Supporting Information

Switchable Aroylation and Diaroylation of Allyl Sulfones with Aldehydes Enabled by Decatungstate Photocatalysis

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1. General Information

1.1 Materials and instruments

All the chemicals were purchased from commercial suppliers, all commercially available reagents were directly used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Proton chemical shifts δ were given in ppm using tetramethylsilane as internal standard. All NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 3 °C). High-resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique. The LEDs used are Kessil® PR160L-390 nm lamp.

Figure S1. Photograph of Photocatalytic reactor used for reactions conducted under irradiation with a Kessil® PR160L-390 nm lamp

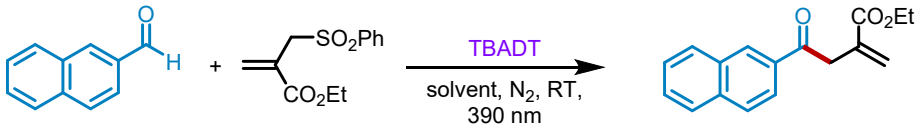
2. Experimental procedures

2.1 Preparation of photocatalyst tetrabutylammonium decatungstate (TBADT)

The photocatalyst was synthesized according to literature report.[1] To a 2 L beaker wrapped in aluminum foil for insulation and equipped with a 4" Teflon stir bar were added tetrabutylammonium bromide (4.80 g, 14.9 mmol, 0.49 equiv.) and deionized water (1600 mL). In a separate 4 L beaker wrapped in aluminum foil for insulation and equipped with a 4" Teflon stir bar were added $Na_2WO_4 \bullet 2H_2O$ (10 g, 30.3 mmol, 1.00 equiv.) and deionized water (1600 mL). Both solutions were rapidly stirred and heated to 90 °C. When both solutions reached 90 °C, concentrated HCl was added to each solution until pH stabilized at 2. At this point, the acidified solutions were combined in the 4 L beaker, and the resultant suspension was stirred at 90 °C for an additional 30 minutes. The reaction mixture was cooled to room temperature, then filtered through a pad of silica gel. The solids were washed with water and left to dry under vacuum. When the silica-supported solids were dry, the receiving flask was exchanged, and the pad was washed with 3 x 200 mL dichloromethane. The filtrate was collected and solvent was removed. The residue was thoroughly dried under vacuum to afford TBADT. Isolated as pale yellow crystals (82% yield). UV-Vis and CV characterization is consistent with literature data.[1]

2.2 Optimization of reaction conditions

Table S1. Optimization of reaction conditions of **3p**



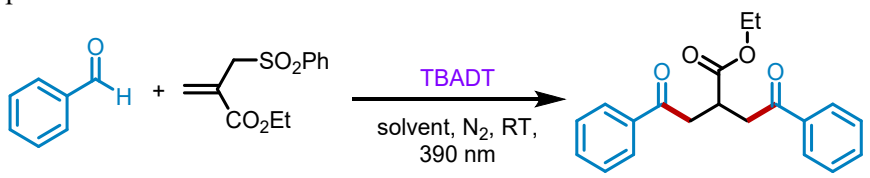
1p **2a** **3p**

Entry	PC	Solvent	Yield (%)
1	TBADT (3 mol %)	Acetone	69
2[b]	TBADT (3 mol %)	Acetone	40
3[c]	TBADT (3 mol %)	Acetone	55
4[d]	TBADT (3 mol %)	Acetone	55
5	TBADT (3 mol %)	MeCN	34
6	TBADT (3 mol %)	DCM	13
7	TBADT (3 mol %)	THF	trace
8	TBADT (2 mol %)	Acetone	44
9	**TBADT (4 mol %)**	**Acetone**	**76**
10	TBADT (5 mol %)	Acetone	48
11[e]	TBADT (4 mol %)	Acetone	38
12[f]	TBADT (4 mol %)	Acetone	47
13[g]	TBADT (4 mol %)	Acetone	63

[a] Reaction conditions: **1p** (0.2 mmol), **2a** (0.6 mmol), TBADT (3 mol %) in solvent (3.0 mL) at room temperature for 6 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N_2 atmosphere. Isolated yields are given. [b] **2a** (0.2 mmol), [c] **2a** (0.4 mmol), [d] **2a** (0.8 mmol), [e] 10 W, [f] 20 W, [g] 30 W.

We began to set up our optimal experimental conditions towards ethyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate using the model reaction of 1p and with 2a in the presence of TBADT under N_2 atmosphere with irradiation of a Kessil® PR160L-390 nm lamp (40 W) at room temperature for 6 h, as summarized in Table S2. Initially, by employing 3 mol% of TBADT as the catalyst, the model reaction was performed smoothly at room temperature in acetone (3 mL), affording the desired product 3p in 69% yield (entry 1). With this intriguing result in hand, the influence of the amount of 2a was examined (entries 1-4). The results showed that 2a (0.6 mmol) was proved to be the best choice. Next, we further investigated other different solvents including acetonitrile, dichloromethane and tetrahydrofuran. Acetone was also proved to be the best one among all the solvents tested. The amount of TBADT was then evaluated. To our delight, the yield of 3p was increased from 69% to 76% as the amount of TBADT increased from 3 mol % to 4 mol %. However, when the model reactions were performed in the different light intensities, yield of 3p has not improved further (entries 11-13). After a wide exploration, the optimal conditions were finally established as follows: 1p (0.2 mmol), 2a (0.6 mmol), TBADT (4 mol %), acetone (3 mL) at room temperature for 6 h under N_2 atmosphere with the irradiation of 40 W 390 nm Kessil lamp.

Table S2. Optimization of reaction conditions of **4a**



1a **2a** **4a**

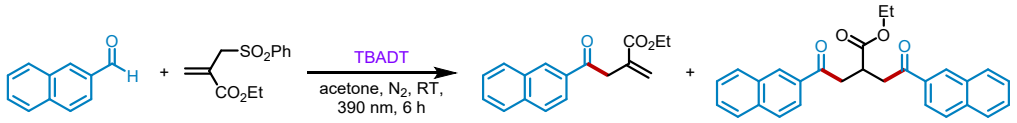
Entry	PC	Base	Solvent	Yield (%)
1	TBADT (3 mol %)	Na_2CO_3	Acetone	58
2	TBADT (3 mol %)	$NaHCO_3$	Acetone	43
3	TBADT (3 mol %)	K_2CO_3	Acetone	trace
4	TBADT (3 mol %)	$KHCO_3$	Acetone	trace
5	TBADT (3 mol %)	---	Acetone	63
6	TBADT (3 mol %)	---	MeCN	42
7	TBADT (3 mol %)	---	THF	34
8	TBADT (3 mol %)	---	DMF	trace
9	TBADT (3 mol %)	---	DCM	21
10	TBADT (2 mol %)	---	Acetone	45
11	TBADT (4 mol %)	---	Acetone	54
12	TBADT (5 mol %)	---	Acetone	48
13[b]	TBADT (3 mol %)	---	Acetone	42
14[c]	TBADT (3 mol %)	---	Acetone	67
15[d]	**TBADT (3 mol %)**	**---**	**Acetone**	**72**
16[e]	TBADT (3 mol %)	---	Acetone	54
17[f]	TBADT (3 mol%)	---	Acetone	17
18[g]	TBADT (3 mol %)	---	Acetone	N.D.
19[h]	TBADT (3 mol %)	---	Acetone	32

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.2 mmol), TBADT (3 mol %) and base (2 equiv) in solvent (3.0 mL) at room temperature for 5 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N_2 atmosphere. Isolated yields are given. [b] **1a** (0.8 mmol), [c] **1a** (1.2 mmol), [d] **1a** (1.4 mmol), [e] **1a** (1.6 mmol), [f] No TBADT, [g] No light, [h] Air.

We initially started our study by using benzaldehyde (**1a**) and ethyl 2-((phenylsulfonyl)methyl)acrylate (**2a**) as the model substrates in the presence of various bases under irradiation of a Kessil® PR160L-390 nm lamp (40 W) to investigate the reaction conditions. To our delight, the optimal isolated yield was 63% without base (entry 5). Next, the effects of various solvents and the amount of TBADT on the reaction were investigated (entries 5-12). The results indicated that the target product **4a** was obtained in the highest yield in acetone and 3 mol % of TBADT. Finally, the amount of **1a** was examined, the results indicated that the yield of **4a** could

be raised to 72% when the amount of **1a** was increased to 1.4 mmol (entry 15). Additionally, poor reactivity was observed when the model reaction was performed without TBADT or 40 W Kessil® PR160L-390 nm lamp respectively (entries 17-18). Therefore, the optimal reaction conditions were thus established as follows: **1a** (1.4 mmol), **2a** (0.2 mmol), and TBADT (3 mol %) in acetone (3 mL) at room temperature for 5 h under N_2 atmosphere with the irradiation of 40 W 390 nm Kessil Lamp.

Table S3. Chemoselectivity of screening of the substrate ratio of aroylation reaction

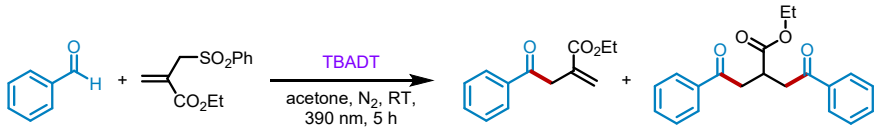


1p 2a 3p 4p

Entry	PC	Substrate ratio (1p:2a)	Product ratios (%)	
			3p	4p
1	TBADT (3 mol %)	1:1	40	25
2	TBADT (3 mol %)	1:2	55	19
3	TBADT (3 mol %)	1:3	69	13
4	TBADT (3 mol %)	1:4	55	10
5[b]	**TBADT (4 mol %)**	**1:3**	**76**	**11**

[a] Reaction conditions: **1p** (0.2 mmol), TBADT (3 mol %) in acetone (3.0 mL) at room temperature for 6 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N_2 atmosphere. Isolated yields are given. [b] TBADT (4 mol %).

Table S4. Chemoselectivity of screening of the substrate ratio of diaroylation reaction



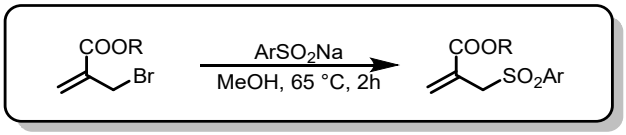
1a 2a 3a 4a

Entry	PC	Substrate ratio (1a:2a)	Product ratios (%)	
			3a	4a
1	TBADT (3 mol %)	4:1	trace	42
2	TBADT (3 mol %)	5:1	trace	63
3	TBADT (3 mol %)	6:1	trace	67
4	**TBADT (3 mol %)**	**7:1**	**trace**	**72**
5	TBADT (3 mol %)	8:1	trace	54

[a] Reaction conditions: **2a** (0.2 mmol), TBADT (3 mol %) in acetone (3.0 mL) at room temperature for 5 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N_2 atmosphere. Isolated yields are given.

2.3 Preparation of starting materials

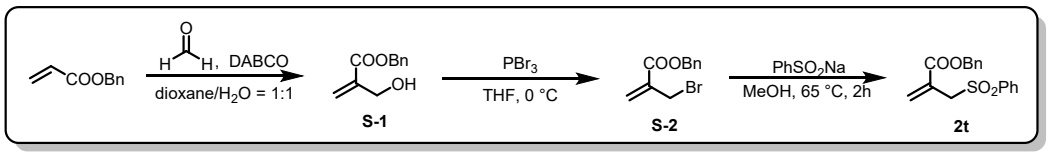
Preparation of 2a and 2s[2]



Scheme S1. General experimental procedures for substrates **2a** and **2s**

2a and **2s** were synthesized according to literature report,[2] to a solution of alkylbromide (1.0 equiv) in dry methanol was added $ArSO_2Na$ (1.5 equiv). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by column chromatography to afford **2a** and **2s**.

Preparation of 2t[2]



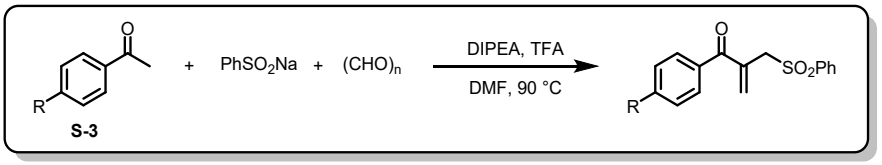
Scheme S2. General experimental procedures for substrate **2t**

Step 1. According to a reported literature procedure,[2] to a solution of paraformaldehyde (1.3 equiv) and benzyl acrylate (1.0 equiv) in dioxane-water (1:1, v/v) was added DABCO (1.3 equiv) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was extracted with EtOAc (× 3) and the combined organic layers were washed with water (x 4) and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford **S-1**.

Step 2. To a solution of **S-1** was added phosphorus (III) bromide (0.33 equiv) in dry THF (20 mL) at -10 ^oC under a nitrogen atmosphere. The temperature was allowed to rise to 20 ^oC and stirring was continued for 3 h. Water (50 mL) was then added and the mixture was extracted with petroleum ether (× 3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **S-2**.

Step 3. 2t was finally prepared by experimental procedures for substrate **2a** from **S-2**.

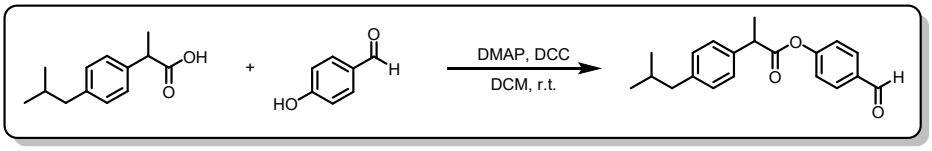
Preparation of 2u-2w[2]



Scheme S3. General experimental procedures for substrates **2u-2w**

According to a reported literature procedure,[2] A mixture of **S-3** (1.0 equiv), DIPEA (1.0 equiv), TFA (2.0 equiv), sodium benzenesulfinate (1.0 equiv) and paraformaldehyde (4.0 equiv) were dissolved in DMF, then, the reaction mixture was heated to 90 °C in a nitrogen atmosphere for 20 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, washed with 3 × 20 mL LiCl (5 wt%), and dried over Na_2SO_4. The solid was filtered off and the organic solvent evaporated. The crude product was purified by column chromatography on silica gel to give the **2u-2w** as a white solid.

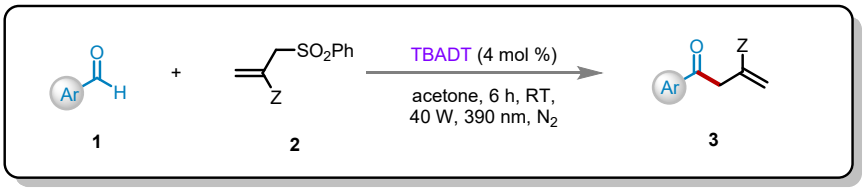
Preparation of 1q[3]



Scheme S4. General experimental procedures for substrate **1q**

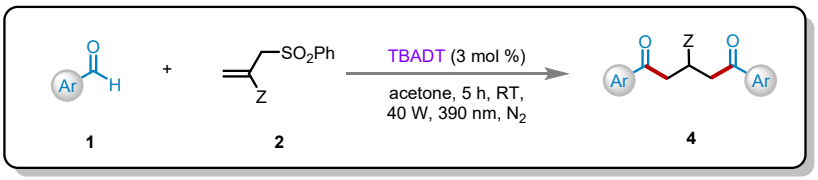
1q was synthesized according to literature report,[3] p-hydroxybenzaldehyde (1.0 equiv) and acid (1.0 equiv) and dry CH_2Cl_2 (20 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.1 equiv) and dicyclohexylcarbodiimide (DCC, 2.0 equiv) were added sequentially. The reaction was allowed to slowly warm to room temperature and further stirred for 8 hours. Upon completion, the solution was concentrated in vacuo and purified by column chromatography on silica to afford the desired product **1q**.

2.4 General experimental procedures for the unsaturated ketones and 1, 5-diketones



Scheme S5. General experimental procedures for the unsaturated ketones

Aldehyde **1** (0.2 mmol, 1.0 equiv), TBADT (26.6 mg, 4 mol %) and allyl sulfone **2** (0.6 mmol, 3.0 equiv) were added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed using a rubber stopper and the reaction mixture was degassed by bubbling with N_2 for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). The reaction tube was irradiated (at approximately 2-3 cm away from the light source) with a Kessil® PR160L-390 nm lamp (40 W) under vigorous stirring at room temperature. After 6 hours the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate (v/v = 40/1) as eluting solvent to give the desired products **3**.

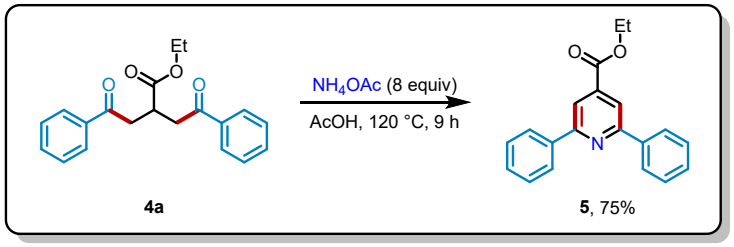


Scheme S6. General experimental procedures for the 1, 5-diketones

TBADT (21 mg, 3 mol %), aldehyde **1** (1.4 mmol, 7.0 equiv) and allyl sulfone **2** (0.2 mmol, 1.0 equiv) were added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed using a rubber stopper and the reaction mixture was degassed by bubbling with N_2 for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N_2 atmosphere). After the reaction, the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate (v/v = 20/1) as eluting solvent to give the desired products **4**.

2.5 Synthetic applications

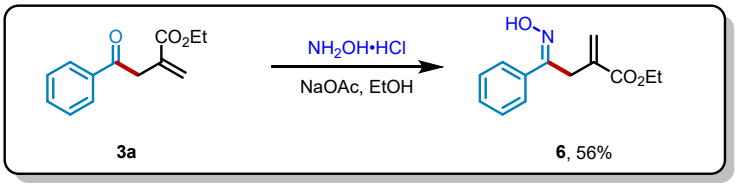
Synthesis of 5[4]



Scheme S7. Experimental procedures for **5**

The reaction was carried out following a modified procedure from Boivin et al.[4] A solution of compound **4a** (65 mg, 0.2 mmol, 1 equiv) in AcOH (5 mL), containing NH_4OAc (123 mg, 1.6 mmol, 8 equiv) was placed into a 10 mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with N_2. The solution was then heated at 120 °C for 5 h after which the solvent was evaporated under reduced pressure and the residue was taken up in Et_2O. The organic layer was washed successively with 2 N aq NaOH and brine, then dried ($MgSO_4$). The residue was chromatographed over silica gel (ethyl ether/petroleum ether = 1:50, R_f = 0.4) to yield the title compound **5** as white solid (45.1 mg, 75%).

Synthesis of 6 [5]



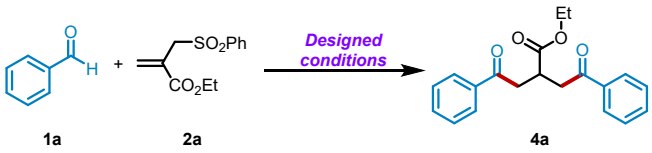
Scheme S8. Experimental procedures for **6**

The reaction was carried out following a modified procedure from Wang et al.[5] To a solution of hydroxylamine hydrochloride (69.5 mg, 1.0 mmol, 5 equiv) in water was added a solution of sodium acetate (114.8 mg, 1.4 mmol, 7 equiv) in ethanol. The mixture was stirred at room temperature while the unsaturated ketone **3b** (43.6 mg, 0.2 mmol, 1 equiv) was added as a solution in ethanol. The mixture was stirred overnight and concentrated in vacuo. Then, the mixture was extracted with ethyl acetate 3 times and the combined extracts were washed with water and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford title compound **6** as colorless oil (26.1 mg, 56%).

2.6 Set of Experiments

A set of experiments that employed **1a** and **2a** were performed to evaluate the reaction-condition-based sensitivity of this conversion, which will be valuable in increasing the insight of this new synthetic method and reproducibility. Various parameters, including concentration, temperature, oxygen level, water level, light intensity, and scale, were chosen with positive and negative direction relative to the standard reaction conditions. Each experiment only deliberately changed one parameter, while keeping others at standard levels.

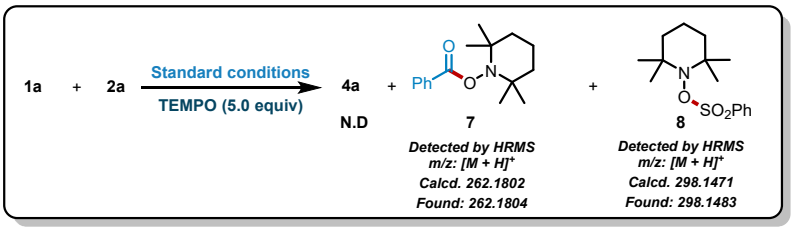
Table S5. Set of Experiments



Parameter	Variation		Description	Yield
Concentration (c)	High c	c + 10% c	2.73 mL Acetone	69%
	Low c	c - 10% c	3.33 mL Acetone	70%
H_2O level	High H_2O	+ H_2O; V_{H2O} = 1%V_{rxn}	30 μL H_2O in 3 mL Acetone	64%
O_2 level	Air		Air instead of N_2	32%
Temperature (T)	High T	T + 10 °C	35 °C	70%
Light intensity (W)	Low W	W/16	2.5 W	0%
Scale	Big scale	n·15	3 mmol of **2a**	59%

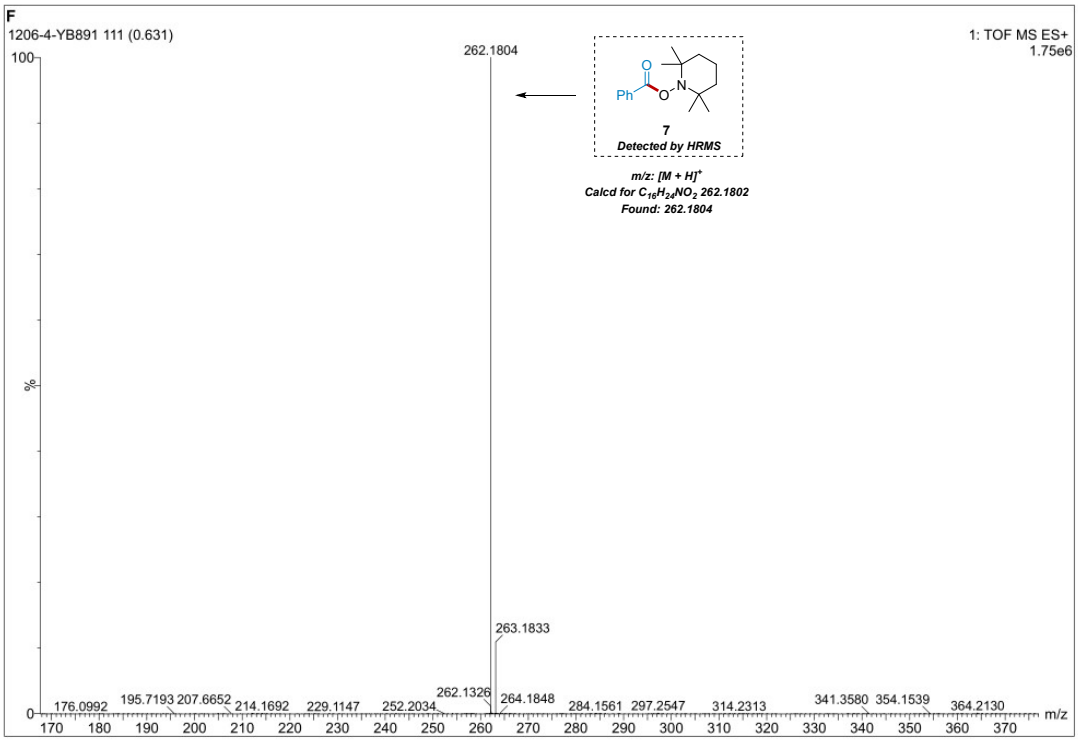
2.7 Investigation of the mechanism

TEMPO was used as a radical scavenger



To a 25 mL Schlenk tube was added TBADT (21 mg, 3 mol %), aldehyde **1a** (1.4 mmol, 7.0 equiv), allyl sulfone **2a** (0.2 mmol, 1.0 equiv) and TEMPO (1.0 mmol, 5.0 equiv). The tube was

sealed with a rubber stopper and the reaction mixture was degassed by bubbling with N_2 for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N_2 atmosphere). As it can be seen, the reaction was completely suppressed, reminding of a radical-involved process. The adduct **7** and **8** were detected by high-resolution mass spectrometry (HRMS) as shown in Figure S2.



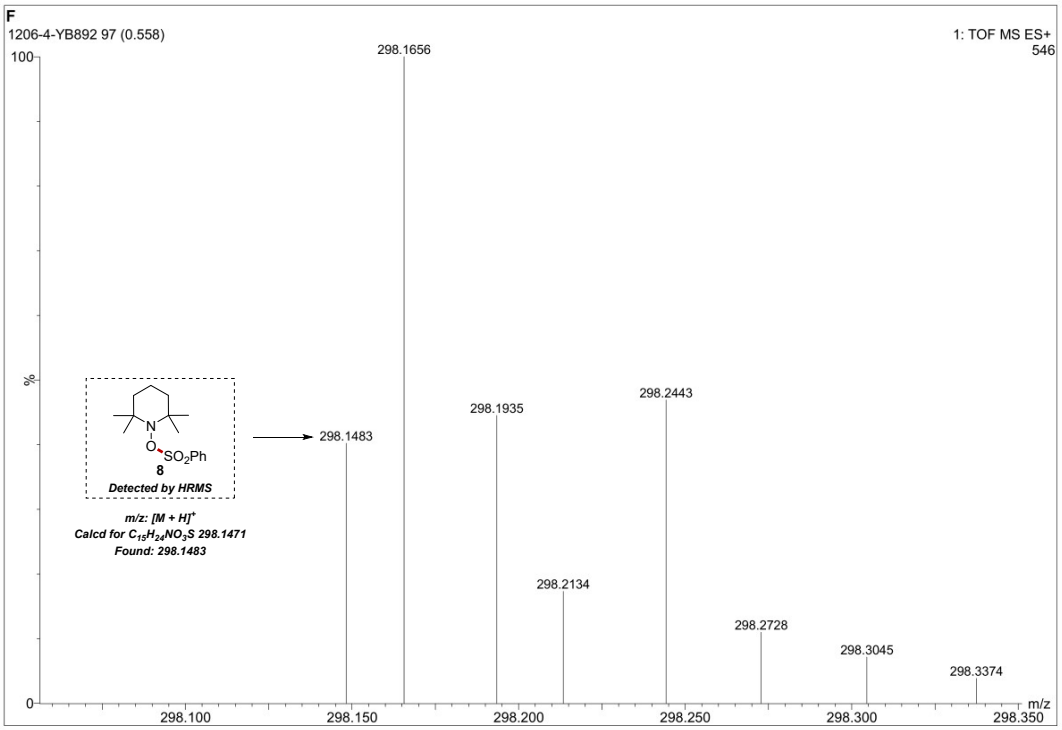
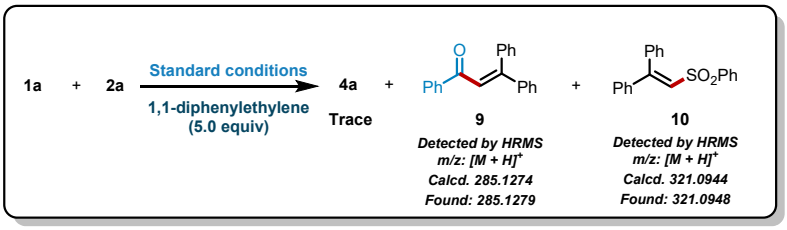


Figure S2. HR-MS of the reaction when TEMPO was used as a radical scavenger

1,1-diphenylethylene was used as a radical scavenger



To a 25 mL Schlenk tube was added TBADT (21 mg, 3 mol %), aldehyde **1a** (1.4 mmol, 7.0 equiv), allyl sulfone **2a** (0.2 mmol, 1.0 equiv) and 1,1-diphenylethylene (1.0 mmol, 5.0 equiv). The tube was sealed with a rubber stopper and the reaction mixture was degassed by bubbling with N_2 for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N_2 atmosphere). As it can be seen, the reaction was severely suppressed and the adduct **9** and **10** were detected by high-resolution mass spectrometry (HRMS) as shown in Figure S3.

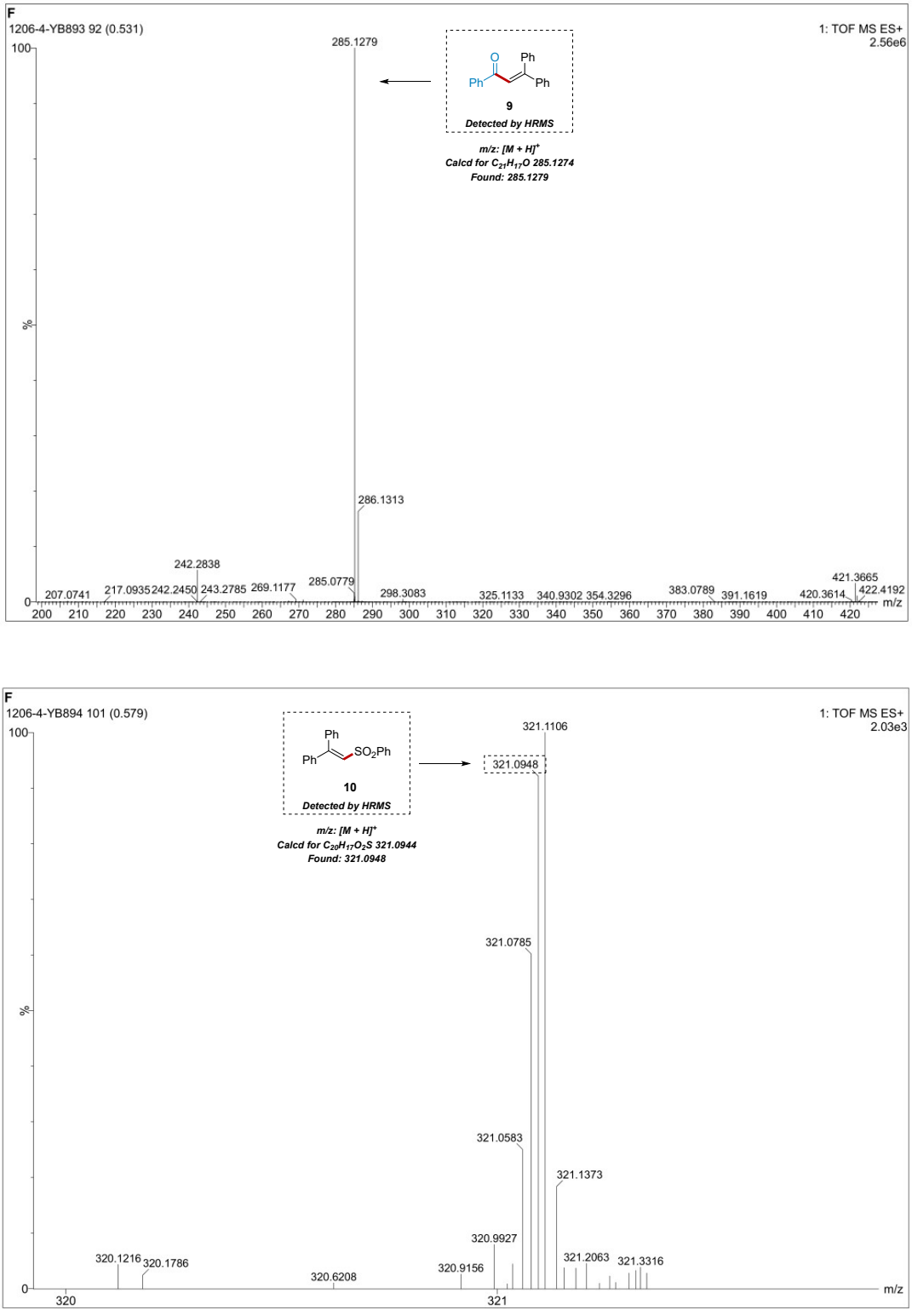


Figure S3. HR-MS of the reaction when 1,1-diphenylethylene was used as a radical scavenger

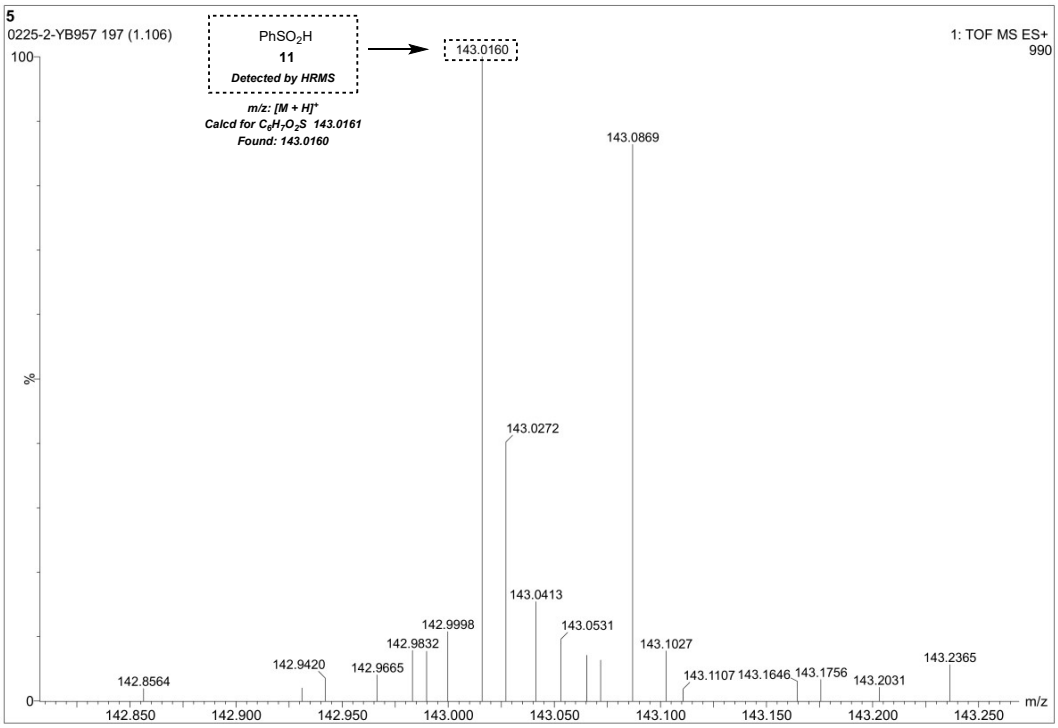
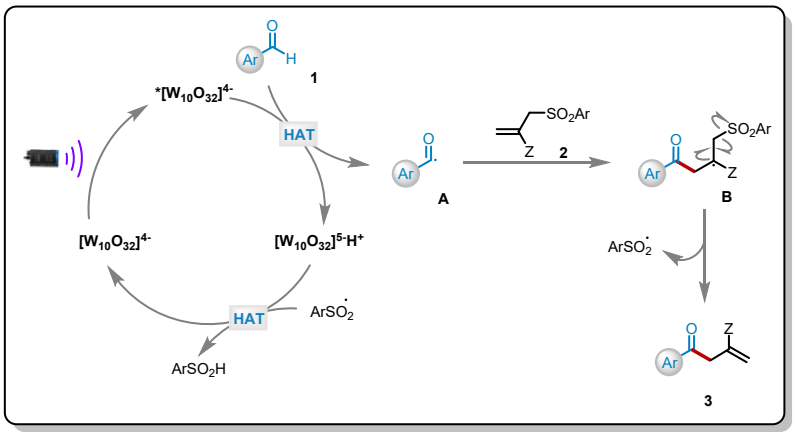


Figure S4. HR-MS of the $PhSO_2H$

2.8 Proposed Reaction Mechanisms

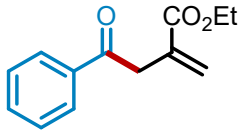
The above mechanistic experiments coupled with precedent related literature collectively point to a plausible mechanism shown in Scheme S9. Initially, the TBADT photocatalyst was excited to generate the triplet excited state $*[W_{10}O_{32}]^{4-}$ under the irradiation of 390 nm Kessil lamp, which abstracted a hydrogen atom from the aldehyde to get a nucleophilic aroyl radical **A** and $[W_{10}O_{32}]^{5-}H^+$. The subsequent interaction of the radical **A** and allyl sulfone **2** through a sequence of radical addition and *β*-fragmentation delivered allyl product **3** while producing phenylsulfonyl radical. Finally, the phenylsulfonyl radical was easily reduced by $[W_{10}O_{32}]^{5-}H^+$, thereby closing the catalyst cycle after the HAT process.



