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Supplementary Material

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Formation of Macrocycles by Catalytic Intramolecular Aromatic Cycloaddition of Metal Carbenes to Remote Arenes

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1,2-Benzenedimethanol. Phthalide (100.0 g, 74.55 mmol) and sodium borohydride (60.0 g, 1.59 mol) were stirred together in 1.0 L of absolute ethanol for four days at room temperature. The solvent was removed under reduced pressure and the resulting voluminous white solid was suspended in 1 L of water. This mixture was acidified to pH 3 using 6 *N* HCl, and the resulting solution was exhaustively extracted with ethyl acetate. The combined organic layer (approximately 1 L) was then washed three times with 150 mL portions of 0.5 *N* NaOH and brine and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent under reduced pressure yielded 89.6 g (87%) of pure 1,2-benzenedimethanol as a white solid, mp 62-64°C (lit[1] mp 63-65°C).

(2-Benzyloxymethyl)benzyl Alcohol. Sodium hydride (1.25 g, 35.0 mmol, 50% dispersion in oil) was washed with hexanes, suspended in 300 mL of freshly distilled THF, and then cooled to 0°C. To this suspension was added 1,2-benzenedimethanol (10.0 g, 77.76 mmol) in 100 mL of THF. After 30 minutes at 0°C, benzyl bromide (3.80 g, 22.2 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature overnight. Water (150 mL) and ethyl acetate (250 mL)

were added, and the layers were separated. The water layer was washed twice with 40-mL portions of ethyl acetate, and the combined organic layer was washed with brine (75 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting clear oil was purified by passing through a plug of silica gel using 2:1 hexanes:ethyl acetate as the eluent to yield 4.54 g (90%) of the title alcohol as a clear liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41-7.29 (comp, 9 H), 4.65 (s, 2 H), 4.64 (s, 2 H), 4.58 (s, 2 H), 2.91 (bs, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.2, 137.3, 135.6, 129.6, 129.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 72.3, 70.8, 63.2; IR ($CHCl_3$) 3467 cm^{-1}. The excess 1,2-benzenedimethanol was recovered in 92% yield by flushing the silica gel with pure ethyl acetate.

(2-Benzyloxymethyl)benzyl Diazoacetate (1). (2-Benzyloxymethyl)benzyl alcohol (4.44 g, 19.62 mmol) was dissolved in 150 mL of anhydrous THF and the solution was cooled to 0°C. Triethylamine (0.28 mL, 1.96 mmol) and diketene (2.14 g, 25.51 mmol) were added sequentially, and the reaction solution was allowed to warm to room temperature overnight. At this point, tlc analysis (3:1 hexanes:ethyl acetate) indicated complete conversion of starting material to the acetoacetate. The reaction solution was again cooled to 0°C, and triethylamine (3.01 mL, 21.6 mmol) was added, followed by methanesulfonyl azide (2.85 g, 23.6 mmol). This solution was allowed to warm to room temperature overnight, and conversion to the diazoacetoacetate was confirmed by tlc analysis. Water (75 mL) and ethyl acetate (200 mL) were added, and the resulting layers were separated. The organic layer was washed twice with 50-mL portions of water, and the combined aqueous layer was back-extracted with ethyl acetate (40 mL). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. Removal of solvent under reduced pressure yielded the crude diazoacetoacetate as a light brown oil (the identity of this material was confirmed by ^{1}H NMR analysis). The diazoacetoacetate was dissolved in 150 mL of THF, and pyrrolidine (4.33 g, 60.8) was added. The cleavage reaction was monitored by tlc (double development of the tlc plate in 5:1 hexanes:ethyl acetate). When the reaction was complete (8 hours), ethyl acetate (150 mL) was added and the organic layer was washed twice with 50 mL portions of brine (50 mL) and dried over anhydrous $MgSO_4$. Removal of solvent under reduced pressure yielded the crude diazoacetate as a light brown oil. Purification via column chromatography on silica gel (3:1 hexanes:ethyl acetate) yielded pure **1** as a bright yellow liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.29 (m, 9 H), 5.30 (s, 2 H), 4.75 (bs, 1 H), 4.62 (s, 2 H), 4.60 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.1, 137.6, 135.5, 130.5, 130.3, 129.6, 129.5, 129.2, 128.9, 128.8, 128.7, 73.6, 71.0, 65.1, 47.3;

IR (neat) 2104 (C=N_2), 1702 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.96; H, 5.40; N. 9.38.

$Rh_2(pfb)_4$-Catalyzed Diazo Decomposition of 1. Diazoacetate **1** (300 mg, 1.01 mmol) was dissolved in 10 mL of freshly distilled CH_2Cl_2 and added to $Rh_2(pfb)_4$ (11 mg, 0.010 mmol, 1.0 mol %) in 10 mL of refluxing CH_2Cl_2 via syringe pump over 10 h. The reaction solution was passed through a plug of silica gel to remove the catalyst, and the crude reaction mixture was purified by column chromatography on silica gel using 5:1 hexanes:ethyl acetate as the eluent to yield three products in 67% combined yield. Two of the products (**3** and **4**) eluted together, and attempts at further separation were not successful.

