Supporting Information for

Palladium-Catalyzed Bisdiene Carbocyclizations: A Facile [3+2] Cycloaddition Reaction Mode.

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General procedure for cyclization of bisdienes 6a-e. To a flame-dried 10 mL flask was added bisdiene **6** (0.2 mmol), $[\text{Pd}(\text{MeCN})(\text{PPh}_3)_3](\text{BF}_4)_2$ (0.02 mmol), dry THF (1.0 mL), dry MeOH (0.05 mL), and dry Et_3N (0.2 mmol). The reaction flask was fitted with an oven-dried reflux condenser (dried at 130 °C overnight), the flask flushed with nitrogen, and the reaction mixture heated to reflux. The course of the reaction was followed by TLC analysis. Upon complete consumption of starting bisdiene, the reaction mixture was cooled and concentrated *in vacuo*. The residue was dissolved in dry dichloromethane (2 mL) and passed through a short silica plug (ca. 5 g, eluent: 50/50 hexane-ethyl acetate). The filtrate was concentrated *in vacuo*. Flash chromatography on silica (eluent: 2% diethyl ether in hexanes) gave the desired cyclization product.

Compound 7a. According to the general procedure, bisdiene **6a** (100 mg, 0.20 mmol) was treated with [Pd(MeCN)(PPh₃)₃](BF₄)₂ (22.0 mg, 0.02 mmol) in THF-MeOH (1.05 mL, 20:1) in the presence of Et₃N (28 μ L, 20 mg, 0.2 mmol) at reflux (1.5 h) to give **7a** (91 mg, 91%) as colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.4 Hz, 2H, H₁₄), 7.33 (t, J = 7.4 Hz, 2H, H₁₅), 7.23 (t, J = 7.4 Hz, 1H, H₁₆), 6.44 (d, J = 15.7 Hz, 1H, H₁), 5.97 (dd, J = 15.7, 8.8 Hz, 1H, H₂), 4.99 (s, 1H, H₁₂), 4.87 (s, 1H, H₁₂), 4.67-4.42 (m, 4H, CO₂CH₂CF₃), 2.76 (dd, J = 11.3, 8.8 Hz, 1H, H₃), 2.63-2.56 (m due to overlapping peaks, 3H, H_{5eq}, H_{10eq}, H_{7eq}), 2.05-1.99 (m due to overlapping peaks, 2H, H_{10ax}, H_{8eq}), 1.81 (ddd, J = 13.6, 13.3, 4.0 Hz, 1H, H_{7ax}), 1.65 (dd, J = 12.8, 12.2 Hz, 1H, H_{5ax}), 1.45 (m, 1H, H₉), 1.34 (dddd, J = 13.3, 13.0, 13.0, 3.4 Hz, 1H, H_{8ax}), 1.24 (dddd, J = 12.2, 11.5, 11.3, 3.1 Hz, 1H, H₄); ¹³C NMR (125 MHz, CDCl₃) δ 170.3 (C=O), 169.0 (C=O), 152.8 (C₆), 137.5, 132.7 (C₁), 130.6 (C₂), 128.7 (C₁₅), 127.4, 126.4 (C₁₄), 124.3 (q, J = 277.6 Hz, CO₂CH₂CF₃), 108.5 (C₁₂), 61.1 (q, J = 37.1 Hz, CO₂CH₂CF₃), 55.9 (C₁₁), 55.0 (C₃), 48.0 (C₄), 43.6 (C₉), 38.0 (C₁₀), 35.2 (C₅), 31.6 (C₇), 28.1 (C₈); FTIR (neat, cm⁻¹) 2937, 1754, 1451, 1410, 1283, 1172, 977, 746, 694; MS (m/z) 490 (M⁺), 438, 386, 307, 154 (100%); HRMS calcd for C₂₄H₂₄F₆O₄ = 490.1579, found 490.1567 m/z .