Scheme S9. Proposed Reaction Mechanism of the aroylation reaction

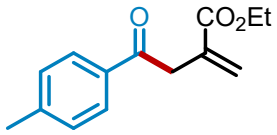
3. Characterization Data for Products

ethyl 2-methylene-4-oxo-4-phenylbutanoate (3a)[6]



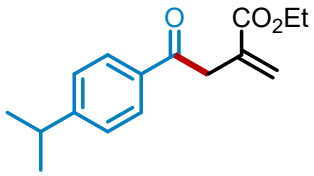
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3a**. Colorless oil (35 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.00 (m, 2H), 7.62 – 7.58 (m, 1H), 7.51 – 7.47 (m, 2H), 6.43 (d, *J* = 0.64 Hz, 1H), 5.71 (d, *J* = 1.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.02 (d, *J* = 0.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 166.4, 136.6, 134.9, 133.2, 128.6, 128.4, 128.3, 61.0, 41.7, 14.1.

ethyl 2-methylene-4-oxo-4-(p-tolyl)butanoate (3b)[6]



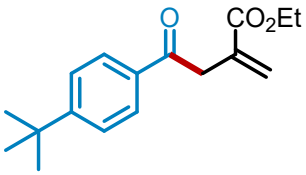
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3b**. Colorless oil (43 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.90 (m, 2H), 7.30 – 7.28 (m, 2H), 6.41 (d, *J* = 0.8 Hz, 1H), 5.70 (d, *J* = 1.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 0.6 Hz, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 166.5, 144.1, 135.0, 134.1, 129.3, 128.4, 128.2, 61.0, 41.6, 21.7, 14.1.

ethyl 4-(4-isopropylphenyl)-2-methylene-4-oxobutanoate (3c)



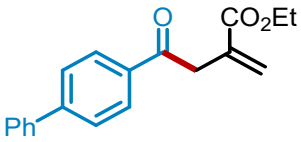
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3c**. Colorless oil (34 mg, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.93 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.41 (d, *J* = 0.7 Hz, 1H), 5.70 (d, *J* = 1.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 0.5 Hz, 2H), 3.04 – 2.94 (m, 1H), 1.30 – 1.26 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 166.5, 154.8, 135.0, 134.4, 128.5, 128.2, 126.7, 61.0, 41.6, 34.3, 23.7, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{21}O_3$, 261.1485; found: 261.1497.

ethyl 4-(4-(tert-butyl)phenyl)-2-methylene-4-oxobutanoate (3d)



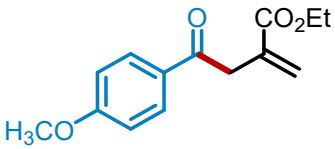
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3d**. Colorless oil (32 mg, 58% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.53 – 7.48 (m, 2H), 6.42 (s, 1H), 5.70 (d, *J* = 1.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 1.37 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 166.5, 157.0, 135.0, 134.0, 128.3, 128.2, 125.6, 61.0, 41.6, 35.1, 31.1, 14.1. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{23}O_3$, 275.1642; found: 275.1638.

ethyl 4-([1,1'-biphenyl]-4-yl)-2-methylene-4-oxobutanoate (3e)[6]



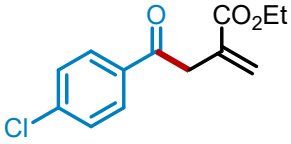
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3e**. White solid (36 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.08 (m, 2H), 7.74 – 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 6.45 (s, 1H), 5.74 (d, *J* = 1.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.30 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 166.4, 145.9, 139.9, 135.3, 134.9, 129.0, 128.9, 128.4, 128.3, 127.3, 61.1, 41.7, 14.1.

ethyl 4-(4-methoxyphenyl)-2-methylene-4-oxobutanoate (3f)[6]



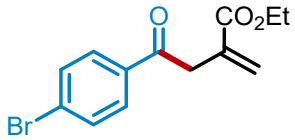
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3f**. Colorless oil (23 mg, 47% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 6.98 – 6.94 (m, 2H), 6.40 (s, 1H), 5.70 (d, *J* = 1.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 3.89 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.5, 166.5, 163.6, 135.1, 130.6, 129.6, 128.2, 113.8, 61.0, 55.5, 41.3, 14.1.

ethyl 4-(4-chlorophenyl)-2-methylene-4-oxobutanoate (3g)[6]



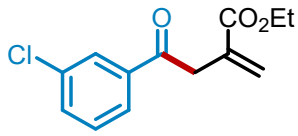
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3g**. Colorless oil (26 mg, 51% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.49 – 7.45 (m, 2H), 6.43 (s, 1H), 5.73 (d, *J* = 0.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.7, 166.3, 139.7, 134.9, 134.6, 129.7, 129.0, 128.5, 61.1, 41.6, 14.1.

ethyl 4-(4-bromophenyl)-2-methylene-4-oxobutanoate (3h)[6]



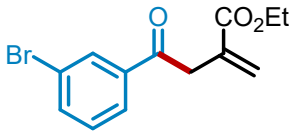
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3h**. Colorless oil (21 mg, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) 7.61 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 5.70 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.9, 166.3, 135.3, 134.5, 131.9, 129.8, 128.6, 128.4, 61.1, 41.6, 14.1.

ethyl 4-(3-chlorophenyl)-2-methylene-4-oxobutanoate (3i)[6]



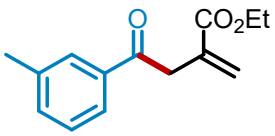
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3i**. Colorless oil (24 mg, 48% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (t, *J* = 1.8 Hz, 1H), 7.88 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 6.44 (s, 1H), 5.73 (d, *J* = 0.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.7, 166.2, 138.1, 135.0, 134.4, 133.2, 130.0, 128.7, 128.4, 126.4, 61.1, 41.8, 14.1.

ethyl 4-(3-bromophenyl)-2-methylene-4-oxobutanoate (3j)[6]



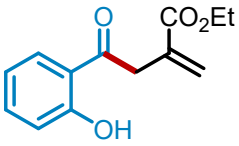
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3j**. Colorless oil (31 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (t, *J* = 1.8 Hz, 1H), 7.91 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.42 (s, 1H), 5.71 (d, *J* = 1.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 0.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.6, 166.2, 138.3, 136.1, 134.4, 131.2, 130.2, 128.7, 126.8, 123.0, 61.1, 41.7, 14.1.

ethyl 2-methylene-4-oxo-4-(m-tolyl)butanoate (3k)



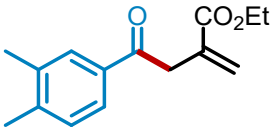
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3k**. Colorless oil (27 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.35 (m, 2H), 6.42 (s, 1H), 5.71 (d, *J* = 0.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.1, 166.4, 138.4, 136.6, 134.9, 134.0, 128.8, 128.5, 128.3, 125.5, 61.0, 41.8, 21.4, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{14}H_{16}NaO_3$, 255.0992; found: 255.0997.

ethyl 4-(2-hydroxyphenyl)-2-methylene-4-oxobutanoate (3l)



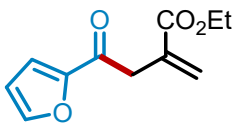
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3l**. Colorless oil (25 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.05 (s, 1H), 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 5.74 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.9, 166.2, 162.5, 136.6, 134.3, 130.0, 128.8, 119.0, 118.6, 61.2, 41.4, 14.1. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{13}H_{15}O_4$, 235.0965; found: 235.0967.

ethyl 4-(3,4-dimethylphenyl)-2-methylene-4-oxobutanoate (3m)[6]



Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3m**. Colorless oil (23 mg, 46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.41 (d, *J* = 0.6 Hz, 1H), 5.69 (d, *J* = 1.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 0.4 Hz, 2H), 2.34 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.8, 166.5, 142.8, 137.0, 135.1, 134.5, 129.8, 129.4, 128.2, 126.0, 61.0, 41.6, 20.0, 19.8, 14.1.

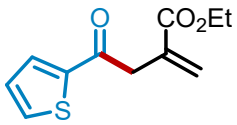
ethyl 4-(furan-2-yl)-2-methylene-4-oxobutanoate (3n)



Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3n**. Colorless oil (25 mg, 59% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.61 (m, 1H), 7.27 (d, *J* = 3.6 Hz,

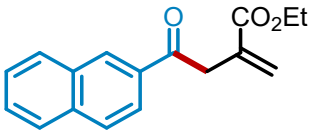
1H), 6.57 (dd, J = 3.4, 1.5 Hz, 1H), 6.43 (s, 1H), 5.76 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.87 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.8, 166.2, 152.3, 146.5, 134.1, 128.8, 117.5, 112.3, 61.1, 41.3, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{11}H_{12}NaO_4$, 231.0628; found: 231.0630.

***ethyl 2-methylene-4-oxo-4-(thiophen-2-yl)butanoate (3o)*[6]**



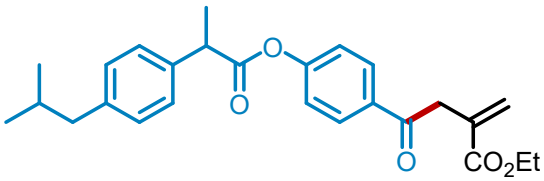
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3o**. Colorless oil (24 mg, 53% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dd, J = 3.8, 1.0 Hz, 1H), 7.67 (dd, J = 4.9, 1.0 Hz, 1H), 7.16 (dd, J = 4.9, 3.8 Hz, 1H), 6.43 (s, 1H), 5.77 (d, J = 1.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.95 (d, J = 0.5 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.6, 166.3, 143.6, 134.3, 133.9, 132.4, 128.7, 128.1, 61.1, 42.2, 14.1.

***ethyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3p)*[6]**



Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3p**, White solid (41 mg, 76% yield), mp 60 – 61 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.06 (dd, J = 8.6, 1.8 Hz, 1H), 8.00 – 7.98 (m, 1H), 7.91 (t, J = 8.5 Hz, 2H), 7.65 – 7.56 (m, 2H), 6.46 (d, J = 0.9 Hz, 1H), 5.76 (d, J = 1.1 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.16 (d, J = 0.7 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 166.5, 135.7, 135.0, 133.9, 132.5, 130.0, 129.6, 128.50, 128.49, 128.4, 127.8, 126.8, 124.0, 61.1, 41.7, 14.1.

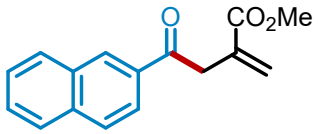
ethyl 4-(4-((2-(4-isobutylphenyl)propanoyl)oxy)phenyl)-2-methylene-4-oxobutanoate (3q)



Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **3q**. Colorless oil (31 mg, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.15 – 7.11 (m, 2H), 6.42 (d, J = 0.5 Hz, 1H), 5.70 (d, J = 0.9 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.00 – 3.95 (m, 3H), 2.50 (d, J = 7.2 Hz, 2H), 1.94 – 1.84 (m, 1H), 1.64 (d, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 0.93 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.7, 172.7, 166.3, 154.7, 141.0, 136.8, 134.7, 134.0, 129.8, 129.6, 128.5, 127.2,

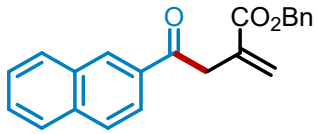
121.7, 61.1, 45.3, 45.1, 41.6, 30.2, 22.4, 18.5, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{30}NaO_5$, 445.1985; found: 445.1992.

methyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3r)



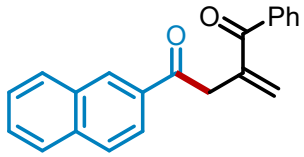
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3r**. White solid (36 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 8.4 Hz, 2H), 7.65 – 7.56 (m, 2H), 6.46 (s, 1H), 5.77 (d, *J* = 0.8 Hz, 1H), 4.17 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.8, 167.0, 135.7, 134.6, 133.8, 132.5, 130.1, 129.6, 128.7, 128.6, 128.5, 127.8, 126.8, 123.9, 52.2, 41.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}NaO_3$, 277.0835; found: 277.0839.

benzyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3s)



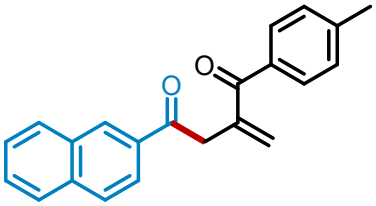
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3s**. White solid (56 mg, 84% yield), mp 76 – 77 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.66 – 7.56 (m, 2H), 7.36 – 7.30 (m, 5H), 6.53 (s, 1H), 5.81 (d, *J* = 0.8 Hz, 1H), 5.24 (s, 2H), 4.19 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.8, 166.3, 135.8, 135.7, 134.6, 133.9, 132.5, 130.1, 129.6, 129.1, 128.6, 128.51, 128.50, 128.2, 128.1, 127.8, 126.8, 124.0, 66.8, 41.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{18}NaO_3$, 353.1148; found: 353.1149.

2-methylene-4-(naphthalen-2-yl)-1-phenylbutane-1,4-dione (3t)



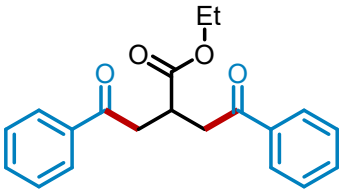
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3t**. White solid (39 mg, 65% yield), mp 102 – 103 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.97 – 7.89 (m, 4H), 7.65 – 7.56 (m, 3H), 7.51 – 7.48 (m, 2H), 6.04 (s, 1H), 5.88 (s, 1H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.4, 197.2, 142.5, 137.4, 135.7, 133.7, 132.5, 132.3, 130.2, 129.9, 129.7, 128.7, 128.6, 128.5, 128.2, 127.8, 126.8, 123.9, 42.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}O_2$, 301.1123; found: 301.1129.

2-methylene-4-(naphthalen-2-yl)-1-(p-tolyl)butane-1,4-dione (3u)



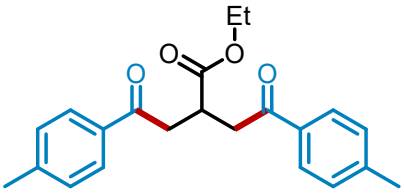
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **3u**. White solid (30 mg, 47% yield), mp 114 – 115 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.98 – 7.69 (m, 5H), 7.65 – 7.56 (m, 2H), 7.31 (s, 1H), 6.00 (s, 1H), 5.86 (s, 1H), 4.39 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.2, 197.1, 143.1, 142.5, 135.7, 134.6, 133.8, 132.5, 130.2, 130.1, 129.7, 128.9, 128.6, 128.5, 128.0, 127.8, 126.8, 123.9, 42.8, 21.7. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{22}H_{19}O_2$, 315.1380; found: 315.1387.

ethyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4a)



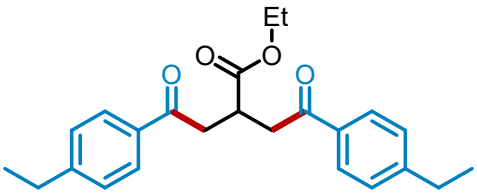
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4a**. Colorless oil (47 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.63 – 3.69 (m, 1H), 3.59 (dd, *J* = 17.8, 5.7 Hz, 2H), 3.39 (dd, *J* = 17.7, 6.3 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 174.3, 136.6, 133.3, 128.6, 128.1, 61.0, 39.5, 36.1, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{20}H_{20}NaO_4$, 347.1254; found: 347.1261.

ethyl 4-oxo-2-(2-oxo-2-(p-tolyl)ethyl)-4-(p-tolyl)butanoate (4b)



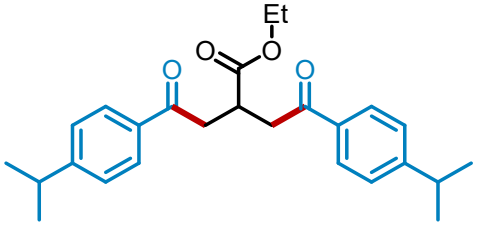
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4b**. Colorless oil (47 mg, 66% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.60 (m, 1H), 3.54 (dd, *J* = 17.7, 5.8 Hz, 2H), 3.35 (dd, *J* = 17.7, 6.4 Hz, 2H), 2.42 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 174.5, 144.1, 134.1, 129.3, 128.2, 60.9, 39.4, 36.2, 21.7, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{22}H_{24}NaO_4$, 375.1567; found: 375.1559.

ethyl 4-(4-ethylphenyl)-2-(2-(4-ethylphenyl)-2-oxoethyl)-4-oxobutanoate (4c)



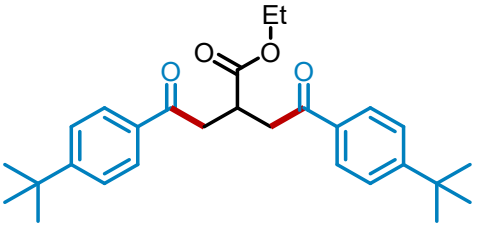
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4c**. Colorless oil (29 mg, 38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, *J* = 17.7, 5.8 Hz, 2H), 3.35 (dd, *J* = 17.6, 6.4 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 4H), 1.29 – 1.23 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 174.5, 150.3, 134.3, 128.3, 128.1, 60.9, 39.4, 36.1, 29.0, 15.2, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{28}NaO_4$, 403.1880; found: 403.1887.

ethyl 4-(4-isopropylphenyl)-2-(2-(4-isopropylphenyl)-2-oxoethyl)-4-oxobutanoate (4d)



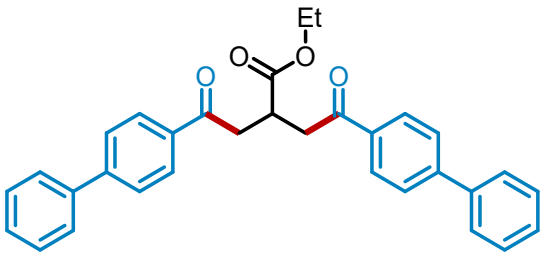
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4d**. Colorless oil (50 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.3 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, *J* = 17.7, 5.7 Hz, 2H), 3.36 (dd, *J* = 17.7, 6.4 Hz, 2H), 3.01 – 2.94 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 174.5, 154.8, 134.5, 128.4, 126.7, 60.9, 39.4, 36.2, 34.3, 23.7, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{32}NaO_4$, 431.2193; found: 431.2188.

ethyl 4-(4-(tert-butyl)phenyl)-2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-4-oxobutanoate (4e)



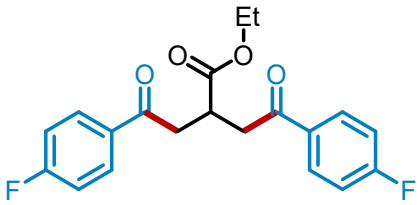
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4e**. Colorless oil (53 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.5 Hz, 4H), 7.49 (d, *J* = 8.5 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, *J* = 17.7, 5.7 Hz, 2H), 3.36 (dd, *J* = 17.6, 6.4 Hz, 2H), 1.35 (s, 18H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 174.5, 157.0, 134.0, 128.1, 125.6, 60.9, 39.4, 36.2, 35.1, 31.1, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{37}O_4$, 437.2686; found: 437.2686.

ethyl 4-([1,1'-biphenyl]-4-yl)-2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-4-oxobutanoate (4f)



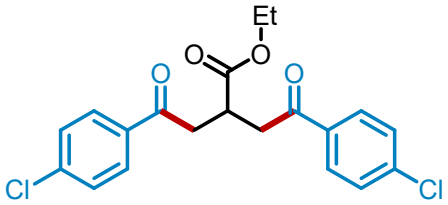
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4f**. White solid (60 mg, 63% yield), mp 85 – 86 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.06 (m, 4H), 7.74 – 7.69 (m, 4H), 7.67 – 7.62 (m, 4H), 7.54 – 7.47 (m, 4H), 7.46 – 7.39 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.75 – 3.69 (m, 1H), 3.65 (dd, *J* = 17.7, 5.7 Hz, 2H), 3.45 (dd, *J* = 17.6, 6.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 174.4, 146.0, 140.0, 135.3, 129.0, 128.7, 128.3, 127.3, 61.1, 39.6, 36.2, 14.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{29}O_4$, 477.2060; found: 477.2067.

ethyl 4-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-oxobutanoate (4g)



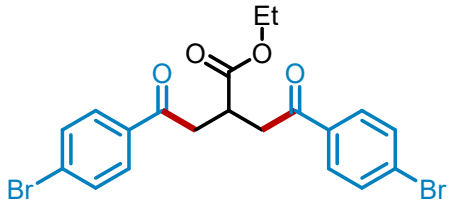
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4g**. Colorless oil (51 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.98 (m, 4H), 7.18 – 7.10 (m, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.60 (m, 1H), 3.55 (dd, *J* = 17.8, 5.7 Hz, 2H), 3.34 (dd, *J* = 17.7, 6.3 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3, 174.1, 165.9 (d, *J* = 255.1 Hz), 133.0 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.4 Hz), 115.8 (d, *J* = 21.8 Hz), 61.1, 39.3, 36.1, 14.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.72. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}F_2NaO_4$, 383.1065; found: 383.1075.

ethyl 4-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-oxobutanoate (4h)



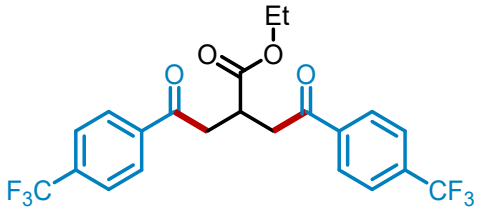
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4h**. Colorless oil (51 mg, 64% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 4H), 7.46 – 7.41 (m, 4H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.65 – 3.59 (m, 1H), 3.53 (dd, *J* = 17.9, 5.7 Hz, 2H), 3.32 (dd, *J* = 17.8, 6.3 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.7, 174.0, 139.8, 134.8, 129.5, 129.0, 61.1, 39.4, 36.0, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}Cl_2NaO_4$, 415.0474; found: 415.0488.

ethyl 4-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-oxoethyl)-4-oxobutanoate (4i)



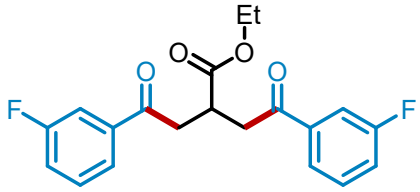
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4i**. Colorless oil (35 mg, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 4H), 7.65 – 7.59 (m, 4H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.64 – 3.60 (m, 1H), 3.54 (dd, *J* = 17.9, 5.6 Hz, 2H), 3.33 (dd, *J* = 17.8, 6.3 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 174.0, 135.2, 132.0, 130.0, 128.6, 61.1, 39.3, 36.0, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ calcd for $C_{20}H_{18}{}^{79}Br_2NaO_4$, 502.9464; found: 502.9470.

ethyl 4-oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-(4-(trifluoromethyl)phenyl)butanoate (4j)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4j**. White solid (52 mg, 56% yield), mp 88 – 89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 4H), 7.76 (d, *J* = 8.3 Hz, 4H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.66 (m, 1H), 3.62 (dd, *J* = 17.9, 5.6 Hz, 2H), 3.41 (dd, *J* = 17.8, 6.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 173.7, 139.1, 134.7 (q, *J* = 32.7 Hz), 128.4, 125.8 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.7 Hz), 61.3, 39.6, 36.0, 14.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.17. HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{22}H_{19}F_6O_4$, 461.1182; found: 461.1188.

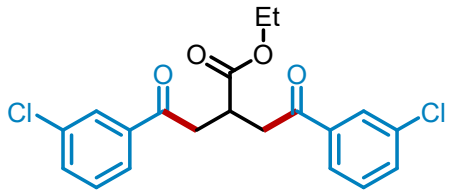
ethyl 4-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-oxoethyl)-4-oxobutanoate (4k)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4k**. Colorless oil (32 mg, 44% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.66 (dt, *J* = 9.4, 2.2 Hz, 2H), 7.47 (td, *J* = 8.0, 5.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.62 (m, 1H), 3.56 (dd, *J* = 17.9, 5.7 Hz, 2H), 3.35 (dd, *J* = 17.9, 6.3 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6 (d, *J* = 2.1 Hz), 173.9, 162.9 (d, *J* = 248.2 Hz),

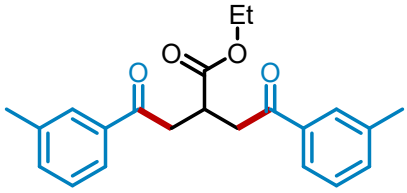
138.6 (d, J = 6.2 Hz), 130.4 (d, J = 7.6 Hz), 123.9 (d, J = 3.0 Hz), 120.4 (d, J = 21.5 Hz), 114.8 (d, J = 22.4 Hz), 61.1, 39.5, 36.0, 14.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.64. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}F_2NaO_4$, 383.1065; found: 383.1072.

ethyl 4-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-oxoethyl)-4-oxobutanoate (4l)



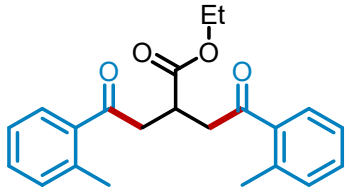
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4l**. Colorless oil (43 mg, 55% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.42 (t, J = 7.9 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, J = 18.0, 5.7 Hz, 2H), 3.34 (dd, J = 17.9, 6.3 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 173.9, 138.0, 135.0, 133.3, 130.0, 128.2, 126.2, 61.2, 39.5, 35.9, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}Cl_2NaO_4$, 415.0474; found: 415.0475.

ethyl 4-oxo-2-(2-oxo-2-(m-tolyl)ethyl)-4-(m-tolyl)butanoate (4m)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4m**. Colorless oil (45 mg, 64% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.2 Hz, 4H), 7.43 – 7.33 (m, 4H), 4.18 (q, J = 7.1 Hz, 2H), 3.68 – 3.62 (m, 1H), 3.56 (dd, J = 17.8, 5.7 Hz, 2H), 3.37 (dd, J = 17.7, 6.4 Hz, 2H), 2.42 (s, 6H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 174.4, 138.4, 136.6, 134.0, 128.6, 128.5, 125.3, 61.0, 39.6, 36.1, 21.3, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_4$, 375.1567; found: 375.1577.

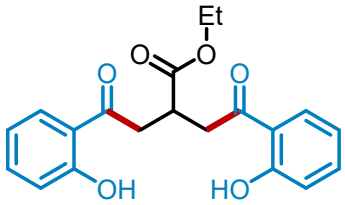
ethyl 4-oxo-2-(2-oxo-2-(o-tolyl)ethyl)-4-(o-tolyl)butanoate (4n)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4n**. Colorless oil (27 mg, 38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.40 (td, J = 7.5, 1.3 Hz, 2H), 7.31 – 7.24 (m, 4H), 4.19 (q, J = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.49 (dd, J = 17.8, 6.2 Hz, 2H), 3.27 (dd, J = 17.8, 6.3 Hz, 2H), 2.52 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

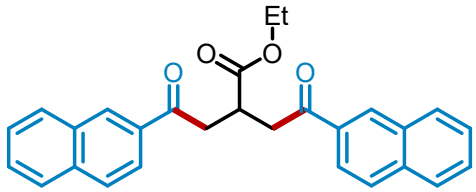
Chloroform-*d*) δ 201.7, 174.3, 138.2, 137.4, 132.0, 131.5, 128.6, 125.7, 61.0, 42.3, 36.5, 21.3, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_4$, 375.1567; found: 375.1571.

ethyl 4-(2-hydroxyphenyl)-2-(2-(2-hydroxyphenyl)-2-oxoethyl)-4-oxobutanoate (4o)



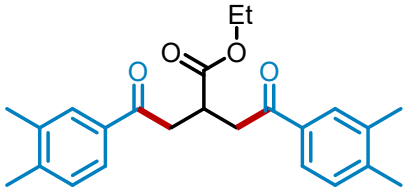
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4o**. Colorless oil (52 mg, 73% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.06 (s, 2H), 7.80 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.90 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.61 (m, 3H), 3.44 – 3.38 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.6, 173.8, 162.4, 136.7, 129.8, 119.2, 119.1, 118.6, 61.3, 39.1, 35.5, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}NaO_6$, 379.1152; found: 379.1165.

ethyl 4-(naphthalen-2-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4p)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4p**. White solid (43 mg, 51% yield), mp 92 – 93 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 2H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.90 (t, *J* = 8.0 Hz, 4H), 7.65 – 7.52 (m, 4H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 – 3.75 (m, 3H), 3.62 – 3.56 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 174.4, 135.7, 133.9, 132.5, 129.9, 129.6, 128.6, 128.5, 127.8, 126.8, 123.7, 61.1, 39.6, 36.3, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{24}NaO_4$, 447.1567; found: 447.1568.

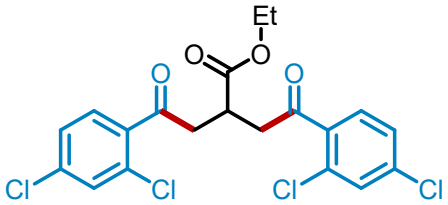
ethyl 4-(3,4-dimethylphenyl)-2-(2-(3,4-dimethylphenyl)-2-oxoethyl)-4-oxobutanoate (4q)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4q**. Colorless oil (61 mg, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 2H), 7.72 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.59 (m, 1H), 3.53 (dd, *J* = 17.7, 5.7 Hz, 2H), 3.34 (dd, *J* = 17.7, 6.5 Hz, 2H), 2.32 (s, 12H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

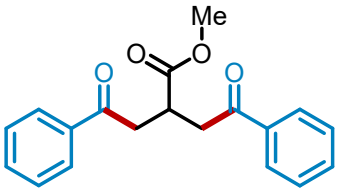
Chloroform-*d*) δ 197.8, 174.5, 142.8, 136.9, 134.5, 129.8, 129.2, 125.8, 60.9, 39.4, 36.2, 20.0, 19.8, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{28}NaO_4$, 403.1880; found: 403.1883.

ethyl 4-(2,4-dichlorophenyl)-2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-4-oxobutanoate (4r)



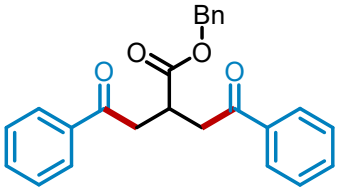
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4r**. Colorless oil (70 mg, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 2.0 Hz, 2H), 7.34 (dd, *J* = 8.3, 2.0 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.60 (m, 1H), 3.50 (dd, *J* = 18.1, 6.3 Hz, 2H), 3.31 (dd, *J* = 18.1, 6.0 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.3, 173.4, 137.7, 136.8, 132.2, 130.5, 130.4, 127.4, 61.3, 43.4, 36.6, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{16}Cl_4NaO_4$, 482.9695; found: 482.9693.

methyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4s)[9]



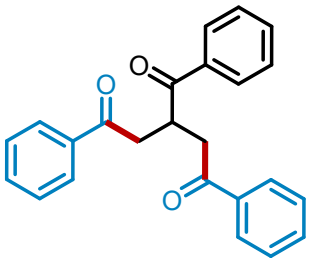
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4s**. White solid (44 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.98 (m, 4H), 7.60 – 7.56 (m, 2H), 7.49 – 7.46 (m, 4H), 3.72 (s, 3H), 3.69 – 3.65 (m, 1H), 3.60 (dd, *J* = 17.9, 5.7 Hz, 2H), 3.40 (dd, *J* = 17.8, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 174.9, 136.5, 133.4, 128.6, 128.1, 52.2, 39.5, 35.9.

benzyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4t)



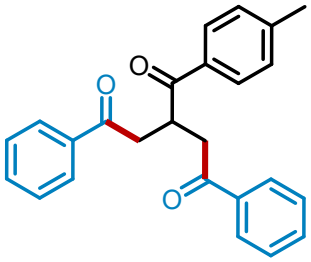
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4t**. White solid (47 mg, 61% yield), mp 65 – 66 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.97 (m, 4H), 7.61 – 7.56 (m, 2H), 7.49 – 7.45 (m, 4H), 7.34 – 7.30 (m, 5H), 5.18 (s, 2H), 3.78 – 3.72 (m, 1H), 3.62 (dd, *J* = 18.0, 5.7 Hz, 2H), 3.42 (dd, *J* = 17.9, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 174.2, 136.5, 135.8, 133.3, 128.6, 128.5, 128.11, 128.10, 66.8, 39.5, 36.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{22}NaO_4$, 409.1410; found: 409.1424.

3-benzoyl-1,5-diphenylpentane-1,5-dione (4u)[9]



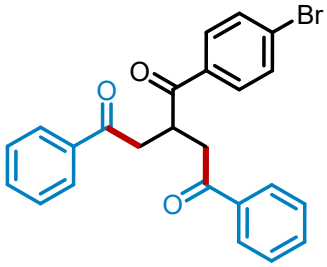
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4u**. Yellow solid (39 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.11 (m, 2H), 7.99 – 7.94 (m, 4H), 7.62 – 7.44 (m, 9H), 4.83 – 4.76 (m, 1H), 3.55 (dd, *J* = 17.9, 6.6 Hz, 2H), 3.36 (dd, *J* = 17.9, 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.4, 197.6, 136.4, 136.0, 133.4, 133.2, 128.8, 128.7, 128.6, 128.1, 40.4, 37.0.

3-(4-methylbenzoyl)-1,5-diphenylpentane-1,5-dione (4v)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4v**. Yellow solid (36 mg, 48% yield), mp 112 – 113 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.97 – 7.95 (m, 4H), 7.60 – 7.56 (m, 2H), 7.48 – 7.45 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.81 – 4.74 (m, 1H), 3.54 (dd, *J* = 17.9, 6.6 Hz, 2H), 3.35 (dd, *J* = 17.9, 6.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.0, 197.6, 144.0, 136.5, 133.4, 133.3, 129.5, 128.8, 128.6, 128.1, 40.4, 36.9, 21.7. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{25}H_{22}NaO_3$, 393.1461; found: 393.1457.

