Electronic Supporting Information

Dioxane promoted photochemical O-alkylation of 1,3-dicarbonyl compounds beyond carbene insertion into C−H and C−C bonds

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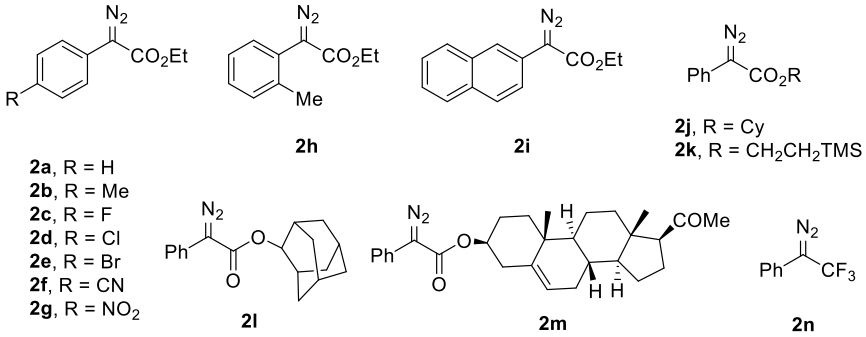
General Information:

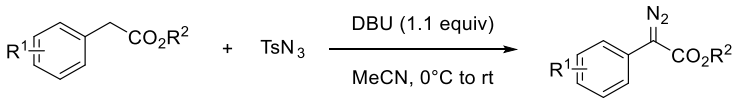
All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 200–300 meshes. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^{1}H in $CDCl_3$ and 77.0 ppm for ^{13}C in $CDCl_3$; 2.50 ppm for ^{1}H in d_6-DMSO and 39.5 ppm for ^{13}C in d_6-DMSO). The HRMS spectra were recorded on a Bruker MicroTOF Q II spectrometer.

Caution! Diazo compounds are reactive compounds that release nitrogen as the only byproduct. Although diazo compounds have been reported to be prone to explosions, we have not encountered any security issues to date. Reaction scales should be limited whenever possible.

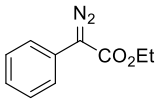
General Procedure for the Preparation of Diazo Compounds.



Diazoacetates **2a−2n** were prepared by the below mentioned method.

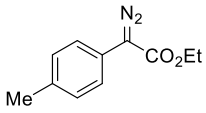


To a stirred solution of 2-phenylacetate (10 mmol, 1 equiv) and TsN_3 (11 mmol, 1.1 equiv, 2.2 g) in MeCN (30 mL) was added DBU (11 mmol, 1.1 equiv, 1.7 g) slowly at 0 °C and stirred at the room temperature for 12 h. Saturated $NaHCO_3$ solution was added to quench the reaction and then this was extracted with EtOAc three times. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and evaporated to give the crude diazoacetate. The crude diazoacetate was then purified by flash column chromatography (PE/EtOAc = 50/1) to give the diazoacetate.



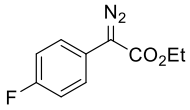
2a

Ethyl 2-diazo-2-phenylacetate (**2a**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2 H), 7.42 – 7.33 (m, 2 H), 7.22 – 7.14 (m, 1 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).



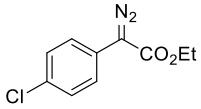
2b

Ethyl 2-diazo-2-(p-tolyl)acetate (**2b**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.34 (t, *J* = 7.1 Hz, 3 H).



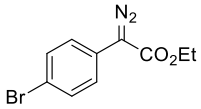
2c

Ethyl 2-diazo-2-(4-fluorophenyl)acetate (**2c**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 2 H), 7.09 (t, *J* = 8.7 Hz, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).



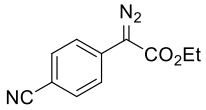
2d

Ethyl 2-(4-chlorophenyl)-2-diazoacetate (**2d**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2 H), 7.37 – 7.32 (m, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).



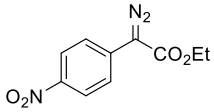
2e

Ethyl 2-(4-bromophenyl)-2-diazoacetate (**2e**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2 H), 7.43 – 7.32 (m, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).



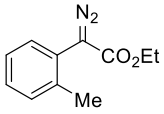
2f

Ethyl 2-(4-cyanophenyl)-2-diazoacetate (**2f**, known compound).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 4 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H).



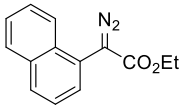
2g

Ethyl 2-diazo-2-(4-nitrophenyl)acetate (**2g**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.0 Hz, 2 H), 7.67 (d, *J* = 9.1 Hz, 2 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 1.37 (t, *J* = 7.1 Hz, 3 H).



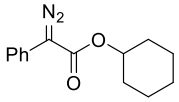
2h

Ethyl 2-diazo-2-(o-tolyl)acetate (**2h**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 1 H), 7.26 (d, *J* = 2.6 Hz, 3 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 2.30 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).



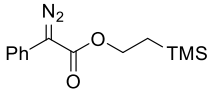
2i

Ethyl 2-diazo-2-(naphthalen-2-yl)acetate (**2i**, known compound).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 3 H), 7.67 – 7.46 (m, 4 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H).



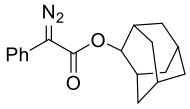
2j

Cyclohexyl 2-diazo-2-phenylacetate (**2j**, known compound).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 4.98 (m, 1 H), 1.97 – 1.83 (m, 2 H), 1.80 – 1.67 (m, 2 H), 1.58 – 1.49 (m, 3 H), 1.47 – 1.30 (m, 3 H).



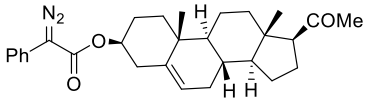
2k

2-(Trimethylsilyl)ethyl 2-diazo-2-phenylacetate (**2k**, known compound).[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2 H), 7.38 (t, *J* = 7.9 Hz, 2 H), 7.22 – 7.07 (m, 1 H), 4.48 – 4.25 (m, 2 H), 1.18 – 0.99 (m, 2 H), 0.07 (s, 9 H).



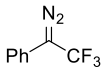
2l

(1R,5R,7S)-Adamantan-2-yl 2-diazo-2-phenylacetate (**2l**, known compound).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 2 H), 7.39 (m, 2 H), 7.22 – 7.12 (m, 1 H), 5.18 – 5.11 (m, 1 H), 2.09 (s, 2 H), 2.05 – 1.96 (m, 2 H), 1.93 – 1.71 (m, 8 H), 1.65 – 1.59 (m, 2 H).



2m

(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-diazo-2-phenyl acetate (**2m**, known compound).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2 H), 7.38 (t, *J* = 7.9 Hz, 2 H), 7.22 – 7.12 (m, 1 H), 5.41 (d, *J* = 5.2 Hz, 1 H), 4.86 – 4.70 (m, 1 H), 4.12 (q, *J* = 7.2 Hz, 1 H), 2.24 – 1.82 (m, 10 H), 1.71 – 1.60 (m, 4 H), 1.53 – 1.43 (m, 4 H), 1.27 – 1.15 (m, 4 H), 1.05 (s, 3 H), 0.64 (s, 3 H).



2n

(1-Diazo-2,2,2-trifluoroethyl)benzene (**2n**, known compound).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2 H), 7.23 – 7.17 (m, 1 H), 7.13 – 7.07 (m, 2 H).

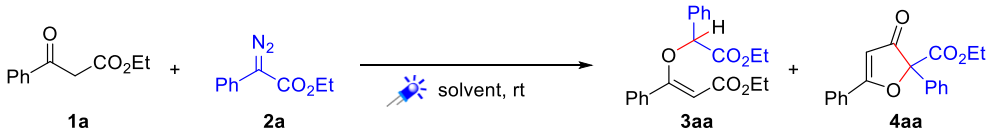
The Reaction Equipment and Light Source

We use RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used have equipped 8 bule light 10W LED. This blue light 10 WLED's energy peak wavelength is 450 nm, peak width at half-height is 25 nm, Iirradiance@10 W is 172 mW/cm^2. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm. No filter between LED and test tube. We conducted the photoreaction in room temperature (about 20°C−30°C). In summer, we controlled the temperature of the reaction mixture to keep in about 25°C using low-temperature cycle.

Figure S1. The Reaction Equipment and Light Source (λ_{max} = 450 nm, $\Delta\lambda$ = 25 nm)

Optimization of Reaction Conditions

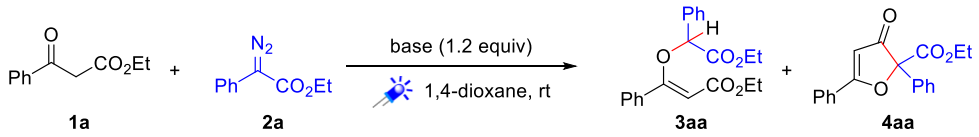
Table S1. Solvent Screening[a]



entry	solvent	yield of **3aa** (%)	yield of **4aa** (%)
1	**1,4-dioxane**	**45**	**0**
2	THF	< 5	0
3	MeCN	< 5	0
4	DMF	< 5	0
5	DMSO	< 5	0
6	MeOH	< 5	0
7	toluene	< 5	0
8	$CHCl_3$	< 5	0
9	EA	< 5	0
10	DCE	< 5	0
11	$MeNO_2$	< 5	0
12	DCM	< 5	0

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), solvent (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 6 h. Yield of the isolated product after column chromatography.

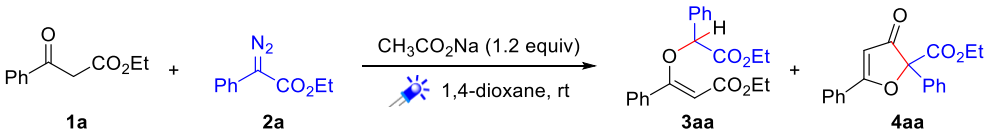
Table S2. Base Screening[a]



entry	base	yield of **3aa** (%)	yield of **4aa** (%)
1	**CH_3CO_2Na**	**86**	**0**
2[b]	**CH_3CO_2Na and DBU**	**0**	**81**
3	Et_3N	67	0
4	DIPEA	52	0
5	DBU	0	31
6	DMAP	44	0
7	K_2CO_3	42	0
8	Na_2CO_3	38	0
9	K_3PO_4	35	0
10	KOH	41	0

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), base (0.48 mmol), 1,4-dioxane (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 6 h. Yield of the isolated product after column chromatography. [b]One pot, two steps. 1.2 equiv DBU was added and continued to react at room temperature for another 2 h.

Table S3. Control Experiments[a]

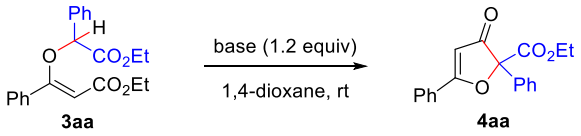


entry	conditions	yield of **3aa** (%)	yield of **4aa** (%)
1	**standard conditions**	**86**	**0**
2	1.0 equiv CH_3CO_2Na	75	0
3	without CH_3CO_2Na	45	0
4	open in Air	61	0
5	in darkness	N.R.	

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), CH_3CO_2Na (0.48 mmol), 1,4-dioxane (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 6 h. Yield of the isolated product after column chromatography. N.R. indicates "no reaction".

Solvent Effect on the Chemoselectivity

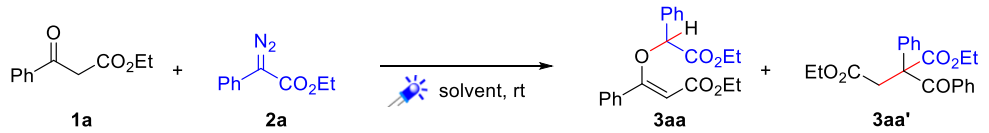
Table S4. Control Experiments of Generation 4aa from 3aa[a]



entry	base	conv. of **3aa** (%)	yield of **4aa**
1	**DBU**	**100**	**quant**
2	CH_3CO_2Na	N.R.	
3	Et_3N	N.R.	
4	DIPEA	N.R.	
5	DMAP	N.R.	
6	K_2CO_3	N.R.	
7	Na_2CO_3	N.R.	
8	K_3PO_4	N.R.	
9	KOH	N.R.	

[a]Reaction conditions: **3aa** (0.4 mmol), base (0.48 mmol), 1,4-dioxane (2 mL), rt, 2 h. Yield of the isolated product after column chromatography. N.R. indicates "no reaction".

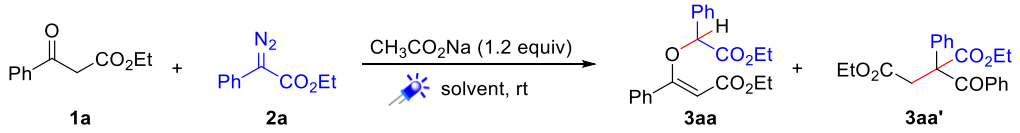
Table S5. Solvent Effect on the Chemoselectivity of β-Ketoester 1a



entry	solvent	yield of **3aa** (%)	yield of **3aa'** (%)
1	**1,4-dioxane**	**45**	**N.D.**
2	THF	< 5	N.D.
3	MeCN	< 5	N.D.
4	DMF	< 5	N.D.
5	DMSO	< 5	N.D.
6	MeOH	< 5	N.D.
7	toluene	< 5	N.D.
8	$CHCl_3$	< 5	N.D.
9	EA	< 5	N.D.
10	DCE	< 5	N.D.
11	$MeNO_2$	< 5	N.D.
12	DCM	< 5	N.D.

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), solvent (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 6 h. Yield of the isolated product after column chromatography. N.D. indicates “no detection”.

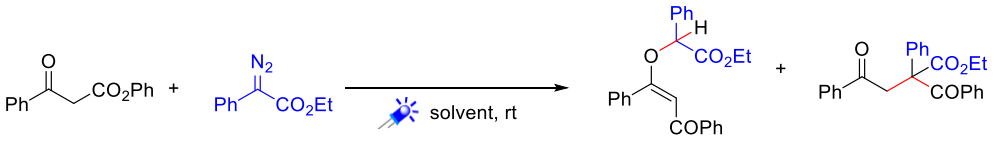
Table S6. Base-Promoted the *O*-alkylation of β-Ketoester 1a



entry	solvent	yield of **3aa** (%)	yield of **3aa'** (%)
1	**1,4-dioxane**	**86**	**N.D.**
2	THF	< 5	N.D.
3	MeCN	36	N.D.
4	DMF	12	N.D.
5	DMSO	< 5	N.D.
6	MeOH	< 5	N.D.
7	toluene	24	N.D.
8	$CHCl_3$	< 5	N.D.
9	EA	27	N.D.
10	DCE	34	N.D.
11	$MeNO_2$	16	N.D.
12	DCM	30	N.D.
13	1,3-dioxane	N.D.	N.D.

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), CH_3CO_2Na (0.48 mmol), solvent (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 6 h. Yield of the isolated product after column chromatography. N.D. indicates “no detection”.

Table S7. Solvent Effect on the Chemoselectivity of 1,3-Diketone 1g

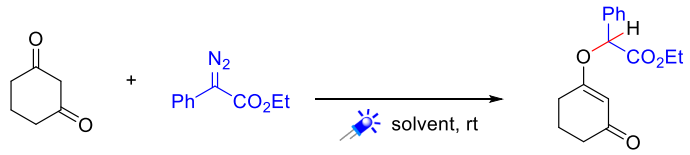


1g **2a** **3ga** **3ga'**

entry	solvent	yield of **3ga** (%)	yield of **3ga'** (%)
1	**1,4-dioxane**	**90**	**N.D.**
2	THF	N.D.	13
3	MeCN	N.D.	28
4	DMF	N.D.	< 5
5	DMSO	N.D.	< 5
6	MeOH	N.D.	< 5
7	toluene	N.D.	22
8	$CHCl_3$	N.D.	25
9	EA	N.D.	11
10	DCE	N.D.	13
11	$MeNO_2$	N.D.	< 5
12	DCM	N.D.	35

[a]Reaction conditions: **1g** (0.4 mmol), **2a** (0.48 mmol), solvent (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 24 h. Yield of the isolated product after column chromatography. N.D. indicates “no detection”.

Table S8. Solvent Effect on the Chemoselectivity of Cyclic 1,3-Diketone 1i



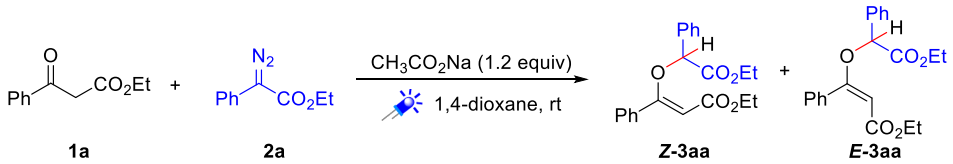
1i **2a** **3ia**

entry	solvent	yield of **3ia** (%)
1	**1,4-dioxane**	**80**
2	THF	< 5
3	MeCN	38
4	DMF	< 5
5	DMSO	< 5
6	MeOH	< 5
7	toluene	17
8	$CHCl_3$	32
9	EA	37
10	DCE	35
11	$MeNO_2$	33
12	DCM	40

[a]Reaction conditions: **1i** (0.4 mmol), **2a** (0.48 mmol), solvent (2 mL), blue LEDs (λ_{max} = 450 nm), rt, 24 h. Yield of the isolated product after column chromatography.

Stereoselectivity of Enol Ethers

Table S9. Stereoselectivity of Enol Ether 3aa

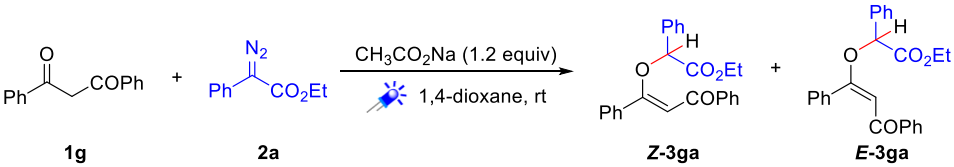


1a **2a** ***Z*-3aa** ***E*-3aa**

entry	T	yield of ***Z*-3aa** (%)	yield of ***E*-3aa** (%)
1	0.5 h	32	N.D.
2	1 h	44	N.D.
3	6 h	86	N.D.
4	24 h	83	N.D.
5	72 h	85	N.D.

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), CH_3CO_2Na (0.48 mmol), 1,4-dioxane (2 mL), blue LEDs (λ_{max} = 450 nm), rt. Yield of the isolated product after column chromatography. N.D. indicates "no detection".

Table S10. Stereoselectivity of Enol Ether 3ga

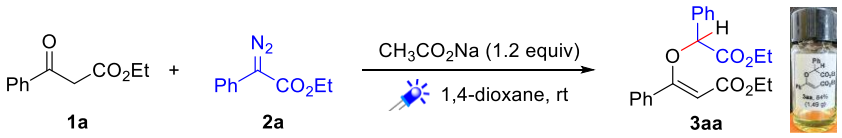


1g **2a** ***Z*-3ga** ***E*-3ga**

entry	T	ratio of ***Z*/*E***
1	1 h	38 : 1
2	3 h	1.1 : 1
3	6 h	1 : 1.4

[a]Reaction conditions: **1g** (0.4 mmol), **2a** (0.48 mmol), CH_3CO_2Na (0.48 mmol), 1,4-dioxane (2 mL), blue LEDs (λ_{max} = 450 nm), rt.

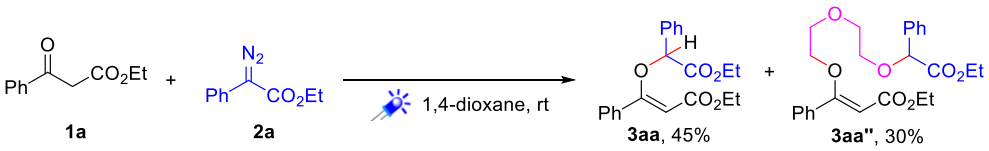
Gram-Scale Synthesis



1a **2a** **3aa**

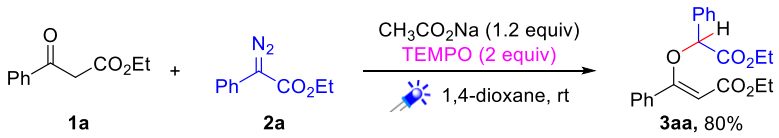
To a 100 mL tube with a stir bar was added ethyl 3-oxo-3-phenylpropanoate **1a** (5 mmol, 1 equiv, 0.96 g), ethyl 2-diazo-2-phenylacetate **2a** (6 mmol, 1.2 equiv, 1.14 g) and 1,4-dioxane (50 mL), followed by CH_3CO_2Na (6 mmol, 1.2 equiv, 0.49 g). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 12 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product **3aa** (1.49 g, 84% yield).

Carbene Trapping Experiment

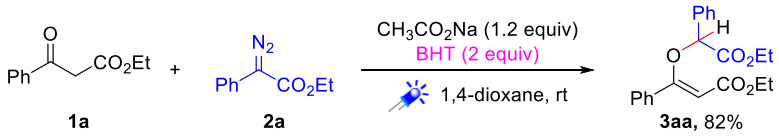


To a 5 mL tube with a stir bar was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 1 equiv, 76.8 mg), ethyl 2-diazo-2-phenylacetate **2a** (0.48 mmol, 1.2 equiv, 91.2 mg) and 1,4-dioxane (2 mL). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product **3aa** (63.7 mg, 45% yield) and **3aa''** (53.1 mg, 30% yield).

Radical Trapping Experiments



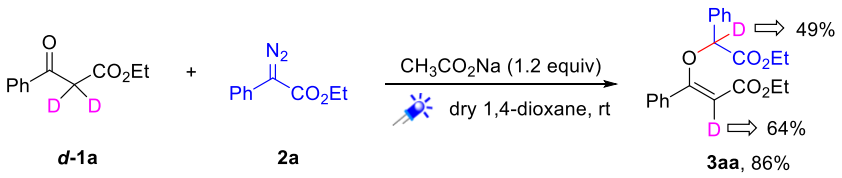
To a 5 mL tube with a stir bar was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 1 equiv, 76.8 mg), ethyl 2-diazo-2-phenylacetate **2a** (0.48 mmol, 1.2 equiv, 91.2 mg), 1,4-dioxane (2 mL) and TEMPO (0.8 mmol, 2 equiv, 125 mg), followed by CH_3CO_2Na (0.48 mmol, 1.2 equiv, 39.4 mg). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product **3aa** (113.3 mg, 80% yield).



To a 5 mL tube with a stir bar was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 1 equiv, 76.8 mg), ethyl 2-diazo-2-phenylacetate **2a** (0.48 mmol, 1.2 equiv, 91.2 mg), 1,4-dioxane (2 mL) and BHT (0.8 mmol, 2 equiv, 176 mg), followed by CH_3CO_2Na (0.48 mmol, 1.2 equiv, 39.4 mg). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the

residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product **3aa** (116.1 mg, 82% yield).

Isotope-Labeling Experiment



To a 5 mL tube with a stir bar was added *d*-bethyl 3-oxo-3-phenylpropanoate ***d*-1a** (0.4 mmol, 1 equiv, 77.6 mg), ethyl 2-diazo-2-phenylacetate **2a** (0.48 mmol, 1.2 equiv, 91.2 mg) and dry 1,4-dioxane (2 mL), followed by CH_3CO_2Na (0.48 mmol, 1.2 equiv, 39.4 mg). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired product **3aa** (121.8 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 4 H), 7.46 – 7.31 (m, 6 H), 5.92 (s, 0.51 H), 5.57 (s, 0.36 H), 4.37 – 3.95 (m, 4 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H).

^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3aa**

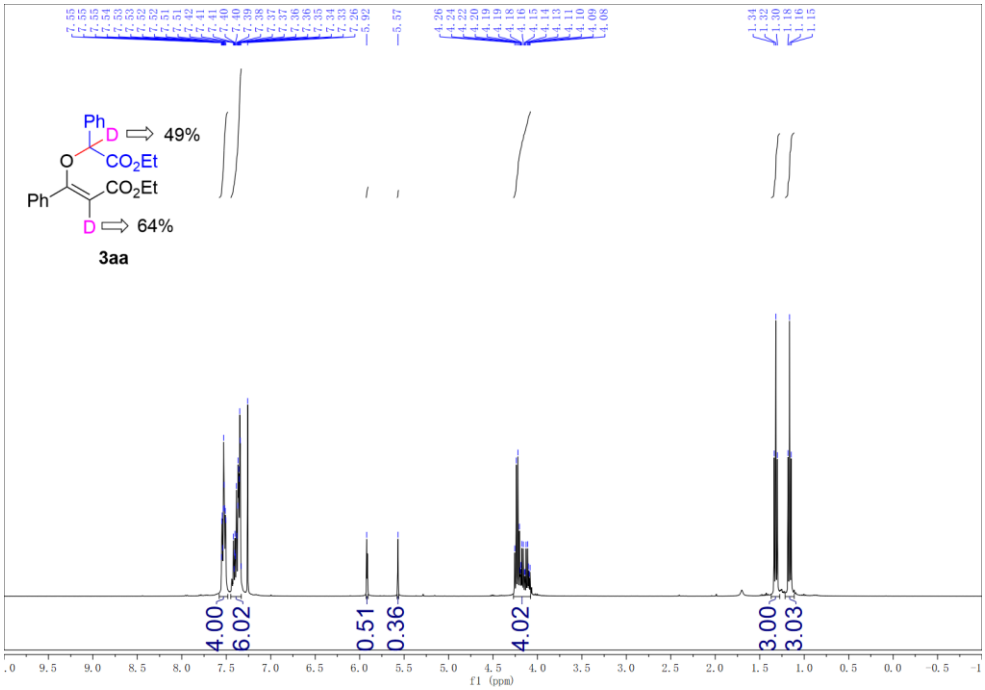


Figure S2

Enolizability of Dibenzoylmethane in 1,4-Dioxane-d_8 and $CDCl_3$

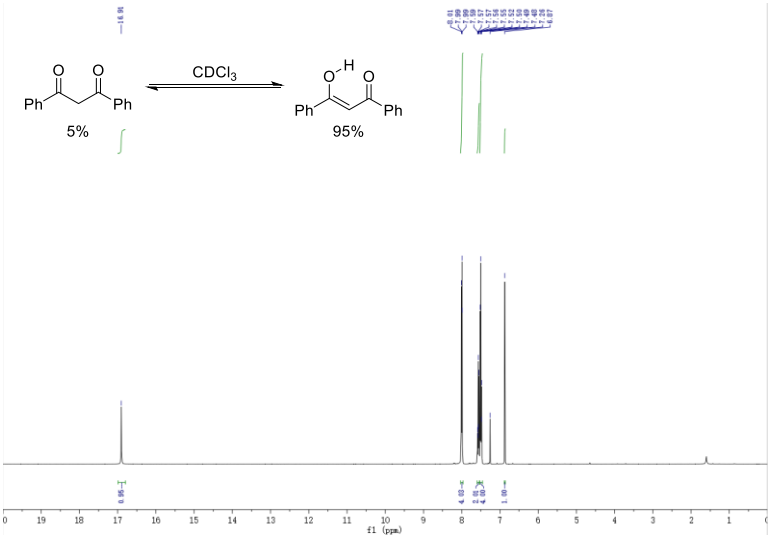


Figure S3

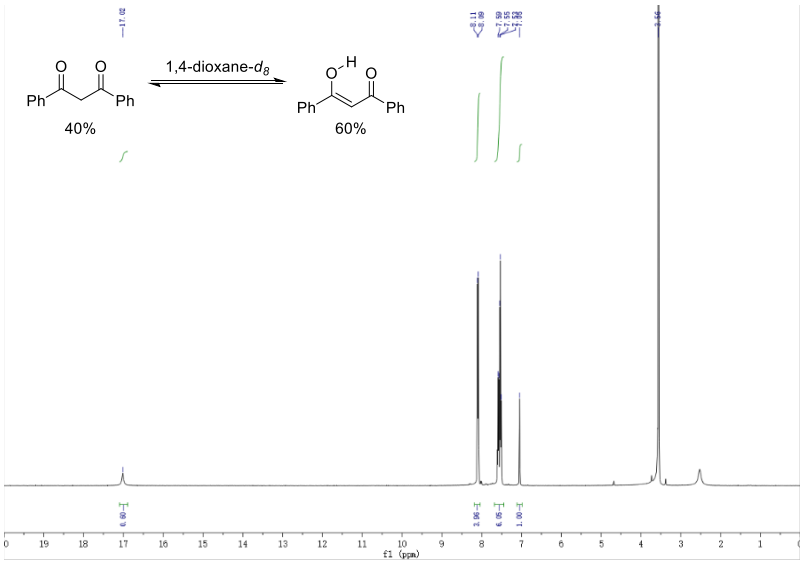


Figure S4

Crystallographic Data for Compound 3ga

Crystallization of **3ga** (30 mg) was dissolved in 1 mL of $CHCl_3$. Then **3ga** were sealed in a 6.5 cm glass ampule with 5 mL of PE, the $CHCl_3$/PE = 1 : 5 (volume ratio). The ampule was placed in a refrigerator at 25 °C and kept at that temperature for 48 hours. Colorless block was crystals deposited in the glass ampule. The data were collected on a Bruker D8 Venture CCD diffractometer.

A good-quality single-crystal of **3ga** was respectively picked carefully and their diffraction intensity data were collected on a Bruker Apex II diffractometer equipped with CCD two-dimensional detector using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150.0 K.

Routine Lorentz and polarization corrections were applied and a multi-scan absorption correction was utilized with the SADABS program. Direct methods were used to solve the structures, refined on F^2 by full-matrix least-squares method, using the SHELXTL-97 program. All H atoms connected to C atoms were generated geometrically and refined isotropically as a riding model using the default Olex2 parameters.

The ellipsoid contour 30% probability levels in the caption for the image of the structure.

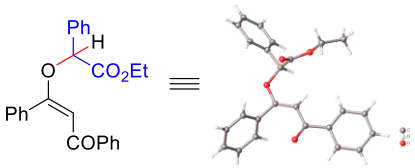


Figure S5: Single crystal structure of **3ga**

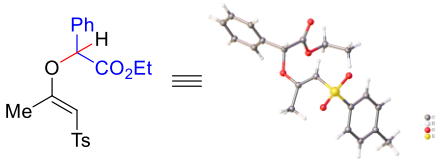
Table S11 Crystal data and structure refinement for **3ga.**	
Identification code	**3ga**
CCDC	2300405
Empirical formula	$C_{25}H_{22}O_4$
Formula weight	386.42
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.2833(18)
b/Å	10.038(2)
c/Å	20.688(4)
α/°	90
β/°	98.406(7)
γ/°	90
Volume/Å^3	2112.7(7)
Z	4
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	0.082
F(000)	816.0
Crystal size/mm^3	0.22 × 0.16 × 0.13
Radiation	MoK*α* (λ = 0.71073)
2Θ range for data collection/°	3.98 to 51.99
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25
Reflections collected	20567
Independent reflections	4160 [R_{int} = 0.0893, R_{sigma} = 0.0761]
Data/restraints/parameters	4160/12/263
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0604, wR_2 = 0.1480
Final R indexes [all data]	R_1 = 0.0982, wR_2 = 0.1723
Largest diff. peak/hole / e Å^{-3}	0.27/-0.22

Crystallographic Data for Compound 3ka

Crystallization of **3ka** (40 mg) was dissolved in 1 mL of DCM. Then **3ka** were sealed in a 6.5 cm glass ampule with 5 mL of PE, the DCM/PE = 1 : 5 (volume ratio). The ampule was placed in a refrigerator at 25 °C and kept at that temperature for 48 hours. Colorless block was crystals deposited in the glass ampule. The data were collected on a Bruker D8 Venture CCD diffractometer.

A good-quality single-crystal of **3ka** was respectively picked carefully and their diffraction intensity data were collected on a Bruker Apex II diffractometer equipped with CCD two-dimensional detector using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150.0 K. Routine Lorentz and polarization corrections were applied and a multi-scan absorption correction was utilized with the SADABS program. Direct methods were used to solve the structures, refined on F^2 by full-matrix least-squares method, using the SHELXTL-97 program. All H atoms connected to C atoms were generated geometrically and refined isotropically as a riding model using the default Olex2 parameters.

The ellipsoid contour 30% probability levels in the caption for the image of the structure.



3ka CCDC: 2297295

Figure S6: Single crystal structure of **3ka**

Table S12 Crystal data and structure refinement for **3ka.**	
Identification code	**3ka**
CCDC	2297295
Empirical formula	$C_{20}H_{22}O_5S$
Formula weight	374.43
Temperature/K	150.0
Crystal system	monoclinic
Space group	C2/c
a/Å	21.549(3)
b/Å	10.8252(14)
c/Å	17.856(3)
α/°	90
β/°	113.929(4)
γ/°	90
Volume/Å^3	3807.4(9)

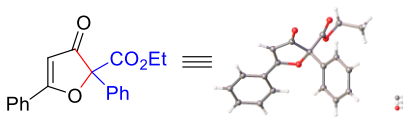
Z	8
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	0.197
F(000)	1584.0
Crystal size/mm^3	0.12 × 0.09 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.136 to 51.994
Index ranges	-26 ≤ h ≤ 25, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	20858
Independent reflections	3739 [R_{int} = 0.0536, R_{sigma} = 0.0374]
Data/restraints/parameters	3739/0/237
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0937
Final R indexes [all data]	R_1 = 0.0624, wR_2 = 0.1089
Largest diff. peak/hole / e Å^{-3}	0.24/-0.33

Crystallographic Data for Compound 4aa

Crystallization of **4aa** (45 mg) was dissolved in 1 mL of DCM. Then **4aa** were sealed in a 6.5 cm glass ampule with 5 mL of PE, the DCM/PE = 1 : 5 (volume ratio). The ampule was placed in a refrigerator at 25 °C and kept at that temperature for 48 hours. Colorless block was crystals deposited in the glass ampule. The data were collected on a Bruker D8 Venture CCD diffractometer.

