Supporting Information for:

Crossed Intermolecular [2+2] Cycloadditions of Acyclic Enones via Visible Light Photocatalysis

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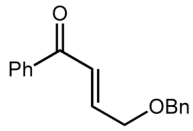
I. General Information

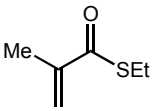
Acetonitrile, CH_2Cl_2, and *i*-Pr_2NEt were distilled from CaH_2 immediately prior to use. $Ru(bipy)_3Cl_2{\cdot}6H_2O$ was purchased from Strem and used without further purification. Methyl acrylate was washed with aqueous NaOH, water, dried with $CaCl_2$ and distilled immediately prior to use. Substrates in Table 1, entries 1–3,[1] 4,[2] 6–8,[3] and Table 2, entry 4[4] were prepared as previously described. Substrates from Table 1, entry 9, and Table 2, entry 5 were synthesized as described below. All other chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography[5] was performed using Purasil 60Å 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 ^{1}H 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 are reported in parts per million (δ) relative to TMS (0.0 ppm) for ^{1}H 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-9974839, CHE-9304546), NIH (RR08389-01) and the University of Wisconsin.

II. Synthesis of substrates



(*E*)-4-(Benzyloxy)-1-phenylbut-2-en-1-one (Table 1, entry 9). A 25 mL round-bottomed flask was charged with 2-(benzyloxy)acetaldehyde (1.0 g, 6.7 mmol), (benzoylmethylene)triphenylphosphorane (2.6 g, 6.7 mmol), and 5 mL CH_2Cl_2 and allowed to reflux overnight. The reaction mixture was cooled to ambient temperature and concentrated. The resulting yellow oil was stirred vigorously with hexane until a white precipitate formed. The solids were washed with hexanes (5x) and the combined organics washed with brine, dried with Na_2SO_4 and concentrated *in vacuo* to afford a yellow oil. Purification by chromatography on silica gel using 5:1 hexanes:EtOAc as the eluent afforded the product as a pale yellow oil (1.1 g, 4.3 mmol, 64% yield). IR (thin film): 1627, 1469, 1382; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, J = 8.1, 2.1 Hz, 2H), 7.56 (tt, J = 6.7, 1.5 Hz, 1H), 7.47 (tt, J = 9.4, 1.8 Hz, 2H), 7.38 (d, J = 4.7 Hz, 3H), 7.32 (m, 1H), 7.22 (dt, J = 15.6, 2.3 Hz, 1H), 7.08 (dt, J = 15.5, 4.1 Hz, 1H), 4.63 (s, 2H), 4.30 (dd, J = 4.1, 2.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 190.3, 144.4, 137.7, 137.6, 132.8, 128.6, 128.6, 128.5, 127.9, 127.7, 124.9, 72.9, 72.9, 69.1; HRMS (ESI^+) calc'd for $[C_{17}H_{16}O_2Na]^+$ requires *m/z* 275.1043, found *m/z* 275.1045.

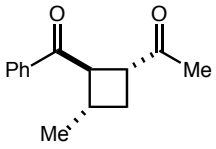


(*S*)-Ethyl-2-methylprop-2-enethioate (Table 2, entry 5). A 1 L round-bottomed flask was charged with methacrylic acid (2.6 mL, 31 mmol), ethanethiol (2.9 mL, 39 mmol), 4-(dimethylamino)pyridine (366 mg, 3 mmol) and 45 mL CH_2Cl_2 and cooled to 0 °C. Dicyclohexylcarbodiimide (6.6 g, 31 mmol) was added in three portions. The reaction mixture was allowed to stir and warm to room temperature overnight. The resulting suspension was filtered through Celite, and the filtrate was washed with saturated $NaHCO_3$, water, and brine and dried with $MgSO_4$. Hydroquinone was added to the solution to prevent polymerization and the solvent was

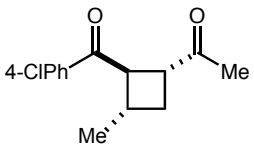
removed by distillation. Purification of the residue by Kugelrohr distillation at reduced pressure (5 mm Hg, 75 °C) afforded the product as yellow oil (1.3 g, 10 mmol, 32% yield). The IR (thin film): 2971, 2930, 1662, 1630; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.56 (q, J = 1.6 Hz, 1H), 2.93 (q, J = 7.5 Hz, 2H), 1.98 (q, J = 1.1 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 193.6, 143.7, 122.7, 23.2, 18.0, 14.6; HRMS (EI^+) calc'd for $[C_6H_{10}OS]^+$ requires *m/z* 130.0447, found *m/z* 130.0454.