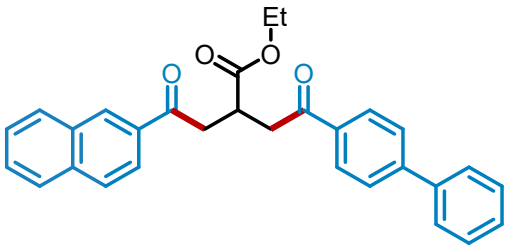
3-(4-bromobenzoyl)-1,5-diphenylpentane-1,5-dione (4w)



Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4w**. Yellow solid (48 mg, 55% yield), mp 123 – 124 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 7.3 Hz, 4H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 4H),

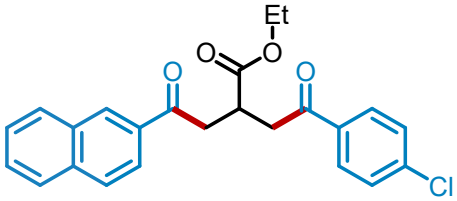
4.72 – 4.66 (m, 1H), 3.50 (dd, *J* = 17.9, 6.8 Hz, 2H), 3.34 (dd, *J* = 17.9, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.6, 197.5, 136.3, 134.9, 133.5, 132.1, 130.3, 128.7, 128.4, 128.1, 40.6, 36.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{19}{}^{79}BrNaO_3$, 457.0410; found: 457.0414.

ethyl 4-([1,1'-biphenyl]-4-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4x)



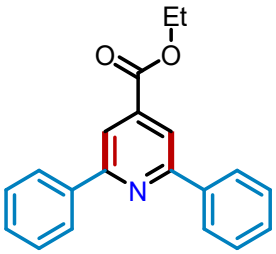
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4x**. White solid (67 mg, 75% yield), mp 77 – 78 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.14 – 8.04 (m, 3H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.53 (m, 4H), 7.53 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.67 (dd, *J* = 17.8, 5.4 Hz, 1H), 3.61 – 3.43 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 197.6, 174.4, 146.0, 139.8, 135.7, 135.3, 133.9, 132.5, 129.9, 129.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.9, 127.3, 126.8, 123.7, 61.0, 39.64, 39.61, 36.3, 14.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{26}NaO_4$, 473.1723; found: 473.1727.

ethyl 4-(4-chlorophenyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4y)



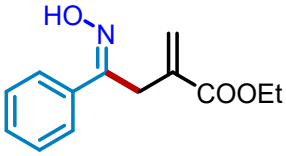
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide **4y**. Yellow oil (63 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.01 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.95 – 7.82 (m, 5H), 7.61 – 7.50 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.66 (m, 2H), 3.61 – 3.46 (m, 2H), 3.35 (dd, *J* = 17.9, 5.8 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.7, 196.8, 174.2, 139.1, 135.7, 134.9, 133.8, 132.5, 129.9, 129.6, 129.5, 128.9, 128.6, 128.5, 127.8, 126.9, 123.7, 61.1, 39.52, 39.50, 36.2, 14.1. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{21}ClNaO_4$, 431.1021; found: 431.1024.

ethyl 2,6-diphenylisonicotinate (5)[10]



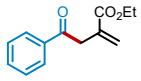
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **5**. White solid (45 mg, 75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (s, 2H), 8.27 – 8.22 (m, 4H), 7.60 – 7.53 (m, 4H), 7.52 – 7.48 (m, 2H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 157.8, 139.5, 138.7, 129.5, 128.8, 127.1, 117.8, 61.9, 14.4.

ethyl (Z)-4-(hydroxyimino)-2-methylene-4-phenylbutanoate (6)

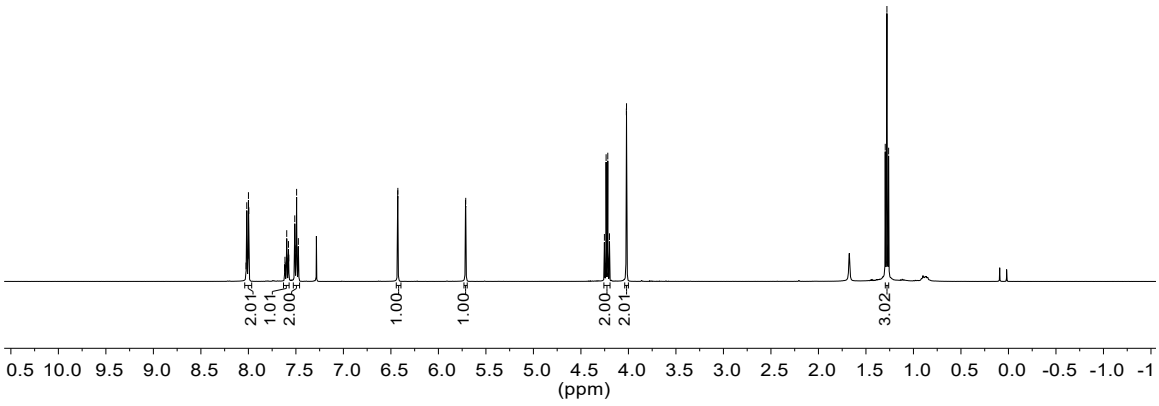


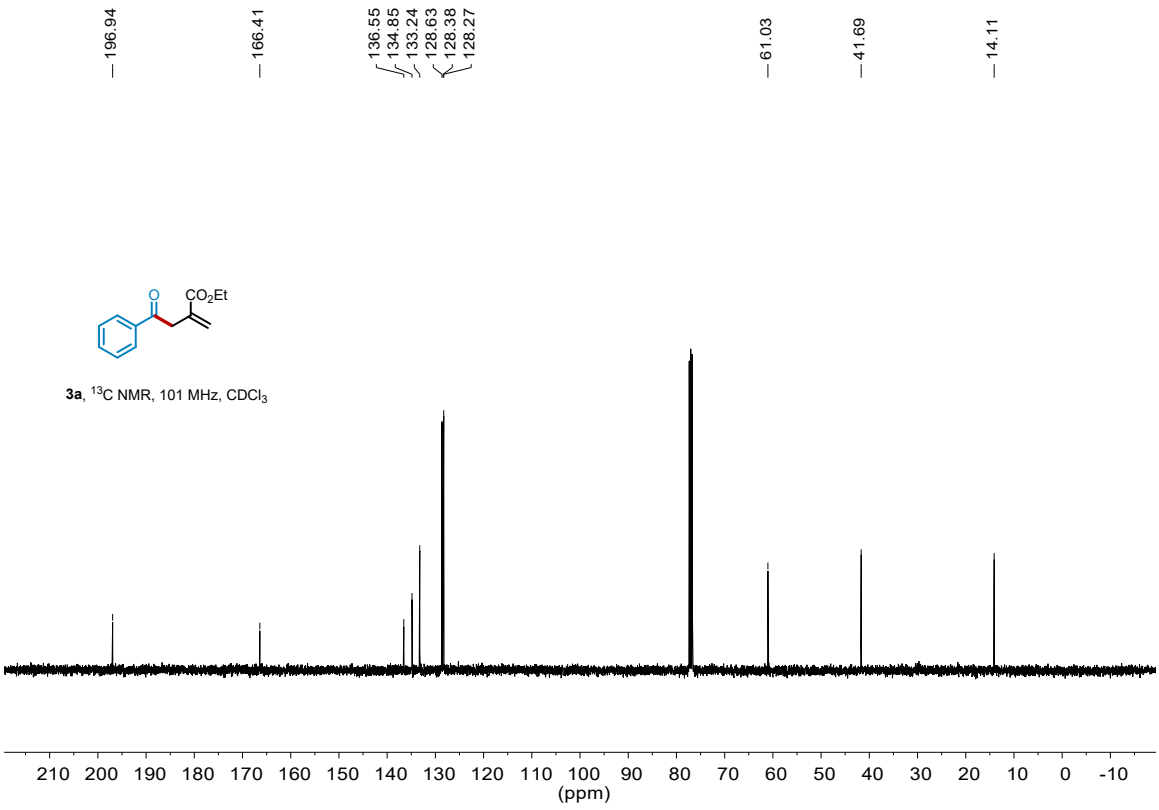
Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **6**. Colorless oil (30 mg, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 14.2 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.41 – 7.37 (m, 3H), 6.27 (d, *J* = 0.8 Hz, 1H), 5.55 (d, *J* = 0.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.88 (t, *J* = 1.6 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 156.6, 135.1, 134.8, 129.4, 128.6, 126.3, 125.8, 61.1, 28.3, 14.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{16}O_3$, 234.1125; found: 234.1136.

