Table of Contents

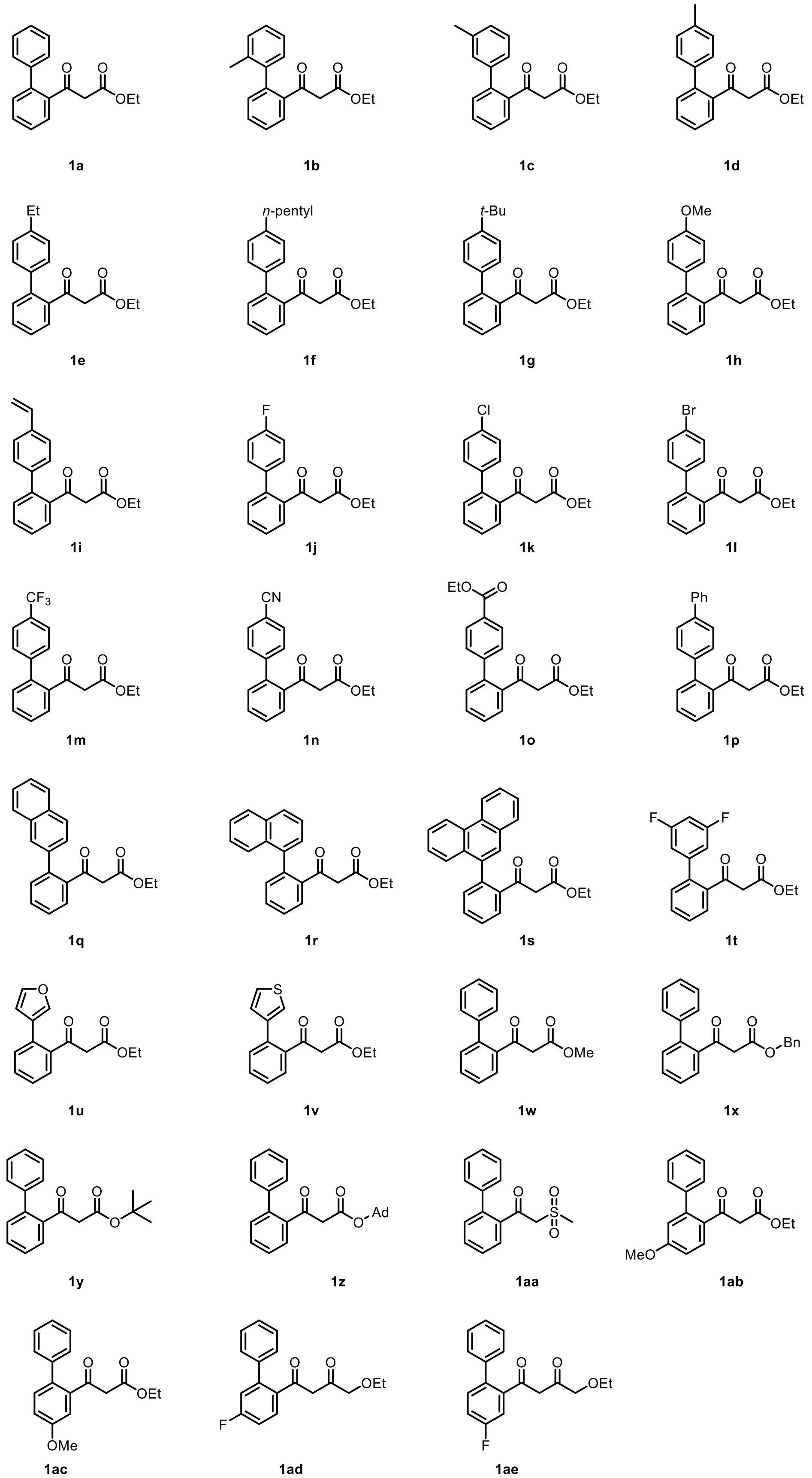
1. General information

All reactions were set up using standard Schlenk techniques and carried out under nitrogen atmosphere with anhydrous solvents, unless otherwise noted. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone. All reagents were purchased from commercial suppliers and used without further purification otherwise noted. Flash chromatography was carried out with silica gel (200 to 300 mesh). Reactions were monitored by thin-layer chromatography (TLC) and carried out on silica gel GF254 plates (0.2± 0.03 mm) using UV light (254 nm) as a visualizing agent and phosphomolybdic acid in ethanol or potassium permanganate ($KMnO_4$) as developing agents. Visible light irradiation was performed with a 30 W LED Light at λ_{ir} = 450 ± 10 nm) for photocatalytic reactions. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR (400 MHz,101 MHz and 376 MHz, respectively) spectra were measured in $CDCl_3$ recorded on Quantum-I 400M Hz spectrometer. Chemical shifts (δ) for^{1}H, ^{13}C, and ^{19}F NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$): δ H = 7.26 ppm, δ C = 77.16 ppm; The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q(quartet), dd (doublet of doublets), etc. The high-resolution mass spectra were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI.

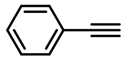
2. Substrates preparation

2.1 Involved substrates

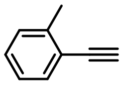
scheme S1



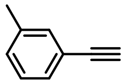
scheme S2



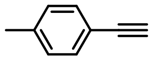
3a



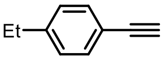
3b



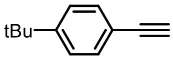
3c



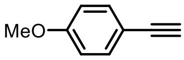
3d



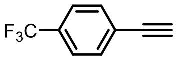
3e



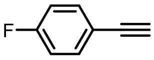
3f



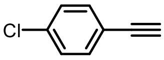
3g



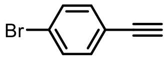
3h



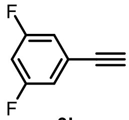
3i



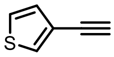
3j



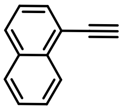
3k



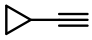
3l



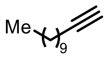
3m



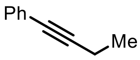
3n



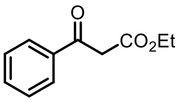
3o



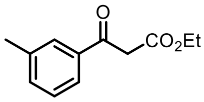
3p



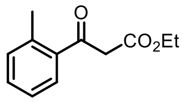
3q



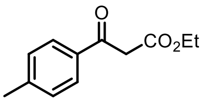
4a



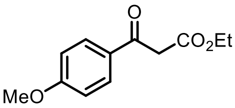
4b



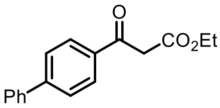
4c



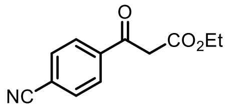
4d



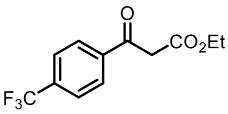
4e



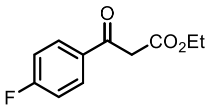
4f



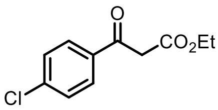
4g



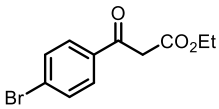
4h



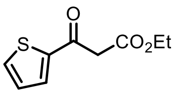
4i



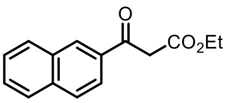
4j



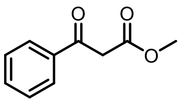
4k



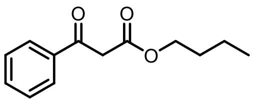
4l



4m

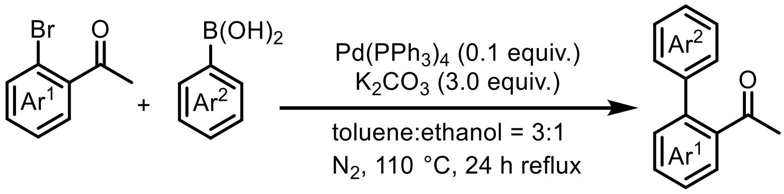


4n

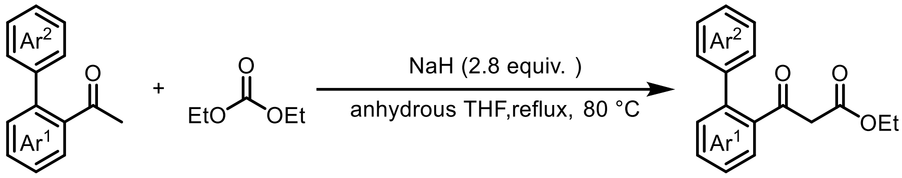


4o

2.2 Synthesis of 1a–1v, 1ab, 1ac, 1ad, 1ae and D_5-1a

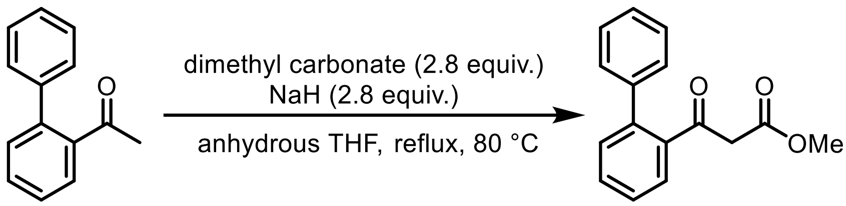


To a stirred solution of aryl bromide (5.0 mmol, 1.0 equiv.) and aryl boronic acid (6 mmol, 1.2 equiv.) in a toluene: ethanol = 3:1 (40 mL) mixture was added potassium carbonate (15.0mmol, 3.0 equiv.) and tetrakis(triphenylphosphine) palladium (0.5 mmol, 0.1 equiv.). The resulting suspension was heated at 110 °C under an atmosphere of N_2 for 12 h. The solvent was removed under reduced pressure and the crude residue was redissolved in water (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water and brine. The filtration was concentrated under reduced pressure and then purified by column chromatography.



To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (60% in mineral oil, 14 mmol, 2.8 equiv.), diethyl carbonate (14 mmol, 2.8 equiv.), and anhydrous THF (10 mL). The mixture was heated to 80 °C under an atmosphere of Ar. A solution of ketone (5.0 mmol, 1.0 equiv.) in anhydrous THF (30 mL) was added dropwise from the dropping funnel over 60 min. After the addition, the mixture was heated to reflux until the biphenyl ketone is completely consumed (12 h). When the reaction was cooled to room temperature, ice water (50 mL) was added dropwise. The THF layer was separated, and the water layer was extracted with EtOAc (3 × 30 mL). The combined organic solution was washed with water and brine. After evaporation of the solvent, the mixture was distilled under reduced pressure. The crude residue was purified by column chromatography to furnish the desired compound **1a–1v, 1ab, 1ac, 1ad, 1ae and D_5-1a.** Data matched those provided in the previous literature.[1,2]

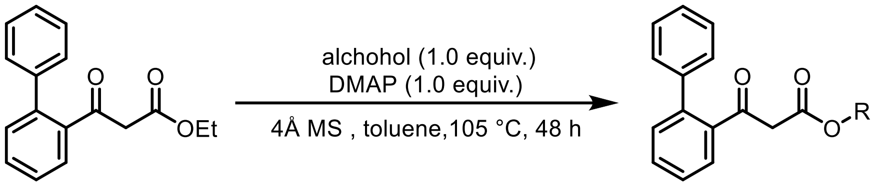
2.3 Synthesis of 1w



1w

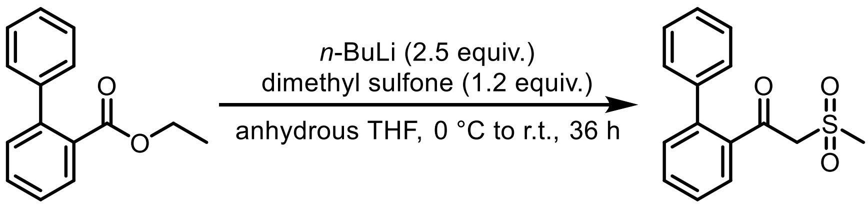
To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (60% in mineral oil, 14 mmol, 2.8 equiv.), dimethyl carbonate (14 mmol, 2.8 equiv.), and anhydrous THF (10 mL). The mixture was heated to 80 °C under N_2 atmosphere. A solution of1-([1,1'-biphenyl]-2-yl)ethan-1-one (5.0 mmol, 1.0 equiv) in anhydrous THF (50 mL) was added dropwise from the dropping funnel over 60 min. After the addition, the mixture was heated to reflux until starting material is completely consumed (about 12 h). After the reaction was cooled to room temperature, ice-water (100 mL) was added. The THF layer was separated, and the water layer was extracted with EtOAc (3 × 30 mL). The combined organic solution was washed with water and brine. After evaporation of the solvent, the mixture was distilled under reduced pressure. The crude residue was purified by column chromatography to furnish the compound **1w** in 72% yield. Data matched those provided in the literature.[1]

2.4 Synthesis of 1x, 1y, 1z



A mixture of corresponding alcohol (5.0 mmol, 1.0 equiv.), **1a** (5.0 mmol,1.0 equiv.), DMAP (5.0 mmol, 1.0 equiv.) was stirred with oven-dried 4Å MS (50 g) in anhydrous toluene (50 mL) at 105 °C for 48 h. The reaction mixture was then cooled to room temperature and filtered to remove the molecular sieves. The solvents were removed under reduced pressure, and EtOAc (3 × 30 mL) and water (90mL) were added to the residue. The layers were separated, filtered, and concentrated. The crude product was purified by column chromatography to furnish the compound **1x** in 60% yield, **1y** in 69% yield, **1z** in 78% yield, respectively. Data matched those provided in the literature.[1]

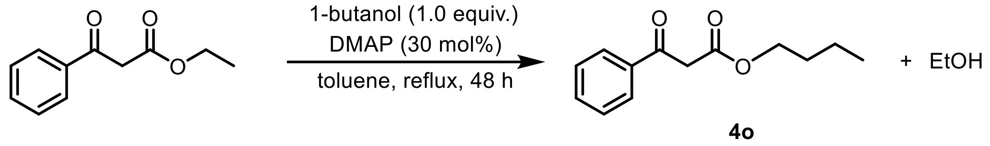
2.5 Synthesis of 1aa



1aa

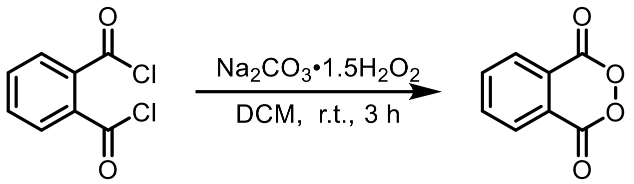
Under N_2 atmosphere, *n*-BuLi (3 mL, 2.5 M in hexane, 7.5 mmol) was dropwise added to a stirred solution of dimethyl sulfone (3.6 mmol) in THF (20 mL) at 0 °C. The resultant white cloudy solution was continued to stir at 0 °C for 40 min, followed by slowly adding with a solution of ethyl biphenyl-2-carboxylate (3 mmol) in THF (11.5 mL) over 5 min. The reaction mixture was then allowed to stir at room temperature for 36 hours, then quenched by H_2O (20 mL), and diluted with EtOAc (3 × 30 mL). The organic layer was separated and washed with saturated aqueous NH_4Cl solution (50 mL x 2), water (50 mL) and brine (50 mL). After concentration, the crude mixture was subjected to chromatography to provide **1aa** in 75% yield. Data matched those provided in the literature.[1]

2.6 Synthesis of 4o



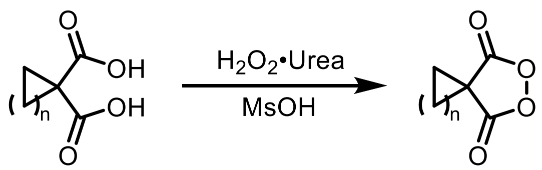
To a flask equipped with a Dean-Stark trap and reflux condenser was added ethyl 3-oxo-3-phenylpropanoate (5 mmol), 1-butanol (10 mmol), DMAP (1.5 mmol) in toluene (40 mL). The mixture was heated to reflux, distilling the ethanol formed during the reaction. After completion, monitored by ^{1}H NMR spectroscopy, the reaction mixture was directly loaded onto silica gel and purified by flash chromatography (eluting in gradient from petroleum ether/ethyl acetate 98:2 to 95:5) to give the **4o** in 66% yield. Data matched those provided in the literature.[3]

2.7 General Procedure for Synthesis of PPO



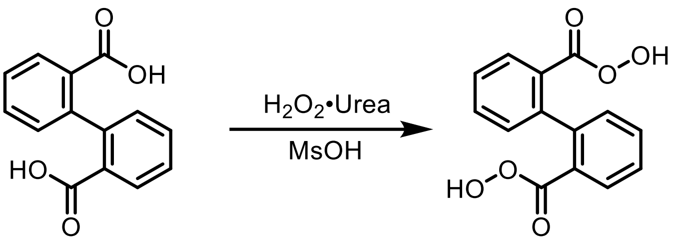
To a solution of phthaloyl chloride (0.40 g, 1.5 mmol, 1.0 equiv.) in CH_2Cl_2 (25 mL), solid sodium percarbonate (H_2O_2: 20-30%) (0.34 g, 2.2 mmol, 1.5 equiv) was added in one portion. The heterogeneous reaction mixture was stirred vigorously for 3 hours (rapid stirring is required). The reaction mixture was filtered through celite and concentrated to provide the phthaloyl peroxide as white solid (0.27 g, 78%). Data matched those provided in the literature [4]

2.8 General Procedure for Synthesis of MPO



Methane sulfonic acid (30 ml) was placed in a round bottomed flask equipped with a large magnetic stirrer bar and immersed in a bath of water at 22 °C. Urea hydrogen peroxide (9.82 g, 104 mmol) was added in a single portion and stirred for 30 seconds. Cycloalkane-1,1-dicarboxylic acid (35 mmol) was added in a single portion and the reaction stirred vigorously for 18 h. The reaction mixture was poured into a mixture of ice (80 g) and ethyl acetate (100 ml) and the layers separated. The aqueous layer was extracted with ethyl acetate (2 × 100 ml) and the combined organics were washed with $NaHCO_3$ (2 × 50 ml), brine (20 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the desired malonoyl peroxide. Data matched those provided in the literature.[5]

2.9 General Procedure for Synthesis of 2,2'-Diperoxyphenic Acid (DPPA)



Methane sulfonic acid (30 mL) was placed in a round bottomed flask equipped with a large magnetic stirrer bar and immersed in a bath of water at 22 °C. Urea hydrogen peroxide (9.82 g, 104 mmol) was added in a single portion and stirred for 30 seconds. Diphenic acid (35 mmol) was added in a single portion and the reaction stirred vigorously for 24 h. The reaction mixture was poured into a mixture of ice (80 g) and ethyl acetate (100 mL) and the layers separated. The aqueous layer was extracted with ethyl acetate (2 × 100 mL) and the combined organics were washed with $NaHCO_3$ (2 × 50 mL), brine (20 mL) and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the 2,2'-diperoxyphenic acid. Data matched those provided in the literature.[6]

3. General experimental procedure

3.1 General experimental procedure for synthesis of 10-phenanthrenols

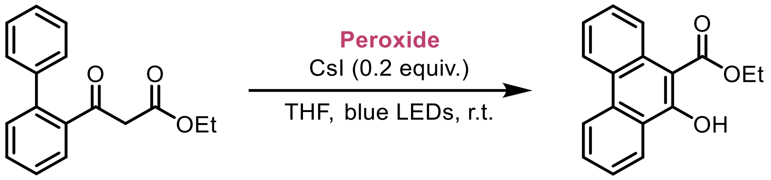
To an oven-dried 10 mL Schlenk tube equipped with a stir bar, CsI (0.04 mmol, 0.2 equiv.) was added. The flask was evacuated under high temperature and backfilled with N_2 three times. While under active N_2, the aromatic β-ketoesters **1** (0.2 mmol, 1.0 equiv.) were added in THF via syringe. Then the Schlenk tube was sealed under N_2. And the reaction mixture was stirred with the PPO (3.0 equiv.) in THF added dropwise through syringe under the irradiation of two 440 nm LEDs (4.5 cm from glass surface on each side of the tube with fan cooling) for 24 h. After reaction completion, the reaction was quenched with 1 mL $NaHCO_3$ (aq.) and extracted with 1 mL EtOAc for three times. The combined EtOAc layer was washed with brine then dried over Na_2SO_4. The mixture was filtered and concentrated in vacuo then purified by flash chromatography with silica.

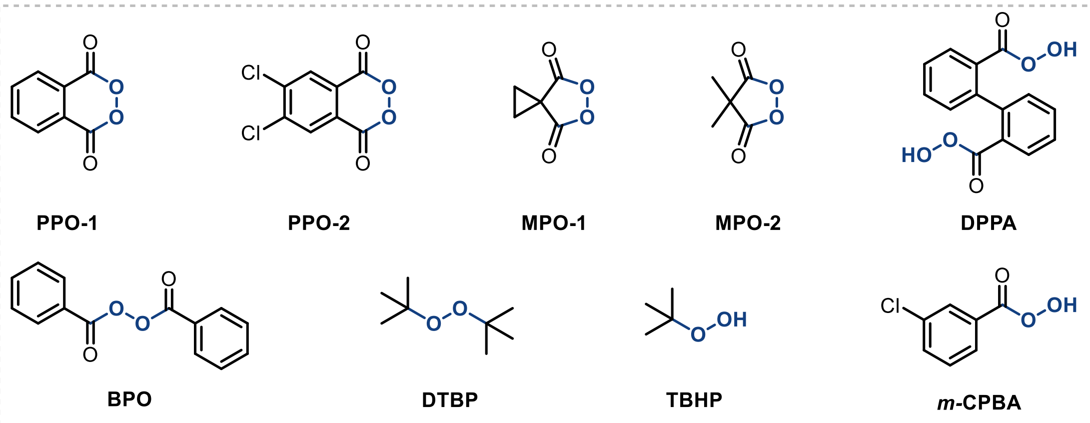
3.2 General experimental procedure for synthesis of 1‑Naphthols

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, CsI (0.04 mmol, 0.2 equiv.) was added. The flask was evacuated under high temperature and backfilled with N_2 three times. While under active N_2, the aromatic β-ketoesters **1** (0.2 mmol, 1.0 equiv.) and alkynes (0.3 mmol, 1.5 equiv.) were added in THF via syringe. Then the Schlenk tube was sealed under N_2. And the reaction mixture was stirred with the MPO (3.0 equiv.) in THF added dropwise through syringe under the irradiation of two 440 nm LEDs (4.5 cm from glass surface on each side of the tube with fan cooling) for 24 h. After reaction completion, the reaction was quenched with 1 mL $NaHCO_3$ (aq.) and extracted with 1 mL EtOAc three times. The combined EtOAc layer was washed with brine then dried over Na_2SO_4. The mixture was filtered and concentrated in vacuo then purified by flash chromatography with silica.

4. Reaction optimization

Table S1 Optimization of the peroxides[a]

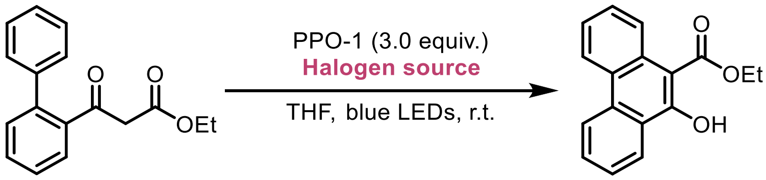




entry	oxidant	equiv.	yield (%)[b]
1	PPO-1	3.0	89
2	PPO-2	3.0	89
3	MPO-1	3.0	65
4	MPO-2	3.0	64
5	DPPA	3.0	41
6	BPO	3.0	30
7	*m*-CPBA	3.0	60
8[c]	TBHP	3.0	N.D.
9	DTBP	3.0	N.D.
10	PPO-1	2.0	67
11	PPO-1	1.0	59
12	PPO-1	none	N.D.

[a]Reaction conditions: **1a** (0.2 mmol. 1.0 equiv.), peroxide (0.6 mmol, 3.0 equiv.) and CsI (0.04 mmol, 0.2 equiv.) in THF (1.0 M) under N_2 with 440 nm blue LEDs irradiation at room temperature for 24 h. N.D.= not detected. [b]Yields of isolated products. [c] TBHP in decane, 5.5 mol/L.

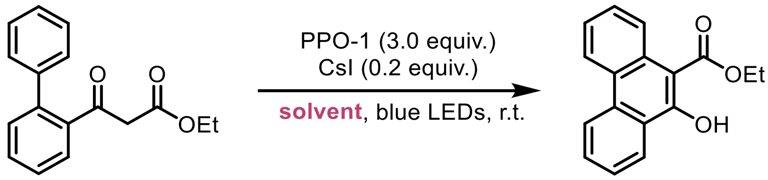
Table S2 Optimization of the halogen sources[a]



entry	halogen source	equiv.	yield (%)[b]
1	NaI	0.2	77
2	CsI	0.2	89
3[c]	NIS	0.2	70
4[d]	TBAI	0.2	59
5	KI	0.2	66
6	I_2	0.2	57
7	CsBr	0.2	22
8	CsCl	0.2	N.D.
9	none	-	N.D.
10	CsI	0.1	40

[a]Reaction conditions: **1a** (0.2 mmol. 1.0 equiv.), PPO-1 (0.6 mmol, 3.0 equiv.) and halogen source (0.04 mmol, 0.2 equiv.) in THF (1.0 M) under N_2 with 440 nm blue LEDs irradiation at room temperature for 24 h. N.D.= not detected. [b]Yields of isolated products. [c]NIS = N-iodosuccinimide. [d]TBAI = tetrabutylammonium iodide.

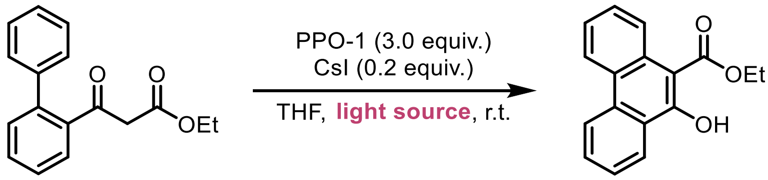
Table S3 Optimization of the solvent[a]



entry	solvent	concentration	yield (%)[b]
1	THF	0.1 M	77
2	MeCN	0.1 M	65
3	DCM	0.1 M	57
4	Chloroform	0.1 M	55
5	toluene	0.1 M	N.D.
6	*i*-PrOH	0.1 M	N.D.
7[c]	THF	0.1 M	67
8	THF	0.5 M	80
9	THF	1.0 M	89
10	THF	2.0M	80

[a]Reaction conditions: **1a** (0.2 mmol. 1.0 equiv.), PPO-1 (0.6 mmol, 3.0 equiv.) and CsI (0.04 mmol, 0.2 equiv.) in corresponding solvent (1.0 M) under N_2 with 440 nm blue LEDs irradiation at room temperature for 24 h. N.D.= not detected. [b]Yields of isolated products. [c]THF was not dried.

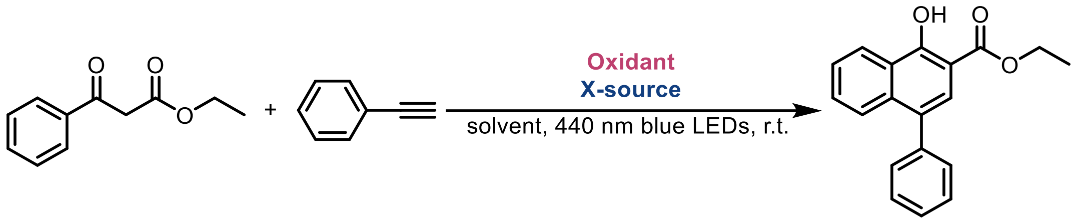
Table S4. Optimization of the light source and reaction time[a]



entry	light source	reaction time	yield (%)[b]
1	440 nm Blue LEDs	24 h	89
1	405 nm Purple LEDs	24 h	70
2	470 nm Blue LEDs	24 h	71
3	White LEDs	24 h	54
4	UV LEDs	24 h	trace
5	sunlight	24 h	58
6	in dark	24 h	41
7	440 nm Blue LEDs	12 h	66
9	440 nm Blue LEDs	36 h	88

[a]Reaction conditions: **1a** (0.2 mmol. 1.0 equiv.), PPO-1 (0.6 mmol, 3.0 equiv.) and CsI (0.04 mmol, 0.2 equiv.) in THF (1.0 M) under N_2 with corresponding light irradiation at room temperature for 24 h. [b]Yields of isolated products.

Table S5 Optimization of the reaction conditions of the intramolecular cycloaromatization for the synthesis of 1-Naphthols[a]



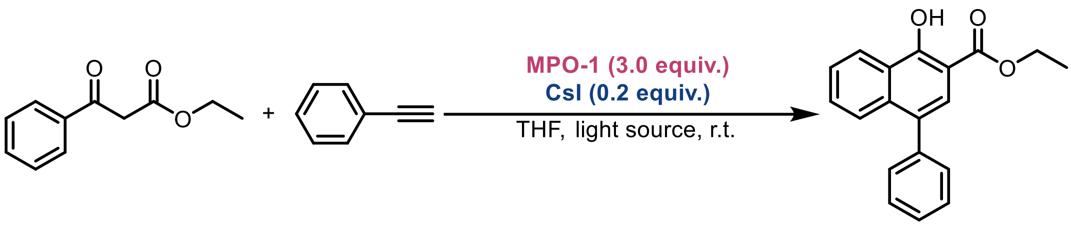
4a 3a 5a

entry	Peroxide	equiv.	X source	solvent	additive	yield (%)[b]
1	PPO-1	3.0	CsI	THF,1.0 M	-	37
2	MPO-1	3.0	CsI	THF,1.0 M	-	54
3	MPO-2	3.0	CsI	THF,1.0 M	-	33
4	DPPA	3.0	CsI	THF,1.0 M	-	30
5	BPO	3.0	CsI	THF,1.0 M	-	N.D.
6	*m*-CPBA	3.0	CsI	THF,1.0 M	-	trace
7	TBHP	3.0	CsI	THF,1.0 M	-	N.D.
8	MPO-1	2.0	CsI	THF,1.0 M	-	40
9	MPO-1	1.0	CsI	THF, 1.0 M	-	19
10	MPO-1	none	CsI	THF, 1.0 M	-	N.D.
11	MPO-1	3.0	CsI	MeCN, 1.0 M	-	27
12	MPO-1	3.0	CsI	EtOH, 1.0 M	-	N.D
13	MPO-1	3.0	CsI	DCE, 1.0 M	-	35
14	MPO-1	3.0	CsI	toluene, 1.0 M	-	trace
15	MPO-1	3.0	CsI	Dioxane, 1.0 M	-	trace
16	MPO-1	3.0	CsI	THF,0.1 M	-	42
17	MPO-1	3.0	CsI	THF,0.5 M	-	41
18	MPO-1	3.0	CsI	THF,2.0 M	-	37
19	MPO-1	3.0	none	THF,1.0 M	-	N.D.
20	MPO-1	3.0	NaI	THF,1.0M	-	33
21	MPO-1	3.0	NIS	THF,1.0M	-	40
22	MPO-1	3.0	TBAI	THF,1.0M	-	17
23	MPO-1	3.0	CsI	THF,1.0M	-	20[c]
24	MPO-1	3.0	CsI	THF,1.0M	-	45[d]
25	MPO-1	3.0	CsI	THF,1.0M	Na_2CO_3	39
26	MPO-1	3.0	CsI	THF,1.0M	$NaHCO_3$	41
27	MPO-1	3.0	CsI	THF,1.0M	NaOAc	44

28	MPO-1	3.0	CsI	THF,1.0M	NaOMe	40
29	MPO-1	3.0	CsI	THF,1.0M	TBAOH	N.D.
30	MPO-1	3.0	CsI	THF,1.0M	NaOH	N.D
31	MPO-1	3.0	CsI	THF,1.0M	Na_2HPO_4	trace

[a]Reaction conditions: **3a** (0.20 mmol, 1.0 equiv.), **4a** (0.20 mmol, 1.0 equiv.), peroxide (0.6 mmol, 3.0 equiv.) and X source (0.04 mmol, 0.2 equiv.) under nitrogen with 440 nm blue LEDs irradiation at room temperature. N.D.= not detected. [b]Yields of isolated products. [c]0.1 equiv. CsI. [d]0.4 equiv. CsI.

Table S6 Optimization of the light source of the intramolecular cycloaromatization for the synthesis of 1-Naphthols [a]



4a **3a** **5a**

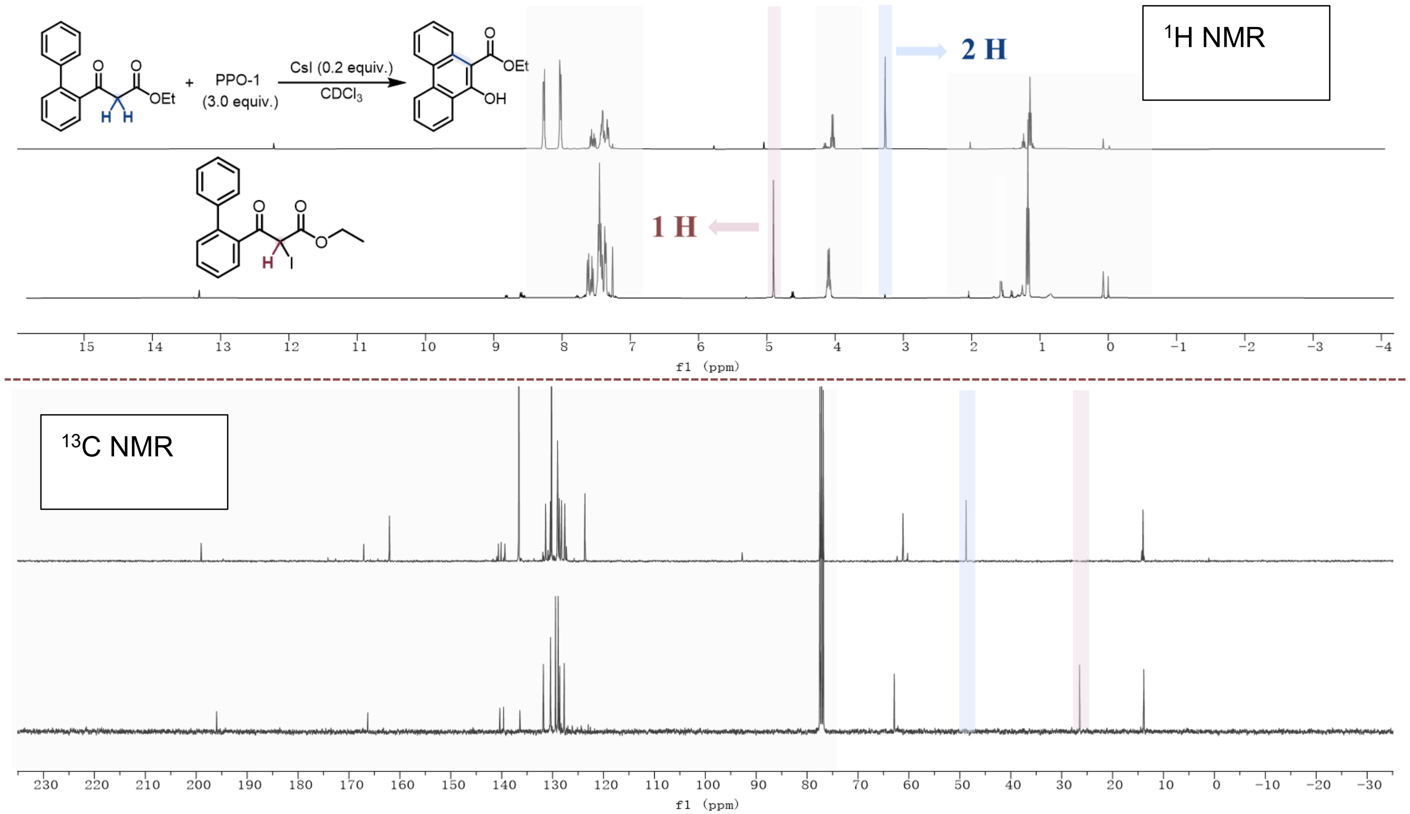
entry	light source	wavelength.	equiv. of **3a**	yield (%)[b]
1	Blue LEDs	470 nm	1.0	40
2	Blue LEDs	405 nm	1.0	45
3	White LEDs	-	1.0	21
4	UV LEDs	260 nm	1.0	trace
5	none	none	1.0	N.D.
6	Blue LEDs	440 nm	0.5	27
7	Blue LEDs	440 nm	1.5	66
8	Blue LEDs	440 nm	2.0	63

[a]Reaction conditions: **4a** (0.20 mmol, 1.0 equiv.), **3a** (x equiv.), MPO-1 (0.60 mmol, 3.0 equiv.) and CsI (0.04 mmol, 0.2 equiv.) under nitrogen with LEDs irradiation at room temperature. N.D.= not detected. [b]Yields of isolated products.

