Experimental Section

General Procedures. Tetrahydrofuran and diethyl ether were distilled from benzophenone sodium ketyl under nitrogen. Benzene was distilled from CaH2. Analytical thin-layer chro-matography was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light and aqueous KMnO4/K2CO3 for visualization. Flash column chromatography was carried out on Baker silica gel (40 ím). Low-resolution mass spectra were obtained by GC-MS using isobutane for chemical ioniza-tion. High-resolution mass spectra were obtained from the mass spectrometry laboratory at the University of Illinois at Urbana/Champaign. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. The light source for all photochemistry was a Hanovia 450-W medium-pressure mer-cury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well and when necessary fitted with a uranyl glass filter to give light with wavelength mainly at 366 nm.

General Procedure. Oxidation of 5 and 9. A 0.2 M solution of **5** or **9** in benzene was cooled to 0 °C, addition of 1 equiv by weight of Celite, 0.2 equiv of pyridinium dichromate, and 3 equiv of *ter*t-butyl hydrogen peroxide in decane was followed by stirring at room temperature for 8-12 h. Filtering through Celite with EtOAc followed by concentration gave the crude oil. Flash chromatography on silica gel with 30% EtOAc in hexane yields **1** and **2**.

1-Methyl-4-oxo-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (1a) was prepared from **5a** in 70% yield. ^{1}H NMR (CDCl$_3$) δ 7.35-7.44 (m, 5 H), 7.09 (m, 2 H), 6.44 (d, J = 9.8 Hz, 1 H), 3.76 (s, 3 H), 1.64 (s, 3 H). CIMS m/z (rel intensity) 243 (M^{+} + 1, 100).

1-(3-Chloro-propyl)-4-oxo-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (1b) was prepared from **5b** as an oil in 65% yield. ^{1}H NMR (CDCl$_3$) δ 7.36-7.43 (m, 5 H), 7.06 (m, 2 H), 6.51 (d, J = 10.0 Hz, 1 H), 3.78 (s, 3 H), 3.52 (t, J = 6.3 Hz, 2 H), 2.22 (m, 2 H), 1.73 (m, 2 H). ^{13}C NMR (CDCl$_3$) δ 27.15, 35.51, 44.10, 51.90, 53.15, 128.03, 128.22, 128.61, 131.10, 135.02, 140.57, 144.48, 146.14, 170.61, 183.60. CIMS m/z (rel intensity) 307 (33), 305 (M^{+} + 1, 100).

1-(3-Azido-propyl)-4-oxo-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (1c) was prepared from **5c** as an oil in 64% yield. ^{1}H NMR (CDCl$_3$) δ 7.41 (m, 5 H), 7.05 (m, 2 H), 6.52 (d, J = 9.7 Hz, 1 H), 3.78 (s, 3 H), 3.31 (t, J = 6.3 Hz, 2 H), 2.14 (m, 2 H), 1.54 (m, 2 H). ^{13}C NMR (CDCl$_3$) δ 23.79, 35.42, 50.82, 52.01, 53.17, 128.05, 128.24, 128.62, 131.12, 135.04, 140.61, 144.44, 146.10, 170.65, 183.61. CIMS m/z (rel intensity) 312 (M^{+} + 1, 100). Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.58; H, 5.50; Found: C, 65.77; H, 5.78;

2-Methoxy-1-methyl-4-oxo-5-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (2a) was prepared from **9a** in 58% yield. ^{1}H NMR (CDCl$_3$) δ 7.34-7.41 (m, 5H), 6.57 (s, 1H), 5.77 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (CDCl$_3$) δ 21.95, 51.00, 53.08, 55.97, 102.88, 127.85, 127.95, 128.71, 134.95, 138.41, 141.24, 170.10, 173.39, 185.66. CIMS m/z (rel intensity) 273 (M^{+} + 1, 100).

