Supporting information for:

# Efficient Visible Light Photocatalysis of [2+2] Enone Cycloadditions

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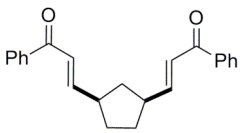
## I. General Information

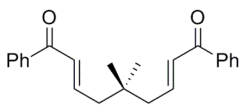
A 275 W GE Sunlamp was used for all photochemical reactions depicted in Table 1, and the solvents for these reactions were degassed with three freeze-pump-thaw cycles. Acetonitrile, $CH_2Cl_2$, and *i*-$Pr_2NEt$ were purified by distillation from $CaH_2$ immediately prior to use. $Ru(bipy)_2 \bullet 6H_2O$ was purchased from Strem and used without further purification. Chromatography was performed with Purasil 60Å silica gel (230–400 mesh) using the method of Still.[1] 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 $^{13}C$ 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 $CDCl_3$ (77 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl or ATR). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. 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.

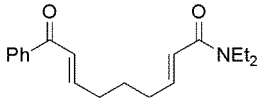
## II. Synthesis of cyclization substrates



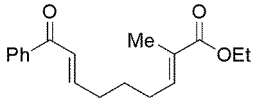
***cis*-1,3-Cyclopentane-(*E*,*E*)-diacrylophenone**:[2] Norbornene (368 mg, 3.9 mmol) was placed in a 50 mL 3-neck round-bottomed flask with 13 mL (0.3 M) $CH_2Cl_2$. The flask was cooled to –78 ºC, and ozone was passed through the reaction mixture until a blue coloration persisted, at which point oxygen was bubbled through the solution to remove excess dissolved ozone. The ozonide was quenched with 3 mL of dimethylsulfide, and the reaction was slowly warmed to room temperature. (Benzoylmethylene)triphenylphosphorane (3.41 g, 8.97 mmol) was added to the flask, and the reaction was stirred for 18 h. The solvent was removed by rotary evaporation, and the crude reaction mixture was purified by chromatography on a silica gel column (8:1 to 4:1 hexanes:EtOAc) to afford 408 mg (1.23 mmol, 31% yield) of the bisenone as a colorless oil. IR(neat) 2956, 1664, 1613, 1447, 1260; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 6.9 Hz, 4H, Ar**H**), 7.55 (t, J = 6.9 Hz, 2H, Ar**H**), 7.47 (t, J = 6.9 Hz, 4H, Ar**H**), 7.05 (dd, J = 14.7, 7.9 Hz, 2H,HC=C**H**), 6.88 (d, J = 14.7 Hz, 2H, HC=C**H**), 2.89 (m, 2H**, -**C$\mathbf{H_2}$), 2.18 (dt, J = 12.8, 6.9 Hz, 1H, C$\mathbf{H_2}$), 2.03 (m, 2H, C$\mathbf{H_2}$), 1.69 (m, 2H, C$\mathbf{H_2}$), 1.48 (q, J = 9.8 Hz, 1H, C**H**); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 190.9, 152.5, 137.9, 132.7, 128.5, 128.5, 124.7, 43.4, 39.4, 31.5. HRMS (EI) calc'd for $[C_{23}H_{22}O_2]^+$ requires *m/z* 330.1615, found *m/z* 330.1631.



**(*E*,*E*)-1,7-Dibenzoyl-4,4-dimethyl-1,6-heptadiene**: 3,3-Dimethylglutardialdehyde[3] was dissolved in 25 mL of dry $CH_2Cl_2$ and treated with 10 g (benzoylmethylene)triphenylphosphorane (26 mmol). The reaction was stirred at room temperature for 80 h. The solvent was then removed by rotary evaporation, and the residue was purified by chromatography on a silica gel column (6:1 to 4:1 hexanes:EtOAc) to afford 547 mg (1.65 mmol, 22% yield) of the bisenone as a colorless oil. IR(neat) 2958, 1669, 1618, 1448, 1282, 1221; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 4H, Ar**H**), 7.57 (t, J = 7.7 Hz, 2H, Ar**H**), 7.47 (t, J = 7.7 Hz, 4H, Ar**H**), 7.12 (dt, J = 15.5, 8.5 Hz, 2H,HC=C**H**), 6.93 (d, J = 15.5 Hz, 2H, HC=C**H**), 2.30 (d, J = 8.5 Hz, 4H**, -**C$\mathbf{H_2}$), 1.06 (s, 6H, C$\mathbf{H_3}$); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 190.3, 145.9, 137.8, 132.8, 128.6, 128.5, 128.4, 45.4, 35.1, 27.3. HRMS ($ESI^+$) calc'd for $[C_{23}H_{24}O_2+H]^+$ requires *m/z* 333.1850, found *m/z* 333.1834.



**(*E*,*E*)-1-Benzoyl-7-(diethylcarbamoyl)-1,6-heptadiene**: A dry 1.5 dram vial was charged with 6-benzoyl-5-hexenal[5] (245 mg, 1.2 mmol), [(diethylcarbamoyl)methyl]triphenylphosphonium chloride[4] (591 mg, 1.4 mmol), and 1.7 mL $CHCl_3$ 1.7 mL. Sodium hydroxide (1.0 M in water, 1.7 mL, 1.7 mmol) was added dropwise to the stirring solution. After 20 min, the organic layer was separated, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by chromatography (2:1 EtOAc:hexanes eluent) to afford 238 mg (0.79 mmol, 66% yield) of the diene as a clear, colorless liquid. IR (thin film) 1727, 1676; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H, Ar**H**), 7.58-7.54 (m, 1H, Ar**H**), 7.47 (t, J = 7.6 Hz, 2H, Ar**H**), 7.05 (dt, J = 15.5, 6.9 Hz, 1H, HC=C**H**), 6.94–6.88 (m, 2H, HC=C**H**), 6.23 (dt, J = 15.2, 1.4 Hz, 1H, HC=C**H**), 3.43 (q, J = 7.1 Hz, 2H, N-C$\mathbf{H}_2$CH$_3$), 3.37 (q, J = 7.0 Hz, 2H, -NC$\mathbf{H}_2$CH$_3$), 2.37 (q, J = 7.2 Hz, 2H, =CHC$\mathbf{H}_2$), 2.29 (q, J = 7.3 Hz, 2H, =CHC$\mathbf{H}_2$), 1.72 (quintet, J = 7.5 Hz, 2H, -CH$_2$C$\mathbf{H}_2$CH$_2$-), 1.19 (t, J = 7.0 Hz, 3H, -NCH$_2$C$\mathbf{H}_3$), 1.14 (t, J = 284.1 Hz, 3H, -NCH$_2$C$\mathbf{H}_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.9, 165.8, 149.1, 145.0, 138.1, 132.9, 128.7, 128.7, 126.5, 121.4, 42.3, 41.0, 32.3, 32.0, 27.2, 15.1, 13.4. HRMS (EI) calc'd for $[C_{19}H_{25}NO_2]^+$ requires *m/z* 299.1880, found *m/z* 299.1882.

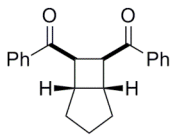


**(*E*,*E*)-1-Benzoyl-7-(ethoxycarbonyl)-7-methyl-1,6-heptadiene**: Ethyl 2-(triphenylphosphoranylidene)propanoate (773 mg, 2.1 mmol) was dissolved in 6 mL $CH_2Cl_2$ in a dry 50 mL round bottom flask. To the stirring solution was added 6-benzoyl-5-hexenal (431 mg, 2.1 mmol) in 7 mL $CH_2Cl_2$. After 1.5 h, the solution was concentrated by rotary evaporation, and the residue was purified by chromatography (3:1 hexanes:EtOAc eluent) to afford 349 mg (1.2 mmol, 57% yield) of the diene as a clear, colorless liquid. IR (thin film) 1707, 1670, 1649; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2 H), 7.55 (tt, J = 7.4, 1.4 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.05 (dt, J = 15.2, 6.8 Hz, 1 H), 6.91 (dt, J = 15.3, 1.5 Hz, 1 H), 6.76 (td, J = 5.5, 3.1 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 2.36 (q, J = 7.3 Hz, 2 H), 2.25 (q, J = 7.4 Hz, 2 H), 1.84 (d, J = 1.3 Hz, 3 H), 1.70 (quintet, J = 7.4 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.7, 168.2, 148.9, 141.1, 138.0, 132.8, 128.6, 128.6, 126.4, 60.6, 32.4, 28.2, 27.2, 14.4, 12.6. HRMS (EI) calculated for $[C_{18}H_{22}O_3]^+$ requires *m/z* 286.1564, found *m/z* 286.1575.

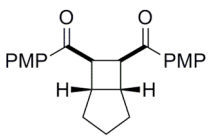
## III. Photocycloadditions

**General procedure A for cyclization of bisenone substrates** (Table 1, entries 1–13): A dry 25 mL Schlenk tube was charged with a solution of the enone (1 equiv), $Ru(bipy)_3Cl_2$•$6H_2O$ (0.05 equiv), $LiBF_4$ (2 equiv), and *i*-$Pr_2NEt$ (2 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 placed in a water bath and irradiated using a floodlight placed at a distance of 20 cm. Upon completion of the reaction, the solvent was removed by rotary evaporation, and the residue was purified by chromatography on a silica gel column.

**General procedure B for intermolecular [2+2] cycloadditions** (Table 1, entries 14 and 15): These experiments were run as above, except with the following molar ratios: 2 equiv enone, 0.05 equiv $Ru(bipy)_3Cl_2$, 2 equiv $LiBF_4$, and 2 equiv *i*-$Pr_2NEt$ in acetonitrile (0.2 M with respect to enone).

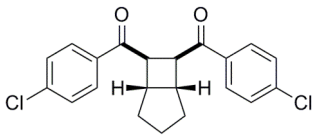


**(1*R*,5*S*,6*R*,7*S*)-6,7-Dibenzoylbicyclo[3.2.0]heptane** (Table 1, entry 1). Experiment 1: Prepared according to general procedure **A** using 104.8 mg (0.34 mmol) (*E*,*E*)-1,7-dibenzoyl-1,6-heptadiene,[5] 14.4 mg (0.019 mmol) $Ru(bpy)_3Cl_2$·$6H_2O$, 72 mg (0.77 mmol) $LiBF_4$, 134 μL (0.77 mmol) *i*-$Pr_2NEt$, 3.8 mL acetonitrile, and an irradiation time of 50 min. Purified by chromatography using a solvent gradient (5:1–2:1 hexanes:EtOAc) to afford 98 mg (0.35 mmol, 90% yield, dr = >10:1) of the cycloadduct. Experiment 2: 55 mg (0.19 mmol) bisenone, 7.1 mg (0.0095 mmol) $Ru(bpy)_3Cl_2$·$6H_2O$, 36 mg (0.38 mmol) $LiBF_4$, 66 μL (0.38 mmol) *i*-$Pr_2NEt$, and 1.9 mL acetonitrile. Isolated 48 mg (0.17 mmol, 87% yield, dr: >10:1). All spectral data were in complete agreement with previously reported values.[6]

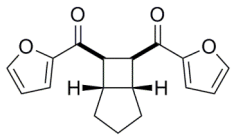


**(1*R*,5*S*,6*R*,7*S*)-6,7-Di(4-methoxybenzoyl)bicyclo[3.2.0]heptane** (Table 1, entry 2). Experiment 1: Prepared according to general procedure **A** using 113 mg (0.31 mmol) (*E*,*E*)-1,7-(4-methoxybenzoyl)-1,6-heptadiene,[7] 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2$·$6H_2O$, 58 mg (0.62 mmol) $LiBF_4$, 108 μL (0.62 mmol) *i*-$Pr_2NEt$, 3.1 mL acetonitrile, and an irradiation time of 20 min. Purified by chromatography using a solvent gradent (4:1 to 2:1 hexanes:EtOAc) to afford

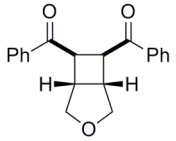
111 mg (0.304 mmol, 98% yield, dr = 10:1) of the cycloadduct as a white solid (mp = 145–147 °C). Experiment 2: 107.3 mg (0.29 mmol) of bisenone, 11 mg (0.015 mmol) of $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 54 mg (0.58 mmol) of $LiBF_4$, 101 μL (0.58 mmol) of *i*-$Pr_2NEt$, and 1.9 mL of acetonitrile. Isolated 104 mg (0.285 mmol, 97% yield, dr = 10:1). IR(neat) 2972, 1740, 1672, 1602, 1358, 1239; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 9.0 Hz, 4H, Ar**H**), 6.83 (d, J = 9.0 Hz, 4H, Ar**H**), 3.81 (s, 8H, -O**Me, -CH**COAr(cyclobutane)), 3.20 (m, 2H, C**H** (cyclobutane)), 2.02 (m, 2H, C**H** (cyclopentane)), 1.83 (ddd, J = 13.5, 5.3, 1.9 Hz, 2H, C**H** (cyclopentane)), 1.69 (m, 2H, C**H** (cyclopentane)); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 197.3, 162.9, 129.9, 129.6, 113.6, 55.3, 48.1, 39.1, 32.5, 25.3. HRMS (ESI$^+$) calculated for $[C_{23}H_{24}O_4H]^+$ requires *m/z* 365.1748, found *m/z* 365.1759.