Compound 7b. According to the general procedure, bisdiene **6b** (91.0 mg, 0.17 mmol) was treated with [Pd(MeCN)(PPh₃)₃](BF₄)₂ (18.0 mg, 0.017 mmol) in THF-MeOH (0.90 mL, 20:1) in the presence of Et₃N (23 μ L, 17 mg, 0.17 mmol) at reflux (1.0 h) to give **7b** (65 mg, 71%) after chromatography on silica as colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ 7.99 (d, J = 8.3

Hz, 2H, H₁₅), 7.47 (d, $J = 8.3$ Hz, 2H, H₁₄), 6.46 (d, $J = 15.7$ Hz, 1H, H₁), 6.09 (dd, $J = 15.7, 8.9$ Hz, 1H, H₂), 5.00 (s, 1H, H₁₂), 4.85 (s, 1H, H₁₂), 4.69-4.41 (m, 4H, CO₂CH₂CF₃), 3.91 (s, 3H, CO₂CH₃), 2.78 (dd, $J = 11.1, 8.9$ Hz, 1H, H₃), 2.62-2.52 (m, 3H, H_{5eq}, H_{10eq}, H_{7eq}), 2.06-1.98 (m, 2H, H_{10ax}, H_{8eq}), 1.83 (ddd, $J = 13.4, 13.1, 4.1$ Hz, 1H, H_{7ax}), 1.66 (dd, $J = 12.8, 12.8$ Hz, 1H, H_{5ax}), 1.44 (m, 1H, H₉), 1.34 (dddd, $J = 13.1, 12.8, 12.8, 3.3$ Hz, 1H, H_{8ax}), 1.26-1.19 (m, 1H, H₄); ¹³C NMR (CDCl₃, 100 MHz) δ 170.2 (C=O), 169.0 (C=O), 167.1 (C=O), 152.3 (C₆), 142.0 (C₁₃), 133.6 (C₂), 131.8 (C₁), 130.2 (C₁₅), 128.9 (C₁₆), 126.3 (C₁₄), 122.9 (q, $J = 277.9$ Hz, CO₂CH₂CF₃), 108.8 (C₁₂), 61.2 (q, $J = 37.1$ Hz, CO₂CH₂CF₃), 55.8 (C₁₁), 54.8 (C₃), 52.2 (CO₂CH₃), 48.0 (C₄), 43.7 (C₉), 38.0 (C₁₀), 35.2 (C₅), 31.9 (C₇), 28.0 (C₈); FTIR (neat, cm⁻¹) 2917, 1753, 1721, 1438, 1412, 1282, 1171, 975, 764; MS (m/z) 548 (M⁺), 517, 421, 386, 321, 293, 258, 192, 163, 129, 83, HRMS calcd for C₂₆H₂₆F₆O₅ = 548.1634, found 548.1640 m/z .

Compound 7c. According to the general procedure, bisdiene **6c** (103.0 mg, 0.20 mmol) was treated with [Pd(MeCN)(PPh₃)₃](BF₄)₂ (20.0 mg, 0.02 mmol) in THF-MeOH (1.05 mL, 20:1) in the presence of Et₃N (28 μ L, 20.0 mg, 0.20 mmol) at reflux (2.25 h) to give **7c** (83 mg, 83%) after chromatography on silica as colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ 7.41 (d, $J = 8.5$ Hz, 2H, H₁₅), 6.88 (d, $J = 8.5$ Hz, 2H, H₁₄), 6.39 (d, $J = 15.7$ Hz, 1H, H₁), 5.81 (dd, $J = 15.7, 8.8$ Hz, 1H, H₂), 4.99 (s, 1H, H₁₂), 4.89 (s, 1H, H₁₂), 4.68-4.42 (m, 4H, CO₂CH₂CF₃), 3.82 (s, 1H, H₁₇), 2.74 (br t, $J = 8.9$ Hz, 1H, H₃), 2.65-2.49 (m due to overlapping peaks, 3H, H_{5eq}, H_{10eq}, H_{7eq}), 2.05-1.99 (m due to overlapping peaks, 2H, H_{10ax}, H_{8eq}), 1.81 (ddd, $J = 13.2, 13.0, 3.5$ Hz, 1H, H_{7ax}), 1.66 (dd, $J = 12.8, 12.8$ Hz, 1H, H_{5ax}), 1.46-1.42 (m, 1H, H₉), 1.35 (dddd, $J = 13.0,$

