Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible light mediated selective α-functionalization of 1,3-dicarbonyl compounds via disulfide induced aerobic oxidation

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1. General Experimental

1.1 Solvents and Reagents

All solvents were commercially supplied or provided by the communal stills of the School of Pharmaceutical Science and Technology, Dalian University of Technology. Anhydrous acetonitrile, toluene, tetrahydrofuran and dichloromethane were dried using Na and stored over thoroughly dried 4 Å molecular sieves.

All other reagents were purchased from various commercial sources and used as received.

1.2 Photoreactor

The photocatalytic reactions were carried out on a WP-TEC-1020 photoreactor purchased from Wattcas Company.

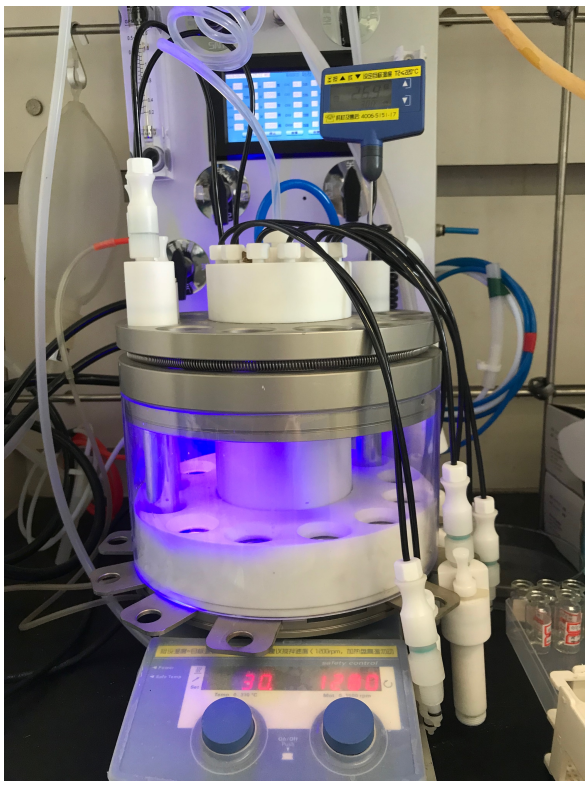


Figure S1. WP-TEC-1020 photoreactor

1.3 Chromatography and Spectroscopy

Analytical TLC was visualized with UV light at 254nm. Thin layer chromatography was carried out on TLC glass sheets with silica gel 60 F254. Purification of reaction products was carried out by chromatography using silica gel 60 (200-300 mesh). All ^{1}H NMR (400/500 MHz) and ^{13}C NMR (101/126 MHz) were recorded on a VARIAN INOVA-400/500M and AVANCE II 400 spectrometer at 25 °C. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26, for ^{1}H NMR and $CDCl_3$: δ 77.0 for ^{13}C NMR). For ^{1}H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry data were obtained with UPLC/Q-Tof Mass Spectrometer and were determined by electrospray ionization (ESI).

2. General Procedures

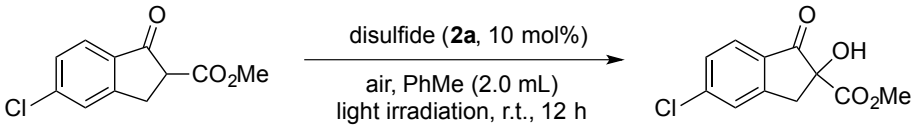
2.1 General experimental procedure for the disulfide catalyzed hydroxylation reaction

The reaction was performed on photochemical reactor. A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), bis(4-fluorophenyl) disulfide (**2d**, 13.01 mg, 0.005mmol) were stirred in 4 mL of DMF in a quartz tube at room temperature under the irradiation of 10 W blue LED for a given time. Meanwhile, the solution was bubbled with an air pump. The solvent was removed under reduced pressure and the reside was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding products.

2.2 Optimization of reaction parameters for the hydroxylation reaction

In our initial screening reactions, the toluene solution of 1-indanone-derived β-keto ester (**1a**) and disulfide (**2a**) was placed under 3W white LED irradiation and stirred for 24h with the reaction vial open to air, the desired α-hydroxylated product **3a** was formed in very low yield (Table S1, entry1). It should be noticed that in the absence of disulfide, none of the products was observed. Meanwhile, we founded that photo irradiation also played an essential role. Various light sources were applied to the model reaction. The results showed that not all of the selected light sources were effective for this transformation and blue LED (450-455nm) was the best choice.

Table S1. Evaluation of light resources[a]



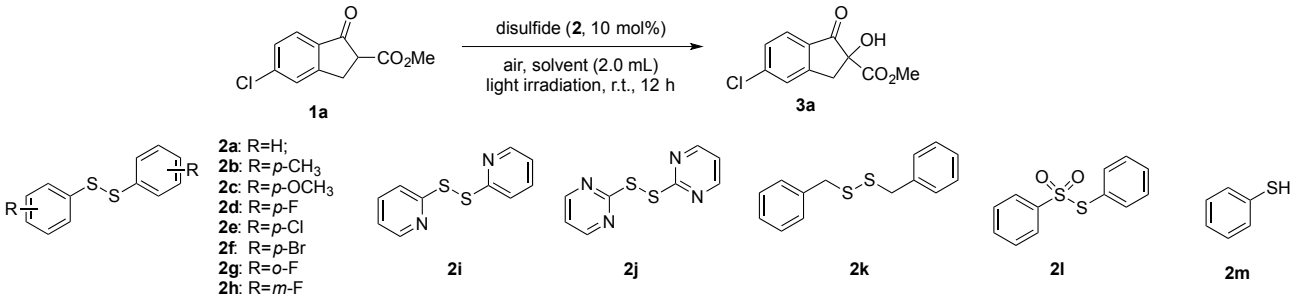
1a **3a**

Entry	disufide	light source	solvent	temp.	yield[b]
1	**2a**	3 W white LED	PhMe	RT	31%
2	--	3 W white LED	PhMe	RT	Trace
3	**2a**	Darkness	PhMe	RT	n.r.
4	**2a**	3 W red LED	PhMe	RT	Trace
5	**2a**	3 W yellow LED	PhMe	RT	Trace
6	**2a**	3 W green LED	PhMe	RT	Trace
7	**2a**	3 W blue LED	PhMe	RT	43%
8	**2a**	3 W purple LED	PhMe	RT	36%
9	**2a**	3 W black LED	PhMe	RT	48%

[a]Reaction conditions: **1a** (0.1 mmol), disulfide (10 mol%), PhMe (2.0 mL), in a 10 mL glass vial at room temperature under the irradiation of 3 W LED for 24 h. Meanwhile, the solution was bubbled with an air pump. [b]Determined by ^{1}H NMR analysis.

When the aromatic ring of disulfide replaced by different functional groups, the reaction efficiency was improved. Among the tested disulfides, bis(4-fluorophenyl) disulfide (**2d**) showed the highest catalytic reactivity. The effect of solvent was also examined. Among the typical solvents, DMF was founded to be the most effective. Overall, the most efficient and environmentally friendly method to prepare a high yield of **2a** involved using 10 mol% bis(4-fluorophenyl) disulfide in DMF under 3 W blue LED irradiation.

Table S2. Evaluation of disulfides and solvents[a]

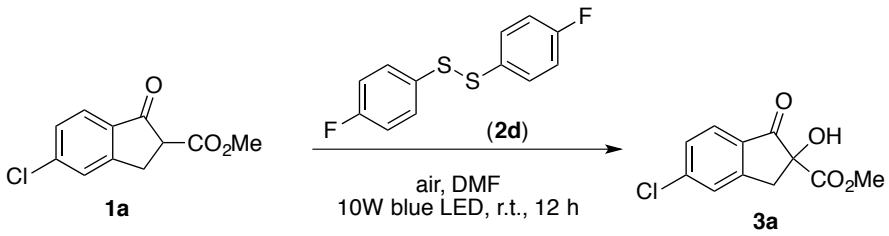


Entry	Disulfide	Light	Solvent	Yield[b]
1	**2a**	3 W blue LED	PhMe	43%
2	**2b**	3 W blue LED	PhMe	30%
3	**2c**	3 W blue LED	PhMe	27%
4	**2d**	3 W blue LED	PhMe	56%
5	**2e**	3 W blue LED	PhMe	47%
6	**2f**	3 W blue LED	PhMe	41%
7	**2g**	3 W blue LED	PhMe	46%
8	**2h**	3 W blue LED	PhMe	31%
9	**2i**	3 W blue LED	PhMe	28%
10	**2j**	3 W blue LED	PhMe	trace
11	**2k**	3 W blue LED	PhMe	trace
12	**2l**	3 W blue LED	PhMe	trace
13	**2m**	3 W blue LED	PhMe	trace
14	**2d**	3 W blue LED	Hexane	Trace
15	**2d**	3 W blue LED	*p*-xylene	24%
16	**2d**	3 W blue LED	THF	Trace

17	**2d**	3 W blue LED	EA	55%
18	**2d**	3 W blue LED	MeCN	Trace
19	**2d**	3 W blue LED	Acetone	20%
20	**2d**	3 W blue LED	DMF	79%
21	**2d**	3 W blue LED	DMAC	3%
22	**2d**	3 W blue LED	DMSO	Trace
23	**2d**	3 W blue LED	MeOH	Trace
24	**2d**	3 W blue LED	EtOH	Trace
25	**2d**	3 W blue LED	Tetralin	Trace
26	**2d**	3 W blue LED	CH_2Cl_2	30%
27	**2d**	3 W blue LED	$CHCl_3$	53%
28	**2d**	3 W blue LED	CCl_4	78%
29	**2d**	3 W blue LED	DMC	7%
30	**2d**	3 W blue LED	Dioxane	7%
31	**2d**	3 W blue LED	Morpholine	Trace

[a]Reaction conditions: **1a** (0.1 mmol), disulfide (10 mol%), solvent (2.0 mL), in a 10 mL glass vial at room temperature under the irradiation of 3 W blue LED for 24 h. Meanwhile, the solution was bubbled with an air pump. [b]Determined by ^{1}H NMR analysis.

Table S3. Evaluation of Concentration



Entry	Cat (x mol%)	concentration	light	yield[b]
1	10	0.050 mol/L	10 W blue LED	90%
2	5	0.050 mol/L	10 W blue LED	86%
3	1	0.050 mol/L	10 W blue LED	33%
4	5	0.0125 mol/L	10 W blue LED	81%
5	5	0.0250 mol/L	10 W blue LED	90%
6	5	0.0500 mol/L	10 W blue LED	82%
7	5	0.1000 mol/L	10 W blue LED	81%
8	5	0.0250 mol/L	10 W white LED	86%
9[d]	5	0.0250 mol/L	10 W white LED	88%
10	5	0.0250 mol/L	10 W blue LED	96%
11[d]	5	0.0250 mol/L	10 W blue LED	96%
12[c]	5	0.0250 mol/L	10 W blue LED	42%

[a]Reaction conditions: **1a** (0.1 mmol), disulfide and DMF in a 10 mL quartz tube at room temperature performed on photochemical reactor under the irradiation of blue LED for a given time. Meanwhile, the solution was bubbled with an air pump for 24h. [b]Determined by HPLC analysis. [c] Performed on glass vial. [d] O_2 balloon.

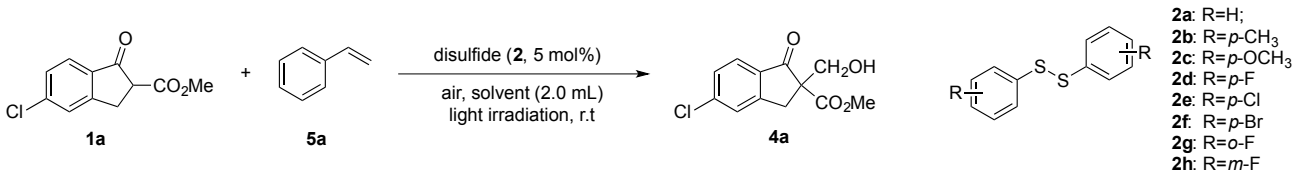
2.3 General experimental procedure for the disulfide catalyzed hydroxymethylation reaction

The reaction was performed on photochemical reactor. A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), styrene (**5a**, 15.67mg) and phenyl disulfide (**2a**, 10.91 mg, 0.005mmol) were stirred in 2 mL of MeCN in a quartz tube at room temperature under the irradiation of 10 W blue LED for a given time. Meanwhile, the solution was bubbled with an air pump. The solvent was removed under reduced pressure and the reside was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding products.

2.4 Optimization of Reaction Parameters for the Hydroxymethylation Reaction

In our initial screening reactions, the toluene solution of 1-indanone-derived β-keto ester (**1a**) styrene (**5a**, 20.83 mg, 2.0 equiv) and disulfide (**2a**) was placed under 3W white LED irradiation and stirred for 24 h with the reaction vial open to air, the desired α-hydroxymethylated product **4a** was formed in very low yield (Table S4, entry1). It should be noticed that in the absence of disulfide, none of the products was observed. Meanwhile, we founded that photo irradiation also played an essential role. Various light sources were applied to the model reaction. The results showed that not all of the selected light sources were effective for this transformation and blue LED (450-455nm) was the best choice.

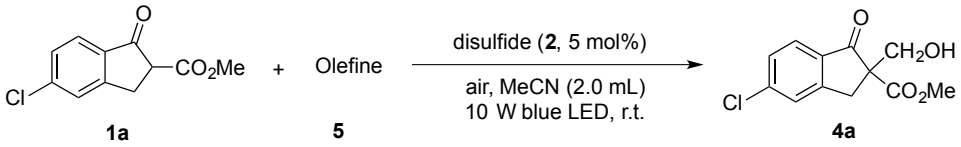
Table S4. Evaluation of solvents and disulfides.[a]

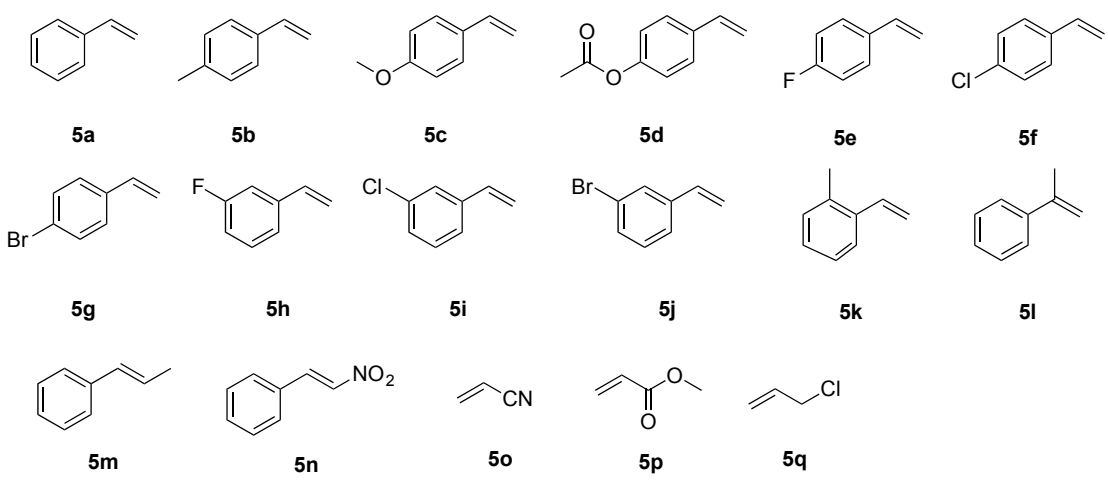


Entry	Disufide	Light	Solvent	Temp.	Yield (%)[b]
1	**2a**	10 W blue LED	MeCN	RT	61
2	**--**	10 W blue LED	MeCN	RT	n.r.
3	**2a**	Darkness	MeCN	RT	n.r.
4	**2b**	10 W blue LED	MeCN	RT	62
5	**2c**	10 W blue LED	MeCN	RT	63
6	**2d**	10 W blue LED	MeCN	RT	54
7	**2e**	10 W blue LED	MeCN	RT	55
8	**2f**	10 W blue LED	MeCN	RT	59
9	**2g**	10 W blue LED	MeCN	RT	57
10	**2h**	10 W blue LED	MeCN	RT	59
11	**2a**	10 W blue LED	PhMe	RT	35
12	**2a**	10 W blue LED	CH_2Cl_2	RT	22
13	**2a**	10 W blue LED	THF	RT	Trace

[a]Reaction conditions: **1a** (0.1 mmol), disulfide (5 mol%), solvent (2.0 mL) and styrene (2.0 eq) in a 10 mL quartz tube performed on photochemical reactor under the irradiation of LED for 12 h. Meanwhile, the solution was bubbled with an air pump. [b]Determined by ^{1}H NMR analysis.

Table S5. Evaluation of Olefines[a]



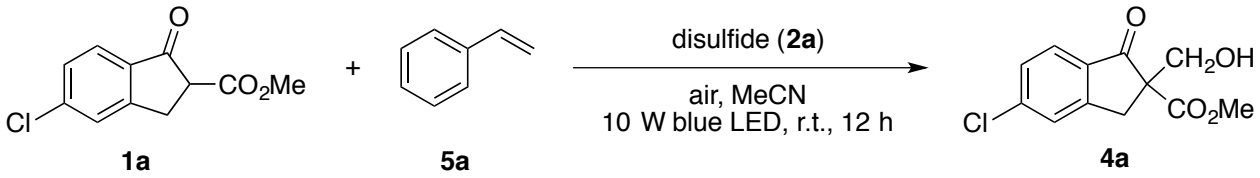


Entry	Disufide	Olefin	**4a** yield (%)[b]
1	**2a**	**5a**	81
2	**2a**	**5b**	63
3	**2a**	**5c**	44
4	**2a**	**5d**	43
5	**2a**	**5e**	84
6	**2a**	**5f**	83.
7	**2a**	**5g**	51
8	**2a**	**5h**	84
9	**2a**	**5i**	76
10	**2a**	**5j**	69
11	**2a**	**5k**	88
12	**2a**	**5l**	66
13	**2a**	**5m**	n.r.

14	**2a**	**5n**	n.r.
15	**2a**	**5o**	n.r.
16	**2a**	**5p**	n.r.
17	**2a**	**5q**	n.r.
18	**2c**	**5a**	77
19	**2d**	**5a**	85

[a]Reaction conditions: Performed on photochemical reactor with quartz tube, **1a** (0.1 mmol), disulfide (5 mol%), MeCN (2.0 mL) and olefine at room temperature under the irradiation of 10W blue LED for 24h. Meanwhile, the solution was bubbled with an air pump. [b]Determined by HPLC analysis.

Table S6. Evaluation of Disulfide and Styrene loading[a]



Entry	PhSSPh	Styrene	**4a** yield (%)[b]
1	5 mol%	1.0 eq	64
2	5 mol%	1.5 eq	81
3[c]	5 mol%	1.5 eq	88
4	5 mol%	4.0 eq	93
5[d]	5 mol%	10.0 eq	95

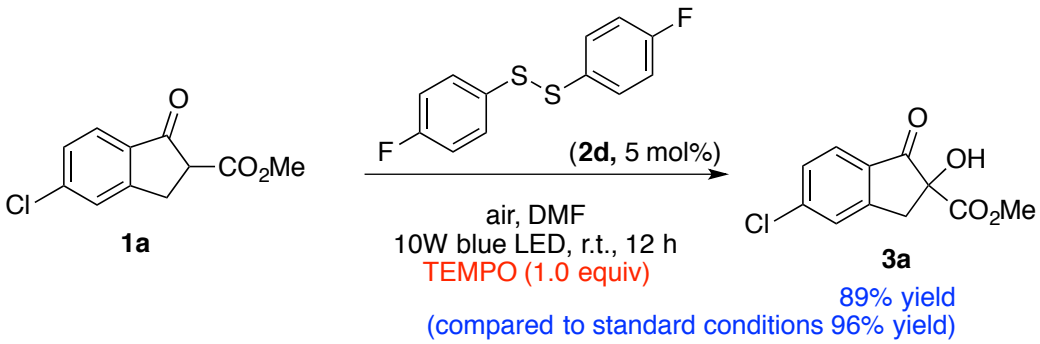
[a]Reaction conditions: Performed on photochemical reactor with quartz tube, **1a** (0.1 mmol), disulfide styrene and MeCN (2.0 mL) in a quartz tube at room temperature under the irradiation of 10 W blue LED for a given time. Meanwhile, the solution was bubbled with an air pump. [b]Determined by HPLC analysis. [c] O_2 balloon. [d] 4h.

3. Preliminary mechanistic studies

3.1 Mechanistic experiments of the disulfide-catalyzed hydroxylation reaction

3.1.1 The addition of TEMPO in the model reaction system

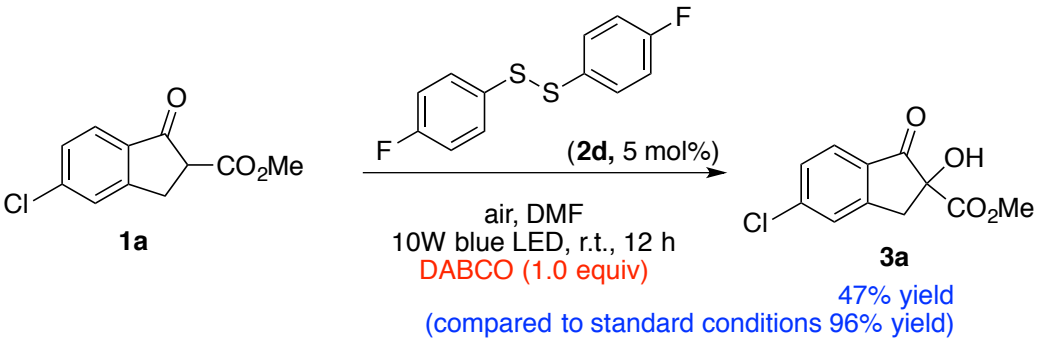
Scheme S1. Addition of TEMPO in disulfide-catalyzed hydroxylation reaction



A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), bis(4-fluorophenyl) (**2d**, 13.01 mg, 0.005mmol) and TEMPO (1.0 equiv) were stirred in 4 mL of DMF in a quartz tube at room temperature under the irradiation of 10 W blue LED for 8h. Meanwhile, the solution was bubbled with an air pump. The solvent was removed under reduced pressure and the reside was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding product **3a** in 89% yield.

3.1.2 The addition of DABCO in the model reaction system

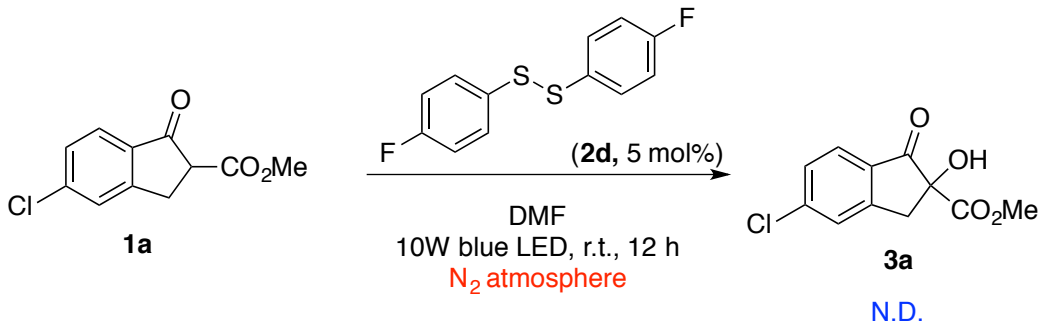
Scheme S2. Addition of DABCO in disulfide-catalyzed hydroxylation reaction



We carried out control experiments trying to verify the presence of photoexcited singlet oxygen. When the single oxygen quencher, 1,4-diazabicyclo[2.2.2]octane (DABCO), was added to the reaction system, a greatly reduced product yield was observed.

3.1.3 The model reaction was carried out under N_2

Scheme S3. Disulfide-catalyzed hydroxylation reaction in N_2 atmosphere

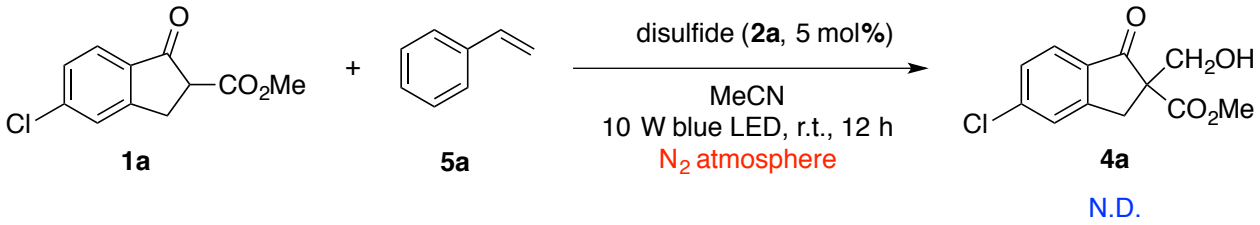


A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), bis(4-fluorophenyl) (**2d**, 13.01 mg, 0.005mmol) were stirred in 4 mL of DMF in a quartz tube at room temperature under the irradiation of 10 W blue LED for 12h under N_2. The solvent was removed under reduced pressure, analysis by NMR and HPLC showed no product formation.

3.2 Mechanistic experiments of the disulfide-catalyzed hydroxymethylation reaction

3.2.1 The model reaction was carried out under N_2

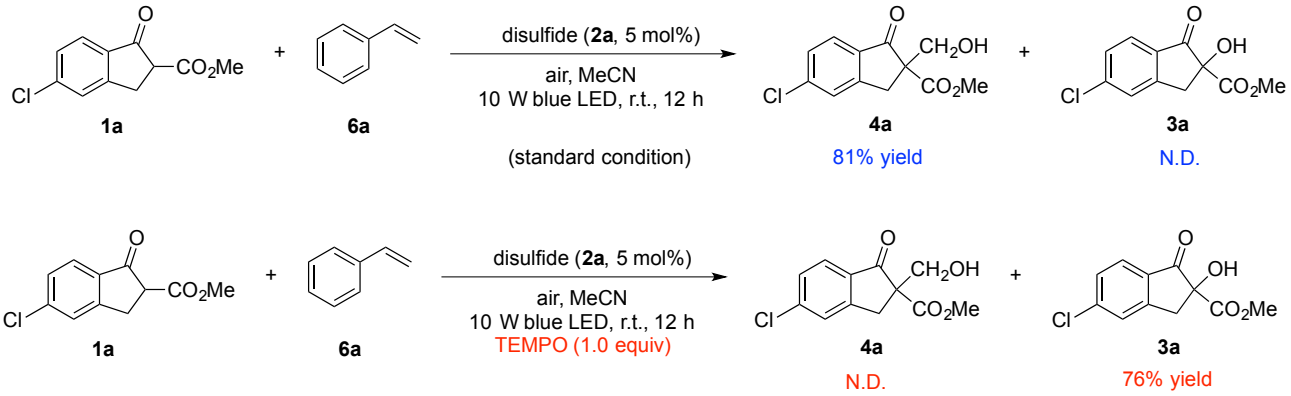
Scheme S4. Disulfide-catalyzed hydroxymethylation reaction in N_2 atmosphere



A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), styrene (**5a**, 15.67mg), phenyl disulfide (**2a**, 10.91 mg, 0.005mmol) and were stirred in 2 mL of MeCN in a quartz tube at room temperature under the irradiation of 10 W blue LED for a given time. The system was protected by N_2. The solvent was removed under reduced pressure, analysis by NMR and HPLC showed no product formation.

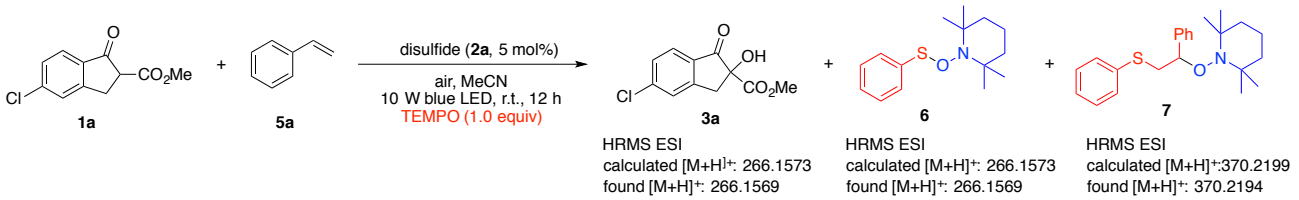
3.2.2 The addition of TEMPO in the model reaction system

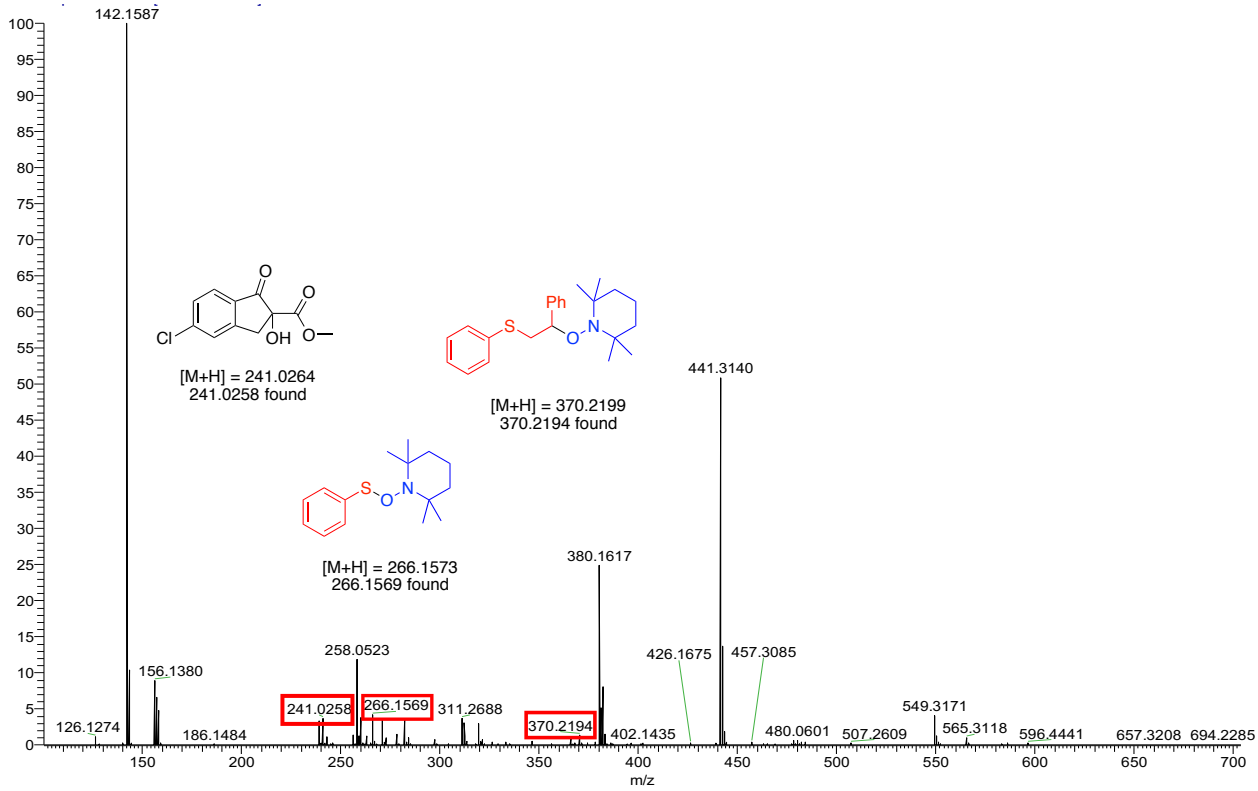
Scheme S5. Addition of TEMPO in disulfide-catalyzed hydroxymethylation reaction



A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), styrene (**5a**, 15.67mg), phenyl disulfide (**2a**, 10.91 mg, 0.005mmol) and TEMPO (15.92mg, 1.0 eq) were stirred in 2 mL of MeCN in a quartz tube at room temperature under the irradiation of 10 W Blue LED for a given time. Meanwhile, the solution was bubbled with an air pump. Analysis by NMR and HPLC showed no product formation. The HRMS spectrum of the system is demonstrated as bellow.

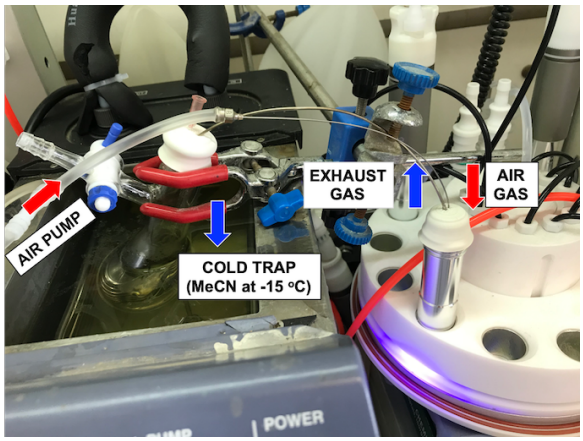
Scheme S6. HRMS evidence of thiyl radical and alkyl radical

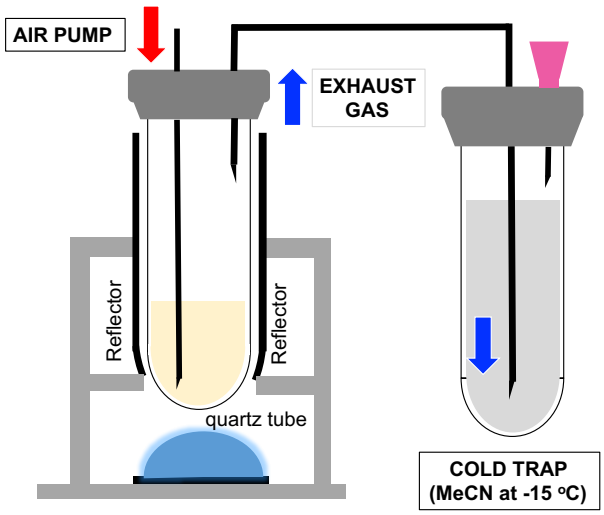


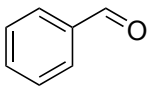


3.2.3 The formation of benzaldehyde.

Due to the volatility of benzaldehyde in the non-closed reaction system, we improved the reaction system and tried to collect the produced benzaldehyde. We used a needle tube instead of the gas line of the photoreactor to introduce air into the system, and add a trap to the system to increase the exhaust gas absorption. The reaction was stopped after 24 hours. Aldehyde was isolated by flash chromatography eluting with CH_2Cl^2/MeOH (50:1) with 0.0086g (53% yield compared to styrene).







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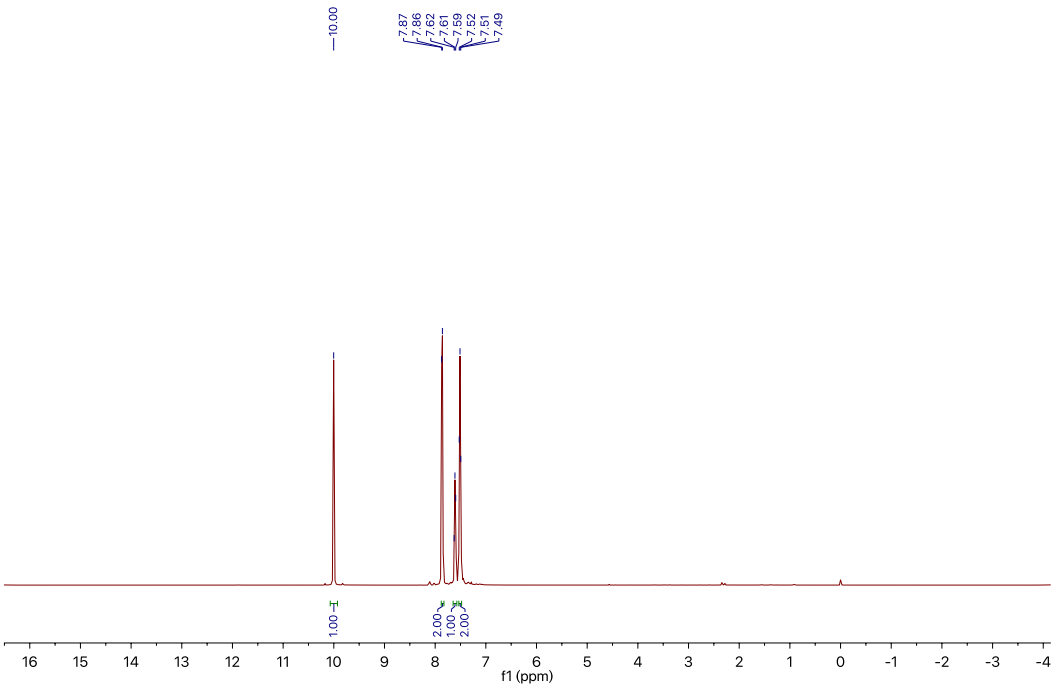
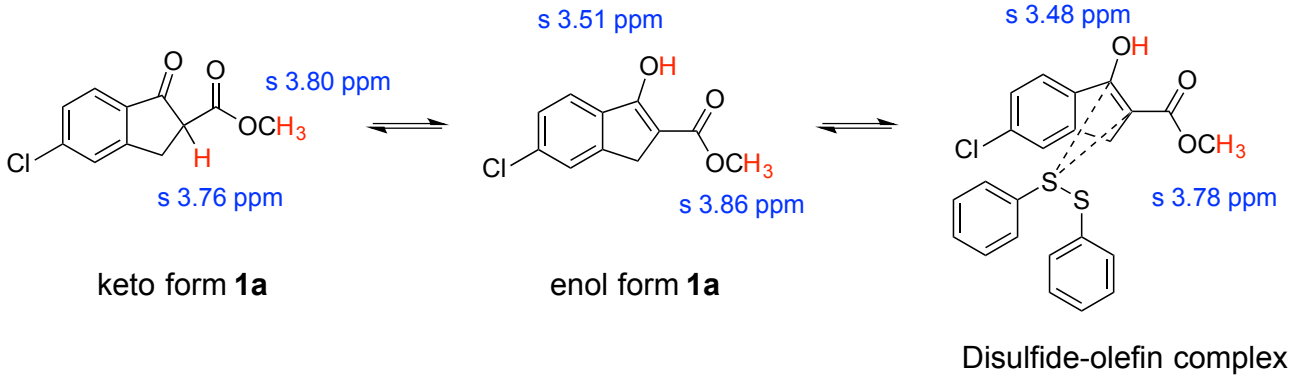
^{1}H NMR (500 MHz, Chloroform-d) δ 10.00 (s, 1H), 7.86 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H).



3.2.4 NMR study of substrate-disulfide complex

We carried out a set of NMR experiments to seek evidence of the substrate-disulfide complex. To a dried 8 mL reaction flask equipped with a magnetic stir bar was charged with substrate **1a** (0.1 mmol, 22.46 mg), **2a** (0.005mmol, 10.91 mg) and $CDCl_3$ (2 mL).



The ^{1}H-NMR (400 MHz, $CDCl_3$) spectra were shown in Figure S2, from which the changes of peaks and chemical shifts were observed at δ 3.90-3.30 ppm as the ratio of disulfide and **1a** increased. The spectra from δ 3.87-3.73 ppm and δ 3.59-3.31 ppm were enlarged in Figure S2b and Figure S2c.

From Figure S2b and Figure S2c, the chemical shift of –$COOCH_3$ (δ 3.80 ppm, 3.86 ppm) from the keto form and enol form of **1a** drifted upfield and the peak of α-H (-CH-) (δ 3.56 ppm) as well as β-H (-CH_2-) (δ 3.35 ppm) were shifted to upfield, which indicated that the electron density on the substrate had increased.

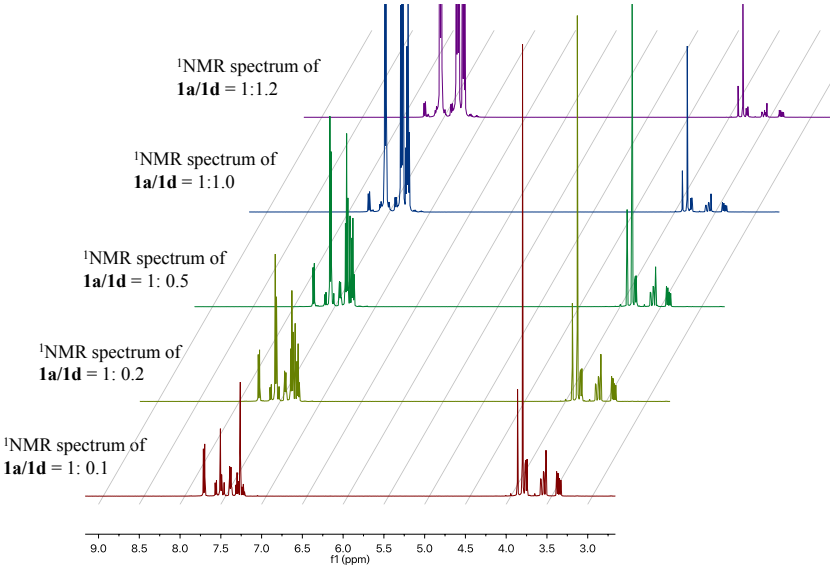


Figure S2. a) The coordination of **2a** and **1a** by ^{1}H-NMR analysis.

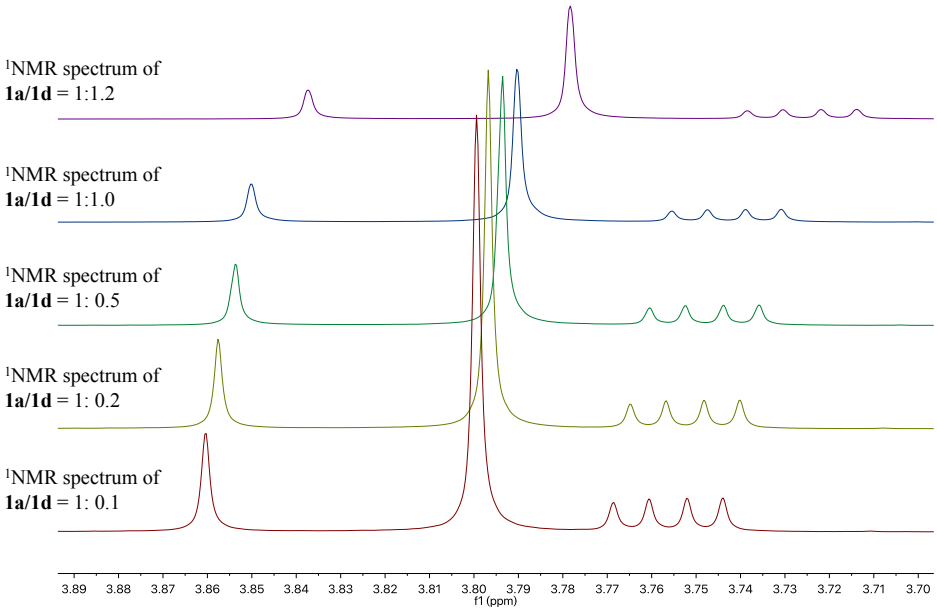


Figure S2. b) The detail view from δ 3.89 – 3.70 ppm of Figure S2

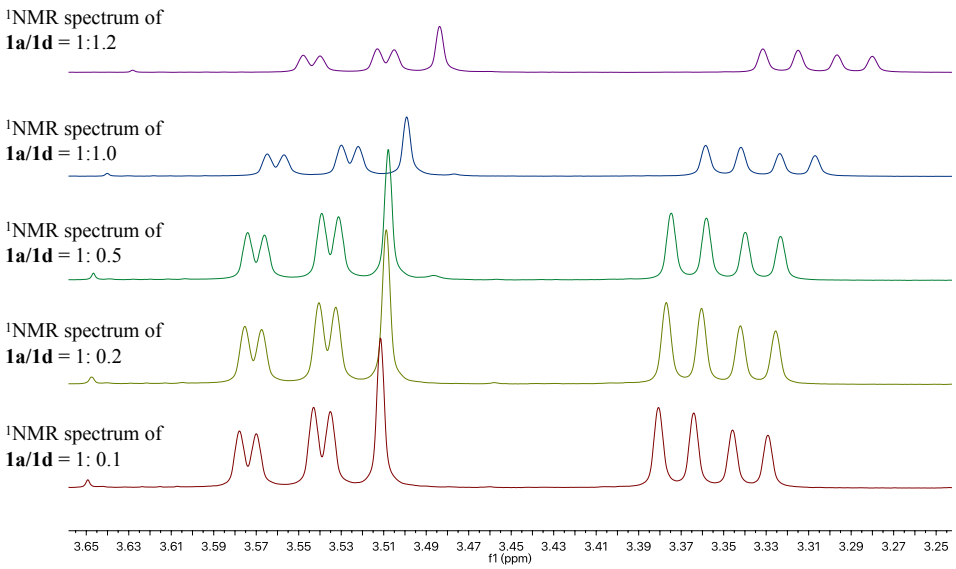


Figure S2. c)The detail view from δ 3.65 – 3.25 ppm of Figure S2

3.2.5 NMR study of disulfide-styrene complex

We carried out a set of NMR experiments to seek evidence of the disulfide–olefin complex. By analyzing a series of ^{1}H NMR of a fixed amount of styrene mixed with increasing amounts of disulfide **2a** in CD3CN, we found that the chemical shift of the styrene CH=CH_2 drifted upfield, which indicated that the electron density on the styrene had increased.

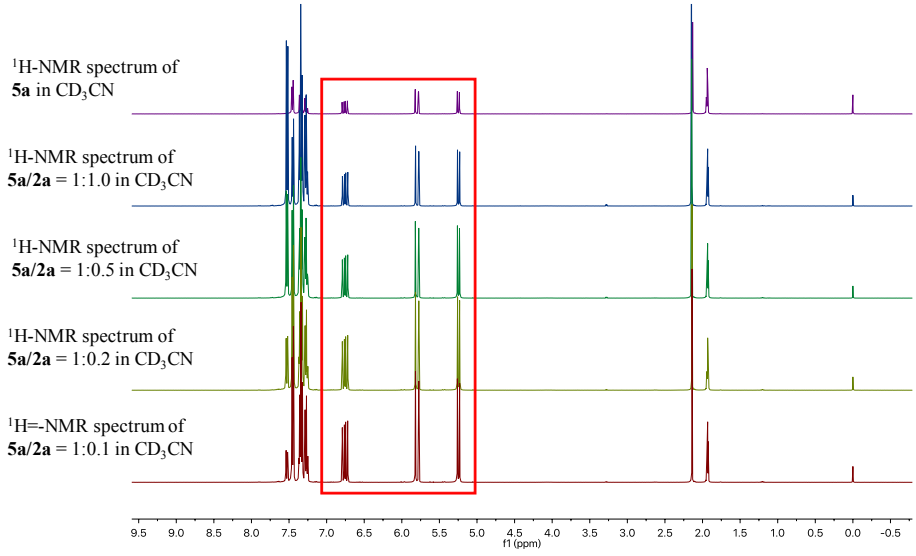


Figure S3. The coordination of **5a** and **1a** by ^{1}H-NMR analysis.

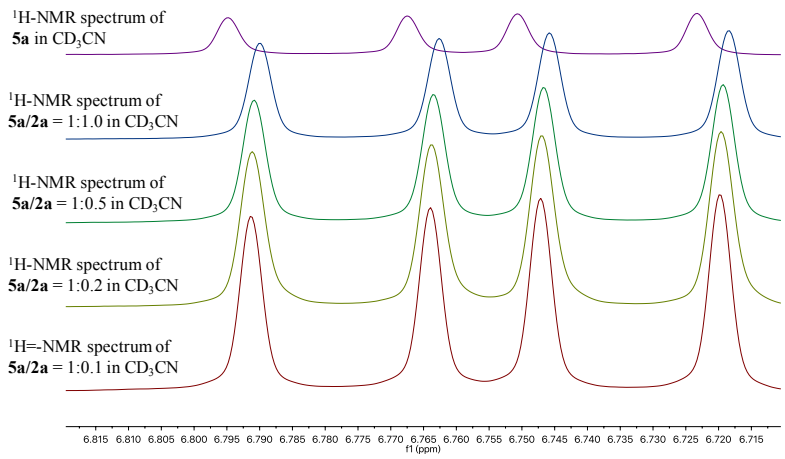


Figure S4. a) The detail view from δ 3.65 – 3.25 ppm of Figure S3

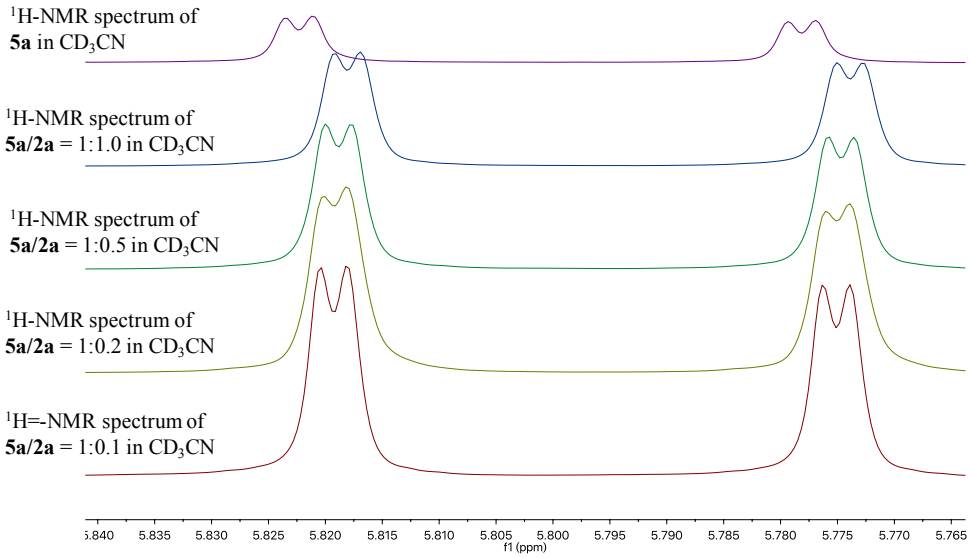


Figure S4. b) The detail view from δ 3.65 – 3.25 ppm of Figure S3

4 The UV-visible spectroscopy and Fluorescence quenching studies

UV-visible spectroscopy of reaction solution was recorded on a UV-9000S spectrophotometer. The sample was prepared by mixing disulfide **2a** and substrate **1a** with MeCN (M[**1a**] = 0.025 mol/L, M[**2a**] = 0.0025 mol/L) in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 328nm. The absorption was collected and result was listed in Figure S5.

A set of UV-Vis spectra scanning experiments were carried out as follows: It can be observed that diphenyl disulfide has little change in absorption spectrum regardless of whether it is irradiated with visible light (below), and the combination of diphenyl disulfide and substrate is formed. There is a clear new absorption peak at around 400 nm, which indirectly proves that the complex may interact with the visible blue light wavelength. This result is also consistent with online nuclear magnetic characterization. The complex formed may be the key to a photocatalytic reaction. Meanwhile, the photographs of reaction solution before and after blue LEDs irradiation indicated that an EDA complex might exist.

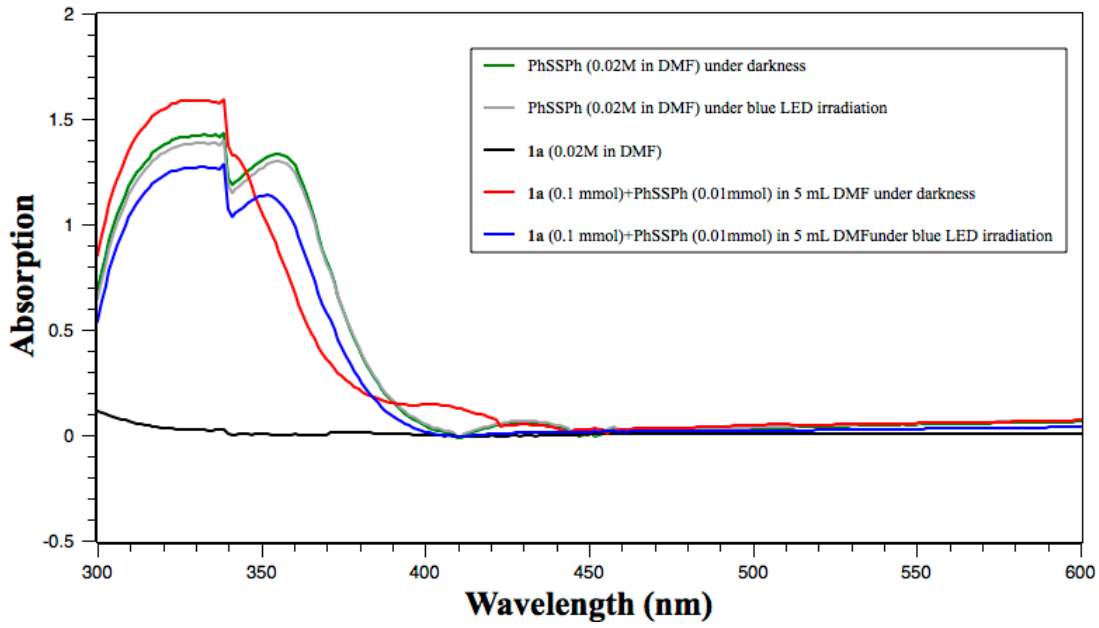


Figure S5. a) UV-visible spectroscopy of hydroxylation system

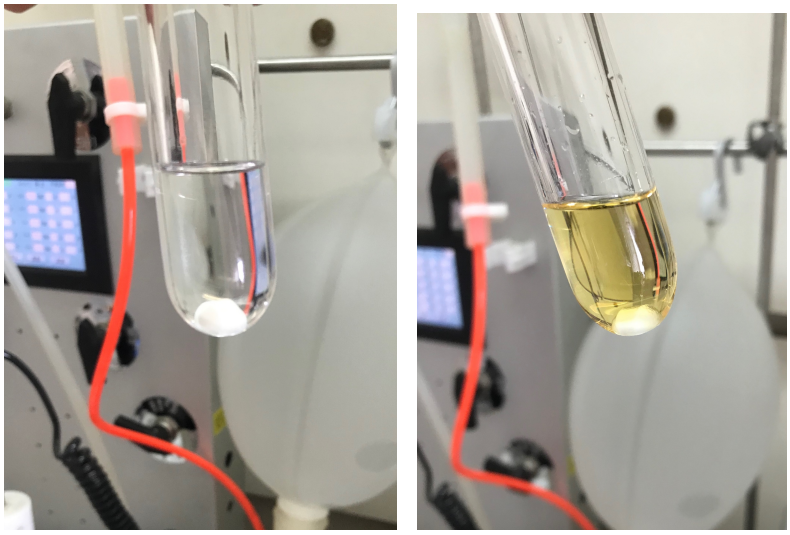


Figure S5. b) The photographs of reaction solution before and after blue LEDs irradiation.

