**Carbocyclization of Aromatic Iodides, Bicyclic Alkenes and Benzyne Involving a
Palladium-Catalyzed C-H Bond Activation as a Key Step**

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Supporting Information

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Experimental Section

General Procedure for the Carbocyclization Reaction of Aromatic Iodides, Bicyclic Alkenes and Benzyne. A 25-mL round-bottomed side-arm flask containing Pd(dba)₂ (0.005 mmol), P(2-furyl)₃ (0.020 mmol) and CsF (4.00 mmol) was evacuated and purged with nitrogen gas three times. To the flask were then added aromatic iodides (**1**) (1.00 mmol), bicyclic alkenes **2** (for **2a** and **2c** 1.50 mmol, **2b** 1.00 mmol), benzyne precursor **3** (1.10 mmol) and CH₃CN (3.0 mL) via syringes. The reaction mixture was allowed to stir at room temperature for 10 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4**.

Spectral data and copy of ¹H and ¹³C NMR spectra of all compounds **4a-r** are listed below (pages 4 – 31). All of these products **4a-r** decomposed during melting point determination, likely undergoing retro Diels-Alder reactions, at temperature >100 °C.

Regioselective Studies

In this reaction, two different kinds of regioisomers are possible **4a** or **4a'**, but we observed only **4a**. The regiochemistry of compound **4a** was established by ¹H NMR NOE experiments.

Stereoselective Studies

The catalytic reaction is highly stereoselective, giving the exo isomer as the exclusive product. Exo stereochemistry of this product was established on the basis of the coupling constants of protons H-1 and H-2 and H-1' and H-2'. It is well-known that for norbornene derivatives the coupling constant between the endo proton at C-2' and the bridgehead proton at C-1' is nearly zero, whereas the value between the exo and a bridgehead proton is ca. 3 Hz and can be clearly observed. For compounds **4a**, **4d** and **4j**, the C1 and C1' protons all appear as singlets in their ^1H NMR spectra at $\sim \delta$ 3., thereby confirming the exo stereochemistry.¹ A similar type of exo stereoisomers was observed for compounds **4b-c**, **4e-i**, and **4k-r**.

References

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Spectral Data of Compounds 4a-r

1-[(4aR*,12bS*)-10,11-Dimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenyl-7-yl]ethanone (4a). Pale yellow solid; $R_f = 0.75$ (3% ethyl acetate in hexanes); IR 1675 cm^{-1} (C=O); ^1H NMR (CDCl_3 , 500 MHz): δ 8.47 (d, $J = 1.5\text{ Hz}$, 1 H), 7.75 (dd, $J = 7.5, 1.5\text{ Hz}$, 1 H), 7.73 (s, 1 H), 7.37 (d, $J = 7.5\text{ Hz}$, 1 H), 7.09 (s, 1 H), 6.37 – 6.33 (m, 2 H), 3.05 – 2.97 (m, 4 H), 2.63 (s, 3 H), 2.31 (s, 3 H), 2.27 (s, 3 H), 1.30 (d, $J = 8.5\text{ Hz}$, 1 H), 1.14 (d, $J = 8.5\text{ Hz}$, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 198.0, 143.4, 137.9, 137.3, 137.0, 135.3, 134.8, 132.7, 131.3, 130.3, 128.5, 127.0, 123.7, 122.0, 55.6, 55.2, 42.8, 41.6, 40.7, 26.6, 19.6, 19.5; HMRS (EI+): calcd for $\text{C}_{23}\text{H}_{22}\text{O}$ 314.1671, found 314.1675.

(4aR*,12bS*)-6,7-Dimethyl-10-nitro-1,4,4a,12b-tetrahydro-1,4-methanotriphenyl-ene (4b). Pale yellow solid; $R_f = 0.70$ (2% ethyl acetate in hexanes); IR cm^{-1} 1509, 1336 (NO_2); ^1H NMR (CDCl_3 , 400 MHz): δ 8.68 (d, $J = 2.0\text{ Hz}$, 1 H), 7.99 (dd, $J = 8.4, 2.4\text{ Hz}$, 1 H), 7.65 (s, 1 H), 7.42 (d, $J = 8.8\text{ Hz}$, 1 H), 7.10 (s, 1 H), 6.38 – 6.33 (m, 2 H), 3.05 – 2.96 (m, 4 H), 2.31 (s, 3 H), 2.28 (s, 3 H), 1.27 (d, $J = 8.8\text{ Hz}$, 1 H), 1.15 (d, $J = 8.8\text{ Hz}$, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.0, 145.5, 138.4, 138.3, 137.5, 135.6, 135.4, 134.2, 131.6, 131.3, 127.6, 124.1, 121.7, 117.5, 56.0, 55.4, 43.0, 42.0, 41.0, 19.9, 19.8; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$ 317.1416, found 317.1420.

