

## Supporting Information

### Synthesis of Benzonorcaradienes via a Gold(I)-Catalyzed [4+3] Annulation Reaction

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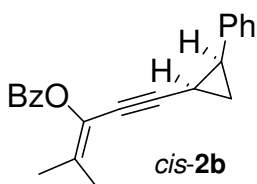
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**General Information.** Unless otherwise noted, all reagents were obtained commercially and used without further purification. Reagent grade nitromethane (NO<sub>2</sub>Me) was obtained from Aldrich. HPLC grade 1,2-dichloroethane was obtained from Fischer Scientific. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates using KMnO<sub>4</sub> stain and UV light to visualize the reaction components. Column chromatography was carried out on Merck 60 silica gel (32-63 μm). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker AV-300, AVQ-400, AVB-400, DRX-500, and AV-500 spectrometers referenced to chloroform, unless otherwise noted. Product ratios were determined by <sup>1</sup>H NMR unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the benzonorcaradiene analogs were obtained at 50 °C in order to minimize broadening and splitting from atropisomers. <sup>2</sup>H NMR spectra were recorded with a Bruker AVB-400 spectrometer. Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

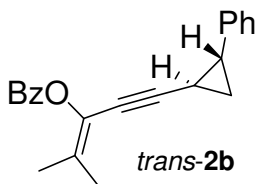
#### General procedure for the synthesis of benzonorcaradiene analogs:

Procedure A: The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF<sub>6</sub> (0.05 equiv.), AuPPh<sub>3</sub>Cl (0.05 equiv.), and NO<sub>2</sub>Me (0.4 M based on the diynyl ester). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of the diynyl ester (1 equiv.) and the appropriate olefin (4 equiv.) in NO<sub>2</sub>Me (0.4 M) was added. The resulting mixture (0.2 M) was left overnight. Analysis by TLC generally indicated complete consumption of starting material within minutes, and subsequent conversion of the enynecyclopropane to the benzonorcaradiene over several hours. The reaction mixture was loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of the described compounds.

Procedure B: The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF<sub>6</sub> (0.05 equiv.), AuPPh<sub>3</sub>Cl (0.05 equiv.), and dichloroethane (0.4 M based on the diyne ester). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of the diyne ester (1 equiv.) and the appropriate olefin (4 equiv.) in dichloroethane (0.4 M) was added. The resulting mixture (0.2 M) was left for 15 minutes and then heated in an oil bath at 50 °C overnight. The reaction mixture was loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of the described compounds.

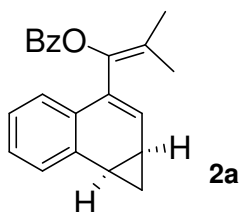


Styrene and **1** were reacted according to general procedure A. The reaction was quenched after 15 minutes by loading the mixture directly onto a silica column. Chromatography yielded enyneecyclopropane **2b** as a single diastereomer in 83% yield (43.0 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.10 (m, 2 H), 7.64 (tt, 1 H, *J* = 7.2, 1.6 Hz), 7.50 (t, 2 H, *J* = 7.2 Hz), 7.05-7.31 (m, 5 H), 2.40 (q, 1 H, *J* = 8.4 Hz), 1.98 (m, 1 H), 1.65 (s, 6 H), 1.43 (m, 1 H), 1.31 (q, 1 H, *J* = 6.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 164.1, 137.6, 133.2, 131.3, 130.0, 129.5, 128.4, 128.3, 127.8, 126.2, 125.6, 93.2, 73.6, 24.0, 20.1, 17.4, 14.7, 10.1; HRMS (FAB) Calcd. For [C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>] 316.1463, Found 316.1468.

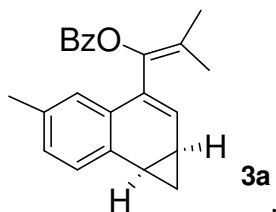


A mixture of diastereomers was obtained from the reaction of **1** (1 equiv.) and styrene (4 equiv.) with PtCl<sub>2</sub> (0.05 equiv) in toluene at 80 °C. The *trans*-diastereomer could be isolated by chromatography as a clear oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.11 (d, 2 H, *J* = 7.6 Hz), 7.60 (tt, 1 H, *J* = 7.6, 1.2 Hz), 7.49 (t, 2 H, *J* = 8.0 Hz), 7.05-7.31 (m, 5 H), 2.31 (m, 1 H), 1.99 (s, 3 H), 1.73 (s, 3 H), 1.68 (m, 1 H), 1.38 (m, 1 H), 1.31 (m, 1 H);

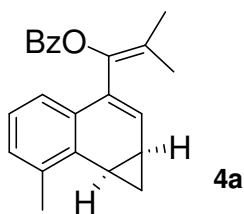
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  164.3, 140.5, 133.3, 131.9, 130.0, 129.5, 128.4, 126.2, 125.9, 125.8, 95.6, 70.5, 26.7, 20.6, 18.1, 17.5, 11.9; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{20}\text{O}_2]$  316.1463, Found 316.1463; Anal. calc'd for  $\text{C}_{22}\text{H}_{20}\text{O}_2$ : C, 83.51; H, 6.37. Found: C, 83.22; H, 6.27.



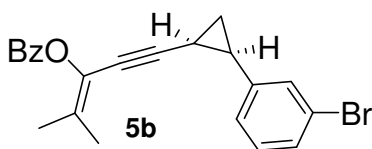
Styrene and **1** were reacted according to procedure A. Due to the larger scale of the reaction, the procedure was modified such that the reaction mixture was subjected to magnetic stirring. Benzonorcaradiene **2a** was isolated as an off-white solid in 80% yield (535 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.06 (d, 2 H,  $J = 8.0$  Hz), 7.30-7.70 (m, 5 H), 7.20 (m, 2 H), 6.60 (bs, 1 H), 2.44 (m, 1 H), 2.04 (bs, 1 H), 1.79 (s, 3 H), 1.71 (s, 3 H), 1.57 (bs, 1 H), -0.18 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  165.0, 136.2, 134.0, 133.3, 130.7, 130.3, 130.0, 128.7, 128.6, 127.4, 126.3, 126.0, 21.6, 20.0, 18.0, 10.3; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{20}\text{O}_2]$  316.1463, Found 316.1465; Anal. calc'd for  $\text{C}_{22}\text{H}_{20}\text{O}_2$ : C, 83.51; H, 6.37. Found: C, 83.15; H, 6.49.



