First Heck Reaction with Arenediazonium Cations with Recovery of Pd-Triolefinic Macrocyclic Catalyst

Judit Masllorens,[†] Marcial Moreno-Mañas,[‡] Anna Pla-Quintana,[†] and Anna Roglans^{*,†}

[†] *Department of Chemistry, Universitat de Girona, Girona, 17071-Girona, Spain.*

[‡] *Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola, 08913-Barcelona, Spain.*

Supporting Information. Details of synthesis and characterization data for all intermediates in the synthesis of the Pd(0) catalyst **1**. Experimental procedure for the Heck reaction and spectroscopic data for compounds **2**, **6**, **7**, and **8**. ESI mass spectra for the detected oxidative addition intermediates and calculated isotope distributions.

General Considerations. IR spectra were recorded with a FT-IR using a single reflection ATR system as a sampling accessory. ¹H NMR (¹³C NMR) were recorded at 200 MHz (50 MHz) using Me₄Si as internal standard. Chemical shifts are given in δ units. EI mass spectra were recorded at 70 eV. ESI mass spectra were acquired using a Navigator quadrupole instrument. Elemental analyses were determined at “Servei d'Anàlisi Química de la Universitat de Girona” and “Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona”.

Preparation of Pd(0)-catalyst, (*E,E,E*)-1-Ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0), **1:**

Palladium(0) complex **1** was previously synthesized and characterized by us¹ according to a previously reported method also described by one of us.² The synthesis was summarized in scheme S1.

Scheme S1. Preparation of palladium(0) catalyst, **1**.

(4-Methylphenyl)sulfonamide and (*E*)-1,4-dibromobutene are commercially available and were used without further purification. Ferrocenesulfonamide was prepared from ferrocene as previously reported.³

Spectral data for all intermediates are described below:

***N*-(*tert*-Butyloxycarbonyl)(4-methylphenyl)sulfonamide (9)⁴**: colorless solid; m.p. 115-116 °C (Lit. m.p. 117-119 °C)⁴; IR (KBr): 3225, 1750, 1439, 1340, 1234, 1149 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.47 (s, 9H), 2.46 (s, 3H), 7.30 (s, 1H), 7.38 (AA' part of the AA'BB' system, *J* = 8.2 Hz, 2H), 7.93 (BB' part of the AA'BB' system, *J* = 8.2 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): 21.6, 27.7, 84.0, 128.1, 129.4, 135.9, 144.6, 149.4; MS: *m/z* (%) = 171 (M⁺ - COO^tBu, 85), 155 (80), 91 (100).

***N*-(*E*)-4-Bromo-2-butenyl)-*N*-(*tert*-butyloxycarbonyl)(4-methylphenyl)sulfonamide (10)^{2a}**: colorless solid; m.p. 64-66 °C; IR (KBr): 2981, 2932, 1720, 1355, 1153 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.36 (s, 9H), 2.43 (s, 3H), 3.97 (d, *J* = 6.6 Hz, 2H), 4.45 (d, *J* = 5.0 Hz, 2H), 5.82-6.07 (m, 2H), 7.32 (AA' part of the AA'BB' system, *J* = 8.4 Hz, 2H), 7.84 (BB' part of the AA'BB' system, *J* = 8.4 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): 21.5, 27.7, 31.5, 47.1, 84.4, 128.0, 129.1, 129.9, 130.0, 136.8, 144.2, 150.5; ESI-MS (*m/z*) = 467-469 [M + Na + CH₃CN]⁺, 442-444 [M + K]⁺, 421-423 [M + NH₄]⁺, 404-406 [M + H]⁺.

