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Supporting Information

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Allylation of Ketones with a Ferrocene-Based Planar Chiral Lewis Acid**

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Materials and General Methods. (*1S*,*2S*)-(+)-Pseudoephedrine, (*1S*,*2S*)-(+)-*N*-methyl pseudoephedrine, and (*4S*,*5S*)-(-)-4,5-dihydro-4-methoxymethyl-2-methyl-5-phenyloxazole) were purchased from Sigma Aldrich and dichlorophenylborane from Acros. All chemicals were used without further purification. (*1R*,*2R*)-(-)-*N*-methyl pseudoephedrine[1], Me_3SnAll[2], and 1,2-$Fc(SnMe_2Cl)(BClMe)$[3] were prepared according to literature procedures. Deuterated chloroform ($CDCl_3$ >99.7%) was obtained from Cambridge Isotope Laboratories (CIL). The solvent was stirred for several days over anhydrous CaH_2, then degassed via several freeze pump thaw cycles and stored over 3Å molecular sieves. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun Glovebox Technology). Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina / copper columns for hydrocarbon solvents) and the chlorinated solvents were subsequently degassed via several freeze pump thaw cycles.

All 499.9 MHz ^1H, 125.7 MHz ^{13}C, 186.4 MHz ^{119}Sn, and 160.3 ^{11}B NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^1H and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{119}Sn and ^{11}B NMR spectra were referenced externally to $SnMe_4$ ($\delta = 0$) and $BF_3 \cdot Et_2O$ ($\delta = 0$) in C_6D_6, respectively. Splittings of NMR signals are abbreviated as pst (pseudo-triplet), dpst (doublet of pseudo-triplet), nr (not resolved).

Two-dimensional ^1H NOESY[4] measurements were obtained with the standard pulse sequence that was followed by a 90° pulse flanked by two 5 G/cm gradient for dephasing any residual transverse magnetization and suppressing potential artifacts, before the relaxation delay. Spectra were recorded in the phase sensitive mode by employing the TPPI improvement[5] of the States-Haberkorn-Ruben Hypercomplex method.[6] Typically, 256 t1 increments of 2K complex data points over 5.0 kHz spectral widths were collected with 32 scans per t1 increment, preceded by 16 or 32 dummy scans, and a relaxation delay of 2 s. Data sets were processed on a Sun Blade 100 workstation (Sun Microsystems Inc., Palo Alto, CA) using the VNMR software package (Varian Inc., Palo Alto, CA). In order to decrease t1 ridges arising from incorrect treatment of the first data point in the discreet Fourier transform (FT) algorithm, the spectrum corresponding to the first t1 value was divided by 2 prior to FT along t1.[7] Unshifted Sine Bell window functions were used in both dimensions. Data sets were zero-filled in the t1 dimension yielding 1K x 1K final matrices.

Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ. Optical rotation analysis was performed on an Autopol II polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at λ = 589 nm. GC analysis was performed on Hewlett Packard 5890 Series II using an Rt-BetaDex-sm chiral column purchased from Restek Corp.

X-Ray data were collected on a Bruker SMART APEX CCD Diffractometer using Cu-Kα (1.54178 Å) radiation. Crystals of $\boldsymbol{S_p}$**-2-(+)-MPE** were grown from toluene/hexanes at –37 °C. SADABS[8] absorption correction was applied, the structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.[9]

Experimental Procedures

Synthesis of 1-OMe: Neat Me_3SiOMe (218 mg; 2 mmol) was added to a solution of **1-Cl** (100 mg; 0.233 mmol) in CH_2Cl_2 (2 mL) via syringe. The reaction mixture was stirred at 40 °C for 48 h. Light orange crystals were obtained from a 2:1 mixture of hexanes/CH_2Cl_2 after two days at –38 °C and dried under vacuum for several hours. Yield: 88.7 mg (0.209 mmol; 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 4.81 (dd, J = 1.0 Hz, 2.5 Hz, 1 H, Cp-H5), 4.73 (pst, J = 2.5 Hz, 1H, Cp-H4), 4.61 (dd, J = 1.0 Hz, 2.5 Hz, 1 H, Cp-H3), 4.16 (s, 5 H, C_5H_5), 3.76 (s, 3 H, OMe), 0.89 (s/d, J ($^{117/119}$Sn, H) = 64/66 Hz, 3 H, Sn-Me), 0.70 (s, 3 H, B-Me), 0.64 (s/d, J ($^{117/119}$Sn, H) = 61/63 Hz, 3 H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 79.2 (s/d, J ($^{117/119}$Sn, C) = 63 Hz, Cp-C5), 77.6 (s/d, J ($^{117/119}$Sn, C) = 59, Cp-C3), 76.3 (s/d, J ($^{117/119}$Sn, C) = 59 Hz, Cp-C4), 68.8 (C_5H_5), 53.6 (OMe), 1.9 (s/d, J ($^{117/119}$Sn, C) = 466/487 Hz, Sn-Me), 0.9 (s/d, J ($^{117/119}$Sn, C) = 422/442 Hz, Sn-Me), 0.1 (br, B-Me), not observed Cp-C1, Cp-C2; ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ = 69.0; ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ = 50.3 ($w_{1/2}$ = 350 Hz). Anal. Calcd for $C_{14}H_{20}BClFeOSn$ (425.13): C, 39.55; H, 4.74. Found C, 39.69; H, 4.59.