12.7, 12.7, 2.6 Hz, 1H, H_{8ax}), 1.27-1.18 (m, 1H, H₄); ¹³C NMR (CDCl₃, 100 MHz) δ 170.3 (C=O), 169.0 (C=O), 159.1 (C₁₆), 153.0 (C₆), 132.0 (C₁), 130.4 (C₁₃), 128.4 (C₂), 127.4 (C₁₅), 122.9 (q, *J* = 277.6 Hz, CO₂CH₂CF₃), 114.2 (C₁₄), 108.3 (C₁₂), 61.2 (q, *J* = 37.0 Hz, CO₂CH₂CF₃), 55.8 (C₁₁), 55.4 (C₁₇), 54.9 (C₃), 48.0 (C₄), 43.5 (C₉), 37.9 (C₁₀), 35.2 (C₅), 31.9 (C₇), 28.0 (C₈); FTIR (neat, cm⁻¹) 2939, 1754, 1607, 1512, 1453, 1411, 1285, 1173, 1035, 976, 834; MS (*m/z*) 520, 393, 258, 226, 171, 135; HRMS calcd for C₂₅H₂₆F₆O₅ = 520.1684, found 520.1679 *m/z*.

Compound 7d. According to the general procedure, bisdiene **6d** (100.0 mg, 0.20 mmol) was treated with [Pd(MeCN)(PPh₃)₃](BF₄)₂ (22.0 mg, 0.02 mmol) in THF-MeOH (1.05 mL, 20:1) in the presence of Et₃N (28 μL, 20 mg, 0.20 mmol) at reflux (4.0 h) to give **7d** (52.0 mg, 52%) after chromatography on silica as colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 1.6 Hz, 1H, H₁₄), 6.37 (dd, *J* = 3.2, 1.6 Hz, 1H, H₁₅), 6.26 (d, *J* = 15.8 Hz, 1H, H₁), 6.20 (d, *J* = 3.2 Hz, 1H, H₁₆), 5.92 (dd, *J* = 15.8, 8.9 Hz, 1H, H₂), 4.98 (s, 1H, H₁₂), 4.88 (s, 1H, H₁₂), 4.63-4.44 (m, 4H, CO₂CH₂CF₃), 2.70 (dd, *J* = 11.3, 8.9 Hz, 1H, H₃), 2.64-2.51 (m due to overlapping peaks, 3H, H_{5eq}, H_{10eq}, H_{7eq}), 2.04-1.97 (m due to overlapping peaks, 2H, H_{10ax}, H_{7eq}), 1.81 (ddd, *J* = 13.5, 13.2, 4.0 Hz, 1H, H_{7ax}), 1.63 (dd, *J* = 12.7, 12.7 Hz, 1H, H_{5ax}), 1.46-1.39 (m, 1H, H₉), 1.36 (dddd, *J* = 13.2, 12.8, 12.8, 3.4 Hz, 1H, H_{8ax}), 1.26-1.18 (m, 1H, H₄); ¹³C NMR (100 MHz, CDCl₃) 170.3 (C=O), 169.0 (C=O), 153.1 (C₁₃), 152.6 (C₆), 141.7 (C₁₄), 129.6 (C₂), 122.9 (q, *J* = 277.6 Hz, CO₂CH₂CF₃), 121.4 (C₁), 111.4 (C₁₅), 108.6 (C₁₂), 106.7 (C₁₆), 61.2 (q, *J* = 37.1 Hz,

CO₂CH₂CF₃), 55.8 (C₁₁), 54.6 (C₃), 48.0 (C₄), 43.6 (C₉), 38.0 (C₁₀), 35.3 (C₅), 31.9 (C₇), 28.0 (C₈); FTIR (neat, cm⁻¹) 2937, 1753, 1452, 1411, 1285, 1171, 978, 739; MS (*m/z*) 480 (M⁺), 440, 418, 386, 341, 307, 246, 192, 129 (100%), HRMS calcd for C₂₂H₂₂F₆O₅ = 480.1371, found 480.1373 *m/z*.