5,6-Benzo-3,8-dioxabicyclo[8.5.0]pentadecan-10,12,14-trien-2-one (2). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.26 (comp, 4 H), 6.72-6.67 (dd, *J* = 11.0, 5.6 Hz, 1 H), 6.61-6.55 (dd, *J* = 11.0, 5.8 Hz, 1 H), 6.28-6.21 (comp, 2 H), 6.04 (d, *J* = 13.0 Hz, 1 H), 5.82-5.77 (dd, *J* = 9.4, 5.9 Hz, 1 H), 4.97 (d, *J* = 10.6 Hz, 1 H), 4.95 (d, *J* = 13.0 Hz, 1 H), 4.39-4.30 (comp, 2 H), 4.09 (d, *J* = 12.6 Hz, 1 H), 2.61 (d, *J* = 5.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 136.2, 135.5, 131.4, 130.6, 129.8, 129.2, 128.4, 125.2, 125.1, 124.4, 121.5, 72.0, 71.6, 66.6, 46.3; mass spectrum, *m/z* (relative abundance): 269 (3, M+1), 268 (15, M), 238 (13), 194 (12), 193 (23), 179 (42), 148 (18), 119 (100), 118 (40), 105 (55), 104 (96), 103 (47), 91 (76), 78 (51), 77 (37), 65 (34). IR ($CHCl_3$): 1746 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.03; H, 6.07.

5,6-Benzo-3,8-dioxabicyclo[8.4.1]pentadeca-11,13,15-trien-2-one (3). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, *J* = 7.3 Hz, 1 H), 7.39 (dt, *J* = 1.6, 7.3 Hz, 2 H), 7.26 (dd, *J* = 7.3, 1.6 Hz, 1 H), 6.41-6.33 (m, 1 H), 6.26 (t, *J* = 8.0 Hz, 1 H), 6.20 (d, *J* = 8.0 Hz, 1 H), 5.35 (d, *J* = 12.2 Hz, 1 H), 4.58 (d, *J* = 12.2 Hz, 1 H), 4.39 (d, *J* = 12.2 Hz, 1 H), 4.26 (d, *J* = 9.5 Hz, 1 H), 4.18 (d, *J* = 9.5 Hz, 1 H), 4.13 (d, *J* = 12.2 Hz, 1 H), 3.80-3.65 (comp, 2 H), 3.14 (t, *J* = 9.5 Hz, 1 H). Assignment made by comparison with **10**. Anal. for **3/4**. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.03; H, 6.12.

5,6-Benzo-3,8-dioxabicyclo[8.3.2]pentadeca-11,13,15-trien-2-one (4). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.47 (d, *J* = 7.5 Hz, 1 H), 7.28 (dt, *J* = 1.4, 7.5 Hz, 2 H), 7.19 (dd, *J* = 7.5, 1.4 Hz, 1 H), 6.60 (d, *J* = 6.0 Hz, 1 H), 6.41-6.33 (comp, 2 H), 5.84 (t, *J* = 9.3 Hz, 1 H), 5.76 (t, *J* = 9.3 Hz, 1 H), 5.49 (d, *J* = 12.2 Hz, 1 H), 4.66 (d, *J* = 12.6 Hz, 1 H), 4.37 (d, *J* = 12.2 Hz, 1 H), 4.29 (d, *J* = 9.6 Hz, 1 H), 4.08 (d, *J* = 9.6 Hz, 1 H), 4.07 (t, *J* = 8.9 Hz, 1 H), 3.92 (d, *J* = 12.6 Hz, 1 H). Assignment made by comparison with **6** and **11**.

[2-(*p*-Methoxybenzyl)oxymethyl]benzyl Diazoacetate (5) was prepared in 52% isolated yield by the same procedure as described for **1**. Purification was performed by column chromatography on silica gel (1:1 hexanes:ethyl acetate) to yield pure **5** as a bright yellow liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.25 (comp, 6 H), 6.91 (dd, *J* = 6.9, 1.8 Hz, 2 H), 5.30 (s, 2 H), 4.76 (br s, C*H*=N_2), 4.59 (s, 2 H), 4.50 (s, 2 H), 3.81 (s, 3 H); IR (film) 2111 (C=N_2), 1694 (C=O); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 136.5, 134.2, 129.9, 129.3, 129.1, 128.3, 127.9, 113.6, 72.0, 69.4, 63.8, 55.1. Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.24; H, 5.56; N, 8.59. Found: C, 66.29; H, 5.61; N, 8.46.

$Rh_2(pfb)_4$-Catalyzed Diazo Decomposition of 5. Diazoacetate **5** (636 mg, 1.95 mmol) was dissolved in 10 mL of freshly distilled CH_2Cl_2 and added to $Rh_2(pfb)_4$ (20.6 mg, 19.5 μmol) in 10 mL of refluxing CH_2Cl_2 via syringe pump over 10 h. The reaction solution was passed through a plug of silica gel to remove the catalyst, and the crude reaction mixture was purified by column chromatography on silica gel using 5:1 hexanes:ethyl acetate as the eluent to yield two products in 85% combined yield (492 mg).