Synthesis of S_p-2-(+)-MPE and R_p-1-OMe: A solution of (1*S*,2*S*)-(+)-*N*-methyl pseudoephedrine (45 mg, 0.25 mmol) in toluene (2 mL) was added dropwise to a stirred solution of **1-OMe** (200 mg, 0.47 mmol) in toluene (2 mL). The reaction mixture was left to stir at RT for 2 h followed by removal of all volatile components. The residue was extracted three times with 3 ml of hexanes each to isolate the unreacted starting material. The solvent was removed from the combined extracts under vacuum and the residue was recrystallized from CH_2Cl_2/hexanes at –38 °C and dried under high vacuum. Yield for ***R*$_p$-1-OMe** 84 mg (0.198 mmol; 84%). The NMR data for ***R*$_p$-1-OMe** are identical to those of the racemate **1-OMe**. For ***R*$_p$-1-OMe** $[\alpha]^D_{22}$ = +104.4 (c = 0.38, CH_2Cl_2). The residue left behind after hexane extraction was redissolved in toluene (2 mL), a small amount of racemic **1-OMe** (10 mg) was added, and the mixture was stirred for 1 h at RT. Toluene was removed under vacuum, and the residue washed with hexanes (3 x 1 mL) and dried under high vacuum. Yield for ***S*$_p$-2-(+)-MPE** 95 mg (0.166 mmol; 71%). For ***S*$_p$-2-(+)-MPE:** $[\alpha]^D_{22}$ = 49.9 (c = 0.54, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.36-7.44 (overlapping, 5 H, aromat.), 4.59 (br, 1 H, Cp-H), 4.48 (overlapped, 1 H, Cp-H), 4.48 (d, J = 10 Hz, 1H, MPE-H), 4.27 (br, 1 H, Cp-H), 4.23 (s, 5 H, Cp), 3.34 (m, 1H, MPE-H), 2.44 (br, 3H, N-Me), 1.93 (br, 3H, N-Me), 1.12 (d, J = 6.5 Hz, 3H, C-Me), 0.63 (s/d, J($^{117/119}$Sn, H) = 69/72 Hz, 3 H, Sn-Me), 0.60 (s/d, J($^{117/119}$Sn, H) = 57/59 Hz, 3 H, Sn-Me), 0.45 (s, 3 H, B-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ = 22.4; ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ = 10.2 ($w_{1/2}$ = 360 Hz). Anal. Calcd for $C_{24}H_{34}BClFeNOSn$ (572.34): C, 50.28; H, 5.98, N 2.44. Found C, 50.67; H, 5.75, N 2.37.

Synthesis of R_p-2-(–)-MPE and S_p-1-OMe: A solution of (1*R*,2*R*)-(–)-*N*-methyl pseudoephedrine (45 mg, 0.25 mmol) in toluene (2 mL) was added dropwise to a stirred solution of **1-OMe** (200 mg, 0.47 mmol) in toluene (2 mL). Using a similar procedure as for the preparation of ***S*$_p$-2-(+)-MPE** and ***R*$_p$-1-OMe**, compounds ***R*$_p$-2-(–)-MPE** and ***S*$_p$-1-OMe** were obtained as a yellow powdery material and orange crystals, respectively. Yield for ***R*$_p$-2-(–)-MPE**: 91 mg (0.159 mmol; 65%). Yield for ***S*$_p$-1-OMe** after recrystallization from CH_2Cl_2/hexanes at –38 °C: 85 mg (0.200 mmol; 85%). The NMR data for ***R*$_p$-2-(–)-MPE** are identical to those of ***S*$_p$-2-(+)-MPE** and the data for ***S*$_p$-1-OMe** are identical to those of the racemate **1-OMe**. For ***S*$_p$-1-OMe**: $[\alpha]^D_{22}$ = –100.6 (c = 0.36, CH_2Cl_2); for ***R*$_p$-2-(–)-MPE**: $[\alpha]^D_{22}$ = –49.4 (c = 0.52, CH_2Cl_2).