Compound 7e. According to the general procedure, bisdiene **6a** (85.0 mg, 0.19 mmol) was treated with [Pd(MeCN)(PPh₃)₃](BF₄)₂ (20.0 mg, 0.019 mmol) in THF-MeOH (1.05 mL, 20:1) in the presence of Et₃N (27 μL, 19 mg, 0.19 mmol) at reflux (6.0 h) to give after chromatography on silica enediyne **7e** (68 mg, 80%, colorless oil) as a 1:1 mixture of (*E,E*)- and (*E,Z*)-stereoisomers: ¹H NMR (400 MHz, CDCl₃) δ 6.33 (dd, *J* = 15.0, 11.0 Hz, 0.5H, H₄), 6.03-5.90 (m due to overlapping peaks, 1.5H, H'₄, H'₃, H₃), 5.71-5.63 (m due to overlapping peaks, 1.5H, H₁₃, H'₂), 5.43-5.33 (m due to overlapping peaks, 1H, H₂, H₅), 5.25 (dd, *J* = 13.5, 7.2 Hz, H'₅), 4.96-4.91 (overlapping peaks, 2H, H₁₄), 4.61-4.42 (overlapping peaks, 4H, CO₂CH₂CF₃), 2.41-2.24 (overlapping peaks, 3H, H_{12a}, H_{9a}, H_{7a}), 2.05-1.73 (overlapping peaks, 3H, H₆, H_{10a}, H_{12b}), 1.71 (d, *J* = 5.8 Hz, 3H, H₁), 1.67-1.52 (overlapping peaks, 2H, H_{7b}, H_{9b}), 1.24-1.12 (m, 1H, H₁₁), 1.09-0.93 (m, 1H, H_{10b}); ¹³C NMR (100 MHz, CDCl₃) δ 170.2 (C=O), 169.0 (C=O), 136.5 (C₁₃), 136.0 (C₅), 133.7 (C'₅), 132.2 (C'₃), 131.5 (C'₄), 129.2 (C₃), 128.5 (C'₂), 127.1 (C₄), 125.7 (C₂), 123.0 (q, *J* = 277.3 Hz, CO₂CH₂CF₃), 116.7 (C₁₄), 61.1 (quartet, *J* = 37.4 Hz, CO₂CH₂CF₃), 55.3 (C₈), 43.2 (C₆, or C'₆), 42.8 (C₆, or C'₆), 40.8 (C₁₁), 38.4 (C₇), 37.8 (C₉), 31.0 (C₁₂), 25.7 (C₁₀), 18.2 (C₁), 13.4 (C'₁); FTIR (neat, cm⁻¹) 2934, 1755 (C=O), 1411, 1284, 1171,

980; MS (m/z) 442 (M^+), 413, 400, 386, 341, 307, 259, 219, 154 (100%); HRMS calcd for $C_{20}H_{24}F_6O_4 = 442.1579$, found 442.1558 m/z .