(*E,E*)-1,11-Bis(*tert*-butyloxycarbonyl)-1,11-bis[(4-methylphenyl)sulfonyl]-6-ferrocenylsulfonyl-1,6,11-triazaundeca-3,8-diene (11): yellow solid; m.p. 55-57 °C¹; IR (KBr): 2975, 2926, 1723, 1351, 1275, 1149 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.32 (s, 18H), 2.44 (s, 6H), 3.71 (d, *J* = 5.6 Hz, 4H), 4.40 (s, 5H), 4.34-4.40 (m, 6H), 4.60 (apparent t, *J* = 1.9 Hz, 2H), 5.48-5.77 (m, 4H), 7.31 (AA' part of the AA'BB' system, *J* = 8.4 Hz, 4H), 7.76 (BB' part of the AA'BB' system, *J* = 8.4 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃): 21.6, 27.9, 47.5, 48.0, 68.6, 70.6, 70.7, 84.2, 87.7, 128.0, 128.4, 129.2, 129.4, 137.2, 144.1, 150.6; ESI-MS (*m/z*) = 934 [M + Na]⁺, 911 [M]⁺; C₄₂H₅₃FeN₃O₁₀S₃ (911.9) calcd: C, 55.32; H, 5.86; N, 4.61. Found: C, 55.63 and 55.50; H, 6.01 and 5.99; N, 4.39 and 4.39.

(*E,E*)-1,11-Bis[(4-methylphenyl)sulfonyl]-6-ferrocenylsulfonyl-1,6,11-triazaundeca-3,8-diene (12): yellow solid; m.p. 46-49 °C¹; IR (KBr): 3279, 2919, 1323, 1149 cm⁻¹; ¹H NMR (200 MHz,

CDCl₃): 2.43 (s, 6H), 3.46-3.56 (m, 8H), 4.39 (s, 5H), 4.40-4.42 (m, 2H), 4.56-4.57 (m, 2H), 4.73 (apparent t, J = 6.3 Hz, 2H), 5.47-5.52 (m, 4H), 7.30 (AA' part of the AA'BB' system, J = 8.4 Hz, 4H), 7.73 (BB' part of the AA'BB' system, J = 8.4 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃): 21.5, 44.3, 48.7, 68.6, 70.5, 70.7, 87.1, 127.1, 128.2, 129.2, 129.7, 136.9, 143.5; ESI-MS (m/z) = 734 [M + Na]⁺, 711 [M]⁺; C₃₂H₃₇Fe N₃O₆S₃ (711.7) calcd. C, 54.01; H, 5.24; N, 5.90. Found: C, 54.50 and 54.46; H, 5.43 and 5.45; N, 5.64 and 5.62.

(*E,E,E*)-1-Ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene (13)¹: yellow solid; m.p. 195-197 °C; IR (KBr): 2922, 2859, 1338, 1151 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 2.44 (s, 6H), 3.55-3.66 (m, 12H), 4.39 (apparent t, J = 1.8 Hz, 2H), 4.41 (s, 5H), 4.57 (apparent t, J = 1.8 Hz, 2H), 5.53-5.55 (m, 6H), 7.31 (m, 4H), 7.65 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): 21.5, 50.5, 50.6, 50.7, 68.6, 70.6, 70.8, 86.2, 127.2, 129.0, 129.4, 129.6, 129.8, 136.1, 143.5; ESI-MS (m/z) = 786 [M + Na]⁺, 781 [M+NH₄]⁺, 764 [M+H]⁺, 763 [M]⁺; C₃₆H₄₁Fe N₃O₆S₃ (763.8) calcd. C, 56.61; H, 5.41; N, 5.50. Found: C, 56.57 and 56.47; H, 5.29 and 5.39; N, 5.50 and 5.42.