5. Mechanistic studies

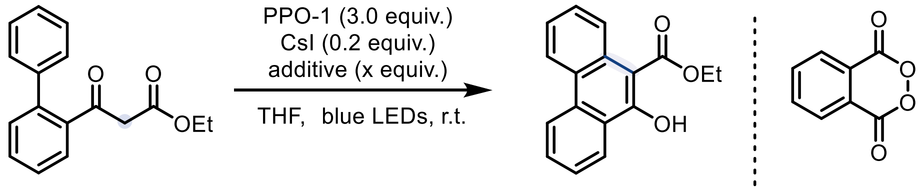
5.1 in situ NMR experiment and radical scavenger experiments

in situ NMR experiments

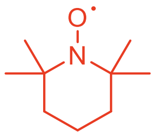
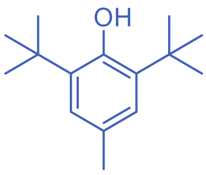


Scheme S1 *in situ* NMR experiment

Table S7 Radical scavenger experiment of intramolecular benzannulation transformations

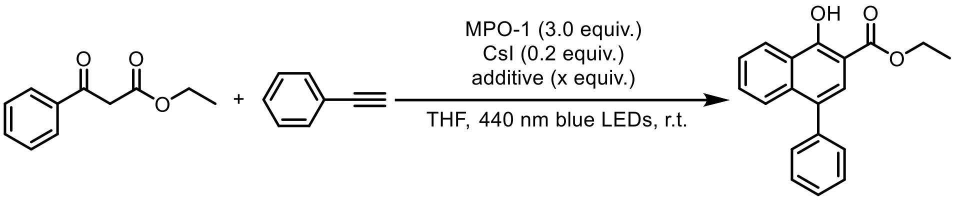


1a **2a** **PPO-1**

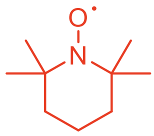
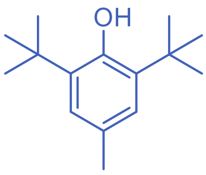
Entry	Additive	Equivalent of additive	Yields of **2a** (%)[a]
1		0	89
2		1.0	60
3	**TEMPO**	2.0	N.D.
4		0	89
5		1.0	41
6	**BHT**	2.0	N.D.

Reaction conditions: **1a** (0.2 mmol. 1.0 equiv.), PPO-1 (0.6 mmol, 3.0 equiv.), CsI (0.04 mmol, 0.2 equiv.) and additive (x equiv.) in THF (1.0 M) under N_2 with 440 nm blue LEDs irradiation at room temperature for 24 h. [a]Yields of isolated products

Table S8 Radical scavenger experiment of intramolecular benzannulation transformations

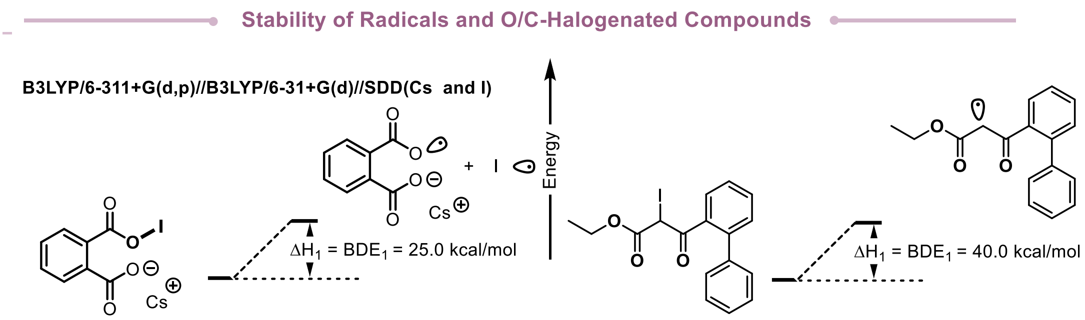


4a **3a** **5a**

Entry	Additive	Equivalent of additive	Yields of **5a** (%)[a]
1		0	66
2		1.0	N.D.
3	**TEMPO**	2.0	N.D.
4		0	66
5		1.0	N.D.
6	**BHT**	2.0	. N.D.

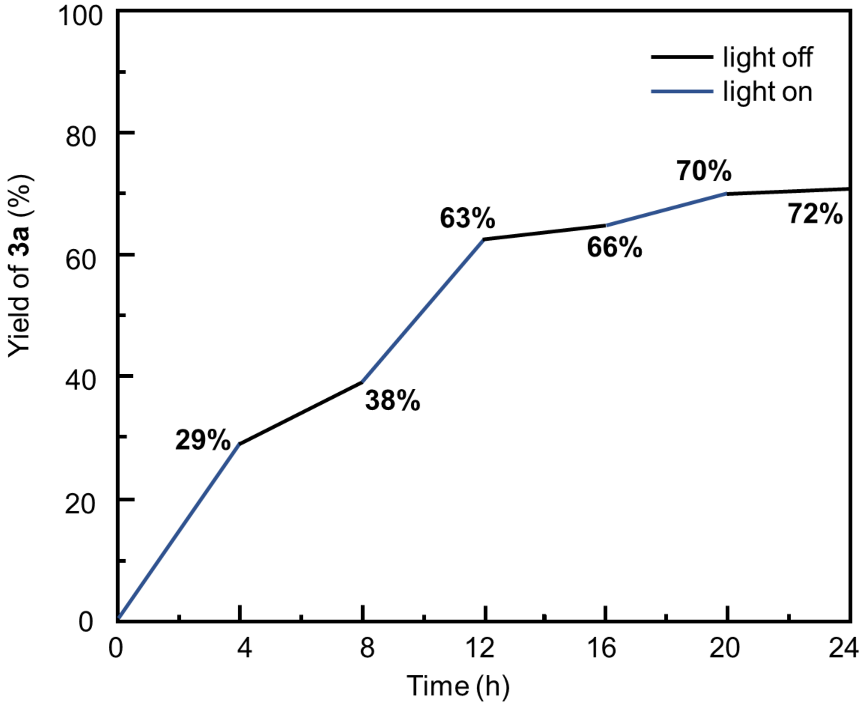
Reaction conditions: **3a** (0.20 mmol, 1.0 equiv.), **4a** (0.20 mmol, 1.0 equiv.), MPO-1 (0.6 mmol, 3.0 equiv.), CsI (0.04 mmol, 0.2 equiv.) and additive (x equiv.) under nitrogen with 440 nm blue LEDs irradiation at room temperature. N.D.= not detected. [a]Yields of isolated products.

5.2 BDE experiments



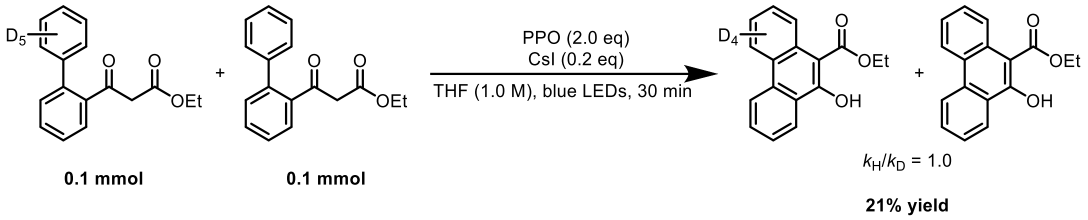
Scheme S2 the BDE values of the O/C-halogenated compounds

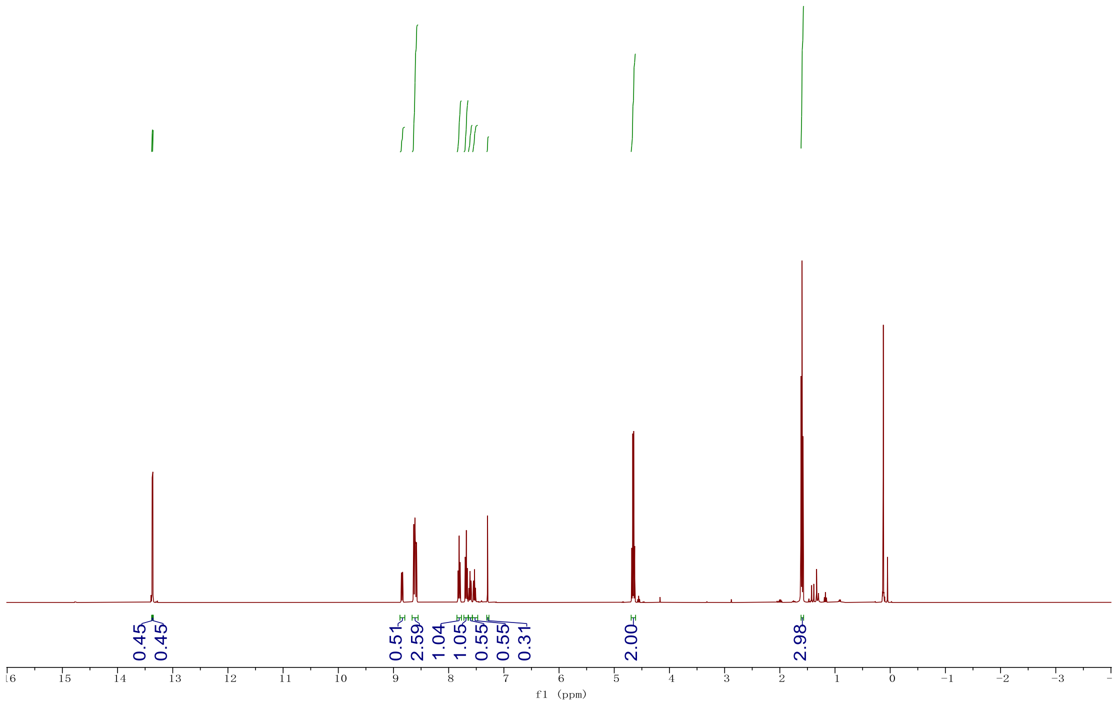
5.3 Light off/on experiment



Scheme S3 Light off/on experiment.

5.4 KIE experiment

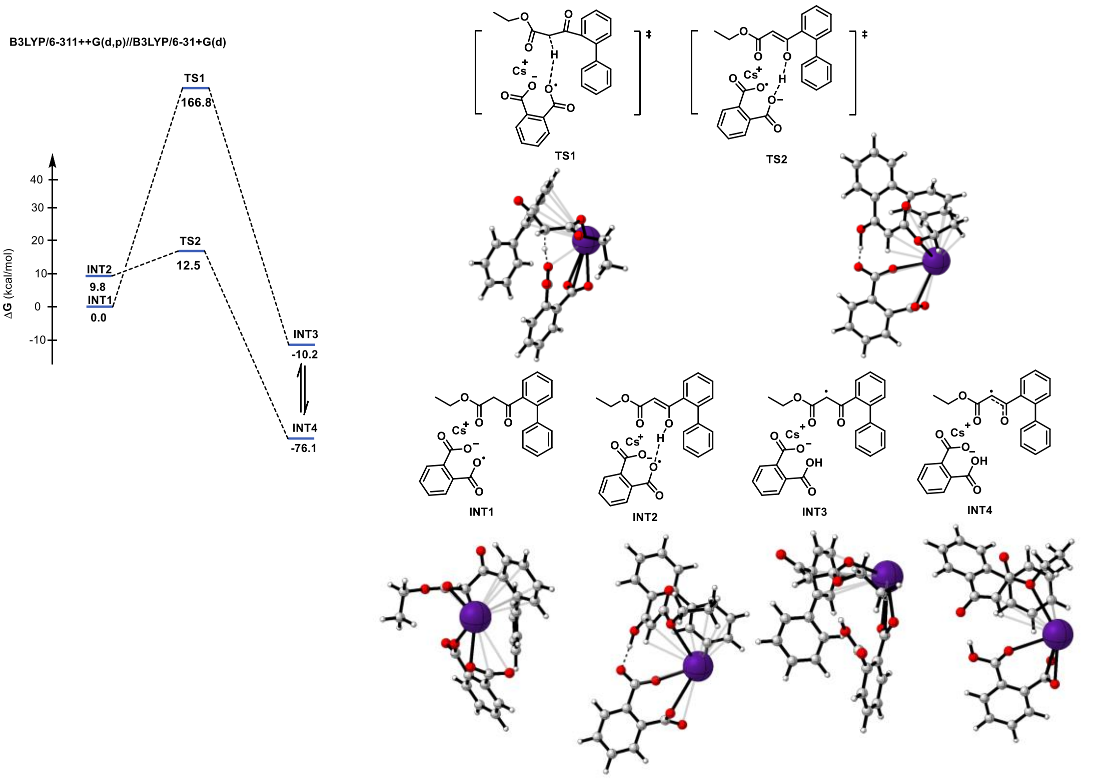




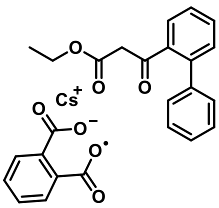
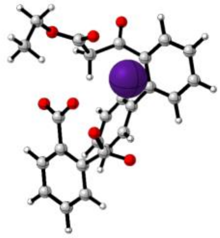
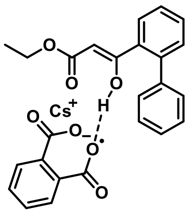
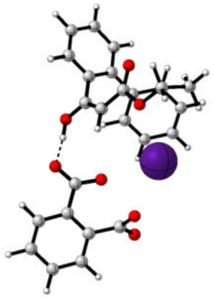
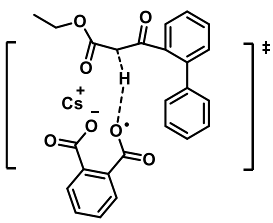
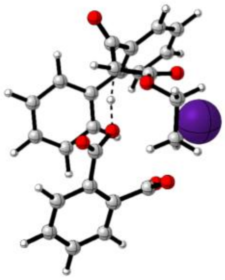
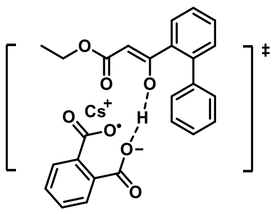
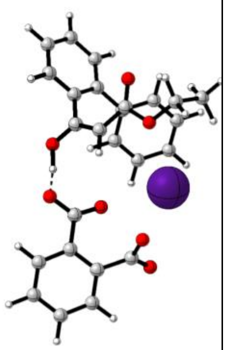
Scheme S4 Intermolecular KIE with D5-**1a** and **1a**

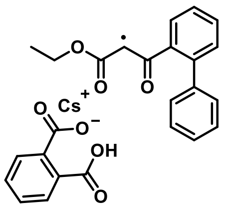
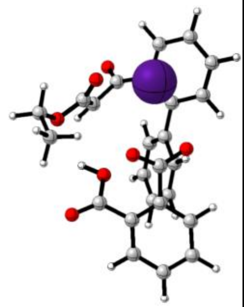
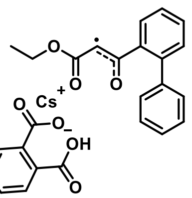
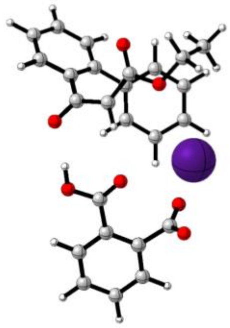
5.5 The DFT calculation of potential energy surface

All computations were performed with the Gaussian 09 Program. Geometries of all stationary points were fully optimized using the dispersion-corrected B3LYP-D3(BJ) functional, with a mixed basis set of SDD for Cs and 6–31+G(d) for other atoms in the gas phase. To verify the stationary points as minima or transition states, vibration frequency calculation was performed for each structure. Solvation energy corrections were applied using the SMD continuum solvation model with tetrahydrofuran(THF) as the solvent. Single-point energy calculations were carried out using the B3LYP-D3(BJ) functional, with a mixed basis set of SDD and 6-311++G(d,p) for other atoms, in THF. All energies discussed are free energies at 298 K and 1 atm in kcal/mol.



Scheme S5 The Gibbs free energy potential surface for the TDRA-induced intermolecular benzannulation of **1a** computed at S64M052X/6-31G(d)/SMD(MeCN)//B3LYP/6-31+G(d) level of theory.

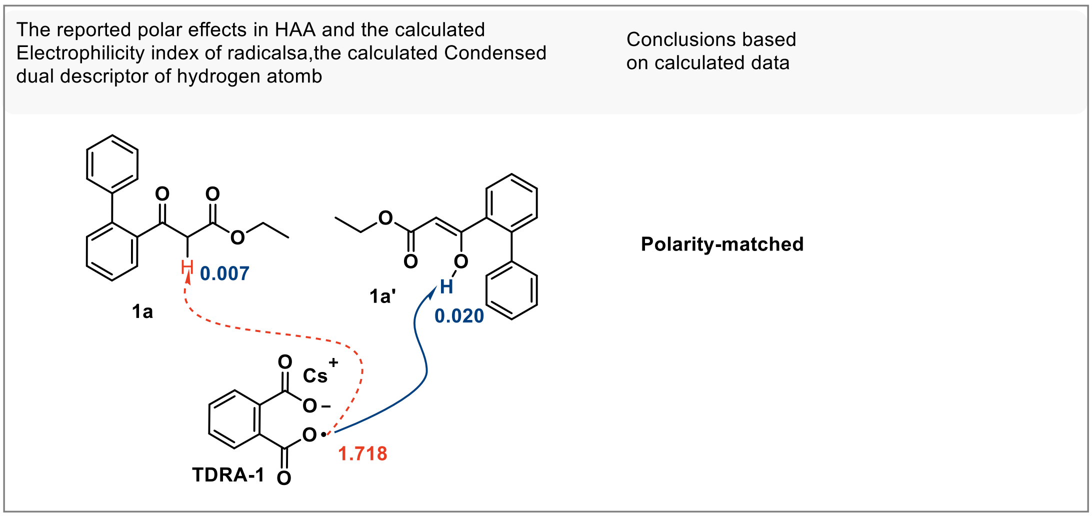
	Species	Optimized Structures	E_0 (Hartree)[b]	E_0+Thermal Free Energy Correction (Hartree)[b,c]	$<S^2>$
INT1			-1512.046	-1511.716	0.757734
INT2			-1512.039	-1511.715	0.758344
TS1			-1512.012	-1511.690	0.758137
TS2			-1512.036	-1511.714	0.75785

INT3			-1512.049	-1511.718	0.760096
INT4			-1512.058	-1511.728	0.760913

[a] Energies, enthalpies, free energies, and entropies of the structures calculated at the SMD(tetrahydrofuran)/B3LYP-D3/6-311+G(d,p) level. [b] 1 Hartree = 627.5095 kcal mol^{-1}. [c] Thermal corrections at 298.15 K.

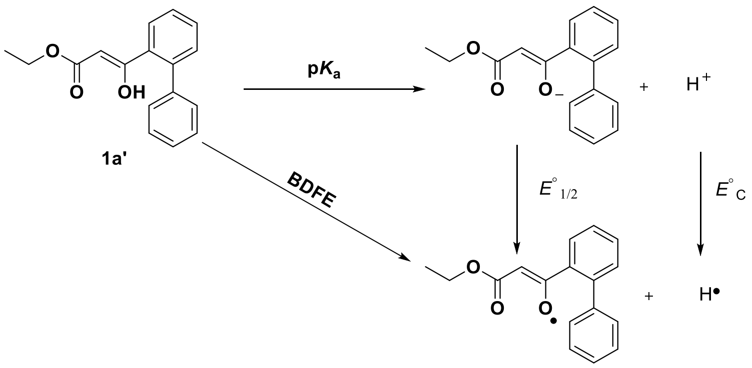
5.6 Polarity matching

The blue arrows represent the experimentally successful abstraction, while the red arrows mean the abstraction pathway not detected. In order to better understand the polarity matching in the intramolecular benzannulation of **1a**, we conducted density functional theory (DFT) calculations for corresponding structures. Specifically, we determined dual descriptor Fukui function values (blue numbers) for hydrogen atom and electrophilicity index (red numbers) for radicals. The more positive condensed dual descriptor (CDD) values are, the more electrophilic the corresponding site hydrogen is. In addition, the higher the values of Electrophilicity index are, the more electrophilic the radicals are.

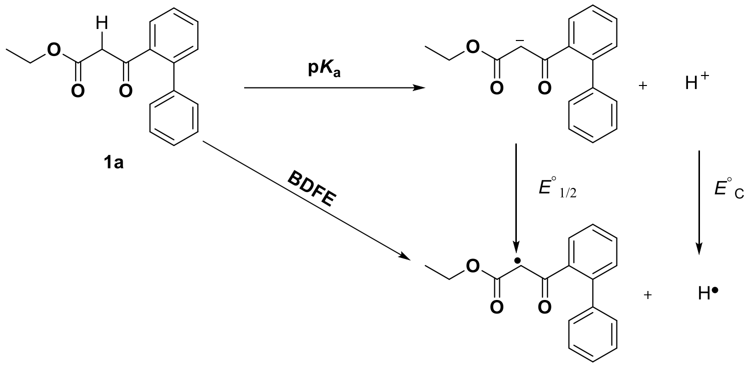


Scheme S6 The polarity matching of intramolecular benzannulation of **1a**

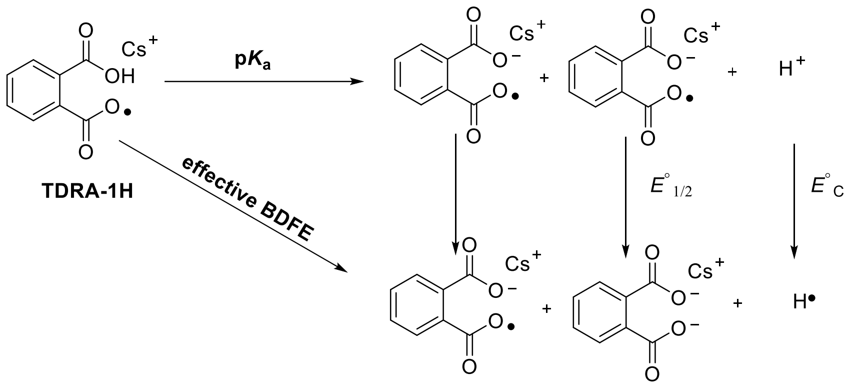
5.7 BDFE evaluations



BDFE (kcal/mol) = 23.06 E° ($R^{\bullet}/R^{-}$) + 1.37 pK_a (RH/R^{-}) +23.06 E° ($H^{+}/H^{\bullet}$)



$$\text{BDFE (kcal/mol)} = 23.06\,E^{\circ}\,(R^{\bullet}/R^{-}) + 1.37\,pK_a\,(RH/R^{-}) + 23.06\,E^{\circ}\,(H^{+}/H^{\bullet})$$



$$\text{BDFE (kcal/mol)} = 23.06\,E^{\circ}\,(Ox^{\bullet+}/Ox) + 1.37\,pK_a\,(BH/B^{-}) + 23.06\,E^{\circ}\,(H^{+}/H^{\bullet})$$

Scheme S7 The thermodynamic cycle separates the BDFE of an R–H bond into two measurable values. Reagent pair and its effective BDFE.

Table S9. A series of O/C-H BDFEs and effective BDFEs are tabulated to show the balancing effect between pK_a and $E°$. $E°$ is computed using Gibbs free energies of species shown in **Table S10**. The free energy change for the reference reaction in the standard hydrogen electrode. In this study, the value -4.44 V is consistently used in all calculations. The pK_a datas are based on http://pka.luoszgroup.com/.[7]

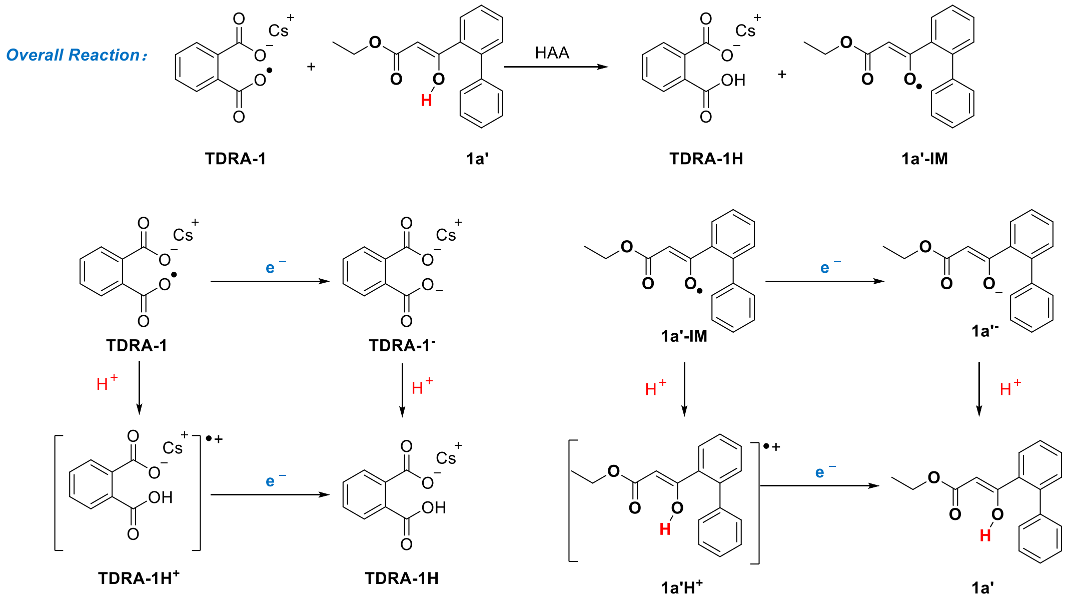
File Description	E°(eV)	pK_a	BDFE
TDRA-1	0.73	14.65	92
1a’	-0.13	20.38	80
1a	0.57	23	100

Table S10. The Gibbs free energy potential surface for the oxidants and substrates computed at M052X/6-31G(d)/SMD(Acetonitrile)//B3LYP/6-31+G(d) level of theory.

File Description	*△G(MeCN)*
TDRA-1	0.189995999999951
1a’	0.158405500000072
1a	0.184051999999951

5.8 Asynchronicity factor

In order to quantify the asynchronicity in the electron and proton transfer in the concerted HAA process, we have computed the asynchronicity factor (***η***) proposed by Srnec and coworkers.[8]



Asynchronicity Factor (η) $= \frac{1}{\sqrt{2}}[-G(\textbf{TDRA-1}^{-})+G(\textbf{1a'}^{-})+G(\textbf{TDRA-1H}^{+})-G(\textbf{1a'H}^{+})]$

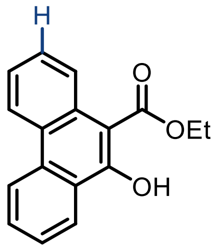
Scheme S8. Species relevant for computing asynchronicity factor. G(species) refers to the Gibbs free energy of the relevant species. [**1a'-IM**] refers to the usual radical product after HAA, [**1a'H$^+$**] is the substrate structure **1a'** oxidized by 1-electron, and [**1a'$^-$**] is the substrate structure after deprotonating the acidic proton from the O–H bond.

η = -203 mV (Calculated asynchronicity factors (***η***) in mV, computed using Gibbs free energies of species shown in **Table S10**)

Table S10. Solution phase Gibbs free energies, G(sol)/Hartree for stationary points involved in **Scheme S8** for the reaction of **TDRA-1** and **1a'** computed at B3LYP/6-311++G(d,p)/SMD(solvent)//B3LYP/6-31+G(d) of theory (T=298K).

File Description	*G*(THF)/a.u.
TDRA-1$^-$	-628.716
TDRA-1H$^+$	-628.967
1a'$^-$	-882.714
1a'H$^+$	-882.954

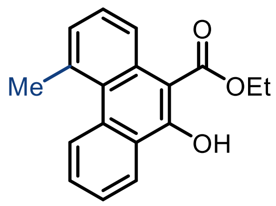
6. The characterization of products



2a, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.34 (s, 1H), 8.81 (d, *J* = 8.6 Hz, 1H), 8.63 – 8.52 (m, 3H), 7.81 – 7.74 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 4.62 (q, *J* = 7.2 Hz, 2H), 1.56 (t, *J* = 7.2 Hz, 3H).

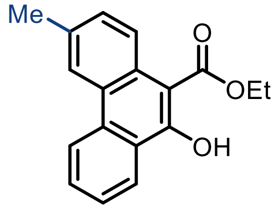
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.97, 162.79, 133.72, 130.45, 129.54, 127.63, 126.88, 126.13, 126.05, 125.32, 125.02, 124.25, 122.89, 122.47, 101.62, 62.09, 14.42.



2b, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.88 (s, 1H), 8.67 – 8.55 (m, 3H), 7.77 – 7.68 (m, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 3.04 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H).

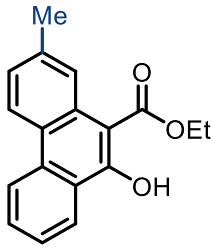
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.66, 161.37, 135.14, 134.41, 130.81, 129.09, 128.81, 127.68, 126.61, 126.50, 126.35, 126.24, 124.51, 123.88, 102.61, 62.08, 27.28, 14.41.



2c, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.26 (s, 1H), 8.67 (d, *J* = 8.7 Hz, 1H), 8.59 – 8.52 (m, 2H), 8.34 (s, 1H), 7.78 – 7.70 (m, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.55 (t, *J* = 7.1 Hz, 3H).

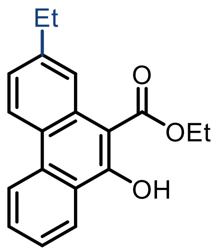
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.02, 162.15, 133.64, 133.49, 130.27, 129.21, 127.15, 126.75, 126.18, 125.93, 125.39, 124.98, 122.78, 122.46, 101.56, 62.03, 21.56, 14.43.



2d, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.25 (s, 1H), 8.61 (s, 1H), 8.56 – 8.50 (m, 2H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.2, Hz, 1H), 7.66 – 7.54 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 1.57 (t, *J* = 7.1 Hz, 3H).

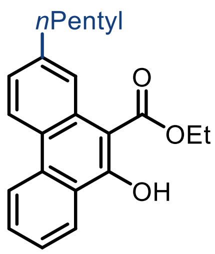
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.99, 162.84, 137.24, 133.77, 130.36, 129.55, 126.38, 126.00, 125.71, 124.96, 124.89, 123.88, 122.73, 122.26, 101.34, 62.02, 22.26, 14.33.



2e, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.28 (s, 1H), 8.66 (s, 1H), 8.60 – 8.46 (m, 3H), 7.79 – 7.69 (m, 1H), 7.66 – 7.56 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 2.85 (q, *J* = 7.6 Hz, 2H), 1.59 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.6 Hz, 3H).

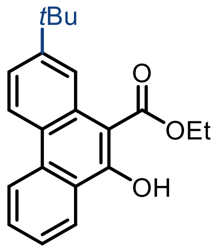
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.05, 162.81, 143.54, 133.80, 130.43, 129.64, 126.48, 124.99, 124.95, 124.77, 124.74, 124.18, 122.86, 122.32, 101.56, 62.02, 29.40, 15.46, 14.35.



2f, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.28 (s, 1H), 8.63 (s, 1H), 8.57 – 8.51 (m, 2H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 2.84 – 2.76 (m, 2H), 1.82 – 1.70 (m, 2H), 1.57 (t, *J* = 7.1 Hz, 3H), 1.40 (q, *J* = 3.6 Hz, 4H), 0.94 (s, 3H).

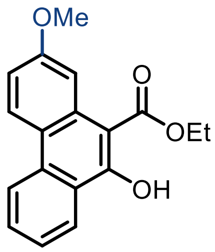
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.03, 162.78, 142.27, 133.81, 130.41, 129.55, 126.45, 125.45, 125.20, 124.98, 124.93, 124.16, 122.77, 122.30, 101.54, 62.01, 36.49, 31.61, 31.09, 22.69, 14.35, 14.14.



2g, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.39 (s, 1H), 8.89 (d, *J* = 2.0 Hz, 1H), 8.59 – 8.48 (m, 3H), 7.75 (t, *J* = 8.3 Hz, 1H), 7.65 – 7.54 (m, 2H), 4.61 (q, *J* = 7.2 Hz, 2H), 1.60 (t, *J* = 7.2 Hz, 3H), 1.47 (s, 9H).

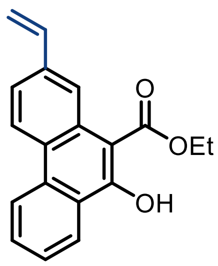
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.24, 163.03, 150.34, 133.68, 130.45, 129.29, 126.51, 125.01 125.01 123.90, 122.63, 122.39, 122.34, 122.34, 101.74, 62.02, 35.28, 31.54, 14.49.



2h, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.44 (s, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.46 (d, *J* = 9.2 Hz, 2H), 8.33 (s, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.63 – 7.50 (m, 1H), 7.11 (d, *J* = 9.1 Hz, 1H), 4.60 (q, *J* = 7.6 Hz, 2H), 3.94 (s, 3H), 1.56 (t, *J* = 7.2 Hz, 3H).

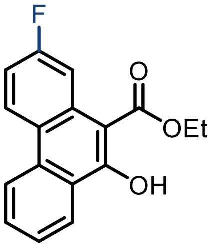
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.05, 163.73, 159.10, 133.90, 131.07, 130.61, 125.86, 125.07, 124.35, 124.21, 121.99, 120.26, 113.63, 108.09, 101.21, 62.03, 55.21, 14.41.



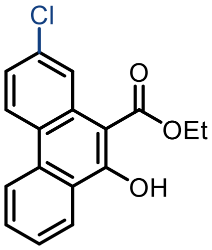
2i, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.36 (s, 1H), 8.85 (s, 1H), 8.58 – 8.47 (m, 3H), 7.76 (t, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.67 – 7.55 (m, 2H), 6.89 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.9 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 1.59 (t, *J* = 6.9 Hz, 3H).

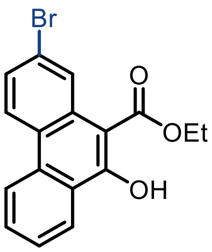
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.94, 163.11, 137.49, 136.59, 133.54, 130.56, 129.70, 126.88, 125.75, 125.27, 125.08, 124.52, 123.16, 122.51, 121.91, 114.29, 101.51, 62.13, 14.38.



2j, White solid
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 13.53 (s, 1H), 8.59 – 8.36 (m, 4H), 7.75 (t, J = 7.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 7.9 Hz, 1H), 4.61 (q, J = 7.1 Hz, 2H), 1.57 (t, J = 7.1 Hz, 3H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.74, 164.05, 163.49 (d, J = 245.0 Hz), 133.38, 131.28 (d, J = 10.3 Hz), 130.82, 126.68, 125.16, 124.94, 124.80, 122.62 (d, J = 1.5 Hz), 122.28, 112.72 (d, J = 24.3 Hz), 111.67 (d, J = 25.8 Hz), 101.05 (d, J = 3.6 Hz), 62.36, 14.37.
^{19}**F NMR** (376 MHz, $CDCl_3$) δ -112.76 (s, 1F).



2k, White solid
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 13.48 (s, 1H), 8.81 (s, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.44 (dd, J = 15.6, 8.5 Hz, 2H), 7.81 – 7.71 (m, 1H), 7.66 – 7.59 (m, 1H), 7.41 (d, J = 8.9 Hz, 1H), 4.61 (q, J = 7.2 Hz, 2H), 1.58 (t, J = 7.1 Hz, 3H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.59, 163.76, 133.80, 133.14, 130.83, 130.64, 127.15, 125.60, 125.16 (×2), 124.51, 124.40, 124.27, 122.38, 100.70, 62.43, 14.31.

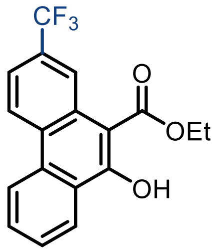


2l, Pale yellow solid

^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.45 (s, 1H), 8.97 (d, *J* = 2.1 Hz, 1H), 8.51 (d, *J* = 9.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.1 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.59 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.53, 163.66, 133.17, 130.97, 130.82, 128.68, 127.24, 127.21, 125.21, 125.16, 124.72, 124.40, 122.32, 122.28, 100.59, 62.42, 14.28.

ESI-HRMS: exact mass calculated for [M+H$^+$] requires m/z 345.0048, found m/z 345.0045.

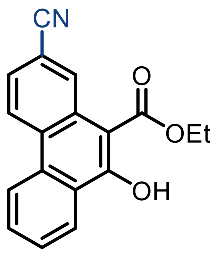


2m, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.49 (s, 1H), 9.15 (s, 1H), 8.57 (d, *J* = 8.6 Hz, 1H), 8.55 – 8.48 (m, 2H), 7.82 – 7.76 (m, 1H), 7.71 – 7.66 (m, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 4.60 (q, *J* = 7.2 Hz, 2H), 1.58 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 163.79, 132.69, 130.90, 129.09, 128.91 (q, *J* = 32.3 Hz), 128.07, 127.93, 125.94, 125.19, 124.7 (q, *J* = 273.3 Hz), 123.55, 123.48, 122.80, 120.14 (q, *J* = 3.0 Hz), 101.11, 62.50, 14.06.

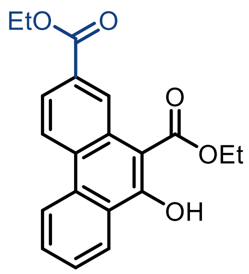
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.38 (s, 3F).



2n, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.55 (s, 1H), 9.10 (d, *J* = 1.6 Hz, 1H), 8.53 (d, *J* = 9.0 Hz, 2H), 8.48 (d, *J* = 8.6 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 8.2 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.63 (q, *J* = 7.2 Hz, 2H), 1.58 (t, *J* = 7.1 Hz, 3H).