13-Methoxy-5,6-benzo-3,8-dioxabicyclo[8.3.2]pentadecan-10,12,14-trien-2-one (6). Pure **6** was isolated as a white crystalline solid (282 mg, 48% yield), mp 155-157°C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47 (d, *J* = 7.6 Hz, 1 H), 7.42-7.34 (m, 1 H), 7.28-7.13 (comp, 2 H), 6.42 (d, *J* = 6.8 Hz, 1 H), 6.37 (d, *J* = 9.5 Hz, 1 H), 5.70 (t, *J* = 9.5 Hz, 1 H), 5.54 (d, *J* = 12.4 Hz, 1 H), 5.49 (d, *J* = 6.8 Hz, 1 H), 4.64 (d, *J* = 12.4 Hz, 1 H), 4.39 (d, *J* = 12.4 Hz, 1 H), 4.25 (d, *J* = 9.5 Hz, 1 H), 4.12 (d, *J* = 9.5 Hz, 1 H), 4.08 (d, *J* = 9.5 Hz, 1 H), 3.89 (d, *J* = 12.4 Hz, 1 H), 3.71 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.2, 154.3, 137.9, 133.9, 132.1, 131.1, 130.8, 130.7, 129.6, 128.0, 127.7, 119.5, 96.0, 75.6, 66.3, 64.6, 57.6, 49.2; IR (film) 1721 cm^{-1}; mass spectrum, *m/z* (relative abundance). 299 (5, M+1), 298 (27, M), 225 (11), 224 (24), 209 (21), 149 (100), 91 (42), 77 (21), 65 (18). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.41; H, 6.10.

13-Methoxy-5,6-benzo-3,8-dioxabicyclo[8.5.0]pentadecan-10,12,14-trien-2-one (7). Pure **7** was isolated after column chromatographic separation from **6** as a colorless oil (29 mg, 5% yield): ^{1}H NMR (C_6D_6, 300 MHz) δ 7.02-6.88 (comp, 3 H), 6.83-6.76 (m, 1 H), 6.17-6.08 (comp, 3 H), 5.87 (d, *J* = 6.6 Hz, 1 H), 5.48 (d, *J* = 6.6 Hz, 1 H), 4.85 (d, *J* = 10.7 Hz, 1 H), 4.66 (d, *J* = 13.0 Hz, 1 H), 4.38 (d, *J* = 12.6 Hz, 1 H), 4.02 (d, *J* = 10.7 Hz, 1 H), 3.79 (d, *J* = 12.6 Hz, 1 H), 3.15 (s, 3 H), 2.92 (d, *J* = 4.2 Hz, 1 H); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.24 (comp, 4 H), 6.17 (d, *J* = 7.0 Hz, 1 H), 6.10 (dd, *J* = 10.0, 1.8 Hz, 1 H), 6.06 (d, *J* = 12.8 Hz, 1 H), 5.94 (dd, *J* =

10.0, 6.0 Hz, 1 H), 5.77 (dd, J = 7.0, 1.8 Hz, 1 H), 4.94 (d, J = 10.4 Hz, 1 H), 4.92 (d, J = 12.8 Hz, 1 H), 4.32 (d, J = 12.5 Hz, 1 H), 4.29 (d, J = 10.4 Hz, 1 H), 4.09 (d, J = 12.5 Hz, 1 H), 3.66 (s, 3 H), 2.80 (d, J = 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 160.5, 136.4, 135.5, 130.6, 129.8, 128.3, 127.8, 124.7, 123.9, 122.3, 102.7, 71.7, 66.6, 54.9, 54.7, 46.2; mass spectrum, *m/z* (relative abundance) 299 (14, M+1), 298 (66, M), 224 (12), 223 (20), 209 (23), 193 (20), 179 (62), 177 (50), 149 (55), 148 (31), 120 (39), 105 (36), 104 (80), 91 (100), 77 (52), 65 (47). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.42; H, 6.15.

***cis*-4-Benzyloxy-2-buten-1-yl Diazoacetate (8)** was prepared from *cis*-4-benzyloxy-2-buten-1-ol (4.02 g, 0.0282 mol) by the standard procedure (acetoacetylation with diketene, diazo transfer with methanesulfonyl azide, and deacylation with lithium hydroxide)[2] and purified by column chromatography on silica gel with 60% overall yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.24 (comp, 5 H), 5.98-5.88 (m, 1 H), 5.87-5.76 (m, 1 H), 4.73 (s, 1 H), 4.70 (d, J = 6.5 Hz, 2 H), 4.51 (s, 2 H), 4.12 (d, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.3, 137.8, 130.7, 128.2, 127.6, 127.5, 126.4, 72.2, 65.4, 60.3, 46.0; IR (film) 2112 (C=N_2), 1695 (C=O) cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.43; H, 5.73; N, 11.38. Found: C, 63.48; H, 5.66; N, 11.30.