(*E,E,E*)-1-Ferrocenylsulfonyl-6,11-bis[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) (1)¹: yellow solid; m.p. 127-129 °C (dec); IR (KBr): 2918, 1333, 1157, 901, 655 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.50-1.70 (m, 4H), 2.38 (s, 6H), 2.76 (apparent t, J = 12 Hz, 2H), 3.03 (apparent q, J = 12 Hz, 2H), 3.70 (m, 2H), 3.93 (m, 2H), 4.41 (s, 5H), 4.32-4.80 (m, 10H), 7.26 (m, 4H), 7.68 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): 21.4, 45.1, 48.1, 48.2, 49.3, 49.4, 68.3, 68.4, 70.6, 70.7, 78.1, 78.2, 78.3, 78.4, 78.6, 78.7, 82.5, 82.6, 82.9, 85.4, 85.8, 126.9, 127.1, 129.7, 129.8, 135.3, 136.0, 143.3, 143.5; ESI-MS (m/z) = 892 [M + Na]⁺, 887 [M + NH₄]⁺, 869 [M]⁺, 781 [M - Pd + NH₄]⁺, 764 [M - Pd + H]⁺, 763 [M - Pd]⁺; C₃₆H₄₁Fe N₃O₆PdS₃ (870.2) calcd. C, 46.69; H, 4.75; N, 4.83. Found: C, 49.50 and 49.66; H, 4.84 and 4.87; N, 4.45 and 4.47.

Arenediazonium Tetrafluoroborates 2a-g, were generally prepared from commercial aromatic amines according to published methods.⁵ The salts could be stored for several weeks at -20°C .

Benzenediazonium Tetrafluoroborate (2a).

Colorless solid (86% yield). M.p.: $100-101^{\circ}\text{C}$ (dec) (Lit m.p. 100°C)⁵

IR (neat): 3107, 2294, 1570, 1022 cm^{-1}

4-Nitrobenzenediazonium Tetrafluoroborate (2b):

Yellow solid (100% yield). M.p. $146-147^{\circ}\text{C}$ (dec) (Lit m.p. 142°C)⁶

IR (neat): 3117, 2306, 1538, 1030 cm^{-1}

4-*tert*-Butylbenzenediazonium Tetrafluoroborate (2c):

Colorless solid (89% yield). M.p. $84-85^{\circ}\text{C}$ (dec) (Lit m.p. 91°C)⁶

IR (neat): 3108, 2274, 1575, 1032 cm^{-1}

2-Methylbenzenediazonium Tetrafluoroborate (2d):

Colorless solid (87% yield). M.p. $88-89^{\circ}\text{C}$ (dec) (Lit m.p. 106°C)⁵

IR (neat): 3103, 2280, 1023, 768 cm^{-1}

3-Methylbenzenediazonium Tetrafluoroborate (2e):

Pale pink solid (88% yield). M.p. $89-90^{\circ}\text{C}$ (dec) (Lit m.p. 108°C)⁵

IR (neat): 3089, 2296, 1026, 791 cm^{-1}

4-Methylbenzenediazonium Tetrafluoroborate (2f):

Colorless solid (69% yield). M.p. $104-105^{\circ}\text{C}$ (dec) (Lit m.p. 110°C)⁵

IR (neat): 3113, 2288, 1581, 1009 cm^{-1}

4-Fluorobenzenediazonium Tetrafluoroborate (2g):

Colorless solid (76% yield). M.p. $153-154^{\circ}\text{C}$ (Lit m.p. 154°C)⁵

IR (neat): 3117, 2295, 1580, 1012 cm^{-1}

Ethyl (*E*)-Cinnamate (**6a**); General Procedure for the Heck Reaction

Ethyl acrylate **3** (0.07 mL, 0.65 mmols) was added to a suspension of benzenediazonium tetrafluoroborate **2a** (0.066 g, 0.34 mmols) and Pd(0) catalyst **1** (0.014 g, 0.016 mmols) in ethanol (15 mL) at 0°C under magnetic stirring. The mixture was stirred at room temperature until gas evolution ceased. After completion of the gas evolution, saturated NaHCO₃ aqueous solution (15 mL) was added and the resulting mixture was extracted with dichloromethane (2 x 15 mL). The combined organic fractions were washed with water, dried over anhydrous sodium sulfate, and evaporated. The oily residue was chromatographed (silica gel; hexane:ethyl acetate, 9:1) to give ethyl (*E*)-cinnamate **6a** (0.058 g, 95% yield) as a colorless oil.⁷ Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (97%).