Synthesis of R_p-1-Cl: A solution of $PhBCl_2$ (29.7 mg, 0.187 mmol) in hexanes (2 mL) was added dropwise to a stirred solution of R_p-**1-OMe** (72 mg, 0.169 mmol) in hexanes (2 mL). The reaction mixture was left to stir at RT for 30 min and a small amount of insoluble material was filtered off. The reaction mixture was placed under high vacuum overnight for removal of all volatile components. The product was identified by comparison to NMR data for racemic **1-Cl**. Yield: 64.6 mg (89%); purity 95% by ^{1}H NMR. Similar results were obtained for the conversion of S_p-**1-OMe** to S_p-**1-Cl**.

Conversion of R_p-1-Cl to R_p-3: A solution of Me_3SnAll (19 mg, 0.093 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of R_p-**1-Cl** (35 mg, 0.081 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was left to stir at RT for 24 h followed by removal of all volatile components. An oily material was obtained. Yield: 35 mg (99%), purity >95% by ^{1}H NMR. The product was used without further purification. For R_p-**3**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.08 (m, 1 H, allyl-β), 4.99 (m, 2 H, allyl-γ), 4.93 (overlapping, 2H, Cp-H), 4.77 (d, J = 1.5, 2.5 Hz, J ($^{117/119}$Sn, H) = 14 Hz, 1 H, Cp-H), 4.19 (s, 5 H, C_5H_5), 2.29 (d, J = 8.0 Hz, 2 H, allyl-α), 0.91 (s/d, J($^{117/119}$Sn, H) = 58/60 Hz, 3 H, Sn-Me), 0.88 (s, 3 H, B-Me), 0.78 (s/d, J($^{117/119}$Sn, H) = 56/58 Hz, 3 H, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ = 130.8; ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ = 70 ($w_{1/2}$ = 600 Hz). The S_p-**3** enantiomer was obtained through similar procedures.

Conversion of R_p-1-OMe or R_p-2-(–)-MPE to R_p-4: A solution of AllMgBr (44 μL, 1 M in Et_2O, 0.044 mmol) in Et_2O (2 mL) was added via syringe to R_p-**1-OMe** (10 mg, 0.023 mmol) or R_p-**2-(–)-MPE** (10 mg, 0.017 mmol) in Et_2O (1 mL) at –35 °C. The reaction mixture was left to stir at RT for 2 h followed by removal of all volatile components. The product was extracted from insoluble magnesium salts by adding 1 ml of hexanes followed by filtration. An oily material was obtained after removal of solvents. Yield from R_p-**1-OMe**: 10 mg (98%); purity ca. 80% by ^{1}H NMR. Yield from R_p-**2-(–)-MPE**: 7.4 mg (98%); purity ca. 65% by ^{1}H NMR. The product was used without further purification. For R_p-**4**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.09 (m, 1H, B-allyl-β), 5.98 (m, 1 H, Sn-allyl-β), 4.99 (m, 1 H, B-allyl-γ), 4.96 (m, 1 H, B-allyl-γ), 4.96 (m, 1 H, Sn-allyl-γ), 4.87 (m, 1 H, Sn-allyl-γ), 4.74 (pst, J = 2.5 Hz, Cp-H4), 4.70 (dd/ddd, J = 1.0 Hz, 2.5 Hz, J ($^{117/119}$Sn, H) = 8 Hz, 1 H, Cp-H3), 4.59 (dd/ddd, J = 1.0 Hz, 2.0 Hz, J ($^{117/119}$Sn, H) = 13 Hz, 1 H, Cp-H5), 4.10 (s, 5 H, C_5H_5), 2.31 (d, J = 8.0 Hz, 2 H, B-allyl-α), 1.99 (dd, J = 3.0 Hz, 8.0 Hz, J ($^{117/119}$Sn, H) = 68 Hz, 2 H, Sn-allyl-α), 0.90 (s, 3 H, B-Me), 0.33 (s/d, J($^{117/119}$Sn, H) = 51/53 Hz, 3 H, Sn-Me), 0.32 (s/d, J($^{117/119}$Sn, H) = 52/54 Hz, 3 H, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ = –14.3; ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ = 71 ($w_{1/2}$ = 690 Hz). The S_p-**4** enantiomer was obtained through similar procedures.

