Electronic Supporting Information

Organophotoredox Catalysed Stereoselective Reductive Dimerization of Chromone-2-Carboxylic Esters

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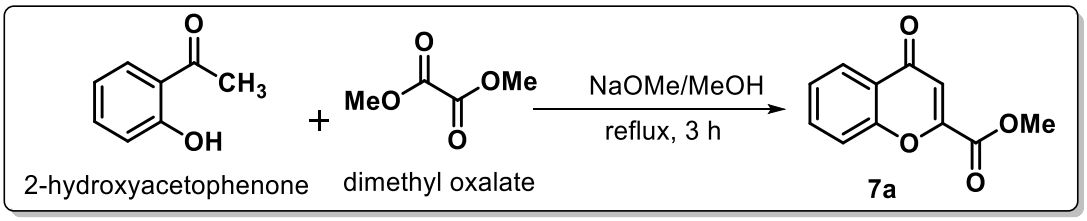
I. General remarks

All commercial reagents were obtained from Sigma-Aldrich Chemical Co., Sisco Research Laboratories, Spectrochem Pvt. Ltd, India, TCI Chemicals Pvt. Ltd, India and Avra synthesis Pvt. Ltd, India. Reactions were monitored by thin-layer chromatography (TLC, 0.25 mm E. Merck silica gel plates, $60F_{254}$) and the plates were visualized by using UV light. Column chromatography was performed on silica gel 60–120/100-200/230–400 mesh obtained from S. D. Fine Chemical Co., India. Evaporation of solvent was achieved using a Büchi water bath B-481 rotary evaporator under reduced pressure (0 – 1000 mbar) with a bath temperature of 40 °C**.** Yields represent chromatographically pure materials. ^{1}H NMR spectra were recorded on Bruker 400 MHz and 400 MHz Ultra Shield instruments using deuterated solvents. Proton coupling constants (***J***) are reported as absolute values in Hz. ^{13}C NMR spectra were recorded on Bruker 400 MHz Ultra Shield instrument operating at 100 MHz. Chemical shifts (δ) of the ^{1}H and ^{13}C NMR spectra are reported in ppm with a solvent resonance as an internal standard. For ^{1}H NMR: chloroform-d_1 7.26; for ^{13}C NMR: chloroform-d_1 77.16. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of a doublet, ddd = doublet of a doublet of doublet, t = triplet, dt = doublet of a triplet, q = quartet, quint = quintet, m = multiplet, br = broad, ar = aromatic. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on an Agilent 6530 Accurate-Mass Q-TOF LC/MS system (Agilent Technologies). UV spectroscopy measurements were performed on Cary 300 UV/Vis spectrophotometer (Agilent Technologies). Cyclic voltammetry (CV) was performed in the Admiral Squidstat Solo electrochemical instrument to measure the reduction potential. For determination of the enantiomeric excess (*ee*) the chiral phases Chiralcel OD-H was used on Agilent Technologies 1260 Infinity HPLC system equipped with OpenLAB CDS v2.3 software.

The Ene reductase (EREDs) enzymes used in this work, namely Yqjm, GluER, NostocER, OYE1, OYE2, OYE3, MorB, NtDBR and the regeneration enzyme GDH were produced in *E. coli* as described elsewhere[1] and used as a cell-free lysate in most experiments unless it is mentioned.

II. General Synthetic Procedures

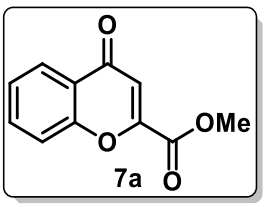
A. Synthesis of chromone-2-carboxylic ester 7a



Scheme S1. Synthesis of chromone-2-carboxylic ester 7**a**

2-hydroxyacetophenone (1.02 g, 7.5 mmol, 1 equiv.) and dimethyl oxalate (1.77 g, 15 mmol, 2 equiv.) were dissolved in methanol (5 ml) and added to the freshly prepared solution of sodium (0.69 g 30 mmol, 4 equiv.) in methanol (50 ml). The reaction mixture was heated at reflux for 3 h, after which it was cooled down and acidified with concentrated HCL until white precipitation was formed. The precipitation was filtered off, and the filtrate was concentrated and extracted with ethyl acetate (3x30 mL), washed with brine, and dried over Na_2SO_4. After evaporation crude mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to give the desired carboxylic ester **7a** (1.15g, 75% yield) as a white crystalline solid.

Methyl 4-oxo-4*H*-chromene-2-carboxylate (7a)



$C_{11}H_8O_4$: 204.18 g. mole^{-1}

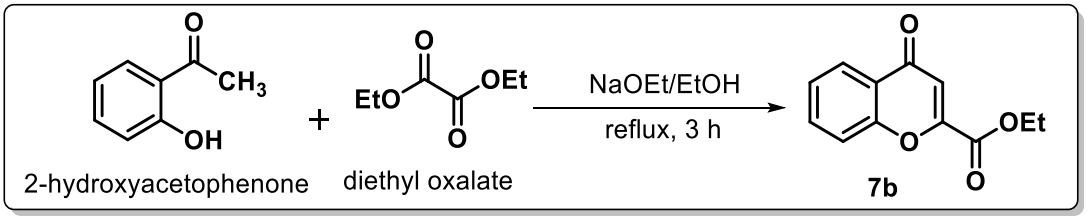
TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.46

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.20 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 4.02 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.5, 161.2, 156.1, 152.1, 134.9, 126.1, 125.9, 124.5, 118.9, 115.0, 53.7.

Exact Mass: M + H]$^+$ Calculated for $C_{11}H_9O_4$ 205.0496; Found 205.0493.

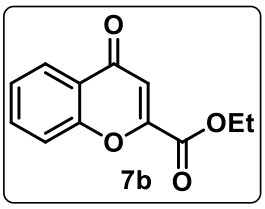
B. Synthesis of chromone-2-carboxylic ester 7b



Scheme S2. Synthesis of chromone-2-carboxylic ester 7**b**

2-hydroxyacetophenone (1.02 g, 7.5 mmol, 1 equiv.) and diethyl oxalate (2.19 g,15 mmol, 2 equiv.) were dissolved in ethanol (5 ml) and added to the freshly prepared solution of sodium (0.69 g 30 mmol, 4 equiv.) in ethanol (50 ml). The reaction mixture was heated at reflux for 3 h, after which it was cooled down and acidified with concentrated HCL until white precipitation was formed. The precipitation was filtered off, and the filtrate was concentrated and extracted with ethyl acetate (3x30 mL), washed with brine, and dried over Na_2SO_4. After evaporation crude mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to give the desired carboxylic ester **7b** (1.32g, 81% yield) as a colorless crystalline solid.

Ethyl 4-oxo-4*H*-chromene-2-carboxylate (7b)



$C_{12}H_{10}O_4$: 218.20 g. mole^{-1}

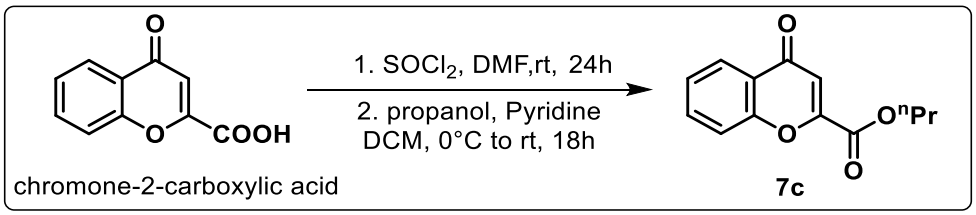
TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.42

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.11 (d, *J* = 7.9 Hz, 1H), 7.68 (t, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.04 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.4, 160.5, 155.9, 152.2, 134.7, 125.9, 125.7, 124.4, 118.8, 114.7, 63.0, 14.1.

Exact Mass [M+H] $^+$: Calculated for $C_{12}H_{11}O_4$ 219.0652; Found 219.0649.

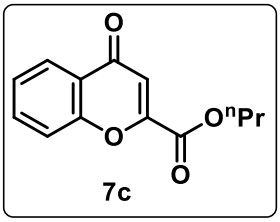
C. Synthesis of chromone-2-carboxylic ester 7c



Scheme S3. Preparation of chromone-2-carboxylic ester 7**c**.

To a flame-dried round bottom flask was added chromone-2-carboxylic acid (0.5 g, 2.63 mmol, 1 equiv.), thionyl chloride (4.5 g, 31.5 mmol, 12.3 equiv.), and dry DMF (10 μL,0.13 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture is homogenous. The reaction mixture is then concentrated under a vacuum to obtain crude chromone-2-acid chloride which was carried to the next step without purification. To the flask containing the crude acid chloride, DCM (25 mL) was added. The solution was cooled to 0ºC then pyridine (0.4 mL, 5 mmol, 1 equiv.) was added dropwise. 0.5 mL n-propyl alcohol was then added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with water (20 mL), and then extracted with DCM (3x20mL). The combined organic phase was washed with brine (2x10 mL), and then dried over Na_2SO_4. The solvent was removed under vacuum to yield crude chromone-2-carboxylate. The crude was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield pure propyl 4-oxo-4H-chromene-2-carboxylate (**7c**) (503 mg, 82% yield) as a white crystalline solid.

Propyl 4-oxo-4*H*-chromene-2-carboxylate (7c)



$C_{13}H_{12}O_4$: 232.24 g. mole^{-1}

TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.41

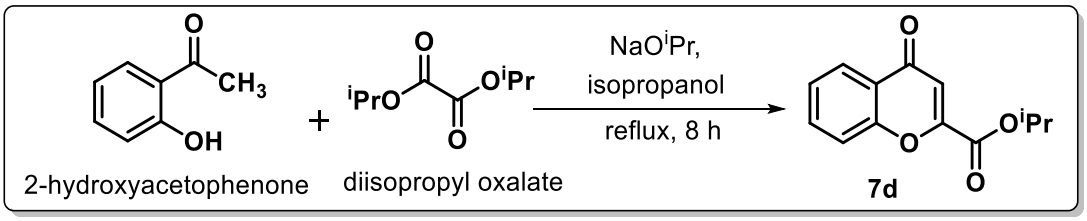
Yield = 82%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.17 (d, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 4.34 (t, *J* = 6.53, 2H), 1.85-1.76 (m, 2H), (t, *J* = 7.37 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.5, 160.7, 156.1, 152.3, 134.8, 126.0, 125.8, 124.5, 118.9, 114.8, 68.5, 21.9, 10.4.

Exact Mass [M+H] $^{+}$: Calculated for $C_{13}H_{13}O_4$ 233.0809; Found 233.0806.

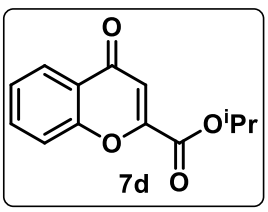
D. Synthesis of chromone-2-carboxylic ester 7d



Scheme S4. Synthesis of chromone-2-carboxylic ester 7**d**

2-hydroxyacetophenone (1.02 g, 7.5 mmol, 1 equiv.) and diisopropyl oxalate (2.61 g, 15 mmol, 2 equiv.) were dissolved in isopropanol (5 ml) and added to the freshly prepared solution of sodium (0.75 g 30 mmol, 4 equiv.) in isopropanol (50 ml). The reaction mixture was heated at reflux for 8 h, after which it was cooled down and acidified with concentrated HCL until white precipitation was formed. The precipitation was filtered off, and the filtrate was concentrated and extracted with ethyl acetate (3x30 mL), washed with brine, and dried over Na_2SO_4. After evaporation crude mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to give the desired carboxylic ester **7d** (1.17g, 67% yield) as a colorless crystal.

Isopropyl 4-oxo-4*H*-chromene-2-carboxylate (7d)



$C_{13}H_{12}O_4$: 232.23 g. mole^{-1}

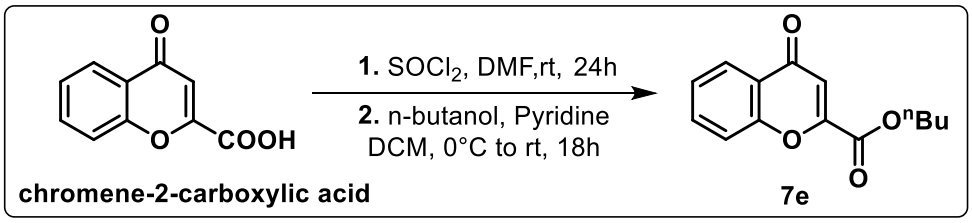
TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.41

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.14 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.06 (s, 1H), 5.30-5.21 (m, 1H), 1.37 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.6, 160.0, 156.0, 152.5, 134.8, 125.9, 125.7, 124.4, 118.9, 114.6, 71.3, 21.7.

Exact Mass: M + H]$^+$ Calculated for $C_{13}H_{13}O_4$ 233.0809; Found 233.0808.

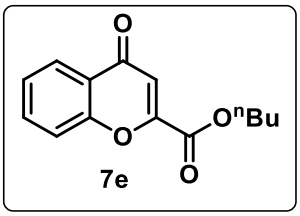
E. Synthesis of chromone-2-carboxylic ester 7e



Scheme S5. Preparation of chromone-2-carboxylic ester **7e**.

Chromone-2-carboxylic ester **7e** was synthesized according to the reported procedure.[2] For that, to a flame-dried round bottom flask was added chromone-2-carboxylic acid (0.95 g, 5 mmol, 1 equiv.), thionyl chloride (4.5 mL, 61.5 mmol, 12.3 equiv.), and dry DMF (20 µL,0.25 mmol, 0.05 equiv.). The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture is homogenous. The reaction mixture is then concentrated under a vacuum to obtain crude chromone-2-acid chloride which was carried to the next step without purification. To the flask containing the crude acid chloride, DCM (25 mL) was added. The solution was cooled to 0ºC then pyridine (0.4 mL, 5 mmol, 1 equiv.) was added dropwise. 1mL Butyl alcohol (5 mmol, 1 equiv.) was then added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with water (20 mL), and then extracted with DCM (3x20mL). The combined organic phase was washed with brine (2x10 mL), and then dried over Na_2SO_4. The solvent was removed under vacuum to yield crude chromone-2- carboxylate. The crude was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield pure butyl 4-oxo-4*H*-chromene-2-carboxylate (**7e**) (0.75g, 61% yield) as a white crystalline solid.

Butyl 4-oxo-4*H*-chromene-2-carboxylate (7e)



$C_{14}H_{14}O_4$: 246.26 g. mole^{-1}

TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.48

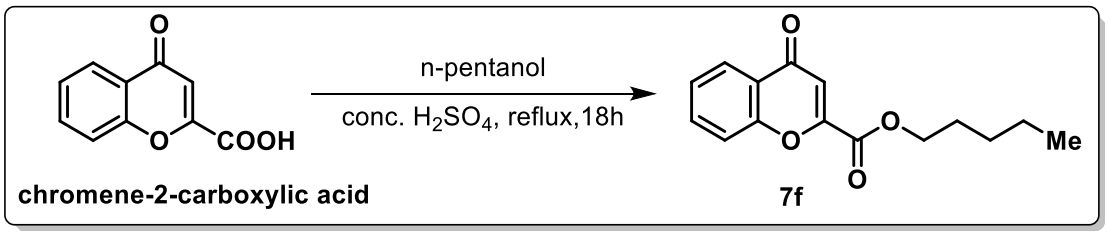
Yield = 61%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.18 (d, *J* = 7.9 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 4.39 (t, *J* = 6.53, 2H), 1.80-1.73 (m, 2H), 1.51-1.42 (m, 2H), 0.98 (d, *J* = 7.37 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.6, 160.7, 156.1, 152.3, 134.8, 126.0, 125.8, 124.5, 118.9, 114.9, 66.9, 30.5, 19.2, 13.8.

Exact Mass [M+H] $^+$: Calculated for $C_{14}H_{15}O_4$ 247.0965; Found 247.0961

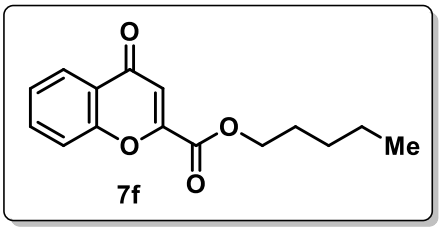
F. Synthesis of pentyl 4-oxo-4H-chromene-2-carboxylate (7f)



Scheme S6. Preparation of chromone-2-carboxylic ester **7f**.

To a 10 mL round bottom flask, chromone-2-carboxylic acid (480 mg, 2.5 mmol, 1 equiv.), and n-pentanol (880 mg, 10 mmol, 4 equiv.) were added. Then 3-5 drops of concentrated H_2SO_4 were added to the reaction mixture and heated to reflux for 12 hours. Upon completion, the reaction mixture is homogenous. The reaction was quenched with water (20 mL), and then extracted with DCM (3x20mL). The combined organic phase was washed with brine (2x10 mL), and then dried over Na_2SO_4. The solvent was removed under vacuum to yield crude chromone-2- carboxylate. The crude reaction mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield pentyl 4-oxo-4H-chromene-2-carboxylate (**7f**) (419 mg, 68% yield) as a white crystalline solid.

Pentyl-4-oxo-4H-chromene-2-carboxylate (7f)



$C_{14}H_{14}O_4$: 260.29 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.43

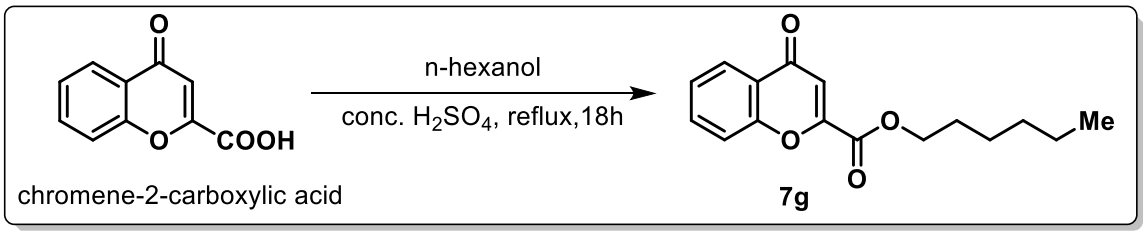
Yield = 68%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.14 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.73-7.68 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.43-7.39 (m, 1H), 7.07 (s, 1H), 4.36 (t, *J* = 6.9 Hz, 2H), 1.79-1.72 (m, 2H), 1.42-1.33 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.5, 160.6, 156.0, 152.2, 134.8, 125.9, 125.7, 124.4, 118.8, 114.8, 67.1, 28.2, 28.0, 22.3, 14.0.

Exact Mass [M+H] $^+$: Calculated for $C_{14}H_{15}O_4$ 261.1122; Found 261.1116.

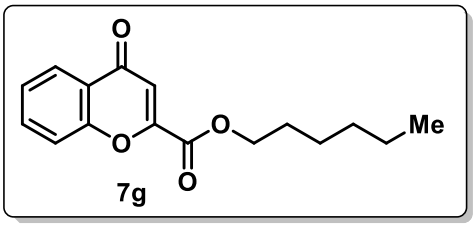
F. Synthesis of hexyl 4-oxo-4H-chromene-2-carboxylate (7g)



Scheme S7. Preparation of chromone-2-carboxylic ester **7g**.

To a 10 mL round bottom flask, chromone-2-carboxylic acid (480 mg, 2.5 mmol, 1 equiv.), and n-pentanol (1.02 mL, 10 mmol, 4 equiv.) were added. Then 3-5 drops of concentrated H_2SO_4 were added to the reaction mixture and heated to reflux for 12 hours. Upon completion, the reaction mixture is homogenous. The reaction was quenched with water (20 mL), and then extracted with DCM (3x20mL). The combined organic phase was washed with brine (2x10 mL), and then dried over Na_2SO_4. The solvent was removed under vacuum to yield crude chromone-2- carboxylate. The crude reaction mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield hexyl 4-oxo-4H-chromene-2-carboxylate (**7f**) (418 mg, 61% yield) as a colorless crystalline solid.

hexyl 4-oxo-4H-chromene-2-carboxylate (7g)



$C_{16}H_{18}O_4$: 274.32 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.44

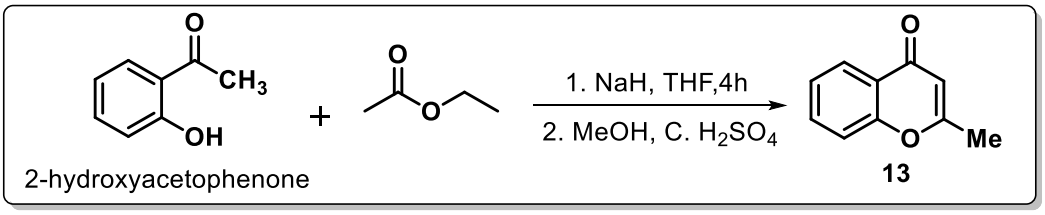
Yield = 61%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.14 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.72-7.68 (m, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.43-7.39 (m, 1H), 7.07 (s, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 1.78-1.71 (m, 2H), 1.43-1.36 (m, 2H), 1.35-1.28 (m, 4H), 0.87 (t, *J* = 6.95 Hz, 3H)

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.5, 160.6, 156.0, 152.2, 134.8, 125.9, 125.7, 124.4, 118.8, 114.8, 67.1, 31.4, 28.4, 25.5, 22.5, 14.1.

Exact Mass [M+H] $^+$: Calculated for $C_{16}H_{19}O_4$ 275.1278; Found 275.1270

F. Synthesis of 2-methyl-4*H*-chromen-4-one (13):

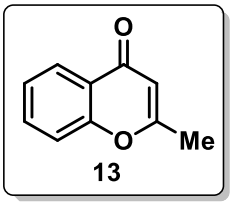


Scheme S8. Synthesis of chromone **13**.

Chromone substrate **13** was synthesized according to the reported procedure.[3] Sodium hydride (60% dispersion in mineral oil, 1.18 g, 29.4 mmol) was rinsed three times with hexanes, and then suspended in THF (9 mL). A mixture of 2-hydroxyacetophenone (0.88 mL, 7.4 mmol) and EtOAc (1.8 mL, 18.4 mmol) in THF (2.5 mL) was added dropwise to the above suspension at room temperature. A vigorous reaction was observed, and the temperature increased to reflux. After complete addition, the reaction mixture was stirred for a further 5 min, then quenched by pouring it on the ice, then acidified to pH 6 with 6 M aq HCl. The resulting precipitate was collected via filtration, washed with water, and dried under a high vacuum. Then the crude reaction mixture was dissolved in methanol (15 mL) and 5-6 drops of concentrated H_2SO_4 were added to the solution and the mixture was allowed to stir at room temperature for 14 h. The mixture was concentrated under reduced pressure and the residue

was diluted with EtOAc (30 mL), then washed successively with solutions of saturated aqueous $NaHCO_3$ (3 x 30 mL), water (30 mL), and brine (30 mL). The organic layer was then dried over Na_2SO_4. The solvent was removed under vacuum to yield the crude product. The crude reaction mixture was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield pure 2-methyl-4*H*-chromen-4-one (**13**) (0.9g, 78% yield) as a white powder.

2-methyl-4*H*-chromen-4-one (13)



$C_{10}H_8O_2$: 160.17 g. mole^{-1}

TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.42

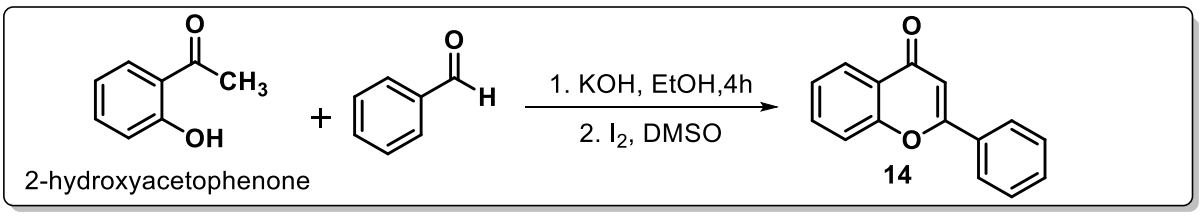
Yield = 78%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.16 (d, *J* = 7.87 Hz, 1H), 7.62 (t, *J* = 8.02 Hz, 1H), 7.41-7.34 (m, 2H), 6.16 (s, 1H), 2.37 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.3, 166.2, 156.5, 133.5, 125.7, 125.0, 123.6, 117.9, 110.6, 20.7.

Exact Mass [M+H] $^+$: Calculated for $C_{10}H_9O_2$ 161.0598; Found 161.0593

G. Synthesis of 2-methyl-4*H*-chromen-4-one (13):

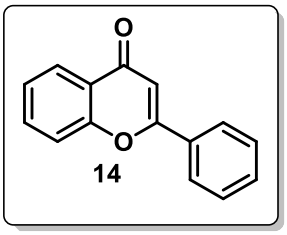


Scheme S9. Synthesis of chromone **13**.

A mixture of 2-hydroxyacetophenone (0.85 mL, 7.3 mmol, 1 equiv.) and benzaldehyde (0.9 mL, 8.8 mmol, 1.2 equiv.) was added to 10% KOH solution (w/v), and stirred at room temperature for overnight. After that, the reaction mixture was quenched by pouring it on the ice, and then acidified with diluted HCl (pH 5). The resulting precipitate was collected via

filtration, washed with water, and dried under a high vacuum. Then the crude reaction mixture was dissolved in DMSO (10 mL) and a catalytic amount of I_2 was added to the solution and the mixture was allowed to reflux at 110^o C temperature for 12 h. The mixture was concentrated under reduced pressure and the residue was diluted with EtOAc (30 mL), then washed successively with solutions of saturated aqueous $NaHCO_3$ (3 x 30 mL), water (30 mL), and brine (30 mL). The organic layer was then dried over Na_2SO_4. The solvent was removed under vacuum to yield the crude product. The crude product was purified by column chromatography (Silica gel 100-200 mess size, hexane: ethyl acetate 4:1) to yield pure 2-phenyl-4H-chromen-4-one (**14**) (1.1g, 68% yield) as a white powder.

2-phenyl-4H-chromen-4-one (14)



$C_{15}H_{10}O_2$: 222.24 g. mole^{-1}

TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.41

Yield = 68%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 8.20 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.90-7.87 (m, 2H), 7.68-7.64 (m, 1H), 7.54-7.46 (m, 4H), 7.40-7.36 (m, 1H), 6.79 (s, 1H).

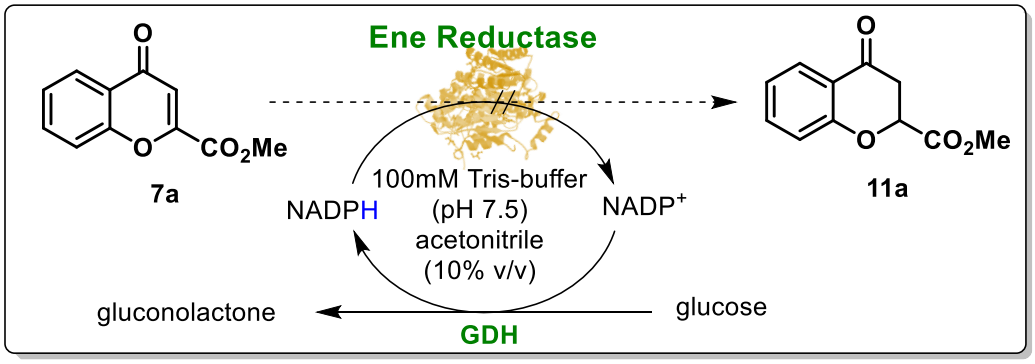
^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 178.4, 163.4, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 125.2, 124.0, 118.1, 107.6.

Exact Mass [M+H] $^+$: Calculated for $C_{15}H_{11}O_2$ 223.0754; Found 223.0751

III. Photodimerization reaction with the model substrate (7a)

A. Attempted biocatalytic reduction of the model substrate 7a to 11a using ene-reductase

For the biocatalytic C=C bond reduction of chromone **7a** preliminary screening of biocatalyst was performed using cell-free lysate of ene reductase (EREDs) enzymes and GDH for cofactor recycling. The general procedure for these biocatalytic reactions is described below



Scheme S10: Ene reductase catalyzed attempted bioreduction of **7a**

To a 25 mL round bottom flask, $NADP^+$ (4 mg, 0.005 mmol, 0.1 equiv.), glucose (44.0 mg, 0.25 mmol, 5 equiv.), and GDH (10 U) were added into 10 mL tris buffer solution (100 mM, pH 7.5), degassed under the counterflow of argon for half an hour, at room temperature. Then, methyl 4-oxo-4*H*-chromene-2-carboxylate (**7a**) (10.0 mg, 0.05 mmol, 1 equiv.) in acetonitrile (1 mL, 10 % v/v) was added slowly, while stirring. Then, ene reductase (Yqjm/GluER/ NostocER/OYE1/OYE2/OYE3/MorB/NtDBR) cell-free lysate (0.5 mL, 2 U) was added to the reaction mixture and kept stirring at 100 rpm at room temperature under argon. After 12 h, the reaction was stopped by the addition of ethyl acetate and the solution was extracted with ethyl acetate (EtOAc, 3 x 10 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. the crude reaction mixture was directly subjected to NMR spectroscopy in $CDCl_3$. The ^{1}H-NMR analysis of the crude reaction mixture shows that only starting material is present in the reaction mixture. **Hence, all the ene reductases (EREDs) used in this study are inactive towards the C=C bond reduction of chromone 7a.**

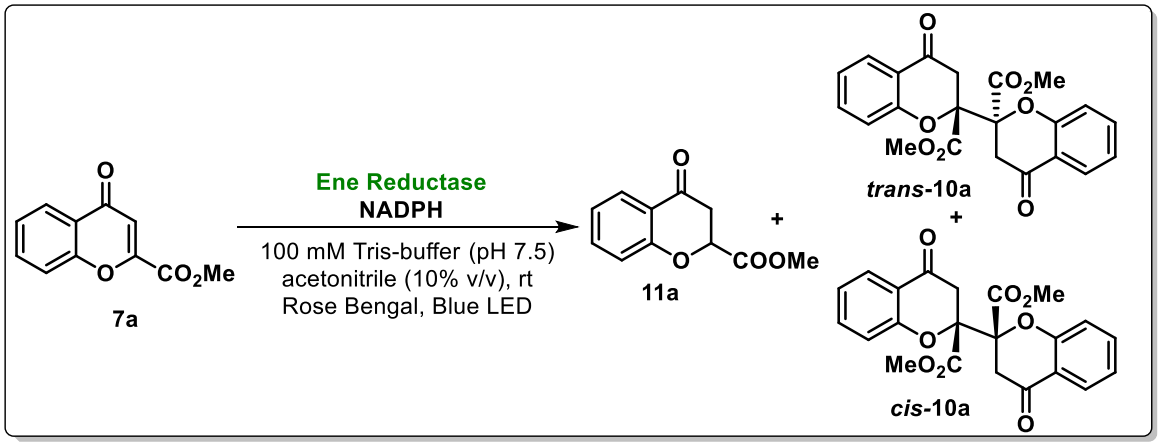
Table S1: Screening of ene reductase (ERED) for C=C bond reduction

Enzyme	YqjM	GluER	NostocER	OYE1	OYE2	OYE3	MorB	NtDBR
Conv. (%)	-	-	-	-	-	-	-	-

B. Attempted photobiocatalytic reduction of the model substrate using ene-reductase and photocatalyst in the presence of light.