4. NMR Copies of Products

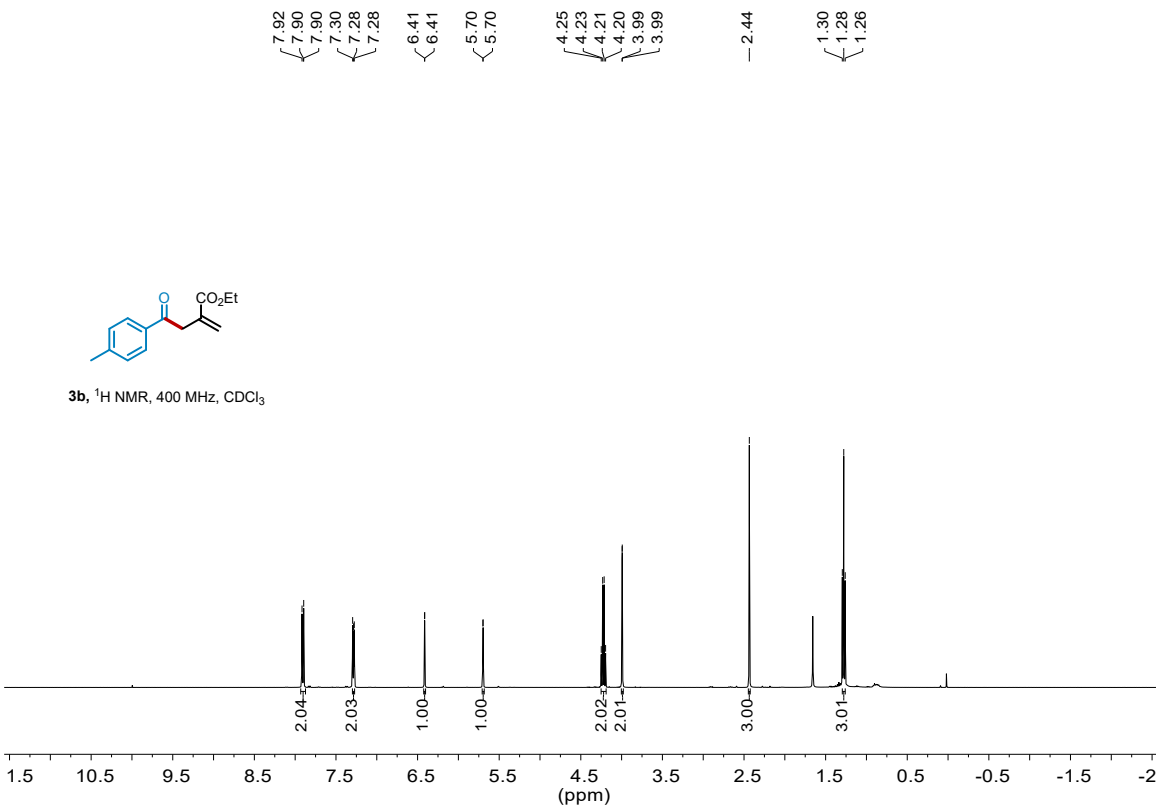


3a, ^{1}H NMR, 400 MHz, $CDCl_3$

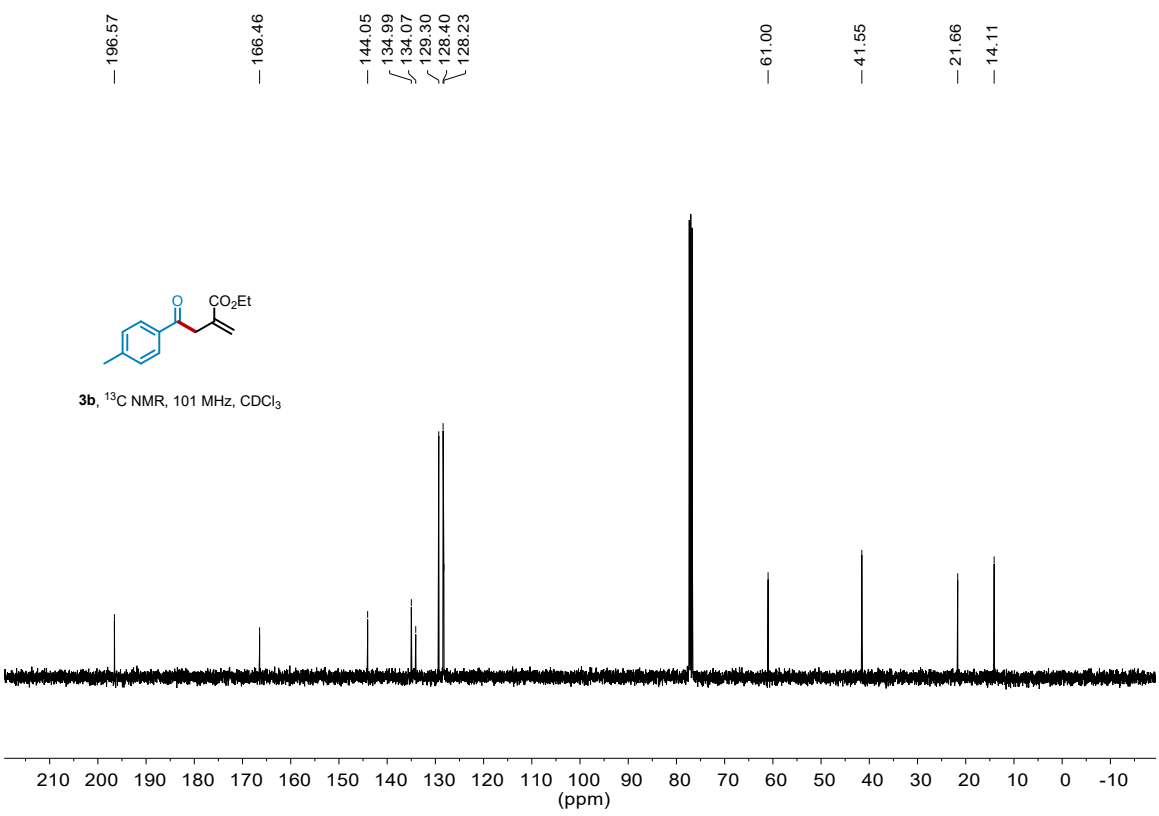




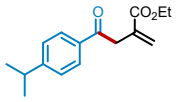
3a, ^{13}C NMR, 101 MHz, $CDCl_3$



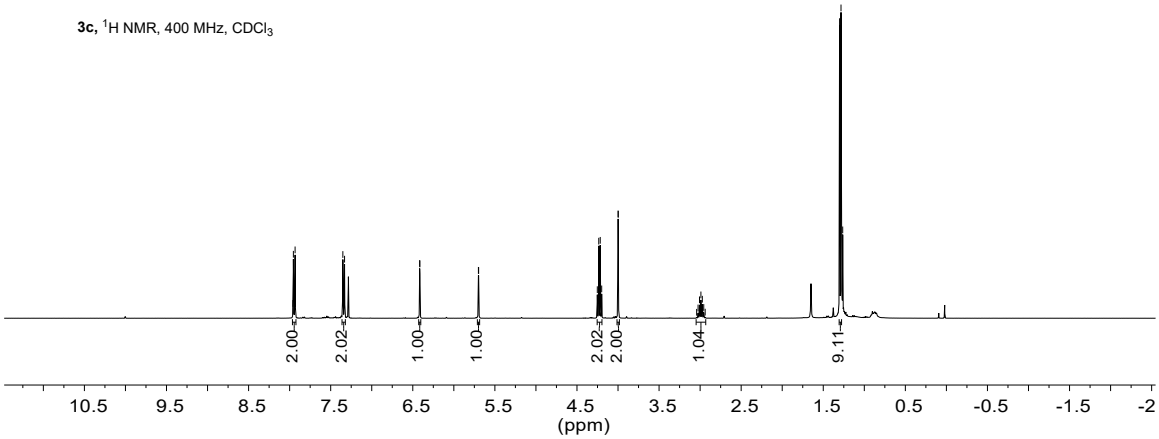
3b, ^{1}H NMR, 400 MHz, $CDCl_3$

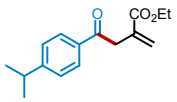


3b, ^{13}C NMR, 101 MHz, $CDCl_3$

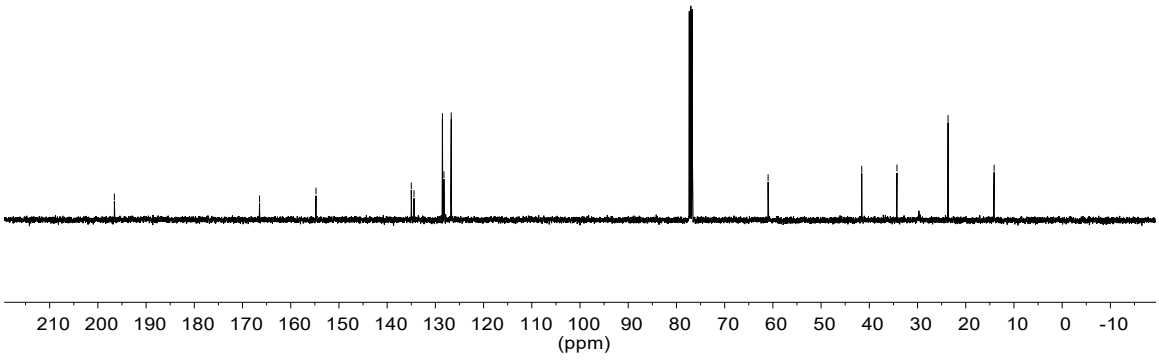


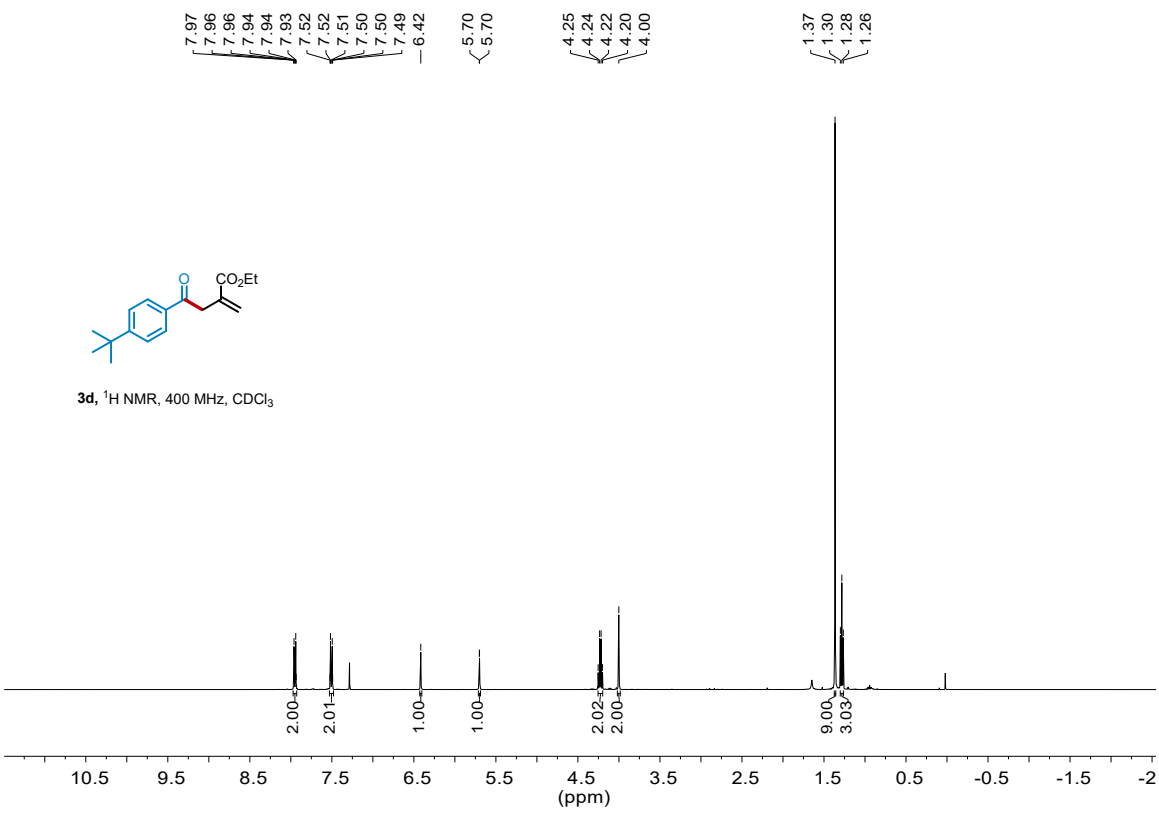
3c, ^{1}H NMR, 400 MHz, $CDCl_3$



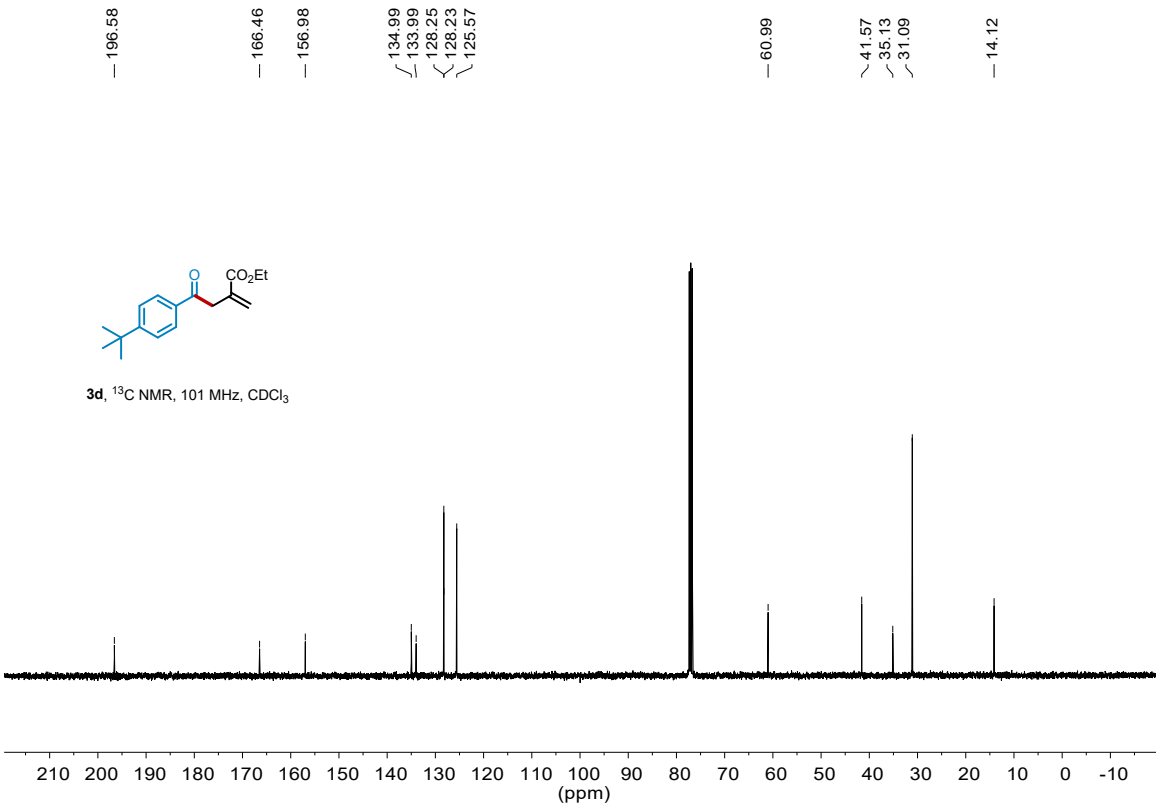


3c, ^{13}C NMR, 101 MHz, $CDCl_3$

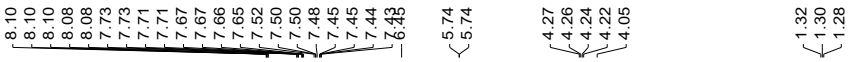


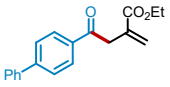


3d, ^{1}H NMR, 400 MHz, $CDCl_3$

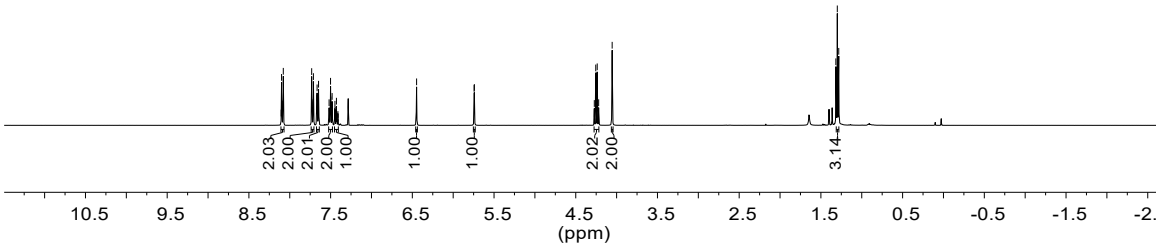


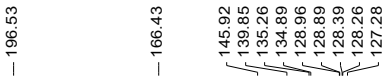
3d, ^{13}C NMR, 101 MHz, $CDCl_3$

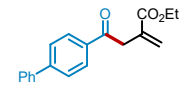




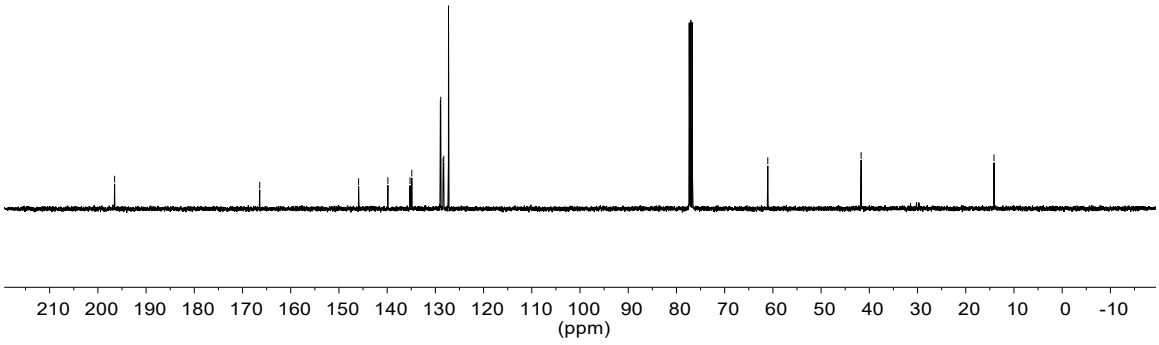
3e, ^{1}H NMR, 400 MHz, $CDCl_3$

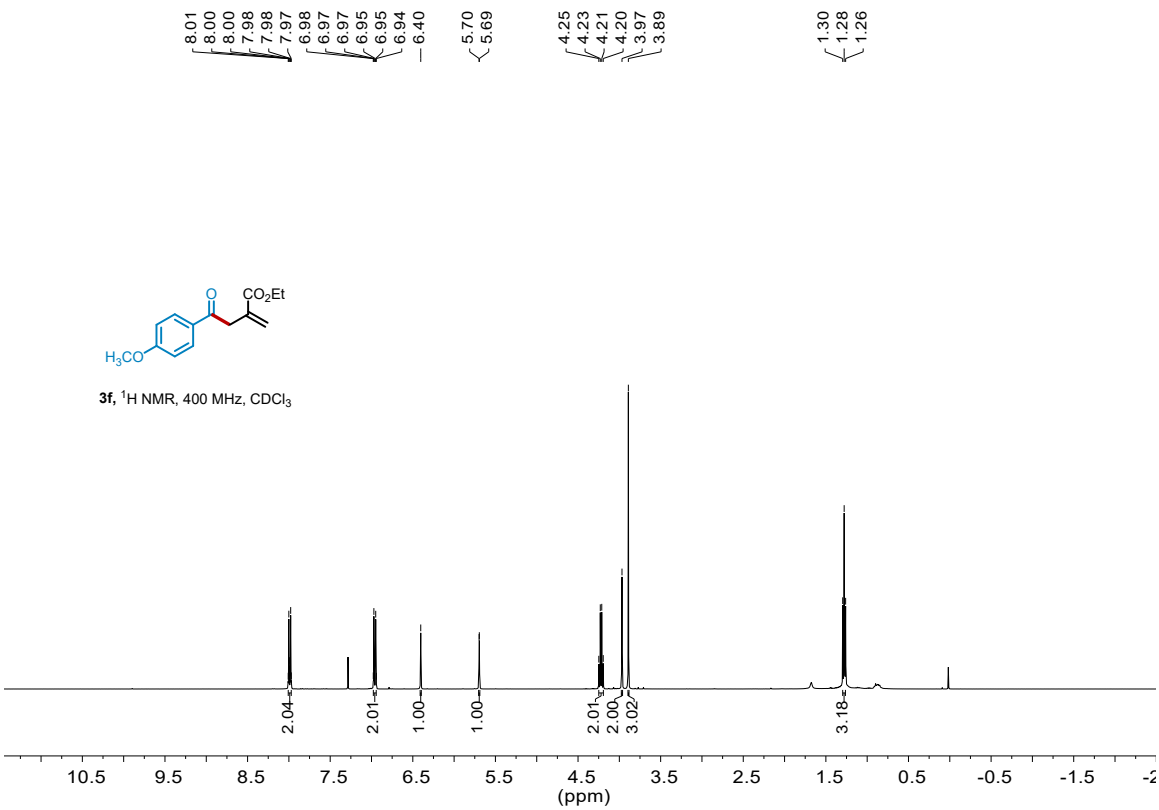




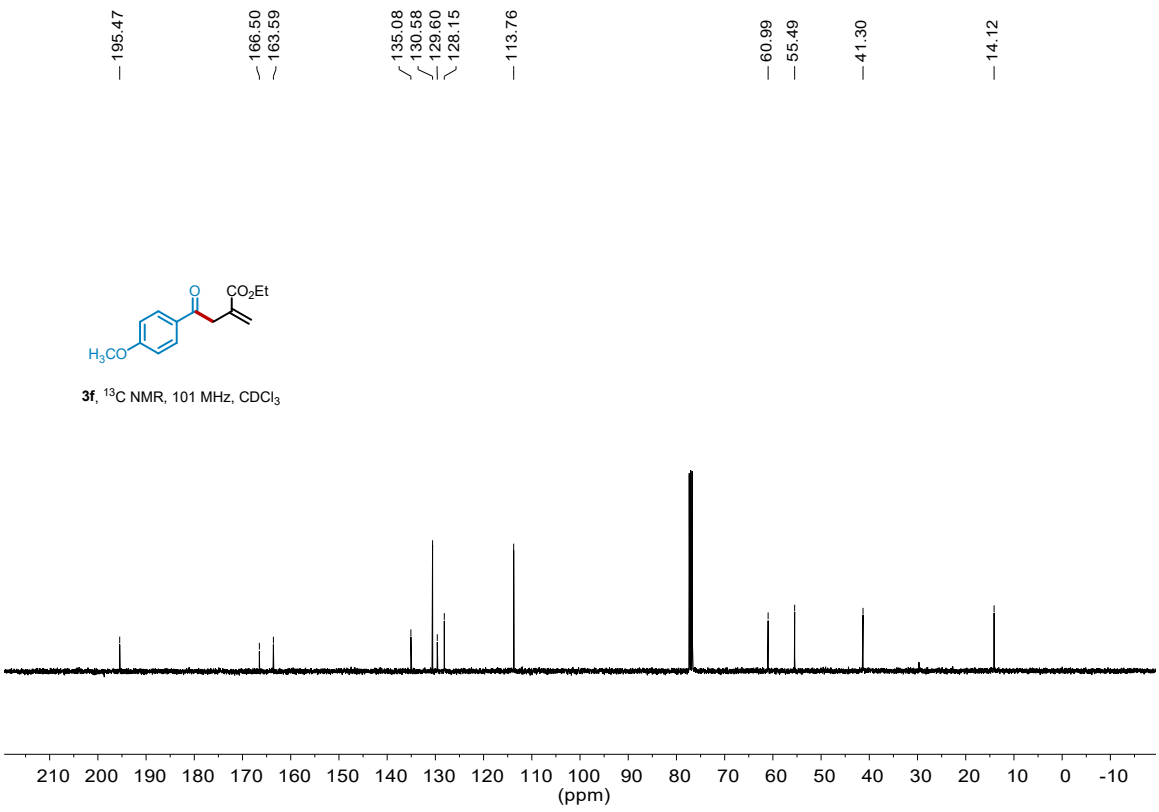


3e, ^{13}C NMR, 101 MHz, $CDCl_3$

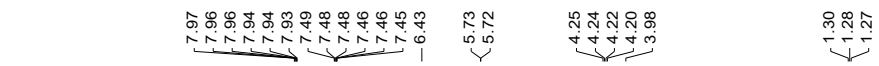


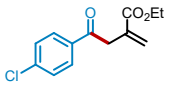


3f, ^{1}H NMR, 400 MHz, $CDCl_3$

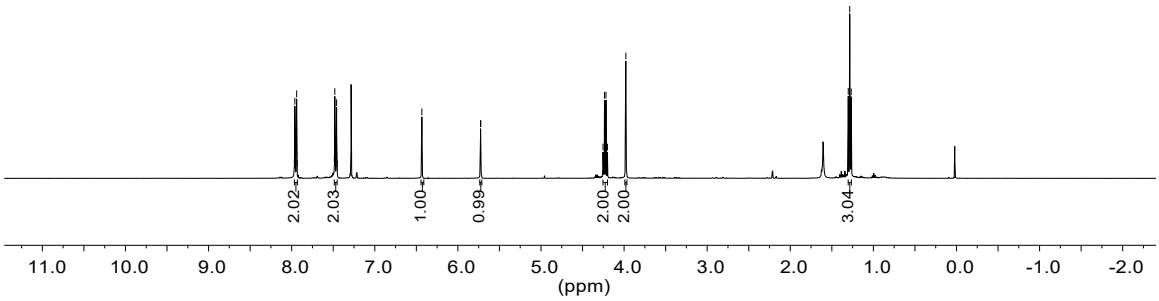


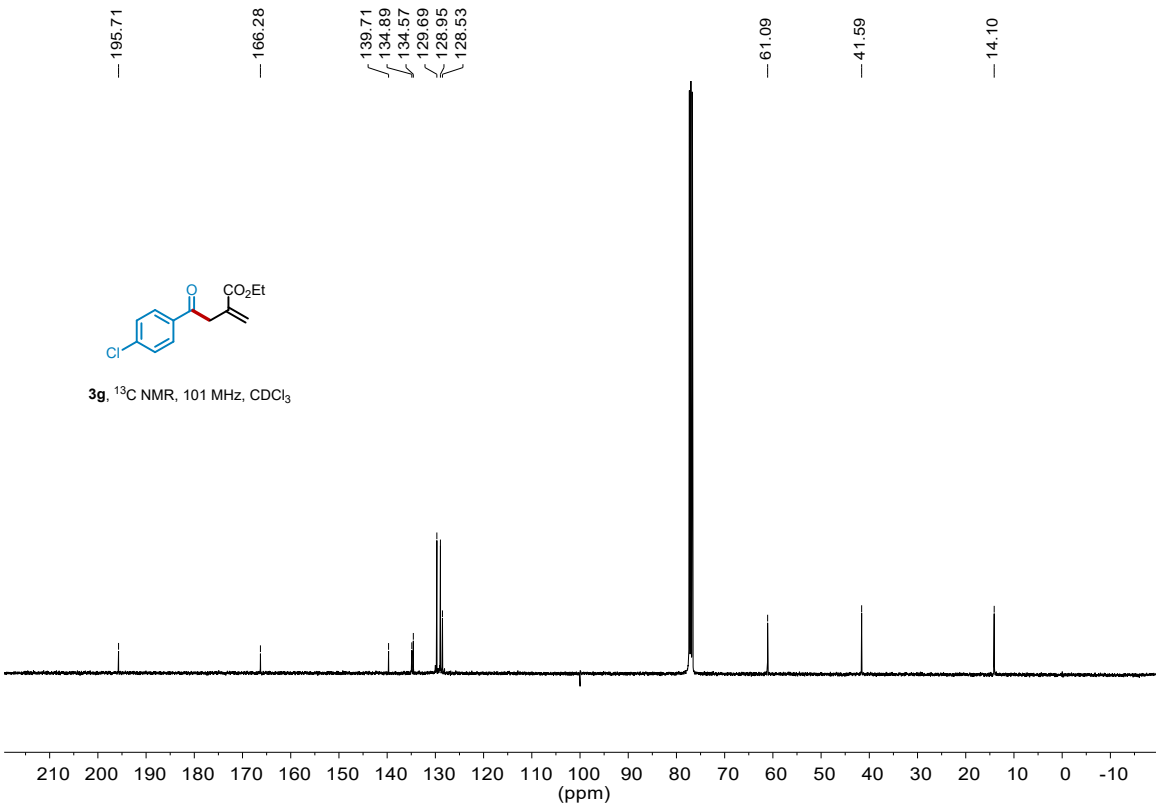
3f, ^{13}C NMR, 101 MHz, $CDCl_3$



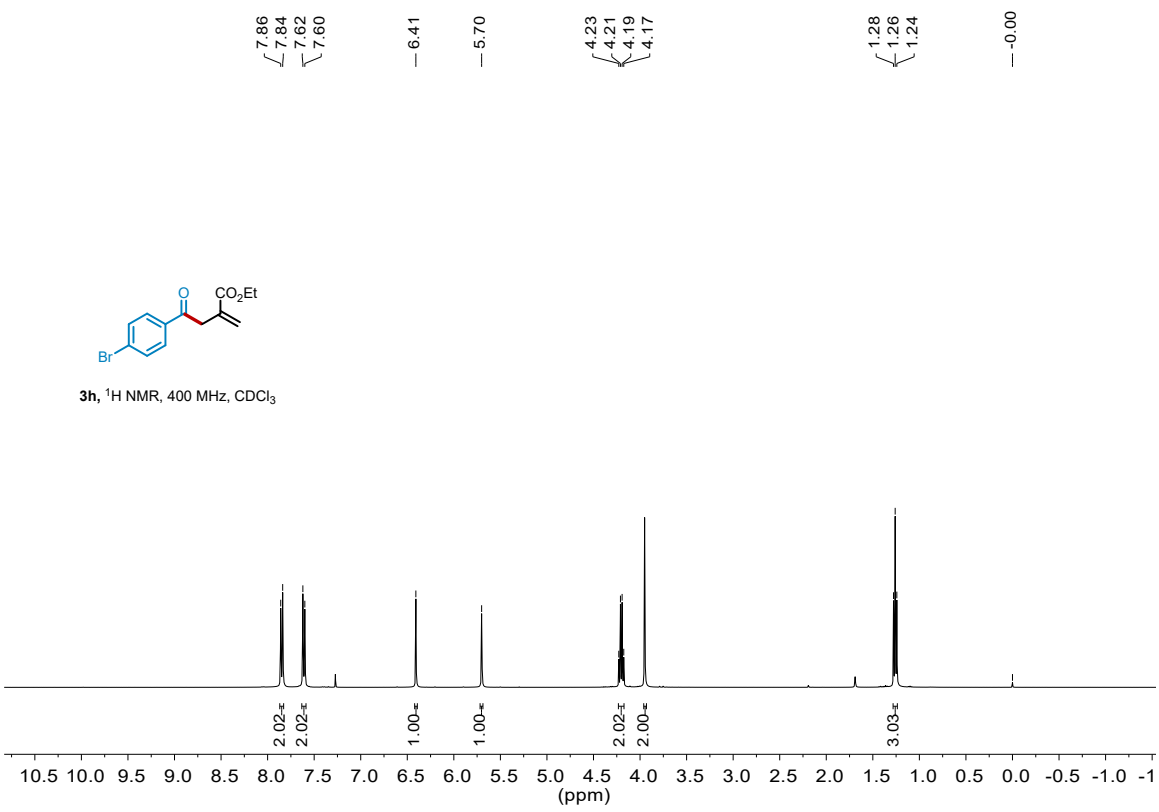


3g, ^{1}H NMR, 400 MHz, $CDCl_3$

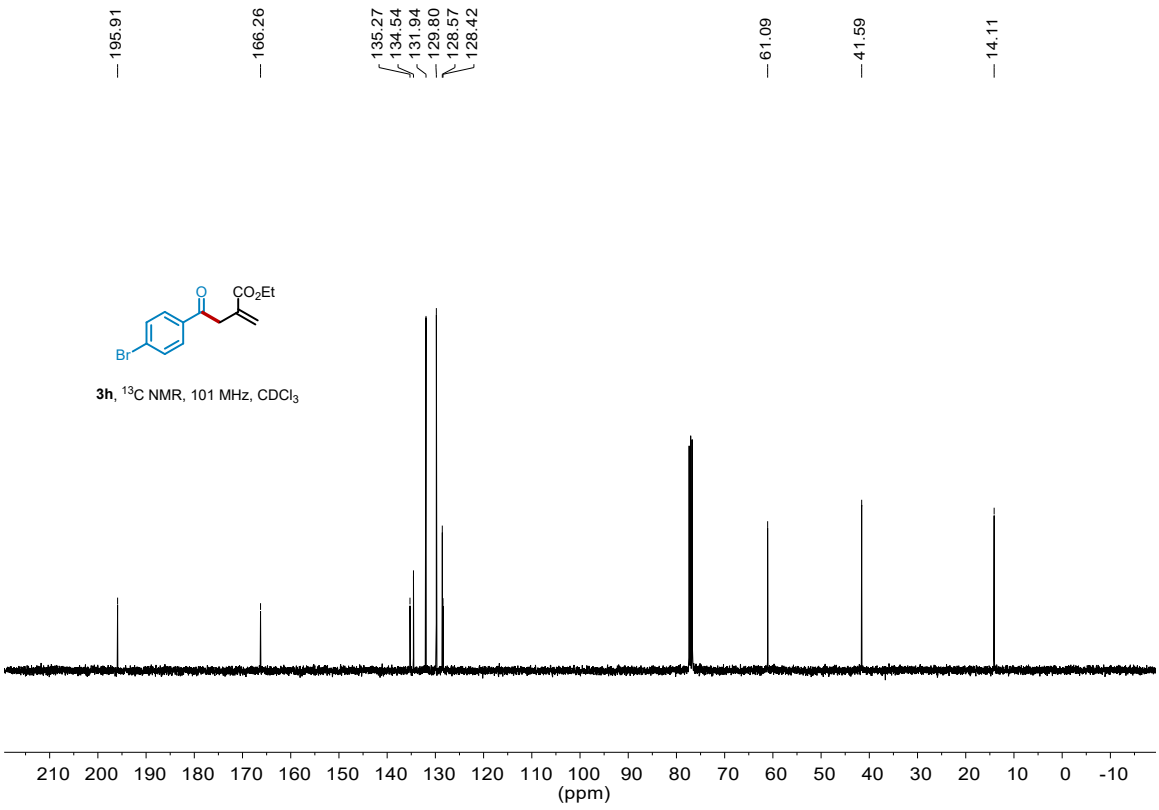




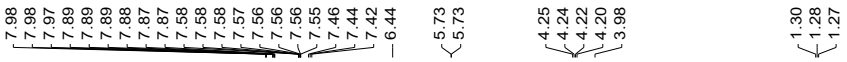
3g, ^{13}C NMR, 101 MHz, $CDCl_3$

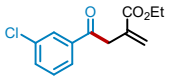


3h, ^{1}H NMR, 400 MHz, $CDCl_3$

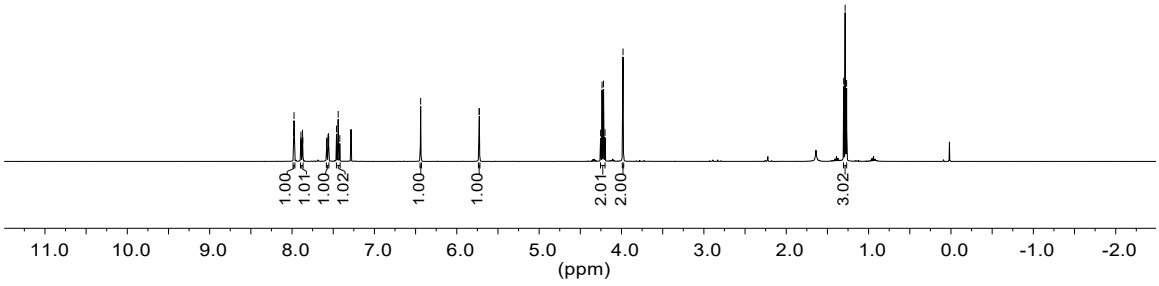


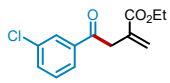
3h, ^{13}C NMR, 101 MHz, $CDCl_3$



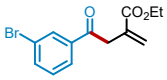


3i, ^{1}H NMR, 400 MHz, $CDCl_3$

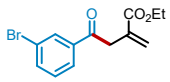




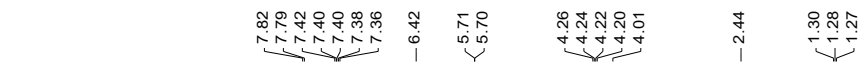
3i, ^{13}C NMR, 101 MHz, $CDCl_3$

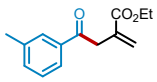


3j, ^{1}H NMR, 400 MHz, $CDCl_3$

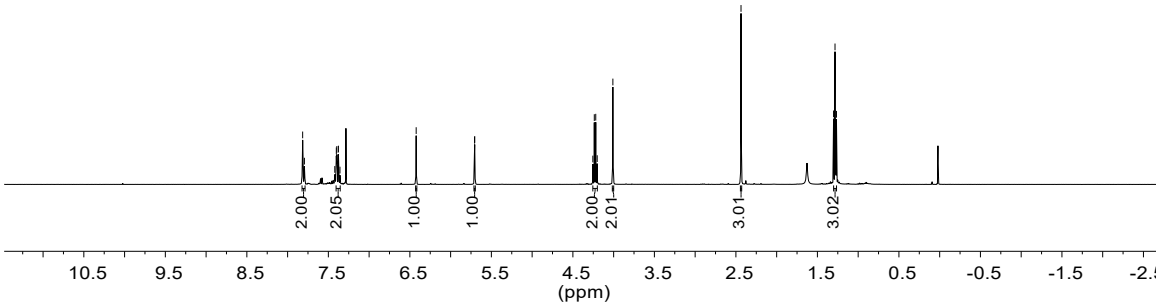


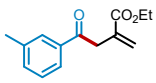
3j, ^{13}C NMR, 101 MHz, $CDCl_3$



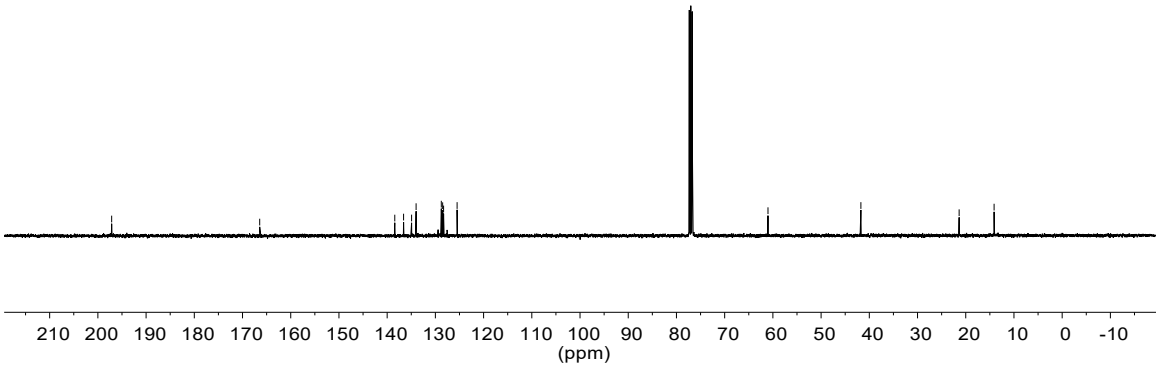


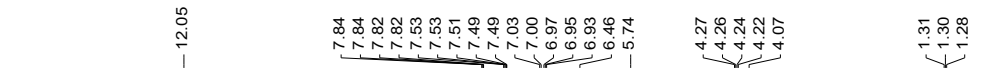
3k, ^{1}H NMR, 400 MHz, $CDCl_3$

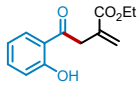




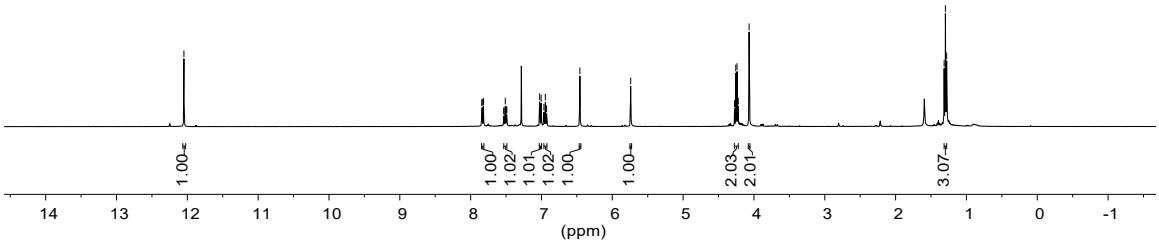
3k, ^{13}C NMR, 101 MHz, $CDCl_3$

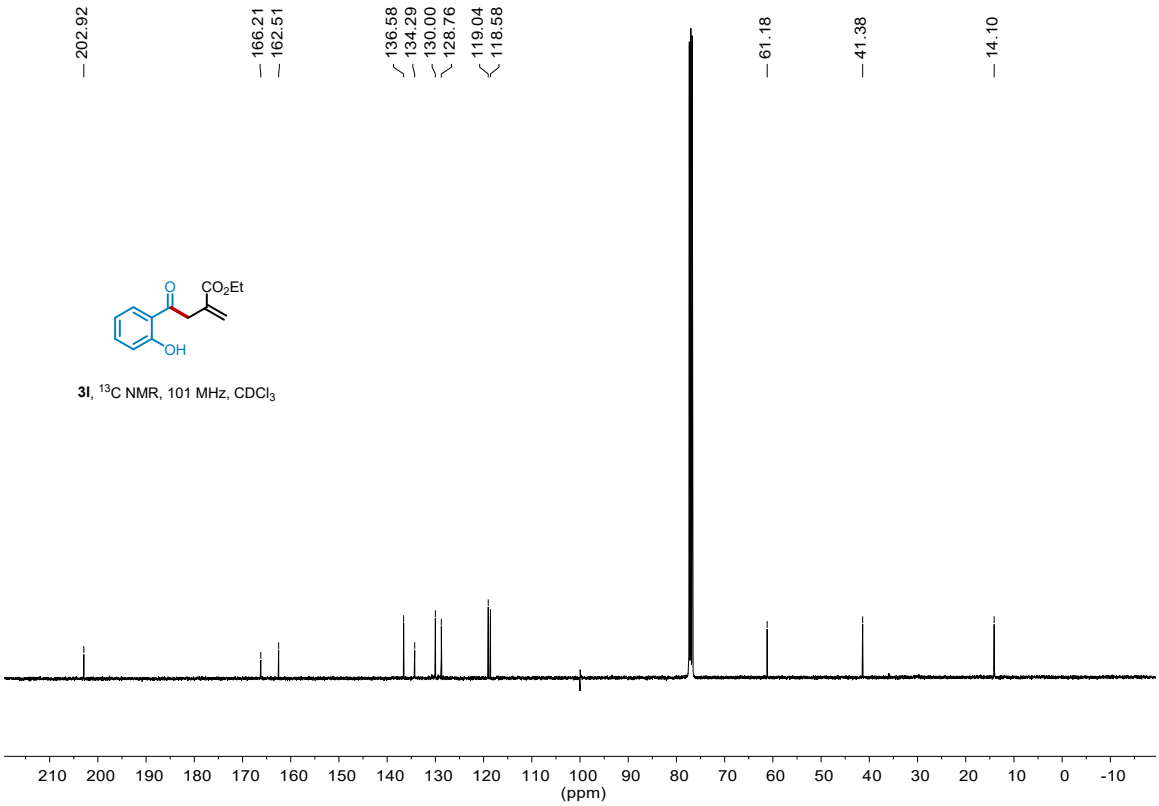




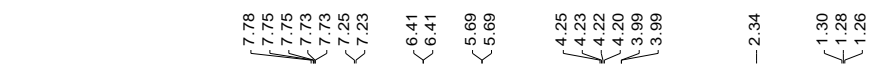


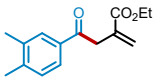
3l, ^{1}H NMR, 400 MHz, $CDCl_3$



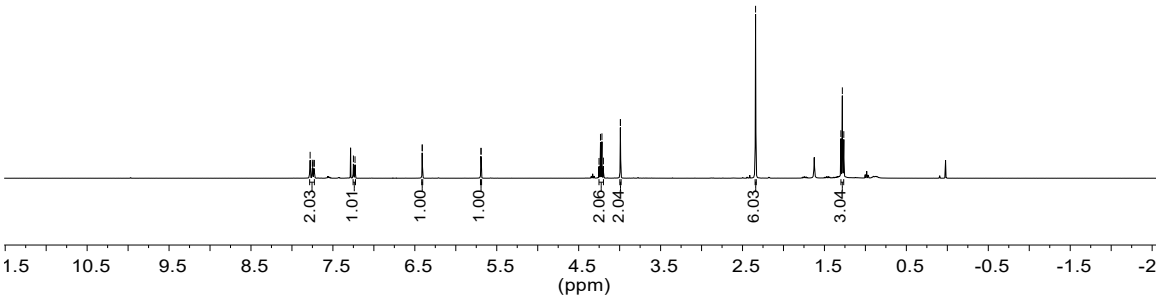


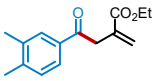
3l, ^{13}C NMR, 101 MHz, $CDCl_3$



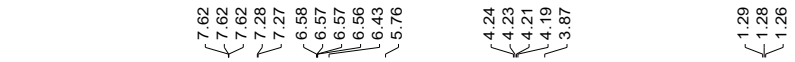


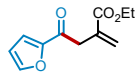
3m, ^{1}H NMR, 400 MHz, $CDCl_3$



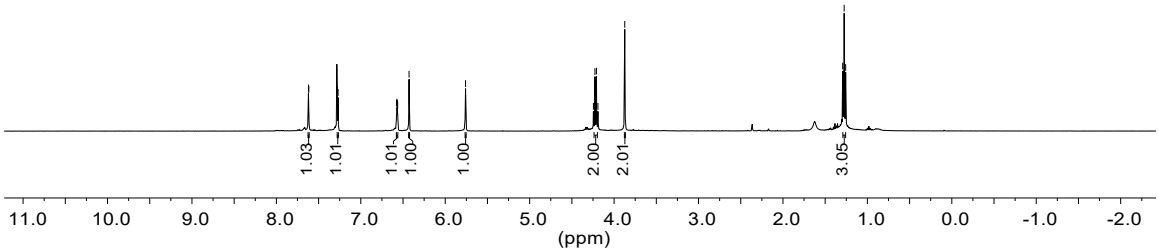


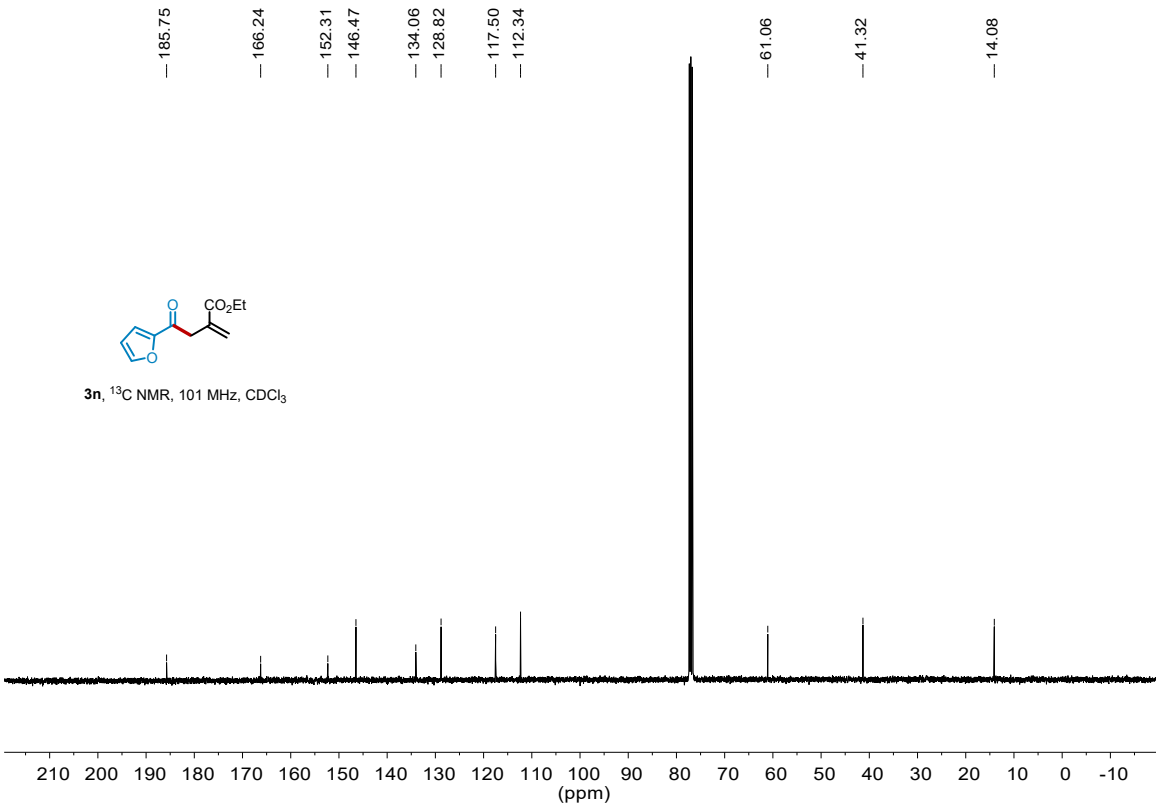
3m, ^{13}C NMR, 101 MHz, $CDCl_3$



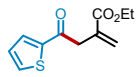


3n, ^{1}H NMR, 400 MHz, $CDCl_3$

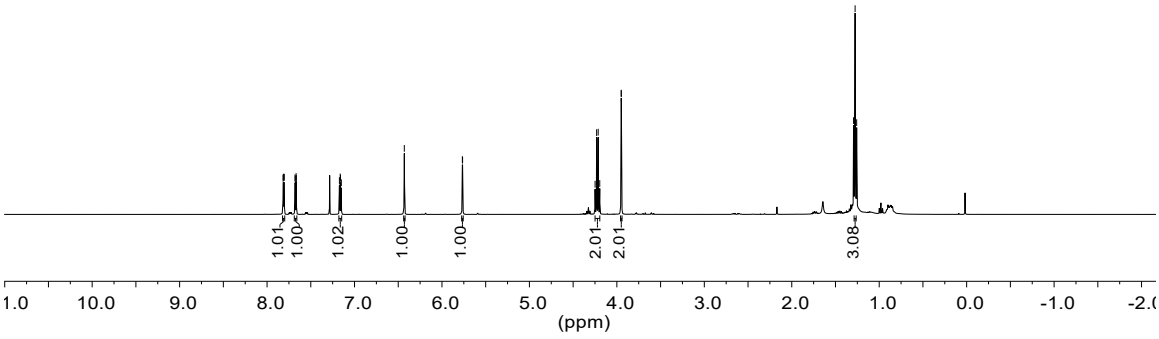


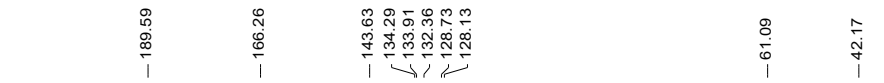


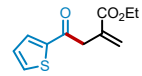
3n, ^{13}C NMR, 101 MHz, $CDCl_3$



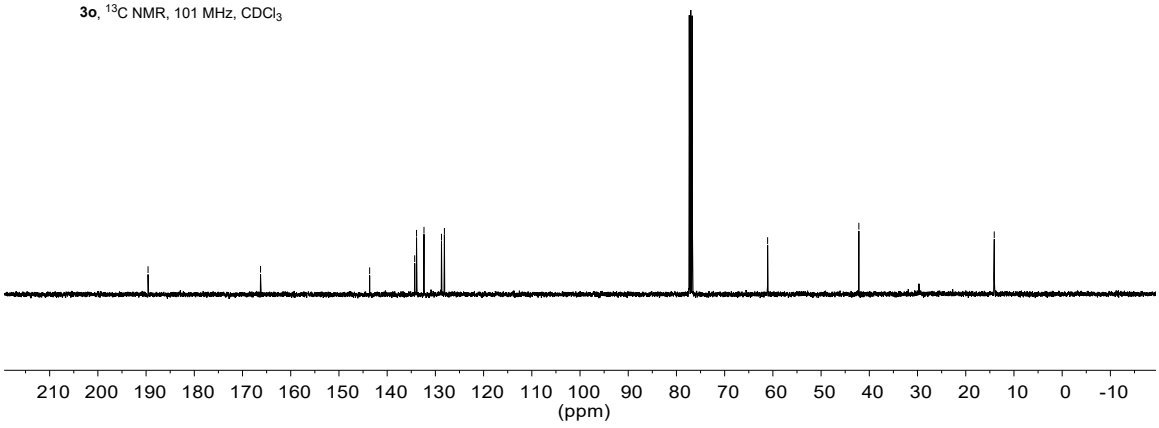
3o, ^{1}H NMR, 400 MHz, $CDCl_3$

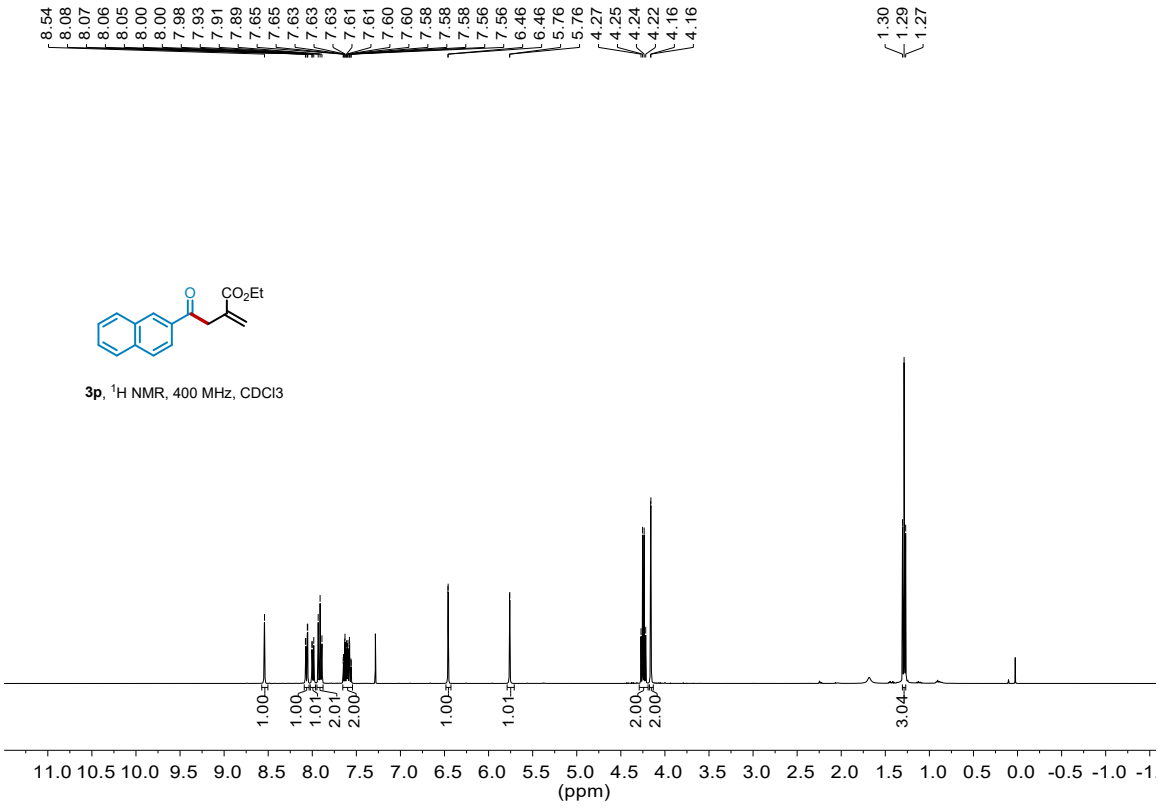






3o, ^{13}C NMR, 101 MHz, $CDCl_3$

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8.08
8.07
8.06
8.05
8.00
8.00
7.98
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7.91
7.89
7.65
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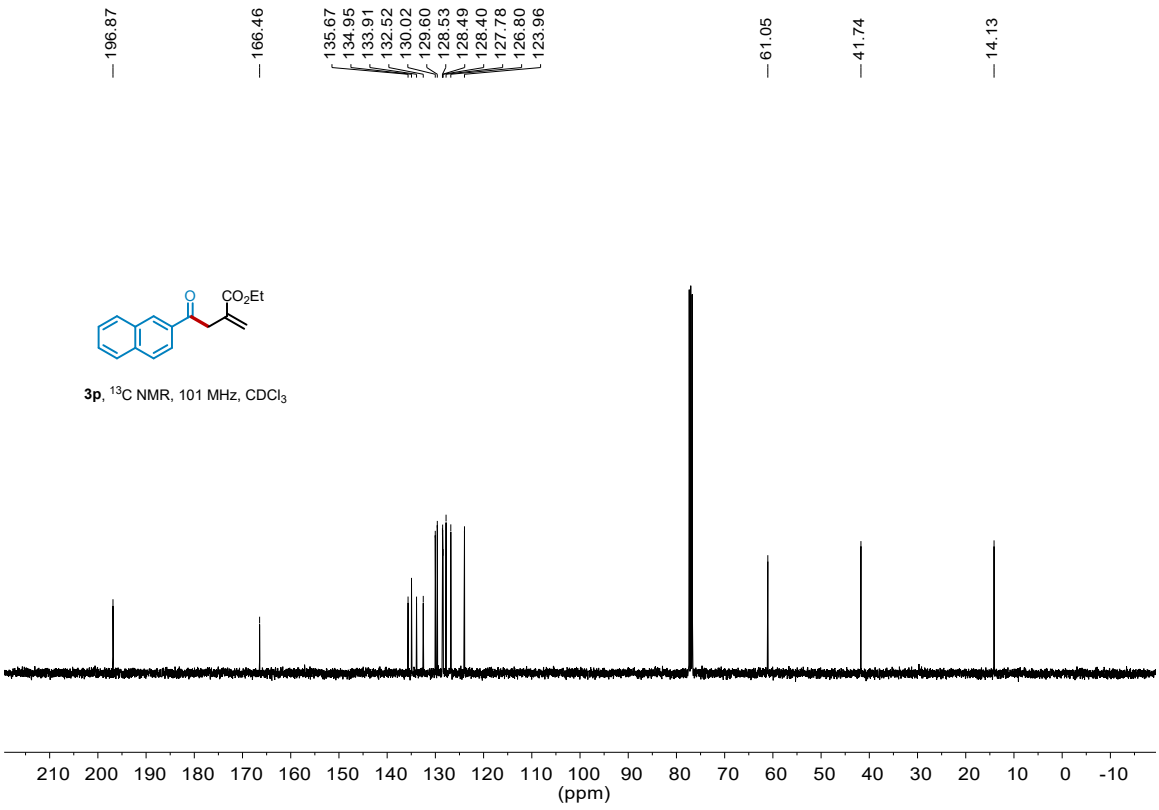
7.63
7.63
7.63
7.61
7.61
7.60
7.60
7.58
7.58
7.56
7.56
6.46
6.46
5.76
5.76
4.27
4.25
4.24
4.22
4.16
4.16
1.30
1.29
1.27
CO2Et
3p, 1H NMR, 400 MHz, CDCl3
1.00
1.00
1.01
2.01
2.00
1.00
1.01
2.00
2.00
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
(ppm)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166.46
135.67
134.95
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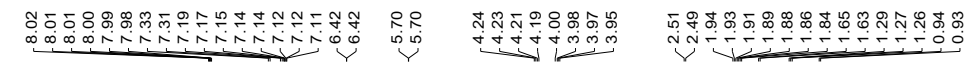
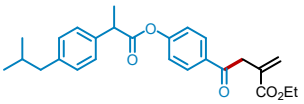
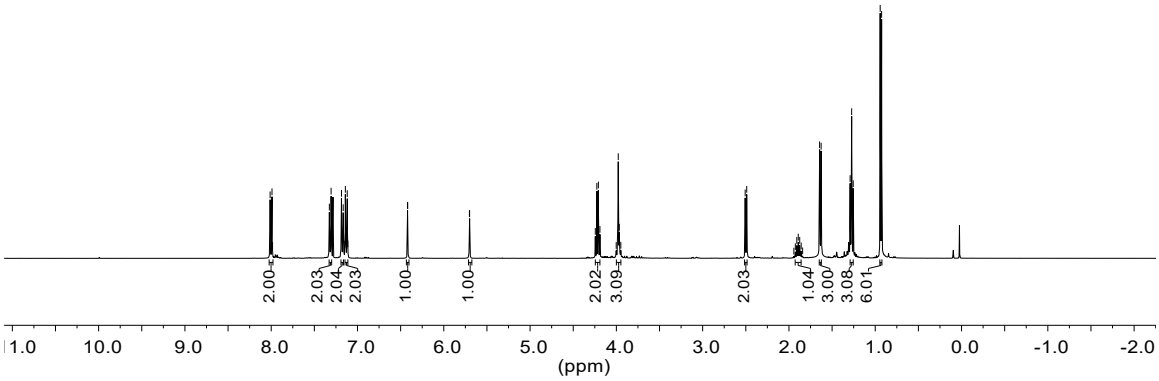
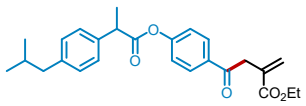
130.02
129.60
128.53
128.49
128.40
127.78
126.80
123.96
61.05
41.74
14.13
CO2Et
3p, 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)



