Supporting Information

Intermolecular Organophotocatalytic Cyclopropanation of Unactivated Olefins

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1. General Remarks

Procedure

Unless otherwise stated, all reactions were carried out under air. 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. When stated, neutral silica from Nacalai Tesque (Silica Gel 60, spherical, neutral, catalog No. 30511-51) was used.

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; DMSO-d_6, ^1H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm; CD_3CN, ^1H: δ = 1.94 ppm, ^{13}C: δ = 1.32 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, 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.

Emission Spectroscopy

The emission spectrum of the blue LED Photoreactor was measured with an Ocean Optics FLAME-S-UV-VIS-ES CCD-Array Spectrometer.

Cyclic Voltammetry

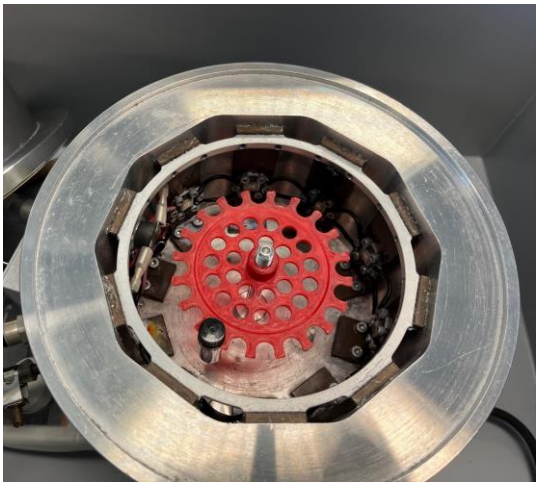
Cyclic voltammetry measurements were conducted on an Autolab PGSTAT204. A glassy carbon rod with a disk diameter of 3 mm (Metrohm, 6.1204.300) was used as the working electrode. A Pt sheet electrode (Metrohm 3.109.0790) was used as the counter electrode. As reference electrode (sat.) $Ag/AgNO_3$ in MeCN was used (Metrohm, 6.0726.100). CVs of compounds (c = 1.00 mM) were recorded in MeCN with a scan rate of 100 mV s^{-1}. Bu_4NPF_6 (0.100 M) was used as supporting electrolyte.

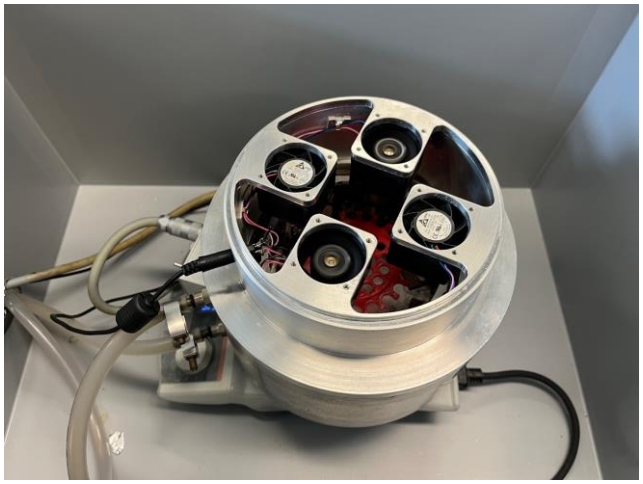
Data Analysis

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

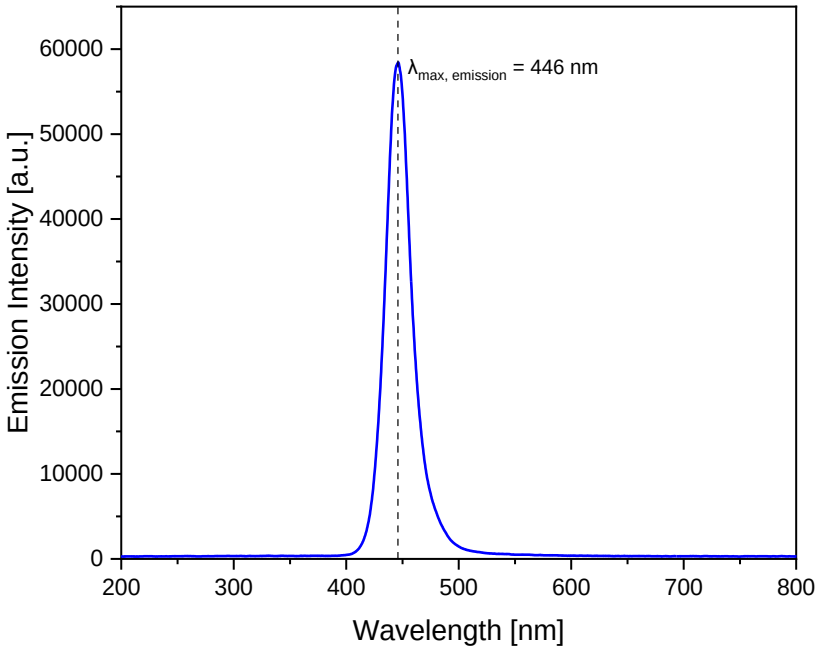
2. Photoreaction Set-up

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). 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.

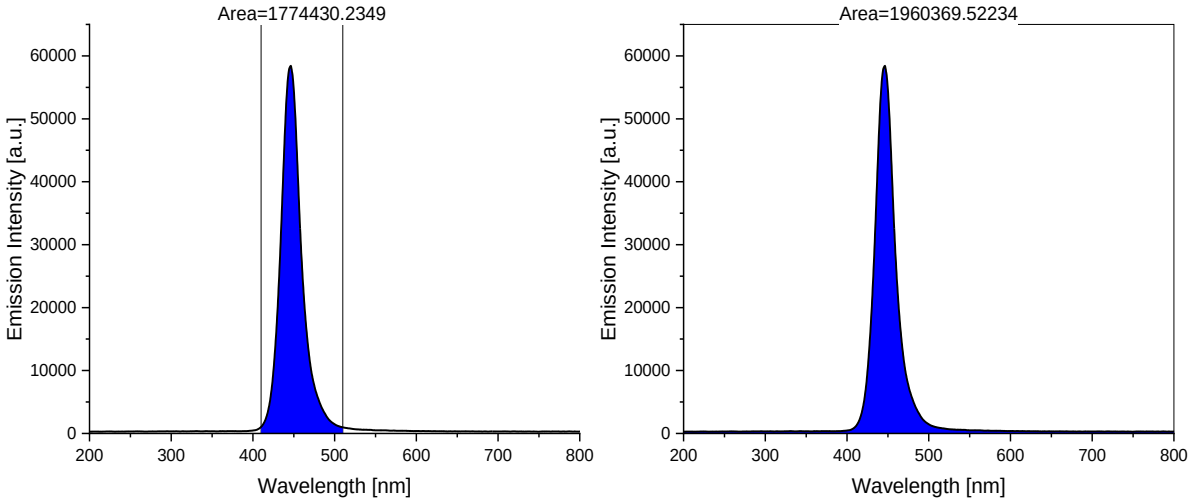




The emission spectrum (see below) of the blue LED reactor shows a maximum intensity at a wavelength of $\lambda_{max,\ emission}$ = 446 nm.



To calculate the percentage of light emitted by the photoreactor between 410 nm and 510 nm ($\%E_{410\text{-}510nm}$), the emission curve was integrated from 410 nm to 510 nm ($\int_{410\text{-}510nm}$) and from 200 nm to 800 nm ($\int_{200\text{-}800nm}$).



Wavelength Range	Integral ∫
410 nm – 510 nm	1774430
200 nm – 800 nm	1960370

The percentage of light emission between 410 nm and 510 nm was subsequently calculated as:

$$\%E_{410\text{-}510nm} = \frac{\int_{410\text{-}510nm}}{\int_{200\text{-}800nm}} = \frac{1774430}{1960370} = 0.905 = 90.5\%$$

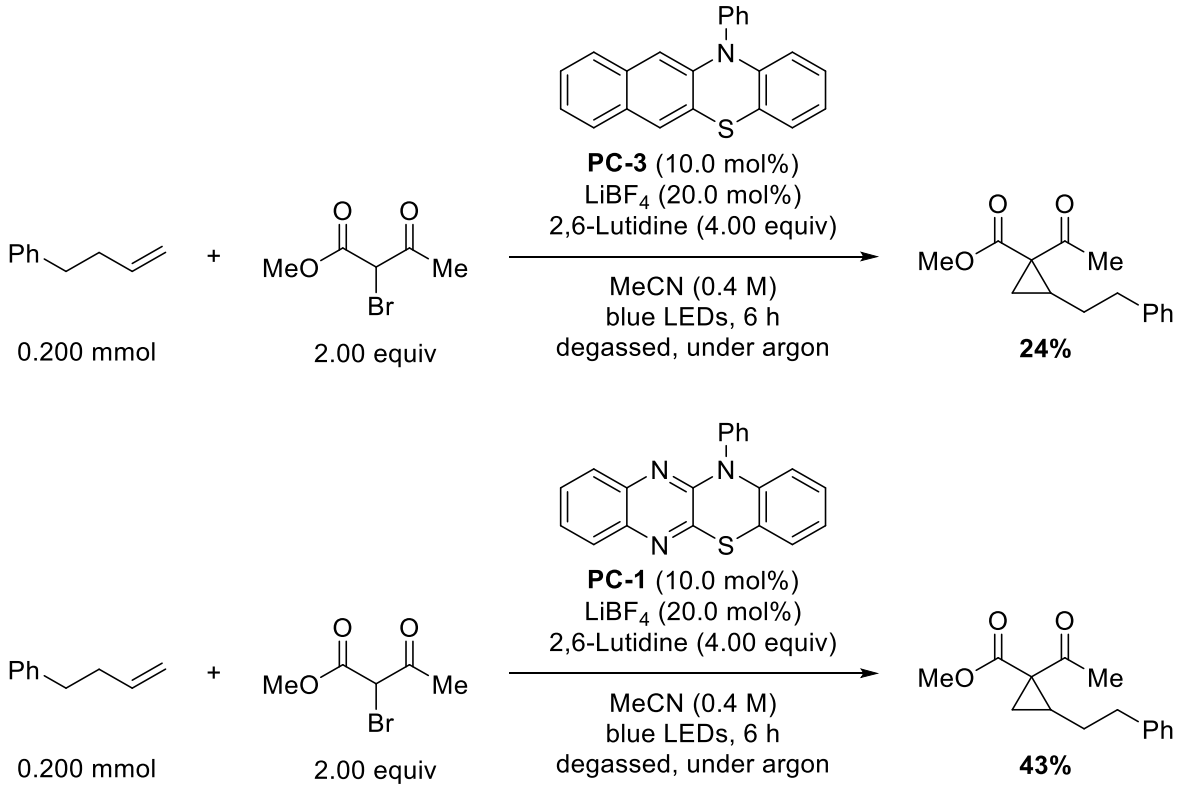
Note: The reaction of phenylbutene **2a** with α-bromo-β-ketoester **1a** or dimethyl bromomalonate **7** could also be conducted with a Kessil PR160L-440nm light (intensity set to 100) with comparable yield, albeit with longer reaction time.

3. Optimization Studies for α-Bromo-β-ketoesters

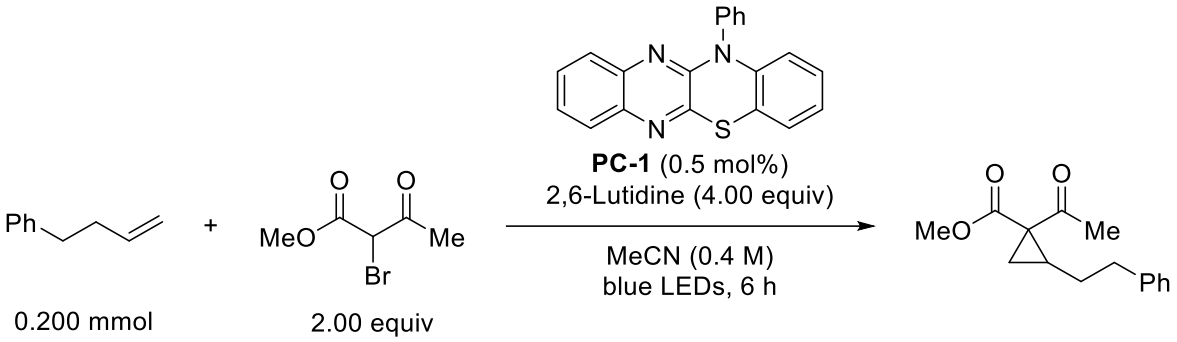
Example of procedure for optimization

To a glass vial charged with **PC-1** (0.33 mg, 0.0010 mmol, 0.50 mol%) in MeCN (500 µL, 0.4 M) were added **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and bromo acetoacetate (78.0 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 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 Experiments

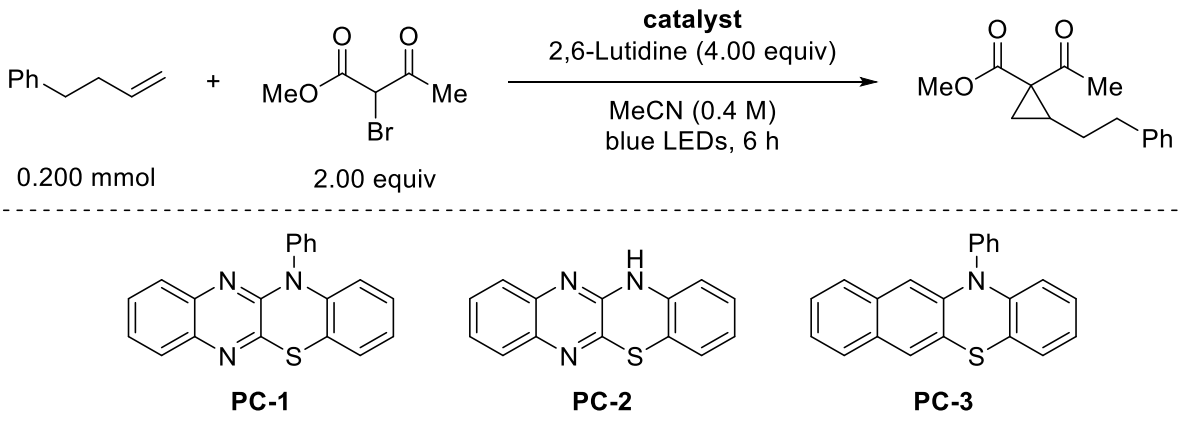


Control Experiments



Entry	Change	Product [%]	SM [%]
1	no base	0	68
2	no PC	0	95
3	in the dark, 40°C	0	97
4	degassed, under Ar	98	0
5	under air	97	0

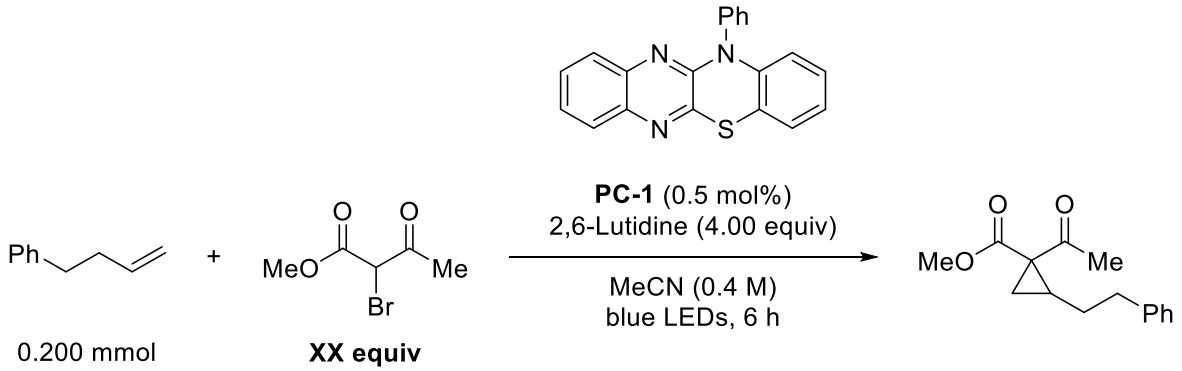
Effect of Catalyst and Catalyst Loading



Entry	Catalyst	Equiv [mol%]	Product [%]	SM [%]
1	**PC-1**	10.0	98	0
2	**PC-1**	5.00	98	0
3	**PC-1**	1.00	96	0
4	**PC-1**	0.500	97	0

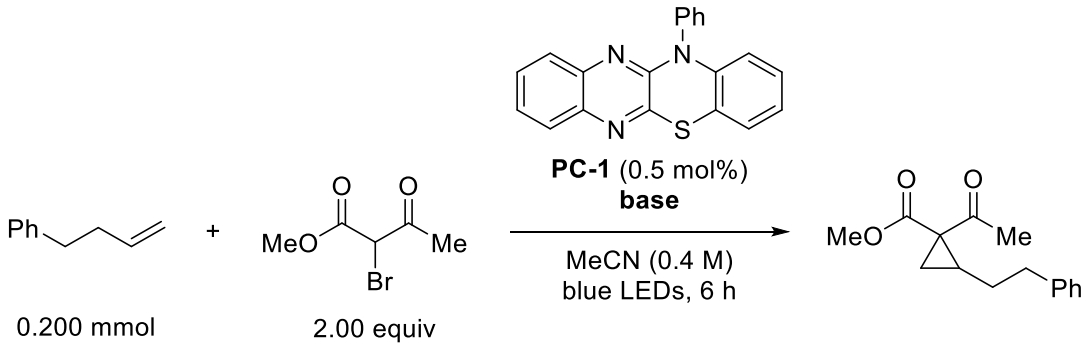
5	**PC-1**	0.100	70	23
6	**PC-2**	0.500	62	31
7	**PC-3**	0.500	52	36
8	Eosin Y	0.500	36	61
9	$Ir(ppy)_3$	0.500	78	16
10	$Ru(bpy)_3Cl_2$	0.500	6	89

Effect of Bromide Equivalents



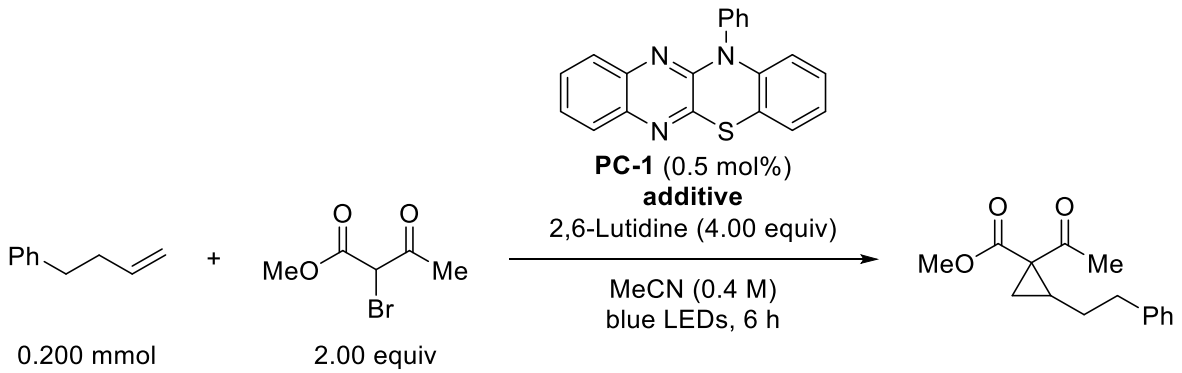
Entry	Equiv	Product [%]	SM [%]
1	1.00	62	31
2	1.20	79	20
3	1.50	93	10
4	2.00	97	0
5	3.00	95	0

Effect of Identity and Amount of Base



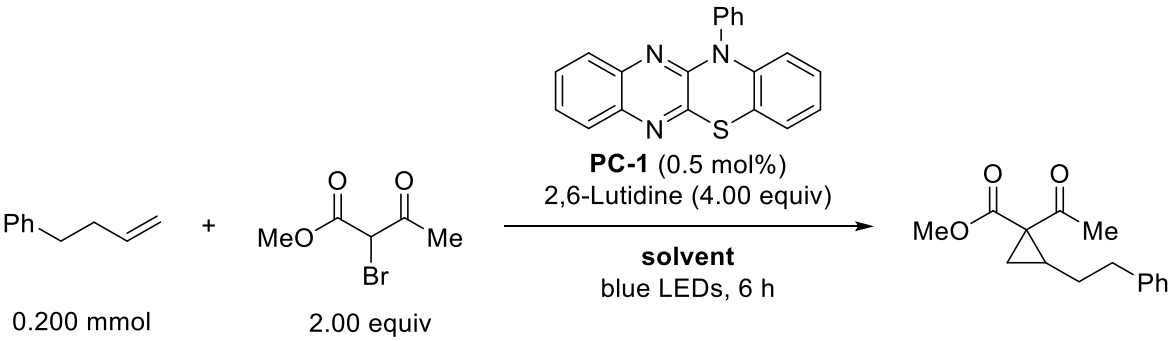
Entry	Base	Equiv	Product [%]	SM [%]
1	Et_3N	4.00	0	95
2	DIPEA	4.00	0	94
3	pyridine	4.00	0	96
4	2,6-lutidine	4.00	97	0
5	DTBMP	4.00	<5	10
6	NMI	4.00	0	96
7	collidine	4.00	54	45
8	2,6-lutidine	1.00	23	6
9	2,6-lutidine	2.00	48	13
10	2,6-lutidine	6.00	98	0
11	2,6-lutidine	12.0	98	0

Effect of Identity and Amount of Additive



Entry	Additive	Equiv	Product [%]	SM [%]
1	$LiBF_4$	1.00	34	42
2	LiBr	1.00	33	63
3	Cs_2CO_3	1.00	71	26
4	$LiClO_4$	1.00	44	43
5	LiOAc	1.00	72	15
6	LiCl	1.00	38	47
7	$LiPF_6$	1.00	60	26
8	$Mg(ClO_4)_2$	1.00	36	47
9	$Mg(OTf)_2$	1.00	41	26
10	KPF_6	1.00	47	0
11	Bu_4NBF_4	1.00	69	21
12	NaOAc	1.00	98	0
13	$NaBF_4$	1.00	82	6
14	$LiBF_4$	none	97	0
15	$LiBF_4$	0.200	68	32
16	$LiBF_4$	0.500	46	37
17	$LiBF_4$	1.00	34	42

Effect of Solvent and Concentration



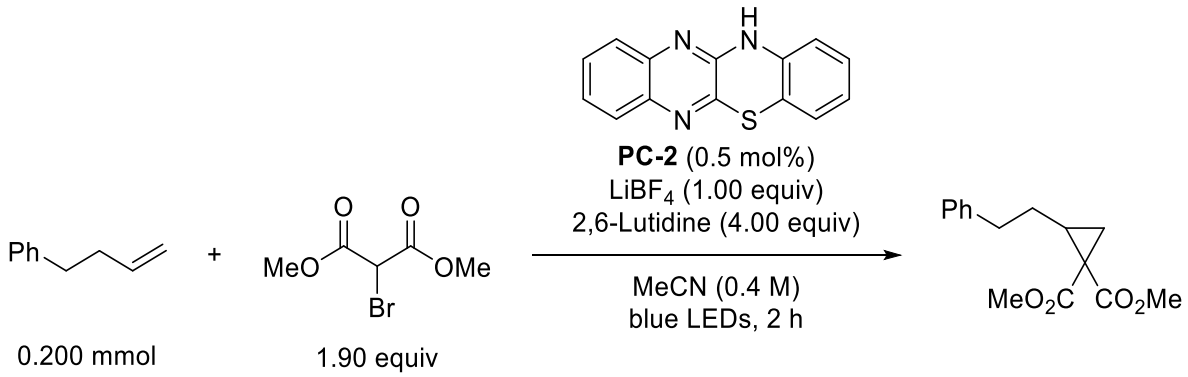
Entry	Solvent	Conc. [M]	Product [%]	SM [%]
1	DMPU	0.400	30	67
2	sulfolane	0.400	97	2
3	DMSO	0.400	68	30
4	DMF	0.400	96	0
5	HFIP	0.400	63	0
6	propionitrile	0.400	90	0
7	chloroform	0.400	41	0
8	THF	0.400	12	16
9	toluene	0.400	0	0
10	hexane	0.400	24	0
11	MeCN	0.800	95	0
12	MeCN	0.600	96	0
13	MeCN	0.400	97	0
14	MeCN	0.200	97	0
15	MeCN	0.100	98	0

4. Optimization Studies for α-Bromomalonate

Example of procedure for optimization

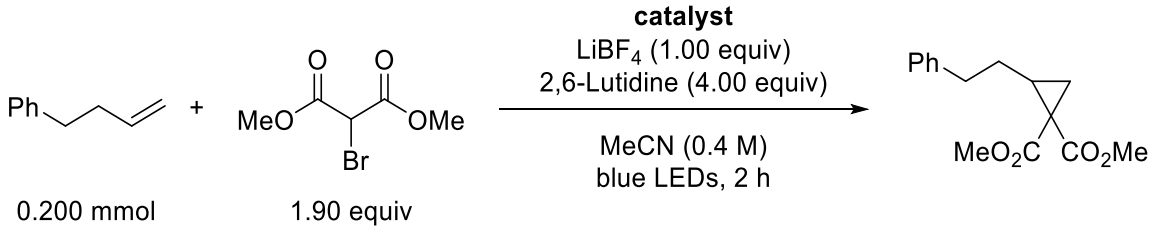
To a glass vial charged with **PC-2** (0.25 mg, 0.0010 mmol, 0.50 mol%) and $LiBF_4$ (18.7 mg, 0.200 mmol, 1.00 equiv) in MeCN (500 µL, 0.4 M) were added **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and bromo dimethylmalonate (50 µL, 0.380 mmol, 1.90 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.

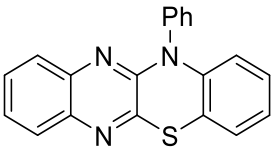
Control Experiments



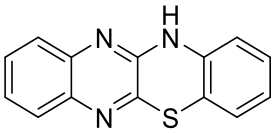
Entry	Change	Product [%]	SM [%]
1	no base	0	68
2	no additive	0	0
3	no PC	0	93
4	in the dark, 40°C	0	95

Effect of Catalyst and Catalyst Loading

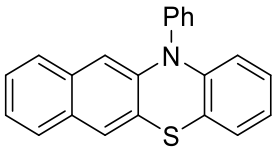




PC-1



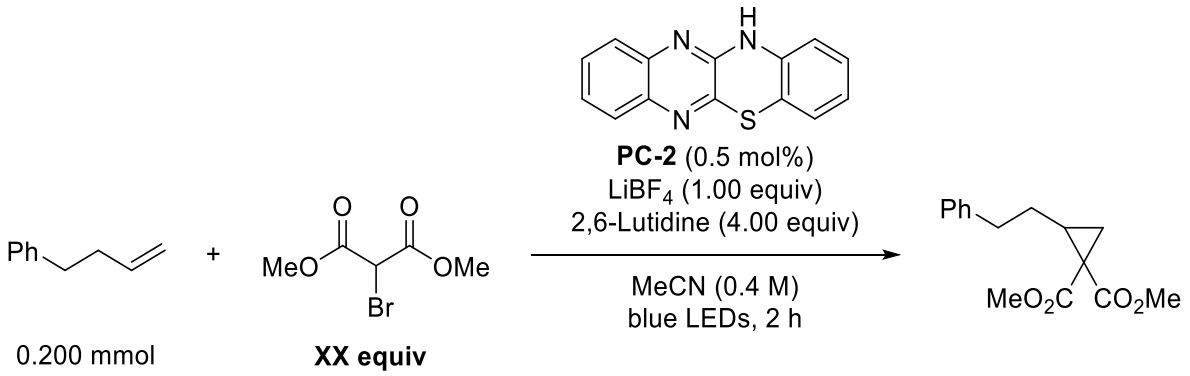
PC-2



PC-3

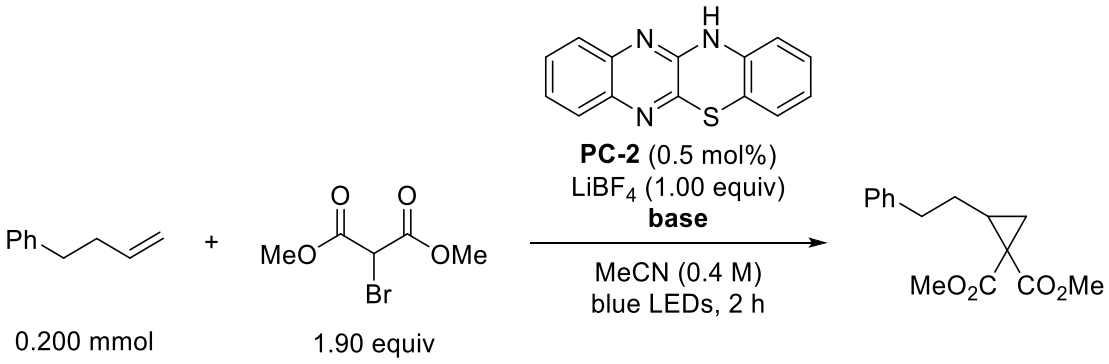
Entry	Catalyst	Equiv [mol%]	Product [%]	SM [%]
1	**PC-2**	10.0	92	0
2	**PC-2**	5.00	94	0
3	**PC-2**	1.00	97	0
4	**PC-2**	0.500	97	0
5	**PC-2**	0.100	70	14
6	**PC-1**	0.500	89	0
7	**PC-3**	0.500	52	43
8	$Ru(bpy)_3Cl_2$	0.500	15	82

Effect of Bromide Equivalents



Entry	Equiv	Product [%]	SM [%]
1	1.00	67	26
2	1.20	69	18
3	1.50	80	10
4	2.00	97	0
5	3.00	96	0

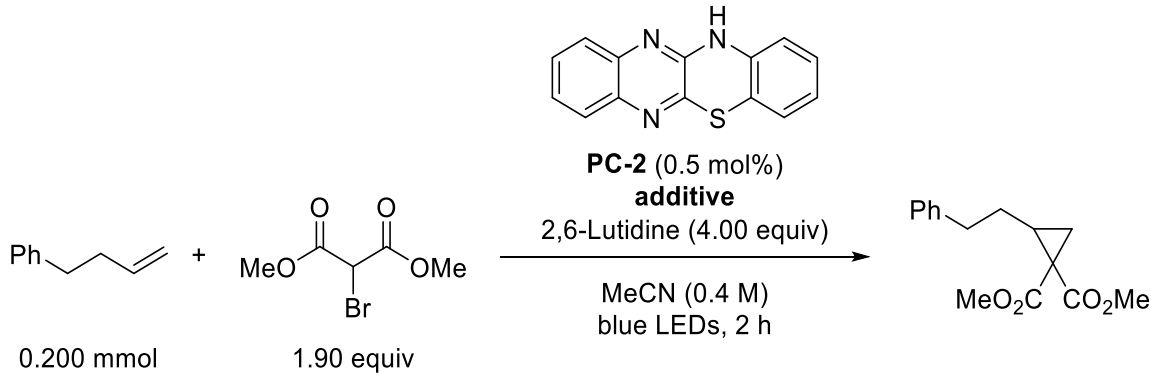
Effect of Identity and Amount of Base



Entry	Base	Equiv	Product [%]	SM [%]
1	Et_3N	4.00	0	95
2	DIPEA	4.00	0	96
3	pyridine	4.00	0	100
4	2,6-lutidine	4.00	93	0

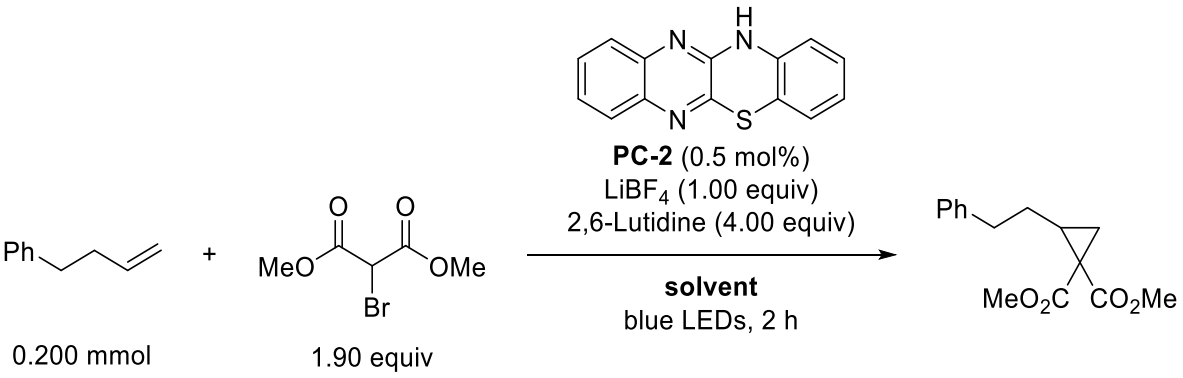
5	collidine	4.00	71	27
6	DTBMP	4.00	0	40
7	2,6-lutidine	1.00	48	0
8	2,6-lutidine	2.00	90	18
9	2,6-lutidine	3.00	97	10
10	2,6-lutidine	6.00	95	0

Effect of Identity and Amount of Additive



Entry	Additive	Equiv	Product [%]	SM [%]
1	$LiBF_4$	1.00	97	0
2	$LiClO_4$	1.00	89	0
3	LiOAc	1.00	56	5
4	$LiPF_6$	1.00	87	0
5	$Mg(ClO_4)_2$	1.00	79	0
6	$Mg(OTf)_2$	1.00	75	0
7	KPF_6	1.00	47	0
8	Bu_4NBF_4	1.00	0	0
9	NaOAc	1.00	0	14
10	$NaBF_4$	1.00	0	18
11	$LiBF_4$	none	0	0
12	$LiBF_4$	0.100	73	0
13	$LiBF_4$	0.500	85	0
14	$LiBF_4$	1.00	97	0
15	$LiBF_4$	2.00	97	0

Effect of Solvent and Concentration

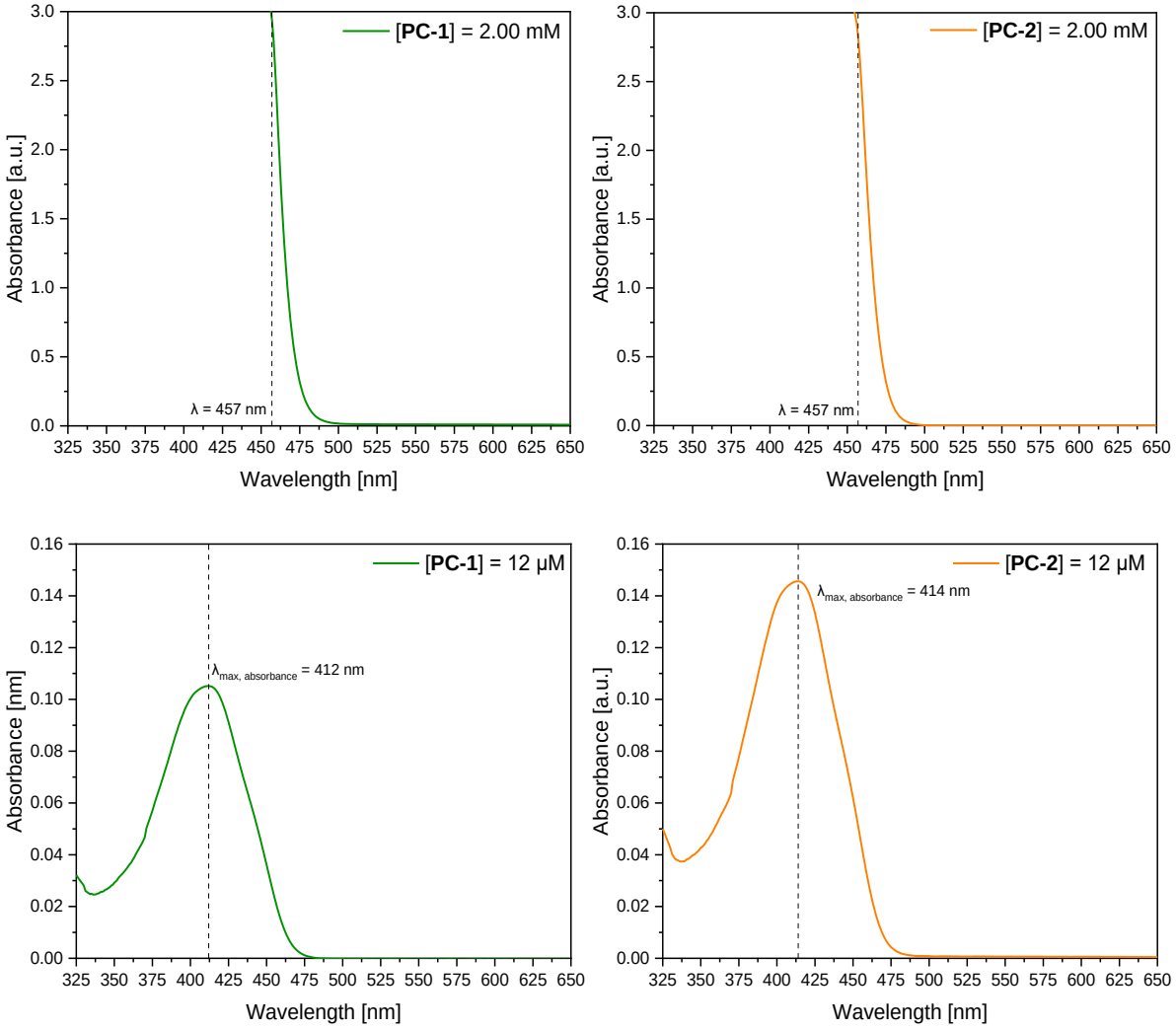


Entry	Solvent	Conc. [M]	Product [%]	SM [%]
1	DMPU	0.400	0	63
2	sulfolane	0.400	62	20
3	DMSO	0.400	0	94
4	DMF	0.400	34	11
5	HFIP	0.400	12	0
6	propionitrile	0.400	72	3
7	chloroform	0.400	0	0
8	THF	0.400	0	12
9	toluene	0.400	0	0
10	hexane	0.400	0	15
11	MeCN	0.800	75	7
12	MeCN	0.600	94	0
13	MeCN	0.400	97	0
14	MeCN	0.200	93	0

5. UV-Vis Spectra of PC-1 and PC-2

UV-Vis spectra of **PC-1** and **PC-2** were measured for two concentrations:

1. A 2.00 mM solution corresponding to 0.5 mol % catalyst loading in 5 mL MeCN (reaction conditions) was prepared and shows an absorbance of >3.0 below 457 nm.
2. The UV-Vis spectra recorded for a 12 µM solution were used to determine $\lambda_{max,\ absorption}$ of **PC-1** and **PC-2** and to determine the extinction coefficient of **PC-1** and **PC-2** at 446 nm (446 nm the emission maximum of the blue LEDs, *vide supra*).



Photocatalyst (12 µM)	**$\lambda_{max,\ absorbance}$**
PC-1	412 nm
PC-2	414 nm

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

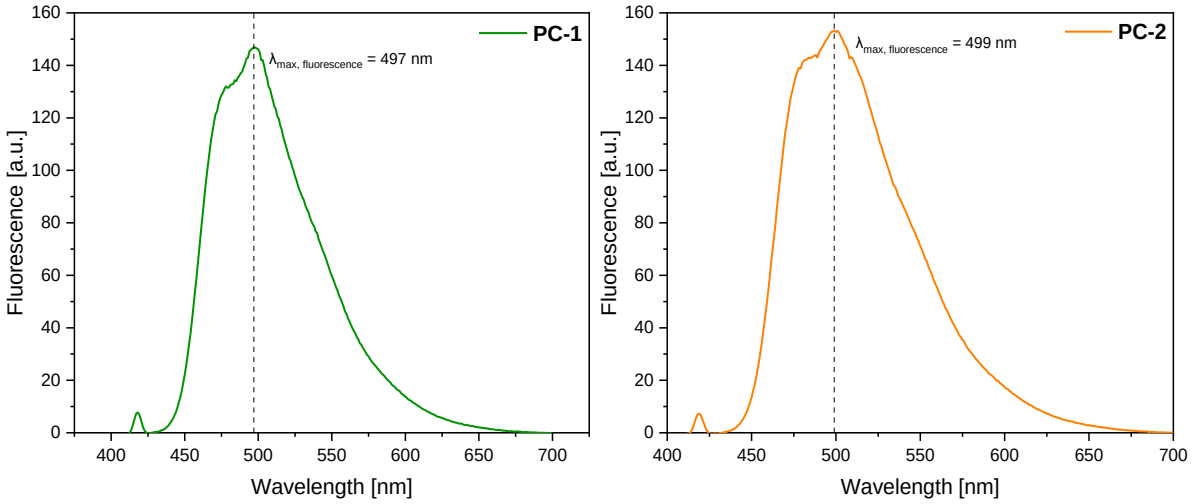
$$\varepsilon_\lambda = \frac{A_\lambda}{c \cdot d}$$

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

Photocatalyst (12 µM)	**Absorbance at 446 nm**	**$\varepsilon_{446\ nm}$**
PC-1	0.04588	3823 $M^{-1}cm^{-1}$
PC-2	0.07390	6158 $M^{-1}cm^{-1}$

6. Fluorescence Spectra of PC-1 and PC-2

To measure the fluorescence spectra of **PC-1** and **PC-2**, a 12 µM solution in degassed MeCN was prepared. The solutions were excited at $\lambda_{max,\ absorbance}$ of the photocatalysts (*vide supra*). The resulting fluorescence spectra are shown below.



Photocatalyst (12 µM)	$\lambda_{max,\ fluorescence}$
PC-1	497.0 nm
PC-2	499.0 nm

7. Stern-Volmer Relationship Studies

For fluorescence quenching studies, all reagents and MeCN were degassed with argon for 30 min while sonicating, and all solutions were prepared in a glove box. For a typical measurement, a 12.00 µM solution of **PC-1** in 5 mL MeCN was added to the appropriate amount of quencher. Different amounts of bromide **1a**, phenylbutene **2a** or 2,6-lutidine resulted in the concentrations indicated in the table below.

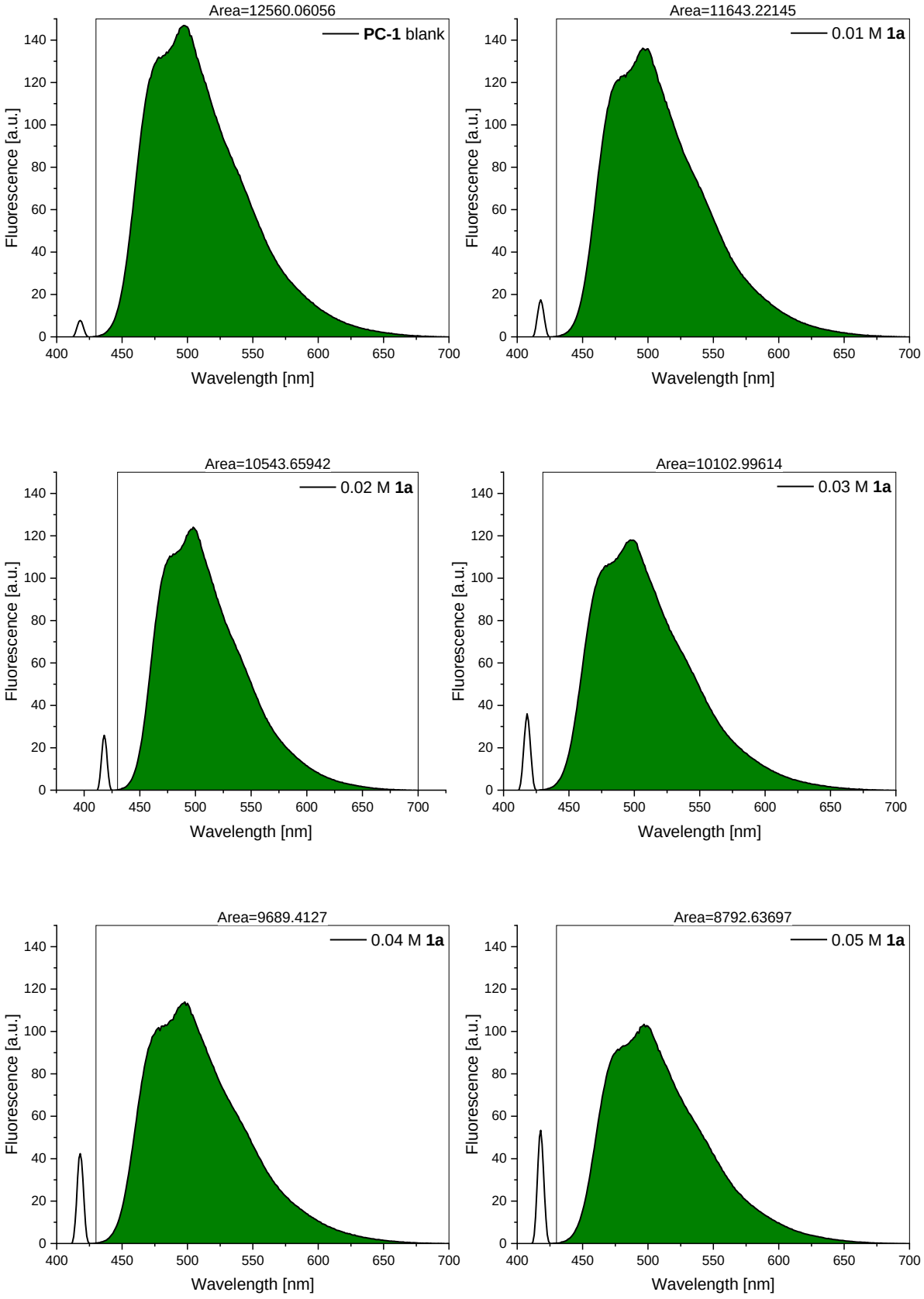
Solution	[**1a**]	[**2a**]	[2,6-lutidine]
1	0.00958 M	0.0111 M	0.00971 M
2	0.0201 M	0.0201 M	0.0194 M
3	0.0302 M	0.0294 M	0.0304 M
4	0.0401 M	0.0398 M	0.0402 M
5	0.0509 M	0.0509 M	0.0519 M

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

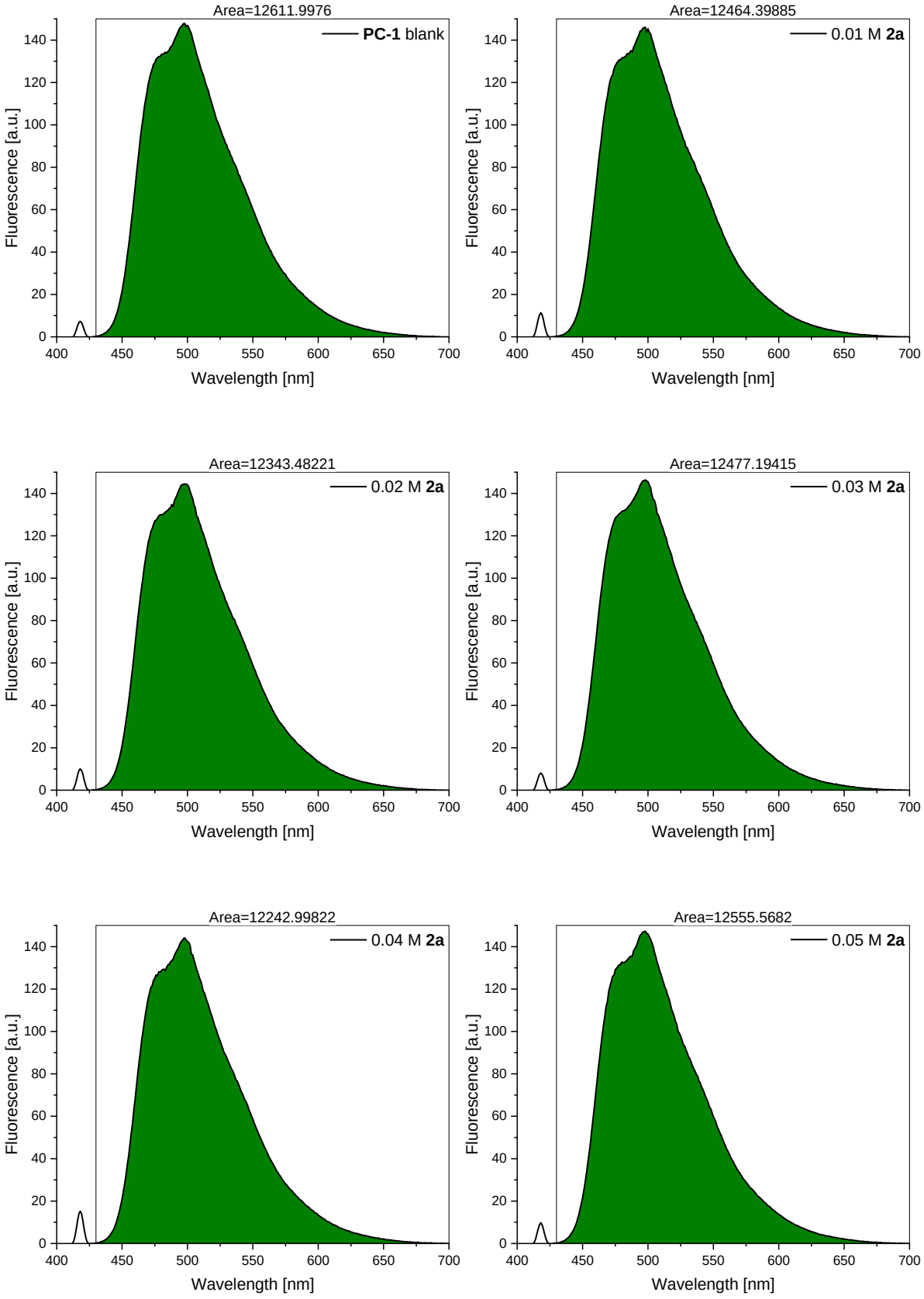
Prior to each compound series, a blank measurement containing only 12 µM **PC-1** in 5 mL MeCN was recorded. For the data analysis the area below the fluorescence curve was integrated from 430 nm to 700 nm.

Solution	$\int_{\lambda=430nm}^{\lambda=700nm} \mathbf{1a}$	$\int_{\lambda=430nm}^{\lambda=700nm} \mathbf{2a}$	$\int_{\lambda=430nm}^{\lambda=700nm} 2{,}6-\text{lutidine}$
Blank	12560	12612	12212
0.01 M	11643	12464	12565
0.02 M	10543	12343	12576
0.03 M	10103	12477	12334
0.04 M	9689.4	12243	12146
0.05 M	8792.6	12556	12457

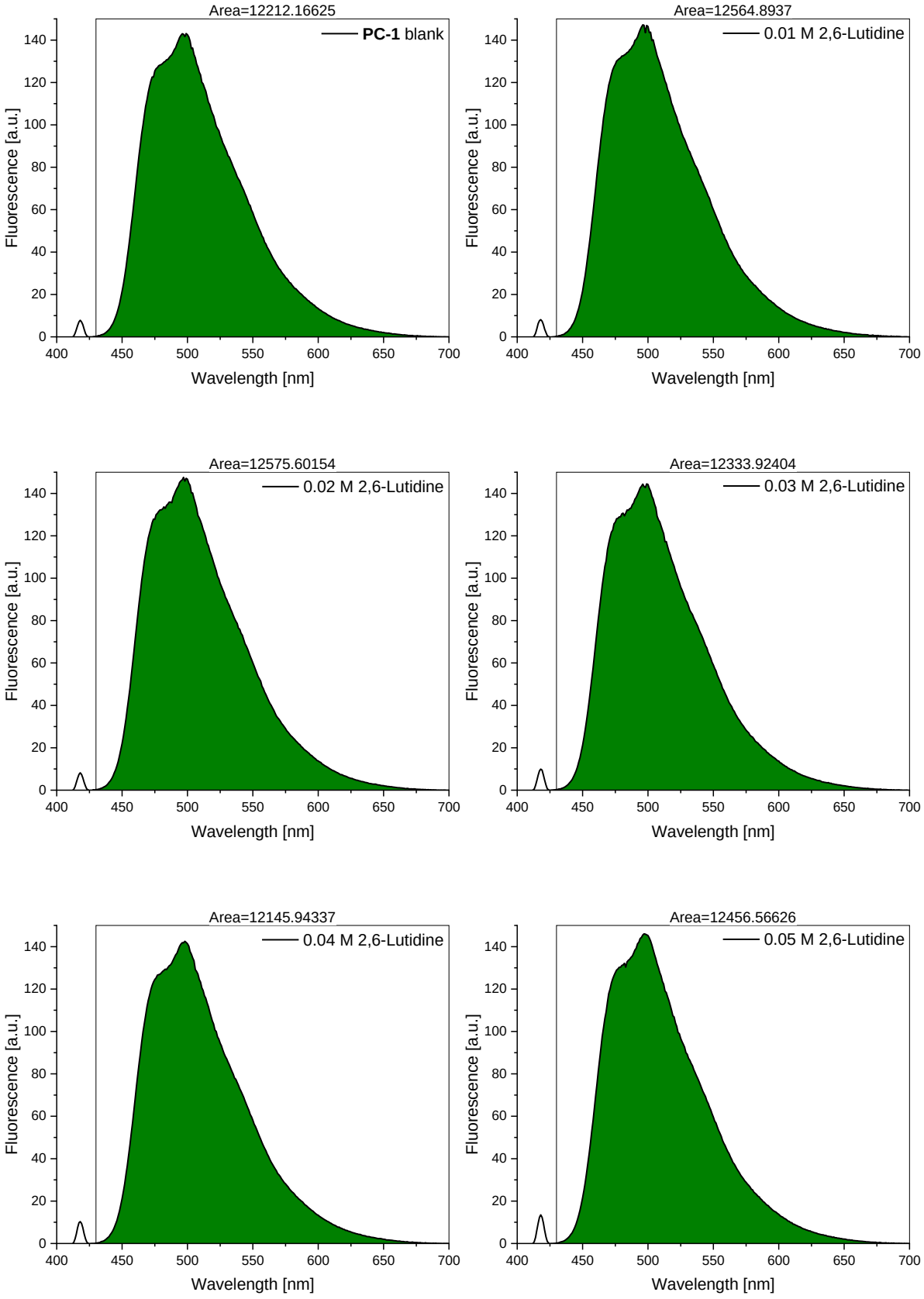
Fluorescence Spectra and Integrated Area for 1a



Fluorescence Spectra and Integrated Area for 2a



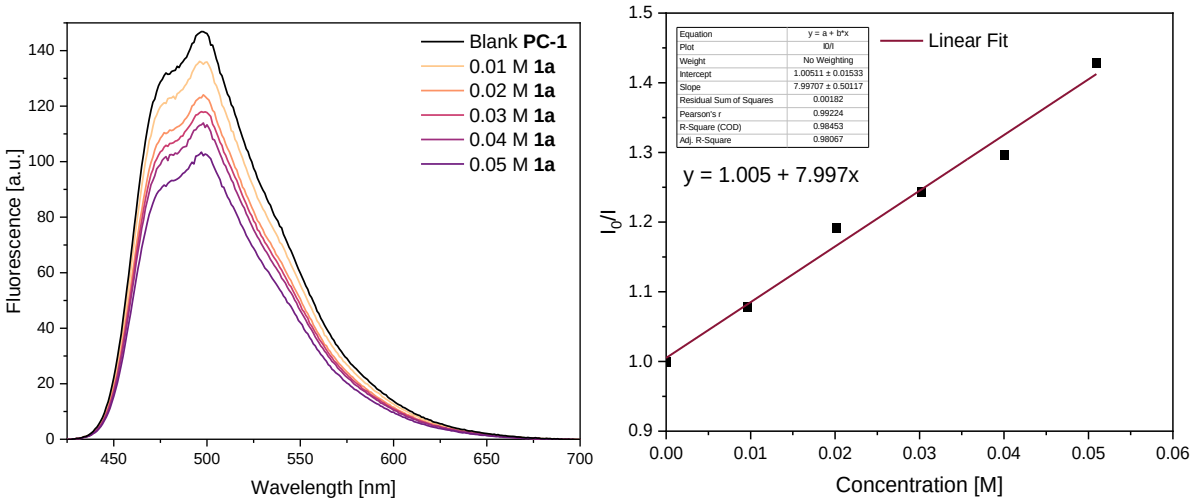
Fluorescence Spectra and Integrated Area for 2,6-Lutidine



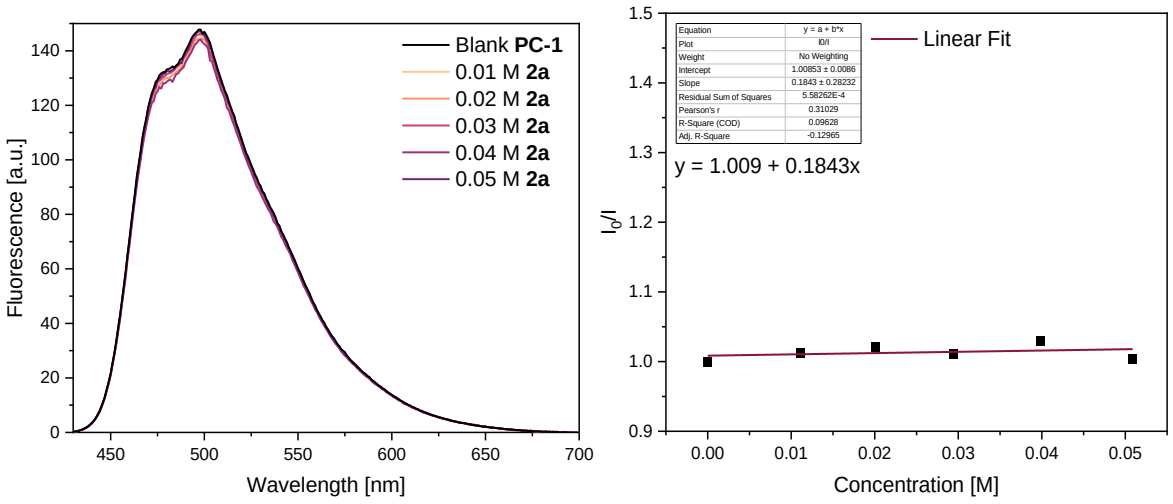
For Stern-Volmer relationships, the integral of the corresponding blank I_0 was divided by the integral I of the solutions 1-5 containing the quencher in different concentrations. The result was plotted against the concentration of the solutions. Only bromide **1a** showed significant quenching of the photocatalyst exited state with a small but significant Stern-Volmer constant of 7.997 M^{-1}. Comparison of UV-Vis absorption spectra taken of **PC-1** before and after Stern-Volmer relationship studies verified that **PC-1** was unchanged.

Note: The UV-Vis spectrum of bromomalonate **1a** at c = 0.05 M in MeCN shows an absorbance of < 0.01. Thus, the absorbance of **1a** is a negligible factor in the observed decrease of fluorescence.

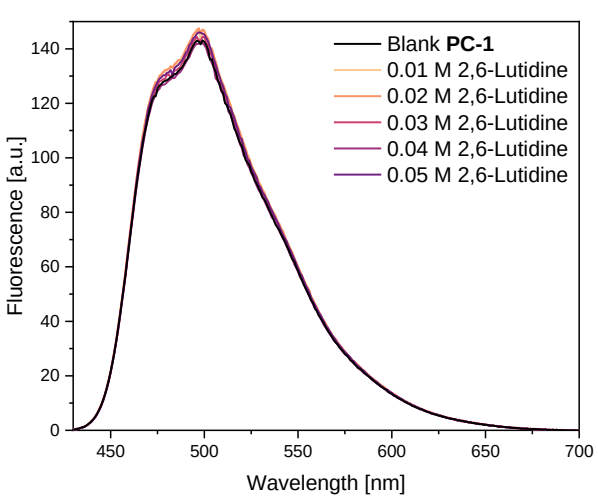
Stern-Volmer Relationship for 1a

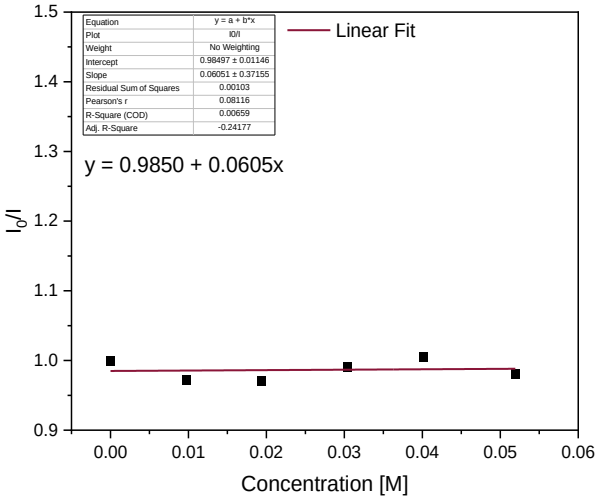


Stern-Volmer Relationship for 2a



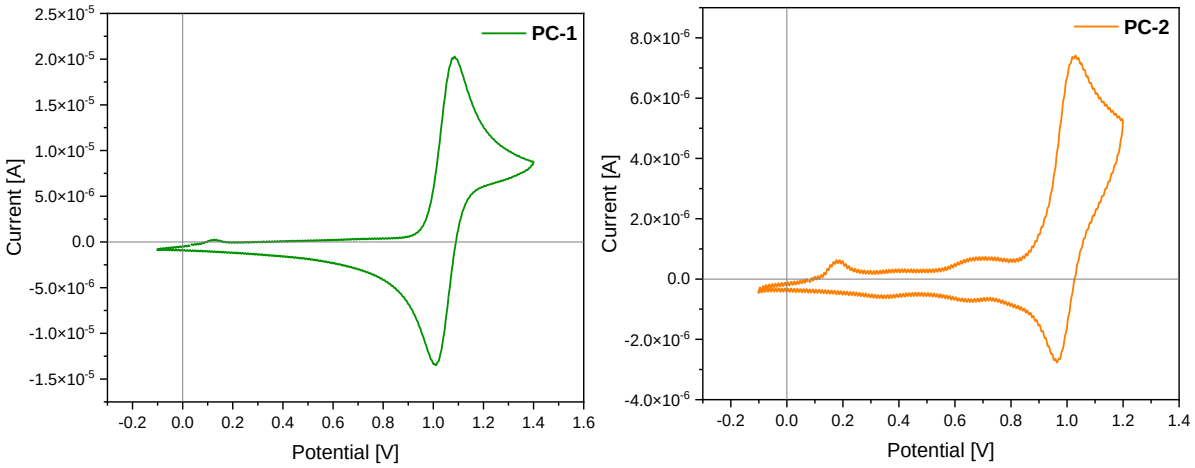
Stern-Volmer Relationship for 2,6-Lutidine





8. Cyclic Voltammetry

The reduction potential of the photocatalyst in its exited state was determined by cyclic voltammetry and fluorescence measurements. For better comparability with the literature, CVs were measured relative to ferrocene (Fc^+/Fc) and converted to the saturated calomel electrode (SCE). According to Nicewicz, $E_{1/2}$ (Fc^+/Fc) in MeCN has a value of +0.420 V against SCE. Our measurement against $Ag/AgNO_3$ was $E_{1/2}$ (Fc^+/Fc) = 0.321. Thus, for the conversion to SCE, +0.099 V were added to our values.[2, 3]



To calculate the reduction potential of **PC-1** and **PC-2** the maximum wavelength of fluorescence was converted into eV using Planck's equation:

$$E_{0,0} = \frac{h \cdot c}{\lambda_{max,\ fluorescence}}$$

where h = 4.1357 $\cdot 10^{-15}$ eVs (Planck's constant) and c = 299792458 m/s (speed of light).

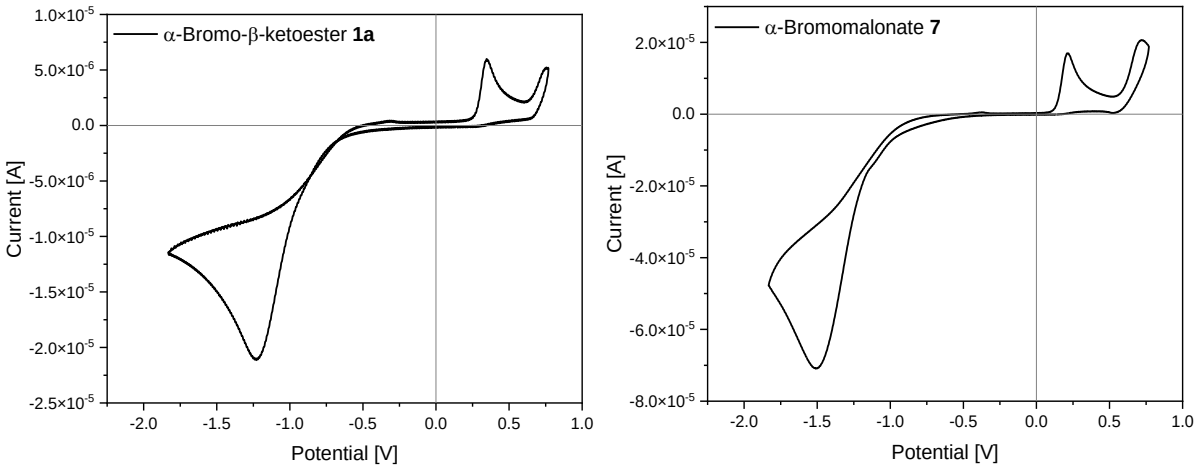
The reduction potential of the photocatalyst in its exited state $E^{*}_{1/2}(PC^{\bullet+}/PC^{*})$ is calculated by subtracting the maximum fluorescence wavelength in eV ($E_{0,0}$) from the half potential $E_{1/2}(PC^{\bullet+}/PC)$ in V of the photocatalyst. Since $E_{0,0}$ and $E_{1/2}(PC^{\bullet+}/PC)$ have different units, a conversion factor of 1 eV/V is applied which is commonplace when approaching single electron transfer on a per molar basis.[4]

This results in the formula:[4]

$$E^{*}_{1/2}(PC^{\bullet+}/PC^{*}) = E_{1/2}(PC^{\bullet+}/PC) - E_{0,0}$$

Photo-catalyst	**$E_{1/2}(PC^{\bullet+}/PC)$ (vs. SCE)[a]**	**$\lambda_{max,\ fluorescence}$**	**$E_{0,0}$**	**$E^{*}_{1/2}(PC^{\bullet+}/PC^{*})$ vs SCE**
PC-1	1.061 V	497.0 nm	2.495 eV	-1.434 V
PC-2	0.9989 V	499.0 nm	2.485 eV	-1.486 V

To determine if the photocatalysts can reduce the starting material bromides, a CV of α-bromo-β-ketoester **1a** and α-bromomalonate **7** was recorded. As for the photocatalysts, the CVs were measured relative to Fc/Fc^{+} and converted to SCE ($E_{1/2}\,(Fc^{+}/Fc)$ = 0.420 V). The value for Fc/Fc^{+} was determined as $E_{1/2}\,(Fc^{+}/Fc)$ = 0.252 which corresponds to a conversion factor of +0.168 V.



Since the reduction is not reversible, the $E_{p/2}$ value which corresponds to the potential at half the maximum current in the CV is used to estimate $E^0_{1/2}$. The peak potential is not used for this estimate as it was found that peak potential estimation leads to consistent overestimation the redox potentials.[3]

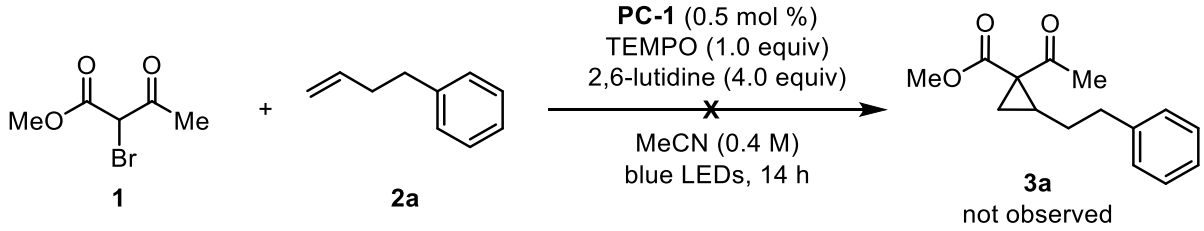
Bromide	**$E_{p/2}$ ($B/B^{\bullet-}$) (vs. SCE)[a]**
α-bromo-β-ketoester **1a**	-1.027 V
α-bromomalonate **7**	-1.288 V

$E^*_{ox}(PC^{\bullet+}/PC^*) < E_{p/2}(B/B^{\bullet-})$ for both photocatalysts and both bromides, a reduction of **1a** and **7** by **PC-1** or **PC-2** is feasible since:

$$\Delta G_{ET} = -F(E_{1/2}(B/B^{\bullet-}) - E_{1/2}(PC^{\bullet+}/PC^*))$$

Where $\mathcal{F}$ is Faraday's constant (23.061 kcal V^{-1} mol^{-1})

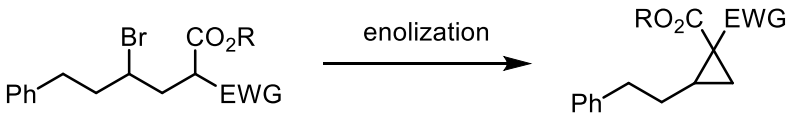
9. TEMPO Experiment



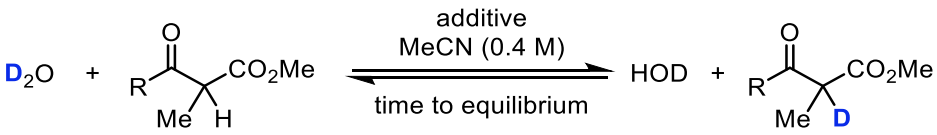
To a glass vial charged with **PC-1** (0.33 mg, 0.0010 mmol, 0.50 mol%) in MeCN (500 µL, 0.4 M) were added **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), 2,2,6,6-Tetramethylpiperidinyloxyl (31.3 mg, 0.200 mmol, 1.00 equiv), and bromoketoester (0.400 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 14 h 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. No product was observed.

10. Kinetic Studies on Enolization

As discussed in the main text and in the further mechanistic considerations, enolization of **10c** to close the cyclopropane is a feasible pathway to product.



To elucidate the kinetics of the enolization of **10c** towards cyclopropane, dimethyl methylmalonate **S-1** and 2-methyl-acetoacetic acid methyl ester **S-2** were chosen as model substrates. To an NMR tube charged with **S-1** or **S-2** (0.20 mmol) was added MeCN (500 µL), D_2O (4.0 µL, 0.20 mmol, 1.00 equiv) and 14 µL 1,3,5-mesitylene (0.093 mmol, 0.50 equiv) as internal standard. Additives were then added according to the table below. The NMR tube was then capped and spectra recorded at regular intervals while heating the sample to 40 °C. The degree of deuteration was determined by comparison of the C-H signal of mesitylene with the C_α-H of the activated bromide.



Compound	No Additive	$LiBF_4$ (50 mol%)	2,6-lutidine (4.0 equiv)	$LiBF_4$ (50 mol%) 2,6-lutidine (4.0 equiv)
S-1	> 16 h	> 16 h	> 16 h	9 min
S-2	> 4 h	> 4 h	2 h	5 min

11. Quantum Yield

The Quantum yield determination was carried out according to the literature.[5]

All experiments were carried out in a red-light room.

The photon flux of the blue LED was determined by Hatchard-Parker ferrioxalate actinometry.[6, 7] A modified procedure with an increased excess of 1,10-phenanthroline was used to account for the high intensity of the light source.[8] The light source in the following experiments is considered monochromatic for the restricted wavelength interval used; a prerequisite for the actinometric determination of quantum yields.[9] Hatchard and Parker showed that the fraction of light absorbed correlates to the optical path length, concentration, and wavelength of irradiated light, but no correlation has been demsonstrated for the impact of the emission intensity of the light source. We chose to employ an optical path length of 10 mm in the experiments reported herein due to the high intensity of the modern LEDs used in this study.

Ferrioxalate solution (0.15 M Ferrioxalate/0.05 M H_2SO_4): A 100 mL volumetric flask was charged with iron(III) chloride hexahydrate (4.05 g, 15.0 mmol). Water (20.0 mL) was added followed by potassium oxalate hydrate (8.29 g, 45.0 mmol) in water (60.0 mL). for the solution was stirred for 1 h, then 0.5 M sulfuric acid (10.0 mL) were added followed by water until the 100 mL graduation mark.

Developer solution (0.05 M phenanthroline/0.75 M sodium acetate/0.2 M H_2SO_4): Sulfuric acid (1.11 ml, 20.0 mmol) was added to water (80 mL) in a 100 mL volumetric flask. Sodium acetate trihydrate (10.2 g, 75.0 mmol) and 1,10-phenanthroline (0.901 g, 5.00 mmol) were added followed by water to give a total volume of 100 mL. The solution was prepared and stored in the dark.

To determine the photon flux of the photoreactor, all measurements were carried out in duplicate. A portion of the ferrioxalate solution (3.0 mL) was added to a reaction vial (⌀ 2.1 cm, borosilicate glass). The path length of the ferrioxalate solution was approximately 1 cm. The vial was placed 15 mm away from a blue LED (40 W, λmax = 440 nm) and vertically irradiated through an aperture (⌀ 6.0 mm) for a specified time (10 s, 20 s, 30 s, 40 s) with magnetic stirring of the solution. After irradiation, a 0.1 mL aliquot of the irradiated solution was added to a vial containing developer solution

(5.0 mL). The solution was allowed to rest for 1 h for full coordination of all ferrous ions to 1,10-phenanthroline. An aliquot of the solution (0.1 mL) was diluted with 1.9 mL developer solution without 1,10-phenanthroline. The absorbance of the diluted solution was measured at 510 nm. A non-irradiated sample was prepared and its absorbance after dilution at 510 nm measured. The amount of ferrous ions formed during irradiation was calculated as follows:

$$\text{mol } Fe^{2+} = \frac{D \cdot V \cdot \Delta A}{l \cdot \varepsilon}$$

Where D is the dilution factor (20), V is the total volume (0.153 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11100 L mol^{-1} cm^{-1}). The photon flux can be calculated as follows:

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximated with the literature known value of 1.01 for a 0.15 M solution at λ = 436 nm), t is the irradiation time, and f is the fraction of light absorbed (approximated with the literature known value of 0.997 at λ = 436 nm). 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 cyclopronation reaction.

<u>For methyl bromoacetoacetate:</u>

To a glass crimp vial charged with **PC-1** (1.6 mg, 0.005 mmol, 0.50 mol %) was added alkene starting material (1.00 mmol) and the atmosphere exchanged to argon (three cycles). MeCN (2.5 mL, 0.4 M, degassed) 2,6-lutidine (5465 µL, 4.0 mmol, 4 equiv, degassed) and methyl bromoacetoacetate (250 µL, 1.9 mmol, 1.9 equiv). The reaction mixture was then degassed by bubbling through Ar for 15 min und cooling with an ice-bath. The vial was placed 15 mm away from a blue LED (40 W, λmax = 440 nm) and vertically irradiated through an aperture (⌀ 6.0 mm) for 120 minutes. 65 µL 1,3,5-mesitylene (0.465 mmol, 0.47equiv) were added as internal standard and an aliquot

analyzed by ^{1}H NMR. After 120 minutes the reaction gave 11% conversion of starting material to product and intermediates, including γ-bromoketoester **S-5** (*vide infra*). After standing at rt in the dark for 12 h the reaction mixture showed 8% product formation and 89% starting material.