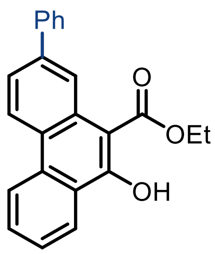
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 164.08, 132.33, 131.15, 131.01, 129.28, 128.60, 128.51, 126.19, 125.85, 125.31, 123.71, 122.93, 119.71, 110.91, 100.46, 62.76, 14.35.



2o, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.44 (s, 1H), 9.57 (s, 1H), 8.55 (t, *J* = 8.2 Hz, 3H), 8.07 (dt, *J* = 8.6, 1.8 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.62 (t, *J* = 7.2 Hz, 3H), 1.46 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.65, 166.95, 163.22, 132.85, 130.65, 129.03, 128.95, 128.24, 127.82, 126.07, 125.08, 124.29, 123.01, 122.85, 101.44, 62.30, 61.04, 14.42, 14.16.

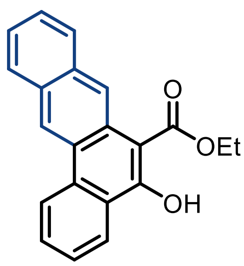


2p, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 9.11 (s, 1H), 8.64 – 8.51 (m, 3H), 7.80 – 7.69 (m, 4H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.60 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.01, 163.26, 141.51, 139.99, 133.52, 130.59, 129.83, 128.96, 127.46, 127.34, 126.89, 125.29, 125.24, 125.10, 124.64, 123.42, 123.26, 122.51, 101.58, 62.15, 14.40.

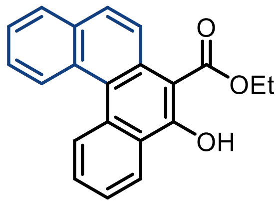
ESI-HRMS: exact mass calculated for [M+H$^+$] requires m/z 343.1256, found m/z 343.1250.



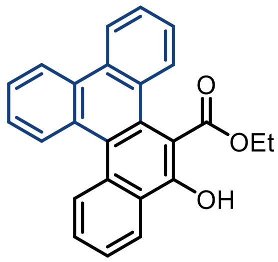
2q, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 9.8 Hz, 1H), 8.49 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H),

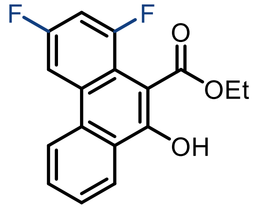
7.86 (d, J = 8.8 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 8.1 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 (t, J = 6.8 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.53, 158.60, 133.28, 133.08, 130.13, 129.60, 129.00, 127.87, 126.81, 126.11, 125.99, 124.73, 124.35, 124.06, 123.02, 120.26, 103.85, 61.74, 13.84.



2r, yellow solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.00 (s, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.85 (d, J = 8.3 Hz, 1H), 8.76 (d, J = 9.1 Hz, 1H), 8.64 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.76 (t, J = 8.3 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.63 – 7.53 (m, 2H), 4.63 (q, J = 7.2 Hz, 2H), 1.58 (t, J = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 161.77, 133.22, 131.77, 129.94, 129.40, 128.45, 128.38, 127.96, 127.90, 127.54, 126.24, 125.99, 125.69, 125.33, 124.54, 124.00, 122.75, 102.66, 62.27, 14.44.



2s, yellow solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.74 (d, J = 7.7 Hz, 1H), 8.68 (ddd, J = 7.7, 4.4, 1.5 Hz, 2H), 8.59 (t, J = 8.4 Hz, 2H), 7.79 (d, J = 6.8 Hz, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.68 – 7.55 (m, 4H), 7.50 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.09 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 159.09, 132.22, 130.38, 130.11, 129.87, 129.84, 129.64, 129.19, 128.26, 127.88, 127.49, 126.61, 126.56, 126.14, 126.05, 125.45, 125.07, 124.82, 123.72, 123.27, 123.06, 103.22, 61.72, 13.71.
ESI-HRMS: exact mass calculated for $[M+H^+]$ requires m/z 367.1256, found m/z 367.1248.



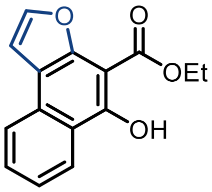
2t, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.45 (d, *J* = 8.1 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 10.3 Hz, 1H), 7.80 – 7.71 (m, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.05 (ddd, *J* = 11.4, 8.4, 2.5 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.80, 157.69, 131.96 (d, *J* = 6.4 Hz), 130.29, 129.07 (d, *J* = 5.9 Hz), 128.17, 125.54, 124.82, 123.02, 115.25 (d, *J* = 10.2 Hz), 104.23 (d, *J* = 3.7 Hz), 104.01 (d, *J* = 3.7 Hz), 103.92, 103.65, 103.38, 100.16, 62.09, 14.08.

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.28 (s, 1F), -110.90 (s, 1F).

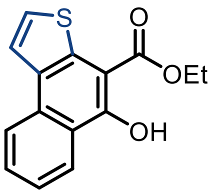
ESI-HRMS: exact mass calculated for [M+H$^+$] requires m/z 303.0755, found m/z 303.0758.



2u, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.63 (m, 2H), 7.51 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.61, 160.72, 148.91, 143.10, 130.38, 130.15, 125.20, 124.60, 123.17, 122.52, 115.59, 105.21, 96.82, 61.95, 14.46.

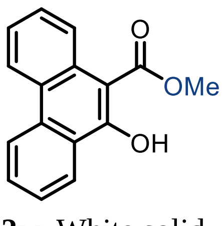


2v, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 5.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.44 (d, *J* = 5.6 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.59 (t, *J* = 7.2 Hz, 3H).

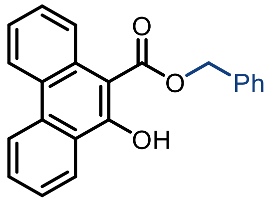
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.69, 161.00, 134.70, 132.22, 130.29, 129.66, 125.40, 124.99, 124.46, 123.56, 123.53, 121.22, 101.91, 62.34, 14.40.

ESI-HRMS: exact mass calculated for [M+H$^+$] requires m/z 273.0507, found m/z 273.0511.

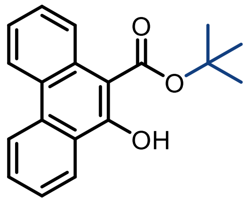


2w, White solid

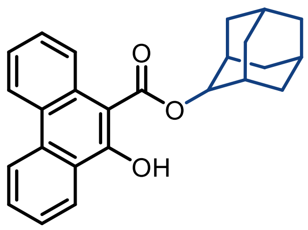
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.25 (s, 1H), 8.74 (d, *J* = 8.6 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 3H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 4.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.45, 162.84, 133.78, 130.57, 129.36, 127.72, 126.95, 126.09 (×2), 125.27, 125.08, 124.37, 122.94, 122.51, 101.54, 52.59.



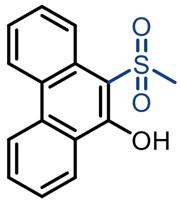
2x, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.23 (s, 1H), 8.83 – 8.77 (m, 1H), 8.60 – 8.53 (m, 3H), 7.77 (t, *J* = 7.0Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.57 – 7.36 (m, 7H), 5.60 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.76, 163.01, 135.35, 133.83, 130.63, 129.42, 128.86, 128.64, 128.48, 127.76, 126.97, 126.15 (×2), 125.27, 125.10, 124.35, 122.93, 122.52, 101.53, 67.69.



2y, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.47 (s, 1H), 8.85 (d, *J* = 10.0 Hz, 1H), 8.63 – 8.53 (m, 3H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 1.81 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.38, 162.39, 133.57, 130.24, 129.84, 127.43, 126.85, 126.17, 126.11, 125.53, 124.93, 124.12, 122.91, 122.47, 102.82, 84.26, 28.69.



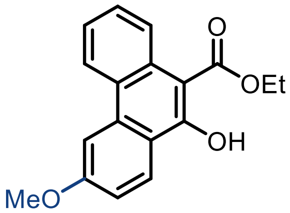
2z, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.50 (s, 1H), 9.00 (d, *J* = 7.0 Hz, 1H), 8.66 – 8.58 (m, 3H), 7.81 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.65 (dddd, *J* = 21.9, 8.5, 6.9, 1.3 Hz, 2H), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 5.51 (s, 1H), 2.36 (s, 2H), 2.27 (d, *J* = 12.9 Hz, 2H), 2.06 – 1.93 (m, 6H), 1.86 (s, 2H), 1.77 (d, *J* = 13.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.47, 162.75, 133.67, 130.41, 129.67, 127.51, 126.90, 126.25, 126.13, 125.45, 125.01, 124.21, 122.91, 122.46, 102.12, 80.20, 37.50, 36.55, 32.32, 32.09, 27.33, 27.13.



2aa, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.65 – 8.50 (m, 4H), 7.82 (t, *J* =7.0 Hz, 1H), 7.67 (q, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 3.36 (s, 3H).

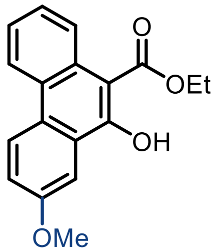
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.32, 133.69, 131.09, 128.49, 127.52, 127.16, 126.38, 125.29, 125.21, 125.18, 123.48, 123.31, 122.56, 108.62, 44.90.



2ab, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.34 (s, 1H), 8.78 (d, *J* = 8.2 Hz, 1H), 8.46 (d, *J* = 9.3 Hz, 2H), 7.87 (d, *J* = 2.8 Hz, 1H), 7.49 (dddd, *J* = 21.7, 8.1, 7.0, 1.4 Hz, 2H), 7.37 (dd, *J* = 9.1, 2.8 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.56 (t, *J* = 7.1 Hz, 3H).

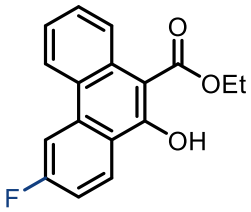
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.13, 162.09, 158.66, 128.39, 127.98, 126.67, 126.51, 126.22, 125.99, 124.31, 124.23, 122.38, 121.17, 104.64, 102.00, 62.13, 55.60, 14.42.



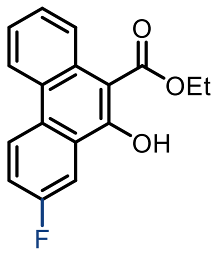
2ac, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.33 (s, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.42 – 8.34 (m, 2H), 7.84 (s, 1H), 7.53 – 7.44 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.13 (m, 1H), 4.52 (q, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H).

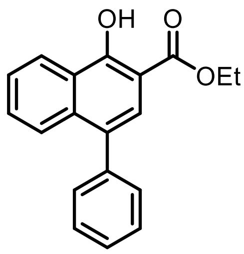
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.10, 163.18, 161.61, 135.80, 130.24, 127.81, 127.03, 126.14, 125.59, 123.92, 122.92, 119.53, 116.40, 104.24, 99.79, 61.93, 55.55, 14.45.



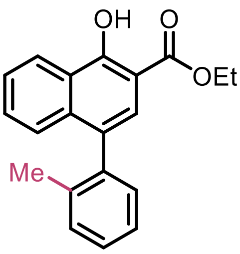
2ad, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.38 (s, 1H), 8.80 (d, *J* = 7.1 Hz, 1H), 8.54 (dd, *J* = 9.0, 6.1 Hz, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 8.16 (dd, *J* = 11.1, 2.6 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.35 (ddd, *J* = 9.0, 7.9, 2.5 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.56 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.92, 165.53 (d, *J* = 250.0 Hz), 162.46, 136.04 (d, *J* = 8.9 Hz), 130.07, 128.31, 128.03 (d, *J* = 9.3 Hz), 126.15, 125.38 (d, *J* = 3.6 Hz), 124.34, 123.12, 121.96, 115.90 (d, *J* = 23.9 Hz), 108.04 (d, *J* = 22.8 Hz), 101.08, 62.19, 14.41.
^{19}F NMR (376 MHz, $CDCl_3$) δ -108.11 (s, 1F).



2ae, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.21 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.57 (dd, *J* = 9.2, 5.1 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.16 (dd, *J* = 9.8, 2.9 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.53 – 7.44 (m, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.74, 162.78 (d, *J* = 246.7 Hz), 161.55 (d, *J* = 3.7 Hz), 130.12, 128.89, 127.40, 126.79 (d, *J* = 8.1 Hz), 126.05, 125.68, 124.93 (d, *J* = 8.7 Hz), 124.49, 122.63, 119.24 (d, *J* = 23.7 Hz), 109.82 (d, *J* = 22.6 Hz), 102.41, 62.28, 14.39.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.81 (s, 1F).



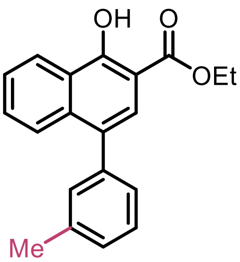
5a, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.56 – 8.44 (m, 1H), 7.85 – 7.79 (m, 1H), 7.75 (s, 1H), 7.58 – 7.52 (m, 2H), 7.52 – 7.40 (m, 5H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 160.44, 140.26, 135.55, 131.21, 130.27, 129.48, 128.43, 127.28, 125.95, 125.73, 125.05, 124.98, 124.19, 105.44, 61.57, 14.34.



5b, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.55 – 8.49 (m, 1H), 7.69 (s, 1H), 7.59 – 7.50 (m, 2H), 7.41 – 7.29 (m, 4H), 7.28 (d, *J* = 3.3 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.06 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

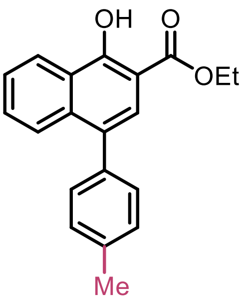
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 160.39, 139.63, 137.35, 135.88, 130.83, 130.56, 129.97, 129.49, 127.76, 125.99, 125.79, 125.65, 124.84, 124.63, 124.14, 105.40, 61.53, 20.14, 14.30.



5c, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H), 8.54 – 8.53 (m, 1H), 7.92 – 7.81 (m, 1H), 7.77 (s, 1H), 7.59 (dd, *J* = 6.8, 3.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 9.4 Hz, 3H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H).

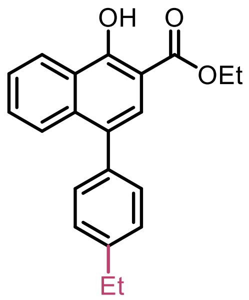
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 160.35, 140.18, 138.06, 135.61, 131.34, 130.94, 129.40, 128.27, 127.99, 127.33, 126.03, 125.66, 125.01, 124.82, 124.13, 105.41, 61.54, 21.56, 14.34.



5d, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.55 – 8.47 (m, 1H), 7.88 – 7.79 (m, 1H), 7.73 (s, 1H), 7.58 – 7.52 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).

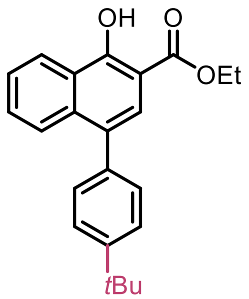
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 160.29, 137.30, 136.95, 135.66, 131.16, 130.11, 129.37, 129.10, 126.00, 125.64, 125.03, 124.88, 124.14, 105.44, 61.52, 21.29, 14.32.



5e, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.06 (s, 1H), 8.65 – 8.26 (m, 1H), 7.87 – 7.81 (m, 1H), 7.74 (s, 1H), 7.57 – 7.52 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.6 Hz, 3H).

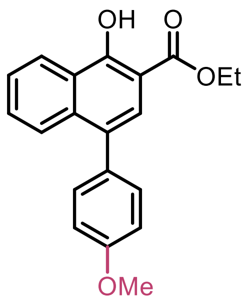
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 160.28, 143.28, 137.52, 135.67, 131.20, 130.16, 129.35, 127.89, 126.03, 125.63, 125.04, 124.90, 124.13, 105.45, 61.50, 28.69, 15.66, 14.32.



5f, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.53 – 8.46 (m, 1H), 7.91 – 7.82 (m, 1H), 7.76 (s, 1H), 7.59 – 7.49 (m, 4H), 7.41 (d, *J* = 8.3 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 – 1.40 (m, 12H).

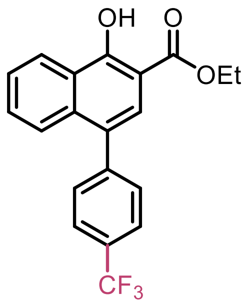
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.21, 160.28, 150.14, 137.23, 135.64, 131.12, 129.88, 129.36, 126.09, 125.65, 125.32, 125.03, 124.94, 124.13, 105.45, 61.52, 34.69, 31.52, 14.34.



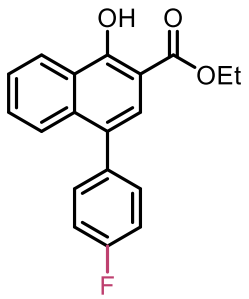
5g, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.06 (s, 1H), 8.65 – 8.34 (m, 1H), 7.87 – 7.78 (m, 1H), 7.72 (s, 1H), 7.59 – 7.50 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H).

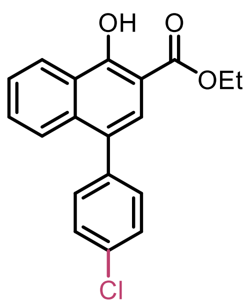
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 160.22, 158.96, 135.80, 132.60, 131.26, 130.83, 129.37, 125.98, 125.64, 125.05, 124.86, 124.14, 113.84, 105.43, 61.52, 55.44, 14.33.



5h, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.69 – 8.36 (m, 1H), 7.81 – 7.69 (m, 4H), 7.63 – 7.54 (m, 4H), 4.47 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 161.00, 144.07, 135.15, 130.65, 129.90, 129.73, 129.40 (q, J = 32.6 Hz), 126.06, 125.49, 125.44 (q, J = 3.6 Hz), 125.35, 125.18, 124.45 (×2), 105.52, 61.78, 14.40.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35 (s, 3F).



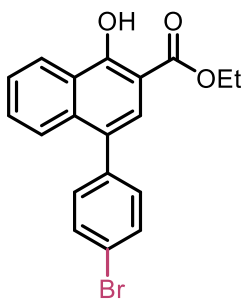
5i, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 8.54 – 8.46 (m, 1H), 7.78 – 7.72 (m, 1H), 7.70 (s, 1H), 7.61 – 7.51 (m, 2H), 7.42 – 7.37 (m, 2H), 7.18 (t, J = 8.1 Hz, 2H), 4.46 (q, J = 7.8 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.11, 163.54 (d, J = 247.2 Hz), 160.57, 136.16 (d, J = 3.5 Hz), 135.59, 131.84, 131.77, 130.11, 129.63, 125.84 (d, J = 10.8 Hz), 125.09 (×2), 124.29, 115.46 (d, J = 21.8 Hz), 105.43, 61.66, 14.38.
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.43 (s, 1F).



5j, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.54 – 8.43 (m, 1H), 7.79 – 7.71 (m, 1H), 7.70 (s, 1H), 7.60 – 7.52 (m, 2H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).

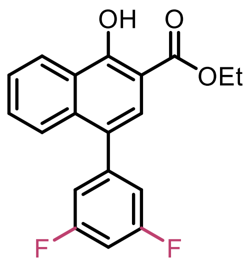
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.02, 160.64, 138.65, 135.30, 133.30, 131.53, 129.85, 129.66, 128.61, 125.85, 125.58, 125.06, 125.03, 124.28, 105.41, 61.64, 14.33.



5k, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.57 – 8.43 (m, 1H), 7.81 – 7.72 (m, 1H), 7.70 (s, 1H), 7.65 – 7.52 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.01, 160.66, 139.15, 135.23, 131.88, 131.57, 129.84, 129.67, 125.86, 125.57, 125.08, 125.00, 124.29, 121.44, 105.42, 61.64, 14.33.



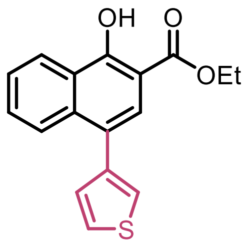
5l, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.15 (s, 1H), 8.51 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.71 (s, 1H), 7.64 – 7.50 (m, 2H), 7.00 (d, *J* = 5.9 Hz, 2H), 6.88 (t, *J* = 9.0 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.89, 164.23 (d, *J* = 13.3 Hz), 161.76 (d, *J* = 13.3 Hz), 161.00, 143.51 (t, *J* = 9.3 Hz), 134.81, 129.91, 128.80, 126.02, 125.22, 125.13, 125.08, 124.39, 113.34 (d, *J* = 7.3 Hz), 113.16 (d, *J* = 6.4 Hz), 105.34, 102.70 (t, *J* = 26.8 Hz), 61.73, 14.33.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.04 (s, 2F).

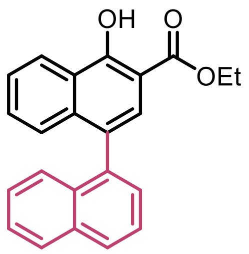
ESI-HRMS: exact mass calculated for $[M+H^+]$ requires m/z 329.0911, found m/z 329.0909.



5m, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 8.53 – 8.37 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.55 (m, 2H), 7.44 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.34 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.24 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

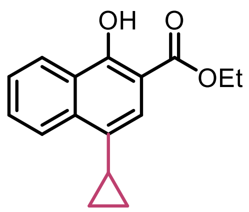
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.08, 160.51, 140.57, 135.72, 129.70, 129.59, 125.86, 125.78 (×2), 125.41, 125.05, 125.02, 124.19, 123.44, 105.43, 61.58, 14.35.



5n, Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 8.54 (d, *J* = 9.2 Hz, 1H), 7.95 (dd, *J* = 8.2, 3.8 Hz, 2H), 7.82 (s, 1H), 7.61 – 7.40 (m, 6H), 7.33 – 7.27 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

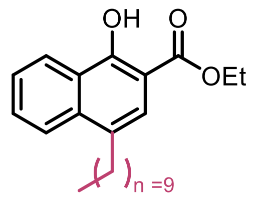
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.19, 160.72, 137.85, 136.70, 133.61, 133.14, 129.46, 129.17, 128.27 (×2), 128.06, 126.51 (×2), 126.11, 125.90, 125.83, 125.73, 125.52, 124.82, 124.05, 105.51, 61.55, 14.27.



5o, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 9.3 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.24 – 2.10 (m, 1H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 8.4 Hz, 2H), 0.72 (d, *J* = 5.5 Hz, 2H).

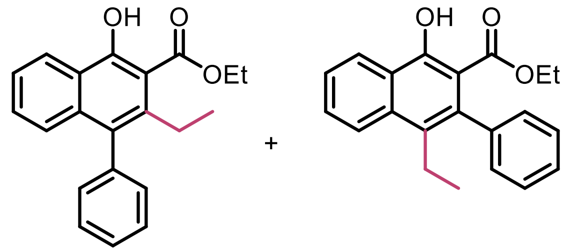
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 159.93, 137.32, 129.54, 129.28, 125.56, 124.96, 124.41, 124.31, 122.24, 105.09, 61.40, 14.39, 12.92, 6.04.



5p, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.55 – 7.45 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.85 (m, 2H), 1.74 – 1.67 (m, 2H), 1.49 – 1.44 (m, 3H), 1.28 (dt, *J* = 11.3, 6.4 Hz, 14H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 159.56, 135.82, 129.34, 129.15, 125.27, 124.52, 123.88, 123.32, 105.28, 61.37, 32.67, 31.94, 30.83, 29.84, 29.66, 29.60, 29.38, 22.72, 14.36, 14.14.

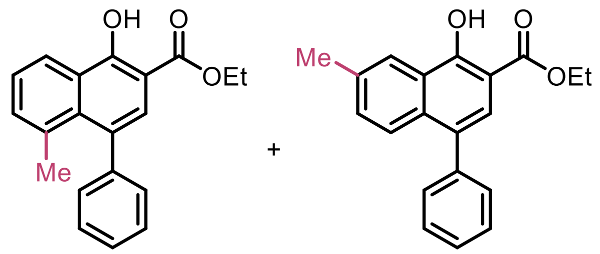


5q (left), **5q'** (right), **5q**:**5q'** = 10:1, Pale yellow solid

5q(major) ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.56 (s, 1H), 8.39 (d, *J* = 8.1 Hz, 1H), 7.42 (ddd, *J* = 7.4, 6.2, 1.6 Hz, 2H), 7.37 (ddt, *J* = 12.2, 5.6, 1.7 Hz, 3H), 7.21 – 7.18 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.81 (q, *J* = 7.3 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

5q(major) ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.73, 161.66, 140.01, 138.40, 136.20, 130.90, 130.85, 129.32, 128.38, 127.03, 126.38, 124.92, 123.85, 123.54, 105.97, 61.86, 25.95, 16.30, 14.06.

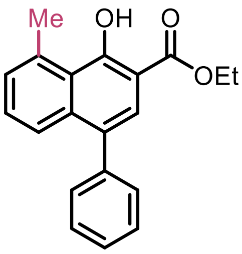
ESI-HRMS: exact mass calculated for $[M+H^+]$ requires m/z 321.1412, found m/z 321.1405.



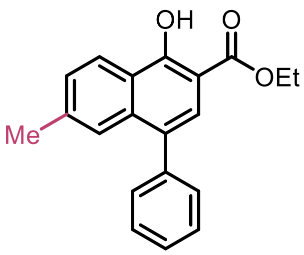
5r (left), **5r'** (right), **5r**:**5r'** = 1:2, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.06 (s, 1H), 12.04 (s, 2H), 8.45 (d, *J* = 10.0 Hz, 2H), 8.29 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.68 (s, 1H), 7.62 (s, 2H), 7.54 – 7.28 (m, 22H), 4.45 (p, *J* = 7.0 Hz, 6.5H), 2.55 (s, 3.2H), 1.99 (s, 6.7H), 1.42 (q, *J* = 7.3 Hz, 10.3H).

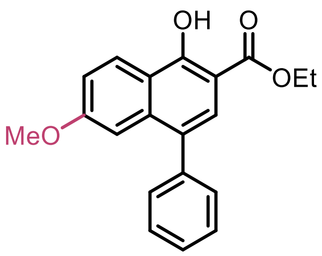
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.25, 170.98, 160.58, 160.00, 144.64, 140.40, 135.60, 135.40, 134.67, 133.71, 133.30, 131.56, 131.27, 131.08, 130.22, 129.94, 128.37, 127.75, 127.17, 127.13, 126.83, 126.14, 125.85, 125.53, 125.11, 124.01, 123.19, 122.63, 105.48, 104.55, 61.51, 24.93, 21.68, 14.34.



5s, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (s, 1H), 7.70 (s, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.32 (m, 4H), 7.27 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 3.04 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.75, 163.75, 141.07, 138.66, 137.50, 131.37, 130.31, 129.00, 128.94, 128.33, 127.12, 125.10, 124.44 (×2), 105.59, 61.50, 25.52, 14.32.

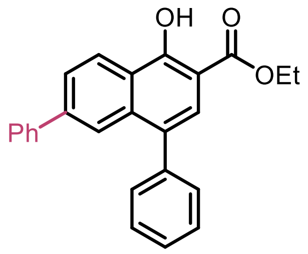


5t, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 1H), 8.39 (d, J = 8.5 Hz, 1H), 7.70 (s, 1H), 7.57 (s, 1H), 7.53 – 7.41 (m, 5H), 7.38 (d, J = 8.6 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 160.47, 140.45, 139.82, 135.80, 130.63, 130.25, 128.39, 127.81, 127.15, 125.17, 125.10, 124.06, 123.08, 104.78, 61.44, 22.18, 14.34.

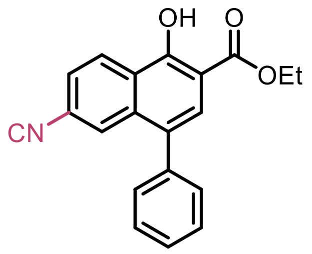


5u, Pale yellow solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 1H), 8.40 (d, J = 9.1 Hz, 1H), 7.70 (s, 1H), 7.48 (d, J = 3.0 Hz, 4H), 7.43 (dd, J = 6.1, 2.6 Hz, 1H), 7.17 (dd, J = 9.1, 2.5 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).

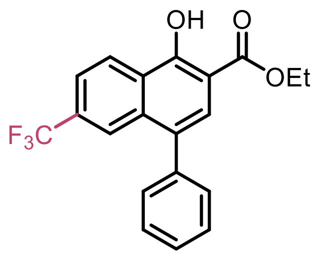
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 160.65, 160.50, 140.46, 137.52, 130.11, 130.07, 128.50, 127.22, 126.05, 125.93, 119.80, 117.23, 105.34, 103.94, 61.36, 55.31, 14.36.



5v, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 8.57 (d, J = 8.7 Hz, 1H), 8.02 (s, 1H), 7.86 – 7.72 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 3.4 Hz, 4H), 7.47 – 7.40 (m, 3H), 7.39 – 7.33 (m, 1H), 4.47 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 160.35, 142.12, 140.82, 140.21, 135.86, 131.42, 130.25, 128.94, 128.52, 127.86, 127.60, 127.32, 125.57, 125.30, 124.83, 124.08, 123.92, 105.49, 61.58, 14.36.
ESI-HRMS: exact mass calculated for [$M+H^+$] requires m/z 369.1412, found m/z 369.1417.

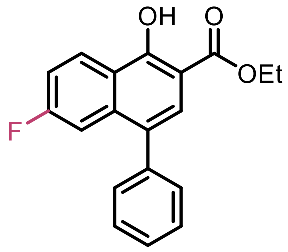


5w, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.58 (d, J = 8.7 Hz, 1H), 8.17 (s, 1H), 7.86 (s, 1H), 7.67 (dd, J = 8.6, 1.7 Hz, 1H), 7.51 (ddd, J = 12.7, 7.6, 5.9 Hz, 3H), 7.44 – 7.38 (m, 2H), 4.49 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 159.58, 138.70, 134.55, 131.90, 131.47, 130.09, 128.82, 127.98, 126.78, 126.61, 126.33, 125.59, 118.96, 112.77, 107.91, 62.09, 14.27.

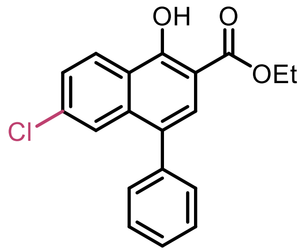


5x, White solid

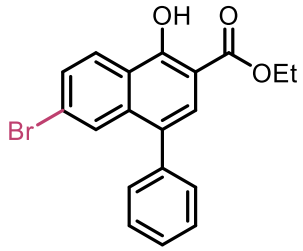
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.15 (s, 1H), 8.66 (d, *J* = 8.7 Hz, 1H), 8.15 (s, 1H), 7.88 (s, 1H), 7.75 (d, *J* = 10.8 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.53 – 7.44 (m, 3H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ170.86, 159.87, 139.29, 134.69, 131.94, 131.03 (q, *J* = 32.3 Hz),130.18, 128.79, 127.82, 126.62, 126.48, 125.54, 124.27 (q, *J* = 273.8 Hz), 123.51 (q, *J* = 4.5 Hz), 121.44 (q, *J* = 2.8 Hz),107.24, 61.99, 14.36.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62 (s, 3F).



5y, White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H), 8.51 (dd, *J* = 9.2, 5.9 Hz, 1H), 7.77 (s, 1H), 7.55 – 7.40 (m, 6H), 7.29 (ddd, *J* = 9.3, 8.1, 2.7 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 164.60 (d, *J* = 250.2 Hz), 160.34, 139.72, 137.38 (d, *J* = 9.2 Hz), 130.62 (d, *J* = 5.0 Hz), 130.05, 128.59, 127.50, 127.24 (d, *J* = 9.5 Hz), 126.24, 121.92, 115.73 (d, *J* = 24.8 Hz), 110.09 (d, *J* = 22.6 Hz), 105.09 (d, *J* = 1.8 Hz), 61.63, 14.32.
^{19}F NMR (376 MHz, $CDCl_3$) δ -108.85 (s, 1F).



5z, Pale yellow solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 8.43 (d, *J* = 8.9 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.54 – 7.41 (m, 6H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 160.20, 139.54, 136.42, 136.02, 130.42, 130.13, 128.61, 127.55, 126.54, 126.32, 125.99, 124.95, 123.32, 105.78, 61.71, 14.31.

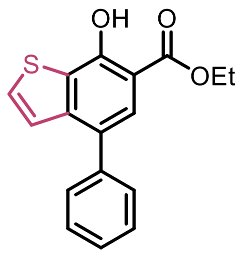


5aa, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 8.35 (d, *J* = 8.9 Hz, 1H), 7.95 (s, 1H), 7.75 (s, 1H), 7.62 (d, *J* = 11.0 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 3H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 160.26, 139.49, 136.68, 130.35, 130.13, 129.15, 128.63, 128.19, 127.56, 126.32, 126.00, 124.70, 123.57, 105.86, 61.73, 14.31.

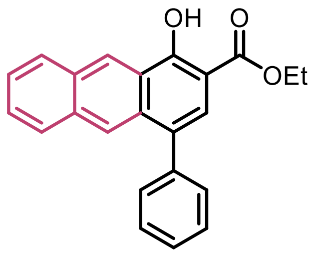
ESI-HRMS: exact mass calculated for $[M+H^+]$ requires m/z 371.0205, found m/z 371.0213.



5ab, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 7.79 (s, 1H), 7.73 – 7.65 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.38 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

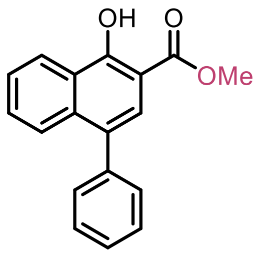
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.05, 157.64, 146.19, 139.92, 130.37, 128.88, 128.20, 127.97, 127.85, 125.73, 124.30, 122.02, 107.43, 61.54, 14.35.



5ac, Pale yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 8.44 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.38 (m, 6H), 7.11 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

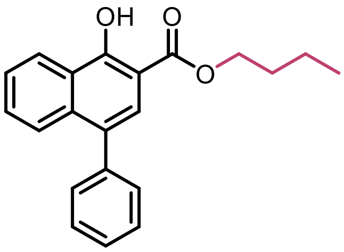
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.80, 159.33, 144.94, 134.84, 133.66, 131.31, 129.81, 129.35, 129.22, 129.04, 128.79, 128.51, 127.42, 127.22, 127.07, 124.98, 123.91, 120.92, 106.90, 61.65, 14.35.



5ad, White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.55 – 8.46 (m, 1H), 7.86 – 7.79 (m, 1H), 7.74 (s, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.41 (m, 5H), 3.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 160.21, 140.02, 135.43, 131.19, 130.06, 129.38, 128.25, 127.11, 125.80, 125.60, 124.88, 124.78, 124.05, 105.08, 52.22.

