Supporting Information for
Photocatalytic [2+2] Cycloadditions of Enones with Cleavable Redox Auxiliaries
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I. General information
A 23 W GE compact fluorescent light bulb was used for all photochemical reactions. i-Pr₂NEt was purified by distillation from CaH₂ immediately prior to use. Ru(bpy)₃Cl₂·6H₂O was purchased from commercial sources and used without further purification. Methyl acrylate was washed with aqueous NaOH, distilled water, brine, dried over CaCl₂, and fractionally distilled immediately prior to use. Benzene, CH₂Cl₂, THF, and MeCN were purified by elution through alumina. All other reagents were purchased from commercial sources and purified immediately prior to use. Chromatography was performed with Purasil 60Å silica gel (230–400 mesh). All glassware was oven-dried for at least 1 h before use. Diastereomer ratios for all compounds were determined by ¹H NMR analysis of the unpurified reaction mixtures. ¹H and ¹³C NMR data for all previously uncharacterized compounds were obtained using Varian Inova-500 and Varian Unity-500 spectrometers and are referenced to TMS (0.00 ppm) and CDCl₃ (77 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl). 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) and the University of Wisconsin. Cyclic voltammetry (CV) was conducted on a BAS Epsilon-EC instrument using MeCN with 0.1 M tetrabutylammonium hexafluorophosphate (nBu₄NPF₆) and 1 mM substrate. The electrodes were as follows: Glassy carbon (working), Pt wire (auxiliary) and Ag/AgNO₃ (0.1 M nBu₄NPF₆, 0.01 M Ag/AgNO₃) (reference). The potentials were referenced versus the ferrocene/ferrocenium redox couple by externally added ferrocene.

II. Synthesis of cyclization substrates

(E)-4,4-Dimethyl-1-(1-methyl-1H-imidazol-2-yl)pent-2-en-1-one: To a flame-dried 100 mL round bottomed flask was added 1-(1-methyl-1H-imidazole-2-yl)-2-(triphenylphosphoranylidene)-ethanone¹ (1.33 g, 3.45 mmol), benzene (18 mL), and freshly distilled trimethylacetaldehyde (2.97 g, 34.5 mmol). The reaction was heated to 75 °C and stirred for 105 h under N₂. After cooling to room temperature, the solvent was removed in vacuo, and the residue was purified by chromatography on a silica gel column (3:1 hexanes:EtOAc) to afford 0.563 g (2.93 mmol, 85 % yield) of a clear, viscous oil. IR (thin film): 2961, 1666, 1619, 1408 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.34 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 0.9 Hz, 1H), 7.13 (d, J = 16.0 Hz, 1H), 7.05 (s, 1H), 4.05 (s, 3H), 1.16 (s, 9H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 181.3, 158.5, 143.9, 129.1, 127.1, 121.2, 36.3, 34.1, 28.7; HRMS (EI) calc’d for [C₁₁H₁₆N₂ONa]⁺ requires m/z 215.1160, found m/z 215.1155.
(E)-4-Benzylxoy-1-(1-methyl-1H-imidazol-2-yl)but-2-en-1-one: To a flame-dried 25 mL round bottomed flask was added 1-(1-methyl-1H-imidazol-2-yl)-2-(triphenylphosphoranylidene)-ethanone (0.782 g, 2.03 mmol), benzene (11 mL), and freshly distilled benzoylacetaldheyde (0.336 g, 2.24 mmol). The reaction was heated to 70 °C and stirred for 5 h under N₂. After cooling to room temperature the solvent was removed *in vacuo*, and the residue was purified by chromatography on a silica gel column (3:2 hexanes:EtOAc) to afford 0.485 g (1.89 mmol, 93% yield) of a clear, viscous oil that turned slightly yellow upon standing. IR (thin film): 2922, 1724, 1669, 1407 cm⁻¹; ¹H NMR: (500.2 MHz, CDCl₃) δ 7.65 (dt, J = 16.0, 2.0 Hz, 1H), 7.36 (m, 4H), 7.29 (m, 1H), 7.17 (d, J = 1.0 Hz, 1H), 7.14 (dt, J = 16.0, 4.5 Hz, 1H), 7.04 (s, 1H), 4.58 (s, 2H), 4.27 (dd, J = 5.0, 2.0 Hz, 2H), 4.03 (s, 3H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 180.3, 143.6, 143.3, 137.9, 129.4, 128.4, 127.8, 127.3, 126.7, 72.7, 69.3, 36.2. HRMS (EI) calc'd for [C₁₅H₁₈N₂O₃Na⁺] requires m/z 279.1109, found m/z 279.1104.

(E)-1-(Methyl-1H-imidazol-2-yl)-6-triisopropylsilyloxy-hex-2-en-1-one: To a flame-dried 25 mL round bottomed flask was added 1-(methyl-1H-imidazole-2-yl)-2-(triphenylphosphoranylidene)-ethanone (0.612 g, 1.59 mmol), benzene (8 mL), and 4-((tris(1-methylethyl)silyloxy)-butanal (0.389 g, 1.59 mmol). The reaction was warmed to 60 °C and stirred for 22 h under N₂. After cooling to room temperature the solvent was removed *in vacuo*, and the residue was purified by chromatography on a silica gel column (4:1 hexanes:EtOAc) to afford 0.318 g (0.907 mmol, 57% yield) of a clear, viscous oil. IR (thin film): 2943, 2866, 1682, 1622, 1409 cm⁻¹; ¹H NMR: (500.2 MHz, CDCl₃) δ 7.42 (dt, J = 15.7, 1.6 Hz, 1H), 7.17 (dt, J = 15.7, 7.1 Hz, 1H), 7.17 (d, J = 0.7 Hz, 1H), 7.04 (s, 1H), 4.05 (s, 3H), 3.74 (t, J = 6.3 Hz, 1H), 2.42 (ddt, J = 7.3, 7.2, 1.5 Hz, 2H), 1.77 (m, 2H), 1.06 (m, 21H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 180.8, 148.6, 143.8, 129.1, 127.1, 126.2, 62.7, 36.3, 31.6, 29.3, 18.0, 11.9; HRMS (EI) calc'd for [C₁₀H₁₃N₃O₄SiNa⁺] requires m/z 373.2287, found m/z 373.2282.

(E)-tert-Butyl 4-(3-(1-methyl-1H-imidazol-2-yl)-3-oxoprop-1-en-1-yl)piperidine-1-carboxylate: To a flame-dried 25 mL round bottomed flask was added 1-(1-methyl-1H-imidazol-2-yl)-2-(triphenylphosphoranylidene)-ethanone (0.587 g, 1.53 mmol), benzene (8 mL), and 4-formylpiperidine-1-carboxylic acid tert-butyl ester (0.391 g, 1.83 mmol). The reaction was heated to 75 °C and stirred for 44 h under N₂. After cooling to room temperature the solvent was removed *in vacuo*, and the residue was purified by chromatography on a silica gel column (7:3 hexanes:EtOAc) to afford 0.354 g (1.11 mmol, 73% yield) of a clear, viscous oil. IR (thin film): 2934, 1690, 1688, 1621, 1410 cm⁻¹; ¹H NMR: (500.2 MHz, CDCl₃) δ 7.41 (dd, J = 15.8, 1.4 Hz, 1H), 7.18 (d, J = 0.8 Hz, 1H), 7.06 (s, 1H), 7.04 (dd, J = 15.8, 6.7 Hz, 1H), 4.13 (m, 2H), 4.05 (s, 3H), 2.79 (m, 2H), 2.41 (m, 1H), 1.80 (d, J = 12.5 Hz, 2H), 1.45 (m, 10H), 1.40 (ddd, J = 13.2, 5.1, 1.1 Hz, 1H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 180.7, 154.8, 150.8, 143.7, 129.3, 127.2, 124.7, 79.5, 43.5, 39.0, 36.3, 30.7, 28.4; HRMS (EI) calc'd for [C₁₃H₂₃N₂O₃Na⁺] requires m/z 342.1794, found m/z 342.1789.

