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 CH₂Cl₂ were purified by elution through alumina as described by Grubbs.¹ i-Pr₂NEt was distilled from CaH₂ immediately prior to use. Ru(bpy)₃Cl₂⋅6H₂O 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 chromatography² 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 CDCl₃ (77.23 ppm) for ¹³C 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

(2E,7E)-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-enal³ (1.89 g, 8.1 mmol) in 6.5 mL CH₂Cl₂ was placed in a 50 mL round-bottomed flask. 3,3-Dimethyl-1-(triphenylphosphoranylidene)butan-2-one² (3.20 g, 8.9 mmol) in 20 mL CH₂Cl₂ 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, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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 [C₂₀H₂₆O₃Na]⁺ requires m/z 337.1775, found m/z 337.1760. (mp = 60–64 °C)

(2E,7E)-S-Ethyl-9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate (Table 2, entry 6). A solution of (E)-7-(4-methoxyphenyl)-7-oxohept-5-enal³ (0.96 g, 4.1 mmol) in 2.0 mL CH₂Cl₂ was placed in a 25 mL round-bottomed flask. S-Ethyl-2-(triphenylphosphoranylidene)ethanethioate⁵ (1.5 g, 4.14 mmol) in 3.0 mL CH₂Cl₂ 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\(_3\)) \(\delta\) 7.95 (dt, \(J = 9.0, 2.6\) Hz, 2H), 7.03 (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); \(^1^C\) 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\(_3\)S\(^+\)] 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 °C. 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-dimethyloxepentaldehyde (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 (0.60 g, 1.9 mmol, 46% yield). IR (thin film): 2932, 1666, 1620, 1599; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.95 (dt, \(J = 8.4\) Hz, 2H), 1.71 (m, 2H), 1.28 (t, 3H); \(^1^C\) 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\(_3\)S\(^+\)] requires \(m/z\) 319.1363, found \(m/z\) 319.1347.

\((2E,7E)\)-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-en-thioate (429 mg, 2.14 mmol), S-ethyl 2-(triphenylphosphoranylidene)propanethioate \(^7\) (1.32 g, 3.2 mmol) and 10 mL CH\(_2\)Cl\(_2\) 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 mmol, 71% yield). IR (thin film): 2931, 1665, 1654, 1618; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.95 (dt, \(J = 9.0, 2.6\) Hz, 2H), 7.03 (m, 1H), 6.95 (dt, \(J = 9.2, 2.6\) Hz, 2H), 6.92 (dt, \(J = 15.1, 1.3\) Hz, 1H), 6.72 (td, \(J = 7.3, 1.2\) 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); \(^1^C\) 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\(_{18}\)H\(_{23}\)O\(_3\)SNa\(^+\)] requires \(m/z\) 355.1339, found \(m/z\) 355.1340.

\((2E,2E')\)-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-dihydrofurane (568 mg, 8.1 mmol) in 27 mL CH\(_2\)Cl\(_2\) was placed in a 100 mL three-necked flask and cooled to −78 °C. 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\(_3\)) \(\delta\) 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); \(^1^C\) NMR (125 MHz, CDCl\(_3\)) 188.3, 163.5, 142.7, 130.9, 130.5,
N,N-Bis((E)-4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methylbenzenesulfonamide (Table 2, entry 9). A solution of N,N-diallyl-p-toluensulfonamide (1.0 g, 4.0 mmol) in 13 mL CH$_2$Cl$_2$ was placed in a 100 mL three-necked flask and cooled to -78 °C. 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 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): 1669, 1624, 1599; $^{1}$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), 2.4 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) 188.9, 163.7, 144.0, 140.3, 136.7, 131.0, 130.0, 130.0, 128.0, 113.9, 55.4, 45.3, 34.9, 27.1; HRMS (ESI$^+$) calc’d for [C$_{29}$H$_{29}$NO$_5$SNa]$^+$ requires m/z 542.1608, found m/z 542.1597. (mp = 72–79 °C)

