Supporting Information

Organophotocatalytic Carbo-Heterofunctionalization of Unactivated Olefins with Pendant Nucleophiles

David M. Fischer‡, Manuel Freis‡, Willi M. Amberg, Henry Lindner, Erick M. Carreira*

Table of Contents

1. General Information

Procedure

All reactions were carried out under air, unless otherwise stated. Reactions carried out at temperatures above room temperature were conducted by placing the reaction flask in a preheated oil bath. Reactions in the photoreactor were performed in 13x40 mm screw-thread vials (ROFRA GmbH, Mat. Nr. 14.020.92) that were charged with a magnetic stirrer bar (PTFE, 3x8 mm, Semadeni Plastics Group, Art. 244) and sealed with a screwcap.

Chemicals

All reagents were purchased from commercial suppliers (ABCR, ACROS, Sigma Aldrich, Fluka, TCI, Strem, Alfa, Combi-Blocks or Fluorochem) and purified where appropriate. Anhydrous solvents over molecular sieves (4Å) were purchased from Acros and used as received.

Thin-Layer Chromatography

For reaction controls TLC glass plates from Supelco® (TLC silica gel 60 F_{254}: 25 glass plates, 20 x 20 cm) were used. Spotted substances were made visible by exposure to ultraviolet light (254 nm or 365 nm) or TLC stain (aqueous potassium permanganate solution or aqueous ceric ammonium molybdate solution followed by heating).

Column Chromatography

For column chromatography Sigma-Aldrich silica gel sorbent (high purity grade (9385), 230-400 mesh particle size, pore size 60) was used as a stationary phase.

Nuclear Magnetic Resonance Spectroscopy

All NMR spectra were measured in deuterated solvents at room temperature with a Bruker Avance 400 (400 MHz, equipped with 9.4 T magnet and BBFO probe), Bruker

Ascend 400 (400 MHz, equipped with 9.4 T magnet and BBFO probe), Bruker Ultrashield 400 (400 MHz, equipped with 9.4 T magnet and BBFO probe), Oxford 400 (400 MHz, equipped with 9.4 T magnet and BBFO probe) or Bruker Avance 500 (500 MHz, equipped with 11.7 T magnet and a BBFO probe). The chemical shifts are referenced to the solvent residual signal ($CDCl_3$, ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm) and reported in parts per million (ppm). The following abbreviations are used in reporting NMR data: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, etc.

High-Resolution Mass Spectrometry

All mass spectra were measured by the mass spectrometry service of the Laboratory of Organic Chemistry at ETH Zurich on a Bruker Daltonics maXis ESI-QTOF or a Bruker Daltonics maXis II ESI-QTOF.

IR Spectroscopy

Infrared spectra were recorded on a Perkin Elmer Two FT-IR spectrometer as thin films. Absorptions are given in wavenumbers (cm^{-1}).

Fluorescence Spectroscopy

Fluorescence spectra were recorded on a Thermo Spectronic AMINCO-Bowman Series 2 Luminescence Spectrometer.

UV-Vis Spectroscopy

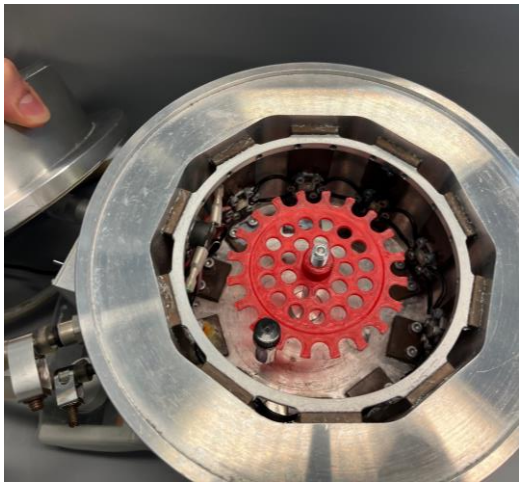
UV-Vis spectra were recorded on a Jasco V-630 UV-Vis Spectrophotometer or an Agilent Cary 60 UV-Vis Spectrophotometer.

Data Analysis

Analysis of all measured data was carried out with the Program OriginPro 2021.

2. Photoreaction Set-up

All photoreactions were carried out in a custom-designed photoreactor.[1] It features 10 circularly arranged blue LEDs, mounted on copper heat sinks, which surround the central reaction vessel holder (see left picture).[2] The reactor is air cooled with four fans (see picture right) and water cooled. Fresh cold water is continuously provided to the reactor. The blue LEDs (manufacturing number: SBR-70-B-R75-KG300; manufacturer: Luminus) were bought from Mouser Electronics.



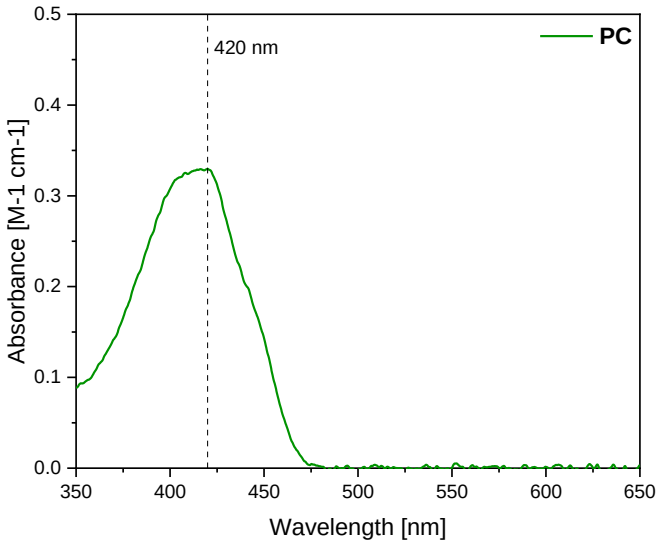

The emission spectrum of the blue LED reactor shows a maximum intensity at a wavelength of $\lambda_{max,\ emission}$ = 446 nm.[2]

It is worth noting that the reaction of diethyl bromomalonate **1a** with pentenoic acid **2a** could also be conducted with a Kessil PR160L-440nm light (intensity set to 100, distance from reaction vessel to light source 5 cm) in identical yield.

[1] Jelier, B. J.; Tripet, P. F.; Pietrasiak, E.; Franzoni, I.; Jeschke, G.; Togni, A., Radical Trifluoromethoxylation of Arenes Triggered by a Visible-Light-Mediated N−O Bond Redox Fragmentation. *Angew. Chem. Int. Ed.* **2018**, *57*, 13784-13789.
[2] Fischer, D. M.; Lindner H; Amberg; W. M.; Carreira; E. M., Intermolecular Organophotocatalytic Cyclopropanation of Unactivated Olefins. *J. Am. Chem. Soc*. **2023**, *145*, 2, 774–780.

3. UV-Vis Spectrum of PC

UV-Vis spectrum of **PC** was measured for a 12 µM solution to determine $\lambda_{max,\ absorption}$ and the extinction coefficient at 446 nm (446 nm is the emission maximum of the blue LEDs).



Photocatalyst (12 µM)	$\lambda_{max,\ absorbance}$
PC	420 nm

The extinction coefficient ε at 446 nm was calculated according to the Lambert-Beer law

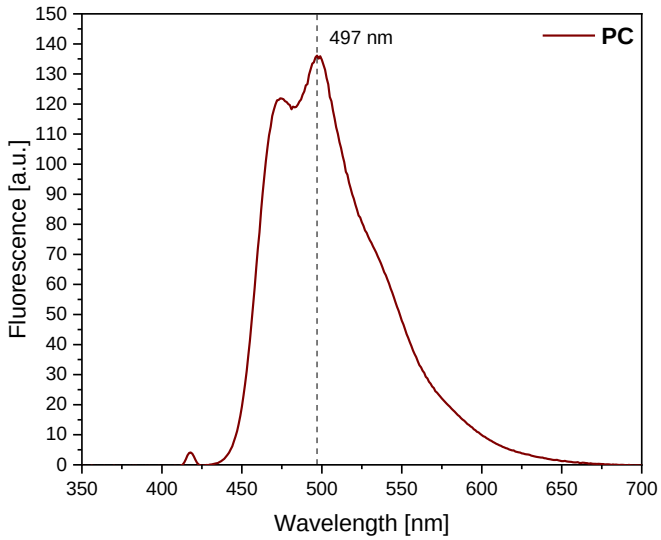
$$\varepsilon_\lambda = \frac{A_\lambda}{c \cdot d}$$

With d = 1.000 cm and c = $12.00 \cdot 10^{-6}$ M

Photocatalyst (12 µM)	Absorbance at 446 nm	$\varepsilon_{446\ nm}$
PC	0.16931	14109 $M^{-1}cm^{-1}$

4. Fluorescence Spectrum of PC

To measure the fluorescence spectrum of **PC**, a 12 µM solution in degassed CH_2Cl_2 was prepared. The solution was excited at $\lambda_{max,\ absorbance}$ of the photocatalysts (*vide supra*). The resulting fluorescence spectrum is shown below



Photocatalyst (12 µM)	**$\lambda_{max,\ fluorescence}$**
PC	497.0 nm

5. Stern-Volmer Relationship Studies

For fluorescence quenching studies, CH_2Cl_2 was degassed with argon for 30 min while sonicating. For a typical measurement, a 24.00 µM solution of **PC** in 5 mL CH_2Cl_2 was added to the appropriate amount of quencher. Different amounts of 2,6-lutidine, bromomalonate **1a**, bromoacetophenone **1l**, pentenoic acid **2a**, methyl ester, pentenol or alcohol **2n**, resulted in the concentrations indicated in the table below. The solutions were stored under exclusion of light.

Solution	1	2	3	4	5
2,6-Lutidine	0.0135 M	0.0263 M	0.0403 M	0.0537 M	0.0660 M
1a	0.0136 M	0.0268 M	0.0408 M	0.0535 M	0.0679 M
1l	0.0136 M	0.0267 M	0.0402 M	0.0534 M	0.0671 M
2a	0.0132 M	0.0268 M	0.0406 M	0.0535 M	0.0667 M
methyl ester	0.0137 M	0.0267 M	0.0406 M	0.0534 M	0.0666 M
pentenol	0.0135 M	0.0262 M	0.0404M	0.0534 M	0.0666 M
2n	0.0135 M	0.0265 M	0.0403 M	0.0536 M	0.0670 M

The measurements were conducted in a dark room. Solutions were transferred to a screw-top quartz cuvette (d = 1.000 cm) and irradiated at $\lambda_{max,\ absorbance}$. The fluorescence spectrum of the sample was recorded.

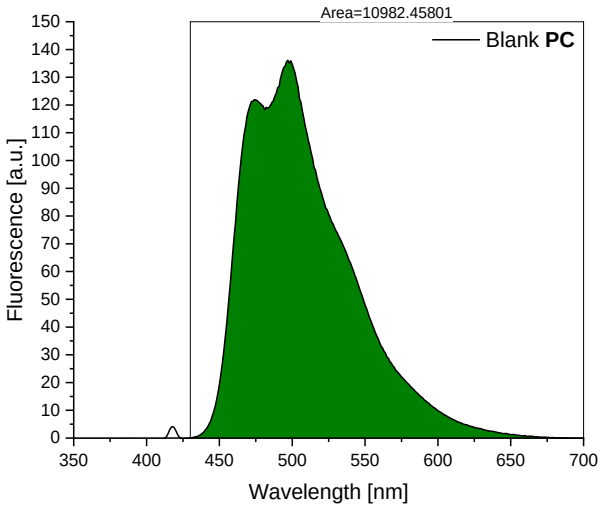
Prior to each compound series, a blank measurement containing only 24.00 µM **PC** in 5 mL CH_2Cl_2 was recorded. For data analysis the area below the curve described by the normalized fluorescence intensity was integrated from 430 nm to 700 nm.

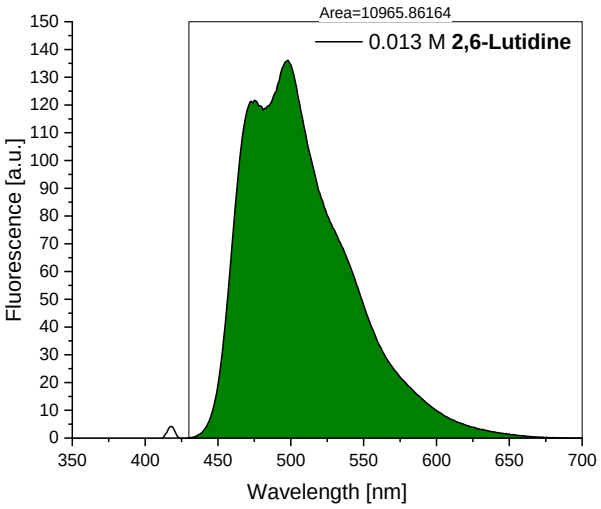
Tabular listing of the integrals of the examined substrates

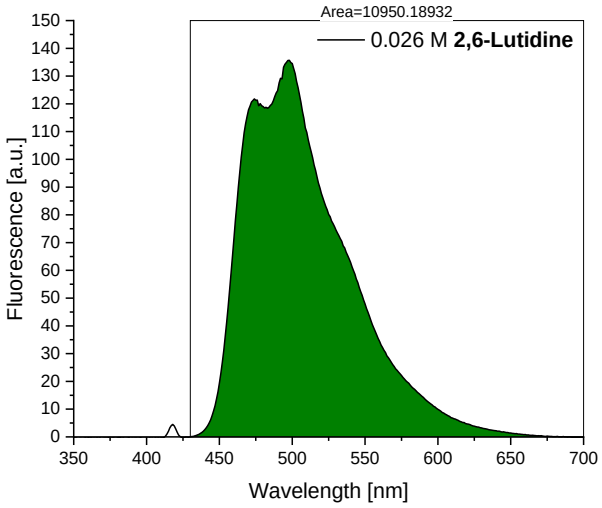
Sample No.	2,6-Lutidine	1a	1l	2a
0	10982	11075	11821	10939
1	10986	10926	9225.0	10649
2	10950	10667	7687.4	10401
3	11039	10576	6076.1	10155
4	10830	10501	5420.4	9932.0
5	10928	10242	4258.8	9721.0

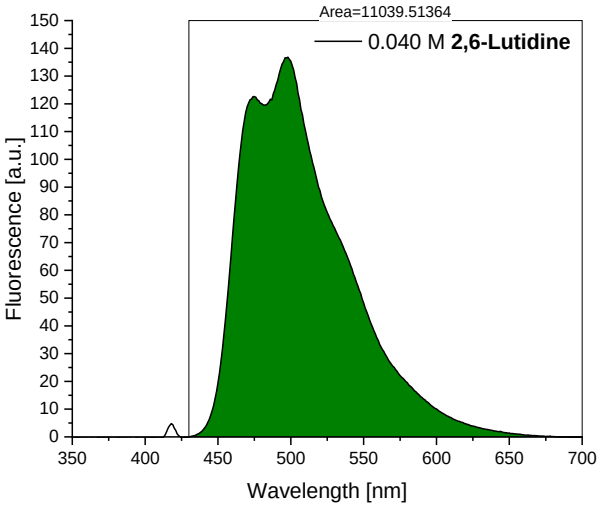
Sample No.	methyl ester	pentenol	2n
0	10669	11025	10786
1	10793	11000	11007
2	10768	10946	10896
3	10767	10940	10873
4	10760	10902	10821
5	10722	10802	10665

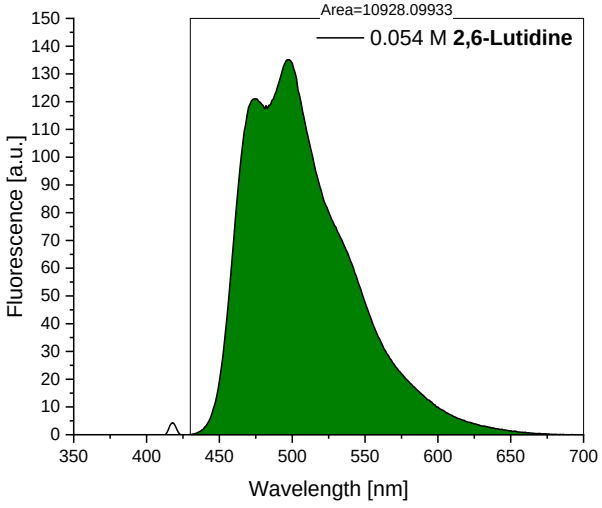
Fluorescence Spectra and Integrated Area for 2,6-Lutidine

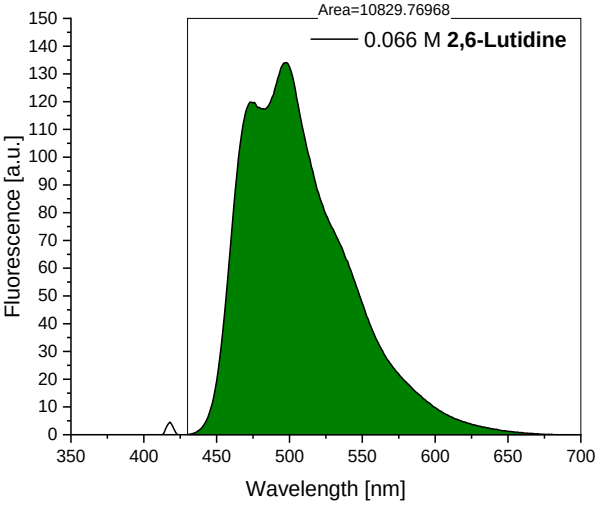




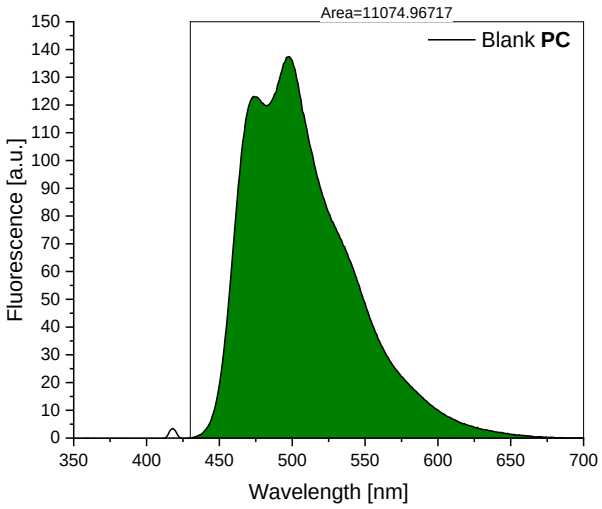


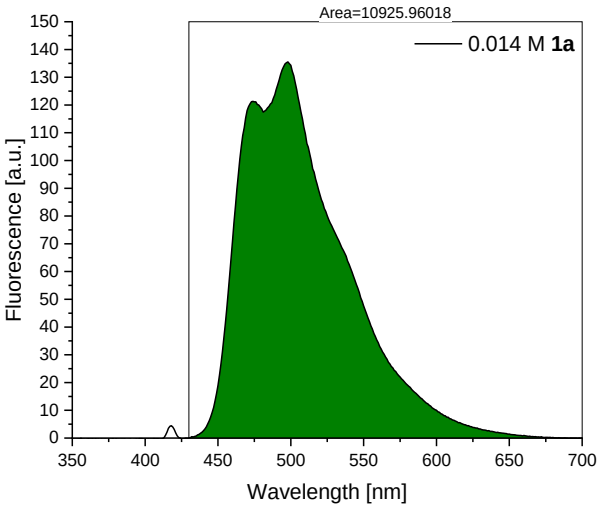


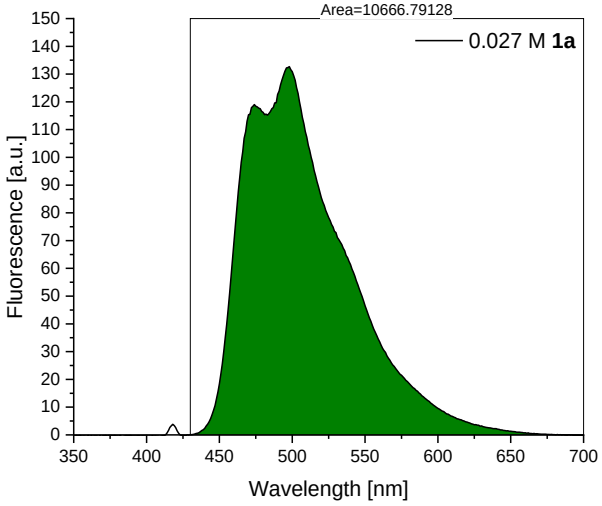


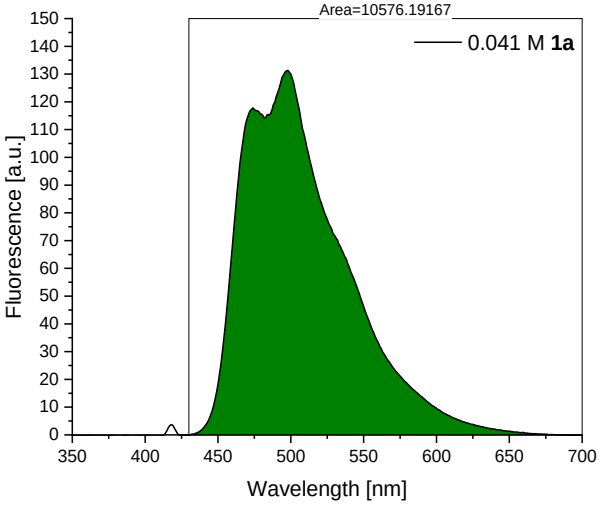


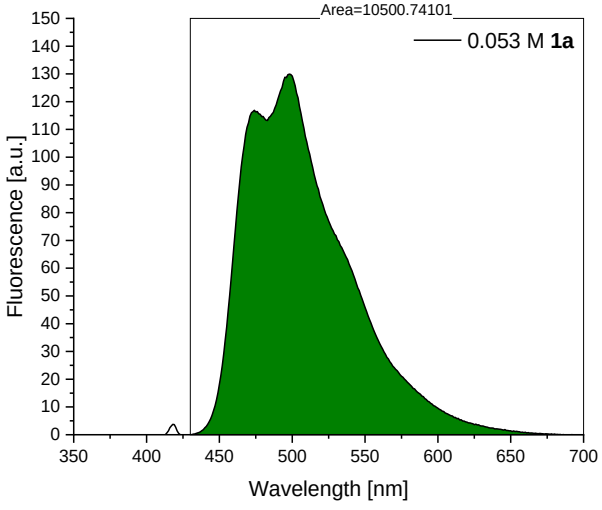
Fluorescence Spectra and Integrated Area for Bromomalonate 1a

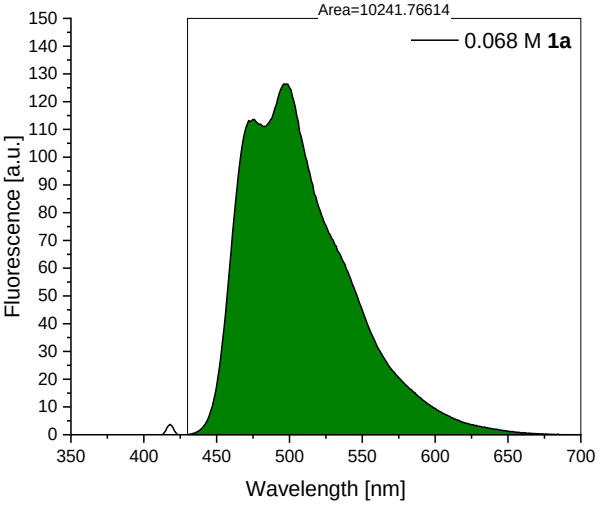




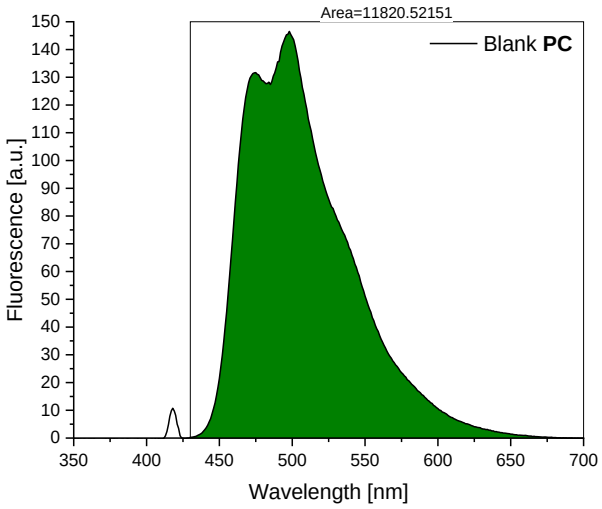


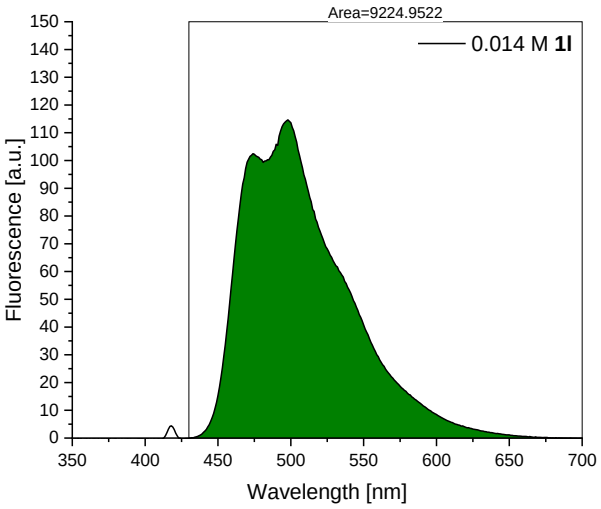


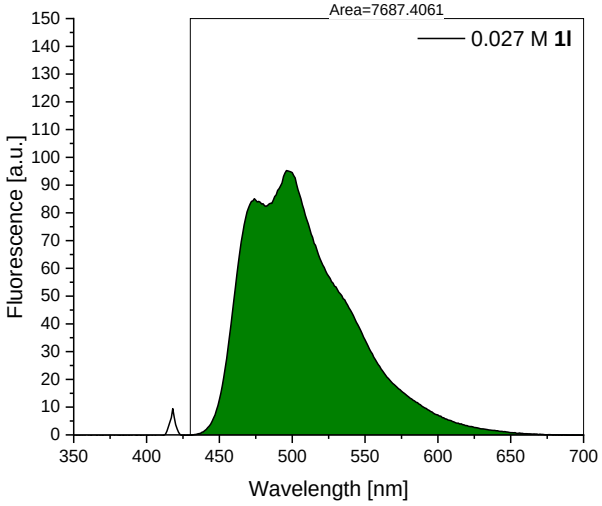


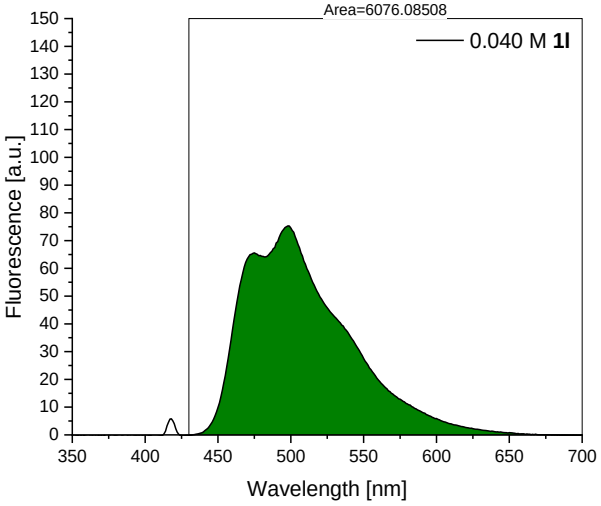


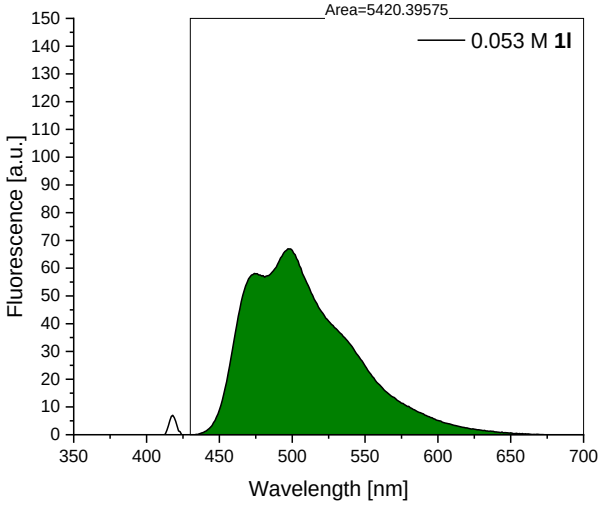
Fluorescence Spectra and Integrated Area for Bromoacetophenone 1l

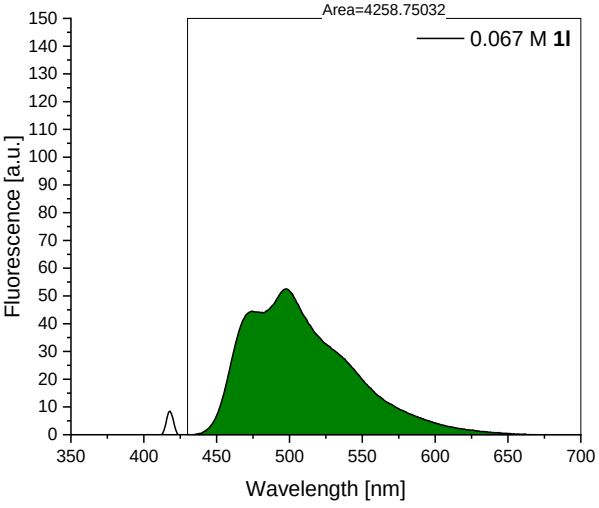




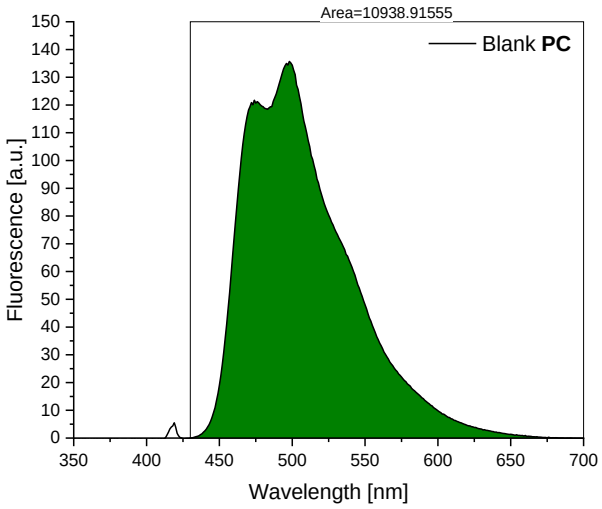


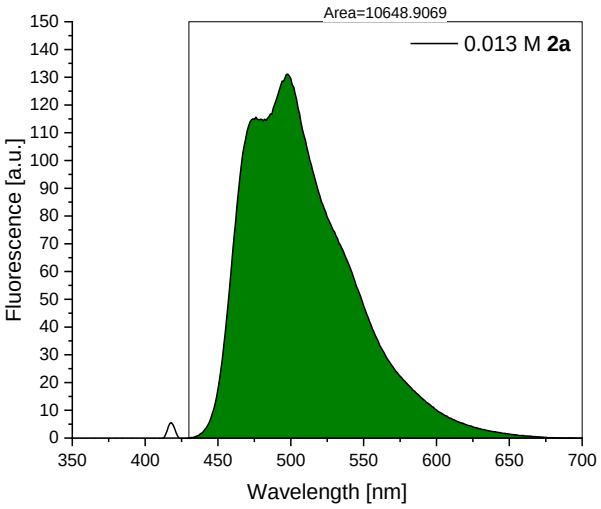


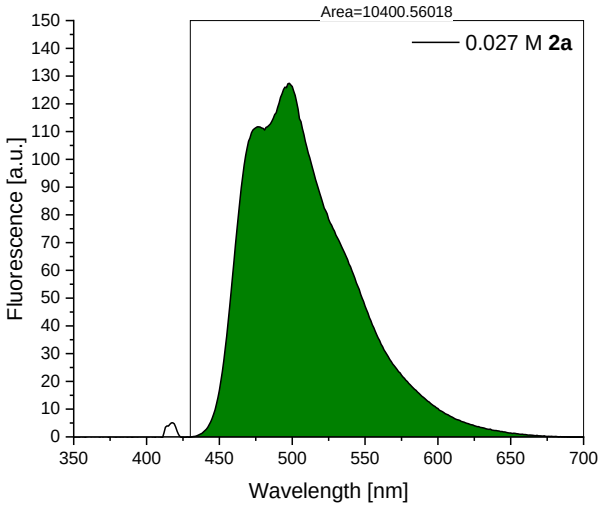


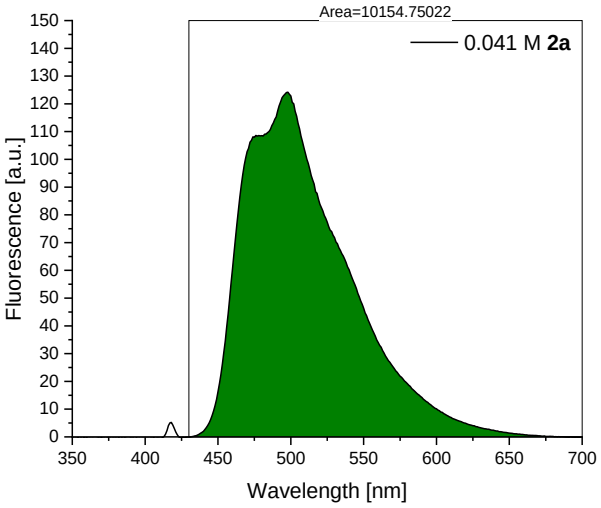


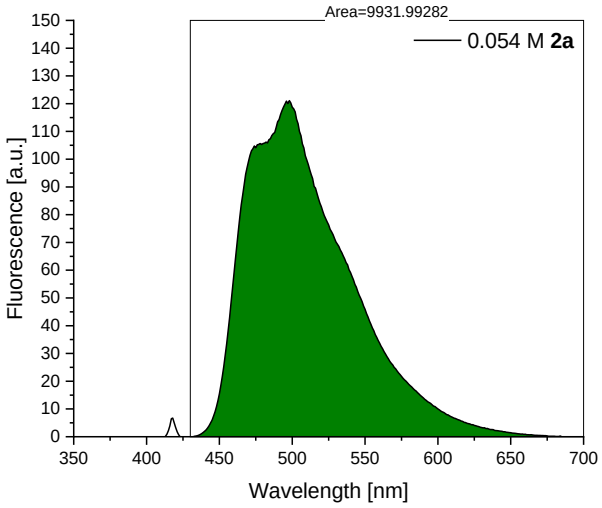
Fluorescence Spectra and Integrated Area for Pentenoic Acid 2a

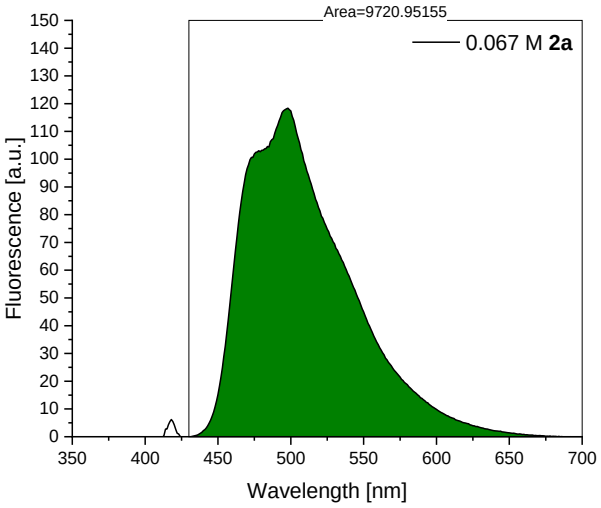




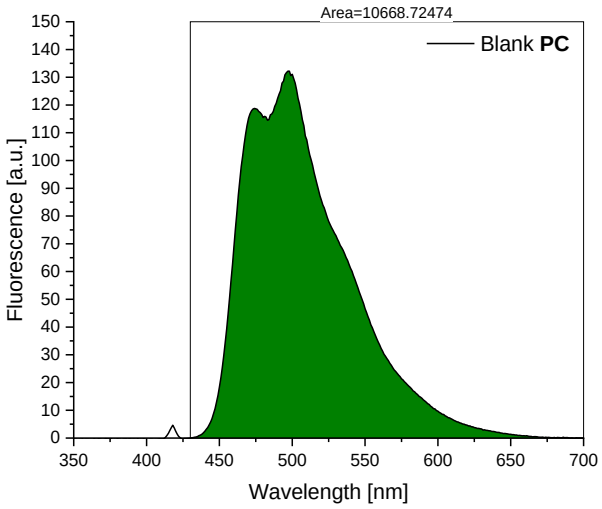


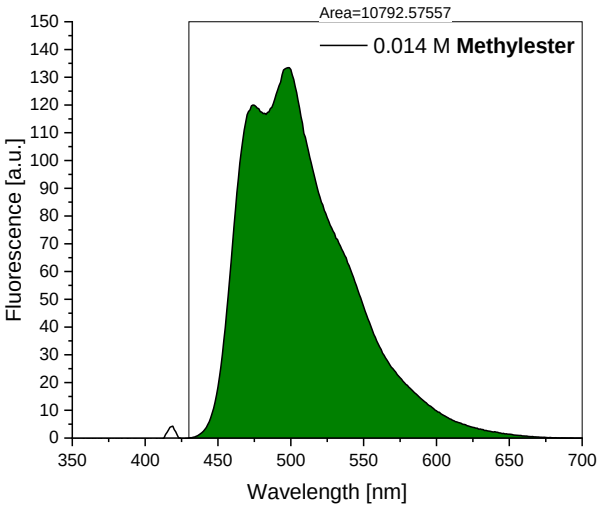


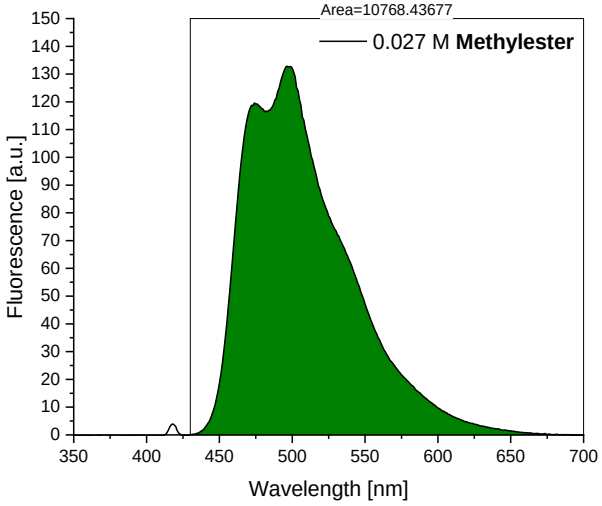


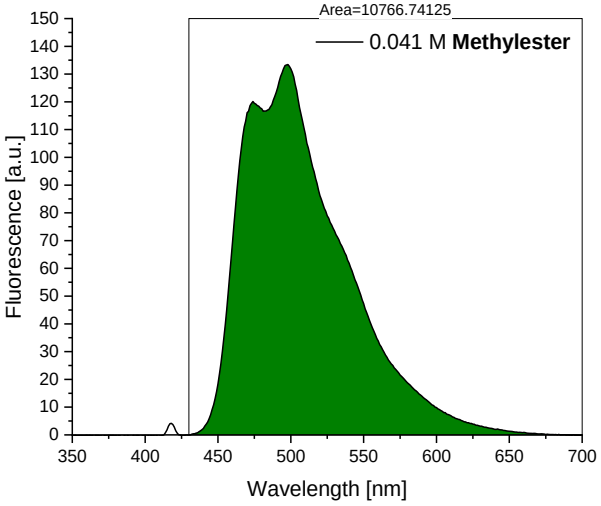


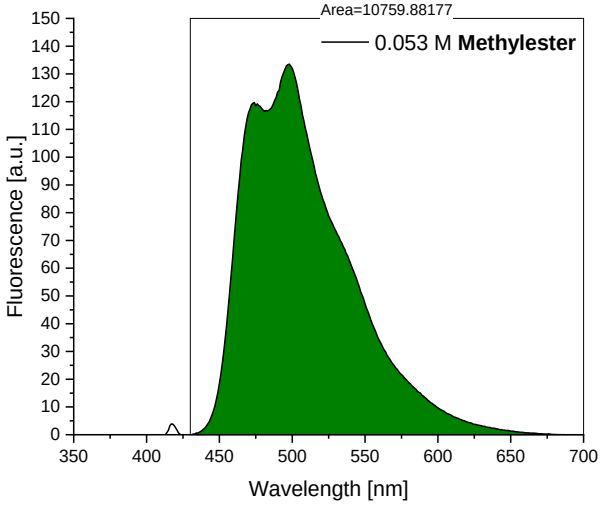
Fluorescence Spectra and Integrated Area for Hexenoic Acid Methyl Ester

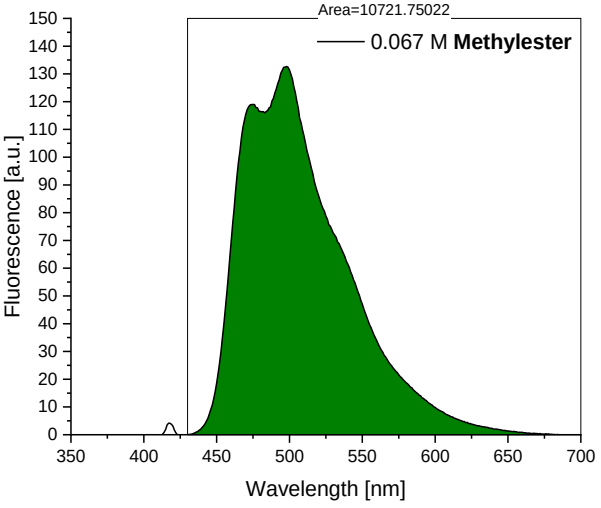




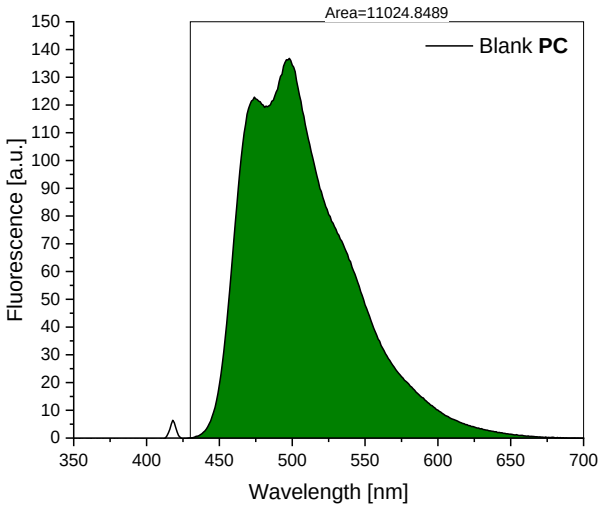


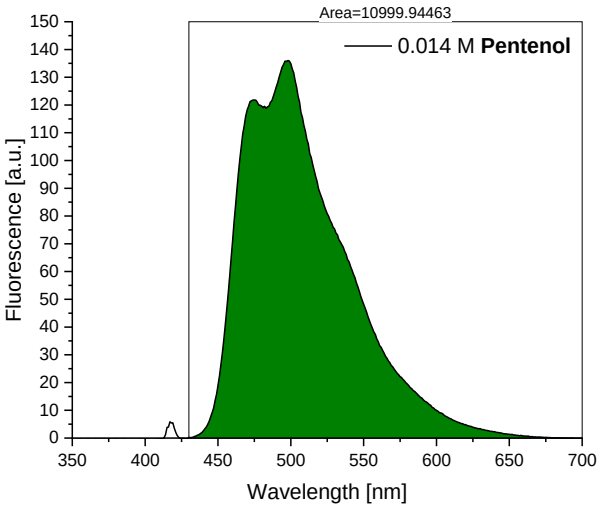


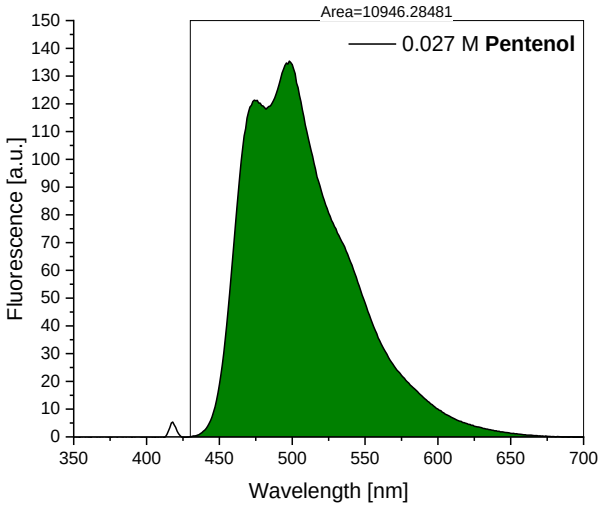


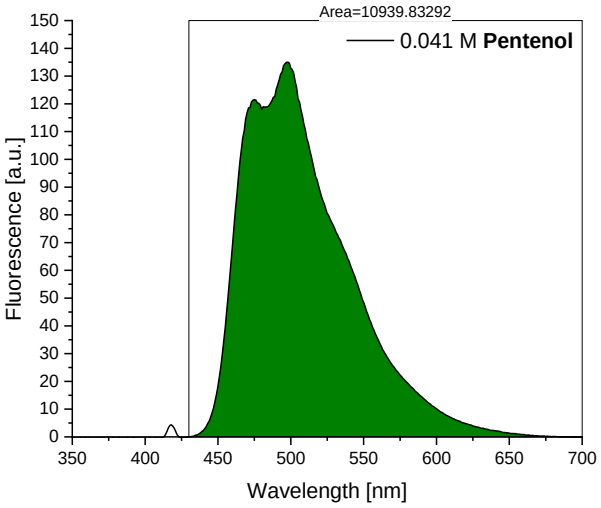


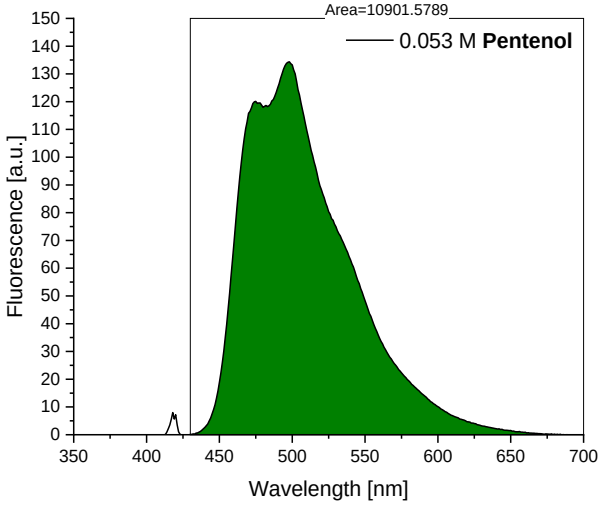
Fluorescence Spectra and Integrated Area for Pent-4-enol