III. Cycloadditions

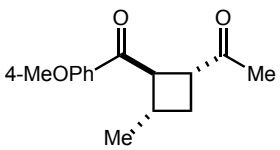
General procedure for intermolecular [2+2] cycloadditions: A dry 25 mL Schlenk tube was charged with the aryl enone (1 equiv), Michael acceptor (2.4 equiv), $Ru(bipy)_3Cl_2{\cdot}6H_2O$ (0.05 equiv), $LiBF_4$ (4 equiv), *i*-Pr_2NEt (2 equiv), and acetonitrile (0.1 M) and degassed by a freeze/pump/thaw cycle (3x) under nitrogen in the dark. The reaction was then allowed to stir and irradiated by a 23 W (1380 lumen) compact fluorescent lamp at a distance of 30 cm. Upon completion, the solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel.



1-((1*R*, 2*R*, 3*S*)-2-Benzoyl-3-methylcyclobutyl)ethanone (Table 1, Entry 1). Experiment 1: Prepared according to the general procedure using 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 121 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 261 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 127 mg (0.59 mmol, 84% yield) of the cycloadduct as a yellow oil. Experiment 2: 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 125 mg (0.58 mmol, 83% yield). IR (thin film): 2957, 1709, 1674; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.1, 1.8 Hz, 2H), 7.57 (tt, J = 6.8, 1.3 Hz, 1H), 7.47 (tt, J = 8.0 Hz, 2H), 3.92 (t, J = 8.4 Hz, 1H), 3.62 (q, J = 9.3 Hz, 1H), 2.5 (m, 1H), 2.38 (m, 1H), 2.08 (s, 3H), 1.75 (q, J = 10.4 Hz, 1H), 1.18 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.2, 199.3, 136.1, 133.3, 128.6, 49.7, 43.4, 30.9, 29.2, 27.6, 20.9; HRMS (EI^+) calc'd for $[C_{14}H_{16}O_2]^+$ requires *m/z* 216.1145, found *m/z* 216.1150.

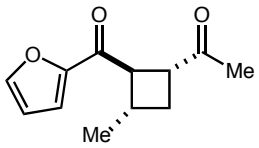


1-((1*R*, 2*R*, 3*S*)-2-(4-Chlorobenzoyl)-3-methylcyclobutyl)ethanone (Table 1, entry 2). Experiment 1: Prepared according to the general procedure using 126 mg (0.70 mmol) (*E*)-1-(4-chlorophenyl)-2-buten-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 148 mg (0.59 mmol, 84% yield) of the cycloadduct as a yellow oil. Experiment 2: 126 mg (0.70 mmol) (*E*)-1-(4-chlorophenyl)-2-buten-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 27 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 140 mg (0.56 mmol, 80% yield). IR (thin film): 1675, 1590, 1093; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, J = 9.1, 2.4 Hz, 2H), 7.44 (dt, J = 9.1, 2.4 Hz, 2H), 3.88 (t, J = 8.3 Hz, 1H), 3.57 (q, J = 9.3 Hz, 1H), 2.52 (m, 1H), 2.41 (q, J = 10.4 Hz, 1H), 2.08 (s, 3H), 1.72 (q, J = 9.7 Hz, 1H), 1.17 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.0, 198.2, 139.8, 134.4, 130.1, 129.0, 49.3, 43.6, 30.6, 29.5, 27.5, 20.9; HRMS (EI^+) calc'd for $[C_{14}H_{15}O_2Cl]^+$ requires *m/z* 250.0756, found *m/z* 250.0764.

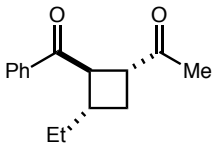


1-((1*R*,2*R*,3*S*)-2-(4-Methoxybenzoyl)-3-methylcyclobutyl)ethanone (Table 1, entry 3). Experiment 1: Prepared according to the general procedure using 125 mg (0.71 mmol) (*E*)-1-(4-methoxyphenyl)-2-buten-1-one, 123 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 92 mg (0.37 mmol, 53% yield) of the