A good-quality single-crystal of **4aa** was respectively picked carefully and their diffraction intensity data were collected on a Bruker Apex II diffractometer equipped with CCD two-dimensional detector using monochromated Mo Kα radiation (λ = 0.71073 Å) at 296.3 K. Routine Lorentz and polarization corrections were applied and a multi-scan absorption correction was utilized with the SADABS program. Direct methods were used to solve the structures, refined on F^2 by full-matrix least-squares method, using the SHELXTL-97 program. All H atoms connected to C atoms were generated geometrically and refined isotropically as a riding model using the default Olex2 parameters.

The ellipsoid contour 30% probability levels in the caption for the image of the structure.



4aa CCDC: 2245771

Figure S7: Single crystal structure of **4aa**

Table S13 Crystal data and structure refinement for **4aa.**

Identification code	**4aa**
CCDC	2245771
Empirical formula	$C_{19}H_{16}O_4$
Formula weight	308.32
Temperature/K	296.3
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9362(6)
b/Å	17.7920(10)
c/Å	8.2146(4)
α/°	90
β/°	108.127(2)
γ/°	90
Volume/Å^3	1519.04(14)
Z	4
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.094
F(000)	648.0
Crystal size/mm^3	0.25 × 0.21 × 0.2
Radiation	MoK*α* (λ = 0.71073)
2Θ range for data collection/°	3.918 to 51.996
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 19, -10 ≤ l ≤ 9
Reflections collected	14415
Independent reflections	2977 [R_{int} = 0.0713, R_{sigma} = 0.0515]
Data/restraints/parameters	2977/0/209
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.0898
Final R indexes [all data]	R_1 = 0.0774, wR_2 = 0.1062
Largest diff. peak/hole / e Å^{-3}	0.18/-0.26

References

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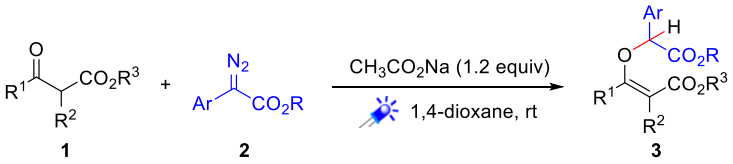
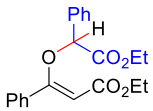
Typical Experimental Procedure and Data of the *Z*-Enol Ethers 3



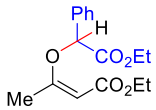
1 2 3

To a 5 mL tube with a stir bar was added β-ketoesters compounds **1** (0.4 mmol, 1 equiv), aryl diazoacetates **2** (0.48 mmol, 1.2 equiv) and 1,4-dioxane (2 mL), followed by CH_3CO_2Na (0.48 mmol, 1.2 equiv, 39.4 mg). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired *Z*-enol ethers **3**.



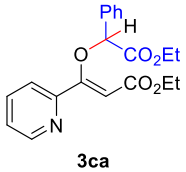
3aa

Ethyl (*Z*)-3-(2-ethoxy-2-oxo-1-phenylethoxy)-3-phenylacrylate (**3aa,** new compound): 121.8 mg of **3aa** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 86% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4 H), 7.44 – 7.31 (m, 6 H), 5.92 (s, 1 H), 5.57 (s, 1 H), 4.39 – 4.00 (m, 4 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.15 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1, 165.1, 164.9, 135.1, 134.8, 130.3, 128.9, 128.4, 128.4, 127.7, 127.6, 101.2, 81.2, 61.3, 59.8, 14.2, 13.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{23}O_5$ 355.1540, found 355.1532.



3ba

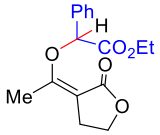
Ethyl (*Z*)-3-(2-ethoxy-2-oxo-1-phenylethoxy)but-2-enoate (**3ba,** new compound): 85.3 mg of **3ba** was obtained from **1b** (52.0 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 73% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 – 7.56 (m, 2 H), 7.48 – 7.31 (m, 3 H), 6.04 (s, 1 H), 5.01 (s, 1 H), 4.25 – 3.90 (m, 4 H), 2.01 (s, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.4, 166.0, 164.1, 135.5, 128.8, 128.5, 127.1, 97.0, 77.2, 61.5, 58.6, 19.1, 14.3, 13.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_5$ 315.1203, found 315.1200.



3ca

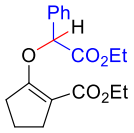
Ethyl (*Z*)-3-(2-ethoxy-2-oxo-1-phenylethoxy)-3-(pyridin-2-yl)acrylate (**3ca,** new compound): 86.6 mg of **3ca** was obtained from **1c** (77.2 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 61% yield. Purified by column

chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.4 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.60 (m, 1 H), 7.49 – 7.39 (m, 2 H), 7.24 (m, 3 H), 7.20 – 7.11 (m, 1 H), 6.48 (s, 1 H), 6.36 (s, 1 H), 4.23 – 3.87 (m, 4 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 1.04 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.6, 165.4, 161.8, 152.7, 148.9, 136.7, 135.3, 129.0, 128.5, 127.6, 124.5, 122.2, 100.8, 82.1, 61.4, 60.1, 14.2, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{21}NNaO_5$ 378.1312, found 378.1310.



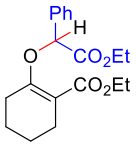
3da

Ethyl (*Z*)-2-(1-(2-oxodihydrofuran-3(2 H)-ylidene)ethoxy)-2-phenylacetate (**3da,** new compound): 75.4 mg of **3da** was obtained from **1d** (51.2 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 65% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.52 – 7.36 (m, 5 H), 6.08 (s, 1 H), 4.28 – 3.99 (m, 4 H), 3.09 – 2.70 (m, 2 H), 2.37 (t, *J* = 2.1 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 171.6, 169.3 163.1, 135.4, 129.1, 128.9, 127.2, 102.3, 76.2, 64.2, 61.6, 25.4, 13.9, 12.6. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{18}NaO_5$ 313.1046, found 313.1050.



3ea

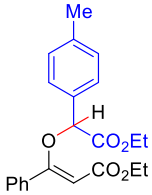
Ethyl 2-(2-ethoxy-2-oxo-1-phenylethoxy)cyclopent-1-ene-1-carboxylate (**3ea,** new compound): 92.9 mg of **3ea** was obtained from **1e** (62.4 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 73% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.59 – 7.50 (m, 2 H), 7.49 – 7.31 (m, 3 H), 5.92 (s, 1 H), 4.25 – 3.97 (m, 4 H), 2.85 – 2.62 (m, 1 H), 2.50 – 2.40 (m, 3 H), 1.97 – 1.63 (m, 2 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 169.3, 166.5, 164.0, 135.4, 128.8, 128.5, 126.9, 105.0, 78.6, 61.4, 58.8, 31.3, 29.1, 18.9, 14.3, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{22}NaO_5$ 341.1359, found 341.1357.



3fa

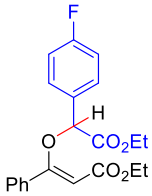
Ethyl 2-(2-ethoxy-2-oxo-1-phenylethoxy)cyclohex-1-ene-1-carboxylate (**3fa,** new compound): 73.0 mg of **3fa** was obtained from **1f** (68.0 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 55% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.58 – 7.50 (m, 2 H), 7.45 – 7.30 (m, 3 H), 5.77 (s, 1 H), 4.21 – 3.92 (m, 4 H), 2.38 – 2.01 (m, 4 H), 1.70 – 1.52 (m, 2 H), 1.46 (q, *J* = 6.3 Hz, 2 H), 1.15 (t, *J* = 6.3 Hz, 3 H), 1.11 (t, *J* = 6.3 Hz, 3

H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 169.6, 167.0, 159.2, 136.1, 128.6, 128.4, 127.2, 108.4, 76.9, 61.1, 59.4, 26.2, 25.2, 22.0, 21.5, 14.1, 13.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{24}NaO_5$ 355.1516, found 355.1510.



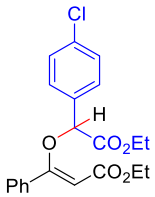
3ab

Ethyl (*Z*)-3-(2-ethoxy-2-oxo-1-(p-tolyl)ethoxy)-3-phenylacrylate (**3ab,** new compound): 129.5 mg of **3ab** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2b** (97.9 mg, 0.48 mmol) in 88% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2 H), 7.46 – 7.31 (m, 5 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 5.88 (s, 1 H), 5.56 (s, 1 H), 4.30 – 3.99 (m, 4 H), 2.34 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.3, 165.2, 165.0, 138.8, 135.0, 132.2, 130.3, 129.2, 128.4, 127.8, 127.6, 101.2, 81.1, 61.3, 59.9, 21.2, 14.3, 13.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{24}NaO_5$ 391.1516, found 391.1511.



3ac

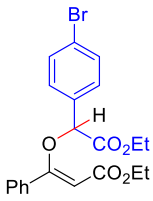
Ethyl (*Z*)-3-(2-ethoxy-1-(4-fluorophenyl)-2-oxoethoxy)-3-phenylacrylate (**3ac,** new compound): 139.9 mg of **3ac** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2c** (99.8 mg, 0.48 mmol) in 94% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 4 H), 7.47 – 7.30 (m, 3 H), 7.04 (t, *J* = 8.5 Hz, 2 H), 5.88 (s, 1 H), 5.57 (s, 1 H), 4.43 – 3.94 (m, 4 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.9, 164.9 (d, $^{2}J_{C\text{-}F}$ = 24.9 Hz), 162.9 (d, $^{1}J_{C\text{-}F}$ = 247.9 Hz), 134.6, 131.0 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 130.3, 129.5 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 128.4, 127.6, 115.5, 115.3, 101.4, 80.3, 61.4, 59.8, 14.2, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.36. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{21}FNaO_5$ 395.1265, found 395.1261.



3ad

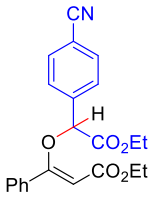
Ethyl (*Z*)-3-(1-(4-chlorophenyl)-2-ethoxy-2-oxoethoxy)-3-phenylacrylate (**3ad,** new compound): 118.0 mg of **3ad** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2d** (107.5 mg, 0.48 mmol) in 76% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (m, 2 H), 7.56 – 7.40 (m, 7 H), 5.94 (s, 1 H), 5.66 (s, 1H), 4.32 – 3.74 (m, 4 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.8, 165.0, 164.8, 134.9, 134.7, 133.7, 130.4, 129.0, 128.7, 128.5, 127.7,

101.5, 80.3, 61.6, 59.9, 14.3, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{21}ClNaO_5$ 411.0970, found 411.0970.



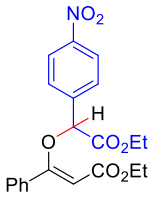
3ae

Ethyl (*Z*)-3-(1-(4-bromophenyl)-2-ethoxy-2-oxoethoxy)-3-phenylacrylate (**3ae,** new compound): 136.8 mg of **3ae** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2e** (129.1 mg, 0.48 mmol) in 79% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 4 H), 7.43 – 7.32 (m, 5 H), 5.87 (s, 1 H), 5.57 (s, 1 H), 4.39 – 3.82 (m, 4 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.7, 165.0, 164.8, 134.6, 134.2, 131.7, 130.4, 129.3, 128.5, 127.7, 123.2, 101.5, 80.4, 61.6, 59.9, 14.3, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{21}BrNaO_5$ 455.0465, found 455.0458.



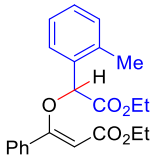
3af

Ethyl (*Z*)-3-(1-(4-cyanophenyl)-2-ethoxy-2-oxoethoxy)-3-phenylacrylate (**3af,** new compound): 95.5 mg of **3af** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2f** (103.2 mg, 0.48 mmol) in 63% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 4 H), 7.56 – 7.48 (m, 2 H), 7.48 – 7.31 (m, 3 H), 5.94 (s, 1 H), 5.58 (s, 1 H), 4.31 – 3.91 (m, 4 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.2, 164.9, 164.8, 140.2, 134.4, 132.3, 130.6, 128.7, 128.2, 127.8, 118.4, 112.8, 101.8, 80.2, 62.0, 60.1, 14.3, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{21}NNaO_5$ 402.1312, found 402.1302.



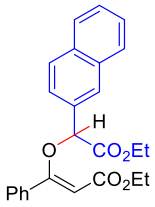
3ag

Ethyl (*Z*)-3-(2-ethoxy-1-(4-nitrophenyl)-2-oxoethoxy)-3-phenylacrylate (**3ag,** new compound): 87.8 mg of **3ag** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2g** (112.8 mg, 0.48 mmol) in 55% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.19 (m, 2 H), 7.81 – 7.74 (m, 2 H), 7.58 – 7.51 (m, 2 H), 7.50 – 7.32 (m, 3 H), 6.01 (s, 1 H), 5.60 (s, 1 H), 4.42 – 3.84 (m, 4 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 167.9, 164.5, 164.2, 147.8, 142.1, 133.7, 130.9, 128.8, 128.7, 127.7, 123.8, 101.0, 79.6, 61.7, 59.7, 14.2, 13.8. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{21}NNaO_7$ 422.1210, found 422.1208.



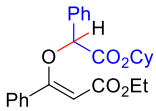
3ah

Ethyl (*Z*)-3-(2-ethoxy-2-oxo-1-(o-tolyl)ethoxy)-3-phenylacrylate (**3ah,** new compound): 98.6 mg of **3ah** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2h** (97.9 mg, 0.48 mmol) in 67% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 – 7.38 (m, 6 H), 7.33 – 7.16 (m, 3 H), 6.14 (s, 1 H), 5.59 (s, 1 H), 4.28 – 3.86 (m, 4 H), 2.23 (s, 3 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 1.06 (t, *J* = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.3, 165.4, 164.9, 136.4, 134.9, 133.8, 130.4, 130.2, 128.8, 128.4, 128.1, 127.8, 126.2, 101.5, 78.0, 61.3, 59.8, 19.0, 14.3, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{24}NaO_5$ 391.1516, found 391.1514.



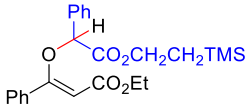
3ai

Ethyl (*Z*)-3-(2-ethoxy-1-(naphthalen-2-yl)-2-oxoethoxy)-3-phenylacrylate (**3ai,** new compound): 114.7 mg of **3ai** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2i** (115.2 mg, 0.48 mmol) in 71% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 – 8.18 (m, 1 H), 8.04 – 7.92 (m, 2 H), 7.68 (d, *J* = 7.1 Hz, 1 H), 7.64 – 7.52 (m, 5 H), 7.50 – 7.35 (m, 3 H), 6.67 (s, 1 H), 5.68 (s, 1 H), 4.17 – 3.98 (m, 4 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 1.02 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.0, 164.8, 164.5, 134.5, 133.5, 131.1, 130.8, 130.6, 129.9, 128.7, 128.7, 127.6, 127.1, 126.8, 126.1, 125.4, 123.7, 80.0, 79.0, 61.4, 59.7, 14.2, 13.8. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{25}H_{24}NaO_5$ 427.1516, found 427.1517.



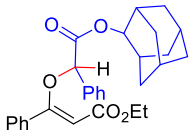
3aj

Ethyl (*Z*)-3-(2-(cyclohexyloxy)-2-oxo-1-phenylethoxy)-3-phenylacrylate (**3aj,** new compound): 135.5 mg of **3aj** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2j** (117.1 mg, 0.48 mmol) in 83% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 – 7.61 (m, 2 H), 7.57 – 7.28 (m, 8 H), 5.98 (s, 1 H), 5.64 (s, 1 H), 4.79 – 4.52 (m, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 1.73 – 1.34 (m, 5 H), 1.33 – 1.10 (m, 8 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 168.0, 164.6, 164.3, 135.2, 134.3, 130.7, 129.1, 128.6, 128.6, 127.6, 127.4, 99.8, 80.6, 73.1, 59.5, 30.6, 30.4, 24.7, 22.6, 22.5, 14.12. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{25}H_{28}NaO_5$ 431.1829, found 431.1830.



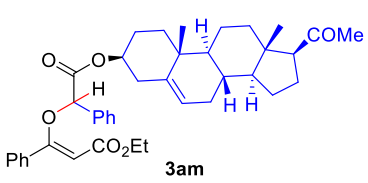
3ak

Ethyl (*Z*)-3-(2-oxo-1-phenyl-2-(2-(trimethylsilyl)ethoxy)ethoxy)-3-phenylacrylate (**3ak,** new compound): 124.4 mg of **3ak** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2k** (125.8 mg, 0.48 mmol) in 73% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 – 7.56 (m, 2 H), 7.53 – 7.34 (m, 8 H), 5.97 (s, 1 H), 5.65 (s, 1 H), 4.24 – 3.94 (m, 4 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 0.80 (t, *J* = 8.3 Hz, 2 H), -0.07 (s, 9 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 168.7, 164.5, 164.4, 135.0, 134.4, 130.7, 129.2, 128.7, 128.7, 127.6, 127.6, 100.0, 80.7, 63.4, 59.6, 16.6, 14.2, -1.6. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{24}H_{30}NaO_5Si$ 449.1755, found 449.1747.



3al

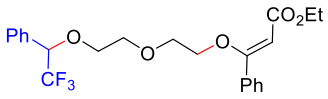
Ethyl (*Z*)-3-(2-(((1R,5R,7S)-adamantan-2-yl)oxy)-2-oxo-1-phenylethoxy)-3-phenylacrylate (**3al,** new compound): 167.4 mg of **3al** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2l** (142.1 mg, 0.48 mmol) in 91% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 – 7.61 (m, 2 H), 7.58 – 7.53 (m, 2 H), 7.50 – 7.35 (m, 6 H), 6.04 (s, 1 H), 5.61 (s, 1 H), 4.77 (s, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 1.83 – 1.58 (m, 11 H), 1.55 – 1.48 (m, 1 H), 1.44 – 1.36 (m, 1 H), 1.34 – 1.28 (m, 1 H), 1.23 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 168.0, 164.7, 164.3, 135.4, 134.4, 130.7, 129.1, 128.7, 128.6, 127.6, 127.3, 99.7, 80.7, 77.7, 59.5, 36.6, 35.5, 35.5, 31.2, 31.1, 31.0, 30.9, 26.5, 26.3, 14.2. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{29}H_{32}NaO_5$ 483.2142, found 483.2136.



3am

Ethyl (*Z*)-3-(2-(((3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-oxo-1-phenylethoxy)-3-phenylacrylate (**3am,** new compound): 124.8 mg of **3am** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2m** (220.8 mg, 0.48 mmol) in 50% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 66.7 – 69.1 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 – 7.60 (m, 2 H), 7.57 – 7.51 (m, 2 H), 7.50 – 7.34 (m, 6 H), 6.08 – 5.90 (m, 1 H), 5.67 (d, *J* = 4.3 Hz, 1 H), 5.43 – 5.17 (m, 1 H), 4.52 – 4.33 (m, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.59 – 2.46 (m, 1 H), 2.22 – 2.11 (m, 1 H), 2.07 – 1.89 (m, 7 H), 1.86 – 1.45 (m, 7 H), 1.43 – 1.28 (m, 4 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 1.11 – 0.86

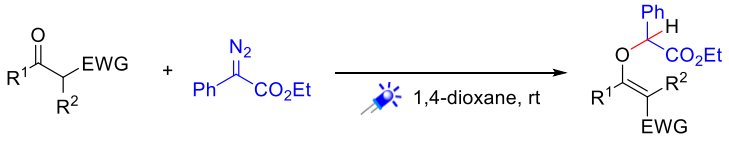
(m, 6 H), 0.51 (s, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 208.1, 168.0, 164.6, 164.5, 164.3, 139.0, 138.8, 135.0, 134.5, 130.6, 129.1, 128.6, 127.6, 127.3, 122.2, 99.8, 80.7, 74.5, 62.5, 59.5, 55.9, 49.2, 43.1, 37.8, 37.0, 36.2, 36.0, 31.2, 31.1, 27.0, 23.9, 22.2, 20.5, 18.8, 14.2, 12.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{40}H_{48}NaO_6$ 647.3343, found 647.3334.



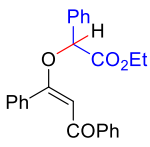
3an

Ethyl (*Z*)-3-phenyl-3-(2-(2-(2,2,2-trifluoro-1-phenylethoxy)ethoxy)ethoxy)acrylate (**3an,** new compound): 113.9 mg of **3an** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2n** (89.3 mg, 0.48 mmol) in 65% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 2 H), 7.52 – 7.31 (m, 8 H), 5.64 (s, 1 H), 4.77 (q, *J* = 6.7 Hz, 1 H), 4.35 – 4.11 (m, 4 H), 3.84 – 3.73 (m, 2 H), 3.73 – 3.62 (m, 4 H), 1.30 (t, *J* = 7.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 165.0, 135.0, 132.7, 130.3, 129.2, 128.4, 128.3, 128.1, 127.4, 123.7 (q, $^1J_{C\text{-}F}$ = 281.7 Hz), 100.2, 79.9 (q, $^2J_{C\text{-}F}$ = 30.9 Hz), 72.2, 70.4, 70.3, 69.7, 59.6, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.62. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{23}H_{25}F_3KO_5$ 477.1286, found 477.1295.

Typical Experimental Procedure and Data of the *E*-Enol Ethers 3



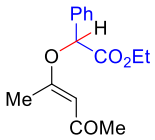
To a 5 mL tube with a stir bar was added 1,3-dicarbonyl compounds **1** (0.4 mmol, 1 equiv), ethyl 2-diazo-2-phenylacetate **2a** (0.48 mmol, 1.2 equiv) and 1,4-dioxane (2 mL). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 24 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired *E*-enol ethers **3**.



3ga

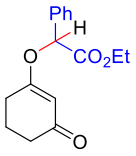
Ethyl (*E*)-2-((3-oxo-1,3-diphenylprop-1-en-1-yl)oxy)-2-phenylacetate (**3ga,** new compound): 139.0 mg of **3ga** was obtained from **1g** (89.6 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 90% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 82.3 – 84.2 ºC. ^1H NMR (400 MHz, DMSO-d_6) δ 7.89 – 7.75 (m, 2 H), 7.68 – 7.53 (m, 3 H), 7.52 – 7.28 (m, 10 H), 6.44 (s, 1 H), 6.37 (s, 1 H), 4.32 – 4.10 (m, 2 H), 1.14 (t, *J* = 7.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-

d_6) δ 189.2, 168.8, 167.2, 138.7, 134.9, 134.6, 132.5, 129.9, 129.3, 129.1, 128.9, 128.5, 128.0, 127.9, 127.4, 101.1, 77.7, 61.6, 14.0. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{25}H_{22}NaO_4$ 409.1410, found 409.1408.



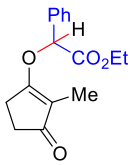
3ha

Ethyl (*E*)-2-((4-oxopent-2-en-2-yl)oxy)-2-phenylacetate (**3ha,** new compound): 90.1 mg of **3ha** was obtained from **1h** (40.0 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 86% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 – 7.49 (m, 2 H), 7.48 – 7.35 (m, 3 H), 5.88 (s, 1 H), 5.62 (s, 1 H), 4.32 – 3.82 (m, 2 H), 2.25 (s, 3 H), 2.07 (s, 3 H), 1.15 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.0, 168.5, 168.5, 134.5, 129.3, 128.9, 127.3, 101.8, 76.9, 61.4, 31.9, 18.9, 13.9. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{18}NaO_4$ 285.1097, found 285.1099.



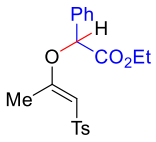
3ia

Ethyl 2-((3-oxocyclohex-1-en-1-yl)oxy)-2-phenylacetate (**3ia,** new compound): 87.7 mg of **3ia** was obtained from **1i** (44.8 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 80% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2 H), 7.38 (m, 3 H), 5.43 (s, 1 H), 5.28 (s, 1 H), 4.26 – 4.07 (m, 2 H), 2.68 – 2.54 (m, 1 H), 2.55 – 2.44 (m, 1 H), 2.39 – 2.27 (m, 2 H), 2.10 – 1.83 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.1, 175.9, 168.0, 133.7, 129.2, 128.7, 126.9, 104.1, 77.9, 61.8, 36.5, 28.7, 20.8, 13.7. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{18}NaO_4$ 297.1097, found 297.1100.



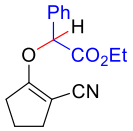
3ja

Ethyl 2-((2-methyl-3-oxocyclopent-1-en-1-yl)oxy)-2-phenylacetate (**3ja,** new compound): 94.3 mg of **3ja** was obtained from **1j** (44.8 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 86% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.36 (m, 5 H), 6.18 (s, 1 H), 4.27 – 4.00 (m, 2 H), 2.81 – 2.53 (m, 2 H), 2.40 – 2.18 (m, 2 H), 1.54 (s, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 204.0, 182.6, 168.9, 135.1, 129.3, 129.0, 127.3, 115.9, 77.7, 61.7, 33.4, 24.7, 13.9, 6.0. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{18}NaO_4$ 297.1097, found 297.1098.



3ka

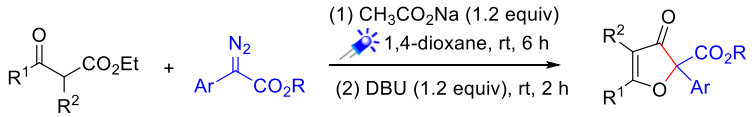
Ethyl (*E*)-2-phenyl-2-((1-tosylprop-1-en-2-yl)oxy)acetate (**3ka,** new compound): 121.2 mg of **3ka** was obtained from **1k** (84.8 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 81% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 63.5 – 64.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2 H), 7.47 – 7.33 (m, 5 H), 7.32 – 7.20 (m, 2 H), 5.51 (s, 1 H), 5.33 (s, 1 H), 4.30 – 3.92 (m, 2 H), 2.42 (s, 3 H), 2.33 (s, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.9, 167.6, 143.5, 140.5, 133.5, 129.6, 129.4, 128.9, 126.9, 126.5, 105.7, 78.5, 62.0, 21.5, 18.1, 13.9. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{20}H_{22}NaO_5S$ 397.1080, found 397.1081.



3la

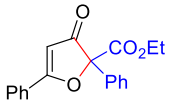
Ethyl 2-((2-cyanocyclopent-1-en-1-yl)oxy)-2-phenylacetate (**3la,** new compound): 90.0 mg of **3la** was obtained from **1l** (43.6 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 83% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2 H), 7.44 – 7.33 (m, 3 H), 5.96 (s, 1 H), 4.30 – 4.13 (m, 2 H), 2.74 – 2.43 (m, 4 H), 2.07 – 1.82 (m, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.0, 168.5, 134.4, 129.2, 128.7, 127.1, 116.5, 81.9, 79.7, 62.1, 33.2, 31.7, 20.1, 13.9. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{16}H_{17}NNaO_3$ 294.1101, found 294.1094.

Typical Experimental Procedure and Data of the Furan-3(2H)-One 4



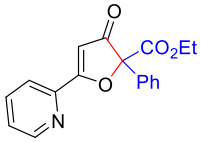
1 2 4

To a 5 mL tube with a stir bar was added β-Ketoesters compounds **1** (0.4 mmol, 1 equiv), aryl diazoacetates **2** (0.48 mmol, 1.2 equiv) and 1,4-dioxane (2 mL), followed by CH_3CO_2Na (0.48 mmol, 1.2 equiv, 39.4 mg). Then tube was tightly screw capped. The mixture was stirred at room temperature under the blue LEDs for 6 h. Then DBU (0.48 mmol, 1.2 equiv, 73.1 mg) was added to the above reaction, and the mixture was stirred at room temperature for another 2 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (PE/EtOAc = 20/1), affording the desired furan-3(2H)-ones **4**.



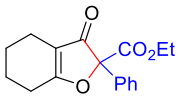
4aa

Ethyl 3-oxo-2,5-diphenyl-2,3-dihydrofuran-2-carboxylate (**4aa,** new compound): 99.8 mg of **4aa** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 81% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 64.6 – 65.7 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2 H), 7.85 – 7.76 (m, 2 H), 7.68 – 7.50 (m, 3 H), 7.47 – 7.35 (m, 3 H), 6.04 (s, 1 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1, 185.2, 164.8, 133.5, 133.2, 129.0, 128.9, 128.4, 128.2, 127.3, 125.7, 99.2, 90.5, 62.9, 13.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{16}NaO_4$ 331.0941, found 331.0937.



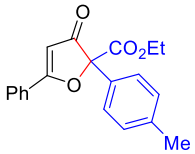
4ca

Ethyl 3-oxo-2-phenyl-5-(pyridin-2-yl)-2,3-dihydrofuran-2-carboxylate (**4ca,** new compound): 68.0 mg of **4ca** was obtained from **1c** (77.2 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 55% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 – 8.72 (m, 1 H), 8.23 (d, *J* = 7.8 Hz, 1 H), 8.11 (m, 1 H), 7.77 – 7.63 (m, 3 H), 7.52 – 7.37 (m, 3 H), 6.54 (s, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.4, 184.6, 164.7, 151.2, 146.5, 138.4, 133.4, 129.6, 129.0, 128.2, 126.0, 123.0, 101.5, 90.9, 63.3, 14.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_4$ 310.1074, found 310.1084.



4fa

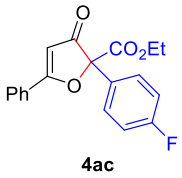
Ethyl 3-oxo-2-phenyl-2,3,4,5,6,7-hexahydrobenzofuran-2-carboxylate (**4fa,** new compound): 49.2 mg of **4fa** was obtained from **1f** (68.0 mg, 0.4 mmol) and **2a** (91.2 mg, 0.48 mmol) in 43% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (m, 2 H), 7.41 (m, 3 H), 4.27 – 4.04 (m, 2 H), 2.71 – 2.59 (m, 2 H), 2.20 – 1.94 (m, 2 H), 1.78 (q, *J* = 6.0 Hz, 2 H), 1.69 – 1.49 (m, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 194.3, 189.1, 164.7, 133.5, 128.9, 128.4, 125.6, 110.4, 89.0, 62.5, 25.2, 21.2, 21.1, 18.0, 13.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{18}NaO_4$ 309.1097, found 309.1087.



4ab

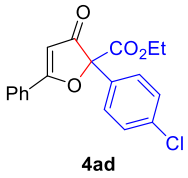
Ethyl 3-oxo-5-phenyl-2-(p-tolyl)-2,3-dihydrofuran-2-carboxylate (**4ab,** new compound): 94.0 mg of **4ab** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2b** (97.9 mg, 0.48 mmol) in 73% yield. Purified by column

chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 2 H), 7.69 – 7.64 (m, 2 H), 7.64 – 7.57 (m, 1 H), 7.57 – 7.50 (m, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 6.03 (s, 1 H), 4.39 – 4.14 (m, 2 H), 2.35 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.4, 185.2, 165.0, 138.9, 133.2, 130.6, 129.1, 129.0, 128.3, 127.4, 125.7, 99.2, 90.6, 62.8, 21.1, 13.9. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{20}H_{18}NaO_4$ 345.1097, found 345.1089.



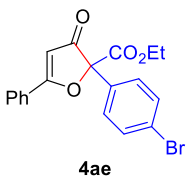
4ac

Ethyl 2-(4-fluorophenyl)-3-oxo-5-phenyl-2,3-dihydrofuran-2-carboxylate (**4ac,** new compound): 106.9 mg of **4ac** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2c** (99.8 mg, 0.48 mmol) in 82% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2 H), 7.84 – 7.76 (m, 2 H), 7.68 – 7.59 (m, 1 H), 7.55 (dd, *J* = 8.3, 6.7 Hz, 2 H), 7.17 – 7.01 (m, 2 H), 6.03 (s, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1, 185.3, 164.7, 163.1 (d, $^{1}J_{C\text{-}F}$ = 248.3 Hz), 133.4, 129.3 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 129.1, 128.2, 127.8 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 127.4, 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 99.2, 89.9, 63.0, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.98. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{19}H_{15}FNaO_4$ 349.0847, found 349.0844.



4ad

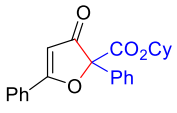
Ethyl 2-(4-chlorophenyl)-3-oxo-5-phenyl-2,3-dihydrofuran-2-carboxylate (**4ad,** new compound): 88.9 mg of **4ad** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2d** (107.5 mg, 0.48 mmol) in 65% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 97.5 – 99.1 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2 H), 7.80 – 7.73 (m, 2 H), 7.68 – 7.60 (m, 1 H), 7.55 (m, 2 H), 7.43 – 7.30 (m, 2 H), 6.03 (s, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.8, 185.4, 164.5, 135.1, 133.4, 131.8, 129.1, 128.5, 128.1, 127.4, 127.2, 99.1, 89.8, 63.1, 13.9. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{19}H_{15}ClNaO_4$ 365.0551, found 365.0552.



4ae

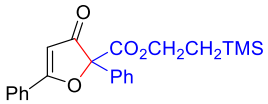
Ethyl 2-(4-bromophenyl)-3-oxo-5-phenyl-2,3-dihydrofuran-2-carboxylate (**4ae,** new compound): 73.3 mg of **4ae** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2e** (129.1 mg, 0.48 mmol) in 48% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 92.3 – 94.7 ºC

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.00 (m, 2 H), 7.79 – 7.56 (m, 7 H), 6.62 (s, 1 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 195.8, 185.6, 164.6, 134.3, 132.9, 131.9, 129.8, 128.2, 127.9, 127.9, 123.1, 99.6, 89.6, 63.4, 14.2. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{15}BrNaO_4$ 409.0046, found 409.0037.