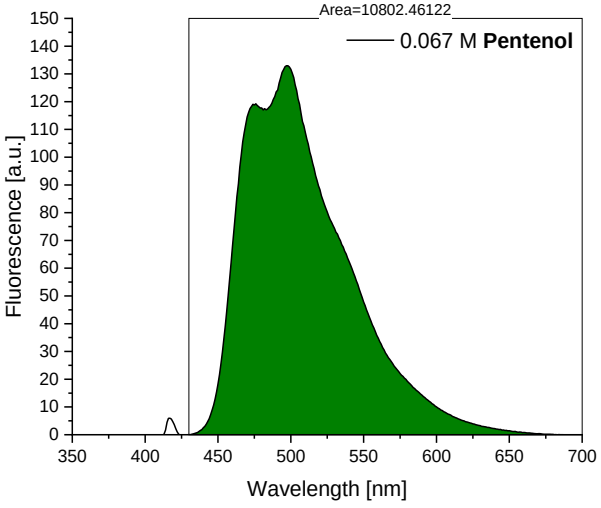




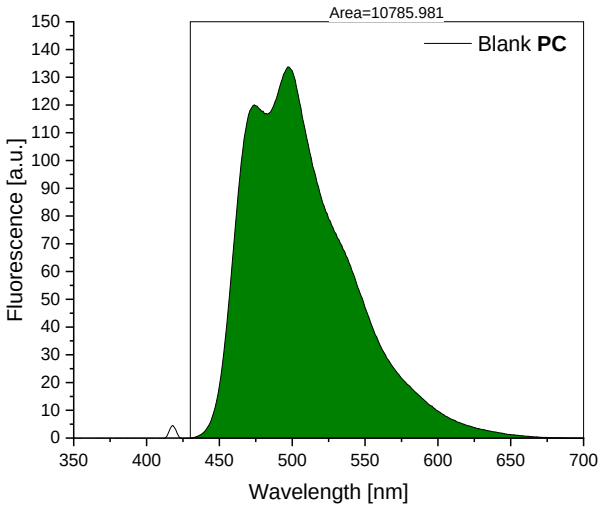


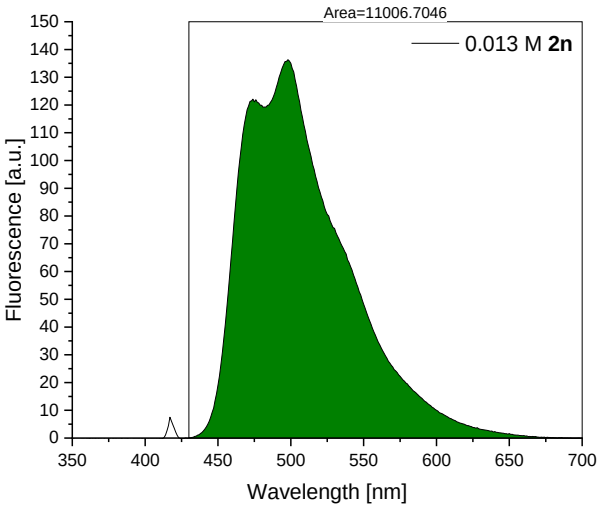


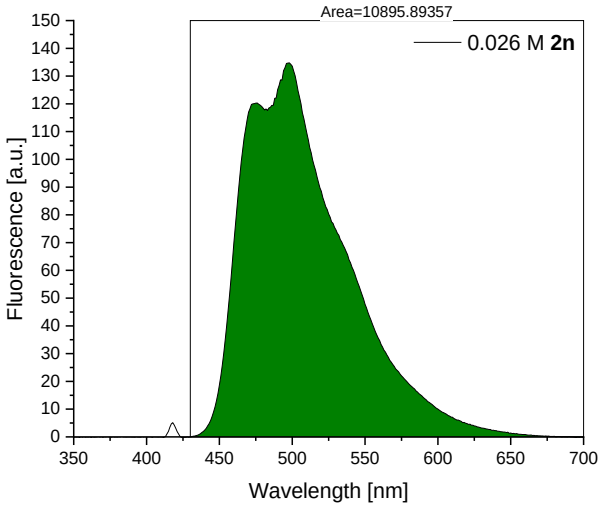


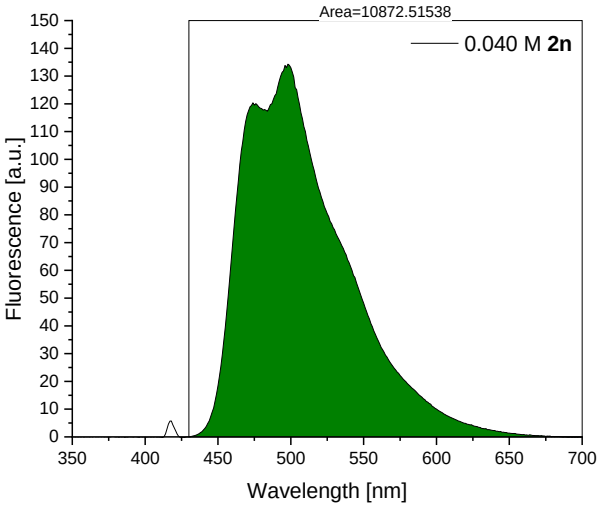


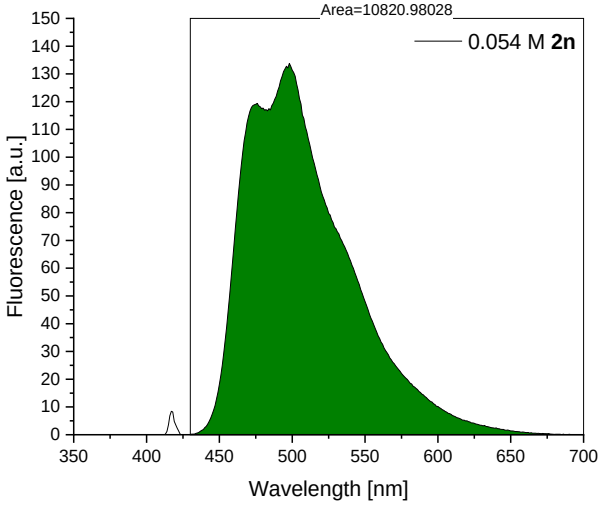
Fluorescence Spectra and Integrated Area for Alcohol 2n

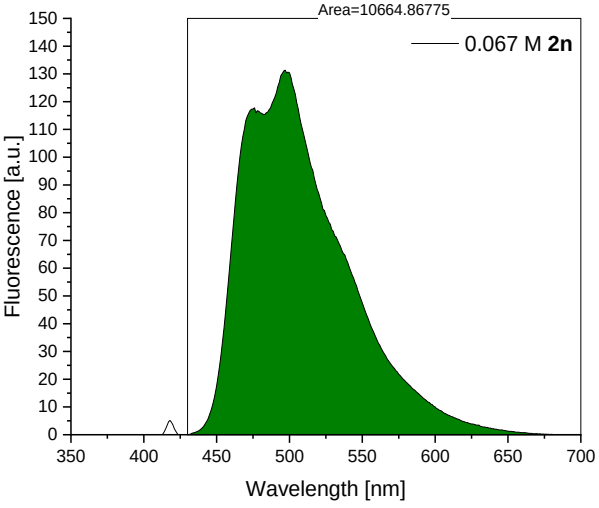








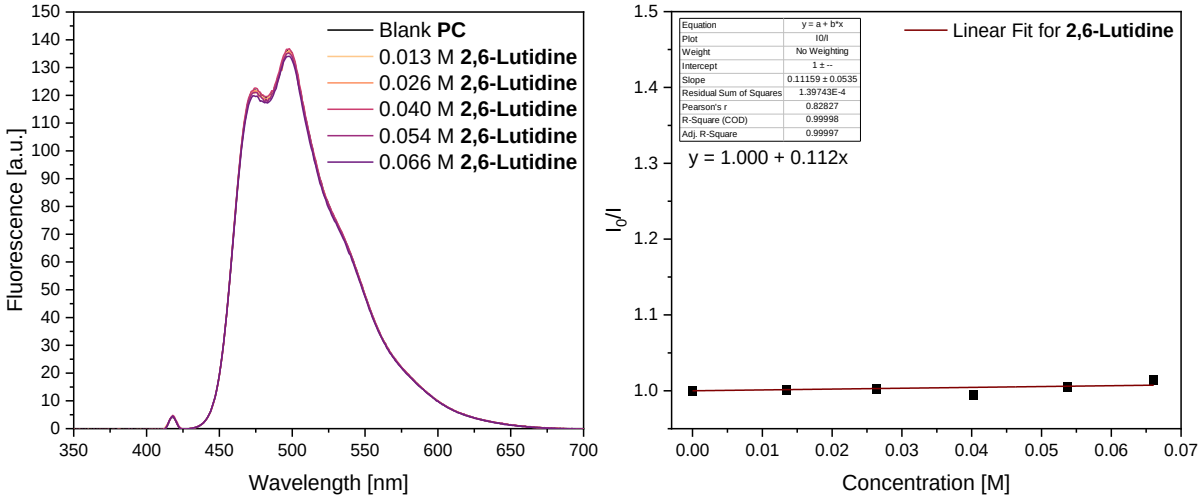




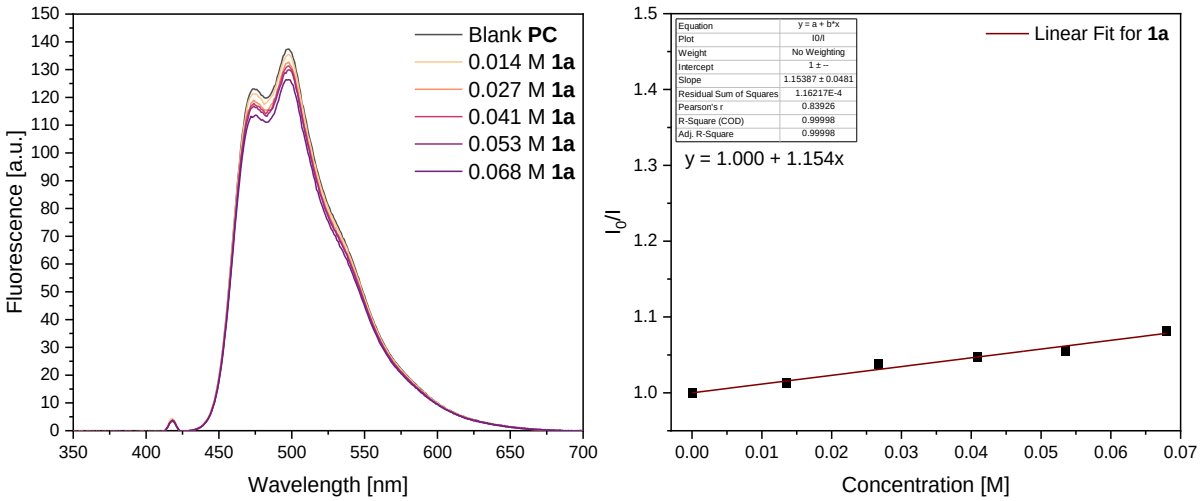
For Stern-Volmer relationship plots, the integral of the corresponding blank I_0 (sample 0) was divided by the integral I of samples 1-5 containing quencher in different concentrations. The result was plotted against the concentration of the samples. Both bromides (bromomalonate **1a** and bromoacetophenone **1l**) showed significant quenching of the photocatalyst exited state. No correlation between fluorescence and concentration of the quencher could be observed for 2,6-Lutidine or alcohol **2n** and photocatalyst fluorescence.

However, pent-4-enoic acid also displayed quenching of the exited state. To assess whether the olefin or the carboxylic acid functionality of pent-4-enoic acid effects quenching of **PC***, we investigated pent-4-enol and the 5-hexenoic acid methyl ester. Both compounds did not quench the exited state of **PC**. This observation led us to conclude that the acid functionality in pent-4-enoic acid is responsible for the quenching of the **PC***.

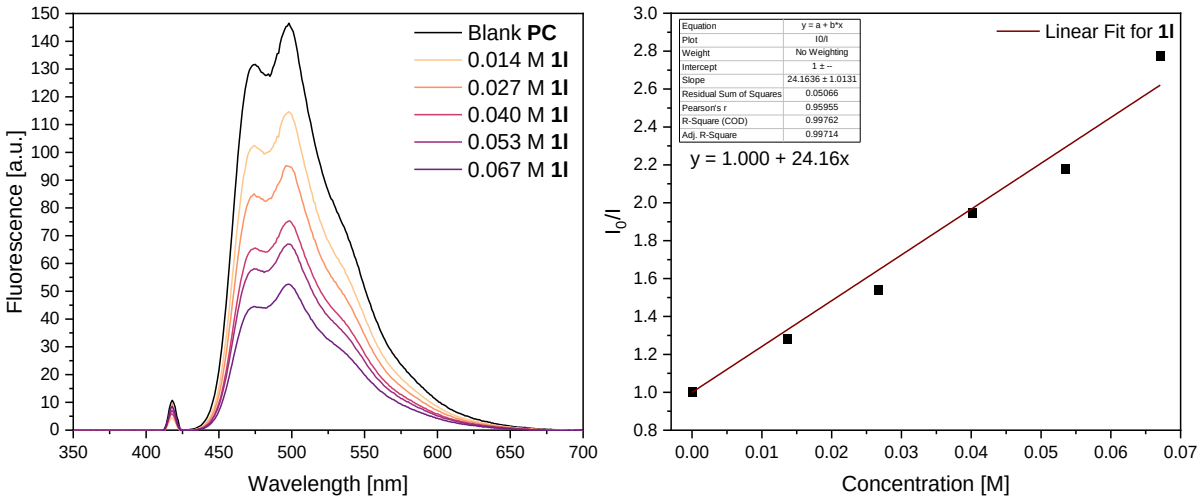
Stern-Volmer Relationship for 2,6-Lutidine



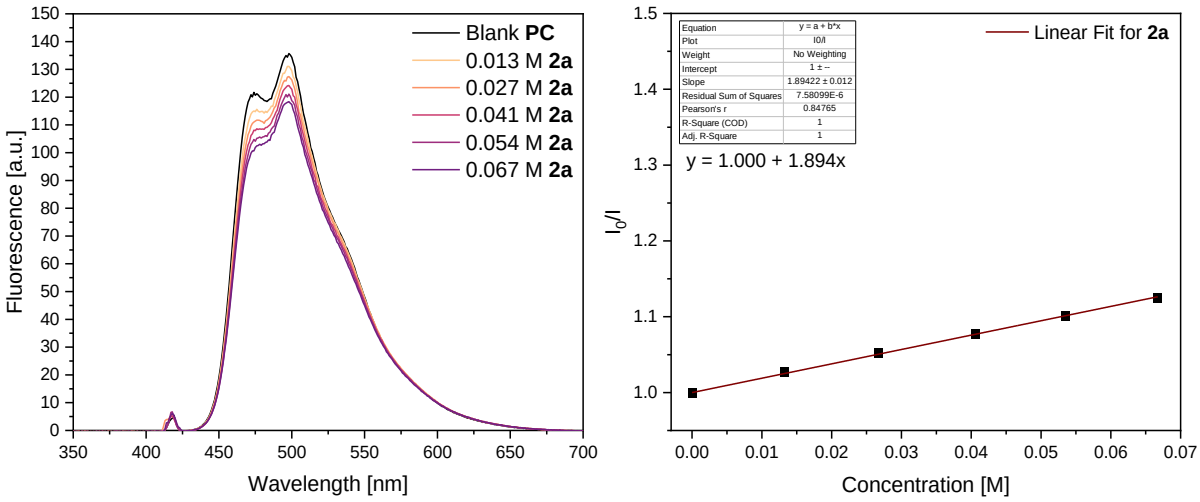
Stern-Volmer Relationship for Bromomalonate 1a



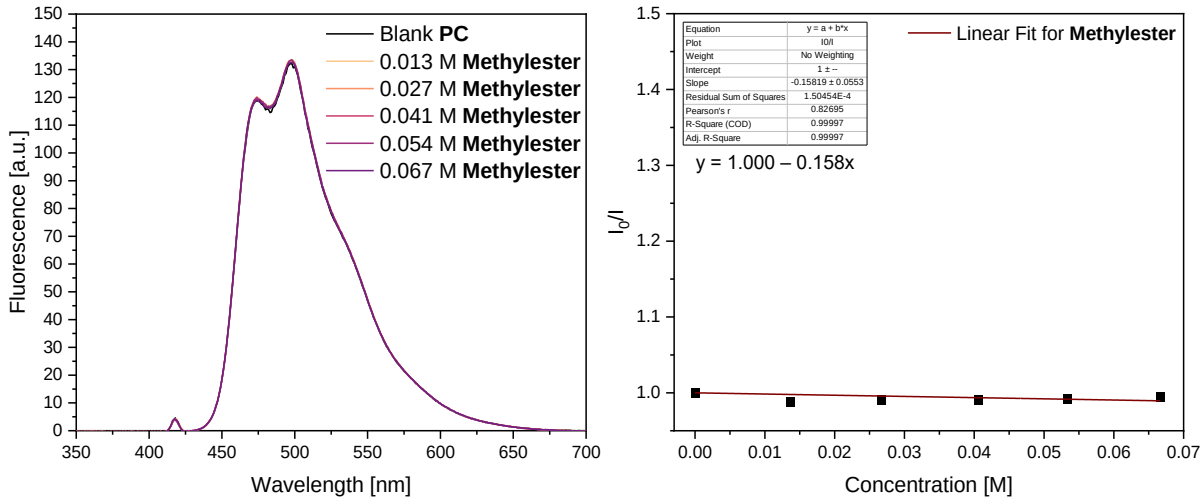
Stern-Volmer Relationship for Bromoacetophenone 1l



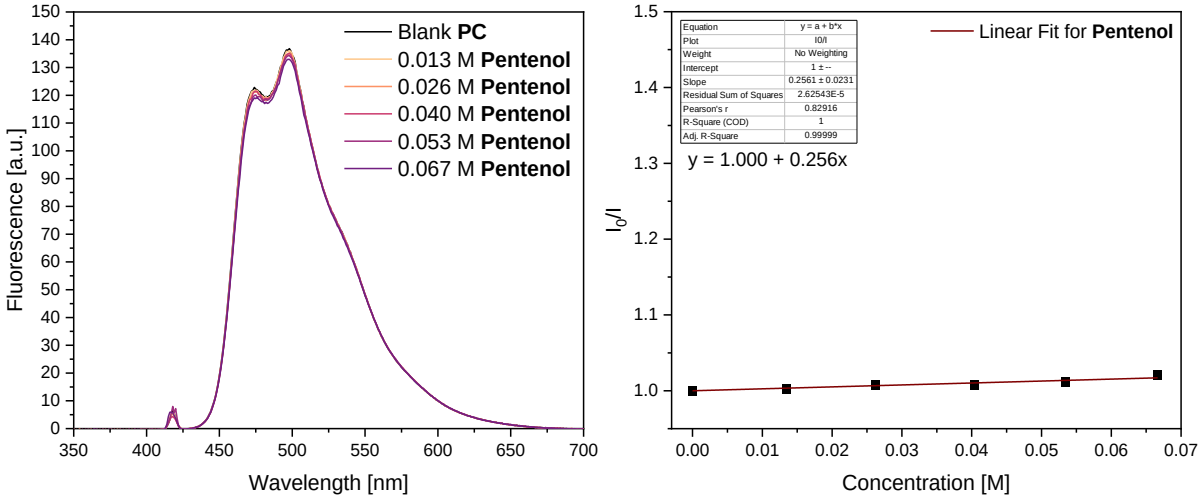
Stern-Volmer Relationship for 4-Pentenoic acid 2a



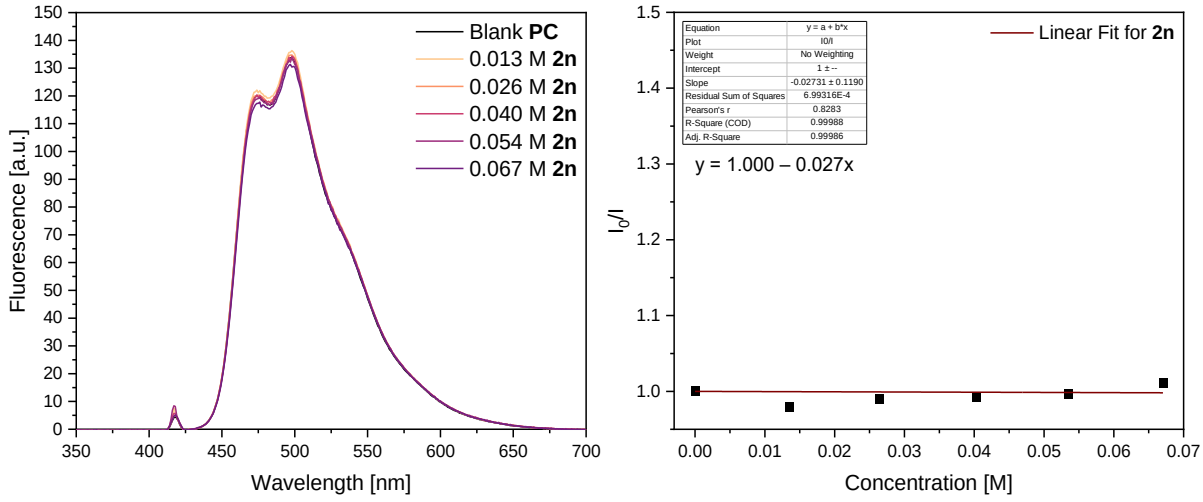
Stern-Volmer Relationship for Methylester



Stern-Volmer Relationship for Pentenol



Stern-Volmer Relationship for Cyclobutanol 2n



6. Quantum Yield

The Quantum yield was determined according to literature.[3]

To determine the phot flux of the light source, Hatchard-Parker ferrioxalate actinometry was carried out as previously described.[4] The photon flux was calculated as the average of the photon flux at 4 different times (each carried out in duplicate) to be 9.12 × 10^{-7} Einstein s^{-1}.

Determination of quantum yield of the heterofuntionalisation reaction.

To a glass crimp vial charged with **PC** (1.6 mg, 0.0050 mmol, 0.50 mol%), under argon atmosphere (three exchange cycles) was added pent-4-enoic acid (1.0 mmol) CH_2Cl_2 (2.5 mL, 0.4 M, degassed), 2,6-lutidine (500 µL, 4.0 mmol, 4 equiv, degassed) and dimethyl bromomalonate (250 µL, 1.5 mmol, 1.5 equiv). The reaction mixture was degassed by bubbling with Ar for 10 min while cooling (ice-bath). The vial was placed 15 mm away from a blue LED (40 W, λ_{max} = 440 nm) and vertically irradiated through an aperture (⌀ 6.0 mm) for 45 minutes. 140 µL 1,3,5-mesitylene (1.00 mmol, 1.00 equiv) were added as internal standard and an aliquot analyzed by ^{1}H NMR. After 45 minutes the reaction showed 20% conversion to products (bromide **5** and **3a**).

The quantum yield was calculated as:

$$\Phi = \frac{\text{mol product}}{f \cdot t \cdot f}$$

where *f* is the photon flux previously determined by ferrioxalate actinometry, t is the time (2700 s), and f is the fraction of light absorbed by the photocatalyst at 446 nm. The absorbance of **PC** at 446 nm is >3 indicating the fraction of light absorbed f is >0.999.[2c] The quantum yield of the reaction was thus determined to be:

$$\mathbf{\Phi = 0.0812}$$

[3] S. L. Rössler, B. J. Jelier, P. F. Tripet, A. Shemet, G. Jeschke, A. Togni and E. M. Carreira, Pyridyl Radical Cation for C−H Amination of Arenes. *Angew. Chem. Int. Ed.* **2019,** *58*, 526-531.
[4] C. G. Hatchard, C. A. Parker and E. J. Bowen, A new sensitive chemical actinometer - II. Potassium ferrioxalate as a standard chemical actinometer. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1956,** *235*, 518-536, H. Kuhn, S. Braslavsky and R. Schmidt, Chemical actinometry (IUPAC technical report). *Pure and Applied Chemistry* **2004,** *76*, 2105-2146, D. M. Fischer, H. Lindner, W. M. Amberg and E. M. Carreira, Intermolecular Organophotocatalytic Cyclopropanation of Unactivated Olefins. *J. Am. Chem. Soc.* **2023,** *145*, 774-780.

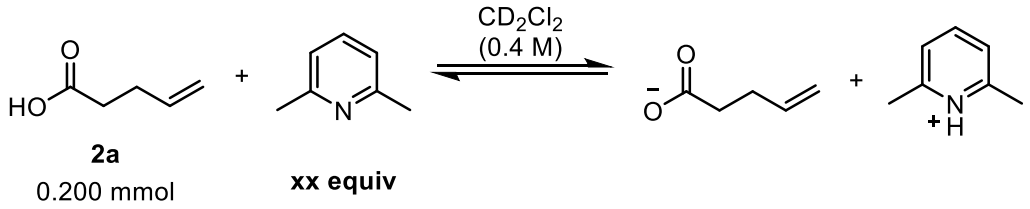
7. Time Series Experiment

To determine the time course of the reaction a times series was set up as follows:
To a glass vial charged with **PC** (0.33 mg, 0.0010 mmol, 0.50 mol%) in CH_2Cl_2 (500 µL, 0.4 M) were added 4-pentenoic acid (20.4 µL, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv) diethyl bromomalonate (51.2 µL, 71.6 mg, 0.300 mmol, 1.50 equiv) sequentially. The vial was equipped with a magnetic stirrer bar and capped with a screwcap. The reaction was irradiated in a 350 W photoreactor (*vide supra*) for the indicated time and quenched by addition of aq HCl (4 M, 0.3 mL, 1.2 mmol, 6.00 equiv). The reaction mixture was diluted with approximately 1 mL deuterated chloroform and 27.8 µL 1,3,5-mesitylene (24.0 mg, 0.200 mmol, 1.00 equiv) were added as internal standard. Reactions were analyzed by removing a 0.6 mL aliquot of solution. The data are given as relative amounts (%, average of two runs).

Time [min]	**2a** [%]	**5** [%]	**3a** [%]
0.5	97	3	0
1	93	7	0
2	81	19	0
3	55	45	0
4	38	60	2
5	22	76	3
10	8	84	8
15	5	83	12
30	0	69	31
45	0	57	43
60	0	48	52
120	0	23	77
180	0	9	91
240	0	2	98

8. Deprotonation Study

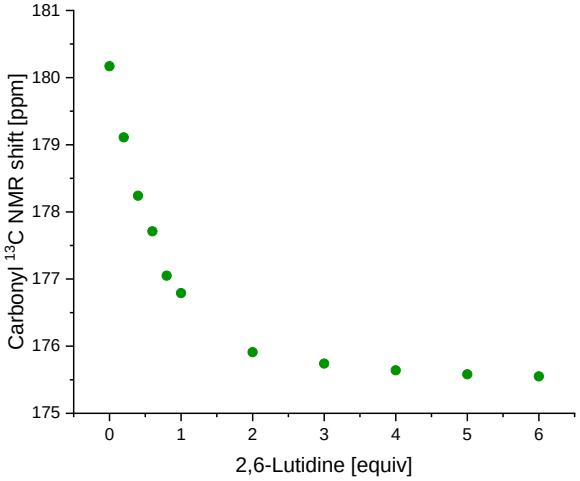
To determine the degree of deprotonation under the reaction conditions solutions of **2a** in the presence of varying amounts of 2,6-lutidine were prepared and ^{13}C and ^{1}H NMR spectra recorded. Only a single species was observed in all cases, suggesting rapid proton exchange. The signal at 180.17 ppm in the ^{13}C NMR, corresponding to the carboxylic acid carbon showed a concentration-dependent upfield shift.



2a
0.200 mmol

xx equiv

Entry	2,6-Lutidine [equiv]	^{13}C carbonyl [ppm]	^{13}C alkene [ppm]
1	0.00	180.17	115.92
2	0.20	179.11	115.74
3	0.40	178.24	115.59
4	0.60	177.71	115.51
5	0.80	177.05	115.43
6	1.00	176.79	115.39
7	2.00	175.91	115.28
8	3.00	175.74	115.27
9	4.00	175.64	115.26
10	5.00	175.58	115.26
11	6.00	175.55	115.26



For comparison the ^{13}C NMR spectrum of methyl pentenoate was recorded in the presence of different amounts of 2,6-lutidine.

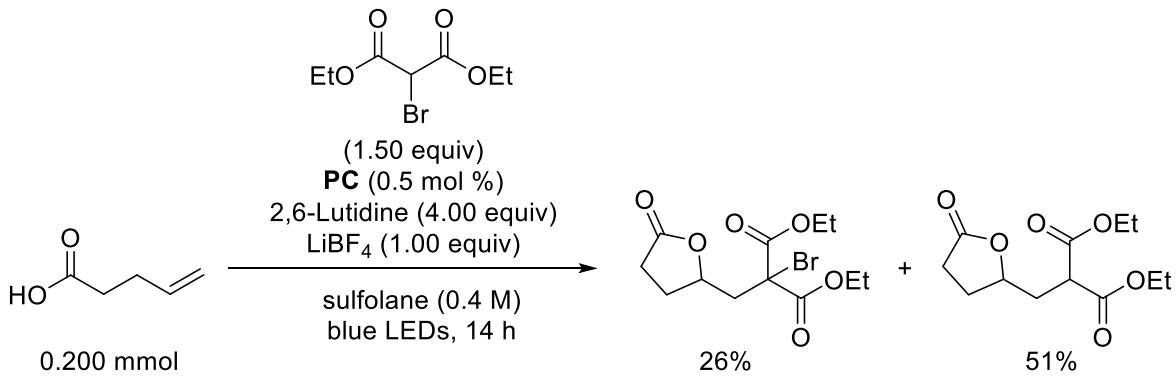
Entry	2,6-Lutidine [equiv]	^{13}C carbonyl [ppm]	^{13}C alkene [ppm]
1	0	173.79	115.92
2	1	173.77	115.74
3	2	173.75	115.59
4	4	173.70	115.51

9. Optimization Studies

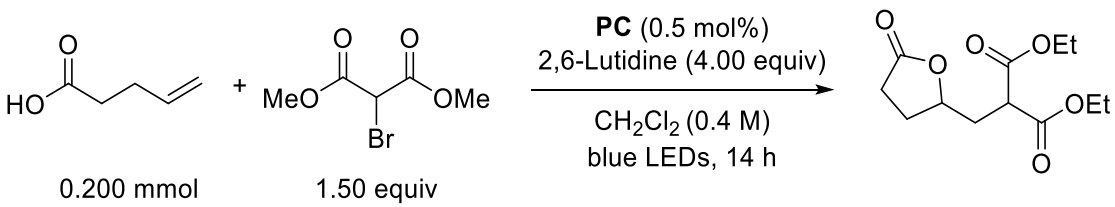
Example of procedure for optimization

To a glass vial charged with **PC** (0.33 mg, 0.0010 mmol, 0.50 mol%) in CH_2Cl_2 (500 µL, 0.4 M) were added pent-4-enoic acid (20.4 µL, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv) and diethyl bromomalonate (51.2 µL, 71.6 mg, 0.300 mmol, 1.50 equiv) sequentially. The vial was equipped with a magnetic stirrer bar and capped with a screwcap. The reaction was irradiated in a 350 W photoreactor (*vide supra*) for the indicated time. The reaction mixture was diluted with approximately 1 mL deuterated chloroform and 27.8 µL 1,3,5-mesitylene (24.0 mg, 0.200 mmol, 1.00 equiv) were added as internal standard. Reactions were analyzed by removing a 0.6 mL aliquot of solution. The above procedure was modified as necessary to investigate the desired variables.

Initial Conditions



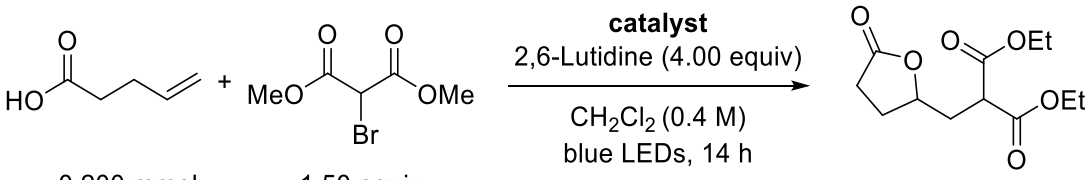
Control Experiments



0.200 mmol 1.50 equiv

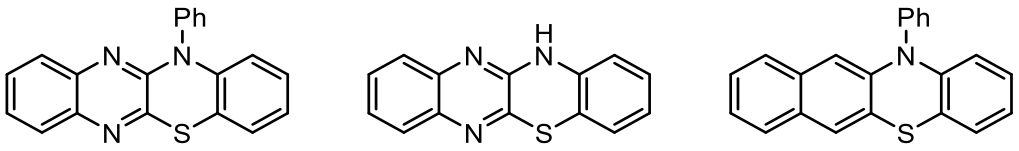
Entry	Change	Product [%]	SM [%]
1	none	93	0
2	no base	6	0
3	no **PC**	0	93
4	in the dark, 40°C	0	90
5	no bromomalonate	0	94
6	under Ar, degassed	90	0

Effect of Catalyst and Catalyst Loading



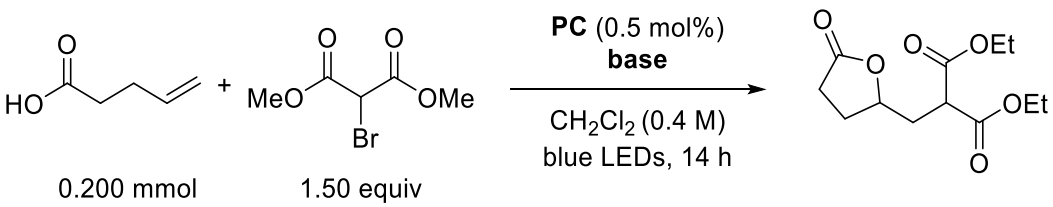
0.200 mmol 1.50 equiv

Entry	Catalyst	Equiv [mol%]	Product [%]
1	**PC**	0.10	81
2	**PC**	0.50	91
3	**PC**	5.0	82
4	**PC-2**	0.50	80
5	**PC-3**	0.50	83



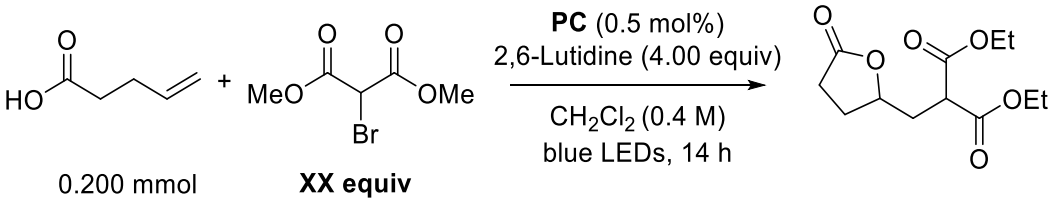
PC **PC-2** **PC-3**

Effect of Base



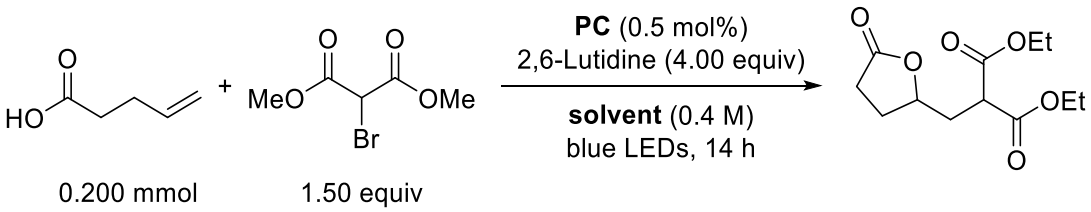
Entry	Base	Equiv	Product [%]	SM [%]
1	2,6-lutidine	1.00	82	0
2	2,6-lutidine	2.00	86	0
3	2,6-lutidine	4.00	92	0
4	2,6-lutidine	8.00	85	0
5	Pyridine	4.00	59	18
6	Et_3N	4.00	0	80
7	DIPEA	4.00	0	75

Effect of Malonate Equivalents



Entry	Equiv	Product [%]	SM [%]
1	1.00	81	0
2	1.50	91	0
3	2.00	86	0
4	4.00	78	0

Effect of Solvent



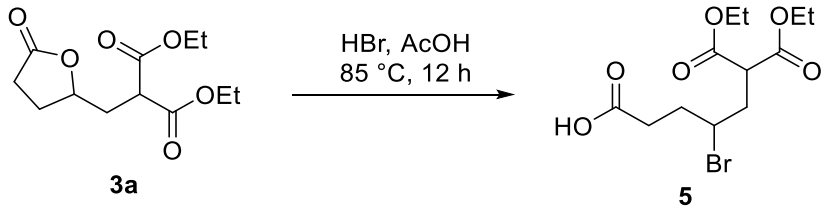
0.200 mmol 1.50 equiv

Entry	Solvent	Product [%]	SM [%]	Bromide 5 [%]
1	MeCN	75	0	12
2	sulfolane	82	0	0
3	CH_2Cl_2	93	0	0
4	DMF	55	0	0
5	*i*-PrOH	60	0	22
6	EtOAc	56	0	25
7	PhMe	66	0	20
8	DCE	81	0	0

10. Investigation of Intermediates

Compound 5:

4-bromo-6-(ethoxycarbonyl)-7-oxooctanoic acid



A solution of lactone **3a** (51.6 mg, 0.2 mmol, 1.00 eq.) in HBr (33% in acetic acid, 2 mL) was heated to 85 °C for 12 h. Upon complete consumption of starting material (TLC) the mixture was cooled to room temperature, diluted with H_2O (5 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified via column chromatography (0-50% EtOAc in hexane) to give **5** as a pale-yellow oil.

Yield: 36.2 mg, 1.17 mmol, 59%

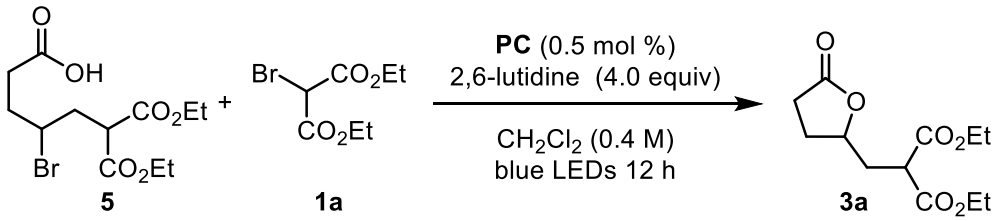
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.29 – 4.15 (m, 4H), 4.06 (ddt, J = 10.5, 9.4, 3.6 Hz, 1H), 3.76 (dd, J = 10.0, 4.5 Hz, 1H), 2.73 – 2.41 (m, 3H), 2.37 – 2.17 (m, 2H), 2.15 – 2.03 (m, 1H), 1.28 (td, J = 7.1, 2.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 178.0, 168.9, 168.8, 62.0, 61.9, 53.3, 50.6, 38.0, 34.0, 32.0, 14.2, 14.2.

IR (thin film, cm^{-1}): 2983, 1732, 1370,1154.

HRMS (ESI+): *m/z* for $C_{12}H_{19}BrNaO_6$ $[M+Na]^+$: calc.: 361.0257, found: 361.0259.

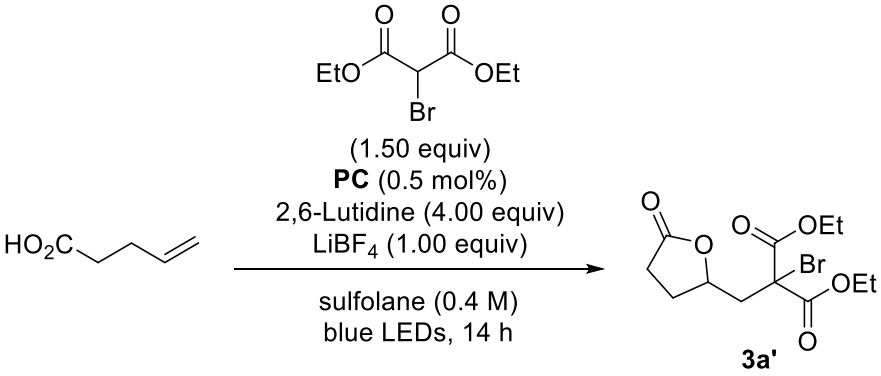
To investigate the role of potential intermediate **5** in the reaction a series of experiments was carried out. The experiments were set-up according to **GP-1** on 0.1 mmol scale, with selected components excluded as indicated in the table below. After 12 h 1,3,5-mesitylene (28 µL, 2.00 equiv) was added as an internal standard and the reaction mixture analyzed by ^{1}H NMR spectroscopy.



Entry	Change from std. conditions	Yield of 3a [%]
1	none	85
2	without **1a**	82
3	dark, 40 °C	87
4	dark, 40 °C no **PC**	81
5	without 2,6-lutidine	5

Compound 3a'

Diethyl 2-bromo-2-((5-oxotetrahydrofuran-2-yl)methyl)malonate 3a'



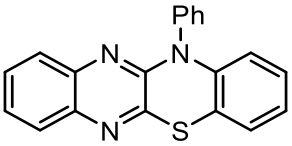
Lactone **3a'** was prepared using diethyl 2-bromomalonate (51.2 µL, 71.6 mg, 0.300 mmol, 1.50 equiv) and $LiBF_4$ (18.8 mg, 0.200 mmol, 1.00 equiv) in sulfolane (0.4 M), and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3a'** as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.85 (m, 1H), 4.37 – 4.25 (m, 4H), 2.73 (dd, J = 15.4, 9.2 Hz, 1H), 2.60 (dd, J = 15.4, 2.9 Hz, 1H), 2.55 – 2.49 (m, 2H), 2.49 – 2.39 (m, 1H), 2.01 – 1.88 (m, 1H), 1.30 (td, J = 7.2, 4.8 Hz, 6H).

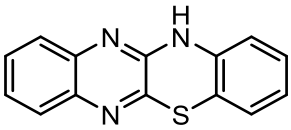
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 175.9, 167.1, 165.8, 76.9, 64.0, 63.4, 60.3, 44.1, 28.4, 28.3, 13.9, 13.9.