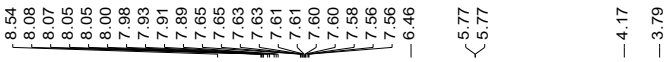


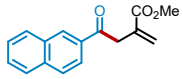
3q, ^{1}H NMR, 400 MHz, $CDCl_3$



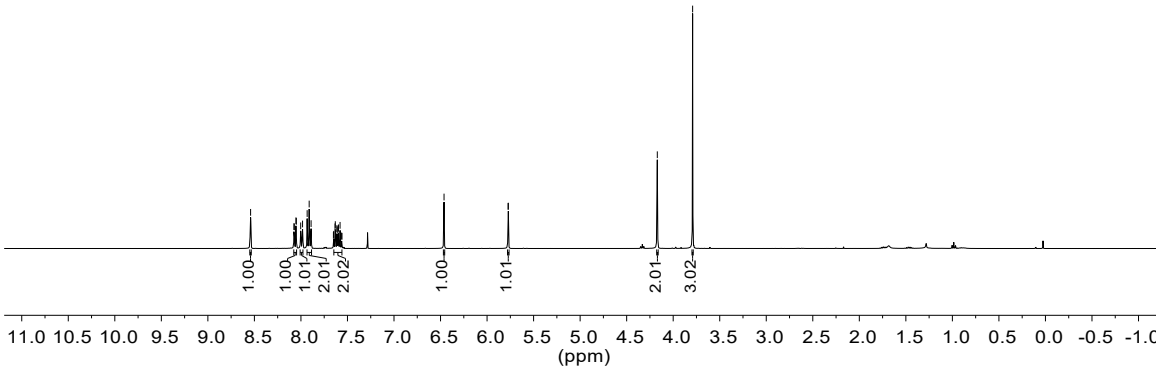


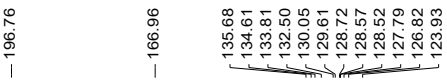
3q, ^{13}C NMR, 101 MHz, $CDCl_3$

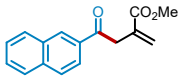




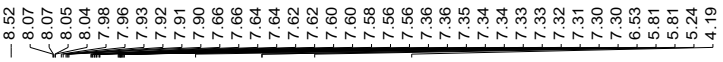
3r, ^{1}H NMR, 400 MHz, $CDCl_3$

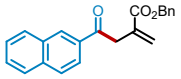




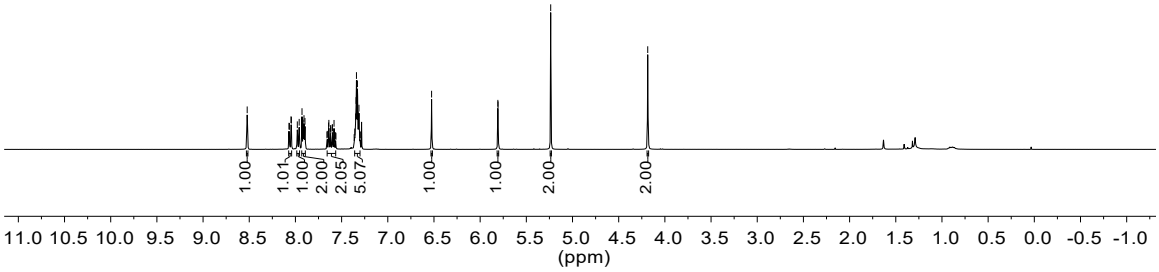


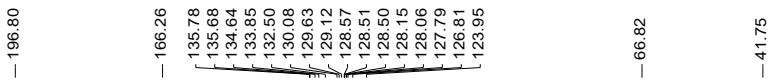
3r, ^{13}C NMR, 101 MHz, $CDCl_3$

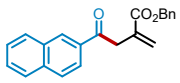




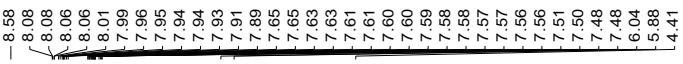
3s, ^{1}H NMR, 400 MHz, $CDCl_3$

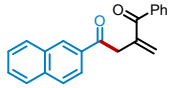




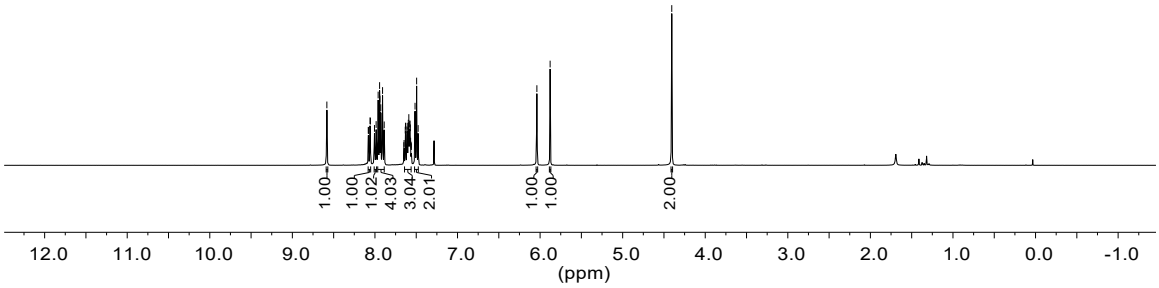


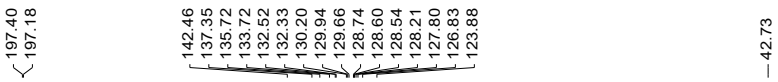
3s, ^{13}C NMR, 101 MHz, $CDCl_3$

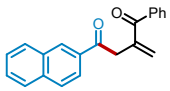




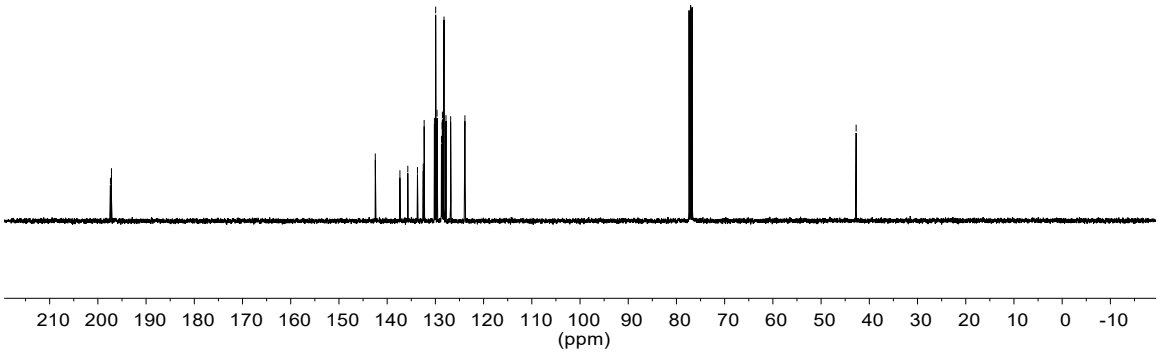
3t, ^{1}H NMR, 400 MHz, $CDCl_3$

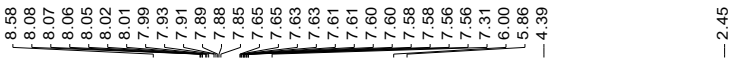


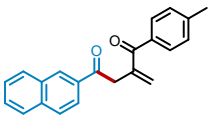




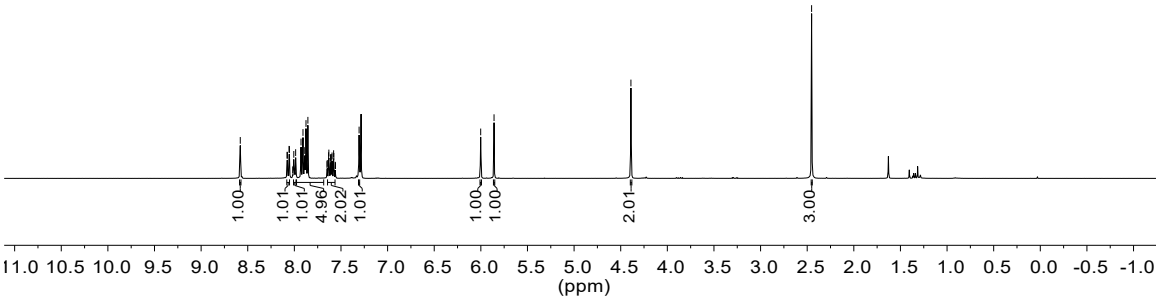
3t, ^{13}C NMR, 101 MHz, $CDCl_3$

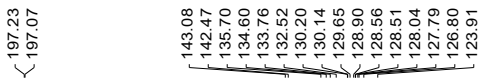


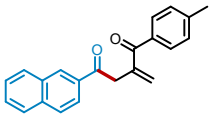




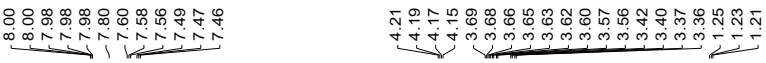
3u, ^{1}H NMR, 400 MHz, $CDCl_3$

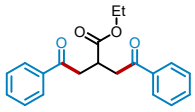




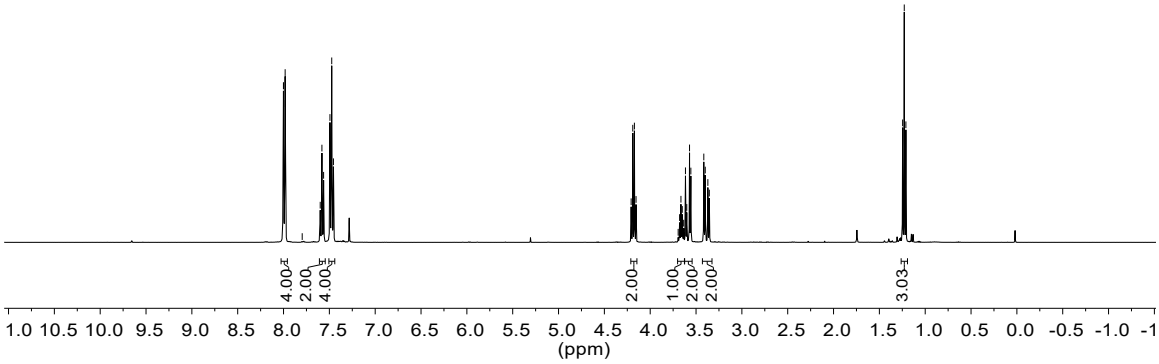


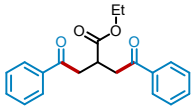
3u, ^{13}C NMR, 101 MHz, $CDCl_3$



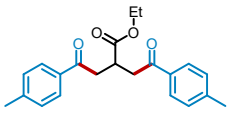


4a, ^{1}H NMR, 400 MHz, $CDCl_3$

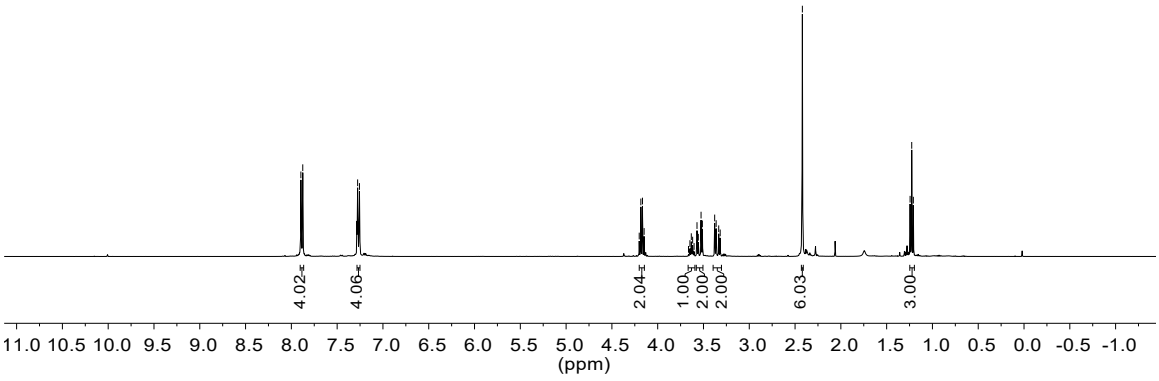


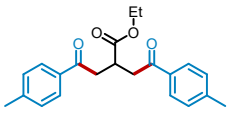


4a, ^{13}C NMR, 101 MHz, $CDCl_3$

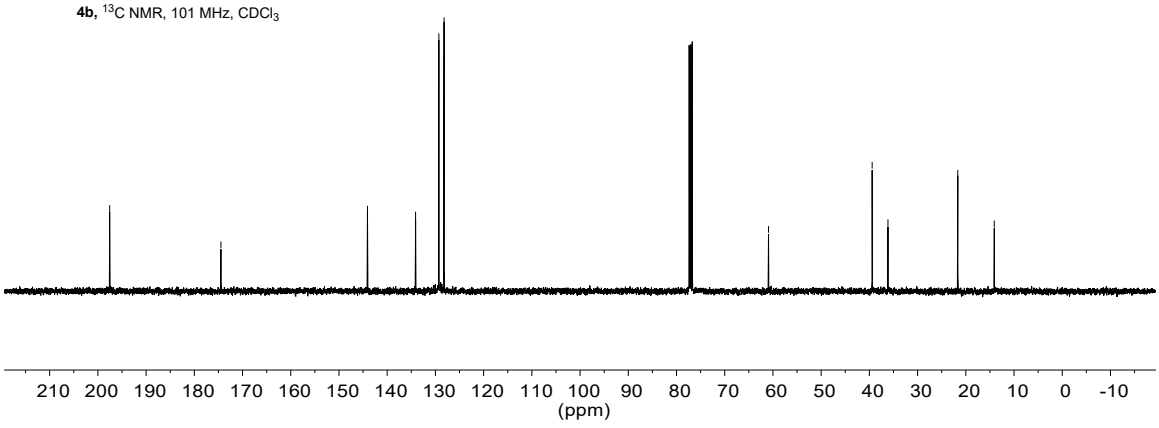


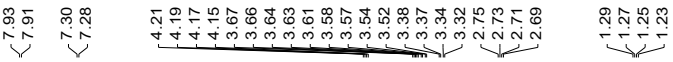
4b, ^{1}H NMR, 400 MHz, $CDCl_3$

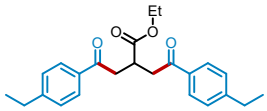




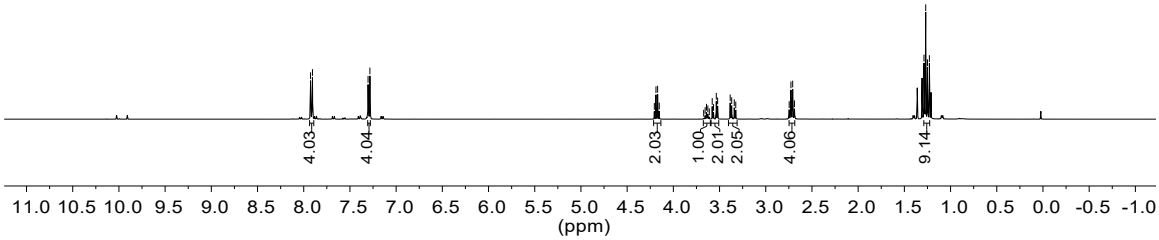
4b, ^{13}C NMR, 101 MHz, $CDCl_3$

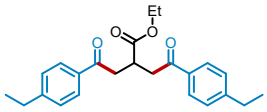




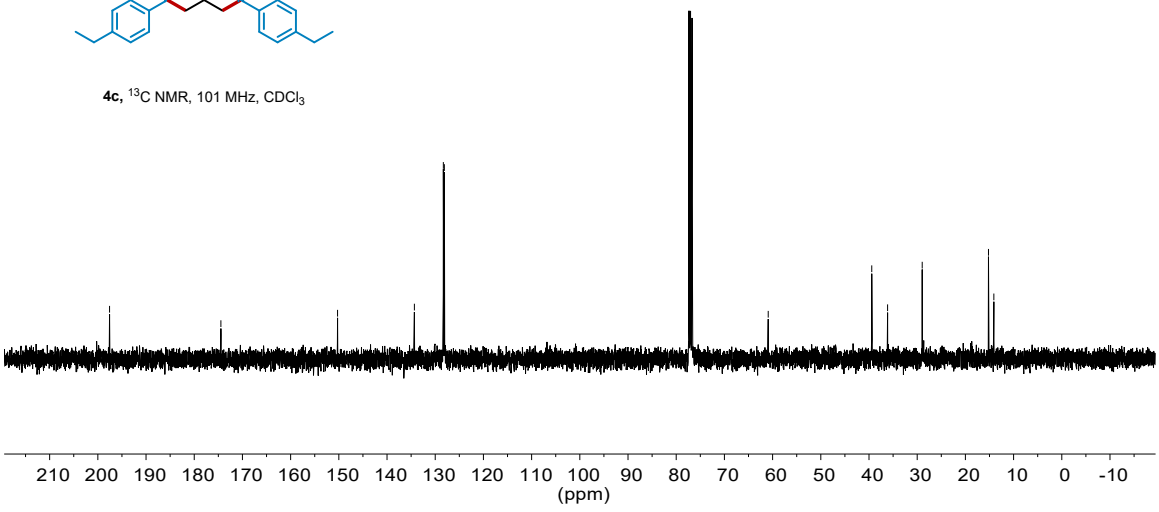


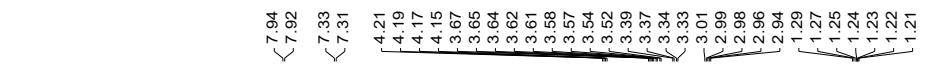
4c, ^{1}H NMR, 400 MHz, $CDCl_3$

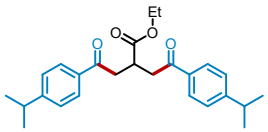




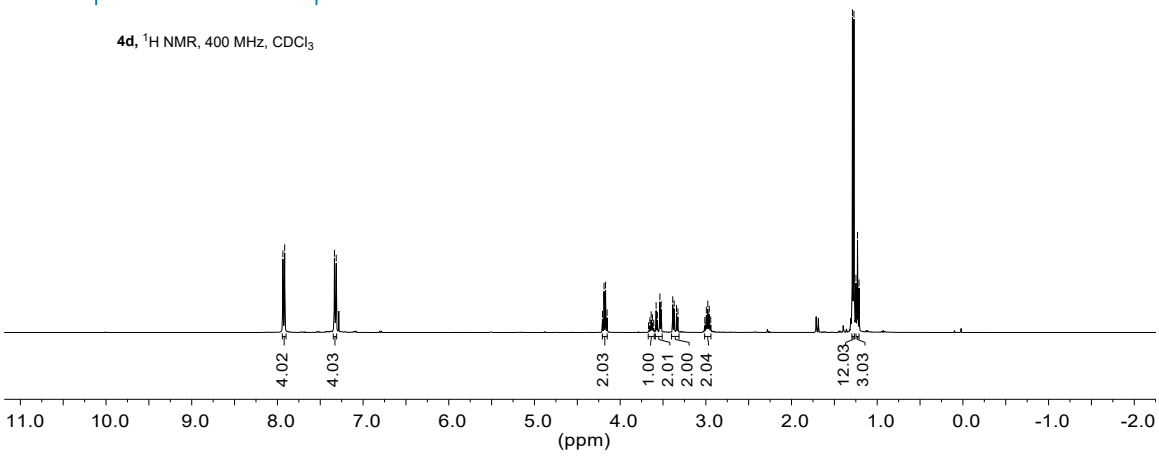
4c, ^{13}C NMR, 101 MHz, $CDCl_3$

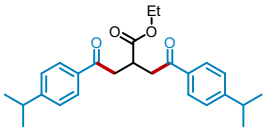




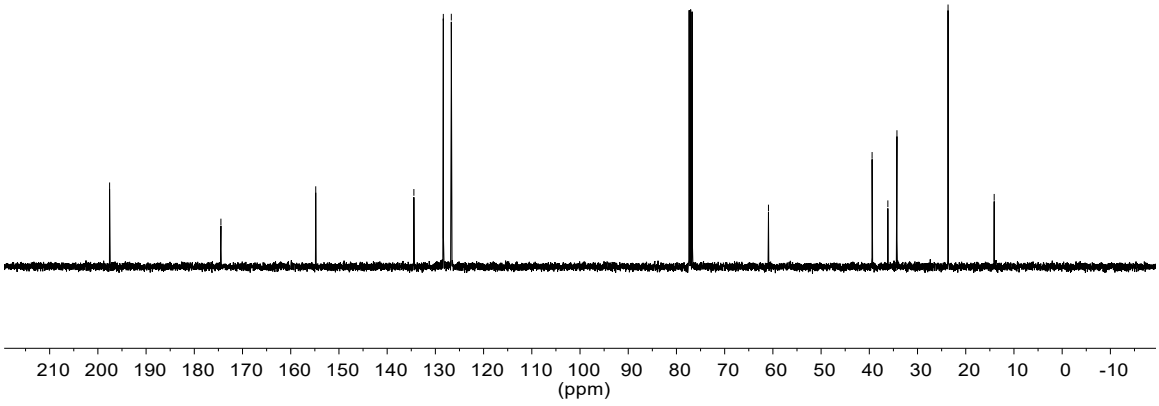


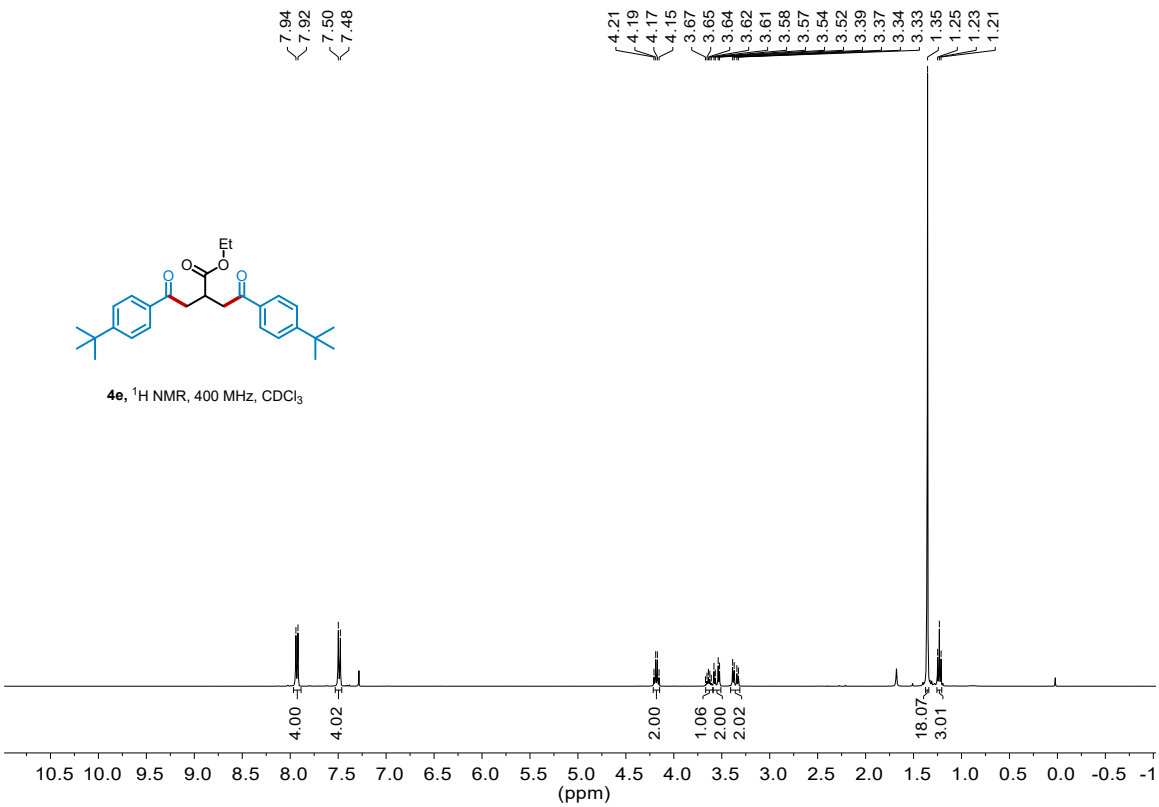
4d, ^{1}H NMR, 400 MHz, $CDCl_3$