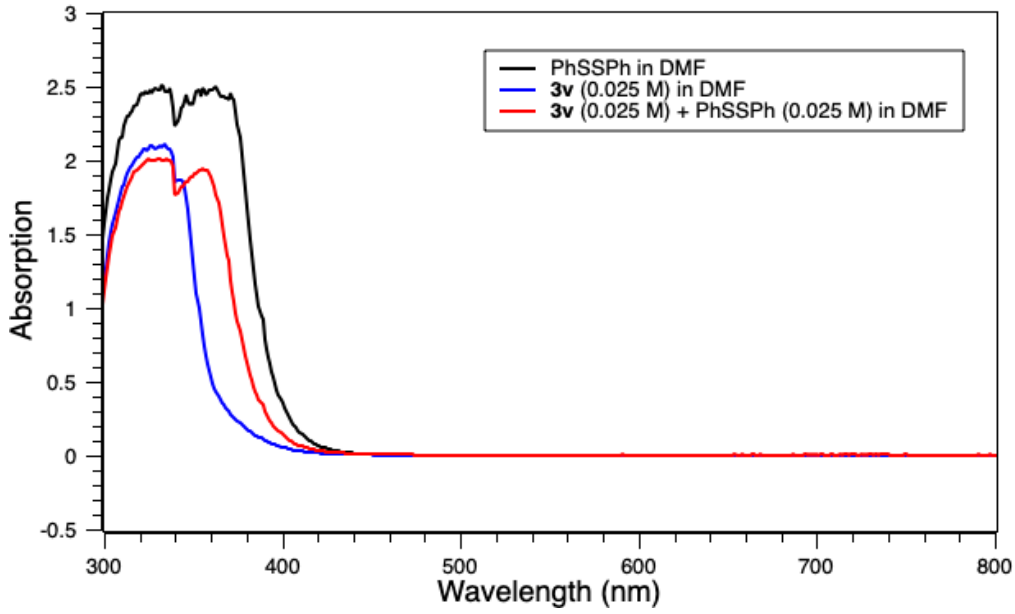


Figure S5. c) UV-visible spectroscopy of **3v** and disulfide mixture

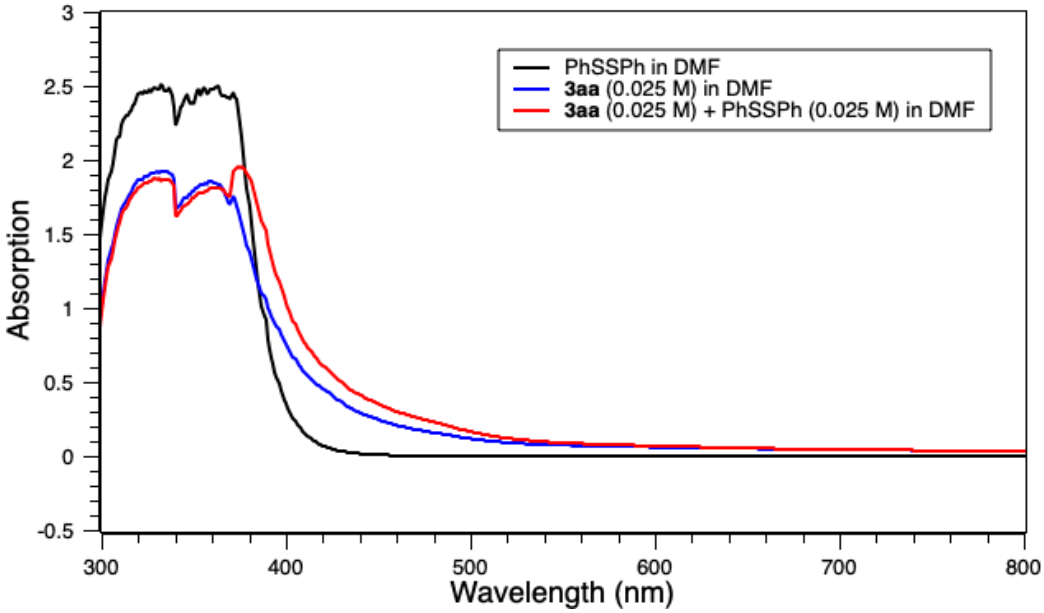


Figure S5. d) UV-visible spectroscopy of **3aa** and disulfide mixture

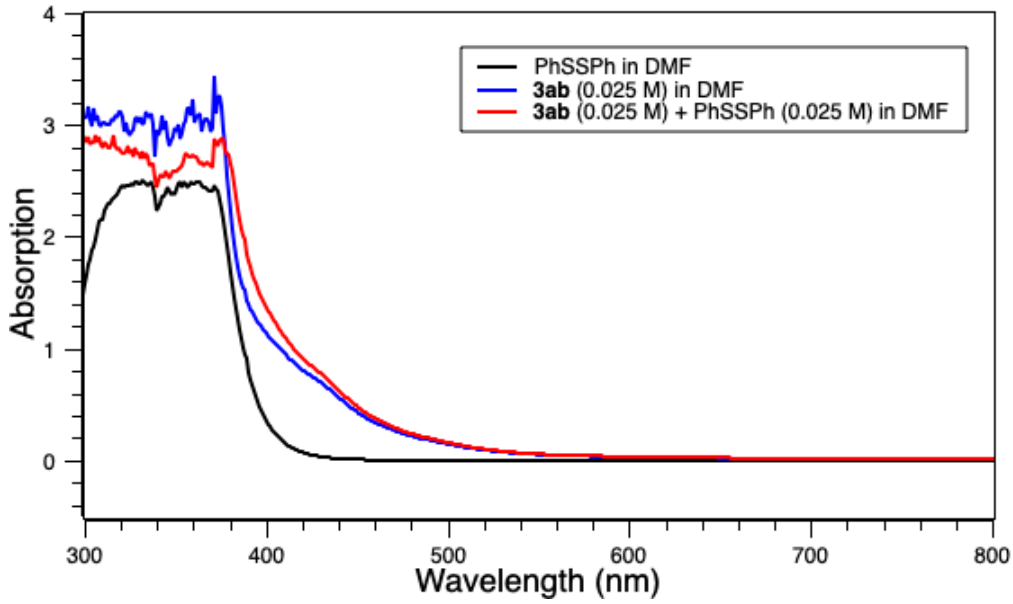


Figure S5. e) UV-visible spectroscopy of **3ab** and disulfide mixture

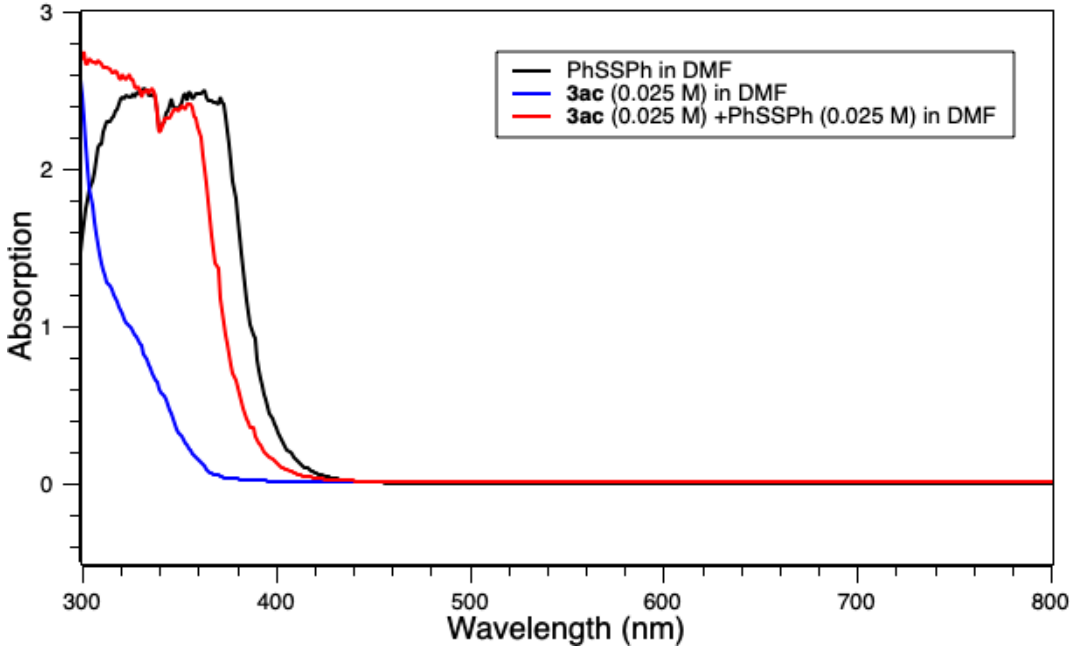


Figure S5. f) UV-visible spectroscopy of **3ac** and disulfide mixture

Emission quenching experiments (Stern-Volmer studies)

Emission intensities were recorded using Hitachi F-7000 Fluorescence Spectrometer for all experiments. The excitation wavelength was fixed at 435nm, and the emission wavelength was measured at 435nm. The sample was prepared by mixing disulfide **2a**, substrate **1a,** styrene **5a**, CuI with solvent DMF and MeCN in a light path quartz fluorescence cuvette. The emission intensity was collected and the results were listed as follows.

The samples were prepared by mixing by PhSSPh (2×10^{-2} mol/L) and different amount of substrate **1a** (2×10^{-3}mol/L to 3×10^{-2}mol/L) in DMF. The emission intensity was collected and the results were presented in Figure S6.

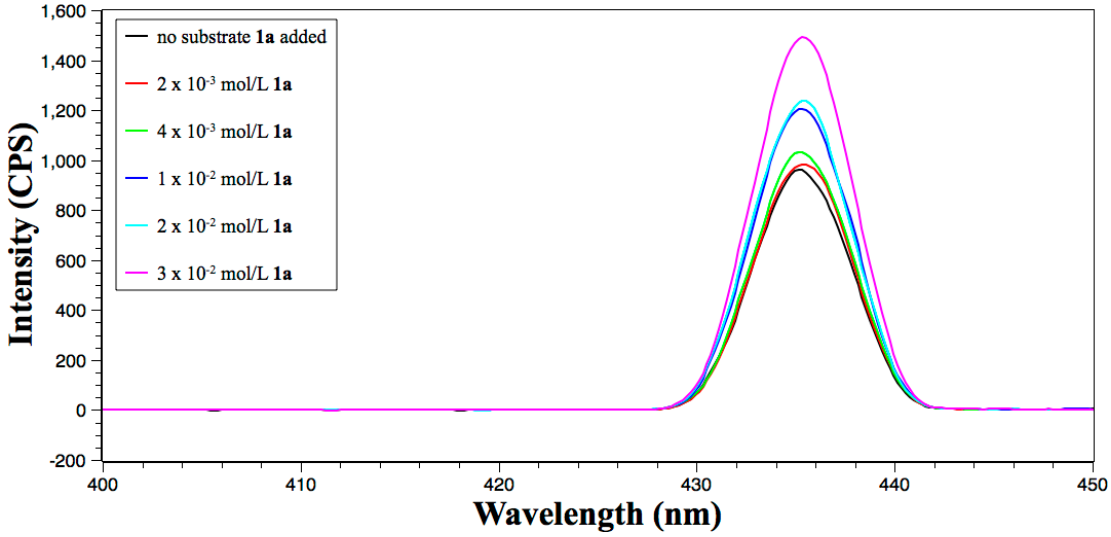


Figure S6. Quenching of PhSSPh fluorescence emission in the presence of **1a**

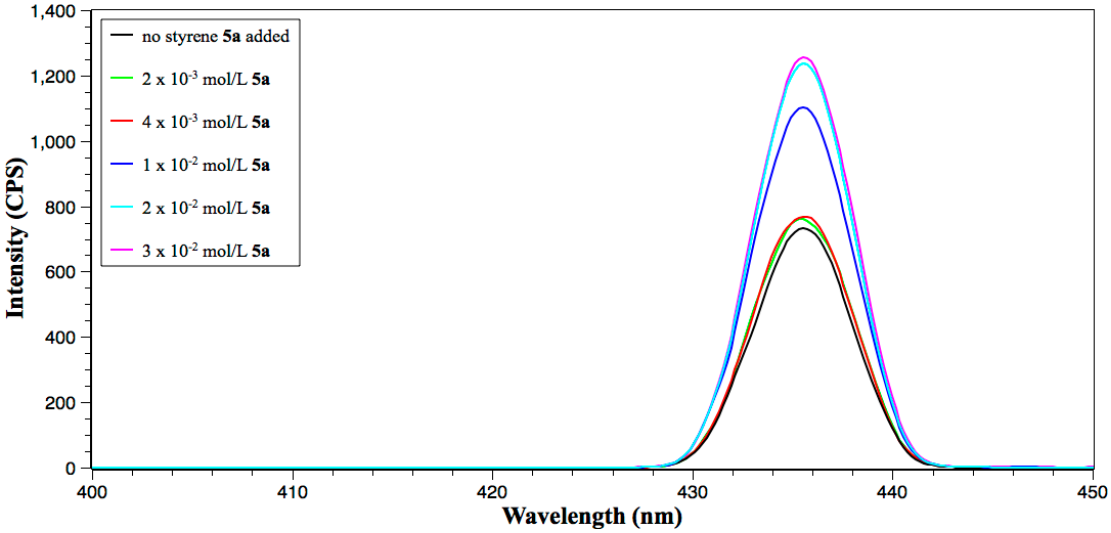


Figure S7. Quenching of PhSSPh fluorescence emission in the presence of **5a**

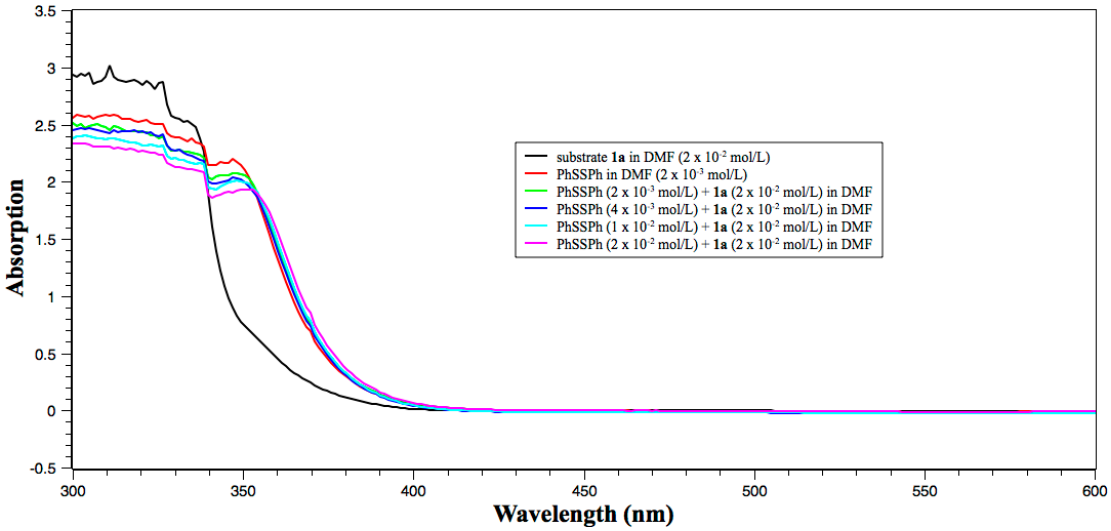


Figure S8. UV-visible spectroscopy of hydroxylation system

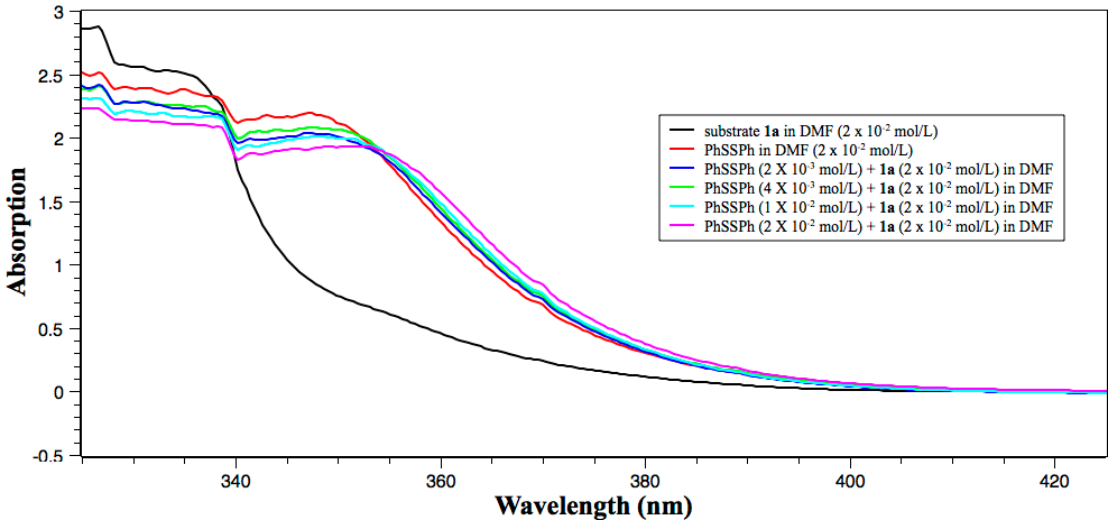


Figure S9. The detail view of Figure S8

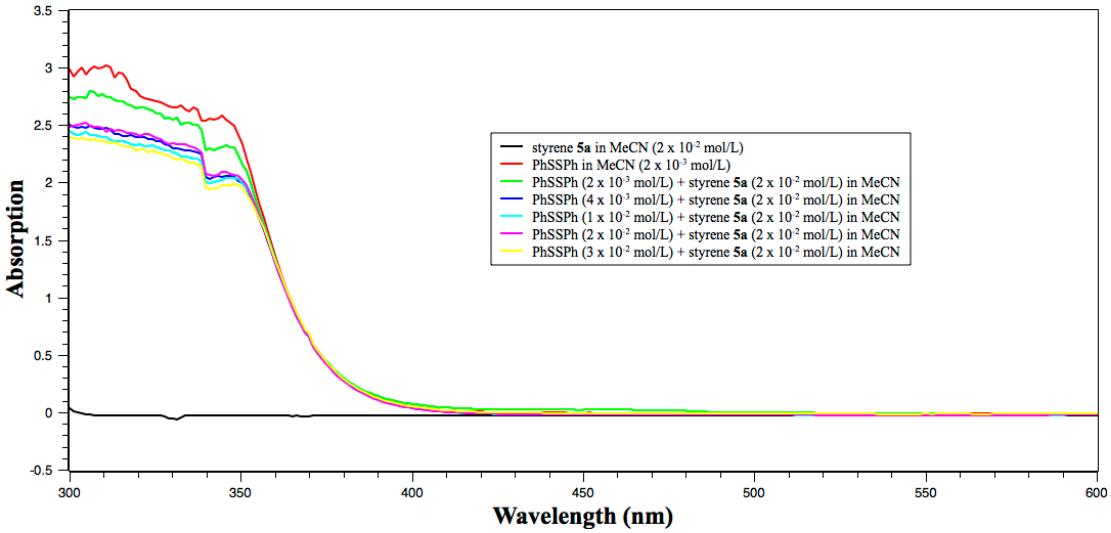


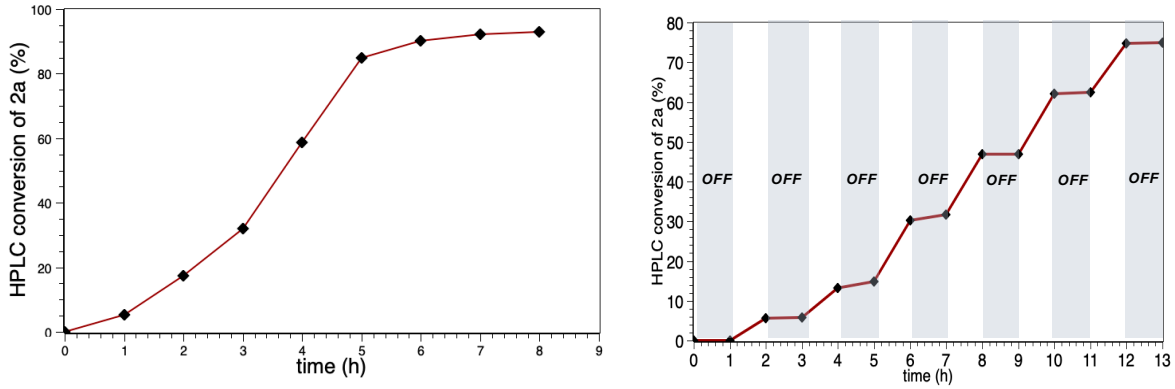
Figure S10. UV-visible spectroscopy of hydroxymethylation system

5 Quantum Yield Measurement

5.1 Visible light irradiation on/off experiment

An on/off visible light irradiation experiment was carried out to verify the effect of photoirradiation, and show that the continuous irradiation of visible light is necessary for promoting the present transformation.

Scheme S7. Visible light on/off experiment of disulfide-catalyzed hydroxylation reaction



5.2 Measurement of quantum yield

According to the procedure of Yoon, the photon flux of the LED was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (2.21 g) in H_2SO_4 (30 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (50 mg) and sodium acetate (11.25 g) in H_2SO_4 (25 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (4.0 mL) was placed in a cuvette and irradiated for 90 s at $\lambda = 450$ nm. After irradiation, the phenanthroline solution (0.7 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using Equation S1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \qquad \text{(Equation S1)}$$

Where V is the total volume (0.00470 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 (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using Equation S2.

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f} \qquad \text{(Equation S2)}$$

Where Φ is the quantum yield for the ferrioxalate actinometer, t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 450$ nm. The photon flux was calculated to be 9.83×10^{-8} einstein s^{-1}.

Determination of fraction of light absorbed at 450 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 450 nm was measured to be 1.187. The fraction of light absorbed (f) by this solution was calculated using Equation S3, where A is the measured absorbance at 450 nm.

$$f = 1 - 10^{-A(450nm)} \qquad \text{(Equation S3)}$$

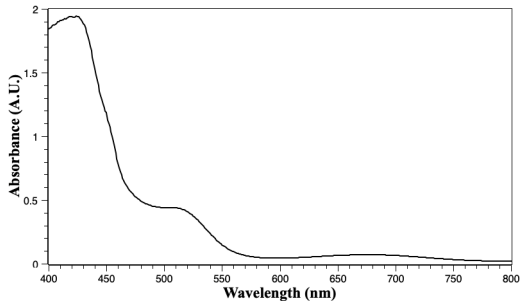
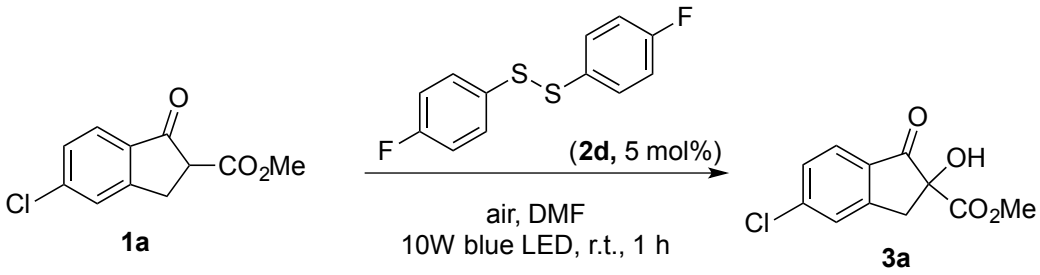


Figure S11. Absorbance of the ferrioxalate actinometer solution.

Determination of the reaction quantum yield:



The reaction was performed on photochemical reactor. A mixture of 5-chloroindanone carboxylic methyl ester (**1a**, 22.46 mg, 0.1 mmol), bis(4-fluorophenyl) disulfide (**2d**, 13.01 mg, 0.005mmol) were stirred in 4 mL of DMF in a quartz tube at room temperature under the irradiation of 10 W blue LED for a 1h. Meanwhile, the solution was bubbled with an air pump. After irradiation, the yield of product **3a** was determined to be 6% (0.006 mmol of **3a**). The reaction quantum yield (Φ) was determined using Equation S4 where the photon flux is 9.83×10^{-8} einstein s^{-1} (determined by actinometry as described above), t is the reaction time (3600 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using Equation S3. An absorbance of the reaction mixture at 450 nm was measured to be 0.032.

$$\emptyset = \frac{\text{mol of product formed}}{\text{photon flux} \cdot t \cdot f} \quad \text{(Equation S4)}$$

The reaction quantum yield (Φ) was thus determined to be 0.23

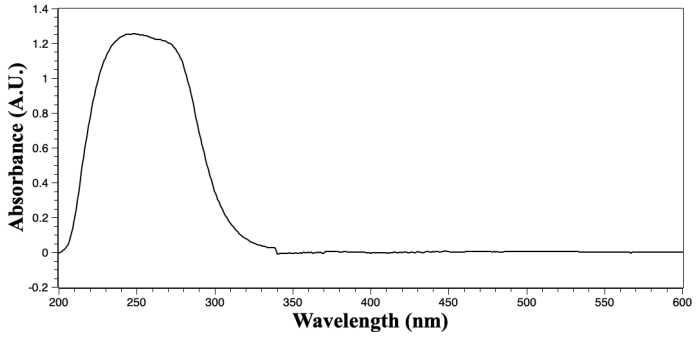


Figure S12. Absorbance of the reaction mixture solution.

6 Continuous-flow setup

6.1 Generalities of photo reactions

The photo reactions were conducted in a commercial continuous-flow reactor (Corning® Advanced Flow™ Lab Photo Reactor) featuring a compact glass mesofluidic module (155 × 125 mm size, 0.8 mm channel height, 2.7 mL internal volume) integrated with a high capacity heat exchanger (2 layer, 22 mL, 1 W mL^{-1} K^{-1}). LED panels were mounted on both sides of the fluidic module (40 mm from the center of the reactive layer), and each LED panel was equipped with multiple wavelengths (20 LEDs for each wavelength) and a heat exchanger (T=15°C). The thermoregulation of both the glass fluidic module and the LED panels was carried out with Huber minichiller 280 thermostats. Meonoethylenglycol was utilized as thermofluid.
The feed solution was conveyed to the photoreactor with a HPLC pump (Corning Intelligent Pump, UI-22, 0.1 – 10 mL min^{-1}) through a section of 1/8" PFA tubing (Swagelok®). The feed solution was installed on a precision scale for accurate flow rate monitoring. A dome-type back-pressure regulator (BPR, Zaiput Flow Technologies®) was inserted downstream the reactor. The gas flow rate was controlled with a Bronkhorst® F210CTM mass flow controller (MFC).

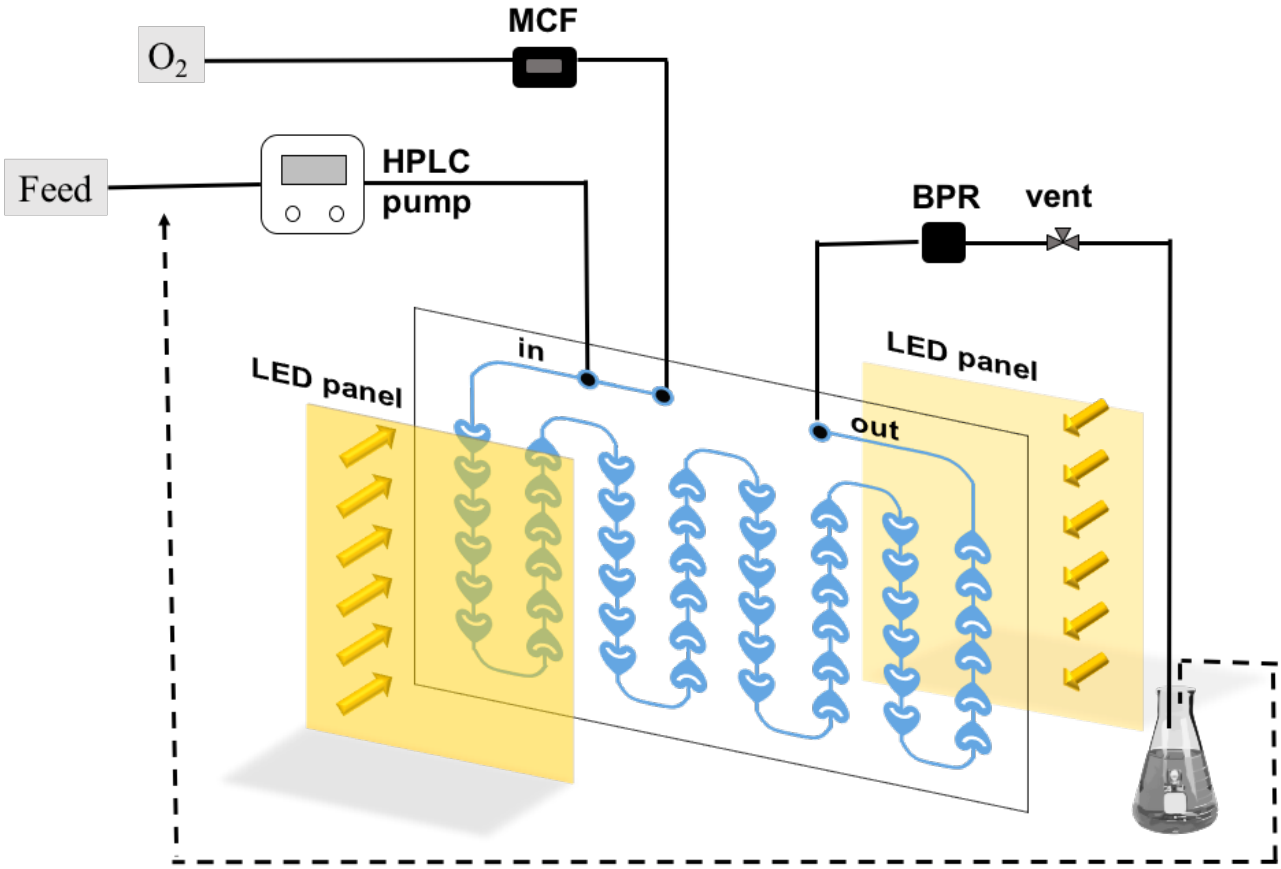


Figure S13. Continuous-Flow setup

6.2 Residence time calculation

The residence time is calculated according to Equation S1:

$$\text{Residence time (min)} = \frac{\text{Internal volume (mL)}}{\text{Flow rate (mL min}^{-1})} \quad \text{(Equation S1)}$$

The total flow rate combines the individual flow rates of all fluids fed into the reactor. The gas flow rate is calculated from the flow rate measured by the MFC according to Equation S2-3:

$$n_{O_2} = \frac{P_N(atm)V_N(L)}{R(L.atm.mol^{-1}.K^{-1})T_N(K)} \quad \text{(Equation S2)}$$

$$V_{real} = \frac{n_{O_2}RT_{real}}{P_{real}} \quad \text{(Equation S3)}$$

For example, the actual volume of O_2 delivered under 5 barg and 30°C when the MFC is set at 1 mL min^{-1} is 0.22 mL min^{-1} (see Equations S4-5):

$$n_{O_2} = \frac{P_N(atm)V_N(L)}{R(L.atm.mol^{-1}.K^{-1})T_N(K)} = \frac{1*0.001}{0.082*273.15} = 0.0446\ mmol \quad \text{(Equation S4)}$$

$$V_{real} = \frac{n_{O_2}RT_{real}}{P_{real}} = \frac{0.0000446*0.082*303.15}{5} = 0.22\ mL \text{ (Equation S5)}$$

Residence (irradiation) time within the reactor time was calculated according to Equation S1:

$$Residence\ Time = \frac{Internal\ volume\ (mL)}{Flow\ rate\ liquid\ phase\ \left(\frac{mL}{\text{min}}\right) + Real\ flow\ rate\ gas\ phase\ \left(\frac{mL}{\text{min}}\right)}$$

$$= \frac{2.7}{0.5 + 0.22}\ min = 3.75\ min$$

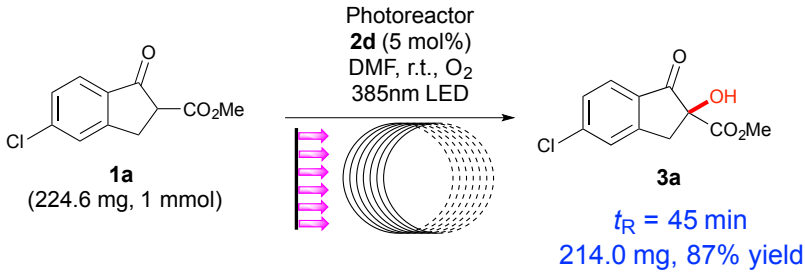
$$Total\ Residence\ Time = \frac{total\ time}{\frac{V_{mixcure}}{flow}rate\ liquid\ phase} \times Residence\ Time$$

$$= \frac{240min}{10mL/0.5mL\ min^{-1}} \times 3.75\ min = 45\ min$$

6.3 Typical runs

The HPLC pump used to deliver a solution of **1a** (0.2246g, 1 mmol, 1.0 equiv) and bis(4-fluorophenyl) disulfide **2d** (0.0127g, 5 mol%) in 10 mL DMF was set to 0.5 mL min^{-1} and the oxygen flow was set to 1 mL min^{-1} with the MCF, and both fluids were conveyed to the continuous-flow photoreactor through perfluoroalkoxyalkane (PFA) tubing (1/8" O.D.). Mixing and irradiation (385nm LED, 100% intensity) occurred along the entire reactor channel (2.7 mL internal volume, min residence time) under 5 barg of pressure.

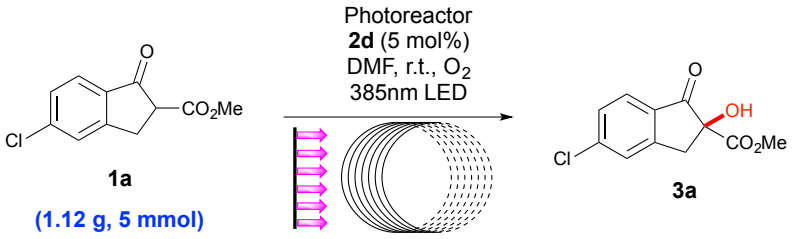
Table S7. Process optimization for the preparation of **3a**



Entry	**1a**	**2d** (eq)	feed 1 (mL min^{-1})	O_2 (mL min^{-1})	T (°C)	back-pressure	light resource	Total time	Res. time	Conv.[a] (yield)[b]
1	0.1M	0.1	0.5	2.5	20	0	385 nm	1h	2.6 min	quant.
2	0.1M	0.1	0.5	2.5	20	5	385 nm	1h	7.8 min	18%
3	0.1M	0.1	0.5	2.5	20	10	385 nm	1h	10.6 min	21%
4	0.1M	0.2	0.5	2.5	20	5	385 nm	1h	10.6 min	21%
5	0.1M	0.1	0.5	5.0	20	5	385 nm	1h	5.2 min	13%
6	0.1M	0.1	0.5	1.0	20	5	385 nm	1h	11.4 min	26%
7	0.1M	0.1	1.0	2.0	20	5	385 nm	1h	11.3 min	28%
8	0.1M	0.1	0.1	0.2	20	5	385 nm	1h	22.7 min	25%
9	0.1M	0.1	0.5	1.0	30	5	385 nm	1h	11.2 min	33%
10	0.1M	0.1	0.5	1.0	50	5	385 nm	1h	11.0 min	37%
11	0.1M	0.1	0.5	1.0	30	5	405 nm	1h	11.2 min	22%
12	0.1M	0.1	0.5	1.0	30	5	white LED	1h	11.2 min	quant.
13	0.1M	0.1	0.5	1.0	30	5	385 nm	2h	22.5 min	59%
14	0.1M	0.1	0.5	1.0	30	5	385 nm	3h	33.8 min	81%
15	0.1M	0.1	0.5	1.0	30	5	385 nm	4h	45.0 min	84% (87%)

[a] Reactions were carried out using continuous-flow reactor. [b] Determined by HPLC analysis. [c] Isolated yield.

Table S8. Gram-scale continuous flow process optimization for the preparation of **3a**

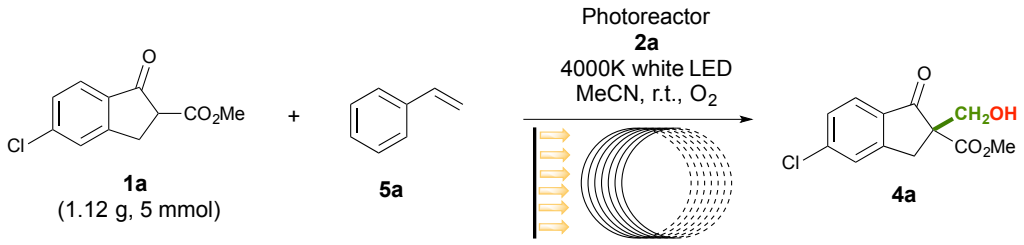


Entry	feed 1[c] (mL min^{-1})	feed 2[d] (mL min^{-1})	O_2 (mL min^{-1})	T (°C)	back-pressure	light resource	Total time	Res. time	yield[b]
1	1.5	0.15	20.0	30	5	385 nm	4h	43.6 min	30%
2	4.0	0.2	20.0	30	0	385 nm	4h	53.3 min	55%
3	4.0	0.2	20.0	30	5	385 nm	4h	67.8 min	82%

[a] Reactions were carried out using continuous-flow reactor. [b] Determined by ^{1}H-NMR. [c] **1a** (1.12g, 5 mmol) in 15 mL DMF [d] **2d** (0.060g, 5 mol%) in 15 mL DMF.

The HPLC pump used to deliver a solution of **1a** (1.12 g, 5 mmol, 1.0 equiv), disulfide **2a** (0.054g, 5 mol%) and styrene **5a** in 15 mL MeCN was set to 1.5 mL min^{-1} and the oxygen flow was set to 2.5 mL min^{-1} with the MCF, and both fluids were conveyed to the continuous-flow photoreactor through perfluoroalkoxyalkane (PFA) tubing (1/8" O.D.). Mixing and irradiation (4000K white LED, 100% intensity) occurred along the entire reactor channel (2.7 * 3 mL internal volume, min residence time).

Table S9. Gram-scale continuous flow process optimization for the preparation of **4a**[a]



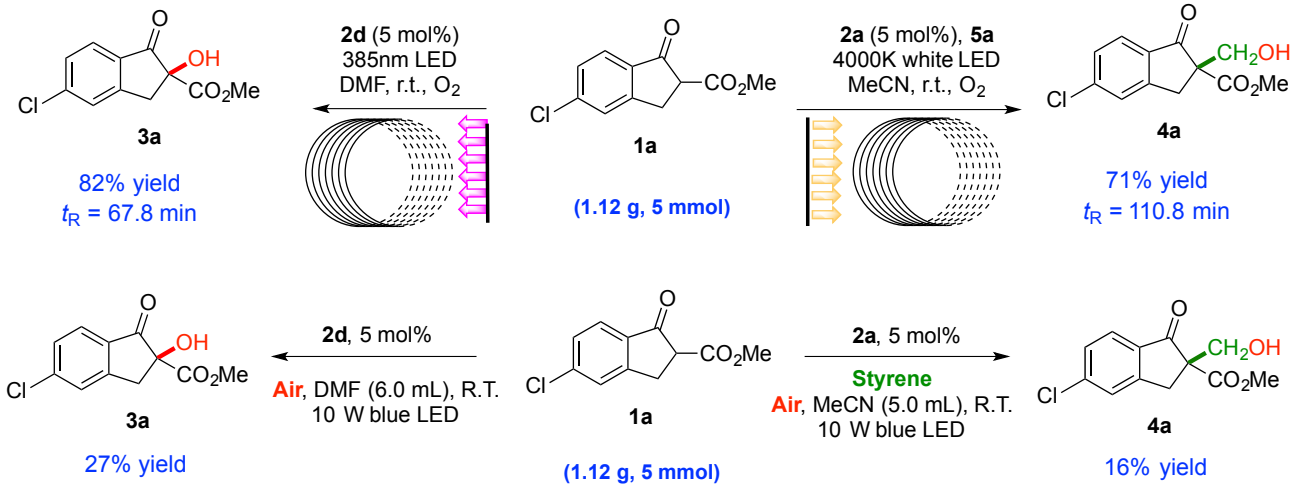
Entry	feed 1[c] (mL min^{-1})	feed 2[d] (mL min^{-1})	O_2 (mL min^{-1})	**5a** (equiv)	T (°C)	back-pressure	light resource	Total time	Res. time	yield[b]
1	1.5	2.5	1.5	30	0	white LED	4h	83.5 min	quant.	
2	1.5	12.5	1.5	30	5	white LED	4h	56.8 min	9%	

3		1.5	2.5	1.5	50	0	white LED	4h	90.4 min	18%
4		1.5	12.5	1.5	50	5	white LED	4h	60.0 min	24%
5		4.0	15.0	1.5	30	0	white LED	4h	56.9 min	35%
6		4.0	20.0	1.5	30	0	white LED	4h	66.5 min	41%
7		4.0	20.0	1.5	30	0	385 nm	8h	133.0 min	37%
8		4.0	20.0	1.5	30	0	405 nm	8h	133.0 min	29%
9	0.2	4.0	20.0	1.5	30	0	white LED	8h	110.1 min	56%
10	0.2	4.0	20.0	4.0	30	5	white LED	8h	110.8 min	71%

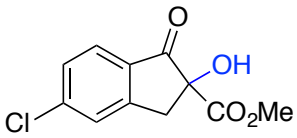
[a] Reactions were carried out using continuous-flow reactor. [b] Determined by ^{1}H-NMR. . [c] **1a** (1.12g, 5 mmol) and **5a** in 15 mL MeCN, [d] **2a** (0.108g, 10 mol%) in 30 mL DMF.

6.4 Gram-scale

Scheme S8. Gram-scale experiments.



7 Characterization data for all products



3a

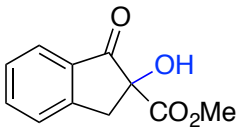
methyl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3a)

Prepared according to the general procedure with a reaction time of 8h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3a** as white solid: 23.11 mg, 96% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.43 – 7.39 (m, 1H), 3.95 (s, 1H), 3.74 (s, 3H), 3.69 (d, *J* = 17.4 Hz, 1H), 3.23 (d, *J* = 17.4 Hz, 1H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.38, 171.51, 153.54, 142.79, 132.00, 129.02, 126.74, 126.36, 80.45, 53.53, 39.01.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9ClO_4$ $[M+H]^+$:241.0262 , found: 241.0263.



3b

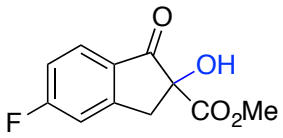
methyl 2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3b)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3b** as white solid: 12.99 mg, 63% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.68 (td, *J* = 7.7, 1.3 Hz, 1H), 7.50 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 3.98 (s, 1H), 3.81 – 3.67 (m, 4H), 3.26 (d, *J* = 17.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.92, 152.21, 136.18, 133.55, 128.17, 126.49, 125.34, 80.39, 53.46, 39.29, 29.70.

HRMS (m/z): (ESI) calc'd for $C_{11}H_{10}O_4$ $[M+H]^+$:207.0652 , found: 207.0651.



3c

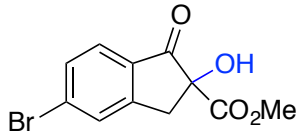
methyl 5-fluoro-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3c)

Prepared according to the general procedure with a reaction time of 8 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3b** as white solid: 17.49 mg, 78% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.14 (q, *J* = 8.4, 5.3 Hz, 2H), 4.00 (s, 1H), 3.75 (s, 3H), 3.72 (d, *J* = 17.5 Hz, 1H), 3.24 (d, *J* = 17.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.78, 170.56, 167.97, 165.91, 154.16, 126.73, 115.54, 112.42, 52.54, 38.12, 28.68.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9FO_4$ $[M+H]^+$:225.0558 , found: 225.0558.



3d

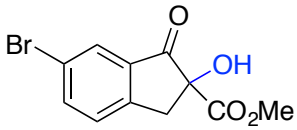
methyl 5-bromo-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3d)

Prepared according to the general procedure with a reaction time of 8 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3d** as white solid: 27.94 mg, 98% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 1H), 3.75 (s, 3H), 3.70 (d, *J* = 17.4 Hz, 1H), 3.24 (d, *J* = 17.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.54, 171.46, 153.55, 132.39, 131.91, 129.83, 126.40, 80.34, 53.59, 38.87, 29.69.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9BrO_4$ $[M+H]^+$:284.9757 , found: 284.9760.



3e

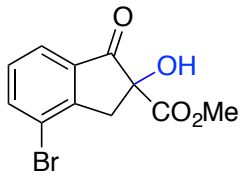
methyl 6-bromo-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3e)

Prepared according to the general procedure with a reaction time of 8 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3e** as white solid: 27.94 mg, 98% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.9 Hz, 1H), 7.77 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.41 – 7.36 (m, 1H), 4.01 (s, 1H), 3.75 (s, 3H), 3.67 (d, *J* = 17.4 Hz, 1H), 3.19 (d, *J* = 17.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.53, 163.53, 161.55, 147.60, 135.21, 127.95, 124.00, 111.13, 53.57, 38.73, 29.68.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9BrO_4$ $[M+H]^+$:284.9757 , found: 284.9760.



3f

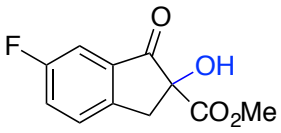
methyl 4-bromo-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3f)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3f** as white solid: 24.23 mg, 85% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 3.99 (s, 1H), 3.77 (s, 3H), 3.68 (d, *J* = 17.8 Hz, 1H), 3.18 (d, *J* = 17.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.14, 171.50, 151.92, 138.84, 135.52, 129.88, 124.06, 121.86, 53.63, 40.38, 29.69.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9BrO_4$ $[M+H]^+$:284.9757 , found: 284.9760.



3g

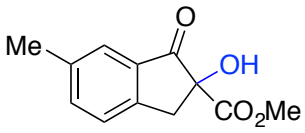
methyl 6-fluoro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3g)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3g** as white solid: 15.24 mg, 68% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 1H), 7.44 (dd, *J* = 7.3, 2.5 Hz, 1H), 7.39 (td, *J* = 8.5, 2.5 Hz, 1H), 3.97 (s, 1H), 3.75 (s, 3H), 3.69 (d, *J* = 16.8 Hz, 1H), 3.22 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.53, 163.53, 161.55, 147.60, 135.21, 127.95, 124.00, 111.13, 53.57, 38.73, 29.68.

HRMS (m/z): (ESI) calc'd for $C_{11}H_9FO_4$ $[M+H]^+$:225.0558 , found: 225.0556.



3h

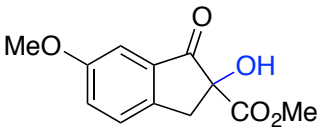
methyl 2-hydroxy-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3h)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3h** as white solid: 17.84 mg, 81% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 1.6 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 3.95 (t, *J* = 4.3 Hz, 1H), 3.73 (s, 3H), 3.68 (d, *J* = 17.1 Hz, 1H), 3.20 (d, *J* = 17.1 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.83, 172.02, 149.60, 138.24, 137.46, 133.68, 126.13, 125.17, 80.73, 53.40, 38.96, 21.06.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{12}O_4$ $[M+H]^+$:221.0808 , found: 221.0808.



3i

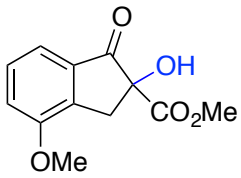
methyl 2-hydroxy-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3i)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3i** as white solid: 7.80 mg, 33% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 3.94 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.65 (d, *J* = 16.9 Hz, 1H), 3.17 (d, *J* = 16.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.75, 171.98, 159.86, 145.15, 134.68, 127.17, 125.63, 106.28, 81.06, 55.65, 53.44, 38.68.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{12}O_5$ $[M+H]^+$:237.0757 , found:237.0758.



3j

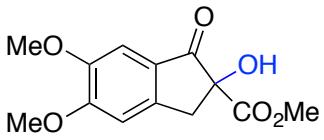
methyl 2-hydroxy-4-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3j)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3j** as white solid: 4.02 mg, 17% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 2H), 7.11 (dd, *J* = 6.9, 1.9 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 3.66 (d, *J* = 17.6 Hz, 1H), 3.11 (d, *J* = 17.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.94, 172.03, 156.73, 141.19, 134.88, 129.66, 116.65, 116.30, 80.24, 55.56, 53.40, 36.16.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{12}O_5$ $[M+H]^+$:237.0757 , found: 237.0758.



3k

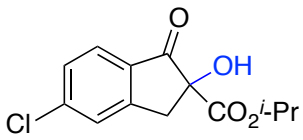
methyl 2-hydroxy-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3k)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3k** as white solid: 3.46 mg, 13% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (s, 1H), 6.90 (s, 1H), 4.00 (s, 3H), 3.94 (s, 1H), 3.92 (s, 3H), 3.75 (s, 3H), 3.64 (d, *J* = 17.0 Hz, 1H), 3.16 (d, *J* = 17.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.20, 156.78, 150.04, 148.09, 126.16, 107.31, 105.38, 80.79, 56.41, 56.18, 53.44, 39.00, 29.71.

HRMS (m/z): (ESI) calc'd for $C_{13}H_{14}O_6$ $[M+H]^+$: 267.0863, found: 267.0864.



3l

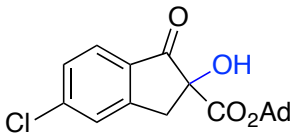
isopropyl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3l)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3l** as white solid: 23.64 mg, 88% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.7 Hz, 1H), 5.08 (hept, *J* = 6.2 Hz, 1H), 3.97 (s, 1H), 3.66 (d, *J* = 17.3 Hz, 1H), 3.21 (d, *J* = 17.3 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 153.68, 142.68, 128.97, 126.69, 126.27, 80.31, 71.17, 38.98, 29.71, 21.56, 21.34.

HRMS (m/z): (ESI) calc'd for $C_{13}H_{13}ClO_4$ $[M+H]^+$: 269.0575, found:269.0577.



3m

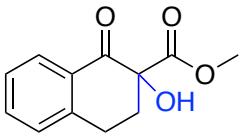
adamantan-1-yl 5-chloro-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3m)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 10/1, Rf = 0.4) to give **3m** as white solid: 33.20 mg, 92% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.04 (s, 1H), 3.64 (d, *J* = 17.3 Hz, 1H), 3.21 (d, *J* = 17.3 Hz, 1H), 2.17 – 2.12 (m, 3H), 1.98 (d, *J* = 3.0 Hz, 6H), 1.62 (d, *J* = 3.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.97, 169.80, 153.68, 142.37, 132.47, 128.77, 126.51, 126.07, 84.25, 80.52, 40.95, 39.26, 35.85, 30.83.

HRMS (m/z): (ESI) calc'd for $C_{20}H_{21}ClO_4$ $[M+H]^+$: 361.1201, found: 361.1200.



3n

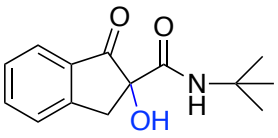
methyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3n)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.3) to give **3n** as white solid: 11.89 mg, 54% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.54 (td, *J* = 7.9, 1.4 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.28 (s, 1H), 4.33 (s, 1H), 3.75 (s, 3H), 3.25 – 2.98 (m, 2H), 2.72 (dt, *J* = 13.6, 5.0 Hz, 1H), 2.25 (ddd, *J* = 13.6, 9.3, 5.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.57, 171.08, 144.05, 134.45, 130.17, 128.96, 128.26, 127.01, 53.01, 32.75, 29.70, 25.58.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{12}O_4$ $[M+H]^+$: 221.0808, found:221.0809.



3o

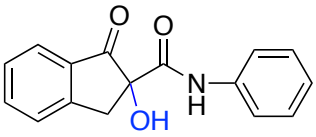
N-(tert-butyl)-2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxamide (3o)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **3o** as white solid: 13.11 mg, 53% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 3.70 (d, *J* = 16.7 Hz, 1H), 3.49 (s, 1H), 3.07 (d, *J* = 16.7 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.75, 169.41, 153.06, 136.18, 134.02, 127.97, 126.32, 125.06, 82.30, 51.41, 40.75, 28.56, 1.03.

HRMS (m/z): (ESI) calc'd for $C_{14}H_{17}NO_3$ $[M+H]^+$: 248.1281, found:248.1281.



3p

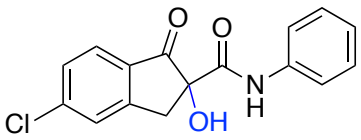
2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (3p)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.3) to give **3p** as white solid: 17.64 mg, 66% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.43 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.10 – 7.03 (m, 1H), 4.12 (s, 1H), 3.81 (d, *J* = 16.8 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.00, 168.22, 152.98, 136.91, 136.50, 133.70, 129.01, 128.18, 126.38, 125.23, 124.78, 119.98, 119.71, 82.73, 40.85.

HRMS (m/z): (ESI) calc'd for $C_{16}H_{13}NO_3$ $[M+H]^+$: 268.0968, found:268.0970.



3q

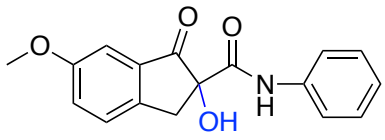
5-chloro-2-hydroxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (3q)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **3q** as white solid: 27.76 mg, 92% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 3.83 (d, *J* = 16.9 Hz, 1H), 3.17 (d, *J* = 16.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.56, 167.85, 154.30, 143.26, 136.75, 132.11, 129.05, 126.67, 126.22, 124.92, 119.72, 82.86, 40.57, 29.70.

HRMS (m/z): (ESI) calc'd for $C_{16}H_{12}ClNO_3$ $[M+H]^+$: 302.0578, found:302.0582.



3r

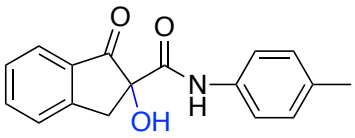
2-hydroxy-6-methoxy-1-oxo-N-phenyl-2,3-dihydro-1H-indene-2-carboxamide (3r)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **3r** as white solid: 25.87 mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.69 (d, *J* = 16.5 Hz, 1H), 3.03 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.00, 168.43, 159.82, 146.07, 136.93, 134.82, 128.98, 127.12, 125.96, 124.74, 119.73, 106.19, 83.24, 55.65, 40.22, 29.70.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{15}NO_4$ $[M+H]^+$: 298.1074, found:298.1079.



3s

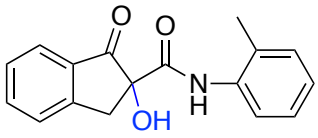
2-hydroxy-1-oxo-N-(p-tolyl)-2,3-dihydro-1H-indene-2-carboxamide (3s)

Prepared according to the general procedure with a reaction time of 12 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **3s** as white solid: 22.22 mg, 79% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.01 – 6.93 (m, 1H), 3.78 (d, *J* = 16.8 Hz, 1H), 3.62 (s, 1H), 3.11 (d, *J* = 16.8 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.06, 167.99, 152.97, 136.46, 134.42, 134.37, 133.74, 129.49, 128.16, 126.37, 125.22, 119.68, 82.72, 40.86, 20.87.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{15}NO_3$ $[M+H]^+$: 282.1125, found:282.1126



3t

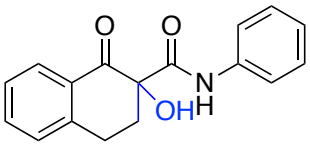
2-hydroxy-1-oxo-N-(o-tolyl)-2,3-dihydro-1H-indene-2-carboxamide (3t)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **3t** as white solid: 14.47 mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.01 – 6.93 (m, 1H), 3.78 (d, *J* = 16.8 Hz, 1H), 3.62 (s, 1H), 3.11 (d, *J* = 16.8 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.26, 168.35, 153.14, 136.37, 134.41, 134.34, 133.79, 129.44, 128.04, 126.38, 125.14, 119.78, 82.57, 77.36, 77.04, 76.72, 40.82, 20.87.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{15}NO_3$ $[M+H]^+$: 282.1125, found:282.1126



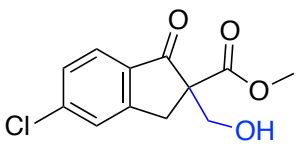
3u

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **3u** as white solid: 15.19 mg, 54% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.32 (dt, *J* = 26.5, 7.7 Hz, 4H), 7.10 (d, *J* = 7.7 Hz, 1H), 4.84 (s, 1H), 3.62 (ddd, *J* = 17.4, 13.0, 5.4 Hz, 1H), 3.01 (ddd, *J* = 17.4, 5.4, 2.1 Hz, 1H), 2.62 (ddd, *J* = 13.0, 5.4, 2.1 Hz, 1H), 2.34 (td, *J* = 13.2, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.05, 167.79, 145.69, 136.94, 134.64, 130.66, 129.01, 128.00, 126.71, 124.66, 119.64, 34.64, 29.70, 27.09, 26.34, 22.69, 14.11.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{15}NO_3$ $[M+H]^+$: 282.1125, found: 282.1124.



4a

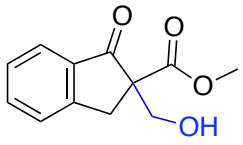
methyl 5-chloro-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4a)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.1) to give **4a** as white solid: 20.62 mg, 81% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 1H), 7.41 – 7.37 (m, 1H), 4.12 (d, *J* = 11.2 Hz, 1H), 3.90 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.54 (d, *J* = 17.5 Hz, 1H), 3.39 (d, *J* = 17.5 Hz, 1H), 2.53 (s, 1H).

^{13}C NMR (126 MHz, CDCl3) δ 200.03, 170.76, 154.99, 142.26, 133.70, 128.70, 126.81, 125.81, 64.64, 62.50, 52.92, 34.58.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{11}ClO_4$ $[M+H]^+$: 255.0419, found: 255.0419.



4b

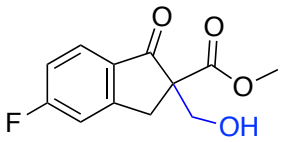
methyl 2-(hydroxymethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4b)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.1) to give **4b** as white solid: 19.60 mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.90 (d, *J* = 11.3 Hz, 1H), 3.74 (s, 3H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.43 (d, *J* = 17.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.19, 135.16, 130.82, 130.14, 128.19, 127.60, 126.49, 125.37, 112.34, 53.48, 52.98, 39.27.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{12}O_4$ $[M+H]^+$: 221.0808, found:221.0811.



4c

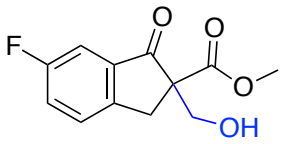
methyl 5-fluoro-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4c)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.2) to give **4c** as white solid: 20.25 mg, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.07 (td, *J* = 8.6, 2.2 Hz, 1H), 4.09 (d, *J* = 11.3 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 1H), 3.68 (s, 2H), 3.50 (d, *J* = 17.7 Hz, 1H), 3.35 (d, *J* = 17.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 199.98, 171.01, 154.81, 134.08, 131.65, 131.22, 129.93, 125.95, 77.34, 77.02, 76.70, 64.90, 62.25, 52.95, 34.68.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{11}FO_4$ $[M+H]^+$: 239.0714, found: 239.0719.