1-(3-Azido-propyl)-2-methoxy-4-oxo-5-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (2b) was prepared from **9b** as an oil in 65% yield. ^{1}H NMR (CDCl$_3$) δ 7.41 (m, 5 H), 6.54 (d, J = 0.6 Hz, 1 H), 5.88 (s, 1 H), 3.82 (s, 3 H), 3.74 (s, 3 H), 3.31 (dt, J = 1.2, 6.6 Hz, 2 H), 2.40 (dt, J = 5.1, 9.0 Hz, 1 H), 2.17 (dt, J = 4.8, 12.0 Hz, 1 H), 1.43 (m, 2 H). ^{13}C NMR (CDCl$_3$) δ 22.97, 31.46, 50.62, 53.09, 54.77, 56.00, 104.78, 127.82, 128.03, 128.59, 134.70, 139.61, 140.38, 169.42, 171.22, 185.55. CIMS m/z (rel intensity) 342 (M^{+} + 1, 70), 314 (M^{+} - N$_2$, 100). Anal. Calcd for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31. Found: C, 63.47; H, 5.78; N, 12.08.

General Procedure. Birch Reduction and Alkylation of Methyl 3-Phenylbenzoate (4) and Methyl 2-methoxy-5-Phenylbenzoate (8). To a flame-dried three-necked flask under argon was added **6** dissolved in 10-15 mL of THF and 1.0 equiv of *t*-BuOH. The solution was cooled to -78 °C and 100 mL of twice distilled NH$_3$ was added. Small pieces of lithium wire (2.5-3.0 equiv) were added until the deep blue coloration persisted for 15-20 min. Excess metal was quenched with piperylene to give a dark orange solution, the appropriate alkylation agent (1.5-2.0 equiv) was added, and the resulting yellow solution was stirred for 1 h at-78 °C before quenching with 1-2 g of solid NH$_4$Cl. The solution was warmed slowly to room temperature while the NH$_3$ was evaporated under a stream of argon. The thick mixture was diluted with H$_2$O and Et$_2$O, the phases were separated, and the organic phase was twice extracted with Et$_2$O. The organic phases were combined, washed with saturated NaHCO$_3$ and saturated NaCl, and dried over

$MgSO_4$. Filtration, removal of solvent in vacuo, and flash chromatography on silica gel with 5% EtOAc in hexane gave the 1,4-cyclohexadiene.

1-Methyl-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (5a) was prepared as colorless oil in 100% yield from **4** and methyl iodide (silica gel, 20:1 hexane/EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 7.1 Hz, 2 H), 7.35 (dt, J = 7.8 Hz, 2 H), 7.28 (t, J = 7.1 Hz, 1 H), 6.16 (dd, J = 2.1, 3.8 Hz, 1 H), 5.98 (m, 1 H), 5.88 (m, 1 H), 3.71 (s, 3 H), 3.07 (m, 2 H), 1.43 (s, 3 H). CIMS m/z (rel intensity) 229 (M^+ + 1, 100). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.50; H, 6.98.

1-(3-Chloro-propyl)-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (5b) was prepared from **4** and 3-chloropropyl iodide as oil (95%); ^{1}H NMR ($CDCl_3$) δ 7.29-7.47 (m, 5 H), 6.09 (m, 2 H), 5.81 (dd, J = 1.8, 8.4 Hz, 1 H), 3.73 (s, 3 H), 3.53 (t, J = 6.6 Hz, 2 H), 3.08 (br s, 1 H), 1.96 (m, 2 H), 1.78 (m, 2 H). CIMS m/z (rel intensity) 291 (M^+ + 1, 62), 213 (63).

1-(3-Azido-propyl)-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (5c) was prepared from **4** and 3-azidopropyl iodide as oil (91%); ^{1}H NMR ($CDCl_3$) δ 7.45 (d, J = 7.1 Hz, 2 H), 7.35 (t, J = 7.3 Hz, 2 H), 7.29 (m, 1 H), 6.08 (m, 2 H), 5.81 (dd, J = 2.2, 10.3 Hz, 1 H), 3.72 (s, 3 H), 3.27 (t, J = 6.8 Hz, 2 H), 3.07 (m, 2 H), 1.86 (m, 2 H), 1.56 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 23.94, 28.17, 36.47, 49.01, 51.36, 52.25, 123.54, 125.94, 125.21, 126.18, 127.52, 128.32, 135.89, 174.84. CIMS m/z (rel intensity) 298 (M^+ + 1, 100). Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44. Found: C, 68.62; H, 6.78.