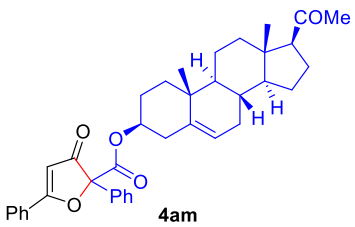
4aj

Cyclohexyl 3-oxo-2,5-diphenyl-2,3-dihydrofuran-2-carboxylate (**4aj,** new compound): 115.8 mg of **4aj** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2j** (117.1 mg, 0.48 mmol) in 80% yield. Purified by column chromatography (PE/EtOAc = 20/1); slightly yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 – 8.04 (m, 2 H), 7.80 – 7.55 (m, 5 H), 7.50 – 7.25 (m, 3 H), 6.59 (s, 1 H), 4.95 – 4.68 (m, 1 H), 1.72 – 1.59 (m, 2 H), 1.56 – 1.18 (m, 8 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 189.0, 177.9, 156.1, 125.4, 125.2, 120.8, 120.6, 119.9, 119.0, 117.4, 90.6, 82.6, 66.8, 22.3, 22.3, 16.8, 14.3. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{23}H_{22}NaO_4$ 385.1410, found 385.1400.



4ak

2-(Trimethylsilyl)ethyl 3-oxo-2,5-diphenyl-2,3-dihydrofuran-2-carboxylate (**4ak,** new compound): 121.6 mg of **4ak** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2k** (125.8 mg, 0.48 mmol) in 80% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 89.7 – 91.2 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2 H), 7.85 – 7.74 (m, 2 H), 7.65 – 7.56 (m, 1 H), 7.54 (m, 2 H), 7.45 – 7.33 (m, 3 H), 6.03 (s, 1 H), 4.38 – 4.20 (m, 2 H), 1.05 – 0.98 (m, 2 H), -0.01 (s, 9 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1, 185.1, 164.9, 133.5, 133.2, 129.0, 128.9, 128.3, 128.2, 127.3, 125.7, 99.2, 90.5, 65.4, 17.1, -1.7. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{24}NaO_4Si$ 403.1336, found 403.1334.



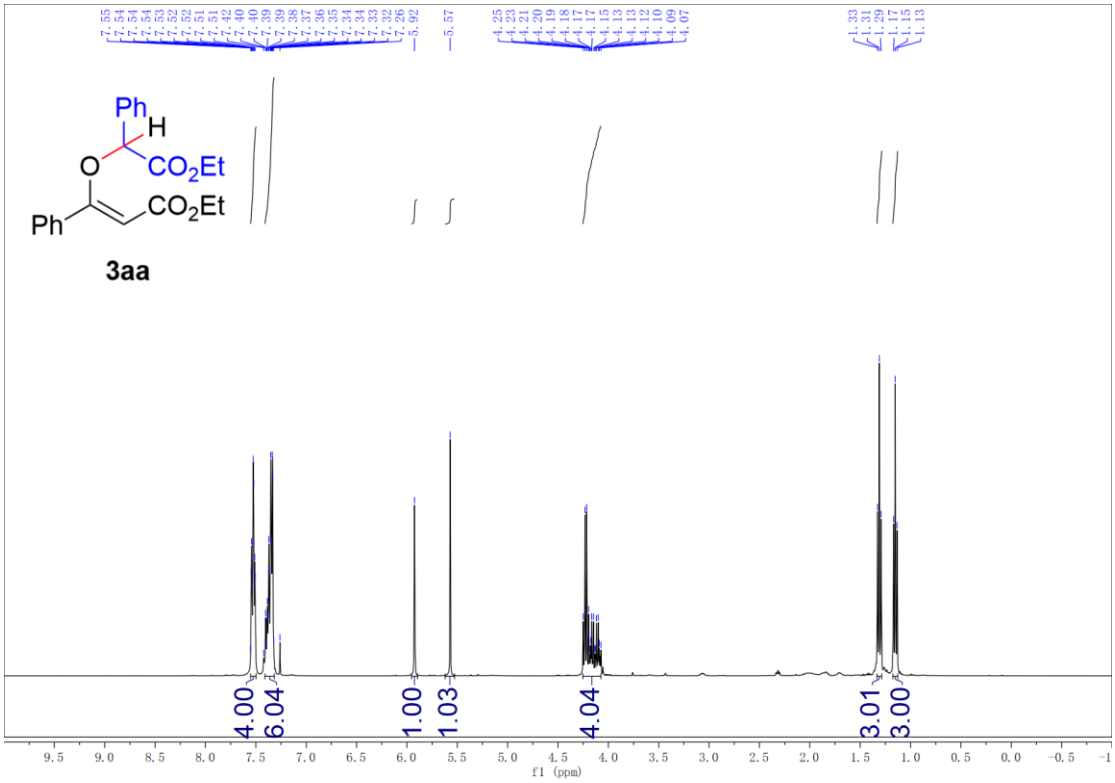
4am

(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-oxo-2,5-diphenyl-2,3-dihydrofuran-2-carboxylate (**4am,** new compound): 94.8 mg of **4am** was obtained from **1a** (76.8 mg, 0.4 mmol) and **2m** (220.8 mg, 0.48 mmol) in 41% yield. Purified by column chromatography (PE/EtOAc = 20/1); white solid; mp 114.8 – 117.2 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 – 8.02 (m, 2 H), 7.79 – 7.58 (m, 5 H), 7.53 – 7.38 (m, 3 H), 6.58 (s, 1 H), 5.35 (s, 1 H), 4.69 – 4.46 (m, 1 H),

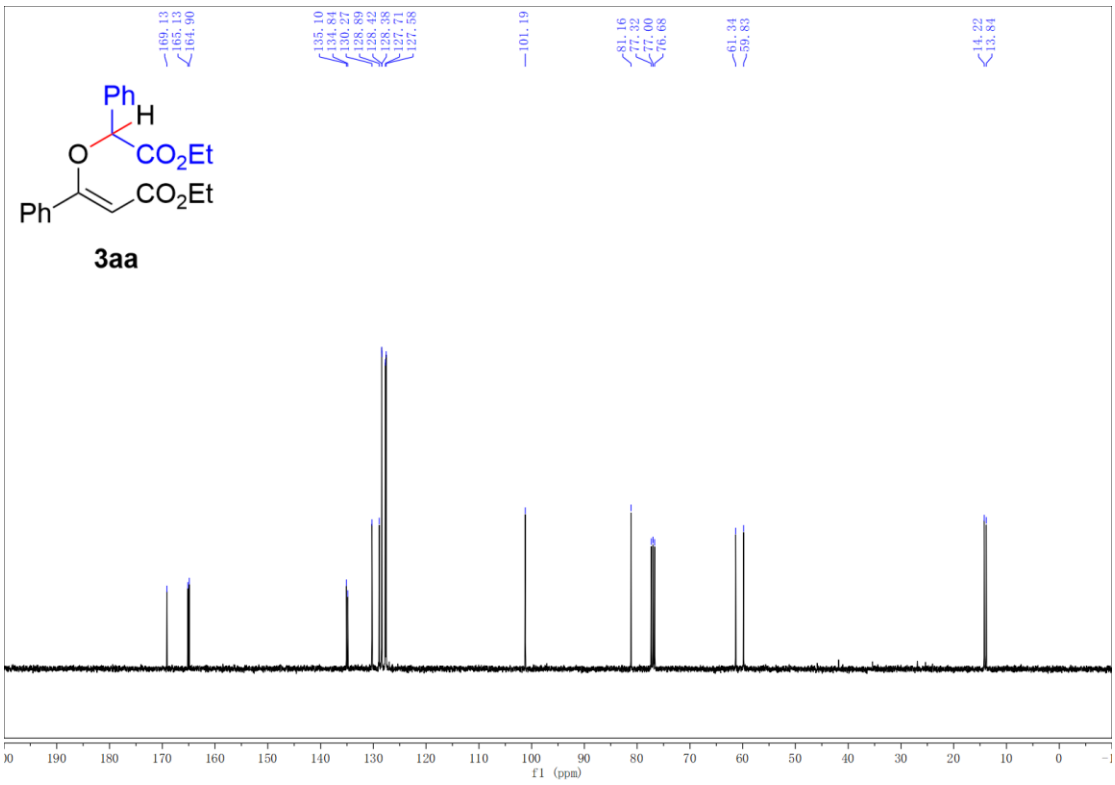
2.62 – 2.50 (m, 1 H), 2.32 – 2.14 (m, 2 H), 2.07 – 1.91 (m, 6 H), 1.80 – 1.67 (m, 1 H), 1.62 – 1.28 (m, 9 H), 1.15 – 0.88 (m, 7 H), 0.50 (s, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 208.3, 195.6, 184.9, 163.8, 138.8, 133.6, 133.2, 129.3, 129.0, 128.4, 127.6, 127.3, 125.5, 122.4, 99.2, 89.8, 76.1, 62.5, 55.9, 54.9, 49.1, 43.2, 37.8, 37.1, 36.2, 36.0, 31.2, 31.1, 27.0, 24.0, 22.2, 20.5, 18.9, 12.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{43}O_5$ 579.3105, found 579.3111.

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of All the Products

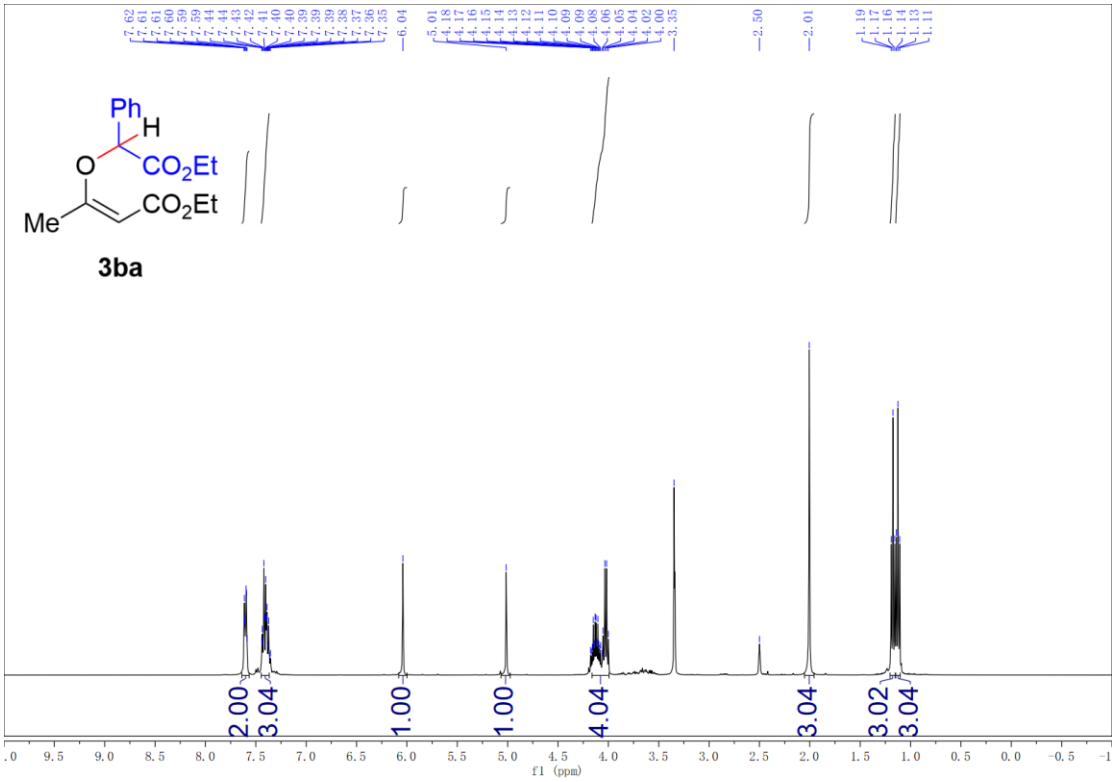
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3aa**



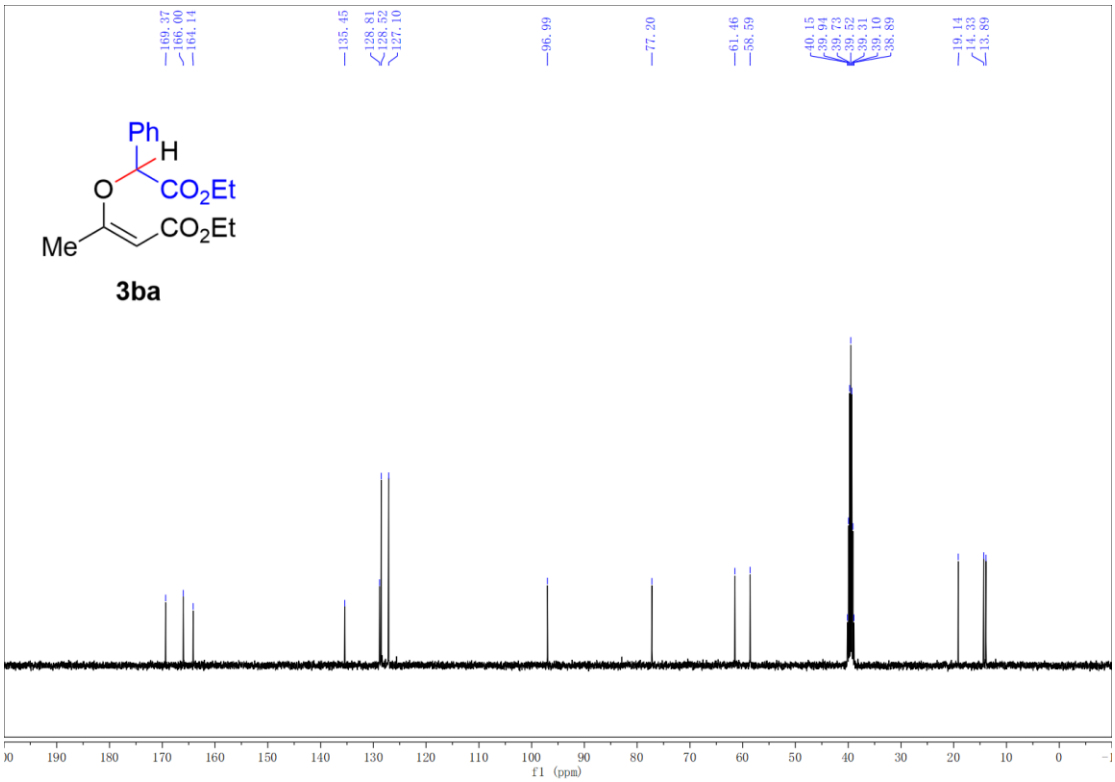
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) Spectrum of **3aa**



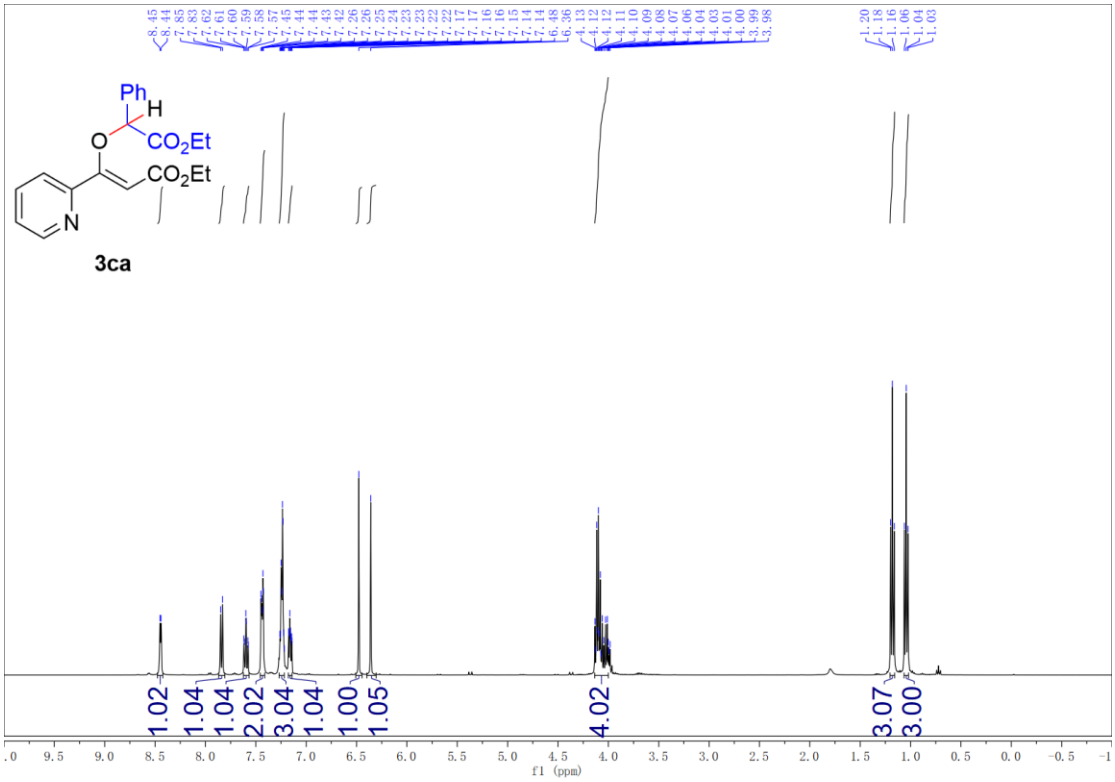
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ba**



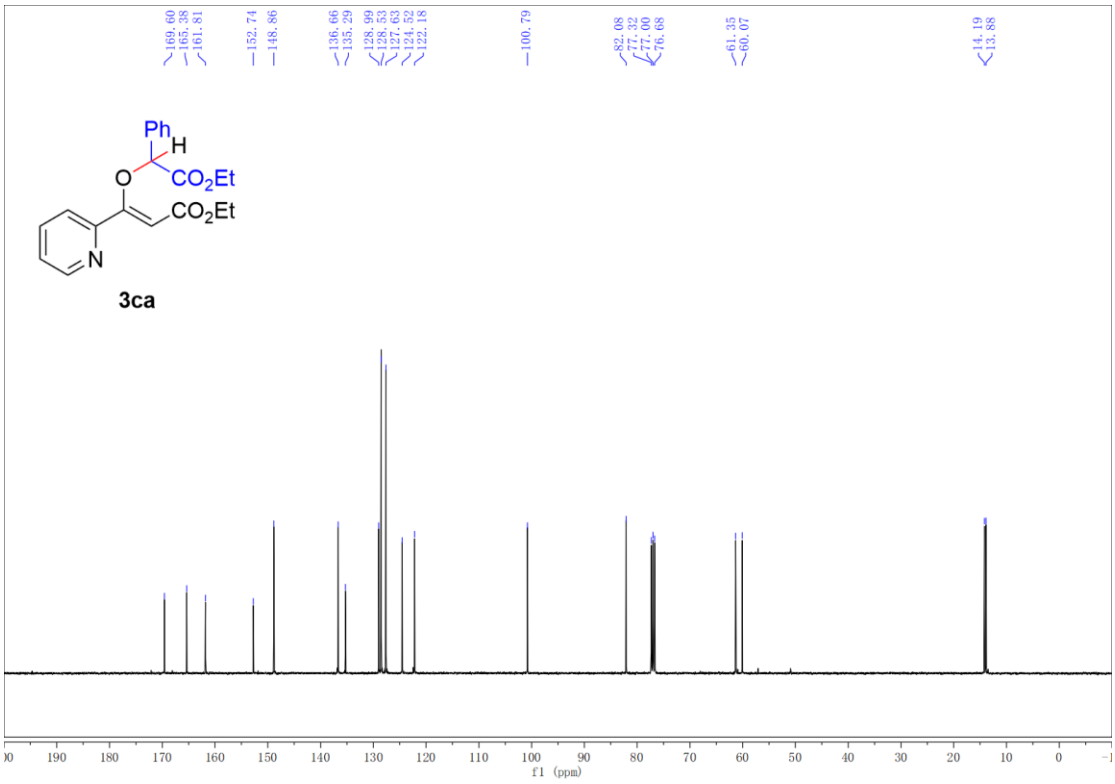
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ba**



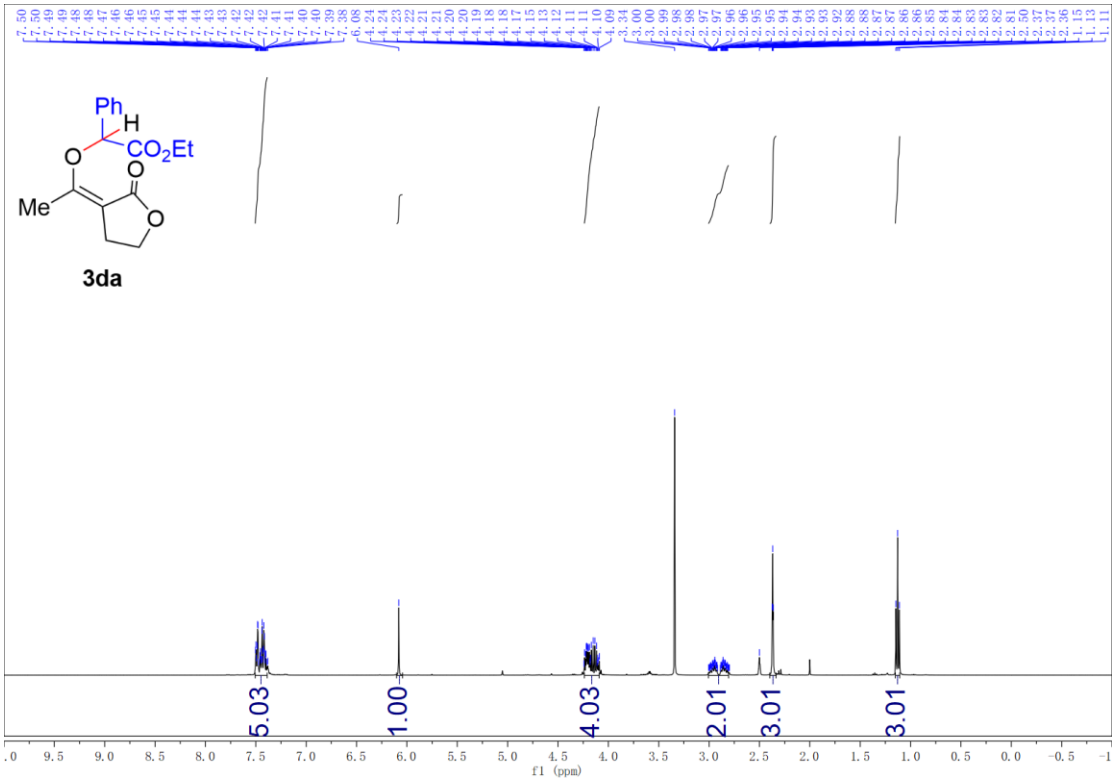
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ca**



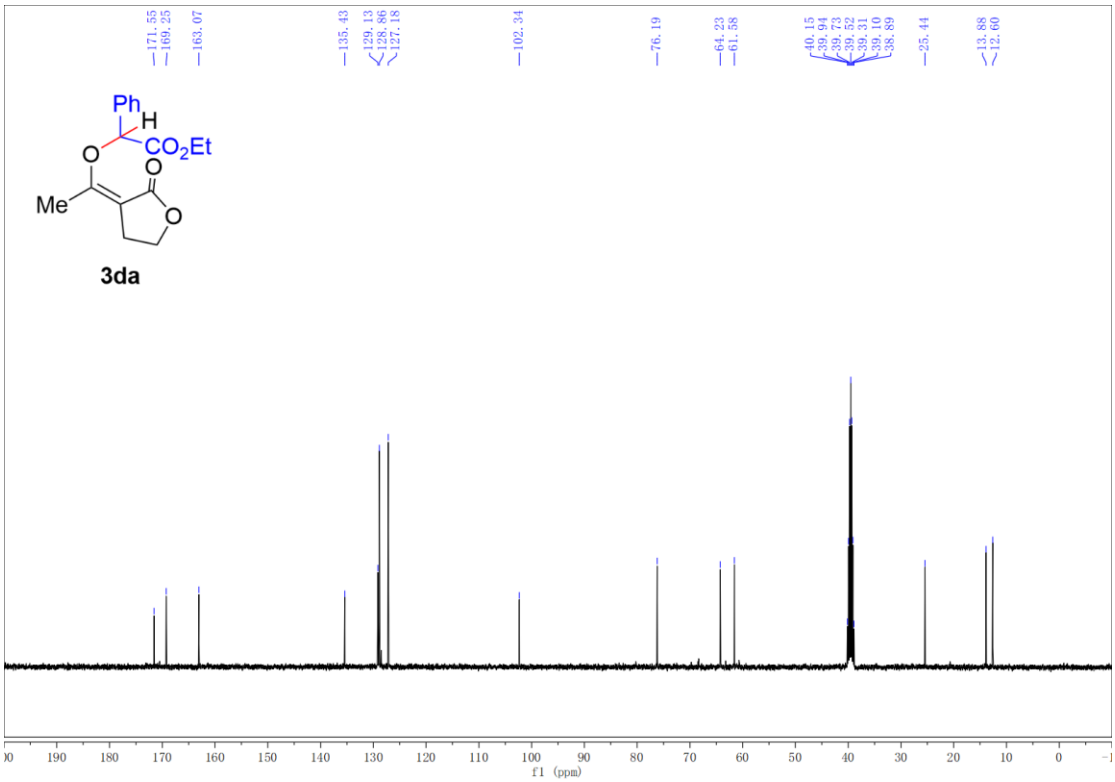
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ca**



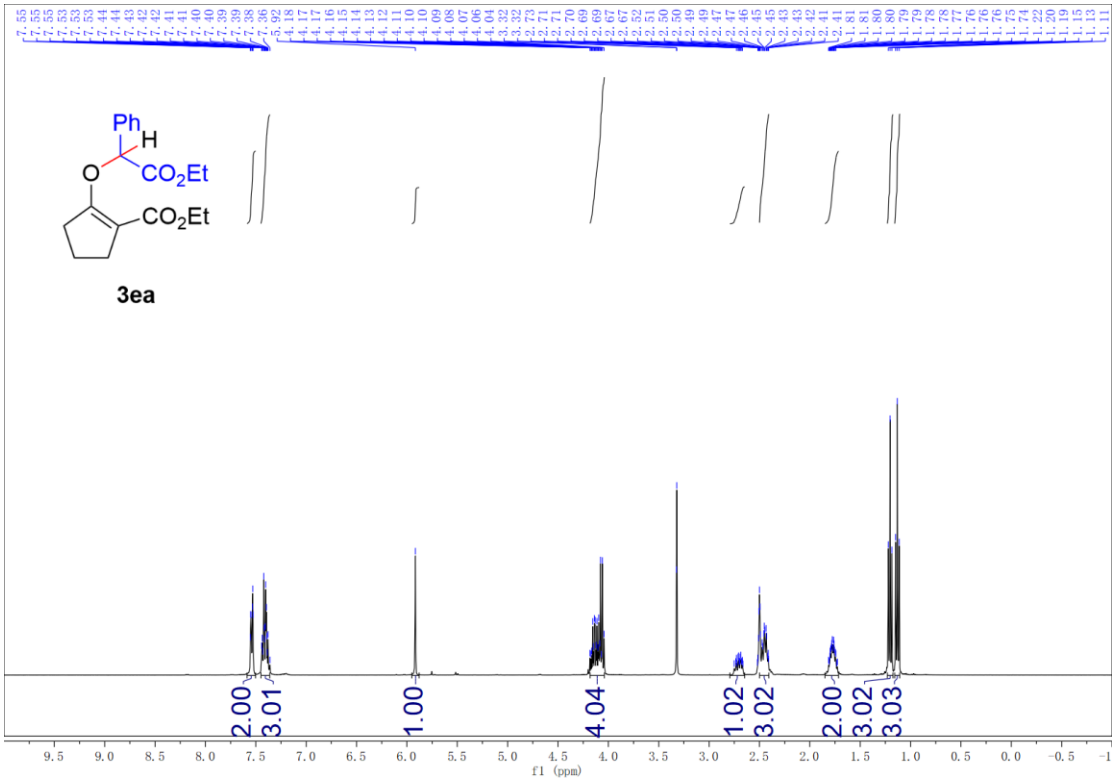
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3da**



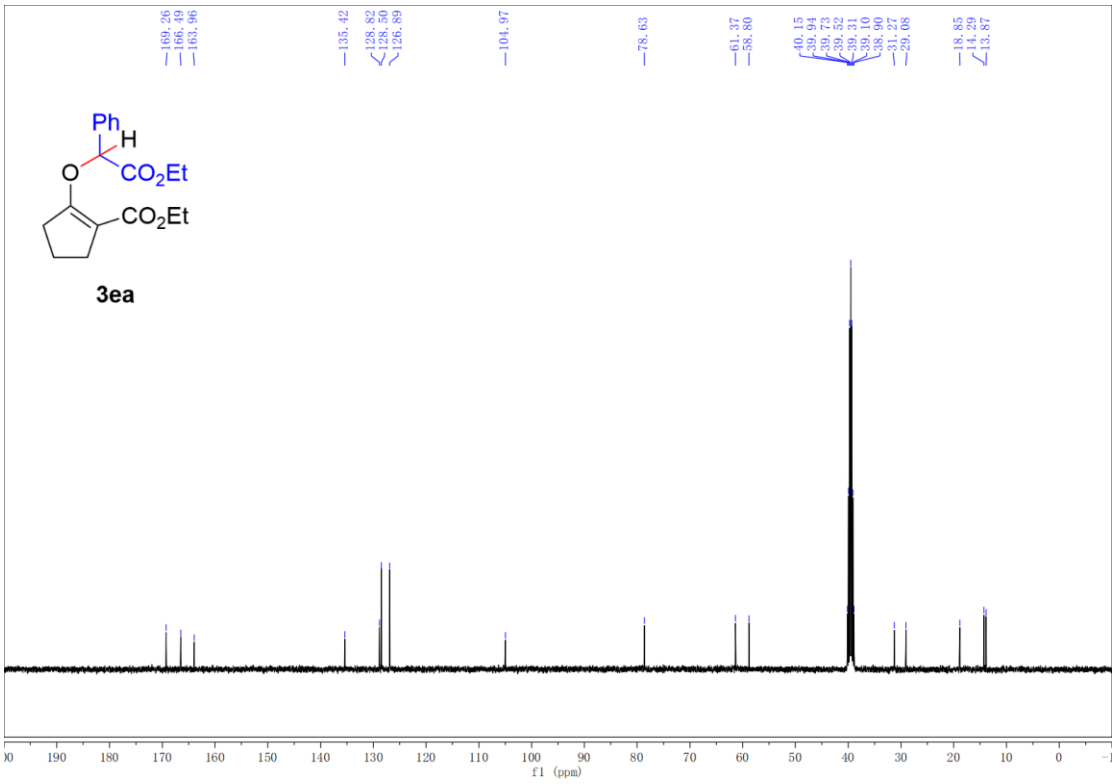
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3da**



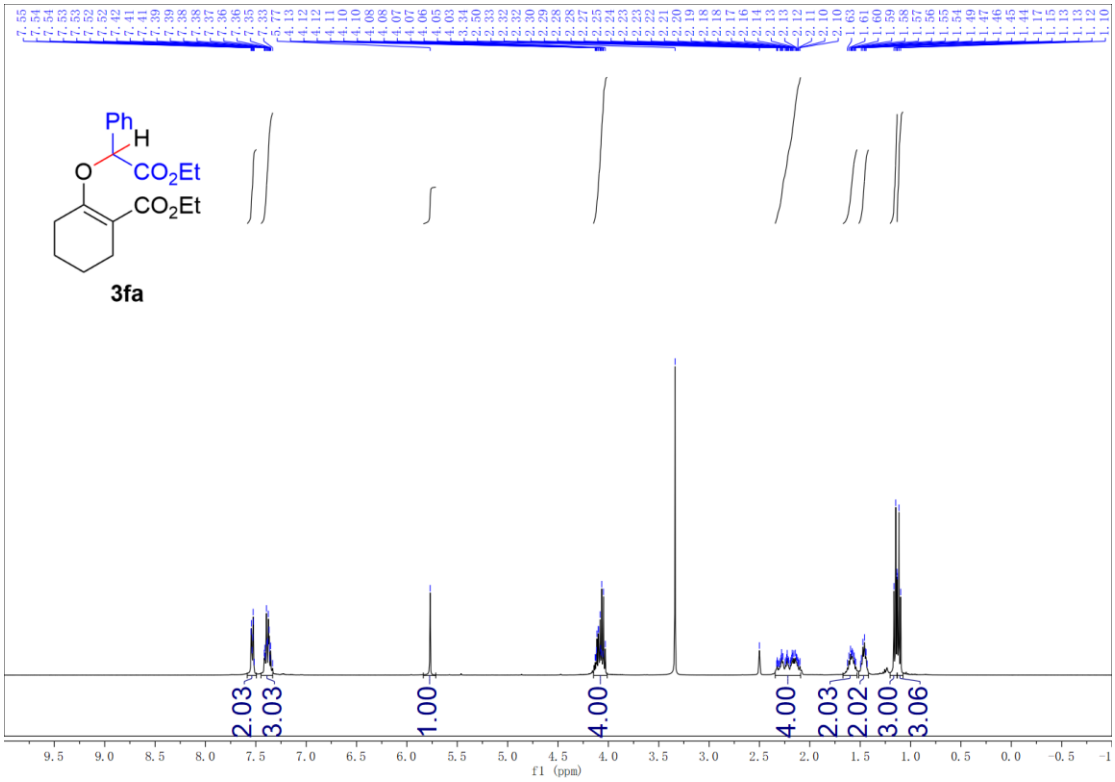
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ea**



