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 $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ (internal standard:
7.26 ppm, $^1$H; 77.36 ppm, $^{13}$C) or DMSO-d$_6$ (internal standard: 2.54 ppm, $^1$H; 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 Pd$_2$(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. $^1$H 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. $^1$H 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. $^1$H NMR (DMSO-d$_6$): 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). $^{13}$C NMR (DMSO-d$_6$): 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.