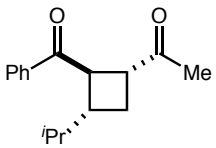
cycloadduct as a yellow oil. Experiment 2: 123 mg (0.70 mmol) (*E*)-1-(4-methoxyphenyl)-2-buten-1-one, 123 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 86 mg (0.56 mmol, 50% yield). IR (thin film): 1794, 1664, 1600; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, J = 9.7, 3.1 Hz, 2H), 6.94 (dt, J = 9.8, 2.8 Hz, 2H), 3.87 (s, 3H), 3.84 (q, J = 5.4 Hz, 1H), 3.61 (q, J = 9.1 Hz, 1H), 2.49 (m, 1H), 2.37 (q, J = 9 Hz, 1H), 2.07 (s, 3H), 1.74 (q, J = 9.3 Hz, 1H), 1.17 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.4, 197.7, 163.7, 130.9, 129.1, 113.8, 55.5, 49.5, 43.5, 30.9, 29.3, 27.7, 20.9; HRMS (EI^+) calc'd for $[C_{15}H_{18}O_3]^+$ requires *m/z* 246.1251, found *m/z* 246.1256.



1-((1*R*,2*R*,3*S*)-2-(Furan-2-carbonyl)-3-methylcyclobutyl)ethanone (Table 1, entry 4). Experiment 1: Prepared according to the general procedure using 95 mg (0.70 mmol) (*E*)-1-(furan-2-yl)but-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 2:1 hexanes:EtOAc to yield 106 mg (0.51 mmol, 73% yield) of the cycloadduct as a yellow oil. Experiment 2: 95 mg (0.70 mmol) (*E*)-1-(furan-2-yl)but-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 106 mg (0.58 mmol, 74% yield). IR (thin film): 1708, 1665, 1467; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.8, 1.0 Hz, 1H), 7.27 (dd, J = 3.7, 0.7 Hz, 1H), 6.54 (dd, J = 3.8, 2.1 Hz, 1H), 3.66 (t, J = 8.6 Hz, 1H), 3.58 (q, J = 9.2 Hz, 1H), 2.54 (m, 1H), 2.37 (q, J = 9.8 Hz, 1H), 2.08 (s, 3H), 1.73 (q, J = 9.4 Hz, 1H), 1.18 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 209.0, 187.8, 152.1, 147.0, 118.5, 112.3, 50.1, 42.8, 30.8, 29.3, 27.5, 20.9; HRMS (EI^+) calc'd for $[C_{12}H_{13}O_3]^+$ requires *m/z* 206.0938, found *m/z* 206.0940.

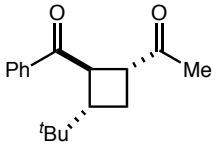


1-((1*R*,*2*R,*3*S)-2-Benzoyl-3-ethylcyclobutyl)ethanone (Table 1, entry 6). Experiment 1: Prepared according to the general procedure using 113 mg (0.70 mmol) (*E*)-1-phenyl-2-penten-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 115 mg (0.50 mmol, 71% yield) of the cycloadduct as a yellow oil. Experiment 2: 106 mg (0.66 mmol) (*E*)-1-phenyl-2-penten-1-one, 116 mg (1.7 mmol), 25 mg (0.033 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 248 mg (2.6 mmol) $LiBF_4$, 229 μL (1.3 mmol) *i*-Pr_2NEt, 6.5 mL acetonitrile and irradiated for 4 h. Isolated 103 mg (0.45 mmol, 68% yield). IR (thin film): 2963, 2254, 1708, 1672; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (dt, J = 8.5, 1.8 Hz, 2H), 7.56 (tt, J = 6.7, 1.3 Hz, 1H), 7.46 (tt, J = 7.9 Hz, 2H), 3.98 (tt, J = 8 Hz, 1H), 3.54 (q, J = 9.3 Hz, 1H), 2.4 (m, 2H), 2.07 (s, 3H), 1.72 (q, J = 9.3 Hz, 1H), 1.57 (m, 1H), 1.47 (m, 1H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 208.1, 199.8, 136.2, 133.2, 128.6, 47.7, 44.1, 36.7, 28.5, 27.5, 27.4, 10.7; HRMS (EI^+) calc'd for $[C_{15}H_{18}O_2]^+$ requires *m/z* 230.1302, found *m/z* 230.1299.