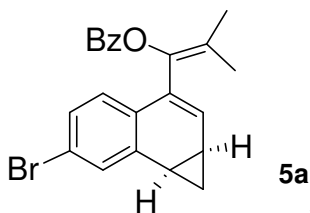
4-Me-Styrene and **1** were reacted according to procedure A. Benzonorcaradiene **3a** was isolated as a clear oil in 85% yield (39.6 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.06 (d, 2 H,  $J = 7.2$  Hz), 7.70-7.20 (m, 5 H), 7.06 (d, 1 H,  $J = 7.6$  Hz), 6.64 (d, 1 H,  $J = 5.2$  Hz), 2.50-2.30 (m, 4 H), 2.05 (m, 1 H), 1.84 (s, 3 H), 1.72 (s, 3 H), 1.54 (bs, 1 H), -0.18 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  164.7, 140.4, 134.9, 133.8, 132.9, 132.8, 130.5, 129.9, 129.4, 128.3, 128.0, 127.9, 126.5, 21.3, 20.5, 19.7, 17.6, 16.9, 9.8; HRMS (FAB) Calcd. For  $[\text{C}_{23}\text{H}_{22}\text{O}_2]$  330.1620, Found 330.1618.



2-Me-Styrene and **1** were reacted according to procedure A. Benzonorcaradiene **4a** was isolated as a clear oil in 82% yield (38.4 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.09 (d, 2 H,  $J = 7.2$  Hz), 7.65-7.35 (m, 4 H), 7.13 (m, 2 H), 6.61 (d, 1 H,  $J = 4.4$  Hz), 2.50 (m, 4 H), 2.05 (m, 1 H), 1.83 (s, 3 H), 1.76 (s, 3 H), 1.63 (bs, 1 H), -0.12 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  164.7, 135.8, 134.3, 133.1, 132.8, 130.4, 129.9, 129.5, 128.8, 128.7, 128.3, 125.1, 123.9, 19.6, 19.5, 17.5, 17.4, 14.0, 8.2; HRMS (FAB) Calcd. For  $[\text{C}_{23}\text{H}_{22}\text{O}_2]$  330.1620, Found 330.1624.

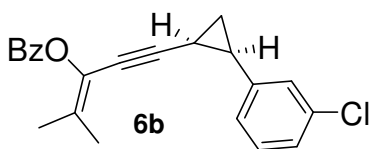


3-Br-Styrene and **1** were reacted according to procedure A. Enynecyclopropane **5b**, a yellow oil, was isolated as a single diastereomer in 59% yield (33.2 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.08 (dd, 2 H,  $J = 8.0, 0.75$  Hz), 7.64 (t, 1 H,  $J = 7.2$  Hz), 7.47 (t, 2 H,  $J = 7.5$  Hz), 7.41 (t, 1 H,  $J = 1.5$  Hz), 7.19 (m, 2 H), 7.04 (t, 1 H,  $J = 7.5$  Hz), 2.34 (q, 1 H,  $J = 8.5$  Hz), 1.97 (m, 1 H), 1.68 (s, 3 H), 1.64 (s, 3 H), 1.41 (m, 1 H), 1.28 (q, 1 H,  $J = 6.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  164.6, 140.7, 133.7, 132.1, 132.0, 130.5, 129.9, 129.8, 127.5, 126.0, 122.4, 93.1, 74.4, 24.1, 20.6, 17.9, 15.3, 10.8; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}]$  394.0568, Found 394.0565; Anal. calc'd for  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}$ : C, 66.85; H, 4.84. Found: C, 66.37; H, 4.96.

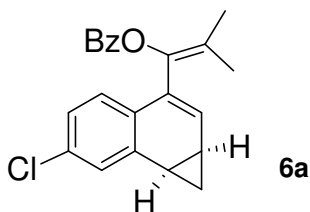


3-Br-Styrene and **1** were reacted according to procedure B. The reaction resulted in a 1:1.2 (**5a**:**5b**) mixture of products isolated in 56% combined yield (29.4 mg). Subsequent

column chromatography afforded pure **5a** as a clear oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.04 (d, 2 H,  $J = 7.0$  Hz), 7.55 (t, 1 H,  $J = 7.0$  Hz), 7.52 (d, 1 H,  $J = 2.0$  Hz), 7.50-7.30 (m, 4 H), 6.62 (d, 1 H,  $J = 5.0$  Hz), 2.43 (m, 1 H), 2.05 (m, 1 H), 1.80 (s, 3 H), 1.70 (s, 3 H), 1.60 (bs, 1 H), -0.16 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  165.0, 138.4, 134.3, 133.4, 131.3, 130.6, 130.3, 129.0, 128.8, 128.2, 127.9, 121.0, 21.0, 19.9, 18.0, 17.8, 10.2; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}]$  394.0568, Found 394.0572. The regiochemistry was assigned by the coupling constant of the  $^1\text{H}$  NMR resonance at 7.52 ppm.