IR (neat): 1708, 1635, 1309, 1169 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.33 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 6.43 (d, *J* = 16 Hz, 1H), 7.34-7.39 (m, 3H), 7.46-7.53 (m, 2H), 7.68 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.2, 60.3, 118.2, 127.8, 128.7, 130.1, 134.4, 144.4, 166.8; MS: *m/z* (%) = 176 (M⁺, 42), 147 (40), 131 (70), 103 (100).

The following compounds were prepared and isolated according to the general procedure.

Ethyl (*E*)-4-Nitrocinnamate (**6b**):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6b** was obtained as a pale yellow solid (95% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (100%).

M.p. 132-134 °C (Lit m.p. 141-142 °C)⁷

IR (neat): 1708, 1643, 1512, 1332, 1174 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.36 (t, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 6.48 (d, *J* = 16.2 Hz, 1H), 7.68 (AA' part of the AA'BB' system, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 16.2 Hz, 1H), 8.25 (BB' part of the AA'BB' system, *J* = 8.6 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): 14.1, 60.8, 122.5, 124.0, 128.5, 140.5, 141.4, 148.3, 165.8; MS: *m/z* (%) = 221 (M⁺, 33), 193 (76), 176 (100), 130 (78), 102 (70).

Ethyl (*E*)-4-*tert*-Butylcinnamate (6c):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6c** was obtained as a pale yellow oil⁸ (quantitative yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (97%).

IR (neat): 2960, 1711, 1635, 1309, 1167 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.32 (s, 9H), 1.33 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 16 Hz, 1H), 7.35-7.48 (m, 4H), 7.68 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.3, 31.1, 34.8, 60.3, 117.3, 125.8, 127.8, 131.7, 144.4, 153.6, 167.1; MS: *m/z* (%) = 232 (M⁺, 53), 217 (100), 128 (65).

Ethyl (*E*)-2-Methylcinnamate (6d):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6d** was obtained as a pale yellow oil⁹ (quantitative yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 1709, 1633, 1311, 1164 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.34 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.15-7.30 (m, 3H), 7.51-7.57 (m, 1H), 7.97 (d, *J* = 15.8 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.2, 19.7, 60.4, 119.2, 126.2, 126.3, 129.9, 130.7, 133.4, 137.5, 142.2, 167.0; MS: *m/z* (%) = 190 (M⁺, 39), 145 (78), 116 (100), 91 (50).

Ethyl (*E*)-3-Methylcinnamate (6e):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6e** was obtained as a pale orange oil¹⁰ (78% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (94%).

IR (neat): 1710, 1638, 1311, 1174 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.32 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 16 Hz, 1H), 7.13-7.30 (m, 4H), 7.65 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.3, 21.2, 60.3, 118.0, 125.2, 128.6, 128.7, 131.0, 134.4, 138.4, 144.7, 166.9; MS: *m/z* (%) = 190 (M⁺, 68), 161 (37), 145 (97), 116 (100), 91 (50).

Ethyl (*E*)-4-Methylcinnamate (6f):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6f** was obtained as a pale yellow oil¹⁰ (97% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (100%).

IR (neat): 1709, 1635, 1310, 1165 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.33 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.38 (d, *J* = 16 Hz, 1H), 7.17 (AA' part of the AA'BB' system, *J* = 8 Hz, 2H), 7.40 (BB' part of the AA'BB' system, *J* = 8 Hz, 2H), 7.66 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.2, 21.3, 60.3, 117.1, 127.9, 129.5, 131.7, 140.5, 144.5, 167.1; MS: *m/z* (%) = 190 (M⁺, 59), 161 (33), 145 (92), 116 (100), 91 (50).

Ethyl (*E*)-4-Fluorocinnamate (6g):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **6g** was obtained as a pale yellow oil¹¹ (78% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (100%).

