Supporting Information

Synthesis of Methyl 1-(2,2-diphenylvinyl)cyclopropanecarboxylate (1b). To a solution of diethyl (diphenylmethyl)phosphonate[7] (12.3 g, 0.04 mol) in dry DME (11 mL) under argon at 0 °C was added n-BuLi (25 mL, 1.6 M in hexane). After 1 h, a solution of the corresponding aldehyde **3a**[6] (1.67 g, 0.013 mol) in DME (10 mL) was added at 0 °C. The reaction mixture was stirred for 2 h, quenched with water and extracted with Et_2O. The extract was washed with water and brine, dried ($MgSO_4$), filtered and evaporated to dryness. The residue was purified by flash chromatography on silica gel using hexane/Et_2O 9:1 to afford the ester **1b** (2.56 g, 71%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (m, 2 H), 1.28 (m, 2 H), 3.63 (s, 3 H), 6.23 (s, 1 H), 7.17-7.33 (m, 10 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.8, 24.5, 52.3, 126.3, 127.5-145.3, 175.4; IR (neat) 1730, 1665 cm^{-1}; MS: 278 (M^+, 34), 219 (100), 204 (26), 105 (22), 91 (34); HRMS calcd for $C_{19}H_{18}O_2$ (M^+) 278.1302, found 278.1311.

Independent synthesis of 7-methoxycarbonyl-9-phenyl-6,7-dihydro-5H-benzocycloheptene (4c). A mixture of 2,3-benzo-2,6-cycloheptadienone[14] (0,92 g, 5.82 mmol), KCN (0.78 g, 12 mmol), NH_4Cl (0.47 g, 8.79 mmol), DMF (25 mL) and water (3 mL) was heated at 100 °C for 6 h. The reaction mixture was cooled, neutralized with diluted acetic acid (10%) and extracted with Et_2O. The extract was dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography on silica gel using hexane/EtOAc 8:2 gave compound **6** (0.85 g, 79%) as a slightly yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (m, 2 H), 3.05 (m, 5 H), 7.24 (m, 1 H), 7.36 (m, 1 H), 7.46 (m, 1 H), 7.69 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 29.4, 30.5, 42.7, 120.9, 127.4-139.2, 199.9; IR (neat) 2255, 1785 cm^{-1}; MS: 185 (M$^+$, 89), 157 (71), 132 (65), 118 (40), 104 (100), 77 (29); HRMS calcd for $C_{12}H_{11}NO$ (M$^+$) 185.0838, found 185.0839. A mixture of **6** (1.2 g, 6.5 mmol) and HCl (3.5 mL conc.) was refluxed for 2h. The reaction mixture was cooled and diluted with water (50 mL) and extracted with $CHCl_3$. The extracts were washed with water, dried with Na_2SO_4 and concentrated to dryness to give a crude product that was recrystallized from EtOAc-hexane to yield 1.14g (86%) of the ketoacid **7** as a white solid: mp 136-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (m, 2 H), 2.86-3.07 (m, 5 H), 7.22 (d, J = 7.7 Hz, 1 H), 7.31 (app t, J = 7.7 Hz, 1 H), 7.44 (app t, J = 7.7 Hz, 1 H), 7.72 (d, J = 7.7 Hz, 1 H), 10.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 30.9, 38.0, 42.3, 127.0-140.5, 180.2, 202.4; IR (KBr) 3420, 3060, 1730, 1640 cm^{-1}; MS: 204 (M$^+$, 80), 186 (19), 159 (86), 131 (100), 115 (36), 104 (93), 91 (64), 77 (73). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88. Found: C, 70.88; H, 5.91. To a stirred suspension of magnesium (180 mg, 7.35 mmol) in anhydrous THF (20 mL) under argon was added a solution of bromobenzene (0.77 mL, 7.35 mmol) in anhydrous THF (2 mL) dropwise. The mixture was refluxed for 30 min. A solution of the ketoacid **7** (0.5 g, 2.45 mmol) in THF (10 mL) was added and the reaction mixture was refluxed for 5h. The crude was poured into HCl (3 N) and ice, and extracted with $CHCl_3$. The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography on silica gel using hexane-EtOAc 98:2 gave the acid **8** (100 mg, 15%) as a white solid: mp 162-163 °C (EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (m, 1H), 2.70 (m, 3H), 3.05 (m, 1H), 6.62 (d, J = 6.6 Hz, 1H), 7.02 (m, 1H), 7.22-7.31 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.2, 39.4, 42.4, 124.4-142.6, 180.8; IR (KBr) 3425, 1700 cm^{-1}; MS: 264 (M$^+$, 20), 219 (16), 202 (15), 192 (37), 107 (25), 91 (100). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.78; H, 6.11. Found: C, 81.50; H, 6.30; and the lactone **9** (203 mg, 31%) as a white solid: mp 135-136 °C (EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08 (m, 1H), 2.42 (m, 1H), 2.68 (d, J = 12.6 Hz, 1H), 2.85