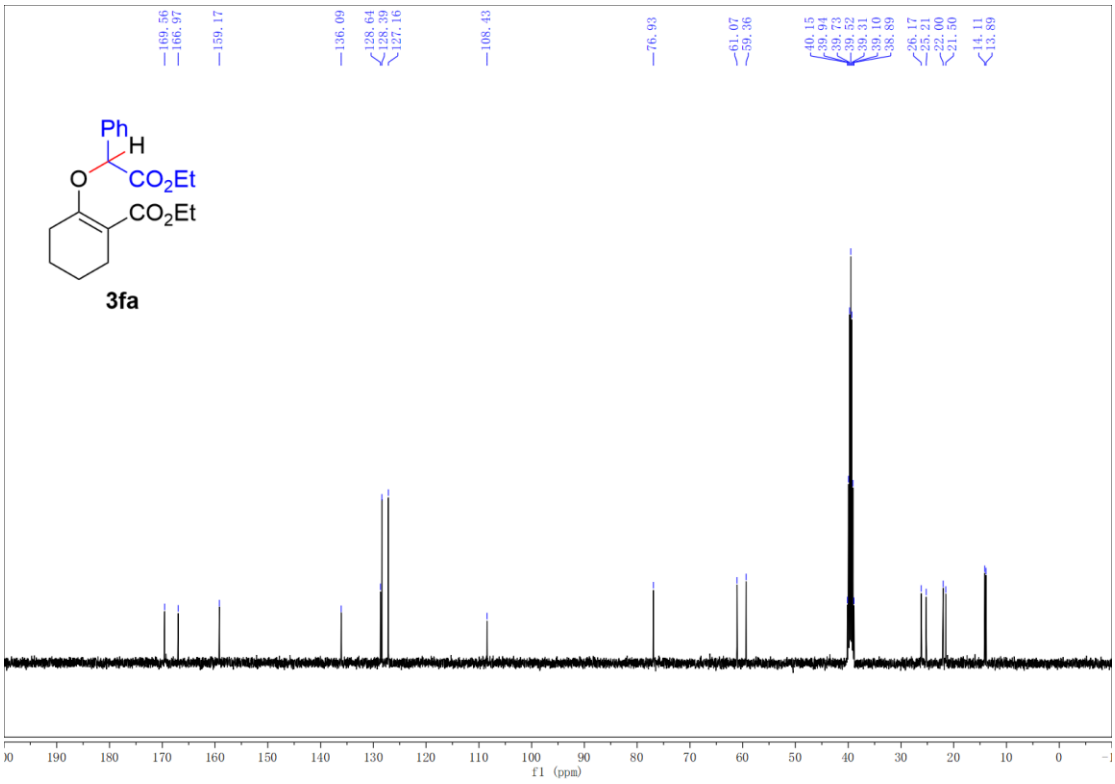
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ea**



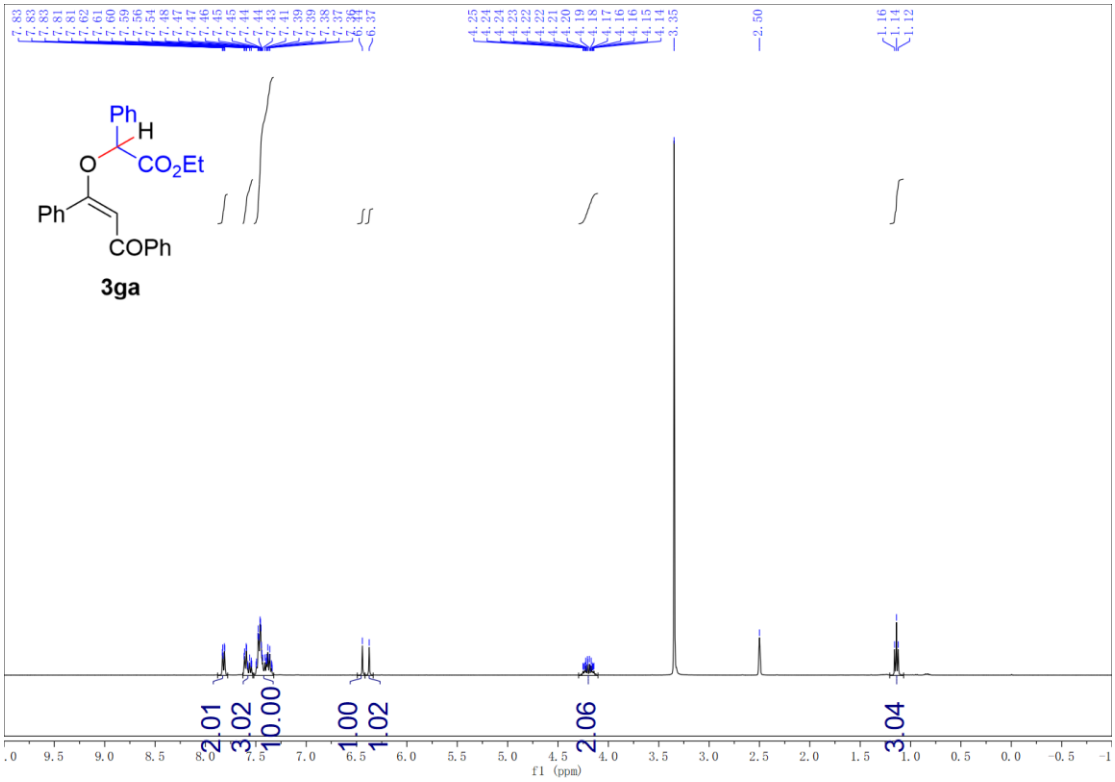
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3fa**



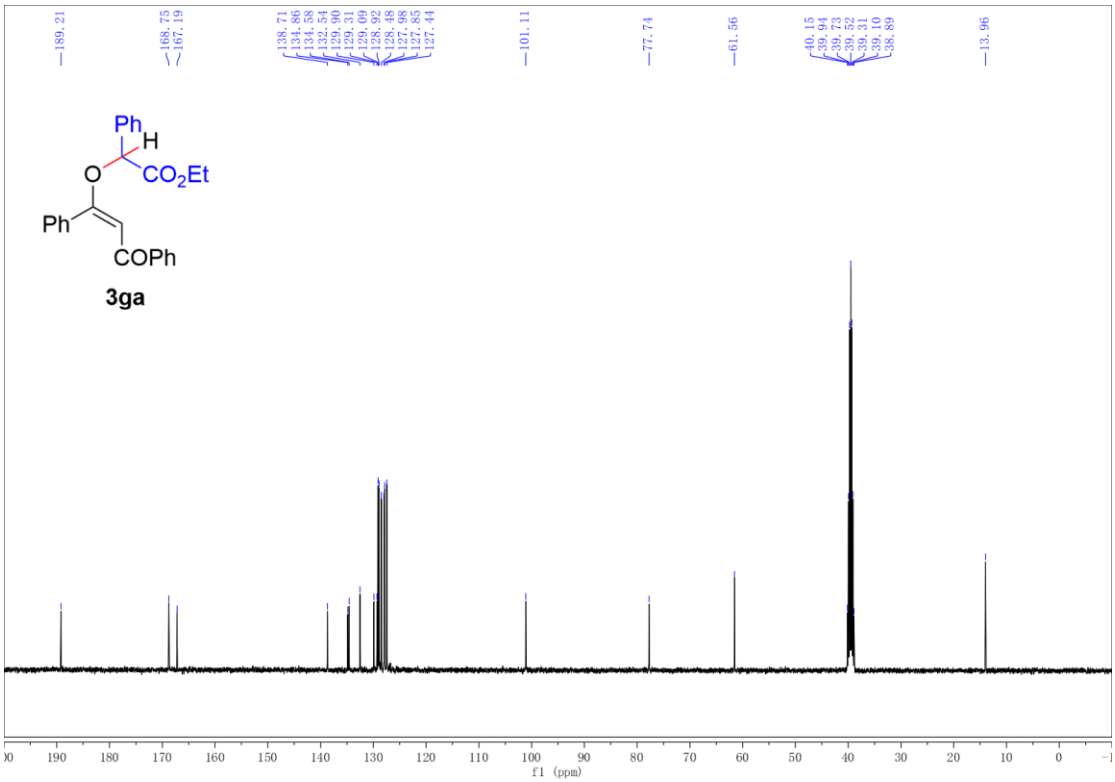
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3fa**



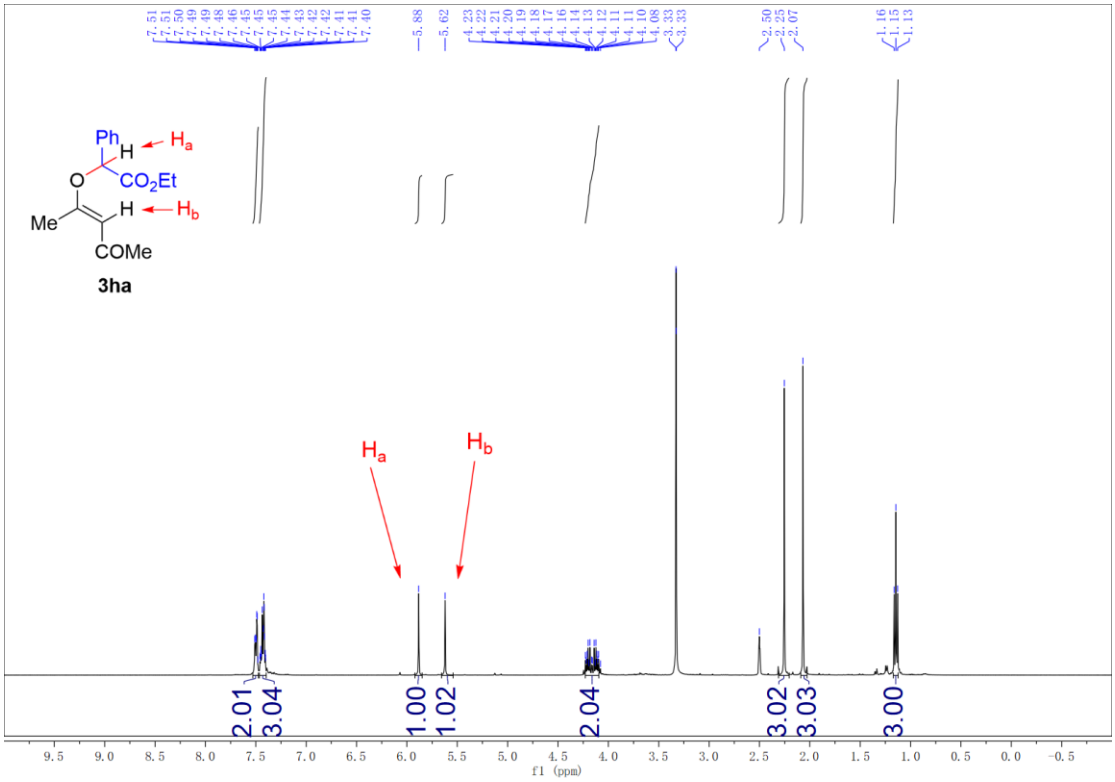
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ga**



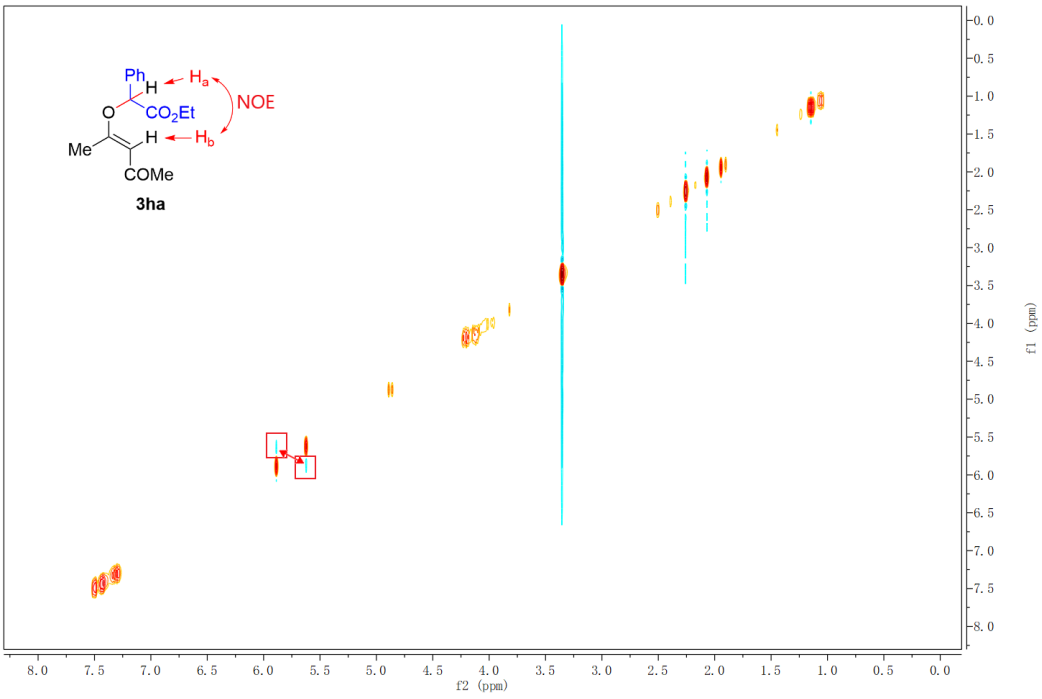
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ga**



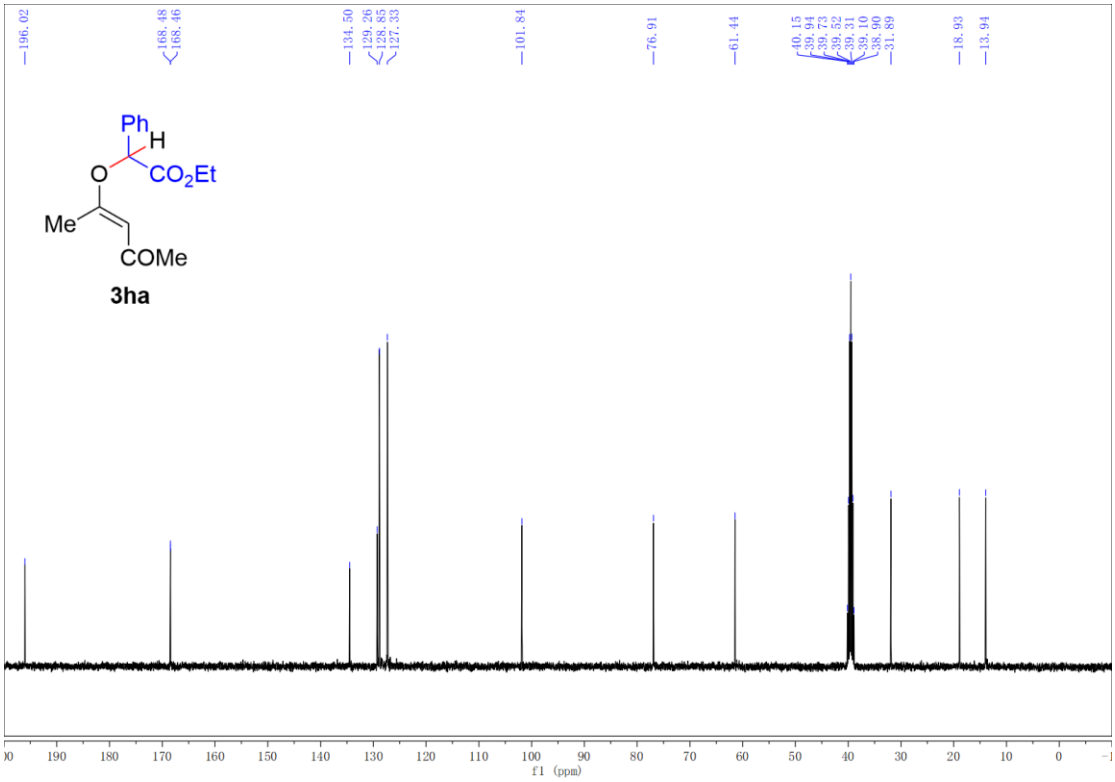
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ha**



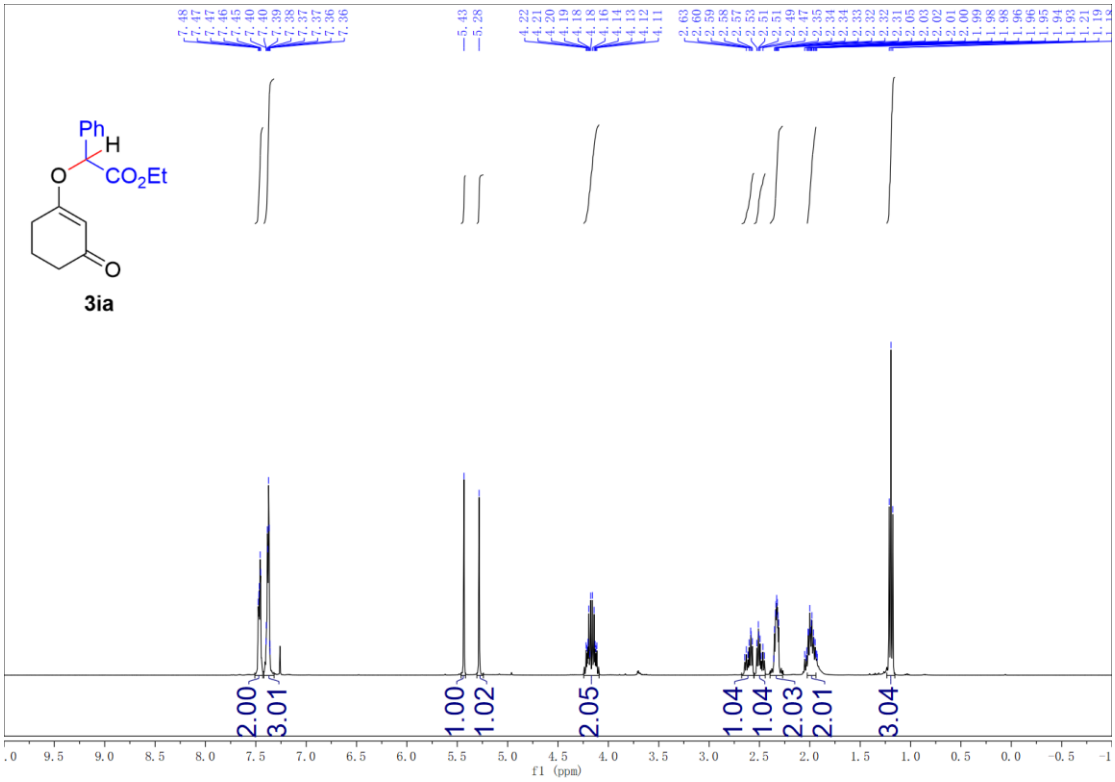
NOESY NMR (400 MHz, DMSO-d_6) Spectrum of **3ha**. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



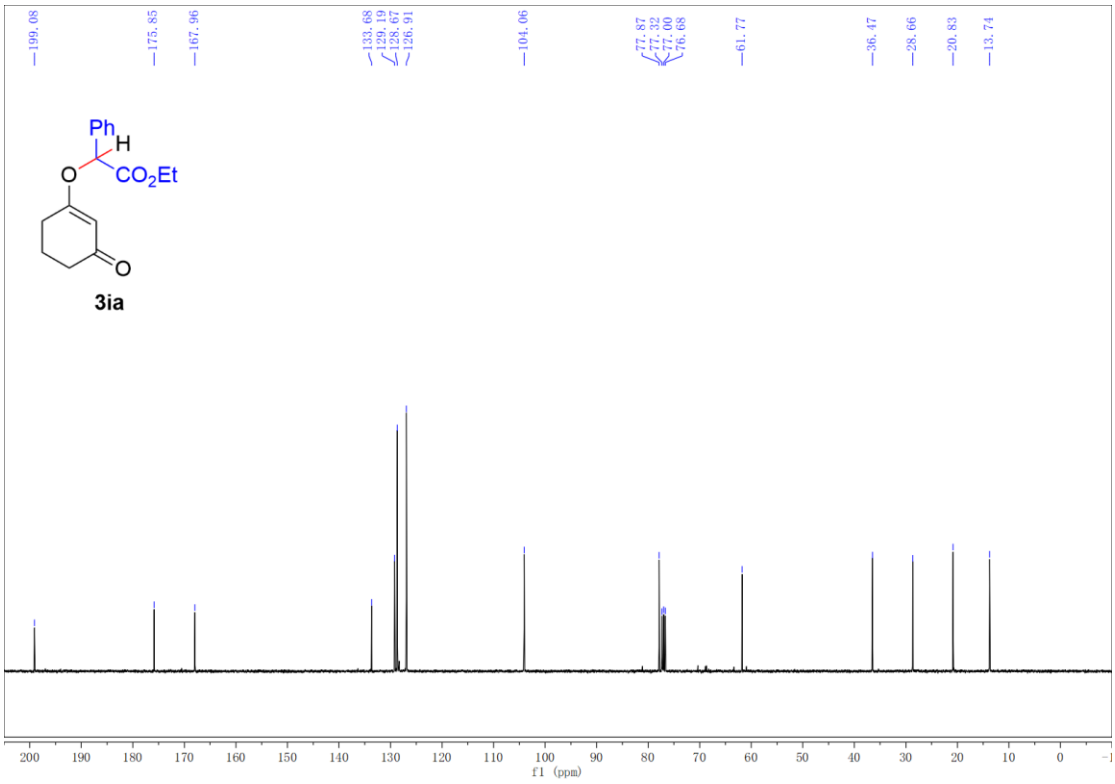
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) Spectrum of **3ha**



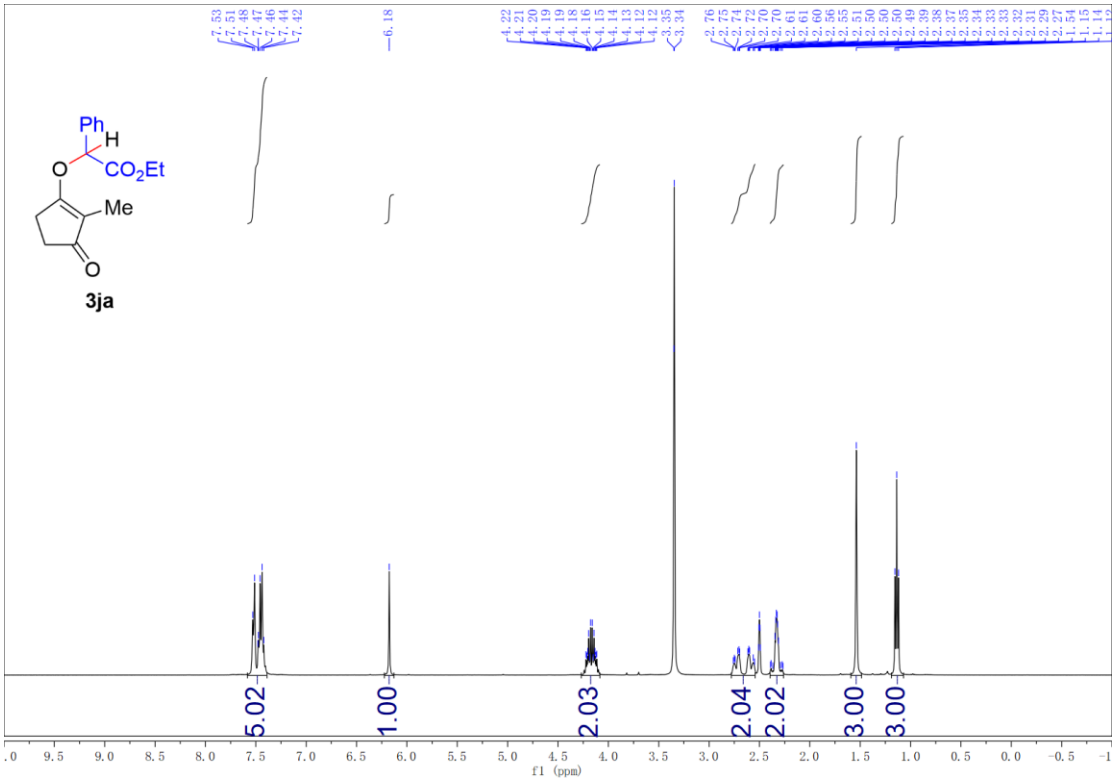
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ia**



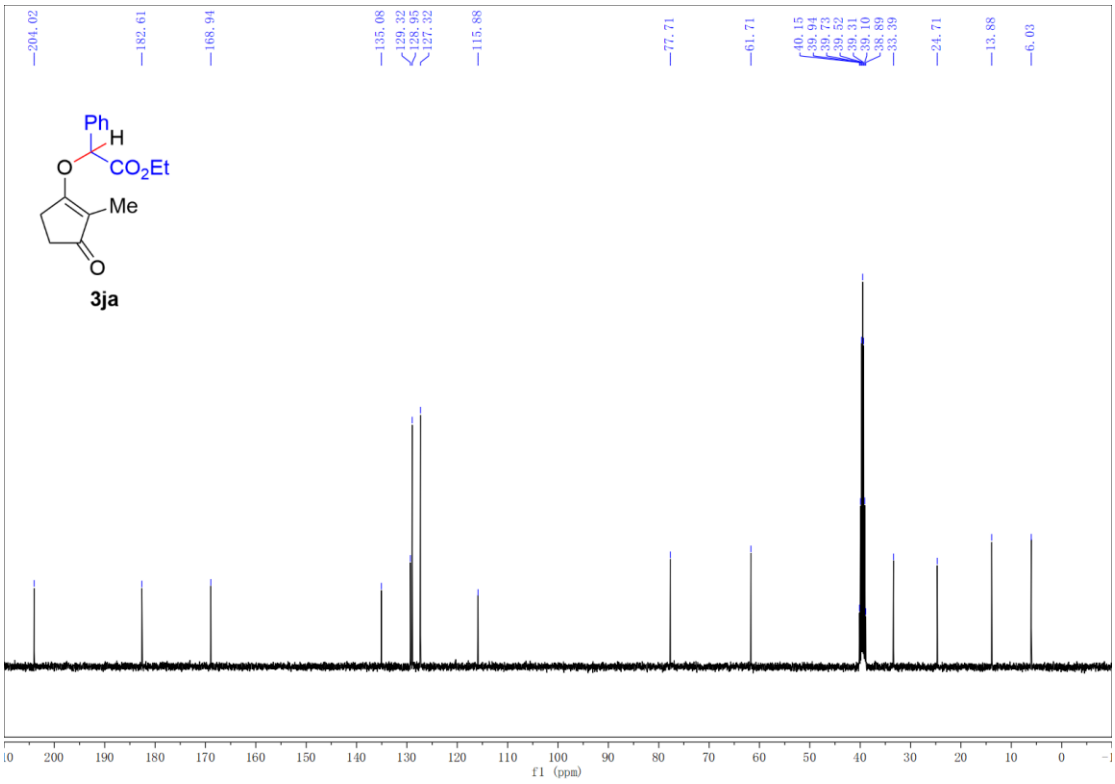
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ia**



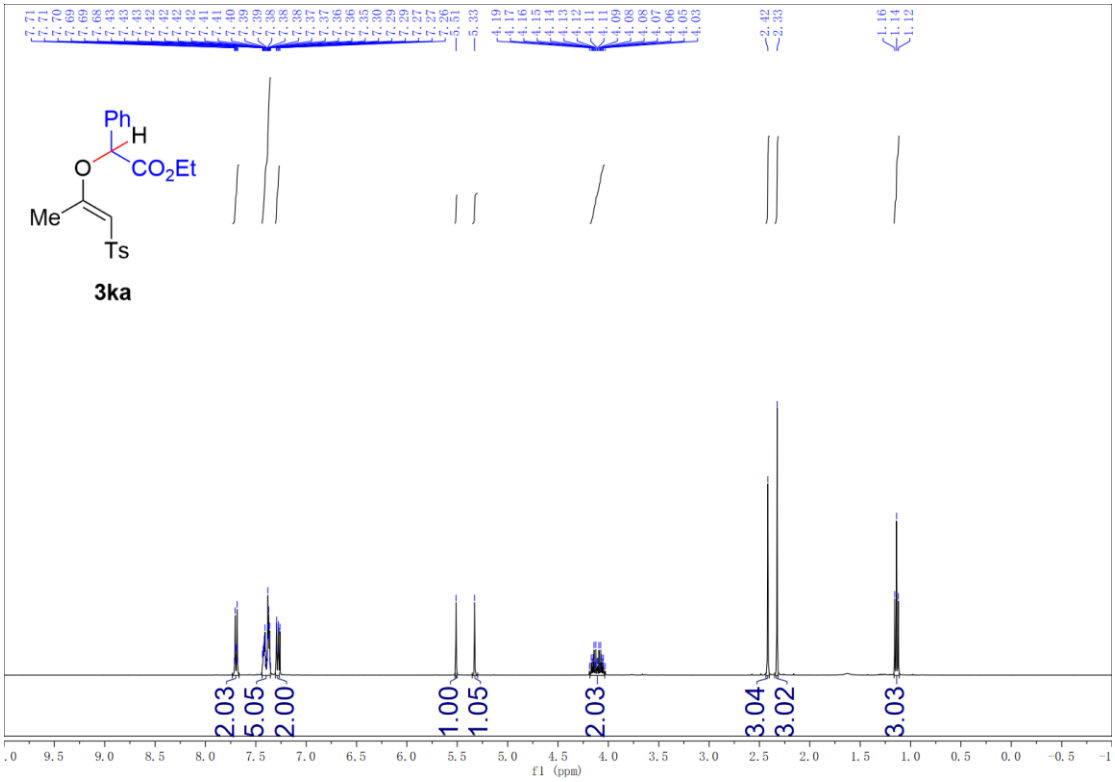
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ja**



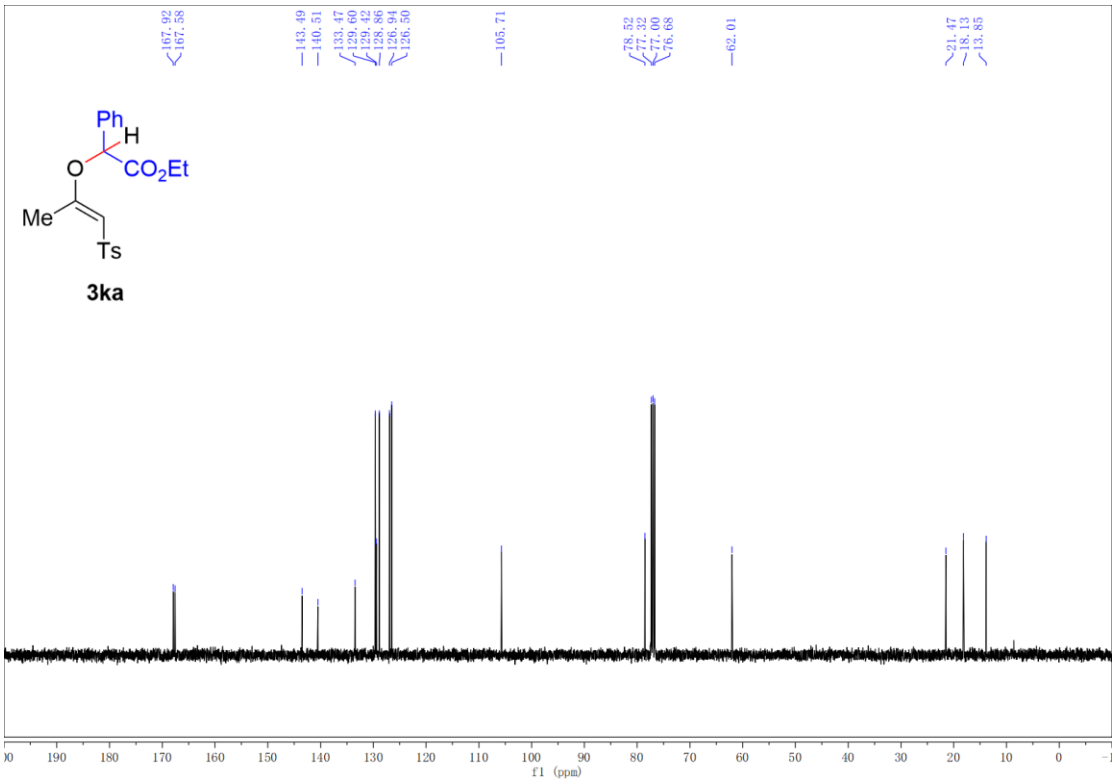
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ja**



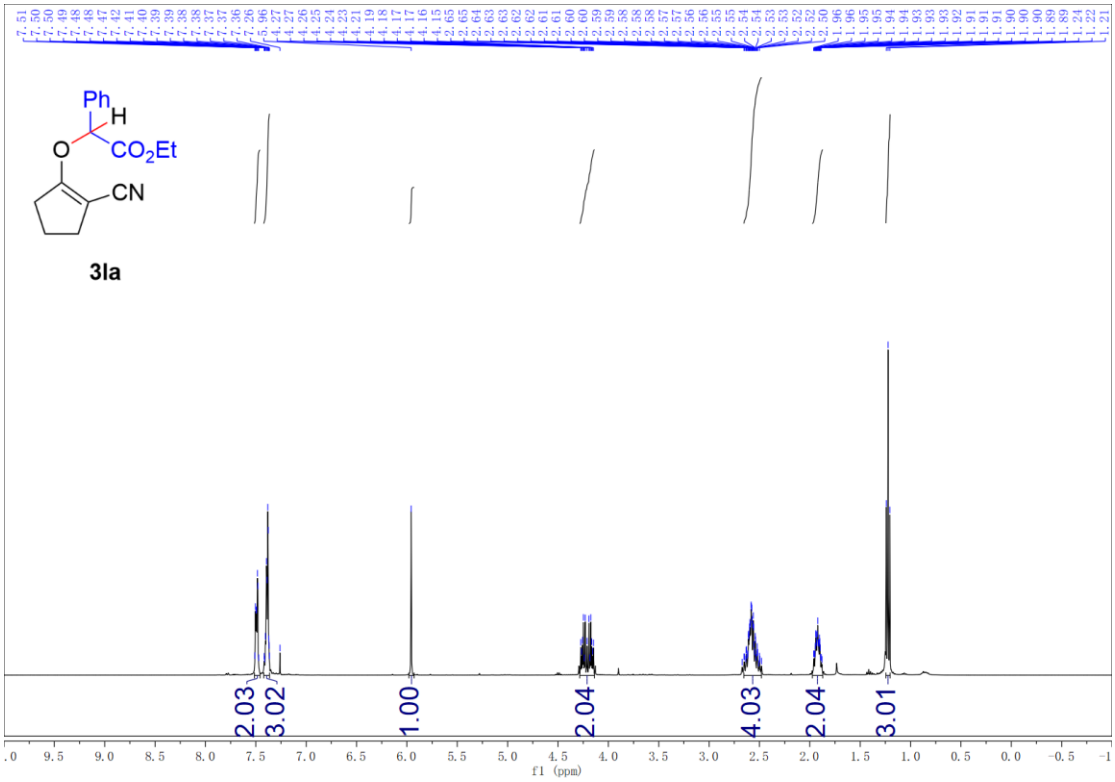
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ka**