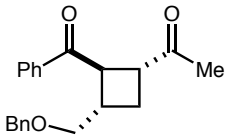


1-((1*R*,2*R*,3*R)*-2-Benzoyl-3-isopropylcyclobutyl)ethanone (Table 1, entry 7). Experiment 1: Prepared according to the general procedure using 122 mg (0.70 mmol) (*E*)-4-methyl-1-phenylpent-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 108 mg (0.44 mmol, 64% yield) of the cycloadduct as a yellow oil. Experiment 2: 122 mg (0.70 mmol) (*E*)-4-methyl-1-phenylpent-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 27 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 107 mg (0.44 mmol, 62% yield). IR (thin film): 2253, 1708, 1671; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dt, J = 8.0, 2.2 Hz, 2H), 7.56 (tt, J = 6.8, 1.3 Hz, 1H), 7.46 (tt, J = 8 Hz, 2H), 4.09 (tt, J = 8.4 Hz, 1H), 3.31 (q, J = 9.2 Hz, 1H), 2.45 (m, 1H), 2.36 (m, 1H), 2.04 (s, 3H), 1.71 (q, J

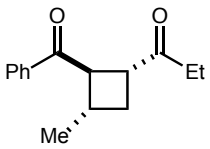
= 9.4 Hz, 1H), 1.55 (m, 1H), 0.83 (d, J = 6.9 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 207.8, 200.6, 136.3, 133.2, 128.6, 128.6, 45.7, 45.1, 41.2, 33.4, 27.6, 26.6, 19.5, 18.7; HRMS (EI^+) calc'd for $[C_{16}H_{20}O_2Na]^+$ requires *m/z* 267.1356, found *m/z* 267.1369.



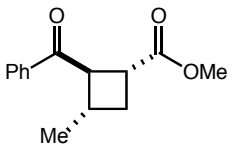
1-((1*R*,2*R*,3*S*)-2-Benzoyl-3-*tert*-butylcyclobutyl)ethanone (Table 1, entry 8). Experiment 1: Prepared according to the general procedure using 131 mg (0.70 mmol) (*E*)-4,4-dimethyl-1-phenylpent-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 14 mg (0.05 mmol, 8% yield) of the cycloadduct as a yellow oil. Experiment 2: 132 mg (0.70 mmol) (*E*)-4,4-dimethyl-1-phenylpent-2-en-1-one, 123 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 9 mg (0.05 mmol, 6% yield).



1-((1*R*,2*R*,3*S*)-2-benzoyl-3-(benzyloxymethyl)cyclobutyl)ethanone (Table 1, entry 9). Experiment 1: Prepared according to the general procedure using 176 mg (0.70 mmol) (*E*)-4-(benzyloxy)-1-phenylbut-2-en-1-one, 122 mg (1.7 mmol) 3-buten-2-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 3:1 hexanes:EtOAc to yield 137 mg (0.42 mmol, 61% yield) of the cycloadduct as a clear oil. Experiment 2: 177 mg (0.70 mmol) (*E*)-4-(benzyloxy)-1-phenylbut-2-en-1-one, 123 mg (1.7 mmol) 3-buten-2-one, 27 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 140 mg (0.43 mmol, 62% yield). IR (thin film): 2254, 1673; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.7 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 (m, 5H), 4.52 (q, J = 12.1 Hz, 2H), 4.28 (t, J = 8.3 Hz, 1H), 3.61 (q, J = 8.9 Hz, 1H), 3.46 (m, 2H), 2.73 (m, 1H), 2.29 (q, J = 10.2 Hz, 1H), 2.08 (s, 3H), 2.07 (m, J = Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 207.9, 199.3, 138.1, 135.8, 133.3, 128.7, 128.6, 128.4, 127.7, 127.6, 73.1, 71.2, 44.5, 43.8, 35.0, 27.4, 24.0; HRMS (EI^+) calc'd for $[C_{21}H_{22}O_3]^+$ requires *m/z* 322.1564, found *m/z* 322.1569.

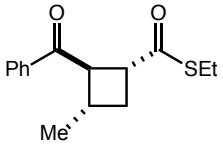


1-((1*R*,2*R*,*3S*)-2-Benzoyl-3-methylcyclobutyl)propan-1-one (Table 2, entry 2). Experiment 1: Prepared according to the general procedure using 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 147 mg (1.7 mmol) 1-penten-3-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 137 mg (0.59 mmol, 85% yield) of the cycloadduct as a yellow oil. Experiment 2: 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 147 mg (1.7 mmol) 1-penten-3-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 133 mg (0.58 mmol, 83% yield). IR (thin film): 2254, 1672, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, J = 8.1, 1.9 Hz, 2H), 7.57 (tt, J = 6.8, 1.3 Hz, 1H), 7.47 (tt, J = 7.9 Hz, 2H), 3.94 (tt, J = 8.6 Hz, 1H), 3.61 (q, J = 8.9 Hz, 1H), 2.43 (m, 4H), 1.75 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 211.0, 211.0, 199.5, 199.5, 136.1, 133.3, 128.6, 127.9, 49.7, 42.5, 33.8, 31.0, 29.5, 20.9, 7.6; HRMS (EI^+) calc'd for $[C_{15}H_{19}O_2]^+$ requires *m/z* 231.1380, found *m/z* 231.1382.

