Supporting Information for:

Photocatalytic Reductive Cyclizations of Enones: Divergent Reactivity of Photogenerated Radical and Radical Anion Intermediates

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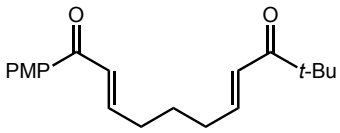
I. General Information

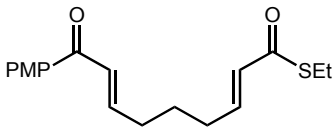
Acetonitrile and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[1] *i*-Pr_2NEt was distilled from CaH_2 immediately prior to use. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ was purchased from Strem and used without further purification. Formic acid was passed through a silica plug immediately prior to use. All other chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography[2] was performed using Silicycle silica gel (230–400 mesh). All glassware was oven-dried at 130 °C for at least 1 h or flame-dried immediately prior to use.

Diastereomer ratios for all compounds were determined by ^1H NMR analysis of the unpurified reaction mixtures. All NMR spectra were obtained at ambient temperature on the Varian Unity-500 and Varian Inova-500 spectrometers. Chemical shifts (δ) are reported in parts per million relative to TMS (0.0 ppm) for ^1H NMR data and $CDCl_3$ (77.23 ppm) for ^{13}C NMR data. IR spectral data were obtained using a Bruker Vector 22 spectrometer. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact). These facilities are funded by the NSF (CHE-8813550, CHE-9629688), NIH (RR04981-01) and the University of Wisconsin.

II. Synthesis of substrates

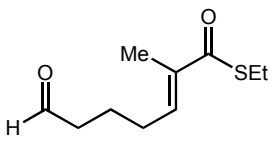


(2*E*,7*E*)-1-(4-Methoxyphenyl)-10,10-dimethylundeca-2,7-diene-1,9-dione (Table 2, entry 5). A solution of (*E*)-7-(4-methoxyphenyl)-7-oxohept-5-enal[3] (1.89 g, 8.1 mmol) in 6.5 mL CH_2Cl_2 was placed in a 50 mL round-bottomed flask. 3,3-Dimethyl-1-(triphenylphosphoranylidene) butan-2-one[4] (3.20 g, 8.9 mmol) in 20 mL CH_2Cl_2 was added dropwise. The resulting solution was allowed to stir for 7 d, after which the reaction was concentrated *in vacuo* to afford a yellow residue. Purification by chromatography on silica gel using 5:1 hexanes:EtOAc as the eluent afforded the product as a yellow solid (1.27 g, 4.0 mmol, 51% yield). IR (thin film): 1687, 1666, 1622, 1600; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 9.1, 2.9 Hz, 2H), 7.02 (dt, J = 15.3, 6.9 Hz, 1H), 6.95 (dt, J = 6.7, 2.1 Hz, 2H), 6.91 (m, 1H), 6.53 (dt, J = 15.3, 1.7 Hz, 1H), 3.88 (s, 3H), 2.35 (q, J = 7.8 Hz, 2H), 2.29 (q, J = 7.3 Hz, 2H), 1.71 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.2, 188.8, 163.3, 147.5, 146.3, 130.8, 130.7, 126.0, 124.8, 113.7, 55.5, 42.9, 32.1, 31.8, 26.8, 26.2; HRMS (ESI^+) calc'd for $[C_{20}H_{26}O_3Na]^+$ requires *m/z* 337.1775, found *m/z* 337.1760. (mp = 60–64 ºC)

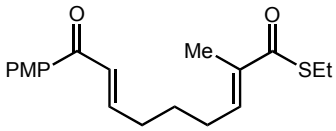


(2*E*,7*E*)-*S*-Ethyl-9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate (Table 2, entry 6). A solution of (*E*)-7-(4-methoxyphenyl)-7-oxohept-5-enal[3] (0.96 g, 4.1 mmol) in 2.0 mL CH_2Cl_2 was placed in a 25 mL round-bottomed flask. *S*-Ethyl-2-(triphenylphosphoranylidene)ethanethioate[5] (1.5 g, 4.14 mmol) in 3.0 mL CH_2Cl_2 was added dropwise. The resulting solution was allowed to stir for 24 h, after which the reaction was concentrated *in vacuo* to afford a

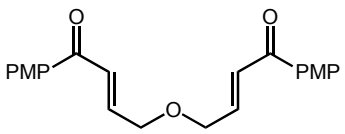
yellow residue. Purification by chromatography on silica gel using 7:3 hexanes:EtOAc as the eluent afforded the product as a yellow oil (0.60 g, 1.9 mmol, 46% yield). IR (thin film): 2932, 1666, 1620, 1599; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 9.0, 2.1 Hz, 2H), 7.01 (m, 1H), 6.95 (dt, J = 9.2, 2.6 Hz, 2H), 6.89 (m, 2H), 6.13 (dt, J = 15.7, 1.4 Hz, 1H), 3.87 (s, 3H), 2.94 (q, J = 7.2 Hz, 2H), 2.34 (q, J = 7.8 Hz, 2H), 2.26 (q, J = 8.4 Hz, 2H), 1.71 (m, 2H), 1.28 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 189.9, 188.7, 163.3, 147.3, 144.0, 130.8, 130.7, 129.3, 126.1, 113.8, 55.5, 32.0, 31.5, 26.5, 23.1, 14.8; HRMS (ESI^+) calc'd for $[C_{18}H_{23}O_3S]^+$ requires *m/z* 319.1363, found *m/z* 319.1347.



(*E*)-*S*-Ethyl 2-methyl-7-oxohept-2-enethioate. A suspension of NaH (35 mg, 8.9 mmol) in 34 mL THF was placed in a 50 mL round-bottomed flask and cooled to 0 ºC. *S*-Ethyl 3-(diethoxyphosphoryl)-2-methylpropanethioate (2.1 g, 8.2 mmol) was added dropwise and the resulting suspension stirred for 30 min, after which 5,5-dimethoxypentanal[6] (1.0 g, 6.8 mmol) was added dropwise. The reaction was allowed to stir for an additional 40 min, after which the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was then dissolved in 16 mL THF and treated with 1 M HCl. After 1 h, the aqueous layer was separated, neutralized with sat. $NaHCO_3$ and extracted with EtOAc (x3). The combined organics were then washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography on silica gel using 9:1 hexanes:EtOAc as the eluent afforded the product as a yellow oil (429 mg, 2.1 mmol, 33% yield). IR (thin film): 2722, 1720, 1652; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 6.67 (td, J= 7.1, 1.0 Hz, 1H), 2.92 (q, J =7.1 Hz, 2H), 2.49 (td, J =7.3, 1.1 Hz, 2H), 2.25 (q, J =7.4 Hz, 2H), 1.87 (s, 3H), 1.81 (quintet, J =7.2 Hz, 2H), 1.27 (t, J= 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 201.9, 193.8, 138.7, 137.0, 43.2, 27.8, 23.3, 20.9, 14.7, 12.4; HRMS (ESI^+) calc'd for $[C_{10}H_{16}O_2SNa]^+$ requires *m/z* 223.0764, found *m/z* 223.0775.

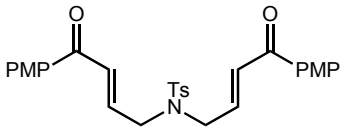


(2*E*,7*E*)-*S*-Ethyl-9-(4-methoxyphenyl)-2-methyl-9-oxonona-2,7-diene thioate (Table 2, entry 7). A solution of (*E*)-7-(4-methoxyphenyl)-7-oxohept-5-enal (429 mg, 2.14 mmol), *S*-ethyl 2-(triphenylphosphoranylidene)propanethioate[5] (1.32 g, 3.2 mmol) and 10 mL CH_2Cl_2 was placed in a 25 mL round-bottomed flask and allowed to stir for 72 h, after which the reaction mixture was concentrated to yield a yellow oil. Purification by chromatography on silica gel using 4:1 hexanes:EtOAc as the eluent afforded the product as a yellow oil (503 mg, 1.5 mmmol, 71% yield). IR (thin film): 2931, 1665, 1654, 1618; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 9.0, 2.6 Hz, 2H), 7.03 (dt, J = 15.3, 7.0 Hz, 1H), 6.95 (dt, J = 8.9, 2.0 Hz, 2H), 6.92 (dt, J = 15.1, 1.3 Hz, 1H), 6.72 (tq, J = 7.3, 1.2 Hz, 1H), 3.88 (s, 3H), 2.92 (q, J = 7.6 Hz, 2H), 2.36 (q, J = 7.9 Hz, 2H), 2.27 (q, J = 7.2 Hz, 2H), 1.88 (s, 3H), 1.72 (m, 2H), 1.27 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 193.8, 188.8, 163.4, 147.5, 139.4, 136.7, 130.8, 130.7, 126.1, 113.8, 55.4, 32.2, 28.0, 27.1, 23.2, 14.7, 12.5; HRMS (ESI^+) calc'd for $[C_{19}H_{24}O_3SNa]^+$ requires *m/z* 355.1339, found *m/z* 355.1340.

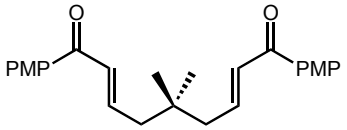


(2*E*,2'*E*)-4,4'-Oxybis(1-(4-methoxyphenyl)but-2-en-1-one) (Table 2, entry 8). Prepared using a modification of a procedure by Montgomery.[7] A solution of 2,5-dihydrofuran (568 mg, 8.1 mmol) in 27 mL CH_2Cl_2 was placed in a 100 mL three-necked flask and cooled to –78 ºC. Ozone was passed through the reaction mixture until a blue coloration persisted, at which point N_2 was bubbled through the solution to remove excess dissolved ozone. The ozonide was then quenched with 1.2 mL dimethylsulfide and 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene) ethanone (10 g, 23 mmol) was added in one portion. The resulting solution was warmed to room temperature and allowed to stir for 16 h. Concentration *in vacuo* and purification by chromatography on silica gel using 2:1 hexanes:EtOAc as the eluent afforded the product as a white solid (1.1 g, 3.0 mmol, 37% yield). IR (thin film): 1668, 1623, 1600; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dt, J = 8.9, 2.9 Hz, 4H), 7.24 (dt, J = 15.1, 1.8 Hz, 2H), 7.06 (dt, J = 15.4, 4.1 Hz, 2H), 6.95 (dt, J = 8.9, 2.9 Hz, 4H), 4.36 (dd, J = 4.1, 2.0 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 188.3, 163.5, 142.7, 130.9, 130.5,

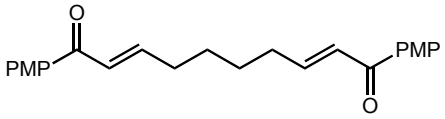
124.9, 113.8, 70.0, 55.5; HRMS (ESI$^+$) calc'd for $[C_{22}H_{22}O_5Na]^+$ requires *m/z* 389.1360, found *m/z* 389.1367. (mp= 81–86 ºC)



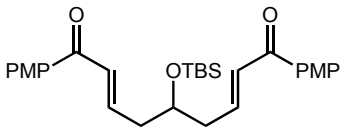
_N,N_-Bis((*E*)-4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methyl benzenesulfonamide (Table 2, entry 9). A solution of *N*,*N*-diallyl-*p*-toluenesulfonamide[8] (1.0 g, 4.0 mmol) in 13 mL CH_2Cl_2 was placed in a 100 mL three-necked flask and cooled to –78 ºC. Ozone was passed through the reaction mixture until a blue coloration persisted, at which point N_2 was bubbled through the solution to remove excess dissolved ozone. The ozonide was then quenched with 1.2 mL dimethylsulfide and warmed to room temperature. 1-(4-Methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone (3.5 g, 8.5 mmol) was added in one portion and the resulting solution was allowed to stir for 2 d. Concentration *in vacuo* and purification by chromatography on silica gel using 1:1 hexanes:EtOAc as the eluent afforded the product as a white solid (555 mg, 1.1 mmol, 26% yield). IR (thin film): 1669, 1624, 1599; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dt, J = 8.9, 2.8 Hz, 4H), 7.76 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 6.99 (d, J = 15.5 Hz, 2H), 6.91 (dt, J = 8.9, 2.5 Hz, 4H), 6.76 (dt, J = 15.2, 5.4 Hz, 2H), 4.12 (d, J = 5.5 Hz, 4H), 3.87 (s, 6H), 2.4 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 187.8, 163.7, 144.0, 140.3, 136.7, 131.0, 130.0, 130.0, 128.0, 127.3, 113.9, 55.5, 48.7, 21.5; HRMS (ESI$^+$) calc'd for $[C_{29}H_{29}NO_6SNa]^+$ requires *m/z* 542.1608, found *m/z* 542.1597. (mp = 72–79 ºC)



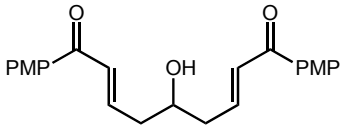
(2*E*,7*E*)-1,9-Bis(4-methoxyphenyl)-5,5-dimethylnona-2,7-diene-1,9-dione (Table 2, entry 10). Prepared using a modification of a procedure by Montgomery.[7] To a solution of 3,3-dimethylglutaraldehyde[9] (0.1 g, 0.8 mmol) in 10 mL CH_2Cl_2 was added 1-(4-methoxyphenyl)-2-(triphenyl phosphoranylidene)ethanone (0.8 g, 2.0 mmol). The resulting solution was allowed to stir for 3 d, after which the reaction was concentrated *in vacuo* to afford a yellow residue. Purification on silica gel using 4:1 hexanes:EtOAc as the eluent afforded a yellow oil that was recrystallized from hexanes:EtOAc to yield the product as a white solid (98 mg, 0.3 mmol, 32% yield). IR (thin film): 1663, 1617, 1257; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J =8.9, 3.1 Hz, 4H), 7.09 (m, 2H), 6.93 (m, 6H), 3.86 (s, 6H), 2.28 (dd., J =7.8, 1.0 Hz, 4H), 1.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 188.9, 163.7, 145.0, 130.8, 128.2, 113.9, 55.4, 45.3, 34.9, 27.1; HRMS (ESI$^+$) calc'd for $[C_{25}H_{28}O_4Na]^+$ requires *m/z* 415.1873, found *m/z* 415.1880. (mp = 51–57 ºC)