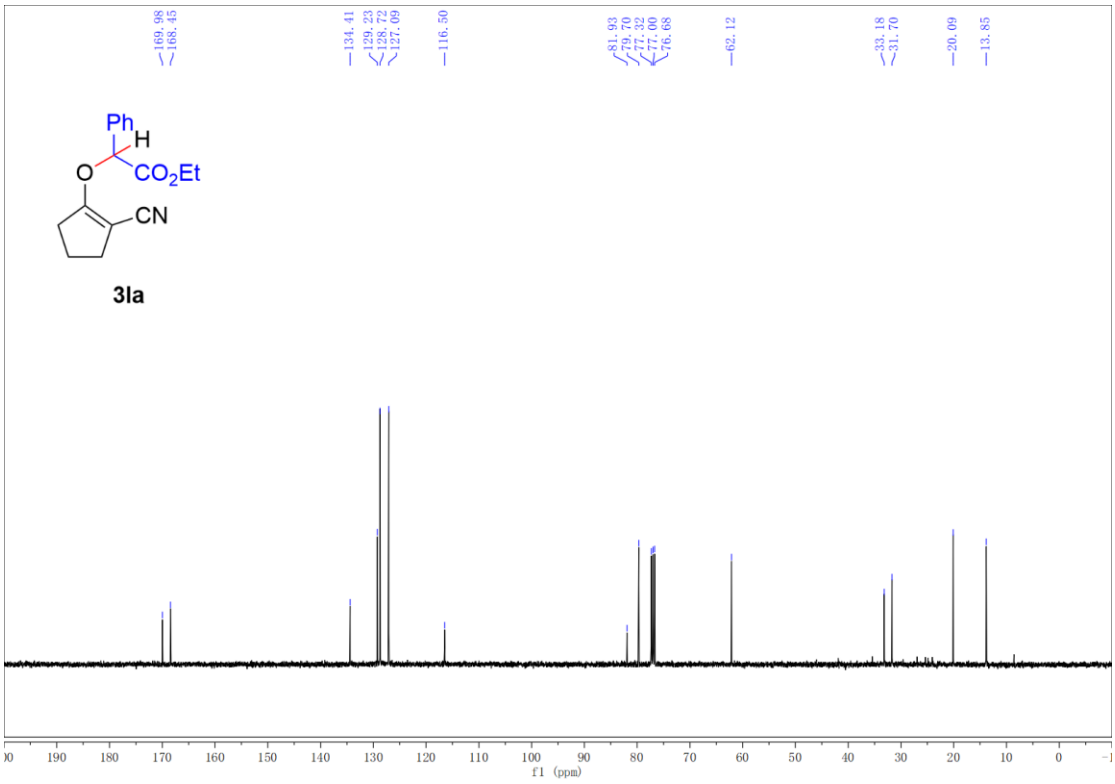
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ka**



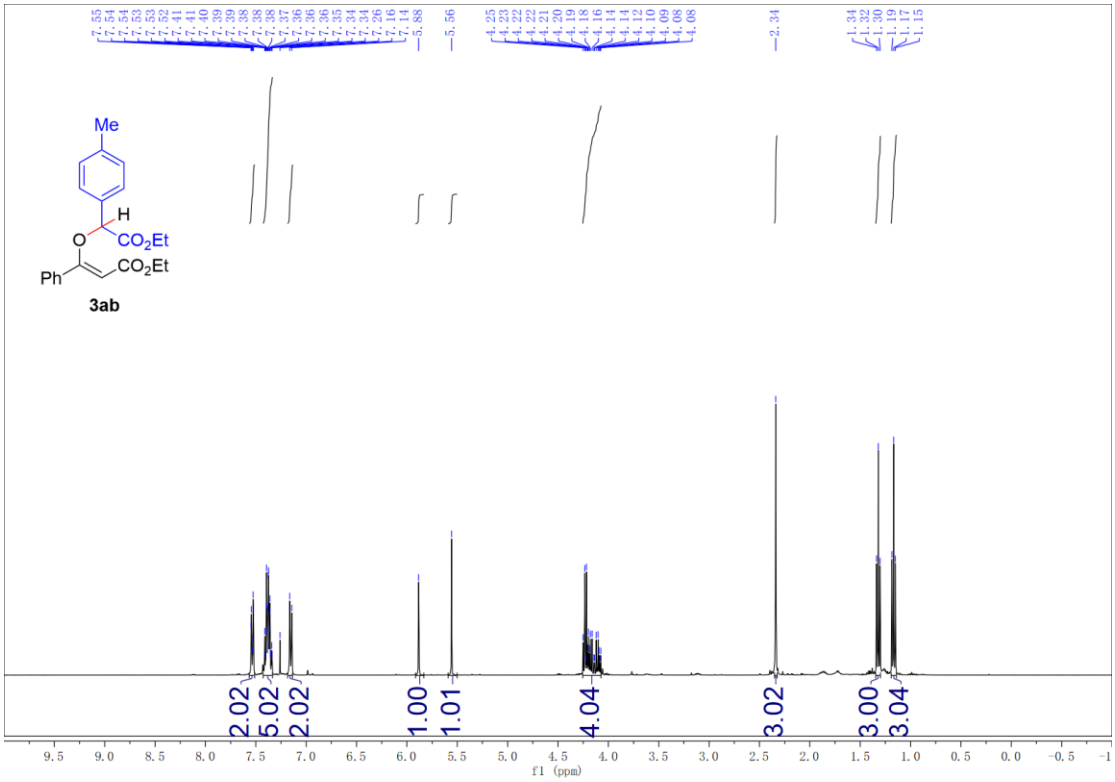
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3la**



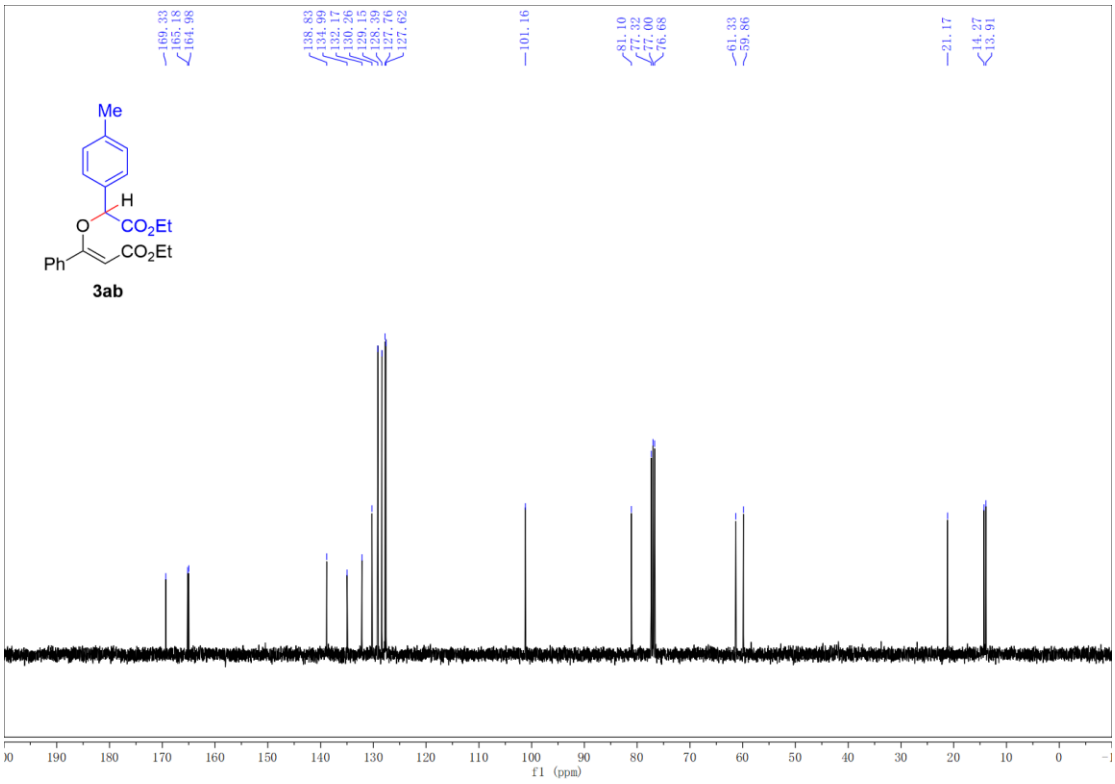
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3la**



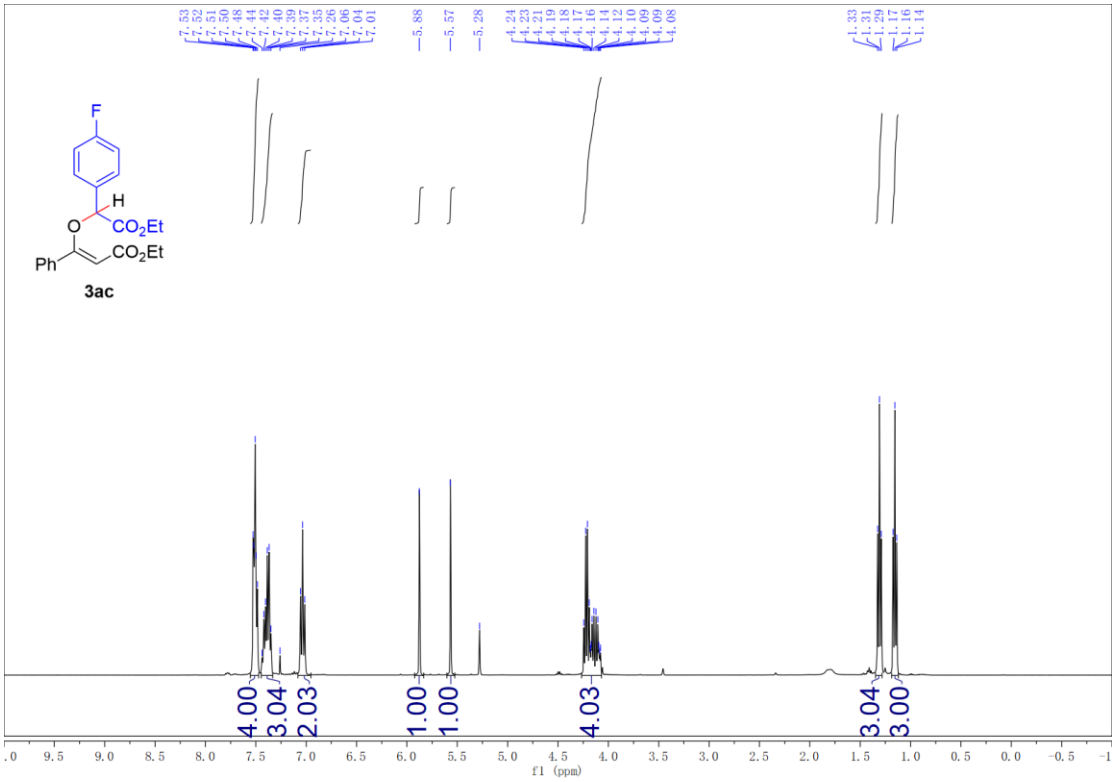
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ab**



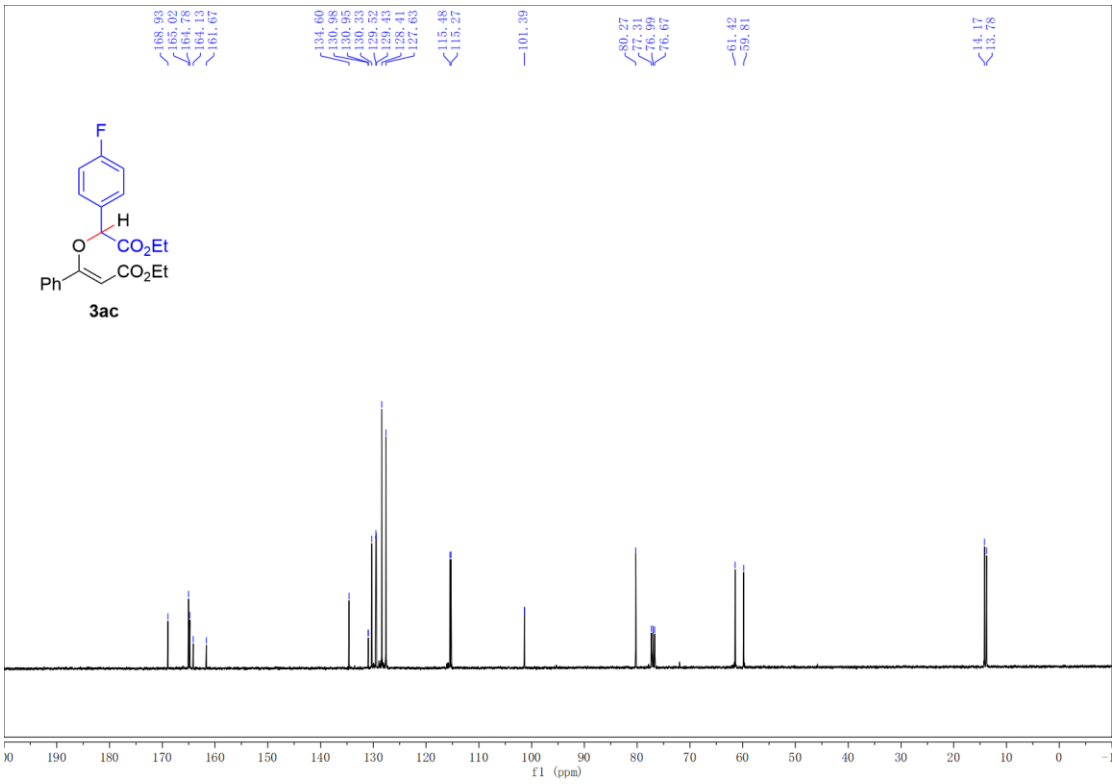
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ab**



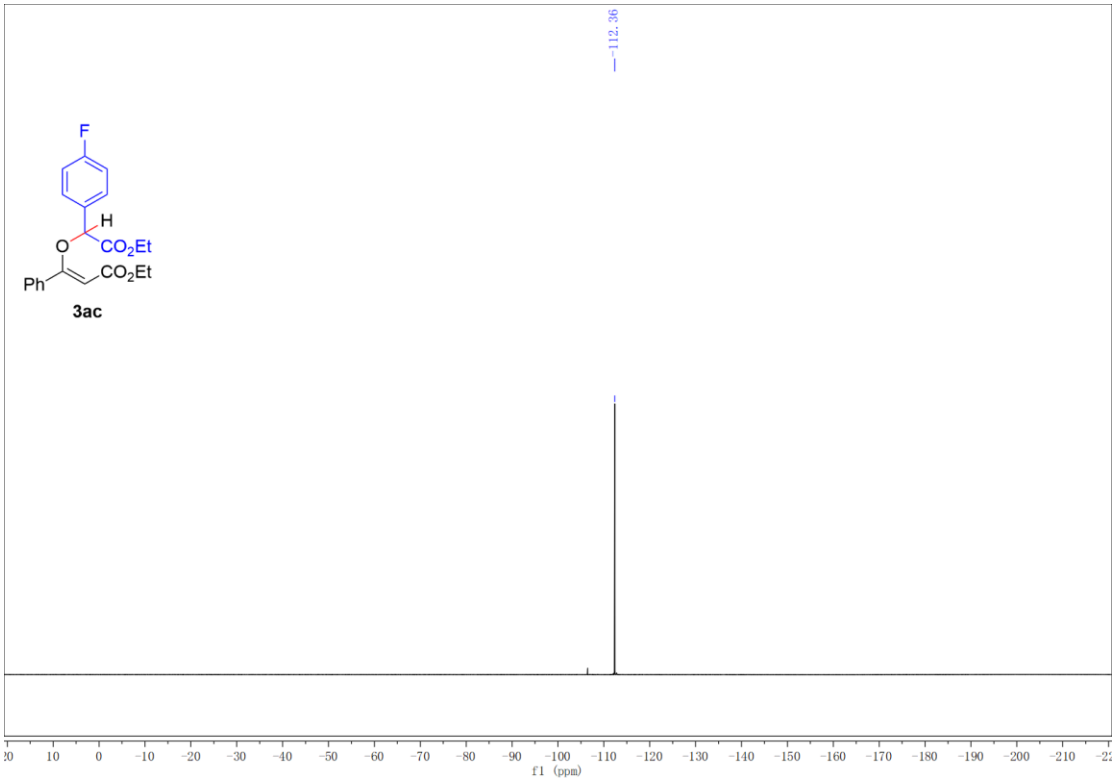
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ac**



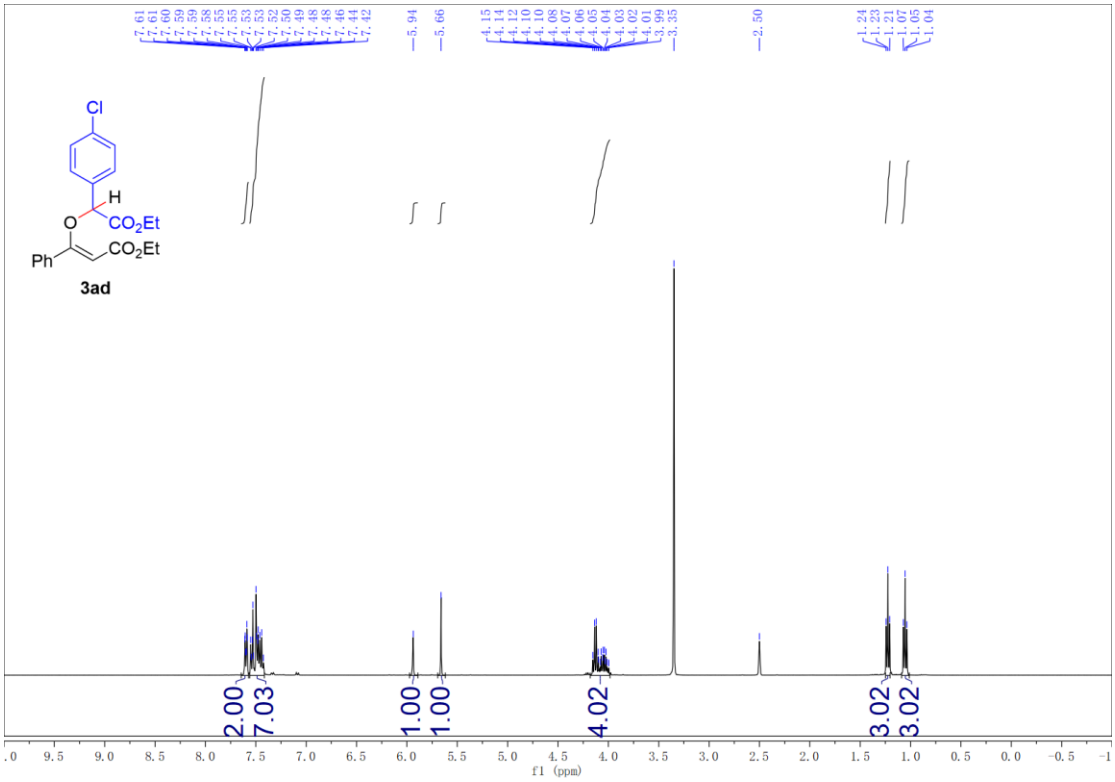
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ac**



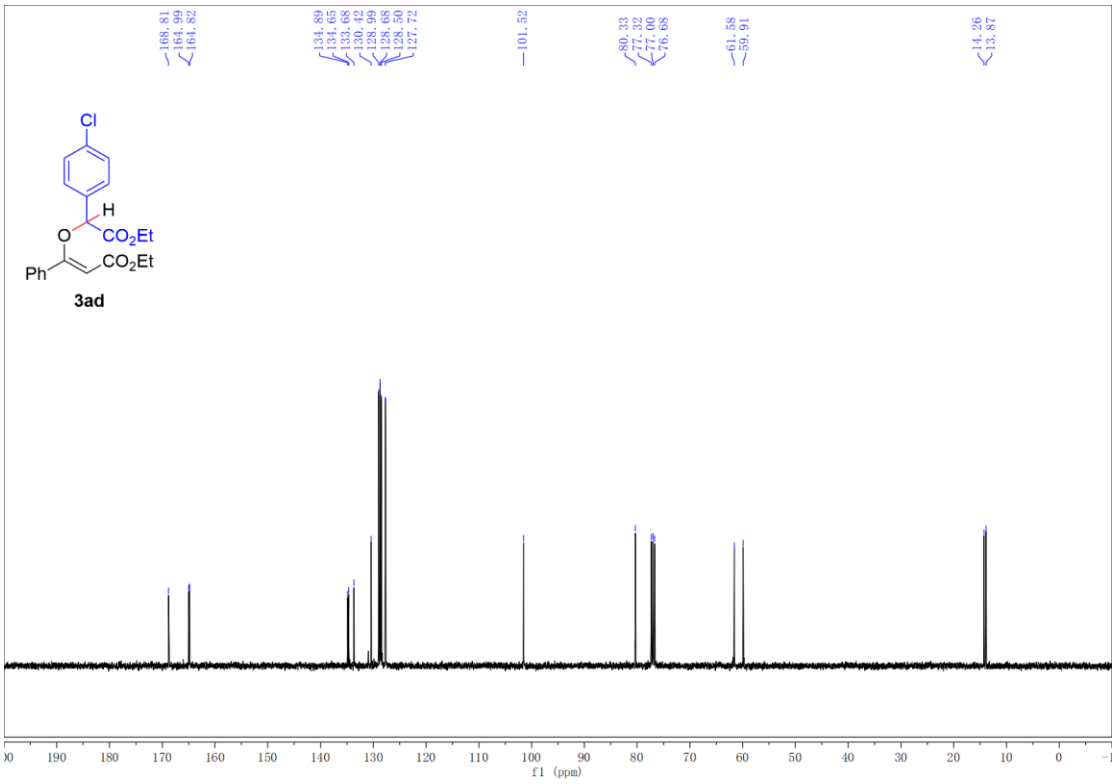
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3ac**



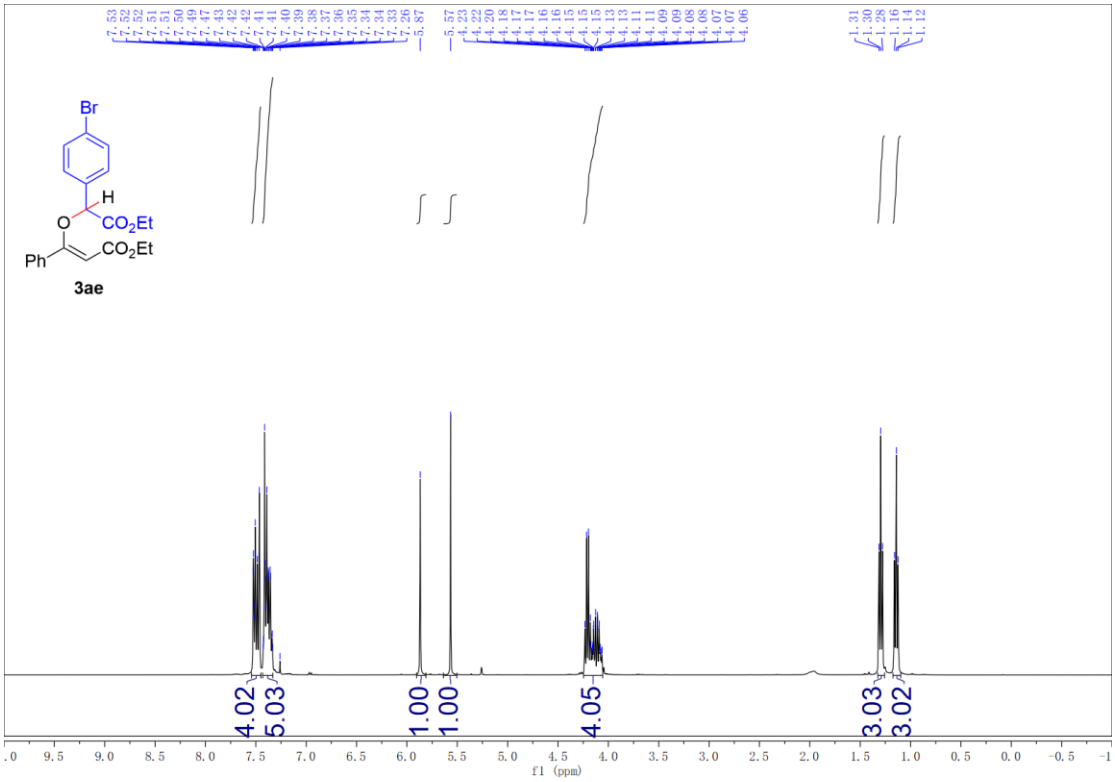
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ad**



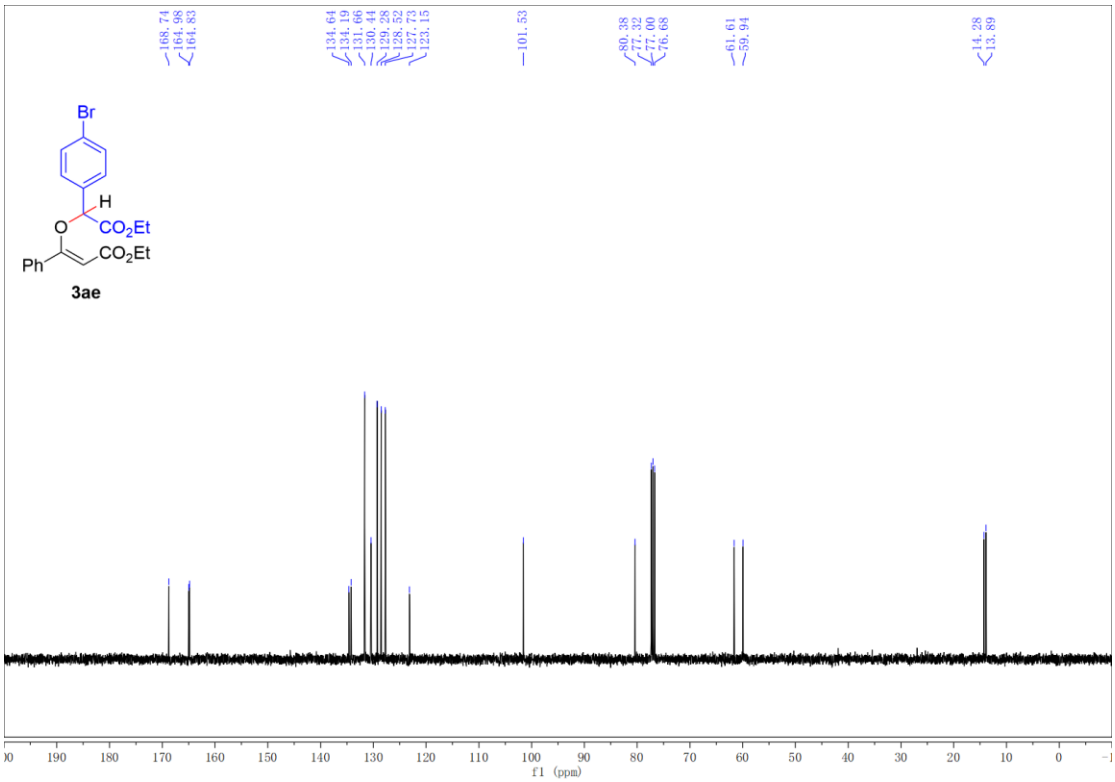
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ad**



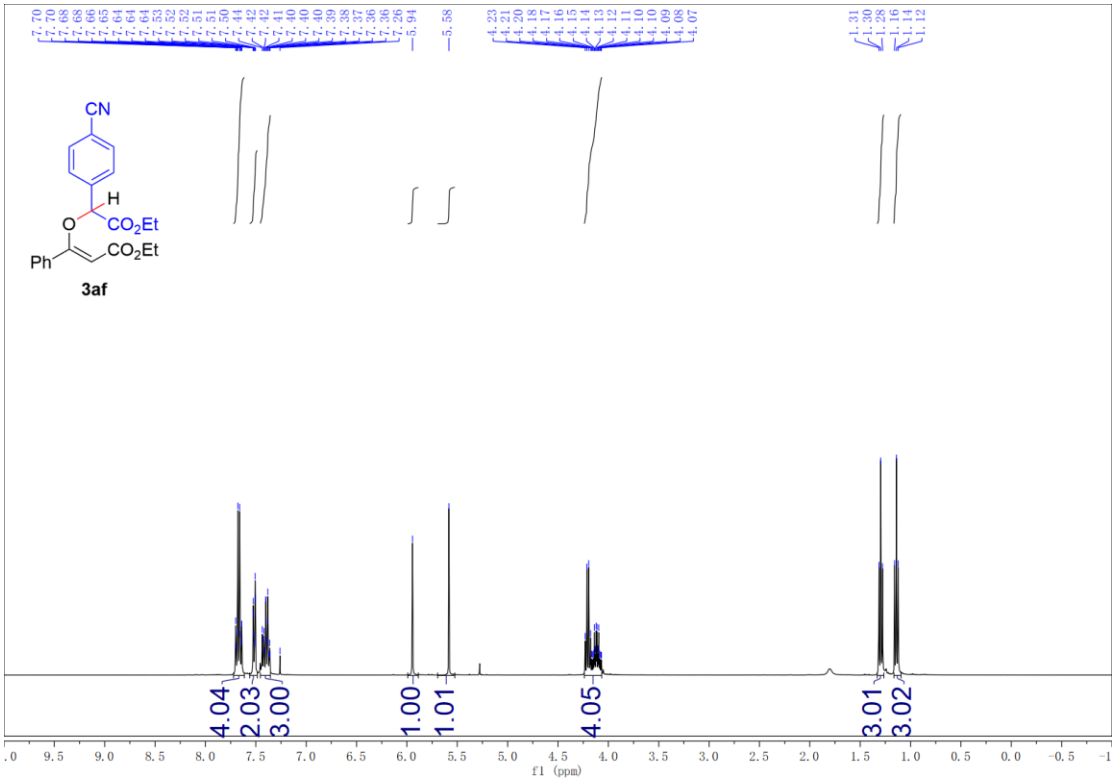
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ae**



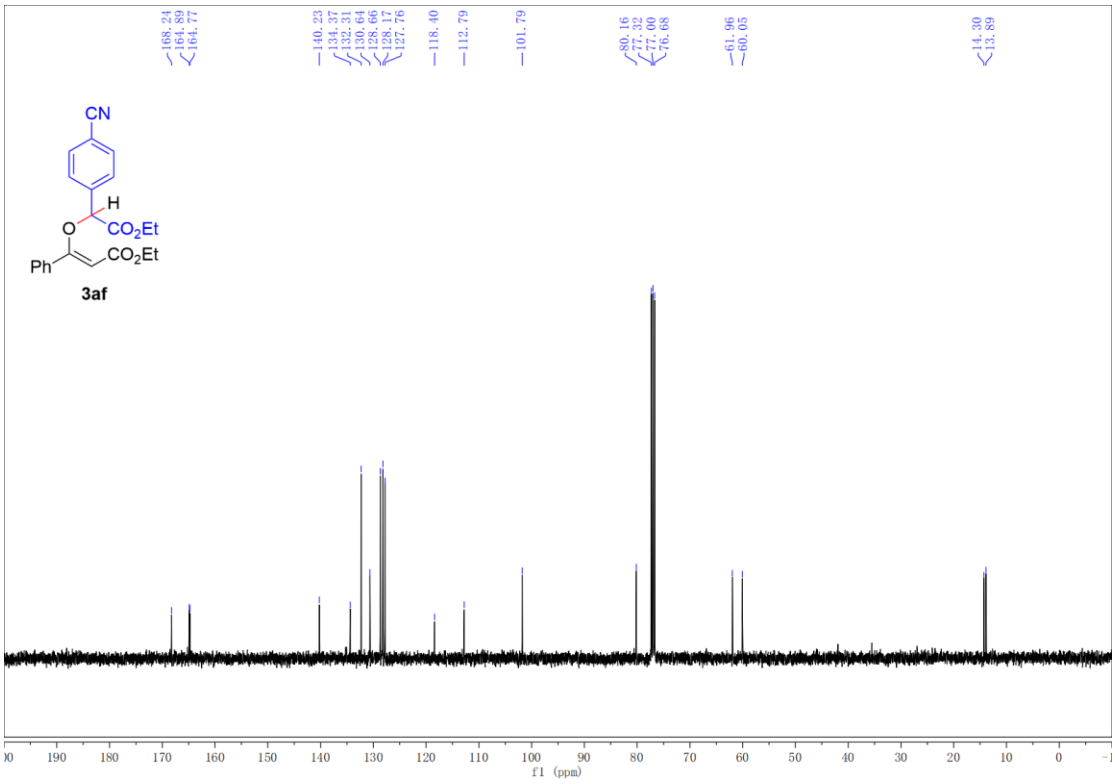
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ae**



