Supporting Information

Photocatalytic Systems with Flavinium Salts: From Photolyase Models to Synthetic Tool for Cyclobutane Ring Opening

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S1 General procedures and methods

NMR spectra were recorded on a Varian Mercury Plus 300 (299.97 MHz for ^{1}H, 75.44 MHz for ^{13}C, and 282.23 MHz for ^{19}F) or Agilent 400-MR DDR2 (399.94 MHz for ^{1}H and 100.58 MHz for ^{13}C) at 298 K unless otherwise indicated. Chemical shifts δ are given in ppm, using residual solvent or tetramethylsilane as an internal standard. Coupling constants *J* are reported in Hz. **UV-VIS spectra** were recorded on a Varian Cary 50 spectrophotometer. **Fluorescence spectra** were recorded on Varian Cary Eclipse. High-resolution **mass spectra** were obtained on Q-Tof Micro (Waters), equipped with a quadrupole and TOF analyzers and MCP detector. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 0.040-0.063 mm (Merck). **Melting points** were measured on a Boetius melting point apparatus and are uncorrected.

Electrochemical measurements were performed using a standard three-electrode system in a methrom type electrochemical cell with a glassy carbon working electrode, silver wire pseudo-reference electrode and a platinum wire auxiliary electrode. Cyclic voltammograms were collected by PGSTAT128N. The cyclic voltammetry measurements were carried out in acetonitrile containing a cyclobutane **3** ($c = 1 \times 10^{-3}$ mol L^{-1}) and tetrabutylammonium hexafluorophosphate ($c = 1 \times 10^{-1}$ mol L^{-1}) as supporting electrolyte under argon atmosphere. The scan rate was 100 mV s^{-1}. The measured redox potentials were converted into values relative to SCE using standard redox couple Fc^{+}/Fc as suggested by Addison and others:[1] conversion of the measured values into those *vs* SCE involved subtraction of the difference between experimental $E_{1/2}$ values for standard redox couple Fc^{+}/Fc measured after each experiment (relative to Ag wire) and $E_{1/2}$ value for standard redox couple Fc^{+}/Fc measured against SCE at the same apparatus (+0.381 V, the value obtained as an average of 5 measurements).

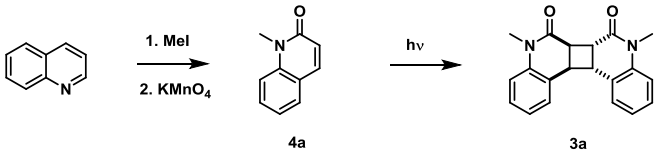
Starting materials, reagents and substrates were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures.[2] Riboflavin tetraacetate (**1**),[3] alloxazinium salts **2**,[4] and isoalloxazinium salt **8**

[1] a) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97; b) Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714.
[2] D. D. Perrin, W. L. F. A. *Purification of Laboratory Chemicals, 4th Ed.*; Elsevier Science Ltd., Oxford, 1996.
[3] Neveselý, T.; Svobodová, E.; Chudoba, J.; Sikorski, M.; Cibulka, R. *Adv. Synth. Catal.* **2016**, *358*, 1654.
[4] Ménová, P.; Dvořáková, H.; Eigner, V.; Ludvík, J.; Cibulka, R. *Adv. Synth. Catal.* **2013**, *355*, 3451.

(ref.[3]) were prepared according to previously reported procedures. NMR and UV spectra are in agreement with previously reported data.[2,3]

S2. Synthetic procedures and characterization of compounds 3

(6a*R**,6b*R**,12b*R**,12c*R**)-5,8-Dimethyl-5,6a,6b,8,12b,12c-hexahydrocyclobuta--[1,2-*c*:4,3-*c*']diquinoline-6,7-dione (3a)

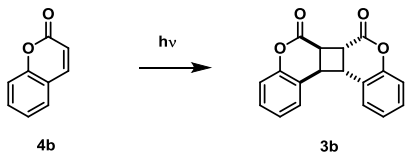


*1-Methylquinolin-2(1H)-one (**4a**)* Quinoline (15 g, 116 mmol) and iodomethane (16.48 g, 116 mmol) were mixed and allowed to stir/stand for 3 hours. Orange solids were dissolved in acetonitrile (250 mL) followed by addition of potassium permanganate (45.9 g, 290 mmol) while stirring. Mixture color changed from violet to brown (MnO_2). Residual permanganate was decomposed with saturated solution of sodium sulfite. Resulting mixture was treated with 10% HCl and extracted with chloroform. Chloroform solution was dried with magnesium sulfate and evaporated. Crude product was crystalized from ethanol to obtain **4a** (9.8 g, 61.6 mmol, 53% yield). M.p. 72-75 °C (ref.[5] 75-76 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 9.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.36 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.71 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.52, 140.22, 139.15, 130.83, 128.94, 122.29, 121.92, 120.86, 114.34, 29.60.

(6aR,6bR*,12bR*,12cR*)-5,8-Dimethyl-5,6a,6b,8,12b,12c-hexahydrocyclobuta[1,2-c:4,3-c']diquinoline-6,7-dione (**3a**)* Solution of 1-methylquinolin-2(1*H*)-one (2 g, 12.56 mmol) in ethanol (100 mL) was irradiated in pyrex glassware for 10 hours using medium pressure mercury lamp (125 W). White precipitate was filtered off, washed with ethanol to give single isomer of **3a** (1.5 g, 4.71 mmol, 75% yield). M.p. 222-223 °C (ref.[6] 220-222 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.07 – 6.98 (m, 4H), 6.92 (dd, *J* = 7.4, 1.7 Hz, 2H), 3.89 – 3.81 (m, 2H), 3.79 – 3.71 (m, 2H), 3.47 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.00, 139.60, 128.40, 127.78, 123.41, 123.19, 115.00, 44.14, 43.40, 29.73. HRMS (ESI+) Calcd for $C_{20}H_{18}O_2N_2$ $[M+H]^+$: 320.14746; found: m/z 320.14764. UV-VIS (acetonitrile): 259 nm.

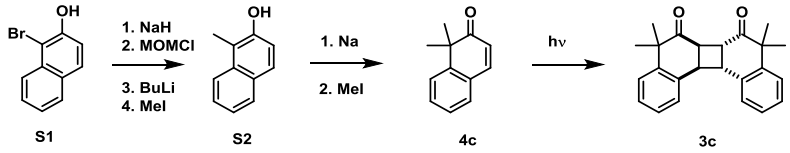
[5] Aksenov, A. V.; Smirnov, A. N.; Aksenov, N. A.; Aksenova, I. V.; Matheny, J. P.; Rubin, M. *RSC Advances* **2015**, *5*, 8647.
[6] Lewis, F. D.; Reddy, G. D.; Elbert, J. E.; Tillberg, B. E.; Meltzer, J. A.; Kojima, M. *J. Org. Chem.* **1991**, *56*, 5311.

(6a*R*,6b*R***,12b*R***,12c*R***)-6a,6b,12b,12c-Tetrahydrocyclobuta[1,2-*c*:4,3-*c*']-**
-dichromene-6,7-dione (3b)



Benzophenone (0.156 g, 0.855 mmol) and coumarine (2.5 g, 17.11 mmol) were dissolved in 150 mL of acetonitrile. Argon was bubbled through solution for 10 minutes followed by irradiation by medium pressure mercury lamp (125 W) in pyrex glassware. After 20 hours of irradiation, white precipitate was collected. Crystaline product was recrystalized from benzene to give **3b** (2.375 g, 8.13 mmol, 95% yield) as a single isomer product. M.p. 176-178 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.30 (m, 2H), 7.23 – 7.07 (m, 6H), 4.03 – 3.78 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.98, 151.18, 129.70, 127.78, 125.39, 120.24, 117.86, 43.86, 40.17. HRMS (ESI+) Calcd for $C_{18}H_{12}O_4$ $[M+Na]^+$: 316.06613; found: m/z 316.06641. UV-VIS (acetonitrile): 271, 280 nm.

(6a*R*,6b*R***,12b*R***,12c*R***)-5,5,8,8-Tetramethyl-5,6a,6b,8,12b,12c-hexahydrodibenzo-**
[*a*,*i*]biphenylene-6,7-dione (3c)



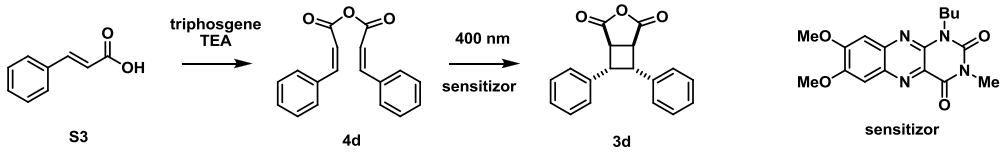
*1-Methylnaphthalen-2-ol (**S2**)* Sodium hydride (2.96 g, 74.0 mmol) was suspended in anhydrous THF (100 ml). Mixture was cooled to 0 °C and 1-bromonaphthalen-2-ol (15 g, 67.2 mmol) was added portion wise. Mixture was stirred for one hour followed by addition of chloro(methoxy)methane (7.66 mL, 101 mmol). Mixture was allowed to warm to room temperature and stirred for 2 hours. Reaction was quenched with ethanol and water. Mixture was extracted twice with ether. Ethereal part was washed with water, brine and dried using magnesium sulfate. Removal of solvent gave brown oil of 1-bromo-2-(methoxymethoxy)naphthalene (17.06 g) which was used without further purification. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.57 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.47 – 7.38 (m, 2H), 5.36 (s, 2H), 3.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 133.1, 130.5, 128.9, 128.1, 127.7, 126.4, 124.9, 117.0, 110.5, 95.6, 56.6. 1-Bromo-2-(methoxymethoxy)naphthalene (8 g, 29.9 mmol) was dissolved in THF (100 mL) under argon and cooled to -70 °C. While stirring, butyllithium (13.18 mL, 32.9

mmol) was added slowly. Mixture was allowed to stir for one hour at - 70 °C, followed by addition of iodomethane (4.66 mL, 74.9 mmol). Solution was allowed to warm to room temperature and stirred for 3 hours. Reaction was quenched by water (10 mL) and extracted with ether. Organic part was washed with water, brine and dried with magnesium sulfate. Ether was evaporated to give brown solid. Solids were dissolved in MeOH (60 mL) and five drops of concentrated HCl were added. Solution was refluxed for 3 hours and evaporated to give **S2** as yellow solid (2.73 g, 17.26 mmol, 58% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.63 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.51 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 3.53 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.41, 133.80, 129.17, 128.44, 127.35, 126.30, 123.12-2 signals, 117.55, 115.18, 10.47.

*1,1-Dimethylnaphthalen-2(1H)-one (**4c**)* Sodium (0.725 g, 31.5 mmol) was dissolved in MeOH (50 mL). Solution of 1-methylnaphthalen-2-ol (**S2**, 4.75 g, 30.0 mmol) in 20 mL of methanol was added. Black solution was stirred overnight. Solvent was evaporated and solids were dried in vacuo. Brown solids were dissolved in iodomethane (28.0 mL, 450 mmol) and refluxed for 20 hours. Iodomethane was evaporated, solids were dissolved in ether and water. Water was separated, extracted with ether. Ethereal part was washed with water, brine and dried with $MgSO_4$. Crude oil was purified by column chromatography (hexane/ethyl acetate 10:1) to give **4c** (2.2 g, 12.77 mmol, 43% yield) as an oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 3H), 7.35 – 7.27 (m, 2H), 6.17 (d, *J* = 9.8 Hz, 1H), 1.47 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.55, 147.65, 144.79, 130.05, 129.44, 128.68, 126.67, 126.23, 124.50, 47.44, 27.86.

(6aR,6bR*,12bR*,12cR*)-5,5,8,8-Tetramethyl-5,6a,6b,8,12b,12c-hexahydrodibenzo--[a,i]biphenylene-6,7-dione (**3c**)* 1,1-Dimethylnaphthalen-2(1*H*)-one (**4c**, 400 mg, 2.323 mmol) was dissolved in ethanol (5 mL) and solution was irradiated in pyrex glassware for 20 hrs using medium pressure mercury lamp (125 W). White precipitate was filtered off, washed with ethanol to give single isomer of **3c** (364 mg, 1.057 mmol, 91% yield). M.p. 192-194 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.28 (m, 8H), 4.21 – 4.11 (m, 2H), 3.81 (dt, *J* = 8.4, 1.4 Hz, 2H), 1.58 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.94, 139.99, 132.63, 123.97, 123.47, 123.30, 121.50, 44.63, 43.54, 38.14, 25.04, 17.23. HRMS (ESI+) calcd for $C_{24}H_{24}O_2$ $[M+Na]^+$: 368.17021; found: 368.17052 m/z. UV-VIS (acetonitrile): 219, 267 nm.

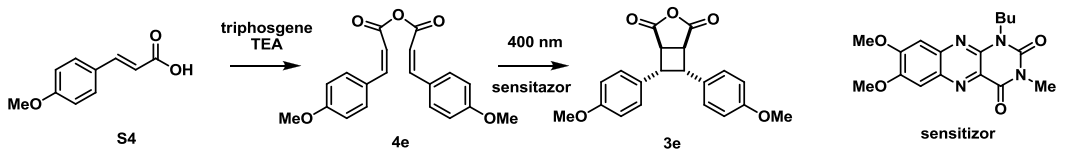
(1*R,5*S**,6*R**,7*S**)-6,7-diphenyl-3-oxabicyclo[3.2.0]heptane-2,4-dione (3d)**



*Cinnamic anhydride (**4d**)* Cinnamic acid (10 g, 67.5 mmol) and triethylamine (6.83 g, 67.5 mmol) were stirred in ethyl acetate (50 mL) and cooled to 0 °C. Bis(trichloromethyl) carbonate (3.91 g, 11.47 mmol) was added portion wise keeping the temperature below 10 °C. Reaction was stirred for one hour, filtered and washed with ethyl acetate. Filtrate was evaporated to give white crystals of **4d** (16.7 g, 60.0 mmol, 89% yield). M.p. 134-135 °C (ref.[7] 134-136 °C). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 15.9 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.47 – 7.39 (m, 6H), 6.53 (dd, *J* = 15.9, 0.8 Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.71, 148.89, 133.94, 131.51, 129.31, 128.81, 116.97.

(1R,5S*,6R*,7S*)-6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane-2,4-dione (**3d**)* Cinnamic anhydride (2 g, 7.19 mmol) and 1-butyl-7,8-dimethoxy-3-methylbenzo[g]pteridine-2,4(1H,3H)-dione[8] **S9** (0.247 g, 0.719 mmol) in acetonitrile (50 mL) were irradiated with 400 nm LED lamp for 3 hours. Solvent was evaporated to give yellow foam of **3d** (1.92 g, 6.90 mmol, 96% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.05 (m, 6H), 6.95 – 6.84 (m, 4H), 4.44 – 4.36 (m, 2H), 3.99 – 3.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.18, 136.32, 128.31, 127.63, 127.19, 46.94, 42.94. HRMS (ESI+) calcd for $C_{18}H_{15}O_3$ $[M+H]^+$: 279.10216; found: 279.10174 m/z. UV-VIS (acetonitrile): 217, 258 nm.

(1*R,5*S**,6*R**,7*S**)-6,7-bis(4-methoxyphenyl)-3-oxabicyclo[3.2.0]heptane-2,4-dione (3e)**



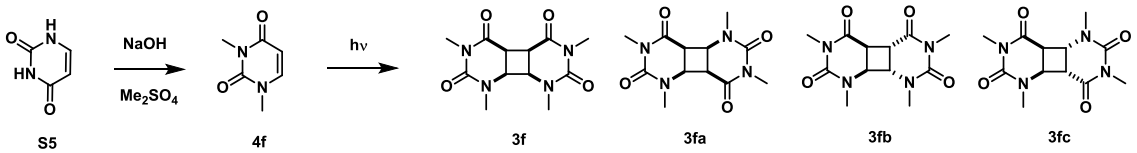
*(E)-3-(4-methoxyphenyl)acrylic anhydride (**4e**)* (*E*)-3-(4-Methoxyphenyl)acrylic acid (8.6 g, 48.3 mmol) and triethylamine (6.94 mL, 48.3 mmol) were stirred in ethyl acetate (50 mL) and cooled to 0 °C. Bis(trichloromethyl) carbonate (2.435 g, 8.20 mmol) was added portion wise keeping the temperature below 10 °C. Reaction was stirred for one hour, filtered and washed with ethyl acetate. Filtrate was evaporated to give white foam of **4e** (6.61 g, 19.55

[7] Konieczynska, M. D.; Dai, C.; Stephenson, C. R. J. *Org. Biomol. Chem.* **2012**, *10*, 4509.
[8] Mojr, V.; Svobodova, E.; Strakova, K.; Nevesely, T.; Chudoba, J.; Dvorakova, H.; Cibulka, R. *Chem. Commun.* **2015**, *51*, 12036.

mmol, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 15.9 Hz, 2H), 7.58 – 7.50 (m, 4H), 6.97 – 6.91 (m, 4H), 6.39 (d, *J* = 15.8 Hz, 2H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.01, 162.15, 148.24, 130.40, 126.52, 114.50, 114.15, 55.42 (d, *J* = 4.5 Hz).

(1R,5S*,6R*,7S*)-6,7-bis(4-methoxyphenyl)-3-oxabicyclo[3.2.0]heptane-2,4-dione (**3e**)* 1-Butyl-7,8-dimethoxy-3-methylbenzo[*g*]pteridine-2,4(1*H*,3*H*)-dione[8] (0.051 g, 0.148 mmol) and (*E*)-3-(4-methoxyphenyl)acrylic anhydride (**4e**, 1 g, 2.96 mmol) were dissolved in acetonitrile (20 mL). Solution was irradiated for 2 hours with LED (400 nm). Solvent was evaporated, crude product was purified by column chromatography (hexane/ethyl acetate 5:1) to gain **3e** (460 mg, 1.360 mmol, 46% yield) as an oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 6.88 – 6.77 (m, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 4.35 – 4.28 (m, 2H), 3.81 (dd, *J* = 5.5, 1.8 Hz, 2H), 3.70 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.27, 158.08, 130.31, 128.80, 113.52, 55.11, 44.11, 43.86. HRMS (ESI+) calcd for $C_{20}H_{18}O_5$ $[M+H]^+$: 339.11542; found: m/z 339.11483. UV-VIS (acetonitrile): 228, 278 nm.

(4a*R,4b*S**,8a*S**,8b*R**)-1,3,6,8-Tetramethylhexahydrocyclobuta[1,2-*d*:4,3-*d*']dipyrimidine-2,4,5,7(3*H*,6*H*)-tetraone (3f)**



*1,3-Dimethylpyrimidine-2,4(1H,3H)-dione (**4f**)* Pyrimidine-2,4(1*H*,3*H*)-dione (15 g, 134 mmol) and sodium hydroxide (12.85 g, 321 mmol) were dissolved in water (150 mL). Mixture was stirred for one hour followed by addition of dimethyl sulfate (30.5 mL, 321 mmol). Solution was heated to 60 °C overnight. Water was evaporated, white solids were dissolved in dichloromethane, washed twice with water, brine and organic part was dried using magnesium sulfate. After solvent removal, white crystals were dried to give **4f** (14.5 g, 103 mmol, 77% yield). M.p. 118-121 °C (ref.[9] 122-124 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 7.9 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 151.92, 142.66, 101.38, 37.02, 27.75.

(4aR,4bS*,8aS*,8bR*)-1,3,6,8-Tetramethylhexahydrocyclobuta[1,2-d:4,3-d']dipyrimidine-2,4,5,7(3H,6H)-tetraone (**3f**)* 1,3-Dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**4f**, 10 g, 71.4 mmol) was irradiated in acetone (200 mL) using quartz glassware and medium pressure

[9] Kolonko, K. J.; Shapiro, R. H.; Barkley, R. M.; Sievers, R. E. *J. Org. Chem.* **1979**, *44*, 3769.

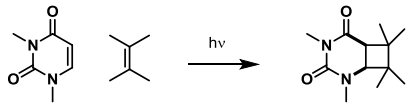
mercury lamp (125 W) for 5 hours. Solvent was evaporated, solids crystalized from ethanol to give mixture of four isomers of uracil dimer in ratio **3f**/**3fa**/**3fb**/**3fc** 50:30:15:5. Mixture was separated by column chromatography on silica gel (hexan/acetone 6:4) as starting eluent and long column 1g/150 g of silica. After elution of first isomer **3fc**, eluent changed to hexane/acetone 4:6, to separate second **3fb** and third isomer **3fa**. Pure acetone was used to elute fourth isomer **3f**. Data for **3f**: M.p. 245-247 °C. (ref.[10] 241-243 °C). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.07 (d, J = 9.8 Hz, 2H), 3.78 (d, J = 9.9 Hz, 2H), 3.15 (s, 6H), 2.99 (s, 6H). ^{13}C NMR of **3f** (101 MHz, Chloroform-d) δ 165.69, 152.63. UV-VIS (acetonitrile): 225 nm.

Data for **3fa**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.09 (t, *J* = 8.5 Hz, 2H), 3.76 (t, *J* = 8.5 Hz, 2H), 3.12 (s, 6H), 3.10 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.94, 152.03, 49.16, 45.22, 35.51, 27.62.

Data for **3fb**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.87 (d, *J* = 8.4 Hz, 2H), 3.61 (d, *J* = 8.4 Hz, 2H), 3.24 (s, 6H), 3.06 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.07, 151.74, 59.28, 39.13, 35.09, 28.27.

Data for **3fc**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.16 – 4.06 (m, 2H), 3.57 – 3.45 (m, 2H), 3.25 (s, 6H), 3.09 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.95, 151.38, 53.41, 44.33, 33.68, 27.93.

(1*S,6*S**)-2,4,7,7,8,8-Hexamethyl-2,4-diazabicyclo[4.2.0]octane-3,5-dione (3g)**

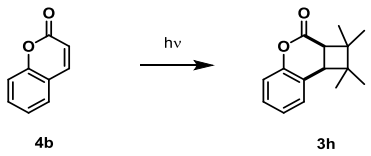


4f 3g

1,3-Dimethylpyrimidine-2,4(1*H*,3*H*)-dione (1.5 g, 10.70 mmol) was dissolved in acetone (150 mL) and 2,3-dimethylbut-2-ene (12.87 mL, 107 mmol) was added. Mixture was bubbled with argon for 15 minutes. Solution was irradiated in quartz glassware by medium pressure mercury lamp (125 W). After 8 hours of irradiation, solvent was removed and oily residual was purified by column chromatography (hexane/acetone 7/3) to give colorless oil of **3g** (1.1 g, 4.90 mmol, 46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.57 (d, *J* = 10.1 Hz, 1H), 3.20 (s, 3H), 3.01 – 2.93 (m, 4H), 1.22 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.43, 153.02, 57.42, 45.25, 44.95, 41.86, 35.87, 27.28, 27.02, 24.51, 20.27, 19.19. HRMS (ESI+) Calcd for $C_{12}H_{20}O_2N_2$ $[M+H]^+$: 225.15975; found: m/z 225.15947. UV-VIS (acetonitrile): < 225 nm.

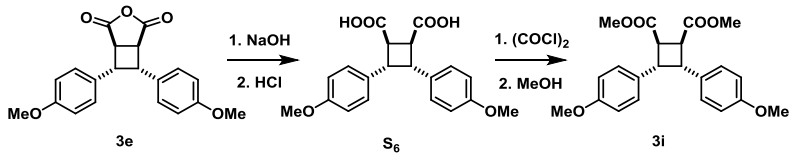
[10] Gorelic, L. S.; Lisagor, P.; Yang, N. C. *Photochem. Photobiol.* **1972**, *16*, 465.

(2a*R,8b*S**)-1,1,2,2-Tetramethyl-1,2,2a,8b-tetrahydro-3*H*-cyclobuta[*c*]chromen-3-one (3h)**



(2aR,8bS*)-1,1,2,2-Tetramethyl-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]chromen-3-one* ***(3h)*** 2*H*-Chromen-2-one (1 g, 6.84 mmol) and benzophenone (0.125 g, 0.684 mmol) were dissolved in dioxane (150mL) and argon was bubbled through solution for 10 minutes. Then 2,3-dimethylbut-2-ene (2.88 g, 34.2 mmol) was added and mixture was irradiated for 6 hours in pyrex glassware using medium pressure mercury lamp (125 W). Solvent was evaporated, crude product purified by column chromatography (hexane/ethyl acetate 10:1) and crystalized from hexane to give **3h** (500 mg, 2.171 mmol, 32% yield). M.p. > 320 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.20 (ddd, J = 7.9, 1.7, 0.7 Hz, 1H), 7.07 (td, J = 7.4, 1.2 Hz, 1H), 7.01 - 6.97 (m, 2H), 3.37 (d, J = 9.7 Hz, 2H), 3.19 (d, J = 9.7 Hz, 2H), 1.26 (s, 3H), 1.21 (s, 3H), 1.01 (s, 3H), 0.75 (s, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 167.24, 151.62, 129.19, 128.18, 124.15, 120.55, 117.10, 45.22, 44.52, 43.07, 41.45, 26.31, 26.01, 21.34, 20.86. HRMS (ESI+) Calcd for $C_{15}H_{18}O_2$ $[M+Na]^+$: 253.11990; found: m/z 253.12021. UV-VIS (acetonitrile): 271, 279 nm.

Dimethyl (1*R,2*S**,3*R**,4*S**)-3,4-bis(4-methoxyphenyl)cyclobutane-1,2-dicarboxylate (3i)**

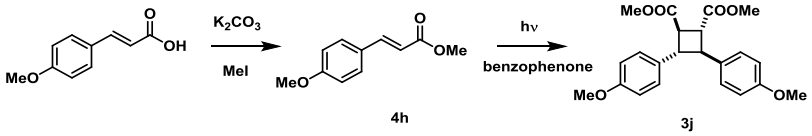


Dimethyl (1R,2S*,3R*,4S*)-3,4-bis(4-methoxyphenyl)cyclobutane-1,2-dicarboxylate* ***(3i)***

3e (850 mg, 2.51 mmol) was dissolved in MeOH (5 mL). Solution of potassium hydroxide (282 mg, 5.02 mmol) in MeOH (5 mL) was added. White precipitate formed immediately. Solids were separated, dissolved in water (2 mL) and dichloromethane (2 mL). Solution was acidified using concentrated HCl. Mixture was stirred for 20 minutes, organic part was separated, water phase was washed with dichloromethane. Organic part was dried with magnesium sulfate and evaporated to give crude acid **S6** (850 mg) which was used in following step without purification. **S6** (480 mg, 1.347 mmol) was suspended in dichloromethane (3 mL) and oxalyl dichloride (289 µl, 3.37 mmol) was added. Reaction was started with 3 drops of DMF. When solution became homogenous, solution of methanol (272

µl, 6.73 mmol) in dichloromethane (3 mL) was added dropwise. Reaction was quenched by water, organic part separated, washed with saturated $NaHCO_3$, brine and dried with magnesium sulfate. Solvent evaporation gave orange oil, which was further purified by column chromatography (hexane/ethyl acetate 5:1). **3i** (310 mg, 0.806 mmol, 60% yield) was obtained as colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (d, *J* = 8.7 Hz, 4H), 6.66 (d, *J* = 8.8 Hz, 4H), 4.33 – 4.27 (m, 2H), 3.76 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 6H), 3.71 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.04, 157.98, 130.67, 128.81, 113.43, 55.11, 52.11, 44.32, 43.55. HRMS (ESI+) Calcd for $C_{22}H_{24}O_6$ [M+Na]$^+$: 407.14651; found: m/z 407.14693. UV-VIS (acetonitrile): 228, 278 nm.