General procedure for the allylation of aldehydes and ketones. A solution of R_p/S_p-**3** or R_p/S_p-**4** (1.1 equiv) in CH_2Cl_2 (0.5 mL) was added dropwise to the desired aldehyde / ketone in CH_2Cl_2 (0.5 mL) and the mixture was stirred at RT for 1 h. The reaction mixture was quenched by addition of 1 drop of MeOH followed by GC/MS and chiral GC analysis without further treatment. Alternatively, one equiv of PE is added and the mixture stirred for 30 min in toluene, followed by evaporation of toluene, extraction with hexanes, and analysis by chiral GC. Low temperature reactions were carried out in a similar fashion by adding R_p/S_p-**3** or R_p/S_p-**4** to a pre-cooled solution of aldehyde / ketone at –78 °C under N_2 atmosphere via syringe.

Synthesis of (+)-(2*R*)-2-Phenylpent-4-en-2-ol. A solution of S_p-**3** (4.0 mg, 9.2 μmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a solution of acetophenone (1.0 mg, 8.4 μmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 1 h at RT followed by addition of (*1S*,*2S*)-(+)-pseudoephedrine (1.6 mg, 10 μmol). The solvents were removed under vacuum and hexanes

(2 mL) were added to extract the product. Conversion: 82%, er = 80:20 (determined by chiral GC analysis).

Figure S1. (a) ^{119}Sn NMR Spectrum of racemic **[1-Cl]•D*** in $CDCl_3$ (b) ^{119}Sn NMR Spectrum of **[R_p-1-Cl]•D*** in $CDCl_3$. (c) ^{119}Sn NMR Spectrum of **[S_p-1-Cl]•D*** in $CDCl_3$. (D* = (*4S*,*5S*)-(-)-4,5-Dihydro-4-methoxymethyl-2-methyl-5-phenyloxazole).

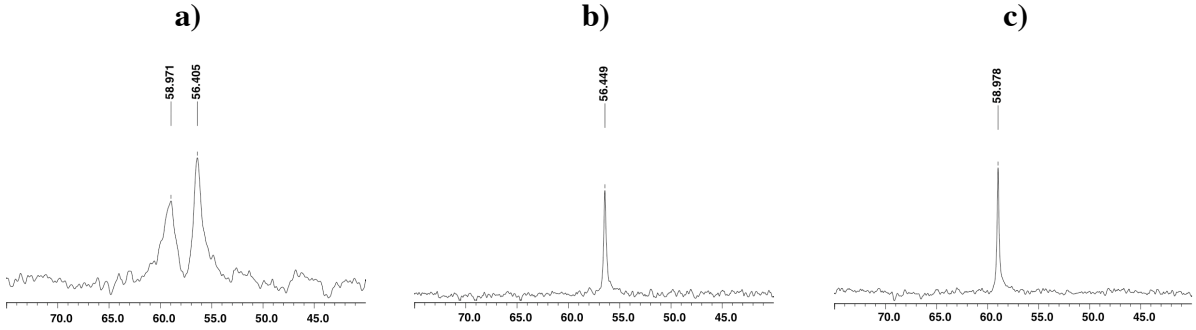


Figure S2. a) GC-FID Trace of 2-Phenylpent-4-en-2-ol b) GC-FID Trace of (+)-(*2R*)-2-Phenylpent-4-en-2-ol prepared from **S_p-3** at RT. c) GC-FID Trace of (–)-(*2S*)-2-Phenylpent-4-en-2-ol prepared from **R_p-4** at RT.