For dimethylbromomalonate:

To a glass crimp vial charged with **PC-2** (1.25 mg, 0.005 mmol, 0.50 mol%) was added alkene starting material (1.0 mmol), $LiBF_4$ (93 mg, 1.0 mmol, 1.00 equiv) the atmosphere exchanged to argon (three cycles). MeCN (2.5 mL, 0.4 M, degassed), 2,6-lutidine (465 µL, 4.0 mmol, 4 equiv, degassed) and dimethyl bromomalonate (250 µL, 1.9 mmol, 1.9 equiv). The reaction mixture was then degassed by bubbling through Ar for 15 min und cooling with an ice-bath. The vial was placed 15 mm away from a blue LED (40 W, λmax = 440 nm) and vertically irradiated through an aperture (⌀ 6.0 mm) for 60 minutes. 65 µL 1,3,5-mesitylene (0.465 mmol, 0.47equiv) were added as internal standard and an aliquot analyzed by ^{1}H NMR. After 60 minutes the reaction showed formation of 7% product.

The quantum yield was calculated as:

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

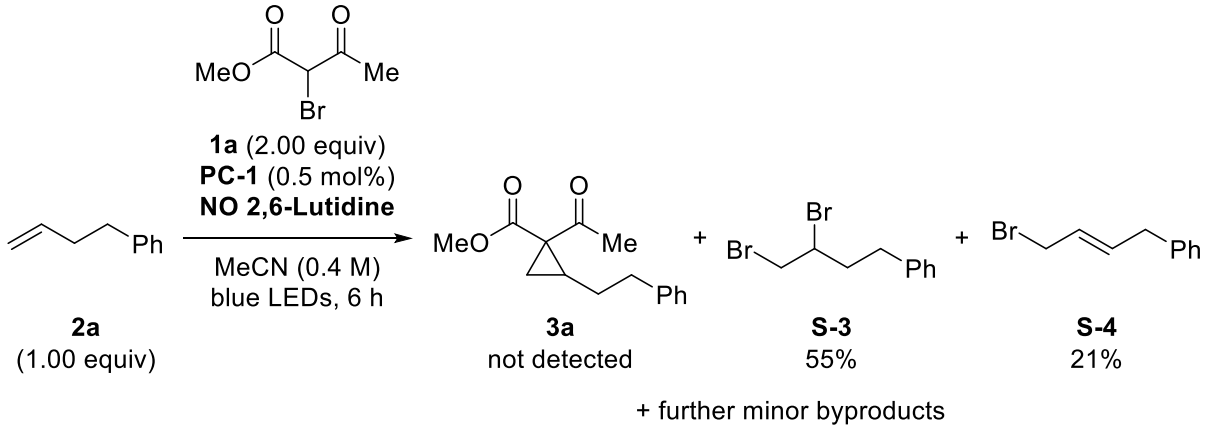
where *f* is the photon flux previously determined by ferrioxalate actinometry (*vide supra),* t is the time (3600 or 7200 s), and f is the fraction of light absorbed by the photocatalyst at 446 nm. The absorbance of **PC-1** and **PC-2** in MeCN were determined at reaction concentration. The absorbance at 446 nm is >3 indicating the fraction of light absorbed f is >0.999. The quantum yield of the reaction was determined to be:

Methyl bromoacetoacetate Φ = 0.0122

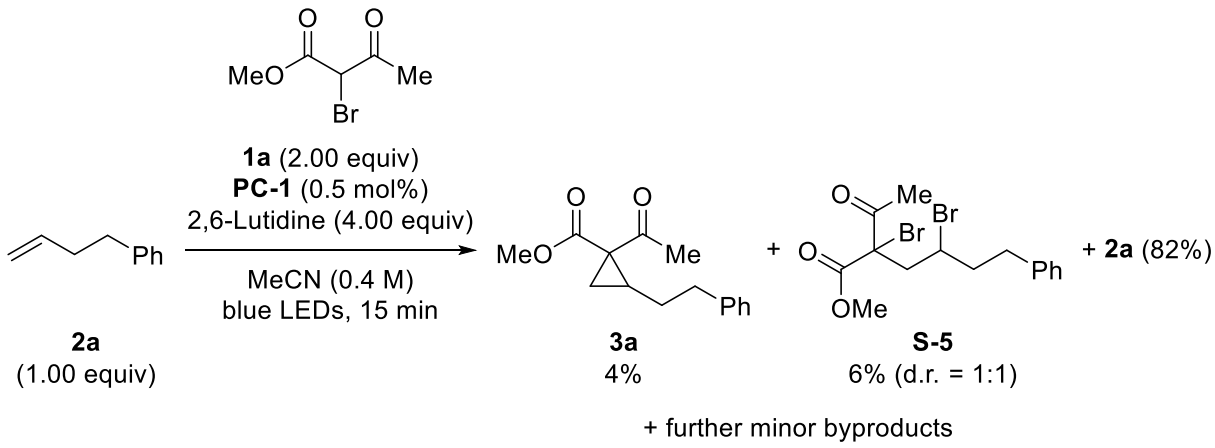
Dimethyl bromomalonate Φ = 0.0213

12. Further Mechanistic Considerations

As a control during optimization studies, the reaction of **1a** with **2a** was conducted without base. The reaction gave a complex mixture where cyclopropane **3a** was not detected. Instead, the dibrominated phenylbutene **S-3** and allylic bromide **S-4** were observed in 55% and 21% yield respectively (NMR yield calculated with mesitylene as internal standard). **S-3** and **S-4** were isolated and characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.



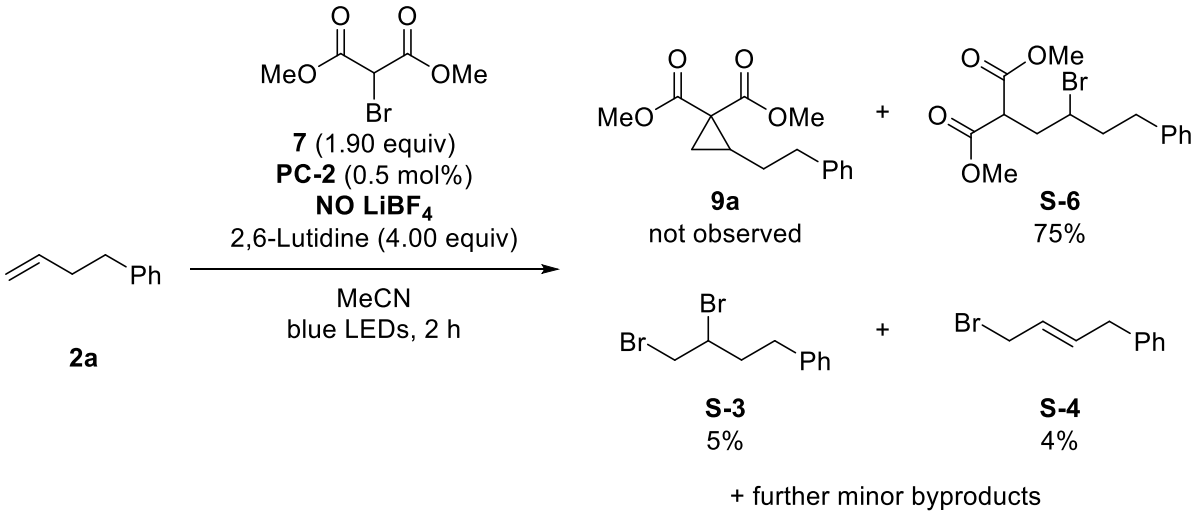
When the cyclopropanation of **2a** was conducted with **1a** under standard conditions and the reaction was interrupted after 15 min, we observed the dibromide **S-5** as major intermediate.



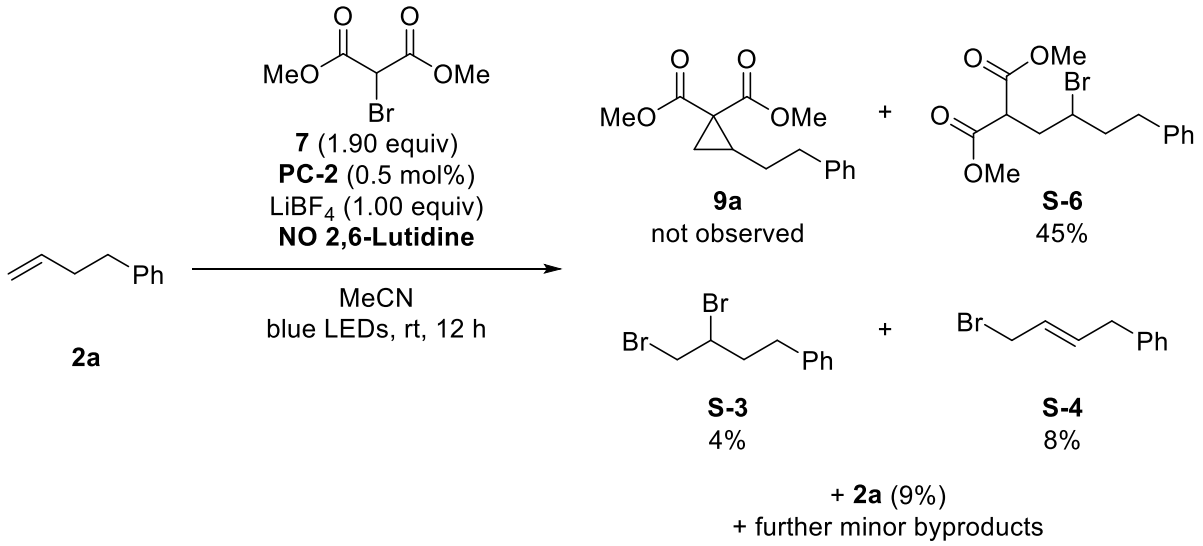
After standing at room temperature in the dark for 12 h the reaction mixture showed 9% of **3a**, and **S-5** was not observed anymore. This indicates that **S-5**, while being an off cycle intermediate, can re-enter the catalytic cycle after α-debromination. This is especially relevant for the quantum yield determination (*vide supra*), since the

quantum yield is defined as conversion to products which require light, thus including formation of bromides.

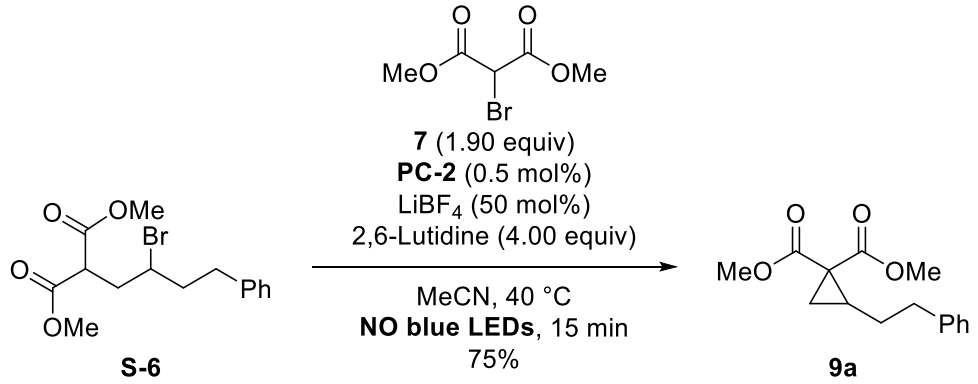
For dimethyl bromomalonate **7**, as a control during optimization studies the reaction of **2a** with **7** was conducted without $LiBF_4$. After 2 h, no starting material remained, and no product formation was observed. Instead, ATRA product **S-6** was observed as major species in 75% yield. Furthermore, **S-3** and **S-4** were observed in minute quantities (5% and 4% respectively; NMR yield calculated with mesitylene as internal standard). **S-6** was isolated and characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.



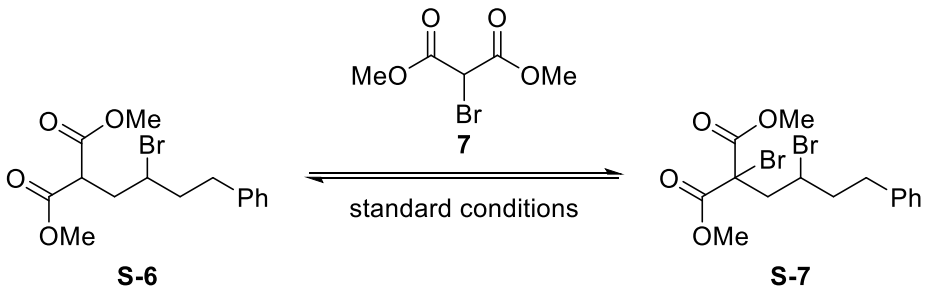
When the cyclopropanation of **2a** with **7** was conducted with 1.00 equiv $LiBF_4$ but no 2,6-lutidine, after 2 h mostly starting material was observed (68%). Therefore, the reaction was run for 12 h. After this time, the ATRA product **S-6** was again observed as major intermediate. Furthermore, **S-3** and **S-4** were observed in 4% and 8% respectively (NMR yield calculated with mesitylene as internal standard). Overall, the reaction proceeded less cleanly.



When **S-6** was resubjected to the reaction conditions without light, cyclopropane **9a** was observed in 75% yield (NMR yield calculated with mesitylene as internal standard). This shows that **S-6** is a viable intermediate towards cyclopropane **9a**.



During kinetic studies of cyclization **S-6** → **9a** we observed an additional, previously unobserved intermediate. Upon closer examination of the NMR data we found it to be α,γ-dibromide **S-7**. The intermediate was isolated and characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS. During the kinetic investigations the amount of **S-7** never exceeded 10%. At the end of the reaction **S-7** was not observed.



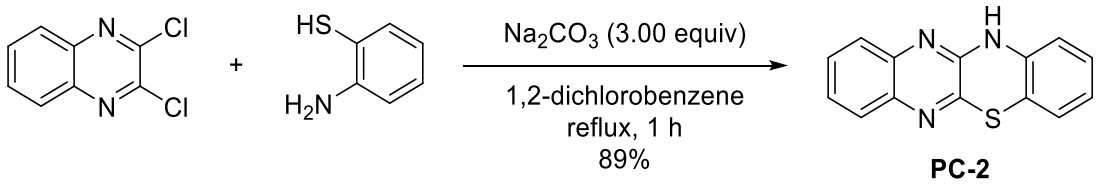
We hypothesize that **S-7** could be formed through enolization of **S-6** and subsequent reaction with bromomalonate **7**. Debromination, which is necessary to form the cyclopropane, could feasibly proceed with malonate or bromomalonate. Intermediate **S-7** could also be observed as minor byproduct if the cyclopropanation reaction is terminated before it goes to completion.

13. Experimental Section

13.1 Preparation of Photocatalysts PC-1 and PC-2

Compound PC-2:

12H-benzo[5,6][1,4]thiazino[2,3-b]quinoxaline



PC-2

In a 250 mL round-bottom flask, a suspension of 2,3-dichloroquinoxaline (3.96 g, 20.0 mmol, 1.00 equiv), 2-aminobenzenethiol (2.14 mL, 2.50 g. 20.0 mmol, 1.00 equiv), and sodium carbonate (6.36 g, 60.0 mmol, 3.00 equiv) in 1,2-dichlorobenzene (35 mL) was heated under reflux for 1 h. After cooling, the reaction mixture was diluted with water (30 ml). The precipitated yellow solid was filtered, washed with water (3 x 30 ml), and dried under reduced pressure (1 mbar, 50 °C) over night to give **PC-2** as yellow crystalline solid.

Yield: 4.47 g, 17.8 mmol, 89%

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.22 (s, 1H), 7.53 (ddd, J = 8.2, 1.4, 0.7 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.31 (ddd, J = 8.3, 6.2, 2.3 Hz, 1H), 7.09 – 6.99 (m, 2H), 6.91 – 6.78 (m, 2H).

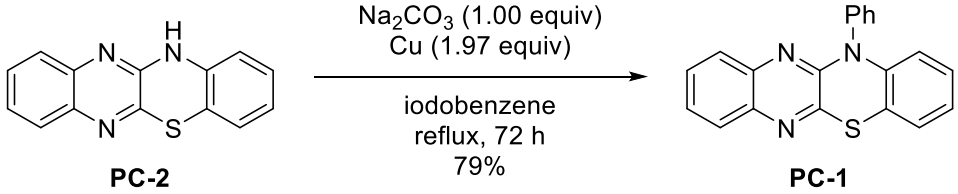
^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 145.5, 145.1, 140.3, 139.1, 136.5, 129.2, 127.9, 126.7, 125.8, 125.8, 125.5, 122.5, 115.9, 115.0.

IR (thin film, cm^{-1}): 3256, 1589, 1569, 1542, 1479, 1407, 1368, 1293, 1264, 1127, 1085, 1074, 932, 862, 751, 598.

HRMS (ESI+): *m/z* for $C_{14}H_{10}N_3S$ $[M+H]^+$: calc.: 252.0590, found: 252.0591

Compound PC-1:

12-phenyl-12H-benzo[5,6][1,4]thiazino[2,3-b]quinoxaline



In a 100 mL round-bottom flask, a suspension of **PC-2** (2.00 g, 7.97 mmol, 1.00 equiv), sodium carbonate (844 mg, 7.97 mmol, 1.00 equiv) and copper turnings (1.00 g, 15.7 mmol, 1.97 equiv) in iodobenzene (20 mL) was heated under strong reflux for 72 h. Unreacted iodobenzene was removed under reduced pressure (1 mbar, 50 °C). The crude product was recrystallized from hot ethanol (1.80 L) to give **PC-1** as yellow crystalline solid.

Yield: 2.05 g, 6.22 mmol, 79%

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.68 – 7.63 (m, 2H), 7.62 – 7.58 (m, 1H), 7.57 – 7.51 (m, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.33 (m, 2H), 7.22 – 7.13 (m, 2H), 7.01 – 6.88 (m, 2H), 6.02 – 5.95 (m, 1H).

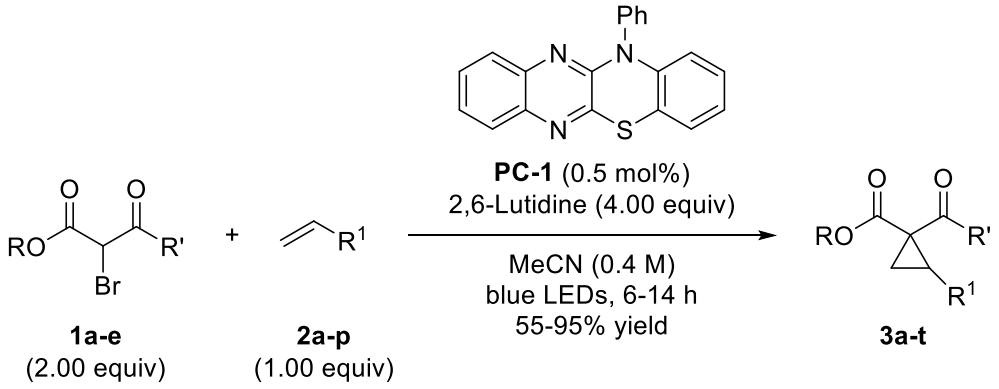
^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 146.5, 145.0, 139.7, 139.2, 139.0, 138.7, 130.4, 130.1, 129.2, 128.5, 127.6, 126.6, 126.6, 126.5, 126.4, 123.1, 117.3, 116.4.

IR (thin film, cm^{-1}): 3065, 1584, 1525, 1479, 1438, 1401, 1360, 1343, 1314, 1287, 1269, 1124, 1087, 749, 737, 694, 666, 599, 576.

HRMS (ESI+): *m/z* for $C_{20}H_{14}N_3S$ $[M+H]^+$: calc.: 328.0903, found: 328.0903

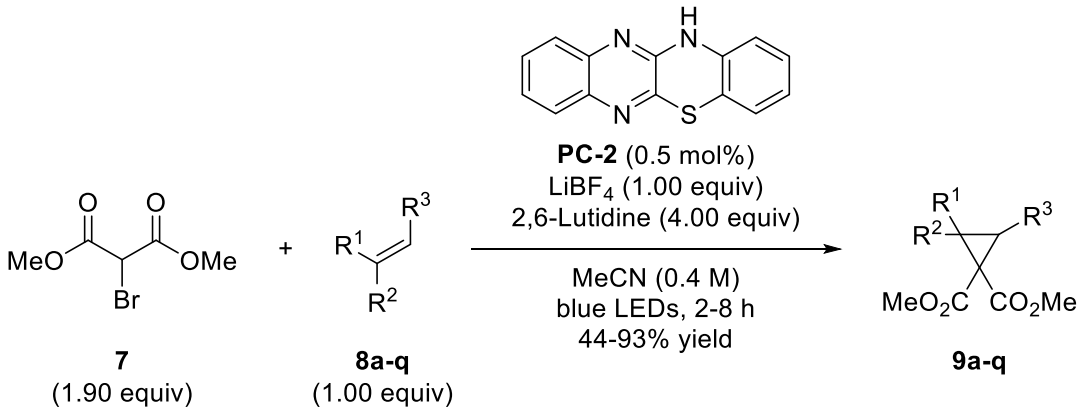
13.2 General Procedures for the Cyclopropanation

GP1: Cyclopropanation of Unactivated Alkenes with α-Bromo-β-ketoesters



To a glass vial charged with **PC-1** (0.33 mg, 0.0010 mmol, 0.50 mol%) in MeCN (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 bromoketoester (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 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.

GP2: Cyclopropanation of Unactivated Alkenes with α-Bromomalonates

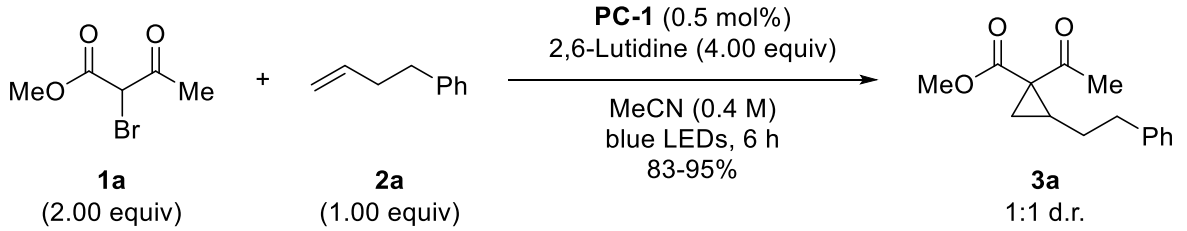


To a glass vial charged with **PC-2** (0.25 mg, 0.0010 mmol, 0.50 mol%) and $LiBF_4$ (18.7 mg, 0.200 mmol, 1.00 equiv) in MeCN (500 µL, 0.4 M) were added alkene starting material (0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and dimethyl bromomalonate (50.0 µL, 0.380 mmol, 1.90 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.

13.3 Substrate Scope for α-Bromo-β-ketoesters

Compound 3a:

Methyl 1-acetyl-2-phenethylcyclopropane-1-carboxylate



1a (2.00 equiv) + **2a** (1.00 equiv) → **3a** 1:1 d.r.

Cyclopropane **3a** was prepared via GP1, using alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 6 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3a** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Note: Cyclopropane **3a** was prepared on larger scale by an adapted procedure based on GP1, using alkene **2a** (300 µL, 264 mg, 2.00 mmol, 1.00 equiv) and bromoketoester **1a** (780 mg, 4.00 mmol, 2.00 equiv) and the reaction was stirred for 6 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3a** as a pale-yellow oil in 83% (408 mg, 1.66 mmol) yield. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 46.6 mg, 0.189 mmol, 95%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.33 – 7.23 (m, 4H), 7.22 – 7.11 (m, 6H), 3.78 (s, 3H), 3.73 (s, 3H), 2.67 (dt, J = 11.2, 6.9 Hz, 4H), 2.35 (d, J = 1.6 Hz, 6H), 2.09 – 1.92 (m, 2H), 1.81 – 1.69 (m, 2H), 1.68 – 1.59 (m, 1H), 1.56 (dd, J = 7.9, 4.2 Hz, 1H), 1.49 – 1.39 (m, 3H), 1.37 (dd, J = 9.0, 4.2 Hz, 1H).

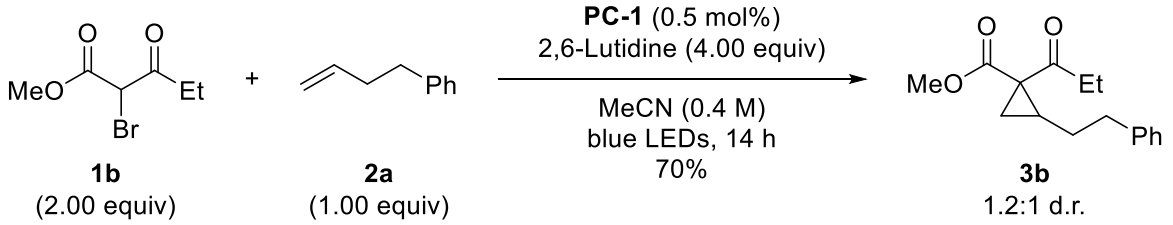
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 201.8, 171.8, 170.3, 141.4, 141.2, 128.8, 128.6, 128.5, 128.5, 128.5, 128.4, 126.2, 126.1, 52.4, 52.4, 41.7, 40.7, 35.7, 35.3, 31.6, 31.3, 30.9, 30.5, 29.4, 29.3, 23.9, 21.1.

IR (thin film, cm^{-1}): 3027, 2952, 2927, 2861, 1726, 1701, 1454, 1437, 1358, 1285, 1197, 981, 749, 700, 607.

HRMS (ESI+): *m/z* for $C_{15}H_{18}NaO_3$ $[M+Na]^+$: calc.: 269.1148, found: 269.1147

Compound 3b:

Methyl 2-phenethyl-1-propionylcyclopropane-1-carboxylate



Cyclopropane **3b** was prepared via GP1, using alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1b** (83.6 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3b** as a pale-yellow oil. The product was isolated as an inseparable 1.2:1 mixture of diastereomers.

Yield: 36.2 mg, 0.139 mmol, 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 – 7.27 (m, 3H), 7.28 – 7.23 (m, 1H), 7.21 – 7.12 (m, 6H), 3.77 (s, $3H_{minor}$), 3.72 (s, $3H_{major}$), 3.04 – 2.78 (m, 2H), 2.73 – 2.52 (m, 5H), 2.50 – 2.36 (m, 1H), 2.08 – 1.92 (m, 2H), 1.83 – 1.67 (m, 2H), 1.66 – 1.58 (m, 1H), 1.55 (dd, J = 7.8, 4.2 Hz, 1H), 1.43 – 1.31 (m, 4H), 1.11 – 1.03 (m, 6H).

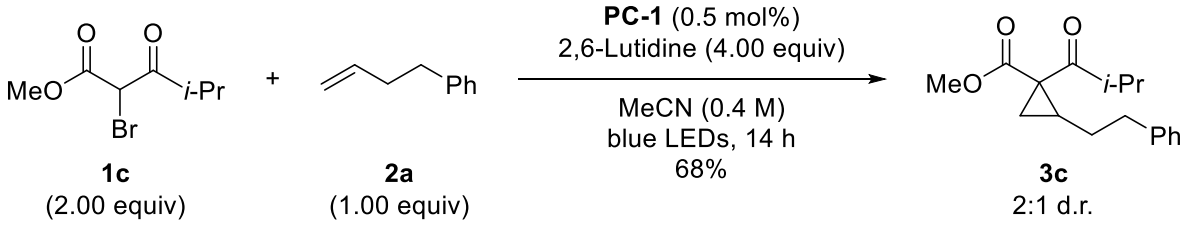
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 205.6, 204.8, 172.0, 170.4, 141.5, 141.3, 128.6, 128.5, 128.5, 126.2, 126.1, 52.4, 52.4, 41.3, 40.3, 36.4, 35.7, 35.3, 34.8, 31.0, 30.7, 30.5, 29.6, 23.6, 20.9, 8.4, 8.3.

IR (thin film, cm^{-1}): 3027, 2979, 2943, 2863, 1725, 1699, 1496, 1455, 1437, 1315, 1287, 1198, 1169, 1096, 979, 891, 749, 700, 579.

HRMS (ESI+): *m/z* for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: calc.: 283.1305, found: 283.1309.

Compound 3c:

Methyl 1-isobutyryl-2-phenethylcyclopropane-1-carboxylate



1c (2.00 equiv) **2a** (1.00 equiv) **3c** 2:1 d.r.

Cyclopropane **3c** was prepared via GP1, using alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1c** (89.2 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3c** as a pale-yellow oil. The product was isolated as an inseparable 2:1 mixture of diastereomers.

Yield: 37.2 mg, 0.136 mmol, 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 – 7.24 (m, 4H), 7.21 – 7.13 (m, 6H), 3.77 (s, $3H_{minor}$), 3.73 (s, $3H_{major}$), 3.17 (hept, J = 6.9 Hz, 2H), 2.69 (t, J = 7.7 Hz, 4H), 2.14 – 1.96 (m, 2H), 1.76 (ddq, J = 22.0, 14.4, 7.4 Hz, 2H), 1.67 – 1.59 (m, 1H), 1.60 – 1.52 (m, 1H), 1.43 (dd, J = 7.7, 4.1 Hz, 1H), 1.36 – 1.20 (m, 3H), 1.14 – 1.11 (m, 6H), 1.10 – 1.06 (m, 6H).

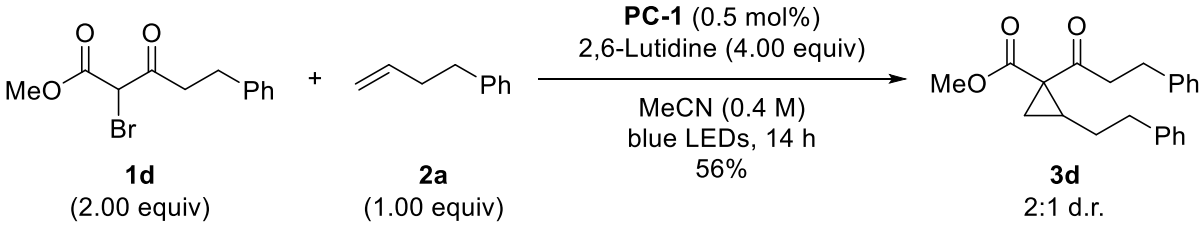
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 208.9, 208.0, 171.9, 170.5, 141.4, 141.3, 128.5, 128.4, 128.4, 126.0, 126.0, 52.3, 40.4, 39.9, 39.6, 39.1, 35.5, 35.2, 31.2, 30.4, 29.5, 29.3, 23.5, 21.2, 19.7, 18.9, 18.5, 18.3.

IR (thin film, cm^{-1}): 3027, 2973, 2935, 2872, 1728, 1698, 1496, 1455, 1437, 1312, 1284, 1198, 1156, 1070, 1031, 749, 700.

HRMS (ESI+): *m/z* for $C_{17}H_{22}NaO_3$ $[M+Na]^+$: calc.: 297.1461, found: 297.1464

Compound 3d:

Methyl 2-phenethyl-1-(3-phenylpropanoyl)cyclopropane-1-carboxylate



1d (2.00 equiv) + **2a** (1.00 equiv) → **3d** 2:1 d.r.

Cyclopropane **3d** was prepared via GP1, using alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1d** (114 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3d** as a pale-yellow oil. The product was isolated as an inseparable 2:1 mixture of diastereomers.

Yield: 37.9 mg, 0.113 mmol, 56%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31 – 7.24 (m, 8H), 7.24 – 7.09 (m, 12H), 3.74 (s, $3H_{minor}$), 3.68 (s, $3H_{major}$), 3.31 (ddd, J = 17.3, 9.2, 5.9 Hz, 1H), 3.21 – 3.09 (m, 1H), 3.04 – 2.83 (m, 5H), 2.81 – 2.59 (m, 5H), 2.07 – 1.91 (m, 2H), 1.74 (dq, J = 14.7, 7.4 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.55 (dd, J = 7.9, 4.2 Hz, 1H), 1.42 – 1.22 (m, 4H).

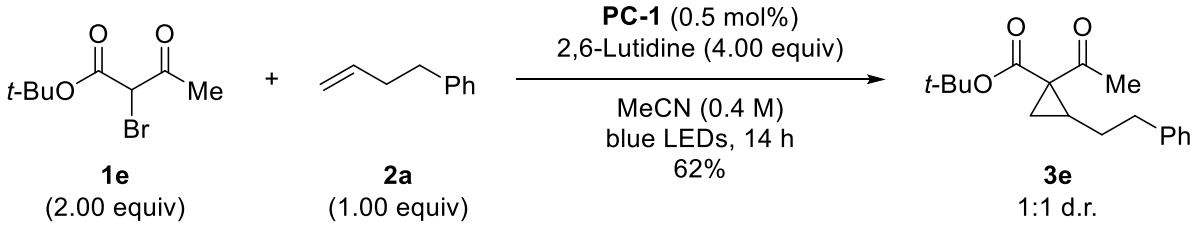
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 204.0, 203.2, 171.8, 170.3, 141.4, 141.3, 141.2, 141.2, 128.6, 128.6, 128.6, 128.5, 128.5, 126.2, 126.2, 126.1, 52.5, 44.9, 43.3, 41.6, 40.4, 35.7, 35.3, 31.4, 30.8, 30.5, 30.3, 30.2, 29.4, 23.6, 21.0.

IR (thin film, cm^{-1}): 3062, 3027, 2950, 2861, 1724, 1699, 1604, 1496, 1454, 1436, 1319, 1289, 1199, 1158, 1089, 1030, 749, 699.

HRMS (ESI+): *m/z* for $C_{22}H_{24}NaO_3$ $[M+Na]^+$: calc.: 359.1618, found: 359.1626

Compound 3e:

Tert-butyl 1-acetyl-2-phenethylcyclopropane-1-carboxylate



1e (2.00 equiv) + **2a** (1.00 equiv) → **3e** 1:1 d.r.

Cyclopropane **3e** was prepared via GP1, using alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1e** (94.8 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3e** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 35.5 mg, 0.123 mmol, 62%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 – 7.24 (m, 4H), 7.21 – 7.12 (m, 6H), 2.77 – 2.61 (m, 4H), 2.37 (s, $3H_{major}$), 2.32 (s, $3H_{minor}$), 2.01 – 1.90 (m, 2H), 1.86 – 1.59 (m, 3H), 1.51 (s, 9H), 1.47 (s, 9H), 1.45 – 1.36 (m, 1H), 1.35 – 1.23 (m, 4H).

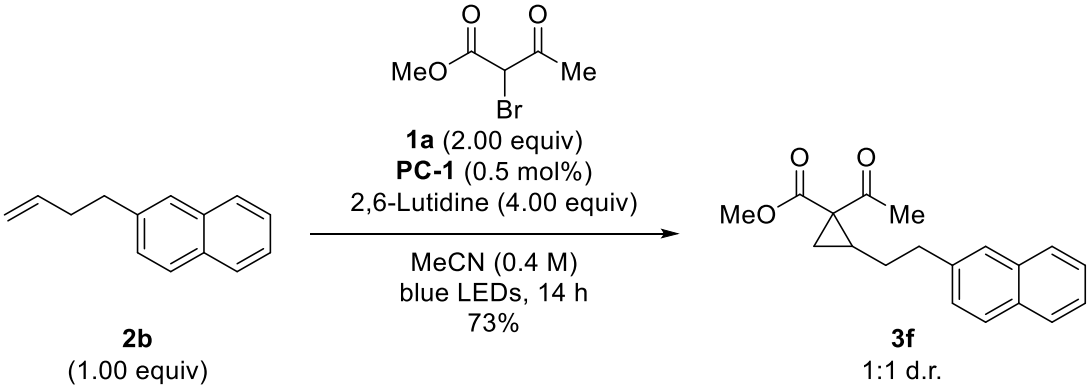
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.3, 202.4, 170.3, 168.9, 141.5, 141.4, 128.6, 128.5, 128.5, 128.5, 126.2, 126.1, 82.2, 82.0, 42.9, 41.9, 35.8, 35.4, 30.8, 30.7, 30.4, 30.1, 29.5, 29.4, 28.2, 28.1, 23.6, 20.6.

IR (thin film, cm^{-1}): 3027, 3004, 2978, 2931, 2863, 1697, 1455, 1368, 1356, 1323, 1256, 1164, 1121, 844, 748, 699, 610.

HRMS (ESI+): *m/z* for $C_{18}H_{24}NaO_3$ $[M+Na]^+$: calc.: 311.1618, found: 311.1614

Compound 3f:

Methyl 1-acetyl-2-(2-(naphthalen-2-yl)ethyl)cyclopropane-1-carboxylate



Cyclopropane **3f** was prepared via GP1, using alkene **2b**[10] (36.5 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3f** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 43.2 mg, 0.146 mmol, 73%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 – 7.73 (m, 6H), 7.59 (s, 2H), 7.49 – 7.38 (m, 4H), 7.29 (dd, J = 8.4, 1.7 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.92 – 2.75 (m, 4H), 2.36 (s, 3H), 2.35 (s, 3H), 2.12 – 1.99 (m, 2H), 1.91 – 1.68 (m, 3H), 1.62 – 1.57 (m, 1H), 1.56 – 1.49 (m, 1H), 1.49 – 1.35 (m, 3H).

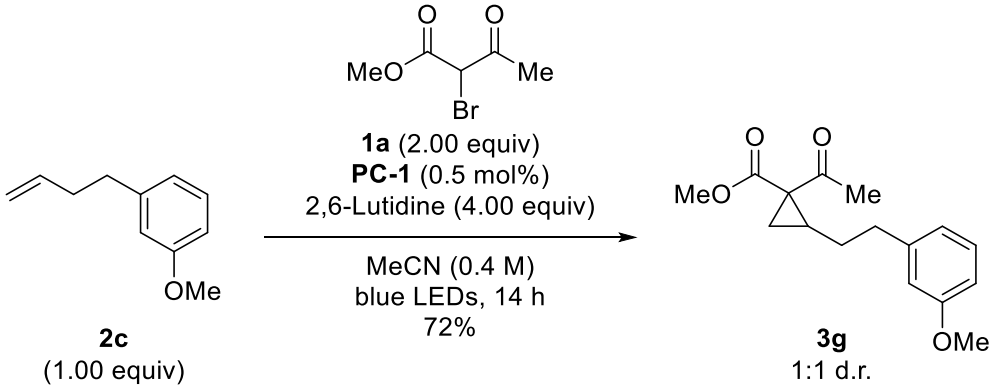
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 201.9, 171.8, 170.3, 138.9, 138.7, 133.7, 133.7, 132.2, 132.2, 128.2, 128.1, 127.7, 127.7, 127.6, 127.3, 127.3, 126.7, 126.6, 126.1, 126.1, 125.4, 125.4, 52.5, 52.4, 41.7, 40.7, 35.8, 35.5, 31.6, 31.3, 31.0, 30.4, 29.4, 29.2, 23.9, 21.1.

IR (thin film, cm^{-1}): 3053, 3010, 2951, 2861, 1726. 1698, 1508, 1436, 1358, 1324, 1283, 1200, 1125, 857, 819, 748.

HRMS (ESI+): *m/z* for $C_{19}H_{20}NaO_3$ $[M+Na]^+$: calc.: 319.1305, found: 319.1304

Compound 3g:

Methyl 1-acetyl-2-(3-methoxyphenethyl)cyclopropane-1-carboxylate



Cyclopropane **3g** was prepared via GP1, using alkene **2c**[11] (32.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3g** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 39.8 mg, 0.144 mmol, 72%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.18 (t, J = 7.9 Hz, 2H), 6.76 – 6.67 (m, 6H), 3.79 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 2.70 – 2.60 (m, 4H), 2.35 (s, 3H), 2.35 (s, 3H), 2.08 – 1.93 (m, 2H), 1.80 – 1.61 (m, 3H), 1.56 (dd, J = 7.9, 4.2 Hz, 1H), 1.48 – 1.34 (m, 4H).

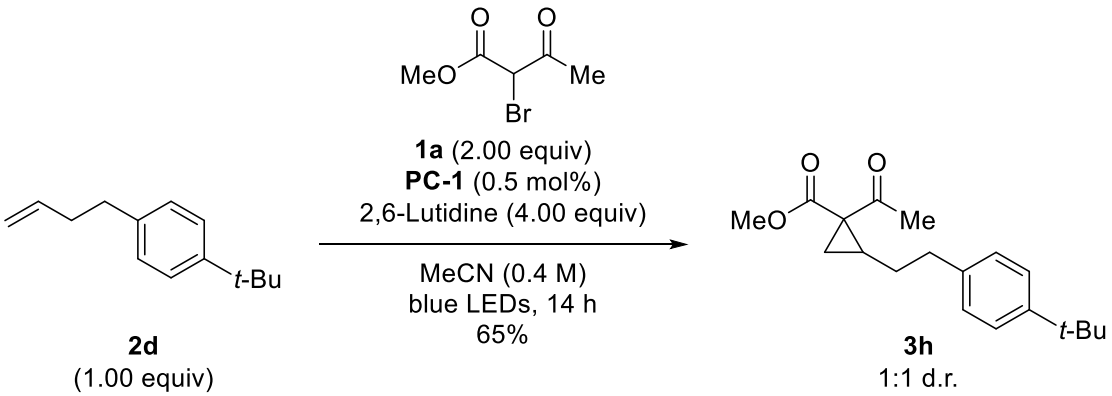
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 201.8, 171.8, 170.3, 159.8, 159.8, 143.0, 142.8, 129.5, 129.5, 121.0, 120.9, 114.3, 114.3, 111.5, 111.4, 77.5, 76.8, 55.3, 55.2, 52.4, 52.4, 41.7, 40.7, 35.7, 35.4, 31.6, 31.3, 30.9, 30.4, 29.4, 29.2, 23.9, 21.0.

IR (thin film, cm^{-1}): 3004, 2951, 2837, 1727, 1698, 1602, 1585, 1489, 1437, 1358, 1323, 1263, 1200, 1153, 1125, 1047, 869, 782, 697, 610.

HRMS (ESI+): *m/z* for $C_{16}H_{20}NaO_4$ $[M+Na]^+$: calc.: 299.1254, found: 299.1255.

Compound 3h:

Methyl 1-acetyl-2-(4-(tert-butyl)phenethyl)cyclopropane-1-carboxylate



Cyclopropane **3h** was prepared via GP1, using alkene **2d**[12] (37.7 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3h** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 39.3 mg, 0.130 mmol, 65%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 (d, J = 8.2 Hz, 4H), 7.08 (d, J = 8.1 Hz, 4H), 3.78 (s, 3H), 3.74 (s, 3H), 2.73 – 2.55 (m, 4H), 2.35 (s, 3H), 2.34 (s, 3H), 2.12 – 1.94 (m, 2H), 1.81 – 1.62 (m, 3H), 1.57 (dd, J = 7.9, 4.2 Hz, 1H), 1.49 – 1.35 (m, 4H), 1.31 (s, 9H), 1.31 (s, 9H).

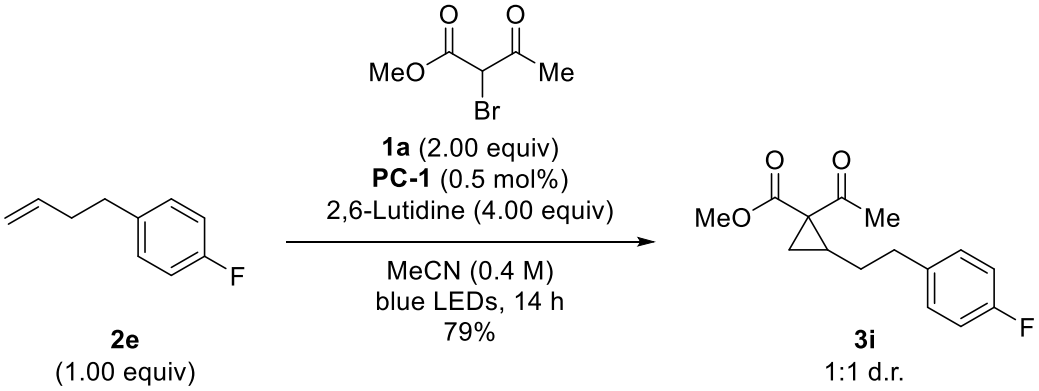
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.9, 201.8, 171.8, 170.3, 149.0, 148.9, 138.3, 138.2, 128.2, 128.2, 125.4, 125.4, 52.4, 41.8, 40.7, 35.1, 34.8, 34.5, 31.7, 31.5, 31.5, 30.9, 30.5, 29.4, 29.3, 23.9, 21.0.

IR (thin film, cm^{-1}): 3003, 2957, 2867, 1727, 1698, 1505, 1436, 1359, 1322, 1271, 1198, 1121, 1020, 979, 825, 608, 569.

HRMS (ESI+): *m/z* for $C_{19}H_{26}NaO_3$ $[M+Na]^+$: calc.: 325.1774, found: 325.1772.

Compound 3i:

Methyl 1-acetyl-2-(4-fluorophenethyl)cyclopropane-1-carboxylate



Cyclopropane **3i** was prepared via GP1, using alkene **2e**[11] (30.0 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3i** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 41.9 mg, 0.159 mmol, 79%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.12 – 7.06 (m, 4H), 6.95 (t, J = 8.6 Hz, 4H), 3.77 (s, 3H), 3.73 (s, 3H), 2.70 – 2.58 (m, 4H), 2.36 (s, 3H), 2.34 (s, 3H), 2.06 – 1.90 (m, 2H), 1.77 – 1.65 (m, 2H), 1.64 – 1.57 (m, 1H), 1.54 (dd, J = 7.9, 4.2 Hz, 1H), 1.45 – 1.33 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 201.8, 171.8, 170.3, 162.7, 162.7, 160.3, 160.3, 137.0, 137.0, 136.8, 136.8, 130.0, 129.9, 129.9, 129.8, 115.4, 115.4, 115.2, 115.2, 52.5, 52.5, 41.7, 40.6, 34.9, 34.5, 31.4, 31.0, 30.9, 30.5, 30.5, 29.4, 23.9, 21.1.

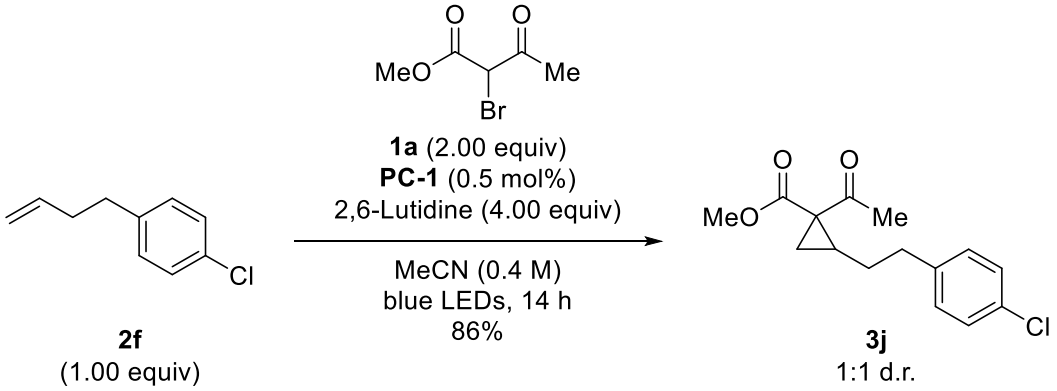
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -117.36 (tt, J = 9.0, 5.5 Hz, 1F), -117.46 (tt, J = 8.8, 5.4 Hz, 1F).

IR (thin film, cm^{-1}): 3007, 2953, 2864, 1728, 1698, 1601, 1510, 1437, 1359, 1324, 1221, 1201, 1125, 828, 609, 545.

HRMS (ESI+): *m/z* for $C_{15}H_{17}FNaO_3$ $[M+Na]^+$: calc.: 287.1054, found: 287.1059

Compound 3j:

Methyl 1-acetyl-2-(4-chlorophenethyl)cyclopropane-1-carboxylate



Cyclopropane **3j** was prepared via GP1, using alkene **2f**[12] (33.3 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3j** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 48.2 mg, 0.172 mmol, 86%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.23 (d, J = 7.8 Hz, 4H), 7.07 (d, J = 8.2 Hz, 4H), 3.77 (s, 3H), 3.74 (s, 3H), 2.68 – 2.60 (m, 4H), 2.36 (s, 3H), 2.34 (s, 3H), 2.05 – 1.91 (m, 2H), 1.77 – 1.66 (m, 2H), 1.66 – 1.56 (m, 1H), 1.54 (dd, J = 7.9, 4.2 Hz, 1H), 1.45 – 1.34 (m, 4H).

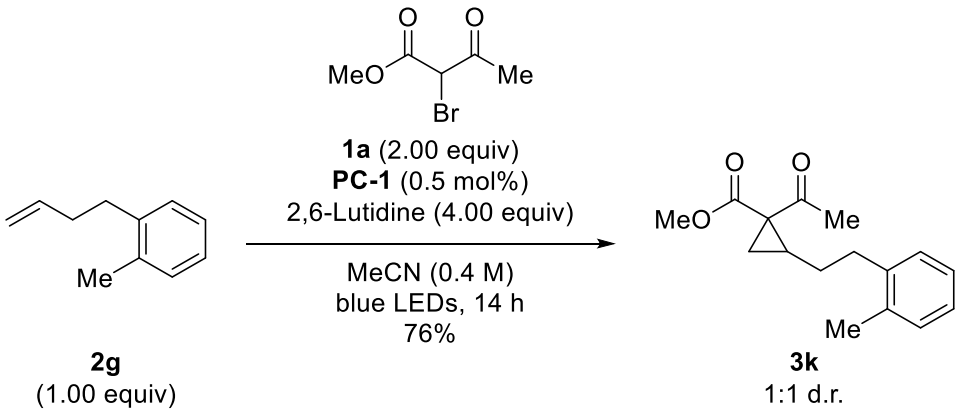
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.7, 201.8, 171.7, 170.3, 139.8, 139.6, 132.0, 131.9, 129.9, 129.9, 128.7, 128.7, 52.5, 52.5, 41.7, 40.6, 35.0, 34.7, 31.4, 31.0, 30.9, 30.3, 29.4, 29.2, 23.9, 21.1.

IR (thin film, cm^{-1}): 3007, 2952, 2864, 1728, 1699, 1493, 1437, 1358, 1324, 1287, 1200, 1118, 1092, 1015, 819.

HRMS (ESI+): *m/z* for $C_{15}H_{18}ClO_3$ $[M+H]^+$: calc.: 281.0939, found: 281.0935

Compound 3k:

Methyl 1-acetyl-2-(2-methylphenethyl)cyclopropane-1-carboxylate



Cyclopropane **3k** was prepared via GP1, using alkene **2g**[12] (29.2 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3k** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 39.6 mg, 0.152 mmol, 76%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.15 – 7.07 (m, 8H), 3.77 (s, 3H), 3.74 (s, 3H), 2.74 – 2.60 (m, 4H), 2.36 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H), 2.28 (s, 3H), 2.13 – 1.98 (m, 2H), 1.77 – 1.63 (m, 2H), 1.63 – 1.56 (m, 2H), 1.49 – 1.35 (m, 4H).

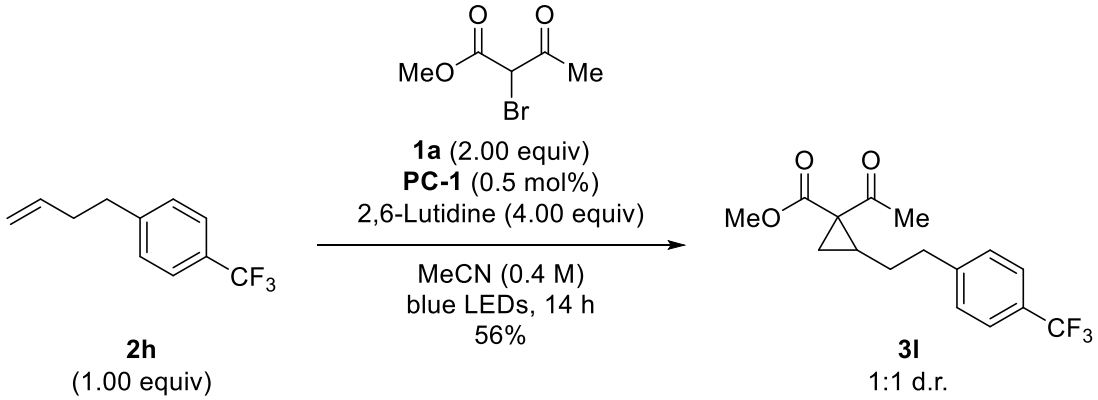
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.9, 201.8, 171.8, 170.3, 139.6, 139.4, 135.9, 135.9, 130.4, 130.4, 129.1, 129.1, 126.4, 126.3, 126.2, 52.5, 41.8, 40.7, 33.0, 32.7, 31.9, 31.5, 30.9, 29.5, 29.2, 28.1, 23.9, 21.1, 19.3.

IR (thin film, cm^{-1}): 3013, 2952, 2867, 1728, 1698, 1436, 1358, 1323, 1282, 1199, 1121, 1068, 870, 752, 608.

HRMS (ESI+): *m/z* for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: calc.: 283.1305, found: 283.1305.

Compound 3l:

Methyl 1-acetyl-2-(4-(trifluoromethyl)phenethyl)cyclopropane-1-carboxylate



Cyclopropane **3l** was prepared via GP1, using alkene **2h**[11] (40.0 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3l** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 35.4 mg, 0.113 mmol, 56%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.53 (d, J = 8.4 Hz, 4H), 7.25 (d, J = 7.3 Hz, 4H), 3.77 (s, 3H), 3.74 (s, 3H), 2.79 – 2.67 (m, 4H), 2.36 (s, 3H), 2.35 (s, 3H), 2.06 – 1.93 (m, 2H), 1.81 – 1.62 (m, 3H), 1.55 (dd, J = 7.9, 4.3 Hz, 1H), 1.50 – 1.35 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.6, 201.8, 171.7, 170.2, 145.5, 145.5, 145.3, 145.3, 128.9, 128.9, 125.5, 125.5, 125.5, 125.5, 52.6, 52.5, 41.6, 40.6, 35.5, 35.2, 31.3, 31.0, 30.7, 30.1, 29.4, 29.0, 23.8, 21.1.

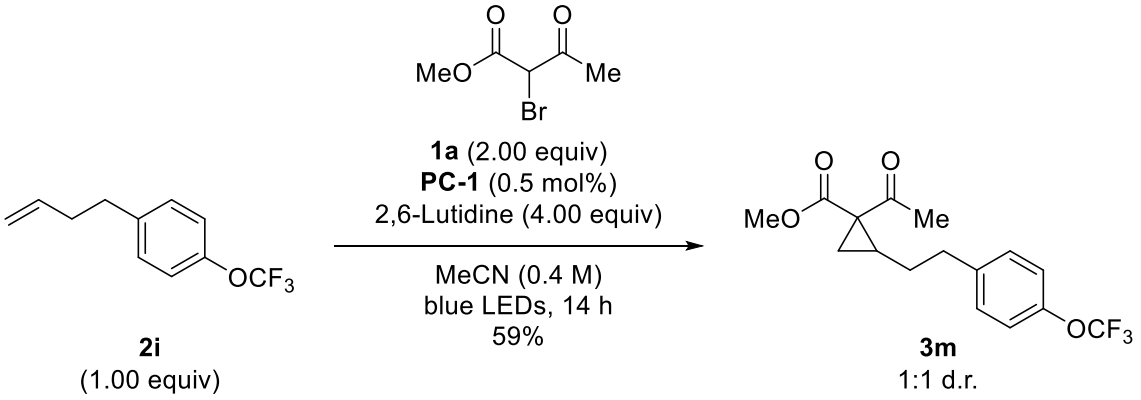
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -62.36 (s, 3F), -62.37 (s, 3F).

IR (thin film, cm^{-1}): 3010, 2955, 1867, 1730, 1699, 1619, 1438, 1359, 1325, 1163, 1119, 1068, 1019, 831, 610.

HRMS (ESI+): *m/z* for $C_{16}H_{17}F_3NaO_3$ $[M+Na]^+$: calc.: 337.1022, found: 337.1024

Compound 3m:

Methyl 1-acetyl-2-(4-(trifluoromethoxy)phenethyl)cyclopropane-1-carboxylate



Cyclopropane **3m** was prepared via GP1, using alkene **2i**[13] (43.2 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3m** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 38.7 mg, 0.117 mmol, 59%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.18 – 7.09 (m, 8H), 3.77 (s, 3H), 3.74 (s, 3H), 2.73 – 2.61 (m, 4H), 2.35 (s, 3H), 2.34 (s, 3H), 2.06 – 1.92 (m, 2H), 1.79 – 1.68 (m, 2H), 1.67 – 1.60 (m, 1H), 1.54 (dd, J = 7.9, 4.2 Hz, 1H), 1.48 – 1.34 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.7, 201.8, 171.7, 170.3, 147.7, 147.7, 147.7, 147.7, 140.1, 140.0, 129.8, 129.8, 121.9, 121.2, 121.2, 121.1, 121.1, 119.4, 52.5, 52.5, 41.7, 40.6, 35.0, 34.7, 31.4, 30.9, 30.9, 30.3, 29.4, 29.2, 23.9, 21.1.

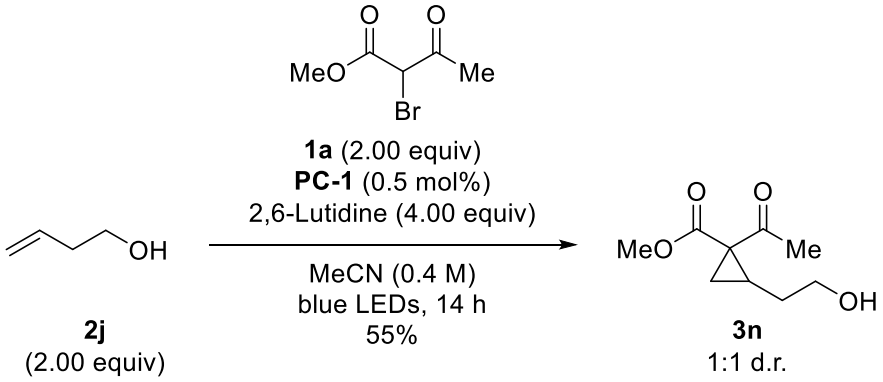
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -57.94 (s, 3F), -57.96 (s, 3F).

IR (thin film, cm^{-1}): 3008, 2955, 2866, 1730, 1700, 1509, 1438, 1359, 1258, 1222, 1198, 1164, 1020, 846, 608.

HRMS (ESI+): *m/z* for $C_{16}H_{17}F_3NaO_4$ $[M+Na]^+$: calc.: 353.0971, found: 353.0967

Compound 3n:

Methyl 1-acetyl-2-(2-hydroxyethyl)cyclopropane-1-carboxylate



Cyclopropane **3n** was prepared via GP1, using alkene **2j** (17.2 µL, 14.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-35% EtOAc in hexane) to give **3n** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 20.3 mg, 0.109 mmol, 55%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3H), 3.75 (s, 3H), 3.73 – 3.67 (m, 4H), 2.41 (s, 3H), 2.36 (s, 3H), 2.11 (dtd, J = 9.1, 7.8, 6.6 Hz, 1H), 2.01 (dq, J = 9.0, 7.4 Hz, 2H), 1.76 – 1.59 (m, 3H), 1.54 – 1.39 (m, 6H).

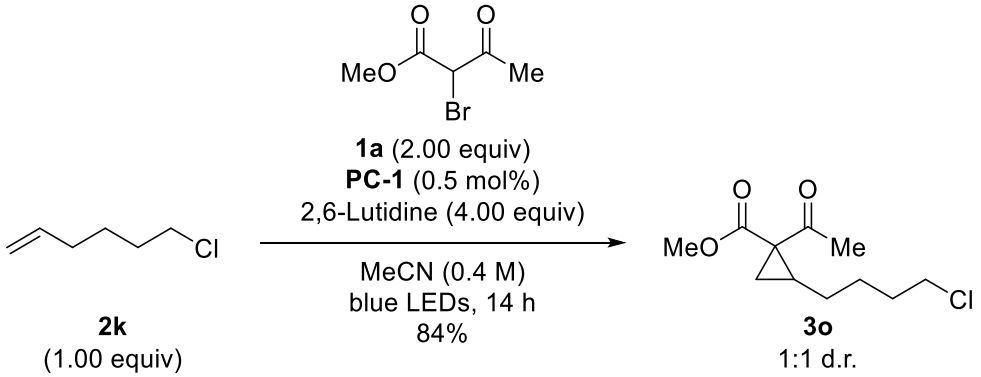
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 202.2, 171.8, 170.5, 62.3, 62.1, 52.6, 41.2, 40.1, 31.5, 31.0, 30.4, 29.4, 28.9, 28.3, 23.2, 20.7.

IR (thin film, cm^{-1}): 3430, 3008, 2954, 2881, 1725, 1696, 1438, 1360, 1326, 1203, 1125, 1044, 890, 610.

HRMS (ESI+): *m/z* for $C_9H_{14}NaO_4$ $[M+Na]^+$: calc.: 209.0784, found: 209.0782.

Compound 3o:

Methyl 1-acetyl-2-(4-chlorobutyl)cyclopropane-1-carboxylate



Cyclopropane **3o** was prepared via GP1, using alkene **2k** (26.5 µL, 23.7 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3o** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 38.9 mg, 0.167 mmol, 84%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3H), 3.74 (s, 3H), 3.51 (t, J = 6.6 Hz, 4H), 2.40 (s, 3H), 2.36 (s, 3H), 2.06 – 1.90 (m, 2H), 1.89 – 1.69 (m, 4H), 1.57 – 1.49 (m, 5H), 1.49 – 1.28 (m, 6H), 1.20 – 1.06 (m, 1H).

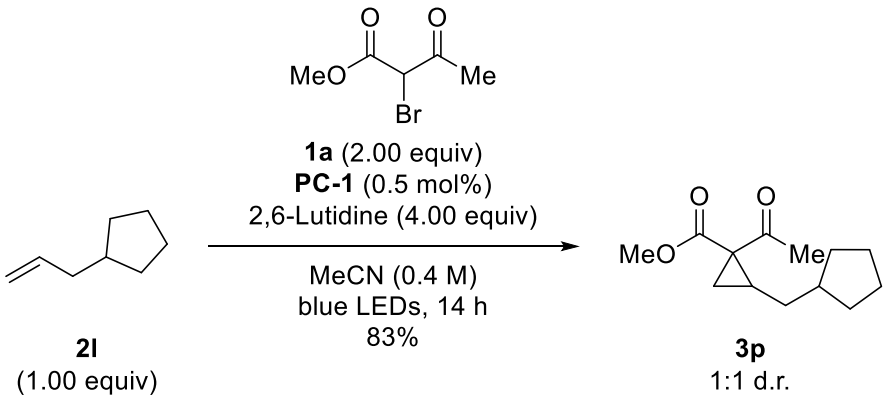
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.9, 201.9, 171.8, 170.3, 52.5, 52.5, 44.9, 41.7, 40.6, 32.2, 32.2, 31.7, 31.2, 31.0, 29.5, 27.7, 26.7, 26.7, 26.3, 24.0, 21.2.

IR (thin film, cm^{-1}): 2951, 2865, 1729, 1699, 1437, 1359, 1325, 1279, 1200, 1126, 983, 871, 736, 650, 609.

HRMS (ESI+): *m/z* for $C_{11}H_{17}ClNaO_3$ $[M+Na]^+$: calc.: 255.0758, found: 255.0758.

Compound 3p:

Methyl 1-acetyl-2-(cyclopentylmethyl)cyclopropane-1-carboxylate



Cyclopropane **3p** was prepared via GP1, using alkene **2l** (27.8 µL, 22.0 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **3p** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 37.1 mg, 0.165 mmol, 83%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.78 (s, 3H), 3.74 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 2.06 – 1.91 (m, 2H), 1.88 – 1.70 (m, 6H), 1.65 – 1.59 (m, 1H), 1.58 – 1.40 (m, 12H), 1.36 (dd, J = 8.9, 4.1 Hz, 1H), 1.22 – 1.15 (m, 1H), 1.14 – 1.04 (m, 4H), 0.99 (ddd, J = 13.7, 9.1, 6.8 Hz, 1H).

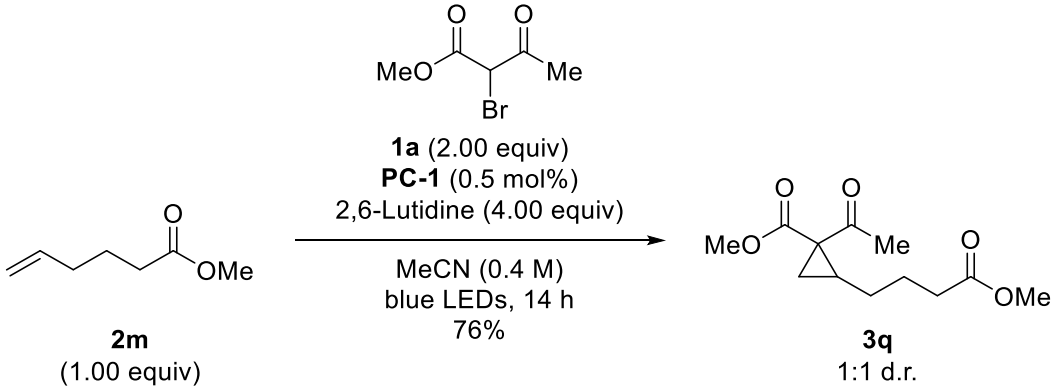
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.1, 202.1, 172.1, 170.5, 52.4, 52.3, 41.7, 40.6, 40.3, 40.0, 34.4, 33.4, 32.7, 32.6, 32.5, 31.4, 31.3, 31.0, 29.5, 25.1, 25.1, 25.1, 25.1, 24.3, 21.3.

IR (thin film, cm^{-1}): 2951, 2867, 1729, 1699, 1437, 1358, 1322, 1272, 1199, 1124, 981, 870, 747, 608.

HRMS (ESI+): *m/z* for $C_{13}H_{20}NaO_3$ $[M+Na]^+$: calc.: 247.1305, found: 247.1304.

Compound 3q:

Methyl 1-acetyl-2-(4-methoxy-4-oxobutyl)cyclopropane-1-carboxylate



Cyclopropane **3q** was prepared via GP1, using alkene **2m** (28.2 µL, 25.6 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-20% EtOAc in hexane) to give **3q** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 36.7 mg, 0.151 mmol, 76%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.78 (s, 3H), 3.74 (s, 3H), 3.66 (s, 6H), 2.39 (s, 3H), 2.35 (s, 3H), 2.34 – 2.28 (m, 4H), 2.05 – 1.88 (m, 2H), 1.76 – 1.64 (m, 4H), 1.56 (dd, J = 7.8, 4.2 Hz, 1H), 1.52 – 1.28 (m, 6H), 1.17 – 1.07 (m, 1H).

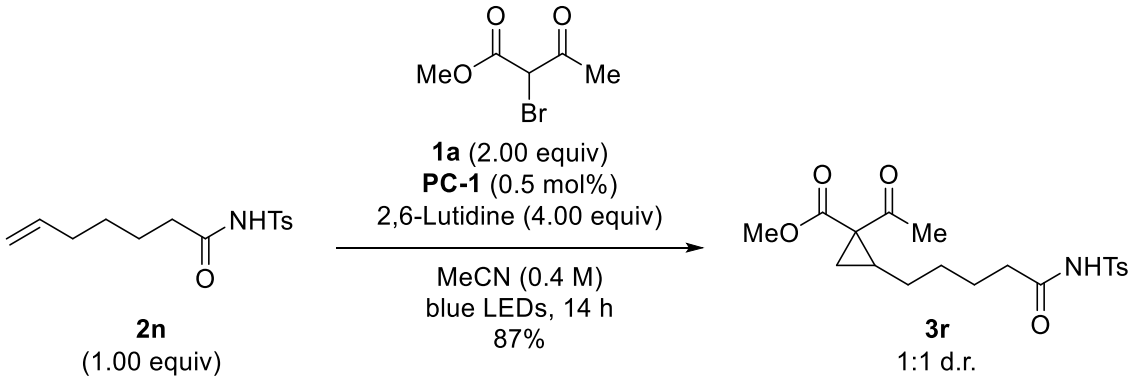
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.8, 201.8, 173.8, 173.8, 171.8, 170.3, 52.5, 52.5, 51.7, 51.7, 41.6, 40.6, 33.6, 33.6, 31.4, 31.0, 31.0, 29.4, 27.8, 26.8, 24.7, 24.3, 23.9, 21.0.

IR (thin film, cm^{-1}): 3006, 2954, 2868, 1734, 1698, 1437, 1359, 1326, 1251, 1200, 1175, 1119, 997, 880, 608.

HRMS (ESI+): *m/z* for $C_{12}H_{18}NaO_5$ $[M+Na]^+$: calc.: 265.1046, found: 265.1050.

Compound 3r:

Methyl 1-acetyl-2-(5-((4-methylphenyl)sulfonamido)-5-oxopentyl)cyclopropane-1-carboxylate



Cyclopropane **3r** was prepared via GP1, using alkene **2n**[14] (53.5 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-30% EtOAc in hexane) to give **3r** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 68.8 mg, 0.174 mmol, 87%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.5 Hz, 4H), 3.76 (s, 3H), 3.73 (s, 3H), 2.44 (s, 6H), 2.36 (s, 3H), 2.34 (s, 3H), 2.27 – 2.18 (m, 4H), 1.98 – 1.81 (m, 2H), 1.63 – 1.47 (m, 5H), 1.44 – 1.21 (m, 10H), 1.11 – 0.97 (m, 1H).

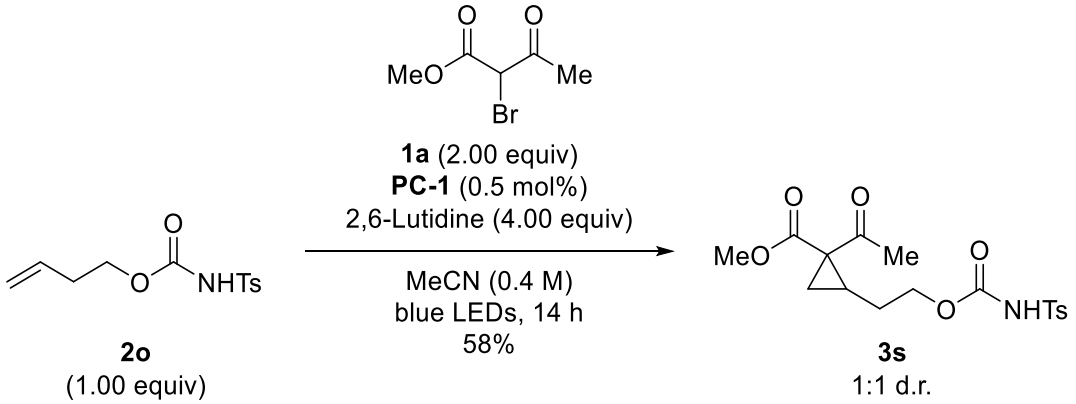
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.0, 202.3, 171.8, 170.6, 170.6, 170.4, 145.3, 145.3, 135.7, 129.8, 128.5, 52.5, 52.5, 41.7, 40.6, 36.1, 36.0, 31.6, 31.2, 31.0, 29.4, 28.5, 28.2, 28.0, 26.9, 23.9, 23.9, 21.8, 21.2.

IR (thin film, cm^{-1}): 3567, 3237, 3940, 2864, 1721, 1696, 1438, 1338, 1172, 1126, 1088, 855, 816, 662, 550.

HRMS (ESI+): *m/z* for $C_{19}H_{25}NNaO_6S$ $[M+Na]^+$: calc.: 418.1295, found: 418.1291.

Compound 3s:

Methyl 1-acetyl-2-(2-((tosylcarbamoyl)oxy)ethyl)cyclopropane-1-carboxylate



Cyclopropane **3s** was prepared via GP1, using alkene **2o**[15] (53.9 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-30% EtOAc in hexane) to give **3s** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 46.2 mg, 0.116 mmol, 58%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, J = 7.6 Hz, 4H), 7.35 (d, J = 8.5 Hz, 4H), 4.12 – 4.02 (m, 4H), 3.77 (s, 3H), 3.76 (s, 3H), 2.45 (s, 6H), 2.38 (s, 3H), 2.35 (s, 3H), 2.02 – 1.89 (m, 2H), 1.70 – 1.61 (m, 4H), 1.53 (dd, J = 7.9, 4.2 Hz, 1H), 1.49 – 1.33 (m, 6H), 1.16 (dq, J = 15.2, 7.9 Hz, 1H).

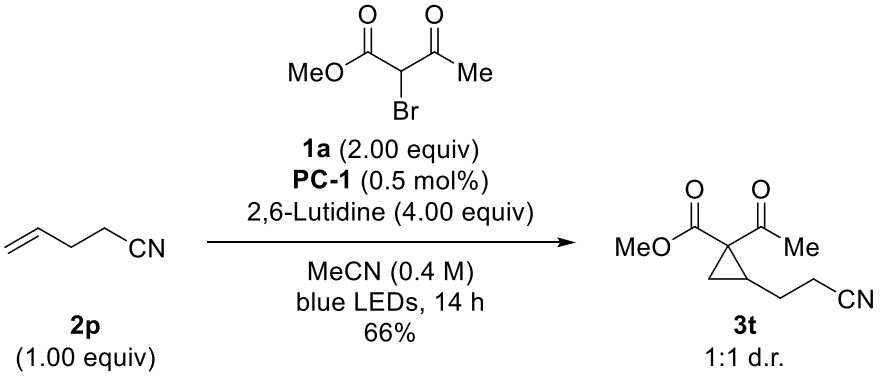
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 202.9, 201.8, 171.8, 170.2, 150.4, 145.3, 135.6, 129.8, 128.5, 66.5, 66.4, 52.7, 52.6, 41.6, 40.6, 31.3, 31.0, 30.2, 29.5, 28.2, 27.8, 24.9, 23.8, 23.8, 21.8, 21.3.

IR (thin film, cm^{-1}): 3242, 2955, 2926, 1728, 1696, 1439, 1341, 1286, 1224, 1158, 1123, 1089, 851, 815, 771, 661, 575, 546.

HRMS (ESI+): *m/z* for $C_{18}H_{23}NNaO_7S$ $[M+Na]^+$: calc.: 420.1087, found: 420.1089.

Compound 3t:

Methyl 1-acetyl-2-(2-cyanoethyl)cyclopropane-1-carboxylate



Cyclopropane **3t** was prepared via GP1, using alkene **2p** (19.9 µL, 16.2 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-20% EtOAc in hexane) to give **3t** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Yield: 25.7 mg, 0.132 mmol, 66%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 3H), 3.76 (s, 3H), 2.47 – 2.38 (m, 7H), 2.37 (s, 3H), 2.11 (qd, J = 8.4, 6.4 Hz, 1H), 2.00 (p, J = 7.9 Hz, 1H), 1.89 – 1.68 (m, 3H), 1.63 – 1.58 (m, 1H), 1.57 – 1.46 (m, 4H).

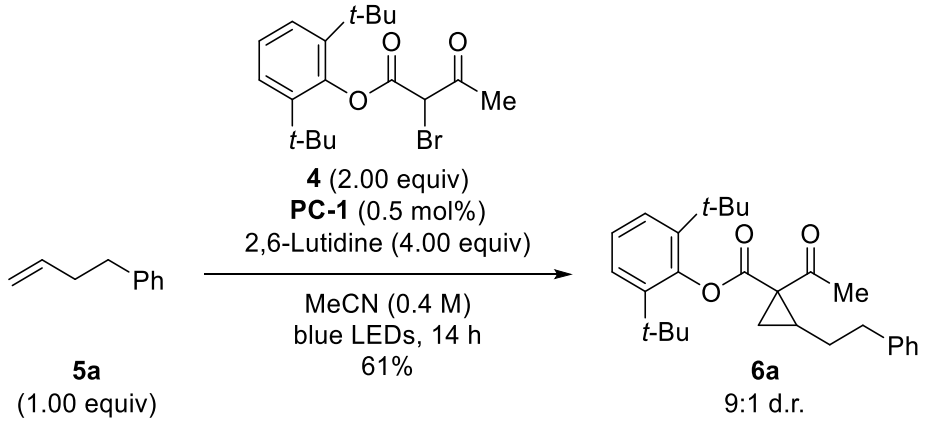
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.9, 201.6, 171.0, 169.9, 118.9, 118.9, 52.8, 52.7, 41.1, 40.1, 31.0, 29.8, 29.3, 28.9, 24.6, 23.5, 23.0, 20.9, 17.2, 16.9.

