Supporting Information – Part 1:

METHOX - a New Pyridine N-Oxide Organocatalyst for the Asymmetric Allylation of Aldehydes with Allyltrichlorosilanes

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Experimental

General Methods. Melting points were determined on a Kofler block and are uncorrected. Optical rotations were recorded in CHCl_3 at 25 °C unless otherwise indicated, with an error of $\leq \pm 0.1$. The $[\alpha]_D$ values are given in $10^{-1} \text{ deg cm}^3 \text{ g}^{-1}$. The NMR spectra were recorded in CDCl_3 , ^1H at 400 MHz and ^{13}C at 100.6 MHz with chloroform- d_1 (δ 7.26, ^1H ; δ 77.0, ^{13}C) as internal standard unless otherwise indicated. Various 2D-techniques and DEPT experiments were used to establish the structures and to assign the signals. The IR spectra were recorded for CHCl_3 solutions. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware, twice evacuated and filled with inert gas. Solvents and solutions were transferred by syringe-septum and cannula techniques. All solvents for the reactions were of reagent grade and were dried and distilled immediately before use (dichloromethane from calcium hydride). Petroleum ether refers to the fraction boiling in the range of 60-80 °C. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior. The chiral GC and HPLC methods were calibrated with the corresponding racemic mixtures. (+)- α -Pinene was purchased from Aldrich; according to GC analysis on a Supelco β -DEX 120 column the ee was 90%. (–)-Pinocarvone (–)-**15** was obtained on a 40 g scale from (+)- α -pinene via the photochemical oxidation (99%) according to the Mihelich procedure (Mihelich, E. D.; Eickhoff, D. J. *J. Org. Chem.* **1983**, 48, 4135.). The Kröhnke salt **14a** was prepared according to the literature (Hartwell, J. L.; Kornberg, S. R. L. *J. Amer. Chem. Soc.*, **1946**, 68, 868; King, L. C.; McWhirter, M.; Rowland, R. L. *J. Amer. Chem. Soc.* **1948**, 70, 239; King, L. C. *J. Amer. Chem. Soc.* **1948**, 70, 242; Alvarez-Builla, J. E.; Cuadro, A. M.; Florencio, F.; Garcia Blanco, S. J. *Heterocycl. Chem.* **1987**, 24, 917).

Kröhnke Salts. The aryl ketone (48.0 mmol) was heated in pyridine (20 mL) until a clear solution was obtained. Crystalline iodine (17.4 g, 57.0 mmol) was added portionwise and the resulting solution was refluxed for 1 h and then cooled to room temperature. The brownish precipitate was filtered off and successively washed with absolute pyridine (3×15 mL) to give the Kröhnke salt as a pale yellow solid, which could be crystallized from water or used directly in the Kröhnke annulation.

1-[2-(2',6'-Dimethoxyphenyl)-2-oxo-ethyl]-pyridinium Iodide (14b) (50%): mp 201-203 °C (water); ^1H NMR (400 MHz, d_6 -DMSO) δ 3.85 (s, 6H), 6.08 (s, 2H), 6.82 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 8.4 Hz, 1H), 8.21 (t, J = 6.7 Hz, 2H), 8.74 (t, J = 7.8 Hz, 1H), 8.94 (d, J = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 56.65 (CH_3O), 69.4 (CH_2), 104.9 (CH), 114.6 (C), 128.4 (CH), 134.0 (CH), 146.4 (CH), 146.9 (CH), 158.0 (C), 194.0 (CO); HRMS (FAB) 258.1132 ($\text{C}_{15}\text{H}_{16}\text{NO}_3$ requires 258.11302).