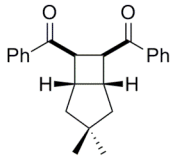
**(1*R*,5*S*,6*R*,7*S*)-6,7-Di(4-chlorobenzoyl)bicyclo[3.2.0]heptane** (Table 1, entry 3). Experiment 1: Prepared according to general procedure **A** using 113 mg (0.30 mmol) of (*E*,*E*)-1,7-(4-chlorobenzoyl)-1,6-heptadiene,[8] 11 mg (0.015 mmol) of $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 57 mg (0.61 mmol) of $LiBF_4$, 106 μL (0.61 mmol) of *i*-$Pr_2NEt$, 3.0 mL acetonitrile, and an irradiation time of 10 min. Purified by chromatography using a solvent gradient (10:1 to 7:1 hexanes:EtOAc) to afford 111 mg (0.30 mmol, 98% yield, dr >10:1) of the cycloadduct. Experiment 2: 111 mg (0.30 mmol, 98% yield, dr >10:1). Experiment 2: 63.9 mg (0.17 mmol) of bisenone, 6.4 mg (0.009 mmol) of $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 32 mg (0.34 mmol) of $LiBF_4$, 59 μL (0.34 mmol) of DIEA, and 1.7 mL of MeCN. Isolated 60 mg (0.16 mmol, 94% yield, dr >10:1). All spectral data were in complete agreement with previously reported values.[8]



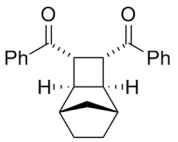
**(1*R*,5*S*,6*R*,7*S*)-6,7-Di(2-furoyl)bicyclo[3.2.0]heptane** (Table 1, entry 4). Experiment 1: Prepared according to general procedure **A** using 109 mg (0.38 mmol) (*E*,*E*)-1,7-(2-furoyl)-1,6-heptadiene,[7] 14.4 mg (0.019 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 72 mg (0.77 mmol) $LiBF_4$, 134 μL (0.77 mmol) *i*-$Pr_2NEt$, 3.8 mL acetonitrile, and an irradiation time of 30 min. Purified by chromatography using a solvent gradient (5:1 to 2:1 hexanes:EtOAc) to afford 98 mg (0.35 mmol, 90% yield, dr = >10:1) of the cycloadduct. Experiment 2: 55 mg (0.19 mmol) bisenone, 7.1 mg (0.0095 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 36 mg (0.38 mmol) $LiBF_4$, 66 μL (0.38 mmol) *i*-$Pr_2NEt$, and 1.9 mL acetonitrile. Isolated 48 mg (0.17 mmol, 87% yield, dr: >10:1). All spectral data were in complete agreement with previously reported values.[6]



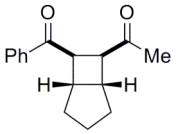
**(1*R*,5*S*,6*R*,7*S*)-6,7-Dibenzoyl-3-oxabicyclo[3.2.0]heptane** (Table 1, entry 7). Experiment 1: Prepared according to general procedure **A** using 115 mg (0.38 mmol) (*E*,*E*)-1,7-dibenzoyl-4-oxa-1,6-heptadiene,[6] 14 mg (0.019 mmol) $Ru(bpy)_3Cl_26H_2O$. 71.3 mg (0.76 mmol) $LiBF_4$, 132 μL (0.76 mmol) *i*-$Pr_2NEt$, 3.8 mL acetonitrile, and an irradiation time of 10 min. Purified by chromatography using a solvent gradient (5:1 to 2:1 hexanes:EtOAc) to afford 106 mg (0.346 mmol, 92% yield, dr = 5:1) of the cycloadduct. Experiment 2: 100 mg (0.33 mmol) bisenone, 13 mg (0.017 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 56 mg (0.66 mmol) $LiBF_4$, 115 μL *i*-$Pr_2NEt$, and 3.3 mL acetonitrile. Isolated 88 mg (0.29 mmol, 88% yield, dr = 5:1). All spectral data were in complete agreement with previously reported values.[6]



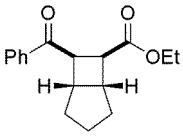
**(1*R*,5*S*,6*R*,7*S*)-6,7-Dibenzoyl-3,3-dimethylbicyclo[3.2.0]heptane** (Table 1, entry 8). Experiment 1: Prepared according to general procedure **A** using 76 mg (0.23 mmol) (*E*,*E*)-1,7-(benzoyl)-3,3-dimethyl-1,6-heptadiene, 9 mg (0.012 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 43 mg (0.46 mmol) $LiBF_4$, 80 μL (0.46 mmol) *i*-$Pr_2NEt$, 2.3 mL acetonitrile, and an irradiation time of 10 min. Purified by chromatography using a solvent gradient (10:1 to 8:1 hexanes:EtOAc) to afford 51 mg (0.153 mmol, 67% yield, dr = 5:1) of the cycloadduct as a white solid (mp = 172–175ºC). Experiment 2: 71.8 mg (0.22 mmol) bisenone, 8.2 mg (0.011 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 41 mg (0.44 mmol) $LiBF_4$, 77 μL (0.44 mmol) *i*-$Pr_2NEt$, and 2.2 mL acetonitrile. Isolated 49 mg (0.147 mmol, 68% yield, dr = 3:1). IR(neat) 2946, 1680, 1220, 1019; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 6.9 Hz, 3H, Ar**H**), 7.48 (t, J = 6.9 Hz, 2H, Ar**H**), 7.38 (t, J = 6.9 Hz, 3H, Ar**H**), 4.11 (m, 2H**, -CH**COAr (cyclobutane)), 3.21 (m, 2H, C**H** (cyclobutane)), 2.01 (m, 2H, C**H** (cyclopentane)), 1.70 (dd, J = 12.7, 5.1 Hz, 2H, C**H** (cyclopentane)), 1.60 (s, 3H, C**H$_3$**), 1.27 (s, 3H, C**H$_3$**); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 199.3, 136.6, 132.8, 128.7, 128.1, 51.5, 48.7, 44.9, 40.0, 29.0, 28.2. HRMS (ESI$^+$) calculated for $[C_{23}H_{24}O_4H]^+$ requires *m/z* 333.2850, found *m/z* 333.1853.



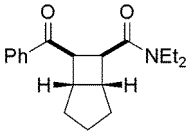
**(1*R*,2*S*,3*S*,4*R*,5*R*,6*S*)-3,4-Dibenzoyltricyclo[4.2.1.0$^{2,5}$]nonane** (Table 1, entry 9). Experiment 1: Prepared according to general procedure **A** using 61 mg (0.18 mmol) *cis*-1,3-cyclopentane-(*E*,*E*)-diacrylophenone, 6.7 mg (0.012 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 34 mg (0.36 mmol) $LiBF_4$, 63 μL (0.36 mmol) *i*-$Pr_2NEt$, 1.8 mL acetonitrile, and an irradiation time of 2 h. Purified by chromatography using 7:1 hexanes:EtOAc as eluent to afford 32 mg (0.097 mmol, 52% yield, dr = 5:1) of the cycloadduct as a white solid (mp = 163–166ºC). Experiment 2: 73.5 mg (0.22 mmol) bisenone, 8.23 mg (0.011 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 41 mg (0.44 mmol) $LiBF_4$, 77 μL (0.44 mmol) *i*-$Pr_2NEt$, and 2.2 mL acetonitrile. Isolated 41 mg (0.12 mmol, 56% yield, dr = 7:1). IR(neat) 2959, 1678, 1596, 1448. 1348, 1222; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 4H, Ar**H**), 7.45 (t, J = 7.4 Hz, 2H, Ar**H**), 7.36 (t, J = 6.9 Hz, 4H, Ar**H**), 3.91 (s, 2H, **-CH**COAr(cyclobutane)), 2.73 (s, 2H, C**H** (cyclobutane)), 2.09 (d, J=10.9 Hz, 1H, C**H** (cyclopentane)), 1.55 (m, 2H, C**H** (cyclopentane)), 1.51 (d, J=11.0 Hz, 1H, C**H** (cyclopentane)), 1.14 (dd, J=7.7, 2.0 Hz, 2H, C**H** (cyclopentane)); $^{13}$C NMR (125 MHz, $CDCl_3$) δ198.1, 136.4, 132.5, 128.5, 127.8, 47.2, 42.4, 38.6, 33.2, 27.3, 0.0. HRMS (EI) calculated for $[C_{23}H_{22}O_2]^+$ requires *m/z* 330.1615, found *m/z* 330.1620.



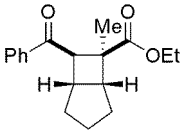
**(1S$^*$,5R$^*$,6S$^*$,7R$^*$)-6-Acyl-7-benzoylbicyclo[3.2.0]heptane** (Table 1, entry 10). Experiment 1: Prepared according to general procedure **A** using 107 mg (0.44 mmol) (*E*,*E*)-7-acetyl-1-benzoyl-1,6-heptadiene,[7] 16 mg (0.022 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 83 mg (0.88 mmol) $LiBF_4$, 153 μL (0.88 mmol) *i*-$Pr_2NEt$, 4.4 mL acetonitrile, and an irradiation time of 75 min. Purified by chromatography using a solvent gradient (4:1 to 3:1 hexanes:EtOAc) to afford 88 mg (0.36 mmol, 82.5% yield, dr >10:1) of the cycloadduct. Experiment 2: 78.3 mg (0.32 mmol) bisenone, 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 60 mg (0.64 mmol) $LiBF_4$, 112 μL *i*-$Pr_2NEt$, and 3.2 mL acetonitrile. Isolated 68 mg (0.28 mmol, 86.8% yield, dr >10:1). All spectral data were in complete agreement with previously reported values.[7]



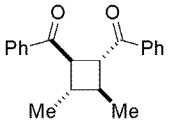
**(1S$^*$,5R$^*$,6S$^*$,7R$^*$)-6-Benzoyl-7-(ethoxycarbonyl)bicyclo[3.2.0]heptane** (Table 1, entry 11). Experiment 1: Prepared according to general procedure **A** using 108 mg (0.40 mmol) (*E*,*E*)-1-benzoyl-7-(ethoxycarbonyl)-1,6-heptadiene,[9] 15 mg (0.020 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 74 mg (0.79 mmol) $LiBF_4$, 141 μL (0.81 mmol) *i*-$Pr_2NEt$, 4.0 mL acetonitrile, and an irradiation time of 45 min. Purified by chromatography using 3:1 hexanes:EtOAc to afford 97 mg (0.36 mmol, 90% yield, dr >10:1) of the cycloadduct as a white solid (m.p. 45–46 °C). Experiment 2: 102 mg (0.37 mmol) diene, 14 mg (0.019 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 70 mg (0.75 mmol) $LiBF_4$, 133 μL (0.75 mmol) *i*-$Pr_2NEt$, and 3.7 mL acetonitrile. Isolated 87 mg (0.32 mmol, 85% yield, dr >10:1) of the cycloadduct. IR (neat) 1722, 1671; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.52 (tt, J = 7.3, 1.4 Hz, 1H, Ar**H**), 7.43 (t, J = 7.8 Hz, 2H, Ar**H**), 3.87 (qd, J = 7.2, 1.8 Hz, 2H, Ar**H**), 3.69 (dd, J = 10.1, 5.2 Hz, 1H, ArCOC**H**), 3.22 (ddd, J = 6.7, 6.7, 6.7 Hz, 1H, C**H** (cyclobutane)), 3.07 (ddd, J = 6.7, 6.7, 6.7 Hz, 1H, C**H** (cyclobutane)), 3.01 (dd, J = 10.1, 5.2 Hz, 1H, -C**H**$CO_2$Et), 1.98–1.86 (m, 2H, **CH** (cyclopentane)), 1.75–1.71 (m, 2H), 1.68–1.57 (m, 2H, -C**H** (cyclopentane)), 0.97 (t, J = 7.2 Hz, 3H, -$CH_2CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.3, 136.4, 133.0, 128.7, 128.3, 60.6, 46.7, 44.6, 39.1, 38.8, 32.5, 32.5, 25.4, 14.0. HRMS (EI) calc'd for $[C_{17}H_{20}O_3+H]^+$ requires *m/z* 273.2486, found *m/z* 273.1475.