IR (thin film, cm^{-1}): 3009, 2956, 2248, 1729, 1700, 1437, 1360, 1325, 1285, 1203, 1119, 977, 881, 609.

HRMS (ESI+): *m/z* for $C_{10}H_{13}NNaO_3$ $[M+Na]^+$: calc.: 218.0788, found: 218.0788.

Compound 6a:

2,6-di-tert-butylphenyl 1-acetyl-2-phenethylcyclopropane-1-carboxylate



Cyclopropane **6a** was prepared via GP1, using alkene **5a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **6a** as a pale-yellow oil. The product was isolated as an inseparable 9:1 mixture of diastereomers.

Yield: 51.5 mg, 0.122 mmol, 61%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.38 – 7.28 (m, 8H), 7.24 – 7.11 (m, 8H), 2.85 – 2.67 (m, 3H), 2.65 (s, $3H_{minor}$), 2.55 (s, $3H_{major}$), 2.41 – 2.29 (m, 2H), 2.16 – 2.04 (m, $2H_{minor}$), 1.96 (dd, J = 9.3, 4.1 Hz, $1H_{minor}$), 1.89 – 1.76 (m, 4H), 1.64 – 1.51 (m, 2H), 1.41 – 1.33 (m, 36H).

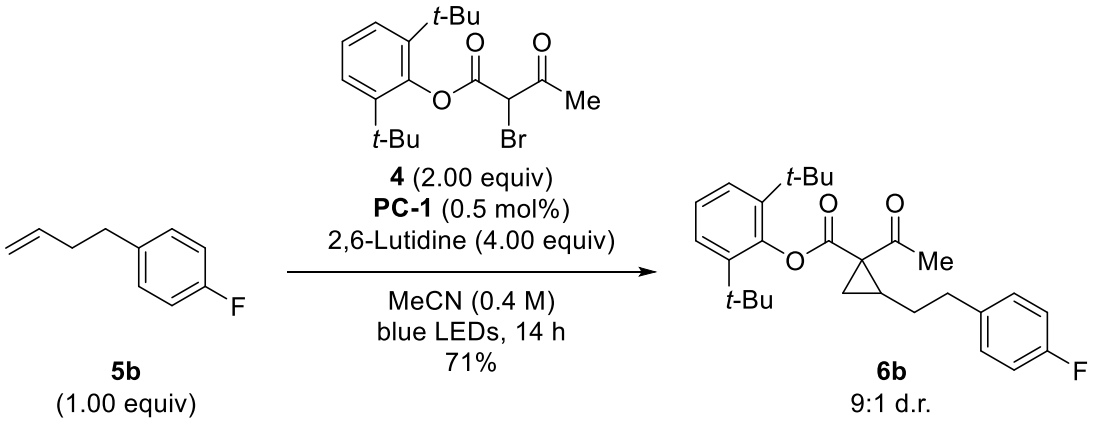
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.6, 171.6, 170.6, 148.0, 142.8, 142.4, 141.0, 128.6, 128.6, 128.5, 128.5, 126.6, 126.6, 126.5, 126.4, 126.3, 126.1, 126.0, 41.8, 41.6, 35.6, 35.6, 35.5, 35.4, 33.8, 32.9, 32.0, 31.7, 31.6, 31.5, 30.8, 30.0, 28.0, 23.9, 21.2.

IR (thin film, cm^{-1}): 3064, 3004, 2963, 2872, 1738, 1705, 1455, 1395, 1362, 1311, 1268, 1176, 1105, 1090, 793, 749, 730, 699, 614.

HRMS (ESI+): *m/z* for $C_{28}H_{36}NaO_3$ $[M+Na]^+$: calc.: 443.2557, found: 443.2556

Compound 6b:

2,6-di-tert-butylphenyl 1-acetyl-2-(4-fluorophenethyl)cyclopropane-1-carboxylate



Cyclopropane **6b** was prepared via GP1, using alkene **5b**[11] (30.0 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **6b** as a pale-yellow oil. The product was isolated as an inseparable 9:1 mixture of diastereomers.

Yield: 62.5 mg, 0.142 mmol, 71%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.36 – 7.29 (m, 4H), 7.18 – 7.08 (m, 6H), 7.02 – 6.91 (m, 4H), 2.81 – 2.65 (m, 3H), 2.64 (s, 3H), 2.54 (s, 3H), 2.39 – 2.25 (m, 2H), 2.07 (q, J = 7.5 Hz, $2H_{minor}$), 1.94 (dd, J = 9.3, 4.1 Hz, $1H_{minor}$), 1.85 (dd, J = 9.1, 4.4 Hz, 2H), 1.82 – 1.73 (m, 3H), 1.60 – 1.47 (m, 1H), 1.45 – 1.24 (m, 36H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.6, 171.5, 162.8, 160.4, 148.0, 142.8, 142.4, 136.7, 129.9, 129.8, 126.6, 126.4, 126.1, 115.5, 115.3, 41.7, 41.5, 35.6, 35.4, 34.8, 34.7, 33.5, 32.7, 32.0, 31.7, 31.6, 31.6, 31.5, 30.8, 30.1, 21.2.

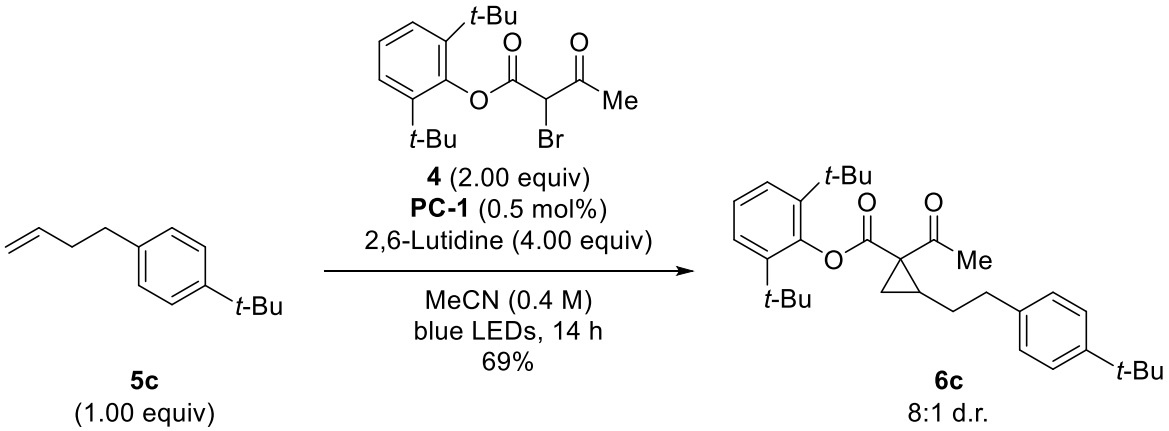
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -117.21 (tt, J = 8.7, 5.3 Hz, 1F), 117.49 (ddd, J = 14.2, 9.0, 5.4 Hz, 1F).

IR (thin film, cm^{-1}): 2964, 2873, 1739, 1706, 1602, 1510, 1415, 1363, 1268, 1223, 1177, 1100, 883, 829, 793, 730.

HRMS (ESI+): *m/z* for $C_{28}H_{35}FNaO_3$ $[M+Na]^+$: calc.: 461.2462, found: 461.2454

Compound 6c:

2,6-di-tert-butylphenyl 1-acetyl-2-(4-(tert-butyl)phenethyl)cyclopropane-1-carboxylate



Cyclopropane **6c** was prepared via GP1, using alkene **5c**[12] (37.7 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **6c** as a pale-yellow oil. The product was isolated as an inseparable 8:1 mixture of diastereomers.

Yield: 66.0 mg, 0.138 mmol, 69%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.35 – 7.29 (m, 4H), 7.18 – 7.09 (m, 3H), 2.81 – 2.62 (m, 2H), 2.52 (s, 3H), 2.39 – 2.30 (m, 1H), 1.87 (dd, J = 9.1, 4.4 Hz, 1H), 1.85 – 1.74 (m, 2H), 1.62 – 1.50 (m, 1H), 1.40 – 1.27 (m, 27H).

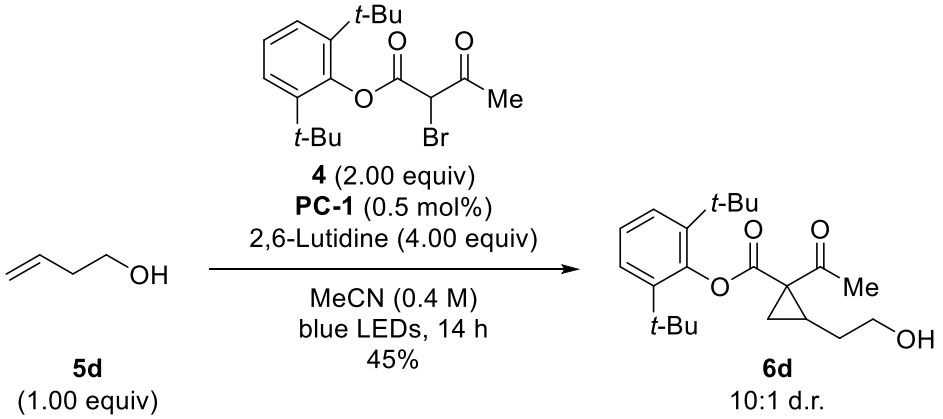
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.6, 171.6, 149.2, 148.0, 142.8, 142.5, 137.9, 128.2, 126.6, 126.4, 126.0, 125.5, 41.9, 35.6, 35.4, 35.0, 34.5, 32.9, 31.6, 31.6, 31.6, 31.5, 31.5, 29.9, 21.2.

IR (thin film, cm^{-1}): 2962, 2871, 1739, 1707, 1631, 1415, 1363, 1269, 1223, 1178, 1106, 792, 729.

HRMS (ESI+): *m/z* for $C_{32}H_{44}NaO_3$ $[M+Na]^+$: calc.: 499.3183, found: 499.3183

Compound 6d:

2,6-di-tert-butylphenyl 1-acetyl-2-(2-hydroxyethyl)cyclopropane-1-carboxylate



Cyclopropane **6d** was prepared via GP1, using alkene **5d** (17.2 µL, 14.4 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-15% EtOAc in hexane) to give **6d** as a pale-yellow oil. The product was isolated as an inseparable 10:1 mixture of diastereomers.

Yield: 32.6 mg, 0.0904 mmol, 45%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.34 – 7.31 (m, 2H), 7.18 – 7.12 (m, 1H), 3.76 (q, J = 5.0 Hz, 2H), 2.55 (s, 3H), 2.49 – 2.38 (m, 1H), 1.90 (dd, J = 9.2, 4.4 Hz, 1H), 1.82 (dd, J = 8.0, 4.4 Hz, 1H), 1.72 (dq, J = 13.5, 6.8 Hz, 1H), 1.62 – 1.51 (m, 1H), 1.37 (s, 9H), 1.33 (s, 9H).

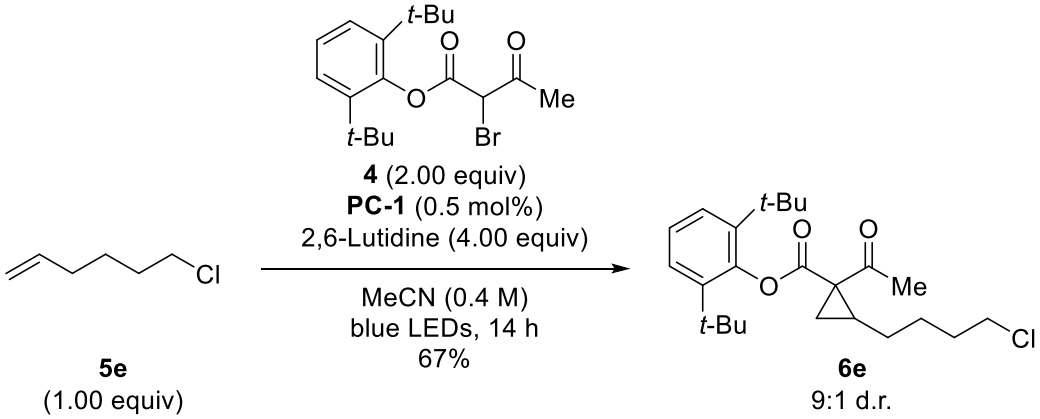
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.9, 171.5, 148.1, 142.8, 142.5, 126.5, 126.5, 126.1, 126.1, 62.2, 56.3, 41.3, 35.6, 35.5, 31.6, 31.5, 31.4, 31.3, 31.0, 30.4, 20.9.

IR (thin film, cm^{-1}): 3462, 2963, 2874, 1739, 1705, 1415, 1363, 1270, 1177, 1104, 1055, 793, 730.

HRMS (ESI+): *m/z* for $C_{22}H_{32}NaO_4$ $[M+Na]^+$: calc.: 383.2193, found: 383.2196

Compound 6e:

2,6-di-tert-butylphenyl 1-acetyl-2-(4-chlorobutyl)cyclopropane-1-carboxylate



Cyclopropane **6e** was prepared via GP1, using alkene **5e** (26.5 µL, 23.7 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **6e** as a pale-yellow oil. The product was isolated as an inseparable 9:1 mixture of diastereomers.

Yield: 54.2 mg, 0.133 mmol, 67%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (d, J = 8.0 Hz, 4H), 7.19 – 7.10 (m, 2H), 3.54 (t, J = 6.5 Hz, $2H_{major}$), 3.41 (t, J = 6.6 Hz, $2H_{minor}$), 2.54 (s, 6H), 2.32 (p, J = 7.8 Hz, 2H), 1.90 – 1.77 (m, 8H), 1.66 – 1.54 (m, 4H), 1.52 – 1.45 (m, 2H), 1.36 (s, 18H), 1.33 (s, 18H), 1.32 – 1.22 (m, 2H).

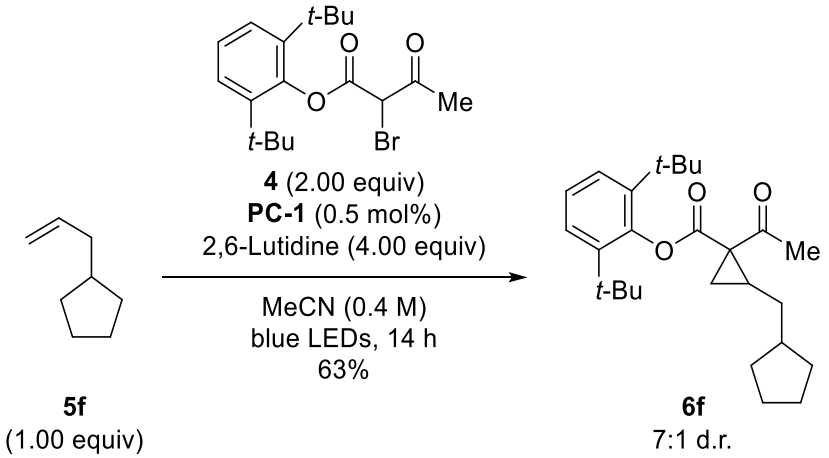
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.6, 171.6, 148.1, 142.8, 142.4, 126.6, 126.5, 126.1, 44.8, 41.8, 35.6, 35.5, 33.2, 32.2, 31.6, 31.6, 27.3, 26.7, 21.3.

IR (thin film, cm^{-1}): 2961, 2870, 1738, 1704, 1415, 1362, 1312, 1269, 1177, 1105, 1094, 883, 793, 779, 730.

HRMS (ESI+): *m/z* for $C_{24}H_{35}ClNaO_3$ $[M+Na]^+$: calc.: 429.2167, found: 429.2164

Compound 6f:

2,6-di-tert-butylphenyl 1-acetyl-2-(cyclopentylmethyl)cyclopropane-1-carboxylate



Cyclopropane **6f** was prepared via GP1, using alkene **5f** (28.7 µL, 22.0 mg, 0.200 mmol, 1.00 equiv) and bromoketoester **4** (147.7 mg, 0.400 mmol, 2.00 equiv) and the reaction was stirred for 14 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **6f** as a pale-yellow oil. The product was isolated as an inseparable 7:1 mixture of diastereomers.

Yield: 50.1 mg, 0.126 mmol, 63%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (d, J = 7.7 Hz, 2H), 7.14 (dd, J = 8.2, 7.5 Hz, 1H), 2.52 (s, 3H), 2.38 – 2.29 (m, 1H), 1.91 – 1.78 (m, 5H), 1.68 – 1.56 (m, 3H), 1.56 – 1.46 (m, 1H), 1.40 – 1.31 (m, 19H), 1.22 – 1.07 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 201.9, 171.8, 148.1, 142.8, 142.5, 126.6, 126.4, 126.0, 41.8, 40.2, 35.6, 35.5, 34.2, 32.9, 32.7, 32.6, 31.6, 31.6, 31.6, 31.5, 31.5, 25.2, 25.1, 21.3.

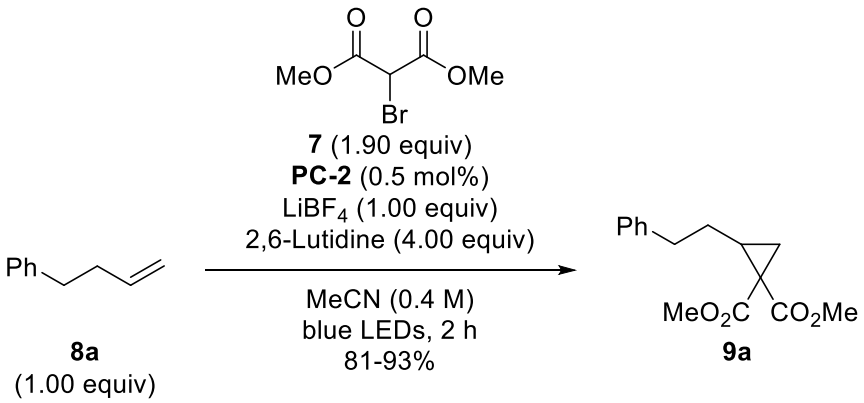
IR (thin film, cm^{-1}): 2957, 2871, 1739, 1706, 1631, 1416, 1363, 1311, 1267, 1223, 1178, 1106, 1095, 1045, 792, 729.

HRMS (ESI+): *m/z* for $C_{26}H_{38}NaO_3$ $[M+Na]^+$: calc.: 421.2713, found: 421.2723

13.4 Substrate Scope for α-Bromomalonate

Compound 9a:

Dimethyl 2-phenethylcyclopropane-1,1-dicarboxylate



Cyclopropane **9a** was prepared via GP2, using alkene **8a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–10% EtOAc in hexane) to give **9a** as a pale-yellow oil.

Note: Cyclopropane **9a** was prepared on larger scale by an adapted procedure based on GP2, using alkene **8a** (300 µL, 264 mg, 2.00 mmol, 1.00 equiv) and and dimethyl bromomalonate **7** (500 µL, 3.80 mmol, 1.90 equiv) the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–10% EtOAc in hexane) to give **9a** as a pale-yellow oil in 81% (425 mg, 1.62 mmol) yield.

Yield: 48.6 mg, 0.185 mmol, 93%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 – 7.23 (m, 2H), 7.23 – 7.12 (m, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 2.81 – 2.64 (m, 2H), 1.94 (dtd, J = 8.9, 7.8, 6.7 Hz, 1H), 1.83 – 1.70 (m, 1H), 1.53 (dddd, J = 13.9, 8.9, 7.8, 7.0 Hz, 1H), 1.46 – 1.34 (m, 2H).

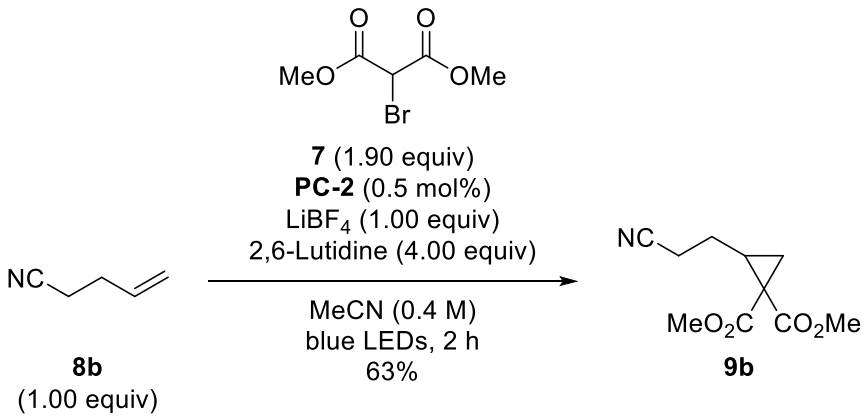
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.9, 168.8, 141.4, 128.5, 128.5, 126.1, 52.7, 52.7, 35.3, 34.1, 30.9, 28.4, 21.4.

IR (thin film, cm^{-1}): 3063, 3027, 2952, 2862, 1724, 1436, 1328, 1286, 1211, 1132, 1072, 1031, 904, 881, 750, 700, 584.

HRMS (ESI+): *m/z* for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: calc.: 285.1097, found: 285.1104.

Compound 9b:

Dimethyl 2-(2-cyanoethyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9b** was prepared via GP2, using alkene **8b** (19.9 µL, 16.2 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–25% EtOAc in hexane) to give **9b** as a pale-yellow oil.

Yield: 26.6 mg, 0.127 mmol, 63%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.78 (s, 3H), 3.74 (s, 3H), 2.51 – 2.43 (m, 2H), 1.98 (dq, J = 9.0, 7.5 Hz, 1H), 1.79 (dtd, J = 14.2, 7.1, 6.6 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.53 (dd, J = 9.0, 4.9 Hz, 1H), 1.44 (dd, J = 7.5, 4.9 Hz, 1H).

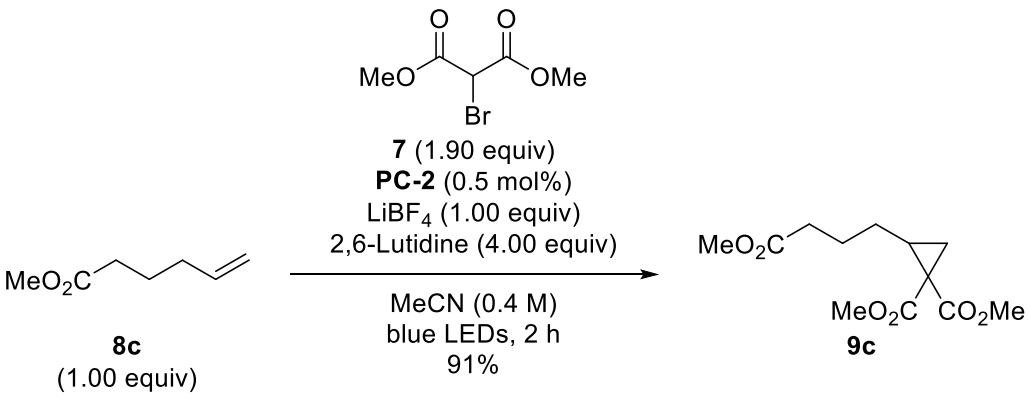
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.1, 168.3, 119.0, 53.0, 53.0, 33.9, 26.6, 25.2, 20.7, 16.8.

IR (thin film, cm^{-1}): 3009, 2956, 2852, 2248, 1723, 1437, 1327, 1285, 1212, 1125, 1075, 986, 882, 822, 705.

HRMS (EI+): *m/z* for $C_{10}H_{13}NO_4$ $[M+H]^+$: calc.: 211.0839, found: 211.0841.

Compound 9c:

Dimethyl 2-(3-methoxy-3-oxopropyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9c** was prepared via GP2, using alkene **8c** (28.5 µL, 25.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–20% EtOAc in hexane) to give **9c** as a pale-yellow oil.

Yield: 46.9 mg, 0.182 mmol, 91%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.74 (s, 3H), 3.70 (s, 3H), 3.64 (s, 3H), 2.31 (td, J = 7.4, 1.9 Hz, 2H), 1.87 (dtd, J = 9.0, 7.8, 6.6 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.52 – 1.43 (m, 1H), 1.42 – 1.34 (m, 2H), 1.26 – 1.17 (m, 1H).

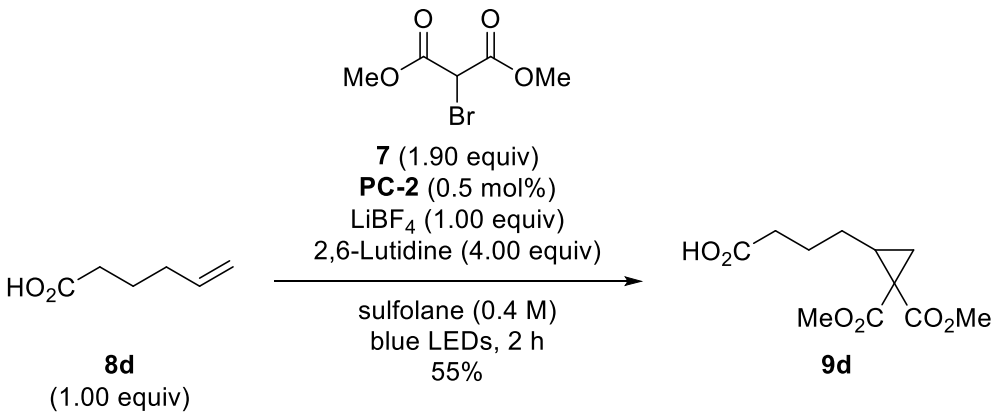
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 178.6, 170.9, 168.7, 52.8, 52.7, 34.0, 33.4, 28.2, 28.1, 24.0, 21.3.

IR (thin film, cm^{-1}): 3005, 2954, 2867, 1725, 1436, 1332, 1278, 1252, 1210, 1121, 1173, 1121, 1079, 993, 885, 739, 705.

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

Compound 9d:

3-(2,2-Bis(methoxycarbonyl)cyclopropyl)propanoic acid



Cyclopropane **9d** was prepared via GP2, but sulfolane was used as solvent instead of MeCN. Alkene **8d** (23.8 µL, 22.8 mg, 0.200 mmol, 1.00 equiv) was added to the vial and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–50% EtOAc in hexane) to give **9d** as a pale-yellow oil.

Yield: 26.9 mg, 0.110 mmol, 55%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.76 (s, 3H), 3.72 (s, 3H), 2.38 (ddd, J = 7.6, 7.1, 3.6 Hz, 2H), 1.90 (dtd, J = 9.0, 7.8, 6.7 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.52 (ddt, J = 13.0, 8.9, 6.5 Hz, 1H), 1.47 – 1.34 (m, 2H), 1.31 – 1.21 (m, 1H).

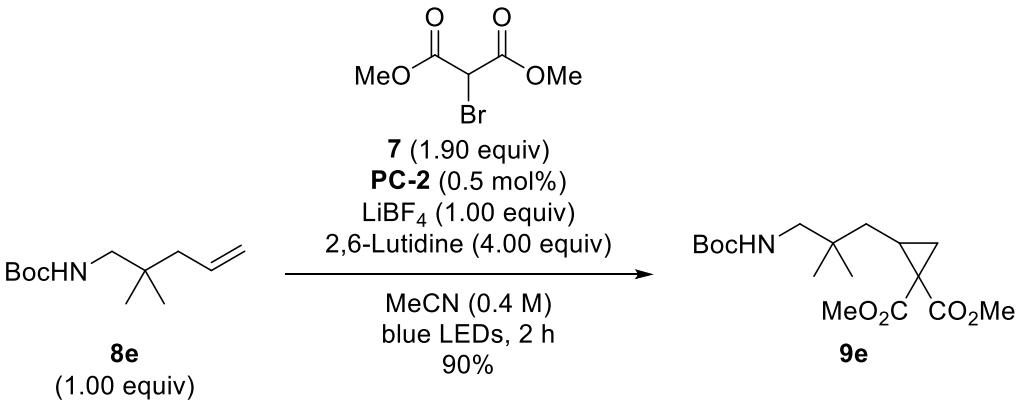
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 178.6, 170.9, 168.7, 52.8, 52.7, 34.0, 33.4, 28.2, 28.1, 24.0, 21.3.

IR (thin film, cm^{-1}): 3009, 2955, 2928, 2864, 1722, 1708, 1437, 1331, 1281, 1212, 1129, 1079, 941, 884, 784, 704.

HRMS (ESI+): *m/z* for $C_{11}H_{16}NaO_6$ $[M+Na]^+$: calc.: 267.0839, found: 267.0840.

Compound 9e:

Dimethyl 2-(3-((tert-butoxycarbonyl)amino)-2,2-dimethylpropyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9e** was prepared via GP2, using alkene **8e**[16] (42.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-40% EtOAc in hexane) to give **9e** as a pale-yellow oil.

Yield: 61.5 mg, 0.179 mmol, 90%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.56 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.00 – 2.91 (m, 2H), 1.94 – 1.83 (m, 1H), 1.63 – 1.58 (m, 1H), 1.50 – 1.36 (s, 11H), 0.92 (s, 6H), 0.85 (dd, J = 14.0, 9.8 Hz, 1H).

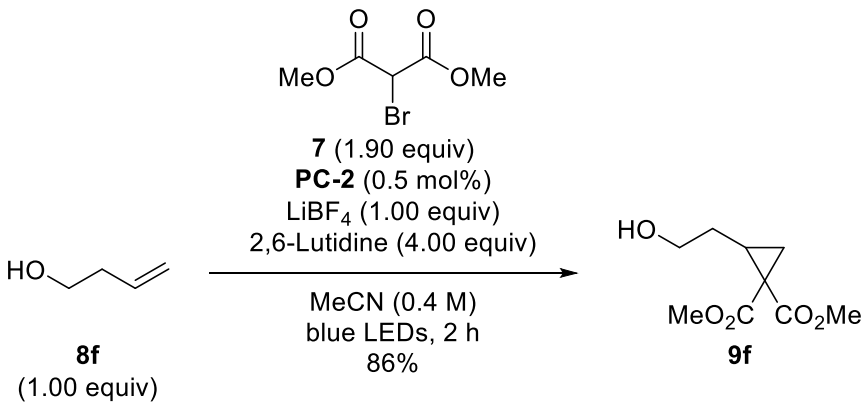
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.0, 168.7, 156.3, 79.3, 52.8, 52.7, 50.6, 38.1, 35.3, 33.2, 28.5, 24.9, 24.9, 24.7, 22.4

IR (thin film, cm^{-1}): 3397, 2960, 2933, 2874, 1716, 1518, 1438, 1366, 1269, 1215, 1168, 1135, 1047, 912, 860, 782.

HRMS (ESI+): *m/z* for $C_{17}H_{29}NNaO_6$ $[M+Na]^+$: calc.: 366.1887, found: 366.1893.

Compound 9f:

Dimethyl 2-(2-hydroxyethyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9f** was prepared via GP2, using alkene **8f** (17.2 µL, 14.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-40% EtOAc in hexane) to give **9f** as a pale-yellow oil.

Yield: 34.9 mg, 0.173 mmol, 86%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.77 (s, 3H), 3.75 (d, J = 6.3 Hz, 1H), 3.73 (s, 3H), 1.99 (dq, J = 9.1, 7.4 Hz, 1H), 1.69 (dq, J = 13.5, 6.7 Hz, 1H), 1.62 – 1.51 (m, 3H), 1.47 (dd, J = 9.1, 4.7 Hz, 1H), 1.41 (dd, J = 7.7, 4.6 Hz, 1H).

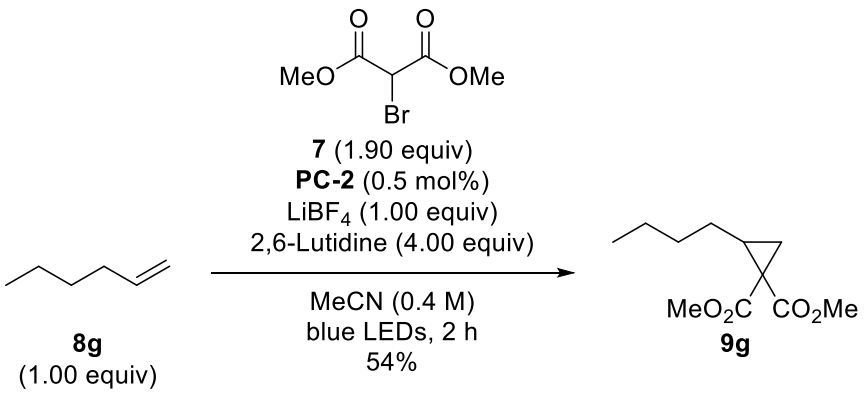
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.8, 168.9, 62.1, 52.8, 52.8, 33.7, 31.9, 25.7, 20.8.

IR (thin film, cm^{-1}): 3431, 3008, 2955, 2883, 1722, 1438, 1333, 1289, 1214, 1130, 1077, 1046, 987, 884, 705.

HRMS (ESI+): *m/z* for $C_9H_{14}NaO_5$ $[M+Na]^+$: calc.: 225.0733, found:. 225.0735

Compound 9g:

Dimethyl 2-butylcyclopropane-1,1-dicarboxylate



Cyclopropane **9g** was prepared via GP2, using alkene **8g** (25.0 µL, 16.8 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **9g** as a pale-yellow oil.

Yield: 23.1 mg, 0.108 mmol, 54%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.76 (s, 3H), 3.72 (s, 3H), 1.96 – 1.84 (m, 1H), 1.51 – 1.29 (m, 7H), 1.23 – 1.10 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H).

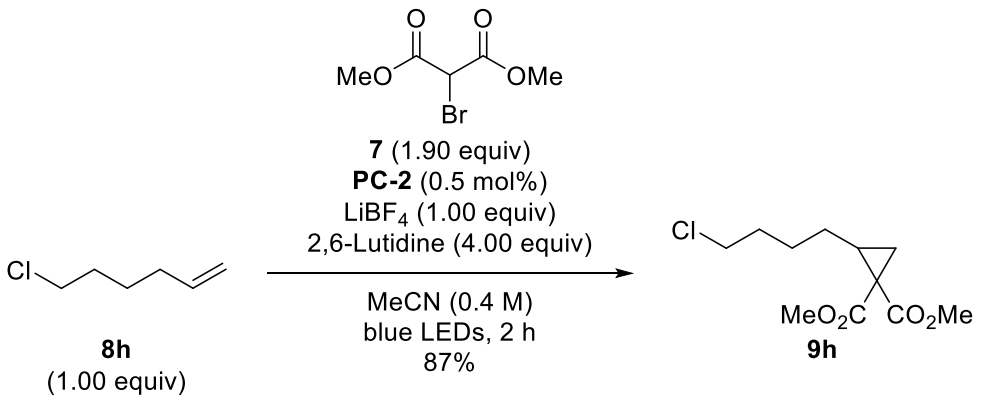
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.2, 168.9, 52.7, 34.1, 31.1, 29.0, 28.5, 22.5, 21.6, 14.1.

IR (thin film, cm^{-1}): 2956, 2930, 2860, 1728, 1437, 1329, 1280, 1211, 1131, 1077, 995, 881, 837.

HRMS (ESI+): *m/z* for $C_{11}H_{18}NaO_4$ $[M+Na]^+$: calc.: 237.1097, found: 237.1101.

Compound 9h:

Dimethyl 2-(4-chlorobutyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9h** was prepared via GP2, using alkene **8h** (26.5 µL, 23.7 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane) to give **9h** as a pale-yellow oil.

Yield: 43.1 mg, 0.173 mmol, 87%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.76 (s, 3H), 3.73 (s, 3H), 3.52 (t, J = 6.6 Hz, 2H), 1.90 (dtd, J = 8.9, 7.8, 6.4 Hz, 1H), 1.83 – 1.73 (m, 2H), 1.63 – 1.55 (m, 2H), 1.49 (dt, J = 14.2, 7.0 Hz, 1H), 1.44 – 1.36 (m, 2H), 1.29 – 1.17 (m, 1H).

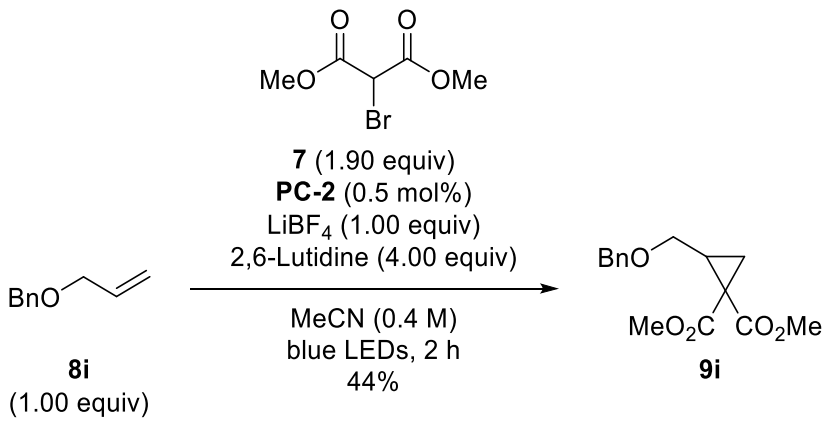
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.9, 168.8, 52.8, 52.7, 44.9, 34.0, 32.3, 28.5, 28.1, 26.3, 21.4.

IR (thin film, cm^{-1}): 3004, 2953, 2865, 1727, 1437, 1332, 1286, 1213, 1133, 1080, 991, 906, 884, 731, 650.

HRMS (ESI+): *m/z* for $C_{11}H_{17}ClNaO_4$ $[M+Na]^+$: calc.: 271.0708 , found: 271.0715

Compound 9i:

Dimethyl 2-((benzyloxy)methyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9i** was prepared via GP2, using alkene **8i** (30.9 µL, 29.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9i** as a pale-yellow oil.

Yield: 24.7 mg, 0.0888 mmol, 44%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.38 – 7.26 (m, 5H), 4.54 – 4.40 (m, 2H), 3.73 (s, 3H), 3.68 (s, 3H), 3.58 (dd, J = 10.5, 5.6 Hz, 1H), 3.46 (dd, J = 10.5, 7.1 Hz, 1H), 2.26 (dtd, J = 9.2, 7.4, 5.6 Hz, 1H), 1.58 (dd, J = 7.6, 4.7 Hz, 1H), 1.46 (dd, J = 9.2, 4.7 Hz, 1H).

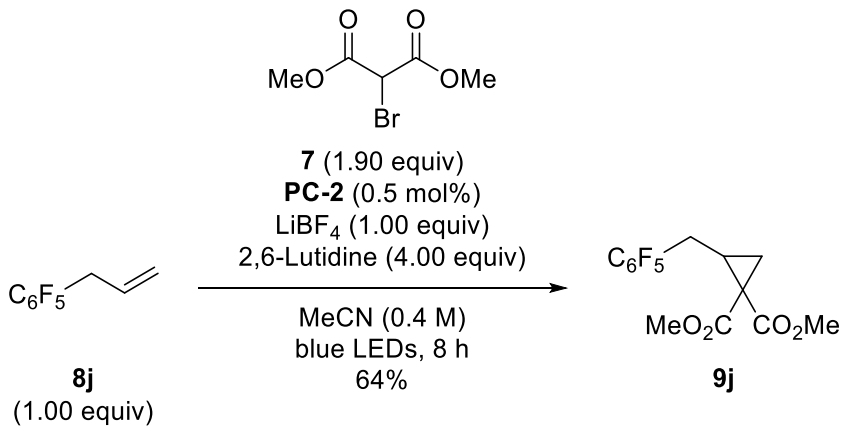
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.5, 168.3, 138.0, 128.5, 127.8, 127.8, 73.0, 67.9, 52.8, 52.7, 32.9, 27.5, 19.0.

IR (thin film, cm^{-1}): 3030, 2953, 2863, 1729, 1437, 1332, 1288, 1212, 1130, 1100, 906, 741, 700.

HRMS (ESI+): *m/z* for $C_{15}H_{18}NaO_5$ $[M+Na]^+$: calc.: 301.1046, found: 301.1047.

Compound 9j:

Dimethyl 2-((perfluorophenyl)methyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9j** was prepared via GP2, using alkene **8j** (30.7 µL, 41.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9j** as a pale-yellow oil.

Yield: 43.3 mg, 0.128 mmol, 64%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 3H), 3.72 (s, 3H), 2.95 (ddt, J = 14.6, 6.3, 1.5 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.20 – 2.12 (m, 1H), 1.59 (dd, J = 7.6, 5.0 Hz, 1H), 1.46 (dd, J = 9.1, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.1, 168.2, 146.3 – 146.2 (m, 1C), 144.4 – 144.2 (m, 1C), 141.4 – 141.1 (m, 1C), 139.3 –139.1 (m, 1C), 138.8 – 138.6 (m, 1C), 136.8 – 136.5 (m, 1C), 113.1 – 112.8 (m, 1C), 53.0, 52.9, 34.3, 26.9, 21.8, 21.1.

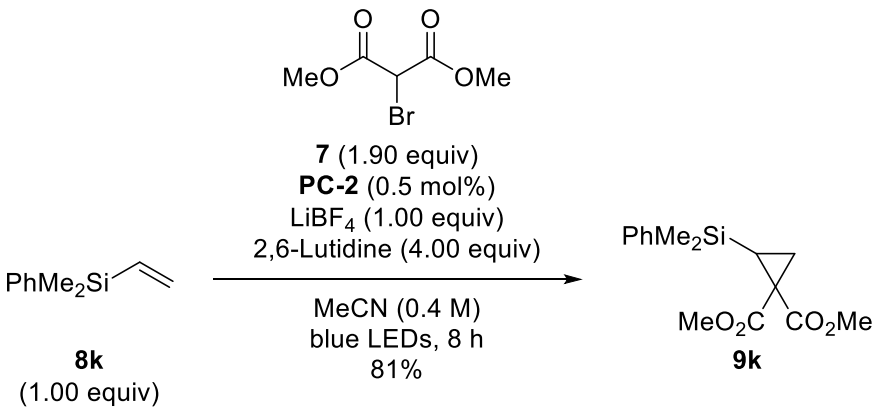
^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -143.13 (dd, *J* = 22.4, 8.4 Hz, 2F), -156.37 (t, *J* = 20.8 Hz, 1F), -162.11 – -162.28 (m, 2F).

IR (thin film, cm^{-1}): 3006, 2958, 1728, 1521, 1503, 1438, 1326, 1276, 1122, 1037, 961, 895, 706, 613.

HRMS (ESI+): *m/z* for $C_{14}H_{11}F_5NaO_4$ $[M+Na]^+$: calc.: 361.0470, found: 361.0472

Compound 9k:

Dimethyl 2-(dimethyl(phenyl)silyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9k** was prepared via GP2, using alkene **8k** (36.4 µL, 32.5 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9k** as a pale-yellow oil.

Yield: 47.6 mg, 0.163 mmol, 81%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.59 – 7.49 (m, 2H), 7.43 – 7.32 (m, 4H), 3.73 (s, 3H), 3.54 (s, 4H), 1.56 (dd, J = 11.1, 3.6 Hz, 1H), 1.44 (dd, J = 9.6, 3.6 Hz, 1H), 1.14 (dd, J = 11.1, 9.6 Hz, 1H), 0.34 (s, 3H), 0.27 (s, 3H).

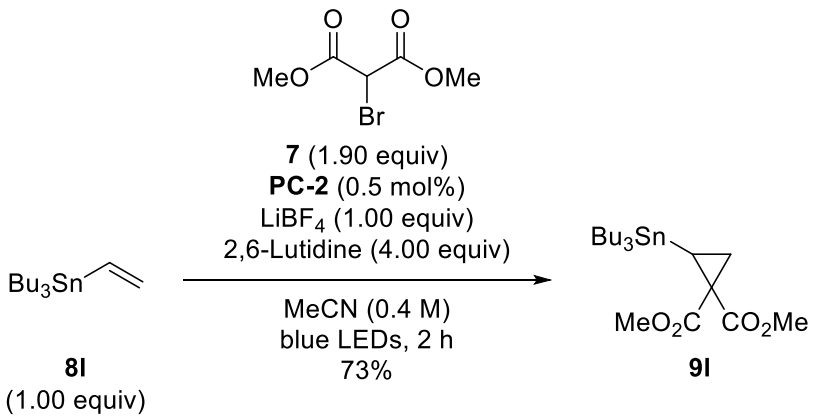
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 171.5, 169.5, 137.7, 133.9, 129.3, 127.9, 52.9, 52.3, 33.1, 18.9, 16.1, -3.1, -3.2.

IR (thin film, cm^{-1}): 3071, 3003, 2954, 2903, 2846, 1730, 1436, 1333, 1247, 1208, 1134, 1078, 878, 837, 818, 781, 735, 703, 669.

HRMS (ESI+): *m/z* for $C_{15}H_{20}NaO_4Si$ $[M+Na]^+$: calc.: 315.1023, found: 315.1026

Compound 9l:

Dimethyl 2-(tributylstannyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9l** was prepared via GP2, using alkene **8l** (58.5 µL, 63.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 8 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9l** as a pale-yellow oil.

Yield: 65.5 mg, 0.146 mmol, 73%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.72 (s, 6H), 1.77 (dd, J = 11.1, 3.4 Hz, 1H), 1.55 – 1.40 (m, 6H), 1.37 – 1.23 (m, 7H), 0.98 – 0.80 (m, 16H).

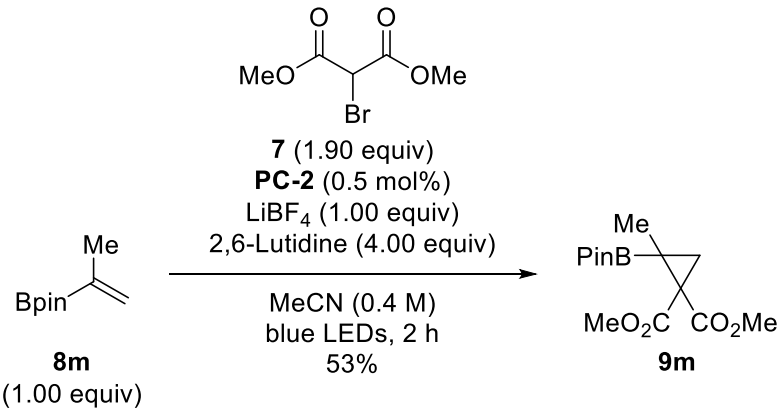
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 172.1, 171.8, 52.7, 52.6, 31.1, 29.1, 27.5, 21.1, 16.0, 13.9, 10.3.

IR (thin film, cm^{-1}): 2954, 2921, 2871, 2851, 1721, 1436, 1321, 1223, 1205, 1134, 1074, 877, 765, 690, 669, 596.

HRMS (ESI+): *m/z* for $C_{19}H_{36}NaO_4Sn$ $[M+Na]^+$: calc.: 471.1528, found: 471.1524.

Compound 9m:

Dimethyl 2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9m** was prepared via GP2, using alkene **8m** (37.6 µL, 33.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (neutral silica, 0-10% EtOAc in hexane) to give **9m** as a pale-yellow oil.

Yield: 28.0 mg, 0.105 mmol, 53%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.73 (s, 3H), 3.70 (s, 3H), 1.51 (d, J = 4.0 Hz, 1H), 1.43 (J = 4.1 Hz, 1H), 1.26 (s, 12H), 1.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 171.3, 168.7, 83.9, 77.4, 52.8, 52.6, 38.9, 25.2, 24.9, 16.3.

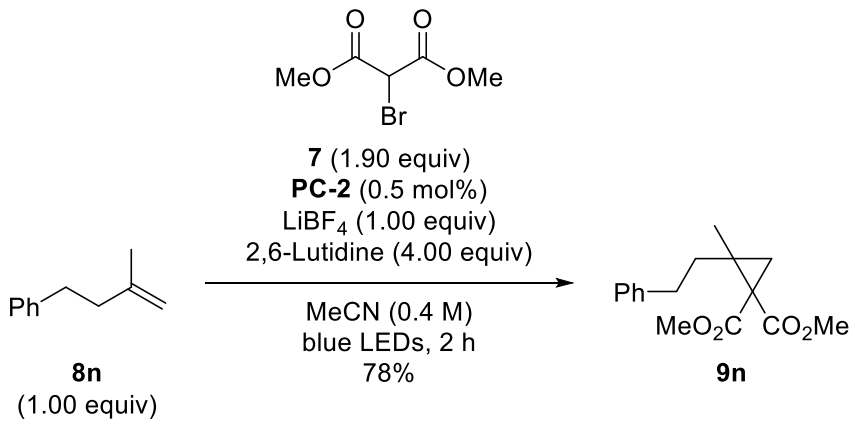
^{11}B NMR (160 MHz, $CDCl_3$): δ (ppm) = 31.95.

IR (thin film, cm^{-1}): 2978, 1728, 1437, 1380, 1318, 1238, 1167, 1142, 1114, 1068, 852, 720, 668.

HRMS (ESI+): *m/z* for $C_{14}H_{23}BNaO_6$ $[M+Na]^+$: calc.: 321.1480, found: 321.1487

Compound 9n:

Dimethyl 2-methyl-2-phenethylcyclopropane-1,1-dicarboxylate



Cyclopropane **9n** was prepared via GP2, using alkene **8n**[17] (29.2 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9n** as a pale-yellow oil.

Yield: 43.1 mg, 0.156 mmol, 78%

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.30 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 2.76 – 2.62 (m, 2H), 1.90 (ddd, J = 13.9, 11.0, 5.5 Hz, 1H), 1.77 (ddd, J = 13.9, 11.0, 6.3 Hz, 1H), 1.49 (d, J = 5.0 Hz, 1H), 1.45 (d, J = 5.0 Hz, 1H), 1.29 (s, 3H).

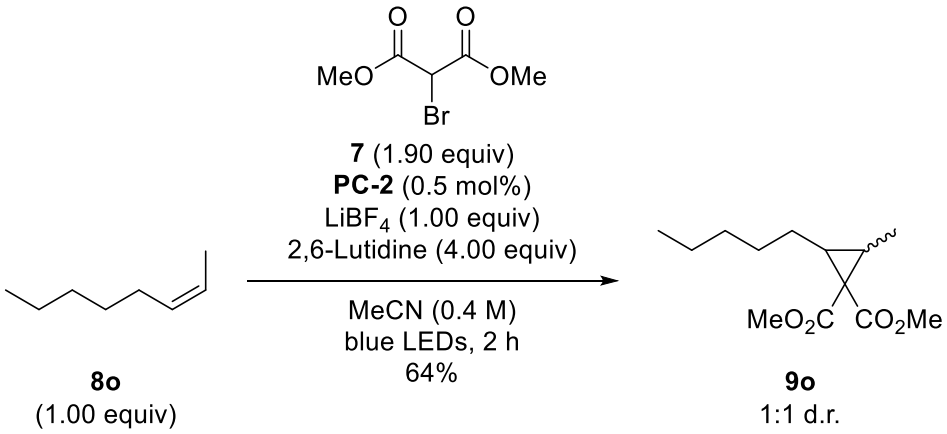
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 169.5, 169.3, 141.9, 128.5, 128.5, 126.0, 52.7, 52.6, 39.4, 36.9, 33.2, 33.2, 27.4, 19.6.

IR (thin film, cm^{-1}): 3062, 3027, 3002, 2952, 2863, 1727, 1455, 1434, 1241, 1111, 895, 749, 701.

HRMS (ESI+): *m/z* for $C_{16}H_{20}NaO_4$ $[M+Na]^+$: calc.: 299.1254, found: 299.1258.

Compound 9o:

Dimethyl 2-methyl-3-pentylcyclopropane-1,1-dicarboxylate



Cyclopropane **9o** was prepared via GP2, using alkene **8o** (31.0 µL, 22.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane), to give **9o** as a pale-yellow oil. The product was isolated as an inseparable 1:1 mixture of diastereomers.

Note: Cyclopropane **9o** was also prepared via GP2, using *E*-oct-2-en (31.0 µL, 22.4 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-5% EtOAc in hexane), to give **9o** as a pale-yellow oil in 64% (30.8 mg, 0.127 mmol) yield. The product was isolated as an inseparable 1:1 mixture of diastereomers

Yield: 31.2 mg, 0.129 mmol, 65%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.73 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H), 1.84 – 1.75 (m, 2H), 1.74 – 1.65 (m, 2H), 1.65 – 1.56 (m, 1H), 1.53 – 1.19 (m, 12H), 1.13 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.2 Hz, 3H), 0.95 – 0.83 (m, 6H).

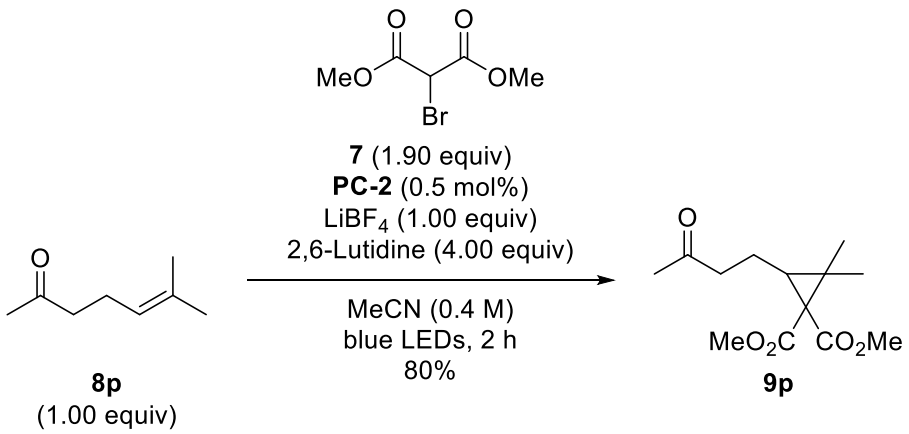
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.8, 169.5, 169.3, 167.9, 52.7, 52.5, 52.2, 40.0, 36.6, 34.5, 32.0, 31.8, 31.5, 29.0, 28.6, 27.8, 27.8, 26.1, 24.6, 22.7, 22.7, 14.2, 14.1, 13.0, 9.4.

IR (thin film, cm^{-1}): 2955, 2930, 2860, 1727, 1436, 1295, 1259, 1213, 1137, 1067, 917.

HRMS (ESI+): *m/z* for $C_{13}H_{22}NaO_4$ $[M+Na]^+$: calc.: 265.1410, found: 265.1414

Compound 9p:

Dimethyl 2,2-dimethyl-3-(3-oxobutyl)cyclopropane-1,1-dicarboxylate



Cyclopropane **9p** was prepared via GP2, using alkene **8p** (29.5 µL, 25.2 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-20% EtOAc in hexane) to give **9p** as a pale-yellow oil.

Yield: 41.2 mg, 0.161 mmol, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.71 (s, 3H), 3.70 (s, 3H), 2.65 – 2.46 (m, 2H), 2.14 (s, 3H), 1.81 – 1.59 (m, 3H), 1.23 (s, 3H), 1.19 (s, 3H).

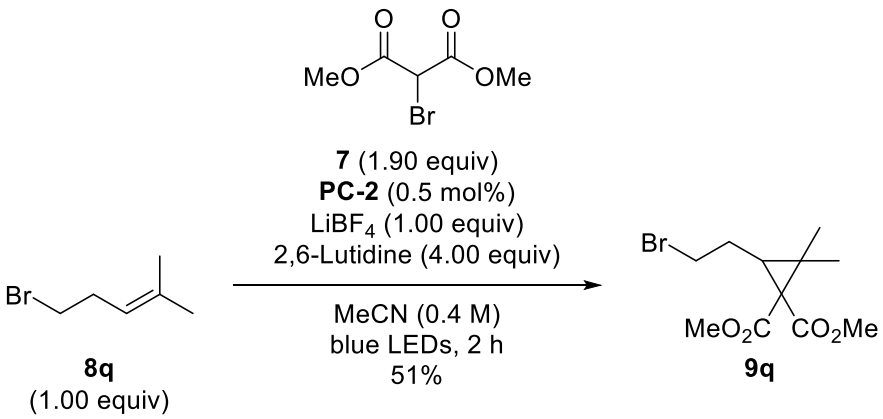
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 208.2, 169.8, 168.1, 52.7, 52.3, 43.0, 41.8, 36.3, 31.1, 30.2, 22.9, 19.5, 17.6.

IR (thin film, cm^{-1}): 2954, 1725, 1435, 1367, 1290, 1244, 1165, 1001, 921, 793.

HRMS (ESI+): *m/z* for $C_{13}H_{20}NaO_5$ $[M+Na]^+$: calc.: 279.1203 , found: 279.1206.

Compound 9q:

Dimethyl 3-(2-bromoethyl)-2,2-dimethylcyclopropane-1,1-dicarboxylate



Cyclopropane **9q** was prepared via GP2, using alkene **8q** (26.8 µL, 32.6 mg, 0.200 mmol, 1.00 equiv) and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0-10% EtOAc in hexane) to give **9q** as a pale-yellow oil.

Yield: 30.0 mg, 102 mmol, 51%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.73 (s, 3H), 3.72 (s, 3H), 3.55 – 3.36 (m, 2H), 2.19 – 2.10 (m, 1H), 1.98 (dq, J = 14.8, 7.4 Hz, 1H), 1.79 (t, J = 7.1 Hz, 1H), 1.24 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 169.5, 168.1, 52.7, 52.4, 41.6, 35.8, 32.2, 31.0, 28.6, 22.8, 17.9.

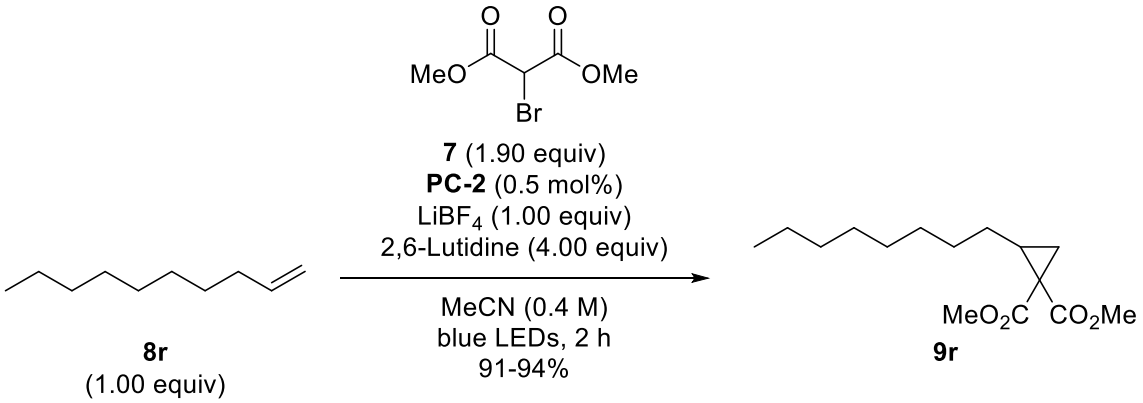
IR (thin film, cm^{-1}): 2954, 1729, 1435, 1310, 1248, 1151, 1116, 1092, 922, 640.

HRMS (ESI+): *m/z* for $[M+Na]^+$: $C_{11}H_{17}BrNaO_4$ calc.: 315.0202, found: 315.0197.

13.5 Synthesis of (±)-Olibanic acid

Compound 9r:

dimethyl 2-octylcyclopropane-1,1-dicarboxylate



Cyclopropane **9r** was prepared via GP2. Alkene **8r** (37.9 µL, 28.1 mg, 0.200 mmol, 1.00 equiv) was added to the vial and the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–20% EtOAc in hexane) to give **9r** as a colourless oil in 91% (49.3 mg, 0.182 mmol) yield.

Note: Cyclopropane **9r** was prepared on 2 mmol scale by an adapted procedure based on GP2, using alkene **8r** (379 µL, 281 mg, 2.00 mmol, 1.00 equiv) and dimethyl bromomalonate **7** (500 µL, 3.80 mmol, 1.90 equiv) the reaction was stirred for 2 h. The crude product was purified via column chromatography (0–20% EtOAc in hexane) to give **9r** as a colourless oil in 94% (508 mg, 1.88 mmol) yield.

Note: When Cyclopropane **9r** was prepared on 15 mmol scale, the catalyst loading could be further decreased and only catalytic amounts of $LiBF_4$ were required. In an adapted procedure based on GP2, a vial was sequentially charged with **PC-2** (3.77 mg, 0.0150 mmol, 0.1 mol %), $LiBF_4$ (281.2 mg, 3.00 mmol, 20 mol %), 7.5 mL MeCN, alkene **8r** (2.84 mL, 2.11 g, 15.0 mmol, 1.00 equiv), 2,6-lutidine (6.95 mL, 6.43 g, 60.0 mmol, 4.00 equiv), and dimethyl bromomalonate **7** (3.75 mL, 28.5 mmol, 1.90 equiv). The reaction was stirred for 2 h. Subsequently, the solvent was evaporated, and the crude product was purified via flash column chromatography

(0–20% EtOAc in hexane) to give **9r** as a colourless oil in 85% (3.45 g, 12.8 mmol) yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.75 (s, 3H), 3.72 (s, 3H), 1.96 – 1.84 (m, 1H), 1.52 – 1.36 (m, 5H), 1.25 (s, 10H), 1.22 – 1.09 (m, 1H), 0.89 – 0.86 (m, 3H).

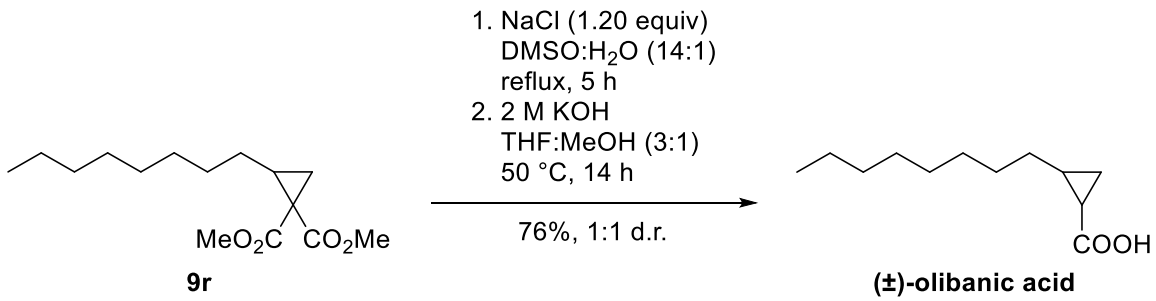
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.2, 168.9, 52.7, 52.6, 34.1, 32.0, 29.6, 29.4, 29.4, 29.0, 29.0, 28.9, 22.8, 21.6, 14.2.

IR (thin film, cm^{-1}): 2953, 2925, 2855, 1726, 1436, 1282, 1209, 1129, 992, 834.

HRMS (ESI+): *m/z* for $C_{15}H_{26}NaO_4$ $[M+Na]^+$: calc.: 293.1723, found: 293.1726.

Compound (±)-Olibanic acid:

2-octylcyclopropane-1-carboxylic acid



9r **(±)-olibanic acid**

To a solution of cyclopropane **9r** (135 mg, 0.500 mmol, 1.00 equiv) in DMSO (1.5 mL) was added NaCl (30.0 mg, 0.510 mmol, 1.02 equiv) and H_2O (0.110 mL). The mixture was stirred at reflux for 5h until complete consumption of starting material (TLC), then cooled to rt and diluted with ethyl acetate (15 mL) and aqueous HCl (1M, 10 mL). The organic phase was isolated, and the aqueous phase extracted with EtOAc (3 x 15 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed in vacuo. The crude product was used directly in the next step.

To the crude product was added 3 mL THF, 1 mL MeOH and 1 mL 2 M aqueous KOH. The reaction was heated to 50 °C and stirred for 14 h. After cooling to room temperature, the reaction was acidified (pH = 2) with aqueous HCl (4 M) and extracted with EtOAc (3 x 20 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via flash column chromatography (0–25% Et_2O in hexane) to give (±)-*cis* and *trans*-olibanic acid in 1:1 d.r.

Yield: 75.4 mg, 0.390 mmol, 76%, 1:1 d.r.

(±)-*cis*-olibanic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.68 (ddd, J = 8.9, 7.8, 5.4 Hz, 1H), 1.55 (ddd, J = 9.8, 5.9, 2.2 Hz, 2H), 1.36 – 1.28 (m, 13H), 1.08 (ddd, J = 8.5, 7.8, 4.5 Hz, 1H), 0.96 (ddd, J = 7.5, 5.4, 4.5 Hz, 1H), 0.90 – 0.86 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 179.2, 32.0, 29.7, 29.7, 29.5, 29.4, 27.1, 23.3, 22.8, 18.0, 14.6, 14.3.

(±)-*trans*-olibanic acid

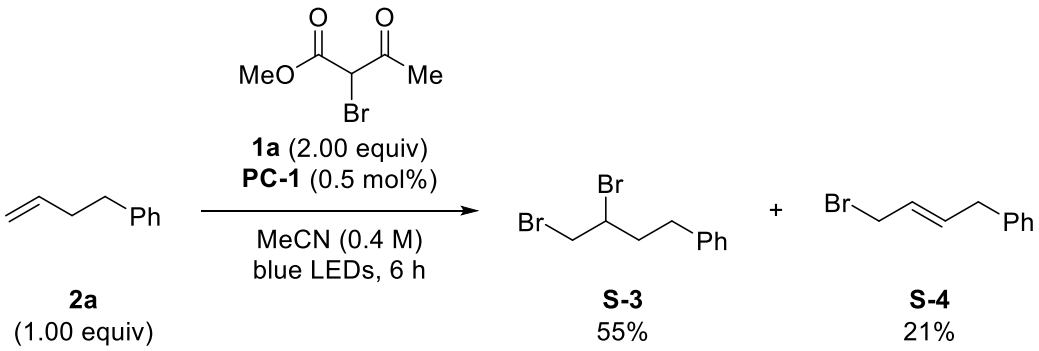
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.50 – 1.31 (m, 4H), 1.33 – 1.26 (m, 13H), 1.24 – 1.20 (m, 1H), 0.88 (t, J = 6.9 Hz, 3H), 0.77 (ddd, J = 8.1, 6.5, 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 179.0, 33.2, 32.0, 29.7, 29.4, 29.4, 29.2, 24.2, 22.8, 19.8, 16.5, 14.3.

Note: For ^{1}H NMR and ^{13}C NMR the the *cis* and *trans* isomers were separated. The analytical data for both isomers matches with the literature.[18]

13.6 Isolation of Intermediates and Side Products

Isolation of Compounds S-3 and S-4:



To a glass vial charged with **PC-1** (0.33 mg, 0.0010 mmol, 0.50 mol%) in MeCN (500 µL, 0.4 M) was added alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), and bromoketoester **1a** (78.0 mg, 0.400 mmol, 2.00 equiv). The vial was equipped with a magnetic stirrer bar and capped with a screwcap. Then, the reaction was irradiated in a 350 W photoreactor for 6 h. The solvent was removed *in vacuo*. Isolation of pure **S-3** and **S-4** was achieved by multiple flash column chromatographies (0–5% Et_2O in hexane).

Note: The yields shown are determined by ^{1}H NMR with mesitylene as internal standard.

Compound S-3

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 4.20 (dddd, J = 9.3, 8.2, 4.9, 3.4 Hz, 1H), 3.90 (dd, J = 10.6, 4.9 Hz, 1H), 3.79 (dd, J = 10.6, 8.0 Hz, 1H), 2.90 (ddd, J = 14.0, 9.4, 4.9 Hz, 1H), 2.74 (ddd, J = 13.7, 9.2, 7.1 Hz, 1H), 2.37 (dddd, J = 14.6, 9.4, 7.0, 3.4 Hz, 1H), 2.13 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, CD_3CN): δ (ppm) = 141.7, 129.5, 129.5, 127.2, 54.1, 38.9, 38.3, 33.7.

IR (thin film, cm^{-1}): 3062, 3027, 2929, 1603, 1496, 1454, 1432, 1233, 1213, 1142, 1030, 910, 748, 699, 646, 569, 551.

HRMS (EI+): *m/z* for $C_{10}H_{12}Br_2$ $[M]^+$: calc.: 289.9300, found: 289.9300.

Compound S-4

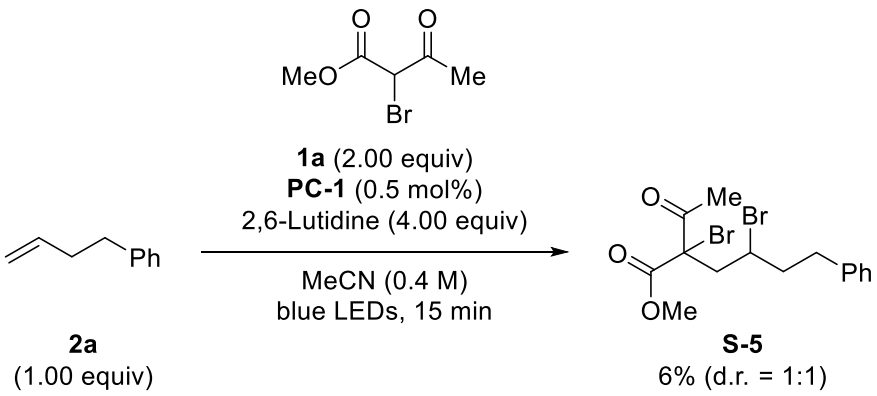
^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 3H), 5.97 (dtt, J = 14.7, 6.9, 0.9 Hz, 1H), 5.78 (dtt, J = 15.1, 7.6, 1.4 Hz, 1H), 4.04 (dq, J = 7.6, 0.8 Hz, 2H), 3.39 (d, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, CD_3CN): δ (ppm) = 140.8, 136.0, 129.5, 129.5, 128.7, 127.2, 38.8, 34.2.

IR (thin film, cm^{-1}): 3062, 3028, 2902, 1659, 1602, 1494, 1453, 1432, 1205, 745, 698, 603, 570, 511.

HRMS (EI+): *m/z* for $C_{10}H_{11}Br$ $[M]^+$: calc.: 210.0039, found: 210.0038.

Isolation of Compound S-5:



To a glass vial charged with **PC-1** (3.3 mg, 0.0100 mmol, 0.50 mol%) in MeCN (5.00 mL, 0.4 M) was added alkene **2a** (0.300 mL, 264 mg, 2.00 mmol, 1.00 equiv), 2,6-lutidine (927 µL, 8.00 mmol, 4.00 equiv), and bromoketoester **1a** (0.780 g, 4.00 mmol, 2.00 equiv). The vial was equipped with a magnetic stirrer bar and capped with a screwcap. Then, the reaction was irradiated in a 350 W photoreactor for 15 minutes. The solvent was removed *in vacuo*. Isolation of **S-5** was achieved by multiple flash column chromatographies (0–50% CH_2Cl_2 in hexane).

Note: The yields shown are determined by ^{1}H NMR with mesitylene as internal standard.

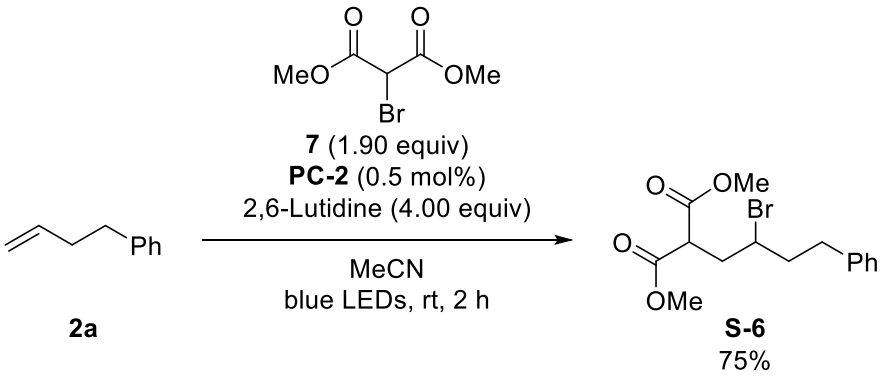
^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.33 – 7.28 (m, 4H), 7.25 – 7.19 (m, 6H), 4.28 – 4.20 (m, 1H), 4.17 – 4.10 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.94 (d, J = 6.0 Hz, 2H), 2.92 – 2.81 (m, 4H), 2.82 – 2.68 (m, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 2.22 – 2.16 (m, 2H), 2.13 – 2.10 (m, 2H).

^{13}C NMR (101 MHz, CD_3CN): δ (ppm) = 198.4, 196.9, 168.7, 168.0, 141.80, 141.76, 129.53, 129.51, 129.5, 127.1, 69.7, 68.2, 54.9, 52.9, 52.8, 46.6, 45.8, 42.2, 41.8, 34.05, 33.98, 27.3, 25.4.

IR (thin film, cm^{-1}): 3027, 2953, 1726, 1454, 1435, 1240, 1178, 1107, 988, 750, 700, 555.

HRMS (ESI+): *m/z* for $C_{15}H_{19}Br_2O_3$ $[M+H]^+$: calc.: 404.9695, found: 404.9687.

Isolation of Compound S-6:



To a glass vial charged with **PC-2** (0.25 mg, 0.0010 mmol, 0.50 mol%) and MeCN (500 µL, 0.4 M) was added alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), 2,6-lutidine (92.7 µL, 0.800 mmol, 4.00 equiv), and dimethyl bromomalonate (50.0 µL, 0.380 mmol, 1.90 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 for 2h. The solvent was removed *in vacuo* and isolation of **S-6** was achieved by flash column chromatography (0–20% Et_2O in hexane).

Note: The yields shown are determined by ^1H NMR with mesitylene as internal standard.

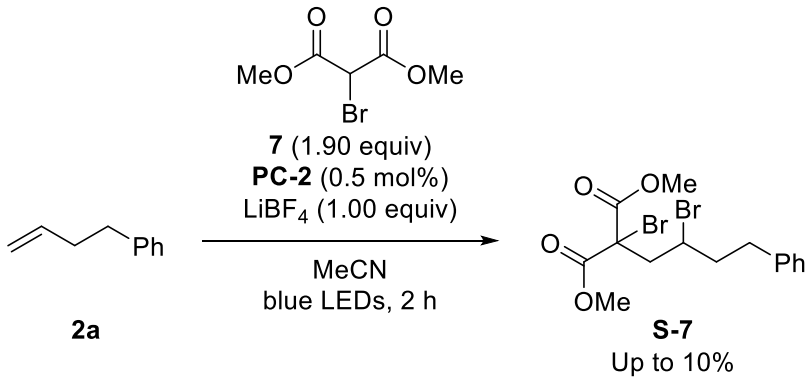
^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.32 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 3.99 (dddd, J = 10.1, 8.3, 4.8, 3.6 Hz, 1H), 3.73 (dd, J = 9.5, 4.9 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 2.87 (ddd, J = 14.3, 8.6, 5.9 Hz, 1H), 2.74 (ddd, J = 13.7, 9.0, 7.1 Hz, 1H), 2.46 (ddd, J = 14.9, 9.5, 3.6 Hz, 1H), 2.30 (ddd, J = 15.0, 10.2, 4.9 Hz, 1H), 2.18 – 2.11 (m, 2H).

^{13}C NMR (101 MHz, CD_3CN): δ (ppm) = 170.2, 170.0, 142.0, 129.48, 129.46, 127.1, 55.6, 53.3, 53.3, 51.2, 41.5, 38.7, 34.1.

IR (thin film, cm^{-1}): 3027, 2953, 1750, 1734, 1454, 1435, 1343, 1260, 1242, 1151, 1017, 846, 750, 700, 521.