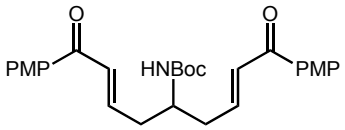
(3*E*,9*E*)-1,12-Bis(4-methoxyphenyl)dodeca-3,9-diene-1,12-dione (Table 2, entry 11). Prepared using a modification of a procedure by Montgomery.[7] A solution of cyclohexenone (756 mg, 9.2 mmol) in 23 mL CH_2Cl_2 was placed in a 100 mL three-necked flask and cooled to –78 ºC. Ozone was passed through the reaction mixture until a blue coloration persisted, at which point N_2 was bubbled through the solution to remove excess dissolved ozone. The ozonide was then quenched with 5.3 mL dimethylsulfide and warmed to room temperature. 1-(4-Methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone (9.4 g, 22 mmol) was added in one portion and the resulting solution was allowed to stir for 2 d. Concentration *in vacuo* and purification by chromatography on silica gel using 2:1 hexanes:EtOAc as the eluent afforded the product as a white solid (1.0 g, 2.8 mmol, 30% yield). IR (thin film): 1664, 1617, 1258, 1170; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.7 Hz, 4H), 7.04 (dt, J = 15.2, 6.9 Hz, 2H), 6.93 (m, 4H), 3.87 (s, 6H), 2.35 (m, 4H), 1.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) 189.0, 163.3, 148.1, 130.8, 130.7, 125.8, 113.7, 55.4, 32.5, 27.8; HRMS (ESI$^+$) calc'd for $[C_{22}H_{26}O_4]^+$ requires *m/z* 378.1826, found *m/z* 378.1829. (mp = 83–88 ºC)



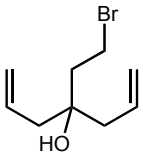
(2*E*,7*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-1,9-bis(4-methoxyphenyl) nona-2,7-diene-1,9-dione. Prepared using a modification of a procedure by Montgomery.[7] A solution of *tert*-butyl(hepta-1,6-dien-4-yloxy)dimethyl silane[10] (2.0 g, 8.9 mmol) in 30 mL CH_2Cl_2 was placed in a 100 mL three-necked flask and cooled to –78 ºC. Ozone was passed through the reaction mixture until a blue coloration persisted, at which point N_2 was bubbled through the solution to remove excess dissolved ozone. The ozonide was then quenched with 2.6 mL dimethylsulfide and warmed to room temperature. 1-(4-Methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone (7.7 g, 19 mmol) was added in one portion and the resulting solution was allowed to stir for 4 d. Concentration *in vacuo* and purification by chromatography on silica gel using 3:2 hexanes:EtOAc as the eluent afforded the product as a yellow oil (2.8 g, 5.7 mmol, 64% yield). IR (thin film): 2931, 1619, 1599, 1258, 1170; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 8.7, 2.9 Hz, 4H), 7.05 (m, 2H), 6.95 (tt, J = 7.0, 2.9 Hz, 6H), 4.05 (m, 1H), 3.87 (s, 6H), 2.51 (m, 4H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 188.5, 163.3, 144.1, 130.8, 130.6, 127.9, 113.6, 70.3, 55.3, 40.6, 25.7, 17.9; HRMS (ESI^+) calc'd for $[C_{29}H_{38}O_5SiNa]^+$ requires *m/z* 517.2381, found *m/z* 517.2396.



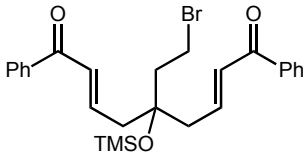
(2*E*,7*E*)-5-Hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione (Table 2, entry 12). Prepared using a modification of a procedure by Shioiri.[11] (2*E*,7*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-1,9-bis(4-methoxy phenyl)nona-2,7-diene-1,9-dione (2.5 g, 5.1 mmol) was allowed to stir in 50 mL of a 13:7:3 AcOH:H_2O:THF mixture. After 2.5 h, the reaction was concentrated, dissolved in Et_2O and washed with H_2O. Purification of the resulting residue by chromatography on silica gel using 3:2 hexanes:EtOAc as the eluent afforded the product as a white solid (638 mg, 1.7 mmol, 33% yield). IR (thin film): 3454, 1600, 1260, 1172; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 8.8, 2.4 Hz, 4H), 7.04 (m, 4H), 6.92 (dt, J = 8.8, 3.6 Hz, 4H), 4.06 (m, 1H), 3.85 (s, 6H), 2.83 (d, J = 4.8 Hz, 1H), 2.56 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) 188.7, 163.5, 143.8, 130.9, 130.5, 128.2, 113.8, 69.4, 55.5, 40.4; HRMS (ESI^+) calc'd for $[C_{23}H_{24}O_5Na]^+$ requires *m/z* 403.1516 found *m/z* 403.1523. (mp = 110–113 ºC)



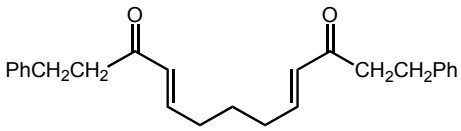
***tert*-Butyl ((2*E*,7*E*)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl)carbamate** (Table 2, entry 13). Prepared using a modification of a procedure by Montgomery.[7] To a solution of 3-amino-1,6-heptadiene (1.5 g, 14 mmol) in 15 mL H_2O was added di-*t*-butyldicarbonate (3.4 g, 16 mmol). The suspension was allowed to stir for 30 min, after which the reaction was extracted with CH_2Cl_2 and concentrated to afford the crude product as a yellow solid.[12] The resulting crude diene was dissolved in 34 mL CH_2Cl_2 in a 100 mL three-necked round-bottomed flask and cooled to –78 ºC. Ozone was passed through the reaction mixture until a blue coloration persisted, at which point N_2 was bubbled through the solution to remove excess dissolved ozone. The ozonide was then quenched with 3.0 mL dimethylsulfide and warmed to room temperature. 1-(4-Methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone (8.9 g, 22 mmol) was added in one portion and the resulting solution was allowed to stir for 2 d. Concentration *in vacuo* and purification by chromatography using 3:2 hexanes:EtOAc as the eluent afforded the product as a yellow solid (1.3 g, 2.6 mmol, 30% yield). IR (thin film): 3366, 1675, 1259, 1170; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 9.1, 2.7 Hz, 4H), 6.99 (m, 4H), 6.94 (dt, J = 9.1, 2.9 Hz, 4H), 4.58 (m, 1H), 4.04 (m, 1H), 3.87 (s, 6H), 2.56 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, CDCl3) 188.4, 163.5, 155.2, 143.1, 130.9, 130.5, 128.3, 113.8, 55.5, 37.6, 28.3; HRMS (ESI^+) calc'd for $[C_{28}H_{33}NO_6Na]^+$ requires *m/z* 480.2381 found *m/z* 480.2387. (mp = 118–121 ºC)



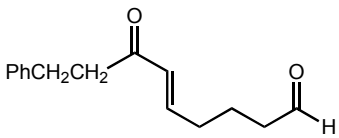
4-(2-Bromoethyl)hepta-1,6-dien-4-ol. Prepared using a modification of a procedure by Wang.[13] Allyl bromide (7.0 mL, 81 mmol) was added dropwise to a suspension of zinc dust (6.1 g, 93 mmol) in 26 mL THF. The suspension was allowed to stir for 10 min, after which ethyl 3-bromopropionate (2.6 mL, 20 mmol) was added slowly. The reaction was then stirred for 2 h, quenched with sat. NH_4Cl, extracted with Et_2O (x3), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to yield a clear oil. Purification by chromatography on silica gel using 9:1 hexanes:EtOAc as the eluent afforded the product as a clear oil (3.7 g, 17 mmol, 83% yield). IR (thin film): 3454, 1640, 1446; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, J = 17.3, 10.1, 7.0 Hz, 2H), 5.16 (dd, J = 16.8, 1.4 Hz, 4H), 3.49 (dd, J = 8.6, 7.8 Hz, 2H), 2.24 (m, 4H), 2.08 (dd, J = 8.4, 8.1 Hz, 2H), 1.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 132.8, 119.6, 73.7, 43.7, 42.6, 27.7; HRMS (EI$^+$) calc'd for $[C_6H_{11}BrO]^+$ requires *m/z* 176.9910, found *m/z* 176.9903.



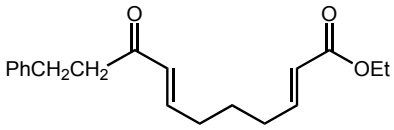
(2*E*,7*E*)-5-(2-Bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-diene-1,9-dione (Table 2, entry 14). A solution of 4-(2-bromoethyl)hepta-1,6-dien-4-ol (2.3 g, 10.5 mmol), acrolein (6.9 mL, 103 mmol), and 2nd generation Grubbs catalyst[14] (446 mg, 0.53 mmol) in 42 mL CH_2Cl_2 was allowed to stir for 48 h.[15] The brown suspension was then concentrated *in vacuo*, treated with pyridine (1.7 mL, 21 mmol) and TMSCl (2.0 mL, 15.8 mmol), and allowed to stir overnight at 35 ºC. The resulting reaction mixture was eluted through two consecutive plugs of silica gel using 2:1 hexanes:EtOAc to completely remove the catalyst and then concentrated *in vacuo* to yield a yellow oil.[16] The crude aldehyde was then dissolved in 0.3 mL THF and cooled to 0 ºC. Phenyl magnesium bromide (1.0 M in THF, 0.56 mL, 0.56 mmol) was added dropwise and the resulting solution was allowed to stir for 1h, after which the reaction was quenched with water, extracted with ether (x3), washed with sat. $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo* to yield 527 mg (1.0 mmol, 10% yield) of the crude diol as a yellow residue.[17] The diol and 2-iodoxybenzoic acid[18] (730 mg, 2.6 mmol) were dissolved in 11 mL CH_2Cl_2 and allowed to stir for 24 h. The reaction mixture was then diluted with CH_2Cl_2, washed with 5% $NaHCO_3$ (x2), water, brine, dried over Na_2SO_4, and concentrated to yield a yellow residue. Purification by chromatography on silica gel using 7:1 hexanes:EtOAc as the eluent afforded the product as a clear oil (332 mg, 0.66 mmol, 64% yield). IR (thin film): 1671, 1620, 1279; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.5 Hz, 4H), 7.57 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 8 Hz, 4H), 7.06 (m, 2H), 6.98 (d, J = 15.3 Hz, 2H), 3.64 (dd, J = 7.9, 7.8 Hz, 2H), 2.59 (m, 4H), 2.10 (dd, J = 7.9, 8.1 Hz, 2H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 189.8, 143.4, 137.5, 132.9, 129.0, 128.6, 128.5, 53.4, 43.6, 43.3, 39.6, 31.6, 22.5, 14.1, 2.5; HRMS (ESI$^+$) calc'd for $[C_{26}H_{31}BrO_3SiNa]^+$ requires *m/z* 521.1119, found *m/z* 521.1109.



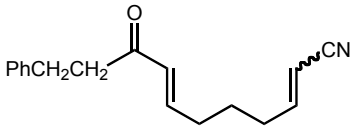
(4*E*,9*E*)-1,13-Diphenyltrideca-4,9-diene-3,11-dione (Table 3, entry 1). A solution of glutaraldehyde (2.0 g, 10 mmol) and 4-phenyl-1-(triphenyl phosphoranylidene)butan-2-one (10.2 g, 25 mmol) in 34 mL CH_2Cl_2 was placed in a 100 mL round-bottomed flask and allowed to stir for 24 h, after which the reaction mixture was concentrated to yield a clear oil. Purification by chromatography on silica gel using 4:1 hexanes:EtOAc as the eluent afforded the product as a white solid (1.13 g, 3.1 mmol, 31% yield). IR (thin film): 1701, 1669, 1629; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dt, J = 7.4, 3.6 Hz, 4H), 7.20 (d, J = 7 Hz, 6H), 6.77 (dt, J = 15.9, 7.0 Hz, 2H), 6.10 (dt, J = 15.9, 1.4 Hz, 2H), 2.93 (dt, J = 7.0, 2.8 Hz, 4H), 2.86 (m, 4H), 2.21 (q, J = 6.6 Hz, 4H), 1.6 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.2, 146.1, 141.2, 130.7, 128.5, 128.3, 126.1, 41.8, 31.7, 30.0, 26.4; HRMS (ESI$^+$) calc'd for $[C_{25}H_{28}O_2Na]^+$ requires *m/z* 383.1982, found *m/z* 383.1985. (mp = 40–44 ºC)



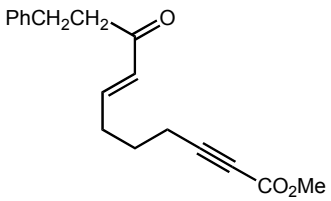
(*E*)-7-Oxo-9-phenylnon-5-enal. A solution of 5,5-dimethoxypentanal[6] (1 g, 6.8 mmol) and 4-phenyl-1-(triphenylphosphoranylidene)butan-2-one (3.6 g, 7.5 mmol) in 23 mL CH_2Cl_2 was placed in a 50 mL round-bottomed flask and allowed to stir for 72 h, after which the reaction mixture was concentrated to yield a yellow oil. The residue was dissolved in 20 mL THF and treated with 1M HCl. After 1 h, the aqueous layer was separated, neutralized with sat. $NaHCO_3$ and extracted with EtOAc (x3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by chromatography on silica gel using 4:1 hexanes:EtOAc as the eluent afforded the product as a yellow oil (401 mg, 1.7 mmol, 26% yield). IR (thin film): 2934, 2724, 1719, 1670, 1628; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (t, J = 1.1 Hz, 1H), 7.28 (m, 2H), 7.19 (m, 3H), 6.76 (dt, J = 15.8, 7.1 Hz, 1H), 6.11 (dt, J = 15.8, 1.6 Hz, 1H), 2.93 (td, J = 8.3, 2.0 Hz, 2H), 2.86 (m, 2H), 2.46 (td, J = 7.5, 1.4 Hz, 2H), 2.24 (qd, J = 7.1, 1.4 Hz, 2H), 1.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 201.5, 199.3, 145.8, 141.2, 130.9, 128.5, 128.4, 126.1, 42.9, 41.7, 31.5, 30.0, 20.3; HRMS (EI$^+$) calc'd for $[C_{15}H_{18}O_2]^+$ requires *m/z* 230.1302, found *m/z* 230.1306.