11. Experimental Section

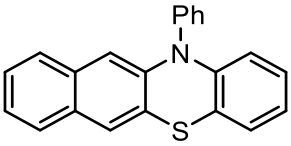
Preparation of Photocatalysts



PC



PC-2

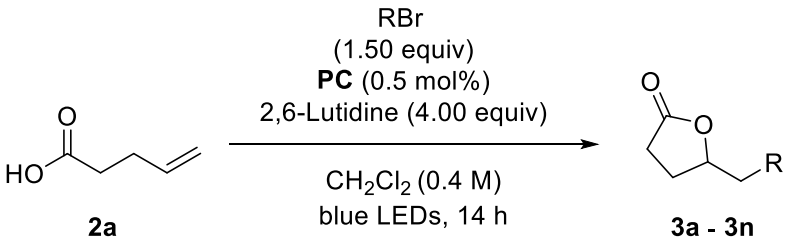


PC-3

Photocatalyst **PC, PC-2** and **PC-3** were prepared according to literature.[5,6]

11.1 General Procedures

GP1: Lactonization of Unactivated Alkenes with Alkyl Bromides

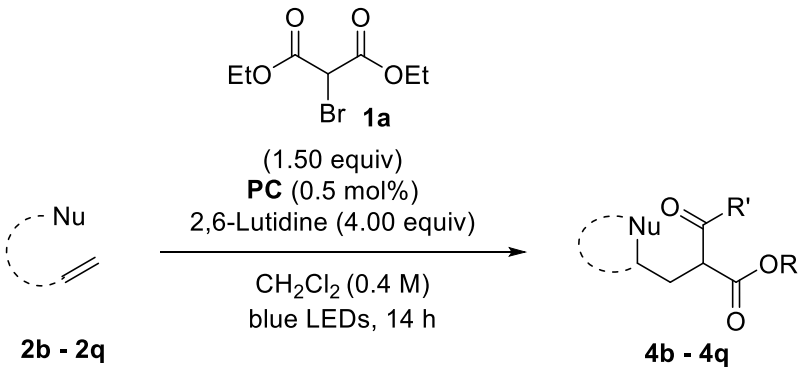


2a **3a - 3n**

To a glass vial charged with **PC** (0.33 mg, 0.0010 mmol, 0.50 mol%) in CH_2Cl_2 (500 µL, 0.4 M) were added 4-pentenoic acid (20.4 µL, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and alkyl bromide (0.300 mmol, 1.50 equiv) sequentially. The vial was equipped with a magnetic stirrer bar and capped with a screwcap. The reaction was irradiated in a 350 W photoreactor (*vide supra*) for the indicated time. The solvent was removed *in vacuo* and purification using silica gel chromatography with the appropriate eluent was employed to obtain pure product.

[5]Fischer, D. M.; Lindner H; Amberg; W. M.; Carreira; E. M., Intermolecular Organophotocatalytic Cyclopropanation of Unactivated Olefins. *J. Am. Chem. Soc*. **2023**, *145*, 2, 774–780.
[6] X. Pan, C. Fang, M. Fantin, N. Malhotra, W. Y. So, L. A. Peteanu, A. A. Isse, A. Gennaro, P. Liu and K. Matyjaszewski, Mechanism of Photoinduced Metal-Free Atom Transfer Radical Polymerization: Experimental and Computational Studies. *J. Am. Chem. Soc.* **2016,** *138*, 2411-2425.

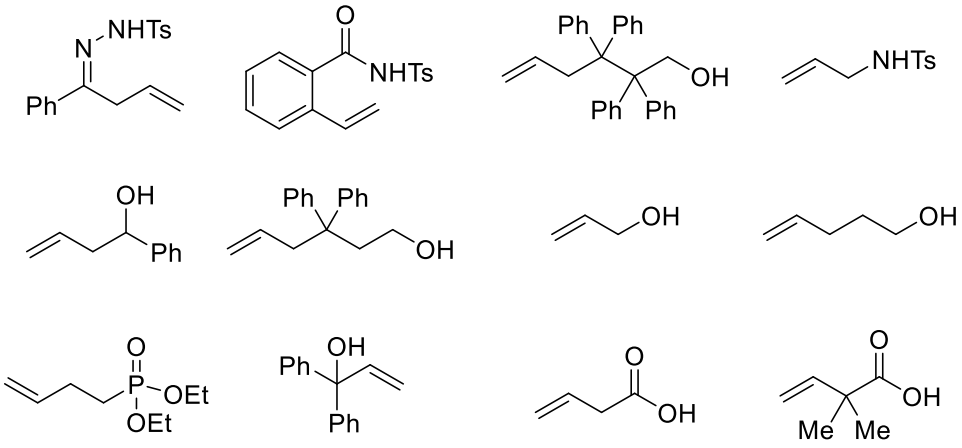
GP2: Cyclization of Unactivated Alkenes with α-Bromomalonates



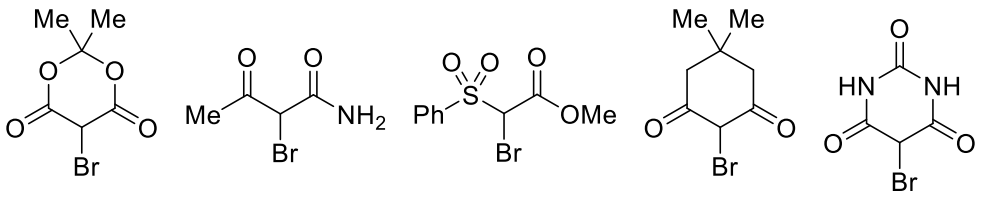
To a glass vial charged with **PC** (0.33 mg, 0.0010 mmol, 0.50 mol%) in CH_2Cl_2 (500 µL, 0.4 M) were added alkene starting material (0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and diethyl bromomalonate (51.2 µL, 71.6 mg, 0.300 mmol, 1.50 equiv) sequentially. The vial was equipped with a magnetic stirrer bar and capped with a screwcap. The reaction was irradiated in a 350 W photoreactor (*vide supra*) for the indicated time. The solvent was removed *in vacuo* and purification using silica gel chromatography with the appropriate eluent was employed to obtain pure product.

Unsuccessful Substrates

Unsuccessful Alkenes



Unsuccessful Bromides

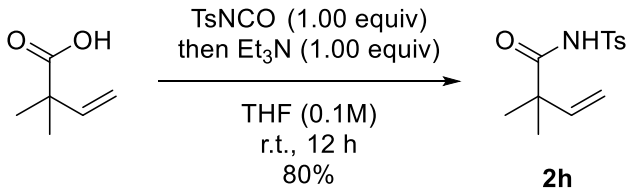


11.2 Starting Material Synthesis

Ketoesters **1b**-**1h** were prepared according to literature.[7]

Compound 2h:

2,2-Dimethyl-N-tosylbut-3-enamide



To a solution of 2,2-dimethylbut-3-enoic acid (500 mg, 4.38 mmol) in dry THF (0.1M) at r.t. under a nitrogen atmosphere, *N*-tosyl isocyanate (669 µL, 4.38 mmol, 1.00 eq.) was added dropwise and the mixture stirred for 10 minutes. Then, Et_3N (316 µL, 4.38 mmol, 1.00 eq.) was added dropwise (caution: gas evolution up addition) and stirring was continued at r.t. for 12 h. The reaction mixture was diluted with EtOAc, washed with aq. HCl (3M) and brine, and dried using anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified via column chromatography (50% EtOAc in hexane) to yield **2h** as an off-white solid.

Yield: 936 mg, 3.50 mmol, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.15 – 8.06 (m, 1H), 7.95 – 7.90 (m, 2H), 7.36 – 7.30 (m, 2H), 5.87 (dd, J = 17.5, 10.6 Hz, 1H), 5.32 – 5.19 (m, 2H), 2.44 (s, 3H), 1.22 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 173.5, 145.2, 141.2, 135.5, 129.7, 128.6, 116.9, 46.6, 24.0, 21.8.

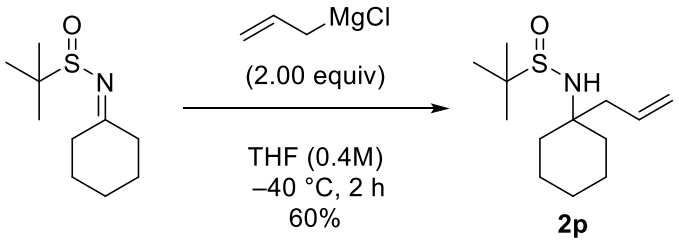
IR (thin film, cm^{-1}): 3277, 2979, 2932, 1717, 1637, 1598, 1495, 1466, 1409, 1342, 1308, 1294, 1188, 1170, 1110, 1084, 1041, 1019, 999, 929, 905, 856, 816, 781, 759, 704, 660, 563, 547

[7] D. M. Fischer, H. Lindner, W. M. Amberg and E. M. Carreira, Intermolecular Organophotocatalytic Cyclopropanation of Unactivated Olefins. Ibid.**2023,** *145*, 774-780.

HRMS (ESI+): *m/z* for $C_{13}H_{17}NNaO_3S$ $[M+Na]^+$: calc.: 290.0821, found: 290.0819.

Compound 2p:

***N*-(1-allylcyclohexyl)-2-methylpropane-2-sulfinamide**



Allyl magnesium chloride (2.00 M, 2.48 ml, 4.96 mmol, 2.00 equiv) was added dropwise to a solution of racemic sulfinamide[8] (500 mg, 2.48 mmol, 1.00 equiv) in THF (6.20 ml) at -40 °C and the mixture stirred at -40 °C for 2 h. After completion (TLC), aq. sat. NH_4Cl (5 ml) was added at -40 °C, the aqueous phase separated and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent removed *in vacuo.* The product was purified via column chromatography (30-50% EtOAc in hexane) to give racemic **2p** as a faint yellow oil.

Yield: 362 mg, 1.49 mmol, 60%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.92 – 5.75 (m, 1H), 5.14 (d, J = 1.2 Hz, 1H), 5.12 – 5.08 (m, 1H), 3.21 (s, 1H), 2.43 (ddt, J = 13.9, 7.4, 1.2 Hz, 1H), 2.36 – 2.25 (m, 1H), 1.88 – 1.77 (m, 2H), 1.70 – 1.40 (m, 8H), 1.20 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 133.5, 119.4, 57.0, 55.9, 37.3, 35.8, 25.7, 22.9, 22.2, 22.2, 21.8.

IR (thin film, cm^{-1}): 3226, 3075, 2977, 2928, 2859, 1714, 1638, 1475, 1453, 1416, 1387, 1362, 1311, 1261, 1221, 1187, 1167, 1154, 1119, 1053, 998, 977, 908, 847, 822, 795, 686, 594, 545.

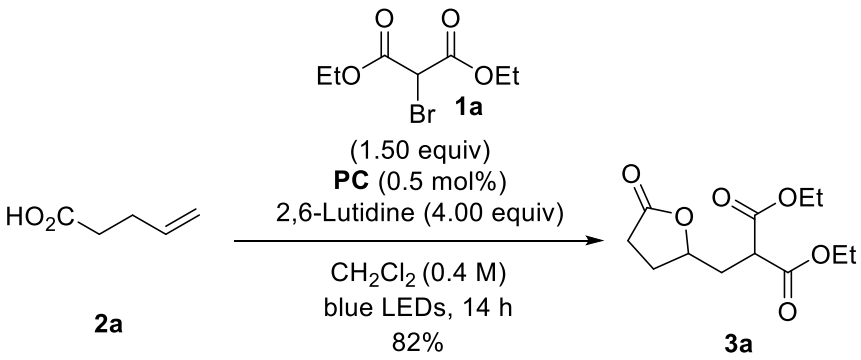
HRMS (ESI+): *m/z* for $C_{13}H_{26}NOS$ $[M+H]^+$: calc.: 244.1730, found: 244.1727.

[8] Rao C. N.; Lentz D.; Reissig H.-U., Synthesis of Polycyclic Tertiary Carbinamines by Samarium DiiodideMediated Cyclizations of Indolyl Sulfinyl Imines. *Angew. Chem. Int. Ed.* **2015**, *54*, 2750–2753.

11.3 Substrate Scope with Pent-4-enoic Acid

Compound 3a:

Diethyl 2-((5-oxotetrahydrofuran-2-yl)methyl)malonate



Lactone **3a** was prepared via GP1, using diethyl 2-bromomalonate (51.2 µL, 71.7 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3a** as a pale-yellow oil.

Note: Lactone **3a** was prepared on larger scale by an adapted procedure based on **GP1**, using 4-pentenoic acid (204 µL, 200 mg, 2.00 mmol, 1.00 equiv) and diethyl 2-bromomalonate (511 µL, 717 mg, 300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3a** as a pale-yellow oil in 77% (398 mg, 1.54 mmol) yield.

Yield: 42.3 mg, 0.164 mmol, 82%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.58 – 4.47 (m, 1H), 4.18 (ddddd, J = 9.7, 8.9, 7.3, 3.5, 2.6 Hz, 4H), 3.59 (dddd, J = 8.6, 5.1, 2.5, 0.9 Hz, 1H), 2.51 (dddt, J = 10.6, 5.8, 2.4, 1.2 Hz, 2H), 2.40 – 2.32 (m, 1H), 2.27 (ddtd, J = 14.7, 9.4, 2.6, 1.3 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.92 – 1.82 (m, 1H), 1.26 – 1.22 (m, 6H).

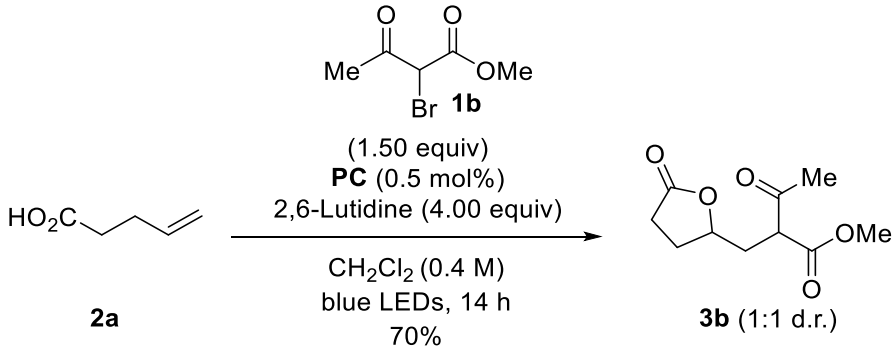
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 176.5, 168.9, 168.8, 78.1, 61.8, 61.8, 48.6, 34.7, 28.6, 28.0, 14.1, 14.1.

IR (thin film, cm^{-1}): 2984, 1778, 1731, 1465, 1370, 1269, 1242, 1179, 1096, 1043, 914, 861.

HRMS (ESI+): *m/z* for $C_{12}H_{18}NaO_6$ $[M+Na]^+$: calc.: 281.0996, found: 281.0994.

Compound 3b:

Methyl 3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)butanoate



Lactone **3b** was prepared via GP1, using methyl 2-bromo-3-oxobutanoate (58.5 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3b** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 30.0 mg, 0.140 mmol, 70%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.51 (dddd, J = 10.5, 7.8, 6.6, 3.0 Hz, 1H), 4.49 – 4.38 (m, 1H), 3.86 – 3.80 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 2.57 – 2.50 (m, 4H), 2.44 – 2.34 (m, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 2.28 – 2.24 (m, 1H), 2.08 – 1.98 (m, 2H), 1.96 – 1.80 (m, 2H).

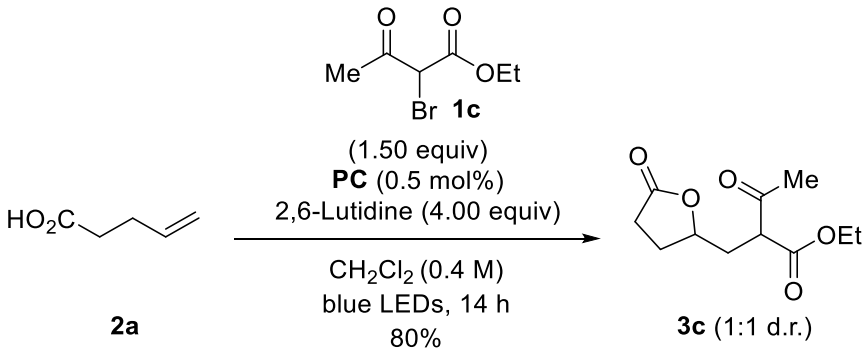
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.2, 202.0, 176.6, 176.5, 169.5, 169.5, 78.3, 78.2, 55.9, 55.5, 53.0, 52.9, 33.9, 33.9, 30.3, 29.6, 28.7, 28.6, 28.3.

IR (thin film, cm^{-1}): 2956, 1773, 1742, 1717, 1649, 1436, 1360, 1241, 1178, 1151, 1047, 1016, 984, 919, 866, 805, 652.

HRMS (ESI+): *m/z* for $C_{10}H_{14}NaO_5$ $[M+Na]^+$: calc.: 237.0733, found: 237.0731.

Compound 3c:

Ethyl 3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)butanoate



Lactone **3c** was prepared via GP1, using ethyl 2-bromo-3-oxobutanoate (61.7 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3c** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 36.5 mg, 0.160 mmol, 80%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.50 (dddd, J = 10.6, 7.7, 6.6, 3.0 Hz, 1H), 4.43 (dddd, J = 10.0, 7.6, 6.6, 3.2 Hz, 1H), 4.25 – 4.16 (m, 4H), 3.79 (ddd, J = 9.8, 6.3, 4.6 Hz, 2H), 2.57 – 2.48 (m, 4H), 2.42 – 2.32 (m, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 2.27 – 2.20 (m, 1H), 2.07 – 1.96 (m, 2H), 1.95 – 1.79 (m, 2H), 1.32 – 1.23 (m, 6H).

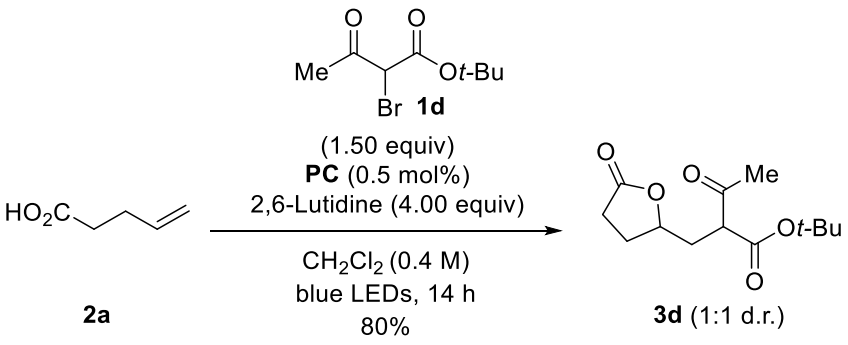
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.4, 202.1, 176.6, 176.6, 169.0, 78.4, 78.3, 62.0, 62.0, 56.1, 55.7, 33.9, 33.8, 30.3, 29.5, 28.7, 28.6, 28.3, 14.2, 14.2.

IR (thin film, cm^{-1}): 2984, 2939, 1774, 1737, 1714, 1645, 1463, 1447, 1423, 1360, 1336, 1297, 1237, 1178, 1148, 1114, 1096, 1046, 1020, 916, 859, 806, 652.

HRMS (ESI+): *m/z* for $C_{11}H_{16}NaO_5$ $[M+Na]^+$: calc.: 251.0890, found: 251.0891.

Compound 3d:

***Tert*-butyl 3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)butanoate**



Lactone **3d** was prepared via GP1, using *tert*-butyl 2-bromo-3-oxobutanoate (71.1 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3d** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 41.2 mg, 0.161 mmol, 80%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.50 (dddd, J = 9.9, 7.7, 6.6, 3.1 Hz, 1H), 4.42 (dddd, J = 10.0, 7.6, 6.6, 3.2 Hz, 1H), 3.70 (ddd, J = 9.8, 6.3, 4.6 Hz, 2H), 2.57 – 2.48 (m, 4H), 2.42 – 2.31 (m, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.27 – 2.15 (m, 1H), 2.04 – 1.92 (m, 2H), 1.93 – 1.79 (m, 2H), 1.46 (s, 9H), 1.46 (s, 9H).

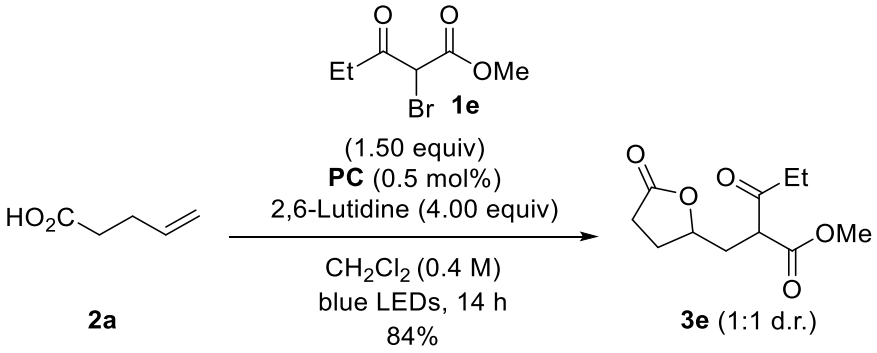
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.7, 202.5, 176.7, 168.1, 168.0, 82.8, 82.7, 78.5, 78.4, 57.1, 56.8, 33.8, 33.7, 30.1, 29.5, 28.7, 28.7, 28.3, 28.0, 28.0.

IR (thin film, cm^{-1}): 2979, 2935, 1774, 1733, 1711,1639, 1478, 1459, 1423, 1394, 1368, 1251, 1168, 1138, 1044, 1014, 984, 964, 915, 843, 805, 735, 653.

HRMS (ESI+): *m/z* for $C_{13}H_{20}NaO_5$ $[M+Na]^+$: calc.: 279.1203, found: 279.1209.

Compound 3e:

Methyl 3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)pentanoate



Lactone **3e** was prepared via GP1, using methyl 2-bromo-3-oxopentanoate (62.7 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3e** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 38.5 mg, 0.169 mmol, 84%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.51 (dddd, J = 10.5, 7.7, 6.6, 2.9 Hz, 1H), 4.43 – 4.34 (m, 1H), 3.82 (td, J = 9.7, 4.6 Hz, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 2.75 – 2.49 (m, 8H), 2.43 – 2.24 (m, 4H), 2.07 – 1.94 (m, 2H), 1.93 – 1.80 (m, 2H), 1.11 – 1.02 (m, 6H).

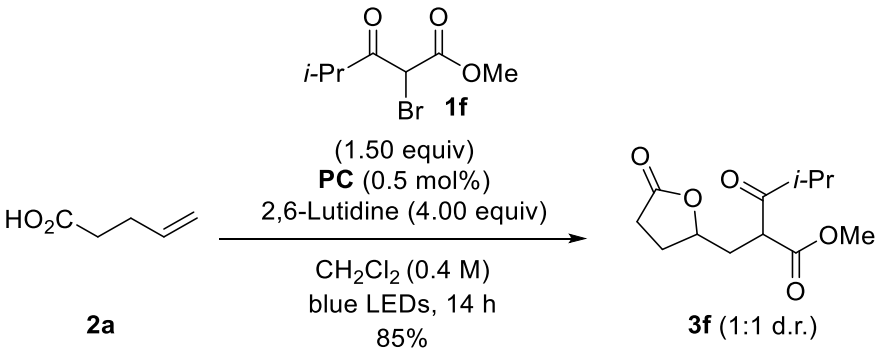
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 205.3, 204.9, 176.6, 176.6, 169.6, 169.6, 78.4, 78.2, 54.9, 54.4, 52.9, 52.8, 36.7, 35.9, 34.2, 34.0, 28.7, 28.6, 28.2, 7.7, 7.7.

IR (thin film, cm^{-1}): 2980, 2954, 1773, 1741, 1715, 1644, 1460, 1436, 1353, 1267, 1232, 1177, 1151, 1121, 1033, 990, 958, 922, 861, 805, 651.

HRMS (ESI+): *m/z* for $C_{11}H_{16}NaO_5$ $[M+Na]^+$: calc.: 251.0890, found: 251.0888.

Compound 3f:

Methyl 4-methyl-3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)pentanoate



Lactone **3f** was prepared via GP1, using methyl 2-bromo-4-methyl-3-oxopentanoate (66.9 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3f** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 41.2 mg, 0.170 mmol, 85%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.52 (dddd, J = 10.6, 7.9, 6.6, 2.8 Hz, 1H), 4.36 – 4.27 (m, 1H), 3.99 (ddd, J = 11.4, 10.1, 4.1 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 2.85 (dp, J = 15.5, 6.9 Hz, 2H), 2.56 – 2.48 (m, 4H), 2.41 – 2.24 (m, 4H), 2.00 (ddd, J = 14.6, 10.6, 4.3 Hz, 1H), 1.95 – 1.79 (m, 3H), 1.14 – 1.07 (m, 12H).

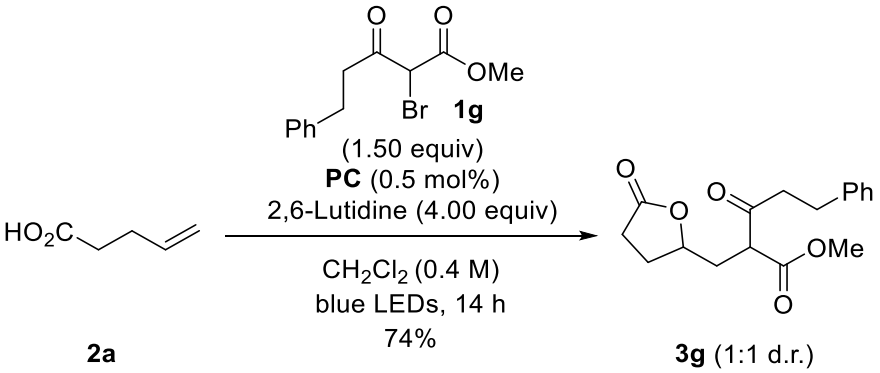
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 208.6, 208.2, 176.6, 176.6, 169.6, 169.5, 78.5, 78.1, 53.1, 52.8, 52.7, 41.3, 40.9, 34.5, 34.3, 28.7, 28.6, 28.3, 28.2, 18.5, 18.4, 18.1, 17.7.

IR (thin film, cm^{-1}): 2973, 2877, 1776, 1742, 1714, 1641, 1464, 1436, 1385, 1340, 1235, 1178, 1150, 1119, 1035, 969, 923, 873, 850, 804, 651

HRMS (ESI+): *m/z* for $C_{12}H_{18}NaO_5$ $[M+Na]^+$: calc.: 265.1046, found: 265.1043.

Compound 3g:

Methyl 3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)-5-phenylpentanoate



Lactone **3g** was prepared via GP1, using methyl 2-bromo-3-oxo-5-phenylpentanoate (85.5 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3g** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 45.3 mg, 0.149 mmol, 74%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 – 7.25 (m, 4H), 7.24 – 7.14 (m, 6H), 4.52 – 4.44 (m, 1H), 4.29 – 4.19 (m, 1H), 3.85 – 3.76 (m, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.05 – 2.85 (m, 8H), 2.57 – 2.45 (m, 4H), 2.39 – 2.21 (m, 4H), 1.98 (dddd, J = 23.2, 14.7, 10.4, 4.6 Hz, 2H), 1.89 – 1.77 (m, 2H).

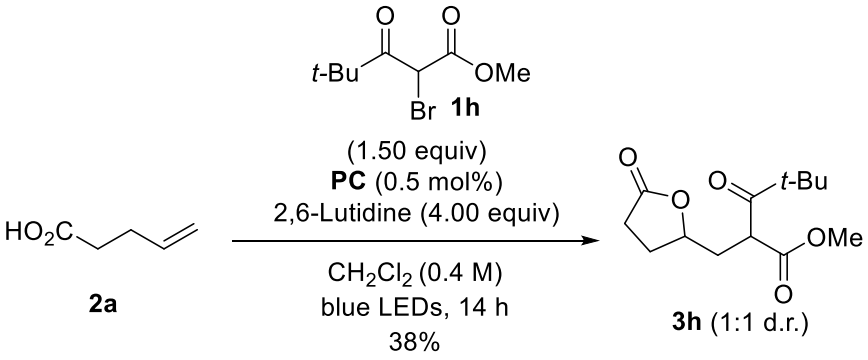
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.8, 203.4, 176.5, 176.5, 169.3, 169.3, 140.6, 140.6, 128.7, 128.6, 128.5, 128.5, 126.4, 78.3, 78.0, 55.3, 54.9, 52.9, 52.8, 44.7, 44.1, 33.9, 29.6, 29.5, 28.7, 28.6, 28.3, 28.2.

IR (thin film, cm^{-1}): 3027, 2953, 1774, 1742, 1715, 1604, 1497, 1454, 1436, 1359, 1340, 1264, 1240, 1176, 1117, 1079, 1041, 991, 920, 864, 804, 751, 701, 651

HRMS (ESI+): *m/z* for $C_{17}H_{20}NaO_5$ $[M+Na]^+$: calc.:327.1203, found: 327.1203.

Compound 3h:

Methyl 4,4-dimethyl-3-oxo-2-((5-oxotetrahydrofuran-2-yl)methyl)pentanoate



Lactone **3h** was prepared via GP2, using methyl 2-bromo-4,4-dimethyl-3-oxopentanoate (71.1 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3h** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 19.5 mg, 0.076 mmol, 38%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.58 (dddd, J = 10.5, 8.0, 6.5, 2.4 Hz, 1H), 4.34 – 4.20 (m, 3H), 3.70 (bs, 6H), 2.57 – 2.49 (m, 4H), 2.44 – 2.32 (m, 4H), 2.03 (ddd, J = 14.4, 10.5, 4.2 Hz, 1H), 1.92 – 1.78 (m, 2H), 1.73 (ddd, J = 14.6, 10.6, 3.2 Hz, 1H), 1.19 (s, 9H), 1.18 (s, 9H).

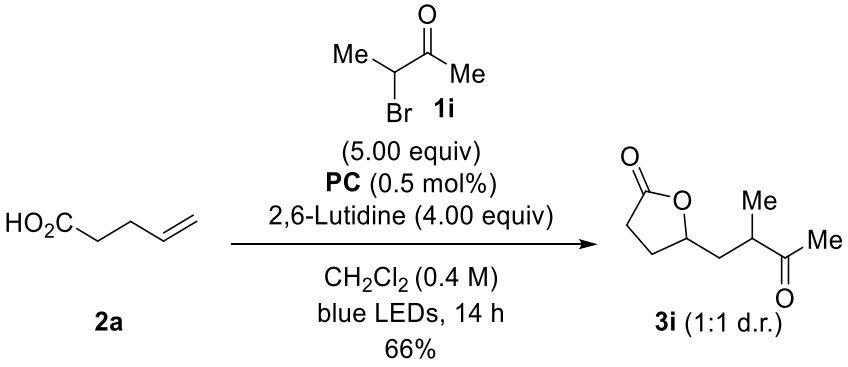
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 209.9, 209.8, 176.6, 176.6, 169.9, 169.8, 78.7, 78.1, 52.8, 52.7, 49.0, 48.7, 45.9, 45.7, 36.1, 35.9, 28.8, 28.6, 28.4, 28.2, 26.3, 26.3.

IR (thin film, cm^{-1}): 2958, 2875, 1776, 1742, 1707, 1480, 1462, 1435, 1397, 1368, 1333, 1303, 1269, 1227, 1176, 1148, 1110, 1081, 1042, 991, 965, 922, 860, 805, 651.

HRMS (ESI+): *m/z* for $C_{13}H_{20}NaO_5$ $[M+Na]^+$: calc.: 279.1203, found: 279.1209.

Compound 3i:

5-(2-methyl-3-oxobutyl)dihydrofuran-2(3H)-one



Lactone **3i** was prepared via GP1, using 3-bromobutan-2-one (105 µL, 151 mg, 1.00 mmol, 5.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (20% EtOAc in hexane) to give **3i** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 22.5 mg, 0.132 mmol, 66%, d.r. = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.59 – 4.51 (m, 1H), 4.43 (dddd, J = 9.8, 8.0, 6.5, 3.1 Hz, 1H), 2.94 – 2.85 (m, 1H), 2.84 – 2.74 (m, 1H), 2.59 – 2.47 (m, 4H), 2.35 (ddtd, J = 12.6, 7.6, 6.3, 3.3 Hz, 2H), 2.19 (s, 3H), 2.18 (s, 3H), 2.13 – 2.01 (m, 2H), 1.93 – 1.74 (m, 2H), 1.65 – 1.49 (m, 2H), 1.21 – 1.14 (m, 6H).

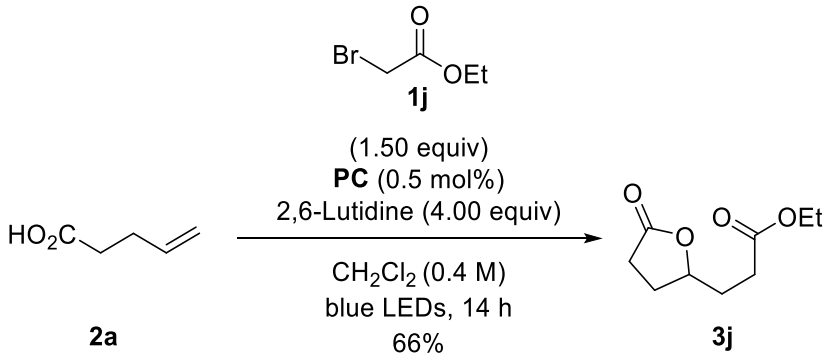
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 211.8, 211.4, 177.1, 176.9, 79.4, 78.3, 43.6, 43.5, 38.7, 38.0, 29.1, 28.8, 28.8, 28.7, 28.5, 28.3, 18.0, 16.1.

IR (thin film, cm^{-1}): 2935, 1772, 1710, 1460, 1423, 1357, 1286, 1219, 1179, 1121, 1079, 1019, 983, 918, 803, 653, 597, 520.

HRMS (ESI+): *m/z* for $C_9H_{14}NaO_3$ $[M+Na]^+$: calc.: 193.0835, found: 193.0837.

Compound 3j:

Ethyl 3-(5-oxotetrahydrofuran-2-yl)propanoate



Lactone **3j** was prepared via GP1, using ethyl bromoacetate (33.3 µL, 50.1 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3j** as a pale-yellow oil.

Yield: 24.6 mg, 0.132 mmol, 66%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.53 (dddd, J = 8.6, 7.9, 6.6, 4.5 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.53 (ddd, J = 9.4, 6.9, 1.1 Hz, 2H), 2.51 – 2.42 (m, 2H), 2.35 (ddt, J = 12.9, 7.6, 6.4 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.90–1.82 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H).

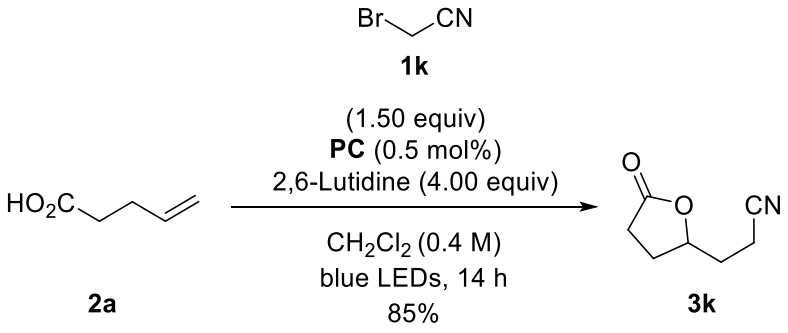
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 176.9, 172.8, 79.8, 60.8, 30.8, 30.3, 28.8, 28.0, 14.3.

IR (thin film, cm^{-1}): 2967, 1773, 1730, 1446, 1422, 1373, 1346, 1262, 1175, 1144, 1097,1042, 956, 912, 859, 807, 652.

HRMS (ESI+): *m/z* for $C_9H_{14}NaO_4$ $[M+Na]^+$: calc.: 209.0784, found: 209.0786.

Compound 3k:

3-(5-oxotetrahydrofuran-2-yl)propanenitrile



Lactone **3k** was prepared via GP1, using bromacetonitrile (21.0 µL, 36.0 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (20% EtOAc in hexane) to give **3k** as a pale-yellow oil.

Yield: 23.7 mg, 0.170 mmol, 85%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.59 (dddd, J = 9.1, 8.1, 6.6, 4.0 Hz, 1H), 2.61 – 2.52 (m, 4H), 2.42 (dddd, J = 12.9, 8.3, 6.6, 5.3 Hz, 1H), 2.06 – 1.96 (m, 2H), 1.96 – 1.86 (m, 1H).

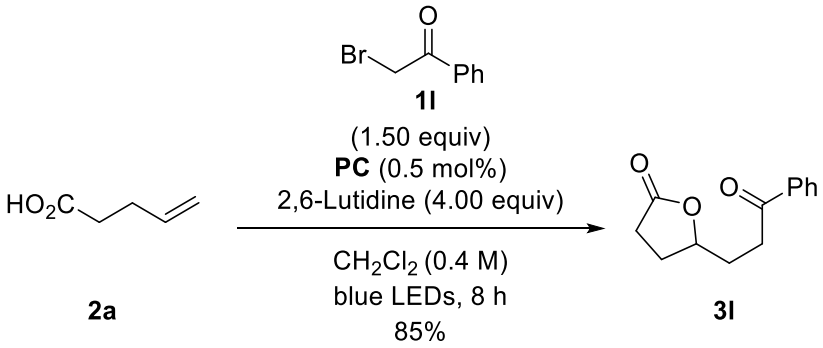
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 176.2, 118.7, 78.3, 31.5, 28.6, 27.7, 14.2.

IR (thin film, cm^{-1}): 2943, 2247, 1767, 1460, 1423, 1392, 1358, 1296, 1283, 1222, 1177, 1146, 1108, 1050, 956, 930, 907, 851, 807, 753, 666, 653.

HRMS (ESI+): *m/z* for $C_7H_9NNaO_2$ $[M+Na]^+$: calc.: 162.0525, found: 162.0526.

Compound 3l:

5-(3-Oxo-3-phenylpropyl)dihydrofuran-2(3*H*)-one



Lactone **3l** was prepared via GP1, using 2-bromoacetophenone (59.7 mg, 0.300 mmol, 1.50 equiv) was added to the vial and the reaction was stirred for 8 h. The crude product was purified via column chromatography (30–50% EtOAc in hexane) to give **3l** as an off-white solid.

Yield: 36.9 mg, 0.169 mmol, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 – 7.95 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 4.61 (dddd, J = 9.9, 7.8, 6.6, 3.6 Hz, 1H), 3.28 – 3.13 (m, 2H), 2.61 – 2.52 (m, 2H), 2.47 – 2.34 (m, 1H), 2.27 – 2.17 (m, 1H), 2.07 – 1.87 (m, 2H).

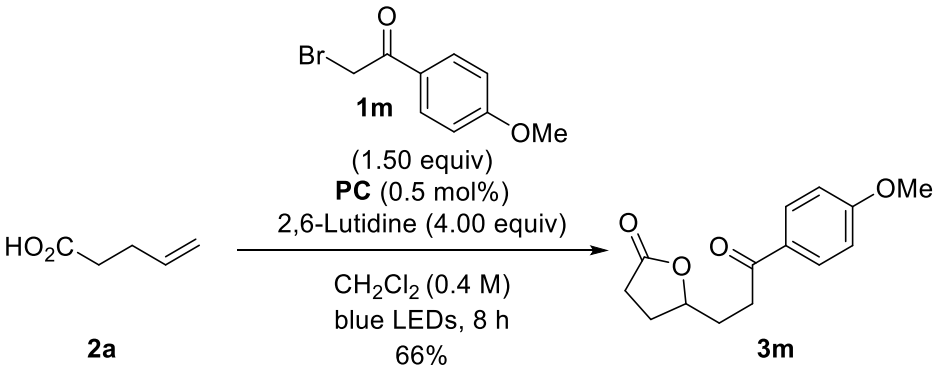
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 199.0, 177.1, 136.7, 133.4, 128.8, 128.1, 80.2, 34.5, 30.0, 28.9, 28.3.

IR (thin film, cm^{-1}): 2934, 1768, 1683, 1597, 1581, 1449, 1417, 1348, 1306, 1269, 1219, 1210, 1176, 1141, 1105, 1075, 1042, 1021, 1001, 960, 917, 865, 804, 747.

HRMS (ESI+): *m/z* for $C_{13}H_{15}O_3$ $[M+H]^+$: calc.: 219.1016, found: 219.1017.

Compound 3m:

5-(3-(4-methoxyphenyl)-3-oxopropyl)dihydrofuran-2(3*H*)-one



Lactone **3m** was prepared via GP1, using 2-bromo-4'-methoxyacetophenone (68.7 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3m** as a colorless solid.

Yield: 32.8 mg, 0.132 mmol, 66%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.95 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.60 (dddd, J = 9.5, 7.9, 6.6, 3.6 Hz, 1H), 3.87 (s, 3H), 3.18 – 3.10 (m, 2H), 2.60 – 2.52 (m, 2H), 2.40 (ddt, J = 12.7, 7.8, 6.2 Hz, 1H), 2.21 (dtd, J = 14.5, 7.5, 3.6 Hz, 1H), 2.03 – 1.86 (m, 2H).

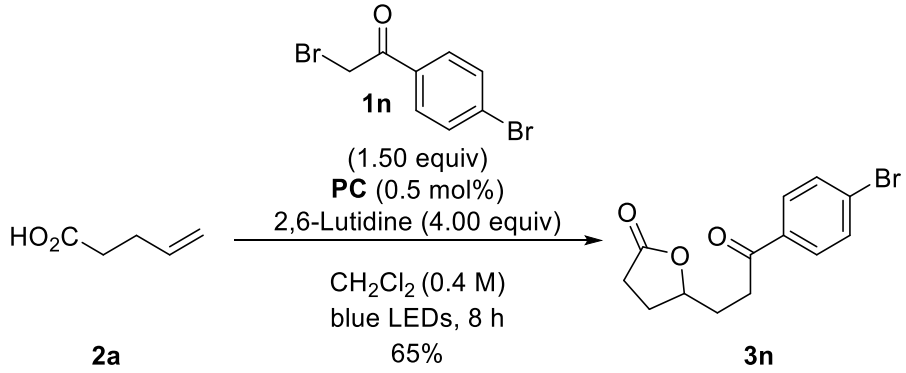
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 197.5, 177.1, 163.8, 130.4, 129.9, 113.9, 80.4, 55.6, 34.1, 30.2, 28.9, 28.3.

IR (thin film, cm^{-1}): 2938, 2842, 1768, 1673, 1599, 1575, 1510, 1460, 1443, 1419, 1348, 1310, 1256, 1216, 1168, 1113, 1025, 993, 963, 934, 917, 839, 809, 788. 719

HRMS (ESI+): *m/z* for $C_{14}H_{17}O_4$ $[M+H]^+$: calc.: 249.1121, found: 249.1124.

Compound 3n:

5-(3-(4-Bromophenyl)-3-oxopropyl)dihydrofuran-2(3*H*)-one



Lactone **3n** was prepared via GP1 using 2,4'-dibromoacetophenone (83.4 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3n** as a colorless solid.

Yield: 38.6 mg, 0.130 mmol, 65%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 4.60 (dddd, J = 9.8, 7.8, 6.6, 3.5 Hz, 1H), 3.21 – 3.12 (m, 2H), 2.61 – 2.52 (m, 2H), 2.41 (ddt, J = 12.8, 7.7, 6.4 Hz, 1H), 2.21 (dddd, J = 14.5, 7.9, 7.2, 3.5 Hz, 1H), 2.05 – 1.86 (m, 2H).

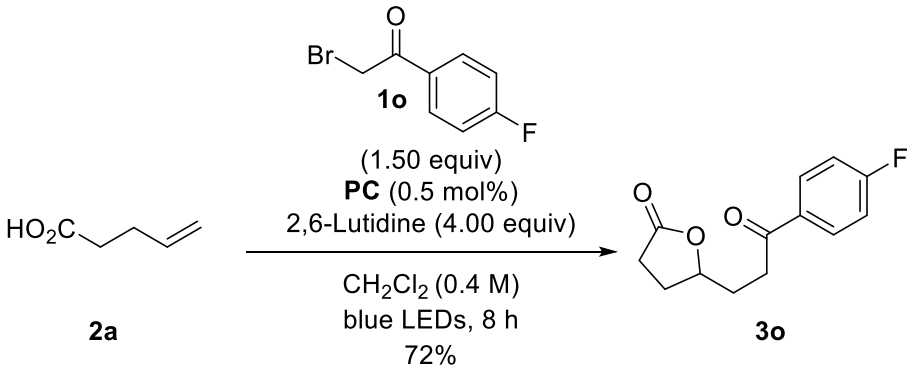
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 198.0, 177.0, 135.5, 132.2, 129.7, 128.7, 80.1, 34.5, 29.9, 28.9, 28.3.