HRMS (ESI+): *m/z* for $C_{15}H_{20}BrO_4$ $[M+H]^+$: calc.: 343.0539, found: 343.0538.

Isolation of Compound S-7:



To isolate a significant amount of **S-7**, the reaction was set up 20 times on 0.20 mmol scale. To a glass vial charged with **PC-2** (0.25 mg, 0.0010 mmol, 0.50 mol%) and MeCN (500 µL, 0.4 M) was added alkene **2a** (30.0 µL, 26.4 mg, 0.200 mmol, 1.00 equiv), $LiBF_4$ (18.7 mg, 0.200 mmol, 1.00 equiv), and dimethyl bromomalonate (50.0 µL, 0.380 mmol, 1.90 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 for 2 h. After this time, all 20 reactions were combined in one flask, the solvent was removed *in vacuo* and isolation of **S-7** was achieved by multiple flash column chromatographies (0–20% Et_2O in hexane).

Note: It is crucial that the reaction is not allowed to go to completion. The best yields of **S-7** were achieved by stirring the reaction for 2 h.

Note: The yields shown are determined by ^1H NMR with mesitylene as internal standard.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.32 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 4.26 – 4.20 (m, 1H), 3.77 (s, 6H), 2.94 – 2.90 (m, 2H), 2.90 – 2.85 (m, 1H), 2.80 – 2.72 (m, 1H), 2.19 – 2.14 (m, 2H).

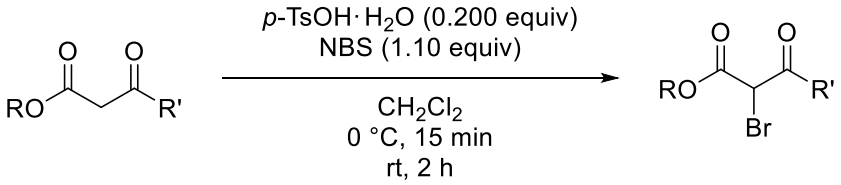
^{13}C NMR (101 MHz, CD_3CN): δ (ppm) = 168.3, 167.2, 141.8, 129.5, 129.5, 127.1, 62.4, 54.9, 54.8, 52.3, 47.1, 41.9, 34.0.

IR (thin film, cm^{-1}): 3027, 2953, 1768, 1749, 1497, 1454, 1435, 1255, 1213, 1177, 1030, 750, 700, 532.

HRMS (ESI+): *m/z* for $C_{15}H_{19}Br_2O_4$ $[M+H]^+$: calc.: 420.9645, found: 420.9645.

13.7 General procedure for the Synthesis of α-Bromo-β-ketoesters

GP3: α-Bromination of β-Ketoesters with *N*-bromosuccinimide

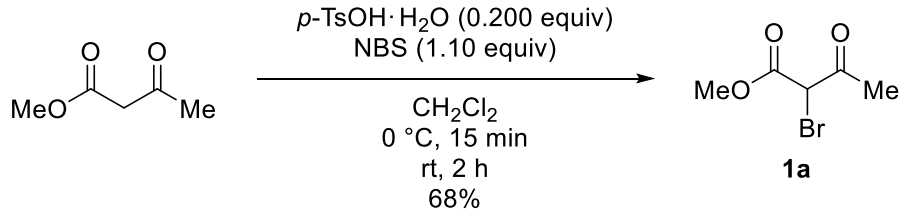


In a 500 mL round-bottom flask, *p*-toluenesulfonic acid monohydrate (761 mg, 4.00 mmol, 0.200 equiv) was added in one portion to a solution of the ketoester starting material (20 mmol, 1.00 equiv) in CH_2Cl_2 (250 mL) . The reaction mixture was cooled to 0 °C and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv) was added in 10 portions over 15 min. The reaction was allowed to warm to room temperature and stirred for 2 h. After complete conversion of starting material, the reaction was quenched with a saturated solution of sodium bicarbonate (100 mL), washed with a saturated solution of sodium thiosulfate (1 x 200 mL), water (2 x 200 mL) and brine (1 x 100 mL). The organic phase was collected, dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified via flash column chromatography with the appropriate eluent to afford the pure bromoketoester.

13.8 Synthesis of α-Bromo-β-ketoesters

Compound 1a:

Methyl 2-bromo-3-oxobutanoate



Bromoketoester **1a** was prepared via GP3, using methyl 3-oxobutanoate (2.16 mL, 2.32 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-50% CH_2Cl_2 in hexane) to give **1a** as a pale-yellow oil.

Yield: 2.65 g, 13.6 mmol, 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.77 (s, 1H), 3.84 (s, 3H), 2.45 (s, 3H).

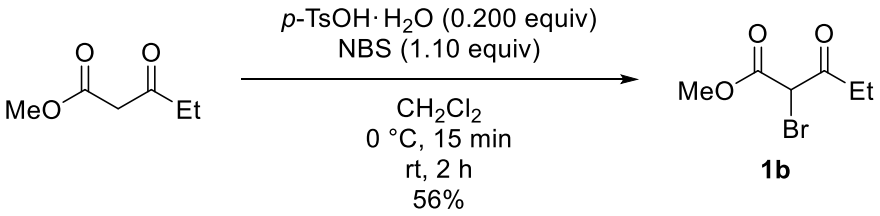
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 196.4, 165.8, 54.0, 48.8, 26.6.

IR (thin film, cm^{-1}): 2959, 1726, 1436, 1360, 1277, 1232, 1145, 1029, 997, 729, 550.

HRMS (ESI+): *m/z* for $C_5H_7BrNaO_3$ $[M+Na]^+$: calc.: 216.9471, found: 216.9468

Compound 1b:

Methyl 2-bromo-3-oxopentanoate



Bromoketoester **1b** was prepared via GP3, using methyl 3-oxopentanoate (2.53 mL, 2.60 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-40% CH_2Cl_2 in hexane) to give **1b** as a pale-yellow oil.

Yield: 2.31 g, 11.1 mmol, 56%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.80 (s, 1H), 3.80 (s, 3H), 2.77 (qd, *J* = 7.2, 0.7 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

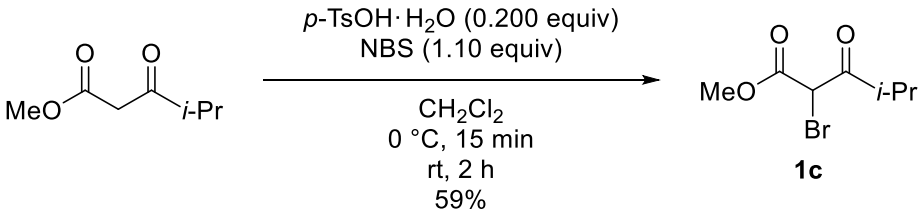
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 199.4, 165.9, 53.9, 48.3, 32.8, 8.1.

IR (thin film, cm^{-1}): 2982, 2957, 1723, 1436, 1301, 1274, 1216, 1144, 1068, 1003, 981, 900, 710, 605.

HRMS (ESI+): *m/z* for $C_6H_9BrNaO_3$ $[M+Na]^+$: calc.: 230.9627, found: 230.9627

Compound 1c:

Methyl 2-bromo-4-methyl-3-oxopentanoate



Bromoketoester **1c** was prepared via GP3, using methyl 4-methyl-3-oxopentanoate (2.85 mL, 2.88 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-40% CH_2Cl_2 in hexane) to give **1c** as a pale-yellow oil.

Yield: 2.59 g, 11.7 mmol, 59%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.96 (s, 1H), 3.82 (s, 3H), 3.11 (hept, *J* = 6.9 Hz, 1H), 1.19 (dd, *J* = 11.3, 6.9 Hz, 6H).

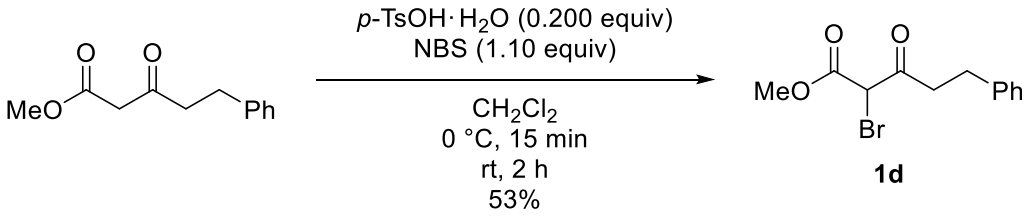
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 202.4, 165.8, 53.9, 47.5, 38.4, 19.3, 18.8.

IR (thin film, cm^{-1}): 2976, 2877, 1761, 1717, 1466, 1436, 1299, 1278, 1219, 1096, 1032, 995, 760, 737, 619.

HRMS (ESI+): *m/z* for $C_7H_{11}BrNaO_3$ $[M+Na]^+$: calc.: 244.9784, found: 244.9787

Compound 1d:

Methyl 2-bromo-3-oxo-5-phenylpentanoate



Bromoketoester **1d** was prepared via GP3, using methyl 3-oxo-5-phenylpentanoate[19] (5.70 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-30% CH_2Cl_2 in hexane) to give **1d** as a pale-yellow oil.

Yield: 3.00 g, 10.6 mmol, 53%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.35 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.77 (s, 1H), 3.78 (s, 3H), 3.09 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H).

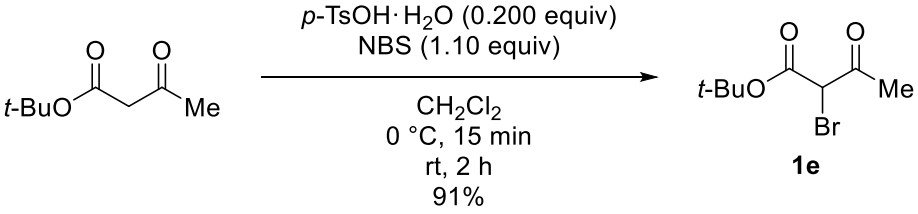
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 197.9, 165.7, 140.2, 128.7, 128.5, 126.5, 53.9, 48.6, 40.9, 30.0.

IR (thin film, cm^{-1}): 3028, 2955, 1721, 1603, 1497, 1454, 1438, 1273, 1151, 1072, 989, 747, 699, 553.

HRMS (ESI+): *m/z* for $C_{12}H_{13}BrNaO_3$ $[M+Na]^+$: calc.: 306.9940, found: 306.9943

Compound 1e:

***tert*-Butyl 2-bromo-3-oxobutanoate**



Bromoketoester **1e** was prepared via GP3, using *tert*-butyl 3-oxobutanoate (3.29 mL, 3.16 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-40% CH_2Cl_2 in hexane) to give **1e** as a pale-yellow oil.

Yield: 4.30 g, 18.2 mmol, 91%

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.67 (s, 1H), 2.42 (s, 3H), 1.49 (s, 9H).

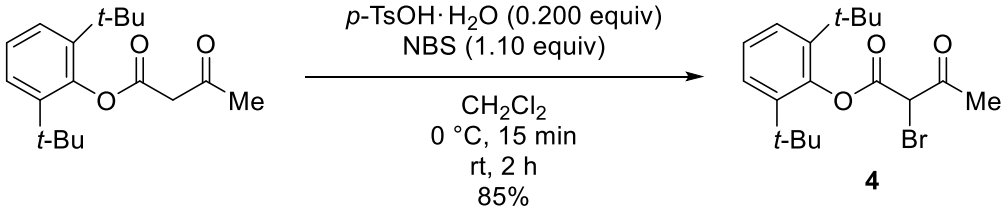
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 196.8, 164.1, 84.6, 50.8, 27.9, 26.4.

IR (thin film, cm^{-1}): 2981, 2936, 1722, 1370, 1359, 1285, 1257, 1132, 846, 845, 780, 752, 550.

HRMS (ESI+): *m/z* for $C_8H_{13}BrNaO_3$ $[M+Na]^+$: calc.: 258.9940, found: 258.9938

Compound 4:

2,6-Di-*tert*-butylphenyl 2-bromo-3-oxobutanoate



4

Bromoketoester **4** was prepared via GP3, using 2,6-di-*tert*-butylphenyl 3-oxobutanoate[20] (7.39 g, 20.0 mmol, 1.00 equiv) and *N*-bromosuccinimide (3.92 g, 22.0 mmol, 1.10 equiv). The crude product was purified via column chromatography (0-30% CH_2Cl_2 in hexane) to give **4** as a pale-yellow oil.

Yield: 6.27 g, 17.0 mmol, 85%

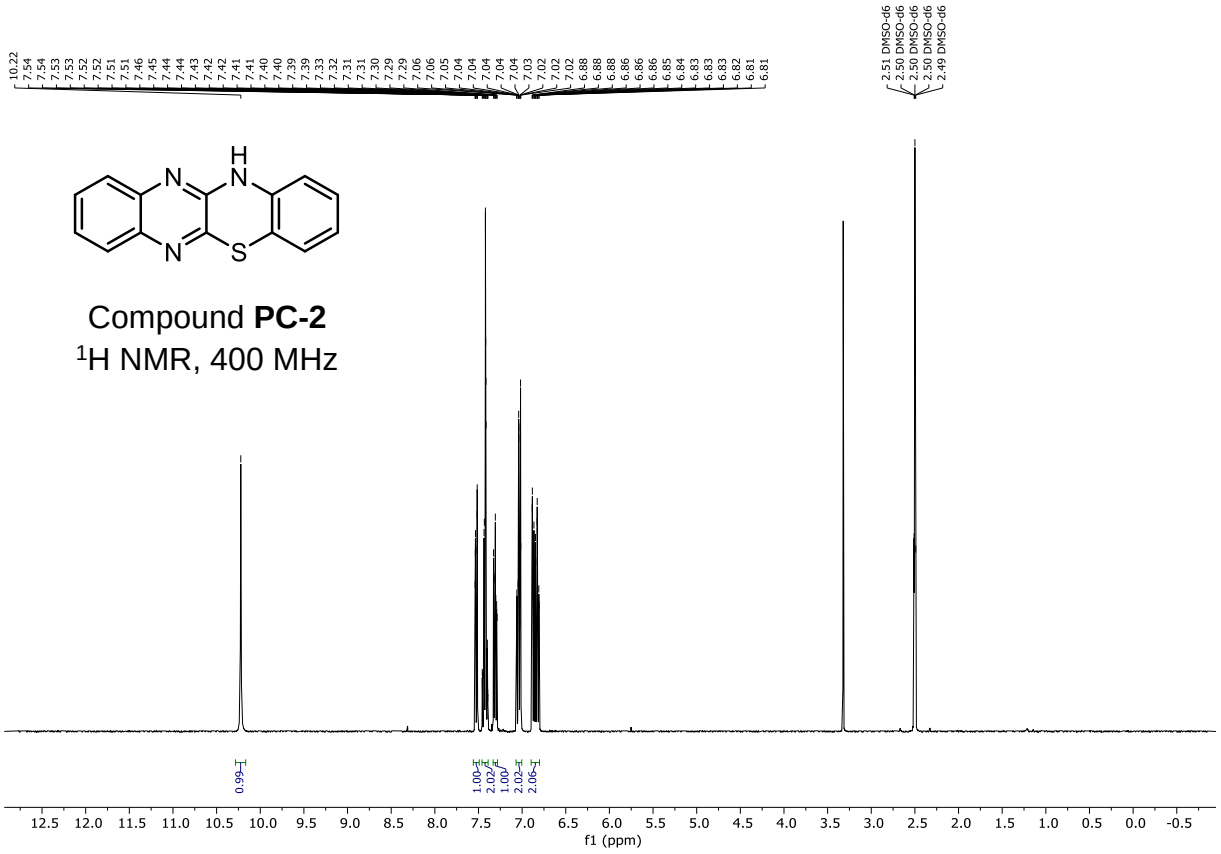
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 12.71 (d, *J* = 0.8 Hz, $1H_{enol}$), 7.34 (d, *J* = 7.7 Hz, 2H), 7.18 (dd, *J* = 8.3, 7.4 Hz, 1H), 5.00 (s, $1H_{keto}$), 2.56 (s, $3H_{keto}$), 2.35 (d, *J* = 0.8 Hz, $3H_{enol}$), 1.35 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 176.5, 170.5, 147.5, 142.6, 126.4, 126.2, 85.1, 35.5, 31.6, 22.6.

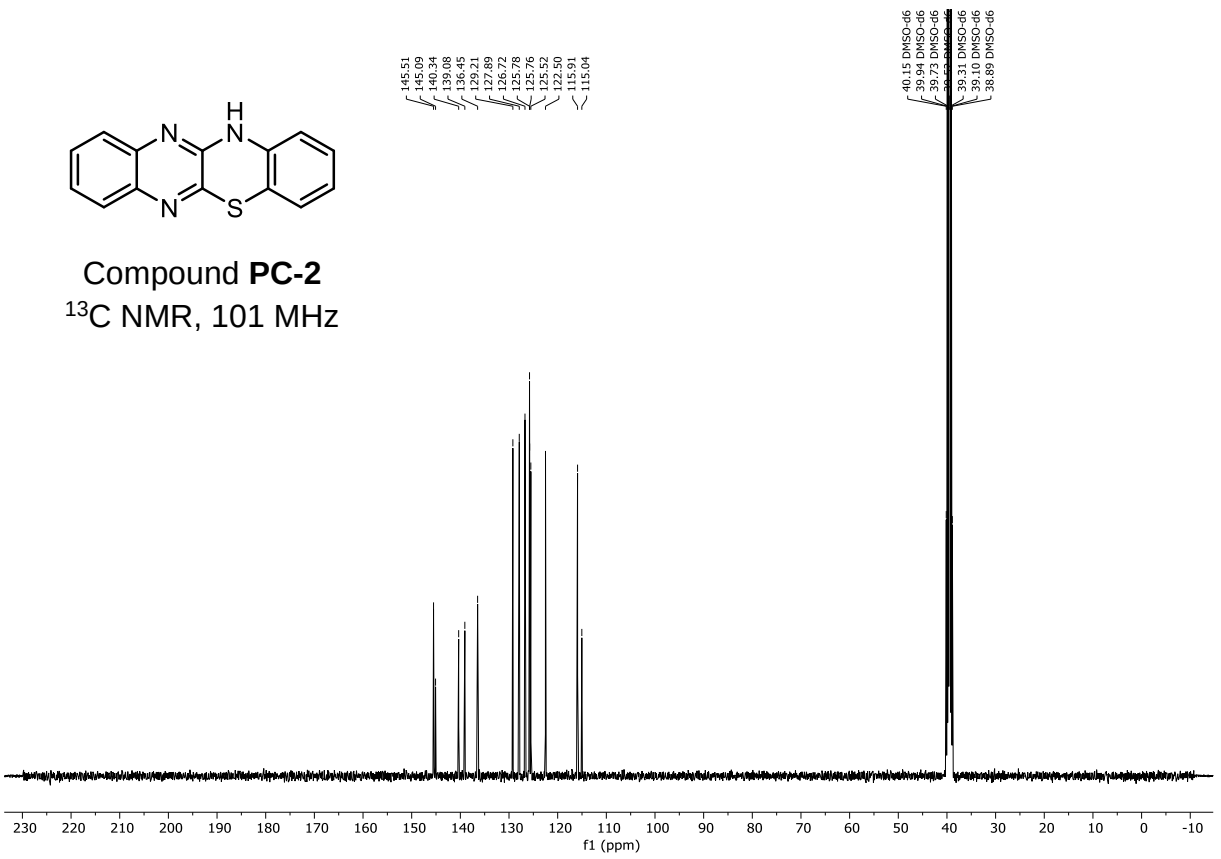
IR (thin film, cm^{-1}): 2963, 2874, 1726, 1601, 1414, 1338, 1236, 1179, 1103,1024, 951, 883, 844, 789, 732, 514.

HRMS (ESI+): *m/z* for $C_{18}H_{25}BrNaO_3$ $[M+Na]^+$: calc.: 391.0879, found: 391.0887

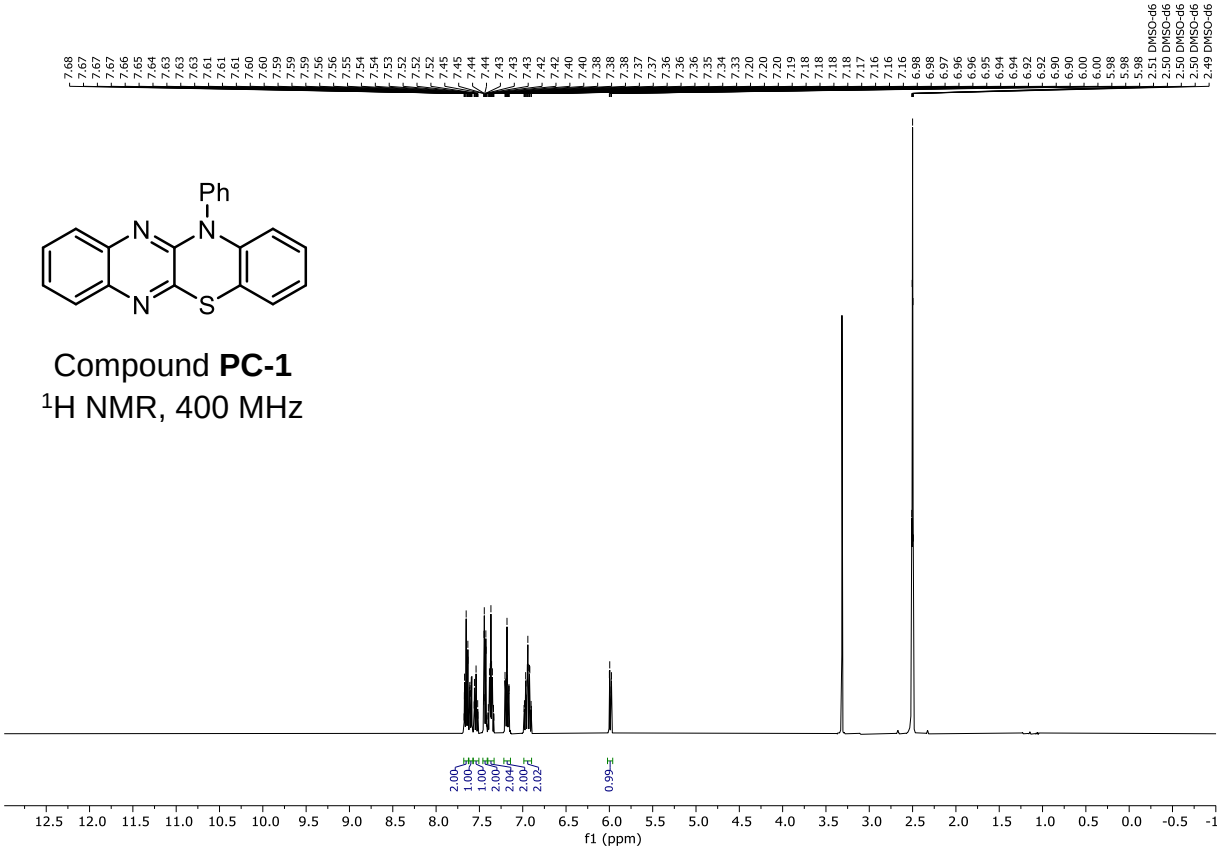
14. ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR Spectra