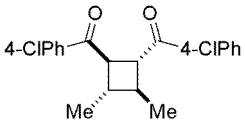
**(1S$^*$,5R$^*$,6S$^*$,7R$^*$)-6-Benzoyl-7-(diethylcarbamoyl)bicyclo[3.2.0]heptane** (Table 1, entry 12). Experiment 1: Prepared according to general procedure **A** using 102 mg (0.34 mmol) (*E*,*E*)-1-benzoyl-7-(diethylcarbamoyl)-1,6-heptadiene, 13 mg (0.017 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 64 mg (0.68 mmol) $LiBF_4$, 118 μL (0.68 mmol) *i*-$Pr_2NEt$, 4.5 mL acetonitrile, and an irradiation time of 30 min. Purified by chromatography using 3:1 hexanes:EtOAc to afford 74 mg (0.25 mmol, 73% yield, dr >10:1) of the cycloadduct as a white solid (m.p. 88–89 °C). Experiment 2: same quantities; isolated 76 mg (0.25 mmol, 75% yield, dr >10:1). IR (neat) 1677, 1614; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H, Ar**H**), 7.12–7.05 (m, 3H, Ar**H**), 3.77 (ddd, J = 6.8, 6.8, 6.8 Hz, 1H, C**H**, cyclobutane), 3.21 (dq, J = 13.8, 6.8 Hz, 1H, -NC**H**$_2$CH$_3$), 3.09–3.05 (m, 1H, -C**H**COAr (cyclobutane)), 2.97–2.93 (m, 1H-C**H**CONEt$_2$ (cyclobutane)), 2.88–2.84 (m, 1H, -C**H** (cyclobutane)), 2.71–2.60 (m, 2H, -NC**H**$_2$CH$_3$), 2.53–2.45 (m, 1H, -NC**H**$_2$CH$_3$), 1.70–1.63 (m, 2H, -C**H** (cyclopentane)), 1.54–1.50 (m, 1H, -C**H** (cyclopentane)), 1.48–1.31 (m, 3H, -C**H** (cyclopentane)), 0.67 (td, J = 7.1, 2.8 Hz, 3H, -$CH_2$C**H**$_3$), 0.60 (t, J = 7.0 Hz, 3H, -$CH_2$C**H**$_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 198.8, 171.6, 137.3, 132.2, 128.5, 127.8, 46.4, 44.8, 42.0, 40.3, 40.0, 38.5, 32.7, 32.7, 25.6, 14.9, 12.7. HRMS (EI) calc'd for $[C_{19}H_{25}NO_2]^+$ requires *m/z* 299.1880, found *m/z* 299.1877.



**(1S*,5R*,6S*,7R*)-6-Benzoyl-7-(ethoxycarbonyl)-7-methylbicyclo[3.2.0]heptane** (Table 1, entry 13). Experiment 1: Prepared according to general procedure **A** using 101 mg (0.35 mmol) (*E*,*E*)-1-benzoyl-7-(ethoxycarbonyl)-7-methyl-1,6-heptadiene, 13 mg (0.017 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 66 mg (0.70 mmol) $LiBF_4$, 123 μL (0.70 mmol) *i*-$Pr_2NEt$, 3.5 mL acetonitrile, and an irradiation time of 60 min. Purified by chromatography using 3:1 hexanes:EtOAc to afford 85 mg (0.30 mmol, 84% yield, dr = 10:1) of the cycloadduct as a clear, colorless liquid. Experiment 2: 100 mg (0.35 mmol) (*E*,*E*)-1-benzoyl-7-ethoxycarbonyl-7-methyl-1,6-heptadiene, 13 mg (0.017 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 65 mg (0.69 mmol) $LiBF_4$, 121 μL (0.69 mmol) *i*-$Pr_2NEt$, and 3.5 mL acetonitrile. Isolated 83 mg (0.29 mmol, 83% yield, dr = 10:1). IR (thin film) 1707, 1670, 1649; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81–7.80 (m, 2H, Ar**H**), 7.53 (tt, J = 7.3, 1.4 Hz, 1H, Ar**H**), 7.45 (t, J = 7.6 Hz, 2H, Ar**H**), 3.95–3.89 (m, 2H, -OC**H**$_2$CH$_3$), 3.45 (ddd, J = 7.2, 7.2, 7.2 Hz, 1H, C**H** (cyclobutane)), 3.19 (dd, J = 7.0, 0.9 Hz, 1H, ArCOC**H**-), 2.94 (dd, J = 8.4, 8.4 Hz, 1H, C**H** (cyclobutane)), 1.98–176 (m, 3H, C**H** (cyclopentane)), 1.67 (dd, J = 12.9, 6.1 Hz, 1H, C**H** (cyclopentane)), 1.63–1.54 (m, 3H, C**H** (cyclopentane)), 1.42 (s, 3H, EtOC(O)CC**H**$_3$), 1.02 (t, J = 7.1 Hz, 3H, -CH$_2$C**H**$_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 200.1, 175.8, 137.7, 132.7, 128.6, 128.2, 60.8, 54.6, 47.7, 42.0, 37.9, 31.9, 27.2, 26.6, 19.1, 13.9. HRMS (EI) calc'd for $[C_{18}H_{22}O_3]^+$ requires *m/z* 286.1564, found *m/z* 286.1554.



**1,2-Dibenzoyl-3,4-dimethylcyclobutane** (Table 1, entry 14). Experiment 1: Prepared according to general procedure **B** using 102 mg (0.70 mmol) (*E*)-1-phenyl-2-buten-1-one, 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 66 mg (0.70 mmol) $LiBF_4$, 122 μL (0.69 mmol) *i*-$Pr_2NEt$, and 3.3 mL acetonitrile, and an irradiation time of 2 h. Purified by chromatography using 9:1 hexanes:EtOAc to afford 81 mg (0.28 mmol, 80% yield) of the cycloadduct as a clear, colorless liquid. Experiment 2: 103 mg (0.70 mmol) enone, 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 66 mg (0.70 mmol) $LiBF_4$, 122 μL (0.69 mmol) *i*-$Pr_2NEt$, and 3.3 mL acetonitrile. Isolated 86 mg (0.29 mmol, 84% yield). IR (thin film) 1669, 1625; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (dt, J = 6.1, 1.8 Hz, 4H, Ar**H**), 7.54 (tt, J = 6.7, 1.2 Hz, 2H, Ar**H**), 7.44 (tt, J = 7.9 Hz, 4H, Ar**H**), 4.04—4.03 (m, 2H, C**H**), 2.18—2.13 (m, J = Hz, 2H, C**H**), 1.21 (dt, J = 4.6, 2.1 Hz, 6H, C**H**$_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 199.7, 136.3, 133.2, 128.6, 128.6, 77.3, 77.0, 76.8, 47.4, 39.4, 19.2. HRMS (EI) calculated for $[C_{20}H_{20}O_2]^+$ requires *m/z* 292.1458, found *m/z* 292.1471.



**1,2-Di(4-chlorobenzoyl)-3,4-dimethylcyclobutane** (Table 1, entry 15). Experiment 1: Prepared according to general procedure **B** using 127 mg (0.71 mmol) (*E*)-1-(4-chlorophenyl)-2-buten-1-one, 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 66 mg (0.70 mmol) $LiBF_4$, 122 μL (0.69 mmol) *i*-$Pr_2NEt$, and 3.3 mL acetonitrile, and an irradiation time of 1 h. Purified by chromatography using 8:1 hexanes:EtOAc to afford 119 mg (0.33 mmol, 93% yield) of the cycloadduct as a white solid (mp = 124–129 °C).. Experiment 2: 125 mg (0.69 mmol) enone, 12 mg (0.016 mmol) $Ru(bpy)_3Cl_2{\cdot}6H_2O$, 66 mg (0.70 mmol) $LiBF_4$, 122 μL (0.69 mmol) *i*-$Pr_2NEt$, and 3.3 mL acetonitrile. Isolated 116 mg (0.32 mmol, 93% yield). IR (neat) 1695, 1645; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (dt, J = 9.2, 2.4 Hz, 4H, Ar**H**), 7.42 (dt, J = 9.2, 2.4 Hz, 4H, Ar**H**), 3.97—3.95 (m, 2H, C**H**), 2.15—2.11 (m, 2H C**H**), 1.20 (dt, J = 6.4 Hz, 6H, C**H**$_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 198.5, 140.0, 134.7, 130.2, 129.1, 77.6, 77.2, 76.8, 47.5, 39.6, 19.4.. HRMS (EI) calculated for $[C_{20}H_{18}Cl_2O_2]^+$ requires *m/z* 360.0679, found *m/z* 360.0689.

**Large-scale photocycloaddition** (eq 1). A dry 50 mL Schlenk flask was charged with a solution of (*E*,*E*)-1,7-(4-methoxybenzoyl)-1,6-heptadiene (1.06 g 2.9 mmol, 1 equiv), $Ru(bipy)_3Cl_2{\bullet}6H_2O$ (109 mg, 0.145 mmol, 0.05 equiv), $LiBF_4$ (543 mg, 5.8 mmol, 2 equiv), and *i*-$Pr_2NEt$ (101 mL, 5.8 mmol 2 equiv) in acetonitrile (29 mL, 0.1 M). The solution was then degassed using three freeze-pump-thaw cycles under nitrogen in the dark. The Schlenk flask was then placed in put into a window ledge with direct sunlight and stirred for 1 h. The solar intensity at the time of this experiment (9:00 am, July 8, 2008)[10] was measured to be 3.9 watts/cm$^2$ using a Scientech Astral Calorimeter (model AC2500). Upon completion of the reaction, the solvent was removed by rotary evaporation, and the residue was purified by chromatography on a silica gel column (4:1 to 2:1 hexanes:EtOAc eluent) to afford 992 mg (2.72 mmol, 94% yield, dr = 10:1) of the cycloadduct.

## IV. NOE assignments for new compounds

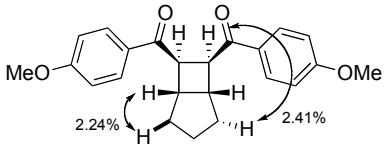



Table 1, Entry 2

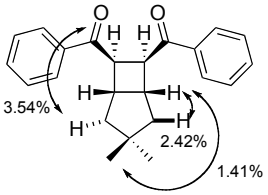



Table 1, Entry 8

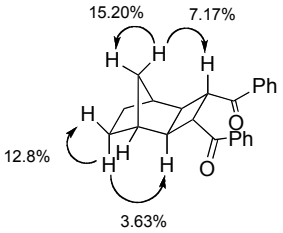



Table 1, Entry 9

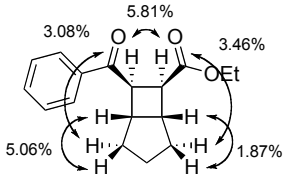



Table 1, Entry 11

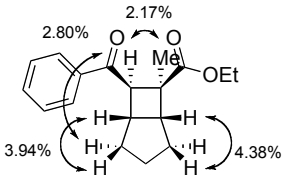



Table 1, Entry 13

Table 1, entries 1, 3, 4, 7, and 10, are known compounds and have been previously characterized. Entry 15 was determined by X-ray crystallographic analysis (vide infra). NOEs for entries 12 and 14 were inconclusive; stereochemistry assigned by analogy.

