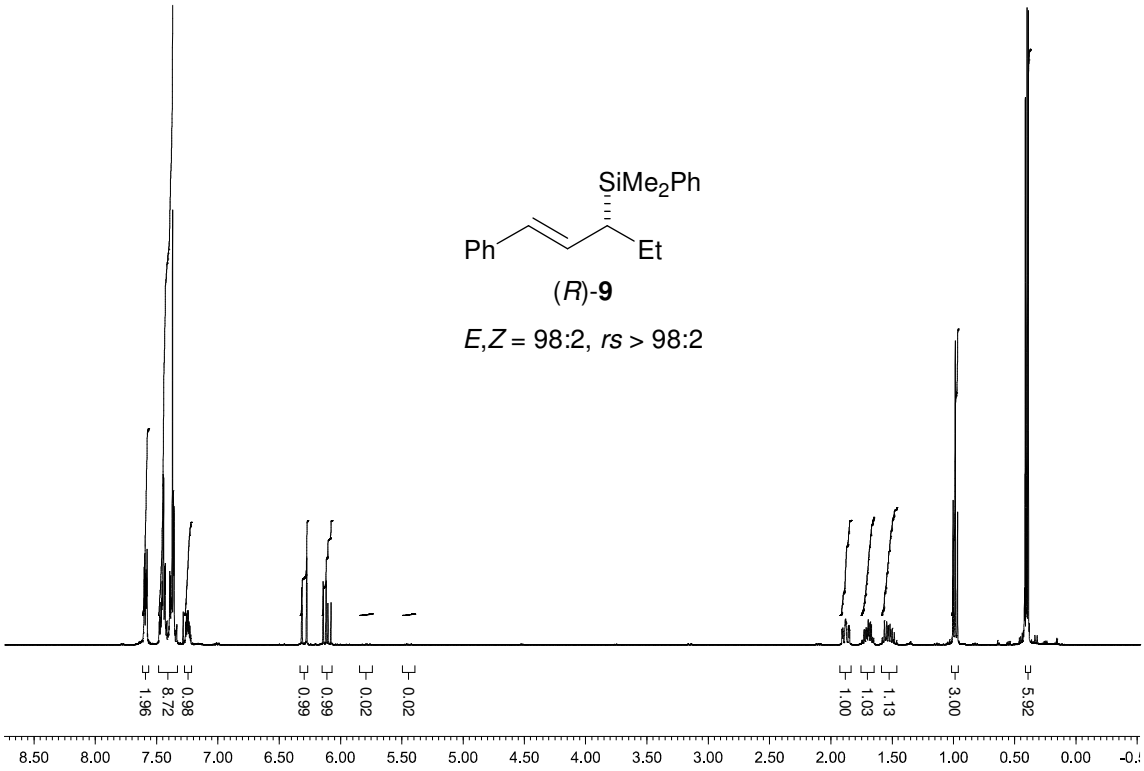
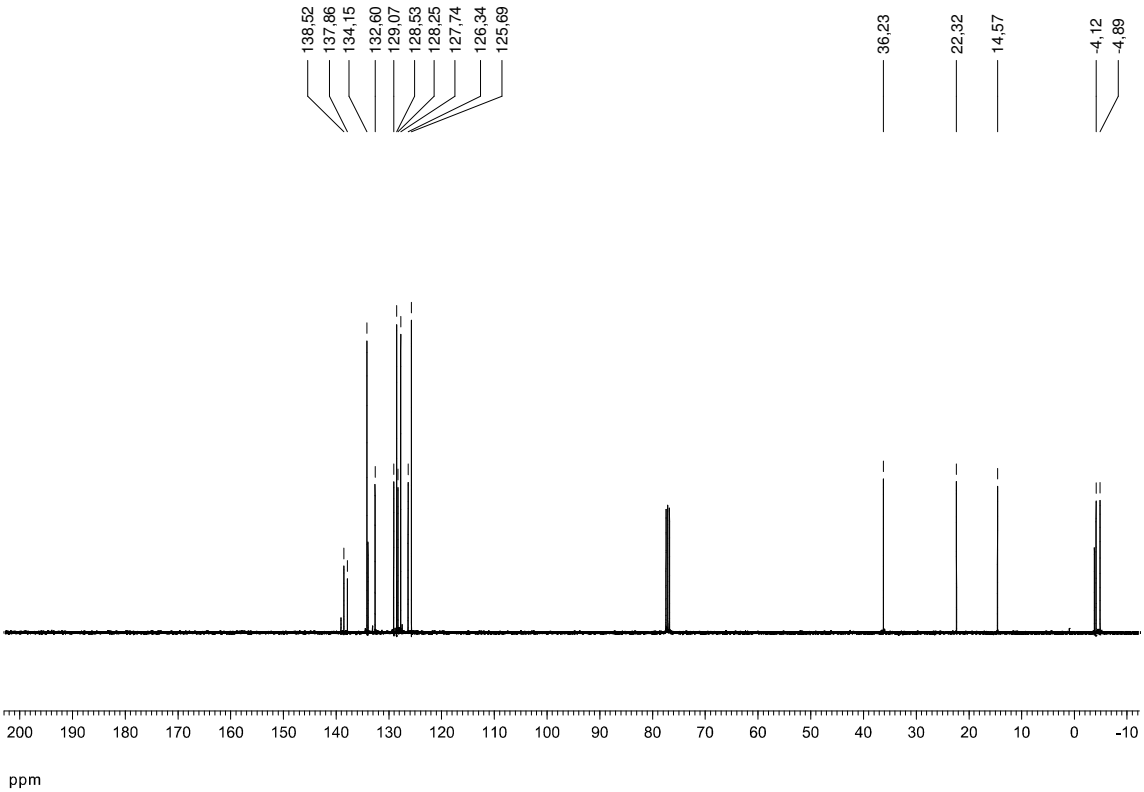
1.00
1.01
10.1
3.02
6.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00


138,28
134,12
133,53
128,90
127,64
121,38
25,62
18,24
14,03
-4,68
-5,31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


SiMe2Ph
Ph
Et
(R)-9
E,Z = 98:2, rs > 98:2
1.96
8.72
0.98
0.99
0.99
0.02
0.02
1.00
1.03
1.13
3.00
5.92
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00


138,52
137,86
134,15
132,60
129,07
128,53
128,25
127,74
126,34
125,69
36,23
22,32
14,57
-4,12
-4,89
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm