**Rhodium-Catalyzed Reactions of Aryl and Alkenylboronic Acids with 2,4-Dienoate Esters:
Conjugate Addition and Heck Reaction Products**

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Supplementary material

General procedures and ^1H , ^{13}C -NMR spectra
(34 pages)

General Methods

All starting boronic acids were commercially available research-grade chemicals, and were used without further purification. The Rh^I-catalysts were commercially available. Dioxane and toluene were research-grade chemicals used without further purification. Ethyl sorbate was commercially available. Deionized water was used as co-solvent. Silica gel 60 F₂₅₄ was used for TLC, and the spots were detected with UV or vanillin solution. Flash column chromatography was carried out on silica gel 60. ¹H-NMR spectra were recorded at 200 MHz, 300 MHz or 500 MHz as indicated, in CDCl₃ solution. ¹³C-NMR spectra were recorded at 50.5 MHz or 75.5 MHz in CDCl₃ solution.

Rhodium-Catalyzed Addition of Aryl and Alkenyl Boronic Acids to 2,4-dienoate esters **1(a-c)**; General Procedure:

The boronic acid (0.34 mmol) and the Rh^I-catalyst (0.005 mmol, see Tables 1-3) were successively introduced in a flask and placed under Ar. A solution of dienoate esters **1a-c** (0.17 mol, see Tables 1-3) in a mixture of dioxane:H₂O (10:1; 0.5 mL) was added. Last, the corresponding additive (Et₃N, Ba(OH)₂, CsF or guanidine) were added (0.17 mol, see Tables 1-3). The reaction mixtures were stirred 16 h at rt. Evaporation under vacuum afforded the crude reaction products, which were purified by column chromatography (hexane-AcOEt, 90:10).

(3Z)-5-Phenylhex-3-enoic acid ethyl ester, **2a**:

¹H NMR (200 MHz, CDCl₃) δ 1.15 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.9 Hz, 3H), 3.10 (m, 2H), 3.65 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 5.50 (m, 1H), 5.65 (m, 1H), 7.18 (m, 5H). ¹³C NMR (50.5 MHz, CDCl₃) δ 14.1, 21.8, 33.1, 37.4, 60.5, 119.8, 125.9, 126.7, 127.1, 128.3, 145.5, 171.6. Anal. Calcd. for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 77.30; H, 8.03.

(3Z)-5-(4-Methoxyphenyl)hex-3-enoic acid ethyl ester, **2b**:

¹H NMR (300 MHz, CDCl₃) δ 1.30 (t, *J* = 7.1 Hz, 3H), 1.33 (d, *J* = 6.9 Hz, 3H), 3.10 (m, 2H), 3.70 (m, 1H), 3.80 (s, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 5.60 (m, 1H), 5.70 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ 14.6, 22.5, 33.6, 37.0, 55.7, 61.1, 114.3, 120.1, 128.2, 128.7, 133.8, 158.8, 171.2. Anal. Calcd. for C₁₅H₂₀O₃: C, 72.55; H, 8.12. Found: C, 72.29; H, 8.39.

(3Z)-5-(4-Trifluoromethylphenyl)hex-3-enoic acid ethyl ester, **2c**:

¹H NMR (300 MHz, CDCl₃) δ 1.30 (t, *J* = 7.1 Hz, 3H), 1.40 (d, *J* = 6.9 Hz, 3H), 3.15 (m, 2H), 3.80 (quint, *J* = 7.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 5.70 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ 14.1, 21.8, 33.1, 37.3, 60.6, 120.9, 125.3, 126.4, 127.2, 127.7, 136.9, 149.6, 171.3. Anal. Calcd. for C₁₅H₁₇F₃O₂: C, 62.93; H, 5.99. Found: C, 63.13; H, 6.26.

(3Z)-5-(Phenyl)pent-3-enoic acid benzyl ester, 2d:

¹H NMR (300 MHz, CDCl₃) δ 3.20 (d, *J* = 5.5 Hz, 2H), 3.30 (d, *J* = 5.9 Hz, 2H), 5.15 (s, 2H), 5.80 (m, 2H), 7.20-7.45 (m, 10H). ¹³C NMR (75.5 MHz, CDCl₃) δ 33.5, 34.0, 66.9, 122.1, 127.6, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 140.4, 145.5, 171.9. Anal. Calcd. for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 81.29; H, 6.95.

(4E)-3,5-Diphenylpent-4-enoic acid methyl ester, 3e:

¹H NMR (300 MHz, CDCl₃) δ 2.80 (d, *J* = 7.6 Hz, 2H), 3.60 (s, 3H), 3.95 (q, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 15.3, 7.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 7.25 (m, 4H), 7.50 (m, 4H), 7.70 (m, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ 40.9, 45.4, 52.1, 127.2, 127.9, 128.6, 128.8, 128.9, 130.5, 132.3, 132.4, 137.5, 142.9, 172.6. Anal. Calcd. for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 80.95; H, 6.99.

(4E)-3-(4-Methoxyphenyl)-5-phenylpent-4-enoic acid methyl ester, 3f:

¹H NMR (300 MHz, CDCl₃) δ 2.70 (dd, *J* = 7.6, 2.7 Hz, 2H), 3.60 (s, 3H), 3.80 (s, 3H), 3.90 (q, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.35 (m, 5H). ¹³C NMR (50.5 MHz, CDCl₃) δ 40.9, 44.3, 51.7, 55.4, 114.1, 126.4, 127.4, 128.3, 128.6, 128.9, 130.1, 132.4, 134.8, 137.4, 158.6, 172.4. Anal. Calcd. for C₁₉H₂₀O₃: C, 77.00; H, 8.80. Found: C, 77.15; H, 8.60.

(4E)- 5-Phenyl-3-(4-trifluoromethylphenyl)pent-4-enoic acid methyl ester, 3g:

¹H NMR (200 MHz, CDCl₃) δ 2.80 (dd, *J* = 7.6, 3.2 Hz, 2H), 3.60 (s, 3H), 4.05 (q, *J* = 7.3 Hz, 1H), 6.30 (dd, *J* = 15.8, 6.9 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 7.15-7.60 (m, 9H). ¹³C NMR (50.5 MHz, CDCl₃) δ 40.6, 44.9, 52.1, 121.1, 126.1, 126.7, 128.1, 128.3, 128.6, 128.9, 129.2, 131.3, 138.2, 146.3, 172.5. Anal. Calcd. for C₁₉H₁₇F₃O₂: C, 68.26; H, 5.13. Found: C, 68.01; H, 5.25.

(3Z, 6E)-5-Methyl-7-phenylhepta-3,6-dienoic acid ethyl ester, 4a:

¹H NMR (200 MHz, CDCl₃) δ 1.15 (d, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 3.10 (d, *J* = 6.9 Hz, 2H), 3.20 (sext, *J* = 7.6 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 5.50 (m, 2H), 6.10 (dd, *J* = 16.0, 6.2 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 7.20 (m, 5H). ¹³C NMR (50.5 MHz, CDCl₃) δ 14.1, 20.7, 34.3, 35.1, 60.7, 120.2, 125.9, 126.9, 128.2, 128.4, 133.8, 136.5, 141.6, 171.2. Anal. Calcd. for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 78.91; H, 8.50.

(3Z, 6E)- 7-(4-Chlorophenyl)-5-methylhepta-3,6-dienoic acid ethyl ester, 4b:

¹H NMR (200 MHz, CDCl₃) δ 1.12 (d, *J* = 6.9 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 3.08 (dd, *J* = 7.1, 1.3 Hz, 2H), 3.20 (sext, *J* = 7.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 5.50 (m, 2H), 6.05 (dd, *J* = 16.0, 6.1 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 7.22 (s, 4H). ¹³C NMR (50.5 MHz, CDCl₃) δ 14.1, 20.6, 33.1, 35.1, 60.5, 120.6, 125.9, 127.1,

127.2, 128.5, 134.5, 135.9, 136.2, 171.3. Anal. Calcd. for C₁₆H₁₉ClO₂: C, 68.93; H, 6.87. Found: C, 69.19; H, 7.15.

(3Z, 6E)- 5-Methyl-7-(4-trifluoromethylphenyl)hepta-3,6-dienoic acid ethyl ester, 4c:

¹H NMR (300 MHz, CDCl₃) δ 1.15 (d, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 3.08 (d, *J* = 6.8 Hz, 2H), 3.25 (sext, *J* = 7.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 5.45 (tt, *J* = 9.5, 1.6 Hz, 1H), 5.60 (m, 1H), 6.25 (dd, *J* = 16.0, 6.1 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (50.5 MHz, CDCl₃) δ 14.3, 20.8, 33.4, 35.4, 60.8, 121.2, 125.5, 125.6, 126.4, 127.3, 129.5, 136.2, 136.8, 139.7, 171.2. Anal. Calcd. for C₁₇H₁₉F₃O₂: C, 65.37; H, 6.13. Found: C, 65.14; H, 5.96.