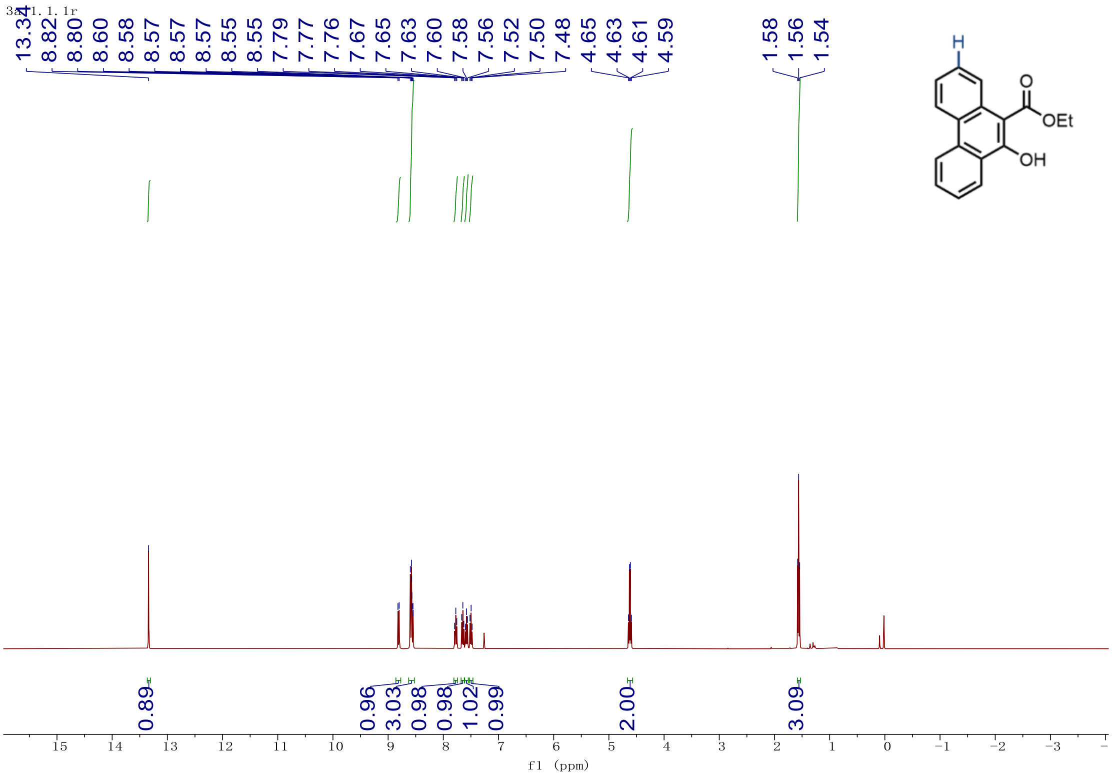


5ae, White solid

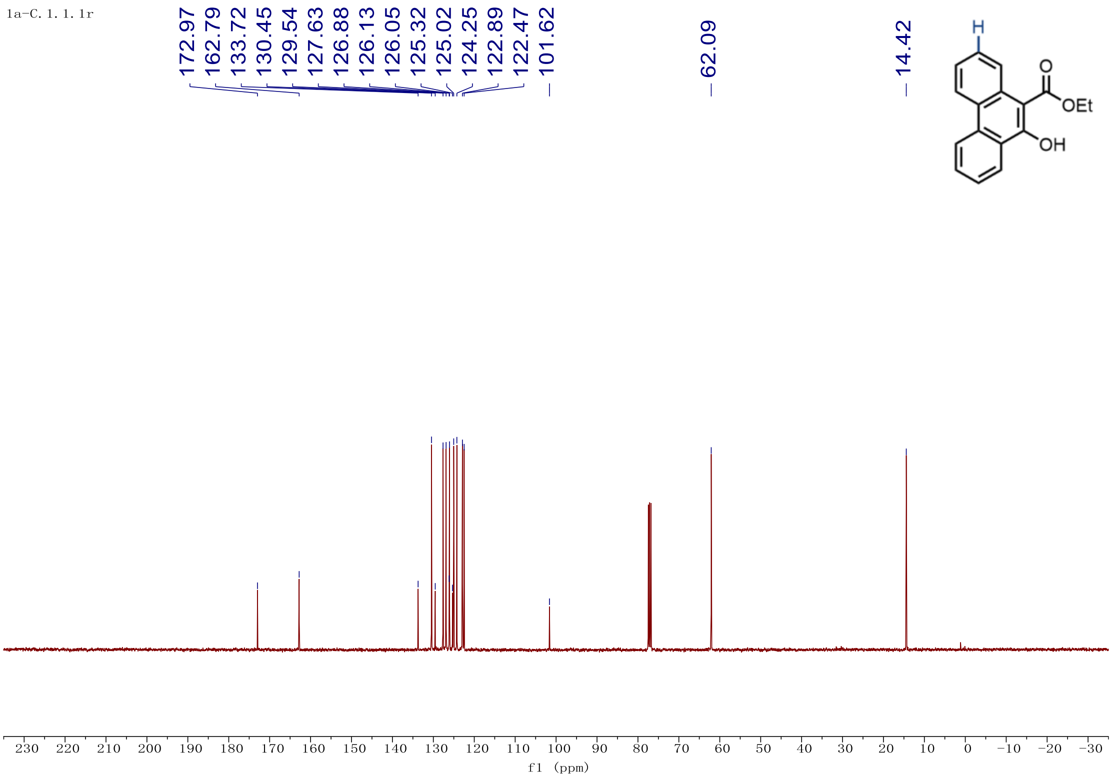
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.56 – 8.46 (m, 1H), 7.85 – 7.79 (m, 1H), 7.73 (s, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.43 (m, 5H), 4.41 (t, J = 6.7 Hz, 2H), 1.79 (p, J = 7.0 Hz, 2H), 1.53 – 1.44 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.23, 160.43, 140.26, 135.53, 131.19, 130.27, 129.46, 128.41, 127.25, 125.93, 125.71, 125.04, 124.87, 124.16, 105.45, 65.41, 30.72, 19.27, 13.80.