To a 25 mL round bottom flask, $NADP^+$ (4 mg, 0.005 mmol, 0.1 equiv.), glucose (44.0 mg, 0.25 mmol, 5 equiv.) and GDH (10 U) were added into 10 mL tris buffer solution (100 mM, pH 7.5), degassed under the counterflow of argon for half an hour, at room temperature. Then, methyl 4-oxo-4*H*-chromene-2-carboxylate (**7a**) (10.0 mg, 0.05 mmol, 1 equiv.) in acetonitrile (1 mL, 10 % v/v) was added slowly, consequently, 2 mole % of Rose Bengal (as a photocatalyst) and the EREDs (2-3 U, used as a cell-free extract) was added to the reaction mixture and it placed in the photo-reactor (**Figure S1**) for the continuous irradiation of blue light while stirring at 100 rpm at room temperature. After 12 h, the reaction was stopped by the addition of ethyl acetate, and the solution was extracted with ethyl acetate (EtOAc, 3 x 10 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. the crude reaction mixture was directly subjected to NMR spectroscopy in $CDCl_3$. The ^{1}H-NMR analysis of the crude reaction mixture showed the formation diastereomeric mixture of dimeric chromone *trans*-**10a** and *cis*-**10a** along with 6-8% corresponding reduced chromone **11a**. **Since same products were obtained even in the absence of an enzyme, therefore the observed photodimerization is non-enzymatic.**

Table S2: Screening of ene reductase (ERED) for photobioacatalytic reduction of C=C bond of model substrate.



Enzyme	YqjM	GluER	NostocER	NtDBR	NIL
Conv. (%)	35	37	31	34	37
Ratio (11a:*trans*-10a:*cis*-10a)	8:62:30	7:64:29	7:65:28	6:64:30	7:64:29

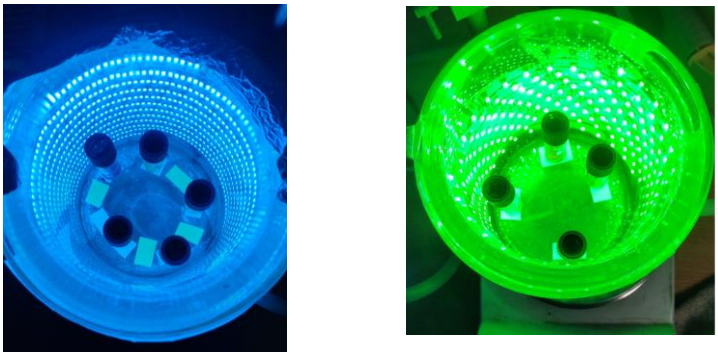
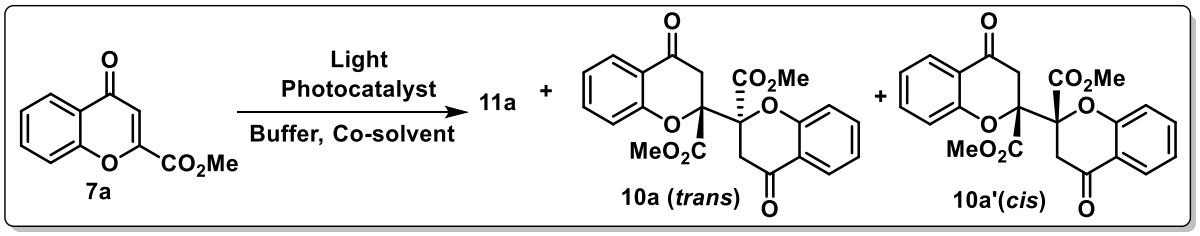


Figure S1: Experimental setup for photocatalytic/ photobiocatalytic reaction.

C. Optimization of reaction conditions for photoreductive dimerization of model substrate (7a).



Analytical photoreactions were performed using a 5W LED strip light for photoactivation (**Fig-S1**). Unless stated otherwise for all reactions, the optimization of the photodimerization reaction was performed by the incubation of 10 mg **7a** (dissolved in 0.4 mL acetonitrile) in 4 mL buffer in a 5 mL glass vial. Then, a 2 mol % photocatalyst was added to the reaction mixture, and the reaction vial was placed in the photoreactor (Figure S1) to start the photoreaction. After 6 h reaction mixture was quenched and extracted into ethyl acetate (2 x reaction volume). The organic fractions were combined and analyzed by ^{1}H-NMR of the crude reaction mixture.

Table S3: Optimization of different buffer and buffer concentrations for the photodimerization of model substrate.

Entry	Solvent	Conversion (%)	Product ratio (**11a**:*trans*-**10a**: *cis*-**10a**)
1	100 mM Kpi (pH 7.5) buffer, 10% ACN (v/v)	-	-
2	100 mM M9 (pH 7.5) buffer, 10% ACN (v/v)	-	-
3	200 mM Tris (pH 7.5) buffer, 10% ACN (v/v)	46	ND
4	100 mM TEOA (pH 7.5) buffer, 10% ACN (v/v)	59	6:67:27

5	200 mM TEOA (pH 7.5) buffer, 10% ACN (v/v)	85	5:70:25
6	50 mM TEOA (pH 7.5) buffer, 10% ACN (v/v)	64	8:66:26
7	200 mM TEOA in ACN	4	-
8	200 mM TEOA in ethanol	12	-

Table S4: Optimization of the buffer pH for the photodimerization of the model substrate.

Entry	**Buffer pH**	**Conversion (%)**	**dr*trans*:*cis*** **(*trans*-10a: *cis*-10a)**
1	200 mM TEOA (pH 5.0) buffer	-	-
2	200 mM TEOA (pH 6.0) buffer	<10	65:35
3	**200 mM TEOA (pH 7.0) buffer**	**98**	**83:17**
4	200 mM TEOA (pH 8.0) buffer	35	67:33
5	200 mM TEOA (pH 9.0) buffer	12	62:38

Table S5: Screening of Photocatalyst and light for photodimerization of model substrate

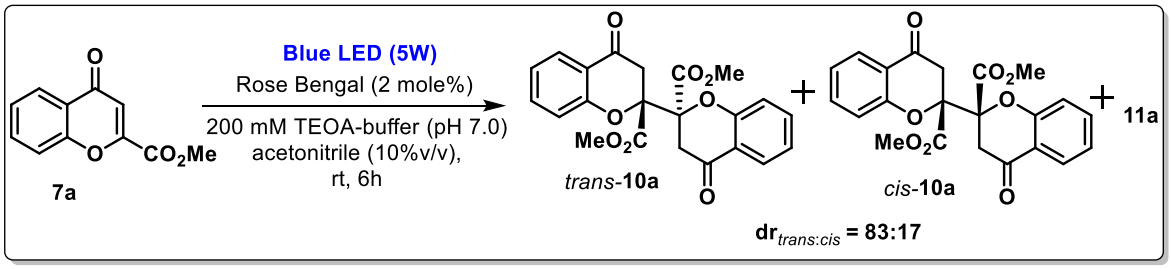
Entry	Photocatalyst (2 mol %)	Light (5W LED)	Conversion	**dr*trans*:*cis*** **(*trans*-10a: *cis*-10a)**
1	**Rose Bengal**	**Blue**	**98%**	**83:17**
2		Green	-	NA
3		Red	-	NA
4	Riboflavin	Blue	-	NA
5		Green	-	NA
6		Red	-	NA
7	Eosin Yellow	Blue	-	NA
8		Green	**60%**	**60:40**
9		Red	-	NA
10	Eosin Blue	Blue	-	NA
11		Green	-	NA
12		Red	-	NA
13	$Ru(bpy)_3Cl_2.6H_2O$	Blue	-	NA
14		Green	-	NA
15		Red	-	NA
16	$Ir(ppy)_3Cl_2$	Blue	-	NA
17		Green	-	NA
18		Red	-	NA

IV. Preparative scale photodimerization of various chromone-2-carboxylic esters (7a-7e)

General Procedure

In a 50 mL round bottom flask, 25 ml TEOA buffer solution (200 mM, pH 7.0) was taken and degassed under the counterflow of argon for half an hour, at room temperature. Then chromone-2-carboxylic ester **7a-7e (**0.5 mM 1 equiv.) was dissolved in acetonitrile pH 7 (10% v/v) and Rose Bengal (2 mol %) was added and the mixture was irradiated with a 5W-LED lamp. After 6 h the crude reaction mixture was extracted with EtOAc (3x20 mL) and the combined organic layer was washed with brine (30 mL), and dried over Na_2SO_4. After the removal of the solvent in vacuo, the crude photo lysate was subjected to chromatography on silica gel, and the product was isolated as a diastereomeric mixture of photodimer.

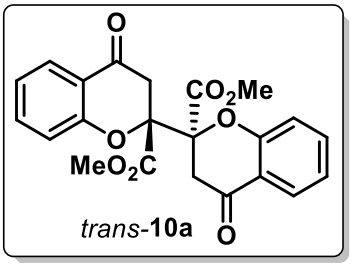
A. Photodimerization of methyl 4-oxo-4*H*-chromene-2-carboxylate (7a)



Scheme S11. Reductive photodimerization of chromone-2-carboxylic ester **7a**

A 96 mg (93% yield) of diastereomeric mixture was obtained. *trans*-**10a** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

Dimethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10a)



$C_{22}H_{18}O_8$: 410.38 g. mole^{-1}

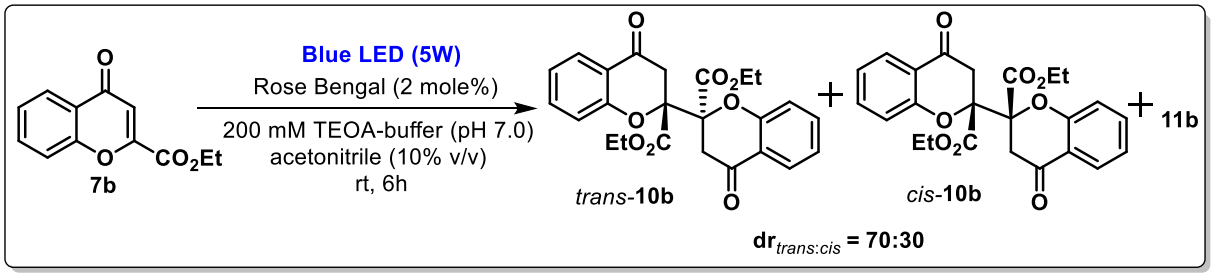
TLC (hexane/ethyl acetate, 7:3 v/v): R_f =0.41

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.85 (dd, *J* = 7.8, *J* = 1.1 Hz, 2H), 7.57-7.53 (m, 2H), 7.12-7.07 (m, 4H), 3.70 (s, 6H), 3.45 (d, *J* = 16.7 Hz, 2H), 3.31 (d, *J* = 16.7 Hz, 2H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 188.4, 168.2, 159.5, 136.9, 126.9, 122.7, 120.5, 118.4, 86.1, 53.7, 40.8.

Exact Mass [M+H] $^+$: Calculated for $C_{22}H_{19}O_8$ 411.1075; Found 411.1077.

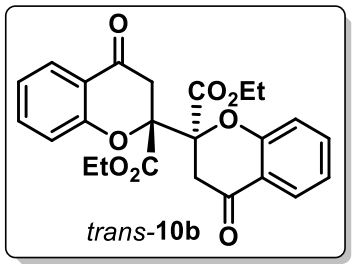
B. Photodimerization of ethyl 4-oxo-4H-chromene-2-carboxylate (7b)



Scheme S12. Reductive photodimerization of chromone-2-carboxylic ester **7b**

A 98 mg (90% yield) of diastereomeric mixture was obtained. *trans*-**10b** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

Diethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10b)



$C_{24}H_{22}O_8$: 438.43 g. mole^{-1}

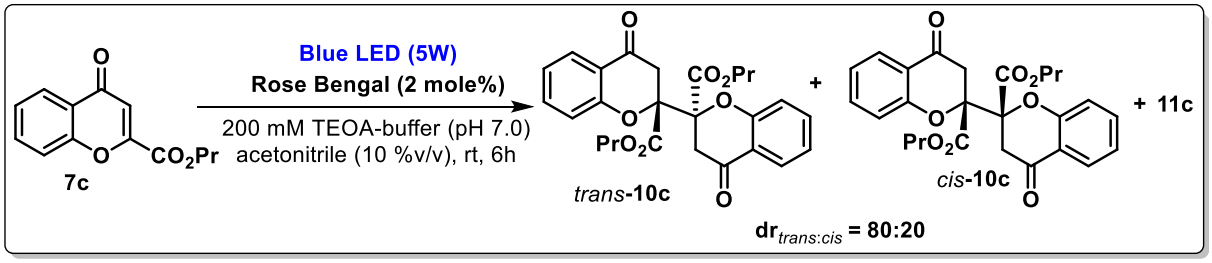
TLC (hexane/ethyl acetate, 7:3 v/v): R_f = 0.39

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.85 (dd, *J* = 7.8, *J* = 1.4 Hz, 2H), 7.56-7.52 (m, 2H), 7.11-7.05 (m, 4H), 4.22-4.09 (m, 4H), 3.46 (d, *J* = 16.7 Hz, 2H), 3.32 (d, *J* = 16.7 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 188.6, 167.6, 159.7, 136.8, 126.8, 122.6, 120.6, 118.4, 85.9, 63.0, 40.9, 13.9.

Exact Mass [M+H] $^+$: Calculated for $C_{24}H_{23}O_8$ 439.1388; Found 439.1394.

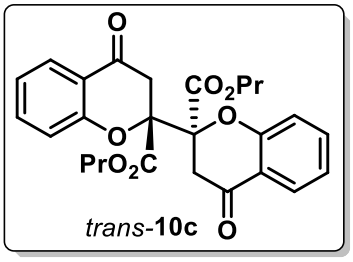
C. Photodimerization of propyl 4-oxo-4*H*-chromene-2-carboxylate (7c)



Scheme S13. Reductive photodimerization of chromone-2-carboxylic ester **7c.**

The product was isolated as a diastereomeric mixture of photodimer (10c: 10c' = 80:20) (94 mg, 81% (isolated yield)) along with **11c** (yield: 16%). In this case, the diastereomers could not be separated.

Dipropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10c)



$C_{26}H_{26}O_8$: 466.49 g. mole^{-1}

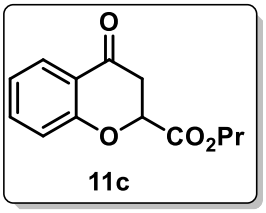
TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.40

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.87-7.84 (m, 2H), 7.56-7.51 (m, 2H), 7.13-7.05 (m, 4H), 4.04-3.98 (m, 4H), 3.70 (d, *J* = 16.7 Hz, 2H), 3.34 (d, *J* = 16.7 Hz, 2H), 1.54-1.43 (m, 4H), 0.73 (t, *J* = 6.2 Hz, 6H)

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.2, 167.7, 159.4, 136.8, 126.9, 122.7, 120.5, 118.3, 86.3, 68.7, 40.3, 21.7, 10.2

Exact Mass [M+H] $^+$: Calculated for $C_{26}H_{27}O_8$ 467.1701; Found 467.1703.

Propyl 4-oxochromane-2-carboxylate (11c)



$C_{13}H_{14}O_4$: 234.25 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.42

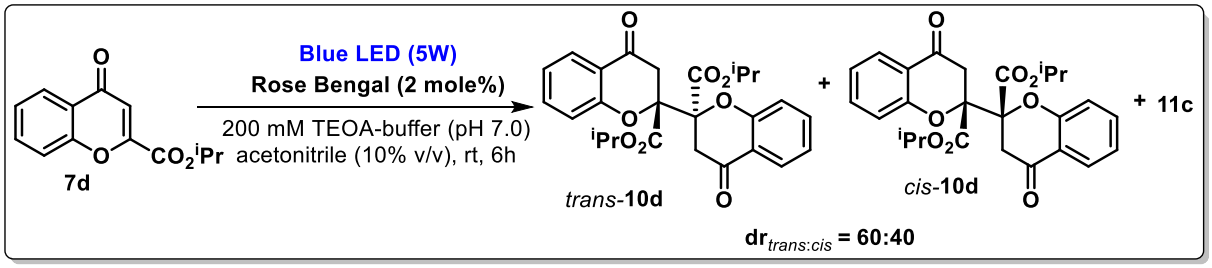
Yield = 16%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.87 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.11-7.04 (m, 2H), 5.11-5.08 (m, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.11-3.01 (m, 2H), 1.70-1.62 (m, 2H), 0.09 (t, *J* = 6.7 Hz, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.8, 169.0, 160.3, 136.6, 127.1, 122.3, 121.0, 118.3, 75.3, 67.7, 39.7, 21.9, 10.3.

Exact Mass [M+H] $^+$: Calculated for $C_{13}H_{15}O_4$ 235.0965; Found 235.0957.

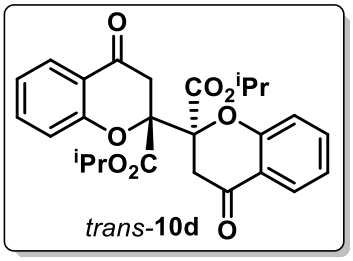
D. Photodimerization of isopropyl 4-oxo-4*H*-chromene-2-carboxylate (7d)



Scheme S14. Reductive photodimerization of chromone-2-carboxylic ester **7d**

A 87 mg, (75% yield) of diastereomeric mixture along with **11d** (19% yield) was obtained. *trans*-**10d** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

diisopropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10d)



$C_{26}H_{26}O_8$: 466.49 g. mole^{-1}

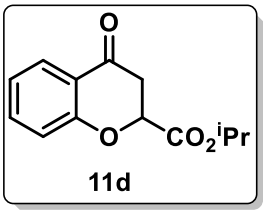
TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.41

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.85 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.10-7.05 (m, 4H), 5.02-4.92 (m, 2H), 3.46 (d, *J* = 16.7 Hz, 2H), 3.32 (d, *J* = 16.7 Hz, 2H), 1.19 (d, *J* = 6.2 Hz, 6H), 0.99 (d, *J* = 6.2 Hz, 6H)

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 188.8, 167.1, 159.8, 136.7, 126.8, 122.5, 120.7, 118.4, 85.8, 71.2, 41.1, 21.6, 21.3.

Exact Mass [M+H] $^+$: Calculated for $C_{26}H_{27}O_8$ 467.1701; Found 467.1697**.**

Isopropyl 4-oxochromane-2-carboxylate (11d)



$C_{13}H_{14}O_4$: 234.25 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.44

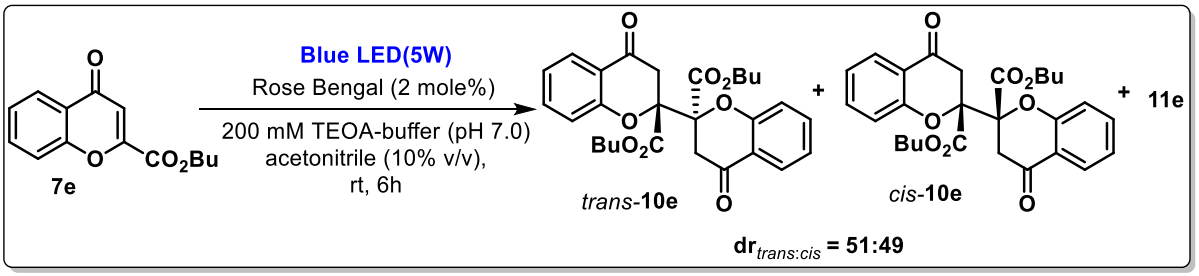
Yield = 19%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.87 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.52-7.48 (m, 1H), 7.10-7.01 (m, 2H), 5.14-5.02 (m, 2H), 3.09-2.98 (m, 2H), 1.24 (q, *J* = 6.3 Hz, 6H)

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.8, 168.4, 160.4, 136.5, 127.0, 122.2, 121.1, 118.3, 75.4, 70.1, 39.7, 21.7, 21.7.

Exact Mass [M+H] $^+$: Calculated for $C_{13}H_{15}O_4$ 235.0965; Found 235.0948.

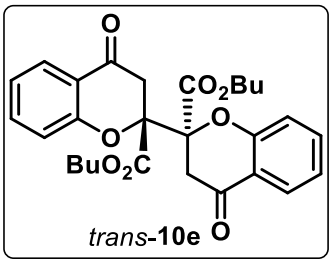
E. Photodimerization of butyl 4-oxo-4*H*-chromene-2-carboxylate (7e)



Scheme S15. Reductive photodimerization of chromone-2-carboxylic ester **7e**

A 70 mg (56% yield) of a diastereomeric mixture along with **11e** (41% yield) was obtained. Solid dimer **10e** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

Dibutyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10e)



$C_{28}H_{30}O_8$: 494.19 g. mole^{-1}

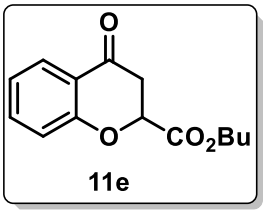
TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.46

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.86 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 2H), 7.56-7.52 (m, 2H), 7.10-7.05 (m, 4H), 4.15-4.03 (m, 4H), 3.48 (d, *J* = 16.7 Hz, 2H), 3.30 (d, *J* = 16.7 Hz, 2H), 1.49-1.38 (m, 4H), 1.19-1.09 (m, 4H), 0.79 (d, *J* = 7.2 Hz, 6H)

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 188.6, 167.9, 159.7, 136.8, 126.9, 122.6, 120.6, 118.4, 85.9, 66.8, 40.9, 30.3, 18.9, 13.6.

Exact Mass [M+H] $^+$: Calculated for $C_{28}H_{31}O_8$ 495.5475; Found 495.5471.

Butyl 4-oxochromane-2-carboxylate (11e)



$C_{14}H_{16}O_4$: 248.10 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.51

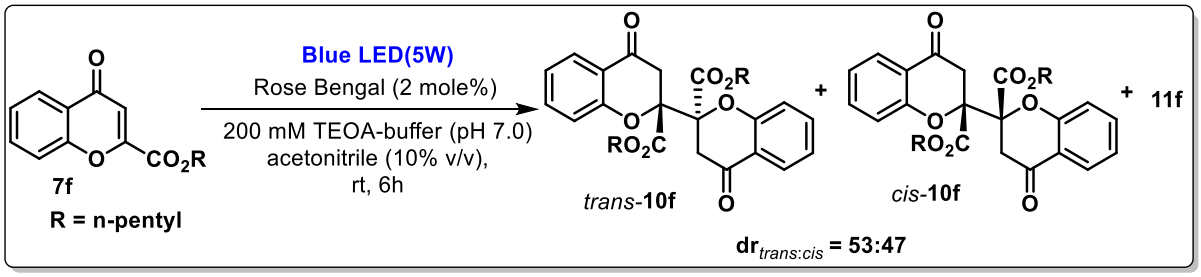
Yield = 41%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.87 (d, *J* = 7.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.10-7.00 (m, 2H), 5.10-5.06 (m, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 6.7 Hz, 2H), 1.64-1.57 (m, 2H), 1.36-1.29 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.8, 168.9, 160.3, 136.6, 127.0, 122.2, 121.0, 118.2, 75.4, 66.0, 39.7, 30.5, 19.0, 13.7.

Exact Mass [M+H] $^+$: Calculated for $C_{14}H_{17}O_4$ 249.1122; Found 249.1124.

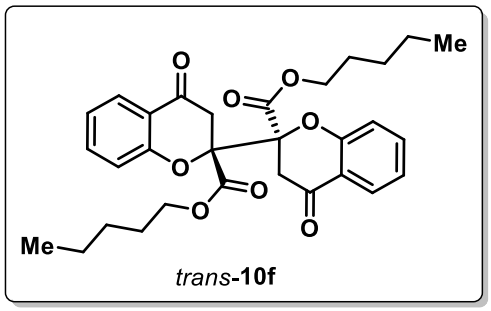
F. Photodimerization of pentyl 4-oxo-4*H*-chromene-2-carboxylate (7f)



Scheme S16. Reductive photodimerization of chromone-2-carboxylic ester **7f**

The photo dimeric products were isolated (68 mg, $dr_{trans:cis}$ 53:47, isolated yield 52 %) along with **11f** (44% yield). Solid dimer **10f** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

dipentyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10f)



$C_{30}H_{34}O_8$: 522.59 g. mole^{-1}

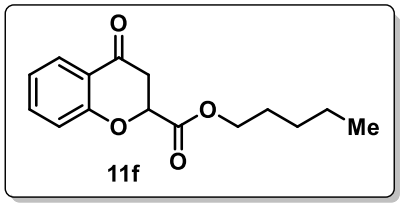
TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.42

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.86 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 2H), 7.56-7.52 (m, 2H), 7.11-7.06 (m, 4H), 4.15-4.03 (m, 4H), 3.48 (d, *J* = 16.7 Hz, 2H), 3.30 (d, *J* = 16.7 Hz, 2H), 1.49-1.40 (m, 4H), 1.21-1.14 (m, 4H), 1.11-1.04 (m, 4H), 0.80 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.2, 167.8, 159.4, 136.7, 126.9, 122.7, 120.6, 118.3, 86.4, 67.2, 40.3, 28.1, 27.8, 22.2, 13.9.

Exact Mass [M+H] $^+$: Calculated for $C_{30}H_{35}O_8$ 523.2327; Found 523.2333.

Pentyl 4-oxochromane-2-carboxylate (11f)



$C_{15}H_{18}O_4$: 262.31 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.44

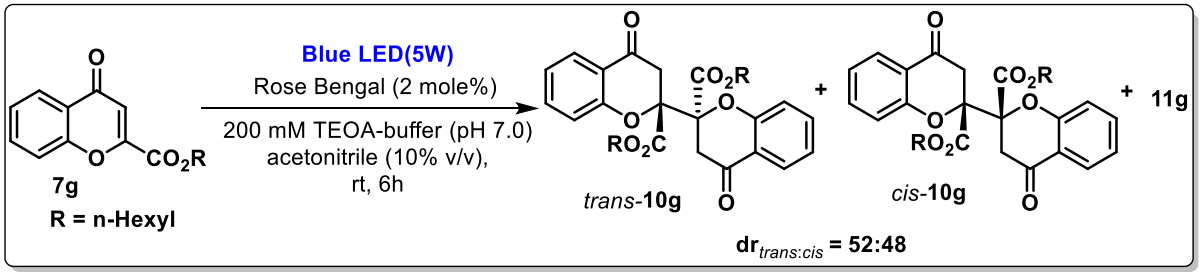
Yield = 44%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.88 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.11-7.03 (m, 2H), 5.09 (dd, *J* = 8.1 Hz, *J* = 6.05 Hz, 1H), 4.19 (td, *J* = 6.7 Hz, *J* = 0.8 Hz, 2H), 3.06 (t, *J* = 5.7 Hz, 2H), 1.66-1.59 (m, 2H), 1.34-1.24 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.8, 169.0, 160.4, 136.6, 127.1, 122.3, 121.1, 118.3, 75.4, 66.3, 39.7, 28.3, 28.0, 22.3, 14.0.

Exact Mass [M+H] $^+$: Calculated for $C_{15}H_{18}O_4$ 263.1278; Found 263.1273

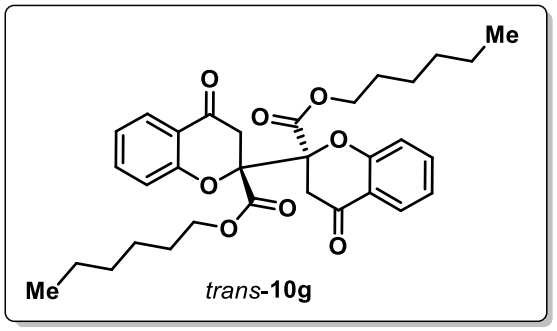
G. Photodimerization of hexyl 4-oxo-4*H*-chromene-2-carboxylate (7g)



Scheme S17. Reductive photodimerization of chromone-2-carboxylic ester **7g**

A 73 mg, $dr_{trans:cis}$ 52:48 (yield 53 %) along with **11g** (45% yield) was isolated. Solid dimer **10g** was separated from the diastereomeric mixture by recrystallization from a mixture of DCM-hexane.

Dihexyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-10g)



$C_{32}H_{38}O_8$: 550.65 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.46

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.86 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 2H), 7.56-7.52 (m, 2H), 7.11-7.06 (m, 4H), 4.14-4.03 (m, 4H), 3.48 (d, *J* = 16.9 Hz, 2H), 3.30 (d, *J* = 16.7 Hz, 2H), 1.50-1.41 (m, 4H), 1.23-1.08 (m, 12H), 0.84 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 188.6, 167.9, 159.7, 136.8, 126.9, 122.6, 120.6, 118.4, 85.9, 67.1, 40.9, 31.3, 28.4, 25.4, 22.6, 14.1.

Exact Mass [M+H]$^+$: Calculated for $C_{32}H_{39}O_8$ 551.2640; Found 551.2645.

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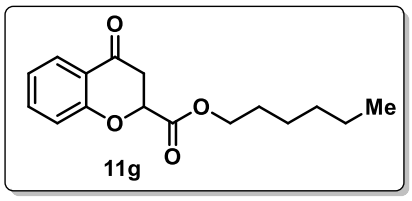
hexyl 4-oxochromane-2-carboxylate (11g)



$C_{16}H_{20}O_4$: 276.33 g. mole^{-1}

TLC (cyclohexane/ethyl acetate, 7:3 v/v): R_f = 0.46

Yield = 45%

^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.88 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.54-7.50 (m, 1H), 7.11-7.04 (m, 2H), 5.08 (dd, *J* = 8.3 Hz, *J* = 6.15 Hz, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.06 (t, *J* = 5.7 Hz, 2H), 1.64-1.59 (m, 2H), 1.32-1.25 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$) δ [ppm]: 189.8, 169.0, 160.4, 136.6, 127.1, 122.3, 121.1, 118.3, 75.4, 66.3, 39.8, 31.4, 28.5, 25.5, 22.6, 14.1.

Exact Mass [M+H]$^+$: Calculated for $C_{15}H_{18}O_4$ 277.1408; Found 277.1403

V. Mechanistic investigations

A. Emission Quenching Experiments (Stern-Volmer Studies)

The solutions for measurement were prepared from stock solutions of **7a** (50 mM) in degassed acetonitrile and Rose Bengal (0.1 mM) in degassed distilled water. The final concentration of each solution for **7a** and Rose Bengal is shown in the following table.

All the solutions were excited at 470 nm in a spectrofluorometer and the emission intensity was measured from 520 to 640 nm. The emission spectrum of each solution was superimposed as shown in **Figure S2**. It can be observed that the greater the concentration of the quencher **7a**, the lower the fluorescence intensity. **Hence, 7a is acting as a reductive quencher for the excited Rose Bengal.**

Table S6: Concentration of **7a** and **photocatalyst** and reaction **buffer** in each solution.

