Supporting Information

Palladium-Catalyzed Coupling of Allyl Acetates with Aldehyde and Imine Electrophiles in the Presence of Bis(pinacolato)diboron

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All reactions were conducted under argon atmosphere by employing standard manifold techniques. The ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 (internal standard: 7.26 ppm, ^1H ; 77.36 ppm, ^{13}C) or $\text{DMSO}-d_6$ (internal standard: 2.54 ppm, ^1H ; 40.45 ppm, ^{13}C) solutions at room temperature by Varian 400 spectrometer. Merck silica gel 60 (230-400 mesh) was used for the chromatography.

General procedure for the allylation reactions. The corresponding electrophile **3-4** (0.3 mmol) and $\text{Pd}_2(\text{dba})_3$ (0.009 mmol) was dissolved in DMSO (3 ml). Thereafter, the allylic substrate **2a-h** (0.36 mmol) was added. This reaction mixture was stirred for 10 min at room temperature under Ar atmosphere. After addition of diboron reagent **1** (0.36 mmol) the reaction mixture was stirred for the allotted temperatures and times listed in Table 1. Thereafter, the reaction mixture was diluted with water (3 ml) and stirred for one hour at room temperature. This solution was extracted with ether (4x6 ml), and the combined ether-phases was dried over MgSO_4 and evaporated. The products **5-6** were isolated by column chromatography using a pentane-EtOAc eluent.

1-[hydroxy(4-nitrophenyl)methyl]allyl acetate (5g). The purification was done by silica gel chromatography using pentane-ethyl acetate (4:1) as eluent. ^1H NMR (CDCl_3): 8.22 (d, 8.8 Hz, 2H), 7.56 (d, 8.8 Hz, 2H), 5.76 (ddd, 6.6 Hz, 10.4 Hz, 17.2 Hz, 1H), 5.45 (dd, 6.6 Hz, 3.9 Hz, 1H), 5.31 (d, 10.4 Hz, 1H, *cis*), 5.26 (d, 17.2 Hz, 1H, *trans*), 5.01 (t, 3.9 Hz, 1H), 2.54 (d, 3.7 Hz, 1H, *OH*) 2.09 (s, 3H). ^{13}C NMR (CDCl_3): 170.3, 146.8, 131.1, 128.8, 127.8, 123.8, 121.0, 78.3, 74.6, 21.4.

2-[hydroxy(4-nitrophenyl)methyl]but-3-enyl acetate (5h). The product was purified by silica gel chromatography using pentane-diethyl ether (2:1) as eluent. ^1H NMR (CDCl_3): 8.20 (d, 8.8 Hz, 2H), 7.50 (d, 8.8 Hz, 2H), 5.70 (ddd, 8.5 Hz, 10.4 Hz, 17.3 Hz, 1H), 5.19 (d, 10.4 Hz, 1H, *cis*), 5.04 (d, 17.3 Hz, 1H, *trans*), 4.90 (d, 3.7 Hz, 1H), 4.32 (dd, 11.2 Hz, 7.7 Hz, 1H), 4.02 (dd, 11.2 Hz, 6.1 Hz, 1H), 2.7 (m, 1H), 2.66 (s, 1H, *OH*), 2.08 (s, 3H). ^{13}C NMR (CDCl_3): 171.7, 149.8, 147.7, 132.8, 127.4, 123.8, 120.9, 72.2, 64.6, 51.1, 21.2.

2-phenyl[(phenylsulfonyl)amino]methylbut-3-enamide (6d). The product was purified by silica gel chromatography using dichloromethane-methanol (20:1) as eluent. ¹H NMR (DMSO-d₆): 8.28 (d, 9.4 Hz, 1H, *NH*), 7.48 (d, 7.4 Hz, 2H), 7.39 (t, 7.4 Hz, 1H), 7.26 (t, 7.4 Hz, 2H), 7.04 (m, 5H), 5.69 (ddd, 10.2 Hz, 10.0 Hz, 17.1 Hz, 1H, *anti*), 5.51 (ddd, 9.4 Hz, 10.2 Hz, 17.2 Hz, 1H, *syn*), 5.22 (d, 17.1 Hz, 1H, *trans*, *anti*), 5.08 (d, 10.0 Hz, 1H, *cis*, *anti*), 4.84 (d, 17.2 Hz, 1H, *trans*, *syn*), 4.80 (d, 10.2 Hz, 1H, *cis*, *syn*), 4.68 (t, 9.4 Hz, 1H, *syn*), 4.55 (t, 10.2 Hz, 1H, *anti*), 3.28 (t, 10.2 Hz, 1H, *anti*), 3.17 (t, 9.4 Hz, 1H, *syn*). ¹³C NMR (DMSO-d₆): 173.4, 142.4, 139.9, 135.7, 132.4, 129.2, 128.6, 128.2, 127.7, 127.2, 118.8, 60.1, 58.1.