(4aR*,12bS*)-6,7-Dimethyl-11-nitro-1,4,4a,12b-tetrahydro-1,4-methanotriphenyl-ene (4c). Pale yellow solid; $R_f = 0.72$ (2% ethyl acetate in hexanes); IR $1524, 1351\text{ cm}^{-1}$ (NO_2); ^1H NMR (CDCl_3 , 400 MHz): δ 8.15 (d, $J = 2.0\text{ Hz}$, 1 H), 8.00 (dd, $J = 8.4, 2.0\text{ Hz}$, 1 H), 7.94 (d, $J = 8.8\text{ Hz}$, 1 H), 7.64 (s, 1 H), 7.12 (s, 1 H), 6.37 (s, 1 H), 6.63 (s, 1 H), 3.08 – 2.98 (m, 4 H), 2.30 (s, 3 H), 2.29 (s, 3 H), 1.27 (d, $J = 8.8\text{ Hz}$, 1 H), 1.17 (d, $J = 8.8\text{ Hz}$, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 146.5, 139.1, 138.8, 138.8, 138.0, 137.3, 136.5, 135.1, 131.5, 127.5, 125.3, 124.7, 122.9, 121.3, 55.9, 55.1, 42.7, 41.3, 40.8, 19.7, 19.6; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$ 317.1416, found 317.1419.

(4aR*,12bS*)-10,11-Dimethyl-5-nitro-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4d). Pale yellow solid; $R_f = 0.70$ (2% ethyl acetate in hexanes); IR 1506, 1334 cm^{-1} (NO_2); ^1H NMR (CDCl_3 , 400 MHz): δ 8.08 (d, $J = 8.0$ Hz, 1 H), 7.61 (dd, $J = 8.0, 1.2$ Hz, 1 H), 7.60 (s, 1 H), 7.29 (t, $J = 8.0$ Hz, 1 H), 7.09 (s, 1 H), 6.31 (s, 1 H), 6.30 (s, 1 H), 3.65 (d, $J = 9.6$ Hz, 1 H), 3.02 (d, $J = 9.6$ Hz, 1 H), 2.96 (s, 1 H), 2.72 (s, 1 H), 2.29 (s, 3 H), 2.28 (s, 3 H), 1.24 (d, $J = 8.8$ Hz, 1 H), 1.14 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.2, 138.0, 137.8, 137.2, 135.1, 134.8, 134.7, 131.5, 131.1, 127.8, 126.5, 126.2, 124.1, 123.3, 55.0, 54.3, 43.0, 40.4, 37.1, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$ 317.1416, found 317.1417.

(4aR*,12bS*)-6,7,10-Trimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4e). Colorless solid; $R_f = 0.75$ (1% ethyl acetate in hexanes); ^1H NMR (CDCl_3 , 400 MHz): δ 7.67 (s, 1 H), 7.66 (s, 1 H), 7.20 (d, $J = 7.6$ Hz, 1 H), 7.10 (s, 1 H), 7.04 (dd, $J = 7.6, 1.2$ Hz, 1 H), 6.35 (s, 1 H), 6.34 (d, $J = 1.6$ Hz, 1 H), 2.99 – 2.95 (m, 4 H), 2.39 (s, 3 H), 2.31 (s, 3 H), 2.28 (s, 3 H), 1.37 (d, $J = 8.8$ Hz, 1 H), 1.14 (d, $J = 8.5$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 137.5, 137.4, 136.0, 135.4, 135.3, 134.7, 134.3, 131.9, 131.3, 130.0, 129.6, 128.0, 123.4, 122.6, 55.4, 55.3, 42.8, 40.8, 40.7, 21.4, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{22}\text{H}_{22}$ 286.1721, found 286.1720.