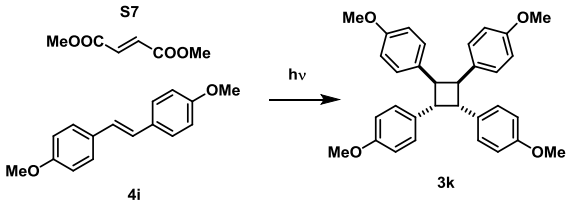
Dimethyl (1*R,2*R**,3*S**,4*S**)-3,4-bis(4-methoxyphenyl)cyclobutane-1,2-dicarboxylate (3j)**



*Methyl (E)-3-(4-methoxyphenyl)acrylate (**4h**)* To a suspension of (*E*)-3-(4-methoxyphenyl)acrylic acid (18.5 g, 104 mmol) and potassium carbonate (28.7 g, 208 mmol) in acetone (300 mL) dimethyl sulfate (19.69 mL, 208 mmol) was added. Mixture was heated to 50 °C overnight. Solids were filtered off, washed with ether. Filtrate was evaporated and crude product crystalized from diisopropyl ether to afford **4h** (14 g, 72.8 mmol, 70% yield). M.p. 89-92 °C . ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, J = 16.0 Hz, 1H), 7.55 - 7.42 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.31 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.75, 161.36, 144.51, 129.70, 127.09, 115.24, 114.30, 55.36, 51.57.

Dimethyl (1R,2R*,3S*,4S*)-3,4-bis(4-methoxyphenyl)cyclobutane-1,2-dicarboxylate (**3j**)*
Benzophenone (0.190 g, 1.041 mmol) and **4h** (1 g, 5.20 mmol) were dissolved in benzene (100 mL). Argon was bubbled through mixture for 10 mins followed by 20 hours of irradiation using medium pressure mercury arc lamp (125 W). Solvent removal and column chromatography (hexane/ethyl acetate 10:1) afforded starting material and mixture of **3i** and **3j**. **3j** (250 mg, 0.650 mmol, 25% yield) was obtained as an oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.20 (d, J = 8.7 Hz, 4H), 6.85 (d, J = 8.7 Hz, 4H), 3.79 (s, 3H), 3.73 (s, 3H), 3.59 (d, J = 9.6 Hz, 2H), 3.42 (d, J = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 173.07, 158.66, 133.07, 127.90, 113.97, 55.26, 52.15, 47.30, 44.55. HRMS (ESI+) Calcd for $C_{22}H_{24}O_6$ [M+Na]$^+$: 407.14651; found: m/z 407.14699. UV-VIS (acetonitrile): 280, 286 nm.

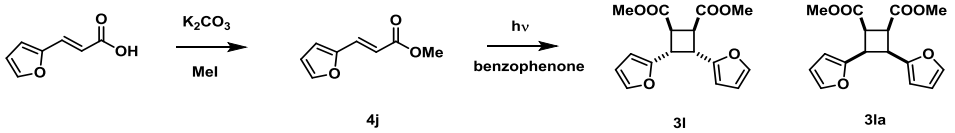
(1*R,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis(4-methoxyphenyl)cyclobutane (3k)**



*(Z)-1,2-Bis(4-methoxyphenyl)ethene (**4i**)* (4-Methoxybenzyl)triphenylphosphonium bromide (37.2 g, 80 mmol) was suspended in toluene (200 mL) and potassium 2-methylpropan-2-olate (10.81 g, 96 mmol) was added. Mixture was stirred at room temperature for 3 hours, followed by addition of 4-methoxybenzaldehyde (14.65 mL, 120 mmol). Solution was stirred overnight. Solvent was evaporated, hexane was added to precipitate triphenylphosphine oxide. Suspension was filtered and evaporated to give crude product, which was used in following isomeration reaction. Crude (*Z*)-1,2-bis(4-methoxyphenyl)-ethene (4 g, 16.65 mmol) was dissolved in THF (50 mL) and 1,2-diphenyldisulfane (0.727 g, 3.33 mmol) was added. Mixture was refluxed for 6 hours and evaporated. Crude product was purified by column chromatography (hexane/ethyl acetate 10:1). Pure **4i** (3 g, 12.48 mmol, 75% yield) was obtained as white crystals. M.p. 211-214 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 8.7 Hz, 4H), 6.93 (s, 2H), 6.89 (d, J = 8.7 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 158.96, 130.44, 127.39, 126.14, 114.07, 55.31.

(1R,2R*,3S*,4S*)-1,2,3,4-Tetrakis(4-methoxyphenyl)cyclobutane (**3k**)* (*E*)-1,2-Bis(4-methoxyphenyl)ethene (800 mg, 3.33 mmol) in benzene was irradiated in pyrex glassware using medium pressure mercury arc lamp (125 W) for 20 hours. Solvent was evaporated and crude yellow oil was purified by column chromatography (hexane/ethyl acetate 10:1). Beside starting material, **3k** (300 mg, 0.624 mmol, 19% yield) was obtained as an oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.01 (d, J = 8.7 Hz, 8H), 6.70 (d, J = 8.7 Hz, 8H), 4.30 (s, 4H), 3.72 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 157.60, 133.10, 129.08, 113.34, 55.10, 47.13. HRMS (ESI+) Calcd for $C_{22}H_{24}O_6$ $[M+Na]^+$: 503.21687; found: m/z 503.21599. UV-VIS (acetonitrile): 281, 287 nm.

Dimethyl (1*R,2*S**,3*R**,4*S**)-3,4-bis(furan-2-yl)cyclobutane-1,2-dicarboxylate (3l)**



*Methyl (E)-3-(furan-2-yl)acrylate (**4j**)* (*E*)-3-(furan-2-yl)acrylic acid (10 g, 72.4 mmol) and potassium carbonate (20.01 g, 145 mmol) were suspended in acetone (150 mL) and dimethyl sulfate (13.73 mL, 145 mmol) was added. Mixture was heated to 50 °C overnight. Solids were filtered off, filtrate evaporated. Residual was dissolved in dichloromethane and washed with water, brine and evaporated to give **4j** (8.5 g, 55.9 mmol, 77% yield) as yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 (dt, J = 1.8, 0.6 Hz, 1H), 7.43 (d, J = 15.7 Hz, 1H), 7.26 (s, 0H), 6.61 (dd, J = 3.4, 0.6 Hz, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H), 6.31 (d, J = 15.7 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.46, 150.85, 144.71, 131.17, 115.43, 114.76, 112.24, 51.64.

Dimethyl (1R,2S*,3R*,4S*)-3,4-di(furan-2-yl)cyclobutane-1,2-dicarboxylate (**3l**)* Methyl (*E*)-3-(furan-2-yl)acrylate (**4j**, 1.5 g, 9.86 mmol) and benzophenone (0.15 g, 0.823 mmol) were dissolved in acetonitrile (150 mL). Solution was irradiated in pyrex glassware using medium pressure mercury acr lamp (125W) for 6 hours. Solvent was evaporated and residual was purified by column chromatography (hexane/ethyl acetate 10:1). The obtained mixture of isomers **3l** and **3la** was separated by column chromatography (hexane/ethyl acetate 20:1). Pure **3l** (170 mg, 0.559 mmol, 6% yield) was obtained. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (dd, J = 1.8, 0.8 Hz, 2H), 6.30 (dd, J = 3.2, 1.9 Hz, 2H), 6.16 (dd, J = 3.2, 0.8 Hz, 2H), 3.77 (d, J = 9.6 Hz, 2H), 3.73 (s, 6H), 3.54 (d, J = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.46, 148.34, 137.47, 105.61, 101.92, 47.49, 38.27, 34.88. HRMS (ESI+) Calcd for $C_{16}H_{16}O_6$ $[M+Na]^+$ 327.08391, found: 327.08395 m/z. UV-VIS (acetonitrile): 223 nm.

S3 [2+2] cycloreversion reactions catalyzed by 1+TfOH

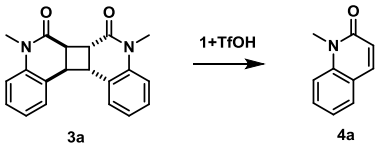
General procedure for cycloreversions on analytical scale

Cyclobutane derivative (0.02 mmol) and riboflavine tetraacetate (**1**, usually 0.001 mmol, 2.5 mol %) were placed in Schlenk tube, anhydrous acetonitrile (0.9 mL) and 0.1 mL of 0.1M triflic acid in acetonitrile were added. Homogenous solution was three-times degassed using freeze-pump-thaw technique. The mixture was irradiated (LED, 400 nm) for given time depending on cyclobutane substrate (usually 10 min). The reaction mixture was analyzed by ^{1}H NMR.

General procedure for cycloreversions on preparative scale

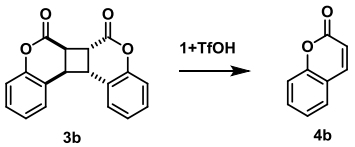
Cyclobutane derivative (0.4 mmol) and riboflavine tetraacetate (**1**, 0.02 mmol, 5 mol %) were placed in Schlenk tube, anhydrous acetonitrile (19.8 mL) and 0.2 mL of 1M triflic acid in acetonitrile were added. Homogenous solution was three-times degassed using freeze-pump-thaw technique. Mixture tube was irradiated (LED, 400 nm) for given time depending on cyclobutane substrate. After irradiation, solvent was removed and crude product was purified by column chromatography to give pure product in good to high yields.

*1-Methylquinolin-2(1H)-one (**4a**)*



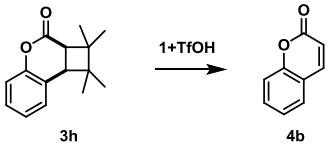
Solution containing **3a** (127 mg, 0.4 mmol) and **1** (10.89 mg, 0.020 mmol) was irradiated with LED (400 nm) for 10 minutes. Crude product was purified by column chromatography (dichloromethane) to afford **4a** (118 mg, 0.741 mmol, 93% yield). M.p. 72-75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 9.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.36 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.71 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.52, 140.22, 139.15, 130.83, 128.94, 122.29, 121.92, 120.86, 114.34, 29.60.

*2H-Chromen-2-one (**4b**) from **3b***



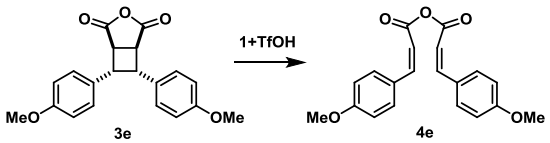
Solution containing **3b** (0.117 g, 0.400 mmol), **1** (10.90 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 10 minutes using LED (400 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 1:1) to afford **4b** (105 mg, 0.718 mmol, 90% yield). M.p. 69-71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 9.6, 0.6 Hz, 1H), 7.60 – 7.44 (m, 2H), 7.39 – 7.26 (m, 3H), 6.43 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.76, 154.05, 143.39, 131.82, 127.83, 124.40, 118.82, 116.92, 116.72.

*2H-Chromen-2-one (**4b**) from **3h***



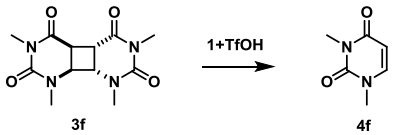
Solution containing **3h** (92 mg, 0.4 mmol), **1** (10.90 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 240 minutes using LED (400 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 1:1) to afford **4b** (40 mg, 0.274 mmol, 68% yield). M.p. 69-71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 9.6, 0.6 Hz, 1H), 7.60 – 7.44 (m, 2H), 7.39 – 7.26 (m, 3H), 6.43 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.76, 154.05, 143.39, 131.82, 127.83, 124.40, 118.82, 116.92, 116.72.

*(Z)-3-(4-Methoxyphenyl)acrylic anhydride (**4e**)*



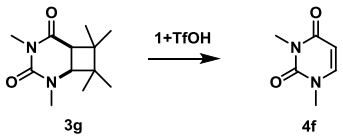
Solution containing **3e** (0.135 g, 0.4 mmol), **1** (10.90 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 30 minutes using LED (400 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4e** (0.111 g, 0.328 mmol, 78% yield). Polymerization of anhydride was observed. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 6.88 – 6.77 (m, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 4.35 – 4.28 (m, 2H), 3.81 (dd, *J* = 5.5, 1.8 Hz, 2H), 3.70 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.27, 158.08, 130.31, 128.80, 113.52, 55.11, 44.11, 43.86.

*1,3-Dimethylpyrimidine-2,4(1H,3H)-dione (**4f**)*



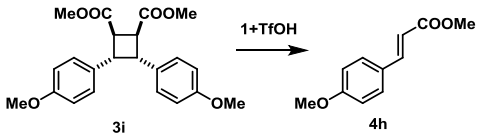
Solution containing **3f** (0.115 g, 0.410 mmol), **1** (0.011 g, 0.021 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 10 minutes. Crude product was purified by column chromatography (dichloromethane/methanol 10:1) to afford **4f** (0.108 g, 0.771 mmol, 94 % yield). M.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 7.9 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 151.92, 142.66, 101.38, 37.02, 27.75.

*1,3-Dimethylpyrimidine-2,4(1H,3H)-dione (**4f**)*



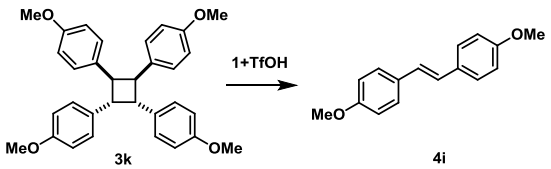
Solution containing **3g** (90 mg, 0.401 mmol), **1** (10.92 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 120 minutes. Crude product was purified by column chromatography (dichloromethane/methanol 10:1) to afford **4f** (35 mg, 0.250 mmol, 62% yield). M.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 7.9 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 151.92, 142.66, 101.38, 37.02, 27.75.

*Methyl (E)-3-(4-methoxyphenyl)acrylate (**4h**)*



Solution containing **3i** (0.154 g, 0.4 mmol), **1** (10.90 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 30 minutes. Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4h** (0.066 g, 0.344 mmol, 86% yield). M.p. 89-92 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.52 – 7.40 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.75, 161.36, 144.51, 129.70, 127.09, 115.24, 114.30, 55.36, 51.57.

*(E)-1,2-Bis(4-methoxyphenyl)ethene (**4i**)*



Solution containing **3k** (0.192 g, 0.4 mmol), **1** (10.90 mg, 0.020 mmol) and trifluoromethanesulfonic acid (0.200 mL, 0.200 mmol) was irradiated for 30 minutes. Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4i** (0.086 g, 0.356 mmol, 89% yield) containing 10% of Z-isomer. M.p. 211-214 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.7 Hz, 4H), 6.93 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.96, 130.44, 127.39, 126.14, 114.07, 55.32. Z-isomer: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (d, J = 7.8 Hz, 4H), 6.78 (d, J = 7.8 Hz, 4H), 6.46 (s, 2H), 3.80 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-d) δ 158.4, 130.0, 129.9, 128.3, 113.5, 55.2.

S4 [2+2] cycloreversion reactions catalyzed by 2c

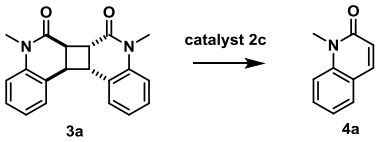
General procedure for cycloreversions on analytical scale

Cyclobutane derivative (0.02 mmol) and 5-ethyl-1,3-dimethyl-8-trifluoromethylalloxazinium perchlorate (**2c**; 0.001 mmol, 2.5 mol %) were placed in Schlenk tube and anhydrous acetonitrile (1 mL) was added. Homogenous solution was three-times deggased using freeze-pump-thaw technique. Solution in Schlenk tube was irradiated (LED, 450 nm) for given time depending on cyclobutane substrate (usually 10 min). The reaction mixture was analyzed by ^{1}H NMR.

General procedure for cycloreversions on preparative scale

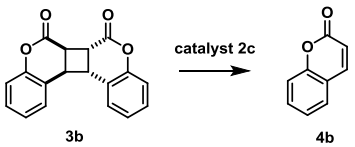
Cyclobutane derivative (0.4 mmol) and 5-ethyl-1,3-dimethyl-8-trifluoromethylalloxazinium perchlorate (**2c**; 0.02 mmol, 5 mol %) were placed in Schlenk tube and anhydrous acetonitrile (20 mL) was added. Homogenous solution was three-times deggased using freeze-pump-thaw technique. Solution in Schlenk tube was irradiated (LED, 450 nm) for given time depending on cyclobutane substrate. After irradiation, solvent was removed and crude product purified by column chromatography to give pure product in good to high yield.

*1-Methylquinolin-2(1H)-one (**4a**)*



Solution containing **2c** (8.77 mg, 0.020 mmol) and **3a** (0.127 g, 0.4 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column cromatography (dihloromethane/methanol 20:1) to afford **4a** (0.056 g, 0.352 mmol, 88% yield). M.p. 72-75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 9.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.36 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.71 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.52, 140.22, 139.15, 130.83, 128.94, 122.29, 121.92, 120.86, 114.34, 29.60.

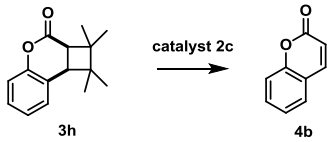
*2H-Chromen-2-one (**4b**) from **3b***



Solution containing **2c** (8.77 mg, 0.020 mmol) and **3b** (0.117 g, 0.4 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by

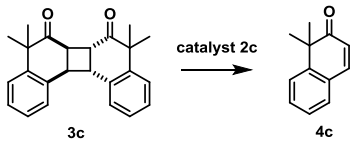
column chromatography (hexane/ethyl acetate 1:1) to afford **4b** (0.108 g, 0.736 mmol, 92% yield). M.p. 69-71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 9.6, 0.6 Hz, 1H), 7.60 – 7.44 (m, 2H), 7.39 – 7.26 (m, 3H), 6.43 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.76, 154.05, 143.39, 131.82, 127.83, 124.40, 118.82, 116.92, 116.72.

*2H-Chromen-2-one (**4b**) from **3h***



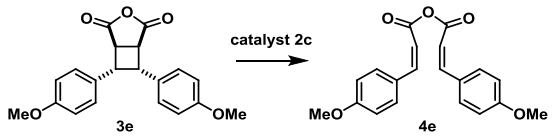
Solution containing **2c** (8.77 mg, 0.020 mmol) and **3h** (0.092 g, 0.4 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 1:1) to afford **4b** (0.029 g, 0.200 mmol, 50% yield). M.p. 69-71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 9.6, 0.6 Hz, 1H), 7.60 – 7.44 (m, 2H), 7.39 – 7.26 (m, 3H), 6.43 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.76, 154.05, 143.39, 131.82, 127.83, 124.40, 118.82, 116.92, 116.72.

*1,1-Dimethylnaphthalen-2(1H)-one (**4c**)*



Solution containing **2c** (8.77 mg, 0.020 mmol) and **3c** (0.138 g, 0.4 mmol) in nitromethane (20 mL) was irradiated for 240 minutes using LED (450 nm). Crude product was purified by column chromatography (hexane/ethylacetate 10:1) to afford **4c** (0.072 g, 0.416 mmol, 52% yield). M.p. 71-74 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.28 (m, 8H), 4.19 – 4.09 (m, 2H), 3.81 (dt, *J* = 8.4, 1.4 Hz, 2H), 1.58 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.94, 139.99, 132.63, 123.97, 123.47, 123.30, 121.50, 44.63, 43.54, 38.14, 25.04, 17.23.

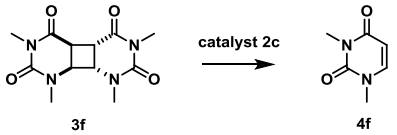
*(Z)-3-(4-Methoxyphenyl)acrylic anhydride (**4e**)*



Solution containing **3e** (0.135 g, 0.4 mmol) and **2c** (8.77 mg, 0.020 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4e** (0.111 g, 0.328 mmol, 86%

yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 6.88 – 6.77 (m, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 4.35 – 4.28 (m, 2H), 3.81 (dd, *J* = 5.5, 1.8 Hz, 2H), 3.70 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.27, 158.08, 130.31, 128.80, 113.52, 55.11, 44.11, 43.86.

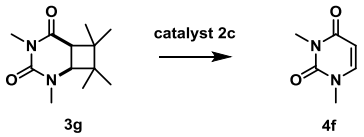
*1,3-Dimethylpyrimidine-2,4(1H,3H)-dione (**4f**) from **3f***



3f 4f

Solution containing **3f** (112 mg, 0.4 mmol) and **2c** (8.77 mg, 0.020 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column chromatography (dichloromethane/methanol 10:1) to afford **4f** (102 mg, 0.728 mmol, 91% yield). M.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 7.9 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 151.92, 142.66, 101.38, 37.02, 27.75.

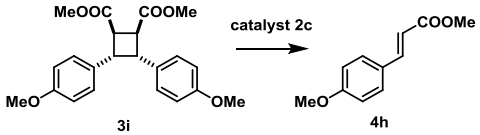
*1,3-Dimethylpyrimidine-2,4(1H,3H)-dione (**4f**) from **3g***



3g 4f

Solution containing **3g** (0.090 g, 0.4 mmol) and **2c** (8.77 mg, 0.020 mmol) in acetonitrile (20 mL was irradiated for 120 minutes using LED (450 nm). Crude product was purified by column chromatography (dichloromethane/methanol 10:1) to affrod **4f** (0.042 g, 0.300 mmol, 75% yield). M.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 7.9 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35, 151.92, 142.66, 101.38, 37.02, 27.75.

*Methyl (E)-3-(4-methoxyphenyl)acrylate (**4h**)*

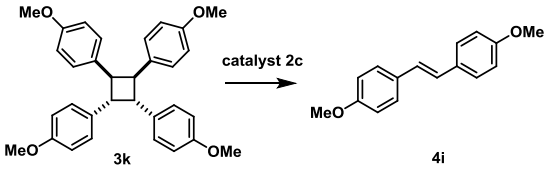


3i 4h

Solution containing **2c** (8.77 mg, 0.020 mmol) and **3i** (0.154 g, 0.4 mmol) in acetonitrile (20 mL was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4h** (0.145 g, 0.752 mmol, 94% yield). M.p. 89-92 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.52 – 7.40 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H).

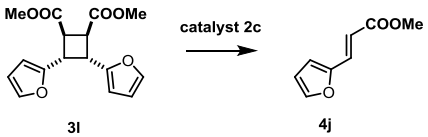
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.75, 161.36, 144.51, 129.70, 127.09, 115.24, 114.30, 55.36, 51.57.

*(E)-1,2-Bis(4-methoxyphenyl)ethene (**4i**)*



Solution containing **3k** (192 mg, 0.4 mmol) and **2c** (8.77 mg, 0.020 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product chromatographed using hexane/ethylacetate 10:1 to give pure (E)-1,2-bis(4-methoxyphenyl)ethene **4i** (143mg, 0.595 mmol, 88% yield) containing 10% of Z-isomer. M.p. 211-214 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.7 Hz, 4H), 6.93 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.96, 130.44, 127.39, 126.14, 114.07, 55.32. Z-isomer: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (d, J = 7.8 Hz, 4H), 6.78 (d, J = 7.8 Hz, 4H), 6.46 (s, 2H), 3.80 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-d) δ 158.4, 130.0, 129.9, 128.3, 113.5, 55.2.

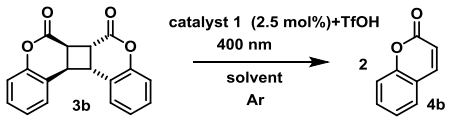
*Methyl (E)-3-(furan-2-yl)acrylate (**4j**)*



Solution containing **2c** (8.77 mg, 0.020 mmol) and **3l** (0.122 g, 0.4 mmol) in acetonitrile (20 mL) was irradiated for 30 minutes using LED (450 nm). Crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to afford **4j** (0.105 g, 0.688 mmol, 86% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 (dt, J = 1.8, 0.6 Hz, 1H), 7.43 (d, J = 15.7 Hz, 1H), 6.61 (dd, J = 3.4, 0.6 Hz, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H), 6.31 (d, J = 15.7 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.46, 150.85, 144.71, 131.17, 115.43, 114.76, 112.24, 51.64.

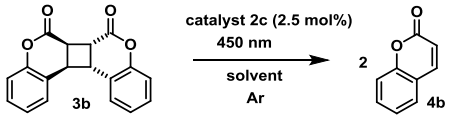
S5 Solvent screening in cycloreversion reactions

Solvent screening was done under conditions of experiments on analytical scale, see S2 and S3 for General procedure.



Solvent	Conversion (10 min)
Acetonitrile	100
$CHCl_3$	8
DMF	0
Dioxane	0
Acetone	24
Toluene	0
MeOH	0
$MeNO_2$	100
Dichloromethane	40

Reaction conditions: **3b** (0.02 mmol), photocatalyst (2.5 mol%), TfOH (0.01 mmol), solvent (1 mL), visible light, rt, Ar.

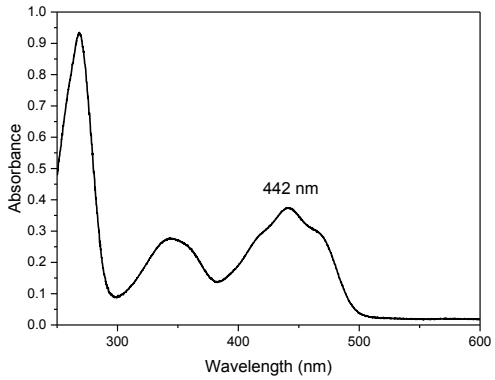


Solvent	Conversion (10 min)
Acetonitrile	100
$CHCl_3$	6
DMF	11
Dioxane	0
Acetone	12
Toluene	6
MeOH	3
$MeNO_2$	85
Dichloromethane	5

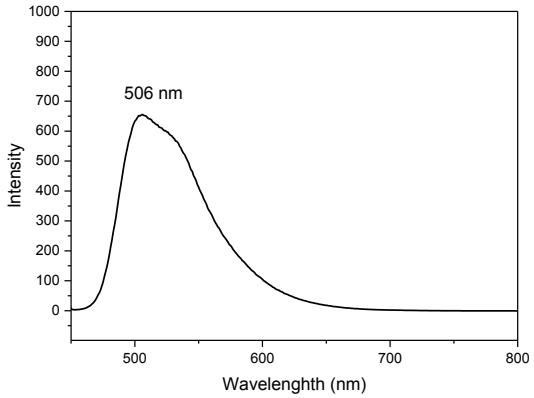
Reaction conditions: **3b** (0.02 mmol), photocatalyst (2.5 mol%), solvent (1 mL), visible light, rt, Ar.

