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

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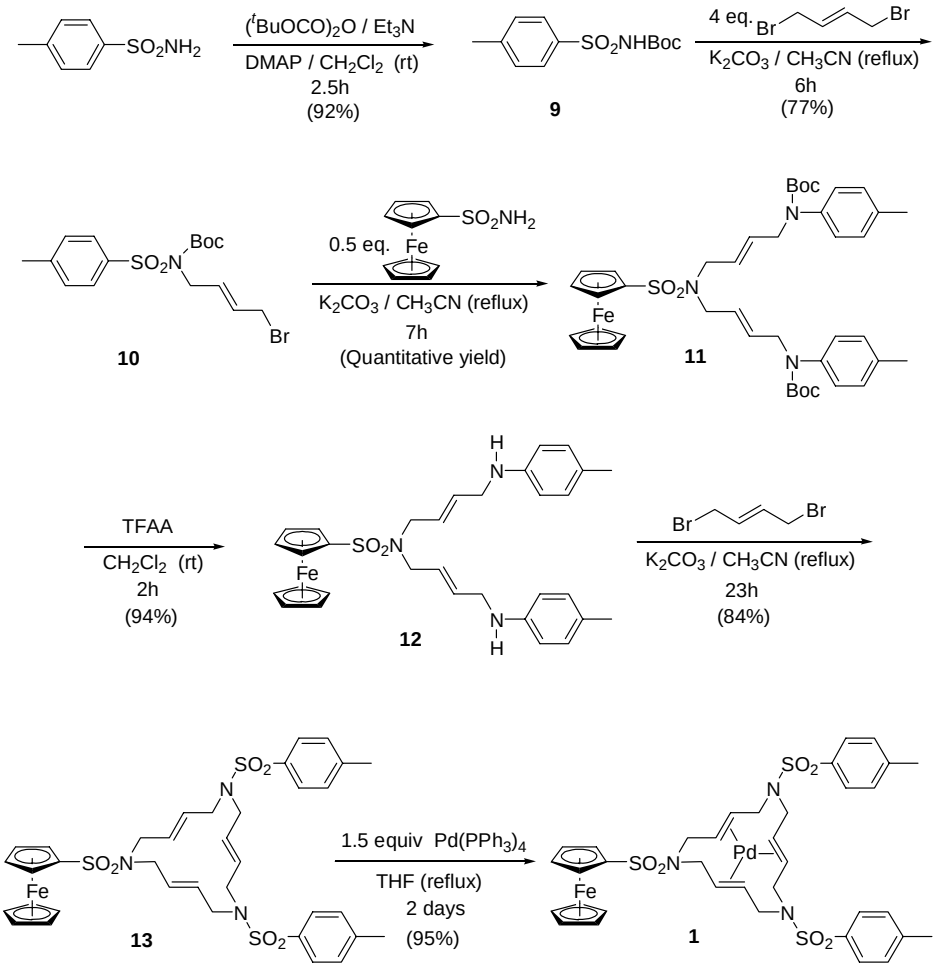
Supporting Information. Details of synthesis and characterization data for all intermediates in the synthesis of the Pd(0) catalyst **1**. Experimental procedure for the Heck reaction and spectroscopic data for compounds **2**, **6**, **7**, and **8**. ESI mass spectra for the detected oxidative addition 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. ^{1}H NMR (^{13}C NMR) were recorded at 200 MHz (50 MHz) using Me_4Si 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-triazaciclopentadeca-3,8,13-trienepalladium(0), 1:

Palladium(0) complex **1** was previously synthesized and characterized by us[1] 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 bellow:

***N*-(*ter*t-Butyloxycarbonyl)(4-methylphenyl)sulfonamide (9)[4]:** colorless solid; m.p. 115-116 ºC (Lit. m.p. 117-119 ºC)[4]; IR (KBr): 3225, 1750, 1439, 1340, 1234, 1149 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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*-(*ter*t-butyloxycarbonyl)(4-methylphenyl)sulfonamide (10)[2a]:** colorless solid; m.p. 64-66 ºC; IR (KBr): 2981, 2932, 1720, 1355, 1153 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 $[M + Na + CH_3CN]^+$, 442-444 $[M + K]^+$, 421-423 $[M + NH_4]^+$, 404-406 $[M + H]^+$.

