Supporting Information

Photocatalyzed Generation of Acyl Radicals from Aryl/Alkyl Acyl Halides via Nucleophilic Substitution

Haowen Zhan[§], Jiansheng Chen[§], Yajing Luo[§], Yang Ke[§] and Xinjun Tang[*§]

[§]Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China

*Email: tangxinjun@cug.edu.cn

Contents

1 General information

Unless otherwise noted, all reactions were carried out under N_2 atmosphere. Acyl halides (**1**), olefins (**2**), and substituted pyridine compounds (used as catalyst precursors) were acquired from commercial reagent suppliers and used without further purification. Acyl fluorides (**1**) were synthesized based on published literature.[1]

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported in δ (ppm) and were referenced to the residual solvent signals of $CDCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C, unless otherwise specified). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet or unresolved, br = broad signal), coupling constant(s) in Hz, and integration. High Resolution Mass Spectrometry (HRMS) were recorded on Bruker micrOTOF II ESI-TOF and Waters G2-XS Qtof using a positive electrospray ionization (ESI). Measured values are reported to 4 decimal places of the calculated value.

UV-Vis: Measurements were recorded on UV-6100 (Shanghai Metash Instruments Co., Ltd). Photochemical reactions were conducted using an RLH-18CU photoreactor (Rogertech, Beijing). Reactions were heated using aluminium alloy heating modules with stirring. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates (Silicyle). Flash column chromatography was performed on silica gel (particle size 300-400 mesh ASTM, purchased from Qingdao, China) and eluted with petroleum ether (PE)/ethyl acetate (EA) or acetone.

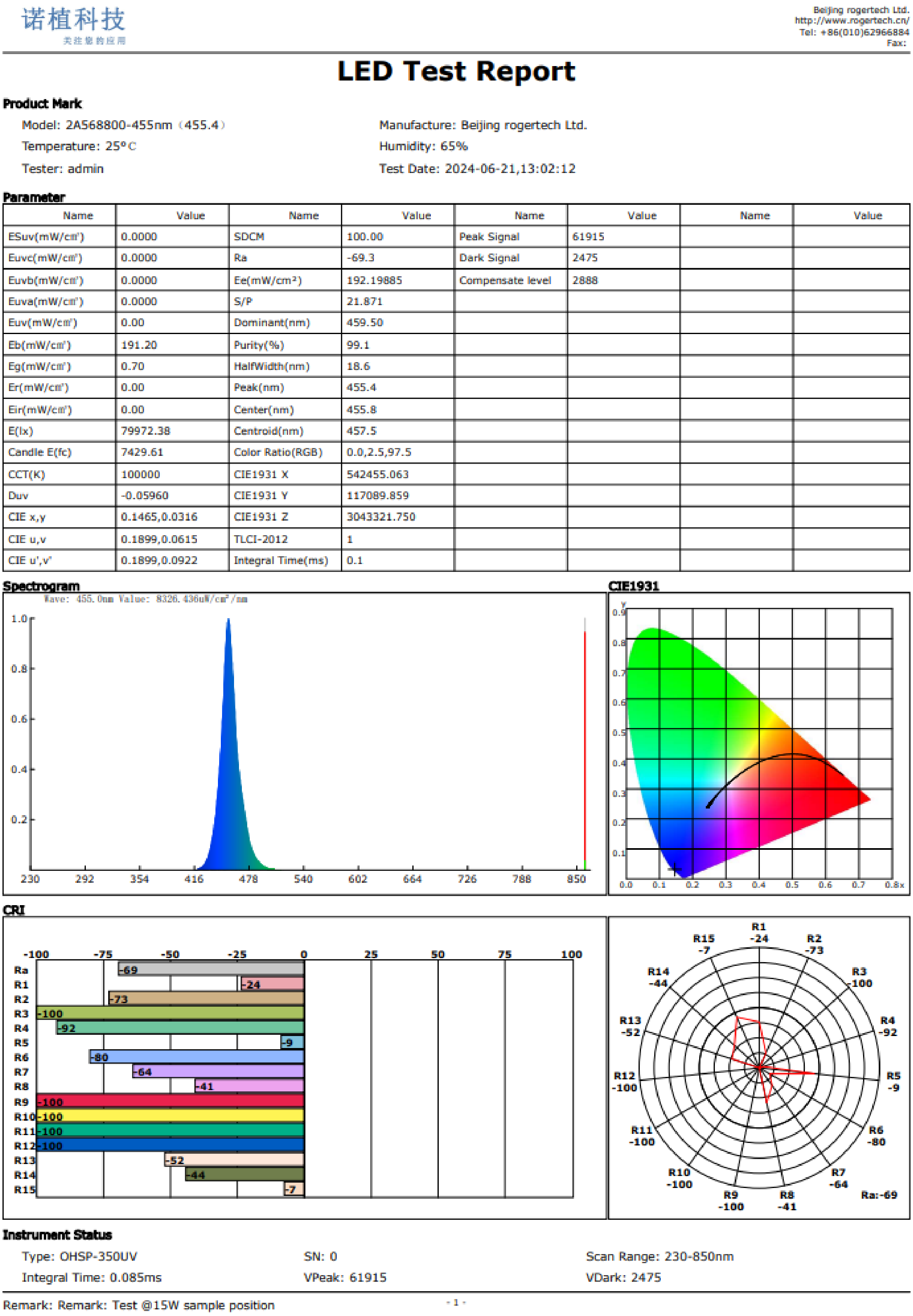
Photoreaction system

Gram scale preparation

Light source

Scheme S1 Photoreactive instrument.

The photoirradiations were conducted using an RLH-18CU 8-position photoreaction system (Beijing Rogertech Ltd.) equipped with blue LEDs. The LEDs have a peak emission wavelength of 455.4 nm and a full width at half maximum (FWHM) of 18.6 nm. The irradiance at the sample position was measured to be 191.20 mW/cm². The reactions were carried out in a borosilicate glass Schlenk tube positioned 2 cm from the LED array without any filters. LED test report is as following：



诺植科技

Beijing rogertech Ltd.
http://www.rogertech.cn/
Tel: +86(010)62966884
Fax:

LED Test Report

Product Mark

Model: 2A568800-455nm（455.4）
Temperature: 25°C
Tester: admin
Manufacture: Beijing rogertech Ltd.
Humidity: 65%
Test Date: 2024-06-21,13:02:12

Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/㎠)	0.0000	SDCM	100.00	Peak Signal	61915		
Euvc(mW/㎠)	0.0000	Ra	-69.3	Dark Signal	2475		
Euvb(mW/㎠)	0.0000	Ee(mW/cm²)	192.19885	Compensate level	2888		
Euva(mW/㎠)	0.0000	S/P	21.871				
Euv(mW/㎠)	0.00	Dominant(nm)	459.50				
Eb(mW/㎠)	191.20	Purity(%)	99.1				
Eg(mW/㎠)	0.70	HalfWidth(nm)	18.6				
Er(mW/㎠)	0.00	Peak(nm)	455.4				
Eir(mW/㎠)	0.00	Center(nm)	455.8				
E(lx)	79972.38	Centroid(nm)	457.5				
Candle E(fc)	7429.61	Color Ratio(RGB)	0.0,2.5,97.5				
CCT(K)	100000	CIE1931 X	542455.063				
Duv	-0.05960	CIE1931 Y	117089.859				
CIE x,y	0.1465,0.0316	CIE1931 Z	3043321.750				
CIE u,v	0.1899,0.0615	TLCI-2012	1				
CIE u',v'	0.1899,0.0922	Integral Time(ms)	0.1				

Spectrogram

Wave: 455.0nm Value: 8326.436uW/cm²/nm

CIE1931

CRI

Instrument Status

Type: OHSP-350UV
Integral Time: 0.085ms
SN: 0
VPeak: 61915
Scan Range: 230-850nm
VDark: 2475

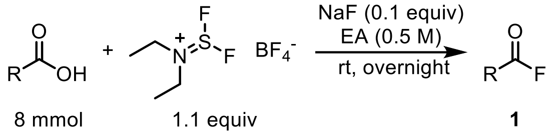
Remark: Remark: Test @15W sample position

- 1 -

Scheme S2 LED test report.

2 General synthetic procedures

2.1 Procedure for the synthesis of acyl fluorides (General procedure A)

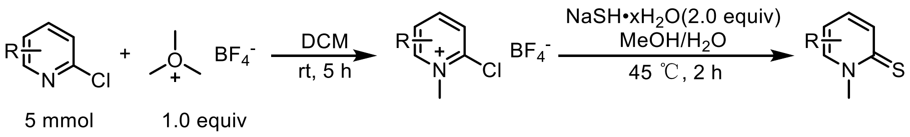


The acyl fluorides were synthesized using a literature procedure with little modification.[1]

A magnetic stir bar was placed in a three-necked flask, followed by the addition of the carboxylic acid (8.0 mmol, 1.0 equiv) and NaF (0.8 mmol, 0.1 equiv). The mixture was then diluted to a concentration of 0.5 M with dry ethyl acetate (EA) or dichloromethane (DCM), followed by the addition of XtalFluor-E (8.8 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature overnight and then concentrated under reduced pressure. The residue was purified directly by passing through a silica plug (3 cm wide × 5 cm deep). The eluent was concentrated under reduced pressure to give the desired acyl fluorides **1** for the following reaction.

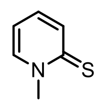
NOTE: Acyl fluorides are unstable on silicon-based materials, therefore, we recommend storing the purified compounds in plastic vials in a freezer.

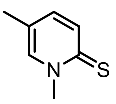
2.2 Procedure for the synthesis of organocatalysts (General procedure B)

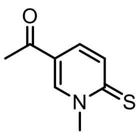


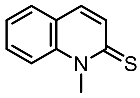
The organocatalysts (**OC**) were prepared according to a literature procedure[2]. Alkylation of 2-chloropyridine (5 mmol, 1.0 equiv) and methyloxonium tetrafluoroborate (5 mmol, 1.0 equiv) was carried out in 40 mL of DCM at room temperature. After stirring for 5 hours, the mixture was concentrated under vacuum to give the pyridine salt, which was used for the next step without further purification.

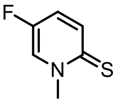
The pyridine salt was dissolved in methanol (30 mL). A solution of NaSH (10 mmol, 2.0 equiv) in water (40 mL) was added dropwise to the methanolic solution at 45 ºC. After stirring for 2 hours, the mixture was poured into water and extracted with DCM (3 × 50 mL). The combined organic phases were dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude organocatalysts, which were purified by column chromatography. The following molecules were synthesized by this method, and the NMR data are consistent with the literature reports.[2]

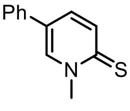

OC1

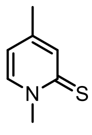

OC2

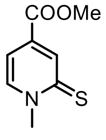

OC3


OC4


OC5

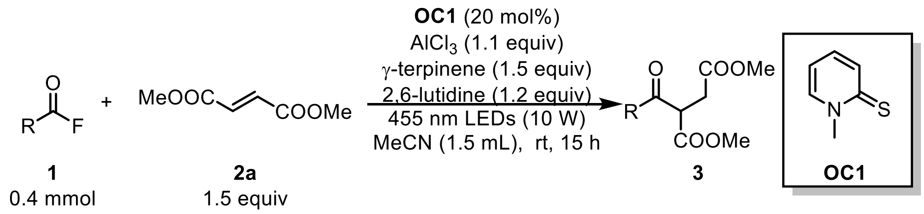

OC6


OC7


OC8

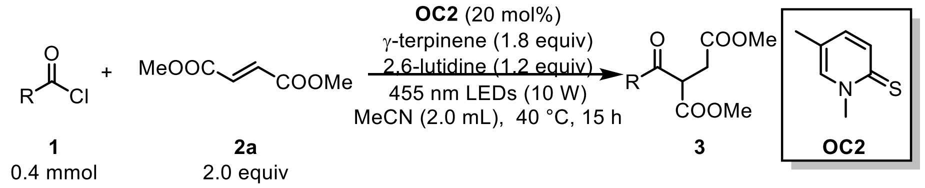
2.3 General procedure for the Giese type reaction

2.3.1 Procedure for the Giese type reaction from acyl fluorides (General procedure C)



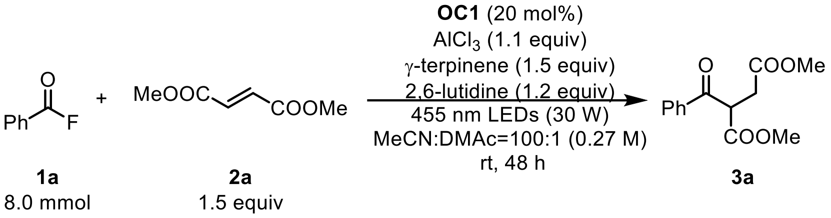
To an oven-dried Schlenk tube equipped with a stir bar were added **OC1** (0.08 mmol, 0.2 equiv), $AlCl_3$ (0.44 mmol, 1.1 equiv), and acyl fluoride **1** (0.4 mmol, 1.0 equiv) under an N_2 atmosphere. (Note: If acyl fluoride **1** is a liquid at room temperature, it should be added after the solvent.) Subsequently, 1.5 mL of MeCN was added to the tube, and the mixture was stirred for 5 minutes. Dimethyl fumarate **2a** (0.8 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), and 2,6-lutidine (0.48 mmol, 1.2 equiv) were then added successively. The reaction mixture was stirred under irradiation from a 10 W 455 nm LED light at room temperature for 15 hours. After the reaction was complete (as monitored by TLC), quenched the reaction with 2.0 mL of MeOH and 0.1 mL of acetic acid. Removal of the solvent under reduced pressure. The residue was then purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product.

2.3.2 Procedure for the Giese type reaction from acyl chlorides (General procedure D)



To an oven-dried Schlenk tube equipped with a stir bar were added **OC2** (0.08 mmol, 0.2 equiv) and acyl chlorides **1** (0.4 mmol, 1.0 equiv) under an N_2 atmosphere. (Note: If acyl chlorides **1** is a liquid at room temperature, it should be added after the addition of 2,6- lutidine.) Subsequently, 2.0 mL of MeCN was added to the tube, and the mixture was stirred for 5 minutes. Dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), and 2,6-lutidine (0.48 mmol, 1.2 equiv) were then added successively. The reaction mixture was stirred under irradiation from a 10 W 455 nm LED light at 40 ºC for 15 hours. After the reaction was complete (as monitored by TLC), quenched the reaction with 2.0 mL of MeOH and 0.1 mL of acetic acid. Removal of the solvent under reduced pressure. The residue was then purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the desired product.

2.3.3 Representative procedure for the preparative scale synthesis

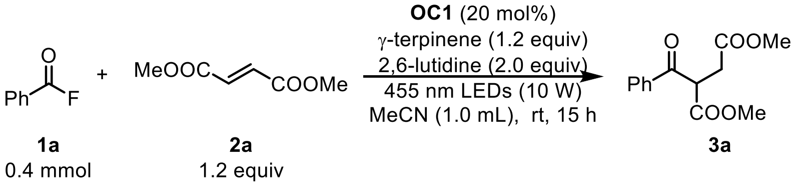


To an oven-dried Schlenk bottle (100 mL) equipped with a stir bar were added **OC1** (1.6 mmol, 0.2 equiv) and $AlCl_3$ (8.8 mmol, 1.1 equiv) under an N_2 atmosphere. Subsequently, 30.0 mL of MeCN was added to the bottle, followed by acyl fluoride **1a** (8.0 mmol, 1.0 equiv). The mixture was stirred for 5 minutes. Dimethyl fumarate **2a** (12.0 mmol, 1.5 equiv), γ-terpinene (12.0 mmol, 1.5 equiv), 2,6-lutidine (9.6 mmol, 1.2 equiv), and 0.3 mL of N, N-dimethylacetamide (DMAc) were then added successively. The reaction mixture was stirred under a 30 W 455 nm LED at room temperature for 48 hours. After the reaction was complete (as monitored by TLC), it was quenched with 0.5 M HCl (20 mL), and the mixture was extracted with ethyl acetate (EA) (3 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by flash column chromatography (PE: EA= 10:1) to afford 1.0613 g of product **3a** as an oily liquid (yield = 53%).

3 Optimization of the reaction conditions

3.1 Screening of the Lewis acid

Table S1 Screening of the Lewis acid

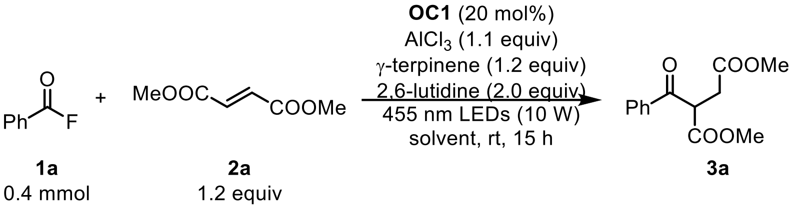


Entry	Lewis acid[a]	NMR yield of **3a**[b]
1	-	8%
2	$Yb(OTf)_3$ (1.2 equiv)	30%
3	$Sc(OTf)_3$ (1.2 equiv)	N.D.
4	$In(OTf)_3$ (1.2 equiv)	N.D.
5	$Zn(OTf)_3$ (1.2 equiv)	N.D.
6	$Fe(OTf)_3$ (1.2 equiv)	N.D.
7	$AlCl_3$ (1.2 equiv)	33%
8	$AlCl_3$ (1.5 equiv)	17%
9	**$AlCl_3$ (1.1 equiv)**	**54%**

[a] **1a** (0.4 mmol), **2a** (1.2 equiv), **OC1** (20 mol%), Lewis acid, γ-terpinene (1.2 equiv), 2.6-lutidine (2.0 equiv), MeCN (1.0 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] Yield determined by ^1H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard. N.D. stands for Not Detected

3.2 Screening of the solvent

Table S2 Screening of the solvent

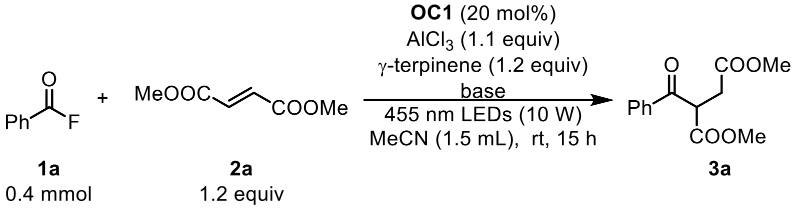


Entry	Solvent[a]	NMR yield of **3a**[b]
1	MeCN (1.0 mL)	54%
2	**MeCN (1.5 mL)**	**60%**
3	MeCN (2 mL)	57%
4	DCM (1.5 mL)	47%
5	DCE (1.5 mL)	47%
6	1,4-Dioxane (1.5 mL)	32%
7	DMSO (1.5 mL)	N.D.
8	DMF (1.5 mL)	37%
9	EA (1.5 mL)	24%
10	Toluene (1.5 mL)	trace
11	THF (1.5 mL)	trace
12	MTBE (1.5 mL)	N.D.

[a] **1a** (0.4 mmol), **2a** (1.2 equiv), **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.2 equiv), 2.6-lutidine (2.0 equiv), solvent with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard. N.D. stands for Not Detected

3.3 Screening of the base

Table S3 Screening of the base



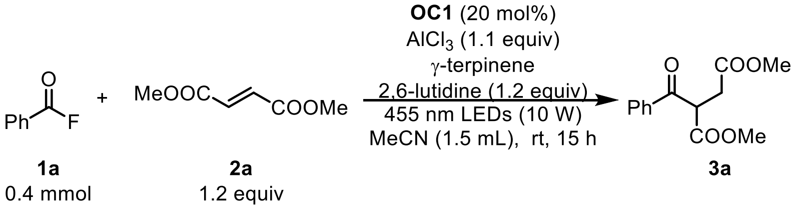
Entry	Base[a]	NMR yield of **3a**[b]
1	2,6-lutidine (2.0 equiv)	60%
2	2,6-lutidine (1.8 equiv)	58%
3	2,6-lutidine (1.5 equiv)	59%
4	**2,6-lutidine (1.2 equiv)**	**65%**
5	K_3PO_4 (1.2 equiv)	23%
6	Cs_2CO_3 (1.2 equiv)	N.D.
7	KOH (1.2 equiv)	N.D.
8	^{t}BuOK (1.2 equiv)	N.D.
9	K_2CO_3 (1.2 equiv)	34%
10	DMAP (1.2 equiv)	20%
11	DBU (1.2 equiv)	trace
12	Et_3N (1.2 equiv)	trace
13	CH_3COONa (1.2 equiv)	N.D.

14	pyridine (1.2 equiv)	36%

[a] **1a** (0.4 mmol), **2a** (1.2 equiv), **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.2 equiv), base, MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard. N.D. stands for Not Detected.

3.4 Screening of the loading of γ-terpinene

Table S4 Screening of the loading of γ-terpinene

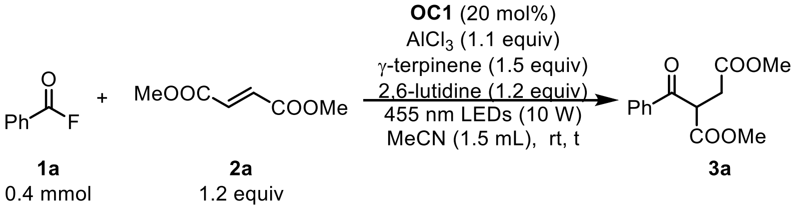


Entry	Loading of γ-terpinene[a]	NMR yield of **3a**[b]
1	γ-terpinene (1.2 equiv)	65%
2	γ-terpinene (1.0 equiv)	60%
3	**γ-terpinene (1.5 equiv)**	**66%**
4	γ-terpinene (1.8 equiv)	62%

[a] **1a** (0.4 mmol), **2a** (1.2 equiv), **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene, 2,6-lutidine (1.2 equiv), MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard.

3.5 Screening of the reaction time

Table S5 Screening of the reaction time

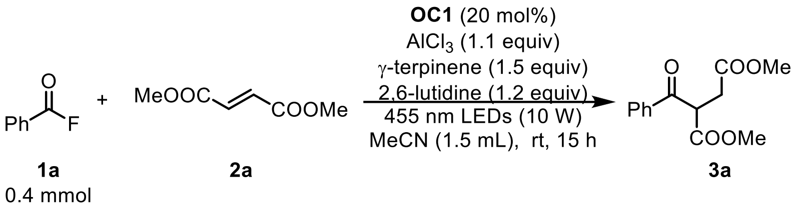


Entry	Reaction time[a]	NMR yield of **3a**[b]
1	**15 h**	**66%**
2	12 h	50%
3	18 h	63%

[a] **1a** (0.4 mmol), **2a** (1.2 equiv), **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.5 equiv), 2,6-lutidine (1.2 equiv), MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for hours under N_2 atmosphere. [b] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard.

3.6 Screening of the material ratio

Table S6 Screening of the material ratio

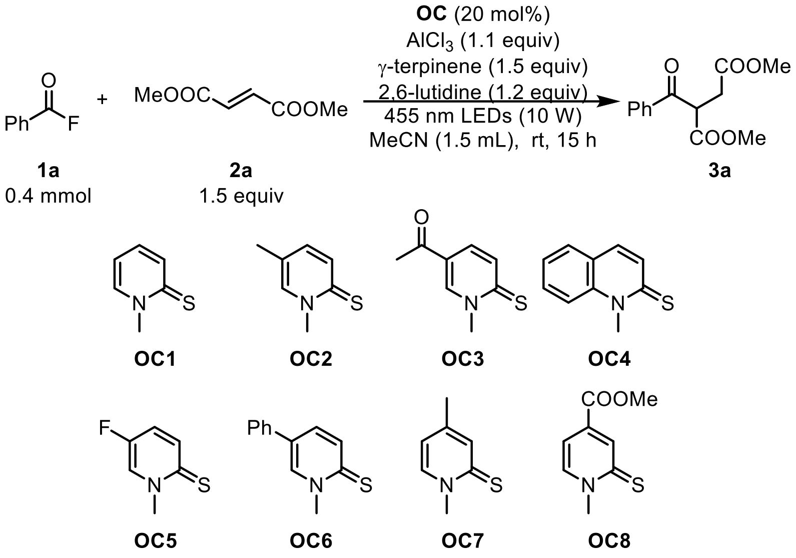


Entry	Material ratio[a]	NMR yield of **3a**[c]
1	**2a** (1.2 equiv)	66%
2	**2a (1.5 equiv)**	**71%**
3	**2a** (1.8 equiv)	53%
4	**2a** (2.0 equiv)	46%
5	**2a** (0.4 mmol), **1a** (1.2 equiv)[b]	54%

[a] **1a** (0.4 mmol), **2a**, **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.5 equiv), 2,6-lutidine (1.2 equiv), MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] $AlCl_3$ (1.32 equiv) were used. [c] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard.

3.7 Screening of the organocatalysts

Table S7 Screening of the organocatalysts

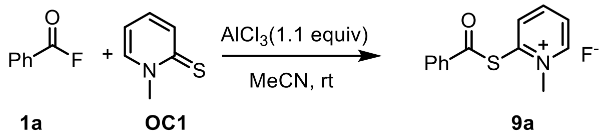


Entry	Organocatalysts[a]	NMR yield of **3a**[b]
1	**OC1**	**71%**
2	**OC2**	19%
3	**OC3**	21%
4	**OC4**	N.D.
5	**OC5**	36%
6	**OC6**	30%
7	**OC7**	15%
8	**OC8**	12%

[a] **1a** (0.4 mmol), **2a** (1.5 equiv), **OC** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.5 equiv), 2,6-lutidine (1.2 equiv), MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] Yield determined by ^{1}H NMR analysis of crude mixture using 0.4 mmol of mesitylene as internal standard.

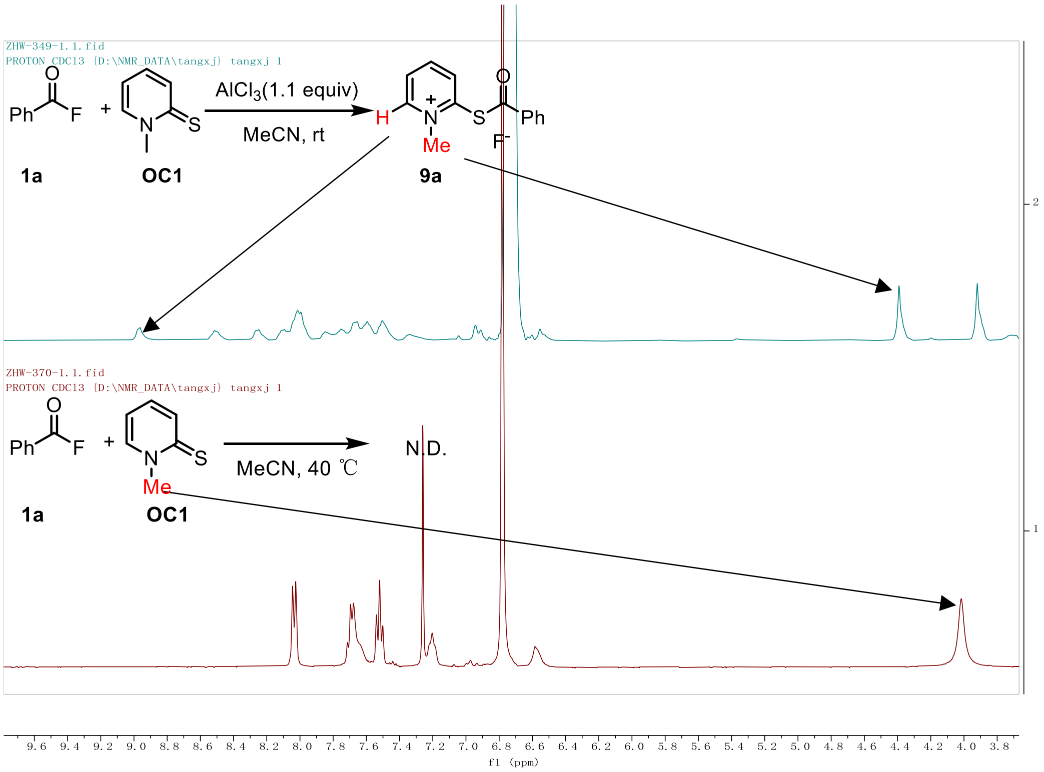
4 Mechanistic Studies

4.1 Procedure for the synthesis of reaction intermediate

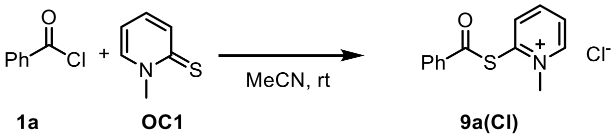


To an oven-dried Schlenk tube equipped with a stir bar were added **OC1** (0.4 mmol, 1.0 equiv) and $AlCl_3$ (0.44 mmol, 1.1 equiv). Subsequently, 1.5 mL of MeCN was added to the tube, followed by the addition of acyl fluoride **1a** (0.4 mmol, 1.0 equiv) under an N_2 atmosphere. After stirring the mixture for 5 minutes, the yield was determined by ^{1}H NMR analysis using mesitylene (0.4 mmol) as an internal standard. The chemical shifts were referenced to the mesitylene signal at δ 6.80 ppm. Various separation methods were attempted without success. The product is inherently unstable, undergoing decomposition under light, in solvents, and on silica gel, accounting for the isolation difficulties—a finding consistent with previous reports.[3] The ^{1}H NMR spectrum in $CDCl_3$ showed that the salt attained an equilibrium with the starting material (**9a**: **1a**=ca. 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02(d, 1H, pyridinium ring proton at 6), 8.61-7.02 (m, ring protons), 4.44(s, 3H, N^+-Me).



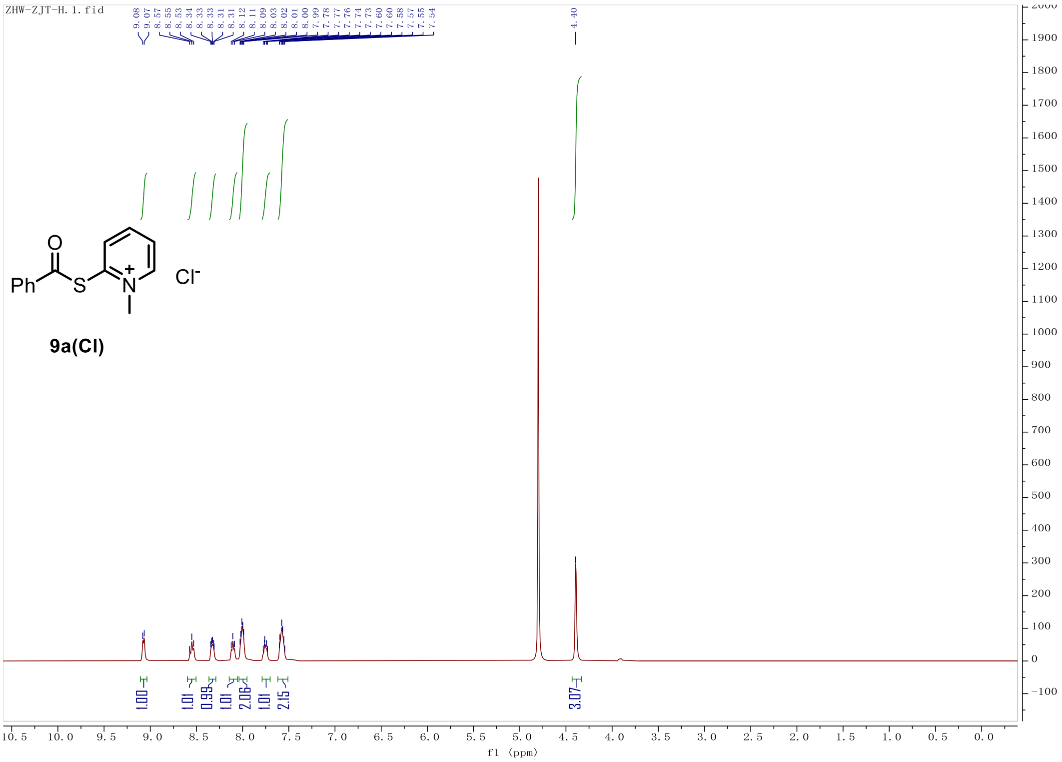
Scheme S3 ^{1}H NMR spectrum of intermediates in the reaction process



To an oven-dried Schlenk tube equipped with a stir bar were added **OC1** (2.0 mmol, 1.0 equiv). Subsequently, 4 mL of MeCN was added to the tube, followed by the addition of acyl chloride **1a** (2.0 mmol, 1.0 equiv) under an N_2 atmosphere. After most of the solvent was removed by rotary evaporation, 10 mL of diethyl ether was added, and the mixture was slowly concentrated at room temperature, resulting in the formation of **9a(Cl)** as a white solid.

^{1}H NMR (400 MHz, D_2O) δ 9.07 (d, *J* = 6.2 Hz, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.37 – 8.29 (m, 1H), 8.11 (t, *J* = 7.2 Hz, 1H), 8.05 – 7.96 (m, 2H), 7.80 – 7.71 (m, 1H), 7.63 – 7.52 (m, 2H), 4.40 (s, 3H).

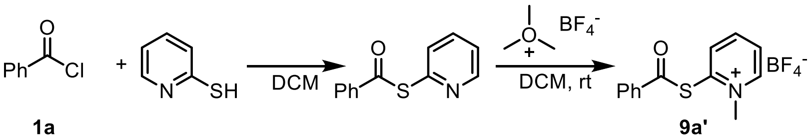
Note: It is recommended to wash the intermediate **9a(Cl)** with ether before use, as it is photosensitive. Additionally, it is stable in H_2O but decomposes in MeCN.



Scheme S4 ^{1}H NMR spectrum of **9a(Cl)**

4.2 Controlled experiment

Considering the low yield and purification difficulties of the reaction intermediate obtained from acyl halides directly, the following route was designed to synthesize intermediate **9a'** based on literature reports.[3]

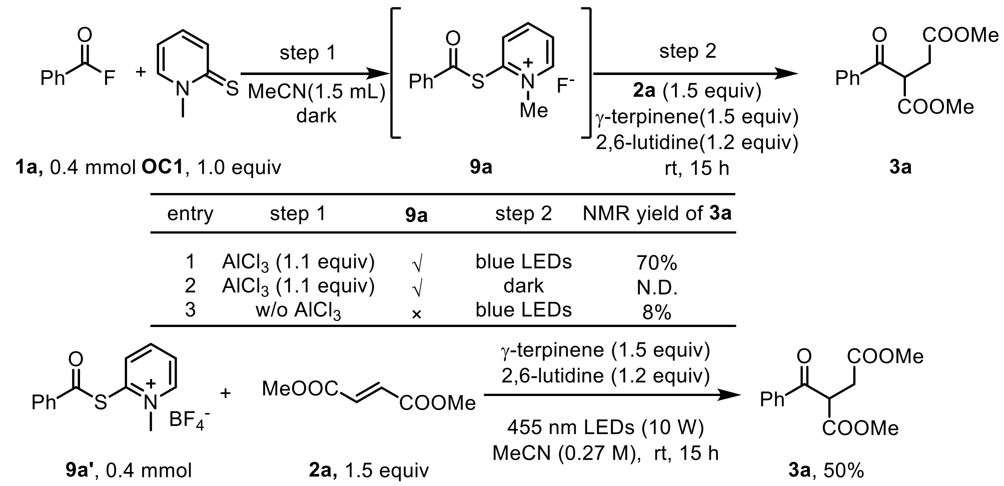


2-Thiopyridine (5.0 mmol) was dissolved in dry DCM (10 mL) and acyl chloride **1a** (5.0 mmol, 1 equiv.) was added dropwise via syringe. The reaction mixture was stirred vigorously for 2 h under N_2 atmosphere. Subsequently, the resulting precipitate was diluted with DCM, quenched by addition of saturated NaHCO3 solution, extracted and the organic phase separated and dried over Na_2SO_4. Filtered and concentrated in vacuo to afford a crude thioester. Thioester in a crystalline form can be obtained via precipitation from EA-hexanes solution.

Then, the obtained thioester was dissolved in DCM and treated with 1.1 equivalents of a trimethyltetrafluoronium salt (relative to the thioester). After stirring for 5 hours, the resulting **9a'** precipitate was collected, washed three times with DCM, and dried under reduced pressure.

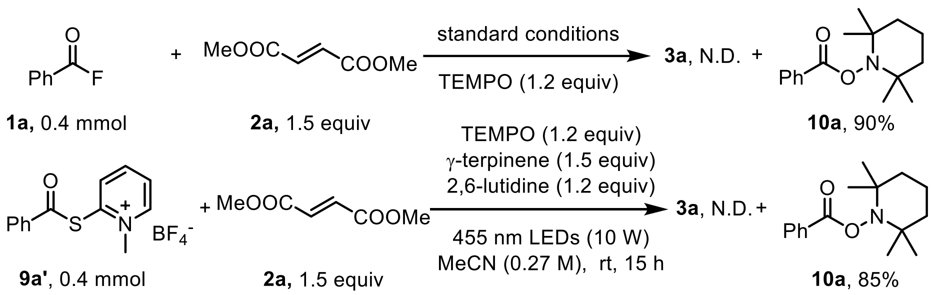
The following experiments were designed (Scheme S5, a). In the present of $AlCl_3$, equivalent of **1a** and **OC1** could form the photoactive intermediate **9a** in dark. **9a** could be photoexcited to generate acyl radical and afford the corresponding product **3a**. The reaction could not work without $AlCl_3$ or without light. In addition, compound **9a'** afforded **3a** in 50% yield upon LEDs irradiation, further confirming this observation. The designed radical trapping experiments also confirm this view (Scheme S5, b). Radical trapping experiments with TEMPO showed that no desired product was found and the adduct **10a** was isolated in 90% and 85% yield, respectively.

a)Synthesis of the photoactive intermediate **9a** and **9a'**



entry	step 1	**9a**	step 2	NMR yield of **3a**
1	$AlCl_3$ (1.1 equiv)	√	blue LEDs	70%
2	$AlCl_3$ (1.1 equiv)	√	dark	N.D.
3	w/o $AlCl_3$	×	blue LEDs	8%

b) Radical trapping experiments

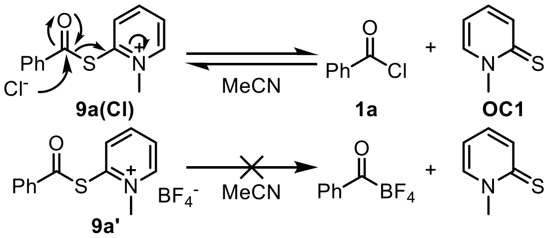


Scheme S5 Controlled experiment. a) Yield determined by ^1H NMR analysis of crude mixture, adding 0.4 mmol of mesitylene as internal standard before the irradiation. b) Standard conditions: **1a** (0.4 mmol), **2a** (1.5 equiv), γ-terpinene (1.5 equiv), 2,6-lutidine (1.2 equiv), MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. TEMPO was added before the irradiation.

4.3 UV-Vis spectroscopic analysis

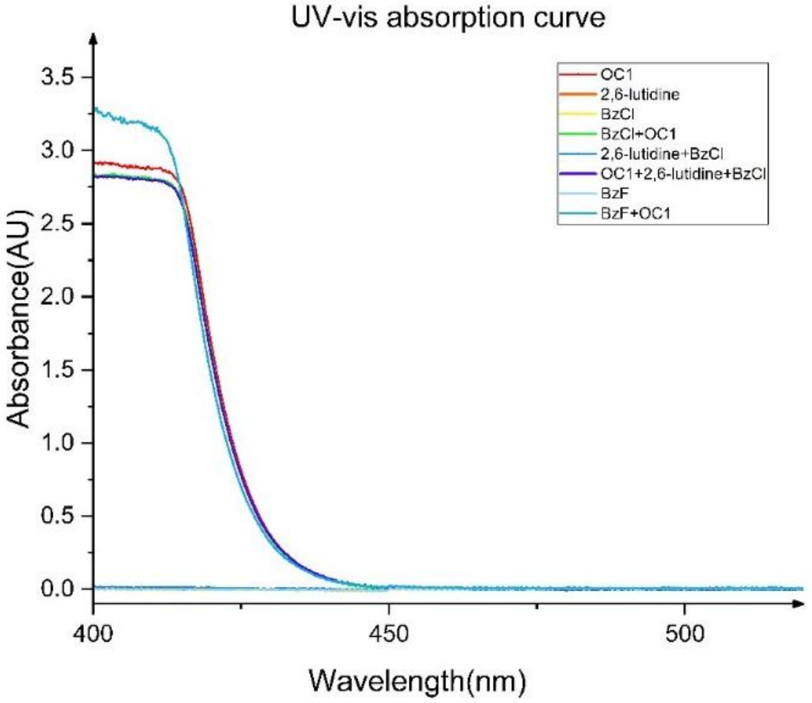
UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a UV-6100 spectrophotometer. Absorption spectra of individual reaction components and mixtures thereof were recorded. No redshift phenomenon was observed.

Extra tests were conducted on the reaction intermediates **9**. The intermediate **9a(Cl)** turned yellow in MeCN and its absorption curve closely overlapped with that of **OC1**, corresponding to the reversible reaction between **OC1** and **9a(Cl)**. In contrast, anomalous negative absorption peaks were observed for **9a(Cl)** in H_2O and for **9a'** in MeCN. Although these negative absorption peaks might potentially arise from the solvent[4], we attempted to use different testing materials and solvents and consistently observed this negative absorption phenomenon. Therefore, we propose that the intermediate is photoexcited at 450nm, and a portion of the intermediate **9** returns from the S_1 state to the S_0 state, emitting fluorescence, which results in the negative absorption peaks.

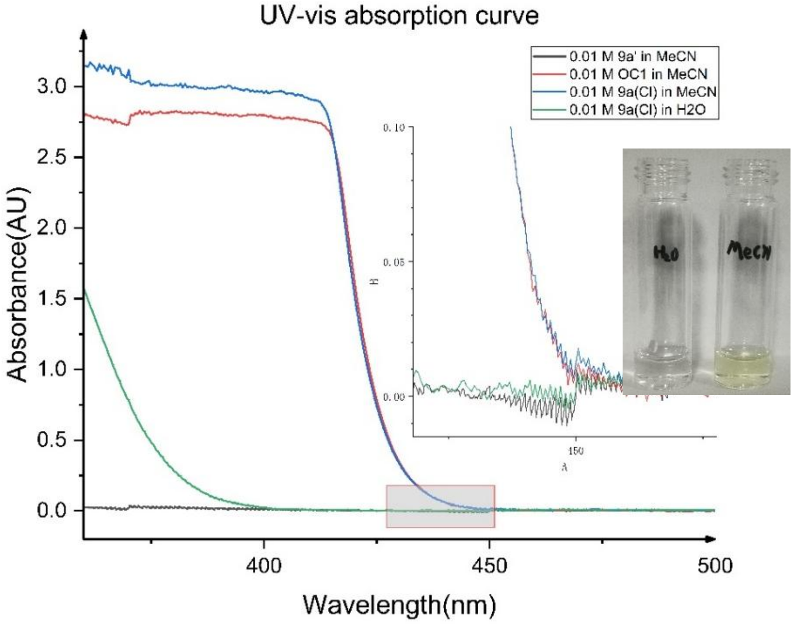


Scheme S6 reversible equilibrium between **9a(Cl)** and **OC1**

Note: No special instructions, the concentration was 0.01 M (in MeCN) for both the individually measured components and for each component in the mixture.



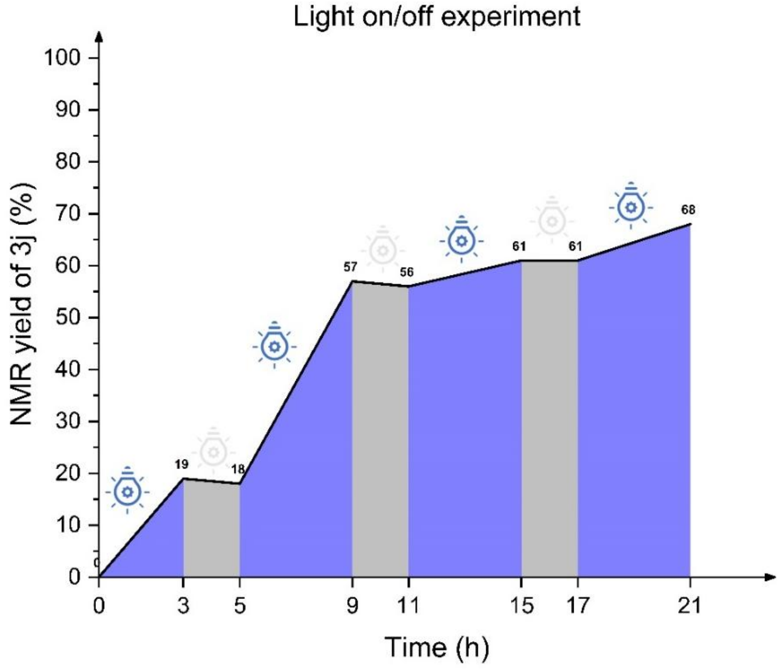
Scheme S7 UV-Vis absorption spectra of individual reaction components and mixtures



Scheme S8 UV-Vis spectroscopic analysis of **9a'** and **9a(Cl)**

4.4 Light ON/OFF experiment

The standard reaction was set up on a 0.4 mmol scale according to the **General Procedure C** for the preparation of **3j**. The internal standard mesitylene was added before the irradiation. The reaction mixture was cooled to room temperature, and the yield was analyzed by ^{1}H NMR. The reaction was initiated with alternating periods of irradiation and darkness to examine the effect of continuous visible light on the reaction progress. The results demonstrated that light is essential for the reaction to proceed.

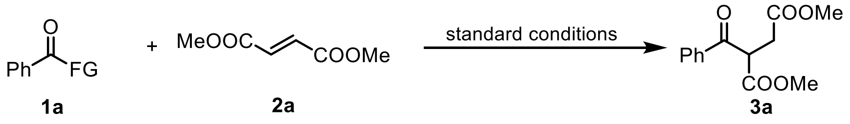


Scheme S9 Light ON/OFF experiment

4.5 Triplet quenching experiment

To investigate the role of the singlet and triplet states of intermediate **9** in the reaction system, we added different types of triplet quenchers to the reaction mixture. When the reaction was conducted under an air atmosphere instead of the a N_2 atmosphere, the reaction was inhibited. To avoid interference from aluminum salts on the additives, benzoyl chloride was used as the substrate. Fc[5], 9-methylanthracene[6], and 2,5-dimethyl-2,4-hexadiene[7] all significantly suppressed the reaction. Meanwhile, the addition of the triplet sensitizer benzil left the reaction yield unchanged. These results indicate the presence of a triplet state during the reaction. Based on the absorption curve of intermediate **9a(Cl)** and **9a'**, we propose that upon visible-light irradiation, **9** is photoexcited to the S_1 state and undergoes intersystem crossing (ISC) to the T_1 state, from which homolytic C–S bond cleavage generates acyl and thiyl radicals.

Table S8 Triplet quenching experiment

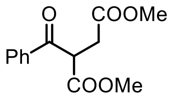


Entry	FG	quencher	GC yield of **3a**[c]
1	F[a]	air	0
2	Cl[b]	air	2%
3	Cl[b]	benzil (0.1 equiv)	71%
4	Cl[b]	Fc (1.5 equiv)	4%

5	Cl[b]	9-methylanthracene (1.5 equiv)	13%
6	Cl[b]	2,5-Dimethyl-2,4-hexadiene (1.5 equiv)	33%

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (1.5 equiv), **OC1** (20 mol%), $AlCl_3$ (1.1 equiv), γ-terpinene (1.5 equiv), 2.6-lutidine (1.2 equiv) in MeCN (1.5 mL) with irradiation of 10 W 455 nm LED at room temperature for 15 h under N_2 atmosphere. [b] **1a** (0.4 mmol), **2a** (2.0 equiv), **OC2** (0.2 equiv), γ-terpinene (1.8 equiv), 2,6-lutidine (1.2 equiv) in MeCN (2.0 mL) with irradiation of 10 W 455 nm LED at 40 ºC for 18 h under a N_2 atmosphere. [c] GC yield.

5 Experimental Procedures and Characterization Data

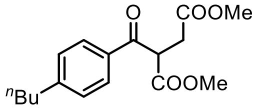


Dimethyl 2-benzoylsuccinate (3a)[8]

LG = F: Synthesized according to **General procedure C** using **1a** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 71.1 mg, 71% yield, oily liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.89 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.10 (dd, *J* = 17.4, 7.7 Hz, 1H), 3.03 (dd, *J* = 17.5, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 171.8, 169.3, 135.9, 133.9, 129.0, 128.9, 53.0, 52.2, 49.4, 33.2.