4d

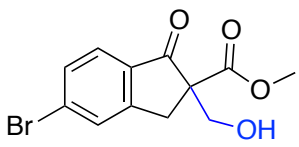
methyl 6-fluoro-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4d)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.2) to give **4d** as white solid: 19.77 mg, 83% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 8.4, 4.2 Hz, 1H), 7.37 (ddt, *J* = 16.7, 8.4, 4.2 Hz, 2H), 4.11 (d, *J* = 11.3 Hz, 1H), 3.89 (d, *J* = 11.3 Hz, 1H), 3.71 (s, 3H), 3.51 (d, *J* = 17.2 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.15, 163.77, 161.29, 148.72, 137.00, 136.92, 128.04, 127.96, 123.56, 110.67, 64.96, 63.04, 52.92, 34.50.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{11}FO_4$ $[M+H]^+$: 239.0714, found: 239.0719.



4e

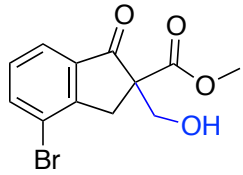
methyl 5-bromo-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4e)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.1) to give **4e** as white solid: 26.62 mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 4.06 (d, *J* = 11.2 Hz, 1H), 3.82 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.48 (d, *J* = 17.7 Hz, 1H), 3.33 (d, *J* = 17.7 Hz, 1H), 1.57 (s, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 199.98, 171.01, 154.81, 134.08, 131.65, 131.22, 129.93, 125.95, 77.34, 77.02, 76.70, 64.90, 62.25, 52.95, 34.68.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{11}BrO_4$ $[M+H]^+$: 298.9913, found:298.9919.



4f

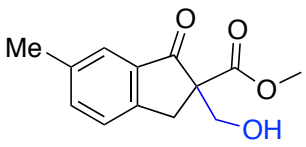
methyl 4-bromo-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4f)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.1) to give **4f** as white solid: 27.52 mg, 92% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 32.2, 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 4.09 (d, *J* = 11.3 Hz, 1H), 3.86 (d, *J* = 11.3 Hz, 1H), 3.68 (s, 3H), 3.44 (d, *J* = 18.0 Hz, 1H), 3.30 (d, *J* = 18.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.98, 171.01, 154.81, 134.08, 131.65, 131.22, 129.93, 125.95, 77.34, 77.02, 76.70, 64.90, 62.25, 52.95, 34.68.

HRMS (m/z): (ESI) calc'd for $C_{12}H_{11}BrO_4$ $[M+H]^+$: 298.9913, found: 298.9916.



4g

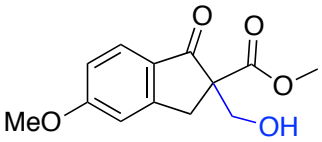
methyl 2-(hydroxymethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4g)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 5/1, Rf = 0.2) to give **4g** as white solid: 21.08 mg, 90% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 4.11 (d, *J* = 11.3 Hz, 1H), 3.85 (d, *J* = 11.3 Hz, 1H), 3.70 (s, 3H), 3.49 (d, *J* = 17.3 Hz, 1H), 3.33 (d, *J* = 17.3 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.41, 171.70, 150.70, 138.02, 136.98, 135.40, 126.26, 124.70, 65.18, 62.43, 52.78, 34.76, 21.07.

HRMS (m/z): (ESI) calc'd for $C_{13}H_{14}O_4$ $[M+H]^+$: 235.0965, found:235.0968.



4h

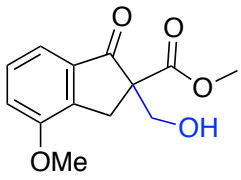
methyl 2-(hydroxymethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4h)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.1) to give **4h** as white solid: 22.02 mg, 88% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 9.2 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 2H), 4.13 (d, *J* = 11.2 Hz, 1H), 3.90 (s, 3H), 3.88 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.51 (d, *J* = 17.5 Hz, 1H), 3.34 (d, *J* = 17.5 Hz, 1H), 2.72 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.26, 171.65, 166.09, 156.44, 128.37, 126.53, 116.14, 109.60, 65.20, 62.41, 55.77, 52.74, 35.01.

HRMS (m/z): (ESI) calc'd for $C_{13}H_{14}O_5$ $[M+H]^+$: 251.0914, found:251.0916.



4i

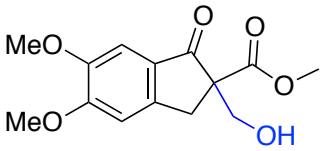
methyl 2-(hydroxymethyl)-4-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4i)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.1) to give **4i** as white solid: 23.77 mg, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 2H), 7.06 (dd, *J* = 6.8, 1.9 Hz, 1H), 4.09 (d, *J* = 11.3 Hz, 1H), 3.90 (s, 3H), 3.88 (d, *J* = 11.3 Hz, 1H), 3.69 (s, 3H), 3.43 (d, *J* = 17.9 Hz, 1H), 3.27 (d, *J* = 17.9 Hz, 1H), 2.60 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.64, 171.62, 156.91, 142.24, 136.64, 129.57, 116.19, 115.75, 77.40, 77.08, 76.76, 65.11, 61.88, 55.55, 52.80, 32.06.

HRMS (m/z): (ESI) calc'd for $C_{13}H_{14}O_5$ $[M+H]^+$: 251.0914, found:251.0916.



4j

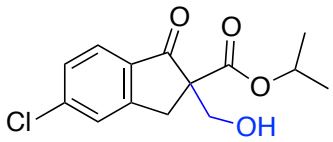
methyl 2-(hydroxymethyl)-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4j)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.1) to give **4j** as white solid: 27.19mg, 97% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (s, 1H), 6.92 (s, 1H), 4.14 (d, *J* = 11.2 Hz, 1H), 3.99 (s, 3H), 3.94 – 3.85 (m, 4H), 3.72 (s, 3H), 3.47 (d, *J* = 17.2 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 2.82 (s, 1H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.73, 171.67, 156.33, 149.86, 149.03, 127.89, 107.32, 104.89, 77.30, 77.05, 76.80, 65.20, 62.46, 56.34, 56.11, 52.72, 34.78.

HRMS (m/z): (ESI) calc'd for $C_{14}H_{16}O_6$ $[M+H]^+$: 281.1020, found:281.1022.



4k

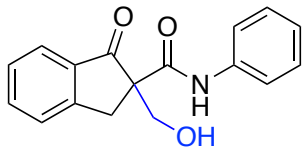
isopropyl 5-chloro-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4k)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.4) to give **4k** as white solid: 15.27mg, 54% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 1H), 7.46 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 5.02 (dq, *J* = 12.6, 6.4 Hz, 1H), 4.05 (d, *J* = 11.2 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 3.32 (d, *J* = 17.6 Hz, 1H), 2.24 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.91, 170.31, 154.74, 142.15, 133.73, 128.75, 126.82, 125.85, 77.34, 77.02, 76.71, 69.71, 64.98, 62.47, 34.77, 21.53, 21.46.

HRMS (m/z): (ESI) calc'd for $C_{14}H_{15}ClO_4$ $[M+H]^+$: 283.0732, found:283.0736.



4l

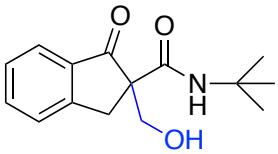
2-(hydroxymethyl)-1-oxo-*N*-phenyl-2,3-dihydro-1*H*-indene-2-carboxamide (4l)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 4/1, Rf = 0.2) to give **4l** as white solid: 20.25mg, 72% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 3H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.02 (d, *J* = 10.9 Hz, 1H), 3.90 (s, 1H), 3.87 (d, *J* = 10.9 Hz, 1H), 3.21 (d, *J* = 10.0 Hz, 1H), 1.55 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.93, 165.47, 152.71, 136.49, 135.36, 133.86, 127.95, 126.88, 125.65, 123.71, 123.67, 123.56, 119.09, 118.67, 67.22, 62.00, 32.81.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{15}NO_3$ $[M+H]^+$: 282.1125, found: 282.1127.



4m

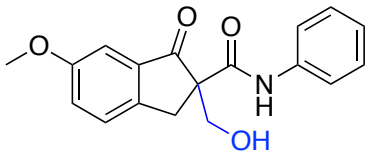
***N*-(*tert*-butyl)-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (4m)**

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.3) to give **4m** as white solid: 10.98 mg, 42% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 3.73 (d, *J* = 16.7 Hz, 1H), 3.10 (d, *J* = 16.7 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.84, 169.46, 153.12, 136.19, 134.01, 127.96, 126.33, 125.06, 82.28, 77.34, 77.03, 76.71, 51.41, 40.74, 28.55.

HRMS (m/z): (ESI) calc'd for $C_{15}H_{19}NO_3$ $[M+H]^+$: 262.1438, found:262.1437.



4n

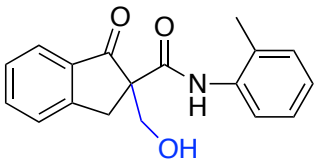
2-(hydroxymethyl)-6-methoxy-1-oxo-*N*-phenyl-2,3-dihydro-1*H*-indene-2-carboxamide (4n)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4n** as white solid: 23.04mg, 74% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.4, 5.8 Hz, 3H), 7.21 – 7.16 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.00 (d, *J* = 10.9 Hz, 1H), 3.87 (d, *J* = 10.9 Hz, 1H), 3.79 – 3.73 (m, 3H), 3.76 (s, 3H), 3.10 (d, *J* = 17.6 Hz, 1H), 2.47 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.80, 165.58, 158.68, 145.75, 136.51, 134.94, 127.95, 126.41, 126.37, 124.88, 123.54, 119.08, 118.93, 104.51, 67.29, 62.82, 54.63, 32.20.

HRMS (m/z): (ESI) calc'd for $C_{18}H_{17}NO_4$ $[M+H]^+$: 312.1230, found:312.1234.



4o

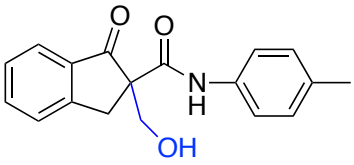
2-(hydroxymethyl)-1-oxo-*N*-(*o*-tolyl)-2,3-dihydro-1*H*-indene-2-carboxamide (4o)

Prepared according to the general procedure with a reaction time of 12h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4o** as white solid: 25.69mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 4.03 (d, *J* = 10.9 Hz, 1H), 3.96 – 3.81 (m, 2H), 3.20 (d, *J* = 10.9 Hz, 1H), 2.34 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.12, 165.50, 152.74, 135.34, 134.72, 133.87, 129.44, 127.55, 126.89, 125.69, 125.63, 123.89, 123.66, 120.93, 67.39, 62.09, 32.85, 16.84.

HRMS (m/z): (ESI) calc'd for $C_{18}H_{17}NO_3$ $[M+H]^+$: 296.1281, found:296.1284.



4p

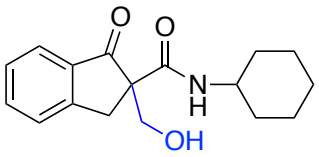
2-(hydroxymethyl)-1-oxo-*N*-(*p*-tolyl)-2,3-dihydro-1*H*-indene-2-carboxamide (4p)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4m** as white solid: 24.51mg, 83% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.01 (d, *J* = 10.9 Hz, 1H), 3.93 – 3.81 (m, 2H), 3.22 (d, *J* = 17.9 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.06, 166.38, 153.78, 136.37, 134.97, 134.25, 129.47, 127.89, 126.70, 126.38, 125.21, 124.69, 120.16, 119.70, 68.27, 62.99, 33.90, 20.90.

HRMS (m/z): (ESI) calc'd for $C_{18}H_{17}NO_3$ $[M+H]^+$: 296.1281, found:296.1283.



4q

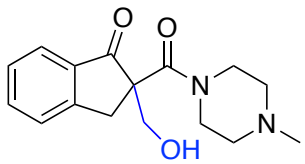
***N*-cyclohexyl-2-(hydroxymethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (4q)**

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4q** as white solid: 25.57mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.82 (d, *J* = 18.0 Hz, 1H), 3.27 (d, *J* = 18.0 Hz, 1H), 2.81 (s, 1H), 1.99 – 1.92 (m, 1H), 1.82 (dd, *J* = 12.8, 4.0 Hz, 1H), 1.72 (dtd, *J* = 17.3, 8.2, 4.0 Hz, 1H), 1.60 (dt, *J* = 12.8, 4.0 Hz, 1H), 1.46 – 1.13 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.17, 167.71, 153.86, 136.09, 135.14, 127.71, 126.68, 124.50 , 68.20, 62.35, 48.44, 33.98, 32.74, 32.60, 25.52, 24.59, 24.55.

HRMS (m/z): (ESI) calc'd for $C_{17}H_{21}NO_3$ $[M+H]^+$:288.1594, found:288.1596.



4r

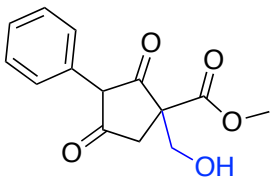
2-(hydroxymethyl)-2-(4-methylpiperazine-1-carbonyl)-2,3-dihydro-1*H*-inden-1-one (4r)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, CH_2Cl_2/CH_3OH = 10/1, Rf = 0.2) to give **4r** as white solid: 23.36mg, 81% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.36 – 7.29 (m, 1H), 4.06 (dd, *J* = 7.9, 3.5 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.81 (dd, *J* = 17.2, 3.5 Hz, 1H), 3.60 (dt, *J* = 12.7, 7.3, 5.3 Hz, 1H), 3.40 (ddd, *J* = 12.7, 7.3, 3.2 Hz, 1H), 3.21 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.66 – 2.60 (m, 2H), 2.55 (dt, *J* = 12.7, 5.3, 3.2 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.53, 166.06, 154.69, 135.36, 135.18, 127.55, 126.55, 124.30, 55.09, 54.42, 50.42, 46.01, 45.61, 41.98, 30.38.

HRMS (m/z): (ESI) calc'd for $C_{16}H_{20}N_2O_3$ $[M+H]^+$: 289.1547, found: 289.1542.



4s

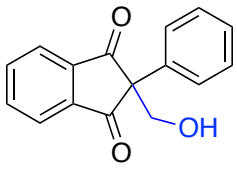
methyl 3-(hydroxymethyl)-2,5-dioxo-1-phenylpyrrolidine-3-carboxylate (4s)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4s** as white solid: 20.19mg, 77% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.54 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.02 – 3.92 (m, 1H), 3.80 (s, 3H), 3.66 (td, *J* = 8.0, 7.0, 3.0 Hz, 1H), 2.55 (dt, *J* = 13.2, 8.0, 7.0 Hz, 1H), 2.46 – 2.33 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25, 168.74, 138.89, 128.88, 125.05, 120.10, 77.38, 77.07, 76.75, 52.77, 49.88, 47.25, 29.70, 22.18, 1.03.

HRMS (m/z): (ESI) calc'd for $C_{14}H_{14}O_5$ $[M+H]^+$: 263.0914, found: 263.0916.



4t

2-(hydroxymethyl)-2-phenyl-1H-indene-1,3(2H)-dione (4t)

Prepared according to the general procedure with a reaction time of 24 h. After column chromatography (silica gel, petroleum ether/ether acetate = 3/1, Rf = 0.2) to give **4t** as white solid: 21.44mg, 85% yield.

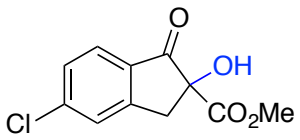
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 – 8.00 (m, 1H), 7.98 – 7.84 (m, 2H), 7.81 – 7.71 (m, 1H), 7.44 (dd, *J* = 31.2, 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 5.12 (s, 1H), 2.96 (s, 1H), 2.89 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.69, 135.62, 133.52, 130.48, 130.13, 129.95, 129.05, 128.93, 128.76, 128.68, 128.65, 128.44, 127.56, 126.26, 124.34, 123.77, 64.46, 36.57, 31.52, 29.70.

HRMS (m/z): (ESI) calc'd for $C_{16}H_{12}O_3$ $[M+H]^+$: 253.0859, found: 253.0856.

8 NMR Spectra

Compound **3a** ^{1}HNMR



3a

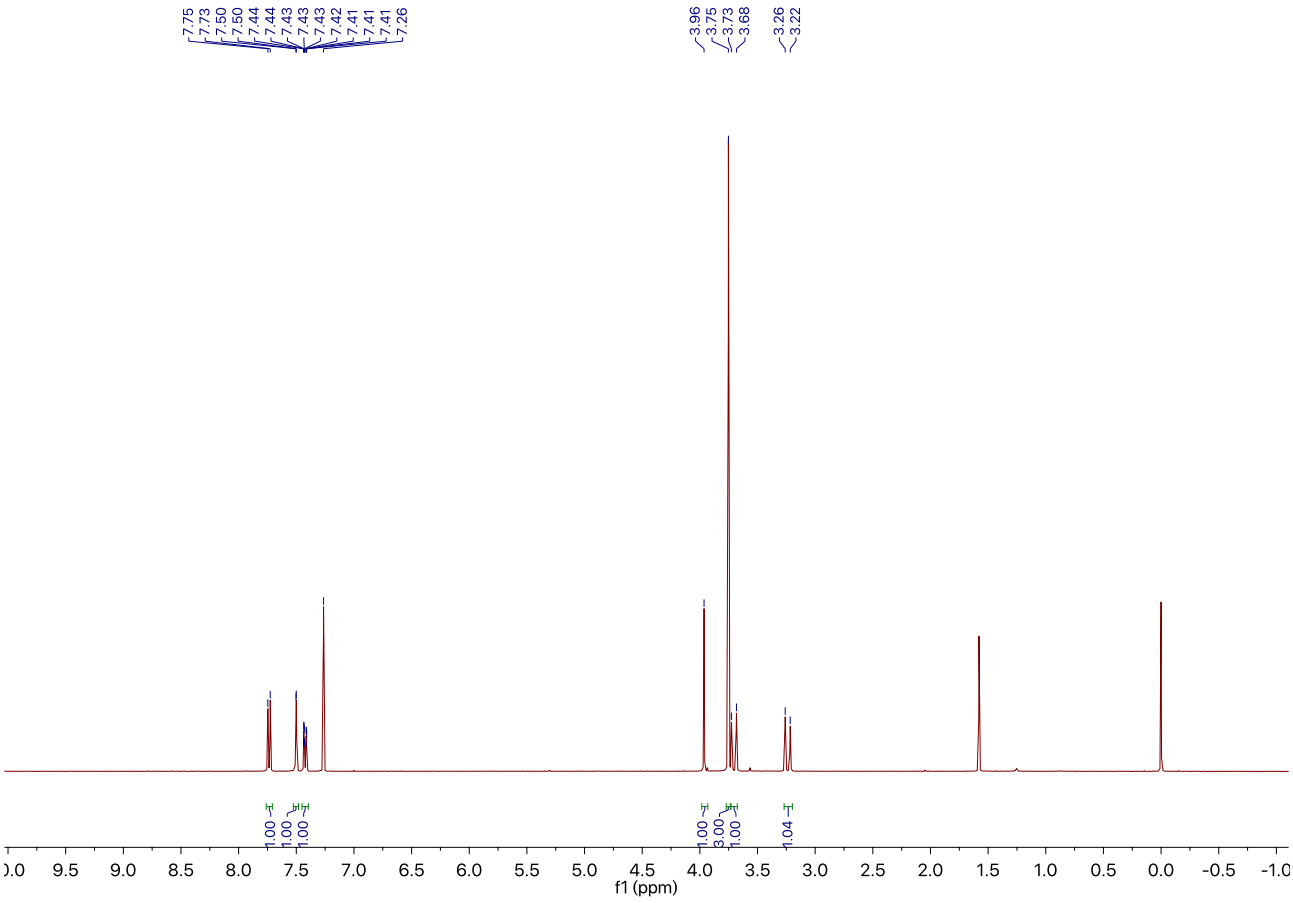
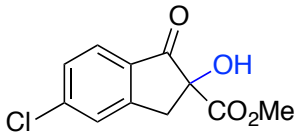


Figure S14. ^{1}HNMR Spectra of Compound **3a**

Compound **3a** ^{13}CNMR



3a

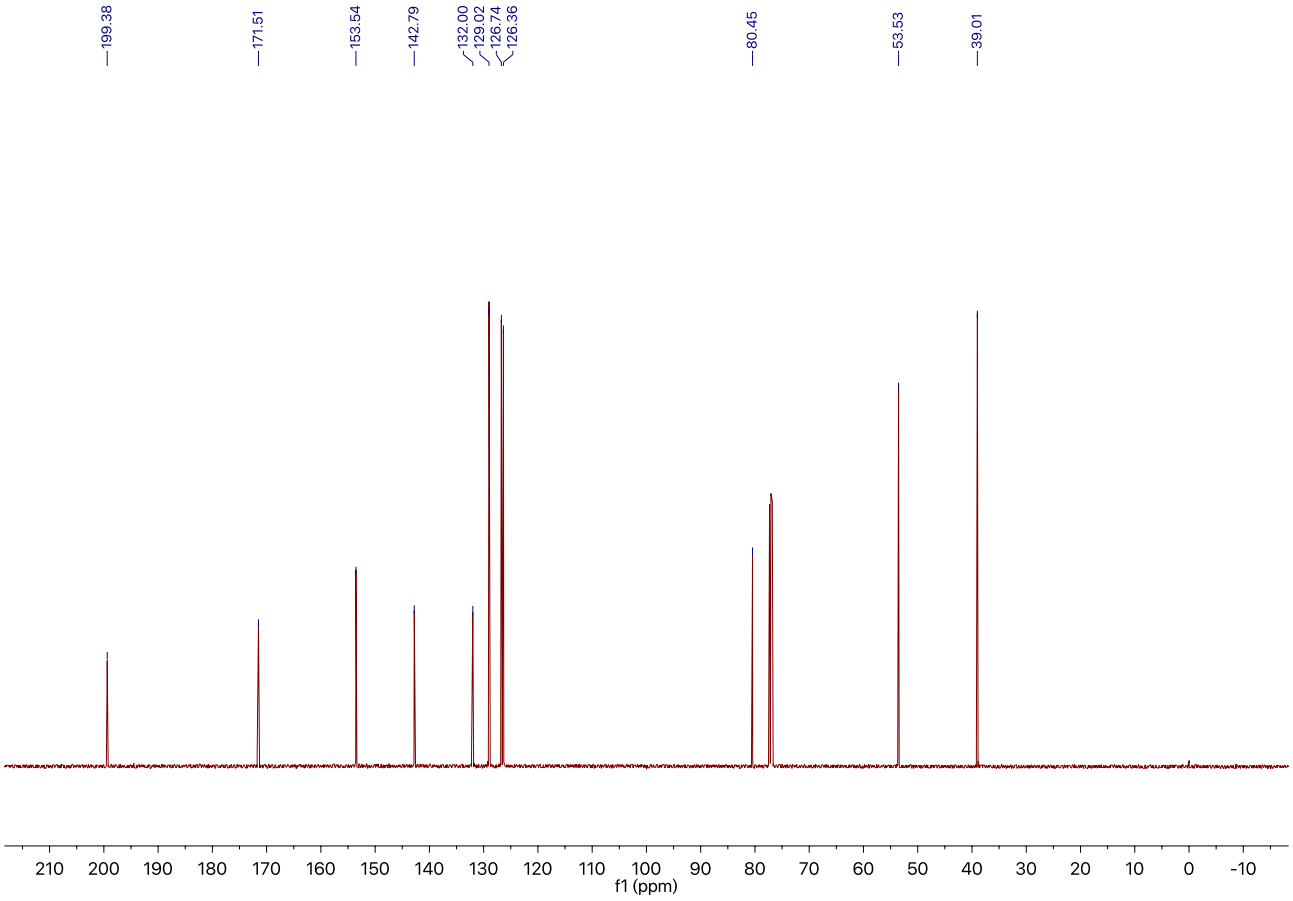
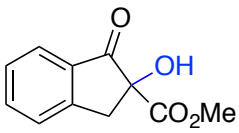


Figure S15. ^{13}CNMR Spectra of Compound **3a**

Compound **3b** [1]HNMR



3b

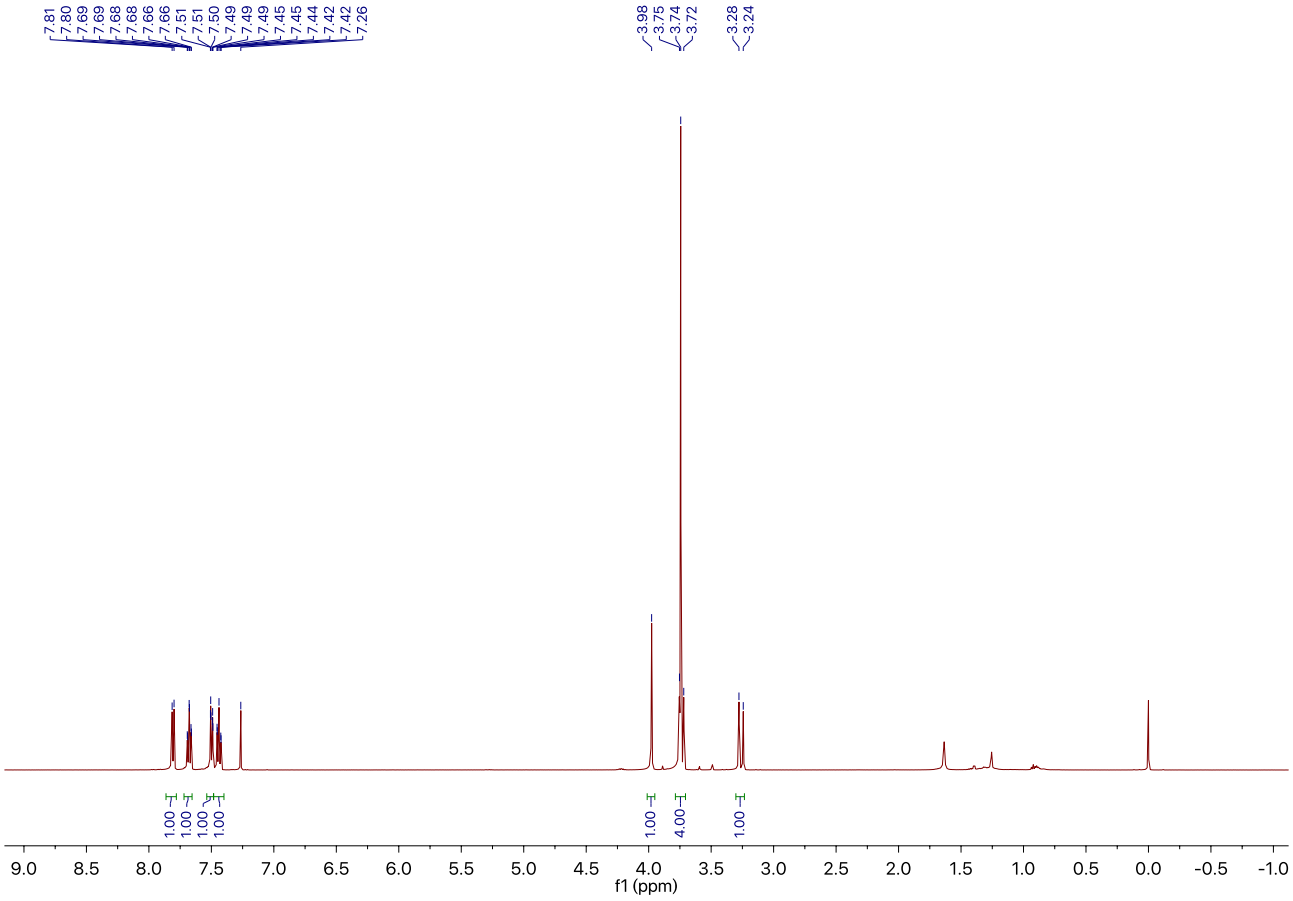
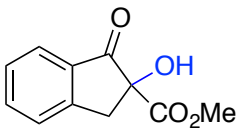


Figure S16. [1]HNMR Spectra of Compound **3b**

Compound **3b** ^{13}CNMR



3b

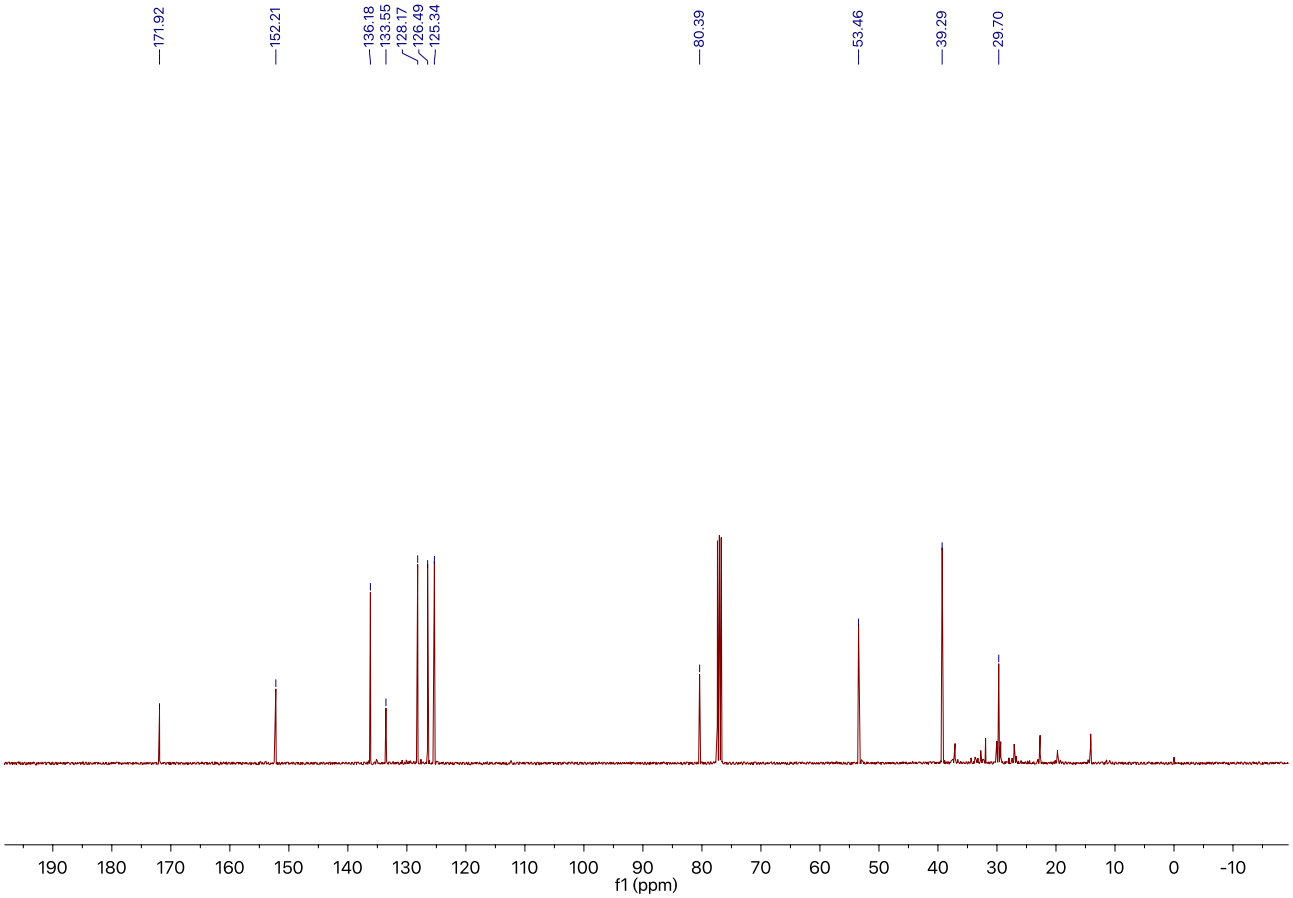
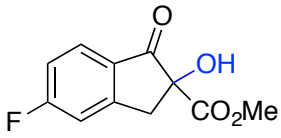


Figure S17. ^{13}CNMR Spectra of Compound **3b**

Compound **3c** ^{1}HNMR



3c

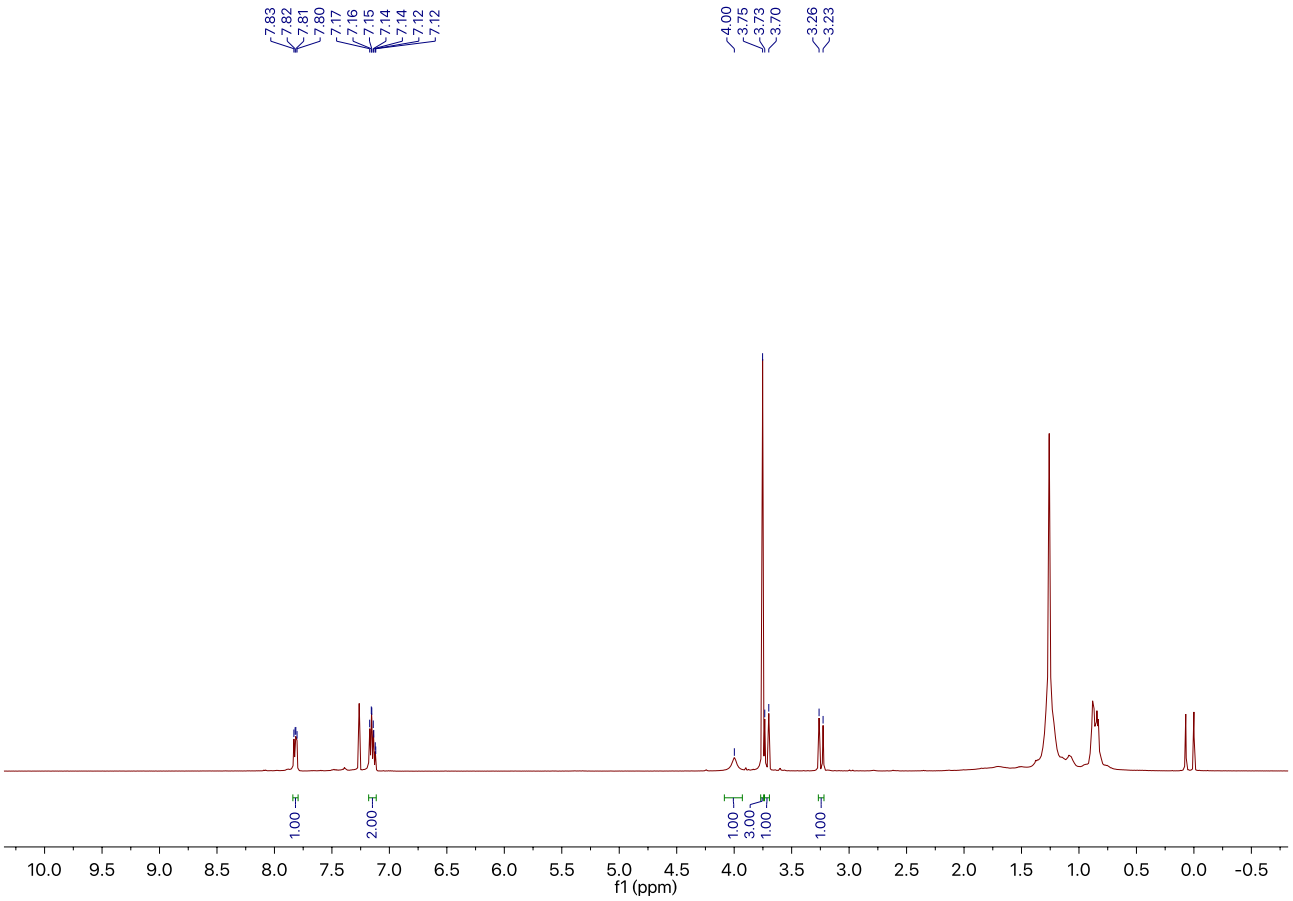
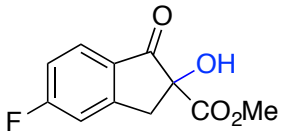


Figure S18. ^{1}HNMR Spectra of Compound **3c**

Compound **3c** ^{13}CNMR



3c

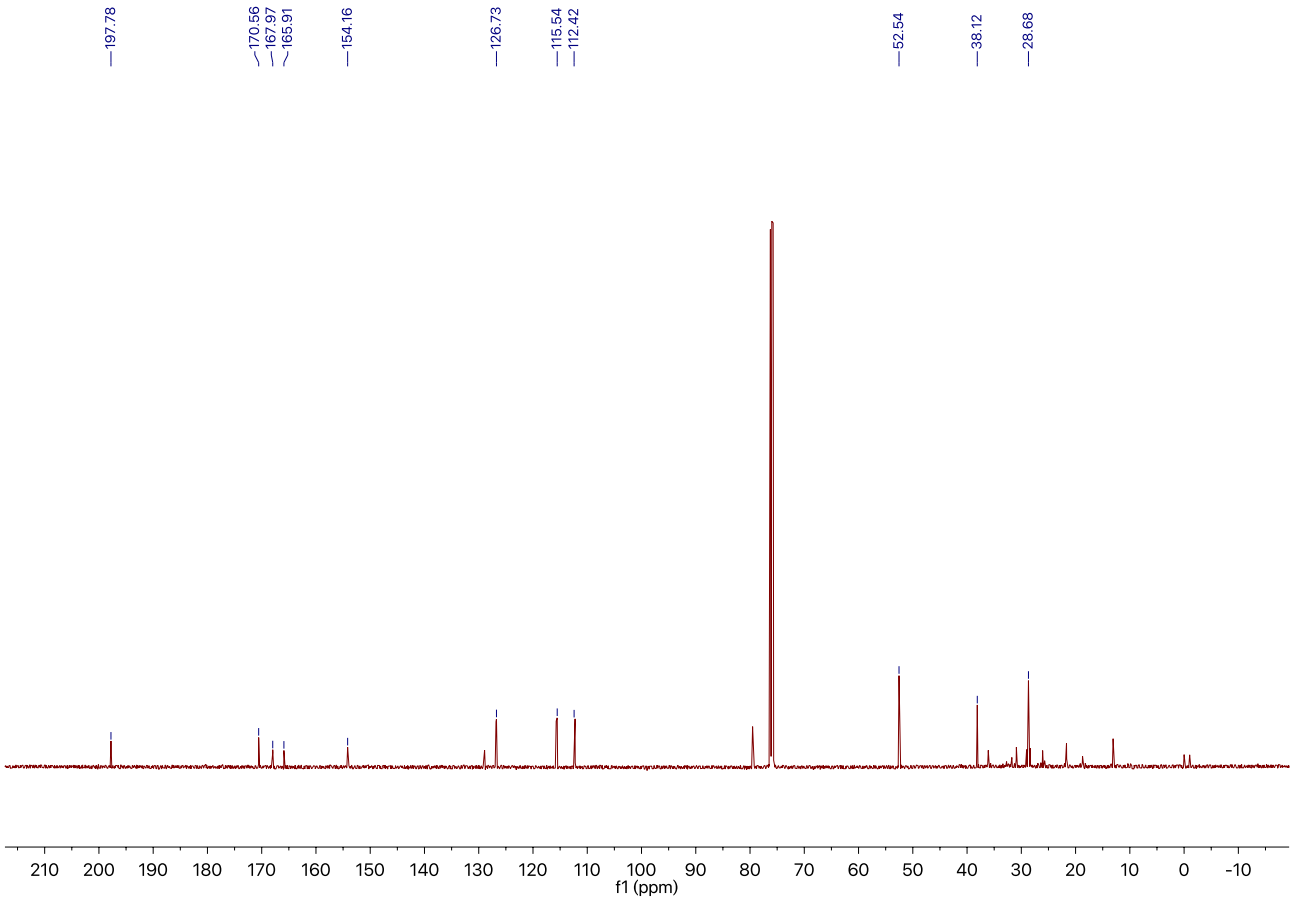
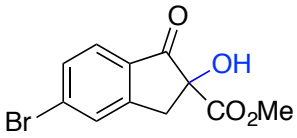


Figure S19. ^{13}CNMR Spectra of Compound **3c**

Compound **3d** [1]HNMR



3d

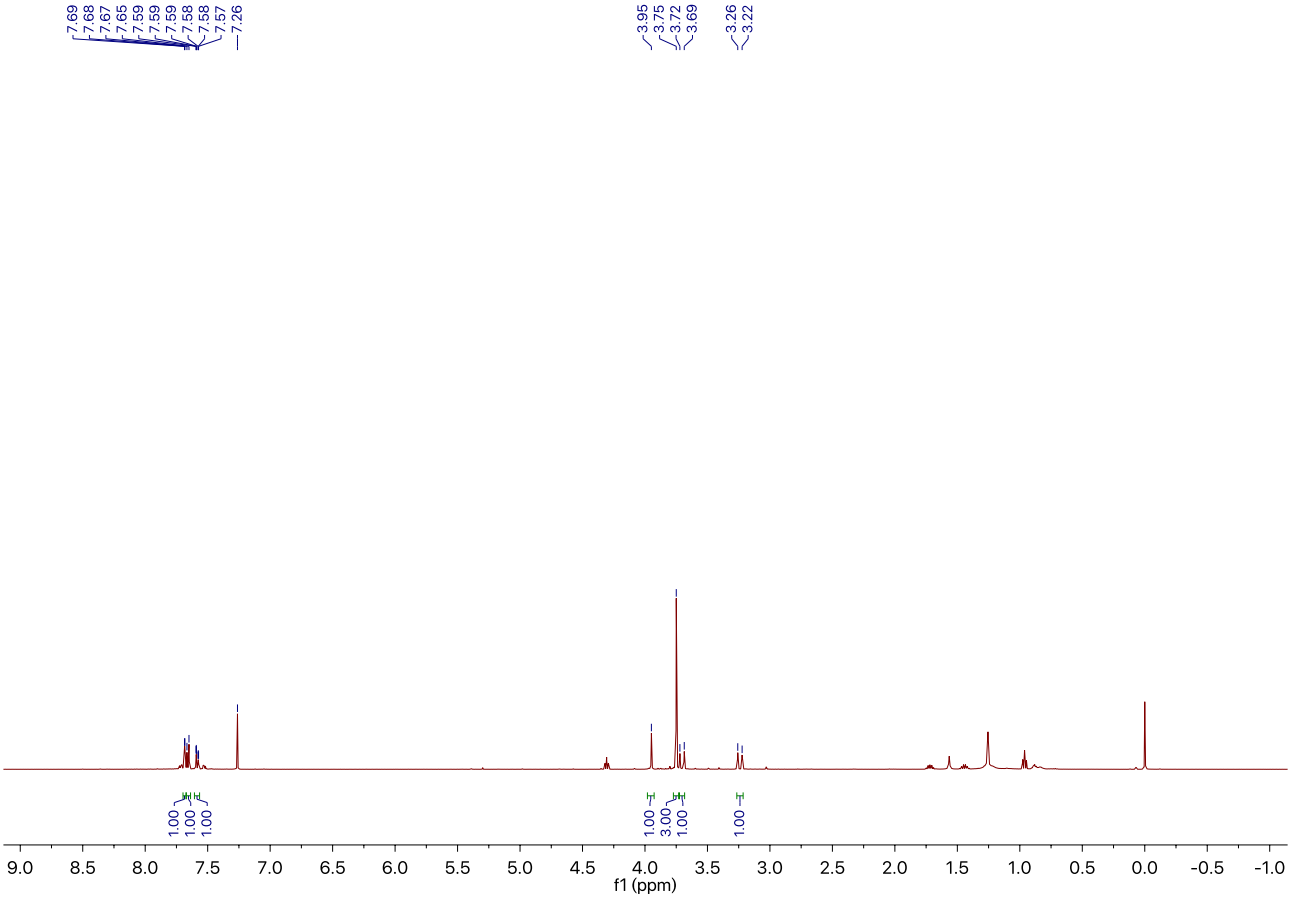
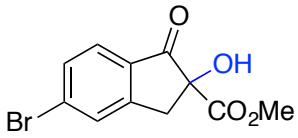


Figure S20. [1]HNMR Spectra of Compound **3d**

Compound **3d** ^{13}CNMR



3d

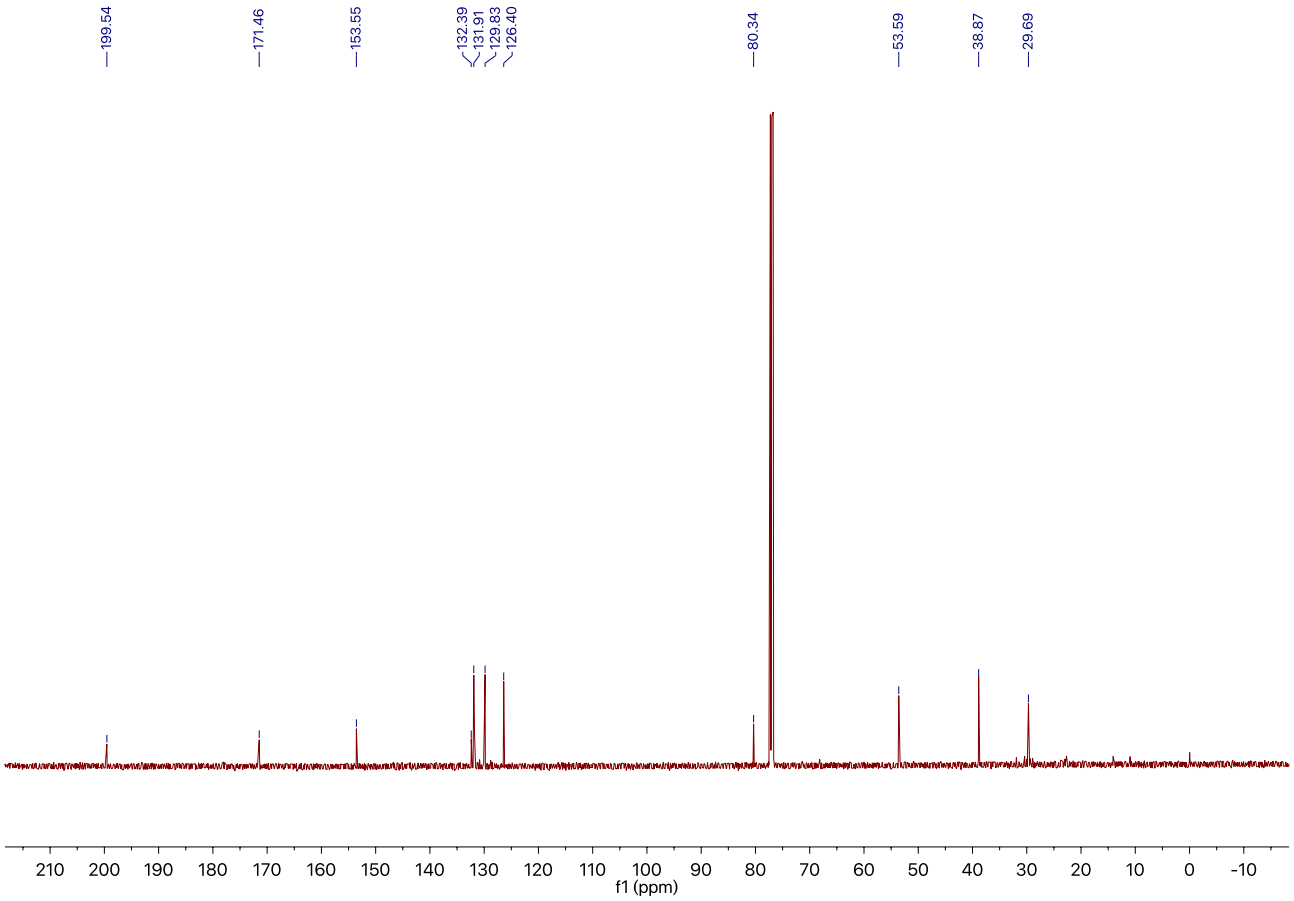
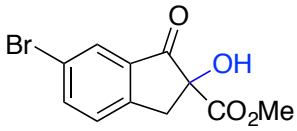


Figure S21. ^{13}CNMR Spectra of Compound **3d**

Compound **3e** ^{1}HNMR



3e

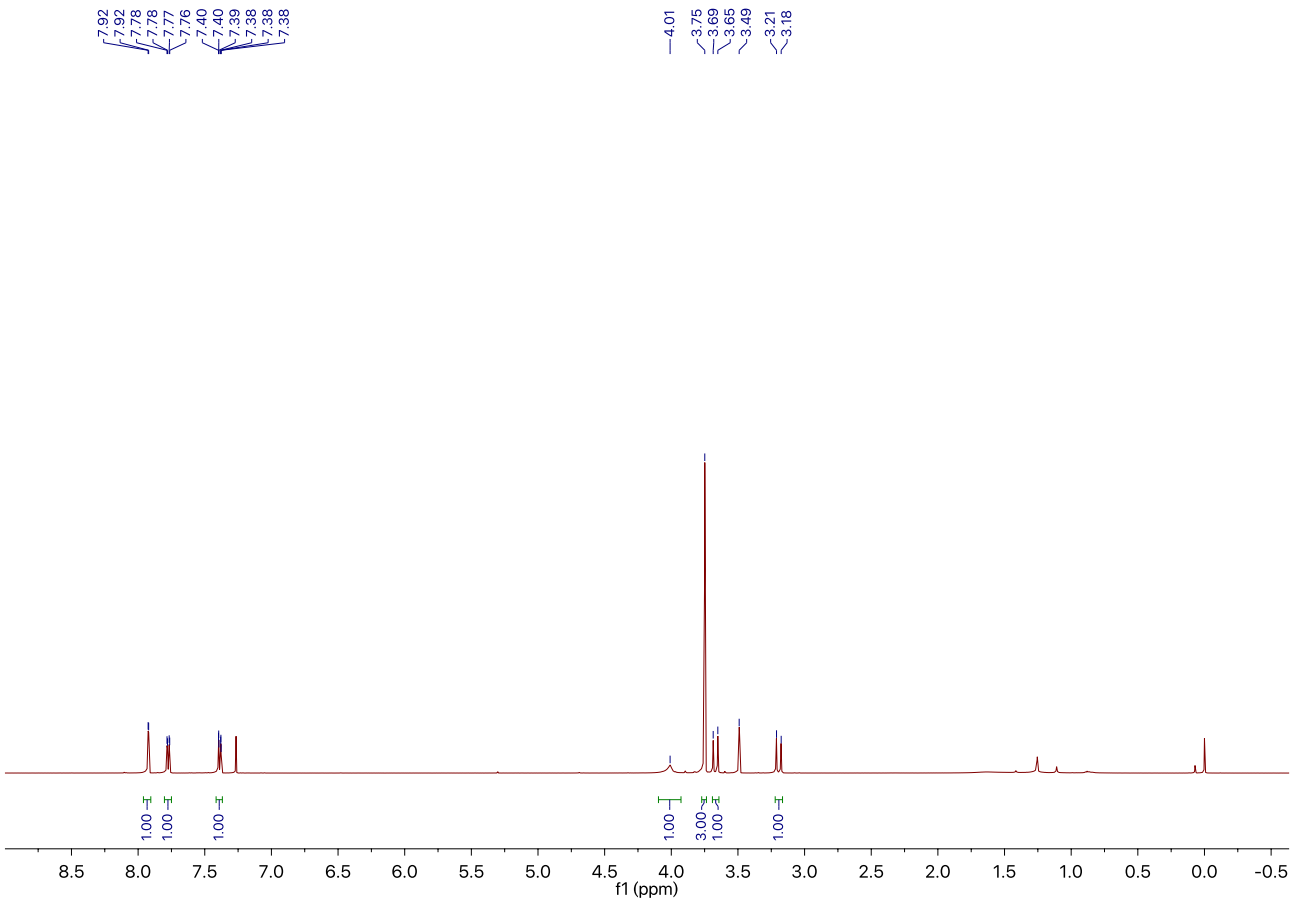
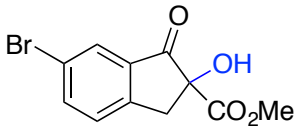


Figure S22. ^{1}HNMR Spectra of Compound **3e**

Compound **3e** ^{13}CNMR



3e

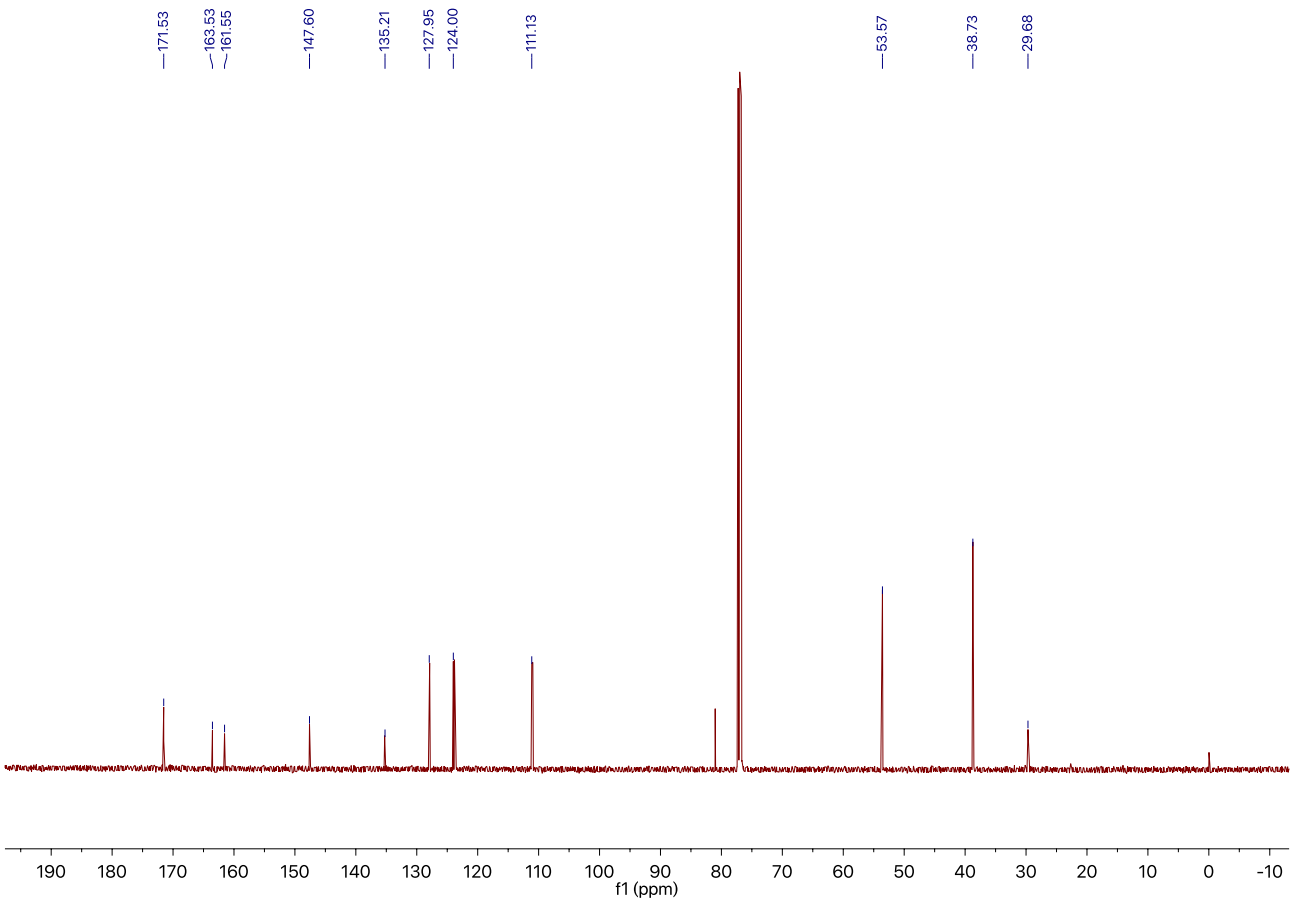
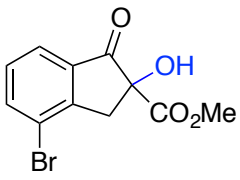