(*E*,*E*)-1,11-Bis(*ter*t-butyloxycarbonyl)-1,11-bis[(4-methylphenyl)sulfonyl]-6-ferrocenylsulfonyl-1,6,11-triazaundeca-3,8-diene (11): yellow solid; m.p. 55-57 ºC[1]; IR (KBr): 2975, 2926, 1723, 1351, 1275, 1149 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 $[M]^+$; $C_{42}H_{53}FeN_3O_{10}S_3$ (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 ºC[1]; IR (KBr): 3279, 2919, 1323, 1149 cm^{-1}; ^1H NMR (200 MHz,

$CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 $[M]^+$; $C_{32}H_{37}Fe\ N_3O_6S_3$ (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-triazaciclopentadeca-3,8,13-triene (13)[1]: yellow solid; m.p. 195-197 ºC; IR (KBr): 2922, 2859, 1338, 1151 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 $[M+NH_4]^+$, 764 $[M+H]^+$, 763 $[M]^+$; $C_{36}H_{41}Fe\ N_3O_6S_3$ (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-triazaciclopentadeca-3,8,13-trienepalladium(0) (1)[1]: yellow solid; m.p. 127-129 ºC (dec); IR (KBr): 2918, 1333, 1157, 901, 655 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 $[M + NH_4]^+$, 869 $[M]^+$, 781 $[M –Pd + NH_4]^+$, 764 $[M - Pd+ H]^+$, 763 $[M - Pd]^+$; $C_{36}H_{41}Fe\ N_3O_6PdS_3$ (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 –20ºC.

Benzenediazonium Tetrafluoroborate (2a).

Colorless solid (86% yield). M.p.: 100-101 ºC (dec) (Lit m.p. 100ºC)[5]

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

4-Nitrobenzenediazonium Tetrafluoroborate (2b):

Yellow solid (100% yield). M.p. 146-147 ºC (dec) (Lit m.p. 142 ºC)[6]

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

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

Colorless solid (89% yield). M.p. 84-85 ºC (dec) (Lit m.p. 91ºC)[6]

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

2-Methylbenzenediazonium Tetrafluoroborate (2d):

Colorless solid (87% yield). M.p. 88-89 ºC (dec) (Lit m.p. 106ºC)[5]

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

3-Methylbenzenediazonium Tetrafluoroborate (2e):

Pale pink solid (88% yield). M.p. 89-90ºC (dec) (Lit m.p. 108ºC)[5]

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

4-Methylbenzenediazonium Tetrafluoroborate (2f):

Colorless solid (69% yield). M.p. 104-105 ºC (dec) (Lit m.p. 110 ºC)[5]

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

4-Fluorobenzenediazonium Tetrafluoroborate (2g):

Colorless solid (76% yield). M.p. 153-154 ºC (Lit m.p. 154 ºC)[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 0ºC under magnetic stirring. The mixture was stirred at room temperature until gas evolution ceased. After completion of the gas evolution, saturated $NaHCO_3$ 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, $CDCl_3$): 1.33 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 6.43 (d, *J* = 16Hz, 1H), 7.34-7.39 (m, 3H), 7.46-7.53 (m, 2H), 7.68 (d, *J* = 16 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC (Lit m.p. 141-142 ºC)[7]

IR (neat): 1708, 1643, 1512, 1332, 1174 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[8] (quantitative yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (97%).

IR (neat): 2960, 1711, 1635, 1309, 1167 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[9] (quantitative yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 1709, 1633, 1311, 1164 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[10] (78% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (94%).

IR (neat): 1710, 1638, 1311, 1174 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[10] (97% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (100%).

IR (neat): 1709, 1635, 1310, 1165 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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 theAA'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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[11] (78% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (100%).

IR (neat): 1713, 1639, 1510, 1232, 1175 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[12] (88% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (99%).

IR (neat): 1706, 1637, 1325, 1150 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC (Lit. m.p. 155-157 ºC)[13]

IR (neat): 1705, 1514, 1310, 1152 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC

IR (neat): 2964, 1708, 1150 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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);]$^+$; $C_{17}H_{24}O_2$ (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 oil[14] (71 % yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 1708, 1150 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 oil[13] (69% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (88%).