1-[2-(2',4',6'-Trimethoxyphenyl)-2-oxo-ethyl]-pyridinium Iodide (14c) (98%): mp 202-206 °C (methanol-toluene); ^1H NMR (400 MHz, d_6 -DMSO) δ 3.85 (s, 6 H), 3.88 (s, 3H), 6.01 (s, 2H), 6.37 (s, 2H), 8.24 (t, J = 7.2 Hz, 2H), 8.69 (t, J = 7.6 Hz, 1H), 8.74, (t, J = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 56.2 (CH_3O), 56.6 (CH_3O), 69.7 (CH_2), 91.6 (CH), 128.2 (CH), 146.4 (CH), 146.6 (CH), 160.8 (C), 164.8 (C), 190.7 (CO); MS (FAB) m/z (%) 288.3 ($\text{M}^+ - \text{I}$, 69); HRMS (FAB) 288.1233 ($\text{C}_{16}\text{H}_{18}\text{NO}_4$ requires 288.1236).

General Procedure for the Kröhnke Annulation Using (–)-Pinocarvone (–)-15 as Michael Acceptor. Anhydrous ammonium acetate (110.0 g) was heated in acetic acid (100 mL) at 110 °C until it dissolved. Kröhnke salt **14** (47.0 mmol) was then added and the mixture was left at 110 °C until the Kröhnke salt dissolved. Pinocarvone (–)-**15** (43.0 mmol) was added and the solution was stirred at 110 °C for 48 h. Water (20 mL) was then added and the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed successively with water (3 × 50 mL) and brine (30 mL), and dried (MgSO₄). The solvent was removed in vacuo to afford an oil that was purified via flash chromatography on silica gel (25 g) using petroleum ether, followed by a 9:1 mixture of petroleum ether and ethyl acetate to give pure product as a yellow oil or solid.

(+)-5-(4'-Methoxyphenyl)-10,10-dimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(16a) (35%): mp 99-101 °C (petroleum ether–ethyl acetate); [α]_D +82.5 (c 1.0, CHCl₃); ¹H NMR δ 0.61 (s, 3H), 1.34 (d, *J* = 5.5 Hz, 1H), 1.44 (s, 3H), 2.42 (m, 1H), 2.71 (dt, *J* = 9.5 and 5.8 Hz, 1H), 2.79 (t, *J* = 5.6 Hz, 1H), 3.19 (d, *J* = 2.6 Hz, 2H), 3.89 (s, 3H), 6.94 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 2H); ¹³C NMR δ 21.7 (CH₃), 26.5 (CH₃), 32.5 (CH₂), 37.2 (CH₂), 40.7 (CH), 46.6 (CH), 56.7 (OCH₃), 113.9 (CH), 116.8 (CH), 128.3 (CH), 133.1 (C), 133.9 (CH), 140.0 (C), 154.9 (C), 157 (C), 160.2 (C); MS (EI) *m/z* (%) 279 (M⁺, 100), 264 (60), 250 (25), 236 (75), 224 (14), 193 (13), 83 (14), 49 (18); HRMS (EI) 279.1623 (C₁₉H₂₁NO requires 279.1623).

(+)-5-(2',6'-Dimethoxyphenyl)-10,10-dimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(16b) (50%): [α]_D +47.1 (c 1.0, CHCl₃); ¹H NMR δ 0.62 (s, 3H), 1.28 (d, *J* = 9.2 Hz, 1H), 1.33 (s, 3H), 2.30 (m, 1H), 2.58 (dt, *J* = 9.6 and 5.7 Hz, 1H), 2.67 (t, *J* = 5.6 Hz, 1H), 3.09 (d, *J* = 2.6 Hz, 2H), 3.63 (s, 6H), 6.52 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 7.16 (m, 2H); ¹³C NMR δ 21.8 (CH₃), 26.5 (CH₃), 32.1 (CH₂), 36.7 (CH₂), 39.9 (C), 40.7 (CH), 46.7 (CH), 56.3 (OCH₃), 104.3 (CH), 119.6 (C), 122.9 (CH), 129.7 (CH), 133.4 (CH), 139.9 (C), 151.4 (C), 156.3 (C), 158.6 (C); MS (EI) *m/z* (%) 309 (M⁺, 60), 294 (45), 266 (15), 83 (100), 47 (21); HRMS (EI) 309.1729 (C₂₀H₂₃NO₂ requires 309.1729).