## V. References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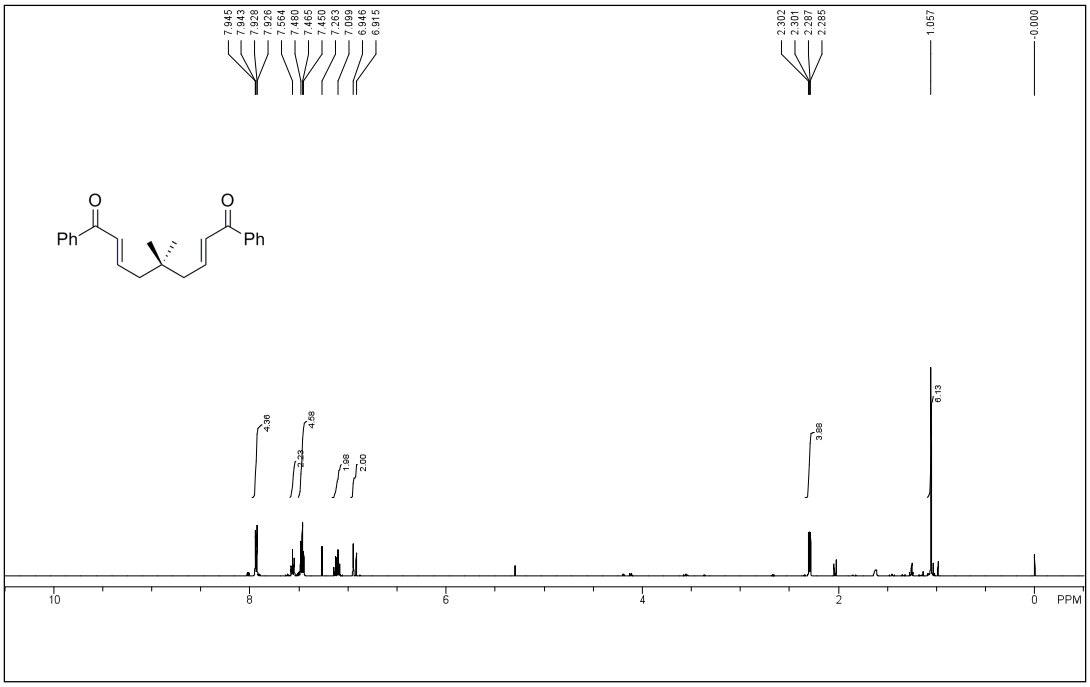
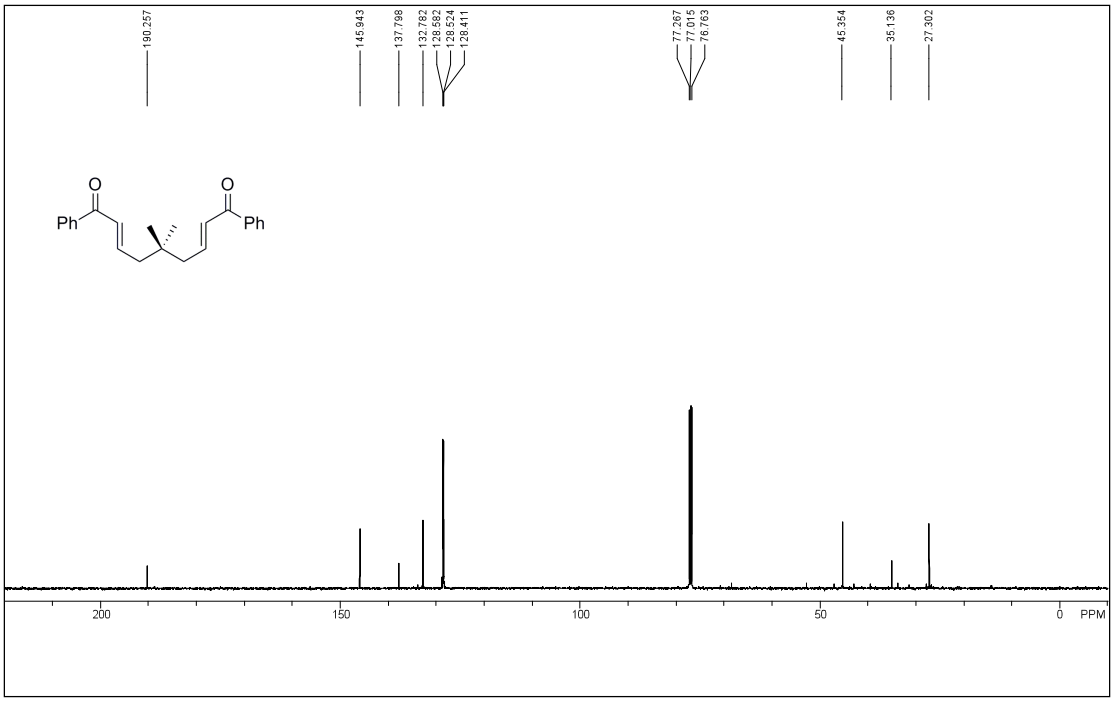
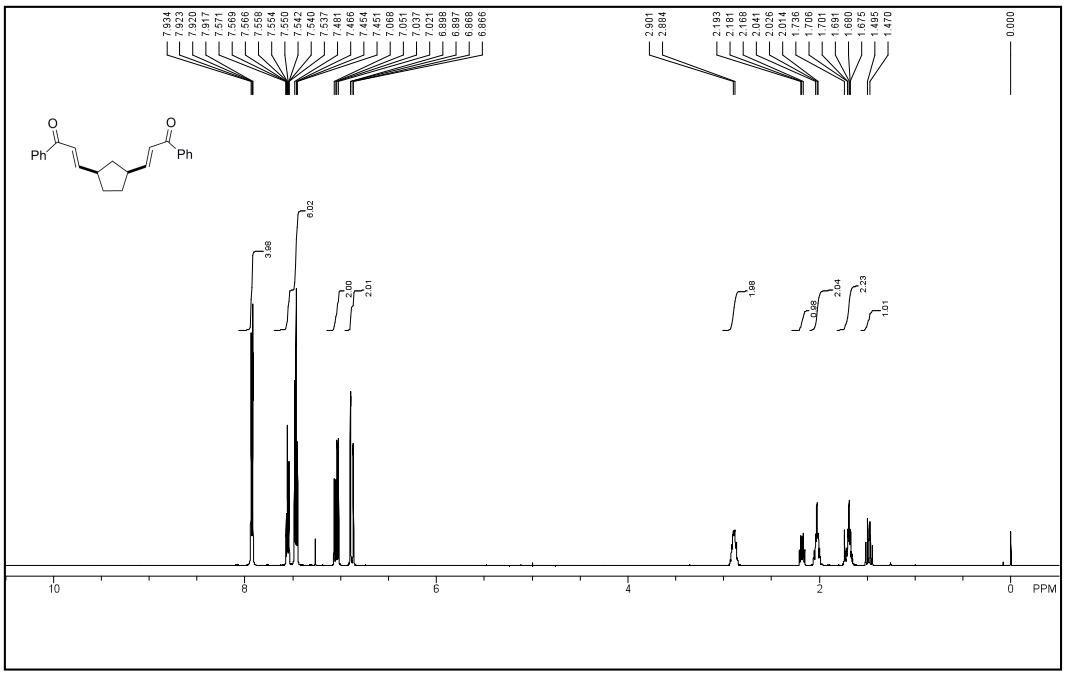
(10) The morning of July 8, 2008, was partly cloudy in Madison, WI.