(m, 2H), 3.17 (m, 1H), 3.32 (m, 1H), 6.39 (d, J = 8.2 Hz, 1H), 6.95 (m, 1H), 7.18 (m, 3H), 7.41 (m, 3H), 7.67 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.8, 33.8, 42.0, 43.2, 91.3, 126.1-143.1, 178.7; IR (KBr) 1765 cm^{-1}; MS: 264 (M^+, 24), 220 (63), 205 (56), 192 (100), 129 (54), 105 (91), 91 (76), 77 (96). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.78; H, 6.11. Found: C, 81.42; H, 6.23. Further elution using hexane-EtOAc 8:2 gave recovered starting material **7** (173 mg, 35%). The acid **8** was converted into **4c** according to the following procedure: a solution of **8** (100 mg, 0.38 mmol) in a mixture of CH_2Cl_2 (25 mL), MeOH (122 mg, 3.8 mmol) and H_2SO_4 conc. (0.1 mL) was refluxed for 6 h. Conventional workup followed by chromatography on silica gel gave **4c** (94 mg, 89%). Lactone **9** (123 mg, 147 mmol) was also converted into the ester **4c** by treatment with MeOH (25 mL) and H_2SO_4 conc. (0.3 mL) at reflux for 30 min. The reaction mixture was cooled, diluted with water (25 mL) and extracted with EtO_2**.** Conventional workup followed by column chromatography on silica gel using hexane/EtOAc 9:1 gave compound **4c** (91 mg, 70%). The spectral data of **4c** obtained by these two procedures are fully coincident with those recorded for the compound obtained in the irradiation of **1b**, demonstrating the proposed structure for **4c**, Compound **4c** is obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (m, 1H), 2.61 (m, 3H), 2.99 (m, 1H), 3.69 (s, 3H), 6.61 (d, J = 6.6 Hz, 1H), 6.98-7.82 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 31.5, 39.7, 42.8, 59.7, 125.5-142.6, 175.3; IR (neat) 1735, 1660 cm^{-1}; MS: 278 (M^+, 45), 219 (56), 192 (30), 182 (75), 105 (100), 91 (68), 77 (74), 51 (25); HRMS calcd for $C_{19}H_{18}O_2$ (M^+) 278.1302, found 278.1299.

Spectral data for compounds 4b, 4d, 4e, 5c, 5d, 5e and 15.

Compound 4b. Was obtained as a white solid (mp 69-70 °C, from hexane): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (m, 2 H), 2.63 (m, 2 H), 3.03 (m, 1 H), 6.25 (d, J = 6.6 Hz, 1 H), 6.94 (m, 1 H), 7.17-7.27 (m, 8 H); ^{13}C NMR (63 MHz

$CDCl_3$) δ 27.9, 30.8, 40.0, 121.3, 121.6, 126.8-145.0; IR (KBr) 2255 cm^{-1}; MS: 245 (M^+, 100), 217 (36), 192 (67), 167 (35), 91 (20), 77 (14); HRMS calcd for $C_{18}H_{15}N$ (M^+) 245.1201, found 245.1212. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.92; H, 6.24; N, 5.64.