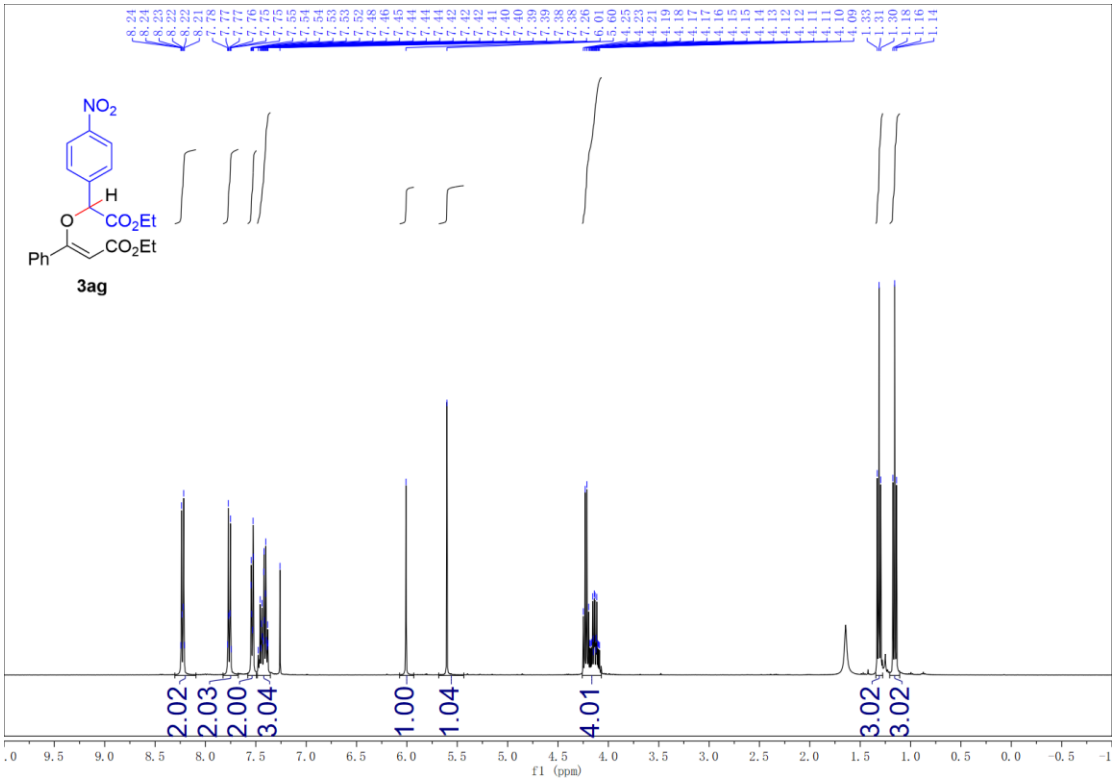
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3af**



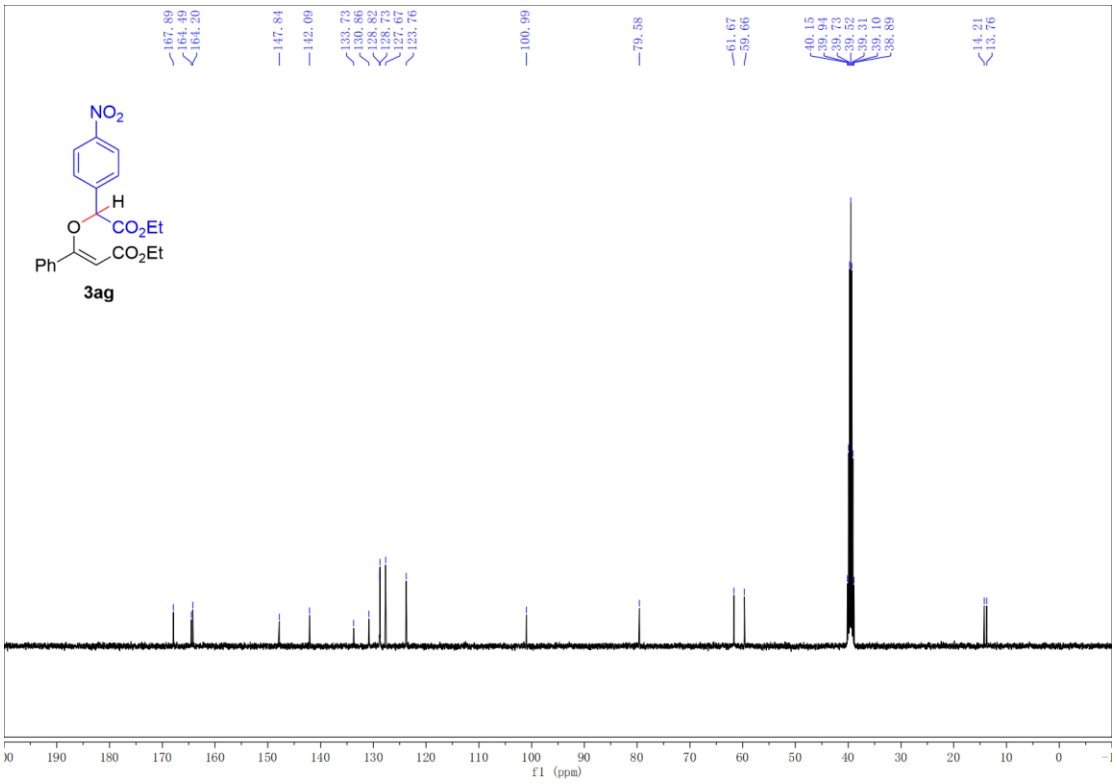
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3af**



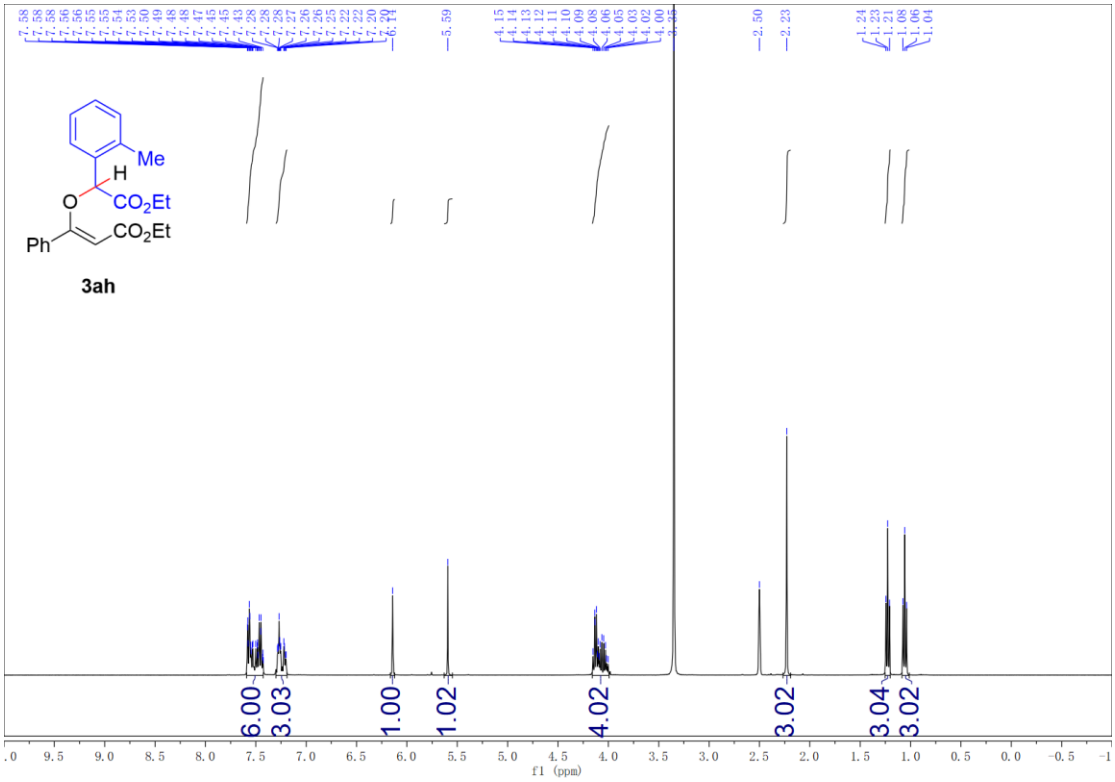
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3ag**



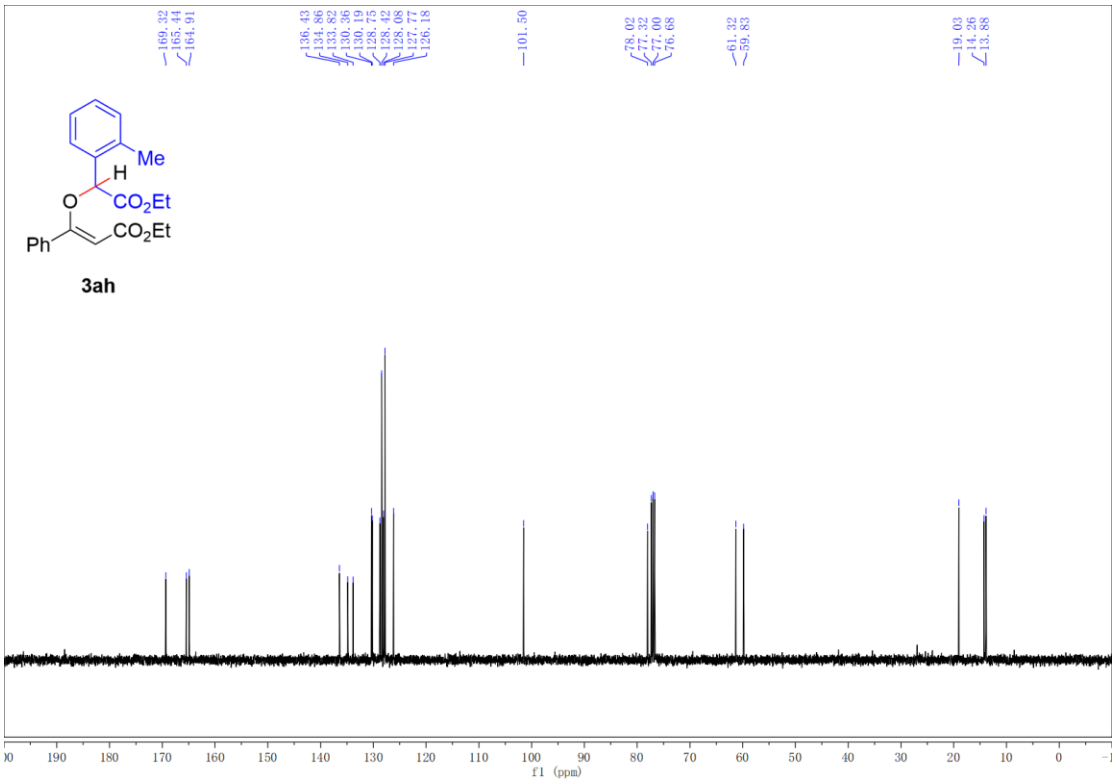
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ag**



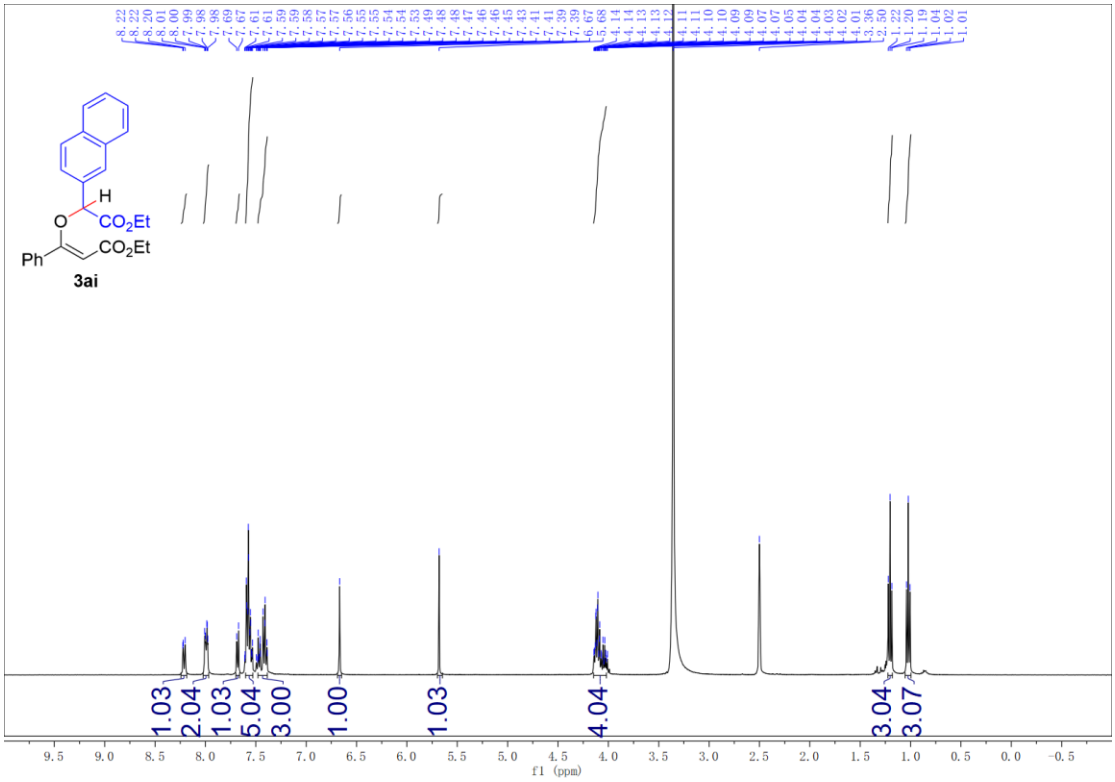
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ah**



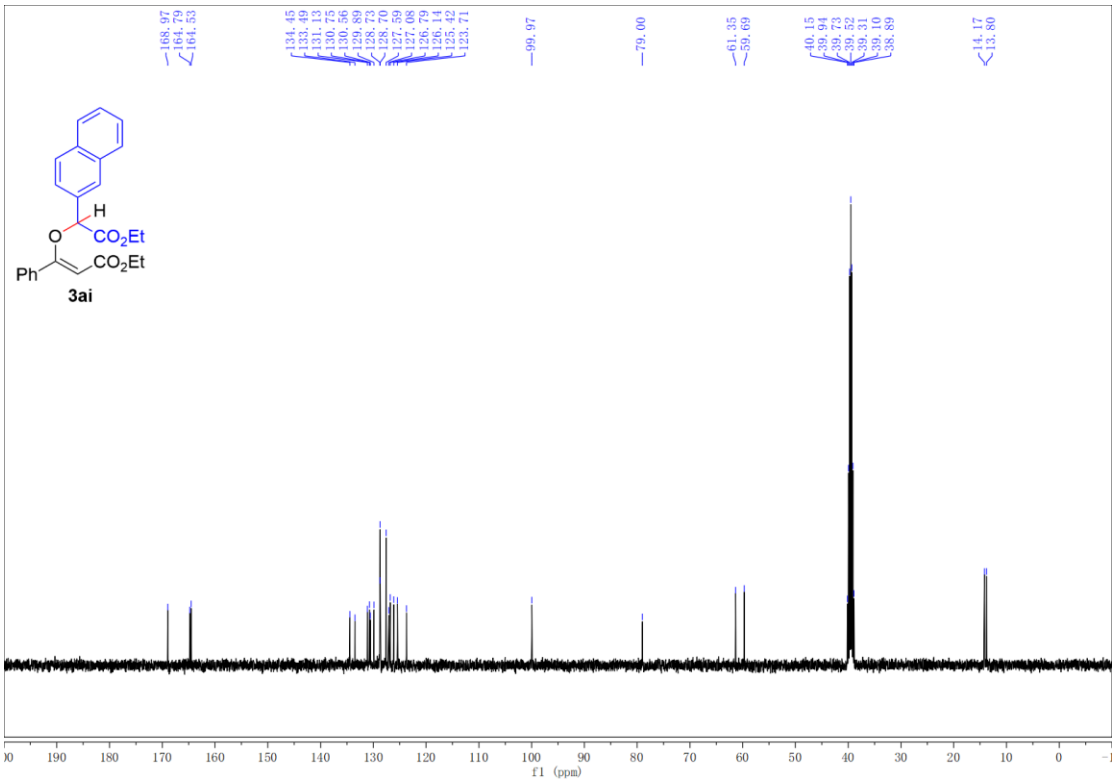
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3ah**



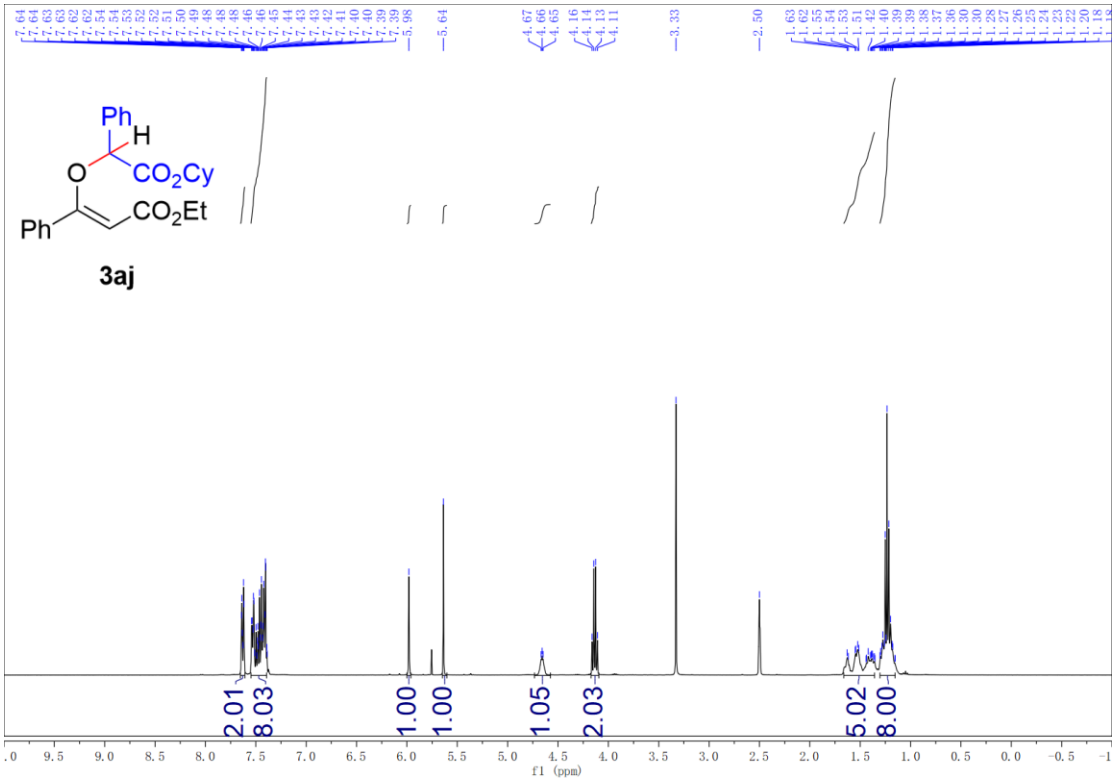
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ai**



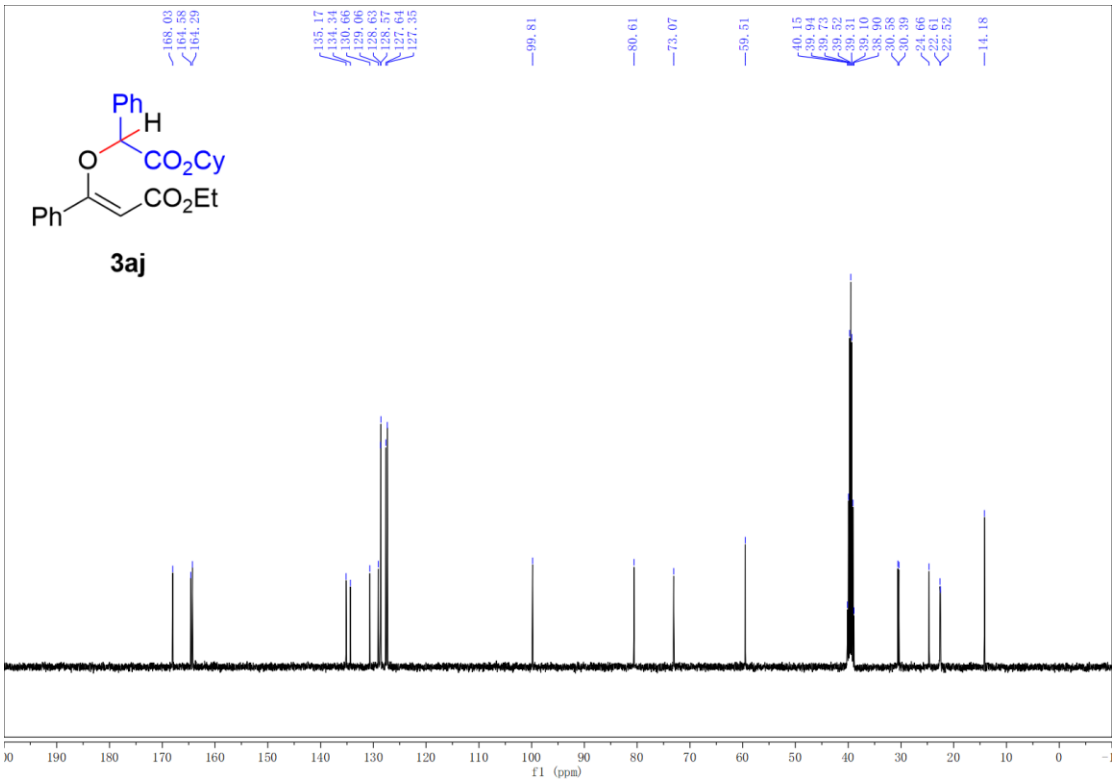
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ai**



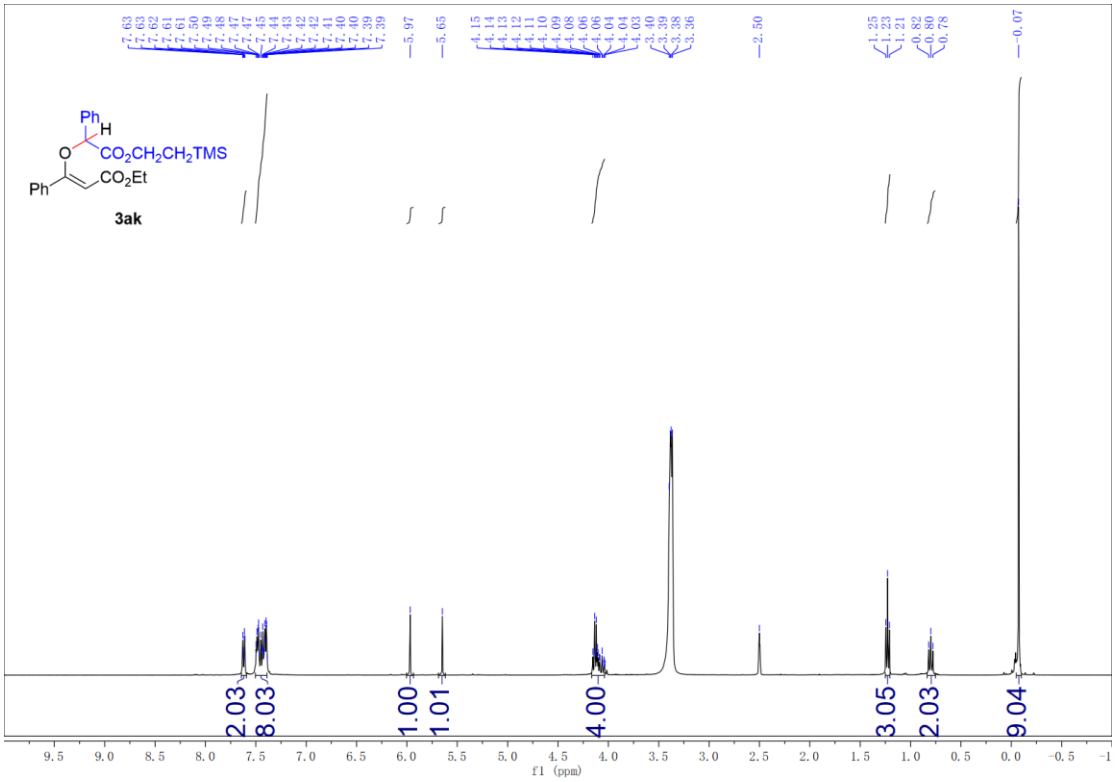
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3aj**



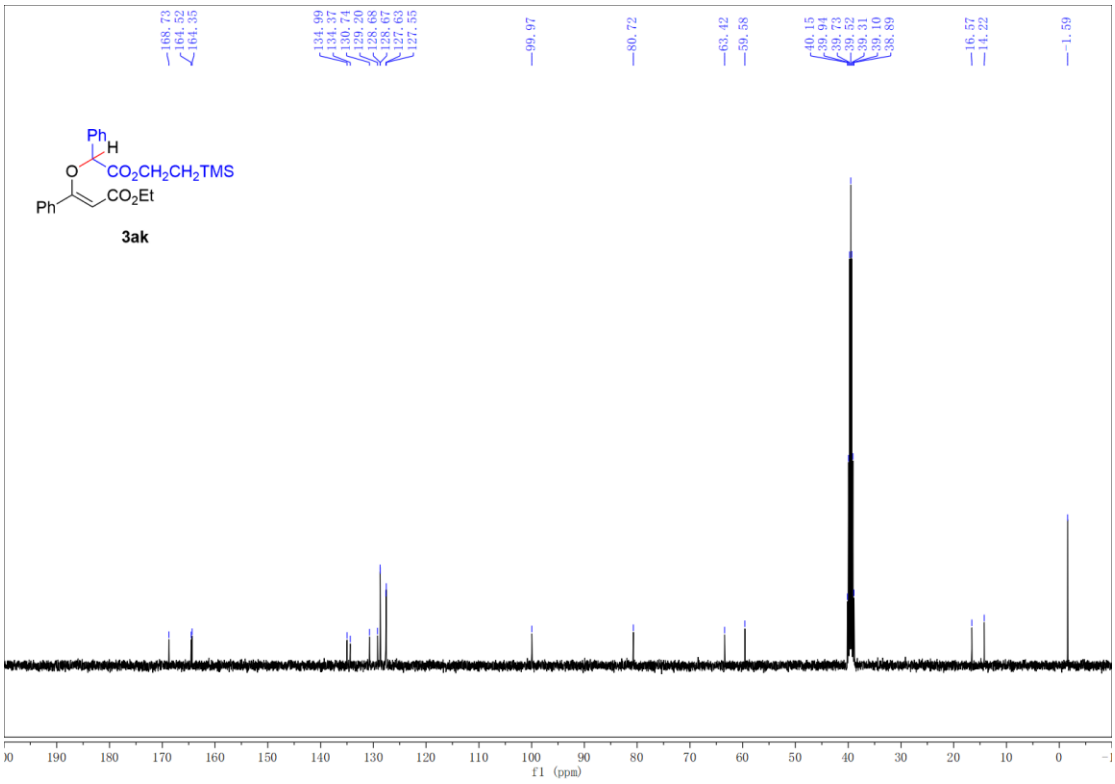
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3aj**



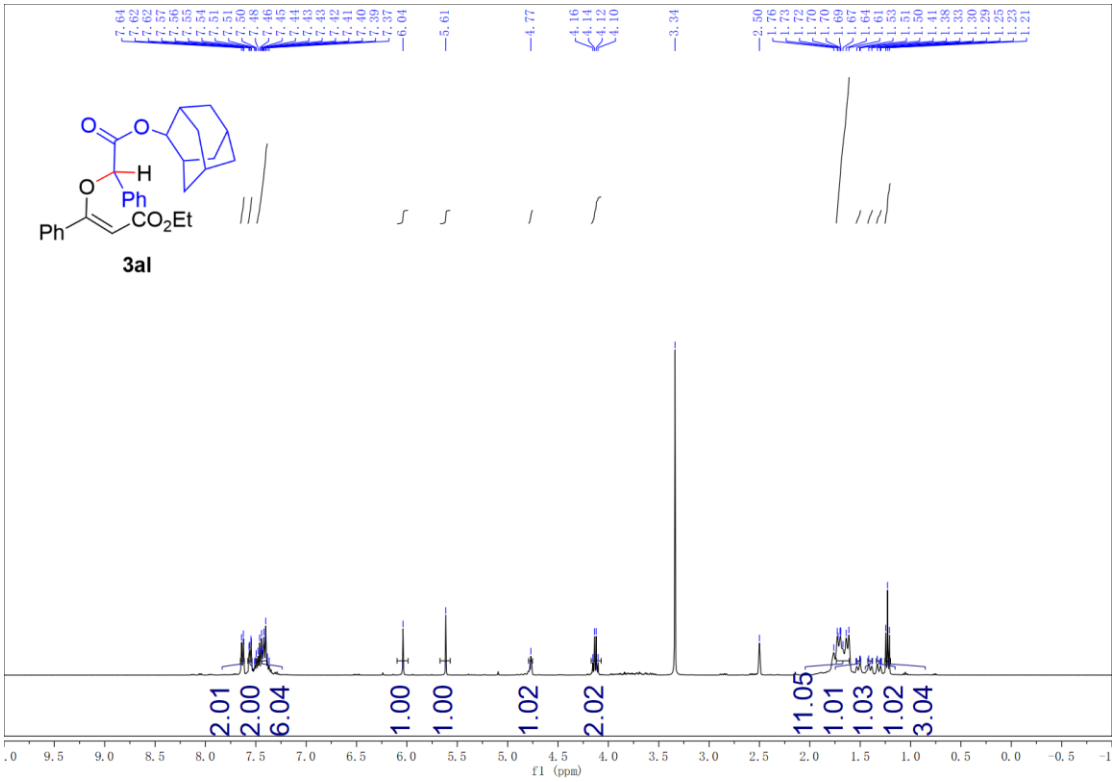
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3ak**



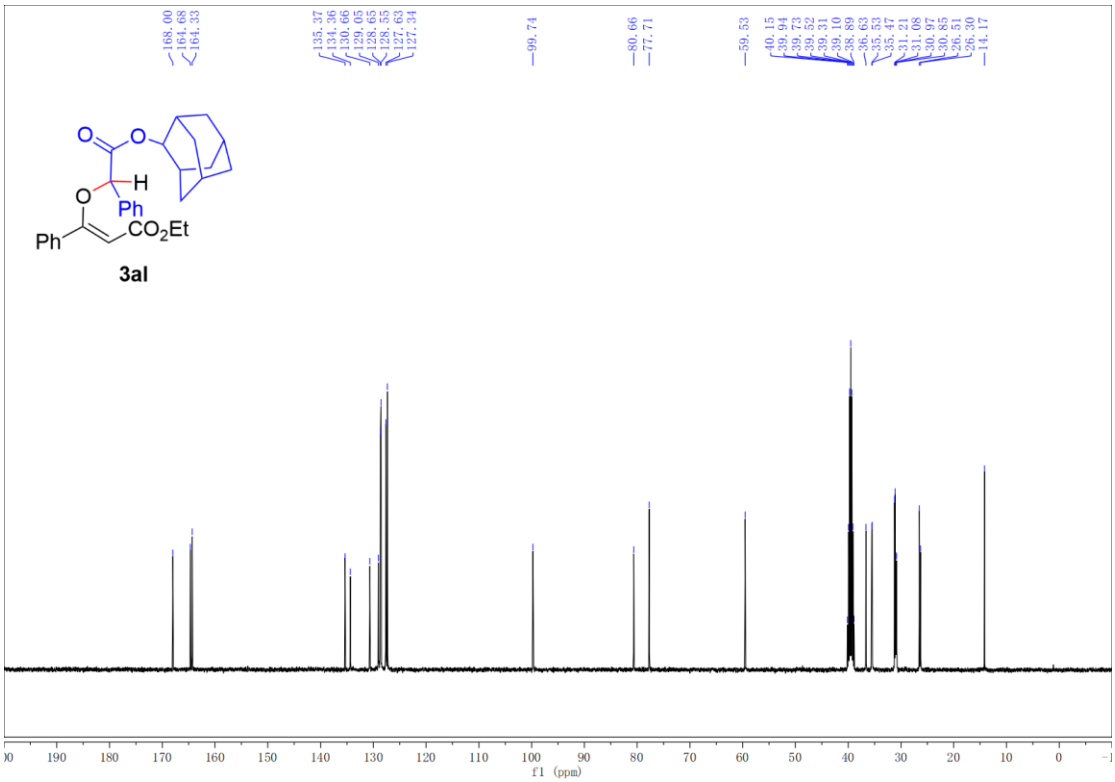
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3ak**