Figure S23 ^{13}CNMR Spectra of Compound **3e**

Compound **3f** [1]HNMR



3f

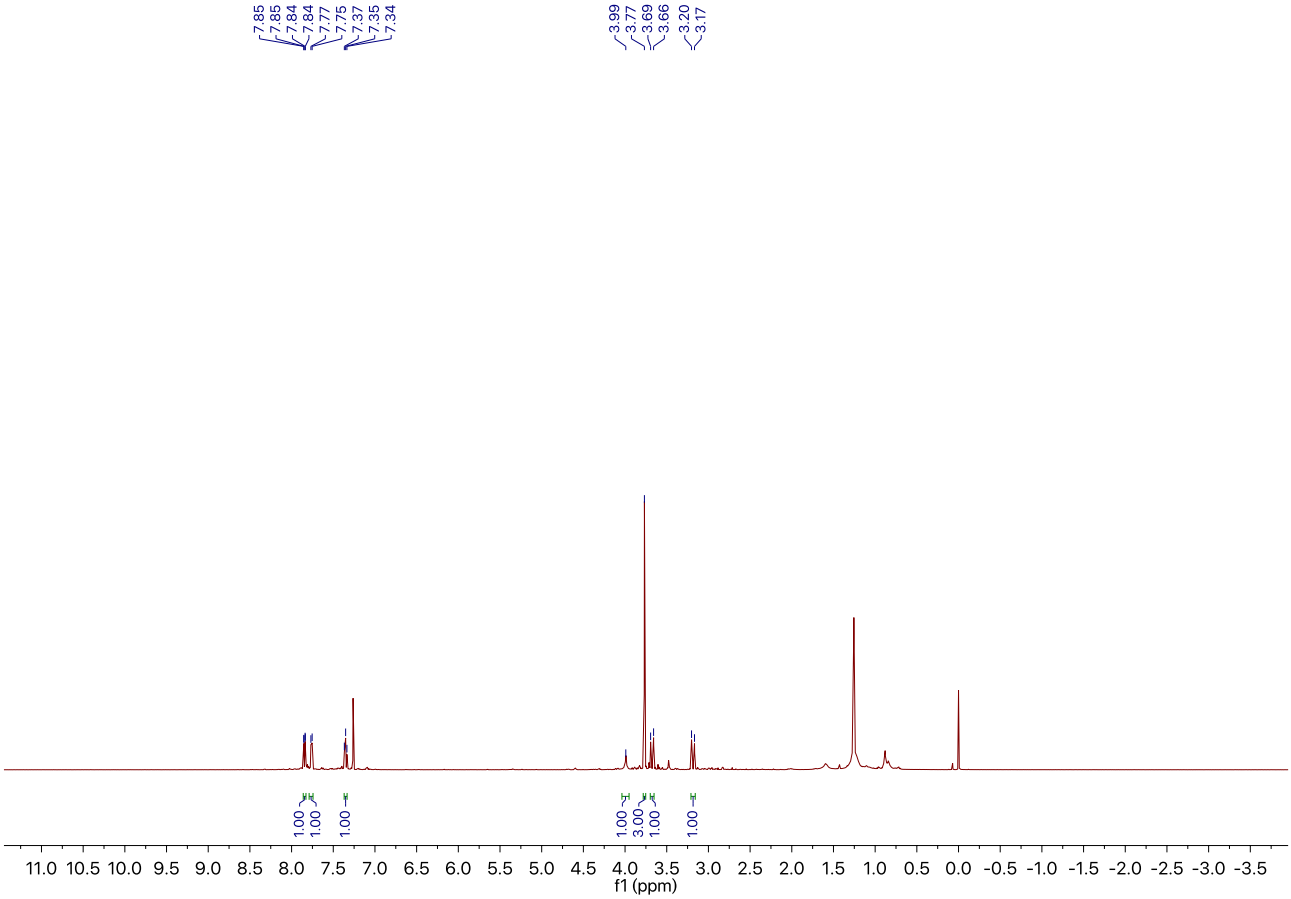
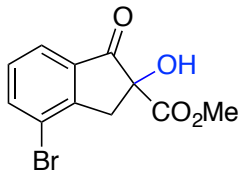


Figure S24. [1]HNMR Spectra of Compound **3f**

Compound **3f** ^{13}CNMR



3f

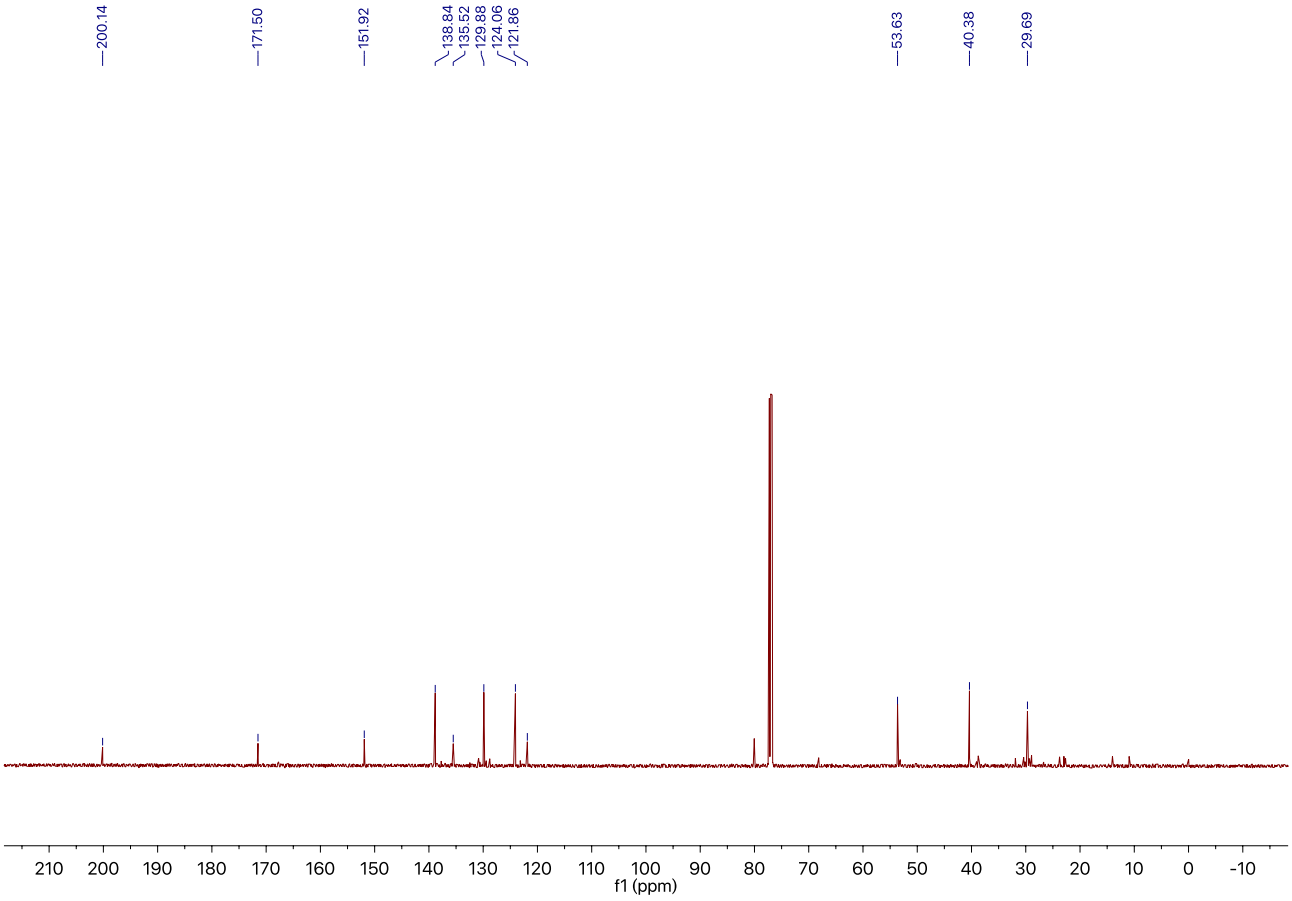
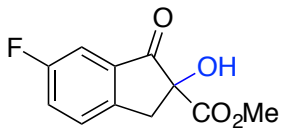


Figure S25 ^{13}CNMR Spectra of Compound **3f**

Compound **3g** ^{1}HNMR



3g

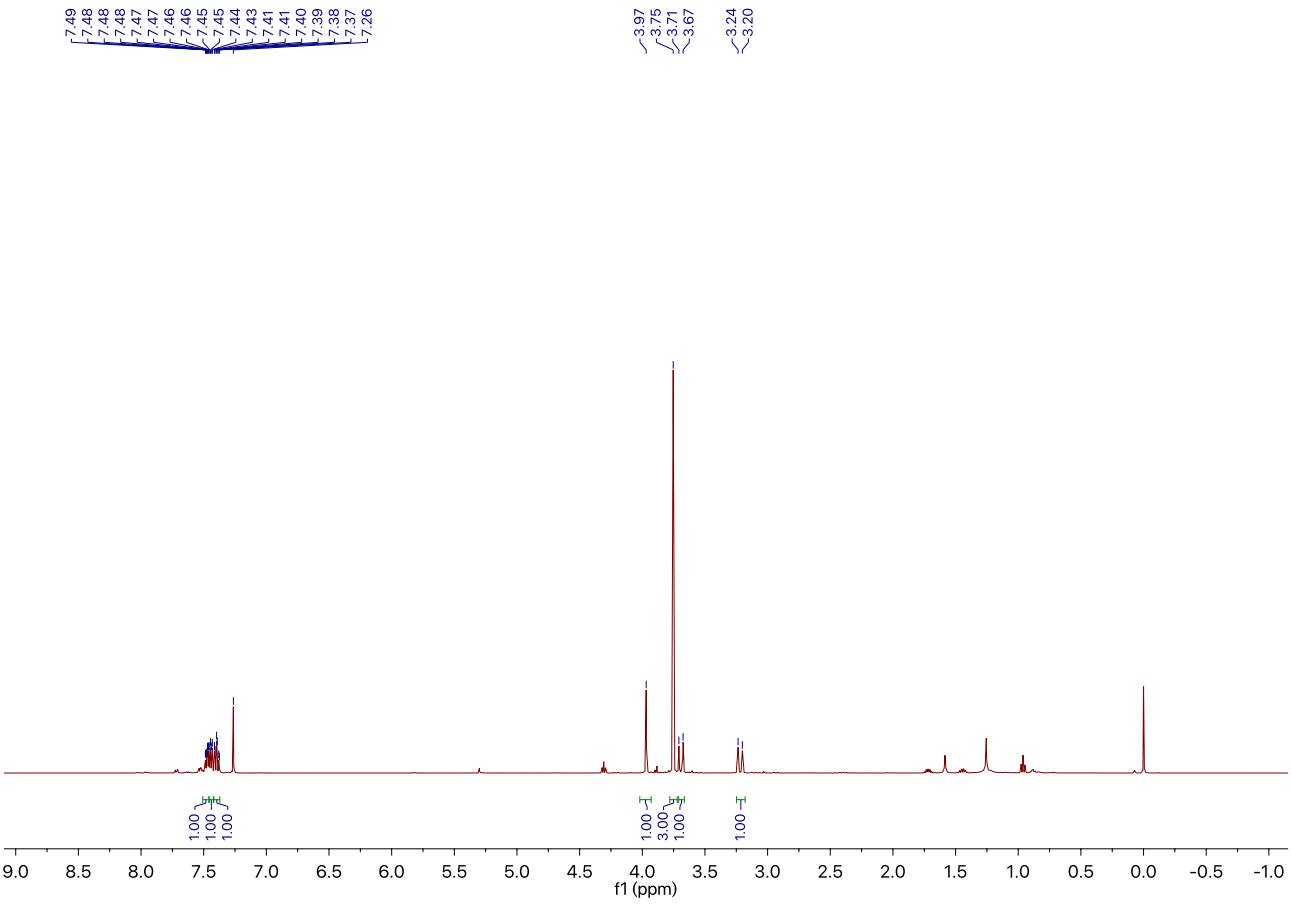
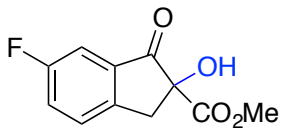


Figure S26. ^{1}HNMR Spectra of Compound **3g**

Compound **3g** ^{13}CNMR



3g

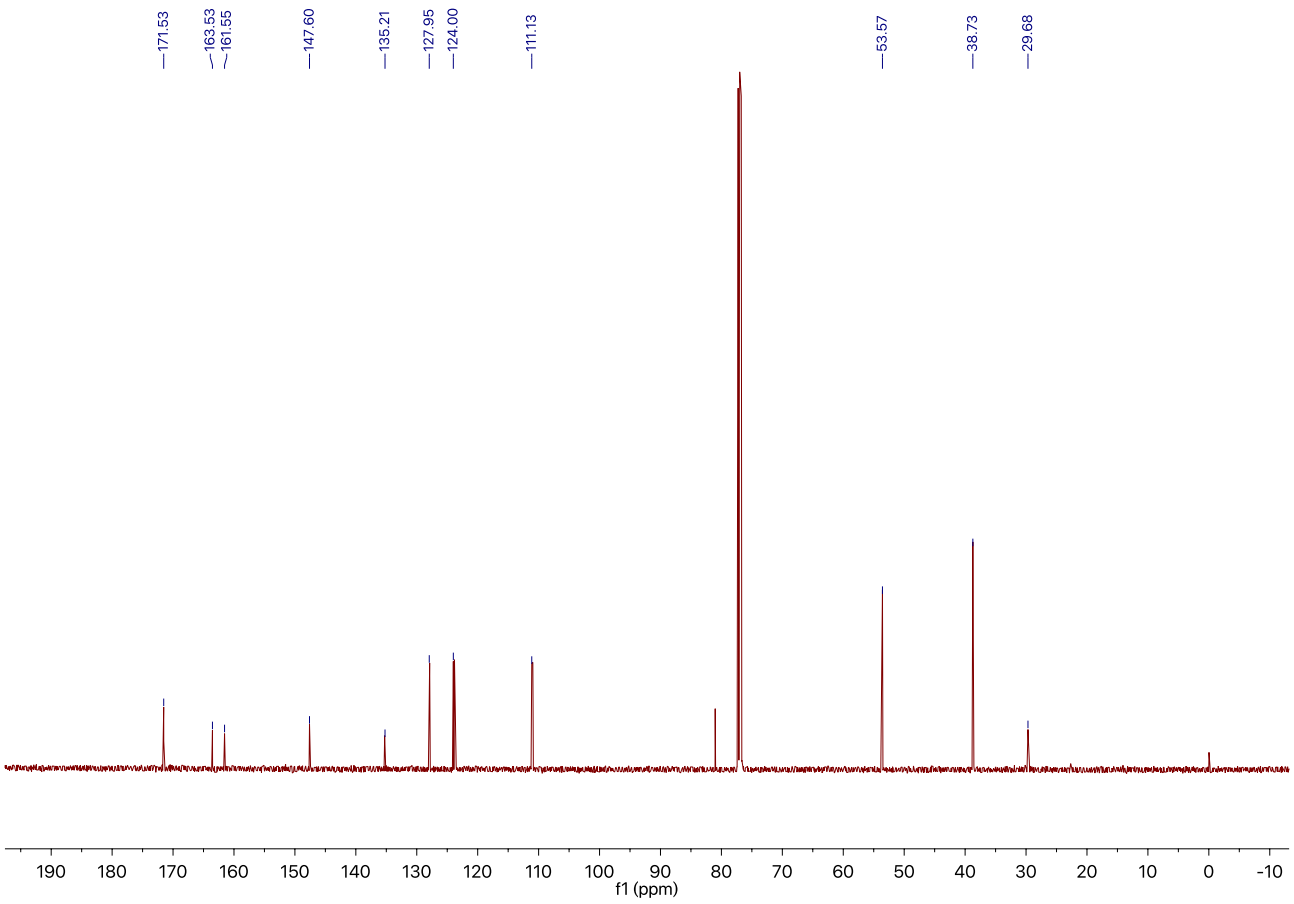
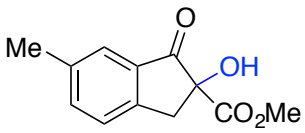


Figure S27 ^{13}CNMR Spectra of Compound **3g**

Compound **3h** [1]HNMR



3h

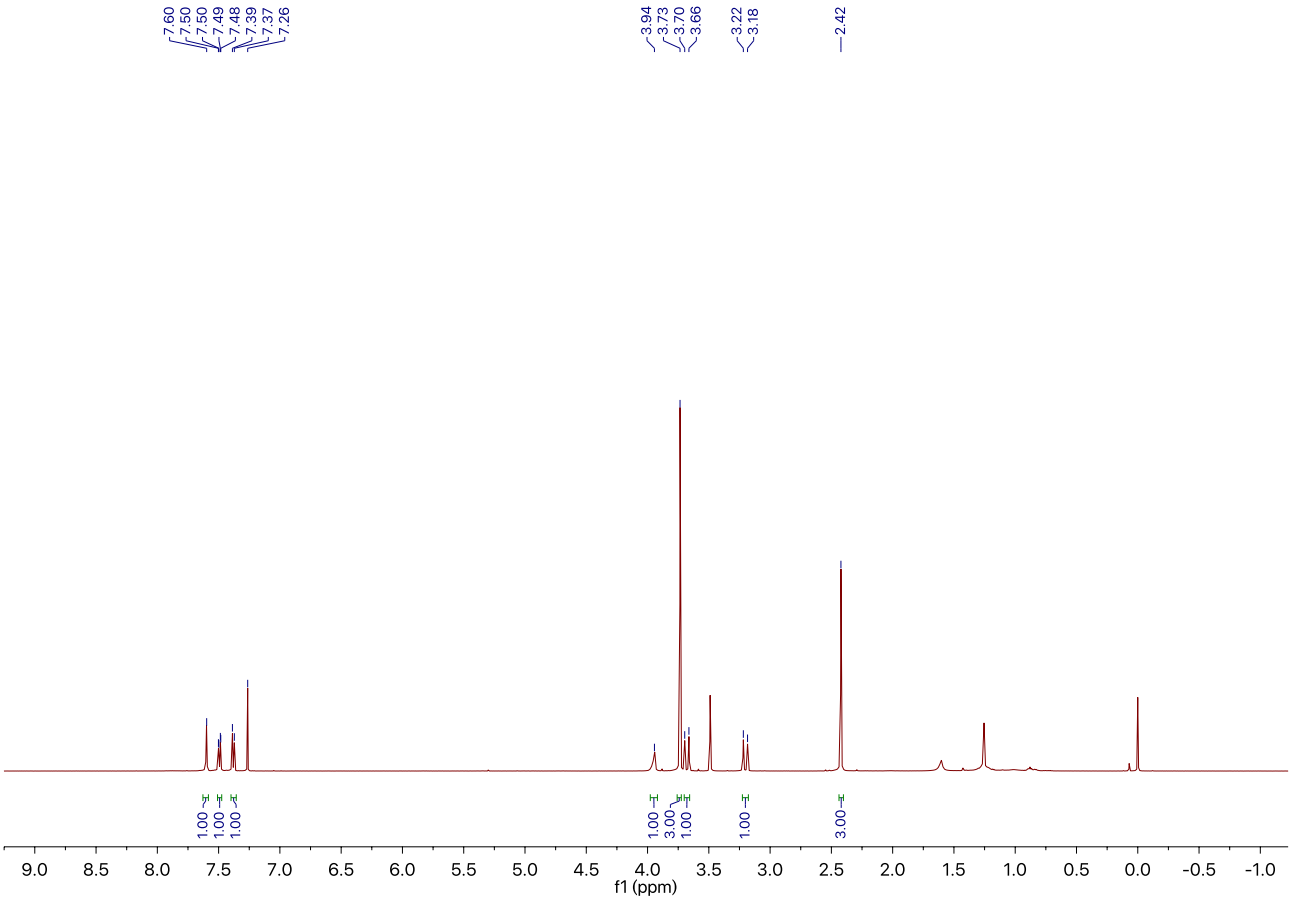
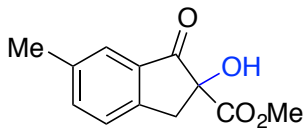


Figure S28. [1]HNMR Spectra of Compound **3h**

Compound **3h** ^{13}CNMR



3h

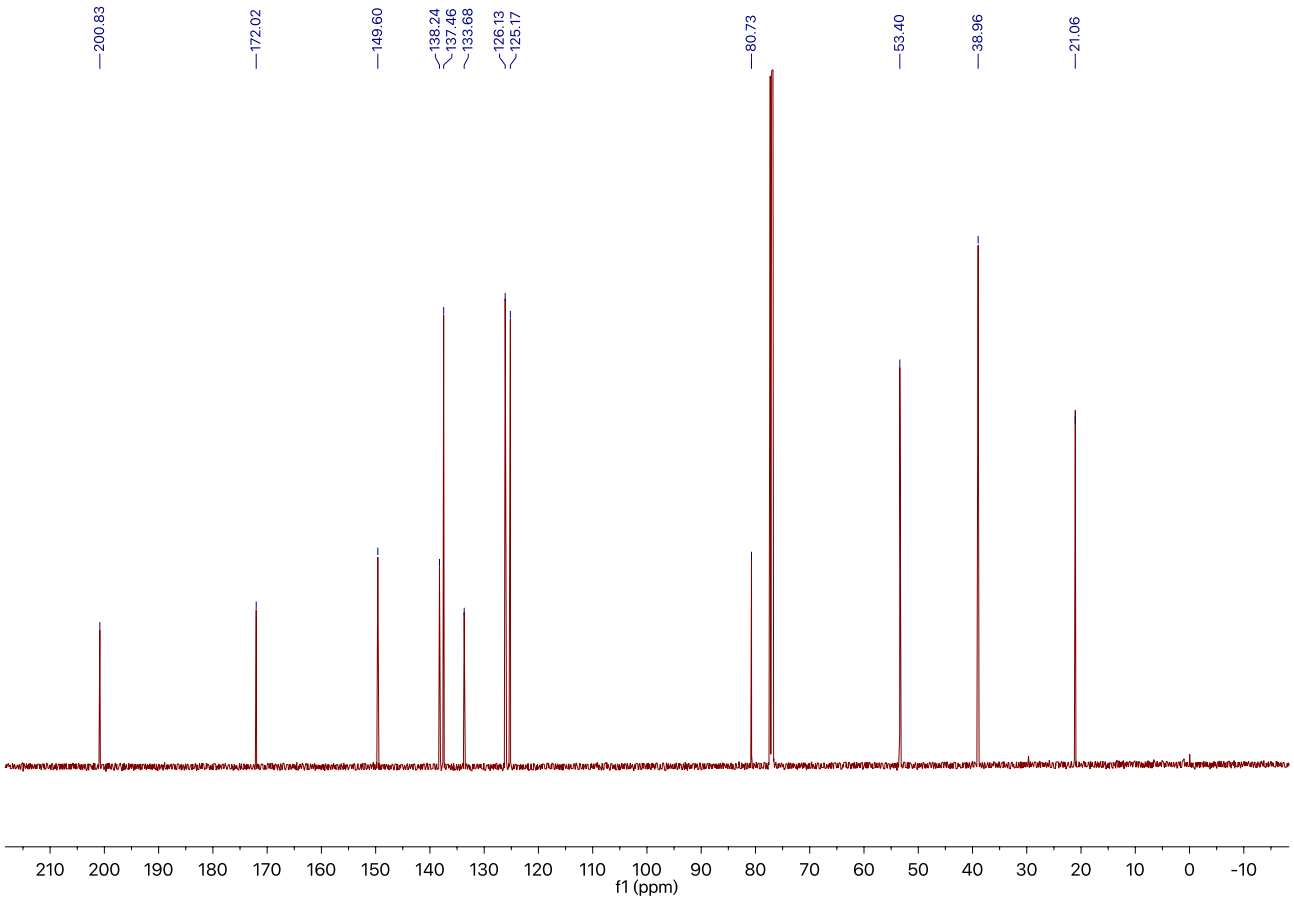
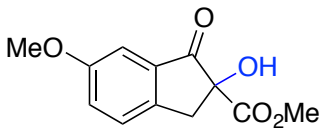


Figure S29 ^{13}CNMR Spectra of Compound **3h**

Compound **3i** [1]HNMR



3i

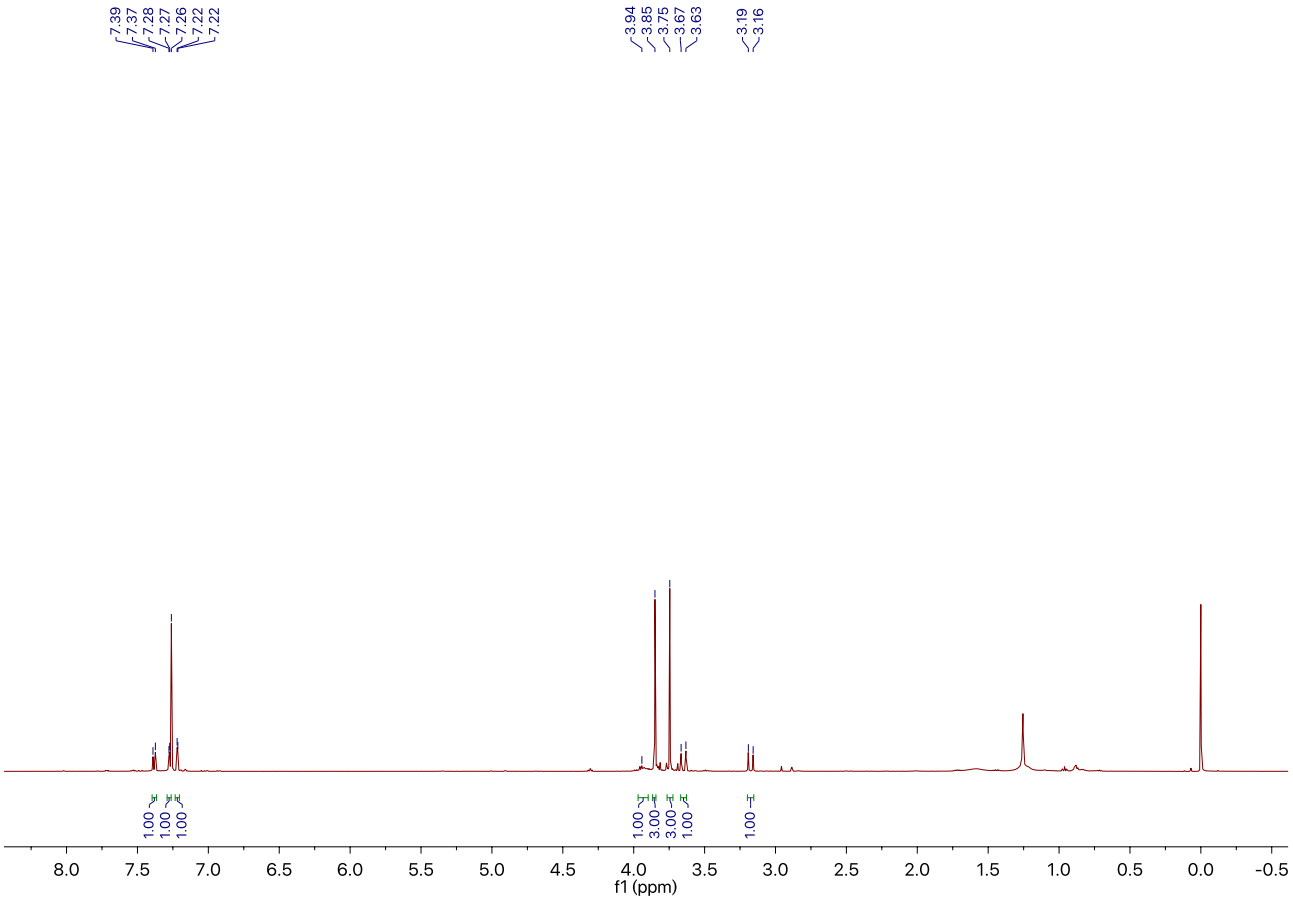
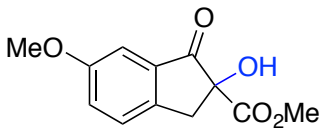


Figure S30. [1]HNMR Spectra of Compound **3i**

Compound **3i** ^{13}CNMR



3i

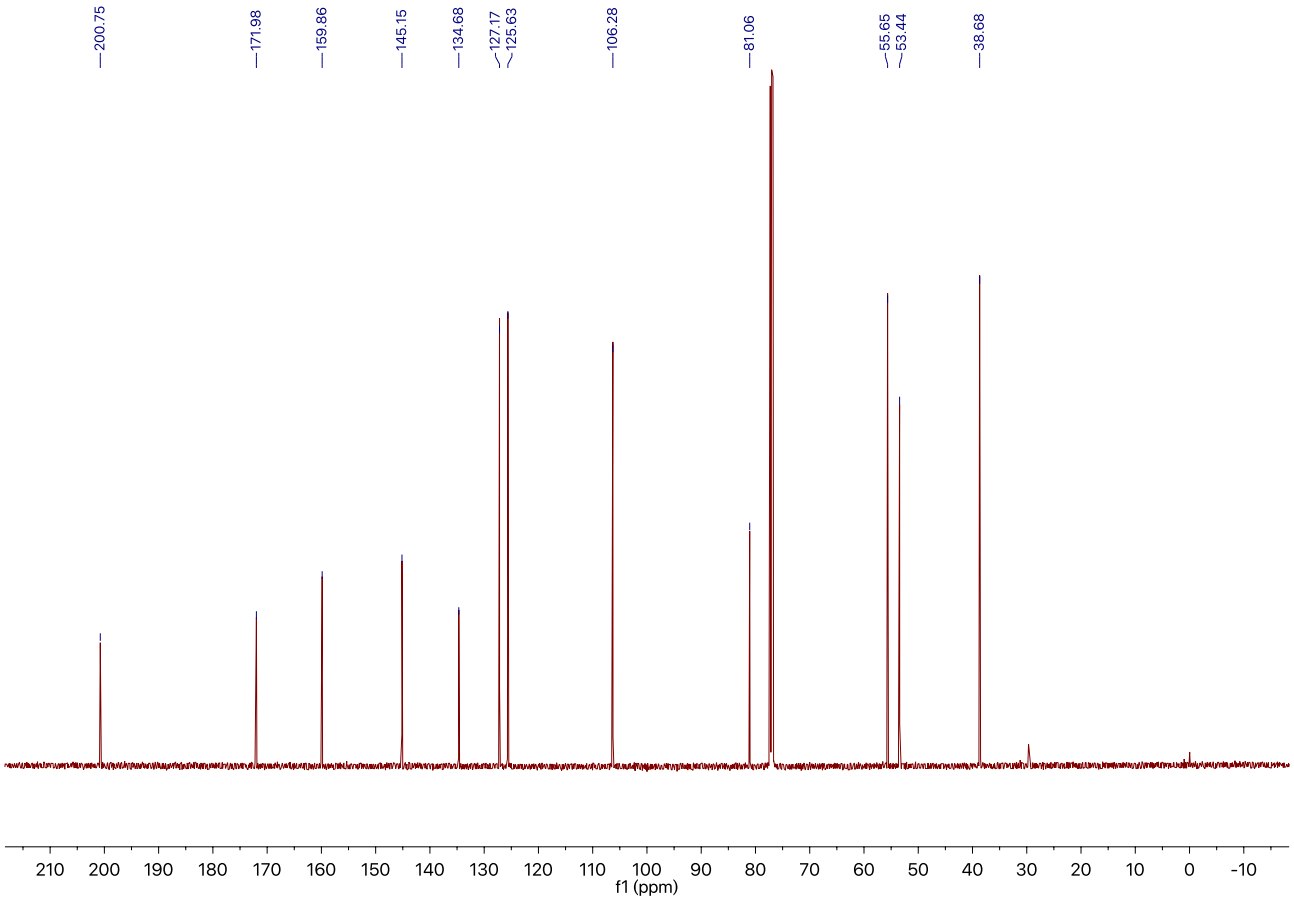
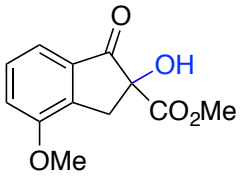


Figure S31 ^{13}CNMR Spectra of Compound **3i**

Compound **3j** ^{1}HNMR



3j

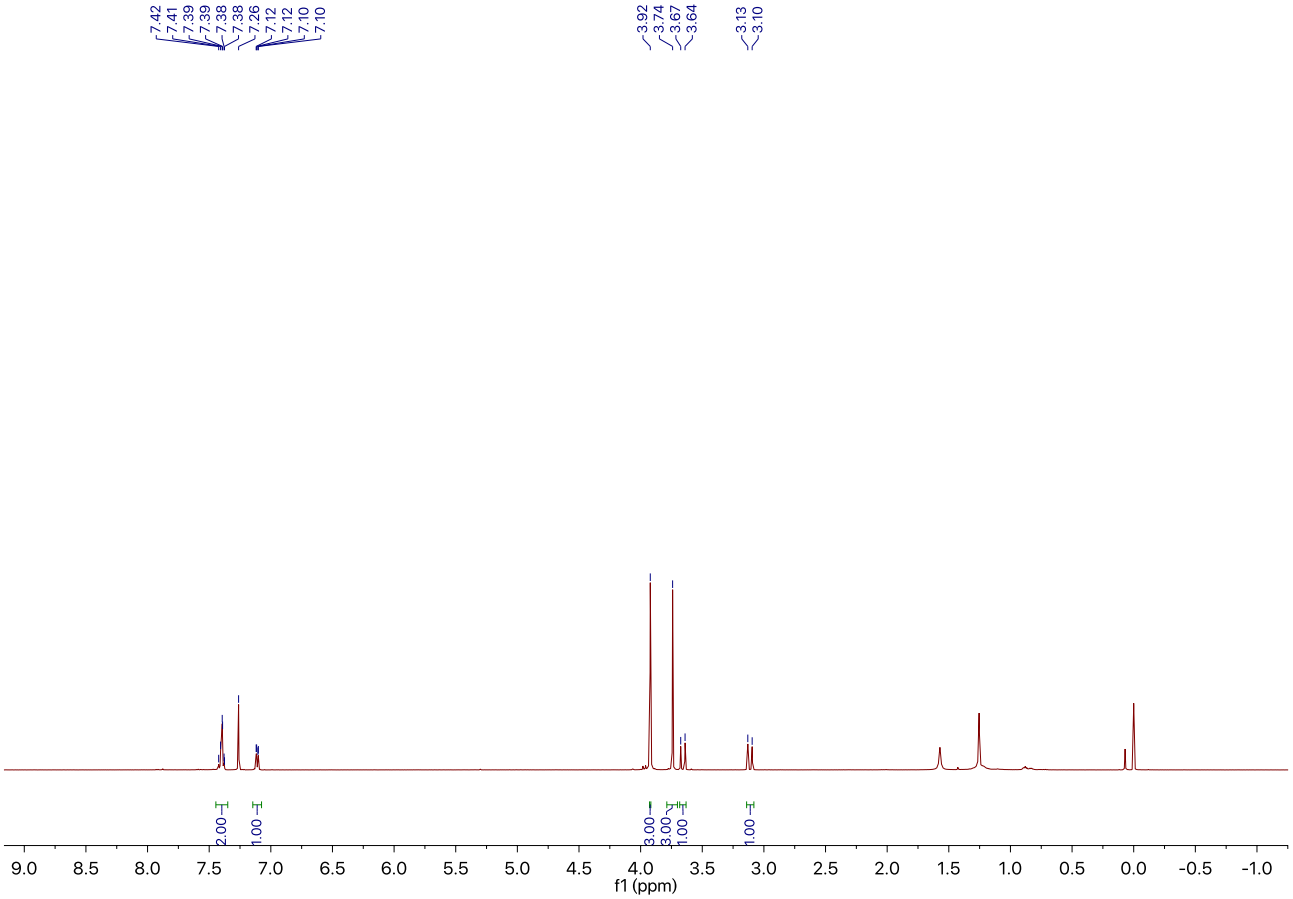
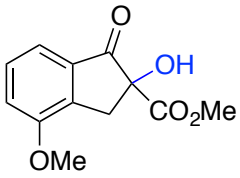


Figure S32. ^{1}HNMR Spectra of Compound **3j**

Compound **3j** ^{13}CNMR



3j

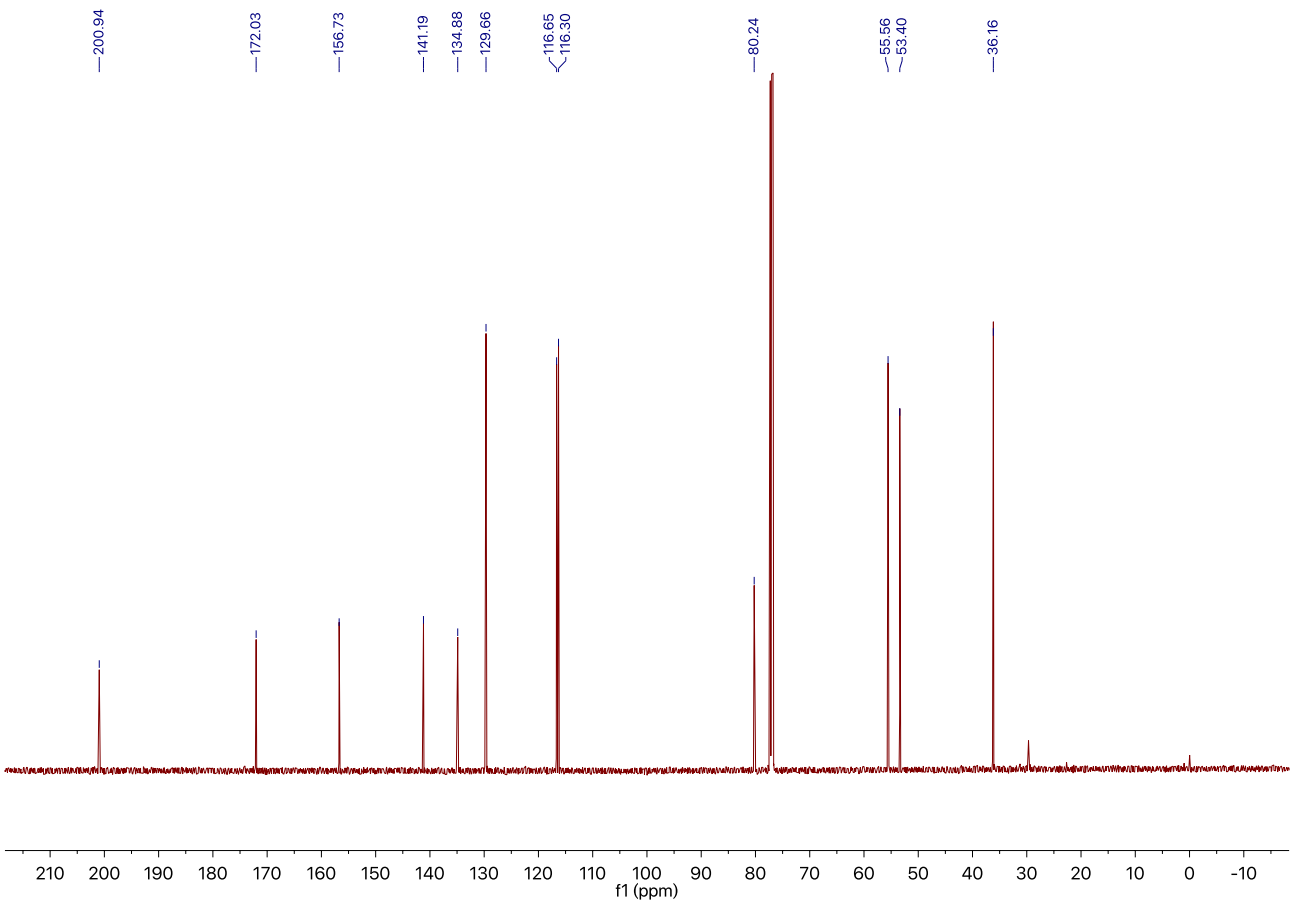
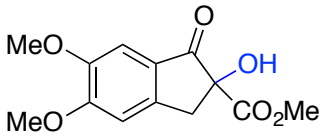


Figure S33 ^{13}CNMR Spectra of Compound **3j**

Compound **3k** [1]HNMR



3k

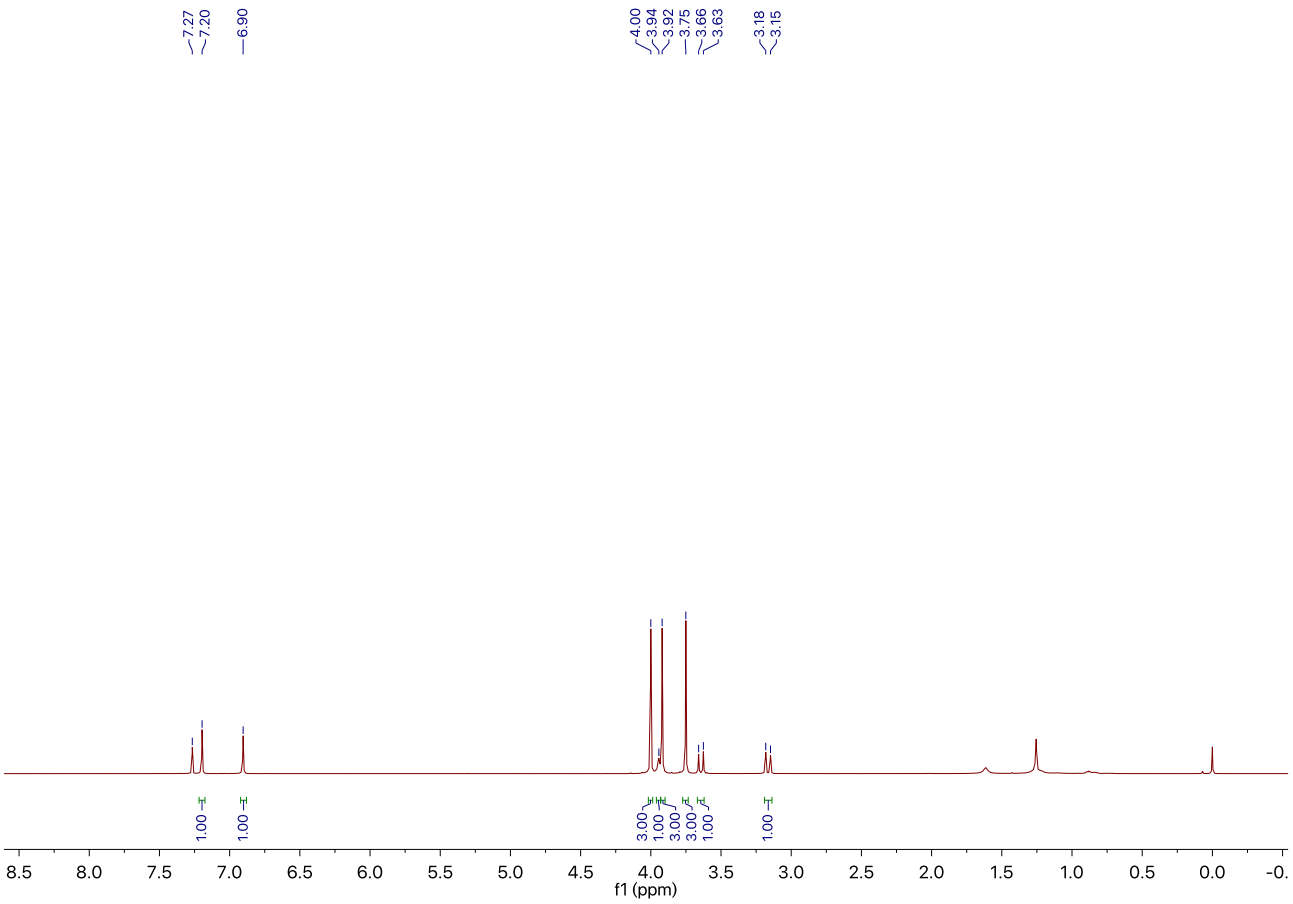
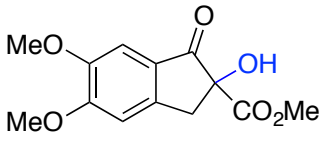


Figure S34. [1]HNMR Spectra of Compound **3k**

Compound **3k** ^{13}CNMR



3k

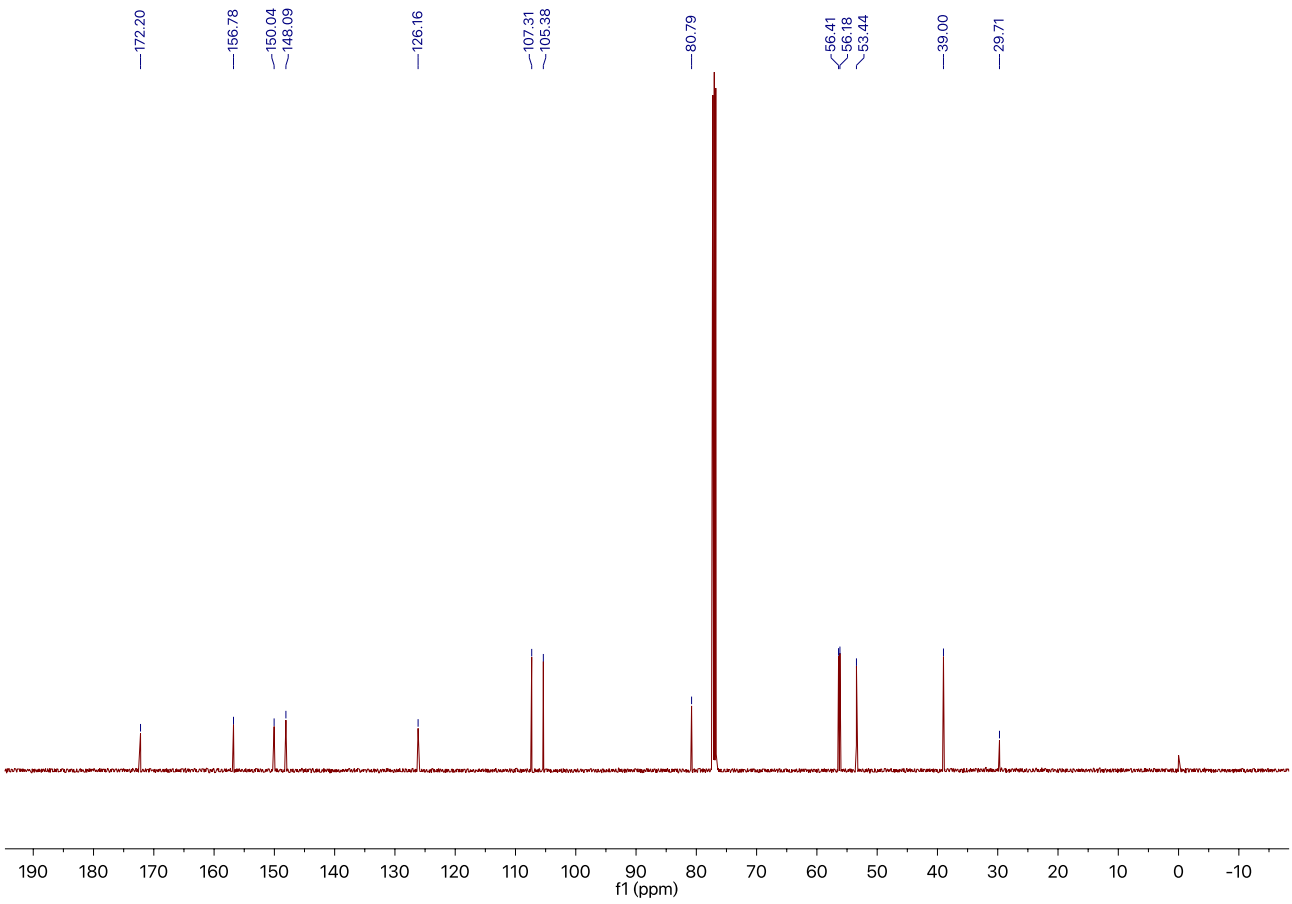
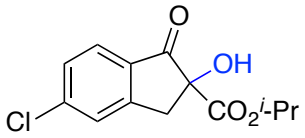


Figure S35 ^{13}CNMR Spectra of Compound **3k**

Compound **3l** [1]HNMR



3l

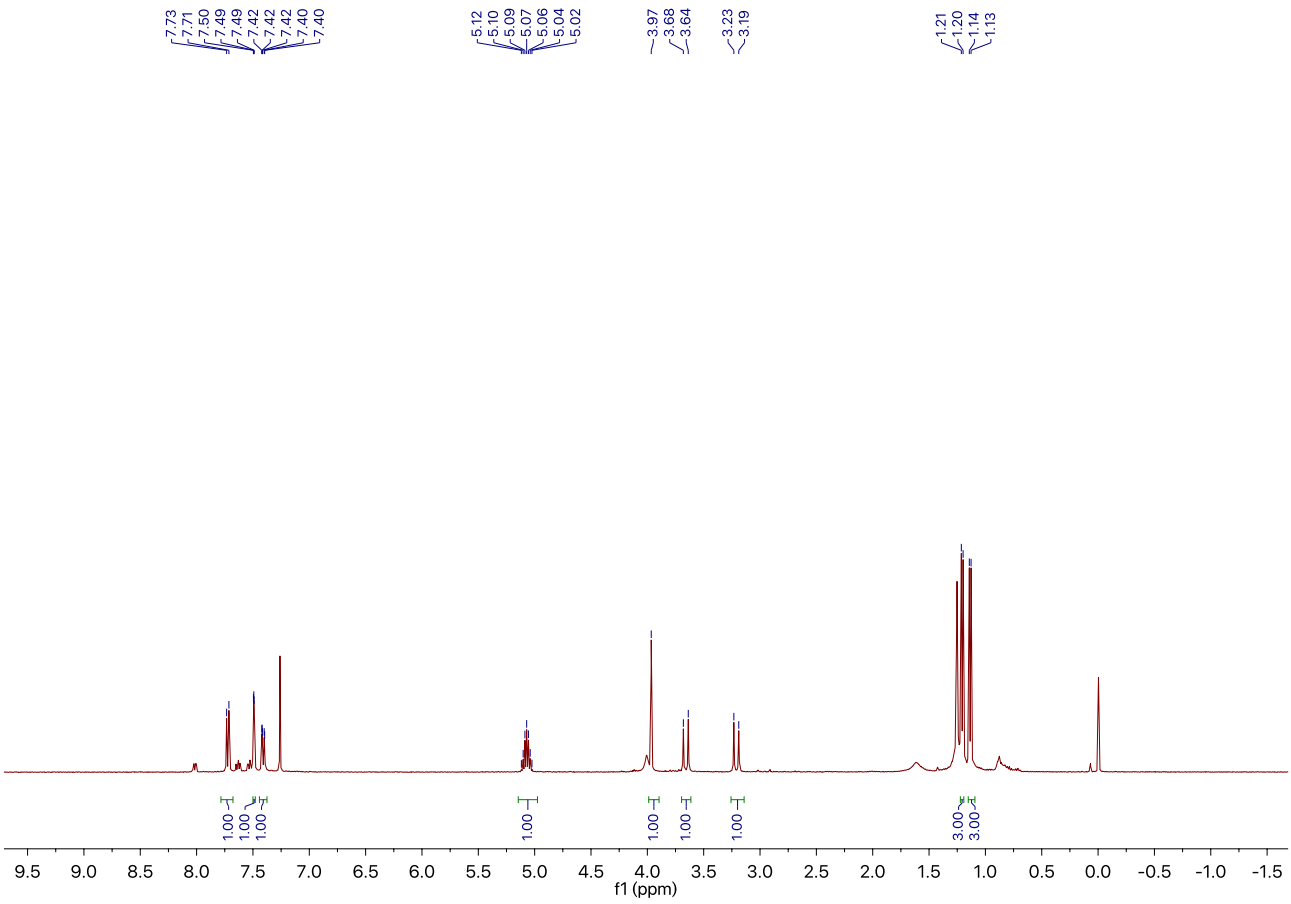
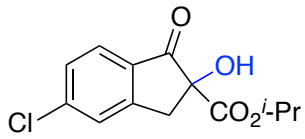


Figure S36. [1]HNMR Spectra of Compound **3l**

Compound **3l** ^{13}CNMR



3l

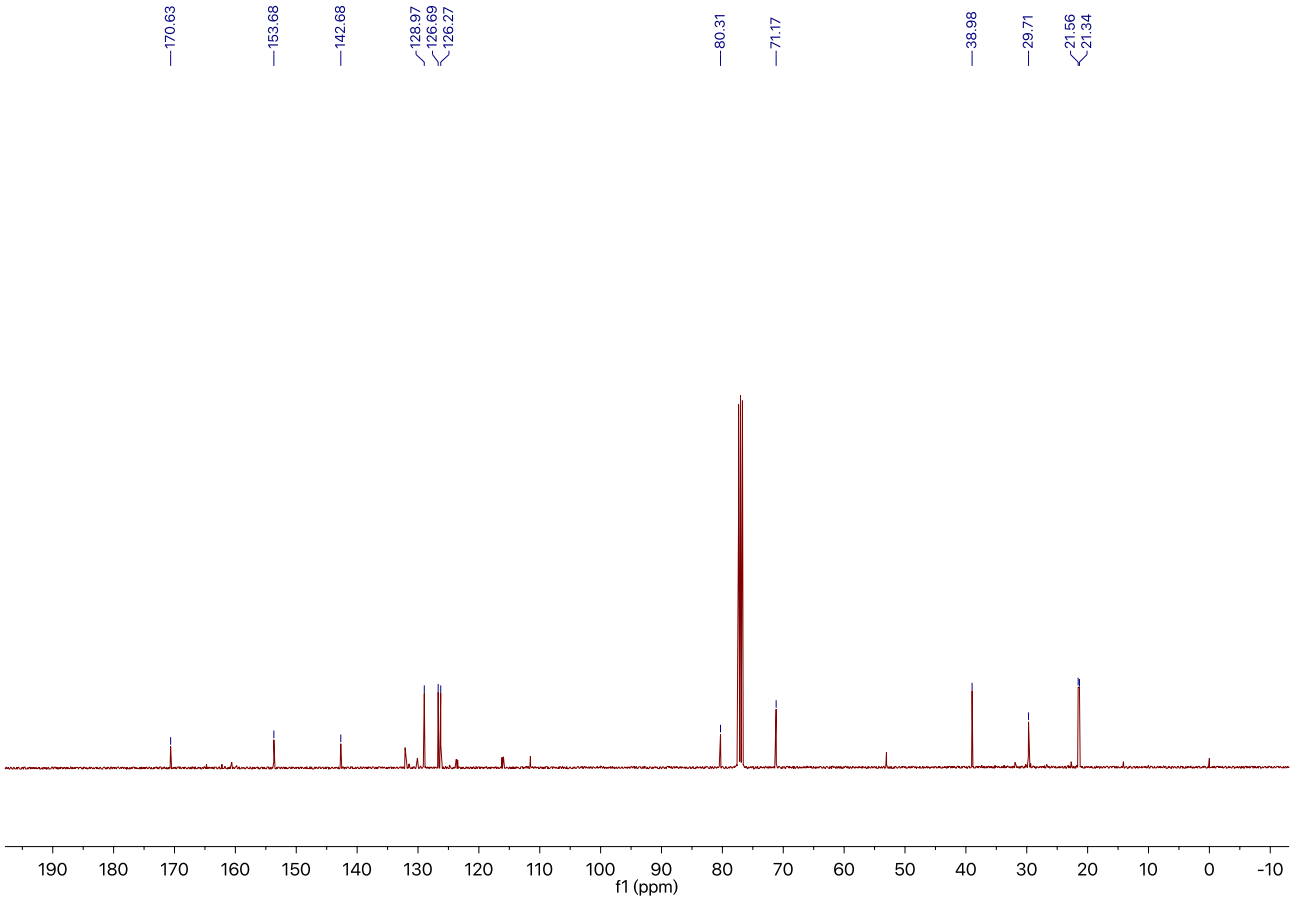
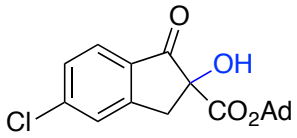