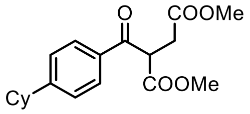
Dimethyl 2-(4-butylbenzoyl)succinate (3b)

LG = F: Synthesized according to **General procedure C** using **1b** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 78.4 mg, 64% yield, oily liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.86 (t, *J* = 7.1 Hz, 1H), 3.65 (s, 2 × 3H), 3.11 – 2.97 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.54 (m, 2H), 1.39 – 1.28 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 171.8, 169.4, 149.7, 133.5, 129.2, 128.9, 52.8, 52.1, 49.2, 35.8, 33.2, 22.4, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}O_5$ 307.1540, found: 307.1544.



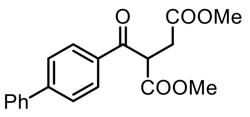
Dimethyl 2-(4-cyclohexylbenzoyl)succinate (3c)

LG = F: Synthesized according to **General procedure C** using **1c** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 86.4 mg, 65% yield, oily liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.87 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.06 (dd, *J* = 17.5, 7.5 Hz, 1H), 3.04 (dd, *J* = 14.0, 3.4 Hz, 1H), 2.62 – 2.50 (m, 1H), 1.92 – 1.81 (m, 4H), 1.80 – 1.72 (m, 1H), 1.49 – 1.33 (m, 4H). 1.32 – 1.19 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 171.9, 169.5, 154.7, 129.3, 127.4, 52.9, 52.2, 49.3, 44.9, 34.2, 33.3, 26.8, 26.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{24}NaO_5$ 355.1516, found: 355.1519.



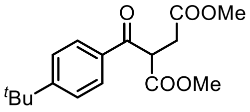
Dimethyl 2-([1,1'-biphenyl]-4-carbonyl) succinate (3d)

LG = F: Synthesized according to **General procedure C** using **1d** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 75.7 mg, 58% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.65 - 7.60 (m, 2H), 7.51 - 7.37 (m, 3H), 4.94 (t, J = 7.2 Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.15 (dd, J = 17.4, 7.7 Hz, 1H), 3.07 (dd, J = 17.4, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.6, 171.8, 169.3, 146.5, 139.7, 134.6, 129.6, 129.1, 128.5, 127.5, 127.4, 52.9, 52.2, 49.3, 33.2.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{19}H_{18}NaO_5$ 349.1046, found: 349.1050.



Dimethyl 2-(4-(tert-butyl)benzoyl)succinate (3e)

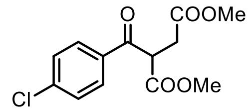
LG = F: Synthesized according to **General procedure C** using **1e** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 68.6 mg, 56% yield, oily liquid.

LG = Cl: Synthesized according to **General procedure D** using **1e** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6-lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 85.8 mg, 70% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.88 (t, J = 7.3 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.13 – 2.97 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.6, 171.8, 169.4, 157.7, 133.2, 129.0, 125.8, 52.9, 52.2, 49.2, 35.3, 33.2, 31.1.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{17}H_{23}O_5$ 307.1540, found: 307.1542.



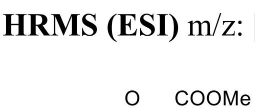
Dimethyl 2-(4-chlorobenzoyl)succinate (3f)

LG = F: Synthesized according to **General procedure C** using **1f** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 71.7 mg, 63% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 4.82 (dd, J = 8.2, 6.2 Hz, 1H), 3.663 (s, 3H), 3.656 (s, 3H), 3.11 (dd, J = 17.5, 8.1 Hz, 1H), 3.01 (dd, J = 17.5, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.0, 171.8, 169.0, 140.5, 134.4, 130.5, 129.2, 53.1, 52.3, 49.3, 33.1.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{13}H_{14}ClO_5$ 285.0524, found: 285.0526.



Dimethyl 2-(4-bromobenzoyl)succinate (3g)

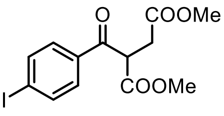
LG = F: Synthesized according to **General procedure C** using **1g** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 68.4 mg, 52% yield, white solid.

LG = Cl: Synthesized according to **General procedure D** using **1g** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6-lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 72.4 mg, 55% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 4.82 (dd, J = 8.2, 6.2 Hz, 1H), 3.674(s, 3H), 3.667 (s, 3H), 3.12 (dd, J = 17.5, 8.2 Hz, 1H), 3.02 (dd, J = 17.5, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.2, 171.8, 168.9, 134.8, 132.2, 130.5, 129.2, 53.1, 52.3, 49.3, 33.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{14}BrO_5$ 329.0019, found: 329.0023.



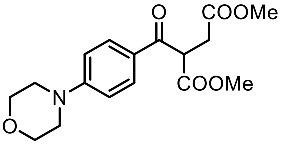
Dimethyl 2-(4-iodobenzoyl)succinate (3h)

LG = F: Synthesized according to **General procedure C** using **1h** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =7:1): 84.2 mg, 56% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 4.80 (dd, *J* = 8.1, 6.3 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.11 (dd, *J* = 17.5, 8.1 Hz, 1H), 3.01 (dd, *J* = 17.5, 6.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 171.8, 168.9, 138.2, 135.3, 130.3, 102.2, 53.0, 52.3, 49.2, 33.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{14}IO_5$ 376.9880, found: 376.9884.



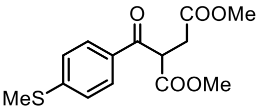
Dimethyl 2-(4-morpholinobenzoyl)succinate (3i)

LG = F: Synthesized according to **General procedure C** using **1i** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6-lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =4:1): 45.6 mg, 34% yield, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.85 – 4.77 (m, 1H), 3.87 – 3.79 (m, 4H), 3.65 (s, 2 × 3H), 3.35 – 3.28 (m, 4H), 3.08 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 172.0, 169.7, 154.7, 131.2, 126.2, 113.3, 66.6, 52.8, 52.1, 48.9, 47.4, 33.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{21}NNaO_6$ 358.1261, found: 358.1262.



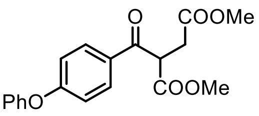
Dimethyl 2-(4-(methylthio)benzoyl)succinate (3j)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 80.6 mg, 68% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.654 (s, 3H), 3.647 (s, 3H), 3.10 – 2.97 (m, 2H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 171.7, 169.2, 147.1, 132.0, 129.3, 125.0, 52.8, 52.1, 49.0, 33.1, 14.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_5S$ 297.0791, found: 297.0794.



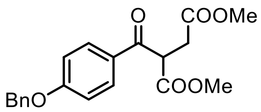
Dimethyl 2-(4-phenoxybenzoyl)succinate (3k)

LG = F: Synthesized according to **General procedure C** using **1k** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 89.0 mg, 65% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 4.84 (t, *J* = 7.3 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.15 – 2.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 171.8, 169.3, 162.8, 155.2, 131.4, 130.4, 130.2, 124.9, 120.5, 117.3, 52.9, 52.1, 49.2, 33.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{19}O_6$ 343.1176, found: 343.1181.



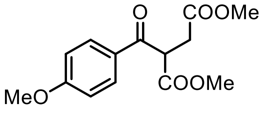
Dimethyl 2-(4-(benzyloxy)benzoyl)succinate (3l)

LG = F: Synthesized according to **General procedure C** using **1l** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 88.4 mg, 62% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.29 (m, 5H), 7.03 (d, *J* = 8.7 Hz, 2H), 5.13 (s, 2H), 4.84 (t, *J* = 7.2 Hz, 1H), 3.673 (s, 3H), 3.665 (s, 3H), 3.11 – 2.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 171.9, 169.4, 163.3, 136.1, 131.4, 129.0, 128.8, 128.4, 127.5, 114.9, 70.3, 52.8, 52.1, 49.1, 33.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}O_6$ 357.1333, found: 357.1337.



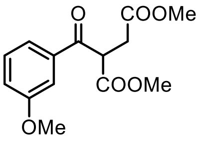
Dimethyl 2-(4-methoxybenzoyl)succinate (3m)

LG = F: Synthesized according to **General procedure C** using **1m** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 76.2 mg, 68% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.84 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.06 (dd, *J* = 18.6, 7.3Hz, 1H), 3.04 (dd, *J* = 17.8, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 172.0, 169.5, 164.2, 131.5, 128.9, 114.1, 55.7, 52.9, 52.2, 49.2, 33.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_6$ 281.1020, found: 281.1023.



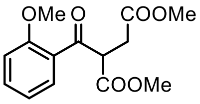
Dimethyl 2-(3-methoxybenzoyl)succinate (3n)

LG = F: Synthesized according to **General procedure C** using **1n** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 57.2 mg, 51% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.37 (t,7.9 Hz, 1H), 7.17 – 7.10 (m, 1H), 4.85 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.09 (dd, *J* = 17.4, 7.7 Hz, 1H), 3.01 (dd, *J* = 17.4, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 171.8, 169.3, 160.0, 137.2, 129.9, 121.6, 120.5, 113.1, 55.6, 52.9, 52.2, 49.5, 33.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_6$ 281.1020, found: 281.1022.



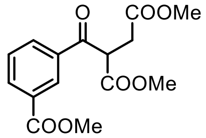
Dimethyl 2-(2-methoxybenzoyl)succinate (3o)

LG = F: Synthesized according to **General procedure C** using **1o** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 38.1 mg, 34% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.82 (dd, *J* = 7.6, 6.5 Hz, 1H), 3.88 (s, 3H), 3.67 (s, 2 × 3H), 3.03 (dd, *J* = 16.9, 7.8 Hz, 1H), 2.88 (dd, *J* = 16.9, 6.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 172.0, 170.4, 158.8, 134.7, 131.4, 126.1, 121.1, 111.7, 55.5, 54.3, 52.5, 52.1, 33.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_6$ 281.1020, found: 281.1023.



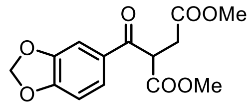
Dimethyl 2-(3-(methoxycarbonyl)benzoyl)succinate (3p)

LG = F: Synthesized according to **General procedure C** using **1p** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.56 mmol, 1.4 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =4:1): 62.9 mg, 51% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 4.91 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.94 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.15 (dd, *J* = 17.4, 8.2 Hz, 1H), 3.04 (dd, *J* = 17.5, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 171.7, 168.9, 166.2, 136.4, 134.5, 133.0, 131.0, 130.1, 129.1, 53.0, 52.5, 52.2, 49.3, 33.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{17}O_7$ 309.0969, found: 309.0971.



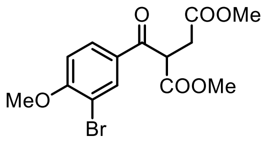
Dimethyl 2-(benzo[d][1,3]dioxole-5-carbonyl)succinate (3q)

LG = F: Synthesized according to **General procedure C** using **1q** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 68.3 mg, 58% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.46 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H), 4.77 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.10 – 2.95 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 171.8, 169.3, 152.6, 148.5, 130.6, 125.7, 108.6, 108.1, 102.1, 52.9, 52.1, 49.2, 33.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{15}O_7$ 295.0812, found: 295.0815.



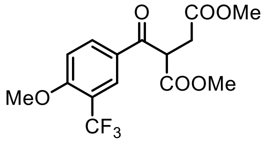
Dimethyl 2-(3-bromo-4-methoxybenzoyl)succinate (3r)

LG = F: Synthesized according to **General procedure C** using **1r** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =3:1): 94.8 mg, 66% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.02 – 7.95 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.77 (t, *J* = 7.2, 1H), 3.94 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 3.07 (dd, *J* = 17.4, 7.9 Hz, 1H), 2.99 (dd, *J* = 17.5, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 171.8, 169.0, 160.2, 134.4, 130.4, 129.8, 112.3, 111.3, 56.6, 52.9, 52.2, 49.0, 33.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}BrO_6$ 359.0125, found: 359.0129.



Dimethyl 2-(4-methoxy-3-(trifluoromethyl)benzoyl)-succinate (3s)

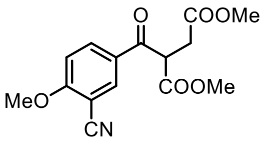
LG = F: Synthesized according to **General procedure C** using **1s** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =4:1): 89.2 mg, 64% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 4.84 – 4.78 (m, 1H), 3.96 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 3.11 (dd, *J* = 17.5, 8.2 Hz, 1H), 3.01 (dd, *J* = 17.5, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 191.7, 171.8, 169.0, 161.7, 134.9, 128.7 (q, *J* = 5.3 Hz), 128.3, 123.1 (q, *J* = 272.7 Hz), 119.3 (q, *J* = 31.7 Hz), 111.9, 56.5, 53.0, 52.2, 49.0, 33.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.01.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{15}H_{16}F_3O_6$ 349.0893, found: 349.0898.



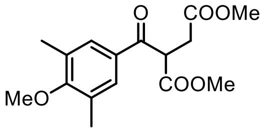
Dimethyl 2-(3-cyano-4-methoxybenzoyl)succinate (3t)

LG = F: Synthesized according to **General procedure C** using **1t** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =1.5:1): 70.8 mg, 58% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 – 8.21 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 4.77 (dd, *J* = 8.2, 6.3 Hz, 1H), 4.01 (s, 3H), 3.67 (s, 3H), 3.65 (s, 3H), 3.14 (dd, *J* = 17.6, 8.5 Hz, 1H), 3.01 (dd, *J* = 17.6, 5.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 191.2, 171.7, 168.6, 164.8, 135.6, 135.3, 129.2, 115.4, 111.5, 102.7, 56.8, 53.1, 52.2, 48.9, 33.0.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{15}H_{16}NO_6$ 306.0972, found: 306.0977.



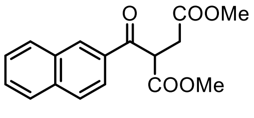
Dimethyl 2-(4-methoxy-3,5-dimethylbenzoyl)succinate (3u)

LG = F: Synthesized according to **General procedure C** using **1u** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 70.3 mg, 57% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (s, 2H), 4.83 (t, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.09 – 2.95 (m, 2H), 2.31 (s, 2 × 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.3, 171.9, 169.4, 162.0, 131.5, 131.4, 130.1, 59.7, 52.8, 52.1, 49.0, 33.2, 16.4.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{16}H_{21}O_6$ 309.1333, found: 309.1337.



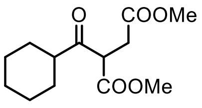
Dimethyl 2-(2-naphthoyl)succinate (3v)

LG = F: Synthesized according to **General procedure C** using **1v** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 49.2 mg, 41% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.60 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.53 (m, 2H), 5.07 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 2 × 3H), 3.21 – 3.07 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.0, 171.9, 169.4, 136.0, 133.3, 132.6, 131.2, 130.0, 129.0, 128.8, 127.9, 127.0, 124.3, 53.0, 52.2, 49.4, 33.3.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{17}H_{17}O_5$ 301.1071, found: 301.1073.



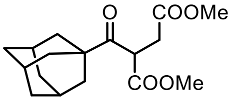
Dimethyl 2-(cyclohexanecarbonyl)succinate (3w)[9]

LG = F: Synthesized according to **General procedure C** using **1w** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate

2a (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 41.2 mg, 40% yield, white solid.
LG = Cl: Synthesized according to **General procedure D** using **1w** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6-lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 59.5 mg, 58% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (dd, *J* = 8.0, 6.4 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.91 (dd, *J* = 17.4, 8.1 Hz, 1H), 2.79 (dd, *J* = 17.4, 6.3 Hz, 1H), 2.68 – 2.58 (m, 1H), 1.99 – 1.90 (m, 1H), 1.82 – 1.71 (m, 3H), 1.67 – 1.60 (m, 1H), 1.46 – 1.33 (m, 1H), 1.32 – 1.12 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 171.8, 169.2, 52.8, 52.2, 52.1, 50.7, 32.3, 29.0, 28.0, 25.8, 25.8, 25.4.

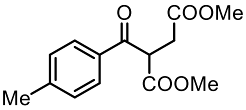


Dimethyl 2-((3r,5r,7r)-adamantane-1-carbonyl)succinate (3x)[9]

LG = F: Synthesized according to **General procedure C** using **1x** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 50.6 mg, 41% yield, oily liquid.
LG = Cl: Synthesized according to **General procedure D** using **1x** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6-lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 75.2 mg, 61% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (t, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 3.62 (s, 3H), 2.77 (d, *J* = 7.2 Hz, 2H), 2.01 (s, 3H), 1.88 – 1.77 (m, 6H), 1.74 – 1.61 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 171.6, 169.5, 52.6, 52.0, 47.7, 47.3, 38.0, 36.4, 33.4, 27.9.



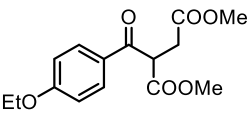
Dimethyl 2-(4-methylbenzoyl)succinate (3y)

LG = Cl: Synthesized according to **General procedure D** using **1y** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 75.0 mg, 71% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.89 (t, *J* = 7.2 Hz, 1H), 3.69 (s, 2 × 3H), 3.15 – 3.00 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 193.7, 171.9, 169.4, 144.9, 133.4, 129.6, 129.2, 52.9, 52.2, 49.3, 33.2, 21.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_5$ 265.1071, found: 265.1069.



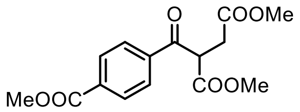
Dimethyl 2-(4-ethoxybenzoyl)succinate (3z)

LG = Cl: Synthesized according to **General procedure D** using **1z** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =5:1): 83.6 mg, 71% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.82 (t, *J* = 7.2 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 3.02 (d, *J* = 7.3 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 192.3, 171.9, 169.5, 163.6, 131.4, 128.6, 114.4, 63.9, 52.8, 52.1, 49.0, 33.2, 14.7.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{15}H_{19}O_6$ 295.1176, found: 295.1173.



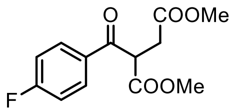
Dimethyl 2-(4-(methoxycarbonyl)benzoyl) succinate (3aa)

LG = Cl: Synthesized according to **General procedure D** using **1aa** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =5:1): 59.2 mg, 48% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H), 4.88 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.95 (s, 3H), 3.67 (s, 2 × 3H), 3.15 (dd, *J* = 17.5, 8.3 Hz, 1H), 3.03 (dd, *J* = 17.5, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 193.9, 171.7, 168.9, 166.2, 139.3, 134.5, 130.0, 128.9, 53.1, 52.6, 52.3, 49.6, 33.1.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{15}H_{16}NaO_7$ 331.0788, found: 331.0784.



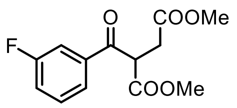
Dimethyl 2-(4-fluorobenzoyl)succinate (3ab)[10]

LG = Cl: Synthesized according to **General procedure D** using **1ab** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 59.0 mg, 55% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (dd, J = 8.8, 5.3 Hz, 2H), 7.17 (t, J = 8.4 Hz, 2H), 4.85 (dd, J = 7.9, 6.5 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 3.13 (dd, J = 17.5, 8.0 Hz, 1H), 3.04 (dd, J = 17.5, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 192.6, 171.8, 169.1, 166.3 (d, *J* = 256.1 Hz), 132.4 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 9.5 Hz), 116.1 (d, *J* = 22.0 Hz), 53.0, 52.3, 49.3, 33.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -103.95.



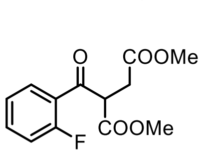
Dimethyl 2-(3-fluorobenzoyl)succinate (3ac)[10]

LG = Cl: Synthesized according to **General procedure D** using **1ac** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 67.7 mg, 63% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 9.4 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 4.87 – 4.79 (m, 1H), 3.69 (s, 3H), 3.68 (s,3H), 3.15 (dd, *J* = 17.5, 8.3 Hz, 1H), 3.04 (dd, *J* = 17.5, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 193.0 (d, *J* = 2.5 Hz), 171.7, 168.9, 163.0 (d, *J* = 248.3 Hz), 138.1 (d, *J* = 6.7 Hz), 130.5 (d, *J* = 7.9 Hz), 124.8 (d, *J* = 3.5 Hz), 120.8 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 22.8 Hz), 53.0, 52.2, 49.5, 33.1.

^{19}F NMR (376 MHz, CDCl$_3$) δ -111.50.

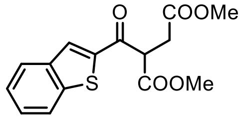


Dimethyl 2-(2-fluorobenzoyl)succinate (3ad)[10]

LG = Cl: Synthesized according to **General procedure D** using **1ad** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =7:1): 27.0 mg, 25% yield, oily liquid.

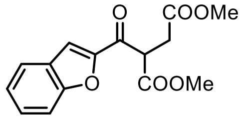
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (t, *J* = 7.8 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.30 – 7.22 (m, 1H), 7.15 (dd, *J* = 11.4, 8.5 Hz, 1H), 4.77 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.14 (dd, *J* = 17.2, 8.4 Hz, 1H), 2.97 (dd, *J* = 17.2, 5.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 192.2 (d, *J* = 4.0 Hz), 171.7, 169.5, 161.9 (d, *J* = 254.8 Hz), 135.4 (d, *J* = 9.5 Hz), 131.3 (d, *J* = 2.4 Hz), 124.8 (d, *J* = 3.7 Hz), 124.7 (d, *J* = 12.0 Hz), 116.9 (d, *J* = 24.2 Hz), 53.4 (d, *J* = 7.8 Hz), 52.8, 52.2, 32.9 (d, *J* = 1.4 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -110.20.



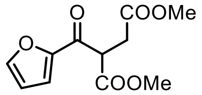
Dimethyl 2-(benzo[b]thiophene-2-carbonyl)succinate (3ae)

LG = Cl: Synthesized according to **General procedure D** using **1ae** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =5:1): 49.0 mg, 40% yield, oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 4.85 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.20 – 3.05 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 171.7, 168.8, 143.2, 142.4, 139.1, 131.2, 128.0, 126.5, 125.3, 123.1, 53.2, 52.3, 50.5, 33.1.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{15}O_5S$ 307.0635, found: 307.0632.



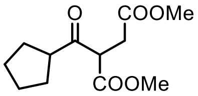
Dimethyl 2-(benzofuran-2-carbonyl)succinate (3af)

LG = Cl: Synthesized according to **General procedure D** using **1af** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =5:1): 31.3 mg, 27% yield, oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 4.82 (t, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.15 (dd, *J* = 17.5, 8.1 Hz, 1H), 3.07 (dd, *J* = 17.5, 6.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 171.6, 168.9, 156.1, 151.6, 128.9, 127.1, 124.2, 123.7, 115.0, 112.7, 53.1, 52.3, 49.9, 32.6.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{15}O_6$ 291.0863, found: 291.0859.



Dimethyl 2-(furan-2-carbonyl)succinate (3ag)

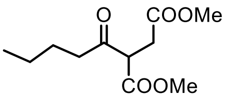
LG = Cl: Synthesized according to **General procedure D** using **1ag** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =5:1): 46.1 mg, 48% yield, oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.34 (d, *J* = 3.3 Hz, 1H), 6.60 – 6.54 (m, 1H), 4.65 (t, *J* = 7.3 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.10 – 2.94 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 171.6, 169.0, 151.8, 147.5, 119.2, 112.9, 52.9, 52.2, 49.6, 32.5.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{13}O_6$ 241.0707, found: 241.0704.



Dimethyl 2-(cyclopentanecarbonyl)succinate (3ah)[11]

LG = Cl: Synthesized according to **General procedure D** using **1ah** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (2.0 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 29.1 mg, 30% yield, oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (t, *J* = 7.2, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.16 (p, *J* = 8.0 Hz, 1H), 2.94 (dd, *J* = 17.5, 7.8 Hz, 1H), 2.82 (dd, *J* = 17.3, 6.5 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.87 – 1.49 (m, 7H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 206.4, 171.9, 169.2, 53.6, 52.8, 52.1, 51.2, 32.4, 30.1, 28.8, 26.1, 26.1.

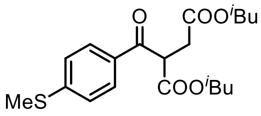


Dimethyl 2-pentanoylsuccinate(3ai) [12]

LG = Cl: Synthesized according to **General procedure D** using **1ai** (0.4 mmol, 1.0 equiv.), **OC2** (0.08 mmol, 0.2 equiv), dimethyl fumarate **2a** (0.8 mmol, 2.0 equiv), γ-terpinene (0.72 mmol, 1.8 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (2.0 mL). Chromatography on silica gel (PE: EA =20:1~10: 1): 55.3 mg, 60% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.98 (dd, J = 8.2, 6.3 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 2.97 (dd, J = 17.5, 8.2 Hz, 1H), 2.82 (dd, J = 17.5, 6.3 Hz, 1H), 2.75 – 2.54 (m, 2H), 1.61 – 1.52 (m, 2H), 1.35 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 204.1, 172.0, 169.1, 53.9, 52.8, 52.2, 42.6, 32.3, 25.6, 22.2, 13.9.



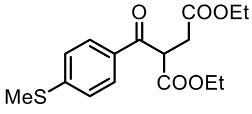
Diisobutyl 2-(4-(methylthio)benzoyl)succinate (4b)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), diisobutyl fumarate **2b** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 92.8 mg, 61% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 4.82 (t, J = 7.1 Hz, 1H), 3.88 – 3.77 (m, 4H), 3.09 (dd, J = 17.4, 7.9 Hz, 1H), 3.01 (dd, J = 17.4, 6.6 Hz, 1H), 2.49 (s, 3H), 1.93 – 1.72 (m, 2H), 0.86 (d, J = 6.8 Hz, 6H), 0.76 (d, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.0, 171.4, 168.7, 146.9, 132.3, 129.4, 125.0, 71.8, 71.2, 49.4, 33.2, 27.7, 27.6, 19.0, 18.9, 14.7.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{20}H_{28}NaO_5S$ 403.1550, found: 403.1554.



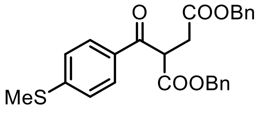
Diethyl 2-(4-(methylthio)benzoyl)succinate (4c)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), diethyl fumarate **2c** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 85.6 mg, 66% yield, oily liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.78 (t, J = 7.2 Hz, 1H), 4.14 – 4.05 (m, 4H), 3.09 – 2.93 (m, 2H), 2.49 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 193.0, 171.3, 168.8, 147.0, 132.2, 129.3, 125.0, 61.8, 61.0, 49.4, 33.3, 14.7, 14.1, 14.0.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{16}H_{21}O_5S$ 325.1104, found: 325.1108.



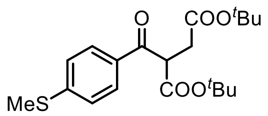
Dibenzyl 2-(4-(methylthio)benzoyl)succinate (4d)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dibenzyl fumarate **2d** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 111.2 mg, 62% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 7.35 – 7.24 (m, 8H), 7.21 (d, J = 8.6 Hz, 2H), 7.16 – 7.11 (m, 2H), 5.08 (s, 3H), 4.87 (t, J = 7.2, 1H), 3.17 (dd, J = 17.4, 7.8 Hz, 1H), 3.08 (dd, J = 17.5, 6.6 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 192.7, 171.1, 168.6, 147.1, 135.6, 135.2, 132.1, 129.4, 128.6, 128.6, 128.4, 128.3, 128.1, 125.0, 67.5, 66.9, 49.5, 33.3, 14.8.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{26}H_{24}NaO_5S$ 471.1237, found: 471.1236.



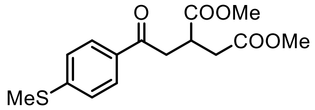
Di-tert-butyl 2-(4-(methylthio)benzoyl)succinate (4e)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), di-tert-butyl fumarate **2e** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 80.7 mg, 53% yield, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.66 (t, *J* = 7.2, 1H), 2.97 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.87 (dd, *J* = 17.2, 6.5 Hz, 1H), 2.53 (s, 3H), 1.40 (s, 9H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 170.7, 168.0, 146.5, 132.6, 129.4, 125.0, 82.4, 81.2, 50.9, 34.4, 28.1, 27.9, 14.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{28}NaO_5S$ 403.1550, found: 403.1552.



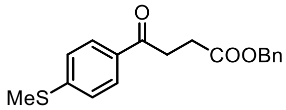
Dimethyl 2-(2-(4-(methylthio)phenyl)-2-oxoethyl)-succinate (4f)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), dimethyl 2-methylenesuccinate **2f** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =5:1): 44.7 mg, 36% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.54 – 3.41 (m, 2H), 3.28 – 3.16 (m, 1H), 2.81 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.69 (dd, *J* = 16.9, 6.1 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 174.3, 172.1, 146.3, 132.7, 128.5, 125.0, 52.2, 51.9, 39.1, 36.6, 35.2, 14.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}O_5S$ 311.0948, found: 311.0952.



Benzyl 4-(4-(methylthio)phenyl)-4-oxobutanoate (4g)

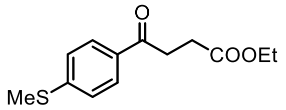
LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), benzyl acrylate **2g** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added.

Chromatography on silica gel (PE: EA =5:1): 45.3 mg, 36% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.30 (m, 5H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.15 (s, 2H), 3.29 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 6.6 Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 172.9, 146.2, 136.0, 132.9, 128.7, 128.6, 128.33, 128.32, 125.1, 66.6, 33.2, 28.4, 14.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}O_3S$ 315.1049, found: 315.1051.



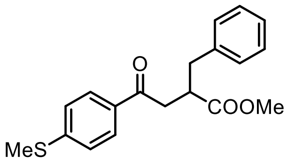
Ethyl 4-(4-(methylthio)phenyl)-4-oxobutanoate (4h)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), ethyl acrylate **2h** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Chromatography on silica gel (PE: EA =5:1): 30.2 mg, 30% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 2.52 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 173.1, 146.1, 133.0, 128.5, 125.1, 60.8, 33.2, 28.4, 14.8, 14.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}O_3S$ 253.0893, found: 253.0895.



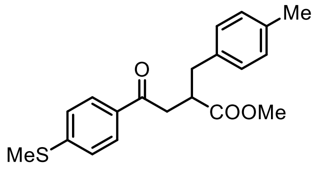
Methyl 2-benzyl-4-(4-(methylthio)phenyl)-4-oxobutanoate (4i)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), methyl 2-benzylacrylate **2i** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =5:1): 39.4 mg, 30% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, J = 7.9 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 5H), 3.65 (s, 3H), 3.42 – 3.28 (m, 2H), 3.10 (dd, J = 13.7, 5.4 Hz, 1H), 3.01 – 2.90 (m, 1H), 2.89 – 2.79 (m, 1H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.1, 175.4, 146.2, 138.6, 133.0, 129.1, 128.6, 128.5, 126.8, 125.0, 51.9, 42.3, 39.2, 37.9, 14.8.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{19}$H$_{21}$O$_3$S 329.1206, found: 329.1208



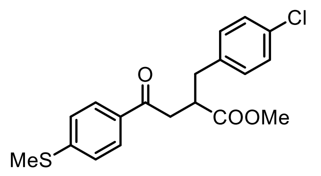
Methyl 2-(4-methylbenzyl)-4-(4-(methylthio)phenyl)-4-oxobutanoate (4j)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), methyl 2-(4-methylbenzyl)acrylate **2j** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =5:1): 45.2 mg, 33% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.12 – 7.04 (m, 4H), 3.67 (s, 3H), 3.41 – 3.27 (m, 2H), 3.12 – 3.02 (m, 1H), 2.95 (d, J = 14.1 Hz, 1H), 2.85 – 2.75 (m, 1H), 2.51 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.2, 175.5, 146.1, 136.3, 135.5, 133.1, 129.4, 129.0, 128.6, 125.1, 52.0, 42.4, 39.2, 37.6, 21.2, 14.9.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{20}$H$_{23}$O$_3$S 343.1362, found: 343.1365



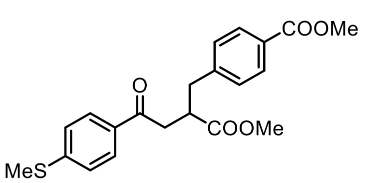
Methyl 2-(4-chlorobenzyl)-4-(4-(methylthio)phenyl)-4-oxobutanoate (4k)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), AlCl$_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), methyl 2-(4-chlorobenzyl)acrylate **2k** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH$_3$CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =5:1): 55.2 mg, 38% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.12 (d, J = 8.1 Hz, 2H), 3.64 (s, 3H), 3.39 – 3.27 (m, 2H), 3.08 – 2.94 (m, 2H), 2.84 (dd, J = 13.8, 7.1 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.8, 175.1, 146.3, 137.1, 132.9, 132.6, 130.4, 128.8, 128.5, 125.1, 52.0, 42.2, 39.3, 37.2, 14.8.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{19}$H$_{20}$ClO$_3$S 363.0816, found: 363.0819.



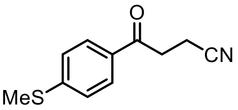
Methyl 4-(2-(methoxycarbonyl)-4-(4-(methylthio) phenyl)-4-oxobutyl)benzoate (4l)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), methyl 4-(2-(methoxycarbonyl)allyl)benzoate **2l** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =5:1): 58.7 mg, 38% yield, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.21 (m, 4H), 3.90 (s, 3H), 3.64 (s, 3H), 3.41 – 3.31 (m, 2H), 3.13 (dd, *J* = 13.6, 6.2 Hz, 1H), 3.02 – 2.89 (m, 2H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 175.1, 167.0, 146.4, 144.1, 132.8, 130.0, 129.2, 128.8, 128.5, 125.1, 52.2, 52.0, 42.1, 39.3, 37.8, 14.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}O_5S$ 387.1261, found: 387.1263.



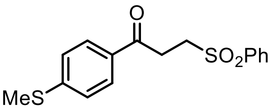
4-(4-(methylthio)phenyl)-4-oxobutanenitrile (4m)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), acrylonitrile **2m** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =3:1): 32.0 mg, 39% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 147.3, 132.0, 128.5, 125.2, 119.4, 34.1, 14.8, 11.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{12}NOS$ 206.0634, found: 206.0637.



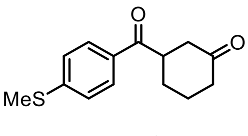
1-(4-(methylthio)phenyl)-3-(phenylsulfonyl)propan-1-one (4n)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), (vinylsulfonyl)benzene **2n** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =3:1): 50.0 mg, 39% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.57 – 3.50 (m, 2H), 3.47 – 3.40 (m, 2H), 2.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 147.1, 139.1, 134.0, 132.1, 129.5, 128.5, 128.1, 125.0, 51.1, 31.2, 14.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}O_3S_2$ 321.0614, found: 321.0615.



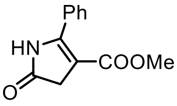
3-(4-(methylthio)benzoyl)cyclohexan-1-one (4o)

LG = F: Synthesized according to **General procedure C** using **1j** (0.4 mmol, 1.0 equiv.), $AlCl_3$ (0.44 mmol, 1.1 equiv), **OC1** (0.08 mmol, 0.2 equiv), cyclohex-2-en-1-one **2o** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), 2,6- lutidine (0.48 mmol, 1.2 equiv) and CH_3CN (1.5 mL). Extra 20 μL of DMAc was added. Chromatography on silica gel (PE: EA =3:1): 31.8 mg, 32% yield, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 3.84 – 3.72 (m, 1H), 2.76 - 2.67 (m, 1H), 2.53 (s, 3H), 2.49 – 2.39 (m, 3H), 2.16 – 2.05 (m, 2H), 1.94 – 1.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 199.4, 146.7, 131.7, 128.9, 125.3, 45.1, 43.3, 41.1, 28.6, 25.0, 14.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_2S$ 249.0944, found: 249.0946.



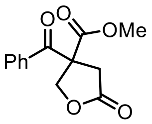
Methyl 5-oxo-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (5)

The product **5** was prepared based on a literature procedure.[13] To an oven-dried Schlenk tube equipped with a stir bar was added $AcONH_4$ (10 mmol, 10 equiv) under an N_2 atmosphere. Subsequently, 1.5 mL of AcOH and **3a** (1.0 mmol, 1.0 equiv) were added to the tube. The reaction mixture was stirred at 80°C overnight. Chromatography on silica gel (PE: EA =2:1): 134.7 mg, 62% yield, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65 – 7.58 (m, 2H), 7.50 - 7.42 (m, 3H), 3.67 (s, 3H), 3.51 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 163.7, 151.7, 130.9, 129.3, 128.7, 128.5, 104.0, 51.4, 38.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{12}NO_3$ 218.0812, found: 218.0815.



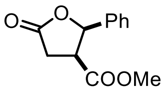
Methyl 3-benzoyl-5-oxotetrahydrofuran-3-carboxylate (6)

The product **6** was prepared based on a literature procedure.[14] Bmim-$FeCl_4$ (0.1 mmol, 0.1 equiv) and 3a (1.0 mmol, 1.0 equiv) were mixed and a 37 % aqueous formaldehyde solution (0.16 mL, 2.0 equiv) was added. The reaction was stirred at 80 °C overnight. Water was evaporated under reduced pressure and the remaining slurry was directly subjected to flash column chromatography. Chromatography on silica gel (PE: EA =5:1): 178.9 mg, 72% yield, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.92 (d, *J* = 9.9 Hz, 1H), 4.79 (d, *J* = 9.8 Hz, 1H), 3.72 (s, 3H), 3.30 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 173.3, 171.0, 134.4, 133.4, 129.3, 128.8, 71.0, 59.9, 54.0, 35.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{13}O_5$ 249.0757, found: 249.0758.



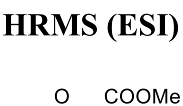
Methyl 5-oxo-2-phenyltetrahydrofuran-3-carboxylate (7)

The product **7** was prepared based on a literature procedure.[15] Sodium borohydride (0.6 mmol, 0.6 equiv) was slowly added to a solution of **3a** (1.0 mmol,1.0 equiv) in 1.0 mL of MeOH, under stirring at 0 °C for 1 h. At the end of the reaction, the solvent was evaporated under reduced pressure, water was added, extracted with ether and dried over Na_2SO_4. Evaporation under reduced pressure afforded the lactones. Chromatography on silica gel (PE: EA =5:1): 133.0 mg, 60% yield, d.r. = 4: 1, oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.28 – 7.23 (m, 2H), 5.76 (d, *J* = 7.9 Hz, 1H-major), 4.91 (d, *J* = 7.5 Hz, 1H-minor), 3.77 – 3.70 (m, 1H), 3.62 (s, 3H-minor), 3.29 (s, 3H-major), 3.09 (dd, *J* = 17.7, 5.2 Hz, 1H-major), 2.80 (dd, *J* = 17.7, 8.8 Hz, 1H-major), 2.60 (dd, *J* = 16.9, 8.8 Hz, 1H-minor), 2.44 (dd, *J* = 16.9, 5.1 Hz, 1H-minor).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 174.2, 172.0, 170.1, 140.9, 135.3, 129.0, 128.7, 128.6, 128.4, 126.5, 125.6, 81.2, 74.6, 52.3, 52.1, 48.7, 46.8, 33.3, 31.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{13}O_4$ 221.0808, found: 221.0806.



Dimethyl 2-benzoyl-2-bromosuccinate (8)

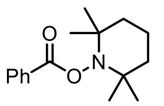
The product **11** was prepared according to a literature procedure.[16, 17] To an oven-dried

Schlenk tube equipped with a stir bar was added NBS (1.1 mmol, 1.1 equiv). Subsequently, 5.0 mL of DCM was added to the tube. DBU (0.2 mmol, 0.2 equiv) and **3a** (1.0 mmol, 1.0 equiv) were then added successively. The reaction mixture was stirred in the dark at room temperature for 4 hours. Purification by chromatography on silica gel (PE: EA= 15:1) afforded the product as an oily liquid (243.6 mg, 74% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 3.74 (s, 3H), 3.67 (s, 3H), 3.58 (d, *J* = 16.7 Hz, 1H), 3.49 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 188.6, 169.3, 167.5, 133.5, 133.4, 129.7, 128.4, 60.1, 54.2, 52.2, 44.5.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{13}H_{14}BrO_5$ 329.0019, found: 329.0015.



2,2,6,6-tetramethylpiperidin-1-yl benzoate (10a)[18]

LG = F: To an oven-dried Schlenk tube equipped with a stir bar was added **OC1** (0.08 mmol, 0.2 equiv), AlCl$_3$ (0.44 mmol, 1.1 equiv), and TEMPO (0.48mmol, 1.2 equiv) under an N$_2$ atmosphere. Subsequently, 1.5 mL of MeCN and acyl fluoride **1a** (0.4 mmol, 1.0 equiv) were added to the tube. The mixture was stirred for 5 minutes. Dimethyl fumarate **2a** (0.6 mmol, 1.5 equiv), γ-terpinene (0.6 mmol, 1.5 equiv), and 2,6-lutidine (0.48 mmol, 1.2 equiv) were then added successively. The reaction mixture was stirred under a 10 W 455 nm LED at room temperature for 15 hours. Chromatography on silica gel (PE: EA =20:1): 94.1 mg, 90% yield, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 1.82 - 1.62 (m, 3H), 1.60 - 1.52 (m, 2H), 1.47 - 1.40 (m, 1H), 1.25 (s, 6H), 1.10 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.4, 132.9, 129.8, 129.6, 128.5, 60.4, 39.1, 32.0, 20.9, 17.0.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for $C_{16}H_{24}NO_2$ 262.1802, found: 262.1800.