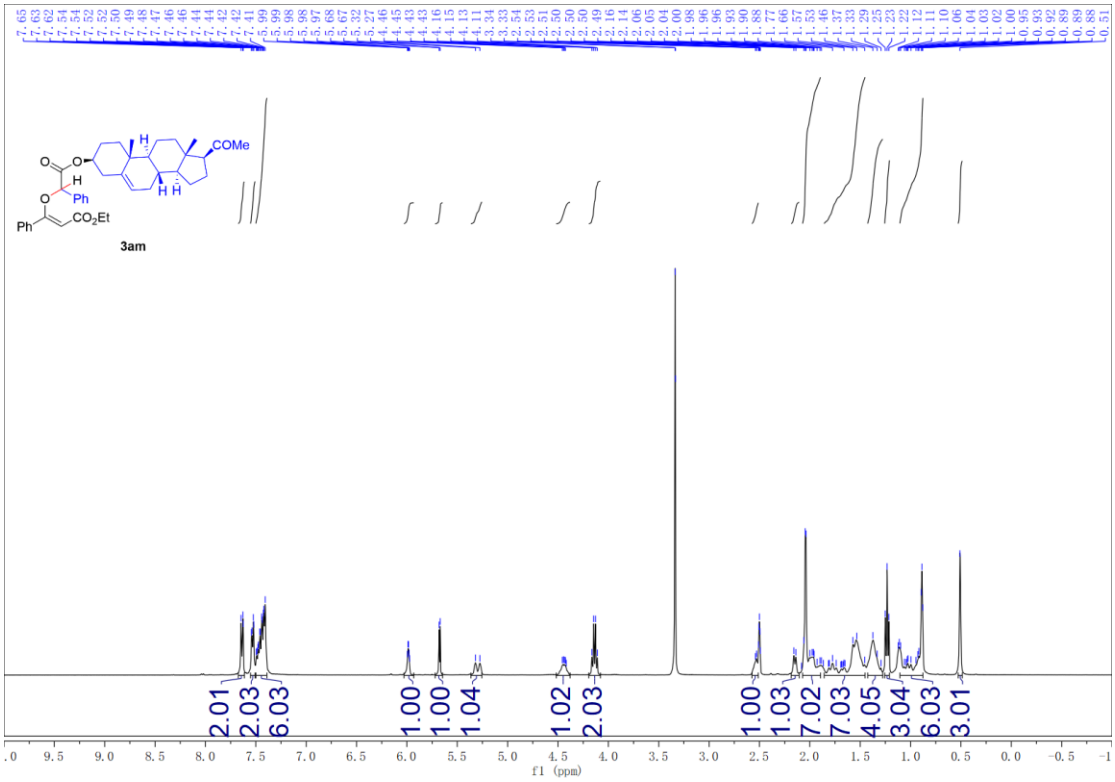
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3al**



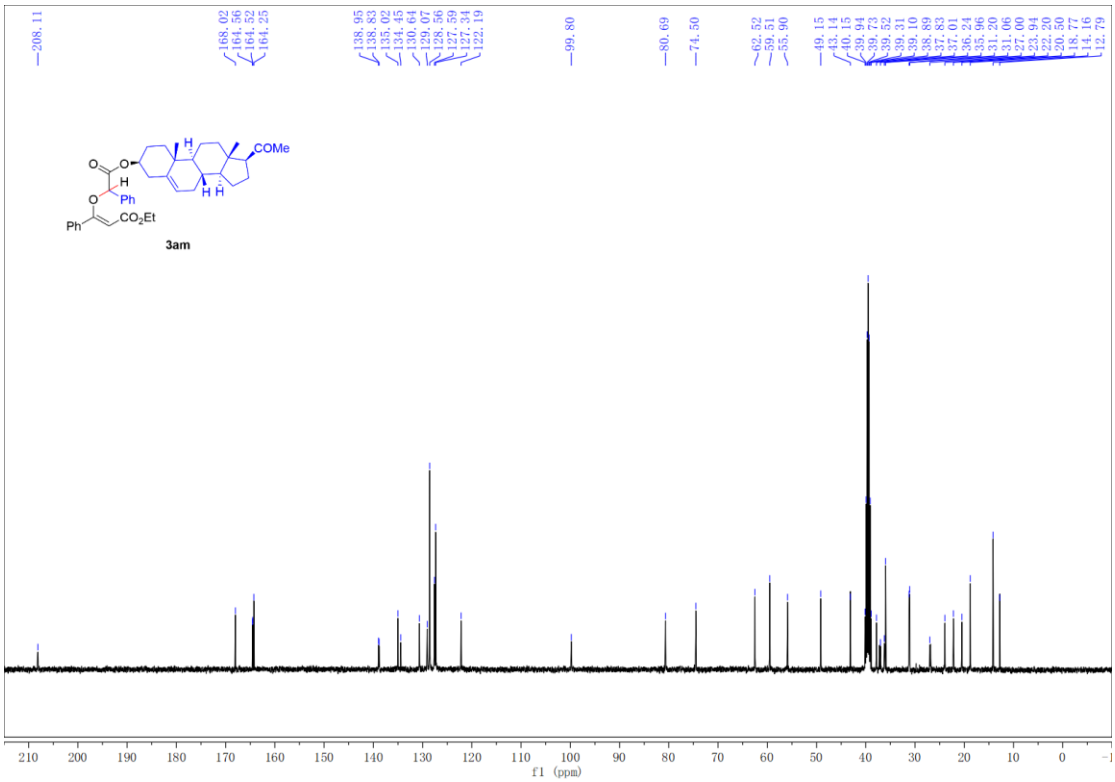
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3al**



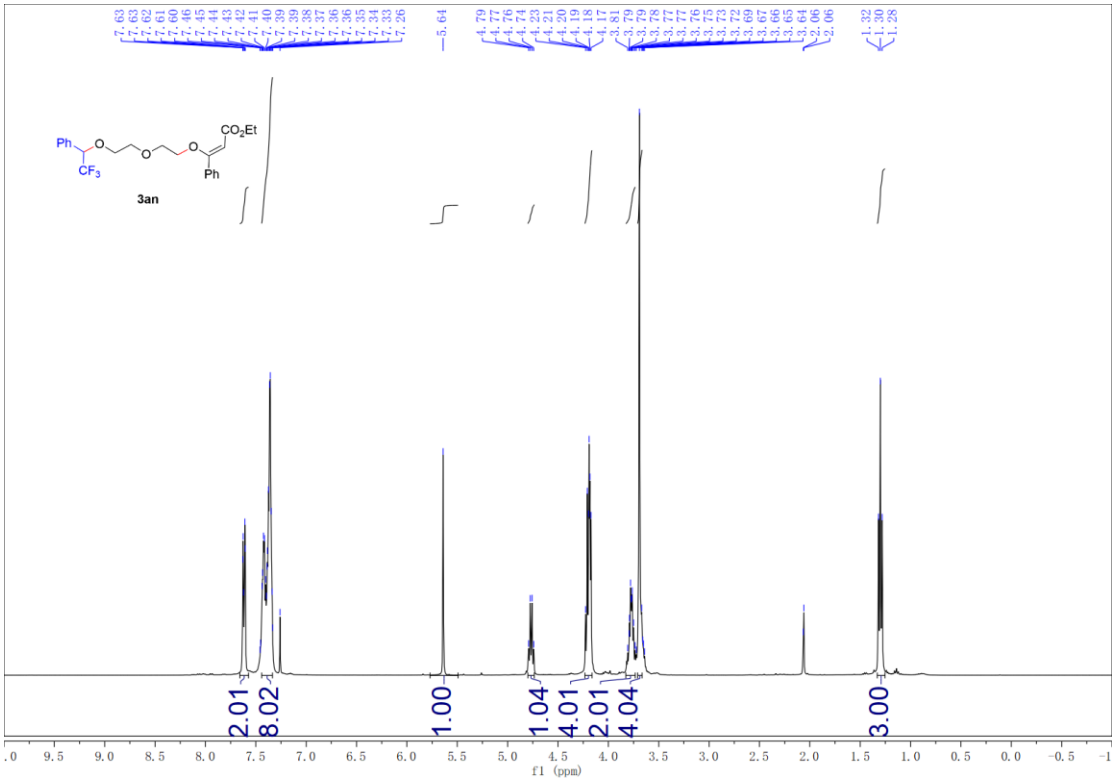
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **3am**



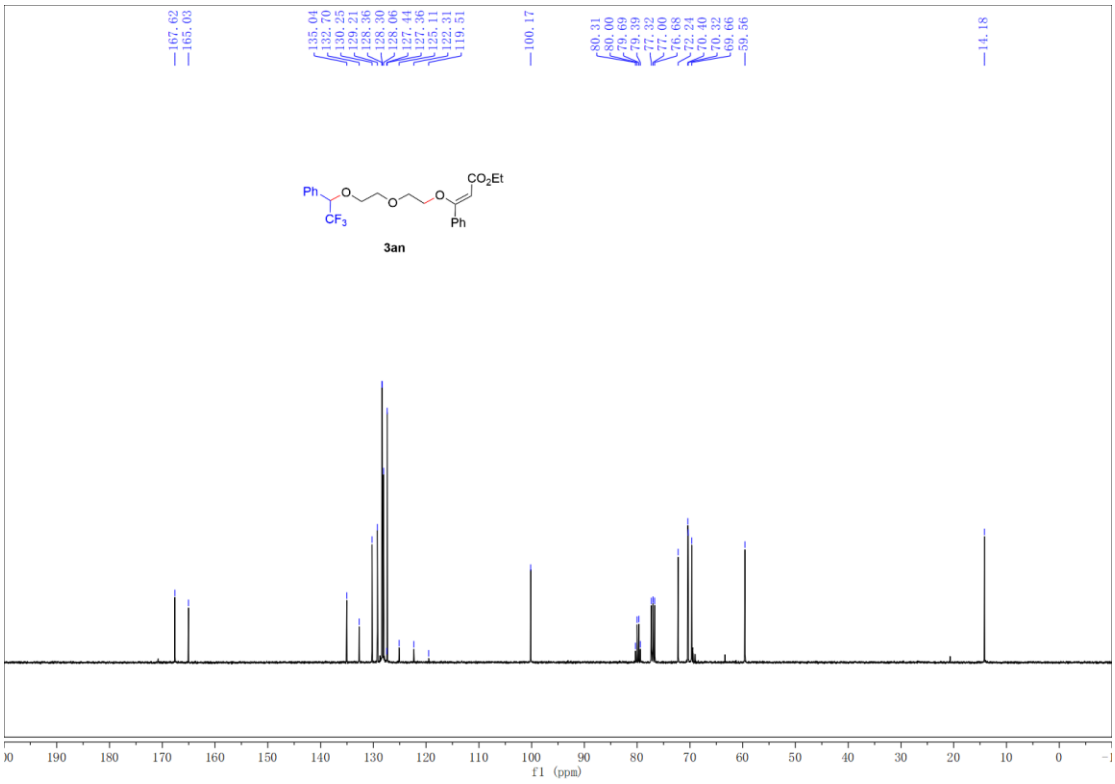
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **3am**



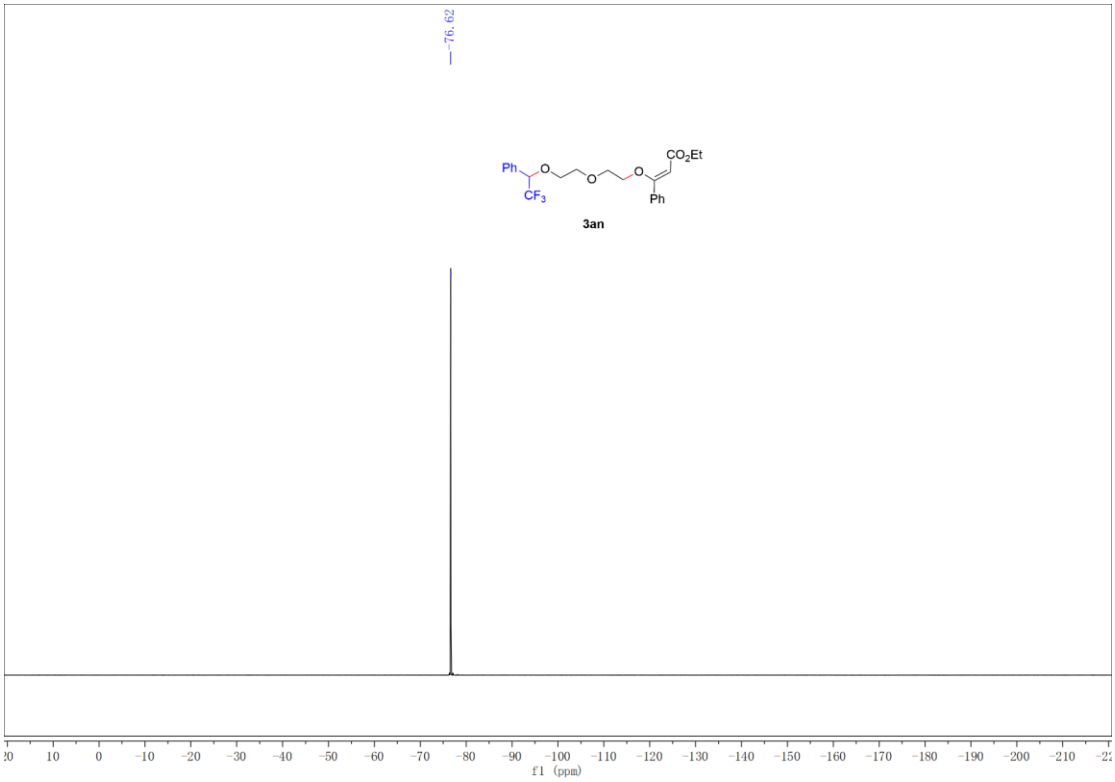
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3an**



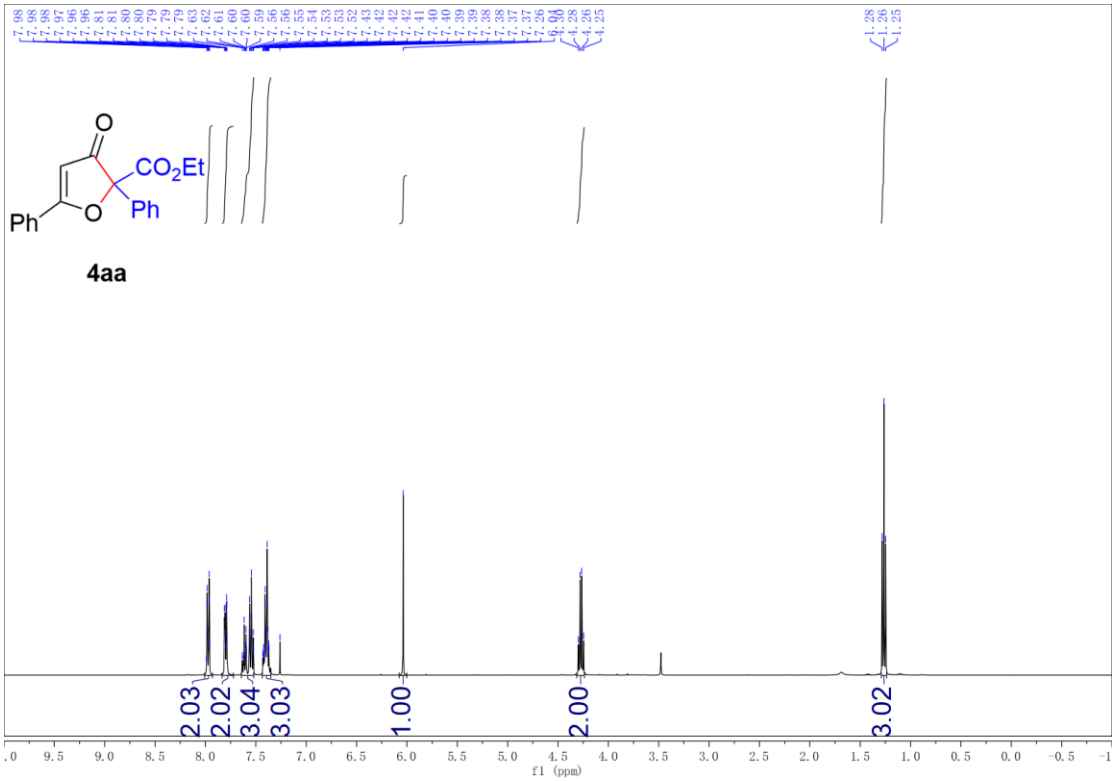
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **3an**



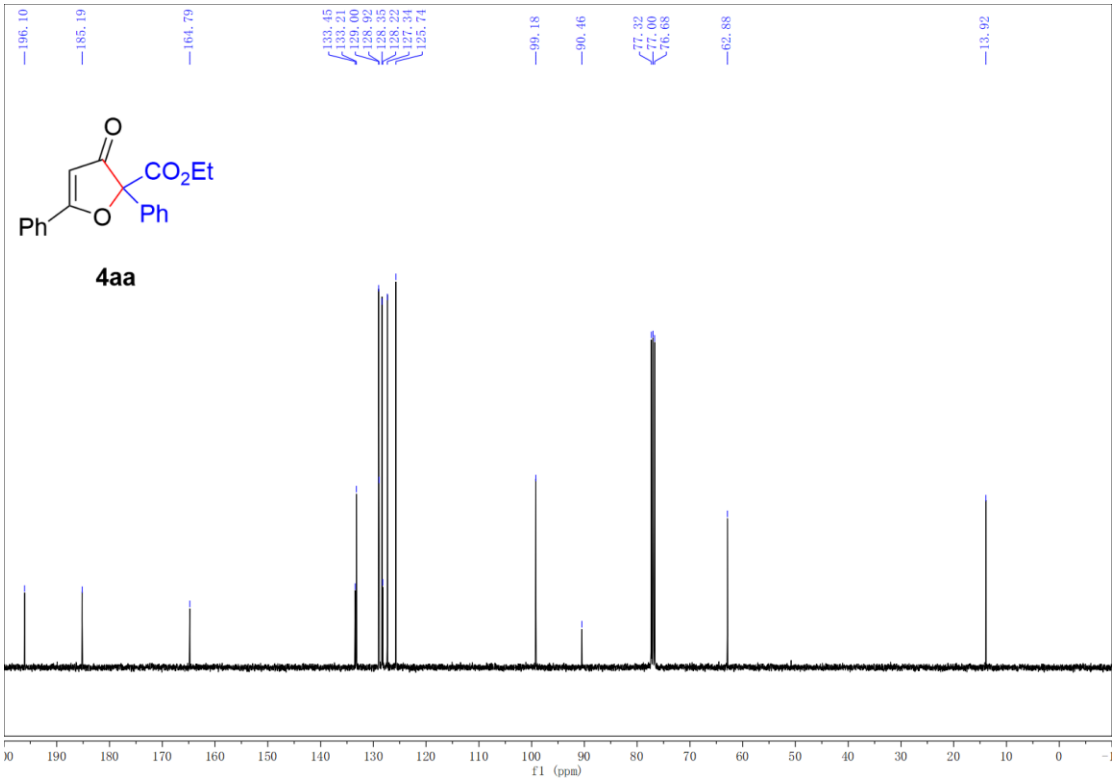
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3an**



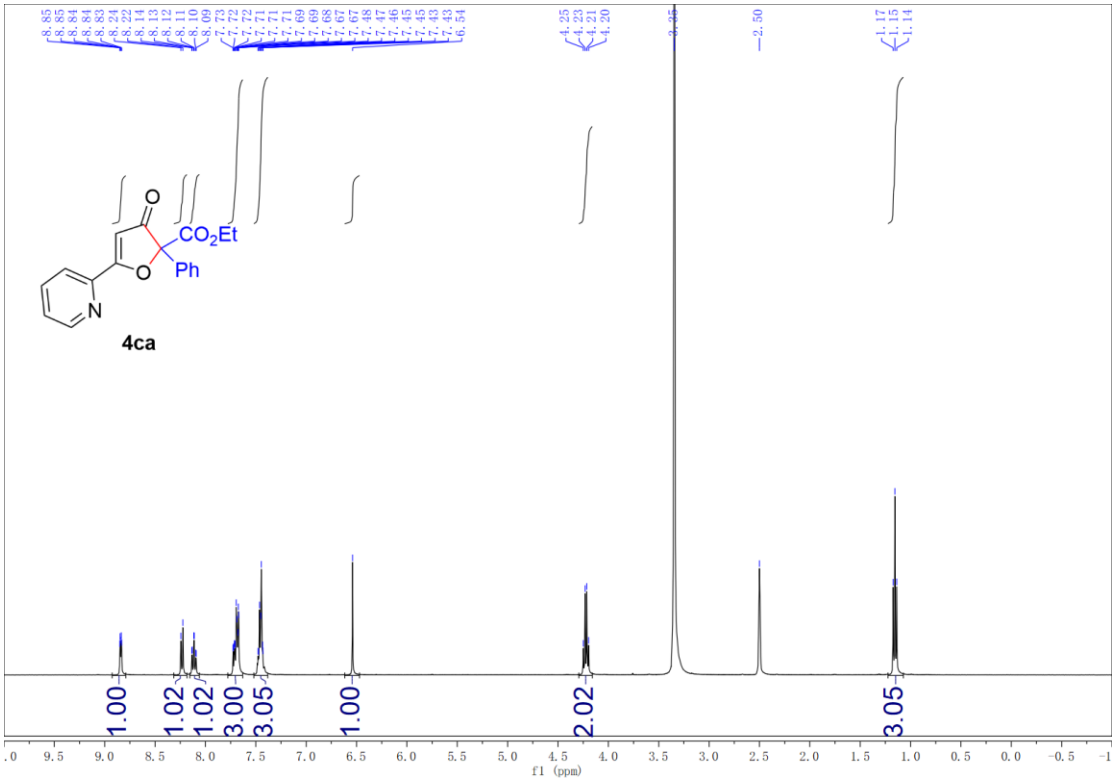
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4aa**



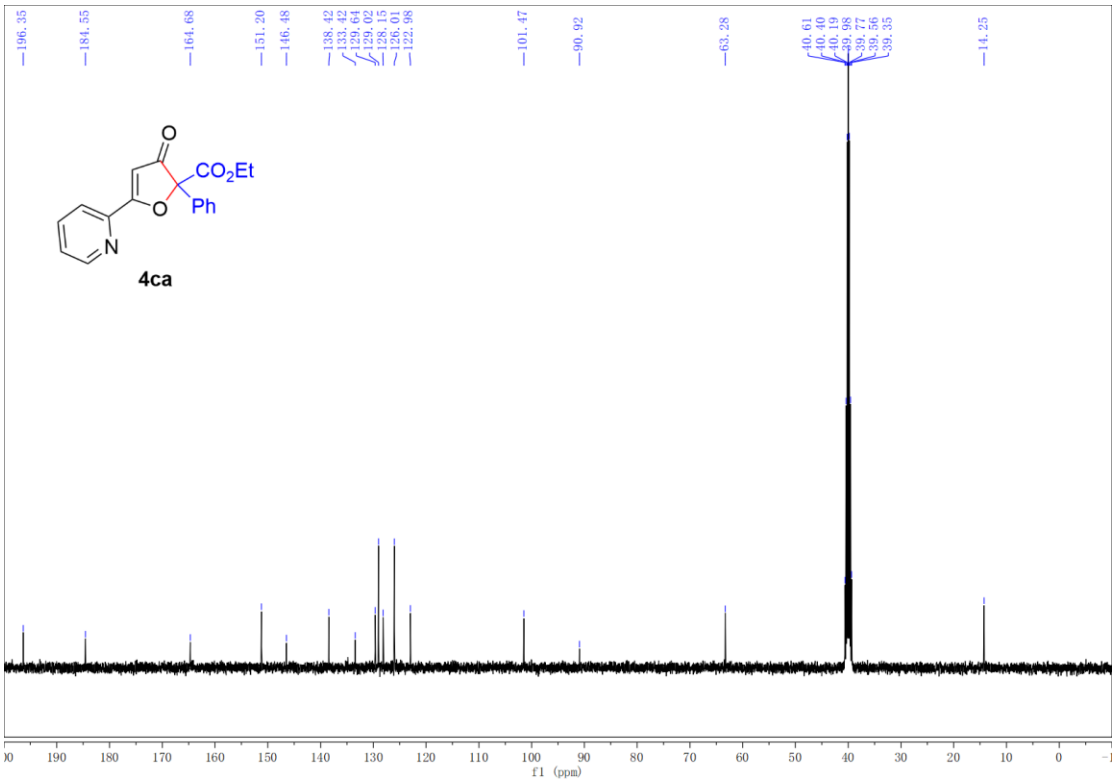
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4aa**



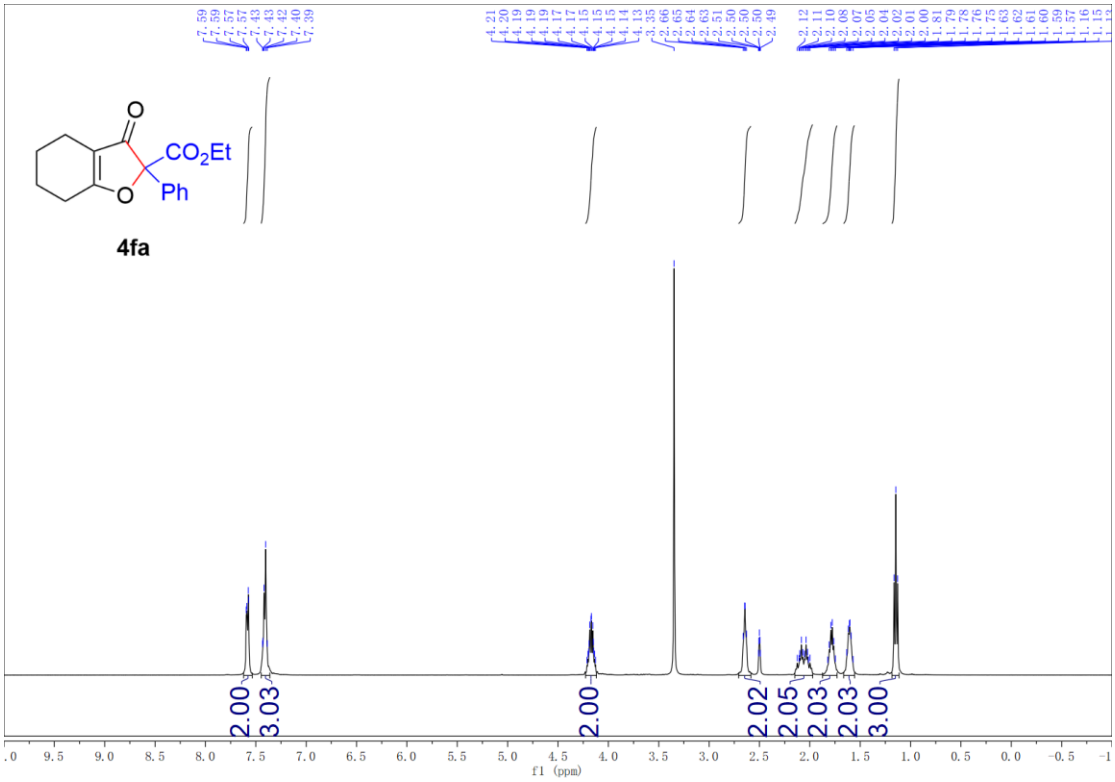
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4ca**



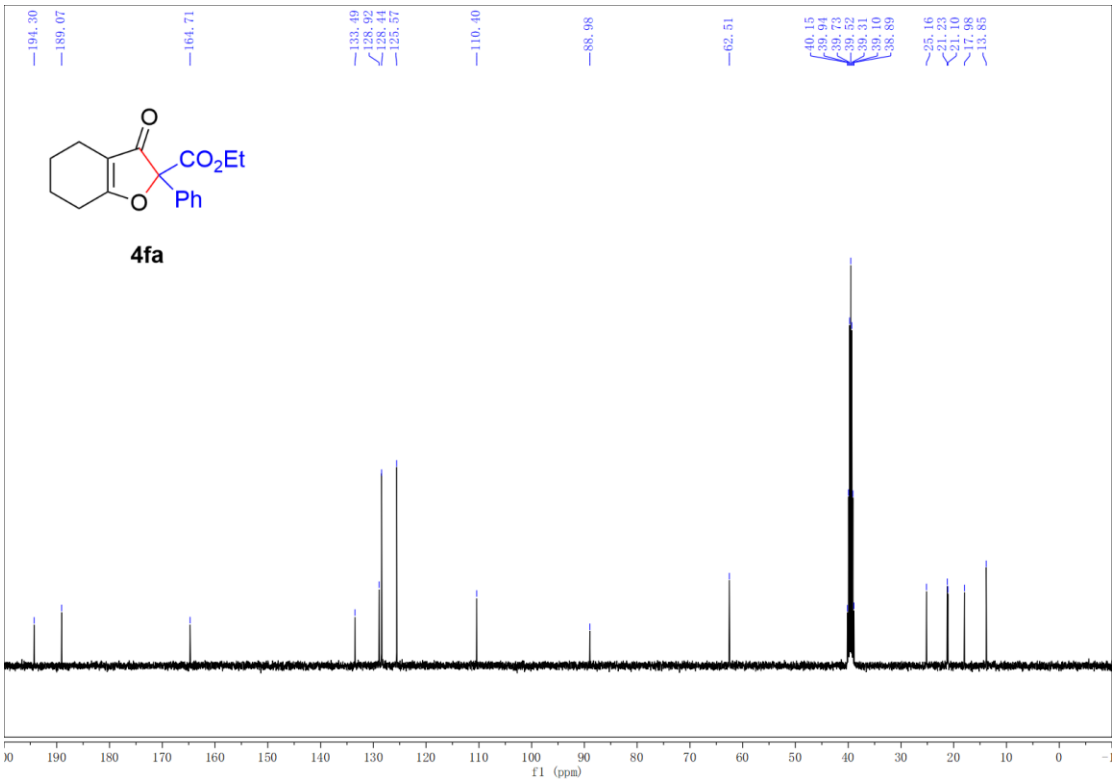
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **4ca**



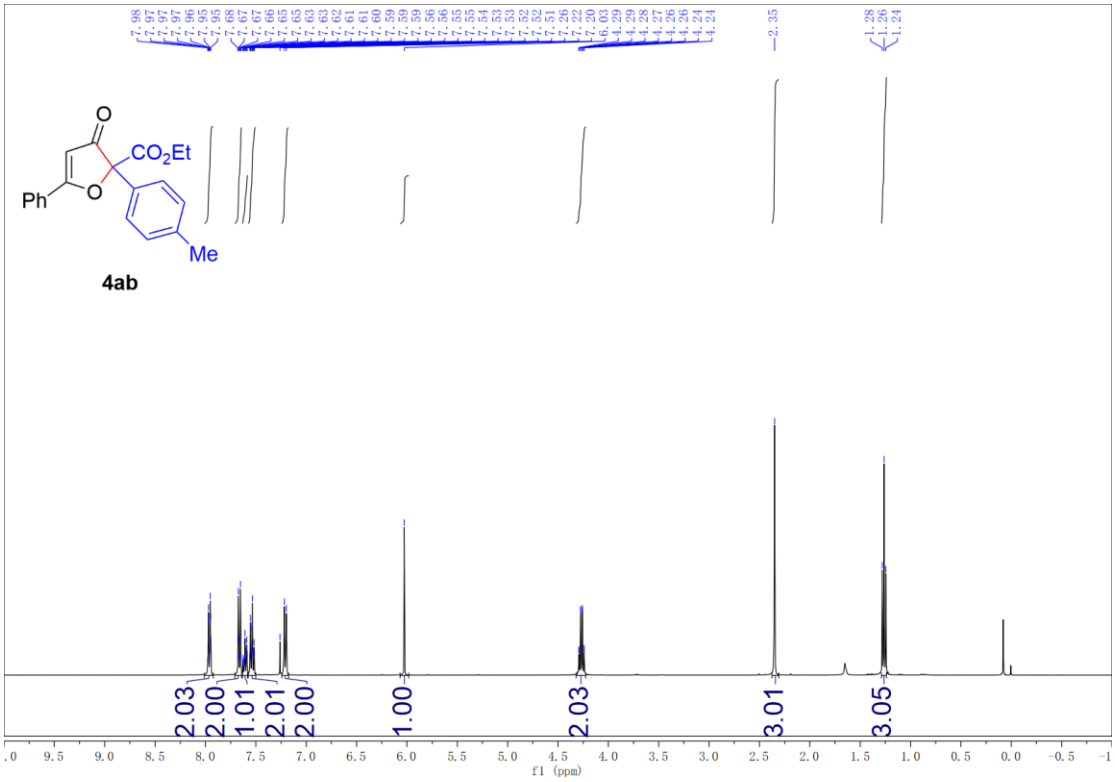
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4fa**



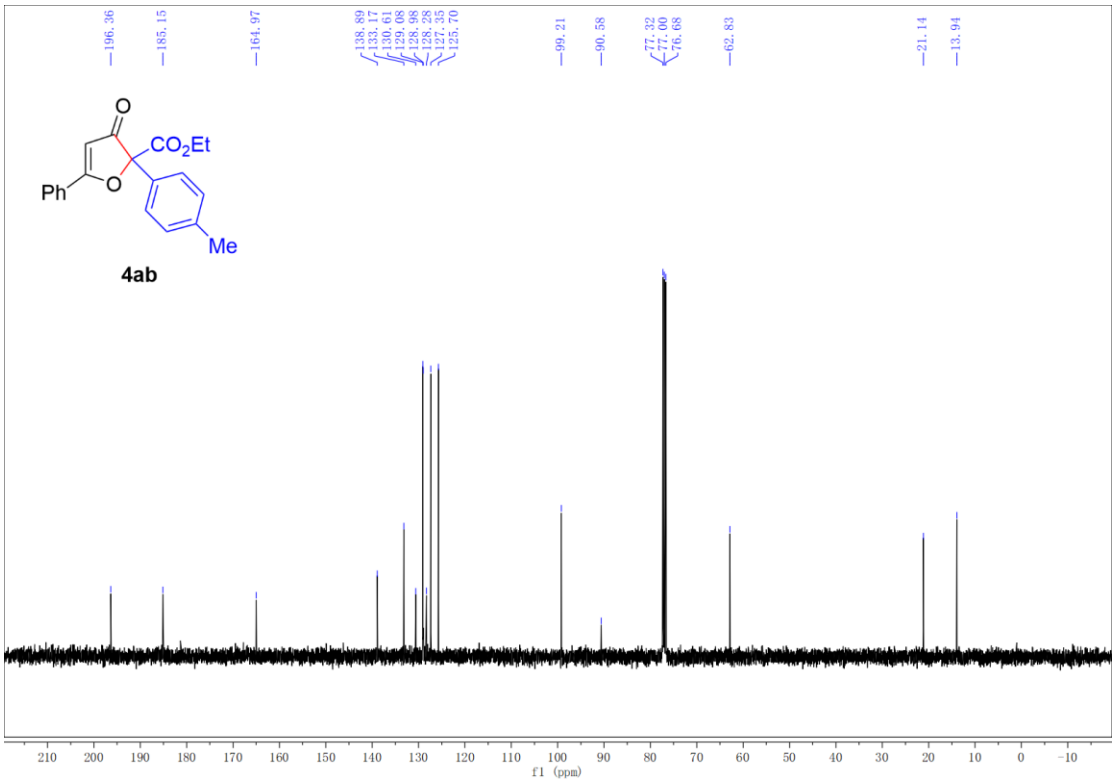
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **4fa**