IR (thin film, cm^{-1}): 2938, 1768, 1684, 1585, 1569, 1484, 1458, 1417, 1397, 1348, 1311, 1267, 1206, 1175, 1141, 1103, 1070, 1042, 1009, 994, 974, 964, 935, 917, 833, 808, 774.

HRMS (ESI+): *m/z* for $C_{13}H_{13}BrNaO_3$ $[M+Na]^+$: calc.: 318.9940, found: 318.9942.

Compound 3o:

5-(3-(4-Fluorophenyl)-3-oxopropyl)dihydrofuran-2(3*H*)-one



Lactone **3o** was prepared via GP1, using 2-bromo-4'-fluoroacetophenone (65.1 mg, 0.300 mmol, 1.50 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **3o** as a pale-yellow oil.

Yield: 34.0 mg, 0.144 mmol, 72%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (dd, J = 8.9, 5.4 Hz, 2H), 7.14 (dd, J = 8.9, 8.3 Hz, 2H), 4.60 (dddd, J = 9.9, 7.9, 6.6, 3.5 Hz, 1H), 3.21 – 3.13 (m, 2H), 2.57 (ddd, J = 9.2, 6.9, 1.7 Hz, 2H), 2.41 (ddt, J = 12.8, 7.7, 6.4 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.04 – 1.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 197.39, 177.03, 166.02 (d, J = 255.1 Hz), 133.21 (d, J = 3.2 Hz), 130.80 (d, J = 9.3 Hz), 115.94 (d, J = 21.9 Hz), 80.12, 34.47, 30.02, 28.91, 28.32.

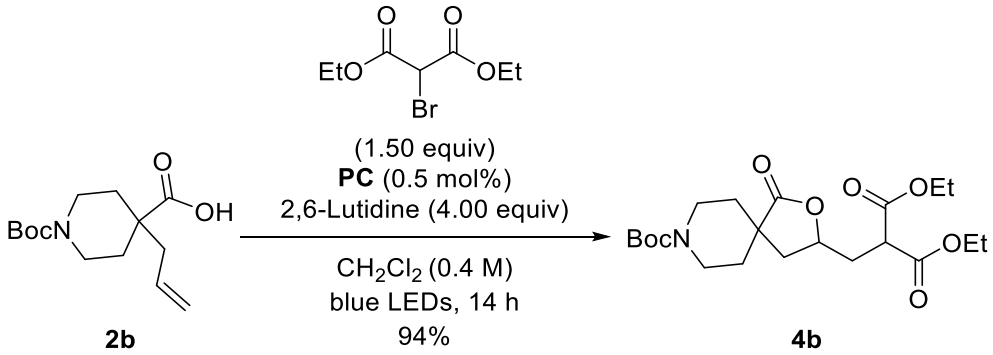
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ (ppm) = -104.8 (s, 1F).

IR (thin film, cm^{-1}): 2942, 1771, 1685, 1597, 1507, 1459, 1411, 1349, 1299, 1269, 1227, 1179, 1158, 1100, 1042, 1013, 995, 964, 935, 918, 843, 822.
HRMS (ESI+): *m/z* for $C_{13}H_{13}FNaO_3$ $[M+Na]^+$: calc.: 259.0741, found: 259.0739.

11.4 Substrate Scope with Diethyl Bromomalonate

Compound 4b:

Diethyl 2-((8-(*tert*-butoxycarbonyl)-1-oxo-2-oxa-8-azaspiro[4.5]decan-3-yl)methyl)malonate



2b **4b**

Lactone **4b** was prepared via GP2 using 4-allyl-1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid[9] (53.8 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4b** as a pale-yellow oil.

Yield: 80.4 mg, 0.188 mmol, 94%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.50 (tdd, J = 9.6, 6.2, 3.3 Hz, 1H), 4.28 – 4.16 (m, 4H), 3.96 (m, 1H), 3.81 (m, 1H), 3.64 (dd, J = 9.8, 4.9 Hz, 1H), 3.16 (ddd, J = 13.5, 9.6, 3.4 Hz, 1H), 3.06 (ddd, J = 13.4, 9.7, 3.5 Hz, 1H), 2.44 – 2.28 (m, 2H), 2.13 (ddd, J = 13.9, 9.7, 4.9 Hz, 1H), 1.94 (ddd, J = 13.8, 9.7, 4.2 Hz, 1H), 1.85 – 1.69 (m, 2H), 1.59 – 1.50 (m, 2H), 1.45 (s, 9H), 1.27 (td, J = 7.2, 2.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 179.3, 168.9, 168.9, 154.7, 80.0, 74.7, 62.0, 62.0, 48.7, 43.0, 39.8, 35.1, 33.6, 31.7, 28.5, 14.2, 14.2.

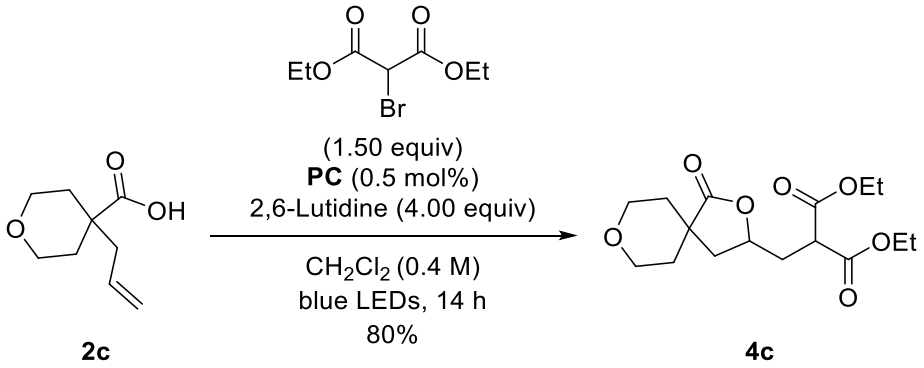
[9] Ferreira A. J.; Solano D. M.; Oakdale J. S.; Kurth M. J., Novel Trinitrogen-Containing Triheterocycles via the Intramolecular Nitrile Oxide Cycloaddition Reaction. *Synthesis* **2011**, *20*, 3241–3246.

IR (thin film, cm^{-1}): 2979, 2936, 1766, 1748, 1731, 1691, 1467, 1446, 1423, 1393, 1366, 1280, 1264, 1247, 1151, 1095, 1064, 1039, 1000, 073, 958, 863, 824, 769, 726, 638, 587.

HRMS (ESI+): *m/z* for $C_{21}H_{33}NNaO_8$ $[M+Na]^+$: calc.: 450.2098, found: 450.2094.

Compound 4c:

Diethyl 2-((1-oxo-2,8-dioxaspiro[4.5]decan-3-yl)methyl)malonate



2c **4c**

Lactone **4c** was prepared via GP2 using 4-allyltetrahydro-2*H*-pyran-4-carboxylic acid[10] (34.0 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (10-50% EtOAc in hexane) to give **4b** as a pale-yellow oil.

Yield: 52.5 mg, 0.160 mmol, 80%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.47 (tdd, J = 9.6, 6.2, 3.3 Hz, 1H), 4.25 – 4.13 (m, 4H), 4.01 (ddd, J = 11.8, 5.1, 4.2 Hz, 1H), 3.87 (ddd, J = 12.0, 5.1, 4.1 Hz, 1H), 3.61 (dd, J = 9.7, 4.9 Hz, 1H), 3.55 (ddd, J = 12.1, 9.4, 3.0 Hz, 1H), 3.46 (ddd, J = 11.8, 9.6, 3.1 Hz, 1H), 2.45 (dd, J = 13.0, 6.2 Hz, 1H), 2.31 (ddd, J = 14.5, 9.7, 3.3 Hz, 1H), 2.08 (m, 2H), 1.86 (ddd, J = 13.5, 9.4, 4.0 Hz, 1H), 1.73 (ddd, J = 13.1, 9.6, 0.9 Hz, 1H), 1.52 (dddd, J = 13.6, 4.9, 2.9, 1.6 Hz, 1H), 1.46 (dddd, J = 13.7, 4.9, 3.1, 1.6 Hz, 1H), 1.24 (td, J = 7.1, 3.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 179.2, 168.8, 168.8, 74.6, 64.0, 63.7, 61.9, 61.9, 48.6, 42.2, 40.1, 35.0, 33.8, 32.1, 14.1, 14.1.

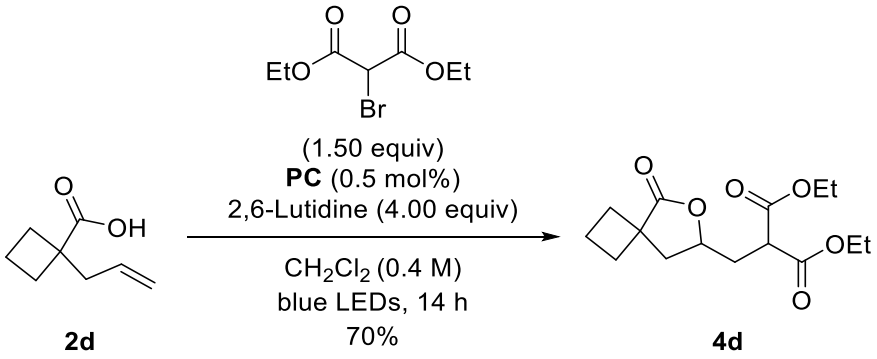
[10] Wang D.; Mück-Lichtenfeld C.; Daniliuc C. G.; Studer A, Radical Aryl Migration from Boron to Carbon. *J. Am. Chem. Soc.* **2021**, *143*, 9320–9326.

IR (thin film, cm^{-1}): 2941, 2852, 2766, 1765, 1746, 1727, 1468, 1444, 1391, 1369, 1331, 1287, 1271, 1244, 1183, 1154, 1106, 1030, 1013, 992, 977, 959, 919, 863, 838, 748, 724, 585, 552, 512.

HRMS (ESI+): *m/z* for $C_{16}H_{24}NaO_7$ $[M+Na]^+$: calc.: 351.1414, found: 351.1413.

Compound 4d:

Diethyl 2-((5-oxo-6-oxaspiro[3.4]octan-7-yl)methyl)malonate



Lactone **4d** was prepared via GP2 using 4-allyltetrahydro-2*H*-pyran-4-carboxylic acid[11] (28.0 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (10-30% EtOAc in hexane) to give **4d** as a pale-yellow oil.

Yield: 41.7 mg, 0.140 mmol, 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.37 (dddd, J = 9.7, 8.2, 6.2, 3.4 Hz, 1H), 4.26 – 4.15 (m, 4H), 3.61 (dd, J = 9.6, 5.0 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.50 (dd, J = 12.9, 6.2 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.27 (ddd, J = 14.5, 9.7, 3.4 Hz, 1H), 2.17 – 1.91 (m, 6H), 1.26 (td, J = 7.1, 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 180.5, 169.0, 168.9, 74.9, 61.9, 61.9, 48.7, 44.4, 42.0, 34.8, 31.7, 29.8, 16.6, 14.1, 14.1.

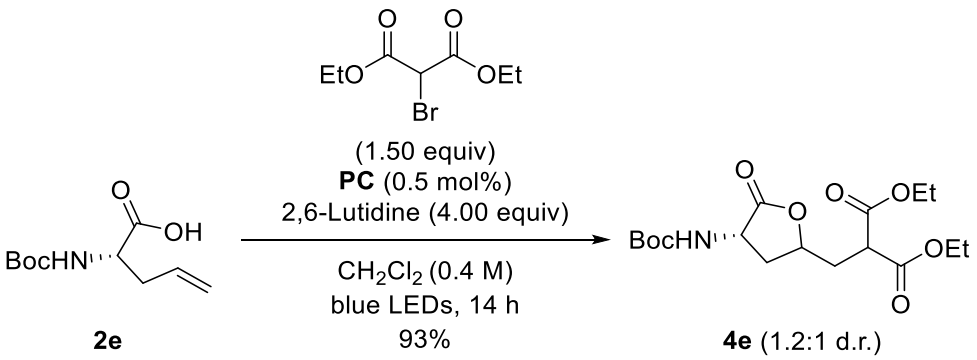
IR (thin film, cm^{-1}): 2982, 2938, 1769, 1746, 1729, 1465, 1446, 1430, 1392, 1369, 1333, 1304, 1270, 1257, 1240, 1172, 1112, 1087, 1028, 955, 924, 861, 801, 736, 670, 596.

HRMS (ESI+): *m/z* for $C_{15}H_{22}NaO_6$ $[M+Na]^+$: calc.: 321.1309, found: 321.1313.

[11] Gao R.; Canney D. J., A modified Prins reaction for the facile synthesis of structurally diverse substituted 5-(2-hydroxyethyl)-3,3-dihydrofurane-2(*3H*)-ones *Tetrahedron Letters* **2009**, *50*, 5914–5916.

Compound 4e:

Diethyl 2-(((4*S*)-4-((*tert*-butoxycarbonyl)amino)-5-oxotetrahydrofuran-2-yl)methyl)malonate



2e **4e** (1.2:1 d.r.)

Lactone **4e** was prepared via GP2 using (*S*)-2-((*tert*-butoxycarbonyl)amino)pent-4-enoic acid (43.1 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4e** as a pale-yellow oil. The product was isolated as an inseparable 1.2:1 mixture of diastereomers.

Yield: 69.5 mg, 0.186 mmol, 93%, d.r. = 1.2:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.08 (s, 2H), 4.68 (td, J = 10.3, 3.5 Hz, 1H), 4.42 – 4.51 (m, 1H) 4.42 – 4.33 (m, 2H), 4.28 – 4.14 (m, 8H), 3.62 (dd, J = 9.4, 5.3 Hz, 1H), 3.57 (dd, J = 8.9, 5.7 Hz, 1H), 2.84 (s, 1H), 2.44 (q, J = 11.2, 10.3 Hz, 1H), 2.34 (ddd, J = 14.6, 9.4, 3.5 Hz, 2H), 2.29 – 2.13 (m, 3H), 1.84 (q, J = 11.7 Hz, 1H), 1.44 (d, J = 1.1 Hz, 18H), 1.29 – 1.24 (m, 12H).

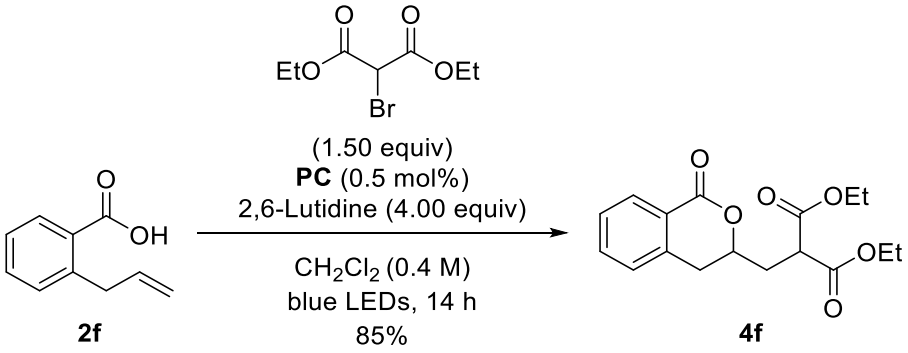
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 174.7, 174.3, 168.8, 168.7, 168.7, 168.7, 155.4 (bs), 80.8 (bs), 75.7, 75.4, 62.0, 62.0 (bs), 51.5, 49.3, 48.5, 48.5, 36.7, 34.7, 34.6, 34.4, 28.4, 28.4, 14.1, 14.1.

IR (thin film, cm^{-1}): 3379, 2980, 2936, 1785, 1716, 1513, 1478, 1453, 1392, 1367, 1334, 1284, 1245, 1153, 1097, 1038, 1028, 988, 960, 907, 859, 812, 781, 618, 561.

HRMS (ESI+): *m/z* for $C_{17}H_{27}NNaO_8$ $[M+Na]^+$: calc.: 396.1629, found: 396.1630.

Compound 4f:

Diethyl 2-((1-oxoisochroman-3-yl)methyl)malonate



Lactone **4f** was prepared via GP2 using 2-allylbenzoic acid[12] (32.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (5-30% EtOAc in hexane) to give **4f** as a pale-yellow oil.

Yield: 54.5 mg, 0.170 mmol, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.06 (dd, J = 7.8, 1.4 Hz, 1H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.38 (tt, J = 7.6, 1.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 4.65 – 4.53 (m, 1H), 4.27 – 4.13 (m, 4H), 3.88 – 3.80 (m, 1H), 3.05 – 2.90 (m, 2H), 2.40 – 2.32 (m, 2H), 1.26 (q, J = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.2, 169.1, 165.0, 138.7, 134.0, 130.4, 127.9, 127.5, 125.1, 76.1, 61.9, 61.8, 47.8, 34.1, 33.5, 14.1.

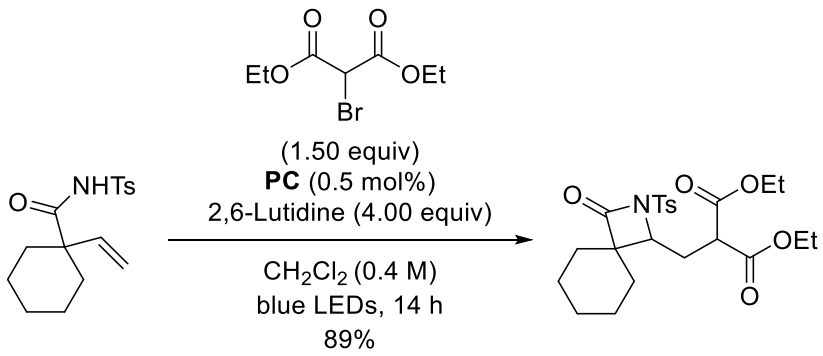
IR (thin film, cm^{-1}): 2982, 1722, 1607, 1460, 1446, 1433, 1391, 1369, 1332, 1281, 1264, 1248, 1231, 1175, 1156, 1124, 1083, 1030, 965, 946, 914, 858, 803, 746, 694, 632, 599, 564.

HRMS (ESI+): *m/z* for $C_{17}H_{20}NaO_6$ $[M+Na]^+$: calc.: 343.1152, found: 343.1153.

[12] Miles K. C.; Le C; Stambuli J. P., Direct Carbocyclizations of Benzoic Acids: Catalyst-Controlled Synthesis of Cyclic Ketones and the Development of Tandem aHH (acyl Heck–Heck) Reactions*Chem. Eur. J.* **2014**, 20, 11336–11339.

Compound 4g:

Diethyl 2-((3-oxo-2-tosyl-2-azaspiro[3.5]nonan-1-yl)methyl)malonate



2g **4g**

N-tosyl lactam **4g** was prepared via GP2 using *N*-tosyl-1-vinylcyclohexane-1-carboxamide[13] (61.5 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4g** as a pale-yellow oil.

Yield: 83.0 mg, 0.178 mmol, 89%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.88 – 7.78 (m, 2H), 7.37 – 7.30 (m, 2H), 4.32 – 4.13 (m, 4H), 3.90 (dd, J = 9.8, 5.5 Hz, 1H), 3.57 (dd, J = 7.9, 4.5 Hz, 1H), 2.43 (s, 3H), 2.36 – 2.19 (m, 2H), 1.85 (m, 1H), 1.60 (m, 4H), 1.53 – 1.38 (m, 3H), 1.35 –1.25 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.9, 169.0, 169.0, 145.3, 135.4, 130.1, 127.5, 63.9, 61.9, 61.8, 58.5, 49.3, 32.4, 29.0, 27.0, 25.2, 22.8, 22.7, 21.8, 14.2, 14.1.

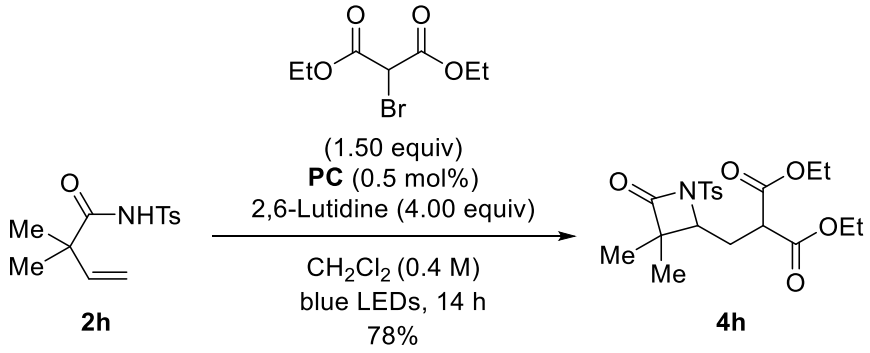
IR (thin film, cm^{-1}): 2982, 2935, 2861, 1787, 1728, 1597, 1495, 1448, 1366, 1285, 1238, 1187, 1166, 1152, 1089, 1027, 979, 916, 857, 815, 801, 765, 733, 705, 667, 589, 547, 530.

HRMS (ESI+): *m/z* for $C_{23}H_{31}NNaO_7S$ $[M+Na]^+$: calc.: 488.1713, found: 488.1710.

[13] Wang D.; Mück-Lichtenfeld C.; Daniliuc C. G.; Studer A, Radical Aryl Migration from Boron to Carbon. *J. Am. Chem. Soc.* **2021**, *143*, 9320–9326.

Compound 4h:

Diethyl 2-((3,3-dimethyl-4-oxo-1-tosylazetidin-2-yl)methyl)malonate



N-tosyl lactam **4h** was prepared via GP2 using 2,2-dimethyl-*N*-tosylbut-3-enamide (53.5 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4h** as a pale-yellow oil.

Yield: 66.4 mg, 0.156 mmol, 78%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 – 7.82 (m, 2H), 7.39 – 7.32 (m, 2H), 4.31 – 4.15 (m, 4H), 3.86 – 3.78 (m, 1H), 3.66 (ddd, J = 7.4, 5.4, 0.7 Hz, 1H), 2.45 (s, 3H), 2.35 (ddd, J = 14.7, 7.4, 5.9 Hz, 1H), 2.24 (ddd, J = 14.7, 9.4, 5.4 Hz, 1H), 1.29 (tdd, J = 7.1, 4.8, 0.6 Hz, 6H), 1.20 (s, 3H), 1.04 (s, 3H).

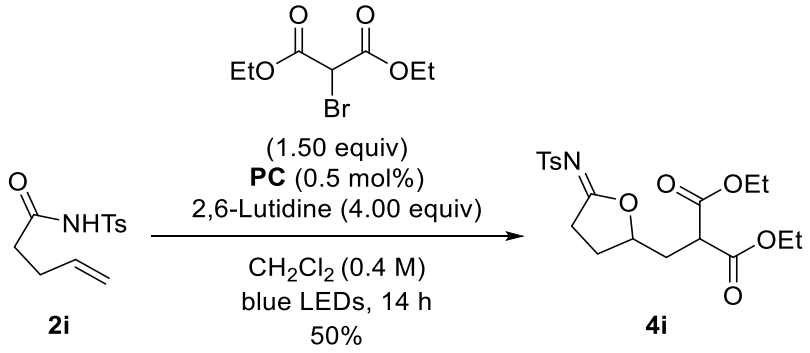
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.4, 168.9, 168.9, 145.5, 135.3, 130.2, 127.6, 63.9, 62.0, 61.9, 54.4, 49.2, 29.5, 21.9, 21.8, 16.7, 14.2, 14.2.

IR (thin film, cm^{-1}): 2980, 2936, 2875, 2118, 1794, 1728, 1597, 1495, 1466, 1448, 1390, 1366, 1328, 1298, 1269, 1237, 1188, 1166, 1107, 1086, 1025, 958, 908, 859, 815, 801, 731, 706, 664, 634, 590, 546

HRMS (ESI+): *m/z* for $C_{20}H_{28}NO_7S$ $[M+H]^+$: calc.: 426.1581, found: 426.1580.

Compound 4i:

Diethyl 2-((5-(tosylimino)tetrahydrofuran-2-yl)methyl)malonate



N-tosyl imidate **4i** was prepared via GP2 using *N*-tosylpent-4-enamide[14] (50.7 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4i** as a pale-yellow oil. The product was isolated as an inseparable 0.4:1 mixture of *E*/*Z* isomers (interconverting at rt).

Yield: 41.1 mg, 0.100 mmol, 50%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.81 (m, 3H), 7.29 (m, 3H), 4.79 (bs, 0.4H), 4.66 (d, J = 8.6 Hz, 1H), 4.27 – 4.13 (m, 6H), 3.64 – 3.54 (m, 1H), 3.43 – 3.38 (m, 1.4H), 3.13 (dt, J = 19.1, 9.4 Hz, 1H), 2.78 (bs, 0.8H), 2.46 (bs, 1H), 2.40 (bs, 4H), 2.37 – 2.28 (m, 1.8H), 2.20–2.10 (m, 1.4H), 1.94 (dq, J = 17.4, 9.3 Hz, 1H), 1.83 (bs, 0.4H), 1.32 – 1.20 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 179.6, 168.6, 143.7, 138.2, 129.5, 127.7, 127.0, 86.0, 81.8, 62.0, 62.0, 48.5, 34.1, 32.3, 30.3, 28.9, 27.8, 21.7, 14.1, 14.1.

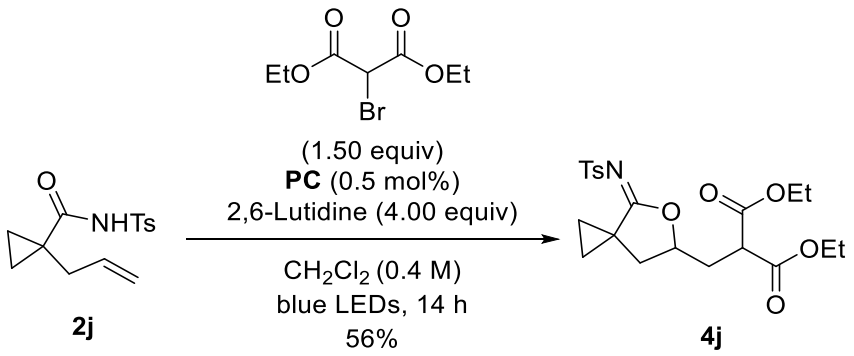
IR (thin film, cm^{-1}): 2983, 1728, 1628, 1446, 1369, 1303, 1241, 1152, 1094, 1031, 816, 769, 691, 663, 581, 556, 541.

[14] Wang D.; Mück-Lichtenfeld C.; Daniliuc C. G.; Studer A, Radical Aryl Migration from Boron to Carbon. *J. Am. Chem. Soc.* **2021**, *143*, 9320–9326.

HRMS (ESI+): *m/z* for $C_{19}H_{26}NO_7S$ $[M+H]^+$: calc.: 412.1425, found: 412.1422.

Compound 4j:

Diethyl 2-((4-(tosylimino)-5-oxaspiro[2.4]heptan-6-yl)methyl)malonate



N-tosyl imidate **4j** was prepared via GP2 using 1-allyl-*N*-tosylcyclopropane-1-carboxamide[15] (55.9 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4j** as a pale-yellow oil.

Yield: 49.0 mg, 0.112 mmol, 56%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.88 – 4.79 (m, 1H), 4.30 –4.16 (m, 4H), 3.43 (dd, J = 10.3, 4.6 Hz, 1H), 2.40 (s, 3H), 2.34 – 2.23 (m, 2H), 2.14 (ddd, J = 14.6, 10.0, 4.7 Hz, 1H), 1.94 (dd, J = 12.7, 6.8 Hz, 1H), 1.45 – 1.39 (m, 1H), 1.30 (m, 7H), 1.11 – 1.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 177.4, 168.7, 168.6, 143.2, 138.7, 129.3, 127.6, 82.8, 62.1, 62.0, 48.2, 35.6, 34.5, 24.5, 21.7, 18.3, 17.4, 14.2, 14.2.

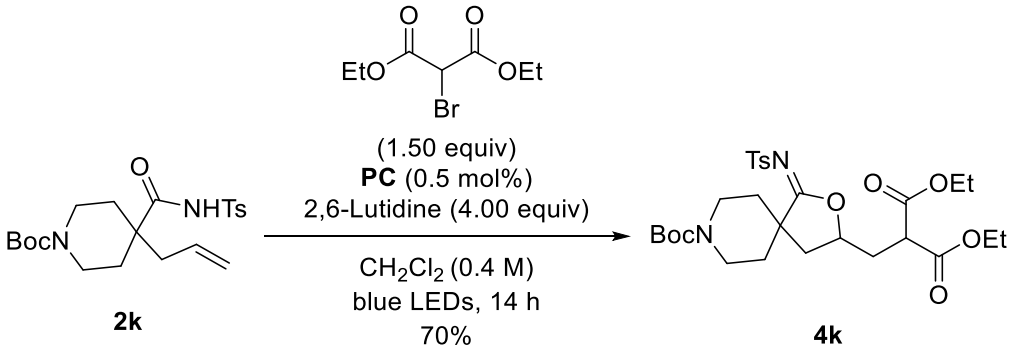
IR (thin film, cm^{-1}): 2983, 2938, 1728, 1620, 1495, 1446, 1370, 1319, 1302, 1289, 1256, 1237, 1150, 1090, 1028, 1020, 987, 919, 835, 804, 788, 726, 707, 664, 579.

HRMS (ESI+): *m/z* for $C_{21}H_{27}NNaO_7S$ $[M+Na]^+$: calc.: 460.1400, found: 460.1406.

[15] Fischer D. M.; Balkenhohl M.; Carreira E. M., Cobalt-Catalyzed Cyclization of Unsaturated N-Acyl Sulfonamides: a Diverted Mukaiyama Hydration Reaction. *JACS Au* **2022**, *2*, 1071–1077.

Compound 4k:

Diethyl 2-((8-(tert-butoxycarbonyl)-1-(tosylimino)-2-oxa-8-azaspiro[4.5]decan-3-yl)methyl)malonate



N-tosyl imidate **4k** was prepared via GP2 using tert-butyl 4-allyl-4-(tosylcarbamoyl)piperidine-1-carboxylate[16] (84.5 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4k** as an off-white solid.

Yield: 81.3 mg, 0.140 mmol, 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (m, 2H), 7.28 (m, 2H), 4.75 – 4.65 (m, 1H), 4.32 – 4.15 (m, 4H), 4.05 – 3.85 (m, 2H), 3.55 (dd, J = 9.9, 4.8 Hz, 1H), 2.97 (t, J = 12.2 Hz, 1H), 2.86 (t, J = 12.2 Hz, 1H), 2.41 (s, 3H), 2.45 – 2.33 (m, 1H), 2.33 – 2.26 (m, 1H) 2.10 (ddd, J = 14.5, 9.5, 4.8 Hz, 1H), 1.96 (ddd, J = 13.6, 10.9, 4.4 Hz, 1H), 1.78 – 1.61 (m, 2H), 1.57 –1.47 (m, 2H), 1.44 (s, 9H), 1.30 (td, J = 7.1, 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 176.7, 168.7, 168.5, 154.5, 143.5, 138.6, 129.4, 127.5, 82.2, 80.1, 62.1, 62.1, 48.5, 47.2, 40.0 (determined by ^{1}H ^{13}C HSQC), 40.0 (determined by ^{1}H ^{13}C HSQC), 38.7, 34.5, 34.1, 32.5 (determined by ^{1}H ^{13}C HSQC), 28.5, 21.7, 14.2.

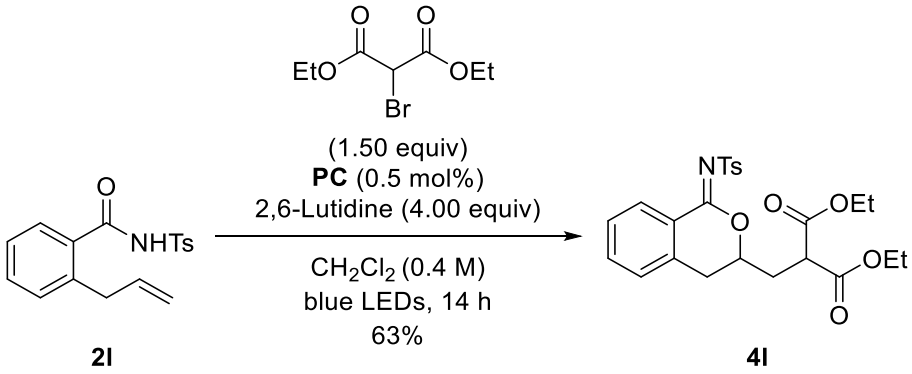
[16] Gao R.; Canney D. J., A modified Prins reaction for the facile synthesis of structurally diverse substituted 5-(2-hydroxyethyl)-3,3-dihydrofurane-2(*3H*)-ones *Tetrahedron Letters* **2009**, *50*, 5914–5916.

IR (thin film, cm^{-1}): 2978, 2934, 1746, 1731, 1689, 1630, 1446, 1424, 1394, 1367, 1324, 1305, 1280, 1264, 1247, 1226, 1154, 1093, 1039, 1019, 971, 918, 861, 817, 806, 788, 731, 707, 688, 663, 577, 554.

HRMS (ESI+): *m/z* for $C_{28}H_{40}N_2NaO_9S$ $[M+Na]^+$: calc.: 603.2347, found: 603.2338.

Compound 4l:

Diethyl 2-((1-(tosylimino)isochroman-3-yl)methyl)malonate



N-tosyl imidate **4l** was prepared via GP2 using 2-allyl-*N*-tosylbenzamide[17] (63.1 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4l** as a pale-yellow oil.

Yield: 59.7 mg, 0.126 mmol, 63%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.11 (dd, J = 8.0, 1.4 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.19 (d, J = 7.6 Hz, 1H), 4.64 – 4.53 (m, 1H), 4.32 – 4.13 (m, 4H), 3.88 (dd, J = 10.5, 4.1 Hz, 1H), 3.03 – 2.87 (m, 2H), 2.42 (s, 3H), 2.41 – 2.19 (m, 2H), 1.30 (q, J = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.1, 169.1, 162.6, 143.2, 139.3, 137.5, 134.5, 130.2, 129.4, 128.1, 127.9, 127.4, 125.0, 78.1, 62.0, 61.9, 47.4, 33.5, 32.9, 21.7, 14.2, 14.2.

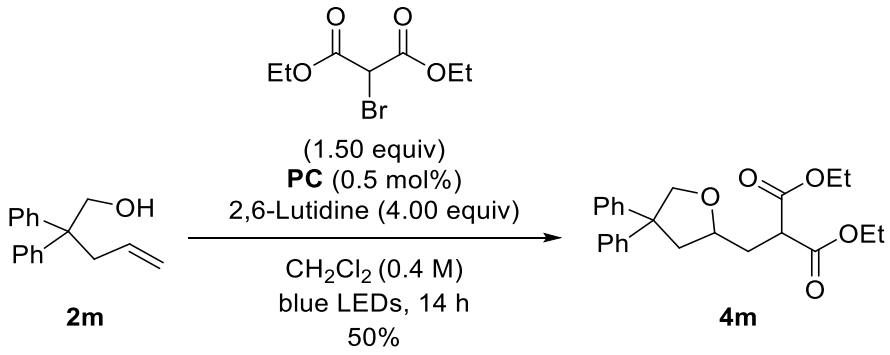
IR (thin film, cm^{-1}): 2982, 2938, 1729, 1614, 1593, 1568, 1462, 1393, 1369, 1319, 1303, 1255, 1237, 1159, 1140, 1085, 1064, 1028, 965, 925, 841,815, 803, 777, 742, 707, 686, 669, 633, 619, 571.

[17] Nicolai S.; Piemontesi C.; Waser J, A Palladium-Catalyzed Aminoalkynylation Strategy towards Bicyclic Heterocycles: Synthesis of (±)-Trachelanthamidine. *Angew. Chem. Int. Ed.* **2011**, *50*, 4680–4683.

HRMS (ESI+): *m/z* for $C_{24}H_{27}NNaO_7S$ $[M+Na]^+$: calc.: 496.1400, found: 496.1394.

Compound 4m:

Diethyl 2-((4,4-diphenyltetrahydrofuran-2-yl)methyl)malonate



Ether **4m** was prepared via GP2 using 2,2-diphenylpent-4-en-1-ol[18] (47.7 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (10-30% EtOAc in hexane) to give **4m** as a pale-yellow oil.

Yield: 39.7 mg, 0.100 mmol, 50%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.31 – 7.25 (m, 6H), 7.23 – 7.16 (m, 4H), 4.56 (dd, J = 8.8, 1.2 Hz, 1H), 4.23 – 4.15 (m, 4H), 4.12 (d, J = 8.8 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.59 (dd, J = 8.9, 5.7 Hz, 1H), 2.69 (ddd, J = 12.2, 6.0, 1.2 Hz, 1H), 2.32 (dd, J = 12.2, 9.2 Hz, 1H), 2.24 (ddd, J = 14.0, 8.9, 4.0 Hz, 1H), 2.13 (ddd, J = 14.2, 8.7, 5.7 Hz, 1H), 1.25 (td, J = 7.1, 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 169.6, 169.4, 146.2, 145.8, 128.6, 128.4, 127.2, 127.1, 126.6, 126.4, 76.8, 76.3, 61.6, 61.5, 56.2, 49.4, 44.8, 35.0, 14.2, 14.1.

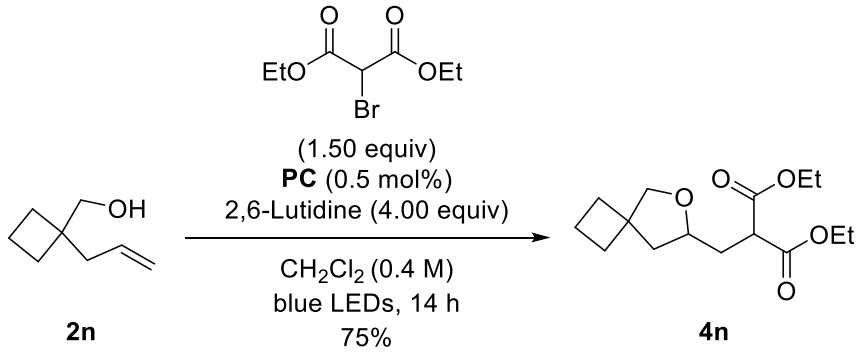
IR (thin film, cm^{-1}): 2939, 1746, 1729, 1493, 1446, 1390, 1369, 1328, 1260, 1238, 1176, 1152, 1078, 1052, 1031, 973, 922, 861, 774, 755, 729, 699, 667, 585, 547, 514.

HRMS (ESI+): *m/z* for $C_{24}H_{28}NaO_5$ $[M+Na]^+$: calc.: 419.1829, found: 419.1831.

[18] Hemric B. N.; Chen A. W.; Wang Q., Copper-Catalyzed Modular Amino Oxygenation of Alkenes: Access to Diverse 1,2-Amino Oxygen-Containing Skeletons. *J. Org. Chem.* **2019**, *84*, 3, 1468–1488.

Compound 4n:

Diethyl 2-((6-oxaspiro[3.4]octan-7-yl)methyl)malonate



Ether **4n** was prepared via GP2 using (1-allylcyclobutyl)methanol[19] (25.2 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (10-30% EtOAc in hexane) to give **4n** as a pale-yellow oil.

Yield: 42.7 mg, 0.150 mmol, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.26 – 4.14 (m, 4H), 3.90 (dddd, J = 8.9, 8.0, 6.4, 4.1 Hz, 1H), 3.74 – 3.65 (m, 2H), 3.54 (dd, J = 8.8, 5.8 Hz, 1H), 2.18 – 1.94 (m, 7H), 1.93 – 1.77 (m, 2H), 1.57 (dd, J = 12.2, 7.8 Hz, 1H), 1.26 (td, J = 7.1, 2.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.8, 169.6, 78.9, 76.4, 61.5, 61.5, 49.5, 46.3, 45.4, 35.0, 33.3, 31.4, 16.6, 14.2, 14.2.

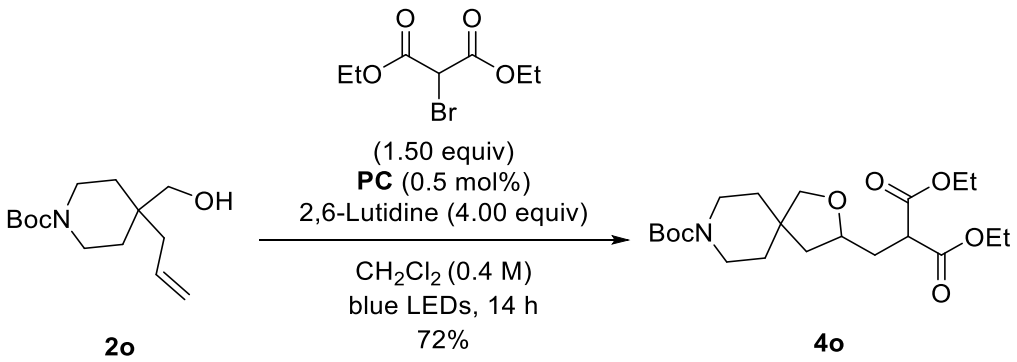
IR (thin film, cm^{-1}): 2976, 2932, 2854, 1731, 1445, 1390, 1368, 1328, 1258, 1151, 1046, 1031, 861

HRMS (ESI+): *m/z* for $C_{15}H_{24}NaO_5$ $[M+Na]^+$: calc.: 307.1516 , found: 307.1520.

[19] Tani K.; Naganawa A.; Ishida A.; Sagawa K.; Harada H.; Ogawa M.; Maruyama T.; Ohuchida S.; Nakai H.; Kondo K.; Toda M., Development of a highly selective EP2-receptor agonist. Part 1: identification of 16-hydroxy-17,17-trimethylene PGE_2 derivatives. *Bioorganic & Medicinal Chemistry* **2002**, *10*, 1093–1106.

Compound 4o:

Diethyl 2-((8-(*tert*-butoxycarbonyl)-2-oxa-8-azaspiro[4.5]decan-3-yl)methyl)malonate



Ether **4o** was prepared via GP2 using *tert*-butyl 4-allyl-4-(hydroxymethyl)piperidine-1-carboxylate (51.1 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4o** as a pale-yellow oil.

Yield: 59.5 mg, 0.144 mmol, 72%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.25 – 4.12 (m, 4H), 3.97 (tdd, J = 8.8, 6.8, 4.0 Hz, 1H), 3.64 – 3.49 (m, 3H), 3.45 – 3.25 (m, 4H), 2.17 (ddd, J = 14.1, 8.8, 3.9 Hz, 1H), 2.06 (ddd, J = 14.0, 9.0, 5.8 Hz, 1H), 1.95 (dd, J = 12.5, 6.7 Hz, 1H), 1.51 (q, J = 5.7 Hz, 4H), 1.44 (s, 9H), 1.34 (dd, J = 12.6, 8.5 Hz, 1H), 1.26 (td, J = 7.1, 2.2 Hz, 6H)

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.6, 169.4, 154.9, 79.6, 77.2, 76.3, 61.6, 61.6, 49.5, 43.4, 42.7, 41,7 (determined by ^{1}H-^{13}C HSQC), 35.9, 35.1, 34.8, 28.6, 28.5, 14.2, 14.2.

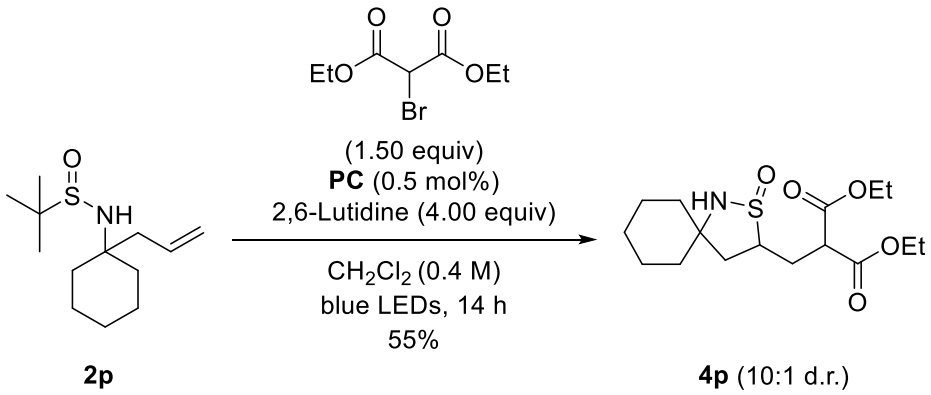
IR (thin film, cm^{-1}): 2977, 2929, 2854, 1748, 1732, 1693, 1466, 1445, 1423, 1392, 1366, 1334, 1262, 1244, 1155, 1114, 1095, 1051, 968, 863, 825, 769, 596, 549,

2936, 1766, 1748, 1731, 1691, 1467, 1446, 1423, 1393, 1366, 1280, 1264, 1247, 1151, 1095, 1064, 1039, 1000, 073, 958, 863, 824, 769, 726, 638, 587.

HRMS (ESI+): *m/z* for $C_{21}H_{35}NNaO_7$ $[M+Na]^+$: calc.: 436.2306, found: 436.2307.