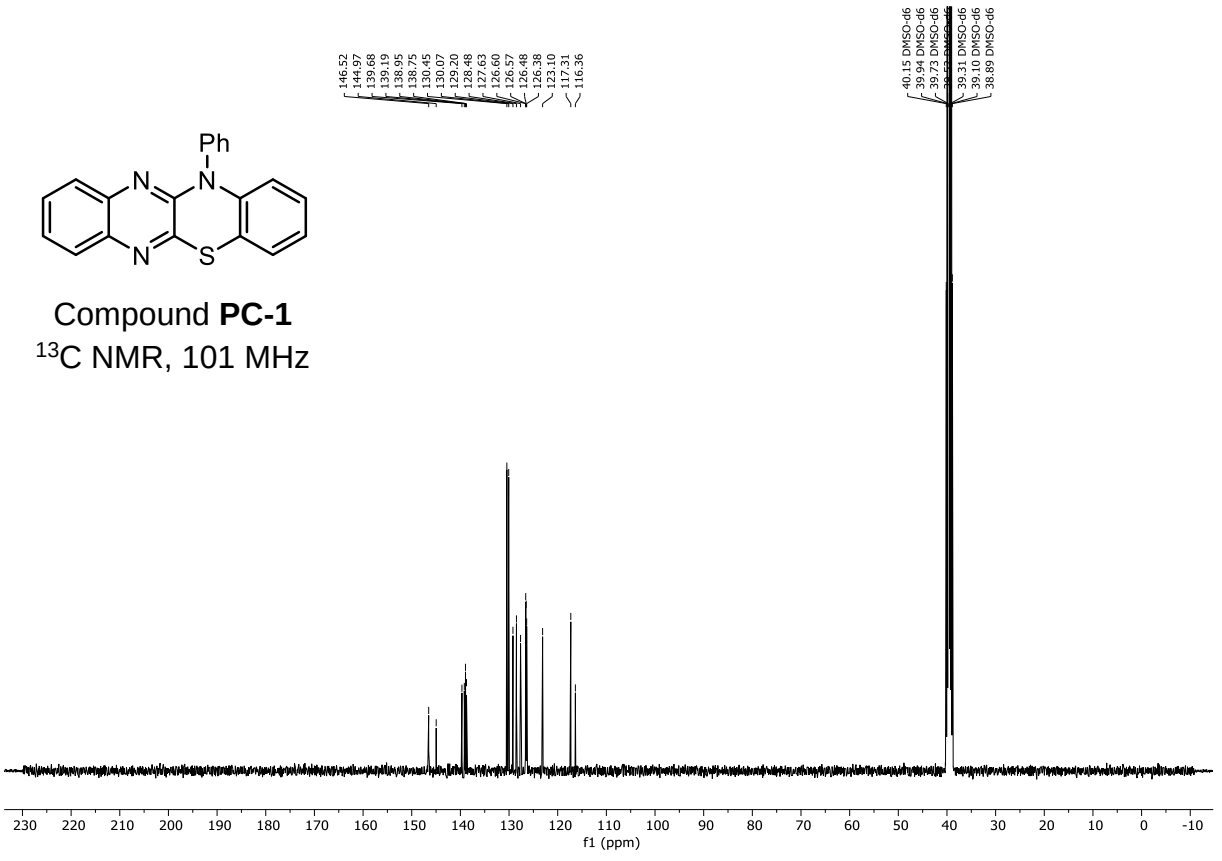
Compound **PC-2**
^{1}H NMR, 400 MHz



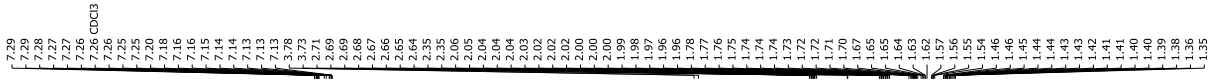
Compound **PC-2**
^{13}C NMR, 101 MHz

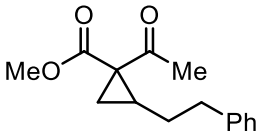


Compound **PC-1**
^{1}H NMR, 400 MHz

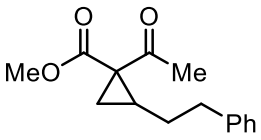


Compound **PC-1**
^{13}C NMR, 101 MHz

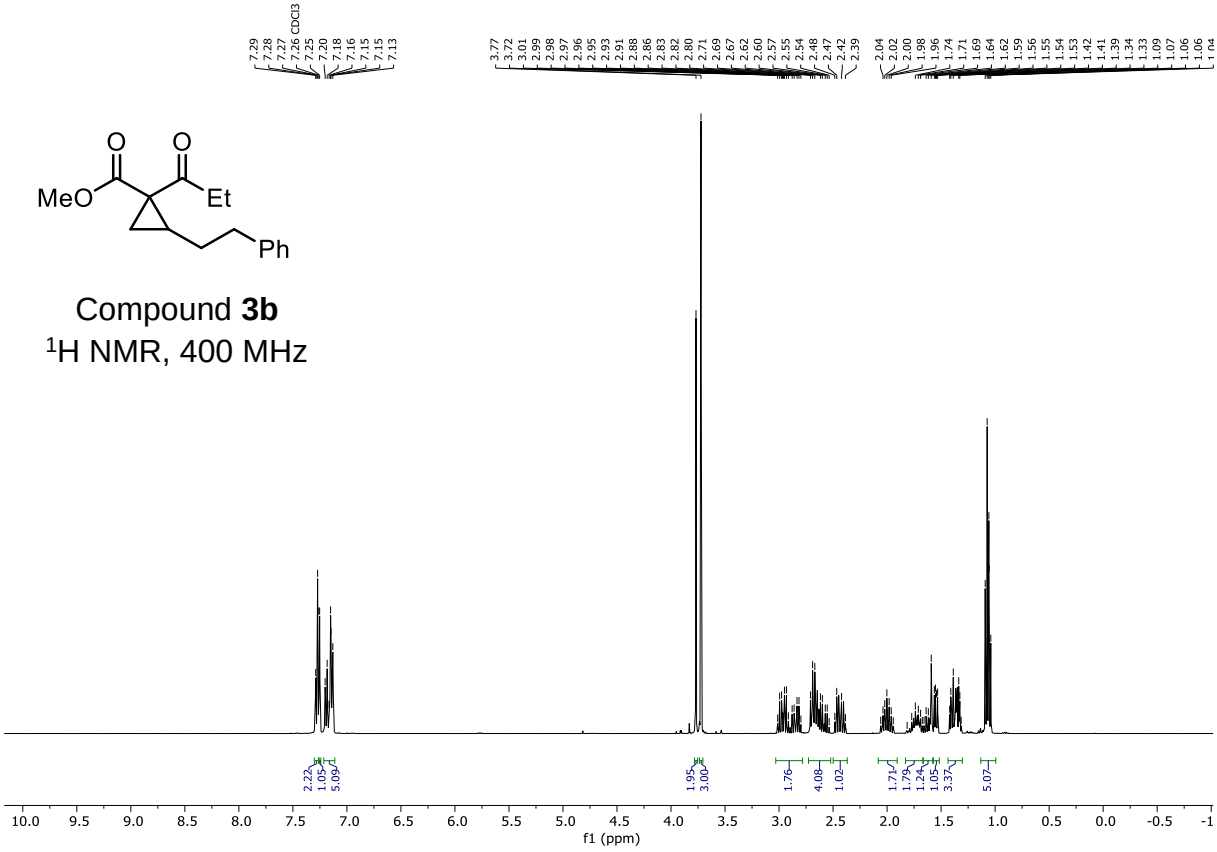




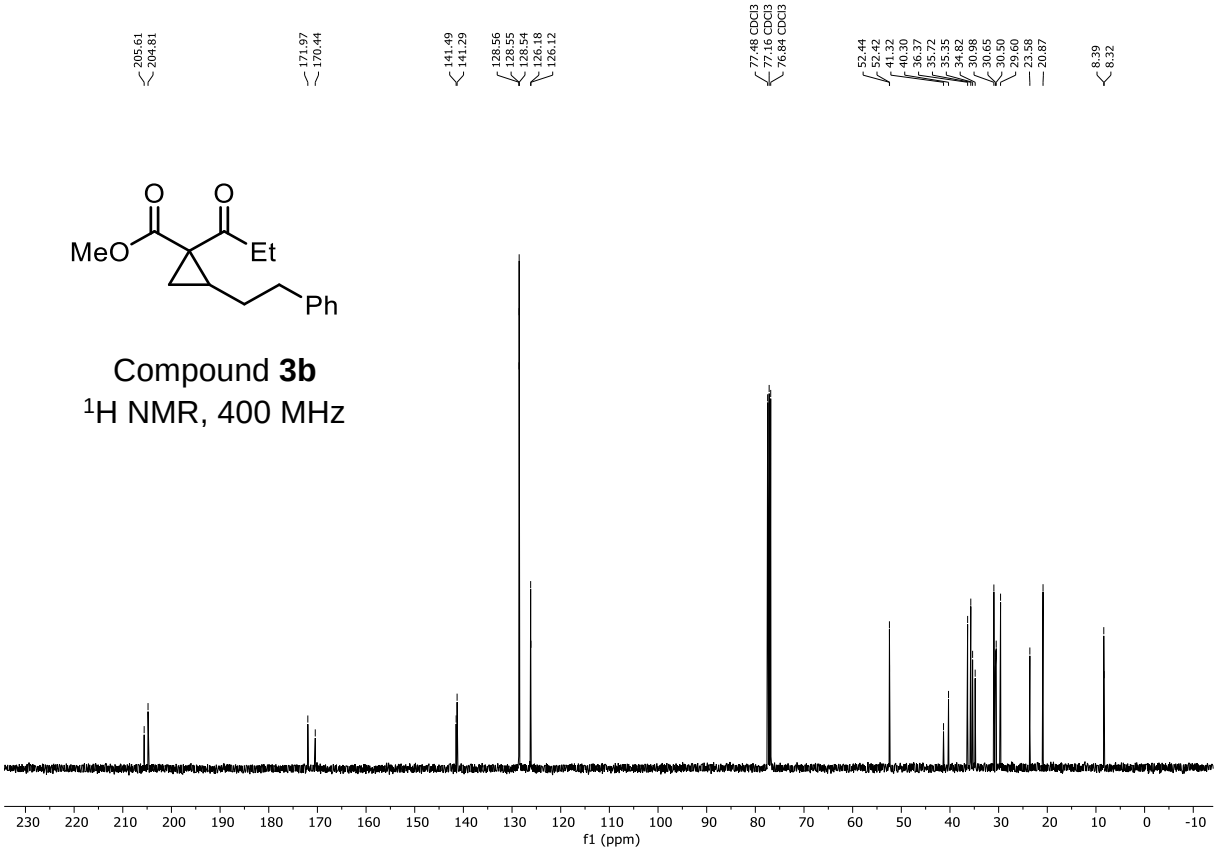
Compound **3a**
^{1}H NMR, 400 MHz



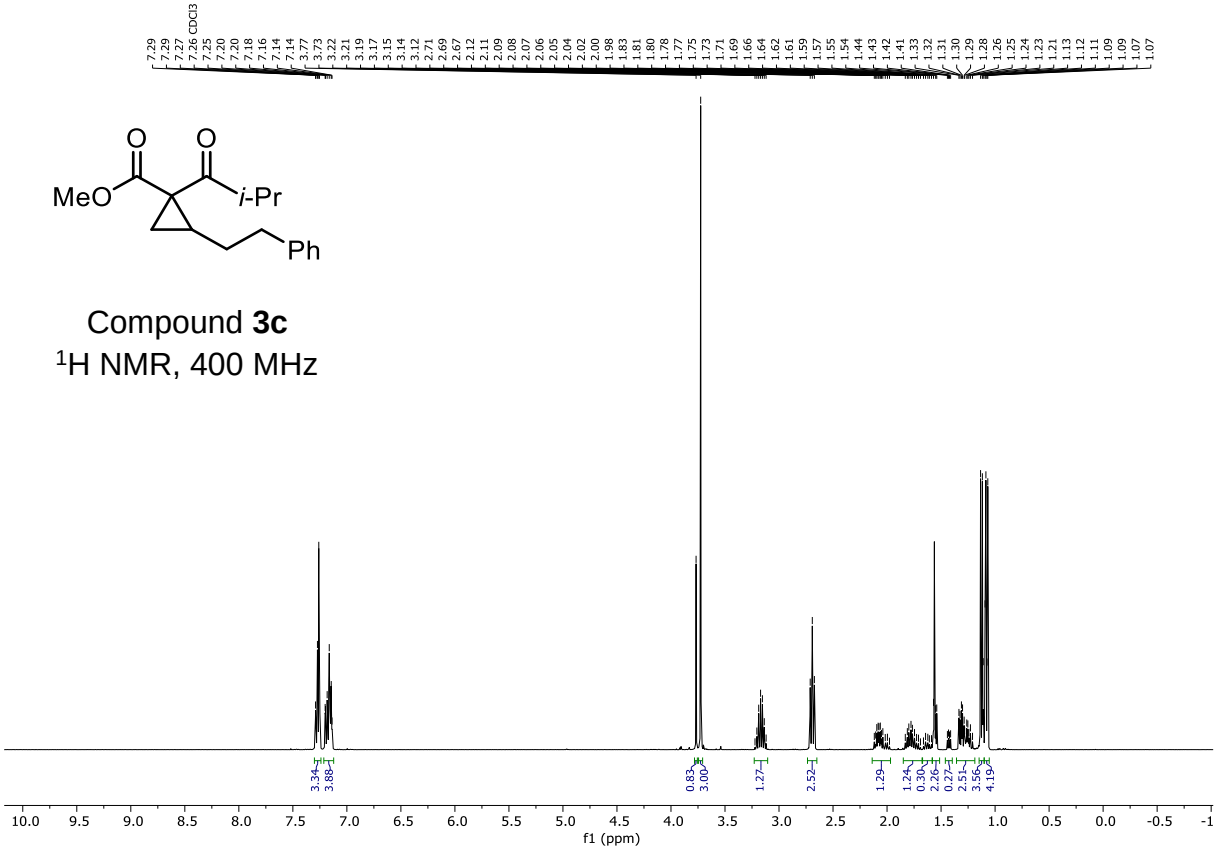
Compound **3a**
^{13}C NMR, 101 MHz



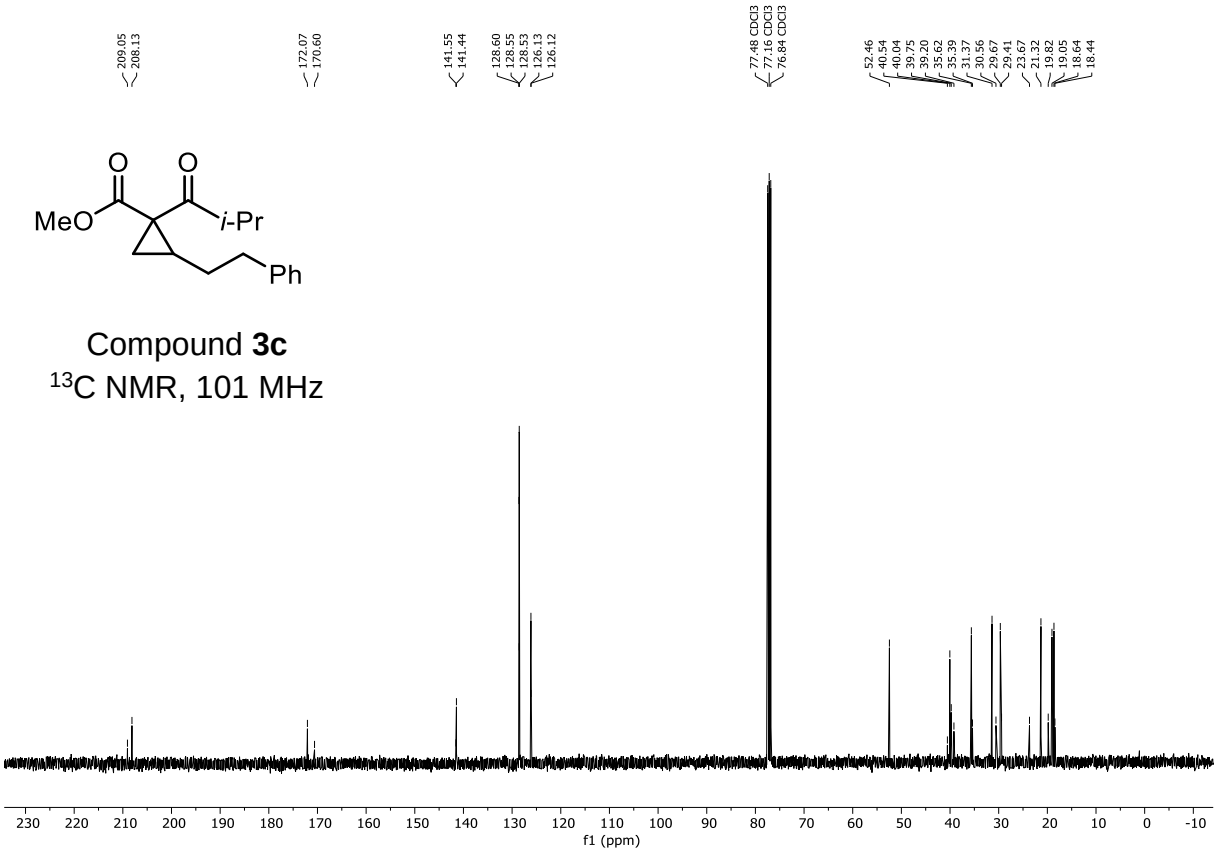
Compound **3b**
^{1}H NMR, 400 MHz



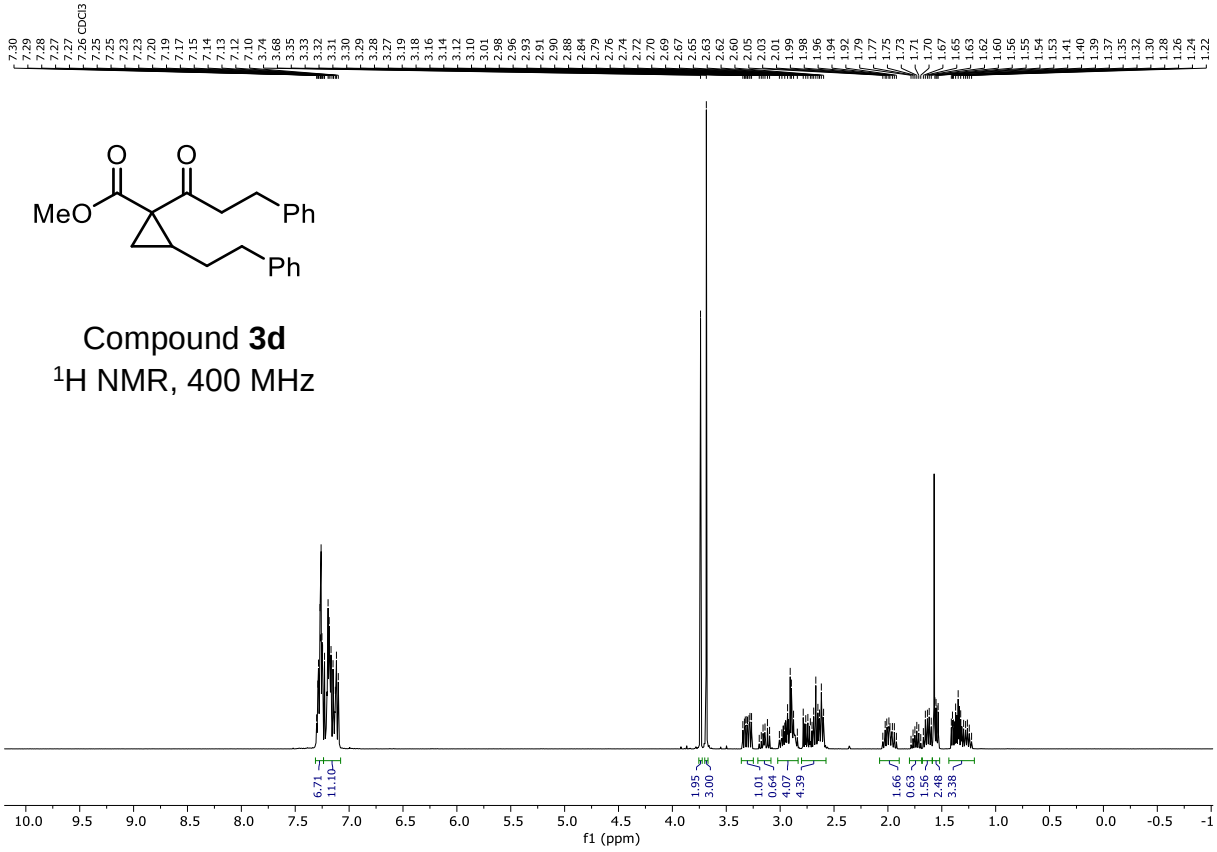
Compound **3b**
^{1}H NMR, 400 MHz



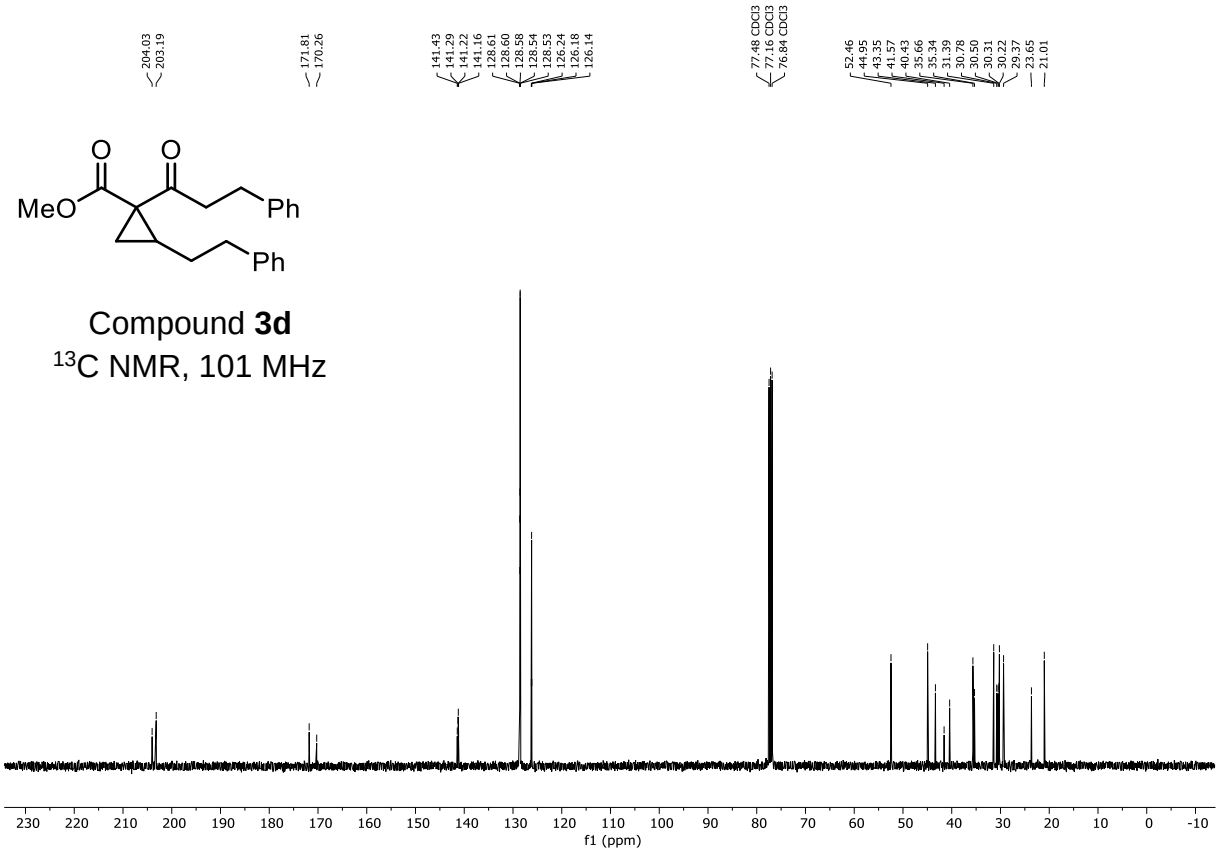
Compound **3c**
^{1}H NMR, 400 MHz



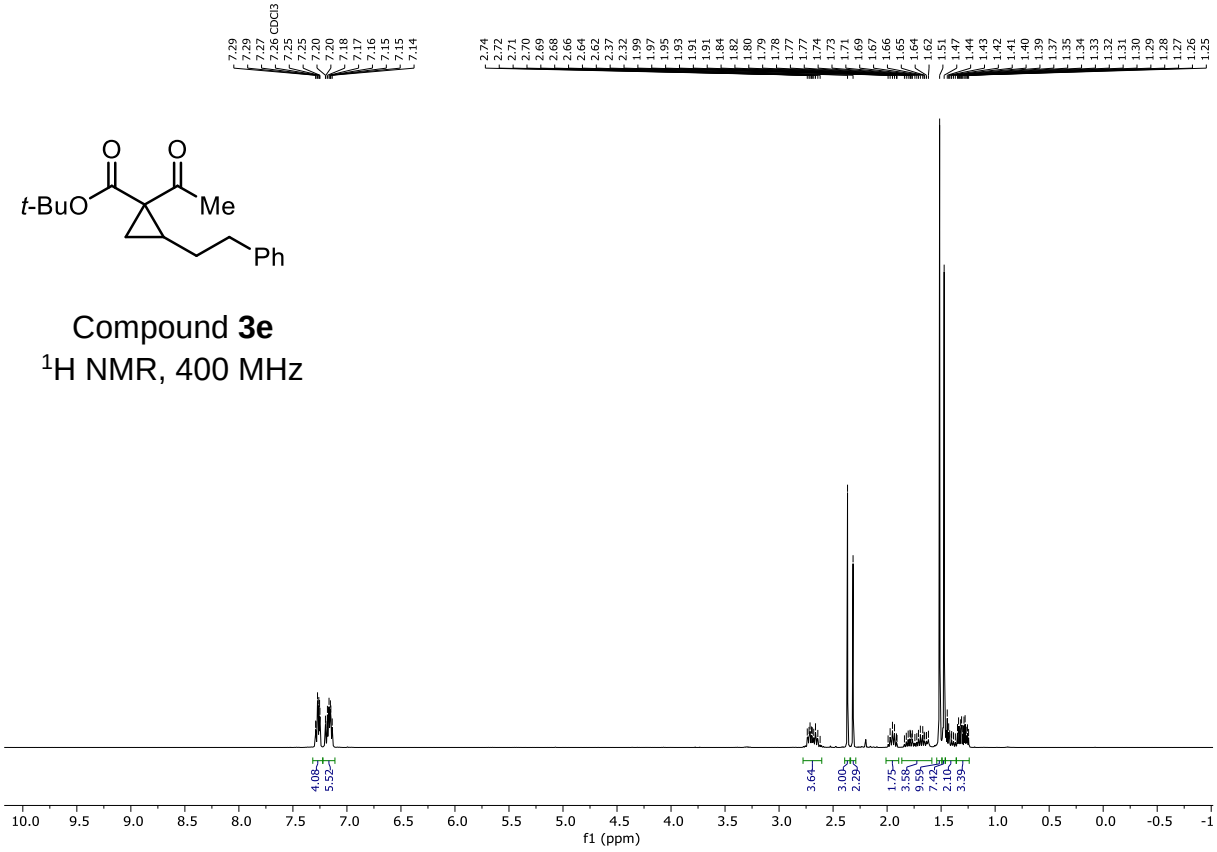
Compound **3c**
^{13}C NMR, 101 MHz



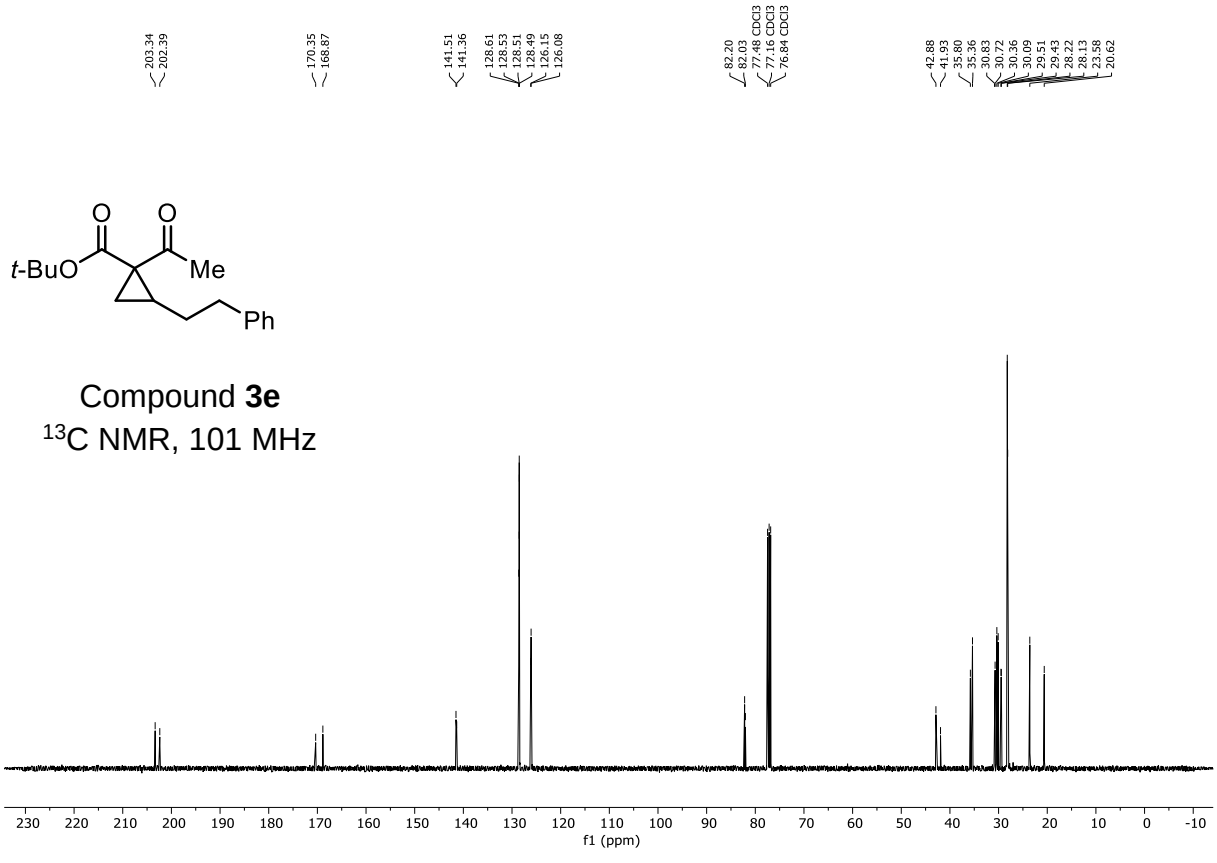
Compound **3d**
^{1}H NMR, 400 MHz



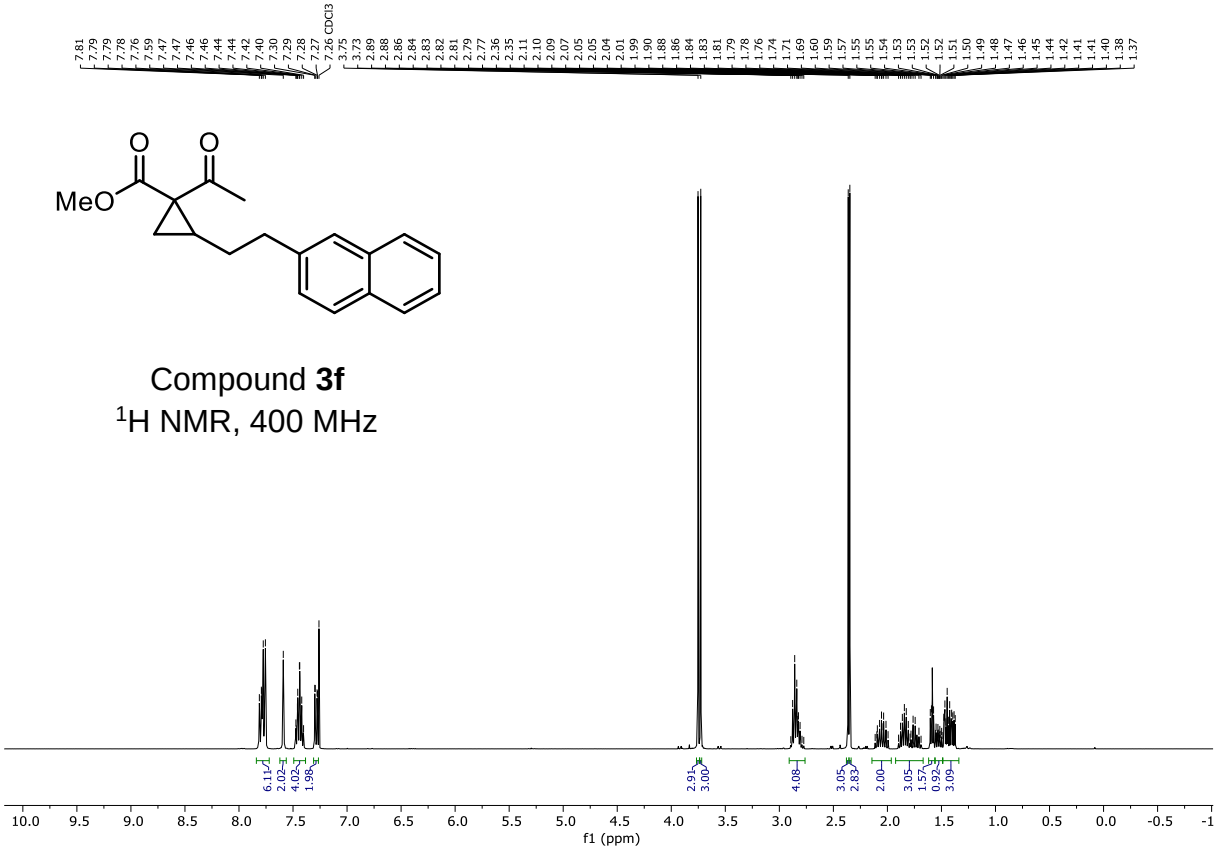
Compound **3d**
^{13}C NMR, 101 MHz



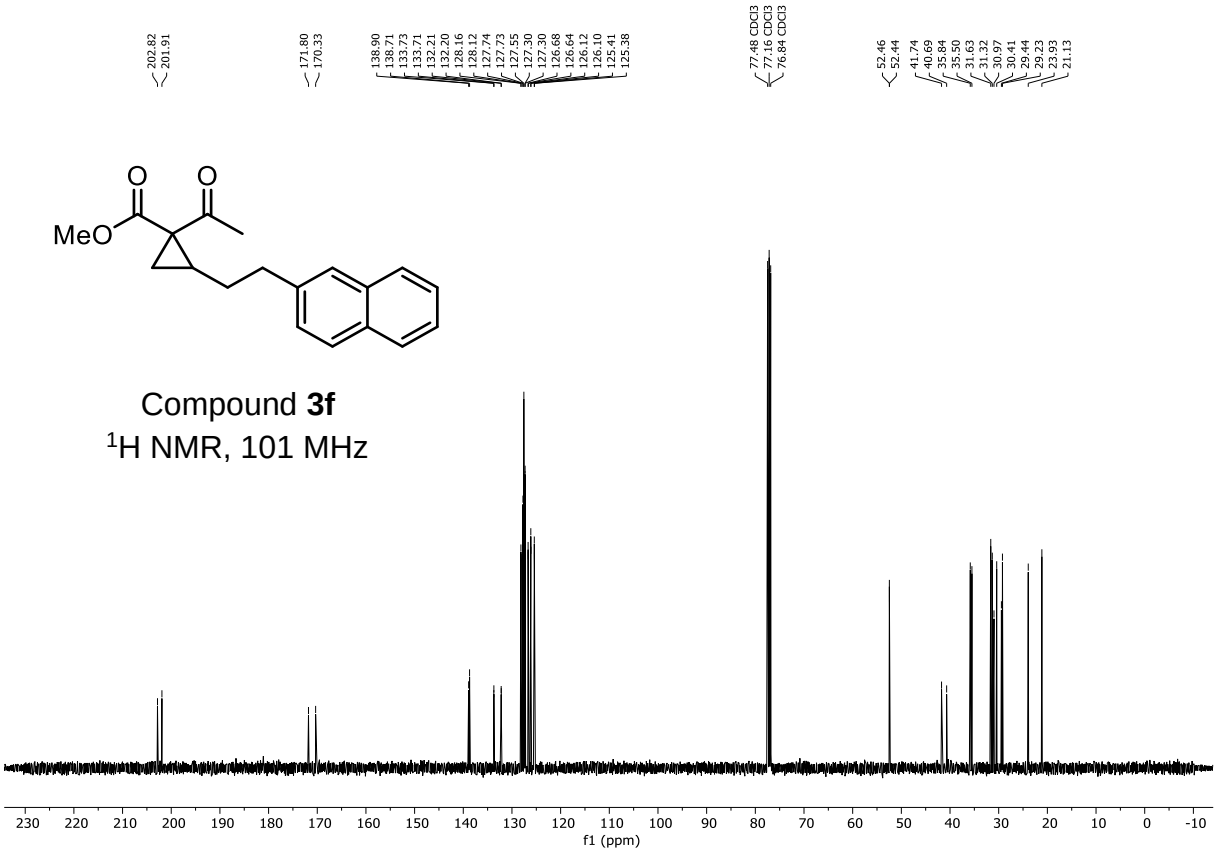
Compound **3e**
^{1}H NMR, 400 MHz



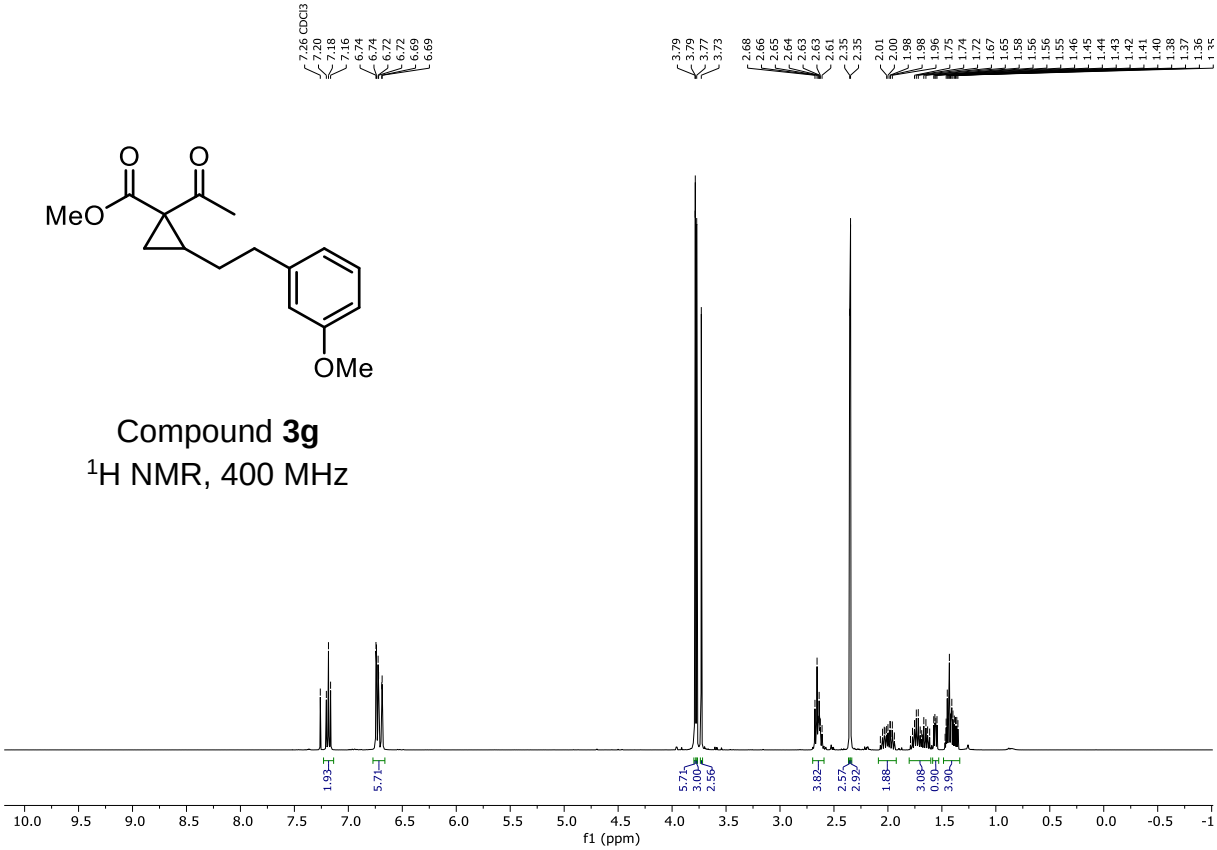
Compound **3e**
^{13}C NMR, 101 MHz



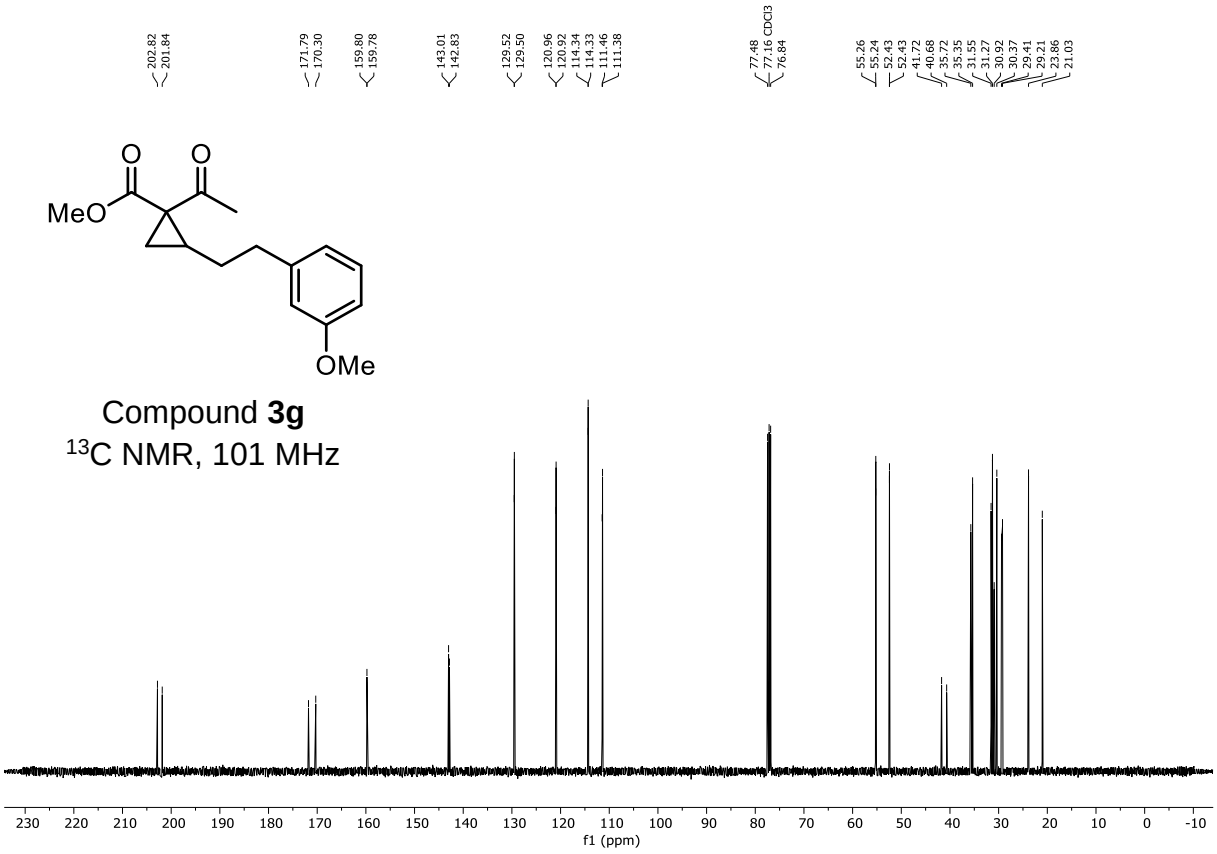
Compound **3f**
^{1}H NMR, 400 MHz



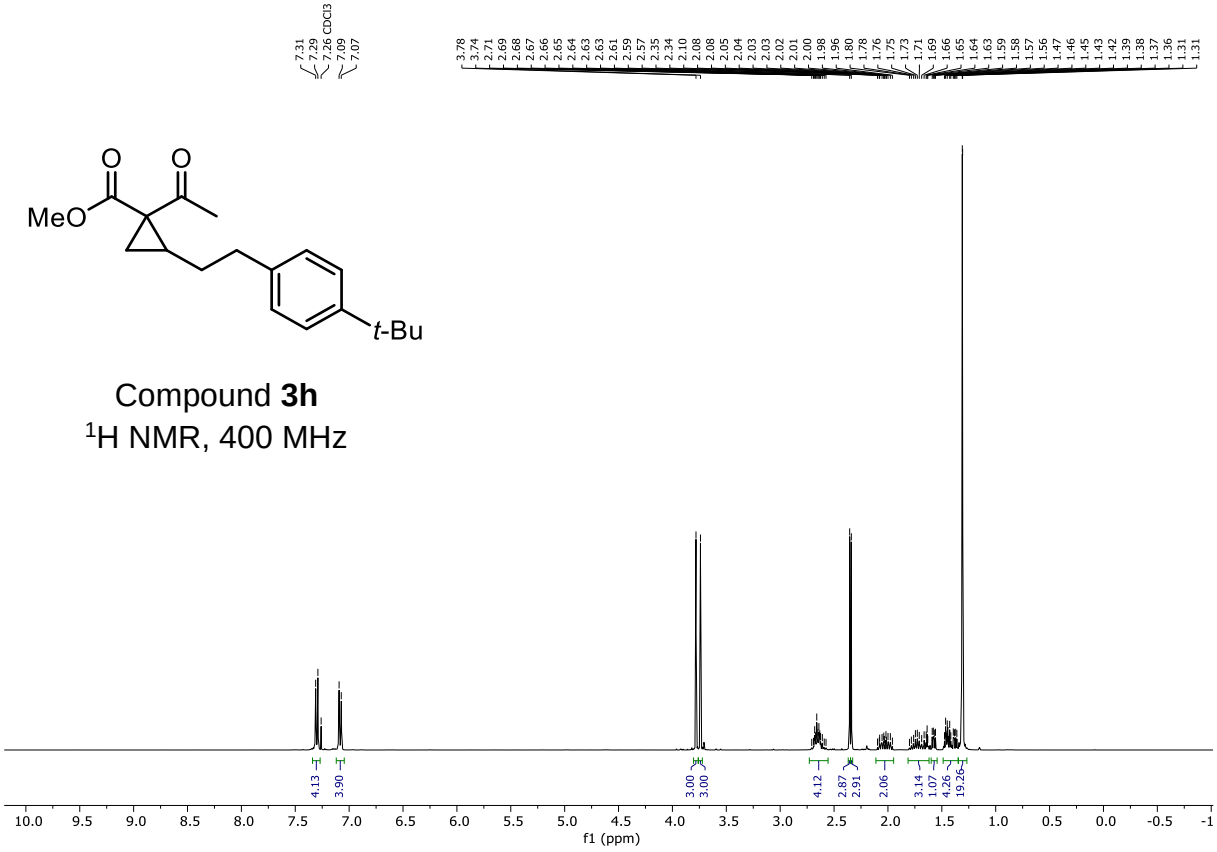
Compound **3f**
^{1}H NMR, 101 MHz



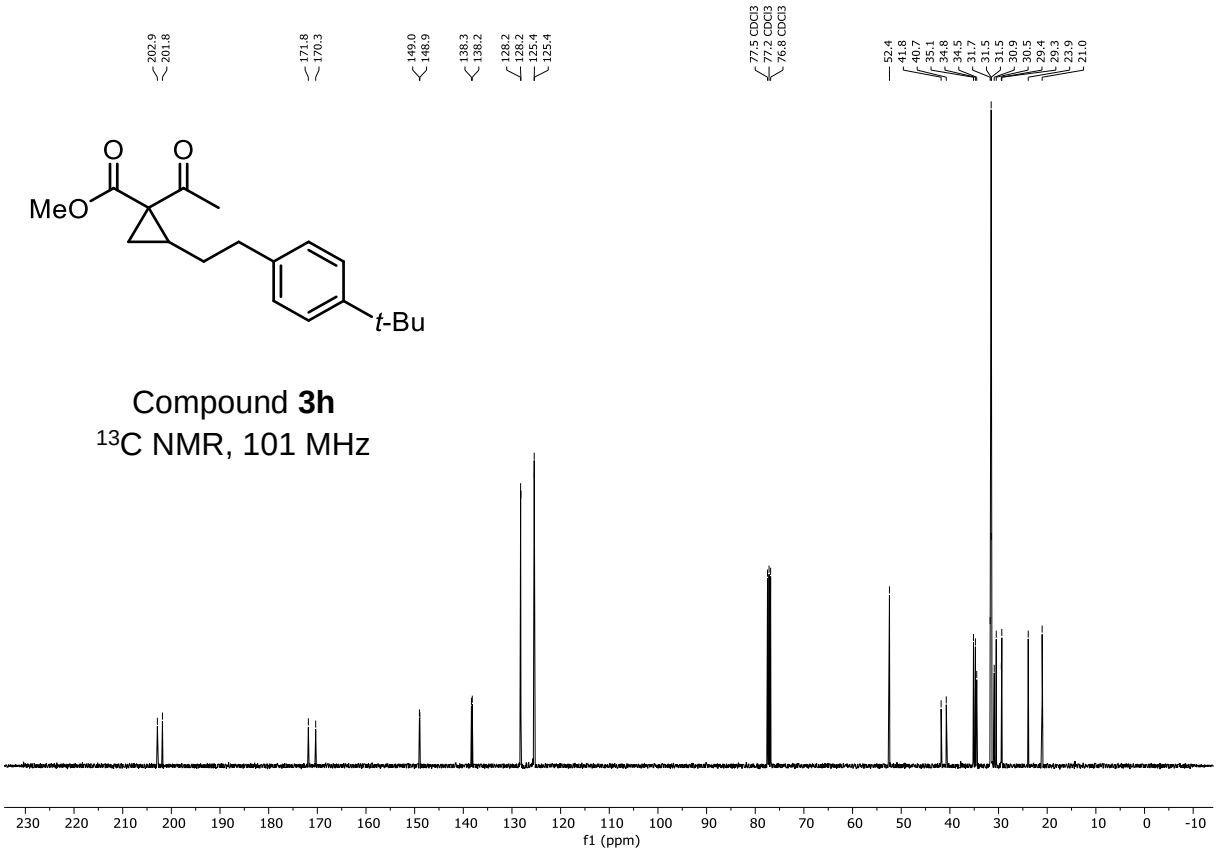
Compound **3g**
^{1}H NMR, 400 MHz



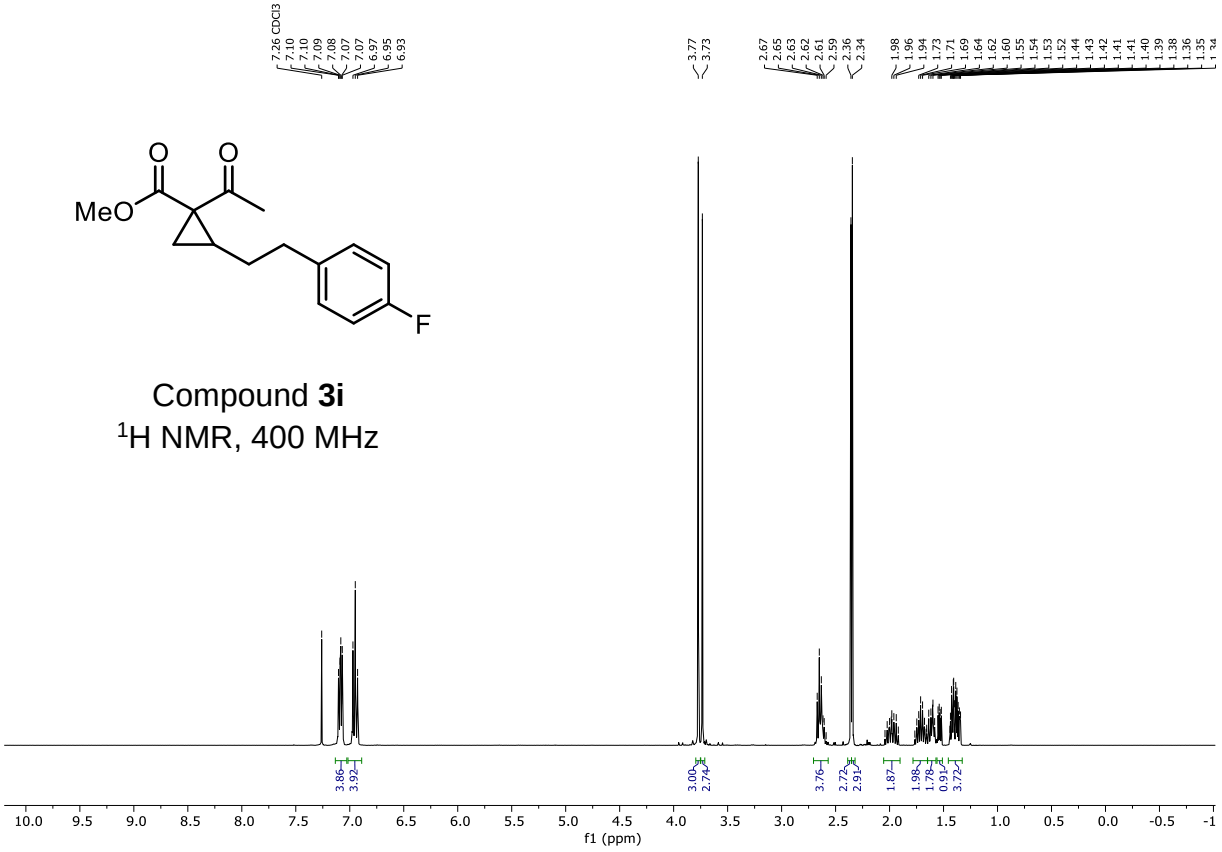
Compound **3g**
^{13}C NMR, 101 MHz



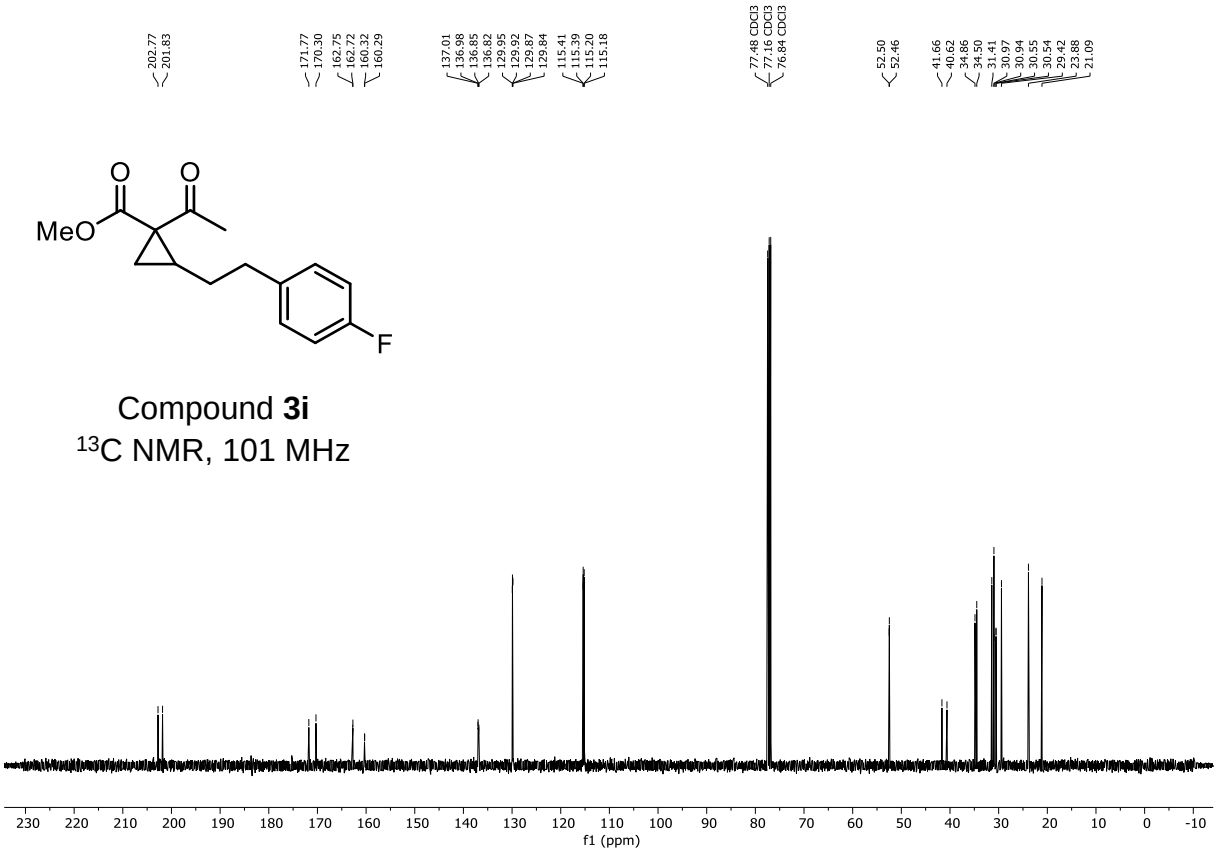
Compound **3h**
^{1}H NMR, 400 MHz



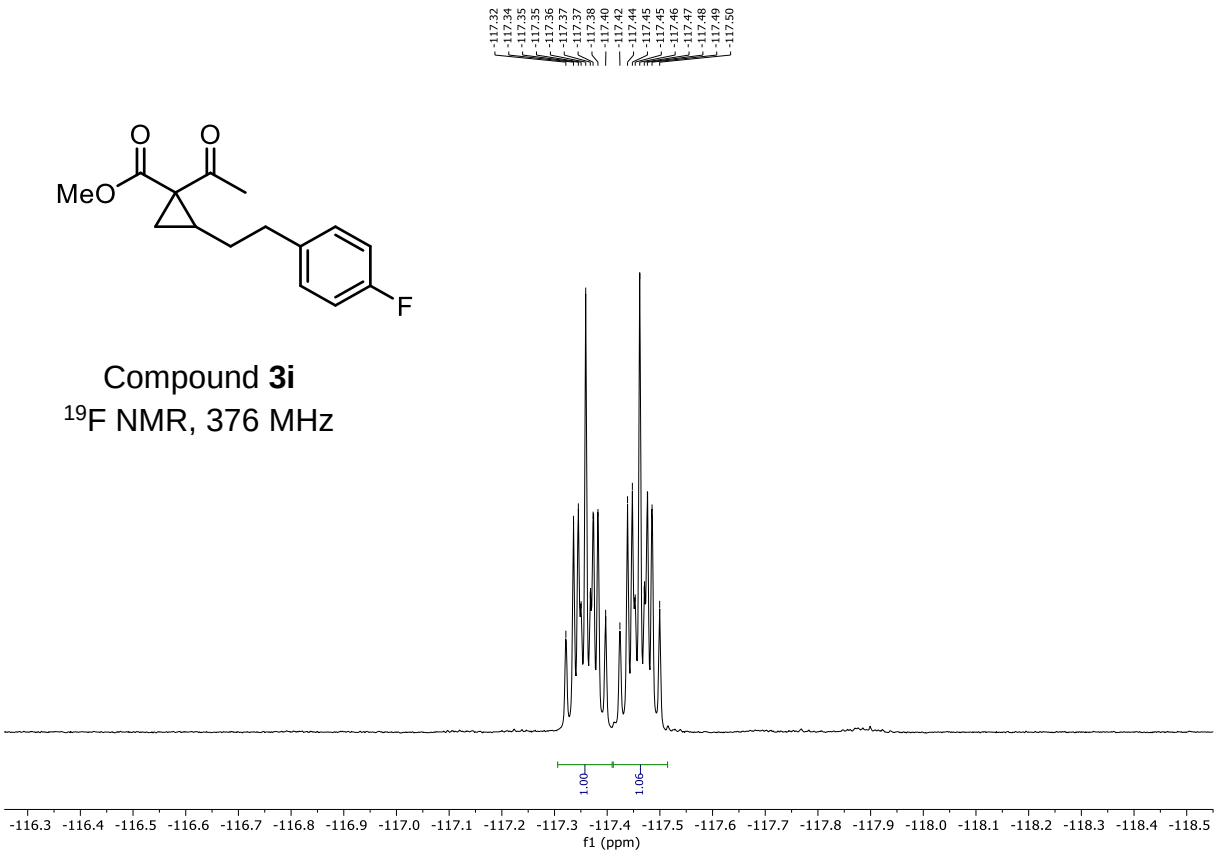
Compound **3h**
^{13}C NMR, 101 MHz



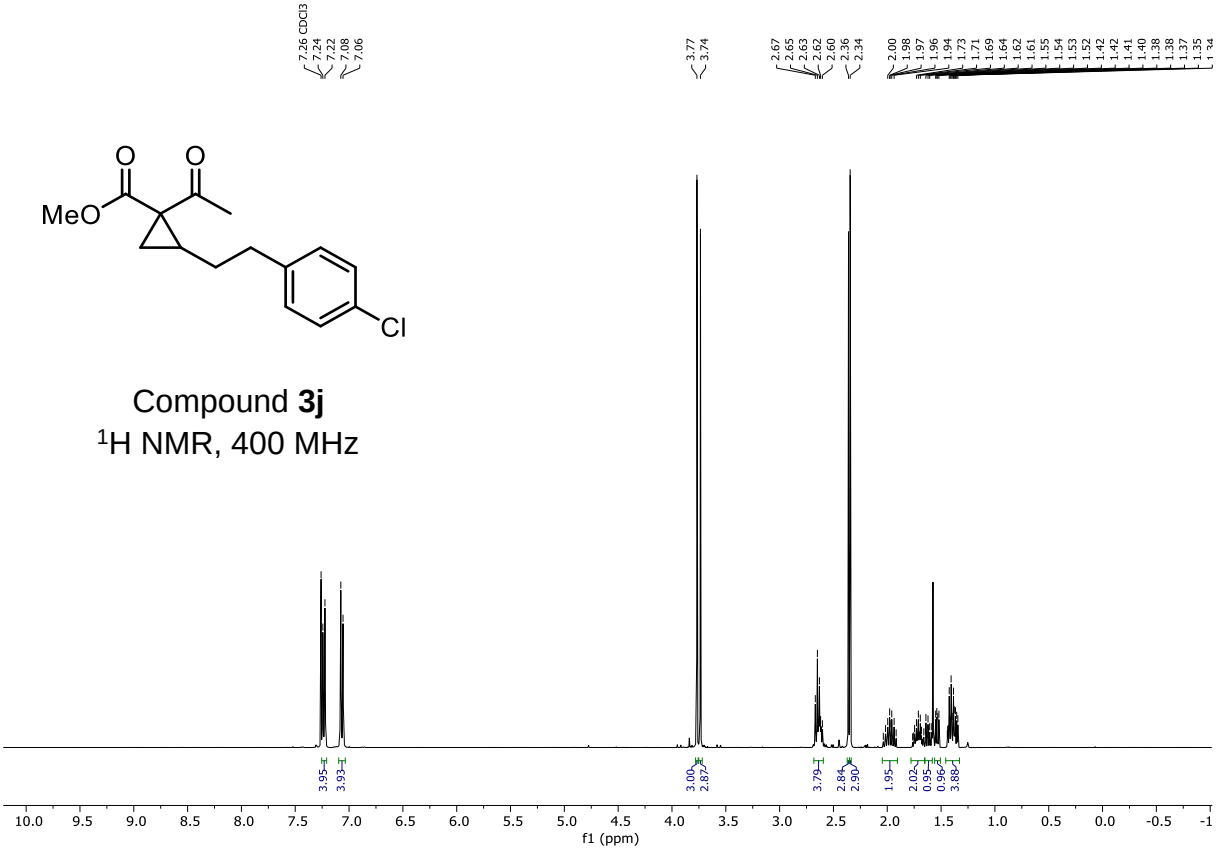
Compound **3i**
^{1}H NMR, 400 MHz



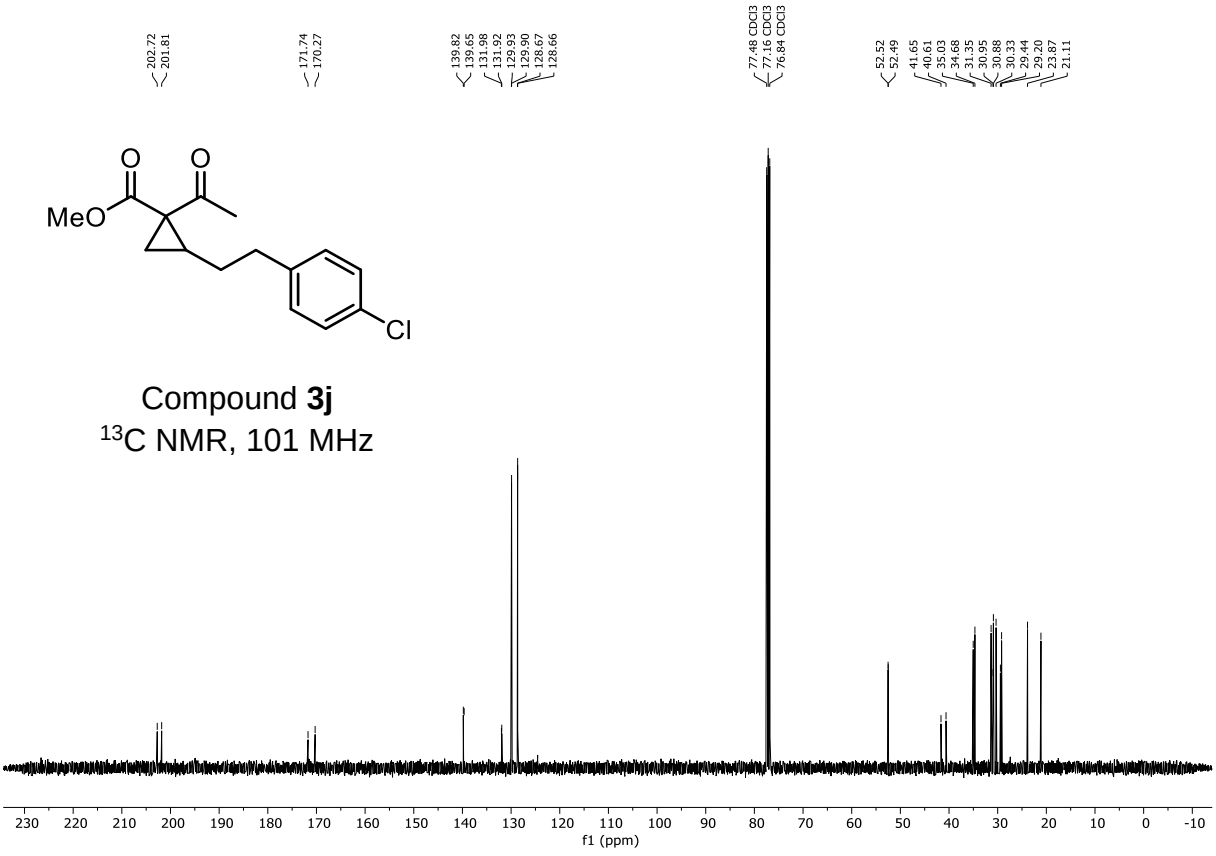
Compound **3i**
^{13}C NMR, 101 MHz



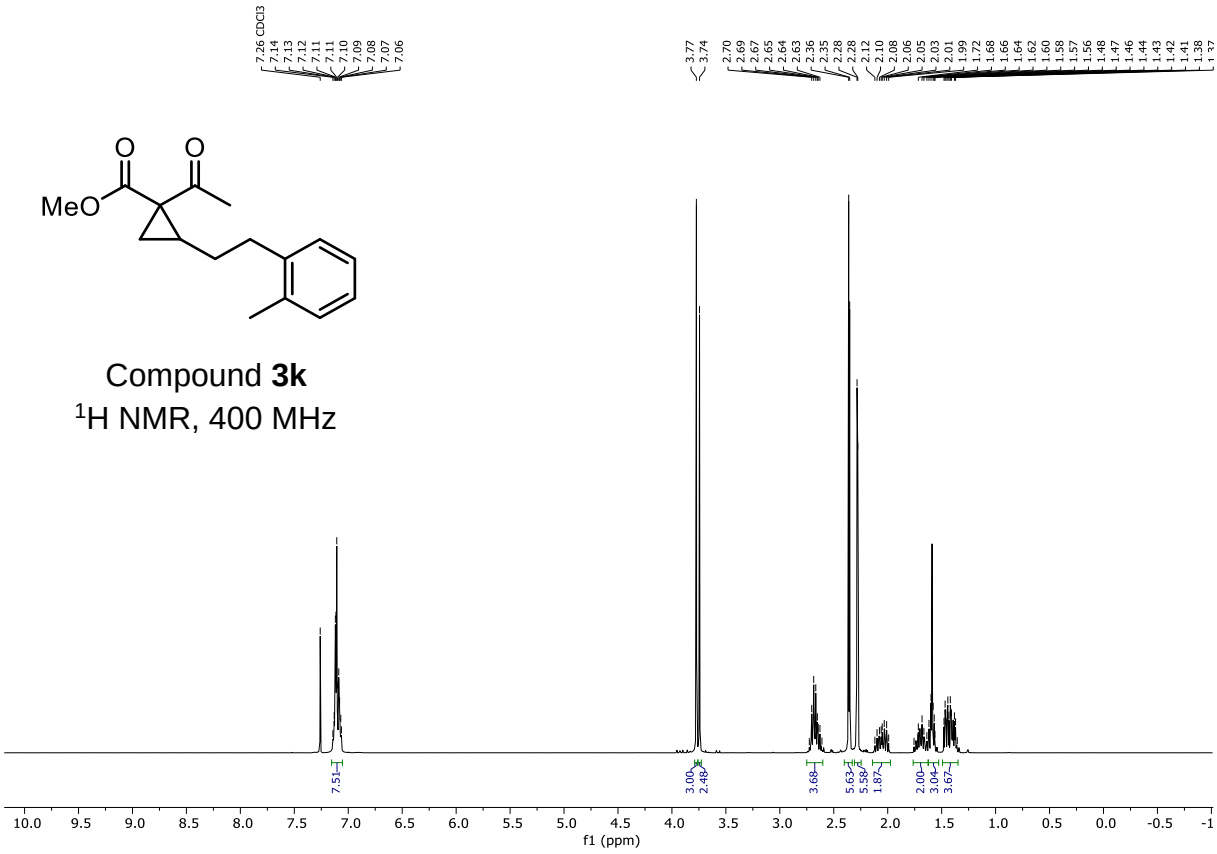
Compound **3i**
^{19}F NMR, 376 MHz



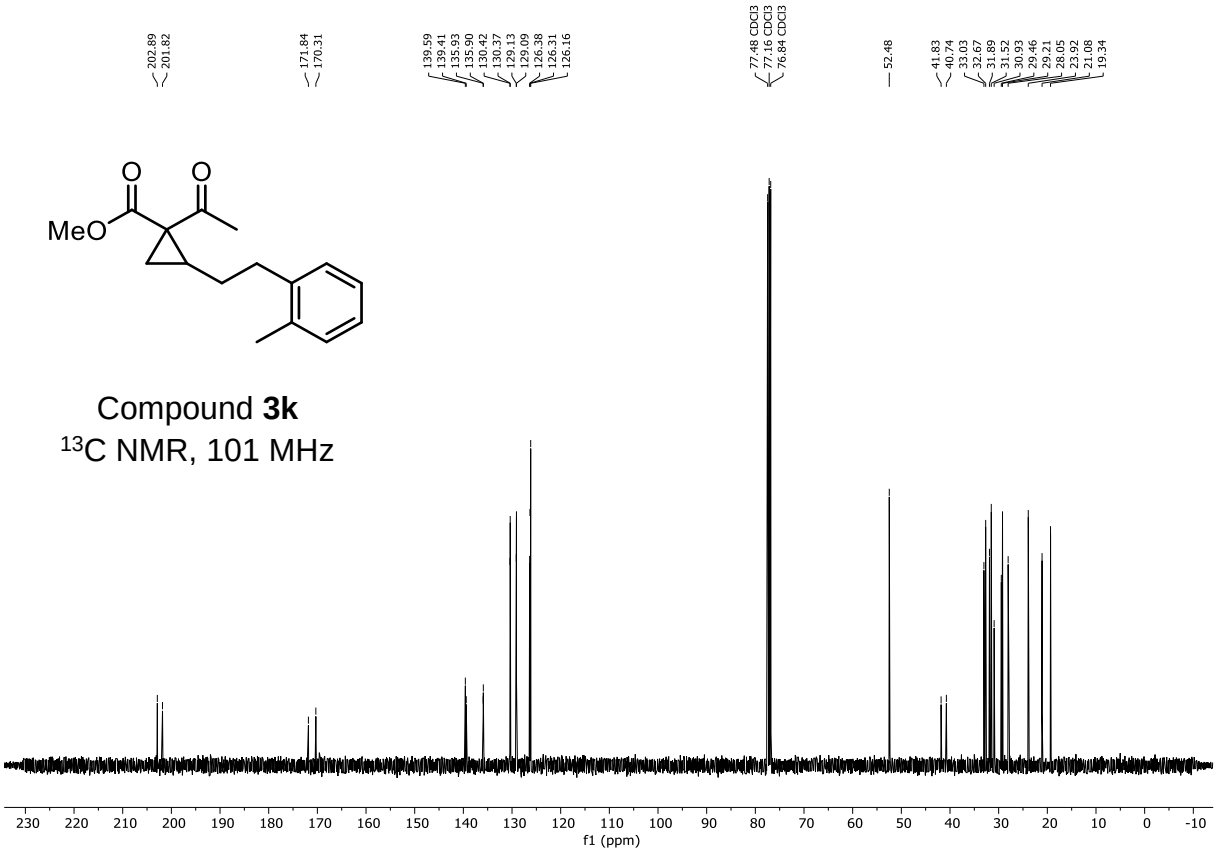
Compound **3j**
^{1}H NMR, 400 MHz



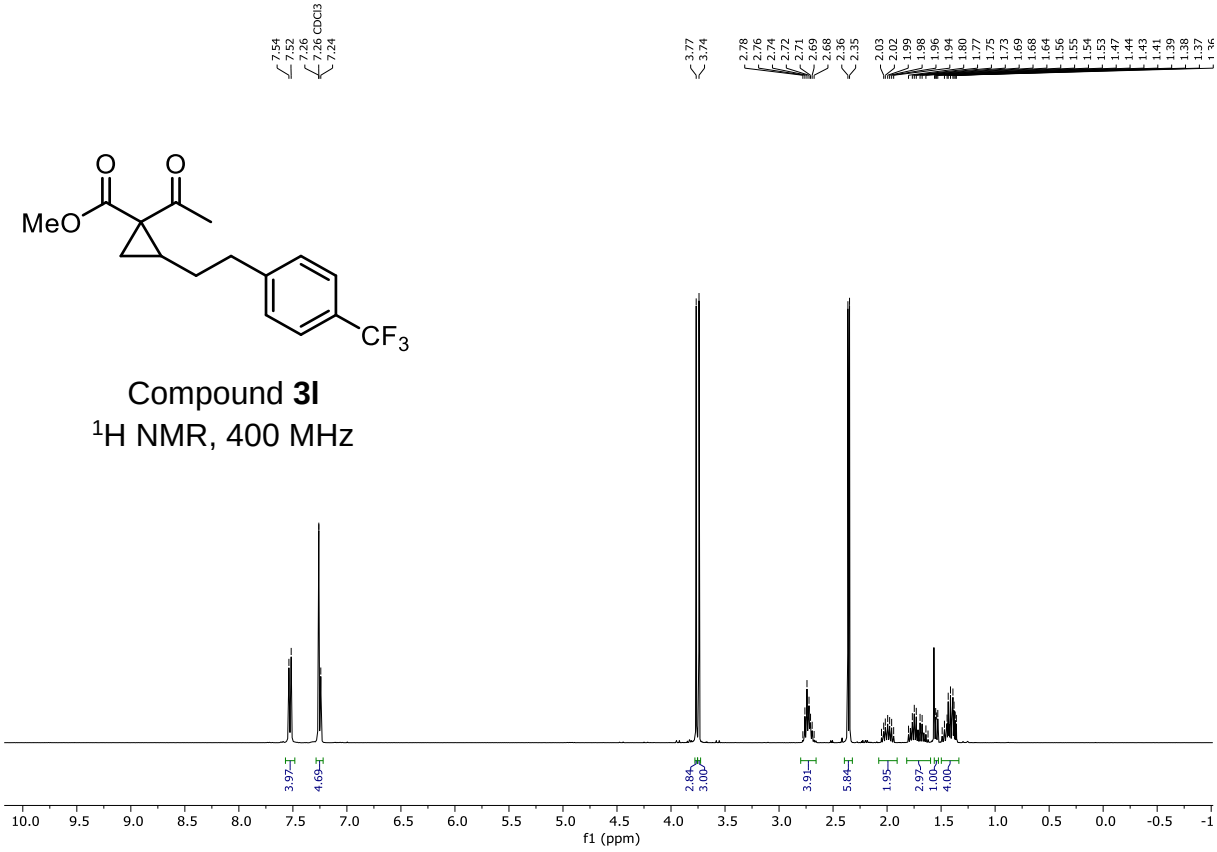
Compound **3j**
^{13}C NMR, 101 MHz



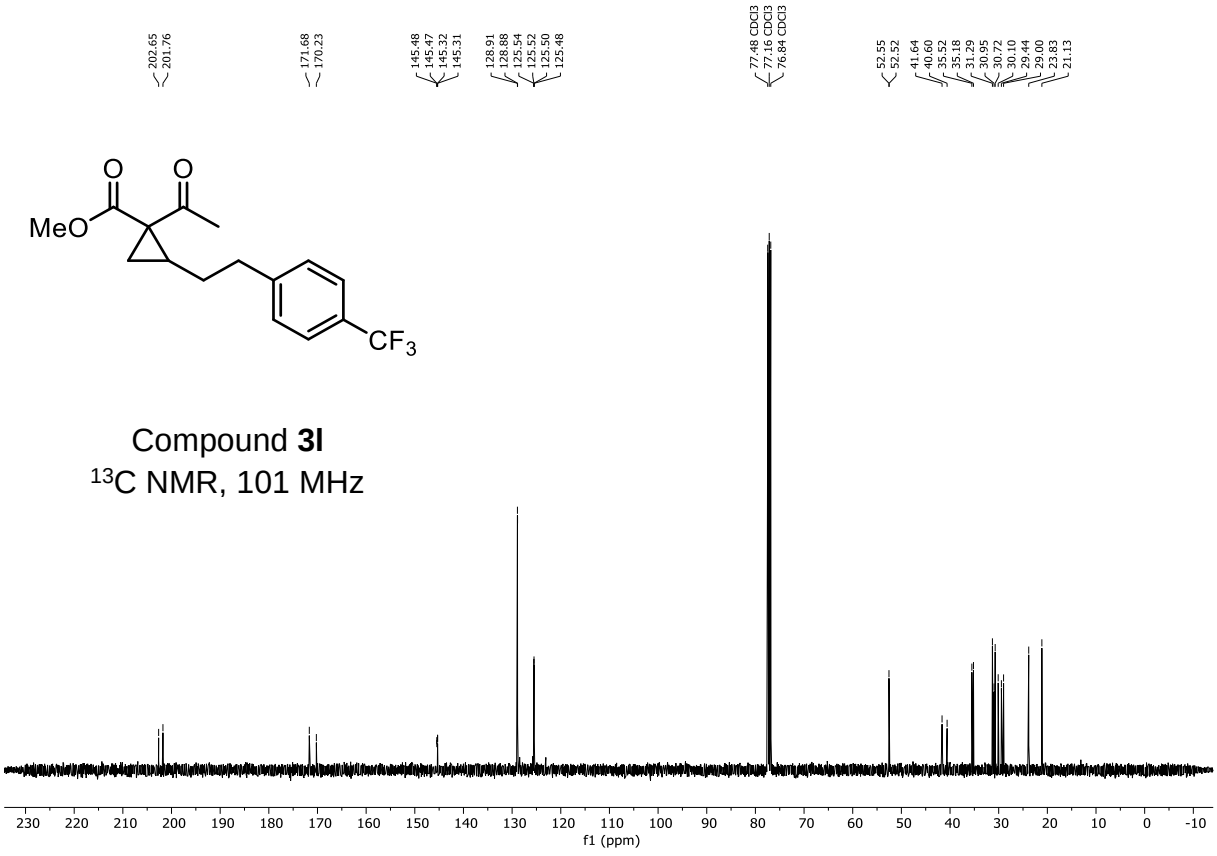
Compound **3k**
^{1}H NMR, 400 MHz



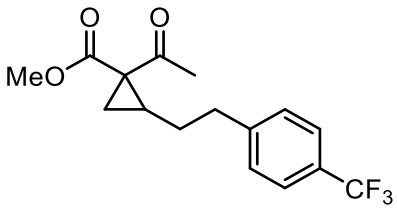
Compound **3k**
^{13}C NMR, 101 MHz



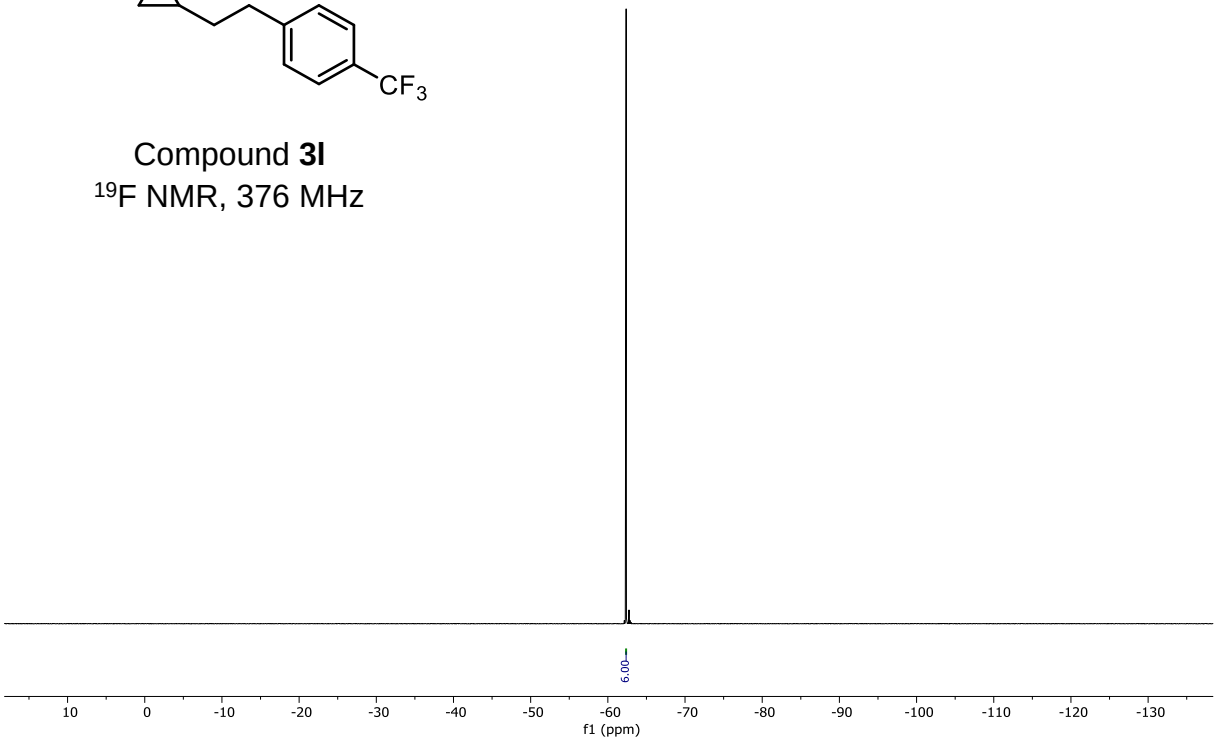
Compound **3l**
^{1}H NMR, 400 MHz

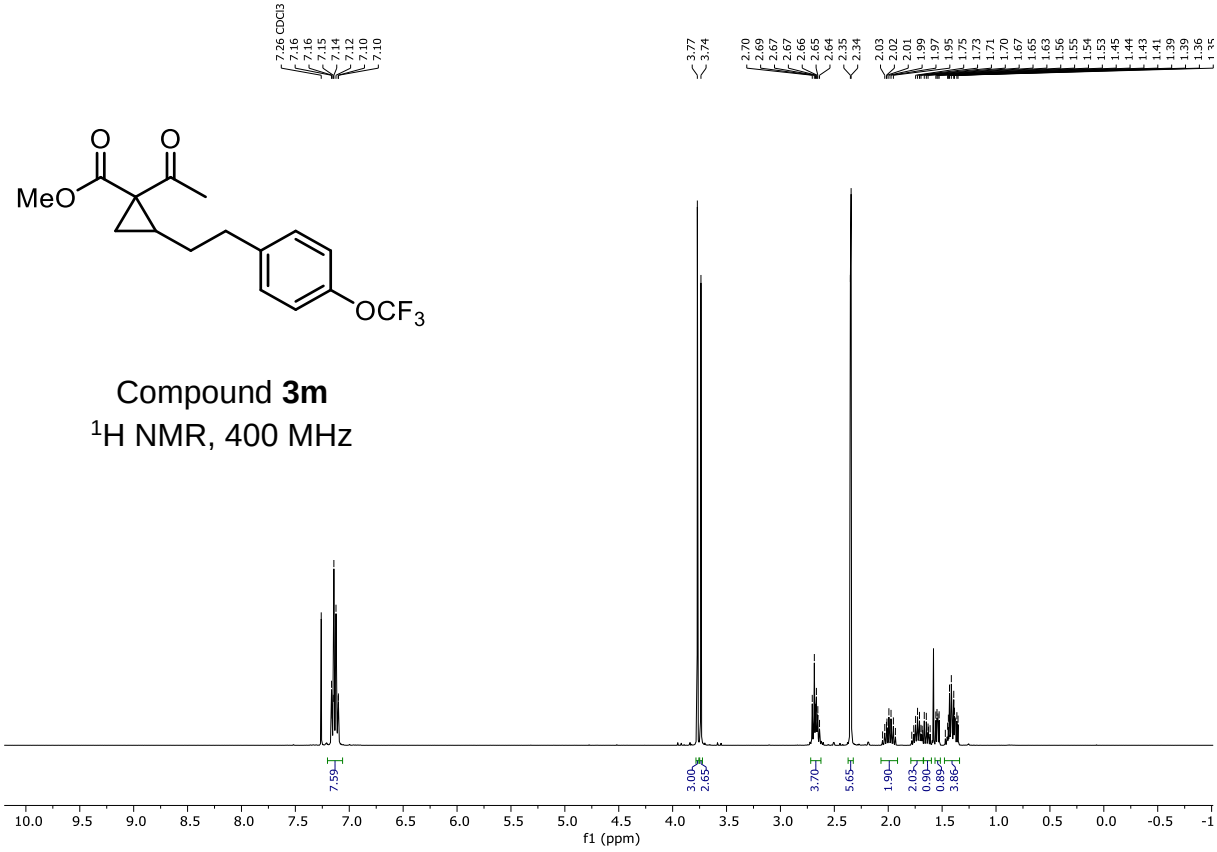


Compound **3l**