## VI. NMR spectra for new compounds

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Ph
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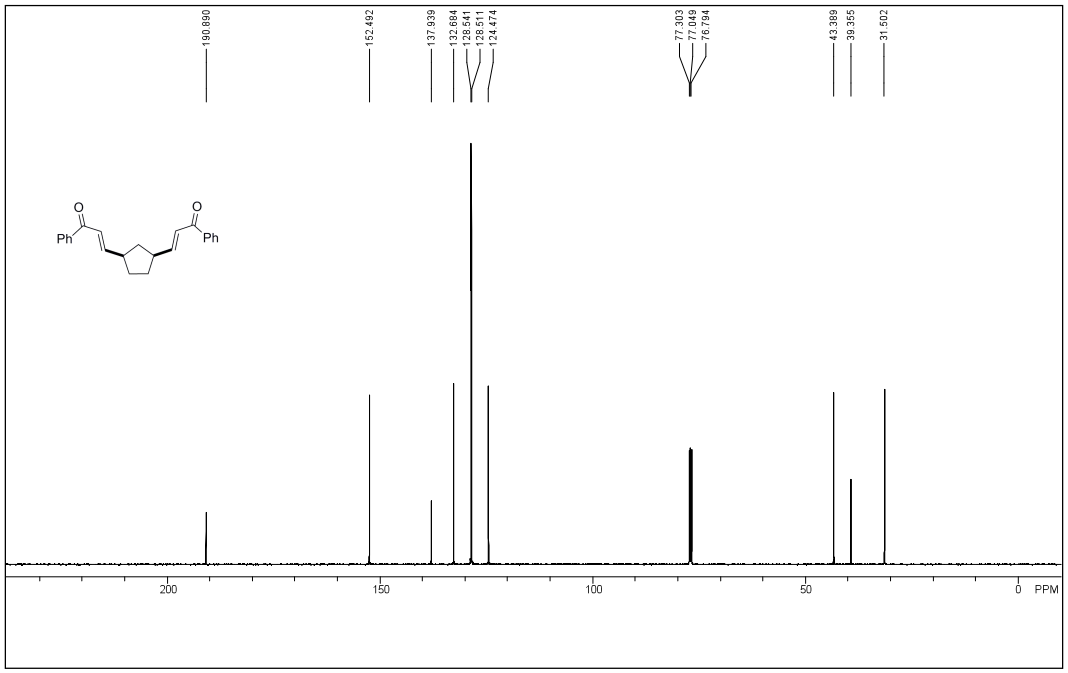
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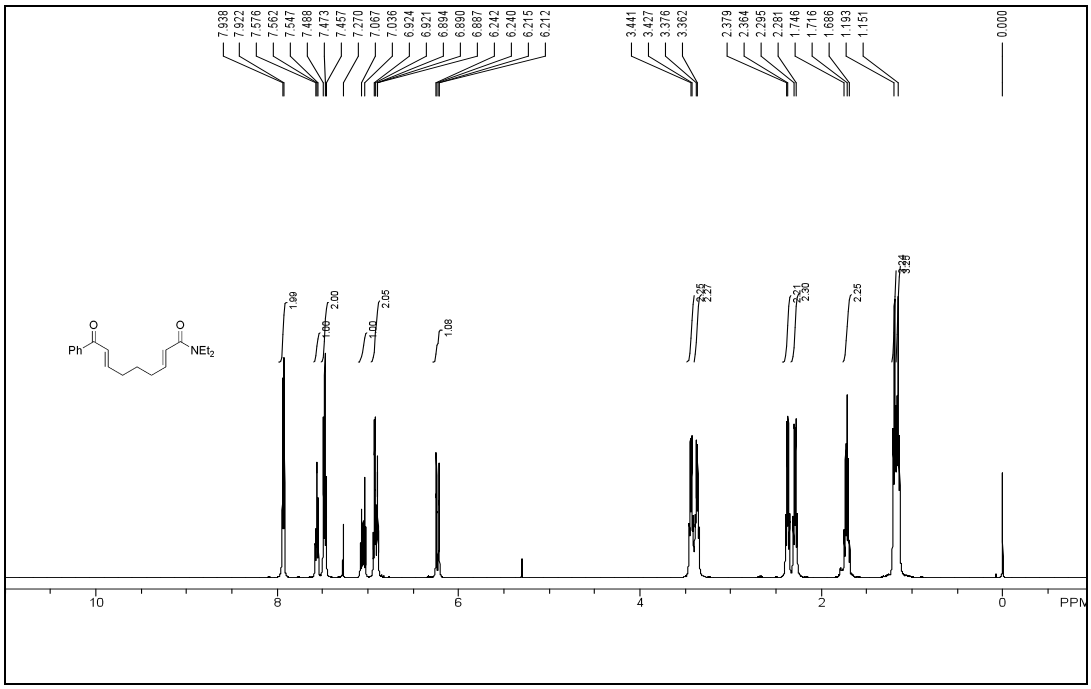
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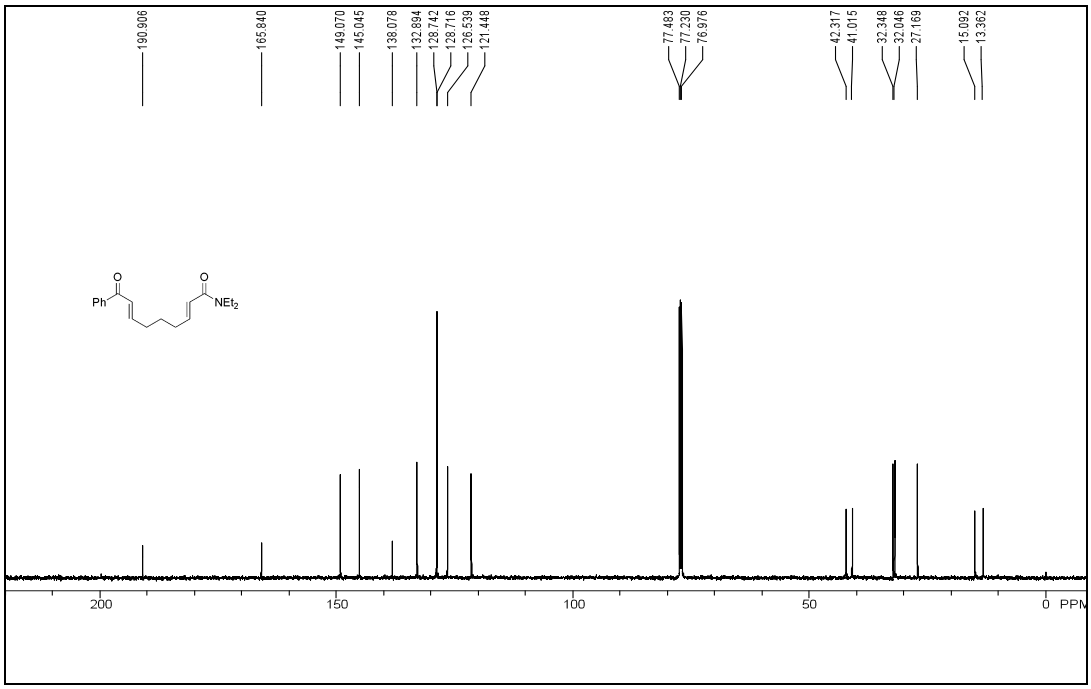
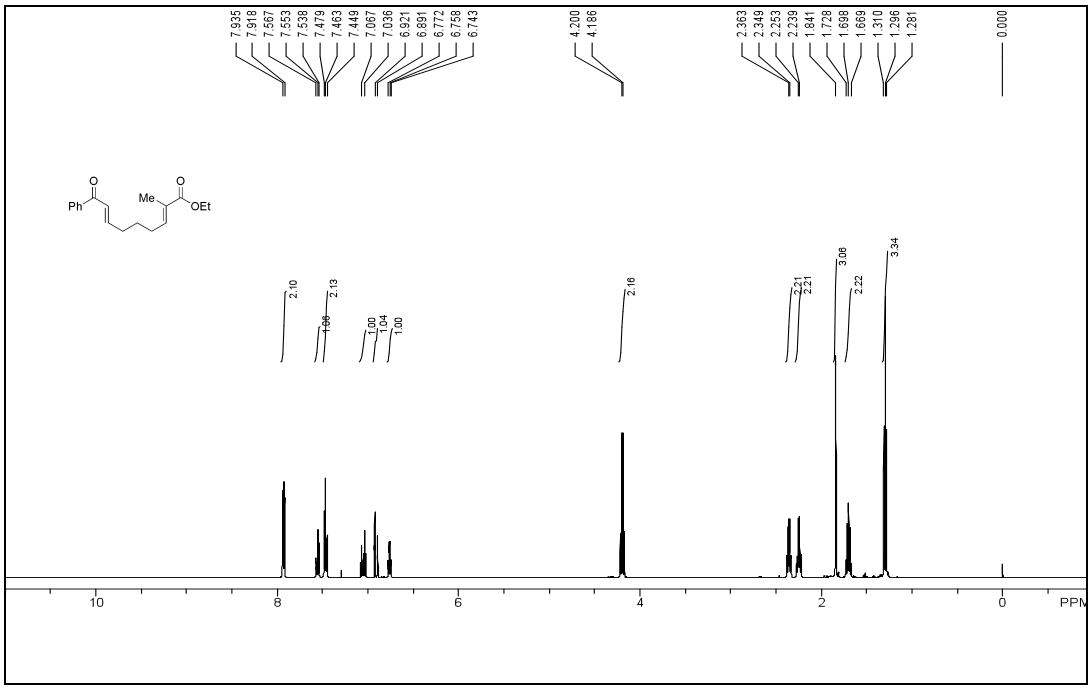
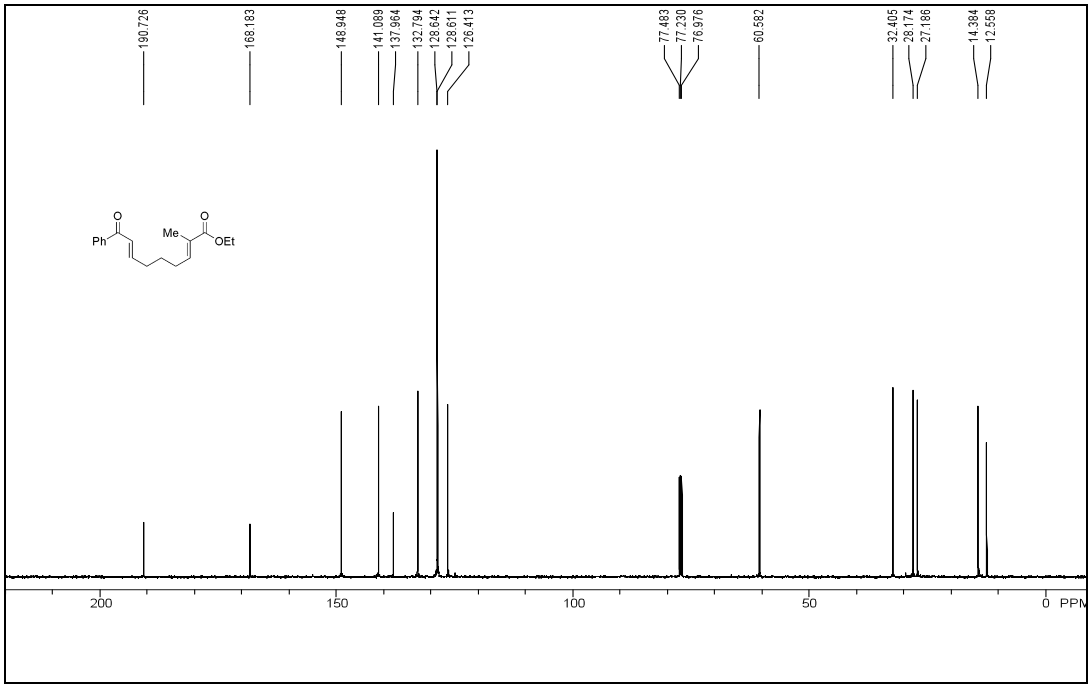
PPM


190.906
165.840
149.070
145.045
138.078
132.894
128.742
128.716
126.539
121.448
77.483
77.230
76.976
42.317
41.015
32.348
32.046
27.169
15.092
13.362
Ph
O
NEt2
200
150
100
50
0
PPM


7.935
7.918
7.567
7.553
7.538
7.479
7.463
7.449
7.067
7.036
6.921
6.891
6.772
6.758
6.743
4.200
4.186
2.363
2.349
2.253
2.239
1.841
1.728
1.698
1.669
1.310
1.296
1.281
0.000
Ph
Me
OEt
2.10
1.66
2.13
1.00
1.04
1.00
2.16
2.21
2.21
3.06
2.22
3.34
10
8
6
4
2
0
PPM


190.726
168.183
148.948
141.089
137.964
132.794
128.642
128.611
126.413
77.483
77.230
76.976
60.582
32.405
28.174
27.186
14.384
12.558
Ph
Me
OEt
200
150
100
50
0
PPM