S6 UV-VIS and fluorescence spectra of the catalysts

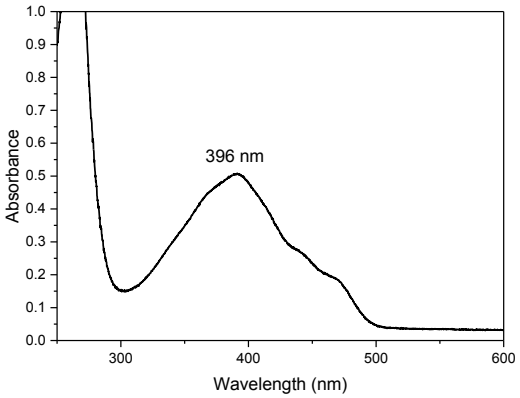
UV-VIS spectrum of **1** in acetonitrile (c(**1**) = 1 × 10^{-5} M)



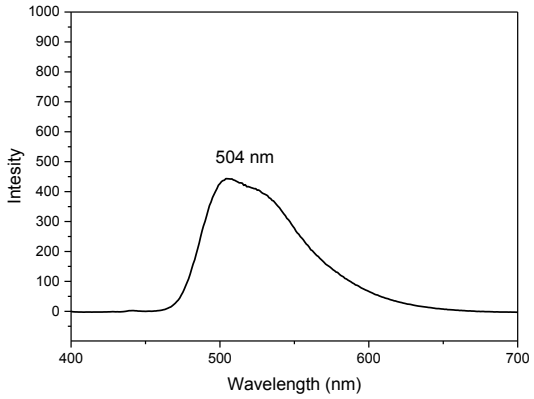
Fluorescence spectrum of **1** in acetonitrile (c(**1**) = 1 × 10^{-6} M)



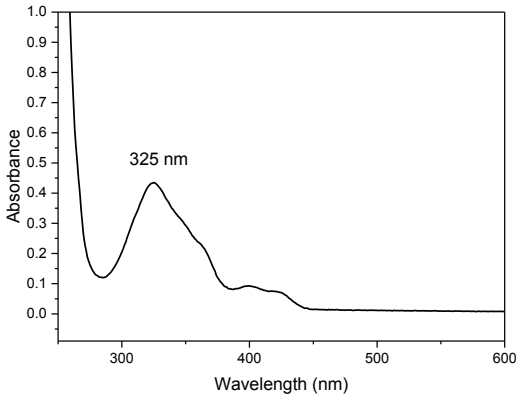
UV-VIS spectrum of **1**+**TfOH** in acetonitrile (c(**1**) = 1 × 10^{-5} M; c(TfOH) = 0.01 M)



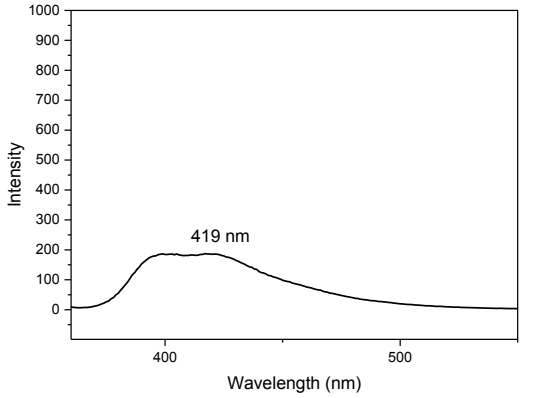
Fluorescence spectrum of **1**+**TfOH** in acetonitrile (c(**1**) = 1 × 10^{-5} M; c(TfOH) = 0.01 M)



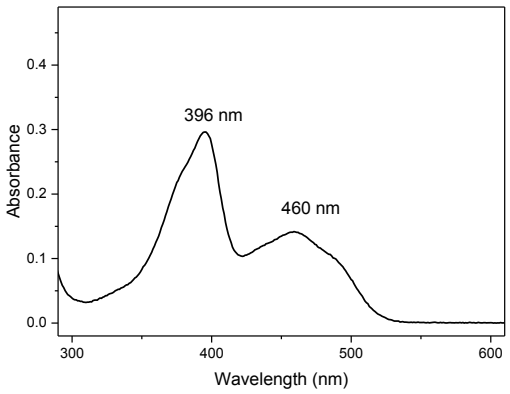
UV-VIS spectrum of **5**+**TfOH** in acetonitrile (c(**5**) = 1 × 10^{-5} M; c(TfOH) = 0.01 M)



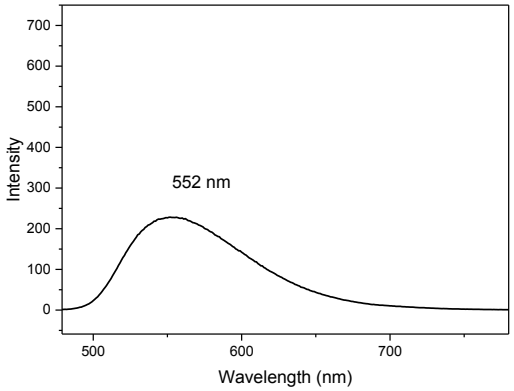
Fluorescence spectrum of **5**+**TfOH** in acetonitrile (c(**5**) = 1 × 10^{-5} M; c(TfOH) = 0.01 M)



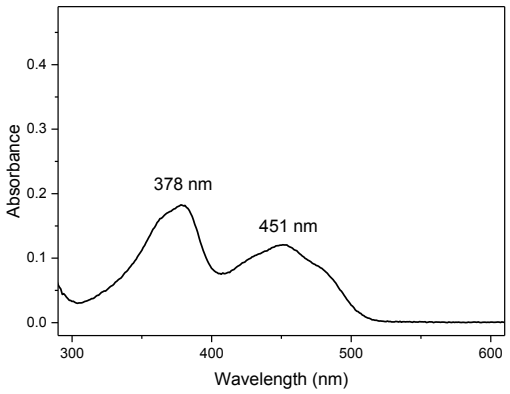
UV-VIS spectrum of **2a** in acetonitrile (c(**2a**) = 3.75 × 10^{-5} M)



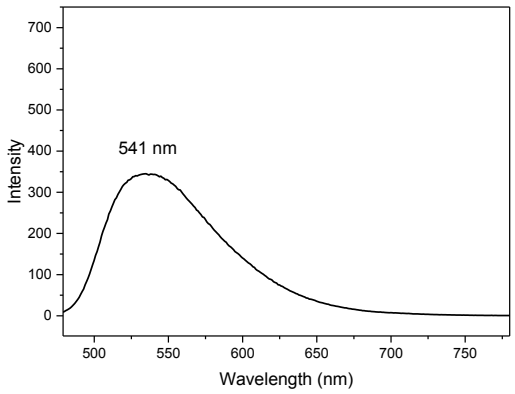
Fluorescence spectrum of **2a** in acetonitrile (c(**2a**) = 2.5 × 10^{-5} M)



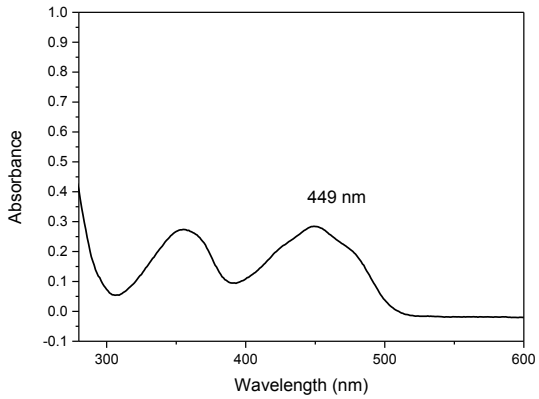
UV-VIS spectrum of **2b** in acetonitrile (c(**2b**) = 3.75 × 10^{-5} M)



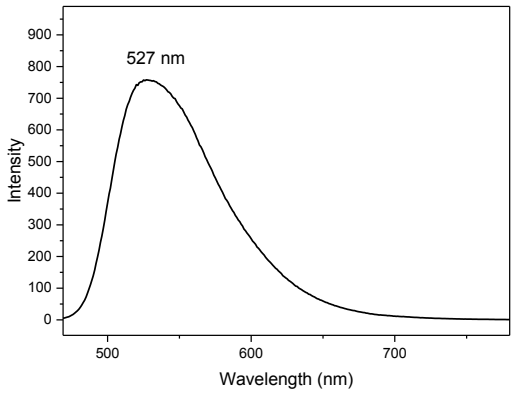
Fluorescence spectrum of **2b** in acetonitrile (c(**2b**) = 2.5 × 10^{-5} M)



UV-VIS spectrum of **2c** in acetonitrile (c(**2c**) = 3.75 × 10^{-5} M)



Fluorescence spectrum of **2c** in acetonitrile (c(**1**) = 2.5 × 10^{-5} M)

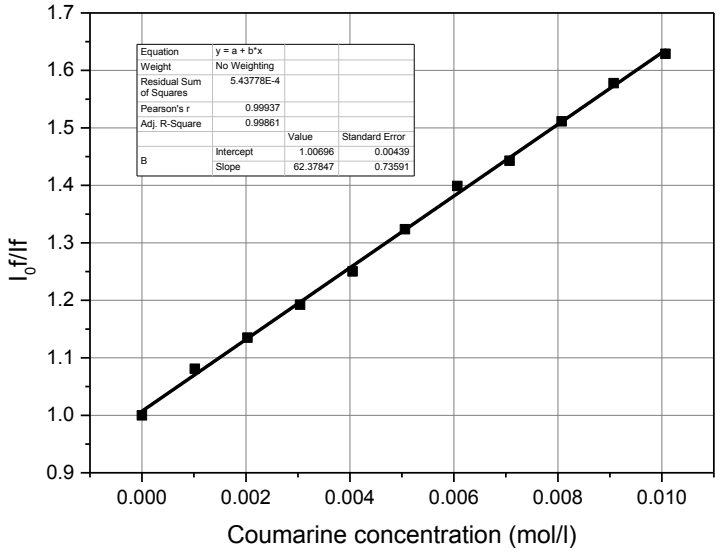


S7 Fluorescence quenching of catalysts 1 and 2 with selected cyclobutanes 3a, 3b

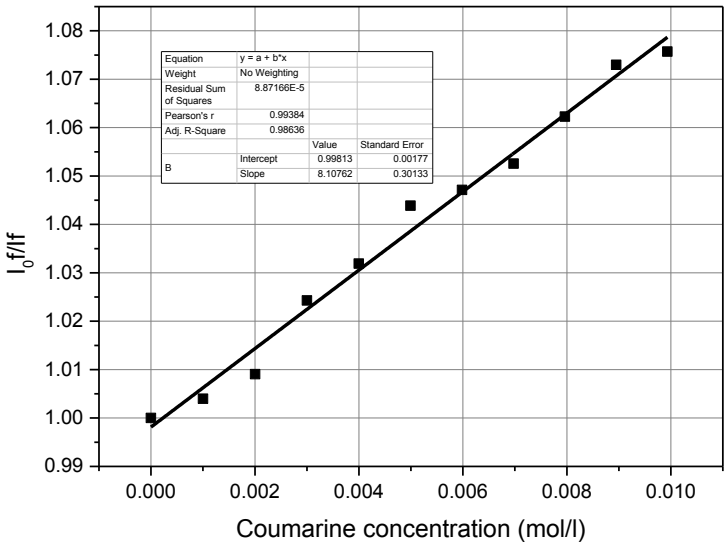
Stern-Volmer constants K_S for the electron transfer from **3a** or **3b** to flavin **1** (in the presence of TfOH, *c*(TfOH = 0.01 M) and **2** in acetonitrile.

catalyst	Quencher	*K*s (L mol^{-1})
1+TfOH	**3b**	62
2a	**3b**	8
2b	**3b**	16
2c	**3b**	29
2c	**3a**	65

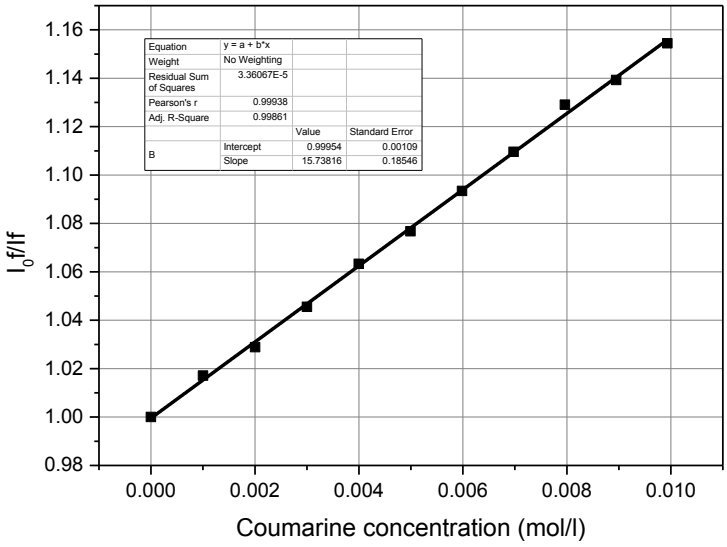
Quenching of **1** with **3b**



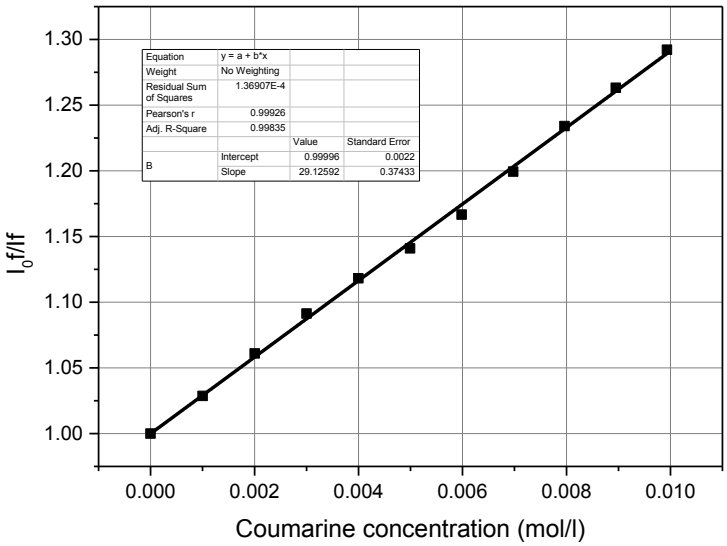
Quenching of **2a** with **3b**



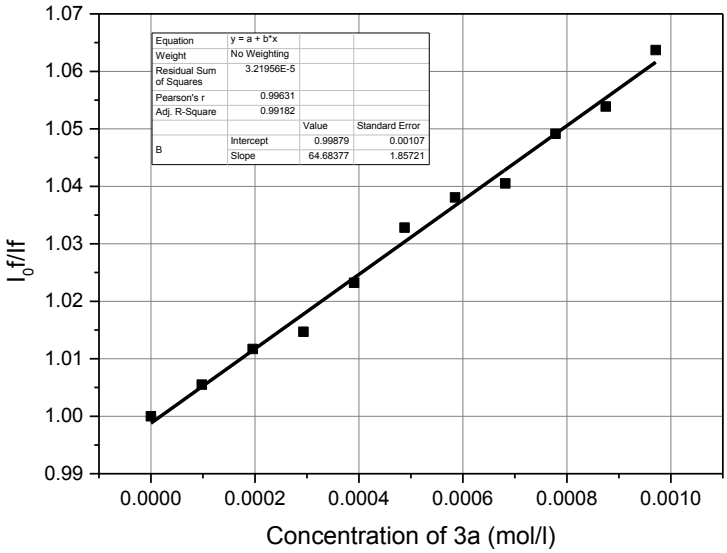
Quenching of **2b** with **3b**



Quenching of **2c** with **3b**



Quenching of **2c** with **3a**



S8 Experimental setup for cycloreversion reaction under sunlight

Cycloreversion experiment using sunlight: Prague, Czech Republic, 19.5.2016 9:30-9:45 am. GPS: N 50.101728, E 014.389929.

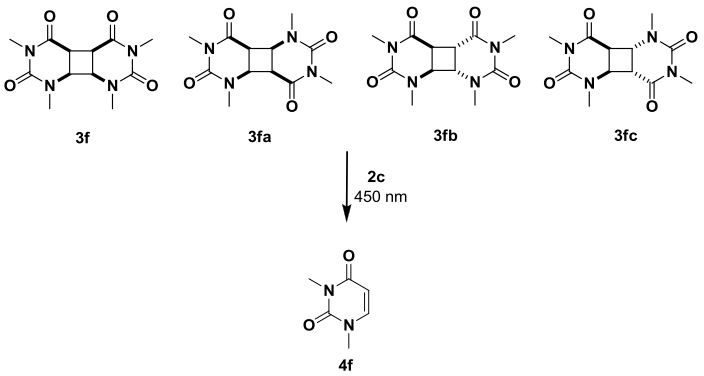
S9 Effect of oxygen concentration on cycloreversion reaction with 2c

Entry	Cyclobutane	Time [min]	Catalyst	Conversion [%]		
				Deggased under Ar[a]	Air[b]	O_2 [c]
1	**3b**	2	**2c**	49	45	47
2	**3f**	4	**2c**	79	79	85

Reaction conditions: **3b** (0.02 mmol), photocatalyst (2.5 mol%), solvent (1 mL), visible light, rt.

[a] Three-times degassed using freeze-pump-thaw technique; [b] Experiment under air; [c] Bubbled with oxygen (2 min) before irradiation.

S10 Cycloreversion of isomeric pyrimidine dimers



Entry	Cyclobutane	Conv. (3 min) [%]
1	**3f**	30
2	**3fa**	17
3	**3fb**	20
4	**3fc**	36

Quantitative conversion was observed within 30 minutes for all isomers

S11 Stern-Volmer plots for quenching of 3b-cycloreversion catalyzed by 2c

Reaction conditions: **3b** (0.02 mmol), **2c** (2.5 mol %), quencher (various concentrations), acetonitrile (1 mL), visible light (450 nm), rt, Ar, 2 min.

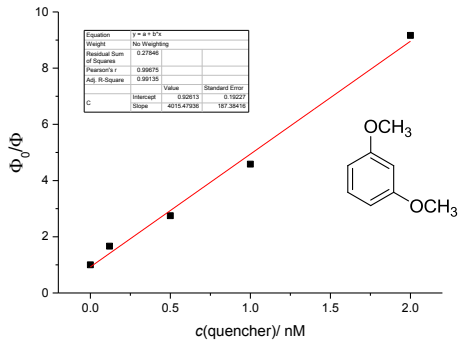


Figure S11-1a

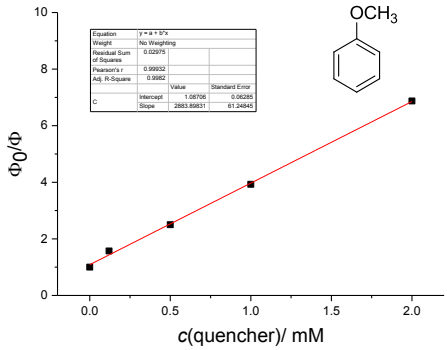


Figure S11-1b

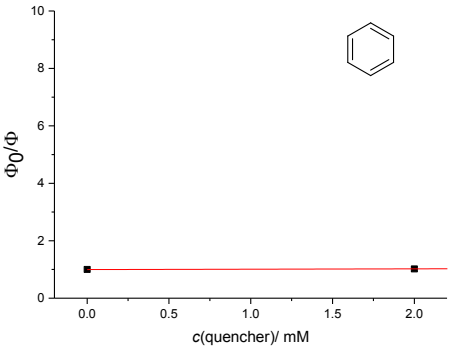


Figure S11-1c

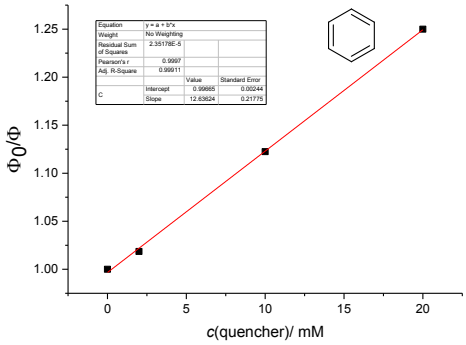


Figure S11-1d

Effective quenching of **3b**-photocycloreversion mediated by catalyst **2c** was observed using quenchers (anisole and 1,3-dimethoxybenzene) with lower oxidation potentials[11] compared to **3b** (E^{ox} = 2.05 V vs SCE). On the other hand benzene[12] having higher oxidation potential did not almost cause quenching of photocycloreversion (see Figure S11-2).

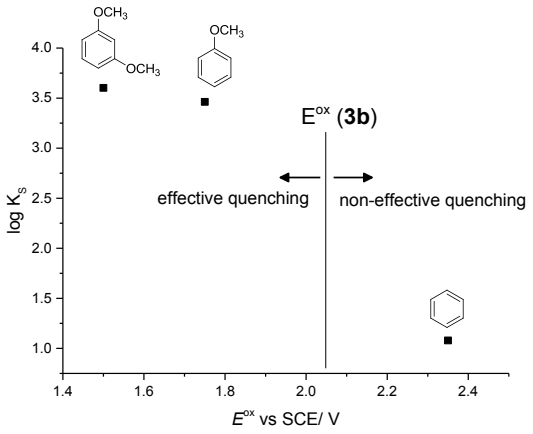
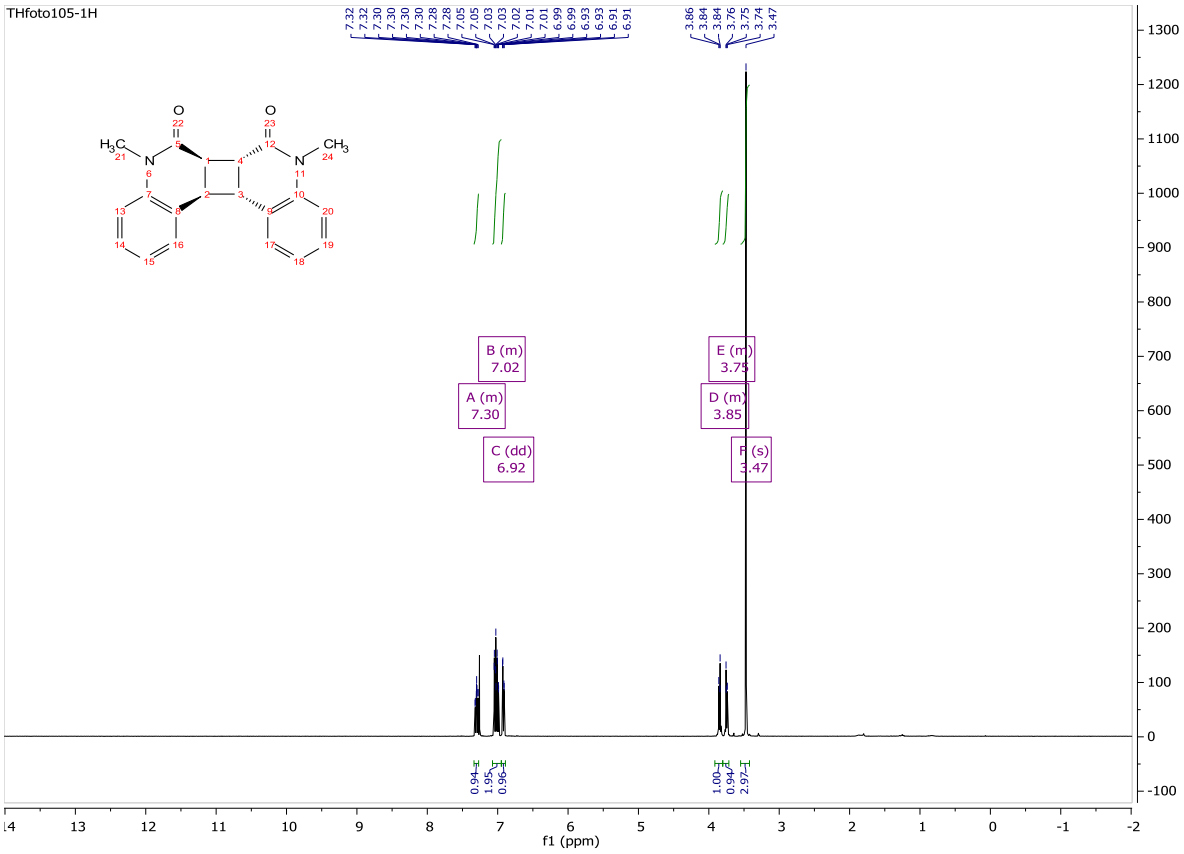


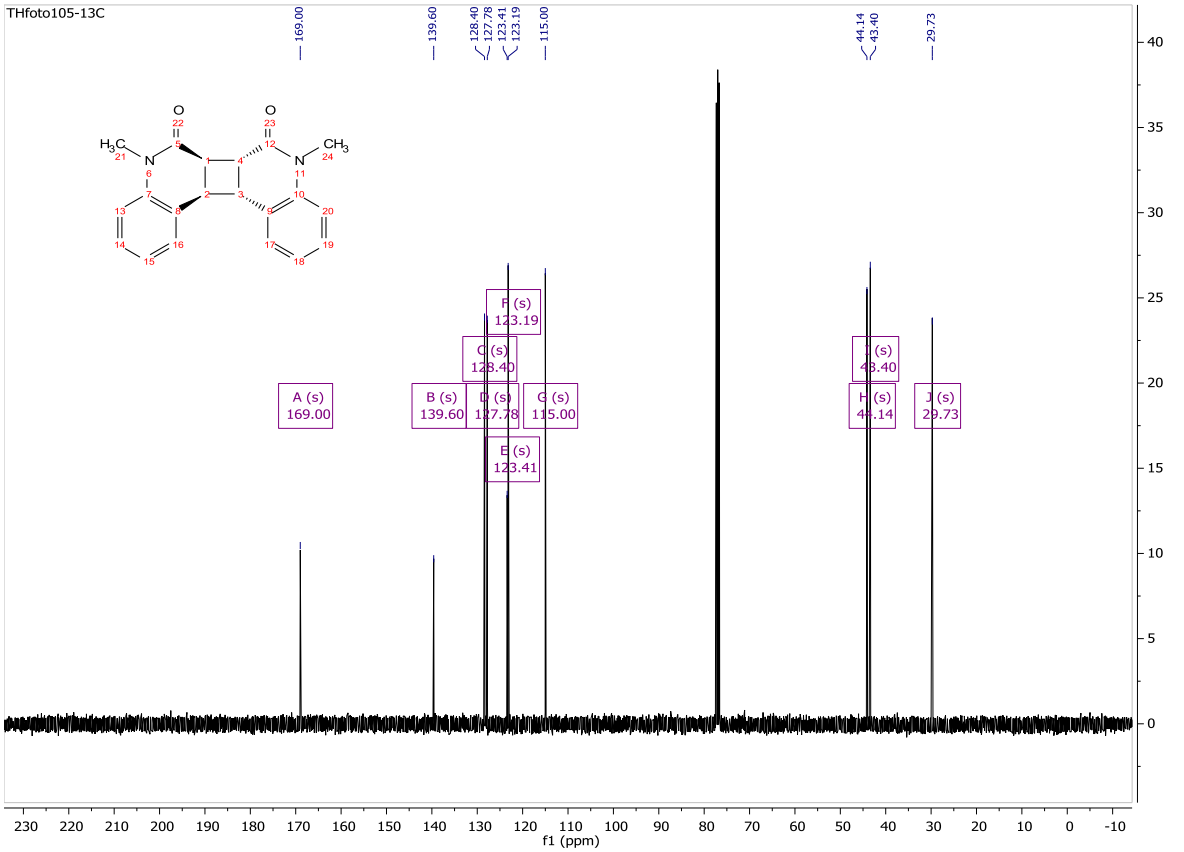
Figure S11-2

[11] Porcal, G.; Bertolotti, S. G.; Previtali, C. M.; Encinas, M. V. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4123.
[12] Fukuzumi, S.; Okhubo, K.; Suenobu, T.; Kato, K.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 8459.