^{13}C NMR, 101 MHz

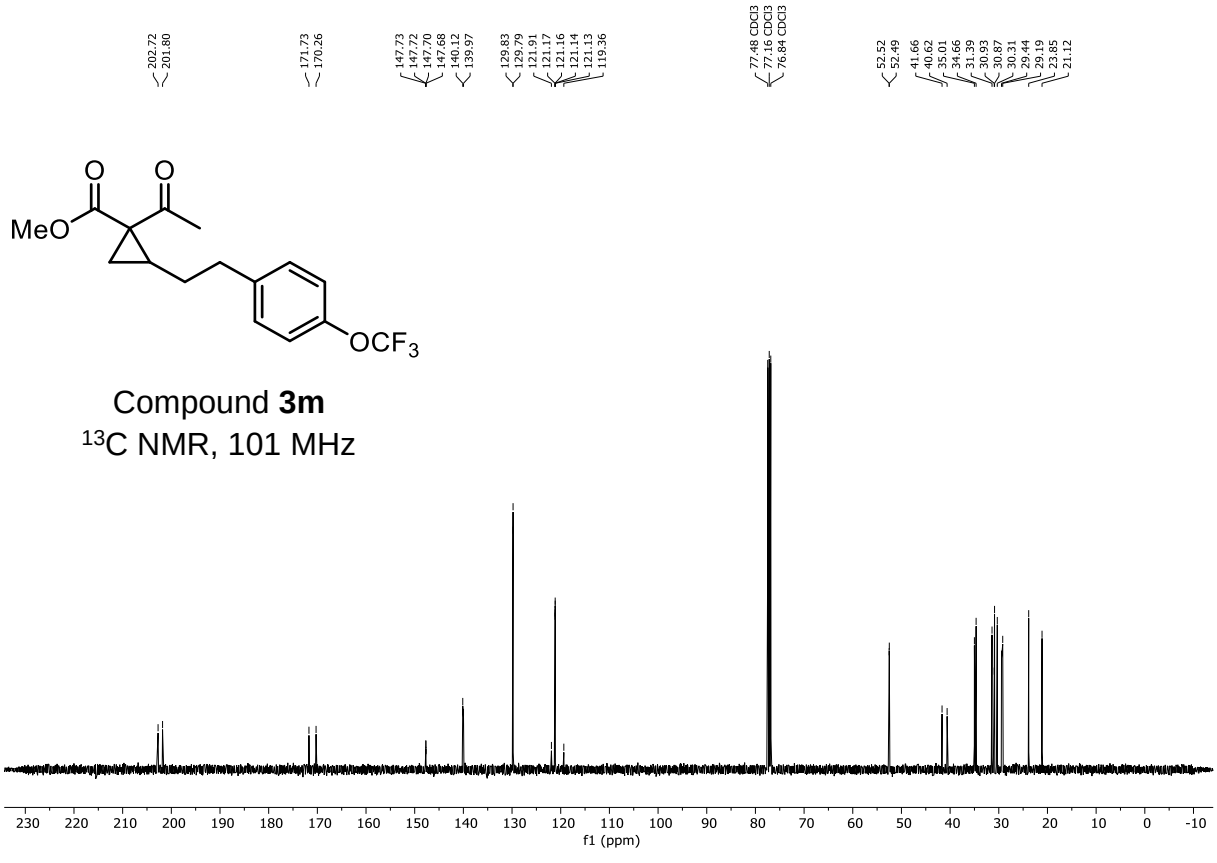


Compound **3l**
^{19}F NMR, 376 MHz

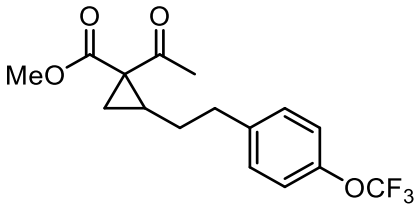




Compound **3m**
^{1}H NMR, 400 MHz

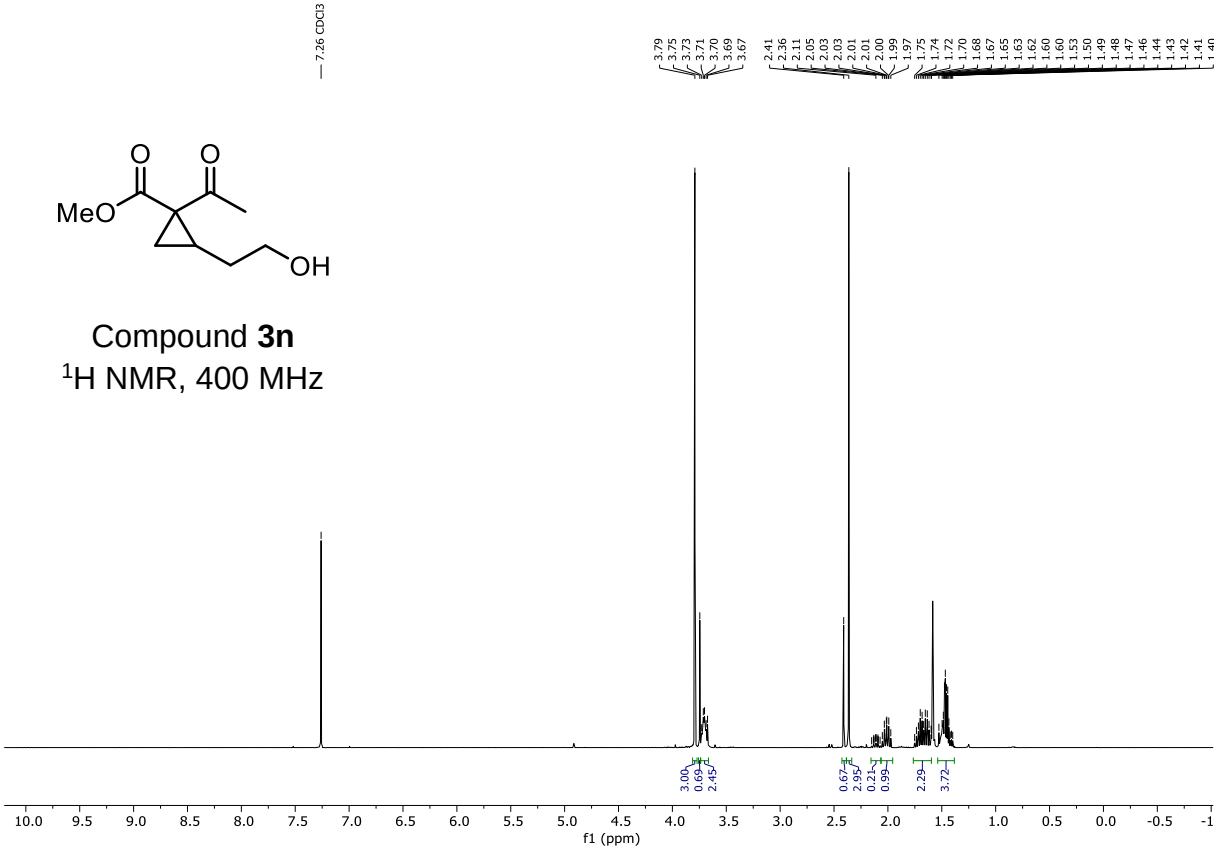


Compound **3m**
^{13}C NMR, 101 MHz

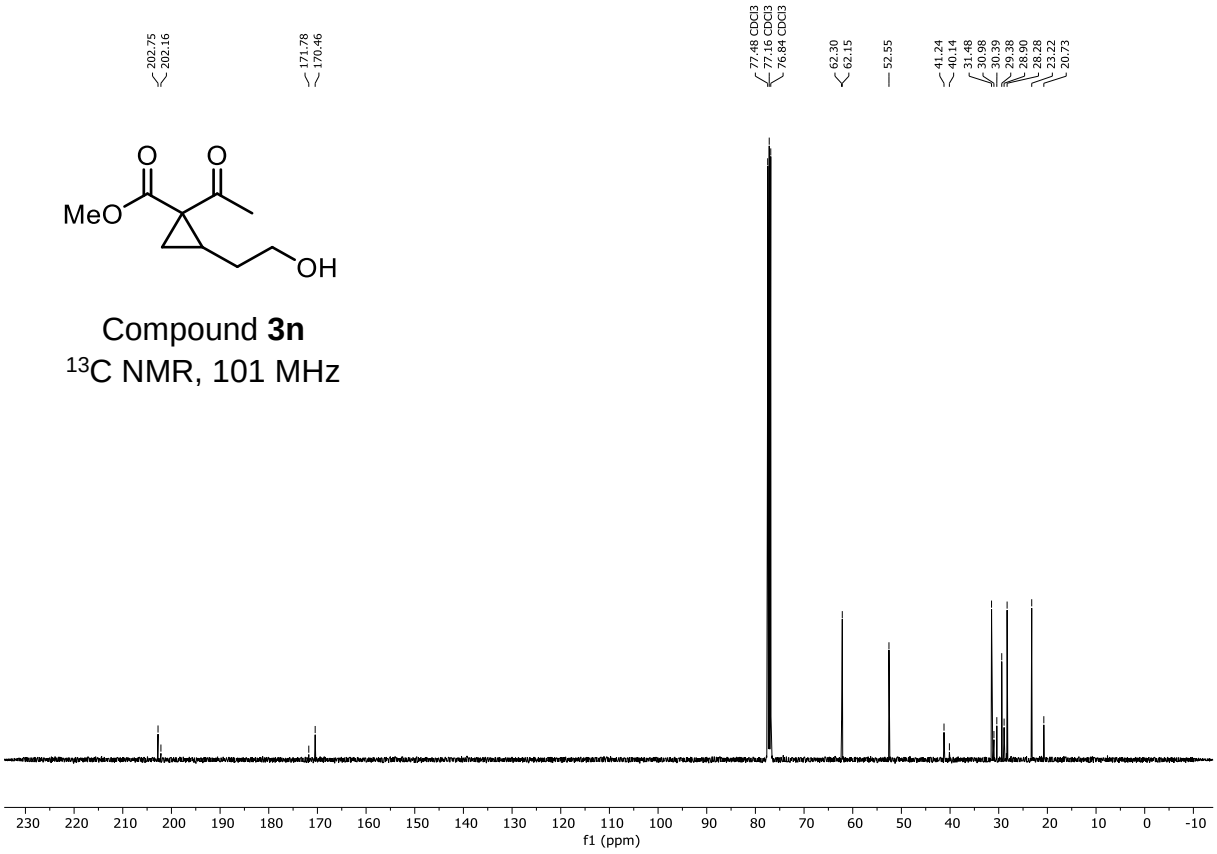


Compound **3m**

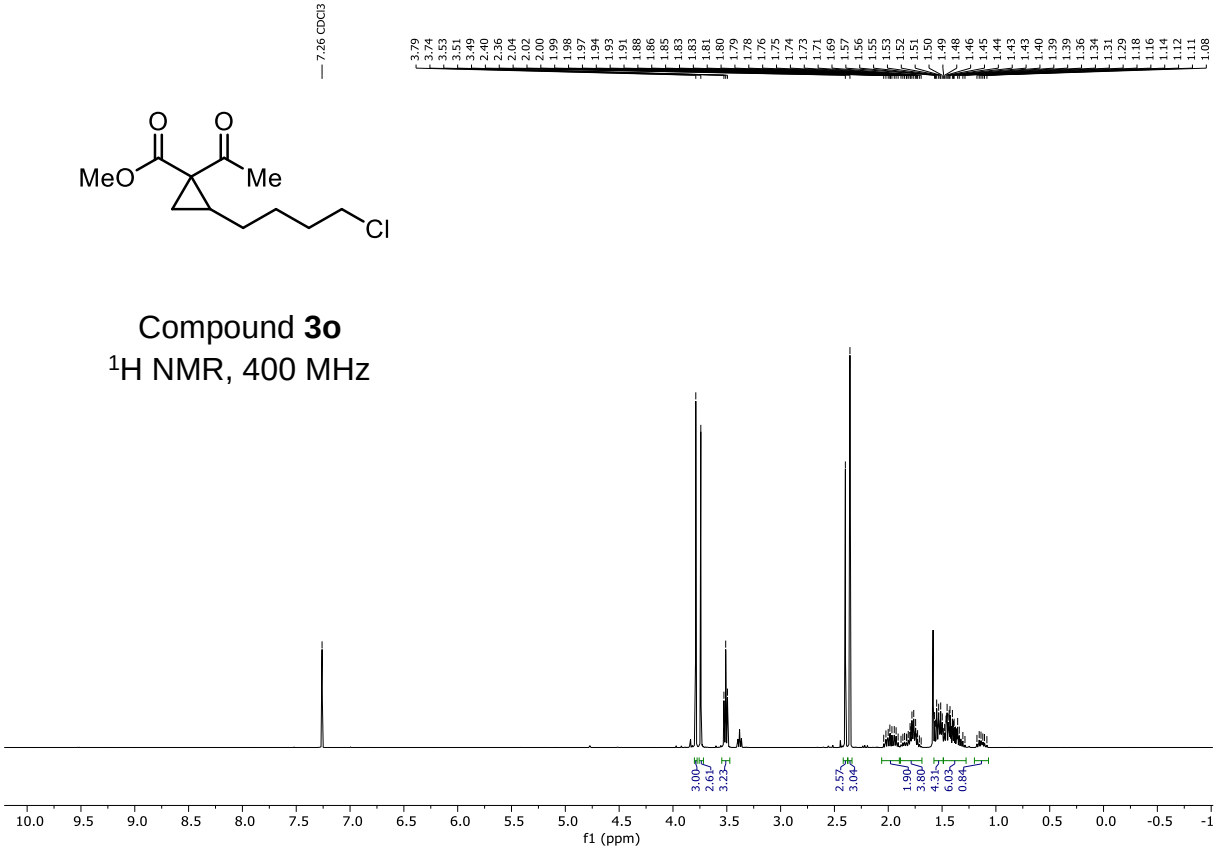
^{19}F NMR, 376 MHz



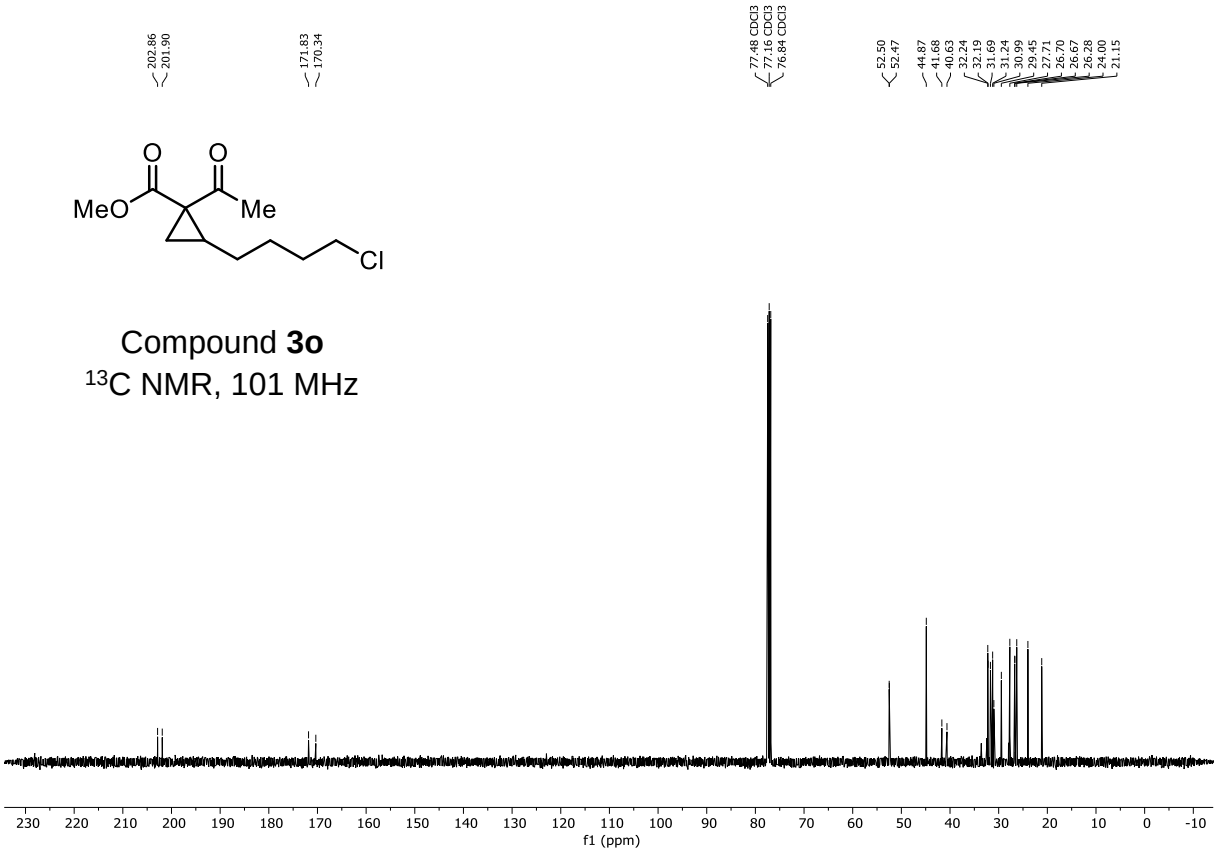
Compound **3n**
^{1}H NMR, 400 MHz



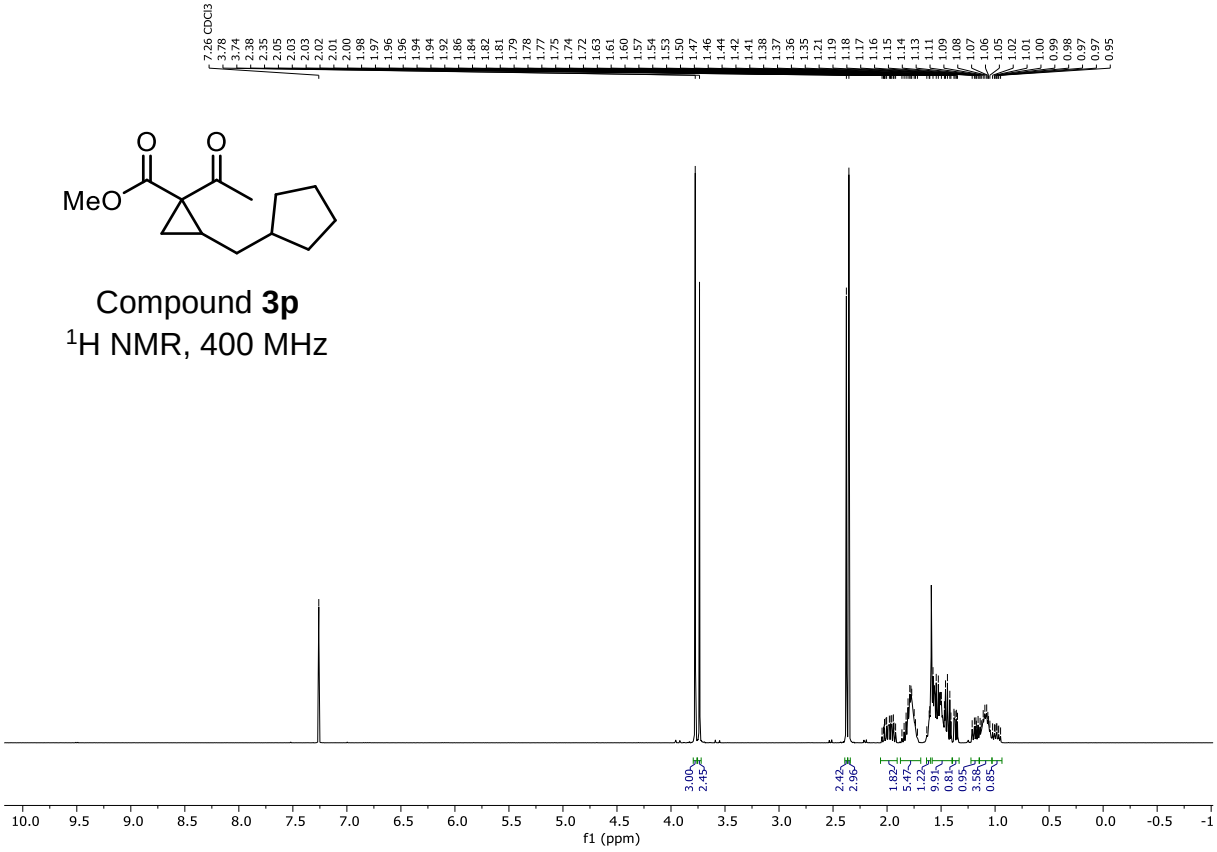
Compound **3n**
^{13}C NMR, 101 MHz



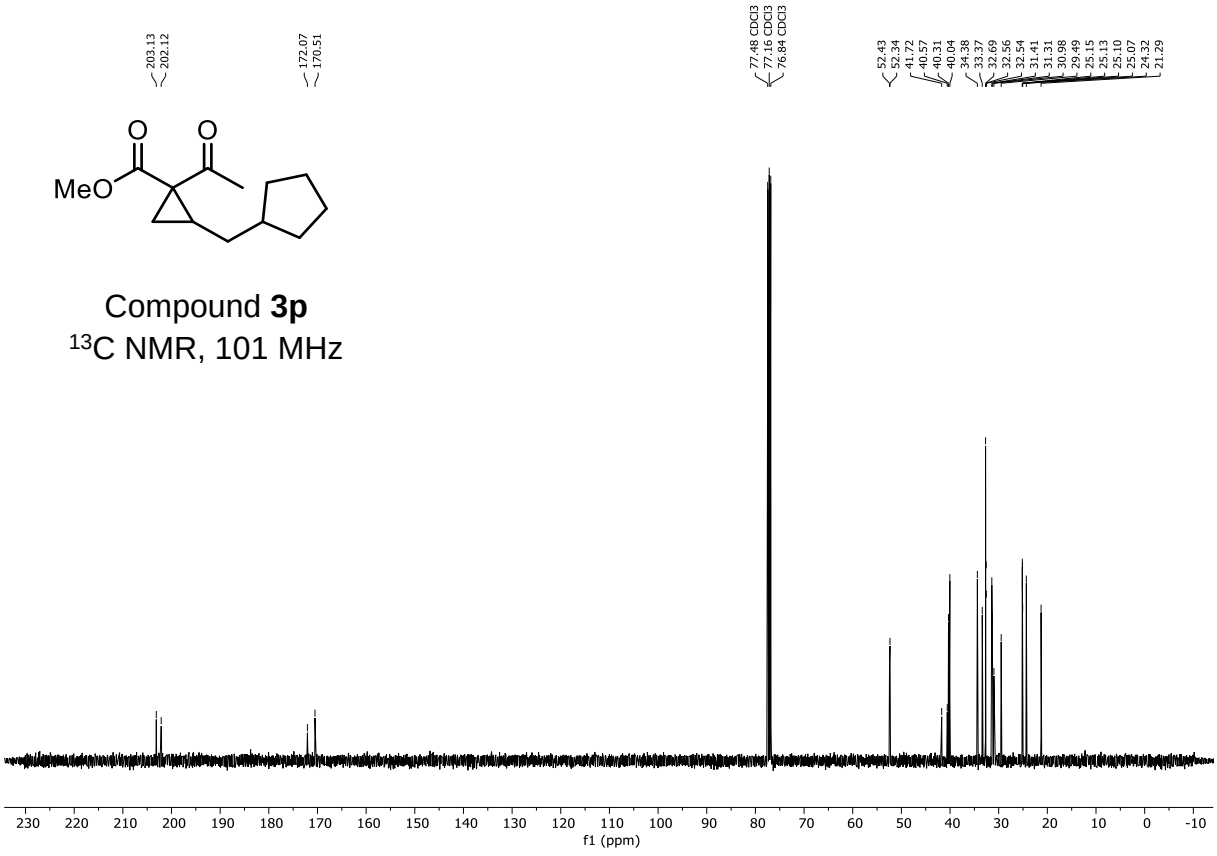
Compound **3o**
^{1}H NMR, 400 MHz



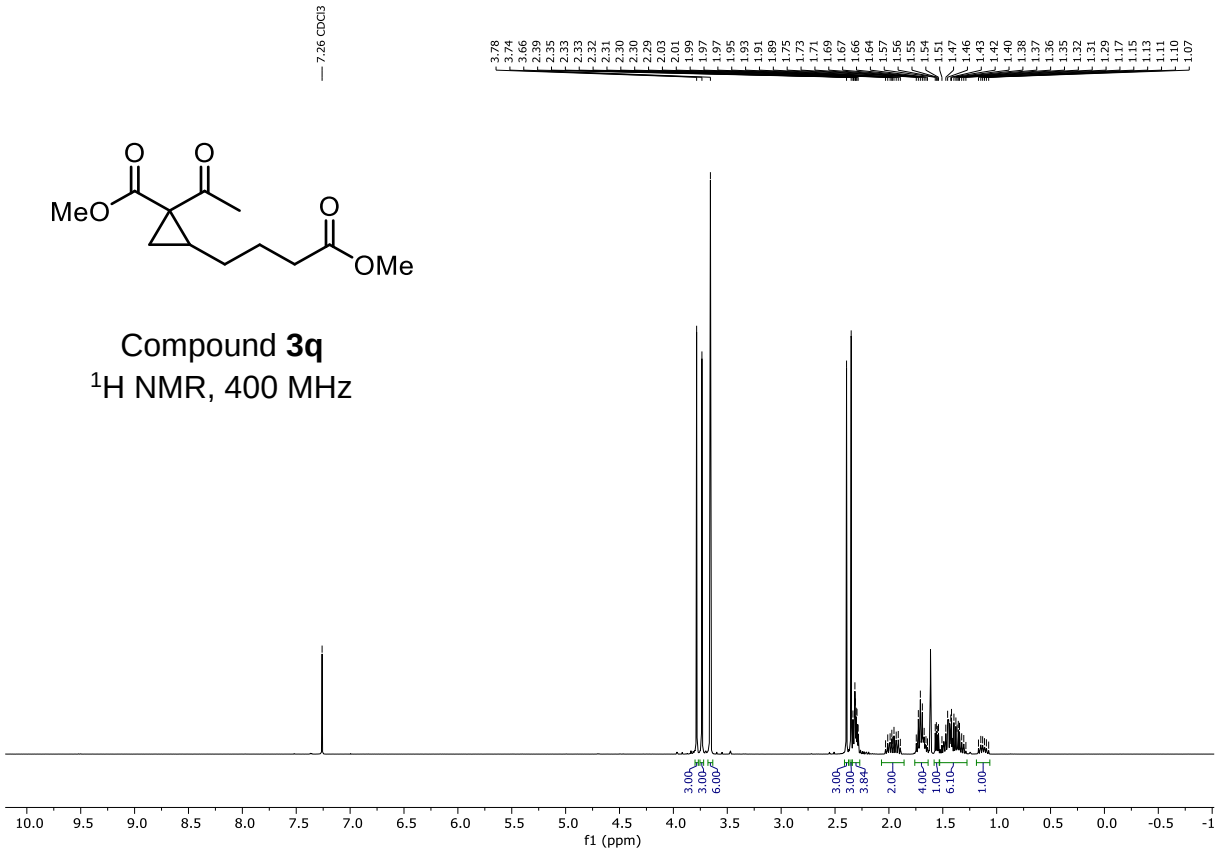
Compound **3o**
^{13}C NMR, 101 MHz



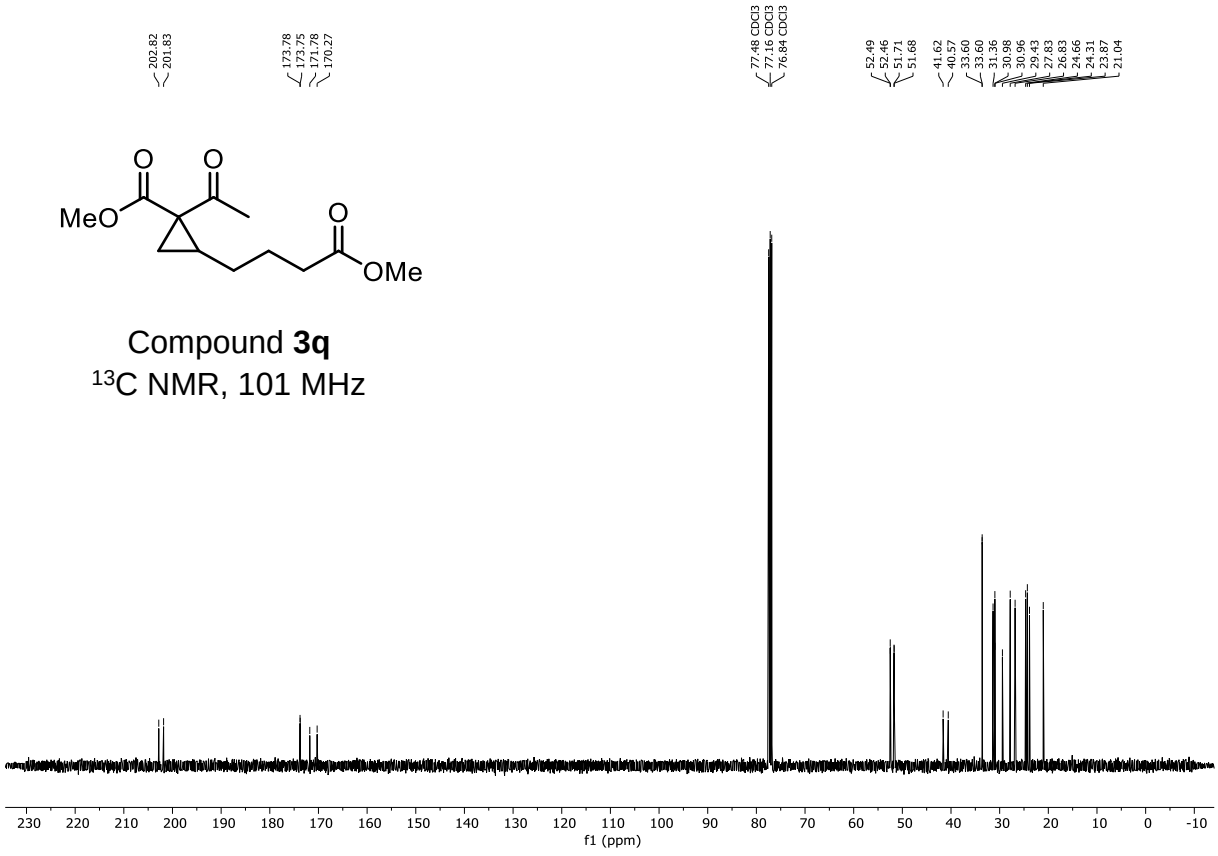
Compound **3p**
^{1}H NMR, 400 MHz



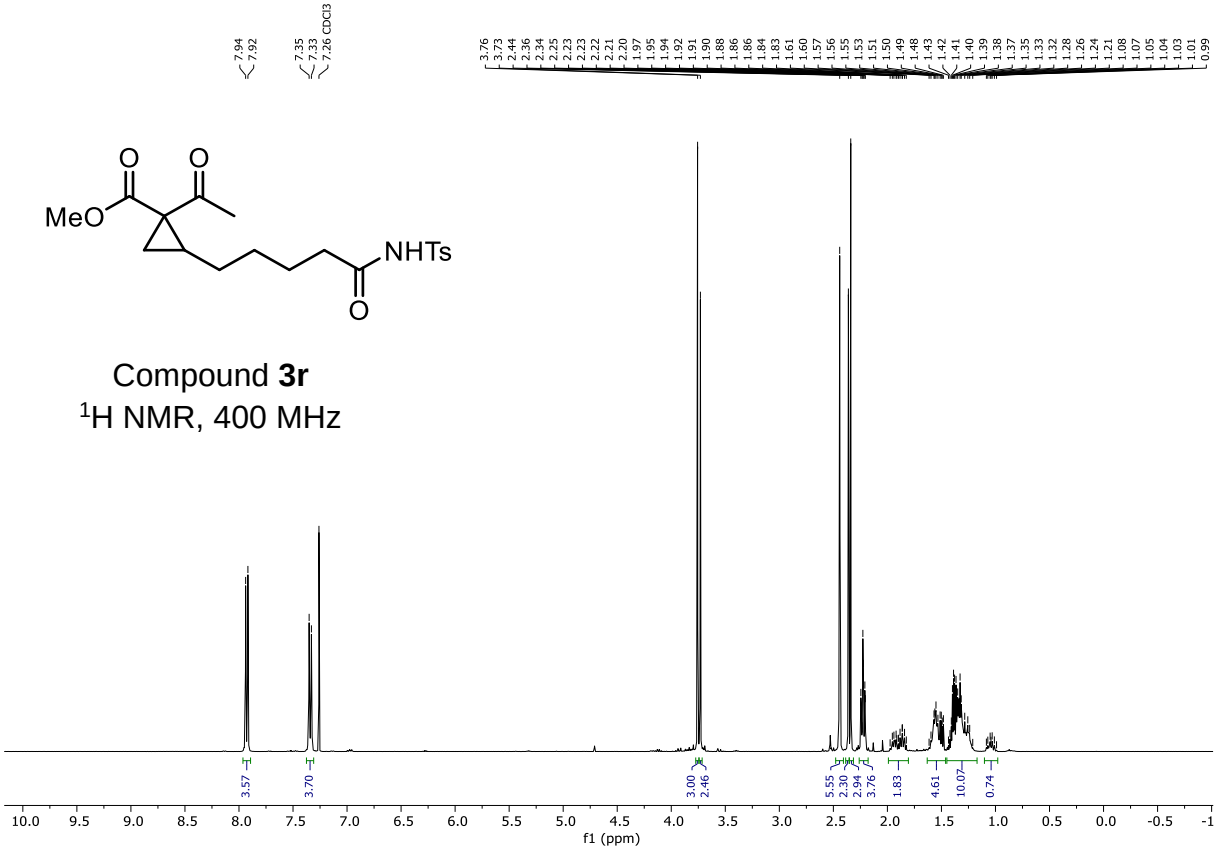
Compound **3p**
^{13}C NMR, 101 MHz



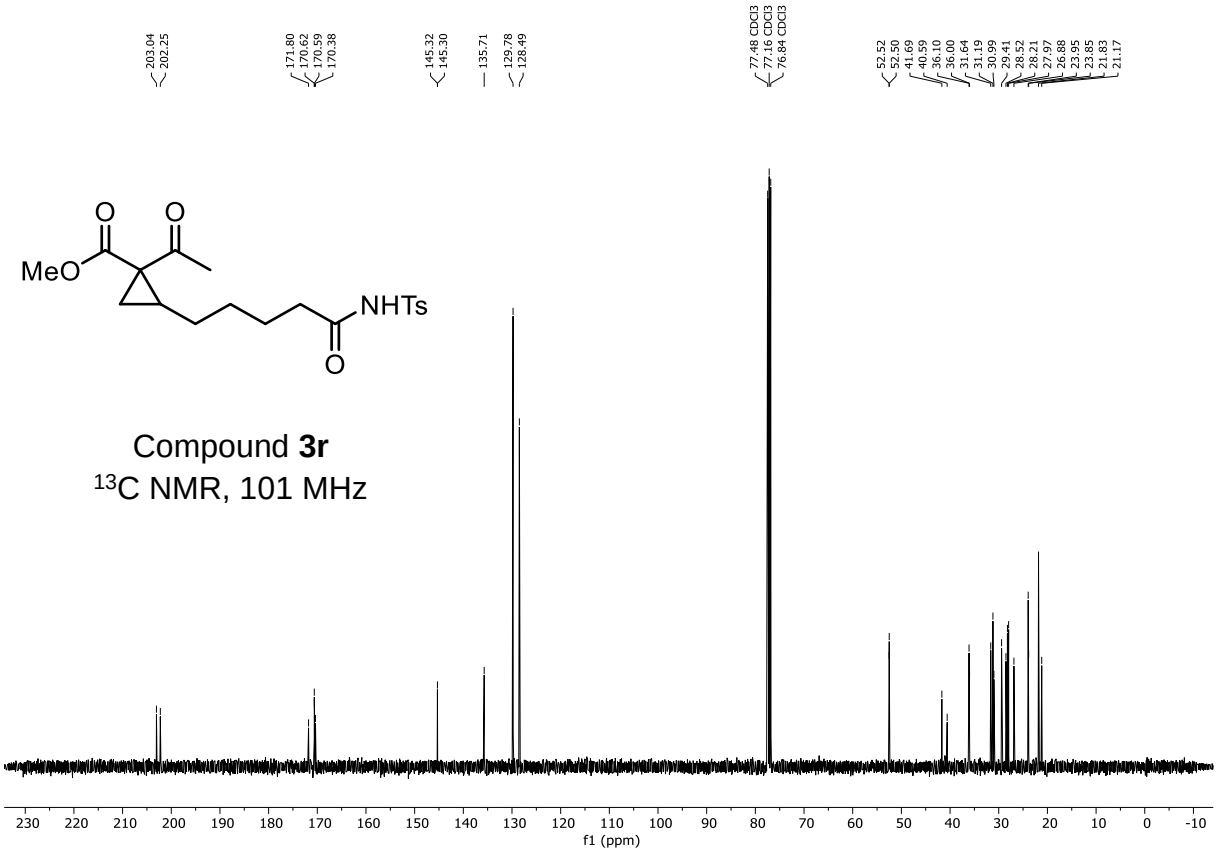
Compound **3q**
^{1}H NMR, 400 MHz



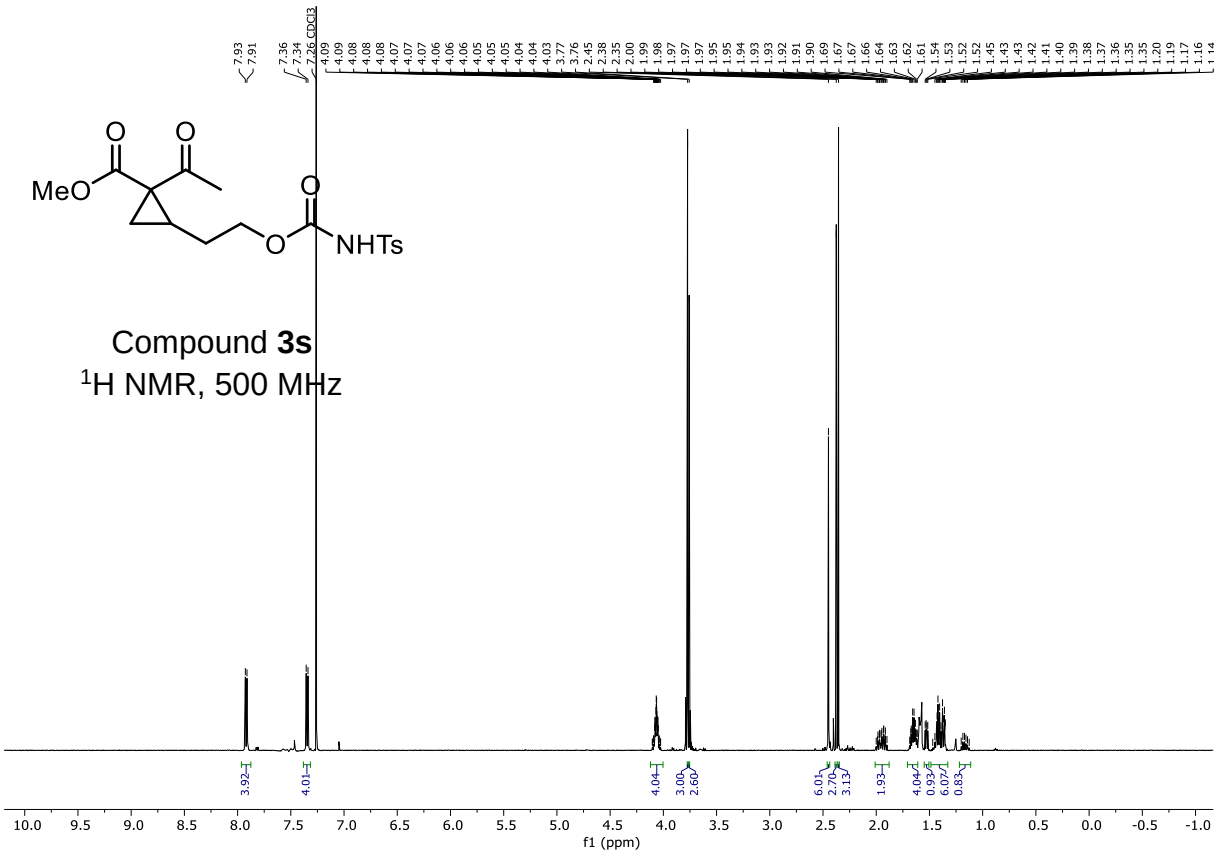
Compound **3q**
^{13}C NMR, 101 MHz



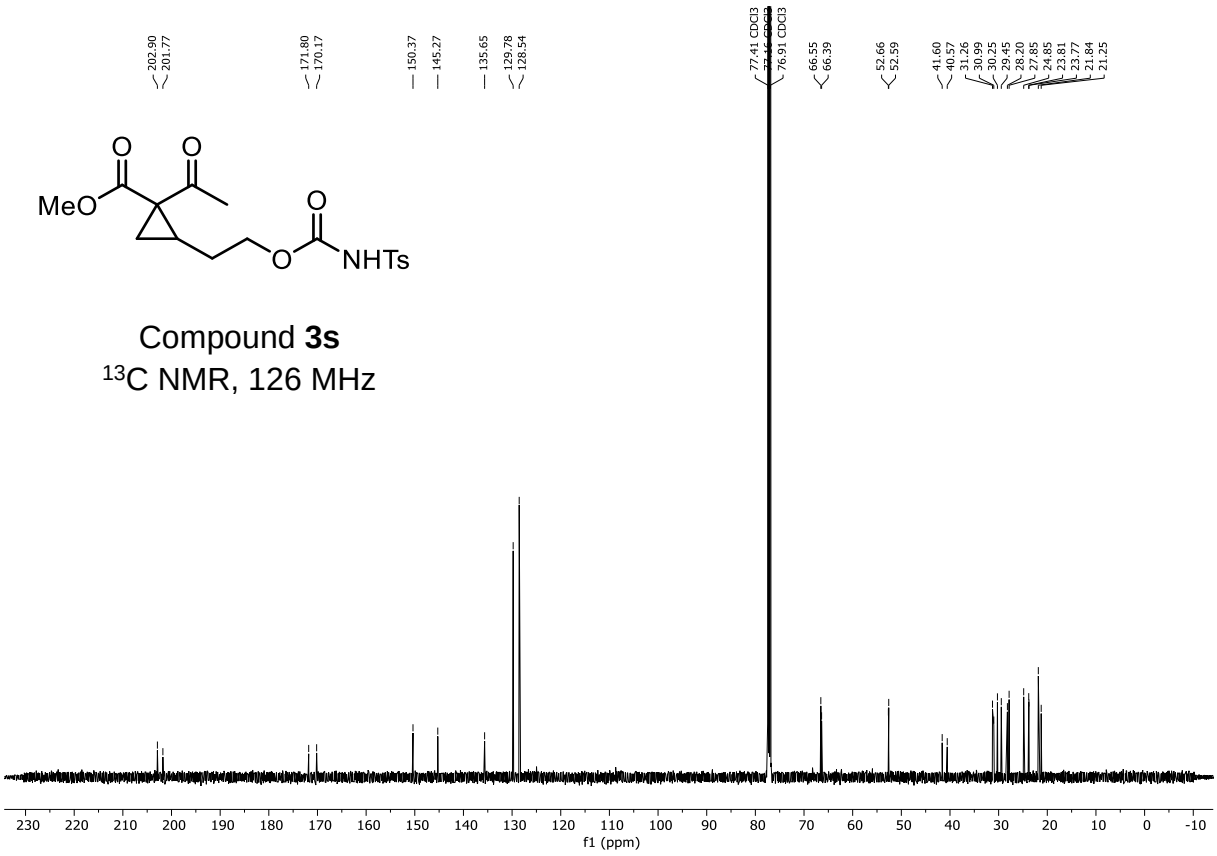
Compound **3r**
^{1}H NMR, 400 MHz



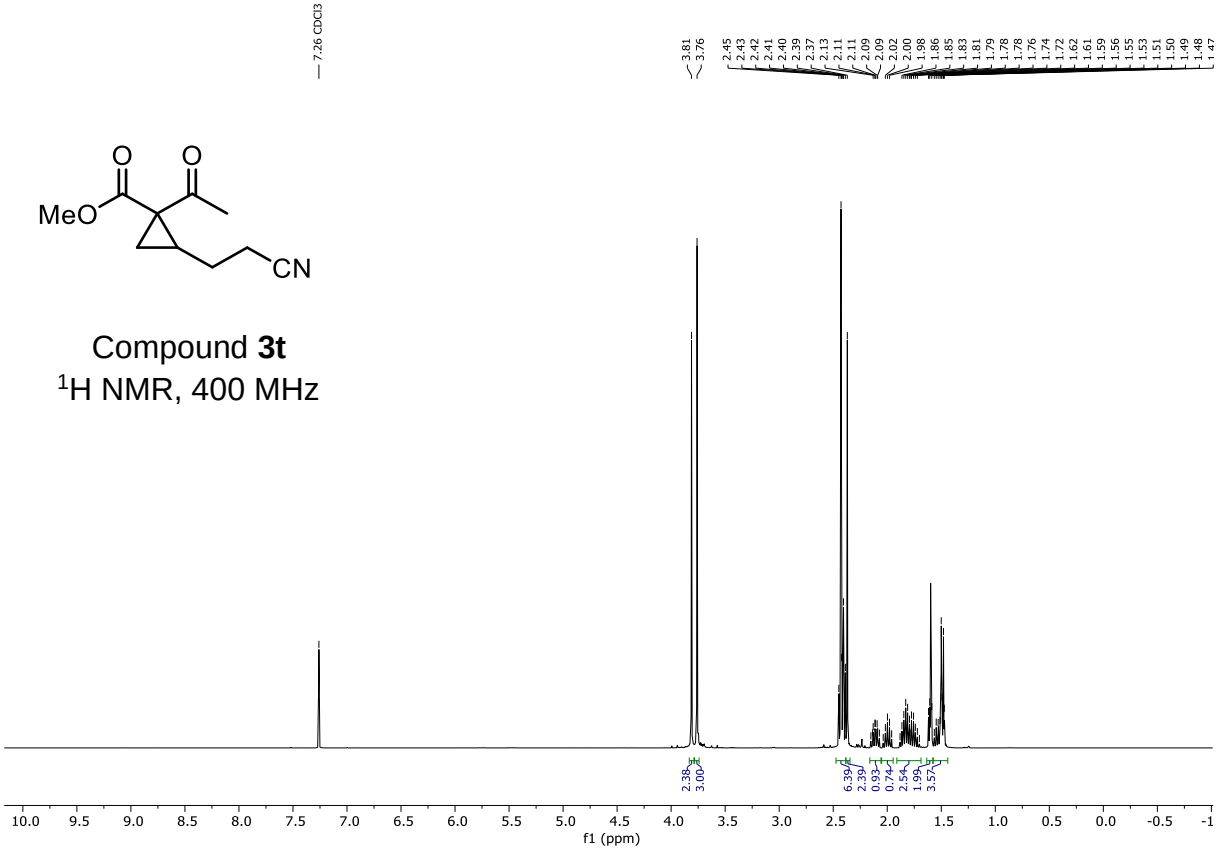
Compound **3r**
^{13}C NMR, 101 MHz



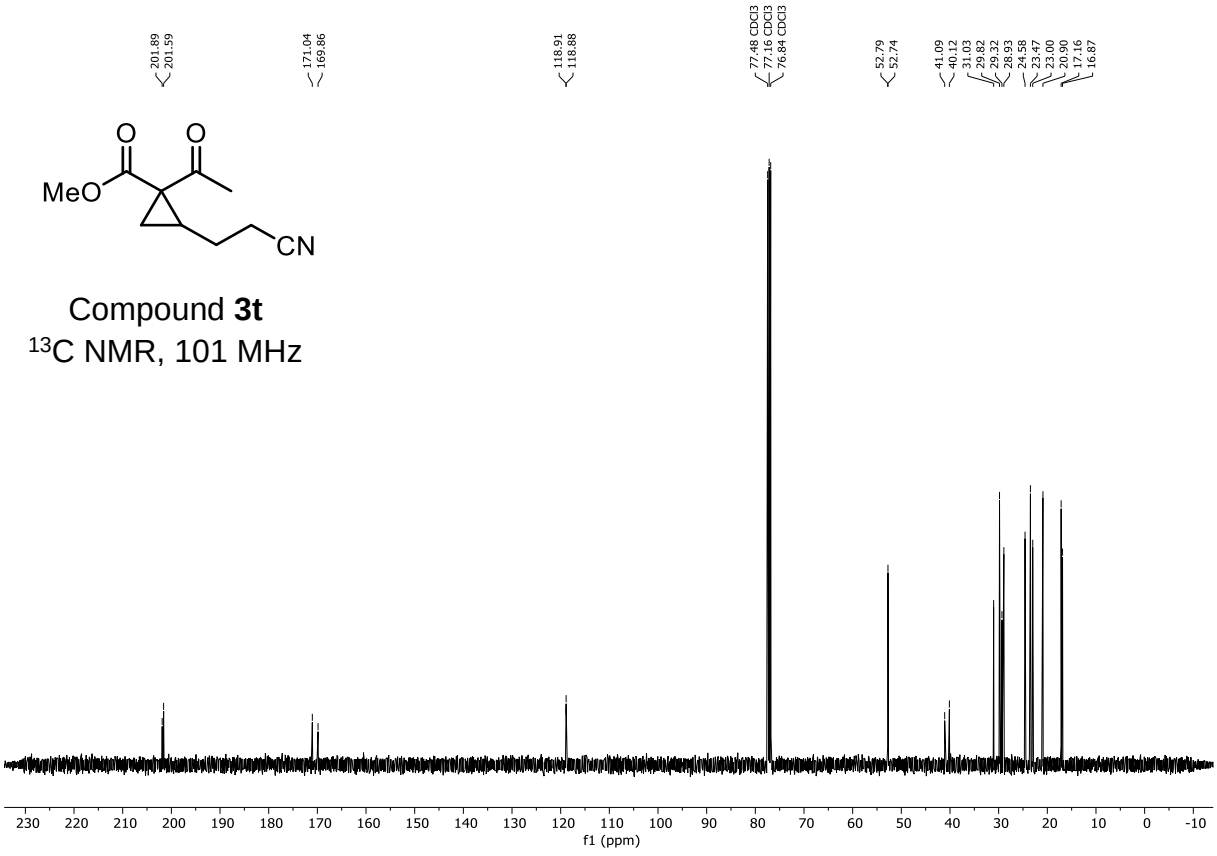
Compound **3s**
^{1}H NMR, 500 MHz



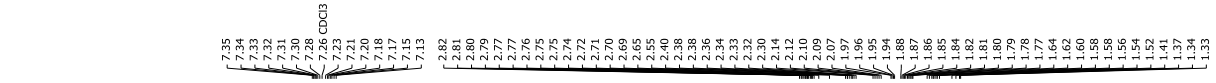
Compound **3s**
^{13}C NMR, 126 MHz

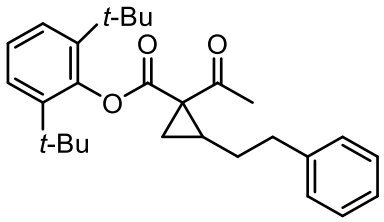


Compound **3t**
^{1}H NMR, 400 MHz

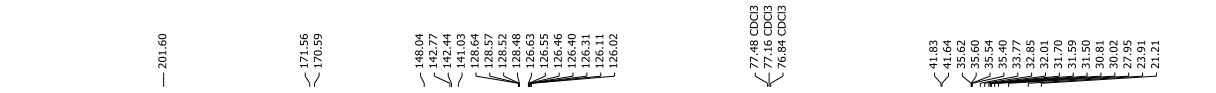


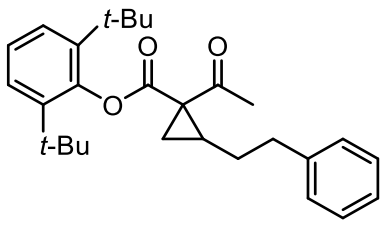
Compound **3t**
^{13}C NMR, 101 MHz



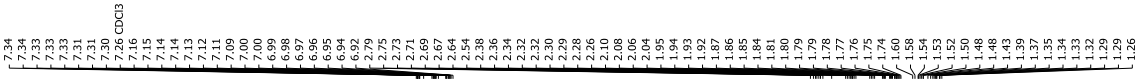


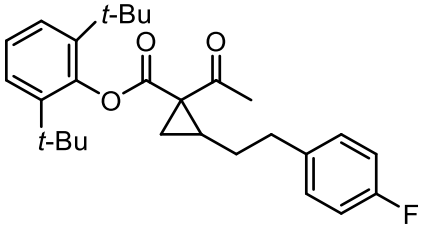
Compound **6a**
^{1}H NMR, 400 MHz



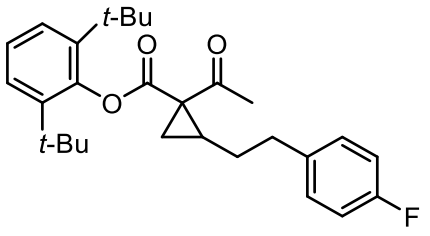


Compound **6a**
^{13}C NMR, 101 MHz

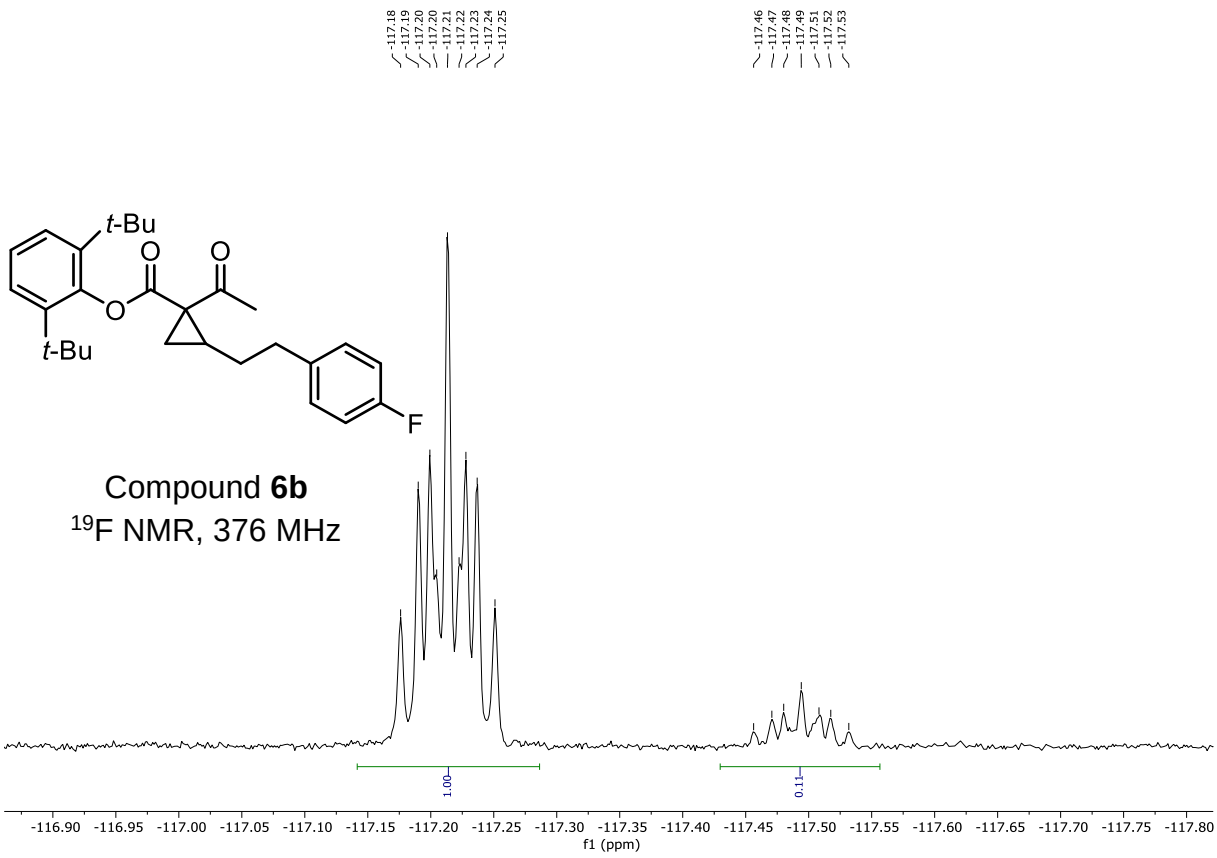


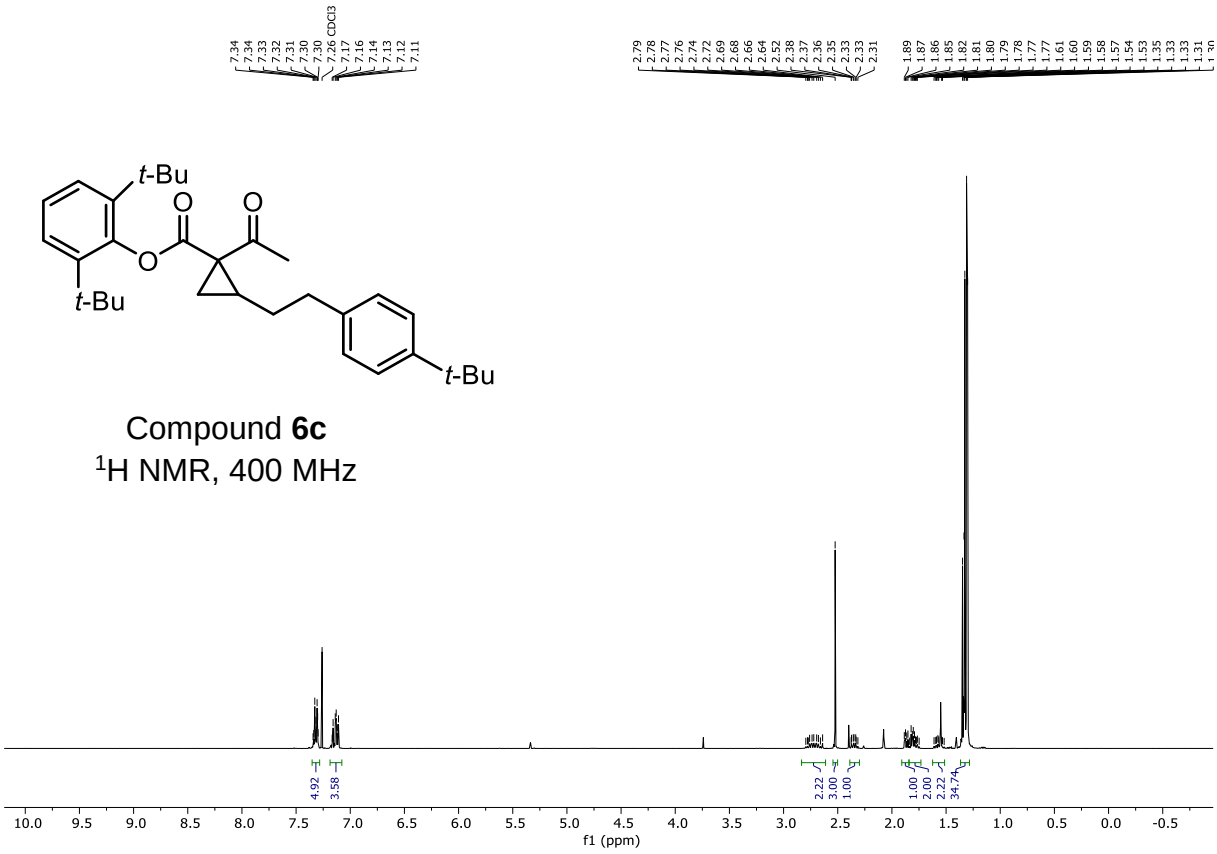


Compound **6b**
^{1}H NMR, 400 MHz

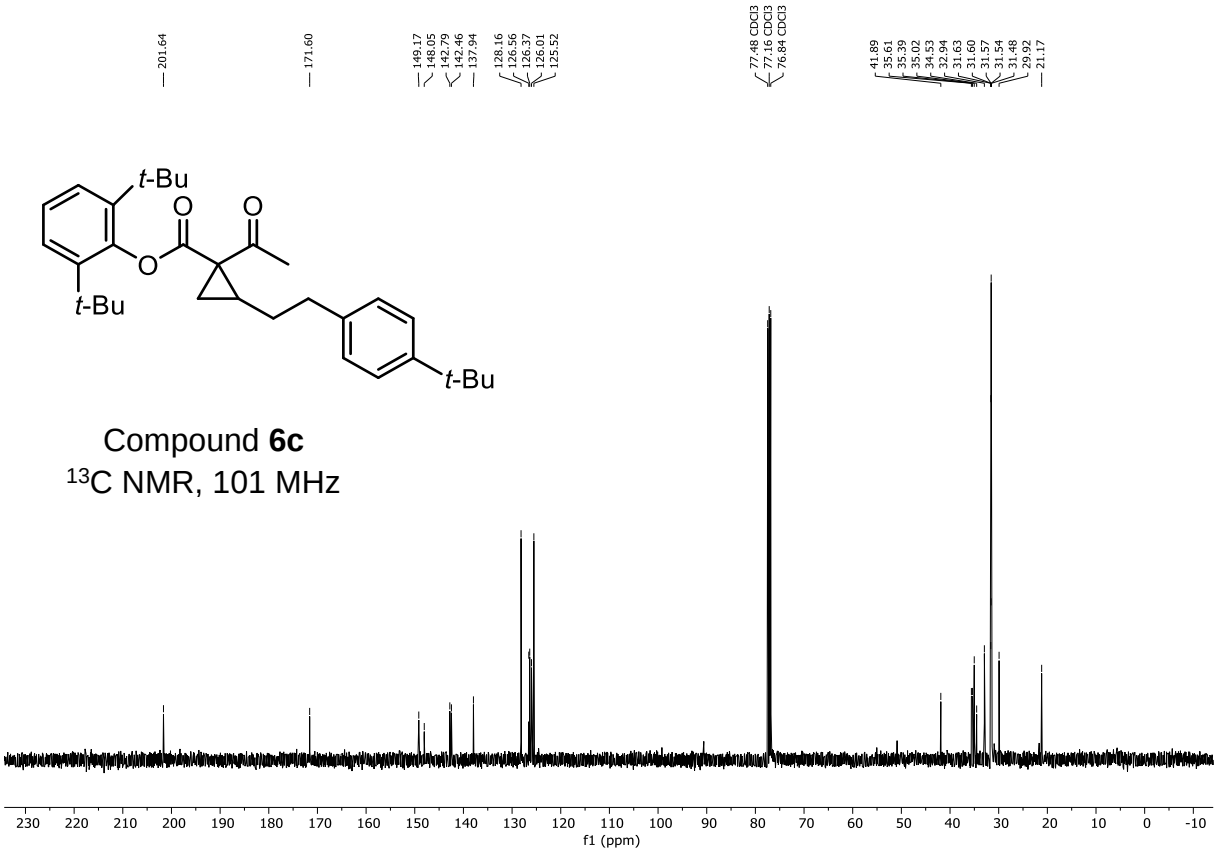


Compound **6b**
^{13}C NMR, 101 MHz

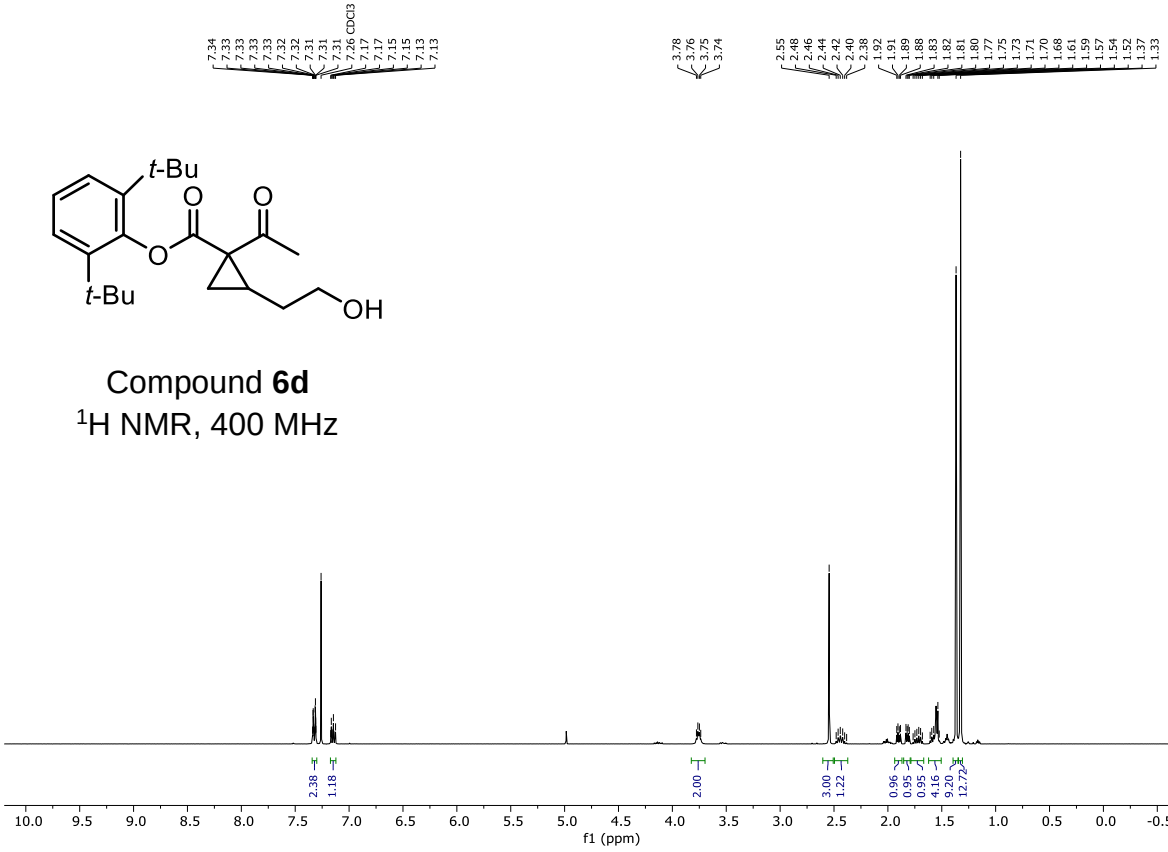

-117.18
-117.19
-117.20
-117.20
-117.21
-117.22
-117.23
-117.24
-117.25
-117.46
-117.47
-117.48
-117.49
-117.51
-117.52
-117.53
t-Bu
O
O
O
t-Bu
F
Compound 6b
19F NMR, 376 MHz
1.00
0.11
-116.90 -116.95 -117.00 -117.05 -117.10 -117.15 -117.20 -117.25 -117.30 -117.35 -117.40 -117.45 -117.50 -117.55 -117.60 -117.65 -117.70 -117.75 -117.80
f1 (ppm)