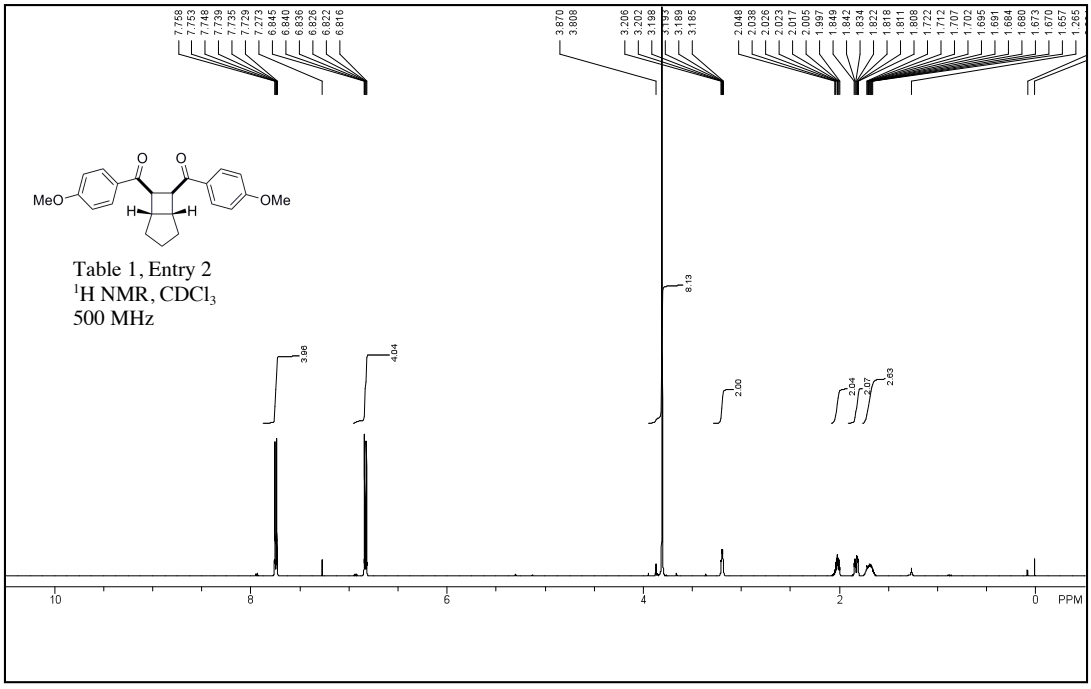



Table 1, Entry 2
$^{1}$H NMR, $CDCl_3$
500 MHz

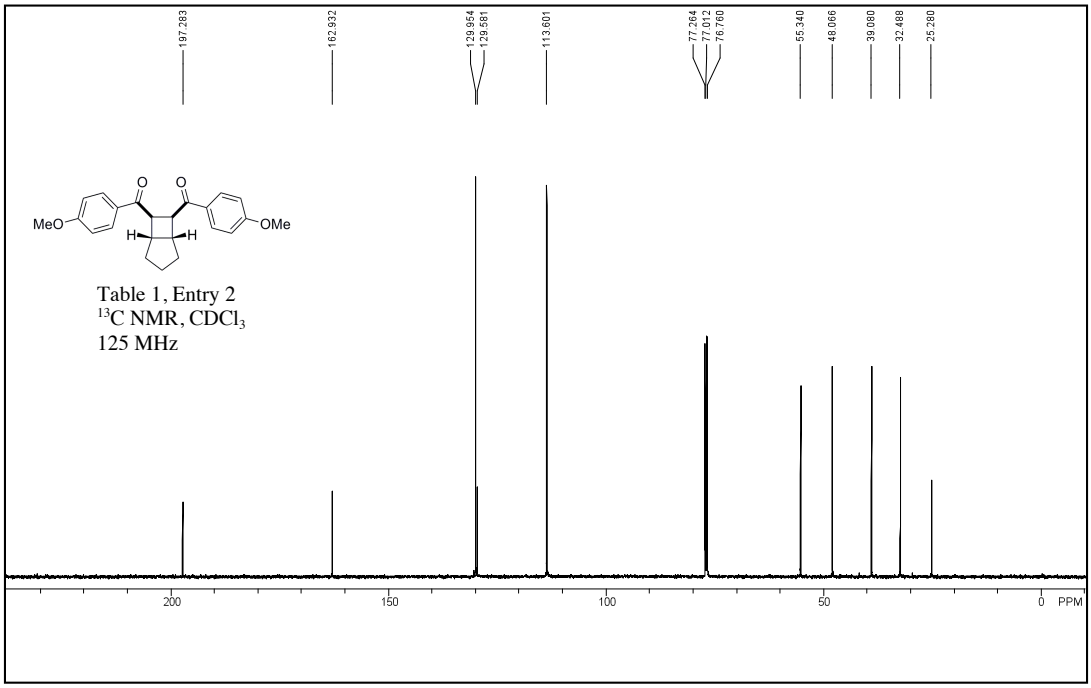



Table 1, Entry 2
$^{13}$C NMR, $CDCl_3$
125 MHz

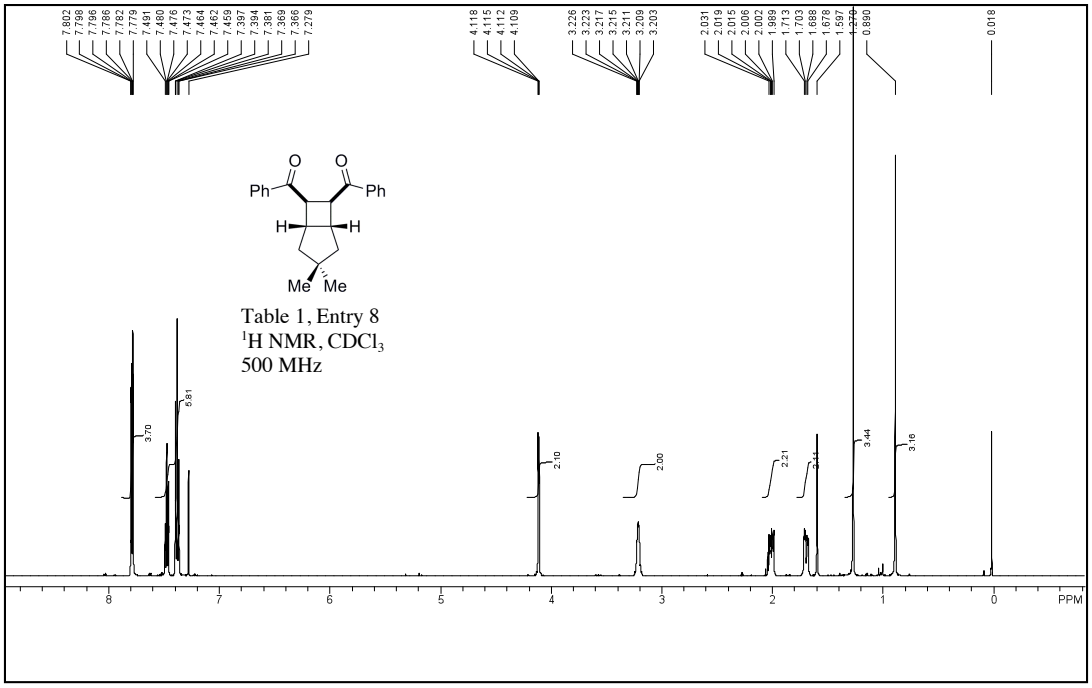


Table 1, Entry 8
1H NMR, CDCl3
500 MHz
PPM

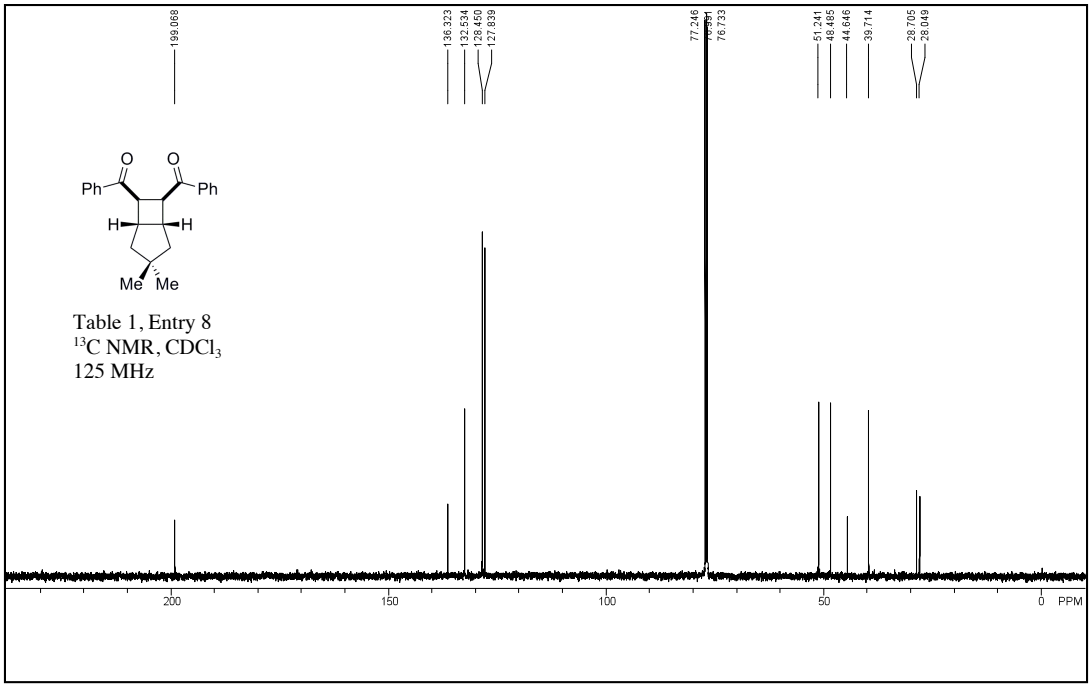


Table 1, Entry 8
13C NMR, CDCl3
125 MHz
PPM

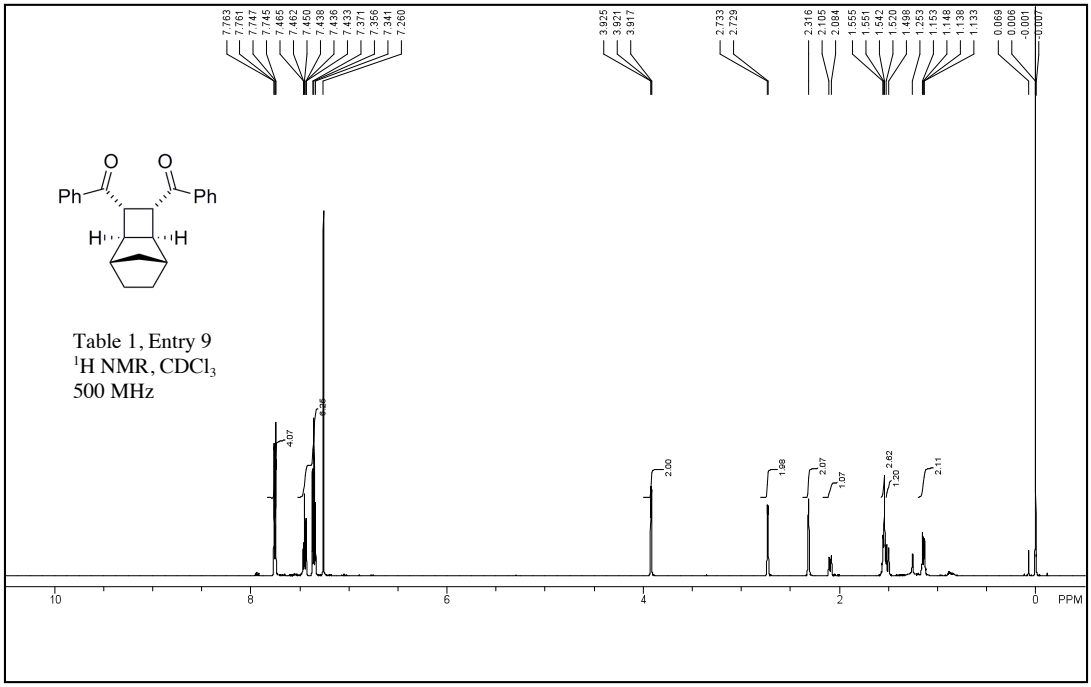



Table 1, Entry 9
$^{1}$H NMR, $CDCl_3$
500 MHz

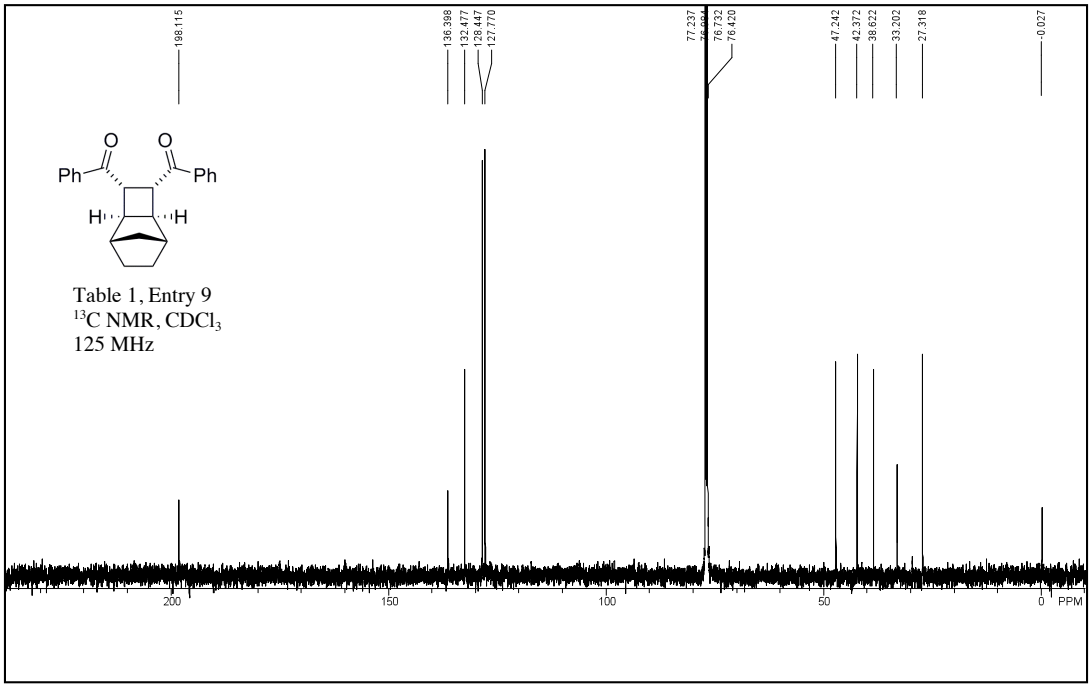



Table 1, Entry 9
$^{13}$C NMR, $CDCl_3$
125 MHz

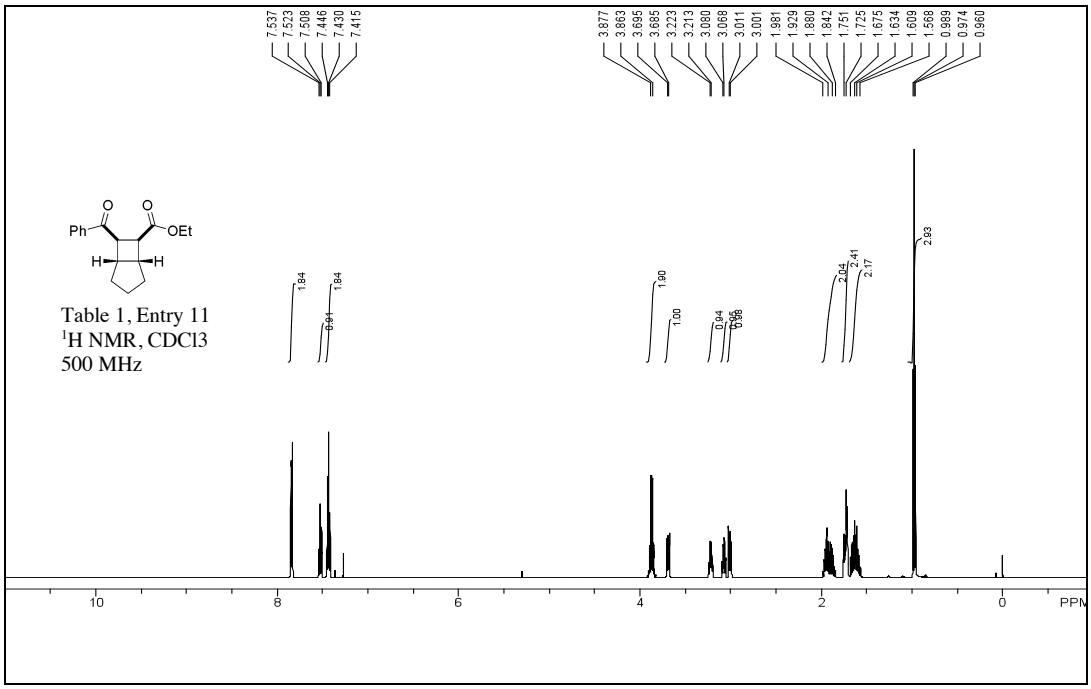



Table 1, Entry 11
$^{1}$H NMR, CDCl3
500 MHz

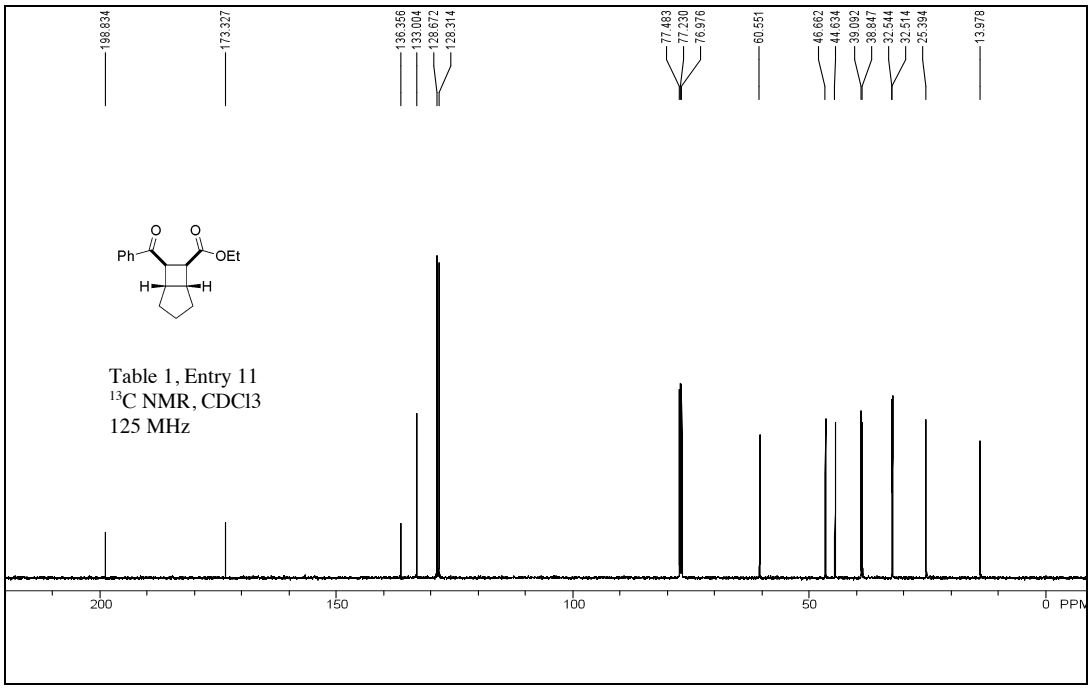