(+)-5-(2',4',6'-Trimethoxyphenyl)-10,10-dimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(16c) (95%): mp 98-100 °C (toluene-ethyl acetate); [α]_D +49.5 (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 0.62 (s, 3H), 1.31 (d, *J* = 9.4 Hz, 1H), 1.38 (s, 3H), 2.29 (m, 1H), 2.59 (dt, *J* = 9.6 and 5.6 Hz, 1H), 2.68 (t, *J* = 5.6 Hz, 1H), 3.07 (d, *J* = 2.8 Hz, 2H), 3.61 (s, 6H), 3.72 (s, 3H), 6.13 (s, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H); ¹³C NMR δ 21.8 (CH₃), 26.5 (CH₃), 32.1 (CH₂), 37.0 (CH₂), 39.9 (C), 40.6 (CH), 46.7 (CH), 55.7 (OCH₃), 56.3 (OCH₃), 91.2 (CH), 113.3 (C), 123.1 (CH), 133.1 (CH), 139.5 (C), 151.6 (C), 156.3 (C), 159.3 (C), 161.3 (C); MS (EI) *m/z* (%) 339 (M⁺, 95), 324 (M⁺-Me, 53); HRMS (EI) 339.1835 (C₂₁H₂₅NO₃ requires 339.1834).

Methylation of Pyridine Derivatives 16a-c. A solution of *n*-butyllithium (1.9 M in hexane, 9.2 mL, 17.7 mmol) was added dropwise to a solution of diisopropylamine (2.76 mL, 19.5 mmol) in THF (30 mL) at -40 °C, the mixture was brought to 0 °C, stirred for 30 min, and cooled to -40 °C. A solution of the pyridine derivative **16a-c** (4.0 g, 11.8 mmol) in THF (30 mL) was added at -40 °C, turning the solution dark red. The mixture was stirred at that temperature for 2 h. Methyl iodide (1.12 mL, 17.7 mmol) was then added dropwise and the mixture was stirred overnight at room temperature. Water (30 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 30 mL). The organic layers were combined and washed with brine (30 mL) and dried (MgSO₄) and the solvent was removed under reduced pressure. The

crude product was purified using flash chromatography on silica gel (80 g) with a mixture of petroleum ether and ethyl acetate (9:1) to give pure product as a white solid.

(+)-5-(4'-Methoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(17a) (52%): $[\alpha]_D +54.3$ (*c* 1.0, CHCl₃); ¹H NMR δ 0.59 (s, 3H), 1.30 (d, *J* = 9.2 Hz, 1H), 1.34 (s, 3H), 1.37 (d, *J* = 7.8 Hz, 3H), 2.08 (m, 1H), 2.46 (dt, *J* = 9.93 and 5.75 Hz, 1H), 2.68 (t, *J* = 5.52 Hz, 1H), 3.17 (dq, *J* = 6.6 and 2.8 Hz, 1H), 3.76 (s, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 2H); ¹³C NMR δ 18.6 (CH₃), 21.3 (CH₃), 26.7 (CH₃), 29.1 (CH₂), 39.3 (CH), 41.8 (CH), 47.2 (CH), 55.7 (OCH₃), 114.4 (CH), 116.6 (CH), 128.2 (CH), 133.2 (C), 133.6 (CH), 139.8 (C), 154.5 (C), 160.3 (C), 160.8 (C); MS (EI) *m/z* (%) 293 (M⁺, 49), 278 (80), 250 (74), 85 (68), 83 (100), 47 (20); HRMS (EI) 293.1780 (C₂₀H₂₃NO requires 293.1780).