Compound *d*₁-7a. According to the general procedure, bisdiene **6a** (52.0 mg, 0.10 mmol) was treated with $[Pd(MeCN)(PPh_3)_3](BF_4)_2$ (11.0 mg, 0.01 mmol) in THF- CD_3OD (0.53 mL, 20:1) in the presence of Et_3N (15 μ L, 10 mg, 0.10 mmol) at reflux (1.75 h) to give **7a** (50 mg, 98%) after chromatography on silica as colorless oil: 1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, $J = 7.2$ Hz, 2H, H_{15}), 7.32 (t, $J = 7.2$ Hz, 2H, H_{16}), 7.23 (t, $J = 7.2$ Hz, 1H, H_{17}), 6.43 (d, $J = 15.7$ Hz, 1H, H_1), 5.96 (dd, $J = 15.7, 8.9$ Hz, 1H, H_2), 4.98 (s, 1H, H_{12}), 4.87 (s, 1H, H_{13}), 4.69-4.41 (m, 4H, $CO_2CH_2CF_3$), 2.75 (dd, $J = 11.2, 8.9$ Hz, 1H, H_3), 2.61 (dd, $J = 13.0, 2.6$ Hz, 1H, H_{5eq}), 2.54 (ddd, $J = 13.4, 5.3, 3.2$ Hz, 1H, H_{7eq}), 2.06-1.99 (overlapping peaks, 2H, H_{8eq} , H_{10}), 1.81 (ddd, $J = 13.4, 13.0, 4.3$ Hz, 1H, H_{7ax}), 1.65 (dd, $J = 13.0, 12.8$ Hz, 1H, H_{5ax}), 1.44 (dddd, $J = 12.2, 11.5, 11.5, 3.2$ Hz, 1H, H_9), 1.34 (dddd, $J = 13.0, 12.7, 12.2, 3.2$ Hz, 1H, H_{8ax}), 1.24 (br ddd, $J = 12.8, 11.5, 11.2$ Hz, 1H, H_4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3 (C=O), 169.0 (C=O), 152.7 (C_6), 137.5, 132.6 (C_1), 130.6 (C_2), 128.7 (C_{15}), 127.4 (C_{16}), 126.4 (C_{14}), 122.9 (q, $J = 277.7$ Hz, $CO_2CH_2CF_3$), 108.5 (C_{12}), 61.1 (q, $J = 37.0$ Hz, $CO_2CH_2CF_3$), 65.8 (C_{11}), 54.9 (C_3), 47.9 (C_4), 43.5 (C_9), 35.2 (C_5), 31.9 (C_7), 28.0 (C_8); FTIR (neat, cm^{-1}) 2927, 2849, 1738, 1449, 1287, 1173, 974, 746, 695; MS (m/z) 491 (M^+), 400, 364, 259, 197, 142, 117, 91 (100%); HRMS calcd for $C_{24}H_{23}DF_6O_4 = 491.1641$, found 491.1621 m/z .

Compound 8'. To a 10mL flame-dried flask was added the phenyl-substituted bisdiene **6a** (100.0 mg, 0.204 mmol), Pd_2dba_3 (9.0 mg, 0.01 mmol), triphenylphosphine (6.0 mg, 0.02 mmol), and dry MeOH (1 mL). The reaction was heated to reflux for 1.5 h. Afterwards, the cooled reaction mixture was concentrated *in vacuo*, dissolved in dry dichloromethane (2 mL), and passed through a short plug of silica (ca. 5 g; 50/50 hexane-ethyl acetate eluent). The filtrate was concentrated and the residue purified via flash chromatography on silica (5% ether in hexane eluent) to afford compound **8'** (39 mg, 42%) as clear oil: 1H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.24 (overlapping peaks, 5H, H_{14} , H_{15} , H_{16}), 5.70-5.58 (overlapping peaks, 2H, H_2 , H_{11}), 5.47 (dd, 15.5 Hz, 8.6 Hz, 1H, H_3), 4.94 (d, 9.6 Hz, 1H, H_{12a}), 4.86 (d, 17.1 Hz, 1H, H_{12b}), 4.65-4.52 (overlapping peaks, 3H, $CO_2CH_2CF_3$, H_1), 3.71 (s, 3H, CO_2CH_3 , or H_{17}), 3.32 (s, 3H, CO_2CH_3 , or H_{17}), 2.41-2.33 (overlapping peaks, 2H, H_{10a} , H_{5eq}), 2.20 (br d, $J = 12.3$ Hz, H_{7eq}), 1.94 (dddd, $J = 11.5, 11.5, 11.5, 3.6$ Hz, 1H, H_4), 1.84-1.77 (m, 1H, H_{8eq}), 1.76-1.61 (overlapping peaks, 3H, H_{10b} , H_{7ax} , H_{5ax}), 1.21 (m, 1H, H_9), 1.03 (dddd, $J = 13.6, 13.6, 13.6, 3.4$ Hz, H_{8ax}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 (C=O), 169.8 (C=O), 141.6 (C_{13}), 136.3 (C_3), 135.8 (C_{11}), 132.5 (C_2), 128.6 (C_{14} , or C_{15}), 127.8 (C_{16}), 126.9 (C_{14} , or C_{15}), 123.0 (q, $J = 277.7$ Hz, $CO_2CH_2CF_3$), 116.6 (C_{12}), 84.3 (C_1), 60.9 (q, $J = 36.9$ Hz, $CO_2CH_2CF_3$), 56.4 (CO_2CH_3 or C_{17}), 55.4 (C_6), 53.0 (CO_2CH_3 or C_{17}), 42.5 (C_4), 40.7 (C_9), 38.4 (C_7), 37.9 (C_5), 31.2 (C_{10}), 27.5 (C_8); FTIR (neat, cm^{-1}) 2931, 2863, 1755 (C=O), 1454, 1410, 1285, 1172, 1076, 979, 656; MS (m/z) 454 (M^+), 422,