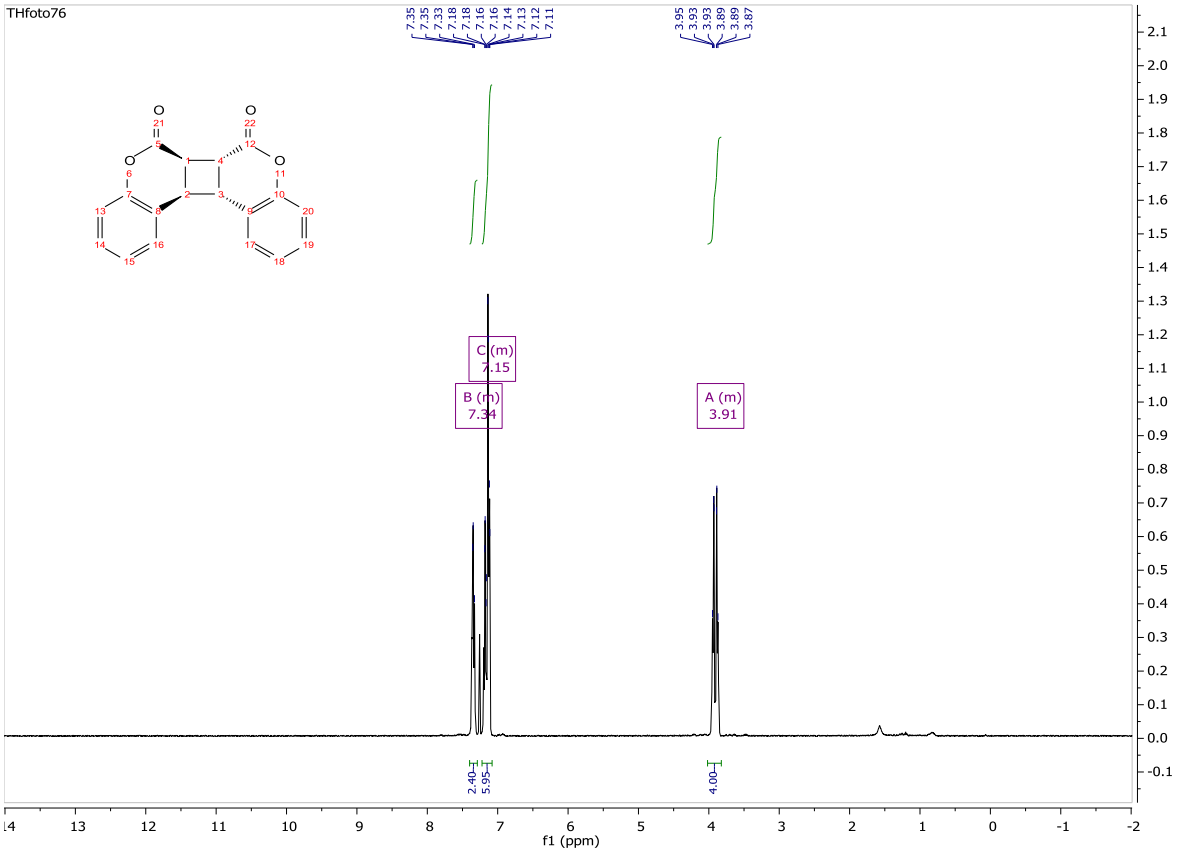
S12 Copy of NMR Spectra of compounds 3

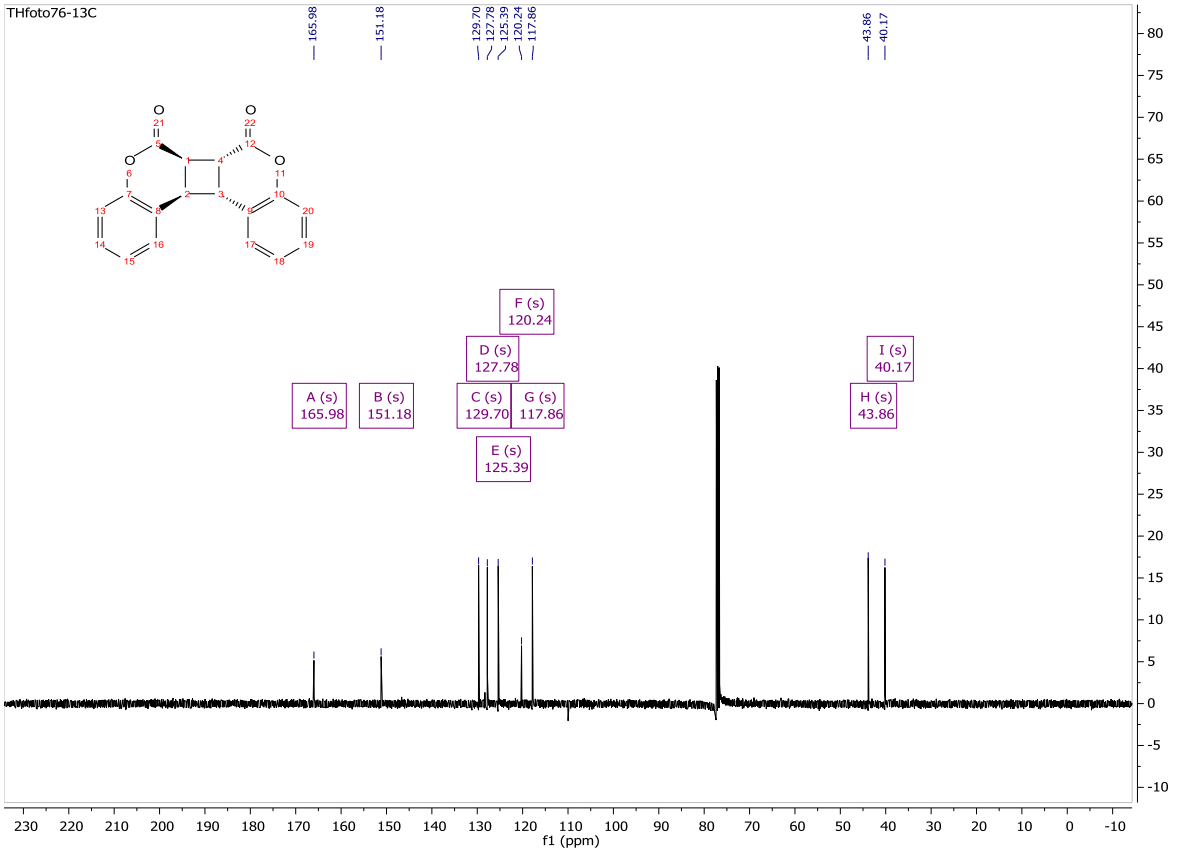
3a



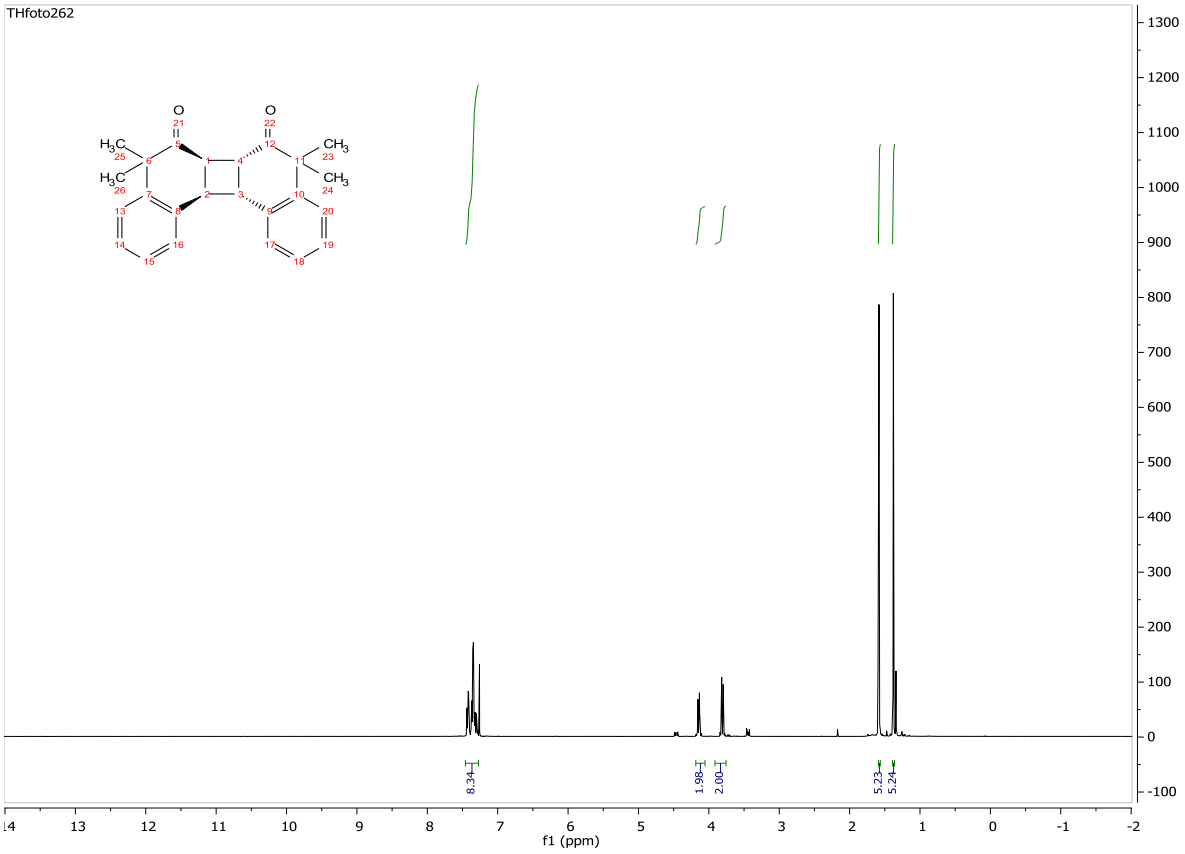


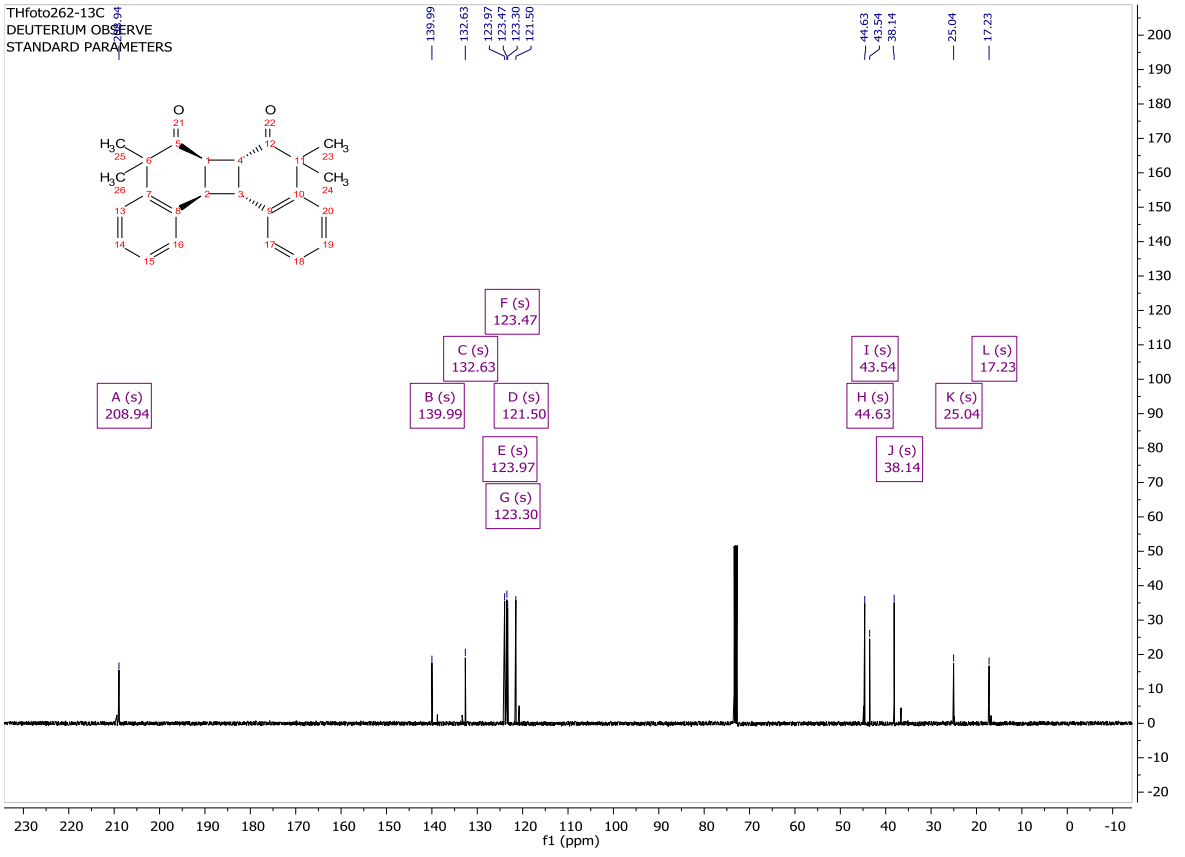
3b


THfoto76
7.35
7.35
7.33
7.18
7.18
7.16
7.16
7.14
7.13
7.12
7.11
3.95
3.93
3.93
3.89
3.89
3.87
C (m)
7.15
B (m)
7.34
A (m)
3.91
2.40
5.95
4.00
f1 (ppm)

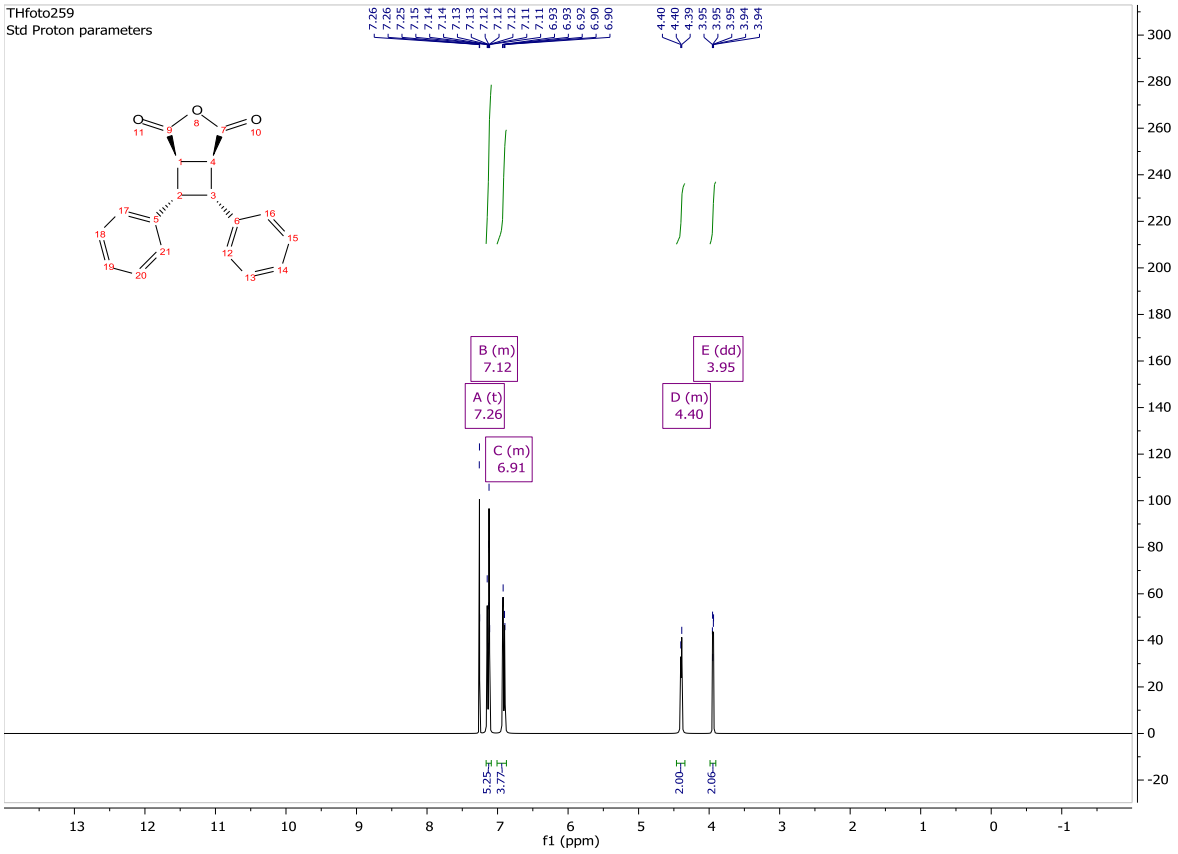

THfoto76-13C
165.98
151.18
129.70
127.78
125.39
120.24
117.86
43.86
40.17
F (s)
120.24
D (s)
127.78
I (s)
40.17
A (s)
165.98
B (s)
151.18
C (s)
129.70
G (s)
117.86
H (s)
43.86
E (s)
125.39
f1 (ppm)

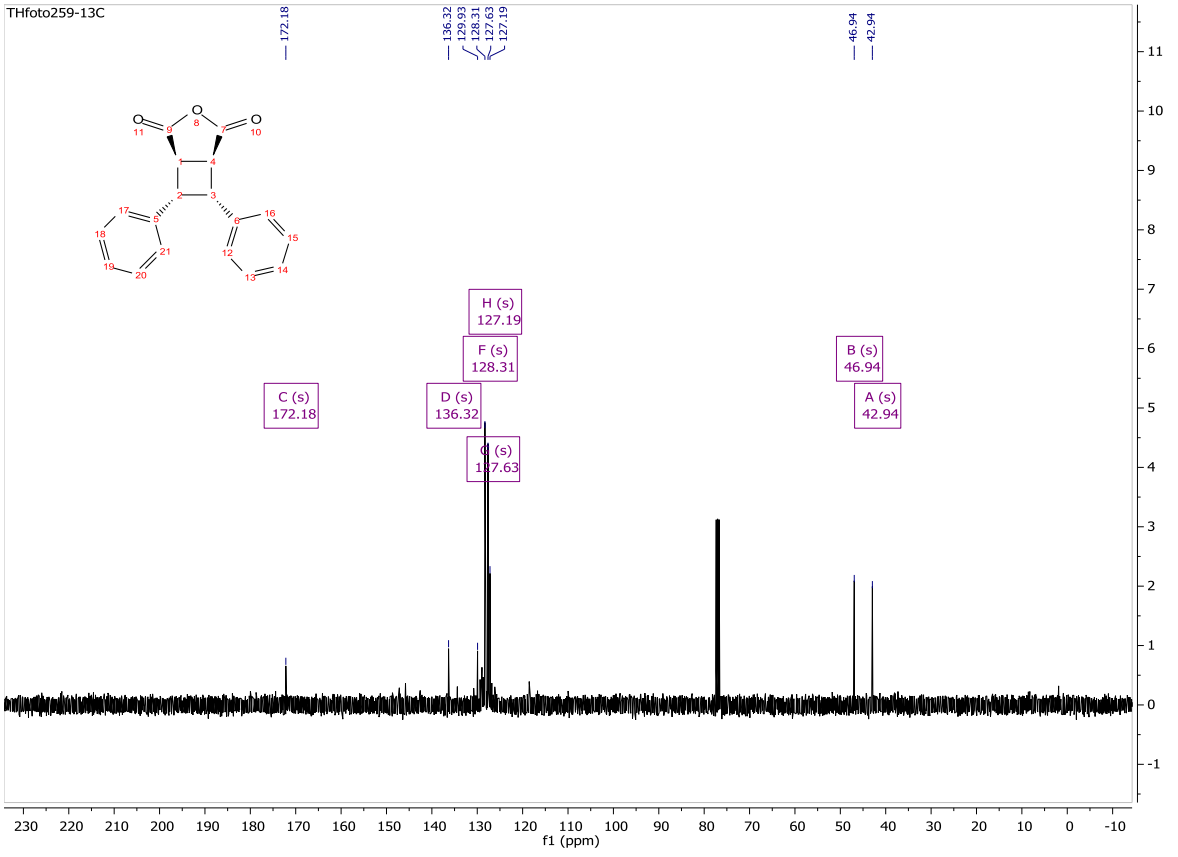
3c


THfoto262
f1 (ppm)

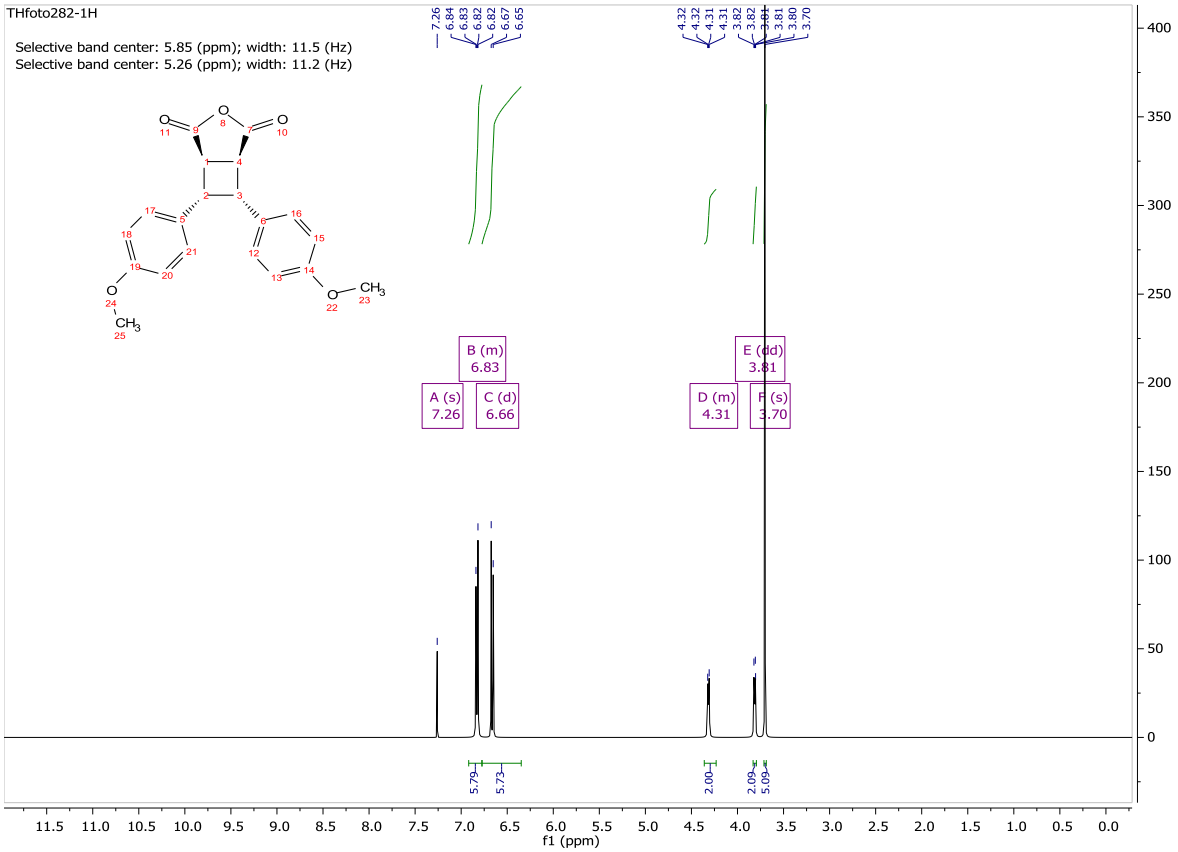

THfoto262-13C
DEUTERIUM OBSERVE
STANDARD PARAMETERS
A (s) 208.94
B (s) 139.99
C (s) 132.63
D (s) 121.50
E (s) 123.97
F (s) 123.47
G (s) 123.30
H (s) 44.63
I (s) 43.54
J (s) 38.14
K (s) 25.04
L (s) 17.23
f1 (ppm)

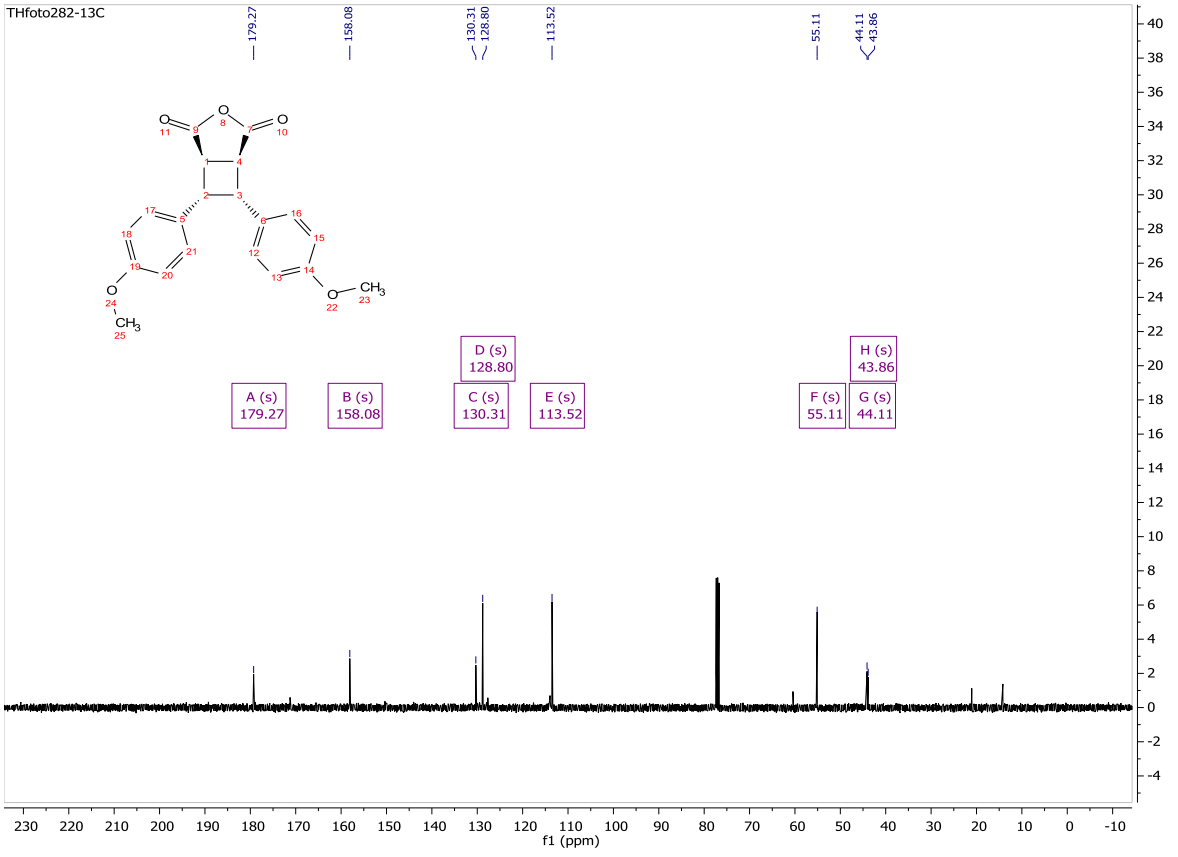
3d


THfoto259
Std Proton parameters
B (m)
7.12
A (t)
7.26
C (m)
6.91
E (dd)
3.95
D (m)
4.40
5.25
3.77
2.00
2.06
f1 (ppm)