IR (neat): 1708, 1151; cm^{-1}; ^{1}H 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 oil[13] (99% yield). Further elution (hexane:ethyl acetate, 7:3) gave recovered **1** (95%).

IR (neat): 2976, 1707, 1636, 1322, 1149 cm^{-1}; ^{1}H 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 theAA'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 ºC (Lit. m.p. = 44-46 ºC)[13]

IR (neat): 1697, 1638, 1509, 1147 cm^{-1}; ^{1}H 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, $CDCl_3$): δ = 28.8, 81.2, 116.6 (d, $^{2}J_{CF}$ = 21.7 Hz), 120.6 (d, $^{5}J_{CF}$ = 2.1 Hz), 130.4 (d, $^{3}J_{CF}$ = 8.4 Hz), 131.6 (d, $^{4}J_{CF}$ = 3.3 Hz), 142.8, 164.4 (d, $^{1}J_{CF}$ = 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 ºC (Lit. m.p. 124-125 ºC)[7]

IR (neat): 3023, 2921, 1494, 1452 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 7.11 (s, 2H), 7.20-7.40 (m, 6H), 7.50-7.54 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ^{1}H 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 ºC (Lit. m.p. 154.5-155.7 ºC)[15]

IR (neat): 2920, 1590, 1503, 1336 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 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); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC (Lit. m.p. 96-98 ºC)[16]

IR (neat): 2953, 1503, 1469 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 1.38 (s, 9H), 7.08 (s, 2H), 7.24-7.53 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC (Lit. m.p. 30-32 ºC)[17]

IR (neat): 2924, 1597, 1496, 1460 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): 2.44 (s, 3H), 7.00 (d, J = 16.2 Hz, 1H), 7.15-7.42 (m, 7H), 7.51-7.62 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): 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 ºC and skimmer cone voltage of 30 eV. Spectra were typically and 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)

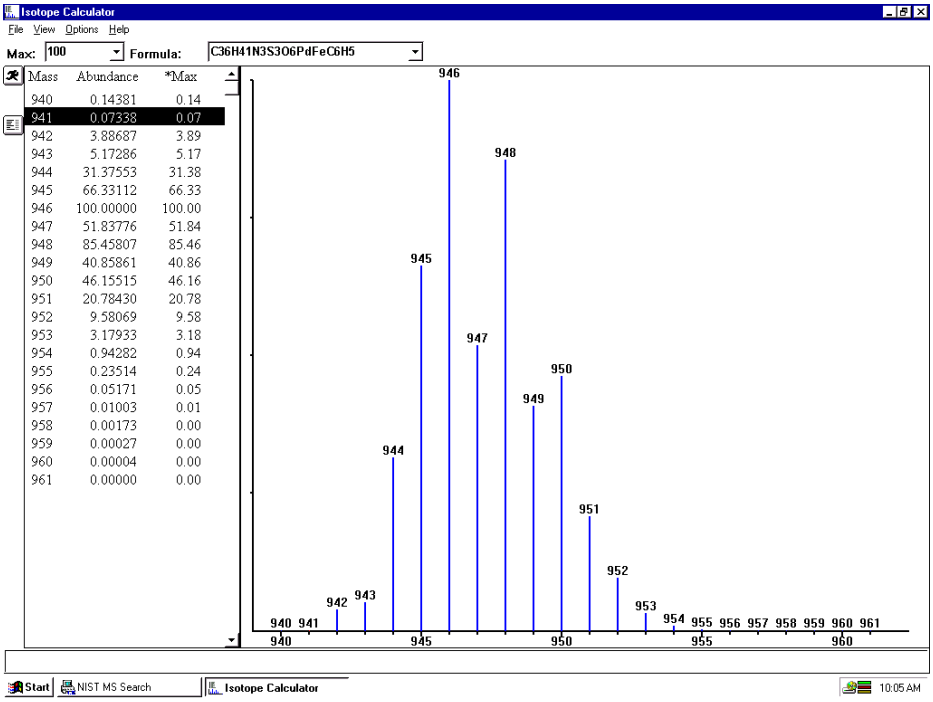


Figure S1. Calculated isotopic distribution for the intermediate resulting from oxidative addition of benzenediazonium tetrafluoroborate **2a** to Pd(0) catalyst **1**.

