Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pyrylium Salts Acting as Both Energy Transfer and Electron Transfer Photocatalysts for *E*→*Z* Isomerization of Activated Alkenes and Cyclization of Cinnamic or Biaryl Carboxylic Acids

Lei Bao[†], Jin-Tang Cheng*[‡], Zhi-Xiang Wang*[†], and Xiang-Yu Chen*[†]

[†]School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

[‡]Institute of Chinese Materia Medica, China Academy of Chinese Medical Sciences, Beijing, 100700, China

Email: jtcheng@icmm.ac.cn; zxwang@ucas.ac.cn; chenxiangyu20@ucas.ac.cn

Table of Contents

1. General Information

- Chemicals were purchased from Alfa Aesar, Leyan, Macklin and Bidepharm used without further purification unless otherwise noted. Solvents were purified using a solvent-purification system (VSPS-8, Vigor) that contained activated alumina and molecular sieves.
- Chromatographic purification of the products was performed on silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- ^{1}H- and ^{13}C- NMR spectra were recorded at ambient temperature on a Shimadzu Avance 400 Spectrometer and Shimadzu Avance 500 Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as the internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, qd = quartet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).
- IR spectra were taken on a Vertex 70 spectrophotometer and reported as wave numbers (cm^{-1}).
- HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. The mass analysis mode of the HRMS was orbitrap.
- Photochemical experiments were performed magnetically stirred in 10 mL glass Schlenk tubes, sealed with a rubber septum (Figure S1). The tubes were irradiated with blue light with a power output of 100 W (a LED lamp with 450nm wavelength) and 10W (a photochemical reactor with 455nm wavelength). All distances from the light source to the irradiation vessel is 2 cm to keep the reaction temperature at 45±5 °C (The purchase link for LED lamp is https://m.tb.cn/h.VCrrHu2?sm=c8b887). To maintain a constant reaction temperature of 25 °C, the setup was cooled by a continuous water-cooling device (The purchase link for the the photochemical reactor is http://www.bjplss.com/productshow_1.html).
- UV/vis absorption spectra were acquired on UV-1900 spectrophotometer (Shimadzu, Japan).

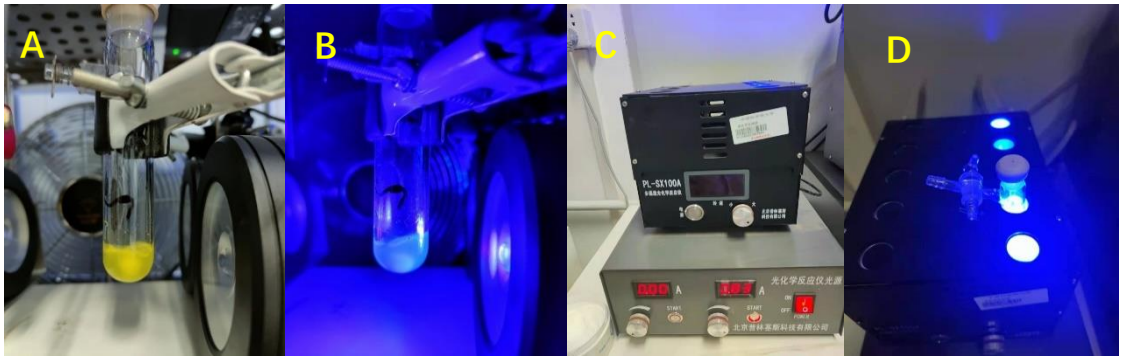


Figure S1 A, B, the LED lamp device for cyclization of **1** to **2** and **5** to **6**; C, D, the photochemical reactor device for *E/Z* isomerization of **3** to **4**.

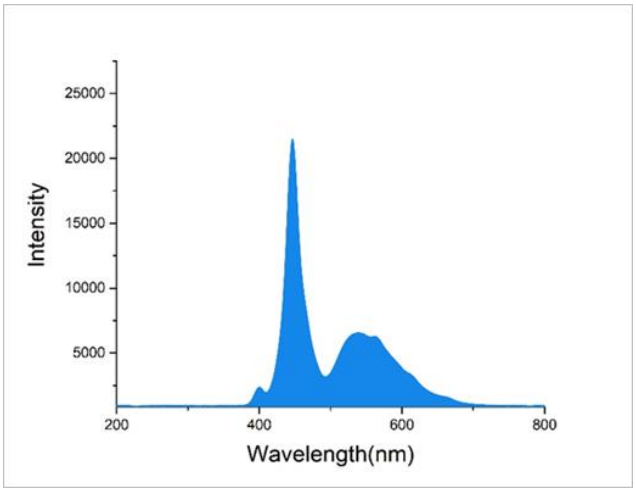


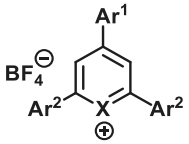
Figure S2 The spectrum of blue LEDs (100 W) employed in the reaction.

2. Experimental Section

2.1 Preparation of the starting materials

The specified α,β-unsaturated esters, nitriles and acids were respectively synthesized according to the literature.[1-3] Except **1a-1e**, **1j**, which are the reactants of **2a-2e**, **2j**, were purchased from Bidepharm. The specified biphenyl-2-carboxylic acids were synthesized according to the literatures.[4-6] Except **5a**, **5c**, **5i**, which are the reactants of **6a**, **6c**, **6i**, were purchased from Bidepharm.

2.2 Preparation of the photocatalysts



PC1: X = O, Ar^1 = Ar^2 = Ph
PC2: X = O, Ar^1 = Ar^2 = 4-MeC_6H_4
PC3: X = O, Ar^1 = Ar^2 = 4-$MeOC_6H_4$
PC4: X = O, Ar^1 = Ar^2 = 4-BrC_6H_4r
PC5: X = S, Ar^1 = Ar^2 = Ph
PC6: X = O, Ar^1 = Mes, Ar^2 = Ph

PC1-PC4 were synthesized according to literature procedure.[7] Freshly distilled BF_3•Et_2O (2.4 equiv.) was slowly added to a mixture of the specified benzaldehyde (1.0 equiv.) and acetophenone (2.0 equiv.) at room temperature. If both starting materials were solids, they were dissolved in a small amount of toluene before addition of BF_3•OEt_2. The mixture was then stirred at 100 °C for 4 h. Upon cooling to room temperature, acetone was added until full dissolution of all solids. Et_2O was then added, which resulted in precipitation of the desired product. The solid was filtered, washed with Et_2O, and dried in vacuo. Multiple recrystallizations in MeCN afforded the pure pyrylium salts. The obtained solid was dried under high vacuum.

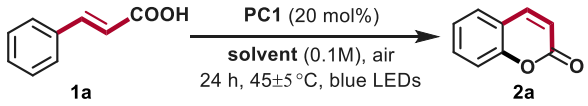
PC5 was synthesized according to literature procedure.[8] An aqueous solution of Na_2S (4 equiv.) was added dropwise to a stirred solution of **PC1** (1 equiv.). Then the mixture was stirred at room temperature for 1 h, upon which the color had changed to red. Afterwards the red solution was added to an Erlenmeyerflask containing aqueous HBF_4 (0.25 M, 48 wt.%) and stirred for another 1 h. The yellow precipitate was filtered, washed with Et_2O. Multiple recrystallizations in MeCN afforded the pure thiapyrylium salt. The obtained solid was dried under high vacuum.

PC6 was synthesized according to literature procedure.[9] To a flame dried 100 mL round bottom flask with a stirring bar was added purchased 2,6-diphenyl-4*H*-pyran-4-one (1 equiv.) under an argon atmosphere. The solid was then dissolved with of anhydrous THF (0.05 M) and 2-mesitylmagnesium bromide (5 equiv., from 1 M solution in THF) was added dropwise. The reaction changed color over time from clear to yellow and to red. After consumption of starting material determined by TLC, the reaction was quenched by sat. $NaHCO_3$ aqueous solution. THF

was removed in vacuo and the remaining mixture was extracted (x3) with DCM. The combined organic layers were then washed with brine and dried over $MgSO_4$. The organic solvent was reduced in vacuo and dried under high vacuum for 30 minutes. The crude material was dissolved into of Et_2O (0.1 M) and stirred, at which point a solution of HBF_4•Et_2O (1.2 equiv., dissolved in Et_2O (0.5 M) was added dropwise. At the onset of addition, a yellow precipitate was observed. After the addition was completed, the mixture was cooled with an ice bath and stirred for 30 minutes. The yellow precipitate was filtered, washed with Et_2O. Multiple recrystallizations in MeCN afforded the pure pyrylium salt. The obtained solid was dried under high vacuum.

2.3 Optimization of the reaction conditions

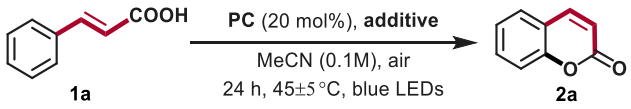
Table S1 Screening of solvents[a]



Entry	Solvent	Yield (%)[b]
1	Acetone	trace
2	DMA	ND
3	DMF	ND
4	THF	ND
5	MeOH	trace
6	DCM	20
7	MeCN	30
8	Ethyl ether	trace
9	DMSO	ND

[a]**1a** (0.2 mmol), solvent (2.0 mL), irradiation with 100 W blue LEDs, ND is 'no product was detected'; [b]Isolated yield.

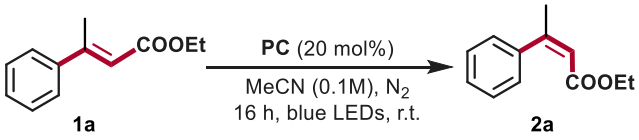
Table S2 Screening of additives[a]



Entry	PC	Additive	Yield (%)[b]
1	**PC1**	10 mol% NaI	34
2	**PC1**	20 mol% NaI	48
3	**PC1**	20 mol% $C_{24}H_{20}PI$	47
4	**PC1**	20 mol% KI	48
5	**PC1**	20 mol% FeI	35
6	**PC1**	20 mol% CuI	28
7	**PC6**	20 mol% NaI	78
8[c]	**PC6**	20 mol% NaI	75

[a]**1a** (0.2 mmol), MeCN (2.0 mL), irradiation with 100 W blue LEDs; [b]isolated yield; [c]in oxygen atmosphere.

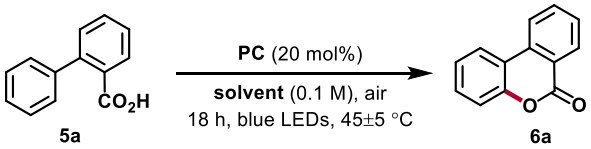
Table S3 Optimization of the *E*→*Z* isomerization reaction[a]



Entry	PC	Yield (%)[b]	*Z/E* ratio[c]
1	**PC1**	30	/
2	**PC2**	20	/
3	**PC3**	trace	/
4	**PC4**	trace	/
5	**PC5**	trace	/
6	**PC6**	85	93:7
7[d]	**PC6**	ND	/

[a]**1a** (0.2 mmol), MeCN (2.0 mL), irradiation with 10 W blue LEDs, ND is 'no product was detected'; [b]isolated yield; [c]*Z/E* ratios were determined by ^{1}H NMR spectroscopy of reaction mixture; [d]no illumination or no **PC6**.

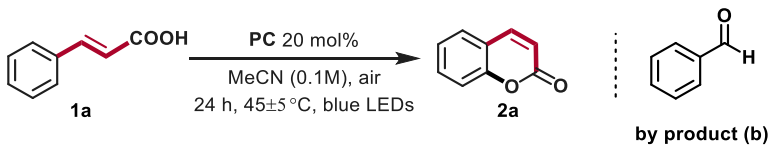
Table S4 Optimization of cyclization of biaryl carboxylic acids[a]



Entry	PC	Solvent	Yield (%)[b]
1	**PC1**	DMF	ND
2	**PC1**	DMA	ND
3	**PC1**	Acetone	trace
4	**PC1**	THF	60
5	**PC1**	DCM	51
6	**PC1**	MeCN	80
7	**PC2**	MeCN	71
8	**PC3**	MeCN	33
9	**PC4**	MeCN	65
10	**PC5**	MeCN	64
11	**PC6**	MeCN	78
12[c]	**PC1**	MeCN	/

[a]**5a** (0.2 mmol), solvent (2.0 mL), irradiation with 100 W blue LEDs, ND is 'no product was detected'; [b]isolated yield; [c]no illumination or no **PC1**.

Table S5 Conversion and by-product analysis of the cascade cyclization[a]

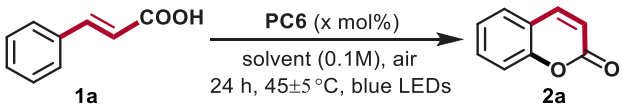


Entry	PC	Conversion (%)[b]	Yield (2a, %)[c]	Yield (b, %)[d]
1	**PC1**	100	35	25
2	**PC2**	100	22	12
3	**PC3**	50	trace	20
4	**PC4**	100	35	30

5	**PC5**	88	20	14
6	**PC6**	100	65	15

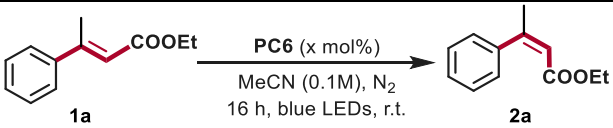
[a]**1a** (0.2 mmol), MeCN(2.0 mL); [c]isolated yield; [b, d]determined by ^{1}H NMR spectroscopy of reaction mixture using 1,1,2,2-tetrachloroethane as internal standard.

Table S6 Optimization of PC's equivalent[a]



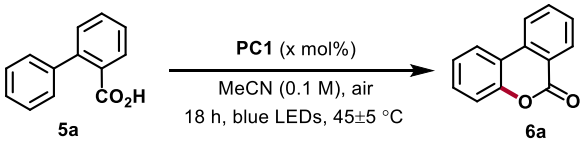
1a 2a

Entry	PC	x	Yield (%)[c]	*Z*/*E* ratio[d]
1	**PC6**	1	14	/
2	**PC6**	2.5	17	/
3	**PC6**	5	30	/
4	**PC6**	10	42	/
5	**PC6**	15	51	/
6	**PC6**	20	65	/
7[b]	**PC6**	1	trace	/
8[b]	**PC6**	2.5	trace	/
9[b]	**PC6**	5	trace	/
10[b]	**PC6**	10	23	/
11[b]	**PC6**	15	41	/
12[b]	**PC6**	20	78	/



1a 2a

Entry	PC	x	Yield (%)[c]	*Z*/*E* ratio[d]
13	**PC6**	1	10	8:92
14	**PC6**	2.5	27	37:63
15	**PC6**	5	52	68:32
16	**PC6**	10	59	88:12
17	**PC6**	15	72	90:10
18	**PC6**	20	85	93:7

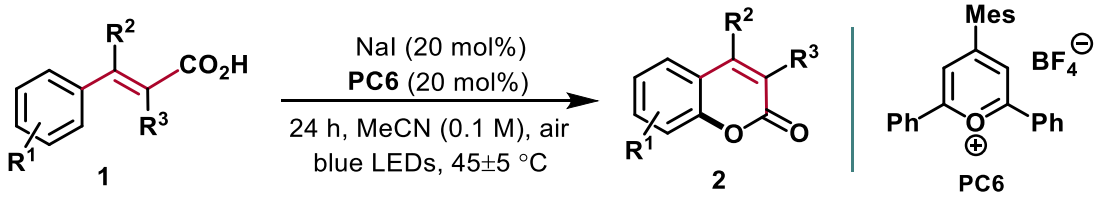


5a 6a

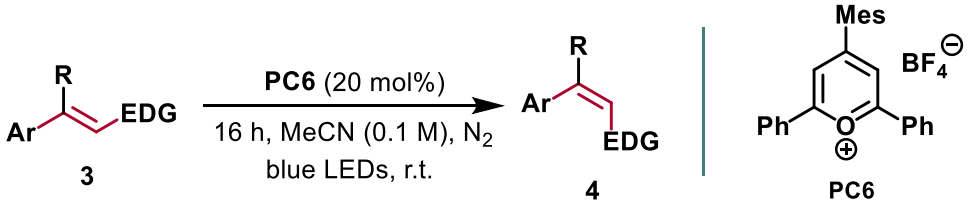
Entry	PC	x	Yield (%)[c]	*Z*/*E* ratio[d]
19	**PC1**	1	21	/
20	**PC1**	2.5	23	/
21	**PC1**	5	36	/
22	**PC1**	10	58	/
23	**PC1**	15	70	/
24	**PC1**	20	80	/

[a]all reactants (0.2 mmol), MeCN (2.0 mL); [b]adding 20 mol% NaI; [c]isolated yield; [d]*Z*/*E* ratios were determined by ^{1}H NMR spectroscopy of reaction mixture.

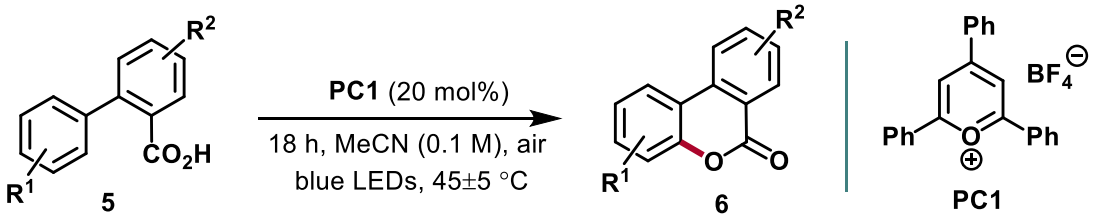
2.4 The general procedure of cyclization and isomerization reactions



General Procedure A: To a dry Schlenk equipped with a stirring bar, the specified cinnamic acid (0.2 mmol), NaI (0.04 mmol, 20 mol%, 6.0 mg), **PC6** (0.04 mmol, 20 mol%, 18.0 mg) were added. After the addition of MeCN (2.0 mL) to the mixture via gastight syringe under air atmosphere, the mixture was stirred 24 h under a 100 W blue LED (450 nm) lamp spaced 2 cm apart. A fan was used to keep the reaction temperature at 45±5 °C (the heat source is from irradiation of LED lamp). The reaction mixture was subjected to silica gel chromatography to afford the desired product (PE/EA = 30:1 – 10:1).



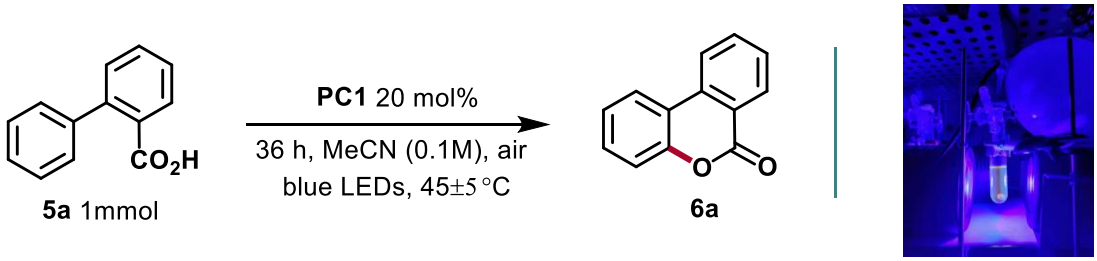
General Procedure B: To a dry Schlenk equipped with a stirring bar, the specified esters, nitrile or phosphonate (0.20 mmol), **PC6** (0.04 mmol, 20 mol%, 18.0 mg) were added. The tube was evacuated and filled with argon (three times). After the addition of MeCN (2.0 mL) to the mixture via gastight syringe under argon atmosphere, the mixture was stirred 16 h at room temperature in a blue LED (455 nm) photoreactor. The reaction mixture was subjected to silica gel chromatography to afford the desired product (PE/EA = 150:1 – 20:1 for esters and nitriles).



General Procedure C: To a dry Schlenk equipped with a stirring bar, the specified 2-phenylbenzoic acid (0.20 mmol), **PC1** (0.04 mmol, 20 mol %, 16.0 mg) were added. After the addition of MeCN (2.0 mL) to the mixture via gastight syringe under air atmosphere, the mixture was stirred 24 h under a 100 W blue LED (450 nm) lamp spaced 2 cm apart. A fan was used to keep the reaction temperature at 45±5 °C (the heat source is from irradiation of LED lamp). The reaction

mixture was subjected to silica gel chromatography to afford the desired product (PE/EA = 30:1 – 10:1).

2.5. Gram-scale reaction



The Procedure: To a Schlenk reaction flask with a stirring bar, the 2-phenylbenzoic acid **5a** (1 mmol, 198.0 mg) and **PC1** (0.2 mmol, 79.2 mg) were added, the flask was filled with air. After the addition of MeCN (10 mL) to the mixture via gastight syringe, the mixture was stirred for 24 h under two 100W blue LEDs (450 nm) lamps spaced 2 cm apart. A fan was used to keep the reaction temperature at 45 ±5 °C (the heat source is from irradiation of LED lamp). The product was purified by silica gel chromatography (PE/EA = 30:1 – 10:1) as a white solid (0.61 mmol, 120.0 mg, 61%).

2.6. Stern-Volmer Emission Quenching Experiment

To 1 mL of a 5 μM solution of **PC6** in a degassed mixture of MeCN was added the specified amount of the quencher (***E*-3a** or ***Z*-3a**, respectively) in 1 mL degassed MeCN. Luminescence intensities were recorded using an Edinburgh instruments FS5 spectrofluorometer excited at 320 nm. All luminescence measurements were recorded using a quartz cuvette (fluorescence quartz cuvette, 10*10 mm, 3.5 mL). Quenching was analyzed by plotting I_0/I according to the Stern-Volmer relationship: $I_0/I = k_q\tau_0[Q]+1$ where I_0 represents the integral of the luminescence over the range of 330 to 600 nm in the absence of a quencher, I is the integral of luminescence over the range of 330 to 600 nm in the presence of a quencher, k_q represents the quenching rate constant, [Q] is the concentration of a given quencher.

Entry	Quencher Concentration (***E*-3a** or ***Z*-3a**)	**PC6** Concentration
1	0 mM	5 μM
2	20 mM	5 μM
3	30 mM	5 μM
4	40 mM	5 μM
5	50 mM	5 μM

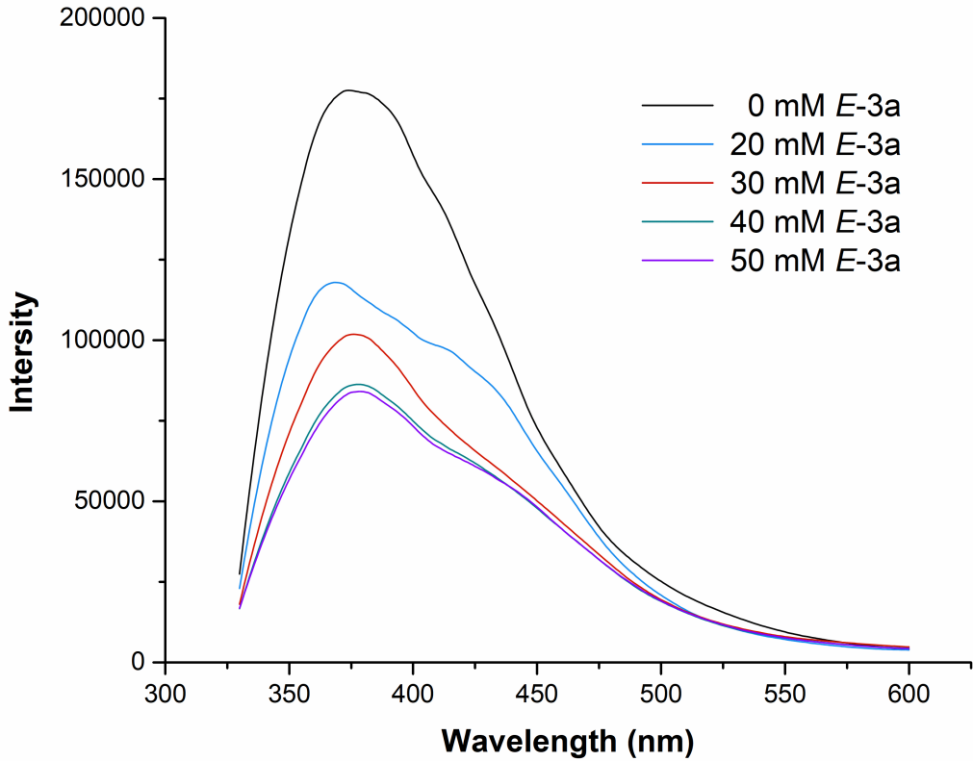


Figure S3 Fluorescence emission spectrum of **PC6** at different concentrations of ***E*-3a**.

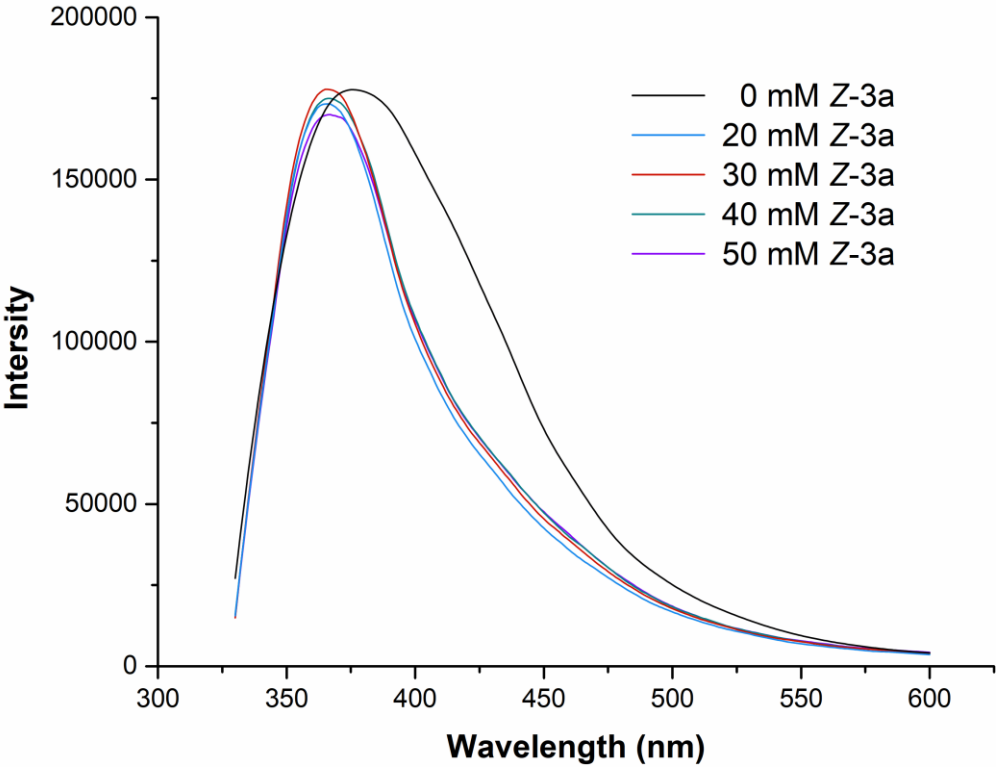
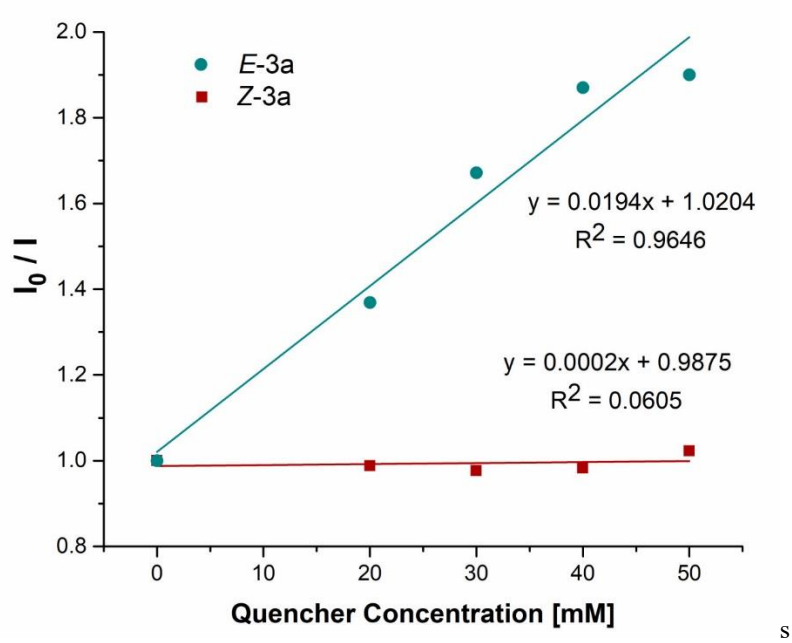


Figure S4 Fluorescence emission spectrum of **PC6** at different concentrations of ***Z*-3a**.



s

Figure S5 Stern-Volmer emission quenching plot of **PC6** at different concentrations of ***E*/*Z*-3a**.