1-Benzyl-3-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (5d) was prepared from **4** and benzyl bromide as oil (83%); ^{1}H NMR ($CDCl_3$) δ 7.17-7.43 (m, 10 H), 6.26 (m, 1 H), 5.96 (d, 2 H), 3.76 (s, 3 H), 3.14 (t, J = 6.3 Hz, 2 H), 3.01 (d, J = 2.2 Hz, 1 H), 2.69 (d, J = 2.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 28.15, 46.52, 50.62, 52.05, 123.95, 125.21, 125.65, 126.23, 126.36, 127.28, 127.60, 128.21, 130.38, 135.47, 136.31, 140.66, 175.51. CIMS m/z (rel intensity) 305 (M^+ + 1, 100).

2-Methoxy-1-methyl-5-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (9a) was prepared from **8** and methyl iodide in high yield. ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 2H), 7.37 (m, 3H), 5.91 (t, J = 1.5 Hz, 1H), 4.90 (t, J = 3.6 Hz, 1H), 3.71 (s, 3H), 3.62 (s, 3H), 3.30 (m, 2H), 1.56 (s, 3H). CIMS m/z (rel intensity) 259 (M^+ + 1, 100).

1-(3-Azido-propyl)-2-methoxy-5-phenyl-cyclohexa-2,5-dienecarboxylic acid methyl ester (9b) was prepared as an oil from **8** and 3-azidopropyl iodide in good yield. ^{1}H NMR ($CDCl_3$) δ 7.27-7.46 (m, 5H), 5.78 (t, J = 1.5 Hz, 1H), 5.03 (t, J = 3.6 Hz, 1H), 3.71 (s, 3H), 3.62 (s, 3H), 3.28 (m, 4H), 2.24 (dt, J = 6.6, 1.5 Hz, 1H), 1.91 (dt, J = 4.5, 7.2 Hz, 1H), 1.49 (m, 2H). CIMS m/z (rel intensity) 329 (M^+ + 1, 100). HRMS (M^+) calcd for $C_{18}H_{21}N_3O_3$: 327.1583, Found: 327.1557.

General Procedure. Irradiation and Preparation of 14, 17, and 18. A 0.06-0.08 M solution of **1, 2,** or **17** in benzene or $CDCl_3$ was degassed by bubbling argon through the solution for 15 min. Irradiation through either uranyl or Pyrex glass was followed by ^{1}H NMR analysis and chromatographic separation on silica gel (4:1 hexane/EtOAc).

6-Hydroxy-2-methyl-biphenyl-3-carboxylic acid methyl ester (14a) was prepared from **1a** in 85% yield (silica gel, 4:1 hexane/EtOAc). ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 1 H), 7.52-7.57 (m, 3 H), 7.28 (d, J = 8.1 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 1 H), 5.11 (br s, 1 H), 3.89 (s, 3 H), 2.31 (s, 3 H). IR (KBr): 3407, 1715, 1584 cm^{-1}. CIMS m/z (rel intensity) 243 (M^+ + 1, 100), 211 (M^+ - OMe, 49). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.62; H, 5.98.

2-(3-Chloro-propyl)-6-hydroxy-biphenyl-3-carboxylic acid methyl ester (14b) was prepared from **1b** in 75% yield. ^{1}H NMR ($CDCl_3$) δ 7.96 (dd, J = 0.9, 7.8 Hz, 1 H), 7.54 (m, 3 H), 7.28 (m, 2 H), 6.93 (dd, J = 0.9, 7.5 Hz, 1 H), 5.01 (br s, 1 H), 3.89 (d, J = 1.2 Hz, 3 H), 3.37 (t, J = 6.6 Hz, 2 H), 2.87 (m, 2 H), 1.88 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 28.51, 33.56, 44.58, 51.52, 112.67, 121.59, 128.56, 129.08, 129.36, 130.19, 132.36, 133.54, 143.13, 155.95, 167.38. IR (neat): 3370, 1682 cm^{-1}. CIMS m/z (rel intensity) 305 (M^+ + 1, 100), 307 (30).