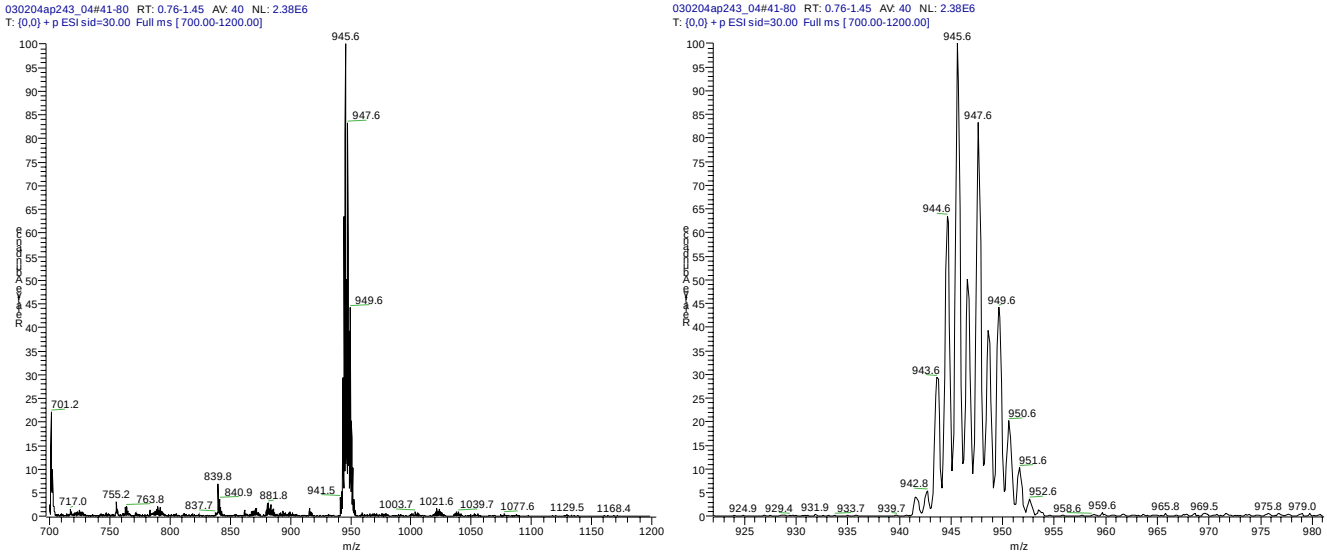


Figure S2. Observed mass spectra for the intermediate resulting from oxidative addition of benzenediazonium tetrafluoroborate **2a** to Pd(0) catalyst **1.**

4-Nitrobenzenediazonium Tetrafluoroborate (2b)