381, 362, 331, 272, 253, 193, 173, 147 (100%) 121; HRMS calcd for $C_{24}H_{29}F_3O_5 = 454.1967$, found 454.1977 m/z .

Compound 7a'. Compound **8'** was treated according to the general procedure. Compound **8'** (40.0 mg, 0.076 mmol) was treated with $[Pd(MeCN)(PPh_3)_3](BF_4)_2$ (8.0 mg, 0.008 mmol) and Et_3N (11 μL , 8 mg, 0.076 mmol) in THF-MeOH (0.53 mL, 20:1) at reflux (4.0 h) to give after chromatography on silica compound **7a'** (39 mg, 99%) as colorless oil: 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J = 7.3$ Hz, 2H, H_{15}), 7.32 (t, $J = 7.3$ Hz, 2H, H_{16}), 7.23 (t, $J = 7.3$ Hz, 1H, H_{17}), 6.43 (d, $J = 15.8$ Hz, 1H, H_1), 5.97 (dd, $J = 15.8, 9.0$ Hz, 1H, H_2), 4.98 (s, 1H, H_{12}), 4.87 (s, 1H, H_{13}), 4.66 (dq, $J = 12.6, 8.4$ Hz, 1H, $CO_2CH_2CF_3$), 4.47 (dq, $J = 12.6, 8.4$ Hz, 1H, $CO_2CH_2CF_3$), 3.71 (s, 3H, CO_2CH_3), 2.75 (br dd, $J = 11.9, 9.0$ Hz, H_3), 2.63-2.56 (overlapping peaks, 2H, H_{5eq}, H_{10eq}), 2.51 (ddd, $J = 13.4, 5.3, 3.2$ Hz, H_{7eq}), 2.05-1.95 (overlapping peaks, 2H, H_{8eq}, H_{10ax}), 1.82 (ddd, $J = 13.4, 13.4, 4.1$ Hz, H_{7ax}), 1.62 (dd, $J = 11.9, 11.9$ Hz, H_{5ax}), 1.44-1.38 (m, 1H, H_9), 1.31 (dddd, $J = 13.4, 13.4, 13.4, 3.2$ Hz, 1H, H_{8ax}), 1.21 (dddd, $J = 11.9, 11.9, 11.9, 3.2$ Hz, 1H, H_4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (C=O), 169.9 (C=O), 153.0 (C_6), 137.6 (C_{13} , or C_{16}), 132.5 (C_1), 130.8 (C_2), 128.7 (C_{15}), 127.3 (C_{16} , or C_{13}), 126.4 (C_{14}), 123.0 (q, $J = 277.7$ Hz, $CO_2CH_2CF_3$), 108.3 (C_{12}), 60.8 (q, $J = 36.7$ Hz, $CO_2CH_2CF_3$), 56.0 (C_{11}), 55.0 (C_3), 53.9 (CO_2CH_3), 48.2 (C_4), 43.7 (C_9), 38.0 (C_{10}), 35.4 (C_5), 32.1 (C_7), 28.2 (C_8); FTIR (neat, cm^{-1}) 2929, 2852, 1740, 1451, 1280, 1173, 971, 740, 697; MS (m/z) 452, 422 (M^+), 363, 318, 295, 258, 235, 190; 155, 131, 91 (100%); HRMS calcd for $C_{23}H_{25}F_3O_4 = 422.1705$, found 422.1705 m/z .