Figure S37 ^{13}CNMR Spectra of Compound **3l**

Compound **3m** ^{1}HNMR



3m

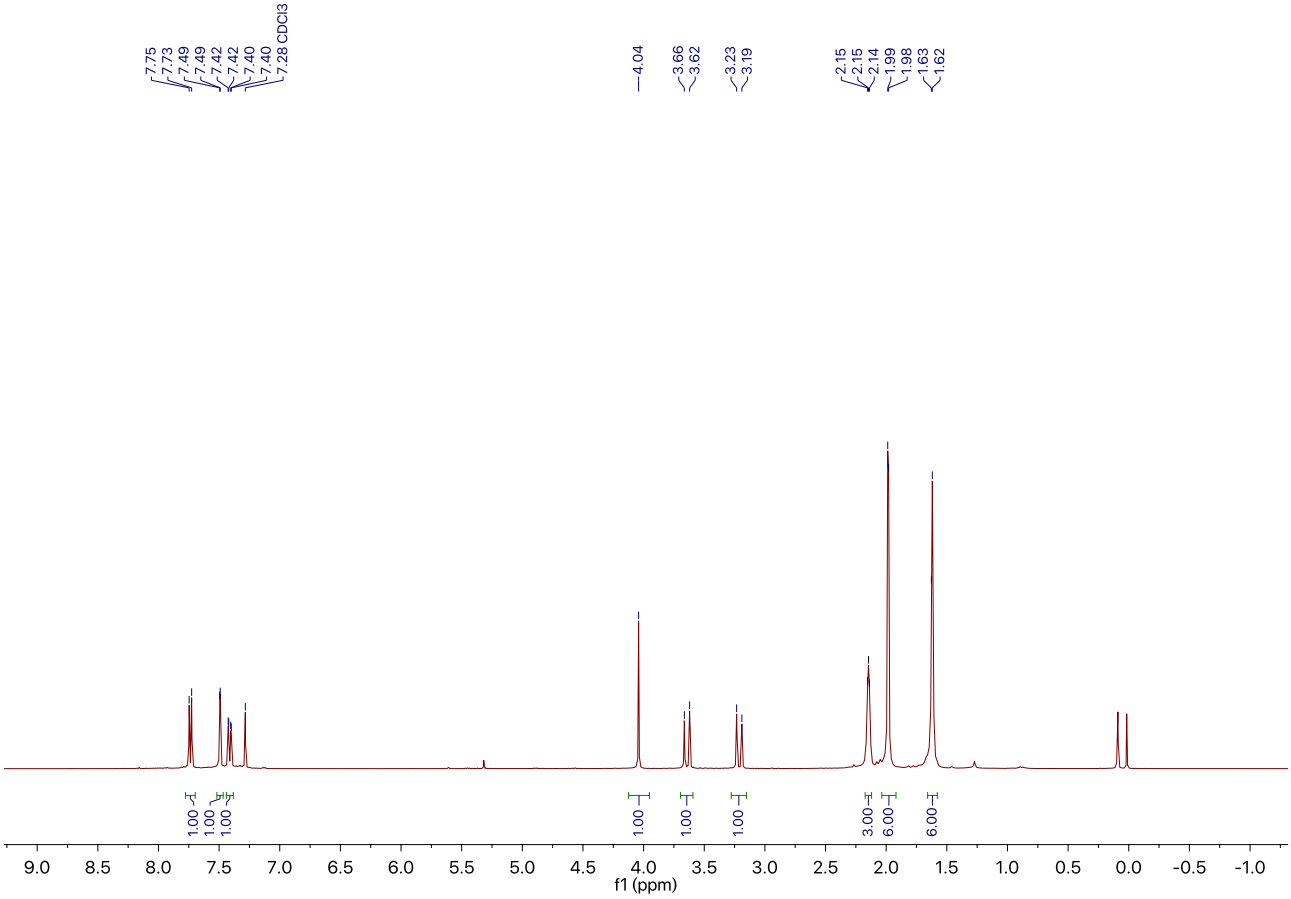
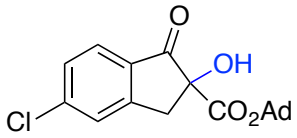


Figure S38. ^{1}HNMR Spectra of Compound **3m**

Compound **3m** ^{13}CNMR



3m

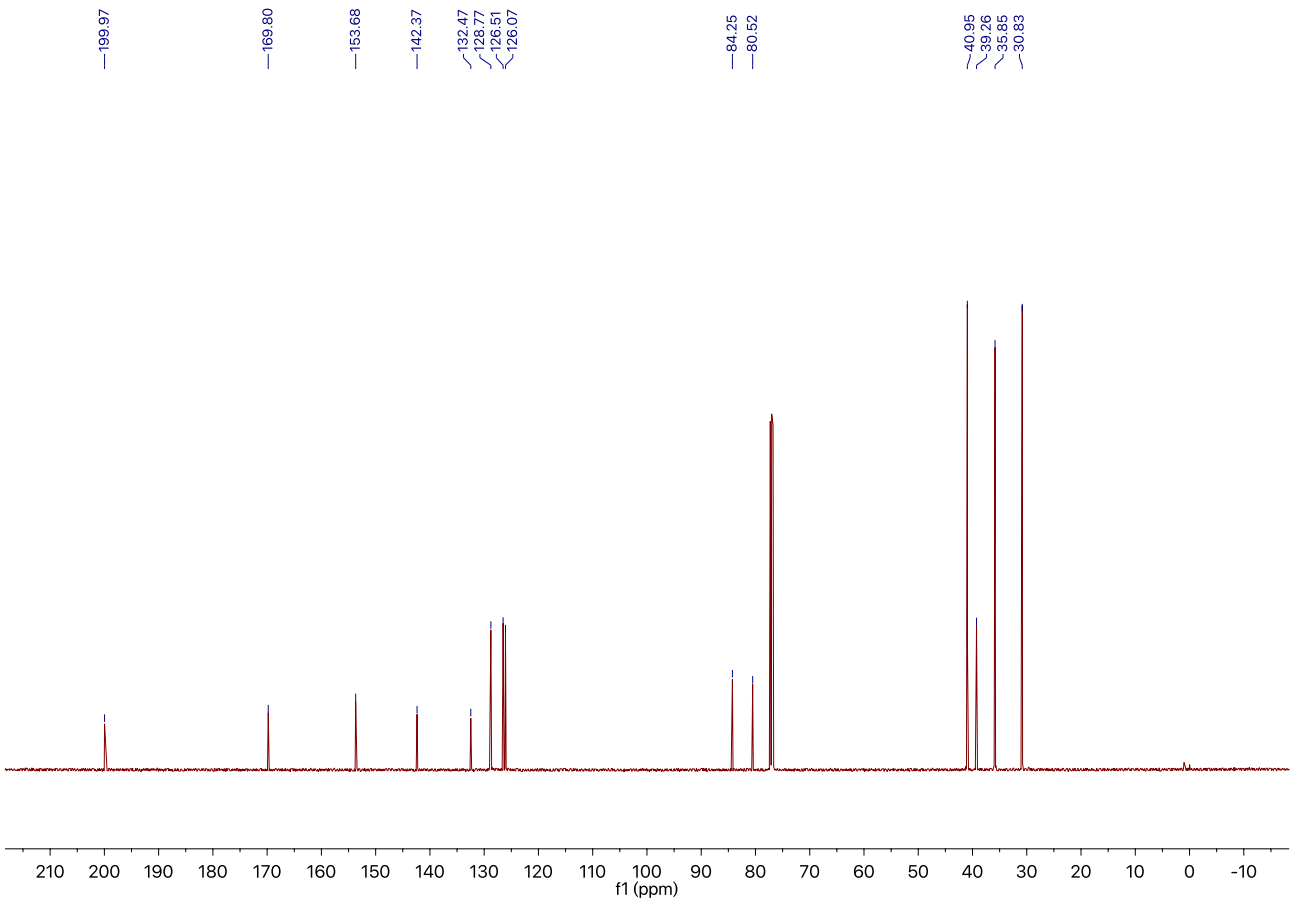
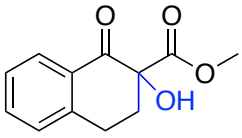


Figure S39 ^{13}CNMR Spectra of Compound **3m**

Compound **3n** [1]HNMR



3n

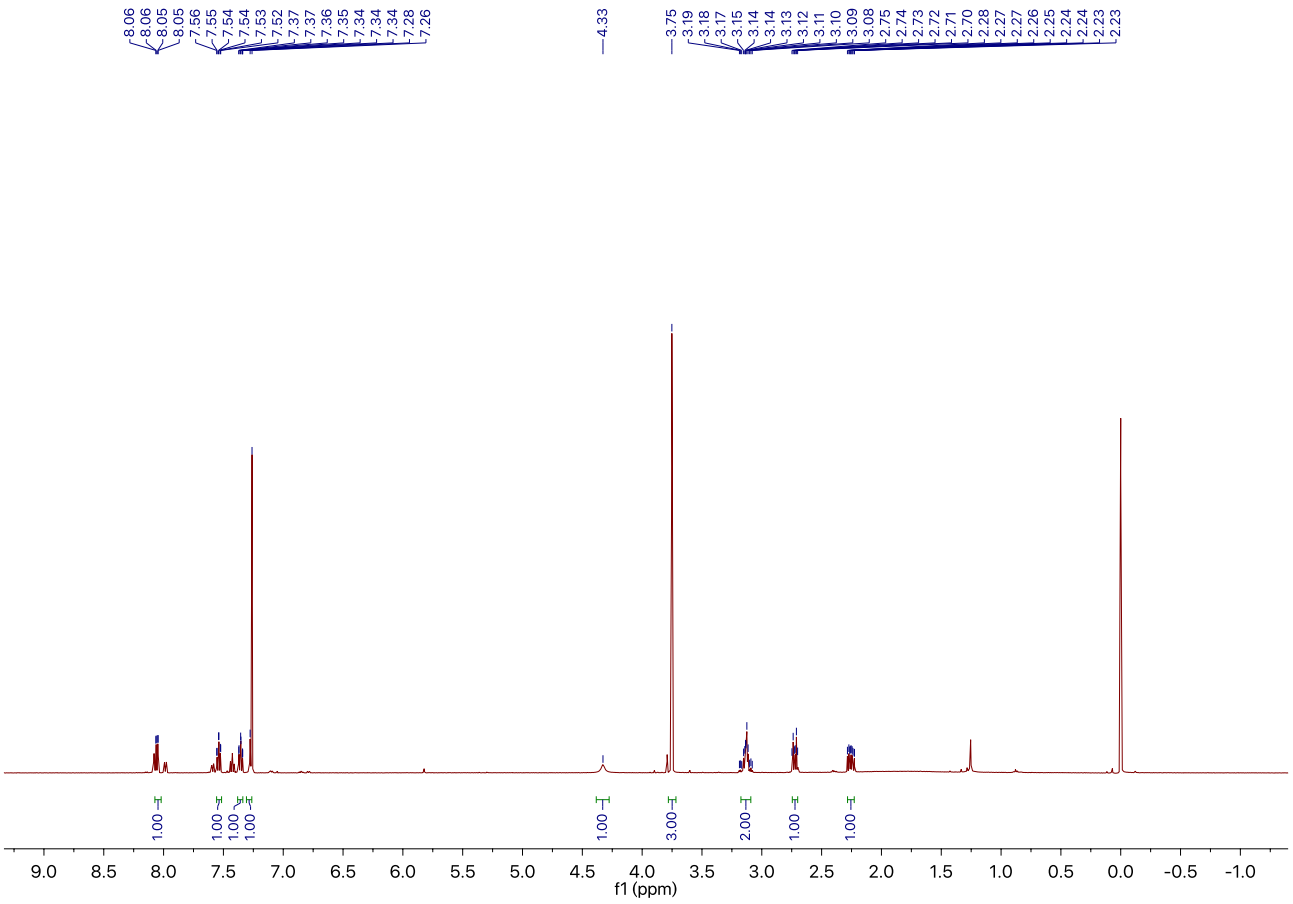
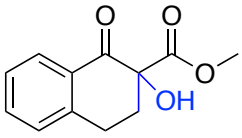


Figure S40. [1]HNMR Spectra of Compound **3n**

Compound **3n** ^{13}CNMR



3n

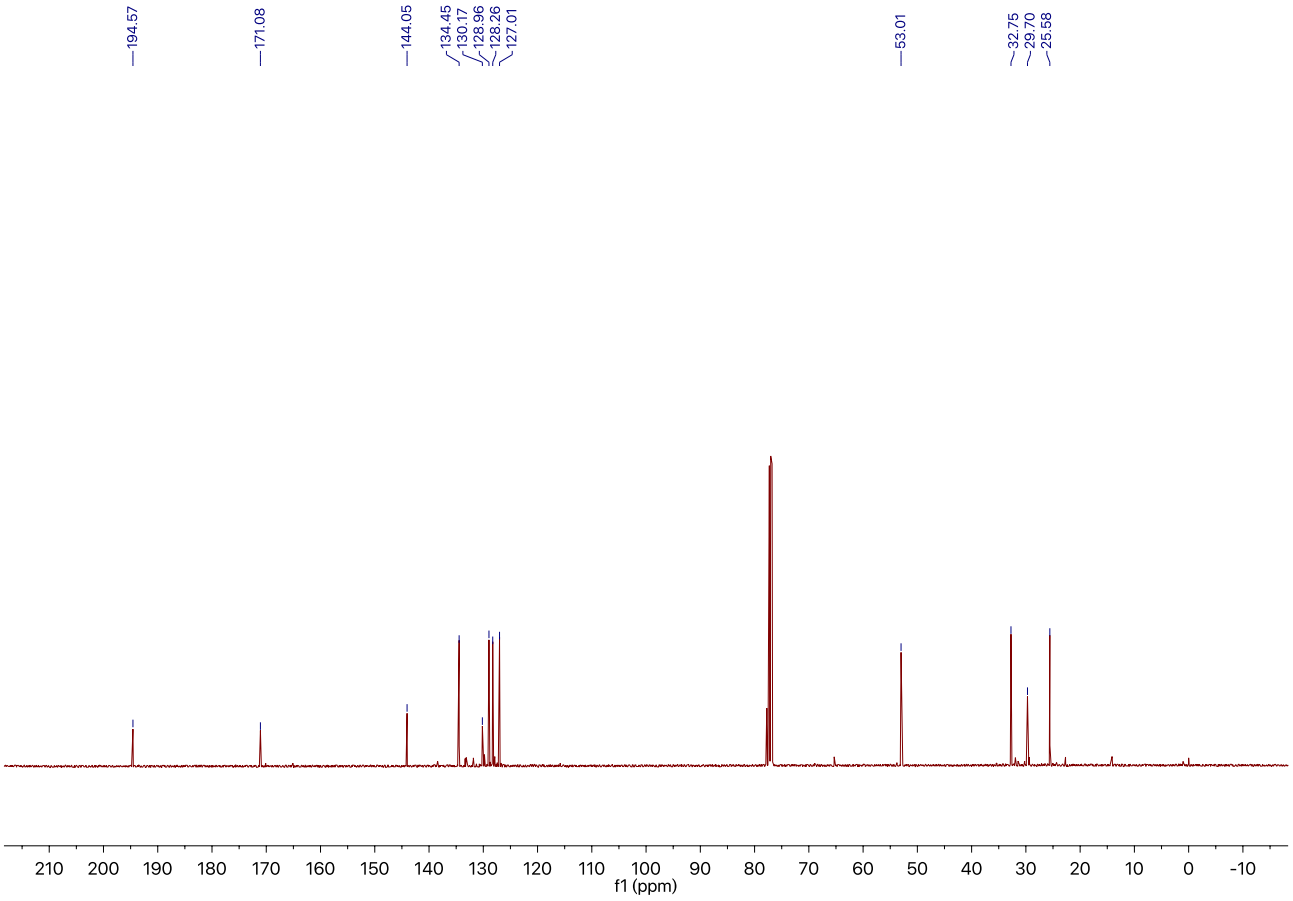
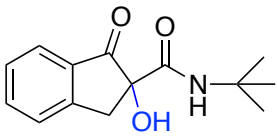


Figure S41 ^{13}CNMR Spectra of Compound **3n**

Compound **3o** [1]HNMR



3o

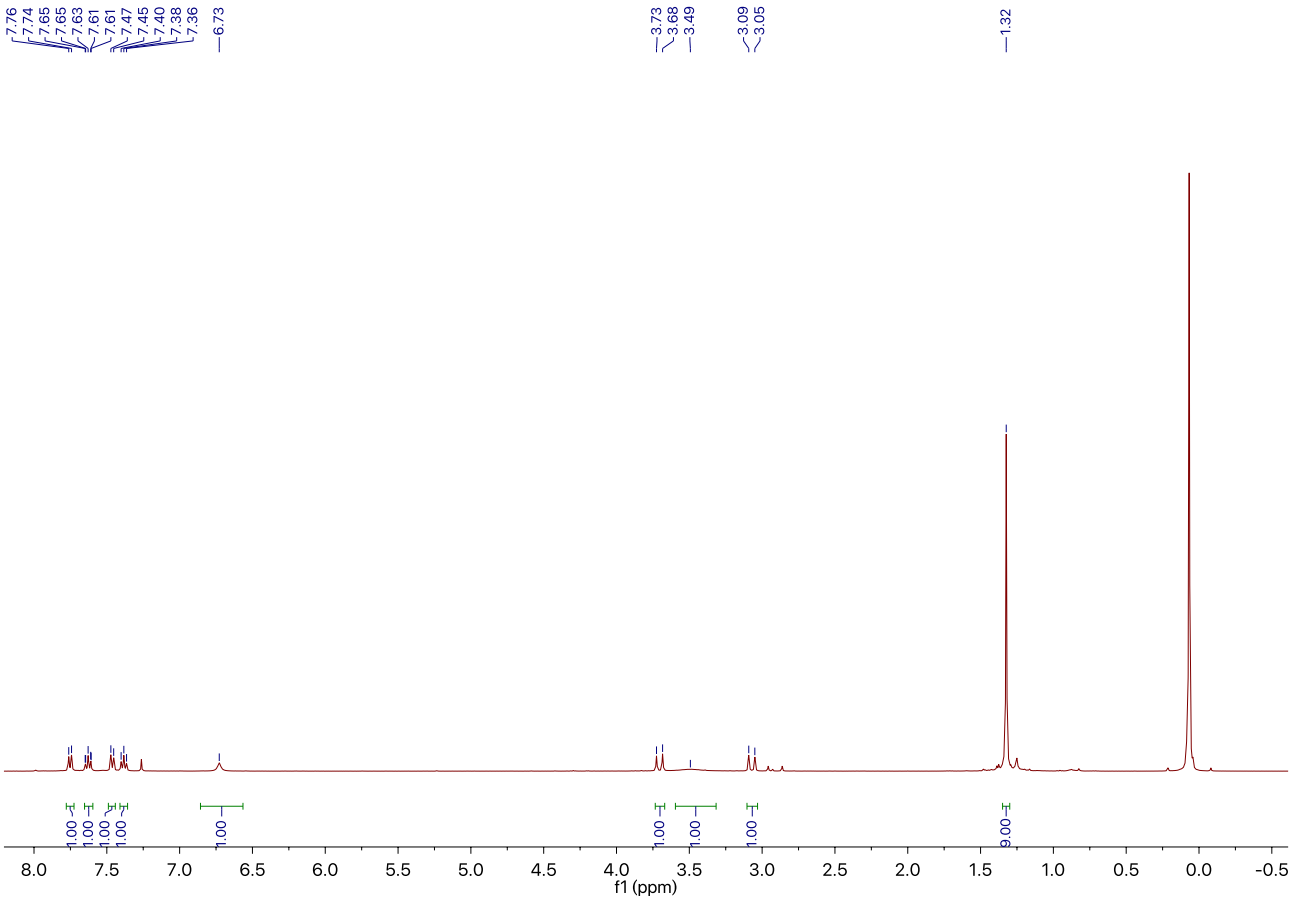
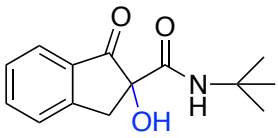


Figure S42. [1]HNMR Spectra of Compound **3o**

Compound **3o** ^{13}CNMR



3o

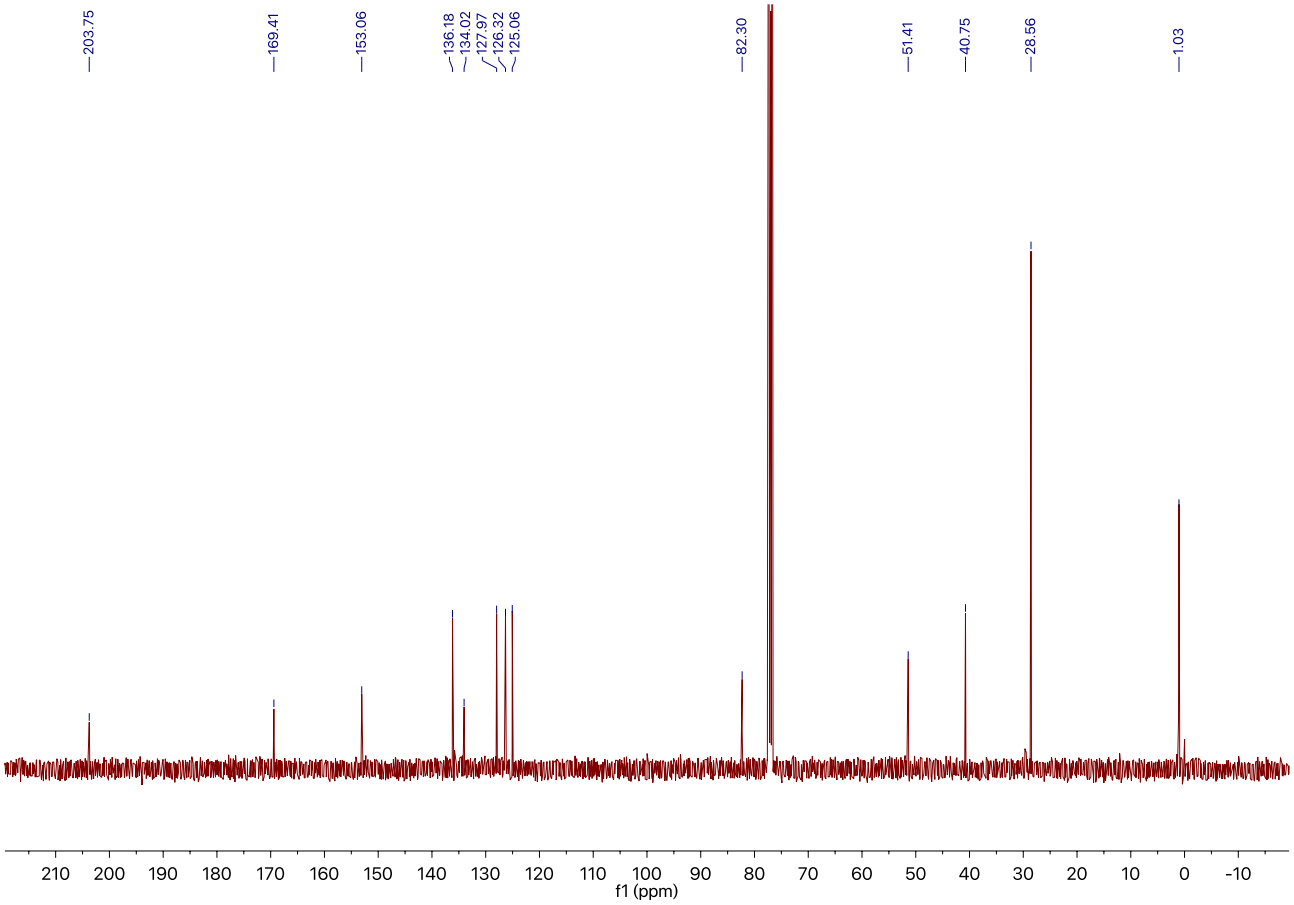
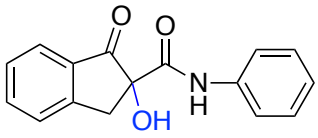


Figure S43 ^{13}CNMR Spectra of Compound **3o**

Compound **3p** [1]HNMR



3p

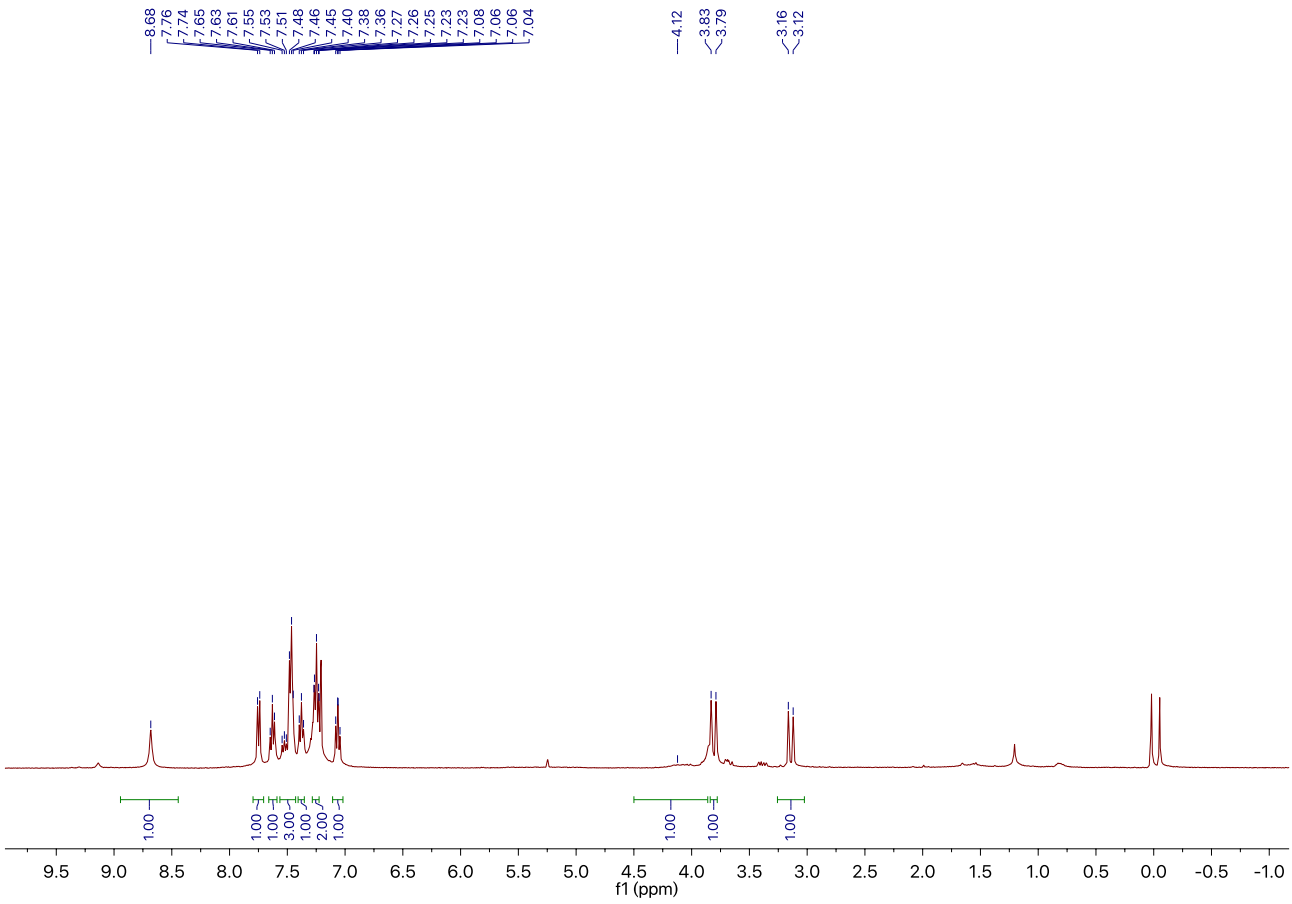
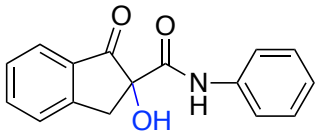


Figure S44. [1]HNMR Spectra of Compound **3p**

Compound **3p** ^{13}CNMR



3p

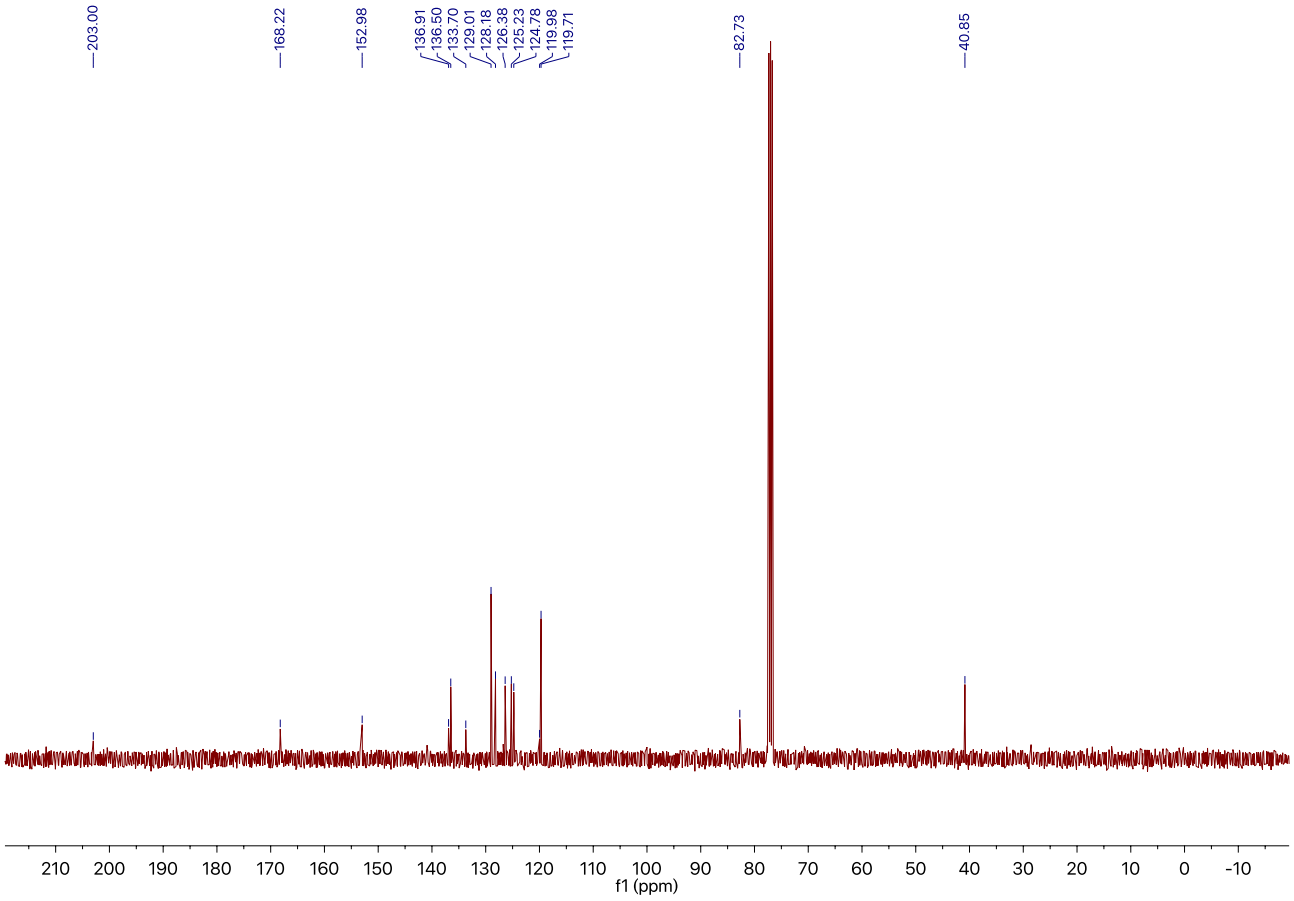
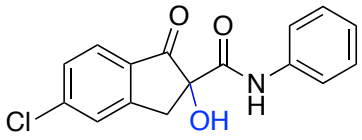


Figure S45 ^{13}CNMR Spectra of Compound **3p**

Compound **3q** [1]HNMR



3q

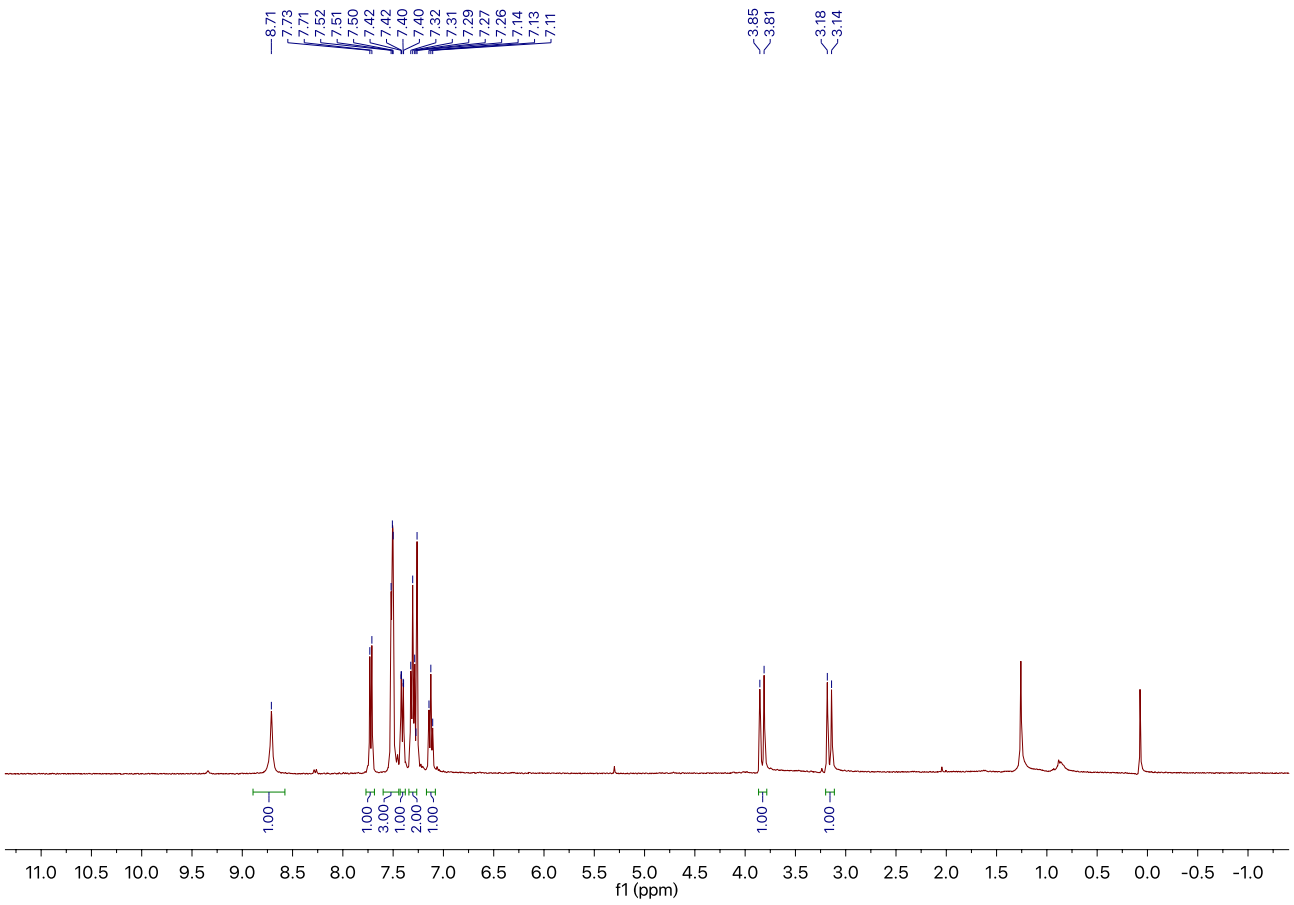
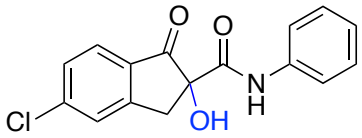


Figure S46. [1]HNMR Spectra of Compound **3q**

Compound **3q** ^{13}CNMR



3q

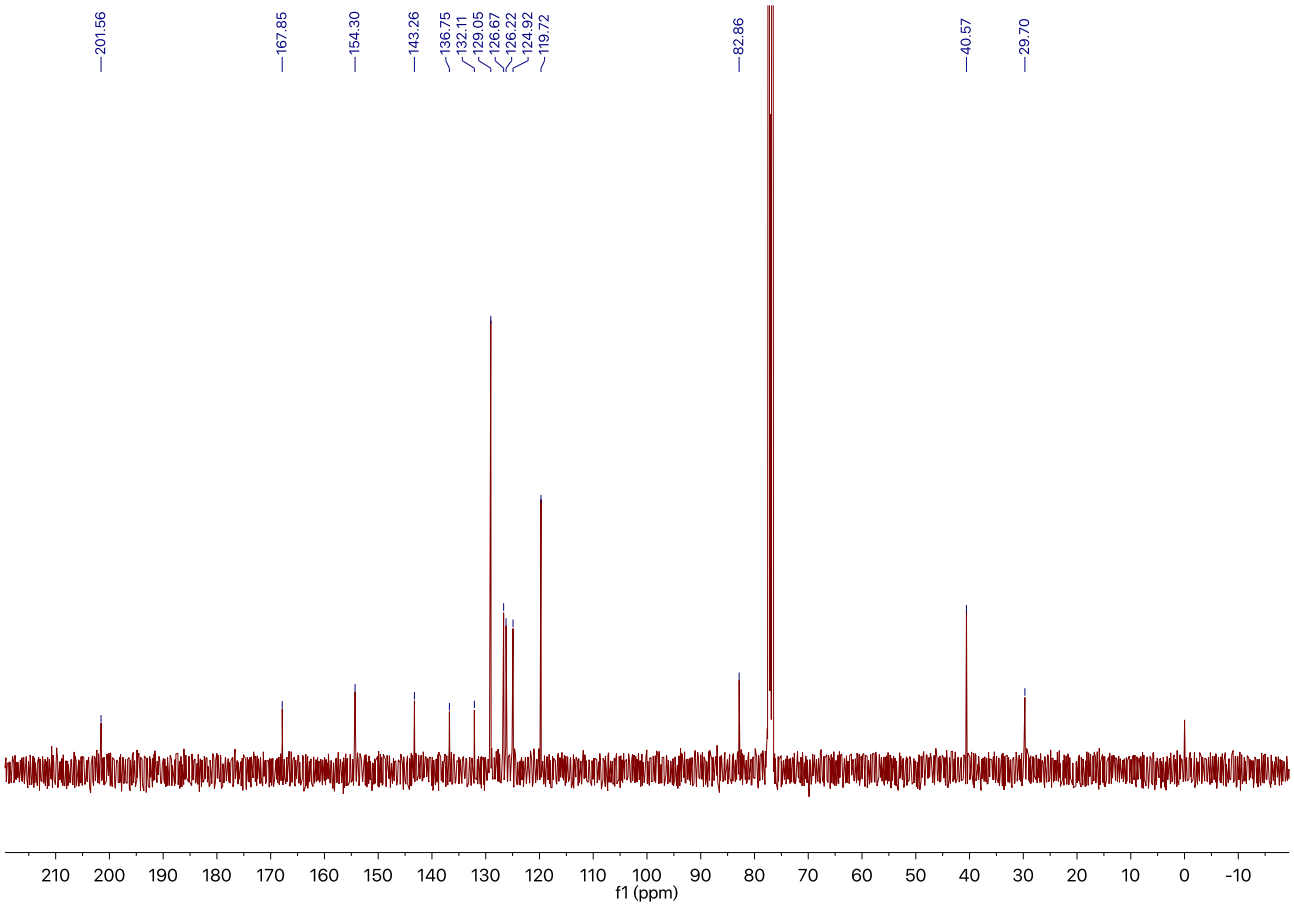
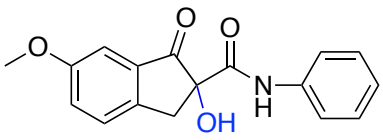


Figure S47 ^{13}CNMR Spectra of Compound **3q**

Compound **3r** [1]HNMR



3r

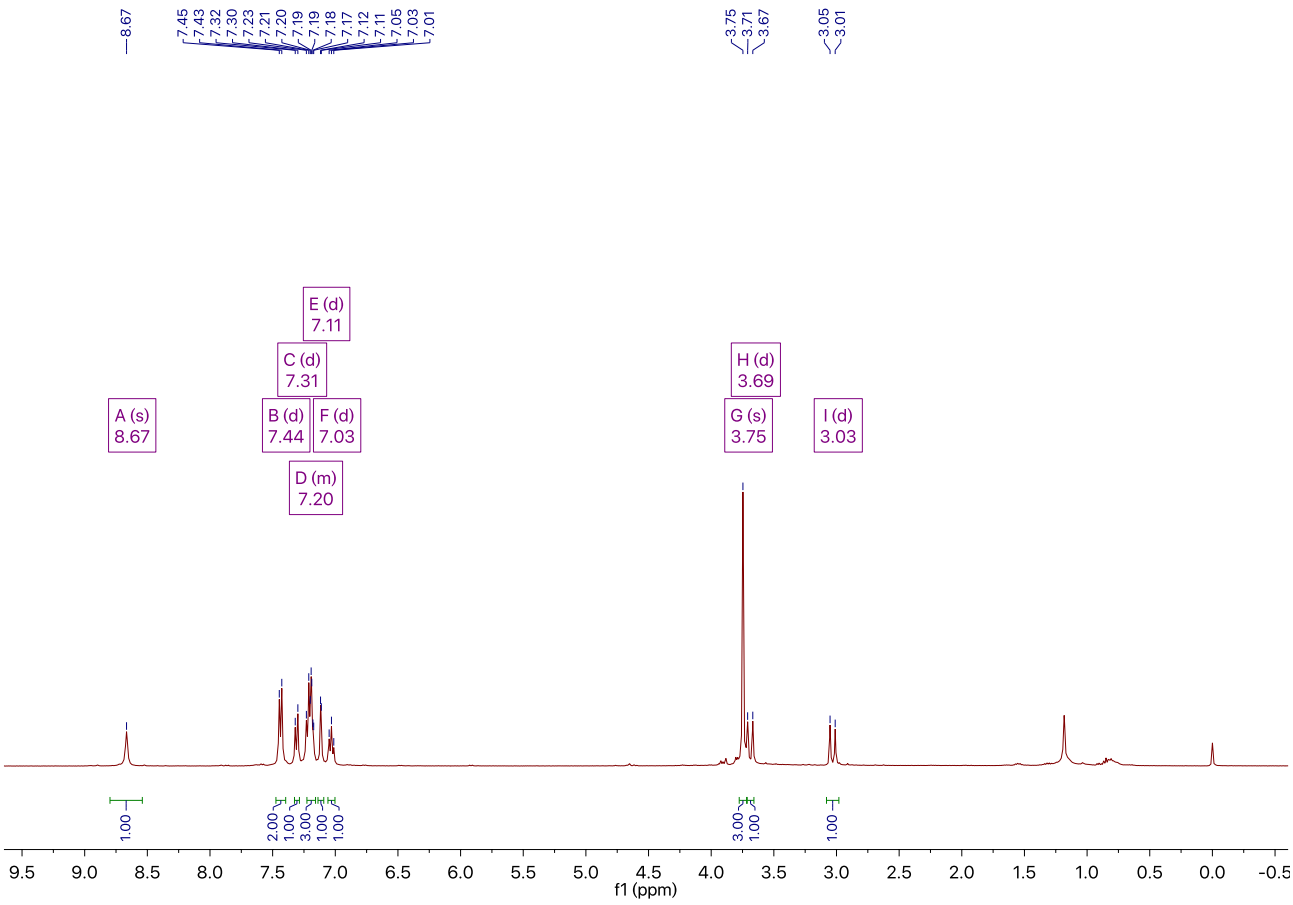
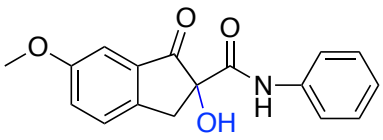


Figure S48. [1]HNMR Spectra of Compound **3r**

Compound **3r** ^{13}CNMR



3r

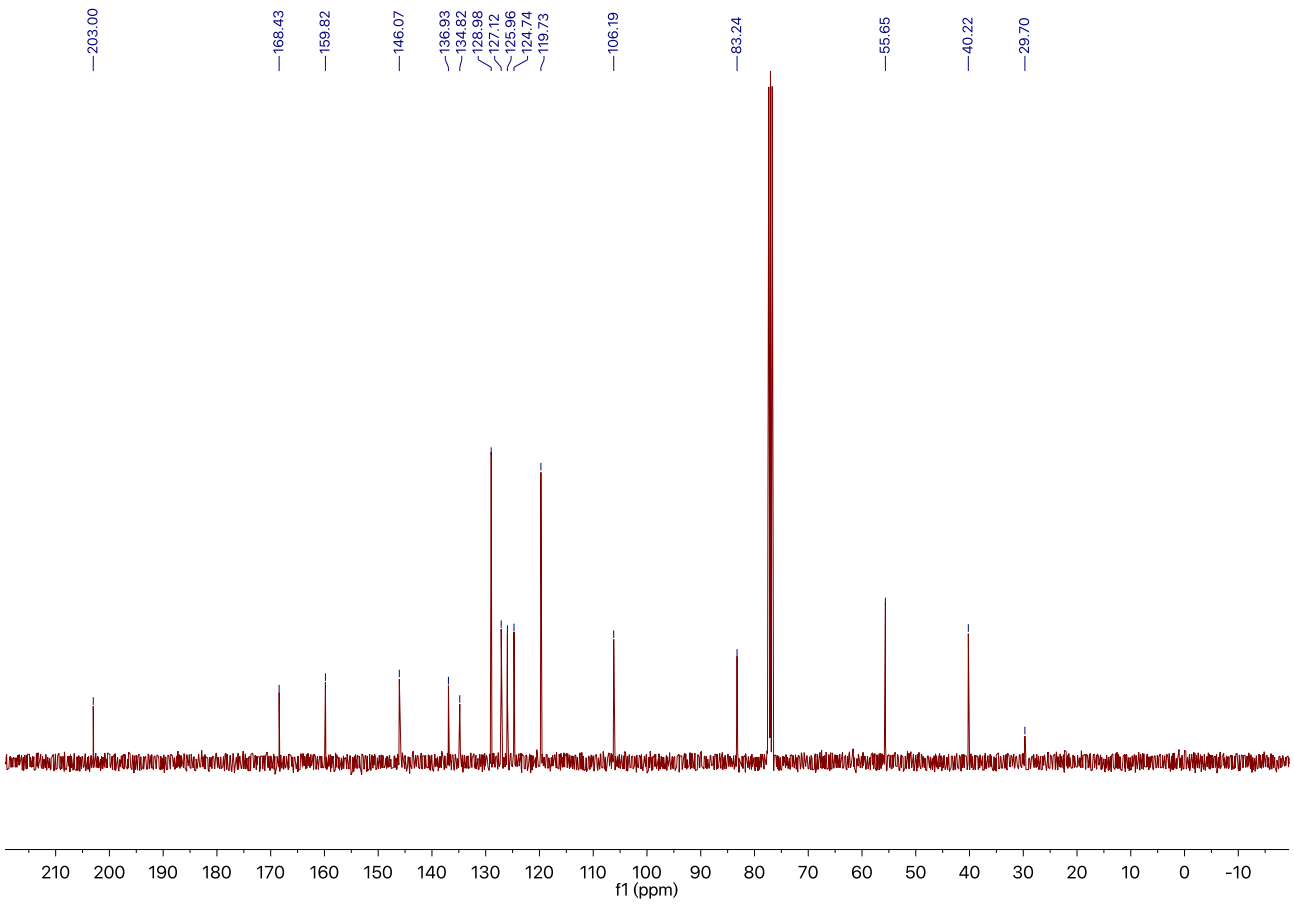
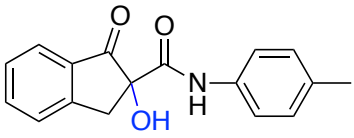


Figure S49 ^{13}CNMR Spectra of Compound **3r**

Compound **3s** ^{1}HNMR



3s

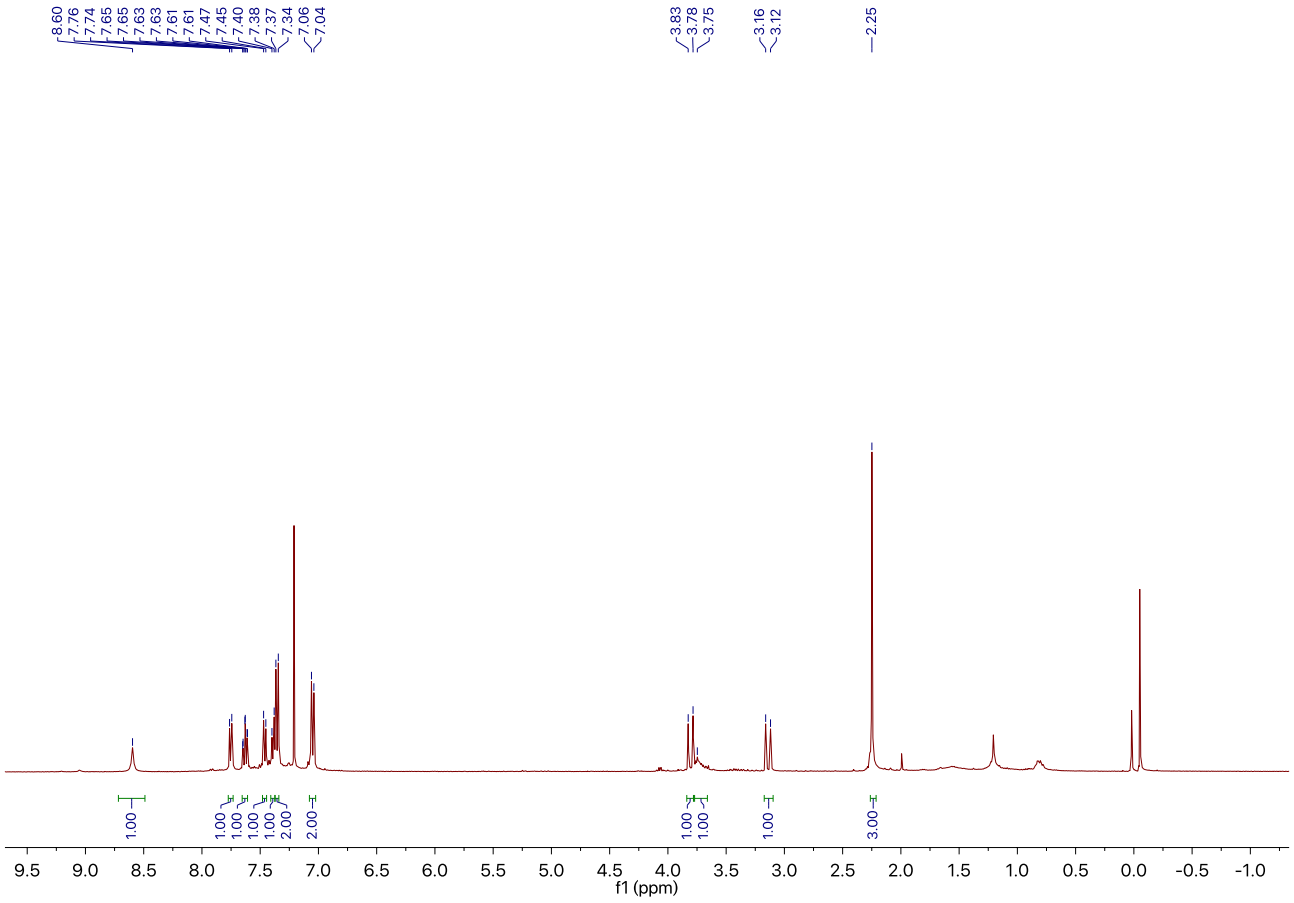
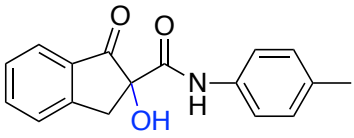


Figure S50. ^{1}HNMR Spectra of Compound **3s**

Compound **3s** ^{13}CNMR



3s

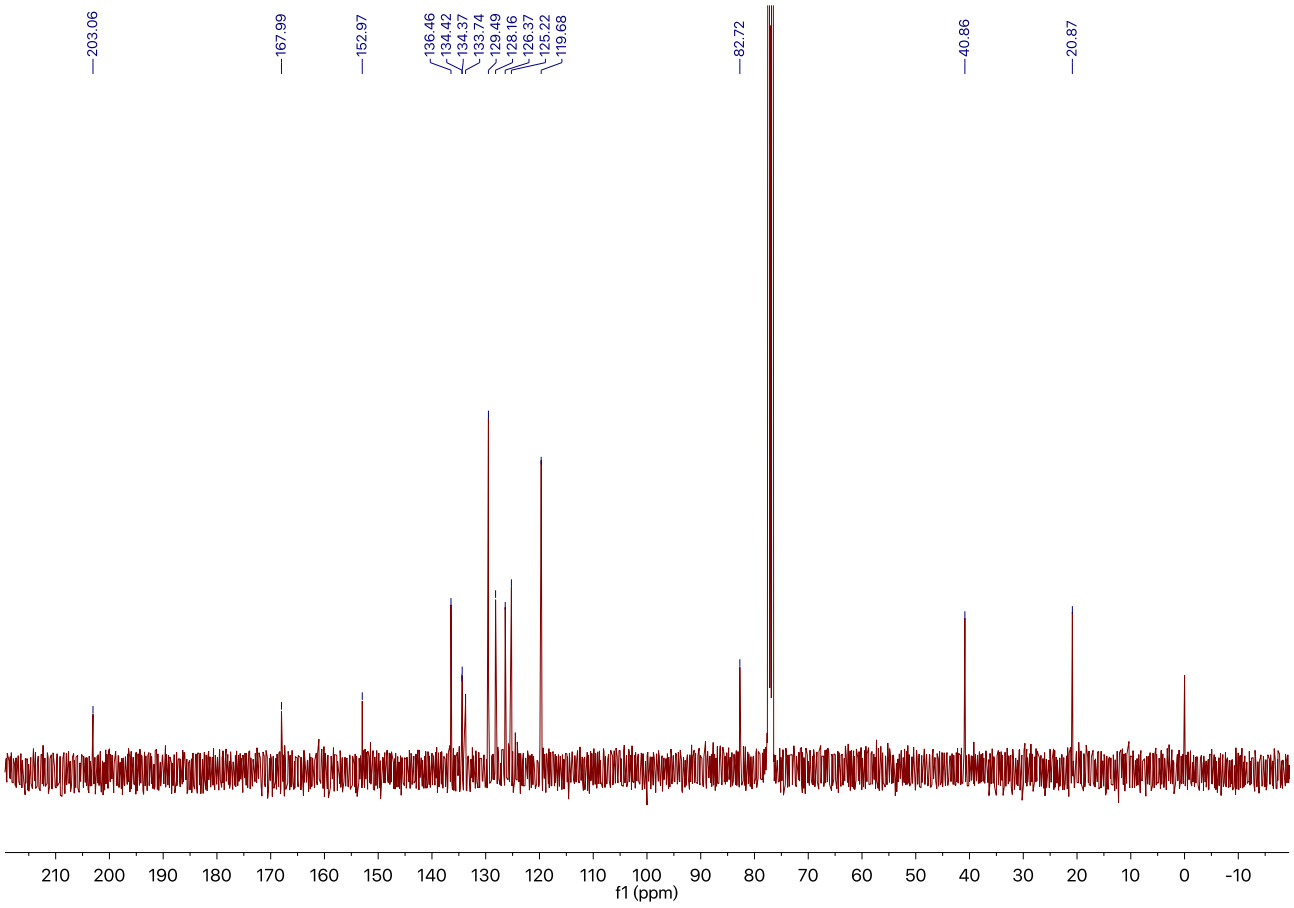
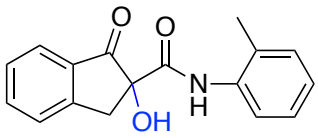


Figure S51 ^{13}CNMR Spectra of Compound **3s**

Compound **3t** [1]HNMR



3t

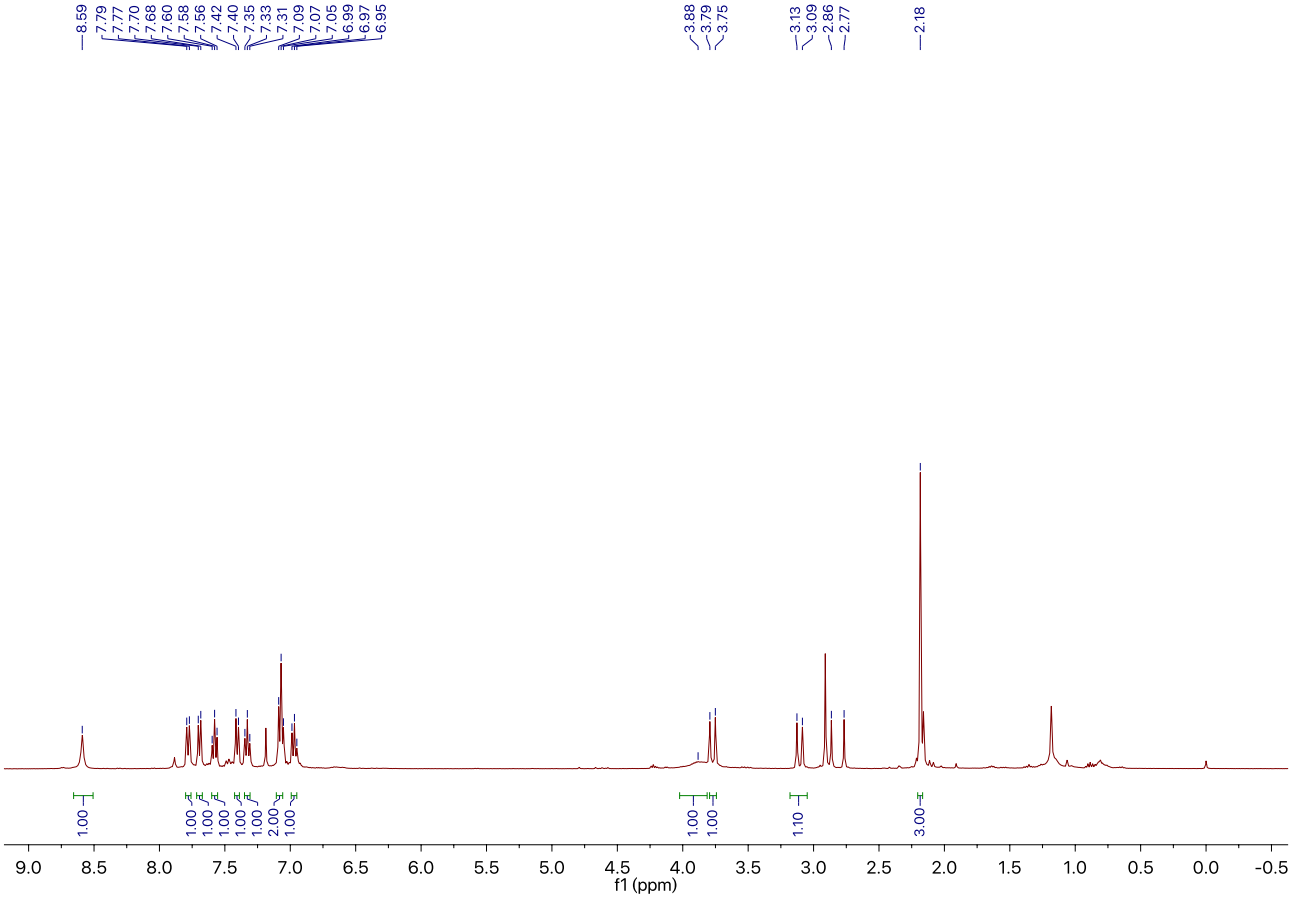
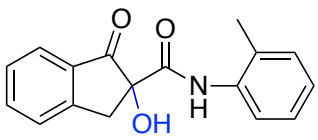