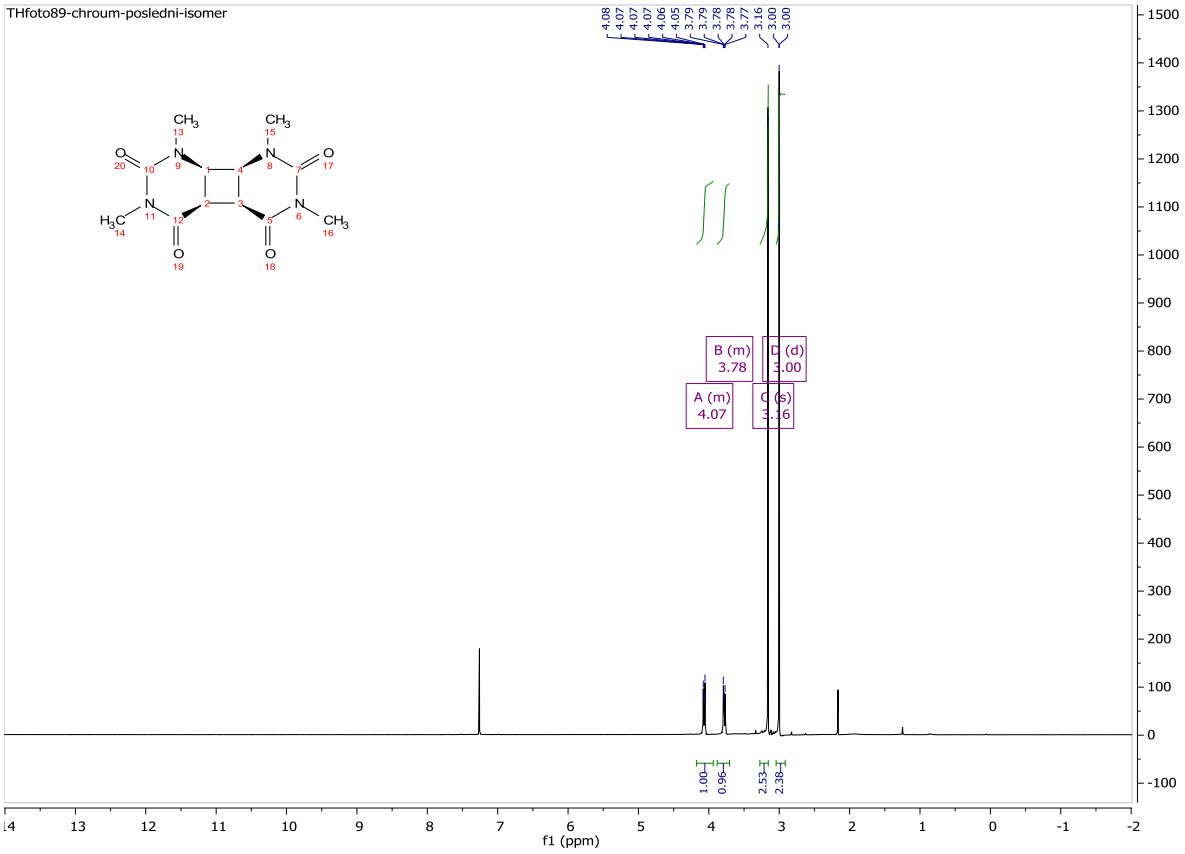

THfoto259-13C
172.18
136.32
129.93
128.31
127.63
127.19
46.94
42.94
H (s)
127.19
F (s)
128.31
B (s)
46.94
C (s)
172.18
D (s)
136.32
A (s)
42.94
f1 (ppm)

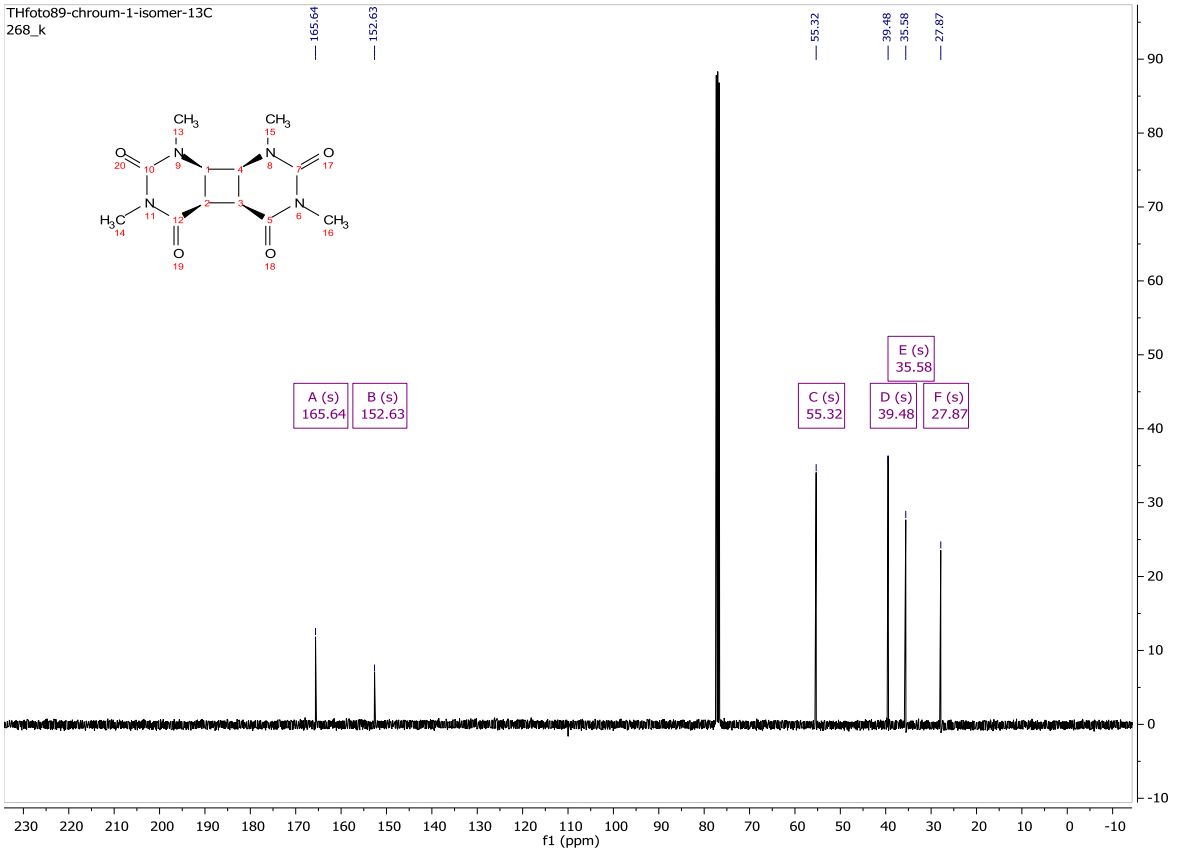
3e


THfoto282-1H
Selective band center: 5.85 (ppm); width: 11.5 (Hz)
Selective band center: 5.26 (ppm); width: 11.2 (Hz)
7.26
6.84
6.83
6.82
6.82
6.67
6.65
4.32
4.32
4.31
4.31
3.82
3.82
3.81
3.80
3.70
B (m) 6.83
A (s) 7.26
C (d) 6.66
E (dd) 3.81
D (m) 4.31
F (s) 3.70
5.79
5.73
2.00
2.09
5.09
f1 (ppm)

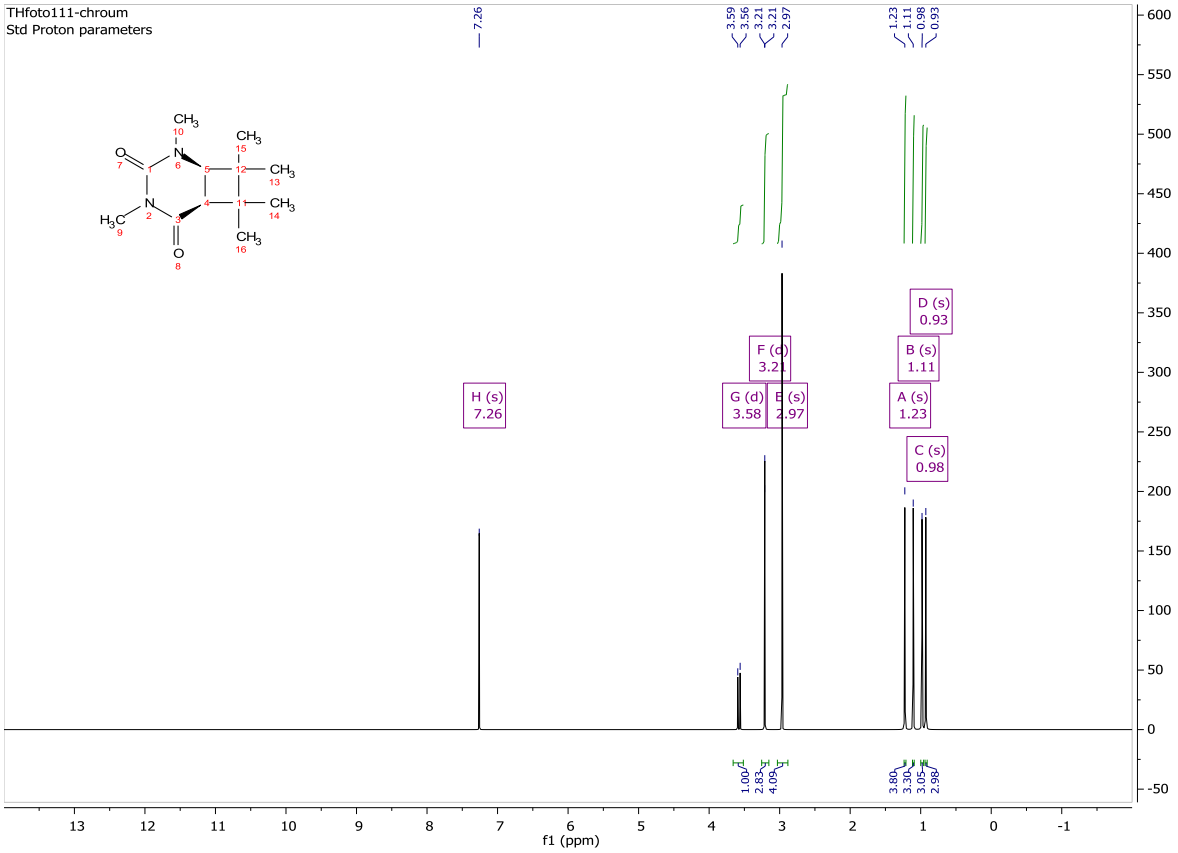

THfoto282-13C
179.27
158.08
130.31
128.80
113.52
55.11
44.11
43.86
D (s) 128.80
H (s) 43.86
A (s) 179.27
B (s) 158.08
C (s) 130.31
E (s) 113.52
F (s) 55.11
G (s) 44.11
f1 (ppm)

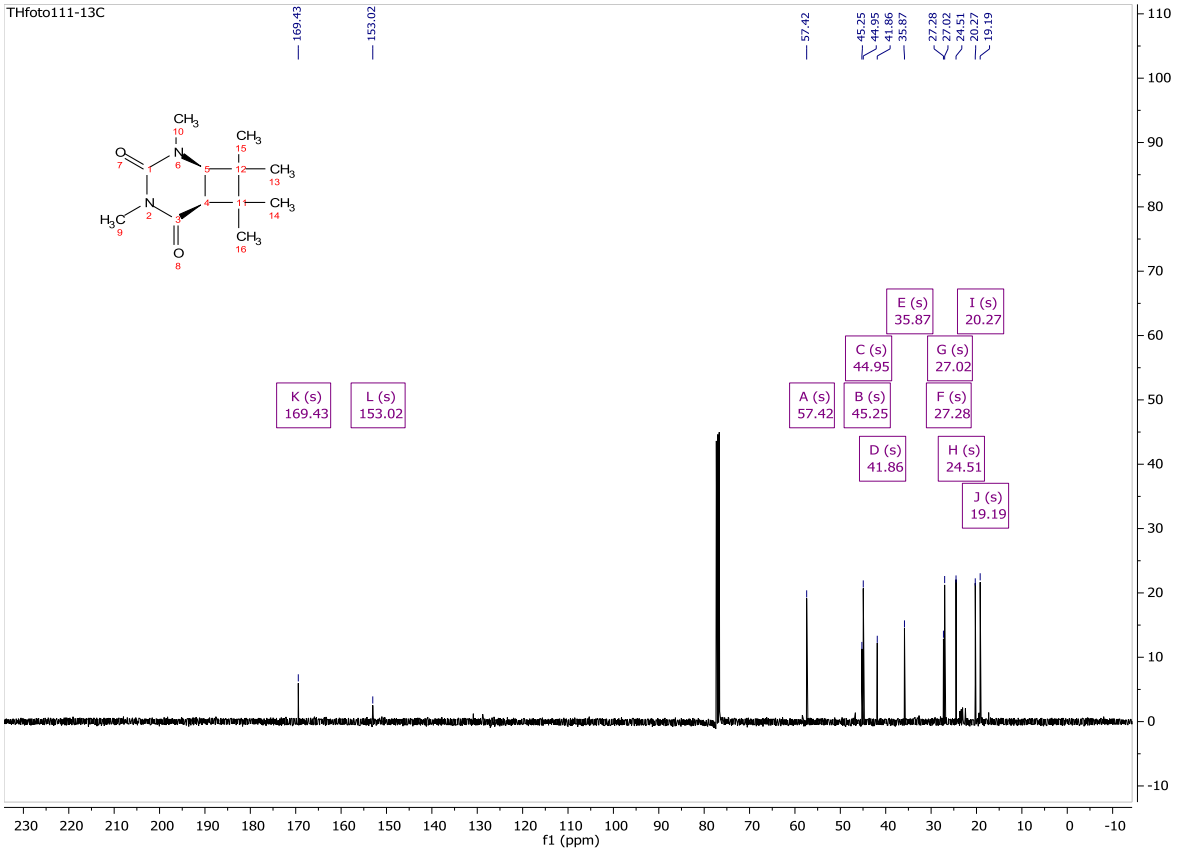
3f


THfoto89-chroum-posledni-isomer
4.08
4.07
4.07
4.07
4.06
4.05
3.79
3.79
3.78
3.78
3.77
3.16
3.00
3.00
B (m)
3.78
D (d)
3.00
A (m)
4.07
C (s)
3.16
1.00
0.96
2.53
2.38
f1 (ppm)

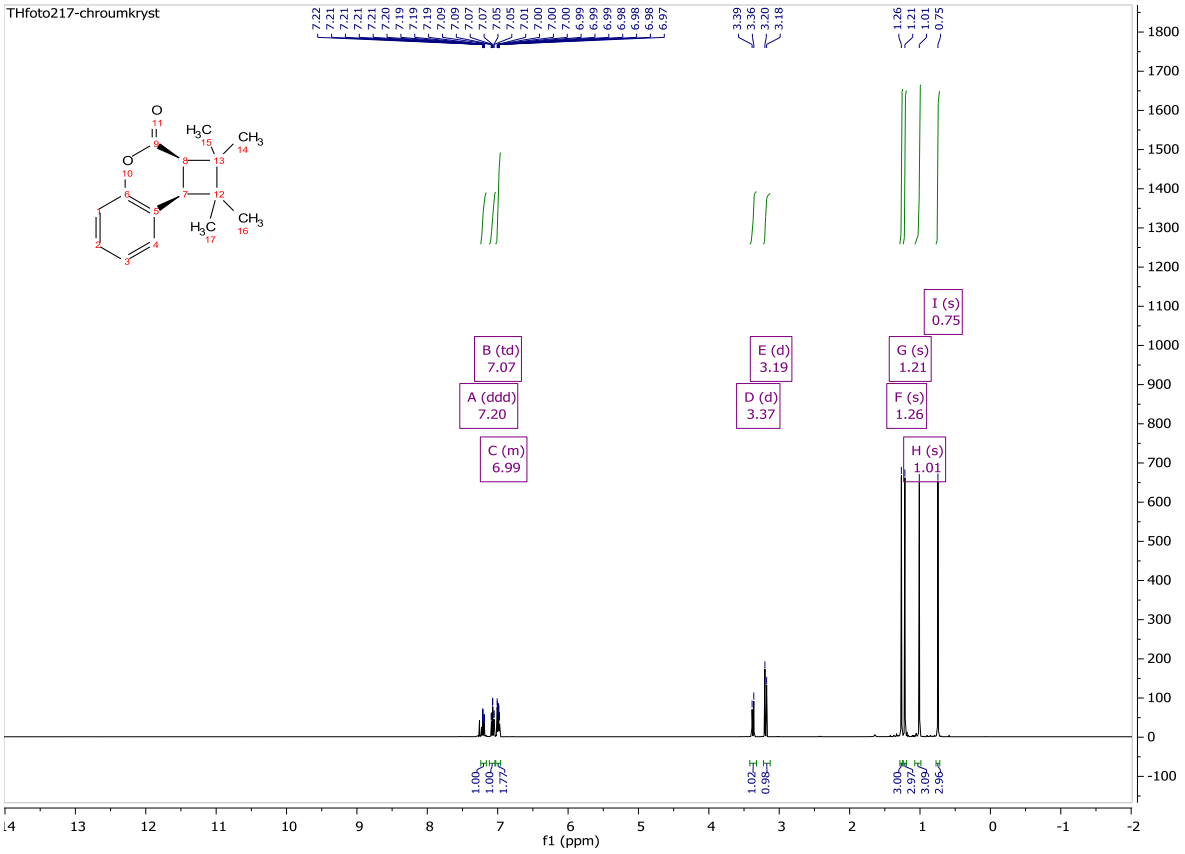

THfoto89-chroum-1-isomer-13C
268_k
165.64
152.63
55.32
39.48
35.58
27.87
A (s)
165.64
B (s)
152.63
C (s)
55.32
D (s)
39.48
E (s)
35.58
F (s)
27.87
f1 (ppm)

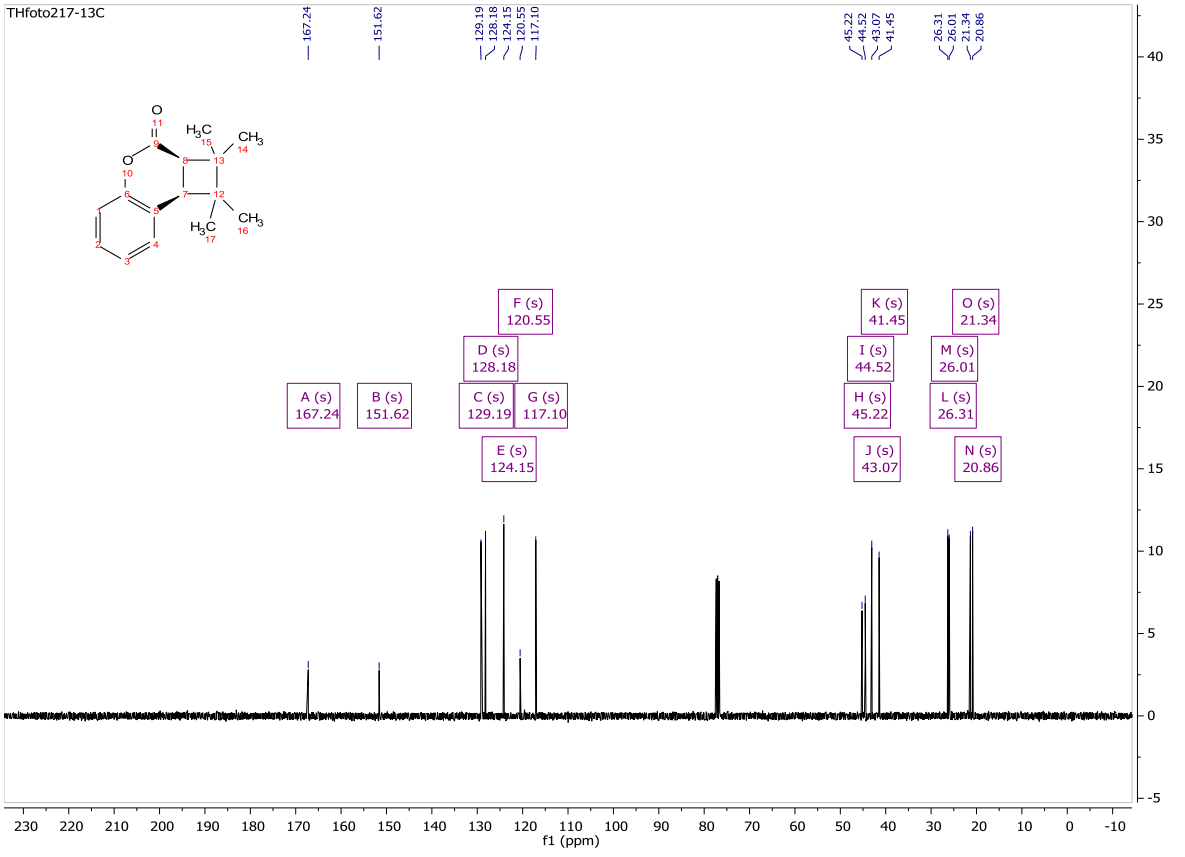
3g


THfoto111-chroum
Std Proton parameters
7.26
3.59
3.56
3.21
3.21
2.97
1.23
1.11
1.11
0.98
0.93
H (s) 7.26
G (d) 3.58
F (d) 3.21
E (s) 2.97
D (s) 0.93
B (s) 1.11
A (s) 1.23
C (s) 0.98
1.00
2.83
4.09
3.80
3.30
3.05
2.98
f1 (ppm)

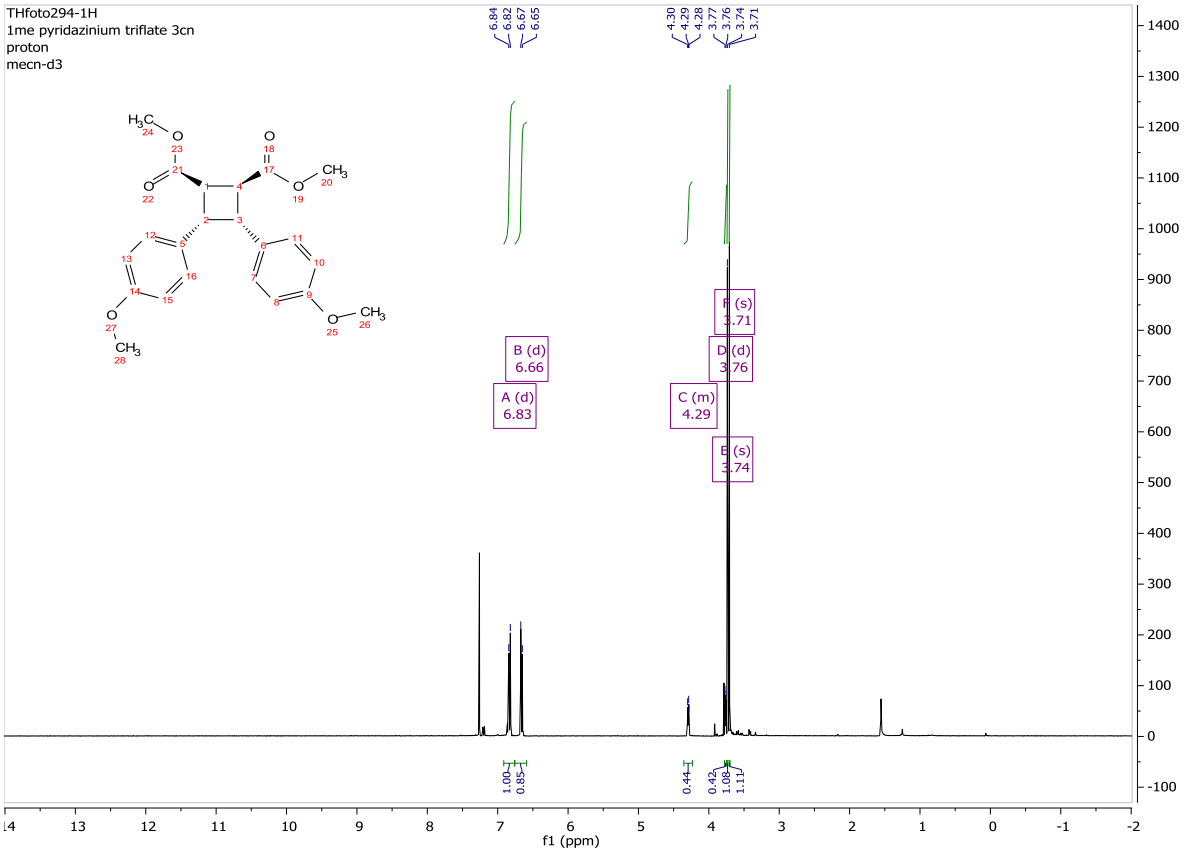

THfoto111-13C
169.43
153.02
57.42
45.25
44.95
41.86
35.87
27.28
27.02
24.51
20.27
19.19
K (s) 169.43
L (s) 153.02
A (s) 57.42
B (s) 45.25
C (s) 44.95
D (s) 41.86
E (s) 35.87
F (s) 27.28
G (s) 27.02
H (s) 24.51
I (s) 20.27
J (s) 19.19
f1 (ppm)