Compound 4p:

Diethyl 2-((2-oxido-2-thia-1-azaspiro[4.5]decan-3-yl)methyl)malonate



2p **4p** (10:1 d.r.)

Isothiazolidine *S*-oxides **4p** was prepared via GP2 using racemic *N*-(1-allylcyclohexyl)-2-methylpropane-2-sulfinamide[20] (48.7 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4p** as a pale-yellow oil. The product was isolated as an inseparable 10:1 mixture of diastereomers.

Yield: 38.0 mg, 0.110 mmol, 55%, d.r. = 10:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.39 (s, 1H), 4.35 (s, 0.1H), 4.26 – 4.16 (m, 4.4H), 3.58 – 3.49 (m, 1.1H), 3.26 – 3.18 (m, 0.1H), 3.09 (ddt, J = 12.6, 8.6, 6.2 Hz, 1H), 2.65 (dd, J = 13.4, 7.6 Hz, 0.10H), 2.39 (ddd, J = 14.9, 8.6, 6.4 Hz, 1H), 2.29 – 2.17 (m, 2H), 2.05 (t, J = 12.9 Hz, 1.20H), 1.89–1.83 (m, 1.20H), 1.67 (ddd, J = 12.8, 8.6, 3.8 Hz, 1H), 1.59 – 1.33 (m, 9H), 1.26 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.0, 168.8, 168.7, 168.6, 69.1, 67.6, 62.0, 62.0, 61.8, 61.8, 61.7, 50.6, 50.3, 43.3, 42.7, 40.3, 38.8, 38.6, 31.0, 27.0, 25.2, 25.1, 24.4, 24.2, 24.1, 14.2, 14.2.

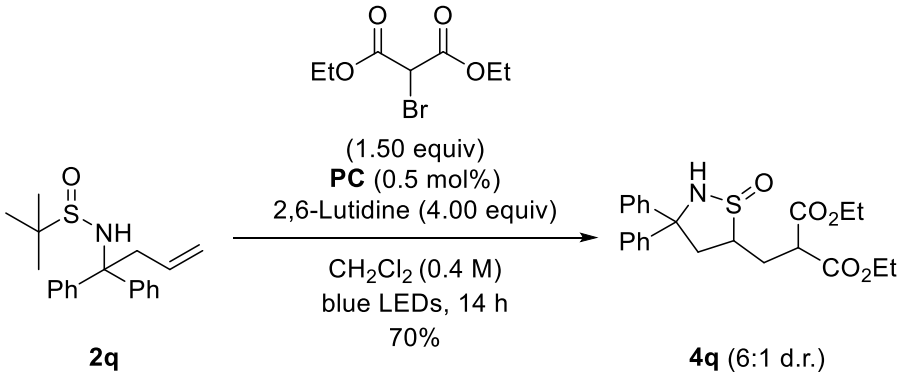
[20] Chen Y.; Wu X.; Yang S.; Zhu C., Asymmetric Radical Cyclization of Alkenes by Stereospecific Homolytic Substitution of Sulfinamides. *Angew. Chem.Int. Ed.* **2022**, *61*, e202201027.

IR (thin film, cm^{-1}): 3235, 2981, 2931, 2856, 1731, 1447, 1391, 1370, 1340, 1300, 1275, 1235, 1177, 1152, 1045, 984, 920, 858, 785, 605, 515.

HRMS (ESI+): *m/z* for $C_{16}H_{27}NNaO_5S$ $[M+Na]^+$: calc.: 368.1502, found: 368.1497.

Compound 4q:

Diethyl 2-((1-oxido-3,3-diphenylisothiazolidin-5-yl)methyl)malonate



2q **4q** (6:1 d.r.)

Isothiazolidine *S*-oxides **4q** was prepared via GP2 using racemic *N*-(1,1-diphenylbut-3-en-1-yl)-2-methylpropane-2-sulfinamide (65.5 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (30-50% EtOAc in hexane) to give **4q** as a pale-yellow oil. The product was isolated as a 6:1 mixture of diastereomers. The characterization data for the major diastereomer is reported.

Yield: 60.1 mg, 0.140 mmol, 70%, d.r. = 6:1

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.39 – 7.19 (m, 10H), 4.91 (s, 1H), 4.24– 4.06 (m, 4H), 3.55 (dd, J = 8.4, 6.9 Hz, 1H), 3.10 – 2.96 (m, 2H), 2.90–2.85 (m, 1H), 2.48 (dt, J = 14.9, 7.4 Hz, 1H), 2.28 (ddd, J = 14.6, 8.5, 5.9 Hz, 1H), 1.21 (td, J = 7.1, 2.3 Hz, 6H)

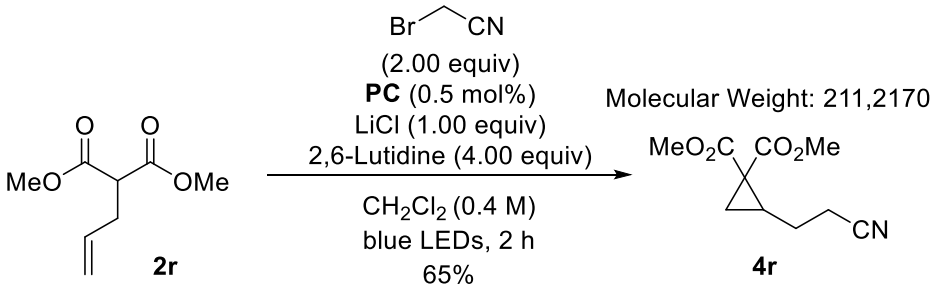
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.8, 168.6, 146.1, 144.4, 128.6 (2C), 128.6 (2C), 127.6, 127.5 (2C), 127.4, 126.5 (2C), 75.6, 62.2 (2C), 61.9, 50.3, 42.4, 26.3, 14.1 (2C).

IR (thin film, cm^{-1}):3230, 3060, 2982, 2935, 1730, 1598, 1492, 1447, 1370, 1340, 1302, 1278, 1234, 1182, 1154, 1050, 1033, 1002, 916, 859, 758, 701, 628, 528.

HRMS (ESI+): *m/z* for $C_{23}H_{27}NNaO_5S$ $[M+Na]^+$: calc.: 452.1502, found: 452.1496.

11.5 Substrate Scope for Cyclopropanation

Compound 4r:



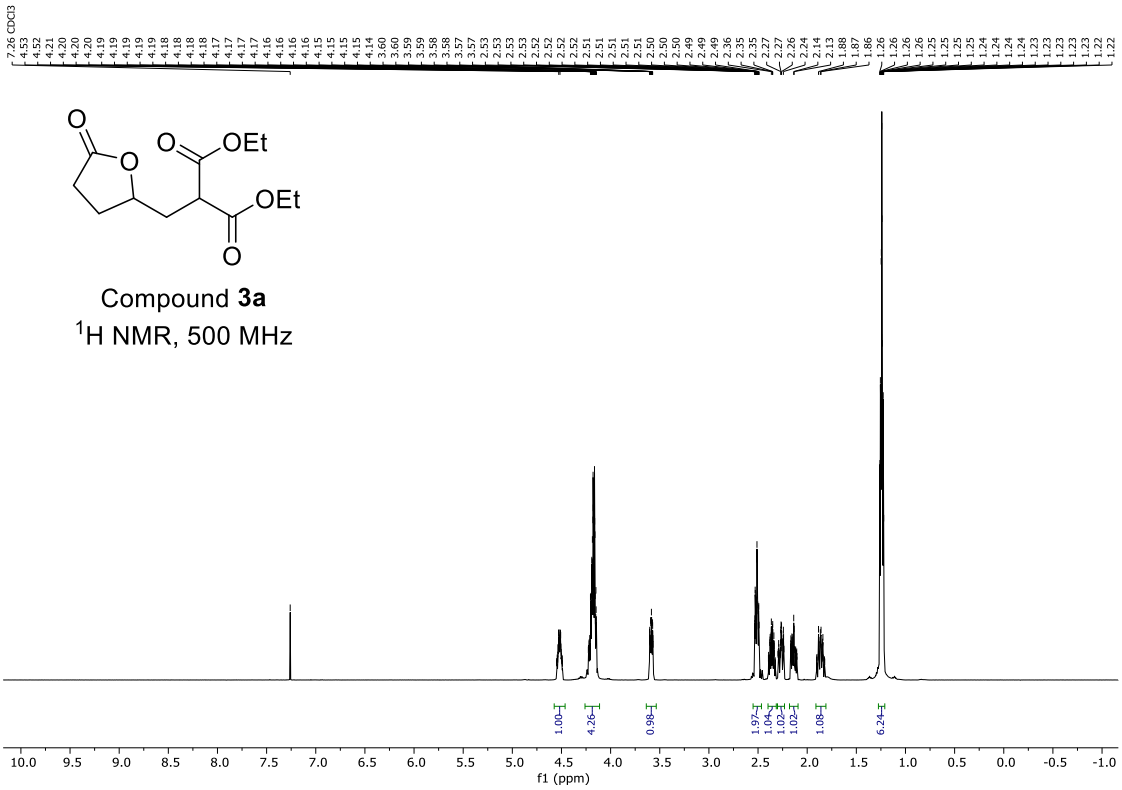
To a glass vial charged with **PC** (0.33 mg, 0.0010 mmol, 0.50 mol%) in CH_2Cl_2 (500 µL, 0.4 M) were added dimethyl allyl malonate (34.4 mg, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), LiCl (8.48 mg, 0.200 mmol, 1.00 equiv) and bromoacetonitrile (48.0 mg, 0.400 mmol, 2.00 equiv) sequentially. The vial was equipped with a magnetic stirrer bar and capped with a screwcap. The reaction was irradiated in a 350 W photoreactor (*vide supra*) for 2 h. The crude product was purified via column chromatography (10-30% EtOAc in hexane) to give **4r** as a pale-yellow oil.

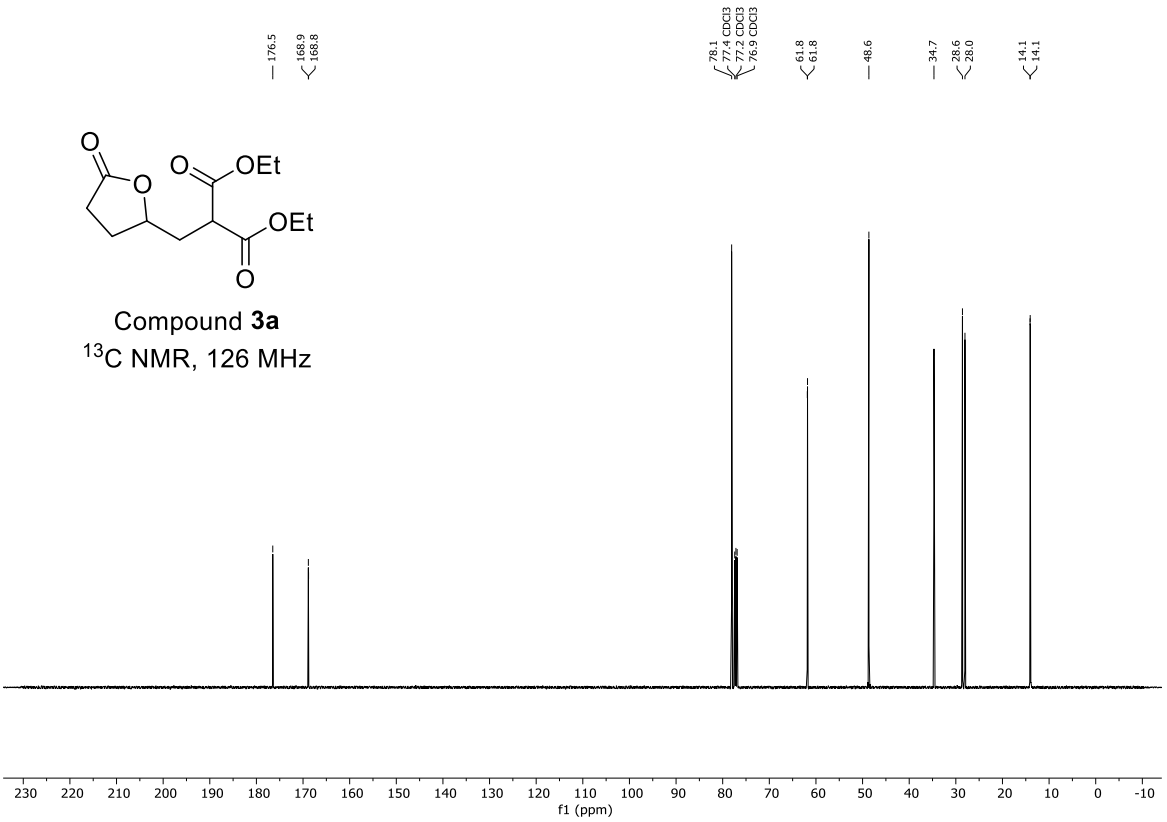
Yield: 27.6 mg, 0.131 mmol, 65%

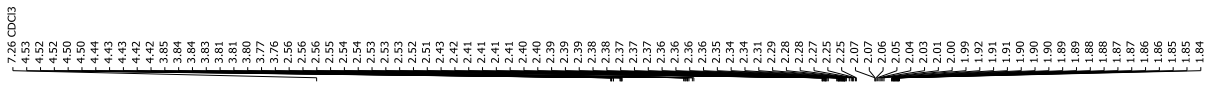
The spectral data match those reported.[21]

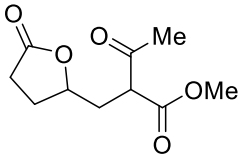
[21] D. M. Fischer, H. Lindner, W. M. Amberg and E. M. Carreira, *J. Am. Chem. Soc.*, 2023, **145**, 774-780