(E)-7-(1-Methyl-1H-imidazol-2-yl)-7-oxohept-5-enal (S-1): 1-(1-Methyl-1H-imidazole-2-yl)-2-(triphenylphosphoranylidene)-ethanone (5.6 g, 14.6 mmol) was placed in a 100 mL round bottomed flask with 36 mL (0.4 M) CH₂Cl₂. 6 mL of a 50 wt. % in water solution of glutaraldehyde (3 g, 30.0 mmol) was added. The mixture was heated to 45 °C and stirred overnight. Upon completion, the reaction was filtered over Celite and the filtrate was concentrated *in vacuo*. The residue was triturated three times with diethyl ether to remove triphenylphosphine oxide. The crude reaction mixture was then purified by chromatography on a silica gel column (2:1 hexanes:acetone) to afford 2.8 g (13.6 mmol, 93% yield) of a light yellow oil. IR (thin film): 2944, 2728, 1720, 1665, 1619, 1408 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 9.78 (t, J = 1.4 Hz, 1H), 7.43 (dt, J = 15.7, 1.6 Hz, 1H), 7.18 (s, 1H), 7.07 (m, = 1H), 7.06 (s, 1H), 4.05 (s, 3H), 2.51 (td, J = 7.4, 1.4 Hz, 2H), 2.37 (qd, J = 7.4, 1.4 Hz, 2H), 1.88 (dq, J = 7.3, 7.4 Hz, 2H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 201.7, 180.4, 146.7, 129.2, 127.2, 127.0, 43.0, 42.7, 36.2, 31.7, 20.5; HRMS (EI) calc'd for [C₁₁H₁₃N₂O₂Na⁺] requires m/z 229.0948, found m/z 229.0958.
(2E,7E)-Benzy1 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate: A 25 mL round-bottomed flask was charged with S-1 (950 mg, 4.6 mmol), benzyl 2-(triphenylphosphoranylidene)acetate (2.5 g, 6.1 mmol) and 5 mL (0.9 M) CH₂Cl₂. The solution was stirred at room temperature for 18 h. The solvent was then removed in vacuo and the residue was triturated three times with diethyl ether to remove triphenylphosphine oxide. The crude reaction mixture was then purified by chromatography on a silica gel column (4:1 to 3:1 hexanes:aceton) to afford 1.4 g (4.1 mmol, 90 % yield) of a clear viscous oil. IR (thin film) 2950, 1732, 1670, 1409 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.41 (dt, J = 15.6, 1.7 Hz, 1H), 7.37 (m, 5H), 7.17 (d, J = 0.9 Hz, 1H), 7.04 (s, 1H), 7.08 (dt, J = 15.7, 7.2 Hz, 1H), 7.00 (dt, J = 16.1, 6.8 Hz, 1H), 5.89 (dt, J = 15.6, 1.5 Hz, 1H), 5.17 (s, J = Hz, 2H), 4.04 (s, 3H), 2.35 (qd, J = 7.4, 1.7 Hz, 2H), 2.26 (qd, J = 7.4, 1.7 Hz, 2H), 1.69 (m, 2H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 180.5, 166.3, 148.9, 147.3, 143.6, 136.1, 129.2, 128.5, 128.2, 128.1, 127.1, 126.8, 121.6, 66.0, 36.3, 31.9, 31.6, 26.4; HRMS (EI) calc’d for [C₃₀H₂₇N₅O₉⁺Na]+ requires m/z 338.1625, found m/z 338.1621.

(2E,7E)-Ethyl 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate: A 25 mL round-bottomed flask was charged with S-1 (750 mg, 3.42 mmol), ethyl 2-(triphenylphosphoranylidene)acetate (2.03 g, 5.33 mmol) and 6 mL (0.6 M) CH₂Cl₂. The solution was stirred at room temperature for 6 h. The solvent was then removed in vacuo and the residue was triturated three times with diethyl ether to remove triphenylphosphine oxide. The crude reaction mixture was then purified by chromatography on a silica gel column (4:1 to 2:1 hexanes:aceton) to afford 1.0 mg (2.93 mmol, 86% yield) of a light yellow viscous oil. IR (thin film) 2936, 1716, 1667, 1408 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.43 (dt, J = 15.5, 1.8 Hz, 1H), 7.17 (d, J = 0.9 Hz, 1H), 7.09 (dt, J = 15.5, 5.7 Hz, 1H), 7.05 (s, 1H), 6.94 (dt, J = 15.5, 6.7 Hz), 5.83 (dt, J = 15.5, 1.5 Hz, 1H), 4.19 (q, J = 7.4 Hz, 2H), 4.05 (s, 3H), 2.35 (qd, J = 7.4, 1.8 Hz, 2H), 2.26 (qd, J = 7.4, 1.8 Hz, 2H), 1.71 (dt, J = 7.4, 1.8 Hz, 2H), 1.29 (s, J = 7.1 Hz, 3H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 180.6, 166.6, 148.1, 147.3, 143.6, 126.9, 129.2, 127.1, 126.8, 121.9, 60.2, 36.25, 31.9, 31.5, 26.5, 14.2; HRMS (EI) calc’d for [C₁₅H₂₇N₅O₉⁺Na]+ requires m/z 276.1469, found m/z 276.1458.

(2E,7E)-1-(1-Methyl-1H-imidazol-2-yl)deca-2,7-diene-1,9-dione: A 25 mL round-bottomed flask was charged with S-1 (250 mg, 1.21 mmol), 1-(triphenylphosphoranylidene)propan-2-one (660 mg, 2.1 mmol) and 10 mL (0.12 M) CH₂Cl₂. The solution was stirred at room temperature for 12 h. The solvent was then removed in vacuo and the crude reaction mixture was loaded directly onto a silica gel column and eluted with 2:1 hexanes:aceton to afford 180 mg (0.73 mmol, 60 % yield) of a colorless viscous oil. IR (thin film) 2932, 1667, 1620, 1407, 1362 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.43 (dt, J = 15.7, 1.4 Hz, 1H), 7.18 (d, J = 0.9 Hz, 1H), 7.09 (dt, J = 15.7, 6.8 Hz, 1H), 7.06 (s, 1H), 6.79 (dt, J = 15.7, 6.8 Hz, 1H), 6.09 (dt, J = 15.7, 1.4 Hz, 1H), 4.05 (s, 3H), 2.35 (qd, J = 7.2, 1.7 Hz, 2H), 2.28 (qd, J = 7.2, 1.3 Hz, 2H), 2.25 (s, 3H), 1.73 (m, 2H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 198.5, 180.4, 147.2, 147.1, 143.5, 131.6, 129.2, 127.1, 126.8, 36.2, 31.9, 31.7, 26.8, 26.5; HRMS (EI) calc’d for [C₁₄H₁₄N₂O₂⁺Na]+ requires m/z 269.1261, found m/z 269.1249.

(2E,7E)-1-(1-Methyl-1H-imidazol-2-yl)-9-morpholinonona-2,7-diene-1,9-dione: A 25 mL round-bottomed flask was charged with 1.0 equivalent NaH dissolved in 3 mL dry THF at room temperature. Diethyl (2-morpholino-2-oxoethyl)phosphonate was added to the stirring solution dropwise (60.5 mg, 0.228 mmol, 1.2 equiv), and the reaction was allowed to stir until solution became clear. A solution of S-1 (40 mg, 0.194 mmol) in 0.5 mL dry THF was added dropwise, and the reaction was stirred for 15 min. The reaction was then diluted with 5 mL diethyl ether and washed with water. The organic layer was separated and dried over Na₂SO₄. After filtration, the solution was concentrated in vacuo and purified by chromatography on a silica gel column (1:1 acetone:hexanes) to afford 35 mg (0.11 mmol, 57 % yield) of a colorless oil. IR (thin film) 2858, 1662, 1618, 1407 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.42 (dt, J = 15.7, 1.5
Upon completion of the reaction, the reaction was diluted with ethyl acetate, passed through a silica plug, and the completion

45 min to the solution containing the Michael acceptor. Additional

then added to the first tube. The solutions were degassed using three freeze

NMR: (500.2 MHz, CDCl$_3$) δ 20.1, 20.1, 20.1, 15.9, 15.9, 15.9, 15.9, 15.9, 15.9. The solution was stirred at room temperature overnight. The solvent was then removed in vacuo and the crude reaction mixture was loaded directly onto a silica gel column and eluted with 3:1 hexanes:acetone to afford 180 mg (0.619 mmol, 38% yield) as a colorless viscous oil. IR (thin film) 2360, 2254, 1700, 1666, 1621 cm$^{-1}$; $^1$H NMR: (499.9 MHz, CDCl$_3$) δ 7.43 (dt, J = 15.5, 1.9 Hz, 1H), 7.17 (dt, J = 1.0 Hz, 1H), 7.11 (dt, J = 15.6, 7.1 Hz, 1H), 7.05 (s, 1H), 6.75 (tq, J = 7.6, 1.7 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 4.05 (s, 3H), 2.36 (qd, J = 7.1, 1.5 Hz, 2H), 2.23 (q, J = 7.3 Hz, 2H), 1.83 (q, J = 1.0 Hz, 3H), 1.70 (dq, J = 7.6, 15.0 Hz, 2H), 1.30 (t, J = 7.0 Hz, 3H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) δ 180.5, 168.1, 147.4, 146.0, 143.6, 129.2, 127.2, 126.8, 120.1, 116.8, 46.1, 42.2, 36.3, 31.9, 131.9, 26.7: HRMS (EI) calc’d for [C$_{17}$H$_{53}$O$_5$+H]$^+$ requires m/z 318.1813, found m/z 318.1812.