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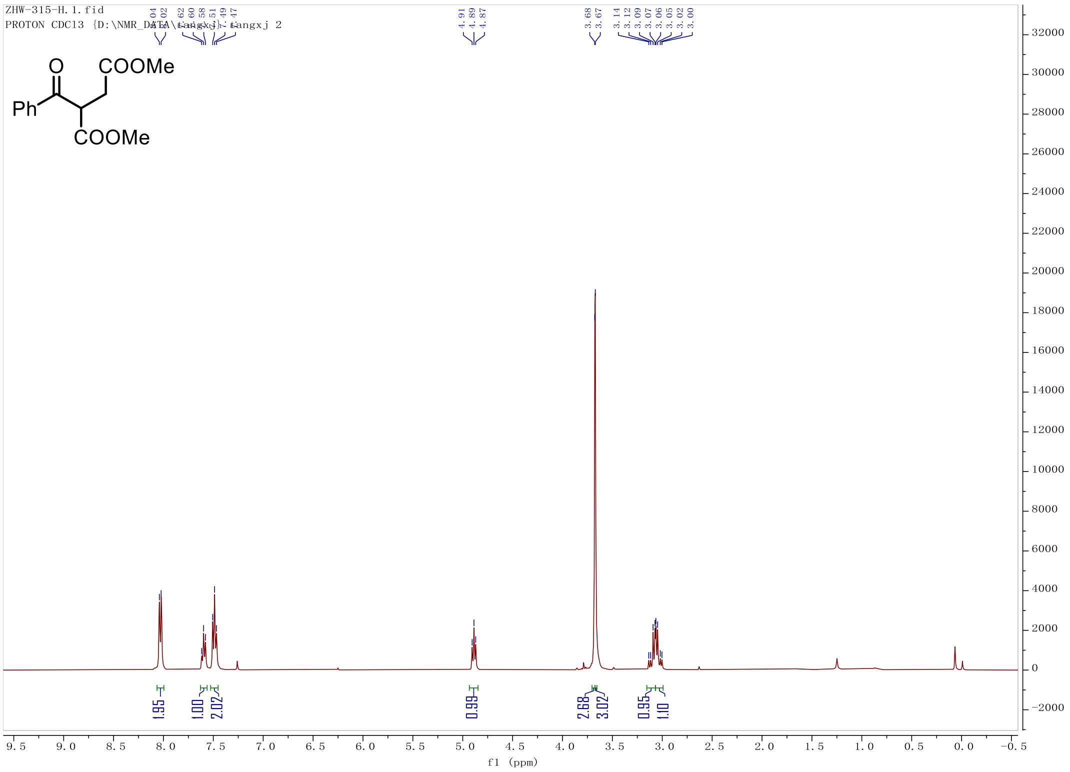
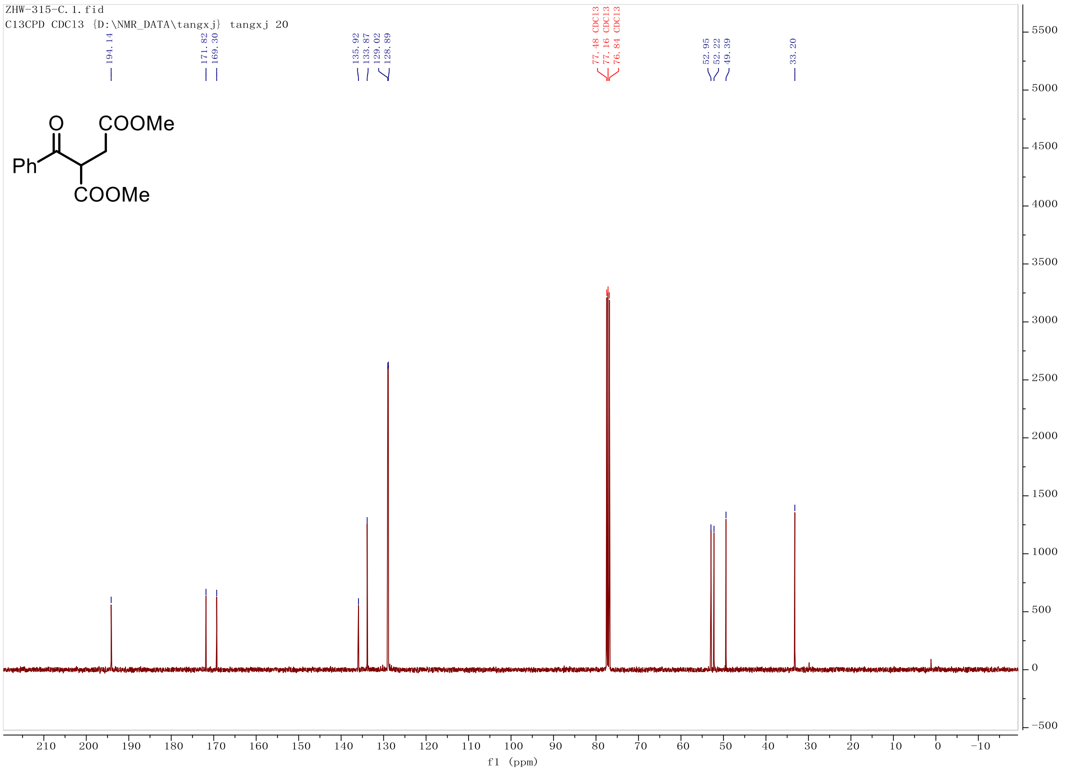
7 ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra

^{1}H NMR of 3a (CDCl$_3$)



^{13}C NMR of 3a (CDCl$_3$)



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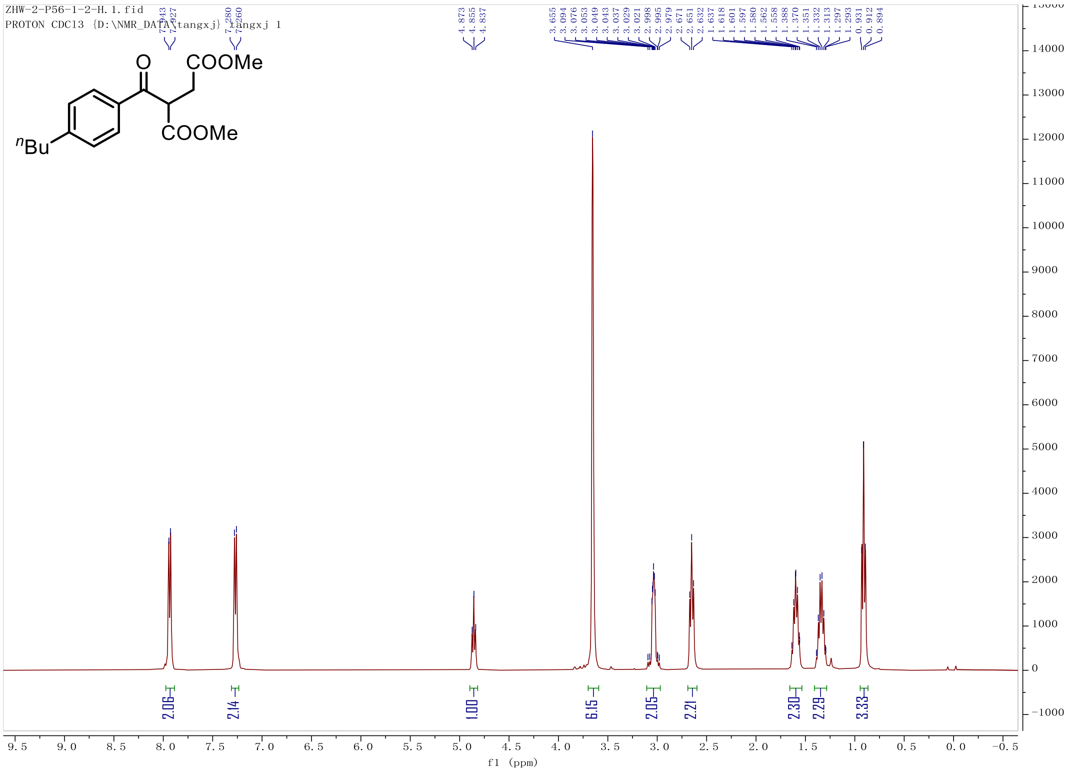

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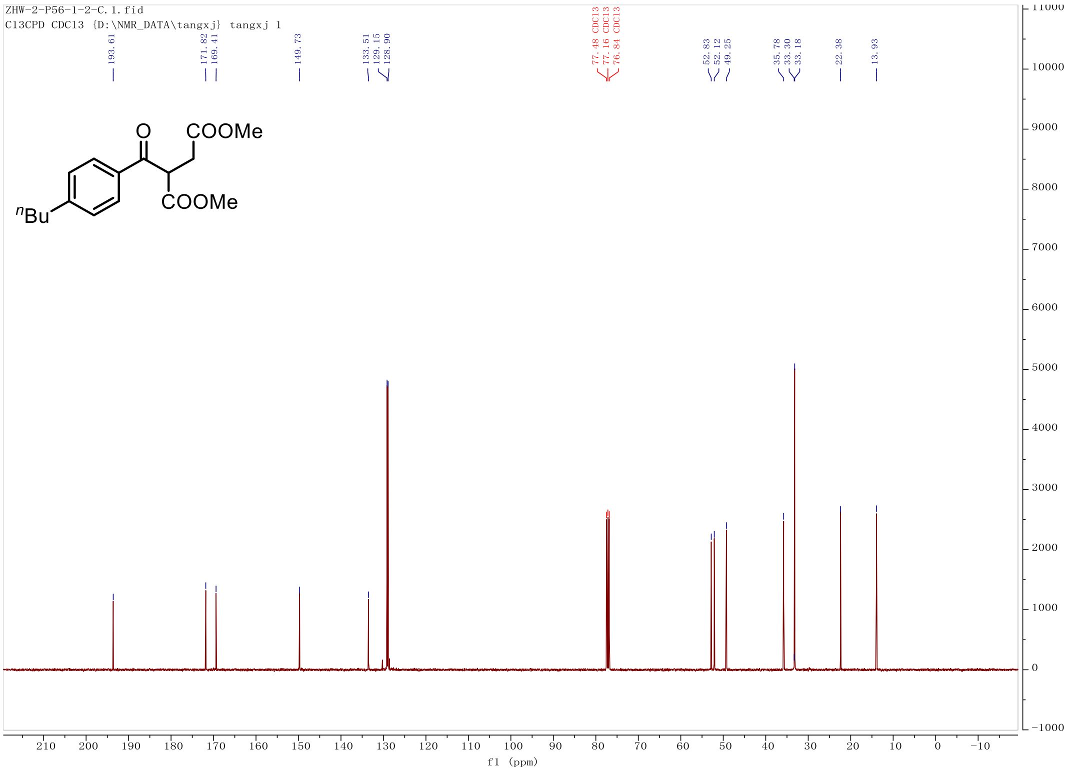
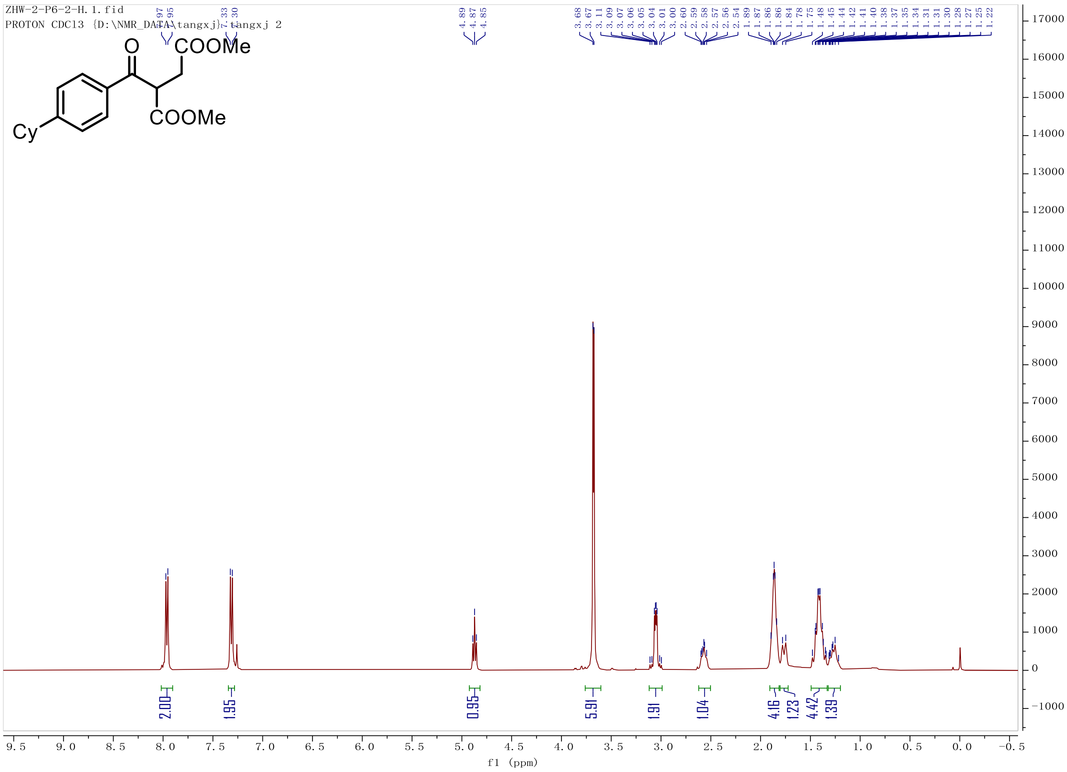


^{1}H NMR of 3c (CDCl$_3$)



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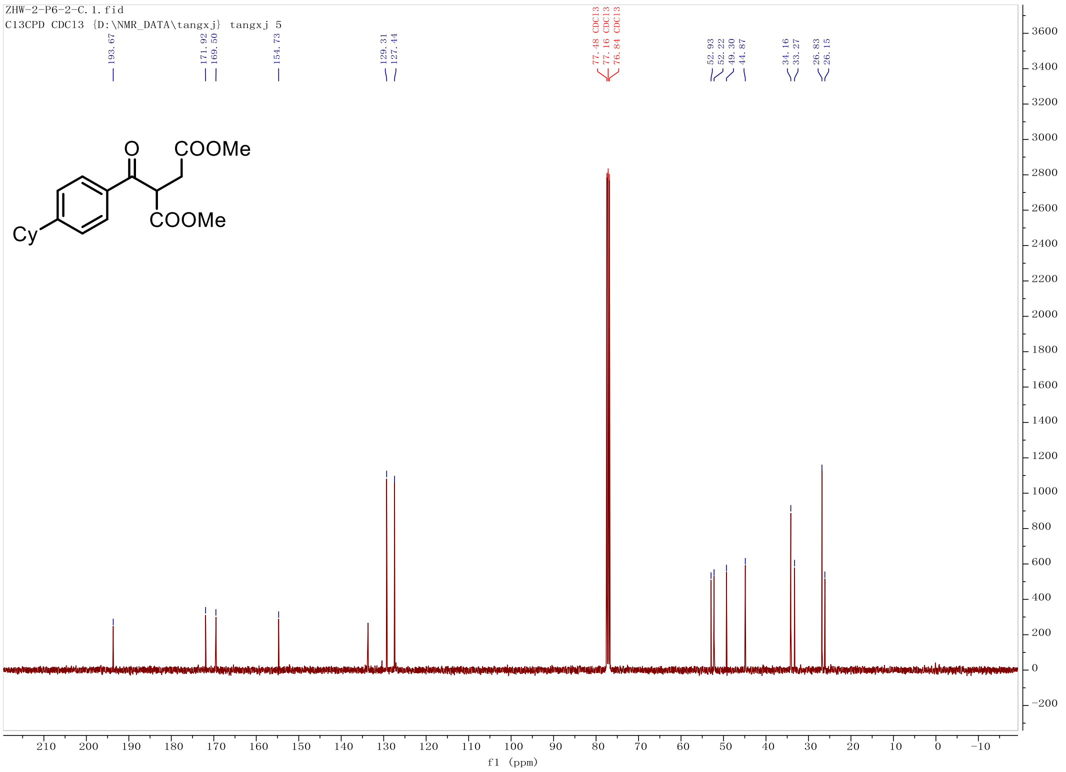

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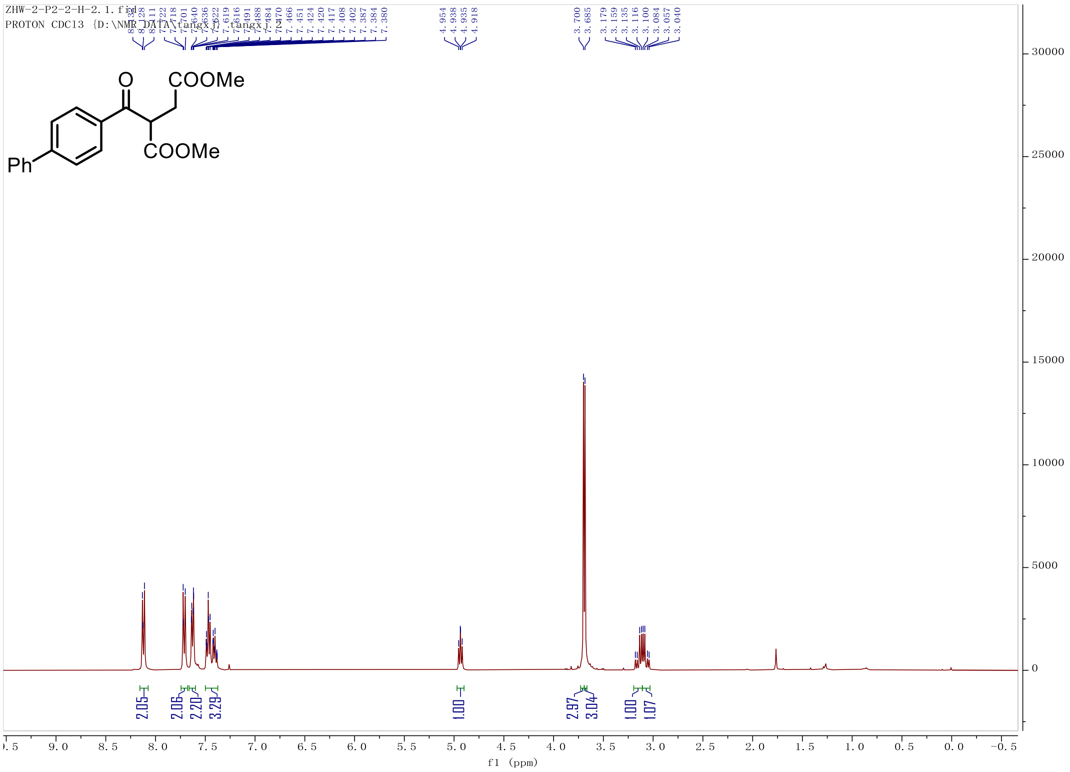

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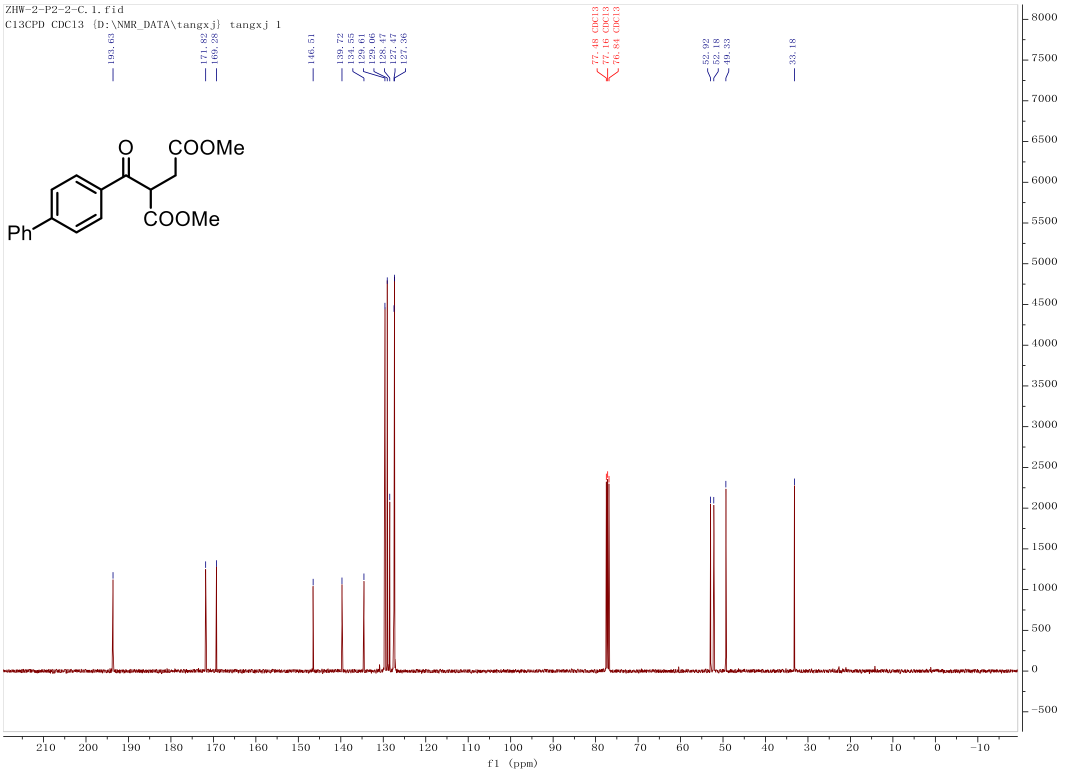

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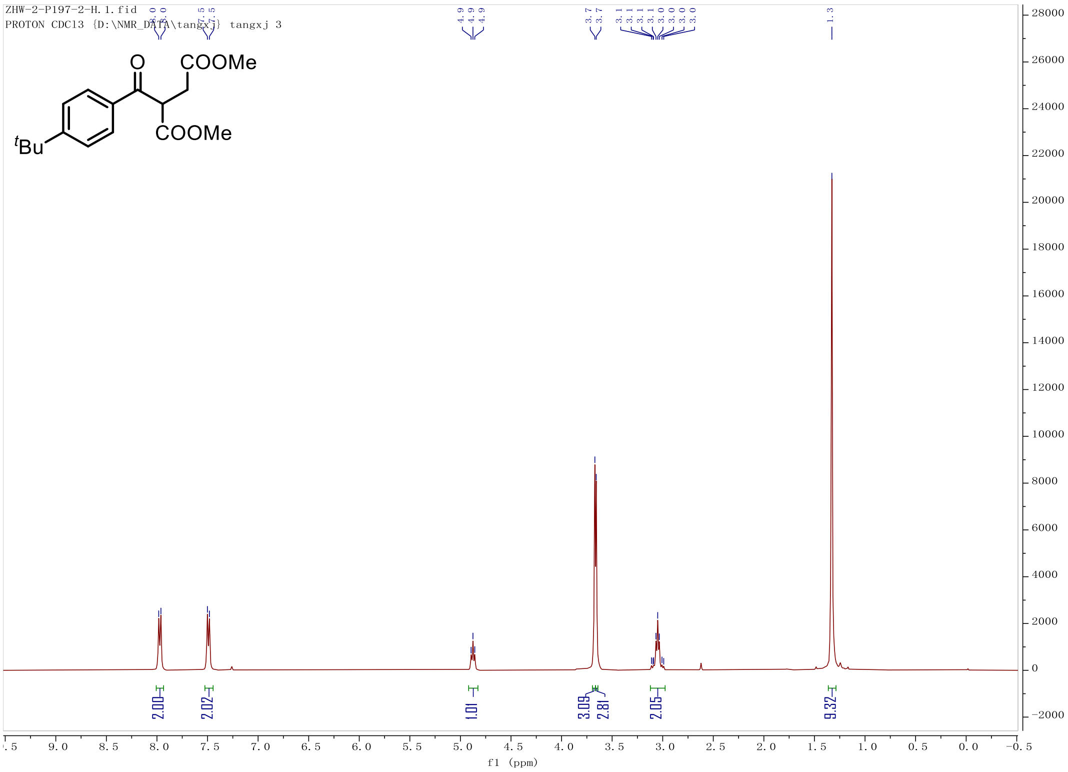

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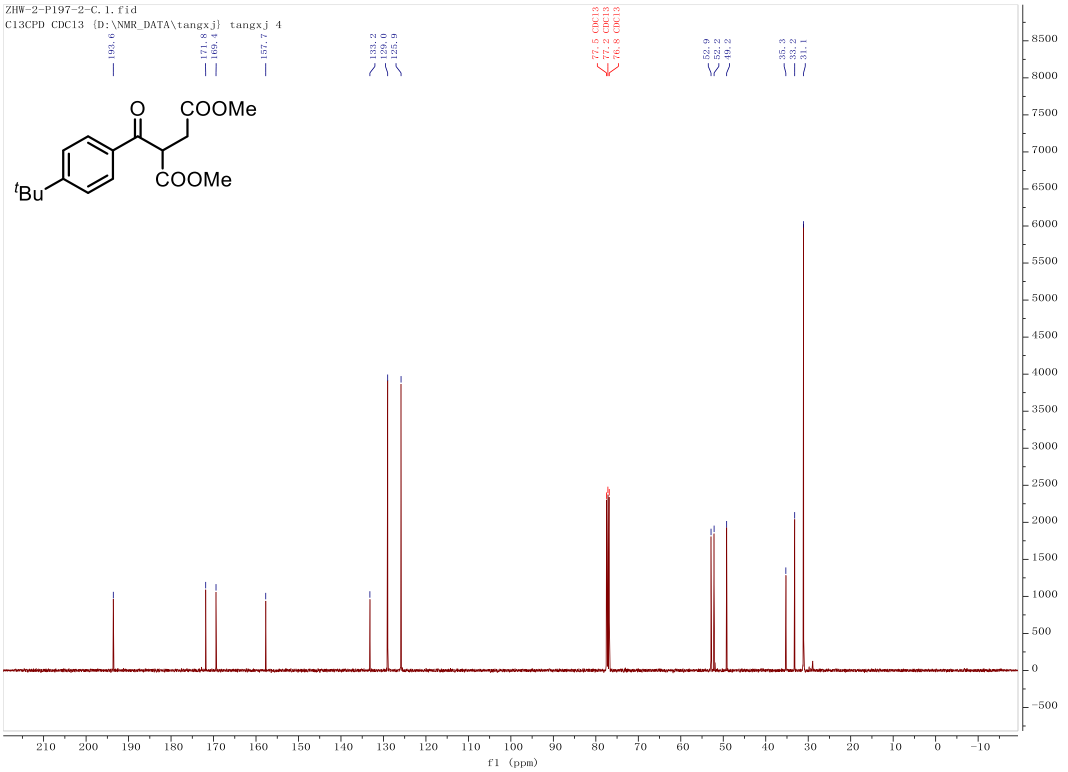

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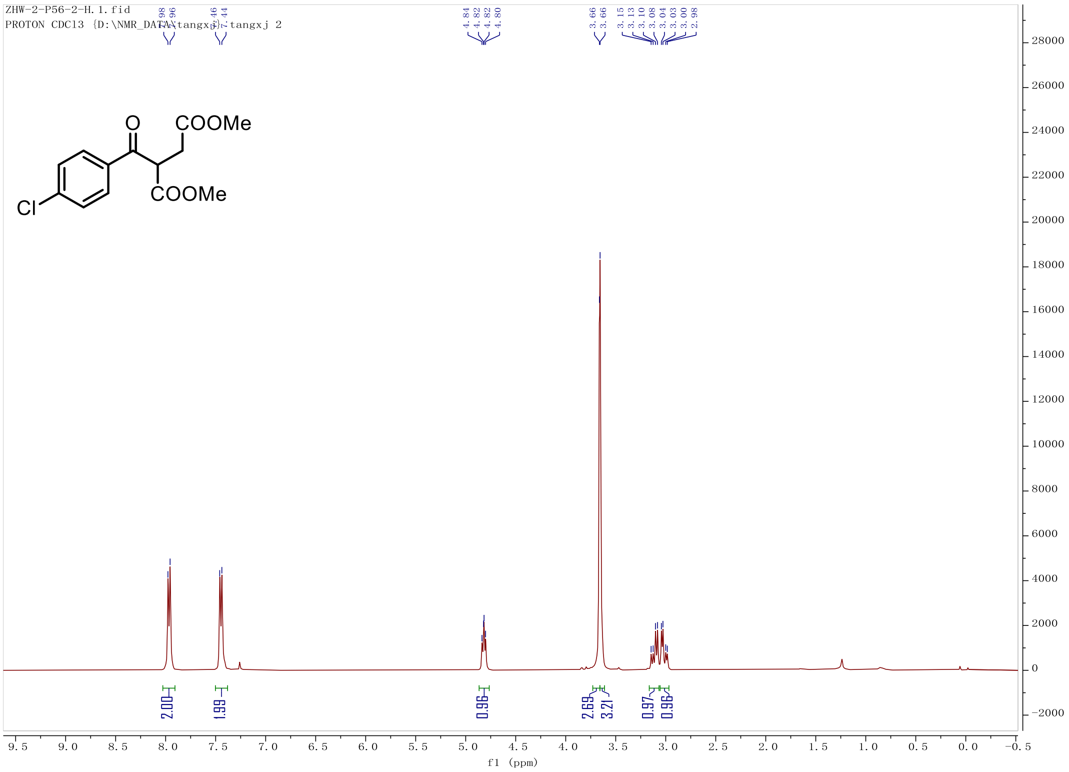

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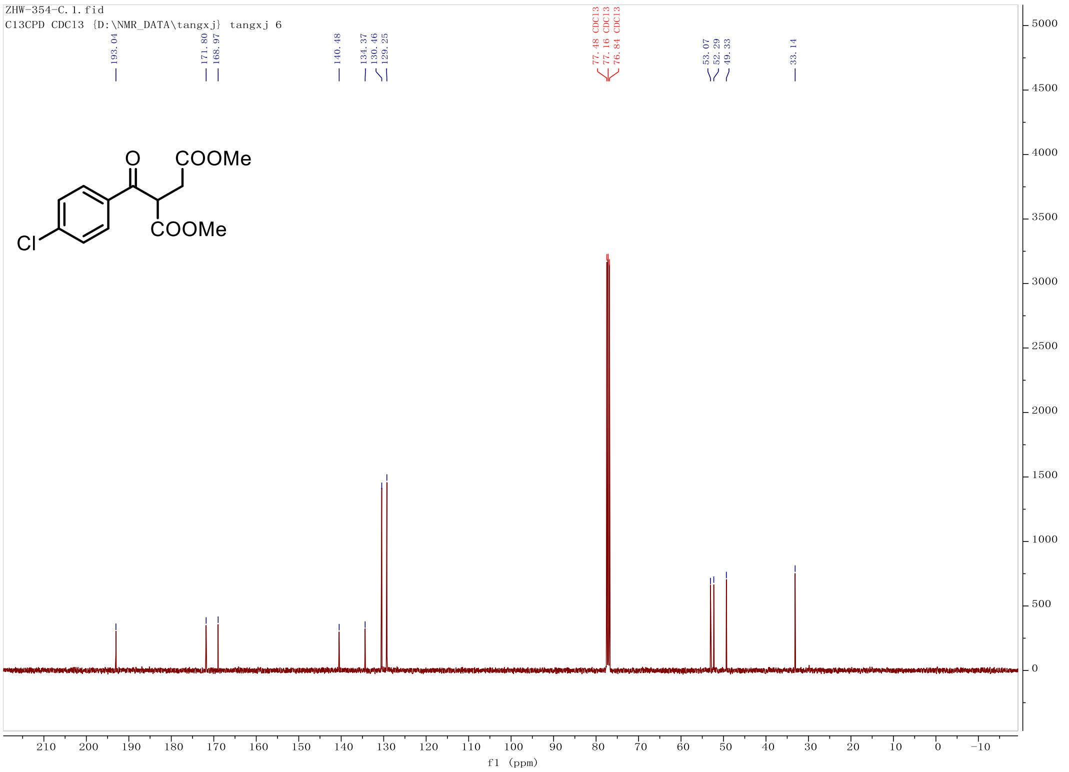

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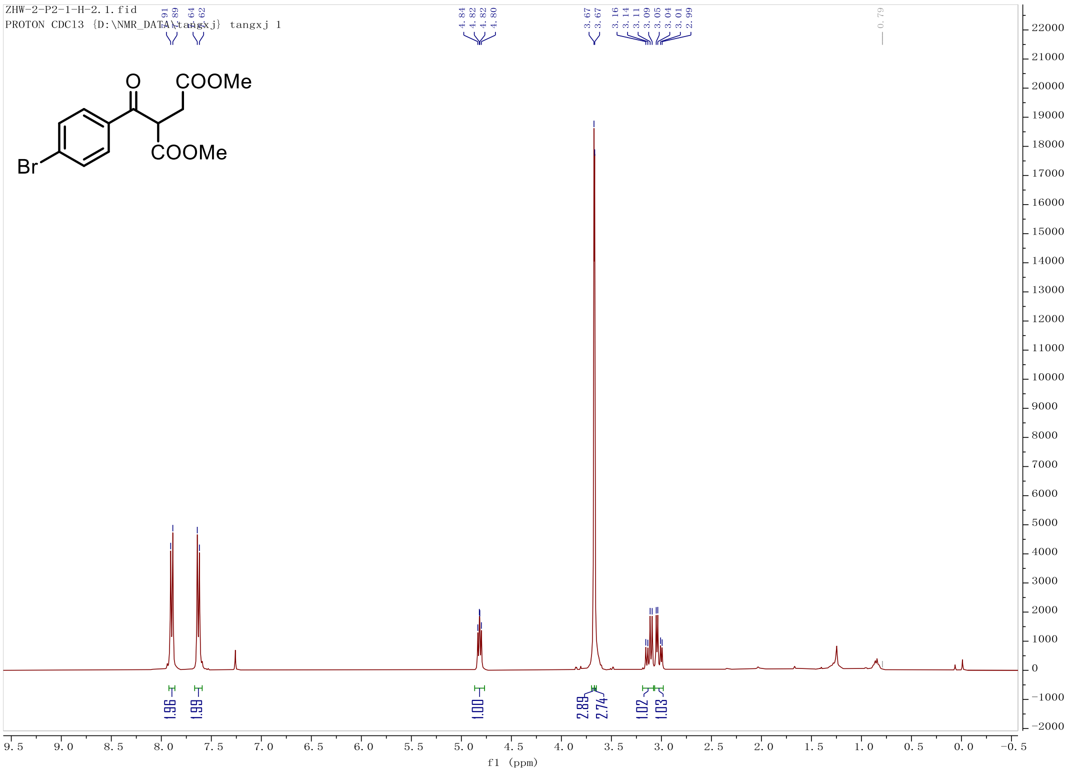

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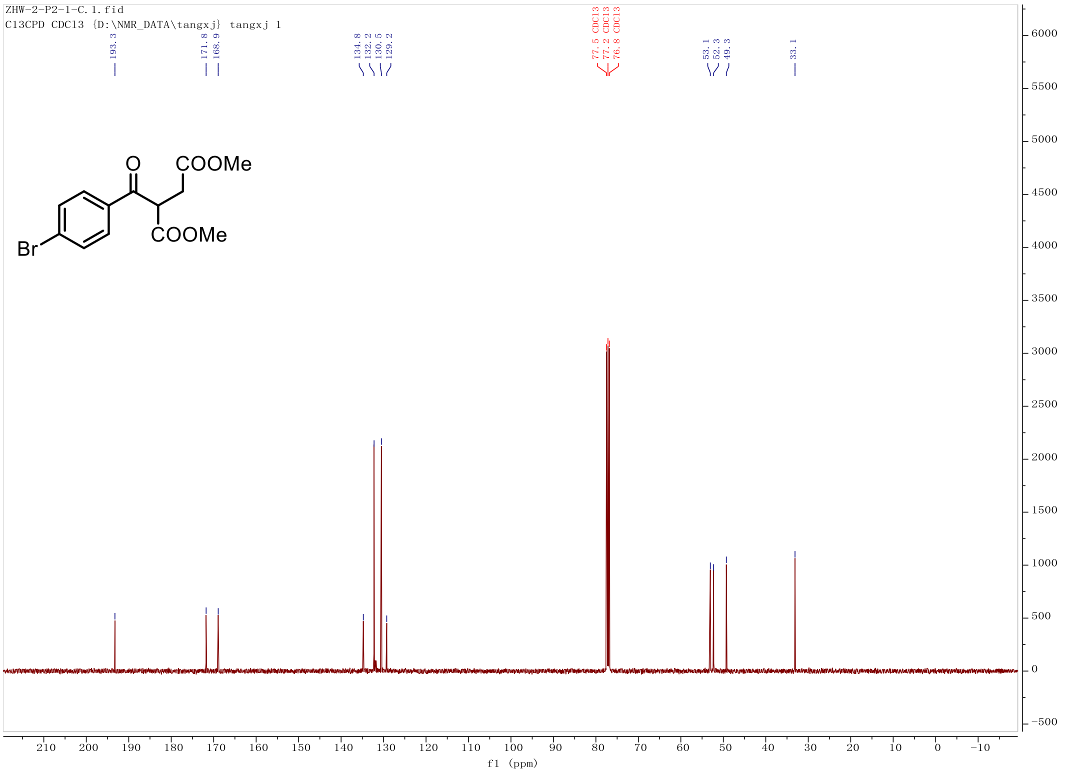

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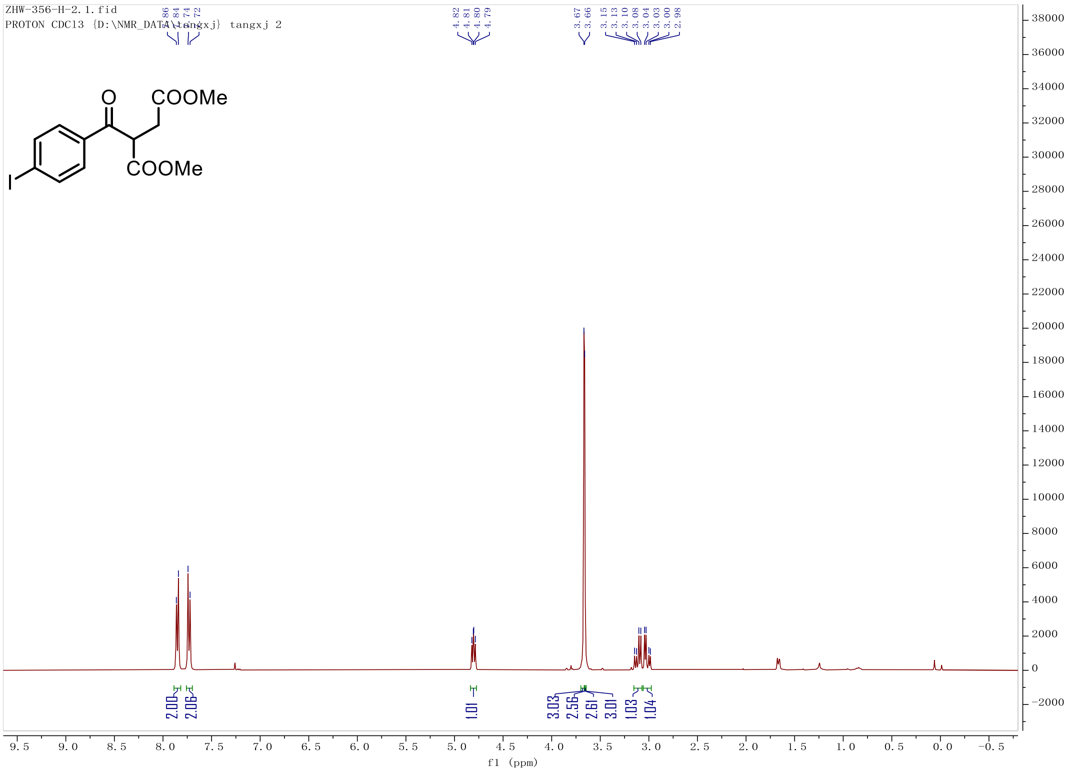

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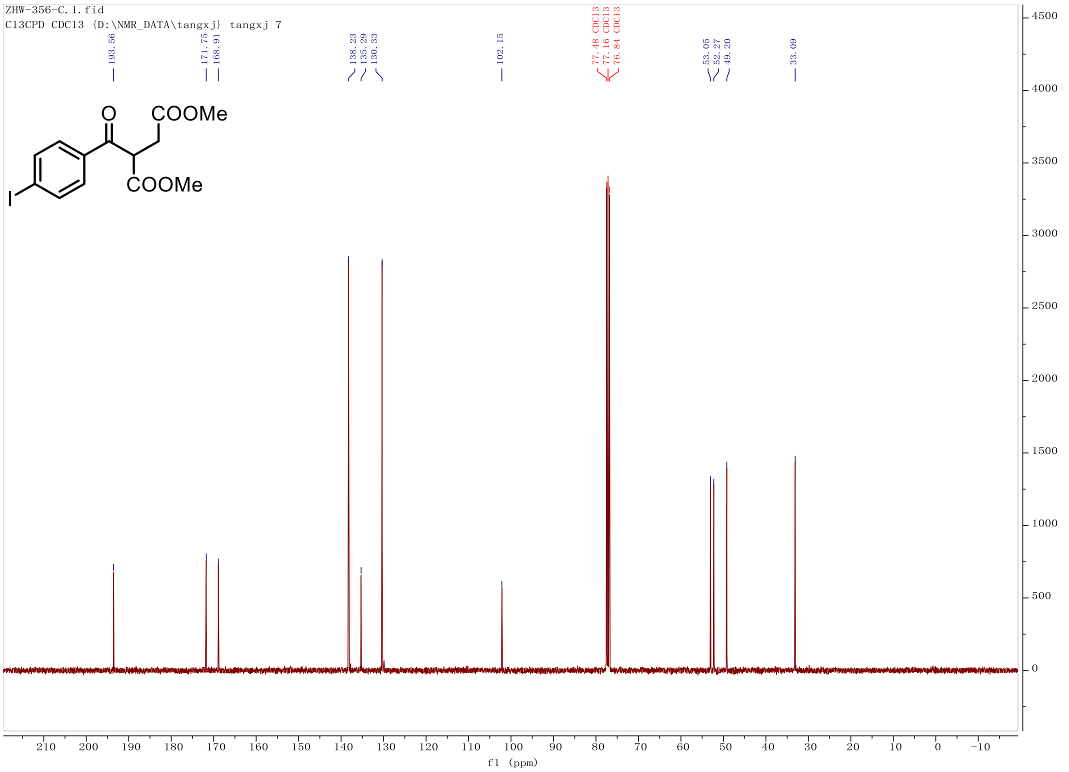

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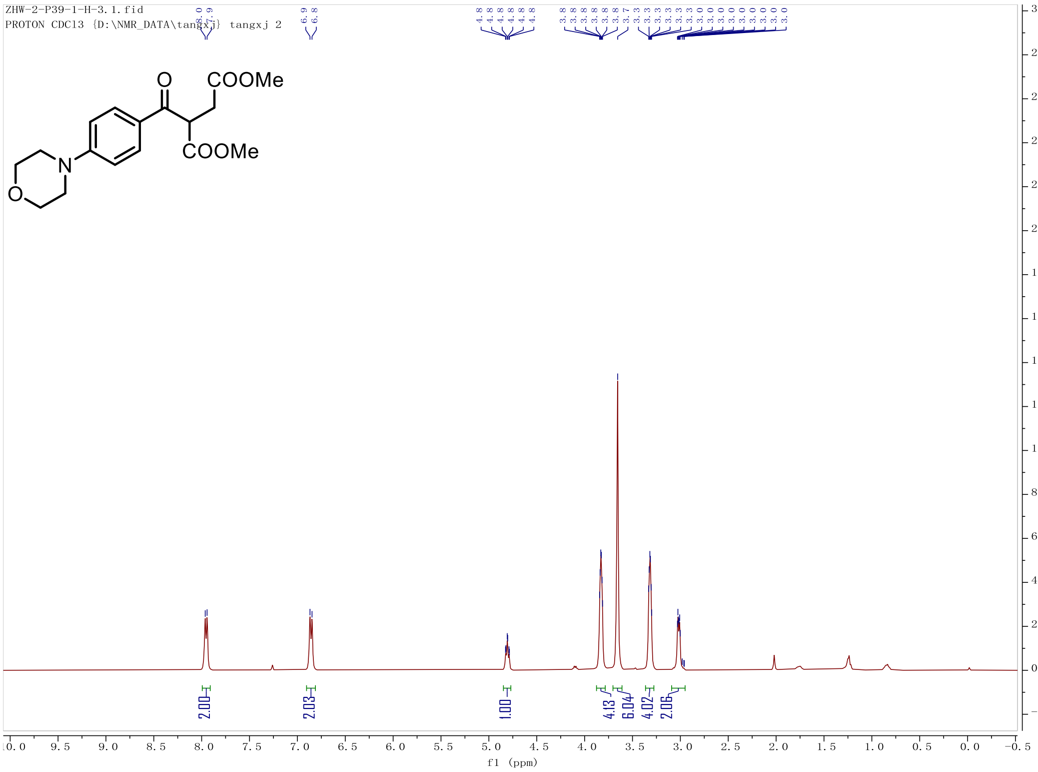

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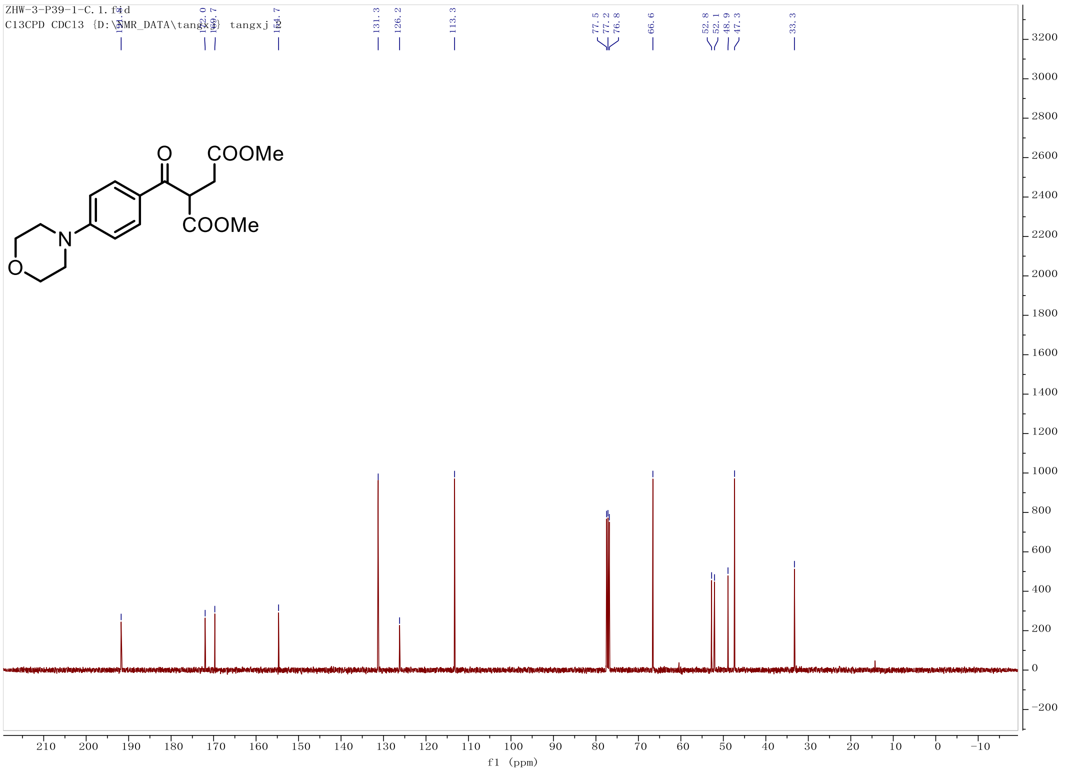

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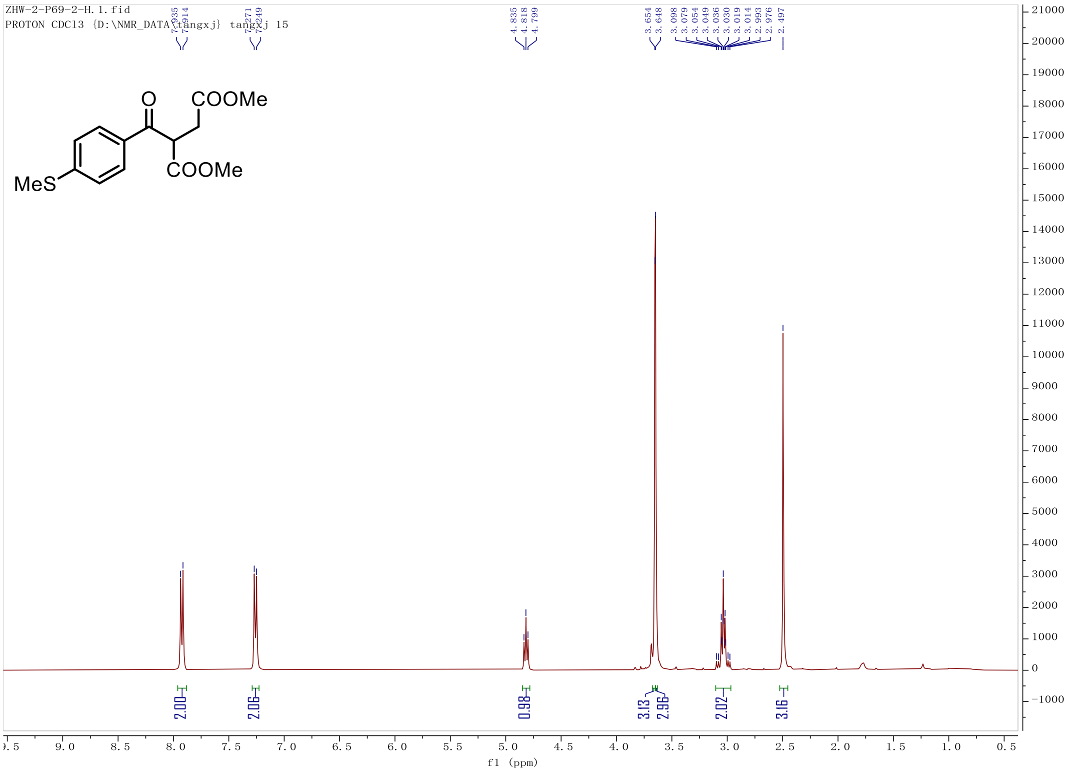

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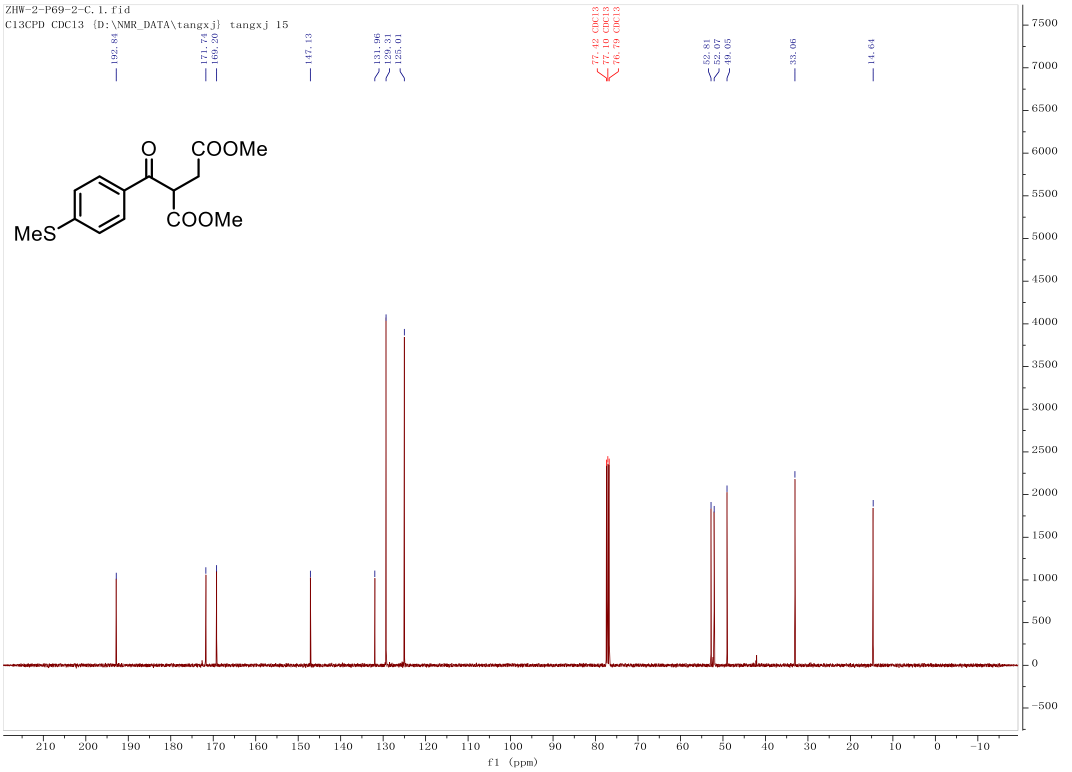

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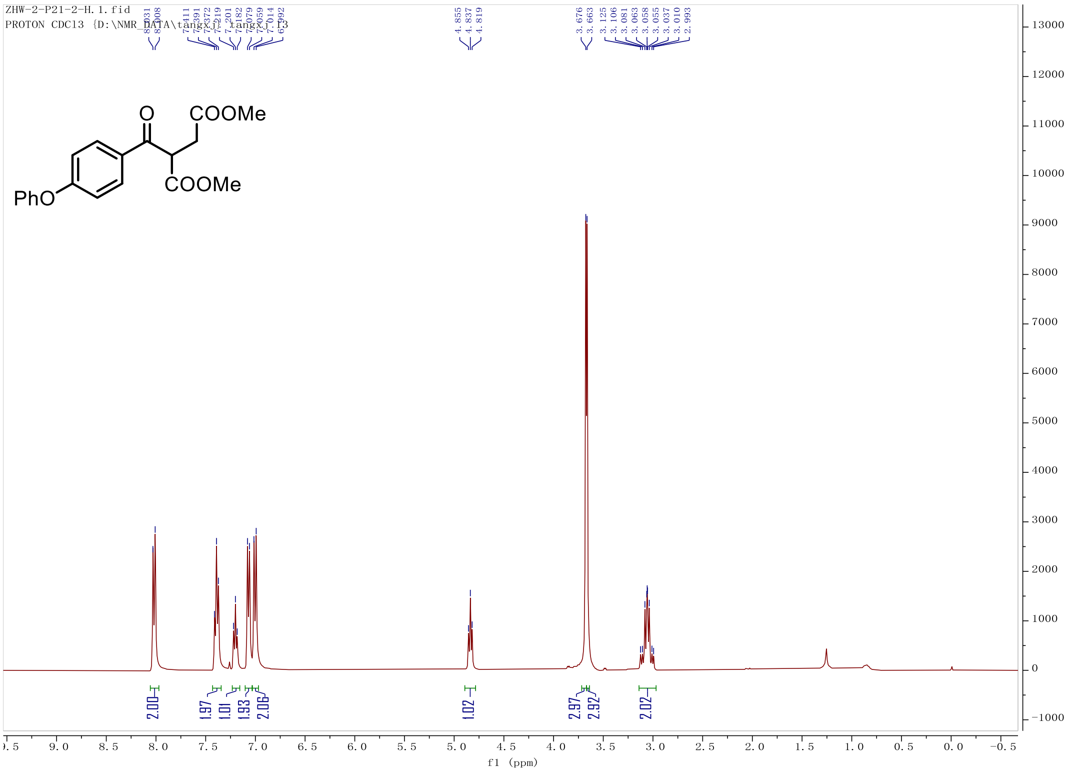