Solution	1	2	3	4	5	6
Substrate conc. (mM)	0	5	10	15	20	30
Rose Bengal conc. (mM)	0.01	0.01	0.01	0.01	0.01	0.01
TEA buffer conc. (mM)	200	200	200	200	200	200

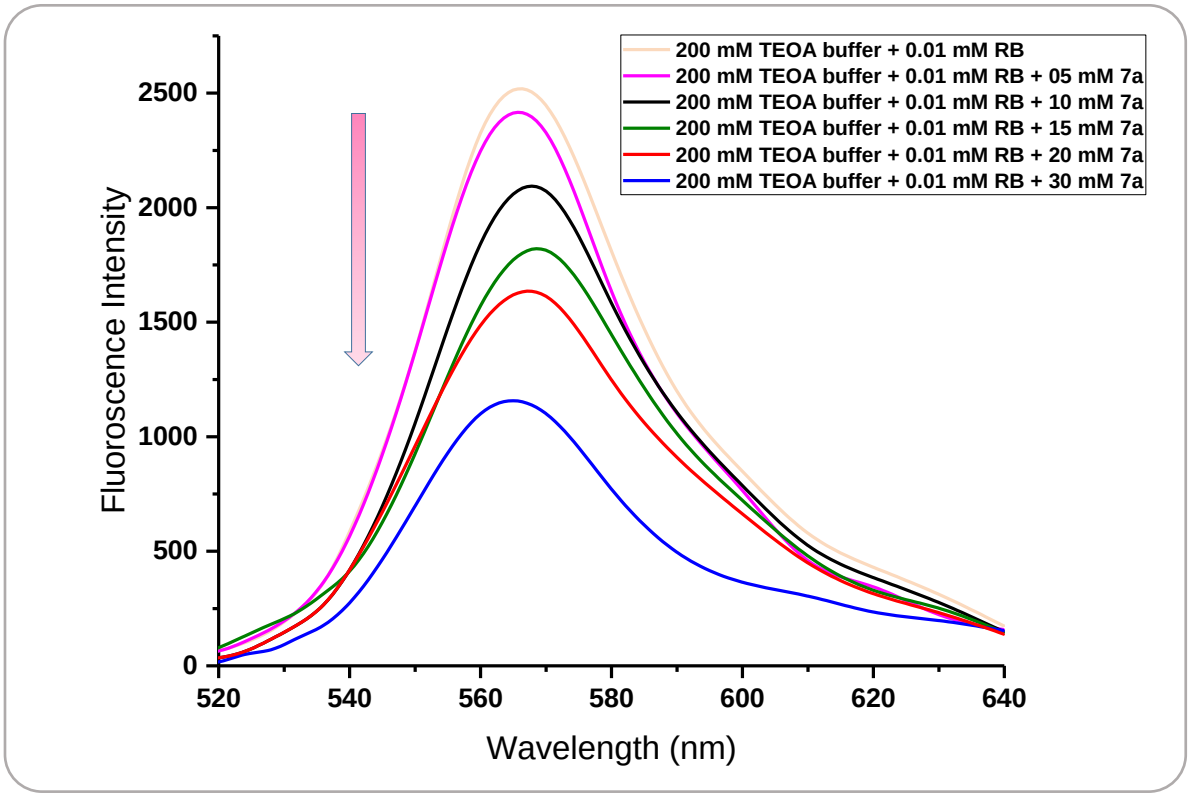


Figure S2: Fluorescence emission spectra for each solution.

Table S7: Fluorescence emission intensity for each solution.

Solution	Substrate conc. (mM)	I_f (571 nm)	I^0_f/I_f
1	0	2523.556	1
2	5	2420.062	1.042
3	10	2097.901	1.202
4	15	1818.548	1.387
5	20	1629.456	1.548
6	30	1156.338	2.182

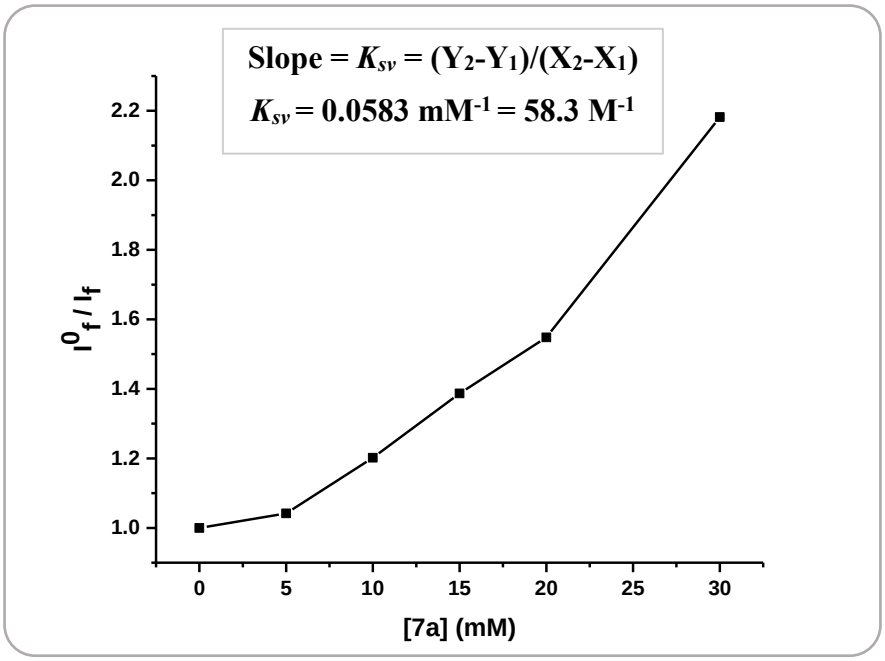
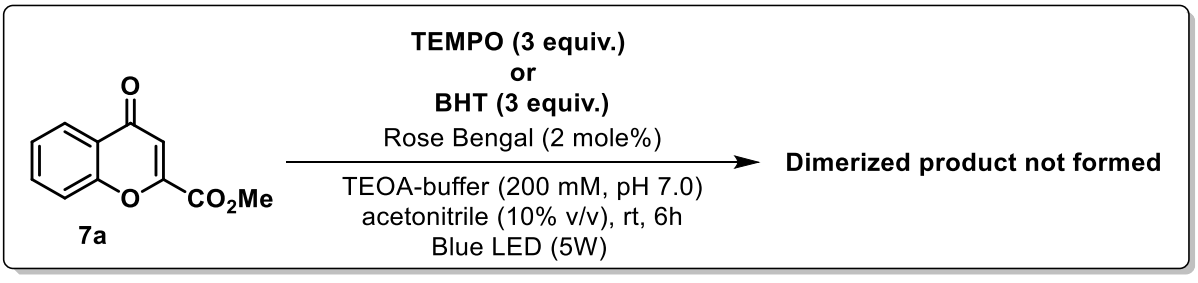


Figure S3: Stern Volmer plot for the fluorescence emission.

B. Radical trapping experiment



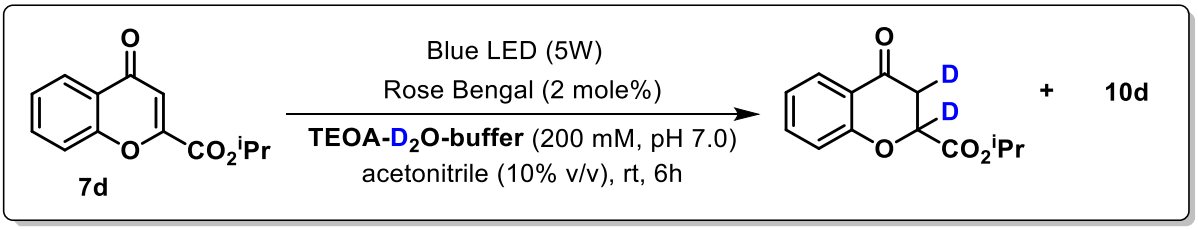
Scheme S18. Radical trapping experiment using radical quencher

In a 25 mL round bottom flask, 10 ml TEOA-buffer solution (200 mM, pH 7.0) was taken and degassed under the counterflow of argon for half an hour, at room temperature. Then chromone-2-carboxylic ester **7a** (23 mg, 0.1 mM, 1 equiv.) was dissolved in acetonitrile (10% v/v) and TEMPO (3 equiv.) or butylated hydroxytoluene (BHT) (3 equiv.) and Rose Bengal (2

mol %) were added and the mixture was irradiated with a 5W-blue LED lamp. After 6 h the crude reaction mixture was extracted with EtOAc and the combined organic layer was washed with brine, and dried over Na_2SO_4. After the removal of the solvent in vacuo, the crude reaction mixture was directly subjected to crude ^{1}H-NMR in $CDCl_3$.

These radical quenching experiments revealed that the photodimerization of **7a** gets completely minimized due to the presence of a radical quencher. Hence, it can be concluded that the developed photodimerization reaction goes through the radical mechanism.

C. Deuterium labelling experiment



Scheme S19. Deuterium incorporating experiment

In a 50 mL round bottom flask, 25 ml TEOA-**D_2O**-buffer solution (200 mM, pH 7.0) was taken and degassed under the counterflow of argon for half an hour, at room temperature. Then chromone-2-carboxylic ester **7d** (47 mg, 0.2 mM 1 equiv.) was dissolved in acetonitrile (10% v/v) and Rose Bengal (2 mol %) was added and the mixture was irradiated with a 5W-blue LED lamp. After 6 h the crude reaction mixture was extracted with EtOAc and the combined organic layer was washed with brine, and dried over Na_2SO_4. After the removal of the solvent in vacuo, the crude reaction mixture was directly subjected to crude ^{1}H-NMR in $CDCl_3$.

From deuterium labelling experiment using D_2O buffer of triethanolamine (200 mM, pH 7.0) shows that two deuterium are incorporated in the reduced chromone-2-carboxylic ester, which is formed by the C=C bond reduction of **7d**, at the time of photodimerization. Hence, the side products (reduced chromone-2-carboxylic ester) formed in the developed photodimerization reaction go through taking hydrogen from the buffer to form the reduced product.

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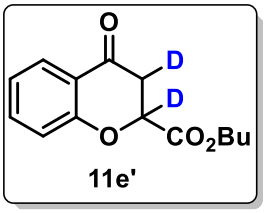
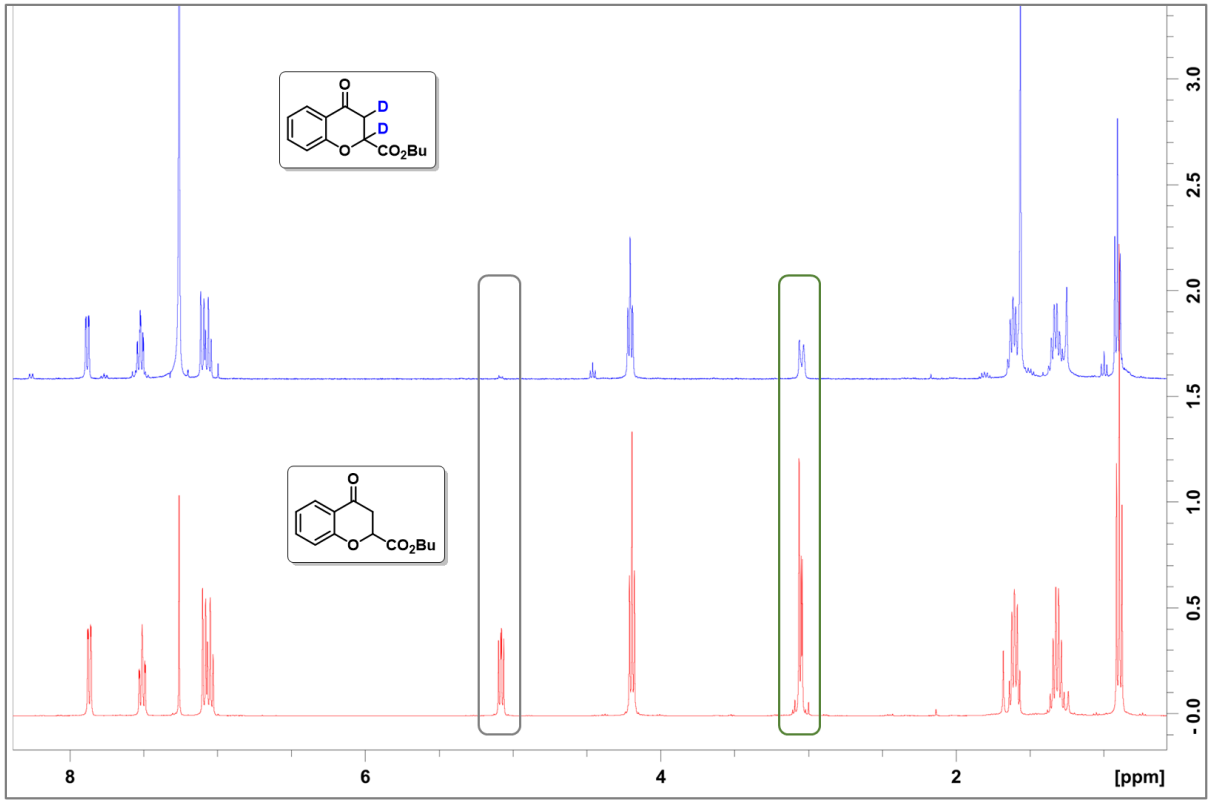
butyl 4-oxochromane-2-carboxylate (11e)

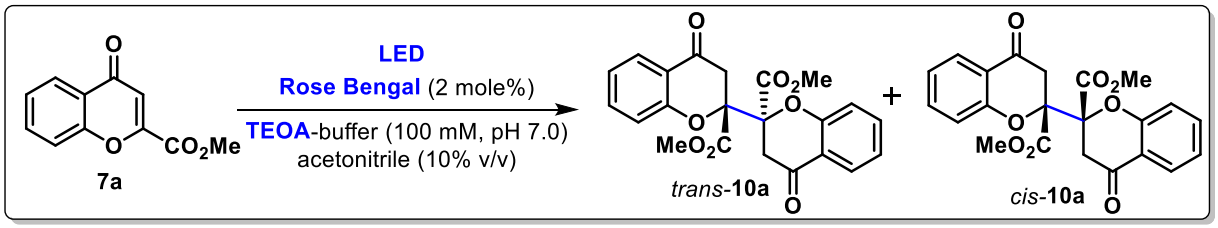


^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm]: 7.88 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.534-7.50 (m, 1H), 7.11-7.04 (m, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.04 (d, *J* = 10.9 Hz, 1H), 1.65-1.60 (m, 2H), 1.38-1.28 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H)

Comparison of ^{1}H NMR of butyl 4-oxochromane-2-carboxylate (11e) and butyl 4-oxochromane-2-carboxylate-2,3-d_2.



D. Switch On-Off Experiment



Scheme S20. Reductive photodimerization of chromone-2-carboxylic ester **7e**

In a 50 mL round bottom flask, 25 ml TEOA-buffer solution (200 mM, pH 7.0) was taken and degassed under the counterflow of argon for half an hour, at room temperature. Then chromone-2-carboxylic ester 7a (102 mg, 0.5 mM 1 equiv.) was dissolved in acetonitrile (10% v/v) and Rose Bengal (2 mol %) was added and the mixture was irradiated with a 5W-blue LED lamp. After 15 min of light irradiation, an aliquot portion (1 mL) was taken from the reaction mixture extracted with diethyl ether washed with brine, and dried over Na_2SO_4. After

the removal of the solvent in vacuo, the crude reaction mixture was directly subjected to crude ^{1}H- NMR in $CDCl_3$. Thereafter, the light was switched off with continuous stirring for 15 min. Once again, an analytical sample solution was prepared for crude ^{1}H-NMR (as mentioned earlier) and analyzed similarly, and the light was switched on for 15 min. This cycle was repeated and the conversion to *trans*- and *cis*-**10a** to time was plotted (**Figure S4**). The nature of the graph indicates that the process is dependent on light.

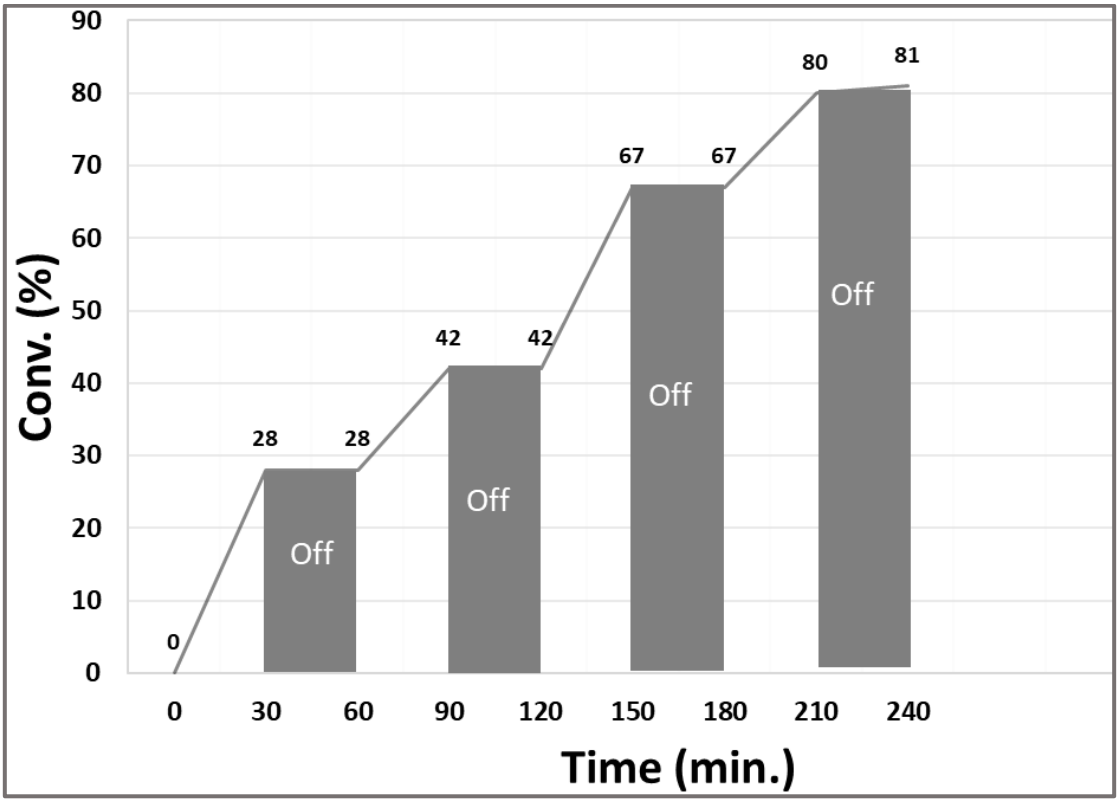
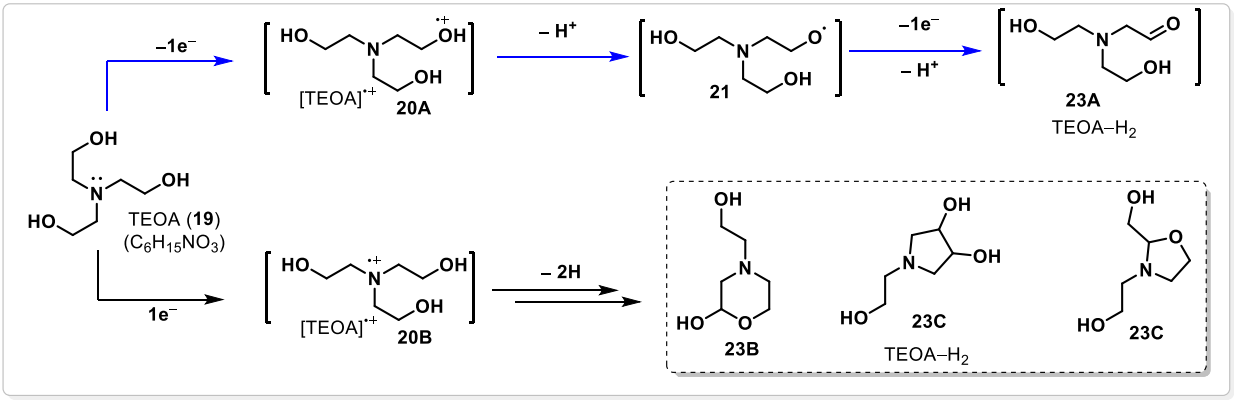


Figure S4: Graph of switch on-off experiment for the formation of *trans* and *cis*-**10a**.

E. Proposed reaction mechanism for photodimerization

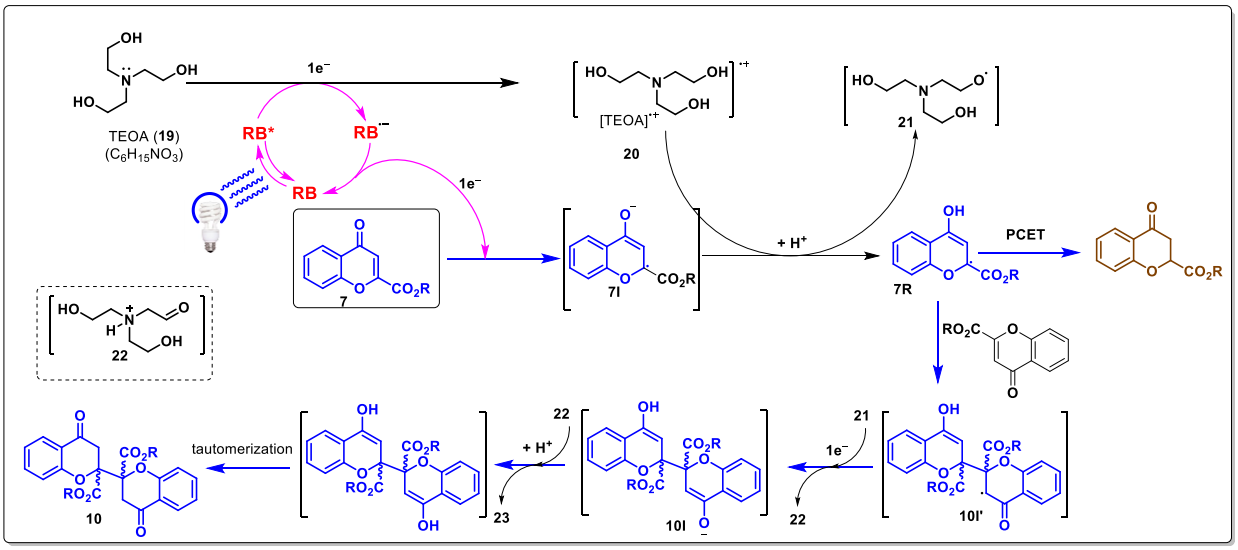
TEOA has been reported earlier to serve as a donor of electrons and protons during photocatalytic reactions (*ACS Catal.* **2019**, *9*, 1531–1538).[4] TEOA has two centers that can undergo oxidation: (1) hydroxyl group and (2) amine function. Accordingly, if the hydroxyl group of TEOA gets oxidized, this process would lead to 2-(bis(2-hydroxyethyl)amino)acetaldehyde (**23A**) and if the amine function gets oxidized it may give a mixture of products (**23B**, **23C or**, **23D**) by the loss of two H molecule during the photoreaction to form TEOA**–**H_2. Therefore, it is difficult to assign exact structure to **23** (see *ACS Catal.* **2019**, *9*, 1531–1538).



Scheme S21. Plausible transformation of TEOA in the photoreaction.

Based on the reported role of TEOA during photodimerization and the experimental result of the optimised photodimerization reaction, we proposed the following reaction mechanism (Scheme **S22**).

First the photocatalyst Rose Bengal can produce the excited-state RB* by the irradiation of 5W blue LED light. Then RB* is prone to accept an electron from the triethanolamine (TEOA) (used as reaction buffer) which serves as an electron donor and results in the formation of $RB^{\bullet-}$ radical anion. Consequently, TEOA forms $[TEOA]^{\bullet+}$ (**20**), which could act as a proton donor.



Scheme S22. Plausible mechanism of photodimerization of chromone-2-carboxylic ester.

After that, $RB^{\bullet-}$ undergoes photocatalytic electron transfer to the chromone-2-carboxylic ester (**7**) to form a chromone radical anion (**7I**) and as a result, $RB^{\bullet-}$ comes to the ground state RB. Then the protonation of **7I** takes place to form **7R** by the use of $[TEOA]^{\bullet+}$ (**20**), which gets further converted to **21.** The chromone radical **7R** in addition to the monomeric chromone-2-

carboxylic ester **7**, followed by the electron transfer from **21** forms dimeric intermediate **10I.** The chromone radical **7R** can also undergo proton-couple electron transfer (PCET) to form reduced chromone (**11**) as a side product. Finally, protonation and consequential tautomerization of intermediate **10I** by **22**, resulted in the formation of dimeric chromone-2-carboxylic ester *trans*- & *cis*-**10**. As a result, **22** gets oxidized to form **23,** with a possibility to form any of the structures shown in Scheme S21.

F: Measurement of reduction potential value for selected compounds.

Cyclic voltammetry (CV) was performed in the Admiral Squidstat Solo electrochemical instrument to measure the reduction potential of selected compounds. In this three-electrode cell system glassy carbon electrode was used as a working electrode, Pt wire was used as a counter, Ag wire in AgNO3 solution in MeCN (0.01 M) and tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte was used as a non-aqueous reference electrode.

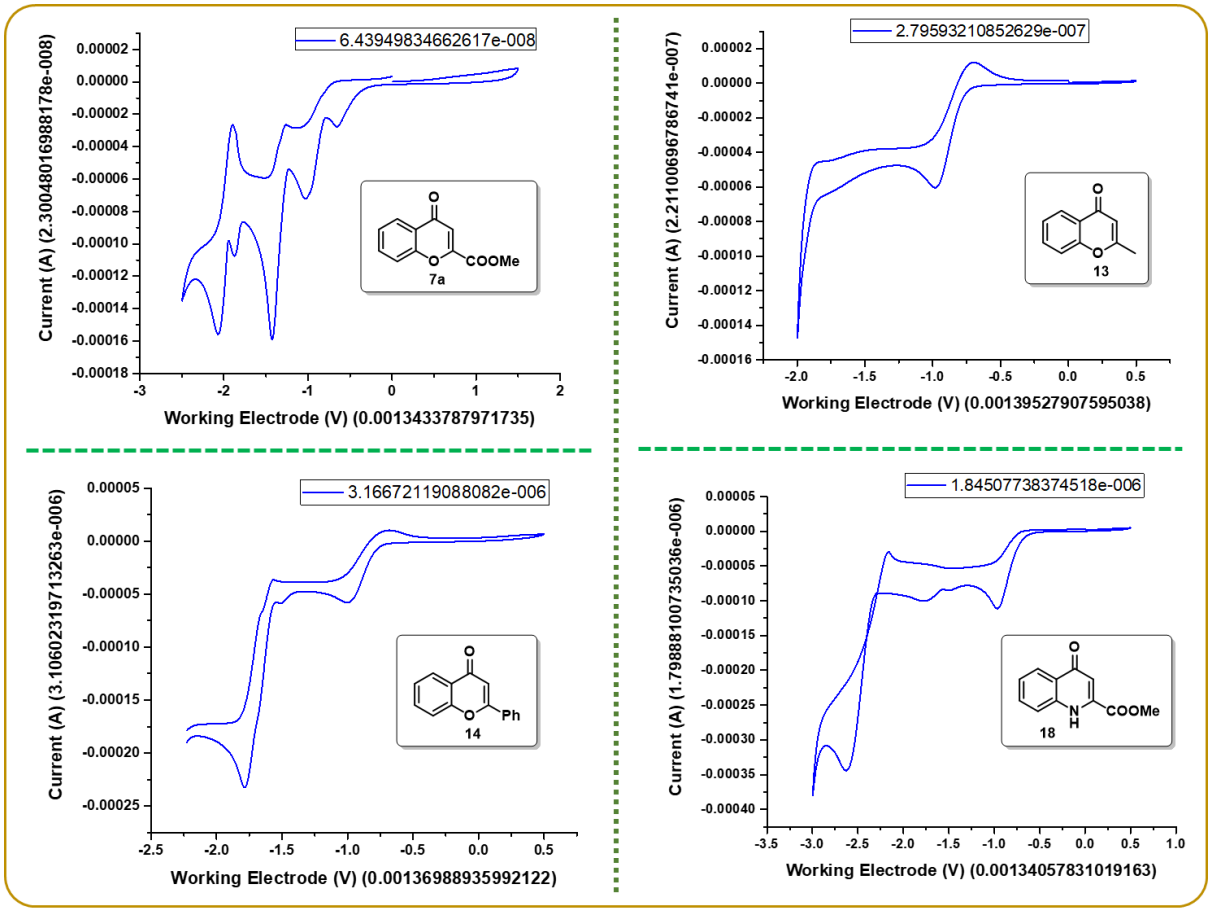


Figure S5: Cyclic voltammetry of selected compounds in acetronitrile.

VI. Crystallographic data of 10b

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

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Temperature:      273 K

                  Calculated                 Reported
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Space group       P 21/n                     P 1 21/n 1
Hall group        -P 2yn                     -P 2yn
Moiety formula    C24 H22 O8                 C12 H11 O4
Sum formula       C24 H22 O8                 C12 H11 O4
Mr                438.42                     219.22
Dx,g cm-3         1.364                      1.365
Z                 2                          4
Mu (mm-1)         0.103                      0.103
F000              460.0                      460.4
F000'             460.28
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Nref              2661                       2617
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Tmin'

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Click on the hyperlinks for more details of the test.