(2E,7E)-1,9-Bis(4-methoxyphenyl)-5,5-dimethylnona-2,7-diene (Table 2, entry 10). Prepared using a modification of a procedure by Montgomery. To a solution of 3,3-dimethylglutaraldehyde (0.1 g, 0.8 mmol) in 10 mL CH$_2$Cl$_2$ was added 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)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 (ddd, 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$_{29}$H$_{29}$NO$_5$SNa]$^+$ requires m/z 415.1873, found m/z 415.1880. (mp = 51–57 °C)

(3E,9E)-1,12-Bis(4-methoxyphenyl)dodeca-3,9-diene (Table 2, entry 11). Prepared using a modification of a procedure by Montgomery. A solution of cyclohexenone (756 mg, 9.2 mmol) in 23 mL CH$_2$Cl$_2$ was placed in a 100 mL three-necked flask and cooled to -78 °C. 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$_{29}$H$_{29}$O$_4$Na]$^+$ requires m/z 378.1826, found m/z 378.1829. (mp = 83–88 °C)
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**1H NMR (125 MHz, CDCl₃)**

δ 188.4, 163.5, 155.2, 143.1, 130.9, 130.5, 128.3, 113.8, 55.5, 37.6, 28.3; 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); hexanes:EtOAc as the eluent afforded the product as a yellow solid (1.3 g, 2.6 mmol, 30% yield).

**IR (thin film)**

δ 3366, 1675, 1259, 1170; 1H NMR (500 MHz, CDCl₃) δ 7.95 (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); 13C NMR (125 MHz, CDCl₃) 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 [C₂₉H₃₈O₂SiNa]⁺ requires m/z 517.2381, found m/z 517.2396.

**2E,7E-5-Hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione**

(2E,7E)-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 (2E,7E)-5-((tert-Butyldimethylsilyloxy)-1,9-bis(4-methoxyphenyl)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:H₂O:THF mixture. After 2.5 h, the reaction was concentrated, dissolved in Et₂O and washed with H₂O. 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): 3459, 1600, 1260, 1172; ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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 [C₂₉H₃₈O₂SiNa]⁺ requires m/z 403.1516 found m/z 403.1523. (mp = 110–113 ºC)

** tert-Butyl (2E,7E)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl)carbamate**

(tert-Butyl (2E,7E)-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 H₂O 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 CH₂Cl₂ and concentrated to afford the crude product as a yellow solid.¹² The resulting crude diene was dissolved in 34 mL CH₂Cl₂ 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 N₂ 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-(triphenylphosphoranyliden)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 (3.4 g, 16 mmol) in 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 N₂ 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-(triphenylphosphoranyliden)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; ¹H NMR (500 MHz, CDCl₃) 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); ¹³C 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 [C₂₆H₃₅NO₆SiNa]⁺ 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. NH4Cl, extracted with Et2O (x3), washed with brine, dried over MgSO4 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 colorless oil (3.7 g, 17 mmol, 83% yield). IR (thin film): 3454, 1640, 1620, 1560; HRMS (ESI) found m/z 128.5, 53.4, 43.6, 43.3, 39.6, 31.6, 22.5, 14.1, 2.5; HRMS (EI) calc’d for [C7H15BrO] requires m/z 176.9903, found m/z 176.9903.

(2E,7E)-5-(2-Bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-dien-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 catalyst14 (446 mg, 0.53 mmol) in 42 mL CH2Cl2 was allowed to stir for 48 h. 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 °C. 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. The crude aldehyde was then dissolved in 0.3 mL THF and cooled to 0 °C. 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 1 h, after which the reaction was quenched with water, extracted with ether (x3), washed with sat. NaHCO3, dried over Na2SO4, 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 acid18 (730 mg, 2.6 mmol) were dissolved in 11 mL CH2Cl2 and allowed to stir for 24 h. The reaction mixture was then diluted with CH2Cl2, washed with 5% NaHCO3 (x2), water, brine, dried over Na2SO4, and concentrated to yield a yellow residue. Purification by chromatography on silica gel using 7:1 hexanes:EtOAc to completely remove the catalyst and then concentrated in vacuo to yield a yellow oil.16

(4E,9E)-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 CH2Cl2 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; 1H NMR (500 MHz, CDCl3) 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); 13C NMR (125 MHz, CDCl3) 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 [C25H26O2Na]+ requires m/z 521.1119, found m/z 521.1109.

