Supporting Information

Palladium-Catalyzed Coupling of Allylboronic Acids with Iodobenzenes. Selective Formation of the Branched Allylic Product in the Absence of Directing Groups

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Experimental Procedures and Characterization of the Prepared Compounds

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 respectively) solutions at 25 °C by Varian 400 spectrometer. Palladium pincer-complex **7** was prepared according to the procedure published by Yao and co-workers.¹ Tetrahydroxydiboron (**6**) was purchased from Boron Molecular Ltd. and were used as received.

General Procedure. To the corresponding vinylcyclopropane (**4a-b**) dissolved in DMSO (0.35 mL) or allylic alcohol (**5a-b**) (0.15 mmol) dissolved in a mixture of DMSO/MeOH (0.30/0.30 mL) were added tetrahydroxydiboron **6** (16.1 mg, 0.18 mmol) and pincer complex **7** (4.2 mg, 0.0075 mmol, 5 mol%). The reaction mixture was stirred for the allotted temperatures (40 °C for **4a-b** and **5b**; 50 °C for **5a**) and times (3 h for **4a**; 5 h for **4b**; 16 h for **5a**, 21 h for **5b**) under Ar atmosphere (see also ref.^{2,3} for details). After centrifugation and filtration, water (0.70 mL) was added to the reaction mixture and the resulting suspension was stirred for 45 minutes at 20°C. This suspension was extracted with ether (3 × 0.50 mL) to obtain the corresponding allylboronic acid (**1a-d**). To this ether solution the corresponding iodoarene (**2a-d**) (0.15 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8.7 mg, 0.0075 mmol, 5mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol) and THF (0.50 mL) were added, and then the volume of the solvents was reduced to 0.5 mL.⁴ Then, the reaction mixture was stirred at 40 °C for 16 h. After evaporation products **3a-j** were purified by silica-gel chromatography.

5,5-Di(Ethoxycarbonyl)-3-Phenyl-1-Butene (3a). This compound was prepared according to the above general procedure from **4a**. ^1H NMR (CDCl_3): 7.31 (t, 7.6 Hz, 2H), 7.21 (t, 7.6 Hz, 1H), 7.19 (d, 7.6 Hz, 2H), 5.93 (ddd, 7.8 Hz, 10.0 Hz, 17.5 Hz, 1H), 5.09 (d, 10.0 Hz, 1H), 5.08 (d, 17.5 Hz, 1H), 4.20 (q, 7.1 Hz, 4H), 4.15 (psq, 7.3 Hz, 1H), 3.30 (dt, 7.3 Hz, 7.8 Hz, 1H), 2.32 (t, 7.3 Hz, 1H), 2.31 (t, 7.3 Hz, 1H), 1.27 (t, 7.1 Hz, 3H), 1.24 (t, 7.1 Hz, 3H). ^{13}C NMR (CDCl_3): 169.7, 143.0, 140.9, 129.0, 128.0, 127.0, 115.7, 61.7, 50.4, 47.9, 34.4, 14.4. MS (EI): m/z (rel intens) 291 ($\text{M}^+ + 1$, 25), 199 (8), 171 (19), 115 (100), 91 (25).

5,5-Di(Ethoxycarbonyl)-3-(4-Chlorophenyl)-1-Butene (3b). This compound was prepared according to the above general procedure from **4a**. ^1H NMR (CDCl_3): 7.28 (d, 8.5 Hz, 2H), 7.12 (d, 8.5 Hz, 2H), 5.88 (ddd, 7.8 Hz, 10.2 Hz, 17.0 Hz, 1H), 5.09 (d, 10.2 Hz, 1H), 5.07 (d, 17.0 Hz, 1H), 4.19 (q, 6.9 Hz, 4H), 4.16 (psq, 7.2 Hz, 1H), 3.28 (q, 7.8 Hz, 1H), 2.27 (dd, 7.2 Hz, 7.8 Hz, 2H), 1.26 (t, 6.9 Hz, 3H), 1.24 (t, 6.9 Hz, 3H). ^{13}C NMR (CDCl_3): 169.6, 141.5, 140.4, 132.8, 129.3, 129.1, 116.1, 61.8, 50.3, 47.2, 34.3, 14.4. MS (EI): m/z (rel intens) 325 ($\text{M}^+ + 1$, 9), 250 (19), 233 (52), 205 (48), 115 (100).