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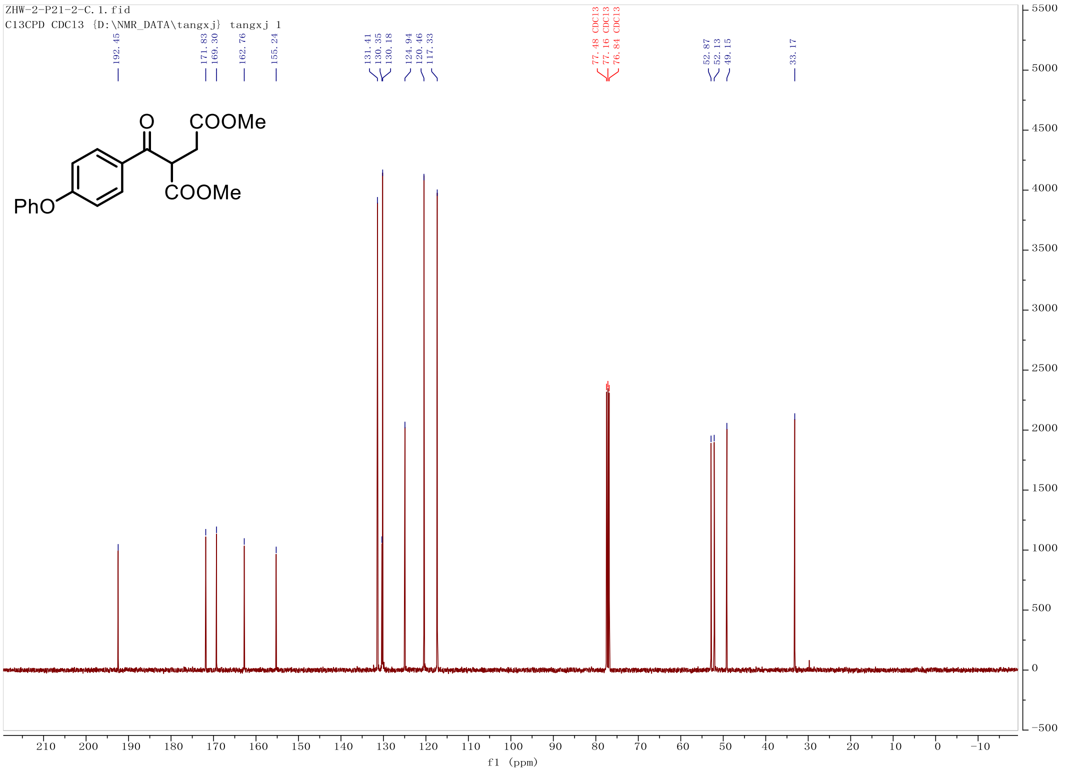

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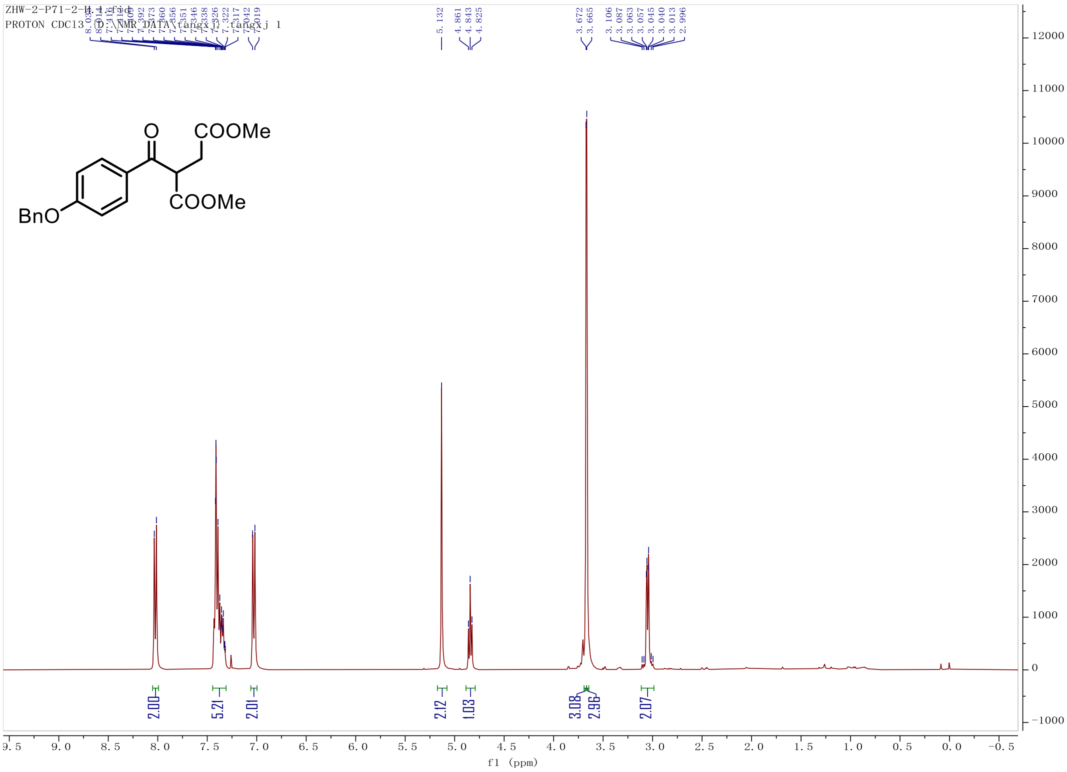

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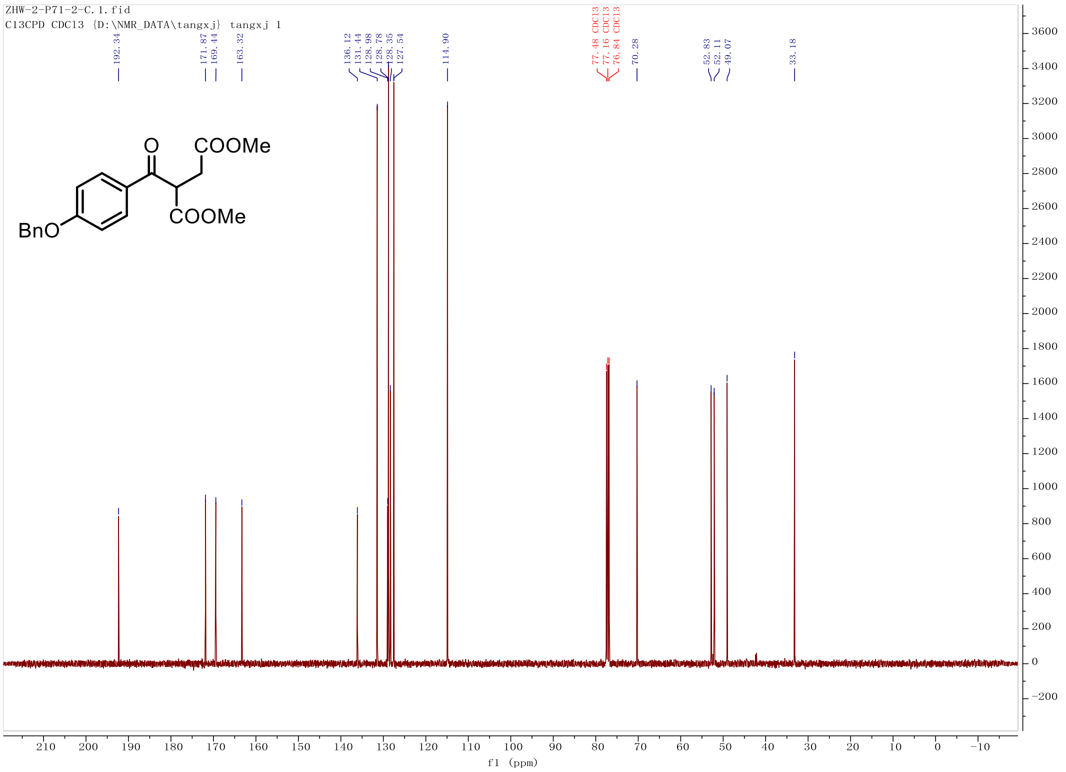

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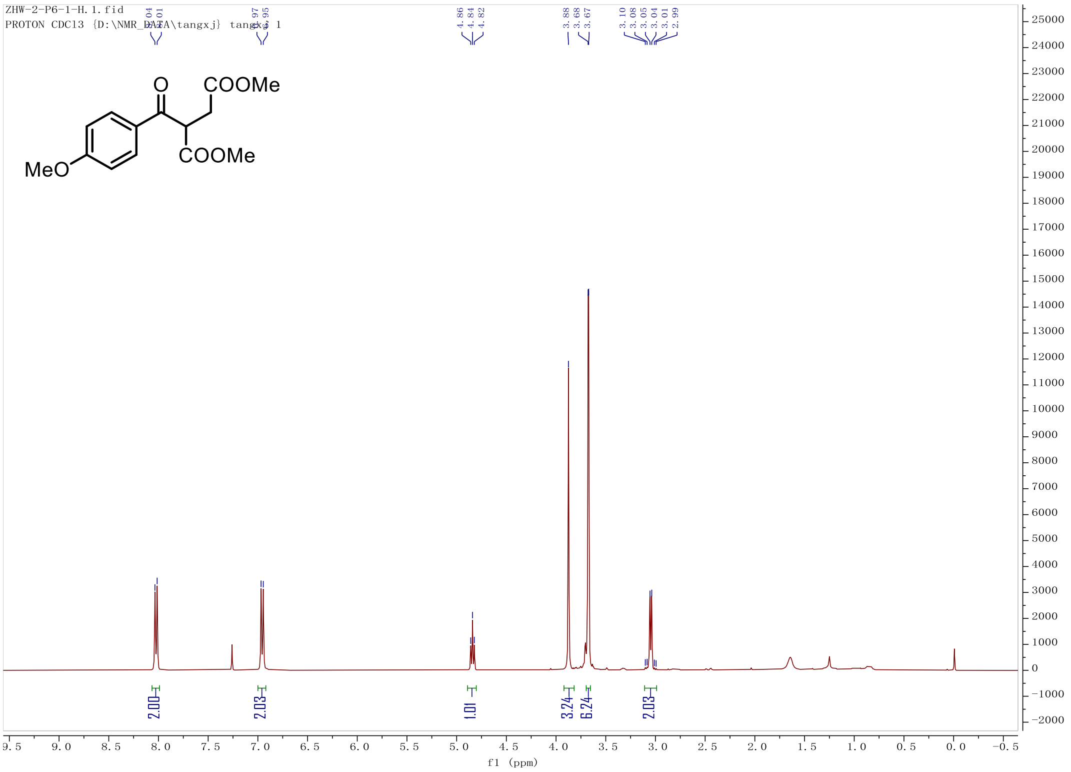

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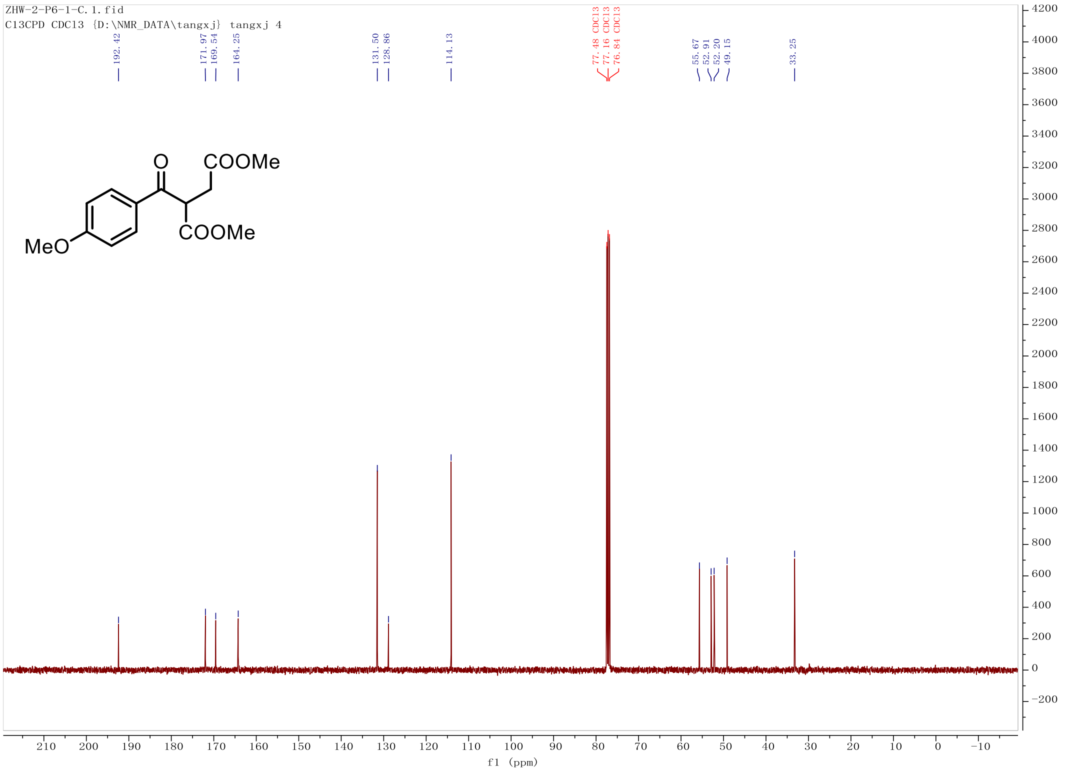

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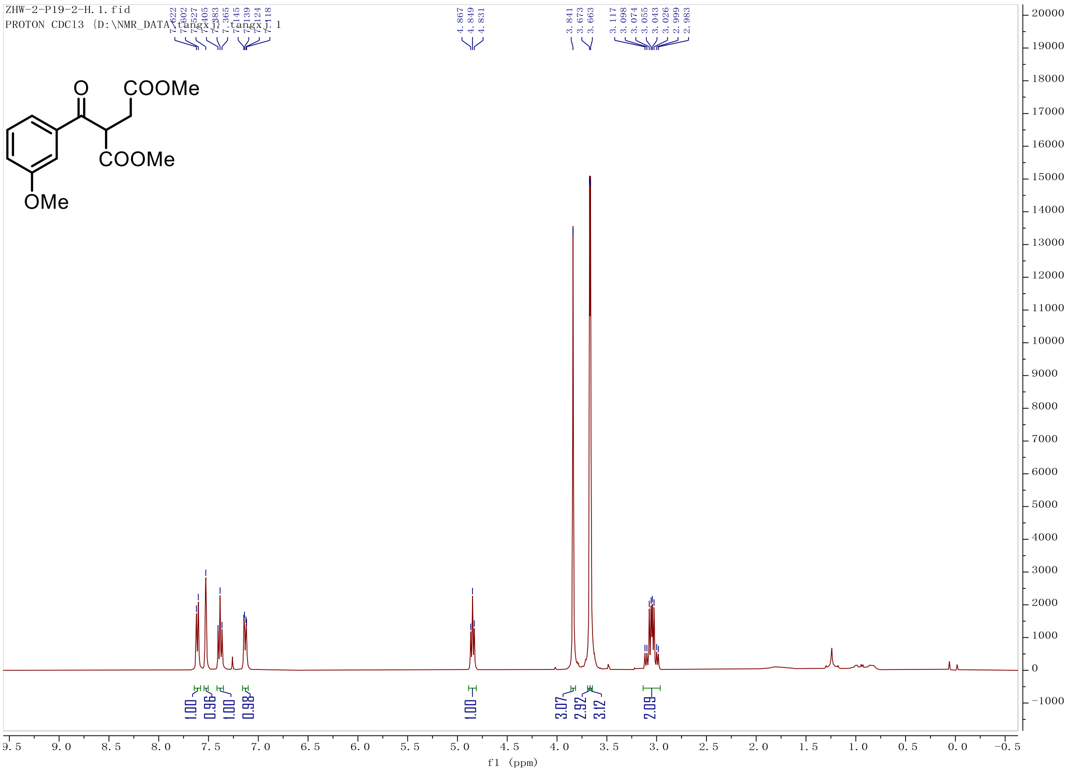

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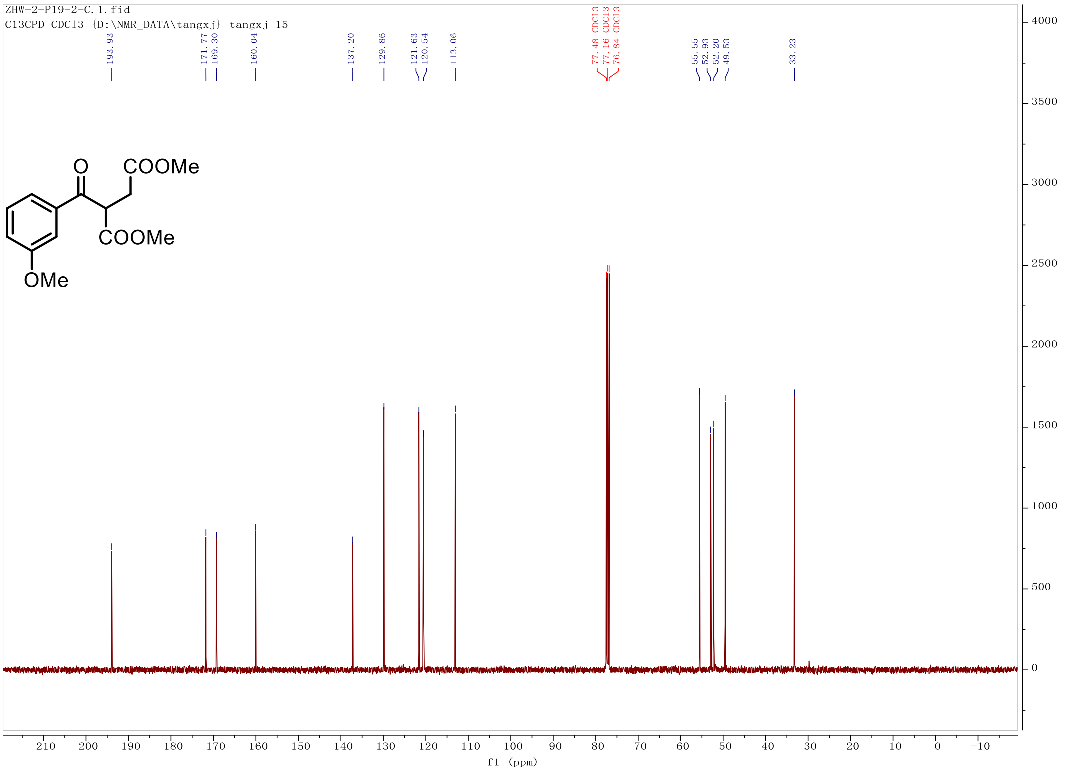
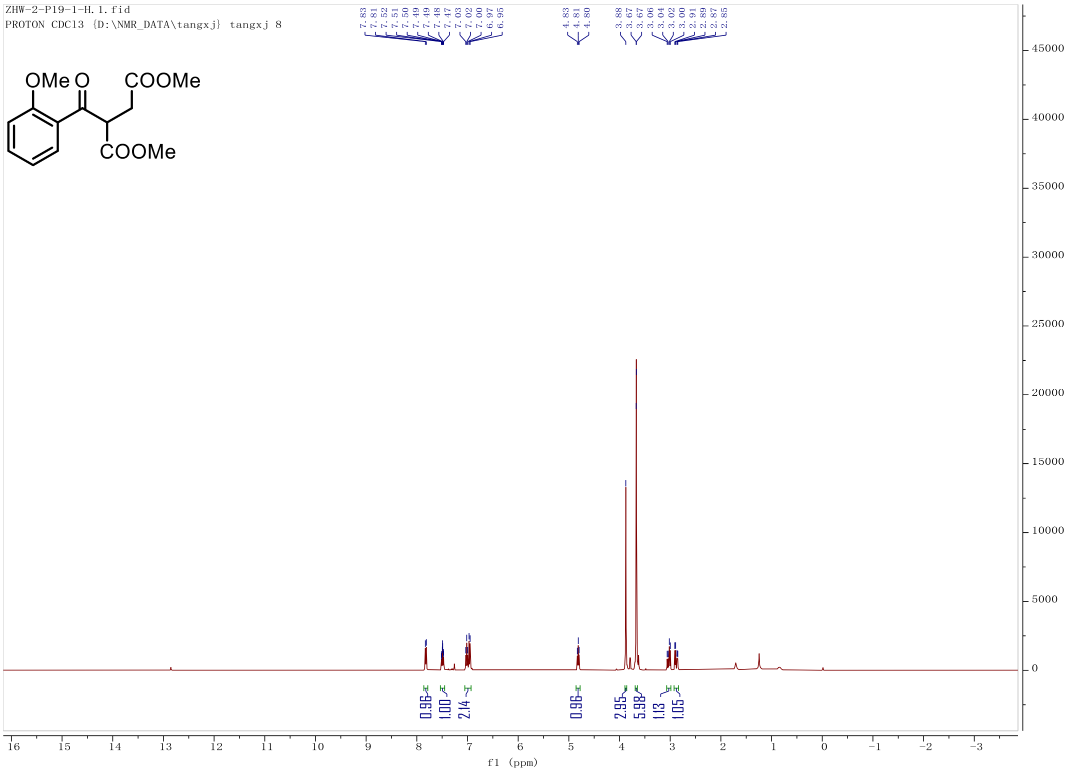


^{1}H NMR of 3o (CDCl$_3$)



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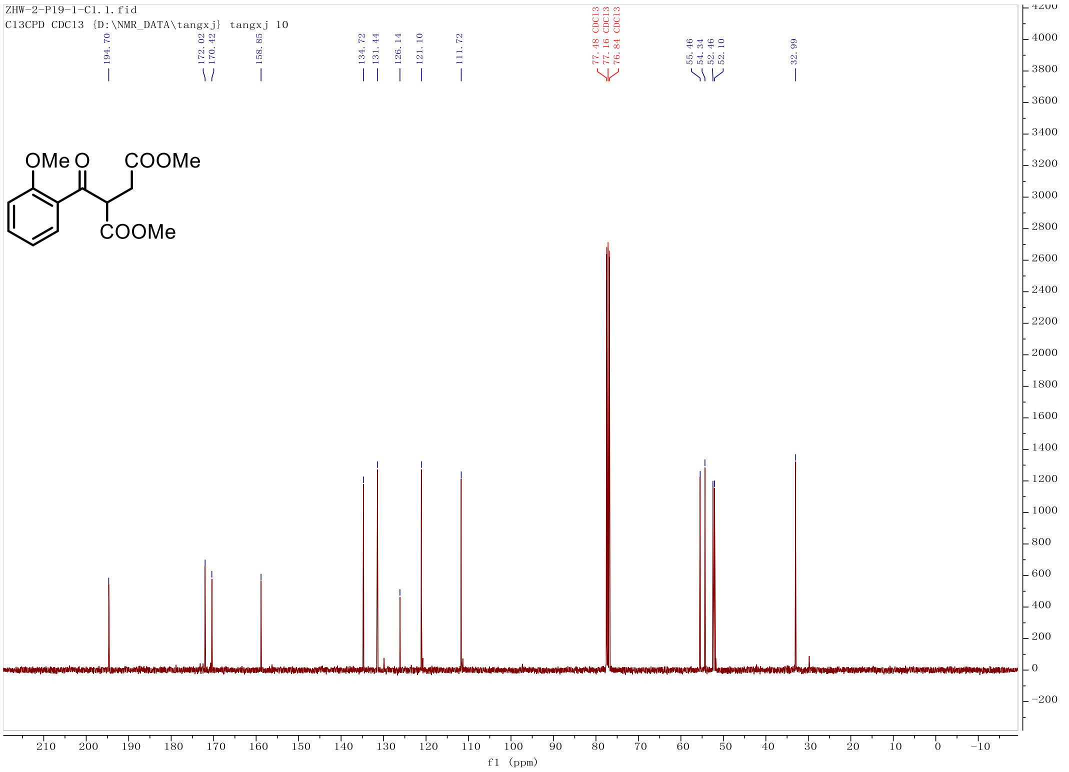

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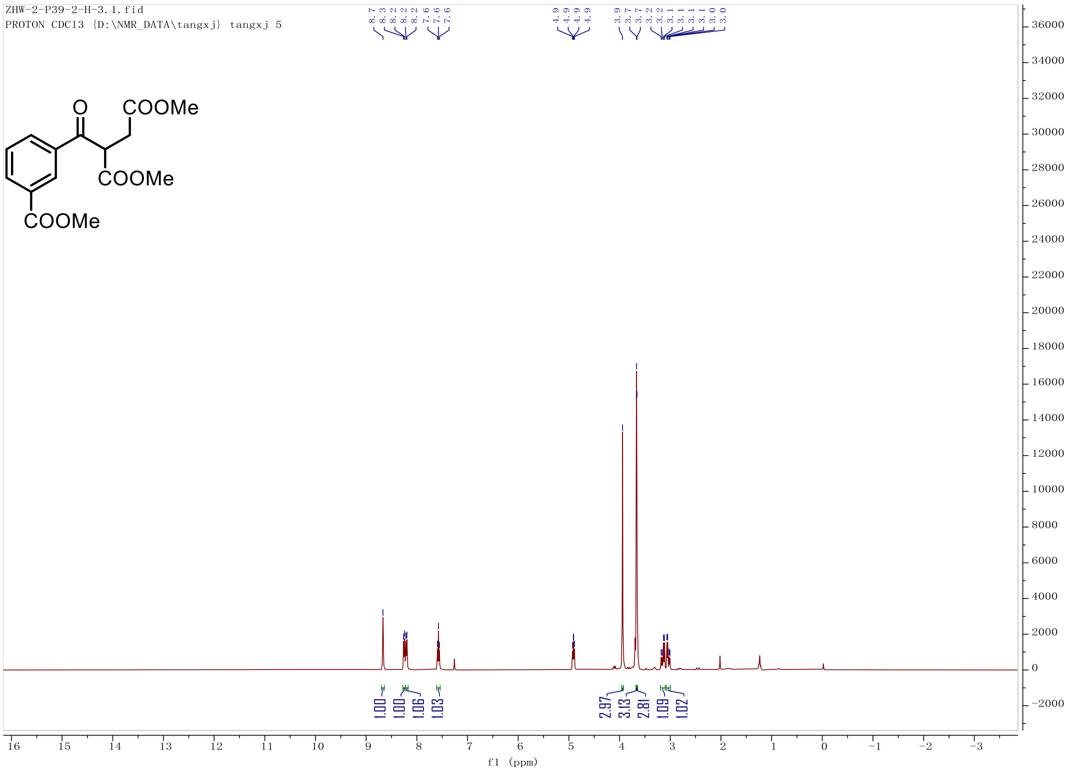

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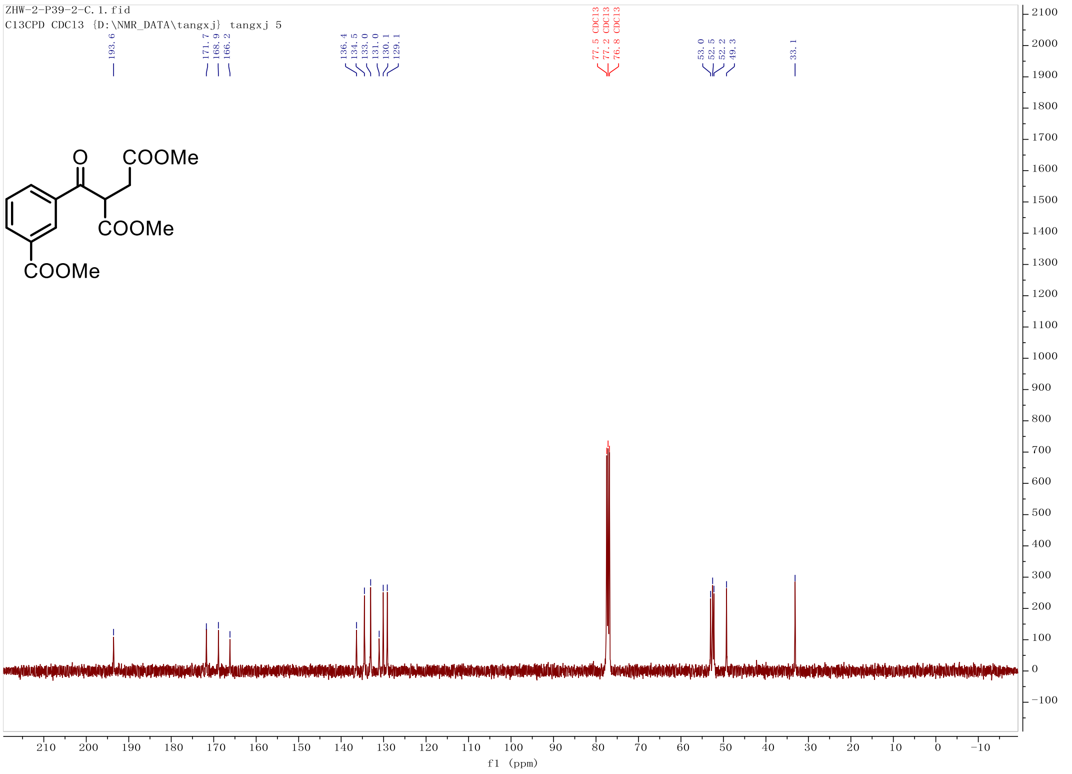

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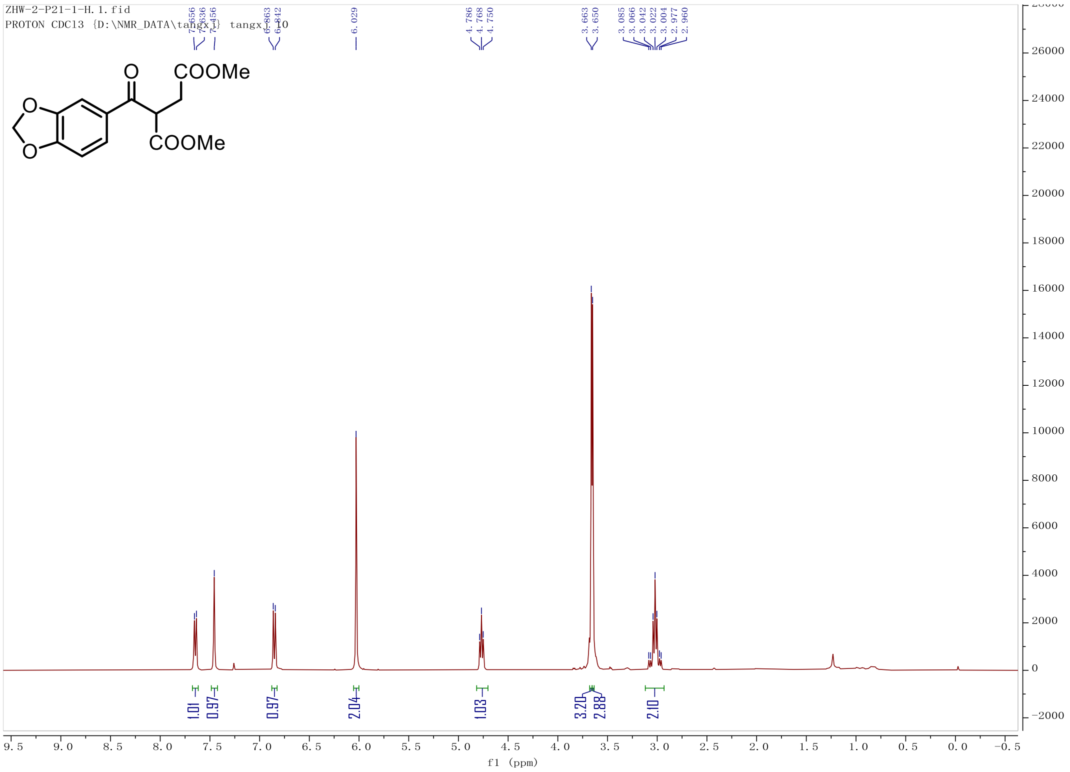
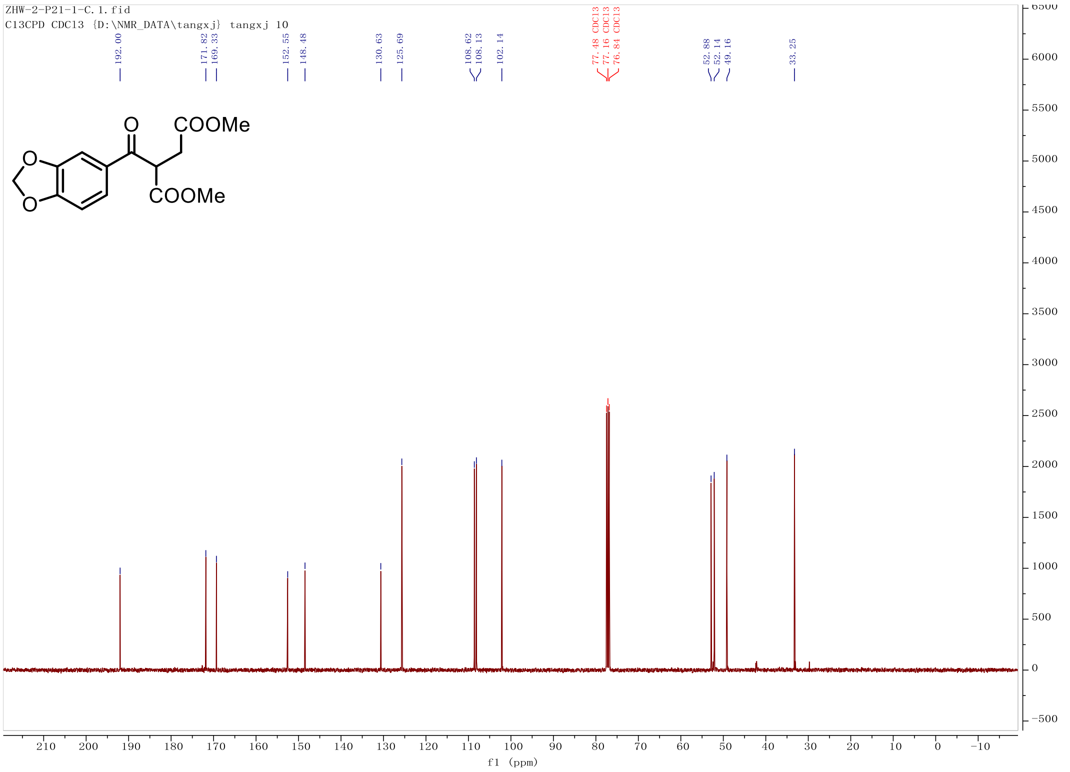
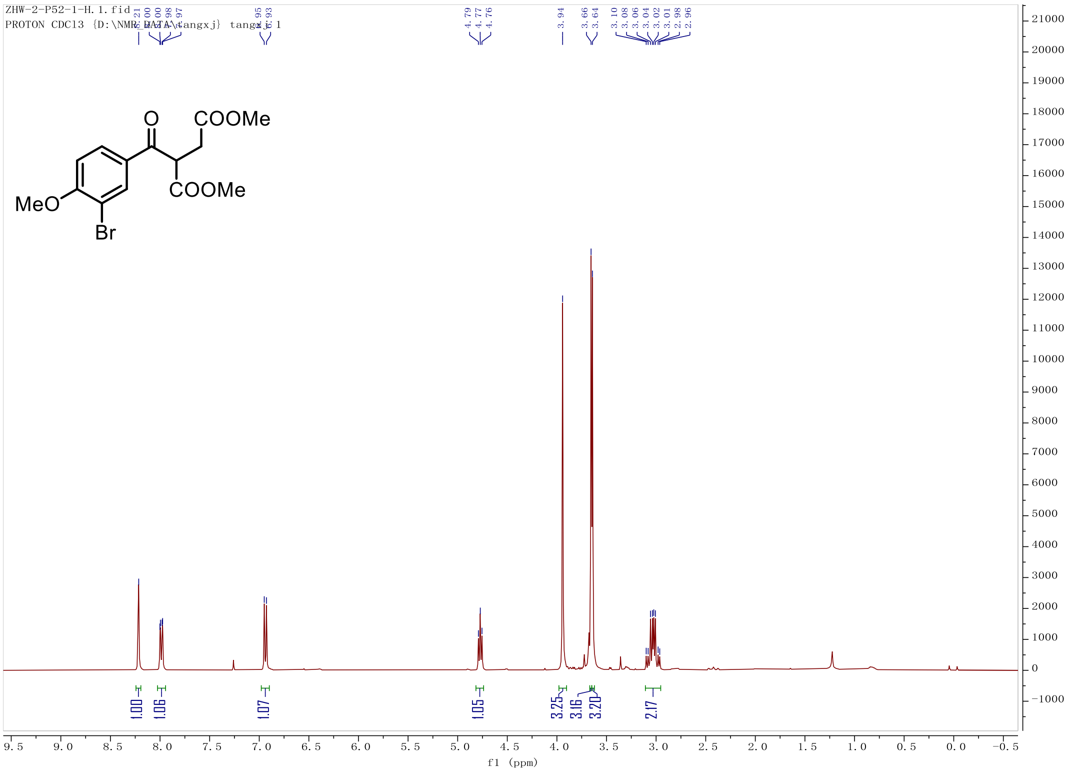


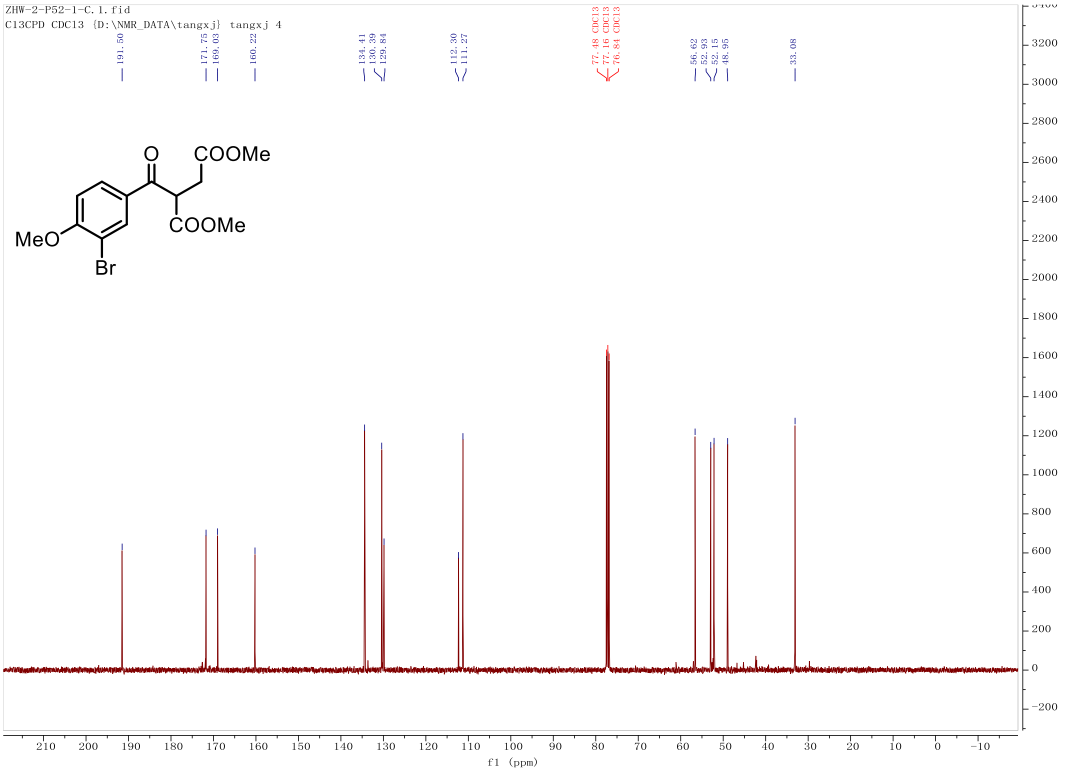
^{13}C NMR of 3q (CDCl$_3$)



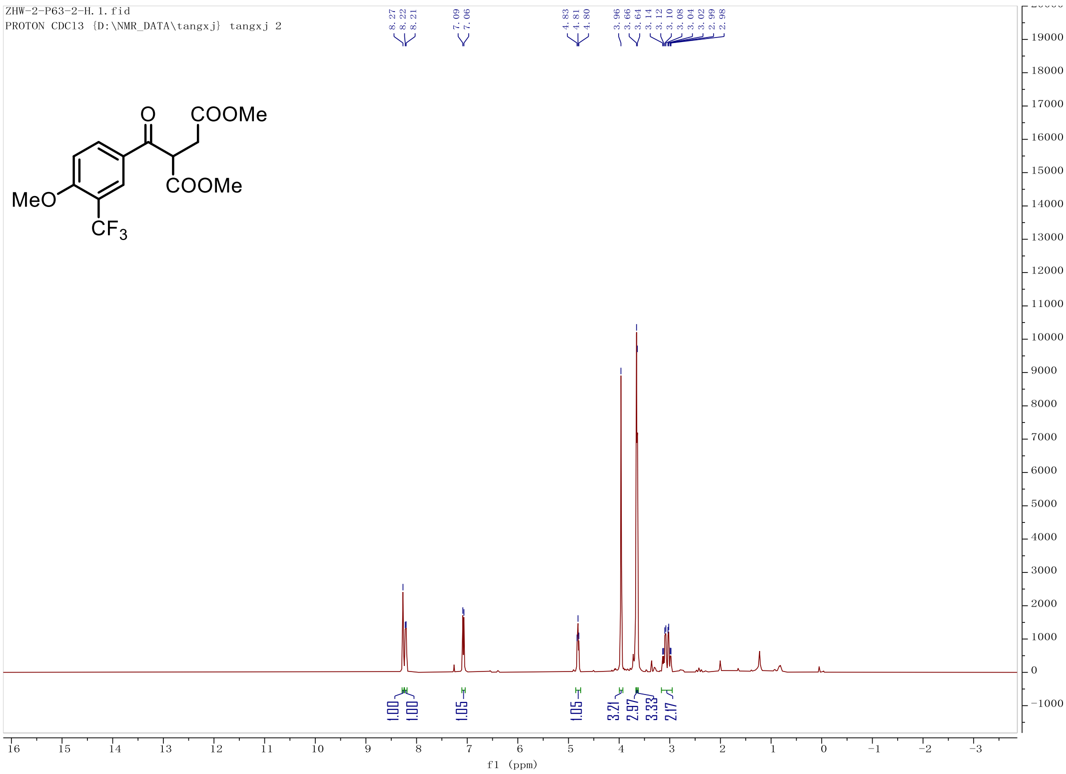
^{1}H NMR of 3r (CDCl$_3$)



^{13}C NMR of 3r (CDCl$_3$)



^{1}H NMR of 3s (CDCl$_3$)



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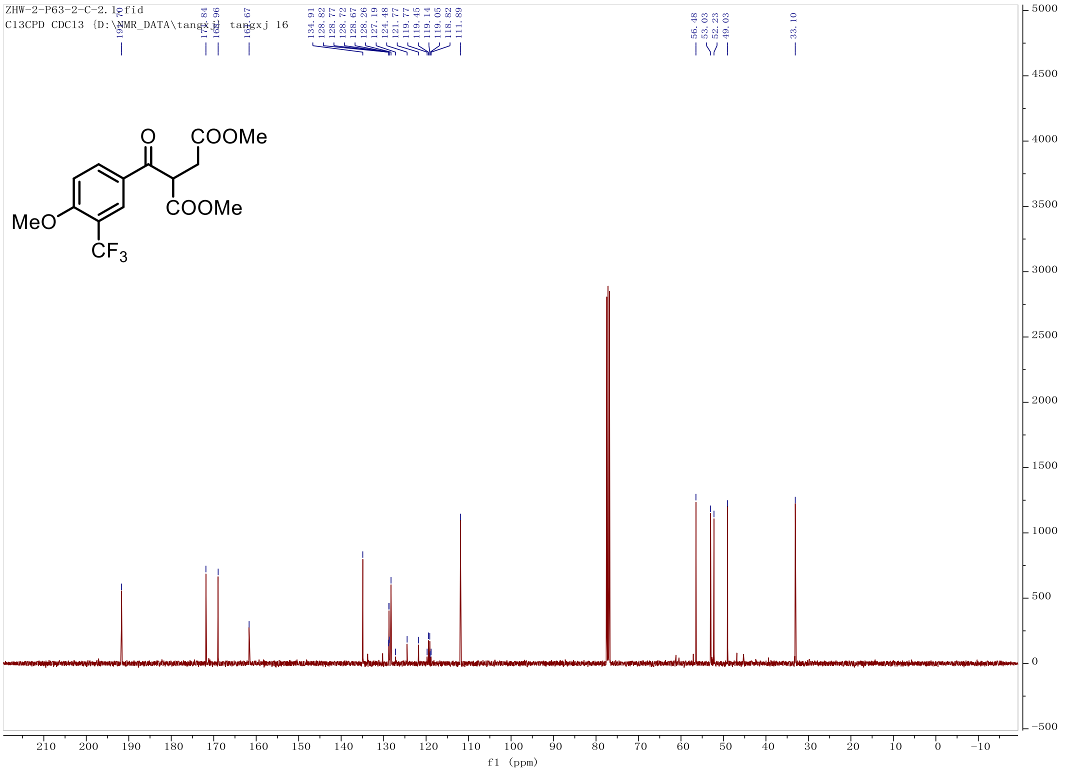
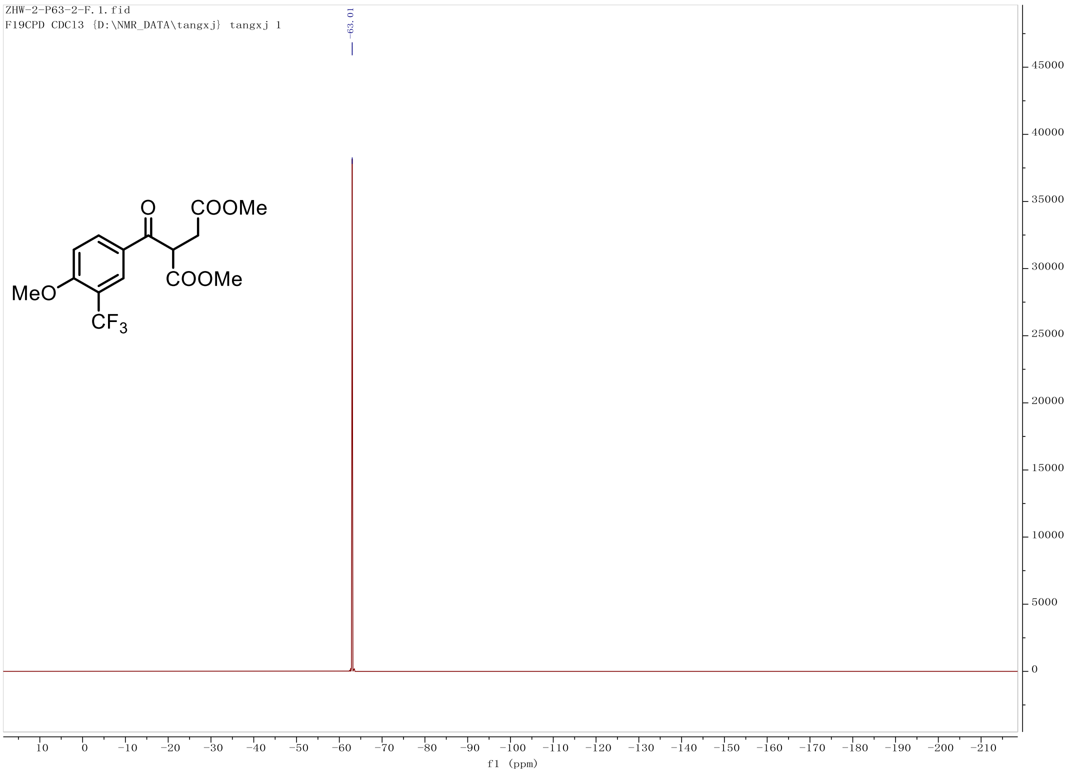
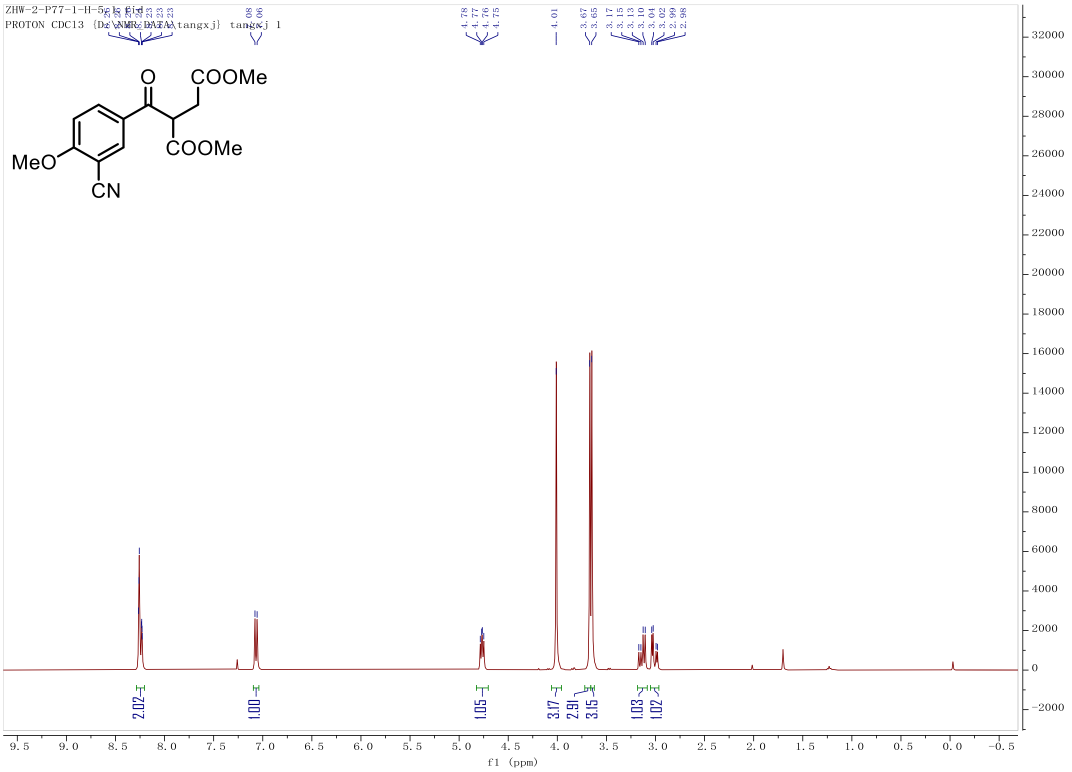