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Alert level C

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Alert level G

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PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        273 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        273 Check
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PLAT769_ALERT_4_G CIF Embedded explicitly supplied scattering data     Please Note
PLAT793_ALERT_4_G Model has Chirality at C006        (Centro SPGR)          S Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         11 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File         43 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

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   3 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

  11 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   8 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

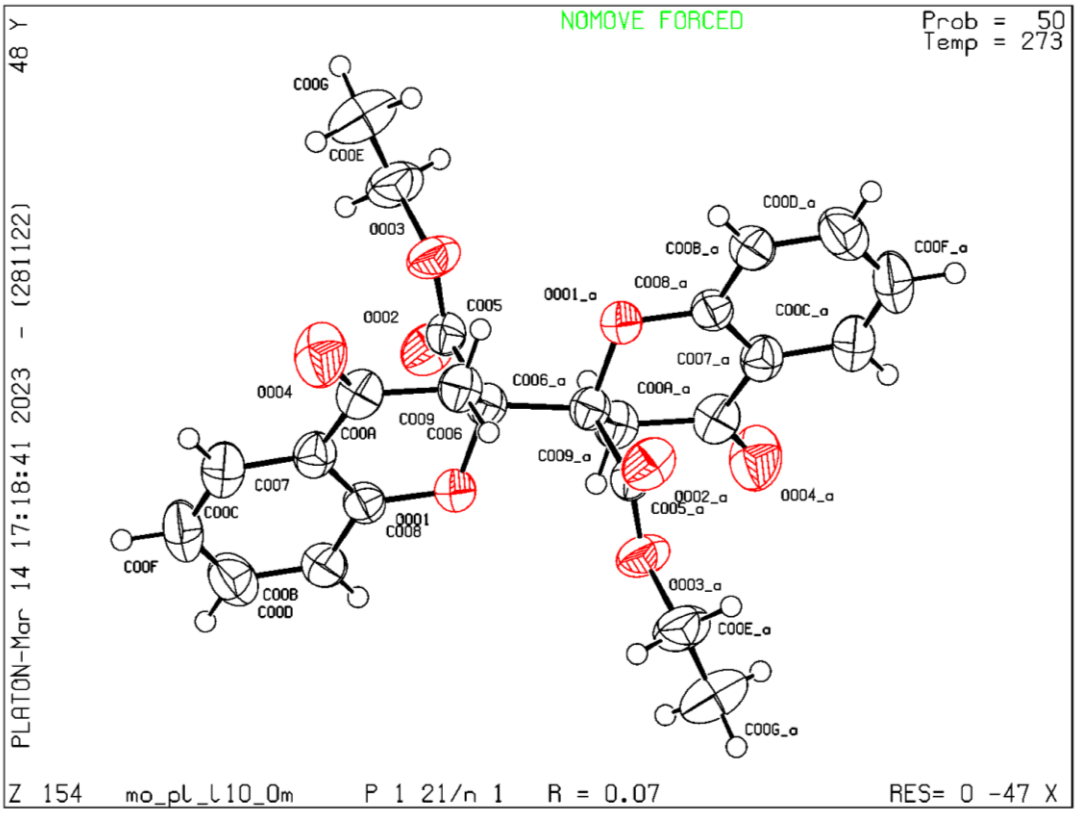
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

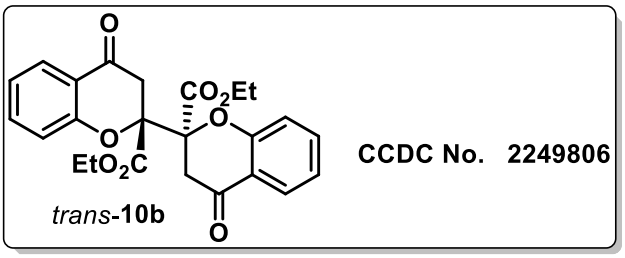
Publication of your CIF in other journals

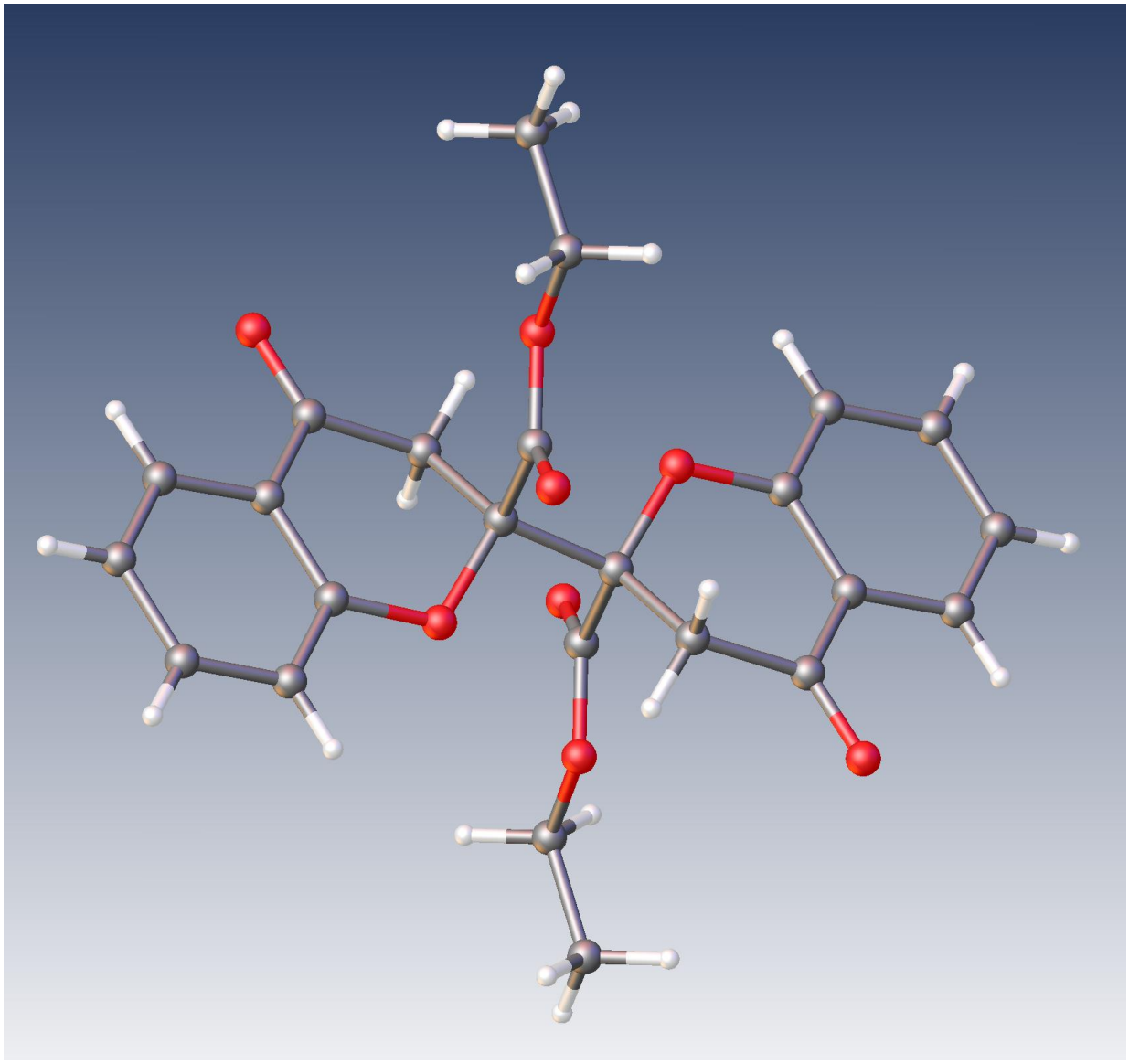
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock mo_pl_l10_0m - ellipsoid plot



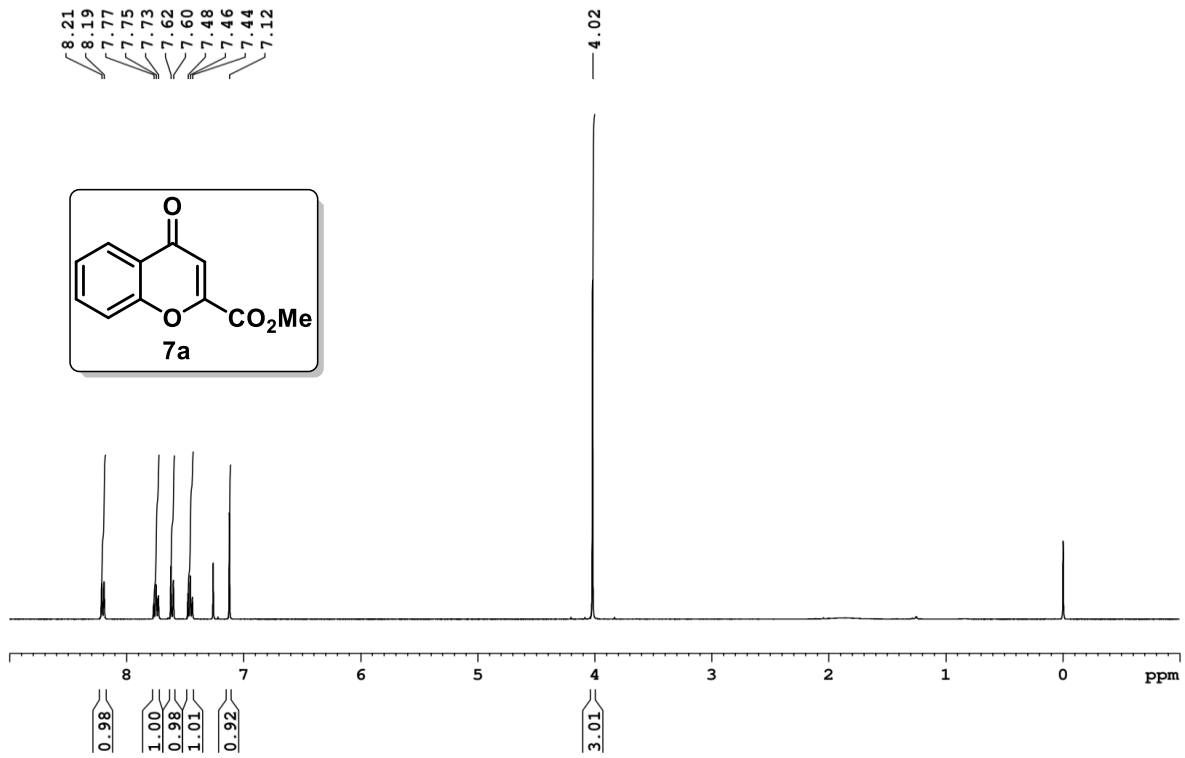




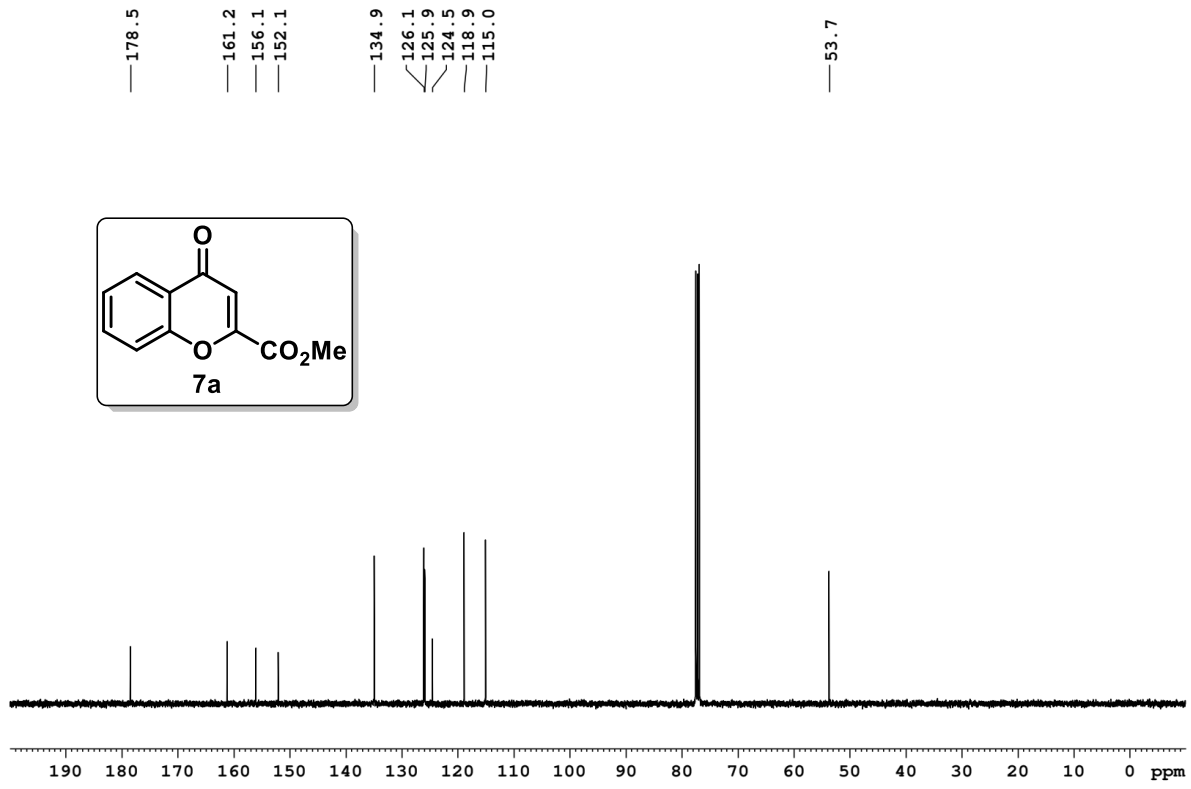
CCDC No. 2249806

VII. NMR spectra

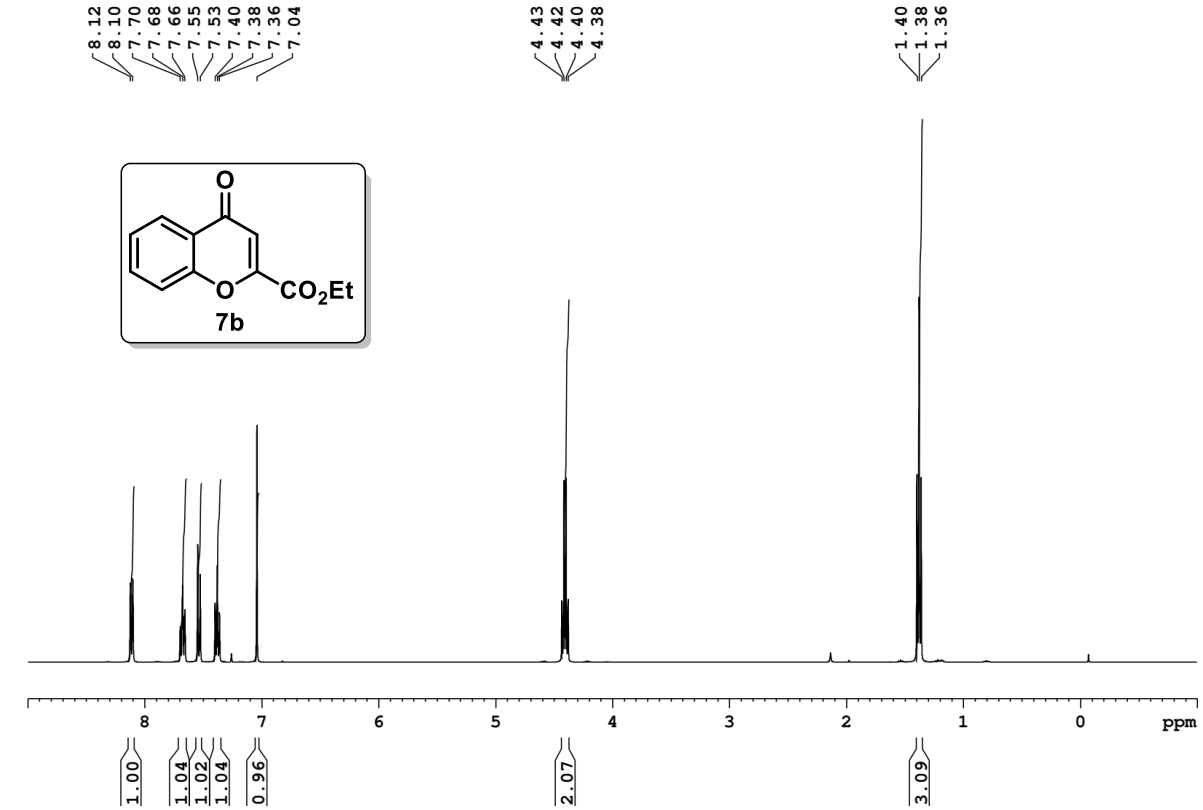
^{1}H NMR (400 MHz, $CDCl_3$) methyl 4-oxo-4*H*-chromene-2-carboxylate (**7a**)



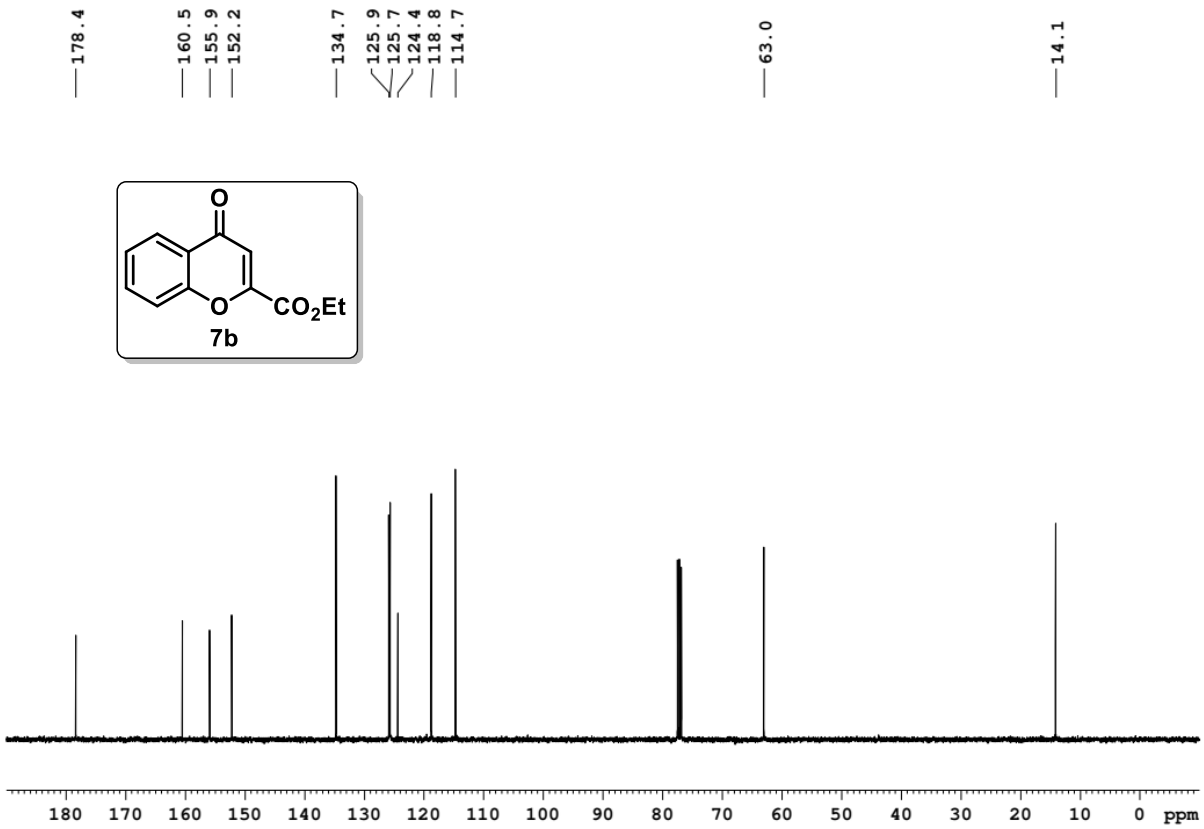
^{13}C NMR (100 MHz, $CDCl_3$) methyl 4-oxo-4*H*-chromene-2-carboxylate (**7a**)



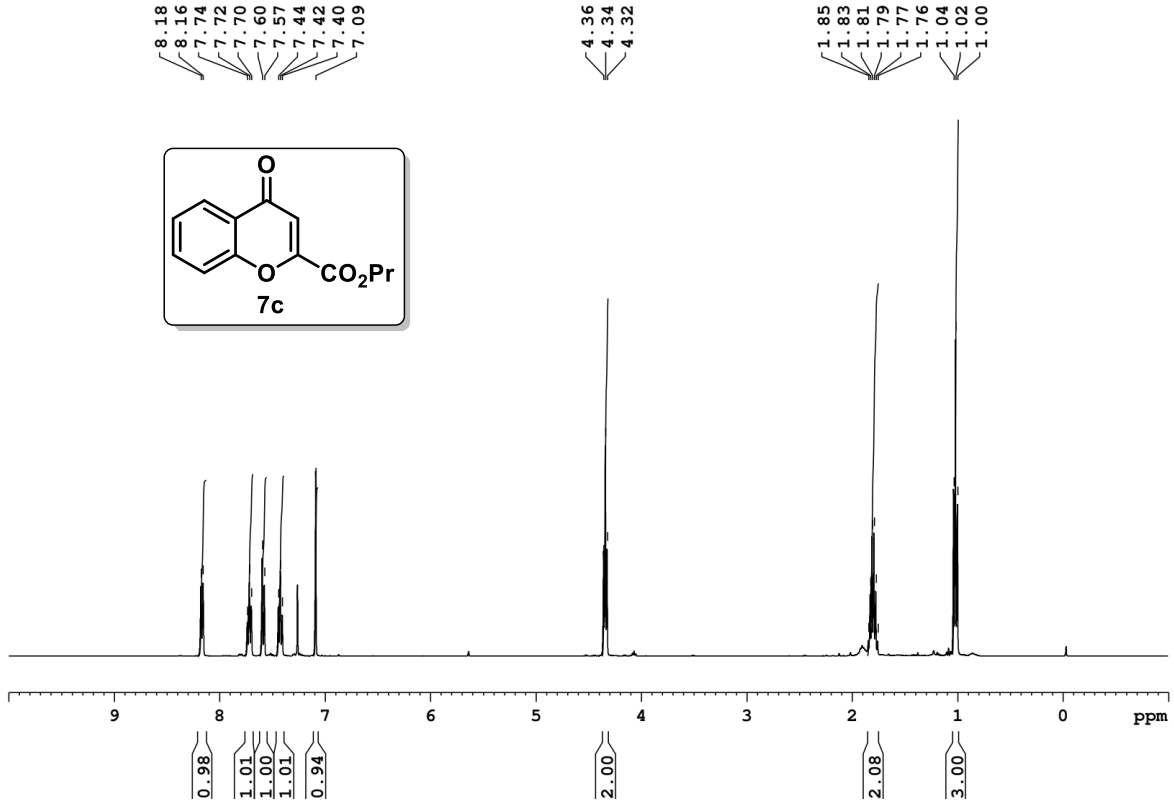
^{1}H NMR (400 MHz, $CDCl_3$) ethyl 4-oxo-4*H*-chromene-2-carboxylate (**7b**)



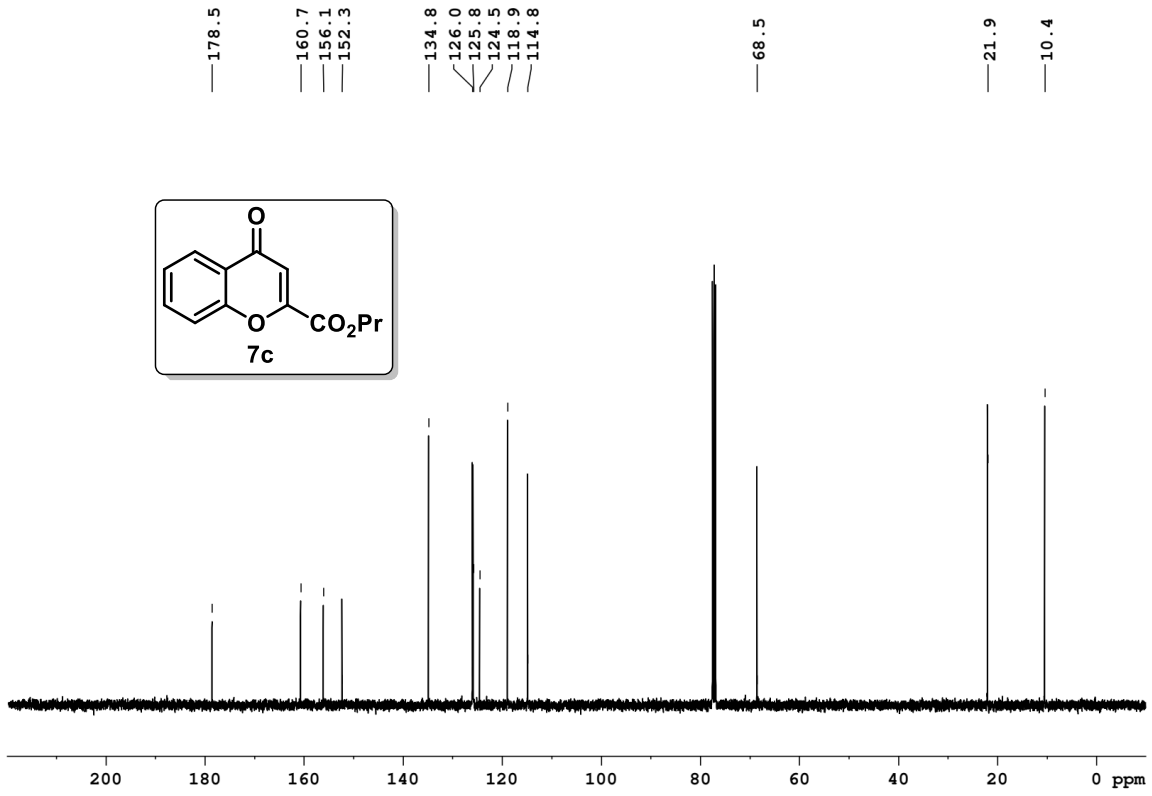
^{13}C NMR (100 MHz, $CDCl_3$) ethyl 4-oxo-4*H*-chromene-2-carboxylate (**7b**)



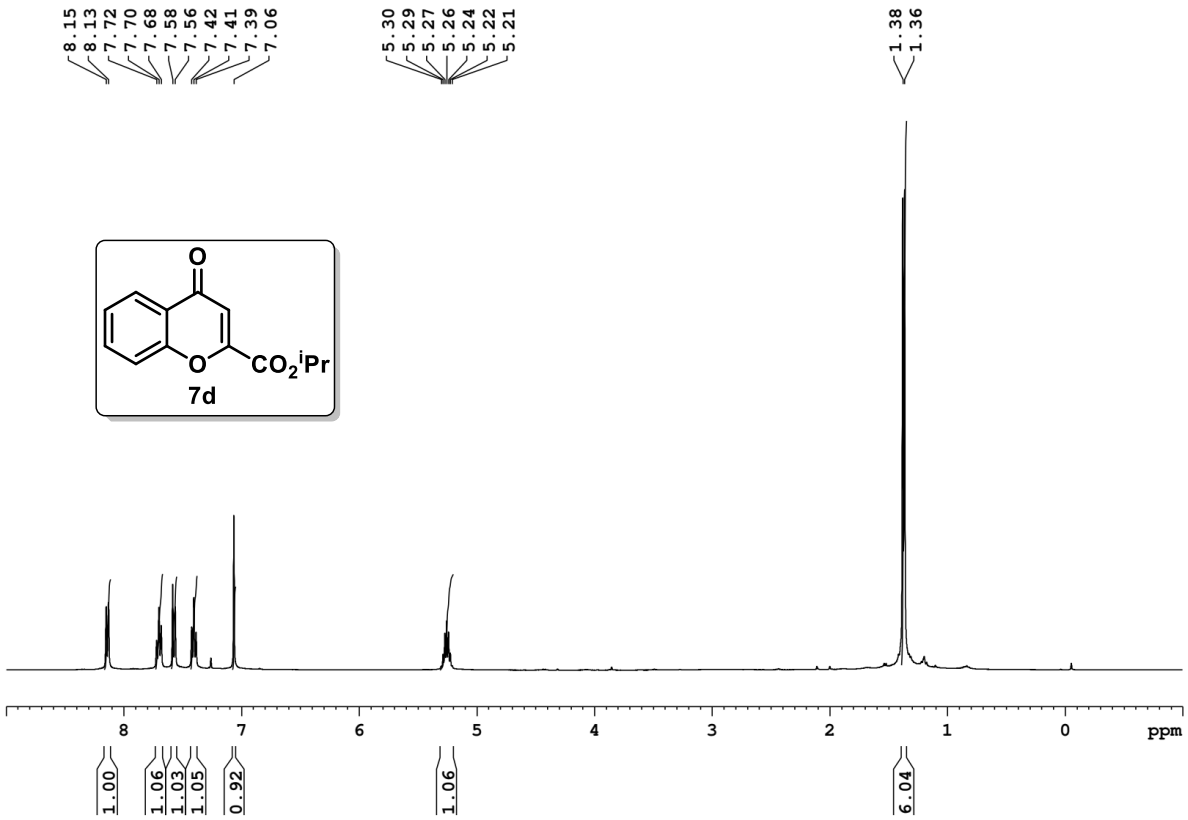
^{1}H NMR (400 MHz, $CDCl_3$) propyl 4-oxo-4*H*-chromene-2-carboxylate (**7c**)



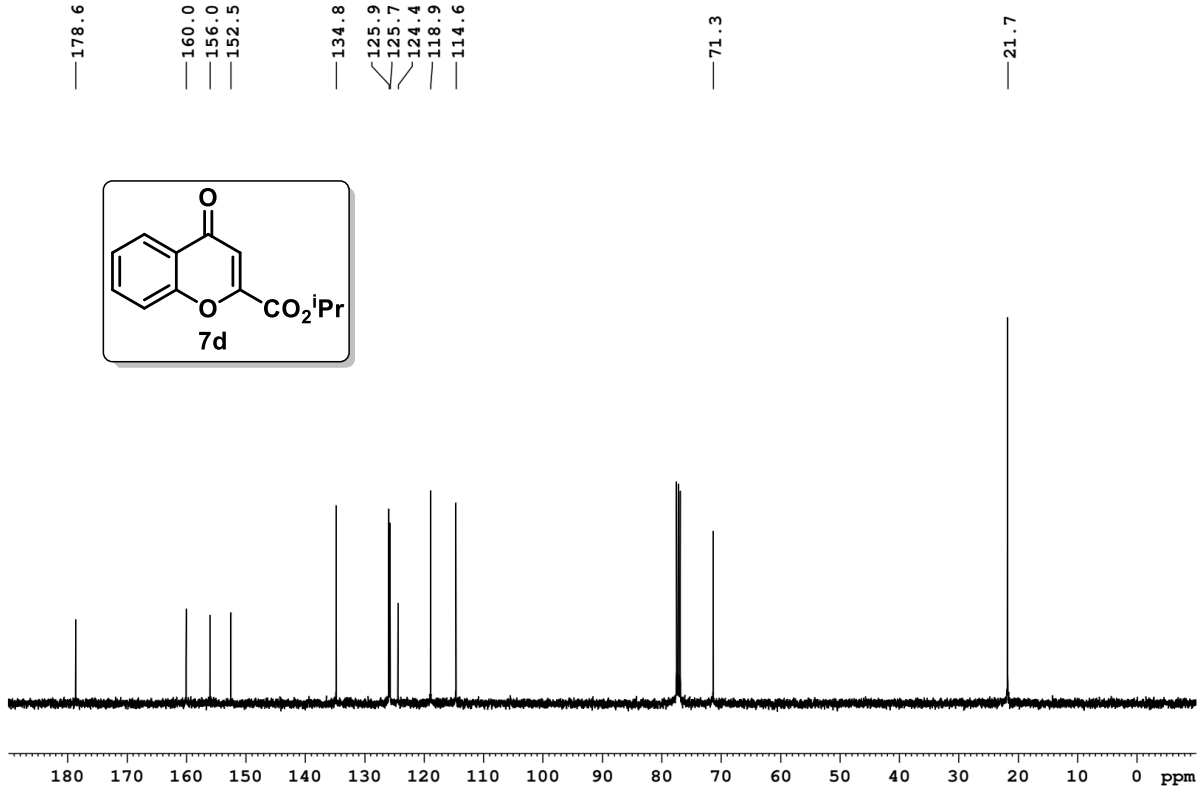
^{13}C NMR (100 MHz, $CDCl_3$) propyl 4-oxo-4*H*-chromene-2-carboxylate (**7c**)