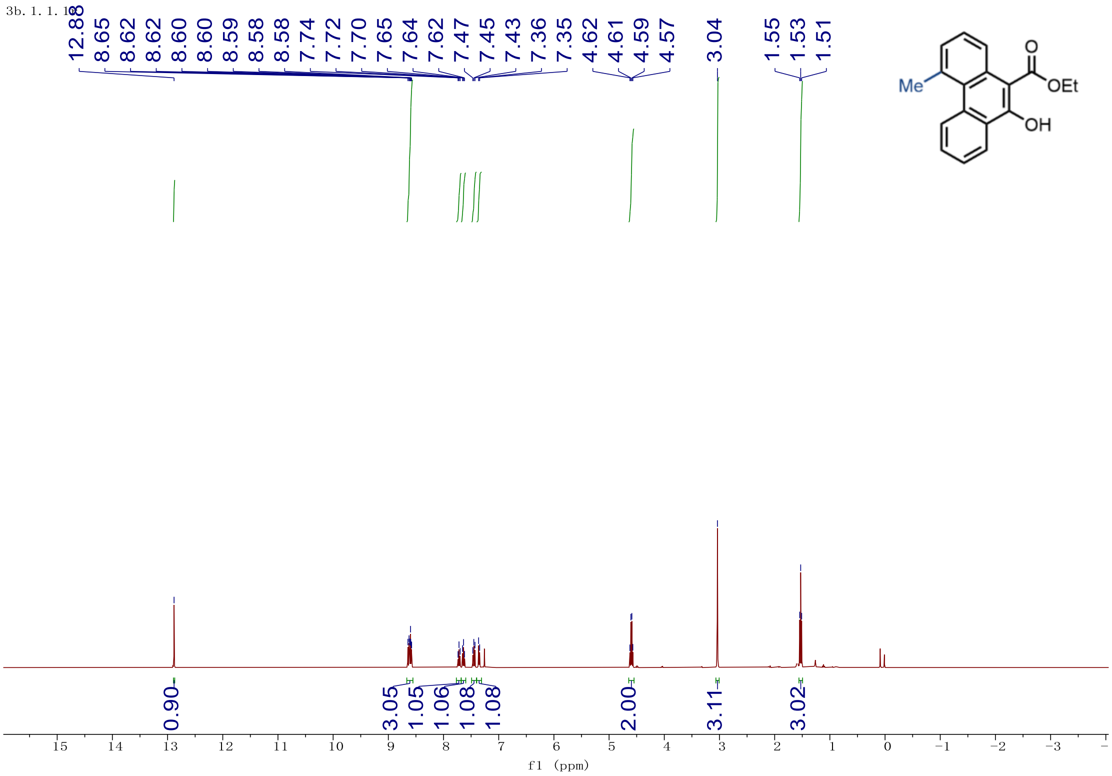
2a ^{1}H NMR



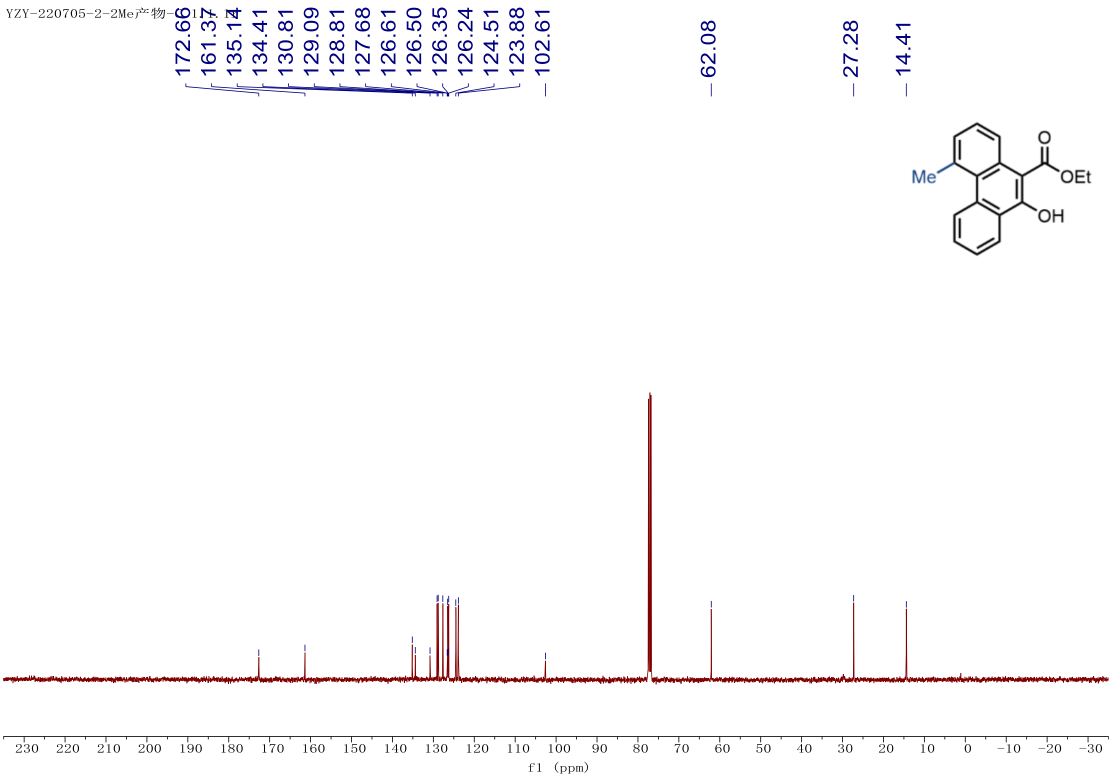
2a ^{13}C NMR



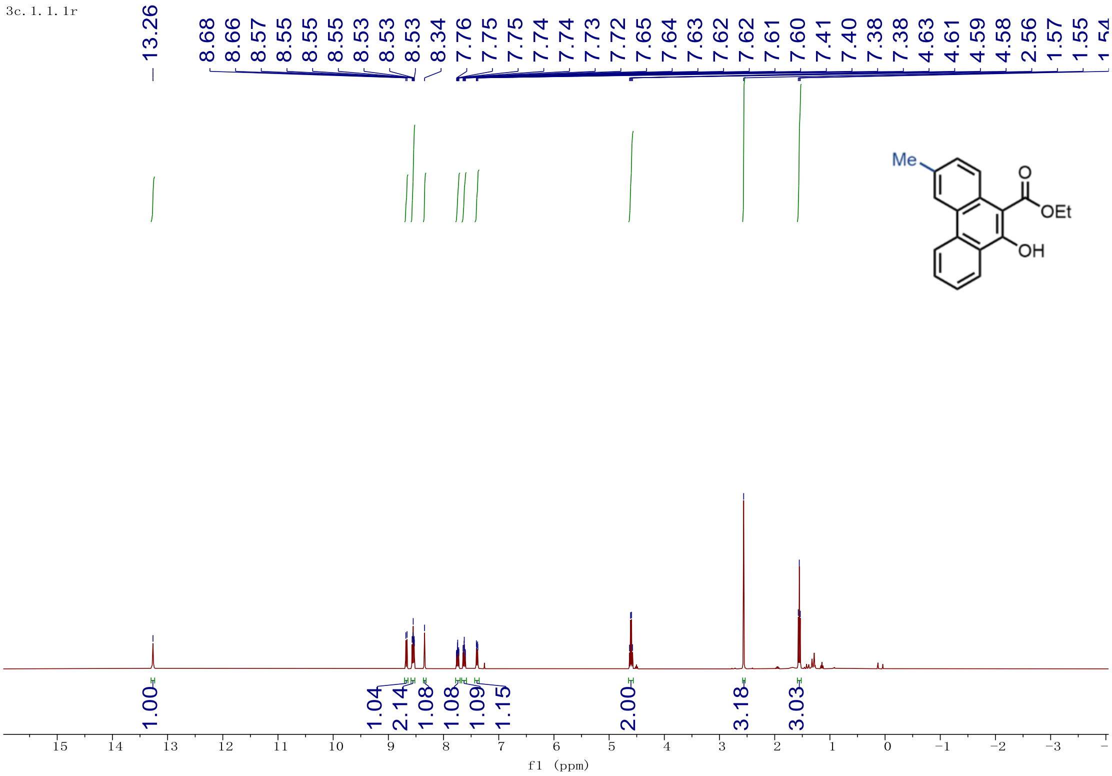
2b ^{1}H NMR



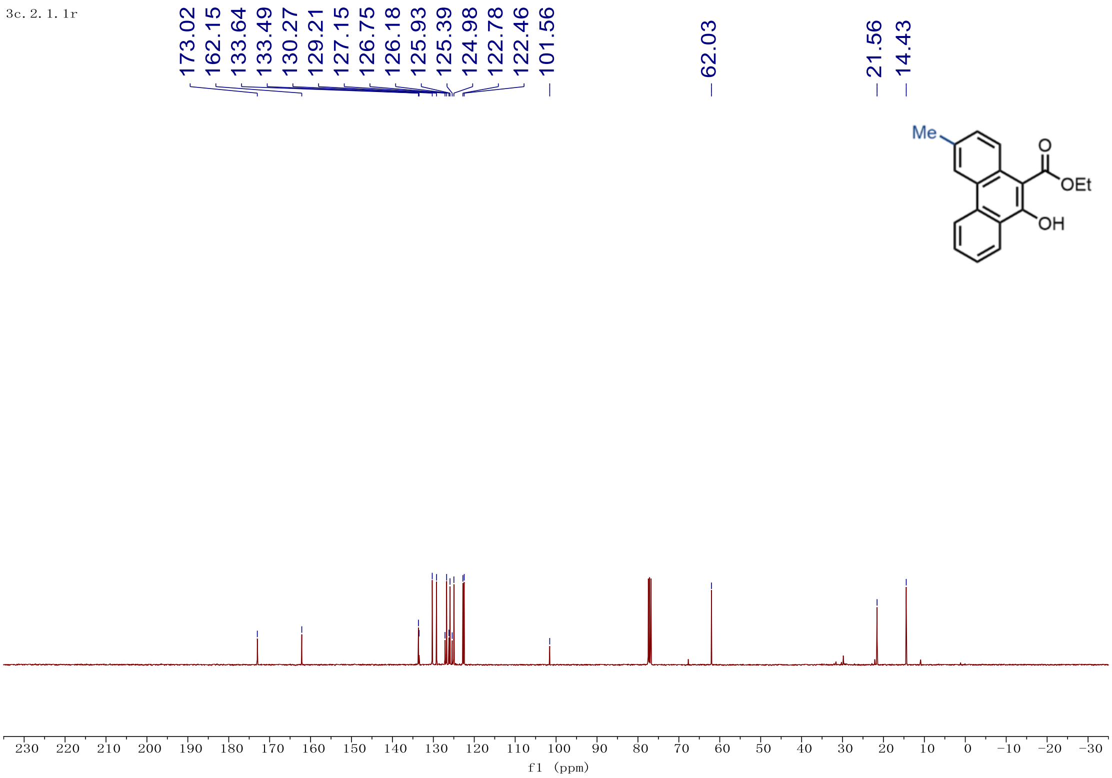
2b ^{13}C NMR



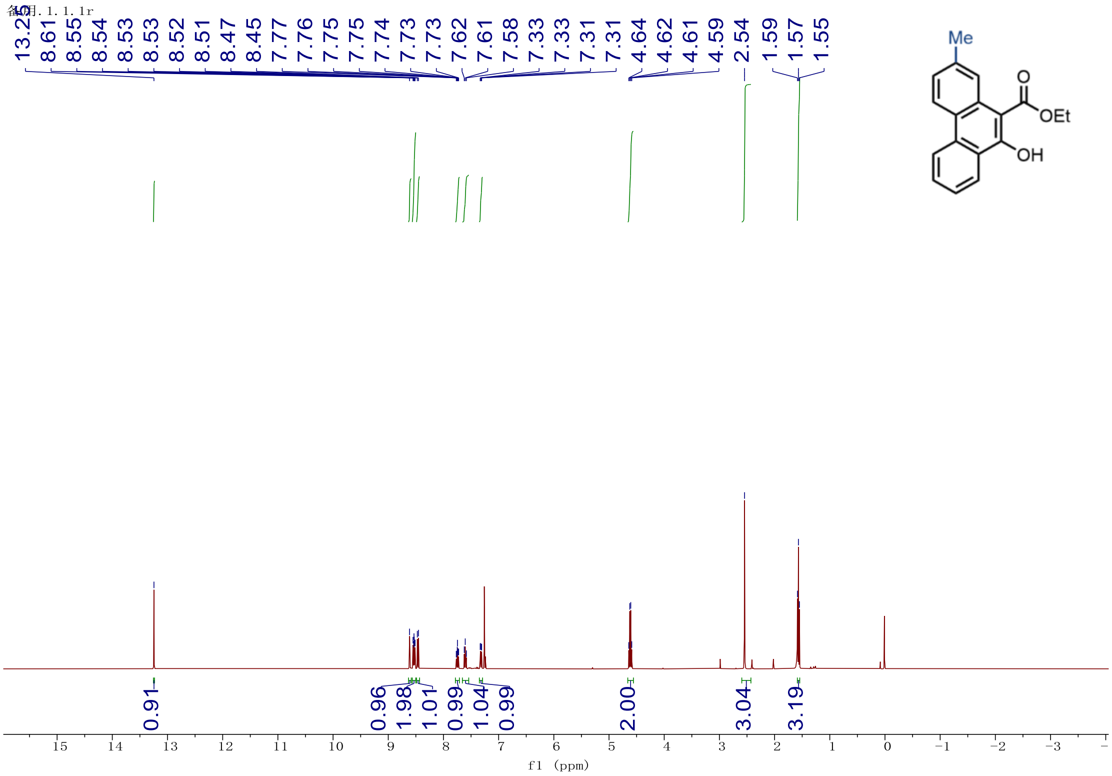
2c ^{1}H NMR



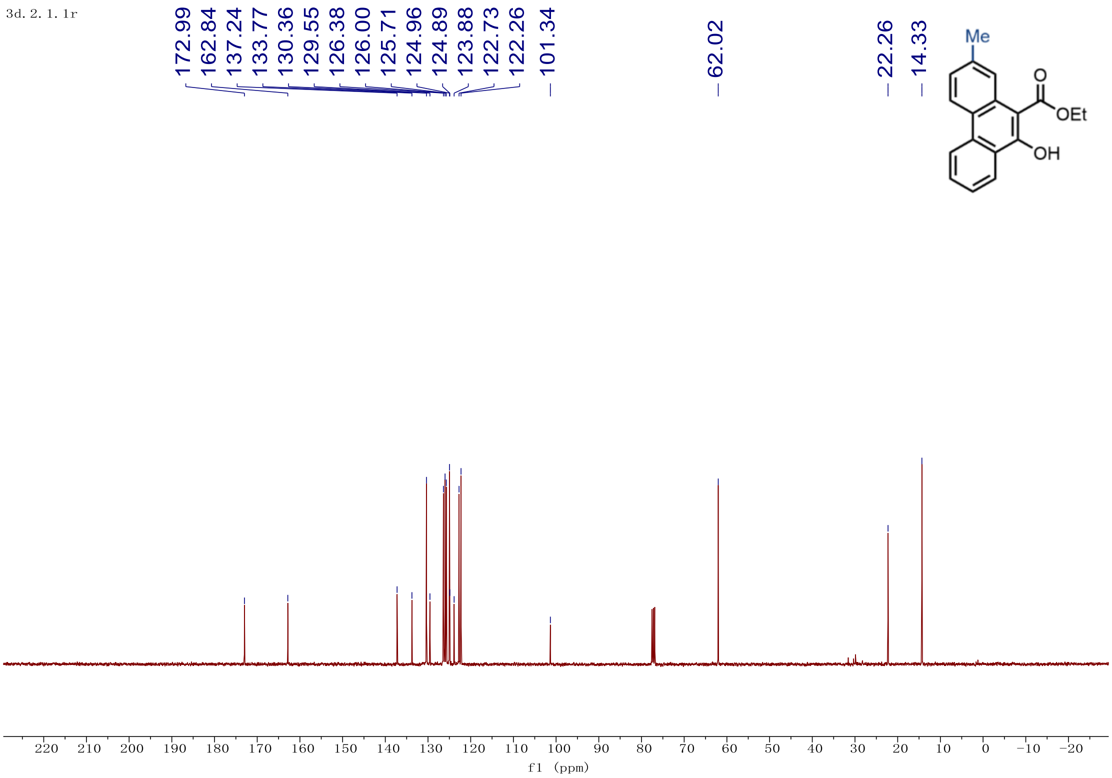
2c ^{13}C NMR



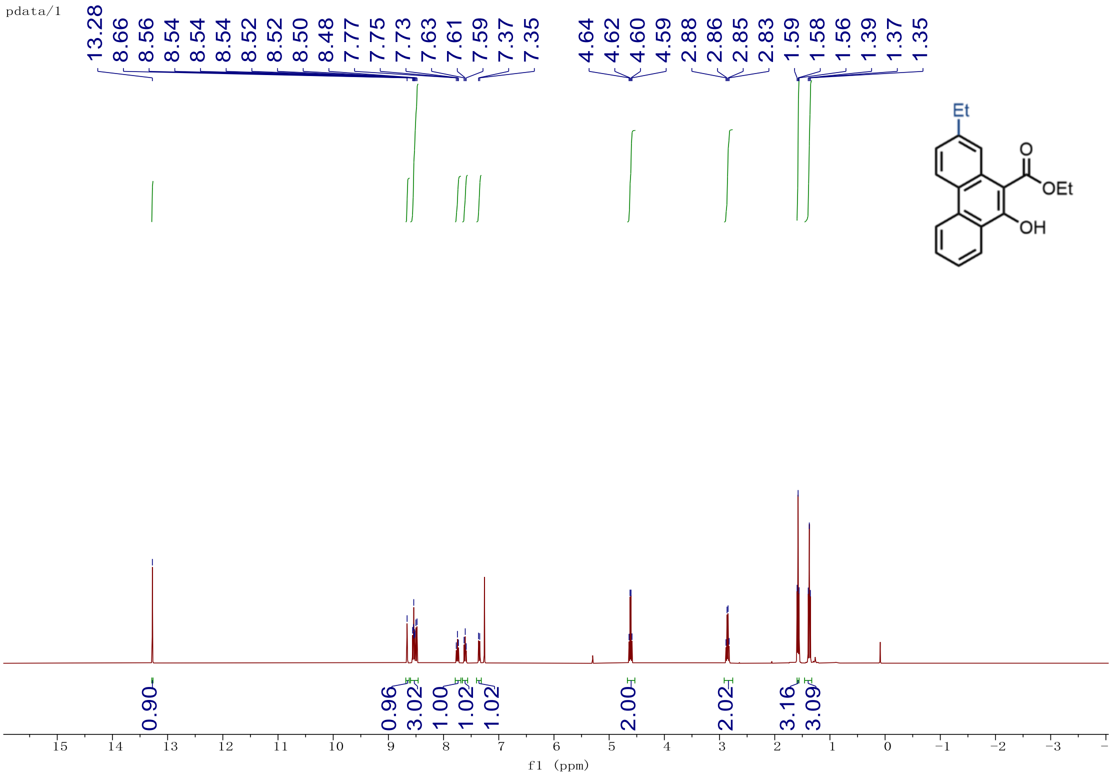
2d ^{1}H NMR



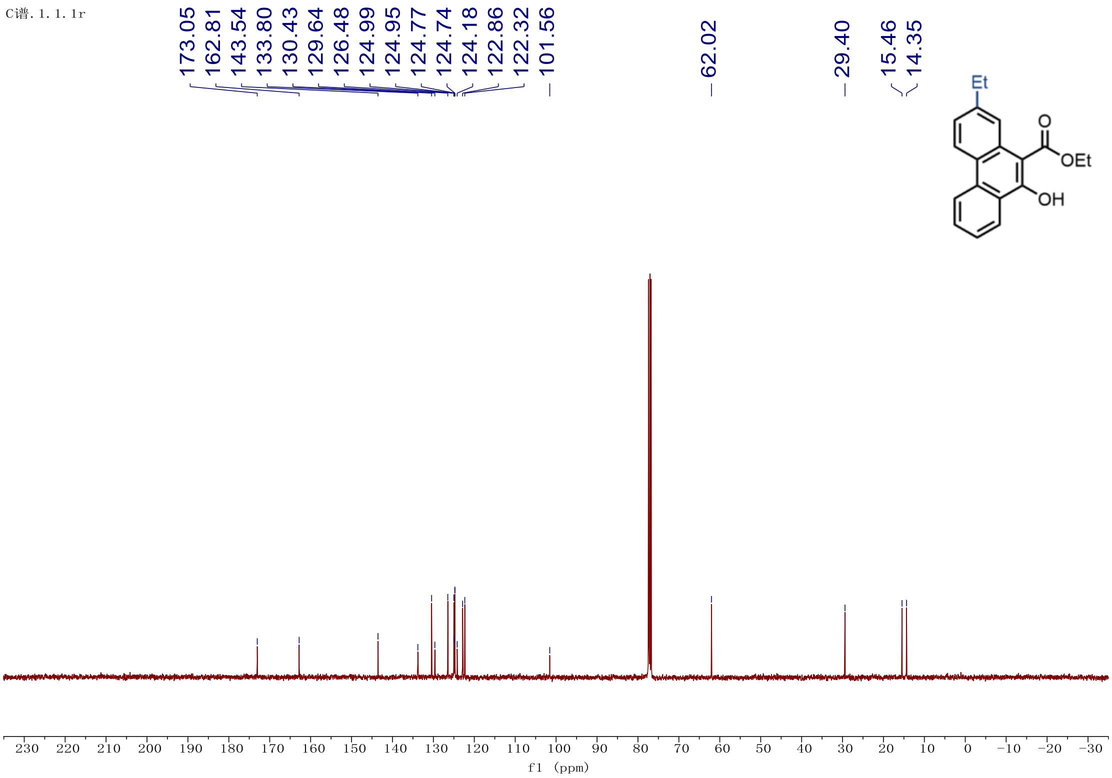
2d ^{13}C NMR



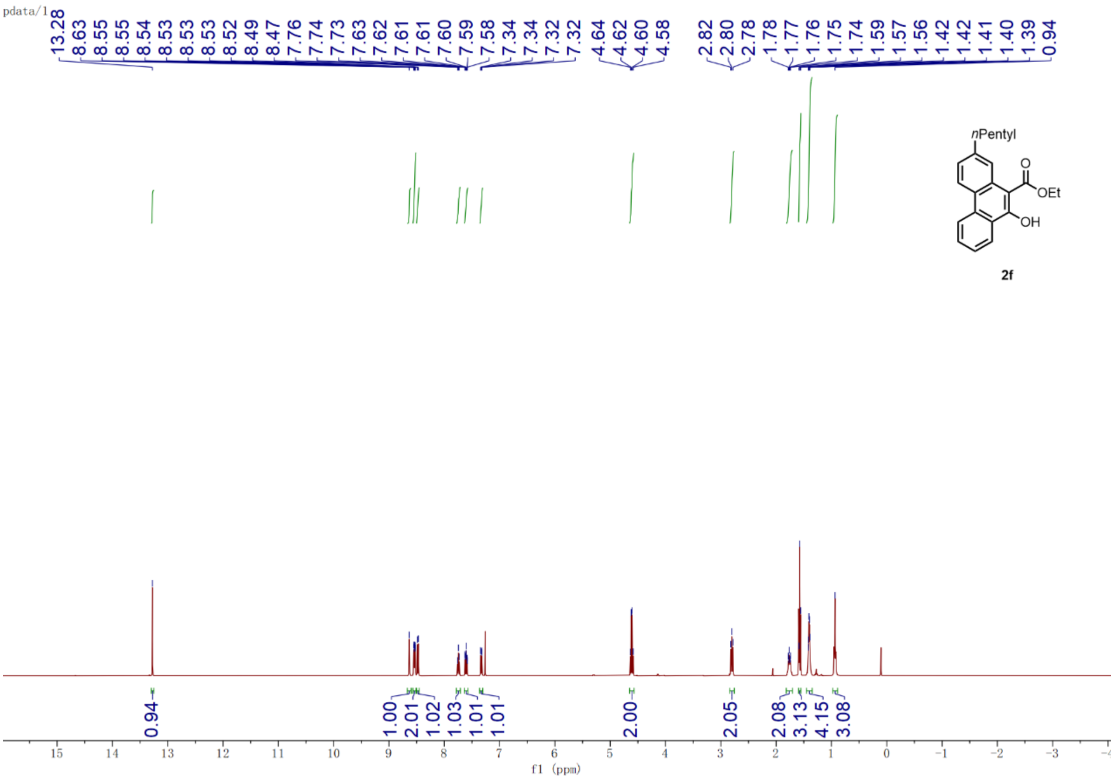
2e ^{1}H NMR



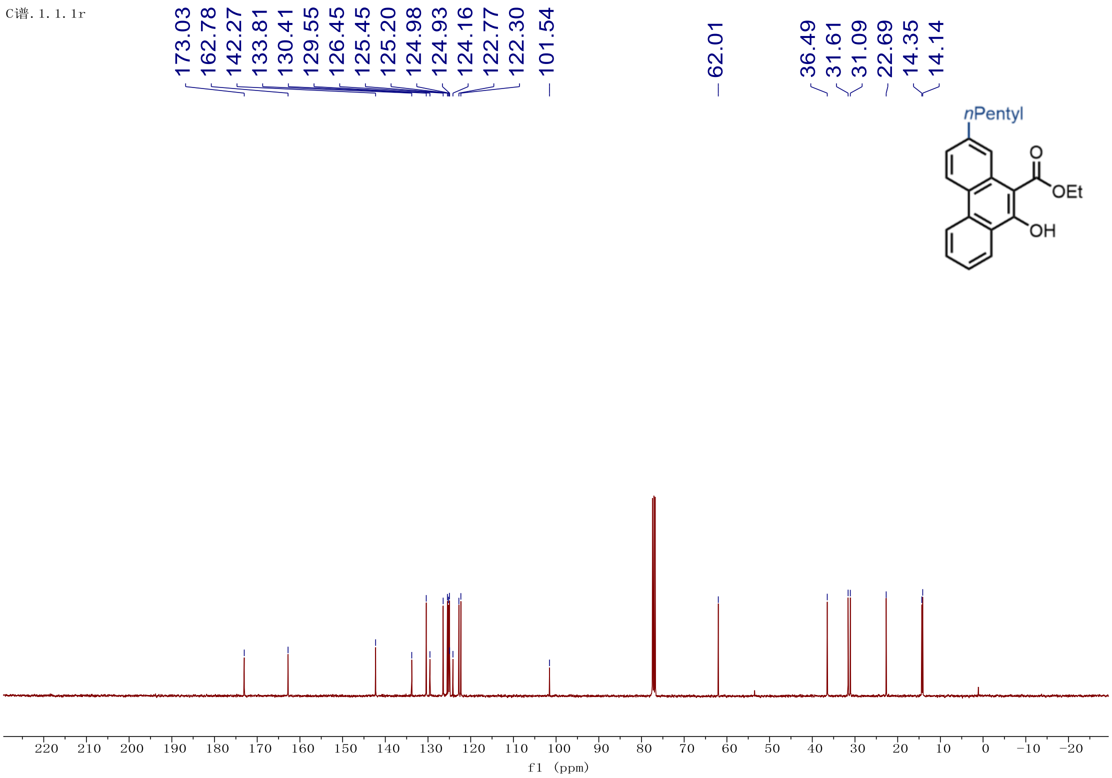
2e ^{13}C NMR



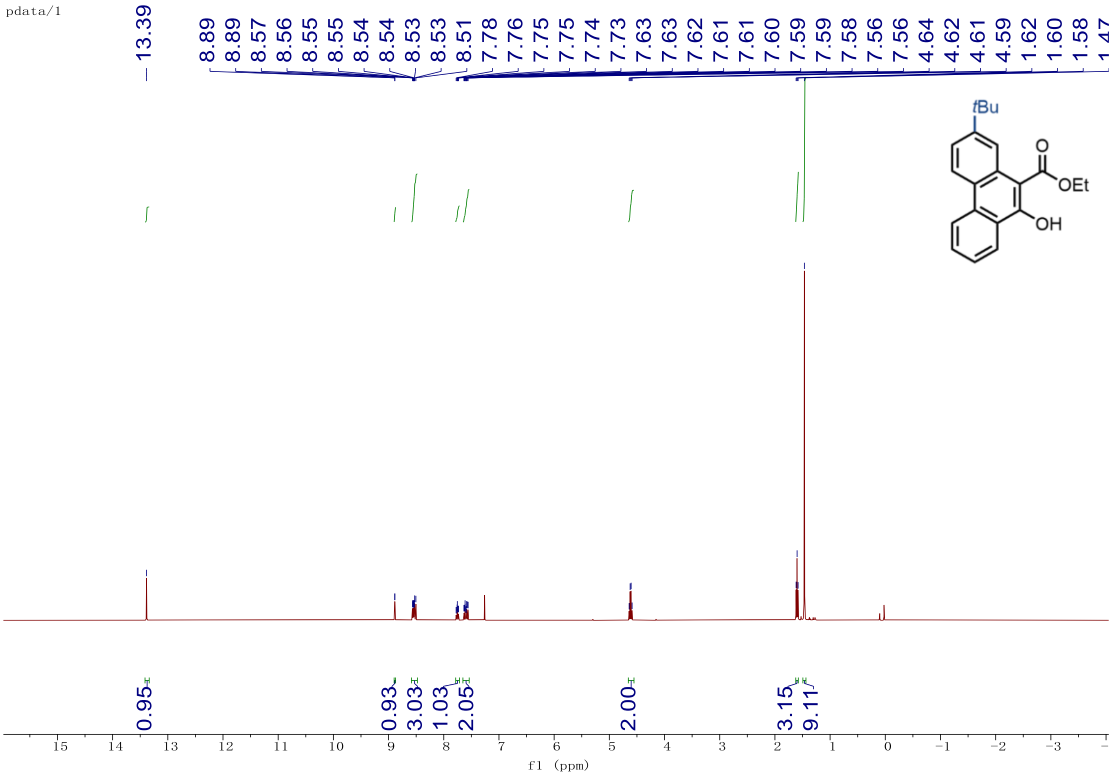
2f ^{1}H NMR



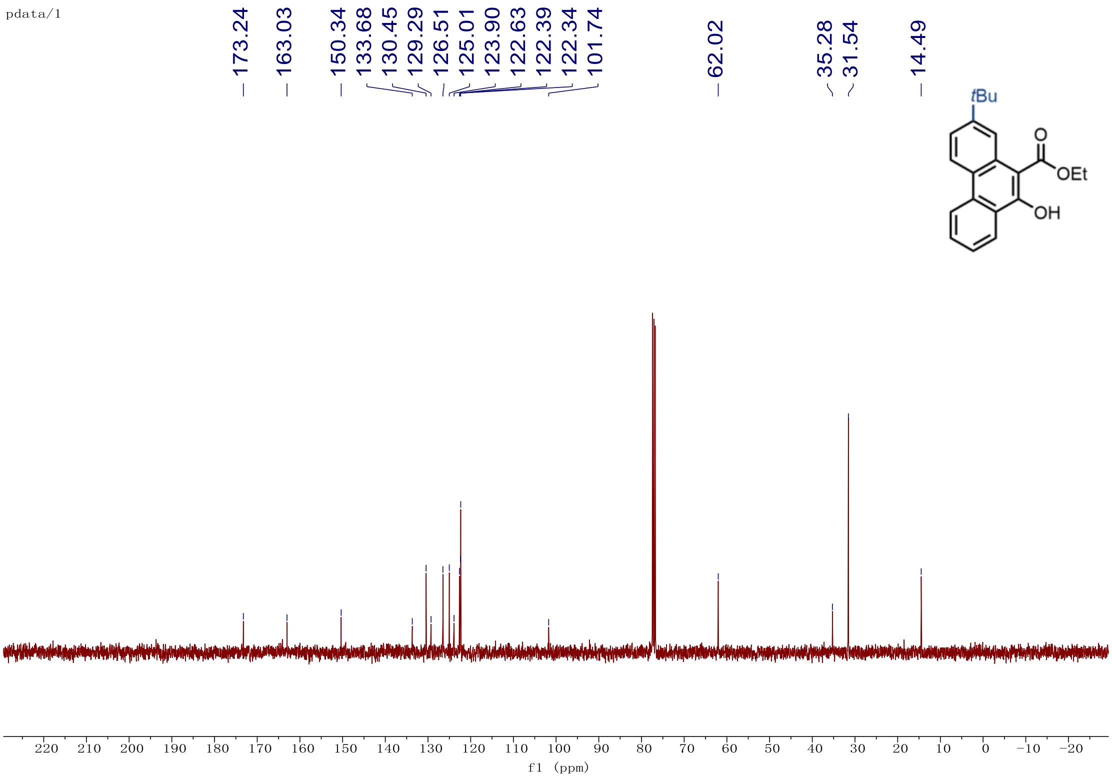
2f ^{13}C NMR



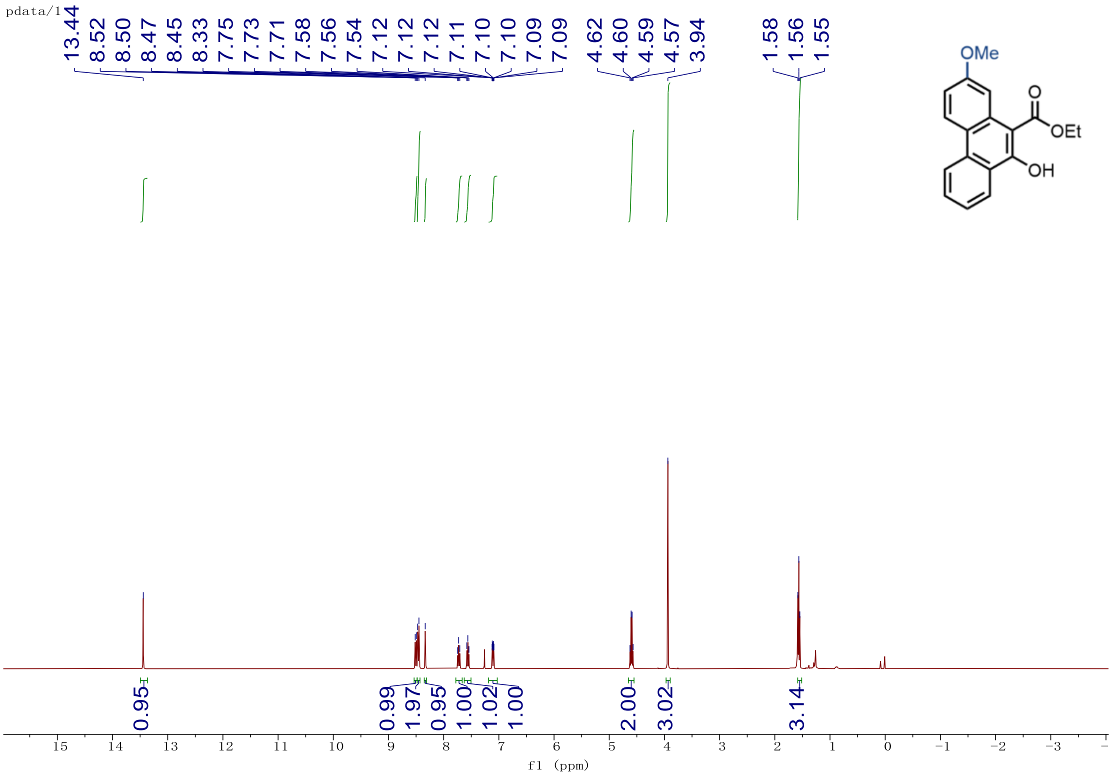
2g ^{1}H NMR



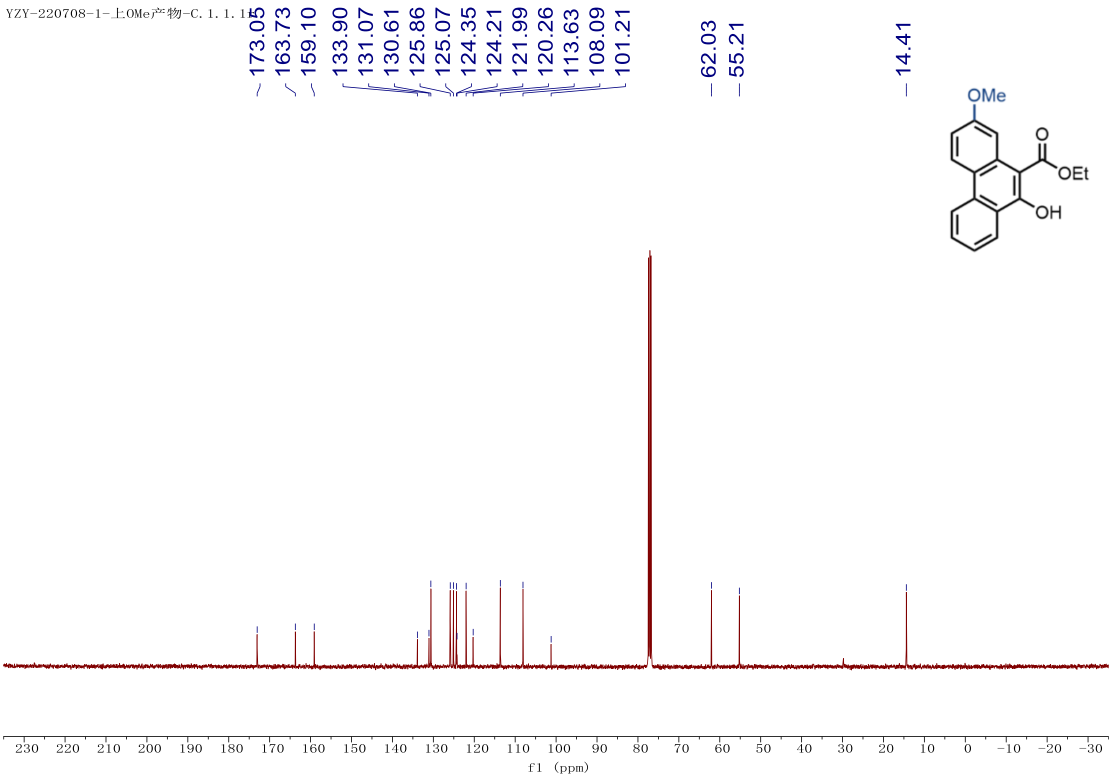
2g ^{13}C NMR



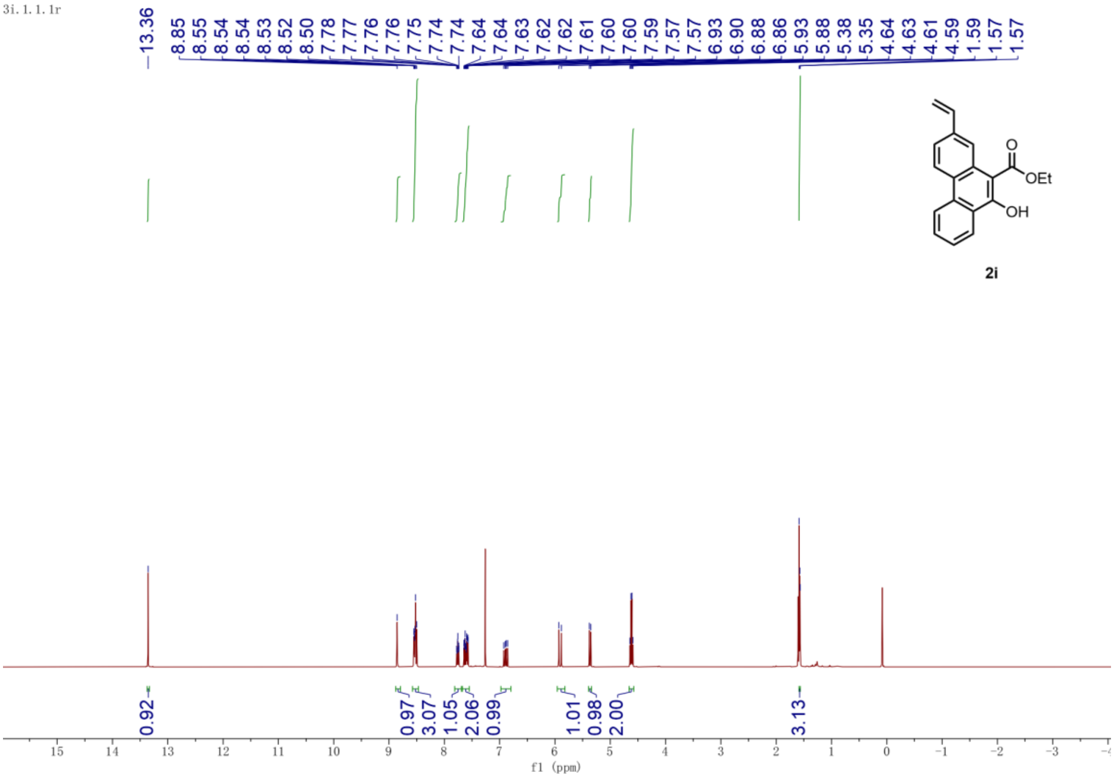
2h ^{1}H NMR



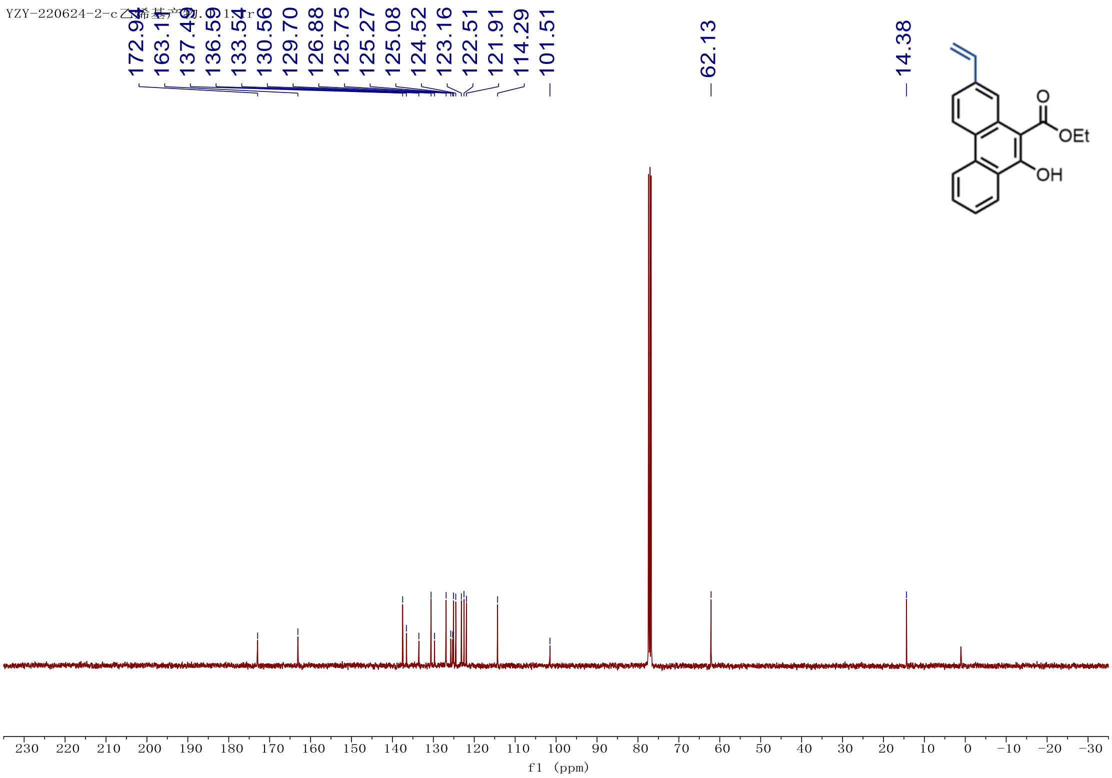
2h ^{13}C NMR



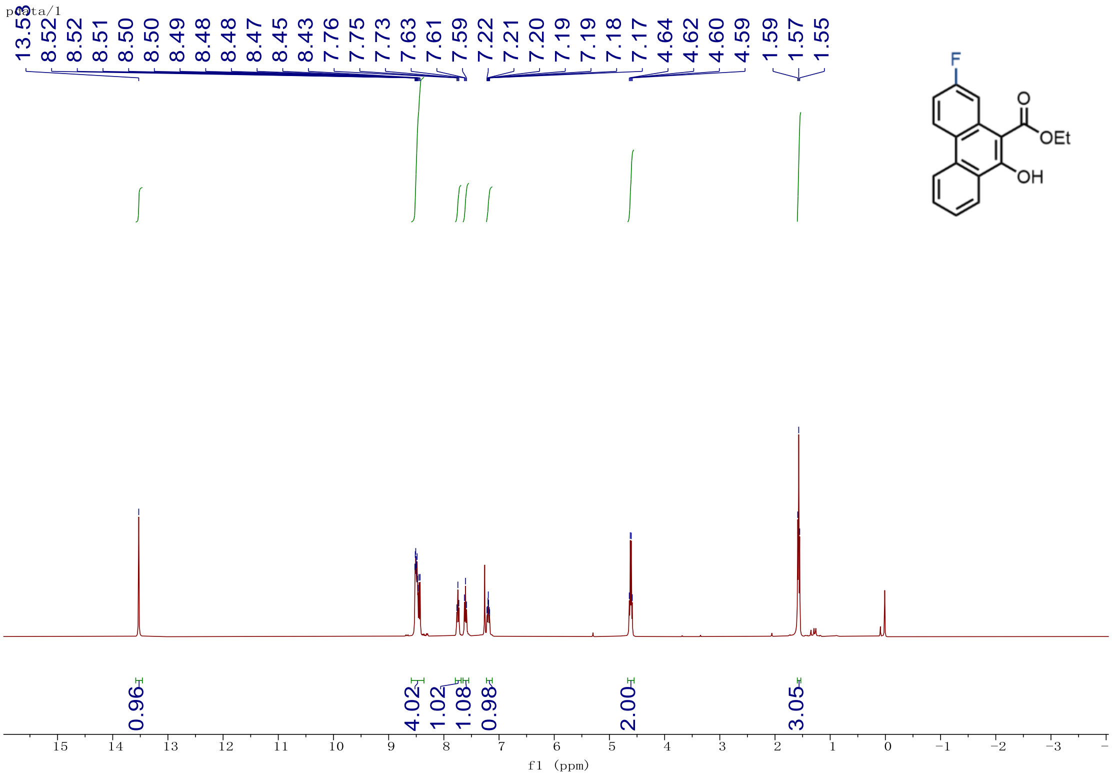
2i ^{1}H NMR



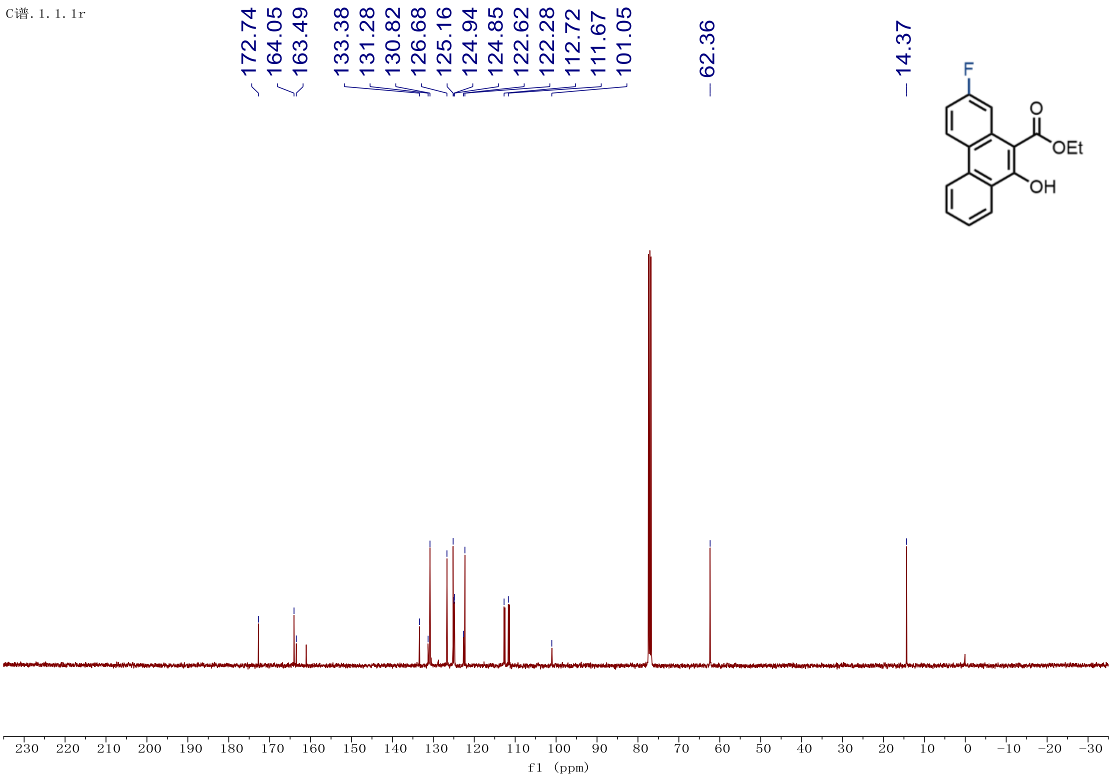
2i ^{13}C NMR



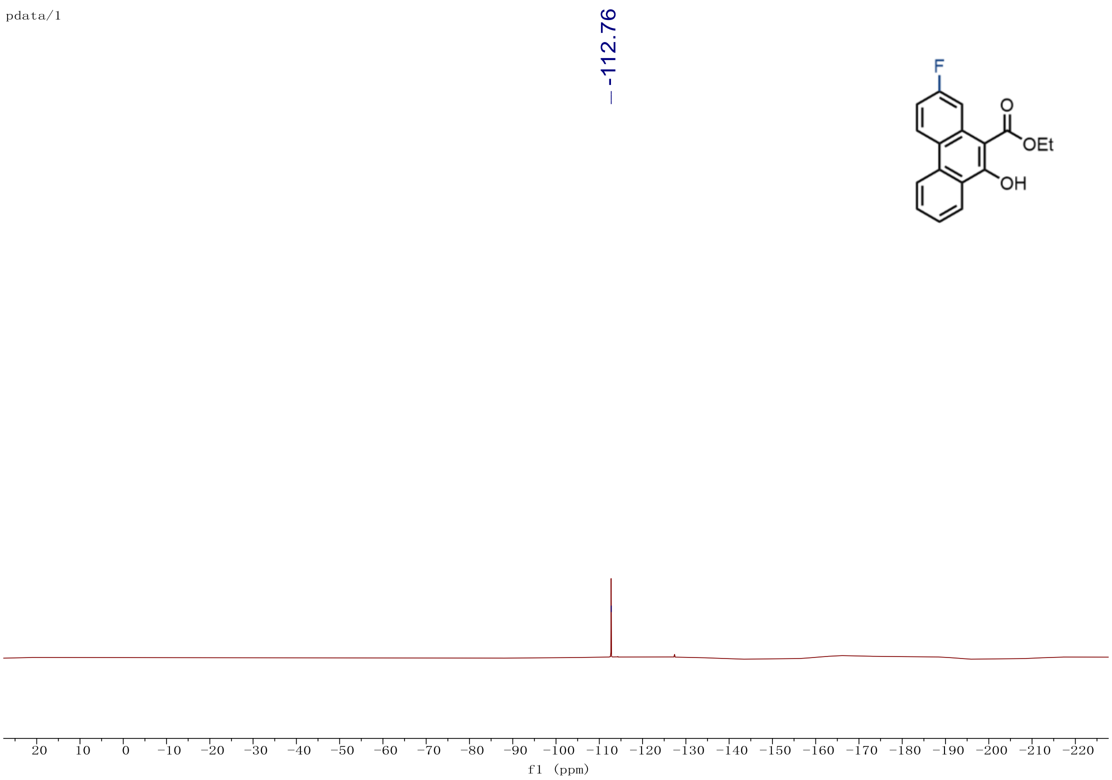