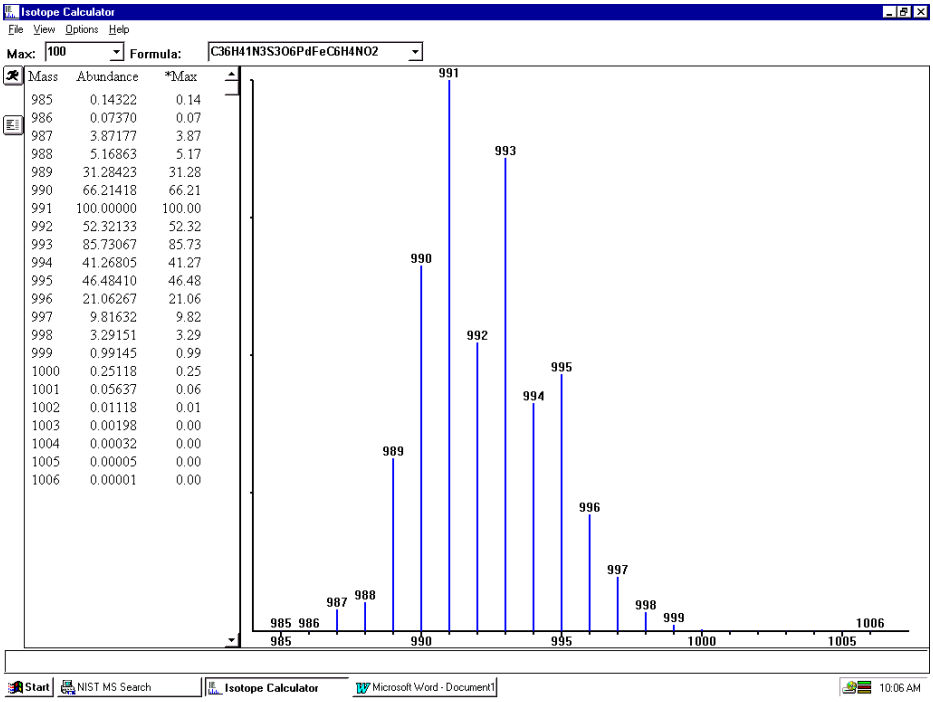


Figure S3. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-nitrobenzenediazonium tetrafluoroborate **2b** to Pd(0) catalyst **1**.

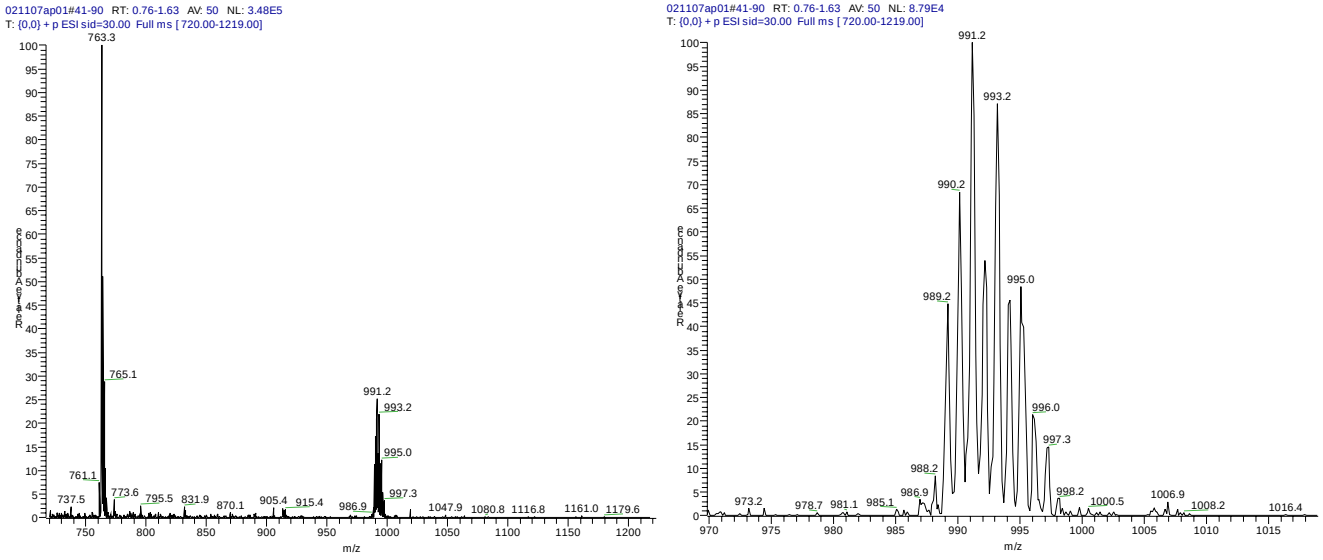


Figure S4. Observed mass spectra for the intermediate resulting from oxidative addition of 4-nitrobenzenediazonium tetrafluoroborate **2b** to Pd(0) catalyst **1.**

4-Methylbenzenediazonium Tetrafluoroborate (2f)