(+)-5-(2',6'-Dimethoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(17b) (71%): mp 143-145 °C (petroleum ether-ethyl acetate); $[\alpha]_D +26.5$ (*c* 1.0, CHCl₃); ¹H NMR δ 0.69 (s, 3H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.42 (d, *J* = 9.5 Hz, 1H), 1.45 (s, 3H), 2.17 (m, 1H), 2.58 (dt, *J* = 9.9 and 5.7 Hz, 1H), 2.79 (t, *J* = 5.6 Hz, 1H), 3.26 (qd, *J* = 6.9 and 2.5 Hz, 1H), 3.74 (s, 6H), 6.66 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 8.4 Hz, 1H); ¹³C NMR δ 19.0 (CH₃), 21.3 (CH₃), 26.7 (CH₃), 28.9 (CH₂), 39.2 (CH), 41.8 (C), 47.4 (CH), 47.5 (CH), 56.5 (OCH₃), 105.2 (CH), 120.6 (C), 122.8 (CH), 129.5 (CH), 132.9 (CH), 139.4 (C), 151.5 (C), 158.8 (C), 160.3 (C); MS (EI) *m/z* (%) 323 (M⁺, 24), 308 (60), 280 (15), 83 (100), 47 (20); HRMS (EI) 323.1885 (C₂₁H₂₅NO₂ requires 323.1885).

(+)-5-(2',4',6'-Trimethoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene (+)-(17c) (79%): mp 110-112 °C (toluene-ethyl acetate); $[\alpha]_D +14.9$ (*c* 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 0.60 (s, 3H), 1.28 (d, *J* = 7.0 Hz, 2H), 1.30 (s, 3H), 1.32 (s, 3H), 2.05 (m, 1H), 2.45 (dt, *J* = 9.8 and 5.6 Hz, 1H), 2.79 (t, *J* = 5.8 Hz, 1H), 3.26 (dq, *J* = 7.1 and 2.8 Hz, 1H), 3.61 (s, 6H), 3.74 (s, 3H), 6.11 (s, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H); ¹³C NMR δ 19.0 (CH₃), 21.3 (CH₃), 26.7 (CH₃), 28.9 (CH₂), 39.0 (CH), 41.8 (C), 47.3 (CH), 47.4 (CH), 55.7 (OCH₃), 56.5 (OCH₃), 91.9 (CH), 113.7 (C), 123.2 (CH), 132.9 (CH), 138.5 (C), 139.2 (C), 151.4 (C), 159.5 (C), 160.2 (C), 161.4 (C); MS (EI) *m/z* (%) 353 (M⁺, 36), 338 (M⁺-Me, 100); HRMS (EI) 353.1991 (C₂₂H₂₇NO₃ requires 353.1991).

N-Oxidation of Pyridine Derivatives 17a-c. *m*-Chloroperoxybenzoic acid (MCPBA) (70%, 1.86 g, 9.38 mmol) was added portion-wise to a solution of the respective pyridine derivative (8.52 mmol) in dichloromethane (60 mL) at 0 °C and the mixture was stirred at room temperature for 2 h. The reaction mixture was then diluted with ether (60 mL) and washed successively with satd. NaHCO₃ (3 × 30 mL) and brine (30 mL). The ethereal solution was dried over Na₂SO₄ and the solvent was evaporated in vacuo. The resulting crude product was purified by column chromatography on silica gel (10 × 2.5 cm) with a mixture of petroleum ether and ethyl acetate (10:1) to elute the unreacted starting material, followed by ethyl acetate, to obtain the *N*-oxide, as a white solid.

(-)-5-(4'-Methoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene 6-Oxide (-)-(10) (83%): mp 110-112 °C (petroleum ether-ethyl acetate); $[\alpha]_D -22.9$ (*c* 1.0, CHCl₃); ¹H NMR δ 0.59 (s, 3H), 1.35 (s, 3H), 1.39 (s, 1H), 1.43 (d, *J* = 6.5 Hz, 3H), 2.10 (m, 1H), 2.48 (dt, *J* = 10.5 and 5.6 Hz, 1H), 2.70 (t, *J* = 5.4 Hz, 1H), 3.35 (qd, *J* = 6.6 and 2.8 Hz, 1H), 3.76 (s, 3H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.7 (d, *J* = 8.6 Hz, 2H); ¹³C NMR δ 15.2 (CH₃), 21.0 (CH₃), 26.3 (CH₃), 28.7 (CH₂), 35.5 (CH), 42.0 (C), 47.3 (CH), 47.9 (CH), 56.7 (OCH₃), 113.8 (CH), 123.2 (CH),

124.0 (CH), 126.3 (C), 131.4 (CH), 144.1 (C), 147.8 (C), 150.5 (C), 160.4 (C); MS (EI) m/z (%) 309 (M^{+} , 60), 292 (100), 278 (44), 250 (100), 236 (45), 224 (20); HRMS (EI) 309.1729 ($C_{20}H_{23}NO_2$ requires 309.1729).

