Supporting Information

Pd-Catalyzed Allylic Substitution Using Nucleophilic *N*-Heterocyclic Carbene as a Ligand

Yoshihiro Sato, Taro Yoshino, and Miwako Mori*

Graduate School of Pharmaceutical Sciences, Hokkaido University,
Sapporo 060-0812, Japan

Typical Procedure for Allylic Substitution of **1 with **4** Using Pd-Carabene Catalyst Generated from PdCl₂, Imidazolium Salt **2d**, and BuLi (Table 1, run 4).**

To a suspension of PdCl₂ (12.6 mg, 0.07 mmol) and imidazolium salt **2d** (29.6 mg, 0.07 mmol) in THF was added BuLi (1.52 M in hexane, 0.14 mL, 0.21 mmol) at 0 °C, and the mixture was stirred at the same temperature for 45 min. To the mixture were added a solution of acetate **1** (353.2 mg, 1.4 mmol) in THF (7 mL) and a solution of sodio dimethylmalonate in THF (21 mL), which was prepared from dimethyl malonate (0.32 mL, 2.8 mmol) and NaH (60% oil suspension, 112.2 mg, 2.8 mmol), at room temperature, and the mixture was heated at 50 °C for 37 hours. To the mixture was added sat. NH₄Cl aqueous solution at 0 °C, and the organic layer was extracted with Et₂O. The combined organic layer was washed with brine, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane-EtOAc, 8/1) to give **5** in 77% yield.

Typical Procedure for Allylic Substitution of **1 with **4** Using Pd-Carabene Catalyst Generated from Pd₂dba₃·CHCl₃ and Imidazolium Salt **2d** in the Presence of Cs₂CO₃ (Table 2, run 2).**

To a suspension of Pd₂dba₃·CHCl₃ (10.4 mg, 0.01 mmol), imidazolium salt **2d** (8.5 mg, 0.02 mmol) and Cs₂CO₃ (273.7 mg, 0.84 mmol) in THF (0.4 mL) were added a solution of acetate **1** (100.9 mg, 0.4 mmol) in THF (2 mL) and a solution of dimethyl malonate (0.9 mL, 0.8 mmol) in THF (2 mL) at 0 °C, and the mixture was heated at 50 °C for 10 hours. To the mixture was added sat. NH₄Cl aqueous solution at 0 °C, and the organic layer was extracted with Et₂O. The combined organic layer was washed with brine, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane-EtOAc, 4/1) to give **5** in 100% yield.

Spectral Data of New Compound

***rel*-4S-Isopropenyl-6R-(1,1-bis(methoxycarbony)methyl)-1-methyl-cyclohexene (**12-α**)**

¹H NMR (400 MHz, CDCl₃) δ 1.62-1.92 (m, 9 H), 2.10-2.20 (m, 2 H), 2.92 (m, 1 H), 3.61 (d, *J* = 7.6 Hz, 1 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 4.69 (s, 1 H), 4.72 (s, 1 H), 5.45 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 20.7, 22.5, 30.5, 31.2, 36.2, 38.9, 52.3, 52.4, 54.8, 108.9, 125.1, 132.5, 148.6, 168.8, 169.3; IR (neat) 2952, 1738, 1645, 1435, 1251 cm⁻¹; EI LRMS *m/z* 266, 234, 207, 203, 191, 149, 134, 119, 105. Anal. Calcd for C₁₅H₂₂O₄: C, 67.64; H, 8.33. Found C, 67.40; H, 8.26.

CAS Registry Numbers of Known Compounds

1: 96482-68-7, **5**: 95071-02-6, **6**: 62668-02-4, **7**: 1566-65-0, **8a**: 119793-72-5, **8b**: 129047-20-7, **8c**: 119784-73-5, **9**: 68217-48-1, **10**: 79644-04-5, **11-α**: 5258-01-5, **11-β**: 76704-27-3, **12-β**: 77517-64-7.