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(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\(_2\)Cl\(_2\) 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).

(2E,7E)-Ethyl 9-oxo-11-phenylnon-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-(triphenylphosphoranylidene)acetate (750 mg, 2.2 mmol) in 5.0 mL CH\(_2\)Cl\(_2\) 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): 2934, 2221, 1670, 1631; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.28 (m, 2H), 7.20 (m, 3H), 6.76 (dt, \(J = 15.8, 7.1\) Hz, 1H), 6.11 (dt, \(J = 15.8, 1.6\) Hz, 1H), 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, 30.0, 26.3, 14.2; HRMS (ESI\(^+\)) calc’d for [C\(_{19}\)H\(_{26}\)O\(_3\)Na\(^+\)] \(m/z\) 323.1618, found \(m/z\) 323.1615.

(2E,7E)-9-Oxo-11-phenylnon-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\(_2\)Cl\(_2\) 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 mmol, 95% yield). IR (thin film): 2934, 2221, 1670, 1631; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)Na\(^+\)] \(m/z\) 276.1357, found \(m/z\) 276.1359.

(E)-Methyl 4-((4-oxo-6-phenylhex-2-en-1-yloxy)buta-2-ynoate (Table 3, entry 5). A solution of methyl 7-oxohept-2-ynoate\(^9\) and 4-phenyl-1-(triphenylphosphoranylidene)butan-2-one in 19 mL CH\(_2\)Cl\(_2\) 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\(_3\)) \(\delta\) 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$_3$) δ 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-phenyleth-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$_2$Cl$_2$ was added DMSO (0.54 mL, 7.6 mmol) in 1.6 mL CH$_2$Cl$_2$. The reaction was stirred for 30 min, after which 2-(cinnamyloxy)ethanol$^{20}$ (565 mg, 3.2 mmol) in 3.2 mL CH$_2$Cl$_2$ was added dropwise. The suspension was allowed to stir for 30 min, after which Et$_3$N (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$_2$O and the product extracted with CH$_2$Cl$_2$ (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$_2$Cl$_2$ 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 clear oil (890 mg, 2.9 mmol, 91% yield). IR (thin film): 3061, 1670, 1636 cm$^{-1}$; $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.27 (m, 3H), 7.20 (m, 3H), 6.84 (dt, J = 15.7, 4.3 Hz, 1H), 6.65 (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$_2$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$_2$O (207 mg, 0.89 mmol), and 0.87 mL CH$_2$Cl$_2$. 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): 1686, 1512, 969 cm$^{-1}$; $^{1}$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); HRMS (ESI$^+$) calc'd for [C$_{13}$H$_{21}$O]$^+$ requires m/z 228.1144, found m/z 228.1144.

(E)-4-(3-(p-Tolyl)allyloxy)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$_2$O. 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$_2$O (x3). The combined organics were washed with H$_2$O, dried over Na$_2$SO$_4$, 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$_2$O (1.57 g, 6.8 mmol), and 6.6 mL CH$_2$Cl$_2$. 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); HRMS (ESI$^+$) calc'd for [C$_{14}$H$_{23}$O]$^+$ requires m/z 250.1746, found m/z 250.1738.
Residue purified by column chromatography on silica gel.

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)$_3$Cl$_2$·6H$_2$O (0.025 equiv), HCO$_2$H (5 equiv), i-Pr$_2$NEt (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)$_3$(dtb-bpy)][PF$_6$]$_2$ (0.025 equiv), HCO$_2$H (5 equiv), i-Pr$_2$NEt (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.