Rh_2(pfb)$_4$-Catalyzed Diazo Decomposition of 8. To a refluxing solution of Rh_2(pfb)$_4$ (30.0 mg, 0.0285 mmol, 2.0 mol %) in 10 mL of anhydrous CH_2Cl_2 was added via syringe pump at 1.25 mL/h a solution of diazoacetate **7** (0.317 g, 1.290 mmol) in 10 mL of CH_2Cl_2. After addition was complete, the reaction mixture was cooled to room temperature and filtered through a plug (1x7 cm) of silica gel which was further rinsed with 15 mL of CH_2Cl_2. After evaporation of the solvent under reduced pressure, an NMR spectrum of the residue showed the formation of cycloheptatrienes in the ratio presented; this spectrum showed no evidence for the formation of **12**. The residue was purified by radial chromatography (10:1 hexanes:ethyl acetate).

3,8-Dioxabicyclo[8.5.0]pentadeca-5,10,12,14-tetraen-2-one (9) was isolated as an oil (28 mg, 0.13 mmol, 10% yield): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.42 (dd, J = 11.0, 5.5 Hz, 1 H), 6.29 (dd, J = 11.0, 5.5 Hz, 1 H), 6.04 (ddd, J = 18.8, 9.3, 5.4, 2 H), 5.79 (ddd, J = 16.0, 2.6, 2.6 Hz, 1 H), 5.72 (d, J = 5.5 Hz, 1 H), 5.54-5.42 (m, 1 H), 5.19 (dddd, J = 11.9, 4.7, 2.4, 2.3 Hz, 1 H), 4.46 (d, J = 14.1 Hz, 1 H), 4.42-4.32 (m, 1 H), 3.75 (dddd, J = 16.0, 4.7, 1.3, 1.3 Hz, 1 H), 3.44 (d, J = 14.1 Hz, 1 H), 3.30 (dd, J = 10.9, 7.0 Hz, 1 H), 2.56 (d, J = 5.7 Hz, 1 H); ^{13}C NMR (C_6D_6, 75 MHz) δ (carbonyl C not detected), 131.5, 129.1, 128.3, 127.8, 126.5, 125.1, 124.1, 122.2, 71.3, 63.6,

62.1, 46.3; HETCOR (short range), COSY, APT experiments performed; HETCOR experiment shows that the methine proton at 2.56 ppm is coupled to only one olefinic proton (at 5.54-5.42 ppm); mass spectrum, *m/z* (relative abundance) 219 (M+1, 0.2), 218 (M, 1.5), 188 (1.6), 174 (8.3) 148 (18), 129 (16), 120 (19), 119 (100), 118 (28), 104 (52), 91 (57), 90 (60), 78 (25), 77 (23). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.37; H, 6.53.

3,8-Dioxabicyclo[8.4.1]pentadeca-5,11,13,15-tetraen-2-one (10) was isolated as an oil (23 mg, 0.11 mmol, 8% yield): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.54 (d, *J* = 11.3 Hz, 1 H), 6.33 (dd, *J* = 11.3, 6.2 Hz, 1 H), 6.20 (dd, *J* = 9.7, 6.2 Hz, 1 H), 5.58 (dddd, *J* = 11.2, 11.1, 4.5, 2.2 Hz, 1 H), 5.16 (t, *J* = 9.2 Hz, 1 H), 5.14-5.04 (m, 1 H), 5.04 (d, *J* = 9.2 Hz, 1 H), 4.74 (dd, *J* = 14.4, 6.1 Hz, 1 H), 4.44 (t, *J* = 11.5 Hz, 1 H), 4.26 (d, *J* = 10.8 Hz, 1 H), 3.85 (dddd, *J* = 11.5, 4.6, 1.8, 1.6 Hz, 1 H), 3.68 (dddd, *J* = 14.4, 3.5, 2.0, 1.8 Hz, 1 H), 3.62 (d, *J* = 11.0 Hz, 1 H), 3.42 (t, *J* = 9.2 Hz, 1 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 169.0, 132.6, 131.8, 131.1, 130.8, 128.5, 128.2, 127.8, 124.3, 73.5, 62.8, 59.7, 41.3; HETCOR (short range) and COSY experiments performed, and they show that methine proton at 3.42 ppm is coupled with vinyl protons at 5.16 and 5.04 ppm; mass spectrum, *m/z* (relative abundance) 218 (M, 0.3), 174 (7.0), 148 (6), 129 (14), 120 (19), 119 (100), 118 (16), 104 (44), 91 (65), 90 (72), 78 (29), 77 (21). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.45; H, 6.41.