2.7. The LED emission spectrum and the UV/vis absorption spectra of pyrylium salts.

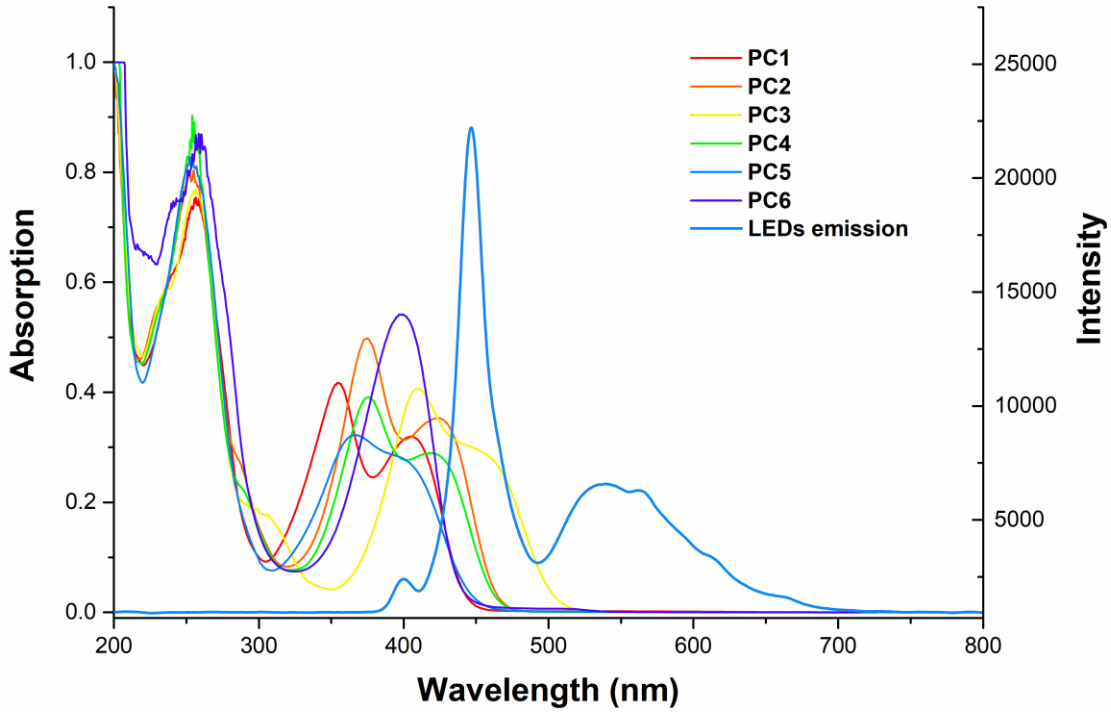
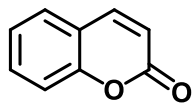


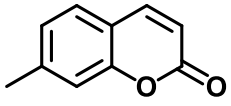
Figure S6. The LED emission spectrum and UV/vis absorption spectra of pyrylium salts **PC1-PC6** (10^{-4} M in acetonitrile)

3. Compound Characterization Data



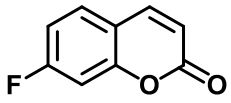
2a

2*H*-chromen-2-one (2a): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA =30:1 - 10:1) as a white solid (22.7 mg, 0.155 mmol, 78%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 9.5, 0.6 Hz, 1H), 7.59 – 7.46 (m, 2H), 7.36 – 7.28 (m, 2H), 6.44 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*). δ 160.9, 154.2, 143.6, 132.0, 128.0, 124.5, 118.9, 117.0, 116.8. These data are in agreement with those reported previously in the literature.[3]



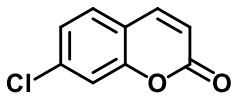
2b

7-methyl-2*H*-chromen-2-one (2b): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (18.6 mg, 0.116 mmol, 58%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 9.5 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.34 (d, *J* = 9.5 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.3, 154.2, 143.6, 143.3, 127.6, 125.7, 117.2, 116.6, 115.6, 21.9. These data are in agreement with those reported previously in the literature.[10]



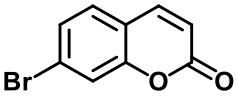
2c

7-fluoro-2*H*-chromen-2-one (2c): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (13.1 mg, 0.080 mmol, 40%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (d, 1H), 7.68 – 7.64 (m, 1H), 7.08 – 6.96 (m, 2H), 6.36 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.3 (d, *J* = 252.2 Hz) 160.4, 155.1 (d, *J* = 12.7 Hz), 143.0, 129.5 (d, *J* = 10.3 Hz), 115.6 115.4 (d, *J* = 3.2 Hz), 112.7 (d, *J* = 22.9 Hz), 104.7 (d, *J* = 25.6 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -104.86 – -104.91 (m). These data are in agreement with those reported previously in the literature.[10]



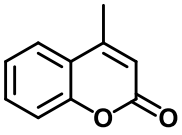
2d

7-chloro-2*H*-chromen-2-one (2d): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (16.2 mg, 0.090 mmol, 45%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 9.6 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.28 - 7.26 (m, 1H), 6.43 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.1, 154.5, 142.8, 138.0, 128.8, 125.2, 117.6, 117.4, 116.8. These data are in agreement with those reported previously in the literature.[10]



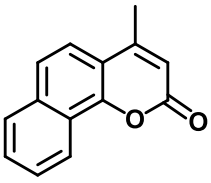
2e

7-bromo-2*H*-chromen-2-one (2e): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (24.8 mg, 0.110 mmol, 55%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 9.6 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.42 - 7.35 (m , 2H), 6.44 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.0, 154.4, 142.9, 128.9, 128.0, 125.9, 120.3, 117.9, 117.0. These data are in agreement with those reported previously in the literature.[10]



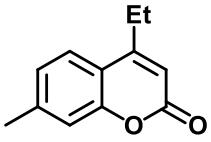
2f

4-methyl-2*H*-chromen-2-one (2f): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (19.2 mg, 0.120 mmol, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 9.6 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.38 – 7.29 (m, 2H), 6.31 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 153.6, 152.6, 131.9, 124.7, 124.3, 120.1, 117.2, 115.2, 18.8. These data are in agreement with those reported previously in the literature.[3]



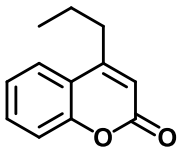
2g

4-methyl-2*H*-benzo[h]chromen-2-one (2g): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (31.1 mg, 0.148 mmol, 74%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.52 – 8.49 (m, 1H), 7.84 – 7.82 (m, 1H), 7.67 – 7.59 (m, 3H), 7.53 (d, *J* = 8.8 Hz, 1H), 6.32 (s, 1H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.0, 153.5, 150.5, 134.8, 128.6, 127.7, 127.2, 124.2, 123.1, 122.6, 120.4, 115.2, 114.3, 19.3. These data are in agreement with those reported previously in the literature.[3]



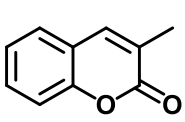
2h

4-ethyl-7-methyl-2*H*-chromen-2-one (2h): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (30.5 mg, 0.162 mmol, 81%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.24 (d, *J* = 1.3 Hz, 1H), 2.80 (q, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.33 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.6, 157.6, 153.8, 142.8, 125.4, 123.9, 117.5, 117.0, 112.0, 24.7, 21.7, 12.2. These data are in agreement with those reported previously in the literature.[11]



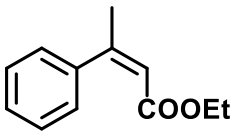
2i

4-propyl-2*H*-chromen-2-one (2j): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (27.4 mg, 0.146 mmol, 73%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 (m, 1H), 7.39 – 7.29 (m, 2H), 6.29 (s, 1H), 2.76 (t, *J* = 7.7 Hz, 2H), 1.76 (dq, *J* = 14.8, 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.2, 156.2, 153.8, 131.7, 124.5, 124.3, 119.4, 117.4, 114.0, 33.8, 21.4, 14.1. These data are in agreement with those reported previously in the literature.[3]



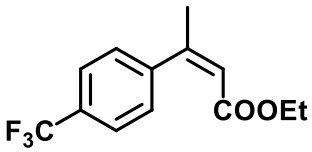
2j

3-methyl-2*H*-chromen-2-one (2k): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (26.9 mg, 0.168 mmol, 84%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (s, 1H), 7.46 – 7.40 (m, 2H), 7.31 - 7.25 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.4, 153.3, 139.4, 130.6, 127.1, 125.9, 124.4, 119.7, 116.6, 17.3. These data are in agreement with those reported previously in the literature.[10]



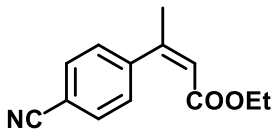
4a

Ethyl (*Z*)-3-phenylbut-2-enoate (4a): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 150:1 - 50:1) as a yellow liquid (32.3 mg, 0.170 mmol, 85%, *Z*/*E* = 93:7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 3H), 7.23 – 7.19 (m, 2H), 5.91 (d, *J* = 1.6 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.18 (d, *J* = 1.5 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.1, 155.6, 141.0, 128.6, 128.0, 127.9, 126.9, 126.4, 117.9, 59.9, 27.3, 14.1. These data are in agreement with those reported previously in the literature.[2]



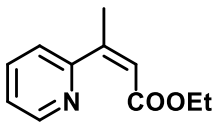
4b

Ethyl (*Z*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (4b): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 150:1 - 50:1) as a yellow liquid (51.6 mg, 0.200 mol, quant., *Z*/*E* = 95:5). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 1.5 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.18 (d, *J* = 1.5 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.6, 154.2, 144.9 (q, *J* = 1.4 Hz), 129.8 (q, *J* = 32.4 Hz), 127.3, 125.4 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 272.2 Hz), 118.9, 60.1, 27.2, 14.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.45 (s). These data are in agreement with those reported previously in the literature.[2]



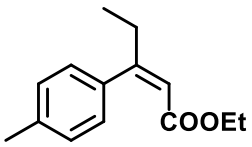
4c

Ethyl (*Z*)-3-(4-cyanophenyl)but-2-enoate (4c): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 150:1 - 50:1) as a yellow liquid (31.8 mg, 0.148 mmol, 74%, *Z*/*E* = 99:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.66 – 7.63 (m, 2H), 7.31-7.28 (m, 2H), 5.97 (q, *J* = 1.5 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.17 (d, *J* = 1.5 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.3, 153.6, 146.1, 131.9, 127.7, 119.2, 118.8, 111.4, 60.1, 26.8, 14.0. These data are in agreement with those reported previously in the literature.[2]



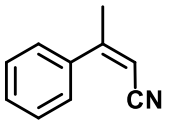
4d

Ethyl (*Z*)-3-(pyridin-2-yl)but-2-enoate (4f): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 150:1 - 50:1) as a yellow liquid (19.1 mg, 0.100 mmol, 50%, *Z*/*E* = 98:2). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.59 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.65 (ddd, *J* = 7.7, 1.8 Hz, 1H), 7.23 (td, *J* =7.9, 1.1 Hz, 1H), 7.20 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 5.99 (q, *J* = 1.5 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.22 (d, *J* = 1.5 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.0, 158.9, 153.5, 149.2, 135.9, 122.6, 119.5, 60.1, 25.1, 14.1. These data are in agreement with those reported previously in the literature.[12]



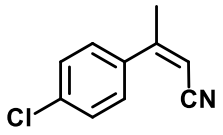
4e

Ethyl (*Z*)-3-(*p*-tolyl)pent-2-enoate (4g): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 150:1 - 50:1) as a yellow liquid (29.2 mg, 0.134 mmol, 67%, *Z*/*E* = 99:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 6.92 – 6.88 (m, 2H), 6.00 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.09 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.7, 161.6, 160.5, 133.2, 128.1, 115.1, 114.0, 59.8, 55.4, 24.1, 14.5, 13.9. **IR (ATR)** ν 2972, 1709, 1626, 1369, 1224, 1155, 1045, 820 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{14}H_{18}O_2K^+$ 257.0938, found 257.0934.



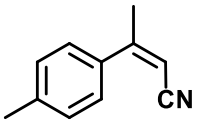
4f

(***Z*)-3-phenylbut-2-enenitrile (4i)**: Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (25.2 mg, 0.176 mmol, 88%, *Z*/*E* = 95:5).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 – 7.52 (m, 2H), 7.45 – 7.40 (m, 3H), 5.40 (q, *J* = 1.6 Hz, 1H), 2.28 (t, *J* = 2.0 Hz, 3H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.1, 138.0, 130.0, 128.9, 128.8, 127.2, 126.0, 117.7, 95.6, 24.8. These data are in agreement with those reported previously in the literature.[1]



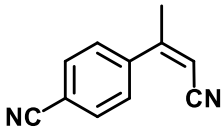
4g

(*Z*)-3-(4-chlorophenyl)but-2-enenitrile (4j): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (25.3 mg, 0.142 mmol, 71%, *Z/E* = 87:13). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 5.41 (q, *J* = 1.5 Hz, 1H), 2.26 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.7, 136.3, 136.0, 129.1, 128.6, 117.4, 96.2, 24.7. These data are in agreement with those reported previously in the literature.[1]



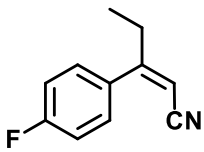
4h

(*Z*)-3-(*p*-tolyl)but-2-enenitrile (4k): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (23.2 mg, 0.148 mmol, 74%, *Z/E* = 92:8). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 5.34 (q, *J* = 1.5 Hz, 1H), 2.37 (s, 3H), 2.25 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.9, 140.3, 135.1, 129.4, 127.1, 118.0, 94.8, 24.7, 21.5. **IR (ATR)** ν 2213, 1606, 1510, 1438, 1377, 823, 720, 595, 475 cm^{-1}. **HRMS** (ESI) *m/z*: [M+Na]$^+$, calcd. for $C_{11}H_{11}NNa^+$ 180.0784, found 180.0780.



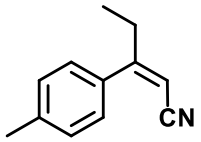
4i

(*Z*)-4-(1-cyanoprop-1-en-2-yl)benzonitrile (4l): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (21.5 mg, 0.128 mmol, 64%, *Z/E* = 99:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 2H), 7.65 – 7.61 (m, 2H), 5.53 (q, *J* = 1.6 Hz, 1H), 2.31 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.1, 142.4, 132.6, 128.0, 118.3, 116.7, 113.5, 98.0, 24.5. These data are in agreement with those reported previously in the literature.[1]



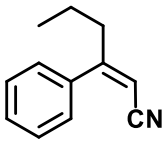
4j

(*Z*)-3-(4-fluorophenyl)pent-2-enenitrile (4n): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (35.0 mg, 0.200 mmol, quant., *Z/E* = 89:11). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H), 7.15 – 7.09 (m, 2H), 5.37 (t, *J* = 1.5 Hz, 1H), 2.58 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.2, 163.4 (d, *J* = 249.9 Hz), 133.7 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 8.4 Hz), 117.6, 115.9 (d, *J* = 21.7 Hz), 94.8, 31.3, 12.3. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -110.86 – -111.00 (m). These data are in agreement with those reported previously in the literature.[1]



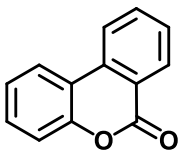
4k

(*Z*)-3-(*p*-tolyl)pent-2-enenitrile (4o): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (29.4 mg, 0.172 mmol, 86%, *Z/E* = 94:6). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 – 7.34 (m, 2H), 7.24 – 7.21 (m, 2H), 5.32 (t, *J* = 1.5 Hz, 1H), 2.58 (m, 2H), 2.38 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.3, 139.9, 134.8, 129.4, 127.3, 118.0, 93.9, 31.1, 21.4, 12.4. These data are in agreement with those reported previously in the literature.[1]



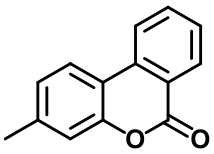
4l

(*Z*)-3-phenylhex-2-enenitrile (4p): Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 50:1 - 20:1) as a yellow liquid (30.4 mg, 0.178 mmol, 89%, *Z/E* = 98:2).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 5H), 5.37 (t, *J* = 1.3 Hz, 1H), 2.54 (m, 2H), 1.42 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.0, 137.6, 129.6, 128.7, 127.4, 117.7, 95.4, 40.2, 21.0, 13.5. These data are in agreement with those reported previously in the literature.[1]



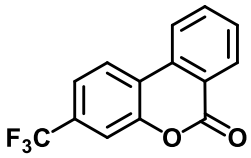
6a

6*H*-benzo[c]chromen-6-one (6a): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (31.4 mg, 0.160 mmol, 80%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 – 8.36 (m, 1H), 8.16-8.10 (m, 1H), 8.06 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.87 – 7.78 (m, 1H), 7.59 (m, *J* = 7.6 Hz, 1H), 7.48 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.40 – 7.32 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.3, 151.4, 135.0, 134.9, 130.7, 130.6, 129.0, 124.7, 122.9, 121.8, 121.4, 118.2, 117.9. These data are in agreement with those reported previously in the literature.[5]



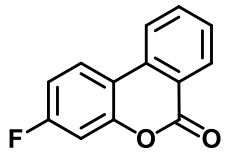
6b

3-methyl-6*H*-benzo[c]chromen-6-one (6b): Following the general procedure C, the title product was obtained after purification by column chromatography PE/EA = 30:1 - 10:1) as a white solid (29.8 mg, 0.142 mmol, 71%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.36 – 8.33 (m, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.55 – 7.48 (m, 1H), 7.13 – 7.11 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.5, 151.3, 141.3, 135.0, 134.8, 130.5, 128.4, 125.7, 122.6, 121.5, 120.9, 117.9, 115.4, 21.5. These data are in agreement with those reported previously in the literature.[6]



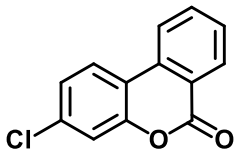
6c

3-(trifluoromethyl)-6*H*-benzo[c]chromen-6-one (6c): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (44.4 mg, 0.168 mmol, 84%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.42 – 8.39 (m , 1H), 8.16 – 8.14 (m, 2H), 7.87 – 7.91 (m, 1H), 7.70 – 7.63 (m, 1H), 7.61 – 7.55 (m, 2H) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.3, 151.0, 135.3, 133.4, 132.3 (q, *J* = 33.5 Hz), 130.9, 130.2, 123.7, 123.5 (q, *J* =272.6 Hz), 122.3, 121.7, 121.2, 121.2 (q, *J* = 3.5 Hz), 115.3 (q, *J* = 4.1 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.69 (s). These data are in agreement with those reported previously in the literature.[5]



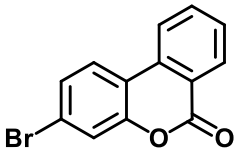
6d

3-fluoro-6*H*-benzo[c]chromen-6-one (6d): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (29.5 mg, 0.138 mmol, 69%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.82 (td, *J* = 7.8, 1.5 Hz, 1H), 7.58 (td, *J* =7.5, 1.1 Hz, 1H), 7.11 – 7.03 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.6 (d, *J* = 252.1 Hz), 160.9, 152.3 (d, *J* = 12.4 Hz), 135.2, 134.3, 130.8, 128.9, 124.5 (d, *J* = 9.8 Hz), 121.6, 120.5, 114.7 (d, *J* = 3.4 Hz), 112.6 (d, *J* = 22.4 Hz), 105.2 (d, *J* = 25.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -108.24 – -108.30 (m). These data are in agreement with those reported previously in the literature.[5]



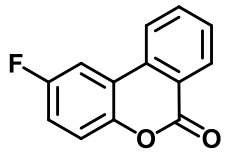
6e

3-chloro-6*H*-benzo[c]chromen-6-one(6e): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (35.1 mg, 0.152 mmol, 76%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 1.5 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.82 (m, 1H), 7.55 – 7.60 (m, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.1 Hz, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.7, 151.6, 136.0, 135.2, 134.1, 130.8, 129.3, 125.1, 123.9, 121.8, 121.0, 118.0, 116.8. These data are in agreement with those reported previously in the literature.[6]



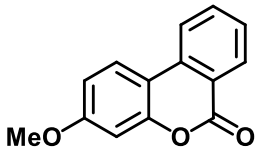
6f

3-bromo-6*H*-benzo[c]chromen-6-one (6f): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (44.6 mg, 0.162 mmol, 81%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 – 8.25 (m, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.61 – 7.54 (m, 1H), 7.48 – 7.39 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.6, 151.6, 135.2, 134.1, 130.9, 129.4, 128.0, 124.1, 123.8, 121.8, 121.1, 121.0, 117.2. These data are in agreement with those reported previously in the litzzerature.[5]



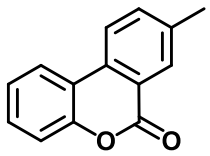
6g

2-fluoro-6*H*-benzo[c]chromen-6-one (6g): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (24.0 mg, 0.112 mmol, 56%).δ 8.41 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.84 (td, *J* = 7.7, 1.5 Hz, 1H), 7.71 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.62 (ddd, *J* = 9.0, 7.5, 1.1 Hz, 1H), 7.34 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.23 – 7.16 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.9, 159.4 (d, *J* = 243.4 Hz), 147.5 (d , *J* = 2.1 Hz), 135.1, 134.0 (d, *J* = 2.7 Hz), 130.8, 129.7, 122.0, 121.4, 119.5 (d, *J* = 8.6 Hz), 119.4 (d, *J* = 8.8 Hz), 117.8 (d, *J* = 24.2 Hz), 108.9 (d, *J* = 24.8 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -117.03 – -117.08 (m). These data are in agreement with those reported previously in the literature.[4]



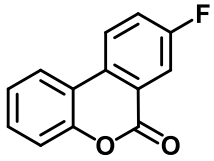
6h

3-methoxy-6*H*-benzo[c]chromen-6-one (6h): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (14.5 mg, 0.064 mmol, 32%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.38 – 8.31 (m, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.78 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 3.88 (s, 3H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.6, 152.8, 135.3, 135.0, 130.7, 127.9, 123.9, 121.2, 120.1, 112.6, 111.3, 101.8, 55.8. These data are in agreement with those reported previously in the literature.[4]



6i

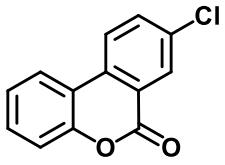
8-methyl-6*H*-benzo[c]chromen-6-one (6i): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (30.2 mg, 0.144 mmol, 72%).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 1.8 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.63 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.45 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.37 – 7.29 (m, 2H), 2.49 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.5, 151.1, 139.4, 136.2, 132.4, 130.5, 130.0, 124.6, 122.7, 121.8, 121.2, 118.3, 117.8, 21.4. These data are in agreement with those reported previously in the literature.[5]



6j

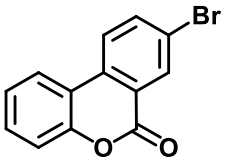
8-fluoro-6*H*-benzo[c]chromen-6-one (6j): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (30.0 mg, 0.140 mmol, 70%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.9, 4.8 Hz, 1H), 8.04 (dd, *J* = 8.5, 2.7 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.53 (ddd, *J* = 8.9, 7.9, 2.8 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.37 – 7.31 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.5 (d, *J* = 251.0 Hz), 160.3 (d, *J* = 3.4 Hz), 150.9, 131.4 (d, *J* = 3.0 Hz), 130.5, 124.9, 124.4 (d, *J* = 7.8 Hz), 123.2 (d, *J* = 22.8 Hz), 122.7,

117.9, 117.5, 116.3 (d, J = 23.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -110.00 – -110.07 (m).These data are in agreement with those reported previously in the literature.[5]



6k

8-chloro-6*H*-benzo[c]chromen-6-one (6k): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (33.7 mg, 0.160 mmol, 73%).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.36 (d, J = 2.3 Hz, 1H), 8.06 (d, J = 8.6 Hz, 1H), 8.01 (dd, J = 7.9, 1.6 Hz, 1H), 7.77 (dd, J = 8.6, 2.3 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.38 – 7.34 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.2, 151.3, 135.3, 135.1, 133.4, 131.0, 130.2, 125.0, 123.6, 122.9, 122.7, 118.0, 117.4. These data are in agreement with those reported previously in the literature.[5]

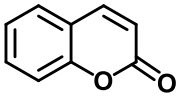


6l

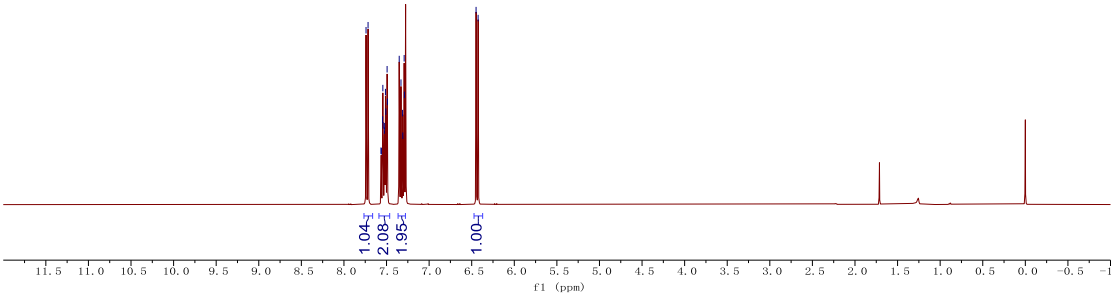
8-bromo-6*H*-benzo[c]chromen-6-one (4l): Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 30:1 - 10:1) as a white solid (50.0 mg, 0.182 mmol, 91%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.45 (d, J = 2.0 Hz, 1H), 7.99 – 7.92 (m, 2H), 7.88 (dd, J = 8.6, 2.0 Hz, 1H), 7.48 (td, J = 7.6, 7.1, 1.5 Hz, 1H), 7.36 – 7.30 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.0, 151.2, 138.0, 133.7, 133.2, 131.0, 125.0, 123.6, 122.9, 122.8, 122.8, 118.0, 117.4. These data are in agreement with those reported previously in the literature.[6]

4. NMR Spectra

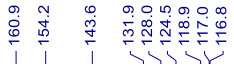
^{1}H NMR of compound **2a** (400 MHz in $CDCl_3$)

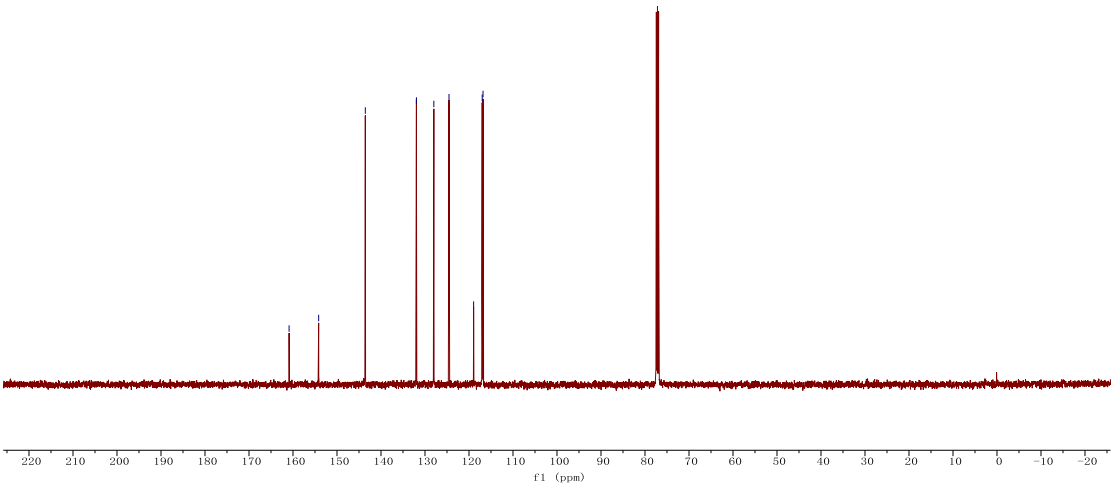


2a

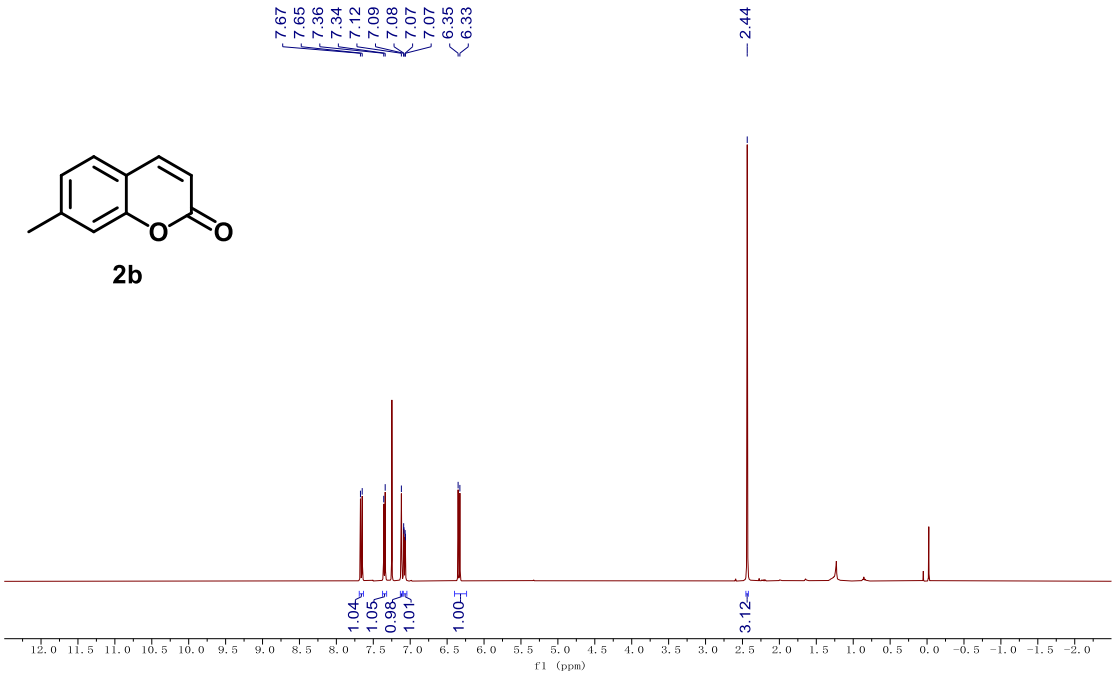


^{13}C NMR of compound **2a** (126 MHz in $CDCl_3$)



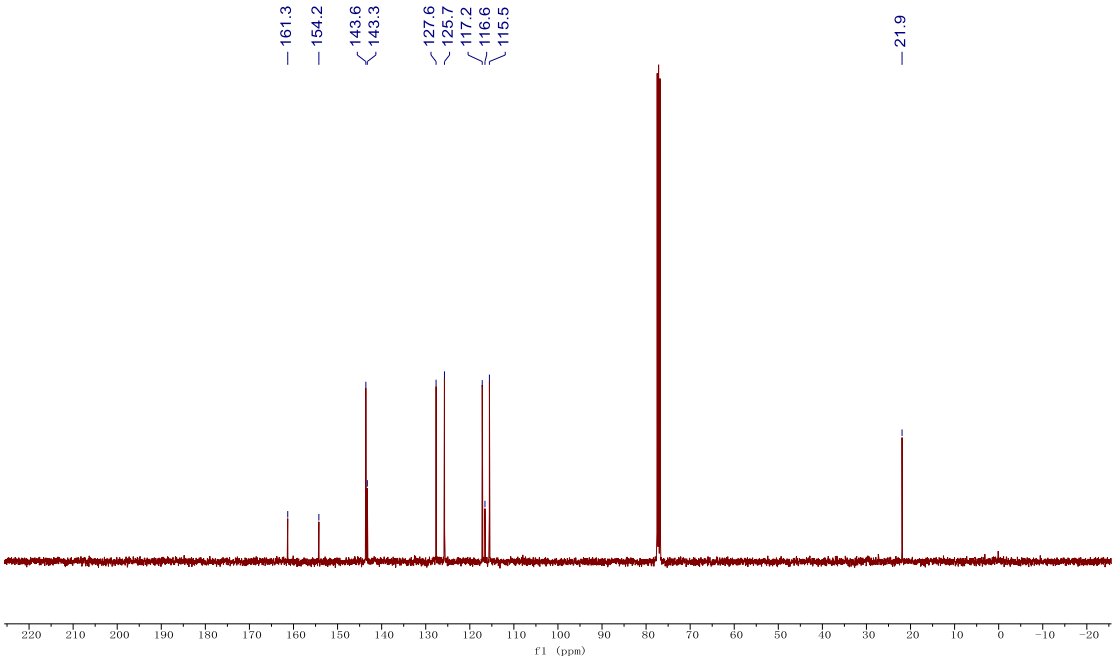


^{1}H NMR of compound **2b** (400 MHz in $CDCl_3$)

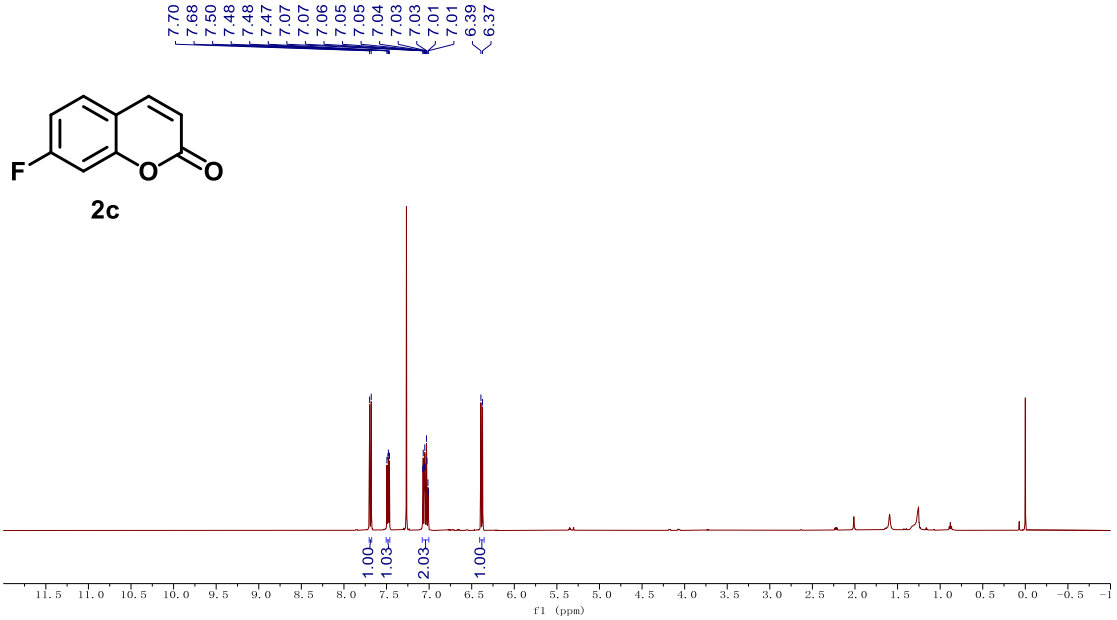


2b

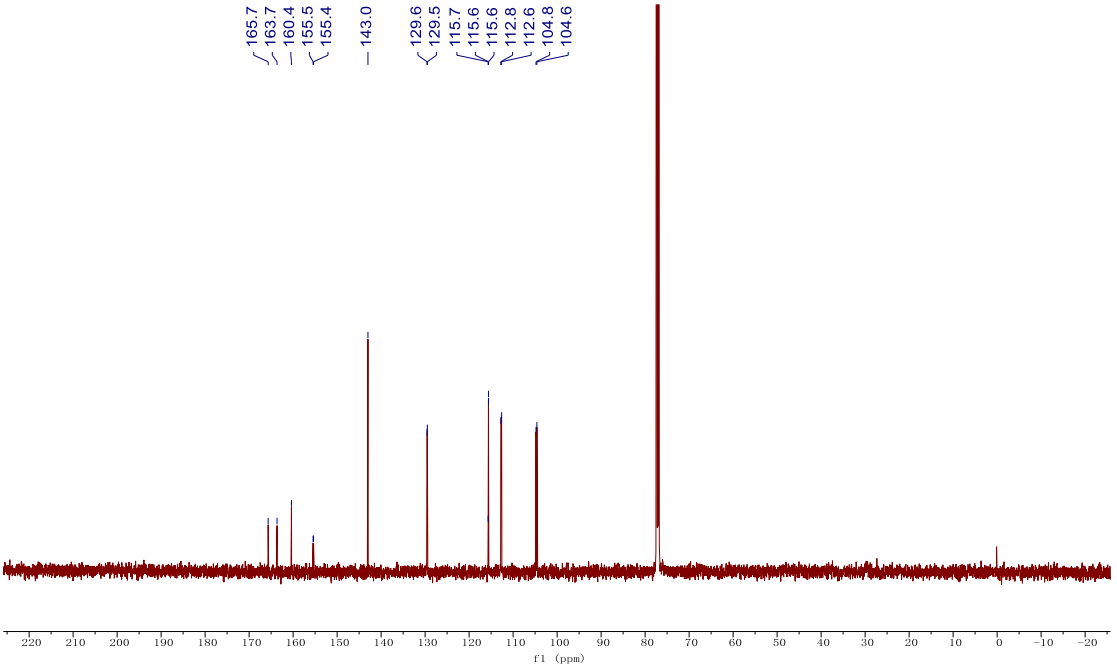
^{13}C NMR of compound **2b** (101 MHz in $CDCl_3$)