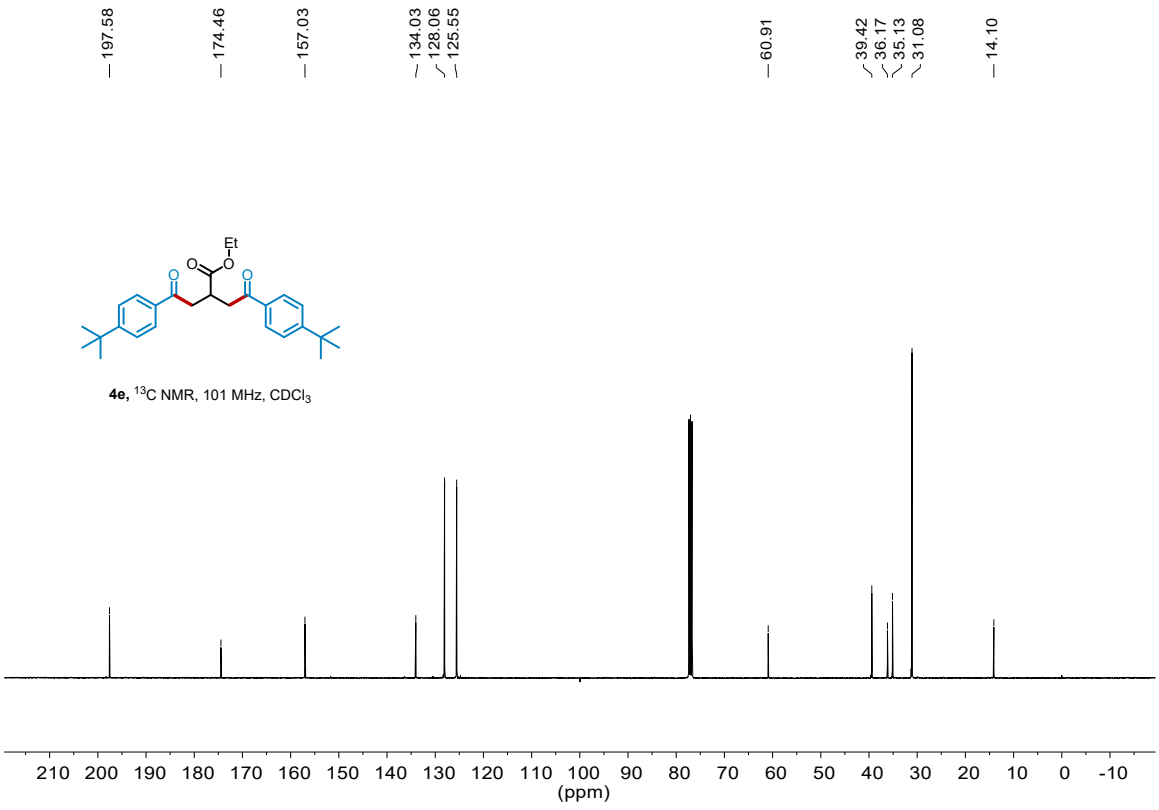


4d, ^{13}C NMR, 101 MHz, $CDCl_3$

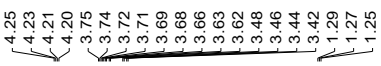


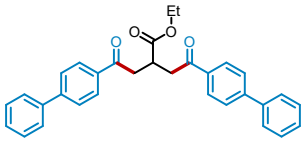


4e, ^{1}H NMR, 400 MHz, $CDCl_3$

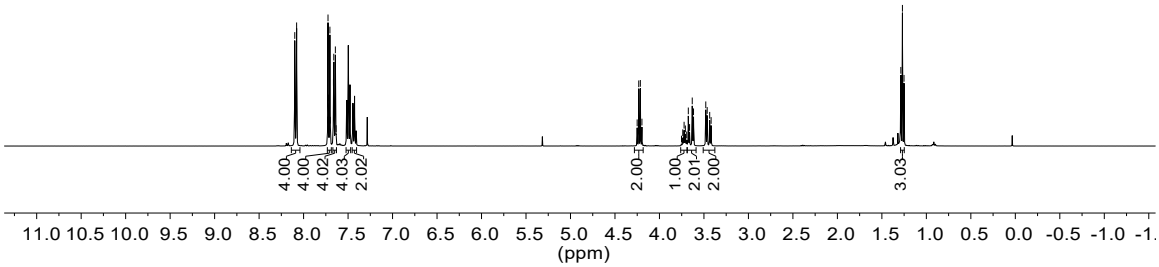


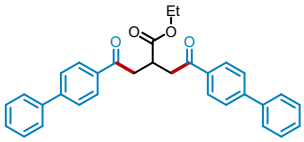
4e, ^{13}C NMR, 101 MHz, $CDCl_3$



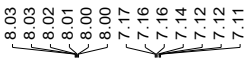


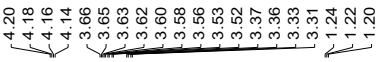
4f, ^{1}H NMR, 400 MHz, $CDCl_3$

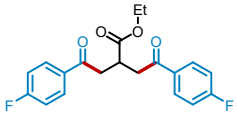




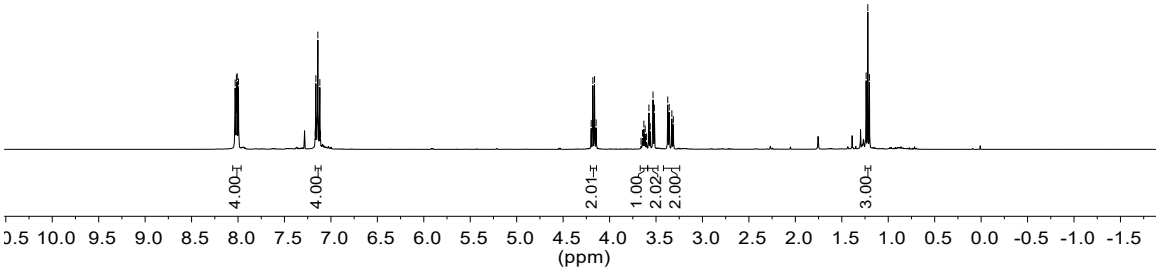
4f, ^{13}C NMR, 101 MHz, $CDCl_3$

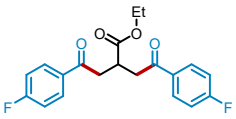




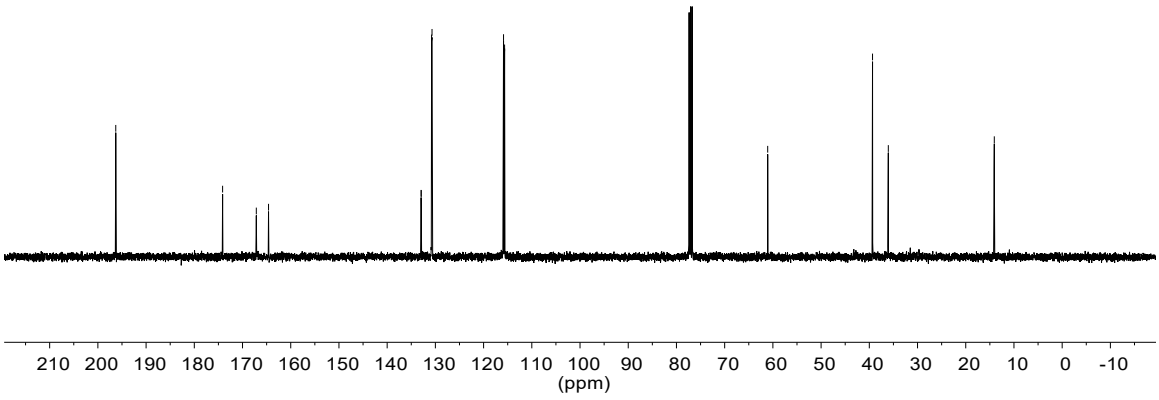


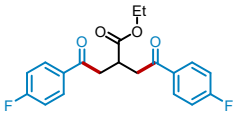
4g, ^{1}H NMR, 400 MHz, $CDCl_3$



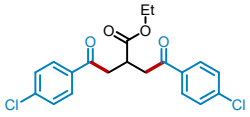


4g, ^{13}C NMR, 101 MHz, $CDCl_3$

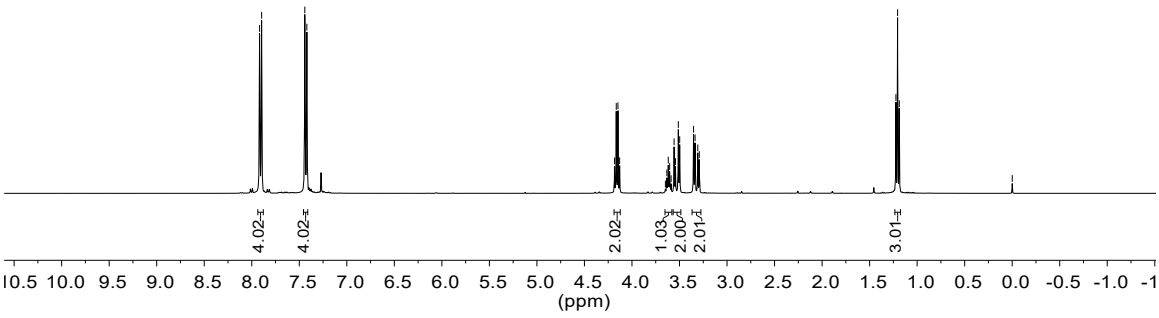


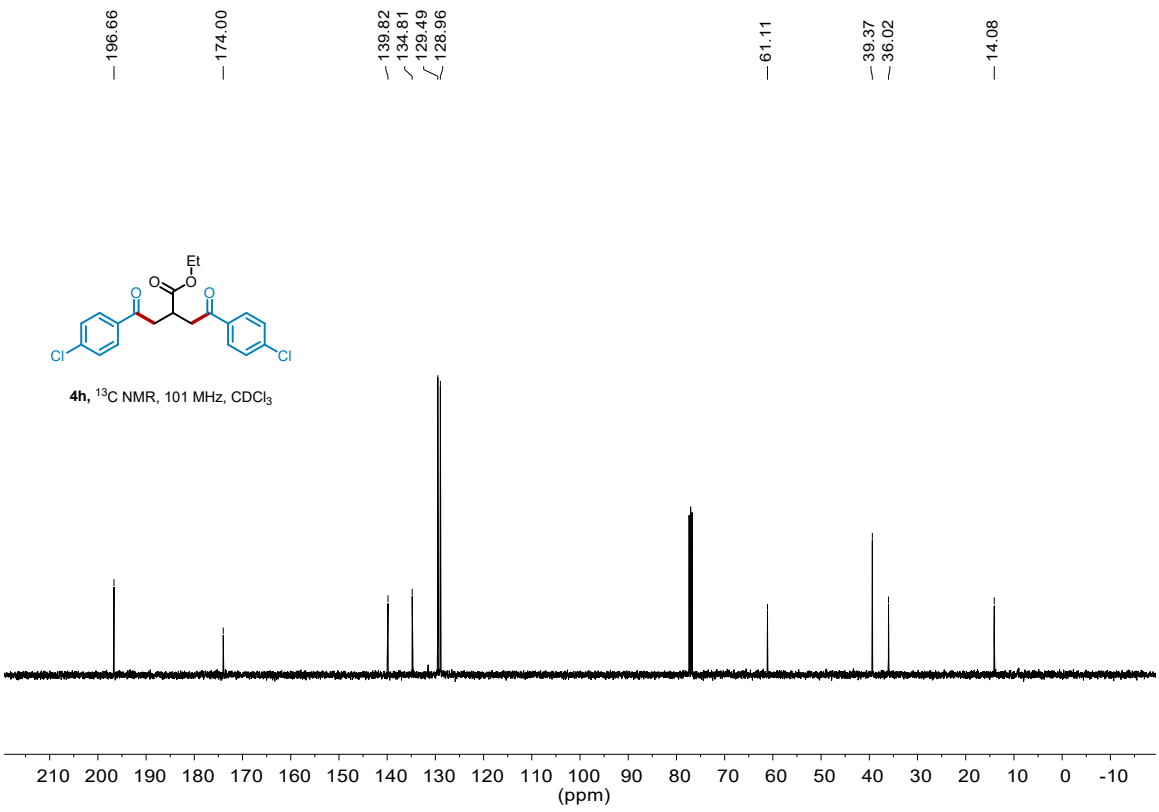


4g, ^{19}F NMR, 376 MHz, $CDCl_3$

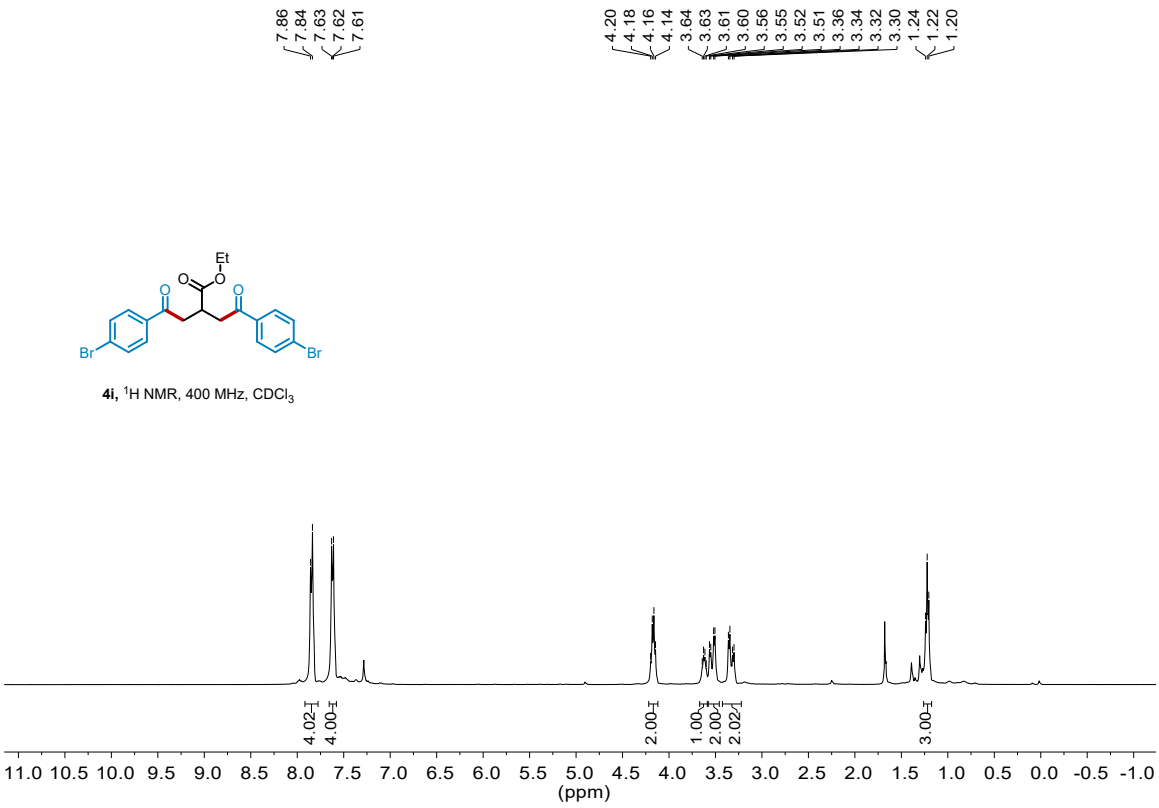


4h, ^{1}H NMR, 400 MHz, $CDCl_3$

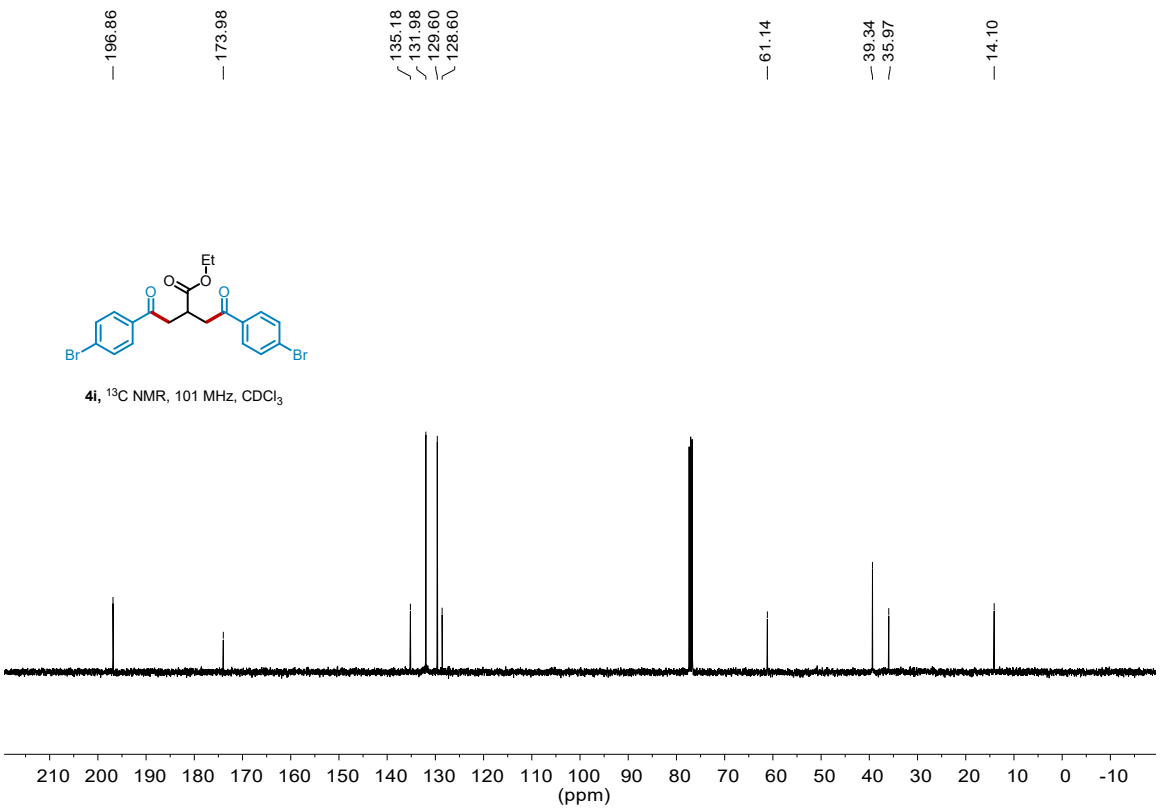




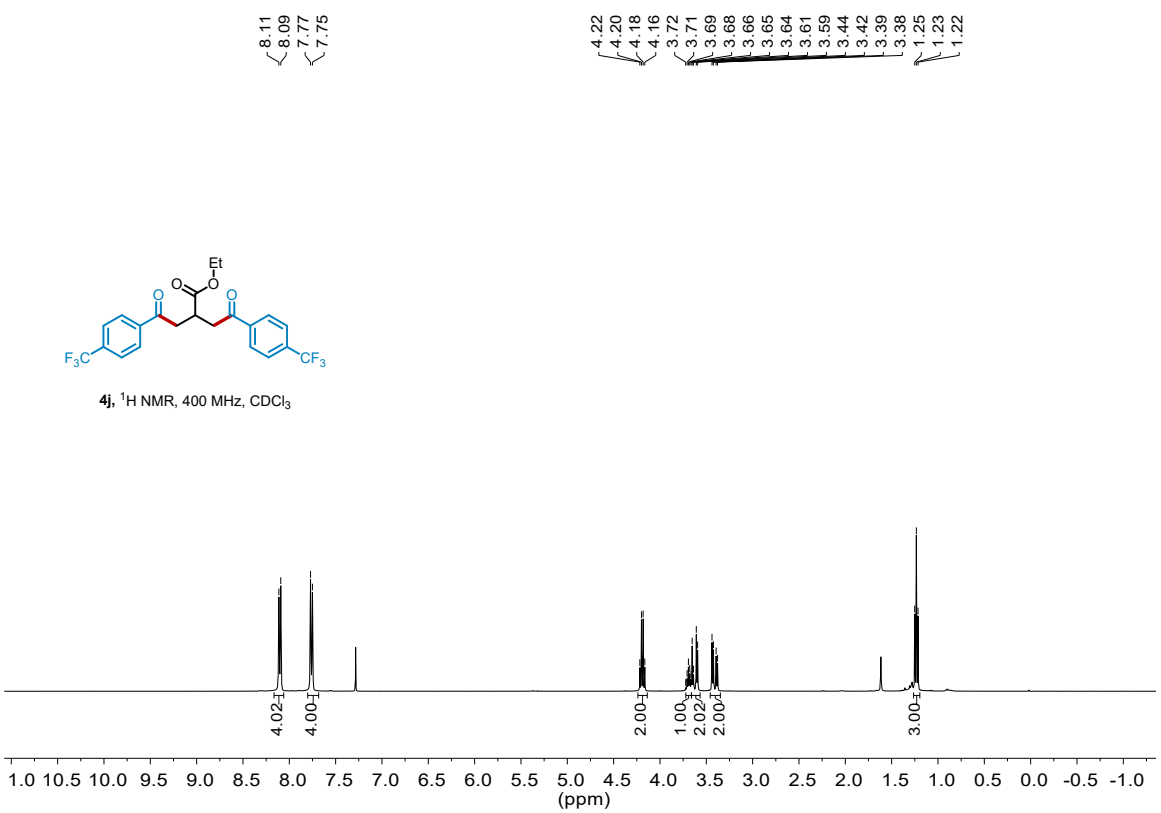
4h, ^{13}C NMR, 101 MHz, $CDCl_3$



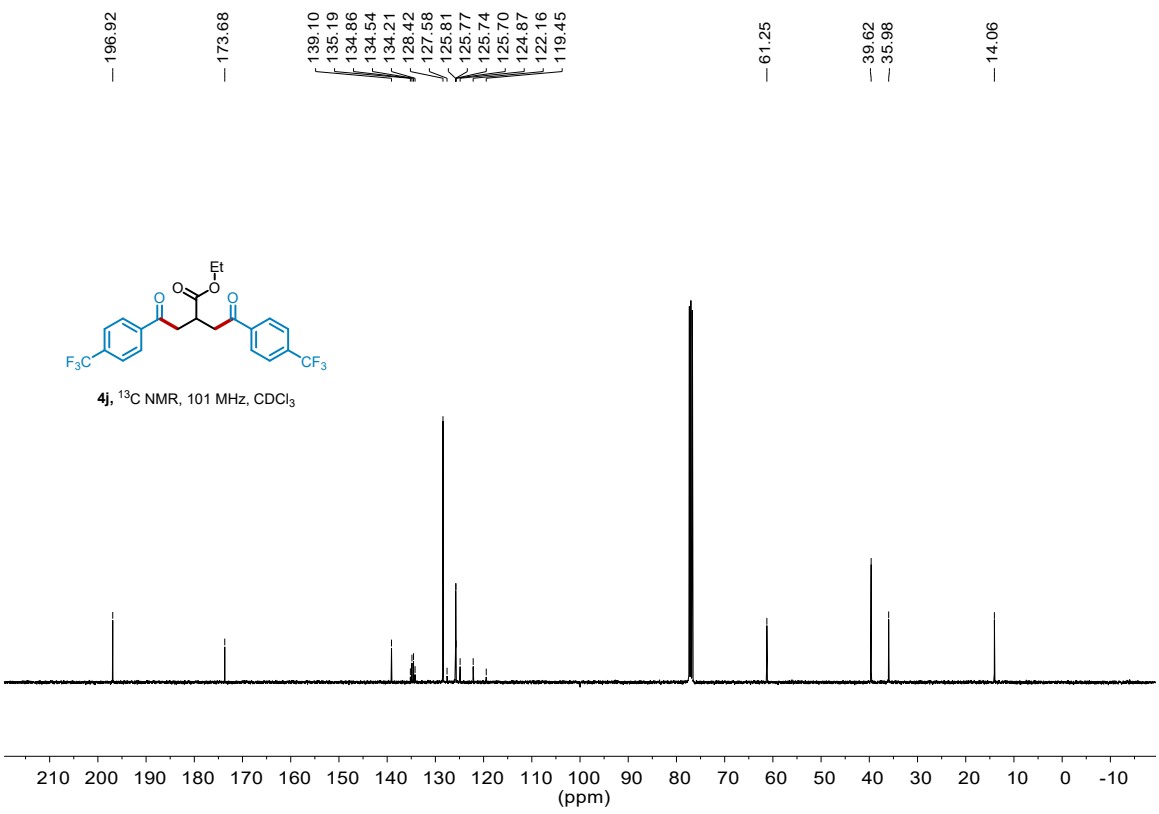
4i, ^{1}H NMR, 400 MHz, $CDCl_3$



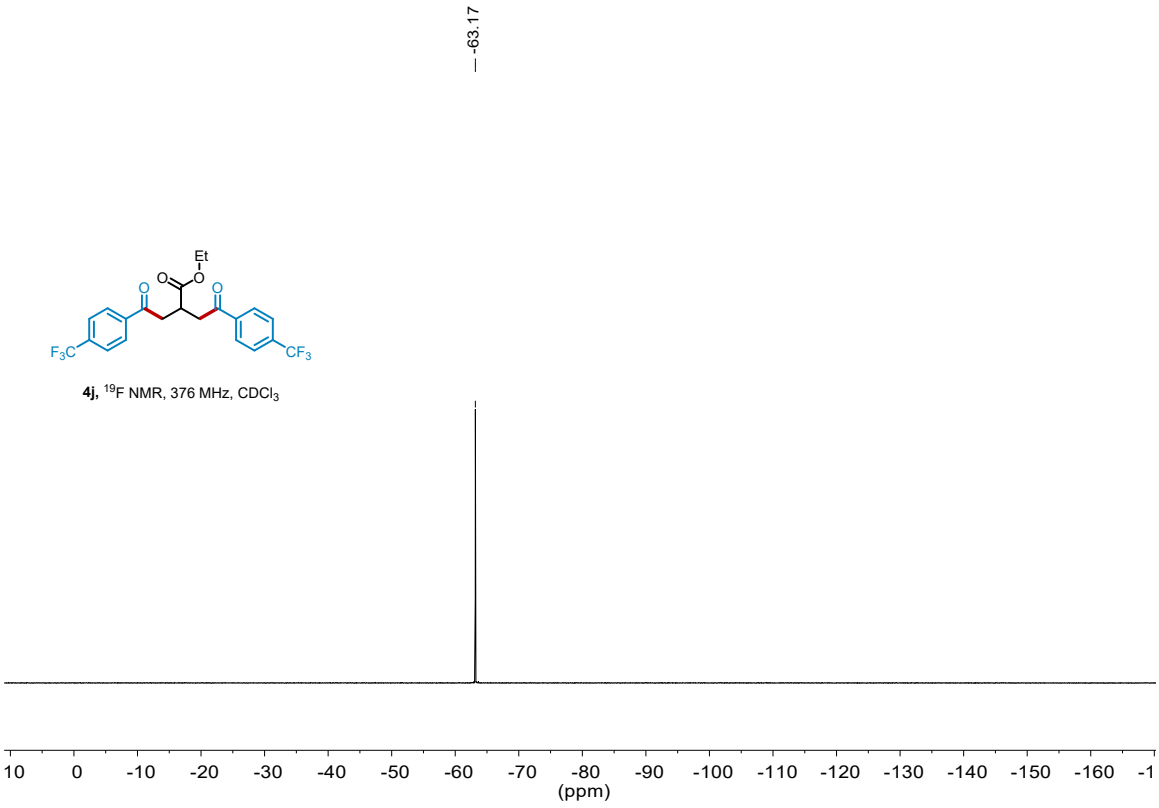
4i, ^{13}C NMR, 101 MHz, $CDCl_3$



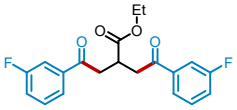
4j, ^{1}H NMR, 400 MHz, $CDCl_3$



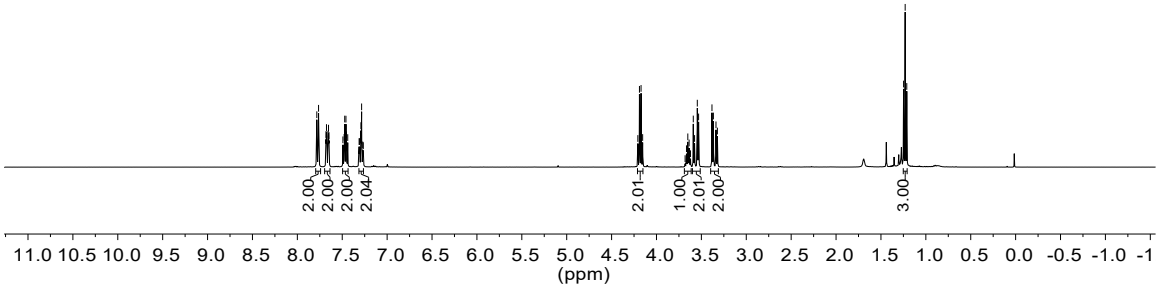
4j, ^{13}C NMR, 101 MHz, $CDCl_3$

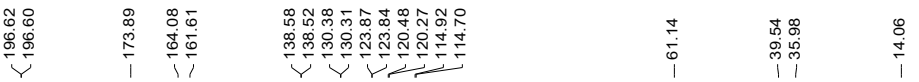


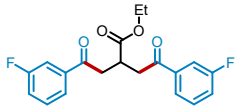
4j, ^{19}F NMR, 376 MHz, $CDCl_3$



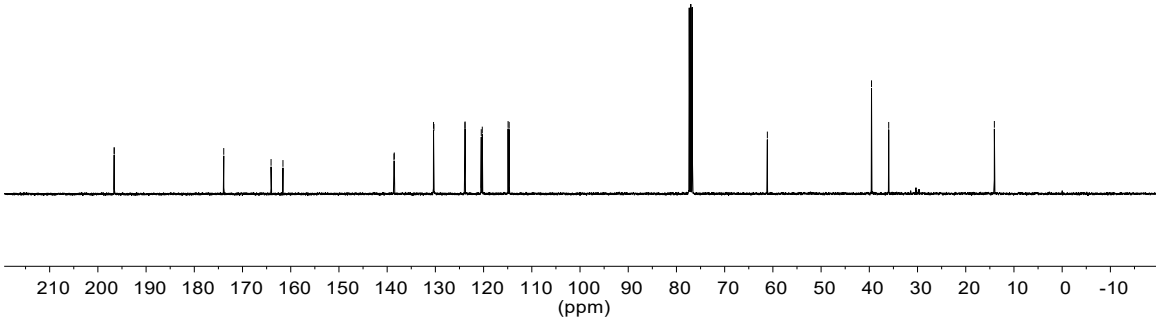
4k, ^{1}H NMR, 400 MHz, $CDCl_3$

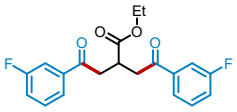




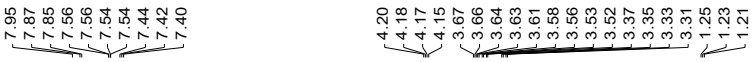


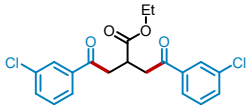
4k, ^{13}C NMR, 101 MHz, $CDCl_3$



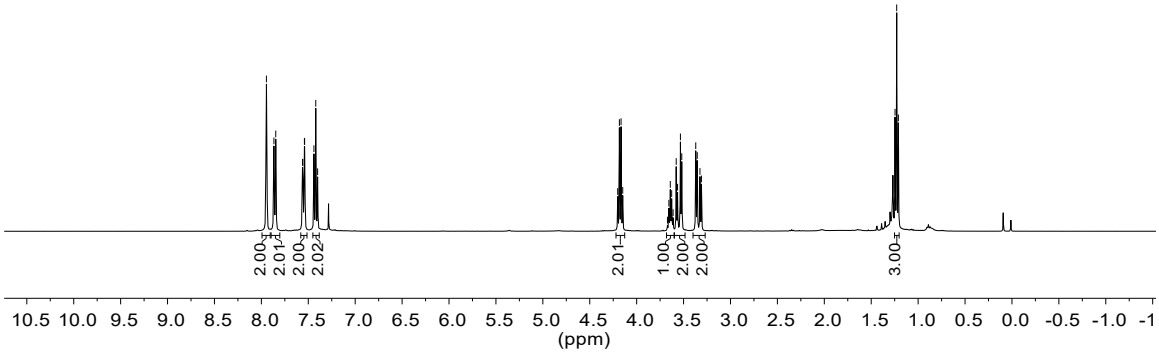


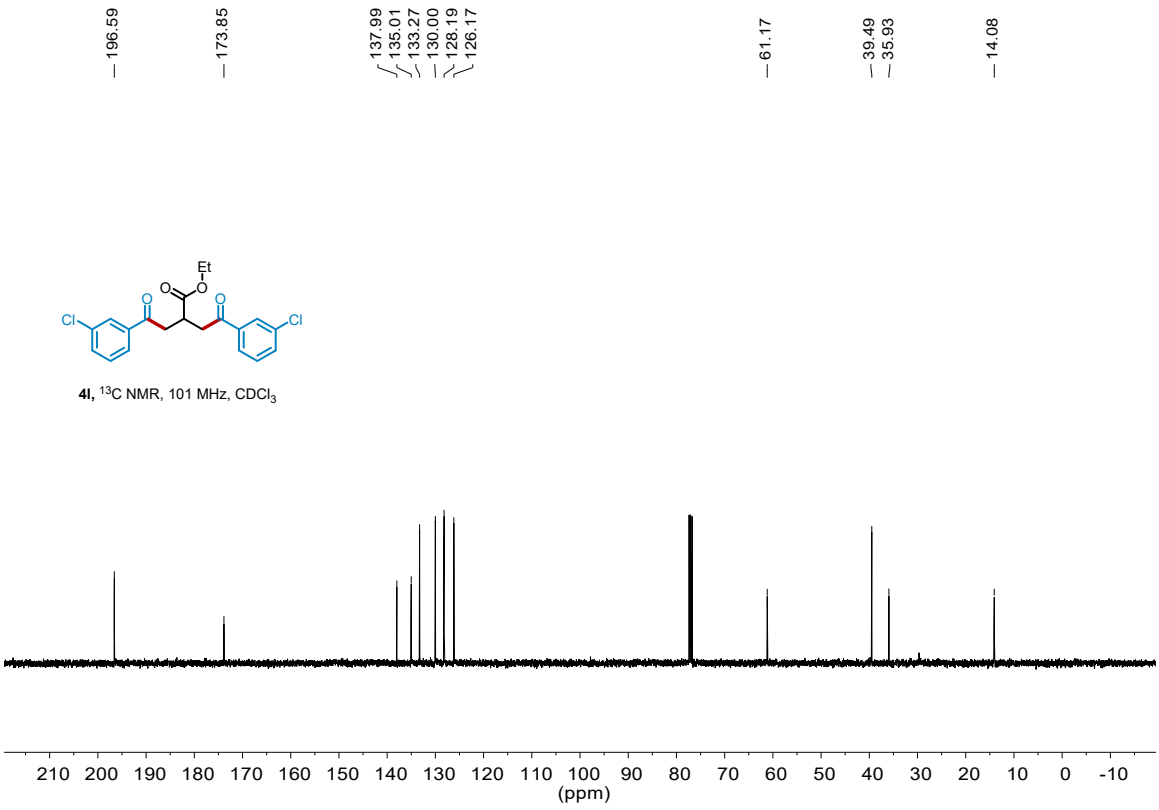
4k, ^{19}F NMR, 376 MHz, $CDCl_3$



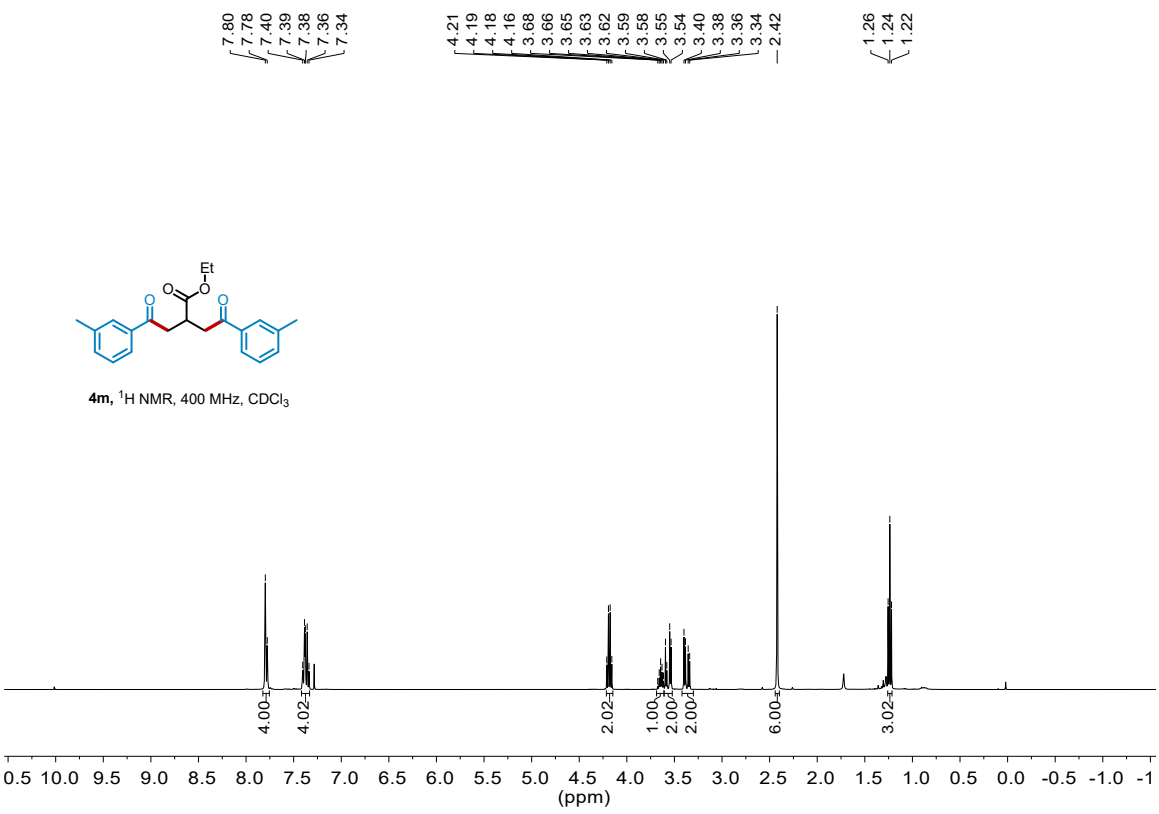


4l, ^{1}H NMR, 400 MHz, $CDCl_3$

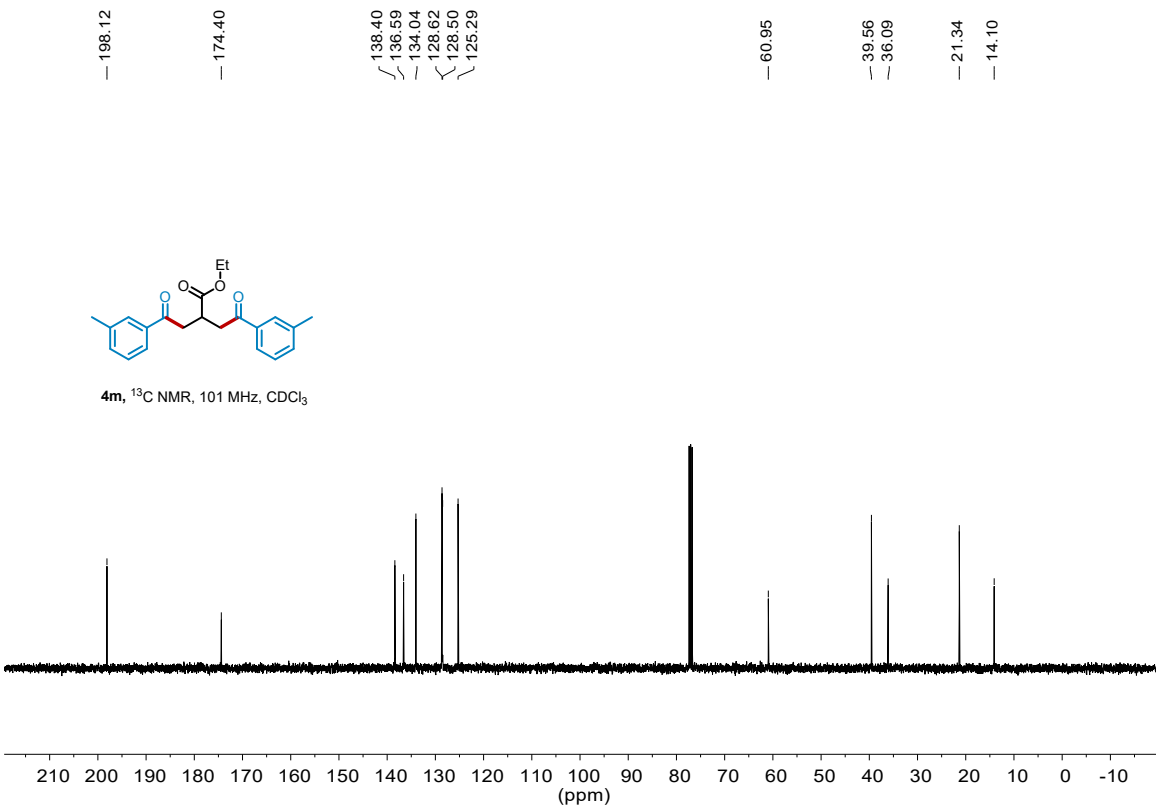




4l, ^{13}C NMR, 101 MHz, $CDCl_3$



4m, ^{1}H NMR, 400 MHz, $CDCl_3$



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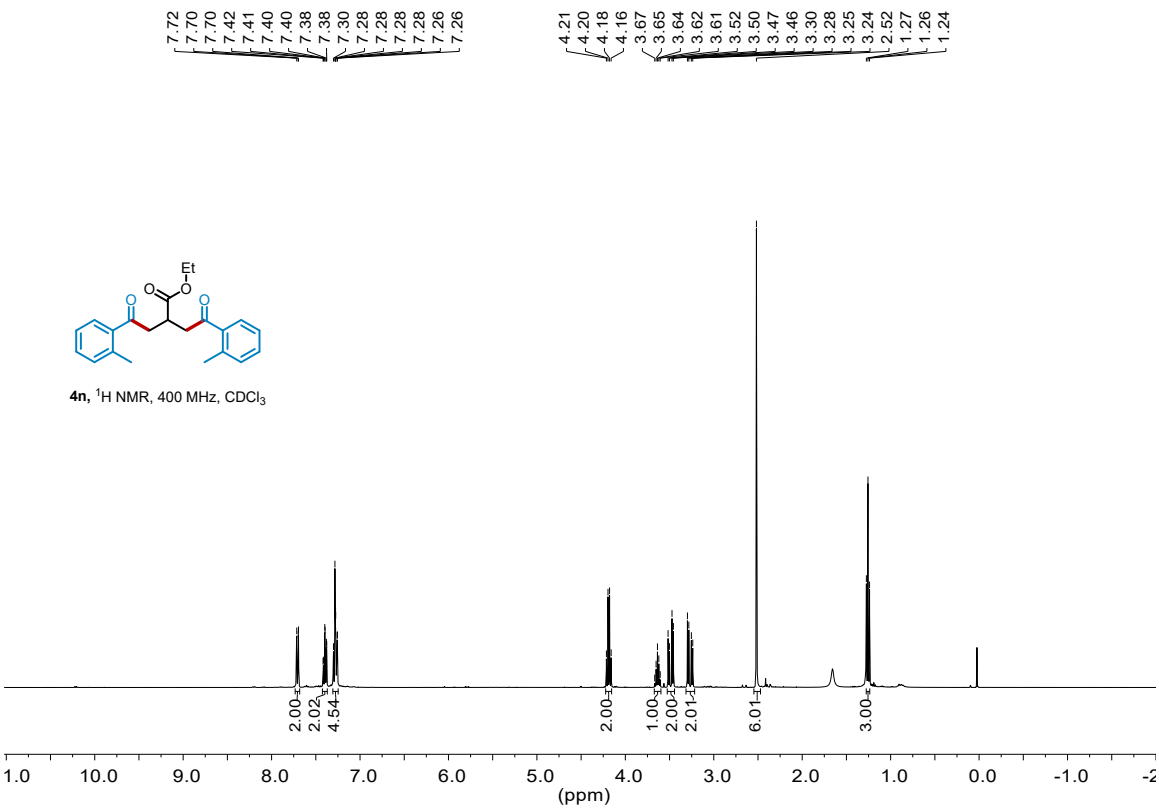
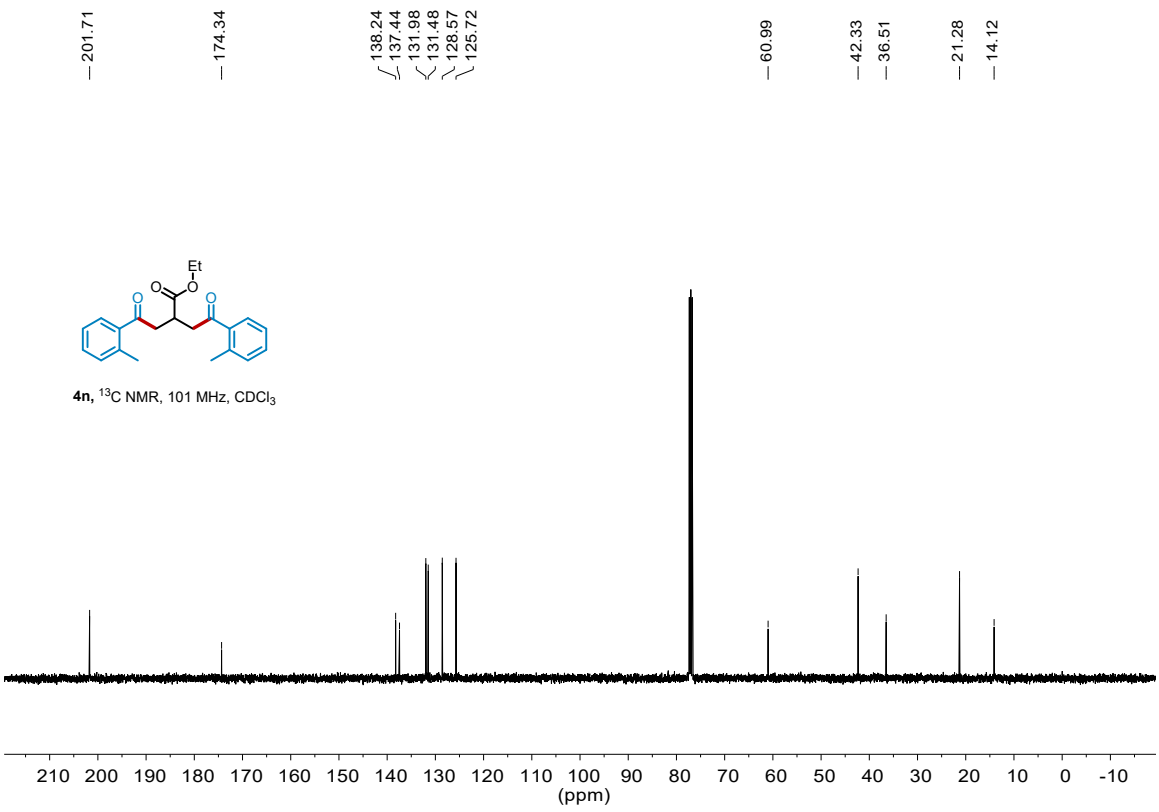
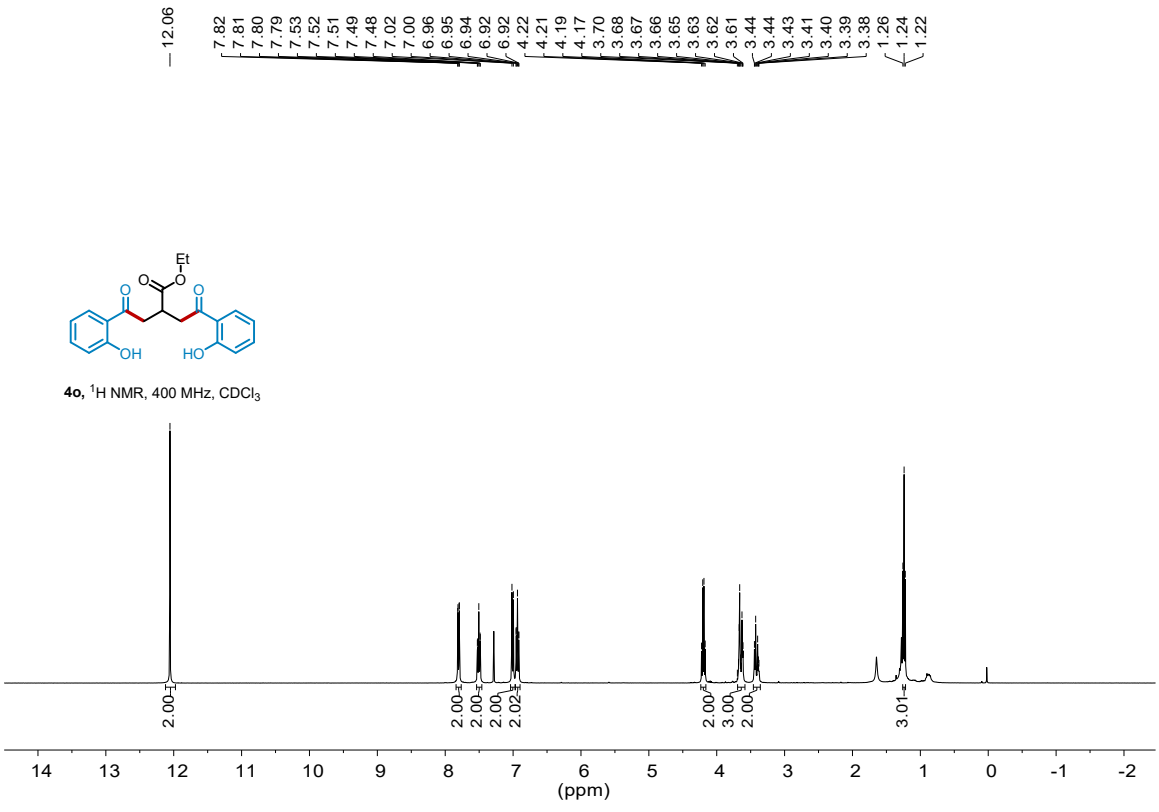