Figure S52. [1]HNMR Spectra of Compound **3t**

Compound **3t** ^{13}CNMR



3t

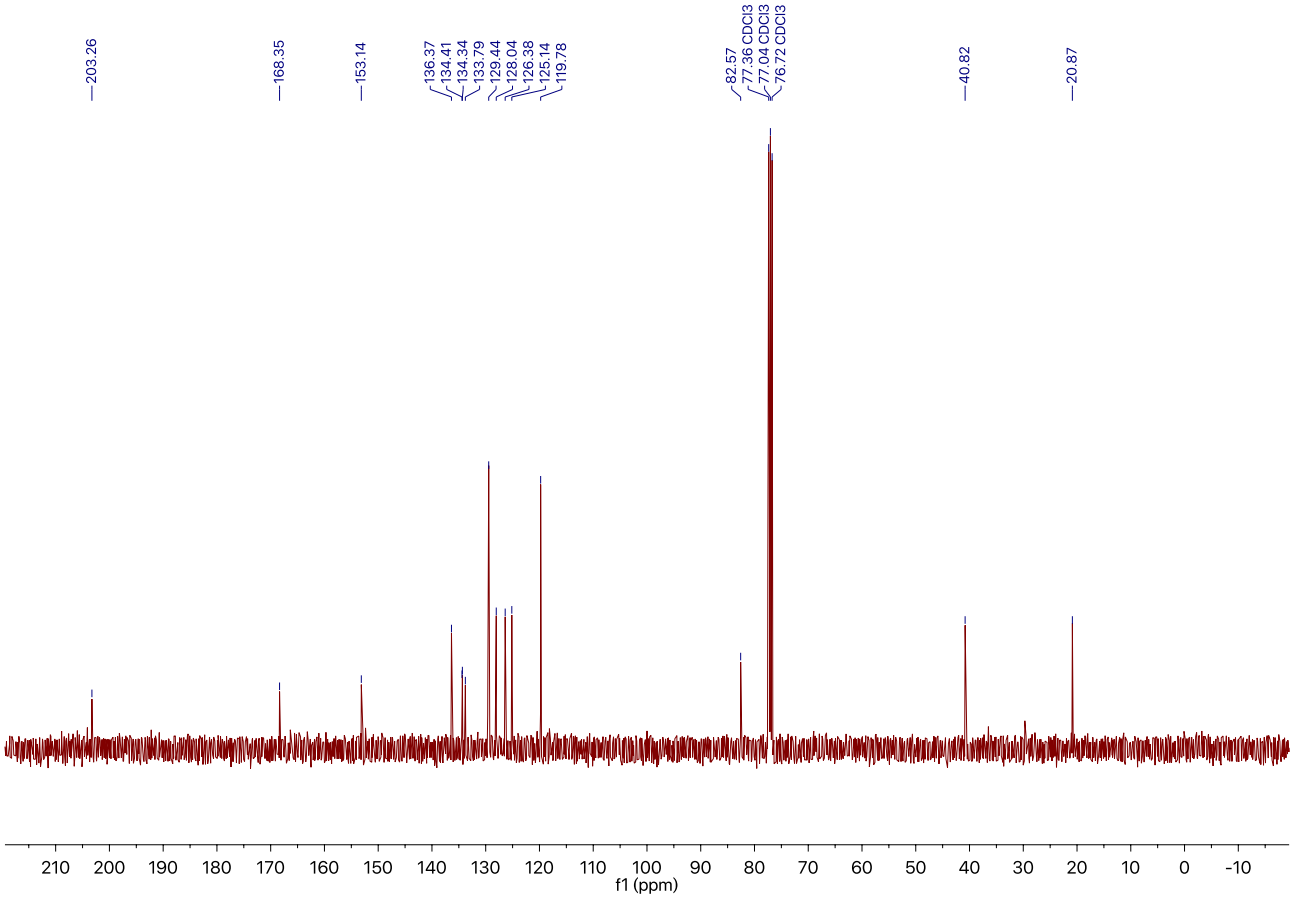
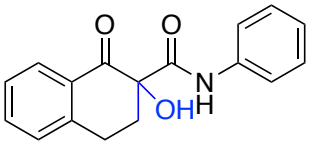


Figure S53 ^{13}CNMR Spectra of Compound **3t**

Compound **3u** [1]HNMR



3u

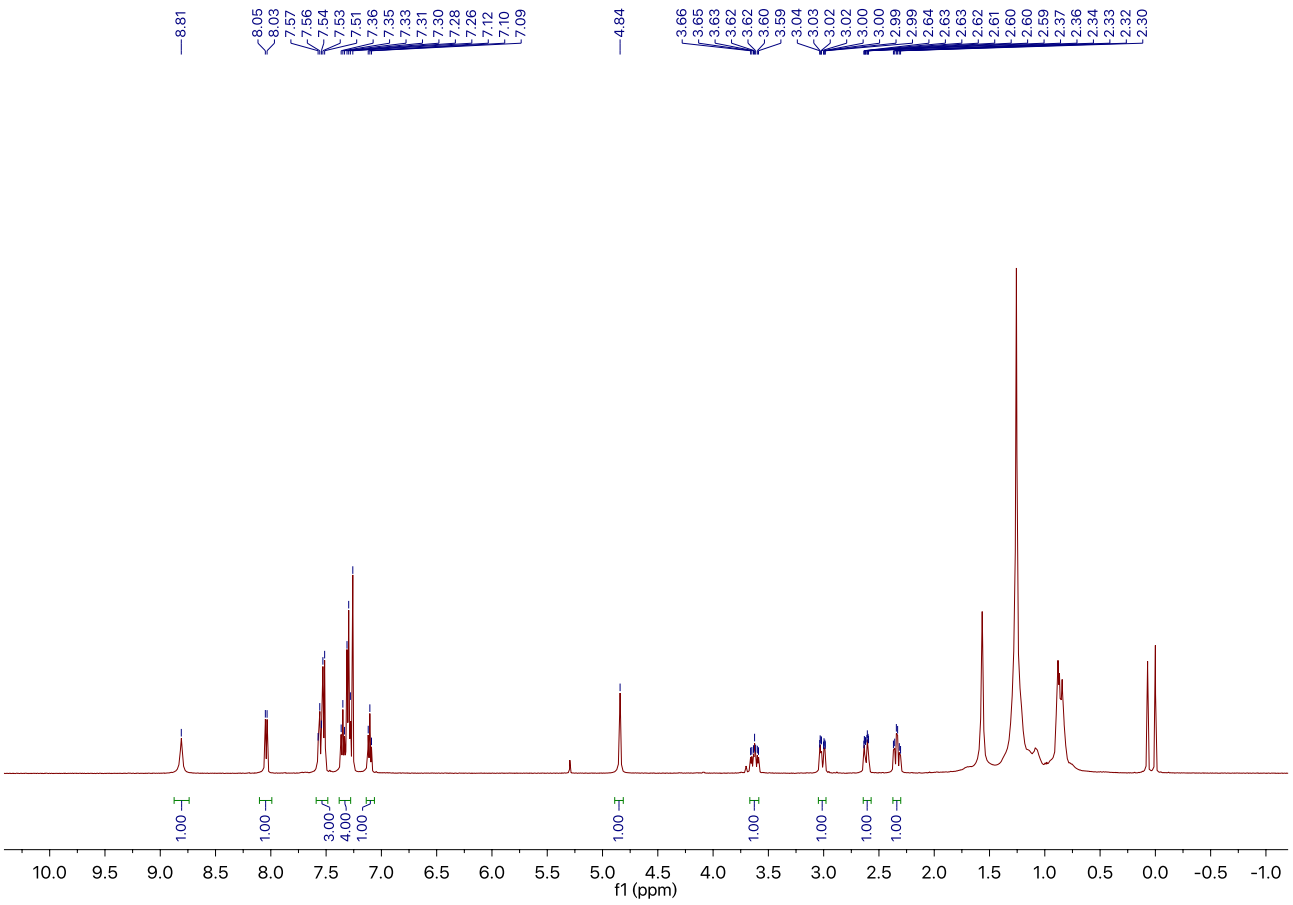
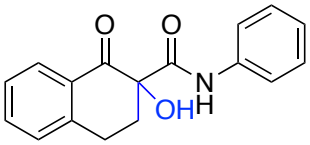


Figure S54. [1]HNMR Spectra of Compound **3u**

Compound **3u** ^{13}CNMR



3u

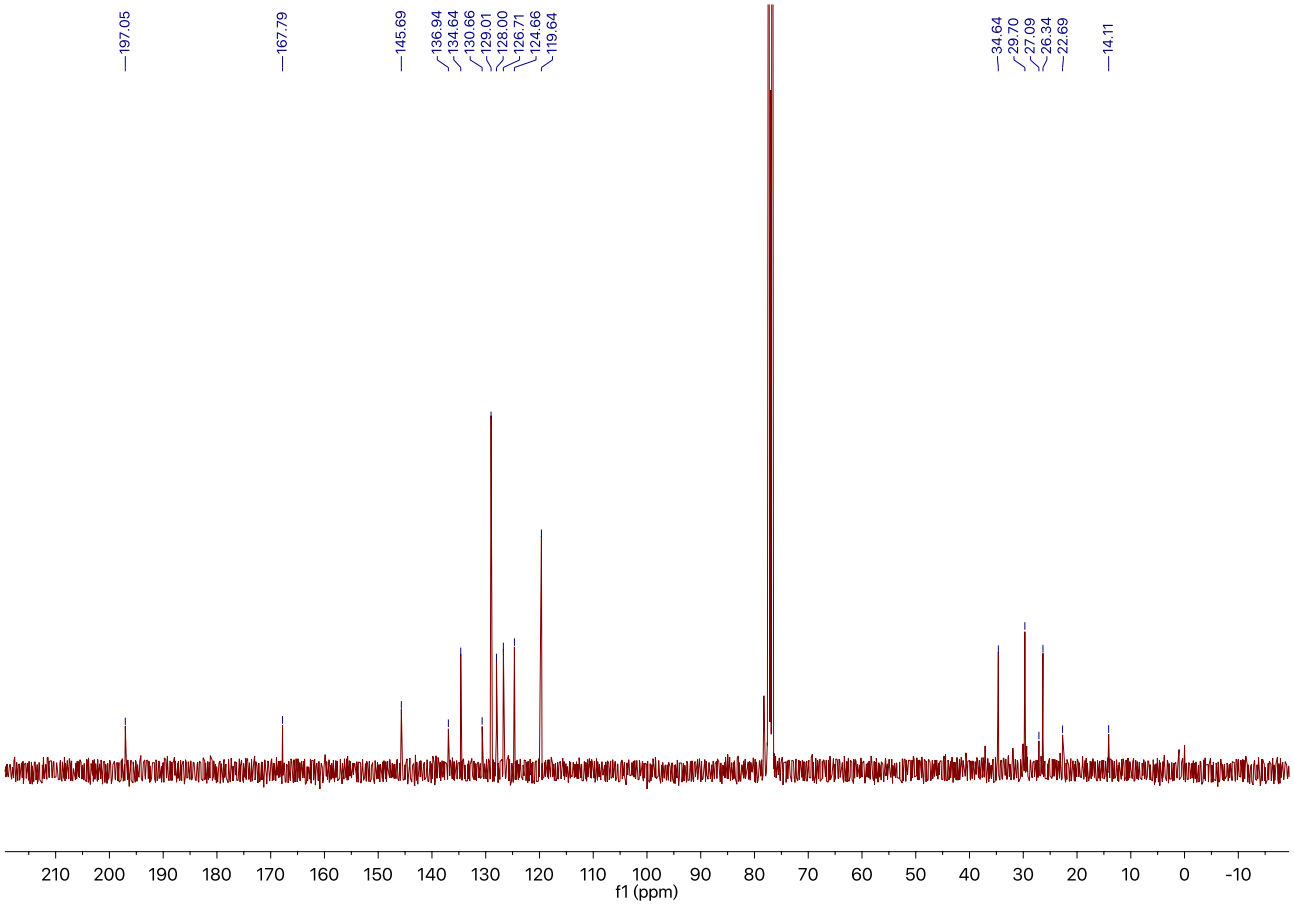
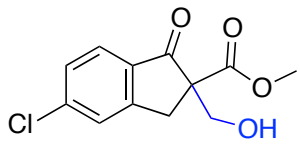


Figure S55 ^{13}CNMR Spectra of Compound **3u**

Compound **4a** [1]HNMR



4a

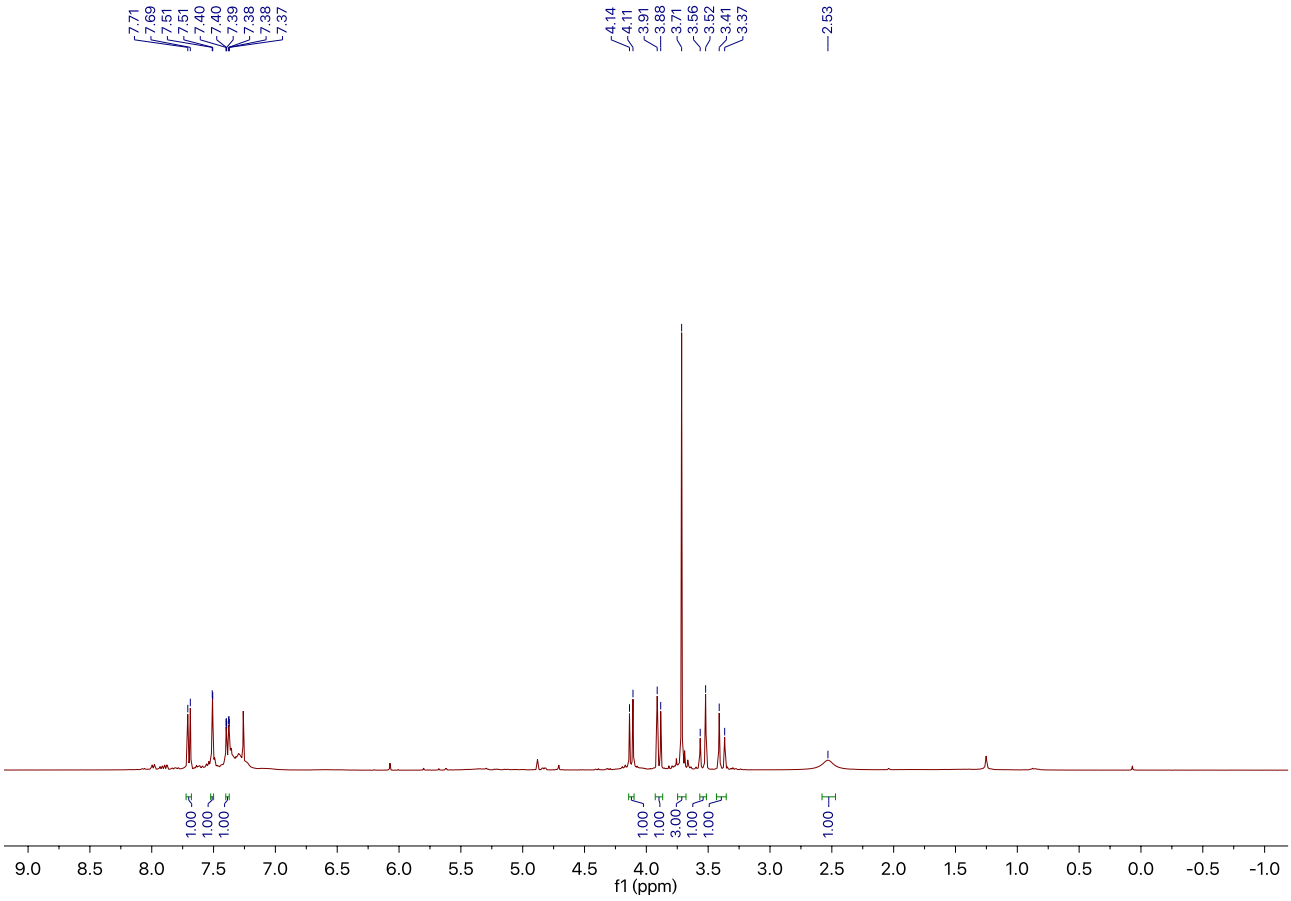
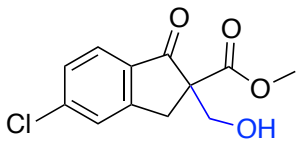


Figure S56. [1]HNMR Spectra of Compound **4a**

Compound **4a** ^{13}CNMR



4a

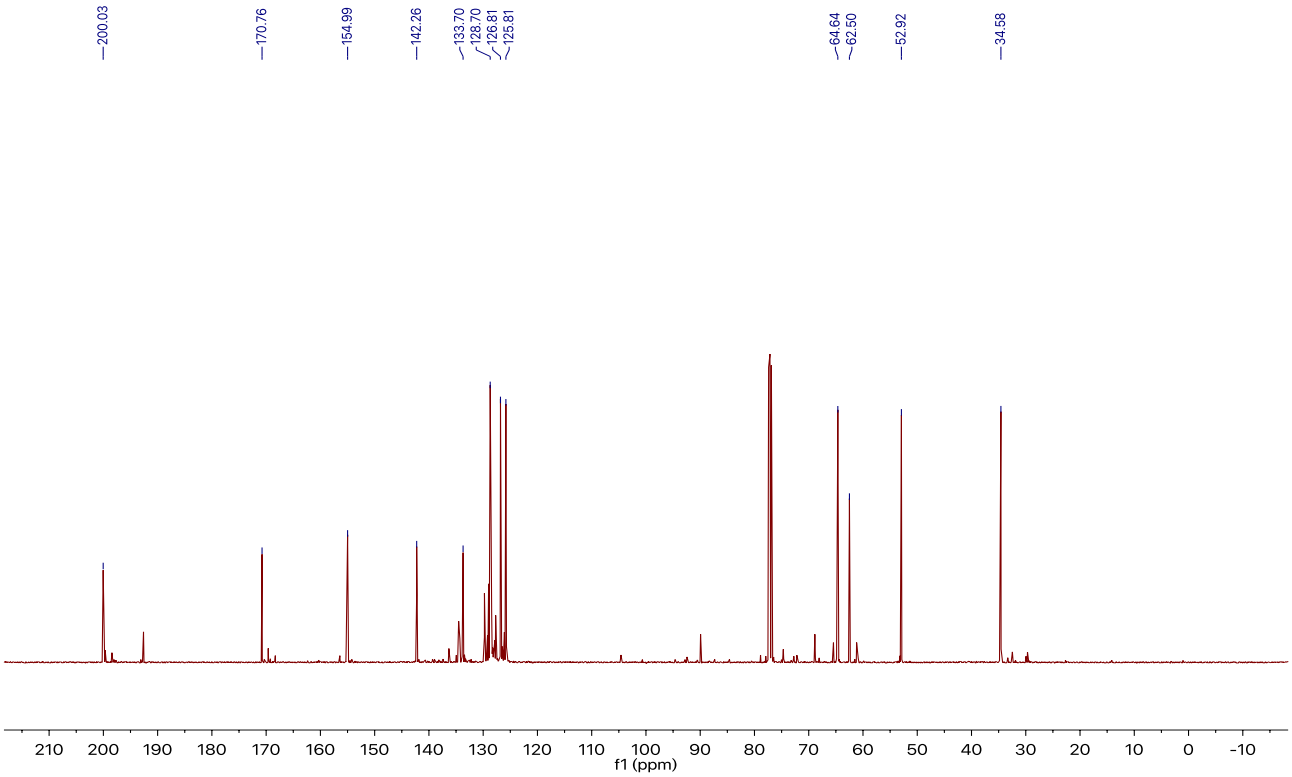
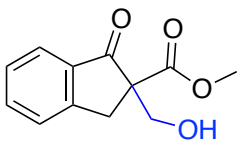


Figure S57. ^{13}CNMR Spectra of Compound **4a**

Compound **4b** [1]HNMR



4b

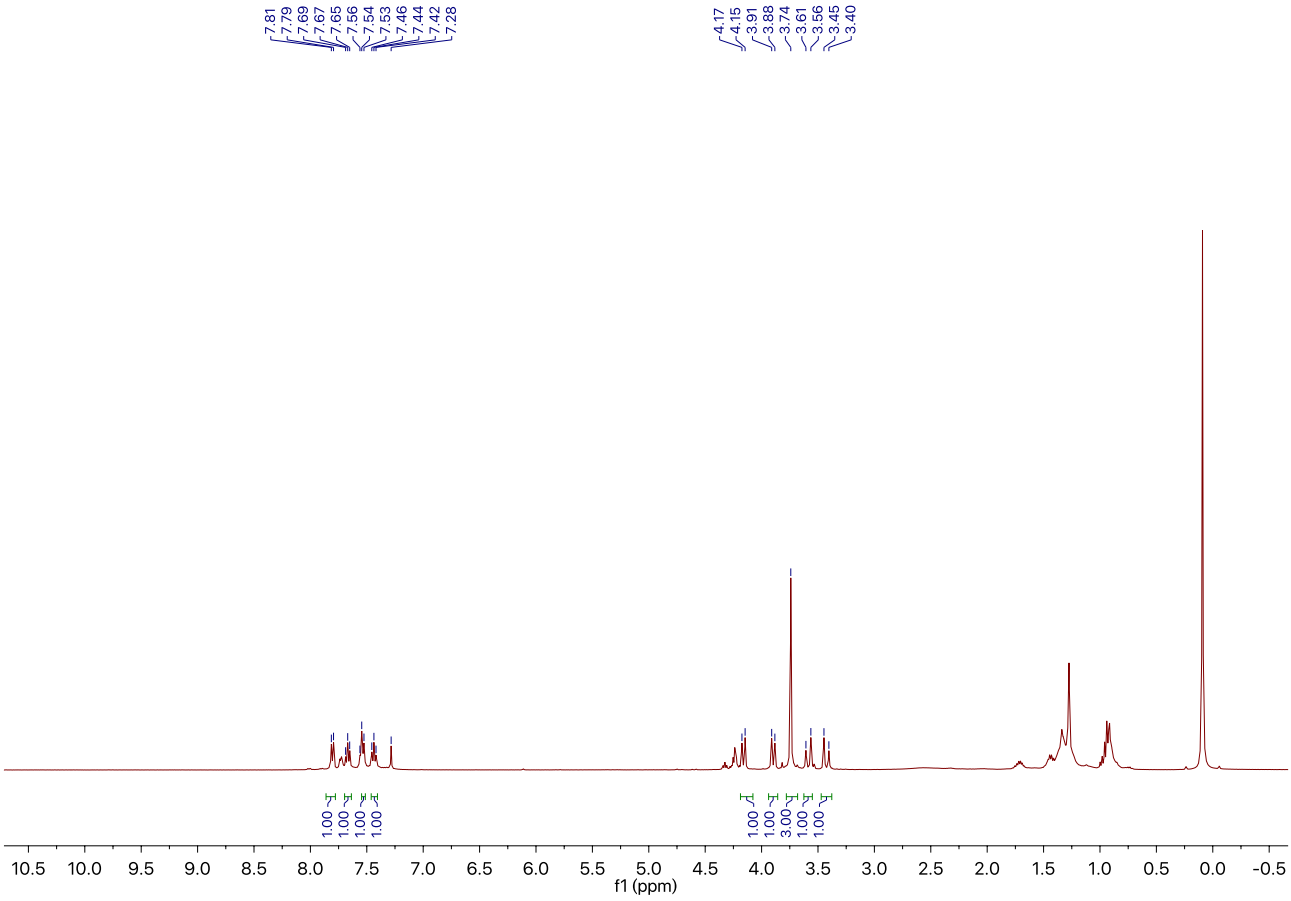
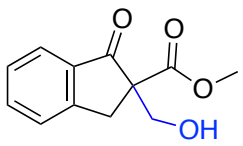


Figure S58. [1]HNMR Spectra of Compound **4b**

Compound **4b** ^{13}CNMR



4b

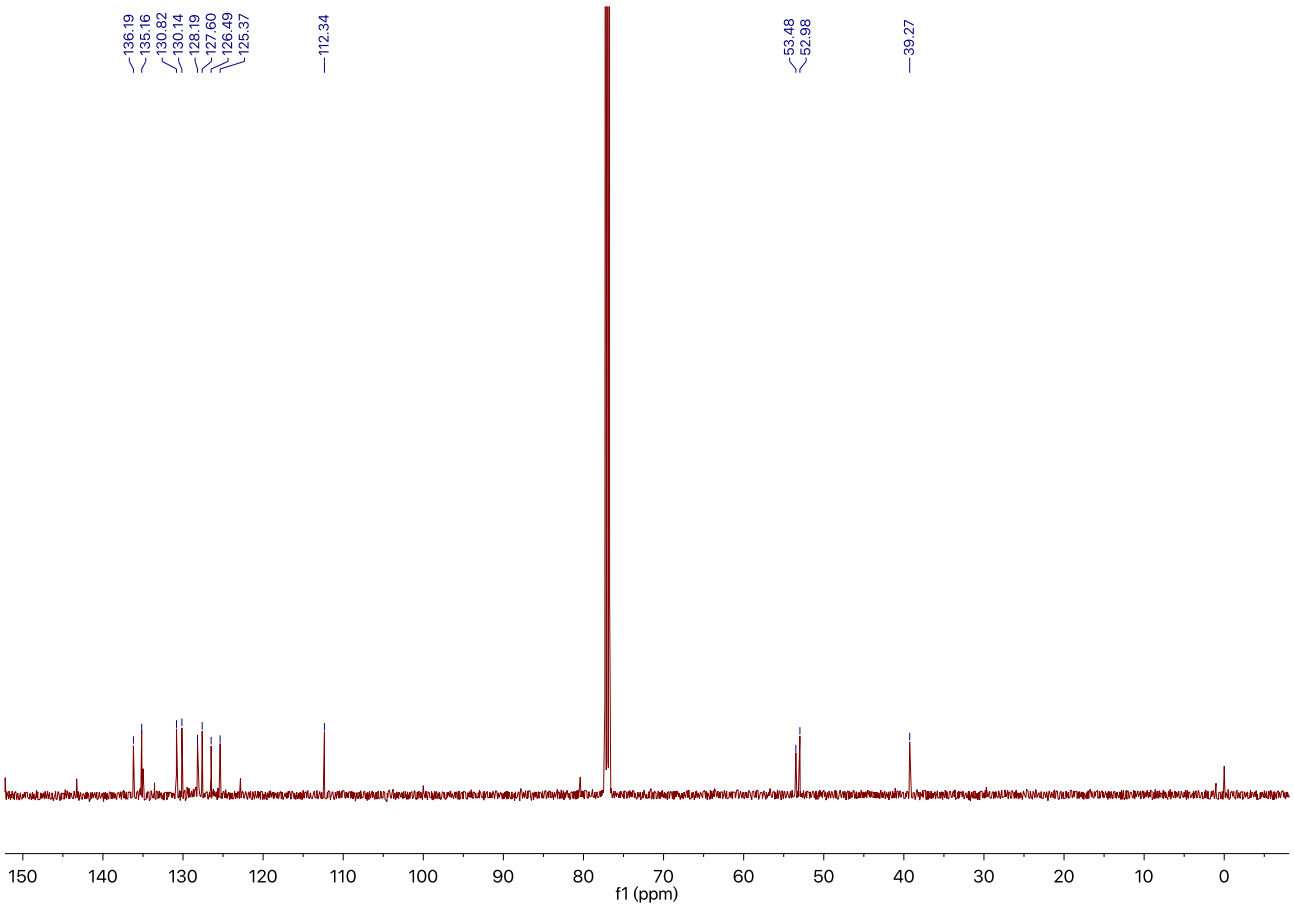
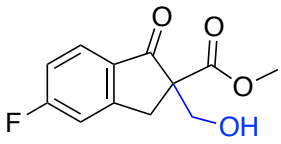


Figure S59. ^{13}CNMR Spectra of Compound **4b**

Compound **4c** ^{1}HNMR



4c

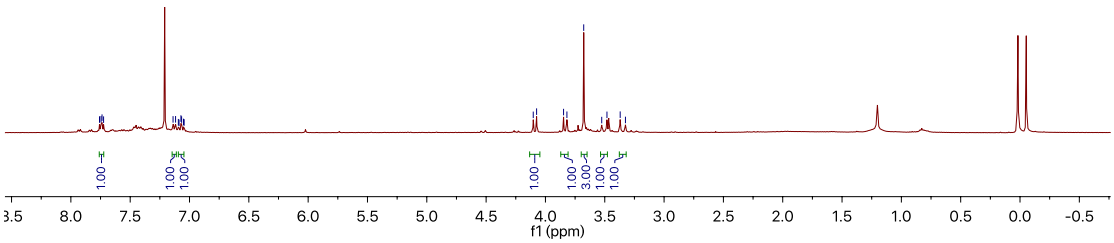
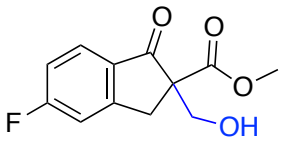


Figure S60. ^{1}HNMR Spectra of Compound **4c**

Compound **4c** ^{13}CNMR



4c

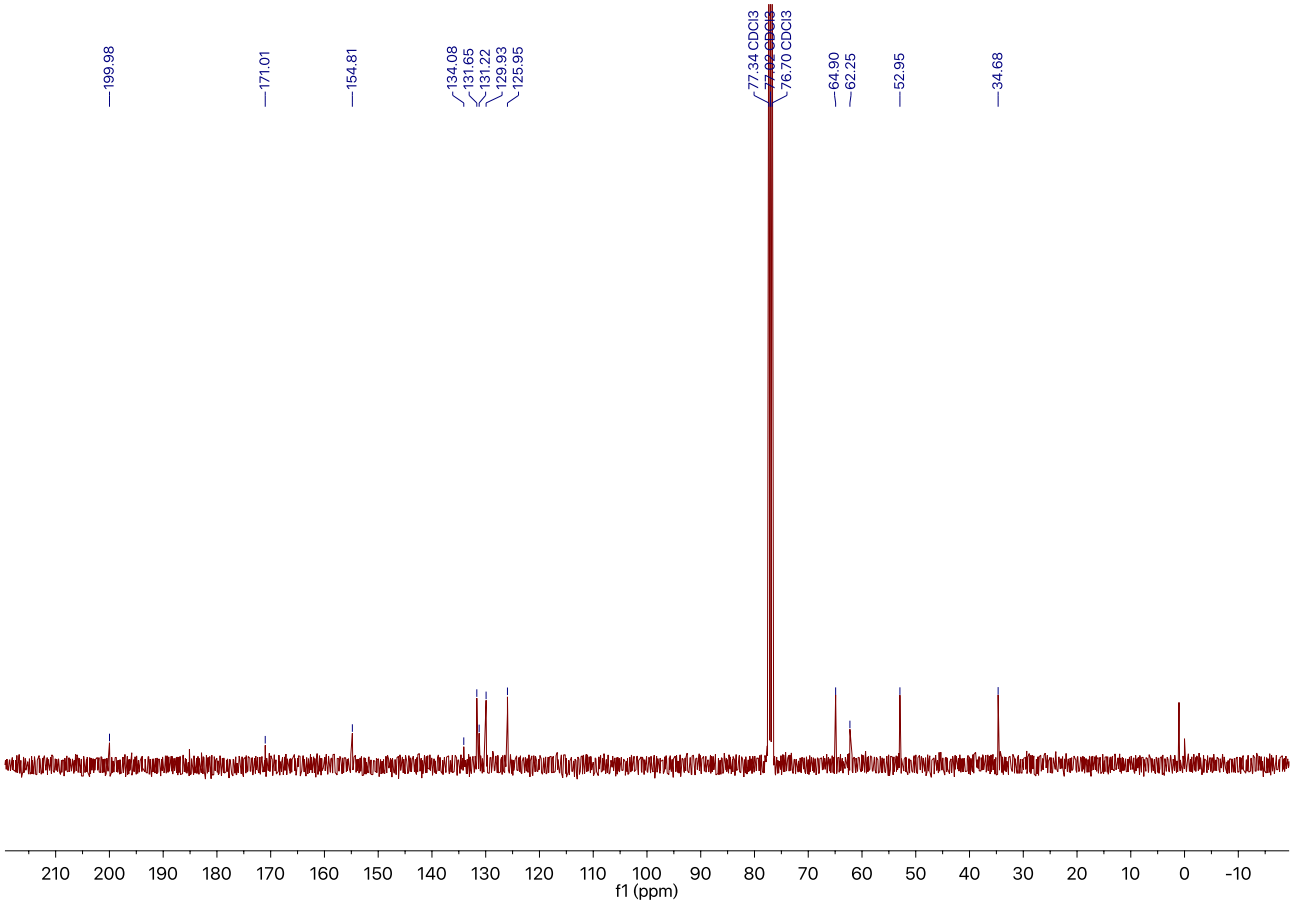
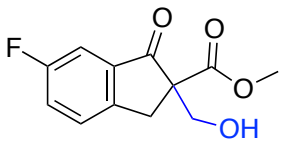


Figure S61. ^{13}CNMR Spectra of Compound **4c**

Compound **4d** [1]HNMR



4d

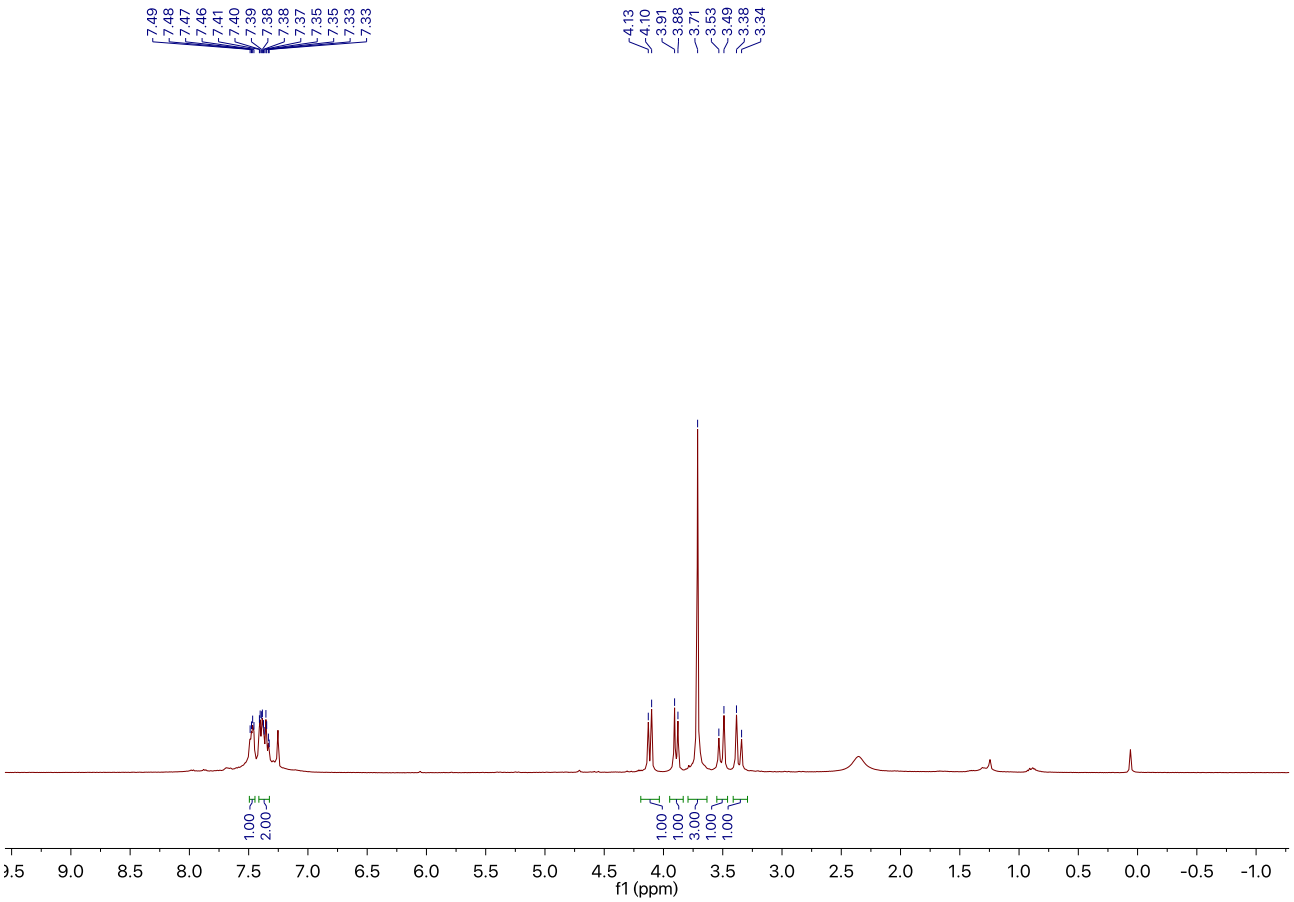
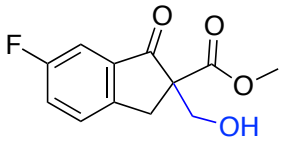


Figure S62. [1]HNMR Spectra of Compound **4d**

Compound **4d** ^{13}CNMR



4d

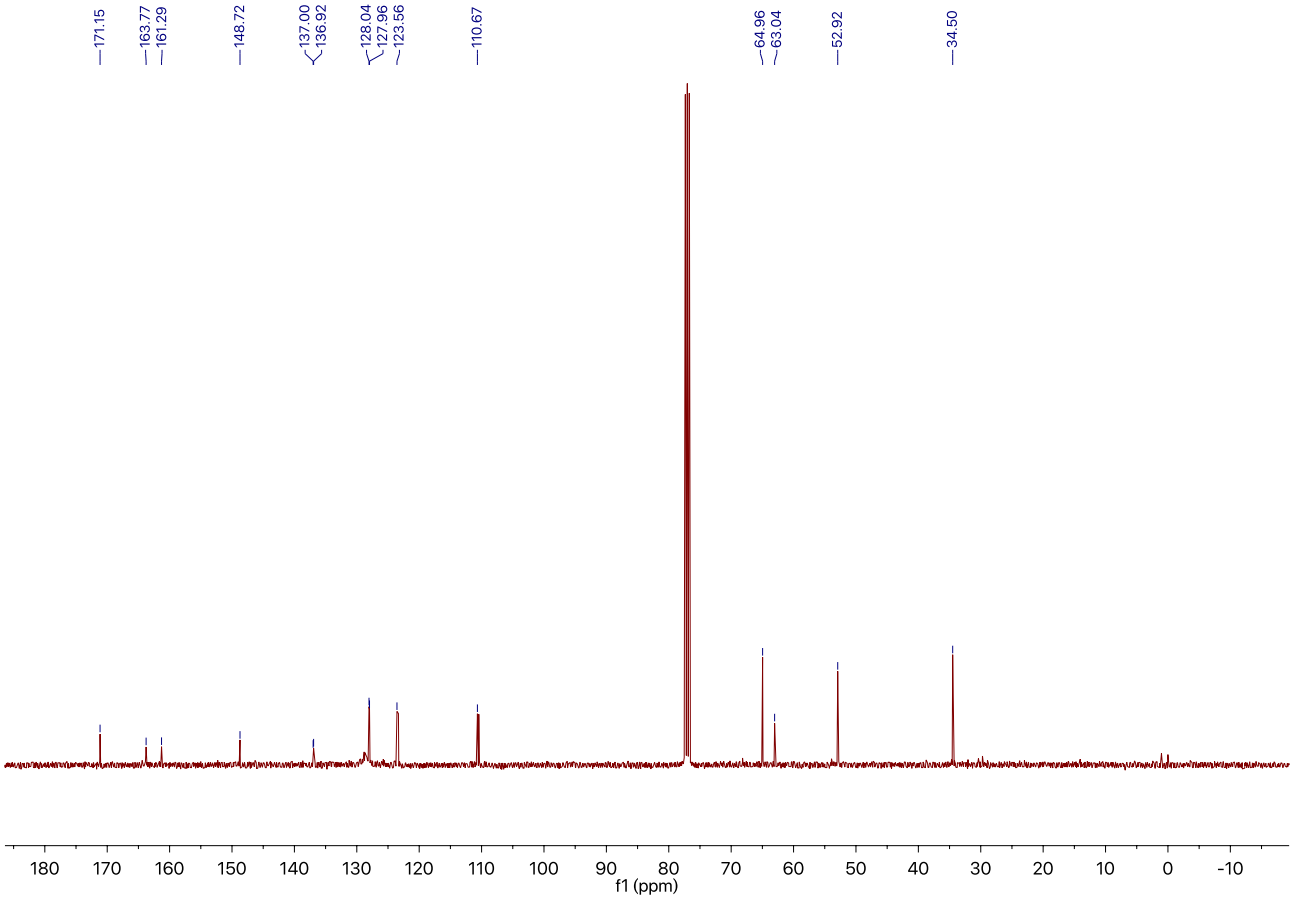
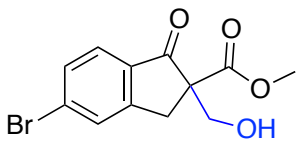


Figure S63. ^{13}CNMR Spectra of Compound **4d**

Compound **4e** ^{1}HNMR



4e

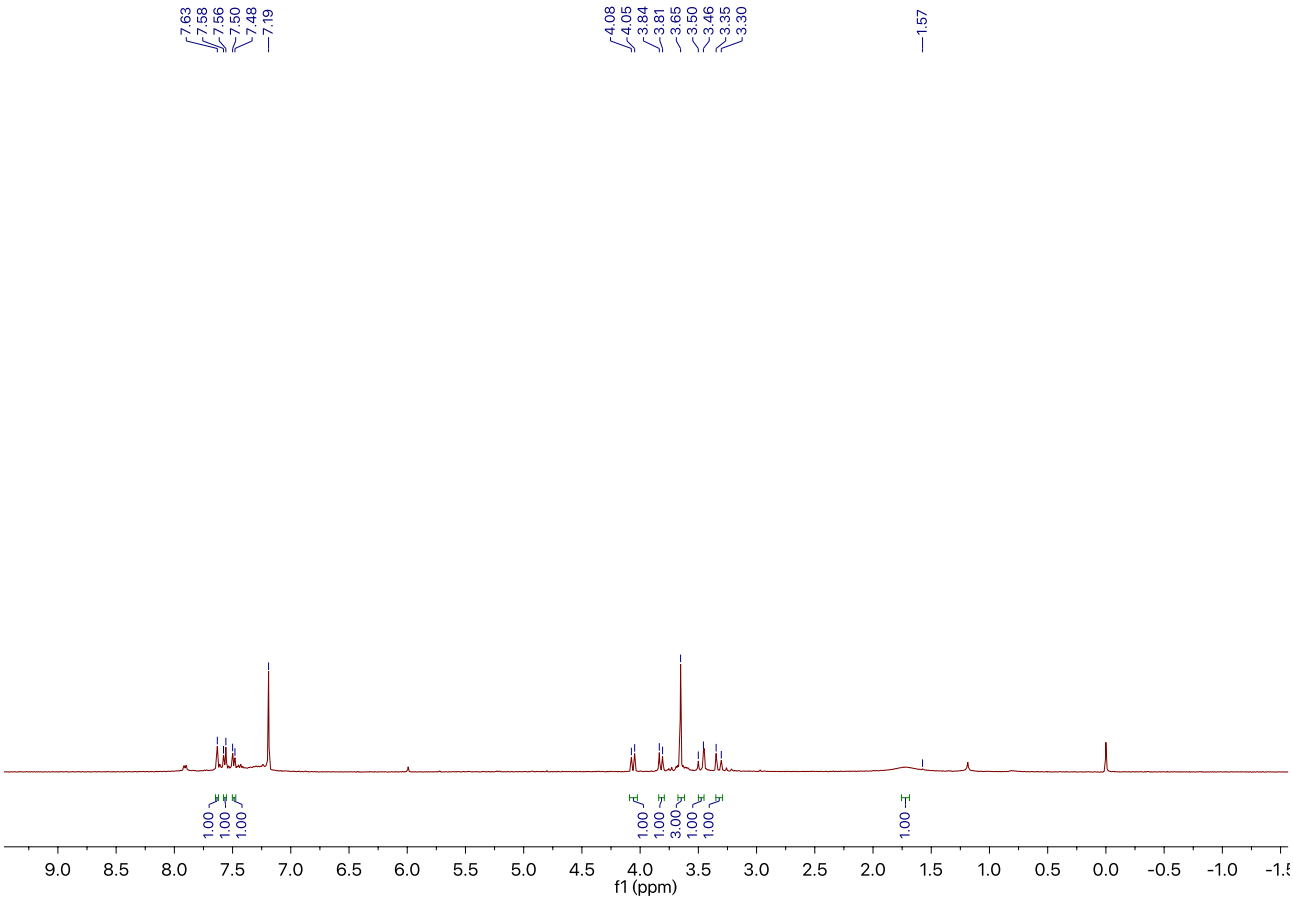
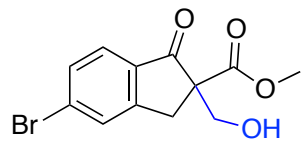


Figure S64. ^{1}HNMR Spectra of Compound **4e**

Compound **4e** ^{13}CNMR



4e

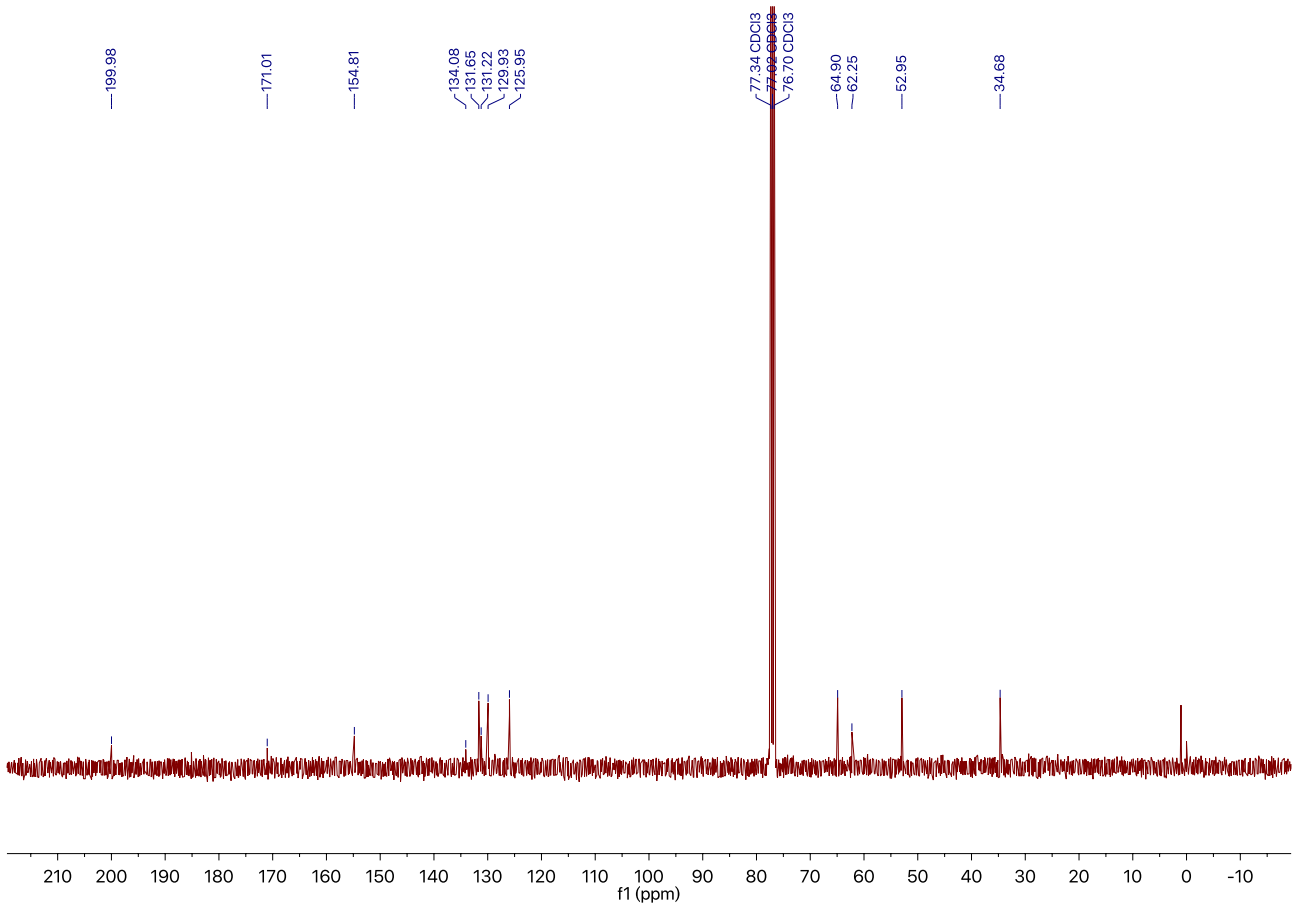
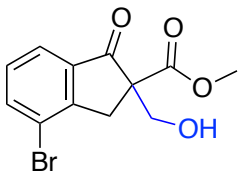


Figure S65. ^{13}CNMR Spectra of Compound **4e**

Compound **4f** ^{1}HNMR



4f

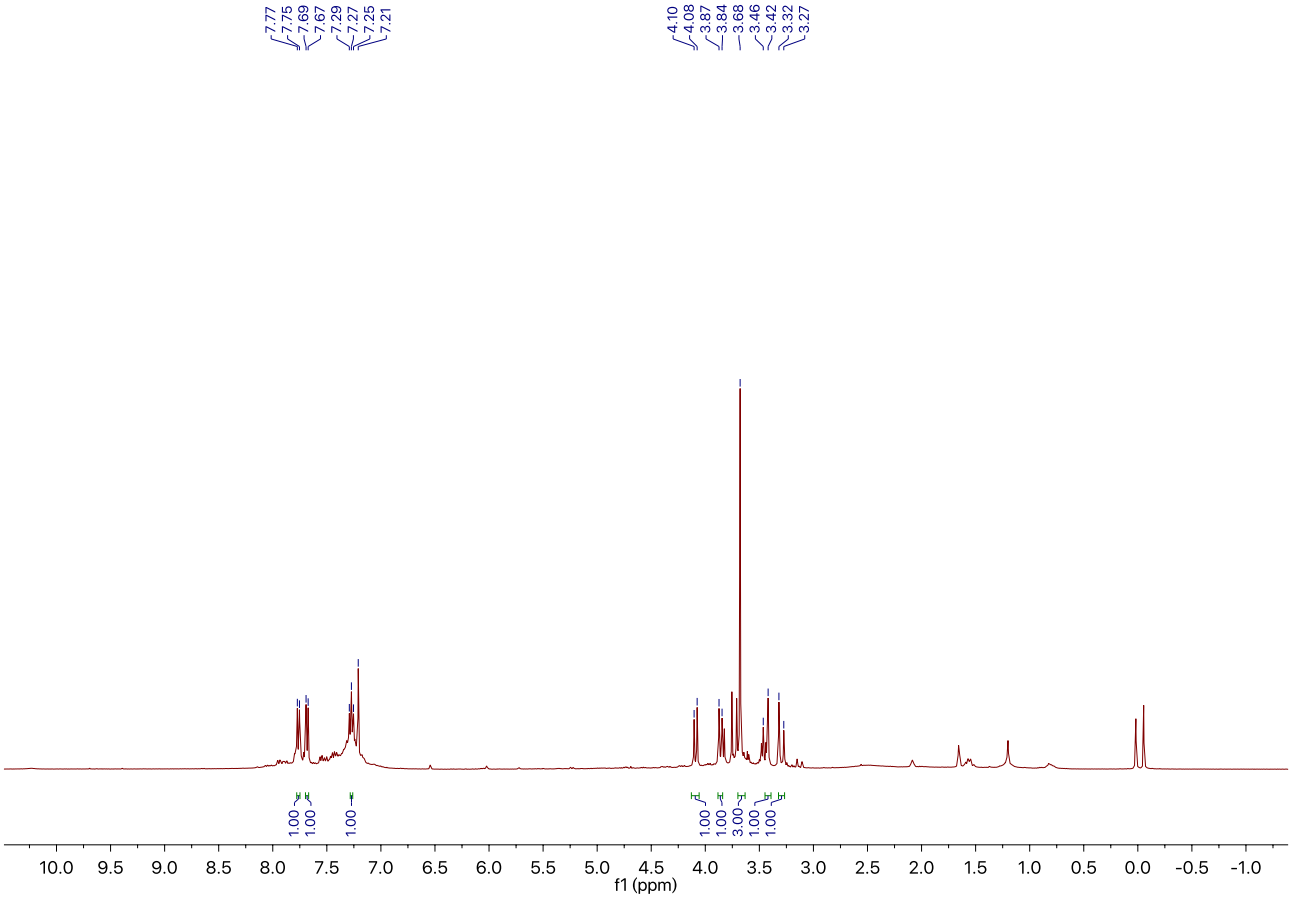


Figure S66. ^{1}HNMR Spectra of Compound **4f**

Compound **4f** ^{13}CNMR

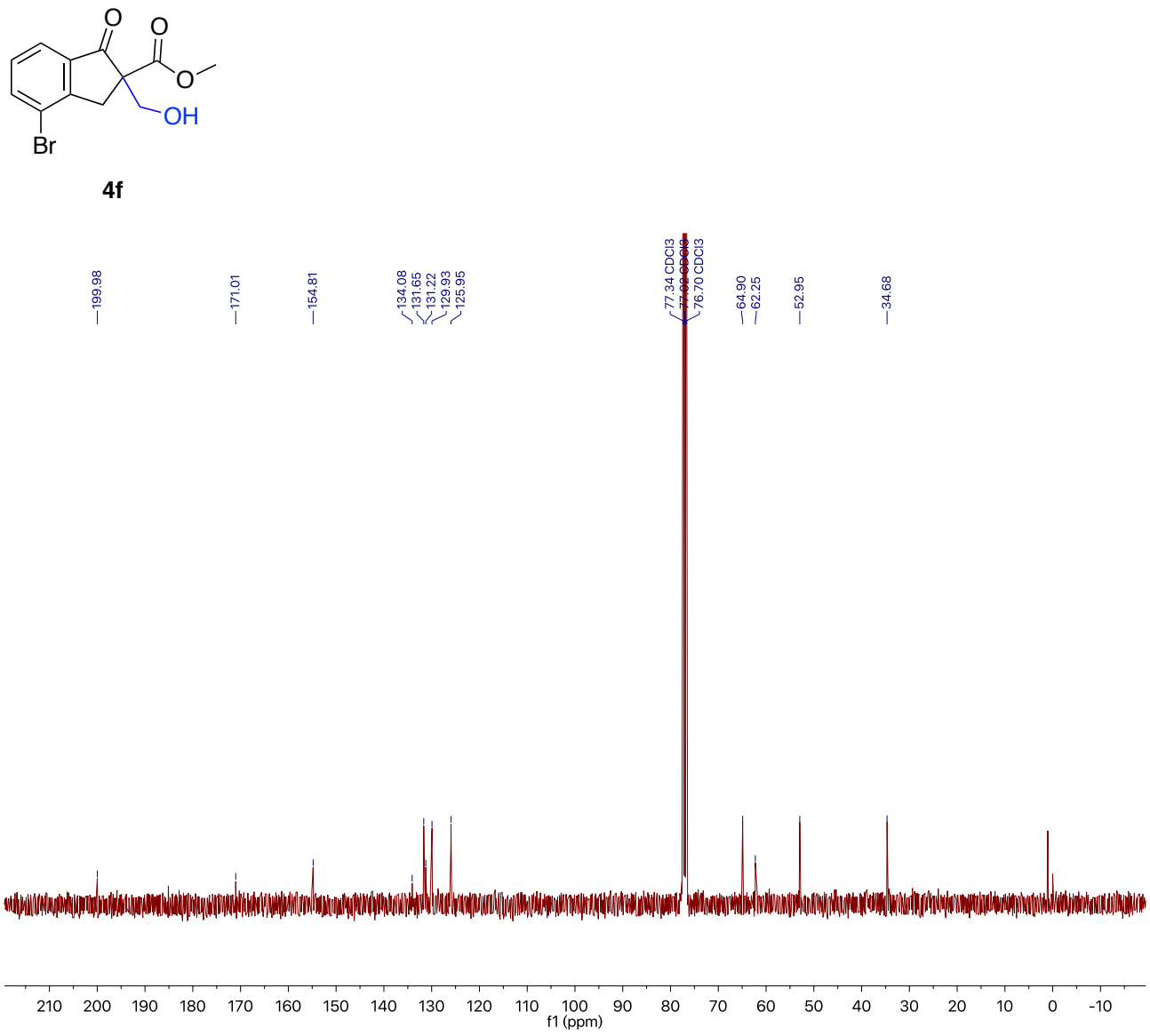
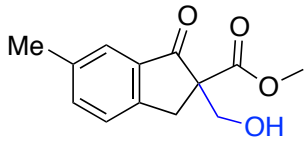