(2*E*,7*E*)-Ethyl 9-oxo-11-phenylundeca-2,7-dienoate (Table 3, entry 3). A solution of (*E*)-7-oxo-9-phenylnon-5-enal (333 mg, 1.4 mmol) and ethyl 2-(triphenyl phosphoranylidene)acetate (750 mg, 2.2 mmol) in 5.0 mL CH_2Cl_2 was placed in a 25 mL round-bottomed flask and allowed to stir for 48 h, after which the reaction mixture was concentrated to yield a yellow oil. Purification by chromatography on silica gel using 4:1 hexanes:EtOAc as the eluent afforded the product as a yellow oil (362 mg, 1.2 mmol, 84% yield). IR (thin film): 1715, 1655; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.19 (dt, J = 15.5, 7.1 Hz, 3H), 6.92 (dt, J = 15.5, 7.1 Hz, 1H), 6.78 (dt, J = 15.8, 6.9 Hz, 1H), 6.11 (dt, J = 15.9, 1.3 Hz, 1H), 5.82 (dt, J = 15.8, 1.6 Hz, 1H), 4.19 (q, J = 6.8 Hz, 2H), 2.93 (m, 2H), 2.86 (m, 2H), 2.22 (m, 4H), 1.63 (m, 2H), 1.29 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.3, 166.5, 147.9, 146.3, 141.2, 130.7, 128.5, 128.3, 126.1, 122.0, 60.2, 41.8, 31.7, 31.4, 30.0, 26.3, 14.2; HRMS (ESI$^+$) calc'd for $[C_{19}H_{24}O_3Na]^+$ requires *m/z* 323.1618, found *m/z* 323.1615.

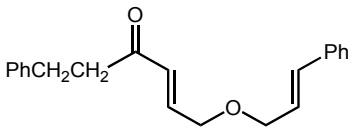


(2*E*,7*E*)-9-Oxo-11-phenylundeca-2,7-dienenitrile (Table 3, entry 4). A solution of (*E*)-7-oxo-9-phenylnon-5-enal (276 mg, 1.2 mmol) and 2-(triphenylphosphoranylidene)acetonitrile (540 mg, 1.8 mmol) in 10 mL CH_2Cl_2 was placed in a 25 mL round-bottomed flask and allowed to stir for 72 h, after which the reaction mixture was concentrated to yield a yellow oil. Purification by chromatography on silica gel using 70:30 hexanes:EtOAc as the eluent afforded the product as a yellow oil and a 1:1 mixture of *trans:cis* isomers (285 mg, 1.1 mmmol, 95% yield). IR (thin film): 2934, 2221, 1670, 1631; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.20 (m, 3H), 6.73 (m, 2H), 6.45 (dt, J =10.9, 7.6 Hz, 1H, minor isomer), 6.12 (m, 1H), 5.33 (dt, J =10.9, 1.2 Hz, 1H, major isomer), 2.93 (m, 2H), 2.87 (m, 2H), 2.45 (qd, J =7.5, 1.3 Hz, 2H, minor isomer), 2.23 (m, 4H), 1.63 (m, 2H), ^{13}C NMR (125 MHz, $CDCl_3$) 199.2, 154.7, 153.8, 145.5, 141.2, 130.9, 128.5, 128.4, 126.1, 117.2, 115.8, 100.5, 41.9, 32.5, 31.6, 31.5, 31.2, 30.0, 26.6, 26.0; HRMS (ESI$^+$) calc'd for $[C_{23}H_{26}O_4Na]^+$ requires *m/z* 276.1357, found *m/z* 276.1359.

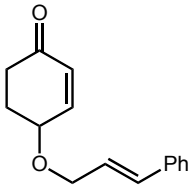


(*E*)-Methyl 4-((4-oxo-6-phenylhex-2-en-1-yl)oxy)but-2-ynoate (Table 3, entry 5). A solution of methyl 7-oxohept-2-ynoate[19] and 4-phenyl-1-(triphenylphosphoranylidene)butan-2-one in 19 mL CH_2Cl_2 was placed in a 25 mL round-bottomed flask and allowed to stir for 48 h, after which the reaction mixture was concentrated to yield a yellow residue. Purification by chromatography on silica gel using 4:1 hexanes: EtOAc as the eluent afforded the product as a yellow oil (1.42 g, 5.0 mmol, 84% yield). IR (thin film): 2235, 1707, 1670, 1630; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.19 (m, 2H), 6.76 (dt, J =

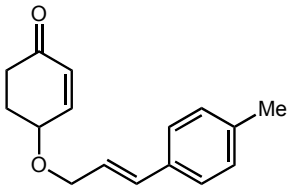
15.9, 6.9 Hz, 1H), 6.14 (dt, J = 15.8, 1.5 Hz, 1H), 3.76 (s, 3H), 2.94 (m, 2H), 2.87 (m, 2H), 2.36 (t, 3H), 2.32 (dt, J = 7 Hz, 1H), 1.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.2, 154.1, 145.3, 141.1, 131.0, 128.5, 126.2, 88.3, 73.8, 52.6, 41.7, 31.2, 25.7, 18.0; HRMS (EI^+) calc'd for $[C_{18}H_{20}O_3]^+$ requires *m/z* 284.1407, found *m/z* 284.1407.



(*E*)-6-(Cinnamyloxy)-1-phenylhex-4-en-3-one (Table 3, entry 6). To a –78 ºC solution of oxalyl chloride (0.55 mL, 6.4 mmol) in 24 mL CH_2Cl_2 was added DMSO (0.54 mL, 7.6 mmol) in 1.6 mL CH_2Cl_2. The reaction was stirred for 30 min, after which 2-(cinnamyloxy)ethanol[20] (565 mg, 3.2 mmol) in 3.2 mL CH_2Cl_2 was added dropwise. The suspension was allowed to stir for 30 min, after which Et_3N (2.2 mL, 16 mmol) was added. The reaction was stirred at –78 ºC for 30 min, warmed to room temperature and stirred for an additional 30 min. The reaction was poured onto H_2O and the product extracted with CH_2Cl_2 (x3). The combined organics were washed with brine, dried over $MgSO_4$ and concentrated to yield a yellow oil. The crude aldehyde was dissolved in 9.4 mL CH_2Cl_2 and treated with 2-(triphenylphosphoranylidene)acetonitrile (2.4 g, 5.8 mmol). The reaction was stirred for 2 d, after which the reaction mixture was concentrated to yield a yellow residue. Purification by chromatography on silica gel using 4:1 hexanes:EtOAc as the eluent afforded the product as a pale yellow oil (890 mg, 2.9 mmol, 91% yield). IR (thin film): 1670, 1636 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.27 (m, 3H), 7.20 (m, 3H), 6.84 (dt, J = 15.7, 4.1 Hz, 1H), 6.62 (d, J = 16.2 Hz, 1H), 6.39 (dt, J = 15.8, 1.7 Hz, 1H), 6.28 (dt, J = 15.8, 5.8 Hz, 1H), 4.19 (m, 4H), 2.96 (m, 2H), 2.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.0, 142.3, 141.1, 136.4, 133.0, 129.2, 128.6, 128.5, 128.3, 127.8, 126.5, 126.1, 125.3, 71.4, 68.7, 42.2, 29.9; HRMS (ESI^+) calc'd for $[C_{21}H_{22}O_2]^+$ requires *m/z* 306.1615, found *m/z* 306.1619.

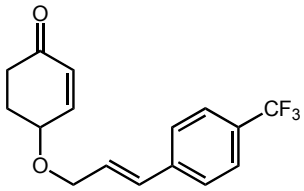


4-(Cinnamyloxy)cyclohex-2-enone (Table 3, entry 7). Prepared using a modification of a procedure by Kibayashi.[21] A 25 mL round-bottomed flask was charged with 4-hydroxycyclohex-2-enone[22] (52 mg, 0.45 mmol), cinnamyl bromide (125 mg, 0.63 mmol), Ag_2O (207 mg, 0.89 mmol), and 0.87 mL CH_2Cl_2. The suspension was allowed to stir overnight and concentrated *in vacuo* to yield a black residue. Purification by chromatography on silica gel using 3:1 hexanes:EtOAc as the eluent afforded the product as a clear oil (16 mg, 0.071 mmol, 16% yield). IR (thin film): 3027, 1683, 1075; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.1 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.27 (m, 1H), 7.00 (d, J = 9.2 Hz, 1H), 6.65 (d, J = 16.1 Hz, 1H), 6.31 (dt, J = 15.9, 6.4 Hz, 1H), 3.01 (d, J = 10.1 Hz, 1H), 4.29 (m, 3H), 2.62 (dt, J = 18.6, 3.9 Hz, 1H), 2.38 (m, 2H), 2.05 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.7, 150.5, 136.4, 133.0, 129.7, 128.6, 127.9, 126.5, 125.4, 72.4, 69.7, 35.3, 29.2; HRMS (ESI^+) calc'd for $[C_{15}H_{16}O_2]^+$ requires *m/z* 228.1145, found *m/z* 228.1144.

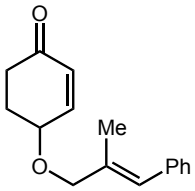


(*E*)-4-((3-(*p*-Tolyl)allyl)oxy)cyclohex-2-enone (Table 3, entry 8). Prepared using a modification of a procedure by Kibayashi.[21] Phosphorous tribromide (0.48 mL, 5.1 mmol) was added dropwise to a solution of (*E*)-3-(*p*-tolyl)prop-2-en-1-ol[23] (690 mg, 4.6 mmol) in 6.2 mL Et_2O. The resulting yellow solution was allowed to stir at 0 ºC for 2.5 h, after which the reaction was quenched with ice and extracted with Et_2O (x3). The combined organics were washed with H_2O, dried over Na_2SO_4, and concentrated to yield the bromide as a white solid.[24] To the crude bromide was added 4-hydroxycyclohex-2-enone[22] (379 mg, 3.4 mmol), Ag_2O (1.57 g, 6.8 mmol), and 6.6 mL CH_2Cl_2. The resulting suspension was allowed to stir overnight and concentrated *in vacuo* to yield a black residue. Purification by chromatography on silica gel using 2:1 hexanes:EtOAc as the eluent afforded the product as a clear oil (93 mg, 0.38 mmol, 11% yield). IR (thin film): 1686, 1512, 969; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.00 (dd, J = 8.8, 1.5 Hz, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.9, 5.9 Hz, 1H), 6.01 (dd, J = 10.0, 1.2 Hz, 1H), 4.27 (m, 3H), 2.62 (dt, J = 16.3, 4.0 Hz, 1H), 2.34 (m, 4H), 2.34 (s, 3H), 2.04 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) 198.7, 150.6, 137.8, 133.5, 133.1, 129.7, 129.3, 126.4, 124.3, 72.3, 69.7, 35.3, 29.3, 21.2; HRMS (EI^+) calc'd for $[C_{16}H_{18}O_2]^+$ requires *m/z* 242.1302, found *m/z* 242.1312.



(*E*)-4-((3-(4-(Trifluoromethyl)phenyl)allyl)oxy)cyclohex-2-enone (Table 3, entry 9). Prepared using a modification of a procedure by Kibayashi.[21] A 25 mL round-bottomed flask was charged with 4-hydroxycyclohex-2-enone[22] (450 mg, 4.0 mmol), (*E*)-1-(3-bromoprop-1-en-1-yl)-4-(trifluoromethyl) benzene[25] (1.48 g, 5.6 mmol), Ag_2O (1.85 g, 8.0 mmol), and 7.8 mL CH_2Cl_2. The suspension was allowed to stir overnight and concentrated *in vacuo* to yield a black residue. Purification by chromatography on silica gel using 1:1 hexanes:EtOAc as the eluent afforded the product as a clear oil (678 mg, 0.57 mmol, 57% yield). IR (thin film): 1687, 1615, 1326, 1120; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.00 (dt, J = 10 Hz, 1H), 6.69 (d, J = 15.8 Hz, 1H), 6.40 (dt, J = 15.7, 5.6 Hz, 1H), 6.02 (d, J = 10.2 Hz, 1H), 4.30 (m, 3H), 2.63 (m, 1H), 2.37 (m, 2H), 2.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.5, 150.1, 139.9, 139.9, 131.0, 129.9, 128.3, 126.6, 125.6, 125.6, 125.5, 125.5, 72.8, 69.2, 35.2, 29.2; HRMS (ESI^+) calc'd for $[C_{16}H_{15}F_3O_2]^+$ requires *m/z* 296.1019, found *m/z* 296.1018.

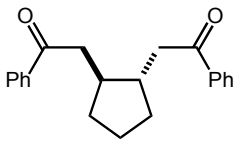


(*E*)-4-((2-Methyl-3-phenylallyl)oxy)cyclohex-2-enone (Table 3, entry 10). Prepared using a modification of a procedure by Kibayashi.[21] A 25 mL round-bottomed flask was charged with 4-hydroxycyclohex-2-enone[22] (645 mg, 5.8 mmol), (*E*)-(3-bromo-2-methylprop-1-en-1-yl)benzene[24] (1.7 g, 8.1 mmol), Ag_2O (2.7 g, 12 mmol), and 11 mL CH_2Cl_2. The suspension was allowed to stir overnight and concentrated *in vacuo* to yield a black residue. Purification by chromatography on silica gel using 3:1 hexanes:EtOAc as the eluent afforded the product as a yellow oil (290 mg, 1.2 mmol, 21% yield). IR (thin film): 1683, 1379, 1087; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.30 (m, 2H), 7.23 (t, J = 5.9 Hz, 1H), 7.01 (d, J = 10.3 Hz, 1H), 6.55 (s, 1H), 6.01 (d, J = 9.9 Hz, 1H), 4.27 (m, 1H), 4.16 (q, J = 12.3 Hz, 2H), 2.62 (dt, J = 15.7, 3.5 Hz, 1H), 2.37 (m, 2H), 2.07 (m, 1H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.7, 150.6, 137.2, 134.7, 129.7, 128.9, 128.2, 127.6, 126.7, 75.3, 72.3, 35.3, 29.2, 15.6; HRMS (ESI^+) calc'd for $[C_{16}H_{28}O_2]^+$ requires *m/z* 242.1302, found *m/z* 242.1303.

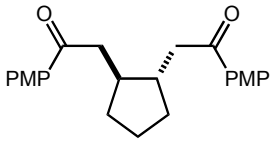
III. Reductive cyclizations

General procedure for reductive cyclizations of aryl enones (A): A dry 25 mL Schlenk tube was charged with the aryl enone (1 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.025 equiv), HCO_2H (5 equiv), *i*-Pr_2NEt (10 equiv), and acetonitrile (0.05 M) and degassed in the dark using three freeze/pump/thaw cycles under nitrogen. The reaction was then stirred vigorously and irradiated with a 23 W (1380 lumen) compact fluorescent lamp. Upon completion of the reaction, the solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel.