III. Reductive cyclizations
2,2′-((1S,2S)-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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 446 μL i-Pr₂NEt (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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 446 μL i-Pr₂NEt (2.6 mmol), 5.1 mL acetonitrile and irradiated for 2.5 h. Isolated 64 mg (0.21 mmol, 82% yield). IR (thin film): 1676, 1588; ¹H NMR (500 MHz, CDCl₃) δ 7.94 (dt, J = 8.7, 2.3 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), 1.96 (m, 2H), 1.62 (m, 2H), 1.27 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) 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 [C₂₅H₂₀O₁₆Na⁺] requires m/z 397.1708, found m/z 397.1708. (mp = 112–116 ºC)

2,2′-((1S,2S)-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, 5.1 mg (0.0068 mmol) Ru(bpy)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 454 μL i-Pr₂NEt (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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 454 μL i-Pr₂NEt (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, CDCl₃) 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 = 16.1, 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); ¹³C NMR (125 MHz, CDCl₃) 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 [C₂₅H₂₀O₁₆Na⁺] requires m/z 397.1708, found m/z 397.1708. (mp = 112–116 ºC)

2,2′-((1S,2S)-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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 453 μL i-Pr₂NEt (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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 454 μL i-Pr₂NEt (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, CDCl₃) δ 7.88 (tt, J = 8.7, 2.3 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 = 16.7, 5.0 Hz, 2H), 2.17 (m, 2H), 1.98 (m, 2H), 1.64 (m, 2H), 1.28 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) 198.9, 139.4, 135.4, 129.5, 128.9, 44.0, 41.4, 32.6, 23.7; HRMS (ESI⁺) calc’d for [C₂₇H₂₆O₁₈Na⁺] requires m/z 397.0733, found m/z 397.0719.

2,2′-((1S,2S)-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)₃Cl₂·6H₂O, 50 μL (1.3 mmol) HCO₂H, 447 μL i-Pr₂NEt (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.

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**1-((1S,2S)-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) (2E,7E)-1-(4-methoxyphenyl)-10,10-dimethylundeca-2,7-diene-1,9-dione, 4.5 mg (0.0060 mmol) Ru(bpy)_2Cl_2·6H_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 4:1 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) (2E,7E)-1-(4-methoxyphenyl)-10,10-dimethylundeca-2,7-diene-1,9-dione, 5.0 mg (0.0067 mmol) Ru(bpy)_2Cl_2·6H_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): 1676, 1600, 1509; ^1^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_20H_20O_3]^+^ requires m/z 317.2112, found m/z 317.2121.

**S'-Ethyl-2,((1S,2S)-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) (2E,7E)-S-ethyl 9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate, 8.2 mg (0.0101 mmol) Ru(bpy)_2Cl_2·6H_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) (2E,7E)-S-ethyl 9-(4-methoxyphenyl)-9-oxonona-2,7-dienethioate, 8.2 mg (0.0101 mmol) Ru(bpy)_2Cl_2·6H_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; ^1^H 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), 3.06 (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, 1H), 1.22 (m, 1H), 1.12 (s, 9H), 1.08 (m, 1H); ^13^C NMR (125 MHz, CDCl_3) 204.8, 198.9, 163.3, 130.3, 113.6, 55.4, 44.1, 43.6, 42.0, 41.5, 40.9, 32.8, 26.4, 23.7; HRMS (ESI^+^) calc’d for [C_30H_28O_3SNa]^+^ requires m/z 434.1339, found m/z 434.1342.