3,8-Dioxabicyclo[8.3.2]pentadeca-5,10,12,14-tetraen-2-one (11) was isolated as a white solid, mp 103-105°C (31 mg, 0.14 mmol, 11% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.52 (d, *J* = 5.8 Hz, 1 H), 6.40 (d, *J* = 9.8 Hz, 1 H), 6.33 (dd, *J* = 9.8, 5.8 Hz, 1 H), 5.92-5.73 (comp, 4 H), 5.02 (dd, *J* = 12.5, 5.8 Hz, 1 H), 4.57 (d, *J* = 12.5 Hz, 1 H), 4.00 (t, *J* = 9.1 Hz, 1 H), 3.82 (dd, *J* = 12.7, 6.6 Hz, 1 H), 3.79 (d, *J* = 12.7 Hz, 1 H), 3.71 (d, *J* = 10.0 Hz, 1 H), 3.65 (d, *J* = 10.0 Hz, 1 H); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.25 (d, *J* = 9.8 Hz, 1 H), 6.16 (d, *J* = 5.8 Hz, 1 H), 6.10 (dd, *J* = 9.5, 5.8 Hz, 1 H), 5.73 (dddd, *J* = 10.7, 10.3, 4.3, 1.3 Hz, 1 H), 5.49 (d, *J* = 9.5 Hz, 1 H), 5.43 (d, *J* = 9.5 Hz, 1 H), 5.35 (dt, *J* = 10.7, 6.4 Hz, 1 H), 4.93 (dddd, *J* = 12.7, 4.3, 1.3, 1.0, 1 H), 4.35 (d, *J* = 12.7 Hz, 1 H), 3.63 (t, *J* = 10.7 Hz, 1 H), 3.52-3.42 (comp, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.1, 140.2, 133.9, 130.8, 129.3, 126.8, 126.5, 123.5, 122.8, 74.9, 61.7, 58.3, 43.2; ^{13}C NMR (C_6D_6, 75 MHz) δ 171.3, 140.8, 134.7, 131.2, 129.8, 127.1, 125.5, 124.0, 123.0, 75.0, 62.1, 58.2, 43.7; HETCOR (short range and long range), COSY, APT experiments performed; APT and HETCOR (short range experiments) identify aliphatic methine at 43.2 ppm and 4.00 ppm in $CDCl_3$ and 43.7 ppm

and within the 3.52-3.42 ppm composite in C_6D_6, and with COSY this CH is coupled to two olefinic protons (at 5.92-5.72 ppm in $CDCl_3$ and 5.49/5.43 ppm in C_6D_6) which are coupled to another two olefinic protons (at 6.40 and 6.33 pm in $CDCl_3$ and at 6.25 and 6.10 ppm in C_6D_6); a HETCOR (long range) experiment demonstrated the connectivity of the aliphatic methine proton to the carbonyl carbon; mass spectrum, *m/z* (relative abundance) 219 (M+1, 0.1), 218 (M, 0.7), 188 (0.1), 174 (9.6), 148 (1.7), 129 (15), 120 (18), 119 (100), 104 (43), 91 (51), 90 (63), 78 (23), 77 (16). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.40; H, 6.35.

$Rh_2(cap)_4$-Catalyzed Diazo Decomposition of 8. To a refluxing solution of $Rh_2(cap)_4$ (7.0 mg, 0.010 mmol, 1.0 mol %) in 10 mL of anhydrous CH_2Cl_2 was added via syringe pump at 1.25 mL/h a solution of diazoacetate **8** (0.246 g, 1.00 mmol) in 5 mL of CH_2Cl_2. After addition was complete, the reaction mixture was cooled to room temperature and filtered through a short plug of silica gel to separate the catalyst. After washing the silica gel plug with 15 mL of CH_2Cl_2, the combined solution was evaporated under reduced pressure to remove the solvent. The residue was purified by radial chromatography (10:1 hexanes:ethyl acetate) to provide a colorless oil (0.122 g, 0.560 mmol, 56% yield) identified as **6-(benzyloxy)methyl-3-oxabicyclo[3.1.0]hexan-2-one (12)**: ^1H NMR (C_6D_6, 300 MHz) δ 7.24-7.04 (comp, 5 H), 4.20 (d, *J* = 12.0 Hz, 1 H), 4.13 (d, *J* = 12.0 Hz, 1 H), 3.57 (d, *J* = 9.8 Hz, 1 H), 3.49 (dd, *J* = 9.8, 5.2 Hz, 1 H), 3.29 (dd, *J* = 10.7, 6.6 Hz, 1 H), 3.13 (dd, *J* = 10.7, 8.3 Hz, 1 H), 1.63 (dd, *J* = 8.9, 6.2 Hz, 1 H), 1.26-1.18 (m, 1 H), 1.14-1.02 (m, 1 H); ^{13}C NMR (C_6D_6, 75 MHz) δ 173.2, 138.7, 128.6, 127.9, 127.8, 73.0, 65.5, 64.9, 22.4, 22.0, 21.3; IR (film) 1770 cm^{-1}; mass spectrum, *m/z* (relative abundance) 219 (M+1, 1), 218 (M, 3), 127 (4), 113 (10), 112 (99), 111 (21), 107 (14), 105 (15), 97 (13), 92 (95), 91 (100), 79 (31), 77 (30). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.38; H, 6.40.