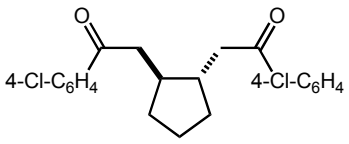
General procedure for reductive cyclizations of aliphatic enones (B): A dry 25 mL Schlenk tube was charged with the aliphatic enone (1 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$[26] (0.025 equiv), HCO_2H (5 equiv), *i*-Pr_2NEt (10 equiv), and acetonitrile (0.05 M) and degassed in the dark using three freeze/pump/thaw cycles under nitrogen. The reaction was then stirred vigorously and irradiated with a 23 W (1380 lumen) compact fluorescent lamp. Upon completion of the reaction, the solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel.



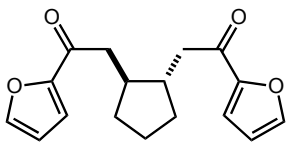
2,2'-((1*S*,2*S*)-Cyclopentane-1,2-diyl)bis(1-phenylethanone) (Table 2, entry 1). Experiment 1: Prepared according to general procedure A using 77 mg (0.25 mmol) (*E*,*E*)-1,7-dibenzoyl-1,6-heptadiene, 5.0 mg (0.0067 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (1.3 mmol), 5.1 mL acetonitrile and irradiated for 2.5 h. Purified by chromatography using 8:1 hexanes:EtOAc to yield 63 mg (0.21 mmol, 81% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure A using 77 mg (0.25 mmol) (*E*,*E*)-1,7-dibenzoyl-1,6-heptadiene, 4.9 mg (0.0065 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (2.6 mmol), 5.1 mL acetonitrile and irradiated for 2.5 h. Isolated 64 mg (0.21 mmol, 82% yield). IR (thin film): 2950, 1683, 1448; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 8.5, 1.7 Hz, 4H), 7.54 (tt, J = 7.3, 1.3 Hz, 2H), 7.44 (t, J = 7.9 Hz, 4H), 3.20 (dd, J = 16.5, 4.3 Hz, 2H), 2.94 (dd, J = 16.5, 8.2 Hz, 2H), 2.19 (m, 2H), 1.99 (m, 2H), 1.63 (m, 2H), 1.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 200.2, 137.2, 132.9, 128.6, 128.1, 44.0, 41.6, 32.5, 23.7; HRMS (ESI^+) calc'd for $[C_{21}H_{23}O_2]^+$ requires *m/z* 307.1693, found *m/z* 307.1708. (mp = 112–116 ºC)



2,2'-((1*S*,2*S*)-Cyclopentane-1,2-diyl)-bis(1-(4-methoxyphenyl)ethanone) (Table 2, entry 2). Experiment 1: Prepared according to general procedure A using 95 mg (0.26 mmol) (*E*,*E*)-1,7-(4-methoxybenzoyl)-1,6-heptadiene, 5.0 mg (0.0067 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 454 μL *i*-Pr_2NEt (2.6 mmol), 5.2 mL acetonitrile and irradiated for 3 h. Purified by chromatography using 3:1 hexanes:EtOAc to yield 90 mg (0.24 mmol, 94% yield) of the cycloadduct as a white solid. Experiment 2: Prepared according to general procedure A using 95 mg (0.26 mmol) (*E*,*E*)-1,7-(4-methoxybenzoyl)-1,6-heptadiene, 5.1 mg (0.0068 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 454 μL *i*-Pr_2NEt (2.6 mmol), 5.2 mL acetonitrile and irradiated for 3 h. Isolated 92 mg (0.25 mmol, 96% yield). IR (thin film): 1671, 1601, 1258, 1171; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, J = 9.0, 2.2 Hz, 4H), 6.92 (dt, J = 8.9, 2.1 Hz, 4H), 3.86 (s, 6H), 3.13 (dd, J = 16.1, 4.8 Hz, 2H), 2.87 (dd, J = 16.1, 8.5 Hz, 2H), 2.15 (m, 2H), 1.96 (m, 2H), 1.62 (m, 2H), 1.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.8, 163.3, 130.4, 130.3, 113.7, 55.4, 43.6, 41.9, 32.5, 23.7; HRMS (ESI^+) calc'd for $[C_{23}H_{26}O_4Na]^+$ requires *m/z* 389.1724, found *m/z* 389.1709. (mp = 117–122 ºC)

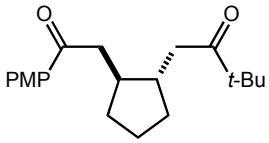


2,2'-((1*S*,2*S*)-Cyclopentane-1,2-diyl)bis(1-(4-chlorophenyl)ethanone) (Table 2, entry 3). Experiment 1: Prepared according to general procedure A using 97 mg (0.26 mmol) (*E*,*E*)-1,7-(4-chlorobenzoyl)-1,6-heptadiene, 5.2 mg (0.0069 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 453 μL *i*-Pr_2NEt (2.6 mmol), 5.2 mL acetonitrile and irradiated for 1.5 h. Purified by chromatography using 12:1 hexanes:EtOAc to yield 73 mg (0.19 mmol, 75% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure A using 97 mg (0.26 mmol) (*E*,*E*)-1,7-(4-chlorobenzoyl)-1,6-heptadiene, 5.0 mg (0.0067 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 454 μL *i*-Pr_2NEt (2.6 mmol), 5.2 mL acetonitrile and irradiated for 1.5 h. Isolated 75 mg (0.20 mmol, 77% yield). IR (thin film): 1676, 1588; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (tt, J = 8.4, 2.6 Hz, 4H), 7.42 (tt, J = 8.7, 2.3 Hz, 4H), 3.16 (dd, J = 16.7, 5.0 Hz, 2H), 2.92 (dd, J = 16.3, 7.9 Hz, 2H), 2.17 (m, 2H), 1.98 (m, 2H), 1.64 (m, 2H), 1.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.9, 139.4, 135.4, 129.5, 128.9, 44.0, 41.4, 32.6, 23.7; HRMS (ESI^+) calc'd for $[C_{21}H_{20}O_2Na]^+$ requires *m/z* 397.0733, found *m/z* 397.0719.

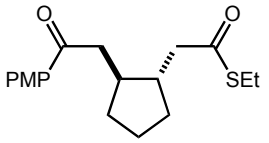


2,2'-((1*S*,2*S*)-Cyclopentane-1,2-diyl)bis(1-(furan-2-yl)ethanone) (Table 2, entry 4). Experiment 1: Prepared according to general procedure A using 73 mg (0.26 mmol) (*E*,*E*)-1,7-(2-furoyl)-1,6-heptadiene, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 447 μL *i*-Pr_2NEt (2.6 mmol), 5.1 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 2:1 hexanes:EtOAc to yield 50 mg (0.18 mmol, 69% yield) of the cycloadduct as a yellow oil.

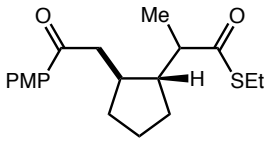
Experiment 2: Prepared according to general procedure A using 91 mg (0.32 mmol) (*E*,*E*)-1,7-(2-furoyl)-1,6-heptadiene, 6.0 mg (0.0080 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 61 μL (1.6 mmol) HCO_2H, 552 μL *i*-Pr_2NEt (3.2 mmol), 6.3 mL acetonitrile and irradiated for 4 h. Isolated 64 mg (0.22 mmol, 69% yield). IR (thin film): 1670, 1568, 1467; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 1.3 Hz, 2H), 7.19 (d, J = 3.3 Hz, 2H), 6.53 (dd, J = 3.2, 2.1 Hz, 2H), 3.01 (dd, J = 15.6, 4.7 Hz, 2H), 2.79 (dd, J = 15.8, 8.7 Hz, 2H), 2.13 (m, 2H), 1.95 (m, 2H), 1.63 (m, 2H), 1.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 189.2, 152.9, 146.3, 117.1, 112.2, 43.5, 41.7, 32.2, 23.5; HRMS (ESI^+) calc'd for $[C_{17}H_{18}O_4]^+$ requires *m/z* 286.1200, found *m/z* 286.1192.



1-((1*S*,2*S*)-2-(2-(4-Methoxyphenyl)-2-oxoethyl)cyclopentyl)-3,3-dimethyl butan-2-one (Table 2, entry 5). Experiment 1: Prepared according to general procedure A using 75 mg (0.24 mmol) (2*E*,7*E*)-1-(4-methoxyphenyl)-10,10-dimethylundeca-2,7-diene-1,9-dione, 4.5 mg (0.0060 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 46 μL (1.2 mmol) HCO_2H, 416 μL *i*-Pr_2NEt (2.4 mmol), 4.8 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 5:1 hexanes:EtOAc to yield 69 mg (0.22 mmol, 92% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure A using 79 mg (0.25 mmol) (2*E*,7*E*)-1-(4-methoxyphenyl)-10,10-dimethylundeca-2,7-diene-1,9-dione, 5.0 mg (0.0067 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 49 μL (1.3 mmol) HCO_2H, 443 μL *i*-Pr_2NEt (2.5 mmol), 5.1 mL acetonitrile and irradiated for 6 h. Isolated 77 mg (0.24 mmol, 97% yield). IR (thin film): 1701, 1671, 1601; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 8.7, 2.0 Hz, 2H), 6.93 (dt, J = 8.9, 1.9 Hz, 2H), 3.87 (s, 3H), 3.06 (dd, J = 16.1, 4.1 Hz, 1H), 2.85 (dd, J = 16.2, 8.7 Hz, 1H), 2.62 (dd, J = 17.8, 4.5 Hz, 1H), 2.52 (dd, J = 17.6, 8.3 Hz, 1H), 2.05 (m, 2H), 1.92 (m, 2H), 1.5 (m, 2H), 1.22 (m, 1H), 1.12 (s, 9H), 1.08 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 215.9, 198.9, 163.3, 130.3, 113.6, 55.4, 44.1, 43.6, 42.0, 41.5, 40.9, 32.6, 26.4, 23.7; HRMS (ESI^+) calc'd for $[C_{20}H_{29}O_3]^+$ requires *m/z* 317.2112, found *m/z* 317.2121.

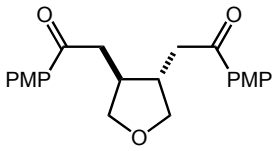


***S*-Ethyl-2-((1*S*,2*S*)-2-(2-(4-methoxyphenyl)-2-oxoethyl)cyclopentyl)ethane thioate** (Table 2, entry 6). Experiment 1: Prepared according to general procedure A using 141 mg (0.44 mmol) (2*E*,7*E*)-*S*-ethyl 9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate, 8.2 mg (0.0101 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 79 μL (2.1 mmol) HCO_2H, 766 μL *i*-Pr_2NEt (4.4 mmol), 9.0 mL acetonitrile and irradiated for 9 h. Purified by chromatography using 4:1 hexanes:ether to yield 113 mg (0.35 mmol, 80% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure A using 141 mg (0.44 mmol) (2*E*,7*E*)-*S*-ethyl 9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate, 8.2 mg (0.0101 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 79 μL (2.1 mmol) HCO_2H, 766 μL *i*-Pr_2NEt (4.4 mmol), 9.0 mL acetonitrile and irradiated for 9 h. Isolated 110 mg (0.34 mmol, 78% yield). IR (thin film): 1676, 1600, 1509; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 8.8, 3.0 Hz, 2H), 6.93 (dt, J = 8.9, 2.9 Hz, 2H), 3.87 (s, 3H), 3.09 (dd, J = 16.3, 4.4 Hz, 1H), 2.87 (q, J = 7.5 Hz, 2H), 2.82 (dd, J = 15.8, 8.8 Hz, 1H), 2.75 (dd, J = 14.7, 5.1 Hz, 1H), 2.49 (dd, J = 14.9, 8.7 Hz, 1H), 2.04 (m, 2H), 1.92 (m, 2H), 1.61 (m, 2H), 1.32 (m, 1H), 1.25 (m, 1H), 1.24 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.3, 198.5, 163.4, 130.4, 130.2, 113.7, 55.4, 49.0, 43.4, 42.8, 41.5, 32.3, 31.9, 23.5, 23.3, 14.7; HRMS (ESI^+) calc'd for $[C_{18}H_{24}O_3SNa]^+$ requires *m/z* 343.1339, found *m/z* 343.1342.

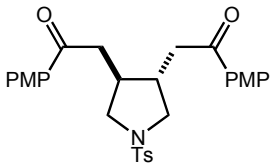


(*R*)-*S*-Ethyl-2-((1*R*,2*S*)-2-(2-(4-methoxyphenyl)-2-oxoethyl)cyclopentyl) propanethioate (Table 2, entry 7). Experiment 1: Prepared according to general procedure A using 90 mg (0.27 mmol) (2*E*,7*E*)-*S*-ethyl 9-(4-methoxyphenyl)-2-methyl-9-oxonona-2,7-dienethioate, 5.1 mg (0.0068 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 49 μL (1.4 mmol) HCO_2H, 472 μL *i*-Pr_2NEt (2.7 mmol), 5 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 4:1 hexanes:EtOAc to yield 68 mg (0.20 mmol, 75% yield) of the cycloadduct as an inseparable 1:1 mixture of diastereomers as a yellow oil. Experiment 2: Prepared according to general procedure A using 90 mg (0.27 mmol) (2*E*,7*E*)-*S*-ethyl 9-(4-

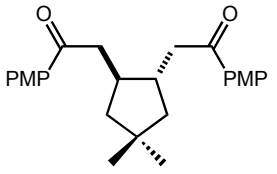
methoxyphenyl)-2-methyl-9-oxonona-2,7-dienethioate, 5.1 mg (0.0068 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 49 μL (1.4 mmol) HCO_2H, 472 μL *i*-Pr_2NEt (2.7 mmol), 5 mL acetonitrile and irradiated for 12 h. Isolated 67 mg (0.20 mmol, 74% yield). IR (thin film): 2961, 1678, 1600, 1258; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (m, H_A = 2H, H_B = 2H), 6.91 (m, H_A = 2H, H_B = 2H), 3.87 (s, H_A = 3H), 3.86 (s, H_B = 3H), 3.14 (dd, J = 14.3, 3.3 Hz, H_B = 1H), 3.06 (dd, J = 15.8, 3.8 Hz, H_A = 1H), 2.91 (q, J = 7.5 Hz, H_B = 2H), 2.84 (q, J = 7.2 Hz, H_A = 2H), 2.76 (dd, J = 15.8, 9.9 Hz, H_A = 1H), 2.63 (m, H_A = 1H, H_B = 1H), 2.55 (m, H_B = 1H), 2.47 (dd, J = 14.0, 12.1 Hz, H_B = 1H), 2.24 (m, H_A = 1H, H_B = 1H), 2.17 (s, H_A = 3H, H_B = 3H), 1.98 (m, H_A = 1H), 1.87 (m, H_A = 2H), 1.8 (m, H_B = 2H), 1.56 (m, H_B = 2H), 1.24 (m, H_A = 3H, H_B = 6H), 1.16 (d, H_A = 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 203.8, 203.5, 199.0, 198.5, 163.3, 163.2, 130.5, 130.4, 113.6, 55.4, 52.2, 50.3, 48.3, 47.1, 44.3, 39.4, 37.9, 37.5, 32.6, 30.9, 30.3, 29.2, 27.7, 23.9, 23.1, 23.1, 21.4, 18.5, 15.0, 14.9, 14.7; HRMS (ESI^+) calc'd for $[C_{19}H_{26}O_3SNa]^+$ requires *m/z* 357.1495, found *m/z* 357.1483.