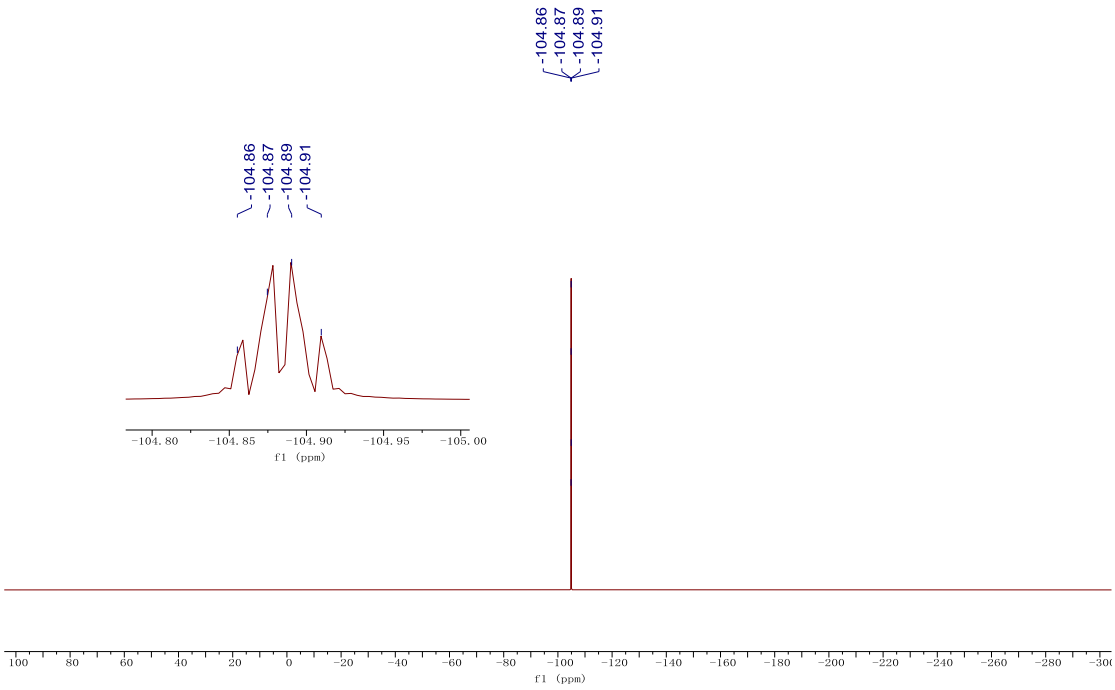


^{1}H NMR of compound **2c** (500 MHz in $CDCl_3$)

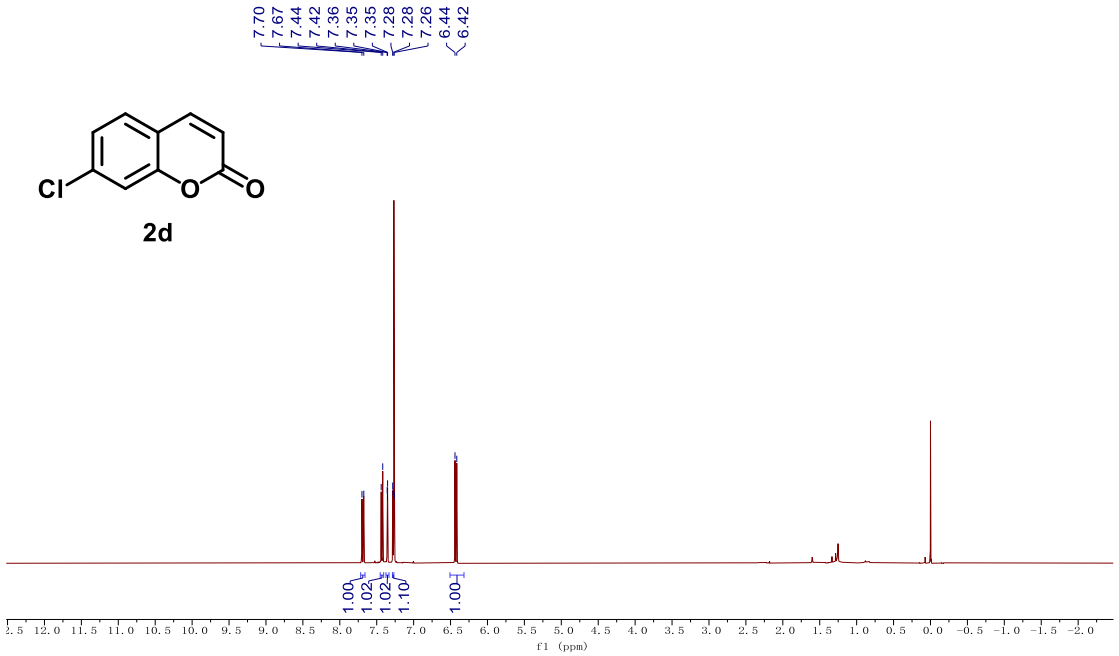


^{13}C NMR of compound **2c** (101 MHz in $CDCl_3$)

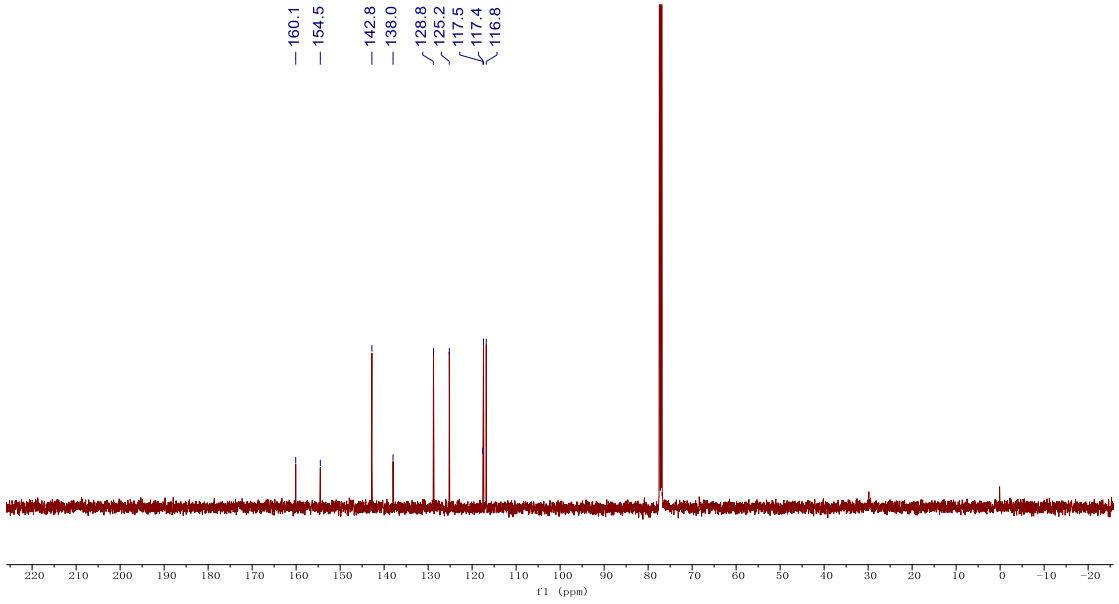



-104.86
-104.87
-104.89
-104.91
-104.86
-104.87
-104.89
-104.91
-104.80
-104.85
-104.90
-104.95
-105.00
f1 (ppm)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

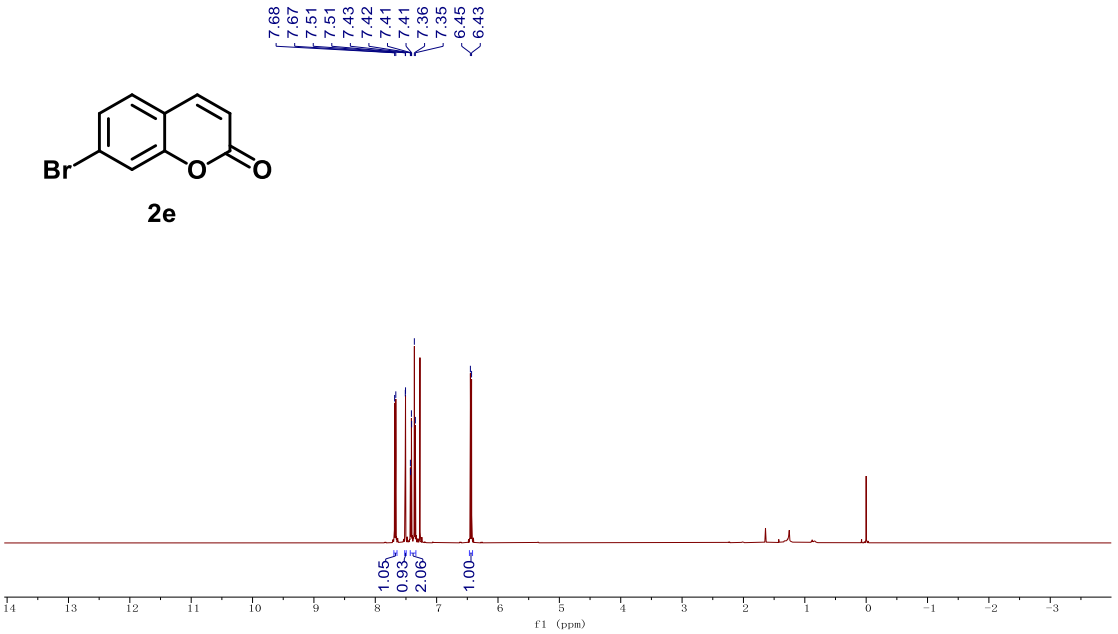
^{1}H NMR of compound **2d** (400 MHz in $CDCl_3$)



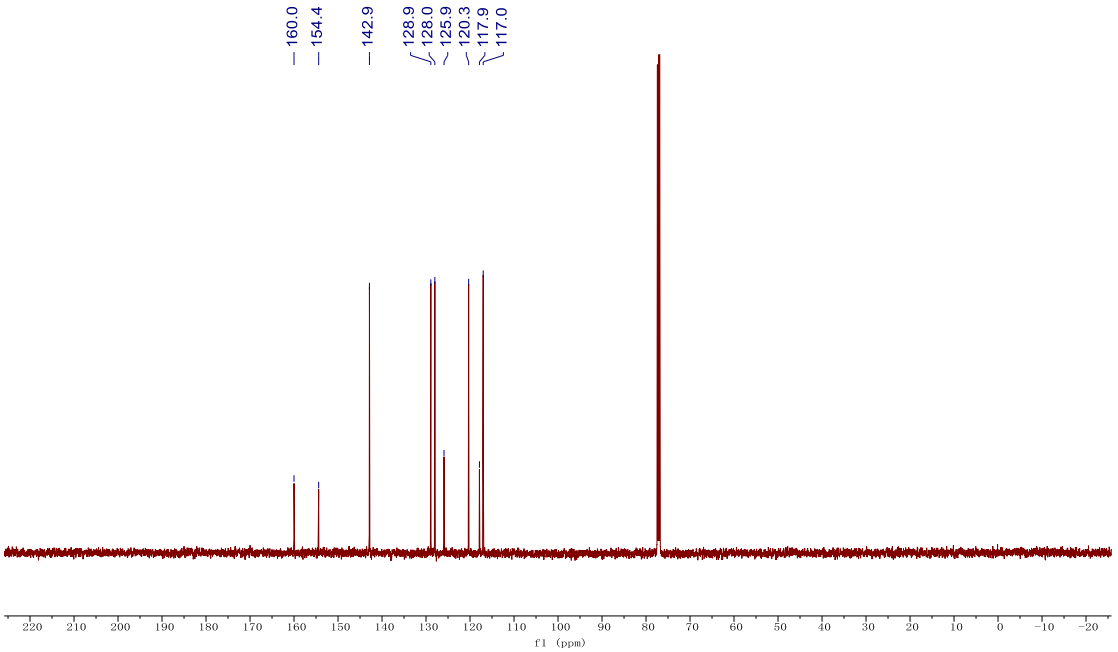
^{13}C NMR of compound **2d** (126 MHz in $CDCl_3$)



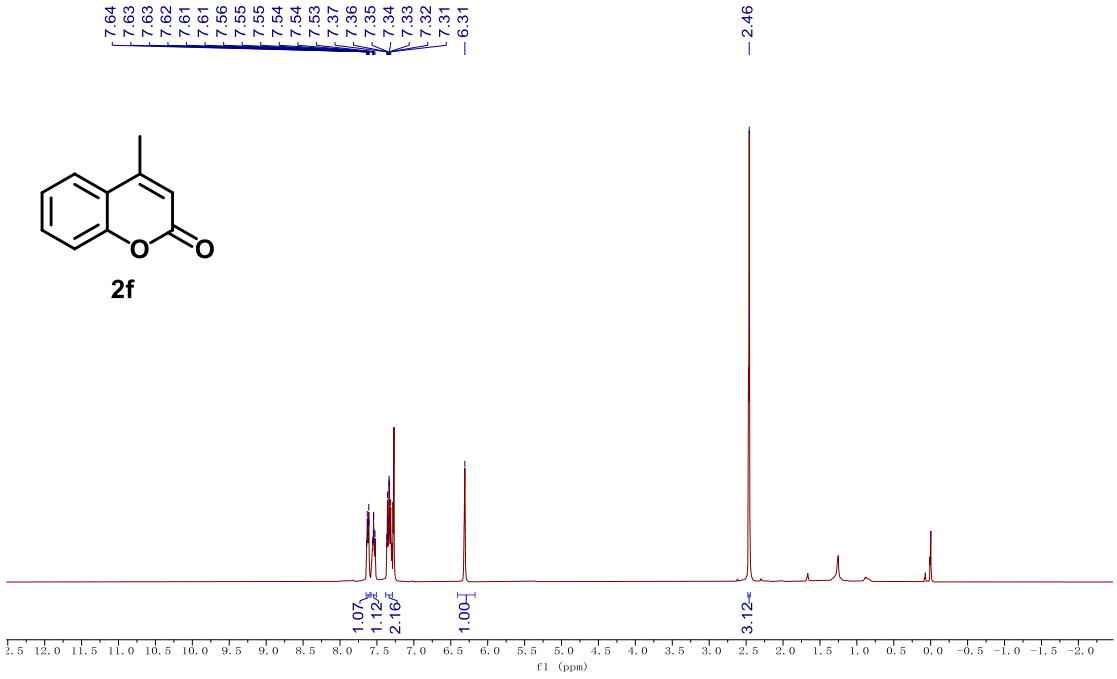
^{1}H NMR of compound **2e** (500 MHz in $CDCl_3$)



^{13}C NMR of compound **2e** (126 MHz in $CDCl_3$)

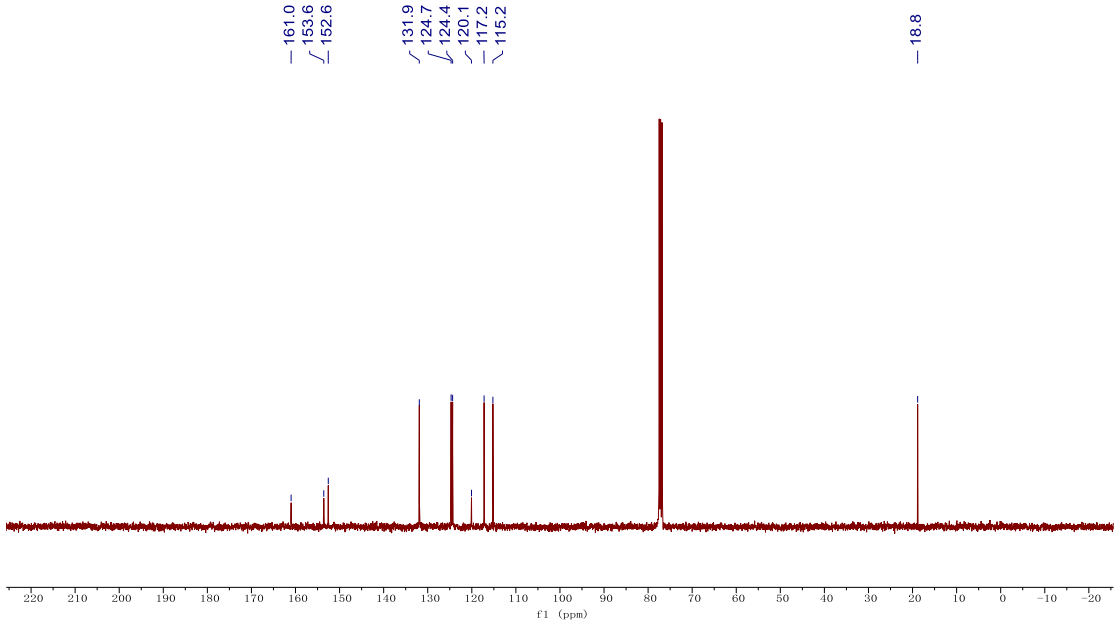


^{1}H NMR of compound **2f** (400 MHz in $CDCl_3$)

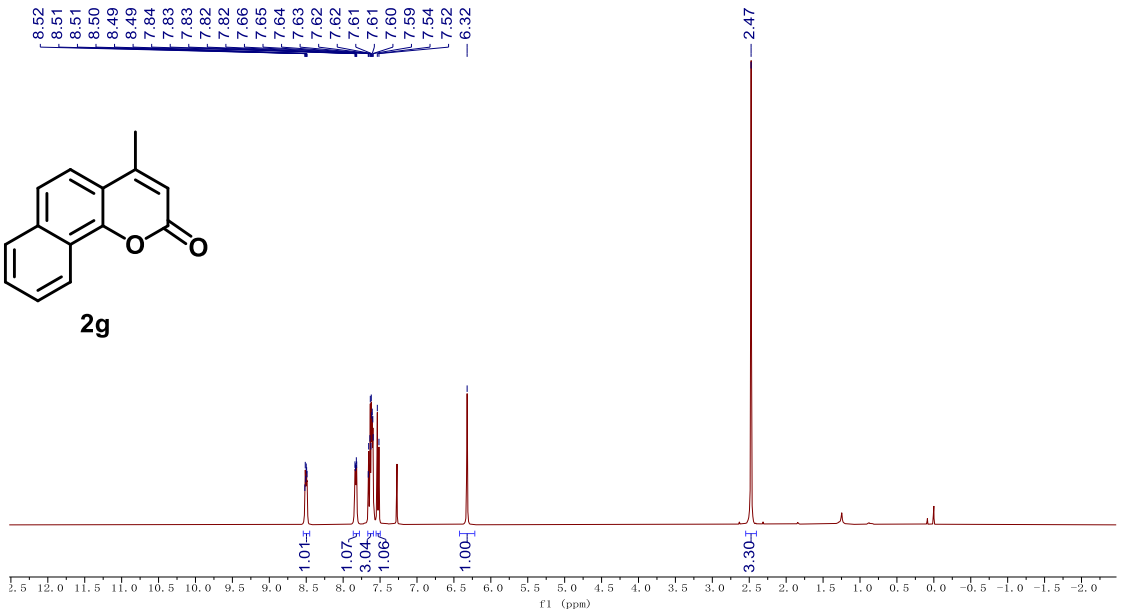


2f

^{13}C NMR of compound **2f** (101 MHz in $CDCl_3$)

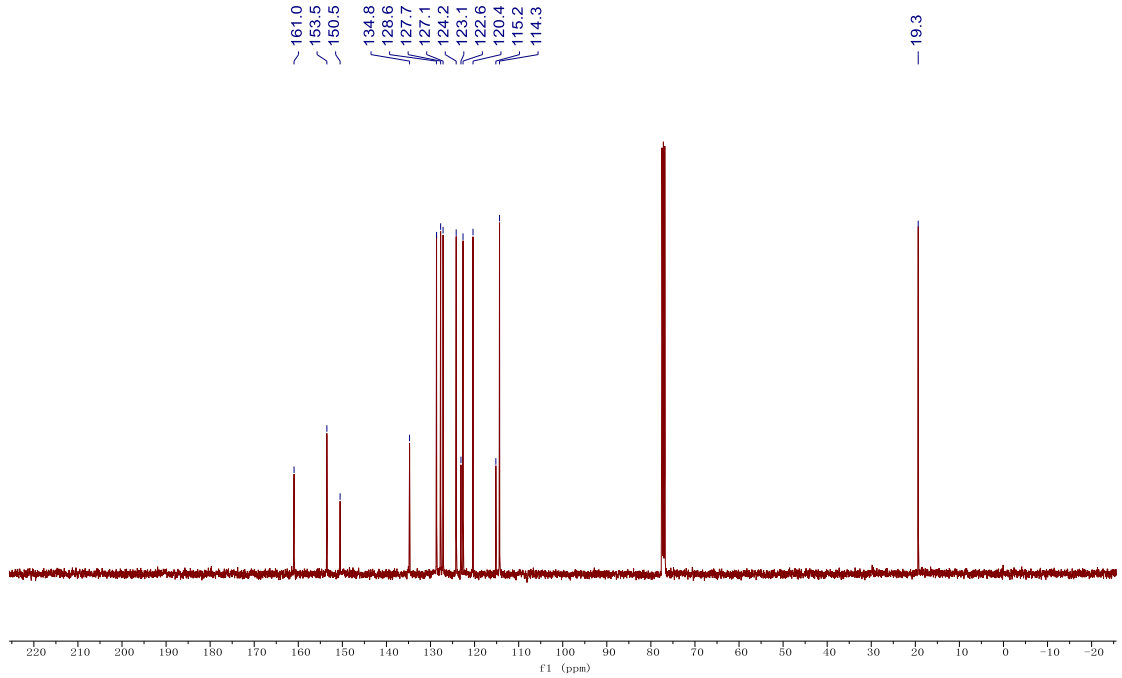


^{1}H NMR of compound **2g** (400 MHz in $CDCl_3$)

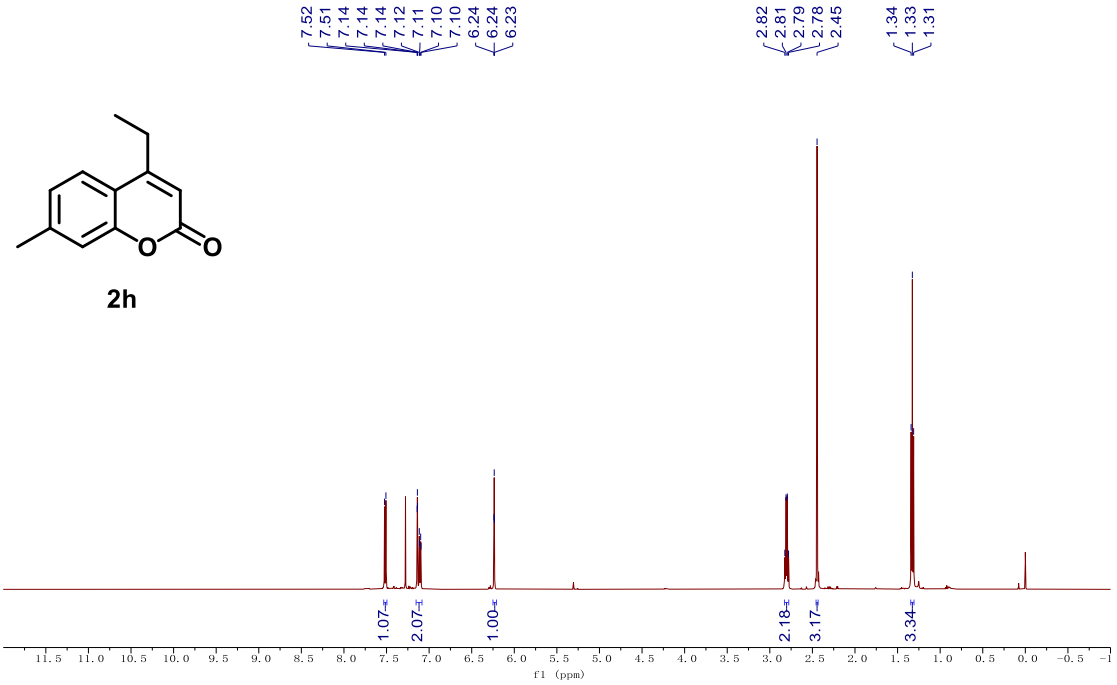


2g

^{13}C NMR of compound **2g** (101 MHz in $CDCl_3$)

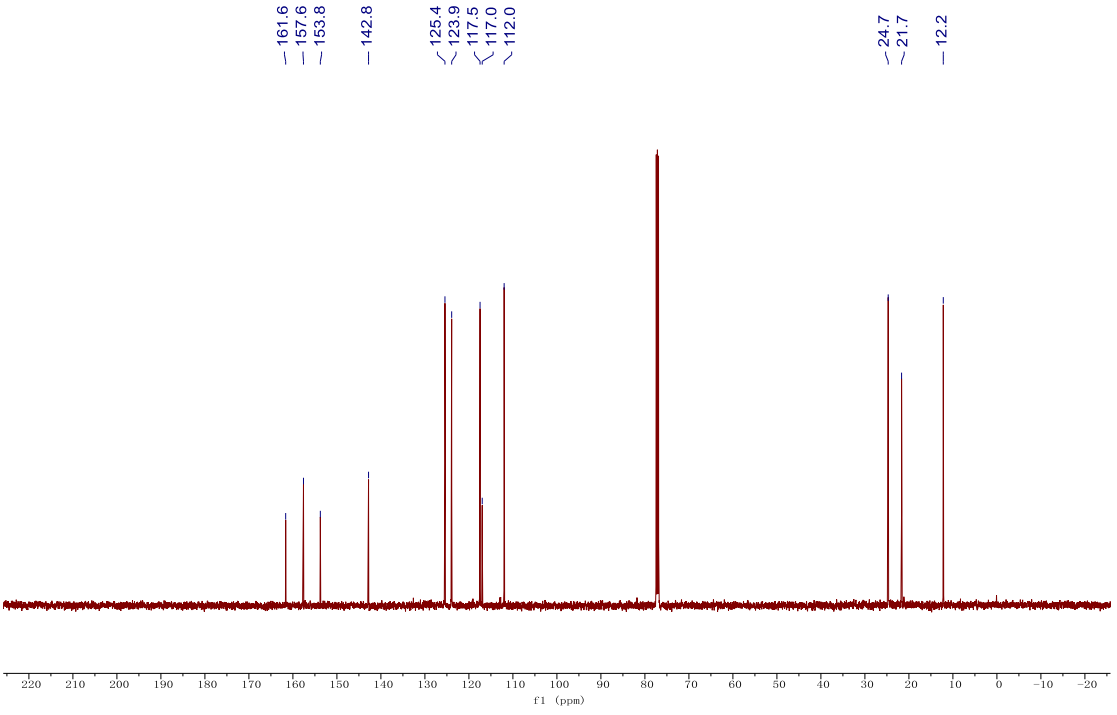


^{1}H NMR of compound **2h** (500 MHz in $CDCl_3$)

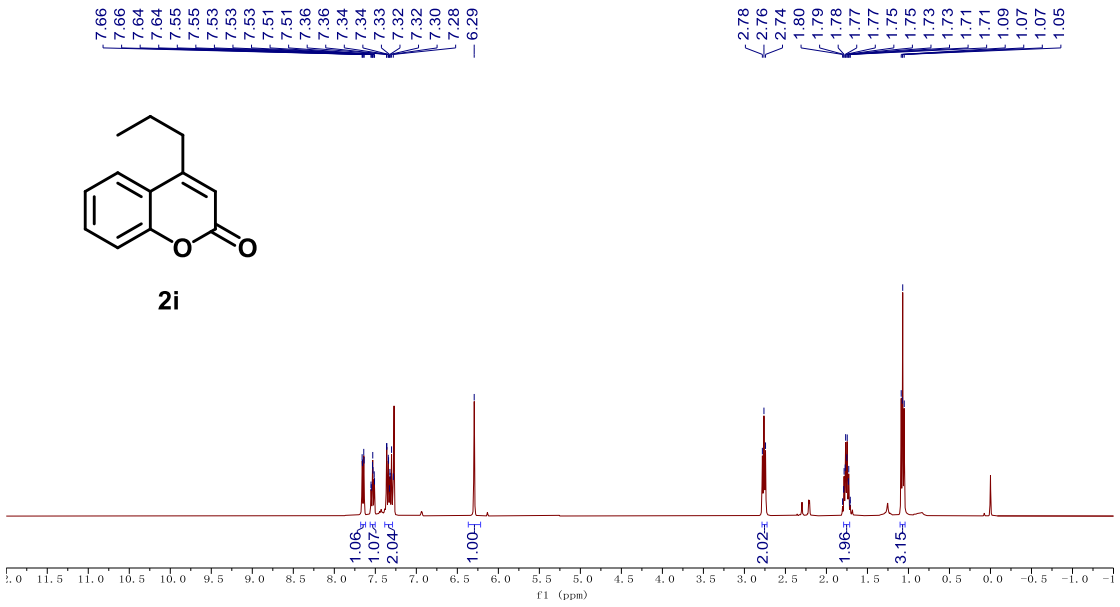


2h

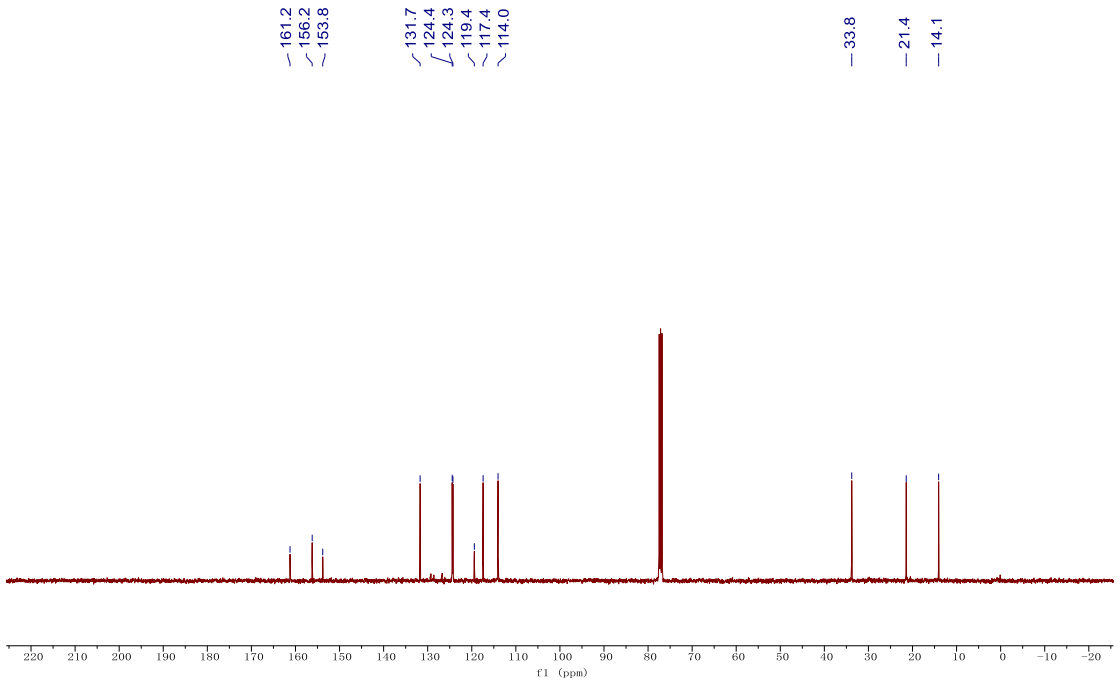
^{13}C NMR of compound **2h** (126 MHz in $CDCl_3$)