^{19}F NMR of 3s (CDCl$_3$)



^{1}H NMR of 3t (CDCl$_3$)



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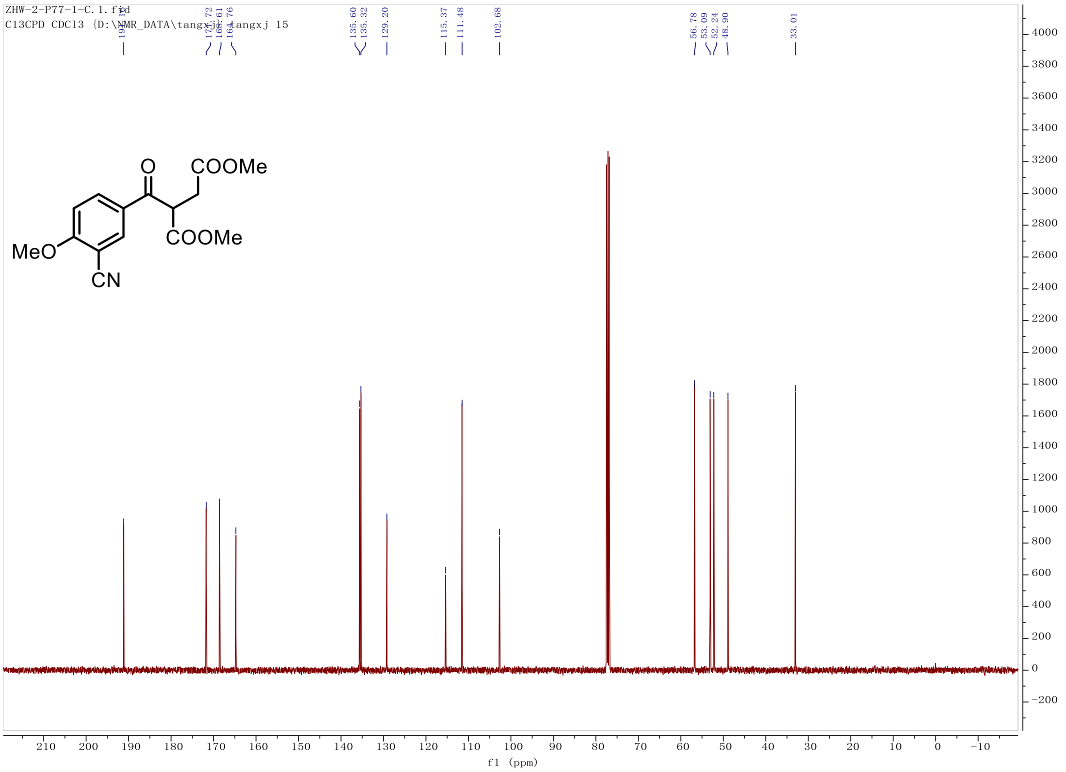
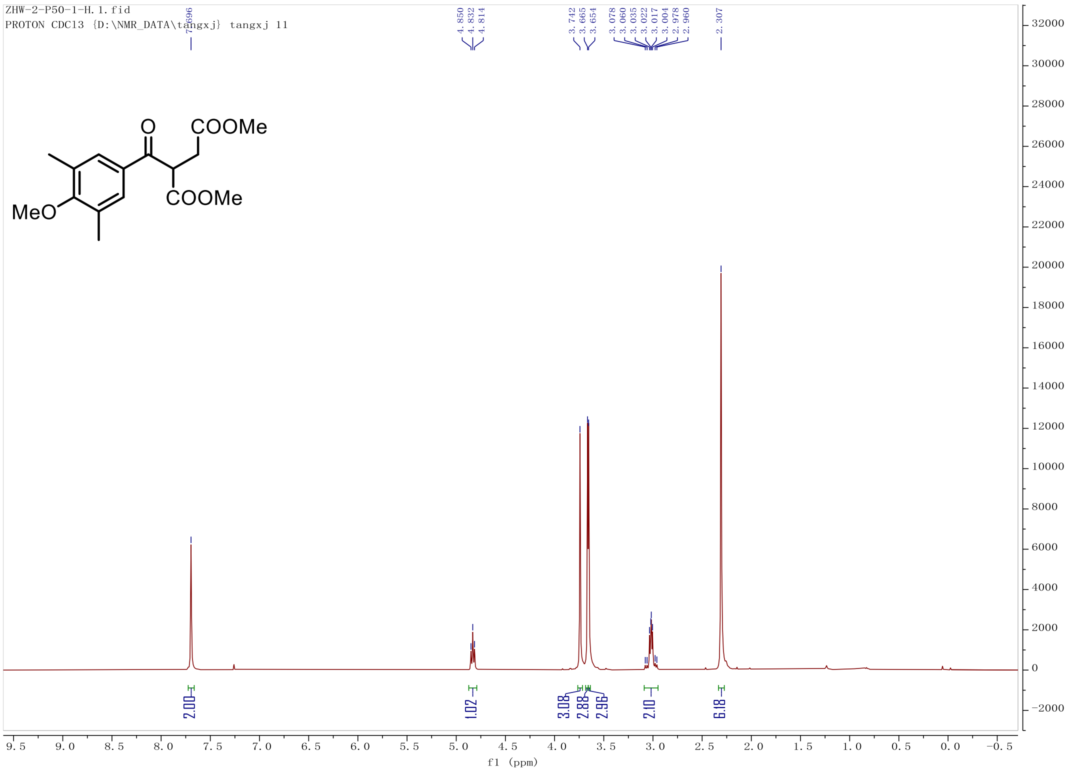


^{1}H NMR of 3u (CDCl$_3$)



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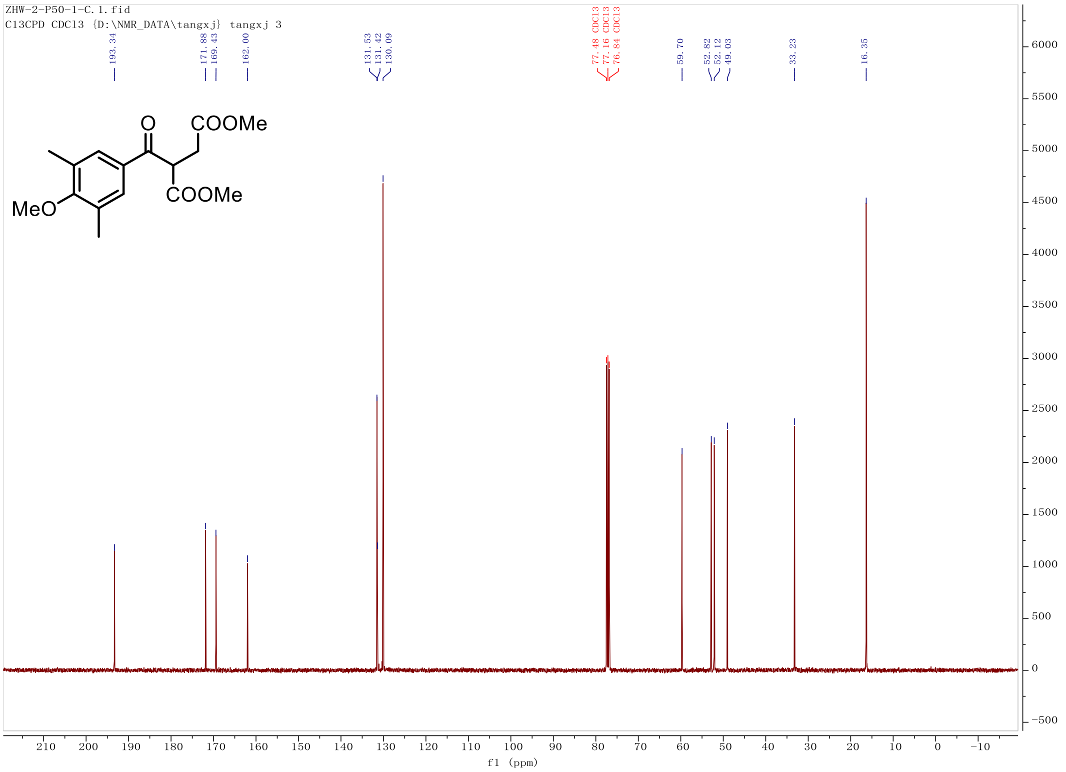

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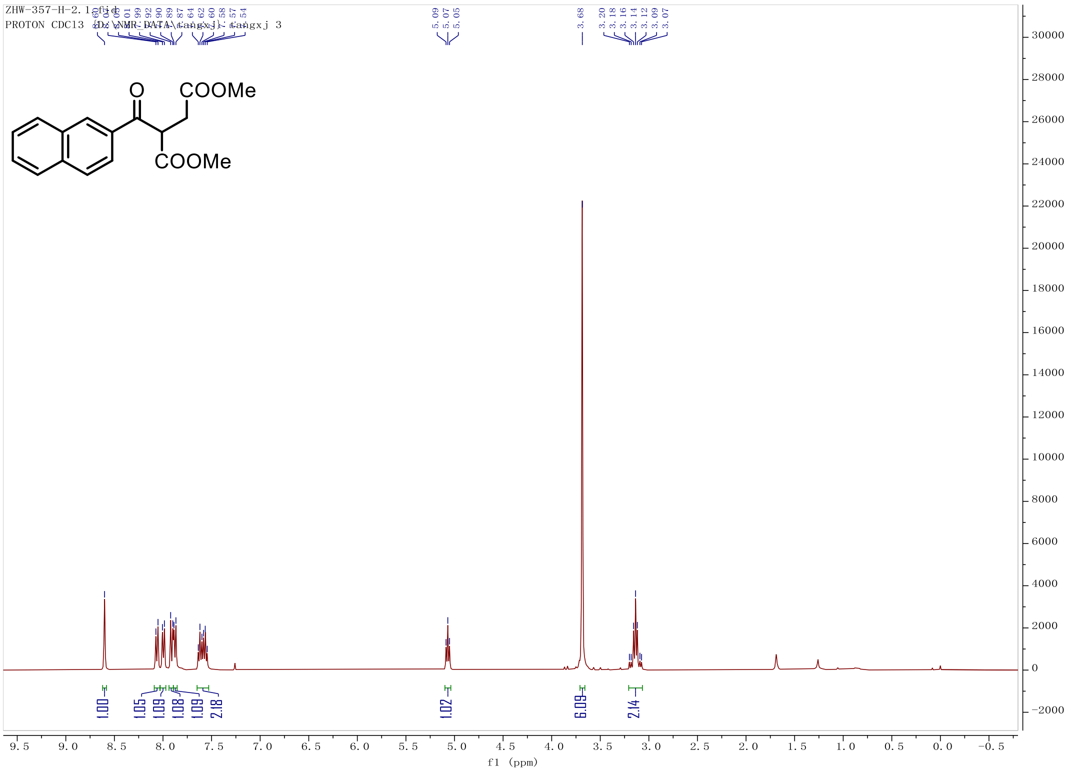
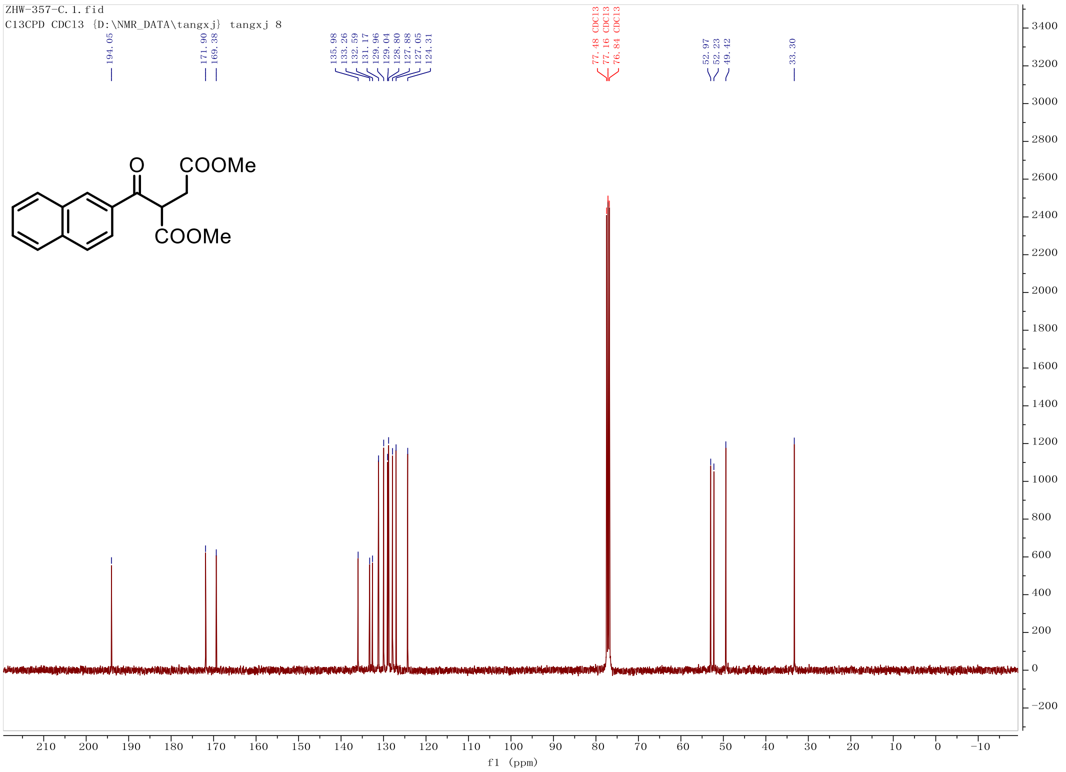
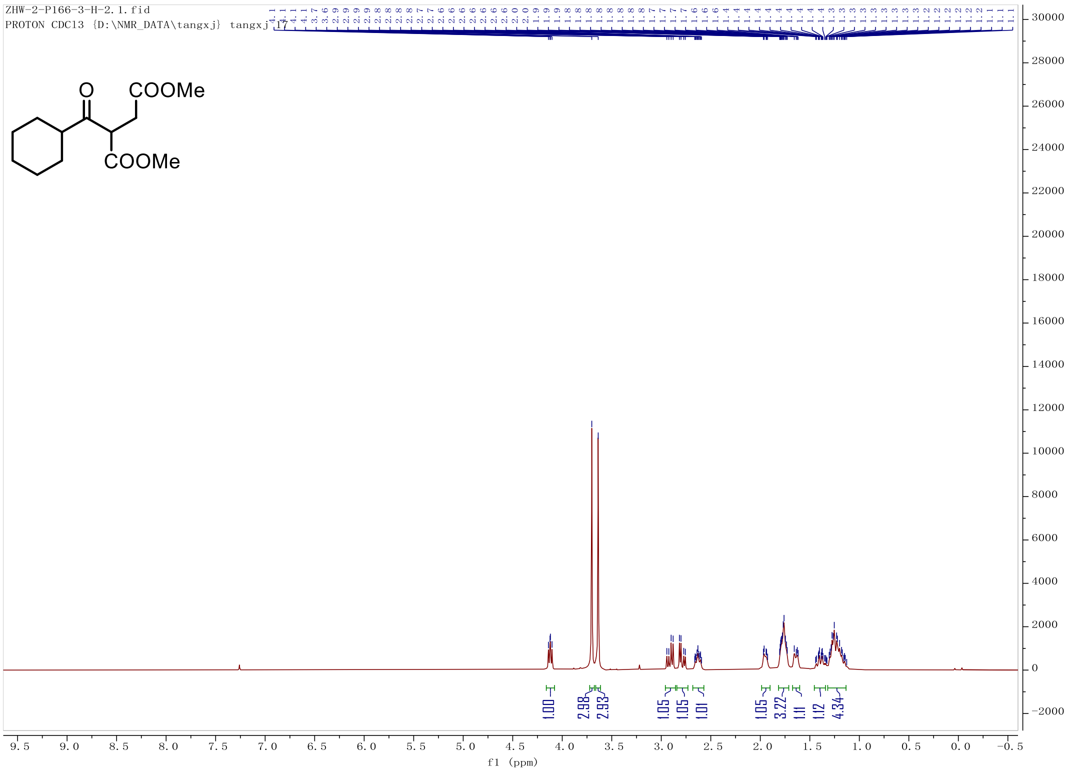


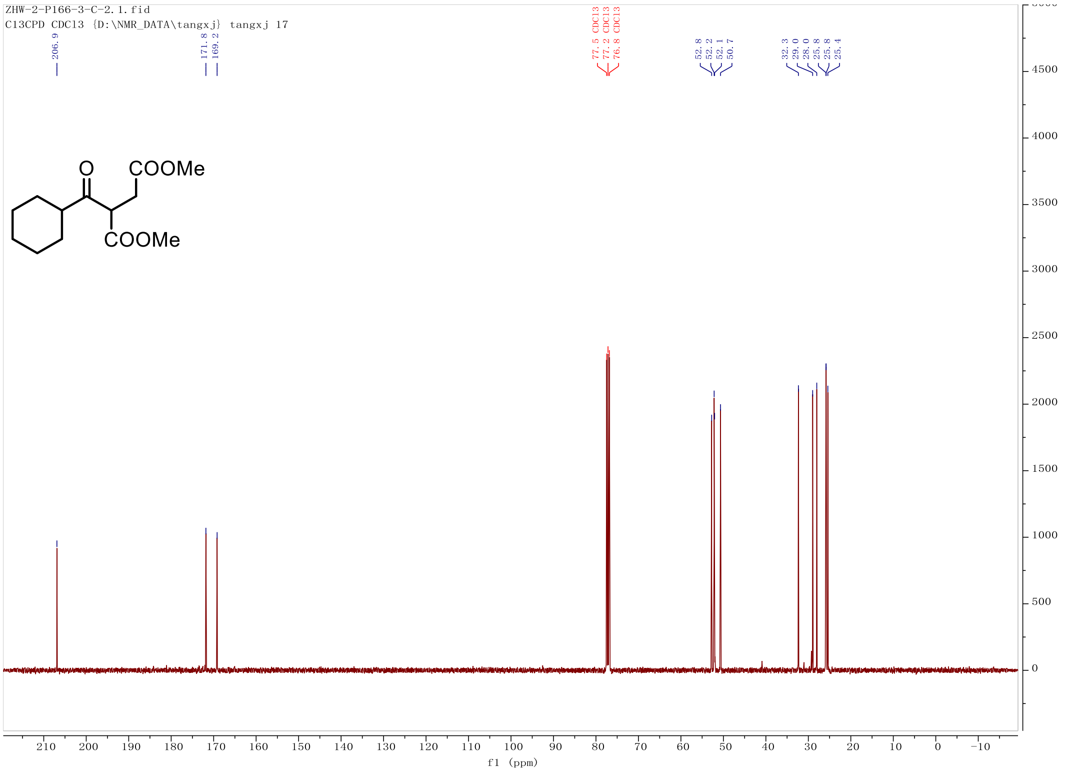
^{13}C NMR of 3v (CDCl$_3$)



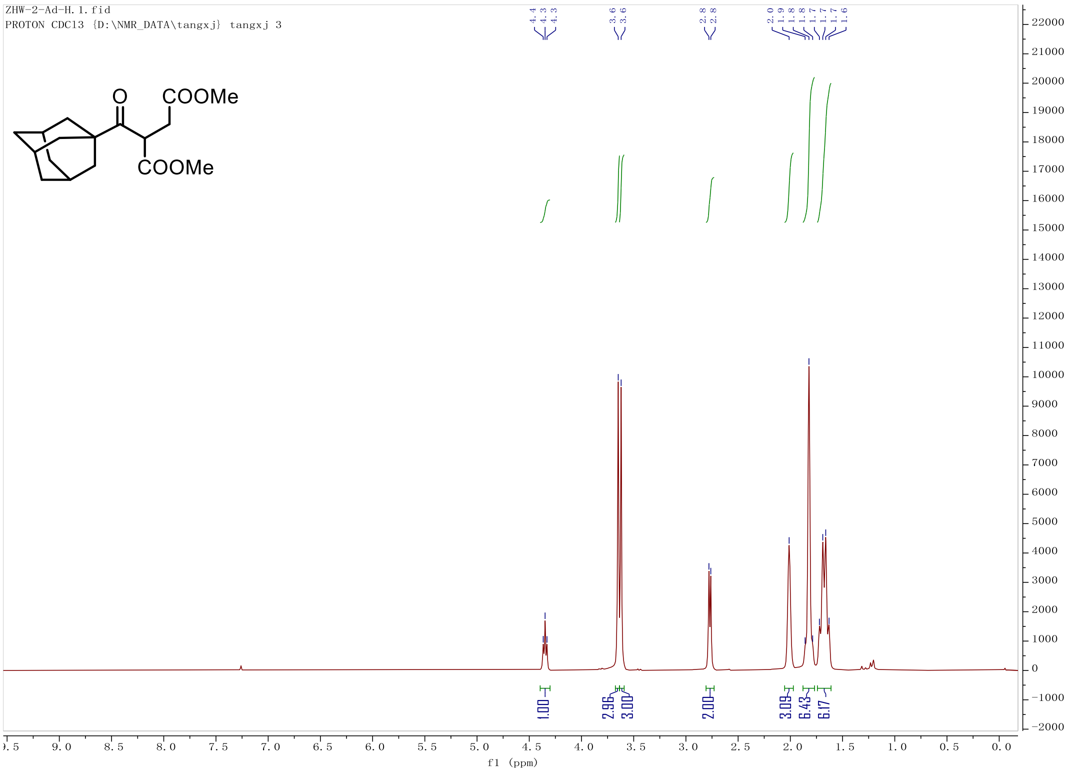
^{1}H NMR of 3w (CDCl$_3$)



^{13}C NMR of 3w (CDCl$_3$)



^{1}H NMR of 3x (CDCl$_3$)



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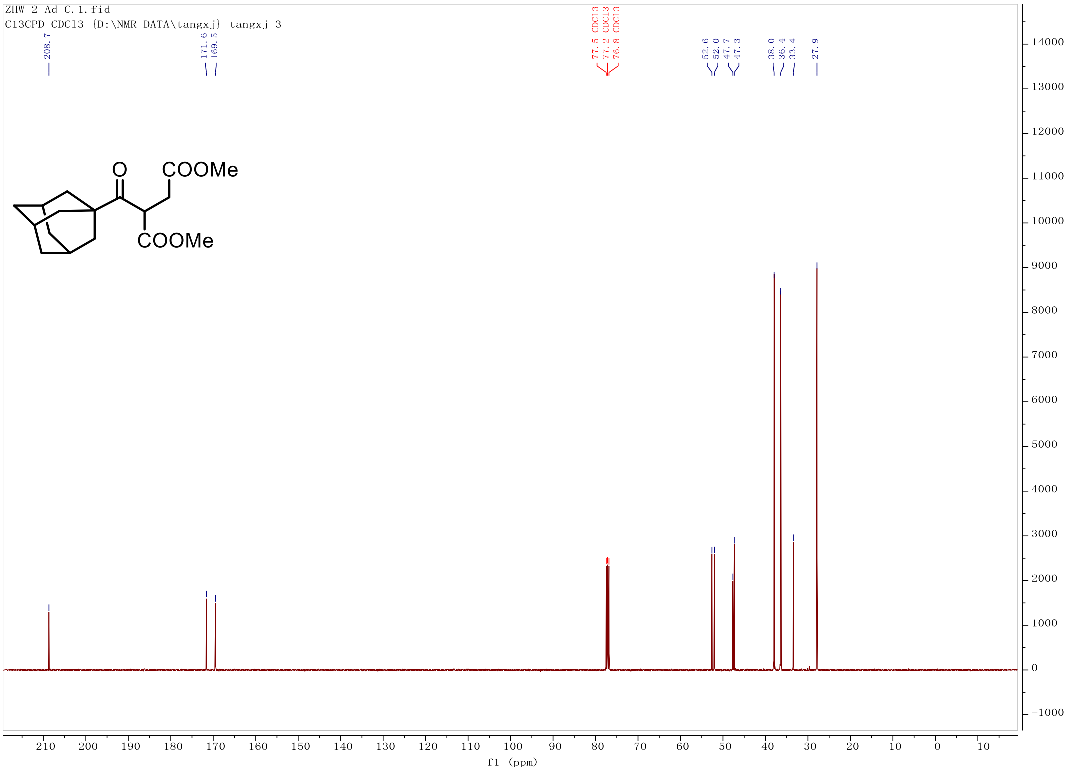

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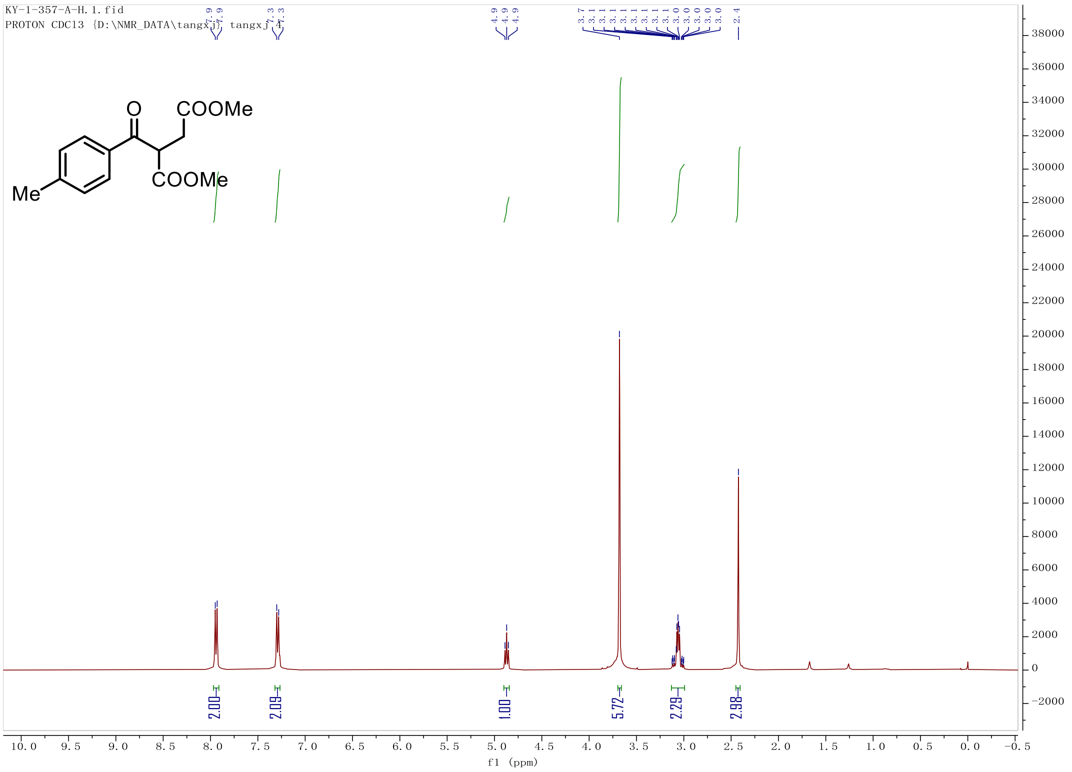

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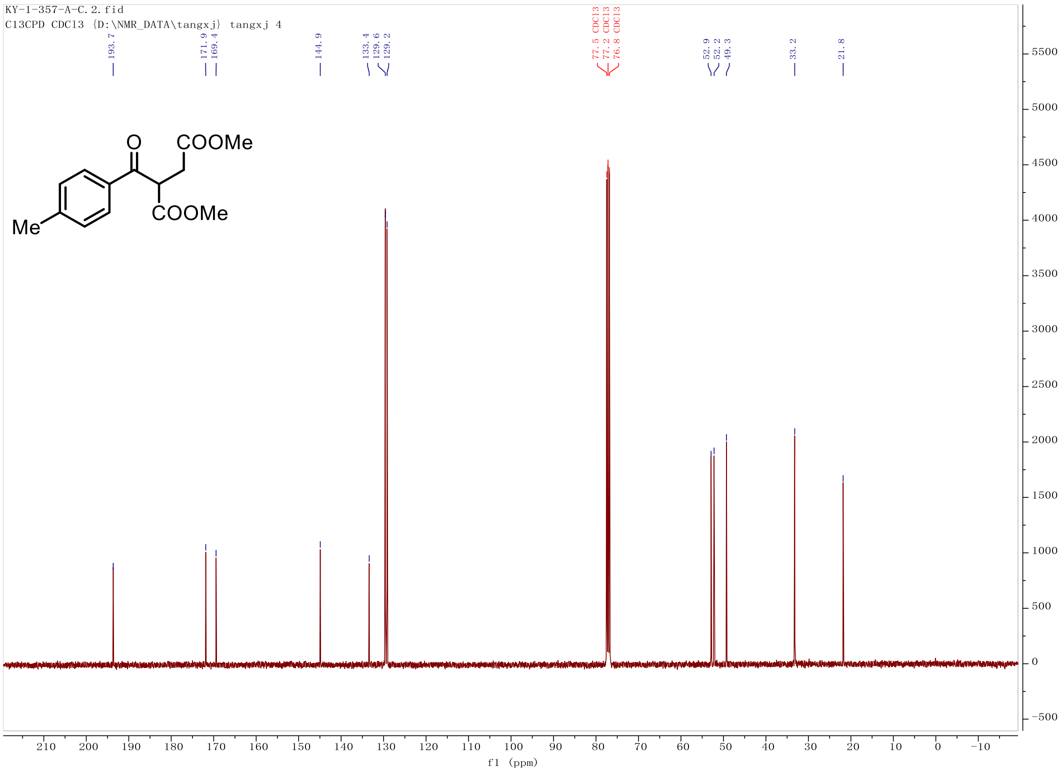

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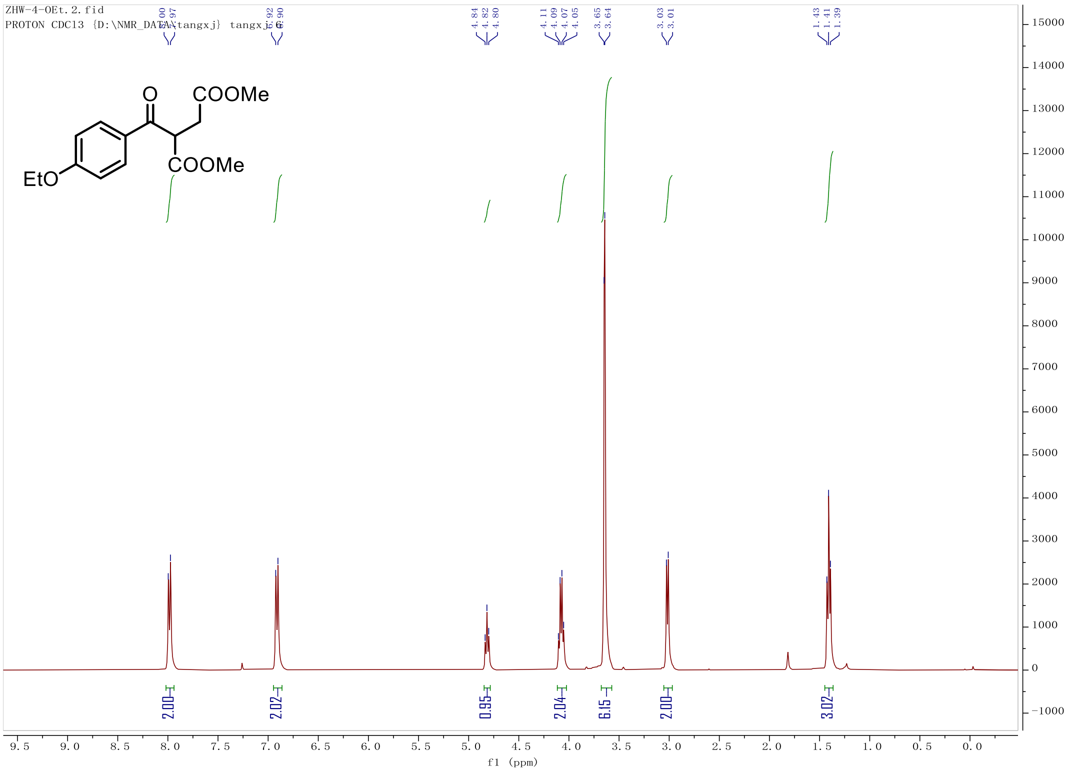

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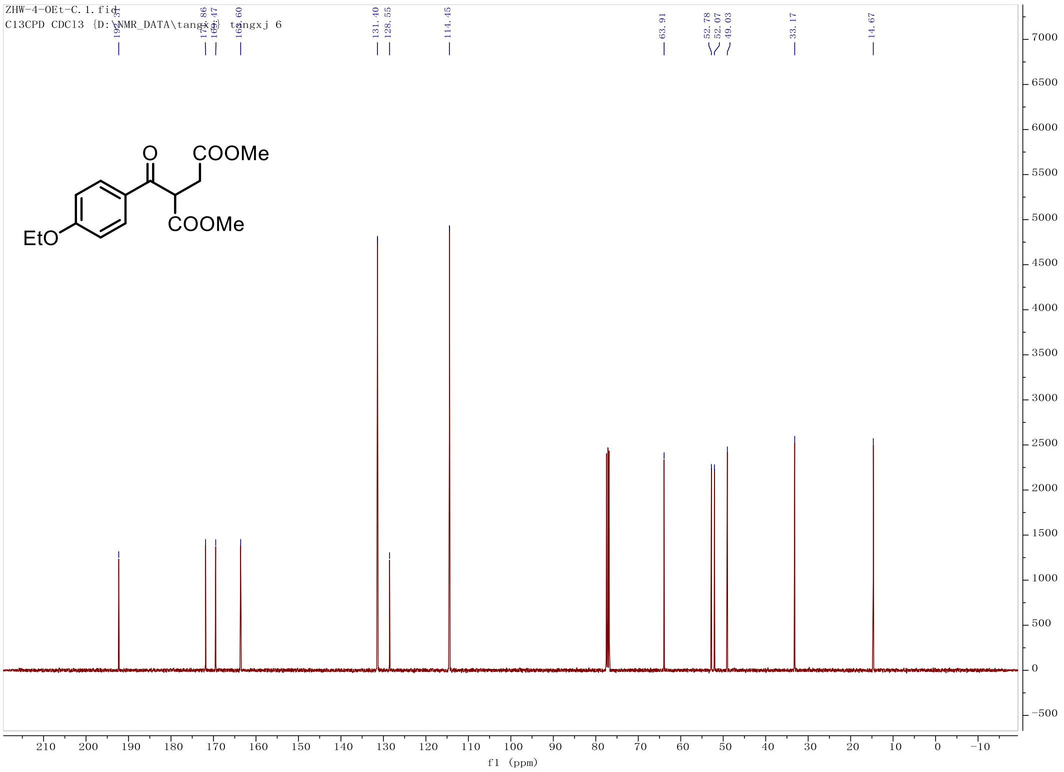
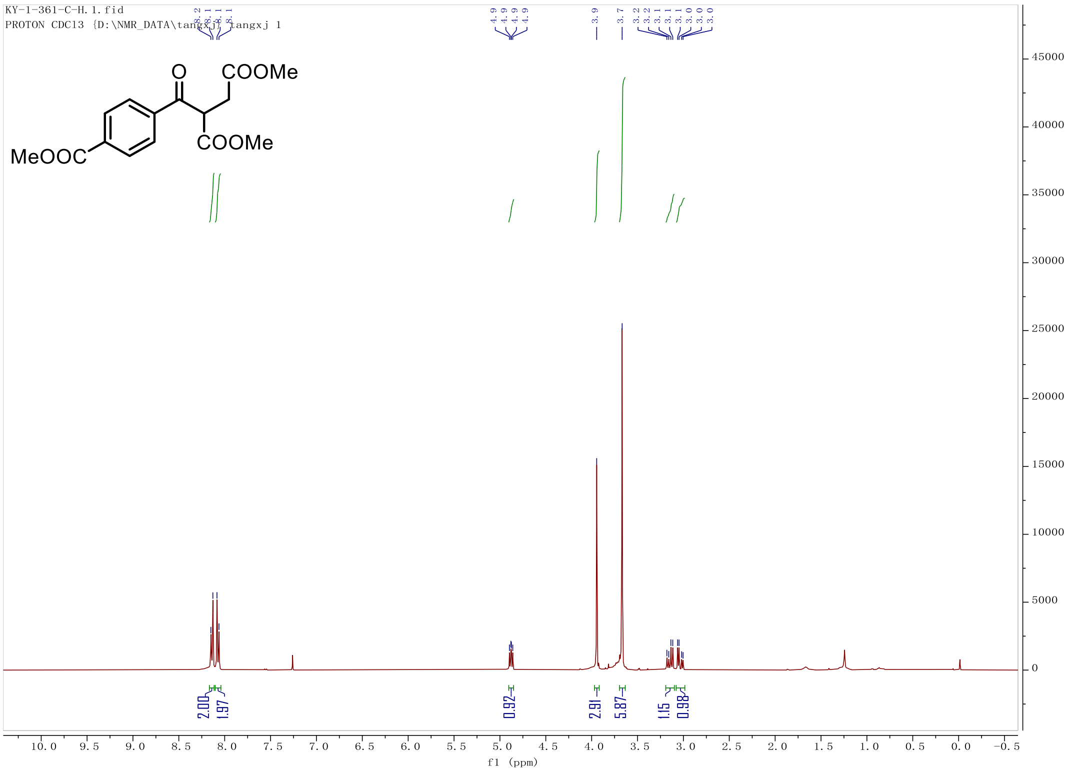
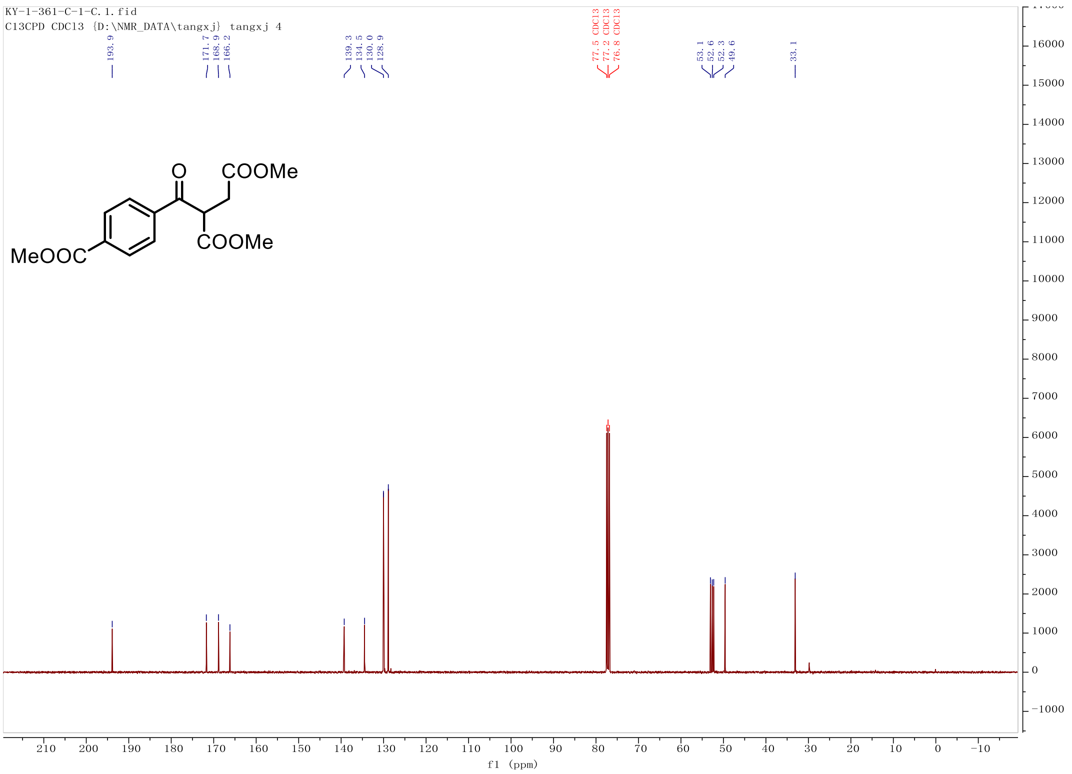


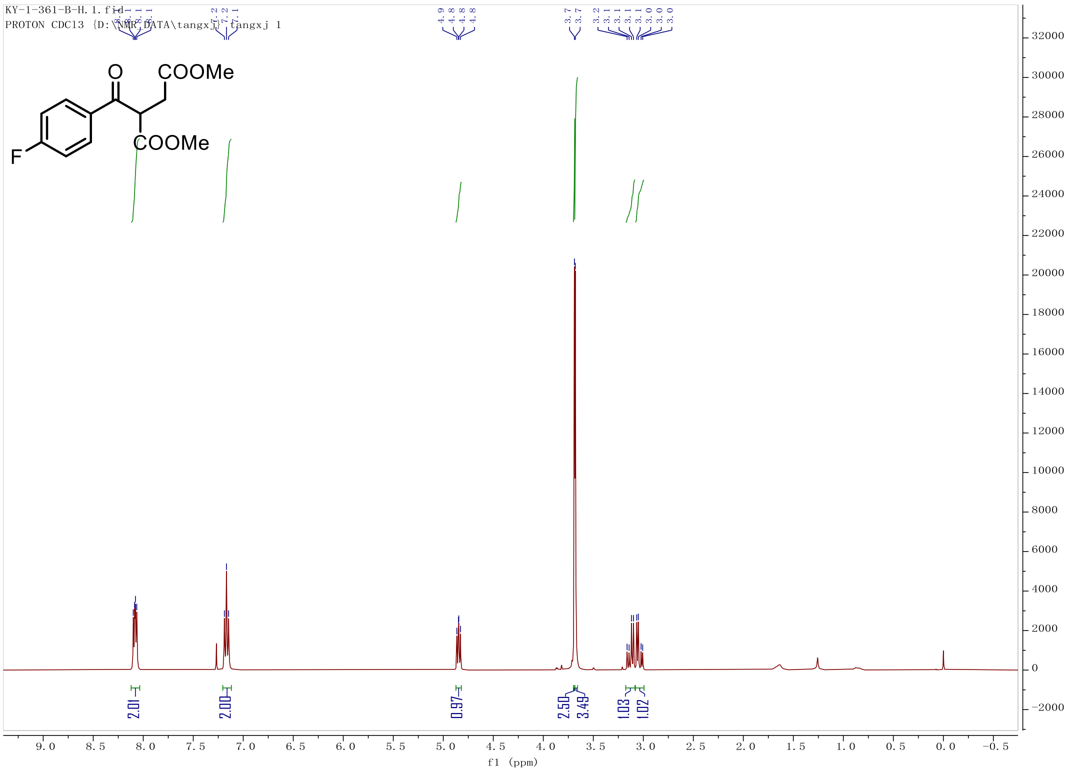
^{1}H NMR of 3aa (CDCl$_3$)



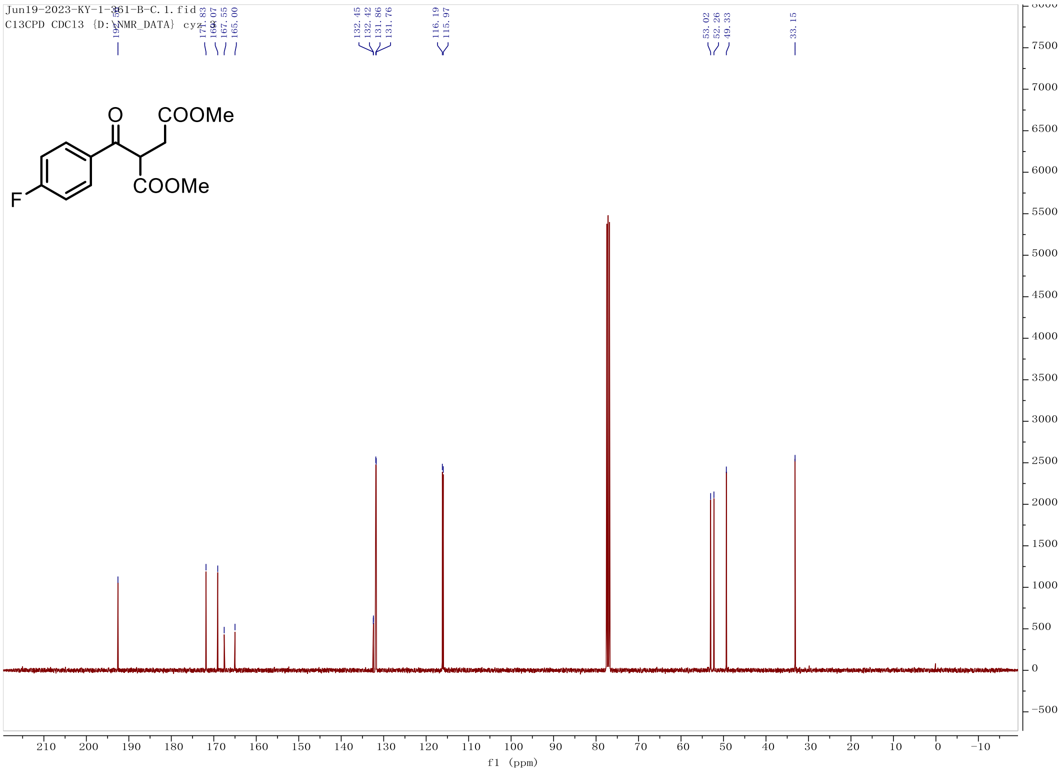
^{13}C NMR of 3aa (CDCl$_3$)