2,2'-((3*S*,4*S*)-Tetrahydrofuran-3,4-diyl)bis(1-(4-methoxyphenyl)ethanone) (Table 2, entry 8). Experiment 1: Prepared according to general procedure A using 92 mg (0.25 mmol) (2*E*,2'*E*)-4,4'-oxybis(1-(4-methoxyphenyl)but-2-en-1-one), 4.8 mg (0.0064 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 49 μL (1.3 mmol) HCO_2H, 437 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 3.5 h. Purified by chromatography using 1:1 hexanes:EtOAc to yield 85 mg (0.23 mmol, 92% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure A using 92 mg (0.25 mmol) (2*E*,2'*E*)-4,4'-oxybis(1-(4-methoxyphenyl)but-2-en-1-one), 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 49 μL (1.3 mmol) HCO_2H, 437 μL *i*-Pr_2NEt (2.5 mmol), 5.1 mL acetonitrile and irradiated for 3.5 h. Isolated 87 mg (0.24 mmol, 94% yield). IR (thin film): 1669, 1601, 1508; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, J = 9.0, 2.7 Hz, 4H), 6.93 (dt, J = 9.2, 2.7 Hz, 4H), 4.15 (dd, J = 8.8, 6.7 Hz, 2H), 3.87 (s, 6H), 3.48 (dd, J = 8.8, 5.8 Hz, 2H), 3.31 (dd, J = 17.5, 5.1 Hz, 2H), 3.04 (dd, J = 17.4, 8.2 Hz, 2H), 2.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 197.6, 163.5, 130.3, 129.9, 113.7, 73.4, 55.5, 42.2, 40.8; HRMS (ESI^+) calc'd for $[C_{22}H_{24}O_5Na]^+$ requires *m/z* 391.1516, found *m/z* 391.1527.

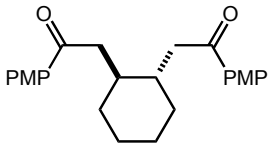


2,2'-((3*S*,4*S*)-1-Tosylpyrrolidine-3,4-diyl)bis(1-(4-methoxyphenyl)ethanone) (Table 2, entry 9). Experiment 1: Prepared according to general procedure A using 74 mg (0.14 mmol) *N,N*-bis((*E*)-4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methyl benzenesulfonamide, 2.7 mg (0.0036 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 26 μL (0.7 mmol) HCO_2H, 251 μL *i*-Pr_2NEt (1.4 mmol), 2.8 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 3:2 hexanes:EtOAc to yield 59 mg (0.11 mmol, 80% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure A using 77 mg (0.15 mmol) *N,N*-bis((*E*)-4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methyl benzenesulfonamide, 2.7 mg (0.0037 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 26 μL (0.7 mmol) HCO_2H, 257 μL *i*-Pr_2NEt (1.5 mmol), 2.9 mL acetonitrile and irradiated for 4 h. Isolated 66 mg (0.13 mmol, 86% yield). IR (thin film): 1673, 1600, 1259, 1160; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (dt, J =9.3, 2.8 Hz, 4H), 7.70 (d, J=8.5 Hz, 2H), 7.28 (d, J =7.7 Hz, 2H), 6.91 (dt, J =9.3, 3.2 Hz, 4H), 3.87 (s, 6H), 3.63 (dd, J =2, 10.3, 6.9 Hz, 2H), 3.09 (dd, J =17.5, 4.5 Hz, 2H), 2.94 (dd, J =10.5, 6.6 Hz, 2H), 2.80 (dd, J =17.8, 8.1 Hz, 2H), 2.47 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 196.7, 163.7, 143.5, 133.0, 130.2, 129.7, 129.6, 127.7, 113.8, 55.5, 52.9, 41.4, 39.4, 30.9, 21.5; HRMS (ESI^+) calc'd for $[C_{29}H_{31}NO_6SNa]^+$ requires *m/z* 544.1765, found *m/z* 544.1741. (mp = 128 ºC (dec.))

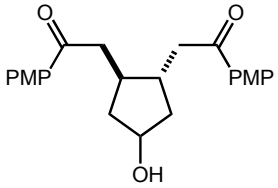


2,2'-((1*S*,2*S*)-4,4-Dimethylcyclopentane-1,2-diyl)bis(1-(4-methoxyphenyl) ethanone) (Table 2, entry 10). Experiment 1: Prepared according to general procedure A using 90 mg (0.23 mmol) (2*E*,7*E*)-1,9-bis(4-methoxyphenyl)-5,5-dimethylnona-2,7-diene-1,9-dione, 4.3 mg (0.0060 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 41 μL (1.2 mmol) HCO_2H, 400 μL *i*-Pr_2NEt (2.3 mmol), 4.6 mL acetonitrile and irradiated for 3 h. Purified by chromatography using 3:1 hexanes:EtOAc to yield

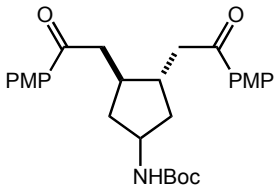
65 mg (0.16 mmol, 72% yield) of the cycloadduct as a white solid. Experiment 2: Prepared according to general procedure A using 92 mg (0.23 mmol) (2*E*,7*E*)-1,9-bis(4-methoxyphenyl)-5,5-dimethylnona-2,7-diene-1,9-dione, 4.4 mg (0.0058 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 42 μL (1.2 mmol) HCO_2H, 406 μL *i*-Pr_2NEt (2.3 mmol), 4.7 mL acetonitrile and irradiated for 3 h. Isolated 68 mg (0.17 mmol, 74% yield). IR (thin film): 1674, 1600, 1256; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (dt, J =9.0, 2.0 Hz, 4H), 6.93 (dt, J =8.9, 1.9 Hz, 4H), 3.87 (s, 6H), 3.11 (dd, J =15.6, 4.5 Hz, 2H), 2.88 (dd, J =16.1, 8.5 Hz, 2H), 2.33 (m, 2H), 1.82 (dd, J =12.8, 6.9 Hz, 2H), 1.16 (dd, J =13.0, 9.7 Hz, 2H), 1.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.9, 163.5, 130.3, 113.7, 55.3, 48.1, 43.4, 41.6, 37.2, 31.0; HRMS (ESI^+) calc'd for $[C_{19}H_{26}O_3SNa]^+$ requires *m/z* 417.2025, found *m/z* 417.2037. (mp = 102–109 ºC)



2,2'-((1*S*,2*S*)-Cyclohexane-1,2-diyl)bis(1-(4-methoxyphenyl)ethanone) (Table 2, entry 11). Experiment 1: Prepared according to general procedure A using 95 mg (0.25 mmol) (3*E*,9*E*)-1,12-bis(4-methoxyphenyl)dodeca-3,9-diene-1,12-dione, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 49 μL (1.3 mmol) HCO_2H, 437 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 6 h. Purified by chromatography using 3:1 hexanes:EtOAc to yield 87 mg (0.23 mmol, 90% yield) of the cycloadduct as a white residue. Experiment 2: Prepared according to general procedure A using 95 mg (0.25 mmol) (3*E*,9*E*)-1,12-bis(4-methoxyphenyl)dodeca-3,9-diene-1,12-dione, 4.8 mg (0.0064 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 49 μL (1.3 mmol) HCO_2H, 437 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 6 h. Isolated 90 mg (0.23 mmol, 93% yield). IR (thin film): 1669, 1600, 1168; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 4H), 6.91 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H), 3.01 (dd, J = 16.0, 3.8 Hz, 2H), 2.77 (dd, J = 16.0, 7.5 Hz, 2H), 1.97 (m, 2H), 1.76 (d, J = 13.3 Hz, 2H), 1.66 (m, 2H), 1.28 (m, 2H), 1.12 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.1, 163.3, 130.5, 130.4, 113.6, 55.4, 43.2, 39.1, 33.2, 26.0; HRMS (ESI^+) calc'd for $[C_{24}H_{28}O_4Na]^+$ requires *m/z* 403.1880, found *m/z* 403.1877.

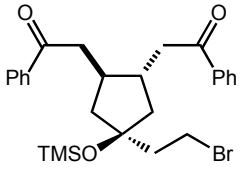


2,2'-((1*S*,2*S*)-4-Hydroxycyclopentane-1,2-diyl)bis(1-(4-methoxyphenyl) ethanone) (Table 2, entry 12). Experiment 1: Prepared according to general procedure A using 95 mg (0.25 mmol) (2*E*,7*E*)-5-hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (1.3 mmol), 5.0 mL acetonitrile and irradiated for 5 h. Purified by chromatography using 2:3 hexanes:EtOAc to yield 73 mg (0.20 mmol, 76% yield) of the cycloadduct as a white solid. Experiment 2: Prepared according to general procedure A using 95 mg (0.25 mmol) (2*E*,7*E*)-5-Hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (2.6 mmol), 5.0 mL acetonitrile and irradiated for 5 h. Isolated 69 mg (0.18 mmol, 72% yield). IR (thin film): 3442, 1664, 1616, 1258; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (t, J = 8.5 Hz, 4H), 6.91 (dd, J = 8.9, 3.6 Hz, 4H), 4.35 (s, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.20 (dd, J = 33.7, 16.7 Hz, 1H), 3.19 (dd, J = 33.9, 16.8 Hz, 1H), 3.07 (dd, J = 16.8, 8.5 Hz, 1H), 2.88 (dd, J = 16.1, 8.5 Hz, 1H), 2.55 (m, 1H), 2.35 (m, 1H), 2.24 (m, 1H), 2.01 (m, 1H), 1.53 (m, 1H), 1.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.8, 198.5, 163.4, 163.4, 130.4, 130.2, 130.1, 113.7, 113.7, 72.5, 55.5, 43.8, 43.5, 42.8, 42.0, 40.0, 39.4; HRMS (ESI^+) calc'd for $[C_{23}H_{26}O_5Na]^+$ requires *m/z* 405.1656, found *m/z* 405.1673. (mp = 88–93 ºC)

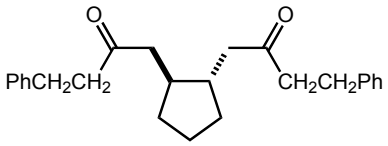


***tert*-Butyl-((3*S*,4*S*)-3,4-bis(2-(4-methoxyphenyl)-2-oxoethyl)cyclopentyl) carbamate** (Table 2, entry 13). Experiment 1: Prepared according to general procedure A using 120 mg (0.25 mmol) *tert*-butyl ((2*E*,7*E*)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl)carbamate, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (1.3 mmol), 5.0 mL acetonitrile and irradiated for 3.5 h. Purified by chromatography using 3:2 hexanes:EtOAc to yield 111 mg (0.23 mmol, 92% yield) of the cycloadduct as a

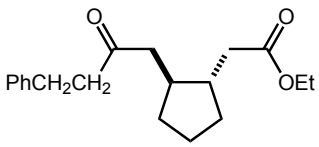
white solid. Experiment 2: Prepared according to general procedure A using 120 mg (0.25 mmol) *tert*-butyl ((2*E*,7*E*)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl)carbamate, 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 50 μL (1.3 mmol) HCO_2H, 446 μL *i*-Pr_2NEt (2.6 mmol), 5.0 mL acetonitrile and irradiated for 3.5 h. Isolated 110 mg (0.23 mmol, 91% yield). IR (thin film): 3345, 1599, 1259, 1171; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.7 Hz, 4H), 6.92 (d, J = 9.1 Hz, 4H), 4.60 (m, 1H), 4.01 (m, 1H), 3.87 (s, 6H), 3.15 (ddd, J = 30.2, 15.9, 5.0 Hz, 2H), 2.92 (dd, J = 16.8, 8.4 Hz, 2H), 2.41 (m, 2H), 2.20 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H), 1.42 (s, 9H), 1.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.2, 198.2, 163.5, 130.3, 130.2, 113.7, 55.5, 43.4, 43.3, 40.3, 39.9, 39.2, 28.4; HRMS (ESI^+) calc'd for $[C_{28}H_{35}NO_6]^+$ requires *m/z* 482.2538, found *m/z* 482.2517. (mp = 107–111 ºC)



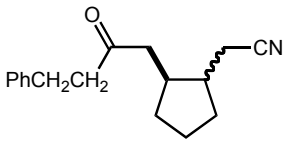
2,2'-((1*S*,2*S*)-4-(2-Bromoethyl)-4-((trimethylsilyl)oxy)cyclopentane-1,2-diyl)bis(1-phenylethanone) (Table 2, entry 14). Experiment 1: Prepared according to general procedure A using 99 mg (0.20 mmol) (2*E*,7*E*)-5-(2-bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-diene-1,9-dione, 3.8 mg (0.0051 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 38 μL (1.0 mmol) HCO_2H, 345 μL *i*-Pr_2NEt (2.6 mmol), 4.0 mL acetonitrile and irradiated for 3 h. Purified by chromatography using 7:1 hexanes:EtOAc to yield 64 mg (0.13 mmol, 64% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure A using 120 mg (0.25 mmol) (2*E*,7*E*)-5-(2-bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-diene-1,9-dione, 4.1 mg (0.0055 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 43 μL (1.1 mmol) HCO_2H, 384 μL *i*-Pr_2NEt (2.2 mmol), 4.4 mL acetonitrile and irradiated for 3 h. Isolated 72 mg (0.14 mmol, 65% yield). IR (thin film): 1685, 1597, 1448, 1251; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (t, J = 7.0 Hz, 4H), 7.56 (m, 2H), 7.46 (m, 4H), 3.58 (m, 1H), 3.28 (m, 2H), 3.12 (dd, J = 16.9, 8.5 Hz, 1H), 2.95 (dd, J = 16.8, 9.0 Hz, 1H), 2.54 (m, 1H), 2.33 (m, 1H), 2.22 (dd, J = 11.8, 5.2 Hz, 1H), 21.2 (m, 1H), 2.02 (m, 2H), 1.56 (m, 1H), 1.31 (m, 2H), 0.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 200.1, 199.9, 137.3, 137.2, 133.3, 128.8, 128.3, 128.2, 83.3, 47.6, 46.8, 45.8, 44.9, 43.9, 40.9, 39.9, 39.9, 2.5; HRMS (ESI^+) calc'd for $[C_{26}H_{33}BrO_3SiNa]^+$ requires *m/z* 523.1275, found *m/z* 523.1291.