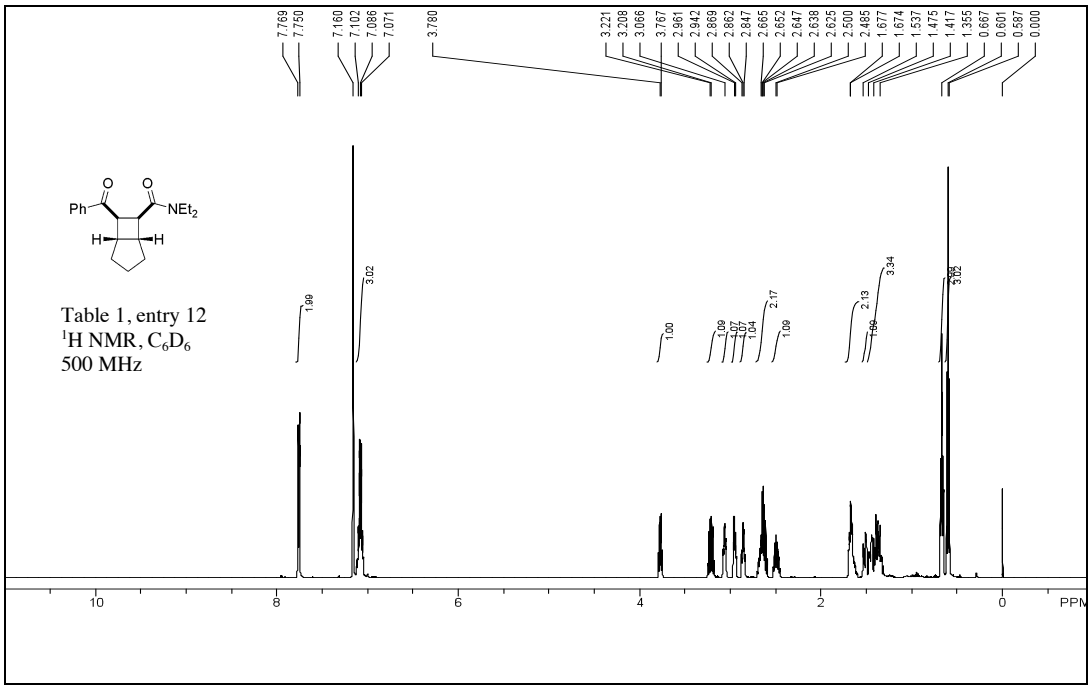
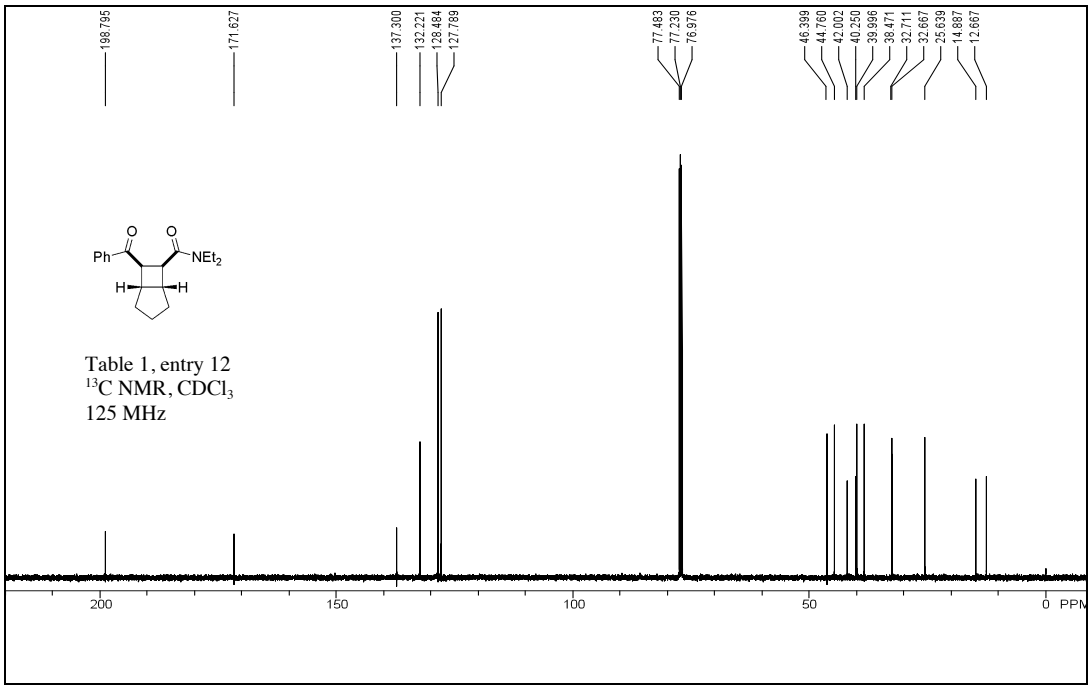



Table 1, Entry 11
$^{13}$C NMR, CDCl3
125 MHz


7.769
7.750
7.160
7.102
7.086
7.071
3.780
3.221
3.208
3.066
3.767
2.961
2.942
2.869
2.862
2.847
2.665
2.652
2.647
2.638
2.625
2.500
2.485
1.677
1.674
1.537
1.475
1.417
1.355
0.667
0.601
0.587
0.000
Ph
O
O
NEt2
H
H
Table 1, entry 12
1H NMR, C6D6
500 MHz
1.99
3.02
1.00
1.09
1.07
1.07
1.04
2.17
1.09
2.13
1.99
3.34
3.02
10
8
6
4
2
0
PPM


198.795
171.627
137.300
132.221
128.484
127.789
77.483
77.230
76.976
46.399
44.760
42.002
40.250
39.996
38.471
32.711
32.667
25.639
14.887
12.667
Ph
O
O
NEt2
H
H
Table 1, entry 12
13C NMR, CDCl3
125 MHz
200
150
100
50
0
PPM