**propanethioate** (Table 2, entry 7). Experiment 1: Prepared according to general procedure A using 90 mg (0.27 mmol) (2E,7E)-S-ethyl 9-(4-methoxyphenyl)-2-methyl-9-oxonona-2,7-dienethioate, 5.1 mg (0.0068 mmol) Ru(bpy)_2Cl_2·6H_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) (2E,7E)-S-ethyl 9-(4-
methoxyphenyl)-2-methyl-9-oxonona-2,7-dienethioate, 5.1 mg (0.0068 mmol) Ru(bpy)_2Cl_2:6H_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, CDCl₃) δ 7.92 (m, H₆ = 2H), 6.91 (dd, J = 15.8, 3.8 Hz, H₂ = 1H), 2.87 (s, H₂ = 3H), 3.14 (dd, J = 14.3, 3.3 Hz, H₄ = 1H), 3.06 (dd, J = 15.8, 3.8 Hz, H₂ = 1H), 2.91 (q, J = 7.5 Hz, H₂ = 2H), 2.84 (q, J = 7.2 Hz, H₂ = 2H), 2.76 (dd, J = 15.8, 9.9 Hz, H₂ = 1H), 2.63 (m, H₆ = 1H, H₂ = 1H), 2.55 (m, H₂ = 1H), 2.47 (dd, J = 14.0, 12.1 Hz, H₂ = 1H), 2.24 (m, H₂ = 1H, H₂ = 1H), 2.17 (s, H₂ = 3H, H₂ = 3H), 1.98 (m, H₆ = 1H), 1.87 (m, H₂ = 2H), 1.8 (m, H₂ = 2H), 1.56 (m, H₂ = 2H), 1.24 (m, H₂ = 3H, H₂ = 6H), 1.16 (d, H₆ = 3H); ¹³C NMR (125 MHz, CDCl₃) 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, 21.3, 21.4, 18.5, 15.0, 14.9, 14.7; HRMS (ESI⁺) calc’d for [C₁₉H₂₀O₂SNa]⁺ requires m/z 357.1495, found m/z 357.1483.

2,2′-(3S,4S)-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) (2E,2′E)-4,4′-oxybis(1-(4-methoxyphenyl)but-2-en-1-one), 4.8 mg (0.0064 mmol) Ru(bpy)_2Cl_2:6H_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) (2E,2′E)-4,4′-oxybis(1-(4-methoxyphenyl)but-2-en-1-one), 4.7 mg (0.0063 mmol) Ru(bpy)_2Cl_2:6H_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, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 197.6, 163.5, 130.3, 129.9, 113.7, 73.4, 55.5, 42.2, 40.8; HRMS (ESI⁺) calc’d for [C₁₉H₂₀O₂SnO₂Na]⁺ requires m/z 391.1516, found m/z 391.1527.

2,2′-(3S,4S)-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(4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methyl benzenesulfonamide, 2.7 mg (0.0036 mmol) Ru(bpy)_2Cl_2:6H_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(4-(4-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methyl benzenesulfonamide, 2.7 mg (0.0037 mmol) Ru(bpy)_2Cl_2:6H_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, CDCl₃) 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 = 2.6, 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); ¹³C NMR (125 MHz, CDCl₃) 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 [C₂₃H₂₃NO₆SnNa]⁺ requires m/z 544.1765, found m/z 544.1741. (mp = 128°C (dec.))

2,2′-(1S,2S)-4,4-Dimethylocyclopentane-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) (2E,7E)-1,9-bis(4-methoxyphenyl)-5,5-dimethyl-1,9-dione, 4.3 mg (0.0060 mmol) Ru(bpy)_2Cl_2:6H_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) (2E,7E)-1,9-bis(4-methoxyphenyl)-5,5-dimethylnona-2,7-diene-1,9-dione, 4.4 mg (0.0058 mmol) Ru(bpy)3Cl2·6H2O, 42 µL (1.2 mmol) HCO2H, 406 µL i-Pr2NEt (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, CDCl3) 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); 13C NMR (125 MHz, CDCl3) 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 [C19H20O3SNa]+ requires m/z 417.2025, found m/z 417.2037. (mp = 102 – 109 °C)

2,2’-(1S,2S)-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) (3E,9E)-1,12-bis(4-methoxyphenyl)dodeca-3,9-diene-1,12-dione, 4.7 mg (0.0063 mmol) Ru(bpy)3Cl2·6H2O, 49 µL (1.3 mmol) HCO2H, 437 µL i-Pr2NEt (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) (3E,9E)-1,12-bis(4-methoxyphenyl)dodeca-3,9-diene-1,12-dione, 4.8 mg (0.0064 mmol) Ru(bpy)3Cl2·6H2O, 49 µL (1.3 mmol) HCO2H, 437 µL i-Pr2NEt (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, CDCl3) 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); 13C NMR (125 MHz, CDCl3) 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 [C32H28O3N2]+ requires m/z 403.1880, found m/z 403.1877.