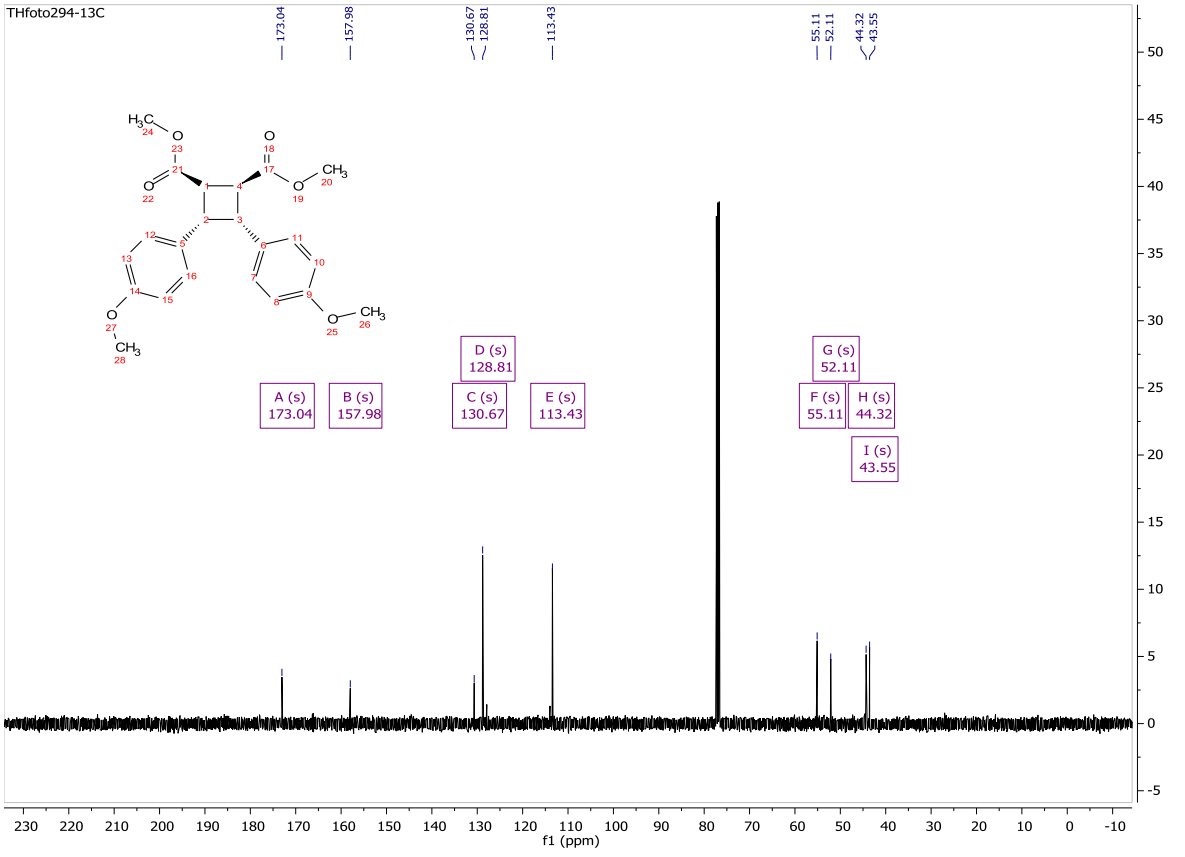
3h


THfoto217-chroumkryst
7.22 7.21 7.21 7.21 7.21 7.20 7.19 7.19 7.09 7.09 7.07 7.07 7.05 7.05 7.01 7.00 7.00 7.00 6.99 6.99 6.98 6.98 6.98 6.97
3.39 3.36 3.20 3.18
1.26 1.21 1.01 0.75
I (s) 0.75
B (td) 7.07
E (d) 3.19
G (s) 1.21
A (ddd) 7.20
D (d) 3.37
F (s) 1.26
C (m) 6.99
H (s) 1.01
1.00 1.00 1.77
1.02 0.98
3.00 2.97 3.09 2.96
f1 (ppm)

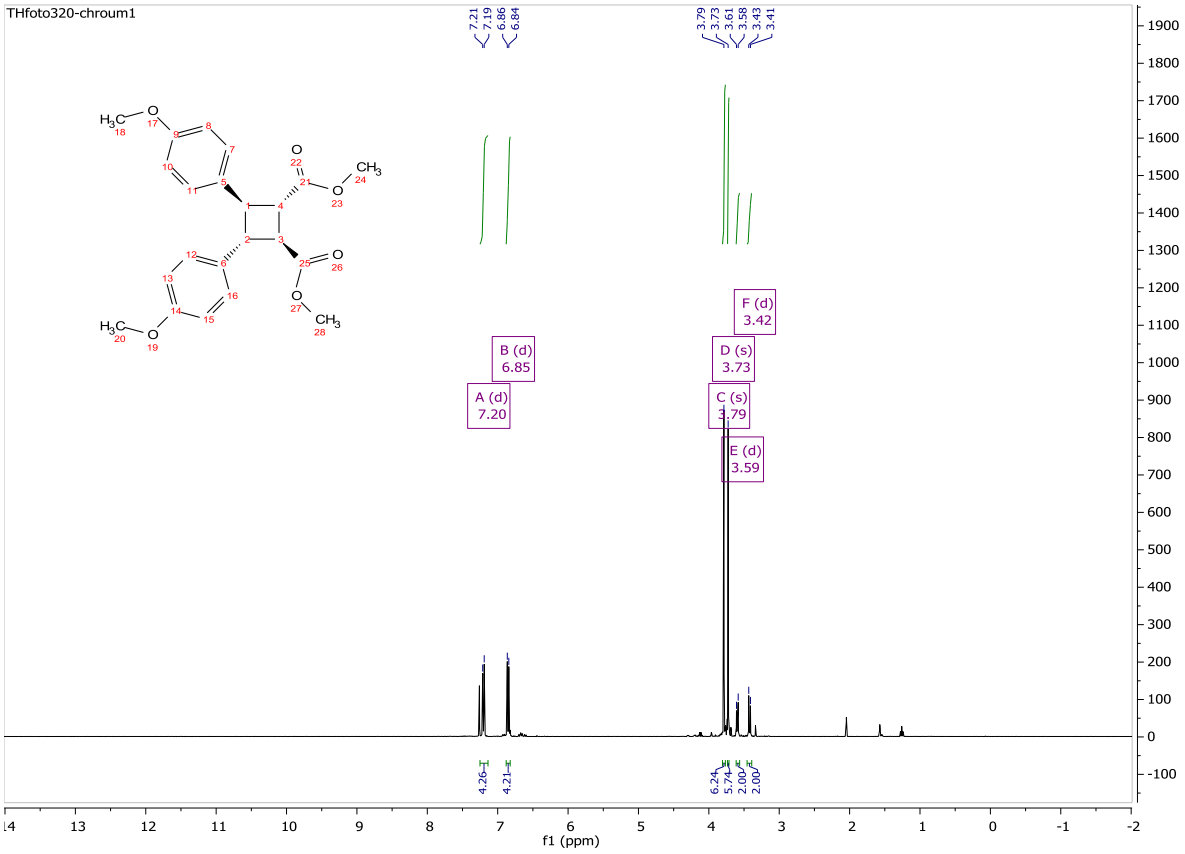

THfoto217-13C
167.24 151.62 129.19 128.18 124.15 120.55 117.10
45.22 44.52 43.07 41.45
26.31 26.01 21.34 20.86
F (s) 120.55
D (s) 128.18
K (s) 41.45
O (s) 21.34
I (s) 44.52
M (s) 26.01
A (s) 167.24
B (s) 151.62
C (s) 129.19
G (s) 117.10
H (s) 45.22
L (s) 26.31
E (s) 124.15
J (s) 43.07
N (s) 20.86
f1 (ppm)

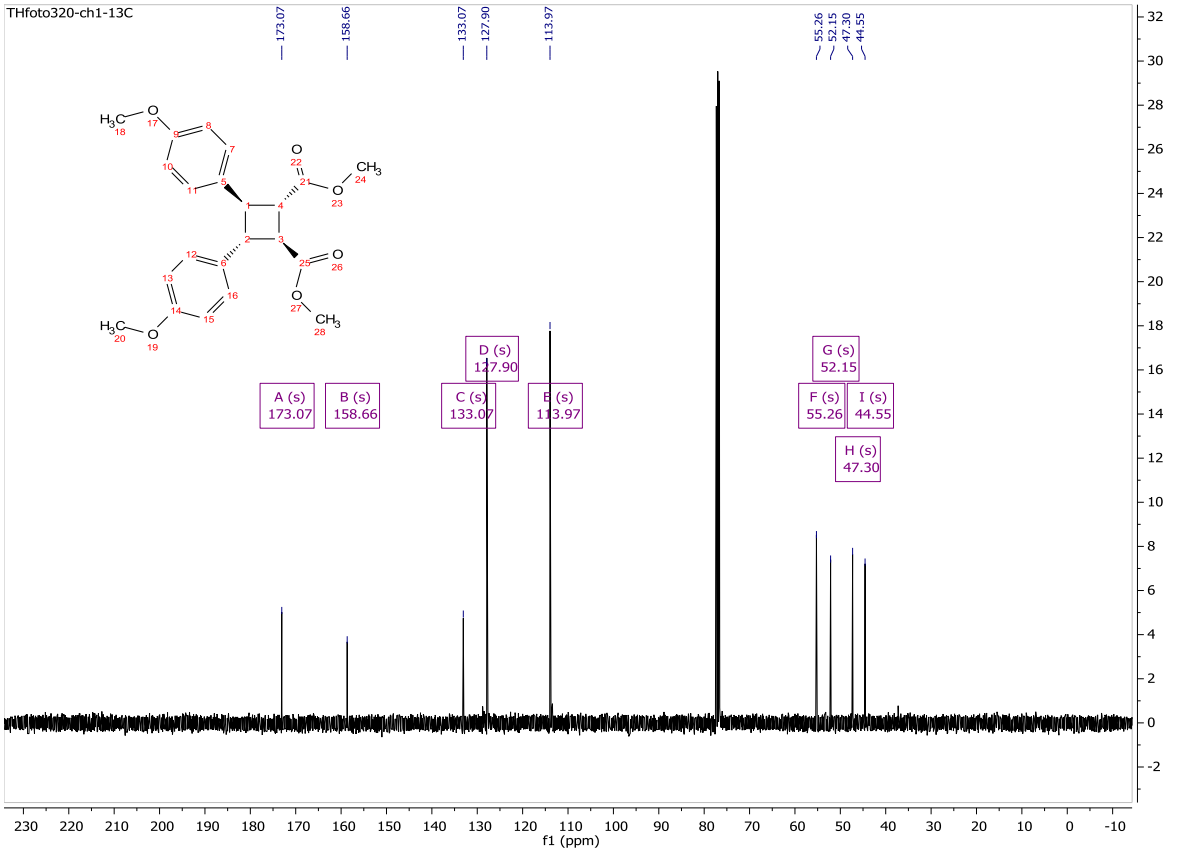
3i


THfoto294-1H
1me pyridazinium triflate 3cn
proton
mecn-d3
6.84
6.82
6.67
6.65
4.30
4.29
4.28
3.77
3.76
3.74
3.71
F (s)
3.71
B (d)
6.66
D (d)
3.76
A (d)
6.83
C (m)
4.29
E (s)
3.74
1.00
0.85
0.44
0.42
1.08
1.11
f1 (ppm)

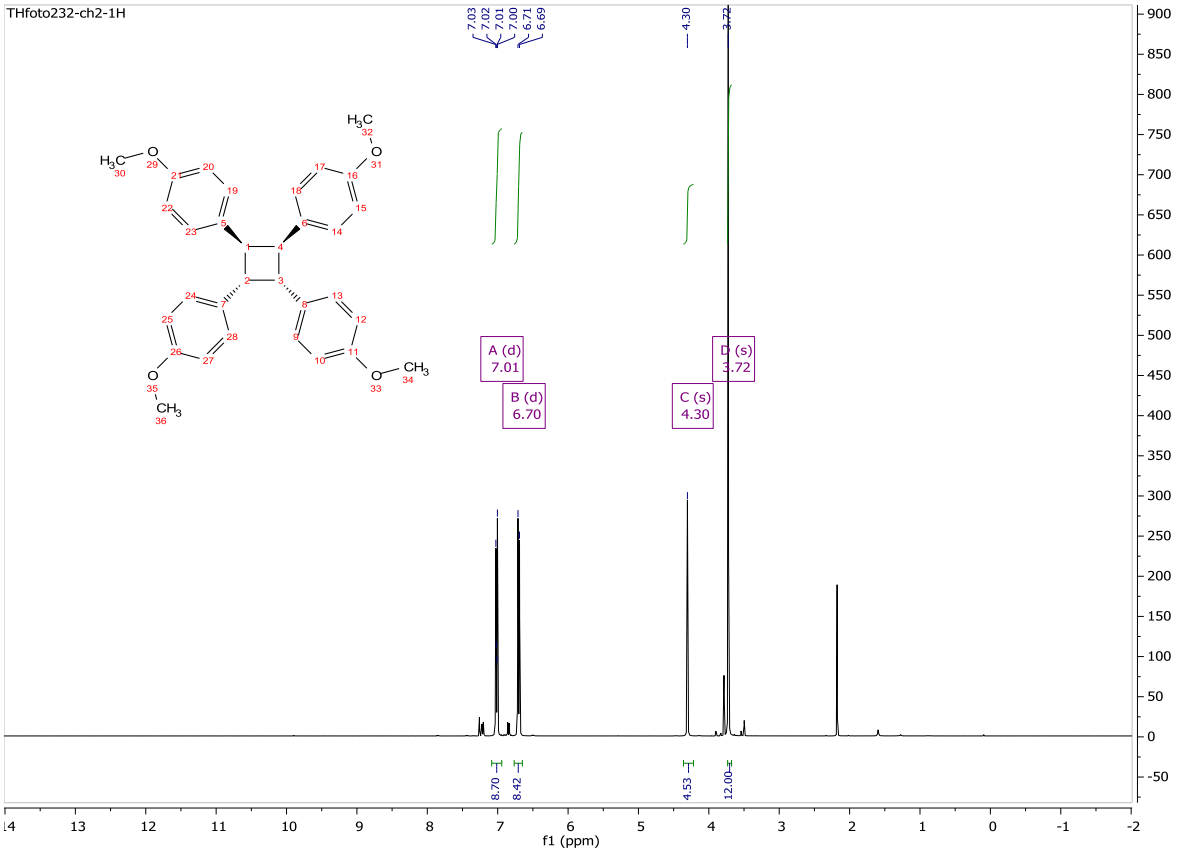

THfoto294-13C
173.04
157.98
130.67
128.81
113.43
55.11
52.11
44.32
43.55
D (s)
128.81
G (s)
52.11
A (s)
173.04
B (s)
157.98
C (s)
130.67
E (s)
113.43
F (s)
55.11
H (s)
44.32
I (s)
43.55
f1 (ppm)

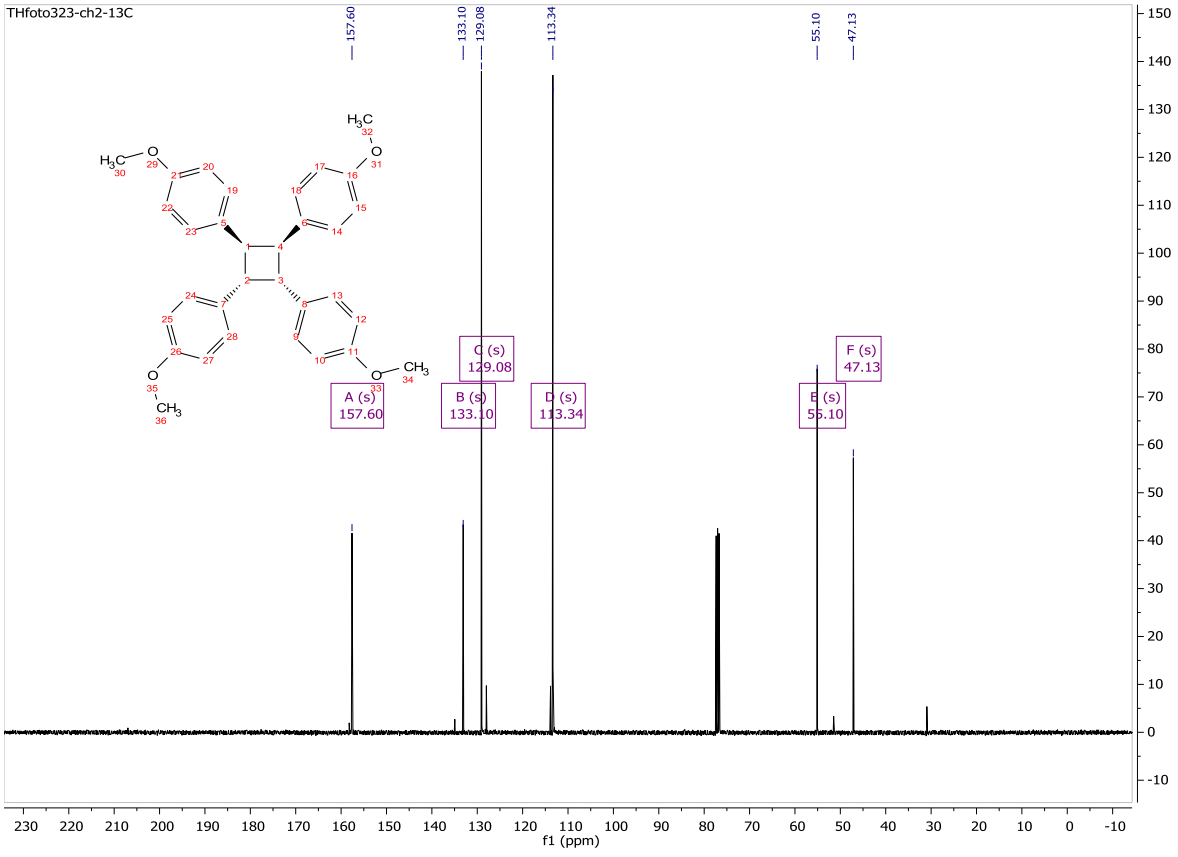
3j


THfoto320-chroum1
7.21
7.19
6.86
6.84
3.79
3.73
3.61
3.58
3.43
3.41
A (d)
7.20
B (d)
6.85
C (s)
3.79
D (s)
3.73
E (d)
3.59
F (d)
3.42
4.26
4.21
6.24
5.74
2.00
2.00
f1 (ppm)

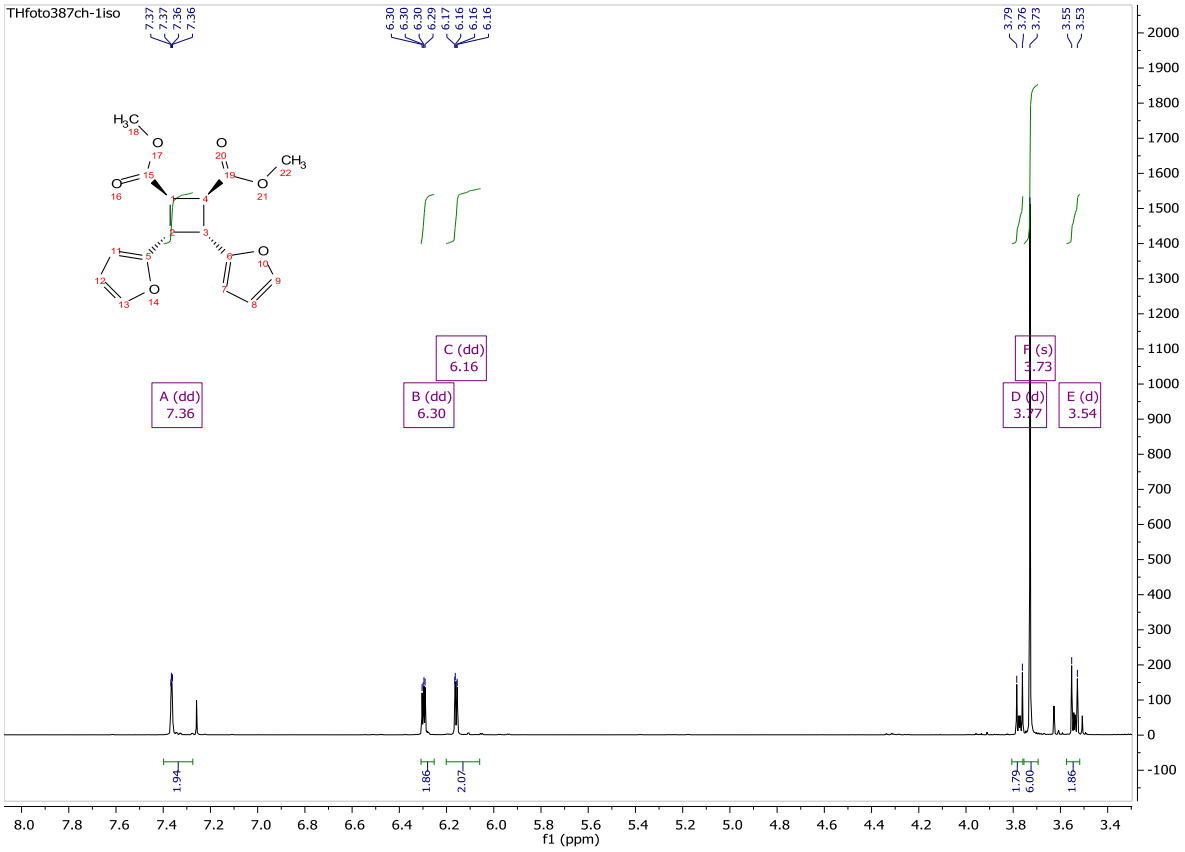

THfoto320-ch1-13C
173.07
158.66
133.07
127.90
113.97
55.26
52.15
47.30
44.55
A (s)
173.07
B (s)
158.66
C (s)
133.07
D (s)
127.90
E (s)
113.97
F (s)
55.26
G (s)
52.15
H (s)
47.30
I (s)
44.55
f1 (ppm)

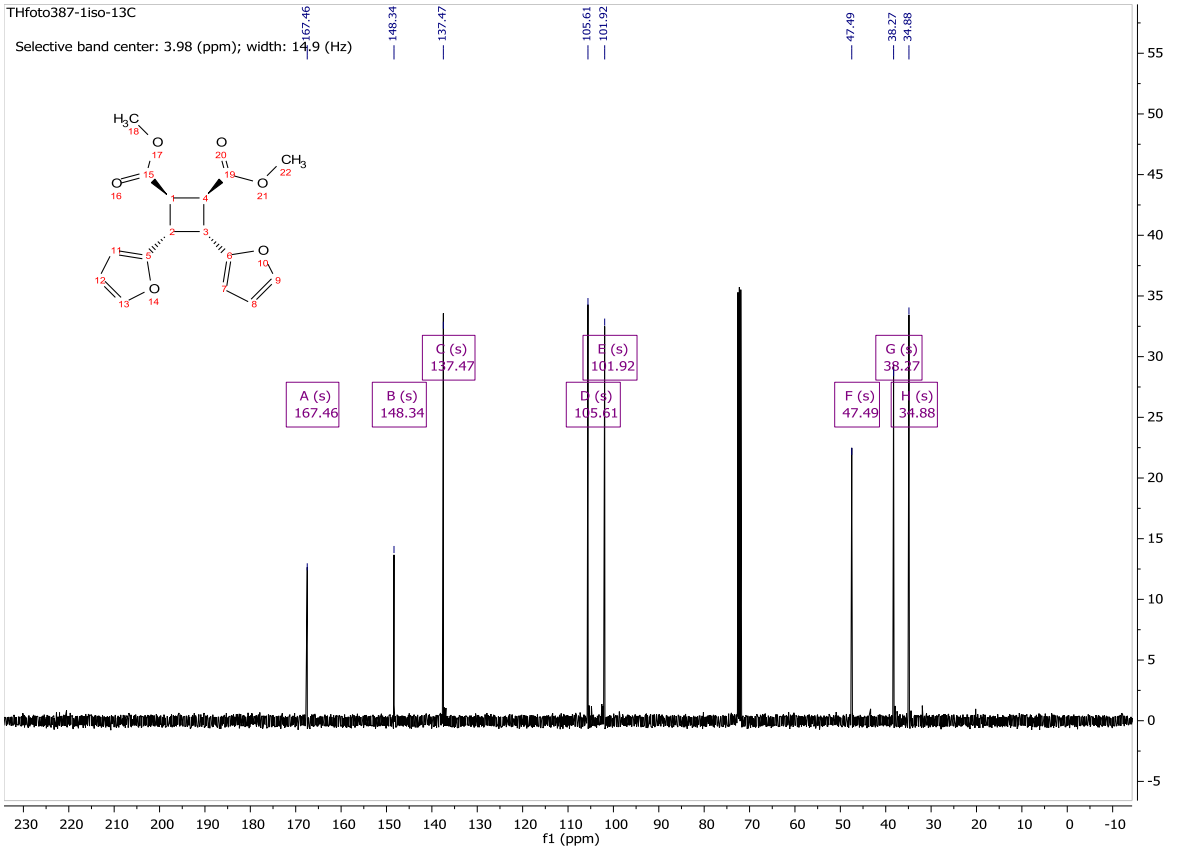
3k


THfoto232-ch2-1H
7.03
7.02
7.01
7.00
6.71
6.69
4.30
3.72
A (d)
7.01
B (d)
6.70
C (s)
4.30
D (s)
3.72
8.70
8.42
4.53
12.00
f1 (ppm)


THfoto323-ch2-13C
157.60
133.10
129.08
113.34
55.10
47.13
A (s)
157.60
B (s)
133.10
C (s)
129.08
D (s)
113.34
E (s)
55.10
F (s)
47.13
f1 (ppm)