(4aR*,12bS*)-6,7,11-Trimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4f). Colorless solid; $R_f = 0.75$ (1% ethyl acetate in hexanes); ^1H NMR (CDCl_3 , 400 MHz): δ 7.78 (d, $J = 8.0$ Hz, 1 H), 7.64 (s, 1 H), 7.14 (s, 1 H), 7.10 (s, 1 H), 7.03 (d, $J = 8.0$ Hz, 1 H), 6.36 (s, 2 H), 3.00 (s, 4 H), 2.37 (s, 3 H), 2.31 (s, 3 H), 2.29 (s, 3 H), 1.40 (d, $J = 8.8$ Hz, 1 H), 1.17 (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 137.6, 137.5, 137.4, 136.7, 135.7, 135.0, 134.3, 131.2, 131.7, 129.6, 129.5, 127.1, 123.3, 122.0, 55.4, 55.3, 43.0, 41.2, 40.7, 21.1, 19.7, 19.4; HMRS (EI): calcd for $\text{C}_{22}\text{H}_{22}$ 286.1722, found 286.1717.

(4aR*,12bS*)-10-Methoxy-6,7-dimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4g). Colorless solid; $R_f = 0.75$ (1% ethyl acetate in hexanes); IR 1506, 1334 cm^{-1} (NO_2); ^1H NMR (CDCl_3 , 400 MHz): δ 8.08 (d, $J = 8.0$ Hz, 1 H), 7.61 (dd, $J = 8.0, 1.2$ Hz, 1 H), 7.60 (s, 1 H), 7.29 (t, $J = 8.0$ Hz, 1 H), 7.09 (s, 1 H), 6.31 (s, 1 H), 6.30 (s, 1 H), 3.65 (d, $J = 9.6$ Hz, 1 H), 3.02 (d, $J = 9.6$ Hz, 1 H), 2.96 (s, 1 H), 2.72 (s, 1 H), 2.29 (s, 3 H), 2.28 (s, 3 H), 1.24 (d, $J = 8.8$ Hz, 1 H), 1.14 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.2, 138.0, 137.8, 137.2, 135.1, 134.8, 134.7, 131.5, 131.1, 127.8, 126.5, 126.2, 124.1, 123.3, 55.0, 54.3, 43.0, 40.4, 37.1, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$ 317.1416, found 317.1417.

riphenylene (4g). Colorless Solid; $R_f = 0.65$ (2% ethyl acetate in hexanes); ^1H NMR (CDCl_3 , 400 MHz): δ 7.59 (s, 1 H), 7.37 (d, $J = 2.4$ Hz, 1 H), 7.21 (d, $J = 8.4$ Hz, 1 H), 7.09 (s, 1 H), 6.80 (dd, $J = 8.4, 2.4$ Hz, 1 H), 6.33 (s, 1 H), 6.32 (s, 1 H), 3.86 (s, 3 H), 2.99 (s, 2 H), 2.95 (s, 1 H), 2.91 (s, 1 H), 2.29 (s, 3 H), 2.27 (s, 3 H), 1.34 (d, $J = 8.8$ Hz, 1 H), 1.47 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 158.0, 137.5, 137.4, 136.4, 135.6, 134.3, 133.2, 131.3, 131.0, 130.2, 129.4, 123.5, 113.0, 107.3, 55.4, 55.3, 55.2, 42.8, 40.8, 40.5, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{22}\text{H}_{22}\text{O}$ 302.1671, found 302.1669.

(4aR*,12bS*)-10-Bromo-6,7-dimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4h). Colorless solid; $R_f = 0.70$ (1% ethyl acetate in hexanes); ^1H NMR (CDCl_3 , 400 MHz): δ 7.96 (d, $J = 2.0$ Hz, 1 H), 7.55 (s, 1 H), 7.29 (dd, $J = 8.0, 2.4$ Hz, 1 H), 7.15 (d, $J = 8.4$ Hz, 1 H), 7.08 (s, 1 H), 6.34 – 6.32 (m, 2 H), 2.96 – 2.91 (m, 4 H), 2.29 (s, 3 H), 2.28 (s, 3 H), 1.31 (d, $J = 8.8$ Hz, 1 H), 1.14 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 137.7, 137.3, 137.0, 136.6, 135.3, 134.6, 134.4, 131.7, 131.3, 129.8, 128.2, 125.0, 123.6, 120.1, 55.4, 55.2, 42.7, 40.9, 40.7, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{19}\text{Br}$ 350.0670, found 350.0673.