2j ^{1}H NMR



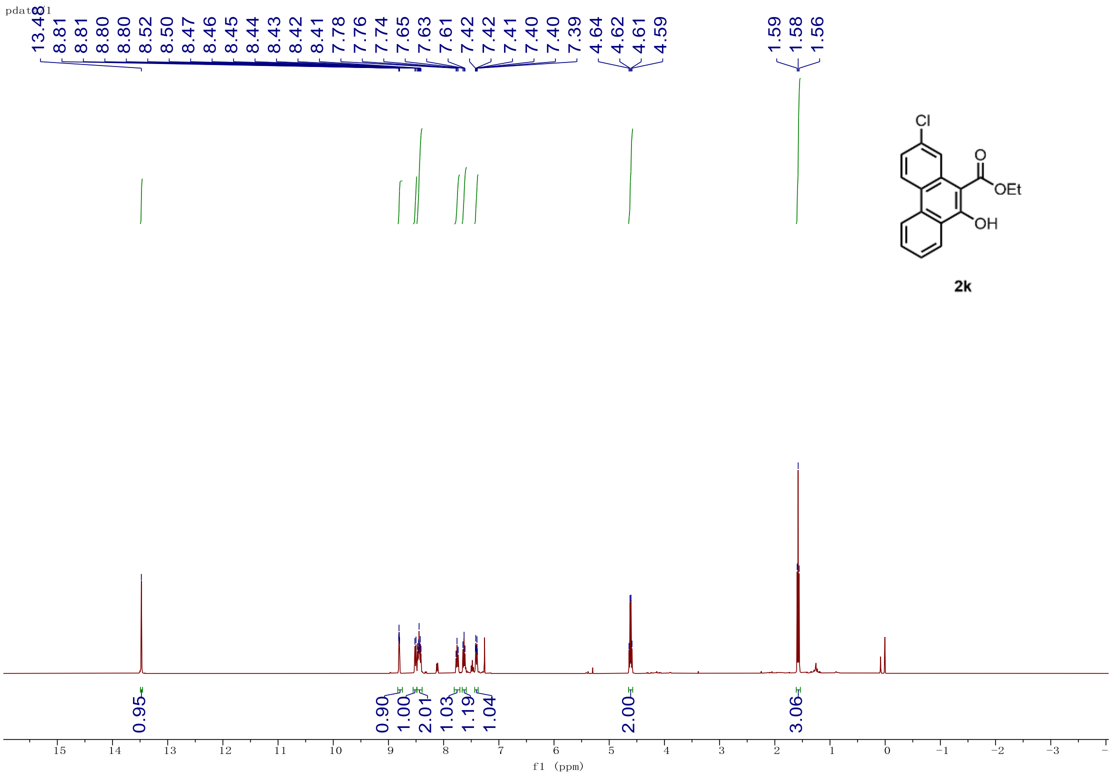
2j ^{13}C NMR



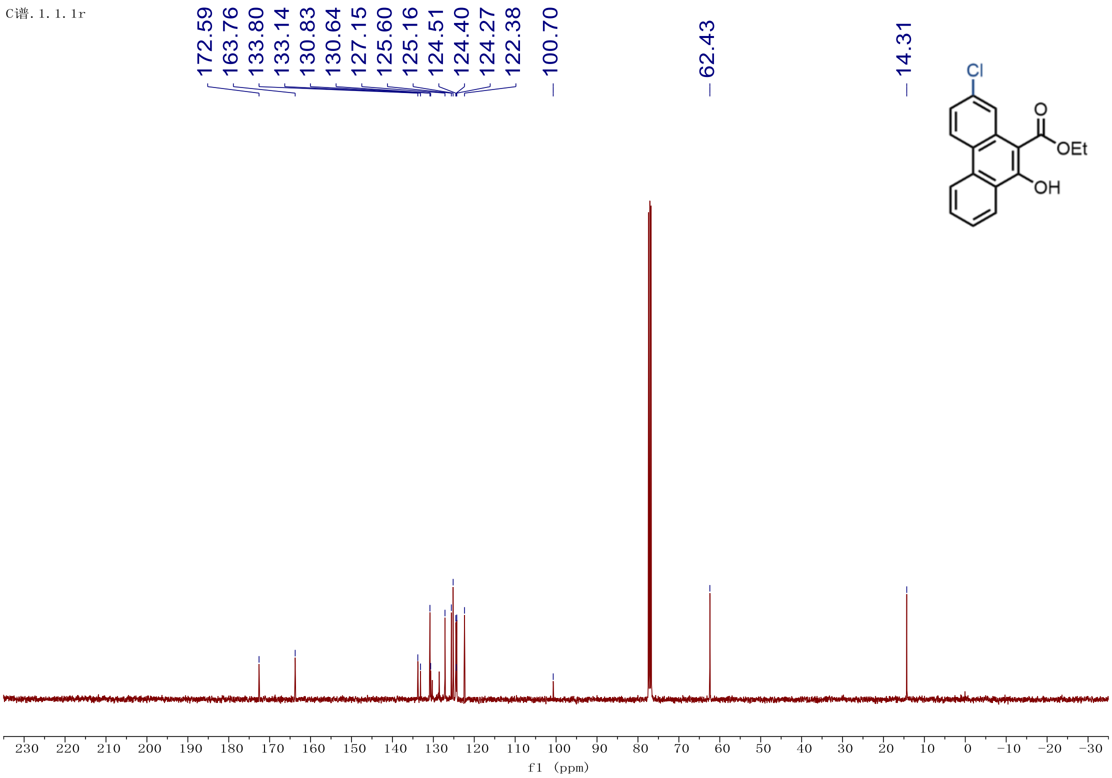
2j ^{19}F NMR


pdata/1
-112.76
F
O
OEt
OH
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

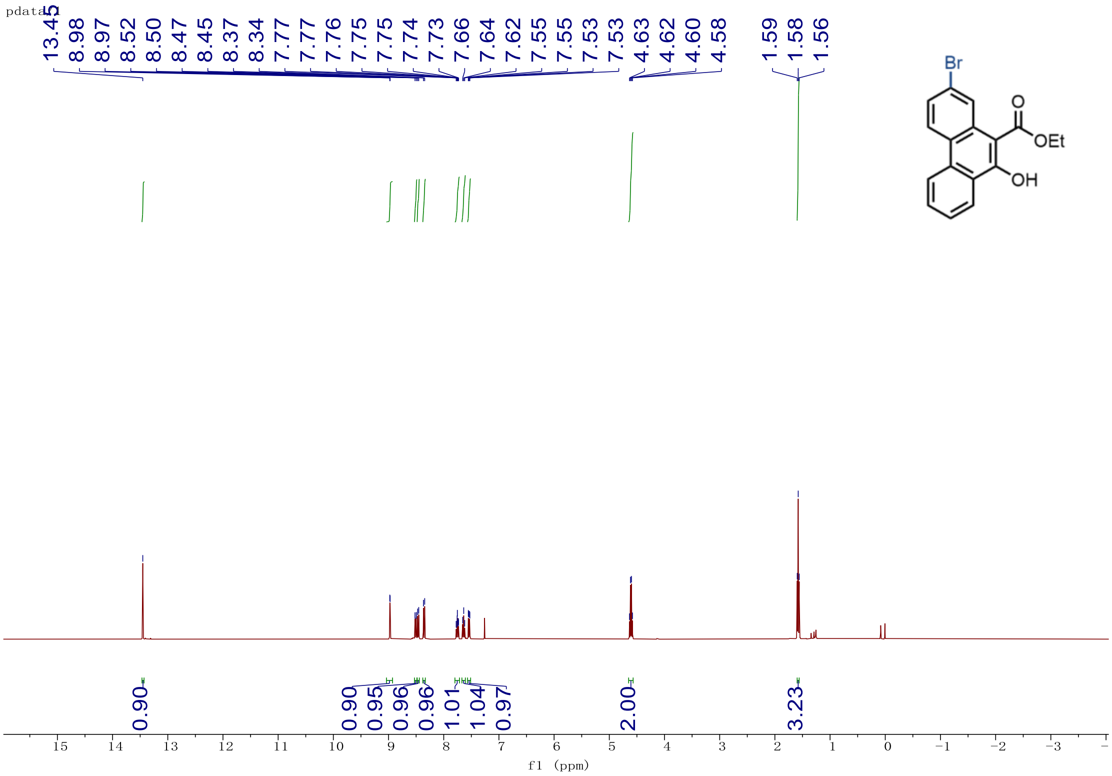
2k ^{1}H NMR



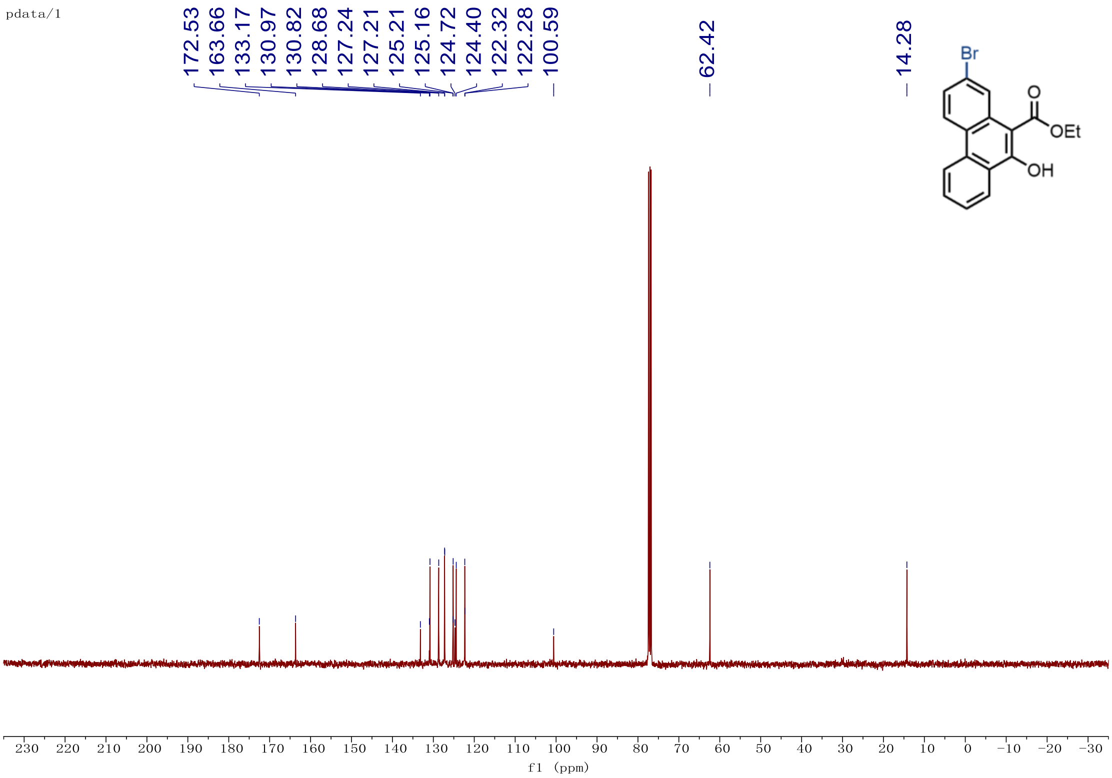
2k ^{13}C NMR



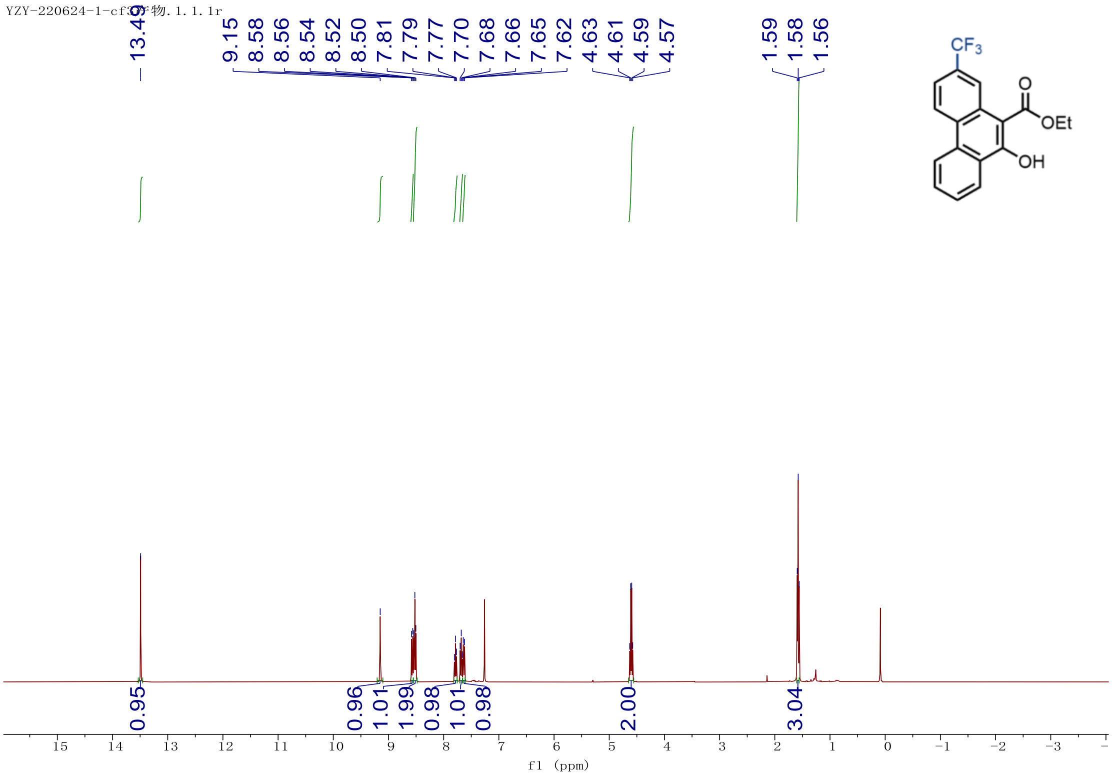
2l ^{1}H NMR



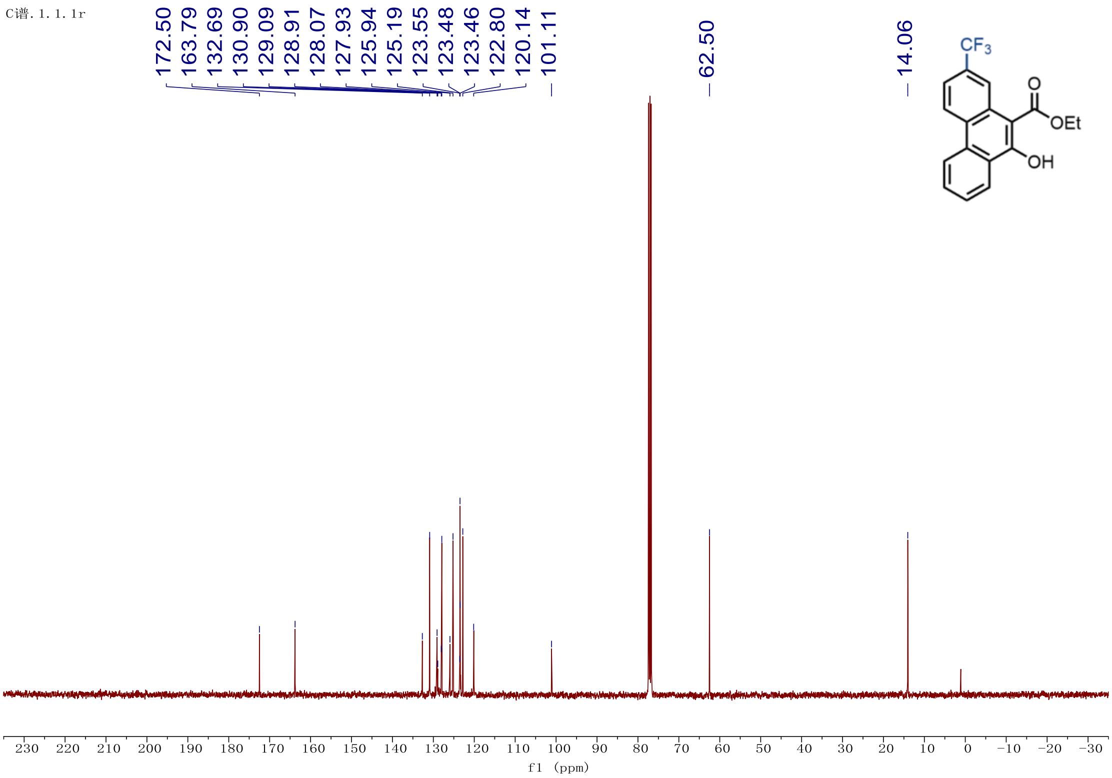
2l ^{13}C NMR



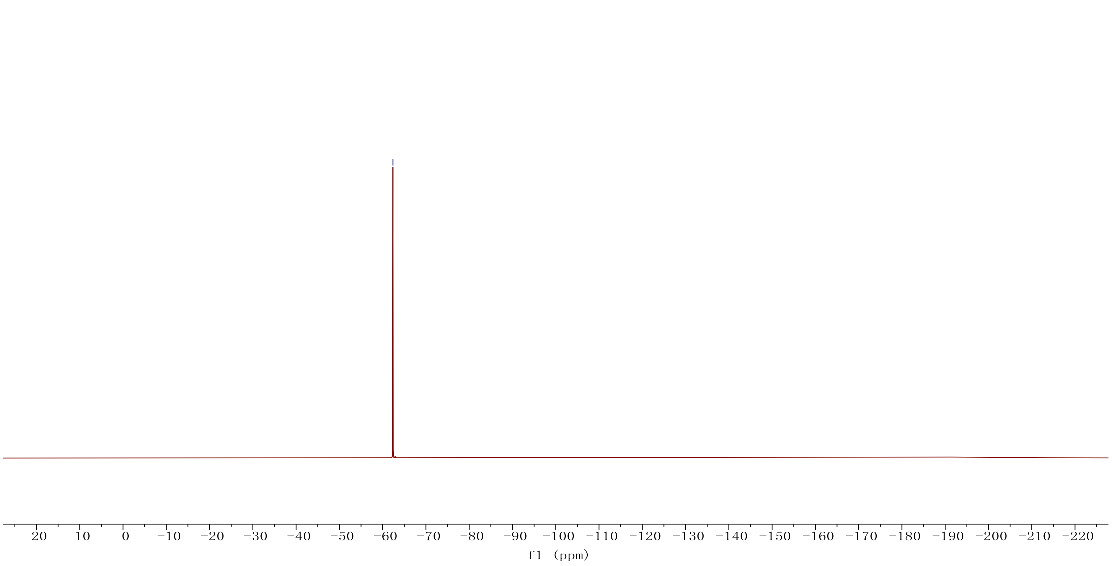
2m ^{1}H NMR

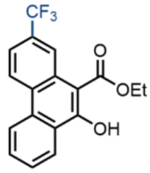


2m ^{13}C NMR

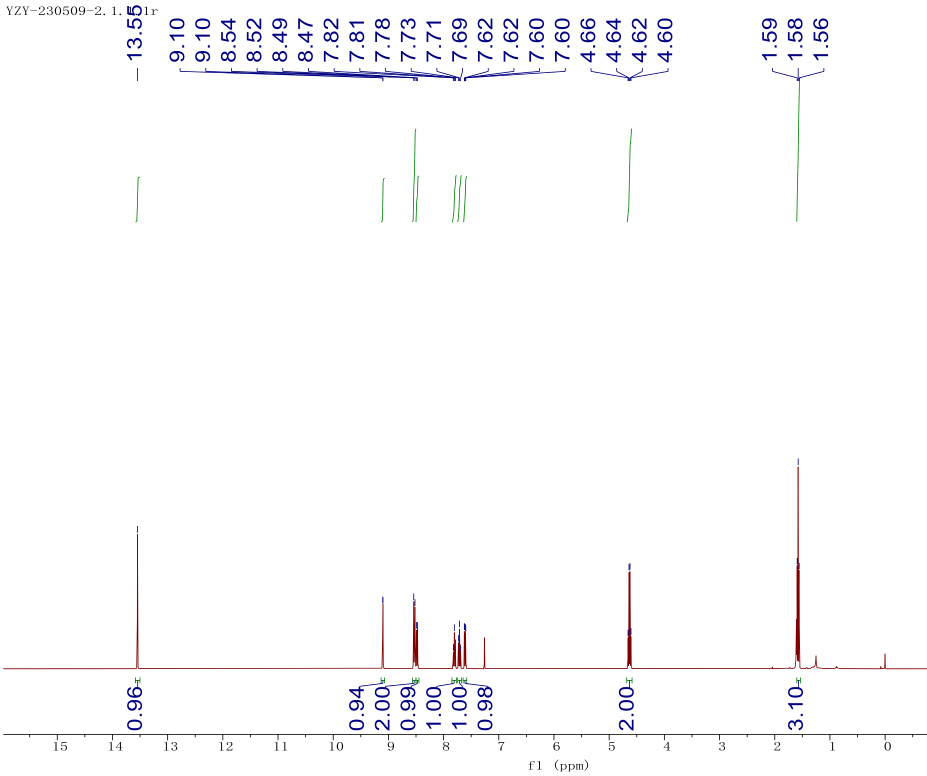


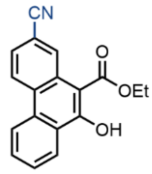
2m ^{19}F NMR



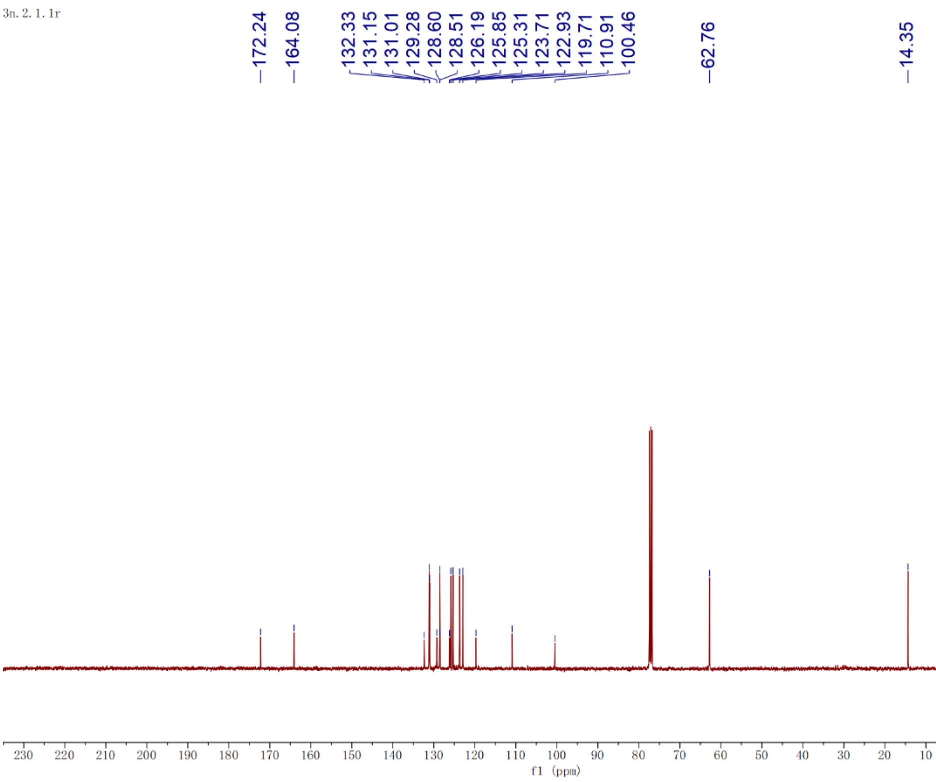


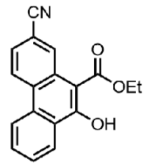
2n ^{1}H NMR





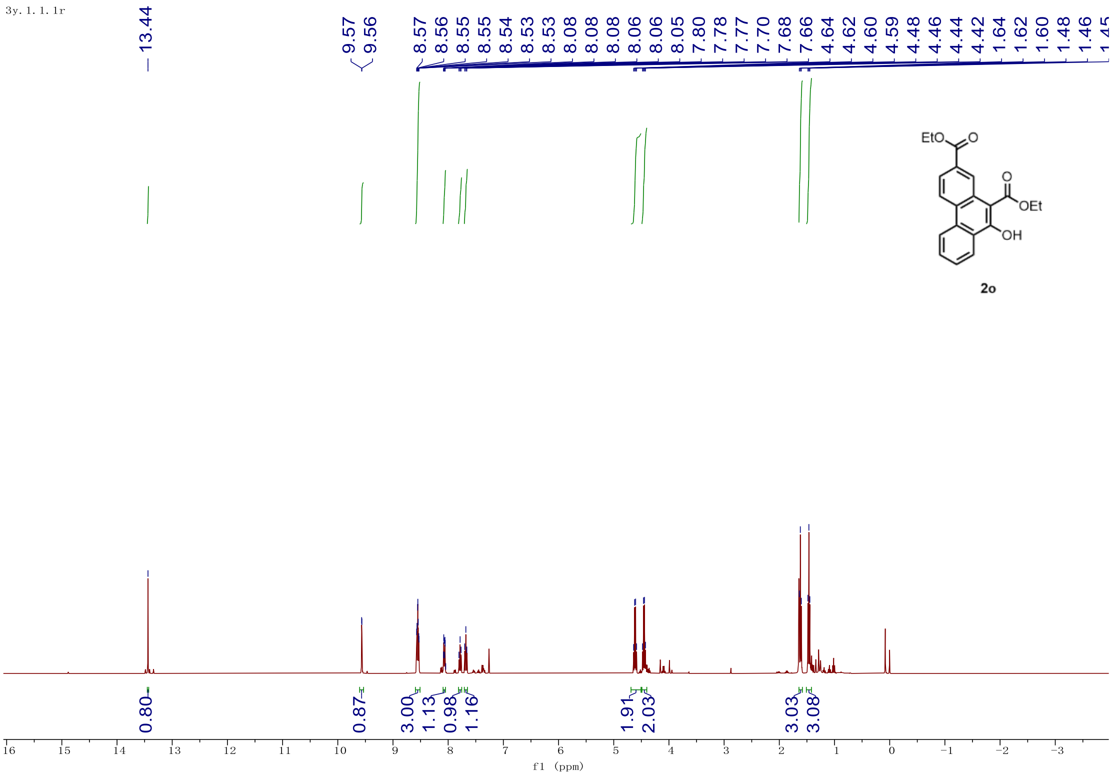
2n ^{13}C NMR



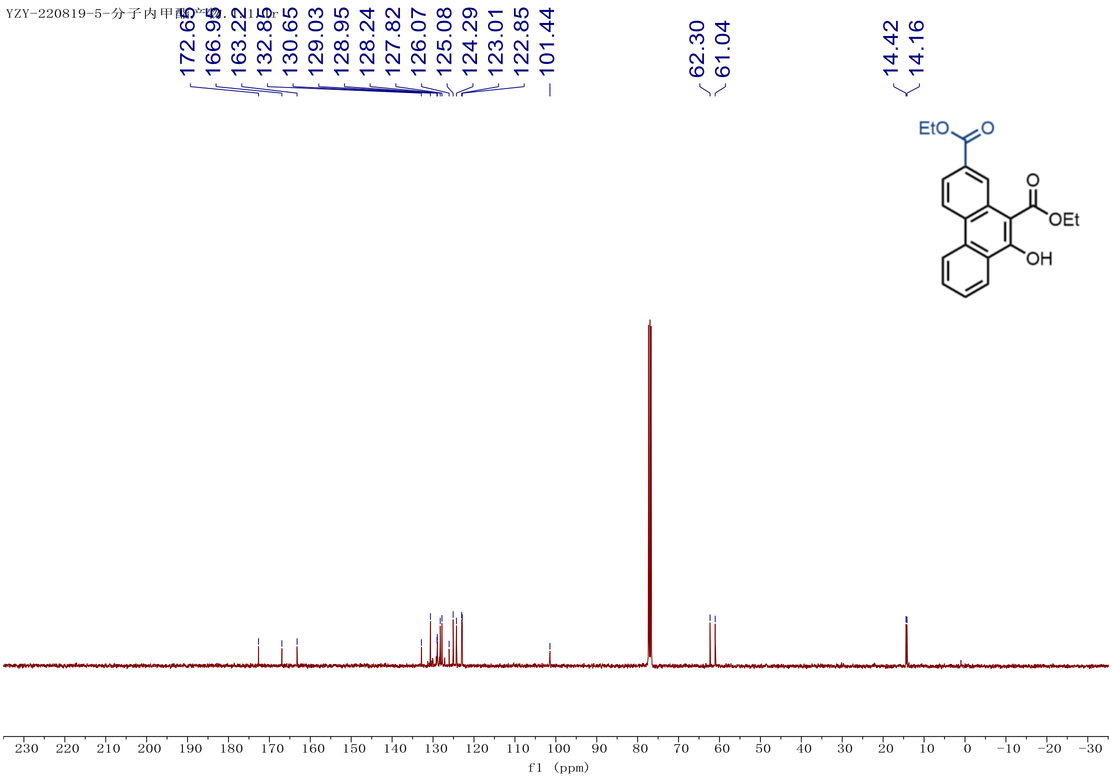


2n

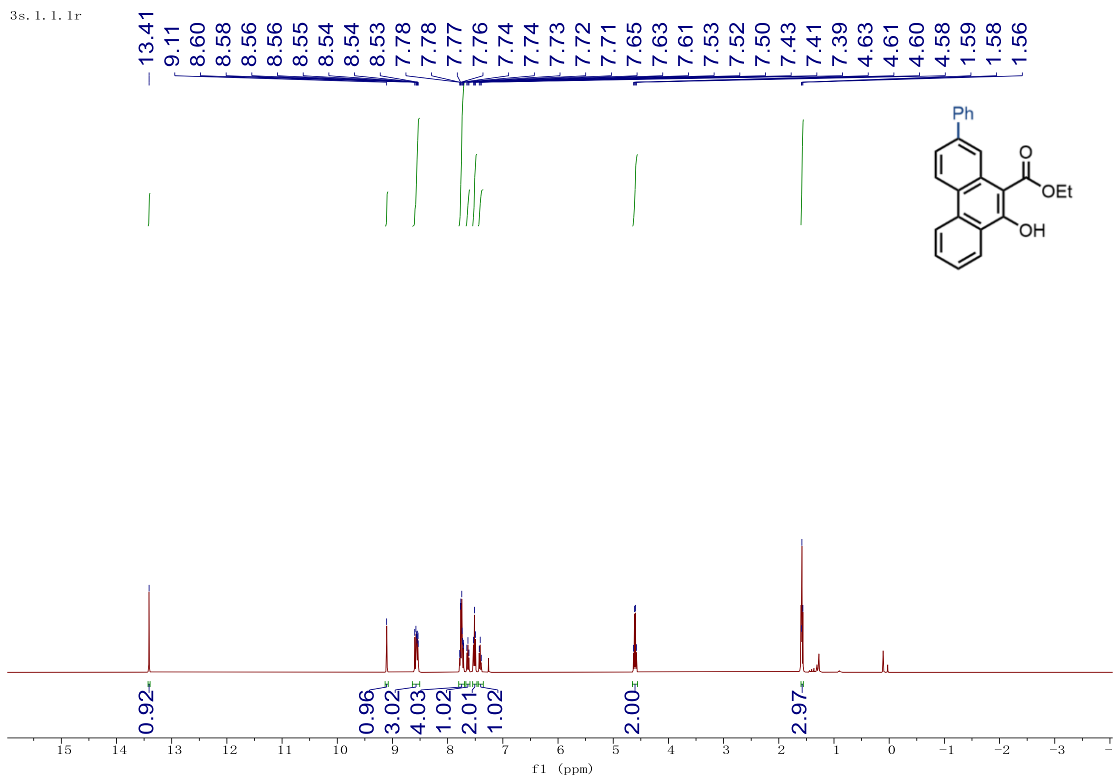
2o ^{1}H NMR



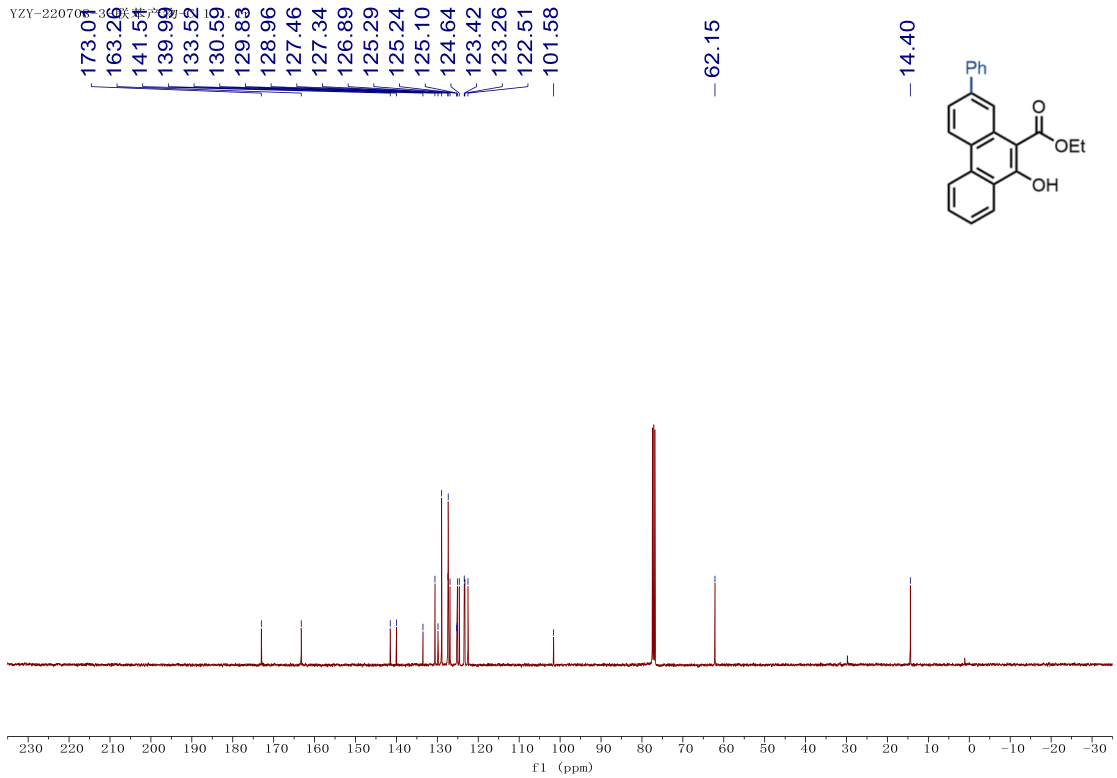
2o ^{13}C NMR



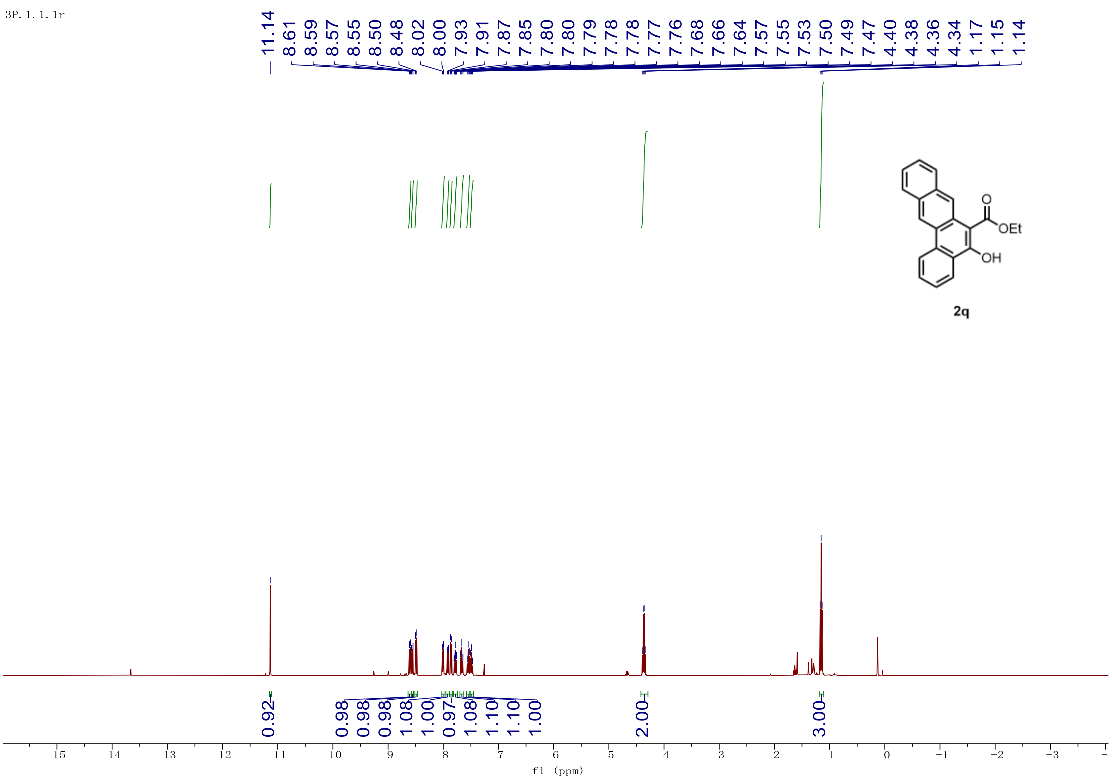
2p ^{1}H NMR



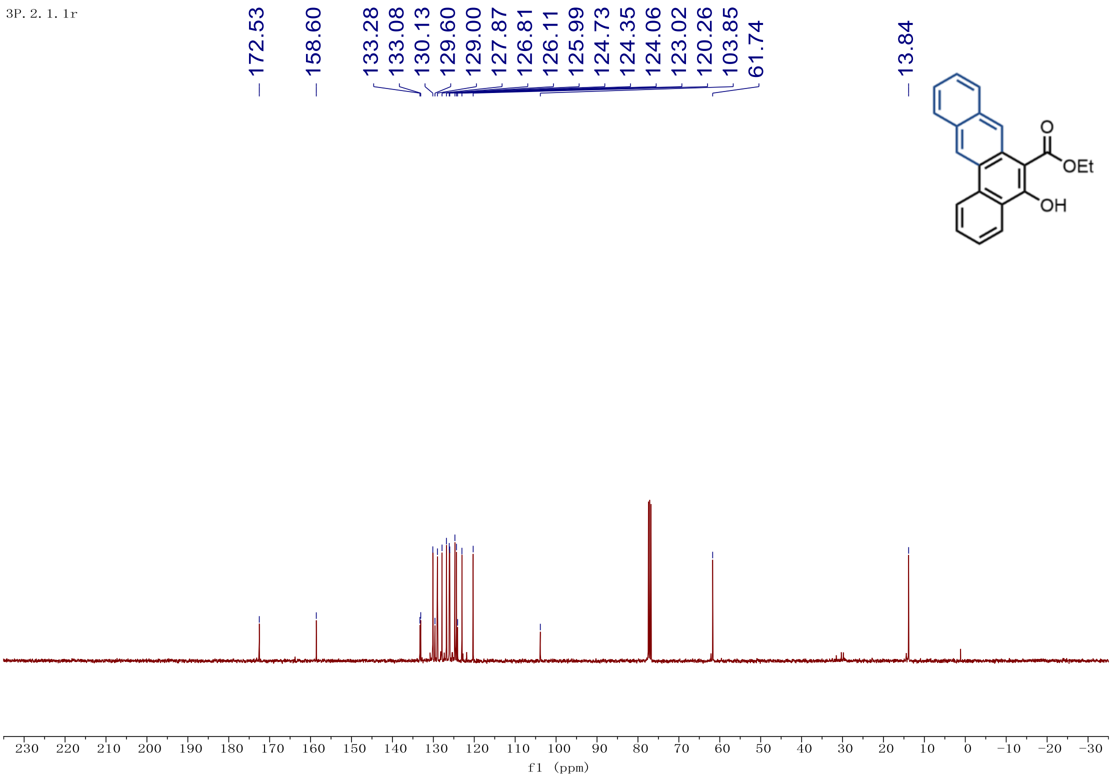