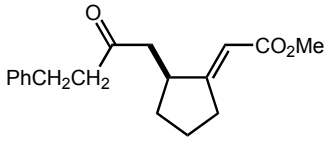
1,1'-((1*S*,2*S*)-Cyclopentane-1,2-diyl)bis(4-phenylbutan-2-one) (Table 3, entry 1). Experiment 1: Prepared according to general procedure A using 90 mg (0.25 mmol) (4*E*,9*E*)-1,13-diphenyltrideca-4,9-diene-3,11-dione, 4.6 mg (0.0061 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 48 μL (1.3 mmol) HCO_2H, 435 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 36 h. Purified by chromatography using 4:1 hexanes:ether to yield 85 mg (0.24 mmol, 94% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure A using 90 mg (0.25 mmol) (4*E*,9*E*)-1,13-diphenyltrideca-4,9-diene-3,11-dione, 4.9 mg (0.0065 mmol) $Ru(bpy)_3Cl_2·6H_2O$, 48 μL (1.3 mmol) HCO_2H, 435 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 36 h. Isolated 83 mg (0.23 mmol, 92% yield). Experiment 3: Prepared according to general procedure B using 90 mg (0.25 mmol) (4*E*,9*E*)-1,13-diphenyltrideca-4,9-diene-3,11-dione, 5.8 mg (0.0063 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 48 μL (1.3 mmol) HCO_2H, 435 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 12 h. Isolated 84 mg (0.23 mmol, 93% yield). Experiment 4: Prepared according to general procedure B using 90 mg (0.25 mmol) (4*E*,9*E*)-1,13-diphenyltrideca-4,9-diene-3,11-dione, 5.8 mg (0.0063 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 48 μL (1.3 mmol) HCO_2H, 435 μL *i*-Pr_2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 12 h. Isolated 82 mg (0.23 mmol, 91% yield). IR (thin film): 1711, 1647; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dt, J = 7.9, 1.7 Hz, 4H), 7.18 (m, 6H), 2.81 (t, J = 7.7 Hz, 4H), 2.7 (m, 4H), 2.49 (dd, J = 16.7, 4.3 Hz, 2H), 2.28 (dd, J = 16.5, 7.6 Hz, 2H), 1.84 (m, 4H), 1.54 (m, 2H), 1.1 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 209.9, 141.1, 128.4, 128.3, 126.1, 48.2, 44.6, 40.8, 32.3, 29.7, 23.5; HRMS (ESI^+) calc'd for $[C_{25}H_{30}O_2]^+$ requires *m/z* 362.2241, found *m/z* 362.2238.



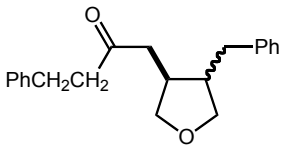
Ethyl 2-((1*S*,2*S*)-2-(2-oxo-4-phenylbutyl)cyclopentyl)acetate (Table 3, entry 3). Experiment 1: Prepared according to general procedure B using 99 mg (0.33 mmol) (2*E*,7*E*)-ethyl 9-oxo-11-phenylundeca-2,7-dienoate, 7.5 mg (0.0082 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 71 μL (1.5 mmol) HCO_2H, 574 μL *i*-Pr_2NEt (3.3 mmol), 6.6 mL acetonitrile and irradiated for 24 h. Purified by chromatography using 9:1 hexanes:EtOAc to yield 76 mg (0.25 mmol, 77% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure B using 90 mg (0.30 mmol) (2*E*,7*E*)-ethyl 9-oxo-11-phenylundeca-2,7-dienoate, 6.8 mg (0.0074 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 54 μL (1.4 mmol) HCO_2H, 519 μL *i*-Pr_2NEt (3.0 mmol), 6.0 mL acetonitrile and irradiated for 24 h. Isolated 69 mg (0.23 mmol, 76 % yield). IR (thin film): 2254, 1716, 1646; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.19 (m, 3H), 4.11 (q, J = 7.0 Hz, 2H), 2.89 (m, 2H), 2.72 (m, 2H), 2.56 (dd, J = 15.4, 4.3 Hz, 1H), 2.41 (dd, J = 14.4, 6.9 Hz, 1H), 2.30 (dd, J = 14.9, 7.4 Hz, 1H), 1.89 (m, 4H), 1.58 (m, 2H), 1.25 (m, 4H), 1.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 209.7, 173.2, 141.1, 128.5, 128.3, 126.1, 60.2, 48.2, 44.6, 42.0, 40.8, 39.3, 32.3, 32.0, 29.8, 23.4; HRMS (ESI$^+$) calc'd for $[C_{19}H_{26}O_3Na]^+$ requires *m/z* 325.1775, found *m/z* 325.1769; HRMS (ESI$^+$) calc'd for $[C_{19}H_{26}O_3Na]^+$ requires *m/z* 325.1775, found *m/z* 325.1789.



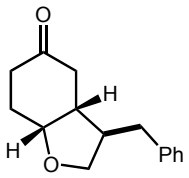
2-((2*S*)-2-(2-Oxo-4-phenylbutyl)cyclopentyl)acetonitrile (Table 3, entry 4). Experiment 1: Prepared according to general procedure B using 120 mg (0.47 mmol) (2*E*,7*E*)-9-oxo-11-phenylundeca-2,7-dienenitrile, 10.8 mg (0.0012 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 85 μL (2.4 mmol) HCO_2H, 824 μL *i*-Pr_2NEt (4.7 mmol), 9.5 mL acetonitrile and irradiated for 9 h. Purified by chromatography using 4:1 hexanes:EtOAc to yield 97 mg (0.38 mmol, 80% yield) of the cycloadduct as an inseparable 1:1 mixture of diastereomers as a yellow oil. Experiment 2: Prepared according to general procedure B using 120 mg (0.47 mmol) (2*E*,7*E*)-9-oxo-11-phenylundeca-2,7-dienenitrile, 10.8 mg (0.0012 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 85 μL (2.4 mmol) HCO_2H, 824 μL *i*-Pr_2NEt (4.7 mmol), 9.5 mL acetonitrile and irradiated for 9 h. Isolated 97 mg (0.38 mmol, 81 % yield). IR (thin film): 3027, 2953, 2244, 1712, 1453; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.17 (m, 3H), 2.88 (m, 4H), 2.72 (m, 2H), 2.52 (dd, J = 17.1, 5.9 Hz, 1H), 2.38 (m, 2H), 2.26 (dd, J = 16.9, 7.7 Hz, 1H), 2.16 (dd, J = 16.4, 6.1 Hz, 1H), 2.01 (dd, J = 16.8, 8.3 Hz, 1H), 1.91 (m, 1H), 1.70 (m, 1H), 1.60 (m, 1H), 1.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 209.2, 208.9, 140.9, 140.9, 128.5, 128.3, 126.2, 126.1, 119.6, 119.2, 48.0, 44.4, 44.3, 43.5, 41.8, 40.1, 38.2, 37.5, 32.6, 32.0, 30.7, 30.3, 29.8, 23.5, 22.2, 21.8, 18.3; HRMS (ESI$^+$) calc'd for $[C_{17}H_{21}ONNa]^+$ requires *m/z* 278.1516, found *m/z* 278.1517.



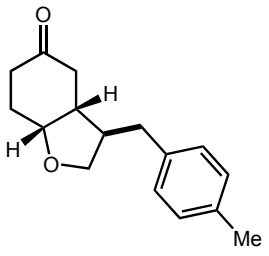
(*S*,*E*)-Methyl 2-(2-(2-oxo-4-phenylbutyl)cyclopentylidene)acetate (Table 3, entry 5). Experiment 1: Prepared according to general procedure B using 101 mg (0.36 mmol) (*E*)-methyl 9-oxo-11-phenylundec-7-en-2-ynoate, 8.2 mg (0.0090 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 69 μL (1.8 mmol) HCO_2H, 621 μL *i*-Pr_2NEt (3.6 mmol), 7.1 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 69 mg (0.24 mmol, 70% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure B using 102 mg (0.36 mmol) bisenone, 8.2 mg (0.0090 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 70 μL (1.8 mmol) HCO_2H, 628 μL *i*-Pr_2NEt (3.6 mmol), 7.2 mL acetonitrile and irradiated for 12 h. Isolated 68 mg (0.24 mmol, 66% yield). IR (thin film): 1712, 1650, 1201; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 7.2 Hz, 2H), 7.19 (m, 3H), 5.61 (q, J = 2.3 Hz, 1H), 3.68 (s, 3H), 2.97 (m, 1H), 2.92 (t, J = 7.4 Hz, 3H), 2.74 (q, J = 7.7 Hz, 3H), 2.73 (m, 1H), 2.64 (dd, J = 17.0, 5.0 Hz, 1H), 2.44 (dd, J = 16.9, 8.5 Hz, 1H), 1.96 (m, 1H), 1.80 (m, 1H), 1.62 (m, 1H), 1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.3, 171.1, 167.2, 140.8, 128.5, 128.3, 126.2, 111.1, 50.9, 47.0, 44.7, 41.7, 32.8, 32.2, 29.8, 24.1; HRMS (ESI$^+$) calc'd for $[C_{18}H_{22}O_3]^+$ requires *m/z* 286.1564, found *m/z* 286.1575.



1-((3*S*)-4-benzyltetrahydrofuran-3-yl)-4-phenylbutan-2-one (Table 3, entry 6). Experiment 1: Prepared according to general procedure B using 100 mg (0.32 mmol) (*E*)-6-(cinnamyloxy)-1-phenylhex-4-en-3-one, 7.5 mg (0.0082 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 63 μL (1.6 mmol) HCO_2H, 483 μL *i*-Pr_2NEt (2.8 mmol), 6.5 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 5:1 hexanes:EtOAc to yield 65 mg (0.21 mmol, 65% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure B using 99 mg (0.32 mmol) (*E*)-6-(cinnamyloxy)-1-phenylhex-4-en-3-one, 7.5 mg (0.0082 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 63 μL (1.6 mmol) HCO_2H, 483 μL *i*-Pr_2NEt (2.8 mmol), 6.5 mL acetonitrile and irradiated for 12 h. Isolated 63 mg (0.20 mmol, 63% yield). Major diastereomer: IR (thin film): 3027, 1713, 1453; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.19 (m, 4H), 7.13 (d, J = 7.3 Hz, 2H), 3.97 (dd, J = 8.3, 6.9 Hz, 1H), 3.74 (dd, J = 8.1, 6.2 Hz, 1H), 3.51 (dd, J = 8.9, 5.5 Hz, 1H), 3.47 (dd, J = 8.2, 6.0 Hz, 1H), 2.89 (t, J = 7.7 Hz, 2H), 2.73 (m, 3H), 2.61 (m, 3H), 2.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.7, 140.8, 140.1, 128.6, 128.5, 128.3, 126.2, 72.7, 71.9, 44.5, 42.5, 41.2, 37.0, 33.9, 29.8; HRMS (ESI^+) calc'd for $[C_{21}H_{24}O_2]^+$ requires *m/z* 308.1771, found *m/z* 308.1757. Minor diastereomer: IR (thin film): 1710, 1603, 1495, 1453; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.19 (m, 2H), 7.14 (m, 4H), 4.09 (dd, J = 8.7, 6.7 Hz, 1H), 3.82 (dd, J = 8.9, 7.2 Hz, 1H), 3.46 (dd, J = 8.6, 7.1 Hz, 1H), 3.32 (dd, J = 8.9, 5.8 Hz, 1H), 2.84 (t, J = 7.7 Hz, 2H), 2.75 (dd, J = 13.6, 6.6 Hz, 1H), 2.62 (m, 3H), 2.43 (m, 1H), 2.34 (m, 2H), 2.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.9, 140.8, 140.2, 128.7, 128.5, 128.3, 126.2, 126.2, 73.6, 72.8, 46.7, 46.6, 44.2, 40.1, 38.9, 29.7; HRMS (ESI^+) calc'd for $[C_{21}H_{24}O_2]^+$ requires *m/z* 308.1771, found *m/z* 308.1787.

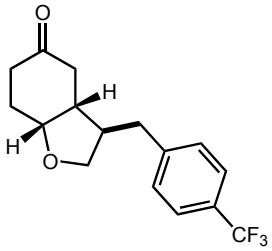


(3a*S*,7a*R*)-3-benzylhexahydrobenzofuran-5(6*H*)-one (Table 3, entry 7). Experiment 1: Prepared according to general procedure B using 104 mg (0.46 mmol) 4-(cinnamyloxy)cyclohex-2-enone, 10.6 mg (0.011 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 88 μL (2.3 mmol) HCO_2H, 794 μL *i*-Pr_2NEt (4.6 mmol), 9.1 mL acetonitrile and irradiated for 20 h. Purified by chromatography using 2:1 hexanes:EtOAc to yield 62 mg (0.27 mmol, 59% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure B using 85 mg (0.37 mmol) 4-(cinnamyloxy)cyclohex-2-enone, 8.5 mg (0.0093 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 72 μL (1.9 mmol) HCO_2H, 649 μL *i*-Pr_2NEt (3.7 mmol), 7.4 mL acetonitrile and irradiated for 20 h. Isolated 52 mg (0.22 mmol, 60% yield). IR (thin film): 2921, 1714; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 4.31 (m, 1H), 3.99 (dd, J = 8.9, 6.7 Hz, 1H), 3.41 (t, J = 8.8 Hz, 1H), 2.77 (dd, J = 13.5, 6.4 Hz, 1H), 2.65 (dd, J = 13.8, 8.5 Hz, 1H), 2.42 (ddd, J = 18.0, 10.8, 5.0 Hz, 1H), 2.34 (m, 2H), 2.19 (m, 2H), 2.09 (m, 2H), 2.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.1, 139.5, 128.6, 128.5, 126.4, 75.6, 72.3, 48.5, 42.5, 41.5, 38.3, 34.6, 30.9, 26.4; HRMS (EI^+) calc'd for $[C_{15}H_{18}O_2]^+$ requires *m/z* 230.1302, found *m/z* 230.1292.