***cis*-4-(*p*-Methoxybenzyloxy)-2-buten-1-yl Diazoacetate** was prepared from *cis*-4-(*p*-methoxybenzyloxy)-2-buten-1-ol by the same procedure employed for the synthesis of **8** and purified by column chromatography on silica gel (2:1 hexanes:ethyl acetate) as a bright yellow oil in 55% overall yield: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, *J* = 8.7 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 5.86-5.77 (m, 1 H), 5.74-5.64 (m, 1 H), 4.75 (br s, 1 H), 4.71 (d, *J* = 6.8 Hz, 2 H), 4.45 (s, 2 H), 4.12 (d, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 130.9, 129.9, 129.2, 126.3, 113.6, 71.9, 65.2, 60.4, 55.0, 46.0; IR (film) 2113 ($C{=}N_2$), 1695 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.68; H, 5.84; N, 10.14. Found: C, 60.72; H:, 5.78; N, 10.13.

$Rh_2(pfb)_4$-Catalyzed Diazo Decomposition of *cis*-4-(*p*-Methoxybenzyloxy)-2-buten-1-yl Diazoacetate. To a refluxing solution of $Rh_2(pfb)_4$ (11 mg, 0.010 mmol, 1.0 mol %) in 10 mL of anhydrous CH_2Cl_2 was added via syringe pump at 1.25 mL/h a solution of the diazoacetate (aaa mg, bbb mmol) in 10 mL of CH_2Cl_2. After addition was complete, the reaction mixture was cooled to room temperature and filtered through a plug of silica gel which was further rinsed with 15 mL of CH_2Cl_2.

13-Methoxy-3,8-dioxabicyclo[8.3.2]pentadeca-5,10,12,14-tetra-en-2-one (13) was isolated as a solid (68 mg, 0.27 mmol, 24% yield), mp 89-90°C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.40 (d, J = 9.5 Hz, 1 H), 6.37 (d, J = 6.9 Hz, 1 H), 5.90 (dddd, J = 10.8, 10.7, 4.9, 1.8 Hz, 1 H), 5.81 (dd, J = 10.7, 6.6 Hz, 1 H), 5.77 (t, 9.5 Hz, 1 H), 5.48 (d, J = 6.9 Hz, 1 H), 5.09 (dd, J = 13.0, 5.4 Hz, 1 H), 4.58 (d, J = 12.4 Hz, 1 H), 4.09 (dd, J = 9.5, 1.8 Hz, 1 H), 3.85 (dd, J = 13.0, 6.6 Hz, 1 H), 3.78 (d, J = 12.4 Hz, 1 H), 3.69 (s, 3 H), 3.71-3.60 (comp, 2 H); ^{1}H NMR (C_6D_6, 300 MHz) δ 6.32 (d, J = 9.5 Hz, 1 H), 6.15 (d, J = 7.0 Hz, 1 H), 5.76 (dddd, J = 10.6, 10.5, 4.8, 1.8 Hz, 1 H), 5.51 (t, J = 9.5 Hz, 1 H), 5.33 (dt, J = 10.6, 6.7 Hz, 1 H), 5.19 (d, J = 6.7 Hz, 1 H), 5.02 (dd, J = 13.0, 6.2 Hz, 1 H), 4.45 (d, J = 13.0 Hz, 1 H), 3.98 (dd, J = 9.5, 1.8 Hz, 1 H), 3.70 (t, J = 10.5 Hz, 1 H), 3.58 (d, J = 12.8 Hz, 1 H), 3.47 (dd, J = 10.5, 4.8 Hz, 1 H), 3.42 (dd, J = 12.8, 7.0 Hz, 1 H), 3.11 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 154.0, 134.1, 130.3, 128.2, 125.1, 119.6, 113.9, 96.2, 75.3, 61.1, 58.6, 55.6, 49.1; ^{13}C NMR (C_6D_6, 75 MHz) δ 170.4, 154.3, 134.6, 130.7, 129.5, 128.4, 124.8, 119.6, 96.7, 75.2, 61.3, 58.3, 55.9, 49.6; HETCOR (short range), COSY, NOESY, APT experiments performed; COSY experiment showed connectivity from absorption at 3.98 ppm to triplet at 5.51 ppm which was connected to doublet at 6.32 ppm (in C_6D_6); IR ($CHCl_3$) 1737 cm^{-1}; mass spectrum, *m/z* (relative abundance) 248 (M, 16), 204 (12), 173 (18), 149 (100), 121 (86), 105 (10), 91 (72), 77 (60).

13-Methoxy-3,8-dioxabicyclo[8.5.0]pentadeca-5,10,12,14-tetraen-2-one (14) was isolated as a mixture with *p*-anisaldehyde and one other, but unidentified, product; ^{1}H NMR ($CDCl_3$, 300 Mz) δ 6.14 (dd, J = 6.5, 1.2 Hz, 1 H), 6.11 (dt, J = 9.8, 1.5 Hz, 1 H), 6.01 (dd, J = 9.8, 6.4 Hz, 1 H), 5.85-5.75 (comp, 2 H), 5.72-5.66 (m, 1 H), 4.47 (d, J = 14.2 Hz, 1 H), 4.44-4.38 (m, 1 H), 4.23 (ddt, J = 15.7, 4.4, 1.2 Hz, 1 H), 4.12-4.07 (m, 1 H), 3.86 (d, J = 14.2 Hz, 1 H), 3.68 (s, 3 H), 3.63 (dd, J = 11.0, 7.0 Hz, 1 H), 2.72 (d, J = 6.4 Hz, 1 H); mass spectrum, *m/z* (relative abundance) 249 (4, M+1), 248 (22, M), 179 (42), 137 (52), 136 (56), 135 (45), 134 (73), 121 (100), 104 (64), 91

(42), 78 (31), 77 (27).