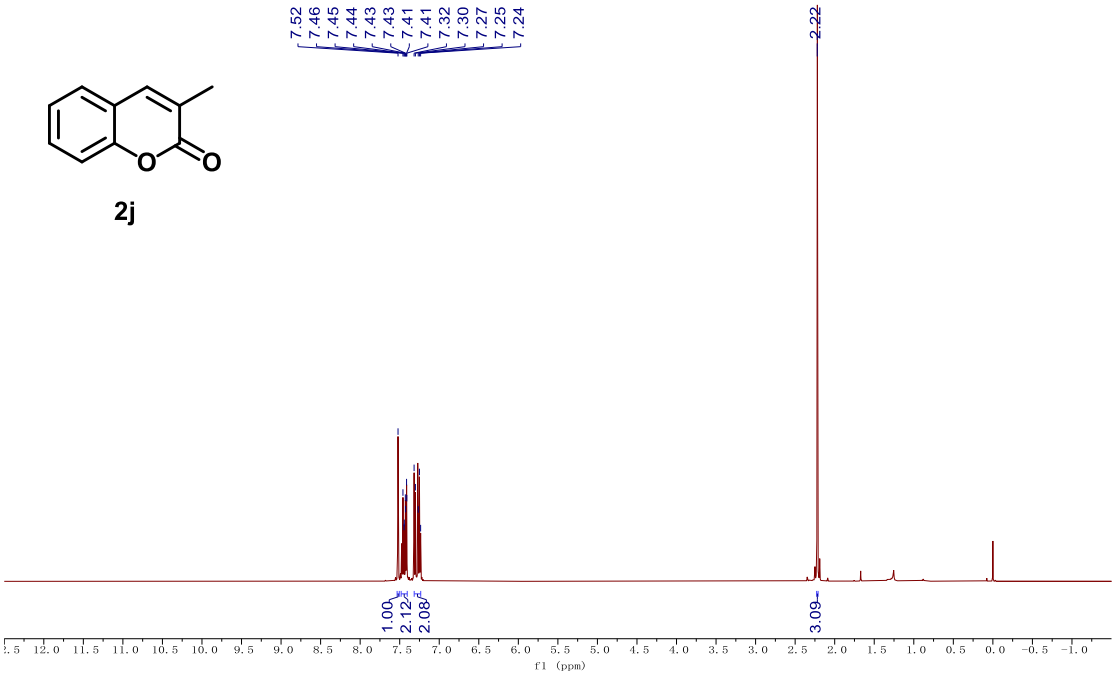
^{1}H NMR of compound **2i** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **2i** (101 MHz in $CDCl_3$)

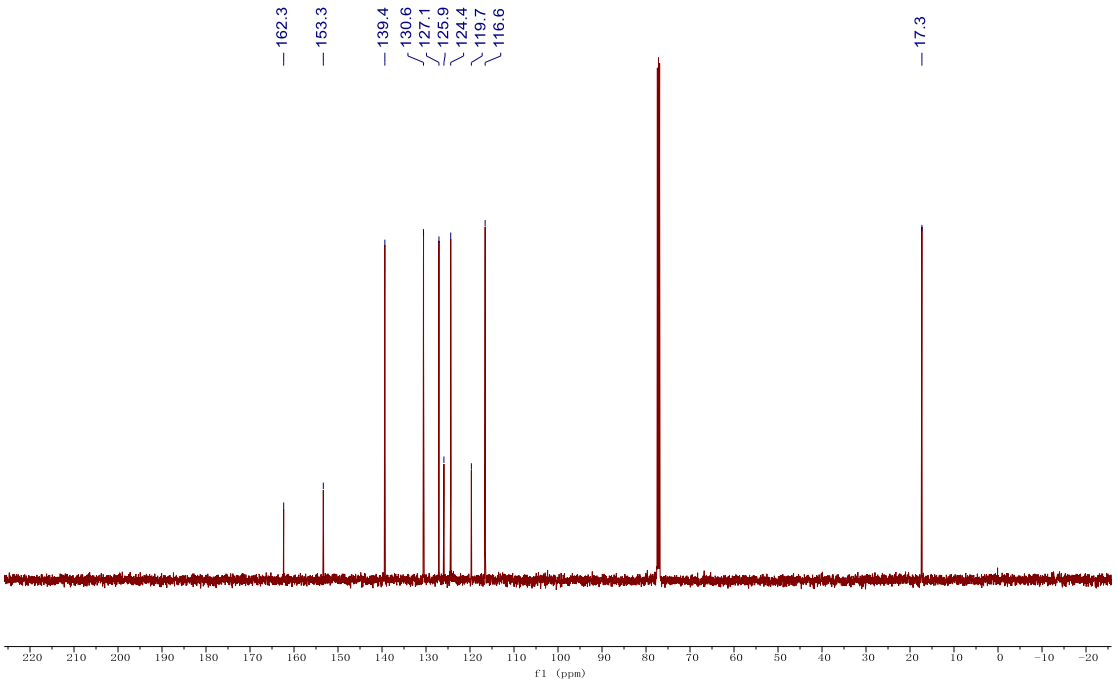


^{1}H NMR of compound **2j** (500 MHz in $CDCl_3$)

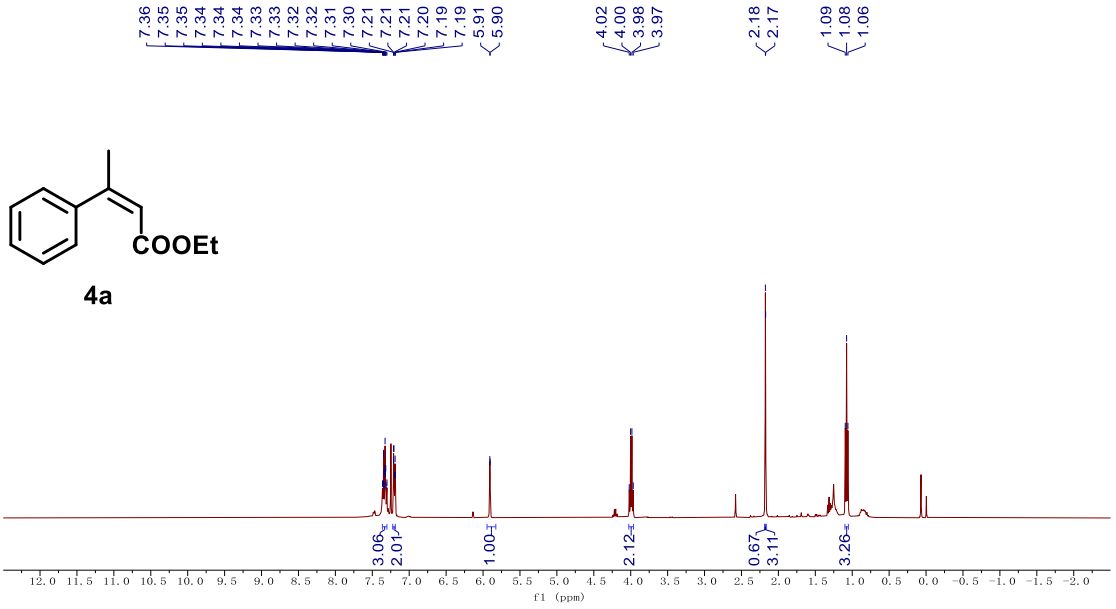


2j

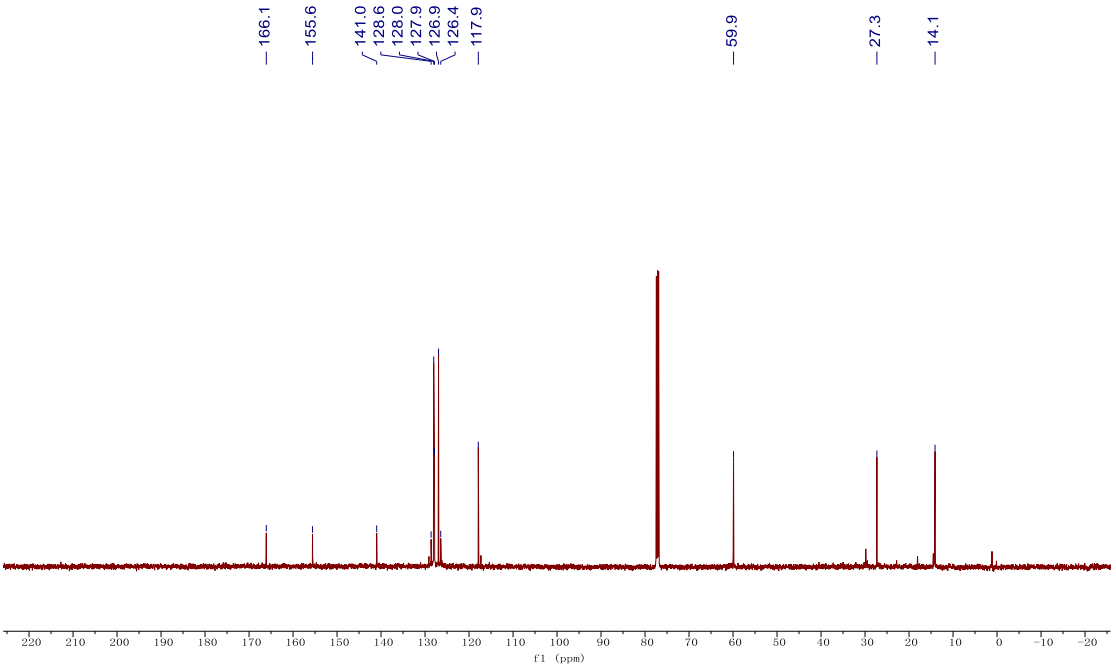
^{13}C NMR of compound **2j** (126 MHz in $CDCl_3$)



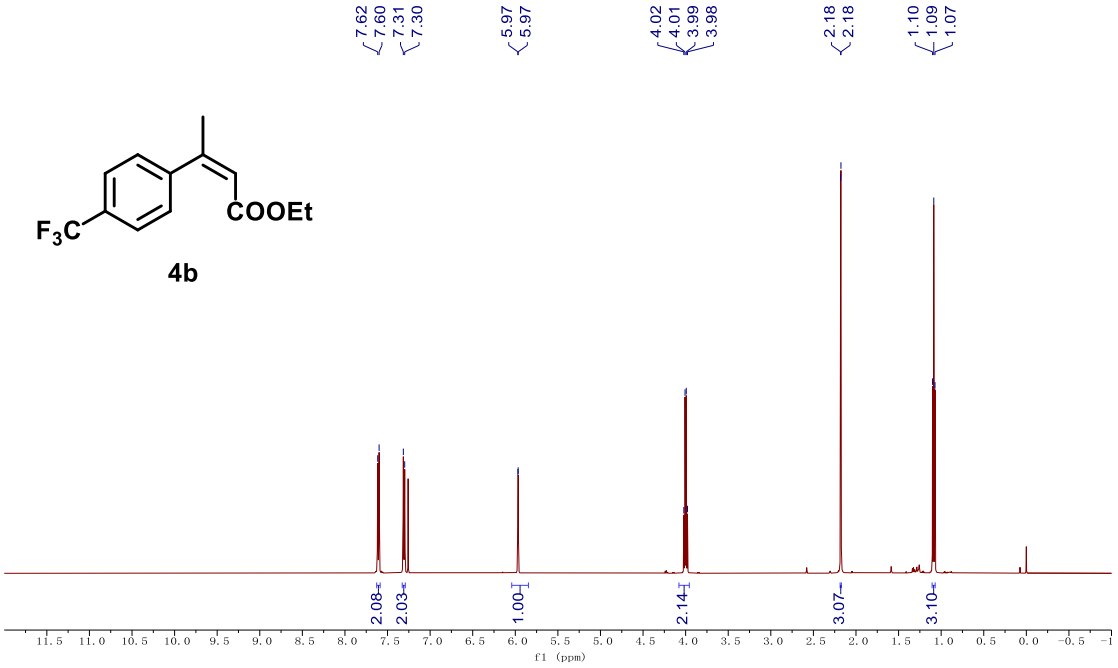
^{1}H NMR of compound **4a** (500 MHz in $CDCl_3$)



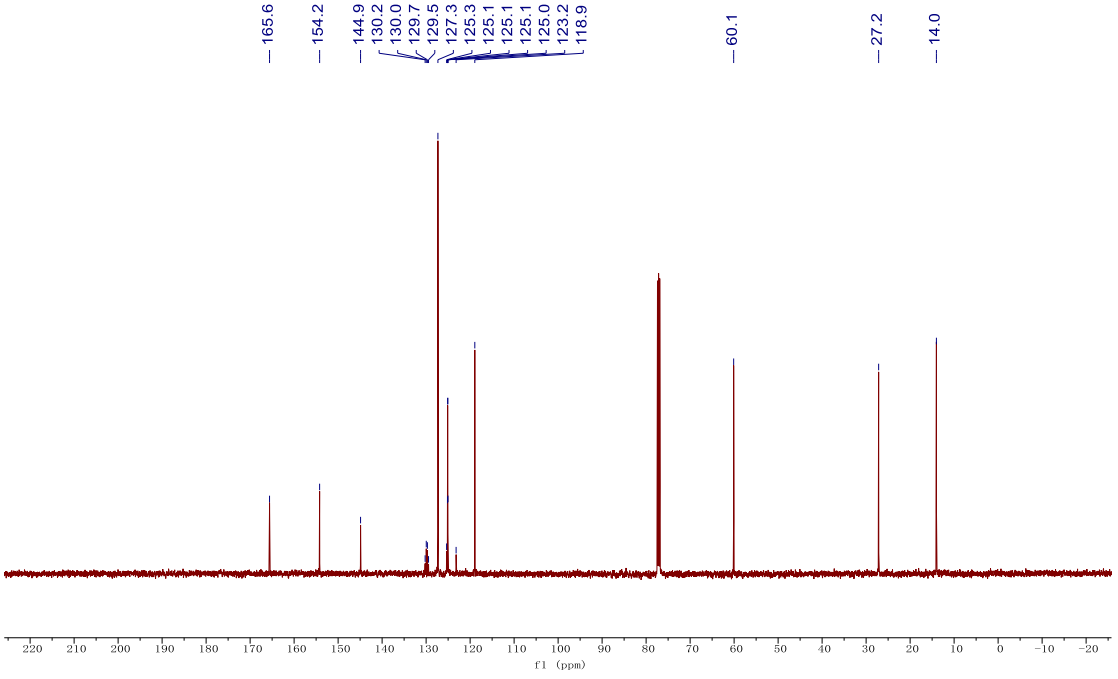
^{13}C NMR of compound **4a** (126 MHz in $CDCl_3$)



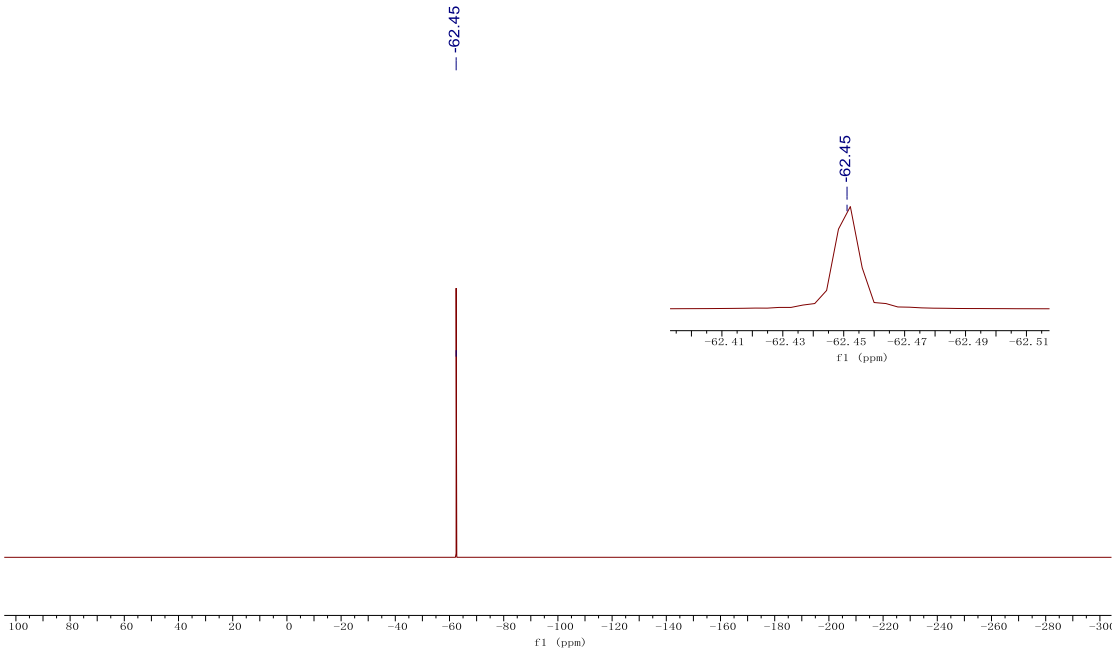
^{1}H NMR of compound **4b** (500 MHz in $CDCl_3$)



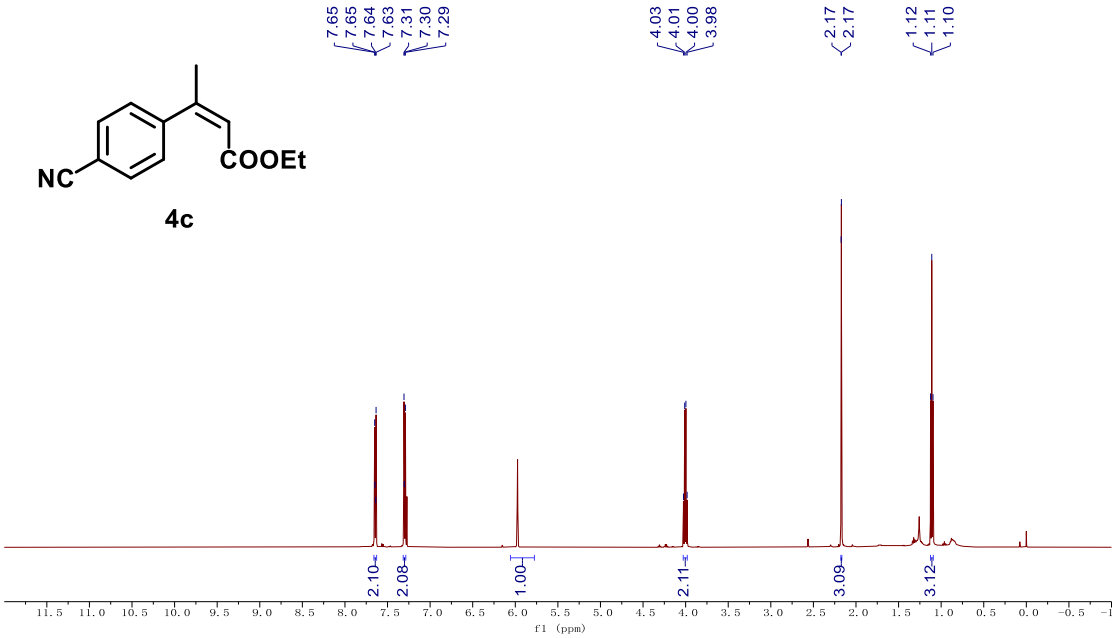
^{13}C NMR of compound **4b** (126 MHz in $CDCl_3$)



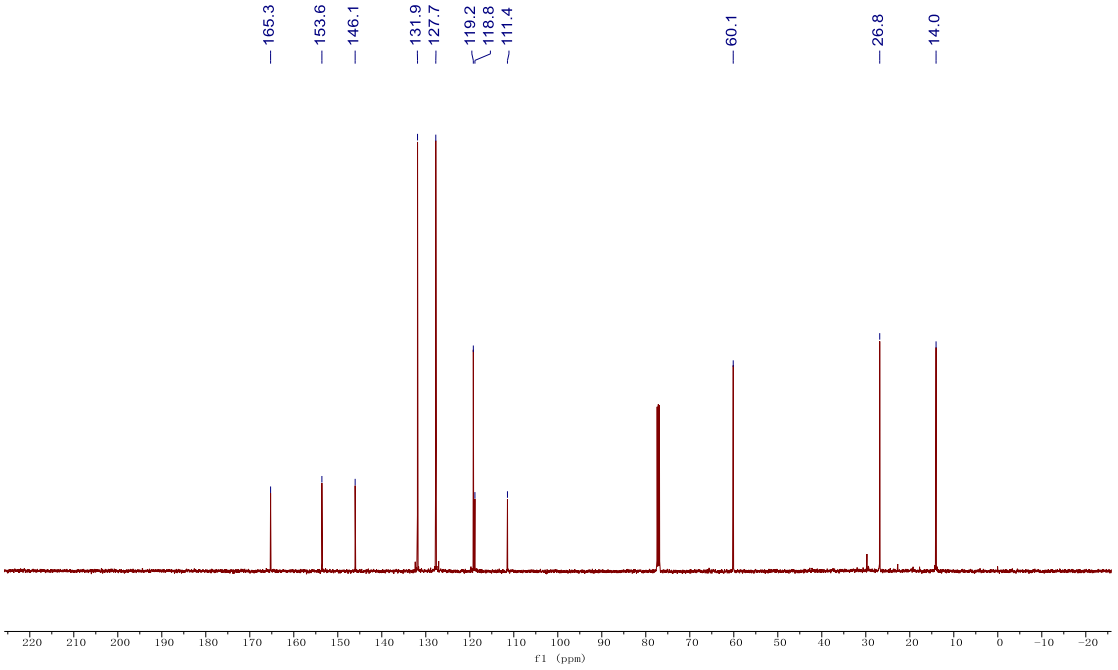
^{19}F NMR of compound **4b** (471 MHz in $CDCl_3$)



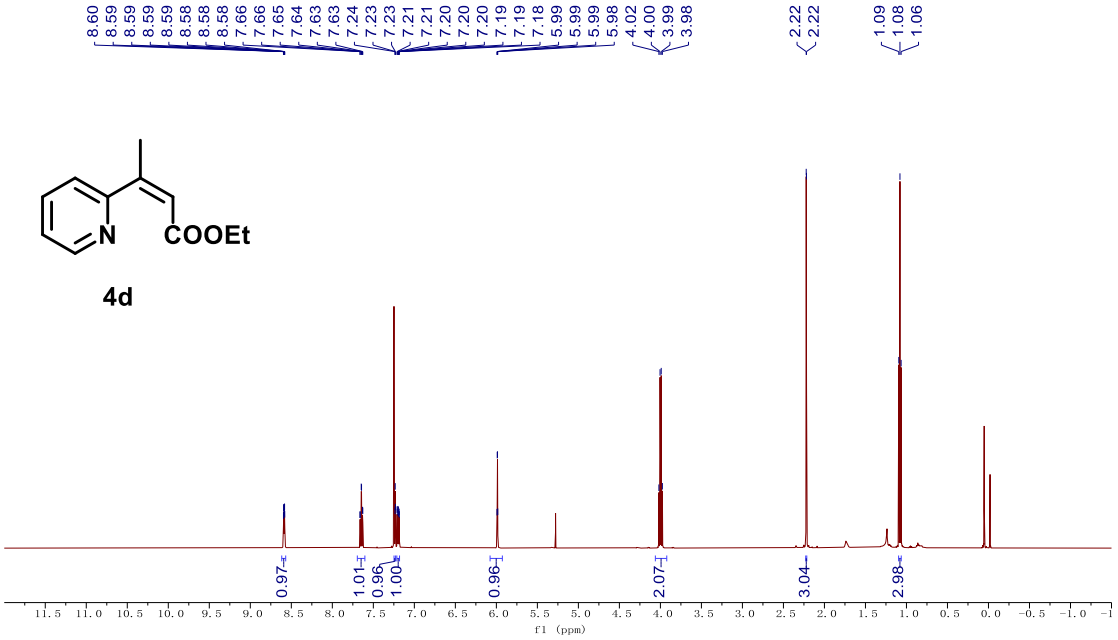
^{1}H NMR of compound **4c** (500 MHz in $CDCl_3$)



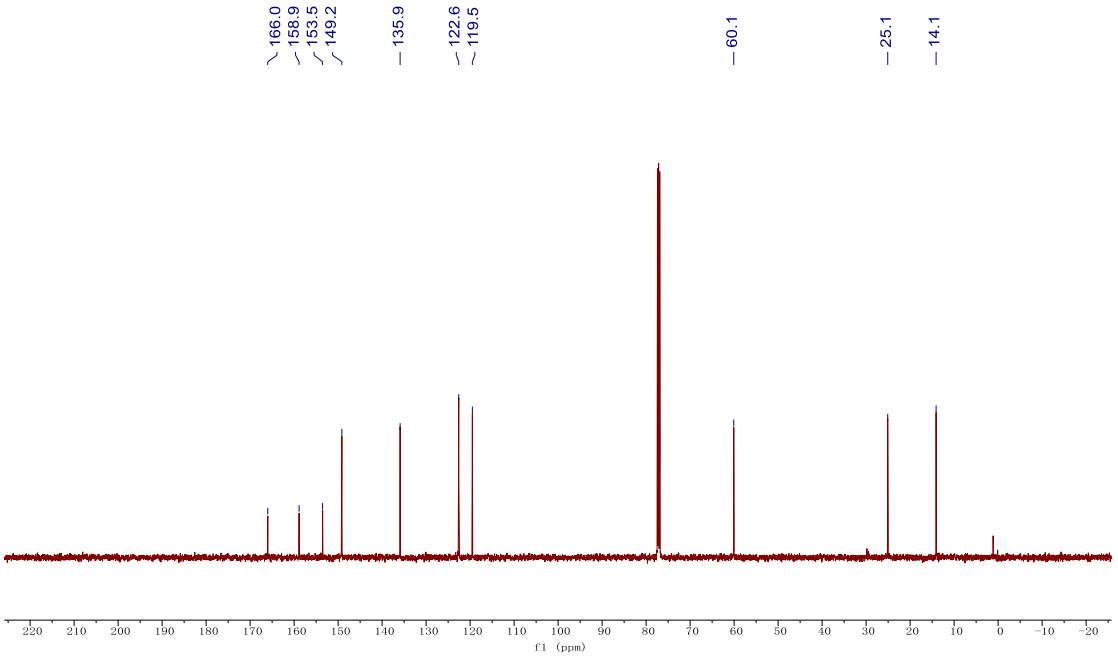
^{13}C NMR of compound **4c** (126 MHz in $CDCl_3$)



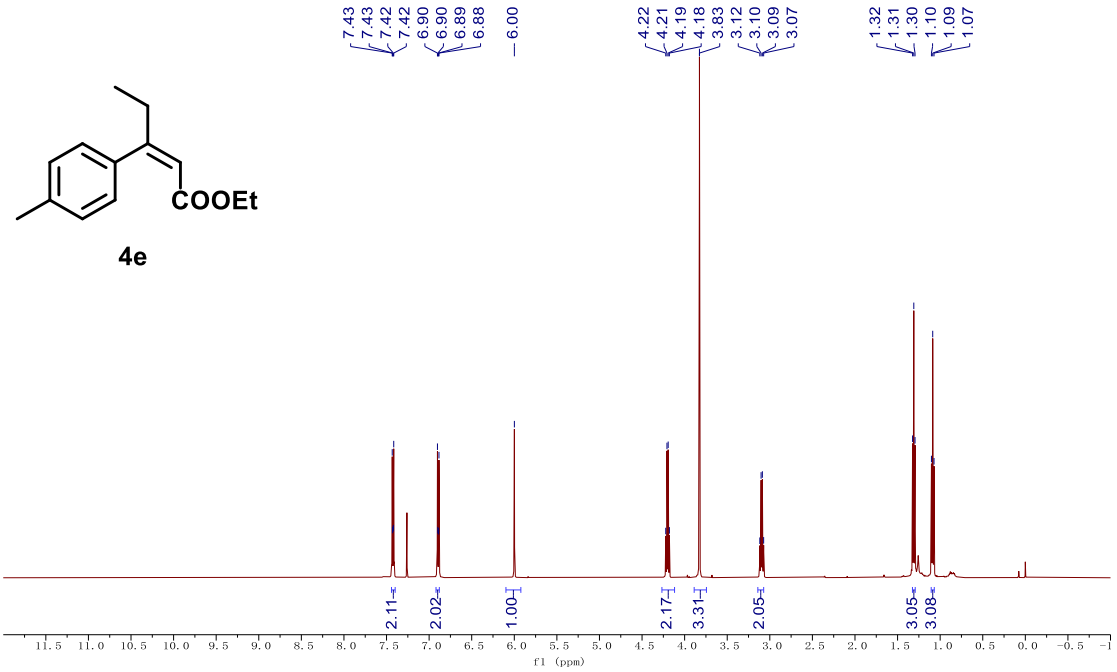
^{1}H NMR of compound **4d** (500 MHz in $CDCl_3$)



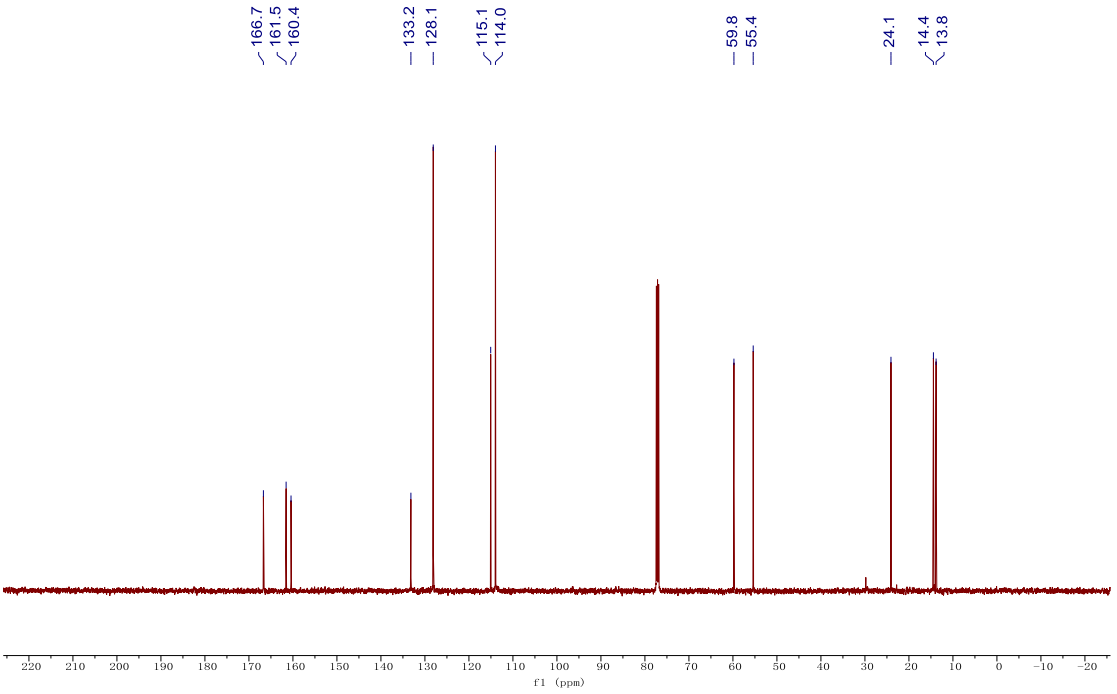
^{13}C NMR of compound **4d** (126 MHz in $CDCl_3$)



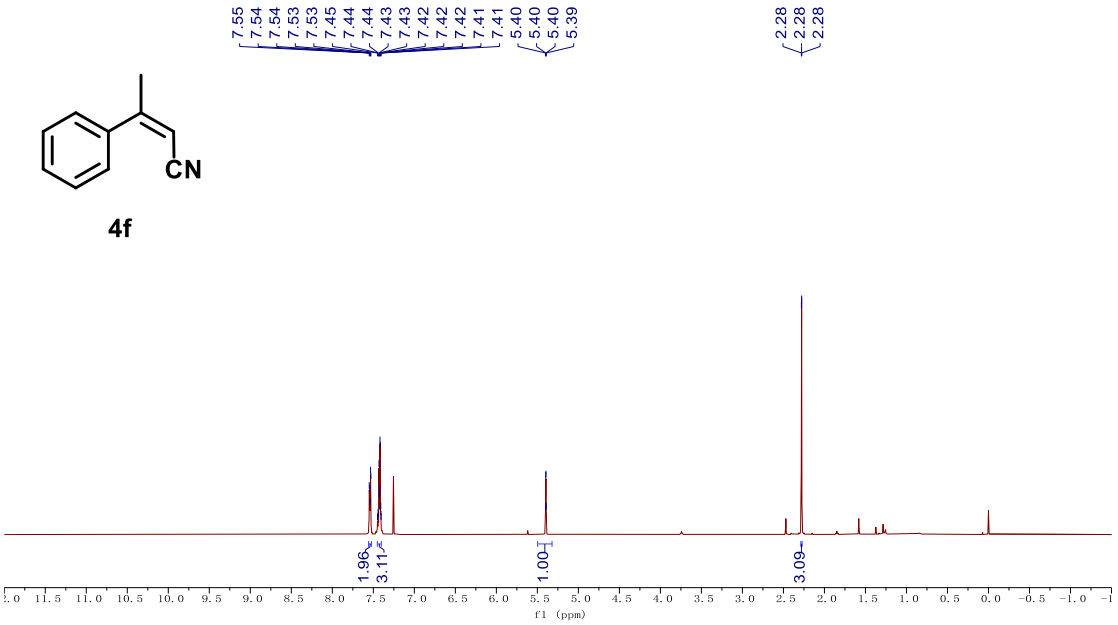
^{1}H NMR of compound **4e** (500 MHz in $CDCl_3$)