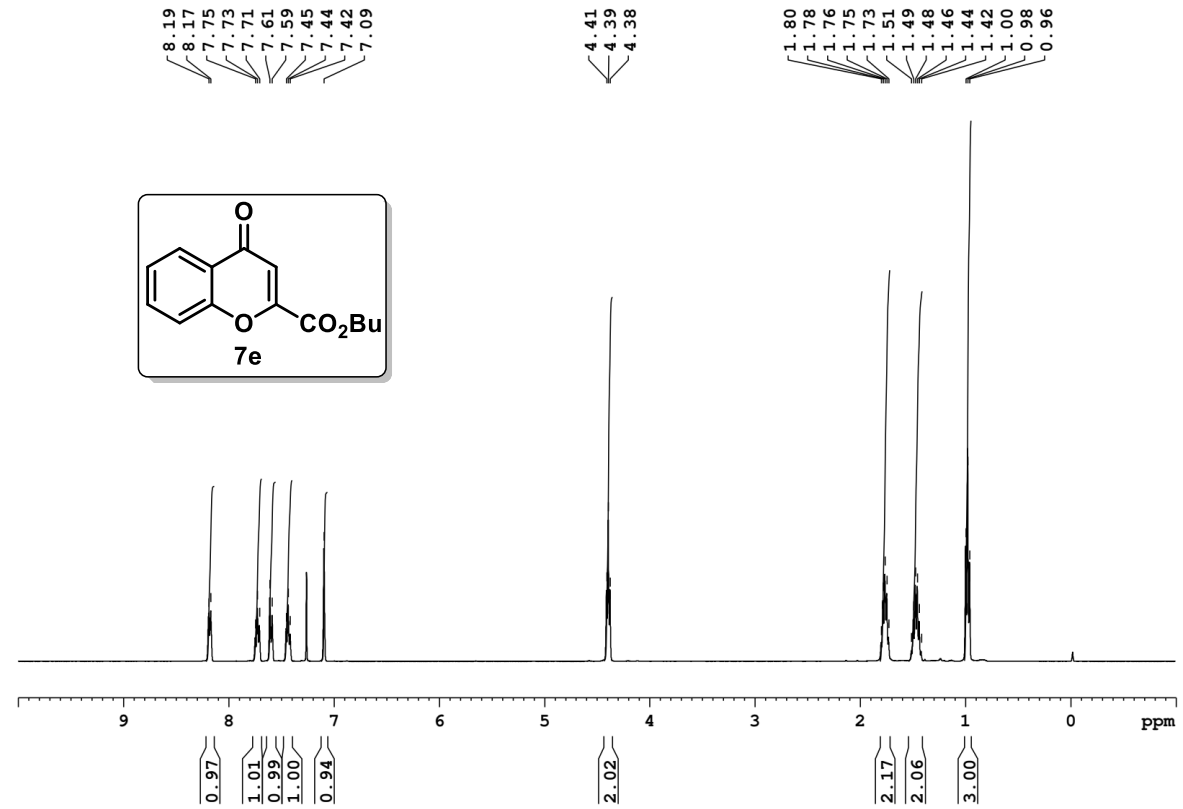
^{1}H NMR (400 MHz, $CDCl_3$) isopropyl 4-oxo-4*H*-chromene-2-carboxylate (**7d**)



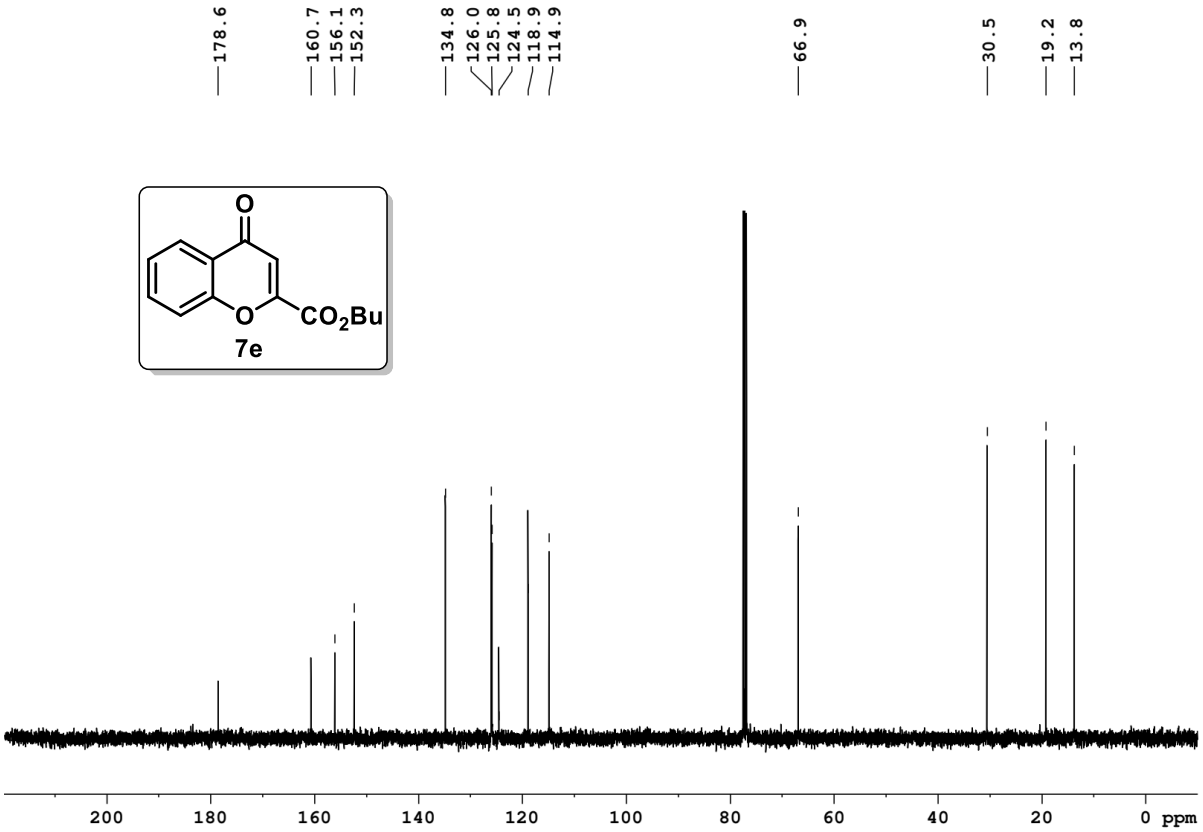
^{13}C NMR (100 MHz, $CDCl_3$) isopropyl 4-oxo-4*H*-chromene-2-carboxylate (**7d**)



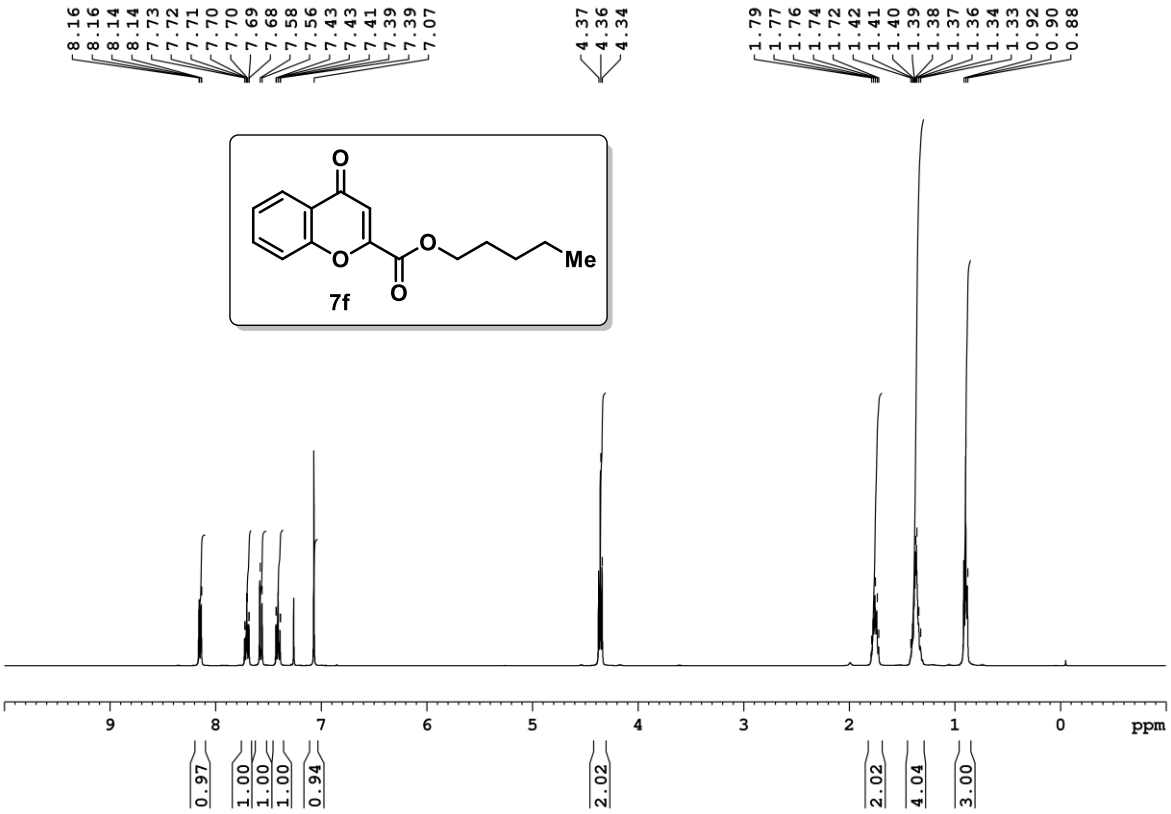
^{1}H NMR (400 MHz, $CDCl_3$) butyl 4-oxo-4*H*-chromene-2-carboxylate (**7e**)



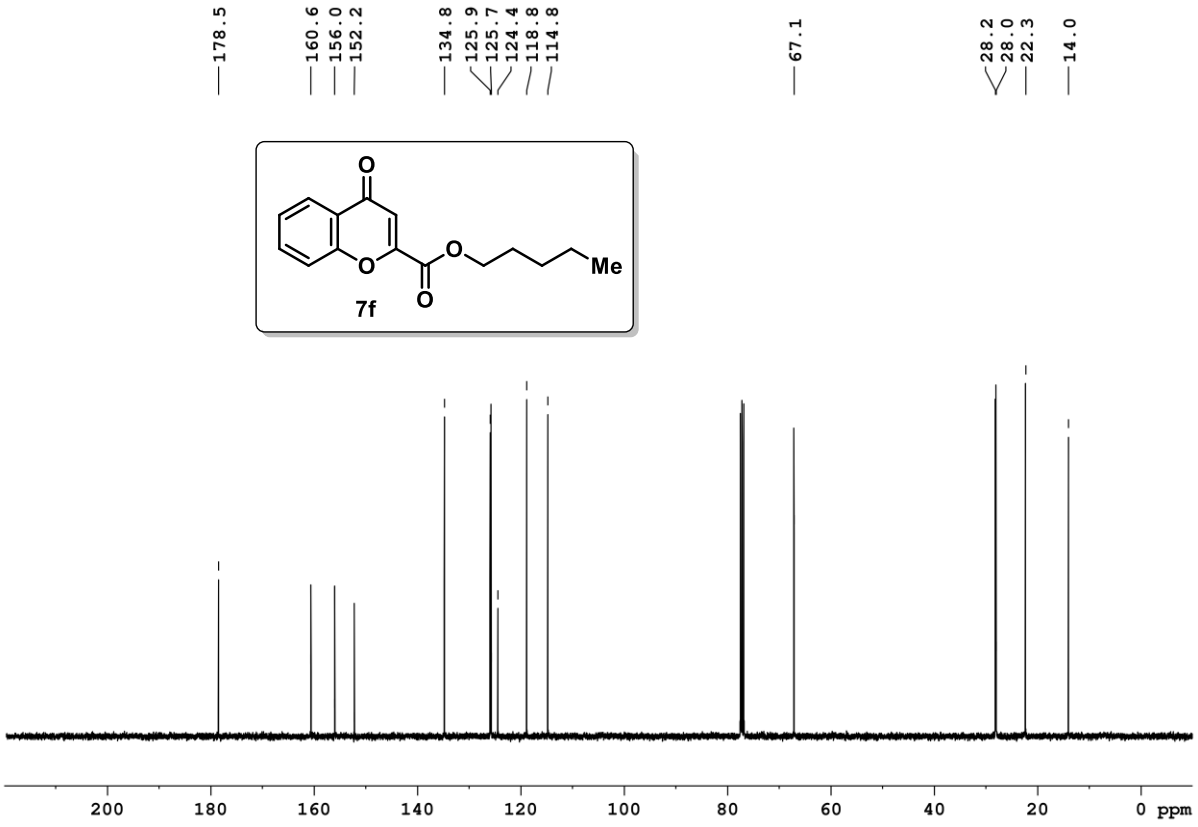
^{13}C NMR (100 MHz, $CDCl_3$) butyl 4-oxo-4*H*-chromene-2-carboxylate (**7e**)



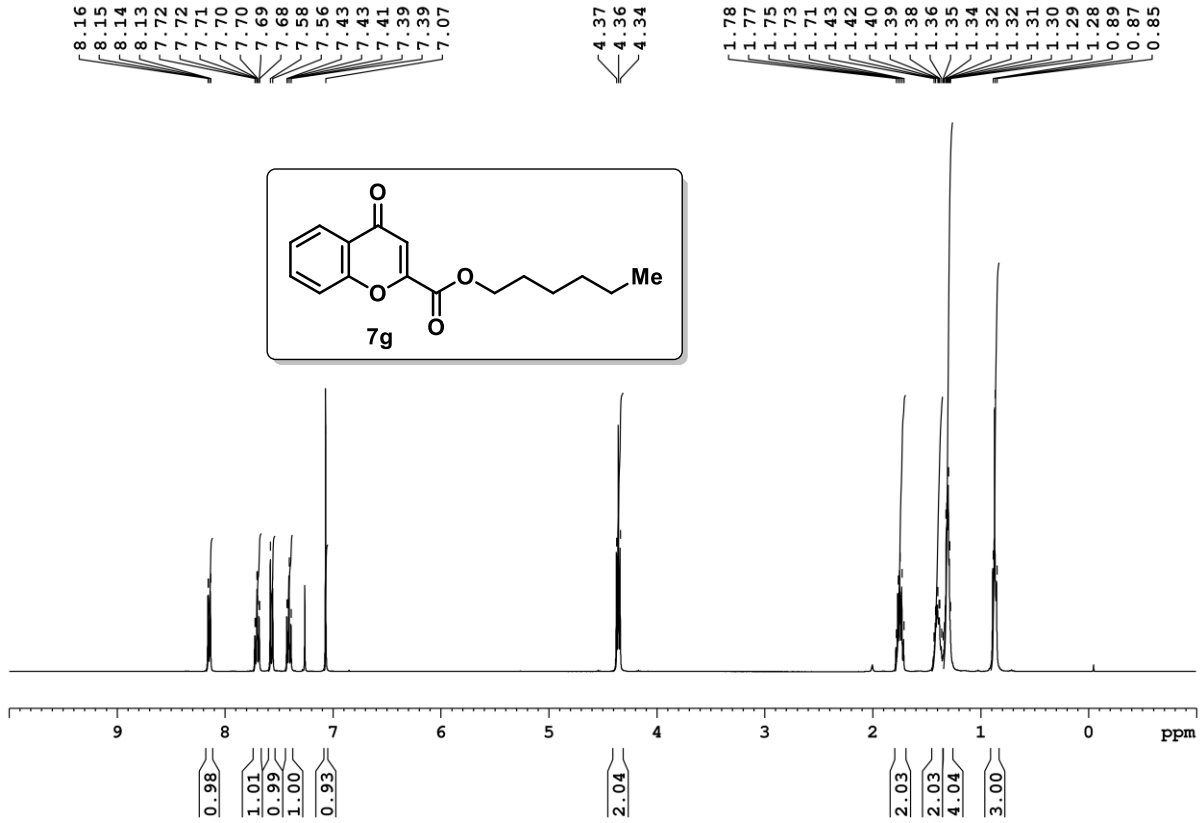
^{1}H NMR (400 MHz, $CDCl_3$) pentyl 4-oxo-4*H*-chromene-2-carboxylate (**7f**)



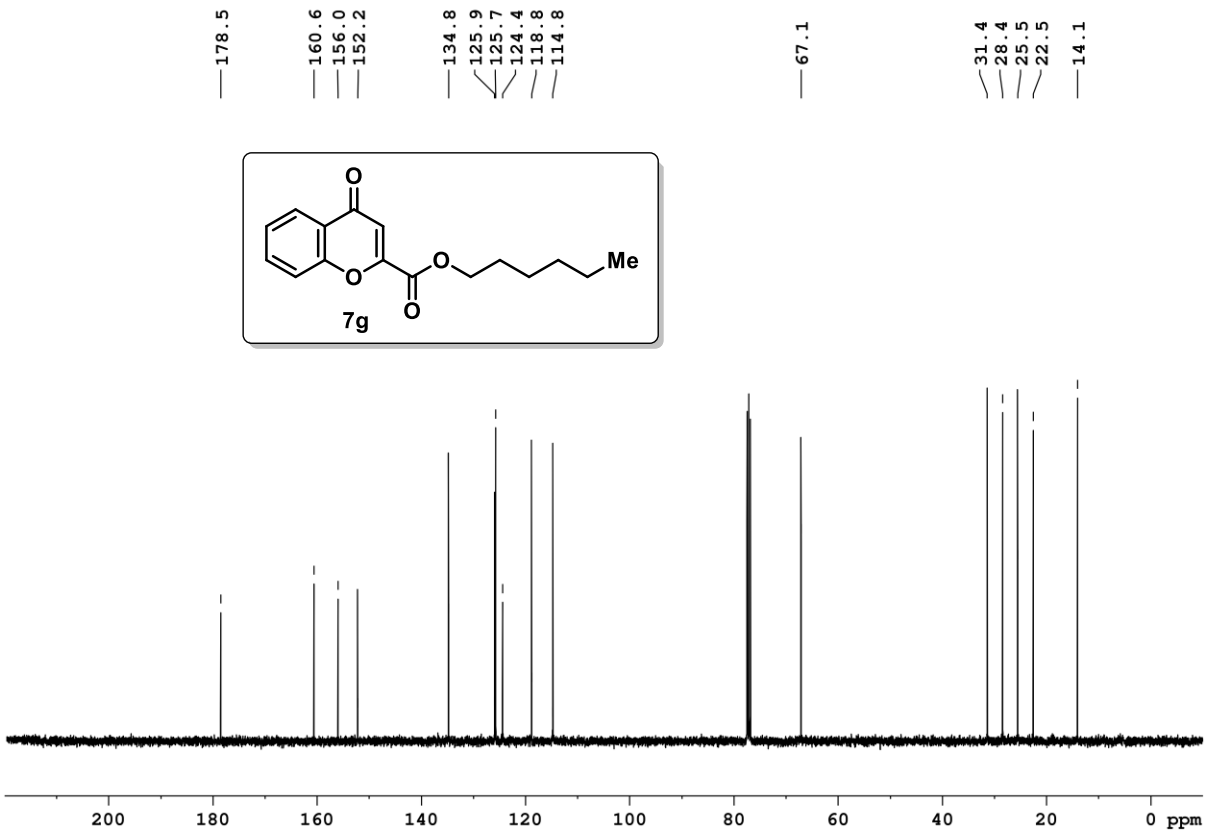
^{13}C NMR (100 MHz, $CDCl_3$) pentyl 4-oxo-4*H*-chromene-2-carboxylate (**7f**)



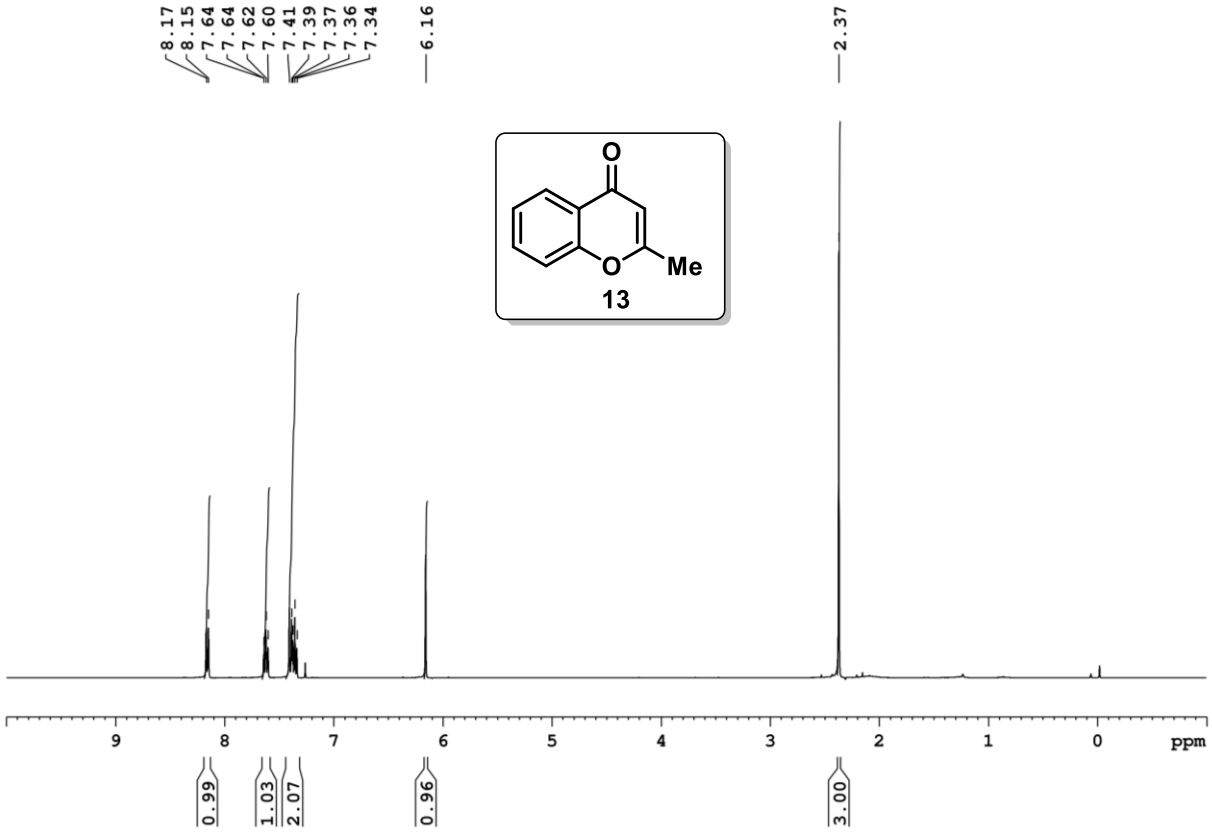
^{1}H NMR (400 MHz, $CDCl_3$) hexyl 4-oxo-4*H*-chromene-2-carboxylate (**7g**)



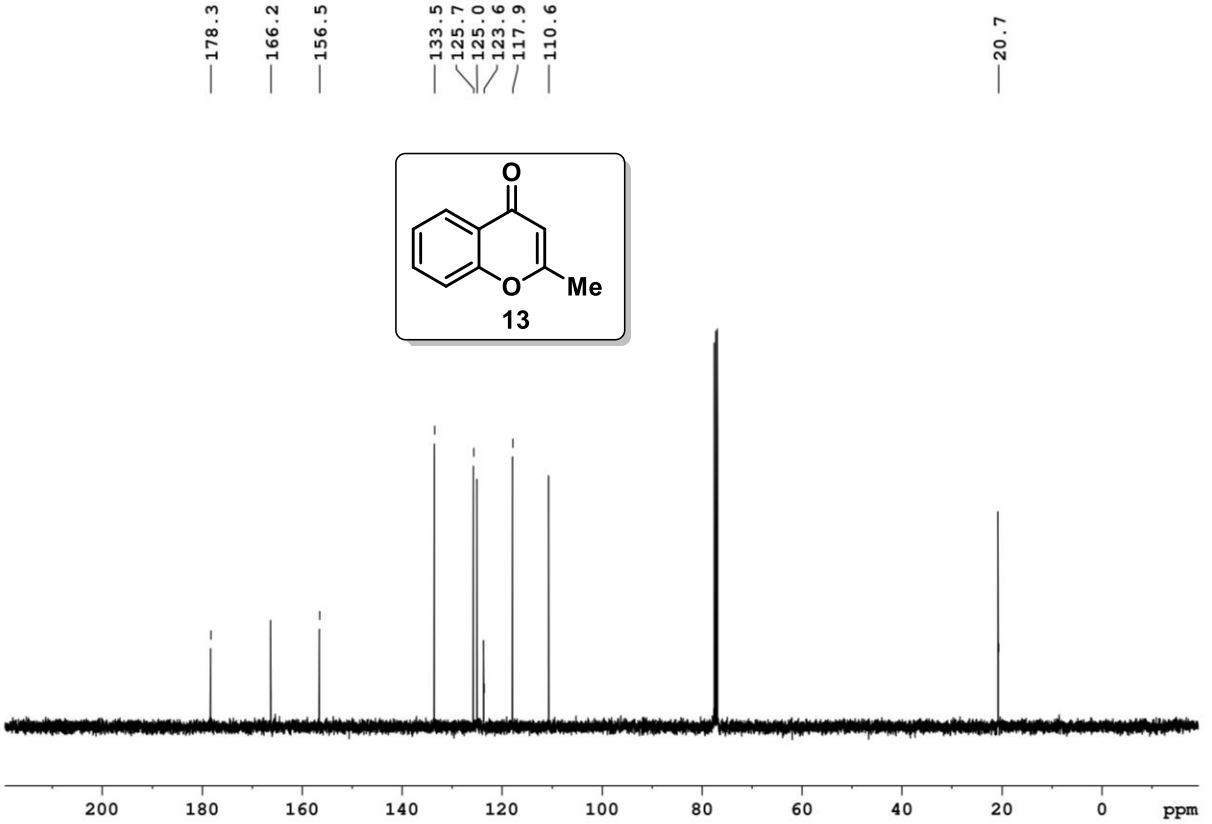
^{1}H NMR (400 MHz, $CDCl_3$) hexyl 4-oxo-4*H*-chromene-2-carboxylate (**7g**)



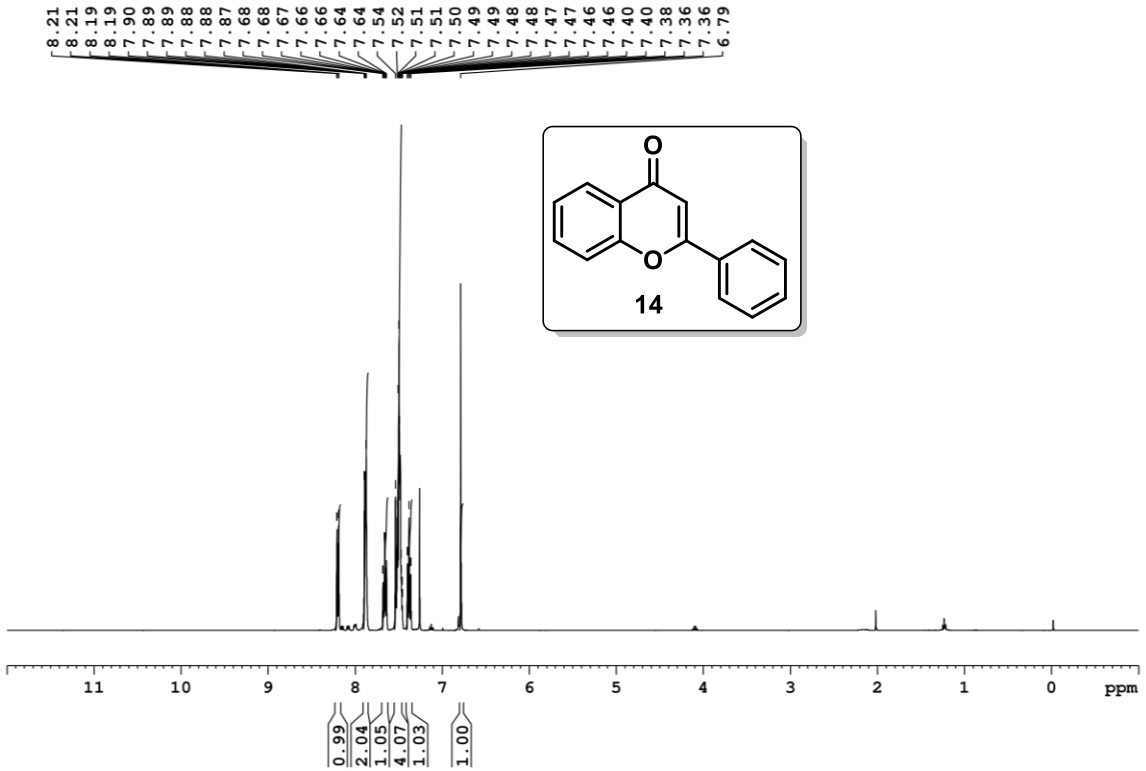
^{1}H NMR (400 MHz, $CDCl_3$) 2-methyl-4*H*-chromen-4-one (**13**)