(-)-5-(2',6'-Dimethoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene 6-Oxide (-)-(11) (70%): $[\alpha]_D$ -48.1 (c 1.0, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 0.53 (s, 3H), 1.34 (s, 3H), 1.39-1.45 (m, 4H), 2.1 (m, 1H), 2.48 (dt, J = 10.2 and 6.6 Hz, 1H), 2.70 (t, J = 6.6 Hz, 1H), 3.34 (qd, J = 6.6 Hz and 2.8 Hz, 1H), 3.67 (s, 3H), 3.69 (s, 3H), 6.52-6.57 (m, 2H), 6.78 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 7.25 (t, J = 8.4 Hz, 1H); ^{13}C NMR δ 15.1 (CH_3), 21.0 (CH_3), 26.3 (CH_3), 28.5 (CH_2), 35.2 (CH), 42.0 (C), 47.3 (CH), 48.3 (CH), 56.3 (OCH_3), 56.5 (OCH_3), 104.2 (CH), 104.6 (CH), 112.4 (C), 122.3 (CH), 125.8 (CH), 130.8 (CH), 143.7 (C), 144.2 (C), 149.9 (C), 158.4 (C), 159.1 (C); MS (EI) m/z (%) 339 (M^{+} , 10), 308 (100), 266 (10), 83 (25); HRMS (EI) 339.1834 ($C_{21}H_{25}NO_3$ requires 339.1834).

(+)-5-(2',4',6'-Trimethoxyphenyl)-8,10,10-trimethyl-6-aza-tricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene 6-Oxide (+)-(12) (51%). The product obtained by chromatography was recrystallized from a hexane-toluene mixture (10:1) to give enantiopure (+)-12 (1.08 g, 67%): mp 112-113 °C; $[\alpha]_D$ +8.6 (c 1.0, CH_2Cl_2); 1H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3H), 1.41 (m, 4H), 2.1 (m, 1H), 2.48 (dt, J = 10.2 and 6.6 Hz, 1H), 2.70 (t, J = 6.6 Hz, 1H), 3.34 (dq, J = 6.6 Hz and 2.8 Hz, 1H), 3.76 (d, J = 5.4 Hz, 6H), 6.55 (t, J = 7.6 Hz, 2H), 6.8 (d, J = 7.8 Hz, 1H), 6.9 (d, J = 7.7 Hz, 1H), 7.25 (t, J = 8.4 Hz, 1H); ^{13}C NMR δ 15.1 (CH_3), 21.0 (CH_3), 26.3 (CH_3), 28.5 (CH_2), 35.2 (CH), 42.0 (C), 47.3 (CH), 47.9 (CH), 55.8 (OCH_3), 56.3 (OCH_3), 56.5 (OCH_3), 91.2 (CH), 91.3 (CH), 105.4 (C), 122.3 (CH), 126.3 (CH), 143.7 (C), 144.0 (C), 149.9 (C), 159.2 (C), 159.9 (C), 162.5 (C); MS (EI) m/z (%) 369 (M^{+} , 10), 338 (M^{+} -Me, -O, 100); HRMS (EI) 369.1940 ($C_{22}H_{27}NO_4$ requires 369.1940).