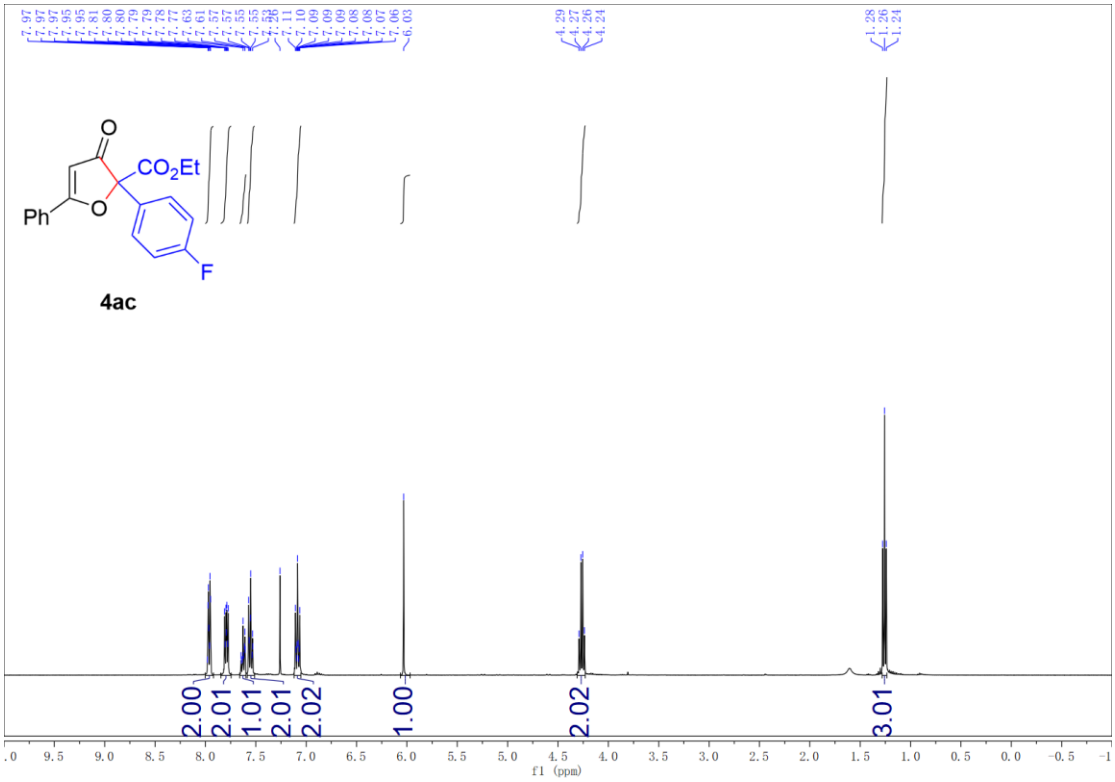
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ab**



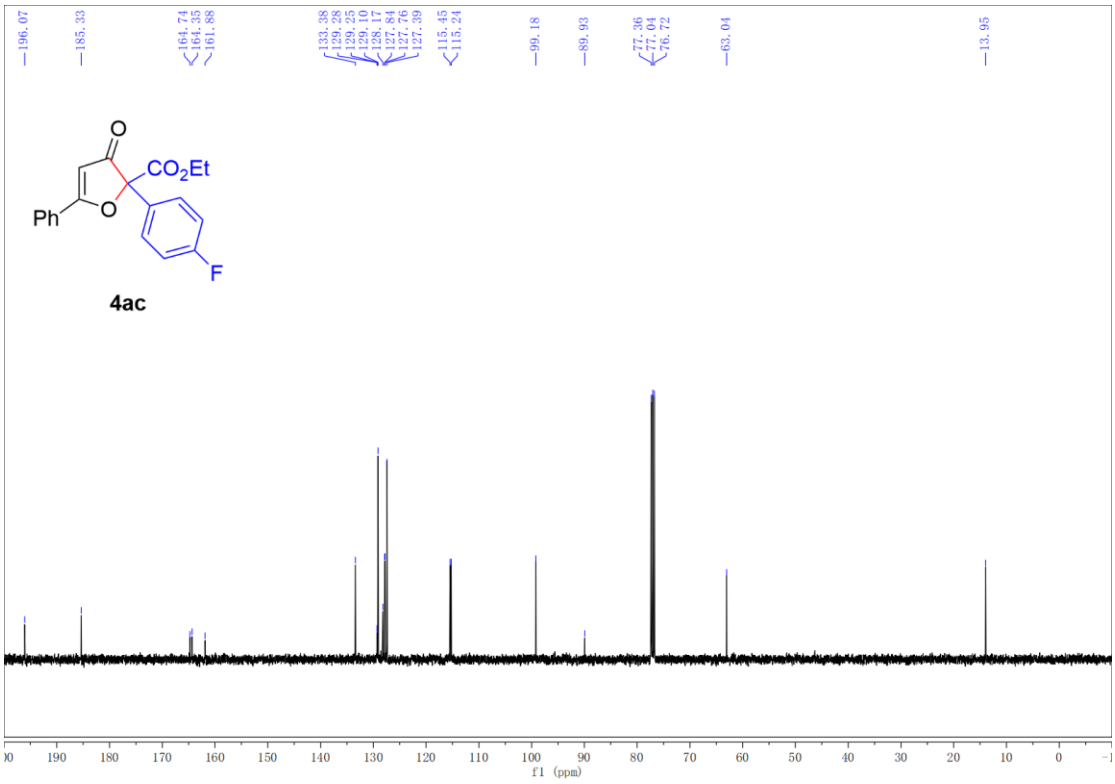
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ab**



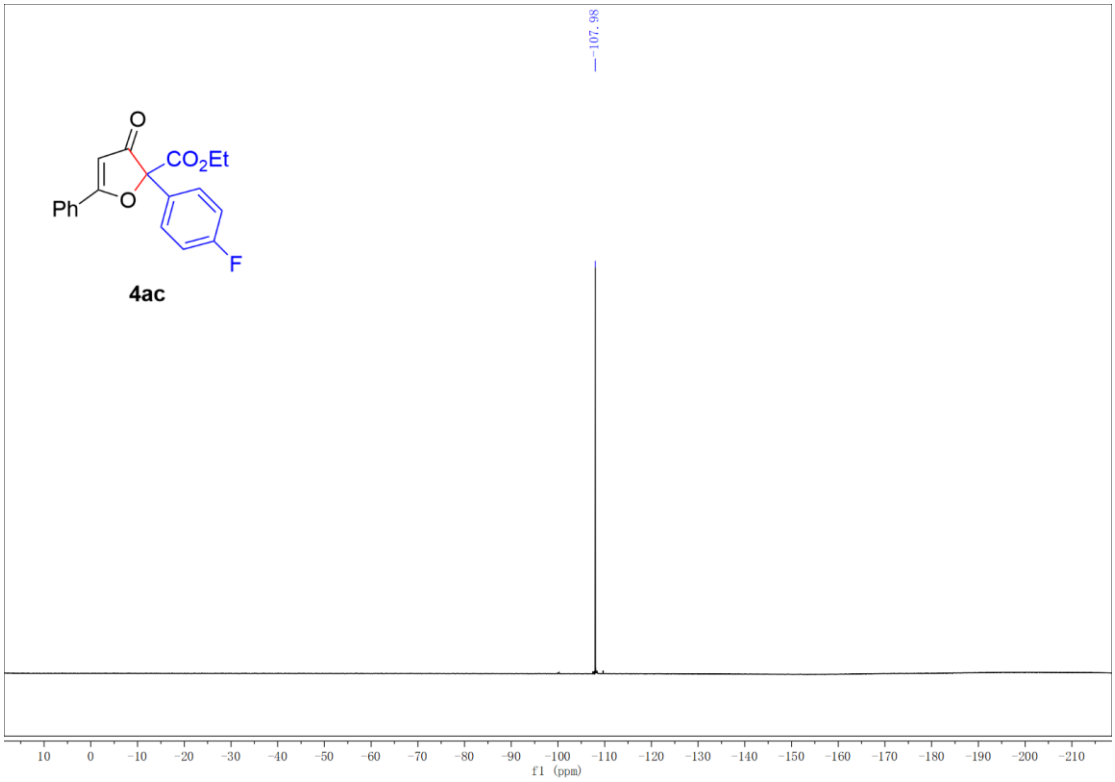
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ac**



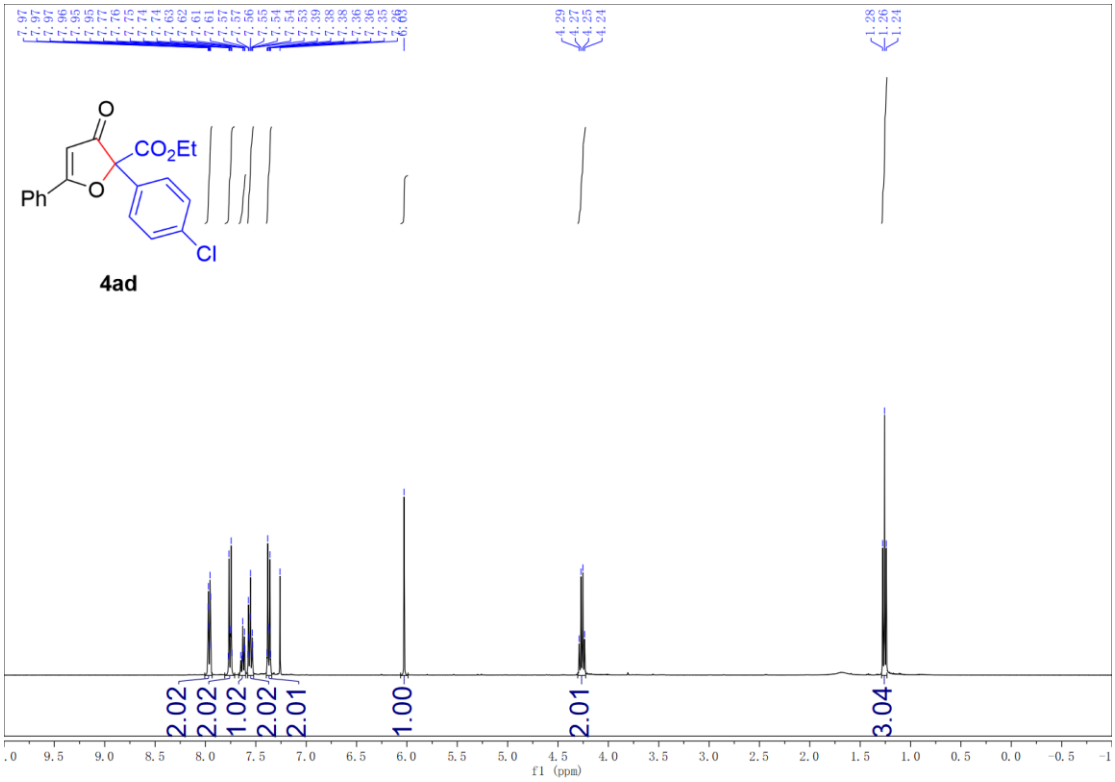
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ac**



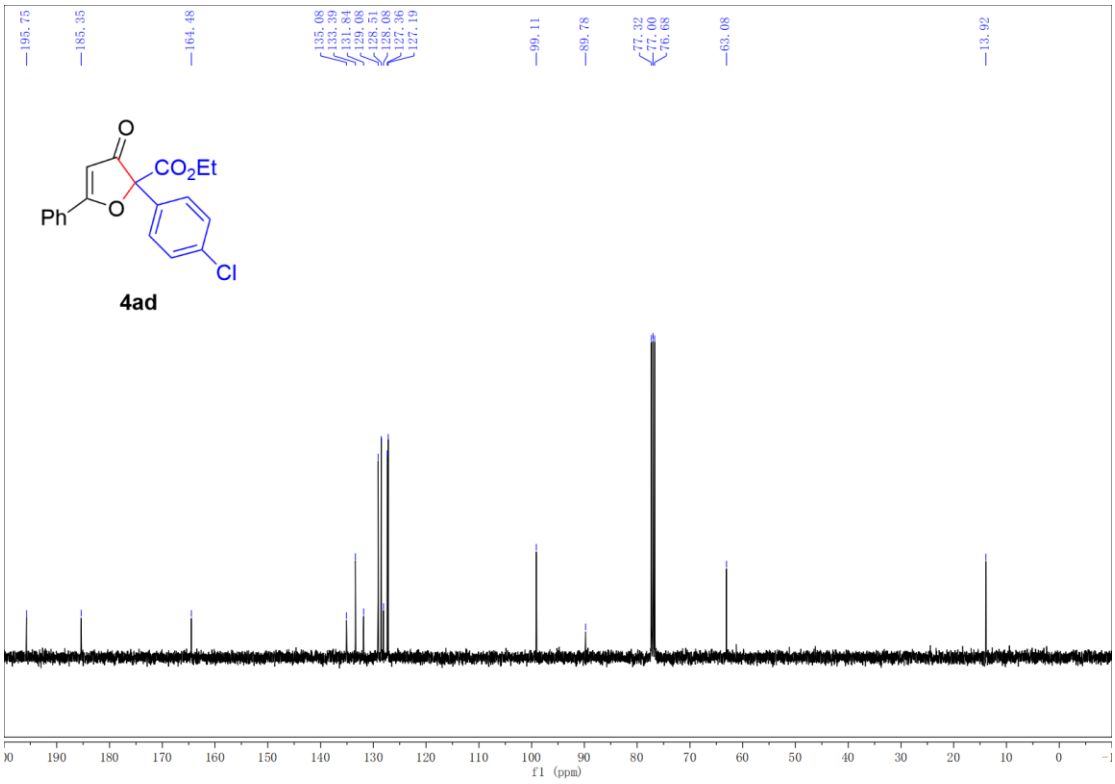
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **4ac**



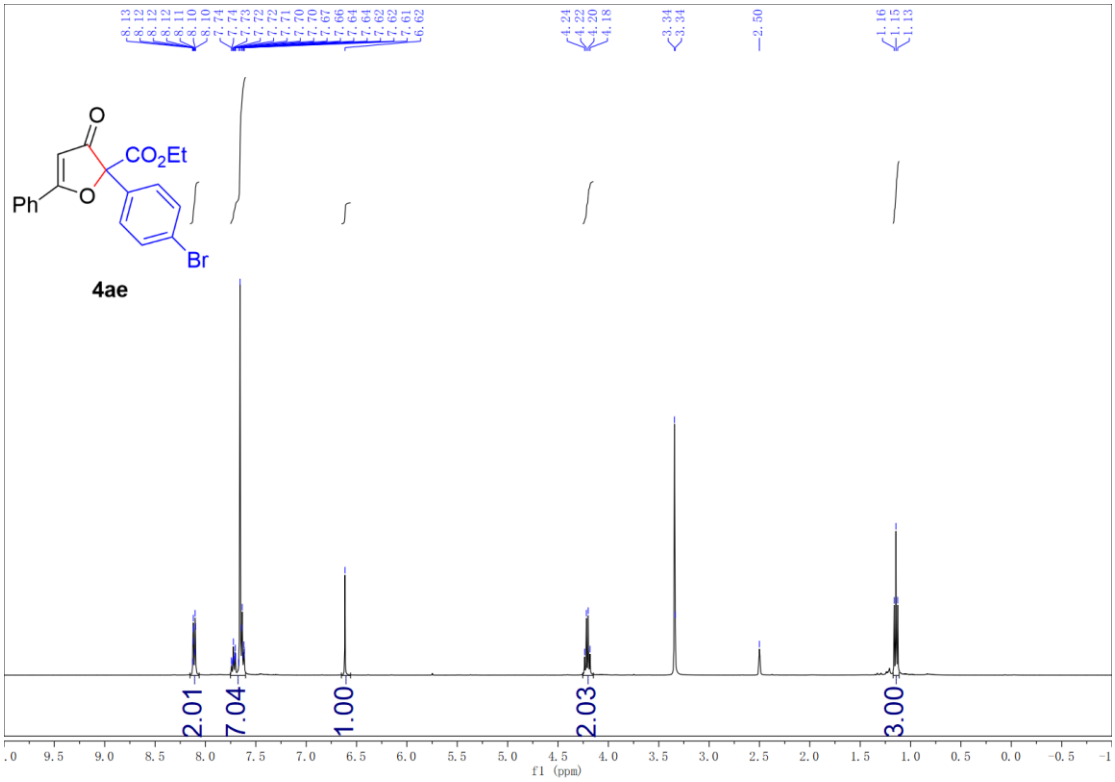
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ad**



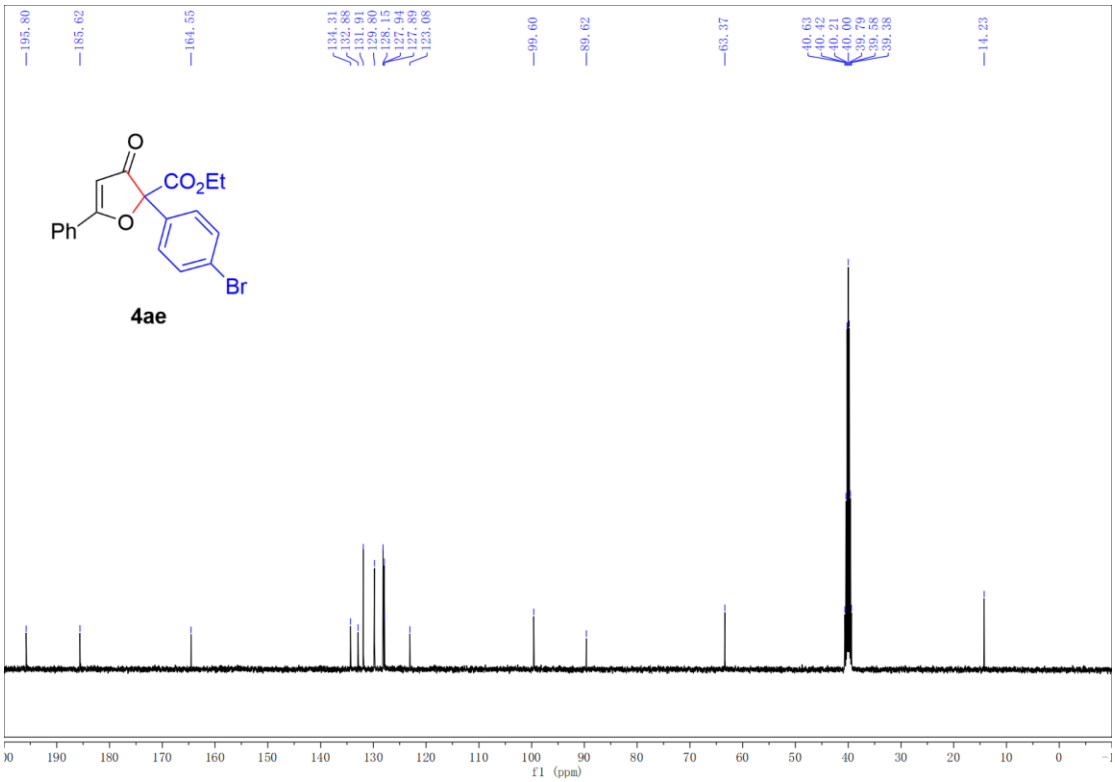
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ad**



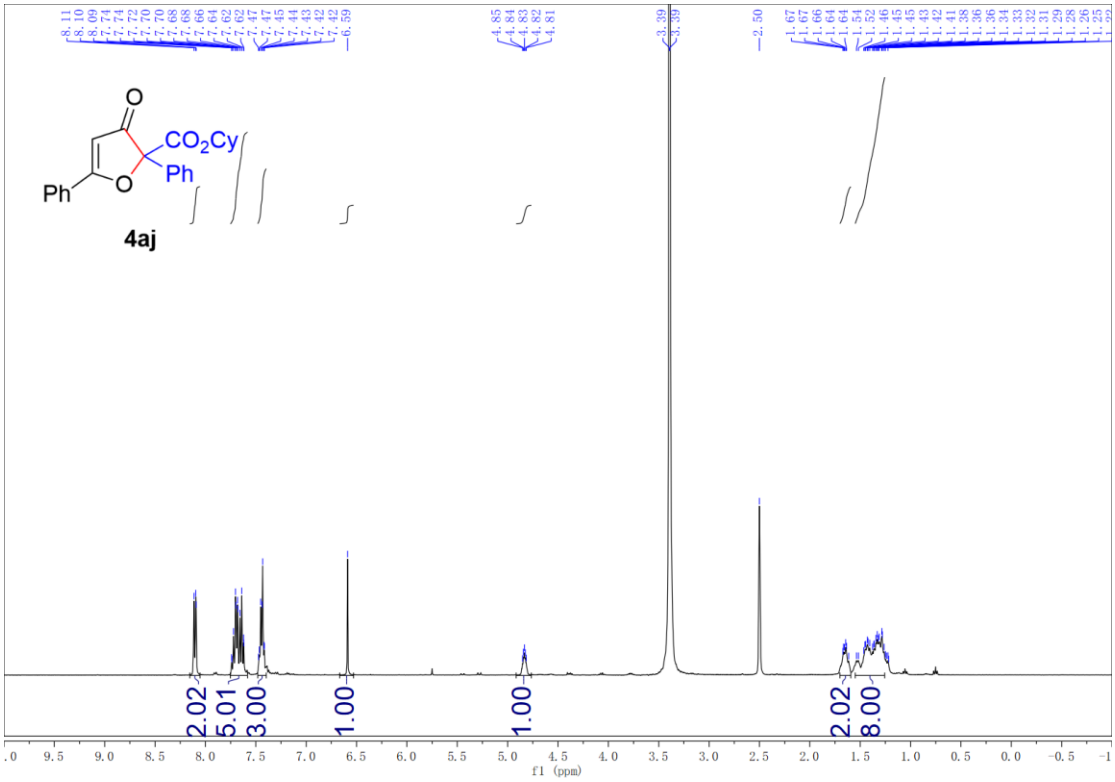
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4ae**



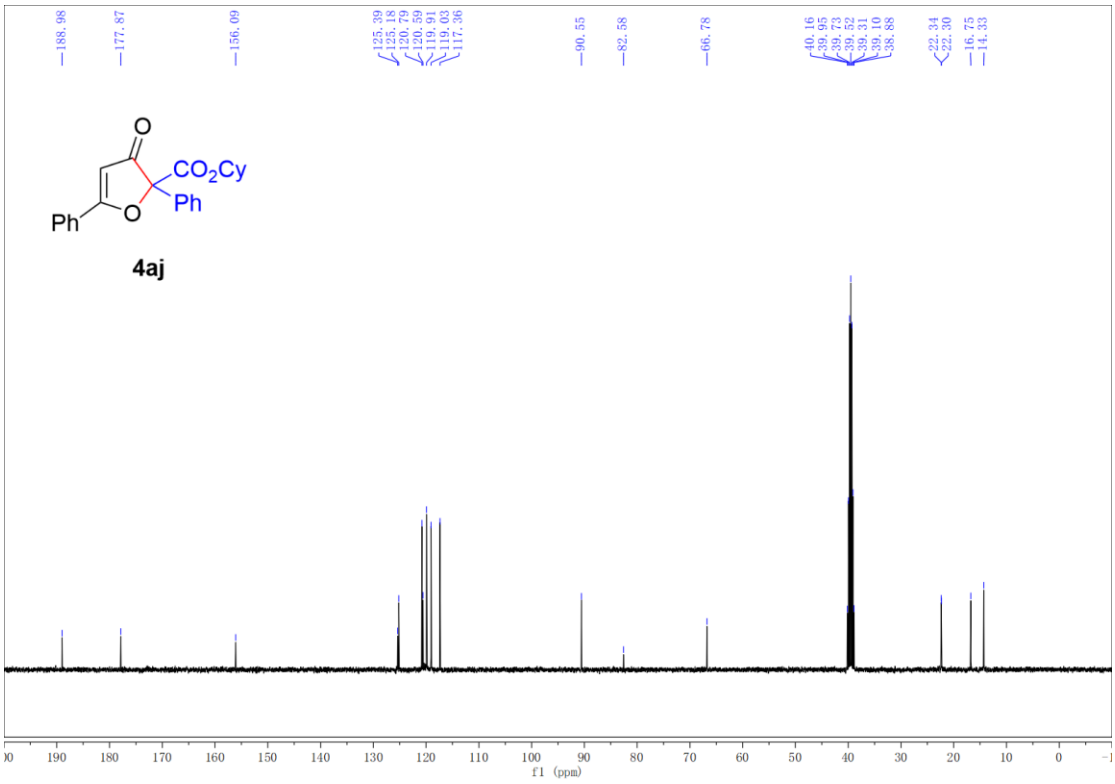
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **4ae**



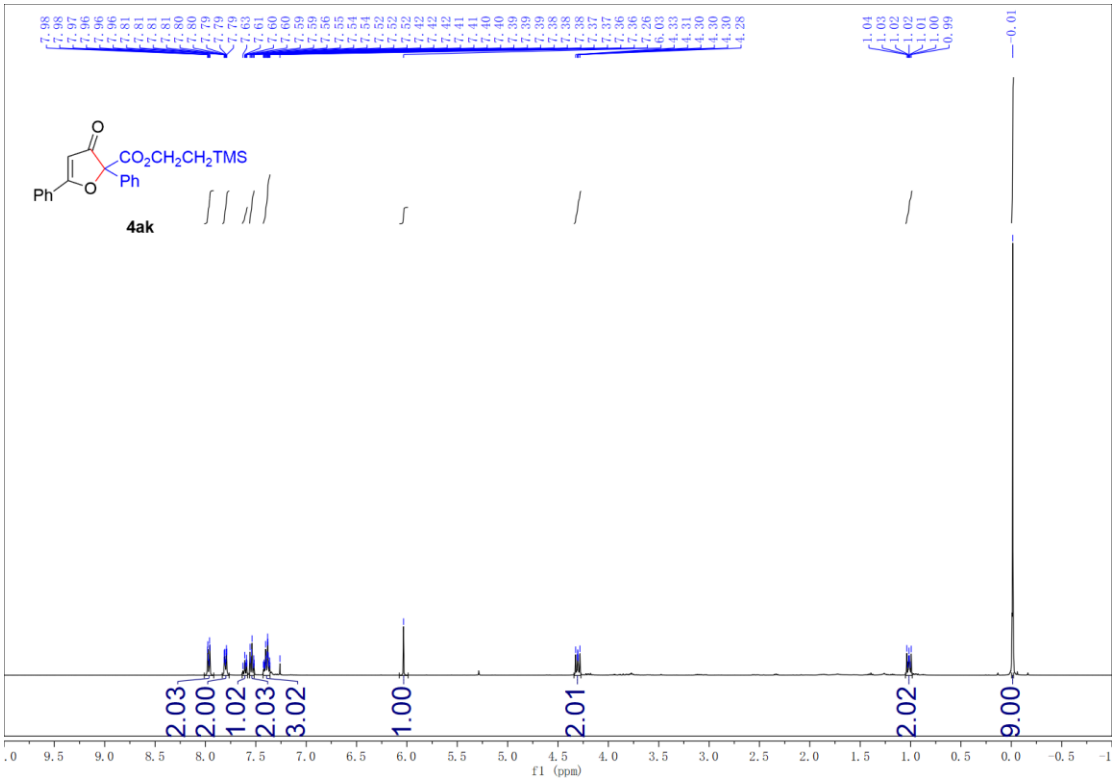
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4aj**



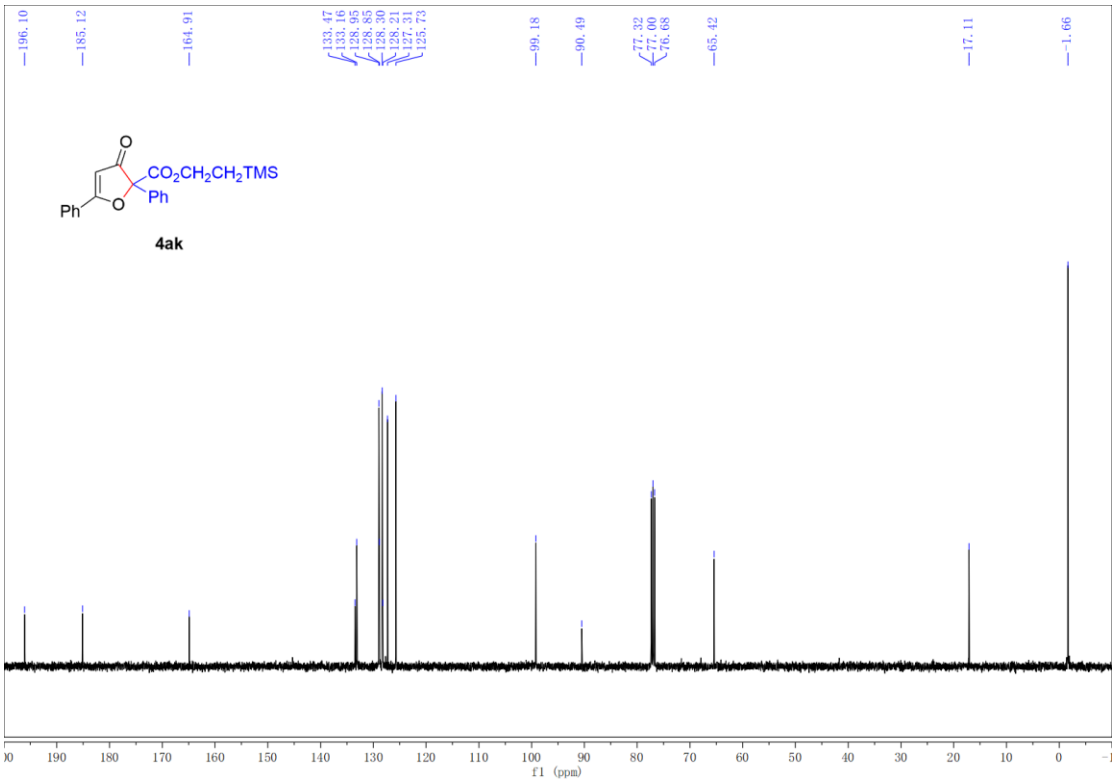
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **4aj**



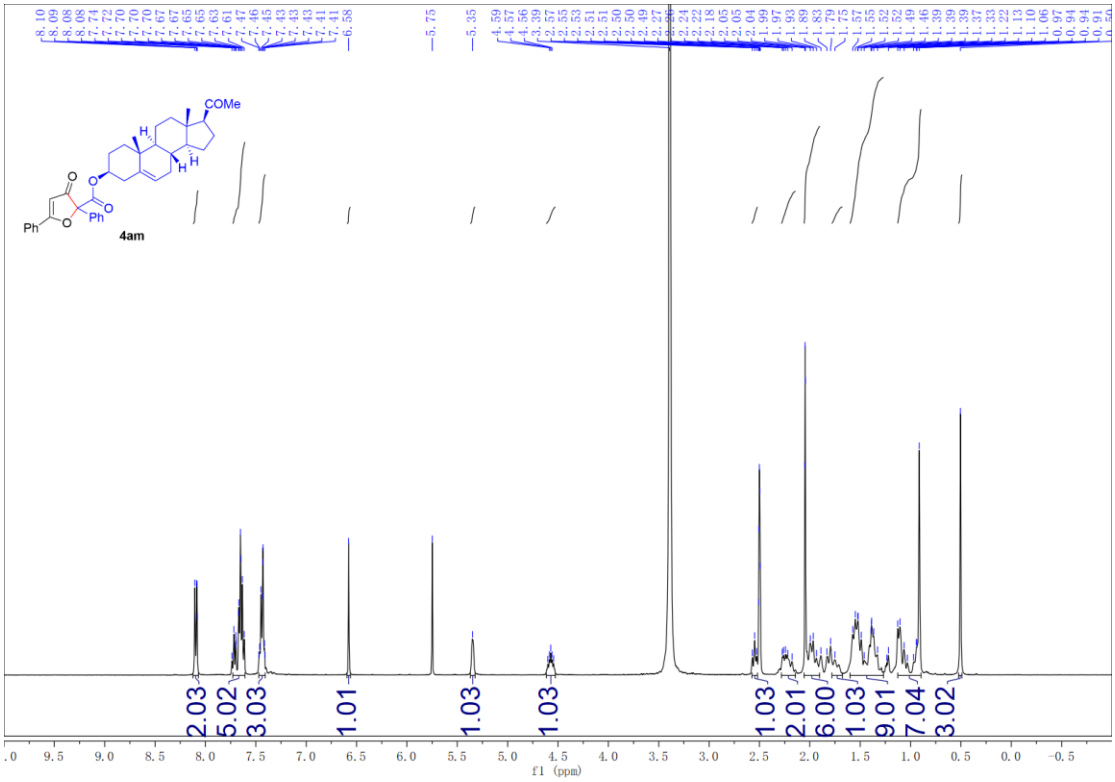
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4ak**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of **4ak**



^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of **4am**



^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) Spectrum of **4am**