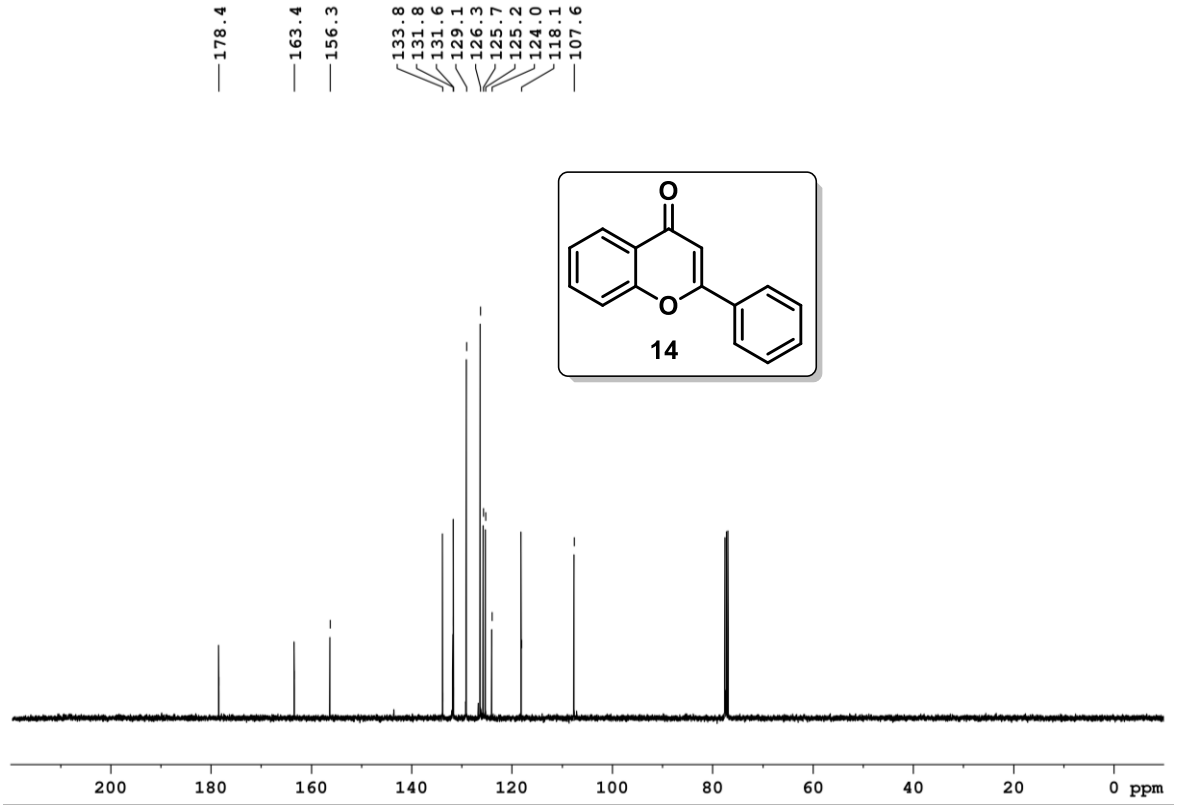
^{13}C NMR (100 MHz, $CDCl_3$) 2-methyl-4*H*-chromen-4-one (**13**)



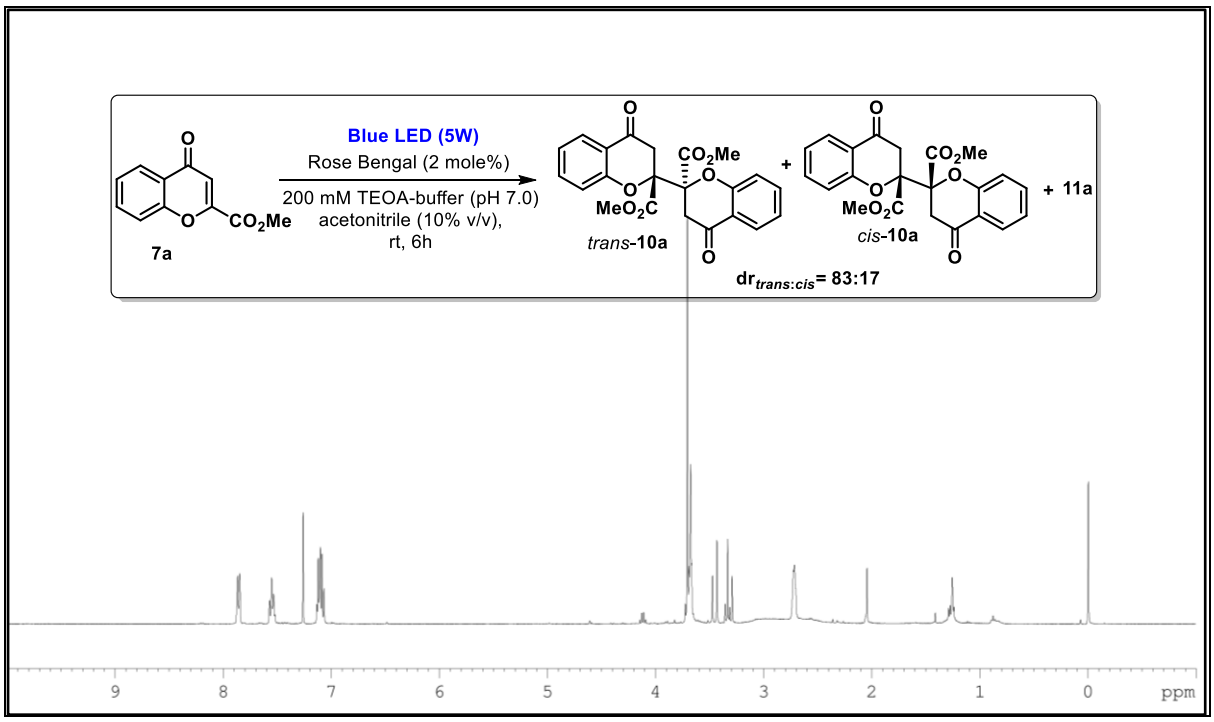
^{1}H NMR (400 MHz, $CDCl_3$) 2-phenyl-4*H*-chromen-4-one (**14**)

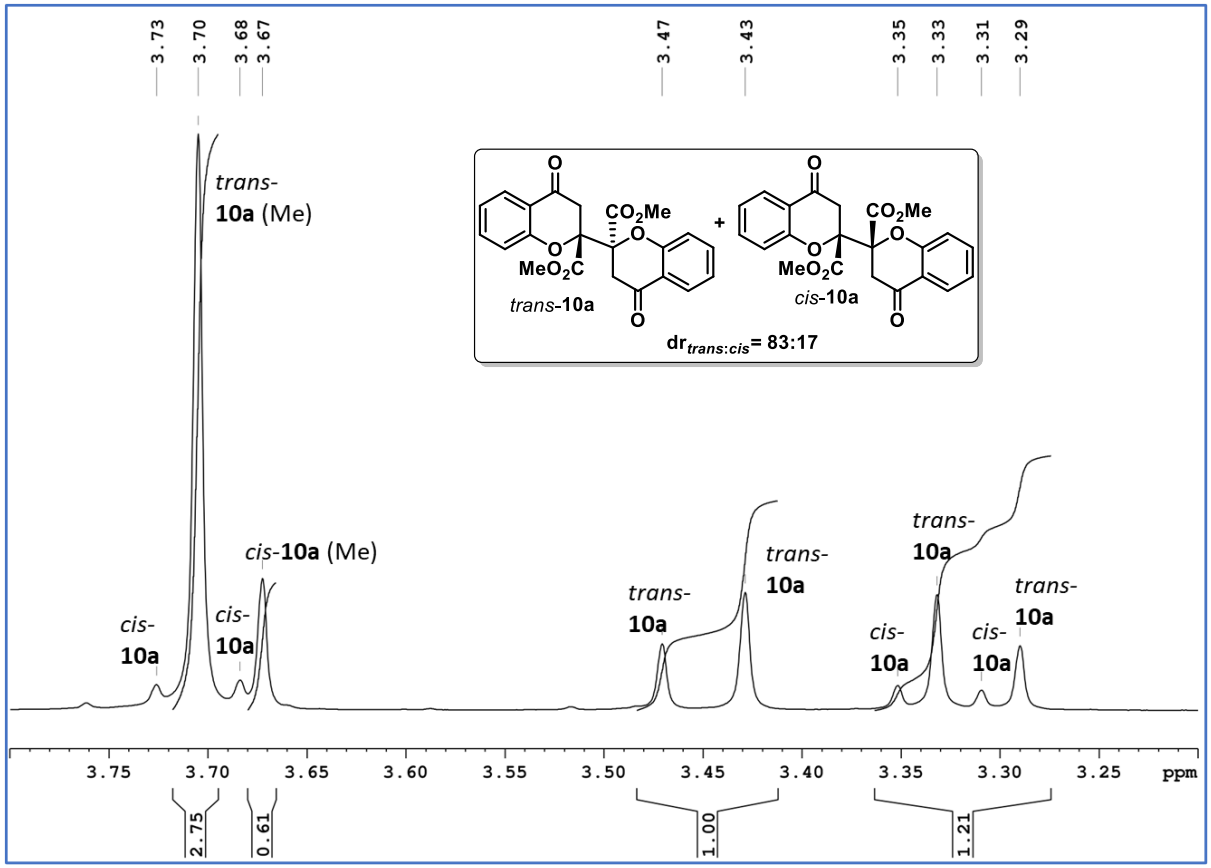


^{13}C NMR (100 MHz, $CDCl_3$) 2-phenyl-4*H*-chromen-4-one (**14**)

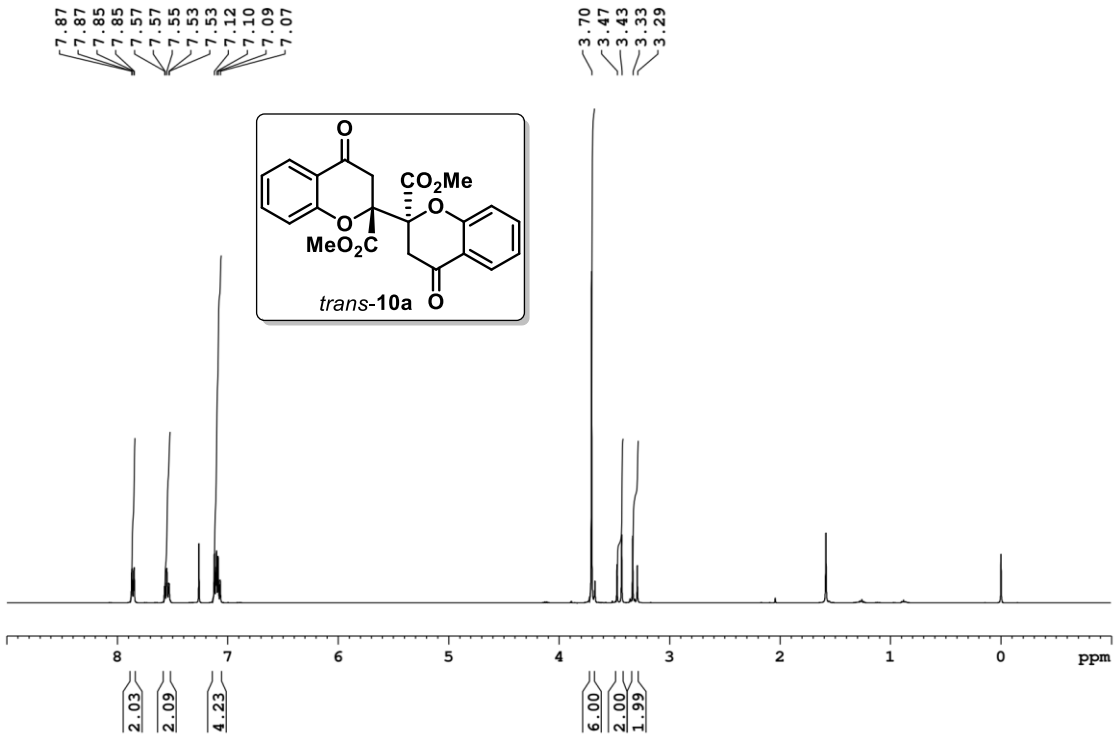


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of unpurified photodimerization reaction mixture of 7a (98% conversion) ($dr_{trans:cis}$ = 83:17)

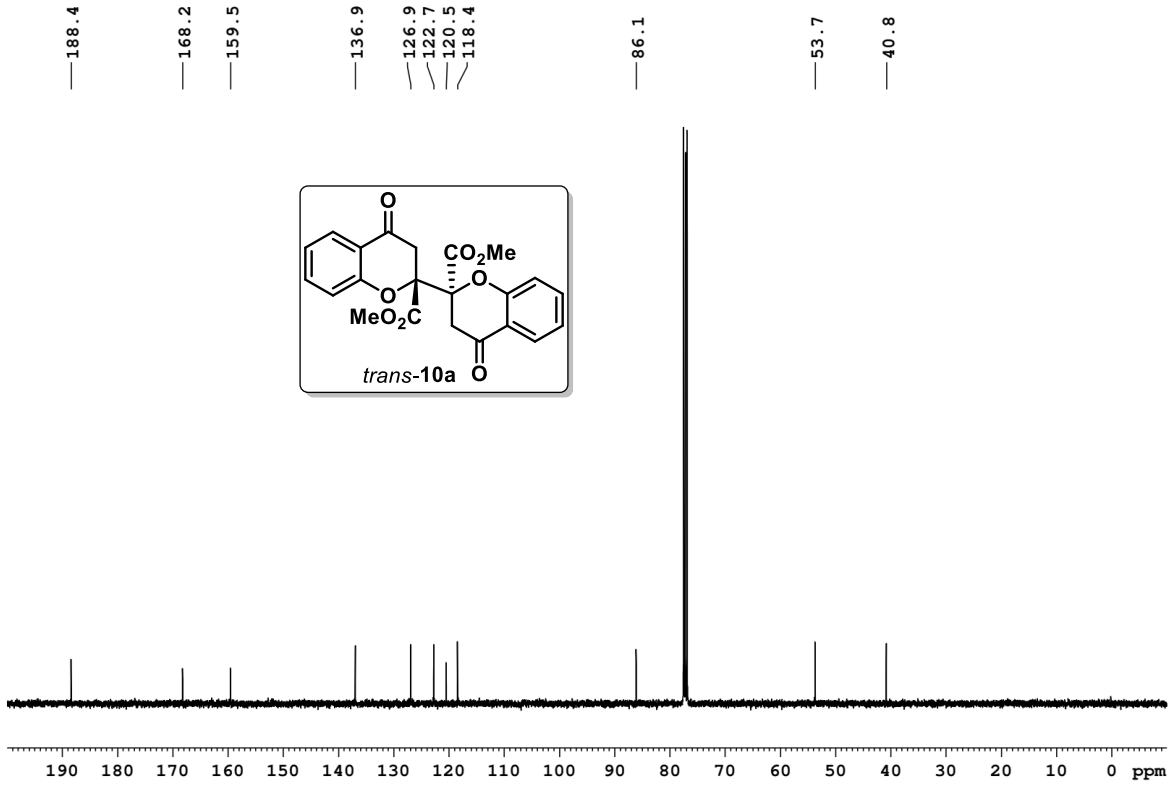




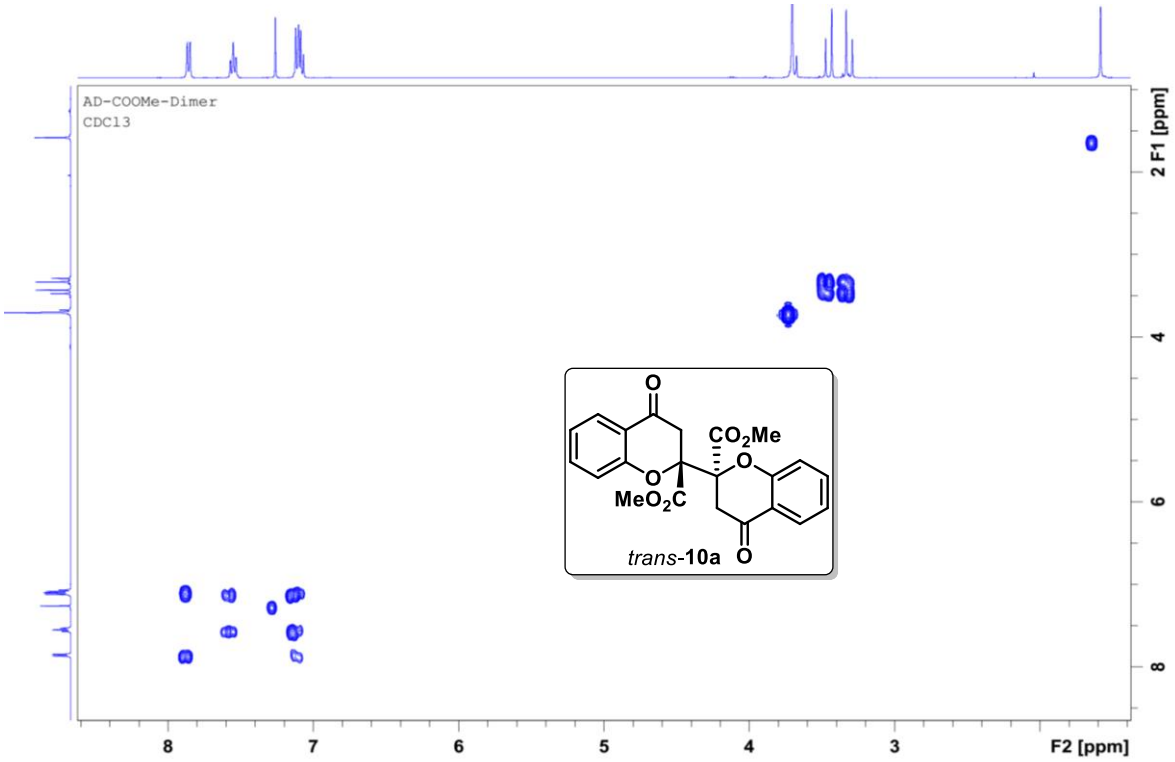
^{1}H NMR (400 MHz, $CDCl_3$) dimethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate. (*trans*-**10a**)



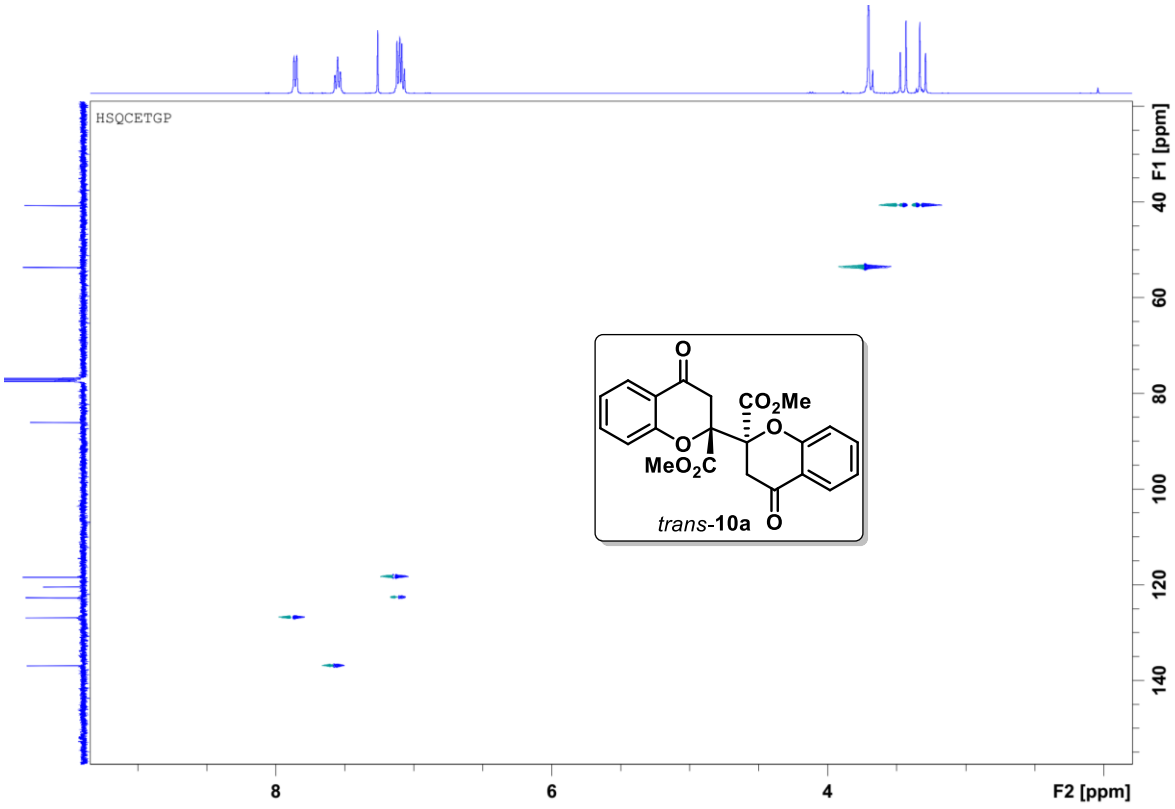
^{13}C NMR (100 MHz, $CDCl_3$) dimethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-**10a**)



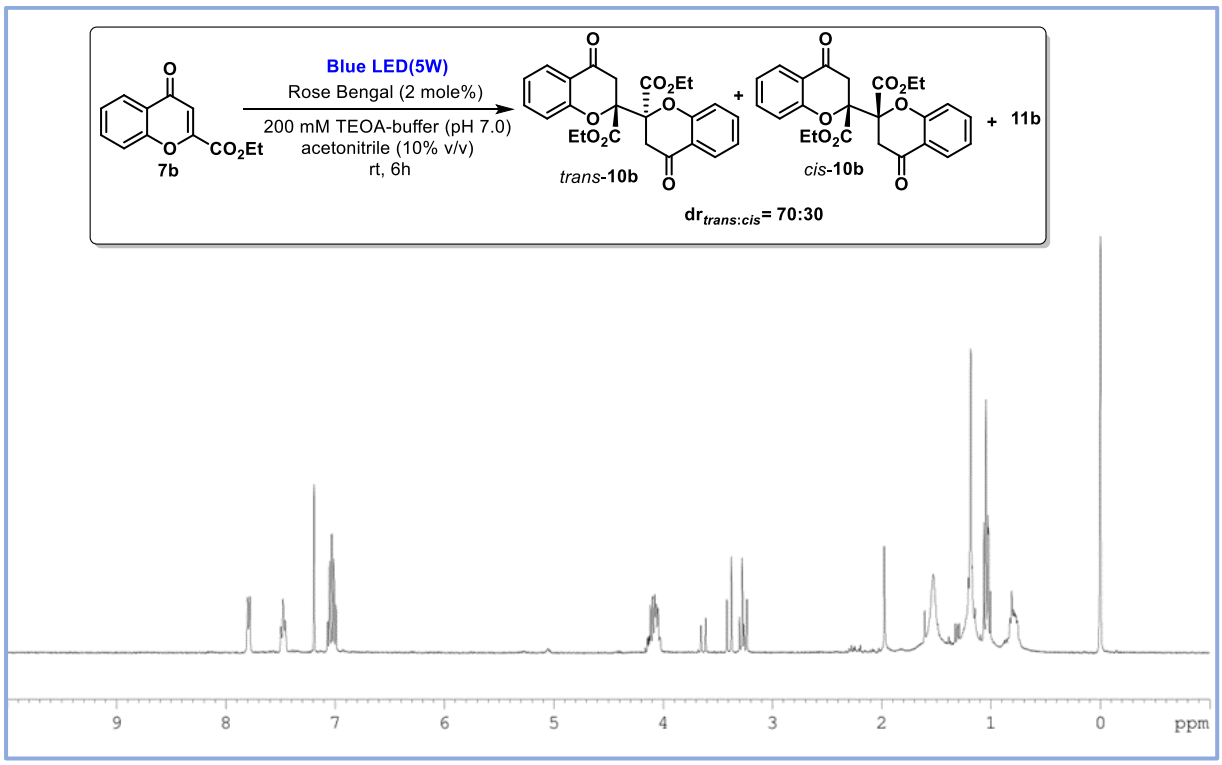
COSY ($CDCl_3$) dimethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-**10a**)

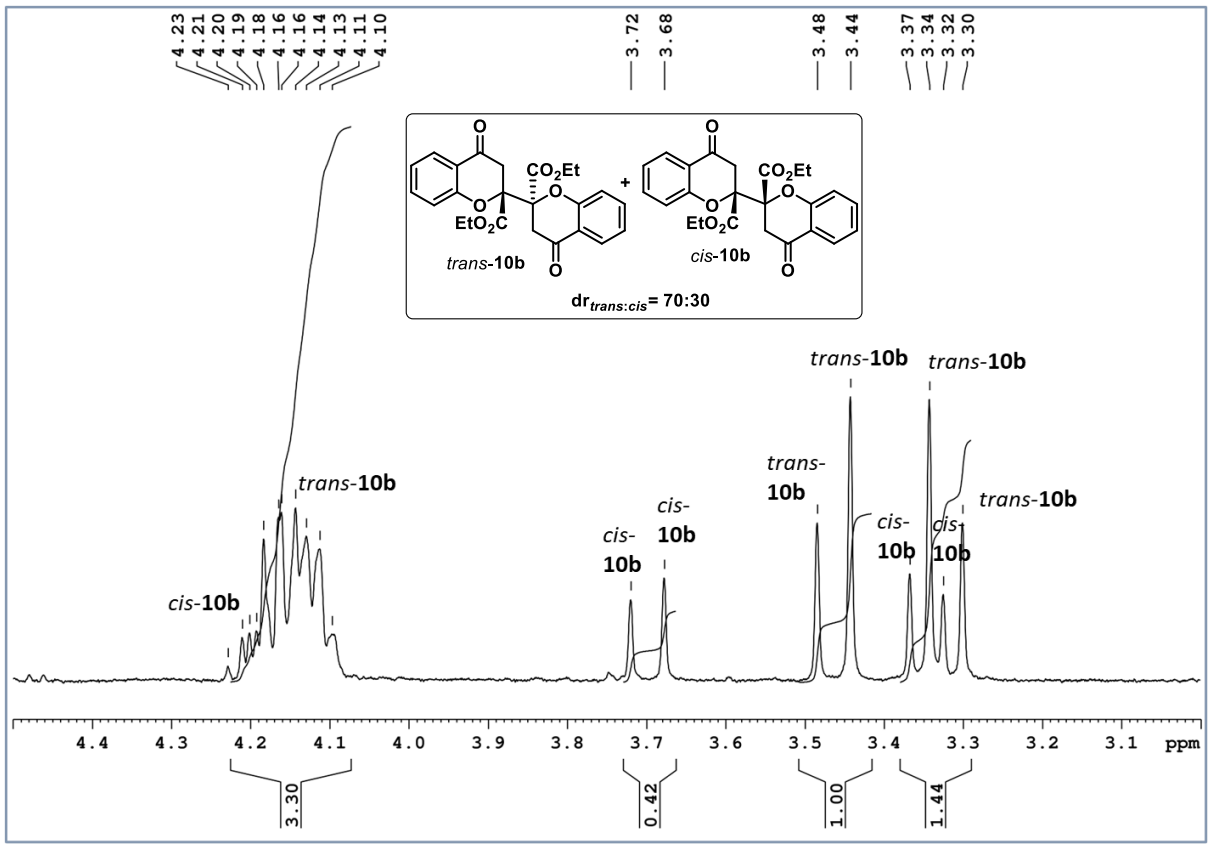


HSQC ($CDCl_3$) dimethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-**10a**)

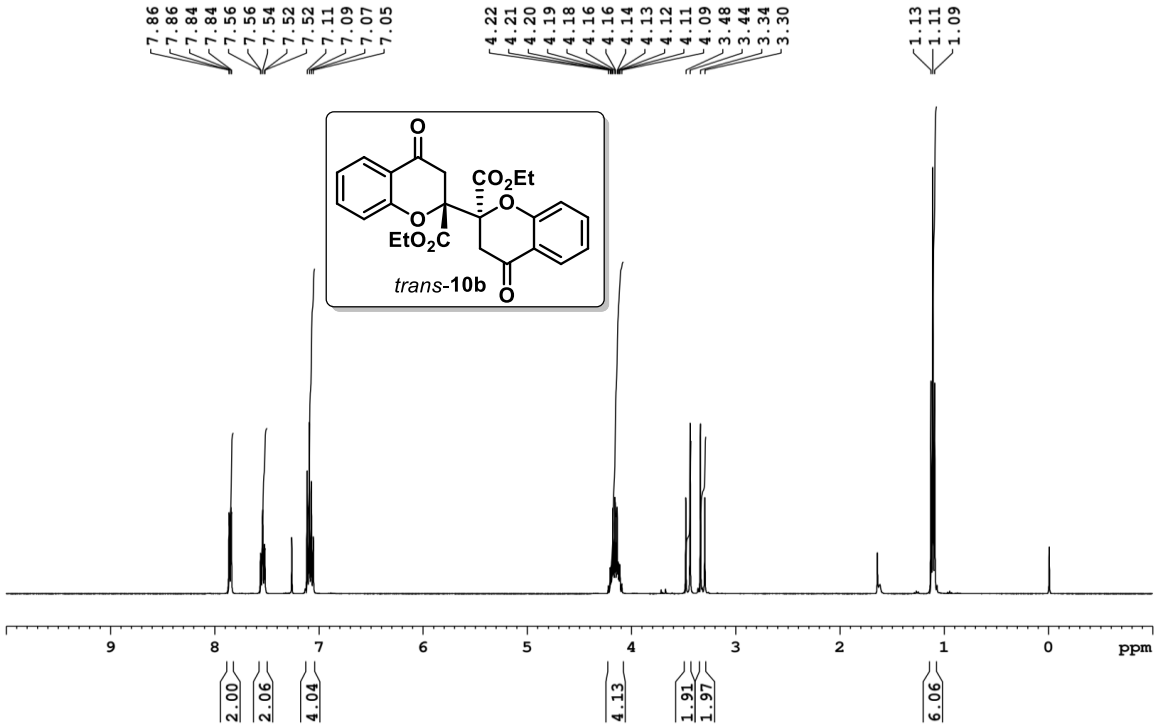


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the unpurified photodimerization reaction mixture of 7b (99% conversion) ($dr_{trans\text{-}10b:cis\text{-}10b}$ = 70:30)