IR (neat): 1713, 1639, 1510, 1232, 1175 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.33 (t, *J* = 7.0 Hz, 3H), 4.25 (q, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 7.07 (apparent t, *J* = 8.6 Hz, 2H), 7.50 (dd, *J*₁ = 6.0 Hz / *J*₂ = 8.6 Hz, 2H), 7.65 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 14.3, 60.5, 116.0 (d, ²*J*_{CF} = 21.8 Hz), 118.0 (d, ⁵*J*_{CF} = 2.1 Hz), 129.8 (d, ³*J*_{CF} = 8.4 Hz), 130.7 (d, ⁴*J*_{CF} = 3.4 Hz), 143.2, 163.0 (d, ¹*J*_{CF} = 249.7 Hz), 166.8; MS: *m/z* (%) = 194 (M⁺, 32), 166 (32), 149 (100), 121 (78), 101 (95).

***tert*-Butyl (*E*)-Cinnamate (7a):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7a** was obtained as a pale yellow oil¹² (88% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (99%).

IR (neat): 1706, 1637, 1325, 1150 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.51 (s, 9H), 6.36 (d, *J* = 16 Hz, 1H), 7.32-7.36 (m, 3H), 7.46-7.52 (m, 2H), 7.59 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 28.1, 80.3, 120.1, 127.9, 128.7, 129.9, 134.6, 143.4, 166.2; MS: *m/z* (%) = 204 (M⁺, 36), 147 (100), 131 (76), 103 (88).

***tert*-Butyl (*E*)-4-Nitrocinnamate (7b):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7b** was obtained as a pale yellow solid (100% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (99%).

M.p. 146-147 °C (Lit. m.p. 155-157 °C)¹³

IR (neat): 1705, 1514, 1310, 1152 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.55 (s, 9H), 6.49 (d, *J* = 16 Hz, 1H), 7.61 (d, *J* = 16 Hz, 1H), 7.65 (AA' part of the system AA'BB', *J* = 8.7 Hz, 2H), 8.23 (BB' part of the system AA'BB', *J* = 8.7 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): 28.9, 82.0, 124.8, 125.3, 129.2, 141.2, 141.6, 149.0, 165.9; MS: *m/z* (%) = 249 (M⁺, 3), 194 (92), 176 (100), 146 (11), 57 (90).

***tert*-Butyl (*E*)-4-*tert*-Butylcinnamate (7c):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7c** was obtained as a colorless solid (100 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (97%).

M.p. 36.5-37.5 °C

IR (neat): 2964, 1708, 1150 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.32 (s, 9H), 1.53 (s, 9H), 6.33 (d, *J* = 16 Hz, 1H), 7.36-7.47 (m, 4H), 7.57 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 28.9, 31.9, 35.5, 81.0, 120.0, 126.5, 128.5, 132.6, 144.1, 154.1, 167.2; MS: *m/z* (%) = 260 (M⁺, 18), 204 (68), 189 (100), 161 (26), 57 (47); ⁺J; C₁₇H₂₄O₂ (260.4) calcd: C, 78.42; H, 9.29. Found: C, 78.10 and 77.97; H, 9.34 and 9.46.

***tert*-Butyl (*E*)-2-Methylcinnamate (7d):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7d** was obtained as a pale yellow oil¹⁴ (71 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 1708, 1150 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.54 (s, 9H), 2.42 (s, 3H), 6.29 (d, *J* = 16 Hz, 1H), 7.16-7.25 (m, 3H), 7.50-7.55 (m, 1H), 7.89 (d, *J* = 16 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): 20.4, 28.9, 81.1, 121.8, 126.9, 127.0, 130.3, 131.4, 134.3, 138.1, 141.9, 167.1; MS: *m/z* (%) = 218 (M⁺, 26), 162 (36), 144 (76), 116 (100), 57 (46).

***tert*-Butyl (*E*)-3-Methylcinnamate (7e):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7e** was obtained as a pale brown oil¹³ (69% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (88%).