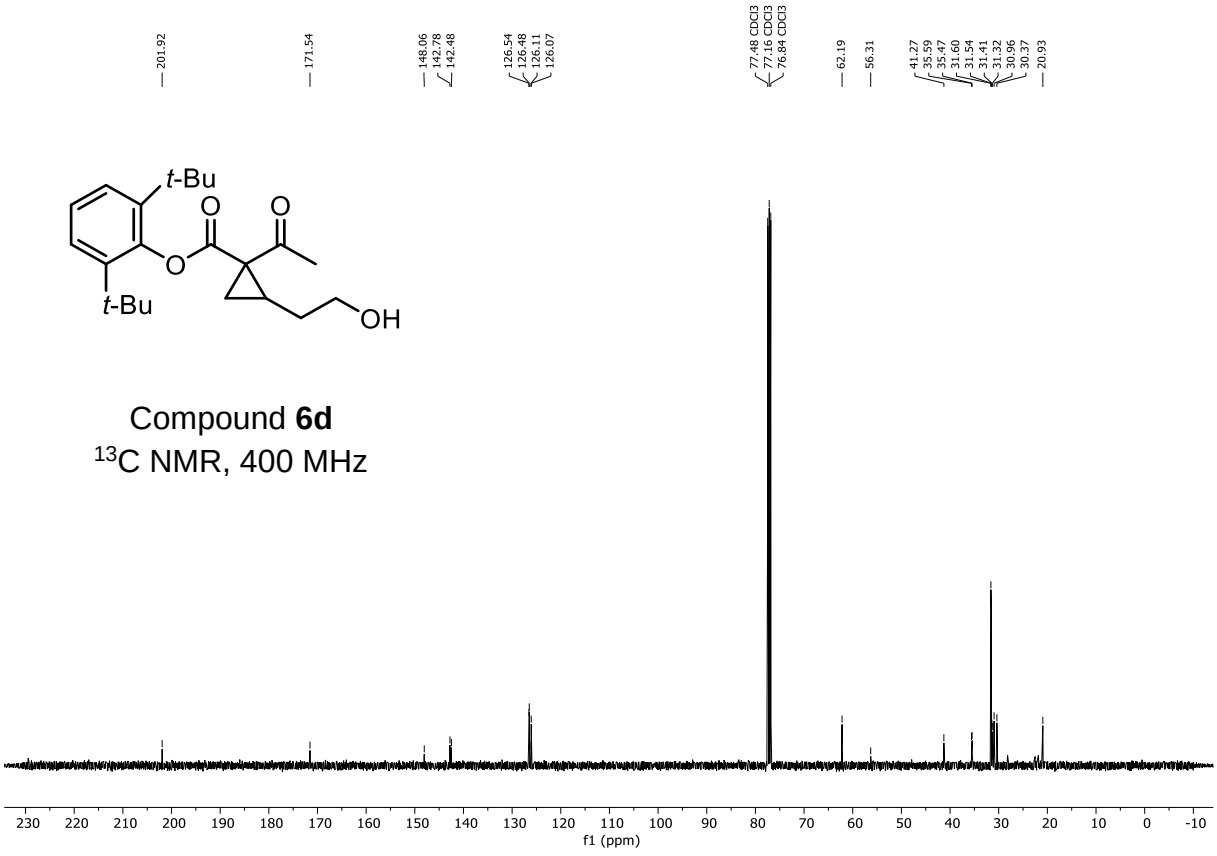
Compound **6c**
^{1}H NMR, 400 MHz



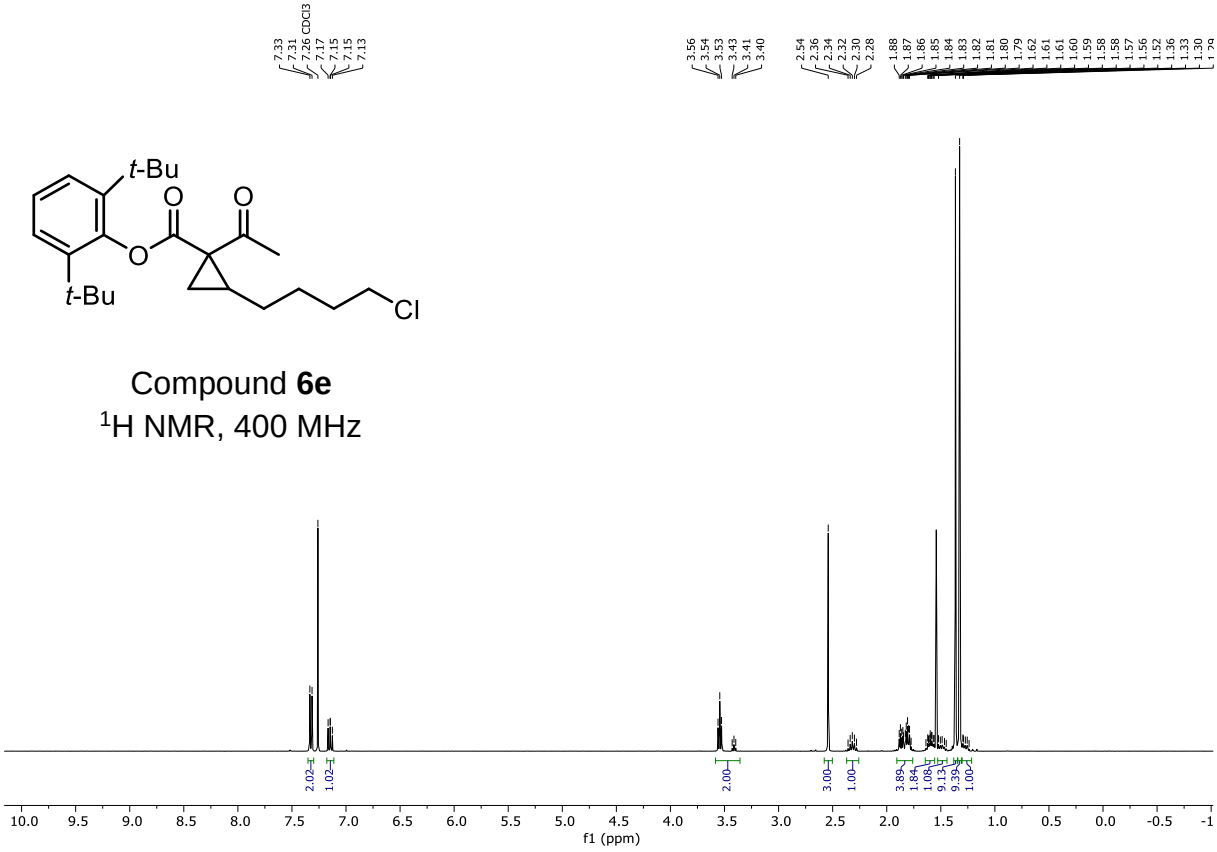
Compound **6c**
^{13}C NMR, 101 MHz



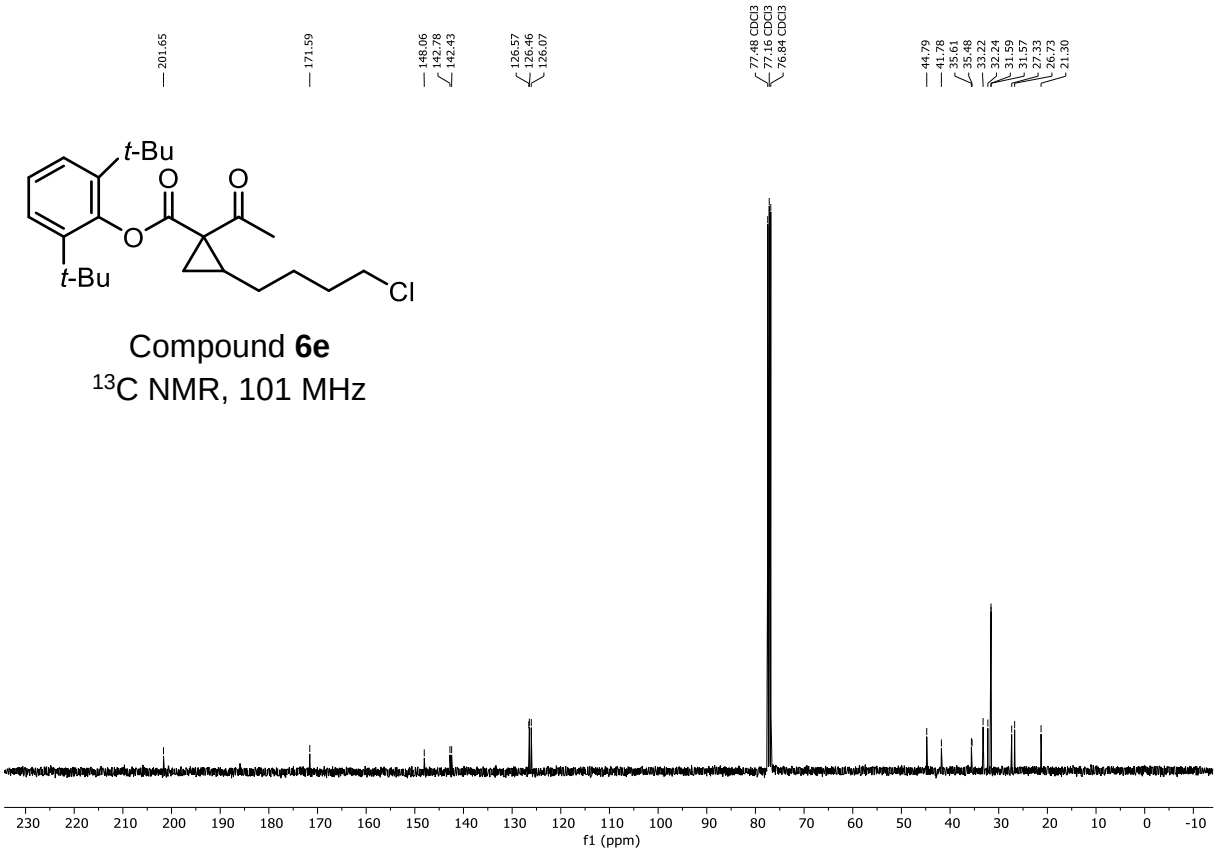
Compound **6d**
^{1}H NMR, 400 MHz



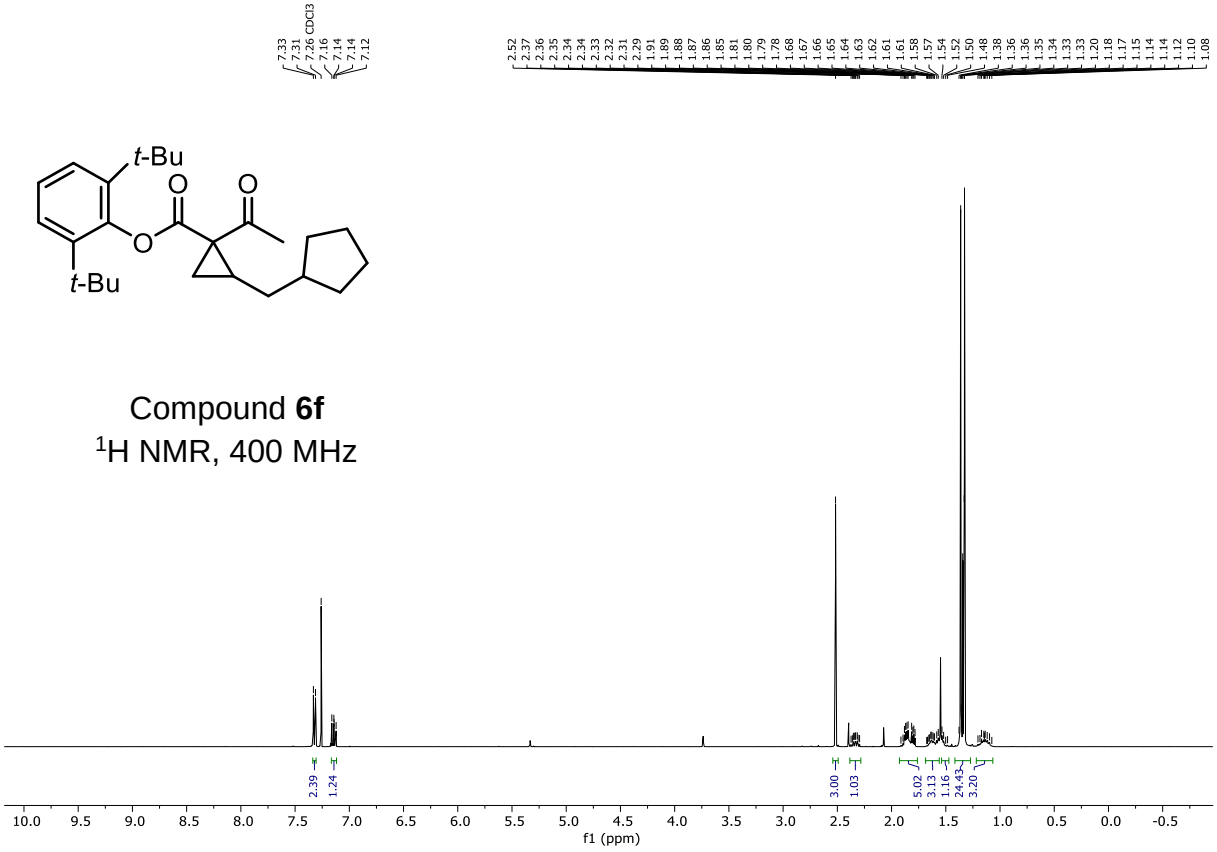
Compound **6d**
^{13}C NMR, 400 MHz



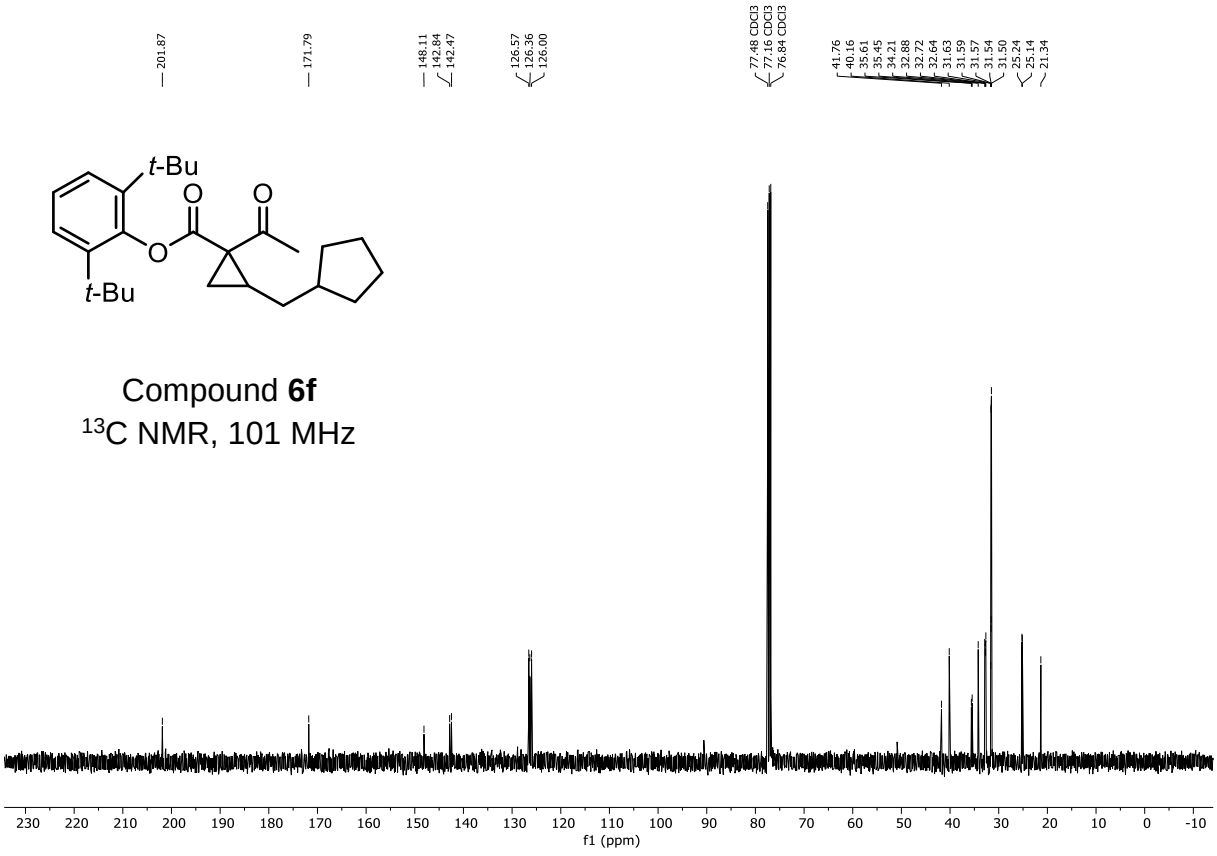
Compound **6e**
^{1}H NMR, 400 MHz



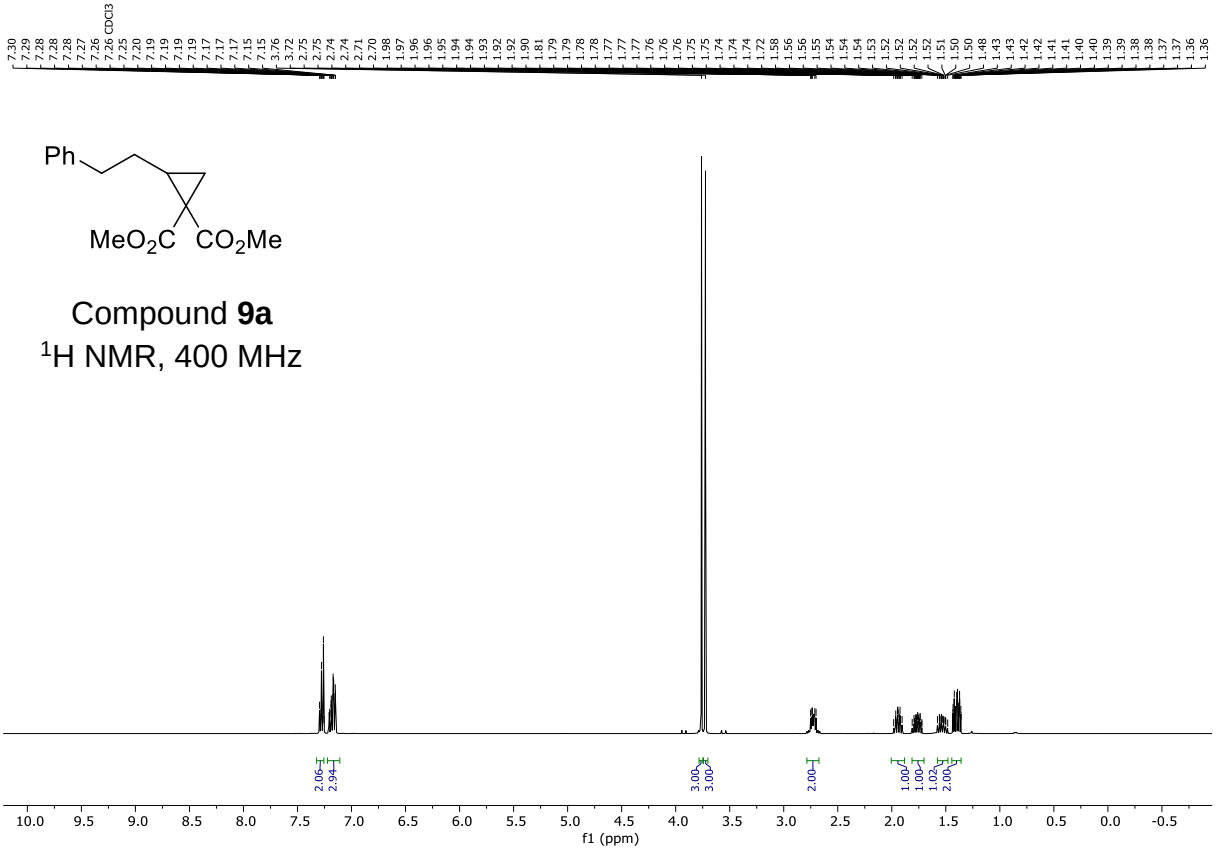
Compound **6e**
^{13}C NMR, 101 MHz



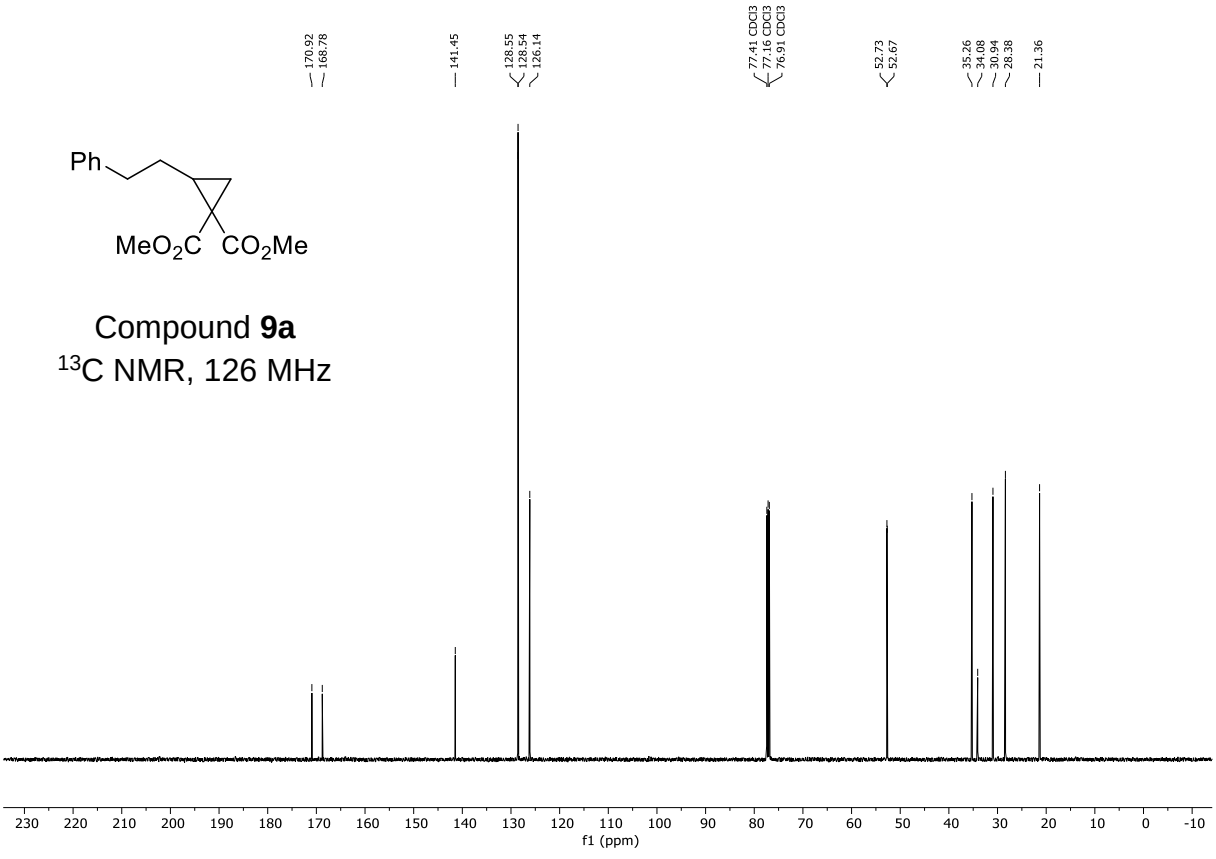
Compound **6f**
^{1}H NMR, 400 MHz



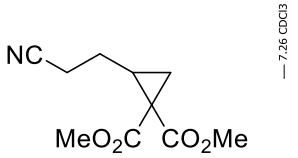
Compound **6f**
^{13}C NMR, 101 MHz



Compound **9a**
^{1}H NMR, 400 MHz

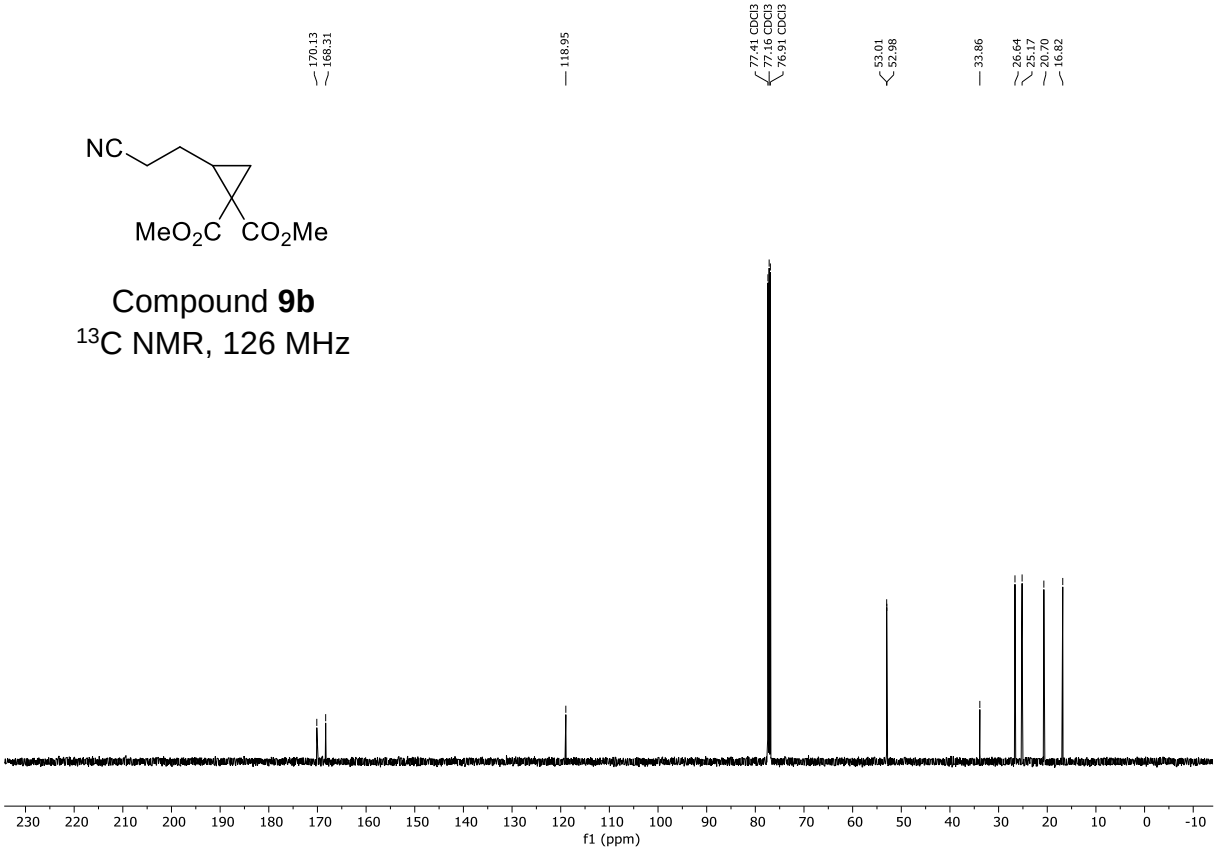


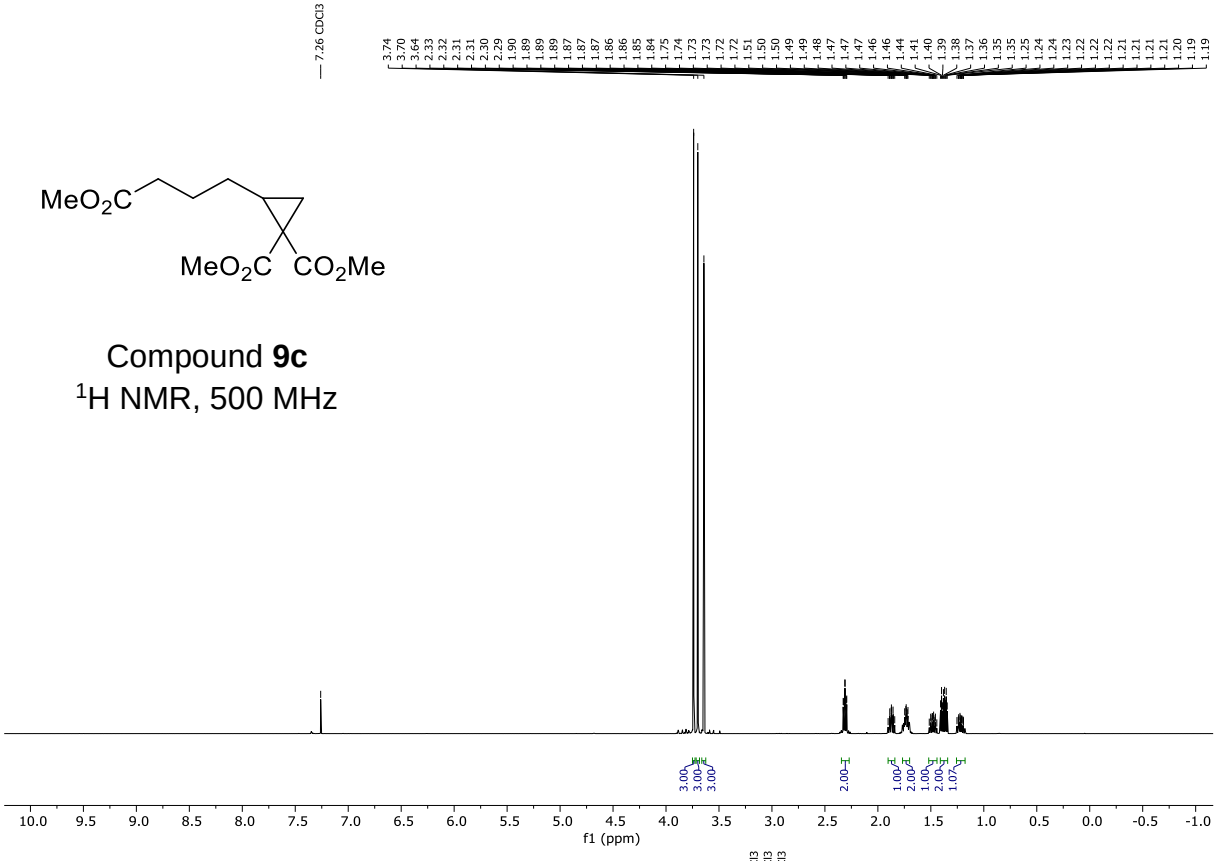
Compound **9a**
^{13}C NMR, 126 MHz



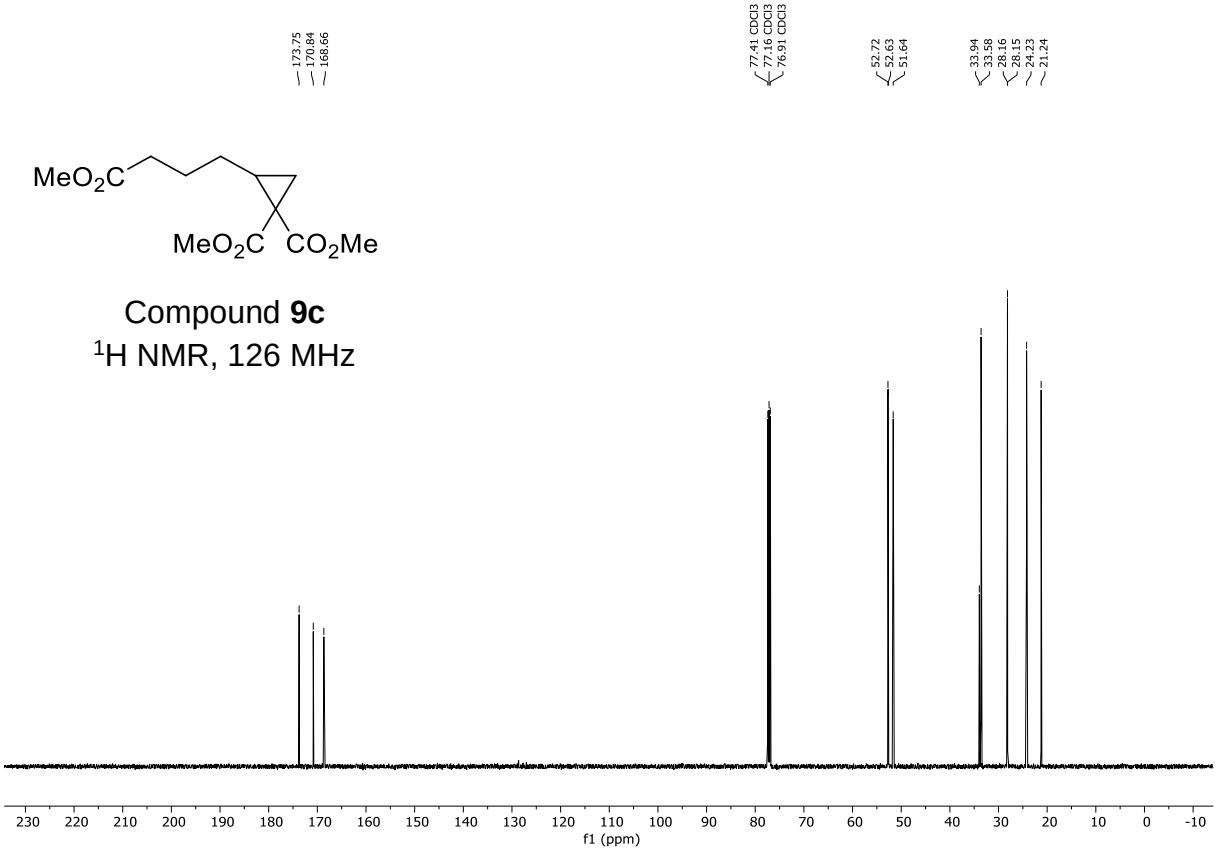
Compound **9b**
^{1}H NMR, 500 MHz

Compound **9b**
^{13}C NMR, 126 MHz

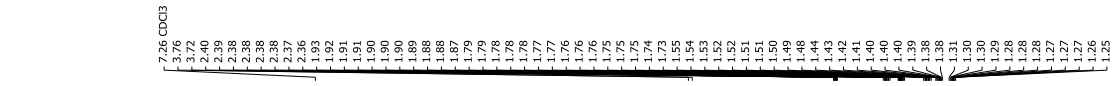


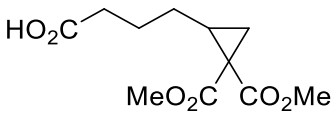


Compound **9c**
^{1}H NMR, 500 MHz

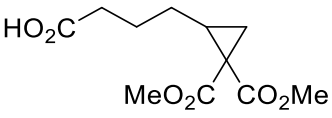


Compound **9c**
^{1}H NMR, 126 MHz

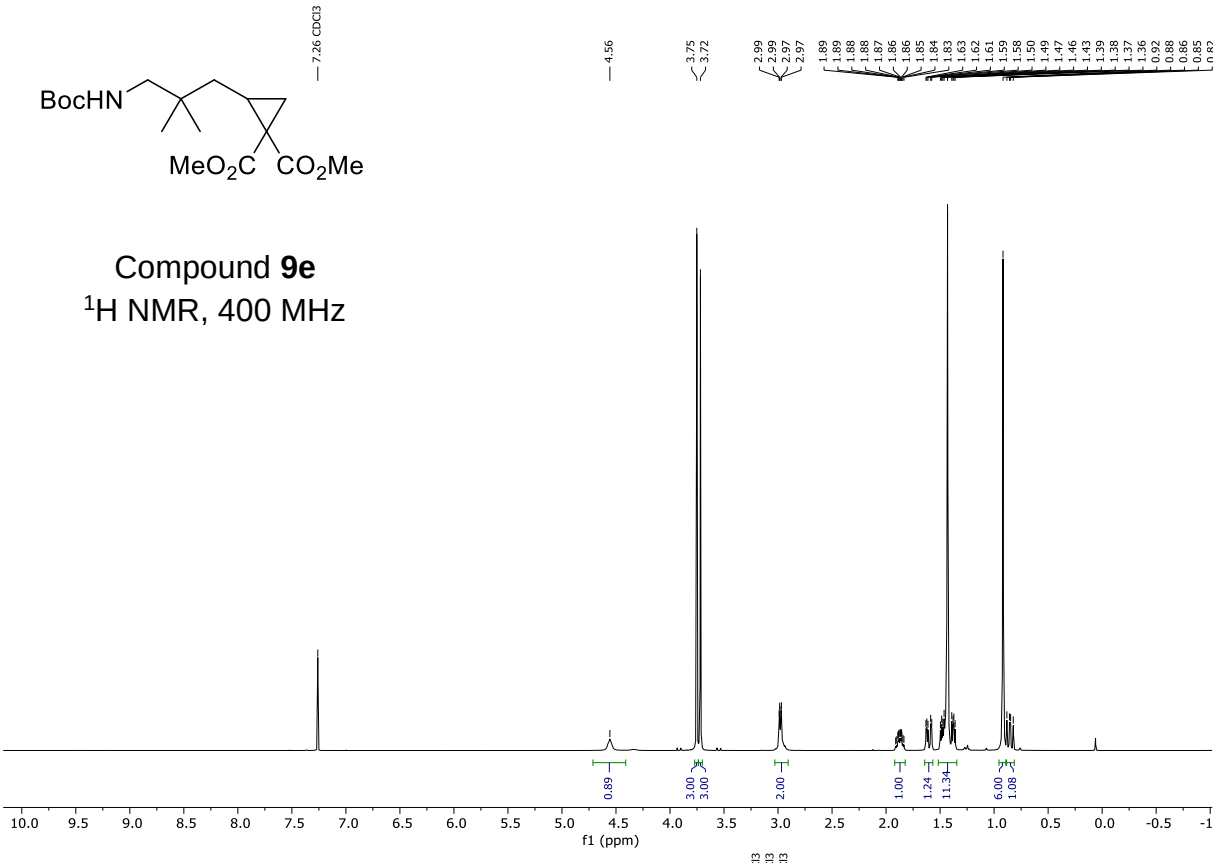




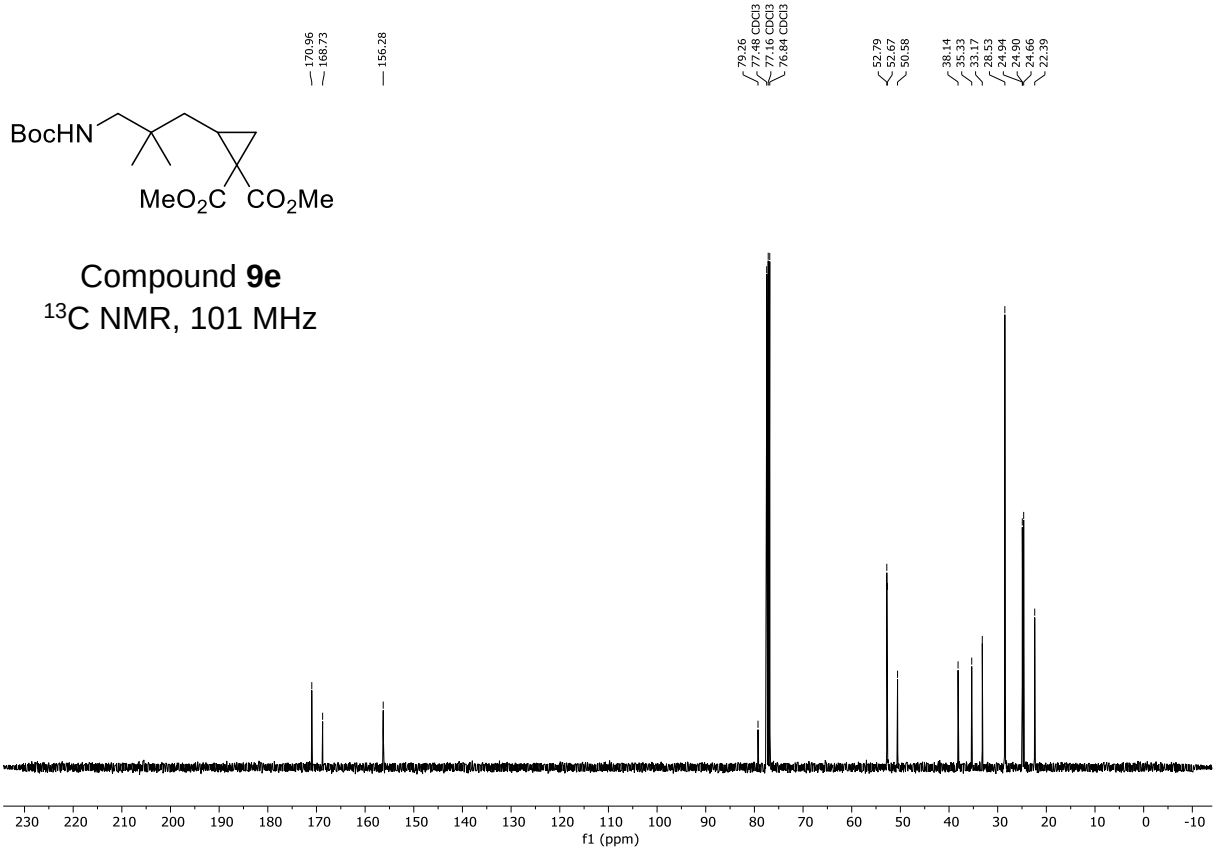
Compound **9d**
^{1}H NMR, 500 MHz



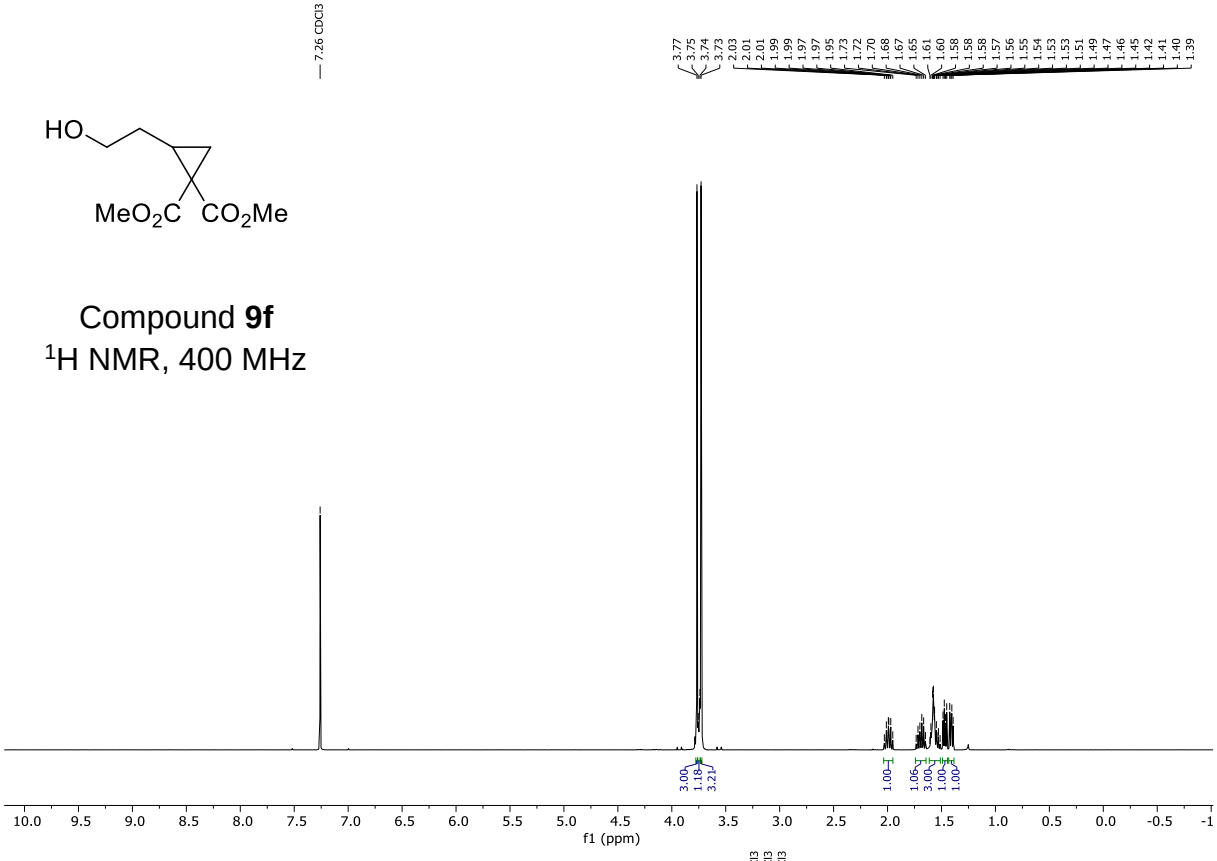
Compound **9d**
^{1}H NMR, 126 MHz



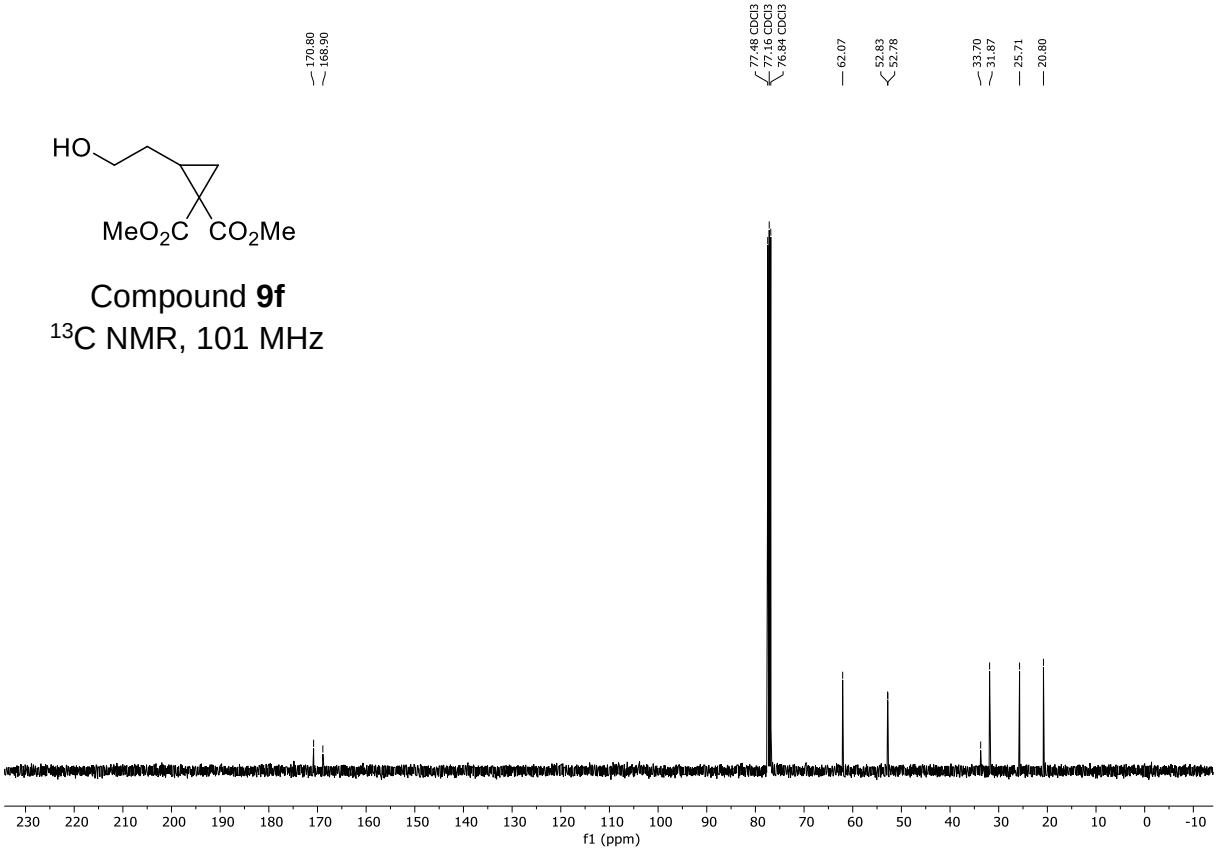
Compound **9e**
^{1}H NMR, 400 MHz



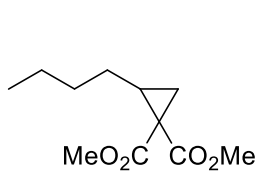
Compound **9e**
^{13}C NMR, 101 MHz



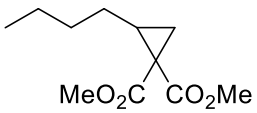
Compound **9f**
^{1}H NMR, 400 MHz



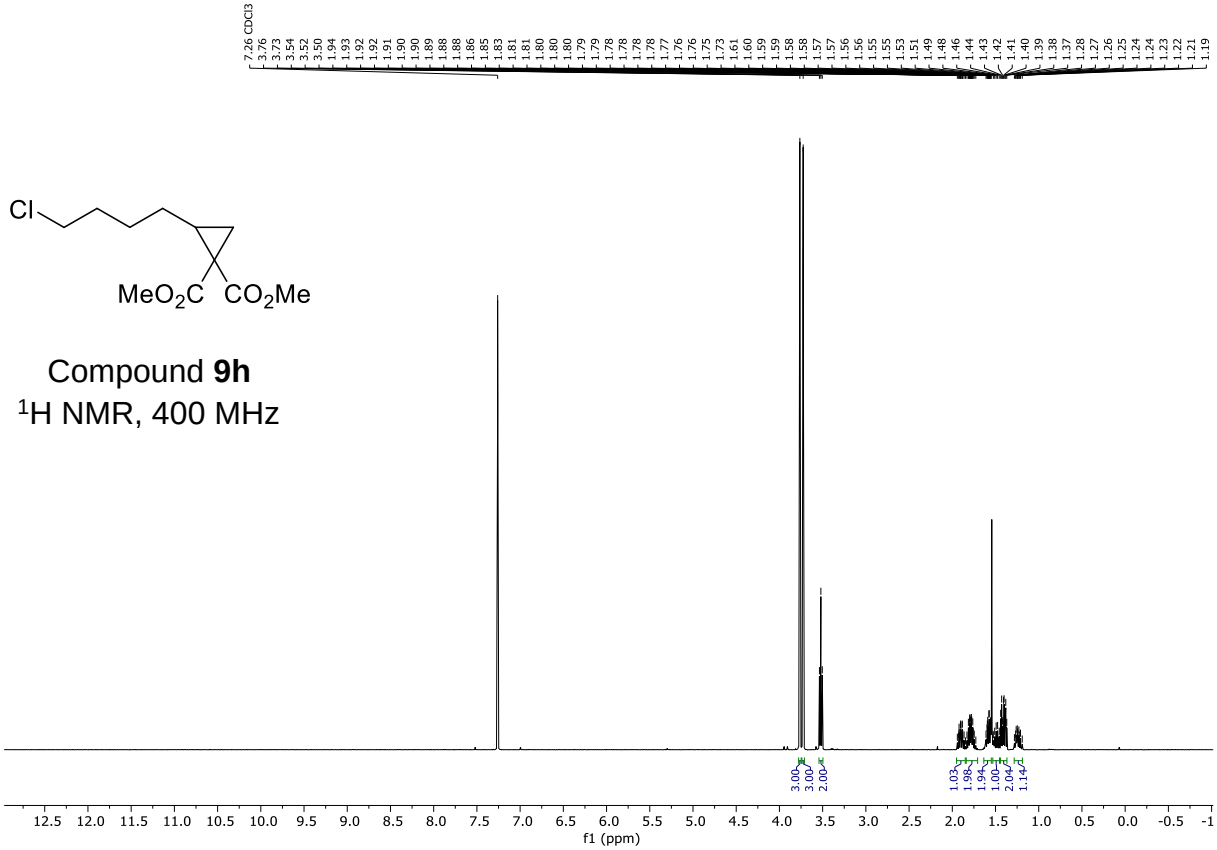
Compound **9f**
^{13}C NMR, 101 MHz



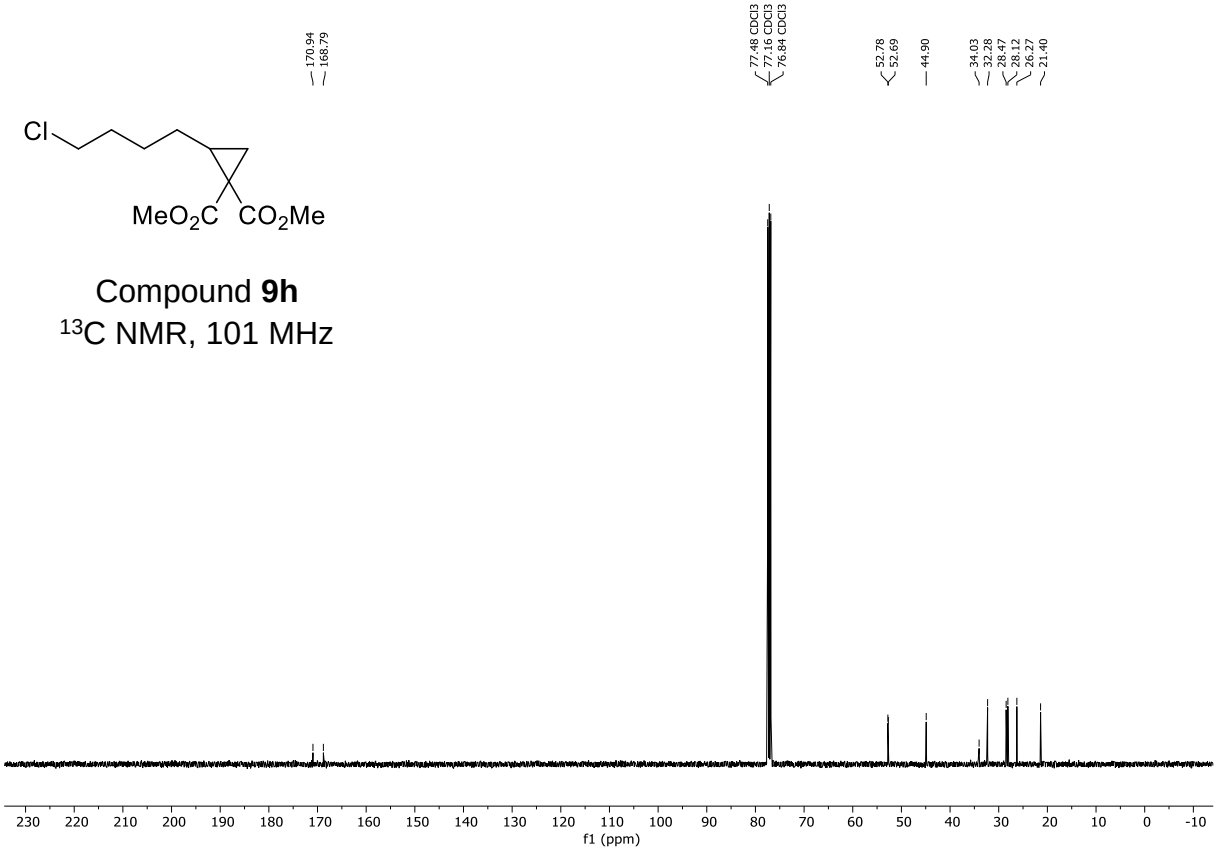
Compound **9g**
^{1}H NMR, 400 MHz



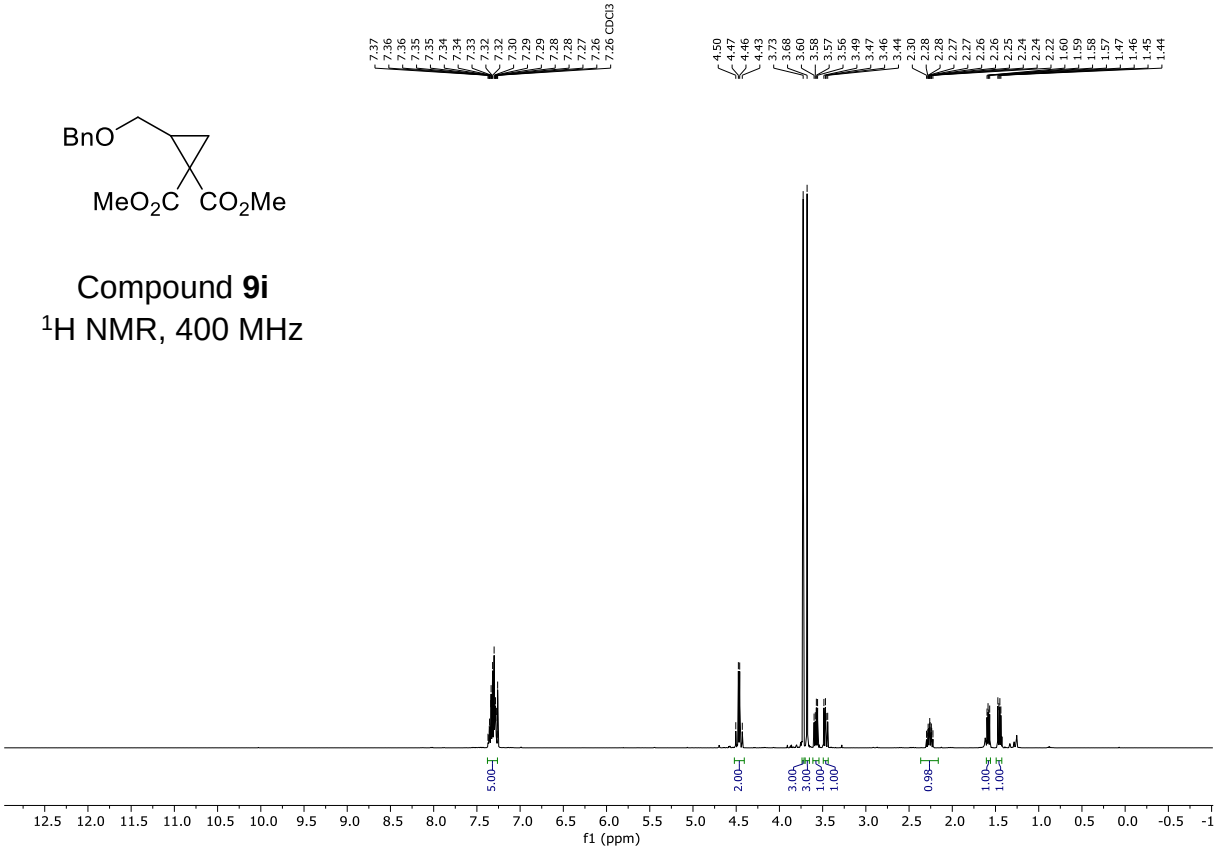
Compound **9g**
^{13}C NMR, 101 MHz



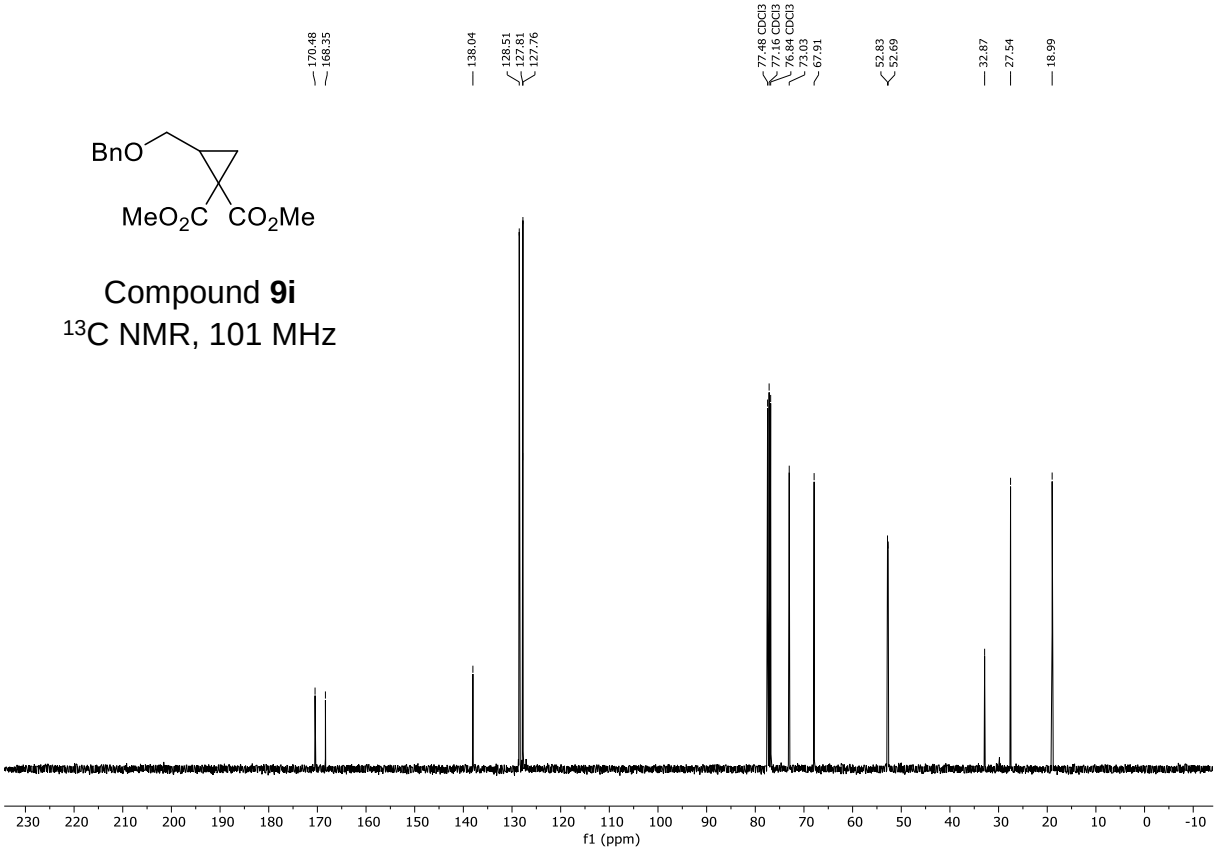
Compound **9h**
^{1}H NMR, 400 MHz



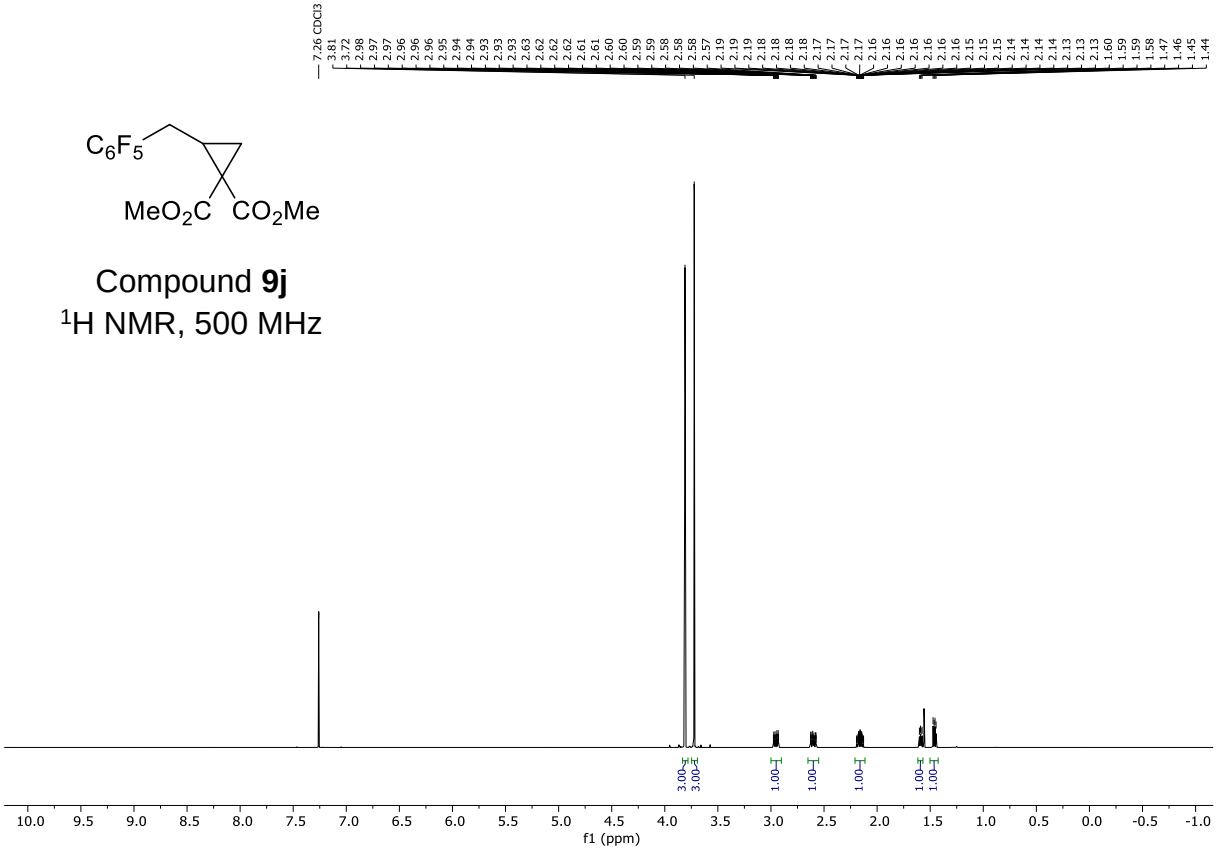
Compound **9h**
^{13}C NMR, 101 MHz



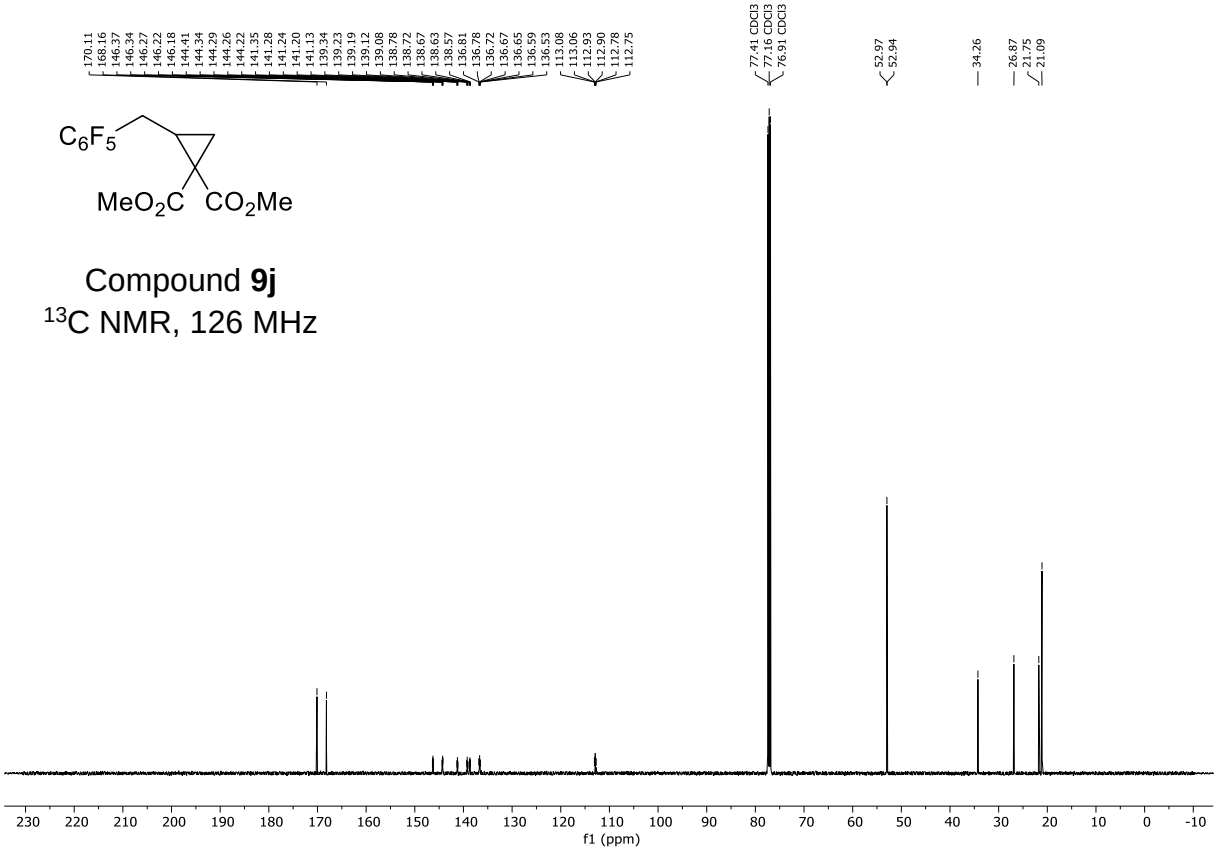
Compound **9i**
^{1}H NMR, 400 MHz



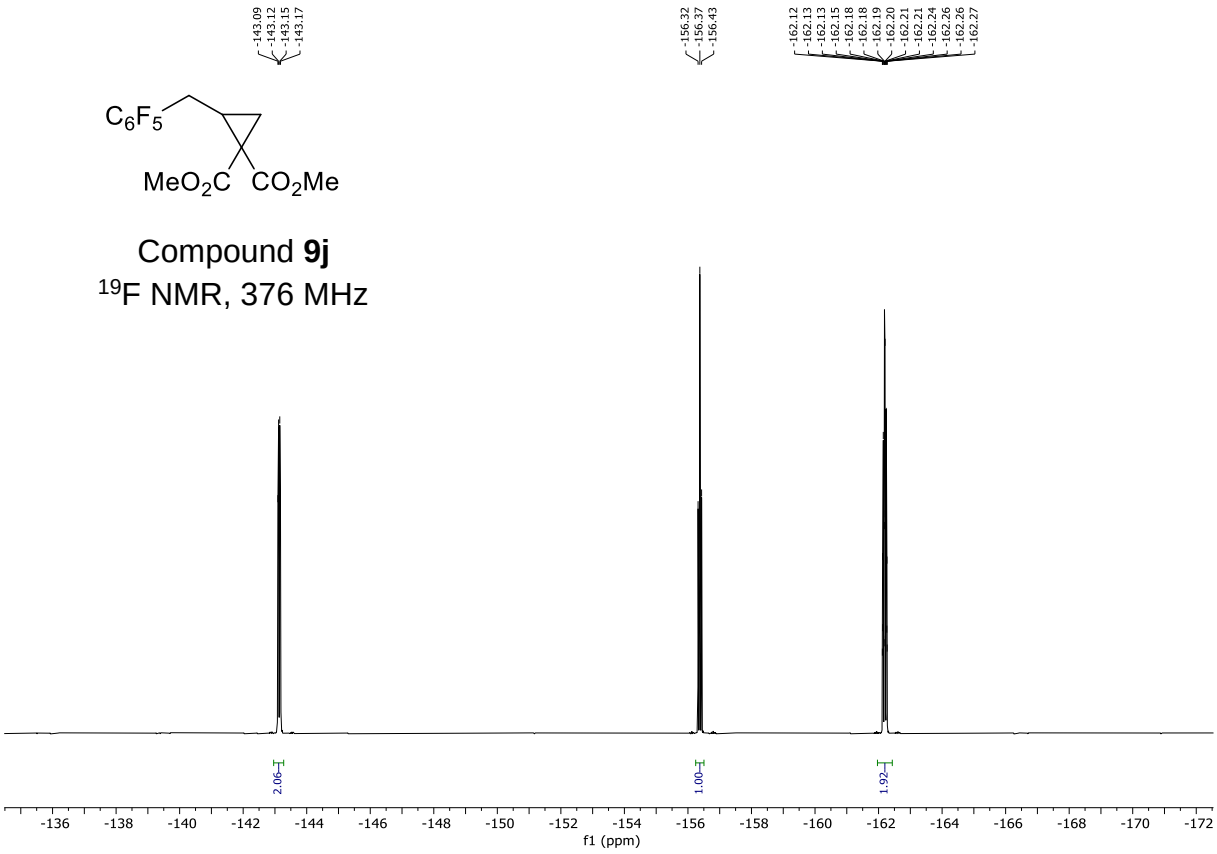
Compound **9i**
^{13}C NMR, 101 MHz

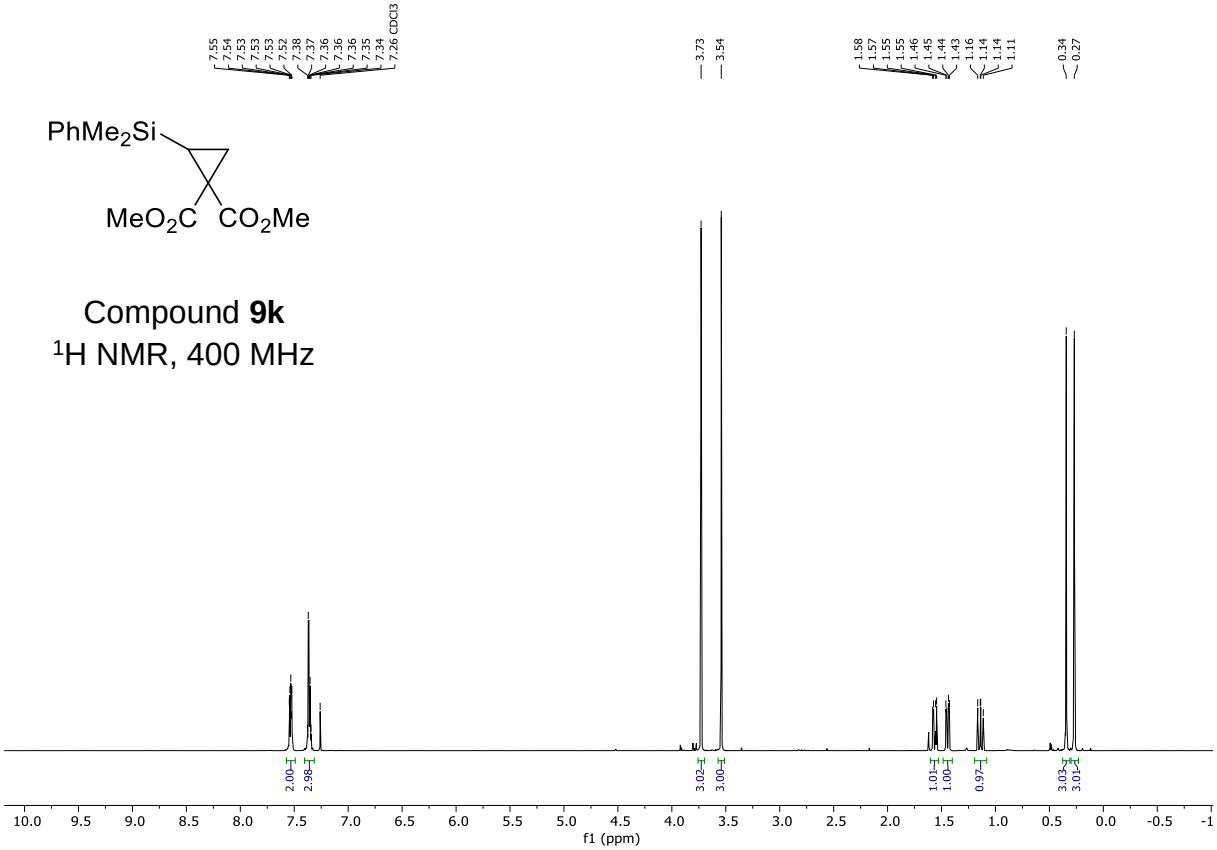


Compound **9j**
^{1}H NMR, 500 MHz

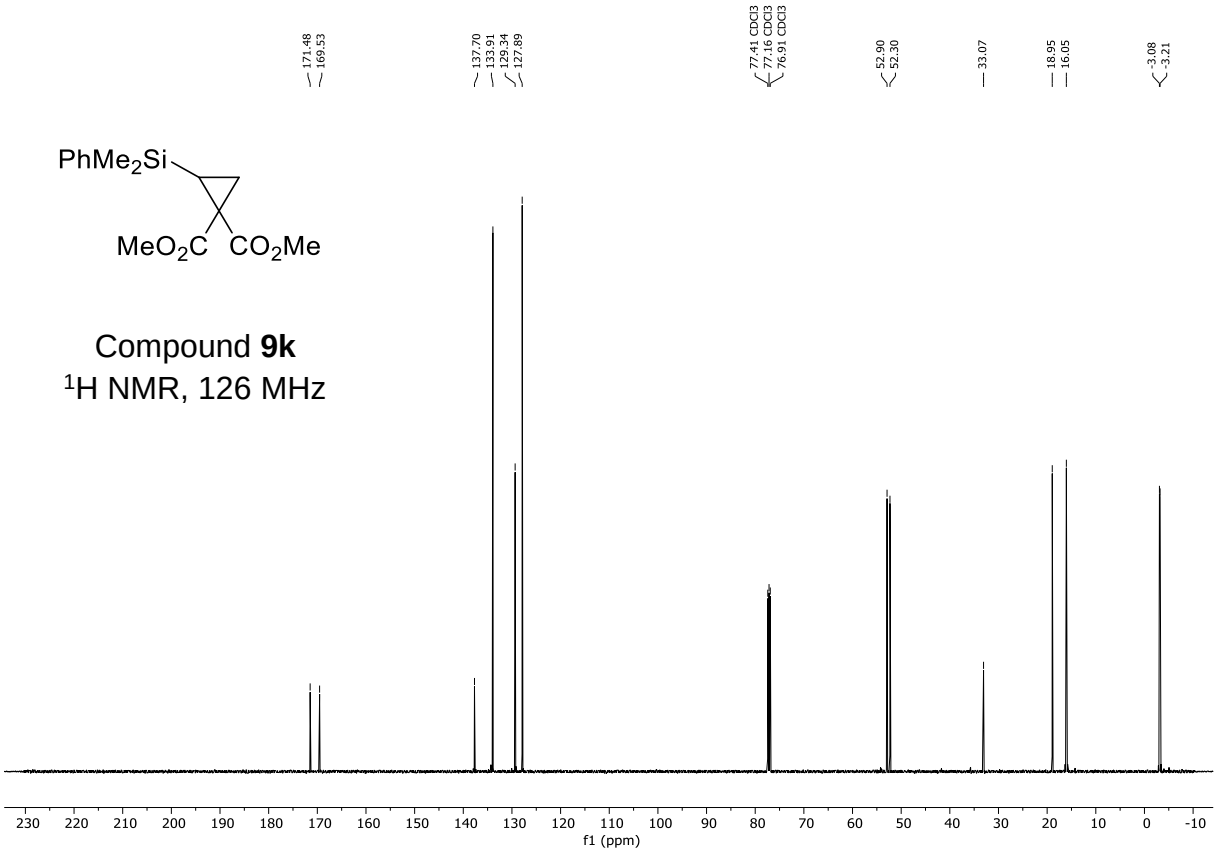


Compound **9j**
^{13}C NMR, 126 MHz

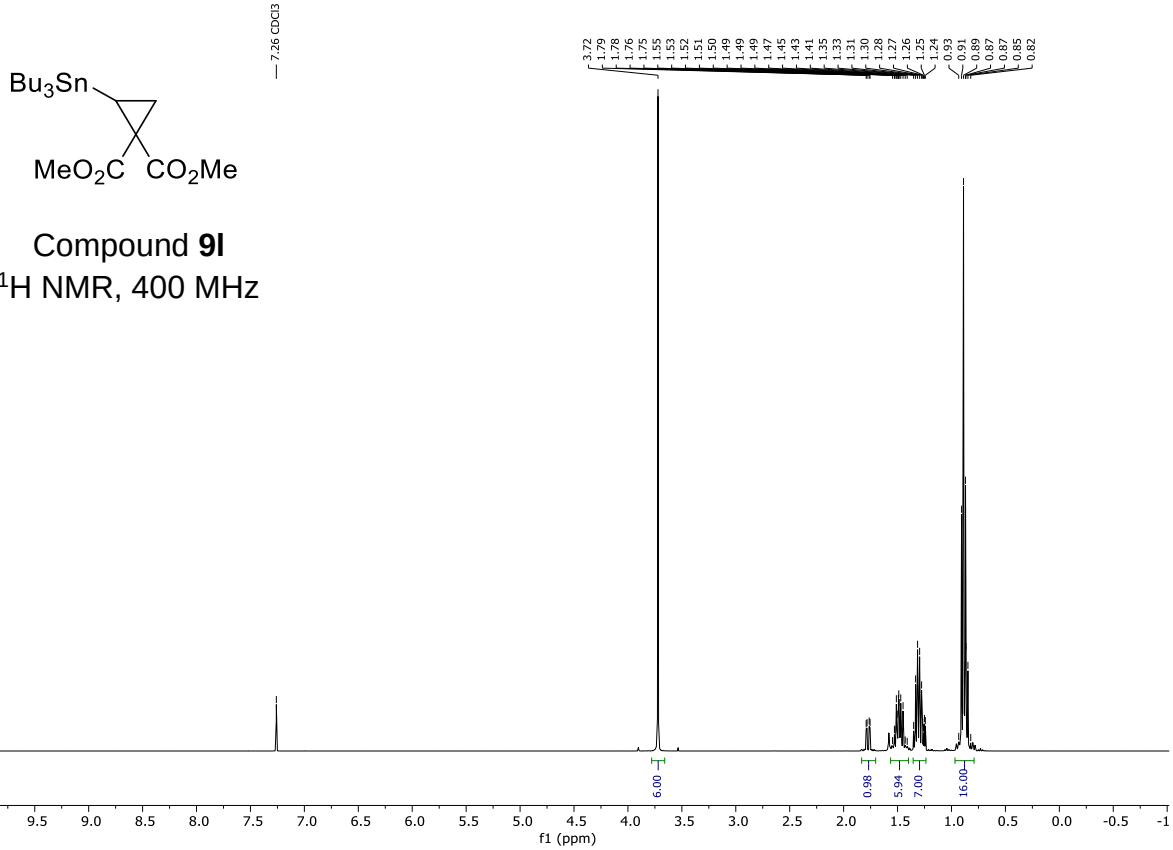

-143.09
-143.12
-143.15
-143.17
-156.32
-156.37
-156.43
-162.12
-162.13
-162.13
-162.15
-162.18
-162.18
-162.19
-162.20
-162.21
-162.21
-162.24
-162.26
-162.26
-162.27
C6F5
MeO2C
CO2Me
Compound 9j
19F NMR, 376 MHz
2.06
1.00
1.92
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
-158
-160
-162
-164
-166
-168
-170
-172
f1 (ppm)