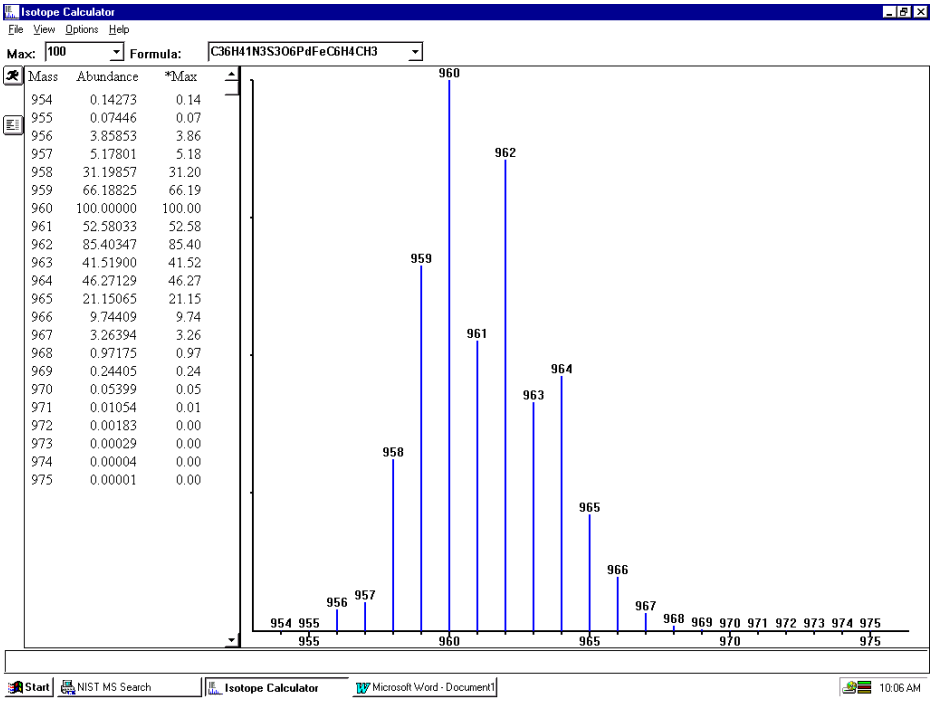


Figure S5. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-methylbenzenediazonium tetrafluoroborate **2f** to Pd(0) catalyst **1**.

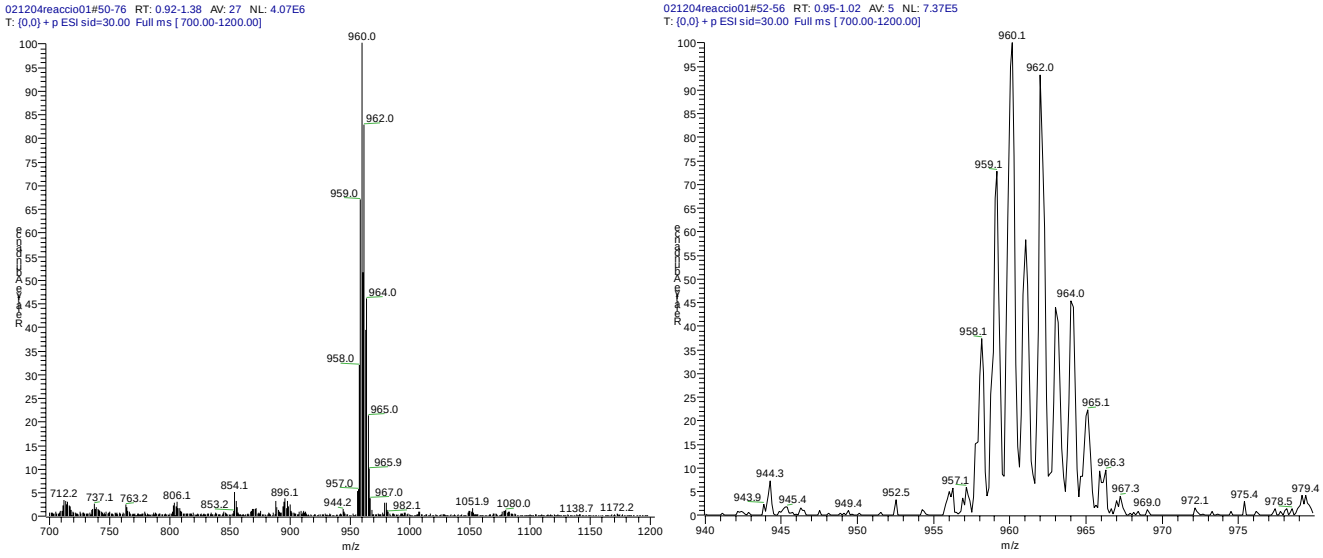


Figure S6. Observed mass spectra for the intermediate resulting from oxidative addition of 4-methylbenzenediazonium tetrafluoroborate **2f** to Pd(0) catalyst **1.**