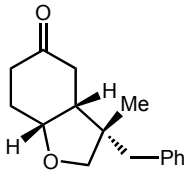


(3a*S*,7a*R*)-3-(4-Methylbenzyl)hexahydrobenzofuran-5(6*H*)-one (Table 3, entry 8). Experiment 1: Prepared according to general procedure B using 90 mg (0.37 mmol) (*E*)-4-((3-(*p*-tolyl)allyl)oxy)cyclohex-2-enone, 8.5 mg (0.0093 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 72 μL (1.9 mmol) HCO_2H, 647 μL *i*-Pr_2NEt (3.7 mmol), 7.4 mL acetonitrile and irradiated for 20 h. Purified by chromatography using 1:1 hexanes:EtOAc to yield 69 mg (0.28 mmol, 76% yield) of the cycloadduct as a yellow oil. Experiment 2: Prepared according to general procedure B using 85 mg (0.35 mmol) (*E*)-4-((3-(*p*-tolyl)allyl)oxy)cyclohex-2-enone, 8.0 mg (0.0088 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 68 μL (1.8 mmol) HCO_2H, 611 μL *i*-Pr_2NEt (3.5 mmol), 7.0 mL acetonitrile and irradiated for 20 h. Isolated 69 mg (0.28 mmol, 80% yield). IR (thin film): 2253, 908, 738, 651; ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 7.9 Hz, 2H), 4.3 (m, 1H), 3.99 (dd, J = 8.9, 6.8 Hz, 1H), 3.40 (t, J = 8.6 Hz, 1H), 2.73 (dd, J = 13.7, 6.8 Hz, 1H), 2.61 (dd, J = 13.7, 8.5 Hz, 1H), 2.42 (m, 1H), 2.32 (s, 3H), 2.21 (m, 2H), 2.08 (m, 2H), 1.99 (m, 1H); ^{13}C NMR

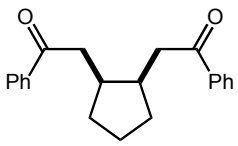
(125 MHz, $CDCl_3$) 212.2, 136.4, 135.9, 129.3, 128.4, 75.6, 72.4, 48.6, 42.4, 41.6, 37.8, 34.6, 26.4, 21.0; HRMS (EI^+) calc'd for $[C_{16}H_{20}O_2]^+$ requires *m/z* 244.1458 found *m/z* 244.1446.



(3a*S*,7a*R*)-3-(4-(Trifluoromethyl)benzyl)hexahydrobenzofuran-5(6*H*)-one (Table 3, entry 9). Experiment 1: Prepared according to general procedure B using 104 mg (0.35 mmol) (*E*)-4-((3-(4-(trifluoromethyl)phenyl)allyl) oxy)cyclohex-2-enone, 8.0 mg (0.0088 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 68 μL (1.8 mmol) HCO_2H, 611 μL *i*-Pr_2NEt (3.5 mmol), 7.0 mL acetonitrile and irradiated for 20 h. Purified by chromatography using 1:1 hexanes:EtOAc to yield 95 mg (0.32 mmol, 91% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure B using 130 mg (0.43 mmol) (*E*)-4-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)cyclohex-2-enone, 9.9 mg (0.011 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 85 μL (2.2 mmol) HCO_2H, 764 μL *i*-Pr_2NEt (4.4 mmol), 8.8 mL acetonitrile and irradiated for 20 h. Isolated 121 mg (0.40 mmol, 92% yield). IR (thin film): 1715, 1325, 1116; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 6.8 Hz, 2H), 4.32 (m, 1H), 3.97 (dd, J = 8.6, 6.6 Hz, 1H), 3.40 (t, J = 9 Hz, 1H), 2.86 (dd, J = 14.0, 6.5 Hz, 1H), 2.69 (dd, J = 13.8, 8.7 Hz, 1H), 2.39 (m, 3H), 2.22 (m, 2H), 2.10 (m, 2H), 2.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 211.7, 128.8, 125.6, 125.6, 75.6, 72.1, 48.2, 42.5, 41.5, 38.1, 34.5, 30.9, 26.3; HRMS (EI^+) calc'd for $[C_{16}H_{17}F_3O_2]^+$ requires *m/z* 298.1176, found *m/z* 298.1175.



(3a*S*,7a*R*)-3-Benzyl-3-methylhexahydrobenzofuran-5(6*H*)-one (Table 3, entry 10). Experiment 1: Prepared according to general procedure B using 91 mg (0.37 mmol) (*E*)-4-((2-methyl-3-phenylallyl)oxy)cyclohex-2-enone, 8.6 mg (0.0094 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 73 μL (1.9 mmol) HCO_2H, 659 μL *i*-Pr_2NEt (3.7 mmol), 7.6 mL acetonitrile and irradiated for 24 h. Purified by chromatography using 2:1 hexanes:EtOAc to yield 68 mg (0.28 mmol, 73% yield) of the cycloadduct as an off-white solid. Experiment 2: Prepared according to general procedure B using 78 mg (0.32 mmol) (*E*)-4-((2-methyl-3-phenylallyl)oxy)cyclohex-2-enone, 7.6 mg (0.0083 mmol) $[Ir(ppy)_2(dtb\text{-}bpy)][PF_6]$, 63 μL (1.6 mmol) HCO_2H, 564 μL *i*-Pr_2NEt (3.2 mmol), 6.5 mL acetonitrile and irradiated for 24 h. Isolated 58 mg (0.24 mmol, 73% yield). IR (thin film): 1642, 1447, 1250; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.24 (m, 1H), 7.13 (d, J = 8.3 Hz, 2H), 4.4 (m, 1H), 3.68 (d, J = 8.8 Hz, 1H), 3.55 (d, J = 8.8 Hz, 1H), 2.71 (m, 2H), 2.45 (m, 1H), 2.38 (m, 1H), 2.27 (dd, J = 15.1, 9.4 Hz, 1H), 2.12 (m, 4H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 212.7, 137.9, 130.2, 128.2, 126.5, 46.9, 45.7, 44.1, 38.8, 34.7, 26.5, 19.4; HRMS (EI^+) calc'd for $[C_{16}H_{20}O_2]^+$ requires *m/z* 244.1458, found *m/z* 244.1458. (mp = 96–100 ºC)



2,2'-((1*R*,2*S*)-Cyclopentane-1,2-diyl)bis(1-phenylethanone) (eq 2). A dry 25 mL Schlenk tube was charged with (1*R*,5*S*,6*R*,7*S*)-bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (76 mg, 0.25 mmol), 4.7 mg (0.0063 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 45 μL (1.3 mmol) HCO_2H, 436 μL *i*-Pr_2NEt (2.5 mmol) and 5.0 mL acetonitrile and degassed in the dark using three freeze/pump/thaw cycles under nitrogen. The reaction was then stirred vigorously and irradiated with a 23 W (1380 lumen) compact fluorescent lamp for 2.5 h. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using 9:1 hexanes:EtOAc to yield 25 mg (0.08 mmol, 32% yield) of the cycloadduct as a yellow oil and 39 mg of the starting cycloadduct (0.13 mmol, 52% yield). IR (thin film): 2950, 1682, 1448; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.1, 1.4 Hz, 4H), 7.56 (dt, J = 7.4, 2.1 Hz, 2H), 7.46 (dt, J = 8.0, 1.6 Hz, 4H), 3.08 (dd, J = 15.4, 6.1 Hz, 2H), 2.80 (dd, J = 15.9, 7.9 Hz, 2H), 2.67 (m, 2H), 1.86 (m, 2H), 1.74 (m, 1H), 1.62 (m, 1H), 1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 200.4, 137.0, 133.0, 128.6, 128.1, 39.6, 38.5, 30.7, 22.4; HRMS (ESI^+) calc'd for $[C_{21}H_{22}O_2Na]^+$ requires *m/z* 329.1512 found *m/z* 329.1501.

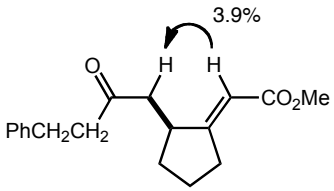
IV. Comparison of DCA to $Ru(bpy)_3^{2+}$ (Table 1, entry 10)

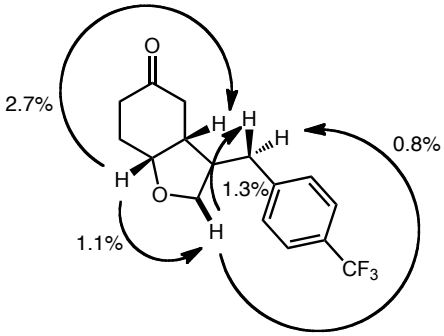
To provide a direct comparison of the effectiveness of $Ru(bpy)_3^{2+}$ and 9,10-dicyanoanthracene (DCA), the cyclization of **6** was attempted using a 23 W compact fluorescent light bulb in place of the 450 W medium-pressure mercury arc lamp in the protocol for photochemical reductive cyclization reported by Pandey,[27] as follows.

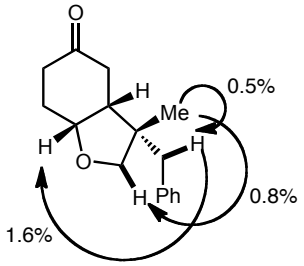
9,10-Dicyanoanthracene (3.1 mg, 0.014 mmol) was added to a 100 mL Schlenk flask containing DMF:*i*-PrOH:H_2O (17.2 mL, 88:10:2) and allowed to stir for 2 h. Bis(enone) **6** (25 mg, 0.069 mmol) and triphenylphosphine (11 mg, 0.042 mmol) were then added, and the resulting solution was stirred for an additional five minutes. The reaction was degassed in the dark using three freeze/pump/thaw cycles under nitrogen and irradiated with a 23 W (1380 lumen) compact fluorescent lamp. After 3 h, the reaction was diluted with Et_2O, washed with water and brine, and concentrated to yield a yellow oil. Dibromomethane (23.3 mg, 0.13 mmol) was added as an internal standard, and this mixture was analyzed by ^1H NMR spectroscopy (RD = 5 s). The reductive cyclization product **7** could not be observed in the resulting spectrum, and 98% of the starting bis(enone) was present by comparison to the internal standard.

V. Stereochemical assignments

The stereochemistry of the major isomer of the reductive cyclization product in Table 2, entry 1 was established by single-crystal X-ray diffraction (*vide infra*). The stereochemistry of the major isomers generated in Table 2, entries 2–14, and Table 3, entries 1–4, were assigned by analogy. NOE correlations were used to determine the relative stereochemistry for the following compounds. Subsequent assignments were made by analogy.







VI. X-Ray Crystallographic Data for Table 2, entry 1

Data Collection

A colorless crystal with approximate dimensions 0.52 x 0.13 x 0.10 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu K_α (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6º in a 25º range about ω with the exposure time of 3 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9853 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 Å. A total of 22130 data were harvested by collecting 19 sets of frames with 0.6º scans in ω with an exposure time 5/12 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[28]

Structure Solution and Refinement

The systematic absences in the diffraction data and the *E*-statistics were consistent for the space groups $Pna2_1$ that yielded chemically reasonable and computationally stable results of refinement[29,30,31].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The space group is asymmetric, but (*S*,*S*) and (*R*,*R*) diastereomers are present.

The final least-squares refinement of 209 parameters against 3010 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0285 and 0.0797, respectively. The final difference Fourier map was featureless.

The molecular diagram is drawn with 50% probability ellipsoids.

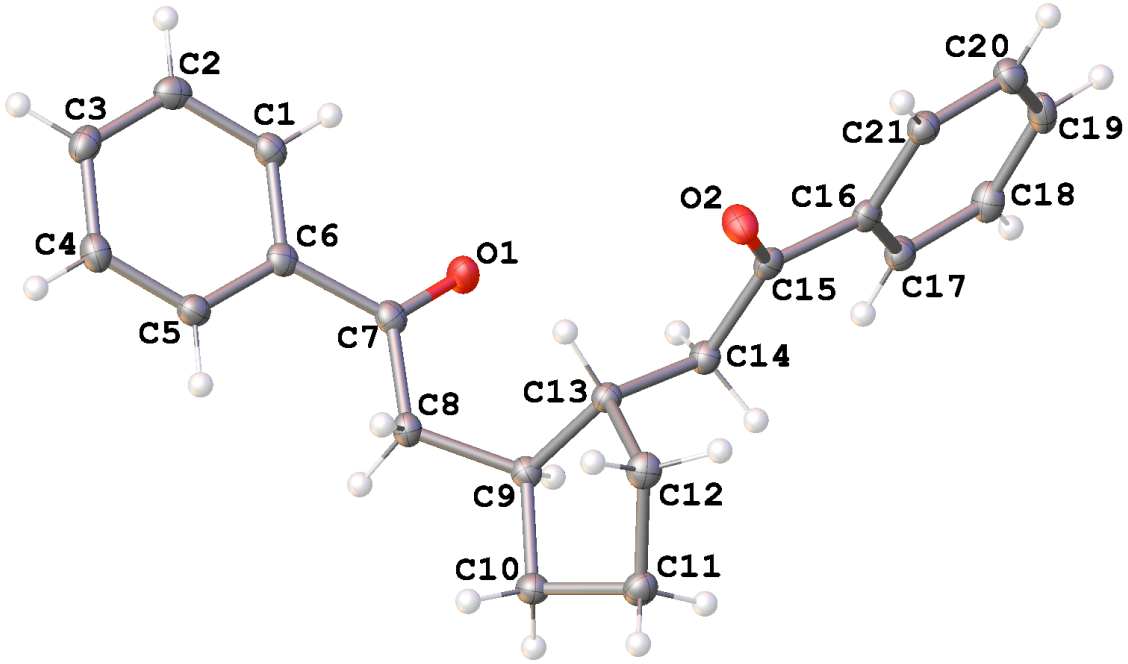


Figure S1. A molecular drawing of Table 2, entry 1.

Table S1. Crystal data and structure refinement.