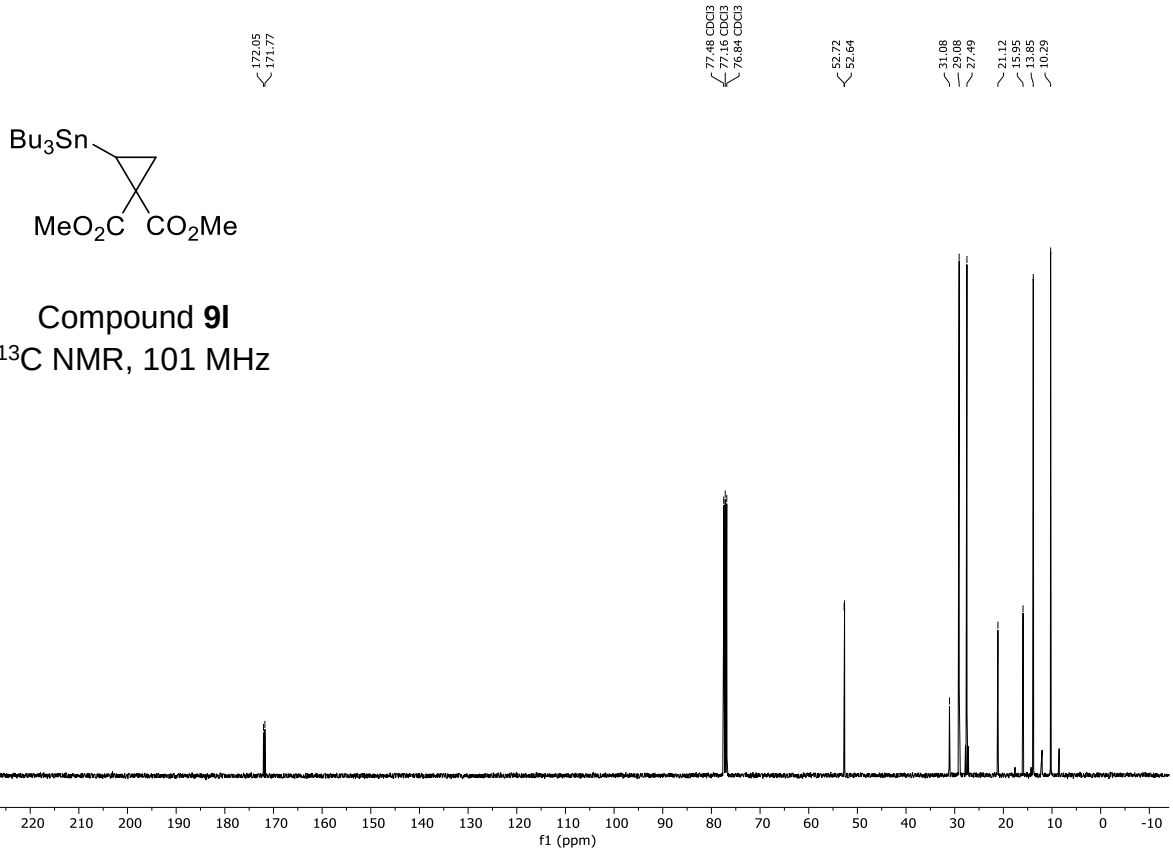
Compound **9k**
^{1}H NMR, 400 MHz



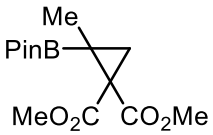
Compound **9k**
^{1}H NMR, 126 MHz



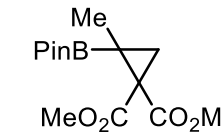
Compound **9l**
^{1}H NMR, 400 MHz



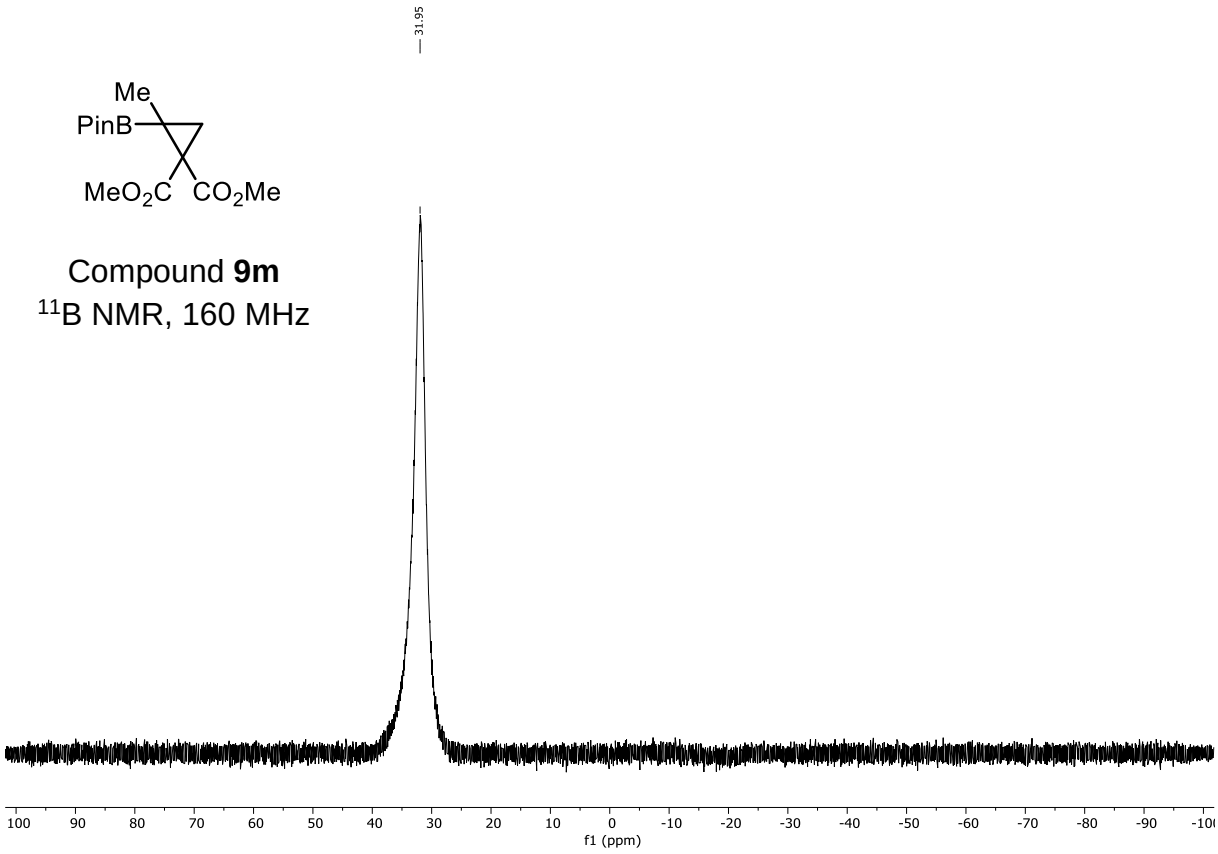
Compound **9l**
^{13}C NMR, 101 MHz

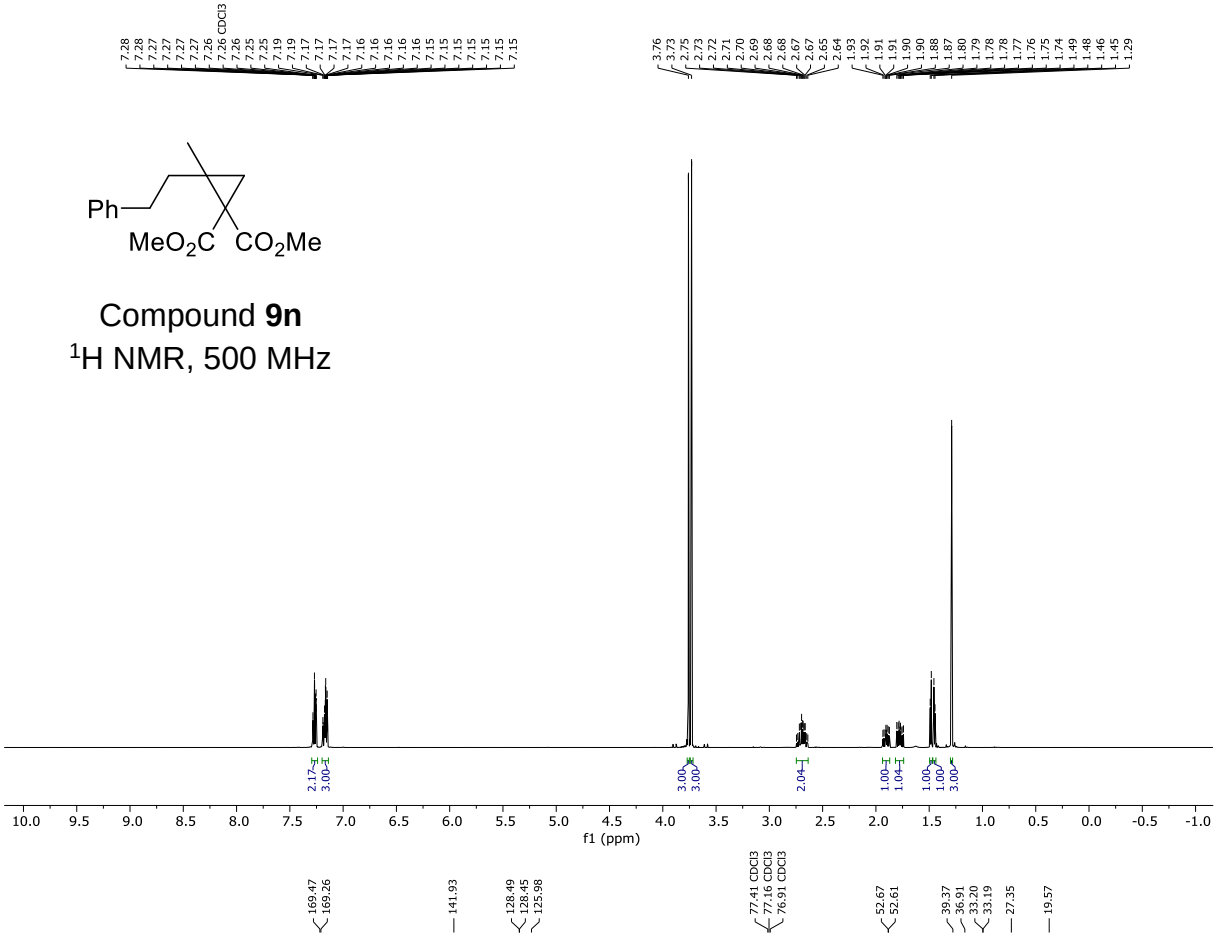


Compound **9m**
^{1}H NMR, 500 MHz

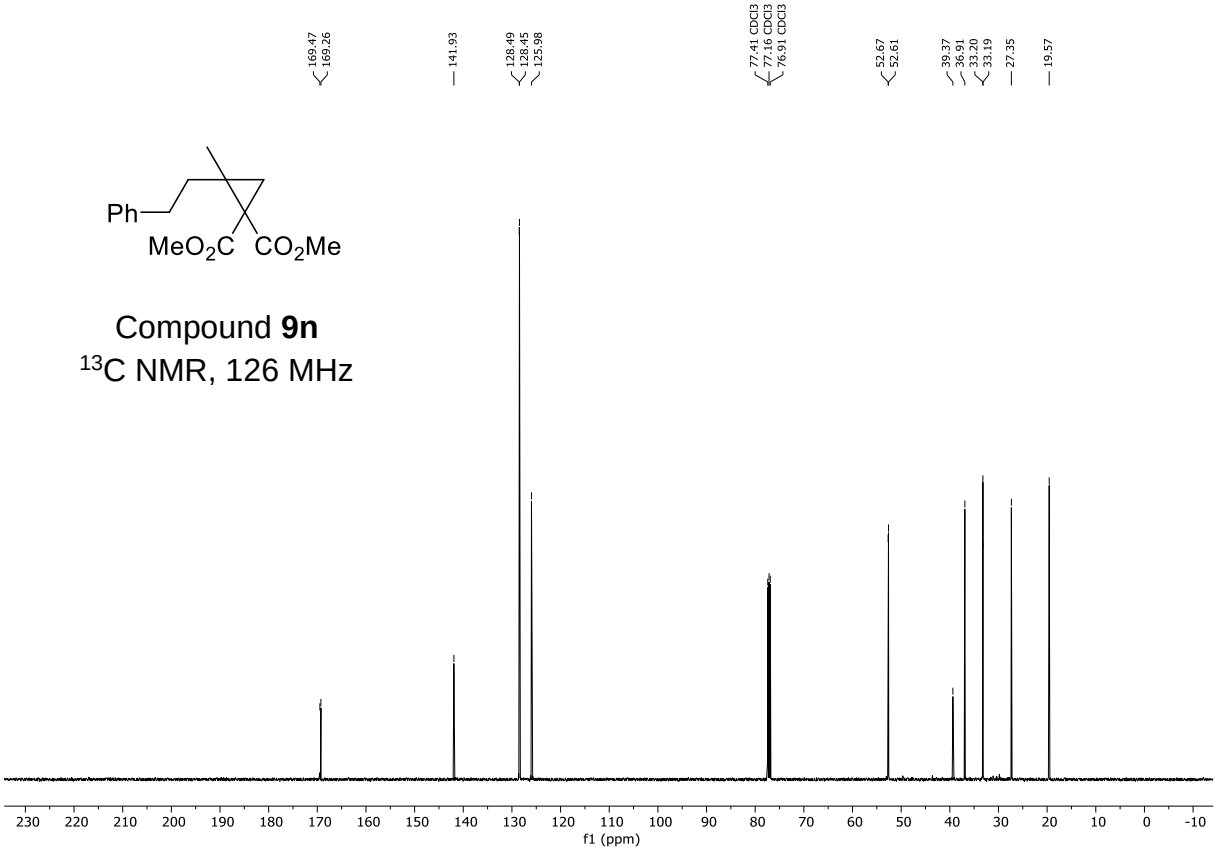


Compound **9m**
^{13}C NMR, 126 MHz

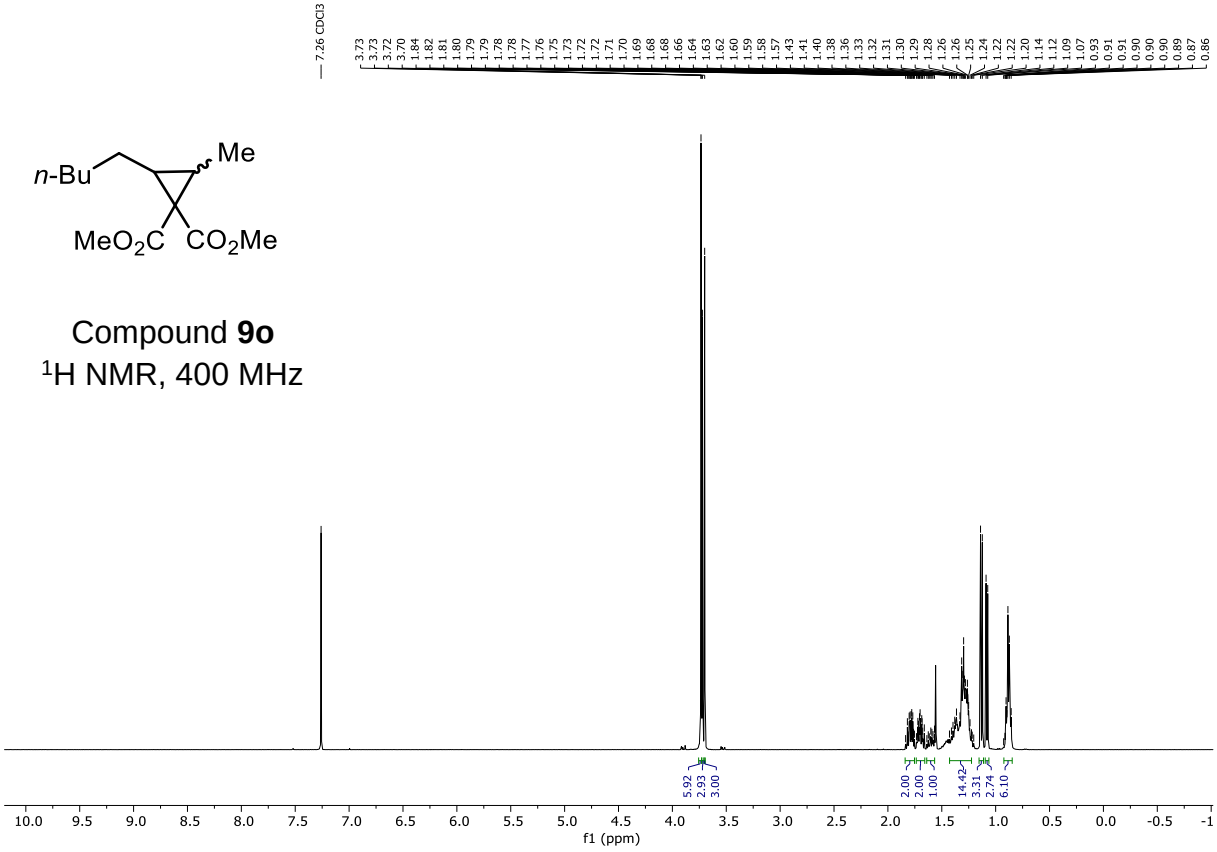

31.95
Me
PinB
MeO2C
CO2Me
Compound 9m
11B NMR, 160 MHz
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)



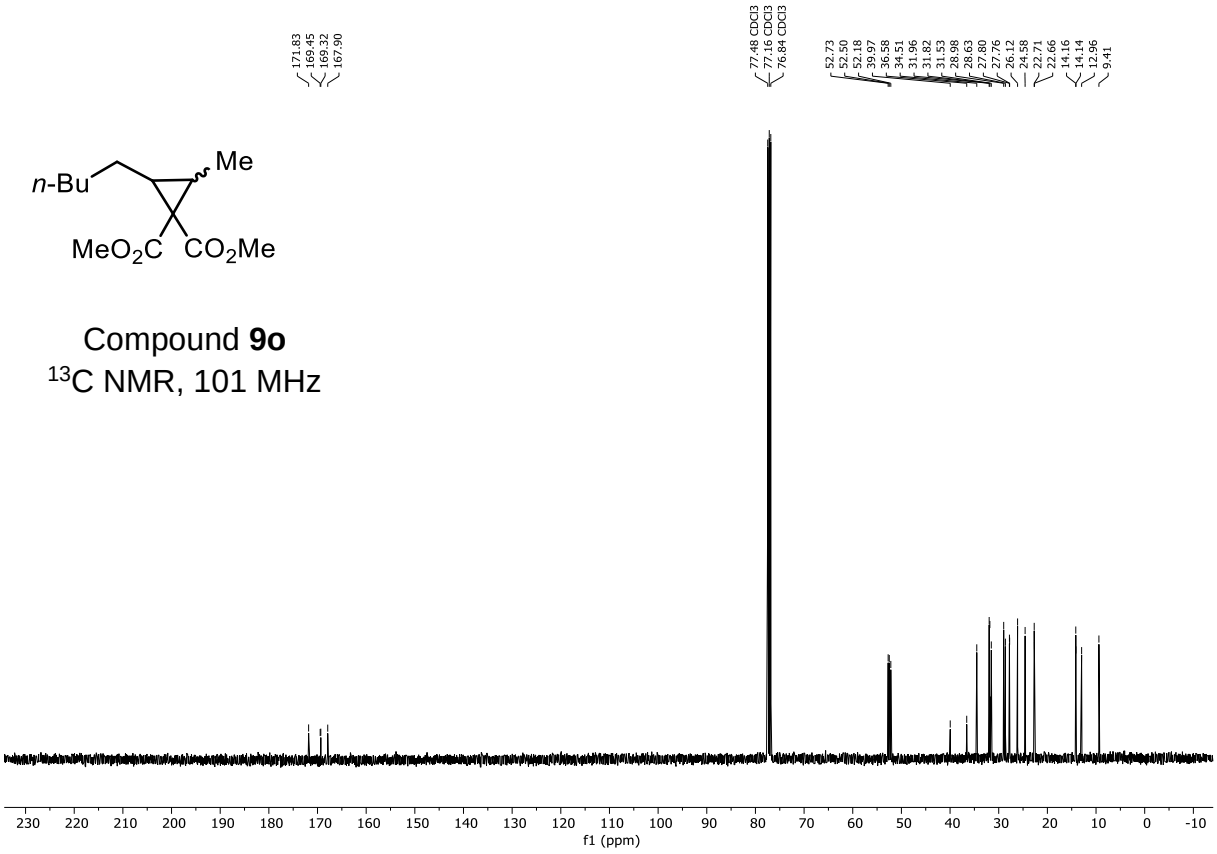
Compound **9n**
^{1}H NMR, 500 MHz



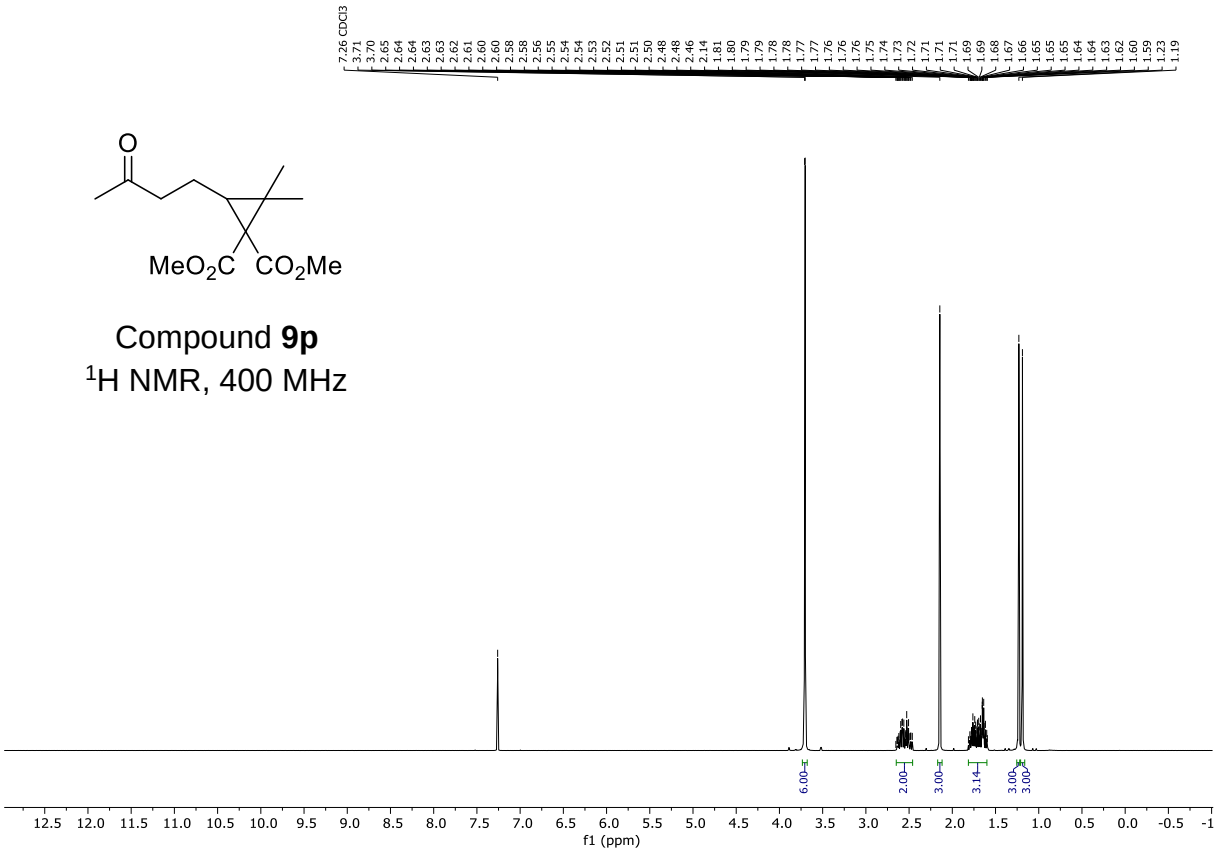
Compound **9n**
^{13}C NMR, 126 MHz



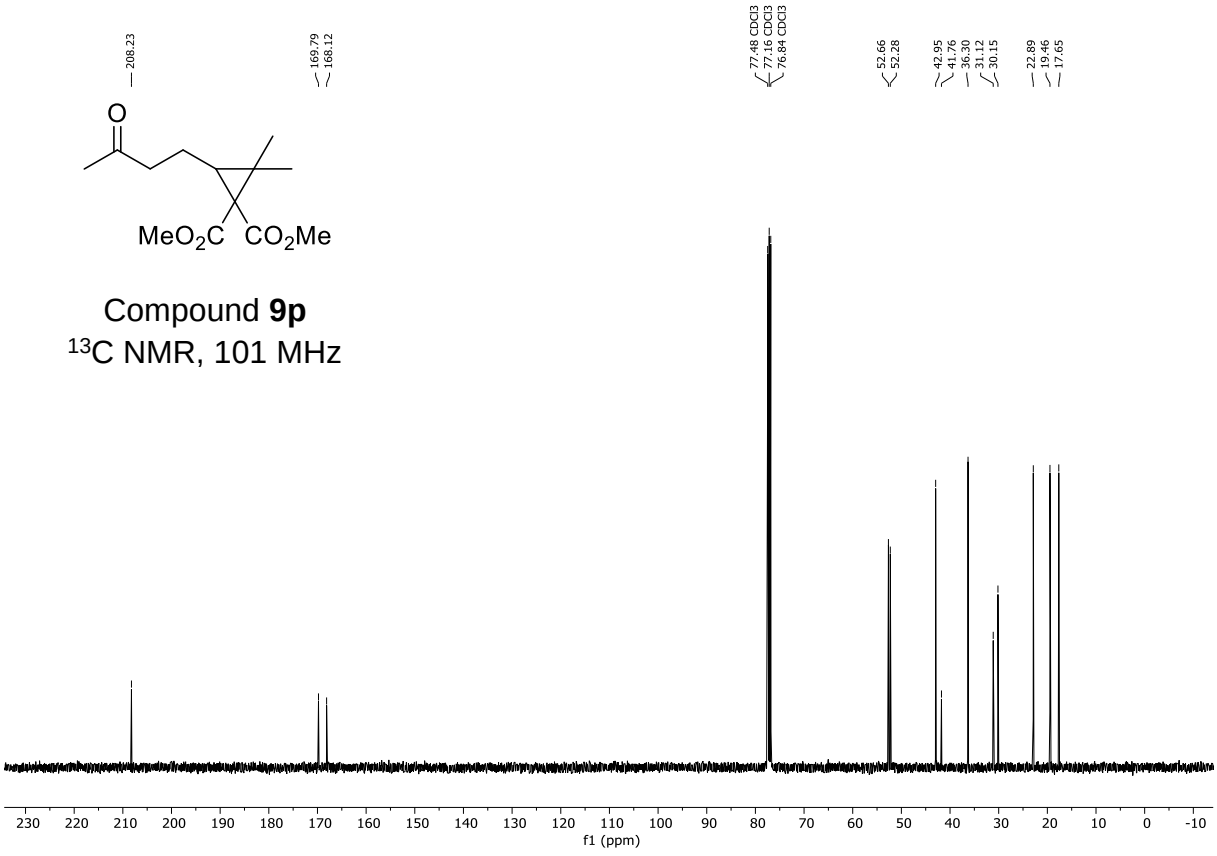
Compound **9o**
^{1}H NMR, 400 MHz



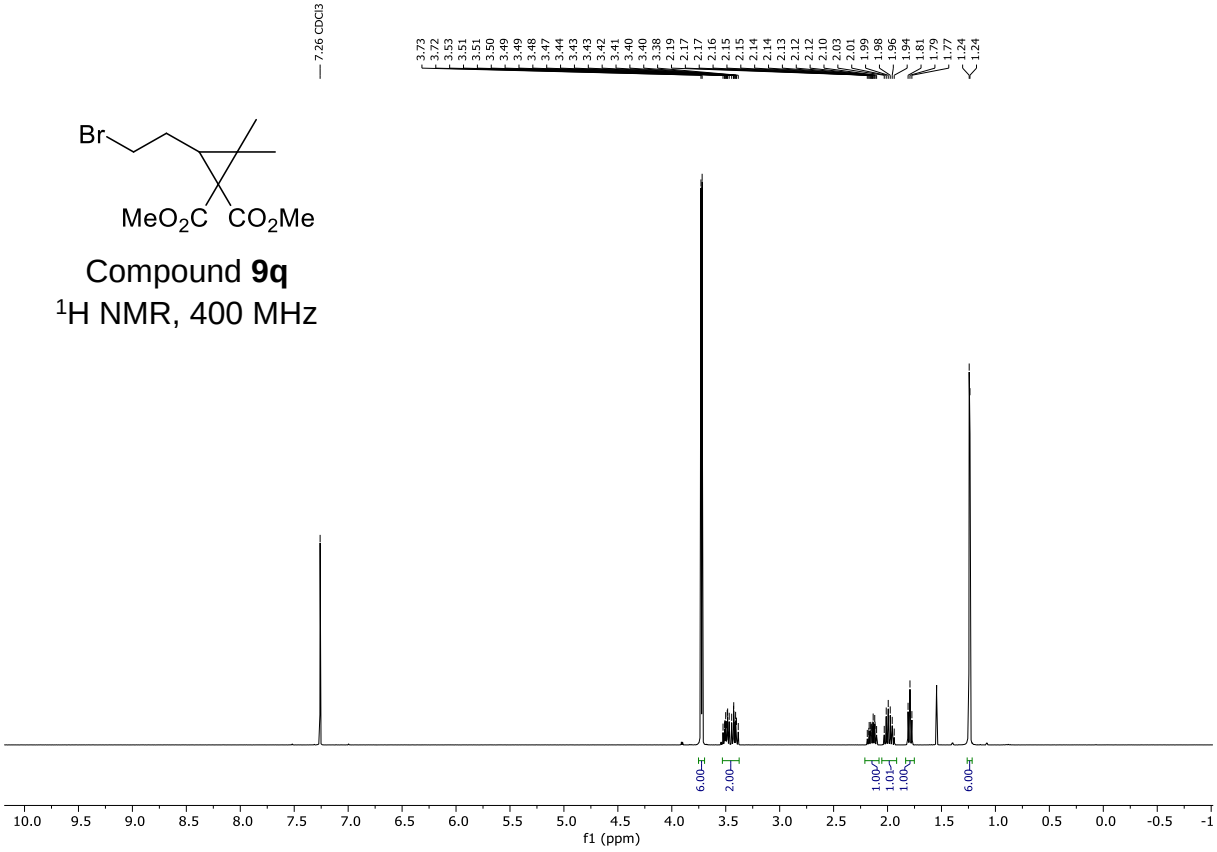
Compound **9o**
^{13}C NMR, 101 MHz



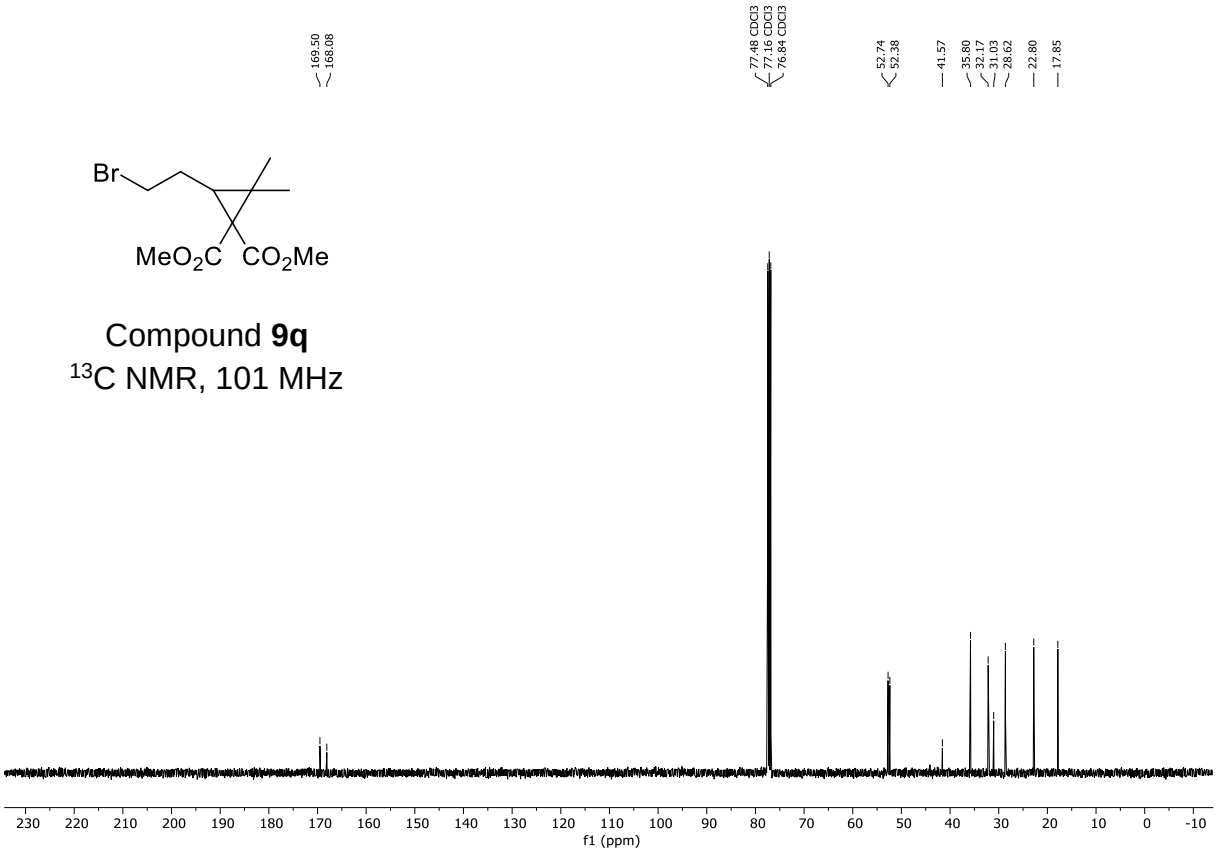
Compound **9p**
^{1}H NMR, 400 MHz



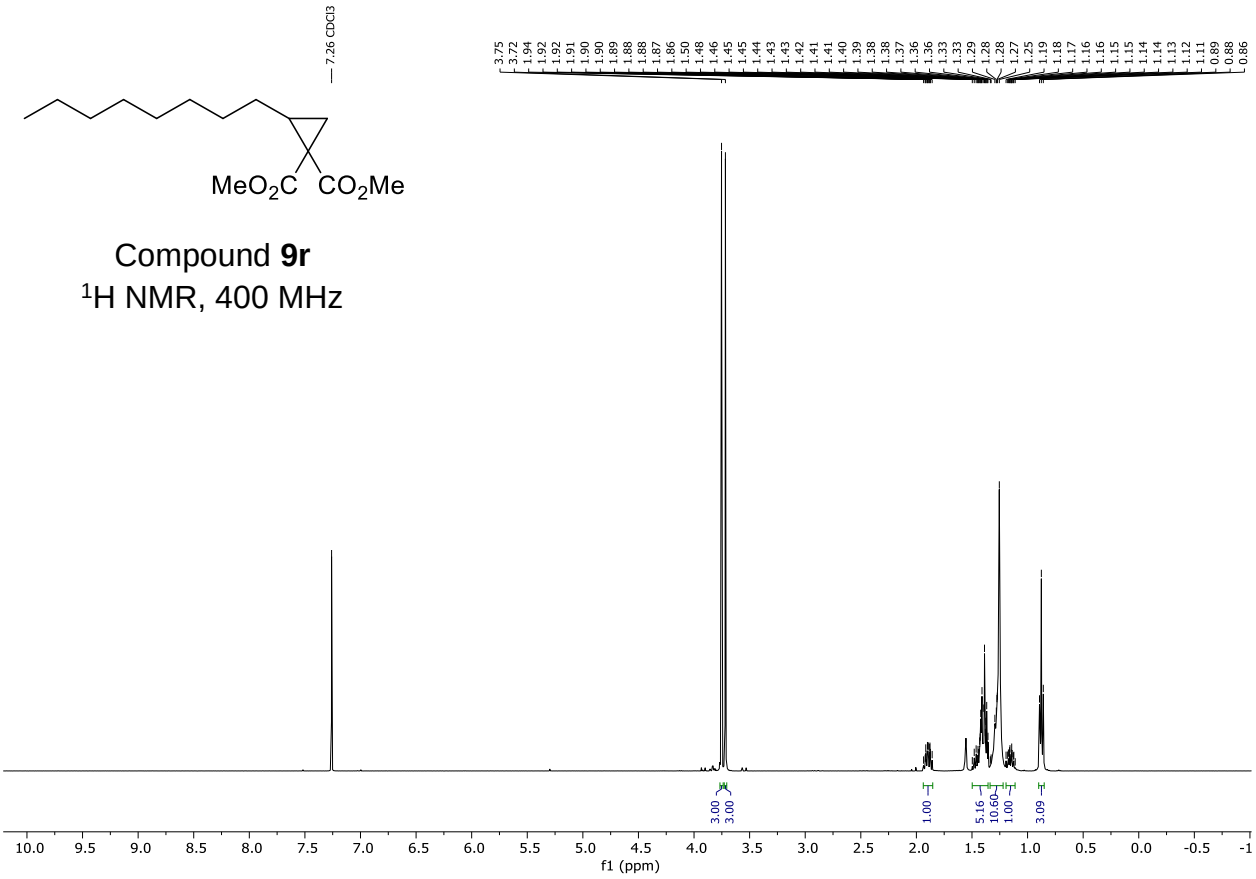
Compound **9p**
^{13}C NMR, 101 MHz



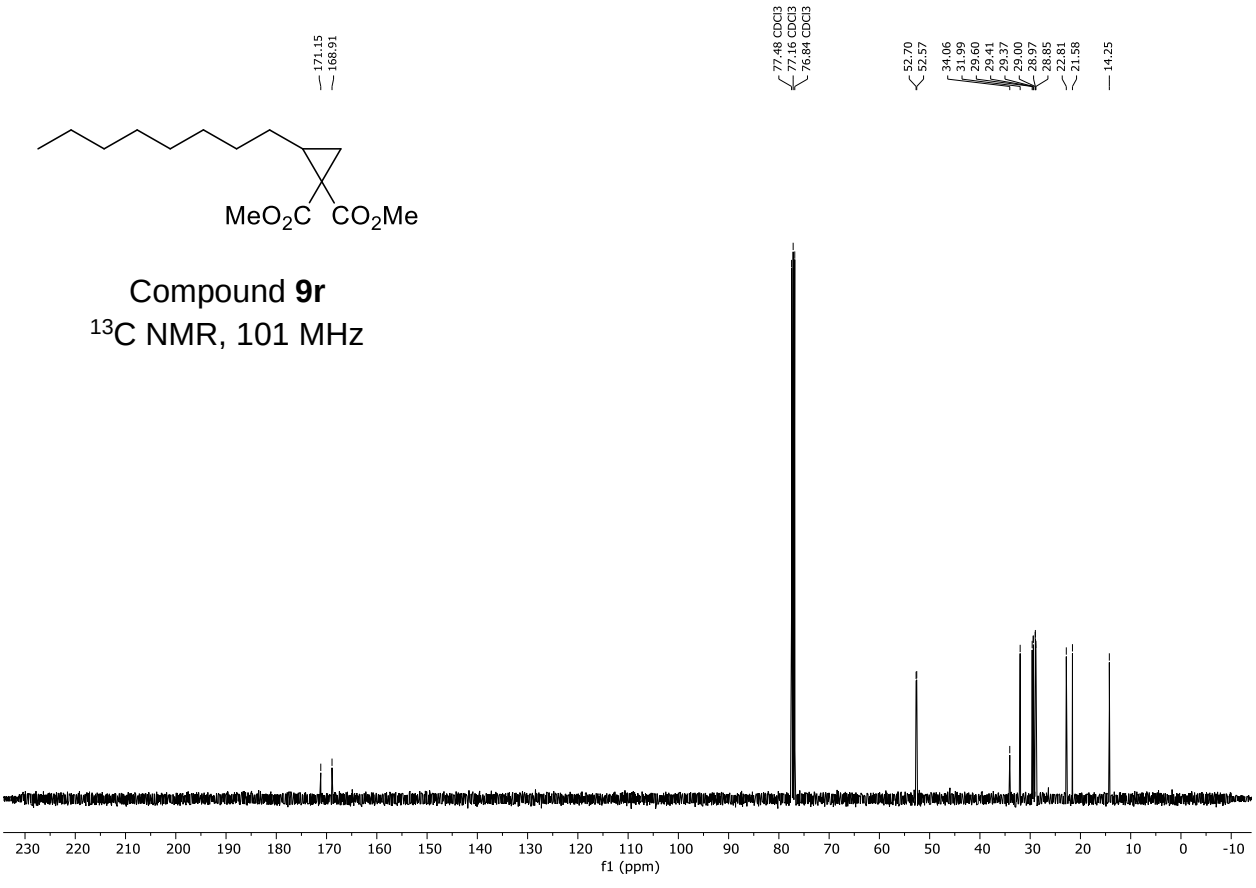
Compound **9q**
^{1}H NMR, 400 MHz



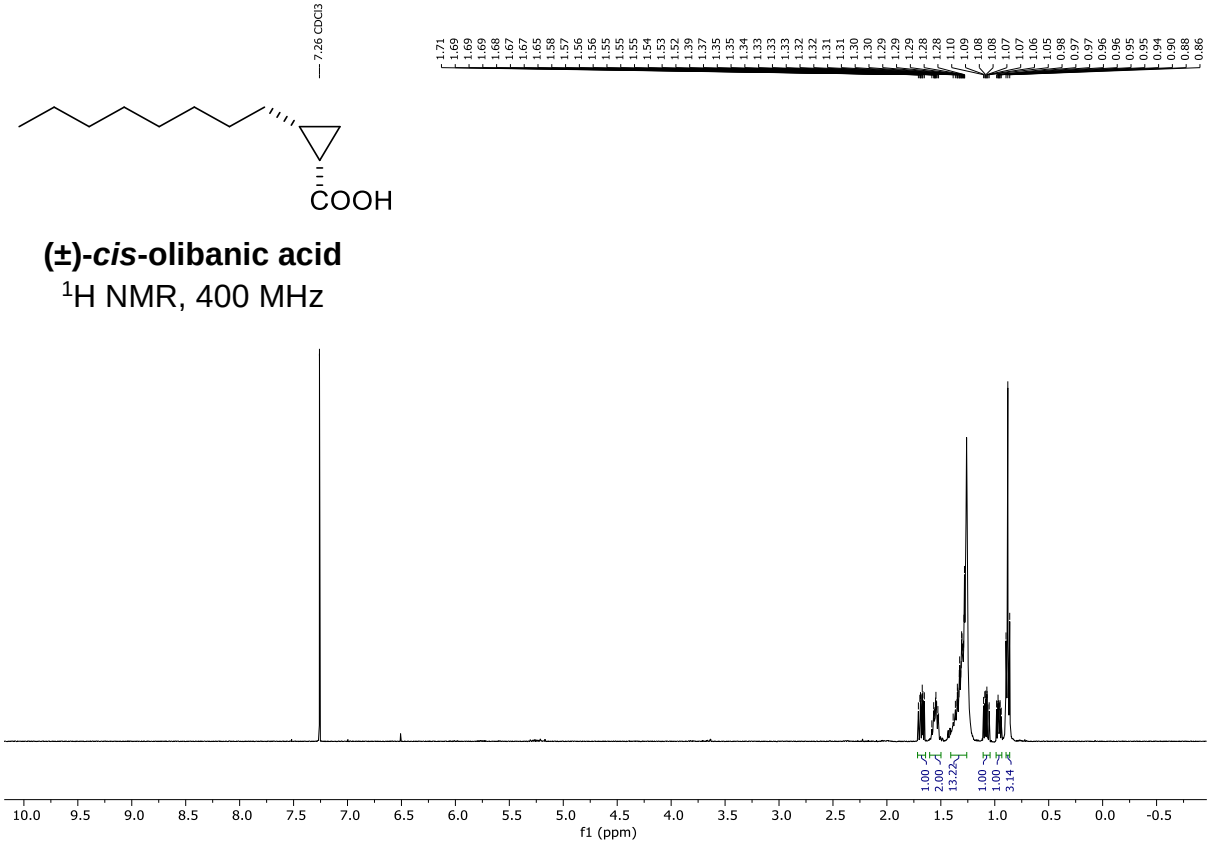
Compound **9q**
^{13}C NMR, 101 MHz



Compound **9r**
^{1}H NMR, 400 MHz

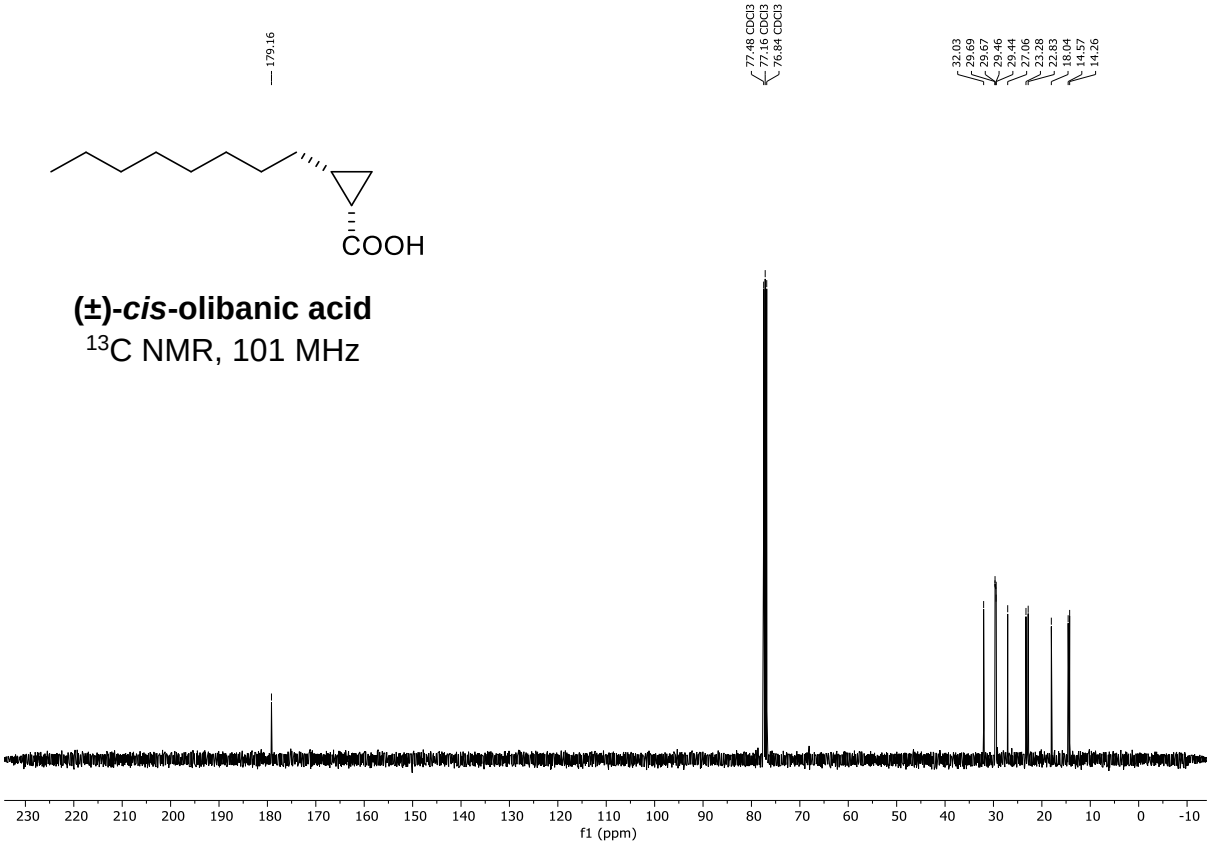


Compound **9r**
^{13}C NMR, 101 MHz



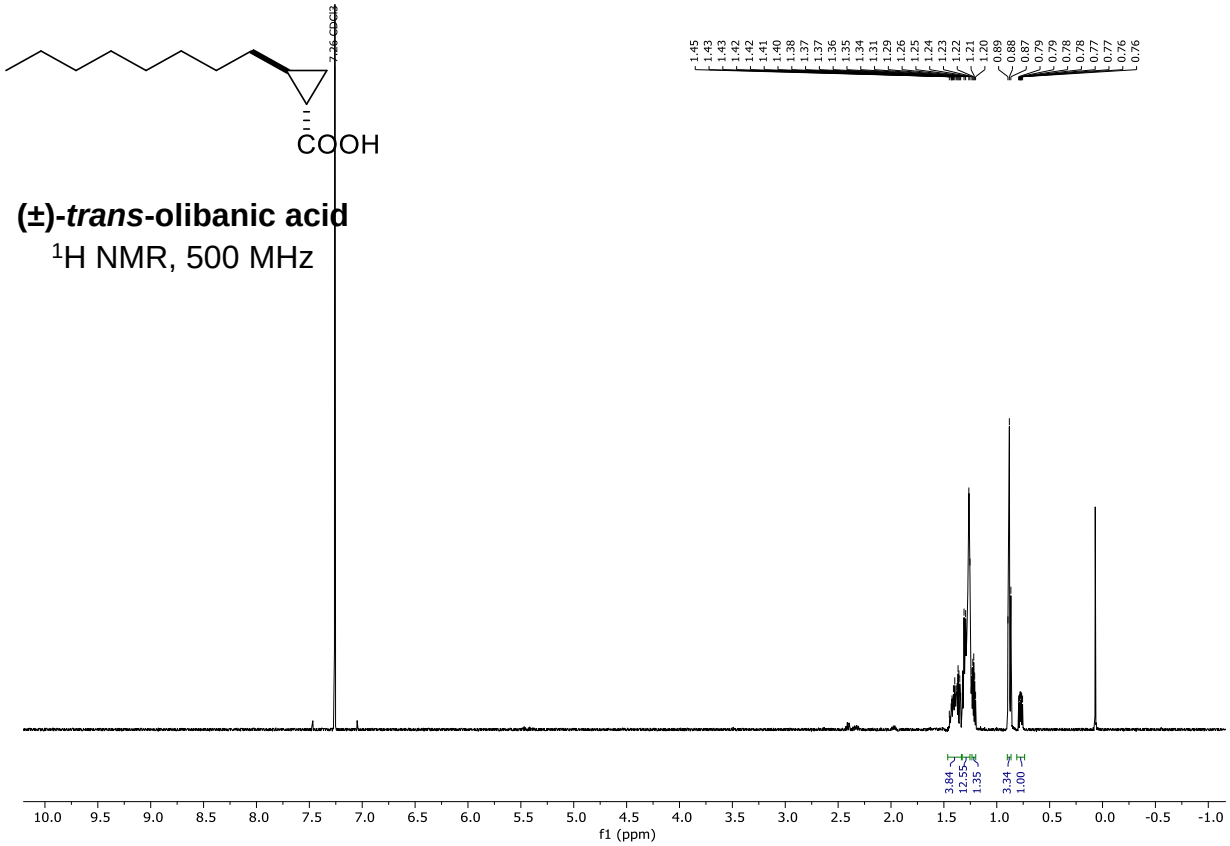
(±)-*cis*-olibanic acid

^{1}H NMR, 400 MHz



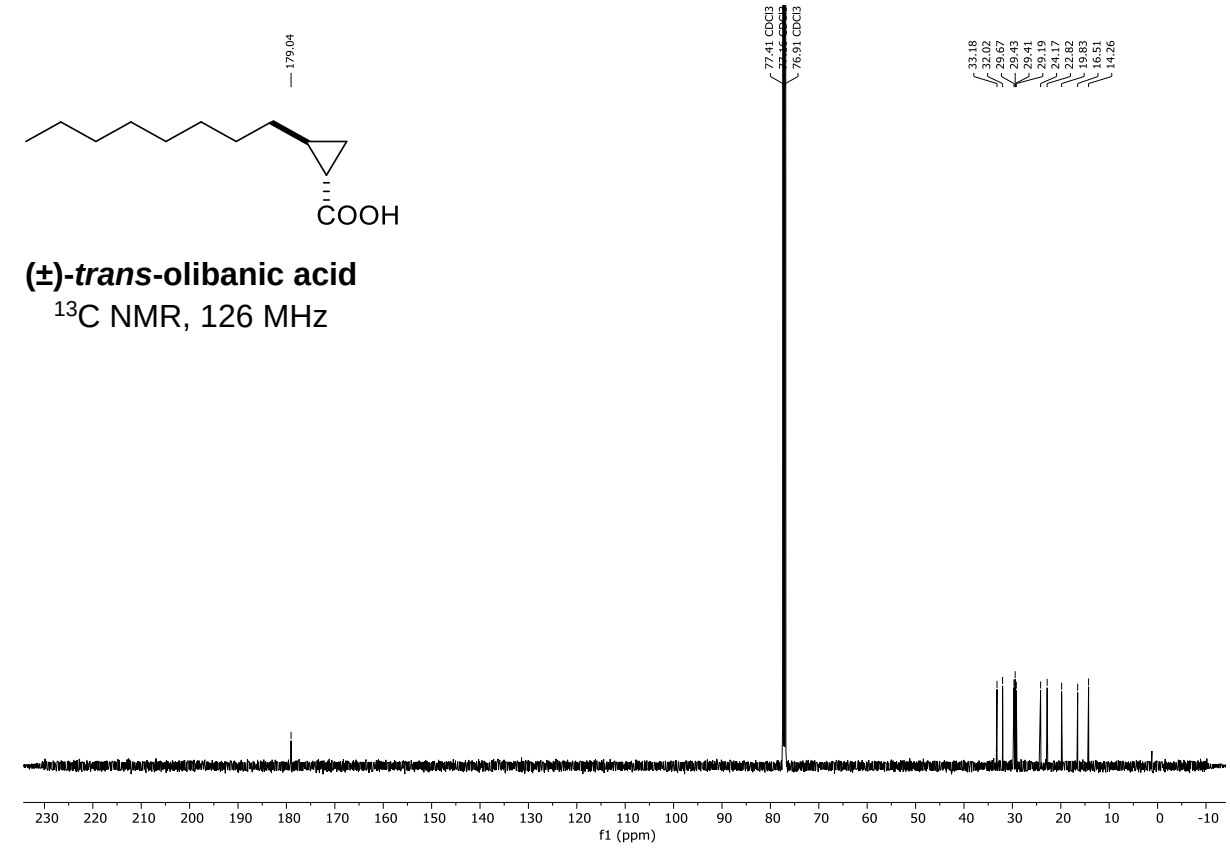
(±)-*cis*-olibanic acid

^{13}C NMR, 101 MHz



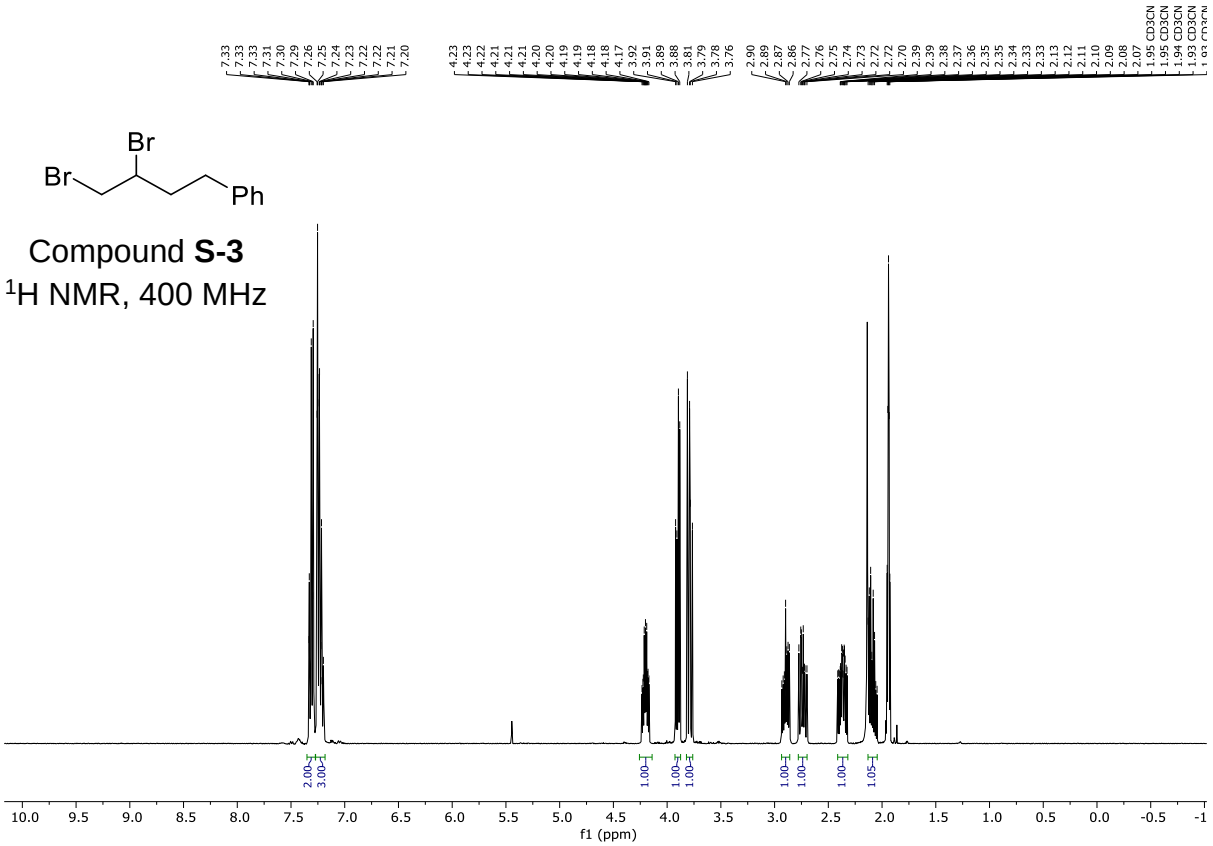
(±)-*trans*-olibanic acid

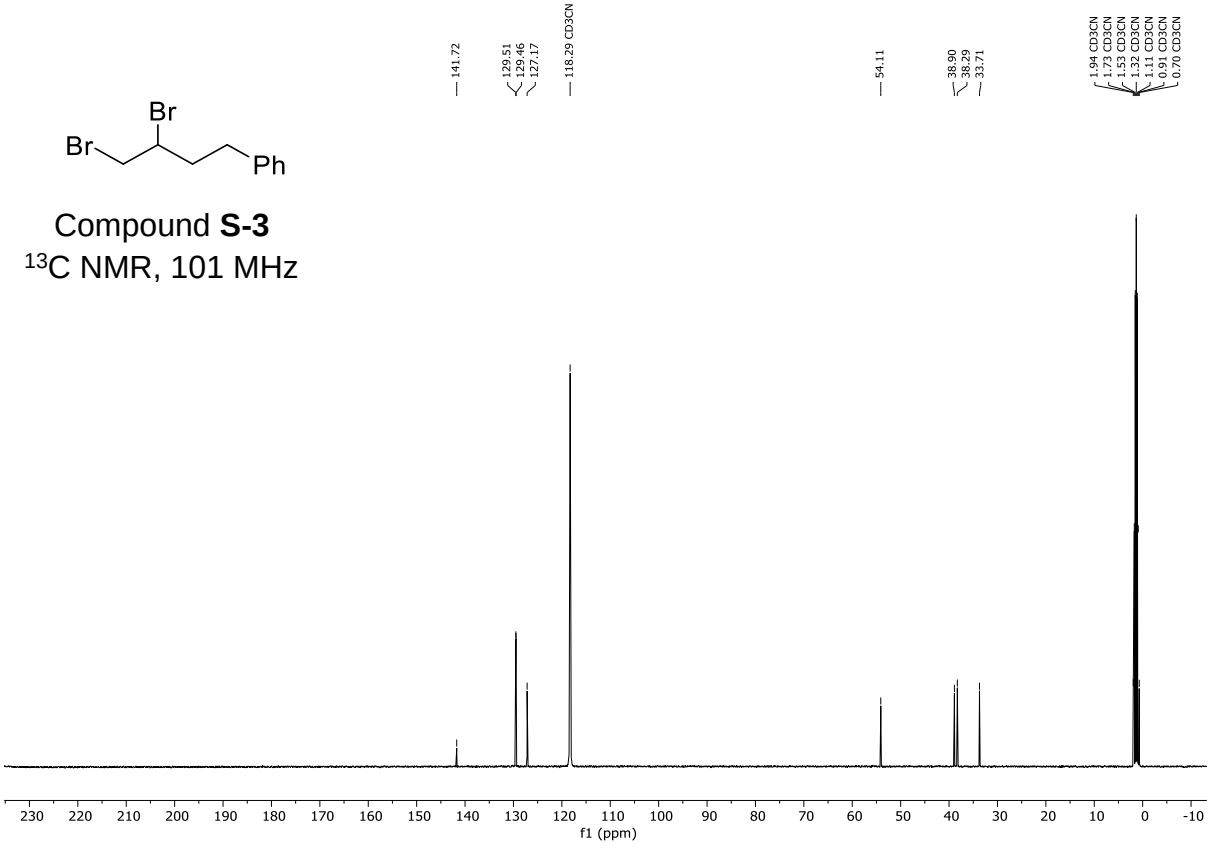
^{1}H NMR, 500 MHz

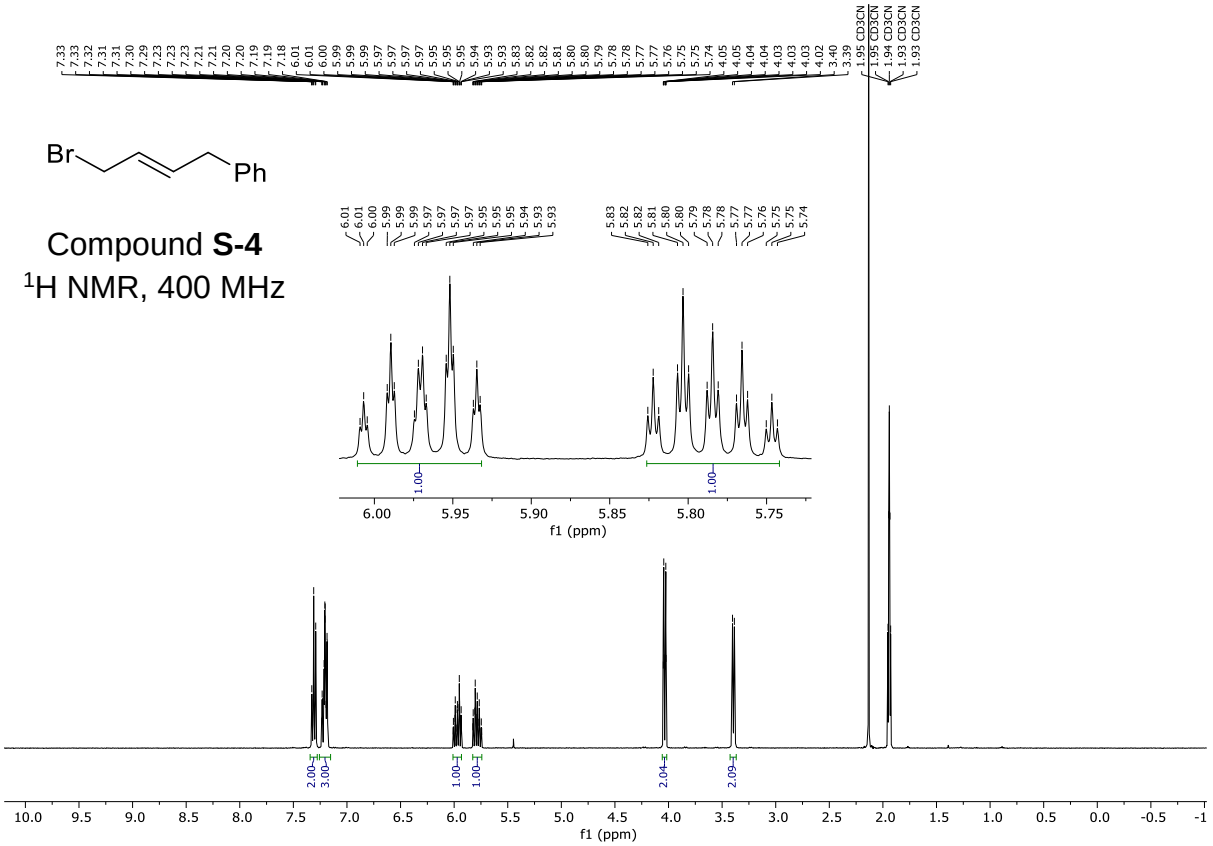


(±)-*trans*-olibanic acid

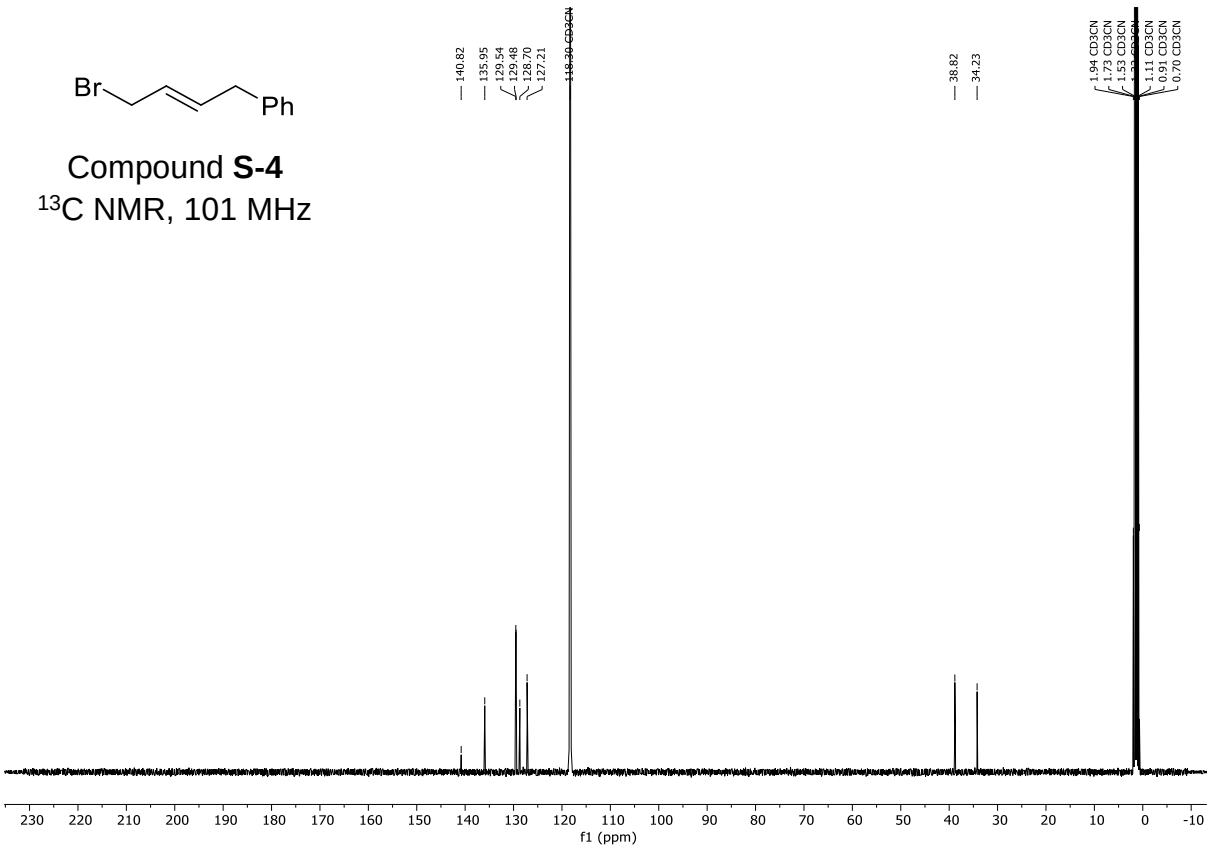
^{13}C NMR, 126 MHz


Br
Br
Ph
Compound **S-3**
^{1}H NMR, 400 MHz
f1 (ppm)

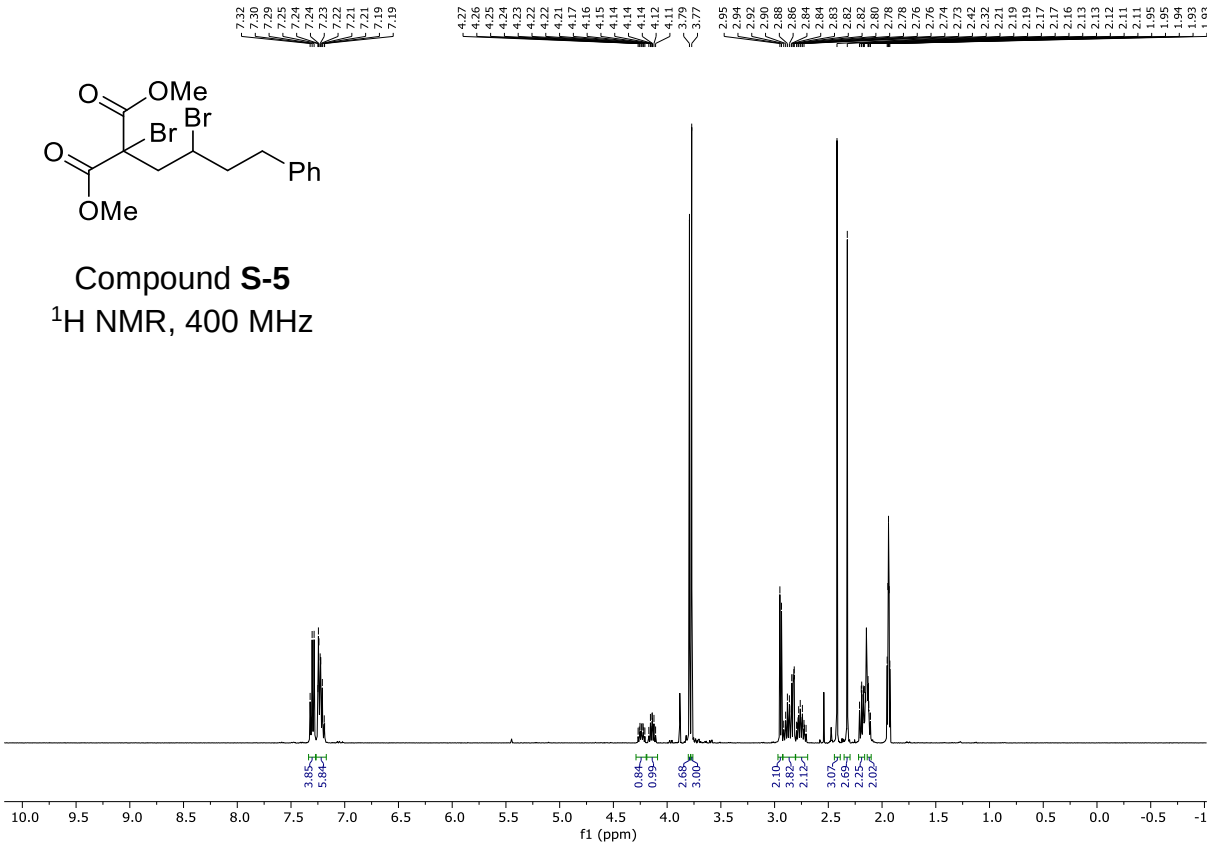

Br
Br
Ph
Compound **S-3**
^{13}C NMR, 101 MHz
f1 (ppm)



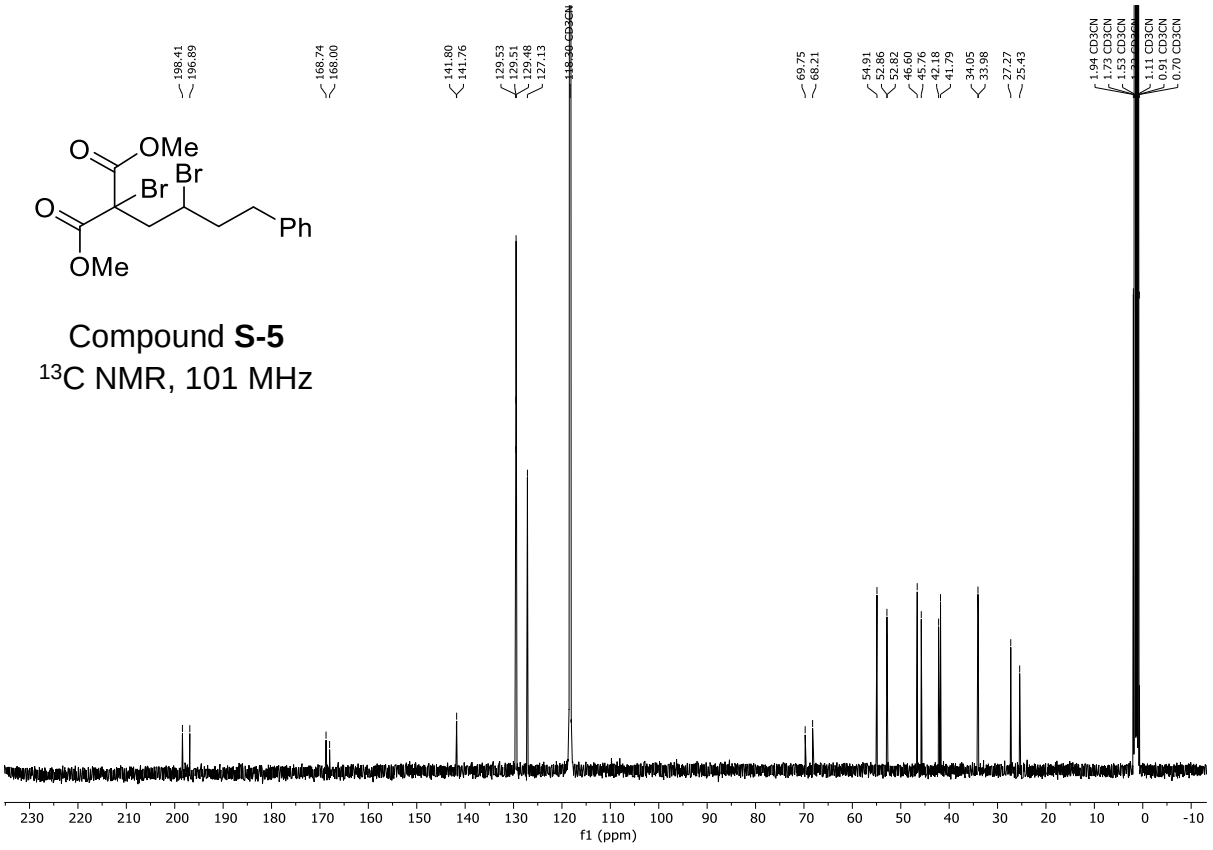
Compound **S-4**
^{1}H NMR, 400 MHz



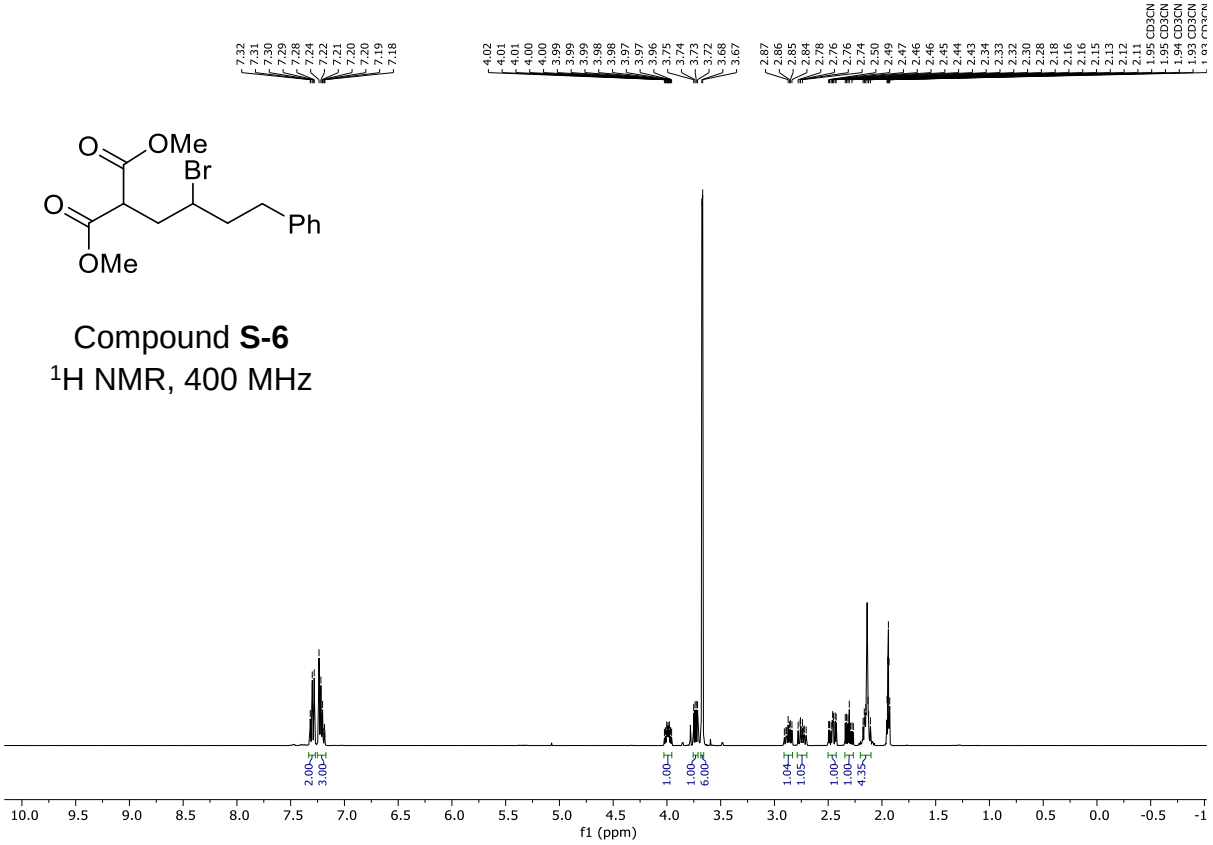
Compound **S-4**
^{13}C NMR, 101 MHz



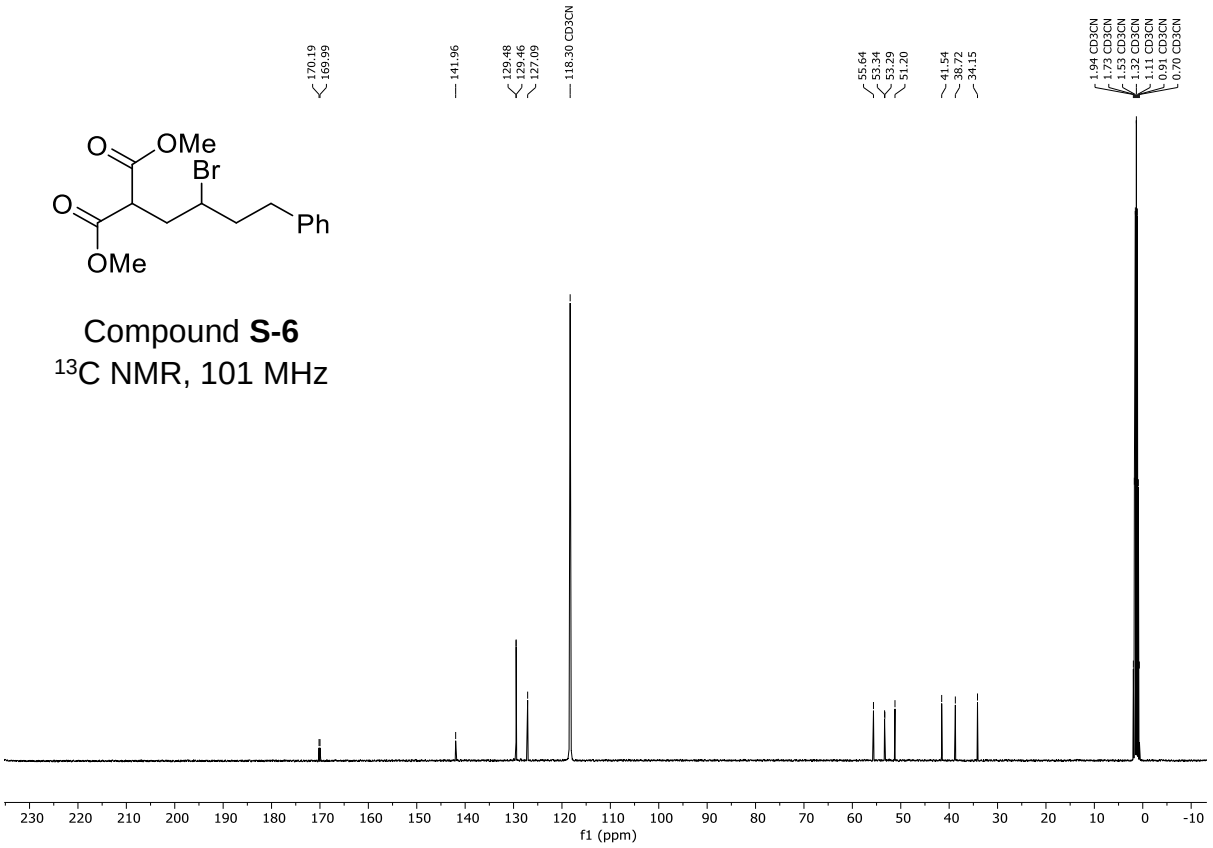
Compound **S-5**
^{1}H NMR, 400 MHz



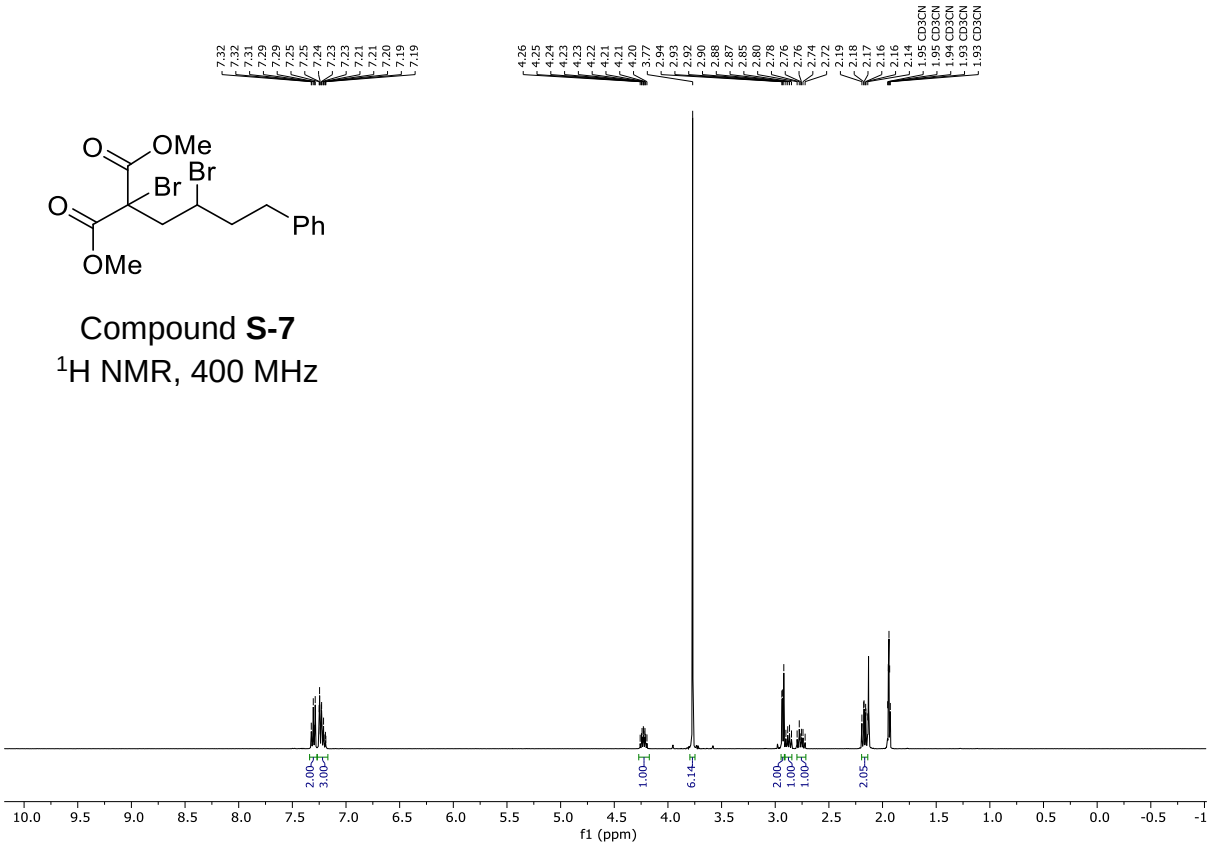
Compound **S-5**
^{13}C NMR, 101 MHz



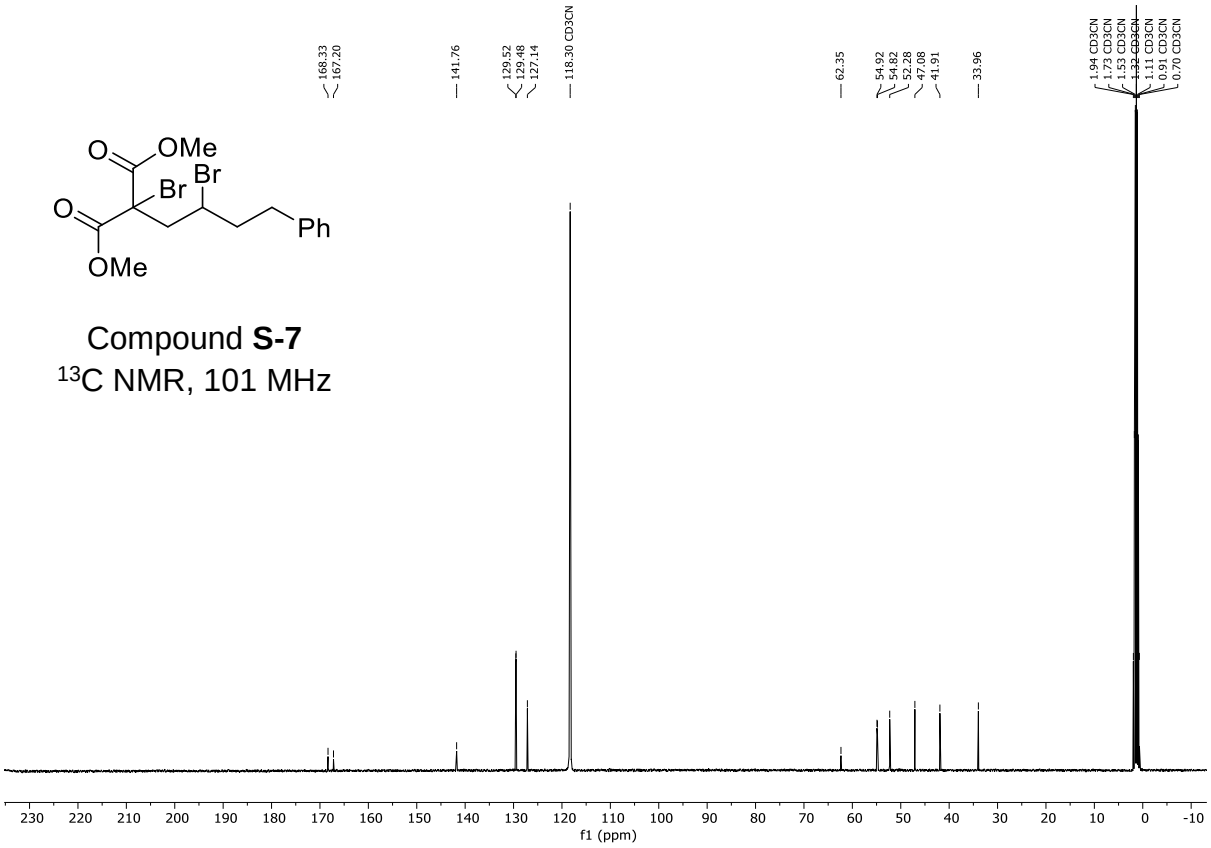
Compound **S-6**
^{1}H NMR, 400 MHz



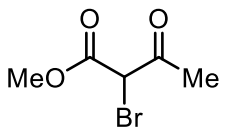
Compound **S-6**
^{13}C NMR, 101 MHz



Compound **S-7**
^{1}H NMR, 400 MHz

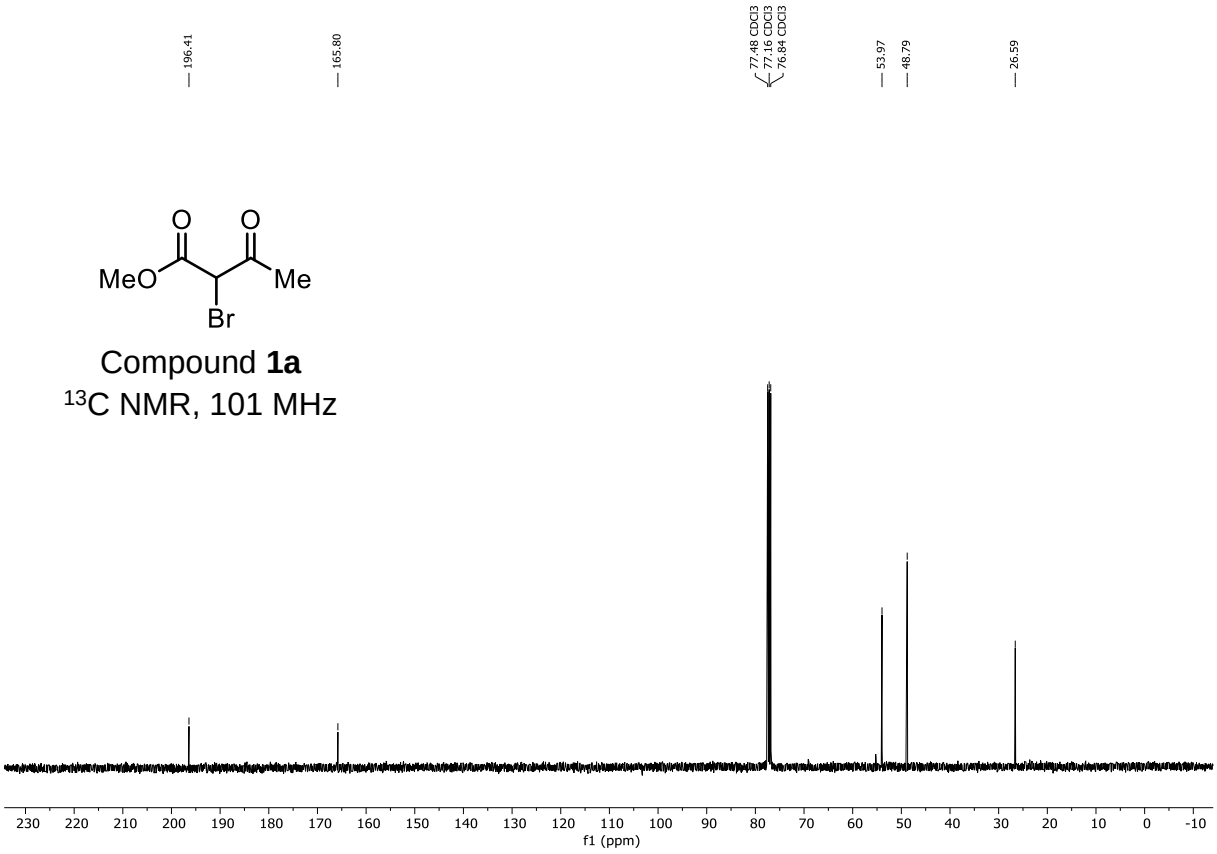


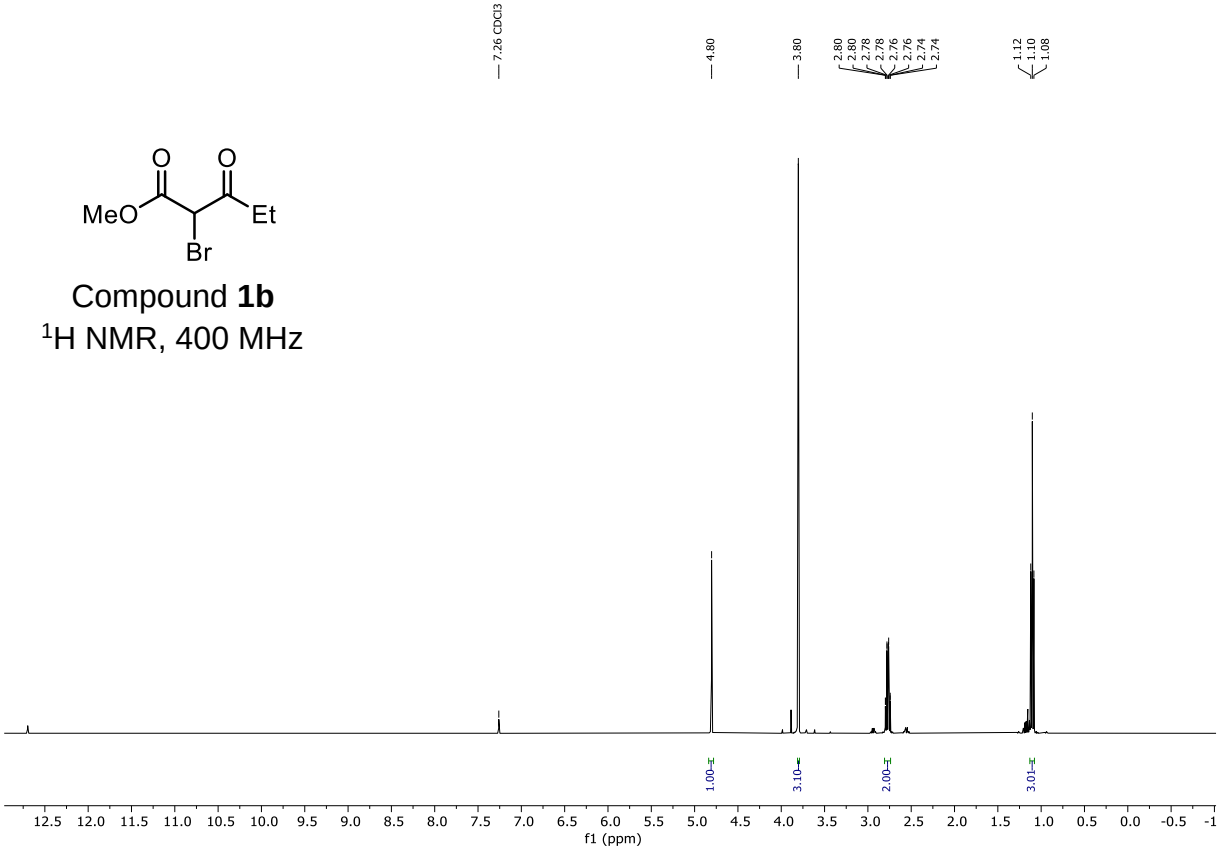
Compound **S-7**
^{13}C NMR, 101 MHz



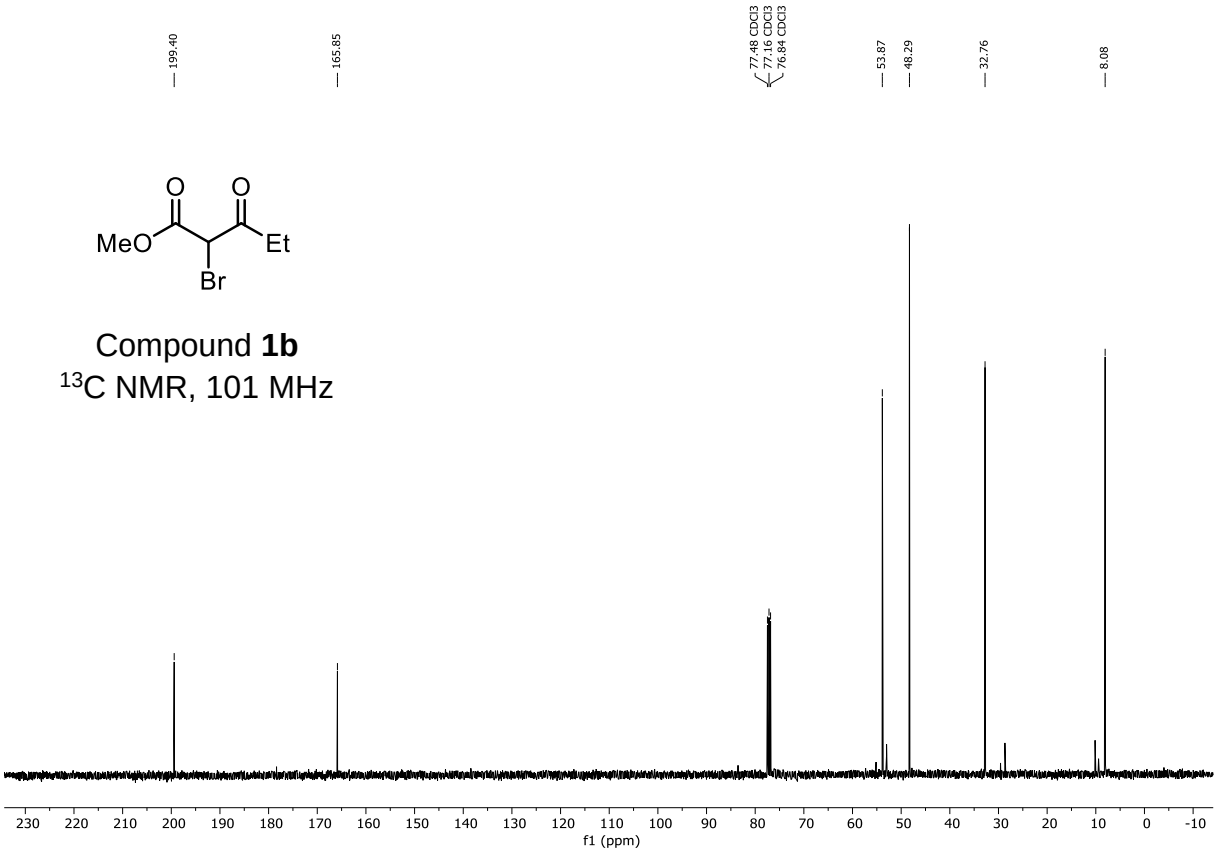
Compound **1a**
^{1}H NMR, 400 MHz

Compound **1a**
^{13}C NMR, 101 MHz

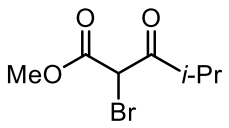




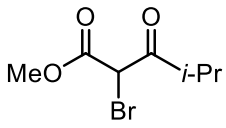
Compound **1b**
^{1}H NMR, 400 MHz



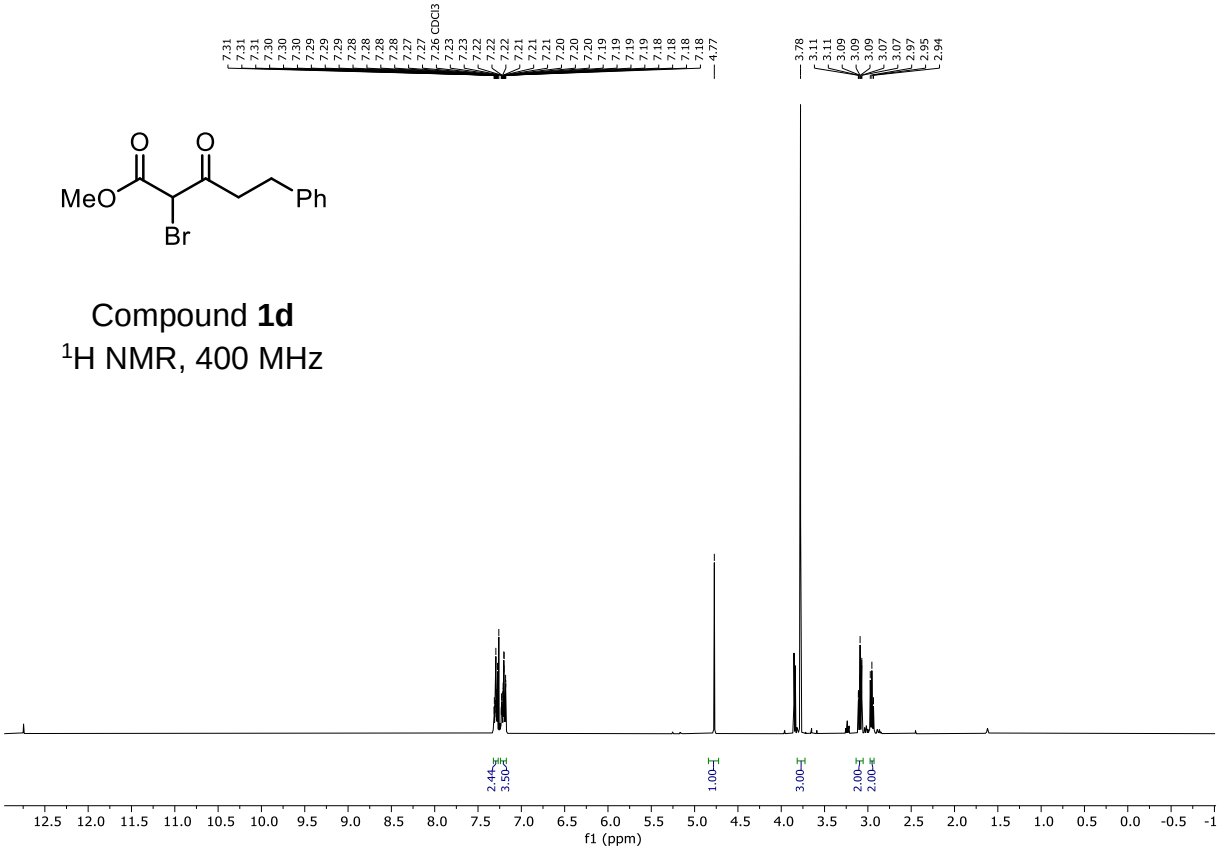
Compound **1b**
^{13}C NMR, 101 MHz



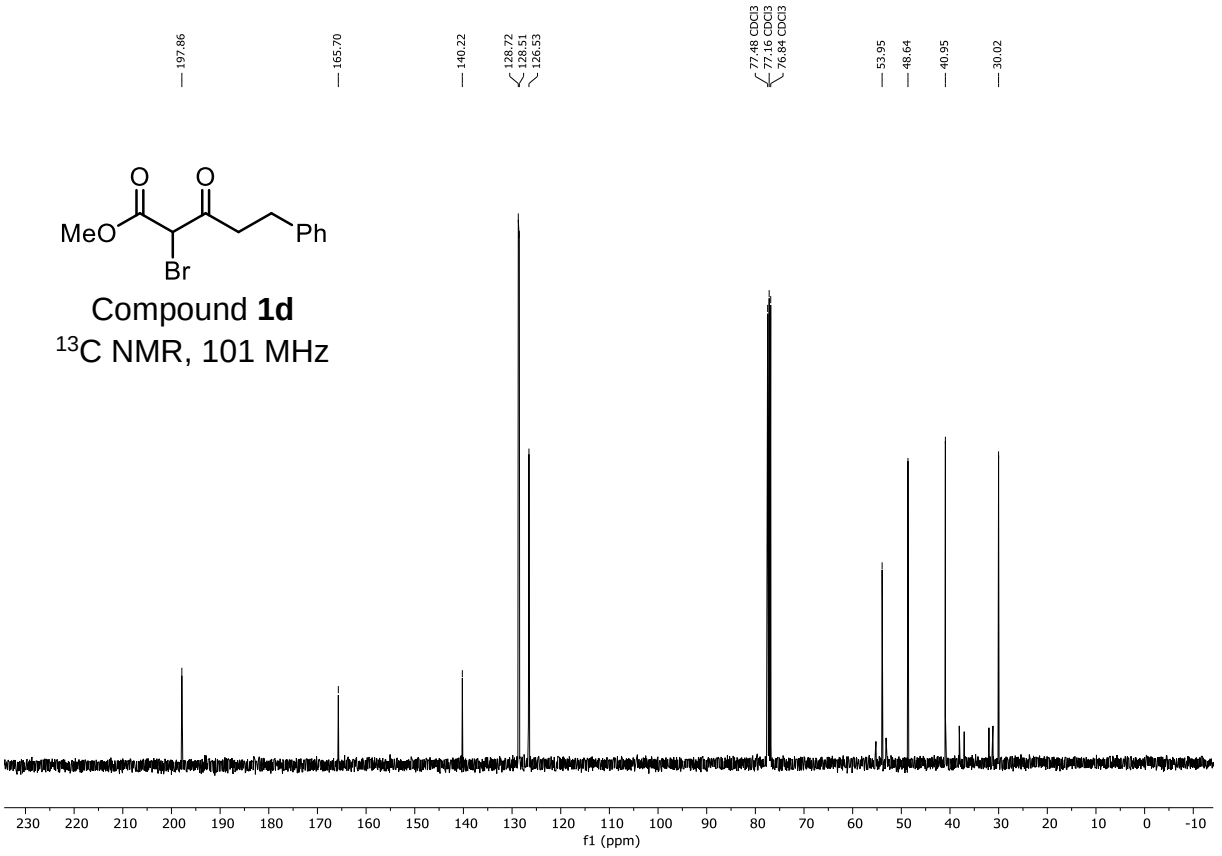
Compound **1c**
^{1}H NMR, 400 MHz



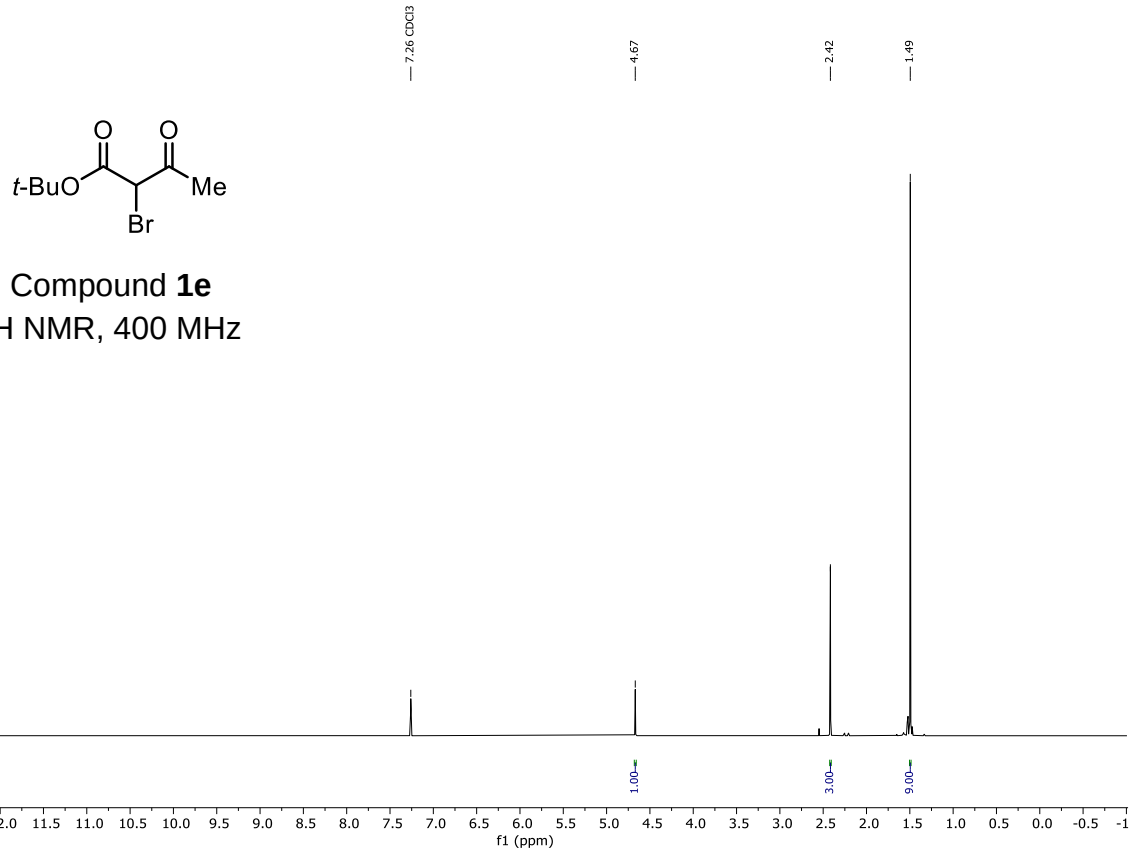
Compound **1c**
^{13}C NMR, 101 MHz



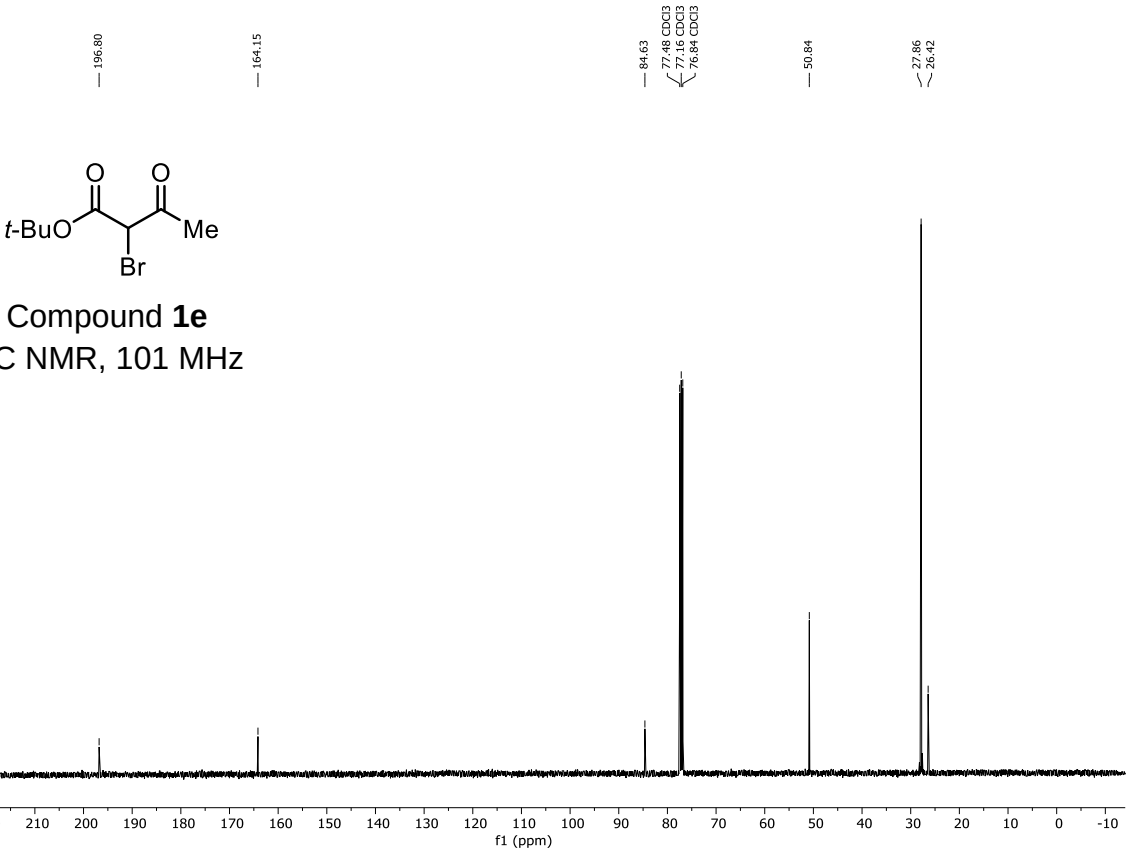
Compound **1d**
^{1}H NMR, 400 MHz



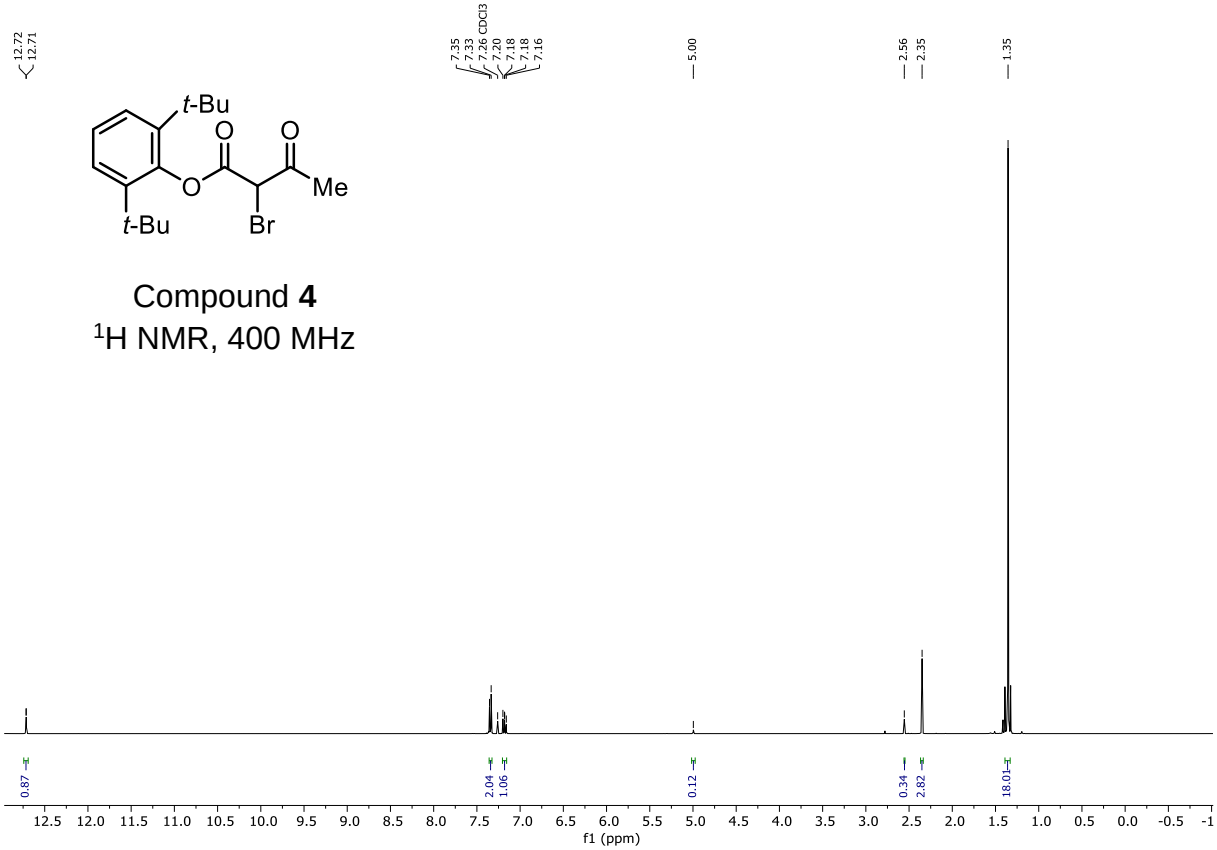
Compound **1d**
^{13}C NMR, 101 MHz



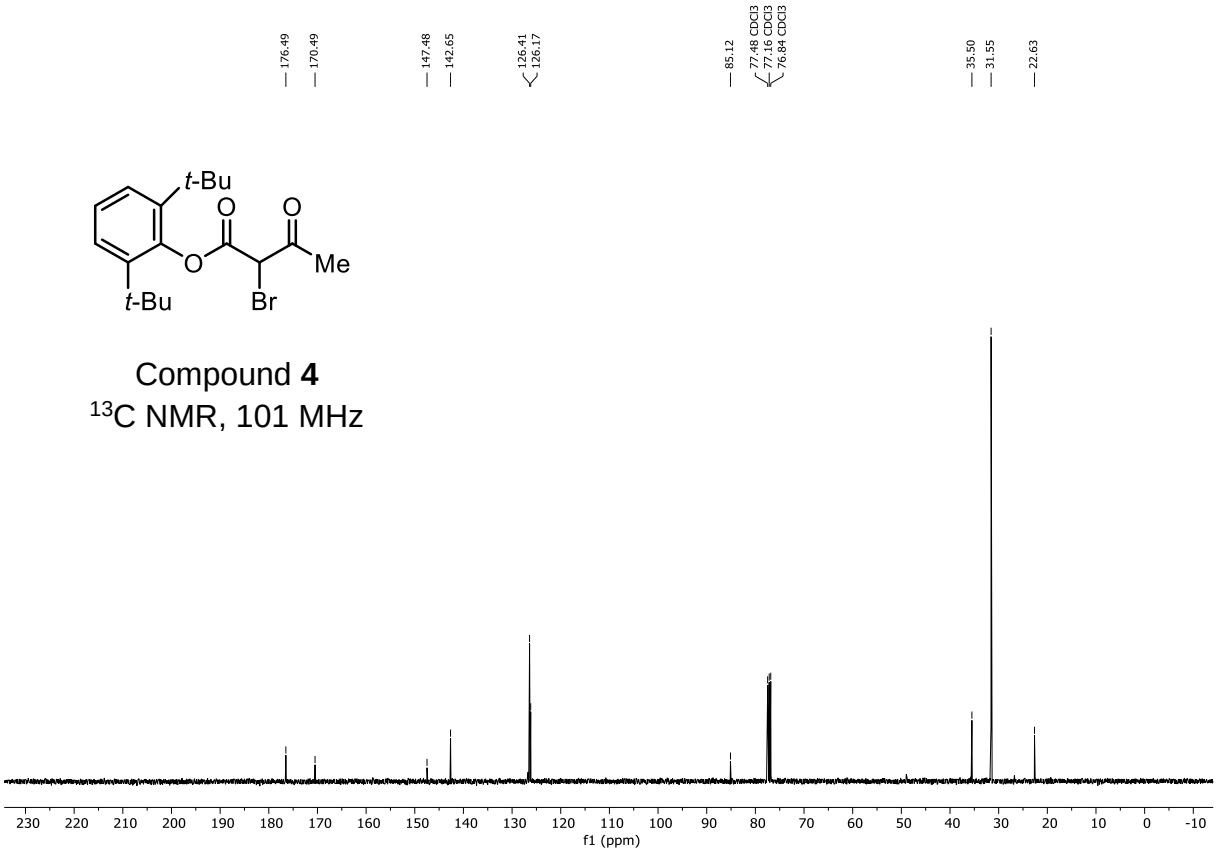
Compound **1e**
^{1}H NMR, 400 MHz



Compound **1e**
^{13}C NMR, 101 MHz



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



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

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