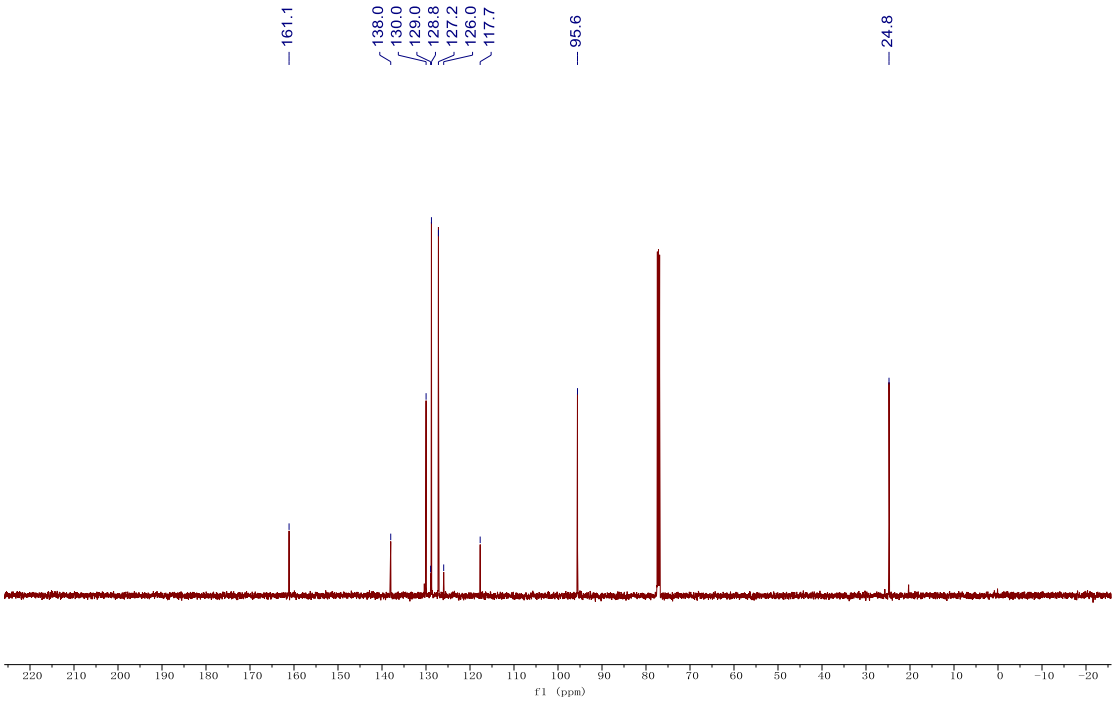
^{13}C NMR of compound **4e** (126 MHz in $CDCl_3$)



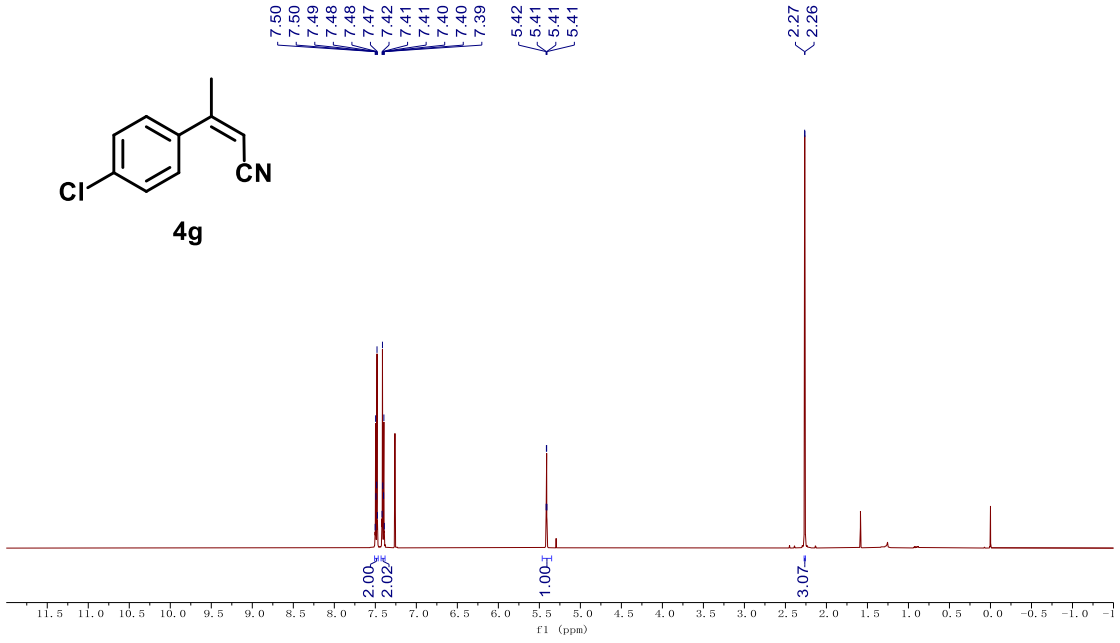
^{1}H NMR of compound **2f** (500 MHz in $CDCl_3$)



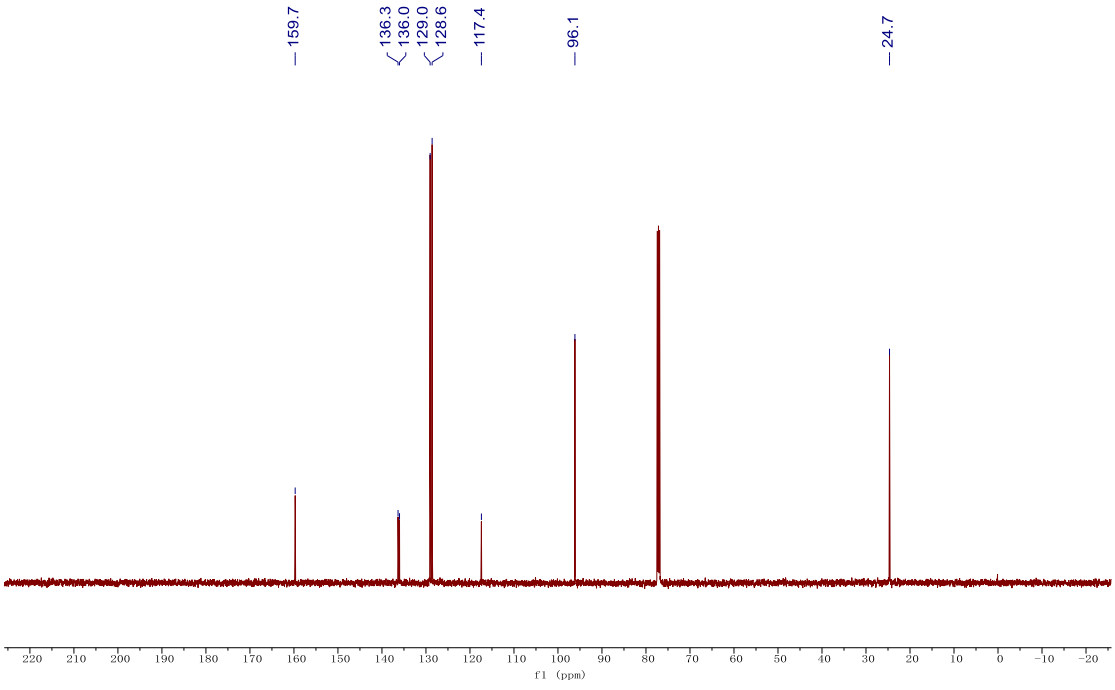
^{13}C NMR of compound **2f** (126 MHz in $CDCl_3$)



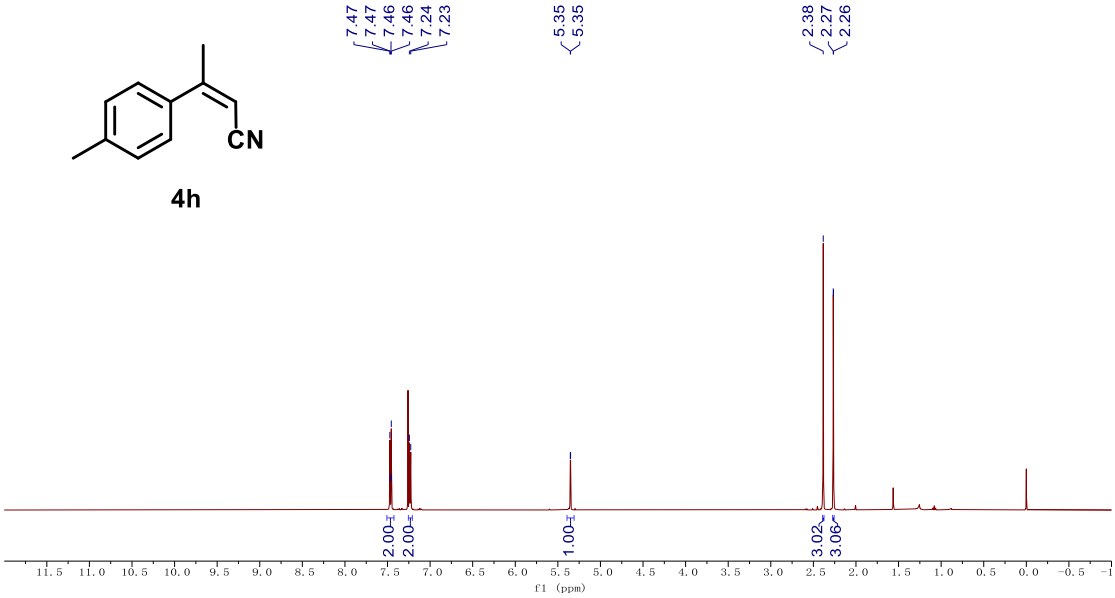
^{1}H NMR of compound **4g** (500 MHz in $CDCl_3$)



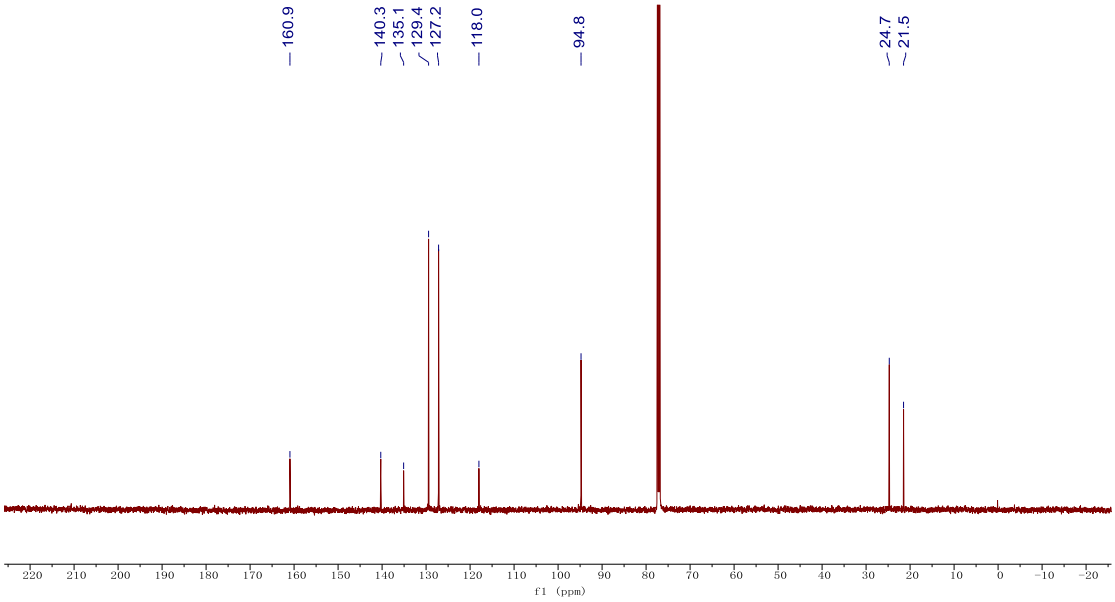
^{13}C NMR of compound **4g** (126 MHz in $CDCl_3$)



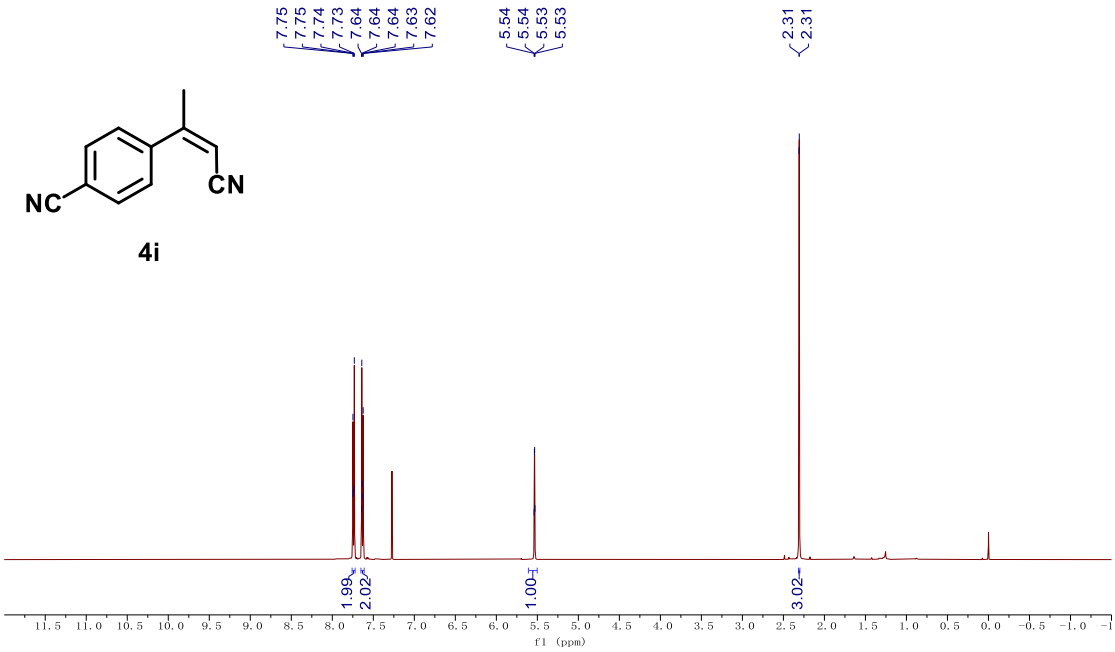
^{1}H NMR of compound **4h** (500 MHz in $CDCl_3$)



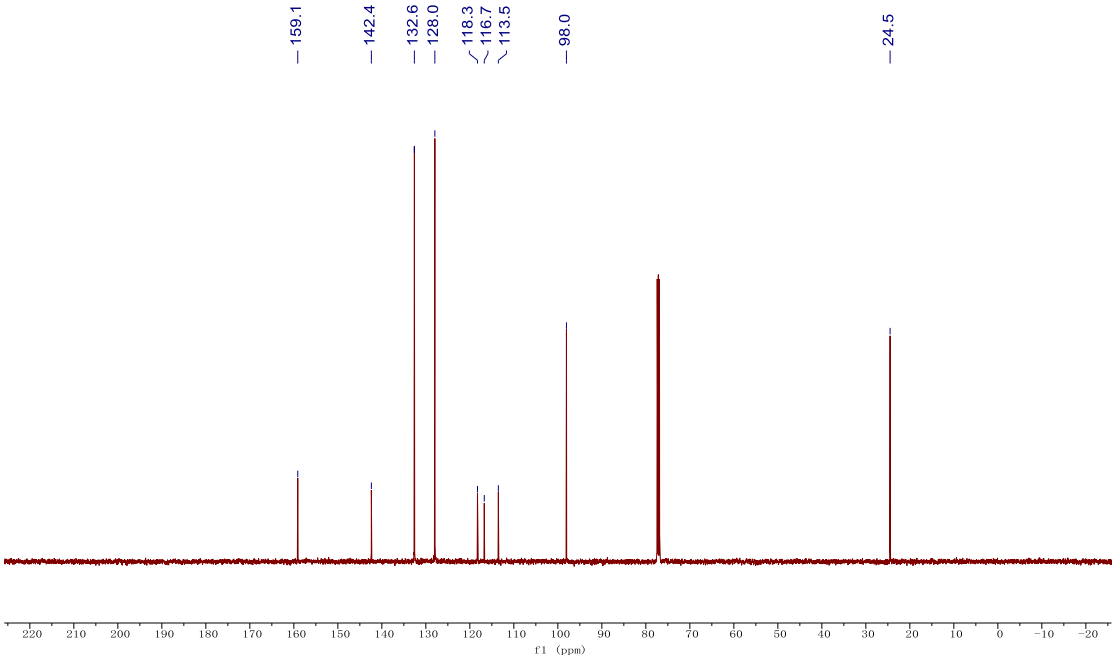
^{13}C NMR of compound **4h** (126 MHz in $CDCl_3$)



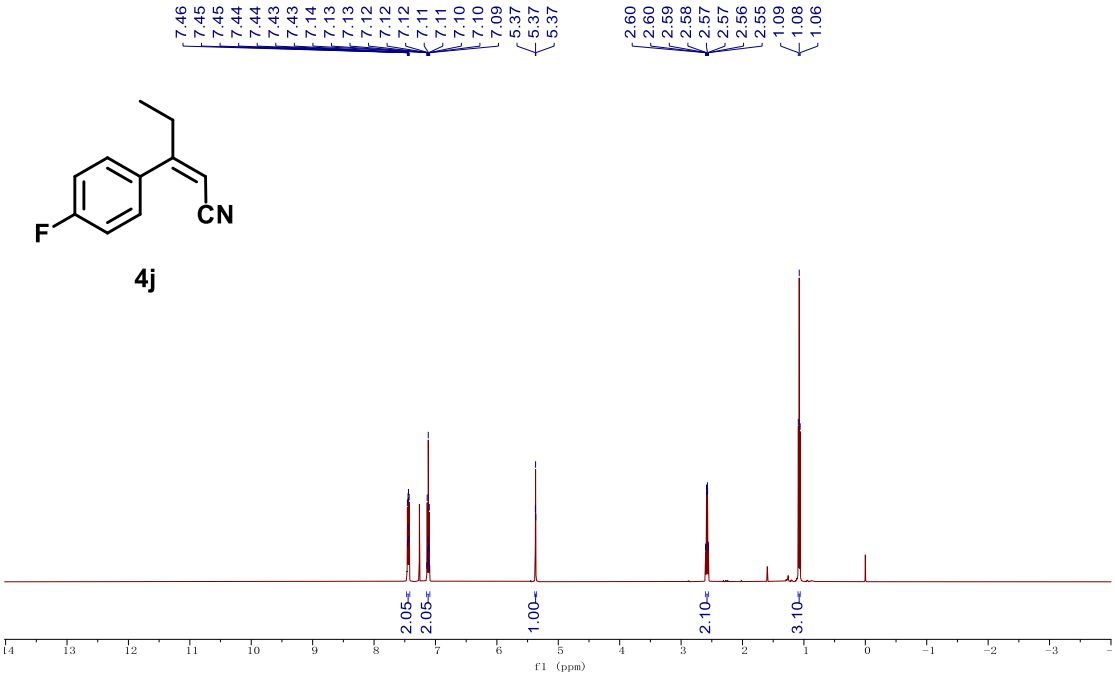
^{1}H NMR of compound **4i** (500 MHz in $CDCl_3$)



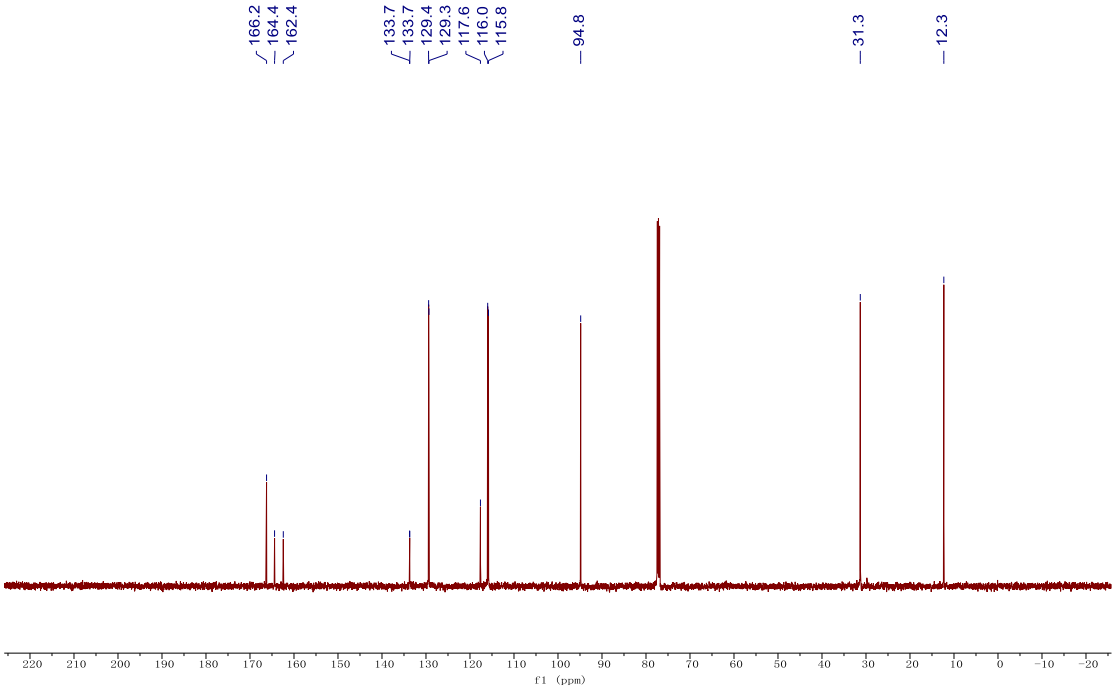
^{13}C NMR of compound **4i** (126 MHz in $CDCl_3$)

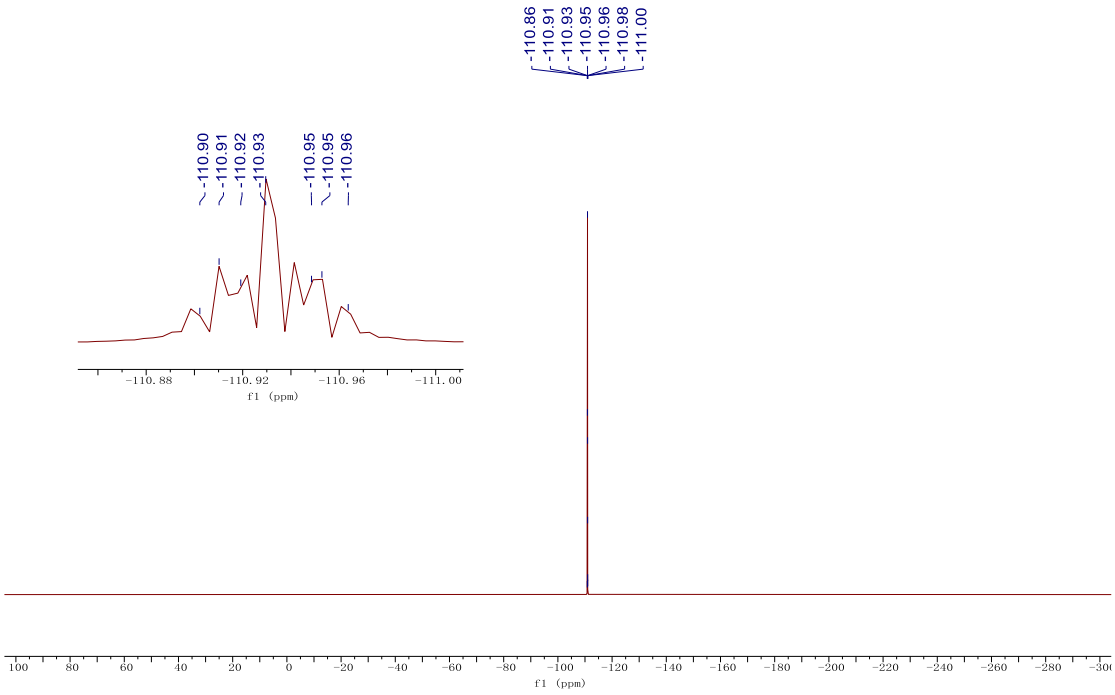


^{1}H NMR of compound **4j** (500 MHz in $CDCl_3$)

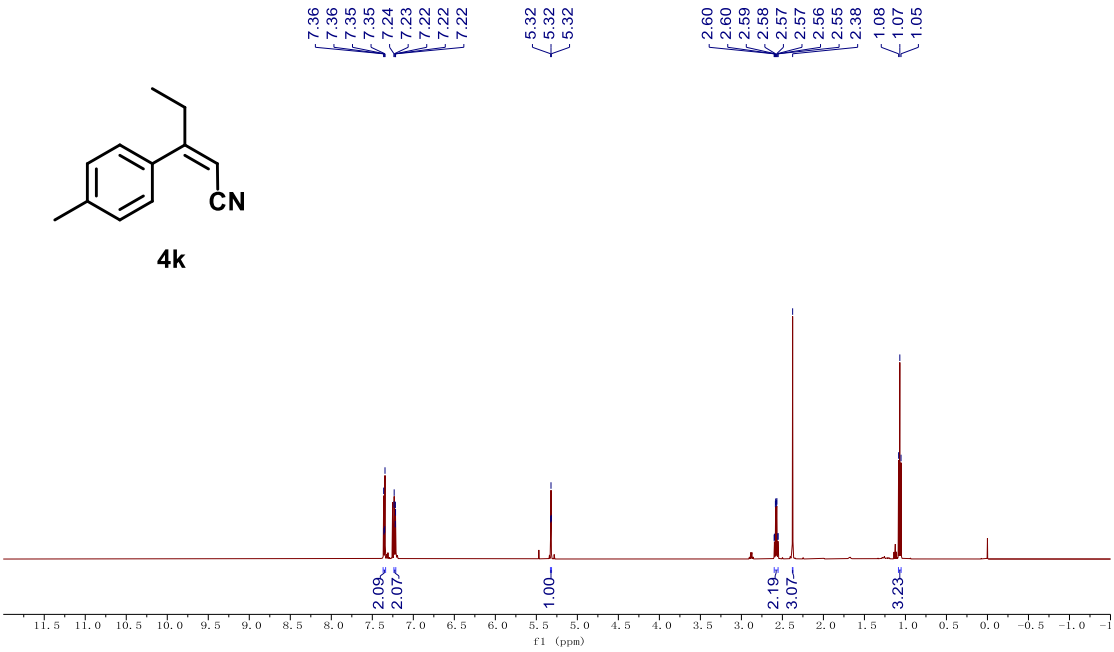


^{13}C NMR of compound **4j** (126 MHz in $CDCl_3$)

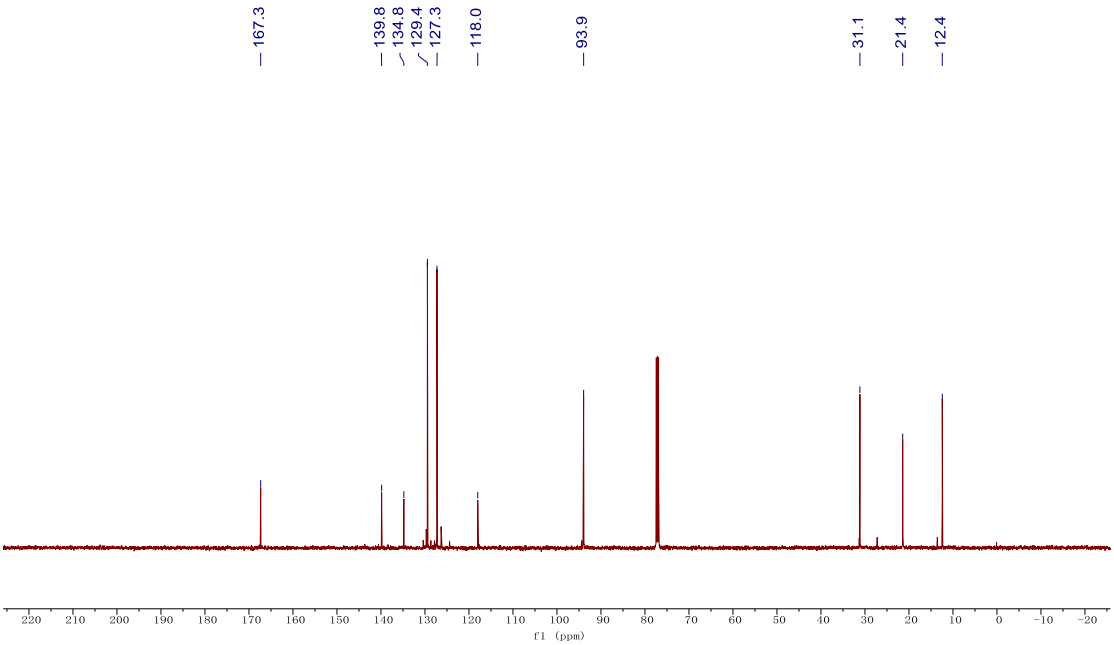



-110.86
-110.91
-110.93
-110.95
-110.96
-110.98
-111.00
-110.90
-110.91
-110.92
-110.93
-110.95
-110.95
-110.96
-110.88
-110.92
-110.96
-111.00
f1 (ppm)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

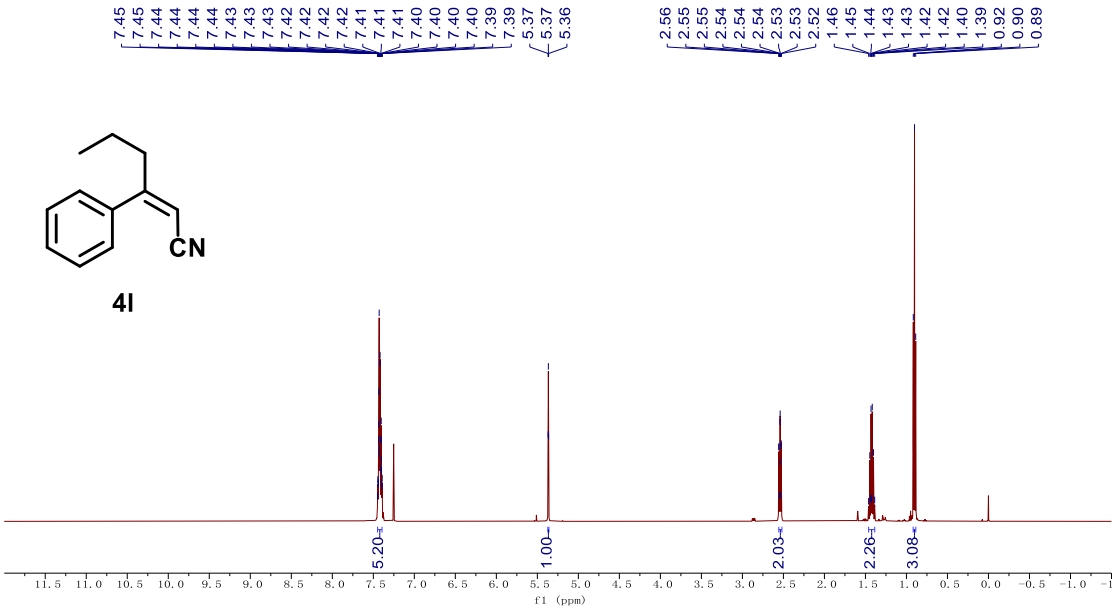
^{1}H NMR of compound **4k** (500 MHz in $CDCl_3$)



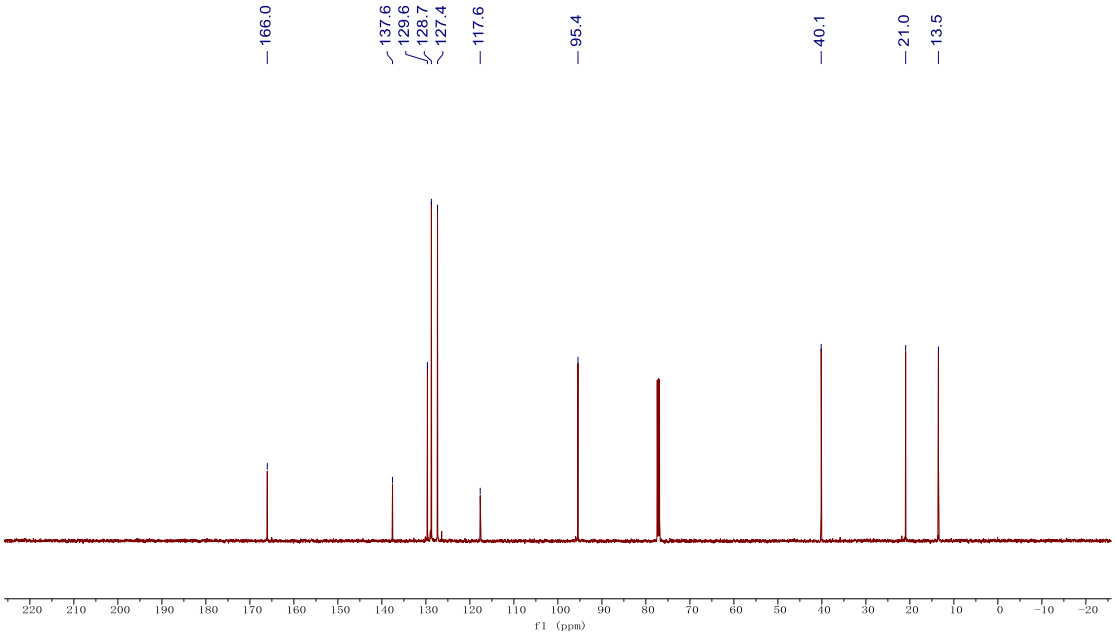
^{13}C NMR of compound **4k** (126 MHz in $CDCl_3$)