### III. Photocycloadditions

(3,4-Dimethylcyclobutane-1,2-diy)bis((1-methyl-1H-imidazol-2-yl)methanone) (2). To an oven-dried 25 mL Schlenk tube was added 99.6 mg (0.663 mmol) (E)-1-(1-methyl-1H-imidazol-2-yl)-2-but-en-1-one, 12.7 mg (0.017 mmol) Ru(bpy)$_3$Cl$_2$·6H$_2$O, 61.7 mg (0.663 mmol) LiBF$_4$, 120 µL (0.651 mmol) i-Pr$_2$NEt, and 3.3 mL acetonitrile. The solution was degassed using three freeze-pump-thaw cycles in the dark. The Schlenk tube was backfilled with nitrogen and irradiated for 4 h. Upon completion of the reaction, the reaction was diluted with acetone, passed through a silica plug, and the solvent was removed in vacuo. Purified by chromatography (2:1 hexanes:acetone) to afford 82.5 mg (0.651 mmol, 83% yield, >10:1 d.r.) of the cycloadduct. Experiment 2: 99.8 mg (0.664 mmol) enone, 12.6 mg (0.017 mmol) Ru(bpy)$_3$Cl$_2$·6H$_2$O, 61.9 mg (0.666 mmol) LiBF$_4$, 120 µL (0.651 mmol) i-Pr$_2$NEt, and 3.3 mL acetonitrile. Isolated 80.7 mg (0.269 mmol, 81% yield, >10:1 d.r.). IR (thin film): 2954, 2921, 1665, 1405 cm$^{-1}$; $^1$H NMR: (500.2 MHz, CDCl$_3$) δ 6.96 (d, J = 0.7 Hz, 2H), 6.94 (s, 2H), 4.14 (dd, J = 5.6, 3.2 Hz, 2H), 4.00 (s, 6H), 2.18 (m, 2H), 1.21 (m, 6H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) δ 191.8, 143.1, 129.0, 126.6, 48.9, 38.5, 36.0, 19.1; HRMS (EI) calc’d for [C$_{17}$H$_{53}$O$_5$+Na]$^+$ requires m/z 323.1484, found m/z 323.1479.

**General procedure A: Intermolecular [2+2] cycloadditions** (Figure 1): A dry 25 mL Schlenk tube was charged with the Michael acceptor (5 equiv) followed by a solution of Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.025 equiv) and LiBF$_4$ (0.5–4.0 equiv) in dry MeCN (1.33 M with respect to the Michael acceptor). A second 25 mL Schlenk tube was charged with a solution of imidazole enone (1 equiv) in dry MeCN (0.16 M with respect to the aryl enone). i-Pr$_2$NEt (2 equiv) was then added to the first tube. The solutions were degassed using three freeze-pump-thaw cycles under nitrogen in the dark. The Schlenk tubes were then placed in a water bath and irradiated using a 23 W compact fluorescent light bulb placed at a distance of 20 cm. The imidazole enone solution was added dropwise via syringe pump over a period of 45 min to the solution containing the Michael acceptor. Additional time was allowed for the reaction to reach completion (total reaction times listed in Table 3 refer to dropwise addition and subsequent irradiation combined). Upon completion of the reaction, the reaction was diluted with ethyl acetate, passed through a silica plug, and the solvent was removed in vacuo. The resulting residue was purified by chromatography on a silica gel column.

**General procedure B: Intramolecular [2+2] cycloadditions** (Figure 2): A dry 25 mL Schlenk tube was charged with a solution of the bisenone (1 equiv), Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.025 equiv), LiBF$_4$ (0.5 equiv), and i-Pr$_2$NEt (2 or 0.5
equiv) in acetonitrile (0.1 M). The solution was then degassed using three freeze-pump-thaw cycles under nitrogen in the dark. The Schlenk tube was then irradiated using a 23 W floodlight placed at a distance of 20 cm. Upon completion of the reaction, the reaction was passed through a silica plug using 100% ethyl acetate or acetone as the eluent, the solvent was removed in vacuo, and the residue was purified by chromatography on a silica gel column.

**Methyl 3-methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutanecarboxylate (3)**

(Figure 1): Prepared according to general procedure A using 104.2 mg (0.694 mmol) \((E)-1-(1-

methyl-1H-imidazole-2-yl)-but-2-en-1-one, 315 \(\mu\)L (3.50 mmol) methyl acrylate, 13.3 mg (0.018 mmol) \(\text{Ru(bpy)}\)_2\(\text{Cl}_2\)\_6H\_2O, 130 mg (1.39 mmol) LiBF\(_4\), 242 \(\mu\)L (1.39 mmol) \(\text{i-Pr}_3\text{NEt}\), 6.94 mL acetonitrile and an irradiation time of 90 min. Purified by chromatography (23:2 hexanes:acetone) to afford 110 mg (0.466 mmol, 67% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 104.7 mg (0.697 mmol) enone, 315 \(\mu\)L (3.50 mmol) methyl acrylate, 13.1 mg (0.017 mmol) \(\text{Ru(bpy)}\)_2\(\text{Cl}_2\)\_6H\_2O, 132 mg (1.41 mmol) LiBF\(_4\), 245 \(\mu\)L (1.41 mmol) \(\text{i-Pr}_3\text{NEt}\), and 6.97 mL acetonitrile. Isolated 111 mg (0.470 mmol, 67% yield, >10:1 d.r.). IR (thin film): 2954, 1733, 1668, 1411 cm\(^{-1}\); \(^1\)H NMR (499.9 MHz, CDCl\(_3\)) \(\delta\) 7.14 (d, \(J = 0.9\) Hz, 1H), 7.05 (s, 1H), 4.21 (dd, \(J = 8.9, 8.9\) Hz, 1H), 4.02 (s, 3H), 3.66 (s, 3H), 3.46 (ddd, \(J = 9.0, 9.0, 9.0\) Hz, 1H), 2.42 (m, 1H), 2.33 (ddd, \(J = 10.2, 8.8, 8.8\) Hz, 1H), 1.92 (ddd, \(J = 10.3, 9.4, 9.4\) Hz, 1H), 1.26 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR: (125.7 MHz, CDCl\(_3\)) \(\delta\) 190.9, 174.4, 142.6, 129.5, 127.3, 52.2, 51.7, 36.1, 35.1, 32.5, 29.3, 20.8; HRMS (EI) calc’d for \([\text{C}_{29}54, 1733, 1668, 1411}\text{M}^+\) requires \(m/z\) 259.1054, found \(m/z\) 259.1054.

**S-Ethyl 3-methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutanecarbothioate (4)**

(Figure 1): Preparing according to general procedure A using 109.4 mg (0.728 mmol) \((E)-1-(1-

methyl-1H-imidazole-2-yl)-but-2-en-1-one, 426 mg (3.67 mmol) ethyl prop-2-enoethioate, 13.4 mg (0.018 mmol) \(\text{Ru(bpy)}\)_2\(\text{Cl}_2\)\_6H\_2O, 136 mg (1.45 mmol) LiBF\(_4\), 255 \(\mu\)L (1.46 mmol) \(\text{i-Pr}_3\text{NEt}\), and 7.23 mL acetonitrile. Isolated 155 mg (0.582 mmol, 80% yield, >10:1 d.r.). IR (thin film): 2963, 2931, 1668, 1410 cm\(^{-1}\); \(^1\)H NMR: (500.2 MHz, CDCl\(_3\)) \(\delta\) 7.15 (s, 1H), 7.06 (s, 1H), 4.26 (dd, \(J = 8.5, 8.5\) Hz, 1H), 4.03 (s, 3H), 3.68 (ddd, \(J = 8.9, 8.9, 8.9\) Hz 1H), 2.86 (q, \(J = 7.5\) Hz, 2H), 2.39 (m, 1H), 2.33 (ddd, \(J = 10.1, 8.7, 8.7\) Hz, 1H), 1.96 (ddd, \(J = 10.4, 9.3, 9.3\) Hz, 1H), 1.26 (d, \(J = 6.6\) Hz, 3H), 1.22 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C NMR: (125.7 MHz, CDCl\(_3\)) \(\delta\) 200.0, 190.7, 142.6, 129.5, 127.3, 52.6, 43.1, 36.1, 32.5, 29.8, 23.0, 20.7, 14.7; HRMS (EI) calc’d for \([\text{C}_{30}53, 1733, 1668, 1411}\text{M}^+\) requires \(m/z\) 289.0987, found \(m/z\) 289.0982.