2,2’-(1S,2S)-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) (2E,7E)-5-hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione, 4.7 mg (0.0063 mmol) Ru(bpy)3Cl2·6H2O, 50 µL (1.3 mmol) HCO2H, 446 µL i-Pr2NEt (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) (2E,7E)-5-Hydroxy-1,9-bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione, 4.7 mg (0.0063 mmol) Ru(bpy)3Cl2·6H2O, 50 µL (1.3 mmol) HCO2H, 446 µL i-Pr2NEt (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, CDCl3) 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); 13C NMR (125 MHz, CDCl3) 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 [C32H28O6N2]+ requires m/z 405.1656, found m/z 405.1673. (mp = 88–93 °C)

tert-Butyl-((3S,4S)-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 ((2E,7E)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl)carbamate, 4.7 mg (0.0063 mmol) Ru(bpy)3Cl2·6H2O, 50 µL (1.3 mmol) HCO2H, 446 µL i-Pr2NEt (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 (2E,7E)-1,9-bis(4-methoxyphenyl)-1,9-dioxonona-2,7-dien-5-yl carbamate, 4.7 mg (0.0063 mmol) Ru(ppy)Cl2·6H2O, 50 µL (1.3 mmol) HCO2H, 446 µL i-Pr2NEt (2.6 mmol), 5.0 mL acetonitrile and irradiated for 3.5 h. Isolated 72 mg (0.14 mmol, 65% yield). IR (thin film): 3345, 1599, 1259, 1171; 1H NMR (500 MHz, CDCl3) δ 7.94 (t, J = 7.9 Hz, 4H), 7.46 (m, 1H), 3.58 (m, 1H), 2.10 (m, 1H); 13C NMR (125 MHz, CDCl3) 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 [C28H33NO6]+ requires m/z 482.2538, found m/z 482.2517. (mp = 107–111 °C)

2,2'-(1(S,2S)-4-(2-Bromoethyl)-4-((trimethylsilyl)oxy)cyclopentane-1,2-diyl)bis(1-phenylethananone) (Table 2, entry 14). Experiment 1: Prepared according to general procedure A using 99 mg (0.20 mmol) (2E,7E)-5-(2-bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-diene-1,9-dione, 3.8 mg (0.0051 mmol) Ru(ppy)Cl2·6H2O, 43 µL (1.1 mmol) HCO2H, 384 µL i-Pr2NEt (2.2 mmol), 4.4 mL acetonitrile and irradiated for 3 h. Isolated 27 mg (0.10 mmol, 43% yield). IR (thin film): 3345, 1685, 1597, 1448, 1251; 1H NMR (500 MHz, CDCl3) δ 7.94 (t, J = 7.9 Hz, 4H), 7.36 (m, 2H), 7.46 (m, 4H), 3.58 (m, 1H), 3.12 (dd, J = 16.8, 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), 1.56 (m, 1H), 1.31 (m, 2H), 0.15 (s, 1H); 13C NMR (125 MHz, CDCl3) 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 [C28H33BrO3SiNa]+ requires m/z 523.1275, found m/z 523.1291.