(4aR*,12bS*)-6,7-Dimethyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylene (4i). Colorless solid; $R_f = 0.70$ (1% ethyl acetate in hexanes); ^1H NMR (CDCl_3 , 400 MHz): δ 7.91 (dd, $J = 6.4, 2.8$ Hz, 1 H), 7.68 (s, 1 H), 7.32 (dd, $J = 5.6, 2.0$ Hz, 1 H), 7.23 – 7.21 (m, 2 H), 7.12 (s, 1 H), 6.38 – 6.37 (m, 2 H), 3.05 – 3.00 (m, 4 H), 2.32 (s, 3 H), 2.30 (s, 3 H), 1.40 (d, $J = 8.8$ Hz, 1 H), 1.18 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 137.6, 137.5, 137.4, 136.2, 135.3, 134.3, 132.1, 131.3, 130.1, 129.5, 127.1, 126.1, 123.5, 122.0, 55.5, 55.3, 42.8, 41.2, 40.7, 19.7, 19.5; HMRS (EI+): calcd for $\text{C}_{21}\text{H}_{20}$ 272.1565, found 272.1569.

1-[(4aR*,12bS*)-6,7-Dimethyl-8b,9,14,14a-tetrahydro-9,14-epoxybenzo[f]tetraphen-3-yl)ethanone (4j). Pale yellow solid; $R_f = 0.60$ (8% ethyl acetate in

hexanes); IR 1675 cm⁻¹ (C=O); ¹H NMR (CDCl₃, 500 MHz): δ 8.51 (d, *J* = 1.5 Hz, 1 H), 7.83 (d, *J* = 7.5 Hz, 1 H), 7.70 (s, 1 H), 7.48 (d, *J* = 8.5 Hz, 1 H), 7.45 – 7.41 (m, 2 H), 7.26 – 7.22 (m, 2 H), 7.18 (s, 1 H), 5.37 (s, 2 H), 3.40 (d, *J* = 9.5 Hz, 1 H), 3.35 (d, *J* = 9.5 Hz, 1 H), 2.65 (s, 3 H), 2.33 (s, 3 H), 2.32 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 198.0, 145.7, 145.5, 140.4, 137.5, 135.7, 132.7, 132.5, 131.1, 130.2, 128.4, 127.3, 127.1, 127.0, 124.1, 122.4, 119.3, 119.2, 90.2, 44.3, 43.5, 26.7, 19.7, 19.6; HMRS (EI⁺): calcd for C₂₆H₂₂O₂ 366.1620, found 366.1615.

2,3-[(4a*R,12b*S**)-Dimethyl-8b,9,14,14a-tetrahydro-9,14-epoxybenzo[*f*]tetraphene (4k).** Colorless solid; *R*_f = 0.65 (7% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.90 (d, *J* = 7.6 Hz, 1 H), 7.68 (s, 1 H), 7.44 – 7.37 (m, 3 H), 7.28 – 7.23 (m, 4 H), 7.22 (s, 1 H), 5.37 (s, 2 H), 3.37 (d, *J* = 9.6 Hz, 1 H), 3.33 (d, *J* = 9.2 Hz, 1 H), 2.31 (s, 3 H), 2.30 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ 145.8, 145.7, 136.6, 134.8, 132.3, 132.1, 130.9, 129.9, 129.4, 127.5, 126.9, 123.9, 122.4, 119.2, 119.1, 90.3, 90.2, 43.9, 43.5, 19.7, 19.5; HMRS (EI⁺): calcd for C₂₄H₂₀O 324.1514, found 324.1518.