**I-(3-Methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (5)**

(Figure 1): Prepared according to general procedure A using 106.8 mg (0.711 mmol) \((E)-1-(1-

methyl-1H-imidazole-2-yl)-but-2-en-1-one, 290 \(\mu\)L (3.57 mmol) 3-buten-2-one, 13.4 mg (0.018 mmol) \(\text{Ru(bpy)}\)_2\(\text{Cl}_2\)\_6H\_2O, 33.6 mg (0.358 mmol) LiBF\(_4\), 250 \(\mu\)L (1.44 mmol) \(\text{i-Pr}_3\text{NEt}\), 7.11 mL acetonitrile and an irradiation time of 90 min. Purified by chromatography (17:3 hexanes:acetone) to afford 119 mg (0.540 mmol, 76% yield, >10:1 d.r.) of the cycloadduct. Experiment 2: 103.4 mg (0.689 mmol) enone, 280 \(\mu\)L (3.45 mmol) 3-buten-2-one, 12.8 mg (0.0171 mmol) \(\text{Ru(bpy)}\)_2\(\text{Cl}_2\)\_6H\_2O, 32.3 mg (0.344 mmol) LiBF\(_4\), 240 \(\mu\)L (1.38 mmol) \(\text{i-Pr}_3\text{NEt}\), and 6.89 mL acetonitrile. Isolated 111 mg (0.504 mmol, 73% yield, >10:1 d.r.) of the cycloadduct as a clear oil, IR (thin film): 2958, 1707, 1665, 1409 cm\(^{-1}\); \(^1\)H NMR: (500.2 MHz, CDCl\(_3\)) \(\delta\) 7.15 (d, \(J = 0.6\) Hz, 1H), 7.05 (s, 1H), 4.13 (dd, \(J = 8.8, 8.8\) Hz, 1H), 4.03 (s, 3H), 3.56 (ddd, \(J = 9.1, 9.1, 9.1\) Hz, 1H), 2.42 (app q, \(J = 8.5, 6.8\) Hz, 1H), 2.27 (ddd, \(J = 10.3, 8.9, 8.9\) Hz, 1H), 2.08 (s, 3H), 1.84 (ddd, \(J = 10.4, 9.5, 9.5\) Hz, 1H), 1.23 (d, \(J = 6.7\) Hz, 3H); \(^{13}\)C NMR: (125.7 MHz, CDCl\(_3\)) \(\delta\) 208.4, 191.4, 142.6, 129.6, 127.3, 51.6, 42.9, 36.1, 32.0, 28.5, 27.5, 20.9; HRMS (EI) calc’d for \([\text{C}_{12}53, 1733, 1668, 1411}\text{M}^+\) requires \(m/z\) 243.1109, found \(m/z\) 243.1104.
1-(3-Ethyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (6) (Figure 1): Prepared according to general procedure A using 103.5 mg (0.630 mmol) (E)-1-(1-methyl-1H-imidazole-2-yl)-pent-2-en-1-one, 260 μL (3.21 mmol) 3-buten-2-one, 11.7 mg (0.016 mmol) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 29.5 mg (0.315 mmol) LiBF$_4$, 220 μL (1.26 mmol) i-Pr$_2$NEt, and an irradiation time of 90 min. Purified by chromatography (17:3 hexanes:acetone) to afford 115 mg (0.491 mmol, 78% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 103.4 mg (0.630 mmol) enone, 255 μL (3.15 mmol) 3-buten-2-one, 11.8 mg (0.016 mmol) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 29.5 mg (0.315 mmol) LiBF$_4$, 220 μL (1.26 mmol) i-Pr$_2$NEt, and 6.30 mL acetonitrile and an irradiation time of 90 min. Purified by chromatography (17:3 hexanes:acetone) to afford 115 mg (0.491 mmol, 78% yield, >10:1 d.r.). IR (thin film): 2960, 2930, 2874, 1709, 1667, 1410 cm$^{-1}$; $^1$H NMR: (500.2 MHz, CDCl$_3$) $\delta$ 7.14 (s, 1H), 7.07 (s, 1H), 4.22 (dd, J = 8.7, 8.7 Hz, 1H), 4.03 (s, 3H), 3.51 (ddd, J = 9.2, 9.2, 9.2 Hz, 1H), 2.31 (m, 1H), 2.23 (ddd, J = 10.2, 9.2, 9.2 Hz, 1H), 2.08 (s, 3H), 1.83 (ddd, J = 10.4, 9.4, 9.4 Hz, 1H), 1.69 (d of quint, J = 12.7, 7.3 Hz, 1H), 1.49 (ddq, J = 12.8, 7.4, 7.3 Hz, 1H), 0.79 (t, J = 7.4 Hz, 3H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 208.5, 191.7, 142.6, 129.5, 127.4, 49.9, 43.5, 37.9, 36.1, 28.5, 27.5, 26.3, 10.8; HRMS (EI) calc’d for [C$_{15}$H$_{23}$N$_2$O$_2$Na]$^+$ requires m/z 257.1266, found m/z 257.1261.

1-(3-iso-Propyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (7) (Figure 1): Prepared according to general procedure A using 108.6 mg (0.609 mmol) (E)-4-methyl-1-(1-methyl-1H-imidazol-2-yl)-pent-2-en-1-one, 250 μL (3.08 mmol) 3-buten-2-one, 11.5 mg (0.015 mmol) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 114 mg (1.22 mmol) LiBF$_4$, 212 μL (1.22 mmol) i-Pr$_2$NEt, 6.09 mL acetonitrile and an irradiation time of 2 h. Purified by chromatography (23:2 hexanes:acetone) to afford 111 mg (0.447 mmol, 73% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 106.7 mg (0.599 mmol) enone, 245 μL (3.02 mmol) 3-buten-2-one, 11.3 mg (0.015 mmol) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 112 mg (1.20 mmol) LiBF$_4$, 210 μL (1.20 mmol) i-Pr$_2$NEt, and 5.99 mL acetonitrile. Isolated 110 mg (0.443 mmol, 74% yield, >10:1 d.r.). IR (thin film): 2957, 2873, 1709, 1665, 1418 cm$^{-1}$; $^1$H NMR: (500.2 MHz, CDCl$_3$) $\delta$ 7.15 (s, 1H), 7.06 (s, 1H), 4.36 (dd, J = 8.7, 8.7 Hz, 1H), 4.02 (s, 3H), 3.32 (ddd, J = 8.9, 8.9, 8.9 Hz, 1H), 2.24 (m, 1H), 2.17 (ddd, J = 10.3, 8.8, 8.8 Hz, 1H), 2.07 (s, 3H), 1.86 (ddd, J = 10.3, 9.4, 9.4 Hz, 1H), 1.64 (m, 1H), 0.83 (d, J = 6.5 Hz, 3H), 0.73 (d, J = 6.5 Hz, 3H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 208.3, 192.4, 142.7, 129.5, 127.5, 48.4, 44.5, 42.6, 36.2, 33.4, 27.7, 24.9, 19.6, 18.8; HRMS (EI) calc’d for [C$_{15}$H$_{25}$N$_2$O$_2$Na]$^+$ requires m/z 271.1422, found m/z 271.1417.

1-(3-(tert-Butyl)-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (8) (Figure 1): To a 25 mL Schlenk tube that had been evacuated and purged with N$_2$ was added 106.4 mg (0.553 mmol, 1.0 equiv) (E)-4,4-dimethyl-1-(1-methyl-1H-imidazol-2-yl)-pent-2-en-1-one, 112 μL (1.38 mmol, 2.5 equiv) 3-buten-2-one, 10.5 mg (0.014 mmol, 0.025 equiv) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 207 mg (2.21 mmol, 4.0 equiv) LiBF$_4$, 193 μL (1.11 mmol, 2.0 equiv) i-Pr$_2$NEt, and 5.53 mL acetonitrile. The solution was subsequently degassed using three freeze-pump-thaw cycles under nitrogen in the dark. The Schlenk tube was then placed in a water bath and irradiated for 14 h. Upon completion of the reaction, the reaction was diluted with ethyl acetate, passed through a silica plug, and the solvent was removed in vacuo. Purified by chromatography (4:1 hexanes:EtOAc) to afford 97 mg (0.370 mmol, 66% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 106.3 mg (0.553 mmol) enone, 110 μL (1.38 mmol) 3-buten-2-one, 10.3 mg (0.014 mmol) Ru(bpy)$_2$Cl$_2$·6H$_2$O, 206 mg (2.20 mmol) LiBF$_4$, 195 μL (1.12 mmol) i-Pr$_2$NEt, and 5.53 mL acetonitrile. Isolated 93 mg (0.354 mmol, 65% yield, >10:1 d.r.). IR (thin film): 2957, 1709, 1666, 1409 cm$^{-1}$; $^1$H NMR: (500.2 MHz, CDCl$_3$) $\delta$ 7.16 (d, J = 0.7 Hz, 1H), 7.06 (s, 1H), 4.53 (dd, J = 9.2 Hz, 1H), 4.02 (s, 3H), 3.25 (ddd, J = 9.2, 9.2, 9.2 Hz, 1H), 2.43 (ddd, J = 10.1, 9.0, 9.0 Hz, 1H), 2.06 (s, 3H), 1.99 (m, 2H), 0.80 (s, 9H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 208.1, 192.7, 142.8, 129.6, 127.6, 46.4, 45.2, 44.2, 36.1, 31.6, 27.6, 26.4, 21.8; HRMS (EI) calc’d for [C$_{15}$H$_{25}$N$_2$O$_2$Na]$^+$ requires m/z 285.1579, found m/z 285.1574.
1-(3-((Benzyloxy)methyl)-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (9) (Figure 1): Prepared according to general procedure A using 108.7 mg (0.424 mmol) (E)-4-benzyloxy-1-(1-methyl-1H-imidazol-2-yl)-but-2-en-1-one, 175 µL (2.16 mmol) 3-buten-2-one, 7.8 mg (0.010 mmol) Ru(bpy)_3Cl_2·6H_2O, 79.9 mg (0.852 mmol) LiBF_4, 148 µL (0.848 mmol) i-Pr_2NEt, 4.24 mL acetonitrile and an irradiation time of 145 min. Purified by chromatography (7.3 hexanes:EtOAc to afford 72 mg (0.221 mmol, 52% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 108.0 mg (0.723 mmol) enone, 170 µL (2.10 mmol) 3-buten-2-one, 7.9 mg (0.011 mmol) Ru(bpy)_3Cl_2·6H_2O, 79.1 mg (0.844 mmol) LiBF_4, 147 µL (0.844 mmol) i-Pr_2NEt, and 4.21 mL acetonitrile. Isolated 70 mg (0.214 mmol, 51% yield, >10:1 d.r.). IR (thin film): 2927, 1708, 1666, 1410 cm⁻¹; ^1H NMR: (500.2 MHz, CDCl_3) δ 7.27 (m, 5H), 7.12 (d, J = 0.7 Hz, 1H), 7.03 (s, 1H), 4.51 (s, 2H), 4.36 (dd, J = 8.7 Hz, 1H), 4.00 (s, 3H), 3.67 (dd, J = 9.7, 5.4 Hz, 1H), 3.59 (dd, J = 9.6, 6.8 Hz, 1H), 3.55 (dd, J = 9.2, 9.2 Hz, 1H), 3.70 (m, 1H), 2.25 (ddd, J = 10.3, 9.0, 9.0 Hz, 1H), 2.11 (s, 3H), 2.10 (ddd, J = 10.3, 9.4, 9.4 Hz, 1H); ^13C NMR: (125.7 MHz, CDCl_3) δ 208.2, 191.1, 142.4, 138.5, 129.5, 128.2, 127.5, 127.4, 127.3, 73.1, 72.8, 46.7, 43.6, 36.0, 35.5, 27.5, 24.3; HRMS (ESI) calc’d for [C_{40}H_{35}N_2O_2Na]^+ requires m/z 349.1528, found m/z 349.1523.