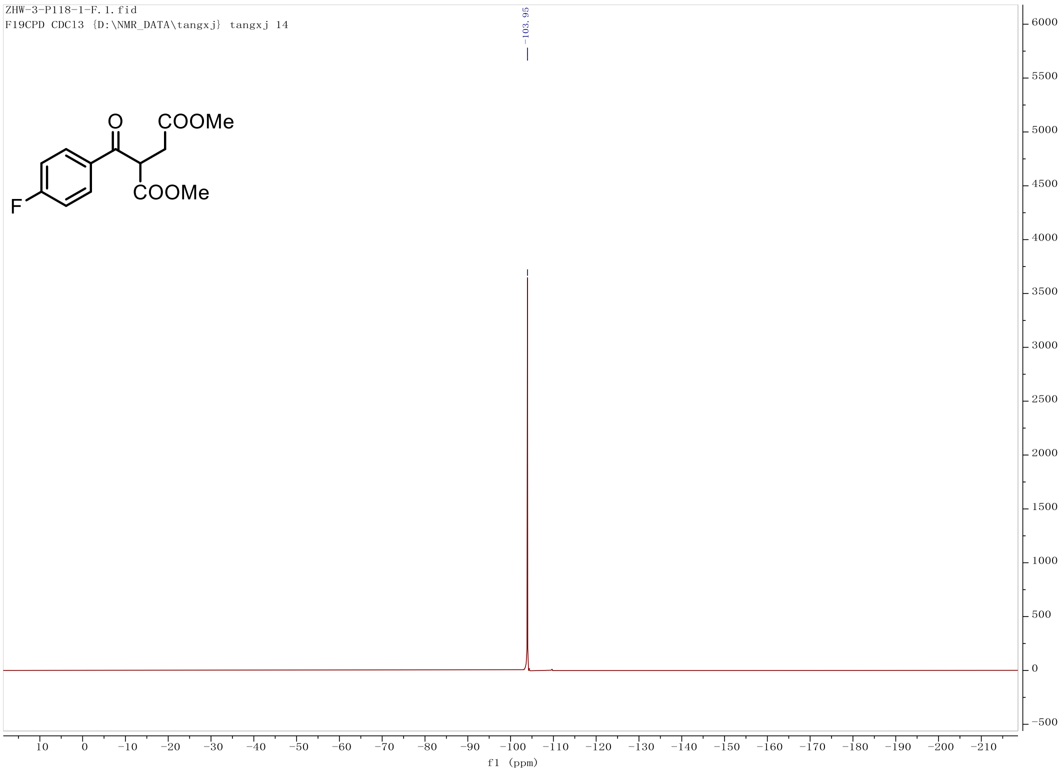
^{1}H NMR of 3ab (CDCl$_3$)



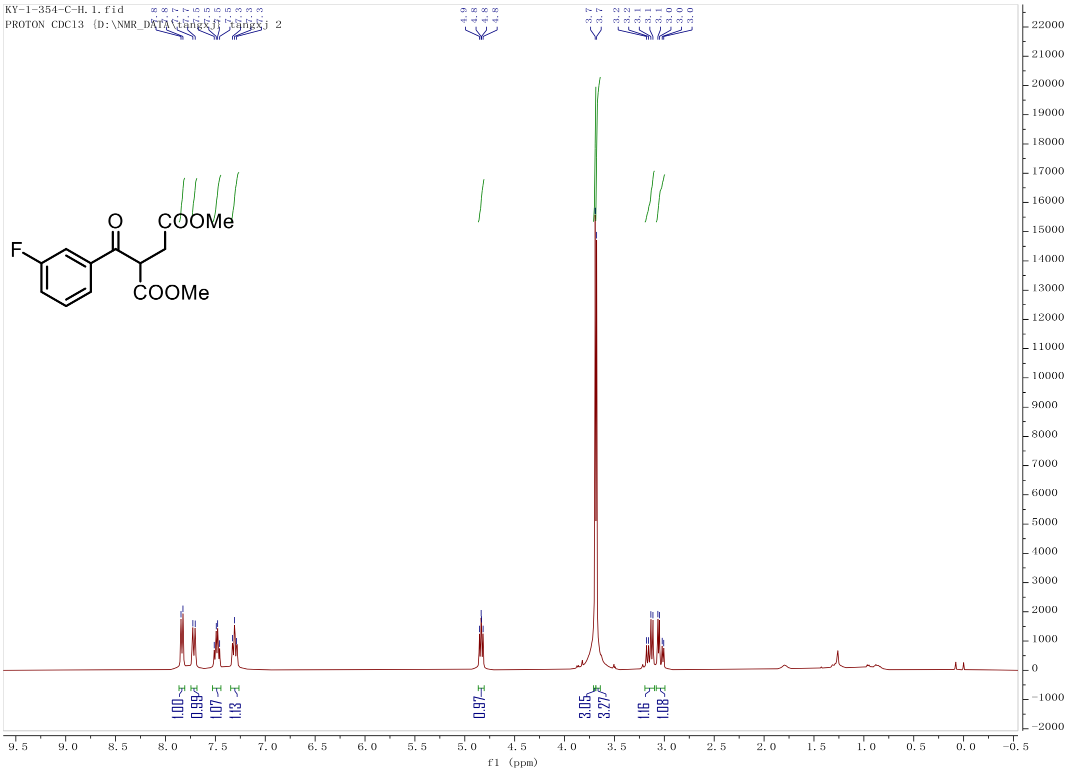
^{13}C NMR of 3ab (CDCl$_3$)



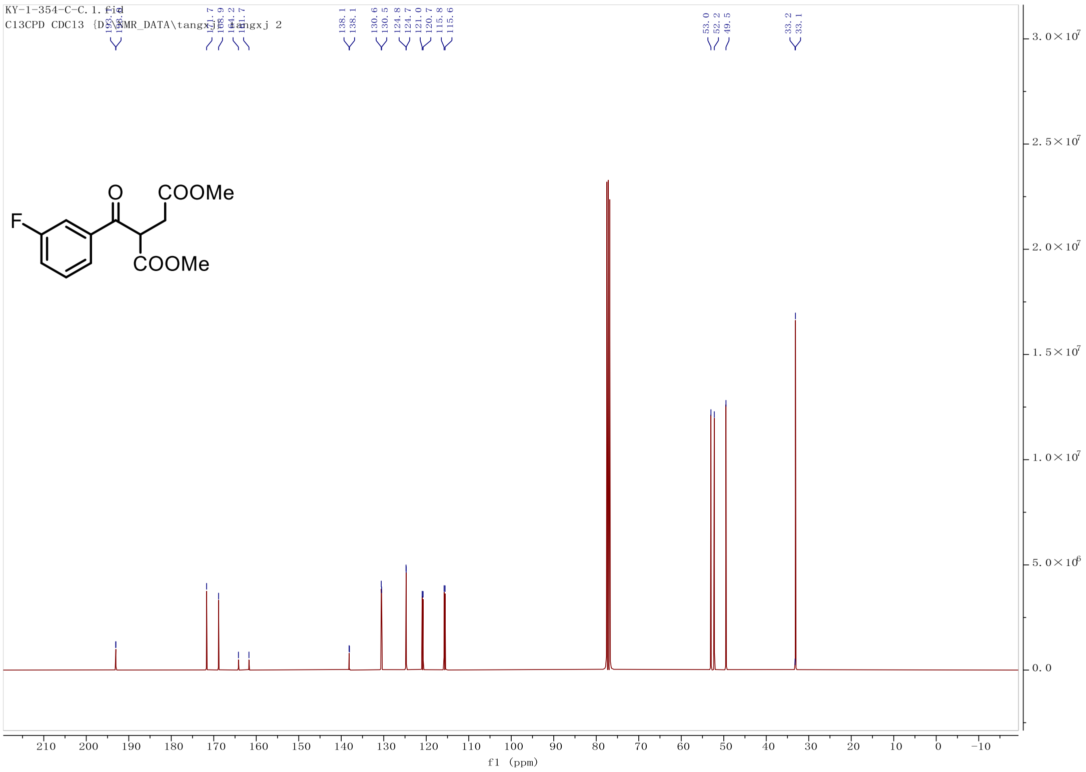
^{19}F NMR of 3ab (CDCl$_3$)



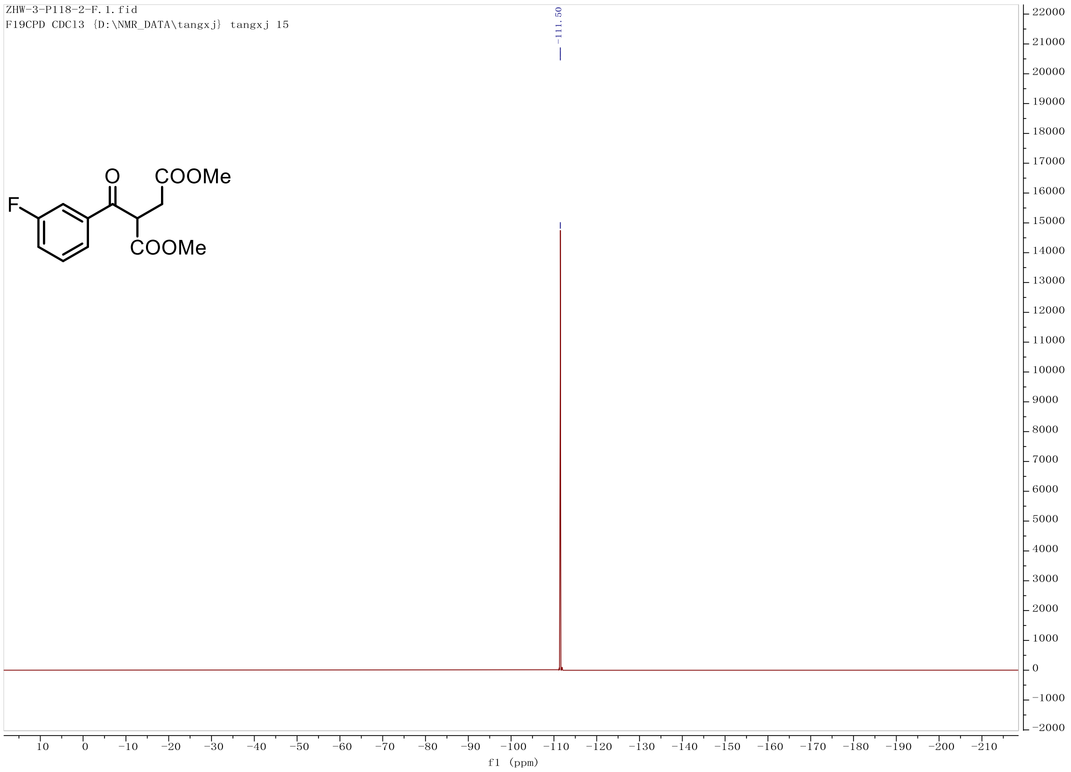
^{1}H NMR of 3ac (CDCl$_3$)



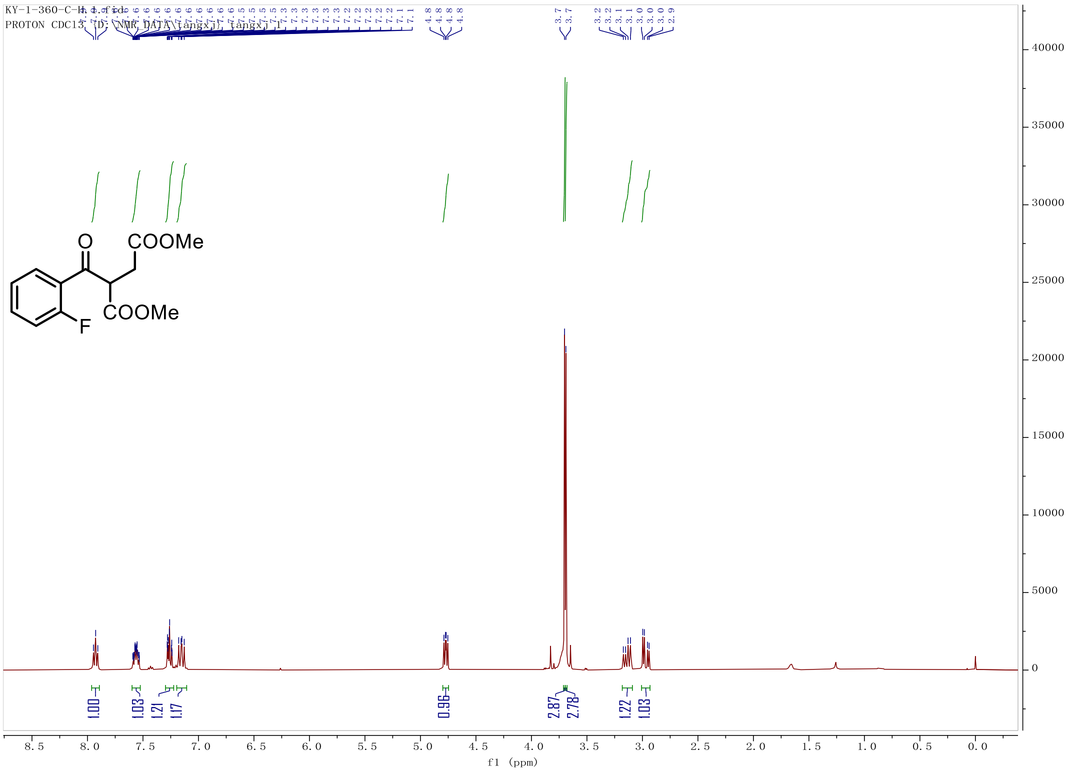
^{13}C NMR of 3ac (CDCl$_3$)



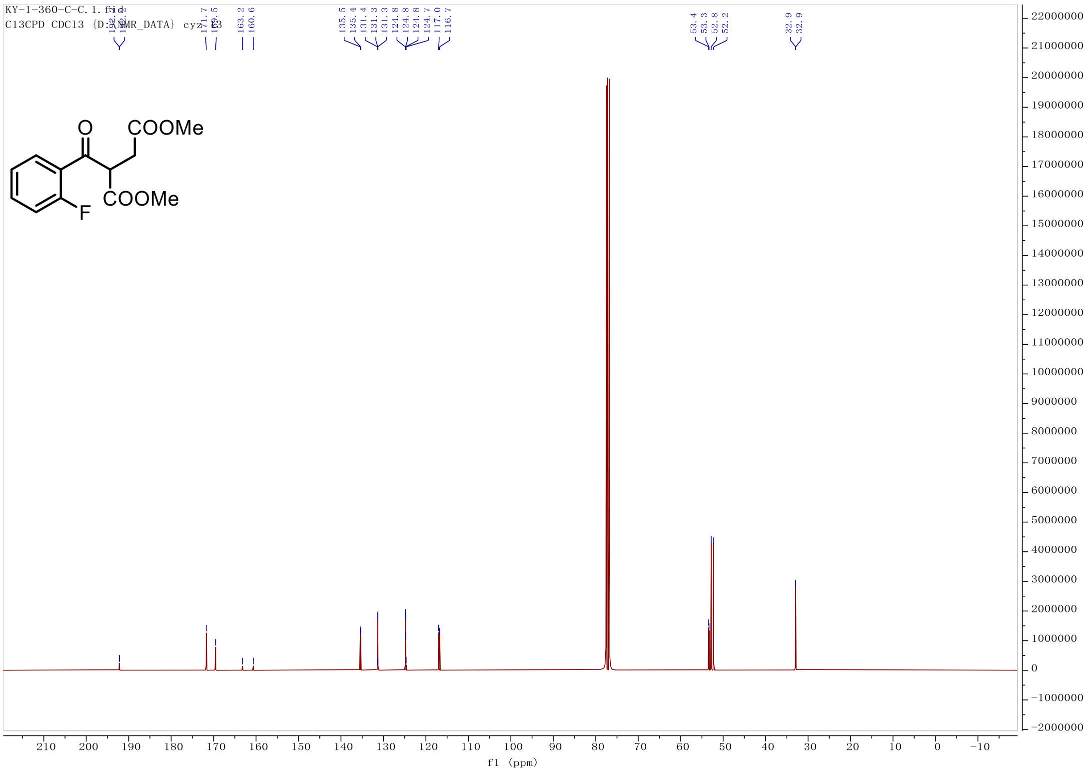
^{19}F NMR of 3ac (CDCl$_3$)



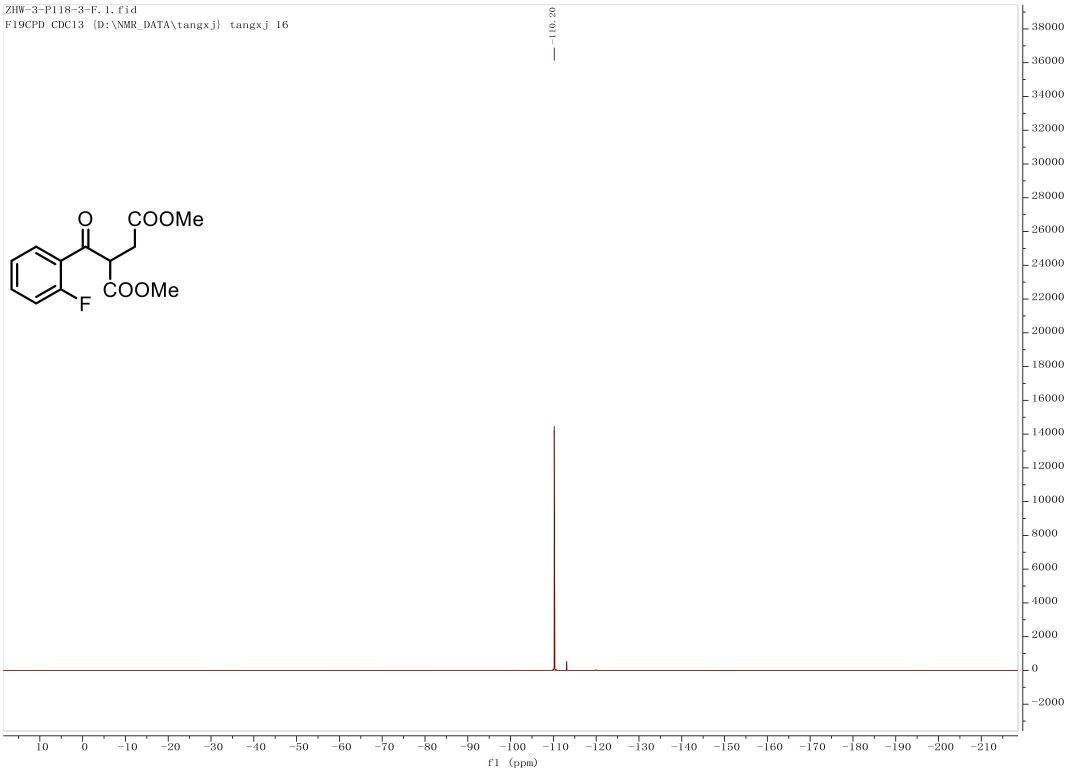
^{1}H NMR of 3ad (CDCl$_3$)



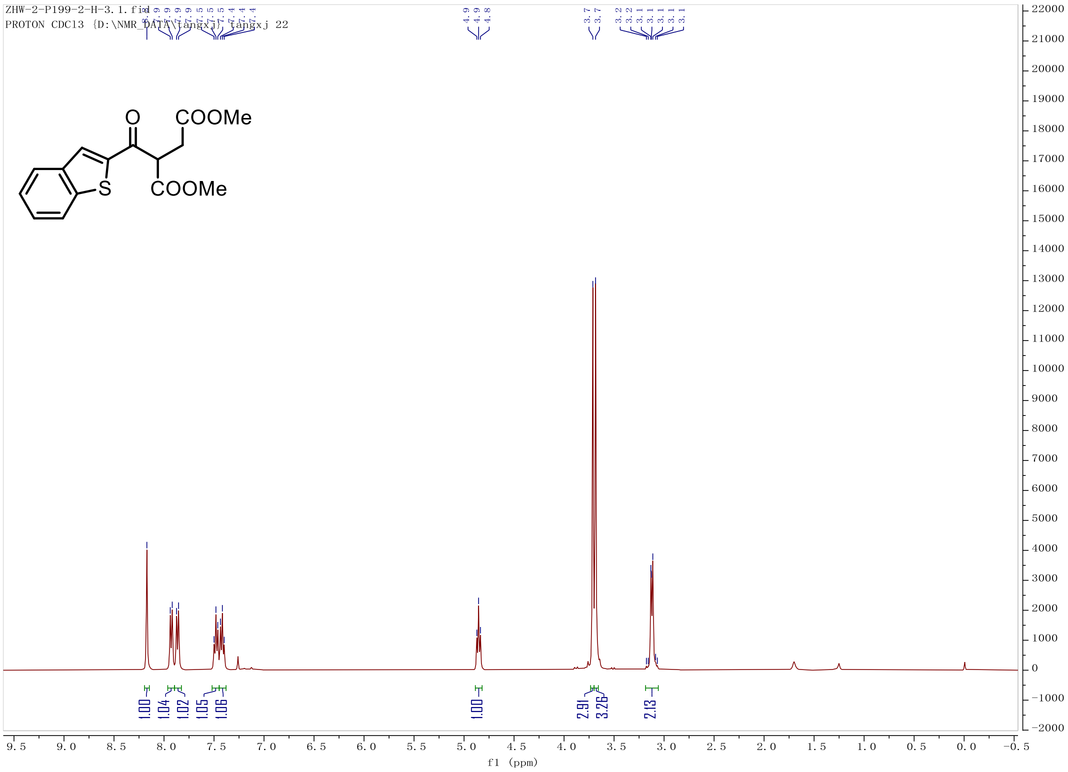
^{13}C NMR of 3ad (CDCl$_3$)



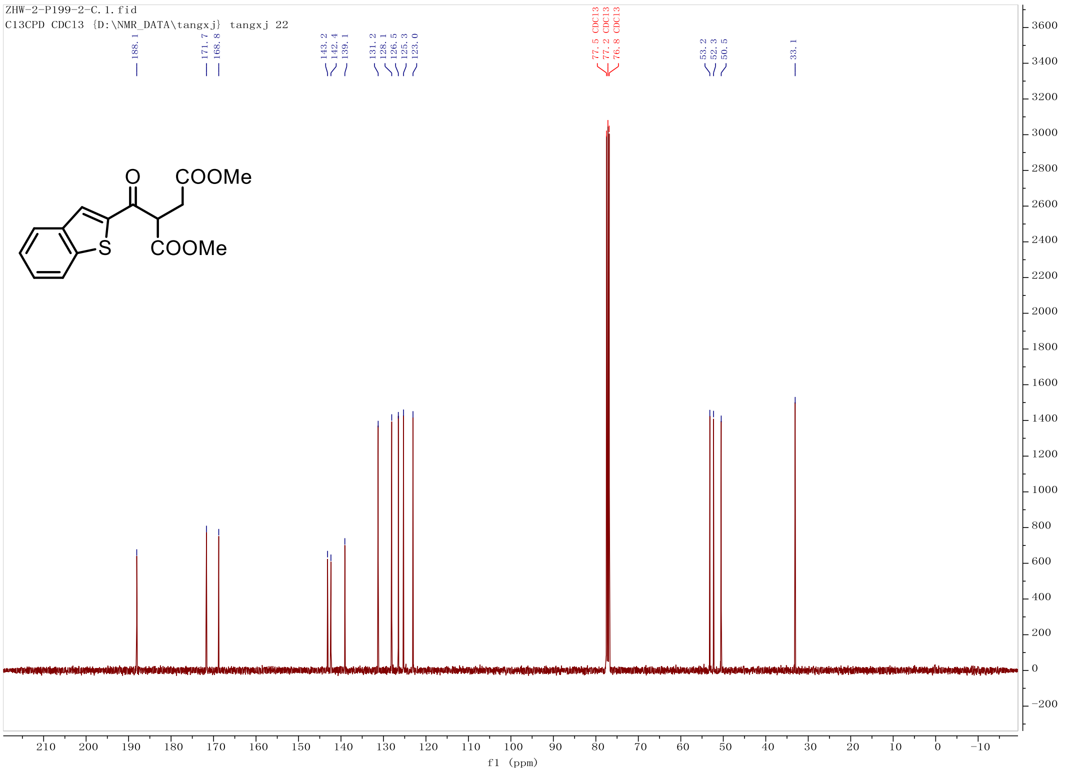
^{19}F NMR of 3ad (CDCl$_3$)



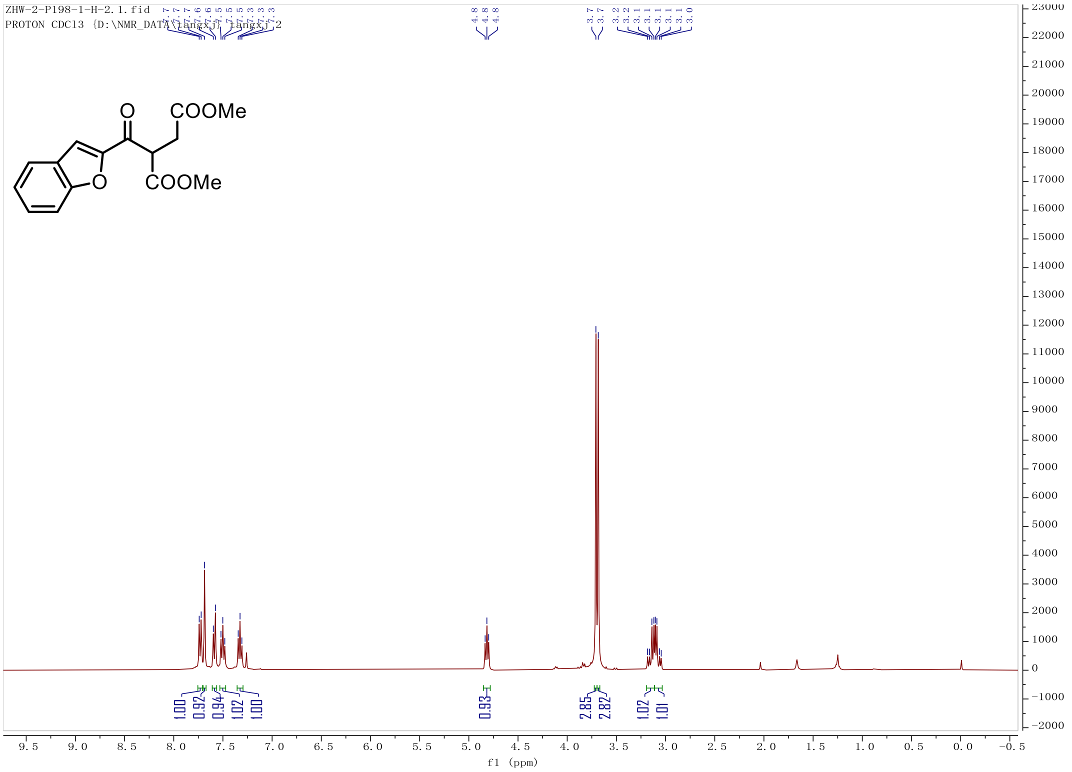
^{1}H NMR of 3ae (CDCl$_3$)



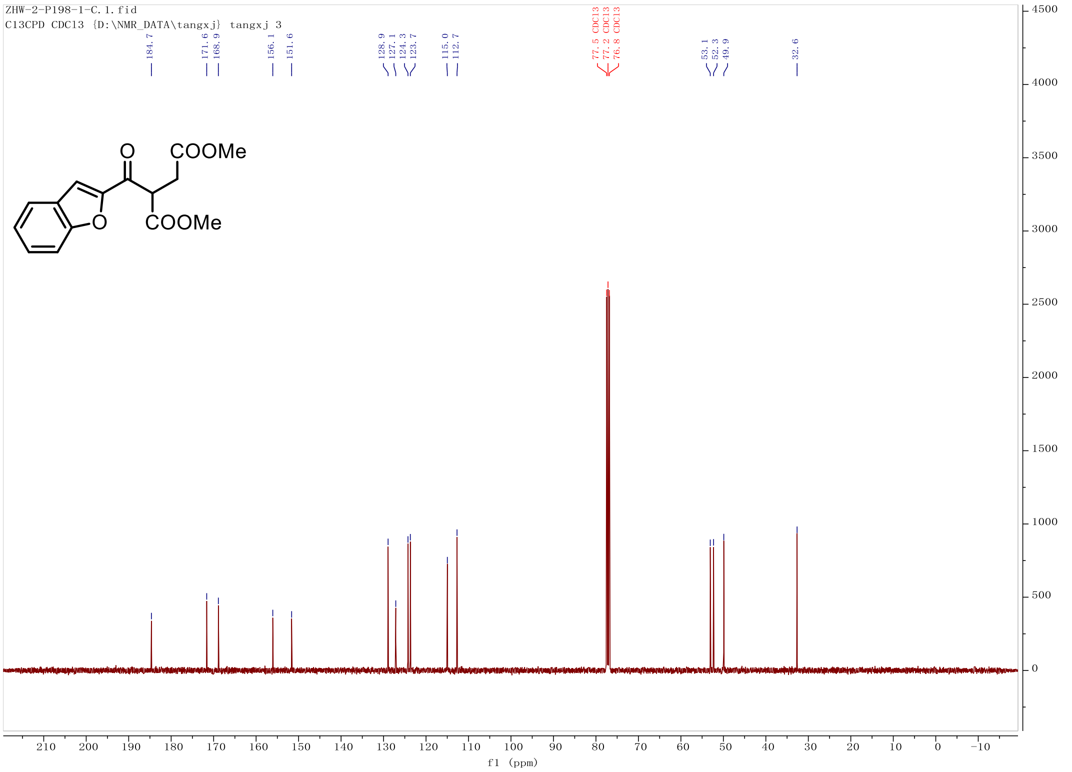
^{13}C NMR of 3ae (CDCl$_3$)



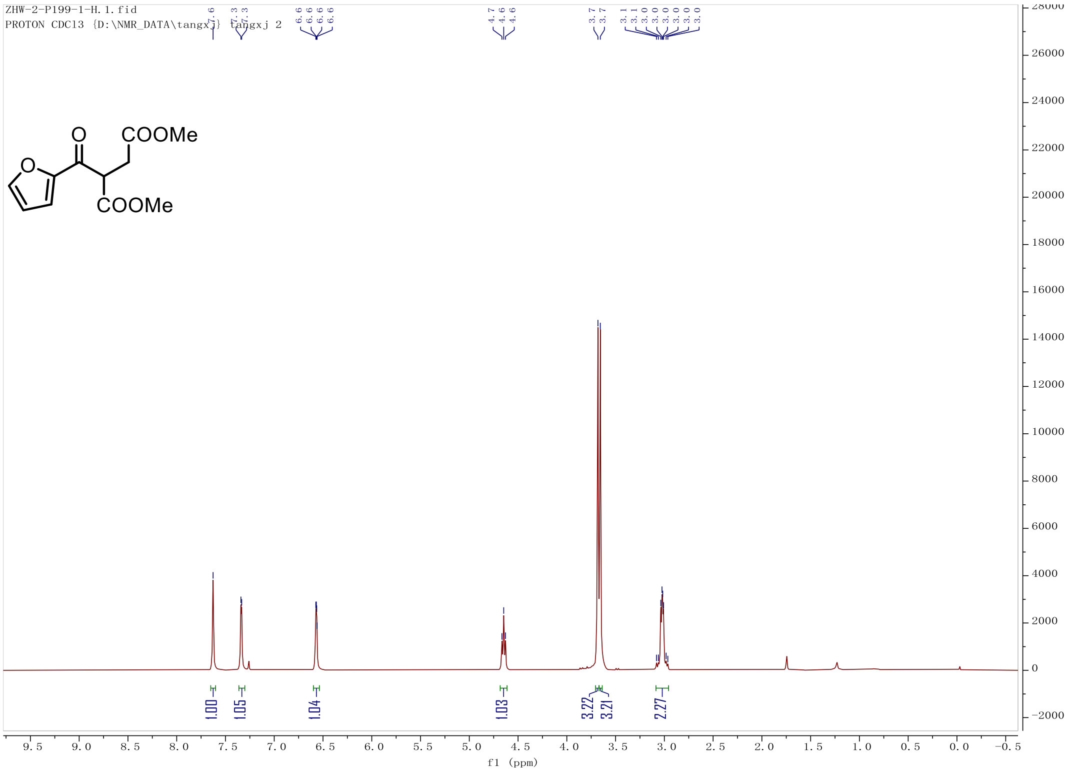
^{1}H NMR of 3af (CDCl$_3$)



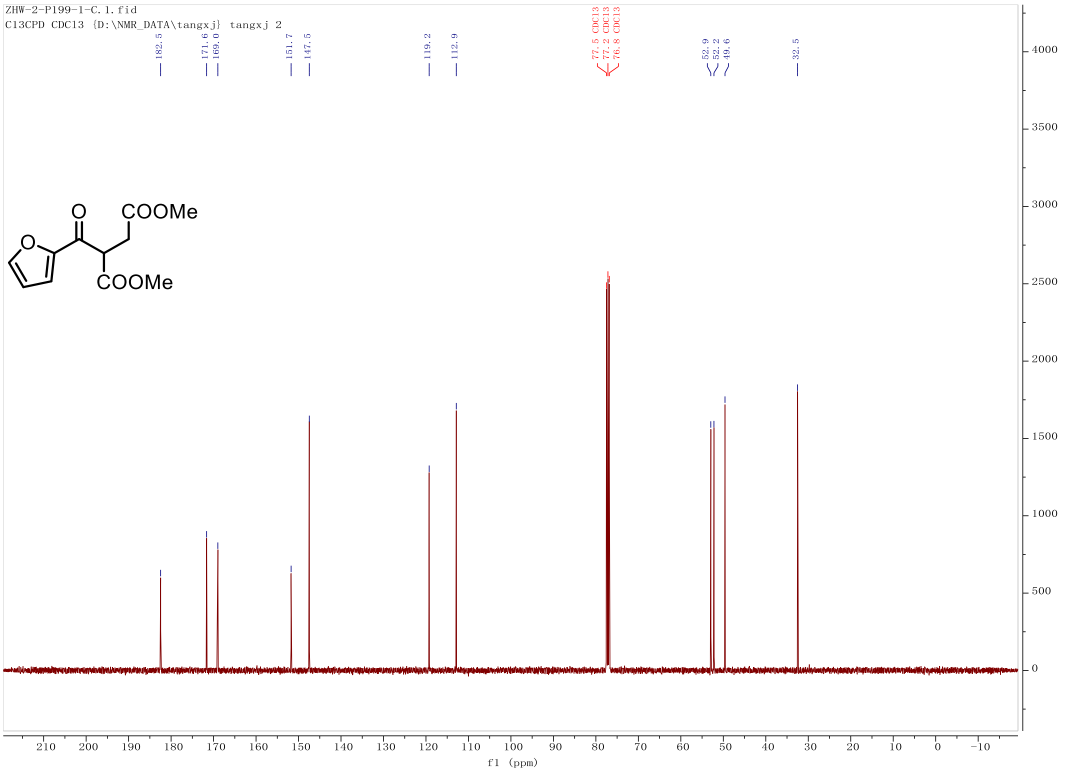
^{13}C NMR of 3af (CDCl$_3$)



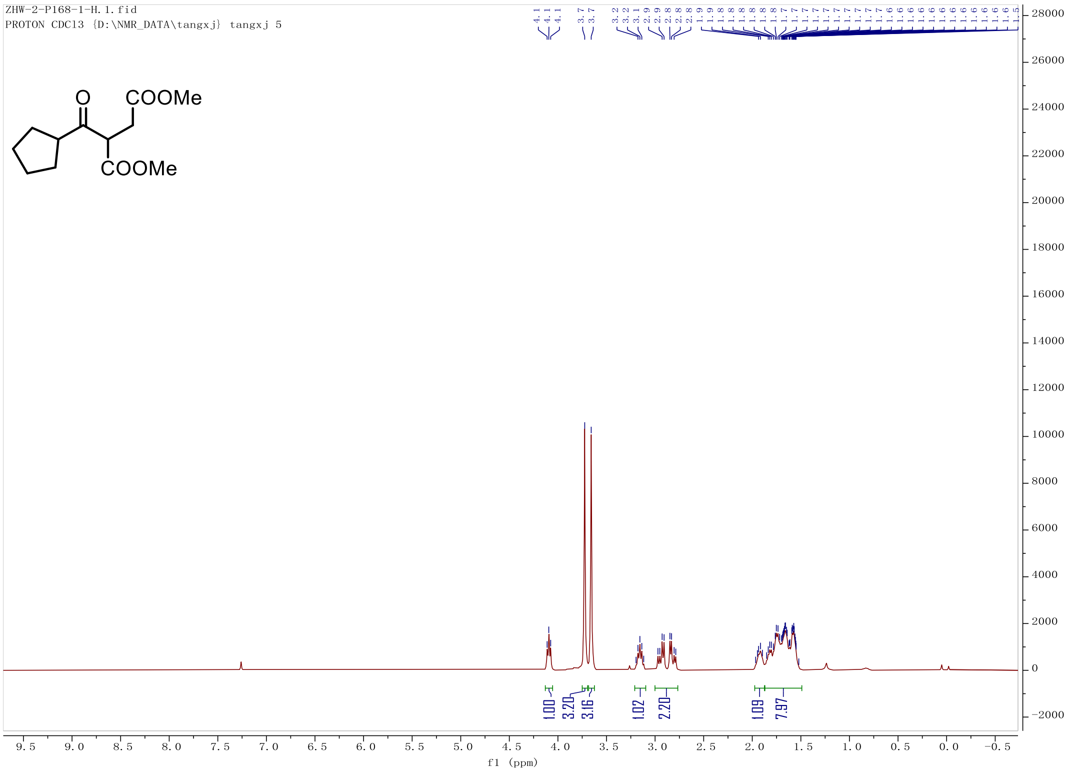
^1H NMR of 3ag ($CDCl_3$)



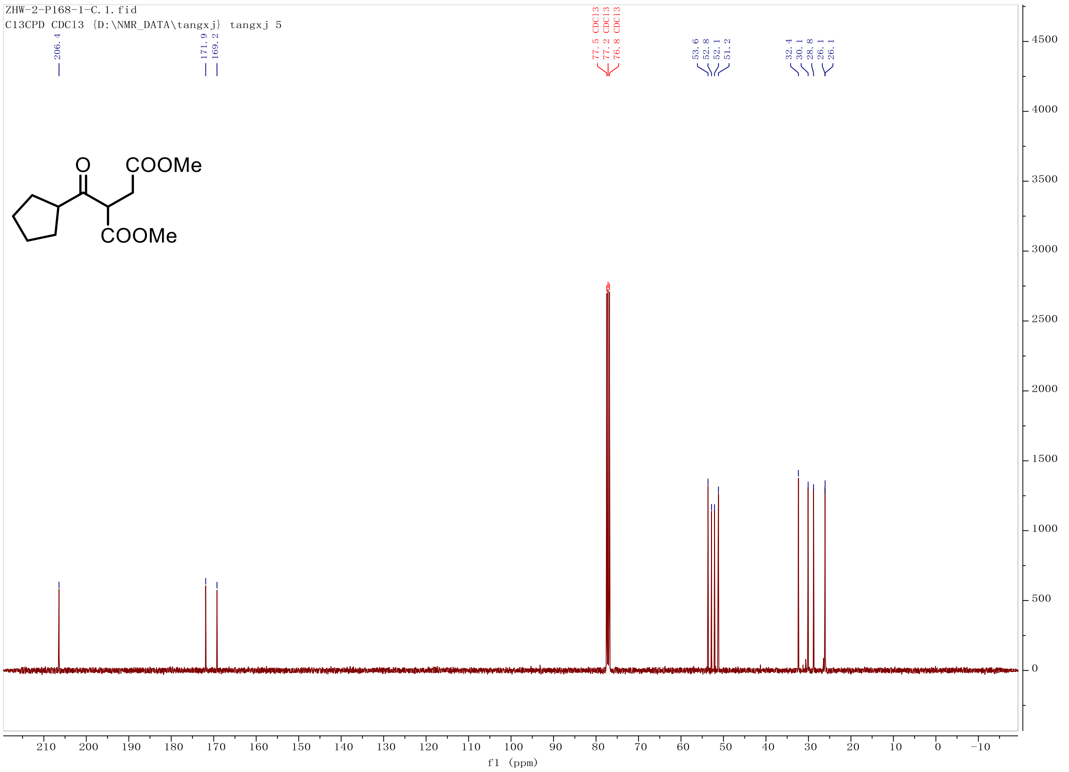
^{13}C NMR of 3ag ($CDCl_3$)



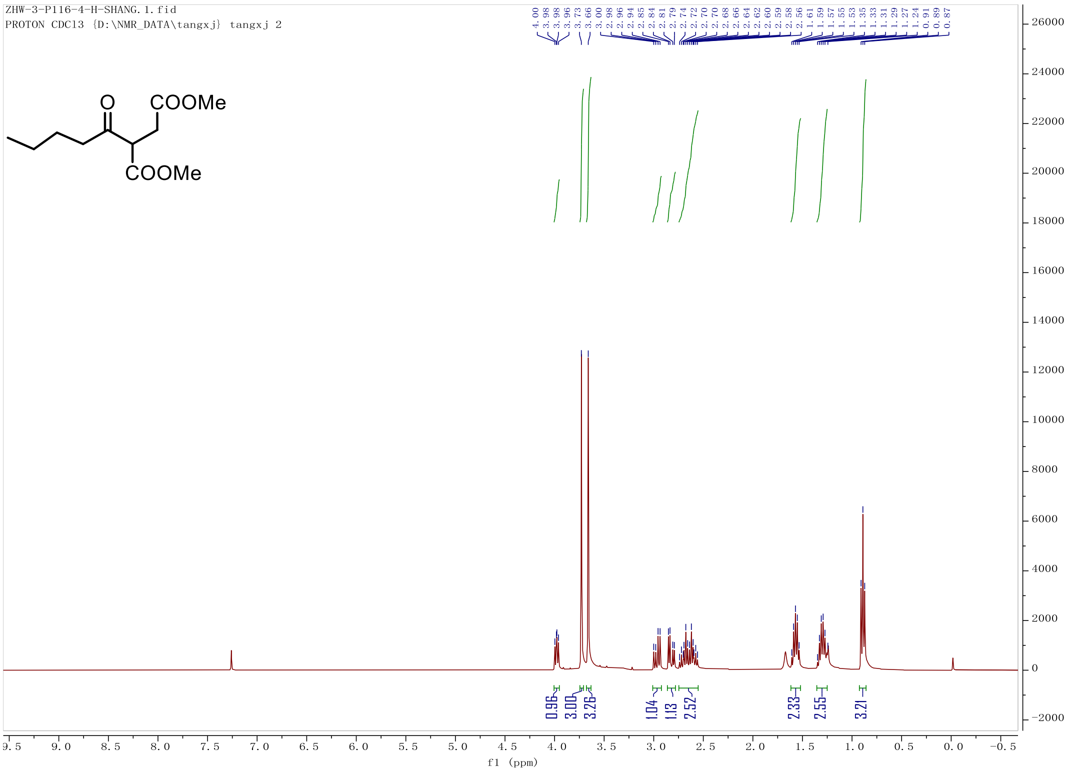
^{1}H NMR of 3ah (CDCl$_3$)



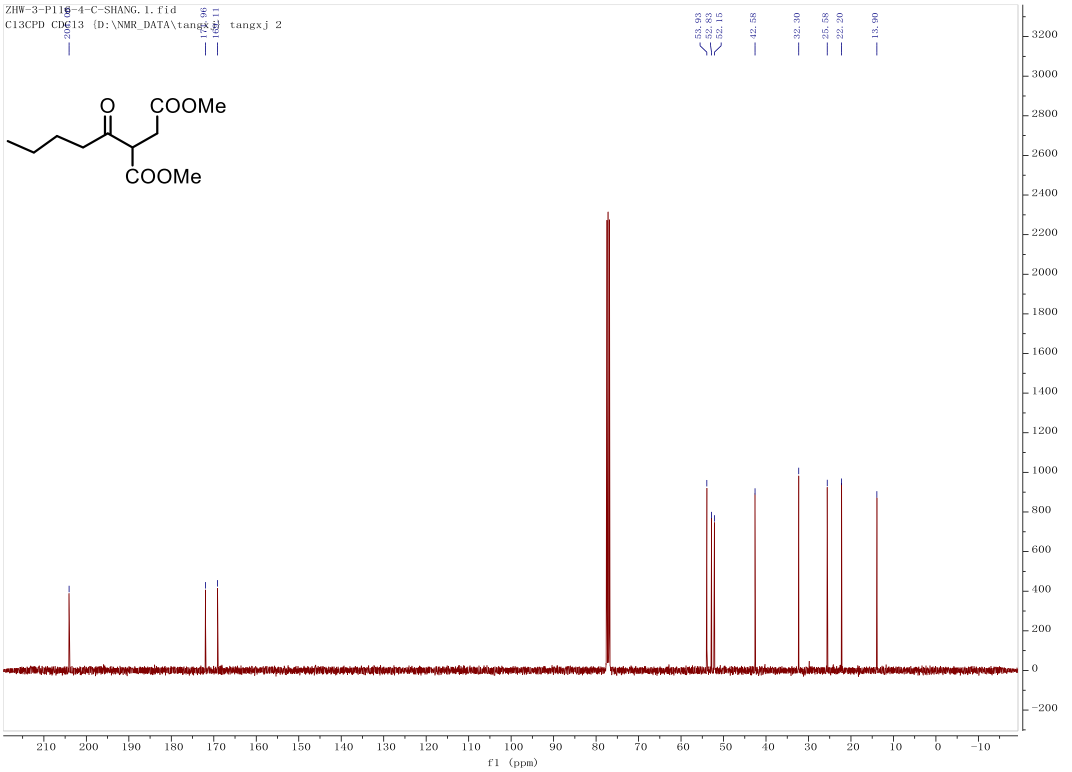
^{13}C NMR of 3ah (CDCl$_3$)



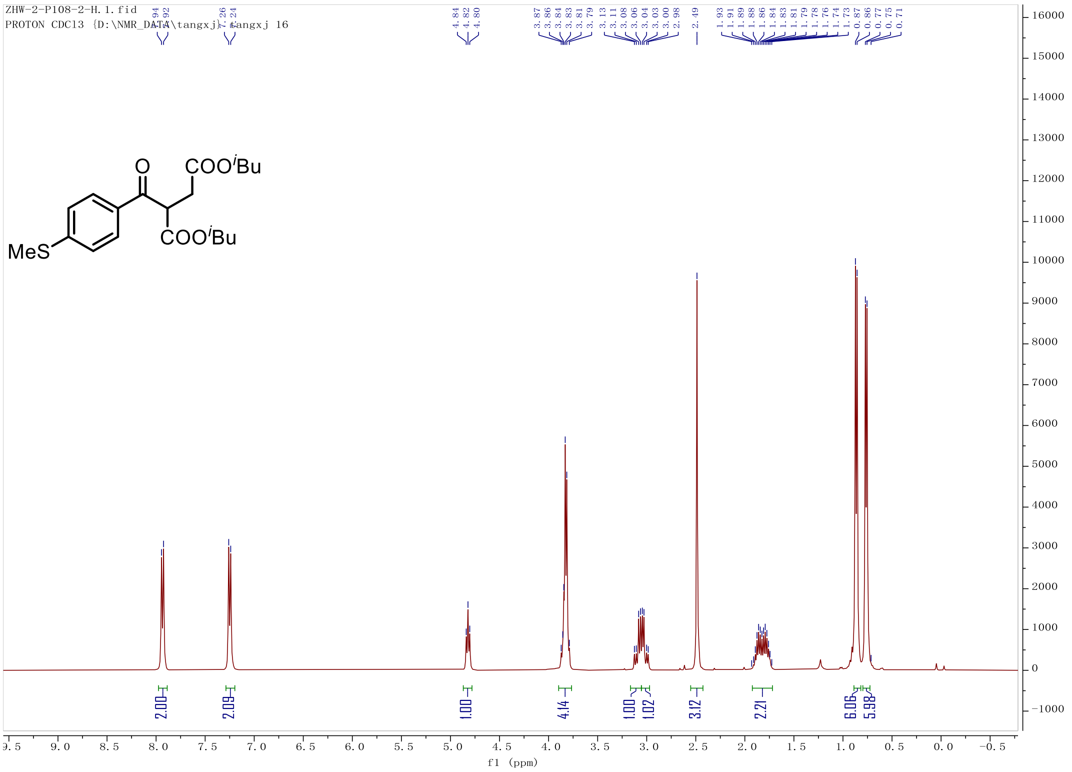
^{1}H NMR of 3ai (CDCl$_3$)