4-Fluorobenzenediazonium Tetrafluoroborate (2g)

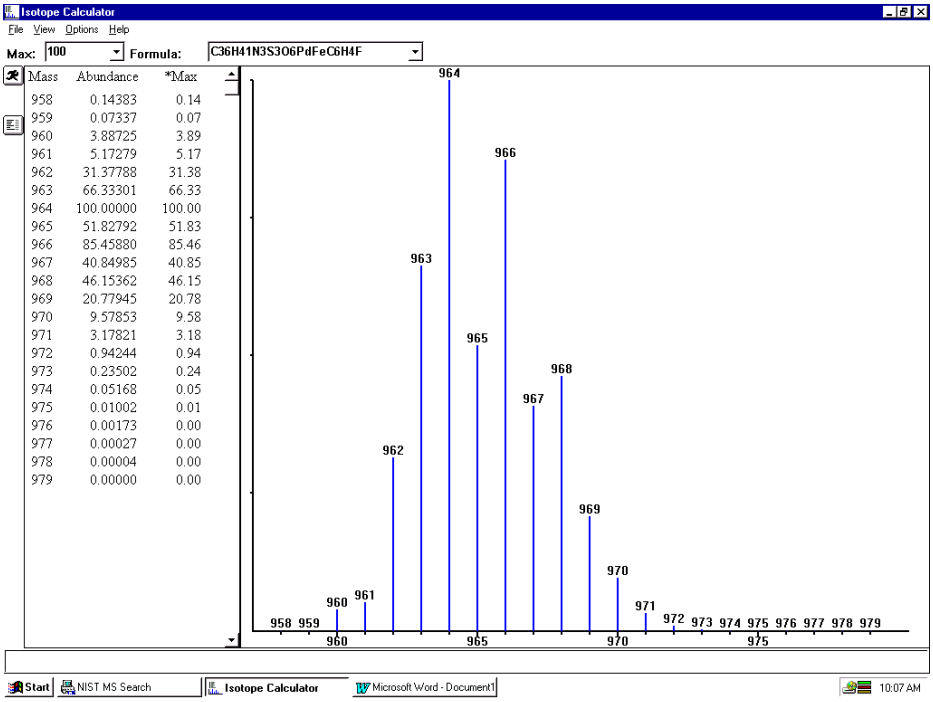


Figure S7. Calculated isotopic distribution for the intermediate resulting from oxidative addition of 4-fluorobenzenediazonium tetrafluoroborate **2g** to Pd(0) catalyst **1**.

