

Supporting Information

A New Preparative Method for Allylic Indium(III) Reagents by Reductive Transmetalation of π -Allylpalladium(II) with Indium(I) Salts

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Detailed experimental procedures and characterization data for the products in Table 4.

2-Methyl-1-phenyl-3-buten-1-ol:¹ To a mixture of indium(I) iodide (0.24 g, 1.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (28 mg, 0.025 mmol) in THF (3 mL) were added 3-chloro-2-butene (0.10 mL, 1.0 mmol) and benzaldehyde (0.052 mL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon for 1.5 h. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel (CH_2Cl_2) to give 2-methyl-1-phenyl-3-buten-1-ol (80 mg, 92 % yield, *syn:anti* = 58:42). ^1H NMR (200 MHz, CDCl_3) δ *syn* isomer 7.40 – 7.22 (m, 5H), 5.91 – 5.68 (m, 1H), 5.26 – 5.01 (m, 2H), 4.62 (dd, J = 5.5, 3.6 Hz, 1H), 2.64 – 2.40 (m, 1H), 1.94 (d, J = 3.6 Hz, 1H), 1.01 (d, J = 6.8 Hz, 3H); *anti* isomer 7.40 – 7.22 (m, 5H), 5.91 – 5.68 (m, 1H), 5.26 – 5.01 (m, 2H), 4.36 (dd, J = 8.0, 2.6 Hz, 1H), 2.64 – 2.40 (m, 1H), 2.15 (d, J = 2.6 Hz, 1H), 0.87 (d, J = 6.8 Hz, 3H).

1,2-Diphenyl-3-buten-1-ol:² To a mixture of indium(I) iodide (0.24 g, 1.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol) in THF (3 mL) were added cinnamyl acetate (0.17 mL, 1.0 mmol) and benzaldehyde (0.052 mL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon for 1.5 h. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel (CH_2Cl_2) to give 1,2-diphenyl-3-buten-1-ol (0.11 g, 100 % yield, *syn:anti* = 14:86). ^1H NMR (200 MHz, CDCl_3) δ *syn* isomer 7.39 – 7.01 (m, 5H), 5.90 (ddd, J = 17, 10, 8.0 Hz, 1H), 5.03 – 4.92 (m, 2H), 4.90 – 4.81 (m, 1H), 3.63 (t, J = 8.0, 1H), 1.96 (d, J = 2.6 Hz, 1H); *anti* isomer 7.39 – 7.01 (m, 5H), 6.25 (ddd, J = 17, 10, 8.3 Hz, 1H), 5.29 – 5.17 (m, 2H), 4.84 (dd, J = 8.3, 2.4 Hz, 1H), 3.55 (t, J = 8.3 Hz, 1H), 2.32 (d, J = 2.4 Hz, 1H).

(Z)-1,2-Diphenyl-3-penten-1-ol:³ To a mixture of indium(I) iodide (0.24 g, 1.0

mmol) and $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol) in THF (3 mL) were added 1-methyl-3-phenyl-2-propenyl acetate (0.11 mL, 0.60 mmol) and benzaldehyde (0.052 mL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon for 30 h. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}=1/1$) to give (*Z*)-1,2-diphenyl-3-penten-1-ol (94 mg, 79 % yield, *syn:anti* = 11:89). ^1H NMR (200 MHz, CDCl_3) δ *syn* isomer 7.26 – 7.02 (m, 10H), 5.97 – 5.68 (m, 2H), 4.76 (d, J = 7.4 Hz, 1H), 3.47 (t, J = 7.4 Hz, 1H), 2.38 (bs, 1H), 1.75 (d, J = 6.4 Hz, 3H); *anti* isomer 7.26 – 7.02 (m, 10H), 5.97 – 5.68 (m, 2H), 4.83 (dd, J = 7.4, 2.3 Hz, 1H), 3.90 (dd, J = 9.5, 7.4 Hz, 1H), 2.25 (d, J = 2.3 Hz, 1H), 1.61 (dd, J = 6.6, 1.5 Hz, 3H).

2-Ethenyl-1,3-diphenyl-1,3-propanediol:⁴ To a mixture of indium(I) iodide (0.14 g, 0.60 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol) in THF (3 mL) were added 2-ethenyl-3-phenyloxirane (*trans:cis* = 31:69, 88 mg, 0.60 mmol) and benzaldehyde (0.052 mL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon for 4 h. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel ($\text{AcOEt}/\text{hexane}=2/1$) to give 2-ethenyl-1,3-diphenyl-1,3-propanediol (0.10 g, 80 % yield, diastereomeric ratio = 85:15). ^1H NMR (200 MHz, CDCl_3) δ major isomer 7.37 – 7.25 (m, 10H), 6.05 (dt, J = 17, 10 Hz, 1H), 5.15 (dd, J = 10, 1.9 Hz, 1H), 4.92 (m, 2H), 4.73 (dd, J = 17, 1.9 Hz, 1H), 2.51 (m, 1H); minor isomer 7.37 – 7.25 (m, 10H), 5.87 – 5.68 (m, 1H), 5.06 – 4.79 (m, 4H), 2.75 (m, 1H).

2-Ethoxy-1-phenyl-3-buten-1-ol:⁵ To a mixture of indium(I) iodide (0.24 g, 1.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol) in THF (3 mL) were added acrolein diethylacetal (0.076 mL, 0.50 mmol) and benzaldehyde (0.10 mL, 1.0 mmol). The reaction mixture was stirred at room temperature under argon for 40 h. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2\text{-AcOEt}$ gradient) to give 2-ethoxy-1-phenyl-3-buten-1-ol (87 mg, 91% yield, *syn:anti* = 64:36) and 2-ethenyl-1,3-diphenyl-1,3-propanediol (12 mg, 9% yield). ^1H NMR (200 MHz, CDCl_3) δ *syn* isomer 7.37 – 7.25 (m, 5H), 5.76 – 5.47 (m, 1H), 5.30 – 5.00 (m, 2H), 4.82 (t, J = 3.3 Hz, 1H), 3.91 – 3.31 (m, 3H), 2.62 (d, J = 3.3 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H); *anti* isomer 7.37 – 7.25 (m, 5H), 5.76 – 5.47 (m, 1H), 5.30 – 5.00 (m, 2H), 4.48 (d, J = 7.9 Hz, 1H), 3.91 – 3.31 (m, 3H), 3.32 (d, J = 1.3 Hz, 1H), 1.24 (t, J = 7.0 Hz, 3H).

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