5,5-Di(Ethoxycarbonyl)-3-(4-Methoxyphenyl)-1-Butene (3c). This compound was prepared according to the above general procedure from **4a**. ^1H NMR (CDCl_3): 7.10 (d, 8.9 Hz, 2H), 6.85 (d, 8.9 Hz, 2H), 5.90 (ddd, 8.0 Hz, 10.0 Hz, 17.5 Hz, 1H), 5.06 (d, 10.0 Hz, 1H), 5.05 (d, 17.5 Hz, 1H), 4.20 (q, 7.2 Hz, 4H), 4.15 (psq, 6.9 Hz, 1H), 3.79 (s, 3H), 3.26 (q, 8.0 Hz, 1H), 2.28 (ddd, 6.9 Hz, 8.0 Hz, 14.0 Hz, 1H), 2.26 (ddd, 6.9 Hz, 8.0 Hz, 14.0 Hz, 1H), 1.27 (t, 7.2 Hz, 3H), 1.24 (t, 7.2 Hz, 3H). ^{13}C NMR (CDCl_3): 169.8, 158.7, 141.3, 135.0, 128.9, 115.3, 114.4, 61.7, 55.6, 50.4, 47.0, 34.5, 14.4. MS (EI): m/z (rel intens) 321 ($\text{M}^+ + 1$, 18), 303 (24), 229 (14), 160 (100), 115 (34).

5,5-Di(Phenylsulfonyl)-3-Phenyl-1-Butene (3d). This compound was prepared according to the above general procedure from **4b** except that the extraction of allylboronic acid **1d** was performed with chloroform and the subsequent cross-coupling reaction was conducted in chloroform. ^1H NMR (CDCl_3): 7.95 (d, 8.0 Hz, 2H), 7.77 (d, 8.0 Hz, 2H), 7.68 (t, 8.0 Hz, 2H), 7.58 (t, 8.0 Hz, 2H), 7.52 (t, 8.0 Hz, 2H), 7.27 (t, 7.6 Hz, 1H), 7.25 (t, 7.6 Hz, 2H), 7.06 (d, 7.6 Hz, 2H), 5.79 (ddd, 7.8 Hz, 9.4 Hz, 17.3 Hz, 1H), 5.11 (d, 9.4 Hz, 1H), 5.09 (d, 17.3 Hz, 1H), 4.38 (t, 5.5 Hz, 1H), 3.75 (q, 7.8 Hz, 1H), 2.52 (dd, 5.5 Hz, 7.8 Hz, 2H). ^{13}C NMR (CDCl_3): 141.4, 140.0, 138.3, 138.2, 135.0, 134.8, 130.1, 129.7, 129.5, 129.4, 129.3, 128.0, 127.5, 116.9, 81.2, 47.6, 31.2. MS (EI): m/z (rel intens) 427 ($\text{M}^+ + 1$, 3), 285 (100), 143 (59), 117 (16), 91 (4).

5,5-Di(Phenylsulfonyl)-3-(4-Chlorophenyl)-1-Butene (3e). This compound was prepared according to the above general procedure from **4b** except that the extraction of allylboronic acid **1d** was performed with chloroform and the subsequent cross-