2-(Benzyloxymethyl)benzyloxyacetic acid. Sodium hydride (1.4 g, 34.2 mmol, 60% dispersion in oil) was washed with hexane, suspended in 70 mL of freshly distilled THF, and then cooled to 0°C. To this suspension was added (2-benzyloxymethyl)benzyl alcohol (5.2 g, 22.8 mmol) in 70 mL of THF. The stirred mixture was allowed to rise room temperature. After 30 min, the suspension was cooled to 0°C, and ethyl bromoacetate (2.8 mL, 25 mmol) was added *via* syringe. The stirred reaction mixture was allowed to come to room temperature and maintained at that temperature for 18 h. An additional 400 mg (17.1 mmol) of sodium hydride and 1.4 mL (12.5 mmol) of ethyl bromoacetate were added, and the yellowish suspension was refluxed for 5 h. Water (100 mL) was added, and most of the THF was removed under reduced pressure, after which the solution was extracted with ethyl acetate (100 mL), washed with brine (50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and then the resulting brown oil was dissolved in 20 mL of ethanol, and 7.2 mL of NaOH aqueous solution (4 M) was added. The mixture was stirred at 80°C overnight. Water (50 mL) was added, and the ethanol was removed under reduced pressure; then extraction was performed with ethyl acetate (50 mL), the aqueous layer was acidified with 1 N HCl solution, and extraction was performed with ethyl acetate. The organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and the solvent was removed to yield 3 g (58%, two steps) of the title acid as a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37-7.35 (comp, 9 H), 4.69 (s, 2 H), 4.64 (s, 2 H), 4.57 (s, 2 H), 4.11 (s, 2 H); IR (neat) 3550-2600 (COO-H), 1733 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.32; H, 6.29. Found, C, 71.17; H 6.10.

3-[2-(Benzyloxymethyl)benzyloxy]-diazo-2-propane (15). To a solution of (2-benzyloxymethyl)benzyloxy acetic acid (4 g, 14 mmol) in dry THF (50 mL) at -10°C and under Ar, was added triethylamine (2.14 mL, 15.4 mmol) and isobutylchloroformate (2 mL, 15.4 mmol). The mixture was stirred for 30 min, and ethereal diazomethane (35 mmol) was added dropwise over 30 min at -10°C. The mixture was then stirred overnight at room temperature. Diethyl ether (50 mL) was added and washed with water, $NaHCO_3$ solution, brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave an oil which was purified by flash column chromatography (1:3 ethyl acetate:hexanes) on silica to give 3 g (69%) of **14** as a bright yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44-7.29 (comp, 9 H), 5.71 (bs, 1 H), 4.62 (s, 2 H), 4.60 (s, 2 H), 4.56 (s, 2 H), 3.99 (bs, 2 H); IR (neat) 2106 ($C=N_2$), 1642 (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.68; H, 5.81; N, 9.03. Found: C, 69.77; H,

5.71; N, 9.14.

$Rh_2(pfb)_4$-Catalyzed Decomposition of Diazoketone 15. Diazoketone **15** (500 mg, 1.6 mmol) was dissolved in 10 mL of freshly distilled CH_2Cl_2 and added to $Rh_2(pfb)_4$ (26 mg, 0.024 mmol, 1.5 mol %) in 10 mL of refluxing CH_2Cl_2 *via* syringe pump over 10 h. The reaction solution was passed through a plug of silica gel, and the crude was purified by column chromatography on neutral alumina with 1:19 ethyl acetate:hexanes to give four products in 52% combined yield.

6,7-Benzo-4,9-dioxabicyclo[9.5.0]hexadecan-12,14,16-trien-2-one (20). Purification via column chromatography on silica gel (10-20% ethyl acetate:hexane), **16**: ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.30 (comp, 6 H), 6.35-6.29 (comp, 3 H), 4.49 (d, J = 12 Hz, 1 H), 4.42 (d, J = 11.7 Hz, 1 H), 4.35 (d, J = 12.8 Hz, 1 H), 4.27 (d, J = 18 Hz, 1 H), 4.22 (d, J = 12.4 Hz, 2 H), 4.41 (d, J = 12 Hz, 1 H), 4.04 (d, J = 18 Hz, 1 H), 1.70 (d, J = 4.7 Hz, 1 H). Purification via column chromatography on neutral alumina (1:19 ethyl acetate: hexane) **20**: ^1H NMR (C_6D_6, 500 MHz) δ 7.56 (d, J = 11.4 Hz, 1 H), 7.20-7.09 (comp, 5 H), 6.37 (dd, J = 11.4, 5.7 Hz, 1 H), 5.96 (dd, J = 9.4, 5.7 Hz, 1 H), 4.91 (dd, J = 9.4, 6.9 Hz, 1 H), 4.41 (d, J = 18.7 Hz, 1 H), 4.23 (d, J = 18.3 Hz, 1 H), 4.10 (d, J = 7.3 Hz, 2 H), 3.99 (d, J = 17.1 Hz, 1 H), 3.80 (d, J = 17.1 Hz, 1 H), 3.19 (t, J = 9.0 Hz, 1 H), 3.10 (dd, J = 9.4, 5.3 Hz, 1 H), 2.18 (m, 1 H), ^{13}C NMR (C_6D_6, 125 MHz) δ 103.2, 147.4, 131.0, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 125.9, 122.1, 73.5, 72.1, 68.1, 67.6, 41.8; HETCOR experiment performed; IR (neat) 3064-3030 (H-C=C), 1683 (C=O) cm^{-1}; mass spectrum, *m/z* (relative abundance) 282 (M^+, 11), 252 (2), 208 (3), 191 (4), 174 (6), 161 (100), 147 (12), 133 (6), 115 (9), 105 (47), 91 (78), 77 (23), 65 (12), 51 (6), 39 (5); MS *m/e* 282.1249 (calcd for $C_{18}H_{18}O_3$ *m/e* 282.1256).