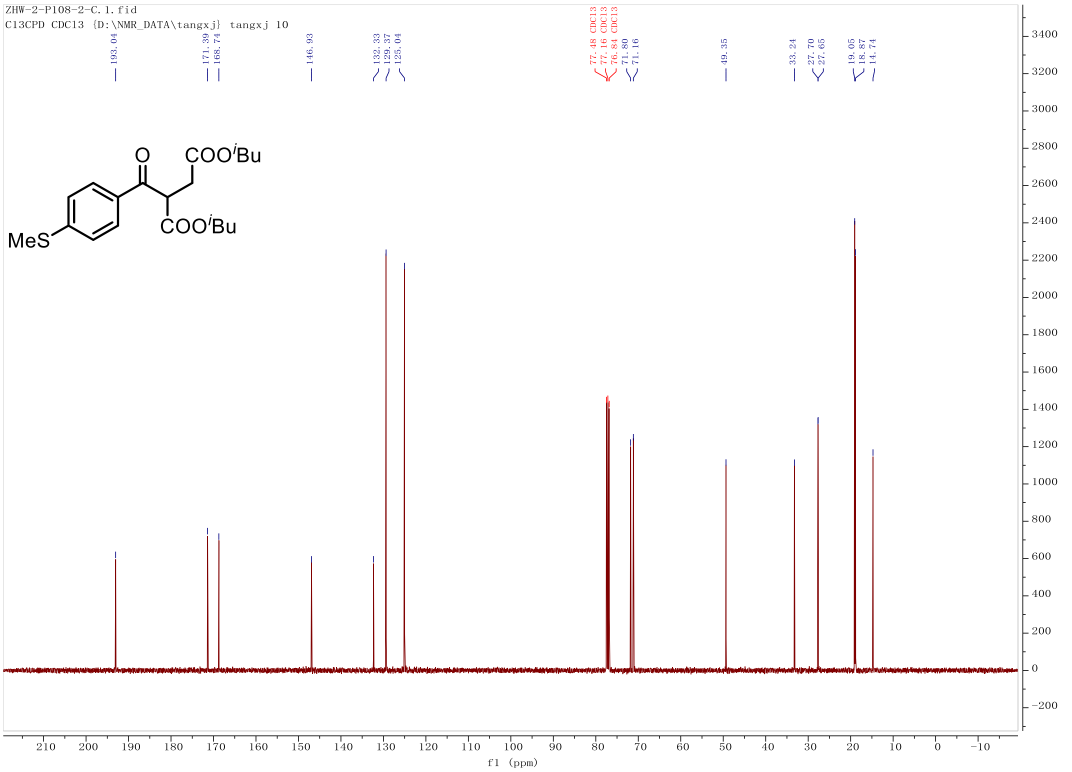
^{13}C NMR of 3ai (CDCl$_3$)



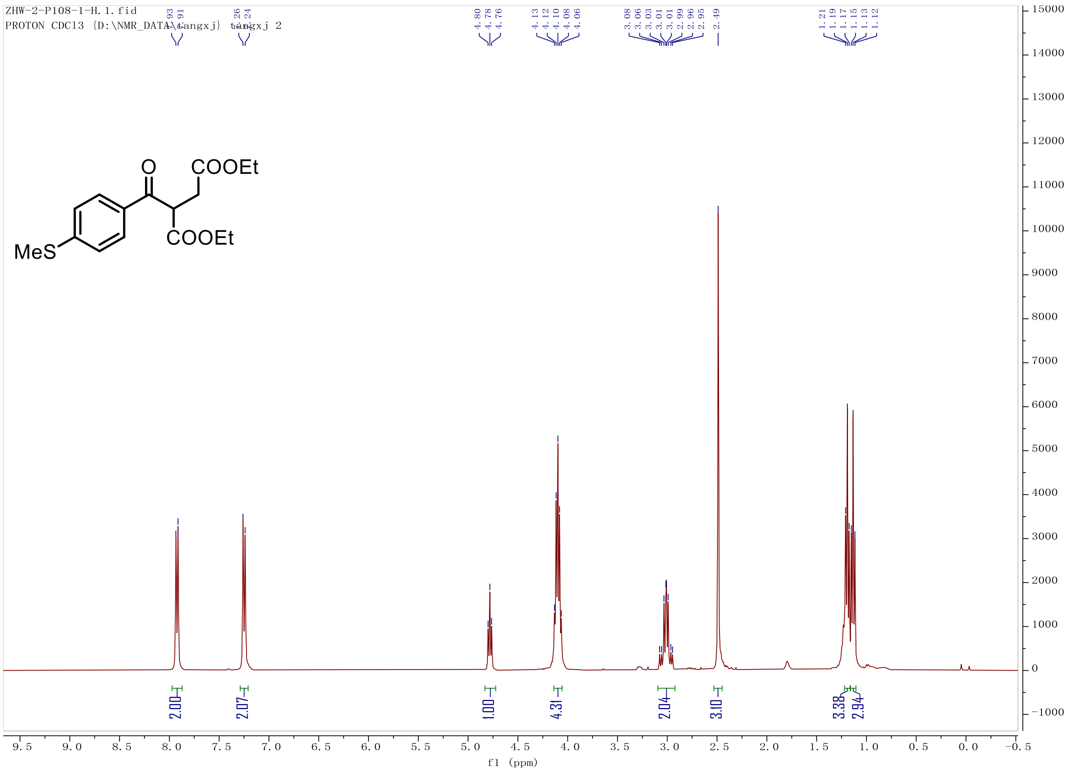
^{1}H NMR of 4b (CDCl$_3$)



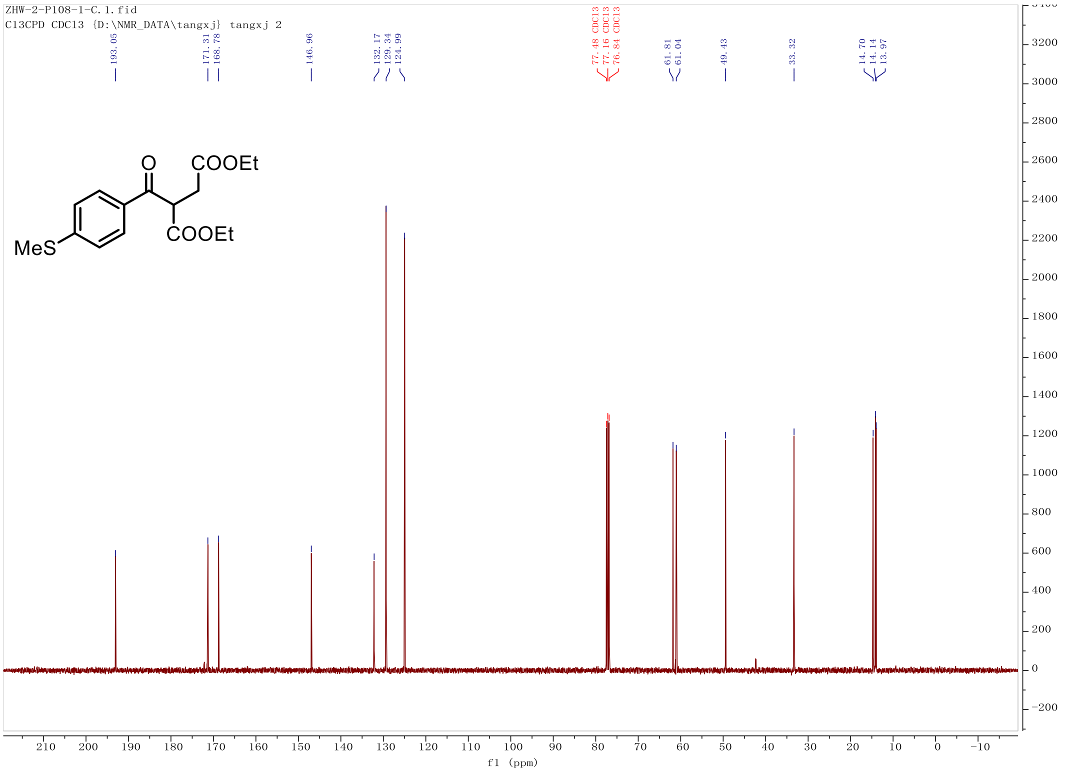
^{13}C NMR of 4b (CDCl$_3$)



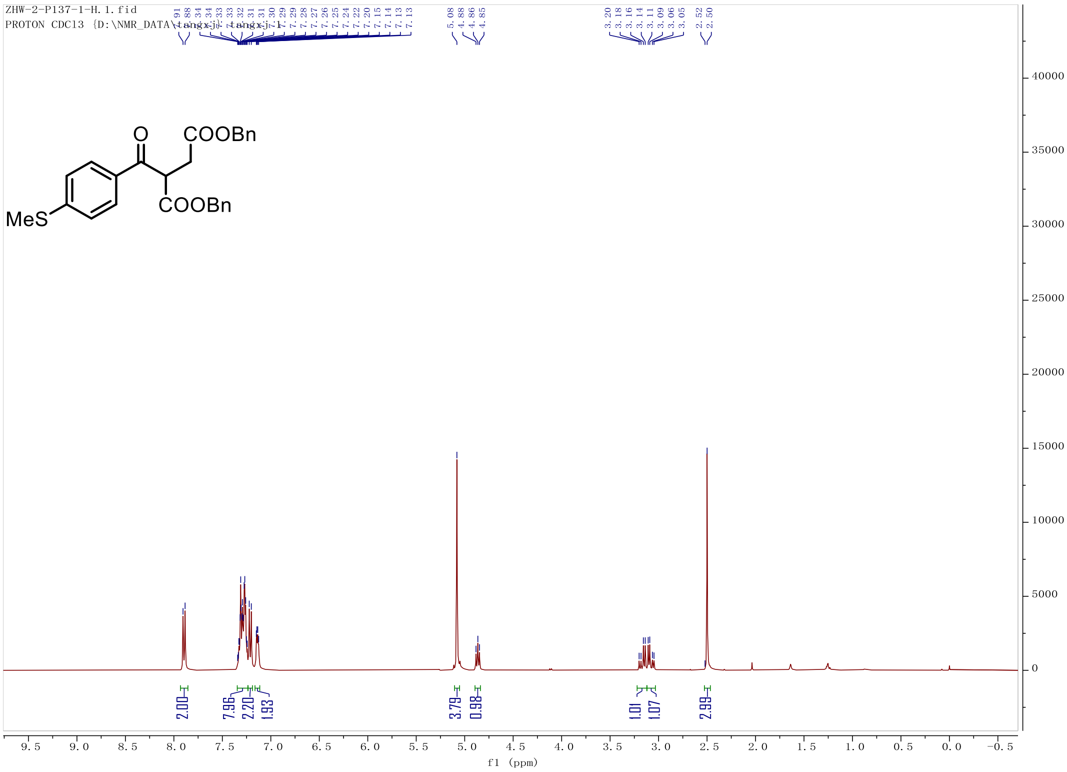
^{1}H NMR of 4c (CDCl$_3$)



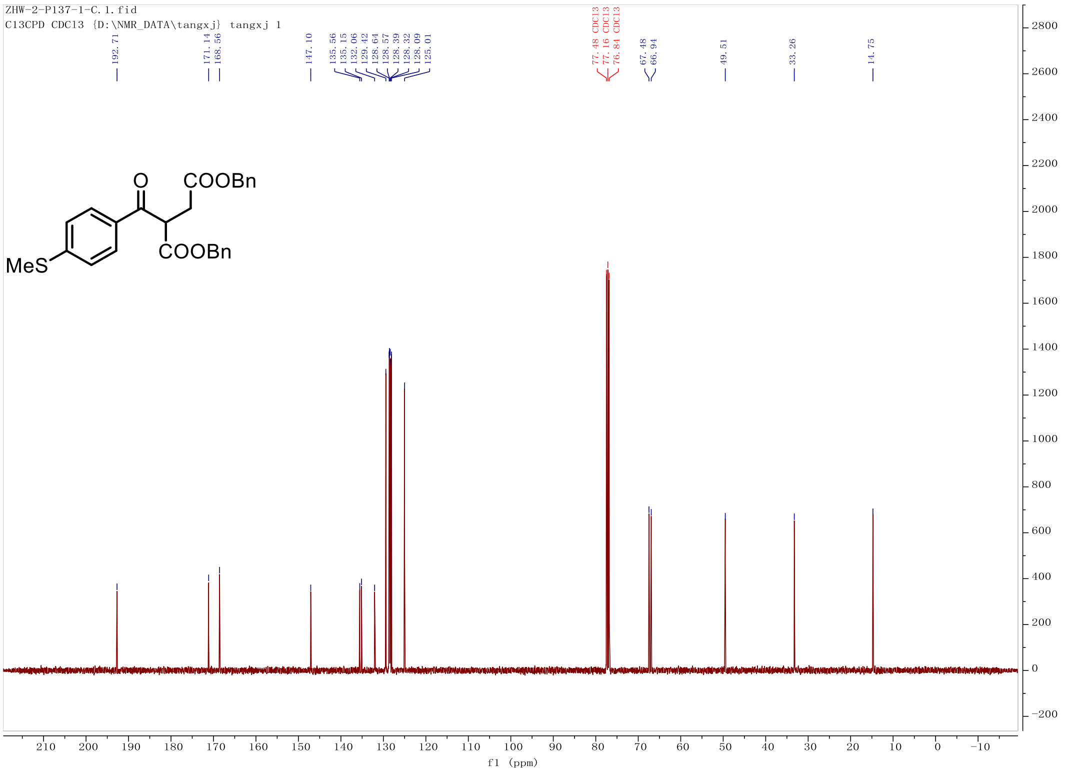
^{13}C NMR of 4c (CDCl$_3$)



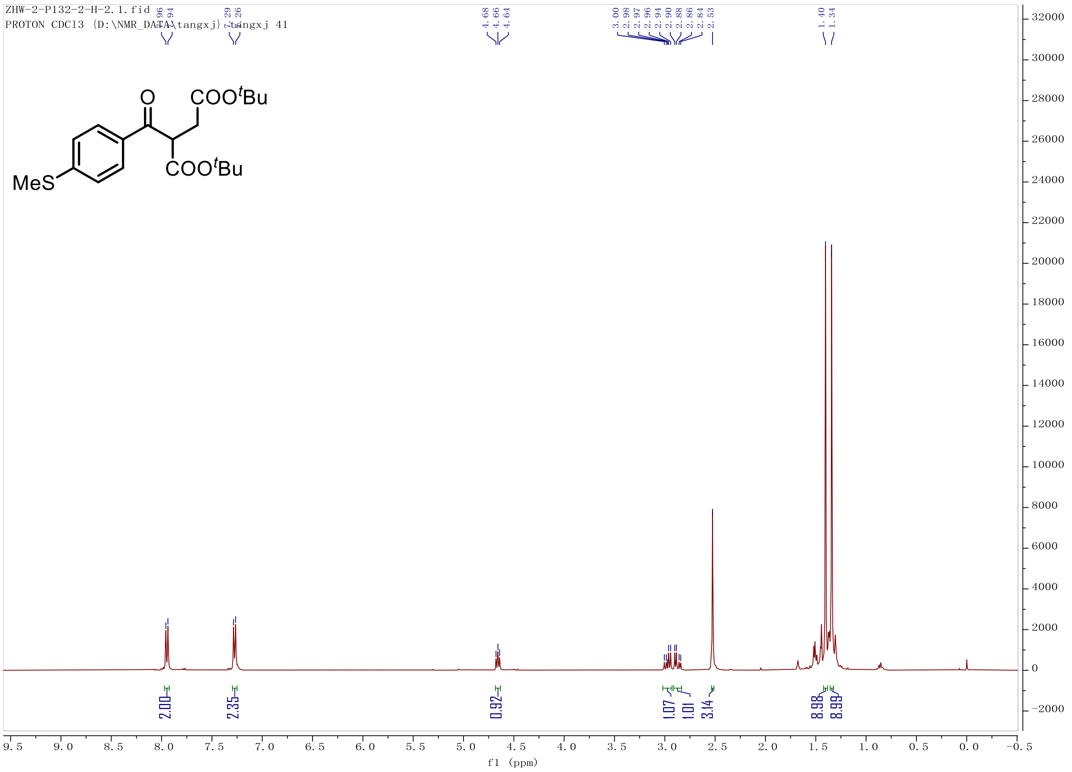
^{1}H NMR of 4d (CDCl$_3$)



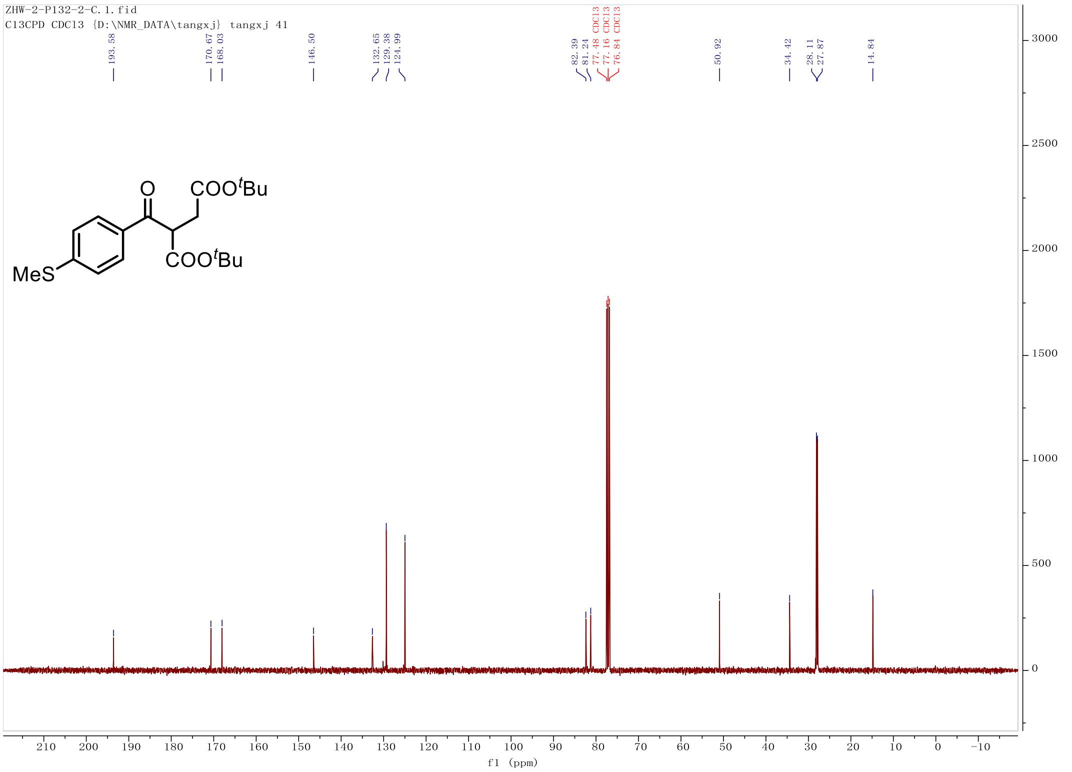
^{13}C NMR of 4d (CDCl$_3$)



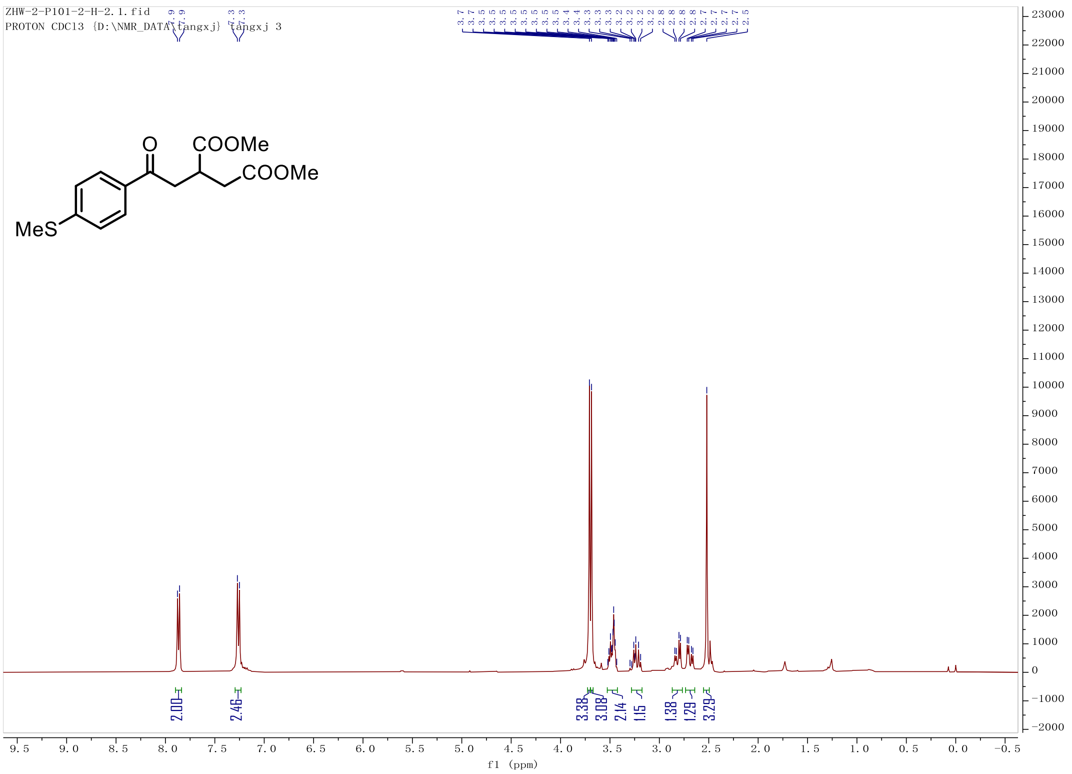
^{1}H NMR of 4e (CDCl$_3$)



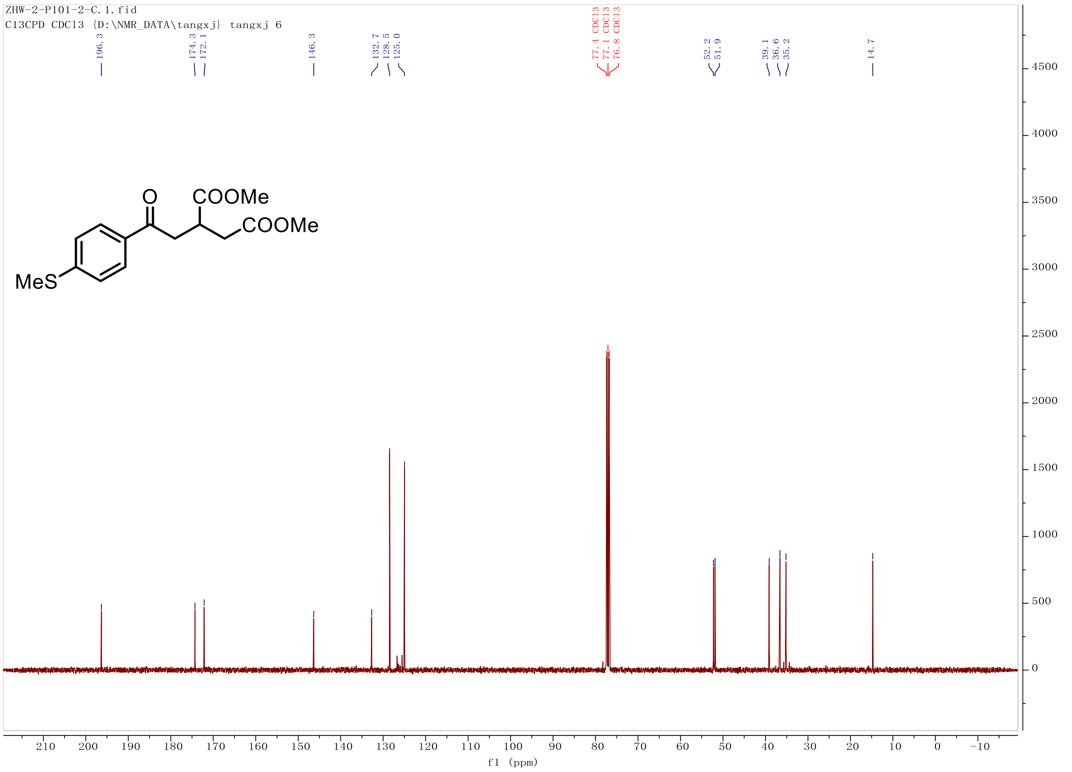
^{13}C NMR of 4e (CDCl$_3$)



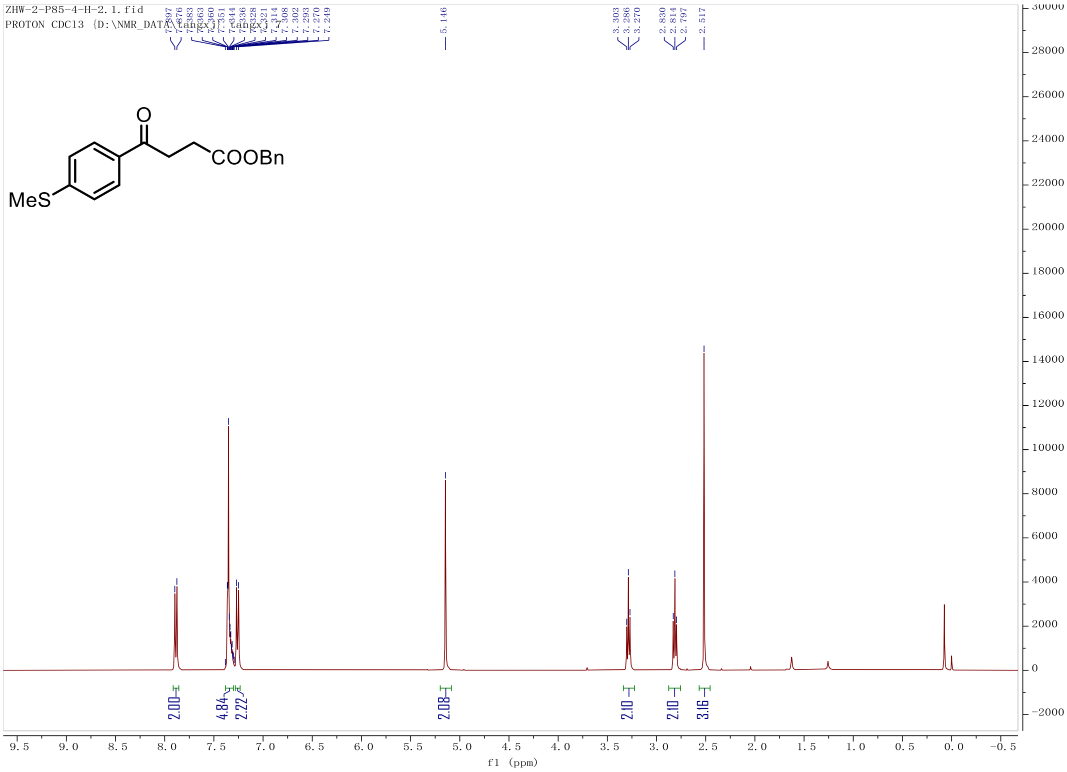
^{1}H NMR of 4f ($CDCl_3$)



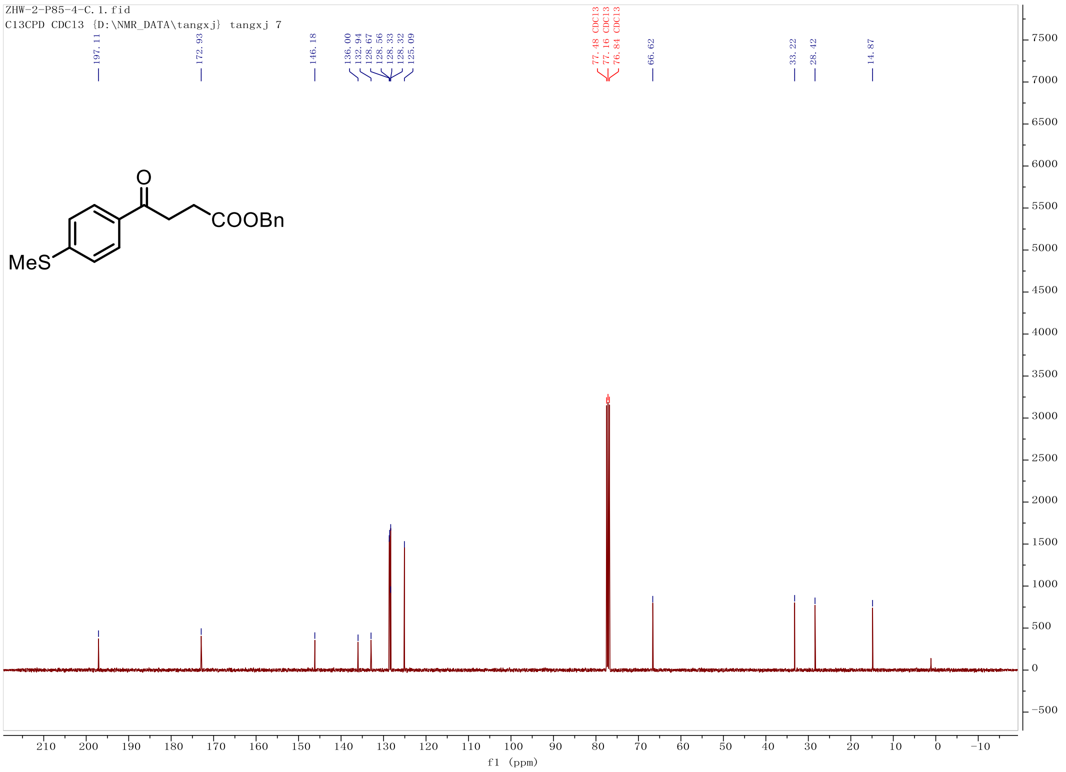
^{13}C NMR of 4f ($CDCl_3$)



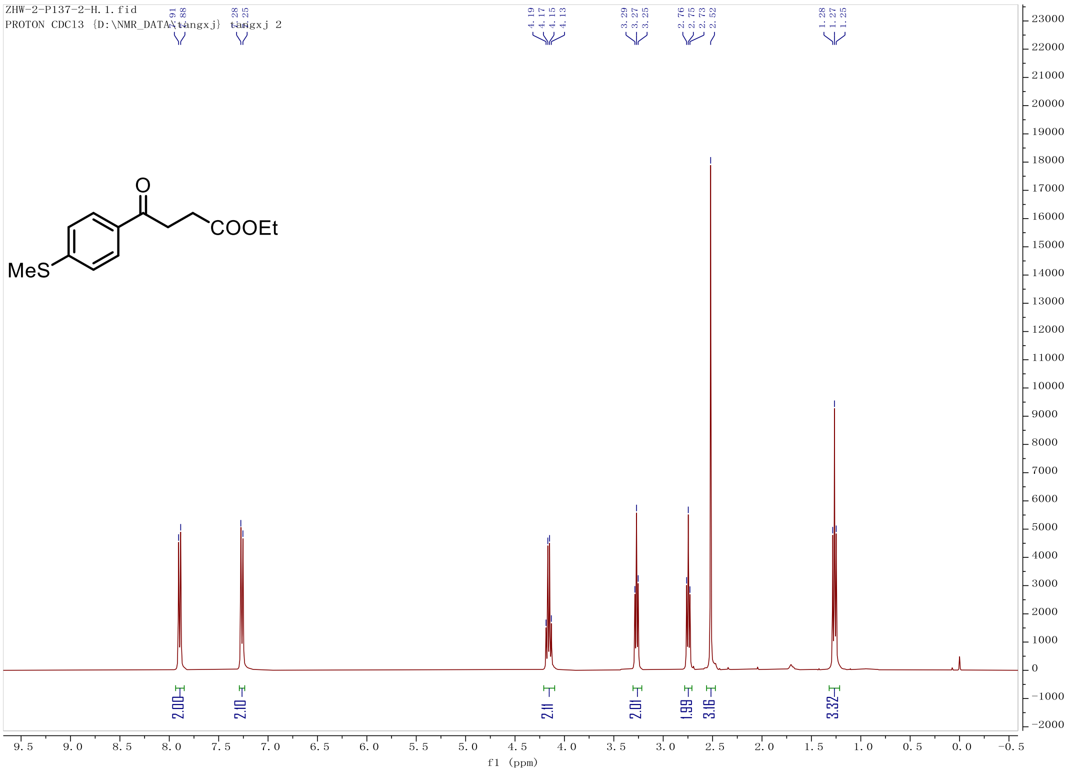
^{1}H NMR of 4g (CDCl$_3$)



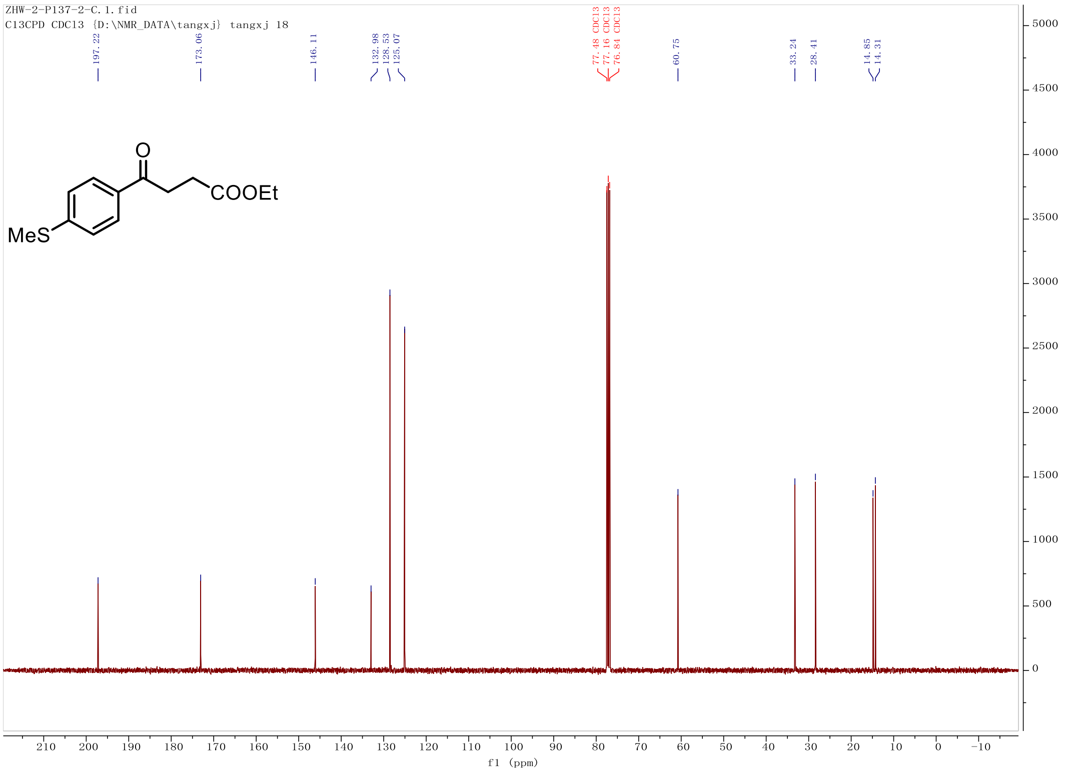
^{13}C NMR of 4g (CDCl$_3$)



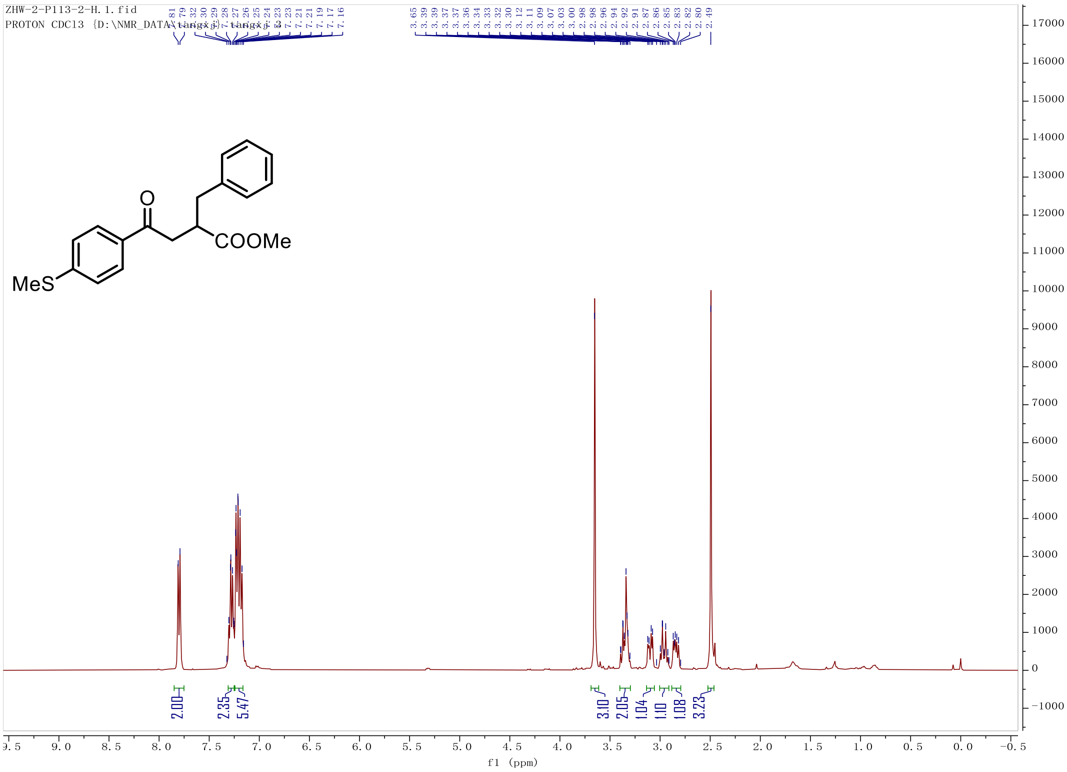
^{1}H NMR of 4h ($CDCl_3$)



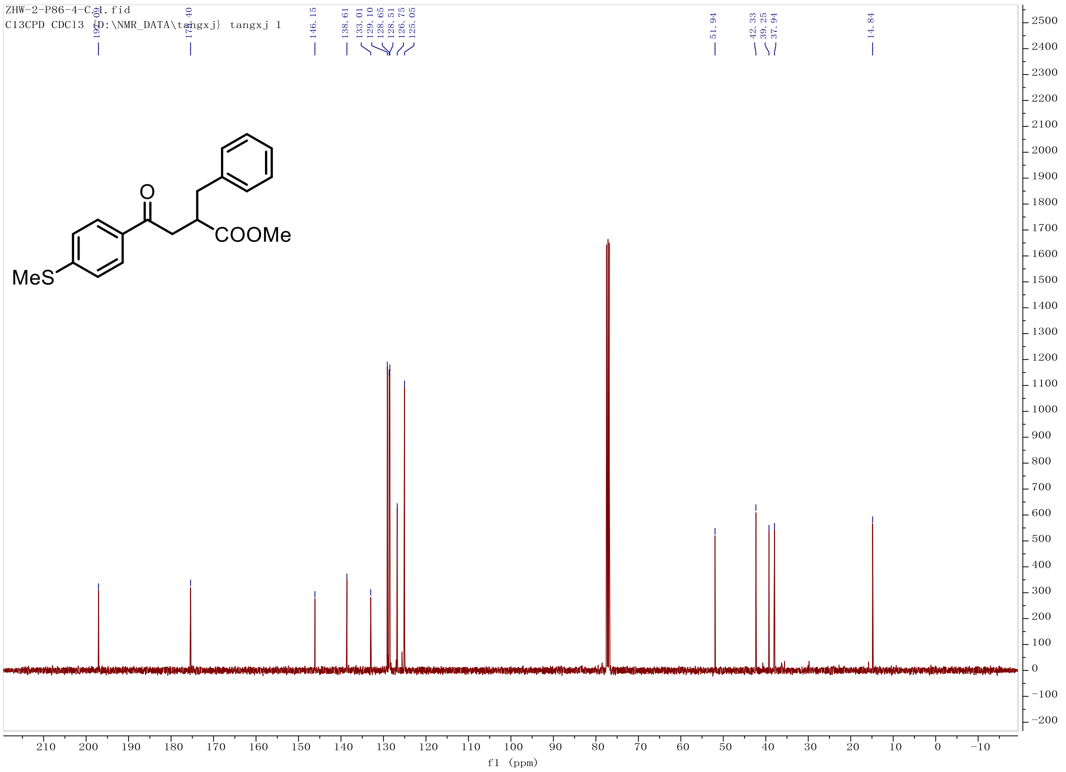
^{13}C NMR of 4h ($CDCl_3$)



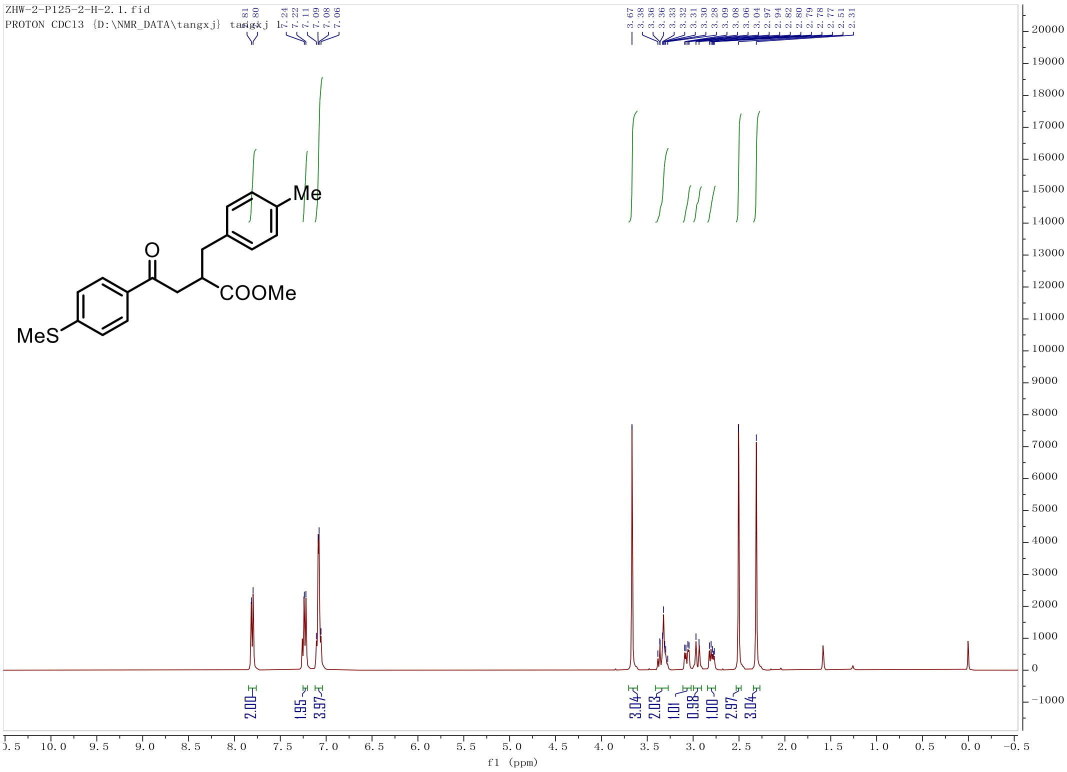
^{1}H NMR of 4i (CDCl$_3$)



^{13}C NMR of 4i (CDCl$_3$)



^{1}H NMR of 4j (CDCl$_3$)



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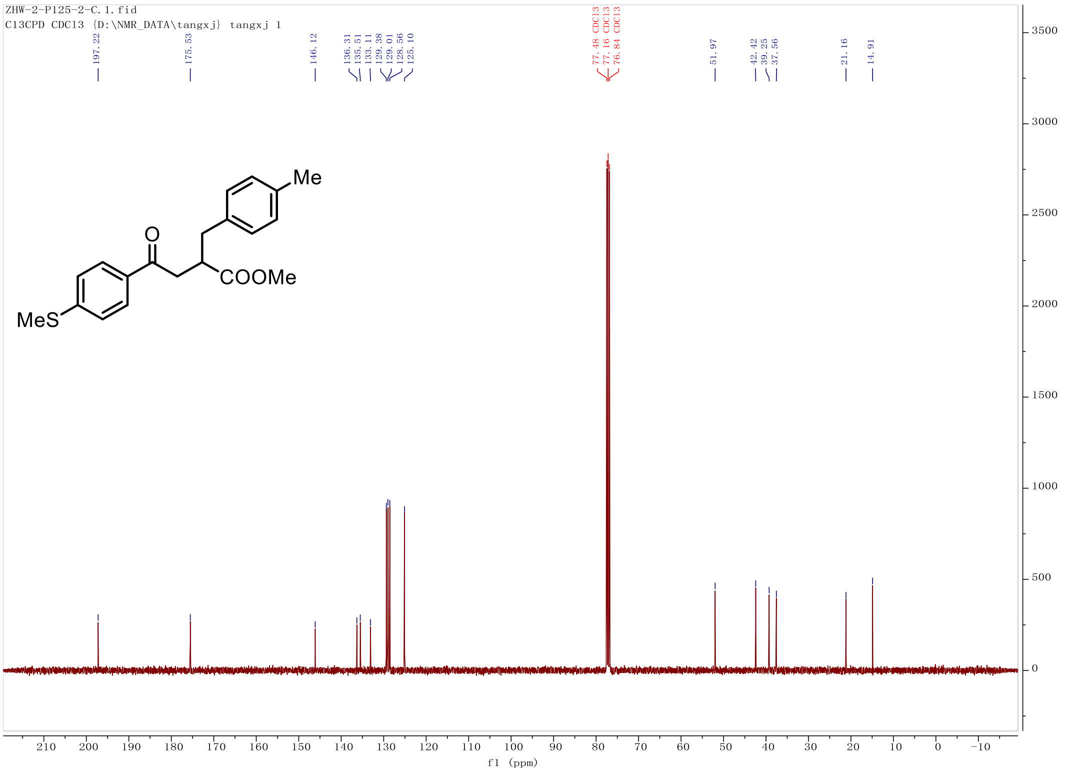
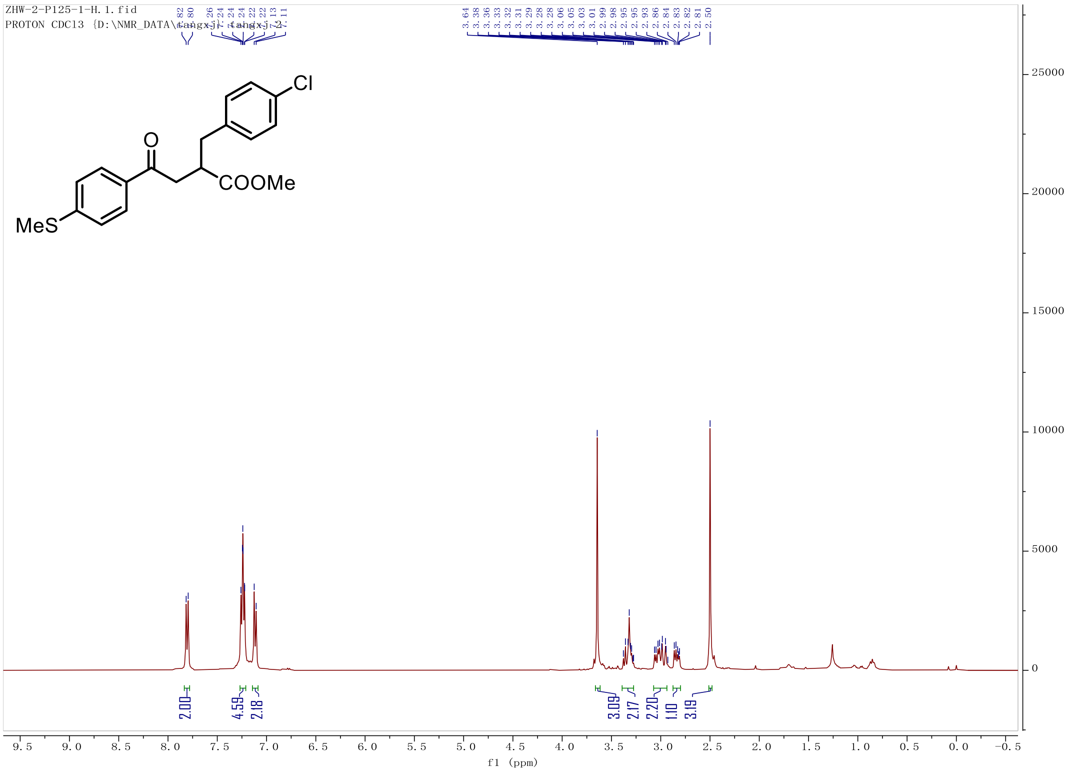


^{1}H NMR of 4k (CDCl$_3$)