(3Z, 6E)- 5-Methylundeca-3,6-dienoic acid ethyl ester, 4d:

¹H NMR (200 MHz, CDCl₃) δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 1.25 (m, 7H), 1.95 (m, 2H), 2.96 (m, 1H), 3.02 (d, *J* = 6.7 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 5.30 (m, 2H), 5.45 (m, 2H). ¹³C NMR (50.5 MHz, CDCl₃) δ 13.8, 14.1, 20.9, 22.1, 31.6, 32.1, 33.1, 34.8, 60.2, 119.5, 129.0, 133.5, 137.5, 171.2. Anal. Calcd. for C₁₄H₂₄O₂: C, 74.95; H, 10.78. Found: C, 75.21; H, 8.54.

(2E, 4E, 6E))-7-Phenylhepta-2,4,6-trienoic acid benzyl ester, 6a:

¹H NMR (300 MHz, CDCl₃) δ 5.10 (s, 2H), 5.90 (d, *J* = 15.2 Hz, 1H), 6.40 (dd, *J* = 15.2, 10.8 Hz, 1H), 6.70 (m, 2H), 6.88 (dd, *J* = 14.9, 10.2 Hz, 1H) 7.22-7.35 (m, 11H). ¹³C NMR (50.5 MHz, CDCl₃) δ 66.1, 120.3, 126.7, 127.2, 127.8, 128.1, 128.3, 128.4, 128.6, 129.0, 130.0, 136.2, 136.7, 140.9, 144.7, 167.2. Anal. Calcd. for C₂₀H₁₂O₂: C, 82.73; H, 6.25. Found: C, 82.89; H, 6.44.

(2E, 4E, 6E))-7-(4-Chlorophenyl)hepta-2,4,6-trienoic acid benzyl ester, 6b:

¹H NMR (500 MHz, CDCl₃) δ 5.15 (s, 2H), 5.90 (d, *J* = 15.2 Hz, 1H), 6.40 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.65 (dd, *J* = 15.2, 10.8 Hz, 1H), 6.70 (d, *J* = 15.3 Hz, 1H), 6.80 (dd, *J* = 15.4, 10.6 Hz, 1H) 7.20-7.35 (m, 10H). ¹³C NMR (50.5 MHz, CDCl₃) δ 66.3, 121.0, 128.1, 128.3, 128.4, 128.7, 128.8, 129.1, 131.2, 135.1, 135.5, 136.2, 138.7, 140.7, 144.8, 167.2. Anal. Calcd. for C₂₀H₁₇ClO₂: C, 73.96; H, 5.28. Found: C, 74.11; H, 5.00.

(2E, 4E, 6E))-7-(4-Trifluoromethylphenyl)hepta-2,4,6-trienoic acid benzyl ester, 6c:

¹H NMR (500 MHz, CDCl₃) δ 5.12 (s, 2H), 5.95 (d, *J* = 15.2 Hz, 1H), 6.45 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.70 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.72 (d, *J* = 15.3 Hz, 1H), 6.90 (dd, *J* = 15.4, 10.6 Hz, 1H), 7.30 (m, 1H), 7.40 (m, 5H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (50.5 MHz, CDCl₃) δ 66.4, 121.7, 125.4, 125.9, 127.0, 128.4, 128.7, 129.1, 130.2, 131.9, 135.5, 135.5, 136.2, 139.8, 140.7, 144.9, 167.2. Anal. Calcd. for C₂₁H₁₇F₃O₂: C, 70.38; H, 4.78. Found: C, 70.21; H, 4.99.

(2*E*, 4*E*, 6*E*)-Undeca-2,4,6-trienoic acid benzyl ester, 6d:

¹H NMR (200 MHz, CDCl₃) δ 0.82 (m, 3H), 1.25 (m, 4H), 2.02 (qd, *J* = 7.1, 1.9 Hz, 2H), 5.12 (s, 2H), 5.85 (d, *J* = 15.2 Hz, 1H), 5.90-6.10 (m, 2H), 6.22 (dd, *J* = 15.4, 10.6 Hz, 1H), 6.55 (dd, *J* = 15.4, 10.6 Hz, 1H), 7.22-7.35 (m, 6H). Anal. Calcd. for C₁₈H₂₂O₂: C, 79.96; H, 8.20. Found: C, 79.77; H, 8.33

6b

6c