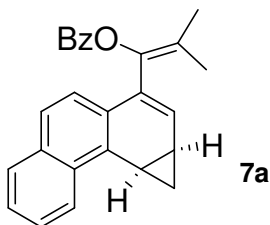


3-Cl-Styrene and **1** were reacted according to procedure A. Enyneecyclopropane **6b** was isolated as a 12:1 mixture with **6a** in 57% yield (23.1 mg). Subsequent column chromatography afforded pure **6b**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.08 (d, 2 H,  $J = 7.2$  Hz), 7.65 (m, 1 H), 7.53 (m, 2 H), 7.12 (s, 1 H), 7.20-7.00 (m, 3 H), 2.34 (m, 1 H), 2.01 (m, 1 H), 1.67 (s, 3 H), 1.63 (s, 3 H), 1.44 (m, 1 H), 1.32 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.2, 139.9, 133.7, 133.3, 131.7, 130.1, 129.6, 129.1, 128.6, 128.4, 126.7, 126.5, 125.6, 92.7, 74.0, 23.7, 20.2, 17.5, 14.9, 10.3; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{19}\text{O}_2\text{Cl}]$  350.1074, Found 350.1072.

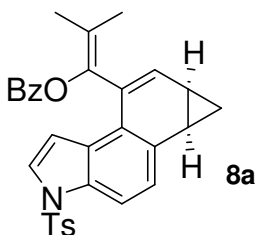


Styrene and **1** were reacted according to procedure B. The reaction resulted in a 2:1 (**6a**:**6b**) mixture of products isolated in 60% yield (39.3 mg). Subsequent column chromatography resulted in isolation of pure benzonorcaradiene **6a** as a clear oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.03 (m, 2 H), 7.70-7.10 (m, 6 H), 6.60 (m, 1 H), 2.39 (m, 1 H), 2.04 (m, 1 H), 1.78 (d, 3 H,  $J = 15.0$  Hz), 1.69 (d, 3 H,  $J = 15.0$  Hz), 1.60 (bs, 1 H), -0.17 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  165.1, 138.3, 134.3, 133.4,

132.9, 130.5, 130.3, 128.7, 128.4, 128.2, 127.7, 126.1, 21.4, 19.9, 18.1, 17.8, 10.3; HRMS (FAB) Calcd. For  $[C_{22}H_{19}O_2Cl]$  350.1074, Found 350.1083; Anal. calc'd for  $C_{22}H_{19}O_2Cl$ : C, 75.32; H, 5.46. Found: C, 74.96; H, 5.25. The regiochemistry was assigned in analogy to **5a**.

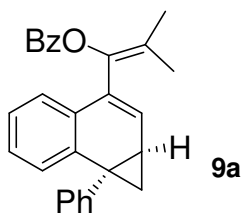


1-Vinyl-naphthalene and **1** were reacted according to procedure A. Benzonorcaradiene **7a** was isolated as a white solid in 74% yield (40.8 mg).  $^1H$  NMR ( $CDCl_3$ , 500 MHz, 50 °C)  $\delta$  8.29 (d, 1 H,  $J = 8.5$  Hz), 8.06 (d, 2 H,  $J = 8.0$  Hz), 7.83 (d, 1 H,  $J = 8.0$  Hz), 7.72 (m, 2 H), 7.65-7.35 (m, 5 H), 6.72 (bs, 1 H), 3.07 (m, 1 H), 2.19 (m, 1 H), 1.84 (s, 3 H), 1.74 (m, 4 H), -0.14 (bs, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz, 50 °C)  $\delta$  164.6, 133.3, 132.9, 132.8, 132.2, 131.3, 130.3, 129.8, 128.8, 128.2, 126.5, 125.9, 125.5, 125.3, 124.5, 123.4, 19.6, 17.6, 16.3, 7.1; HRMS (FAB) Calcd. For  $[C_{26}H_{22}O_2]$  366.1620, Found 366.1612.

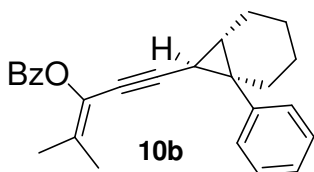


5-Vinyl-*N*-tosyl-indole and **1** were reacted according to procedure A. Benzonorcaradiene **8a**, a white solid, was isolated as a 10:1 mixture of regioisomers in 54% yield (45.5 mg).  $^1H$  NMR ( $CDCl_3$ , 500 MHz, 50 °C)  $\delta$  The following resonances could be resolved for the major regioisomer: 8.00-7.10 (m, 13 H), 6.90 (m, 1 H), 2.52 (m, 1 H), 2.32 (d, 3 H,  $J = 8.0$  Hz), 2.09 (m, 1 H), 1.90-1.50 (m, 7 H), -0.30 (dbs, 1 H,  $J = 43$  Hz). The following resonances could be resolved for the minor regioisomer: 8.15 (m, 2 H), 6.56 (m, 1 H), -0.17 (m, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  164.3, 144.5 (d), 141.4 (d), 136.3 (d), 135.7 (d), 134.2 (d), 132.8 (d), 131.3 (d), 130.4-129.4 (m, at least 5 signals), 128.2 (d), 127.5 (d), 126.7 (d), 126.6 (d), 125.5 (d), 125.4 (d), 123.8, 122.5 (d), 122.1, 21.6, 21.3

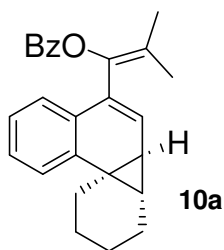
(d), 19.5 (d), 17.8 (d), 17.3 (d), 9.0 (d); HRMS (FAB) Calcd. For  $[C_{31}H_{27}NO_4S]$  509.1666, Found 509.1659. The major regioisomer was assigned by  $^1H$  COSY.