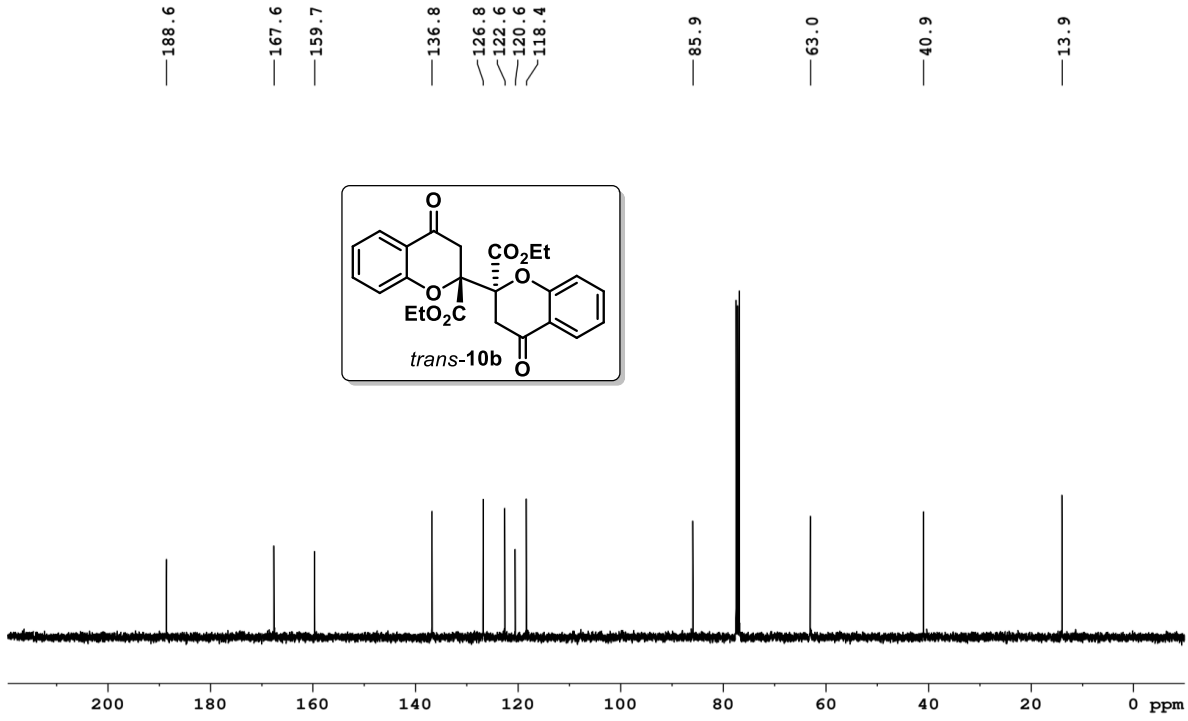




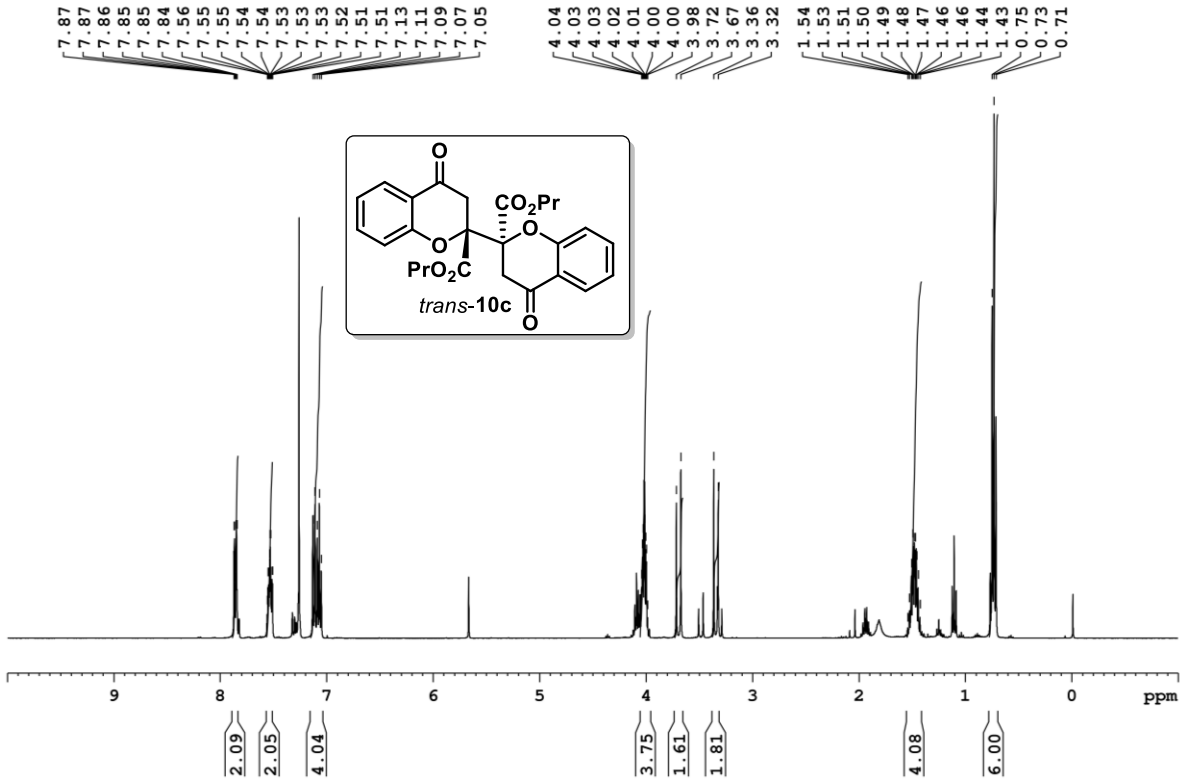
^{1}H NMR (400 MHz, $CDCl_3$) diethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-**10b**)



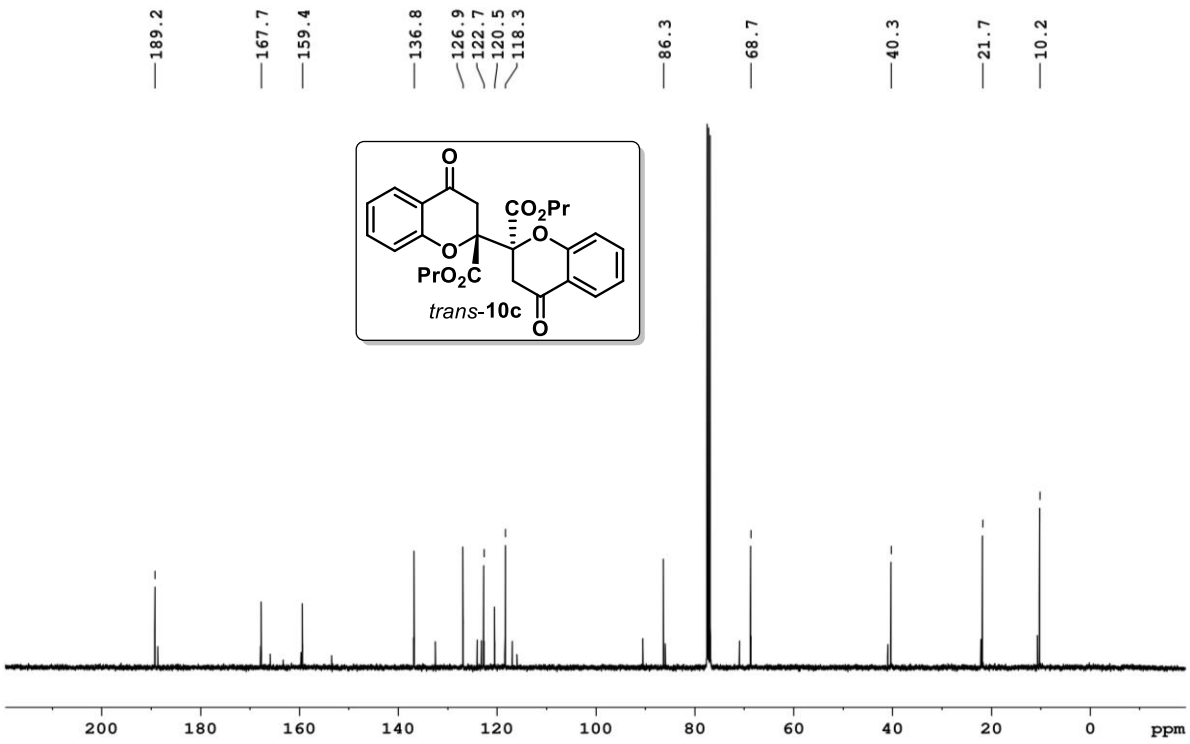
^{13}C NMR (100 MHz, $CDCl_3$) diethyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (*trans*-**10b**)



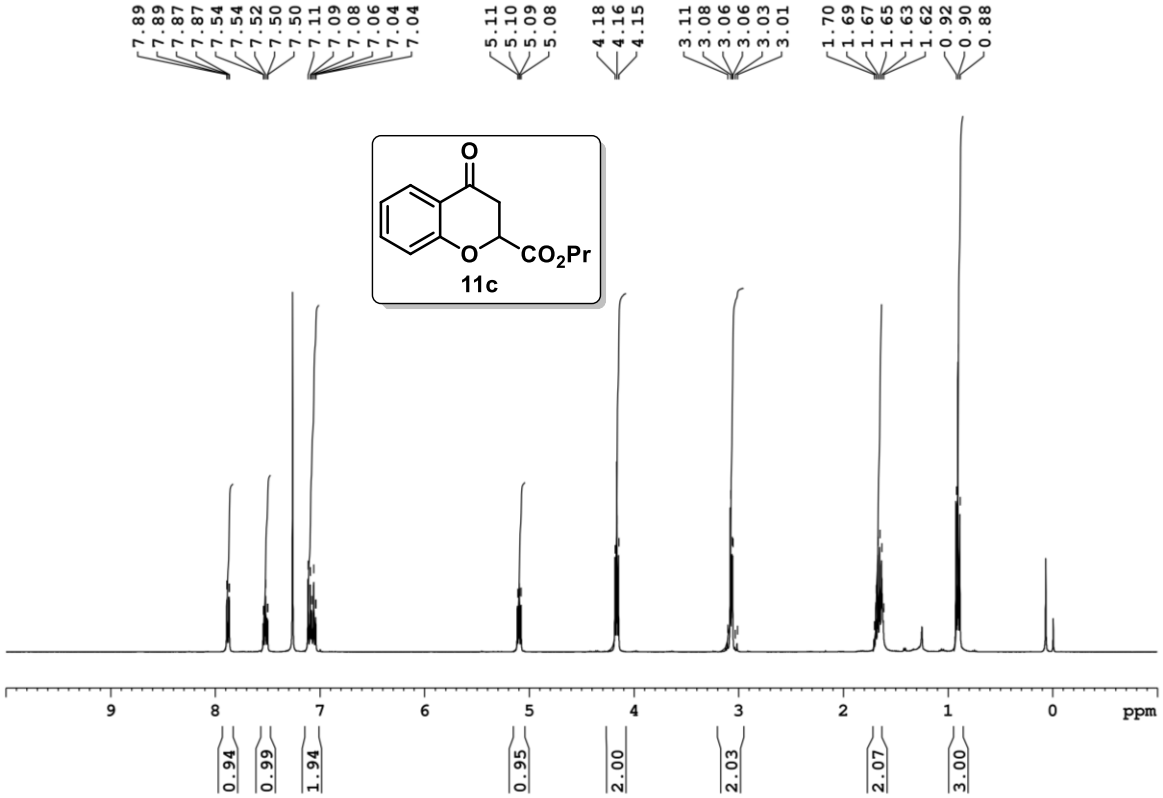
^{1}H NMR (400 MHz, $CDCl_3$) dipropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10c**)



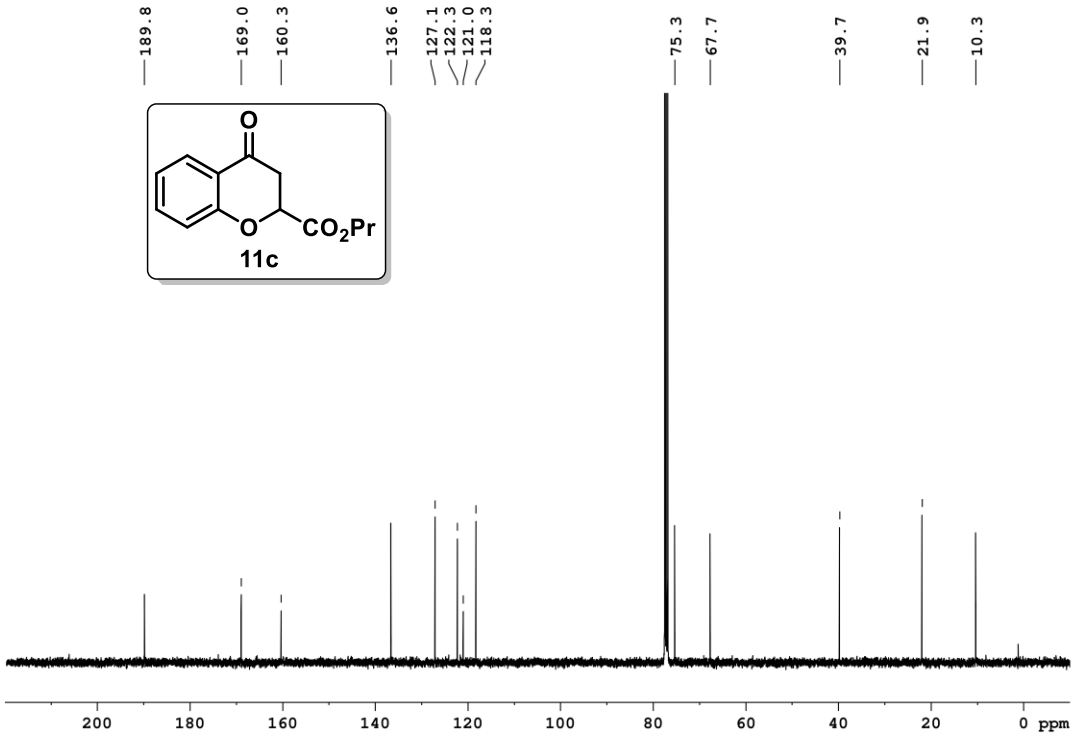
^{13}C NMR (100 MHz, $CDCl_3$) dipropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10c**)



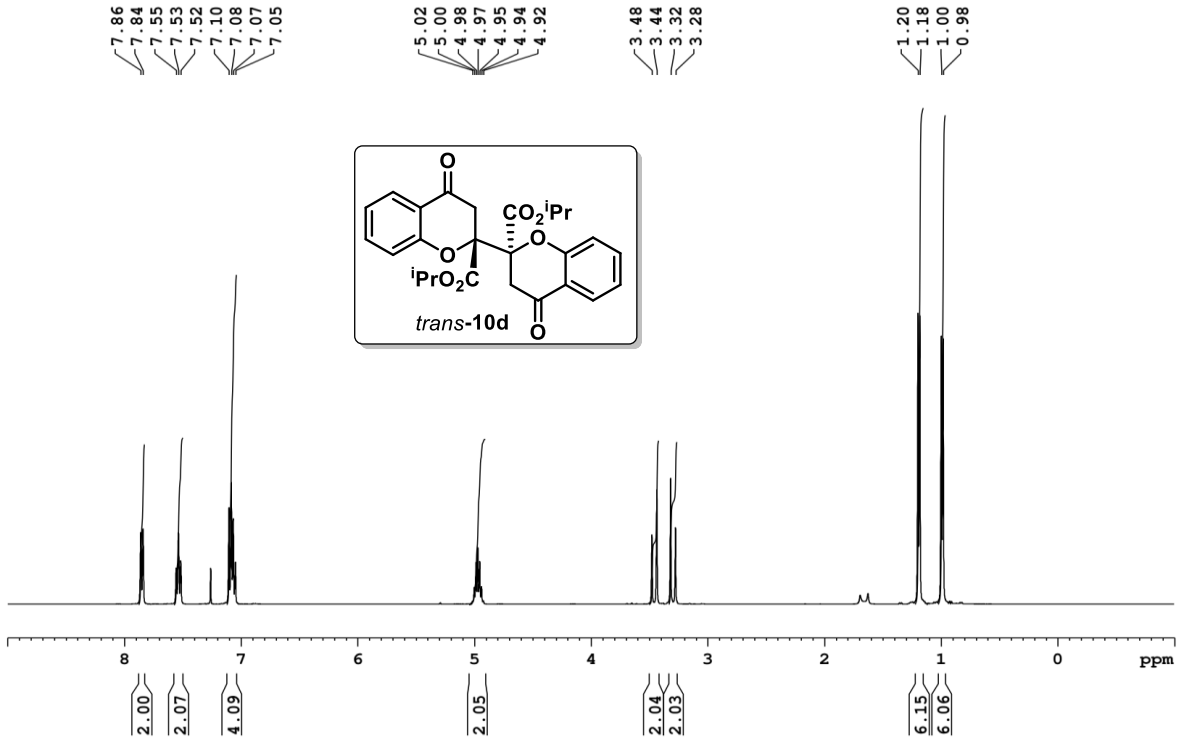
^{1}H NMR (400 MHz, $CDCl_3$) propyl 4-oxochromane-2-carboxylate (**11c**)



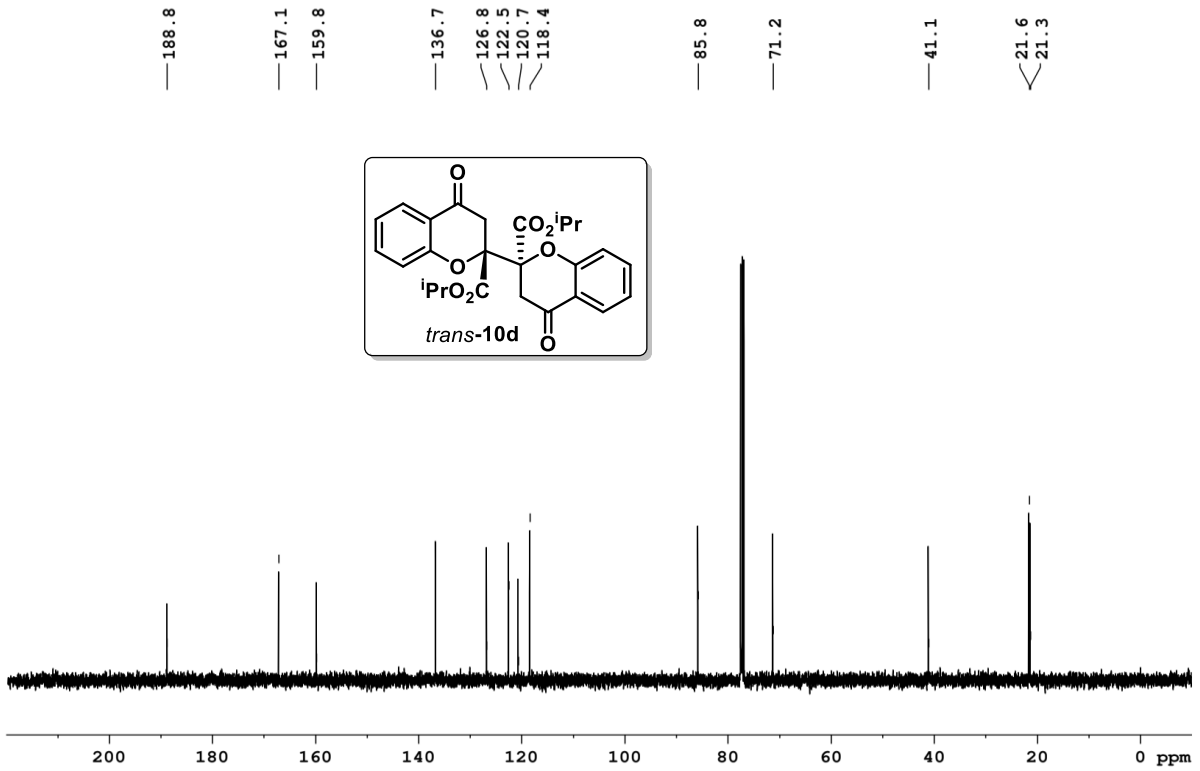
^{13}C NMR (100 MHz, $CDCl_3$) propyl 4-oxochromane-2-carboxylate (**11c**)



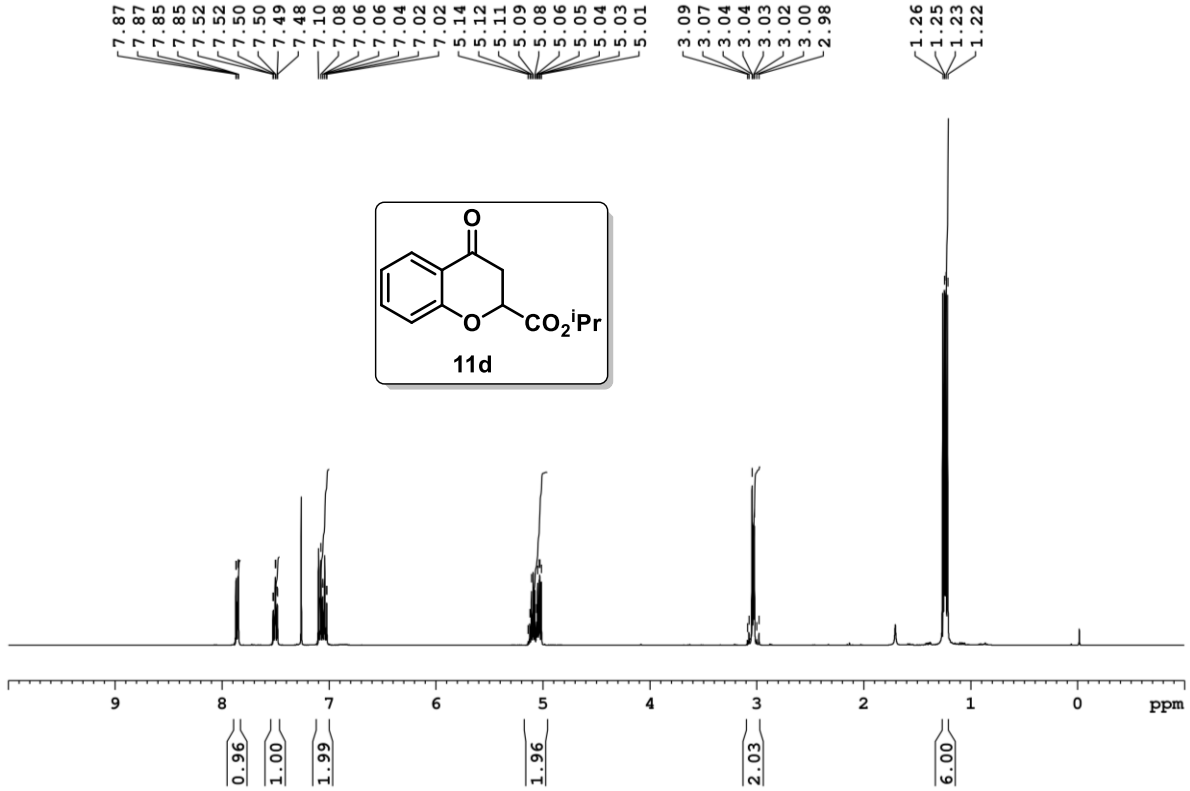
^{1}H NMR (400 MHz, $CDCl_3$) diisopropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10d**)



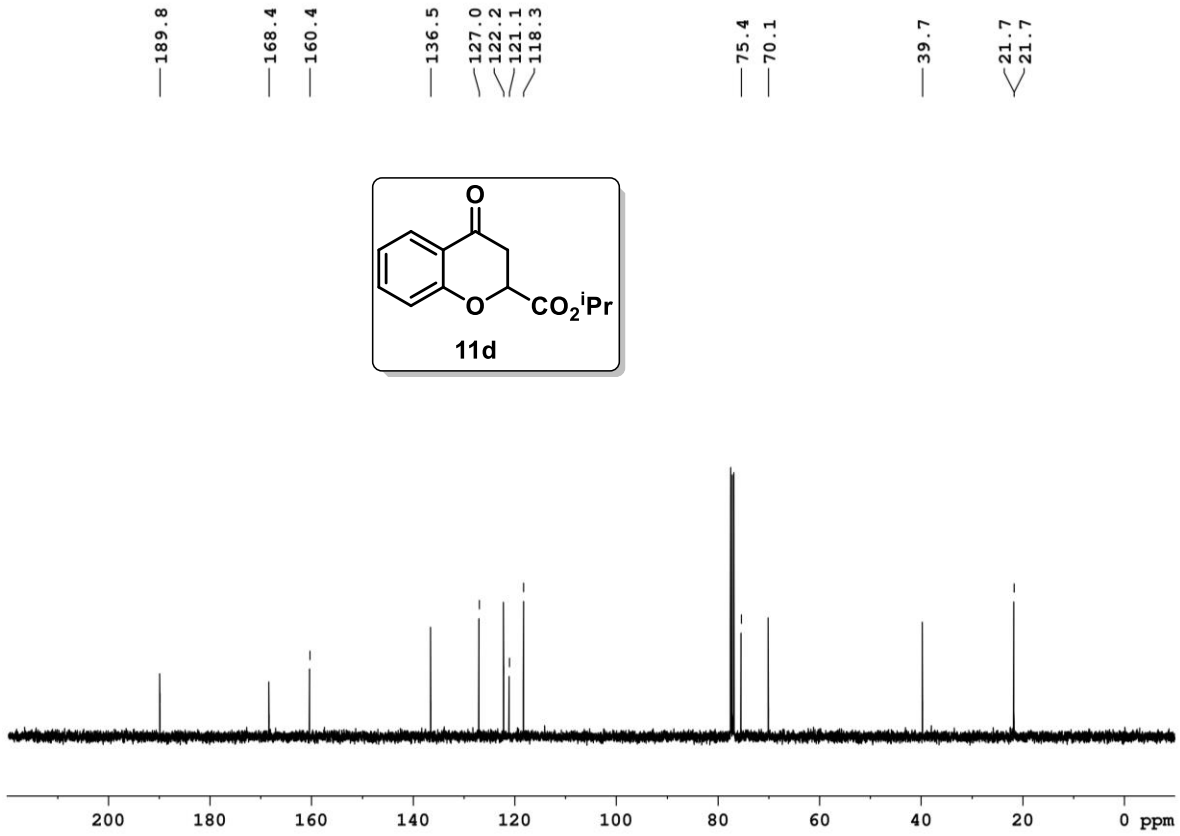
^{13}C NMR (100 MHz, $CDCl_3$) diisopropyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10d**)



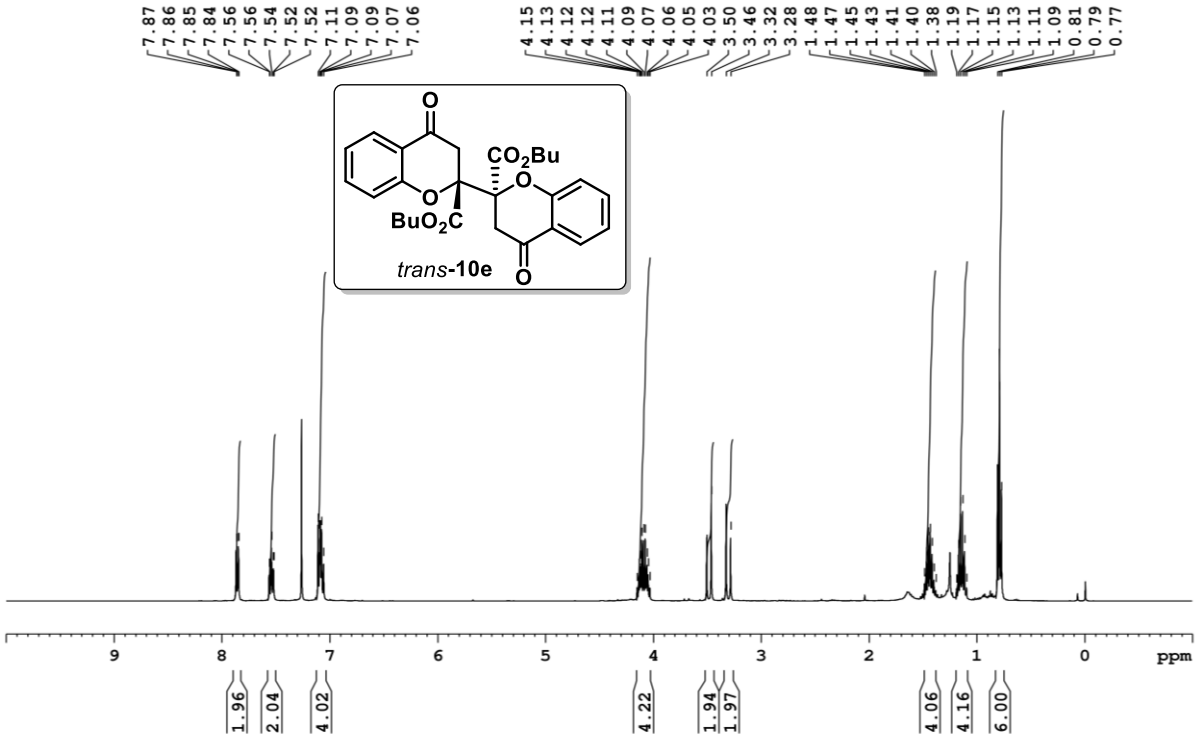
^{1}H NMR (400 MHz, $CDCl_3$) isopropyl 4-oxochromane-2-carboxylate (**11d**)



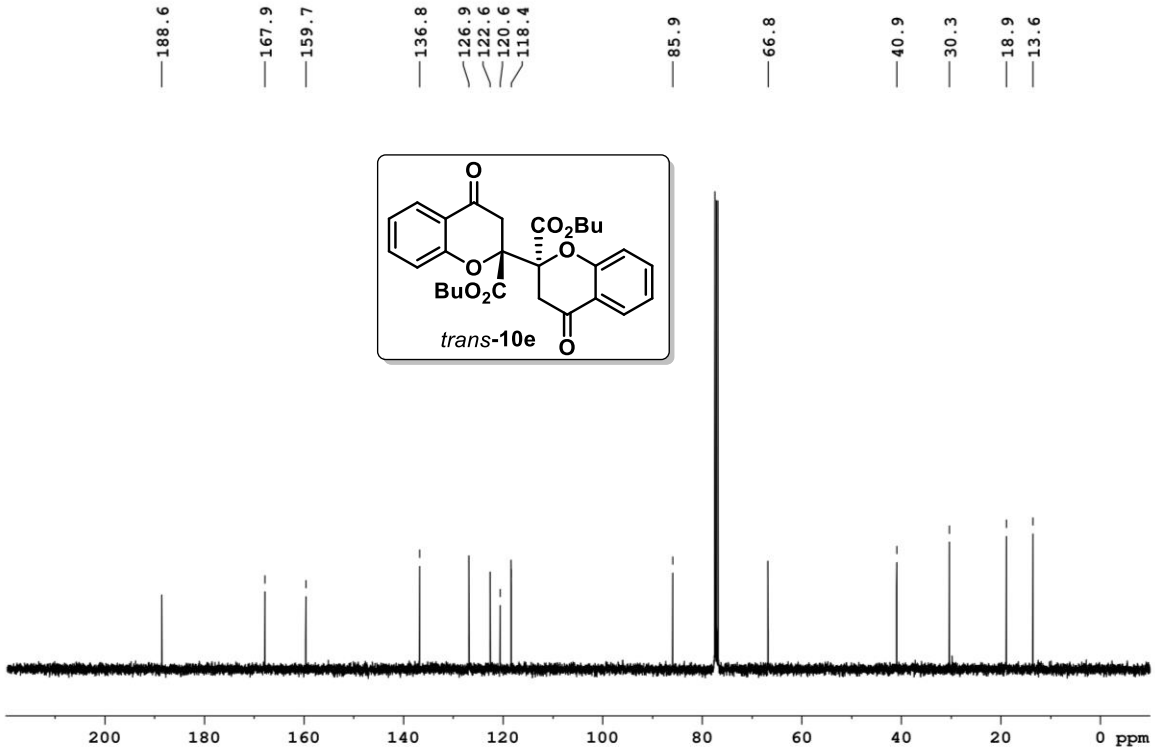
^{13}C NMR (100 MHz, $CDCl_3$) isopropyl 4-oxochromane-2-carboxylate (**11d**)