1,1'-(1(S,2S)-Cyclopentanet-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) (4E,9E)-1,13-diphenyltrideca-4,9-diene-3,11-dione, 4.6 mg (0.0061 mmol) Ru(ppy)Cl2·6H2O, 48 µL (1.3 mmol) HCO2H, 435 µL i-Pr2NEt (2.5 mmol), 5.0 mL acetonitrile and irradiated for 36 h. Purified by chromatography using 4:1 hexanes:ether to yield 85 mg (0.13 mmol, 94% yield) of the cycloadduct as a clear oil. Experiment 2: Prepared according to general procedure A using 120 mg (0.25 mmol) (2E,7E)-5-(2-bromoethyl)-1,9-diphenyl-5-((trimethylsilyl)oxy)nona-2,7-diene-1,9-dione, 4.1 mg (0.0055 mmol) Ru(ppy)Cl2·6H2O, 43 µL (1.1 mmol) HCO2H, 384 µL i-Pr2NEt (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; 1H NMR (500 MHz, CDCl3) δ 7.94 (t, J = 7.9 Hz, 4H), 7.36 (m, 2H), 7.46 (m, 4H), 3.58 (m, 1H), 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), 1.56 (m, 1H), 1.31 (m, 2H), 0.15 (s, 1H); 13C NMR (125 MHz, CDCl3) 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 [C28H33BrO3SiNa]+ requires m/z 523.1275, found m/z 523.1291.
**Ethyl 2-((1S,2S)-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) (2E,7E)-ethyl 9-oxo-11-phenylundec-2,7-dienoate, 7.5 mg (0.0082 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 71 µL (1.5 mmol) HCO$_2$H, 574 µL i-Pr$_2$NEt (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) (2E,7E)-ethyl 9-oxo-11-phenylundec-2,7-dienoate, 6.8 mg (0.0074 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 85 µL (2.4 mmol) HCO$_2$H, 824 µL i-Pr$_2$NEt (4.7 mmol), 9.5 mL acetonitrile and irradiated for 24 h. Isolated 69 mg (0.23 mmol, 76% yield). IR (thin film): 1712, 1650, 1201; HRMS (ESI$^+$) calc’d for [C$_{19}$H$_{20}$O$_2$Na]$^+$ requires m/z 325.1775, found m/z 325.1769; HRMS (ESI$^+$) calc’d for [C$_{19}$H$_{20}$O$_2$Na]$^+$ requires m/z 325.1775, found m/z 325.1789.

**2-(2S)-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) (2E,7E)-9-oxo-11-phenylundec-2,7-dieniencitrile, 10.8 mg (0.0012 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 85 µL (2.4 mmol) HCO$_2$H, 824 µL i-Pr$_2$NEt (4.7 mmol), 9.5 mL acetonitrile and irradiated for 2 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) (2E,7E)-9-oxo-11-phenylundec-2,7-dieniencitrile, 10.8 mg (0.0012 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 85 µL (2.4 mmol) HCO$_2$H, 824 µL i-Pr$_2$NEt (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, 81% yield) of the cycloadduct as an inseparable 1:1 mixture of diastereomers as a yellow oil. IR (thin film): 3307, 3293, 2953, 2244, 1712, 1453; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (m, 2H), 7.17 (m, 3H), 2.81 (m, 2H), 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$_3$) 209.7, 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$_{15}$H$_{15}$O$_2$Na]$^+$ requires m/z 325.1775, found m/z 325.1769; HRMS (ESI$^+$) calc’d for [C$_{15}$H$_{15}$O$_2$Na]$^+$ requires m/z 325.1775, found m/z 325.1789.

**E 1.1S,2S)-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-bpy)][PF$_6$], 69 µL (1.8 mmol) HCO$_2$H, 621 µL i-Pr$_2$NEt (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-bpy)][PF$_6$], 70 µL (1.8 mmol) HCO$_2$H, 628 µL i-Pr$_2$NEt (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$_3$) $\delta$ 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, 121.1, 50.9, 47.0, 44.7, 41.7, 32.8, 32.2, 29.8, 24.1; HRMS (ESI$^+$) calc’d for [C$_{19}$H$_{20}$O$_2$Na]$^+$ requires m/z 326.1564, found m/z 326.1575.
1-((3S)-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-(cinnamylamoxy)-1-phenylhex-4-en-3-one, 7.5 mg (0.0082 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 63 µL (1.6 mmol) HCO$_2$H, 483 µL i-Pr$_2$NEt (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 (0.28 mmol) benzyltetrahydrofuran 8, 5.0 Hz, 1H), 2.34 (m, 2H), 2.07 (m, 1H); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.9 (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 (dd, 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); $^1$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 (ESI$^+$) calc'd for [C$_{13}$H$_{18}$O$_2$]$^+$ requires m/z 230.1302, found m/z 230.1292.