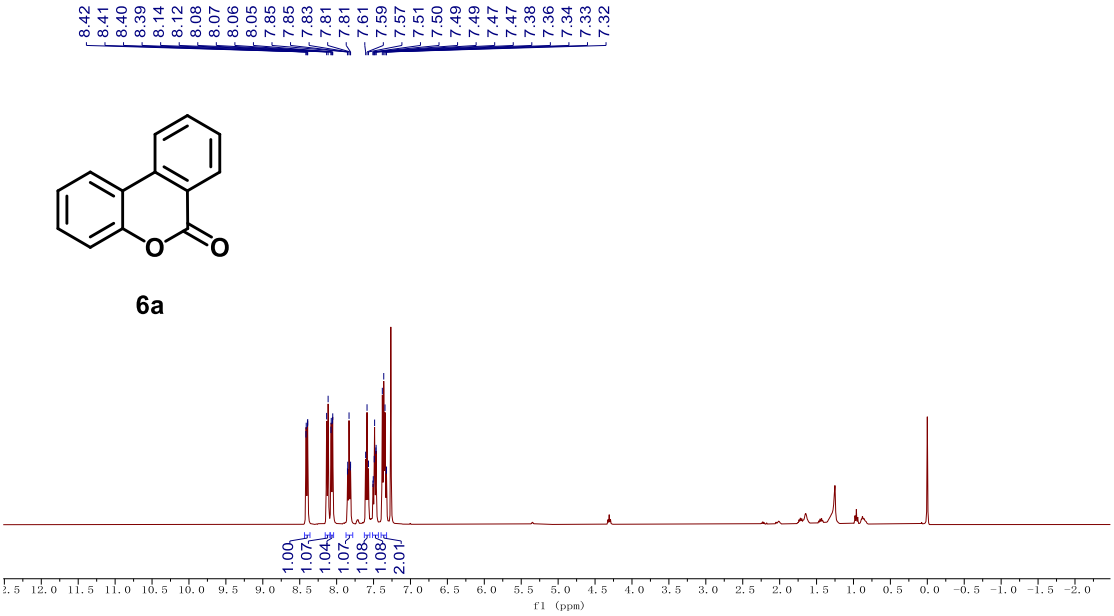
^{1}H NMR of compound **4l** (500 MHz in $CDCl_3$)



^{13}C NMR of compound **4l** (126 MHz in $CDCl_3$)

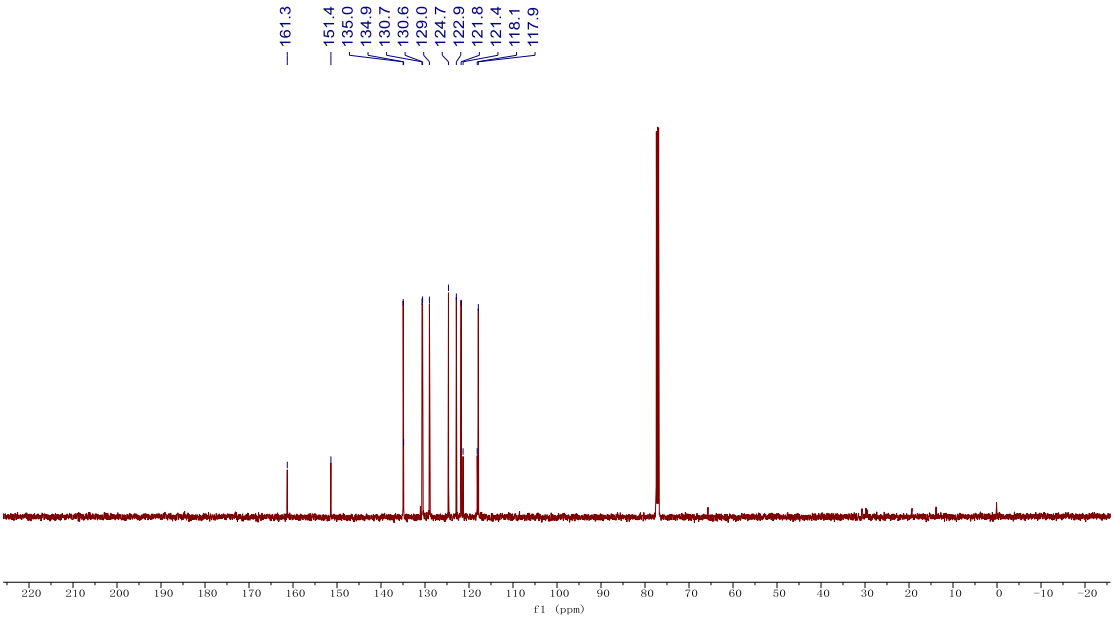


^{1}H NMR of compound **6a** (400 MHz in $CDCl_3$)

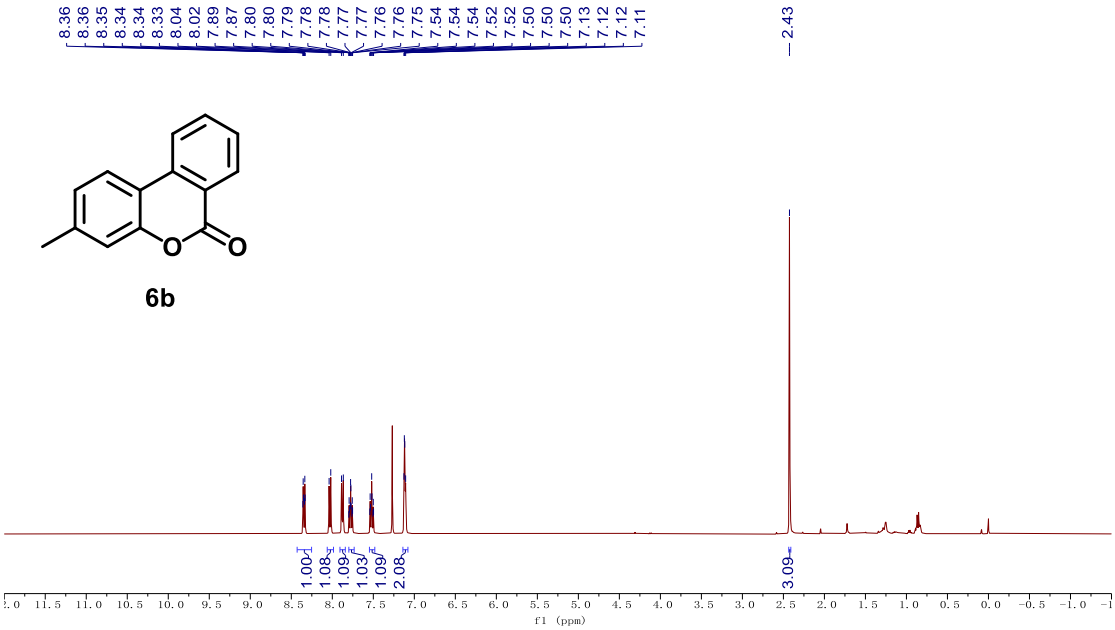


6a

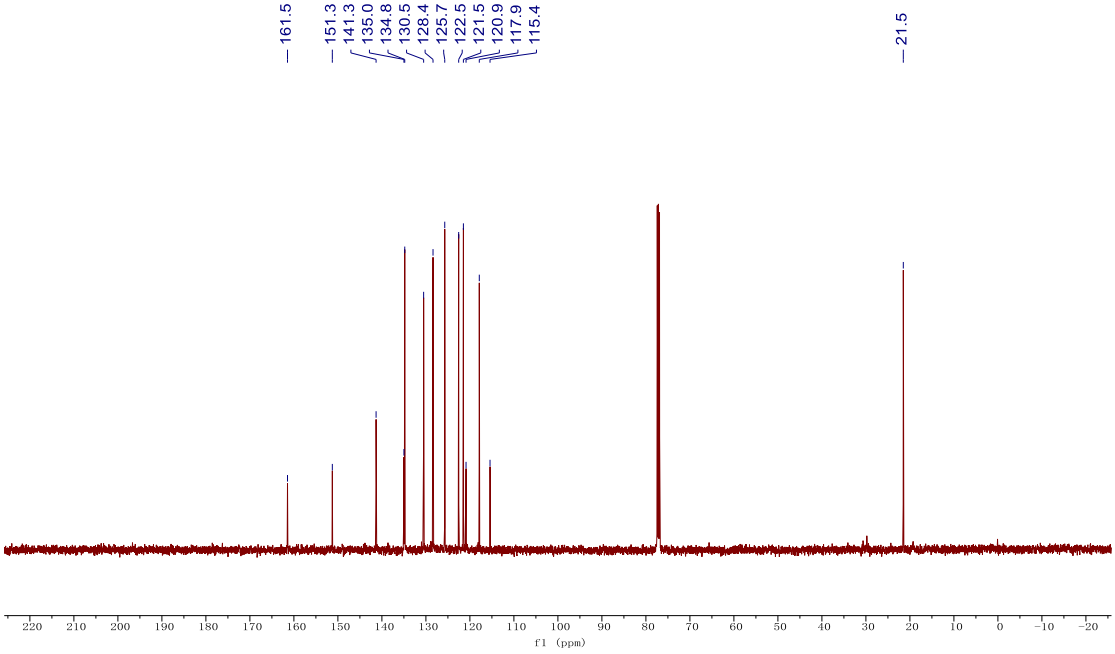
^{13}C NMR of compound **6a** (126 MHz in $CDCl_3$)



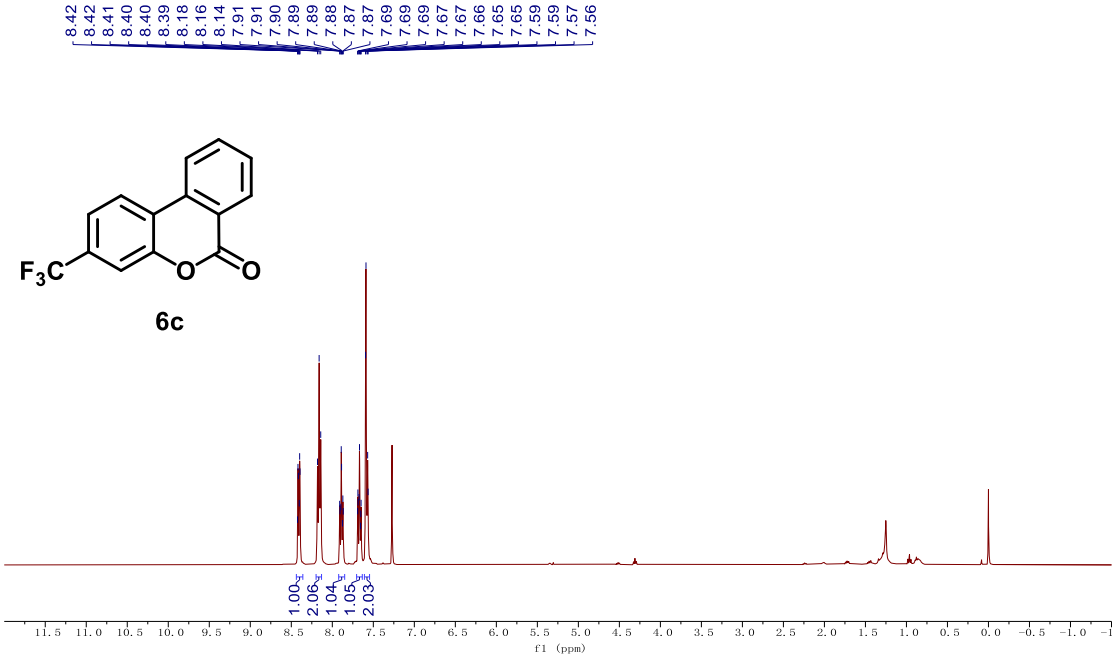
^{1}H NMR of compound **6b** (400 MHz in $CDCl_3$)



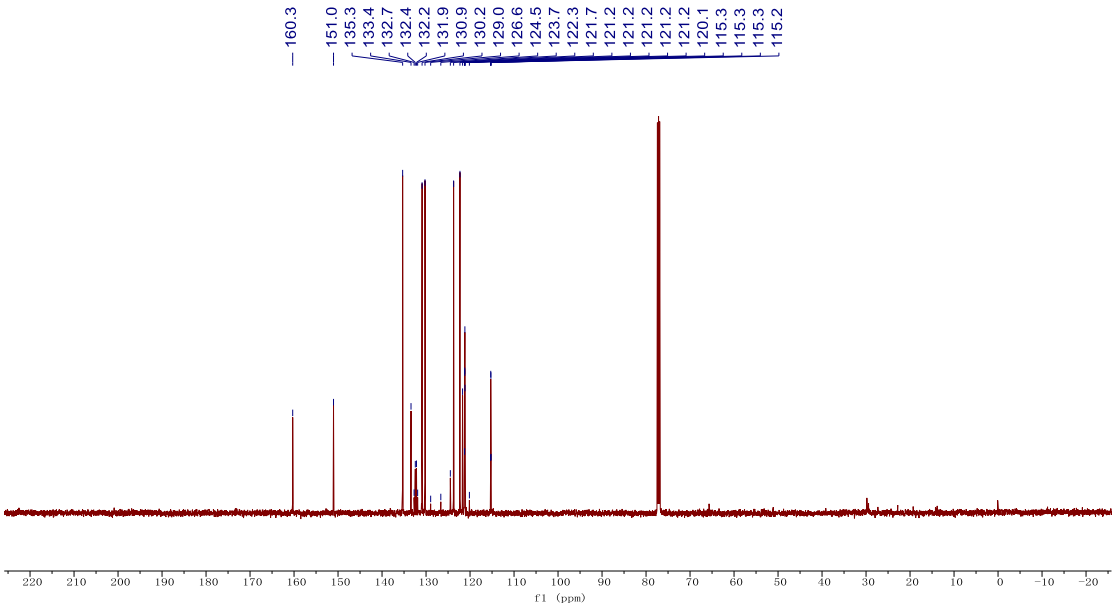
^{13}C NMR of compound **6b** (126 MHz in $CDCl_3$)



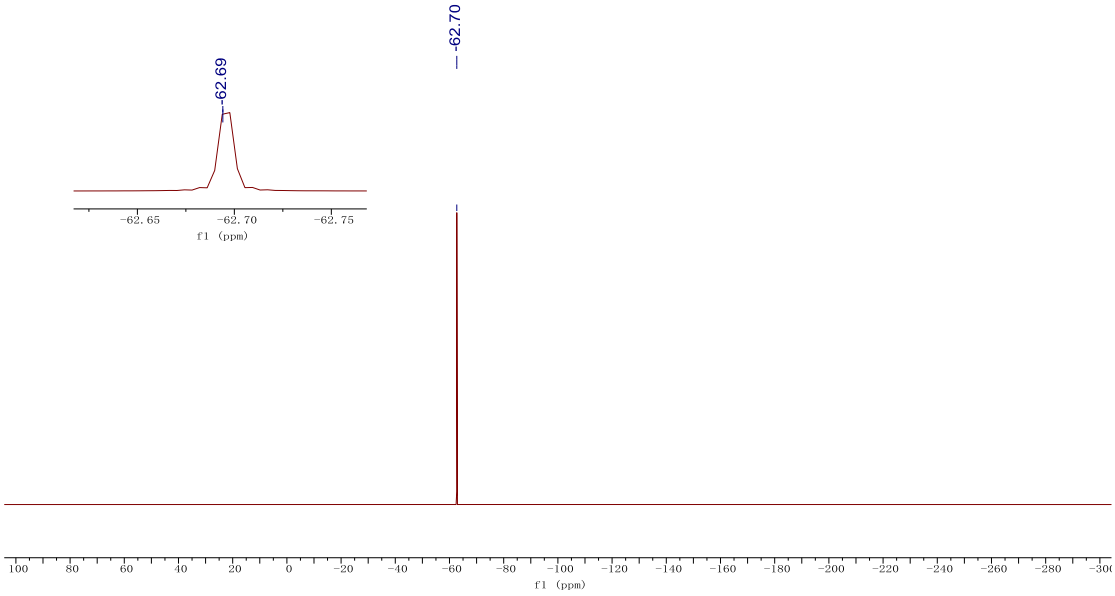
^{1}H NMR of compound **6c** (400 MHz in $CDCl_3$)



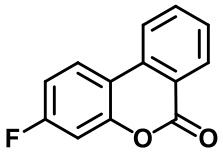
^{13}C NMR of compound **6c** (126 MHz in $CDCl_3$)



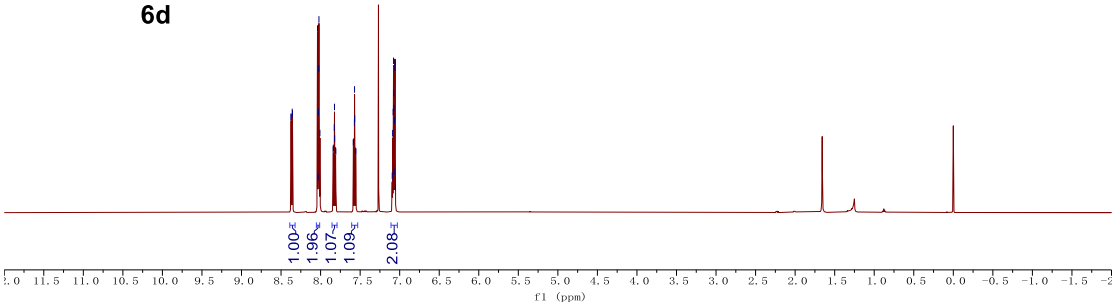
^{19}F NMR of compound **6c** (471 MHz in $CDCl_3$)



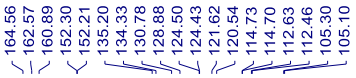
^{1}H NMR of compound **6d** (500 MHz in $CDCl_3$)

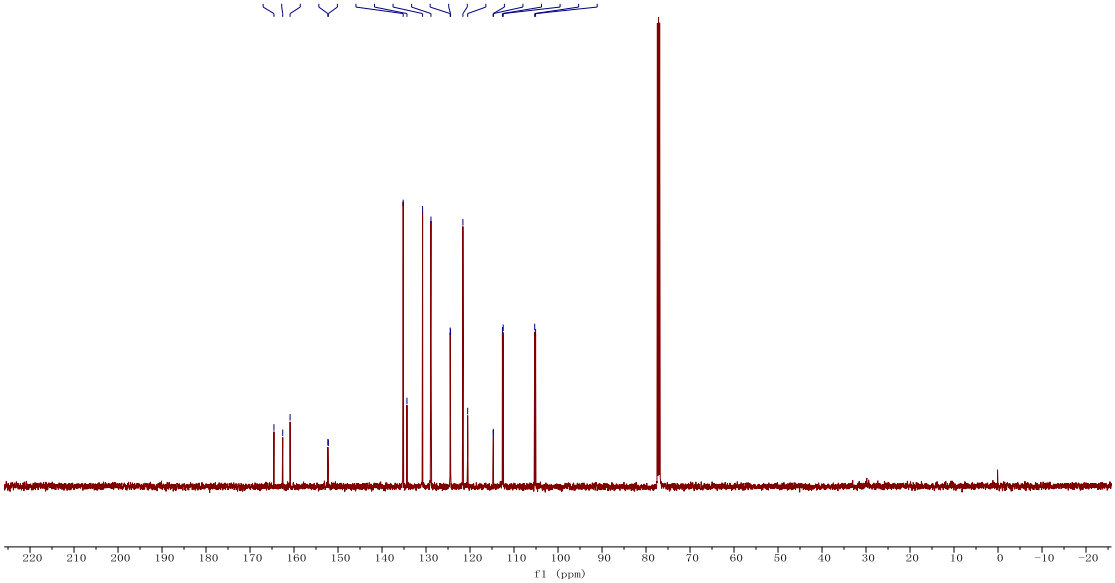


6d

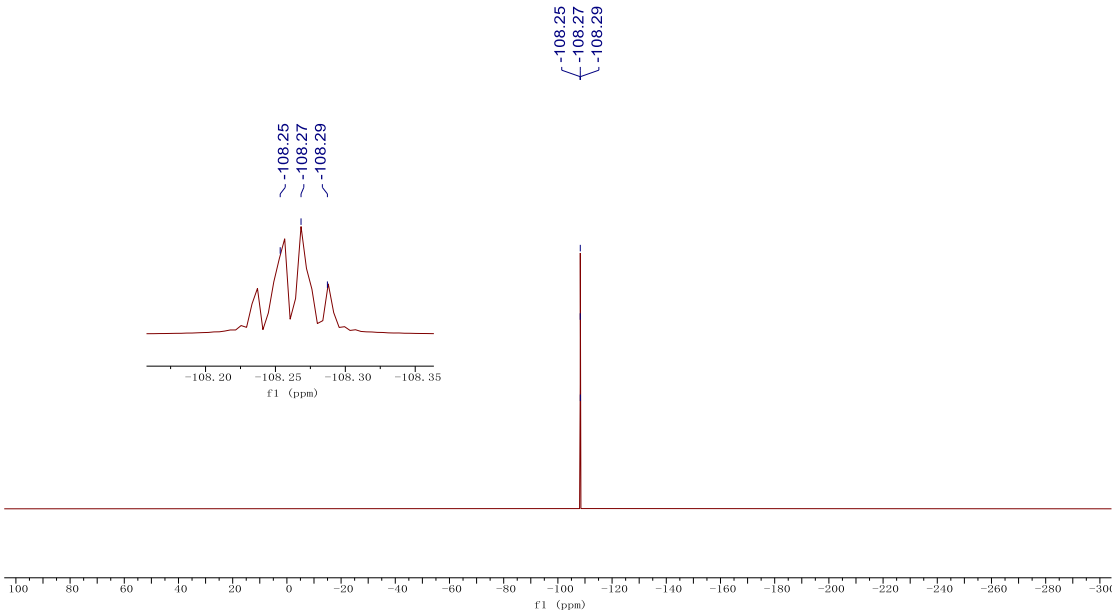


^{13}C NMR of compound **6d** (126 MHz in $CDCl_3$)

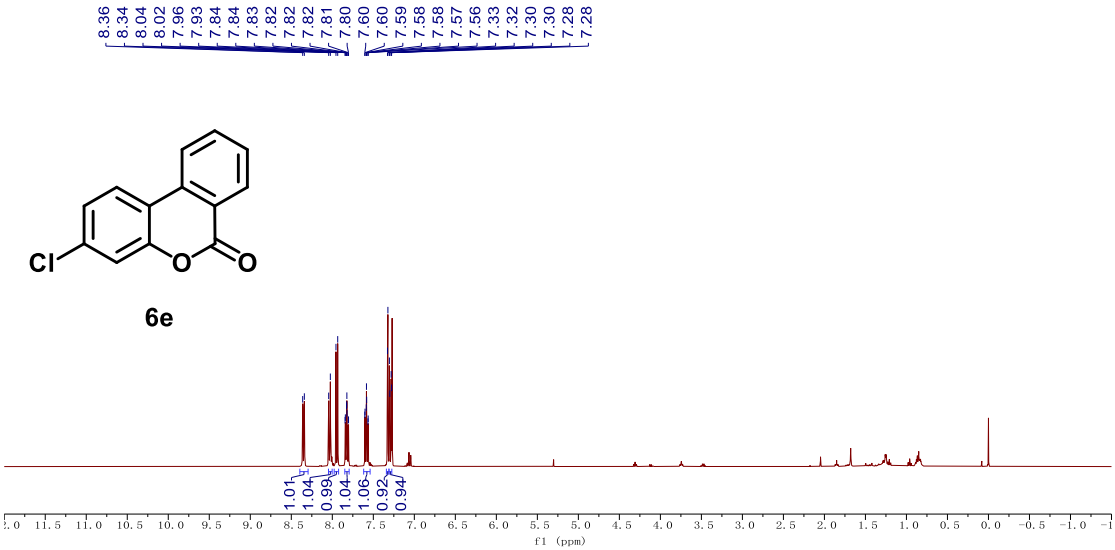




^{19}F NMR of compound **6d** (471 MHz in $CDCl_3$)

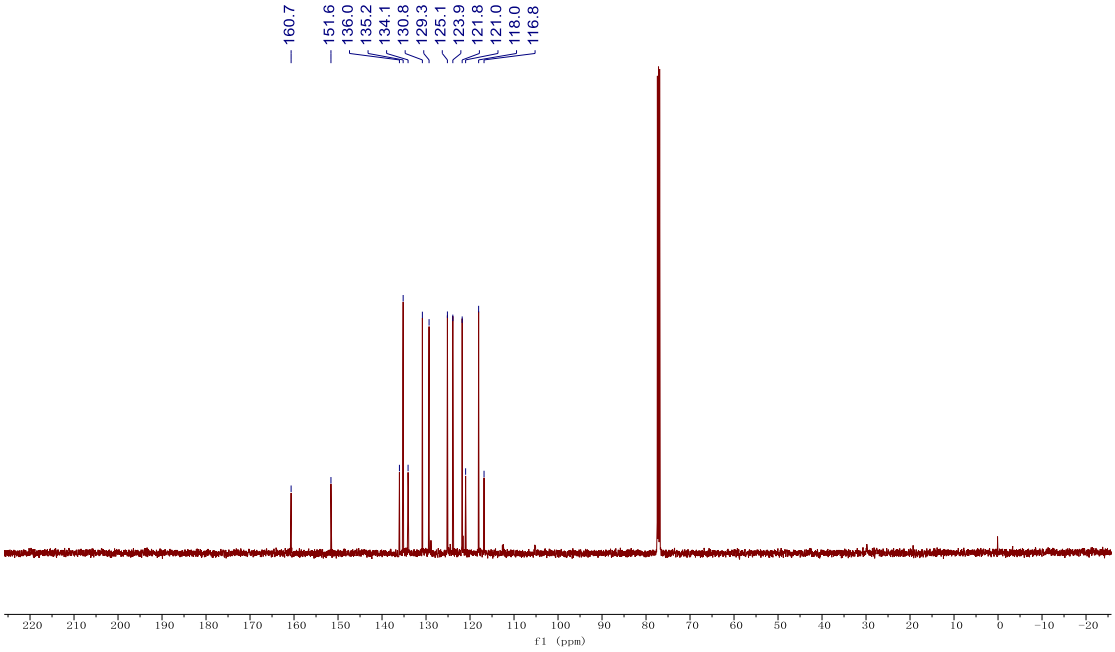


^{1}H NMR of compound **6e** (400 MHz in $CDCl_3$)

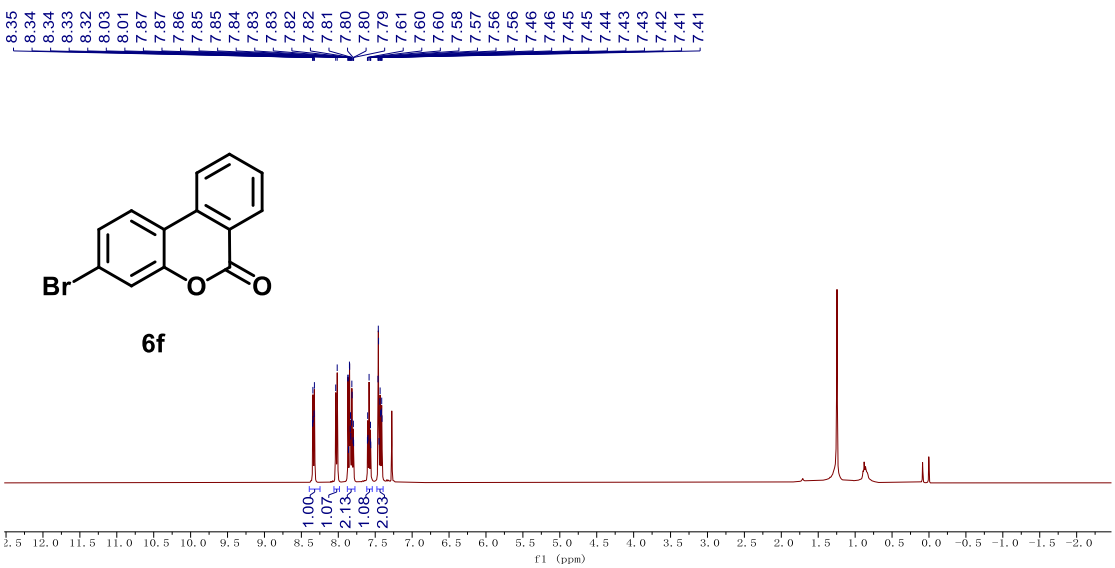


6e

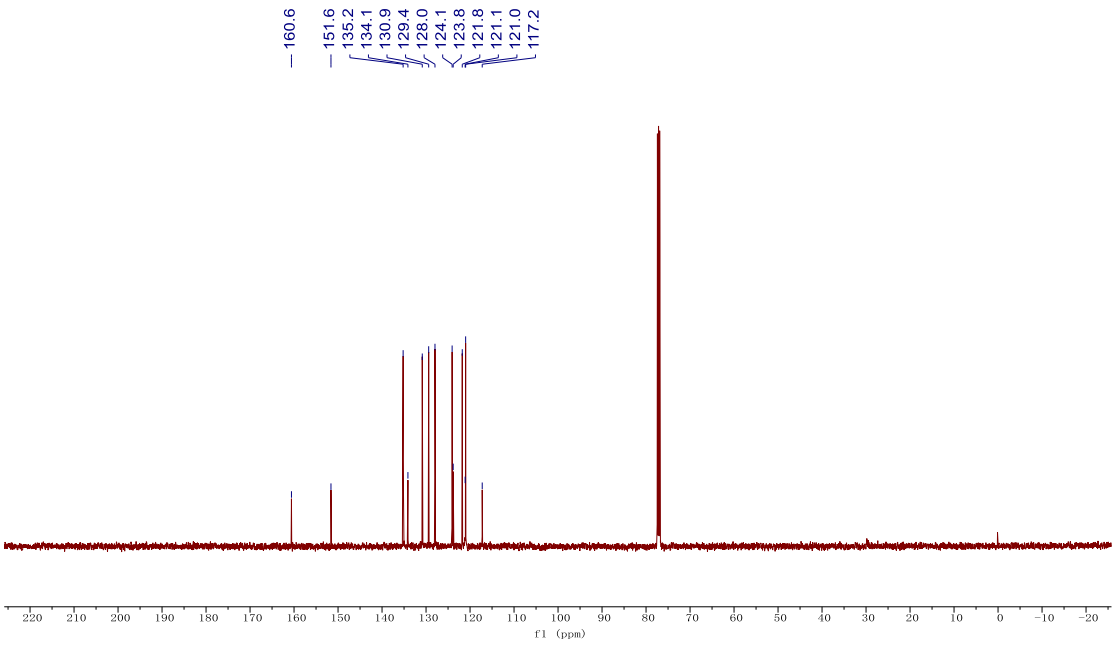
^{13}C NMR of compound **6e** (126 MHz in $CDCl_3$)



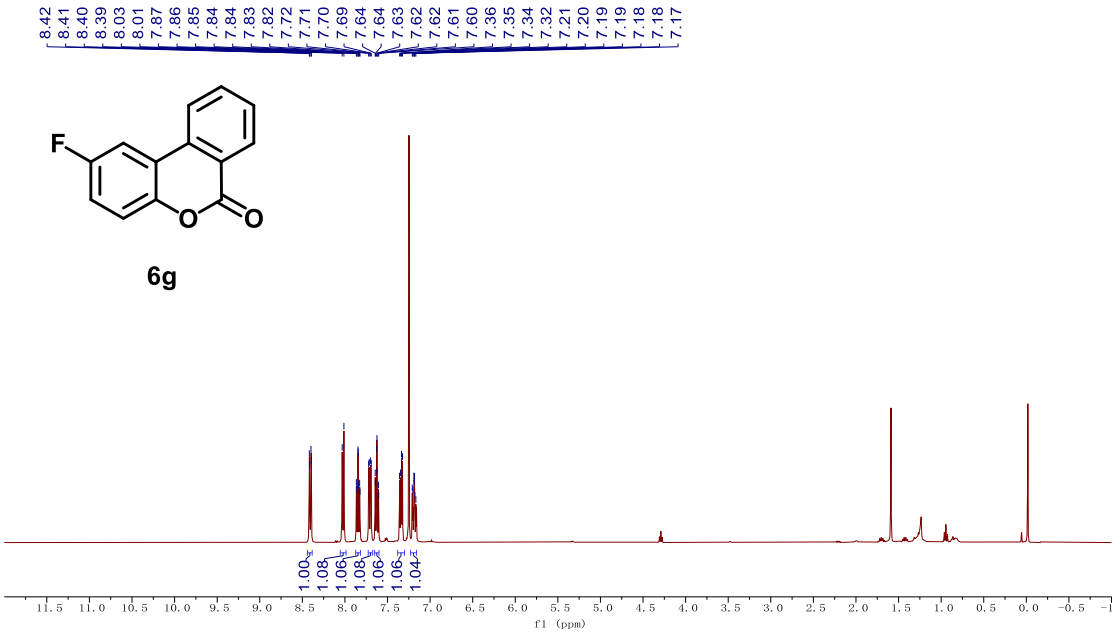
^{1}H NMR of compound **6f** (500 MHz in $CDCl_3$)