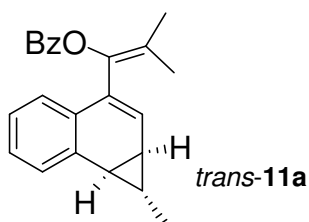
1,1-Diphenyl-ethylene and **1** were reacted according to procedure B. Benzonorcaradiene **9a** was isolated as a white solid in 71% yield (41.9 mg).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 50  $^{\circ}C$ )  $\delta$  8.13 (d, 2 H,  $J = 7.2$  Hz), 7.80-7.00 (m, 12 H), 6.76 (d, 1 H,  $J = 4.8$  Hz), 2.27 (bs, 1 H), 2.16 (m, 1 H), 1.81 (s, 3 H), 1.68 (s, 3 H), 0.27 (bs, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz, 50  $^{\circ}C$ )  $\delta$  164.8, 138.8, 132.9, 132.3, 130.6, 130.4, 130.0, 128.8, 126.7, 126.6, 125.8, 125.4, 33.8, 26.9, 19.7, 17.6, 15.2; HRMS (FAB) Calcd. For  $[C_{28}H_{24}O_2]$  392.1776, Found 392.1776; Anal. calc'd for  $C_{28}H_{24}O_2$ : C, 85.68; H, 6.16. Found: C, 85.35; H, 6.33.



1-phenyl-cyclohexene and **1** were reacted according to procedure A. The reaction was quenched after 15 minutes by loading the mixture directly onto a silica column. Chromatography yielded enyneecyclopropane **10b** as a 5:1 (*cis:trans*) mixture of diastereomers. Subsequent column chromatography resulted in isolation of enyneecyclopropane **10b** as a single diastereomer in 67% yield (37.4 mg).  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  8.05 (d, 2 H,  $J = 8.0$  Hz), 7.60 (t, 1 H,  $J = 8.0$  Hz), 7.44 (t, 2 H,  $J = 8.0$  Hz), 7.30 (m, 2 H), 7.17 (t, 2 H,  $J = 8.0$  Hz), 7.02 (t, 1 H,  $J = 7.5$  Hz), 2.15 (m, 2 H), 1.90-1.70 (m, 3 H), 1.63 (d, 1 H,  $J = 5.0$  Hz), 1.57 (s, 3 H), 1.50 (s, 3 H), 1.50-1.10 (m, 4 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  146.1, 144.9, 133.1, 130.4, 130.0, 129.6, 128.7, 128.3, 128.0, 126.0, 125.8, 94.6, 74.2, 22.9, 32.3, 27.3, 23.0, 21.2, 21.1, 20.0, 19.2, 17.3; HRMS (FAB) Calcd. For  $[C_{26}H_{26}O_2]$  370.1933, Found 370.1926.



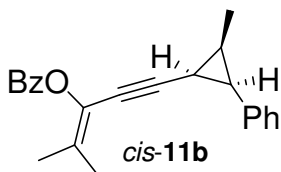
The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF<sub>6</sub> (0.05 equiv.), AuPPh<sub>3</sub>Cl (0.05 equiv.), and NO<sub>2</sub>Me (0.4 M based on **10b**). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of **10b** (1 equiv.) in NO<sub>2</sub>Me (0.4 M) was added. The resulting mixture (0.2 M) was left overnight. The reaction mixture was loaded directly onto a silica column and chromatographed to yield benzonorcaradiene **10a** as a clear oil in 90% yield (31.6 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 50 °C) δ 8.04 (d, 2 H, *J* = 7.5 Hz), 7.70-7.10 (m, 7 H), 6.58 (bs, 1 H), 2.61 (m, 1 H), 2.02 (bs, 2 H), 1.78 (s, 3 H), 1.72 (m, 5 H), 1.60-1.20 (m, 4 H), 0.41 (bs, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 50 °C) δ 164.6, 140.3, 133.6, 132.7, 130.3, 129.9, 128.2, 127.2, 126.5, 125.8, 125.7, 124.9, 30.3, 29.8, 27.4, 23.8, 22.6, 21.5, 21.0, 19.6, 17.5; HRMS (FAB) Calcd. For [C<sub>26</sub>H<sub>26</sub>O<sub>2</sub>] 370.1933, Found 370.1937.



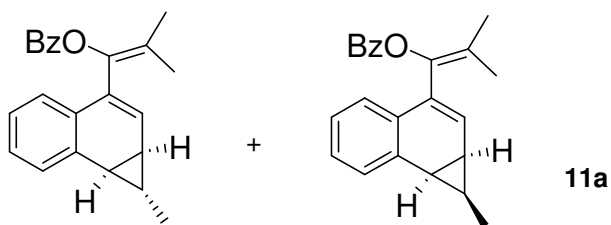
*trans*-β-Methyl styrene and **1** were reacted according to procedure A. Benzonorcaradiene *trans*-**11a** was isolated as a single diastereomer as an inseparable 10:1 mixture with the enynecyclopropane *trans*-**11b** in 90% yield (39.2 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 50 °C) δ The following resonances could be resolved for the major product: 8.06 (d, 2 H, *J* = 8.0 Hz), 7.55-7.15 (m, 7 H), 6.58 (bs, 1 H), 2.17 (m, 1 H), 1.80-1.70 (m, 7 H), 1.28 (bs, 3 H), 0.18 (bs, 1 H) The following resonances could be resolved for the minor product: 8.14 (d, 2 H, *J* = 8.0 Hz), 7.62 (m, 1 H), 7.04 (d, 2 H, *J* = 7.0 Hz), 2.51 (t, 1 H, *J* = 8.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 50 °C) δ The following resonances could be resolved for the major product:: 164.6, 135.5, 132.9, 132.8, 129.8, 128.2, 127.9, 126.8, 125.7, 125.4, 29.7, 25.5, 19.6, 17.8, 17.5, The following resonances could be resolved for the



minor product: 164.4, 34.3, , 23.3, 20.5, 14.5, The following resonances could not be resolved: 134.0, 131.1, 130.3, 129.5, 129.3, 128.3, 128.4, 128.0, 126.9, 126.0, 125.8, 125.3, 18.3; HRMS (FAB) Calcd. For  $[C_{23}H_{22}O_2]$  330.1620, Found 330.1627.