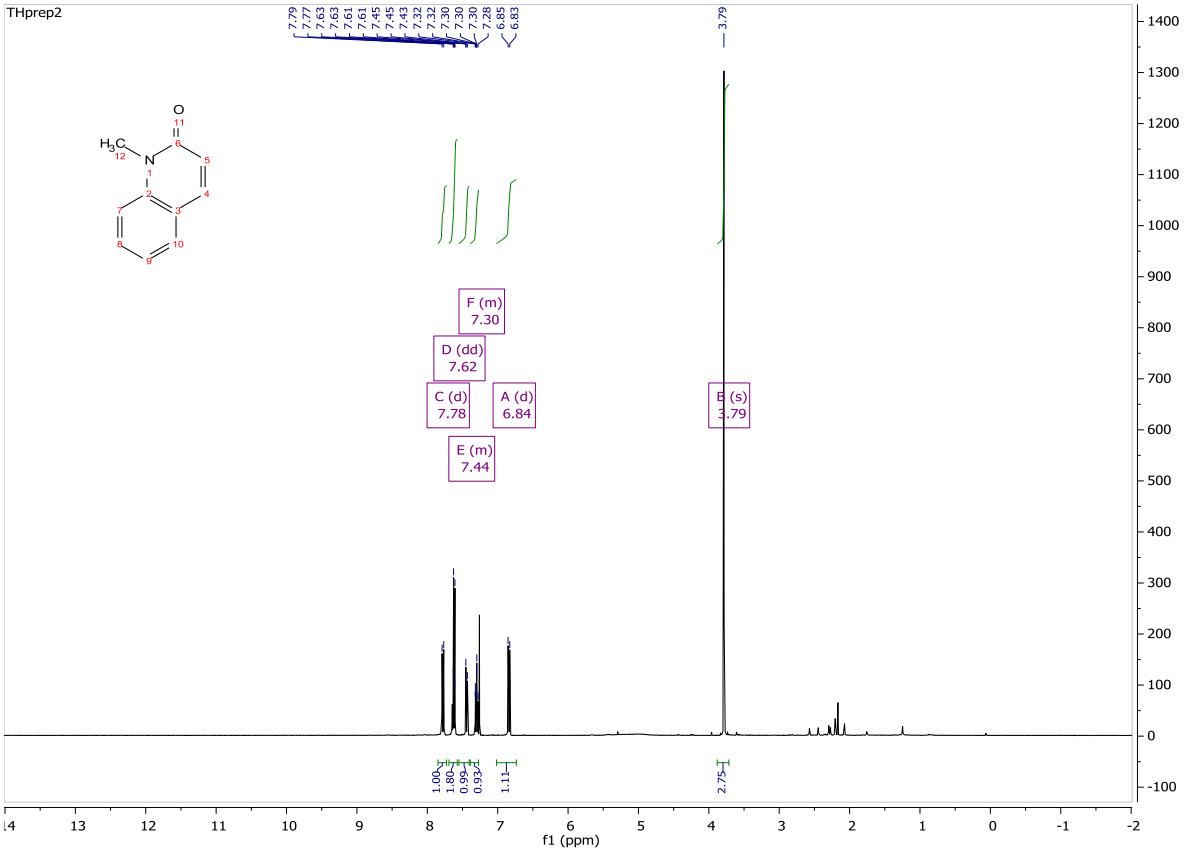
3l

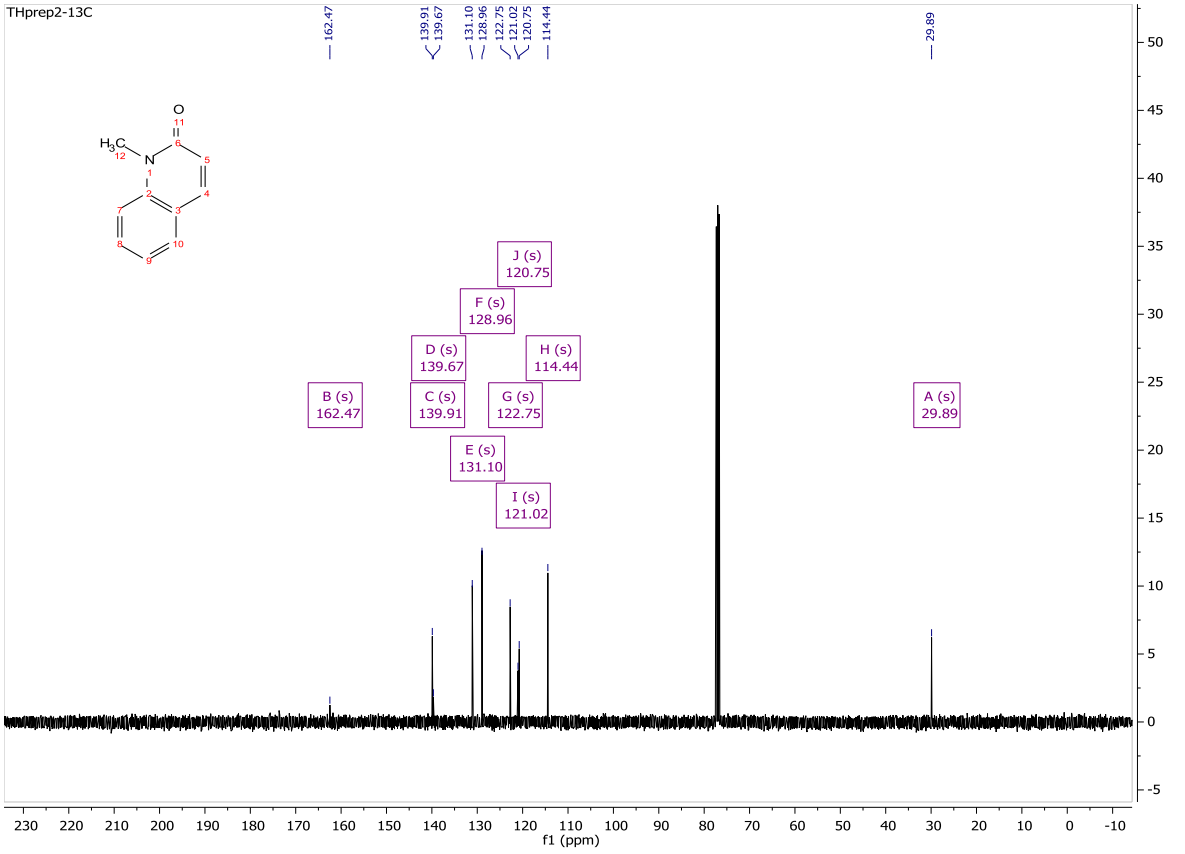

THfoto387ch-1iso
7.37
7.37
7.36
7.36
6.30
6.30
6.30
6.29
6.17
6.16
6.16
6.16
3.79
3.76
3.73
3.55
3.53
A (dd)
7.36
B (dd)
6.30
C (dd)
6.16
D (d)
3.77
E (d)
3.54
F (s)
3.73
1.94
1.86
2.07
1.79
6.00
1.86
f1 (ppm)


THfoto387-1iso-13C
Selective band center: 3.98 (ppm); width: 14.9 (Hz)
167.46
148.34
137.47
105.61
101.92
47.49
38.27
34.88
A (s)
167.46
B (s)
148.34
C (s)
137.47
D (s)
105.61
E (s)
101.92
F (s)
47.49
G (s)
38.27
H (s)
34.88
f1 (ppm)

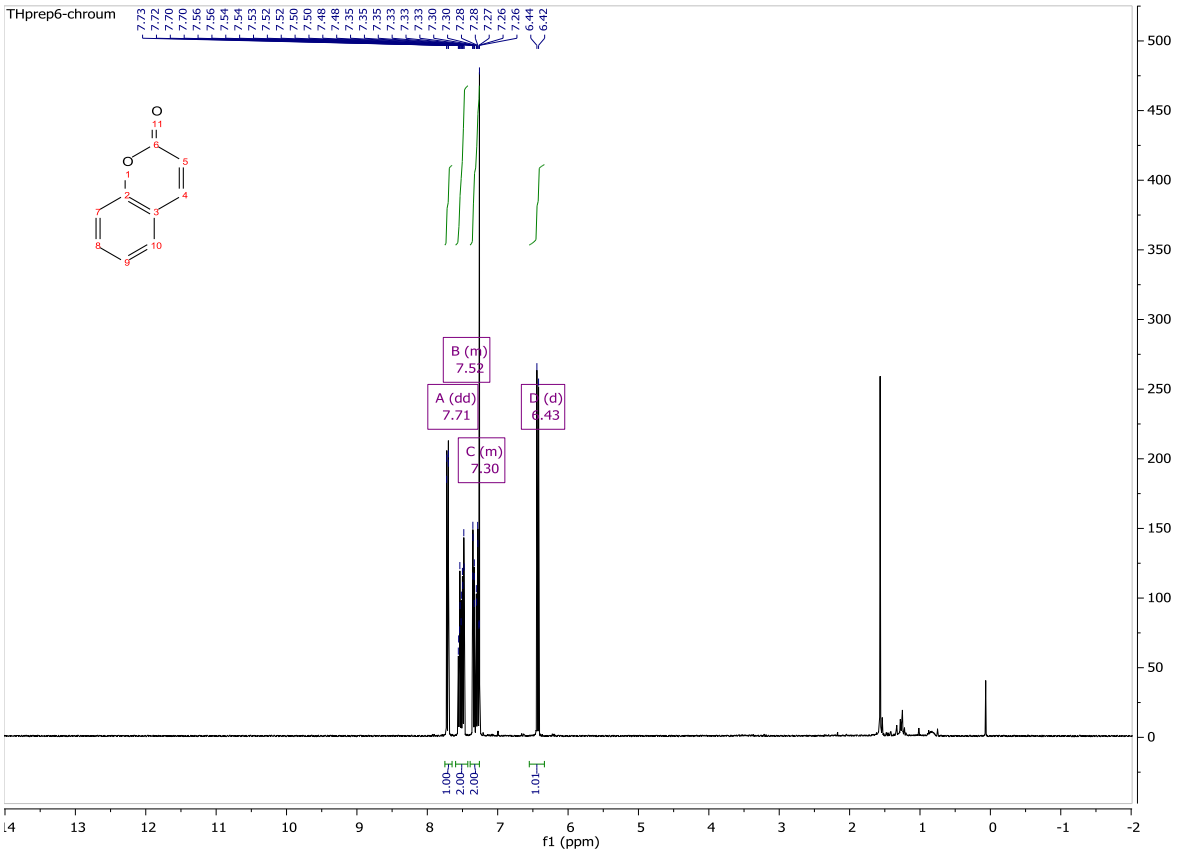
S13 Copy of NMR Spectra of compounds 4

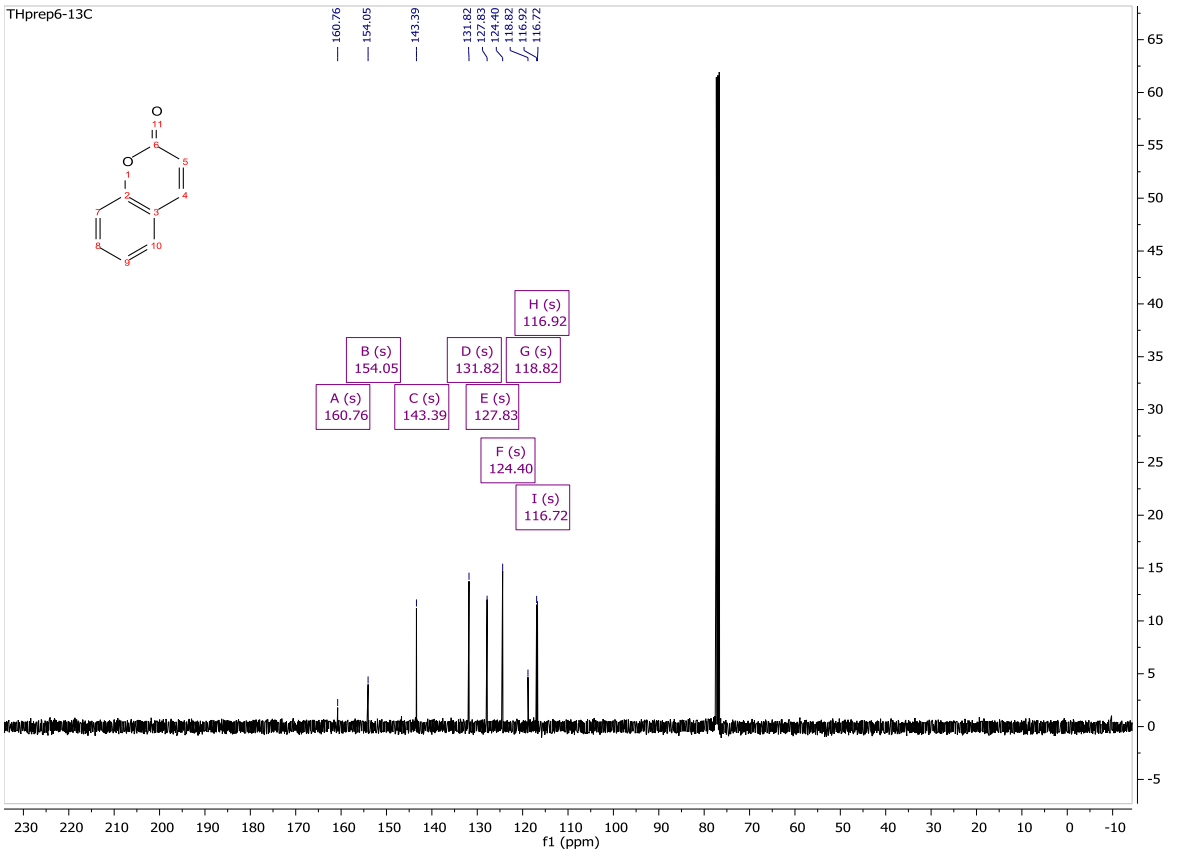
4a



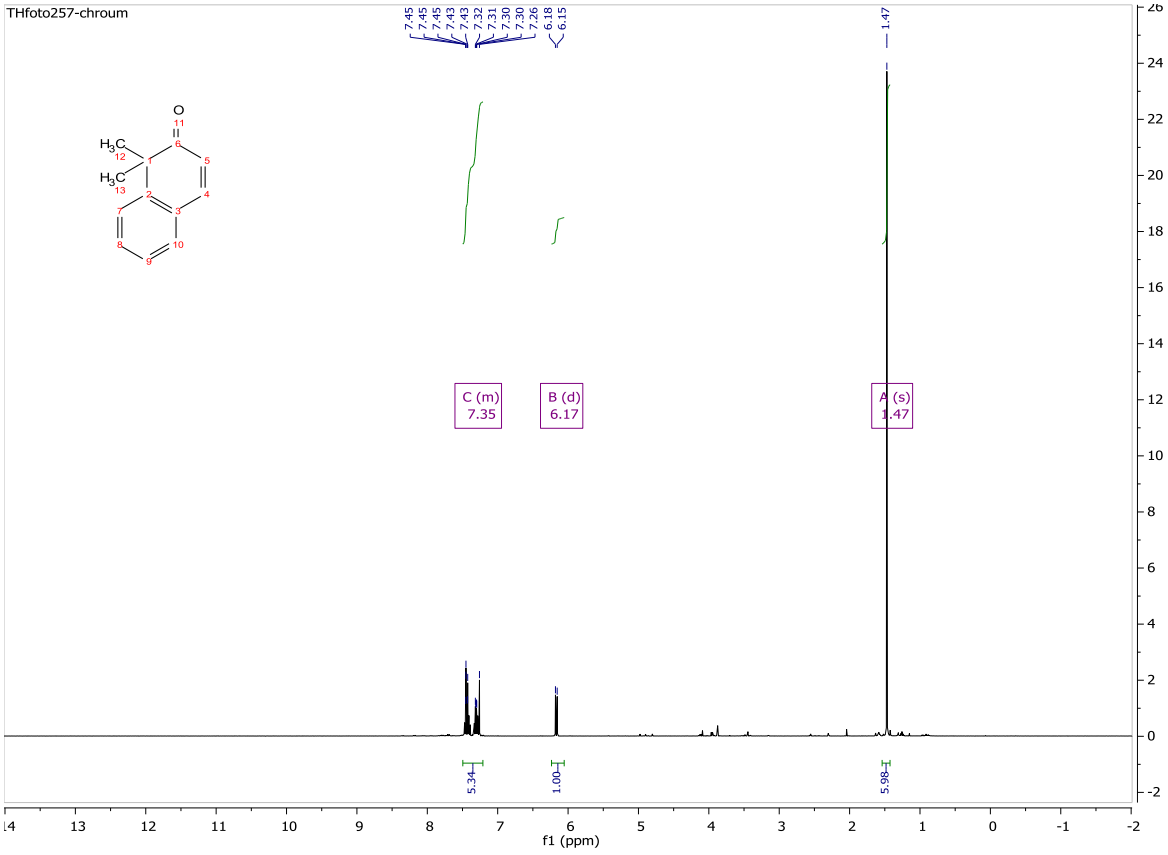


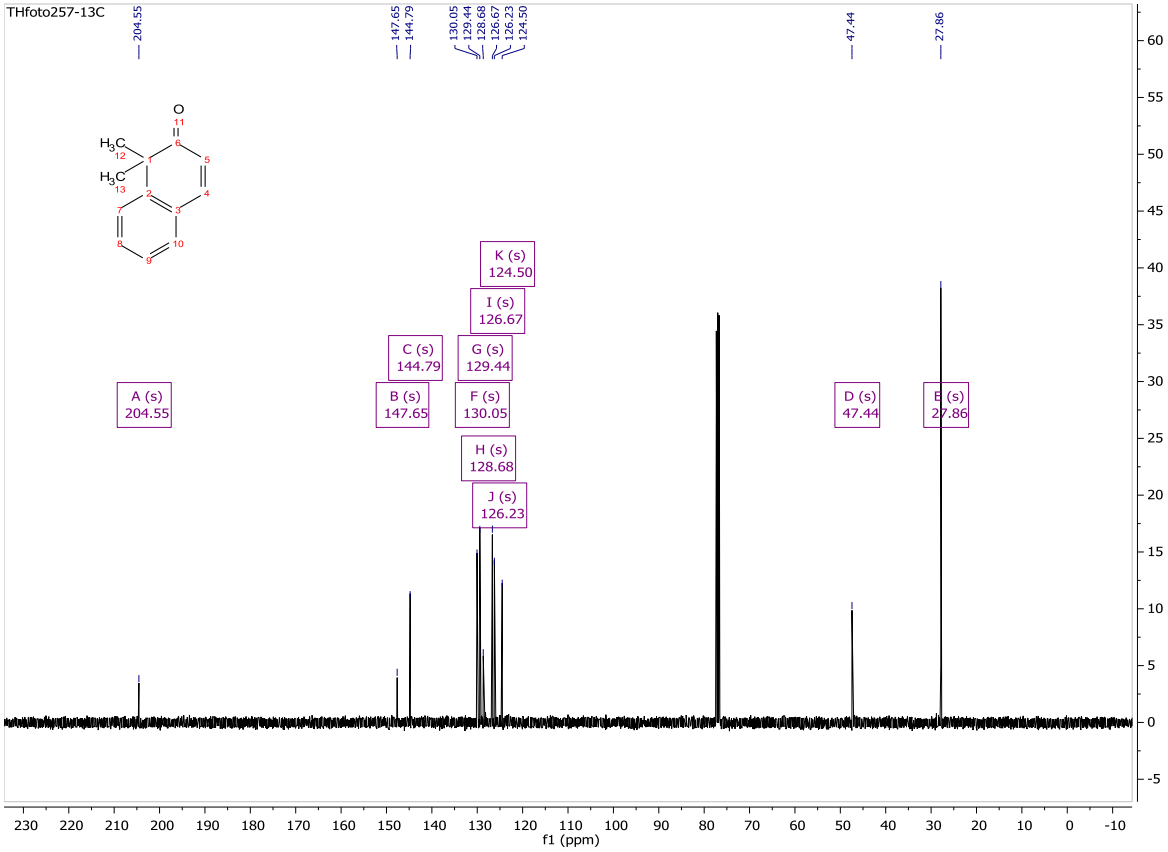
4b


THprep6-chroum
7.73 7.72 7.70 7.70 7.56 7.56 7.54 7.54 7.53 7.52 7.52 7.50 7.50 7.48 7.48 7.35 7.35 7.33 7.33 7.33 7.30 7.30 7.28 7.28 7.27 7.26 7.26 6.44 6.42
B (m) 7.52
A (dd) 7.71
D (d) 6.43
C (m) 7.30
1.00
2.00
2.00
1.01
f1 (ppm)

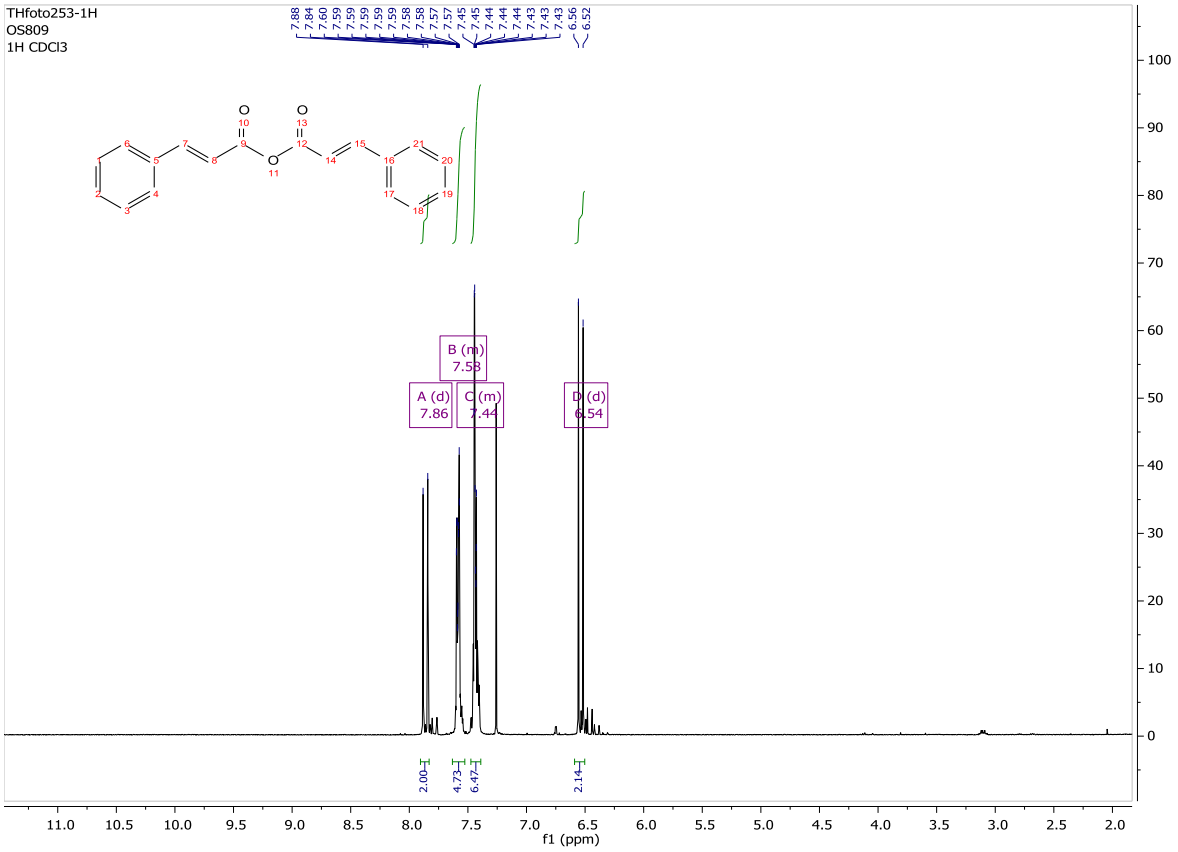

THprep6-13C
160.76 154.05 143.39 131.82 127.83 124.40 118.82 116.92 116.72
H (s) 116.92
B (s) 154.05
D (s) 131.82
G (s) 118.82
A (s) 160.76
C (s) 143.39
E (s) 127.83
F (s) 124.40
I (s) 116.72
f1 (ppm)

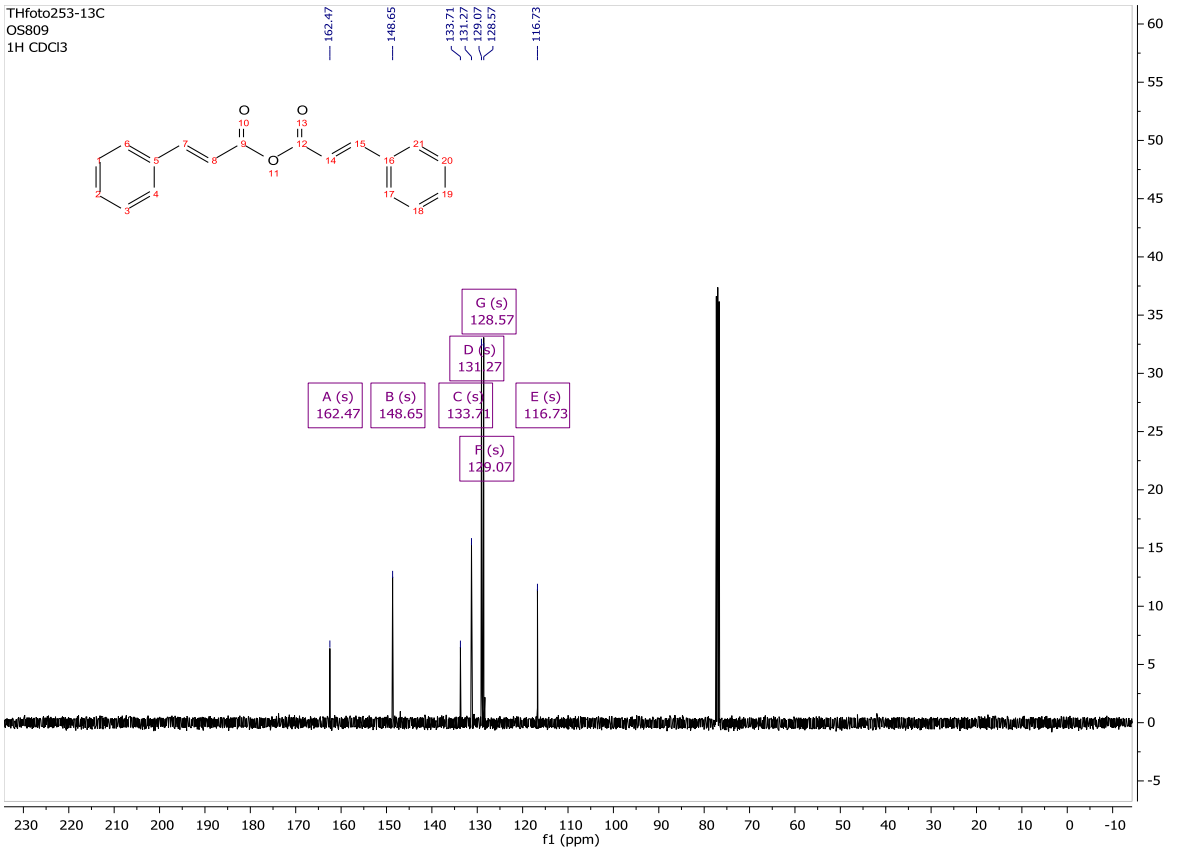
4c


THfoto257-chroum
7.45
7.45
7.45
7.43
7.32
7.31
7.30
7.30
7.26
6.18
6.15
1.47
C (m)
7.35
B (d)
6.17
A (s)
1.47
5.34
1.00
5.98
f1 (ppm)

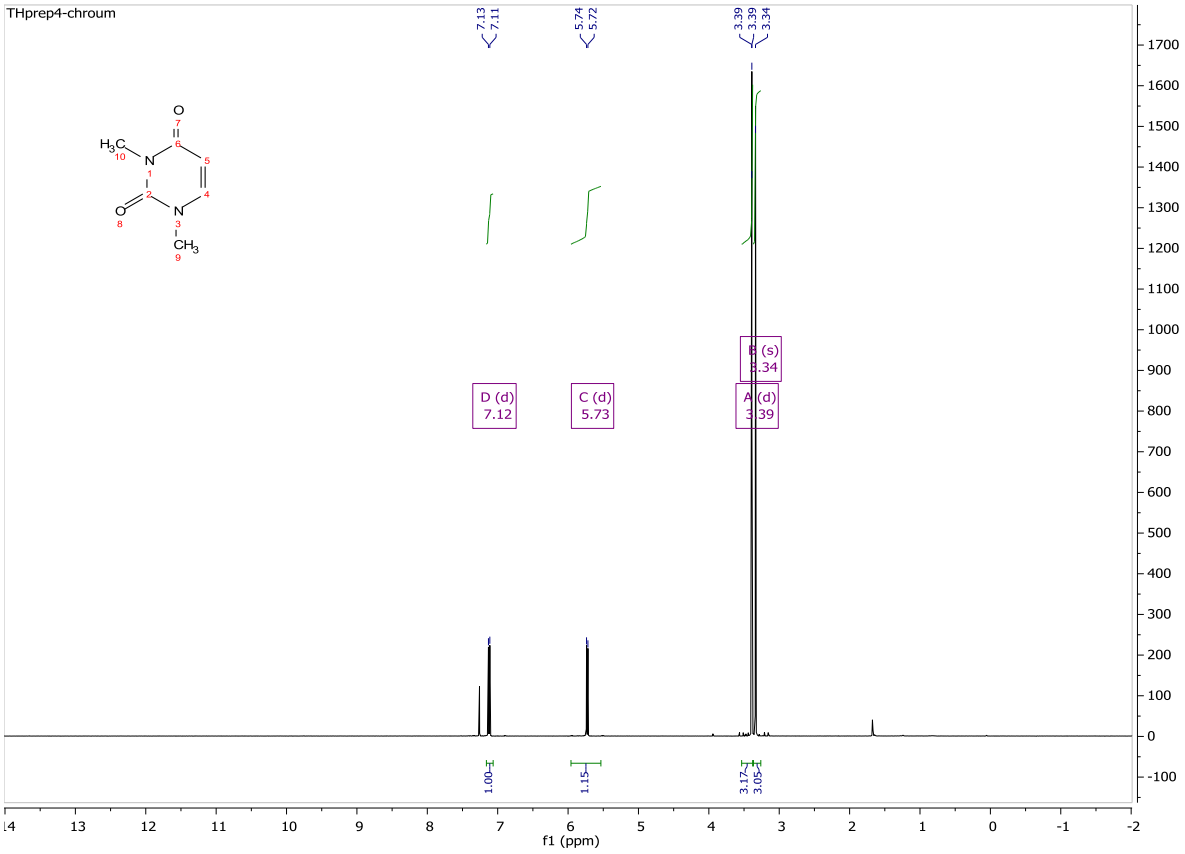

THfoto257-13C
204.55
147.65
144.79
130.05
129.44
128.68
126.67
126.23
124.50
47.44
27.86
K (s)
124.50
I (s)
126.67
C (s)
144.79
G (s)
129.44
A (s)
204.55
B (s)
147.65
F (s)
130.05
D (s)
47.44
E (s)
27.86
H (s)
128.68
J (s)
126.23
f1 (ppm)