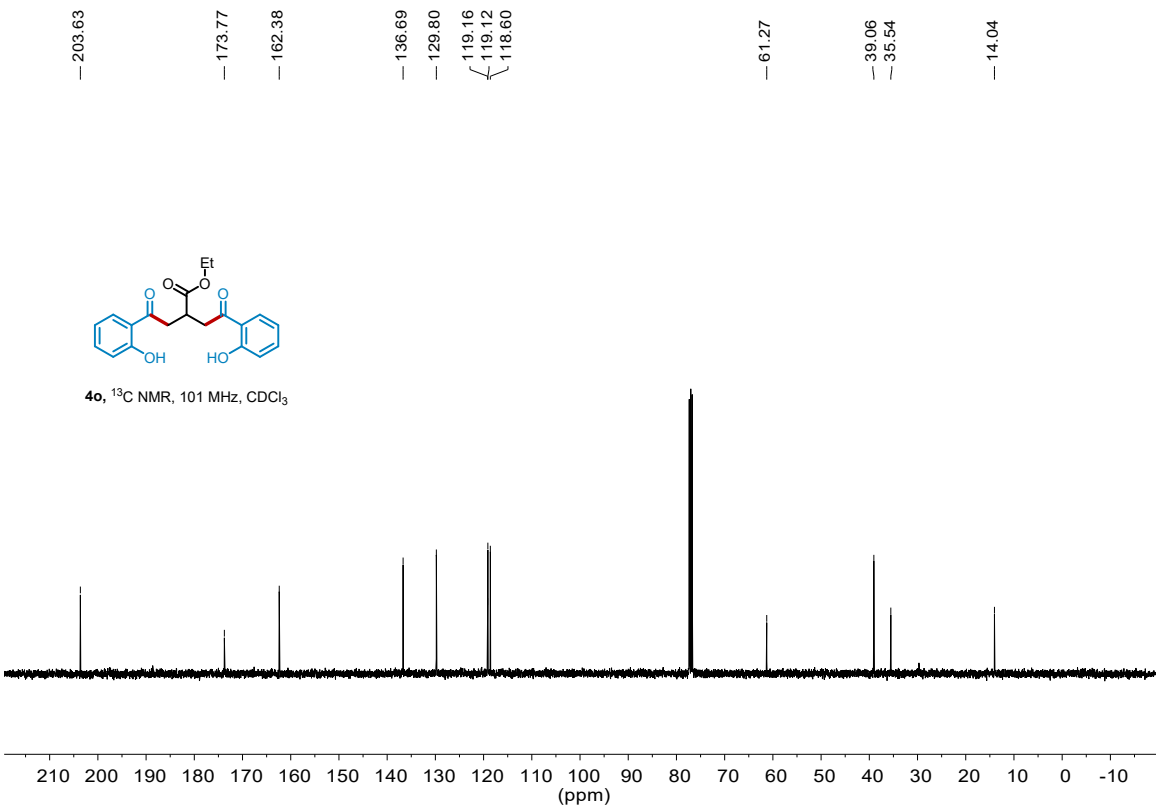
4n, ^{1}H NMR, 400 MHz, $CDCl_3$



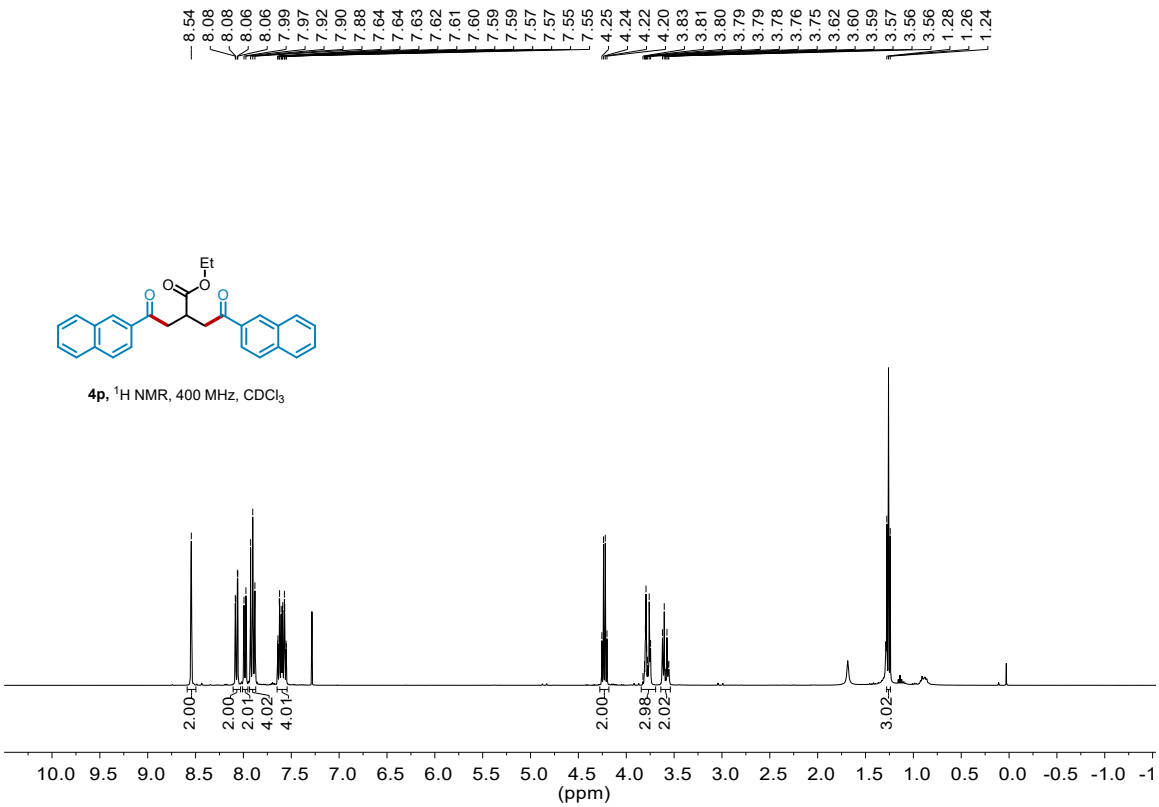
4n, ^{13}C NMR, 101 MHz, $CDCl_3$



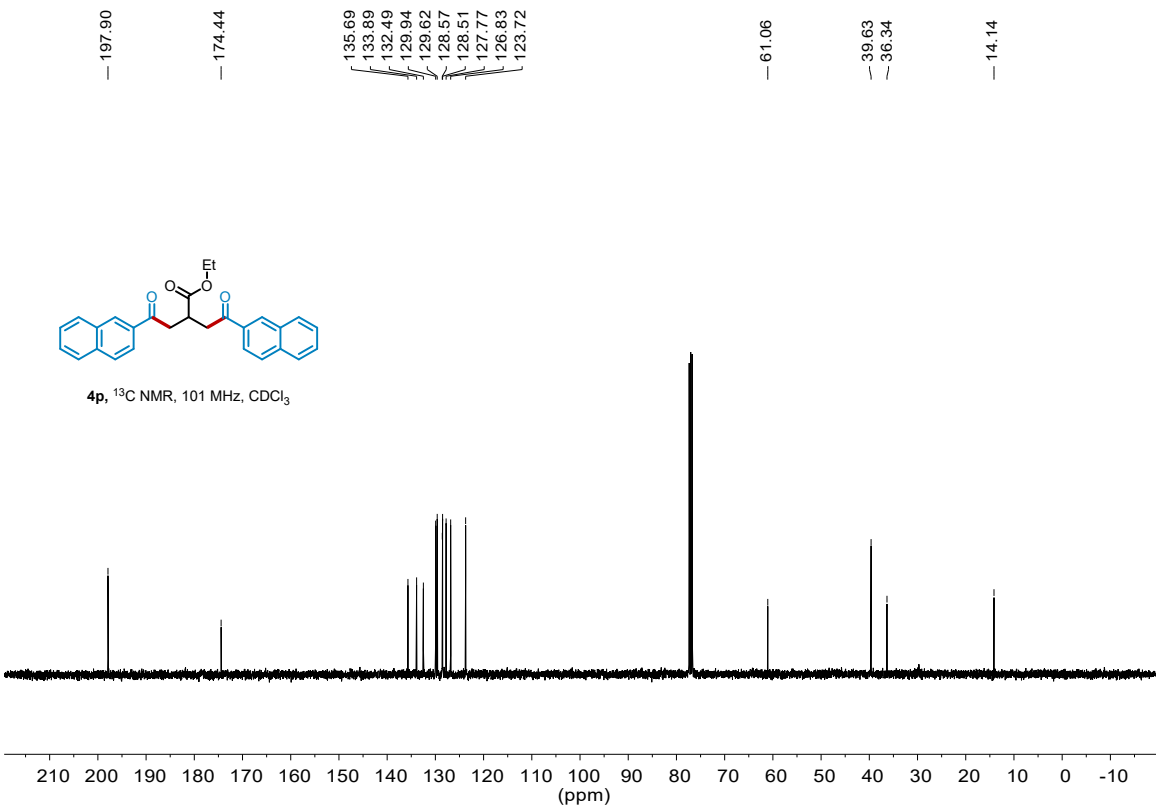
4o, ^{1}H NMR, 400 MHz, $CDCl_3$



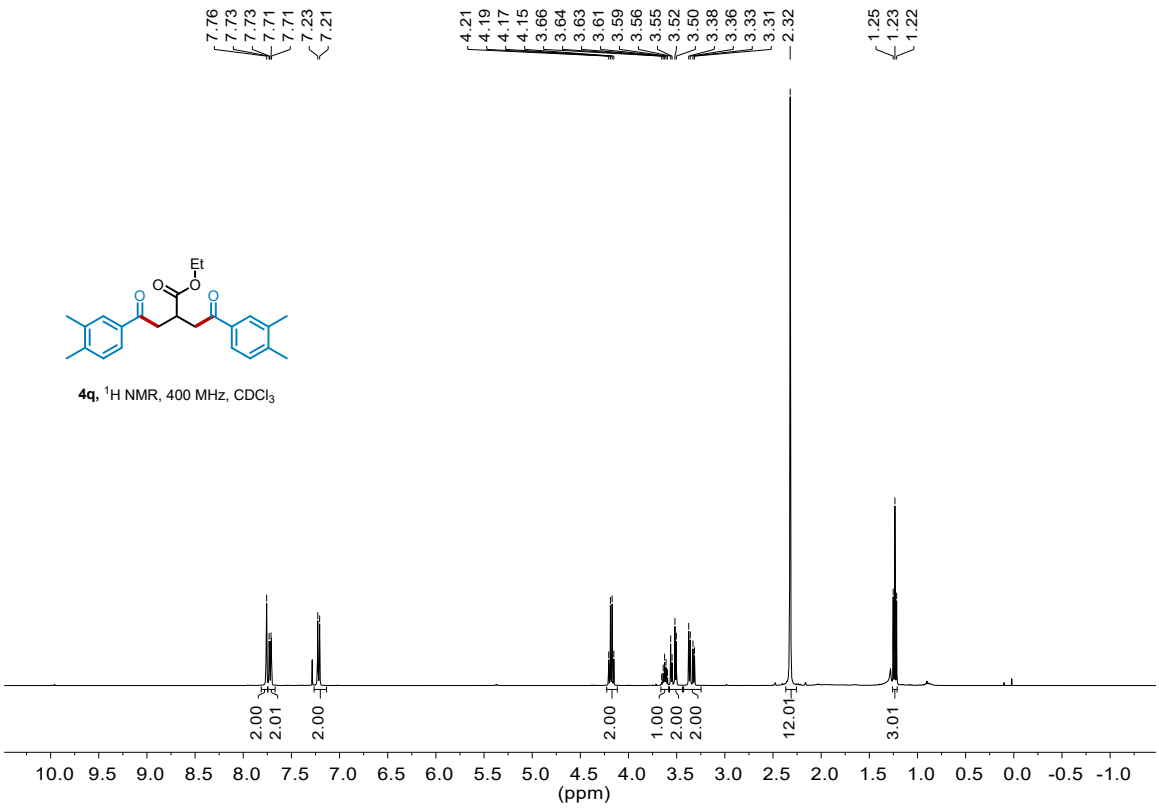
4o, ^{13}C NMR, 101 MHz, $CDCl_3$



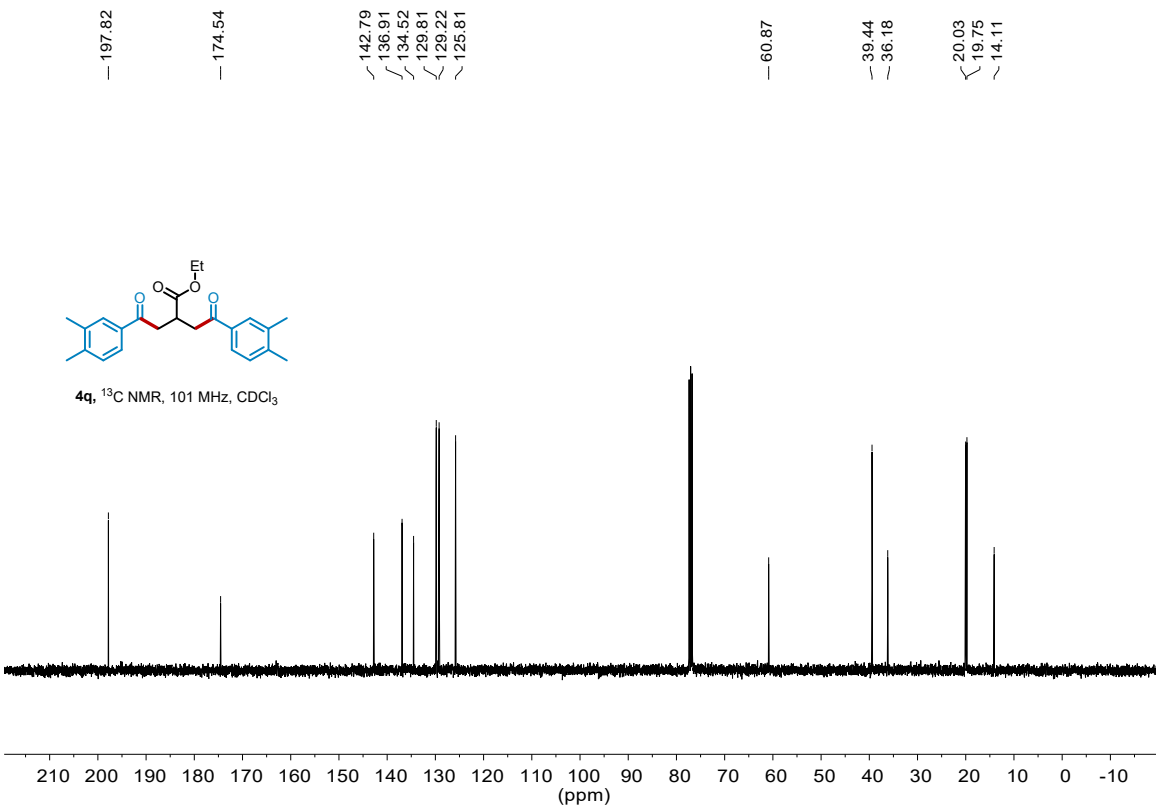
4p, ^{1}H NMR, 400 MHz, $CDCl_3$



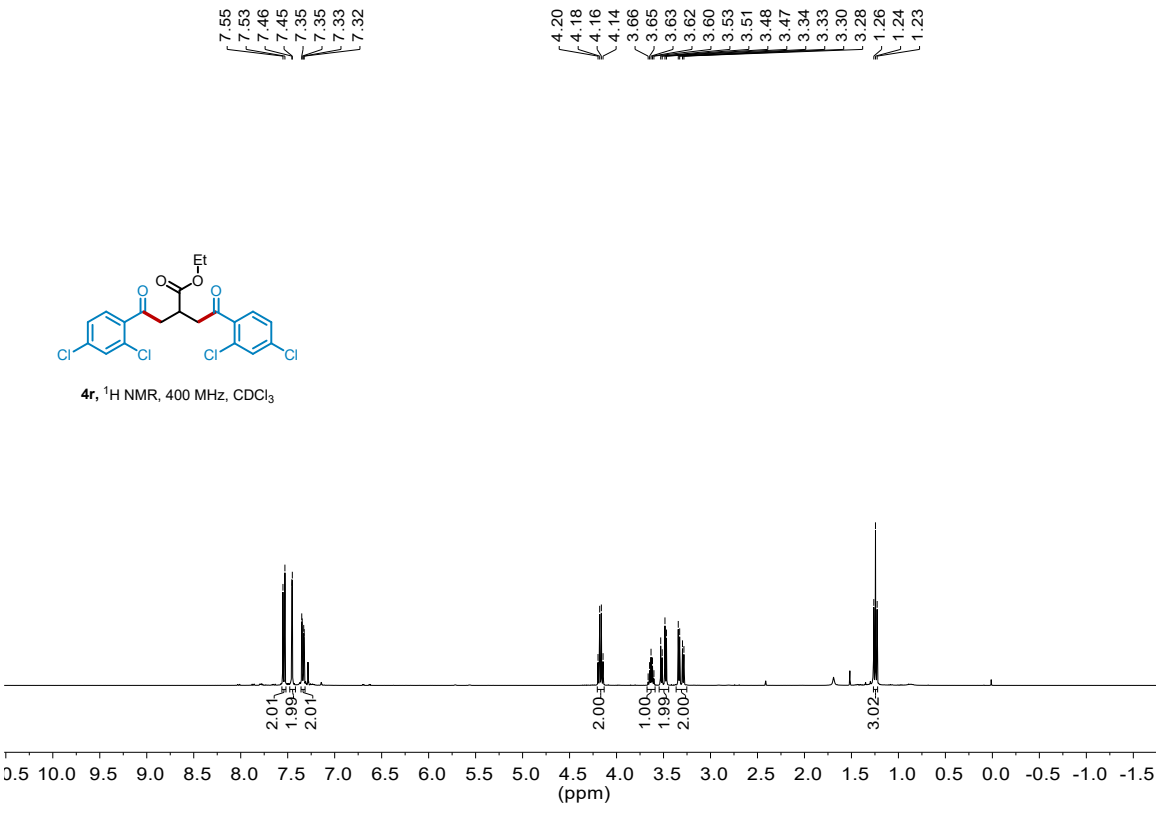
4p, ^{13}C NMR, 101 MHz, $CDCl_3$



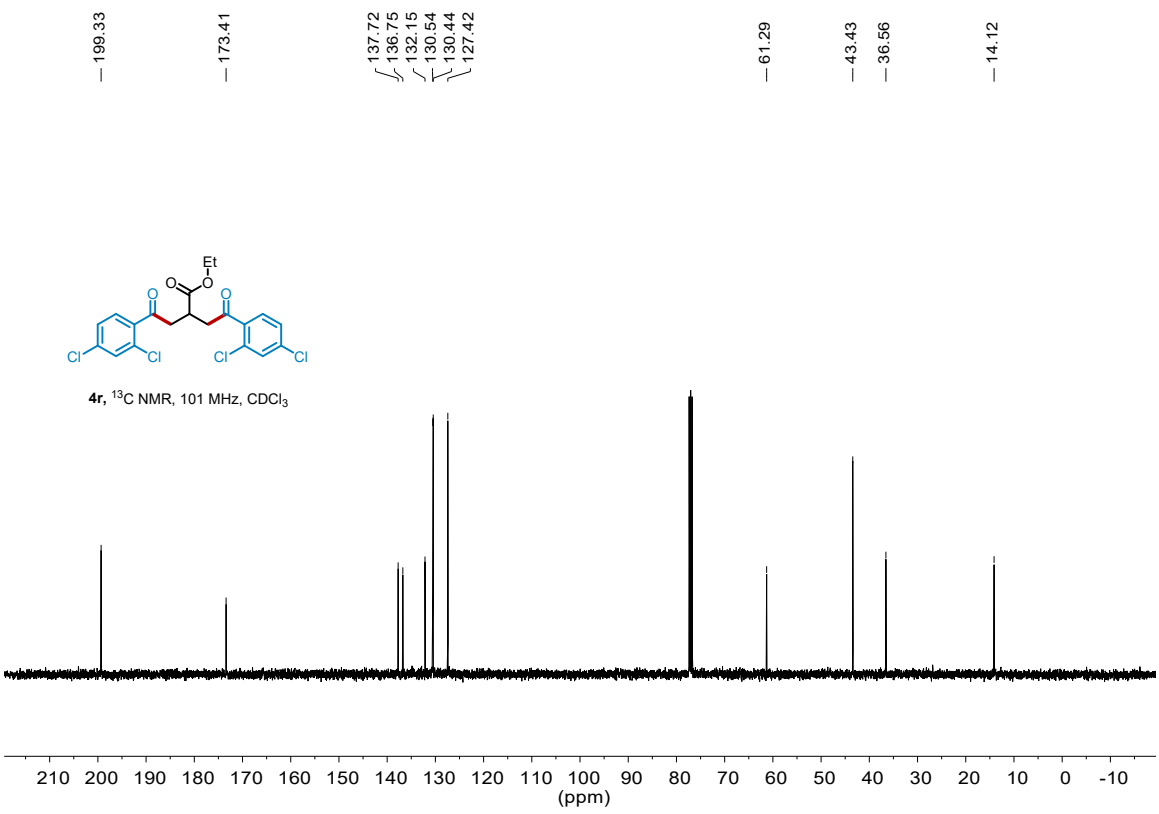
4q, ^{1}H NMR, 400 MHz, $CDCl_3$



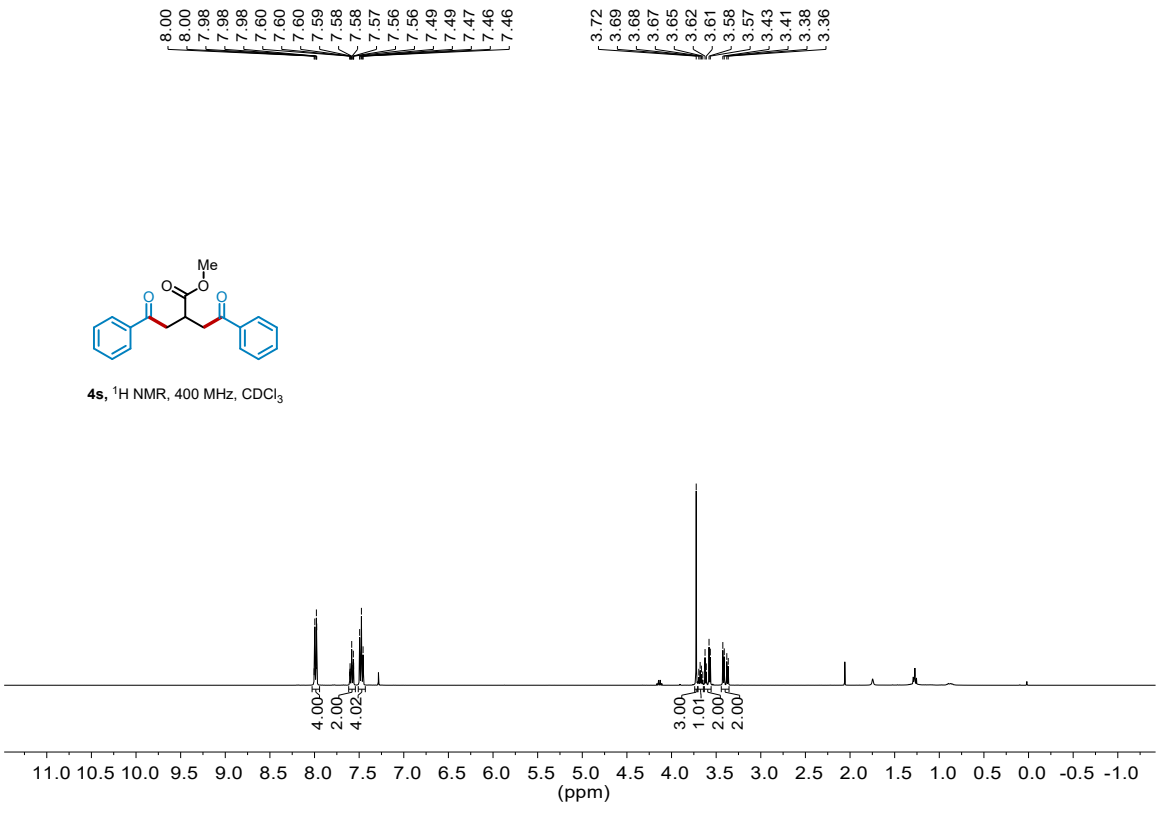
4q, ^{13}C NMR, 101 MHz, $CDCl_3$



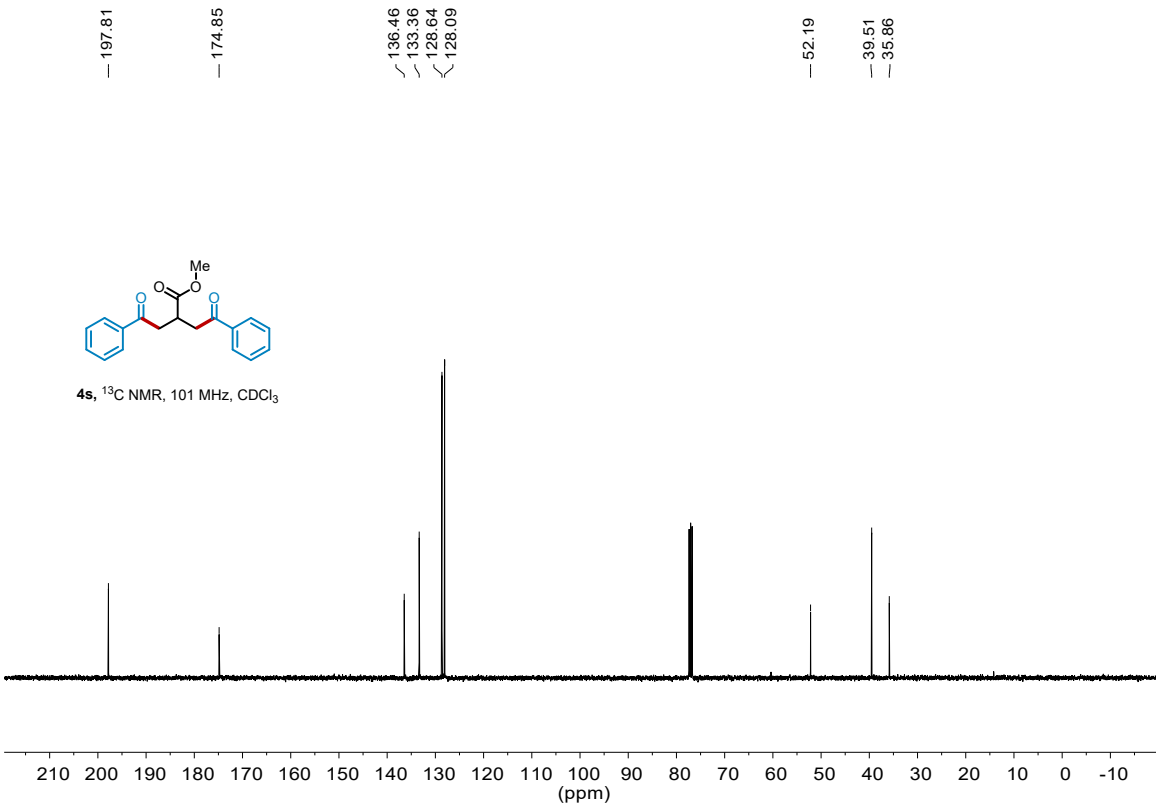
4r, ^{1}H NMR, 400 MHz, $CDCl_3$



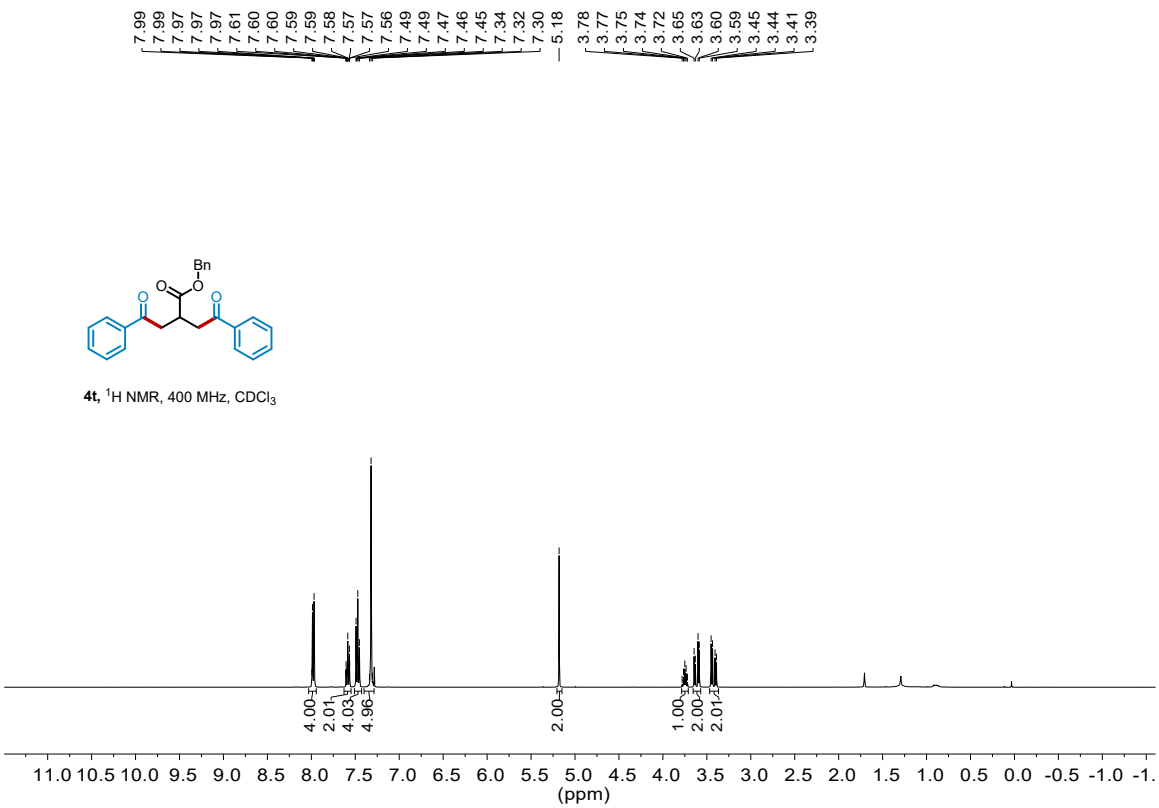
4r, ^{13}C NMR, 101 MHz, $CDCl_3$



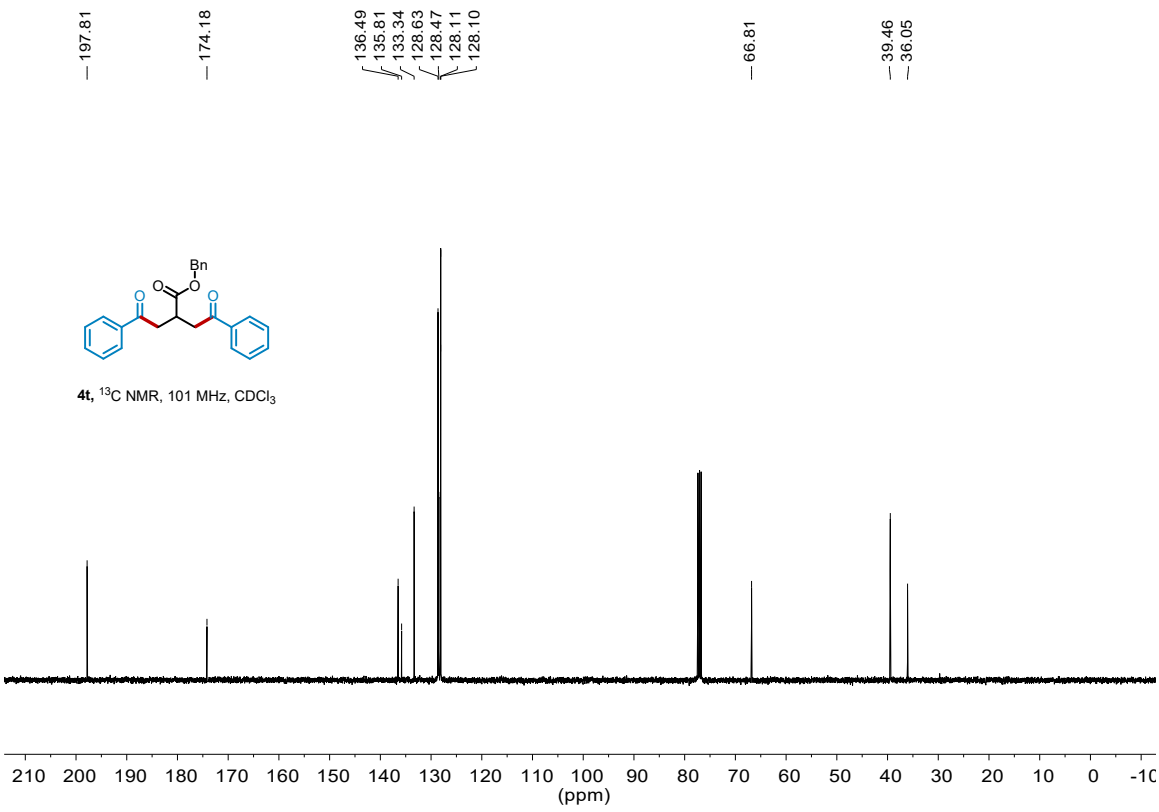
4s, ^{1}H NMR, 400 MHz, $CDCl_3$



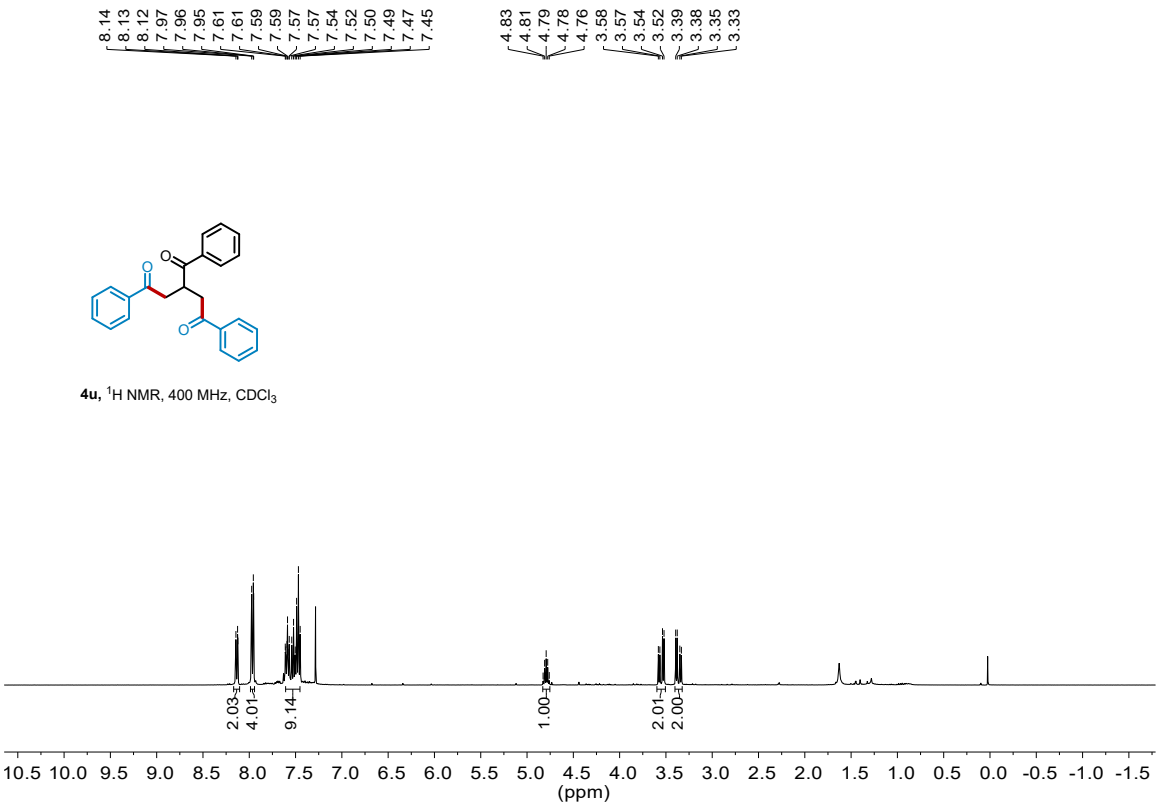
4s, ^{13}C NMR, 101 MHz, $CDCl_3$



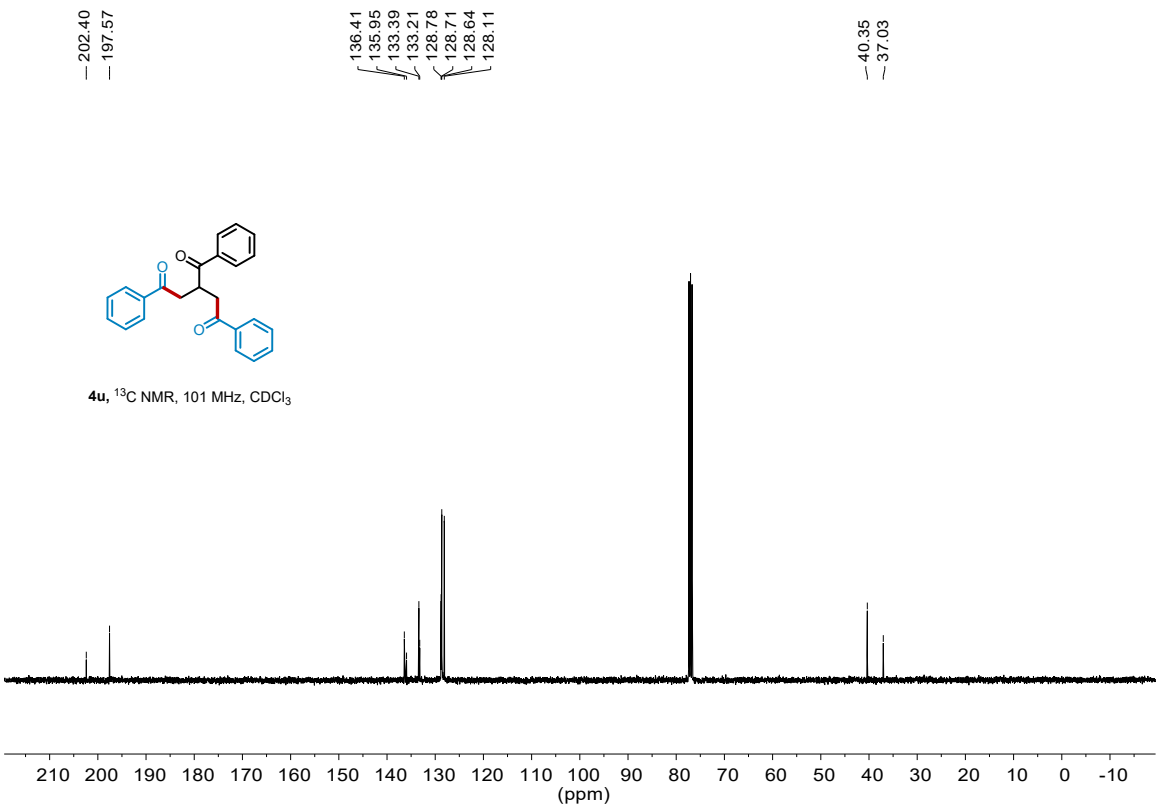
4t, ^{1}H NMR, 400 MHz, $CDCl_3$



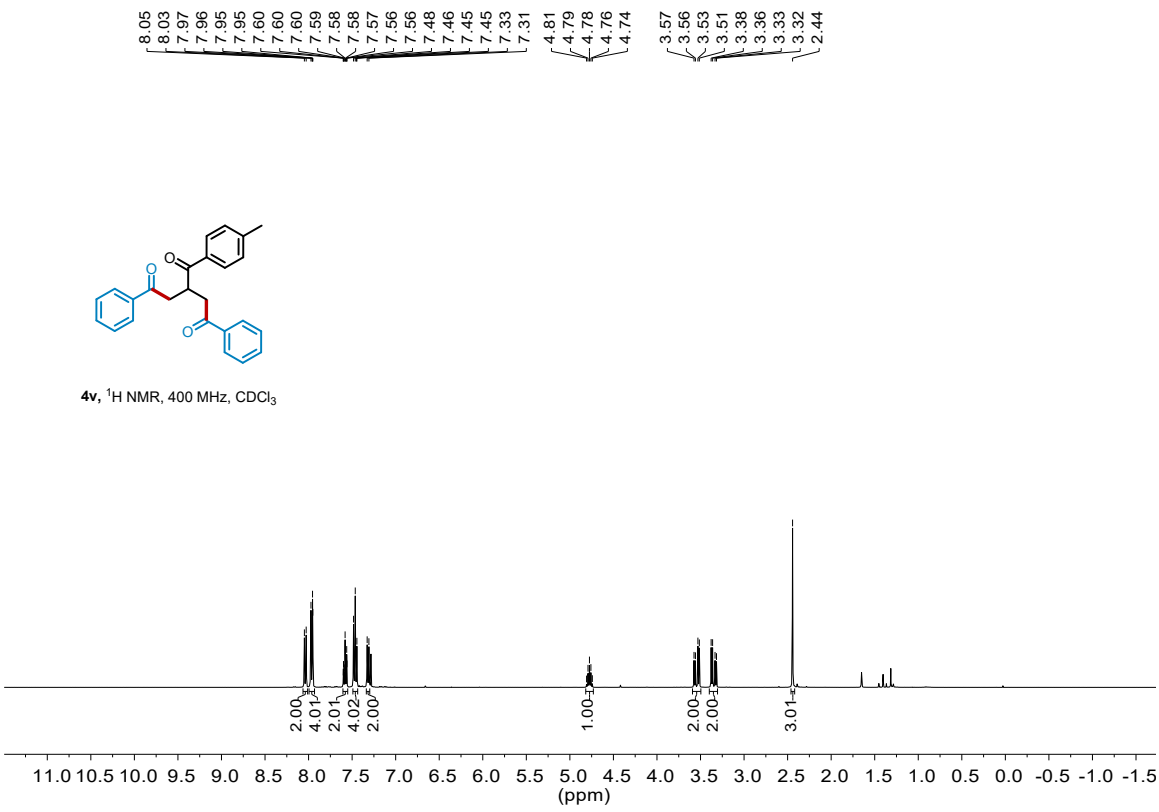
4t, ^{13}C NMR, 101 MHz, $CDCl_3$



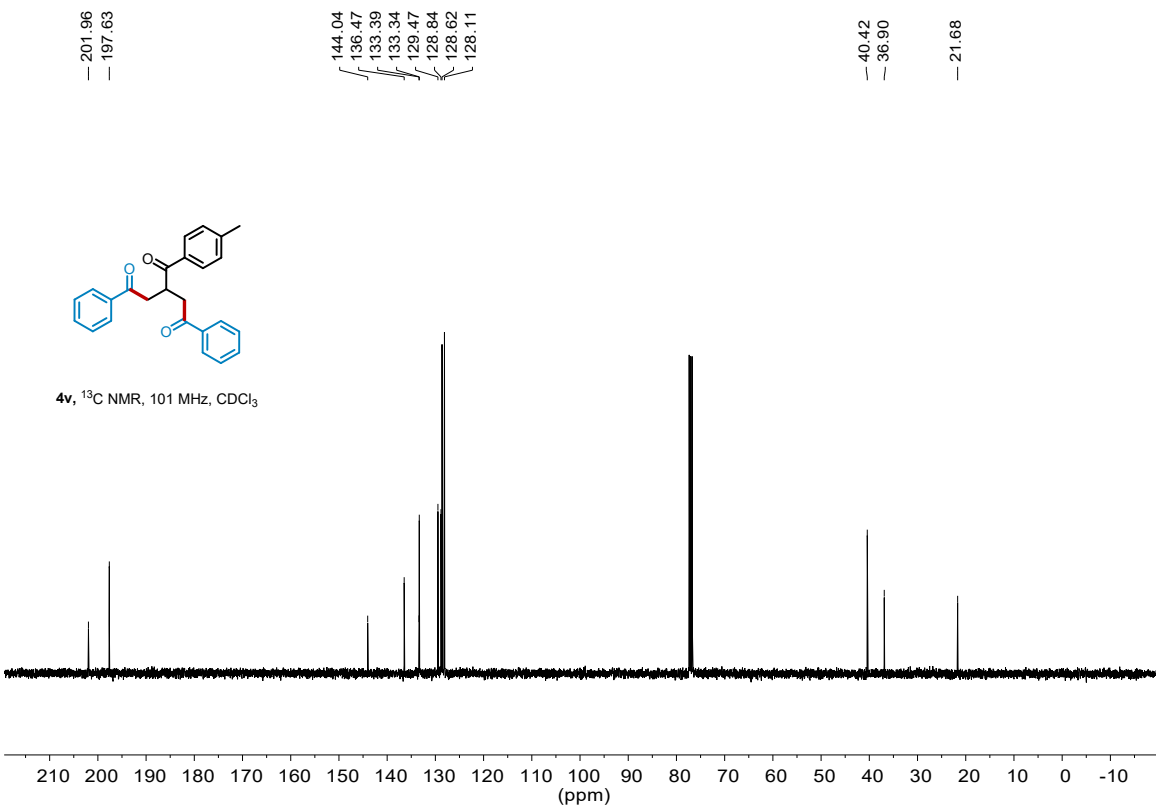
4u, ^{1}H NMR, 400 MHz, $CDCl_3$



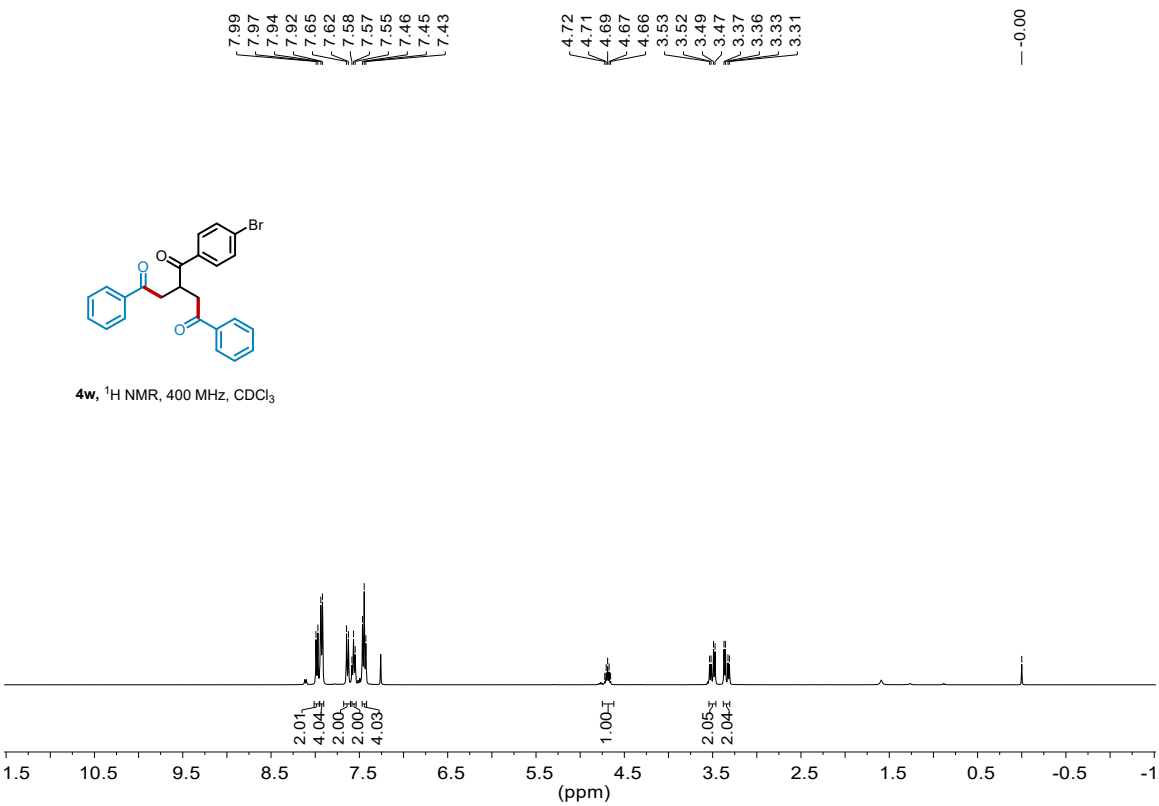
4u, ^{13}C NMR, 101 MHz, $CDCl_3$



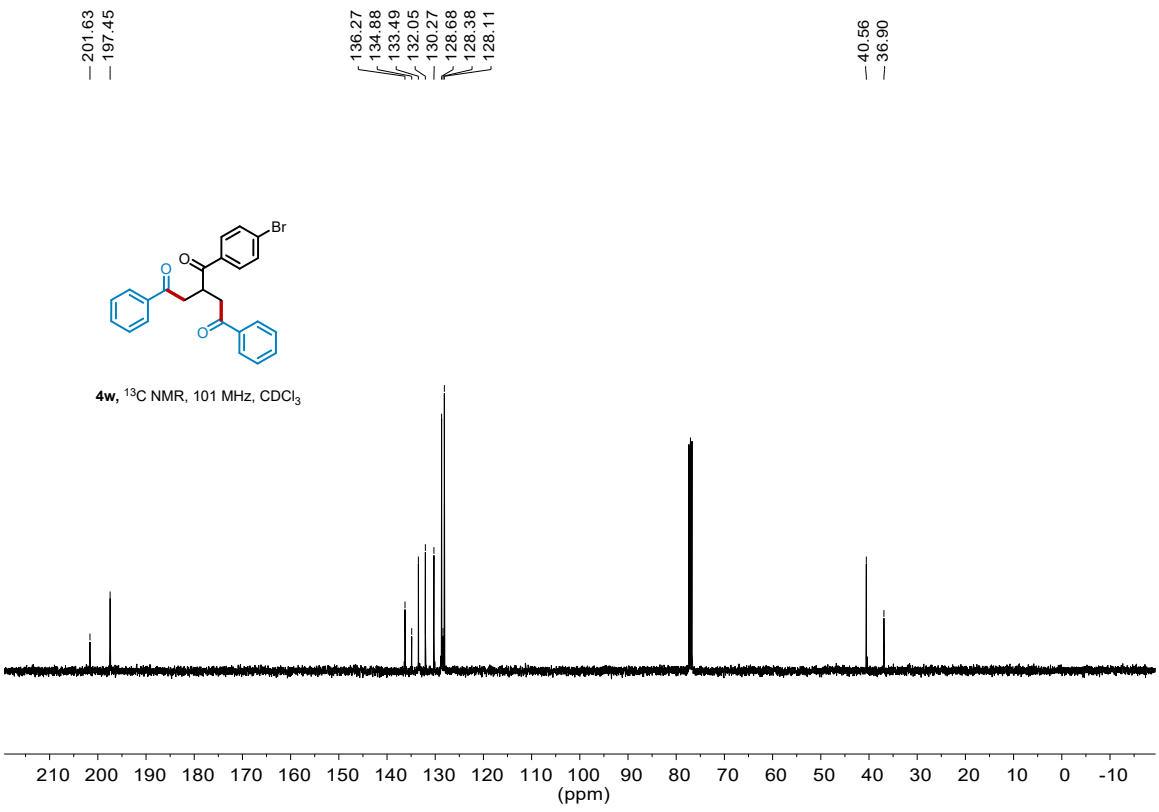
4v, ^{1}H NMR, 400 MHz, $CDCl_3$