12. ^{1}H, ^{13}C, ^{19}F NMR Spectra

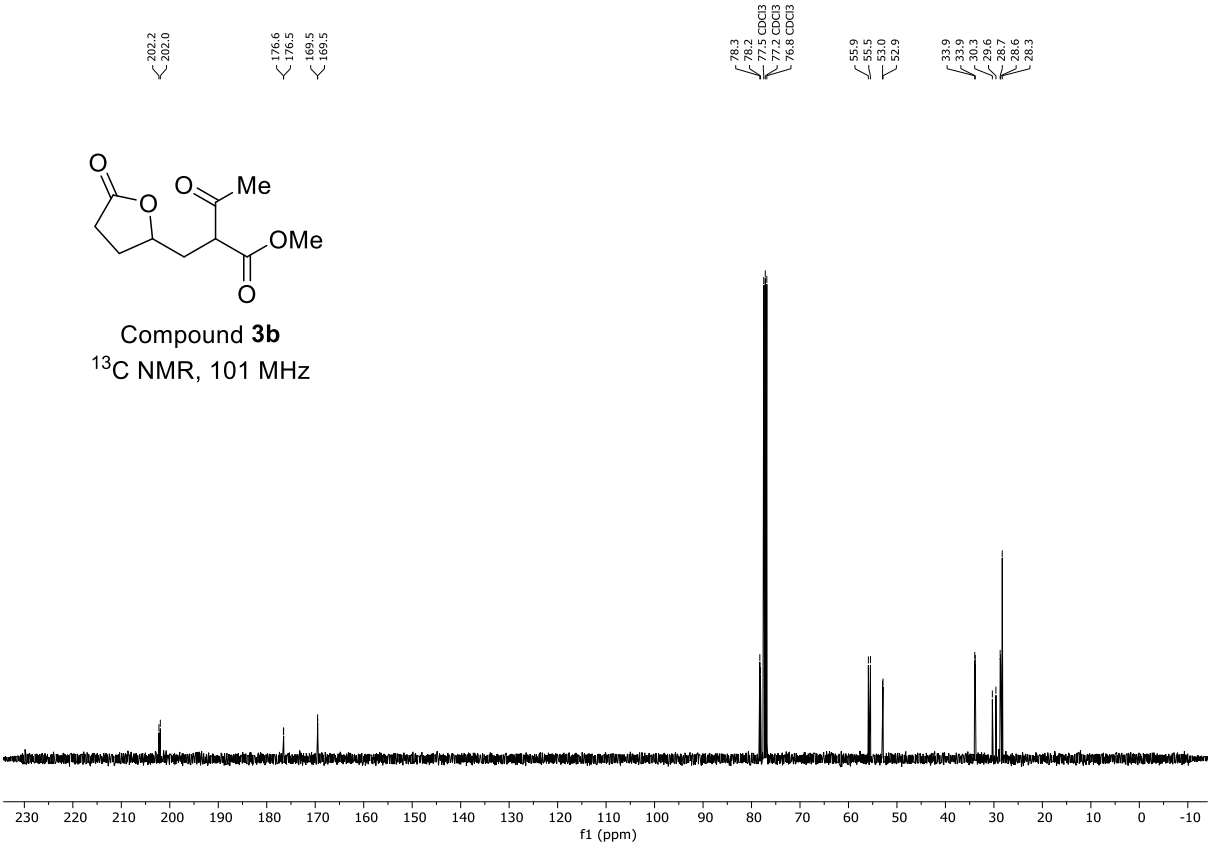




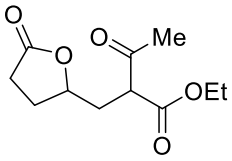




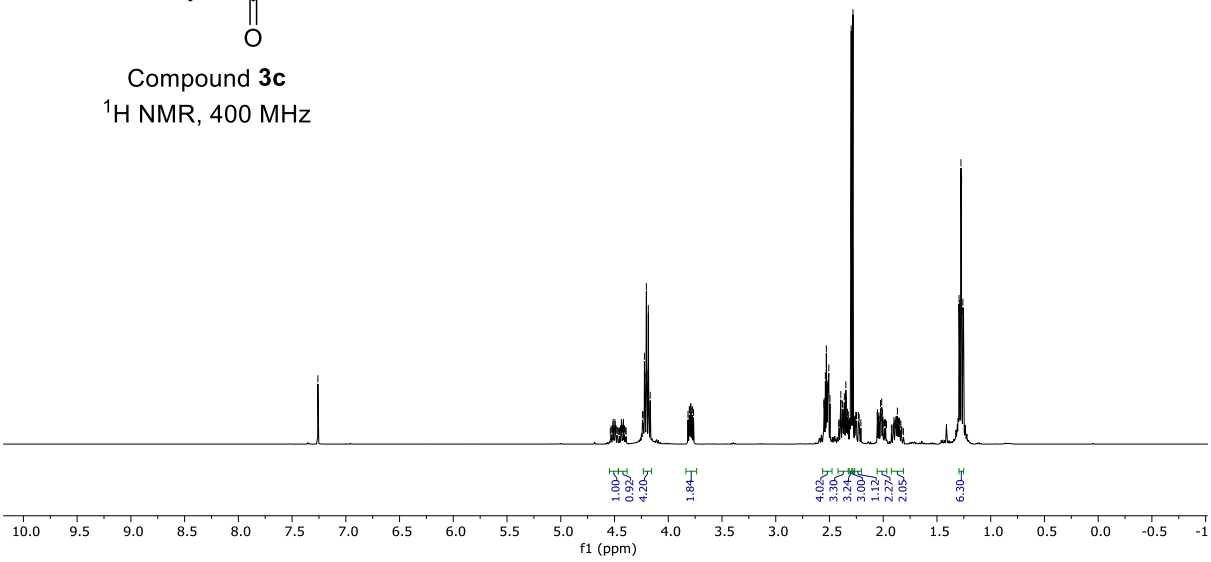
Compound **3b**
^{1}H NMR, 400 MHz

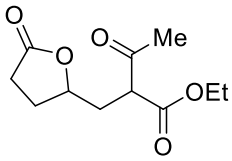


Compound **3b**
^{13}C NMR, 101 MHz

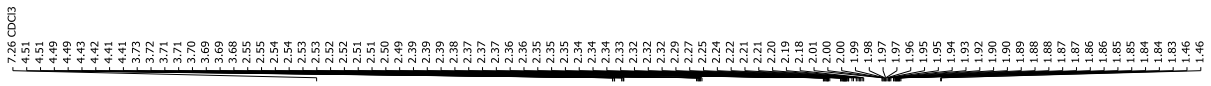


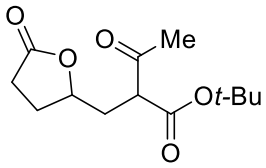
Compound **3c**
^{1}H NMR, 400 MHz



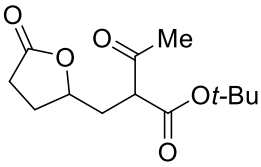


Compound **3c**
^{13}C NMR, 101 MHz

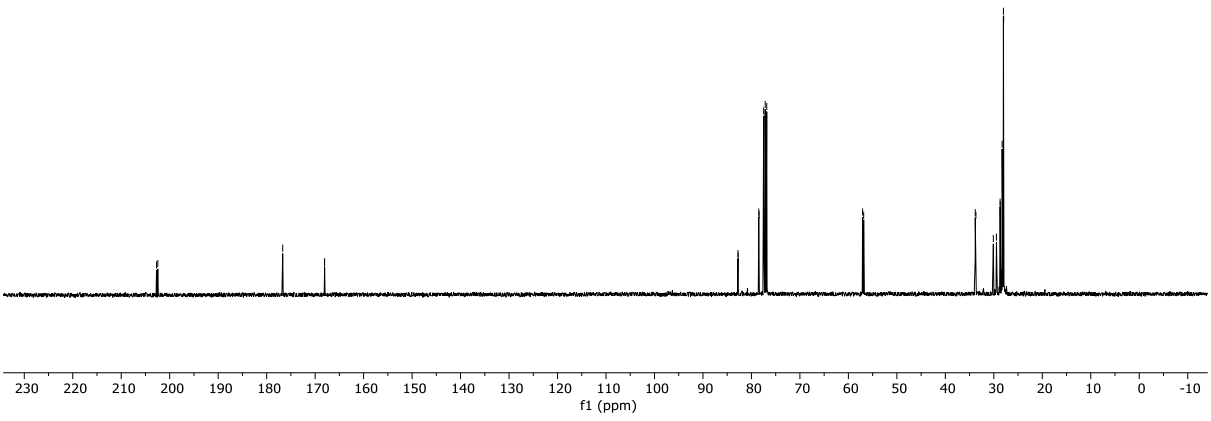


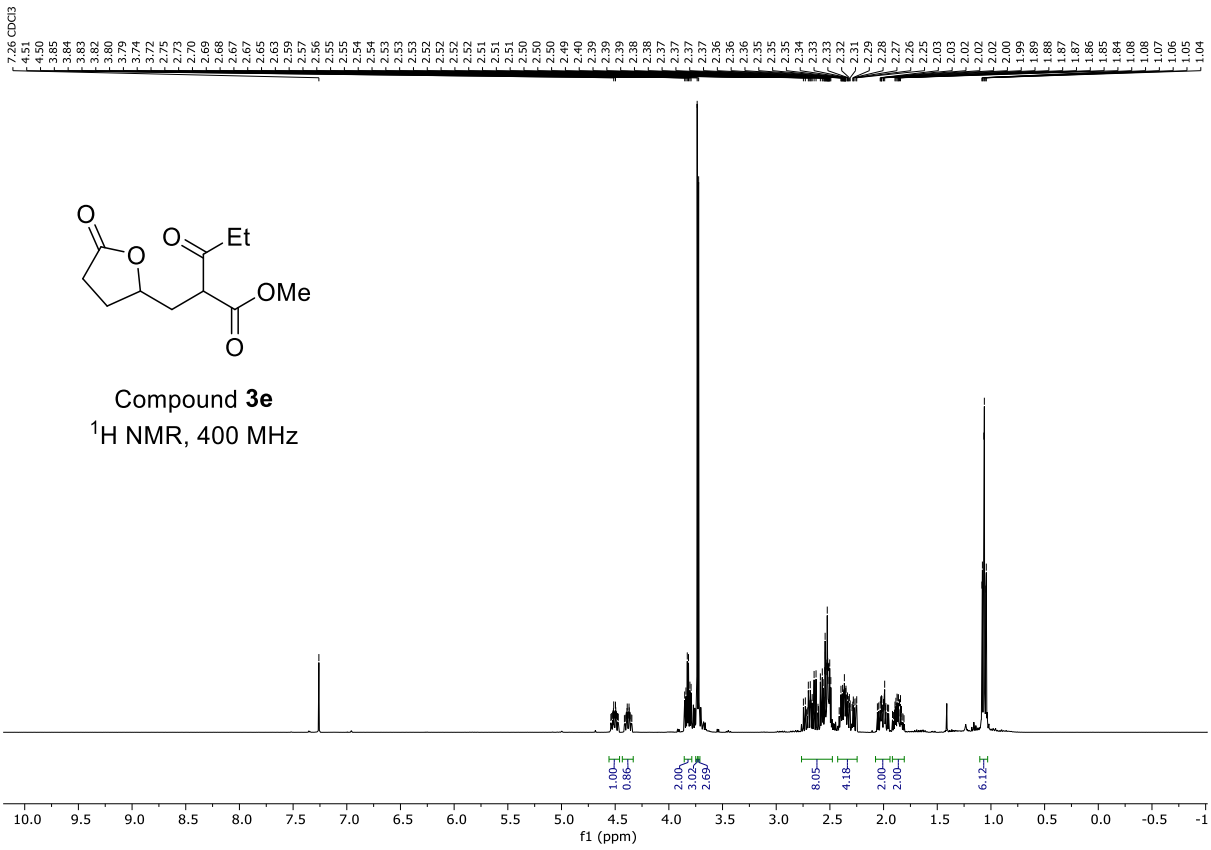


Compound **3d**
^{1}H NMR, 400 MHz

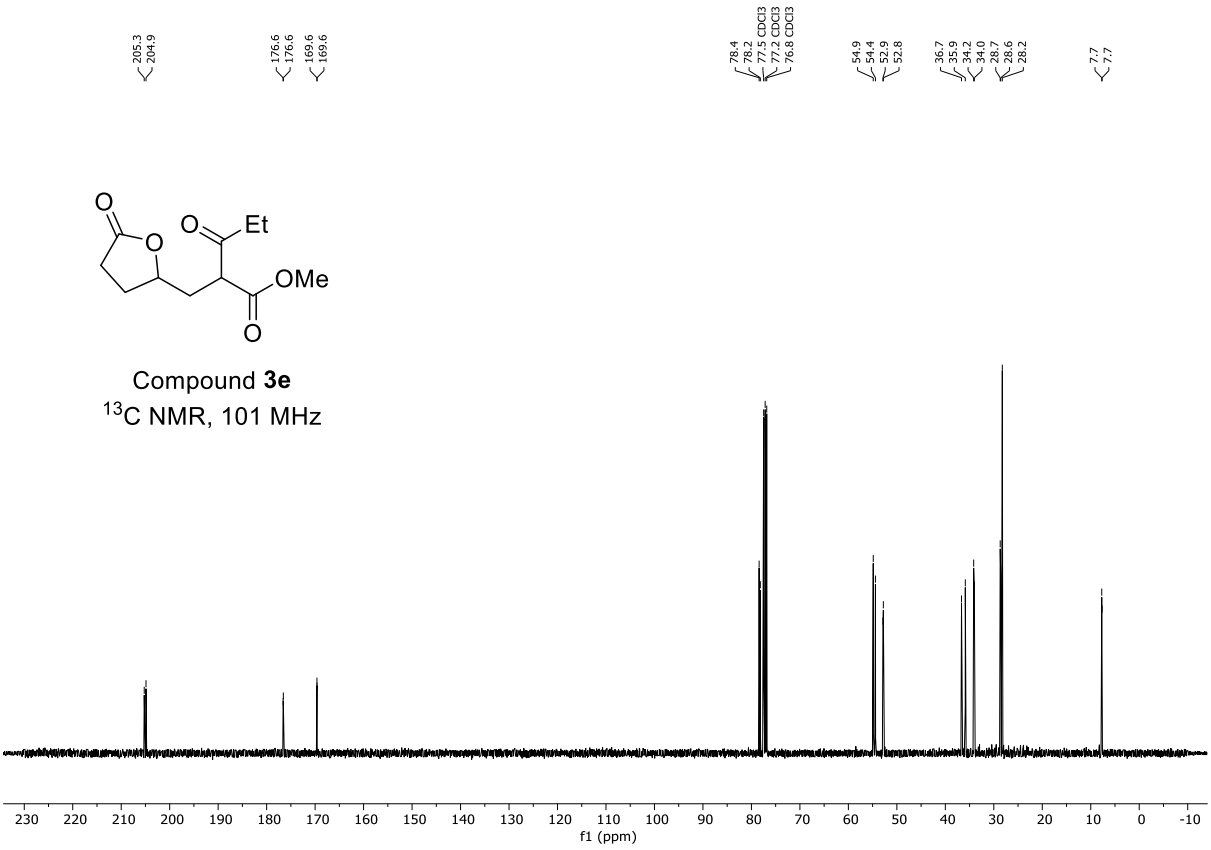


Compound **3d**
^{13}C NMR, 101 MHz

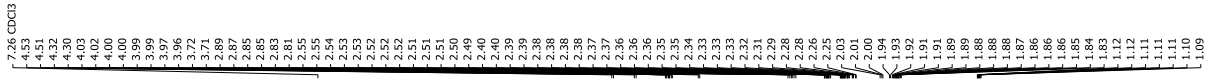


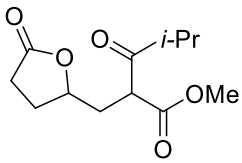


Compound **3e**
^{1}H NMR, 400 MHz

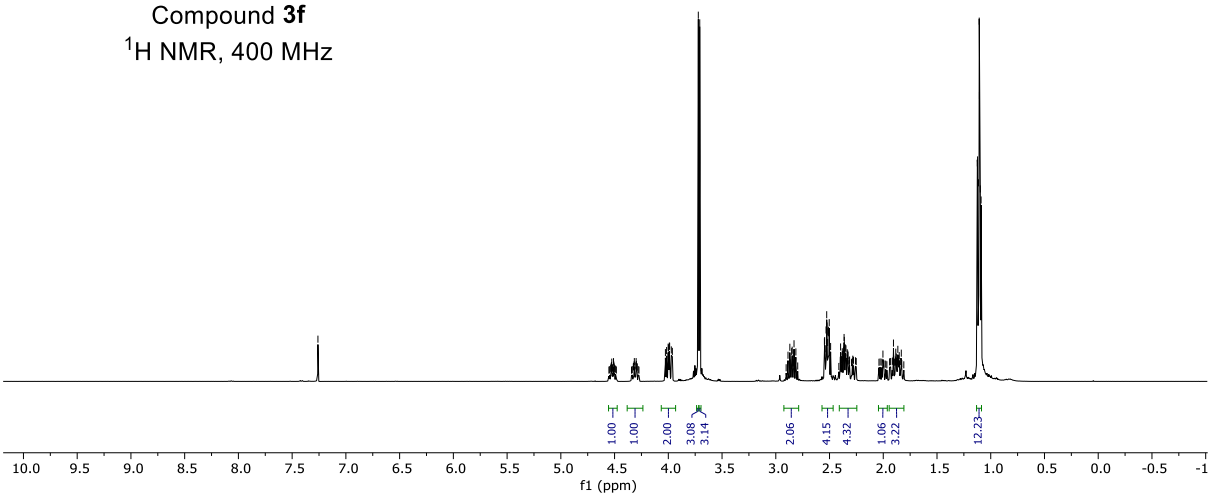


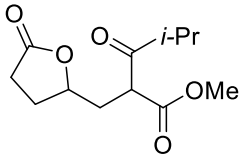
Compound **3e**
^{13}C NMR, 101 MHz



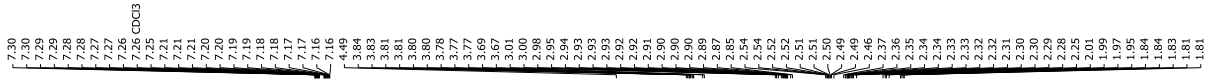


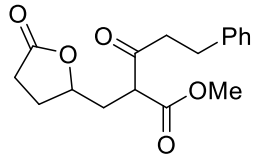
Compound **3f**
^{1}H NMR, 400 MHz



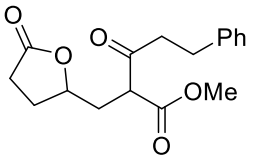


Compound **3f**
^{13}C NMR, 101 MHz

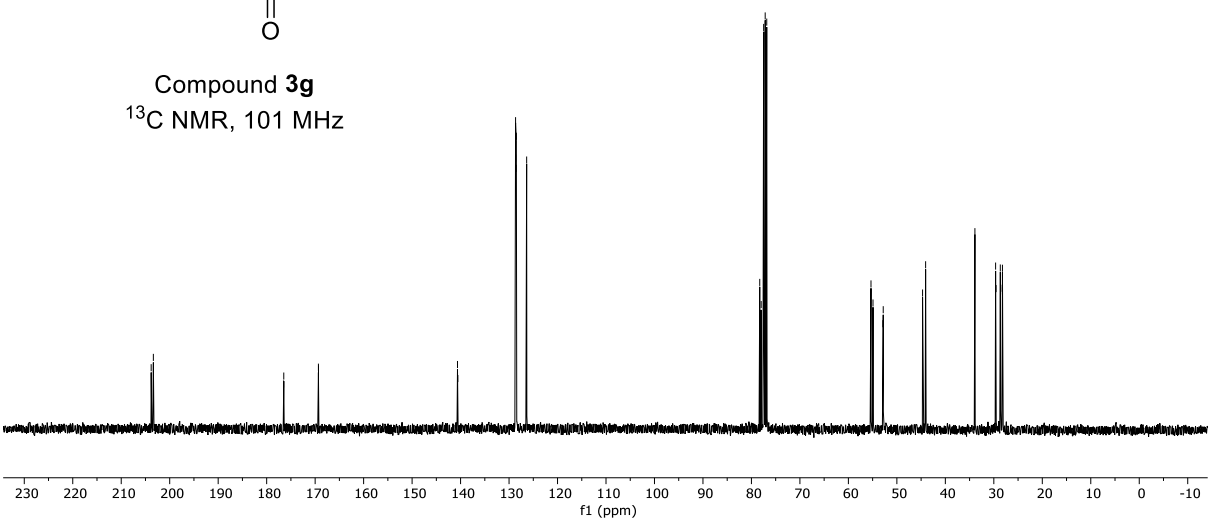


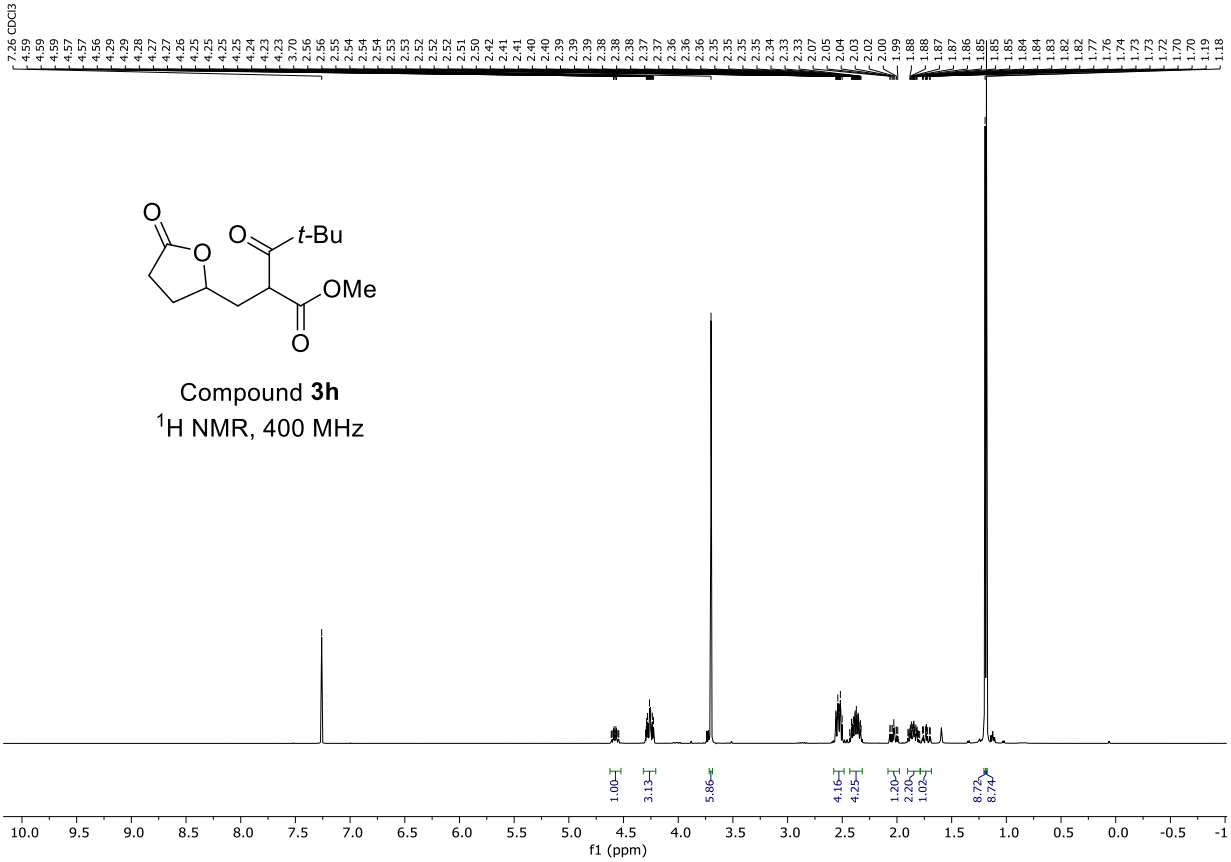


Compound **3g**
^{1}H NMR, 400 MHz

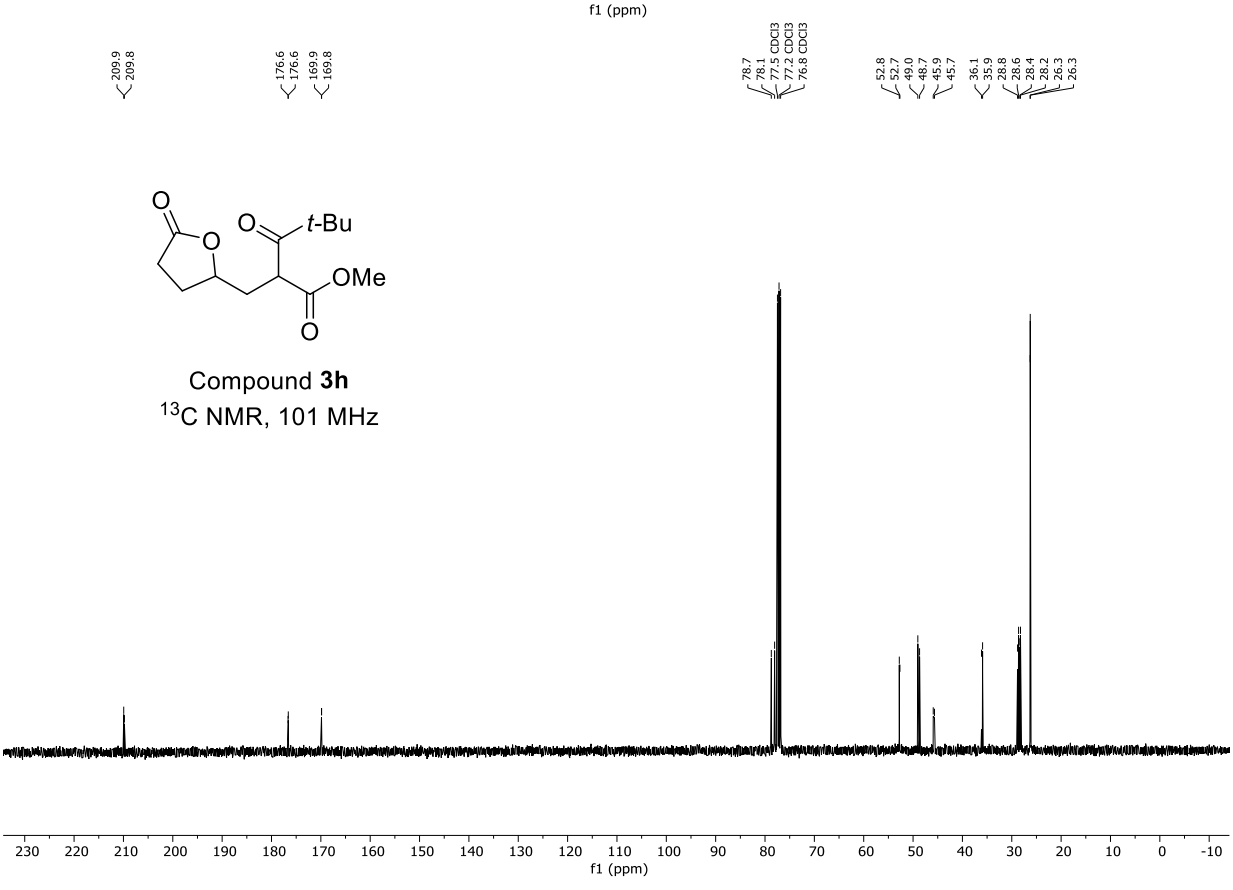


Compound **3g**
^{13}C NMR, 101 MHz

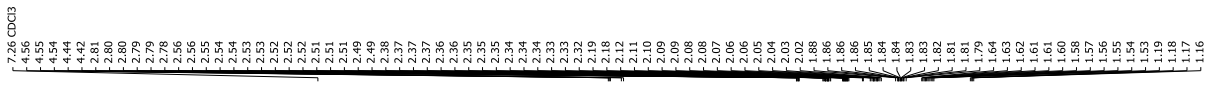


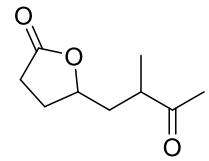


Compound **3h**
^{1}H NMR, 400 MHz

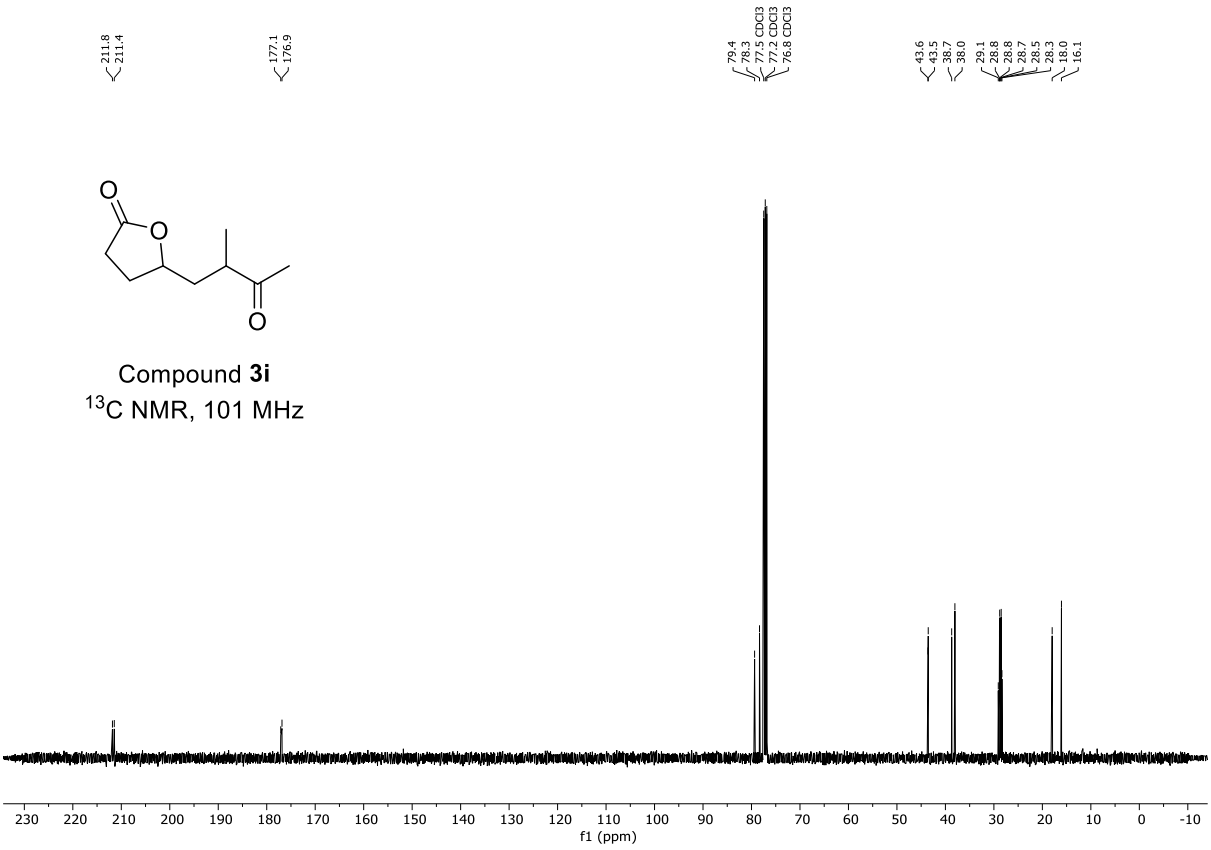


Compound **3h**
^{13}C NMR, 101 MHz

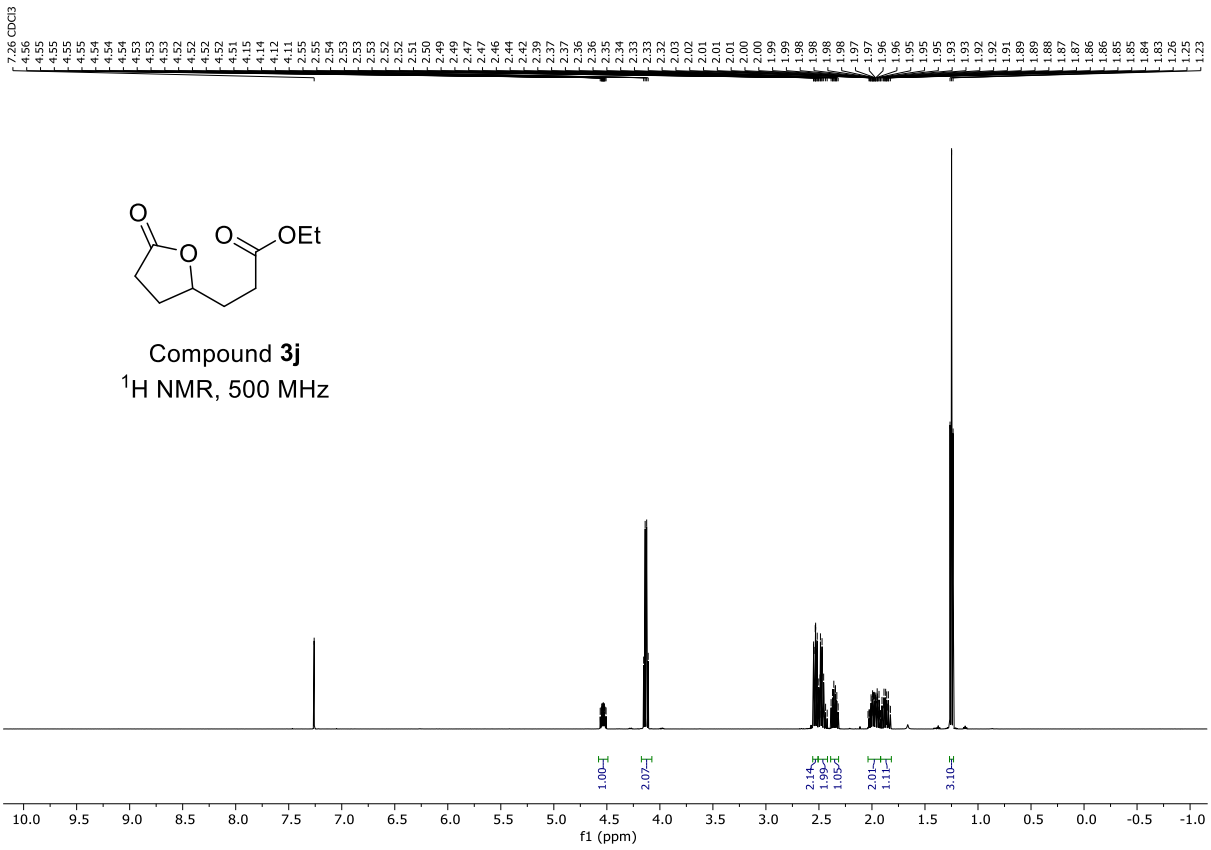




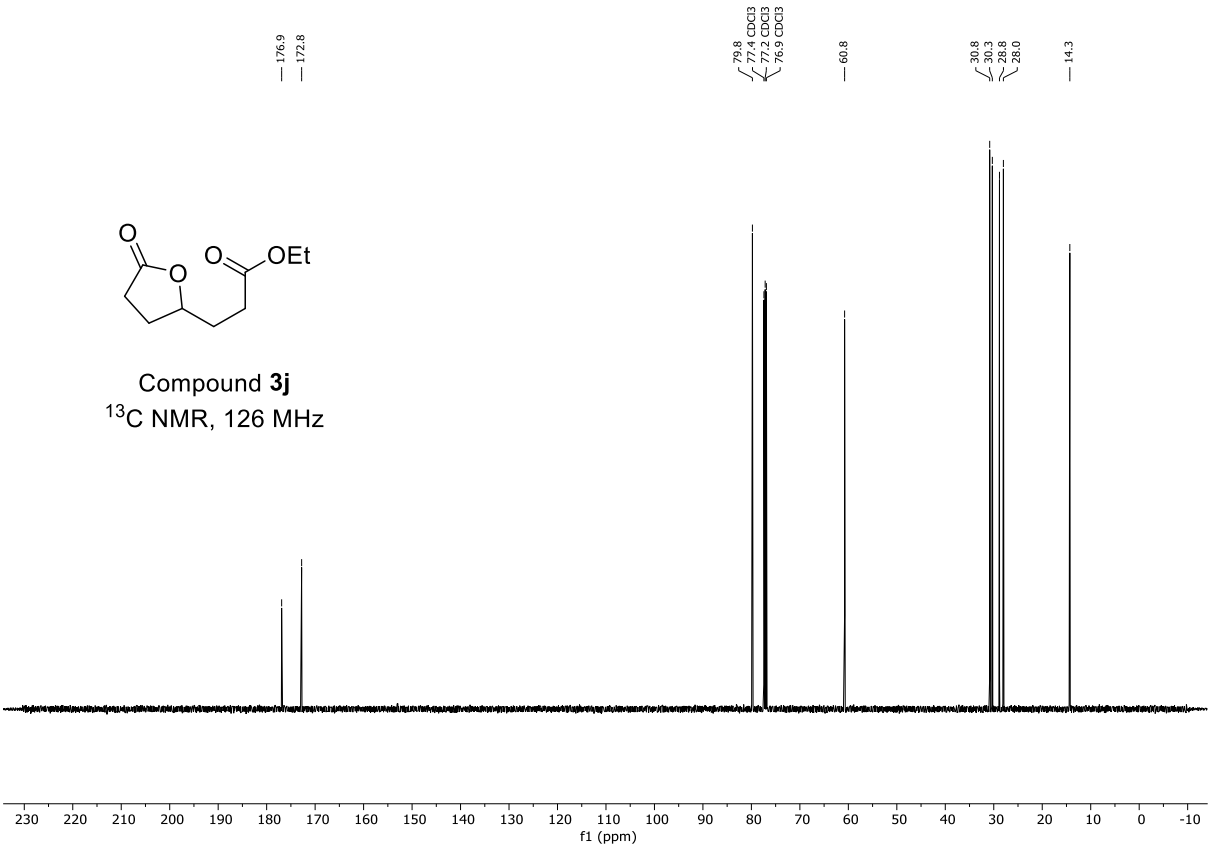
Compound **3i**
^{1}H NMR, 400 MHz



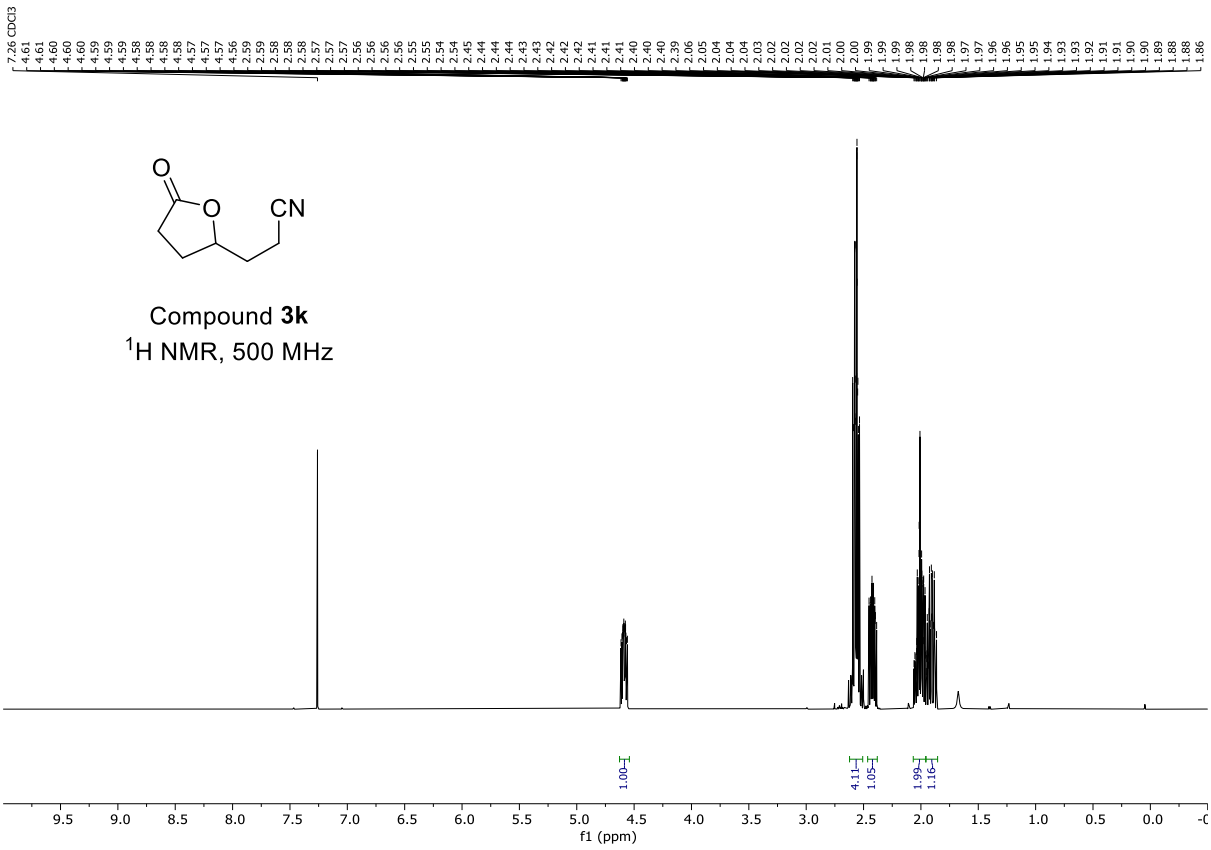
Compound **3i**
^{13}C NMR, 101 MHz



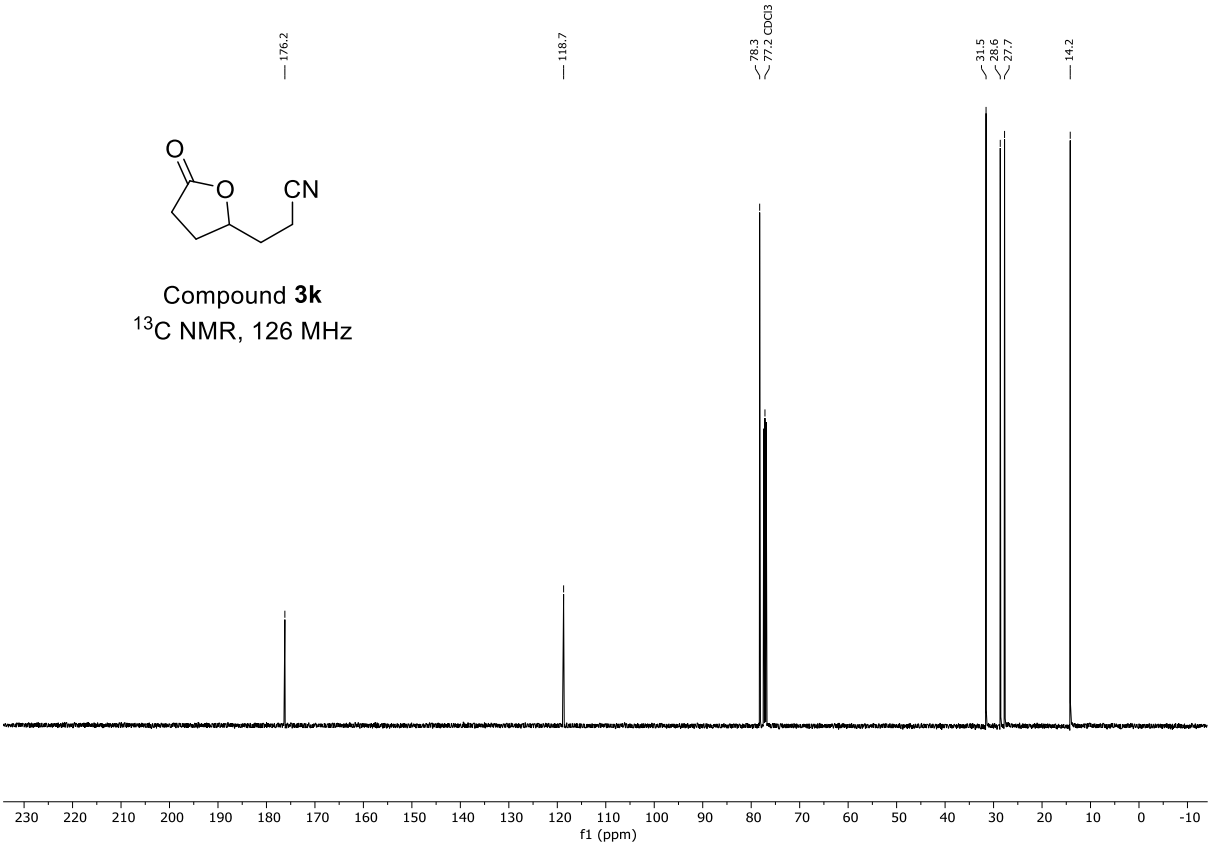
Compound **3j**
^{1}H NMR, 500 MHz



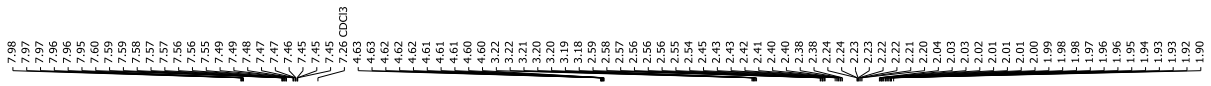
Compound **3j**
^{13}C NMR, 126 MHz

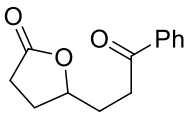


Compound **3k**
^{1}H NMR, 500 MHz

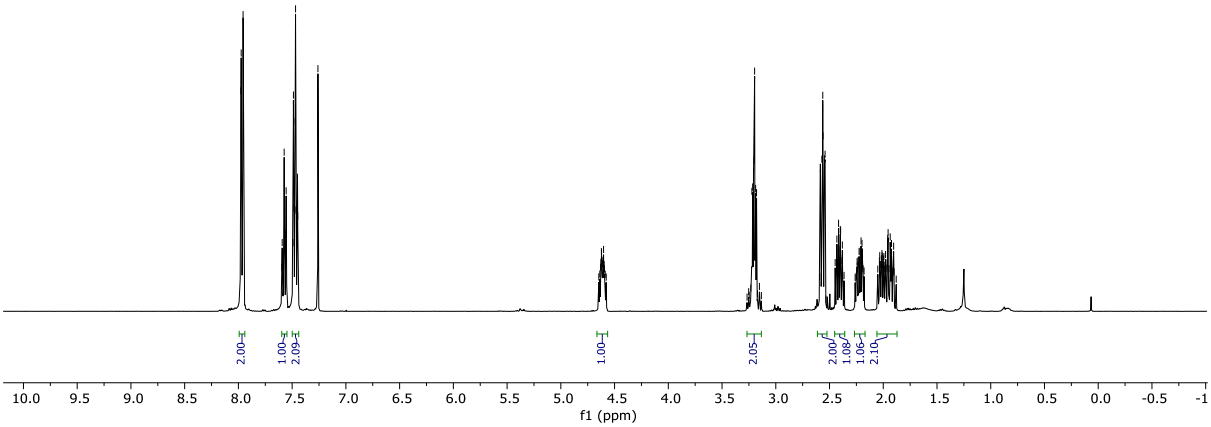


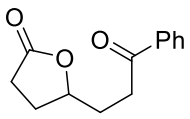
Compound **3k**
^{13}C NMR, 126 MHz



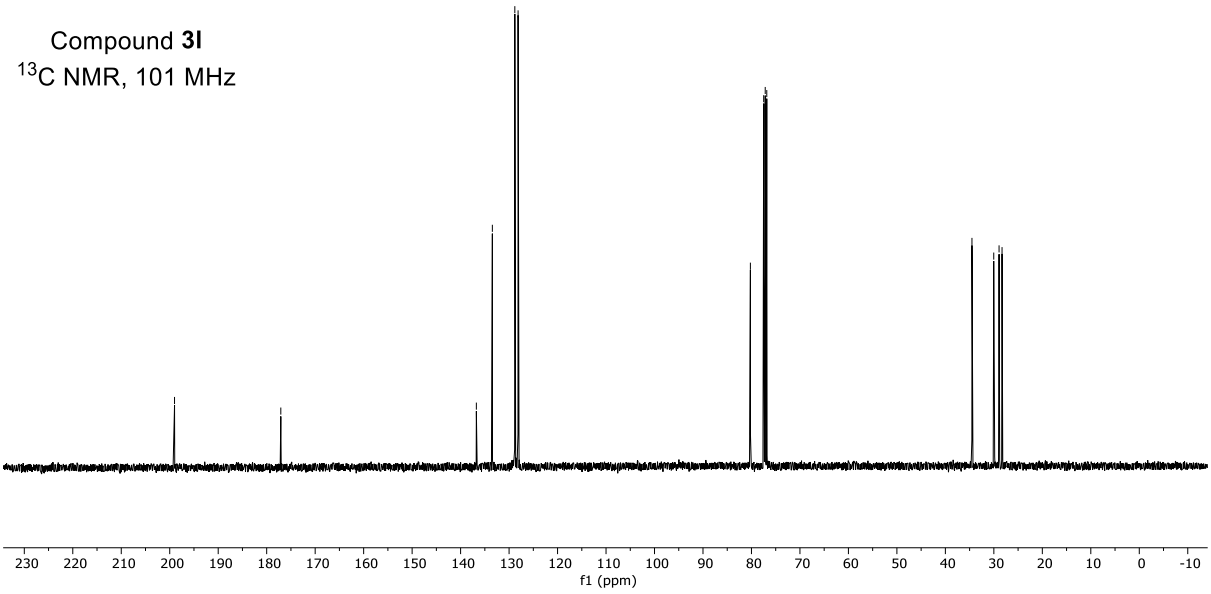


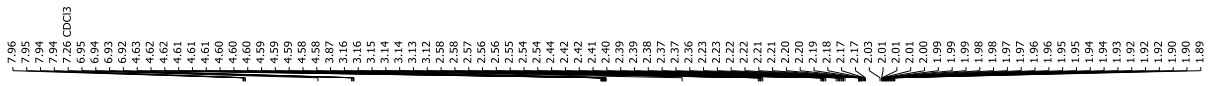
Compound **3l**
^{1}H NMR, 400 MHz

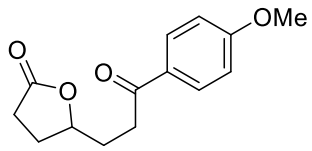




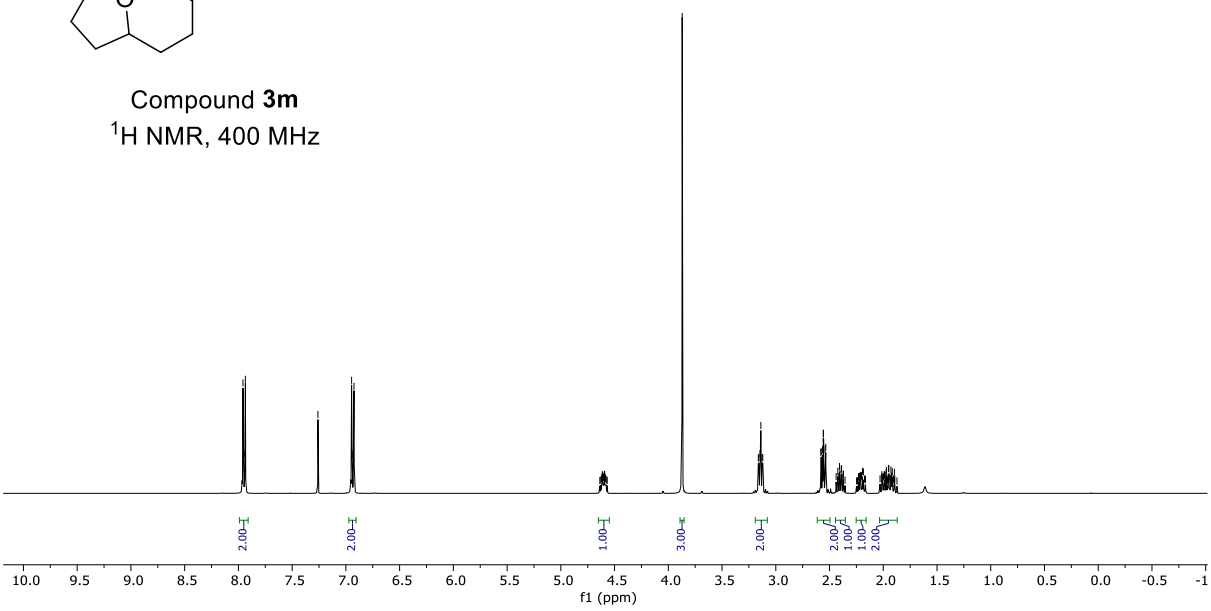
Compound **3l**
^{13}C NMR, 101 MHz

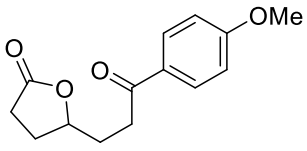




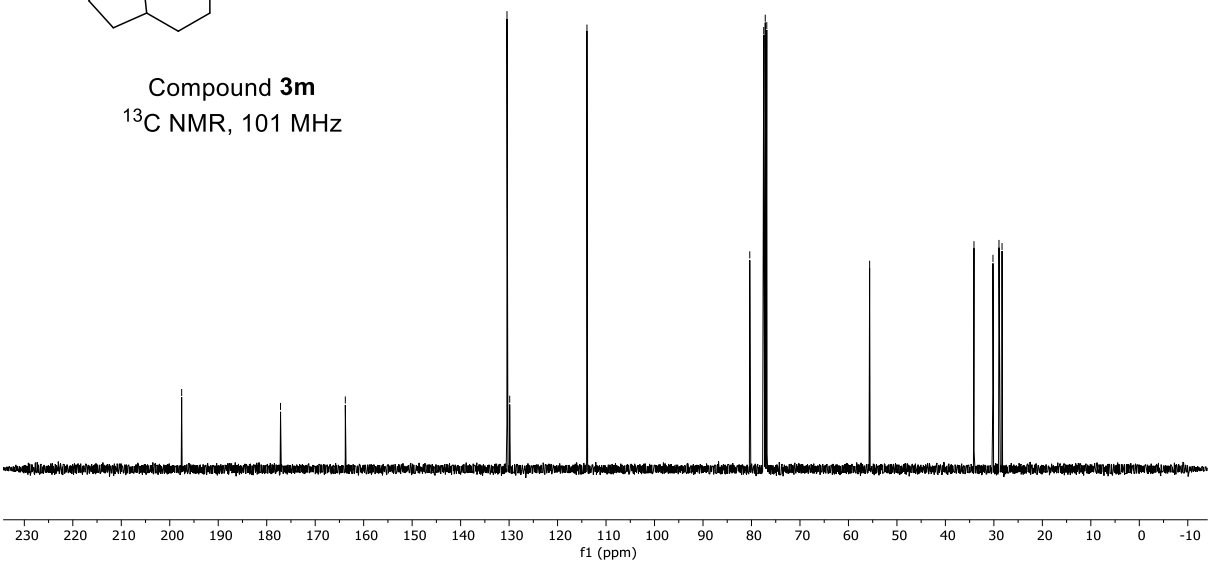


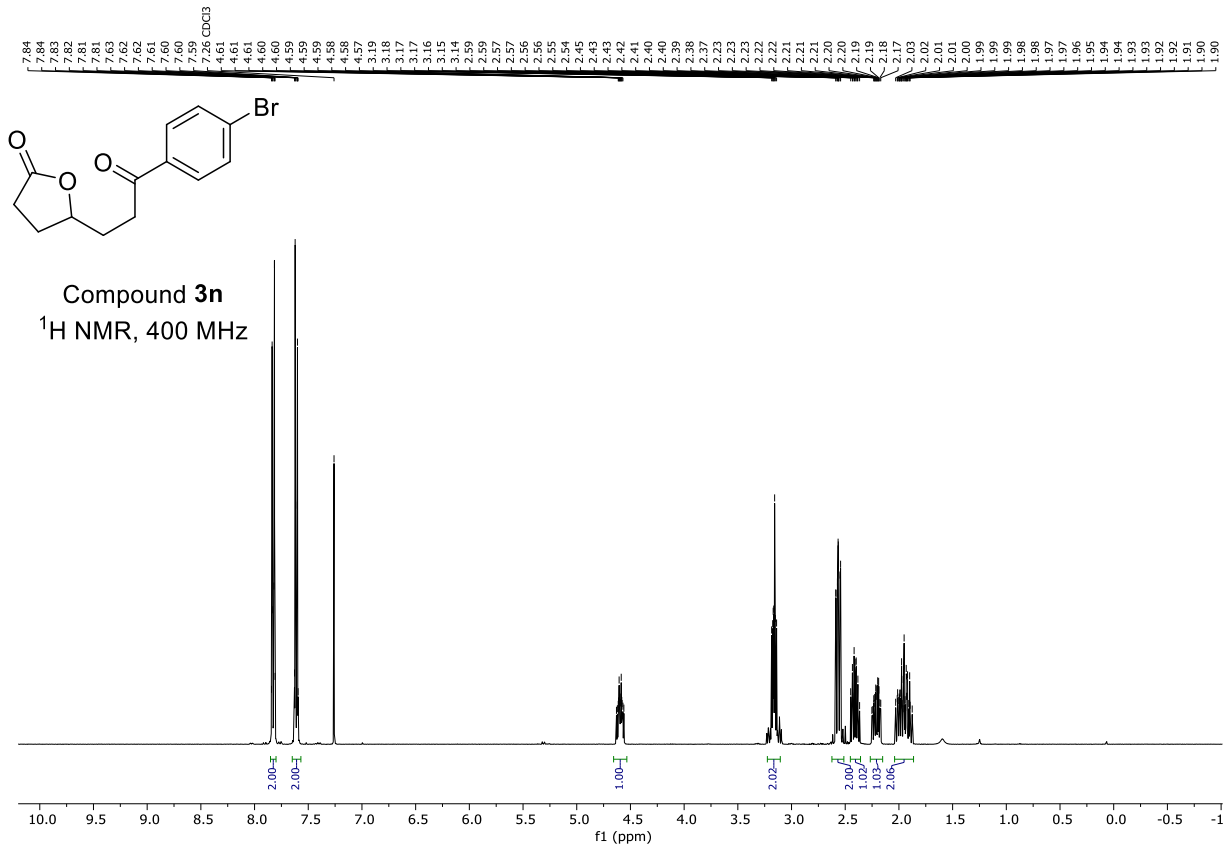
Compound **3m**
^{1}H NMR, 400 MHz

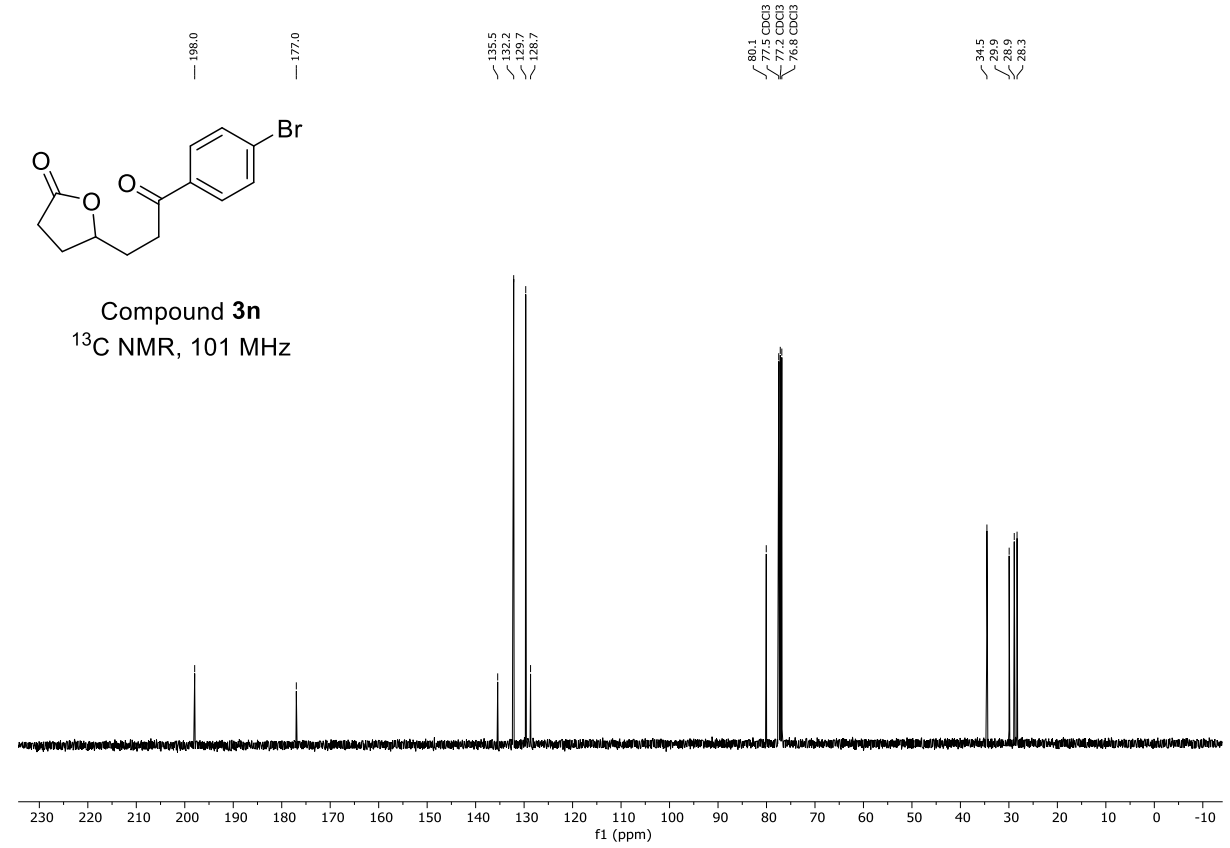


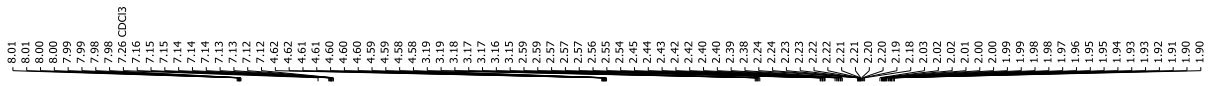


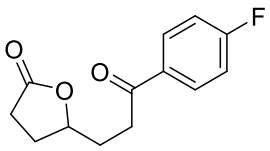
Compound **3m**
^{13}C NMR, 101 MHz



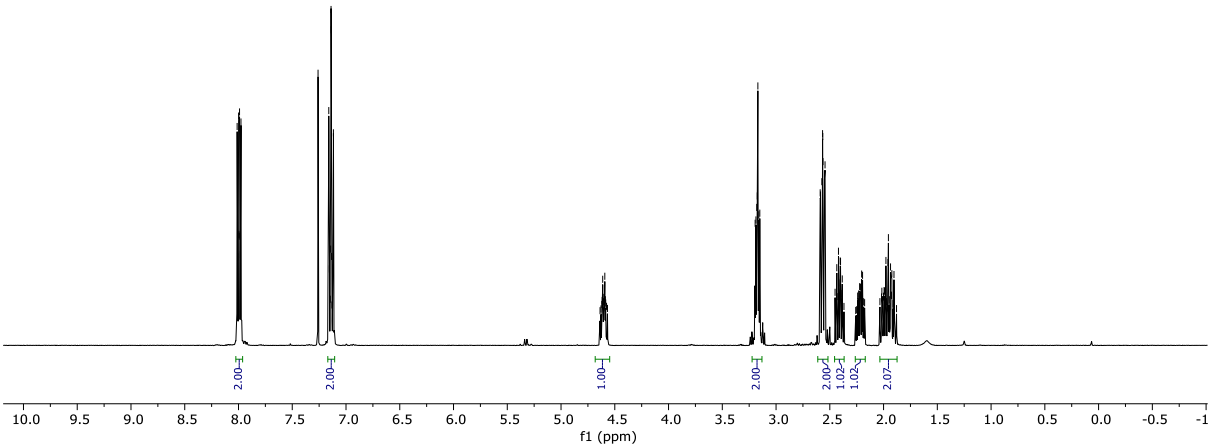

Br
O
O
O
Compound **3n**
^{1}H NMR, 400 MHz
f1 (ppm)

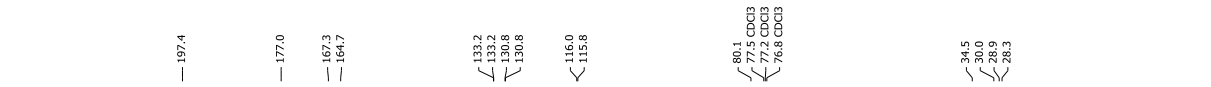

Br
O
O
O
Compound **3n**
^{13}C NMR, 101 MHz
f1 (ppm)