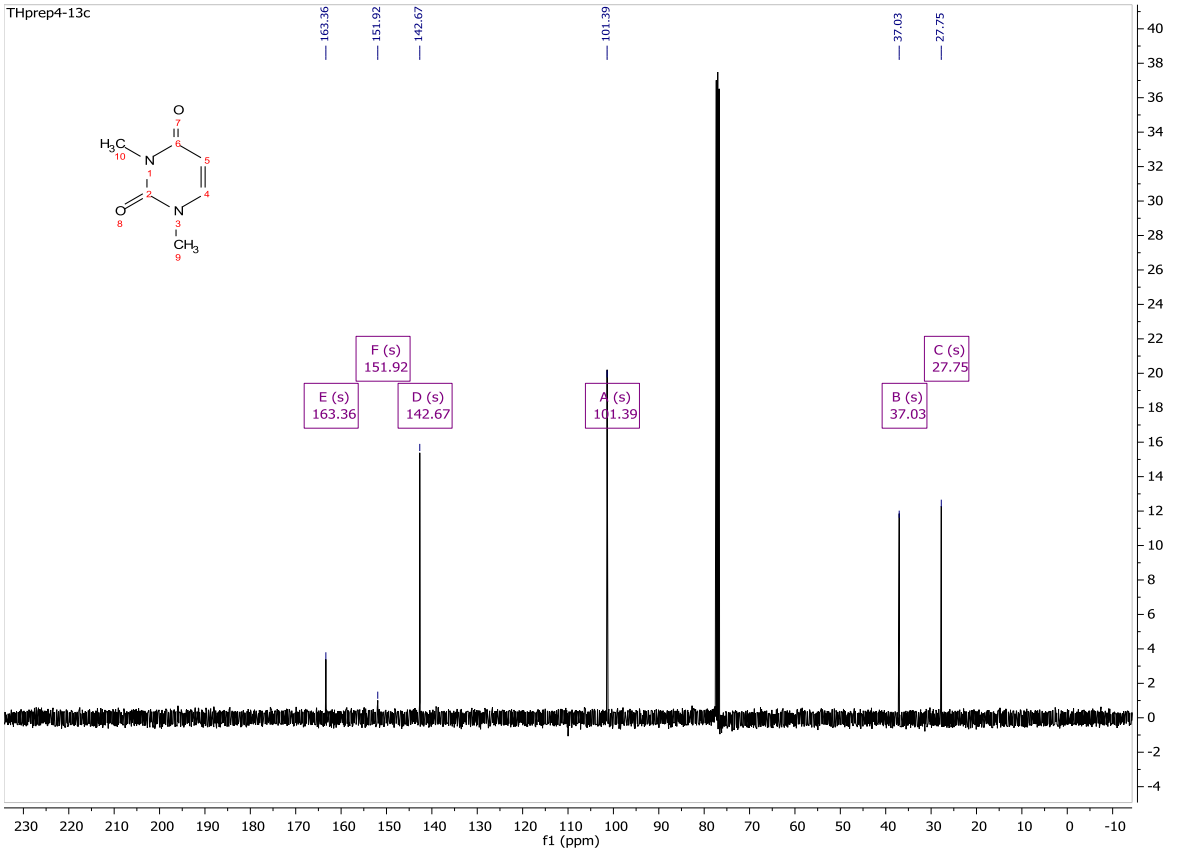
4e


THfoto253-1H
OS809
1H CDCl3
7.88
7.84
7.60
7.59
7.59
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.43
6.56
6.52
B (m)
7.53
A (d)
7.86
C (m)
7.44
D (d)
6.54
2.00
4.73
6.47
2.14
f1 (ppm)

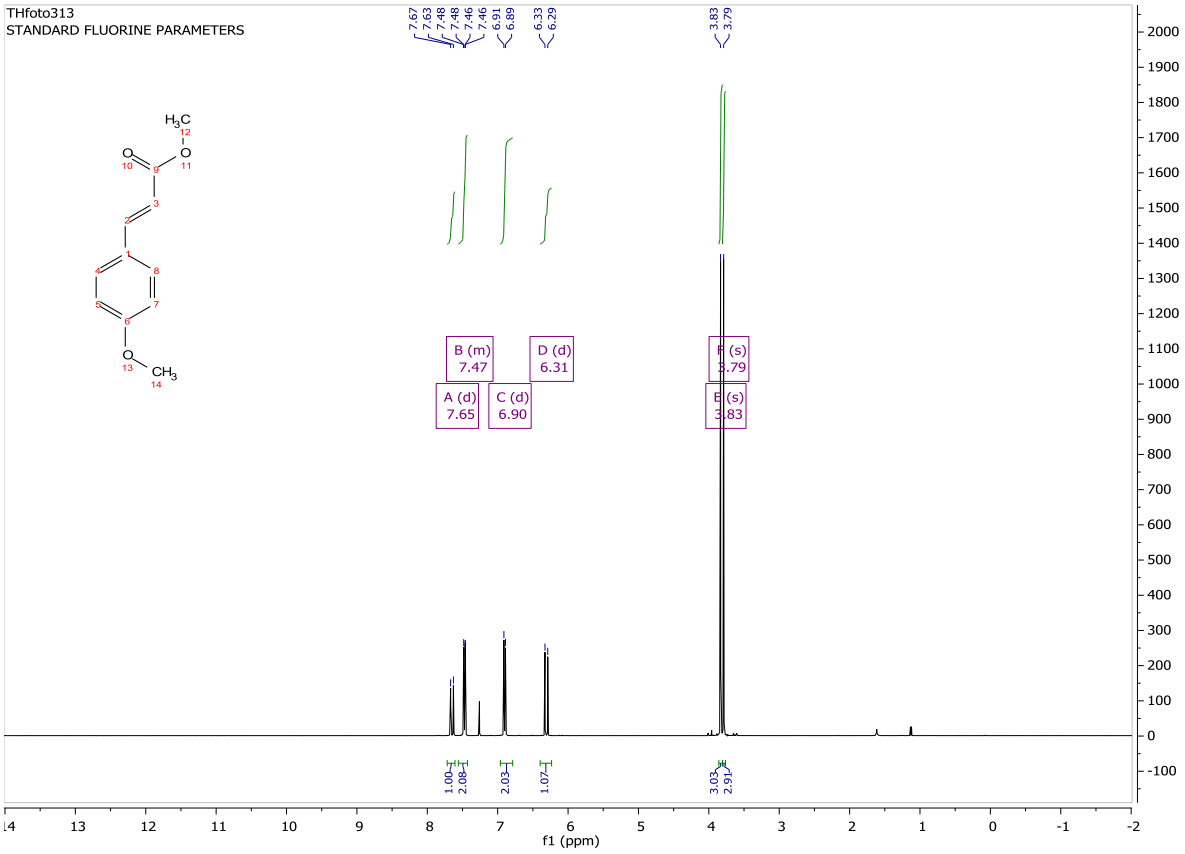

THfoto253-13C
OS809
1H CDCl3
162.47
148.65
133.71
131.27
129.07
128.57
116.73
G (s)
128.57
D (s)
131.27
A (s)
162.47
B (s)
148.65
C (s)
133.71
E (s)
116.73
F (s)
129.07
f1 (ppm)

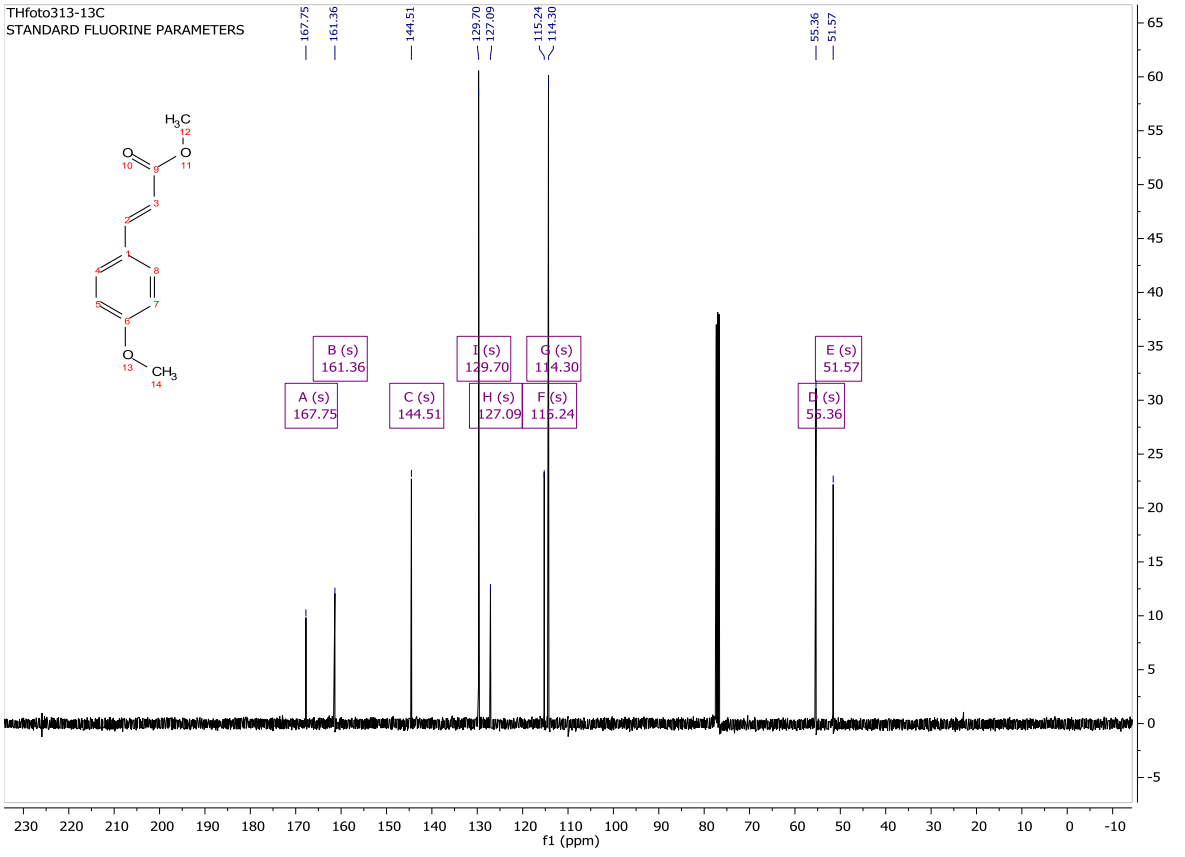
4f


THprep4-chroum
7.13
7.11
5.74
5.72
3.39
3.39
3.34
D (d)
7.12
C (d)
5.73
A (d)
3.39
1.00
1.15
3.17
3.05
f1 (ppm)

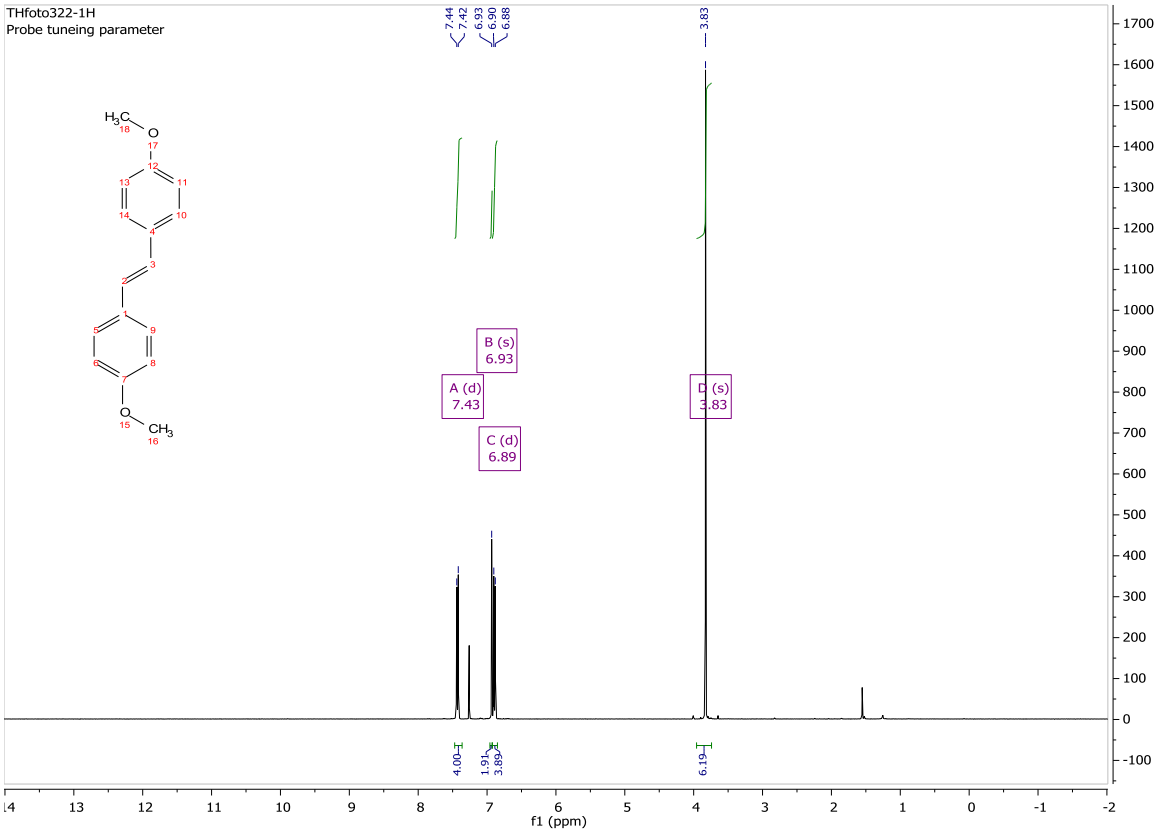

THprep4-13c
163.36
151.92
142.67
101.39
37.03
27.75
F (s)
151.92
E (s)
163.36
D (s)
142.67
A (s)
101.39
C (s)
27.75
B (s)
37.03
f1 (ppm)

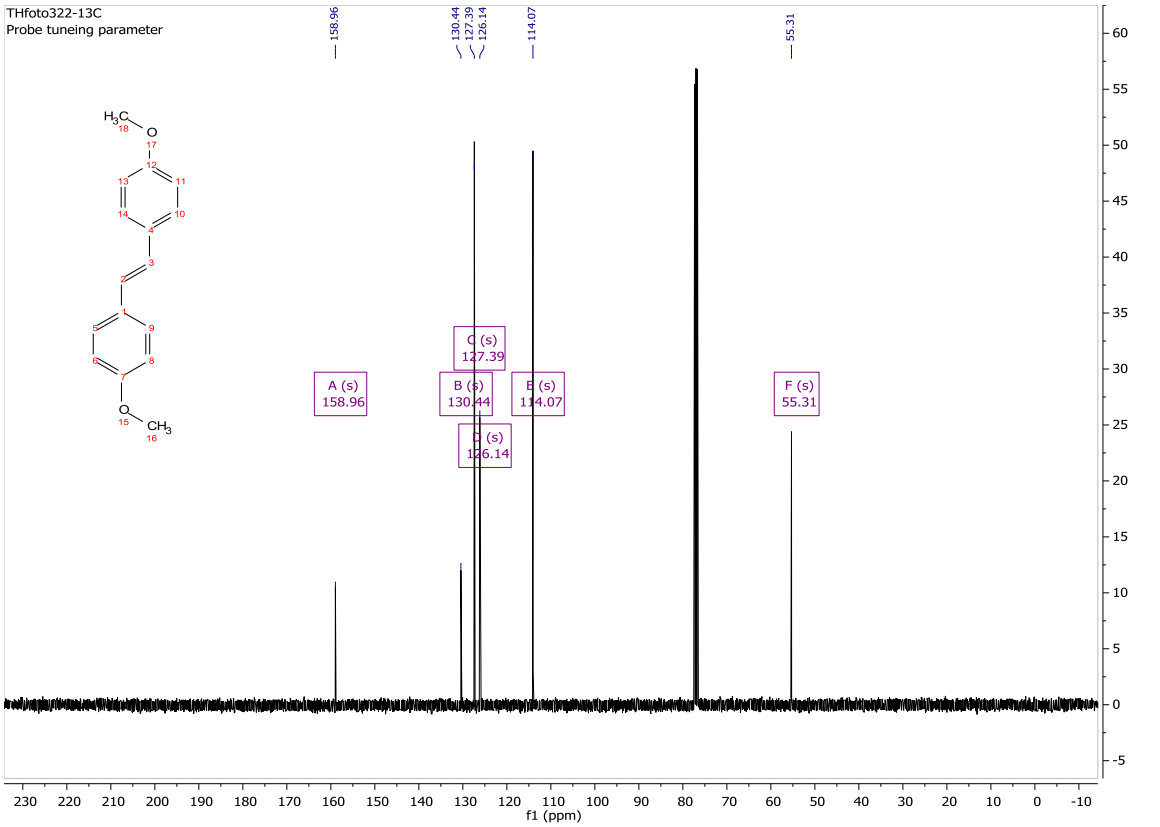
4h


THfoto313
STANDARD FLUORINE PARAMETERS
7.67
7.63
7.48
7.48
7.46
7.46
6.91
6.89
6.33
6.29
3.83
3.79
B (m)
7.47
D (d)
6.31
A (d)
7.65
C (d)
6.90
E (s)
3.83
1.00
2.08
2.03
1.07
3.03
2.91
f1 (ppm)

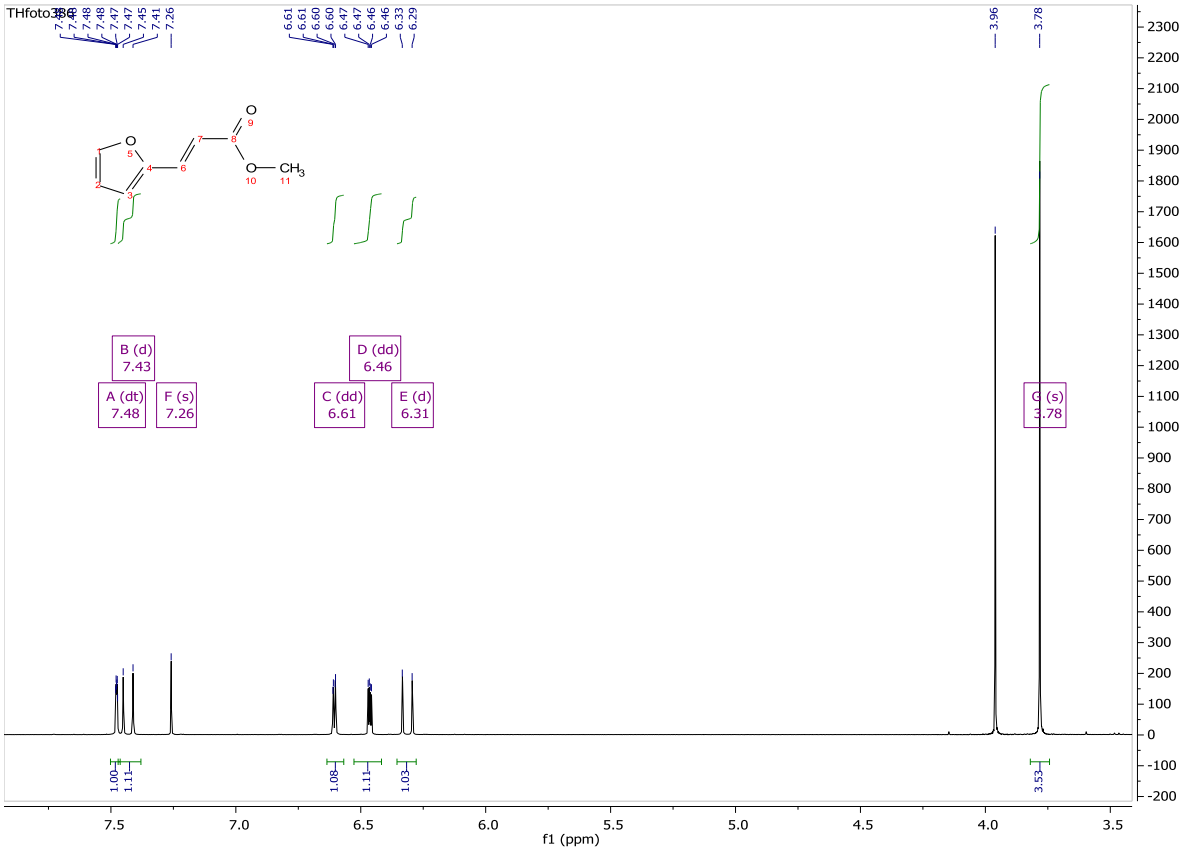

THfoto313-13C
STANDARD FLUORINE PARAMETERS
167.75
161.36
144.51
129.70
127.09
115.24
114.30
55.36
51.57
B (s)
161.36
A (s)
167.75
C (s)
144.51
I (s)
129.70
H (s)
127.09
G (s)
114.30
F (s)
115.24
E (s)
51.57
D (s)
55.36
f1 (ppm)

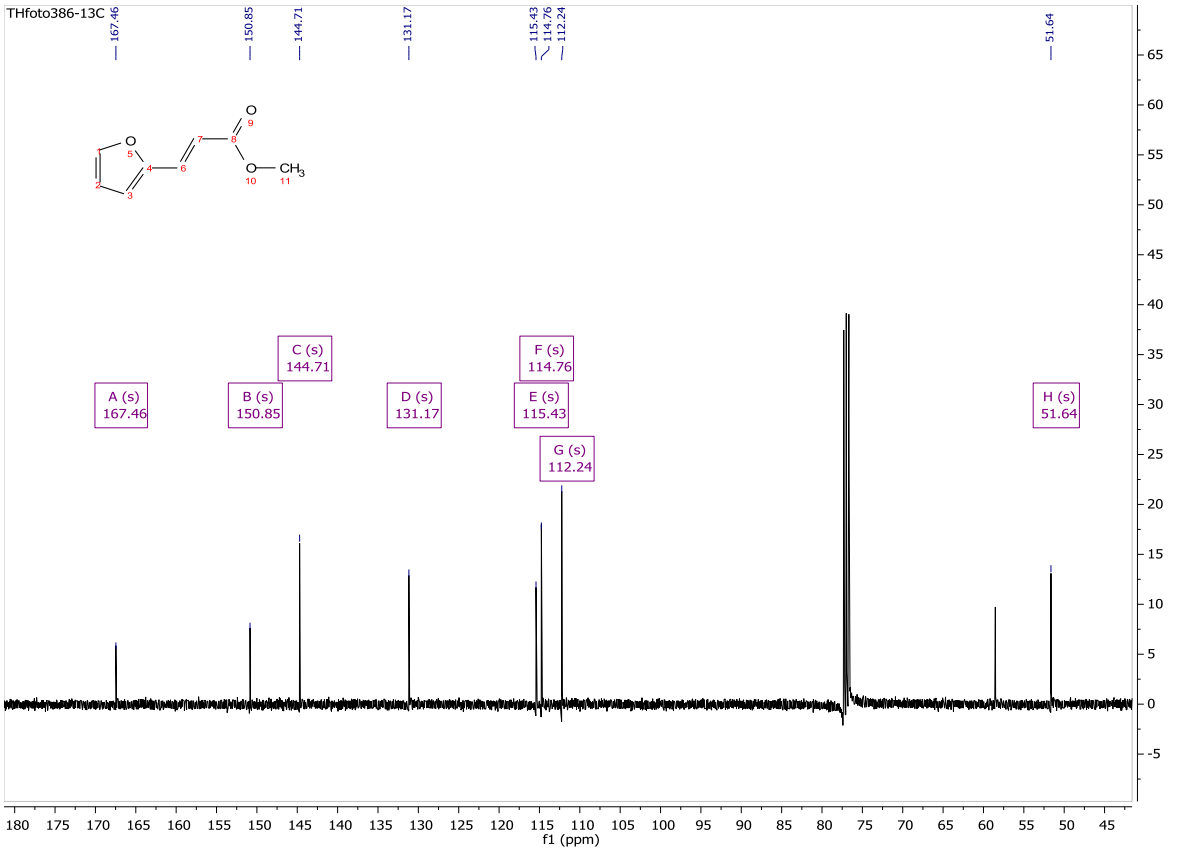
4i


THfoto322-1H
Probe tuneing parameter
7.44
7.42
6.93
6.90
6.88
3.83
B (s)
6.93
A (d)
7.43
C (d)
6.89
D (s)
3.83
4.00
1.91
3.89
6.19
f1 (ppm)


THfoto322-13C
Probe tuneing parameter
158.96
130.44
127.39
126.14
114.07
55.31
A (s)
158.96
C (s)
127.39
B (s)
130.44
E (s)
114.07
D (s)
126.14
F (s)
55.31
f1 (ppm)

4j


THfoto386
7.48
7.47
7.45
7.41
7.26
6.61
6.60
6.47
6.46
6.33
6.29
3.96
3.78
B (d) 7.43
A (dt) 7.48
F (s) 7.26
D (dd) 6.46
C (dd) 6.61
E (d) 6.31
G (s) 3.78
1.00
1.11
1.08
1.11
1.03
3.53
f1 (ppm)


THfoto386-13C
167.46
150.85
144.71
131.17
115.43
114.76
112.24
51.64
A (s) 167.46
B (s) 150.85
C (s) 144.71
D (s) 131.17
E (s) 115.43
F (s) 114.76
G (s) 112.24
H (s) 51.64
f1 (ppm)

S14 Copy of NMR Spectra of compound **2c**