Identification code	yoon25	
Empirical formula	$C_{21}H_{22}O_2$	
Formula weight	306.39	
Temperature	100(1) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 18.0449(4) Å	α= 90°.
	b = 16.5511(4) Å	β= 90°.
	c = 5.37980(10) Å	γ = 90°.
Volume	1606.75(6) $Å^3$	
Z	4	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.625 mm^{-1}	
F(000)	656	
Crystal size	0.10 x 0.13 x 0.52 mm^3	
Theta range for data collection	3.62 to 69.53°.	
Index ranges	-21<=h<=21, -19<=k<=17, -6<=l<=6	
Reflections collected	23965	
Independent reflections	3010 [R(int) = 0.0236]	
Completeness to theta = 69.53°	99.8 %	
Absorption correction	Numerical with SADABS	
Max. and min. transmission	0.9379 and 0.7358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3010 / 1 / 209	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0786	
R indices (all data)	R1 = 0.0292, wR2 = 0.0797	
Absolute structure parameter Flack x	-0.05(17)	
Absolute structure parameter Hooft y	-0.04(4)	
Largest diff. peak and hole	0.198 and -0.176 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7561(1)	9379(1)	2275(2)	22(1)
O(2)	5555(1)	7847(1)	288(2)	22(1)
C(1)	8544(1)	9695(1)	-1652(2)	18(1)
C(2)	9052(1)	9840(1)	-3532(3)	20(1)
C(3)	9679(1)	9355(1)	-3749(3)	20(1)
C(4)	9793(1)	8725(1)	-2084(3)	20(1)
C(5)	9282(1)	8577(1)	-208(2)	18(1)
C(6)	8648(1)	9058(1)	20(2)	17(1)
C(7)	8071(1)	8908(1)	1983(2)	17(1)
C(8)	8144(1)	8147(1)	3540(2)	16(1)
C(9)	7462(1)	7936(1)	5081(2)	16(1)
C(10)	7609(1)	7167(1)	6659(2)	18(1)
C(11)	6880(1)	6694(1)	6595(2)	20(1)
C(12)	6613(1)	6834(1)	3924(2)	19(1)
C(13)	6770(1)	7739(1)	3447(2)	15(1)
C(14)	6106(1)	8272(1)	4108(2)	16(1)
C(15)	5493(1)	8247(1)	2182(2)	16(1)
C(16)	4808(1)	8747(1)	2587(2)	16(1)
C(17)	4723(1)	9246(1)	4654(2)	18(1)
C(18)	4095(1)	9733(1)	4867(3)	21(1)
C(19)	3556(1)	9726(1)	3031(3)	22(1)
C(20)	3633(1)	9220(1)	984(3)	21(1)
C(21)	4255(1)	8731(1)	769(2)	18(1)

Table S3. Bond lengths [Å] and angles [°].

O(1)-C(7)	1.2171(14)	C(11)-C(12)	1.5329(18)
O(2)-C(15)	1.2207(16)	C(11)-H(11B)	0.9900
C(1)-C(2)	1.3862(19)	C(11)-H(11A)	0.9900
C(1)-C(6)	1.3979(17)	C(12)-C(13)	1.5464(16)
C(1)-H(1)	0.9500	C(12)-H(12A)	0.9900
C(2)-C(3)	1.3919(18)	C(12)-H(12B)	0.9900
C(2)-H(2)	0.9500	C(13)-C(14)	1.5296(15)
C(3)-C(4)	1.390(2)	C(13)-H(13)	1.0000
C(3)-H(3)	0.9500	C(14)-C(15)	1.5152(16)
C(4)-C(5)	1.3886(19)	C(14)-H(14A)	0.9900
C(4)-H(4)	0.9500	C(14)-H(14B)	0.9900
C(5)-C(6)	1.3984(17)	C(15)-C(16)	1.5040(16)
C(5)-H(5)	0.9500	C(16)-C(21)	1.3970(18)
C(6)-C(7)	1.5039(17)	C(16)-C(17)	1.3940(18)
C(7)-C(8)	1.5188(17)	C(17)-C(18)	1.3951(17)
C(8)-C(9)	1.5238(16)	C(17)-H(17)	0.9500
C(8)-H(8B)	0.9900	C(18)-C(19)	1.3855(19)
C(8)-H(8A)	0.9900	C(18)-H(18)	0.9500
C(9)-C(10)	1.5524(16)	C(19)-C(20)	1.390(2)
C(9)-C(13)	1.5624(16)	C(19)-H(19)	0.9500
C(9)-H(9)	1.0000	C(20)-C(21)	1.3892(17)
C(10)-C(11)	1.5299(16)	C(20)-H(20)	0.9500
C(10)-H(10A)	0.9900	C(21)-H(21)	0.9500
C(10)-H(10B)	0.9900		

C(2)-C(1)-C(6)	120.73(11)	C(12)-C(11)-H(11A)	111.3
C(2)-C(1)-H(1)	119.6	C(10)-C(11)-H(11A)	111.3
C(6)-C(1)-H(1)	119.6	H(11B)-C(11)-H(11A)	109.2
C(1)-C(2)-C(3)	119.91(12)	C(11)-C(12)-C(13)	104.15(10)
C(1)-C(2)-H(2)	120.0	C(11)-C(12)-H(12A)	110.9
C(3)-C(2)-H(2)	120.0	C(13)-C(12)-H(12A)	110.9
C(2)-C(3)-C(4)	119.89(12)	C(11)-C(12)-H(12B)	110.9
C(2)-C(3)-H(3)	120.1	C(13)-C(12)-H(12B)	110.9
C(4)-C(3)-H(3)	120.1	H(12A)-C(12)-H(12B)	108.9
C(5)-C(4)-C(3)	120.22(12)	C(14)-C(13)-C(12)	112.11(9)
C(5)-C(4)-H(4)	119.9	C(14)-C(13)-C(9)	112.08(10)
C(3)-C(4)-H(4)	119.9	C(12)-C(13)-C(9)	104.75(9)
C(4)-C(5)-C(6)	120.35(12)	C(14)-C(13)-H(13)	109.3
C(4)-C(5)-H(5)	119.8	C(12)-C(13)-H(13)	109.3
C(6)-C(5)-H(5)	119.8	C(9)-C(13)-H(13)	109.3
C(1)-C(6)-C(5)	118.89(11)	C(15)-C(14)-C(13)	113.39(10)
C(1)-C(6)-C(7)	118.88(10)	C(15)-C(14)-H(14A)	108.9
C(5)-C(6)-C(7)	122.23(11)	C(13)-C(14)-H(14A)	108.9
O(1)-C(7)-C(6)	120.60(11)	C(15)-C(14)-H(14B)	108.9
O(1)-C(7)-C(8)	121.72(11)	C(13)-C(14)-H(14B)	108.9
C(6)-C(7)-C(8)	117.67(10)	H(14A)-C(14)-H(14B)	107.7
C(7)-C(8)-C(9)	114.89(10)	O(2)-C(15)-C(16)	119.61(11)
C(7)-C(8)-H(8B)	108.5	O(2)-C(15)-C(14)	121.29(10)
C(9)-C(8)-H(8B)	108.5	C(16)-C(15)-C(14)	119.08(10)
C(7)-C(8)-H(8A)	108.5	C(21)-C(16)-C(17)	119.41(11)
C(9)-C(8)-H(8A)	108.5	C(21)-C(16)-C(15)	118.37(11)
H(8B)-C(8)-H(8A)	107.5	C(17)-C(16)-C(15)	122.17(11)
C(8)-C(9)-C(10)	110.40(9)	C(18)-C(17)-C(16)	119.82(12)
C(8)-C(9)-C(13)	112.78(10)	C(18)-C(17)-H(17)	120.1
C(10)-C(9)-C(13)	105.85(9)	C(16)-C(17)-H(17)	120.1
C(8)-C(9)-H(9)	109.2	C(19)-C(18)-C(17)	120.41(12)
C(10)-C(9)-H(9)	109.2	C(19)-C(18)-H(18)	119.8
C(13)-C(9)-H(9)	109.2	C(17)-C(18)-H(18)	119.8
C(11)-C(10)-C(9)	105.12(9)	C(18)-C(19)-C(20)	120.00(12)
C(11)-C(10)-H(10A)	110.7	C(18)-C(19)-H(19)	120.0
C(9)-C(10)-H(10A)	110.7	C(20)-C(19)-H(19)	120.0
C(11)-C(10)-H(10B)	110.7	C(19)-C(20)-C(21)	119.83(12)
C(9)-C(10)-H(10B)	110.7	C(19)-C(20)-H(20)	120.1
H(10A)-C(10)-H(10B)	108.8	C(21)-C(20)-H(20)	120.1
C(12)-C(11)-C(10)	102.39(10)	C(20)-C(21)-C(16)	120.50(12)
C(12)-C(11)-H(11B)	111.3	C(20)-C(21)-H(21)	119.7
C(10)-C(11)-H(11B)	111.3	C(16)-C(21)-H(21)	119.7

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	18(1)	20(1)	27(1)	4(1)	4(1)	3(1)
O(2)	20(1)	27(1)	19(1)	-7(1)	-2(1)	2(1)
C(1)	16(1)	15(1)	22(1)	-1(1)	-2(1)	-2(1)
C(2)	22(1)	17(1)	21(1)	2(1)	-5(1)	-5(1)
C(3)	19(1)	24(1)	18(1)	-1(1)	2(1)	-6(1)
C(4)	15(1)	22(1)	24(1)	-2(1)	0(1)	0(1)
C(5)	17(1)	17(1)	20(1)	2(1)	-2(1)	-1(1)
C(6)	15(1)	16(1)	18(1)	-2(1)	-3(1)	-4(1)
C(7)	15(1)	17(1)	19(1)	-2(1)	-3(1)	-2(1)
C(8)	14(1)	17(1)	19(1)	-1(1)	0(1)	0(1)
C(9)	15(1)	16(1)	16(1)	-1(1)	0(1)	0(1)
C(10)	18(1)	20(1)	17(1)	2(1)	-1(1)	1(1)
C(11)	20(1)	18(1)	21(1)	2(1)	2(1)	-1(1)
C(12)	20(1)	16(1)	21(1)	-2(1)	0(1)	-2(1)
C(13)	15(1)	15(1)	14(1)	0(1)	0(1)	-1(1)
C(14)	16(1)	17(1)	16(1)	-1(1)	1(1)	-1(1)
C(15)	16(1)	15(1)	17(1)	1(1)	2(1)	-3(1)
C(16)	15(1)	15(1)	18(1)	2(1)	1(1)	-4(1)
C(17)	16(1)	20(1)	18(1)	0(1)	0(1)	-3(1)
C(18)	20(1)	18(1)	24(1)	-4(1)	4(1)	-2(1)
C(19)	15(1)	19(1)	32(1)	2(1)	4(1)	2(1)
C(20)	17(1)	24(1)	24(1)	2(1)	-3(1)	-2(1)
C(21)	18(1)	18(1)	17(1)	0(1)	0(1)	-3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(1)	8120	10031	-1498	21
H(2)	8973	10270	-4670	24
H(3)	10028	9454	-5034	25
H(4)	10221	8395	-2229	24
H(5)	9363	8146	927	22
H(8B)	8572	8211	4675	20
H(8A)	8255	7688	2419	20
H(9)	7343	8397	6213	19
H(10A)	8017	6844	5935	22
H(10B)	7741	7313	8387	22
H(11B)	6963	6112	6926	24
H(11A)	6521	6909	7819	24
H(12A)	6077	6715	3768	23
H(12B)	6890	6490	2740	23
H(13)	6898	7818	1655	18
H(14A)	5903	8094	5728	20
H(14B)	6277	8836	4298	20
H(17)	5092	9256	5914	22
H(18)	4036	10071	6280	25
H(19)	3135	10066	3171	26
H(20)	3261	9209	-264	26
H(21)	4306	8383	-626	21

Table S6. Torsion angles [°].

C(6)-C(1)-C(2)-C(3)	-0.76(18)
C(1)-C(2)-C(3)-C(4)	0.10(19)
C(2)-C(3)-C(4)-C(5)	0.2(2)
C(3)-C(4)-C(5)-C(6)	0.10(19)
C(2)-C(1)-C(6)-C(5)	1.07(18)
C(2)-C(1)-C(6)-C(7)	-178.23(11)
C(4)-C(5)-C(6)-C(1)	-0.73(17)
C(4)-C(5)-C(6)-C(7)	178.53(12)
C(1)-C(6)-C(7)-O(1)	-7.32(17)
C(5)-C(6)-C(7)-O(1)	173.41(11)
C(1)-C(6)-C(7)-C(8)	171.75(11)
C(5)-C(6)-C(7)-C(8)	-7.52(16)
O(1)-C(7)-C(8)-C(9)	11.86(16)
C(6)-C(7)-C(8)-C(9)	-167.20(10)
C(7)-C(8)-C(9)-C(10)	-178.06(10)
C(7)-C(8)-C(9)-C(13)	63.77(13)
C(8)-C(9)-C(10)-C(11)	-141.42(10)
C(13)-C(9)-C(10)-C(11)	-19.08(12)
C(9)-C(10)-C(11)-C(12)	37.74(12)
C(10)-C(11)-C(12)-C(13)	-42.22(11)
C(11)-C(12)-C(13)-C(14)	-91.52(12)
C(11)-C(12)-C(13)-C(9)	30.26(12)
C(8)-C(9)-C(13)-C(14)	-124.26(11)
C(10)-C(9)-C(13)-C(14)	114.93(10)
C(8)-C(9)-C(13)-C(12)	113.95(11)
C(10)-C(9)-C(13)-C(12)	-6.86(12)
C(12)-C(13)-C(14)-C(15)	-76.73(13)
C(9)-C(13)-C(14)-C(15)	165.80(9)
C(13)-C(14)-C(15)-O(2)	-1.52(16)
C(13)-C(14)-C(15)-C(16)	-179.65(10)
O(2)-C(15)-C(16)-C(21)	0.47(16)
C(14)-C(15)-C(16)-C(21)	178.63(11)
O(2)-C(15)-C(16)-C(17)	-176.78(11)
C(14)-C(15)-C(16)-C(17)	1.38(16)
C(21)-C(16)-C(17)-C(18)	-0.96(18)
C(15)-C(16)-C(17)-C(18)	176.27(11)
C(16)-C(17)-C(18)-C(19)	-0.31(18)
C(17)-C(18)-C(19)-C(20)	1.24(19)
C(18)-C(19)-C(20)-C(21)	-0.89(19)
C(19)-C(20)-C(21)-C(16)	-0.39(19)
C(17)-C(16)-C(21)-C(20)	1.31(18)
C(15)-C(16)-C(21)-C(20)	-176.02(11)

Symmetry transformations used to generate equivalent atoms:

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