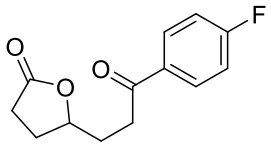




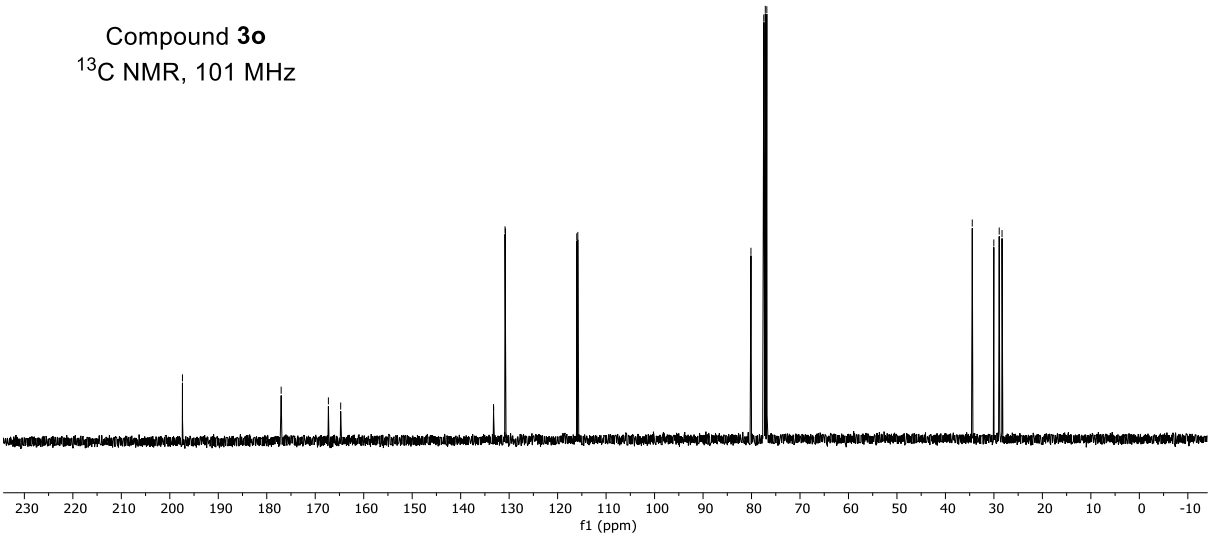
Compound **3o**
^{1}H NMR, 400 MHz

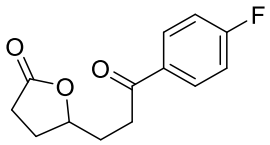






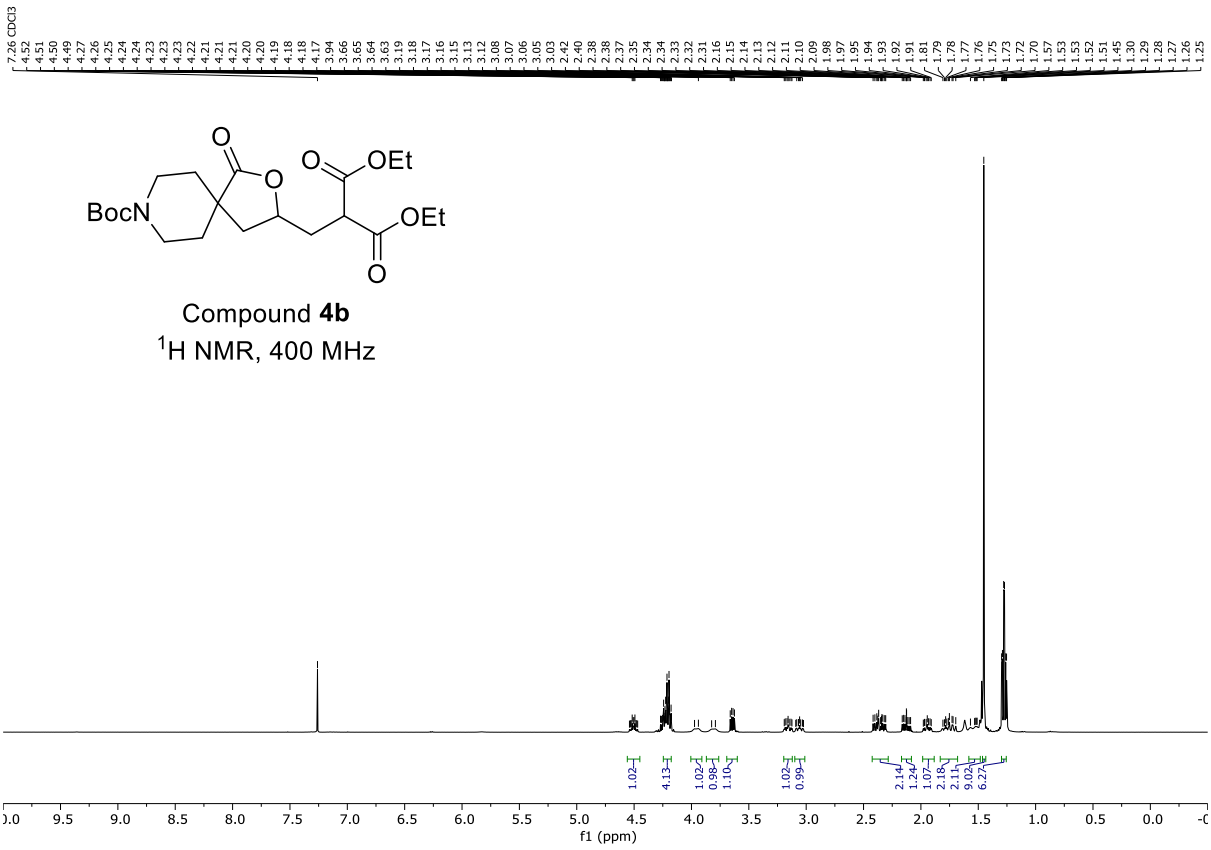
Compound **3o**
^{13}C NMR, 101 MHz



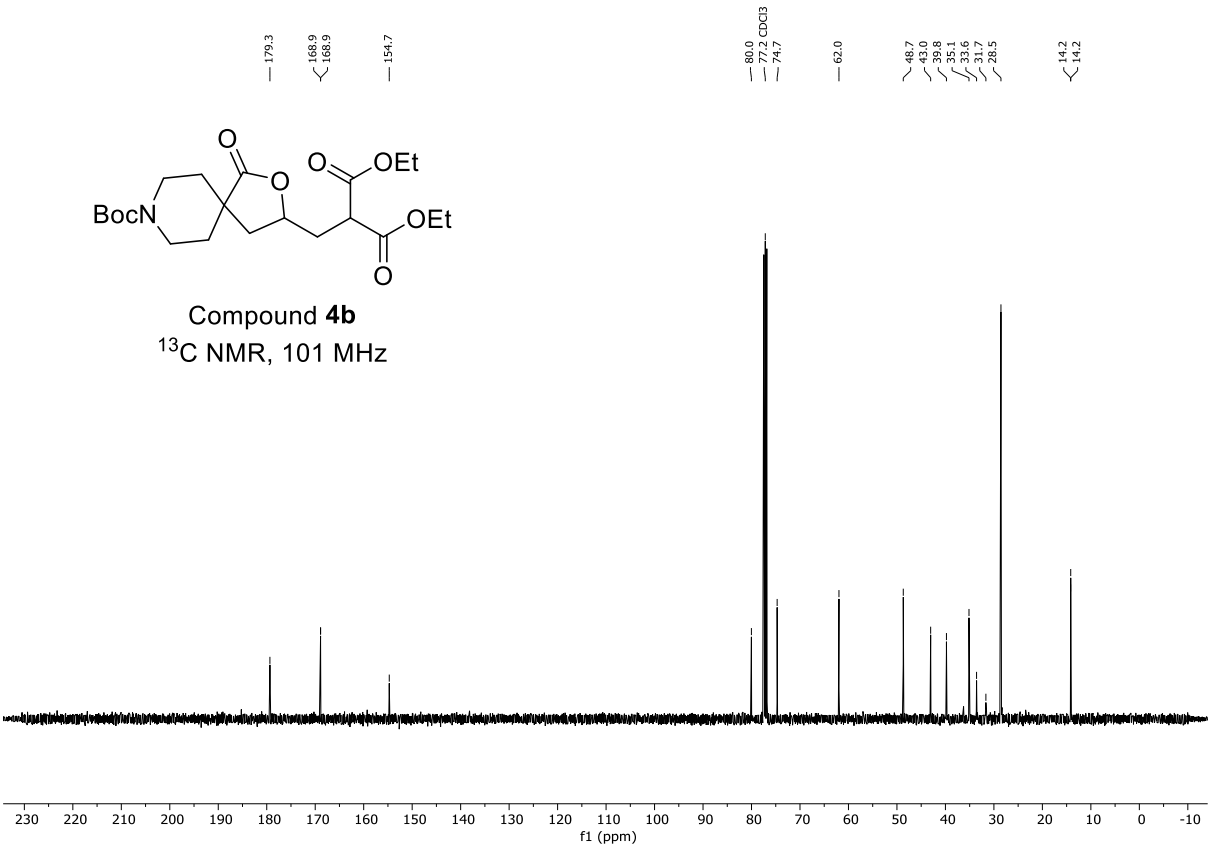


Compound **3o**

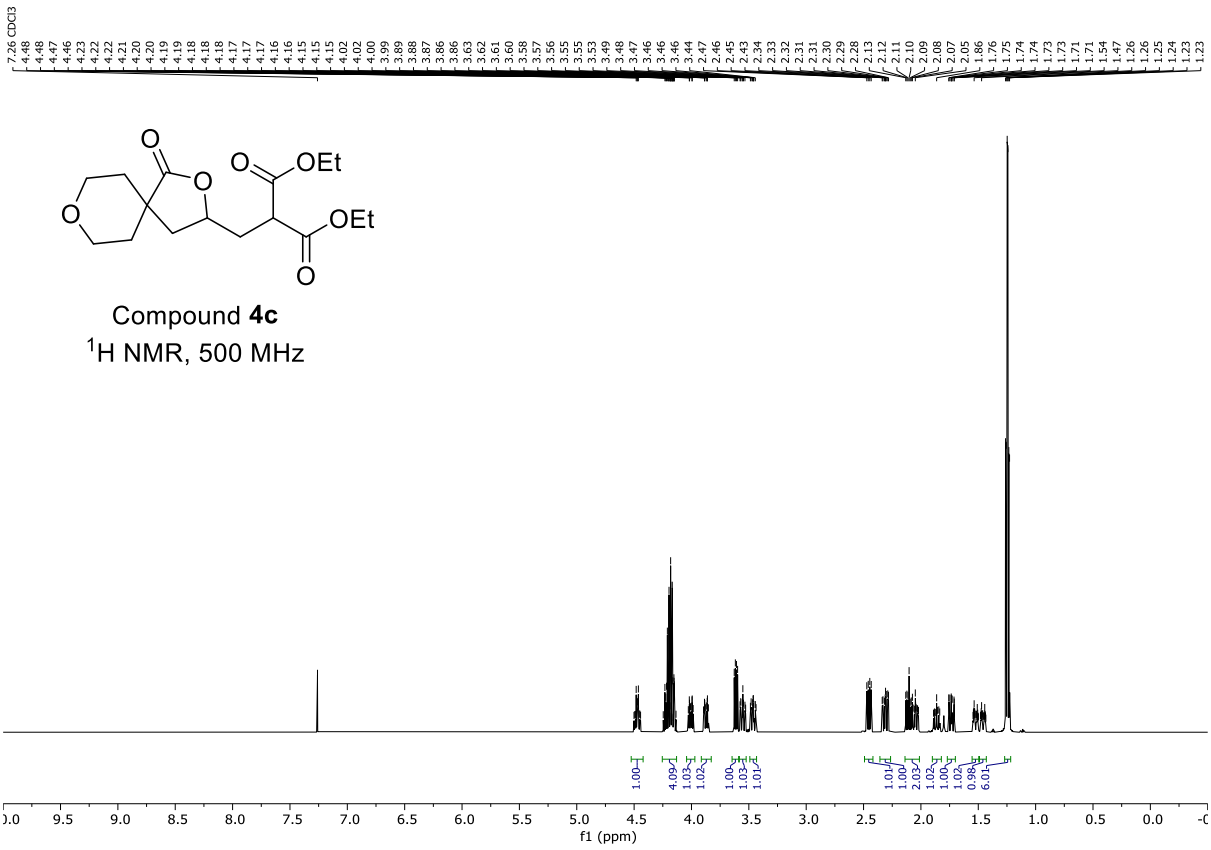
$^{19}F\{^{1}H\}$ NMR, 377 MHz

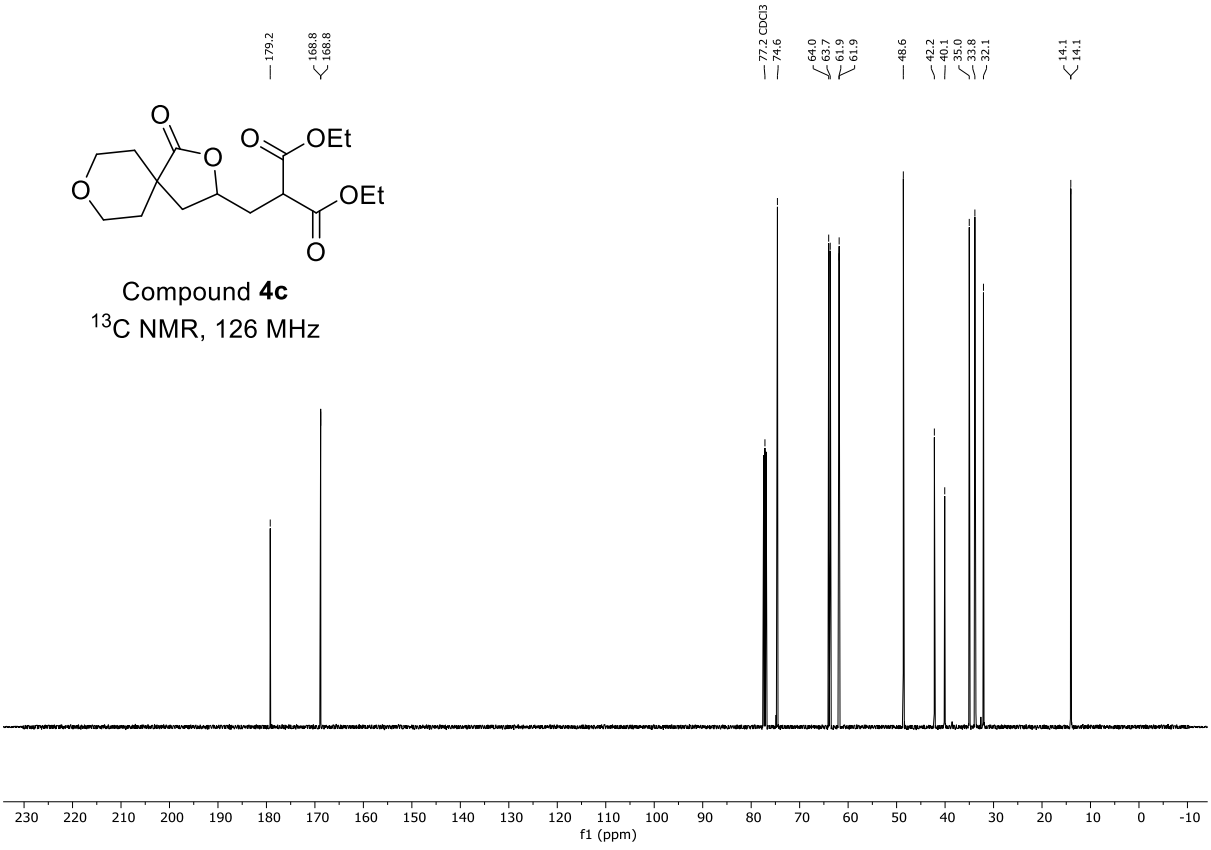


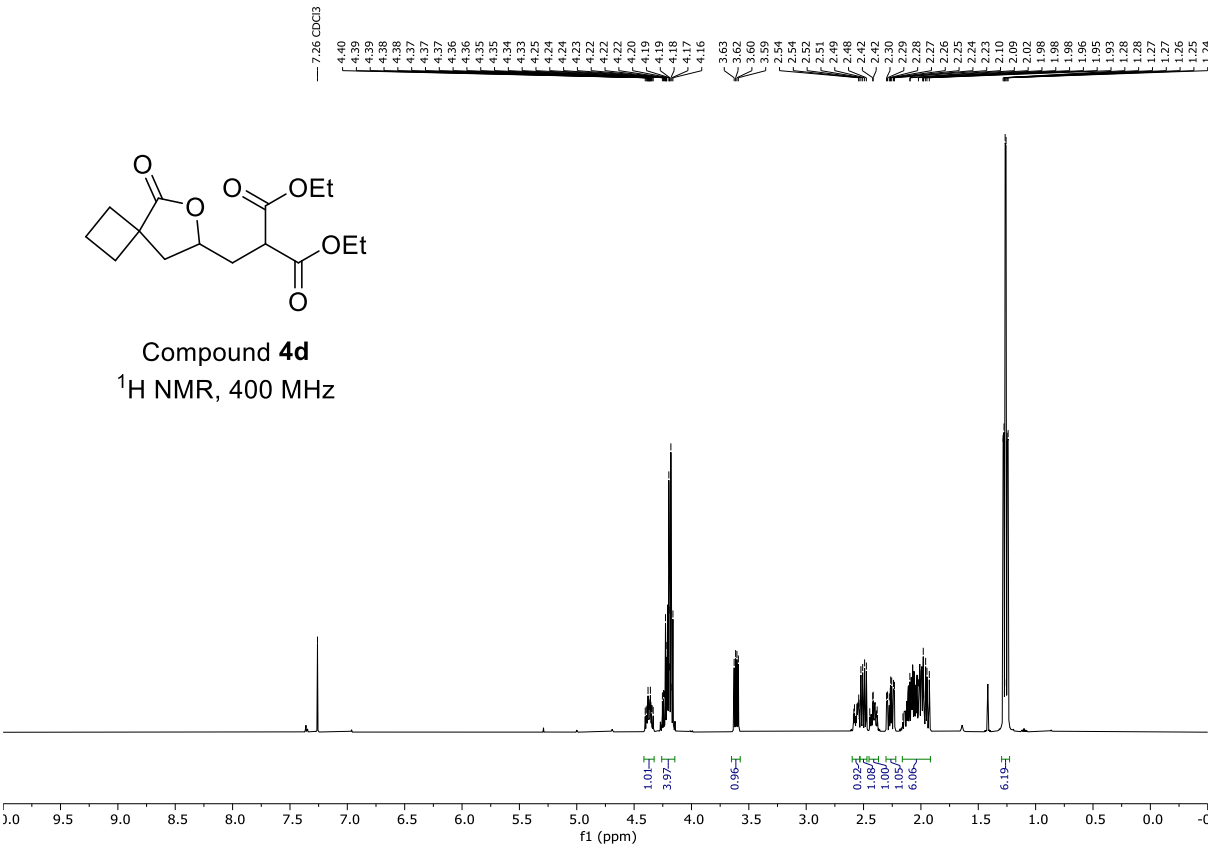
Compound **4b**
^{1}H NMR, 400 MHz



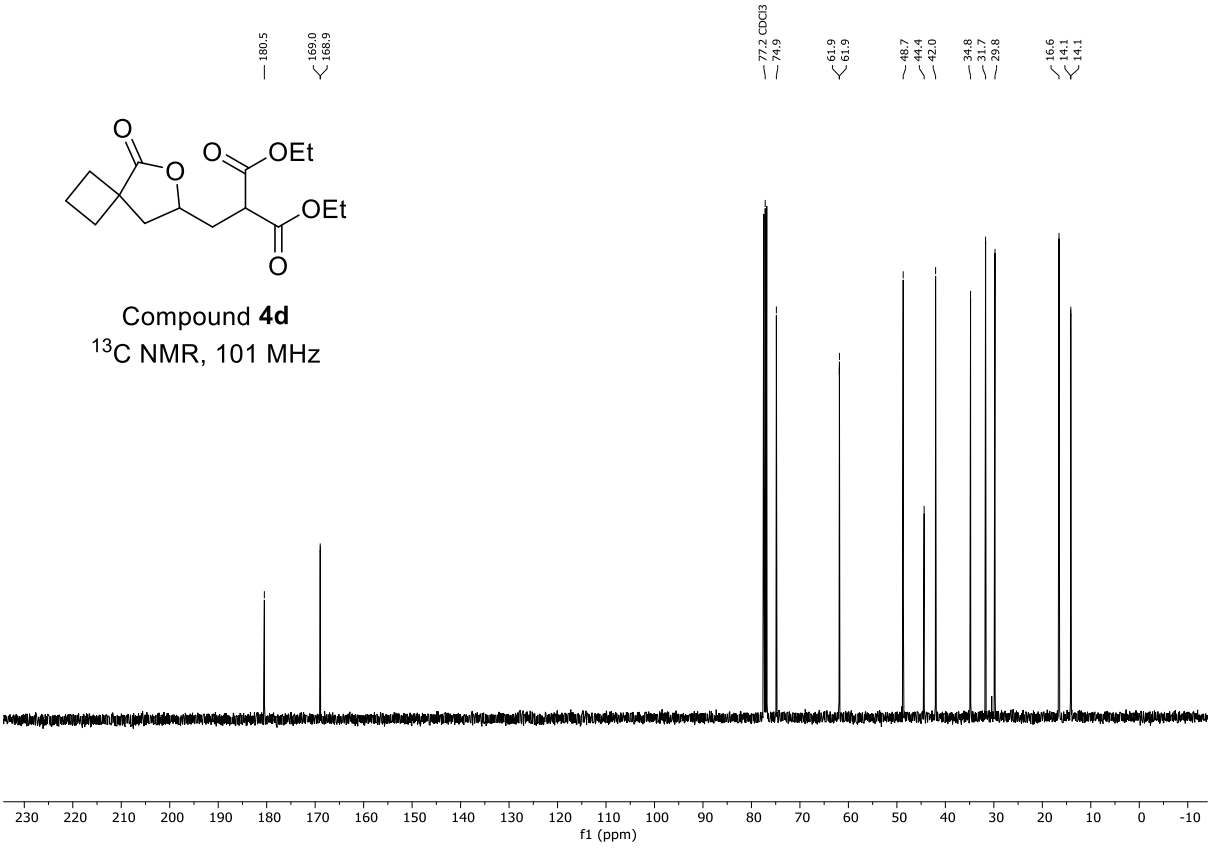
Compound **4b**
^{13}C NMR, 101 MHz


7.26 CDCl3
Compound 4c
1H NMR, 500 MHz
f1 (ppm)

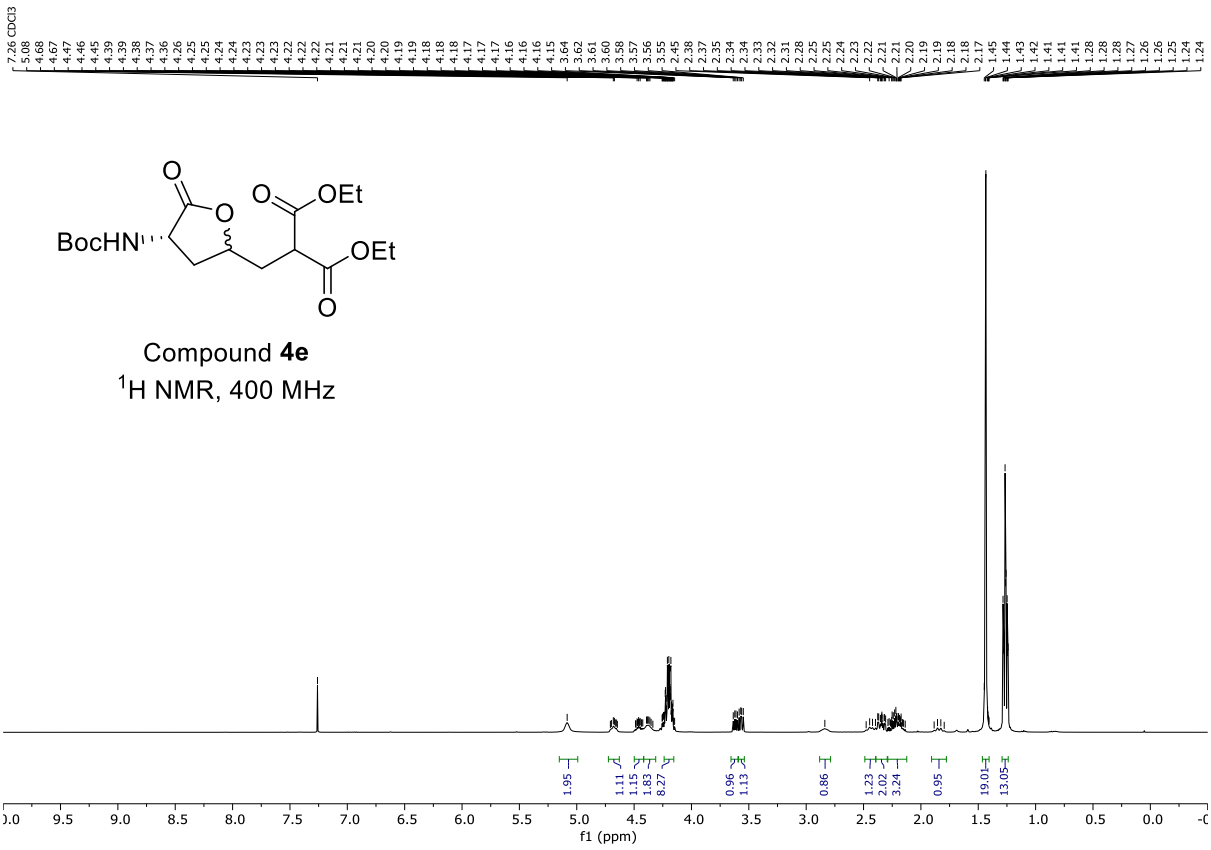

179.2
168.8
168.8
77.2 CDCl3
74.6
64.0
63.7
61.9
61.9
48.6
42.2
40.1
35.0
33.8
32.1
14.1
14.1
Compound 4c
13C NMR, 126 MHz
f1 (ppm)



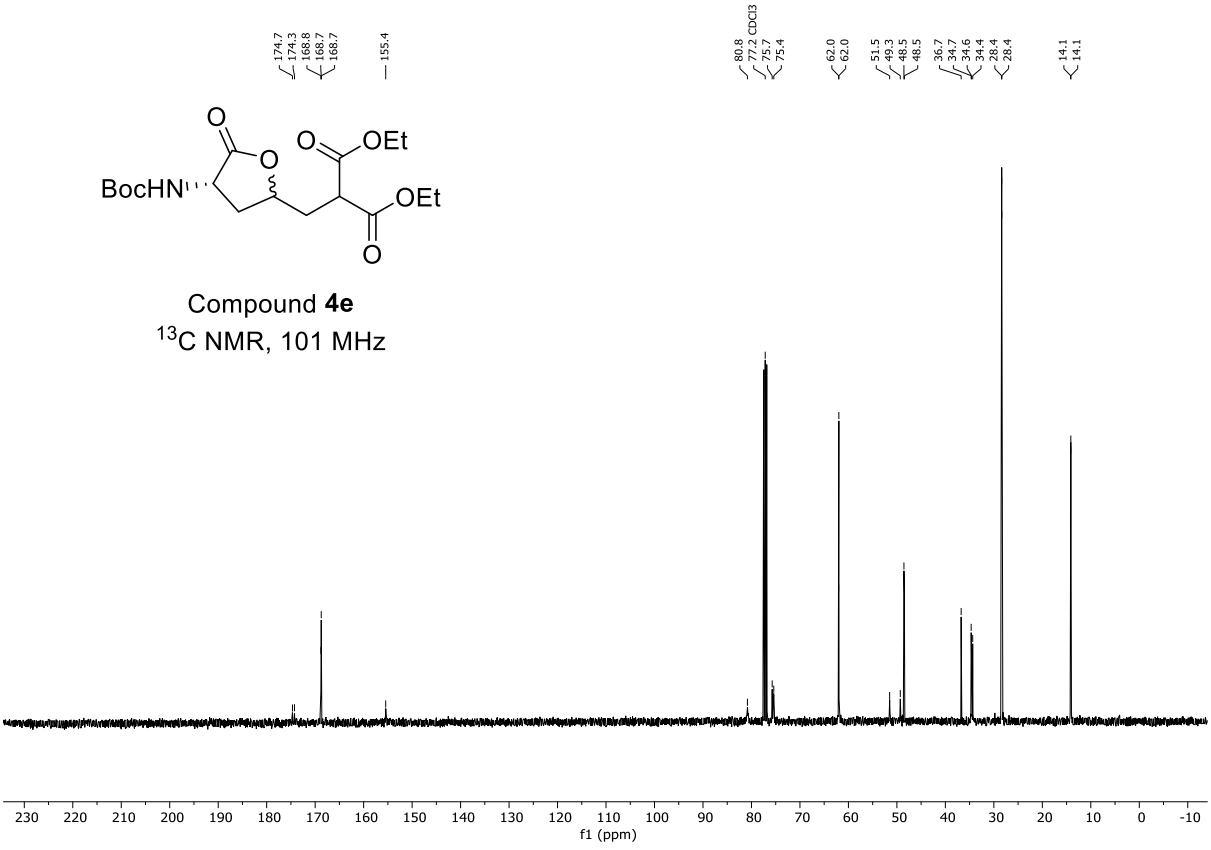
Compound **4d**
^{1}H NMR, 400 MHz



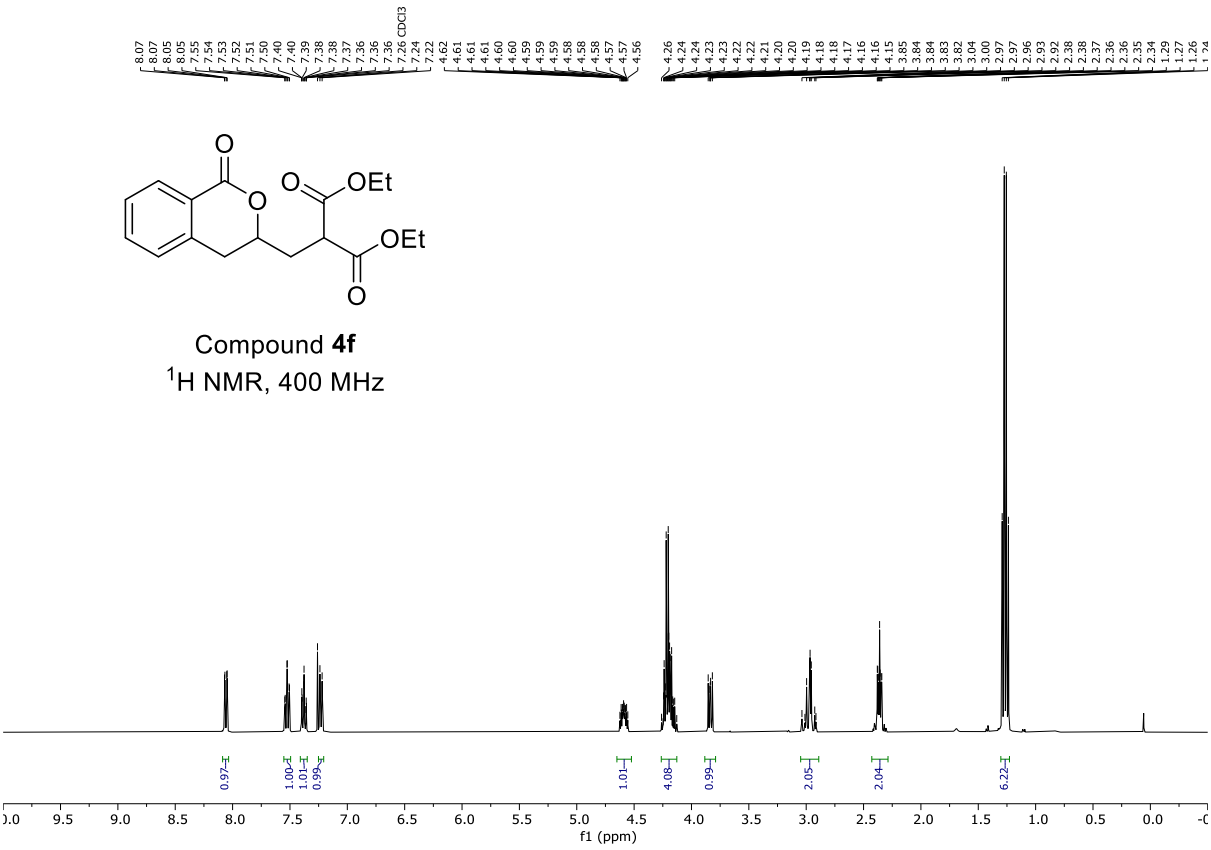
Compound **4d**
^{13}C NMR, 101 MHz



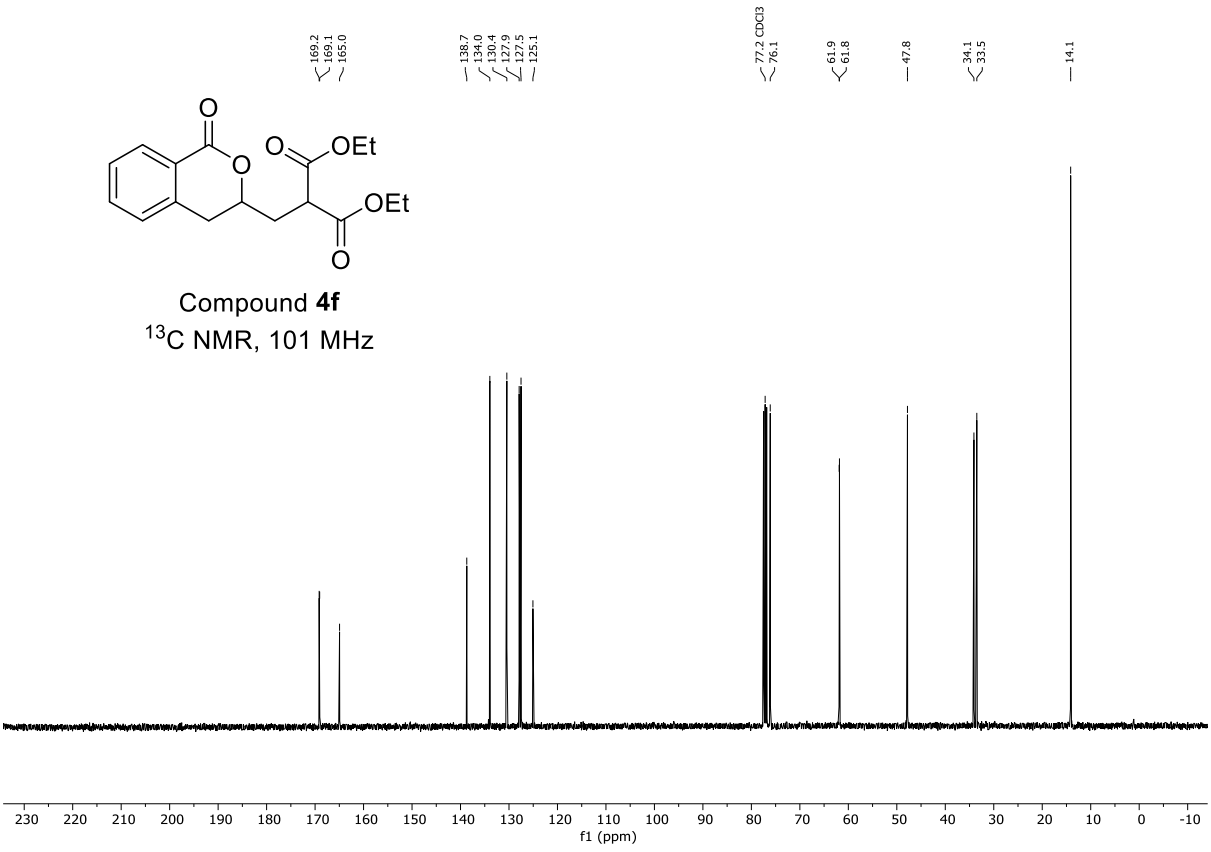
Compound **4e**
^{1}H NMR, 400 MHz



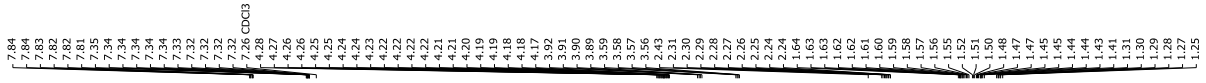
Compound **4e**
^{13}C NMR, 101 MHz

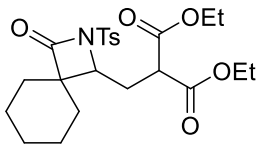


Compound **4f**
^{1}H NMR, 400 MHz

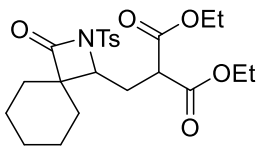


Compound **4f**
^{13}C NMR, 101 MHz

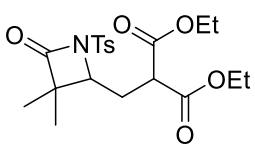




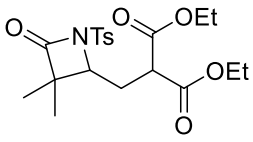
Compound **4g**
^{1}H NMR, 400 MHz



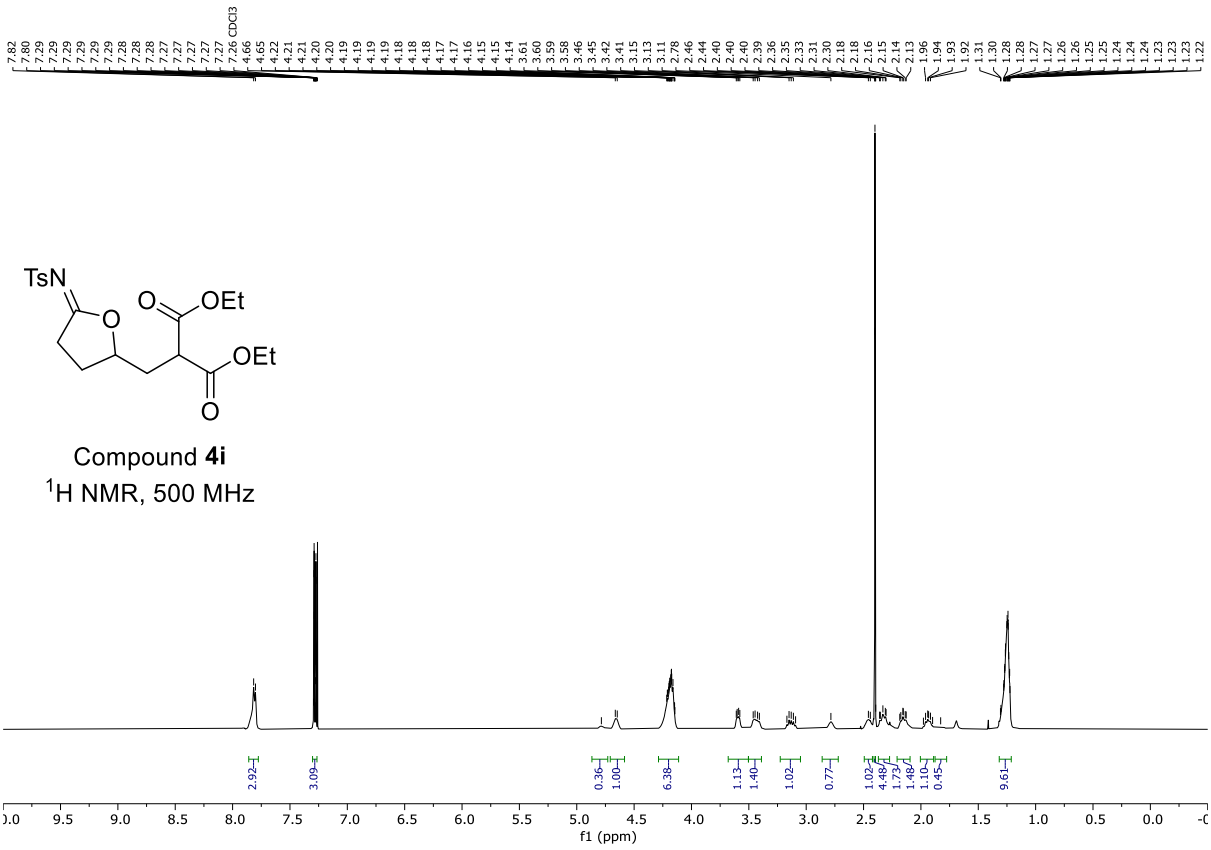
Compound **4g**
^{13}C NMR, 101 MHz



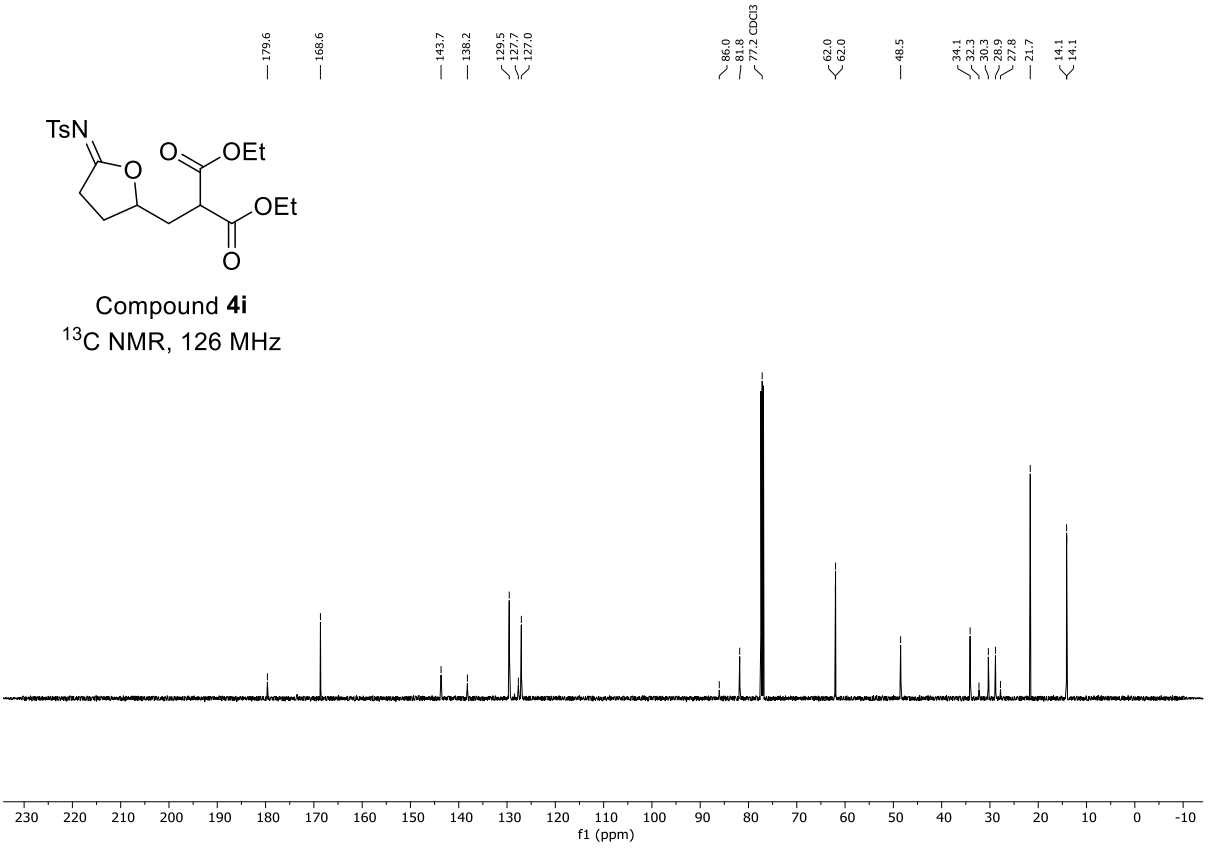
Compound **4h**
^{1}H NMR, 400 MHz



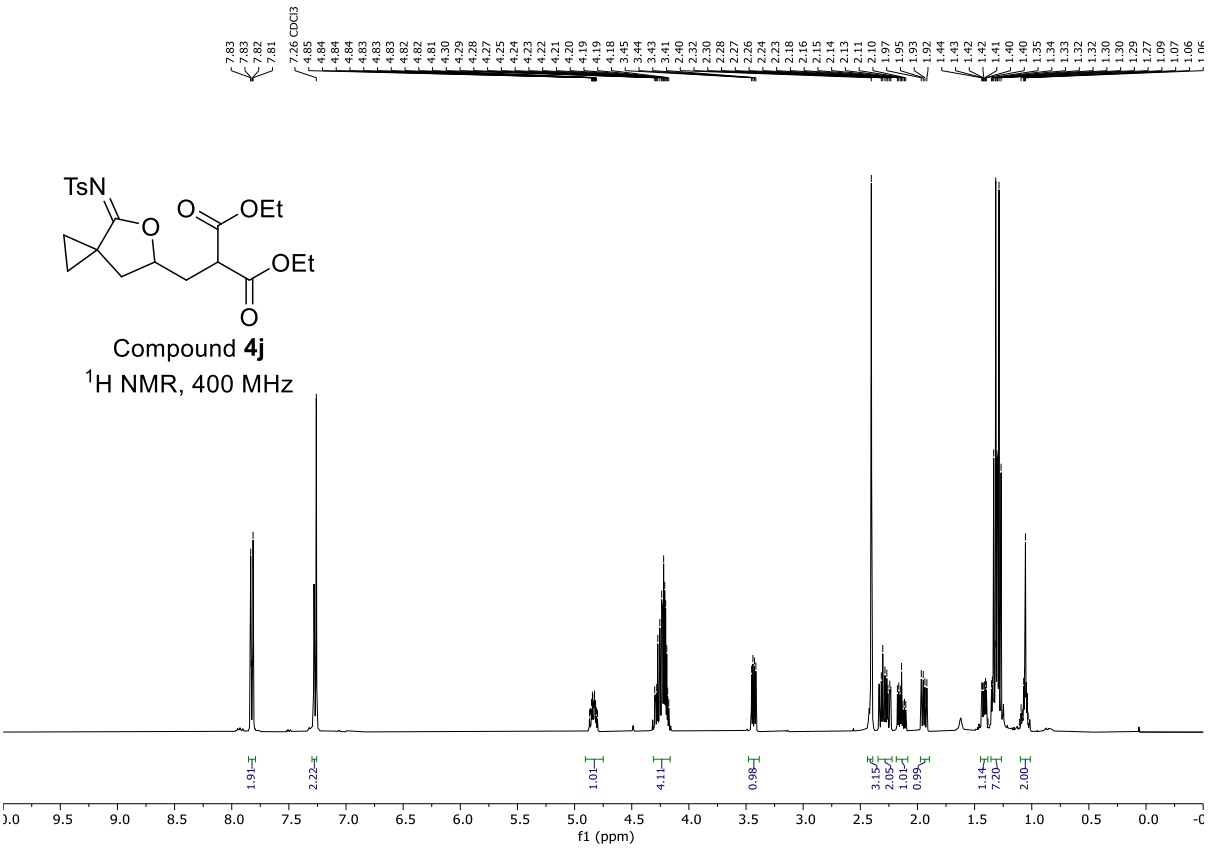
Compound **4h**
^{13}C NMR, 101 MHz

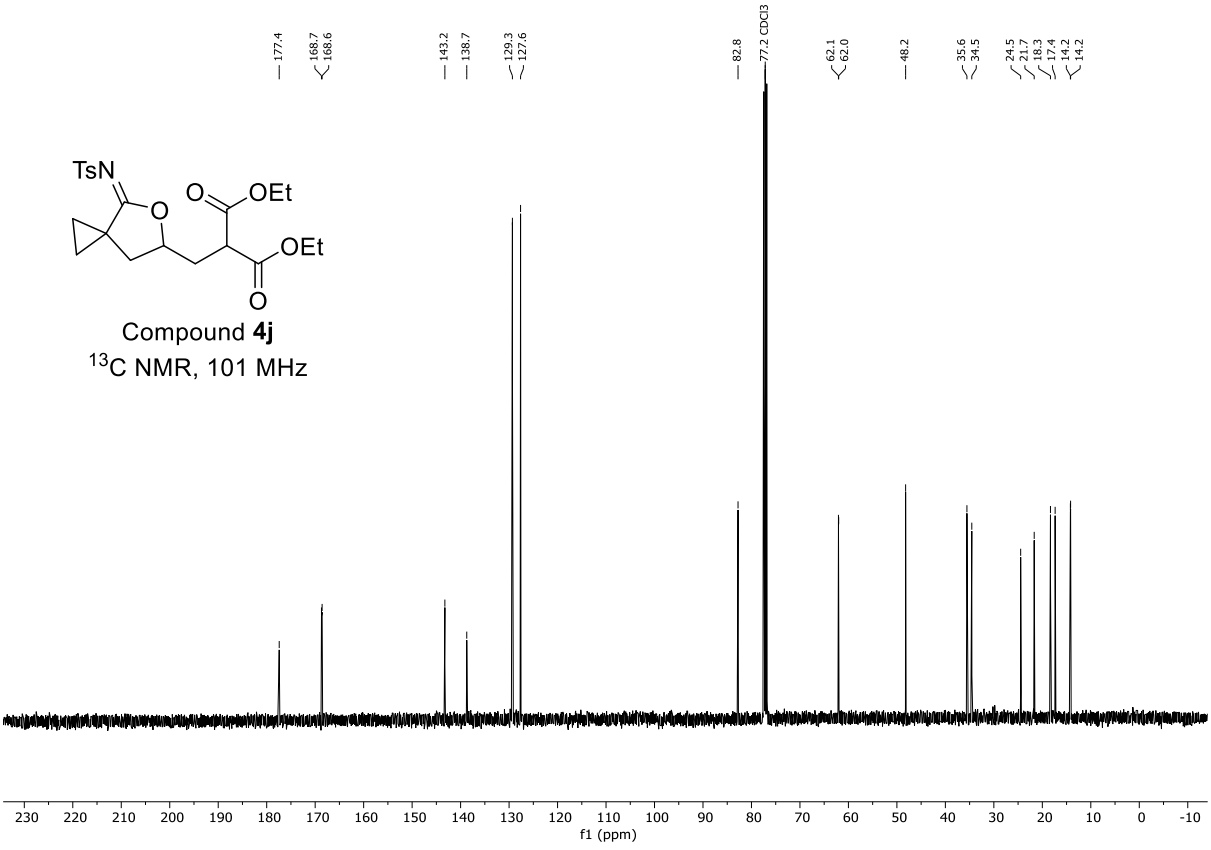


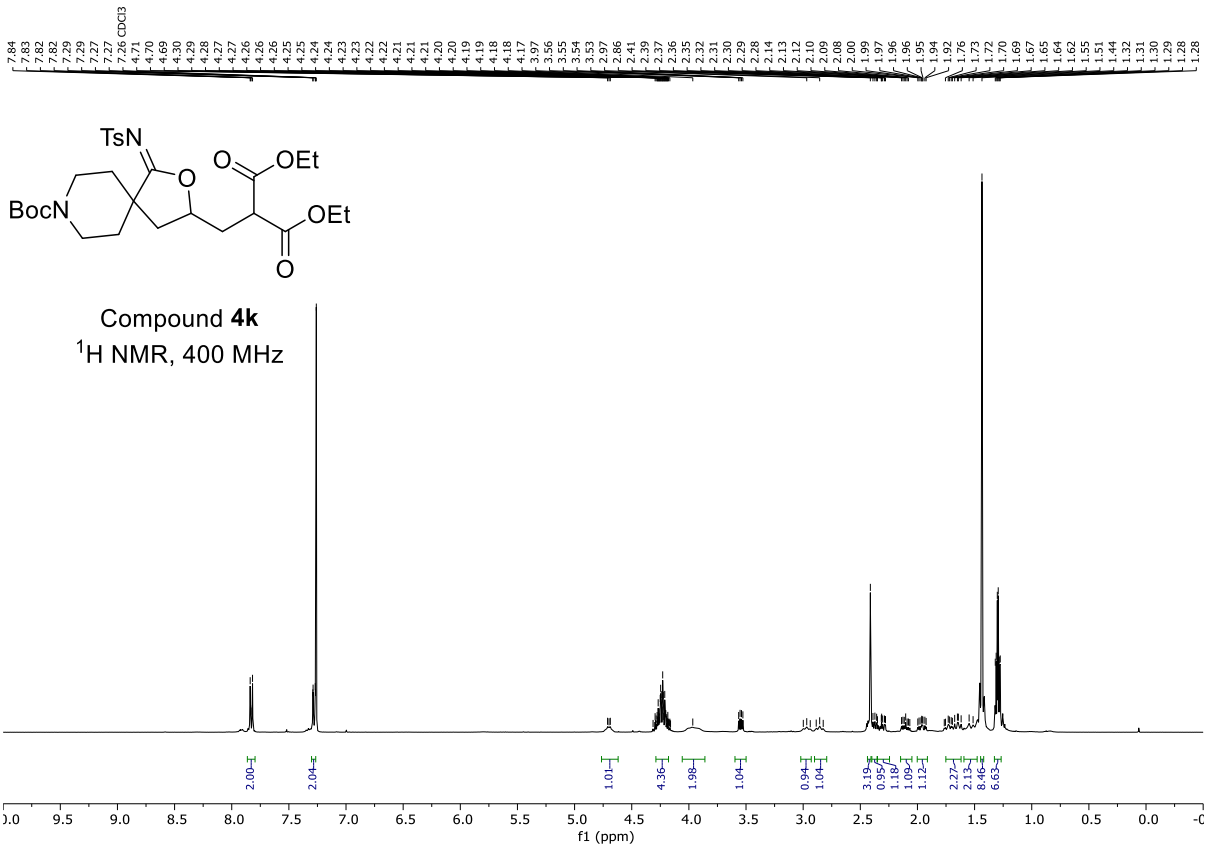
Compound **4i**
^{1}H NMR, 500 MHz

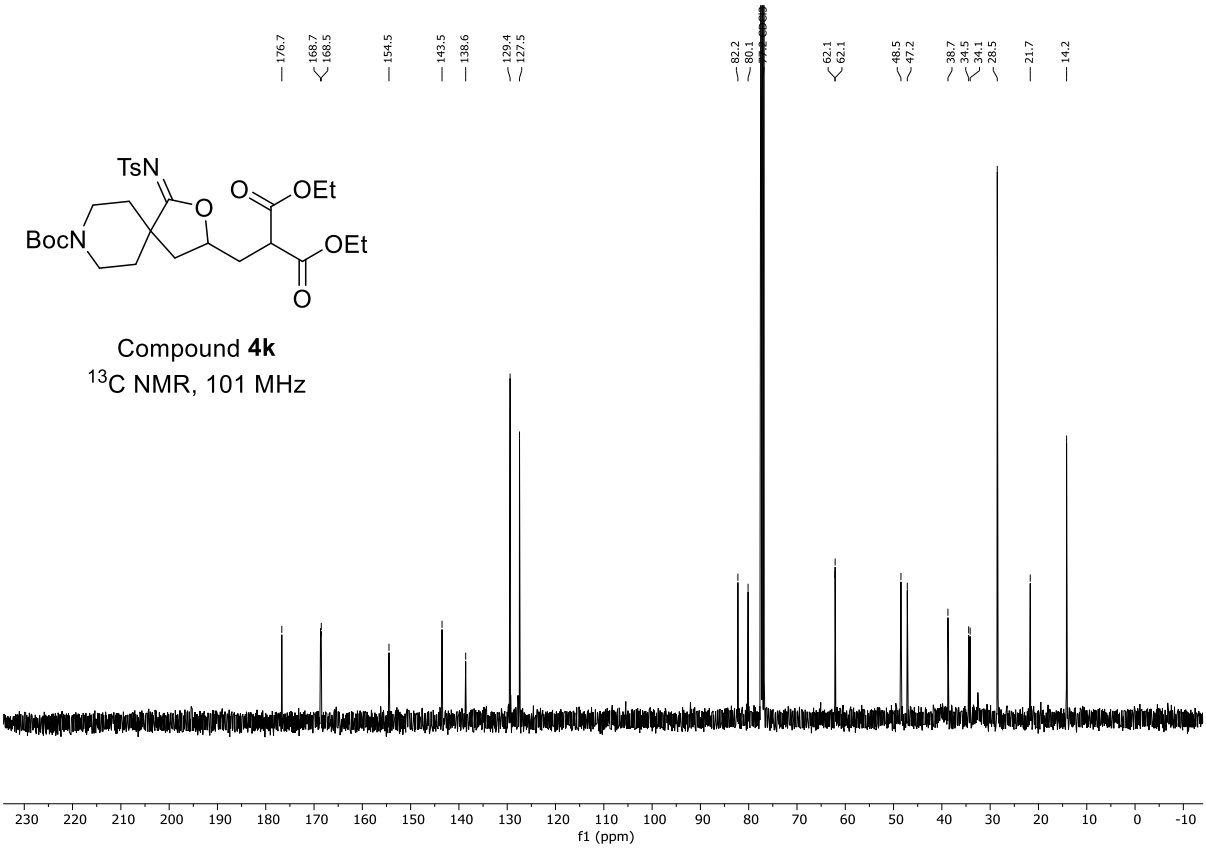


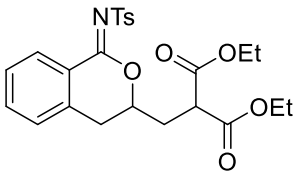
Compound **4i**
^{13}C NMR, 126 MHz


TsN
O
OEt
OEt
O
Compound 4j
1H NMR, 400 MHz
f1 (ppm)