2p ^{13}C NMR



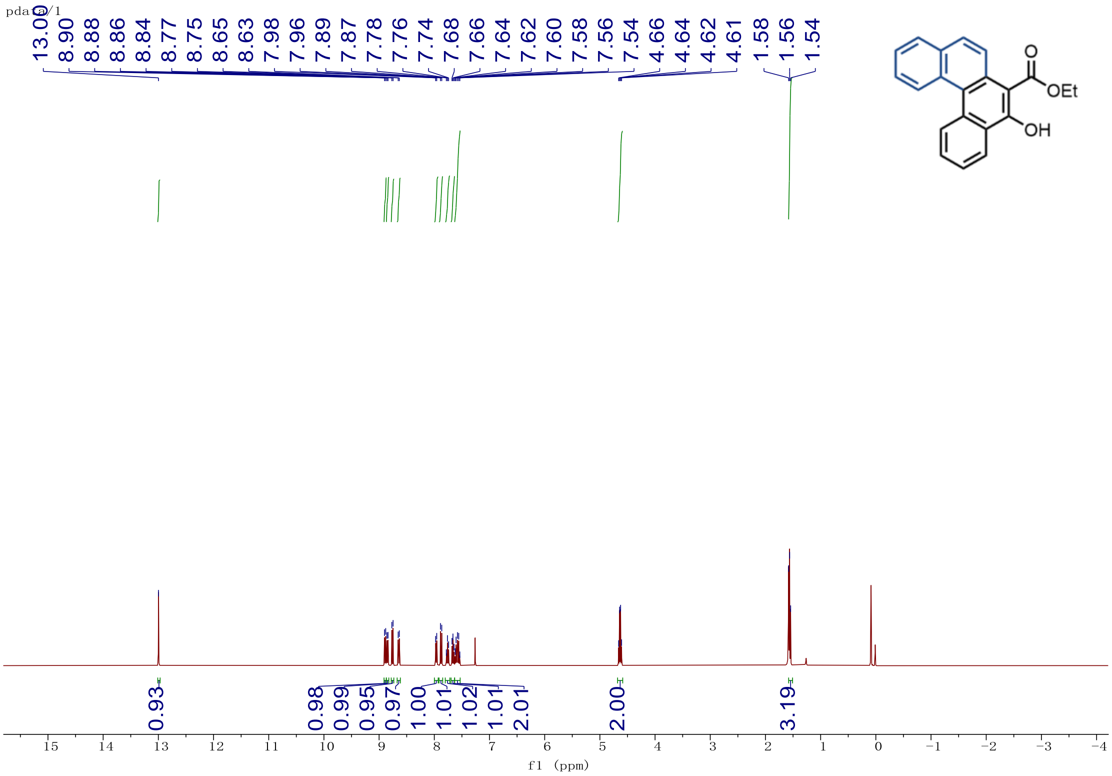
2q ^{1}H NMR



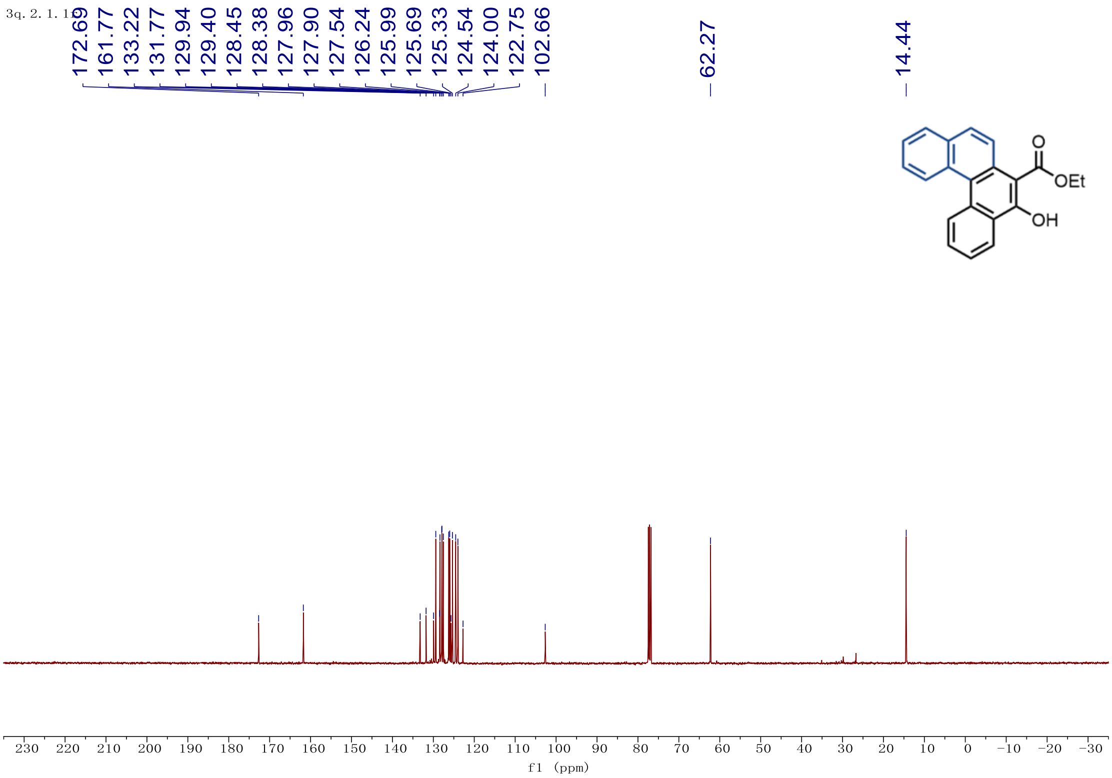
2q ^{13}C NMR



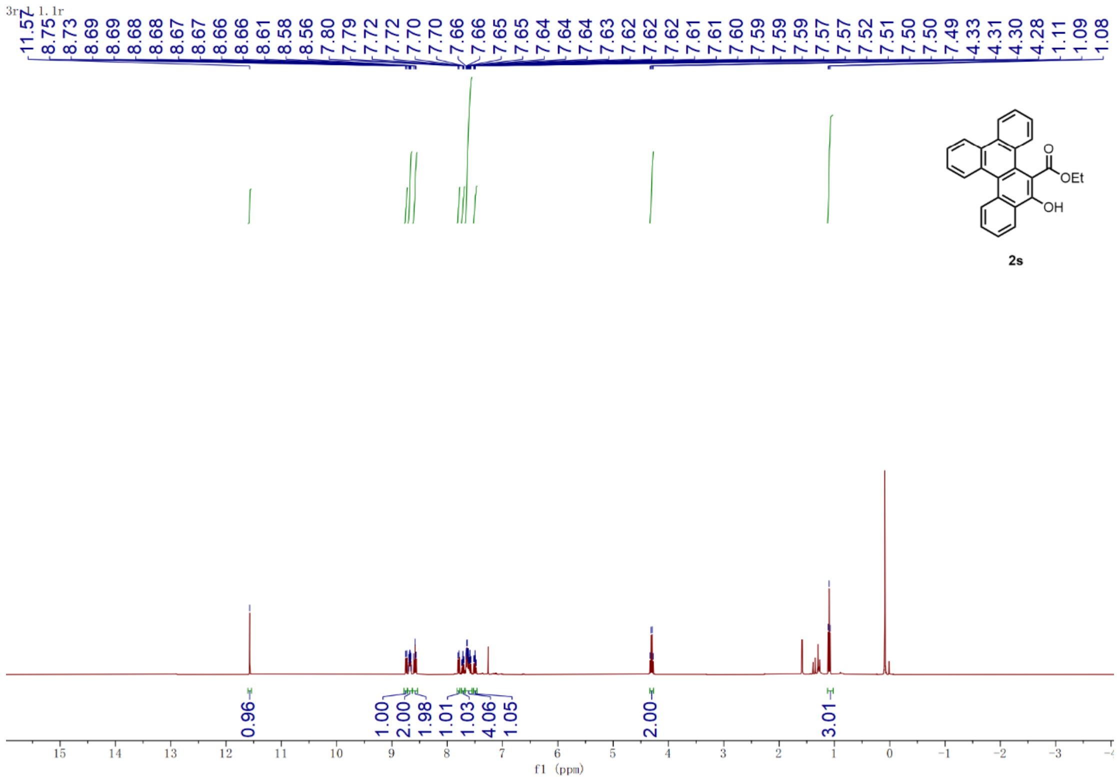
2r ^{1}H NMR



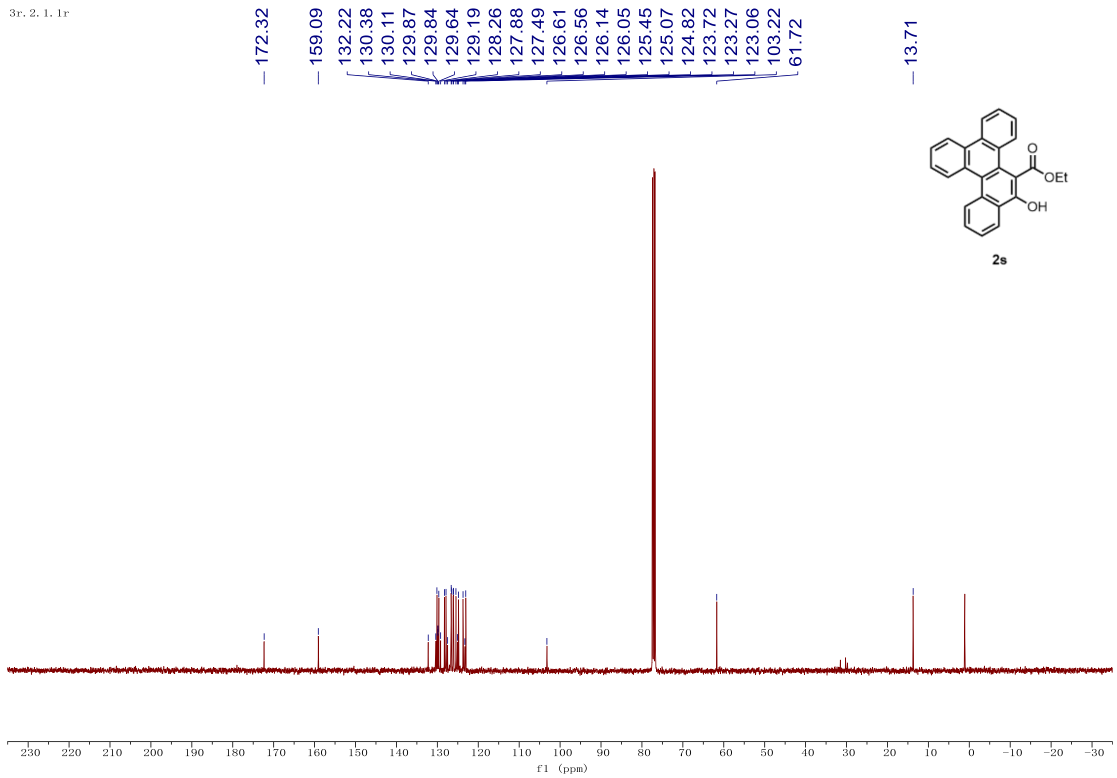
2r ^{13}C NMR



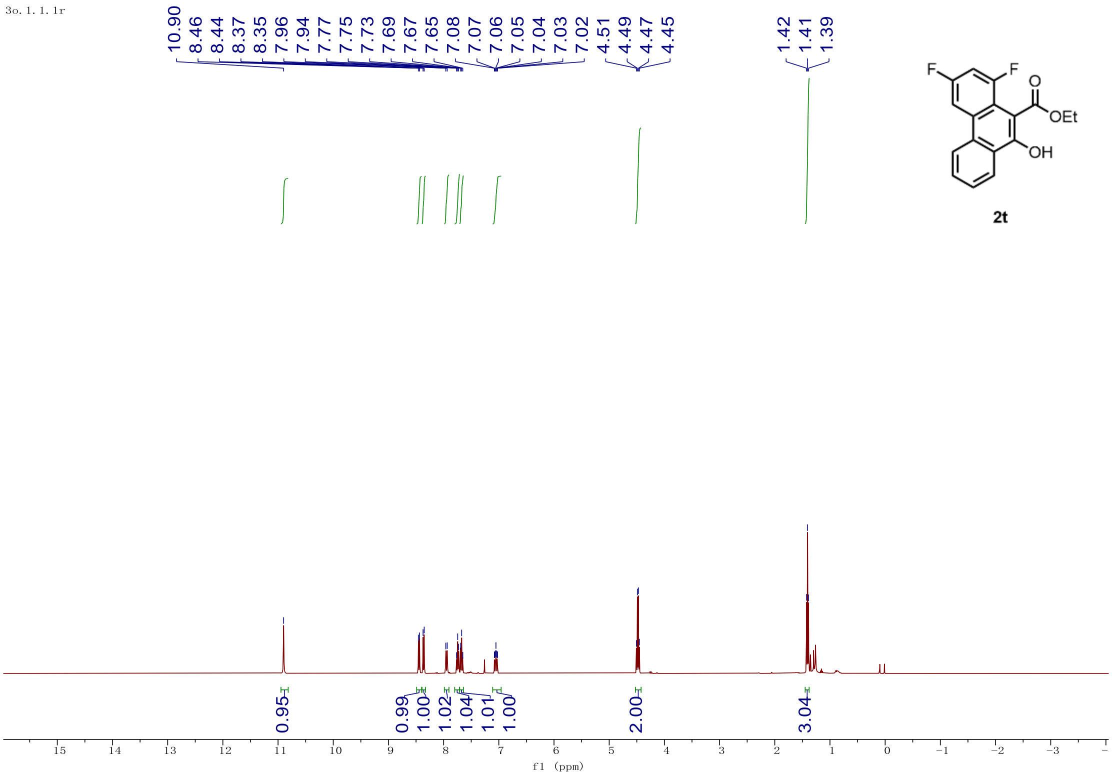
2s ^{1}H NMR



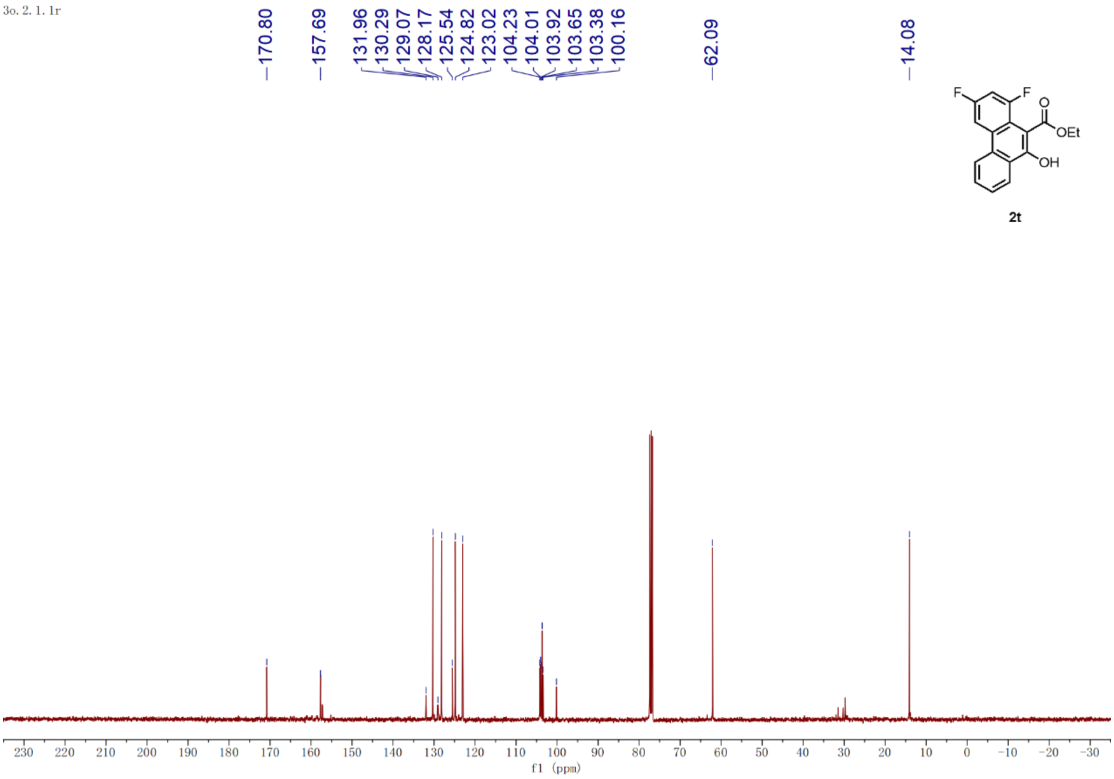
2s ^{13}C NMR



2t ^{1}H NMR

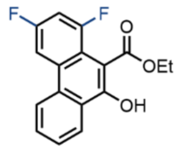


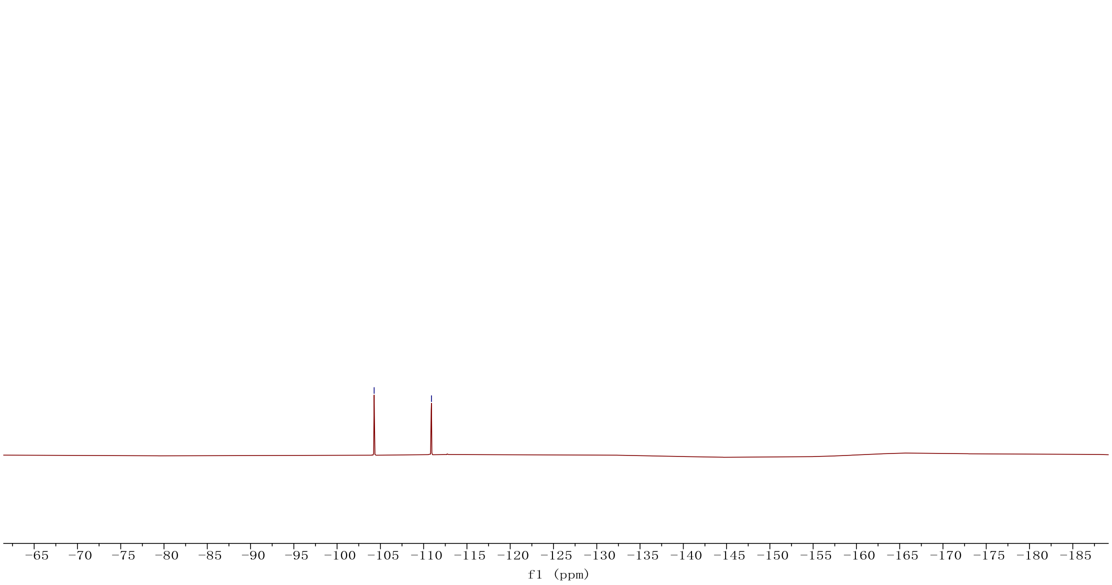
2t ^{13}C NMR



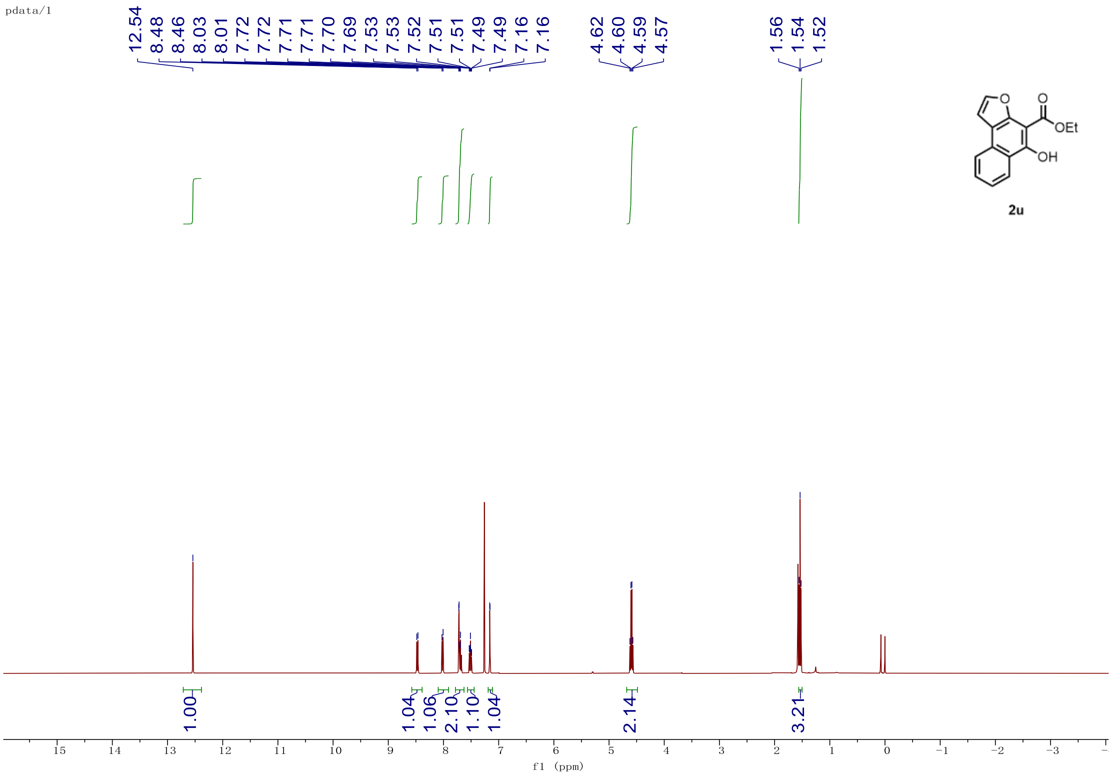
2t ^{19}F NMR

YZY-226027-2-DIFchanwu.1.1.1r

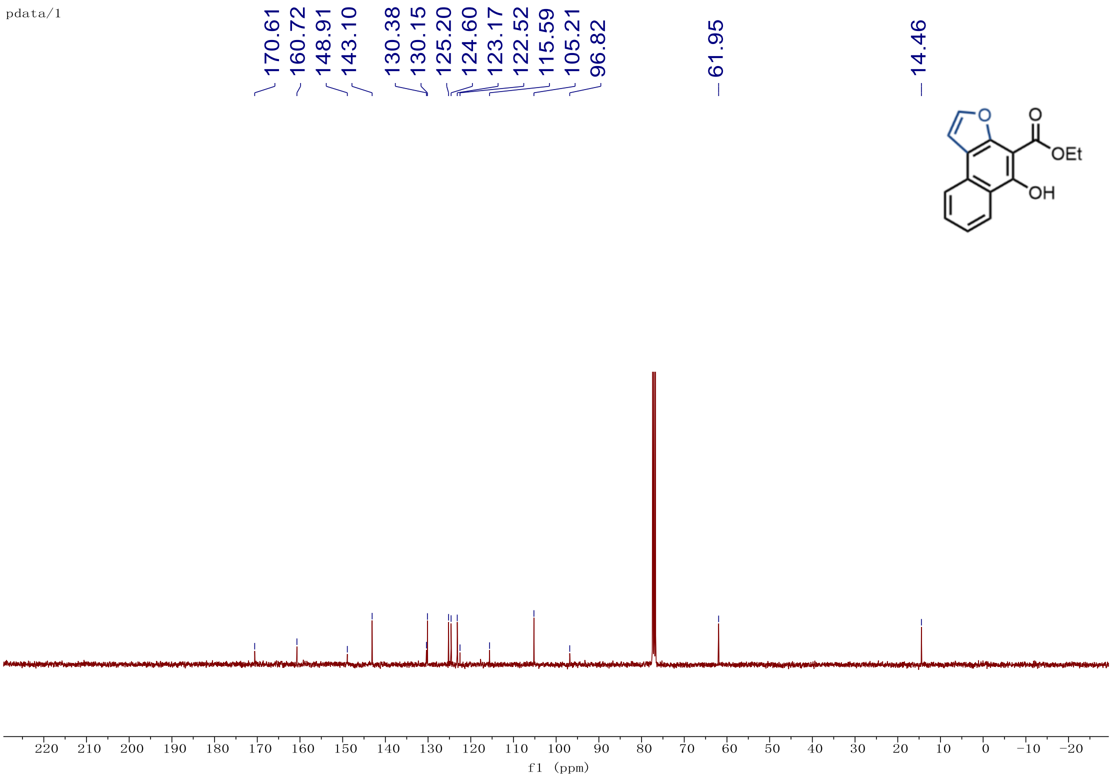




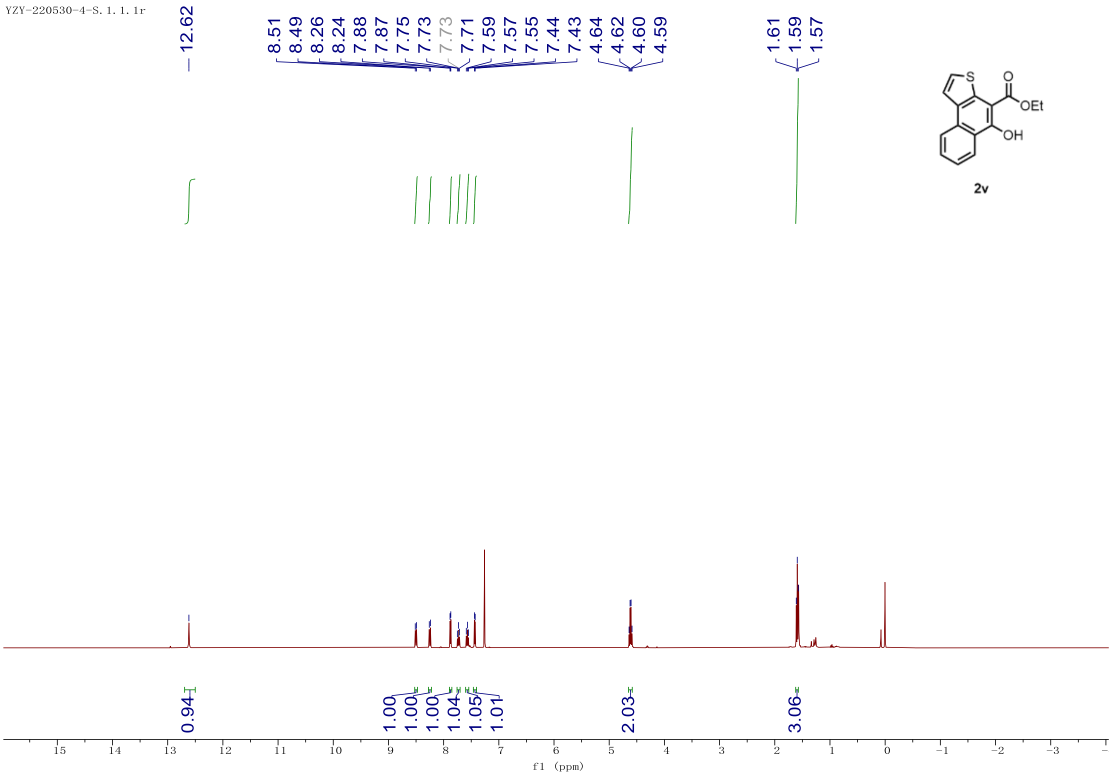
2u ^{1}H NMR



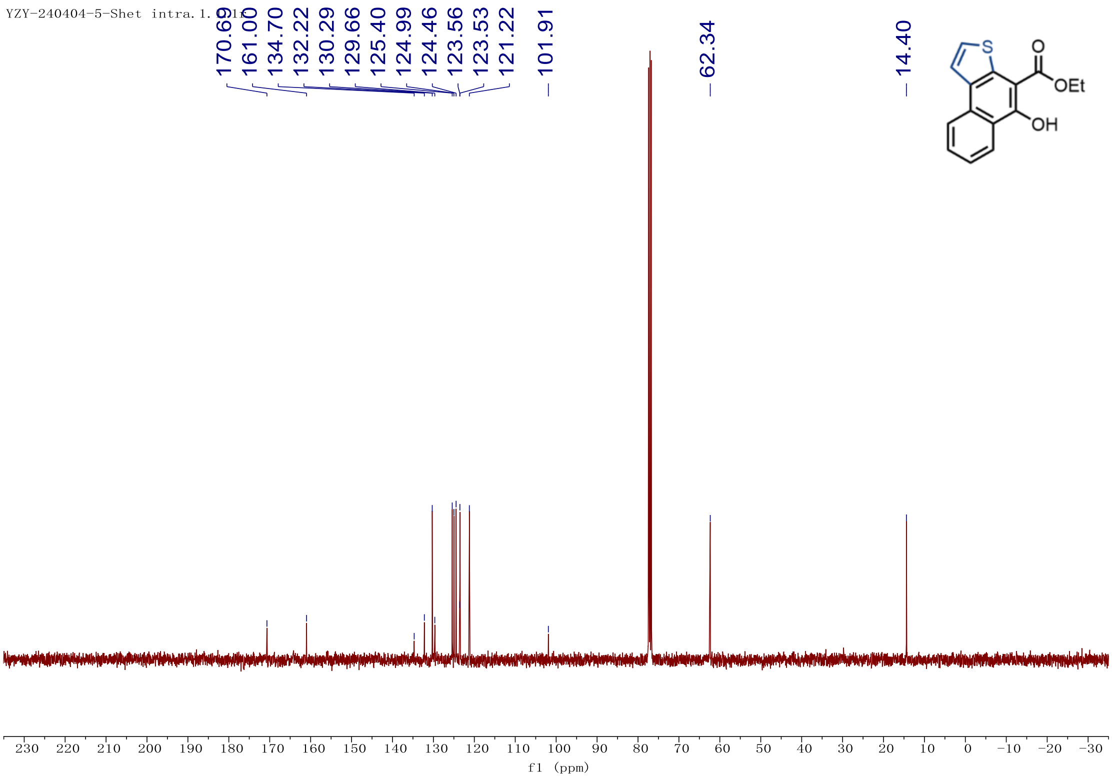
2u ^{13}C NMR



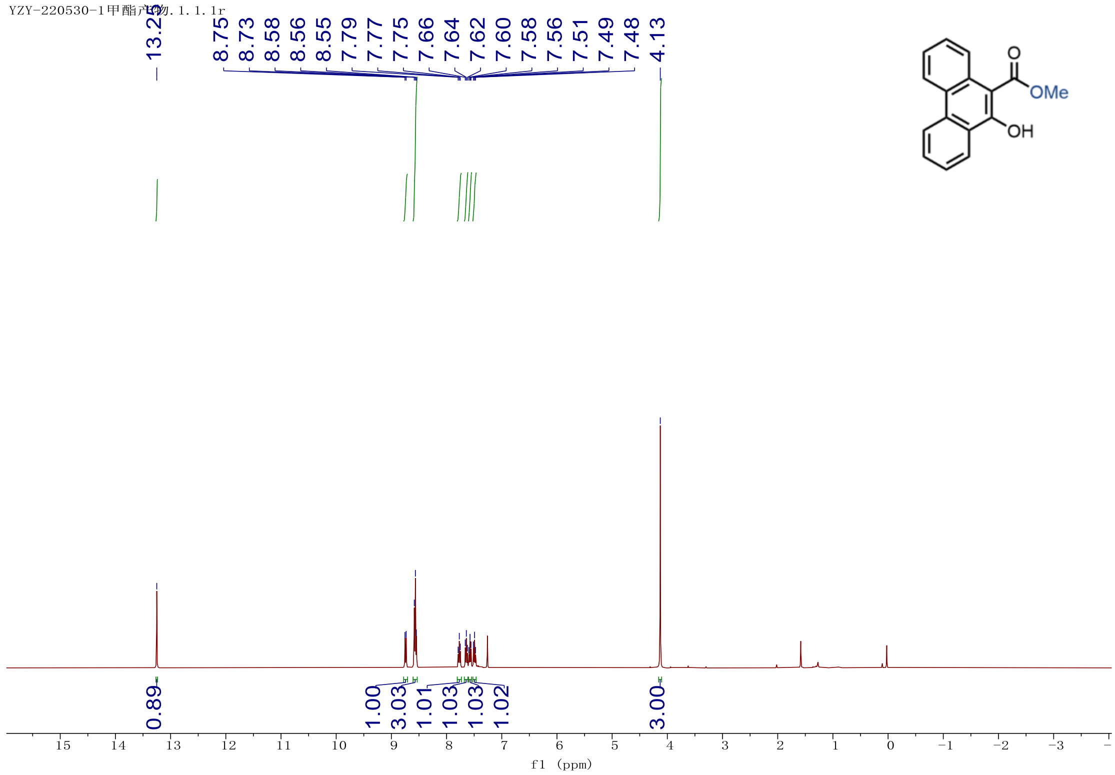
2v ^{1}H NMR



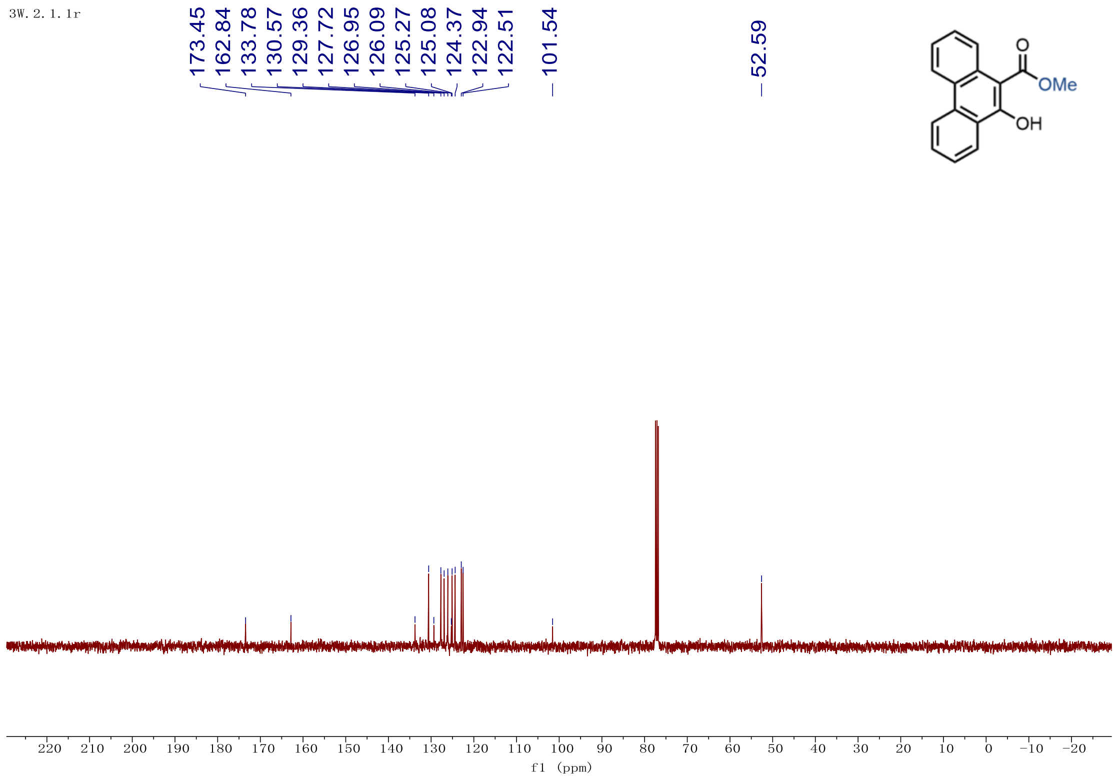
2v ^{13}C NMR



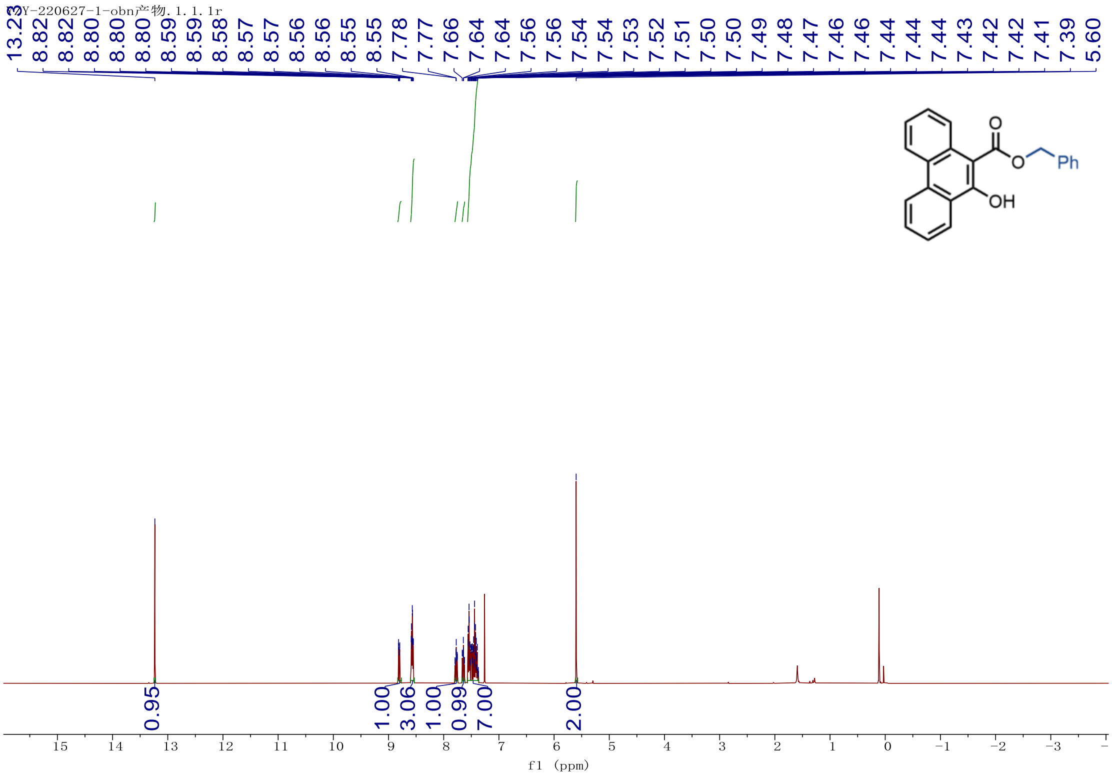
2w ^{1}H NMR



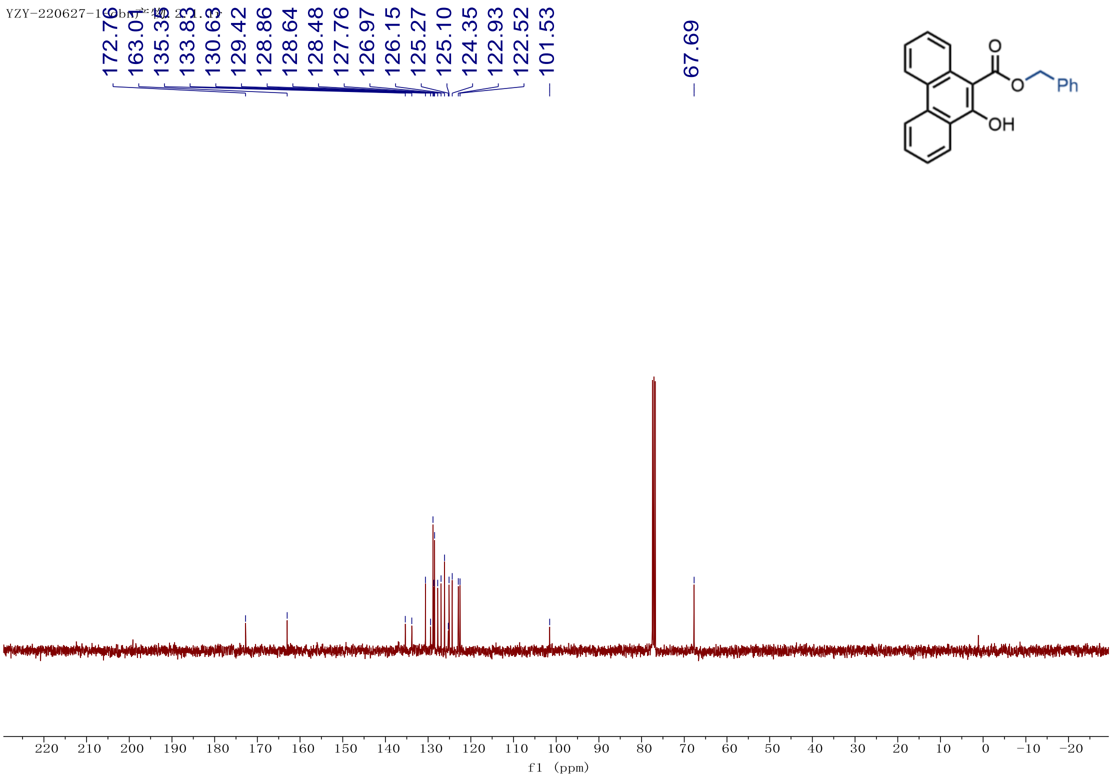
2w ^{13}C NMR



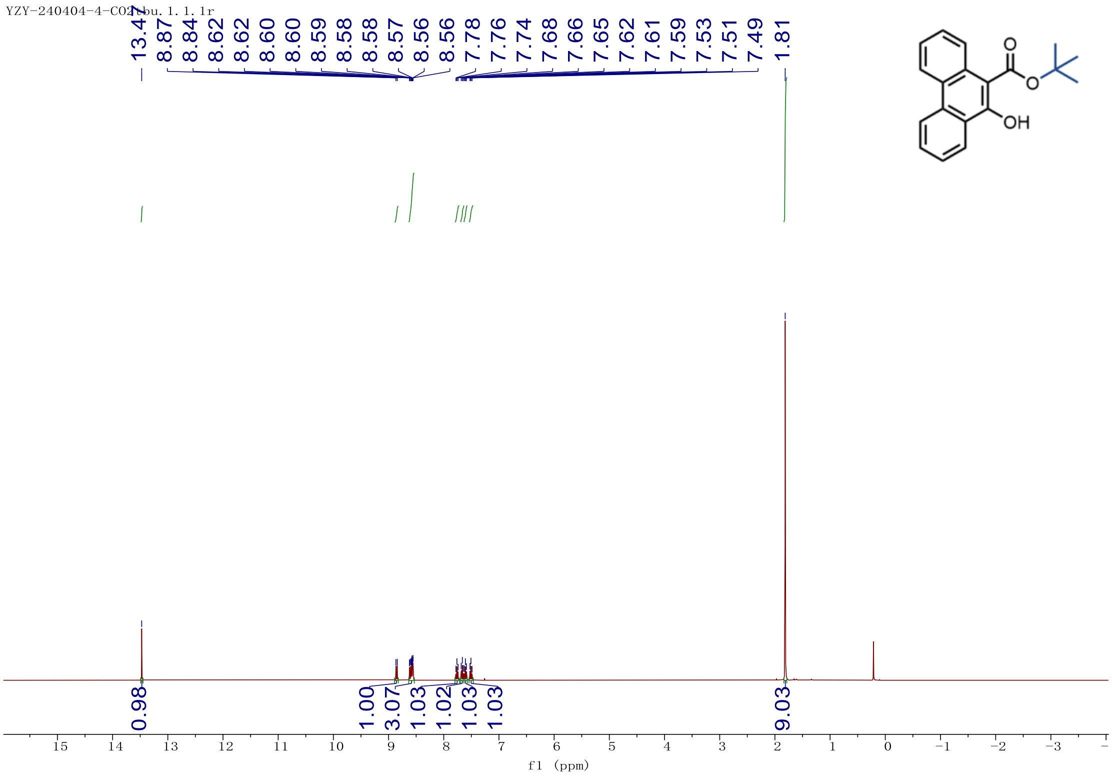
2x ^{1}H NMR



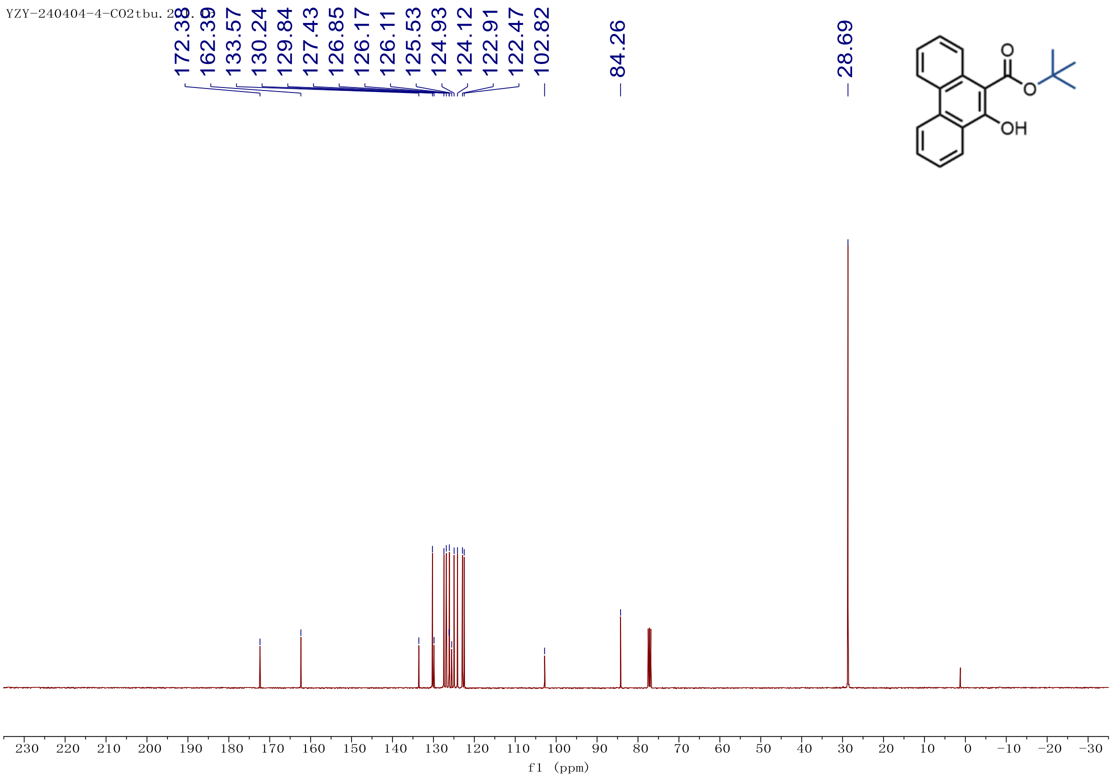
2x ^{13}C NMR