8,9-[(4a*R,12b*S**)-Dimethyl-10b,11,16,16a-tetrahydro-11,16-epoxydibenzo[*a*,*f*]tetraphene (4l).** Colorless solid; *R*_f = 0.70 (7% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 8.10 (d, *J* = 9.2 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.79 (s, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.65 – 7.59 (m, 2 H), 7.52 – 7.48 (m, 2 H), 7.35 – 7.31 (m, 2 H), 7.25 (s, 1 H), 5.50 (s, 1 H), 5.41 (s, 1 H), 3.92 (d, *J* = 9.6 Hz, 1 H), 3.52 (d, *J* = 9.6 Hz, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.5, 145.3, 136.8, 135.2, 133.4, 132.5, 132.2, 130.7, 130.1, 129.4, 129.1, 128.9, 127.6, 127.1, 127.0, 126.7, 125.2, 124.6, 123.4, 121.2, 119.7, 118.5, 90.6, 88.5, 43.3, 41.5, 19.8, 19.5; HMRS (EI⁺): calcd for C₂₈H₂₂O 374.1671, found 374.1668.

5,6-[(4a*R,12b*S**)-Dimethyl-7b,8,13,13a-tetrahydro-8,13-epoxytetrapheno[6,5-*b*]thiophene (4m).** Colorless Solid; *R*_f = 0.70 (7% ethyl acetate in hexanes); ¹H

NMR (CDCl₃, 400 MHz): δ 7.43 – 7.39 (m, 2 H), 7.32 (d, J = 7.2 Hz, 1 H), 7.31 (s, 1 H), 7.25 – 7.22 (m, 2 H), 7.14 (s, 1 H), 5.45 (s, 1 H), 5.41 (s, 1 H), 3.51 (d, J = 9.6 Hz, 1 H), 3.41 (d, J = 9.6 Hz, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ 145.9, 145.3, 136.6, 135.7, 135.4, 134.1, 131.4, 130.8, 128.5, 127.0, 126.9, 124.4, 124.0, 122.8, 119.8, 119.3, 90.1, 88.9, 45.3, 41.5, 19.6, 19.4; HMRS (EI): calcd for C₂₂H₁₈OS 330.1078, found 330.1083.

1-[(4a*R,12b*S**)-10,11-Dimethyl-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylen-7-yl]ethano-ne (4n).** Colorless Solid; R_f = 0.75 (2% ethyl acetate in hexanes); IR 1674 cm⁻¹ (C=O); ¹H NMR (CDCl₃, 400 MHz): δ 8.41 (s, 1 H), 7.71 (dd, J = 8.0, 1.6 Hz, 1 H), 7.67 (s, 1 H), 7.26 (d, J = 8.0 Hz, 1 H), 6.99 (s, 1 H), 3.18 (d, J = 10.0 Hz, 1 H), 3.13 (d, J = 10.0 Hz, 1 H), 2.61 (s, 3 H), 2.60 (s, 1 H), 2.29 (s, 3 H), 2.24 (s, 3 H), 1.70 – 1.62 (m, 2 H), 1.32 (d, J = 10.0 Hz, 1 H), 1.01 (dd, J = 10.4, 1.6 Hz, 1 H); ¹³C NMR (CDCl₃, 100 MHz): δ 198.0, 143.2, 136.9, 135.2, 134.9, 134.7, 132.1, 131.2, 130.3, 127.9, 126.9, 123.4, 121.6, 49.7, 49.2, 46.1, 45.3, 33.2, 30.2, 30.1, 26.5, 19.5, 19.4; HMRS (EI+): calcd for C₂₃H₂₄O 316.1827, found 316.1822.

1-[(4a*R,12b*S**)-1,4,4a,12b-Tetrahydro-1,4-methanotriphenylen-7-yl]ethano-ne (4o).** Pale yellow Solid; R_f = 0.70 (2% ethyl acetate in hexanes); IR 1675 cm⁻¹ (C=O); ¹H NMR (CDCl₃, 500 MHz): δ 8.50 (d, J = 1.5 Hz, 1 H), 7.97 (d, J = 9.5 Hz, 1 H), 7.77 (dd, J = 7.5, 1.5 Hz, 1 H), 7.38 (d, J = 8.0 Hz, 1 H), 7.33 (t, J = 2.0 Hz, 1 H), 7.27 – 7.25 (m, 2 H), 6.37 – 6.36 (m, 2 H), 3.06 (s, 2 H), 2.99 – 2.98 (m, 2 H), 2.63 (s, 3 H), 1.31 (d, J = 8.5 Hz, 1 H), 1.15 (d, J = 8.5 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz): δ 197.8, 143.5, 137.9, 137.8, 137.5, 135.4, 132.4, 130.9, 130.4, 128.3, 127.4, 126.5, 122.7, 122.5, 55.6, 55.4, 42.7, 41.6, 41.3, 26.5; HMRS (EI+): calcd for C₂₁H₁₈O 286.1358, found 286.1360.