TsN
O
OEt
OEt
O
Compound 4j
13C NMR, 101 MHz
f1 (ppm)

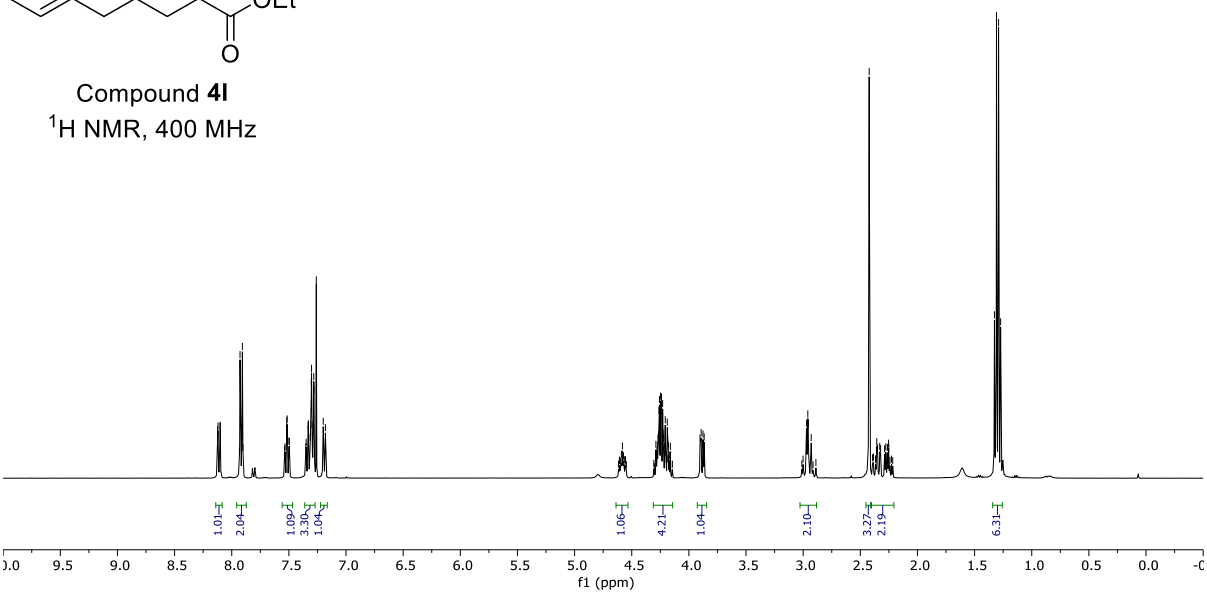

TsN
O
OEt
BocN
OEt
O
Compound **4k**
^{1}H NMR, 400 MHz
f1 (ppm)

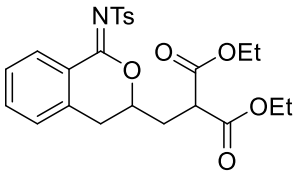

TsN
O
OEt
BocN
OEt
O
Compound **4k**
^{13}C NMR, 101 MHz
f1 (ppm)



Compound **4l**

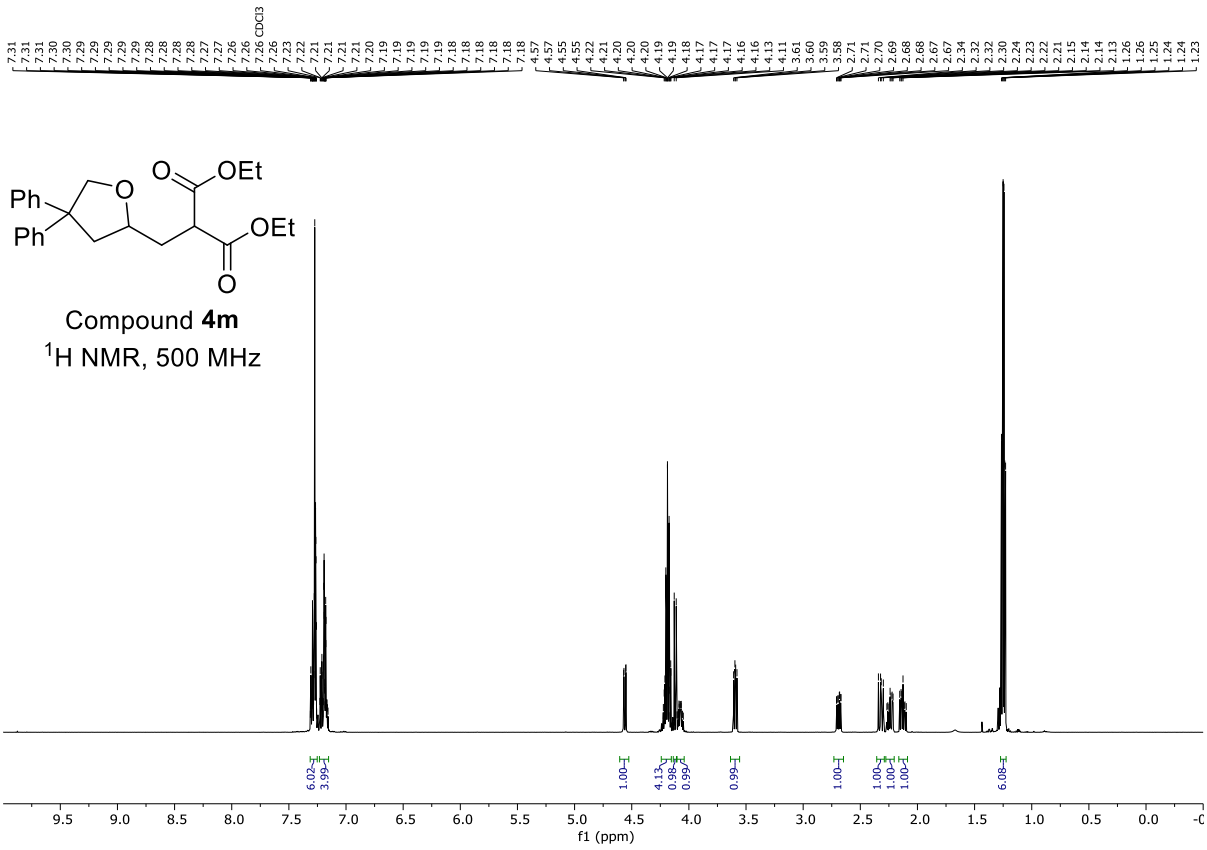
^{1}H NMR, 400 MHz

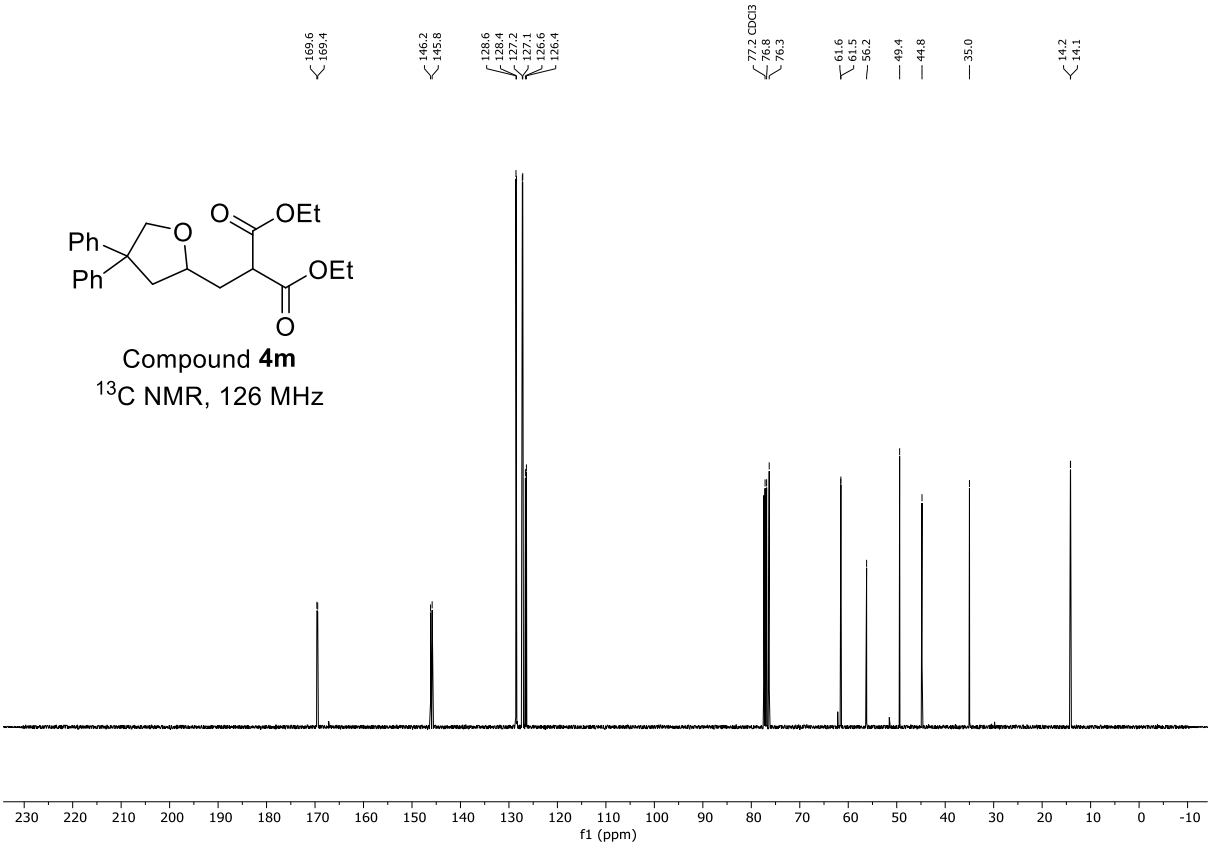


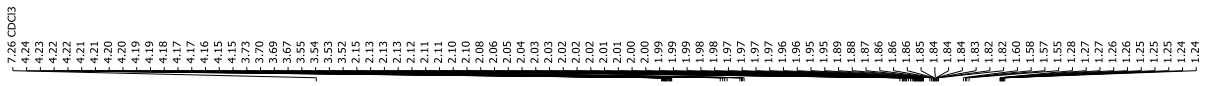


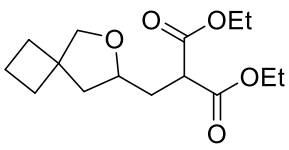
Compound **4l**

^{13}C NMR, 101 MHz


Ph
Ph
O
O
OEt
OEt
O
Compound 4m
1H NMR, 500 MHz
f1 (ppm)

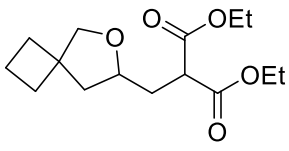

Ph
Ph
O
O
OEt
OEt
O
Compound 4m
13C NMR, 126 MHz
f1 (ppm)





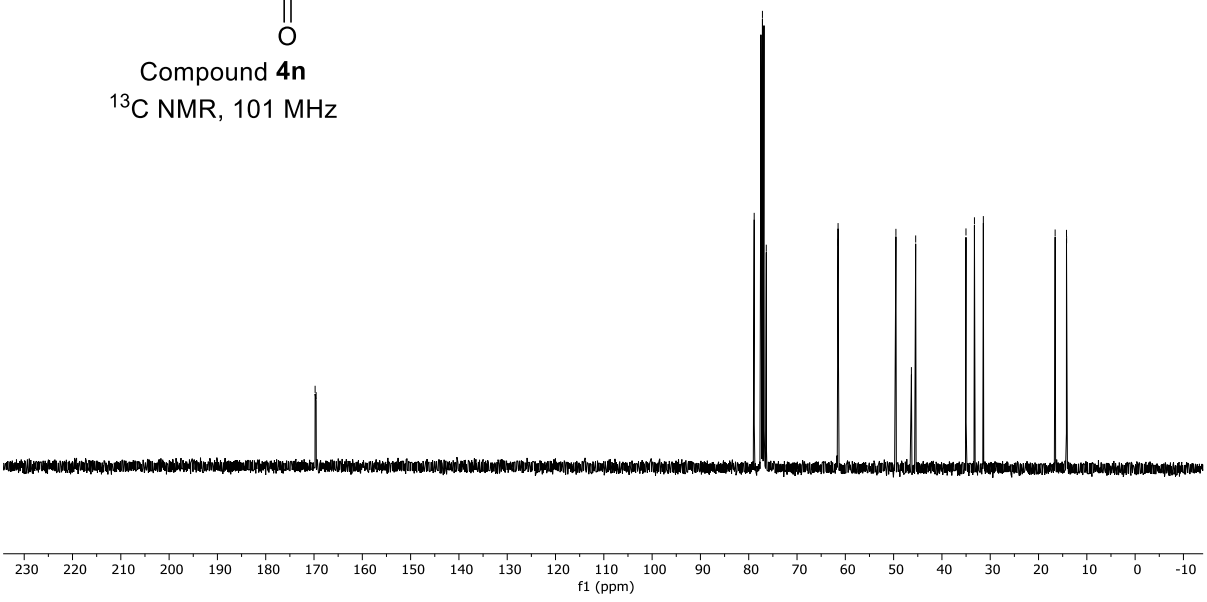
Compound **4n**

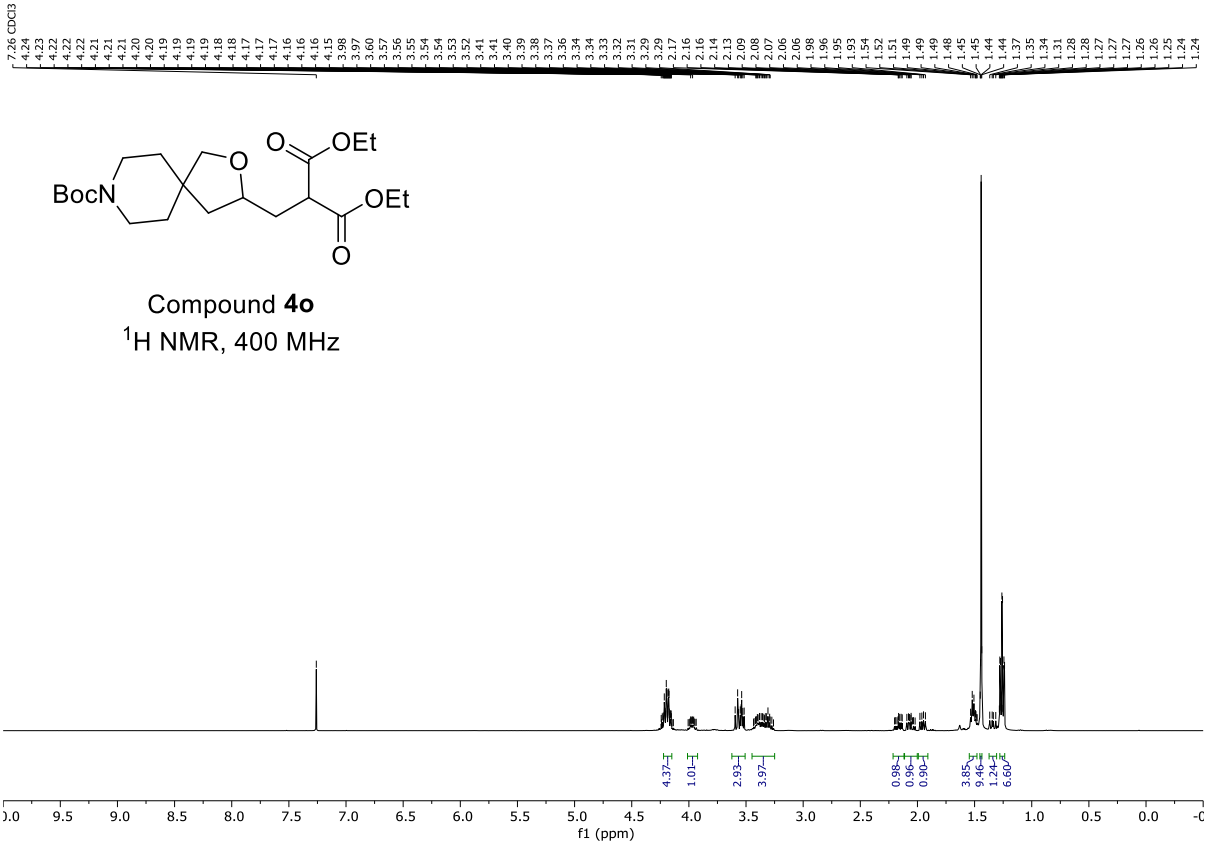
^{1}H NMR, 400 MHz



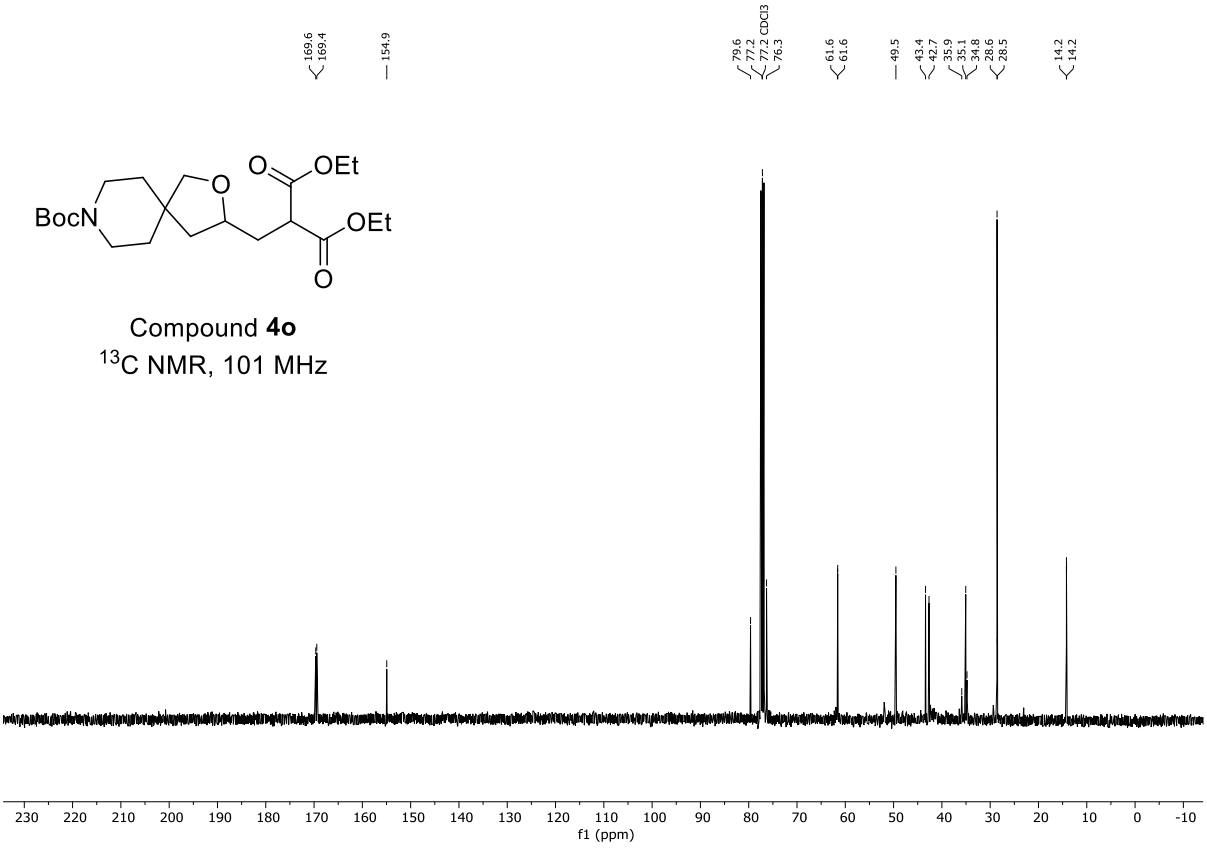
Compound **4n**

^{13}C NMR, 101 MHz

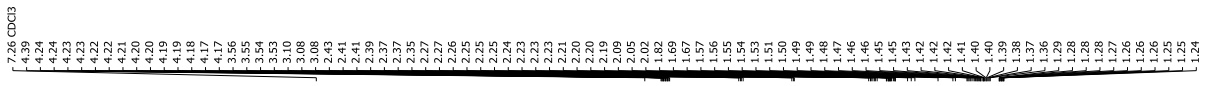


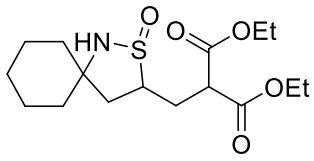


Compound **4o**
^{1}H NMR, 400 MHz



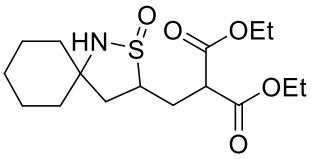
Compound **4o**
^{13}C NMR, 101 MHz





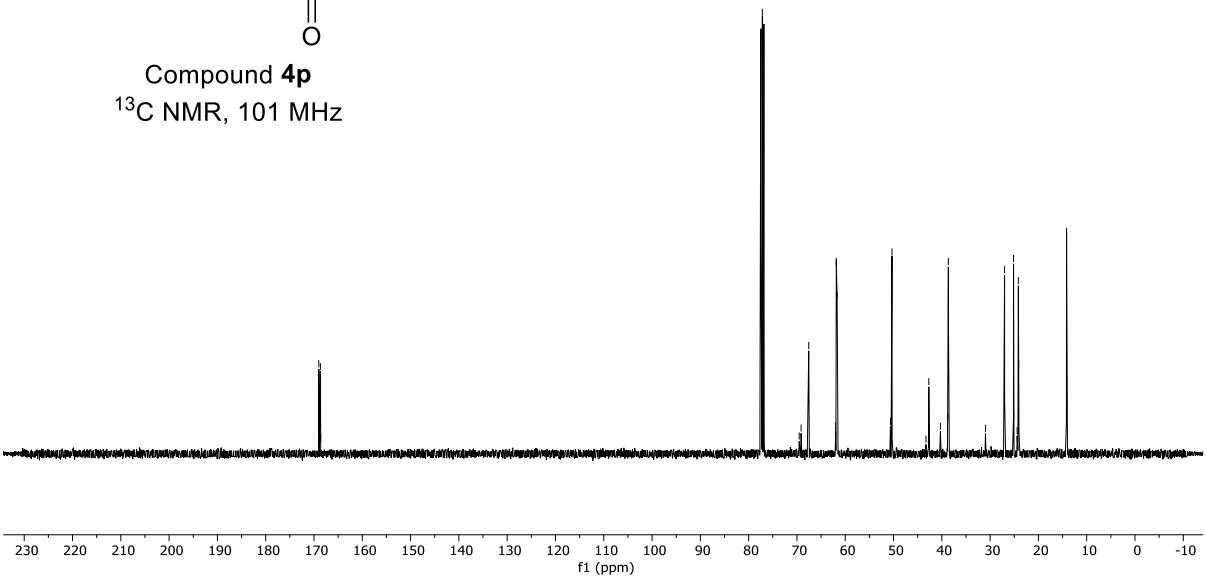
Compound **4p**

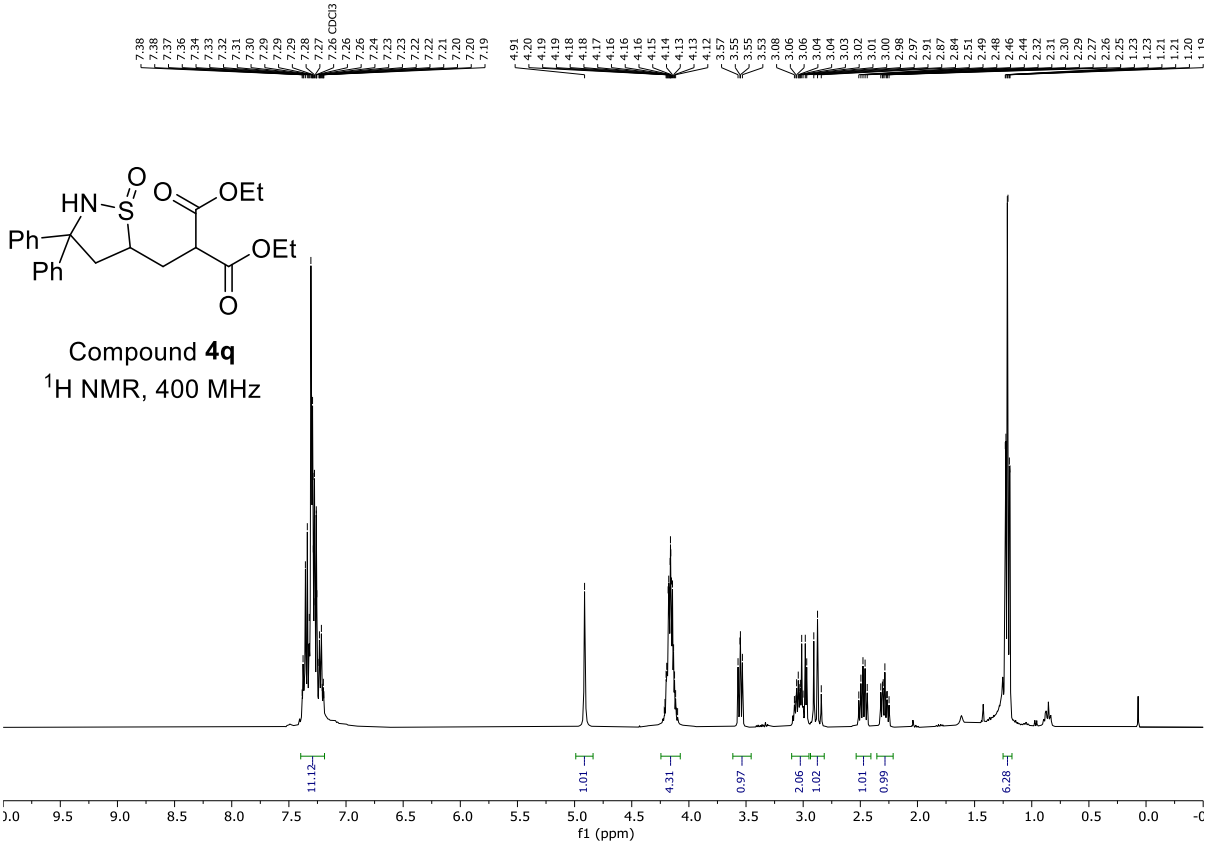
^{1}H NMR, 400 MHz

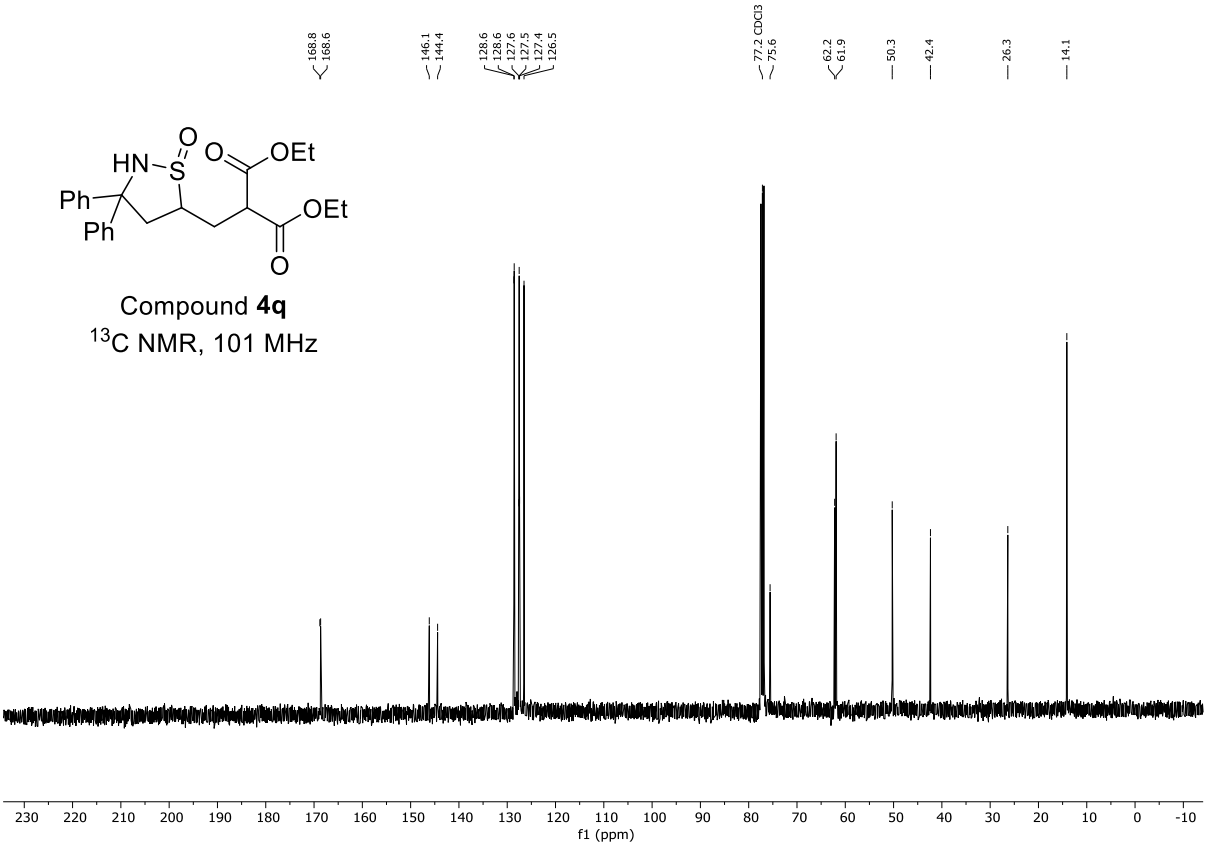


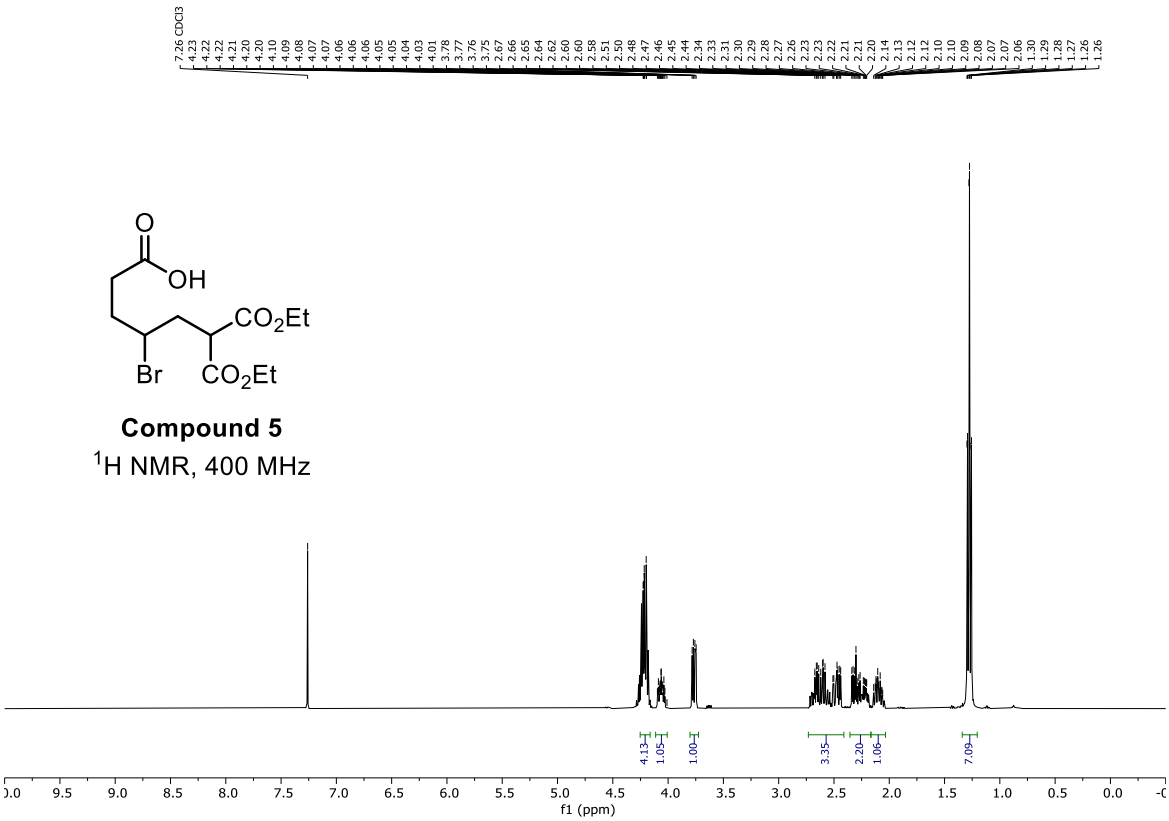
Compound **4p**

^{13}C NMR, 101 MHz



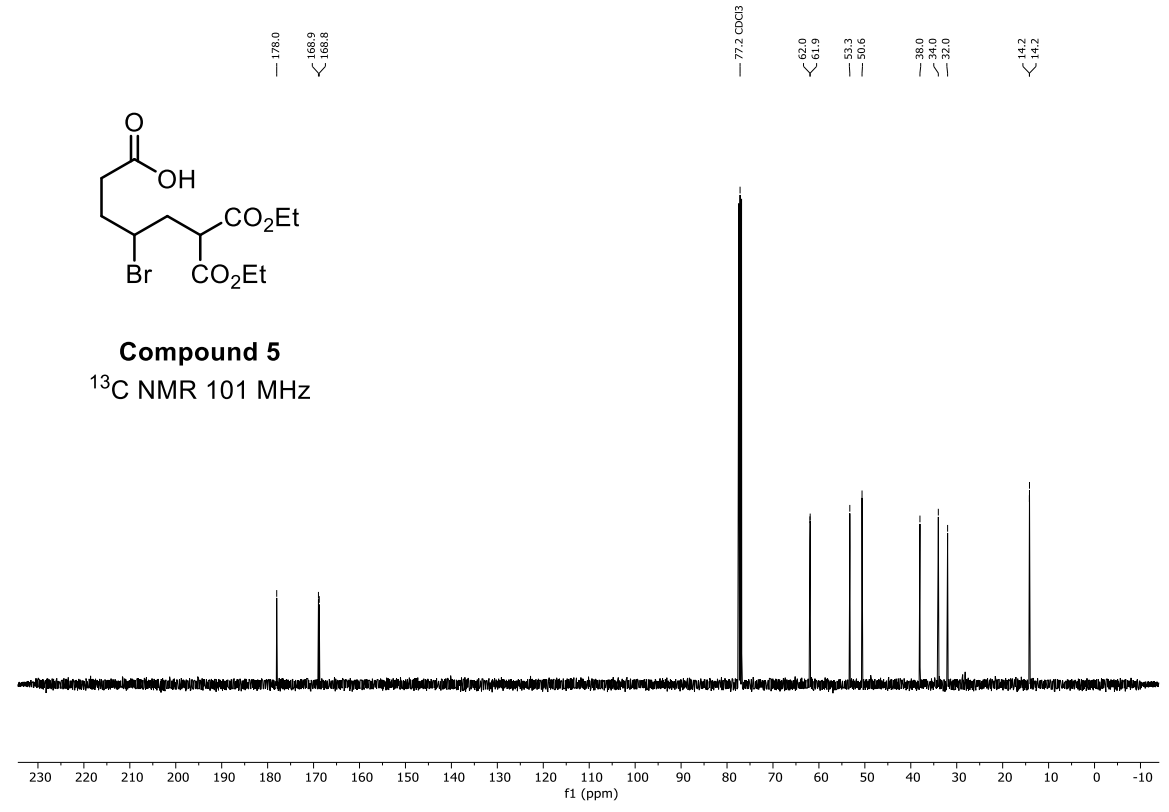

Compound **4q**
^{1}H NMR, 400 MHz
f1 (ppm)


Compound **4q**
^{13}C NMR, 101 MHz
f1 (ppm)



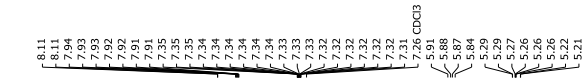
Compound 5

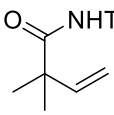
^{1}H NMR, 400 MHz



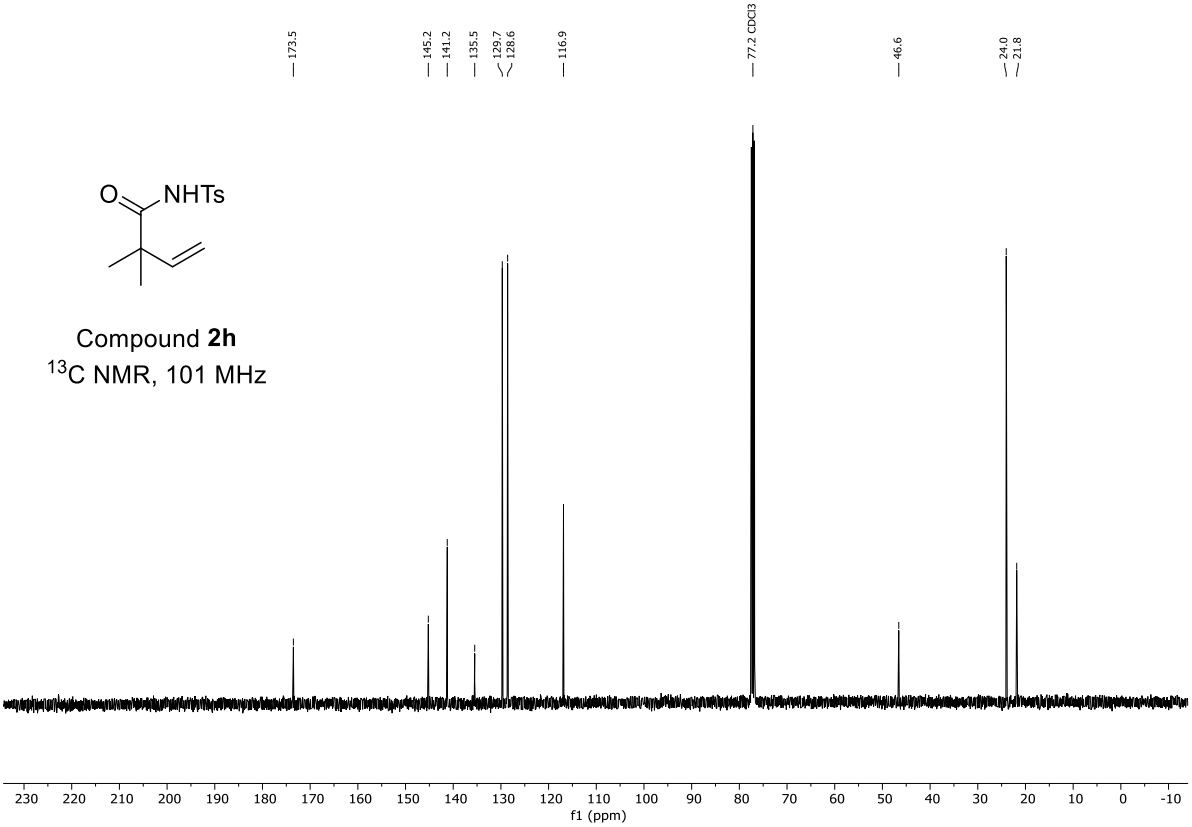
Compound 5

^{13}C NMR 101 MHz

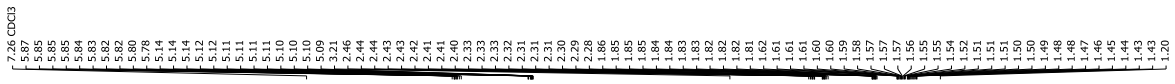


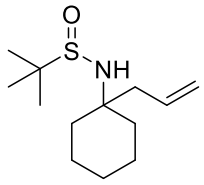


Compound **2h**
^{1}H NMR, 400 MHz

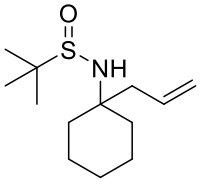


Compound **2h**
^{13}C NMR, 101 MHz

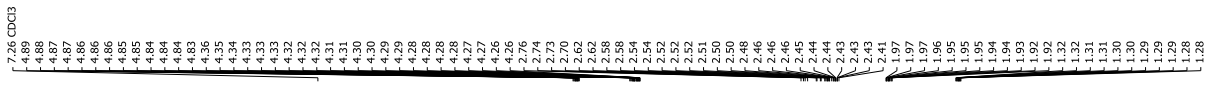


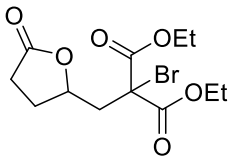


Compound **2p**
^{1}H NMR, 400 MHz



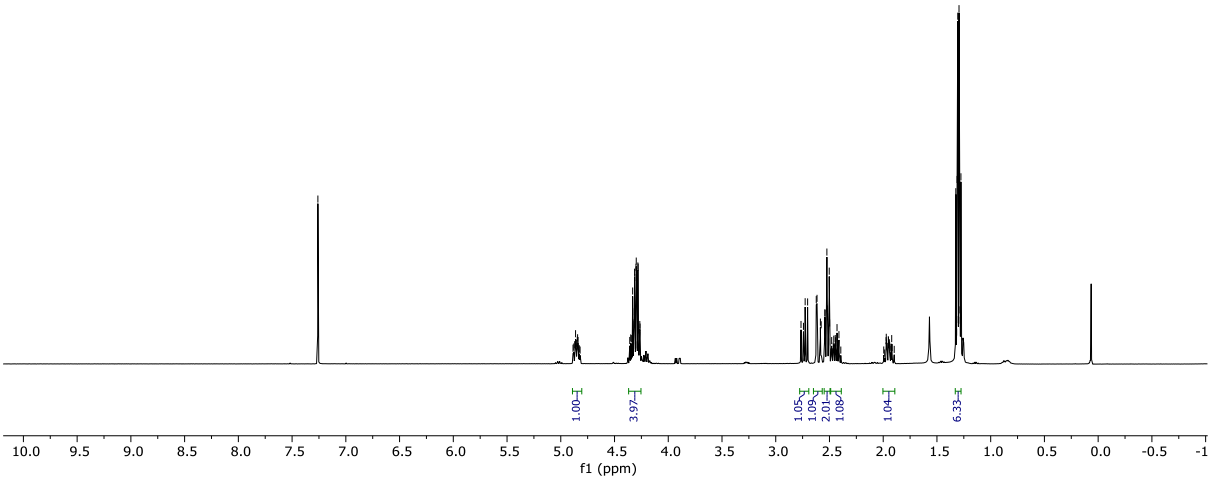
Compound **2p**
^{13}C NMR, 101 MHz

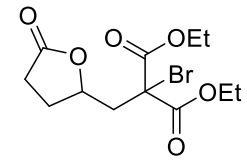




Compound **3a'**

^{1}H NMR, 400 MHz





Compound **3a'**

^{13}C NMR, 101 MHz