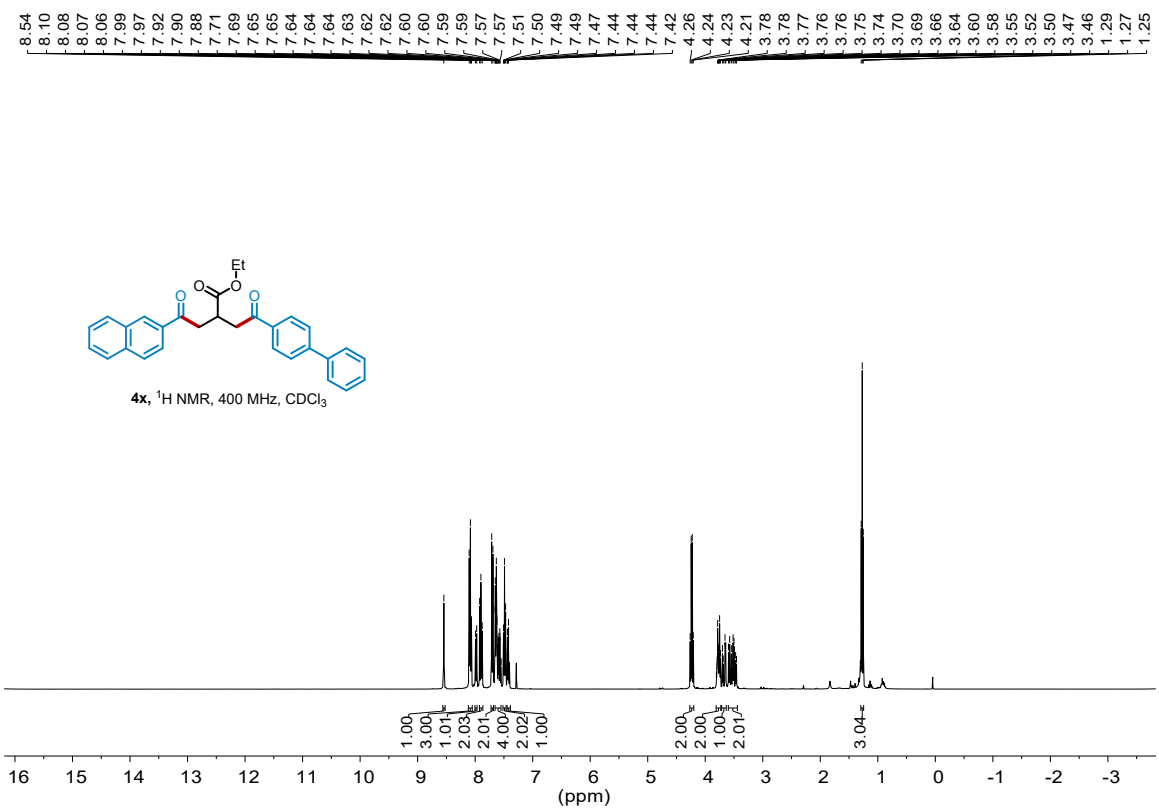


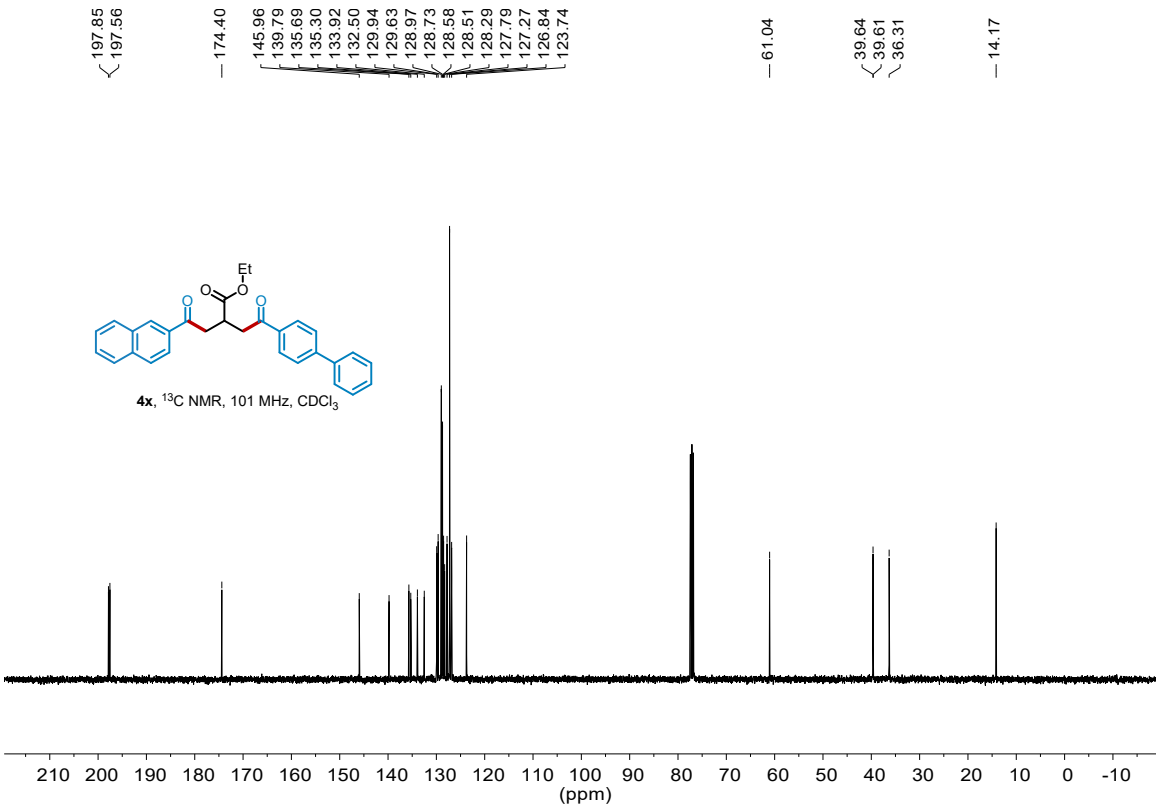
4v, ^{13}C NMR, 101 MHz, $CDCl_3$



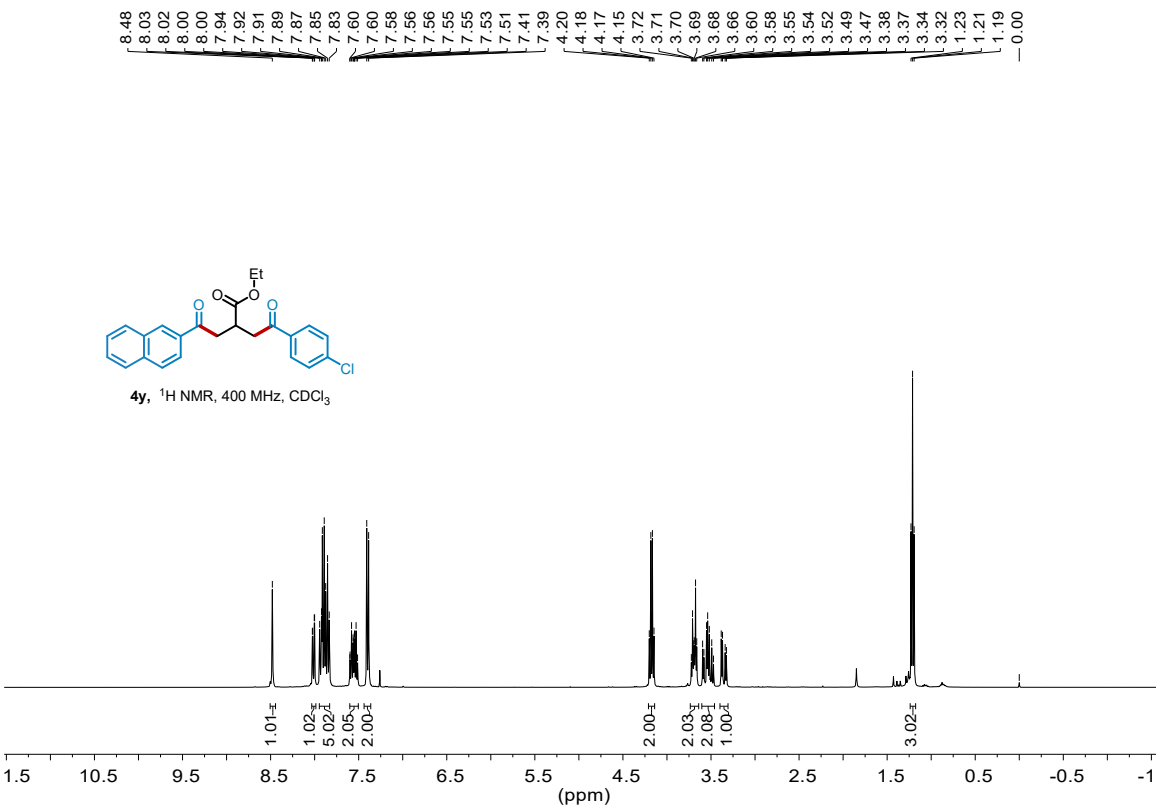
4w, ^{1}H NMR, 400 MHz, $CDCl_3$


201.63
197.45
136.27
134.88
133.49
132.05
130.27
128.68
128.38
128.11
40.56
36.90
Br
O
O
O
4w, 13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

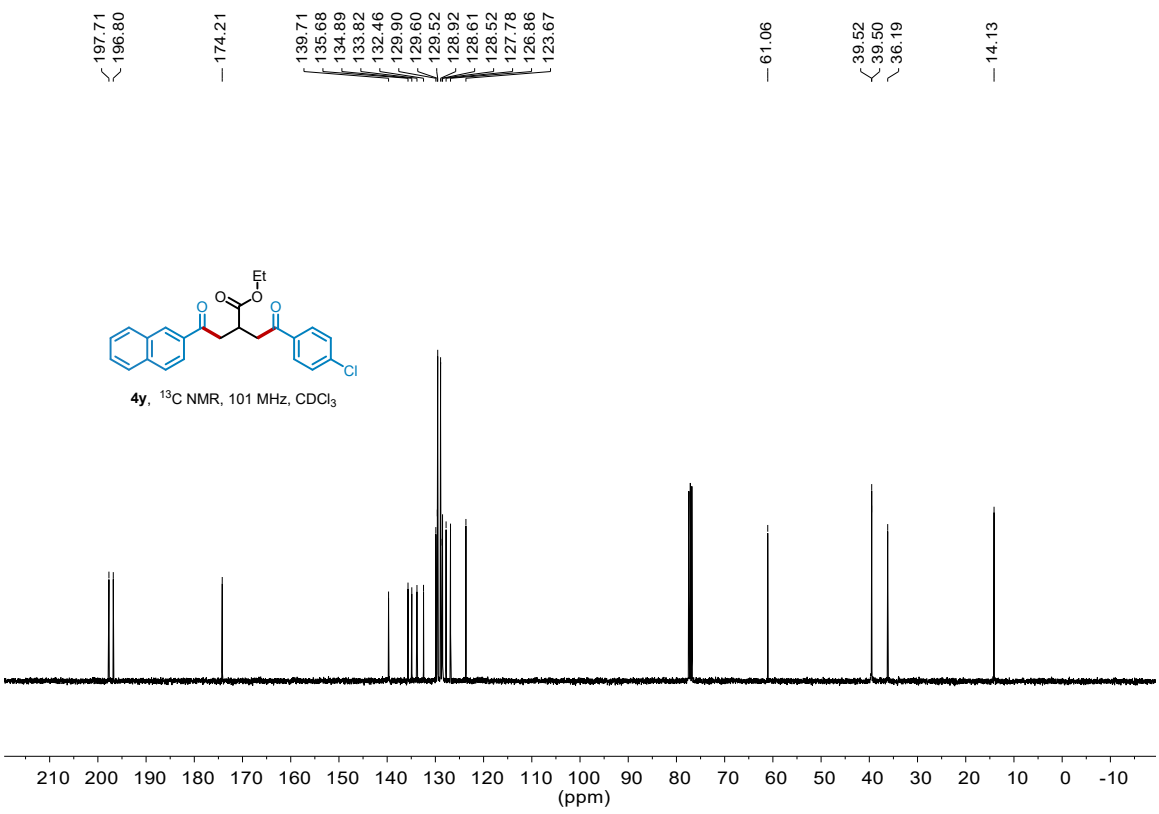

8.54
8.10
8.08
8.07
8.06
7.99
7.97
7.92
7.90
7.88
7.71
7.69
7.65
7.65
7.64
7.64
7.64
7.63
7.62
7.62
7.60
7.60
7.59
7.59
7.57
7.57
7.51
7.50
7.49
7.49
7.47
7.44
7.44
7.44
7.42
4.26
4.24
4.23
4.21
3.78
3.78
3.77
3.76
3.76
3.75
3.74
3.70
3.69
3.66
3.64
3.60
3.58
3.55
3.52
3.50
3.47
3.46
1.29
1.27
1.25
Et
O
O
O
O
4x, 1H NMR, 400 MHz, CDCl3
1.00
3.00
1.01
2.03
2.01
4.00
2.02
1.00
2.00
2.00
1.00
2.01
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
(ppm)



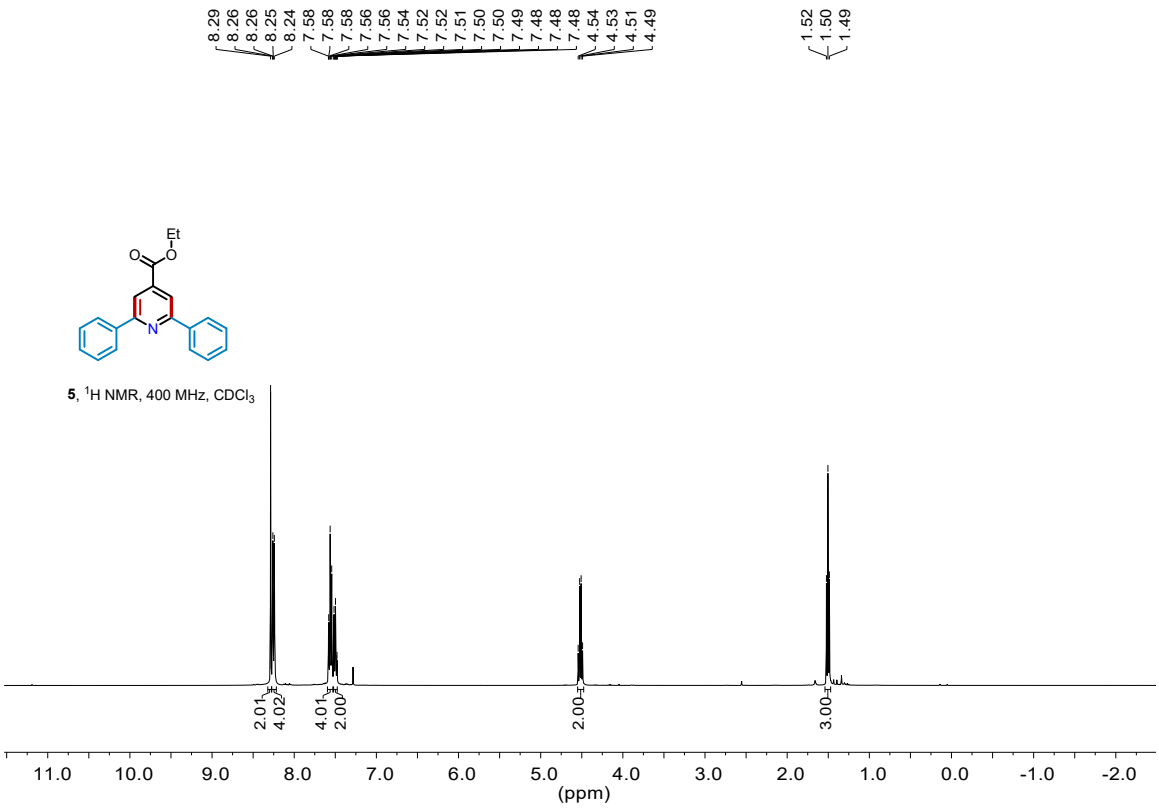
4x, ^{13}C NMR, 101 MHz, $CDCl_3$



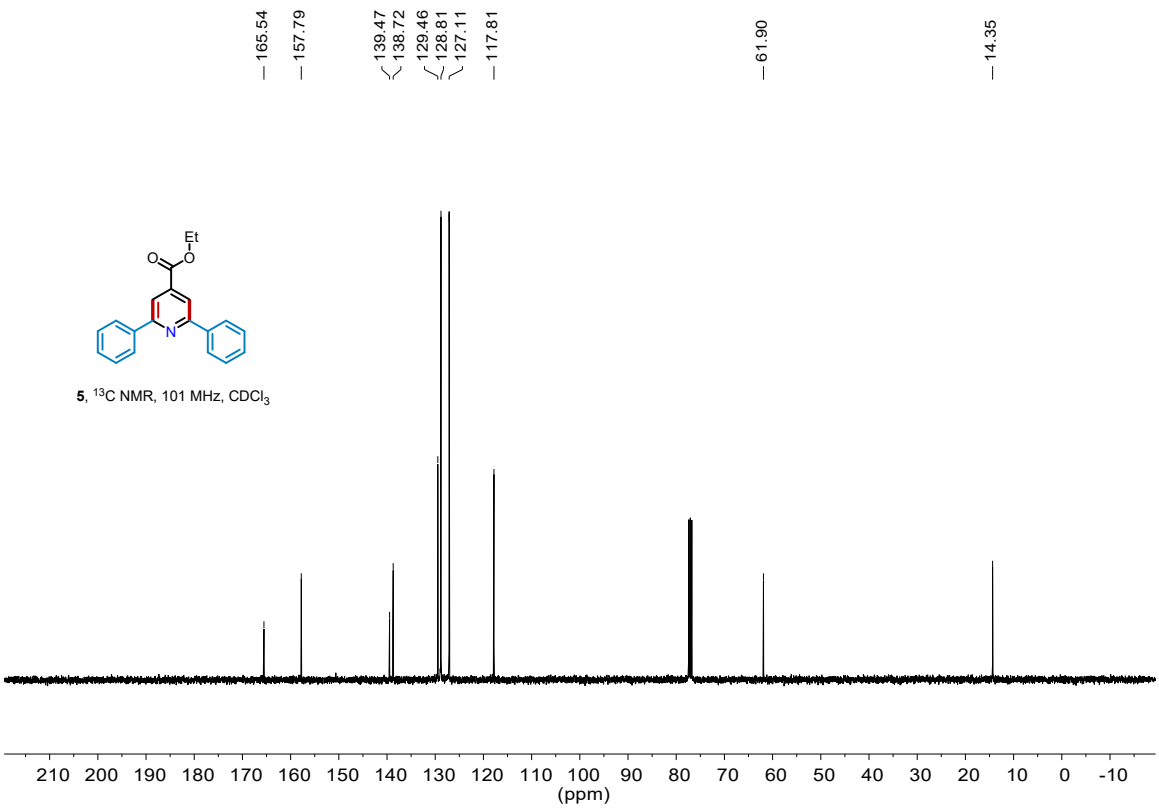
4y, ^{1}H NMR, 400 MHz, $CDCl_3$



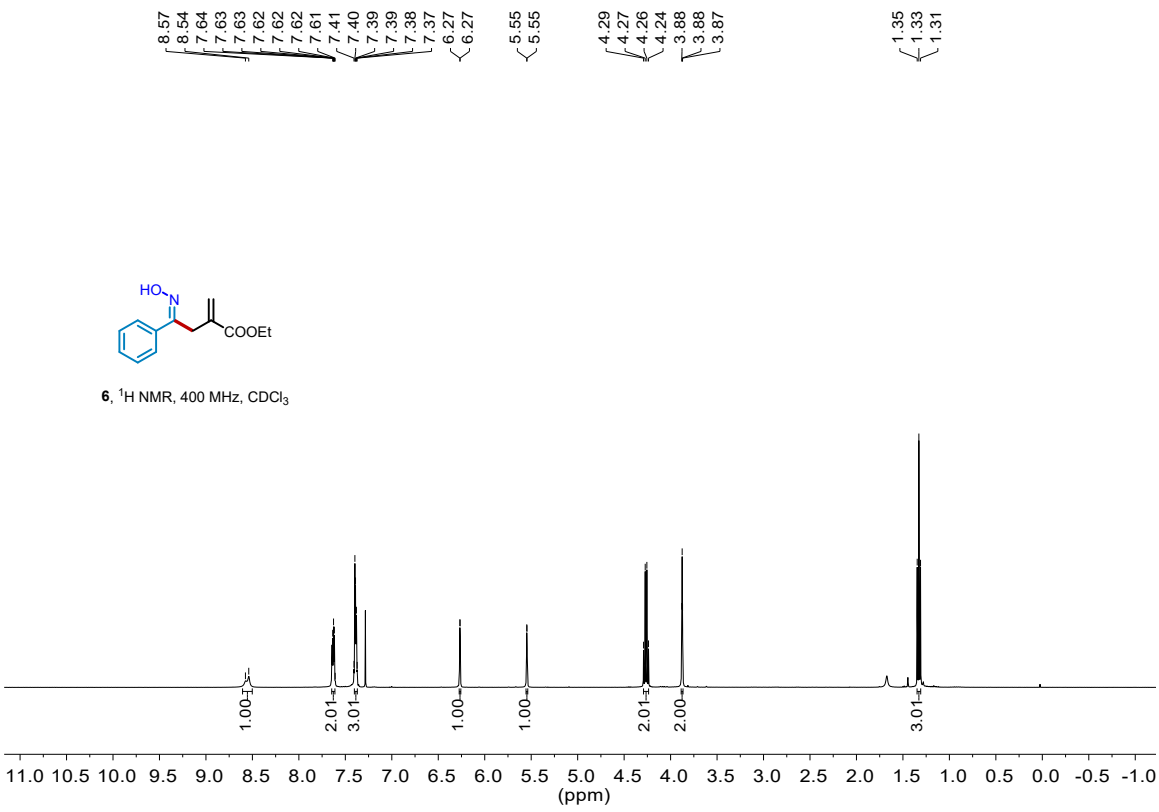
4y, ^{13}C NMR, 101 MHz, $CDCl_3$



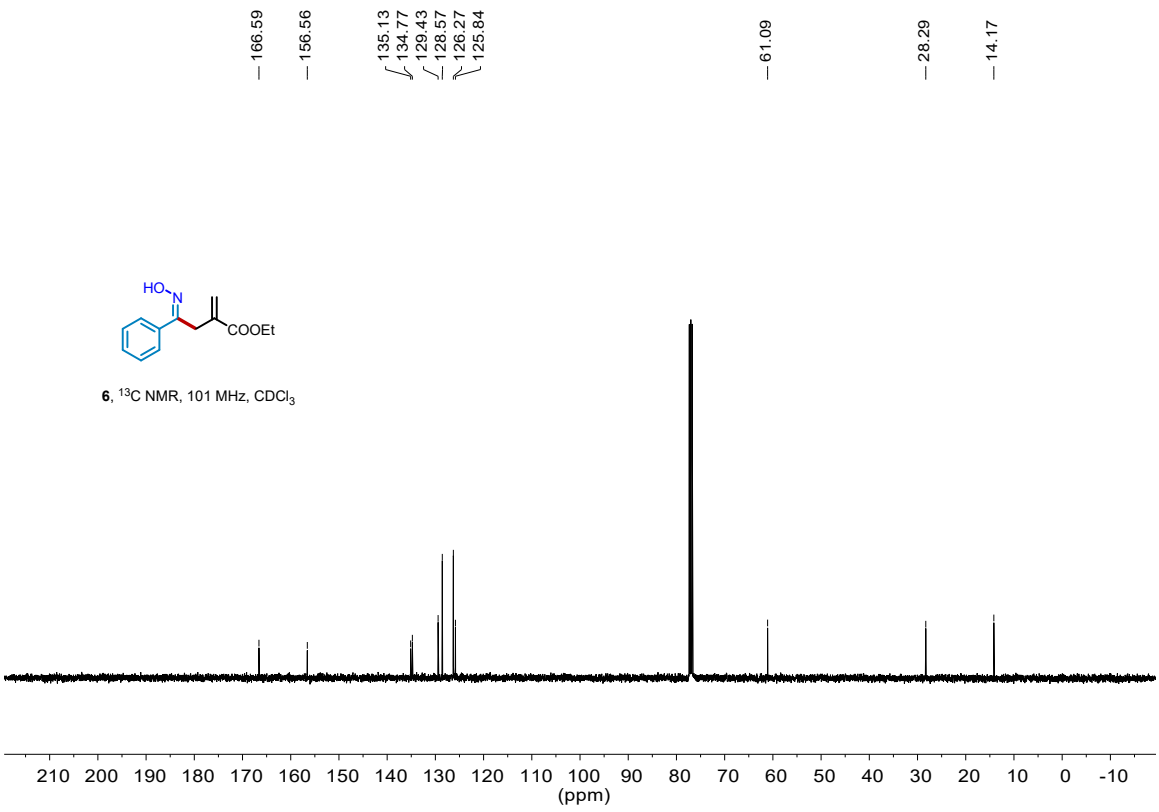
5, ^{1}H NMR, 400 MHz, $CDCl_3$



5, ^{13}C NMR, 101 MHz, $CDCl_3$



6, ^{1}H NMR, 400 MHz, $CDCl_3$



5. Reference

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