1-[(4a*R,12b*S**)-4,4a,10,11,12,13b-Hexahydro-1*H*-1,4-methanocyclopenta[*b*]triphenylen-7-yl]ethanone (4p).** Pale yellow Solid; R_f = 0.75 (2% ethyl acetate in

hexanes); IR 1677 cm^{-1} (C=O); ^1H NMR (CDCl_3 , 400 MHz): δ 8.48 (d, J = 2.0 Hz, 1 H), 7.85 (s, 1 H), 7.77 (dd, J = 8.0, 1.6 Hz, 1 H), 7.37 (d, J = 8.0 Hz, 1 H), 7.19 (s, 1 H), 6.36 – 6.34 (m, 2 H), 3.03 (s, 2 H), 2.97 – 2.90 (m, 6 H), 2.63 (s, 3 H), 2.11 – 2.07 (m, 2 H), 1.32 (d, J = 8.8 Hz, 1 H), 1.13 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.0, 144.8, 143.4, 142.8, 137.9, 137.3, 135.9, 135.2, 133.0, 130.3, 128.9, 126.9, 125.9, 122.2, 118.4, 55.6, 55.5, 42.7, 41.6, 41.4, 32.6, 26.6, 25.4; HMRS (EI⁺): calcd for $\text{C}_{24}\text{H}_{22}\text{O}$ 326.1671, found 326.1670.

1-[(4aR*,12bS*)-1,4,4a,13b-Tetrahydro-1,4-methanotriphenyleno[2,3-d][1,3]dioxol-7-yl)ethanone (4q). Pale yellow Solid; R_f = 0.75 (2% ethyl acetate in hexanes); IR 1675 cm^{-1} (C=O); ^1H NMR (CDCl_3 , 400 MHz): δ 8.29 (s, 1 H), 7.75 (dd, J = 7.2, 2.8 Hz, 1 H), 7.42 (s, 1 H), 7.36 (d, J = 8.0 Hz, 1 H), 6.76 (s, 1 H), 6.34 (s, 2 H), 5.96 (s, 2 H), 3.05 – 2.96 (m, 4 H), 2.61 (s, 3 H), 1.24 (d, J = 9.4 Hz, 1 H), 1.15 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.2, 147.0, 142.8, 137.8, 137.5, 135.6, 132.6, 132.3, 130.7, 128.3, 126.8, 120.9, 109.4, 102.6, 101.2, 55.7, 55.2, 42.7, 41.7, 41.6, 22.6; HMRS (EI⁺): calcd for $\text{C}_{22}\text{H}_{18}\text{O}_3$ 330.1253, found 330.1257.

1-[(4aR*,12bS*)-10-Methyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylen-7-yl)ethanone and 1-[(4aR*,12bS*)-11-Methyl-1,4,4a,12b-tetrahydro-1,4-methanotriphenylen-7-yl)ethanone (4r and 4r'). Pale yellow Solid; R_f = 0.70 (2% ethyl acetate in hexanes); IR 1675 cm^{-1} (C=O); ^1H NMR (CDCl_3 , 400 MHz): δ 8.49 (d, J = 1.6 Hz, 1 H), 8.46 (d, J = 1.6 Hz, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.79 – 7.75 (m, 3 H), 7.39 – 7.37 (m, 2 H), 7.21 (d, J = 7.6 Hz, 1 H), 7.14 (s, 1 H), 7.08 – 7.05 (m, 2 H), 6.36 – 6.35 (m, 4 H), 3.06 – 2.96 (m, 8 H), 2.63 (s, 3 H), 2.62 (s, 3 H), 2.39 (s, 3 H), 2.35 (s, 3 H), 1.31 – 1.28 (m, 2 H), 1.15 – 1.13 (m, 2 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.9, 143.2, 142.8, 137.9, 137.7, 137.4, 137.3, 135.9, 135.2, 134.9, 132.5, 132.4, 130.7, 130.6, 130.4, 130.3, 130.0, 129.3, 128.2, 127.5, 127.4, 126.9, 123.1, 122.6, 122.3, 55.6, 55.5, 55.3, 55.2, 42.8, 42.7, 41.6, 41.2, 40.8, 26.6, 21.3, 21.1;