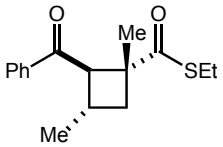


(1*R*,2*R*,3*S*)-Methyl-2-benzoyl-3-methylcyclobutanecarboxylate (Table 2, entry 3). Experiment 1: Prepared according to the general procedure using 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 361 mg (4.2 mmol) methyl acrylate, 27 mg (0.035 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 103 mg (0.44 mmol, 64% yield) of the cycloadduct as a yellow oil.

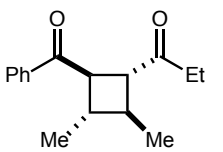
Experiment 2: 101 mg (0.69 mmol) (*E*)-1-phenyl-2-buten-1-one, 360 mg (4.2 mmol) methyl acrylate, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 106 mg (0.46 mmol, 66% yield). IR (thin film): 1728, 1675; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, J = 8.2, 2.1 Hz, 2H), 7.57 (tt, J = 7.1, 1.8 Hz, 1H), 7.47 (tt, J = 7.9, 1.9 Hz, 2H), 3.93 (t, J = 8.5 Hz, 1H), 3.67 (s, 3H), 3.49 (q, J = 9.4 Hz, 1H), 2.50 (m, 1H), 2.39 (q, J = 10.1 Hz, 1H), 1.88 (q, J = 9.4 Hz, 1H), 1.22 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.8, 174.7, 136.1, 133.3, 128.6, 51.8, 51.1, 35.7, 31.6, 29.6, 20.9; HRMS (ESI^+) calc'd for $[C_{14}H_{16}O_3]^+$ requires *m/z* 233.1173, found *m/z* 233.1179.



(1*R*,2*R*,3*S*)-*S*-Ethyl-2-benzoyl-3-methylcyclobutanecarbothioate (Table 2, entry 4). Experiment 1: Prepared according to the general procedure using 103 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 203 mg (1.7 mmol) (*S*)-ethyl-prop-2-enethioate, 27 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 4 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 159 mg (0.61 mmol, 86% yield) of the cycloadduct as a yellow oil. Experiment 2: 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 203 mg (1.7 mmol) (*S*)-ethyl-prop-2-enethioate, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 165 mg (0.63 mmol, 89% yield). IR (thin film): 2254, 1673; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, J = 8.2, 1.7 Hz, 2H), 7.57 (tt, J = 6.9, 1.6 Hz, 1H), 7.47 (t, J = 8 Hz, 2H), 3.96 (t, J = 8.5 Hz, 1H), 3.68 (q, J = 8.8 Hz, 1H), 2.87 (q, J = 7.1 Hz, 2H), 2.5 (m, 1H), 2.41 (m, 1H), 1.92 (q, J = 9.4 Hz, 1H), 1.24 (t, J = 7.5 Hz, 3H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 200.3, 198.6, 136.0, 133.3, 128.6, 128.6, 128.6, 51.3, 44.2, 31.1, 30.4, 23.2, 20.7, 14.7; HRMS (EI^+) calc'd for $[C_{15}H_{17}O_2S]^+$ requires *m/z* 262.1023, found *m/z* 262.1033.



(1*R*,2*R*,3*S*)-*S*-Ethyl-2-benzoyl-1,3-dimethylcyclobutanecarbothioate (Table 2, entry 5). Experiment 1: Prepared according to the general procedure using 103 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 546 mg (4.2 mmol) (*S*)-ethyl-2-methylprop-2-enethioate, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 108 mg (0.39 mmol, 56% yield) of the cycloadduct as a yellow oil. Experiment 2: 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 547 mg (4.2 mmol) (*S*)-ethyl-2-methylprop-2-enethioate, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 262 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 112 mg (0.40 mmol, 58% yield). IR (thin film): 2256, 1672, 1459, 1384; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 6.5 Hz, 1H), 7.42 (t, J = 7.9 Hz, 2H), 4.18 (d, J = 8.8 Hz, 1H), 3.06 (m, 1H), 2.93 (m, 2H), 2.01 (m, J = 7.1 Hz, 2H), 1.28 (t, J = Hz, 3H), 1.21 (s, 3H), 1.13 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.6, 198.8, 136.6, 133.1, 128.5, 128.5, 53.1, 51.4, 39.3, 24.4, 23.3, 20.4, 18.5, 14.7; HRMS (EI^+) calc'd for $[C_{16}H_{19}O_2S]^+$ requires *m/z* 276.1179, found *m/z* 276.1176.