2-Methoxy-6-methyl-4-oxo-5-phenyl-bicyclo[3.1.0]hex-2-ene-6-carboxylic acid methyl ester (17a) was isolated as a single diastereomer (silica gel, 9:1 hexane/EtOAc) after 17 hours' irradiation of **2a**. ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.59 (s, 3 H), 2.69 (d, J = 1.2 Hz, 1 H), 3.28 (s, 3 H), 3.48 (d, J = 1.0 Hz, 1 H), 3.71 (s, 3 H), 3.85 (s, 3 H), 3.88 (s, 3 H), 4.84 (d, J = 1.3 Hz, 1 H), 5.09 (d, J = 1.0 Hz, 1 H), 7.25-7.40 (m, 10 H). ^{1}H NMR ($CDCl_3$) (major) δ 1.12 (s, 3 H), 2.68 (d, J = 1.0 Hz, 1 H), 3.71 (s, 3 H), 3.85 (s, 3 H), 4.84 (d, J = 1.0 Hz, 1 H), 7.33 (m, 2 H), 7.38 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 18.74, 35.48, 48.23, 52.52, 54.44, 59.04, 97.37, 127.79, 128.37, 30.04, 130.67, 170.82, 186.41. CIMS m/z (rel intensity) 273 (M^+ + 1, 100). HRMS (M^+) calcd for $C_{16}H_{16}O_4$: 272.1049, Found: 272.1055.

6-(3-Azido-propyl)-2-methoxy-4-oxo-5-phenyl-bicyclo[3.1.0]hex-2-ene-6-carboxylic acid methyl ester (17b) was obtained as a mixture (2:1) from **2b** in good yield (silica gel, 9:1 hexane/EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.60 (m, 4 H), 1.89 (m, 2 H), 2.32 (m, 2 H), 2.74 (d, J = 2.7 Hz, 1 H), 3.10 (m, 2 H), 3.27 (s, 3 H), 3.20-3.35 (m, 2 H), 3.53 (d, J = 0.9 Hz, 1 H), 3.72 (s, 3 H), 3.85 (s, 3 H), 3.90 (s, 3 H), 4.84 (d, J = 1.5 Hz, 1 H), 5.12 (d, J = 1.2 Hz, 1 H), 7.25-7.43 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 21.64, 25.67, 26.88, 29.75, 33.28, 34.13, 47.78, 48.00, 50.11, 50.64, 51.90, 52.43, 54.69, 58.21, 59.03, 97.42, 100.62, 127.62, 127.82, 127.96, 128.27, 129.44, 129.87, 130.18, 131.03, 168.06, 169.47, 184.58, 186.42, 196.78, 197.14. CIMS m/z (rel intensity) 342 (M^+ + 1, 100), 128 (100).

6-Hydroxy-4-methoxy-2-methyl-biphenyl-3-carboxylic acid methyl ester (18a) was isolated (silica gel, 4:1 hexane/EtOAc) in 81% yield from irradiation of **2a** for 5 hours at 300 nm. ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3 H), 3.82 (s, 3 H), 3.90 (s, 3 H), 4.94 (br s, 1 H, exchangeable with D_2O), 6.46 (s, 1 H), 7.25 (m, 2 H), 7.42 (m, 1 H), 7.50 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 17.51, 52.13, 55.78, 96.30, 128.32, 129.51, 130.72, 134.25, 135.36, 154.62, 156.99, 169 (?), 186 (?). IR (CH_2Cl_2): 3340, 2885, 1715 cm^{-1}. CIMS m/z (rel intensity) 273 (M^+ + 1, 100), 241 (6). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.22; H, 6.04.

2-(3-Azido-propyl)-6-hydroxy-4-methoxy-biphenyl-3-carboxylic acid methyl ester (18b) was isolated from **2b** in 86% yield (silica gel, 4:1 hexane/EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.59 (m, 2 H), 2.42 (m, 2 H), 2.99 (t, 2 H), 3.83 (s, 3 H), 3.91 (s, 3 H), 4.91 (s, 1 H, exchangeable), 6.49 (s, 1 H), 7.27 (m, 2 H), 7.50 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 28.38, 29.71, 51.02, 52.09, 55.80, 96.88, 120.39, 128.58, 129.51, 130.82, 133.61, 138.65, 154.87, 157.25. IR (CH_2Cl_2): 3372, 2952, 1728, 1592 cm^{-1}. CIMS m/z (rel intensity) 342 (M^+ + 1, 100). Anal. Calcd for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61. Found: C, 63.12; H, 5.62.