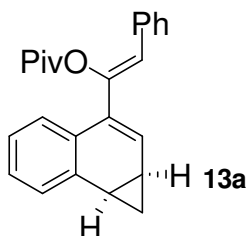


*cis*- $\beta$ -Methyl styrene and **1** were reacted according to procedure A. Enyne cyclopropane *cis*-**11b** was initially isolated as a 5:1 mixture with the benzonorcaradiene **11a** in 89% yield (55.2 mg). Subsequent chromatography resulted in isolation of pure *cis*-**11b**.  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  8.14 (m, 2 H), 7.65 (tt, 1 H,  $J = 7.0, 1.2$  Hz), 7.53 (t, 2 H,  $J = 7.2$  Hz), 7.42 (d, 2 H,  $J = 7.6$  Hz), 7.30-7.10 (m, 3 H), 2.39 (t, 1 H,  $J = 8.8$  Hz), 2.08 (t, 1 H,  $J = 8.8$  Hz), 1.84 (s, 3 H), 1.70 (s, 3 H), 1.54 (m, 1 H), 1.08 (d, 3 H,  $J = 6.4$  Hz);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  164.3, 135.7, 133.3, 131.0, 130.9, 130.1, 129.7, 128.4, 127.9, 126.2, 126.1, 92.0, 76.5, 26.4, 20.4, 18.0, 17.6, 12.3, 11.1; HRMS (FAB) Calcd. For  $[C_{23}H_{22}O_2]$  330.1620, Found 330.1618; Anal. calc'd for  $C_{23}H_{22}O_2$ : C, 83.60; H, 6.71. Found: C, 83.27; H, 6.78. The stereochemistry of *cis*-**11b** was confirmed by  $^1H$  NOE.

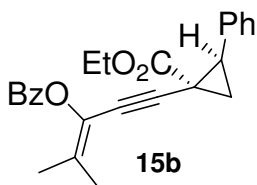


*cis*- $\beta$ -Methyl styrene and **1** were reacted according to procedure B. The reaction resulted in a 1.6:1 (**11a**:**11b**) mixture of products isolated in 64% yield (37.1 mg). **11a** was formed as a 0.8:1 mixture of diastereomers (the major isomer is the same as that formed in the reaction of *trans*- $\beta$ -methyl styrene) while **11b** was formed as a single (*cis*) diastereomer. Subsequent column chromatography resulted in isolation of pure benzonorcaradiene **11a** as a clear oil. Attempts to perform VT NMR in order to characterize the minor diastereomer resulted in increased formation of the major

diastereomer; the spectral data of the major diastereomer matched those reported for *trans*-**11a** above.

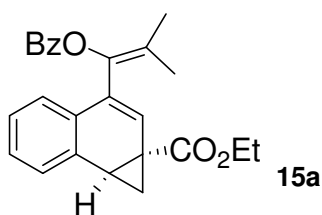


The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF<sub>6</sub> (0.05 equiv.), AuP(t-Bu)<sub>3</sub>Cl (0.05 equiv.), and dichloroethane (0.4 M based on the diyne ester). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of **12** (1 equiv.) and styrene (4 equiv.) in dichloroethane (0.4 M) was added. The resulting mixture (0.2 M) was left for 15 minutes and then heat in an oil bath at 50 °C overnight. The reaction mixture was loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of benzonorcaradiene **13a** as a 19:1 mixture of olefin isomers in 68% combined yield (29.2 mg) contaminated with the enyne cyclopropane (10:1 **13a**:**13b**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 50 °C) δ The following resonances could be identified for the major product: 7.80-7.10 (m, 9 H), 6.70 (d, 1 H, *J* = 5.6 Hz), 6.32 (s, 1 H), 2.60 (m, 1 H), 2.15 (m, 1 H), 1.72 (m, 1 H), 1.26 (s, 9 H), 1.57 (bs, 1 H), -0.15 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 50 °C) δ The following resonances could be identified for the major product: 175.6, 147.8, 135.9, 134.5, 132.4, 130.5, 128.7, 128.3, 127.4, 127.3, 126.2, 125.5, 119.3, 39.0, 27.1, 21.2, 17.2, 10.1; HRMS (FAB) Calcd. For [C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>] 316.1463, Found 316.1465; Anal. calc'd for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>: C, 83.51; H, 6.37. Found: C, 83.15; H, 6.49.

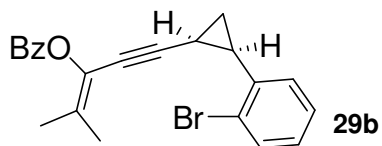


A solution of styrene (4 equiv.) and **14** (1 equiv.) in NO<sub>2</sub>Me (0.2 M) was added to a 1 dram vial containing AuCl (0.05 equiv.). The reaction was left overnight, and then loaded directly onto a silica column. Chromatography yielded enyne cyclopropane **15b** as

a single diastereomer in 83% yield (42.0 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.04 (d, 2 H,  $J = 7.5$  Hz), 7.61 (t, 1 H,  $J = 7.5$  Hz), 7.47 (t, 2 H,  $J = 7.5$  Hz), 7.20 (d, 2 H,  $J = 8.0$  Hz), 7.13 (t, 2 H,  $J = 7.5$  Hz), 7.03 (t, 1 H,  $J = 7.5$  Hz), 4.20 (m, 2 H), 3.05 (t, 1 H,  $J = 8.5$  Hz), 2.06 (dd, 1 H,  $J = 9.0, 4.5$  Hz), 1.82 (dd, 1 H,  $J = 8.0, 4.5$  Hz), 1.68 (s, 3 H), 1.62 (s, 3 H), 1.27 (t, 3 H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  171.1, 163.4, 135.1, 133.2, 132.2, 130.0, 129.5, 128.6, 128.3, 127.9, 127.1, 125.3, 88.9, 61.9, 36.0, 25.4, 24.6, 20.1, 17.4, 14.0; HRMS (FAB) Calcd. For  $[\text{C}_{25}\text{H}_{24}\text{O}_4]$  388.1675, Found 388.1669. The relative stereochemistry was assigned based upon the subsequent reactivity.