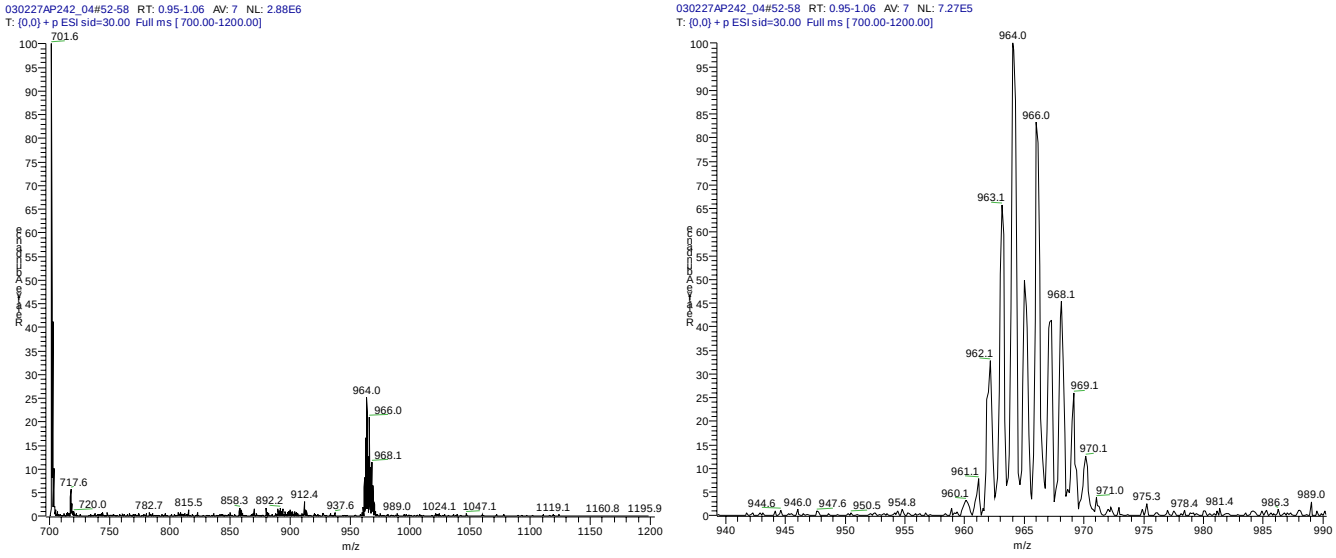


Figure S8. Observed mass spectra for the intermediate resulting from oxidative addition of 4-fluorobenzenediazonium tetrafluoroborate **2g** to Pd(0) catalyst **1.**

[1] Llobet, A.; Masllorens, E.; Moreno-Mañas, M.; Pla-Quintana, A.; Rodríguez, M.; Roglans, A. *Tetrahedron Lett.* **2002**, *43*, 1425.

[2] (a) For preparation of nitrogen-containing 15-membered triolefinic macrocycles, see: Cerezo, S.; Cortès, J.; Galvan, D.; Lago, E.; Marchi, C.; Molins, E.; Moreno-Mañas, M.; Pleixats, R.; Torrejón, J.; Vallribera, A. *Eur. J. Org. Chem.* **2001**, 329. (b) For a general preparation of palladium(0) complexes of 15-membered triolefinic macrocycles, see: Cerezo, S.; Cortès, J.; Lago, E.; Molins, E.; Moreno-Mañas, M.; Parella, T.; Pleixats, R.; Torrejón, J.; Vallribera, A. *Eur. J. Inorg. Chem.* **2001**, 1999.

[3] Slocum, D. W.; Achermann, W. *Synth. React. Inorg. Met. Org. Chem.* **1982**, *12*, 397.

[4] Neustadt, B. R. *Tetrahedron Lett.* **1994**, *35*, 379.

[5] Roe, A. *Org. React.* **1949**, *5*, 193.

[6] Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536.

[7] *Handbook of Chemistry and Physics*, 64rd ed; CRC Press Inc.: Boca Raton, 1983-1984.

[8] Hosoya, N.; Hatayama, A.; Irie, R.; Sasaki, H.; Katsuki, T. *Tetrahedron* **1994**, *50*, 4311.

[9] Norcross, B. E.; Lansinger, J. M.; Martin, R. L. *J. Org. Chem.* **1977**, *42*, 369.

[10] Kikukawa, K.; Nagira, K.; Wada, F.; Matsuda, T. *Tetrahedron* **1981**, *37*, 31.

[11] Silver, R. F.; Kerr, K. A.; Frandsen, P. D.; Kelley, S. J.; Holmes, H. L. *Can. J. Chem.* **1967**, *45*, 1001.

[12] Sato, Y.; Takeuchi, S. *Synthesis* **1983**, 734.

[13] Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P.; Westmoreland, I.; Thickitt, C. P.; Scott, P. *J. Org. Chem.* **2002**, *67*, 3450.

[14] De Vries, A. H. M.; De Vries, J. G. DSM N.V., Neth. PCT Int. Appl. NL 1017138, 2001.

[15] Kikukawa, K.; Maemura, K.; Kiseki, Y.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1981**, *46*, 4885.

[16] Smith, J. G.; Oliver, E.; Boettger, T. J. *Organometallics* **1983**, *2*, 1577.

[17] Ohta, A.; Tonomura, Y.; Odashima, H.; Fujiwara, N.; Shimazaki, M. *Heterocycles* **1989**, *29*, 1199.