(3aS,7aR)-3-benzylhexahydrobenzofuran-5(6H)-one (Table 3, entry 7). Experiment 1: Prepared according to general procedure B using 104 mg (0.46 mmol) 4-(cinnamylamoxy)cyclohex-2-enone, 10.6 mg (0.011 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 88 µL (2.3 mmol) HCO$_2$H, 794 µL i-Pr$_2$NEt (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-(cinnamylamoxy)cyclohex-2-enone, 8.5 mg (0.0093 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 72 µL (1.9 mmol) HCO$_2$H, 649 µL i-Pr$_2$NEt (3.7 mmol), 7.4 mL acetonitrile and irradiated for 20 h. Isolated 52 mg (0.022 mmol, 60% yield). IR (thin film): 3027, 1710, 1603, 1495, 1453; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (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); $^1$C NMR (125 MHz, CDCl$_3$) 208.9, 140.8, 140.2, 128.7, 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$_{13}$H$_{18}$O$_2$]$^+$ requires m/z 308.1771, found m/z 308.1787.

(3aS,7aR)-3-(4-Methylbenzyl)hexahydrobenzofuran-5(6H)-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-bpy)][PF$_6$], 72 µL (1.9 mmol) HCO$_2$H, 647 µL i-Pr$_2$NEt (3.7 mmol), 7.4 mL acetonitrile and irradiated for 20 h. Purified by chromatography using 1:1 hexanes:EtOAc to yield 69 mg (0.028 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-bpy)][PF$_6$], 68 µL (1.8 mmol) HCO$_2$H, 611 µL i-Pr$_2$NEt (3.5 mmol), 7.0 mL acetonitrile and irradiated for 20 h. Isolated 69 mg (0.028 mmol, 80% yield). IR (thin film): 2253, 908, 738, 651; $^1$H 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); $^1$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.

**3aS,7aR)-3-(4-(Trifluoromethyl)benzyl)hexahydrobenzofuran-5(6H)-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-bpy)][PF$_6$], 68 µL (1.8 mmol) HCO$_2$H, 611 µL i-Pr$_2$NEt (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-bpy)][PF$_6$], 85 µL (2.2 mmol) HCO$_2$H, 764 µL i-Pr$_2$NEt (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; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.05 (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, 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$_3$O$_2$]$^+$ requires m/z 298.1176, found m/z 298.1175.

(3aS,7aR)-3-Benzyl-3-methylhexahydrobenzofuran-5(6H)-one (Table 3, entry 10). Experiment 1: Prepared according to general procedure B using 91 mg (0.37 mmol) (E)-4-((2-methyl-3-phenallyl)oxy)cyclohex-2-enone, 7.6 mg (0.0094 mmol) [Ir(ppy)$_2$(dtb-bpy)][PF$_6$], 73 µL (1.9 mmol) HCO$_2$H, 659 µL i-Pr$_2$NEt (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-phen allyl)oxy)cyclohex-2-enone, 63 µL (1.6 mmol) HCO$_2$H, 564 µL i-Pr$_2$NEt (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; $^1$H 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°C)

2,2$^\cdot$-(1R,2S)-Cyclopentane-1,2-diylibis(1-phenylethanone) (eq 2). A dry 25 mL Schlenk tube was charged with (1R,5S,6R,7S)-bicyclo[3.2.0]heptane-6,7-diylibis(phenylmethanone) (76 mg, 0.25 mmol), 4.7 mg (0.0063 mmol) Ru(bpy)$_3$Cl$_2$·6H$_2$O, 45 µL (1.3 mmol) HCO$_2$H, 436 µL i-Pr$_2$NEt (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; $^1$H 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, 4H), 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$_{32}$H$_{32}$O$_3$Na]$^+$ 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,\textsuperscript{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$_2$O (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$_2$O, 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 $^1$H 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 (\textit{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$_\alpha$ ($\lambda = 1.54178$ Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6° in a 25° range about $\omega$ 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 0.6° scans in $\omega$ 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 $Pna\overline{2}_1$ 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.

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**Table S2.** Atomic coordinates ($10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$). $U(eq)$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table S3. Bond lengths [Å] and angles [°].
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Symmetry transformations used to generate equivalent atoms:
References