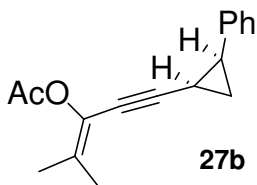


The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of  $\text{AgSbF}_6$  (0.05 equiv.),  $\text{AuPPh}_3\text{Cl}$  (0.05 equiv.), and dichloroethane (0.4 M based on **15b**). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of **15b** (1 equiv.) in dichloroethane (0.4 M) was added. The resulting mixture (0.2 M) was then heat in an oil bath at 50  $^\circ\text{C}$  overnight. The reaction mixture was loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of benzonorcaradiene **15a** as a clear oil in 75% yield (19.8 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.04 (d, 2 H,  $J = 7.5$  Hz), 7.58 (d, 1 H,  $J = 7.5$  Hz), 7.53 (t, 1 H,  $J = 7.5$  Hz), 7.46-7.20 (m, 5 H), 6.93 (bs, 1 H), 4.22 (m, 2 H), 3.13 (dd, 1 H,  $J = 9.5, 6.0$  Hz), 2.16 (m, 1 H), 1.82 (s, 3 H), 1.74 (s, 3 H), 1.29 (t, 3 H,  $J = 7.0$  Hz), 0.30 (bs, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  171.6, 164.5, 139.5, 133.7, 132.8, 130.2, 128.8, 129.5-129.0 (at least two broad resonances), 128.2, 128.0, 127.3, 126.4, 126.3, 123.6, 61.0, 30.9, 27.8, 19.6, 18.9, 17.6, 14.1; HRMS (FAB) Calcd. For  $[\text{C}_{25}\text{H}_{24}\text{O}_4]$  388.1675, Found 388.1683.

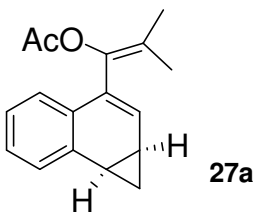


2-Br-Styrene and **1** were reacted according to procedure A. Enynecyclopropane **29b**, a yellow oil, was isolated as a single diastereomer in 64% yield (31.1 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.04 (dd, 2 H,  $J = 8.2, 0.75$  Hz), 7.60 (t, 1 H,  $J = 7.5$  Hz), 7.44 (m, 3 H), 7.14 (m, 2 H), 6.92 (td, 1 H,  $J = 8.0, 1.5$  Hz), 2.48 (q, 1 H,  $J = 7.0$  Hz), 2.07 (m, 1 H), 1.58 (s, 3 H), 1.55 (s, 3 H), 1.42 (m, 1 H), 1.33 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  164.8, 137.3, 133.2, 132.2, 131.4, 130.0, 129.6, 129.4, 128.3, 127.9, 126.9, 126.8, 125.5, 93.2, 72.5, 25.2, 20.0, 17.4, 14.6, 9.8; HRMS (FAB) Calcd. For  $[\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}]$  394.0568, Found 394.0575.

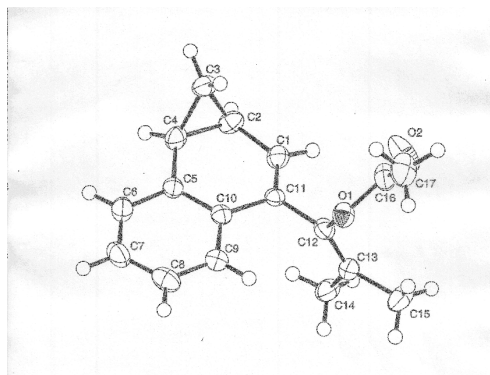
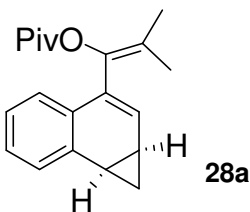
#### Reaction of styrene with other diyne esters:



The acetate analog of **1** and styrene were reacted according to procedure A. The reaction resulted in a 1.2:1 (**27a**:**27b**) mixture of products (determined by  $^1\text{H}$  NMR), which could be separated by column chromatography. Enynecyclopropane **27b** was isolated as clear oil in 25% yield (7.2 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.40-7.15 (m, 5 H), 2.37 (q, 1 H,  $J = 8.5$  Hz), 2.06 (s, 3 H), 1.93 (m, 1 H), 1.67 (s, 3 H), 1.66 (s, 3 H), 1.40 (m, 1 H), 1.27 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.0, 138.0, 131.2, 128.9, 128.3, 126.7, 125.9, 93.8, 74.2, 24.5, 20.1, 20.5, 17.8, 15.2, 10.5; Anal. calc'd for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : C, 80.28; H, 7.13. Found: C, 80.10; H, 7.22.