1-((1*R*,2*R*,3*S*,4*S*)-2-benzoyl-3,4-dimethylcyclobutyl)propan-1-one (Table 2, entry 6). Experiment 1: Prepared according to the general procedure using 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 412 mg (4.2 mmol) 4-hexen-3-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 261 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, 6.9 mL acetonitrile and irradiated for 12 h. Purified by chromatography using 6:1 hexanes:EtOAc to yield 60 mg (0.25 mmol, 35% yield) of the cycloadduct as a pale yellow oil. Experiment 2: 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 412 mg (4.2 mmol) 4-hexen-3-one, 26 mg (0.035 mmol) $Ru(bipy)_3Cl_2 \cdot 6H_2O$, 263 mg (2.8 mmol) $LiBF_4$, 243 μL (1.4 mmol) *i*-Pr_2NEt, and 6.9 mL acetonitrile. Isolated 70 mg (0.27 mmol, 38% yield). IR (thin film): 1691, 1675, 1449; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, J = 8.5, 1.3 Hz, 2H), 7.56 (tt, J = 6.8, 1.3 Hz, 1H), 7.46 (tt, J = 8.0, 1.6 Hz, 2H), 3.80 (t, J = 8.9 Hz, 1H), 3.17 (t, J = 8.8 Hz, 1H), 2.37 (dd, J = 13.9, 7.5 Hz, 1H), 2.37 (m, 1H), 1.99 (m,

2H), 1.20 (d, J = 6.7 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 210.5, 199.6, 136.3, 133.2, 128.6, 128.6, 51.2, 47.0, 39.1, 39.0, 34.9, 19.4, 19.1, 7.5; HRMS (ESI^+) calc'd for $[C_{16}H_{20}O_2]^+$ requires *m/z* 245.1537 found *m/z* 245.1532.

Large scale photocycloaddition (eq 3)**.** A dry 100 mL Schlenk flask was charged with 846 mg (5.8 mmol) (*E*)-1-phenyl-2-buten-1-one, 1.02 g (14.6 mmol) 3-buten-2-one, 217 mg (0.29 mmol) $Ru(bipy)_3Cl_2{\cdot}6H_2O$, 2.18 g (23.1 mmol) $LiBF_4$, 2.0 mL (11.5 mmol) *i*-Pr_2NEt, and 57 mL acetonitrile (0.1 M) and degassed by a freeze/pump/thaw cycle (3x) under nitrogen in the dark. The Schlenk flask was then brought onto the roof and allowed to stir in direct sunlight for 4 h. Upon completion, the solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel with 6:1 hexanes:EtOAc as the eluent to afford 1.04 g (4.8 mmol, 84% yield, >10:1 d.r.) of the cycloadduct as a yellow oil.

IV. NOE Correlations

NOE correlations were used to determine the relative stereochemistry of the following compounds. Subsequent assignments were made by analogy.

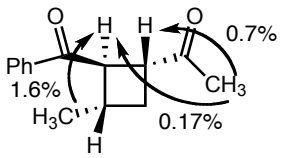


Table 1, entry 1

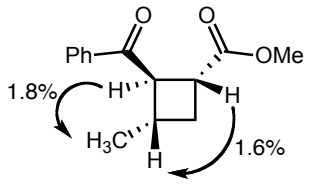


Table 2, entry 3

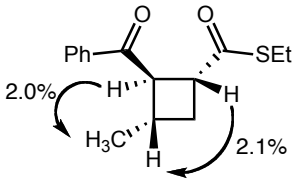


Table 2, entry 4

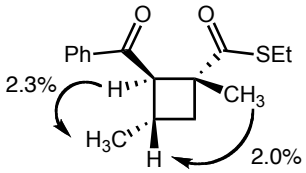


Table 2, entry 5

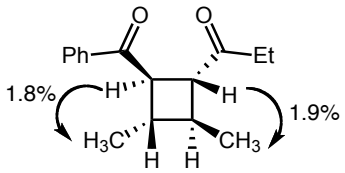


Table 2, entry 7

V. References

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