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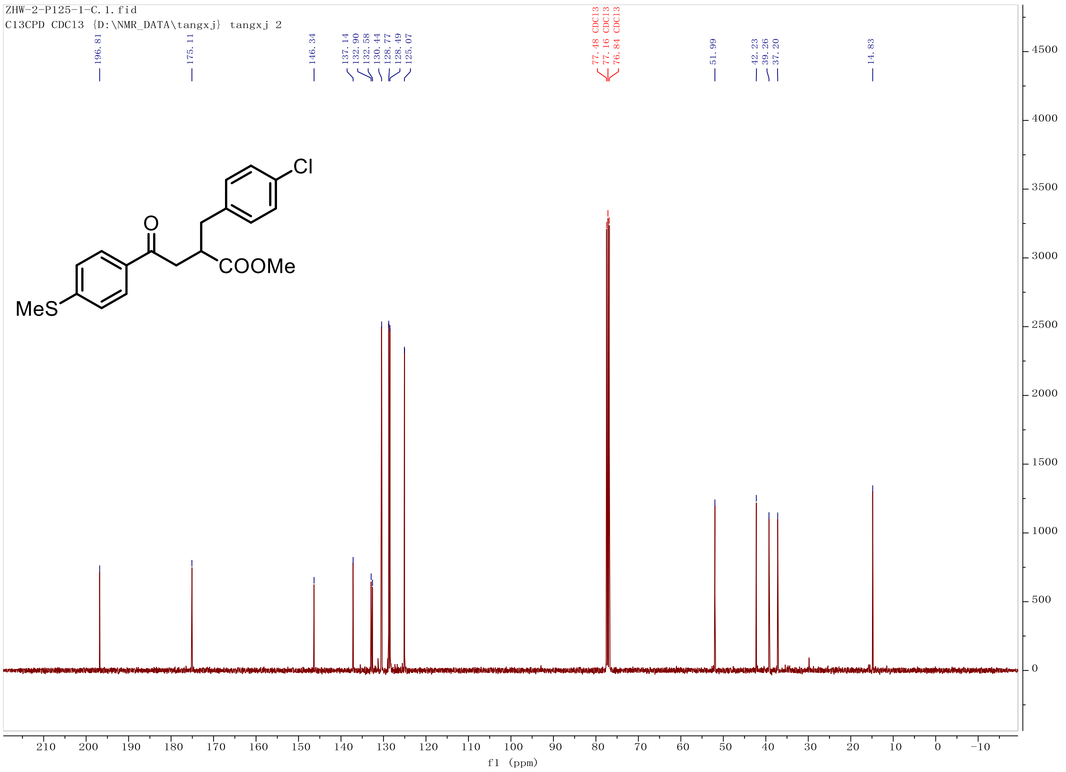
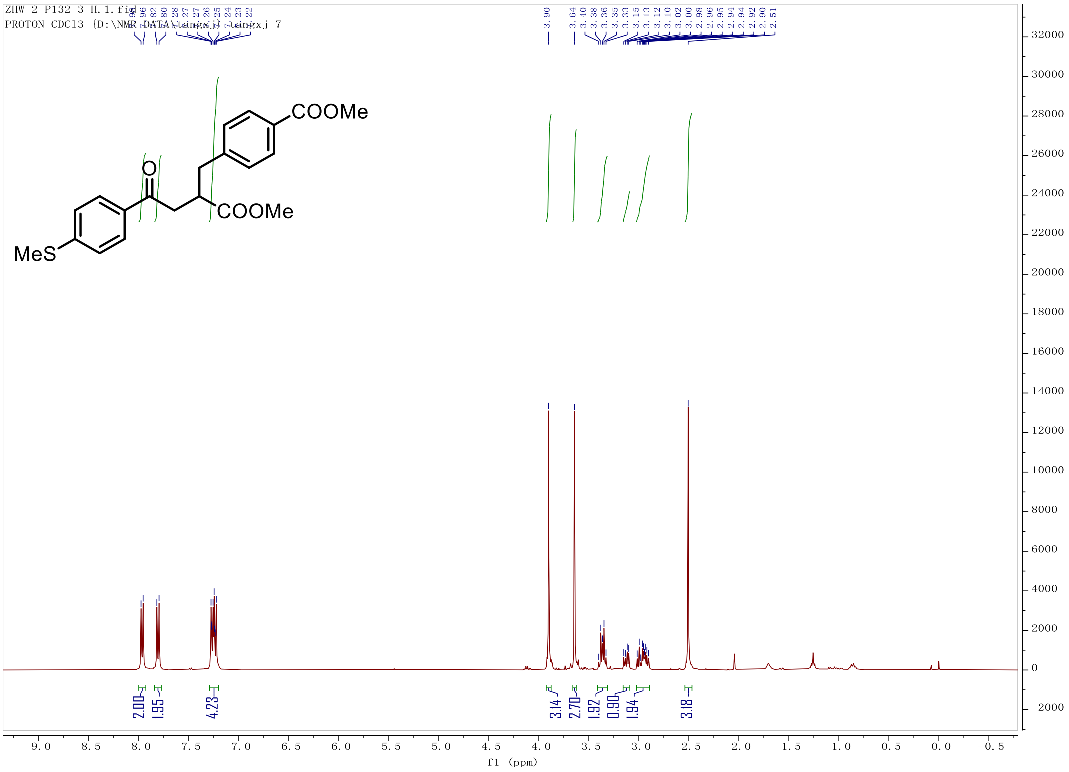
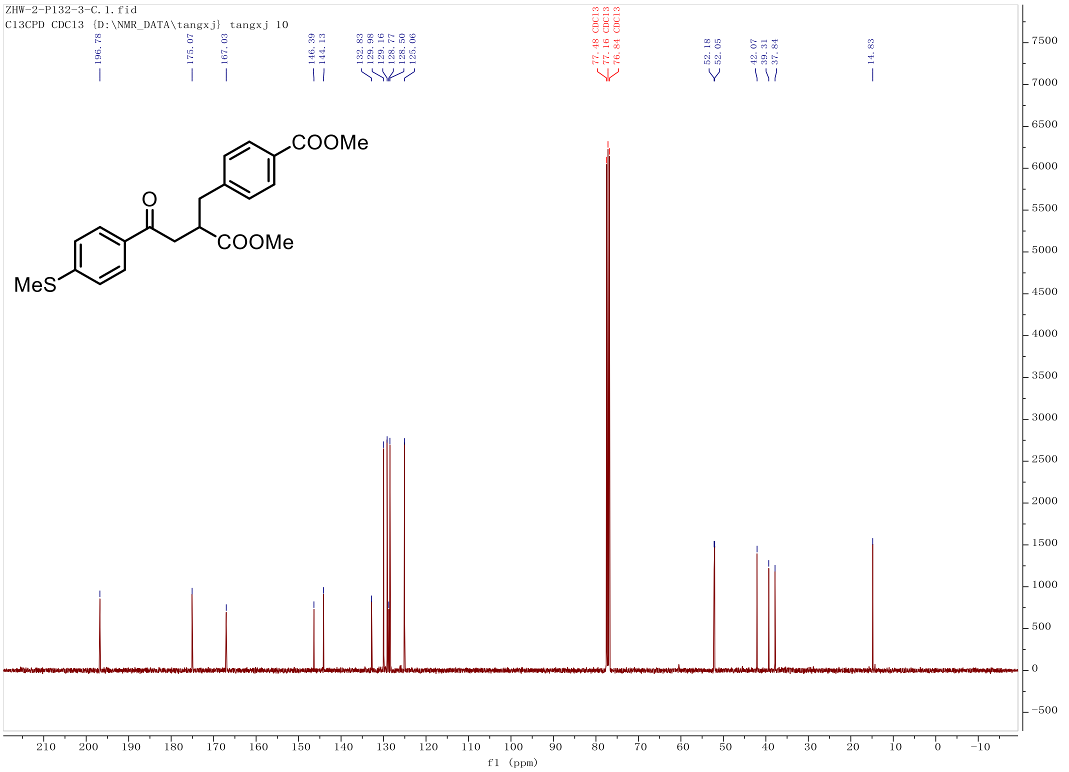


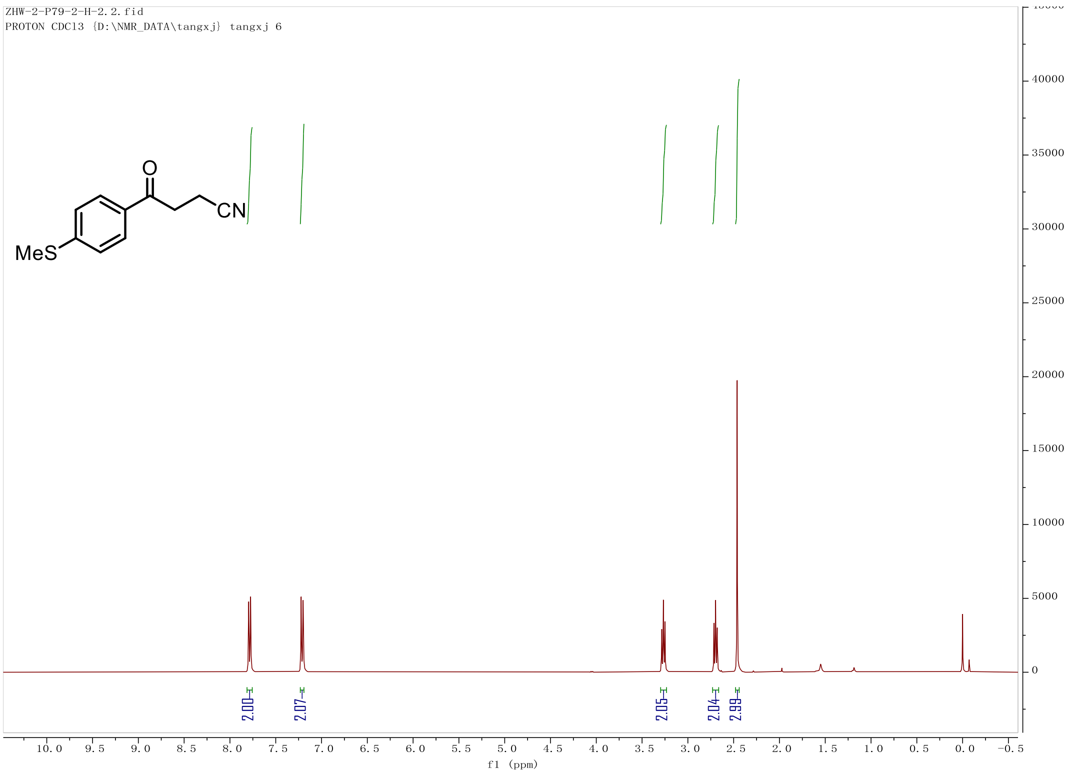
^{1}H NMR of 4l (CDCl$_3$)



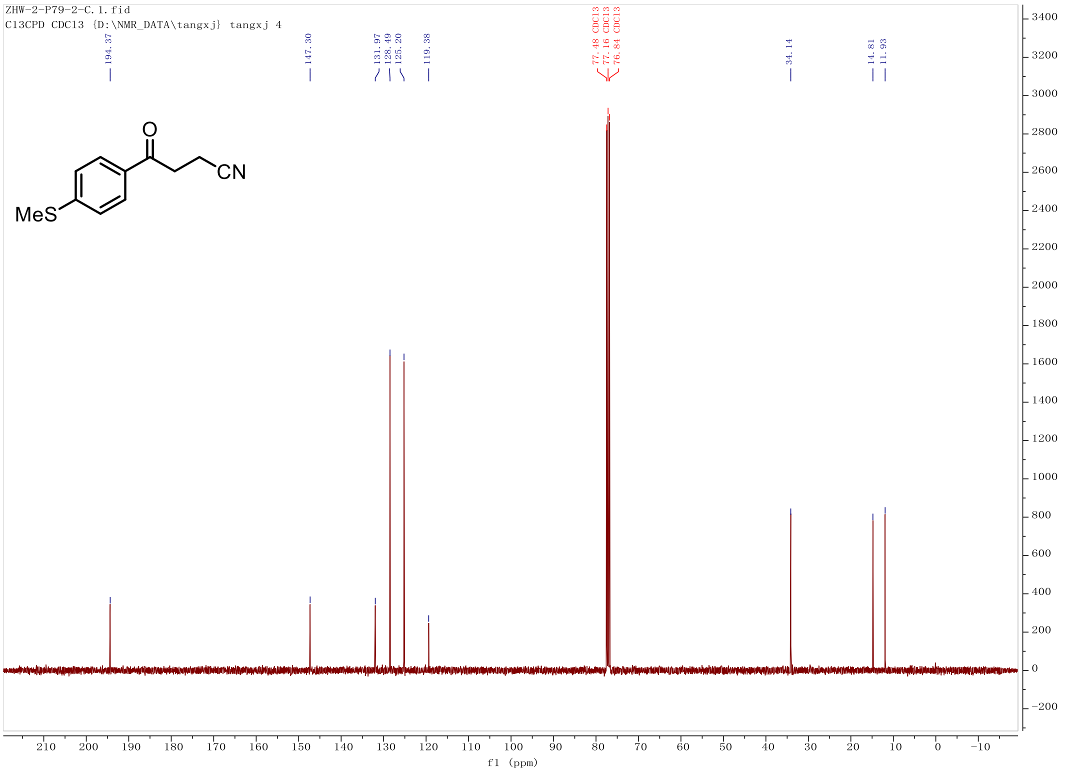
^{13}C NMR of 4l (CDCl$_3$)



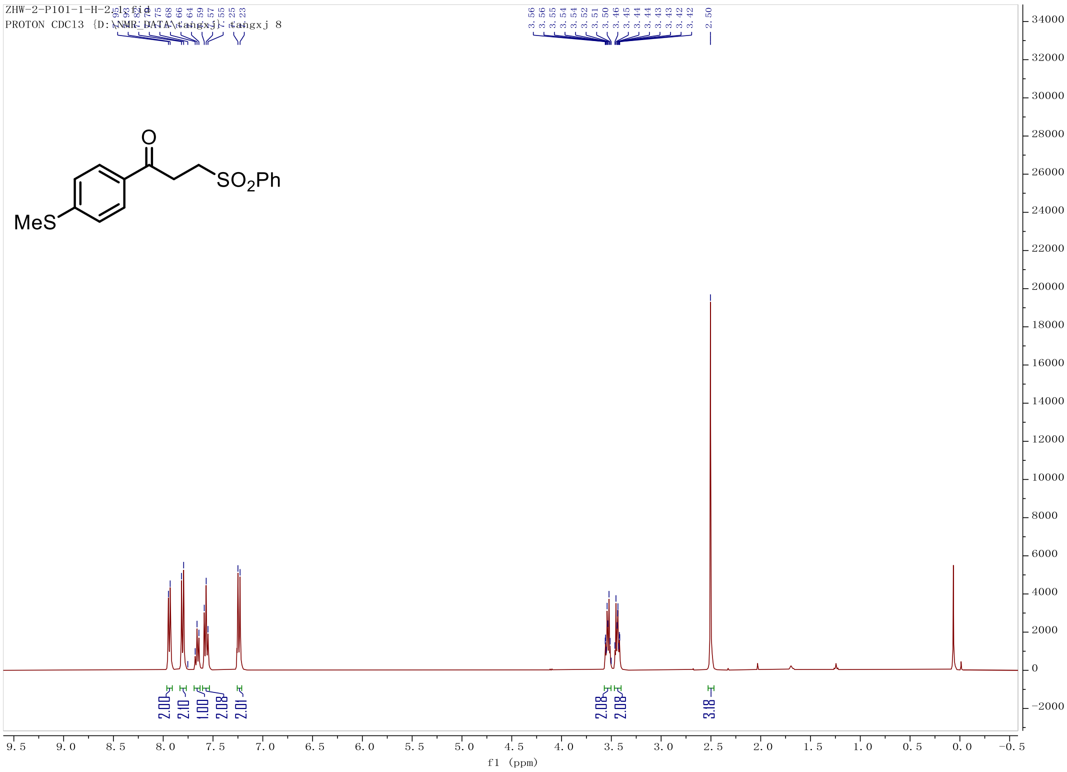
^{1}H NMR of 4m (CDCl$_3$)



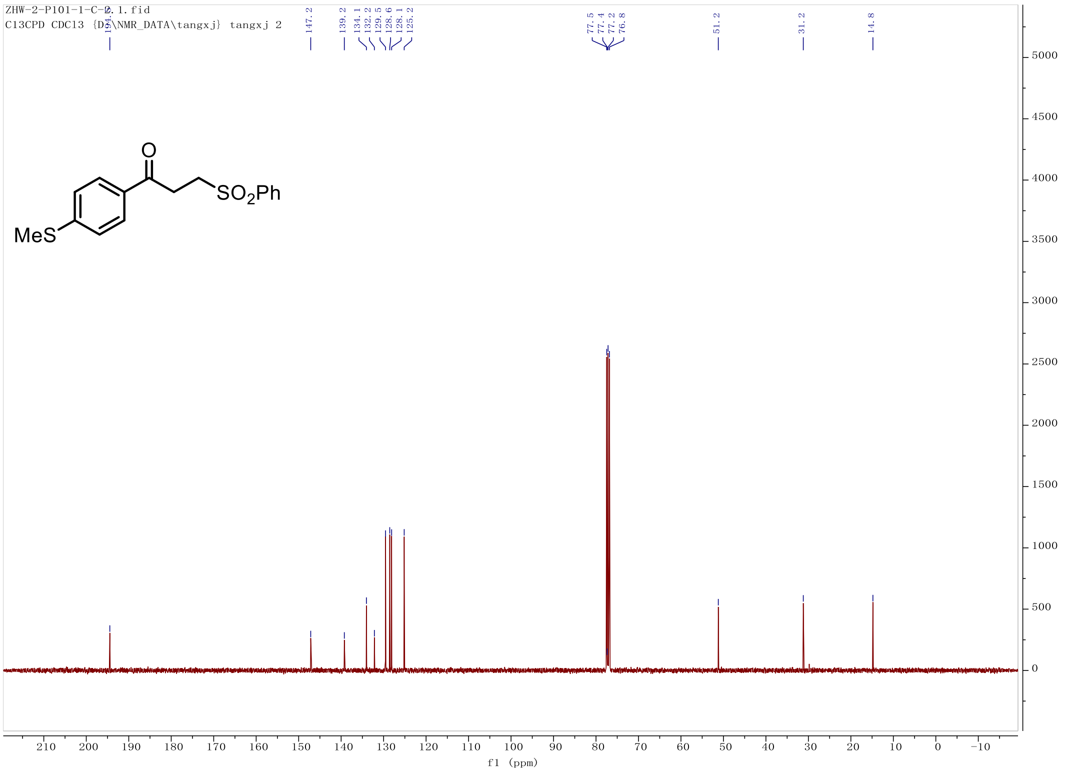
^{13}C NMR of 4m (CDCl$_3$)



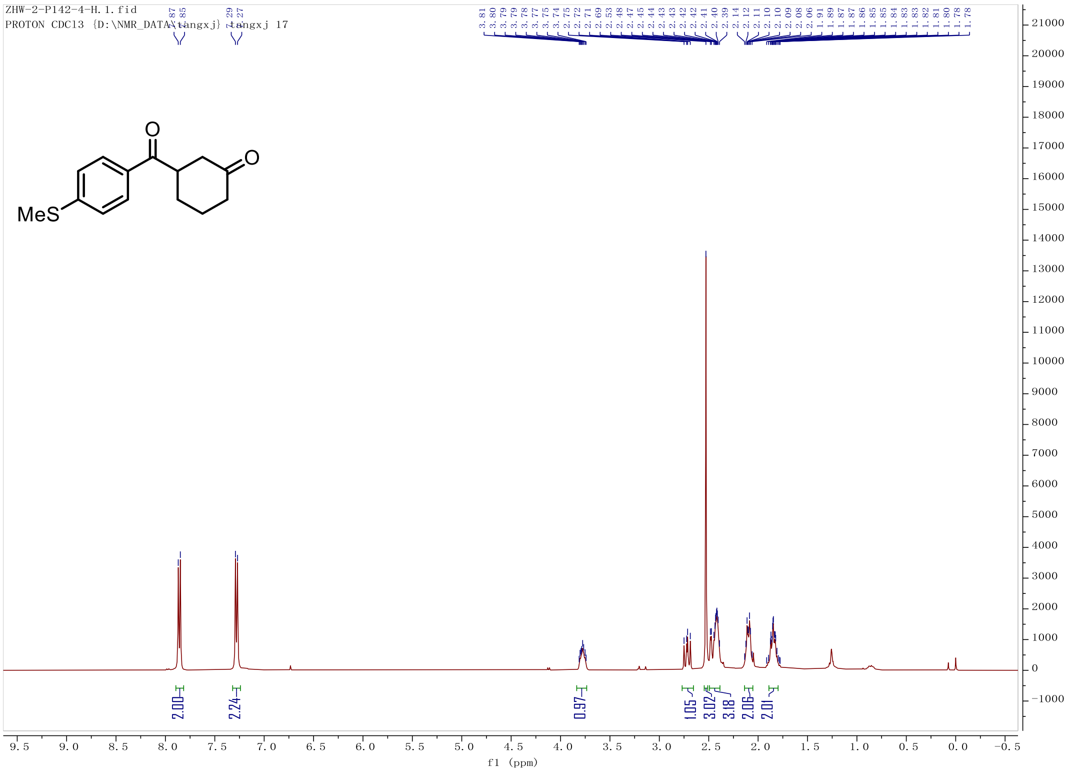
^{1}H NMR of 4n ($CDCl_3$)



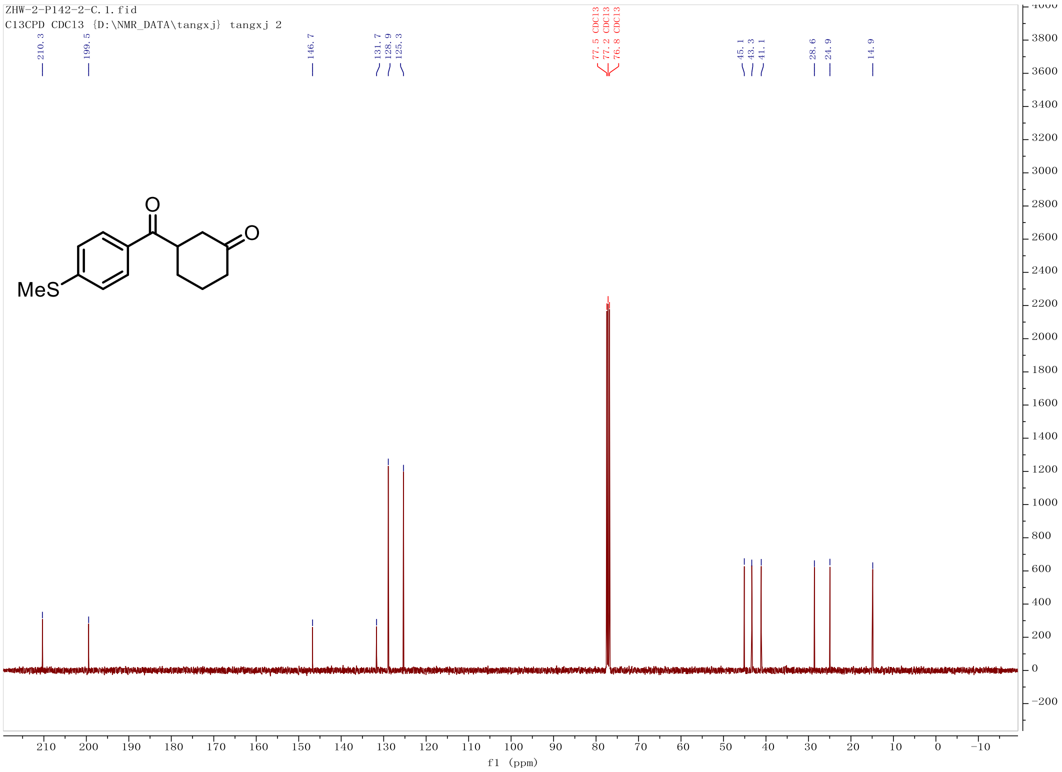
^{13}C NMR of 4n ($CDCl_3$)



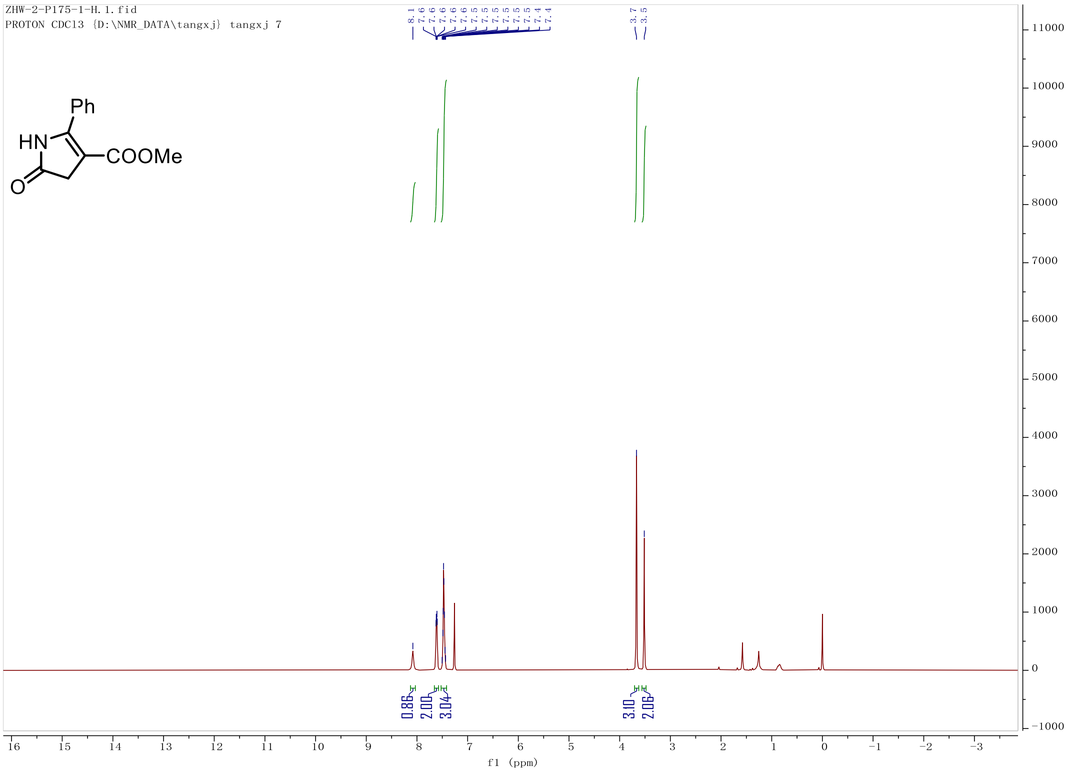
^{1}H NMR of 4o (CDCl$_3$)



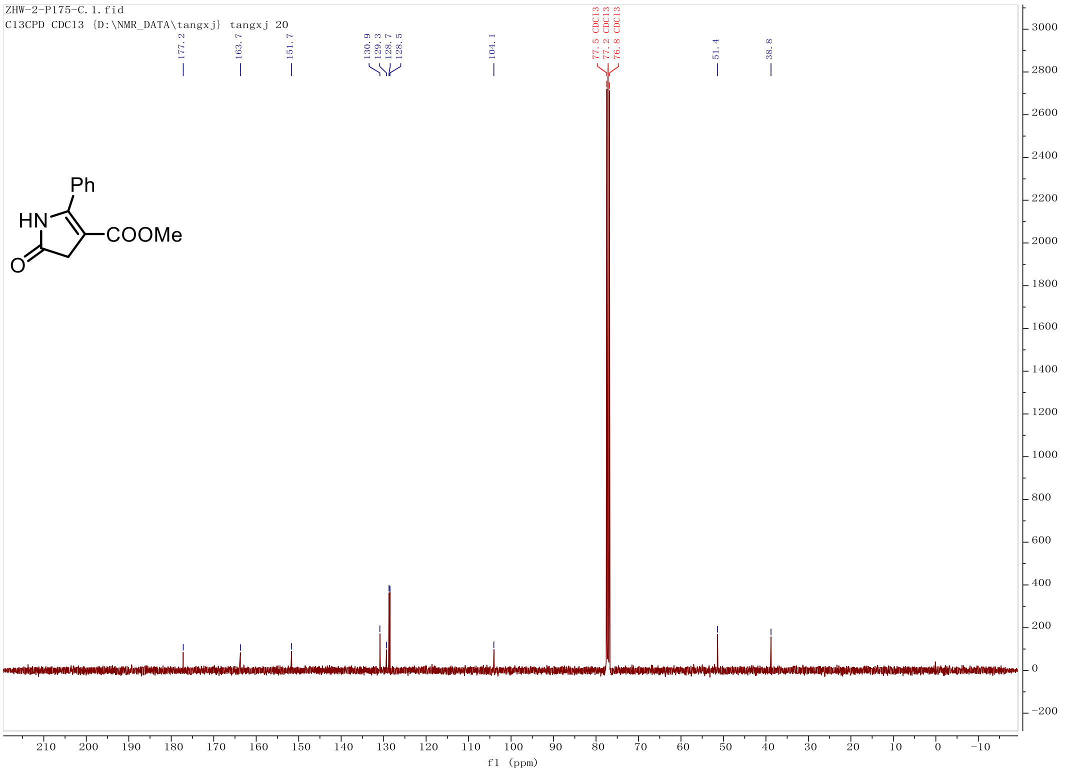
^{13}C NMR of 4o (CDCl$_3$)



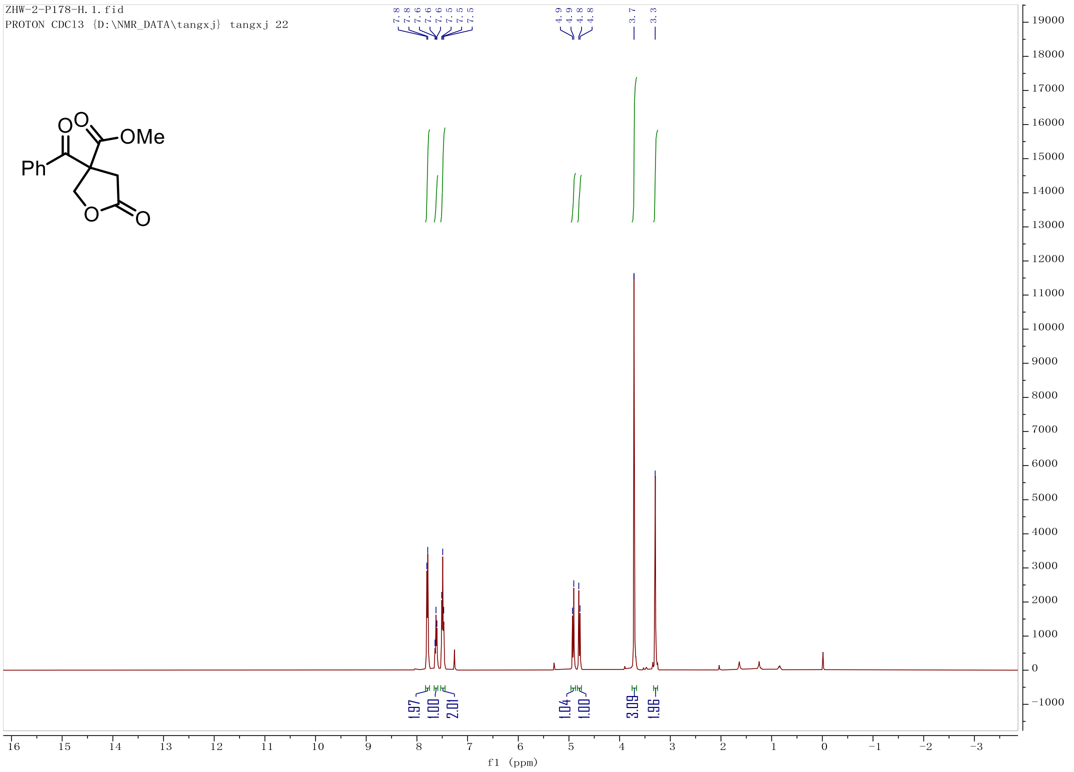
^{1}H NMR of 5 (CDCl$_3$)



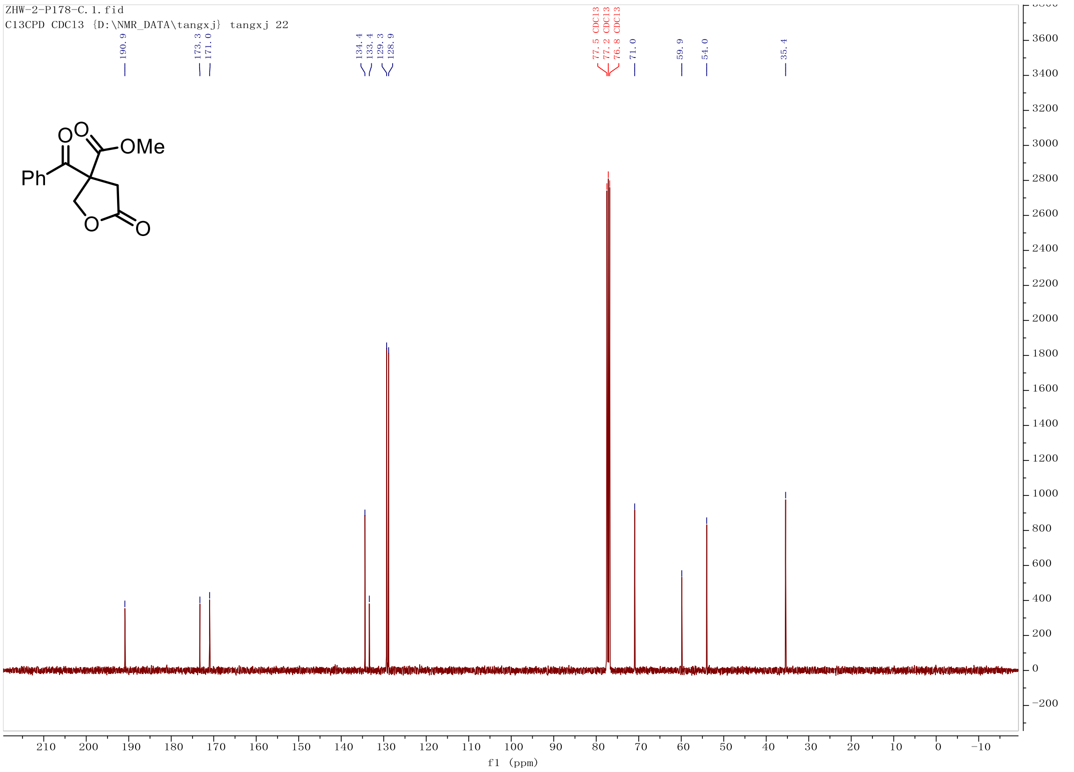
^{13}C NMR of 5 (CDCl$_3$)



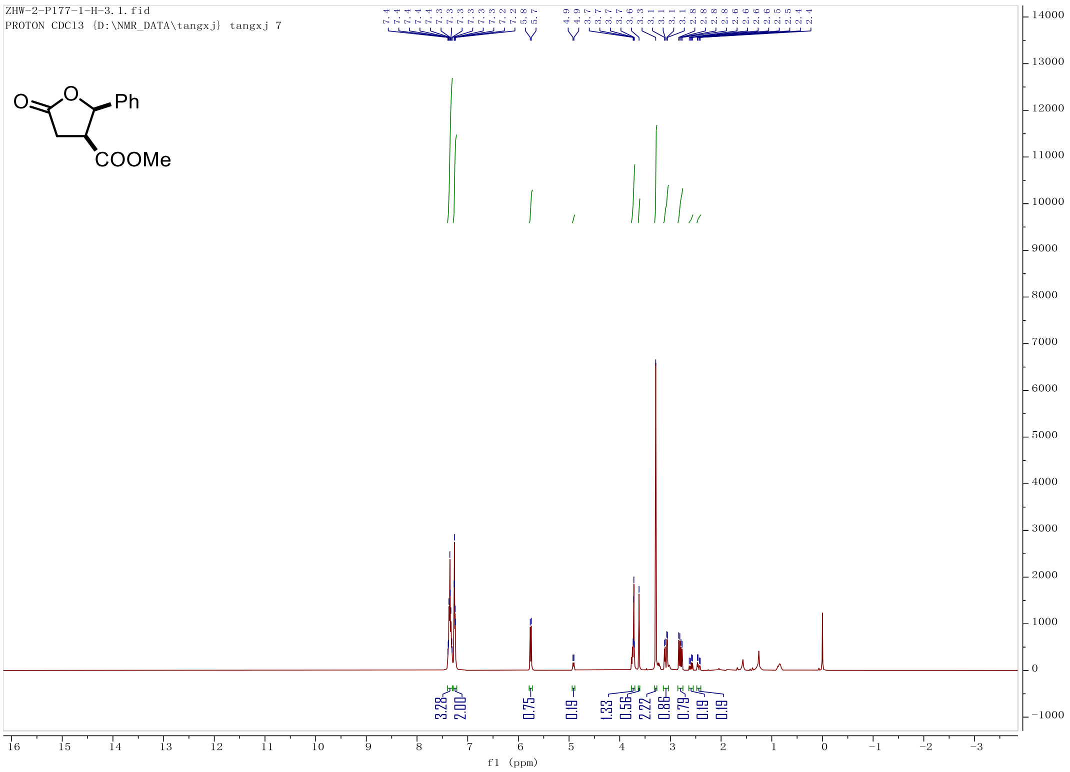
^{1}H NMR of 6 (CDCl$_3$)



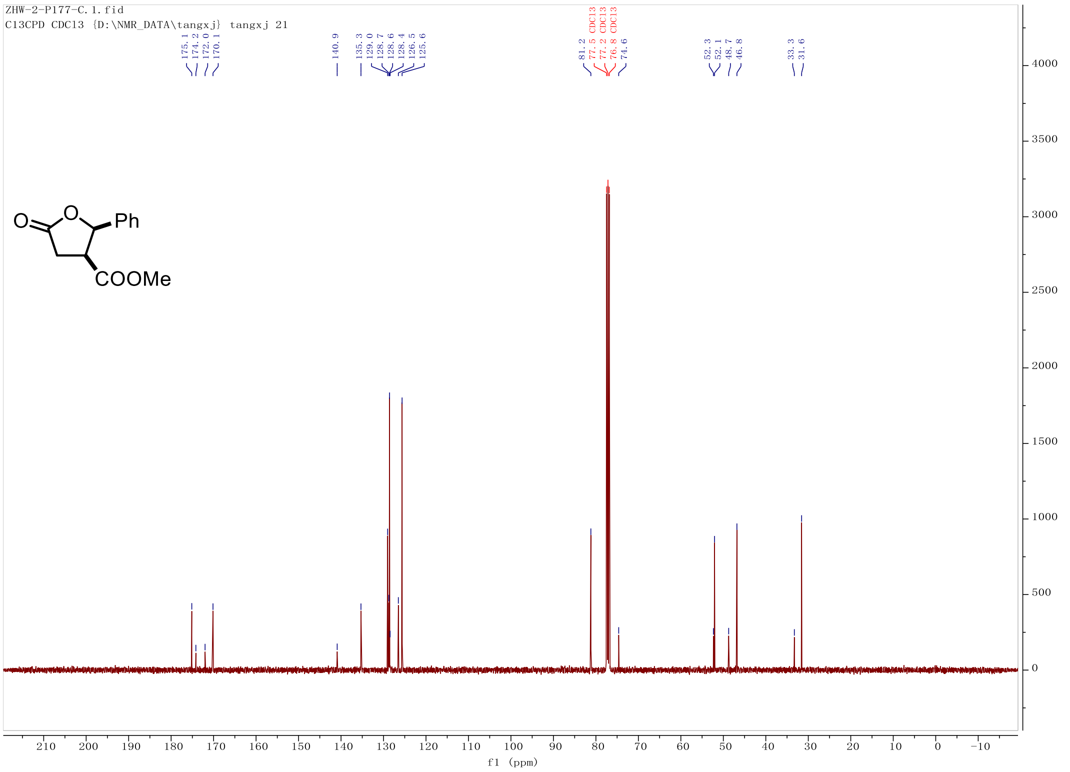
^{13}C NMR of 6 (CDCl$_3$)



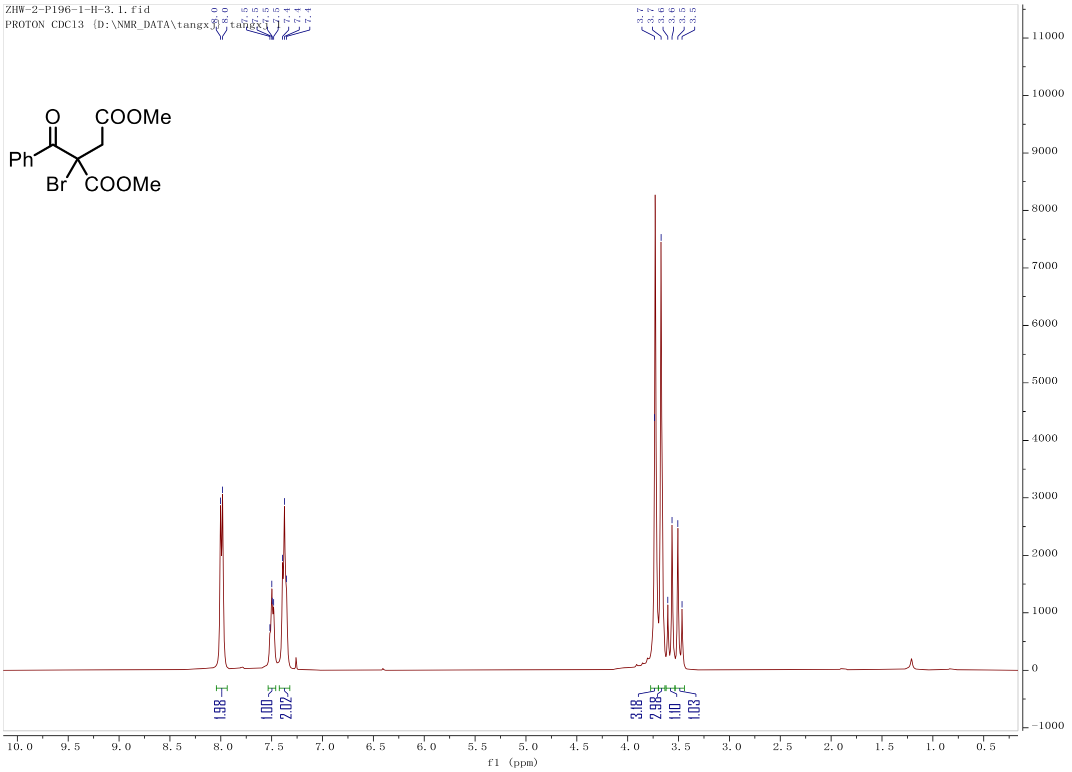
^{1}H NMR of 7 (CDCl$_3$)



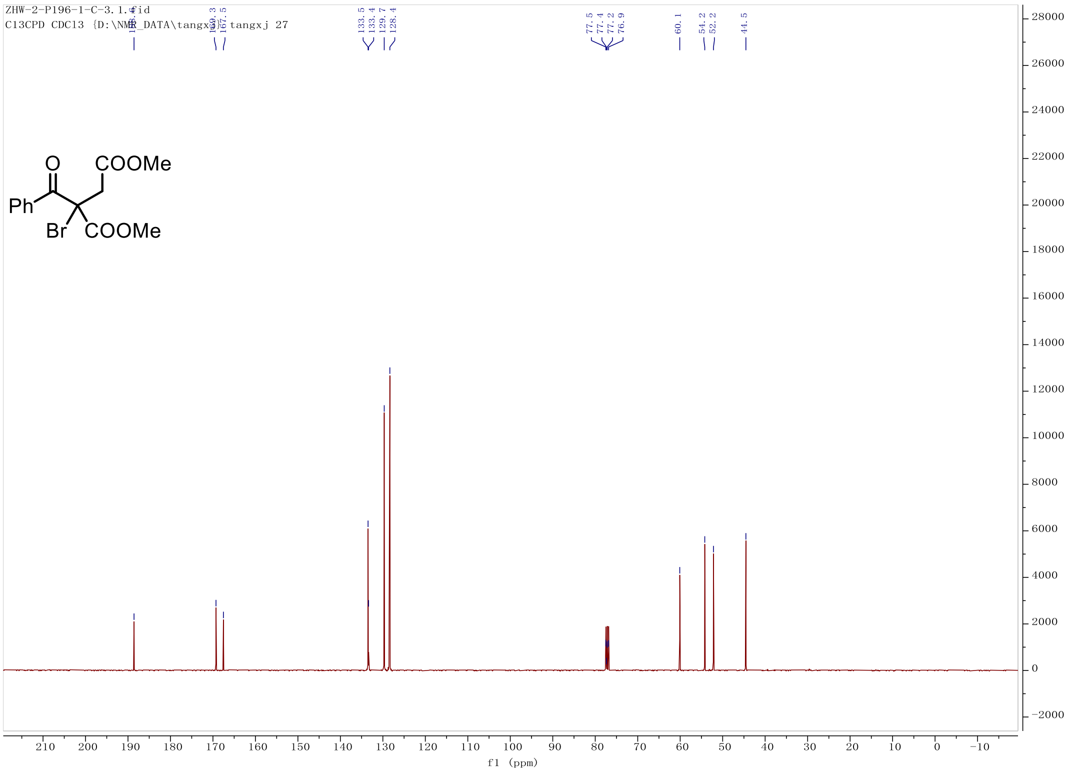
^{13}C NMR of 7 (CDCl$_3$)



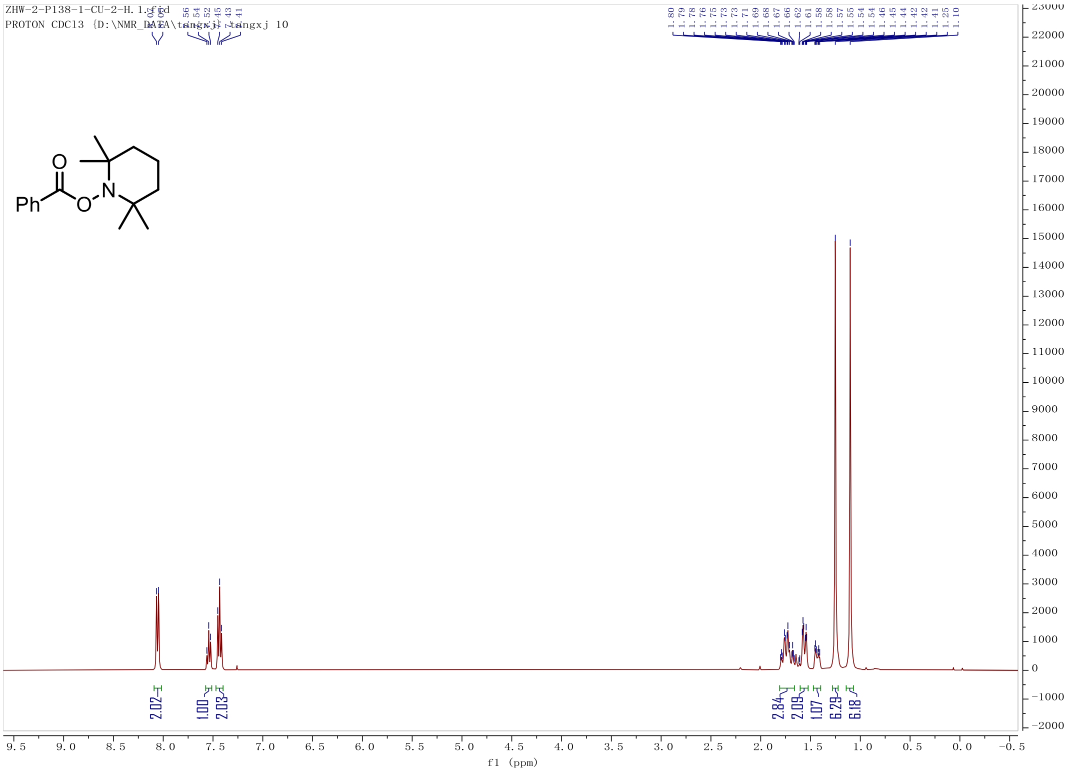
^{1}H NMR of 8 ($CDCl_3$)



^{13}C NMR of 8 ($CDCl_3$)



^{1}H NMR of 10a (CDCl$_3$)



^{13}C NMR of 10a (CDCl$_3$)