Figure S67. ^{13}CNMR Spectra of Compound **4f**

Compound **4g** [1]HNMR



4g

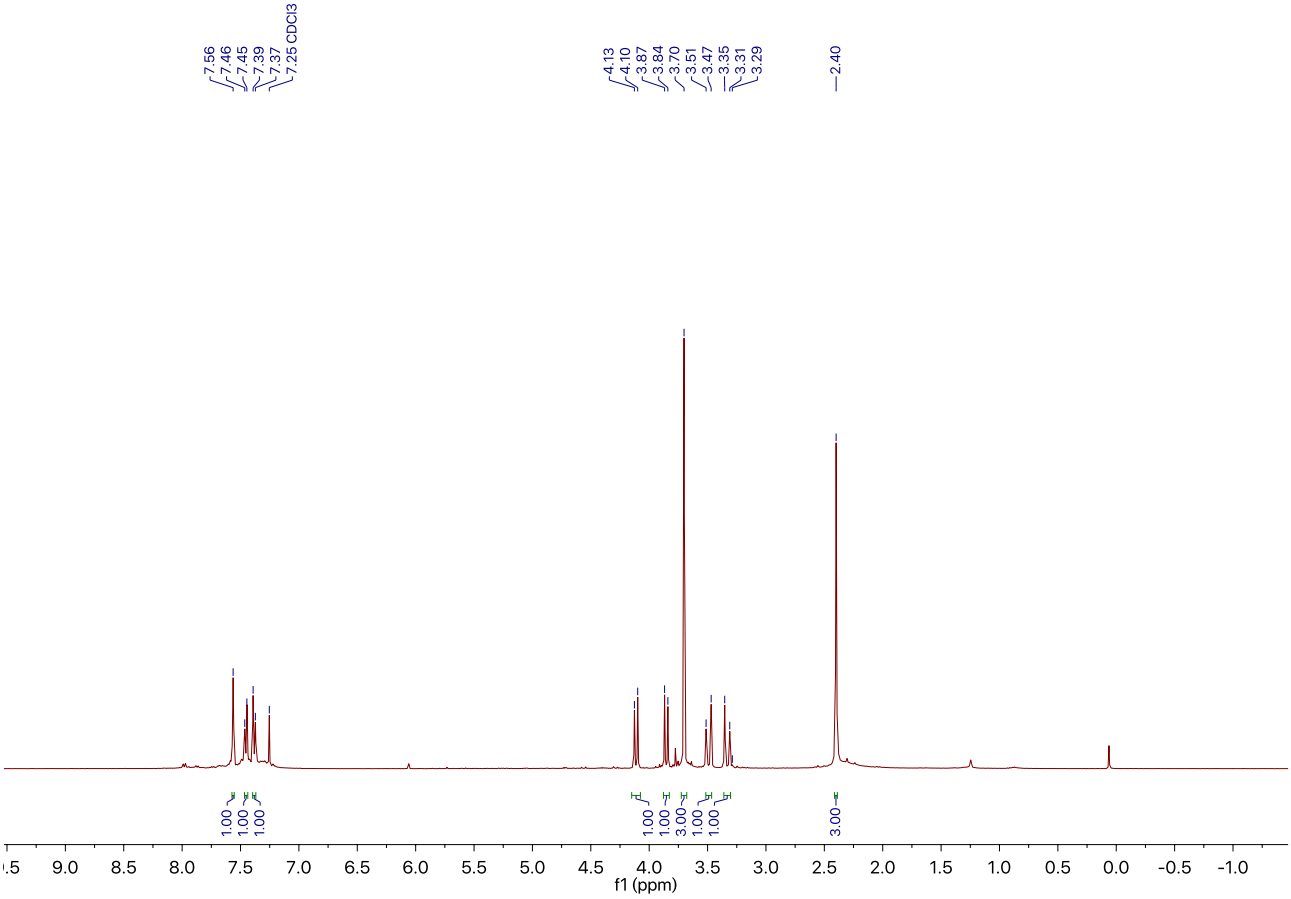
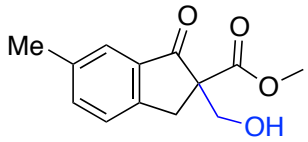


Figure S68. [1]HNMR Spectra of Compound **4g**

Compound **4g** ^{13}CNMR



4g

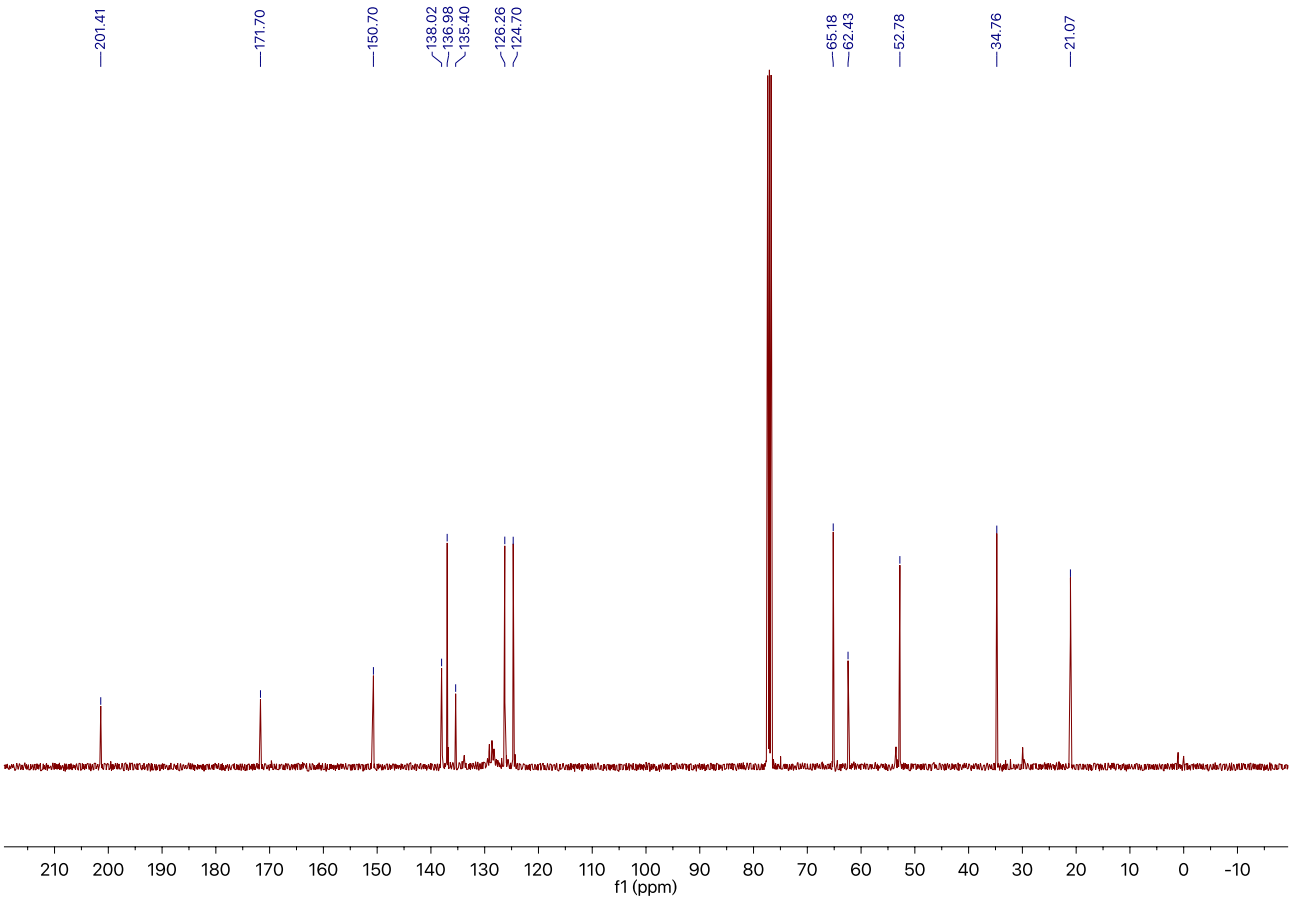
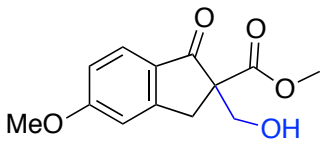


Figure S69. ^{13}CNMR Spectra of Compound **4g**

Compound **4h** [1]HNMR



4h

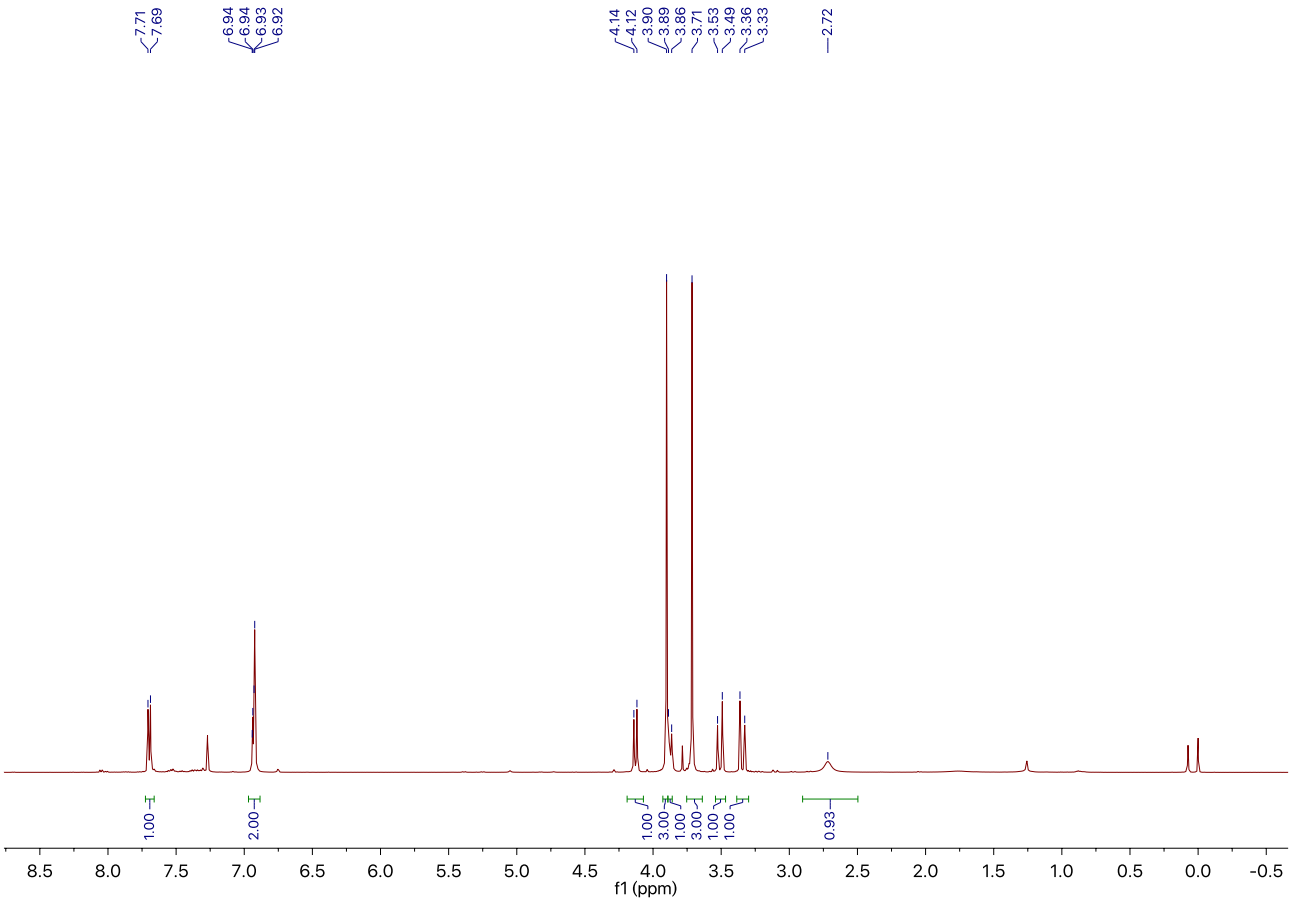
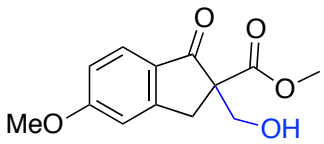


Figure S70. [1]HNMR Spectra of Compound **4h**

Compound **4h** ^{13}CNMR



4h

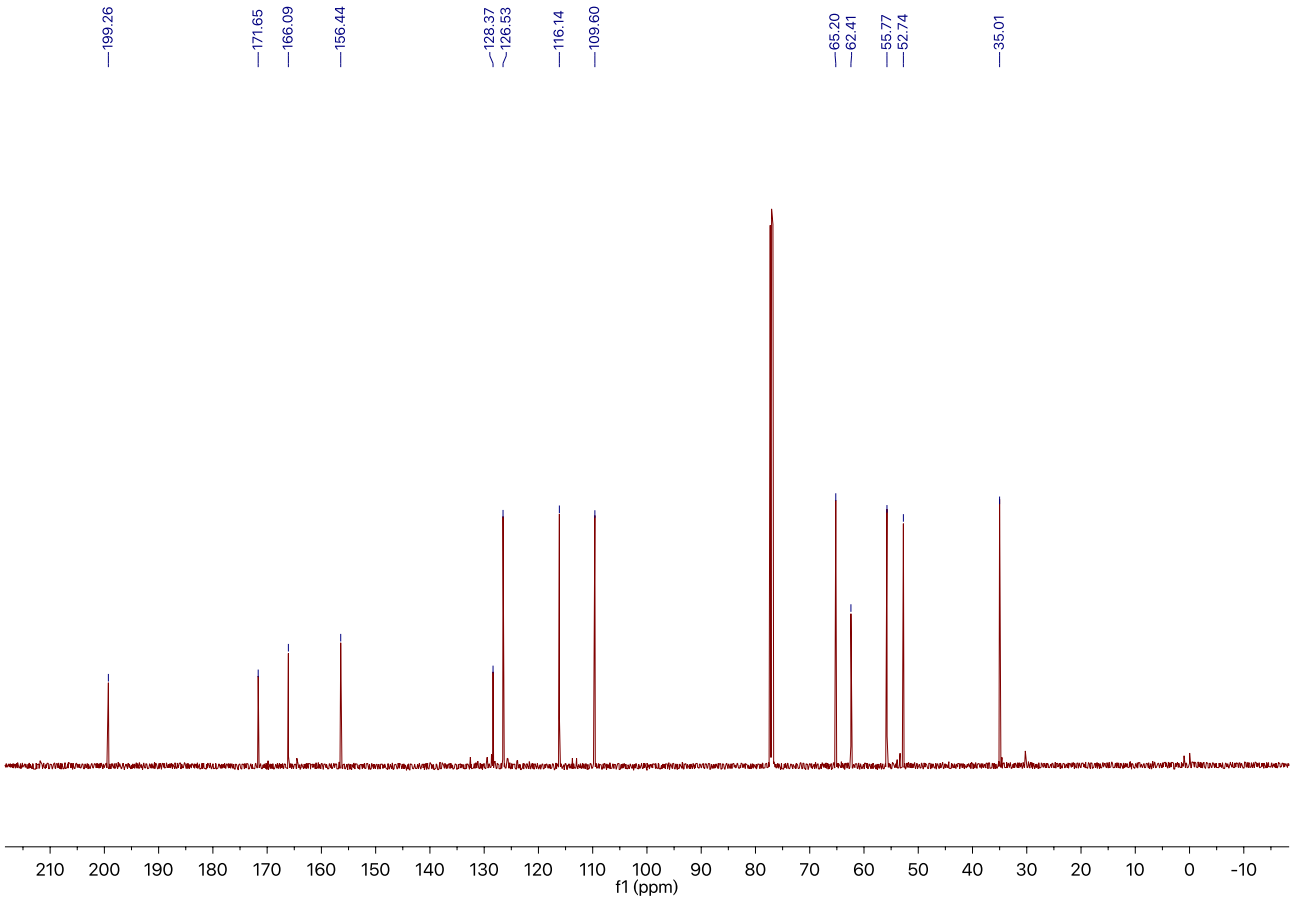
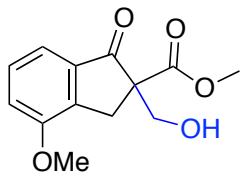


Figure S71. ^{13}CNMR Spectra of Compound **4h**

Compound **4i** [1]HNMR



4i

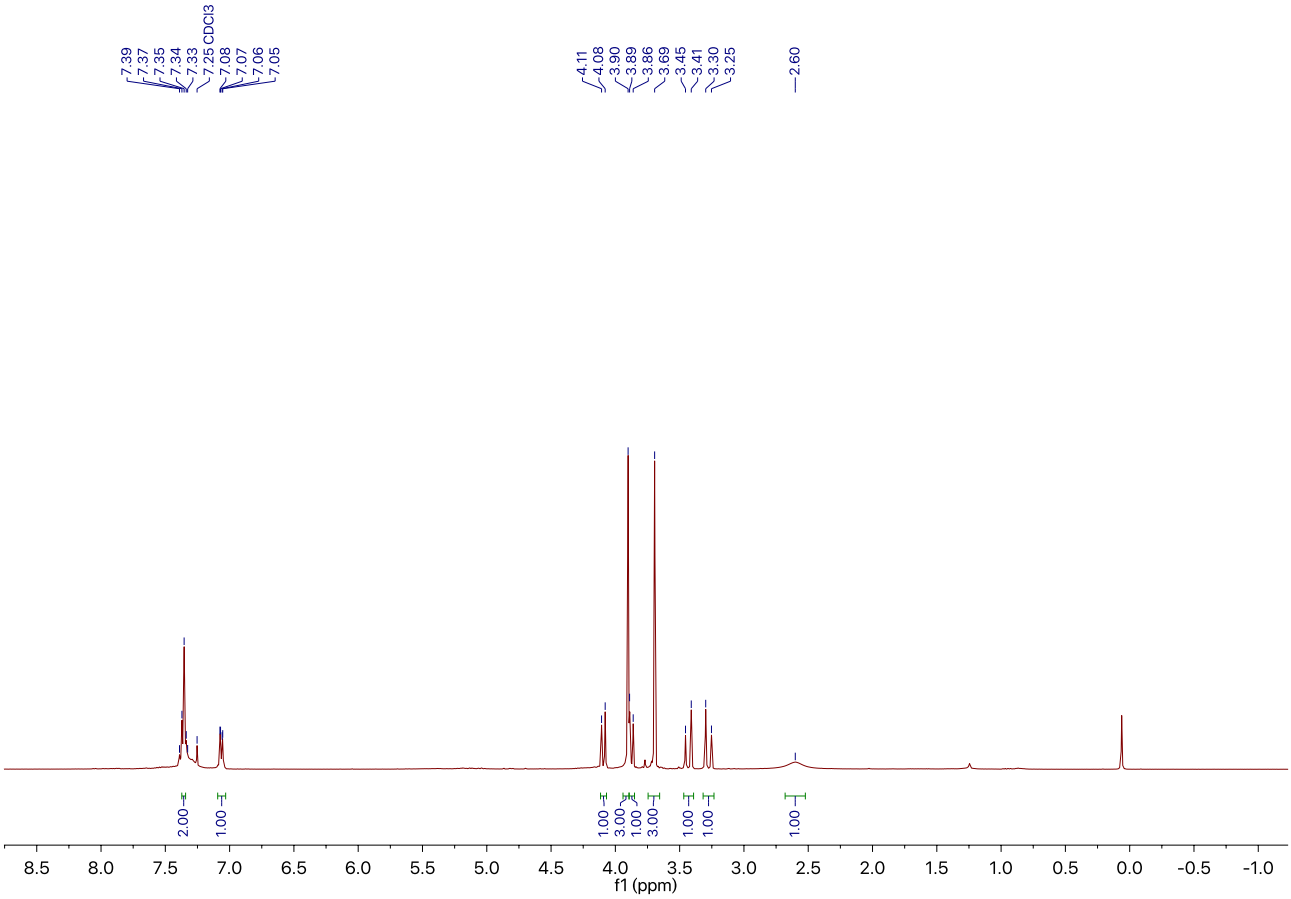
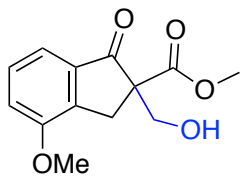


Figure S72. [1]HNMR Spectra of Compound **4i**

Compound **4i** ^{13}CNMR



4i

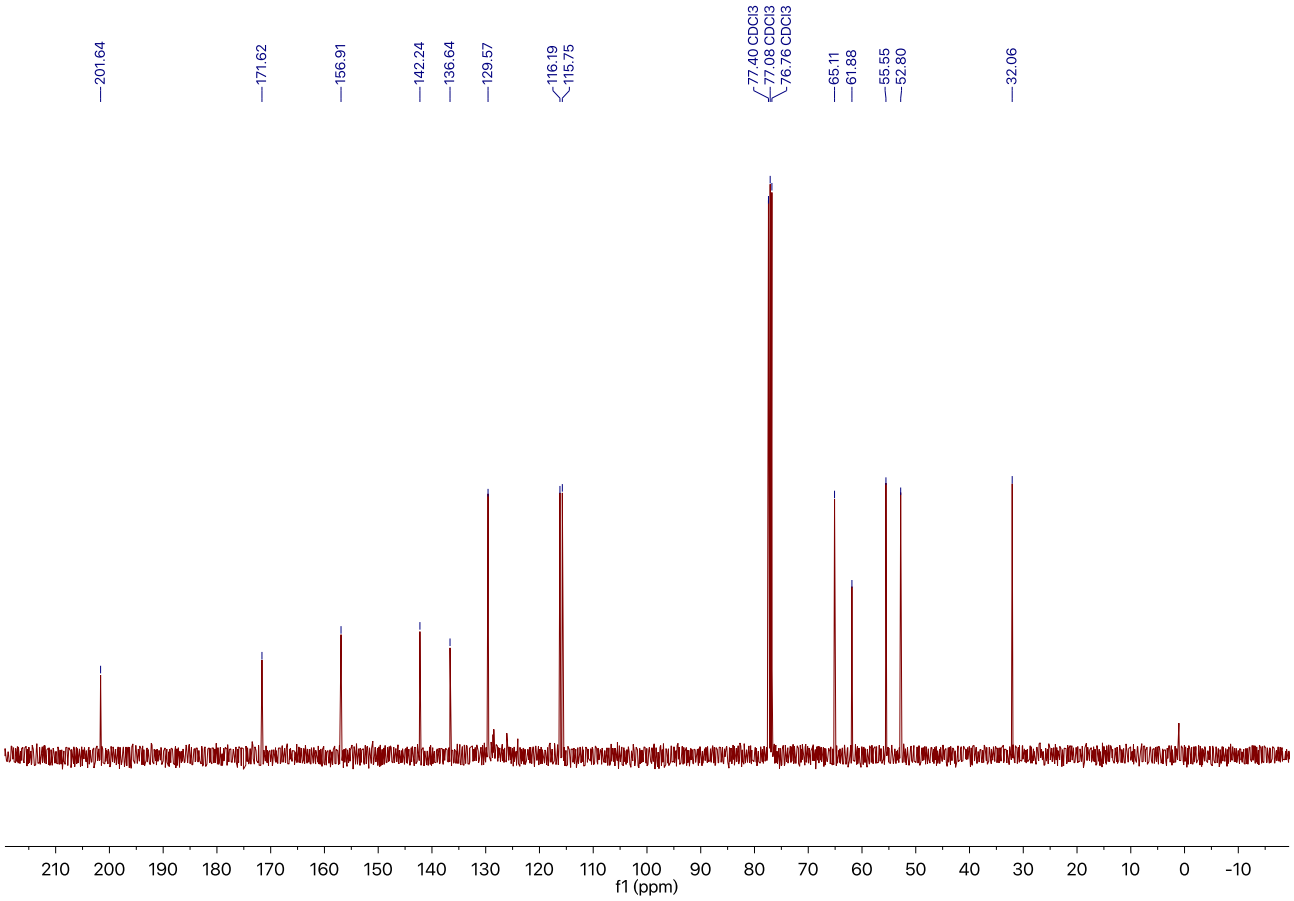
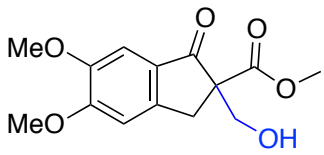


Figure S73. ^{13}CNMR Spectra of Compound **4i**

Compound **4j** [1]HNMR



4j

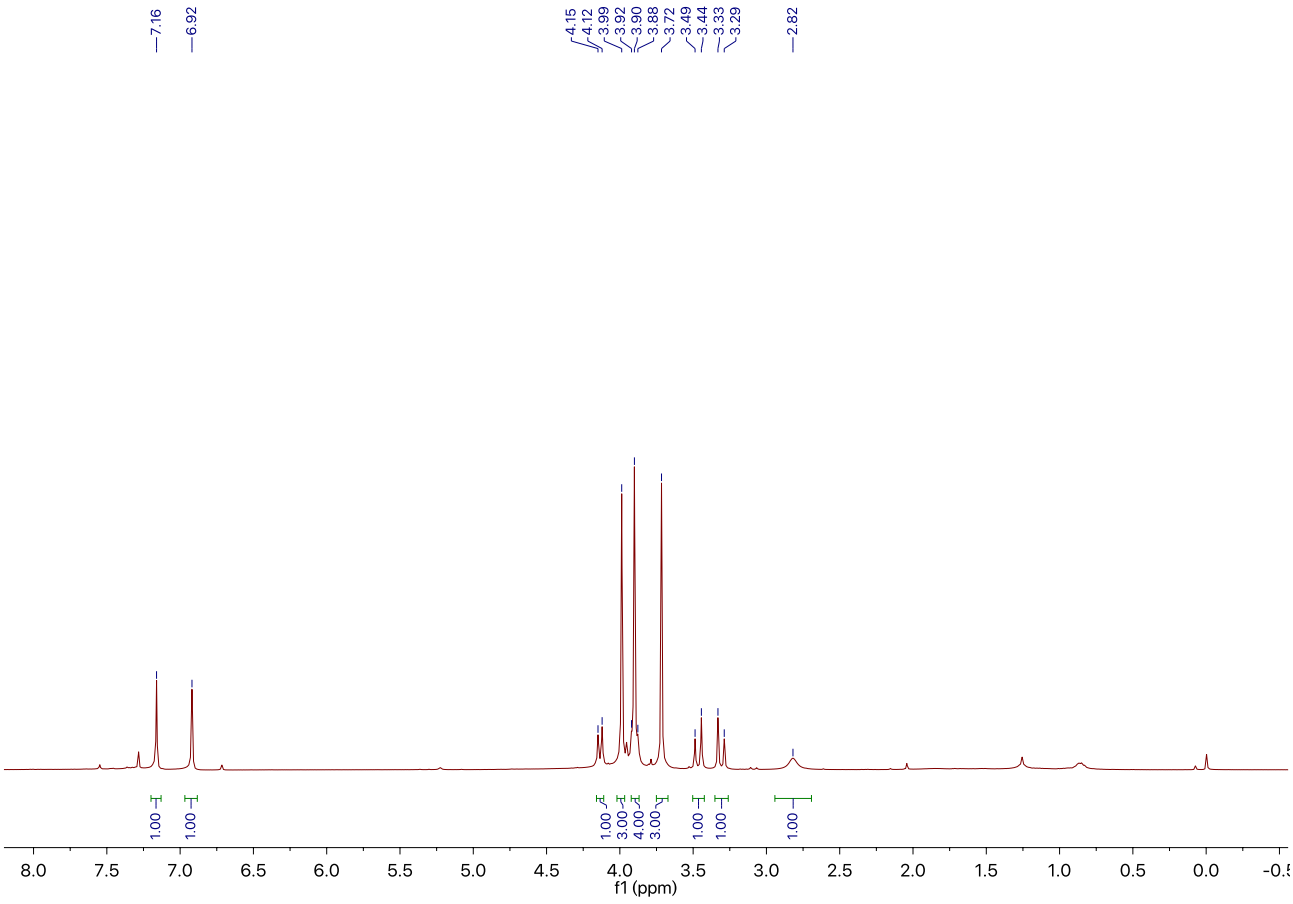
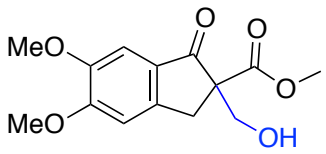


Figure S74. [1]HNMR Spectra of Compound **4j**

Compound **4j** ^{13}CNMR



4j

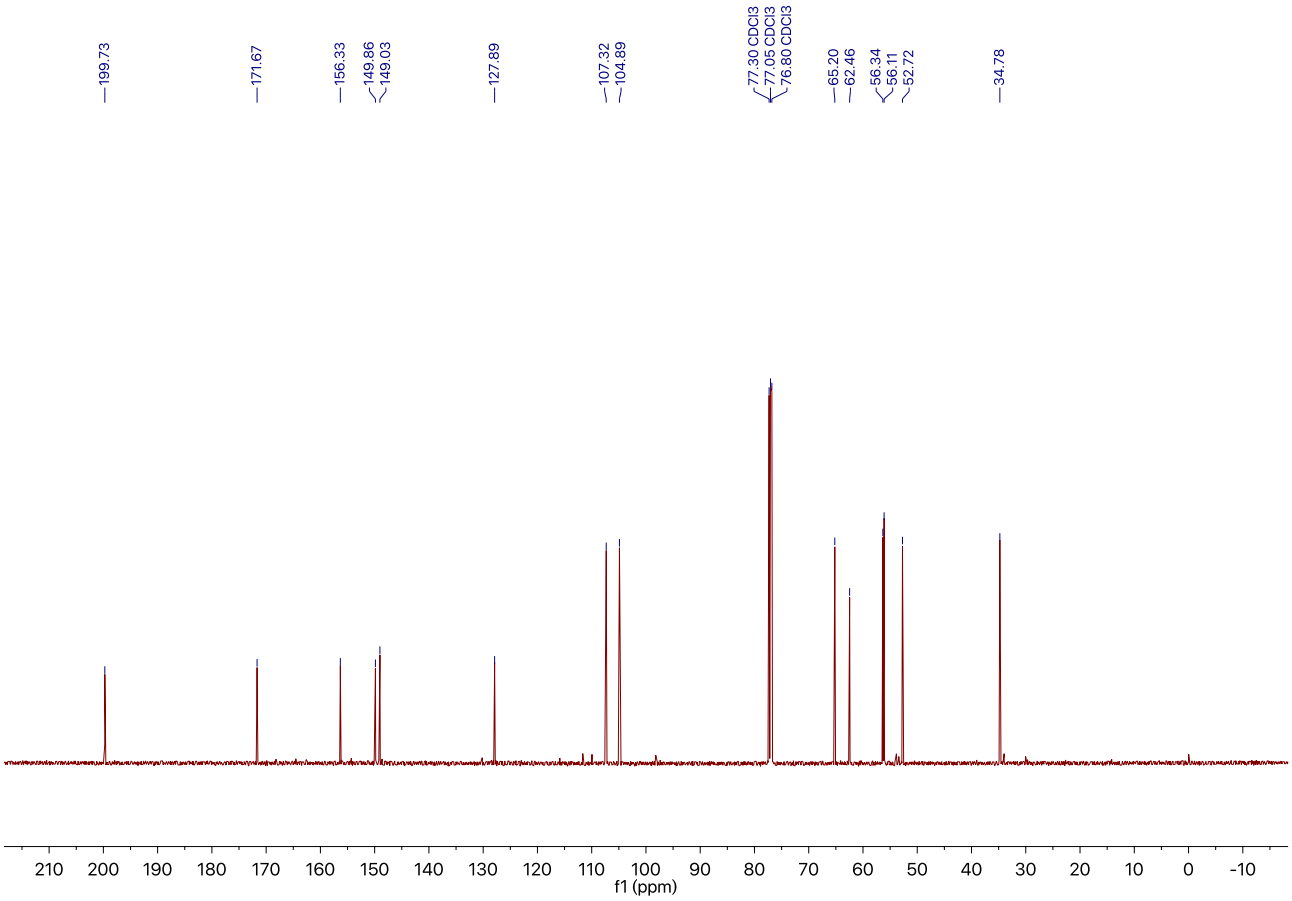
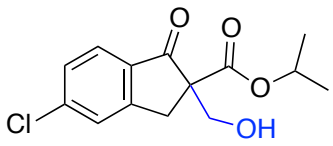


Figure S75. ^{13}CNMR Spectra of Compound **4j**

Compound **4k** [1]HNMR



4k

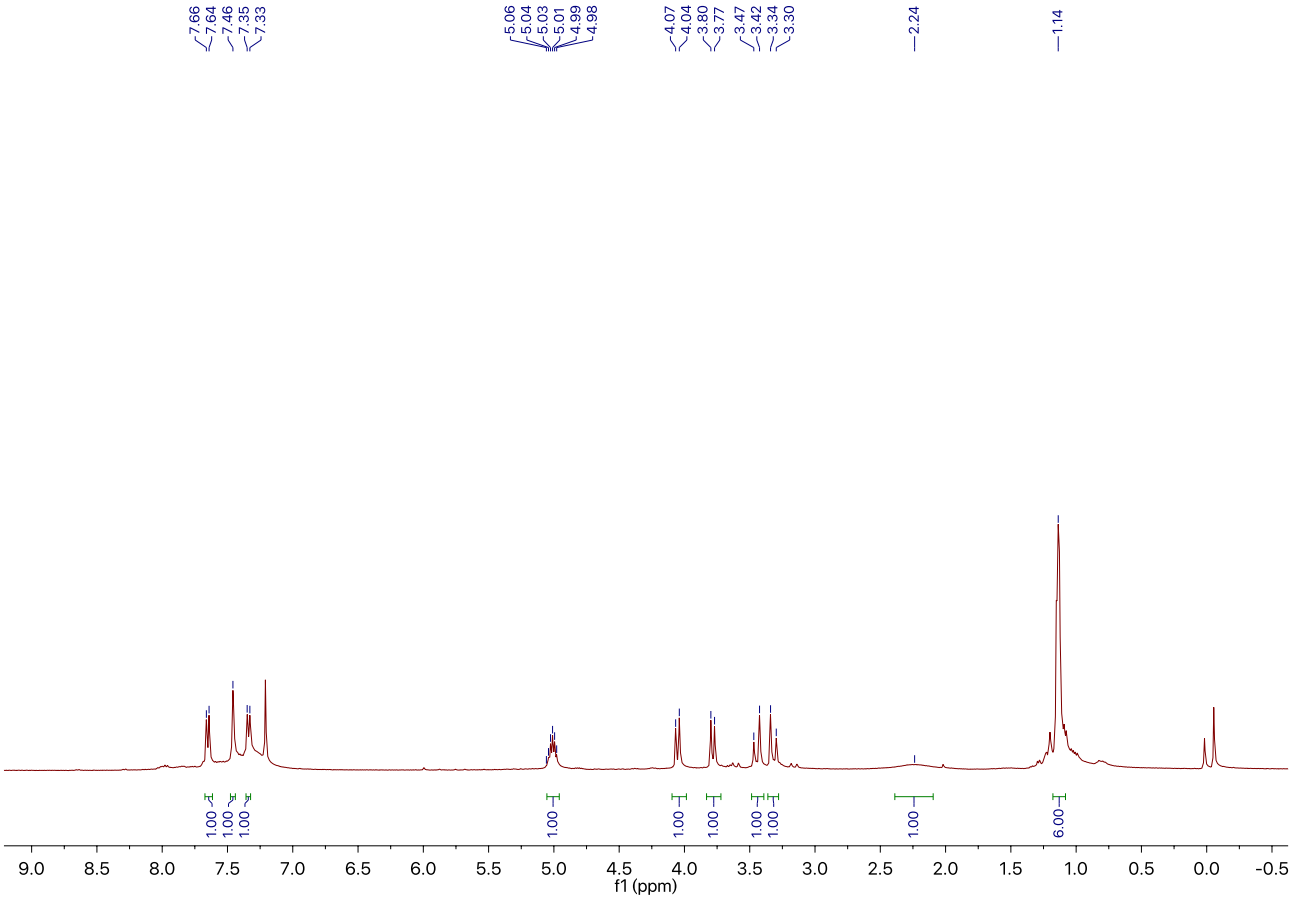
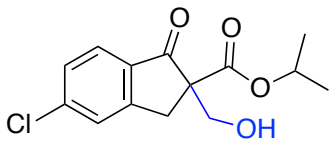


Figure S76. [1]HNMR Spectra of Compound **4k**

Compound **4k** ^{13}CNMR



4k

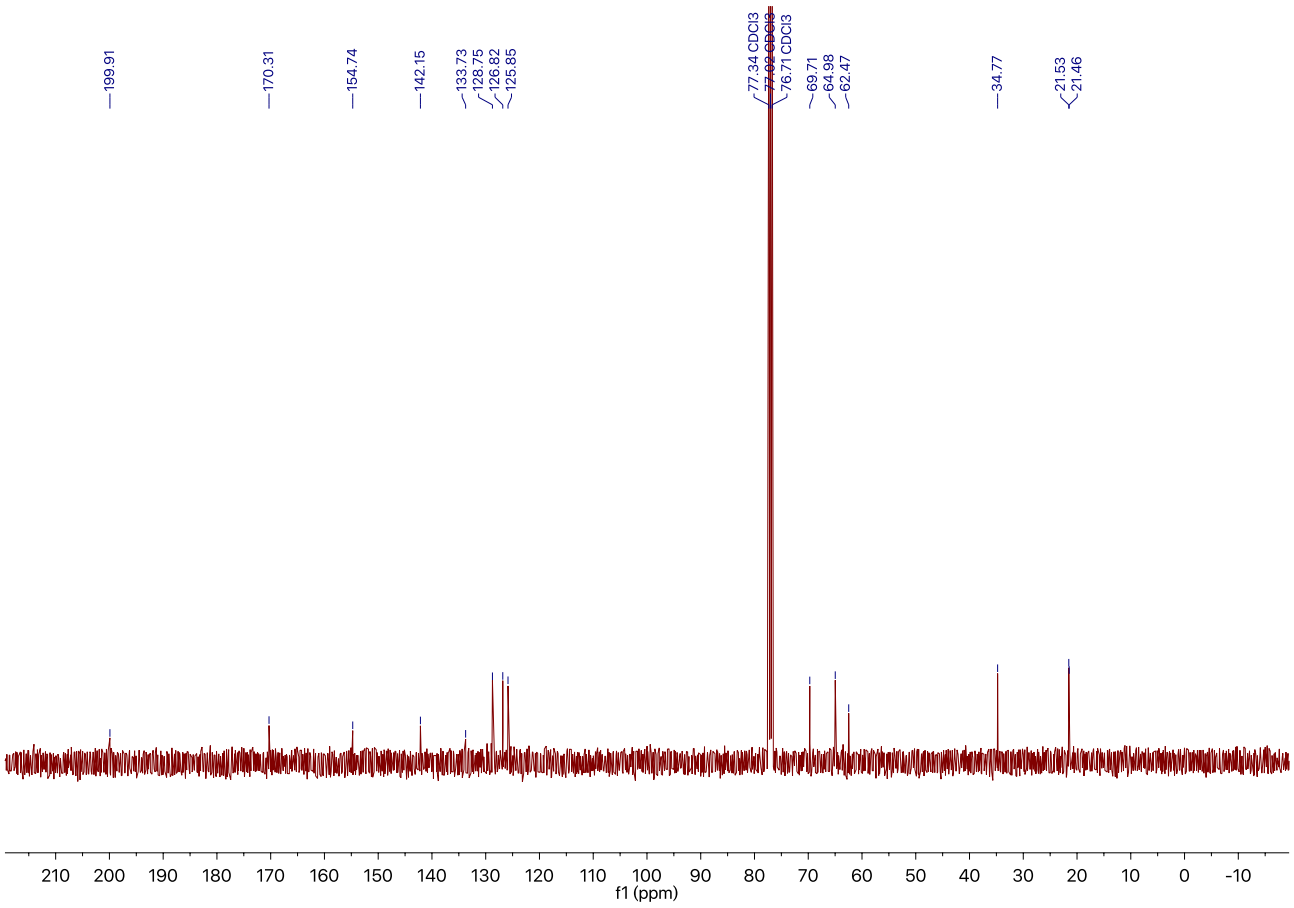
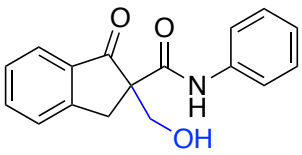


Figure S77. ^{13}CNMR Spectra of Compound **4k**

Compound **4l** [1]HNMR



4l

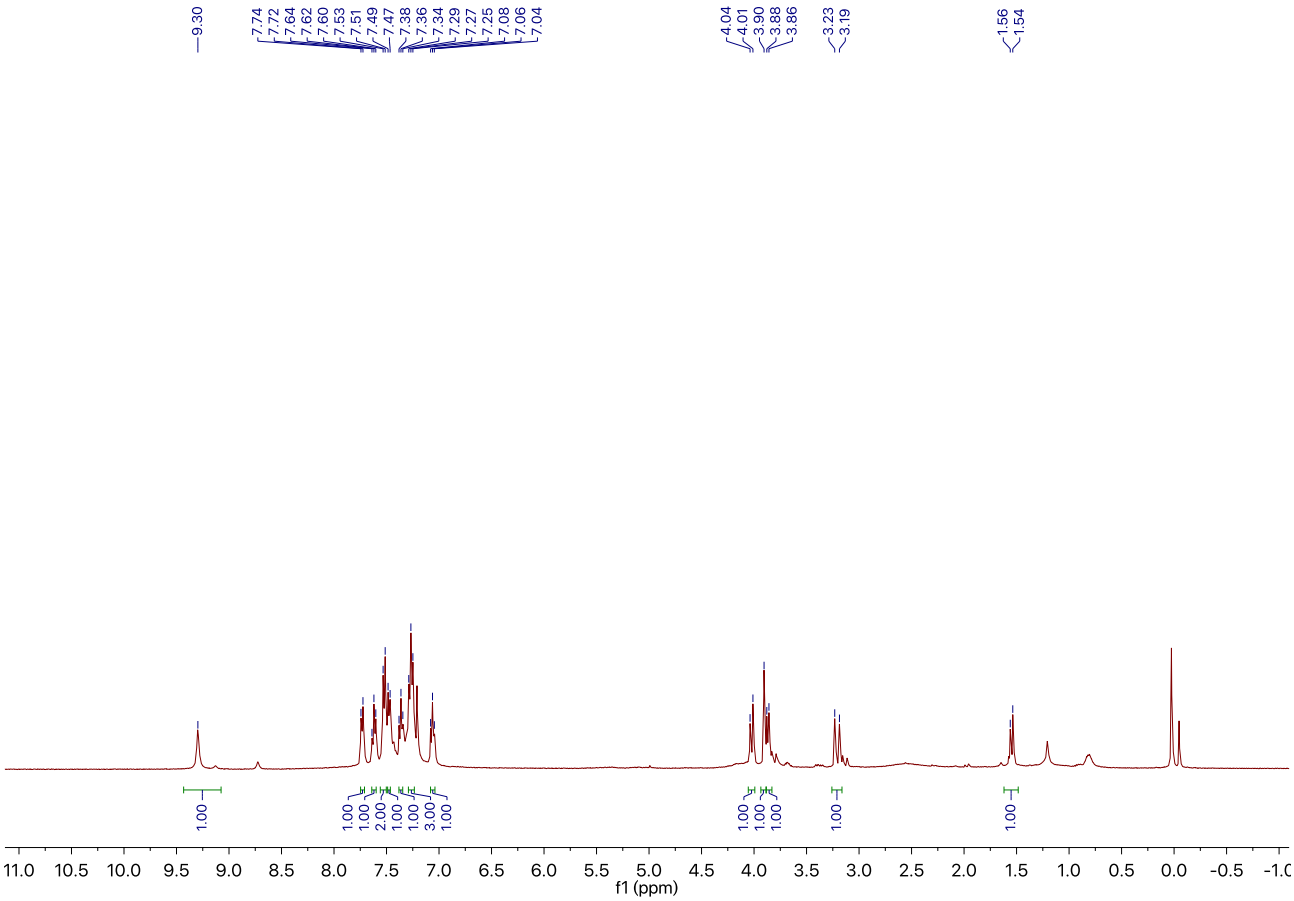
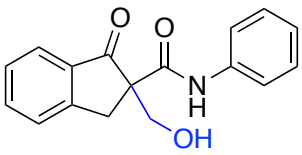


Figure S78. [1]HNMR Spectra of Compound **4l**

Compound **4l** ^{13}CNMR



4l

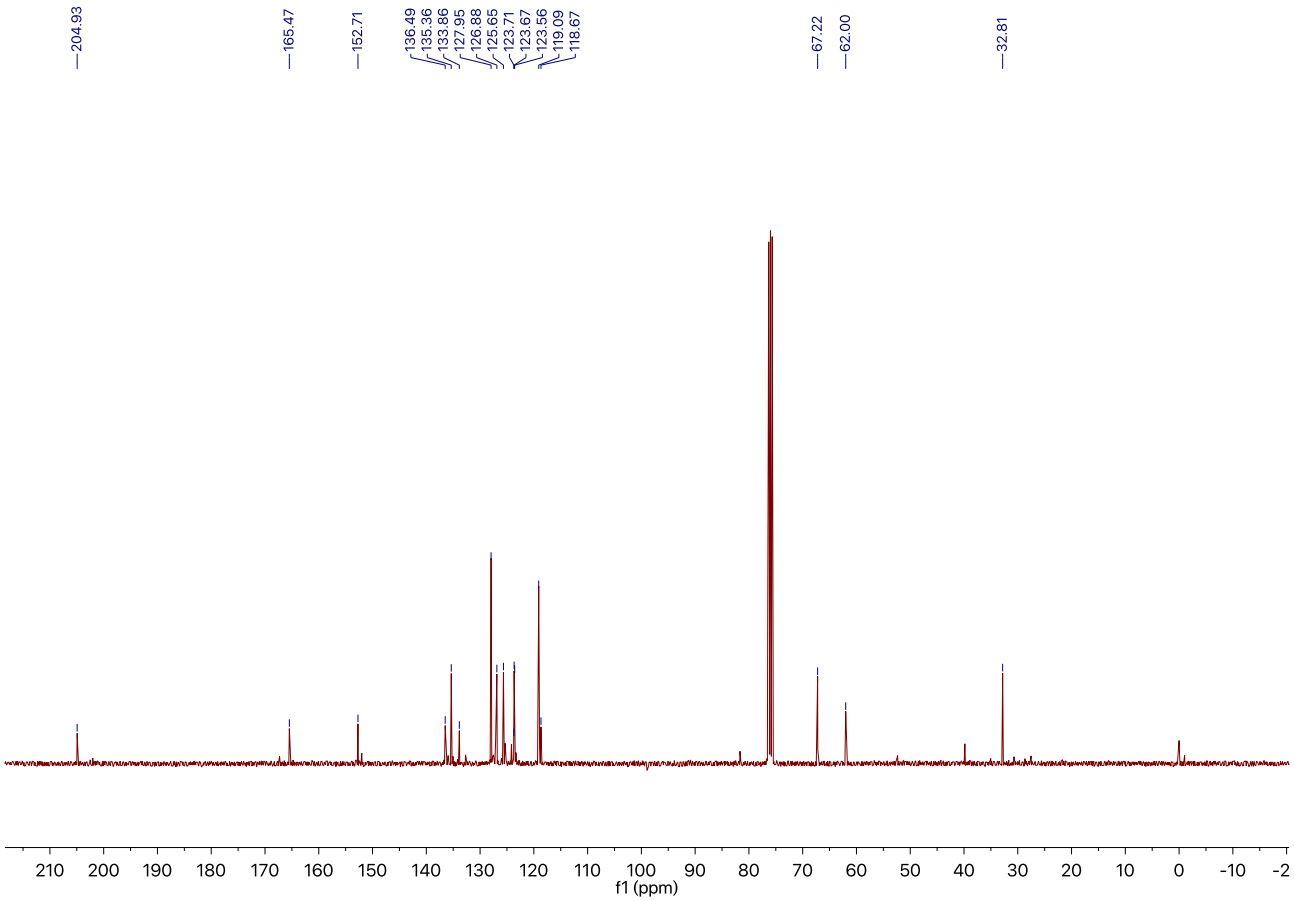
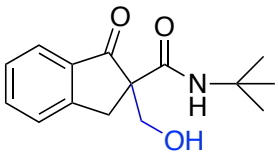


Figure S79. ^{13}CNMR Spectra of Compound **4l**

Compound **4m** [1]HNMR



4m

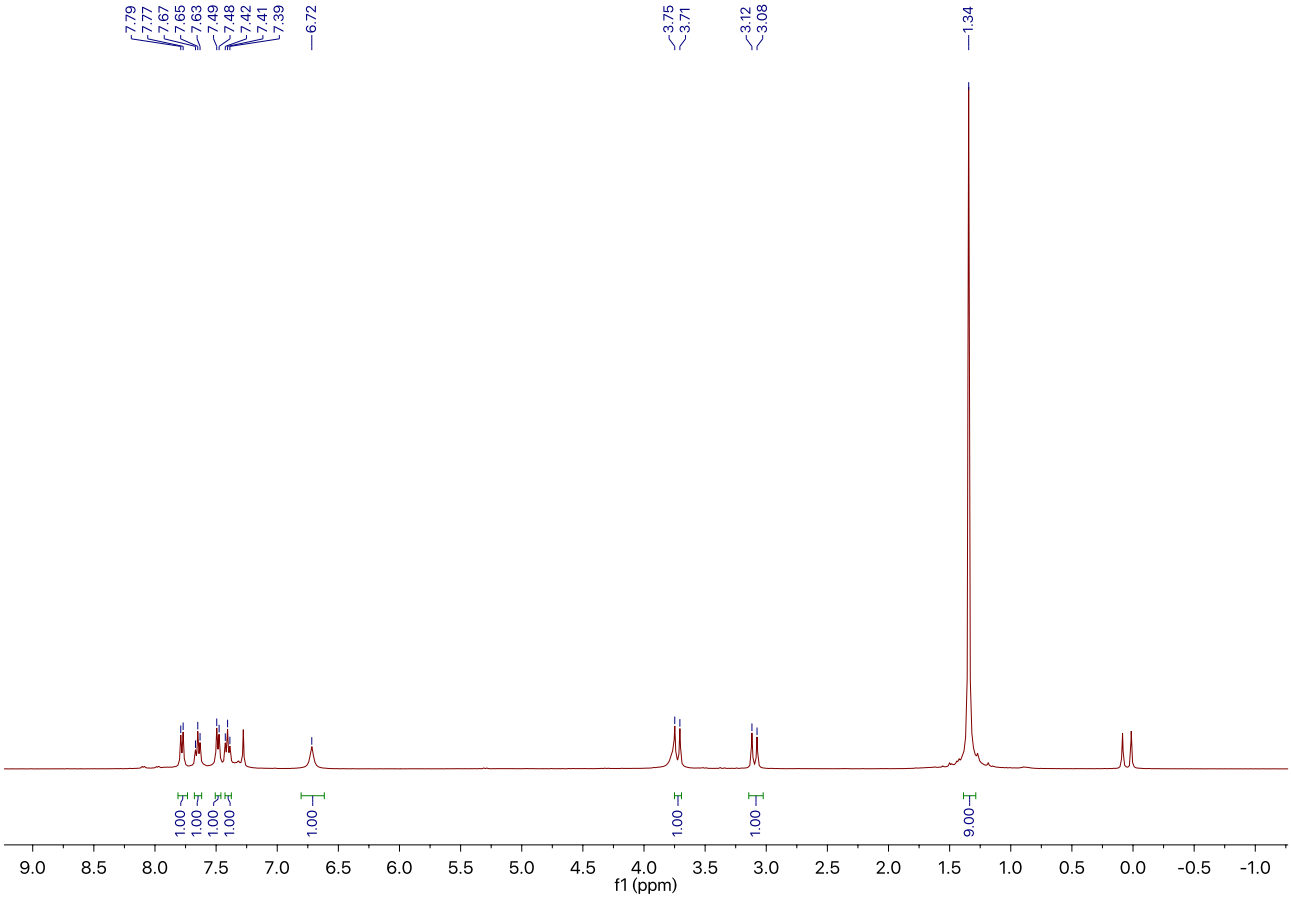
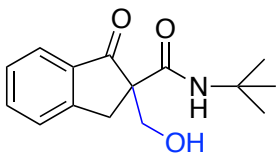


Figure S80. [1]HNMR Spectra of Compound **4m**

Compound **4m** ^{13}CNMR



4m

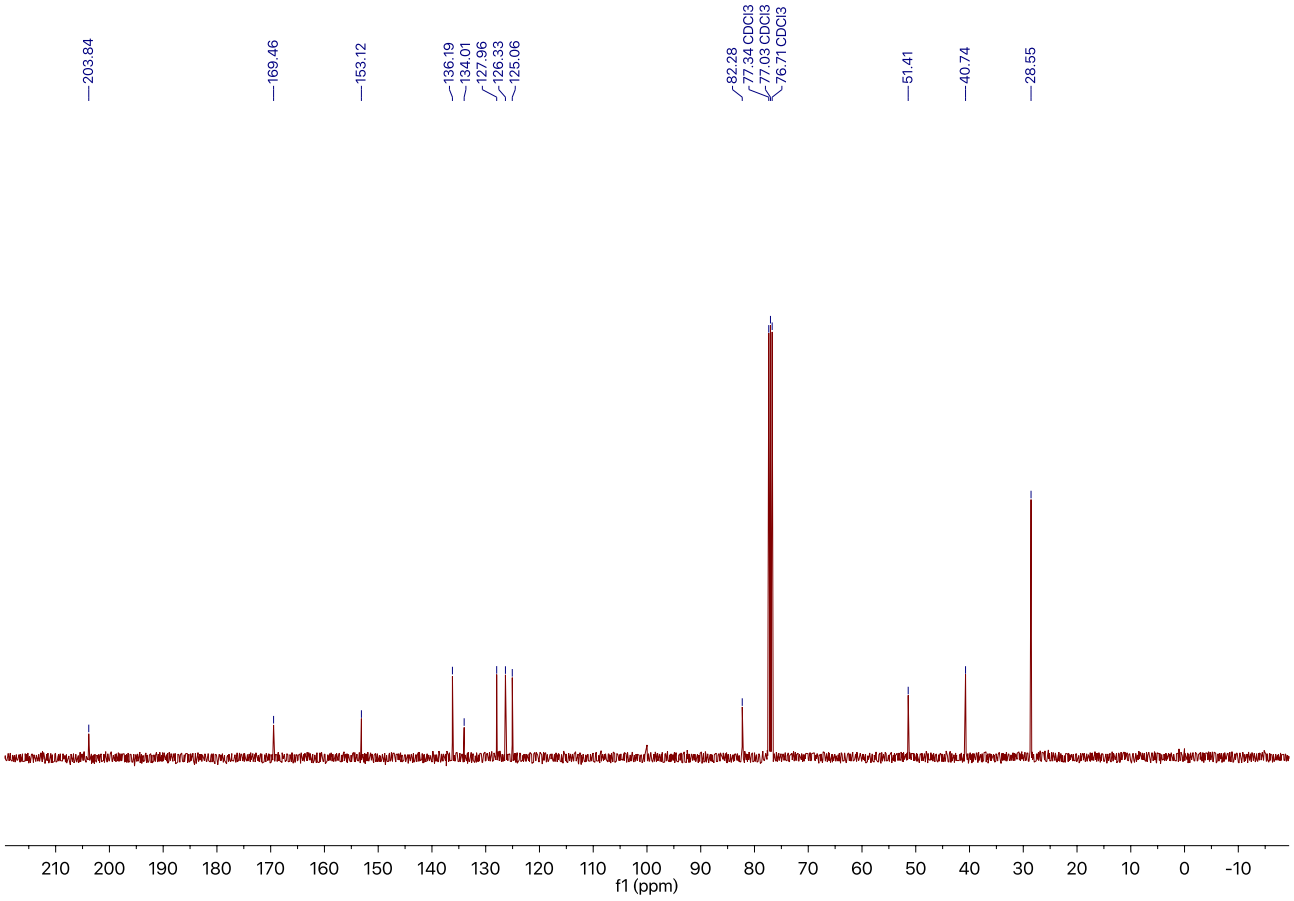
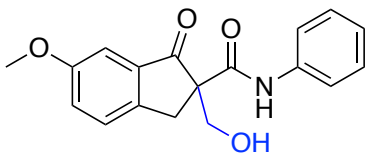