HMRS (EI+): calcd for C₂₂H₂₀O 300.1514, found 300.1515.

Procedure for Deoxyaromatization of 4j to Benzo[b]triphenylenes (7a). A round-bottom sidearm flask (25 mL) containing **4j** (1.00 mmol) was evacuated and purged with nitrogen gas three times. Dichloromethane (3.0 mL) and BF₃·OEt₂ (1.50 mmol) were added. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then poured into a saturated aqueous NaHCO₃ solution and extracted with dichloromethane. The organic layer was washed with brine, dried with MgSO₄, and concentrated under reduced pressure. The residue was recrystallized from a mixture of dichloromethane and hexane (1:3) to afford the desired product **7a**. Product **7b** was also prepared according to this procedure using **4k** as the substrate.

1-(6,7-Dimethylbenzo[f]tetraphen-3-yl)ethanone (7a). Colorless Solid; m.p. 276 – 277 °C, IR 1675 cm⁻¹ (C=O), ¹H NMR (CDCl₃, 500 MHz): δ 9.08 (d, *J* = 1.5 Hz, 1 H), 9.01 (s, 1 H), 8.90 (s, 1 H), 8.72 (d, *J* = 9.0, Hz, 1 H), 8.43 (s, 1 H), 8.32 (s, 1 H), 8.10 (dd, *J* = 9.5, 1.5 Hz, 2 H), 8.05 (d, *J* = 8.0 Hz, 2 H), 7.58 – 7.53 (m, 2 H), 2.76 (s, 3 H), 2.52 (s, 3 H), 2.51 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz): δ 198.1, 137.1, 136.9, 135.5, 133.7, 132.8, 131.9, 130.0, 128.8, 128.3, 128.2, 128.0, 127.5, 127.4, 126.6, 126.2, 126.1, 124.3, 124.2, 123.9, 123.6, 123.2, 121.7, 26.6, 20.3, 20.2; HMRS (EI+): calcd for C₂₆H₂₀O 348.1514, found 348.1520.

2,3-Dimethylbenzo[f]tetraphene (7b). Colorless Solid; m.p. 270 – 271 °C, ¹H NMR (CDCl₃, 400 MHz): δ 9.01 (s, 1 H), 8.98 (s, 1 H), 8.71 (dd, *J* = 6.0, 3.6 Hz, 1 H), 8.50 (dd, *J* = 6.0, 3.2 Hz, 1 H), 8.44 (s, 1 H), 8.26 (s, 1 H), 8.04 (d, *J* = 6.8 Hz, 2 H), 7.60 – 7.52 (m, 4 H), 2.50 (s, 3 H), 2.48 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ 136.5, 136.3, 132.2, 131.9, 130.1, 129.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.4, 126.9, 125.9, 125.7, 124.3, 124.1, 123.6, 123.1, 121.9, 121.5, 20.2; HMRS (EI+): calcd for C₂₄H₁₈ 306.1409, found 306.1403.

Procedure for the Isolation of Intermediate C (R = H and L = PPh₃). A round-bottom side-arm flask containing Pd(PPh₃)₄ (1.00 mmol), iodobenzene (1.00 mmol) and CsF (1.50 mmol) was purged with nitrogen gas three times. To the flask were added CH₃CN (6 mL) and norbornadiene (5.00 mmol), and the solution was stirred at ambient temperature for 6 h. At the end of the reaction, the solvent and the unreacted norbornadiene were removed in vacuo, and the residue was then washed with ether three times and ether layer was concentrated to give orthometallation intermediate **C** (R = H and L = PPh₃) in 69% yield.