coupling reaction was conducted in chloroform. ^1H NMR (CDCl_3): 7.94 (d, 8.0 Hz, 2H), 7.77 (d, 8.0 Hz, 2H), 7.73 (t, 8.0 Hz, 1H), 7.68 (t, 8.0 Hz, 1H), 7.59 (t, 8.0 Hz, 2H), 7.53 (t, 8.0 Hz, 2H), 7.23 (d, 8.2 Hz, 2H), 7.00 (d, 8.2 Hz, 2H), 5.76 (ddd, 7.9 Hz, 10.0 Hz, 17.2 Hz, 1H), 5.13 (d, 10.0 Hz, 1H), 5.10 (d, 17.2 Hz, 1H), 4.33 (t, 5.6 Hz, 1H), 3.76 (q, 7.9 Hz, 1H), 2.52 (ddd, 5.6 Hz, 7.9 Hz, 15.0 Hz, 1H), 2.44 (ddd, 5.6 Hz, 7.9 Hz, 15.0 Hz, 1H). ^{13}C NMR (CDCl_3): 139.9, 139.4, 138.1, 135.1, 134.9, 133.3, 130.0, 129.7, 129.5, 129.5, 129.4, 129.3, 117.3, 81.1, 47.0, 31.2. MS (EI): m/z (rel intens) 460 (M^+ , 10), 458 (100), 355 (9), 285 (18), 151 (5).

3-Phenyl-1-Octene (3f). This compound was prepared according to the above general procedure from **5a**. ^1H NMR (CDCl_3): 7.30 (t, 7.7 Hz, 2H), 7.18 (t, 7.7 Hz, 1H), 7.18 (d, 7.7 Hz, 2H), 5.95 (dt, 7.5 Hz, 11.5 Hz, 1H), 5.03 (d, 7.5 Hz, 1H), 5.00 (d, 11.5 Hz, 1H), 3.23 (q, 7.5 Hz, 1H), 1.69 (q, 7.5 Hz, 2H), 1.27 (m, 6H), 0.86 (t, 6.6 Hz, 3H). ^{13}C NMR (CDCl_3): 145.1, 142.9, 128.7, 127.9, 126.4, 114.2, 50.3, 35.8, 32.2, 27.5, 22.9, 14.4. MS (EI): m/z (rel intens) 188 (M^+ , 9), 131 (5), 117 (100), 91 (12), 78 (3).

3-(4-Nitrophenyl)-1-Octene (3g). This compound was prepared according to the above general procedure from **5a**. ^1H NMR (CDCl_3): 8.16 (d, 8.8 Hz, 2H), 7.34 (d, 8.8 Hz, 2H), 5.91 (ddd, 7.6 Hz, 10.0 Hz, 17.1 Hz, 1H), 5.08 (d, 10.0 Hz, 1H), 5.05 (d, 17.1 Hz, 1H), 3.36 (q, 7.6 Hz, 1H), 1.72 (m, 2H), 1.27 (m, 5H), 1.19 (m, 1H), 0.86 (t, 7.7 Hz, 3H). ^{13}C NMR (CDCl_3): 152.8, 146.8, 141.1, 128.8, 124.1, 115.7, 50.1, 35.6, 32.0, 27.4, 22.8, 14.4. MS (EI): m/z (rel intens) 234 ($\text{M}^+ + 1$, 8), 217 (13), 177 (13), 146 (14), 116 (100).

4-Benzyloxy-3-Phenyl-1-Butene (3h). This compound was prepared according to the above general procedure from **5b** except that the extraction of allylboronic acid **1c** was performed with chloroform and the subsequent cross-coupling reaction was conducted in chloroform. ^1H NMR (CDCl_3): 7.28 (m, 10H), 6.06 (ddd, 6.7 Hz, 10.7 Hz, 17.4 Hz, 1H), 5.15 (d, 10.7 Hz, 1H), 5.12 (d, 17.4 Hz, 1H), 4.54 (s, 2H), 3.70 (m, 3H). ^{13}C NMR (CDCl_3): 141.8, 139.4, 138.7, 128.8, 128.7, 128.4, 127.9, 127.9, 126.9, 116.3, 74.0, 73.4, 50.1. MS (EI): m/z (rel intens) 238 (M^+ , 10), 132 (13), 117 (100), 104 (29), 91 (50).