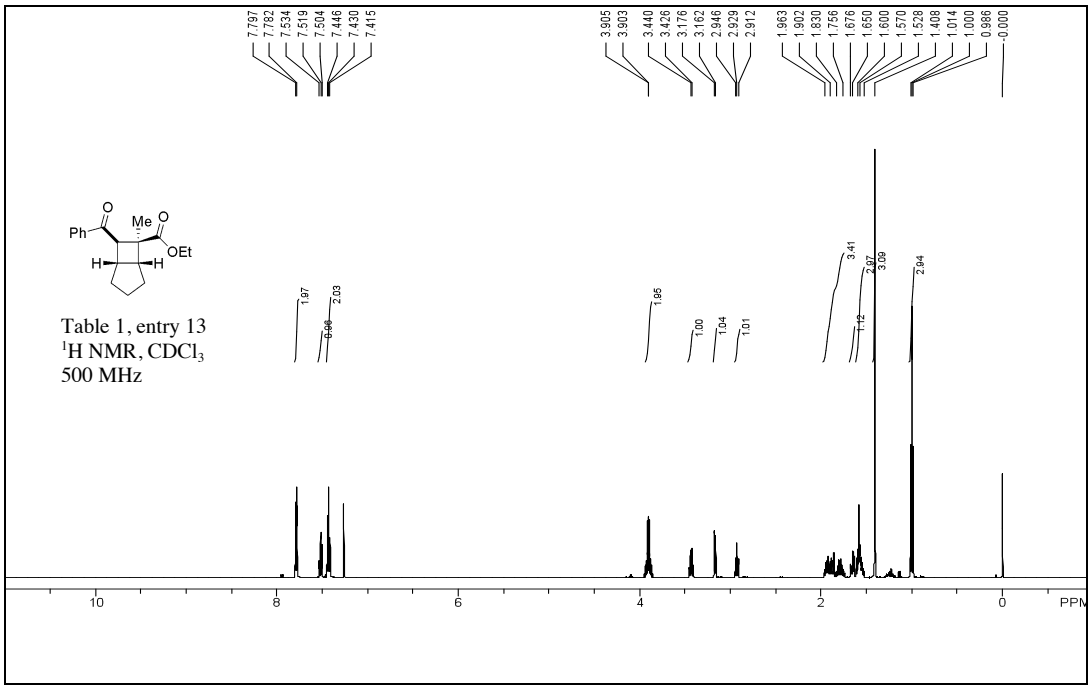



Table 1, entry 13
$^{1}$H NMR, $CDCl_3$
500 MHz

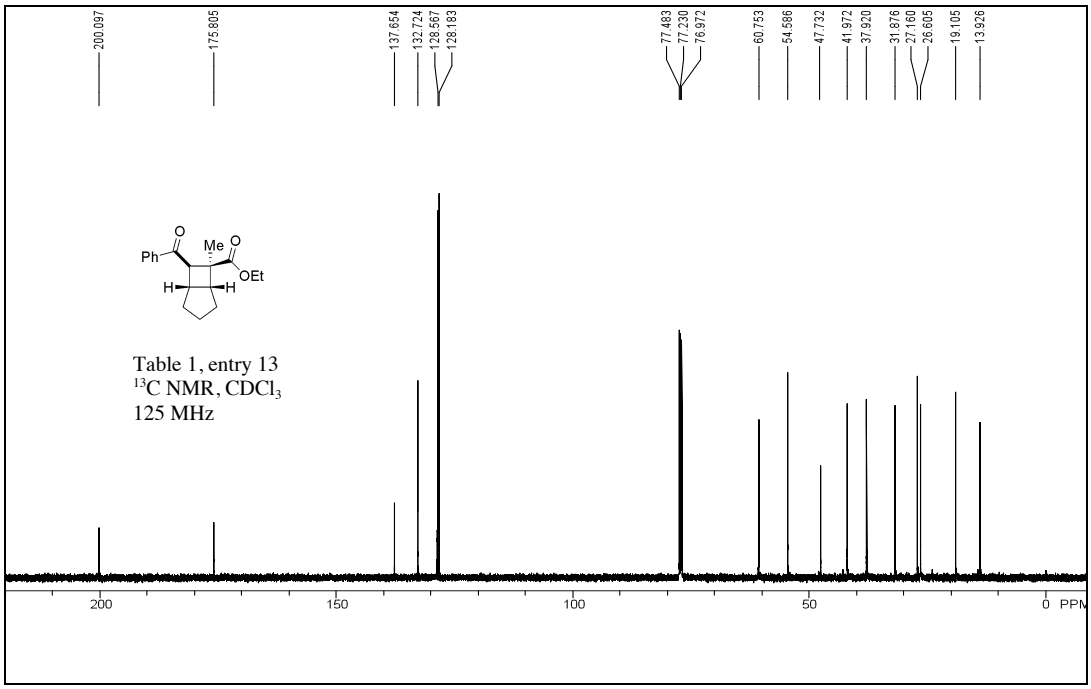
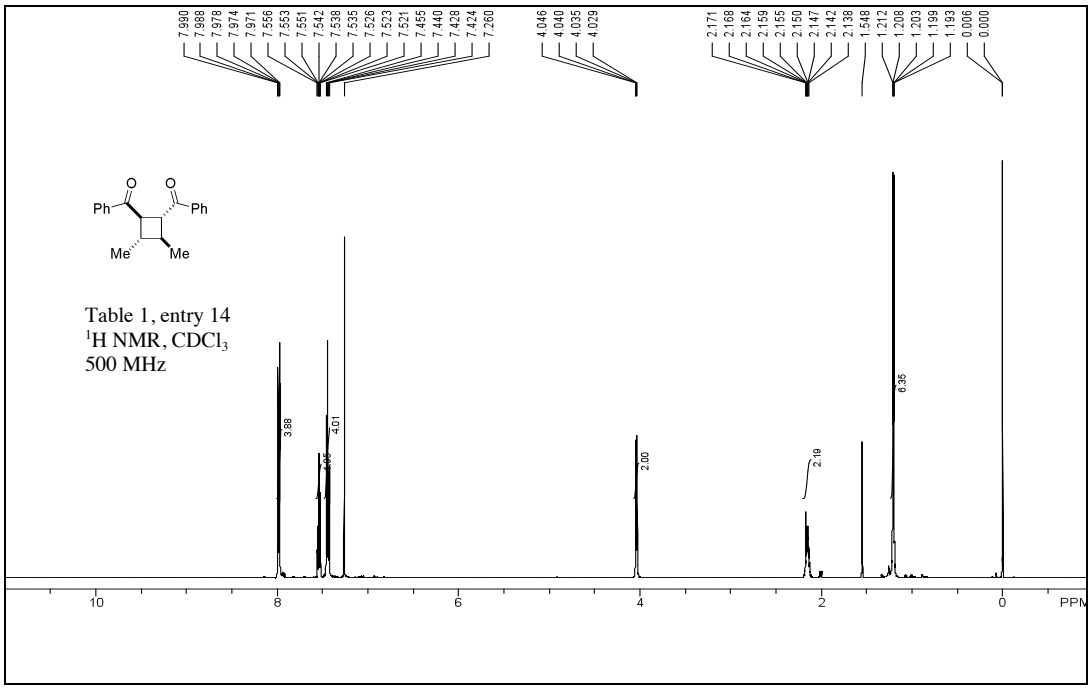
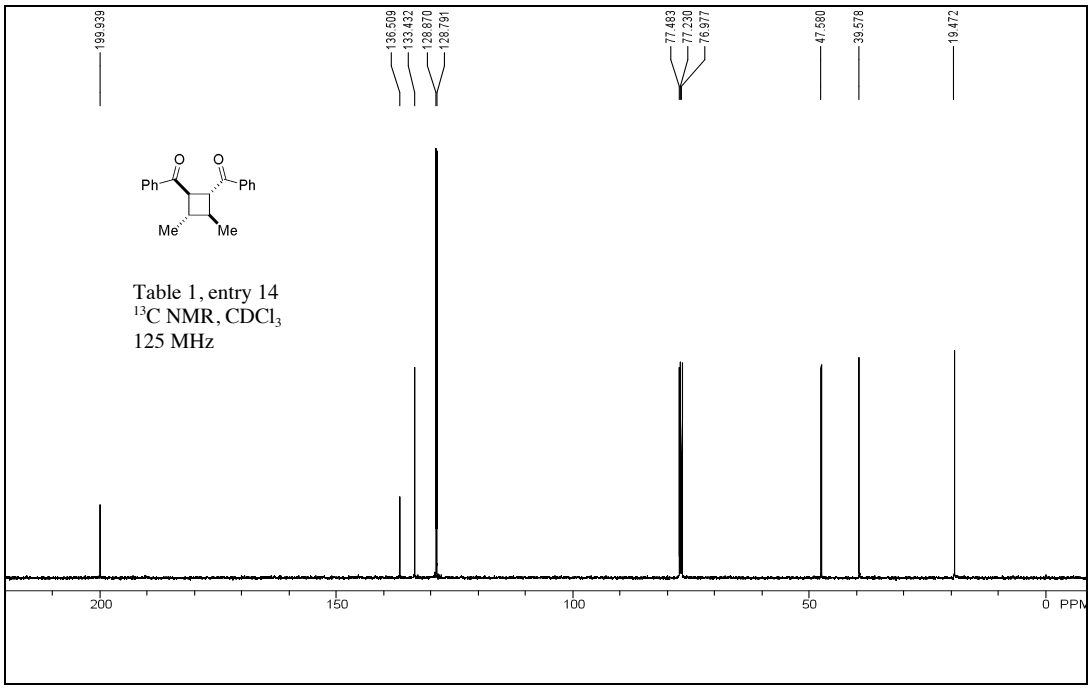
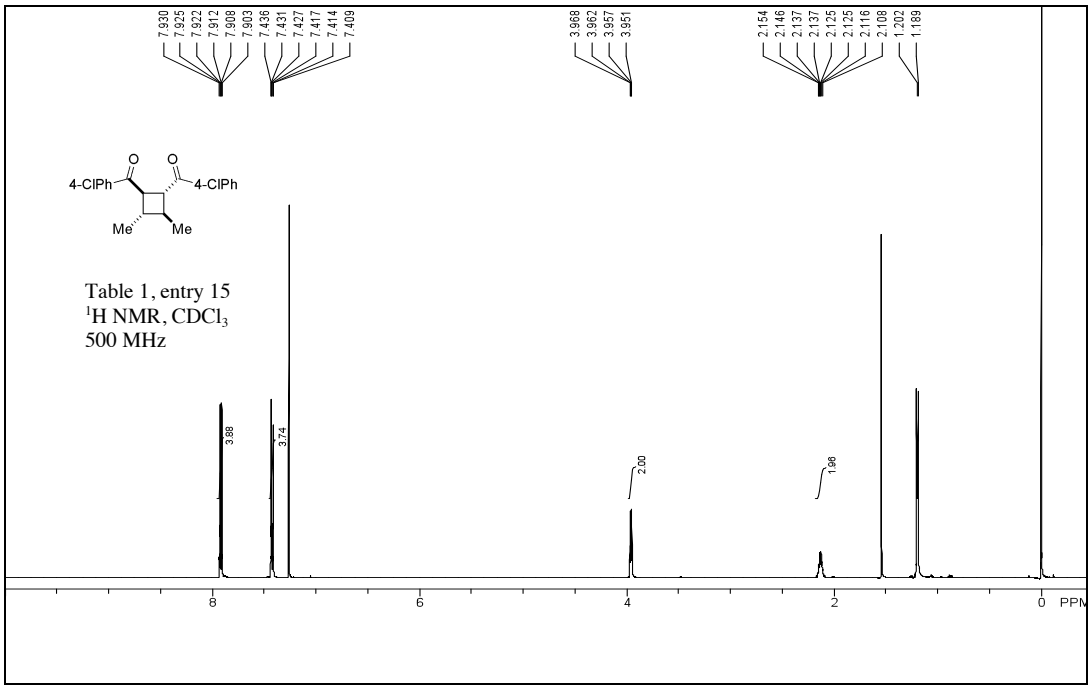
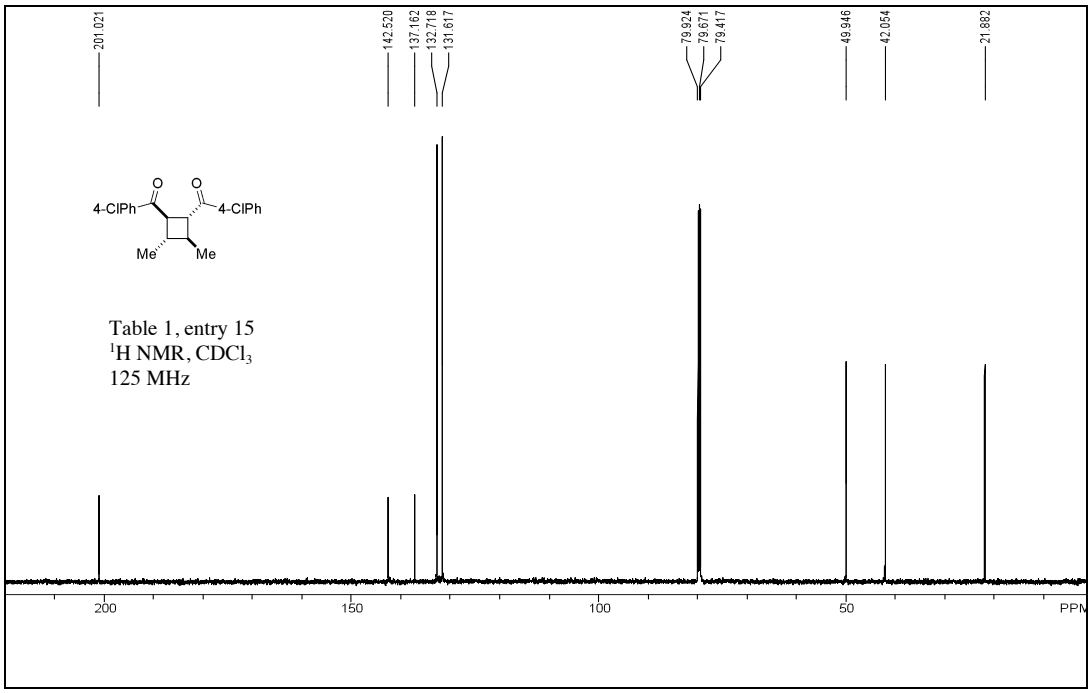



Table 1, entry 13
$^{13}$C NMR, $CDCl_3$
125 MHz


7.990
7.988
7.978
7.974
7.971
7.556
7.553
7.551
7.542
7.538
7.535
7.526
7.523
7.521
7.455
7.440
7.428
7.424
7.260
4.046
4.040
4.035
4.029
2.171
2.168
2.164
2.159
2.155
2.150
2.147
2.142
2.138
1.548
1.212
1.208
1.203
1.199
1.193
0.006
0.000
Ph
Ph
Me
Me
Table 1, entry 14
1H NMR, CDCl3
500 MHz
3.88
4.01
2.00
2.19
6.95
10
8
6
4
2
0
PPM


199.939
136.509
133.432
128.870
128.791
77.483
77.230
76.977
47.580
39.578
19.472
Ph
Ph
Me
Me
Table 1, entry 14
13C NMR, CDCl3
125 MHz
200
150
100
50
0 PPM


7.930
7.925
7.922
7.912
7.908
7.903
7.436
7.431
7.427
7.417
7.414
7.409
3.968
3.962
3.957
3.951
2.154
2.146
2.137
2.137
2.125
2.125
2.116
2.108
1.202
1.189
4-ClPh
4-ClPh
Me
Me
Table 1, entry 15
1H NMR, CDCl3
500 MHz
3.88
3.74
2.00
1.90
8
6
4
2
0
PPM


201.021
142.520
137.162
132.718
131.617
79.924
79.671
79.417
49.946
42.054
21.882
4-ClPh
4-ClPh
Me
Me
Table 1, entry 15
1H NMR, CDCl3
125 MHz
200
150
100
50
PPM