IR (neat): 1708, 1151; cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): 1.54 (s, 9H), 2.35 (s, 3H), 6.35 (d, $J = 16$ Hz, 1H), 7.14-7.31 (m, 4H), 7.55 (d, $J = 16$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): 21.9, 28.9, 81.0, 120.6, 125.8, 129.2, 129.3, 131.4, 135.3, 139.1, 144.3, 167.0; MS: m/z (%) = 218 (M^+ , 38), 162 (100), 145 (77), 115 (55), 57 (64).

***tert*-Butyl (*E*)-4-Methylcinnamate (7f):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7f** was obtained as a pale yellow oil¹³ (99% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 2976, 1707, 1636, 1322, 1149 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): 1.49 (s, 9H), 2.34 (s, 3H), 6.31 (d, $J = 16$ Hz, 1H), 7.15 (AA' part of the AA'BB' system, $J = 8$ Hz, 2H), 7.38 (BB' part of the AA'BB' system, $J = 8$ Hz, 2H), 7.56 (d, $J = 16$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): 21.3, 28.1, 80.2, 119.1, 127.9, 129.5, 131.9, 140.1, 143.4, 166.4; MS: m/z (%) = 218 (M^+ , 40), 161 (100), 145 (77), 117 (44), 115 (60), 91 (50).

***tert*-Butyl (*E*)-4-Fluorocinnamate (7g):**

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **7g** was obtained as a colorless solid (94% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (98%).

M.p. = 47.5-48.5 °C (Lit. m.p. = 44-46 °C)¹³

IR (neat): 1697, 1638, 1509, 1147 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): 1.53 (s, 9H), 6.28 (d, $J = 16.2$ Hz, 1H), 7.00-7.10 (m, 2H), 7.42-7.51 (m, 2H), 7.54 (d, $J = 16.2$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 28.8, 81.2, 116.6$ (d, $^2J_{\text{CF}} = 21.7$ Hz), 120.6 (d, $^5J_{\text{CF}} = 2.1$ Hz), 130.4 (d, $^3J_{\text{CF}} = 8.4$ Hz), 131.6 (d, $^4J_{\text{CF}} = 3.3$ Hz), $142.8, 164.4$ (d, $^1J_{\text{CF}} = 249.1$ Hz), 166.8; MS: m/z (%) = 222 (M^+ , 2), 166 (60), 149 (56), 121 (51), 101 (100), 75 (67), 57 (75).

(E)-Stilbene (8a):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **8a** was obtained as a colorless solid (97 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (98%).

M.p. 123-124 °C (Lit. m.p. 124-125 °C)⁷

IR (neat): 3023, 2921, 1494, 1452 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 7.11 (s, 2H), 7.20-7.40 (m, 6H), 7.50-7.54 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): 127.2, 128.2, 129.3, 138.0; MS: *m/z* (%) = 181 ([M+H]⁺, 20), 179 (100), 165 (45), 89 (35).

(E)-4-Nitrostilbene (8b):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **8b** (100% yield) was obtained as a mixture of *E* and *Z* isomers (93:7). The ratio *E/Z* was calculated by ¹H NMR integration. Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%). A pure sample of (*E*)-**8b** was isolated by flash chromatography (silica gel; hexane:ethyl acetate, 9.9:0.1) as a yellow solid.

M.p. 151-153 °C (Lit. m.p. 154.5-155.7 °C)¹⁵

IR (neat): 2920, 1590, 1503, 1336 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 7.13 (d, *J* = 16.5 Hz, 1H), 7.28 (d, *J* = 16.5 Hz, 1H), 7.34-7.46 (m, 3H), 7.50-7.62 (m, 2H), 7.61 (AA' part of the AA'BB' system, *J* = 8.8 Hz, 2H), 8.21 (BB' part of the AA'BB' system, *J* = 8.8 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): 124.8, 127.0, 127.5, 127.7, 129.5, 129.6, 134.0, 136.9, 144.6, 147.5; MS: *m/z* (%) = 225 (M⁺, 100), 178 (92), 152 (72), 89 (50), 76 (48).