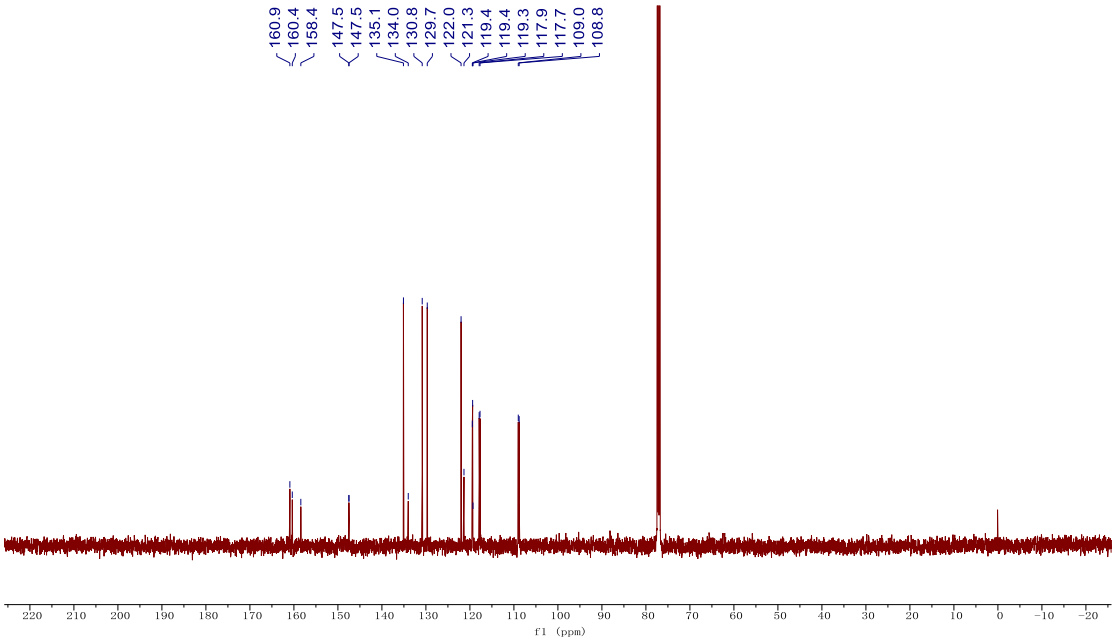
^{13}C NMR of compound **6f** (126 MHz in $CDCl_3$)

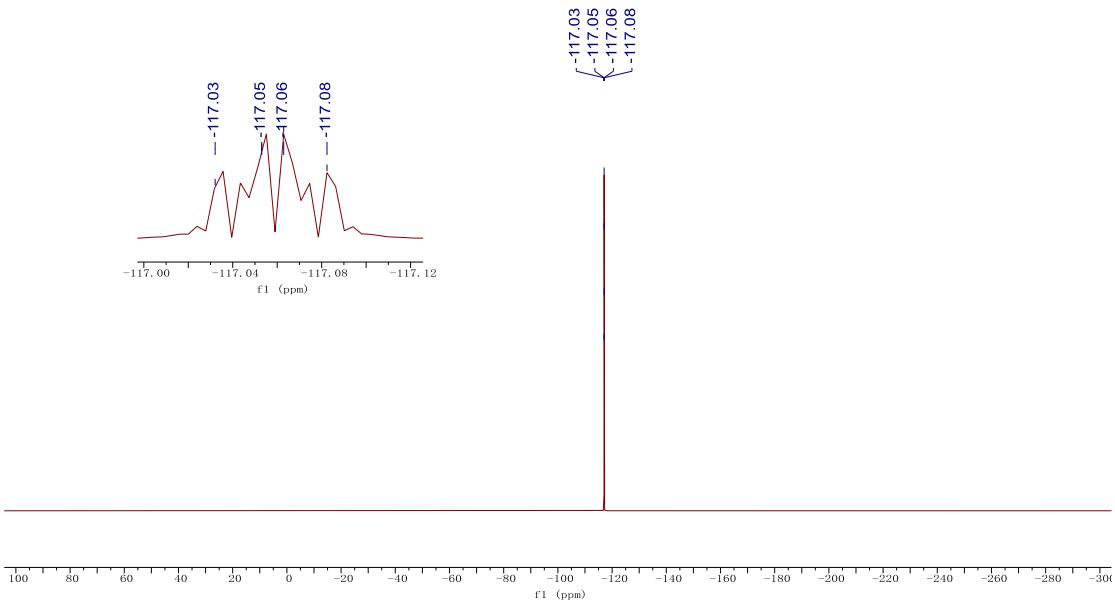


^{1}H NMR of compound **6g** (400 MHz in $CDCl_3$)



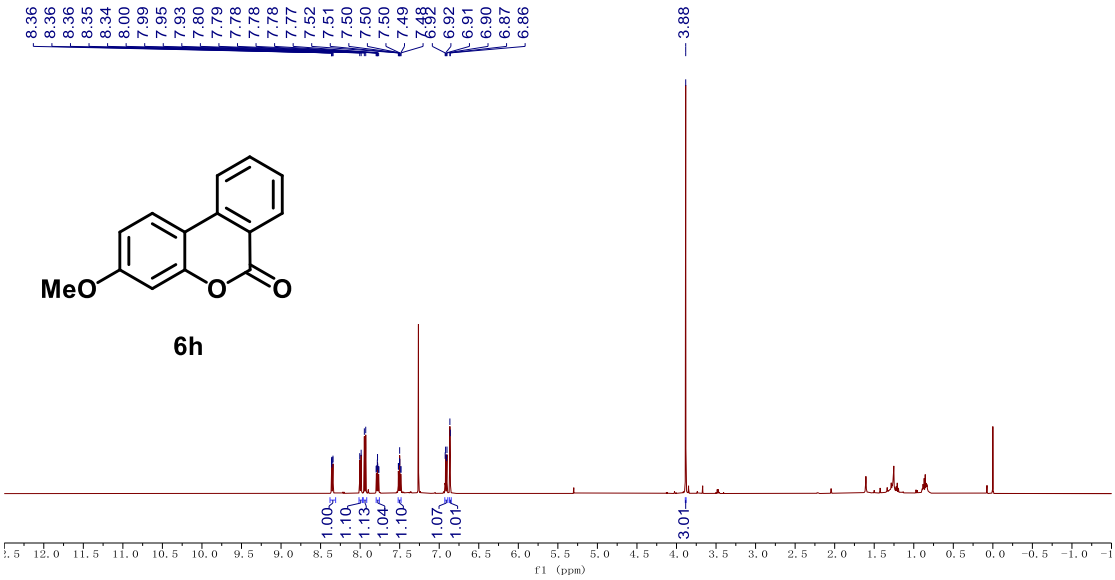
^{13}C NMR of compound **6g** (126 MHz in $CDCl_3$)



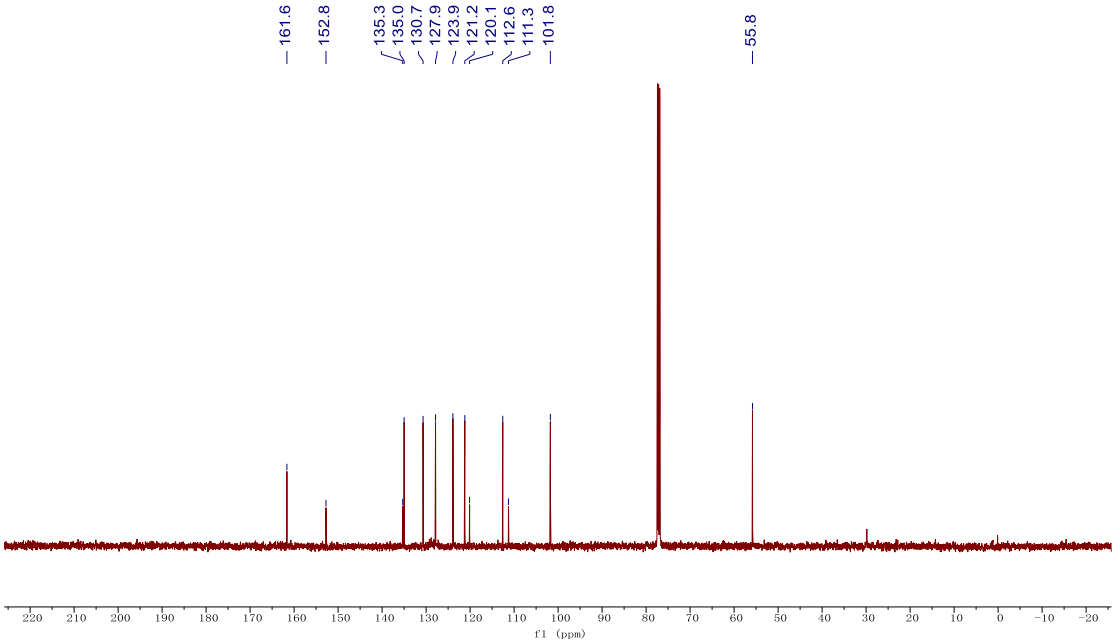

-117.03
-117.05
-117.06
-117.08
-117.03
-117.05
-117.06
-117.08
-117.00
-117.04
-117.08
-117.12
f1 (ppm)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

zz

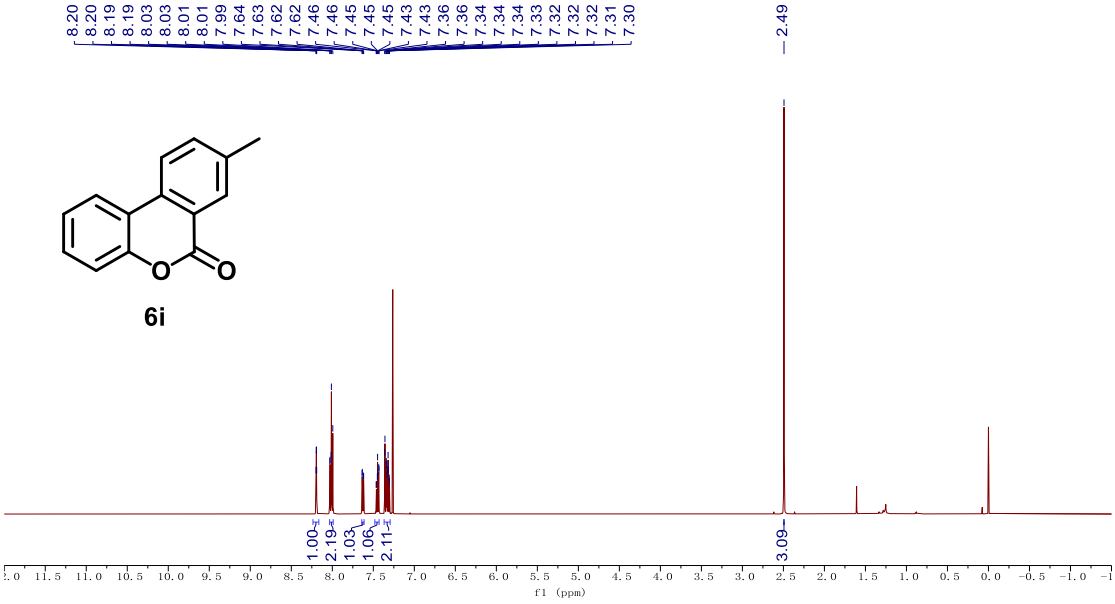
^{1}H NMR of compound **6h** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **6h** (126 MHz in $CDCl_3$)

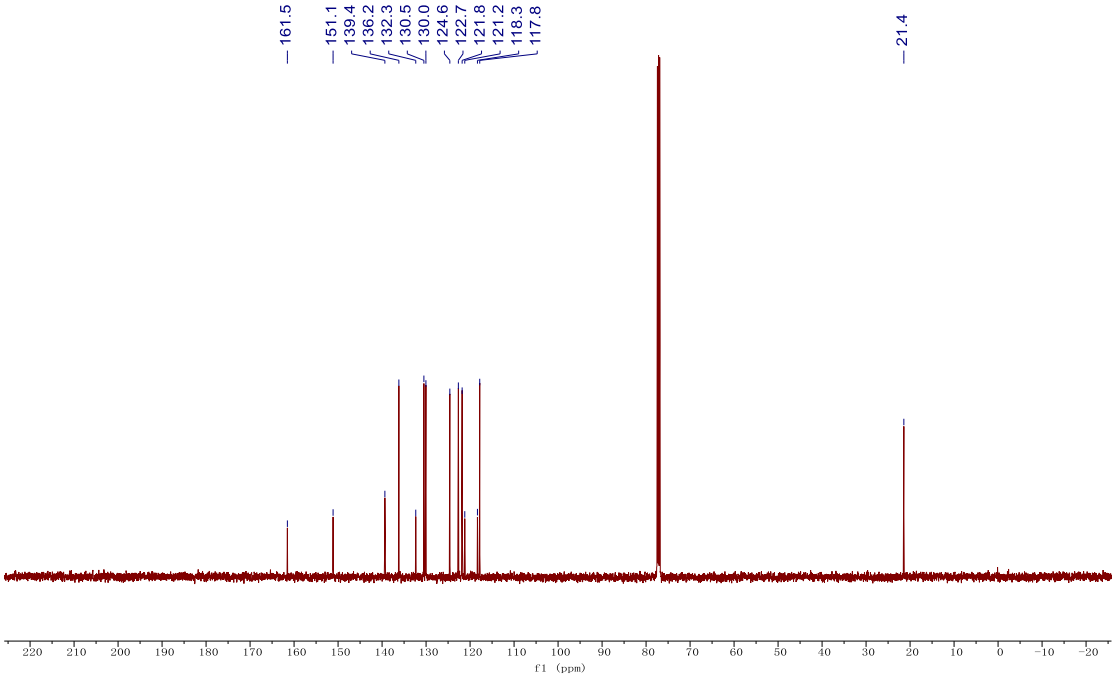


^{1}H NMR of compound **6i** (400 MHz in $CDCl_3$)

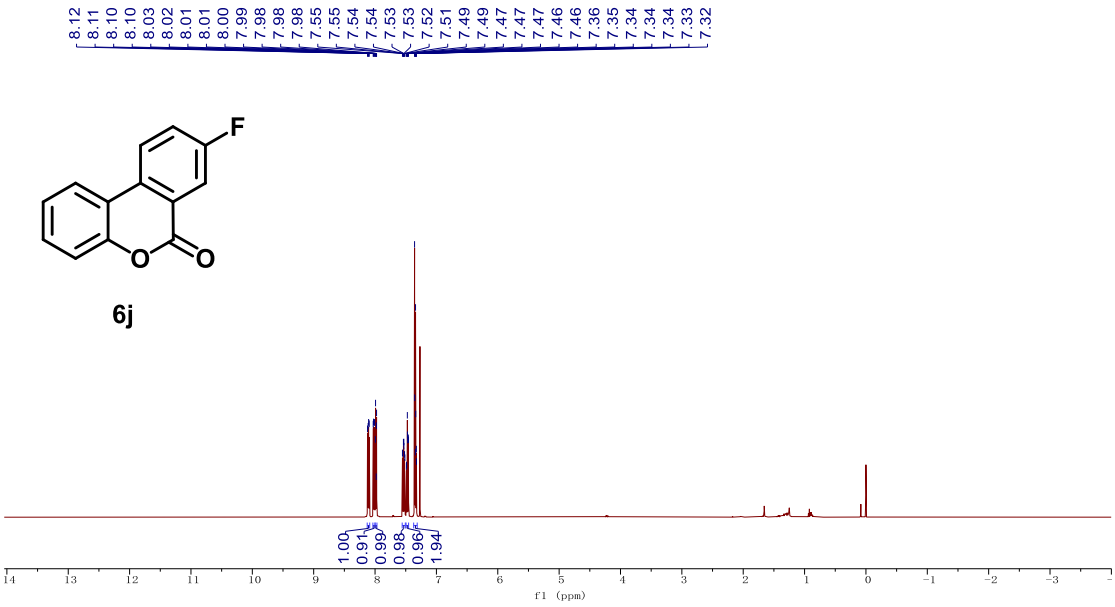


6i

^{13}C NMR of compound **6i** (126 MHz in $CDCl_3$)

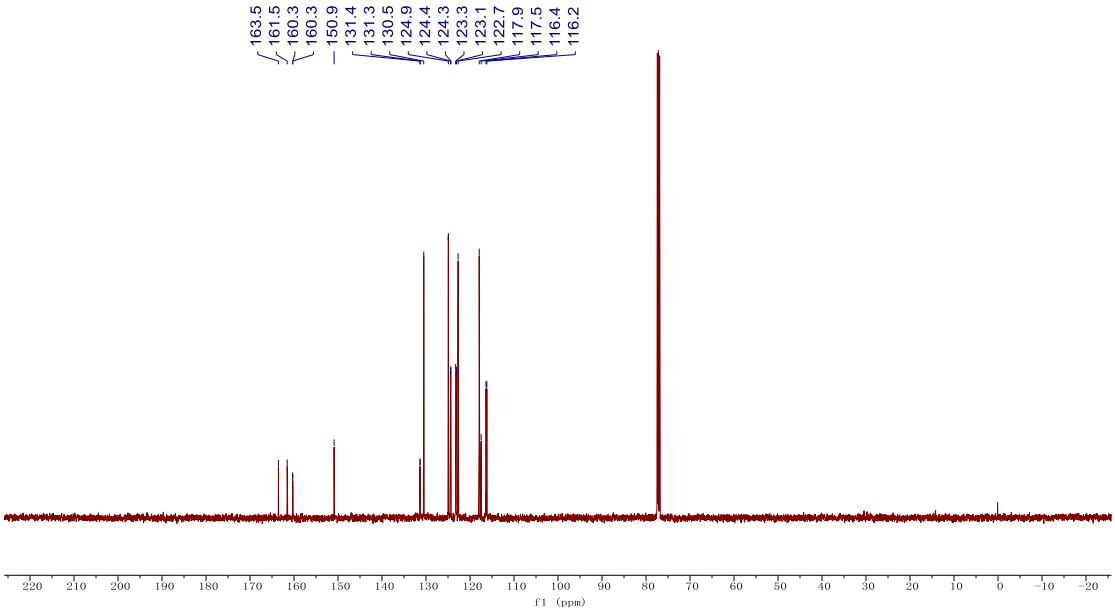


^{1}H NMR of compound **6j** (400 MHz in $CDCl_3$)

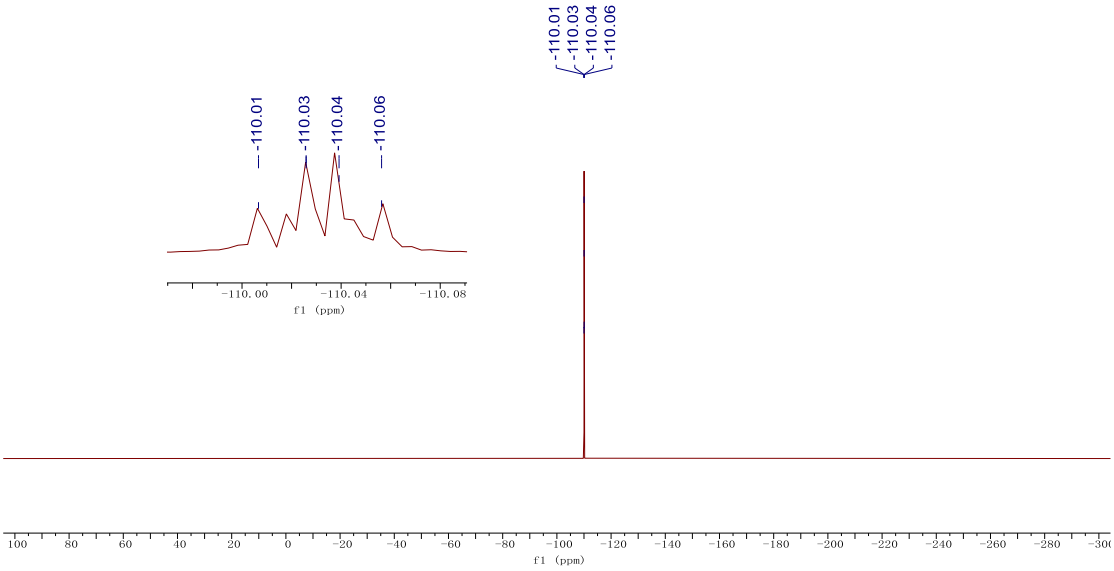


6j

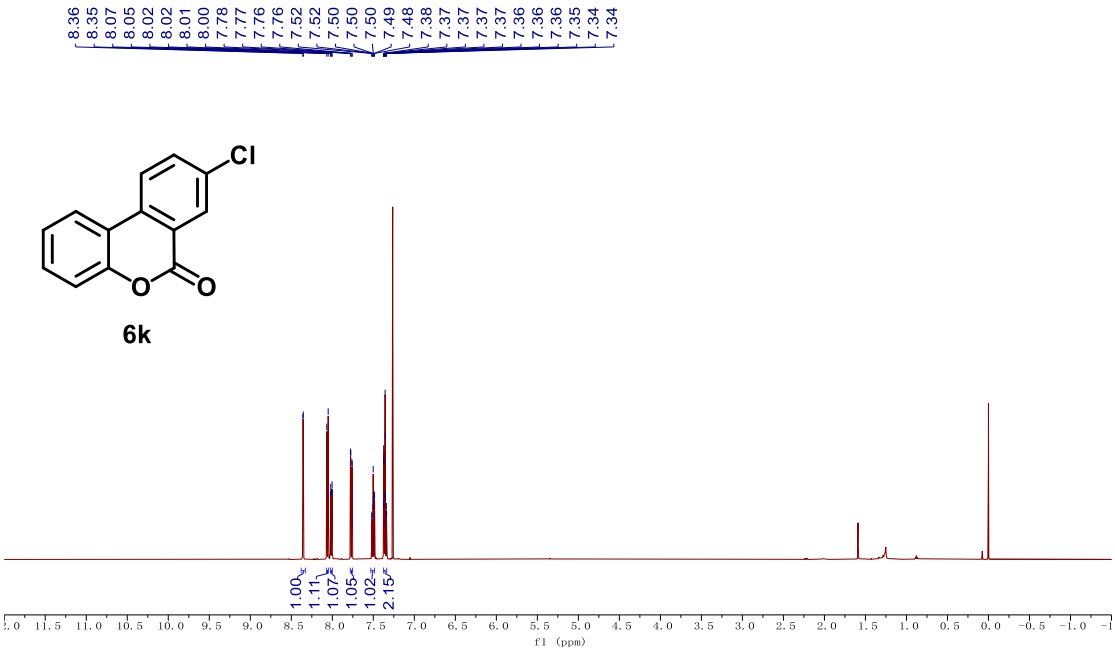
^{13}C NMR of compound **6j** (126 MHz in $CDCl_3$)



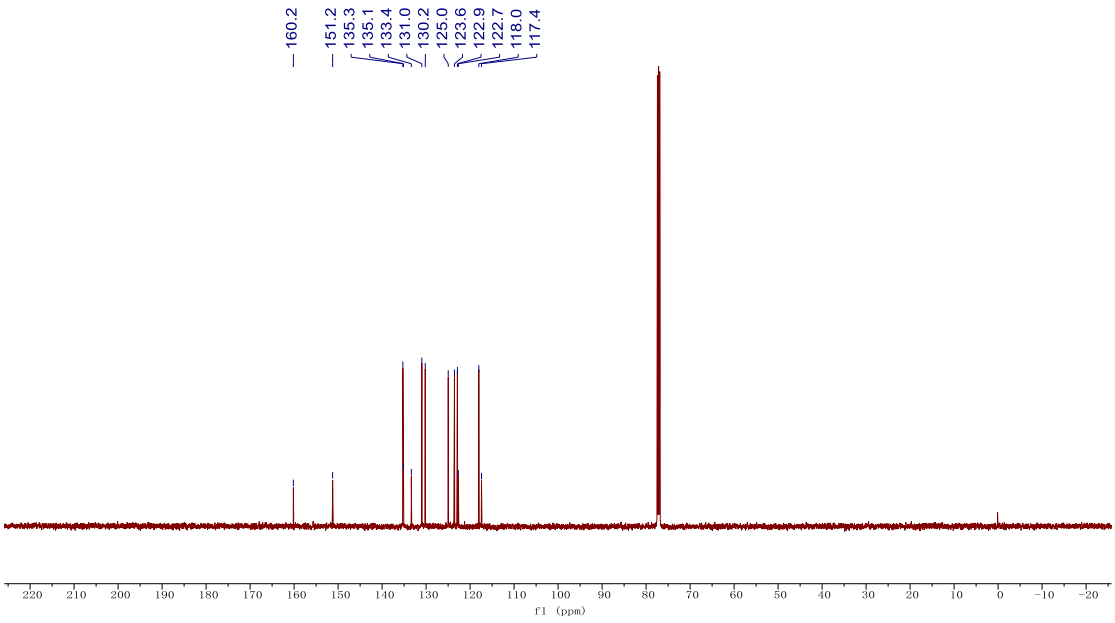
^{19}F NMR of compound **6j** (471 MHz in $CDCl_3$)



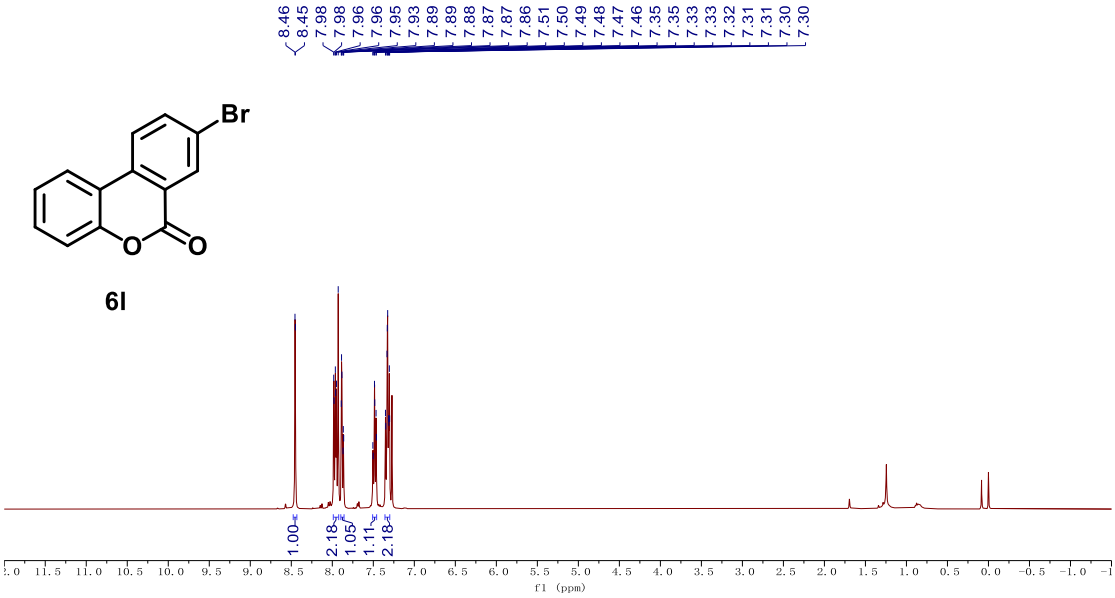
^{1}H NMR of compound **6k** (400 MHz in $CDCl_3$)



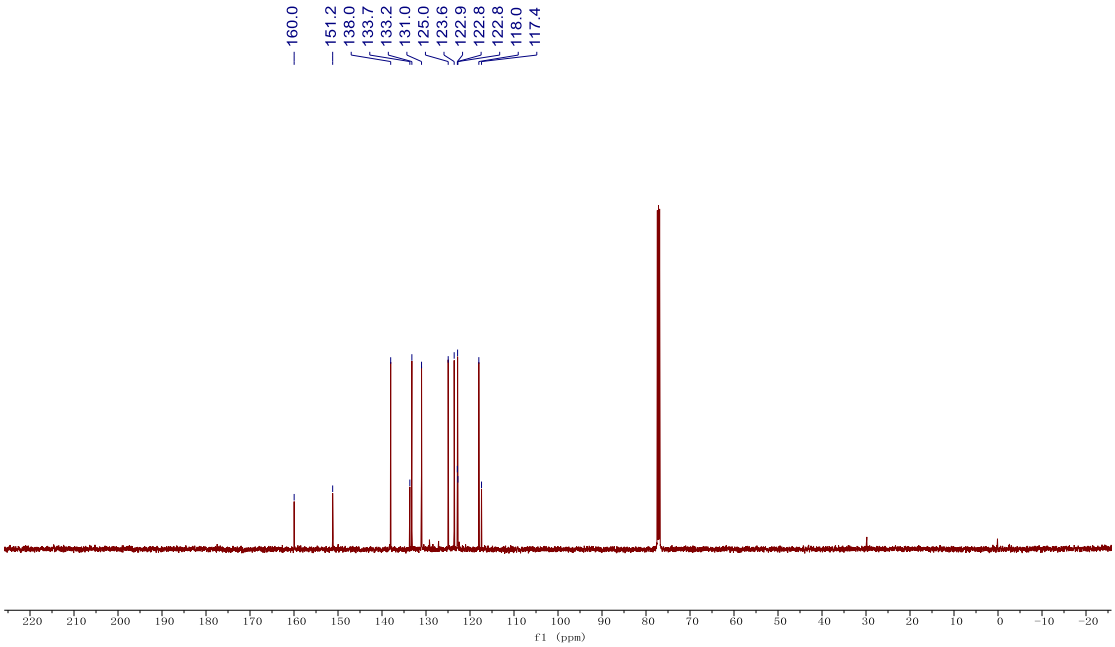
^{13}C NMR of compound **6k** (126 MHz in $CDCl_3$)



^{1}H NMR of compound **6l** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **6l** (126 MHz in $CDCl_3$)



5. Computational Details

The geometries were optimized in MeCN solvent with the implicit solvent model SMD[13] at B3LYP-D3[14]/TZVP[15] level. Harmonic vibrational frequency analyses were performed at the same level to verify the nature of stationary points (no imaginary frequency for minima and only one imaginary frequency for transition states). The energies were further improved by B3LYP-D3/def2-TZVP single-point calculations with solvent effects of MeCN accounted by the SMD solvent model. Harmonic vibration frequencies at B3LYP-D3/TZVP level were used to correct the singlet-point energies to free energies at 298.15 K, which are used in the main text. The vertical excitation energy of the photocatalyst **PC6** was calculated at TD[16]-B3LYP-D3/def2-TZVP level with solvent effects of MeCN accounted by the SMD solvent model. All DFT and TD-DFT calculations were carried out by using Gaussian 09 program.[17] The SET barriers were calculated on the basis of Marcus electron transfer theory.[18]

6. Plausible Rationalizations of no Reaction for NO_2- and MeO-substituted 1a.

Figure S7 (A) compares the experimental results for the reactions of **1a**, **1a-NO_2**, and **1a-OMe**. In the case of **1a-NO_2**, the reaction did not occur with 100% substrate recovery. In the case of **1a-OMe**, the reaction took place poorly with 88% substrate recovery. The mixture contained minor Z-**2-OMe** and benzaldehyde side-product. According to the experimental results, we reason that the EnT step for the two substrates could not go smoothly.

Using DFT calculations, we attempted to understand why the reactions of **1a-NO_2** and **1a-OMe** could not take place effectively. We calculated the energetics for SET and EnT processes of the three reactions (see Figure S7). For **1a**, because the SET process is endergonic by 11.4 kcal/mol, the substrate would disfavor SET and favor EnT to give the cyclization product. For **1a-NO_2**, the electron withdrawing effect of NO_2 group makes both EnT and SET processes endergonic, which could be the reason for no reaction of the substrate. Compared to **1a,** the electron-donating effect of OMe group in **1a-OMe** benefits both EnT and SET processes thermodynamically. Because there is no method to estimate the EnT barrier, we were not able to compare the kinetic favorability of the two processes. Nevertheless, the thermodynamics of SET indicates that **1a-OMe** could undergo

reversible SET. Thus, we reason that the reversible SET could suppress the EnT process to give the cyclization product.