Figure S81. ^{13}CNMR Spectra of Compound **4m**

Compound **4n** [1]HNMR



4n

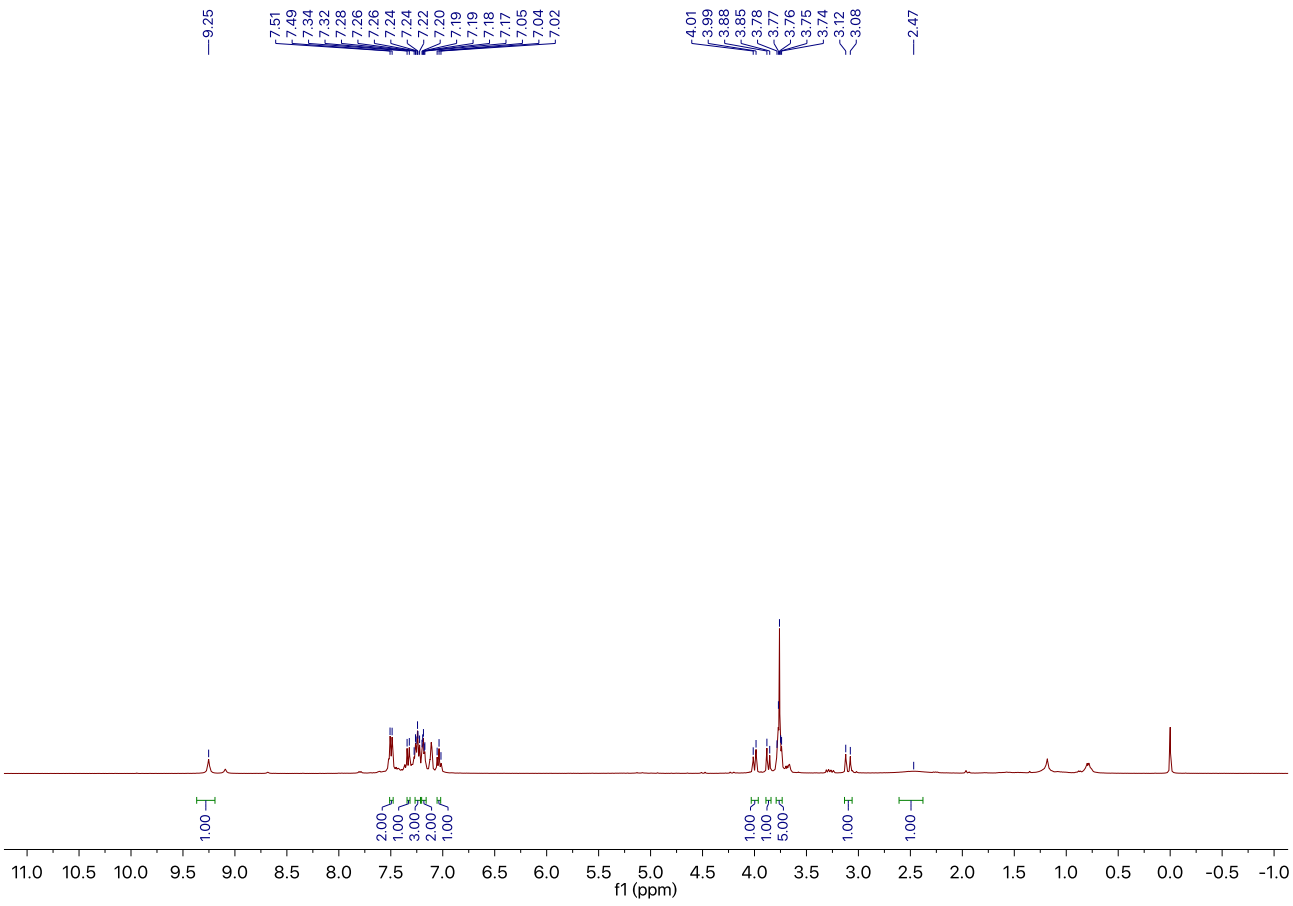
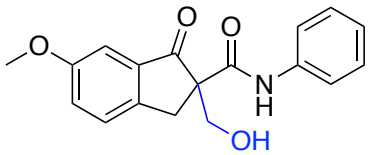


Figure S82. [1]HNMR Spectra of Compound **4n**

Compound **4n** ^{13}CNMR



4n

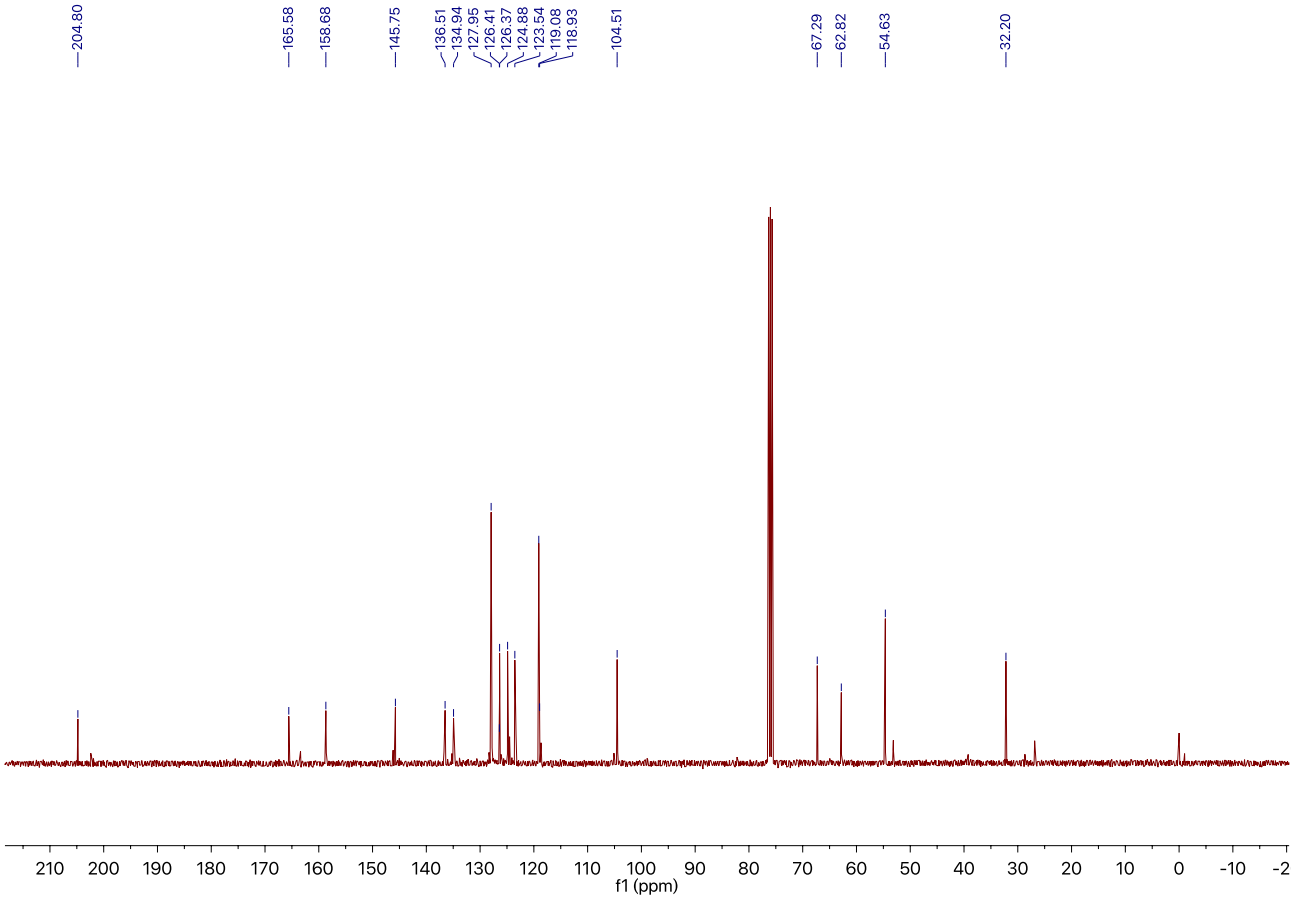
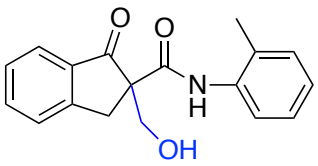


Figure S83. ^{13}CNMR Spectra of Compound **4n**

Compound **4o** [1]HNMR



4o

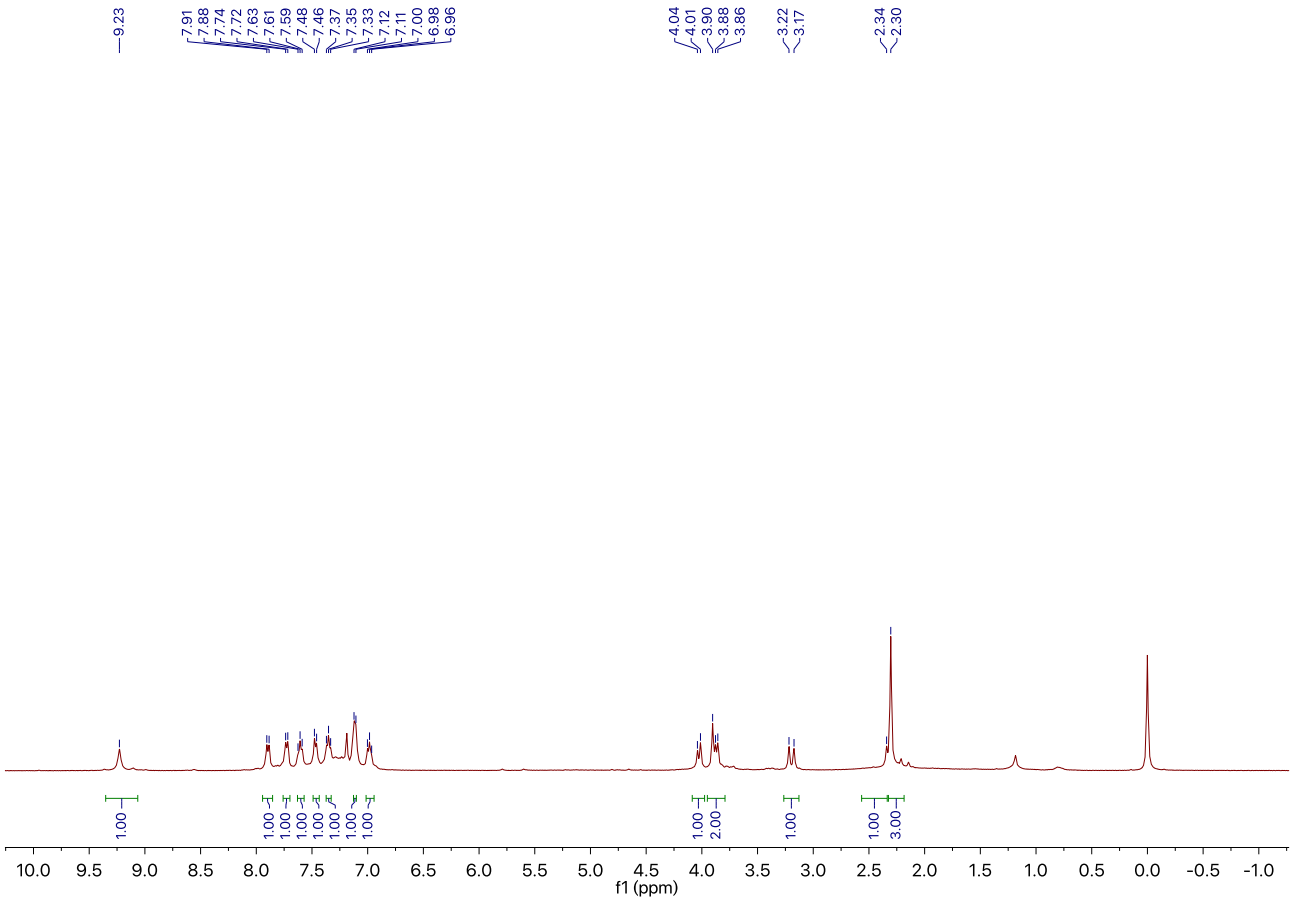
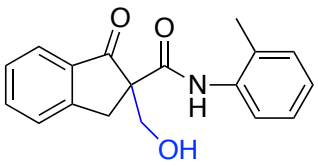


Figure S84. [1]HNMR Spectra of Compound **4o**

Compound **4o** ^{13}CNMR



4o

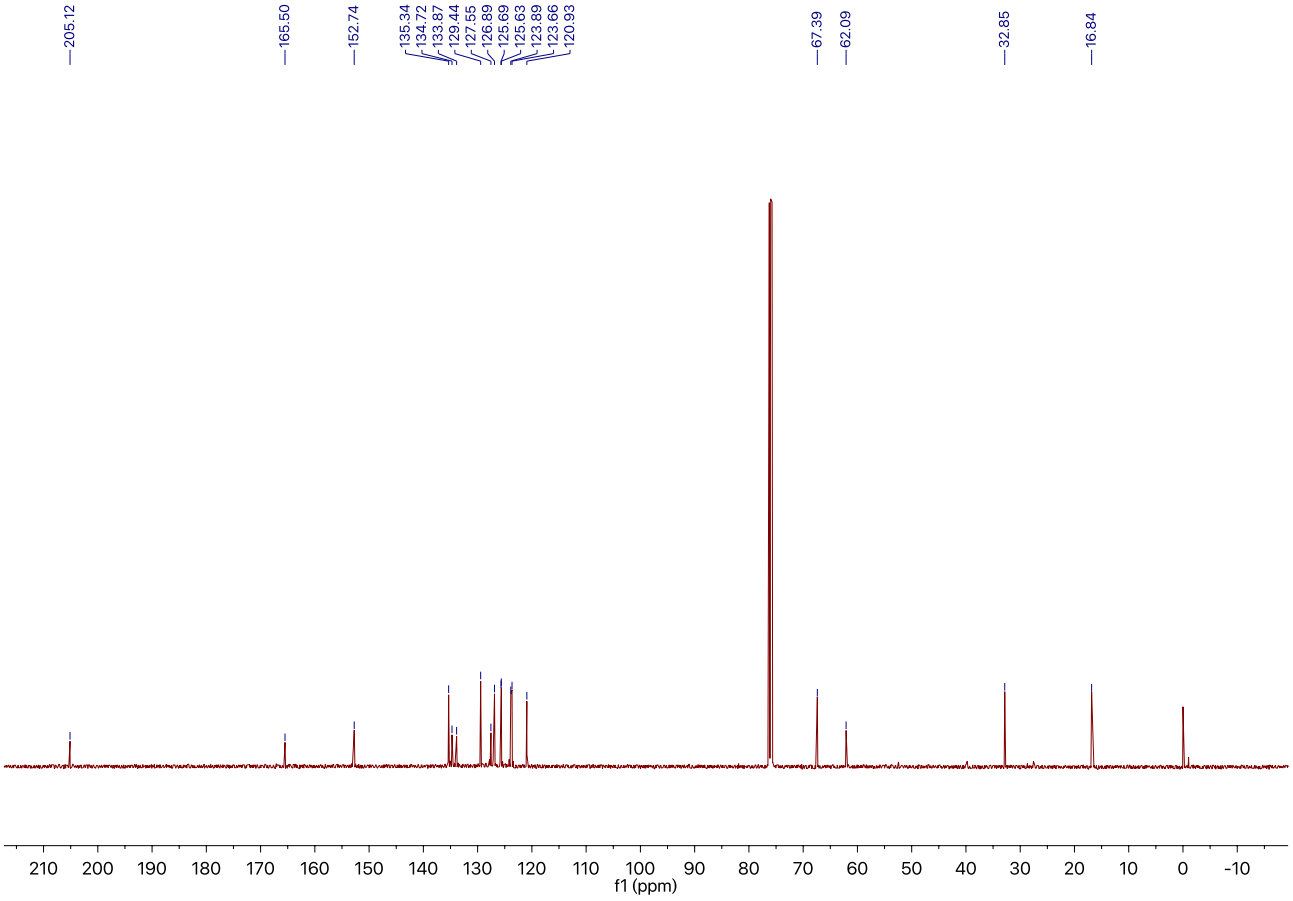
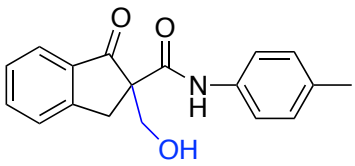


Figure S85. ^{13}CNMR Spectra of Compound **4o**

Compound **4p** [1]HNMR



4p

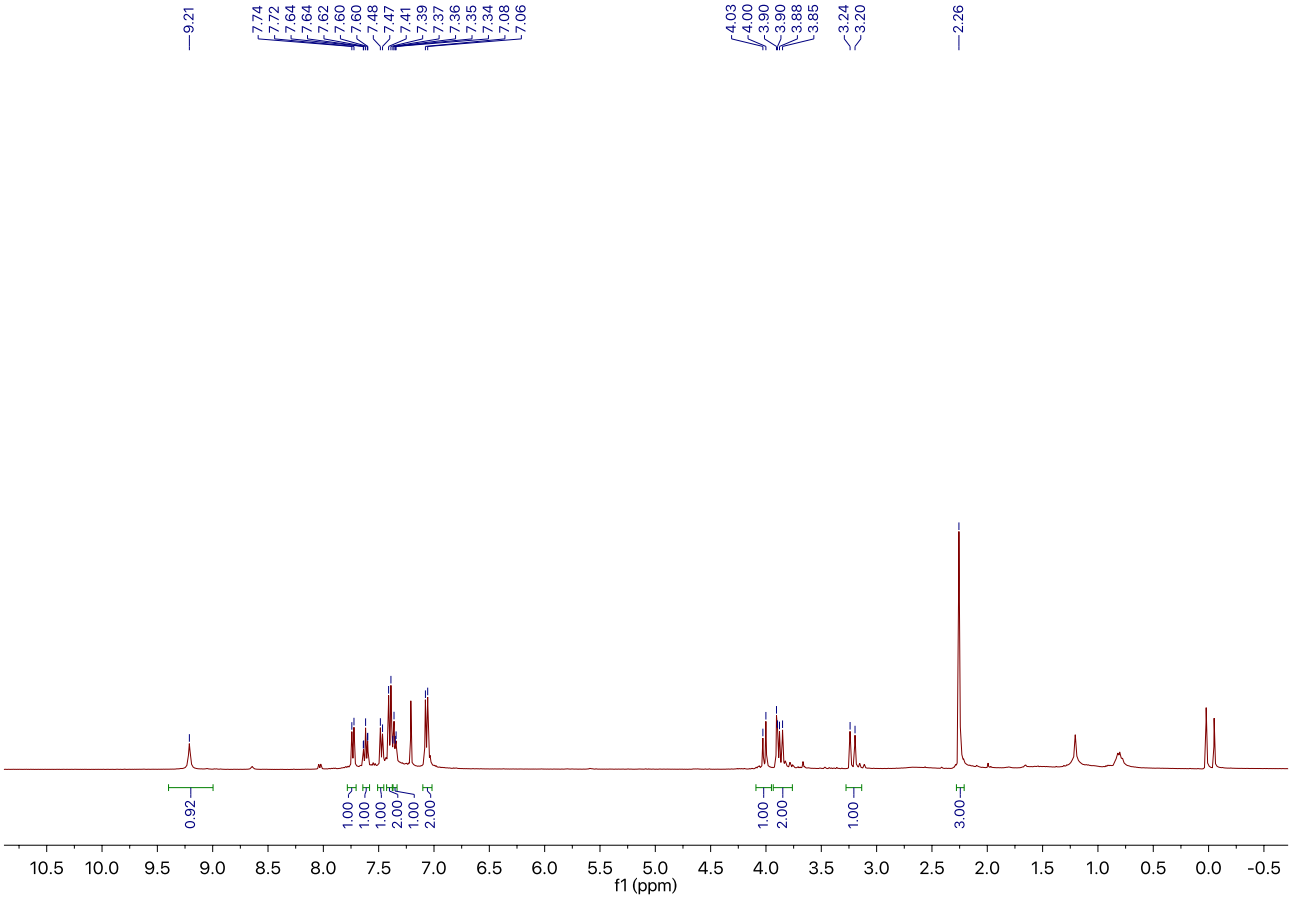
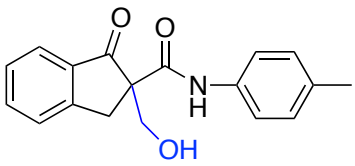


Figure S86. [1]HNMR Spectra of Compound **4p**

Compound **4p** ^{13}CNMR



4p

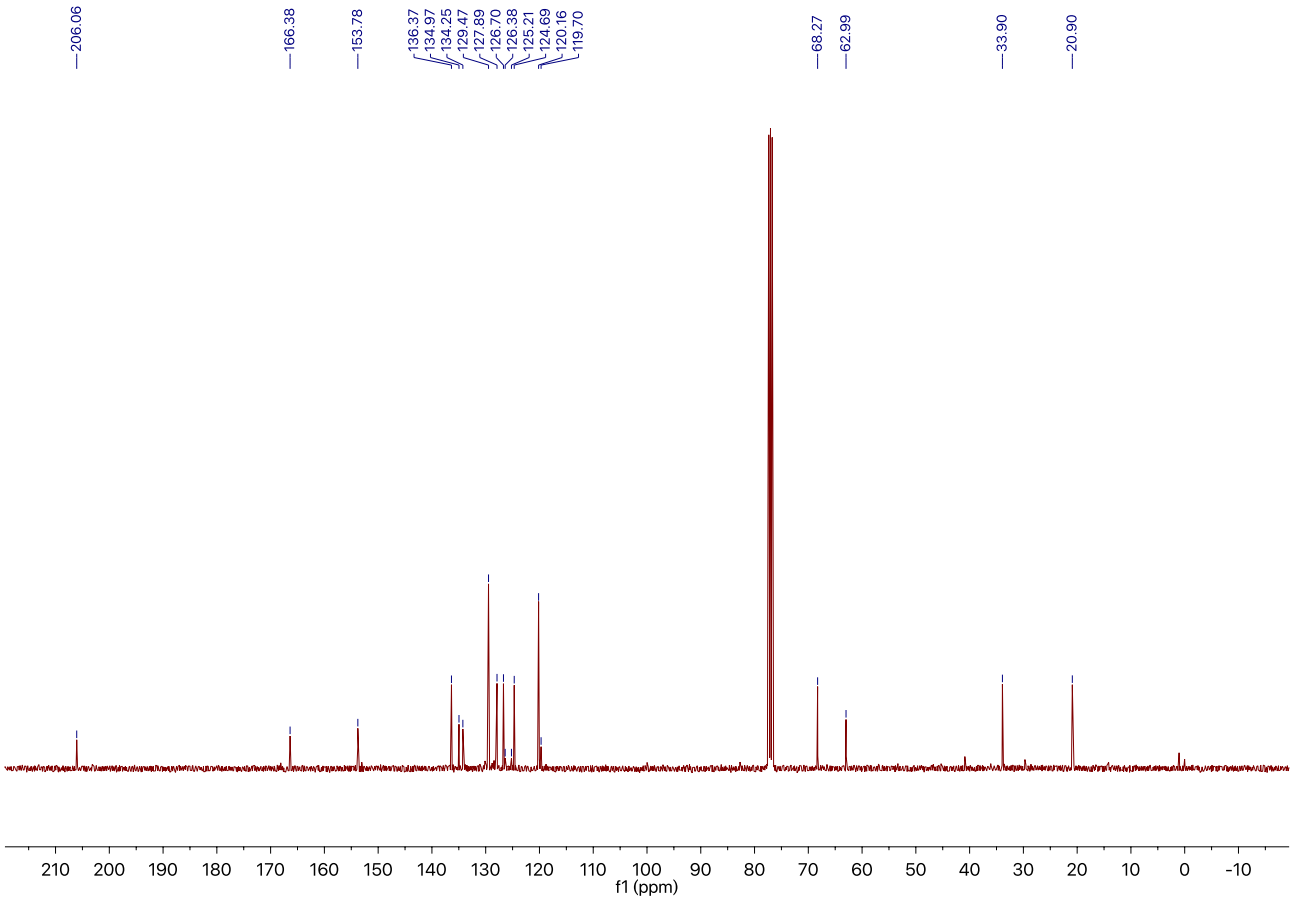
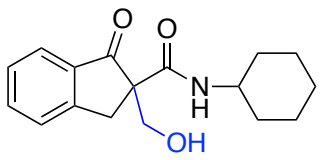


Figure S87. ^{13}CNMR Spectra of Compound **4p**

Compound **4q** [1]HNMR



4q

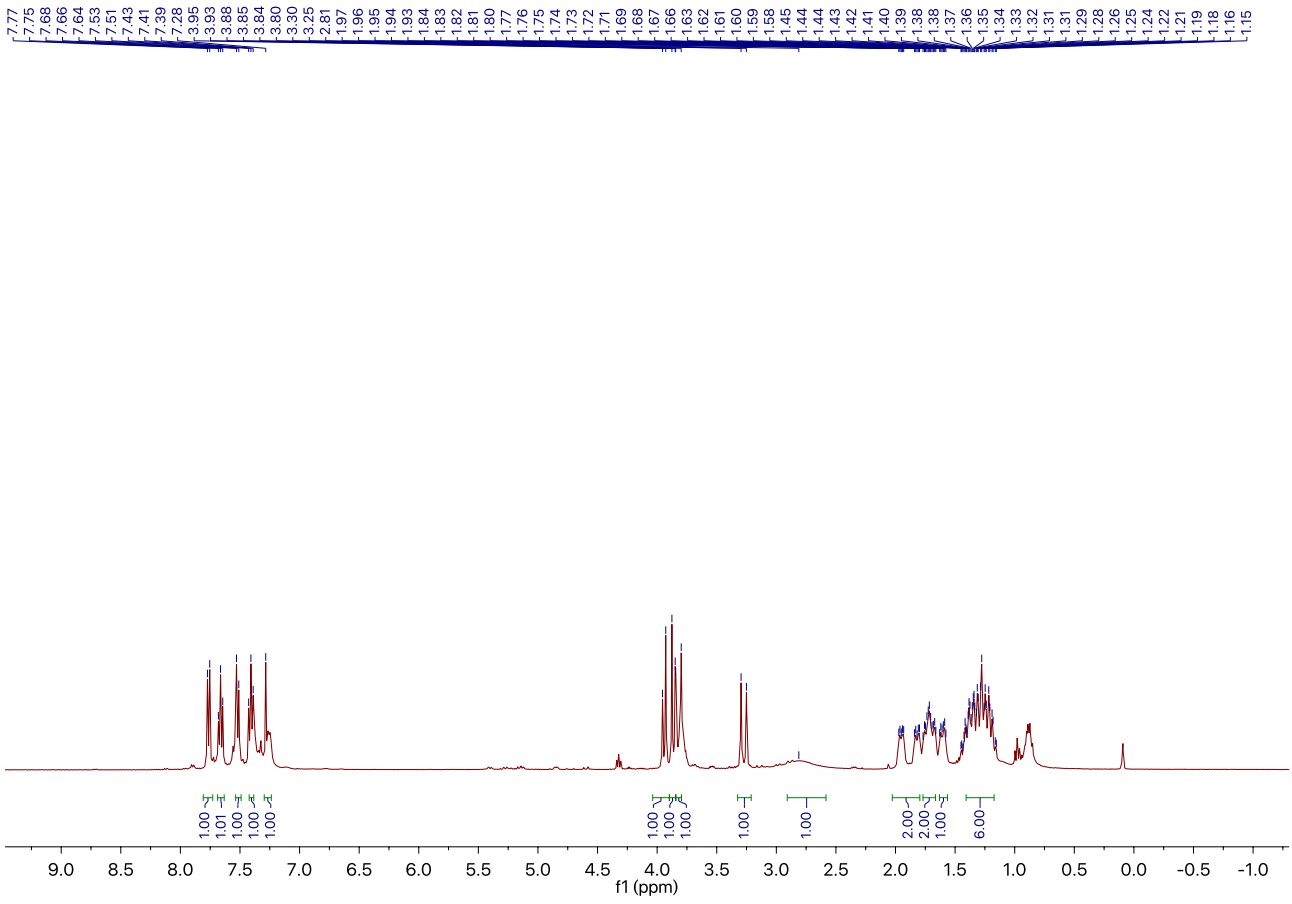
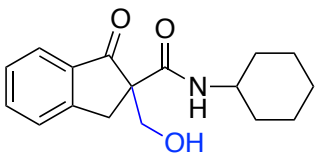


Figure S88. [1]HNMR Spectra of Compound **4q**

Compound **4q** ^{13}CNMR



4q

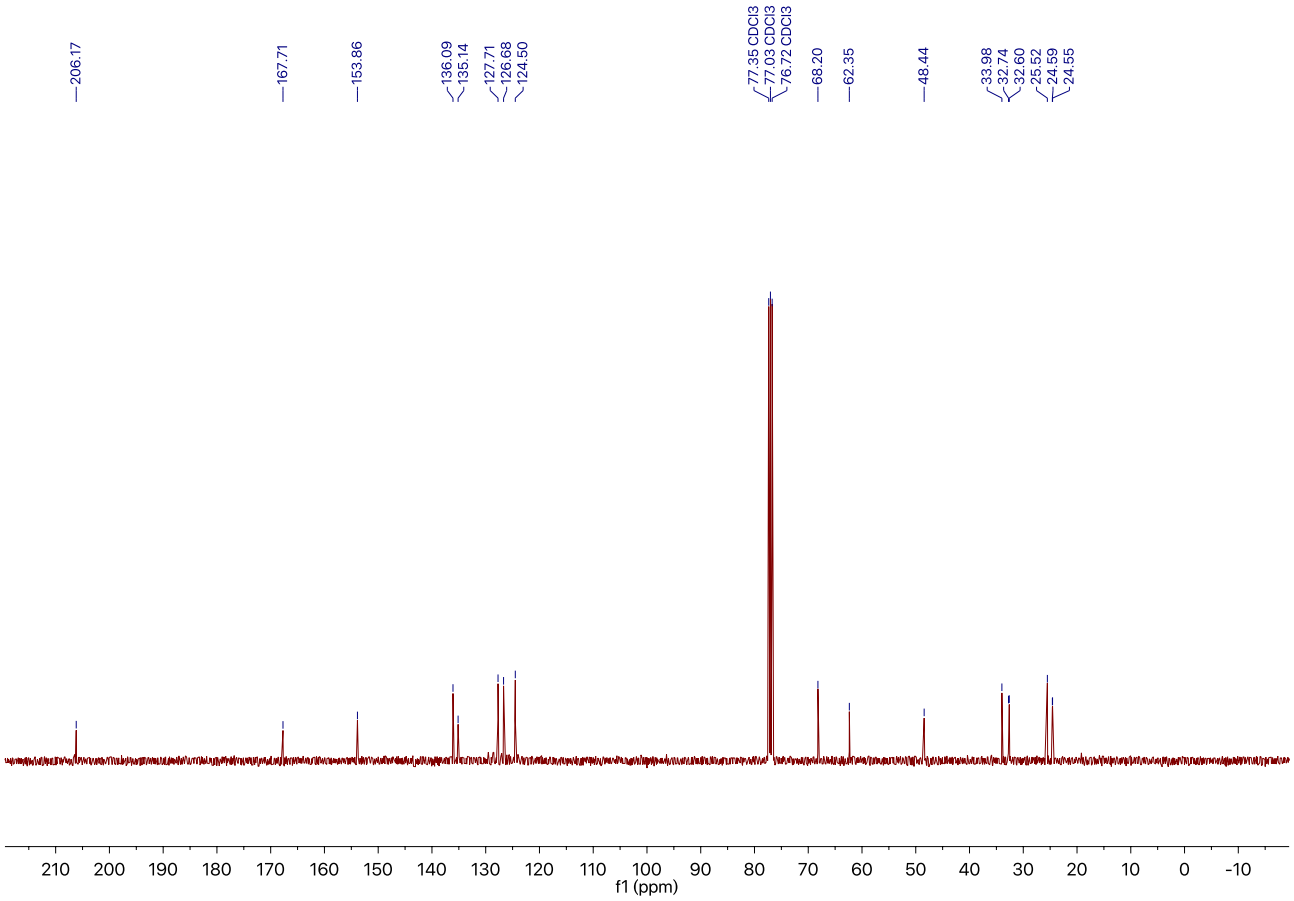
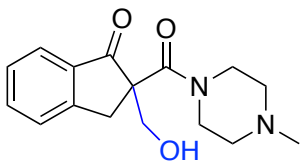


Figure S89. ^{13}CNMR Spectra of Compound **4q**

Compound **4r** [1]HNMR



4r

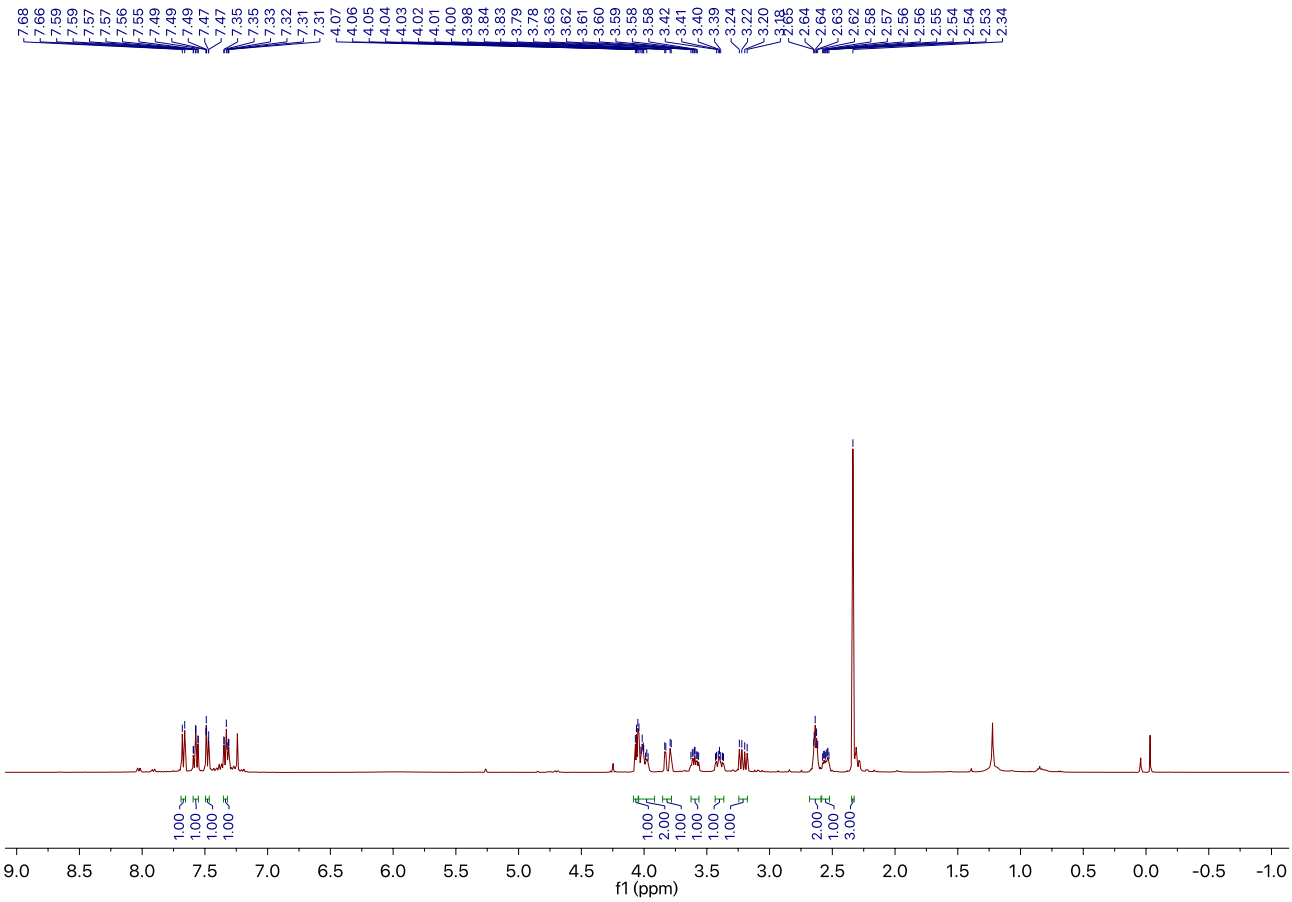
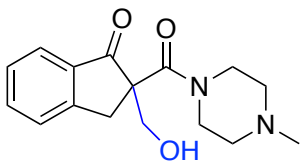


Figure S90. [1]HNMR Spectra of Compound **4r**

Compound **4r** ^{13}CNMR



4r

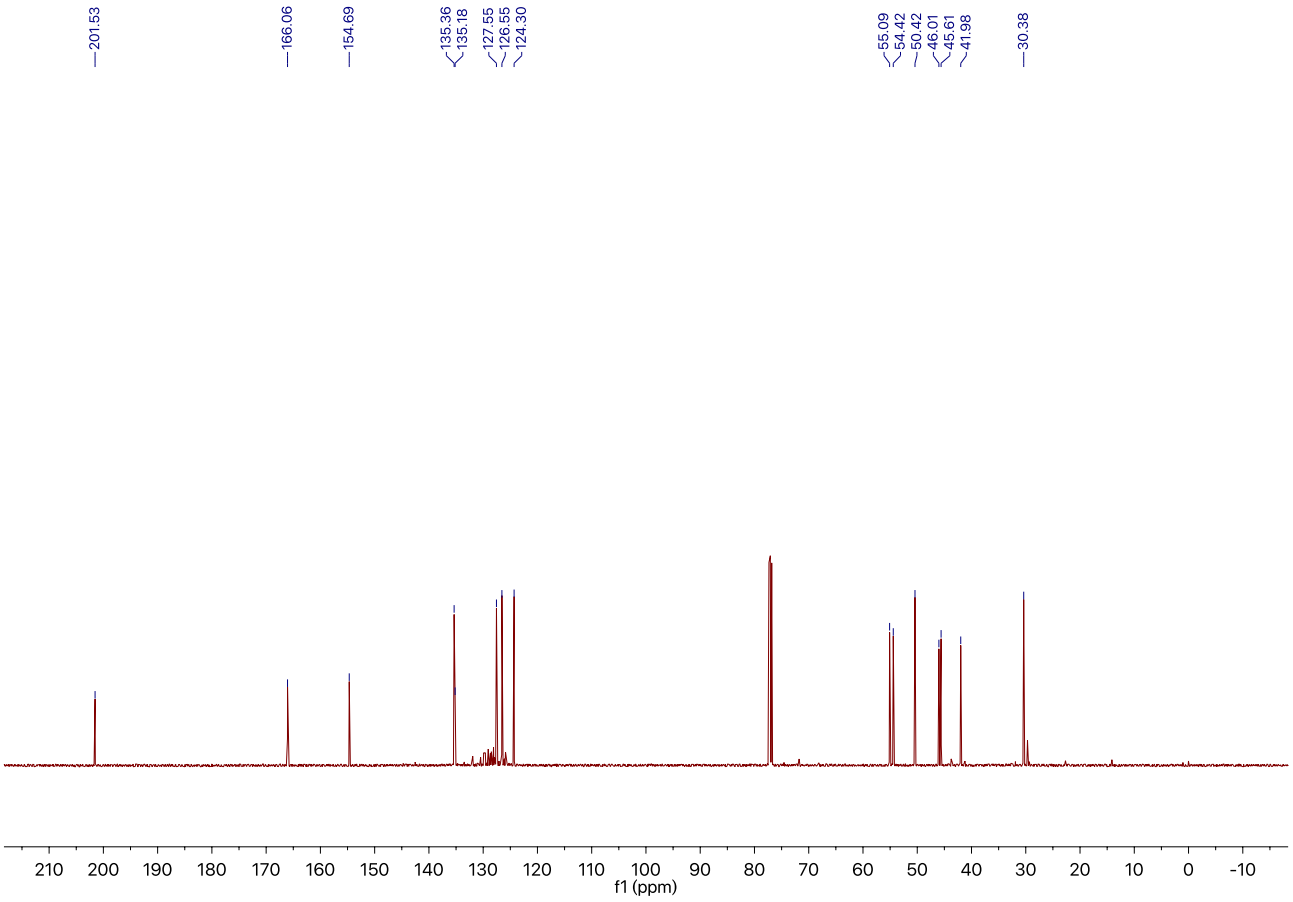
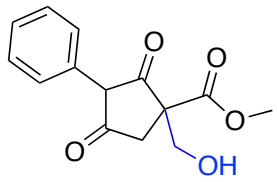


Figure S91. ^{13}CNMR Spectra of Compound **4r**

Compound **4s** ^{1}HNMR



4s

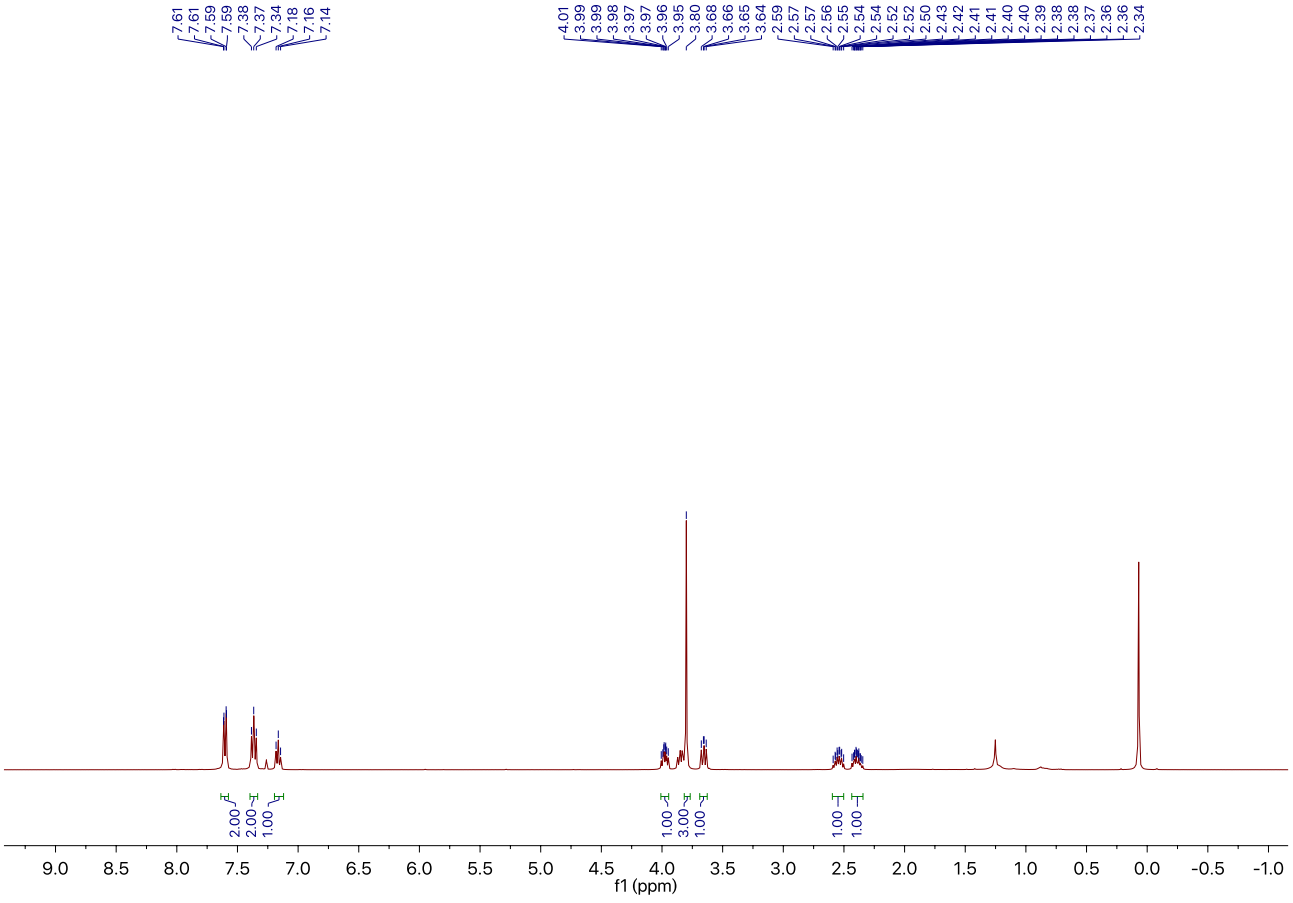
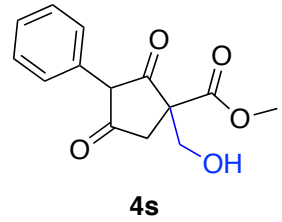


Figure S92. ^{1}HNMR Spectra of Compound **4s**

Compound **4s** ^{13}CNMR



4s

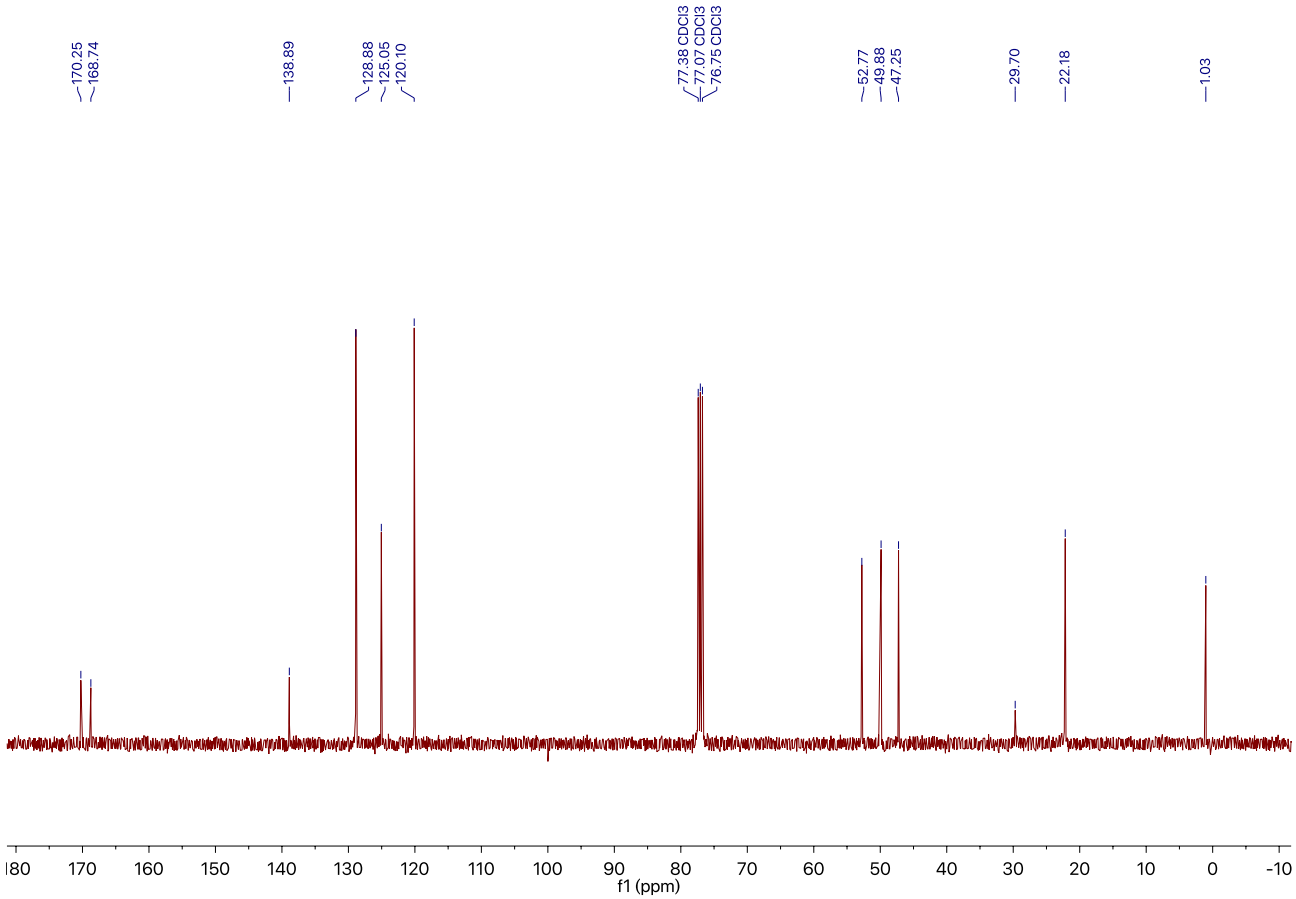
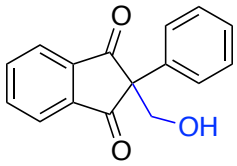


Figure S93. ^{13}CNMR Spectra of Compound **4s**

Compound **4t** ^{1}HNMR



4t

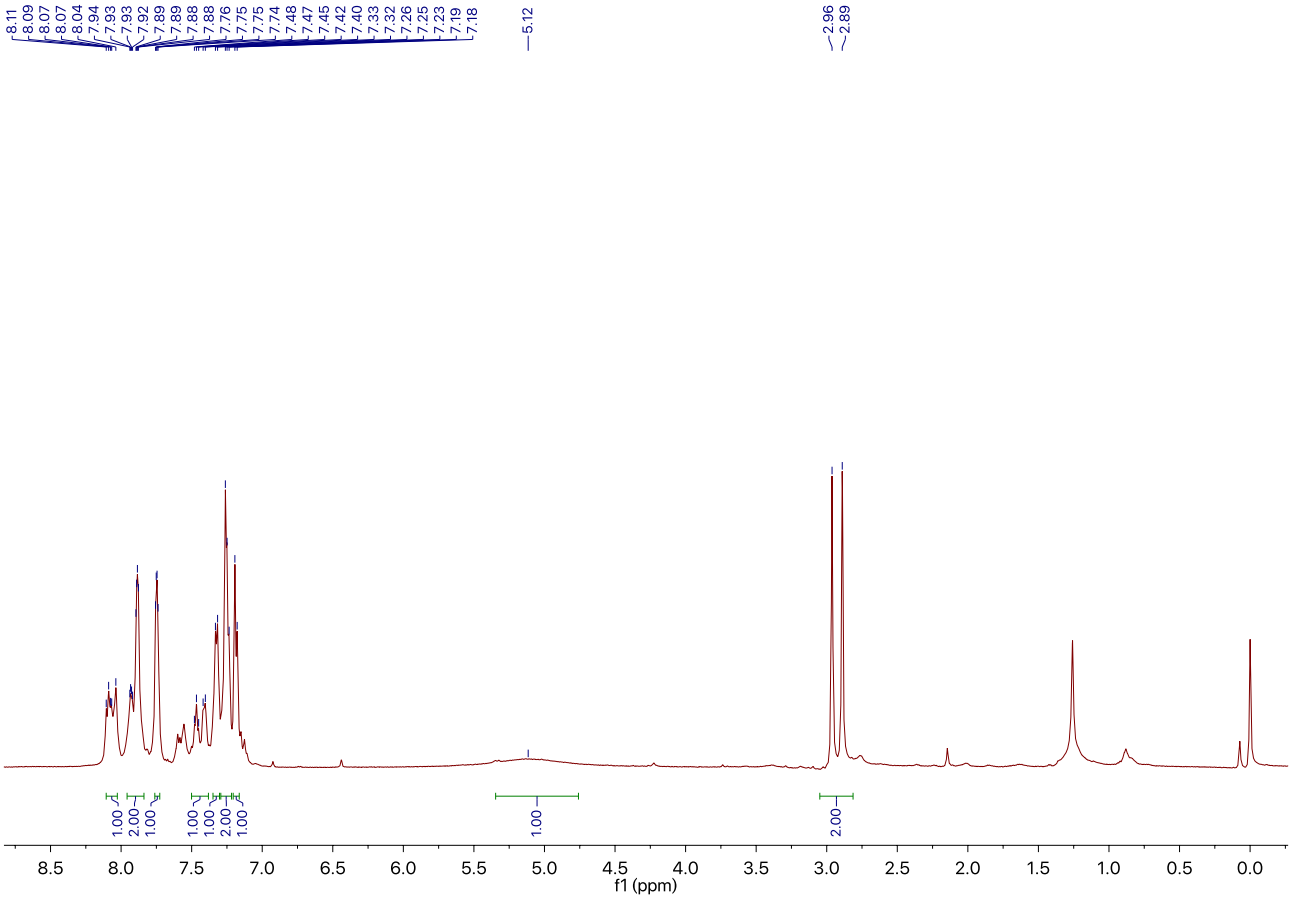
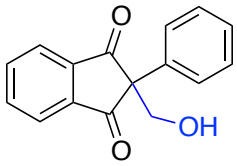


Figure S94. ^{1}HNMR Spectra of Compound **4t**

Compound **4t** ^{13}CNMR



4t

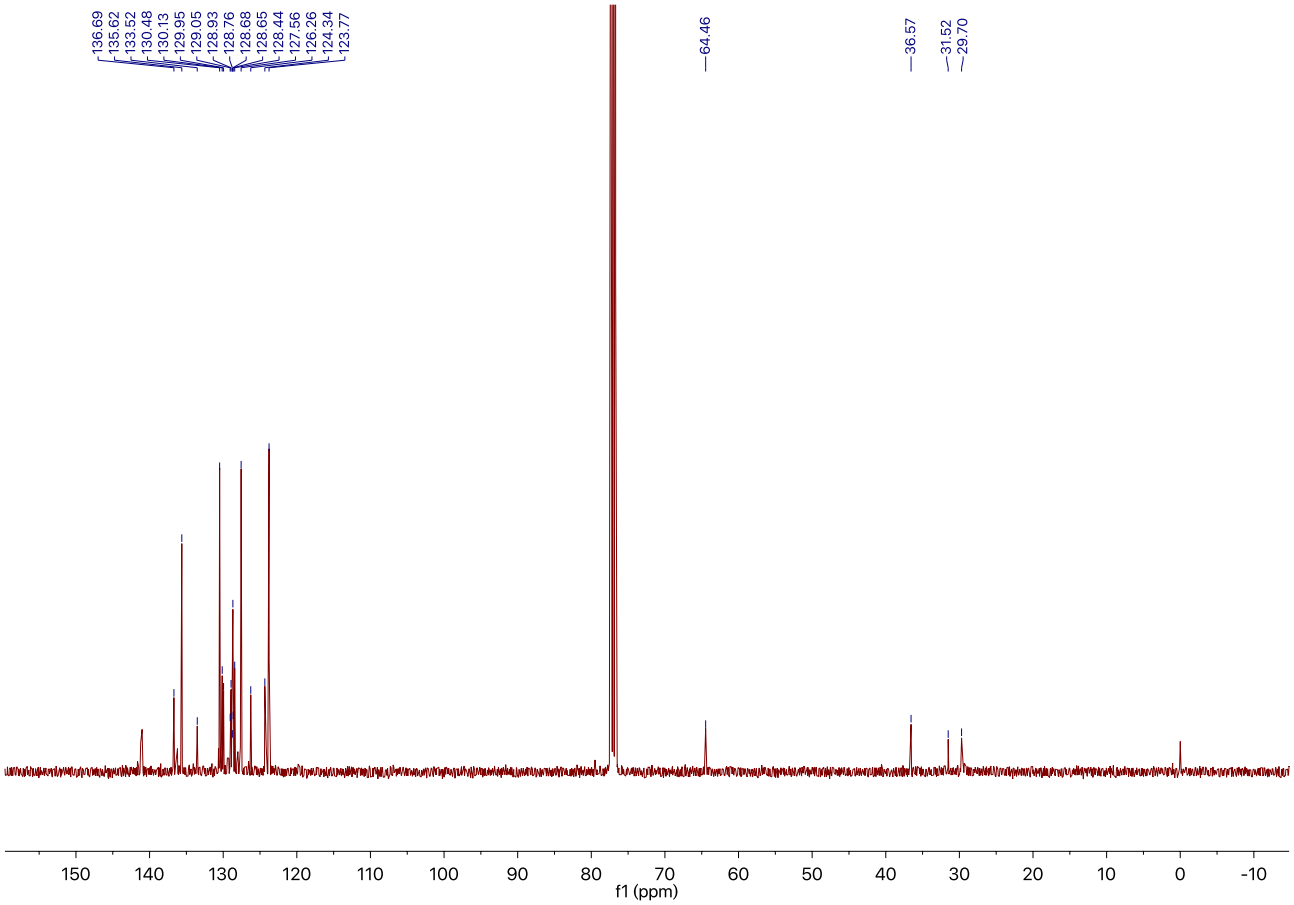


Figure S95. ^{13}CNMR Spectra of Compound **4t**