1-(2-(1-Methyl-1H-imidazole-2-carbonyl)-3-((triisopropylsilyloxy)propyl)cyclobutyl)ethanone (10) (Figure 1): Prepared according to general procedure A using 112.5 mg (0.320 mmol) (E)-1-(1-methyl-1H-imidazol-2-yl)-6-triisopropylsilanyloxy-hex-2-en-1-one, 130 µL (1.60 mmol) 3-buten-2-one, 6.0 mg (0.008 mmol) Ru(bpy)_3Cl_2·6H_2O, 60.4 mg (0.644 mmol) LiBF_4, 112 µL (0.641 mmol) i-Pr_2NEt, 3.20 mL acetonitrile and an irradiation time of 90 min. Purified by chromatography (4:1 hexanes:EtOAc to afford 92 mg (0.219 mmol, 68% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 113.2 mg (0.323 mmol) enone, 131 µL (1.61 mmol) 3-buten-2-one, 6.1 mg (0.008 mmol) Ru(bpy)_3Cl_2·6H_2O, 60.7 mg (0.647 mmol) LiBF_4, 113 µL (0.649 mmol) i-Pr_2NEt, and 3.23 mL acetonitrile. Isolated 92 mg (0.219 mmol, 68% yield, >10:1 d.r.). IR (thin film): 2942, 2866, 2360, 1711, 1667, 1409 cm⁻¹; ^1H NMR: (500.2 MHz, CDCl_3) δ 7.13 (s, 1H), 7.04 (s, 1H), 4.22 (dd, J = 8.8, 8.8 Hz, 1H), 4.02 (s, 3H), 3.60 (t, J = 6.7 Hz, 2H), 3.51 (ddd, J = 9.2, 9.2, 9.2 Hz, 1H), 2.39 (m, 1H), 2.24 (ddd, J = 10.3, 9.4, 9.4 Hz, 1H), 2.08 (s, 3H), 1.84 (ddd, J = 10.1, 9.6, 9.6 Hz, 1H), 1.75 (m, 1H), 1.46 (m, 3H), 1.01 (m, 2H); ^13C NMR: (125.7 MHz, CDCl_3) δ 208.3, 191.6, 142.6, 129.6, 127.4, 63.2, 50.2, 43.5, 36.2, 36.1, 31.9, 30.1, 27.5, 26.8, 18.0, 11.9; HRMS (ESI) calc’d for [C_{25}H_{29}N_2O_2SiNa]^+ requires m/z 443.2706, found m/z 443.2701.

tert-Butyl 4-(3-acetyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)piperidine-1-carboxylate (11) (Figure 1): Due to the hygroscopic nature of the piperidine enone, benzene (3 x 1 mL) was added to the enone, and the volatiles were removed in vacuo three times immediately prior to the reaction. Prepared according to general procedure B using 109.5 mg (0.343 mmol) 4-[(E)-3-(1-methyl-1H-imidazol-2-yl)-3-oxo-propienyl]-piperidine-1-carboxylic acid tert-butyl ester, 140 µL (1.73 mmol) 3-buten-2-one, 6.4 mg (0.009 mmol) Ru(bpy)_3Cl_2·6H_2O, 65.3 mg (0.697 mmol) LiBF_4, 121 µL (0.698 mmol) i-Pr_2NEt, and 3.49 mL acetonitrile. Isolated 105 mg (0.270 mmol, 77% yield, >10:1 d.r.). IR (thin film): 2976, 2930, 2853, 1688, 1667, 1410, 1366 cm⁻¹; ^1H NMR: (500.2 MHz, CDCl_3) δ 7.14 (s, 1H), 7.07 (s, 1H), 4.37 (dd, J = 8.7, 8.7 Hz, 1H), 4.02 (s, 3H), 4.02 (m, 2H), 3.37 (ddd, J = 9.4, 9.4, 9.4 Hz, 1H), 2.62 (m, 1H), 2.31 (pent, J = 8.9 Hz, 1H), 2.19 (ddd, J = 10.1, 9.5, 9.5 Hz, 1H), 2.07 (s, 3H), 1.90 (ddd, J = 10.2, 9.6, 9.6 Hz, 1H), 1.66 (m, 1H), 1.50 (m, 2H), 1.42 (s, 9H), 0.99 (qd, J = 12.5, 4.3 Hz, 1H), 0.88 (qd, J = 12.1, 4.2 Hz, 1H); ^13C NMR: (125.7 MHz, CDCl_3) δ 208.0, 191.9, 154.8, 142.4, 129.6, 127.7, 79.2, 47.9, 44.8, 41.3, 39.9, 36.2, 29.1, 28.5, 27.9, 24.7; HRMS (ESI) calc’d for [C_{32}H_{37}N_2O_3Na]^+ requires m/z 412.2212, found m/z 412.2207.
Benzyl 7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (12) (Figure 2): Prepared according to general procedure B using 203.3 mg (0.601 mmol) (2E,7E)-benzyl 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate, 11.3 mg (0.015 mmol) Ru(bpy)_2Cl_2·6H_2O, 27.8 mg (0.300 mmol) LiBF_4, 220 µL (1.194 mmol) i-Pr_2NEt, 6.0 mL acetonitrile, and an irradiation time of 90 min. Purified by chromatography (3:1 hexanes:acetone) to afford 166.7 mg (0.493 mmol, 82% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 202.6 mg (0.600 mmol) bisenone, 11.5 mg (0.015 mmol) Ru(bpy)_2Cl_2·6H_2O, 27.7 mg (0.300 mmol) LiBF_4, 220 µL (1.19 mmol) i-Pr_2NEt, and 6.0 mL acetonitrile. Isolated 160.8 mg (0.476 mmol, 79% yield, >10:1 d.r.). IR (thin film) 2930, 2361, 1667, 1623 cm\(^{-1}\); ^1H NMR: (499.9 MHz, CDCl_3) δ 7.26 (m, 3H), 7.16 (m, 2H), 7.03 (d, J = 0.9 Hz, 1H), 6.90 (s, 1H), 4.93 (s, 2H), 4.01 (dd, J = 10.5, 5.7 Hz, 1H), 3.83 (s, 3H), 3.21 (1H), 3.16 (dd, J = 10.5, 5.7 Hz, 1H), 3.02 (m, 1H), 1.90 (m, 2H), 1.73 (m, 2H), 1.58 (m, 2H); ^13C NMR: (125.7 MHz, CDCl_3) δ 191.5, 173.3, 142.6, 135.8, 128.6, 128.2, 127.8, 127.8, 77.3, 77.0, 76.7, 65.9, 46.1, 44.8, 39.5, 37.9, 35.7, 32.3, 32.1, 25.0; HRMS (EI) calc’d for [C_{14}H_{19}N_2O_4+H]^+ requires m/z 338.1625, found m/z 338.1614.