Compound 4d. Was obtained as an oil: ^1H NMR (250 MHz, $CDCl_3$) δ 1.39 (d, J = 7.1 Hz, 3 H), 2.22 (m, 1 H), 2.74 (m, 1 H), 3.14 (m, 1 H), 3.44 (m, 1 H), 6.28 (d, J = 7.8 Hz, 1 H), 7.00 (m, 1 H), 7.19-7.41 (m, 8 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.7, 27.5, 34.9, 47.5, 120.5, 120.9, 126.8-146.5; IR (neat) 2250 cm^{-1}; MS: 259 (M^+, 100), 230 (43), 205 (90), 191 (82), 167 (60), 115 (30), 91 (51), 77 (30), 51 (28).

Compound 4e. Was obtained as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 2.89 (m, 1 H), 3.07 (m, 1 H), 3.61 (m, 1 H), 4.36 (app t, J = 7.4 Hz, 1 H), 6.30 (d, J = 8.1 Hz, 1 H), 7.18-7.31 (m, 14 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 27.3, 43.7, 45.7, 120.6, 120.9, 126.7-146.9; IR (neat) 2270 cm^{-1}; MS: 321 (M^+, 68), 268 (100), 267 (91), 243 (54), 230 (38), 202 (32), 191 (36), 91 (44), 77 (32), 51 (38).

Compound 5c. Was obtained as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (m, 2 H), 2.54 (m, 2 H), 3.23 (s, 3 H), 3.93 (s, 2 H), 6.02 (s, 1 H), 7.05-7.15 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.2, 39.9, 58.1, 61.2, 71.3, 125.7-148.6; IR (neat) 1600, 1490, 1450, 1220 cm^{-1}; MS: 264 (M^+, 6), 220 (19), 219 (100), 187 (16), 155 (22), 91 (18); HRMS calcd for $C_{19}H_{20}O$ (M^+) 264.1509, found 264.1514.

Compound 5d. Was obtained as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3 H), 2.38 (m, 2 H), 2.57 (m, 2 H), 5.78 (s, 1 H), 7.15-7.28 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 36.3, 40.3, 61.5, 125.5-149.3; IR (neat) 1655, 1600, 1490, 1445, 1215 cm^{-1}; MS: 234 (M^+, 30), 219 (100), 157 (57), 129 (12), 91 (15); HRMS calcd for $C_{18}H_{18}$ (M^+) 234.1404, found 234.1408.

Compound 5e. Was obtained as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (m, 1 H), 3.16 (m, 1 H), 4.48 (app t, J = 7.5 Hz, 1 H), 6.67-7.41 (m, 16 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 41.3, 53.2, 66.9, 113.8, 116.3, 126.8-145.0, 154.6; IR (neat) 2240, 1610 cm^{-1}; MS: 321 (M$^+$, 10), 230 (100), 229 (47), 92 (53), 91 (33), 77 (22), 51 (24).

Compound 15. Was obtained as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (m, 1 H), 2.54 (m, 2H), 2.74 (m, 1H), 3.00 (m, 1 H), 3.69 (s, 3 H), 3.81 (s, 3 H), 3.83 (s, 3H), 6.45 (d, J = 6.6 Hz, 1 H), 6.75 (dd, J_1 = 2.4 Hz, J_2 = 8.7 Hz, 1 H), 6.83-6.85 (m, 3 H), 6.95 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 31.9, 39.5, 42.9, 52.0, 55.3, 55.4, 111.7-159.3, 175.4; IR (neat) 1735 cm^{-1}; MS: 338 (M$^+$, 44), 279 (76), 121 (100), 91 (15), 77 (18), 59 (27).