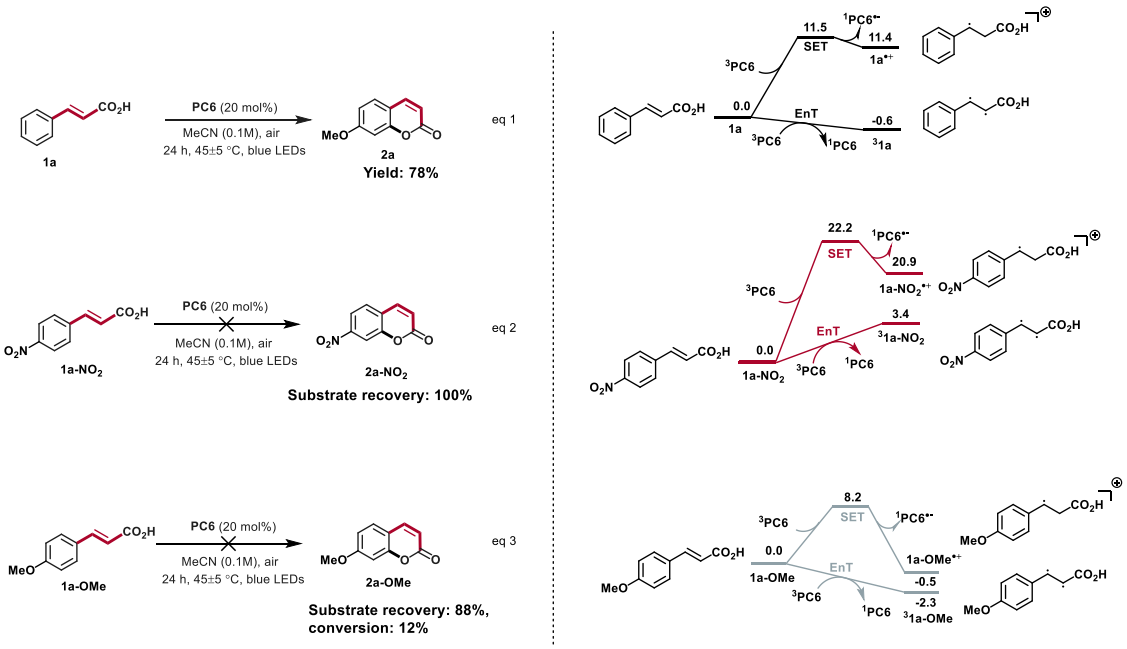


Figure S7 (**A**) Comparing the experimental results of **1a**, **1a-NO$_2$** and **1a-OMe.** (**B**) The energetics for the three substrates to undergo SET and EnT processes.

Energies and Cartesian coordinates for all structures (Energies are given in Hartree and coordinates in angstroms)

^{1}PC6

B3LYP-D3/TZVP SCF energy in MeCN solvent: -1505.008532

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -1505.066551

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -1504.705572

C	-0.735481	-0.891775	-0.929682
C	0.619000	-1.020095	-0.741228
C	1.393795	0.103631	-0.436392
C	0.752046	1.340865	-0.321282
C	-0.605857	1.427974	-0.504401
H	1.082446	-1.985174	-0.863869
H	1.307144	2.222350	-0.044539
C	-1.430563	2.619292	-0.372367
C	-2.810570	2.498784	-0.152874
C	-0.850242	3.893542	-0.447550
C	-3.591427	3.635658	-0.012116
H	-3.260360	1.519672	-0.070915
C	-1.640434	5.024247	-0.309312
H	0.209810	4.002245	-0.632460
C	-3.010449	4.899185	-0.090545
H	-4.654354	3.536518	0.167015
H	-1.187842	6.005166	-0.376306
H	-3.623390	5.784810	0.020428
C	-1.671844	-1.947627	-1.284368
C	-2.948353	-1.630491	-1.771309
C	-1.306925	-3.292581	-1.129407
C	-3.836371	-2.642323	-2.101612
H	-3.238944	-0.597119	-1.897127
C	-2.202711	-4.297434	-1.459768
H	-0.334917	-3.554847	-0.735351
C	-3.467643	-3.976513	-1.946583
H	-4.818421	-2.390226	-2.480700
H	-1.916548	-5.333246	-1.330410

H	-4.164542	-4.764533	-2.202948
C	2.851625	-0.016979	-0.235009
C	3.348418	-0.858600	0.778548
C	3.734691	0.708843	-1.061005
C	4.728162	-0.947205	0.955112
C	5.103950	0.563999	-0.861801
C	5.621627	-0.250916	0.145218
H	5.111100	-1.577716	1.749492
H	5.785024	1.101419	-1.512230
O	-1.299885	0.321772	-0.816987
B	-1.936716	-0.800015	2.522481
F	-3.065904	-0.740019	1.682381
F	-1.240858	-2.005134	2.294258
F	-2.350225	-0.745038	3.869816
F	-1.086655	0.291848	2.249290
C	7.106179	-0.352568	0.359248
H	7.634624	-0.470863	-0.589093
H	7.491958	0.555504	0.832348
H	7.357394	-1.195765	1.003487
C	3.243825	1.602559	-2.171087
H	2.421864	1.149840	-2.727595
H	2.886952	2.560720	-1.785735
H	4.053359	1.812911	-2.870065
C	2.440445	-1.633950	1.698998
H	1.581862	-1.044007	2.020243
H	2.052964	-2.534859	1.216844
H	2.988899	-1.948935	2.586700

^{3}PC6

B3LYP-D3/TZVP SCF energy in MeCN solvent: -1504.923120

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -1504.981260

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -1504.627941

C	-0.829624	-0.814262	-1.001280
C	0.540955	-0.954241	-0.798315
C	1.364011	0.131171	-0.478986
C	0.715580	1.365742	-0.331704
C	-0.653180	1.512752	-0.528709
H	0.971365	-1.938066	-0.900072
H	1.282051	2.230124	-0.021177
C	-1.402721	2.708079	-0.334452
C	-2.818797	2.685882	-0.438091
C	-0.763139	3.941721	-0.034174
C	-3.549224	3.839525	-0.244697
H	-3.323314	1.756691	-0.655829
C	-1.508012	5.084642	0.150847
H	0.313143	3.993700	0.042408
C	-2.903984	5.044943	0.049262
H	-4.628642	3.809807	-0.318666
H	-1.009303	6.018533	0.375273
H	-3.482948	5.947056	0.199350
C	-1.740276	-1.856827	-1.319818
C	-3.114946	-1.561537	-1.531675
C	-1.314465	-3.211591	-1.418890
C	-4.005941	-2.568878	-1.831135
H	-3.456506	-0.540604	-1.457395
C	-2.218792	-4.204017	-1.718259
H	-0.278841	-3.471734	-1.256511
C	-3.569675	-3.894905	-1.926229
H	-5.049969	-2.332108	-1.990530
H	-1.883912	-5.230665	-1.788801
H	-4.274780	-4.682266	-2.159016
C	2.822108	-0.018171	-0.279663
C	3.314998	-0.879391	0.719576
C	3.718919	0.700528	-1.095275
C	4.694097	-1.003151	0.884397
C	5.088751	0.539475	-0.899379
C	5.597861	-0.304450	0.087010
H	5.069188	-1.659174	1.662323
H	5.775340	1.081562	-1.540369
O	-1.408809	0.434405	-0.922946
B	-1.803817	-1.022512	2.569103
F	-3.073749	-0.881950	1.973367
F	-1.228135	-2.246883	2.170957
F	-1.941009	-1.006041	3.973622
F	-0.973946	0.043924	2.169557
C	7.081591	-0.433086	0.301865
H	7.628234	-0.329957	-0.637263
H	7.446339	0.346817	0.977795
H	7.336262	-1.396196	0.746979
C	3.231919	1.614644	-2.190224
H	2.442490	1.148228	-2.782870
H	2.825387	2.546996	-1.789669
H	4.051853	1.877003	-2.859291

C	2.392801	-1.653578	1.626485
H	1.541988	-1.052634	1.948840
H	1.990265	-2.541601	1.131415
H	2.930529	-1.991765	2.512675

^{1}1a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.456313

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.478237

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.366226

C	2.746779	1.336608	0.000093
C	1.378369	1.117014	0.000099
C	0.866234	-0.190743	0.000000
C	1.768932	-1.264377	-0.000083
C	3.140522	-1.042092	-0.000090
C	3.633271	0.258898	-0.000002
H	3.128050	2.350211	0.000169
H	0.703752	1.963187	0.000185
H	1.384006	-2.277227	-0.000146
H	3.823405	-1.882552	-0.000159
H	4.701638	0.436123	-0.000004
C	-1.569322	0.400686	-0.000065
H	-1.405649	1.469862	-0.000163
C	-0.561468	-0.484491	-0.000001
H	-0.819604	-1.539293	0.000077
C	-2.963953	-0.051350	0.000011
O	-3.354458	-1.202582	0.000214
O	-3.823238	0.997078	-0.000172
H	-4.730211	0.642804	-0.000065

^{3}*E*-1a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.372779

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.394645

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.287577

C	2.107675	0.522198	0.129432
C	0.887828	0.904411	0.331628
C	0.762511	-0.508049	0.231057
C	1.930197	-1.253946	-0.087748
C	3.142240	-0.622232	-0.288267
C	3.243566	0.768739	-0.180707
H	2.182399	2.599966	0.210970
H	0.012402	1.497538	0.567139
H	1.854762	-2.331730	-0.170721
H	4.020187	-1.209214	-0.529864
H	4.195769	1.259482	-0.337752
C	-1.706120	-0.493758	0.794713
H	-1.988298	-0.381153	1.837535
C	-0.468990	-1.164679	0.433915
H	-0.498457	-2.247458	0.333922
C	-2.613852	0.031691	-0.203160
O	-2.447097	-0.027314	-1.411241
O	-3.705805	0.621625	0.348660
H	-4.265874	0.951825	-0.375763

^{3}*Z*-1a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.372781

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.394645

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.287567

C	-2.109778	-1.522197	-0.126790
C	-0.889343	-0.905647	-0.329356
C	-0.763041	0.506879	-0.231064
C	-1.930424	1.254103	0.085994
C	-3.143037	0.623619	0.286817
C	-3.245313	-0.767457	0.181458
H	-2.185186	-2.600056	-0.206499
H	-0.014265	-1.499876	-0.563240
H	-1.854254	2.331970	0.167209
H	-4.020697	1.211626	0.526962
H	-4.197961	-1.257270	0.338714
C	0.468820	1.162603	-0.434172
H	0.498526	2.245489	-0.335367
C	1.705746	0.491124	-0.794803
H	1.986506	0.376104	-1.837738
C	2.615514	-0.031202	0.202780

O	2.451485	0.031332	1.411018
O	3.706568	-0.622375	-0.349733
H	4.268041	-0.950591	0.374499

***Z*-1a**

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.447301

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.468961

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.356990

C	-2.072936	-1.491708	0.026334
C	-0.832417	-0.869059	0.054408
C	-0.738487	0.532984	0.027265
C	-1.934395	1.275480	-0.024386
C	-3.171296	0.649083	-0.055436
C	-3.244937	-0.740970	-0.029635
H	-2.125668	-2.573465	0.048845
H	0.068917	-1.458486	0.096133
H	-1.880834	2.357485	-0.043085
H	-4.076018	1.242696	-0.097997
H	-4.208089	-1.235886	-0.052183
C	0.494053	1.315163	0.054665
H	0.284538	2.380858	0.081946
C	1.817787	1.048232	0.044599
H	2.473084	1.909889	0.064203
C	2.546384	-0.221398	-0.007100
O	2.110594	-1.356850	-0.001207
O	3.882977	0.011960	-0.067008
H	4.332980	-0.850805	-0.096425

***Z*-1a$^{\bullet+}$**

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.213626

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.236980

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.126900

C	-1.718328	-1.544225	0.214456
C	-0.579805	-0.791071	0.310896
C	-0.644178	0.626303	0.137366
C	-1.918209	1.238106	-0.089052
C	-3.048210	0.471131	-0.197375
C	-2.954680	-0.922099	-0.046261
H	-1.677071	-2.615869	0.352137
H	0.353549	-1.276793	0.551173
H	-1.961675	2.313730	-0.197855
H	-4.008220	0.929774	-0.390467
H	-3.848020	-1.528547	-0.123350
C	0.479985	1.486500	0.186208
H	0.258102	2.547202	0.233746
C	1.815311	1.168859	0.146784
H	2.538105	1.967714	0.276796
C	2.435930	-0.172697	-0.025661
O	2.968627	-0.715116	0.909932
O	2.426512	-0.727605	-1.239083
H	1.977228	-0.160286	-1.893128

PC6$^{\bullet-}$

B3LYP-D3/TZVP SCF energy in MeCN solvent: -1505.136774

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -1505.193711

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -1504.839965

C	-0.773217	-0.772150	-1.055929
C	0.569521	-0.932107	-0.862289
C	1.393436	0.144613	-0.479589
C	0.762157	1.390546	-0.290799
C	-0.579659	1.548672	-0.489161
H	1.002739	-1.908371	-1.017546
H	1.340471	2.238103	0.044812
C	-1.357143	2.761034	-0.295996
C	-2.761720	2.728538	-0.364396
C	-0.733089	3.995832	-0.034577
C	-3.507984	3.884567	-0.171006
H	-3.264854	1.792321	-0.558062
C	-1.485274	5.142687	0.158435
H	0.345663	4.060283	0.011198
C	-2.879021	5.097570	0.091674
H	-4.588978	3.834428	-0.223362
H	-0.982280	6.081302	0.357350
H	-3.462620	5.997195	0.242191

C	-1.731835	-1.791190	-1.447416
C	-3.064670	-1.445547	-1.734403
C	-1.363787	-3.147287	-1.535850
C	-3.985470	-2.417069	-2.106409
H	-3.373734	-0.412718	-1.667275
C	-2.288000	-4.108781	-1.909689
H	-0.353402	-3.453503	-1.301179
C	-3.606638	-3.752659	-2.198539
H	-5.006272	-2.126634	-2.324172
H	-1.981986	-5.146293	-1.968374
H	-4.326282	-4.508592	-2.487013
C	2.848874	-0.025895	-0.273025
C	3.329703	-0.919036	0.704279
C	3.767502	0.706222	-1.056239
C	4.707429	-1.060648	0.881023
C	5.133503	0.529697	-0.849766
C	5.626552	-0.347784	0.116548
H	5.068108	-1.740709	1.645309
H	5.831380	1.086365	-1.466582
O	-1.347729	0.474669	-0.895274
B	-1.924043	-1.165978	2.705531
F	-3.170546	-1.061676	2.053898
F	-1.188804	-2.233336	2.151924
F	-2.135722	-1.409216	4.080673
F	-1.207198	0.036512	2.549217
C	7.108368	-0.502043	0.331273
H	7.629306	-0.683940	-0.612025
H	7.539616	0.404708	0.765914
H	7.325861	-1.330924	1.006161
C	3.304378	1.651782	-2.135306
H	2.518590	1.205696	-2.748088
H	2.896939	2.576186	-1.718861
H	4.136141	1.922181	-2.786888
C	2.394980	-1.707828	1.585691
H	1.554912	-1.101890	1.926705
H	1.973030	-2.569087	1.061477
H	2.926737	-2.084541	2.460223

O_2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -150.386380

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -150.394051

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -150.410325

O	0.000000	0.000000	0.603839
O	0.000000	0.000000	-0.603839

$O_2^{\bullet-}$

B3LYP-D3/TZVP SCF energy in MeCN solvent: -150.501262

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -150.505831

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -150.522951

O	0.000000	0.000000	0.675344
O	0.000000	0.000000	-0.675344

$HO_2^{\bullet}$

B3LYP-D3/TZVP SCF energy in MeCN solvent: -150.980104

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -150.986798

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -150.995048

O	0.055639	-0.609904	0.000000
H	-0.890231	-0.880162	0.000000
O	0.055639	0.719924	0.000000

^{2}IM1

B3LYP-D3/TZVP SCF energy in MeCN solvent: -497.777471

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -497.799668

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -497.701772

C	1.736182	-1.536099	-0.087398
C	0.566987	-0.804151	-0.106342
C	0.607453	0.608385	-0.021878
C	1.871205	1.241973	0.062361

C	3.036737	0.501300	0.082156
C	2.973335	-0.890573	0.007875
H	1.695355	-2.615830	-0.149352
H	-0.373762	-1.325512	-0.191581
H	1.910080	2.322622	0.117907
H	3.995210	0.998677	0.153299
H	3.884928	-1.474553	0.022732
C	-0.546576	1.454941	-0.022600
H	-0.328848	2.518491	-0.016717
C	-1.879846	1.129736	0.009086
H	-2.599787	1.936392	-0.079072
C	-2.484161	-0.227007	0.092261
O	-2.694455	-0.564840	-1.115960
O	-2.739429	-0.839075	1.122167

^{2}TS1

B3LYP-D3/TZVP SCF energy in MeCN solvent: -497.770339

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -497.791986

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -497.690999

C	1.543958	-1.375450	0.510709
C	0.442145	-0.510405	0.774477
C	0.488256	0.843609	0.291669
C	1.626399	1.305656	-0.356994
C	2.687521	0.439292	-0.602054
C	2.631850	-0.906296	-0.180199
H	1.517696	-2.388394	0.889941
H	-0.140692	-0.700300	1.666321
H	1.662989	2.328315	-0.711076
H	3.559286	0.795518	-1.135565
H	3.474878	-1.557575	-0.373117
C	-0.729156	1.620727	0.399251
H	-0.653063	2.696092	0.521805
C	-1.932160	1.035235	0.275295
H	-2.845338	1.609337	0.362778
C	-2.115321	-0.364109	-0.193113
O	-3.214156	-0.733365	-0.607289
O	-1.090432	-1.180703	-0.234627

^{2}TS1a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.202441

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -648.790337

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -648.681274

C	1.508568	-1.439458	0.385787
C	0.437407	-0.531400	0.702693
C	0.547007	0.852949	0.266486
C	1.737357	1.309414	-0.271451
C	2.780863	0.414631	-0.511849
C	2.645807	-0.959685	-0.197687
H	1.418040	-2.474602	0.685393
H	-0.037452	-0.681484	1.669041
H	1.831225	2.350054	-0.554224
H	3.694774	0.769026	-0.969188
H	3.472859	-1.628840	-0.396019
C	-0.641331	1.652564	0.317019
H	-0.544844	2.731704	0.345169
C	-1.871943	1.094600	0.227972
H	-2.767848	1.700622	0.250065
C	-2.012338	-0.301557	-0.120108
O	-1.074550	-1.141993	-0.136213
O	-3.175846	-0.765164	-0.524204
H	-3.851973	-0.061572	-0.540075

^{2}IM1a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -498.212018

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -498.236372

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -498.120886

C	-1.358129	-1.504117	0.124357
C	-0.520508	0.874820	0.127282
C	-1.825629	1.295586	-0.111031
C	-2.851023	0.370973	-0.227584
C	-2.594246	-1.031444	-0.153242
H	-1.139877	-2.562436	0.179003
H	-2.019064	2.350477	-0.261143
H	-3.855225	0.710793	-0.442707

H	-3.405677	-1.721352	-0.344720
C	0.603400	1.707392	0.087019
H	0.474783	2.778033	-0.012590
C	1.873064	1.165144	0.104714
H	2.761939	1.779578	0.084123
C	2.006903	-0.222515	-0.048691
C	-0.276587	-0.557982	0.491110
H	-0.143488	-0.602833	1.586040
O	1.003256	-1.055210	-0.046332
O	3.135883	-0.834982	-0.299195
H	3.870033	-0.197871	-0.387389

^{2}IM2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -497.787392

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -497.810108

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -497.707488

C	-1.338523	-1.490421	0.146942
C	-0.468437	0.867732	0.112461
C	-1.765039	1.303355	-0.125012
C	-2.814279	0.398416	-0.218949
C	-2.571945	-1.006434	-0.125797
H	-1.139832	-2.552730	0.209799
H	-1.942271	2.360036	-0.289169
H	-3.815471	0.751626	-0.427349
H	-3.394187	-1.690281	-0.297122
C	0.678722	1.695816	0.096358
H	0.555996	2.772081	0.047447
C	1.921962	1.142997	0.109128
H	2.818673	1.746072	0.116782
C	2.119343	-0.290849	-0.080684
O	3.200296	-0.801923	-0.306391
C	-0.219740	-0.566419	0.476988
H	-0.060361	-0.600275	1.569497
O	1.015338	-1.087038	-0.103421

^{2}TS2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -648.742459

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -648.771441

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -648.664042

C	1.509249	0.523457	-1.398991
C	0.674241	-0.763291	0.611813
C	2.026260	-0.898455	1.022713
C	3.036373	-0.356514	0.287440
C	2.771065	0.333403	-0.961695
H	1.292372	1.015220	-2.338620
H	2.236440	-1.469561	1.919044
H	4.063916	-0.474630	0.605453
H	3.610197	0.672771	-1.555269
C	-0.413235	-1.330379	1.244787
H	-0.274319	-1.893574	2.159605
C	-1.687550	-1.188119	0.697882
H	-2.566831	-1.576905	1.190043
C	-1.883213	-0.658032	-0.629519
O	-2.927418	-0.681215	-1.247712
C	0.387984	0.134610	-0.556621
H	0.084089	1.284121	0.081447
O	-0.776570	-0.152815	-1.294992
O	-1.649246	1.888267	1.051681
H	-1.593001	1.496214	1.943753
O	-0.319253	2.216547	0.751984

2a

B3LYP-D3/TZVP SCF energy in MeCN solvent: -497.243004

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -497.267593

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -497.173962

C	-1.293203	-1.484538	-0.000111
C	-0.473198	0.809705	-0.000626
C	-1.799522	1.269486	-0.000237
C	-2.850994	0.371390	-0.000332
C	-2.594319	-1.004449	0.000329
H	-1.081142	-2.545584	0.000763
H	-1.980744	2.337349	-0.000532
H	-3.872028	0.729977	-0.000022
H	-3.418434	-1.706553	0.000311
C	0.672039	1.674288	0.000334

H	0.513440	2.746113	0.000503
C	1.920716	1.164931	0.000392
H	2.800772	1.792083	0.001023
C	2.152951	-0.264848	0.000006
O	3.232161	-0.815546	-0.000545
C	-0.244201	-0.573439	0.000507
O	1.029905	-1.075521	0.000093

H_2O_2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -151.624639

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -151.630402

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -151.626022

O	0.000000	-0.727517	-0.062798
H	-0.768637	-0.914998	0.502385
O	0.000000	0.727517	-0.062798
H	0.768637	0.914998	0.502385

1a-NO_2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -703.034177

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -703.070807

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -702.961426

C	-1.595344	-1.146318	-0.048793
C	-0.220960	-1.006514	-0.034945
C	0.369580	0.265897	0.029175
C	-0.460409	1.395384	0.082978
C	-1.839269	1.270700	0.068906
C	-2.387864	-0.002990	0.002166
H	-2.051050	-2.123934	-0.097227
H	0.392927	-1.895382	-0.072856
H	-0.014781	2.380447	0.135311
H	-2.476775	2.141159	0.109522
C	1.815770	0.474087	0.037540
H	2.103217	1.517390	0.131509
C	4.210595	-0.239565	0.000531
O	5.001283	-1.132362	0.215496
O	4.680953	1.014092	-0.194543
H	3.973520	1.629689	-0.446822
N	-3.848755	-0.149899	-0.011312
O	-4.535638	0.867232	0.033750
O	-4.317537	-1.283671	-0.066732
C	2.755158	-0.476702	-0.050414
H	2.498185	-1.526276	-0.106885

1a-$NO_2^{\bullet+}$

B3LYP-D3/TZVP SCF energy in MeCN solvent: -702.787198

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -702.824929

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -702.716097

C	1.578995	-1.156871	0.010789
C	0.214599	-1.025703	-0.013224
C	-0.379073	0.273518	-0.049356
C	0.460048	1.427313	-0.070624
C	1.825365	1.295515	-0.060345
C	2.355053	0.004188	-0.010779
H	2.049063	-2.128651	0.041517
H	-0.40183	-1.912237	-0.006294
H	0.003207	2.407358	-0.094058
H	2.476798	2.156852	-0.078212
C	-1.778441	0.486419	-0.043094
H	-2.107098	1.519507	-0.081308
C	-4.184009	-0.204351	-0.042170
O	-4.827586	-0.659950	-0.956836
O	-4.739259	0.573346	0.882379
H	-4.099376	0.837797	1.570133
N	3.826239	-0.143675	0.024596
O	4.490687	0.717372	-0.532135
O	4.277371	-1.115785	0.611439
C	-2.730951	-0.505813	0.017639
H	-2.483649	-1.560053	0.004256

^{3}1a-NO_2

B3LYP-D3/TZVP SCF energy in MeCN solvent: -702.957786

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -702.994140
B3LYP-D3/def2-TZVP free energy in MeCN solvent: -702.889283

C	1.210984	-1.011901	-0.299107
C	-0.10134	-0.633923	-0.448252
C	-0.486081	0.732735	-0.329745
C	0.526849	1.694293	-0.048778
C	1.838903	1.317369	0.099765
C	2.175204	-0.035234	-0.026850
H	1.503314	-2.047444	-0.389560
H	-0.854379	-1.382236	-0.658816
H	0.249382	2.736398	0.043383
H	2.606341	2.047186	0.309776
C	-1.818642	1.143175	-0.481063
H	-2.040024	2.205431	-0.392876
C	-3.795472	-0.375293	0.156453
O	-4.738034	-1.080844	-0.156319
O	-3.535646	-0.166459	1.471313
H	-2.755113	0.403525	1.585606
N	3.562297	-0.435930	0.129961
O	4.397004	0.432424	0.395045
O	3.848383	-1.627597	-0.007996
C	-2.924491	0.261020	-0.816947
H	-3.174733	0.075009	-1.856430

1a-OMe

B3LYP-D3/TZVP SCF energy in MeCN solvent: -613.029984
B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -613.058258
B3LYP-D3/def2-TZVP free energy in MeCN solvent: -612.919354

C	1.799664	-1.370487	-0.026240
C	0.437860	-1.162675	-0.029474
C	-0.097584	0.140199	-0.013623
C	0.801063	1.214342	0.004376
C	2.176136	1.020952	0.009736
C	2.684306	-0.279990	-0.005433
H	2.208537	-2.372795	-0.039564
H	-0.221897	-2.020355	-0.046051
H	0.412880	2.225973	0.015895
H	2.834166	1.877157	0.025030
C	-1.521852	0.419235	-0.012511
H	-1.781455	1.472700	-0.021117
C	-3.937757	-0.117872	0.010669
O	-4.847368	-0.927501	0.057587
O	-4.180685	1.216293	-0.038145
H	-5.145197	1.339950	-0.018771
C	-2.524418	-0.478543	0.002916
H	-2.342639	-1.545096	0.019689
O	4.001648	-0.587970	-0.002378
C	4.952984	0.482571	0.029160
H	5.930832	0.007428	0.030025
H	4.856558	1.119069	-0.853321
H	4.837042	1.083002	0.934205

1a-OMe$^{\bullet+}$

B3LYP-D3/TZVP SCF energy in MeCN solvent: -612.819438
B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -612.848718
B3LYP-D3/def2-TZVP free energy in MeCN solvent: -612.708119

C	-1.763799	1.388729	-0.028719
C	-0.422640	1.175527	-0.022755
C	0.099681	-0.154075	0.009906
C	-0.815605	-1.249530	0.041988
C	-2.164325	-1.052736	0.038869
C	-2.661132	0.278624	-0.002580
H	-2.181899	2.385719	-0.055699
H	0.249337	2.021277	-0.043860
H	-0.41774	-2.255417	0.070078
H	-2.842625	-1.891923	0.063255
C	1.493433	-0.450302	0.006715
H	1.757164	-1.500838	0.023379
C	3.924670	0.116741	-0.000312
O	4.803158	0.947692	0.091419
O	4.161218	-1.203379	-0.094472
H	5.124209	-1.349977	-0.062560
C	2.493356	0.471084	-0.013066
H	2.303253	1.535251	-0.019285
O	-3.932363	0.585086	-0.019753
C	-4.955350	-0.449727	0.001561

H	-5.895980	0.089247	-0.036034
H	-4.844845	-1.091963	-0.870698
H	-4.876718	-1.022582	0.924230

^{3}1a-OMe

B3LYP-D3/TZVP SCF energy in MeCN solvent: -612.943402

B3LYP-D3/def2-TZVP SCF energy in MeCN solvent: -612.971633

B3LYP-D3/def2-TZVP free energy in MeCN solvent: -612.838011

C	-1.745891	1.360760	-0.000091
C	-0.402133	1.126462	0.000048
C	0.124516	-0.224030	0.000151
C	-0.855933	-1.290018	0.000237
C	-2.198772	-1.044225	0.000131
C	-2.672942	0.291422	-0.000077
H	-2.131354	2.372797	-0.000204
H	0.276903	1.966757	0.000037
H	-0.497557	-2.311916	0.000366
H	-2.893952	-1.871501	0.000183
C	1.474737	-0.527400	0.000128
H	1.761315	-1.570769	0.000149
C	3.923505	0.154623	-0.000034
O	4.823307	0.997140	0.000190
O	4.212415	-1.182390	-0.000444
H	5.180270	-1.267705	-0.000460
C	2.526810	0.456460	0.000114
H	2.297754	1.512122	0.000338
O	-3.973016	0.637666	-0.000291
C	-4.972206	-0.394928	0.000011
H	-5.926972	0.124020	-0.000354
H	-4.888985	-1.014349	-0.894770
H	-4.889214	-1.013545	0.895367

7. References

1. Metternich, J. B.; Artiukhin, D. G.; Holland, M. C.; von Bremen-Kühne, M.; Neugebauer, J.; Gilmour, R., Photocatalytic *E* → *Z* Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity. *J. Org. Chem.* **2017,** *82*, 9955-9977.

2. Metternich, J. B.; Gilmour, R., A Bio-Inspired, Catalytic *E*→*Z* Isomerization of Activated Olefins. *J. Am. Chem. Soc.* **2015,** *137*, 11254-11257.

3. Metternich, J. B.; Gilmour, R., One Photocatalyst, n Activation Modes Strategy for Cascade Catalysis: Emulating Coumarin Biosynthesis with (−)-Riboflavin. *J. Am. Chem. Soc.* **2016,** *138*, 1040-1045.

4. Li, Y.; Ding, Y.-J.; Wang, J.-Y.; Su, Y.-M.; Wang, X.-S., Pd-Catalyzed C–H Lactonization for Expedient Synthesis of Biaryl Lactones and Total Synthesis of Cannabinol. *Org. Lett.* **2013,** *15*, 2574-2577.

5. Morack, T.; Metternich, J. B.; Gilmour, R., Vitamin Catalysis: Direct, Photocatalytic Synthesis of Benzocoumarins via (−)-Riboflavin-Mediated Electron Transfer. *Org. Lett.* **2018,** *20*, 1316-1319.

6. Xia, S.; Hu, K.; Lei, C.; Jin, J., Intramolecular Aromatic C–H Acyloxylation Enabled by Iron Photocatalysis. *Org. Lett.* **2020,** *22*, 1385-1389.

7. Zhao, Y.; Huang, B.; Yang, C.; Li, B.; Gou, B.; Xia, W., Photocatalytic Cross-Dehydrogenative Amination Reactions between Phenols and Diarylamines. *ACS Catal.* **2017,** *7*, 2446-2451.

8.Michaudel, Q.; Chauviré, T.; Kottisch, V.; Supej, M. J.; Stawiasz, K. J.; Shen, L.; Zipfel, W. R.; Abruña, H. D.; Freed, J. H.; Fors, B. P., Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.* **2017,** *139*, 15530-15538.

9. Alfonzo, E.; Alfonso, F. S.; Beeler, A. B., Redesign of a Pyrylium Photoredox Catalyst and Its Application to the Generation of Carbonyl Ylides. *Org. Lett.* **2017,** *19*, 2989-2992.

10. Zhao, B.; Xu, B., Visible-light promoted oxidative cyclization of cinnamic acid derivatives using xanthone as the photocatalyst. *Org. Bio. Chem.* **2021,** *19*, 568-573.

11. Wang, Z.; Li, X.; Wang, L.; Li, P., Photoinduced cyclization of alkynoates to coumarins with N-Iodosuccinimide as a free-radical initiator under ambient and metal-free conditions. *Tetrahedron* **2019,** *75*, 1044-1051.

12. Cruché, C.; Neiderer, W.; Collins, S. K., Heteroleptic Copper-Based Complexes for Energy-Transfer Processes: *E*→*Z* Isomerization and Tandem Photocatalytic Sequences. *ACS Catal.* **2021,** *11*, 8829-8836.

13. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Chem. Phys.* **1994,** *98*, 11623-11627.

14. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010,** *132*, 154104.

15. Davidson, E. R.; Feller, D., Basis set selection for molecular calculations. *Chem. Rev.* **1986,** *86*, 681-696.

16. Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J., An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules. *J. Chem. Phys.* **1998,** *109*, 8218-8224.

17. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;

Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov , V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*: Wallingford, CT, 2016.

18. Marcus, R. A., Electron transfer reactions in chemistry: theory and experiment (Nobel lecture). *Angew. Chem. Int. Ed.,* **1993**, *32*, 1111-1222.