Benzonorcaradiene **27a** was isolated as a white solid in 30% yield (8.6 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  7.40-7.10 (m, 4 H), 6.49 (d, 1 H,  $J$  = 5.0 Hz), 2.45 (m, 1 H), 2.06 (s, 3 H), 2.01 (m, 1 H), 1.77 (s, 3 H), 1.65, (s, 3 H), 1.56 (m, 1 H), -0.18 (q, 1 H,  $J$  = 4.5 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz, 50  $^\circ\text{C}$ )  $\delta$  168.8, 135.7, 133.3, 129.3, 128.3, 128.1, 127.0, 125.8, 125.5, 20.7, 19.4, 17.4, 17.0, 9.6; HRMS (FAB) Calcd. For  $[\text{C}_{17}\text{H}_{18}\text{O}_2]$  254.1307, Found 254.1305; Anal. calc'd for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : C, 80.28; H, 7.13. Found: C, 80.40; H, 7.30. X-ray structure:

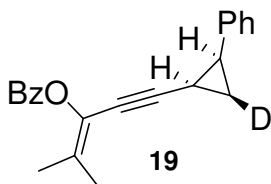


Styrene and the pivaloyl analog of **1** were reacted according to procedure A. Benzonorcaradiene **28a** was isolated as a mixture with the enynecyclopropane (7:1) in 73% yield (43.9 mg). Subsequent chromatography afforded pure **28a**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 50  $^\circ\text{C}$ )  $\delta$  7.45-7.15 (m, 4 H), 6.49 (d, 1 H,  $J$  = 4.4 Hz), 2.48 (m, 1 H), 2.06 (bs, 1 H), 1.77 (s, 3 H), 1.69, (s, 3 H), 1.60 (bs, 1 H), 1.21 (s, 9 H), -0.17 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 50  $^\circ\text{C}$ )  $\delta$  176.3, 140.3, 135.7, 133.2, 129.4, 128.2, 128.0, 126.9, 126.0, 125.4, 38.9, 33.3, 27.0, 20.8, 19.6, 17.2, 9.9; Anal. calc'd for  $\text{C}_{20}\text{H}_{24}\text{O}_2$ : C, 81.04; H, 8.16. Found: C, 80.66; H, 8.22.

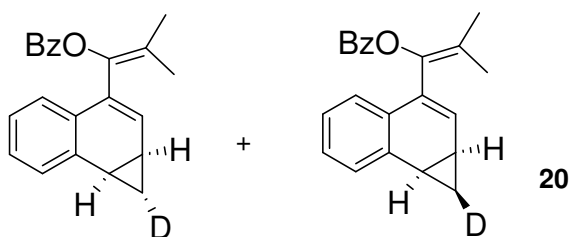
#### Reaction of **1** with *cis*-beta-d-styrene:

The reaction was run according to procedure A. After 16 hours, the reaction mixture was loaded directly onto a silica column and chromatographed to yield the enynecyclopropane **19** in 38% yield and the benzonorcaradiene **20** in 38% yield.  $^1\text{H}$  and

$^2\text{H}$  NMR analysis of **19** indicates deuterium incorporation at a single position.  $^1\text{H}$  and  $^2\text{H}$  NMR analysis of **20** indicates deuterium incorporation into two epimeric positions in a 60:40 ratio.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.10 (m, 2 H), 7.64 (tt, 1 H,  $J = 7.2, 1.6$  Hz), 7.50 (t, 2 H,  $J = 7.2$  Hz), 7.05-7.31 (m, 5H), 2.40 (q, 1 H,  $J = 8.4$  Hz), 1.98 (t, 1 H,  $J = 8.4$  Hz), 1.65 (s, 6 H), 1.43 (t, 1 H,  $J = 8.4$  Hz);  $^2\text{H}$  NMR ( $\text{CDCl}_3$ , 60 MHz)  $\delta$  1.1.

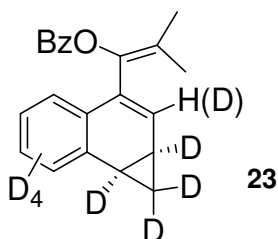


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50  $^\circ\text{C}$ )  $\delta$  8.06 (d, 2 H,  $J = 8.0$  Hz), 7.30-7.70 (m, 5 H), 7.20 (m, 2 H), 6.60 (bs, 1 H), 2.44 (m, 1 H), 2.04 (bs, 1 H), 1.79 (s, 3 H), 1.71 (s, 3 H), 1.57 (bs, 0.56 H), -0.18 (bs, 0.42 H);  $^2\text{H}$  NMR ( $\text{CDCl}_3$ , 61 MHz)  $\delta$  1.4, -0.3.

### Mechanistic experiments regarding the hydroarylation reaction:

#### Reaction of **1** with $\text{D}_8$ -styrene:

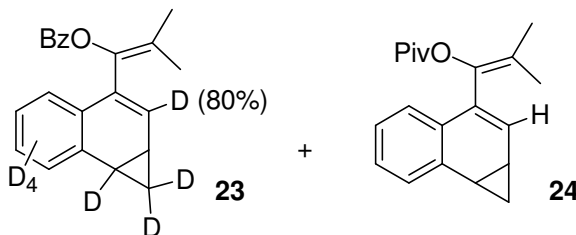
The reaction was run according to procedure A. After 16 hours, the reaction mixture was loaded directly onto a silica plug and eluted to remove styrene and the catalyst.  $^1\text{H}$  analysis of the benzonorcaradiene **23** indicates 20% H-incorporation at the vinyl position. The reaction was run a second time with addition of 2 equiv.  $\text{H}_2\text{O}$ , resulting in 40% H-incorporation by  $^1\text{H}$  NMR.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50 °C)  $\delta$  8.06 (d, 2 H,  $J = 8.0$  Hz), 7.70-7.40 (m, 3 H), 6.60 (bs, 1 H, 0.2 H), 2.04 (bs, 1 H), 1.79 (s, 3 H), 1.71 (s, 3 H).