General Procedure for the Reaction of Allyltrichlorosilane (2) and Crotyltrichlorosilane (18/19) with Aldehydes. Allyltrichlorosilane (0.47 mmol) or crotyltrichlorosilane (0.47 mmol) was added to a solution of the catalyst (0.04 mmol), diisopropylethylamine (2 mmol) and aldehyde (0.4 mmol) in dichloromethane (2 mL) or chloroform (2 mL), or acetonitrile (2 mL) under nitrogen at the specified of temperature (see Table 1). The mixture was stirred at the same temperature for 18 h and then quenched with aqueous satd. $NaHCO_3$ (1 mL). The aqueous layer was extracted with ethyl acetate (3 $\times$ 10 mL) and the combined organic extracts were washed with brine and dried over Na_2SO_4 . The solvent was removed in vacuo and the residue was purified by flash chromatography on a silica gel column (15 cm $\times$ 1 cm) with a petroleum ether-ethyl acetate mixture (95:5). The isolated yields and ee are given in Table 1. The enantiopurity of the resulting alcohol was determined by chiral GC, using a Supelco β -DEX 120 column, unless specified otherwise (see below).

(S)-(-)-1-Phenyl-but-3-en-1-ol (S)-(-)-(3a):^{4,6} 1H -NMR δ 2.08 (s, 1H), 2.37-2.49 (m, 2H), 4.62-4.66 (m, 1H), 5.05-5.15 (m, 2H), 5.68-5.78 (m, 1H), 7.17-7.29 (m, 5H); chiral GC (Supelco β -DEX 120 column, oven: 100 °C for 5 min, then 1 °C/min to 200 °C, 10 min at that temperature) showed ee given in Table 1 (t_R = 31.06 min, t_S = 31.49 min).

(S)-(-)-1-[(4-Trifluoromethyl)-phenyl]-but-3-en-1-ol (S)-(-)-(3b):⁶ 1H -NMR δ 2.00 (s, 1H), 2.35-2.51 (m, 2H), 4.71-4.75 (m, 1H), 5.08-5.13 (m, 2H), 5.67-5.77 (m, 1H), 7.39-7.41 (m, 2H), 7.52-7.54 (m, 2H); chiral GC (Supelco β -DEX 120 column, oven: 100 °C for 5 min, then 1 °C/min to 200 °C, 10 min at that temperature) showed 93% ee (t_R = 32.12 min, t_S = 33.33 min). [For reference, see also: Doucet, H.; Santelli, M. *Tetrahedron: Asymmetry* **2000**, *11*, 4163.]

(S)-(-)-1-(4-Methoxyphenyl)-but-3-en-1-ol (S)-(-)-(3c):^{4,6} 1H -NMR δ 1.97 (s, 1H), 2.43 (t, J = 6.4 Hz, 2H), 3.73 (s, 3H), 4.64 (t, J = 5.6 Hz, 1H), 5.05-5.11 (m, 2H), 5.70-5.76

(m, 1H), 6.81 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.6$ Hz, 2H); chiral HPLC (Chiralcel OD-H, hexane/2-propanol 97:3, 1 mL/min) showed 96% ee ($t_R = 14.80$ min, $t_S = 17.30$ min).

(-)-1-(2-Methoxyphenyl)-but-3-en-1-ol (-)-(3d): $[\alpha]_D -25.6$ (c 0.47, CH_2Cl_2), ^1H -NMR δ 2.39-2.55 (m, 3H), 3.77 (s, 3H), 4.87-4.90 (m, 1H), 5.01-5.09 (m, 2H), 5.72-5.82 (m, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 6.86-6.90 (t, $J = 7.6$ Hz, 1H), 7.15-7.19 (m, 1H), 7.25 (d, $J = 8.4$ Hz, 1H); chiral GC (Supelco β -DEX 120 column, oven: 100 °C for 5 min, then 1 °C/min to 200 °C, 10 min at that temperature) showed 89% ee ($t_S = 46.62$ min, $t_R = 49.18$ min). The absolute configuration of **3d** does not seem to have been rigorously established. In this paper, it is assumed to be (*S*)-(-)-**3d** on the basis of these and previous results. For reference, see: Kobayashi, S.; Nagayama, S.; Busujima, T. *Chem. Lett.* **1997**, 9, 959.