(E)-4-tert-Butylstilbene (8c):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **8c** was obtained as a colorless solid (100 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

M.p. 95-97 °C (Lit. m.p. 96-98 °C)¹⁶

IR (neat): 2953, 1503, 1469 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 1.38 (s, 9H), 7.08 (s, 2H), 7.24-7.53 (m, 9H); ¹³C NMR (50 MHz, CDCl₃): δ = 32.0, 35.3, 126.3, 127.0, 127.1, 128.1, 128.6, 129.2, 129.3, 135.3, 138.2, 151.4; MS: *m/z* (%) = 236 (M⁺, 86), 221 (100), 178 (76), 91 (70).

(E)-2-Methylstilbene (8d):

After purification by flash chromatography (silica gel; hexane:ethyl acetate, 9:1) **8d** was obtained as a colorless solid (38 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (93%).

M.p. = 31-32 °C (Lit. m.p. 30-32 °C)¹⁷

IR (neat): 2924, 1597, 1496, 1460 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): 2.44 (s, 3H), 7.00 (d, *J* = 16.2 Hz, 1H), 7.15-7.42 (m, 7H), 7.51-7.62 (m, 3H); ¹³C NMR (50 MHz, CDCl₃): 20.6, 126.1, 126.9, 127.3, 128.2, 128.3, 129.4, 130.7, 131.1, 136.5, 137.1, 138.4; MS: *m/z* (%) = 194 (M⁺, 74), 178 (100), 115 (44).

Electrospray Mass Spectra Studies

All experiments were performed using a commercially available quadrupole mass spectrometer equipped with an electrospray ion source. Equimolar amounts of arenediazonium salt **2a** (0.002 g, 0.012 mmols) and Pd(0) complex **1** (0.010 g, 0.012 mmols) were dissolved in methanol (6 mL) and the solution was introduced into the mass spectrometer ion source directly through a Rheodyne injector with a 20 µL sample loop. The mobile phase flow (150 µL/min of 70:30 v/v methanol/water) was delivered by a P2000 HPLC pump to the vaporization nozzle of the electrospray ion source and nitrogen was employed as both a drying and a nebulizing gas. The instrument was operated in the positive ion mode (ESI+). Typical ESI conditions used were: probe tip voltage of 3 kV, capillary temperature of 160 °C and skimmer cone voltage of 30 eV. Spectra were typically an average of 10-20 scans. Theoretical isotope patterns were calculated by use of the *Isoform* program and used to aid in assignment.

Benzenediazonium Tetrafluoroborate (2a)

Figure S1. Calculated isotopic distribution for the intermediate resulting from oxidative addition of benzenediazonium tetrafluoroborate **2a** to Pd(0) catalyst **1**.

Figure S2. Observed mass spectra for the intermediate resulting from oxidative addition of benzenediazonium tetrafluoroborate **2a** to Pd(0) catalyst **1**.

4-Nitrobenzenediazonium Tetrafluoroborate (2b)

Figure S3. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-nitrobenzenediazonium tetrafluoroborate **2b** to Pd(0) catalyst **1**.

Figure S4. Observed mass spectra for the intermediate resulting from oxidative addition of 4-nitrobenzenediazonium tetrafluoroborate **2b** to Pd(0) catalyst **1**.

4-Methylbenzenediazonium Tetrafluoroborate (2f)

Figure S5. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-methylbenzenediazonium tetrafluoroborate **2f** to Pd(0) catalyst **1**.

Figure S6. Observed mass spectra for the intermediate resulting from oxidative addition of 4-methylbenzenediazonium tetrafluoroborate **2f** to Pd(0) catalyst **1**.

4-Fluorobenzenediazonium Tetrafluoroborate (2g)

Figure S7. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-fluorobenzenediazonium tetrafluoroborate **2g** to Pd(0) catalyst **1**.

Figure S8. Observed mass spectra for the intermediate resulting from oxidative addition of 4-fluorobenzenediazonium tetrafluoroborate **2g** to Pd(0) catalyst **1**.

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