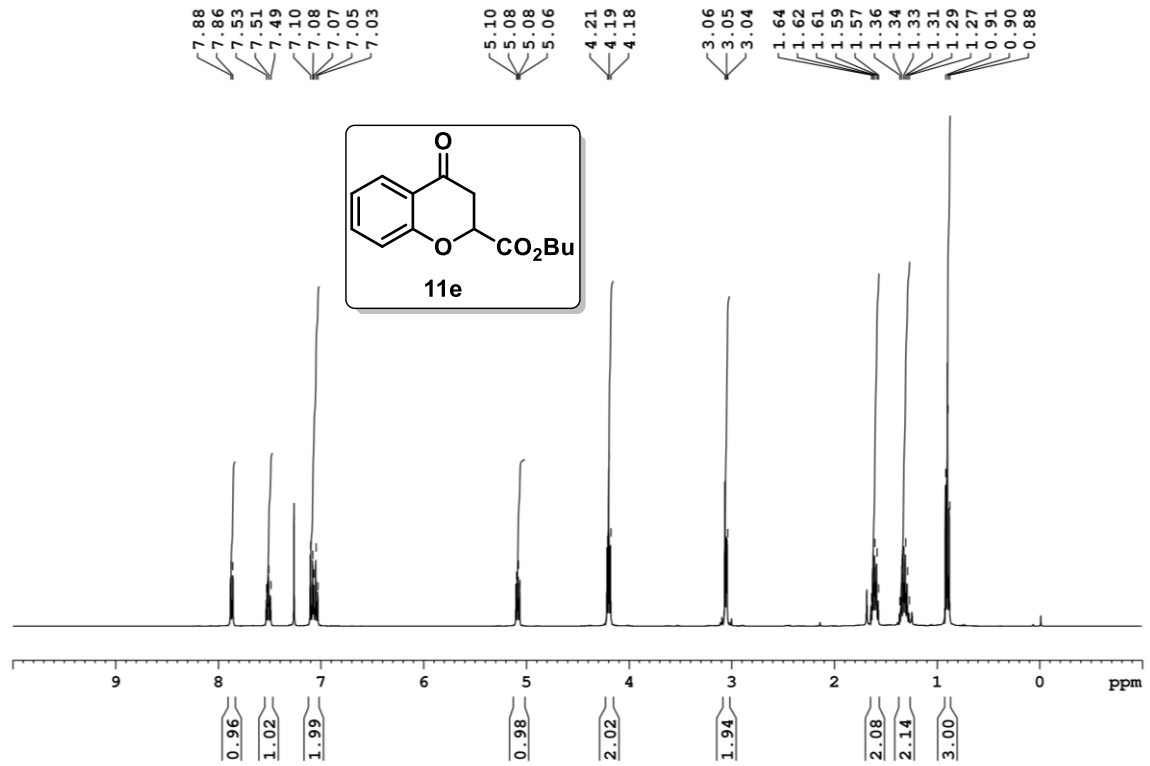
^{1}H NMR (400 MHz, $CDCl_3$) dibutyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10e**)



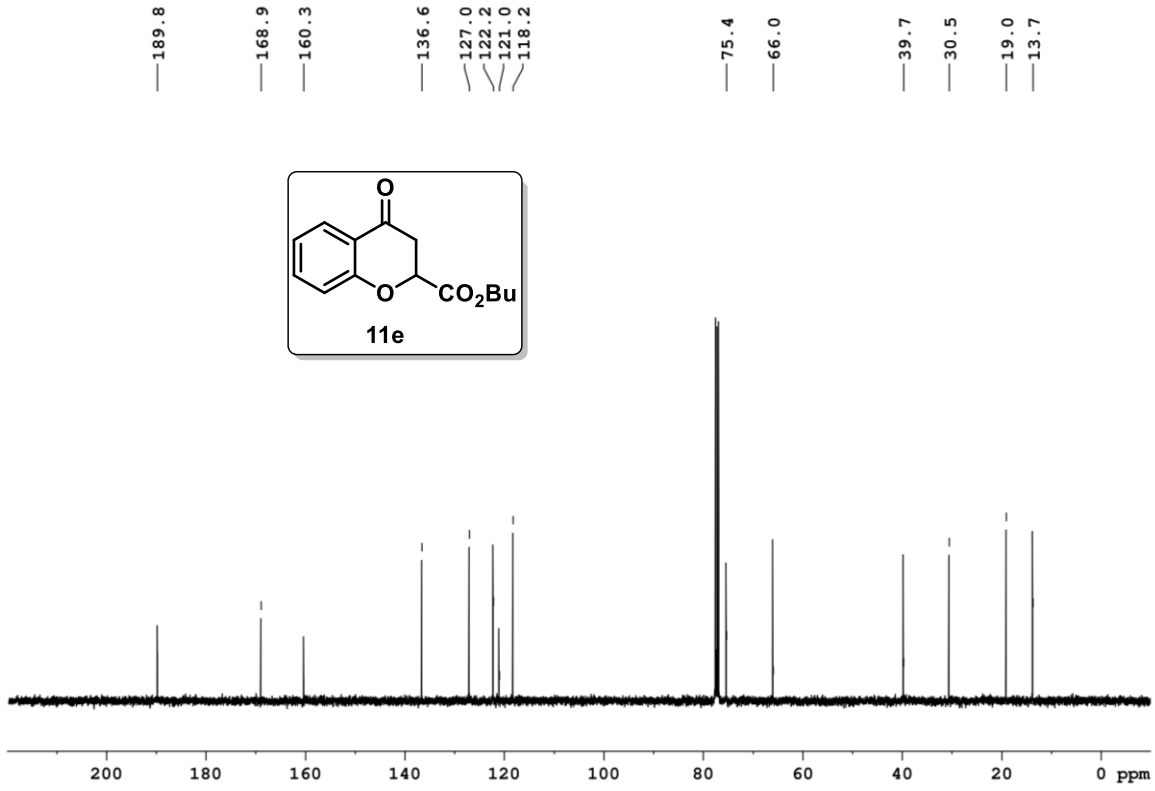
^{13}C NMR (100 MHz, $CDCl_3$) dibutyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2' dicarboxylate (*trans*-**10e**)



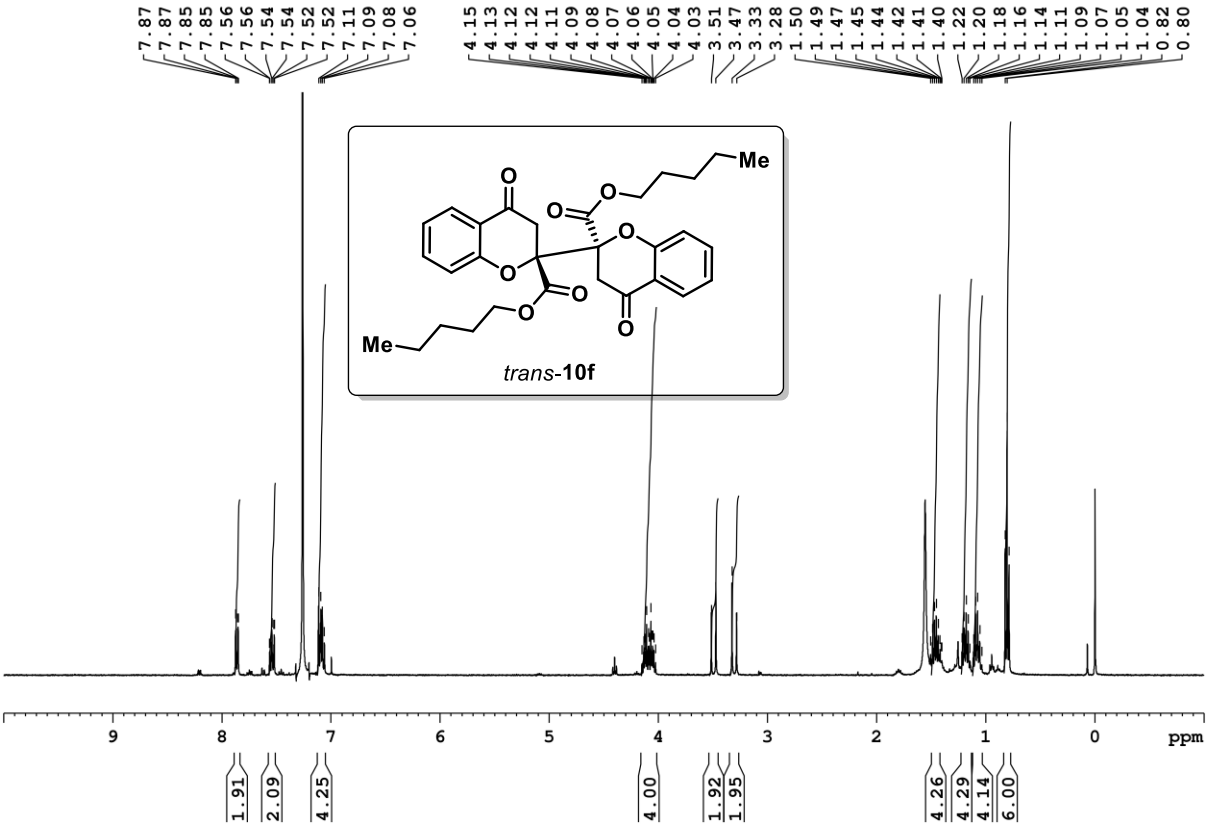
^{1}H NMR (400 MHz, $CDCl_3$) butyl 4-oxochromane-2-carboxylate (**11e**)



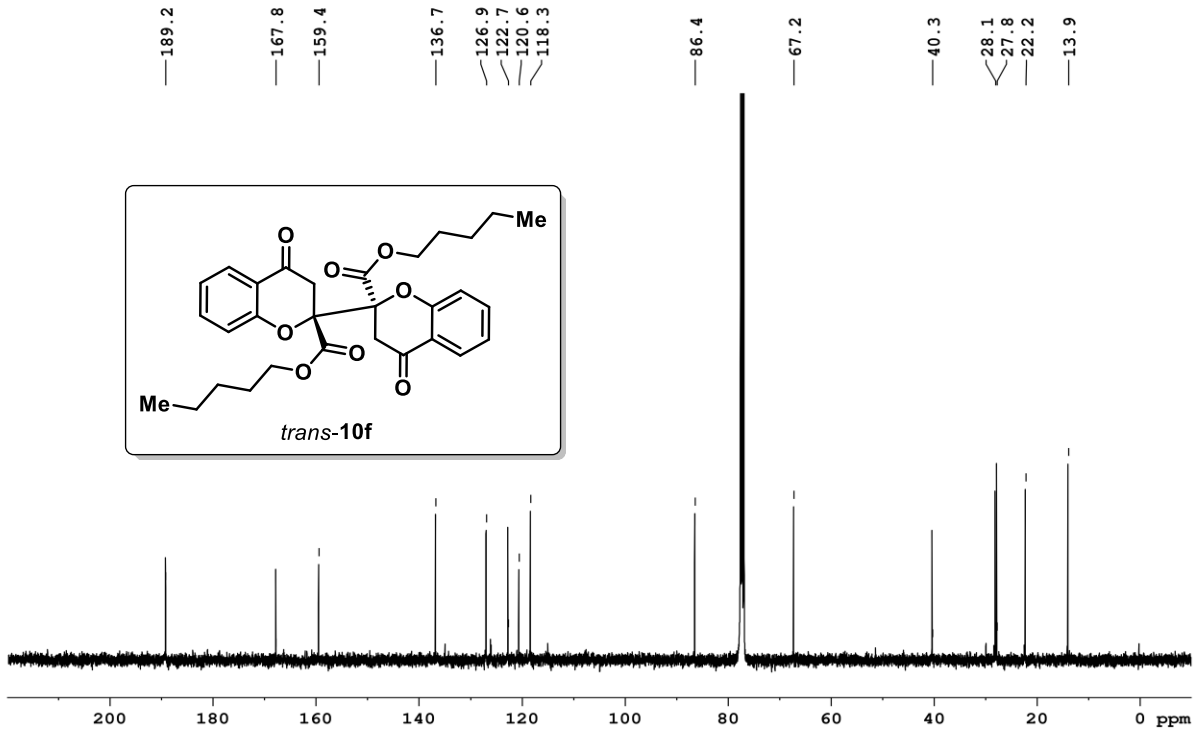
^{13}C NMR (100 MHz, $CDCl_3$) butyl 4-oxochromane-2-carboxylate (**11e**)



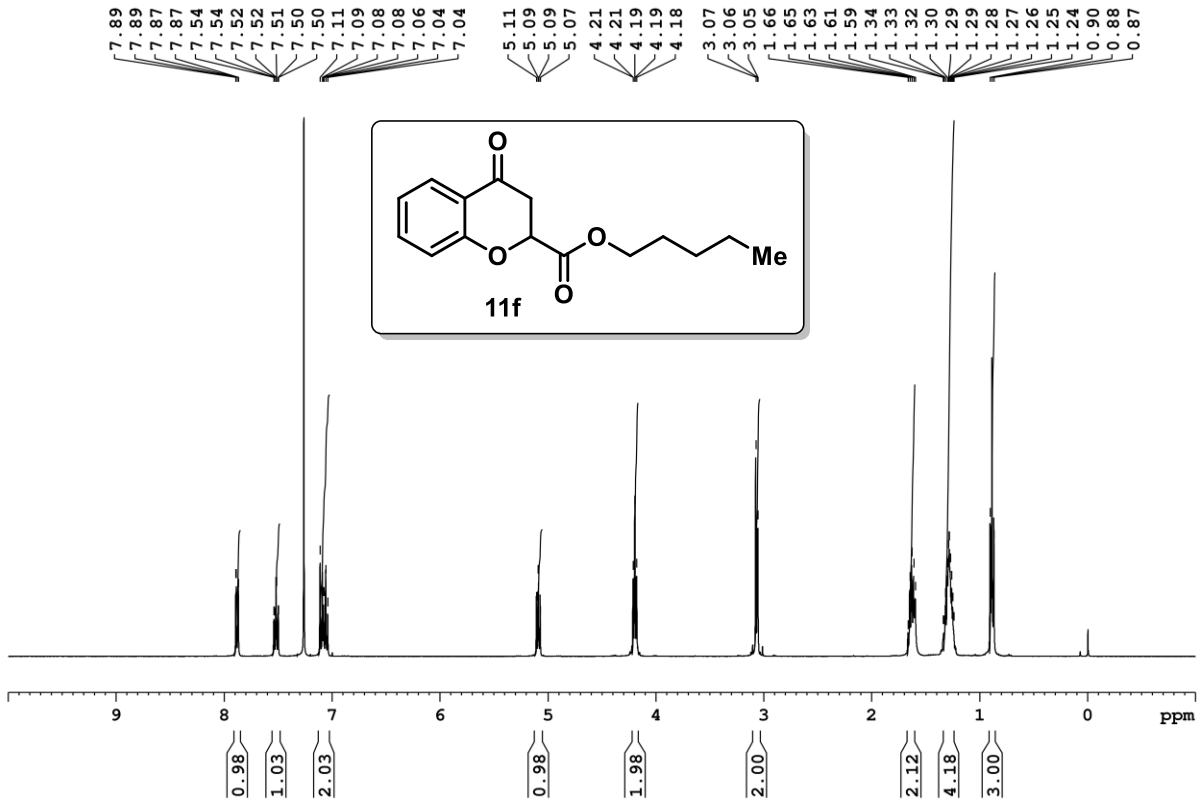
^{1}H NMR (400 MHz, $CDCl_3$) dipentyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (***trans*-10f**)



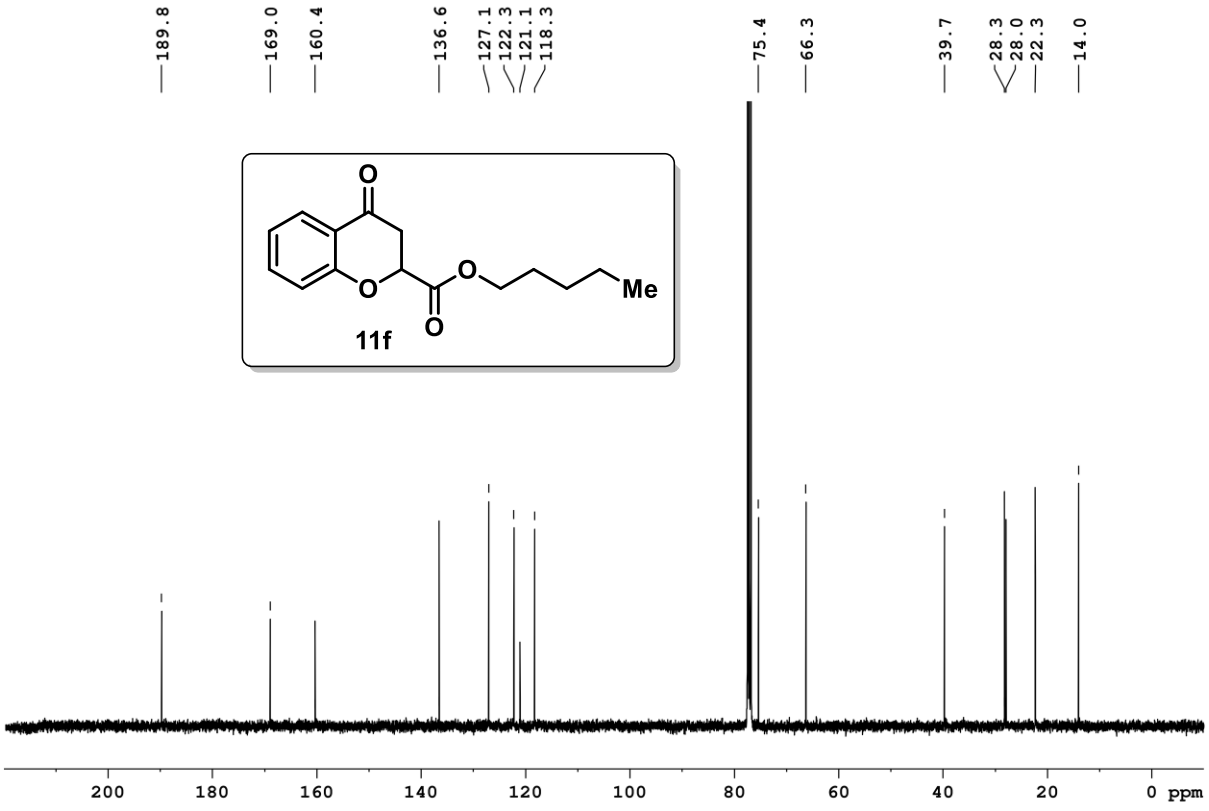
^{13}C NMR (100 MHz, $CDCl_3$) dipentyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (***trans*-10f**)



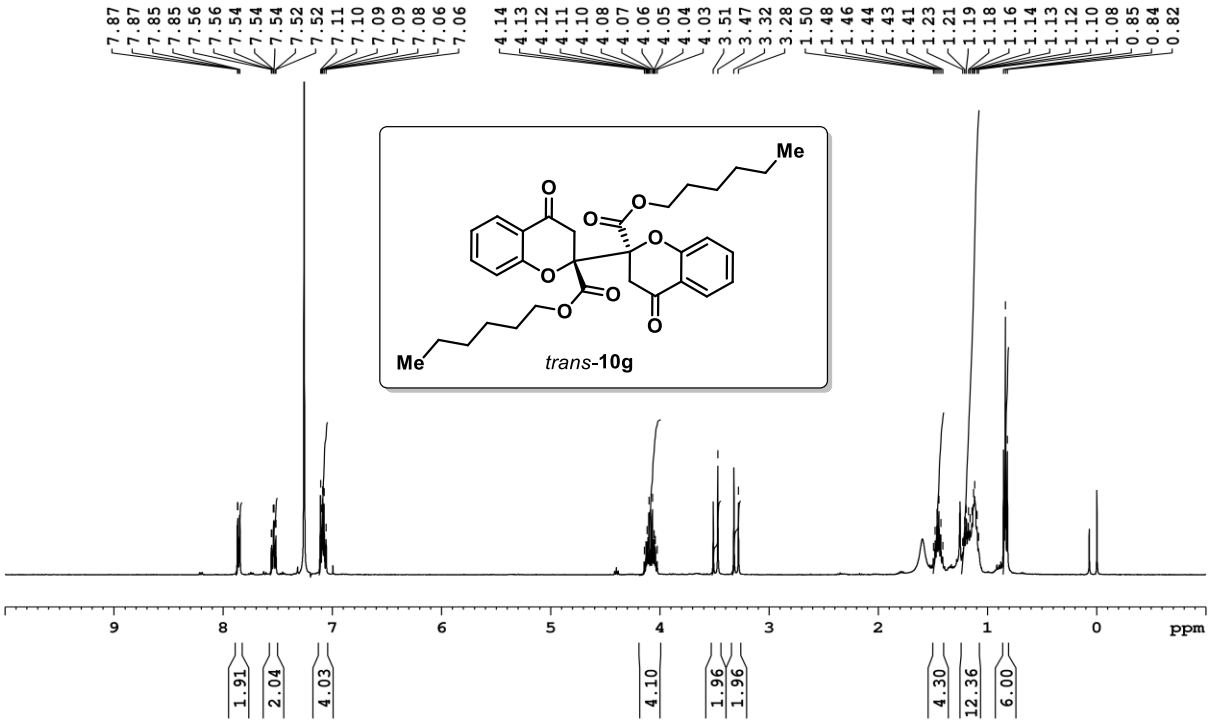
^{1}H NMR (400 MHz, $CDCl_3$) pentyl 4-oxochromane-2-carboxylate (**11f**)



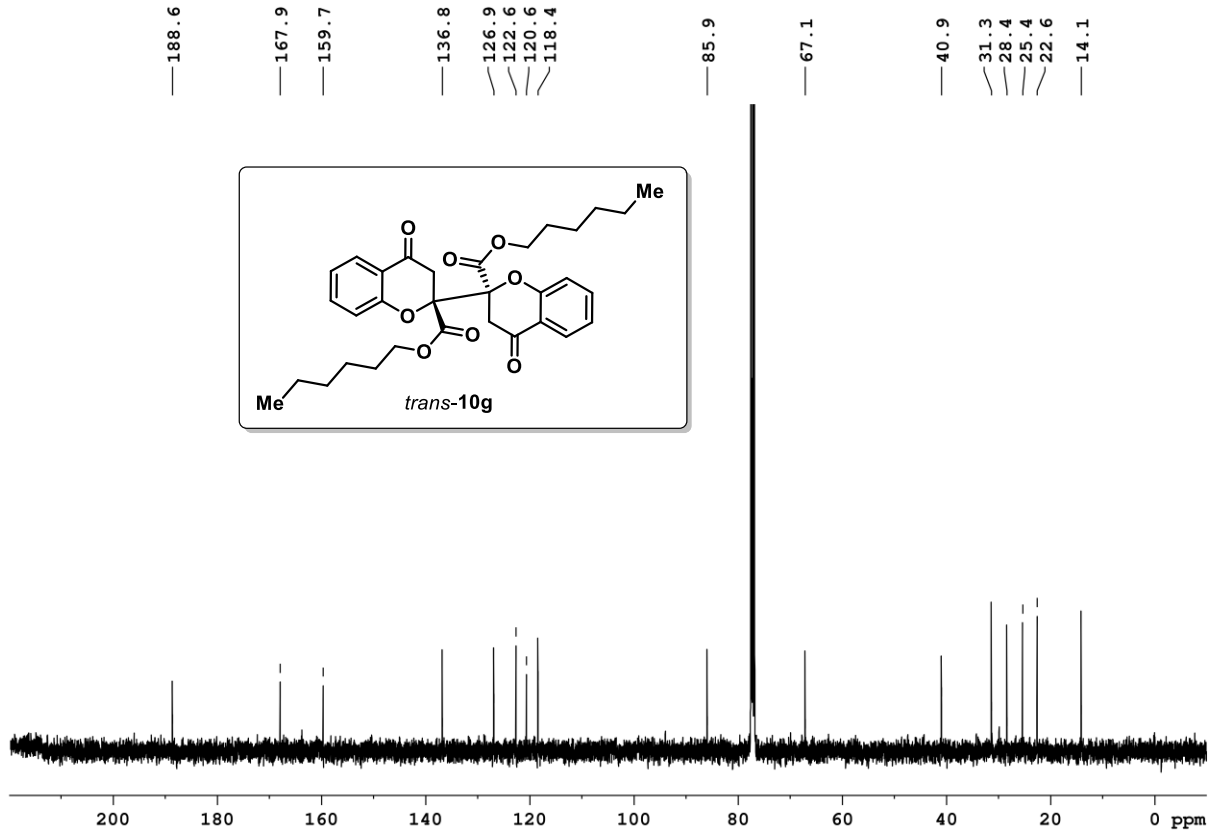
^{13}C NMR (100 MHz, $CDCl_3$) pentyl 4-oxochromane-2-carboxylate (**11f**)



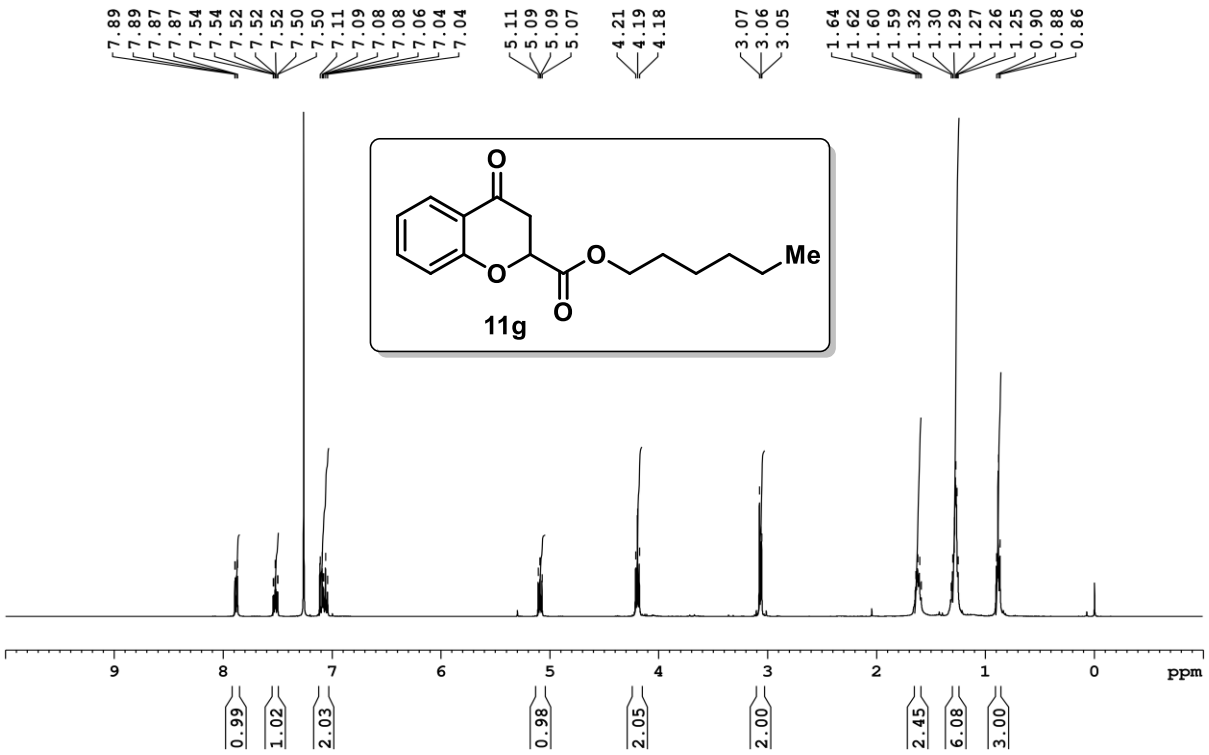
^{1}H NMR (400 MHz, $CDCl_3$) dihexyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (***trans*-10g**)



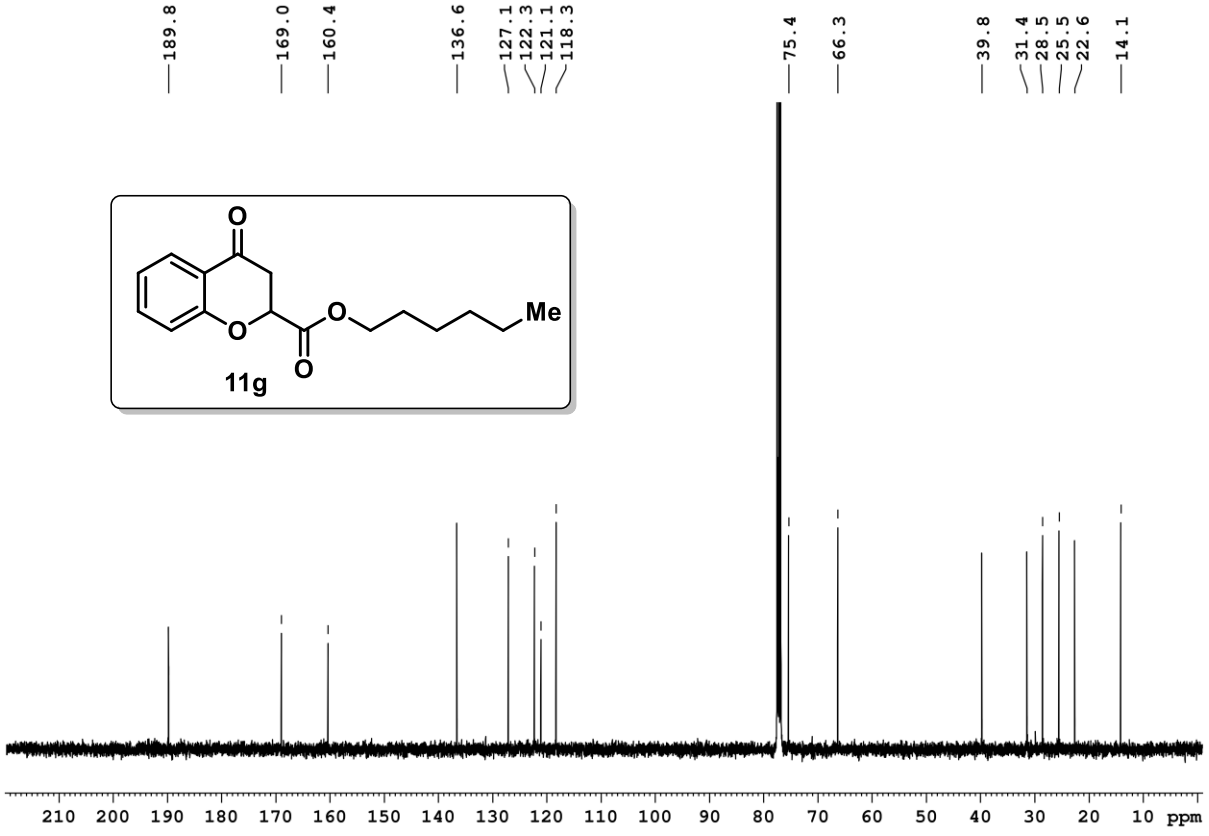
^{13}C NMR (100 MHz, $CDCl_3$) dihexyl (2*R*,2'*S*)-4,4'-dioxo-[2,2'-bichromane]-2,2'-dicarboxylate (***trans*-10g**)



^{1}H NMR (400 MHz, $CDCl_3$) hexyl 4-oxochromane-2-carboxylate (**11g**)



^{13}C NMR (100 MHz, $CDCl_3$) hexyl 4-oxochromane-2-carboxylate (**11g**)



VIII. References

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