Ethyl 7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (13) (Figure 2): Prepared according to general procedure B using 99.6 mg (0.361 mmol), (2E,7E)-ethyl 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate, 6.7 mg (0.009 mmol) Ru(bpy)_2Cl_2·6H_2O, 16.8 mg (0.181 mmol) LiBF_4, 135 µL (0.733 mmol) i-Pr_2NEt, and 3.6 mL acetonitrile, and an irradiation time of 135 min. Purified by chromatography (2:1 hexanes:acetone) to afford 84 mg (0.493 mmol, 85% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 101.1 mg (0.366 mmol) bisenone, 6.6 mg (0.009 mmol) Ru(bpy)_2Cl_2·6H_2O, 16.7 mg (0.179 mmol) LiBF_4, 135 µL (0.733 mmol) i-Pr_2NEt, and 3.6 mL acetonitrile. Isolated 82 mg (0.476 mmol, 82% yield, >10:1 d.r.). IR (thin film) 2952, 2855, 1730, 1672, 1409 cm\(^{-1}\); ^1H NMR: (499.9 MHz, CDCl_3) δ 7.08 (d, J = 0.9 Hz, 1H), 6.99 (s, 1H), 4.00 (s, 3H), 3.97 (ddd, J = 10.2, 5.2, 1.0 Hz, 1H), 3.93 (dq, J = 7.3, 0.9 Hz, 2H), 3.23 (m, 1H), 3.11 (ddd, J = 10.5, 5.6, 0.9 Hz, 1H), 2.97 (m, 1H), 1.90 (m, 2H), 1.73 (m, 2H), 1.60 (m, 2H); HRMS (EI) calc’d for [C_{12}H_{18}N_2O_4+H]^+ requires m/z 276.1469, found m/z 276.1461.

1-7-(1-Methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptan-6-yl)ethanone (14) (Figure 2): Prepared according to general procedure B using 101.6 mg (0.413 mmol) (2E,7E)-1-(1-methyl-1H-imidazol-2-yl)dec-2,7-diene-1,9-dione, 17.5 mg (0.010 mmol) Ru(bpy)_2Cl_2·6H_2O, 19.2 mg (0.206 mmol) LiBF_4, 37 µL (0.201 mmol) i-Pr_2NEt, 4.0 mL acetonitrile, and an irradiation time of 16.5 h. Purified by chromatography (3:1 hexanes:acetone) to afford 66.7 mg (0.271 mmol, 66% yield, >10:1 d.r.) of the cycloadduct as a clear oil. Experiment 2: 100.5 mg (0.408 mmol) bisenone, 7.4 mg (0.010 mmol) Ru(bpy)_2Cl_2·6H_2O, 18.7 mg (0.201 mmol) LiBF_4, 37 µL (0.201 mmol) i-Pr_2NEt, and 4.0 mL acetonitrile. Isolated 64.5 mg (0.262 mmol, 65% yield, >10:1 d.r.). IR (thin film) 2949, 2862, 704, 1671, 1409 cm\(^{-1}\); ^1H NMR: (499.9 MHz, CDCl_3) δ 7.02 (d, J = 0.9 Hz, 1H), 6.97 (s, 1H), 4.02 (s, 3H), 3.84 (ddd, J = 10.2, 5.5, 1.0 Hz, 1H), 3.33 (dd, J = 10.5, 5.2 Hz, 1H), 3.22 (m, 1H), 2.84 (m, 1H), 1.96 (s, 3H), 1.93 (m, 2H), 1.73 (m, 2H), 1.60 (m, 2H); ^13C NMR: (125.7 MHz, CDCl_3) δ 207.9, 192.2, 143.2, 128.4, 126.2, 53.8, 46.3, 39.9, 36.6, 35.8, 32.8, 32.0, 26.3, 25.0; HRMS (EI) calc’d for [C_{14}H_{19}N_2O_2Na]^+ requires m/z 269.1261, found m/z 269.1266.

(1-Methyl-1H-imidazol-2-yl)-7-(morpholine-4-carbonyl)bicyclo[3.2.0]heptan-6-yl)methanone (15) (Figure 2): Prepared according to general procedure B using 98.5 mg (0.311 mmol), (2E,7E)-1-(1-methyl-1H-imidazol-2-yl)-9-morpholinonona-2,7-diene-1,9-dione, 5.8 mg (0.008 mmol) Ru(bpy)_2Cl_2·6H_2O, 14.7 mg (0.158 mmol) LiBF_4, 110 µL (0.597 mmol) i-Pr_2NEt, 3.1 mL acetonitrile, and an irradiation time of 3 h. Purified by chromatography (1:3 hexanes:acetone) to afford 70.0 mg (0.220 mmol, 70% yield, >10:1 d.r.) of the cycloadduct as a light yellow oil.
Experiment 2: 100.6 mg (0.317 mmol) bisenone, 6.1 mg (0.008 mmol) Ru(bpy)$_2$Cl$_2$6H$_2$O, 14.5 mg (0.156 mmol) LiBF$_4$, 110 µL (0.597 mmol) i-Pr$_2$NEt, and 3.1 mL acetonitrile. Isolated 68.4 mg (0.216 mmol, 68% yield, >10:1 d.r.). IR (thin film) 3055, 2987, 1677, 1636, 1422 cm$^{-1}$; $^1$H NMR: (499.9 MHz, CDCl$_3$) $\delta$ 7.02 (d, J = 0.9 Hz, 1H), 6.97 (s, 1H), 4.01 (s, 3H), 3.83 (ddd, J = 10.1, 5.9, 1.2 Hz, 1H), 3.53 (m, 2H), 3.25-3.47 (m, 8H), 2.91 (m, 1H), 1.92 (m, 2H), 1.53-1.76 (m, 4H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 191.4, 171.6, 143.2, 128.1, 126.0, 66.7, 66.3, 46.0, 45.8, 44.3, 41.9, 39.6, 37.1, 35.8, 32.3, 32.2, 25.2; HRMS (EI) calc’d for [C$_7$H$_{13}$N$_3$O$_3$+H]$^+$ requires m/z 318.1813, found m/z 318.1810.

**Ethyl 6-methyl-7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (16)** (Figure 2): Prepared according to general procedure B using 88.7 mg (0.305 mmol) (2E,7E)-ethyl 2-methyl-9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate, 6.0 mg (0.008 mmol) Ru(bpy)$_2$Cl$_2$6H$_2$O, 14.3 mg (0.154 mmol) LiBF$_4$, 115 µL (0.624 mmol) i-Pr$_2$NEt, 3.1 mL acetonitrile, and an irradiation time of 24 h. Purified by chromatography (5:1 hexanes:acetone) to afford 59.0 mg (0.203 mmol, 66% yield, >10:1 d.r.) of the cycloadduct as a light yellow oil. Experiment 2: 84.9 mg (0.294 mmol) bisenone, 5.7 mg (0.008 mmol) Ru(bpy)$_2$Cl$_2$6H$_2$O, 14.5 mg (0.156 mmol) LiBF$_4$, 115 µL (0.624 mmol) i-Pr$_2$NEt, and 3.1 mL acetonitrile. Isolated 56.7 mg (0.195 mmol, 66% yield, >10:1 d.r.). IR (thin film) 2956, 2254,1719, 1669, 1410 cm$^{-1}$; $^1$H NMR: (499.9 MHz, CDCl$_3$) $\delta$ 7.06 (s, 1H), 6.97 (s, 1H), 3.98 (s, 3H), 3.96 (m, 2H), 3.41 (m, 1H), 3.38 (m, 1H), 2.86 (dd, J = 7.7, 7.7 Hz, 1H), 1.89 (m, 2H), 1.79 (m, 1H), 1.64 (dd, J = 13.4, 6.7 Hz, 1H), 1.52 (m, 2H), 1.48 (s, 3H), 1.05 (t, J = 7.2 Hz, 3H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 191.8, 176.2, 143.4, 128.6, 126.1, 60.3, 54.2, 48.9, 42.2, 36.4, 35.7, 31.4, 27.0, 26.3, 18.7, 13.9; HRMS (EI) calc’d for [C$_{16}$H$_{23}$N$_3$O$_3$+Na]$^+$ requires m/z 313.1523, found m/z 313.1520.

**IV. Cleavage of the auxiliary group**

2-(7-((Benzyloxy)carbonyl)bicyclo[3.2.0]heptane-6-carbonyl)-1,3-dimethyl-1H-imidazol-3-ium triflate: In an oven-dried round-bottomed flask was placed a solution of cyclobutane 12 (405 mg, 1.20 mmol) in dry dichloromethane (12 mL, 0.1 M). Neat methyl trifluoromethanesulfonate (135 µL, 1.193 mmol) was added dropwise, and the solution was stirred for 16 h. Upon completion, the reaction was quenched with acetone and the volatiles were removed in vacuo. The triflate salt was recrystallized from acetone/diethyl ether to afford 282.5 mg (0.800 mmol, 67%) of a colorless solid (m.p.: 135–140 ºC). IR (thin film) 3629, 3093, 2262, 1634 cm$^{-1}$; $^1$H NMR: (500.2 MHz, CD$_2$CN) $\delta$ 7.30 (m, 5H), 7.19 (m, 2H), 5.00, 4.92 (ABq, 2H, $J_{AB}$ = 12 Hz), 3.87 (s, 6H), 3.54 (ddd, J = 10.0, 4.4, 0.9 Hz, 1H), 3.35 (ddd, J = 10.0, 5.6, 1.0 Hz, 1H), 3.13 (m, 1H), 3.05 (m, 1H), 1.88 (m, 2H), 1.71 (m, 2H), 1.59 (m, 2H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 191.4, 171.6, 143.2, 128.1, 126.0, 66.7, 66.3, 46.0, 45.8, 44.3, 41.9, 39.6, 37.1, 35.8, 32.3, 32.2, 25.2; HRMS (EI) calc’d for [C$_{16}$H$_{23}$N$_3$O$_3$+Na]$^+$ requires m/z 353.1860, found m/z 353.1851.