The ¹H NMR spectrum of intermediate **C** was compared with our previous report.¹ In our previous report,¹ we have synthesized the intermediate **C** and characterized it very well.

Further, intermediate **C** (0.500 mmol) and CsF (0.750 mmol) was taken in 25 mL round-bottom flask and purged with nitrogen gas three times. To the flask were added CH₃CN (3 mL) and benzyne precursor (**3a**) (0.600 mmol), and the solution was stirred at ambient temperature for 6 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4i** in 75% yield.

References

1. Liu, C.-H.; Li, C.-S.; Cheng, C.-H. *Organometallics* **1994**, *13*, 18.

¹H and ¹³C NMR Spectra of Compound **4a**.

¹H and ¹³C NMR Spectra of Compound 4b.

¹H and ¹³C NMR Spectra of Compound 4c.

^1H and ^{13}C NMR Spectra of Compound **4d**.

^1H and ^{13}C NMR Spectra of Compound **4e**.

^1H and ^{13}C NMR Spectra of Compound **4f**.

¹H and ¹³C NMR Spectra of Compound 4g.

^1H and ^{13}C NMR Spectra of Compound **4h**.

^1H and ^{13}C NMR Spectra of Compound **4i**.

¹H and ¹³C NMR Spectra of Compound 4j.

^1H and ^{13}C NMR Spectra of Compound **4k**.

^1H and ^{13}C NMR Spectra of Compound **4l**.

^1H and ^{13}C NMR Spectra of Compound **4m**.

^1H and ^{13}C NMR Spectra of Compound **4n**.

¹H and ¹³C NMR Spectra of Compound **4o**.

^1H and ^{13}C NMR Spectra of Compound **4p**.

¹H and ¹³C NMR Spectra of Compound **4q**.

STANDARD 1H OBSERV

exp1 stah

SAMPLE REC-2-VT

date Apr 28 2006 dfrq 400.446

solvent CDC13 dn HI

file exp dpr 30

ACQUISITION

sfrq 400.447 dm nnn

tn 01 c

et 2.728 def 200

np 32768

sw 6006.0 lb 0.10

fb 3400

bs 4 wfile

tpwr 59 fn 65536

pw 6.8

g1 1.000 verr

tof 596.3 wekp

nt 32 vbx

ct 8 wnt

elock not used

gain

FLAGS

l1 n

ln n

dp y

DISPLAY

sp -200.4

vp 4094.6

vs 150

vc 0

wc 250

hzmm 16.82

ls 278.28

rfl 3307.1

rff 2893.2

th 6

lms 100.000

nm cdc ph

2.62 2.57 5.27 7.21 9.71 20.26 15.20 4.45

2.38 7.44 2.54 8.71 14.90 4.43

3.061 3.037 3.013 2.989 2.965 2.941 2.917 2.893 2.869 2.845 2.821 2.797 2.773 2.749 2.725 2.701 2.677 2.653 2.629 2.605 2.581 2.557 2.533 2.509 2.485 2.461 2.437 2.413 2.389 2.365 2.341 2.317 2.293 2.269 2.245 2.221 2.197 2.173 2.149 2.125 2.101 2.077 2.053 2.029 2.005 1.981 1.957 1.933 1.909 1.885 1.861 1.837 1.813 1.789 1.765 1.741 1.717 1.693 1.669 1.645 1.621 1.597 1.573 1.549 1.525 1.501 1.477 1.453 1.429 1.405 1.381 1.357 1.333 1.309 1.285 1.261 1.237 1.213 1.189 1.165 1.141 1.117 1.093 1.069 1.045 1.021 0.997 0.973 0.949 0.925 0.901 0.877 0.853 0.829 0.805 0.781 0.757 0.733 0.709 0.685 0.661 0.637 0.613 0.589 0.565 0.541 0.517 0.493 0.469 0.445 0.421 0.397 0.373 0.349 0.325 0.301 0.277 0.253 0.229 0.205 0.181 0.157 0.133 0.109 0.085 0.061 0.037 0.013

COCH₃

COCH₃

ppm

¹H and ¹³C NMR Spectra of Compound 7a.

^1H and ^{13}C NMR Spectra of Compound **7b**.