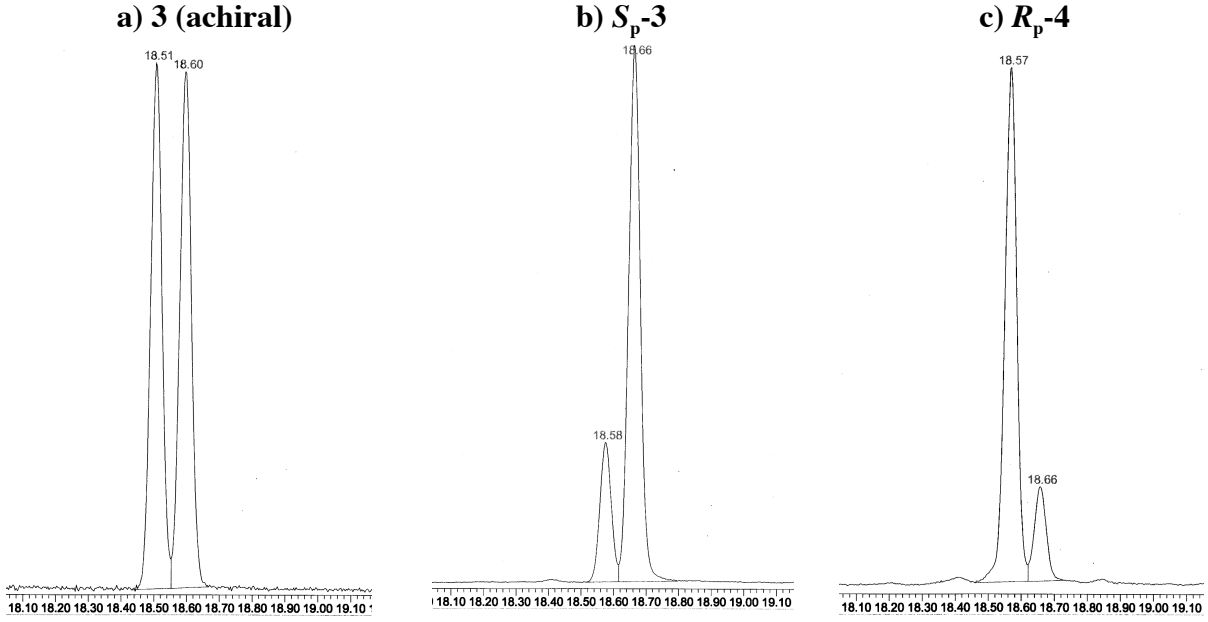
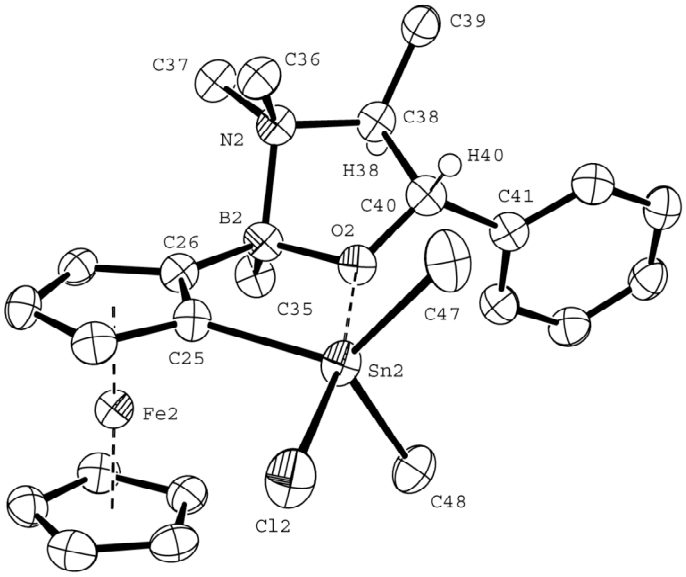


Figure S3. ORTEP plot of the second molecule of ***S*$_p$-2-(+)-MPE** (50% probability). A cocrystallized toluene molecule is omitted and only hydrogens attached to stereogenic carbon atoms are shown. Selected interatomic distances (Å) and angles (°): Sn(2)-Cl(2) 2.4699(13), Sn(2)-C(25) 2.109(5), Sn(2)-C(47) 2.137(6), Sn(1)-C(48) 2.126(6), Sn(2)···O(2) 2.475(3), B(2)-C(26) 1.579(7), B(2)-C(35) 1.612(7), B(2)-O(2) 1.517(7), B(2)-N(2) 1.683(7), Fe(2)···B(2) 3.290; C(25)-Sn(2)-C(47) 122.0(2), C(25)-Sn(2)-C(48) 120.7(2), C(47)-Sn(2)-C(48) 112.8(2), C(48)-Sn(2)-Cl(2) 99.48(17), C(25)-Sn(2)-O(2) 76.53(16), C(47)-Sn(2)-Cl(2) 97.37(17), O(2)-Sn(2)-Cl(2) 170.44(9), C(26)-B(2)-C(35) 115.5(4), C(26)-B(2)-O(2) 108.1(4), C(26)-B(2)-N(2) 110.9(4), C(35)-B(2)-N(2) 108.9(4).



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