7-((Benzyloxy)carbonyl)bicyclo[3.2.0]heptane-6-carboxylic acid (Table 3, entry 1): In an oven-dried 1.5 dram vial was placed 49.6 mg (0.099 mmol) of the imidazolium triflate salt in 1.5 mL dry diethyl ether. The vial was sealed with a septum and flushed with a nitrogen atmosphere. 50 µL (0.33 mmol, 3.5 equiv) of DBU was added, and the reaction was stirred for several minutes before addition of 0.2 mL (11.1 mmol, 111 equiv) H$_2$O. After 2 h, the solution was acidified with 1 mL acetic acid, concentrated in vacuo and purified by chromatography on a silica column (3:l Hex:EtOAc + 1% AcOH) to afford 14 mg (0.051 mmol, 52% yield, >10:1 d.r.) of a clear oil. IR(thin film) 3629, 3093, 2262, 1634 cm$^{-1}$; $^1$H NMR: (499.9 MHz, CDCl$_3$) $\delta$ 7.33 (m, 5H), 5.08, 5.11 (ABq, 2H, $J_{AB}$ = 12.6 Hz), 3.07 (m, 2H), 2.90 (m, 2H), 1.89 (m, 1H), 1.52-1.79 (m, 5H); $^{13}$C NMR: (125.7 MHz, CDCl$_3$) $\delta$ 173.0, 135.8, 128.5, 128.3, 128.2, 66.6, 43.2, 39.5, 39.2, 32.1, 24.9; HRMS (EI) calc’d for [C$_{16}$H$_{20}$O$_4$+H]' requires m/z 273.1132, found m/z 273.1130.
6-Benzyl 7-methyl bicyclo[3.2.0]heptane-6,7-dicarboxylate (Table 3, entry 2): In an oven-dried 1.5 dram vial was placed 51.4 mg (0.102 mmol) of the imidazolium triflate salt in 1.5 mL dry ethyl ether. The vial was sealed with a septum and flushed with a nitrogen atmosphere. 50 µL (0.33 mmol, 3.5 equiv) of DBU were added, and the reaction was stirred for several minutes before addition of 0.5 mL (12.3 mmol, 111 equiv) methanol. After 2 h, the solution was concentrated in vacuo and purified by chromatography on a silica column (10:1 Hex:EtOAc) to afford 25.4 mg (0.088 mmol, 86% yield, >10:1 d.r.) of a clear oil. IR (thin film) 2953, 1731,1647, 1309 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.34 (m, 5H), 5.13 (s, 2H), 3.69 (s, 3H), 3.59 (dd, J = 10.4, 8.6 Hz, 1H), 3.09 (dd, J = 6.5, 0.8 Hz, 1H), 2.98 (m, 1H), 2.88 (m, 1H), 1.76 (m, 3H), 1.62-1.42 (m, 3H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 174.1, 172.4, 136.0, 128.5, 128.1, 128.0, 66.3, 51.5, 41.6, 40.8, 39.7, 38.2, 32.4, 28.5, 25.3; HRMS (EI) calc’d for [C₇H₂₅O₂Na⁺] requires m/z 311.1254, found m/z 311.1259.

6-Benzyl 7-iso-propyl bicyclo[3.2.0]heptane-6,7-dicarboxylate (Table 3, entry 3): In a 1.5 dram vial was placed 49.2 mg (0.098 mmol) of the imidazolium triflate salt in 1.5 mL dichloromethane. The vial was sealed with a septum and flushed with a nitrogen atmosphere. 50 µL (0.33 mmol, 3.5 equiv) of DBU were added, and the reaction was stirred for several minutes before addition of 0.2 mL (2.59 mmol, 26 equiv) isopropanol. After 2 h, the solution was concentrated in vacuo and purified by column chromatography (9:1 Hex:EtOAc) to afford 27.6 mg (0.087 mmol, 88% yield) of a clear oil. IR (thin film) 2957, 1725, 1263, 1194 cm⁻¹; ¹H NMR: (499.9 MHz, CDCl₃) δ 7.34 (m, 5H), 5.13 (s, 2H), 5.04 (sept, J = 6.3 Hz, 1H), 3.52 (dd, J = 8.8, 10.1 Hz, 1H), 3.09 (dd, J = 6.5, 8.7 Hz, 1H), 2.98 (m, 1H), 2.87 (m, 1H), 1.82-1.62 (m, 4H), 1.48 (m, 2H), 1.24 (t, J = 5.5 Hz, 6H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 174.2, 171.4, 136.1, 128.5, 128.1, 127.9, 77.3, 77.0, 76.7, 67.9, 66.2, 41.6, 40.7, 39.9, 38.3, 32.4, 28.2, 25.3, 22.0, 21.9; HRMS (EI) calc’d for [C₉HₓO₂Na⁺] requires m/z 339.1567, found m/z 339.1562.

Benzyl 7-(tert-butylthio)carbomoyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 5): In a 1.5 dram vial was placed 51.2 mg (0.1023 mmol) of the imidazolium triflate salt in 1.5 mL dichloromethane. The vial was sealed with a septum and flushed with a nitrogen atmosphere. 50 µL (0.33 mmol, 3.5 equiv) of DBU were added and let stir for several minutes before addition of 0.150 mL (1.33 mmol, 13 equiv) tert-butylthiol. After 3.5 h, the reaction was concentrated in vacuo and purified by column chromatography (10:1 Hex:EtOAc) to afford 35.1 mg (0.101 mmol, 88% yield, >10:1 d.r.) of a clear oil. IR (thin film) 3629, 3093, 2262, 1634 cm⁻¹; ¹H NMR: (500.2 MHz, CDCl₃) δ 7.33 (m, 5H), 5.12 (m, 2H), 3.66 (dd, J = 10.1, 8.7 Hz, 1H), 3.19 (dd, J = 8.7, 6.3 Hz, 1H), 2.99 (m, 1H), 2.86 (m, 1H), 1.78 (m, 4H), 1.47 (s, 9H), 1.44 (m, 2H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 198.1, 173.9, 136.1, 128.5, 128.1, 127.9, 66.2, 48.2, 47.6, 40.6, 40.1, 32.2, 30.0, 27.3, 25.3; HRMS (EI) calc’d for [C₂₁HₓNₓO₆⁺H⁺] requires m/z 353.1860, found m/z 353.1851.

Benzyl 7-(benzylicarbamoyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 6): In a 1.5 dram vial was placed 47.0 mg (0.099 mmol) of the imidazolium triflate salt in 1.5 mL dichloromethane. The vial was sealed with a septum and flushed with a nitrogen atmosphere. 200 µL (1.83 mmol, 20 equiv) benzylamine were added. After 2 h, the solution was concentrated in vacuo and purified by chromatography on a silica column (5:1 Hex:EtOAc) to afford 33.3 mg of a colorless oil (0.916 mmol, >10:1 d.r.). IR (thin film) 3305, 2954, 1729, 1649 cm⁻¹; ¹H NMR: (500.2 MHz, CDCl₃) δ 7.29 (m, 10H), 5.73 (t, J = 5.6 Hz, 1H), 5.11 (ABq, 2H), 4.43 (d, J = 5.6 Hz, 2H), 3.37 (t, J = 9.8 Hz, 1H), 3.17 (dd, J = 8.4, 5.6 Hz, 1H), 2.89 (m, 2H), 1.80 (m, 4H), 1.48 (m, 2H); ¹³C NMR: (125.7 MHz, CDCl₃) δ 174.3, 170.7, 138.3, 135.9, 128.7, 128.5, 128.2, 128.0, 127.8, 127.5, 66.4, 43.5, 41.7, 41.0, 40.5, 38.1, 32.3, 27.9, 25.7; HRMS (EI) calc’d for [C₂₃H₂₄N₂O₆H⁺] requires m/z 353.1860, found m/z 353.1851.
Benzyl 7-(pyrrolidine-1-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 7): In an oven-dried 1.5 dram vial was placed 50.1 mg (0.099 mmol) of the imidazolium triflate salt in 1.5 mL dichloromethane. 100 µL (1.20 mmol, 12.0 equiv) distilled pyrrolidine were added and the residue was dissolved in 1.5 mL dry dichloromethane (0.2 M) was stirred under N₂ before careful addition of freshly distilled MeOTf (40 µL, 0.341 mmol, 1.1 equiv). The flask was sealed, and the reaction was stirred at room temperature for 90 min. The volatiles were removed in vacuo, and the residue was dissolved in 1.5 mL dichloromethane. To this solution were added 100 µL DBU (0.669 mmol, 2.3 equiv) and 500 µL (12.5 mmol, 44 equiv) freshly distilled methanol. The vessel was sealed and the reaction was stirred for 90 min under N₂. The reaction was then concentrated and the crude residue loaded directly onto silica for purification by chromatography (4:1 Hex:EtOAc) to afford 49.5 mg of a colorless oil (0.1717 mmol, 58% yield).

