Copper(I) Hydride-Catalyzed Asymmetric Hydrosilylation of Heteroaromatic Ketones

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Supporting Information

Following the representative procedure provided in reference 14, the following amounts of reagents were used for entries 2-8 in Table 1. Characterization data is provided for new compounds.

Entry 2. 3-Acetylpyridine. 3-Acetylpyridine (0.50 mL, 4.50 mmol), CuCl (4.5 mg, 0.045 mmol), NaO-*t*-Bu (4.4 mg, 0.045 mmol), (-)-DTBM-SEGPHOS (2.7 mg, 2.25×10^{-3} mmol), PMHS (1.10 mL, 18.0 mmol), toluene (9.0 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 1.¹

Entry 3. 4-Acetylpyridine. 4-Acetylpyridine (1.00 mL, 9.04 mmol), CuCl (18.5 mg, 0.187 mmol), NaO-*t*-Bu (18.3 mg, 0.190 mmol), (-)-DTBM-SEGPHOS (6.0 mg, 5.1×10^{-3} mmol), PMHS (3.0 mL, 45.5 mmol), toluene (15.7 mL), THF (2.3 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 1.¹

Entry 4. 2-Acetylfuran. 2-Acetylfuran (630 mg, 5.72 mmol), CuCl (5.7 mg, 0.057 mmol), NaO-*t*-Bu (5.5 mg, 0.057 mmol), (-)-DTBM-SEGPHOS (3.4 mg, 2.58×10^{-3} mmol), PMHS (1.50 mL, 22.9 mmol), toluene (5.75 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 1.¹

Entry 5. 1-Furan-2-ylheptan-1-one. 1-Furan-2-yl-heptan-1-one (0.82 mL, 5.00 mmol), CuCl (4.95 mg, 0.050 mmol), NaO-*t*-Bu (4.80 mg, 0.050 mmol), (-)-DTBM-SEGPHOS (2.95 mg, 2.50×10^{-3} mmol), PMHS (1.30 mL, 20.0 mmol), toluene (5.00 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 2.²

Entry 6. 2-Acetylthiazole. 2-Acetylthiazole (0.630 mL, 6.08 mmol), CuCl (6.02 mg, 0.0608 mmol), NaO-*t*-Bu (5.84 mg, 0.0608 mmol), (-)-DTBM-SEGPHOS (3.59 mg, 3.04×10^{-4} mmol), PMHS (1.58 mL, 24.3 mmol), toluene (6.00 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 1.¹

Entry 7. 2,5-Dimethyl-4-acetylthiazole. 2,5-Dimethyl-4-acetylthiazole (0.20 mL, 1.48 mmol), CuCl (4.5 mg, 0.045 mmol), NaO-*t*-Bu (4.2 mg, 0.044 mmol), (-)-DTBM-SEGPHOS (0.9 mg, 7.4×10^{-4} mmol), PMHS (0.19 mL, 3.0 mmol), toluene (1.50 mL). Known compound; spectral data can be obtained from the Supporting Information within reference 3.³

Entry 8. 1-(5-Methylisoxazol-3-yl)-pentan-1-one. 1-(5-Methylisoxazol-3-yl)-pentan-1-one (57 mg, 0.34 mmol), CuCl (0.34 mg, 0.0034 mmol), NaO-*t*-Bu (0.33 mg, 0.0034 mmol), (-)-DTBM-SEGPHOS (0.2 mg, 1.7×10^{-4} mmol), PMHS (0.09 mL, 1.36 mmol), toluene (0.34 mL). Spectral data was obtained for the acetate derivative. Colorless oil. 300 MHz ¹H NMR (CDCl₃) δ = 0.89 (t, *J* = 5.4 Hz, 3H, methyl), 1.33 (m, 2H, methylene), 2.10 (m, 2H, methylene), 2.11 (s, 3H, acetate methyl), 2.14 (m, 2H, methylene), 2.20 (s, 3H, oxazole methyl), 5.86 (t, *J* = 4.8 Hz, 1H, methine), 5.95 (s, 1H, oxazole ring); IR (cm⁻¹) 2253, 1711, 1647, 1412, 909; exact mass calcd for C₁₁H₁₇NO₃ 211.1208, found: 211.1207.

¹ Ohkuma, T.; Koizumi, M.; Noyori, R. *Org. Lett.* **2000**, *12*, 1749.

² Maurizio, D.; Rocco, R.; Gianfranco R. *Eur. J. Org. Chem.* **2000**, *19*, 3265.

³ Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P.; Poli, S. *Tetrahedron: Asymmetry* **1993**, *4*, 1607.