6,7-Benzo-4,9-dioxabicyclo[9.3.2]hexadecan-11,13,16-trien-2-one (17). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.05 (comp, 8 H), 6.41 (dd, J = 17.6, 1.2 Hz, 1 H), 6.13 (dd, J = 17.6, 10.6 Hz, 1 H), 5.83 (dd, J = 10.3, 1.5 Hz, 1 H), 5.30 (bs, 2 H), 4.64 (bs, 2 H), 4.57 (bs, 2 H), 1.6 (bs, 1 H); ^1H NMR (C_6D_6, 500 MHz) δ 7.31-7.05 (comp, 8 H), 6.25 (dd, J = 17.3, 1.2 Hz, 1 H), 5.93 (dd, J = 17.3, 10.4 Hz, 1 H), 5.36 (bs, 2 H), 5.20 (dd, J = 10.4, 1.5 Hz, 1 H), 4.43 (bs, 2 H), 4.30 (s, 2 H), 1.32 (m, 1 H); ^{13}C NMR (C_6D_6), 500 MHz) δ 165.8, 133.75, 132.9, 132.8, 130.9, 130.8, 129.8, 129.4, 128.9, 128.8, 128.6, 128.3, 128.0, 72.7, 70.4, 64.1, 30.5; HETCOR experiment performed; mass spectrum, m/z (relative abundance) 282 (M^+, 4), 250 (7), 227 (30), 210 (12), 192 (7), 135 (45), 120 (27), 104 (58), 91 (100), 77 (15), 65 (15), 55 (28), 39 (5); MS *m/e* 282.1257 (calcd for

$C_{18}H_{18}O_3$ *m/e* 282.1256).

2-(Benzyloxymethyl)-9-oxabicyclo[5.4.0]dodecan-2,4,6-trien-12-one (19). ^1H NMR (C_6D_6, 500 MHz) δ 7.12-7.07 (comp, 5 H), 6.25 (m, 2 H), 5.79 (d, *J* = 5.4 Hz, 1 H), 5.65 (d, *J* = 5.1, 1 H), 4.29 (d, *J* = 11.1 Hz, 1 H), 4.21 (d, *J* = 13.7 Hz, 1 H), 4.17 (s, 2 H), 4.06 (d, *J* = 12 Hz, 2 H), 4.03 (d, *J* = 13.7 Hz, 1 H), 3.73 (d, *J* = 11.1 Hz, 1 H), 2.67 (s, 1 H); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.36-7.27 (comp, 5 H), 6.59-6.55 (comp, 2 H), 6.18 (d, *J* = 4.7 Hz, 1 H), 6.10 (d, *J* = 5.1 Hz, 1 H), 4.37-4.31 (comp, 5 H), 4.22 (d, *J* = 17.1 Hz, 1 H), 4.13 (d, *J* = 17.6 Hz, 1 Hz), 3.99 (d, *J* = 11.1 Hz, 1 H), 2.65 (s, 1 H); mass spectrum, *m/z* (relative abundance) 282 (M^+, 0.5), 224 (28), 191 (5), 177 (13), 162 (14), 148 (55), 131 (12), 118 (100), 104 (31), 91 (86), 84 (10), 77 (27), 63 (20), 57 (7), 51 (19), 39 (17); MS *m/e* 282.1253 (calcd for $C_{18}H_{18}O_3$ *m/e* 282.1256).

2-Benzyloxymethyl(benzaldehyde) (18). ^1H NMR ($CDCl_3$, 300 MHz) δ 10.22 (s, 1 H), 7.87 (d, *J* = 7.5 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.60 (t, *J* = 7.1 Hz, 1 H), 7.48 (t, *J* = 7.3 Hz, 1 H), 7.40-7.30 (comp, 5 H), 4.99 (s, 2 H), 4.66 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.3, 133.9, 132.4, 128.5, 128.5, 128.3, 127.7, 72.85, 69.48.

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