One-pot methylation-esterification procedure: An oven-dried Schlenk flask containing 99.8 mg (0.295 mmol) cyclobutane 12 and 1.5 mL dry dichloromethane (0.2 M) was stirred under N₂ before careful addition of freshly distilled MeOTf (40 µL, 0.341 mmol, 1.1 equiv). The flask was sealed, and the reaction was stirred at room temperature for 90 min. The volatiles were removed in vacuo, and the residue was dissolved in 1.5 mL dichloromethane. To this solution were added 100 µL DBU (0.669 mmol, 2.3 equiv) and 500 µL (12.5 mmol, 44 equiv) freshly distilled methanol. The vessel was sealed and the reaction was stirred for 90 min under N₂. The reaction was then concentrated and the crude residue loaded directly onto silica for purification by chromatography (4:1 Hex:EtOAc) to afford 49.5 mg of a colorless oil (0.1717 mmol, 58% yield).

V. Stereochemical determinations by NOE
VI. References


- 2.39 V
  (-2.09 V vs. SCE)

- 1.32 V
  (-1.02 V vs. SCE)

- 1.27 V
  (-0.97 V vs. SCE)
(E)-4,4-Dimethyl-1-(1-methyl-1H-imidazol-2-yl)-pent-2-en-1-one

$^1$H NMR (500 MHz, CDCl$_3$)

(1H NMR (500 MHz, CDCl$_3$))

$^13$C NMR (125.7 MHz, CDCl$_3$)
**(E)-4-Benzylxy-1-(1-methyl-1H-imidazol-2-yl)-but-2-en-1-one**

**1H NMR (500 MHz, CDCl₃)**

![1H NMR spectrum](image1)

**(E)-4-Benzylxy-1-(1-methyl-1H-imidazol-2-yl)-but-2-en-1-one**

**13C NMR (125.7 MHz, CDCl₃)**

![13C NMR spectrum](image2)
(E)-1-((1-Methyl-1H-imidazol-2-yl)-6-triisopropylsilanyloxy-hex-2-en-1-one

$^1$H NMR (500 MHz, CDCl$_3$)

\[(E)-1-(1\text{-Methyl-1H-imidazol-2-yl})-6\text{-triisopropylsilanyloxy-hex-2-en-1-one}\]

$^{13}$C NMR (125.7 MHz, CDCl$_3$)
(E)-tert-butyl 4-(3-(1-methyl-1H-imidazol-2-yl)-3-oxoprop-1-en-1-yl)piperidine-1-carboxylate

$^1$H NMR (500 MHz, CDCl$_3$)

\[ \text{13C NMR (125.7 MHz, CDCl}_3\) } \]
(E)-7-(1-methyl-1H-imidazol-2-yl)-7-oxohept-5-enal

$^1$H NMR (500 MHz, CDCl$_3$)

\[
\begin{align*}
\text{NMe} & \quad \text{CH} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
7.46 & 7.44 & 7.43 & 7.18 & 7.08 & 7.06 \\
4.04 & 2.52 & 2.50 & 2.49 & 2.38 & 2.36 \\
1.89 & 1.88 & 1.87 & 1.78 & & \\
1.03 & 0.93 & 0.88 & & & \\
\end{align*}
\]

$^{13}$C NMR (125.7 MHz, CDCl$_3$)

\[
\begin{align*}
201.70 & 180.39 & 146.74 & 129.22 & 127.18 & 127.03 \\
43.03 & 42.72 & 36.22 & 31.67 & 20.46 & \\
\end{align*}
\]
(2E,7E)-Benzyl 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate
$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (125.7 MHz, CDCl$_3$)
(2E,7E)-Ethyl 9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate

$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (127.5 MHz, CDCl$_3$)
(2E,7E)-1-(1-Methyl-1H-imidazol-2-yl)deca-2,7-diene-1,9-dione

$^1$H NMR (500 MHz, CDCl$_3$)

(2E,7E)-1-(1-Methyl-1H-imidazol-2-yl)deca-2,7-diene-1,9-dione

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
$2E,7E$-1-(1-Methyl-1H-imidazol-2-yl)-9-morpholinonona-2,7-diene-1,9-dione

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
(2E,7E)-ethyl 2-methyl-9-(1-methyl-1H-imidazol-2-yl)-9-oxonona-2,7-dienoate

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
(3,4-dimethyloclobutane-1,2-diyl)bis((1-methyl-1H-imidazol-2-yl)methanone) (2)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125.7 MHz, CDCl$_3$)
methyl 3-methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutanecarboxylate (3)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125.7 MHz, CDCl$_3$)
S-ethyl 3-methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutane carbothioate (4)

$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125.7 MHz, CDCl$_3$)

S-ethyl 3-methyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutane carbothioate (4)

$^{13}C$ NMR (125.7 MHz, CDCl$_3$)
1-[3-Methyl-2-(1-methyl-1H-imidazole-2-carbonyl)-cyclobutyl]-ethanone (5)

$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (125.7 MHz, CDCl$_3$)
1-(3-ethyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (6)
$^1$H NMR (500 MHz, CDCl$_3$)
1-(3-Isopropyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (7)

$^1$H NMR (500 MHz, CDCl$_3$)

![NMR Spectrum](image1)

$^1$C NMR (125.7 MHz, CDCl$_3$)

![NMR Spectrum](image2)
1-(3-(tert-butyl)-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobuty1)ethanone (8)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125.7 MHz, CDCl$_3$)
1-(3-((benzlyoxy)methyl)-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)ethanone (9)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125.7 MHz, CDCl$_3$)
1-(2-(1-Methyl-1H-imidazole-2-carbonyl)-3-(3-triisopropylsilanyloxy-propyl)cyclobutyl)ethanone (10)

$^1$H NMR (500 MHz, CDCl$_3$)

13C NMR (125.7 MHz, CDCl$_3$)

S–33
tert-butyl 4-(3-acetyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)piperidine-1-carboxylate (11)

$^1$H NMR (500 MHz, CDCl$_3$)

![NMR spectrum of tert-butyl 4-(3-acetyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)piperidine-1-carboxylate (11)](image)

$^{13}$C NMR (125.7 MHz, CDCl$_3$)

![NMR spectrum of tert-butyl 4-(3-acetyl-2-(1-methyl-1H-imidazole-2-carbonyl)cyclobutyl)piperidine-1-carboxylate (11)](image)
benzyl 7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (12)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
ethyl 7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (13)

$^1$H NMR (500 MHz, CDCl₃)

![NMR spectrum](image)

ethyl 7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (13)

$^{13}$C NMR (127.5 MHz, CDCl₃)

![NMR spectrum](image)
1-7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptan-6-yl)ethanone (14)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
(1-methyl-1H-imidazol-2-yl)-7-(morpholine-4-carbonyl)bicyclo[3.2.0]heptan-6-yl) methanone (15)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
ethyl 6-methyl-7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (16)

$^1$H NMR (500 MHz, CDCl$_3$)

ethyl 6-methyl-7-(1-methyl-1H-imidazole-2-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (16)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
2-((7-((benzyloxy)carbonyl)bicyclo[3.2.0]heptane-6-carbonyl)-1,3-dimethyl-1H-imidazol-3-ium triflate

$^1$H NMR (500 MHz, CD$_3$CN)

$^{13}$C NMR (127.5 MHz, CD$_3$CN)
7-((benzyloxy)carbonyl)bicyclo[3.2.0]heptane-6-carboxylic acid (Table 3, entry 1)

$^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (127.5 MHz, CDCl$_3$)
6-benzyl 7-methyl bicyclo[3.2.0]heptane-6,7-dicarboxylate (Table 3, entry 2)

$^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (127.5 MHz, CDCl$_3$)
6-benzyl 7-isopropyl bicyclo[3.2.0]heptane-6,7-dicarboxylate (Table 3, entry 3)

$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (127.5 MHz, CDCl$_3$)
Benzyl 7-((tert-butylthio)carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 5)

$^1$H NMR (500 MHz, CDCl$_3$)

Benzyl 7-((tert-butylthio)carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 5)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
Benzyl 7-(benzylcarbamoyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 6)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)
benzyl 7-(pyrrolidine-1-carbonyl)bicyclo[3.2.0]heptane-6-carboxylate (Table 3, entry 7)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (127.5 MHz, CDCl$_3$)