4-Benzyloxy-3-(4-Chlorophenyl)-1-Butene (3i). This compound was prepared according to the above general procedure from **5b** except that the extraction of allylboronic acid **1c** was performed with chloroform and the subsequent cross-coupling reaction was conducted in chloroform. ^1H NMR (CDCl_3): 7.33 (t, 7.4 Hz, 2H), 7.28 (d, 8.5 Hz, 2H), 7.25 (m, 3H), 7.15 (d, 8.5 Hz, 2H), 6.00 (ddd, 6.3 Hz, 10.5 Hz, 17.3 Hz, 1H), 5.13 (d, 10.5 Hz, 1H), 5.08 (d, 17.3 Hz, 1H), 4.52 (s, 2H), 3.67 (m, 3H). ^{13}C NMR (CDCl_3): 140.3, 138.8, 138.5, 132.6, 129.8, 128.9, 128.7, 127.9, 127.9, 116.7, 73.7, 73.4, 49.4. MS (EI): m/z (rel intens) 272 (M^+ , 3), 165 (4), 153 (27), 151 (78), 91 (100).

4-Benzyloxy-3-(4-Nitrophenyl)-1-Butene (3j). This compound was prepared according to the above general procedure from **5b** except that the extraction of allylboronic acid **1c** was performed with chloroform and the subsequent cross-coupling reaction was conducted in chloroform. ^1H NMR (CDCl_3): 8.17 (d, 8.8 Hz, 2H), 7.39 (d, 8.8 Hz, 2H), 7.27 (m, 5H), 6.00 (ddd, 5.8 Hz, 10.3 Hz, 17.2 Hz, 1H), 5.21 (d, 10.3 Hz, 1H), 5.11 (d, 17.2 Hz, 1H), 4.51 (s, 2H), 3.76 (dt, 5.8 Hz, 10.8 Hz, 1H), 3.72 (d, 10.8 Hz, 2H). ^{13}C NMR (CDCl_3): 149.7, 138.2, 137.6, 134.1, 129.4, 128.7, 128.1, 127.9, 124.0, 117.7, 73.6, 73.1, 49.9. MS (EI): m/z (rel intens) 283 (M^+ , 3), 207 (7), 129 (5), 91 (100), 65 (16).

Diethyl-4-phenylbut-2-enylmalonate (9). Diethyl-2-vinylcyclopropane-1,1-dicarboxylate (**4a**) (34.0 mg, 0.160 mmol) in THF (0.30 mL) was added to a mixture of phenylboronic acid (23.4 mg, 0.192 mmol), Pd_2dba_3 (2.9 mg, 0.0032 mmol, 2 mol%), and Cs_2CO_3 (125 mg, 0.384 mmol). After addition of water (0.030 mL) the resulting reaction mixture was stirred 5 h at 40 °C. After evaporation of the solvents the crude reaction mixture was purified by silica-gel chromatography yielding 42 mg (91%) of product. The spectral data obtained for **9** is identical with the literature values.⁵ ^1H NMR (CDCl_3): 7.28 (m, 2 H), 7.17 (m, 3 H), 5.70 (dt, 1.3 Hz, 6.9 Hz, 15.1 Hz, 1 H), 5.48 (dt, 1.3 Hz, 7.0 Hz, 15.1 Hz, 1 H), 4.17 (q, 7.1 Hz, 2H), 4.17 (q, 7.1 Hz, 2H), 3.40 (t, 7.4 Hz, 1H), 3.32 (bd, 6.9 Hz, 2H), 2.63 (bt, 7.2 Hz, 2H), 1.24 (t, 7.1 Hz, 6H). ^{13}C NMR (CDCl_3): 169.3, 140.6, 132.7, 128.8, 128.7, 127.2, 126.3, 61.7, 52.5, 39.2, 32.1, 14.4.

References and Notes:

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- (4) Note, that complete evaporation of the solvents leads to decomposition of the allylboronic acids.
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