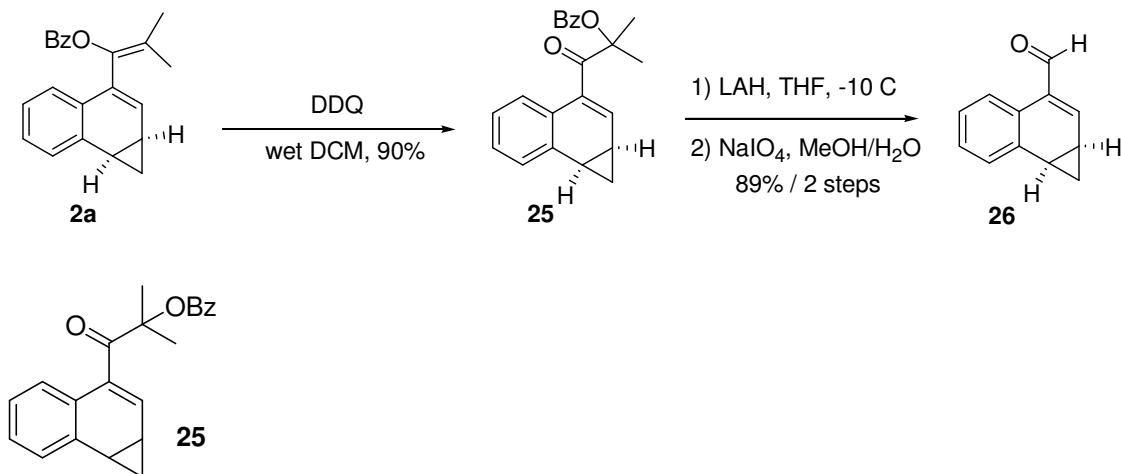
#### Double-labeled cross-over experiment. Reaction of **21** and **22**:

The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of  $\text{AgSbF}_6$  (0.05 equiv.),  $\text{AuPPh}_3\text{Cl}$  (0.05 equiv.), and  $\text{NO}_2\text{Me}$  (0.4 M based on the diynal ester). After allowing the catalyst mixture to sit without stirring for 10 minutes, a solution of **21** (0.5 equiv.) and **22** (0.5 equiv.) in  $\text{NO}_2\text{Me}$  (0.4 M) was added. The resulting mixture (0.2 M) was left overnight. The reaction mixture was loaded directly onto a silica plug and eluted to remove the catalyst.  $^1\text{H}$  NMR analysis of the resulting product mixture indicated 2:1 mixture of **24** and **23**. There was no D-incorporation into **24**, and 20% H-incorporation into the vinyl position of **23**.



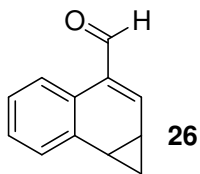
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz, 50 °C)  $\delta$  The following resonances could be resolved for the major product: 7.35 (m, 2 H), 7.15 (m, 2 H), 6.45 (m, 1 H), 2.48 (m, 1 H), 2.04 (bs, 1 H), 1.13 (s, 9 H), -0.25 (dd, 1 H,  $J = 59.0, 4.0$  Hz). The following resonances could be resolved for the minor product: 8.06 (d, 2 H,  $J = 8.0$  Hz), 7.55 (t, 1 H,  $J = 8.0$  Hz), 7.41 (t, 2 H,  $J = 8.0$  Hz), 6.60 (bs, 0.2 H), 2.04 (bs, 1 H), 1.79 (s, 3 H), 1.71 (s, 3 H), 1.57 (bs, 0.56 H), -0.18 (bs, 0.42 H). The following resonances could not be assigned: 1.5-1.8 (m).

**Procedure for the oxidative cleavage of **2a**:**



To **2a** (21 mg, 0.07 mmol) in wet CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at room temperature was added DDQ (75 mg, 0.33 mmol). Upon completion, the reaction was neutralized by the addition of an aqueous sodium bicarbonate solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over magnesium sulfate, concentrated under reduced pressure and the residue purified by flash chromatography (5% ethyl acetate/hexanes) to give the desired ketone **25** (26 mg, 90%) as a pale yellow oil:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (dd, 2 H, *J* = 7.4 Hz); 7.57-7.53 (m, 2 H); 7.40 (t, 2 H, *J* = 7.8 Hz); 7.32 (dd, 1 H, *J* = 5.6, 3.3 Hz); 7.23-7.20 (m, 2 H); 6.88 (d, 1 H, *J* = 5.5 Hz); 2.42 (dd, 1 H, *J* = 13.2, 8.2 Hz); 1.95-1.91 (m, 1 H); 1.85 (s, 6 H); 1.48-1.43 (m, 1 H); 0.39 (bs, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.7, 165.5, 135.4, 133.0, 131.8, 131.6, 130.4, 129.6, 128.3, 128.0, 127.6, 127.0, 126.6, 125.9, 84.9, 26.4, 26.2, 21.3, 16.5, 9.9. HRMS (EI<sup>+</sup>) calc'd for [C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>]: 332.1412, found 332.1415.



Ketone **25** (18 mg, 0.05 mmol) was dissolved in 1 mL THF, cooled to -10 °C and lithium aluminium hydride (10 mg, 0.25 mmol) was added. Upon completion, the reaction was quenched by the addition of an HCl 1M solution and extracted with ether. The combined



organic fractions were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure.

The crude residue was then dissolved in wet methanol (0.5 mL) and sodium periodate (115 mg, 0.5 mmol) was added. The reaction was allowed to stir at room temperature and quenched with water upon completion. The heterogenous mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , dried over magnesium sulfate and concentrated under reduced pressure.

Purification of the crude residue by flash chromatography (20% ethyl acetate/hexanes) provided the desired aldehyde **26** (8 mg, 89% over 2 steps).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.65 (s, 1 H); 8.68 (d, 1 H,  $J = 7.7$  Hz); 7.42 (d, 1 H,  $J = 7.3$  Hz); 7.31-7.20 (m, 3 H); 2.69-2.65 (m, 1 H); 2.29-2.24 (m, 1 H); 1.91-1.87 (m, 1 H); 0.01 (bs, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.2, 154.3, 135.5, 131.8, 128.4, 127.9, 126.4, 126.1, 125.9, 23.6, 18.7, 12.5. HRMS ( $\text{EI}^+$ ) calc'd for  $[\text{C}_{12}\text{H}_{10}\text{O}]$ : 170.0731, found 170.0727.