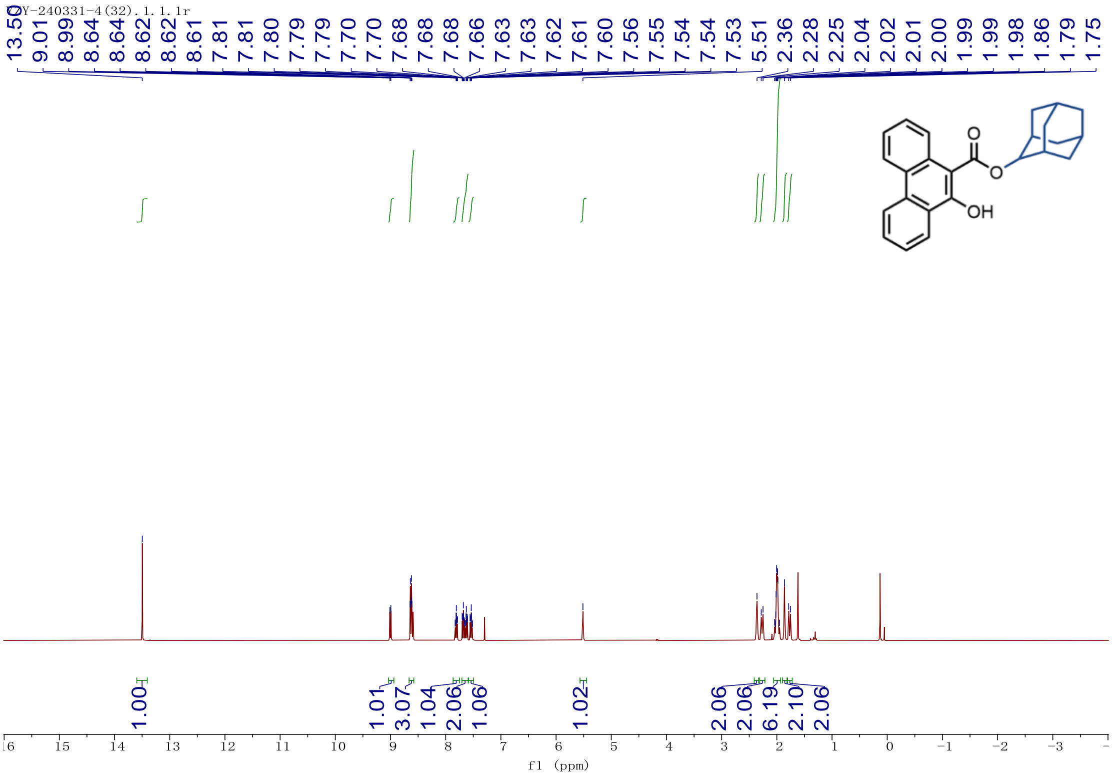
2y ^{1}H NMR



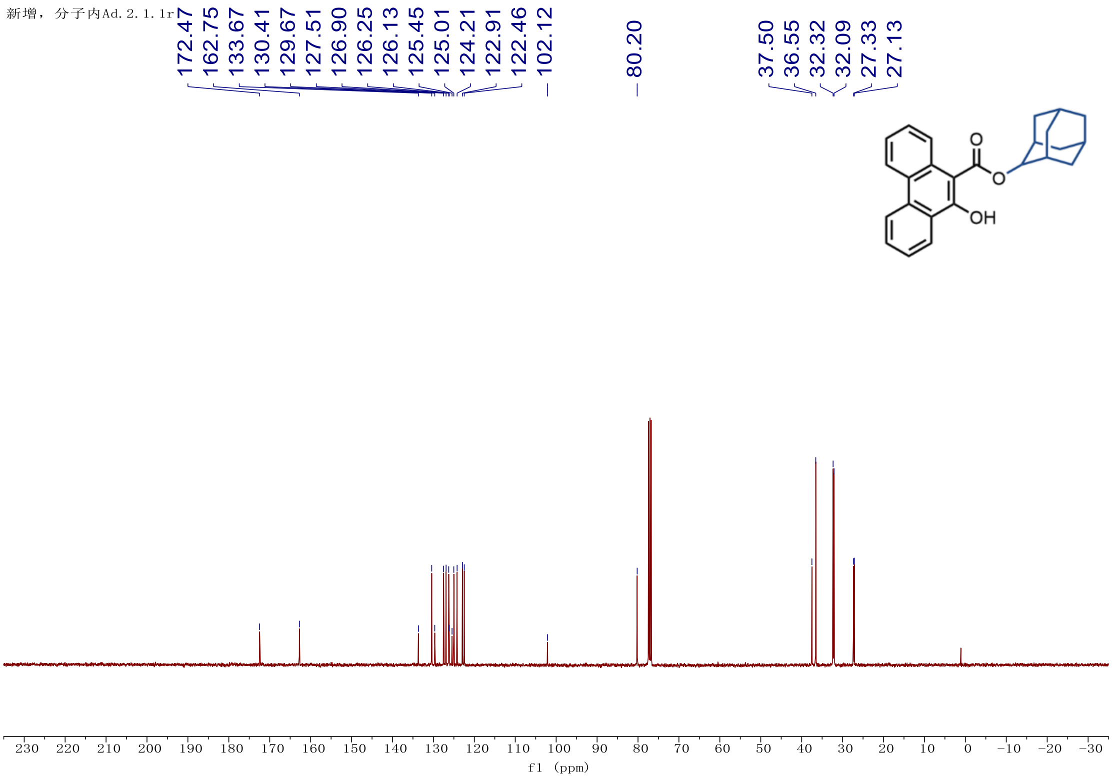
2y ^{13}C NMR



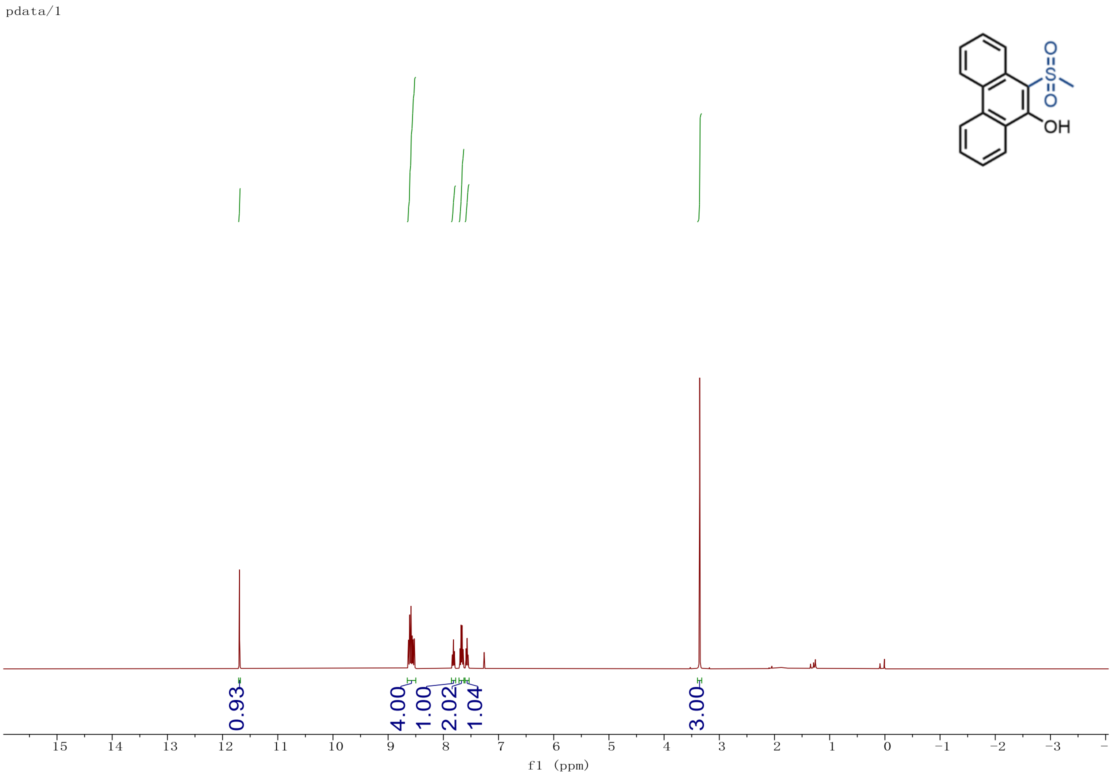
2z ^{1}H NMR



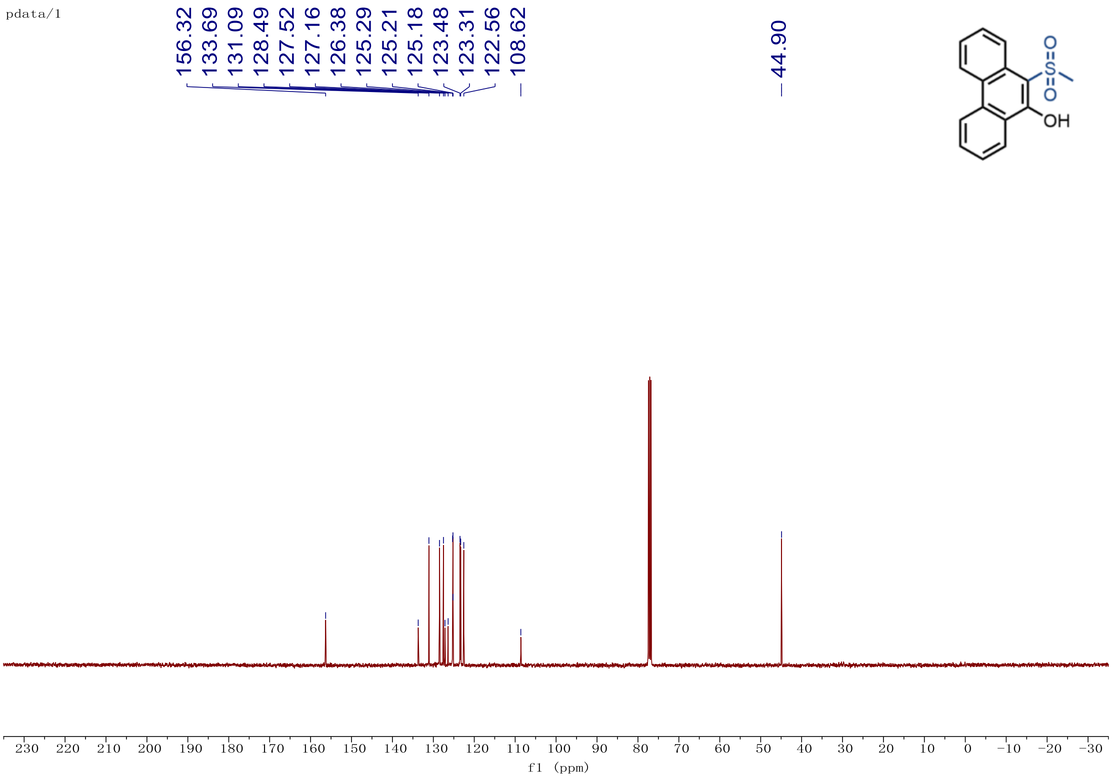
2z ^{13}C NMR



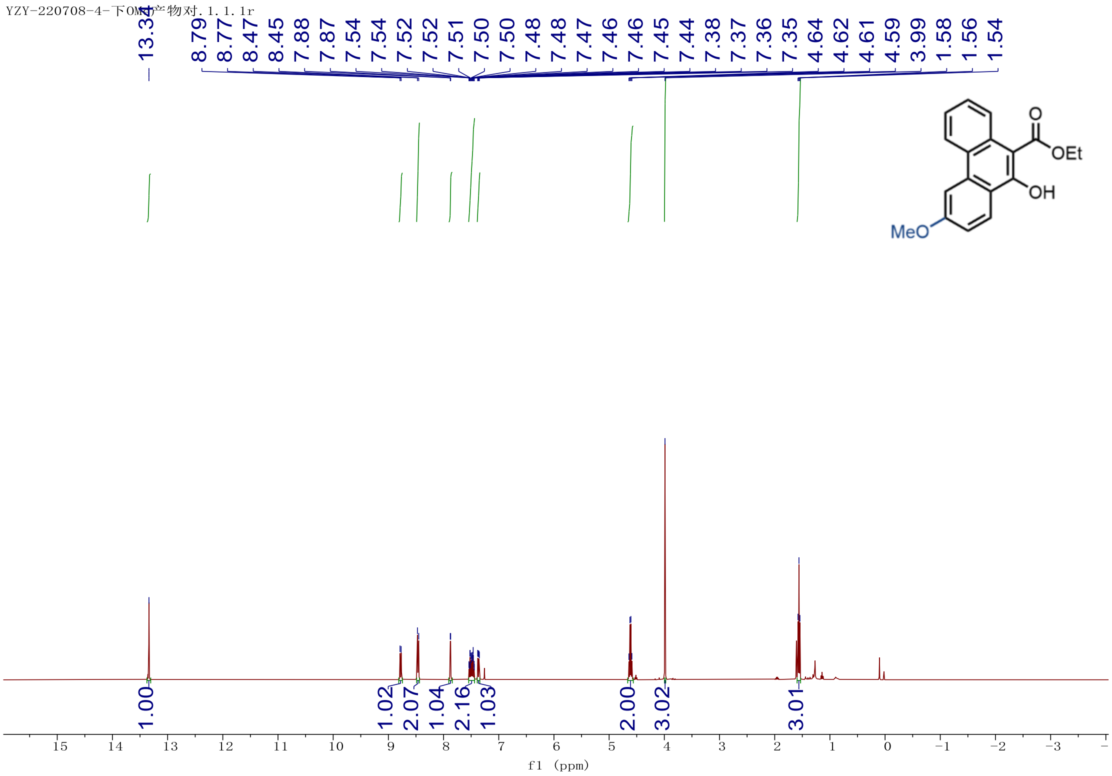
2aa ^{1}H NMR



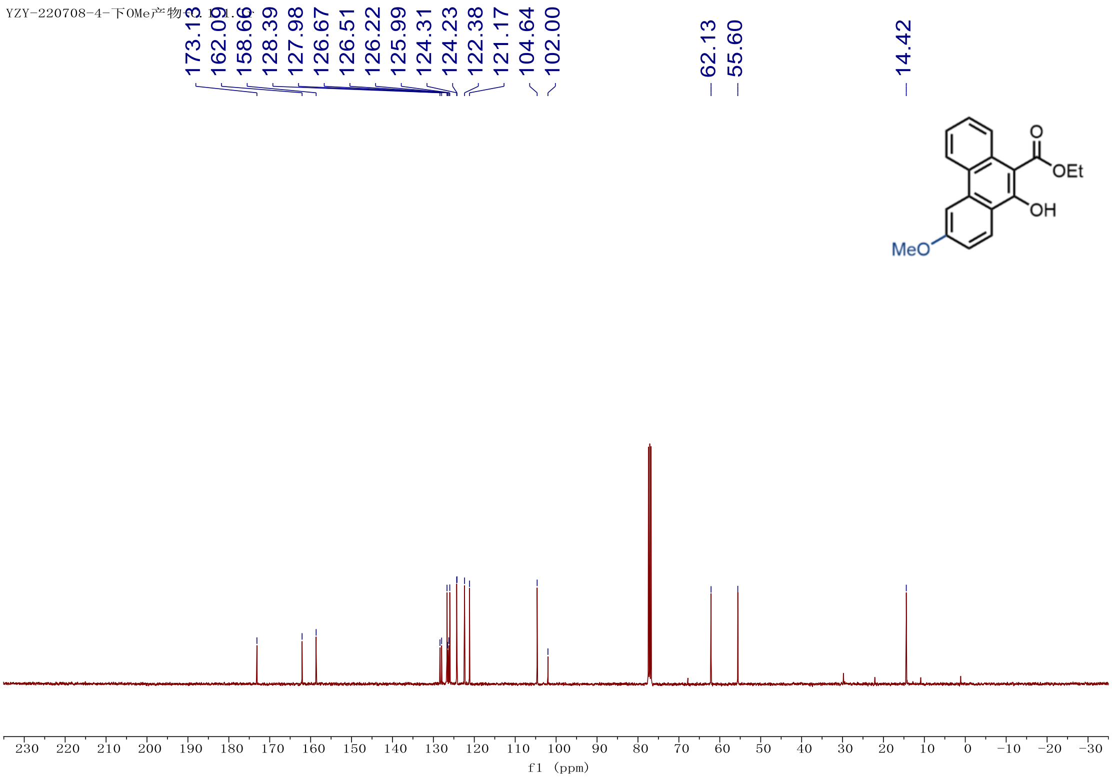
2aa ^{13}C NMR



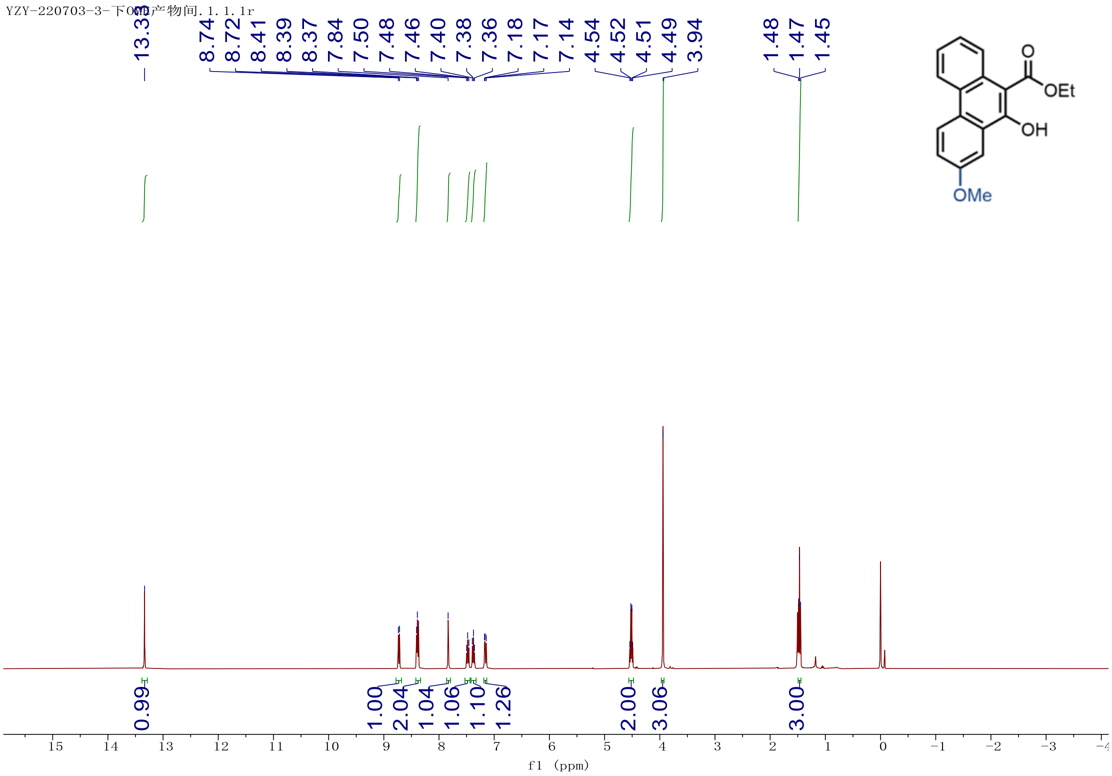
2ab ^{1}H NMR



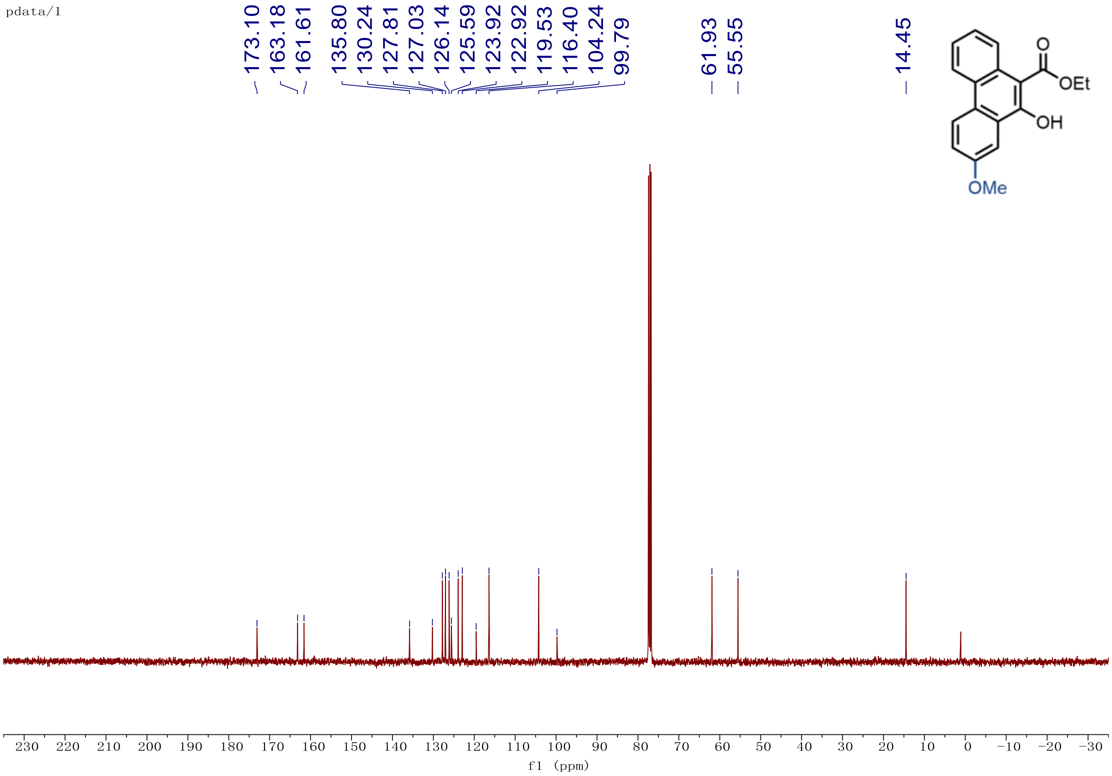
2ab ^{13}C NMR



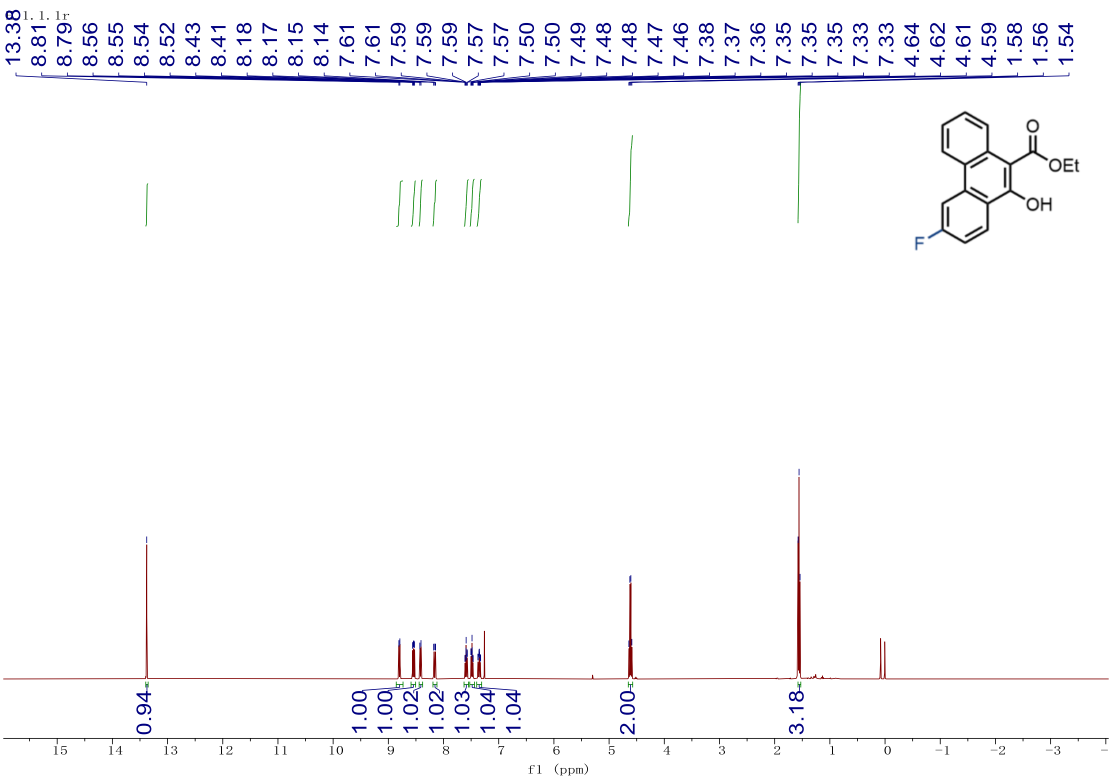
2ac ^{1}H NMR



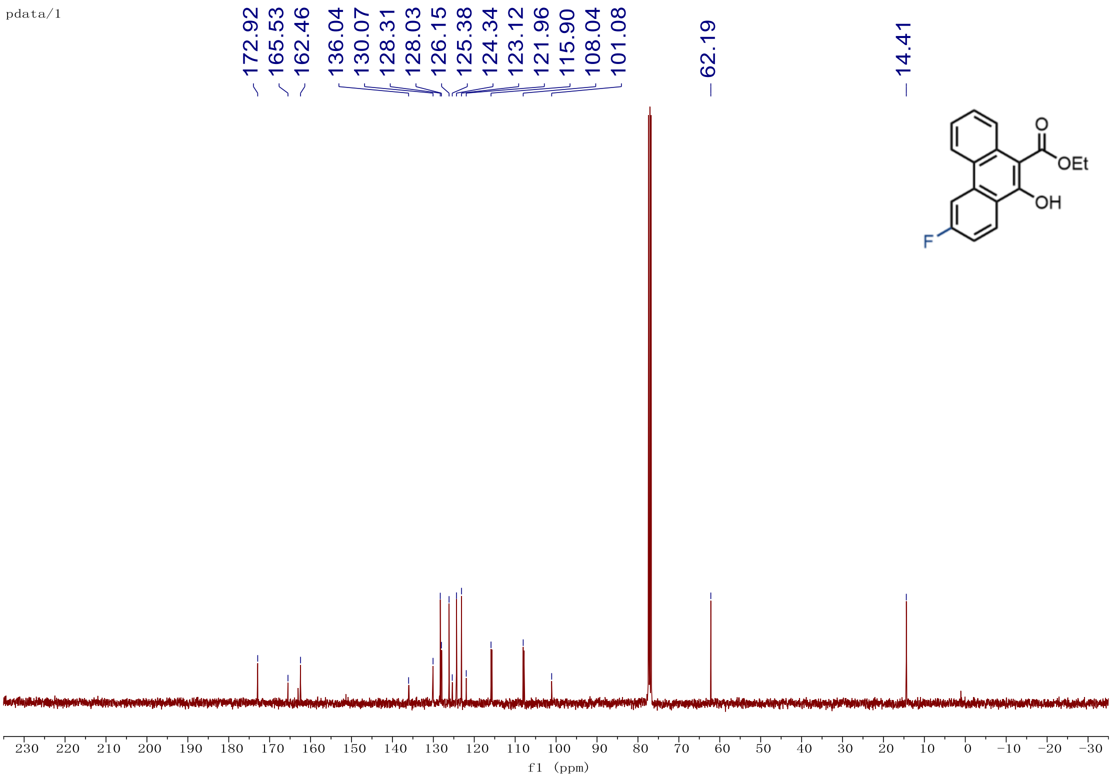
2ac ^{13}C NMR



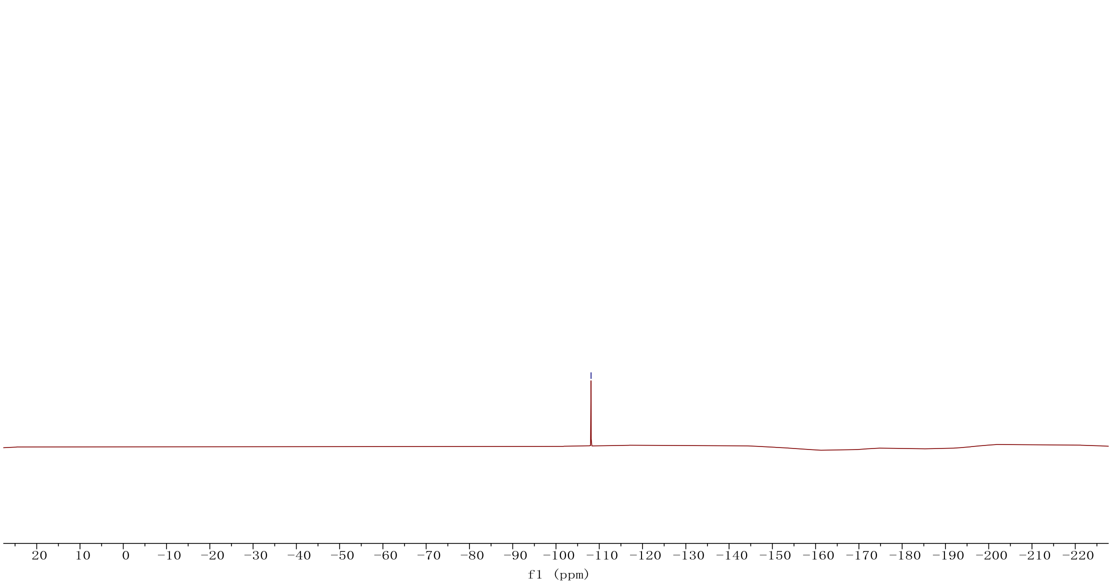
2ad ^{1}H NMR

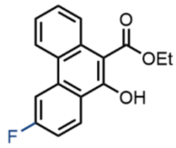


2ad ^{13}C NMR

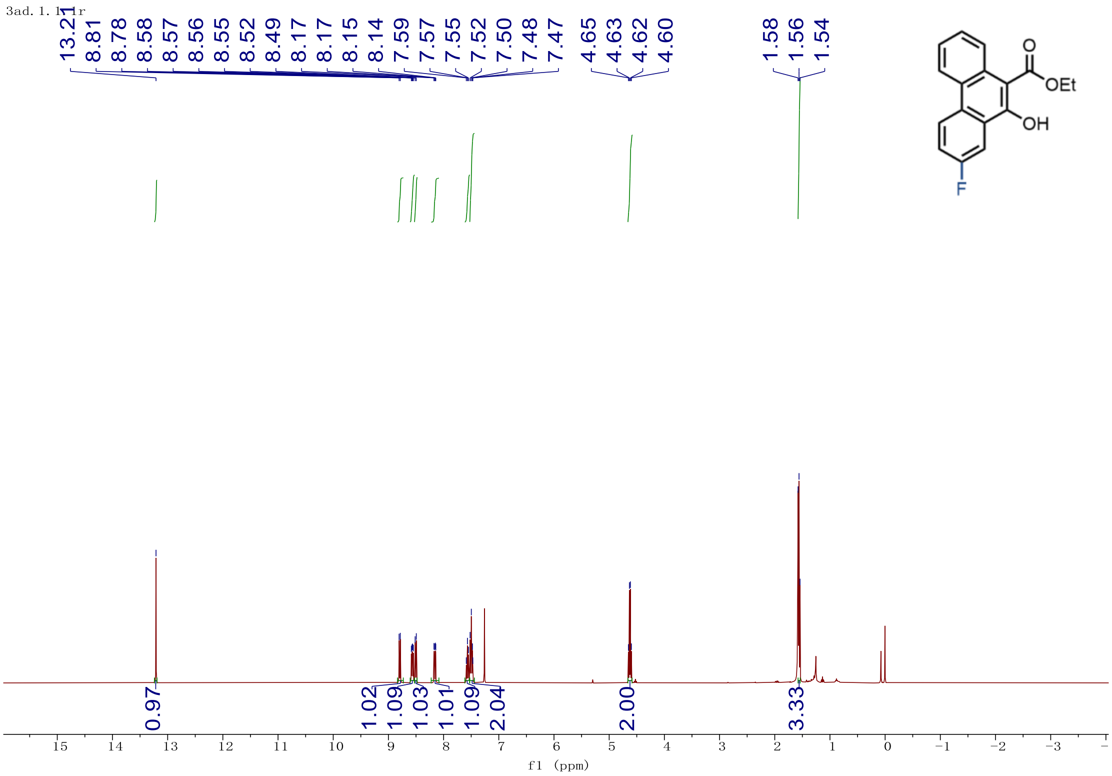


2ad ^{19}F NMR

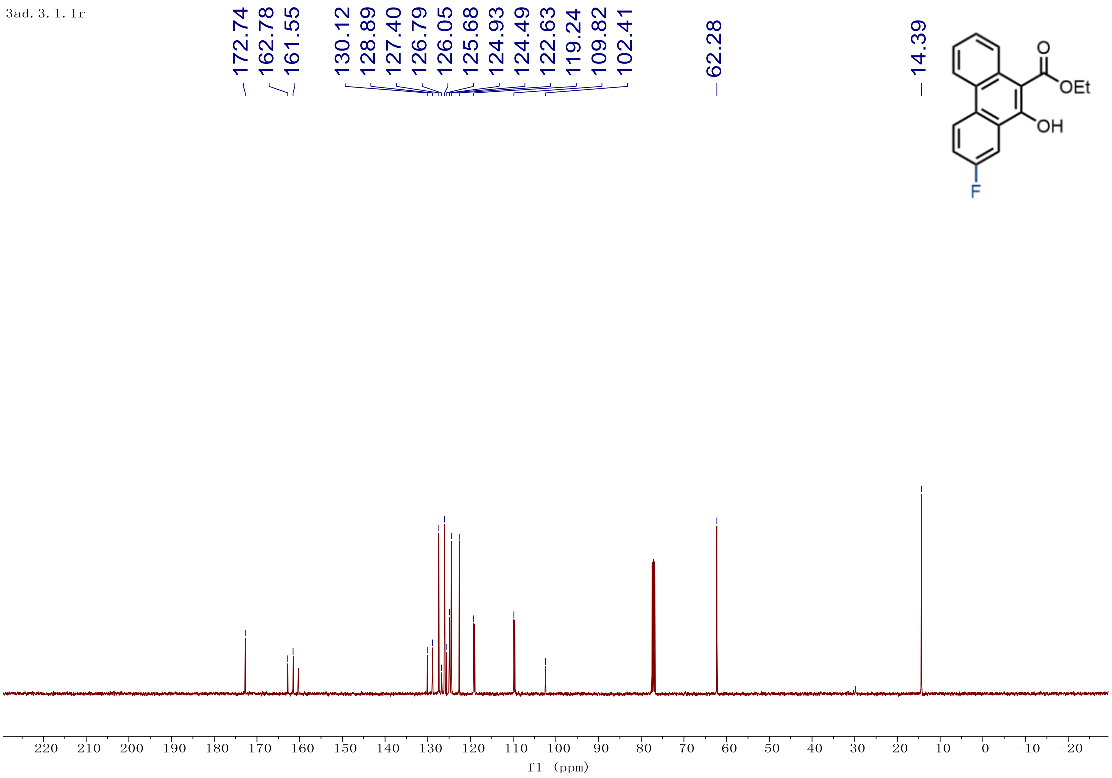

pdata/1
-108.11
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)


O
OEt
OH
F

2ae ^{1}H NMR

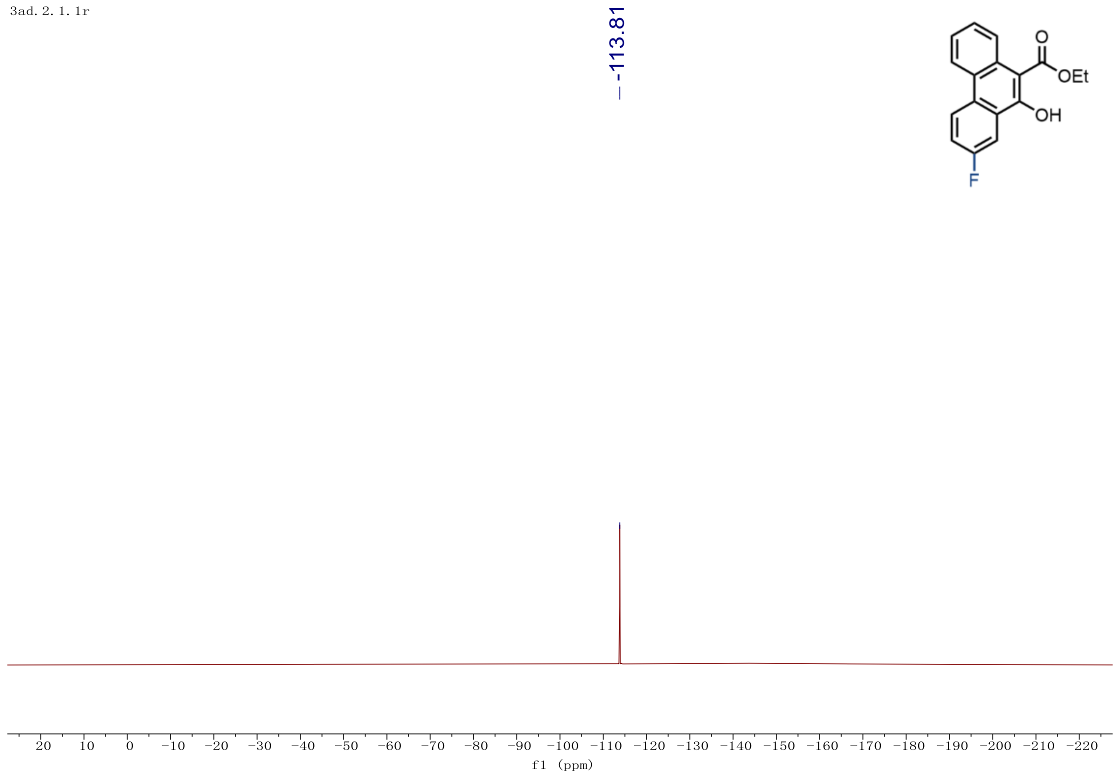


2ae ^{13}C NMR

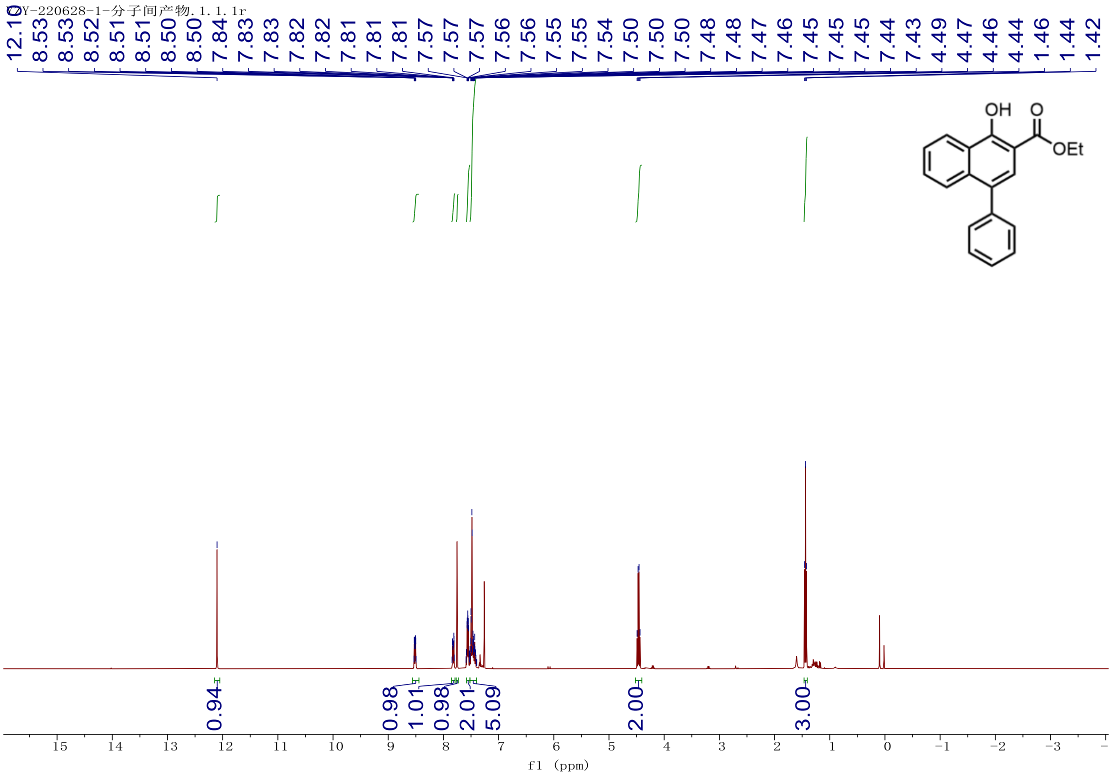


2ae ^{19}F NMR

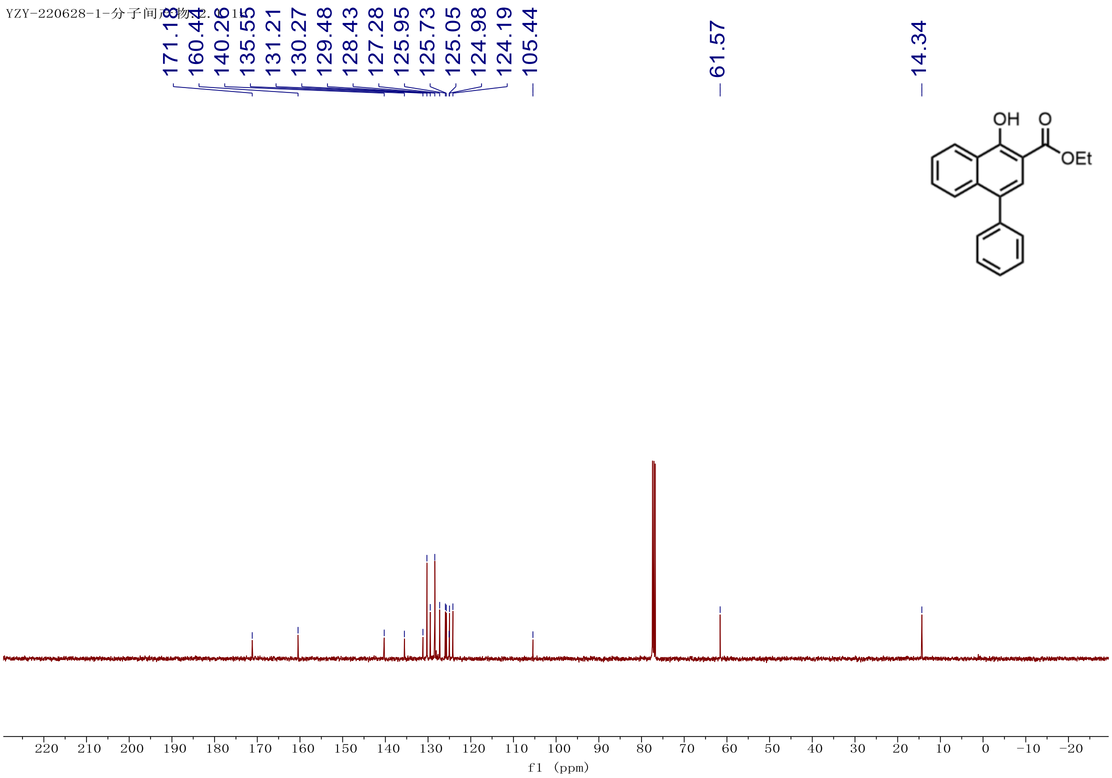
3ad.2.1.1r



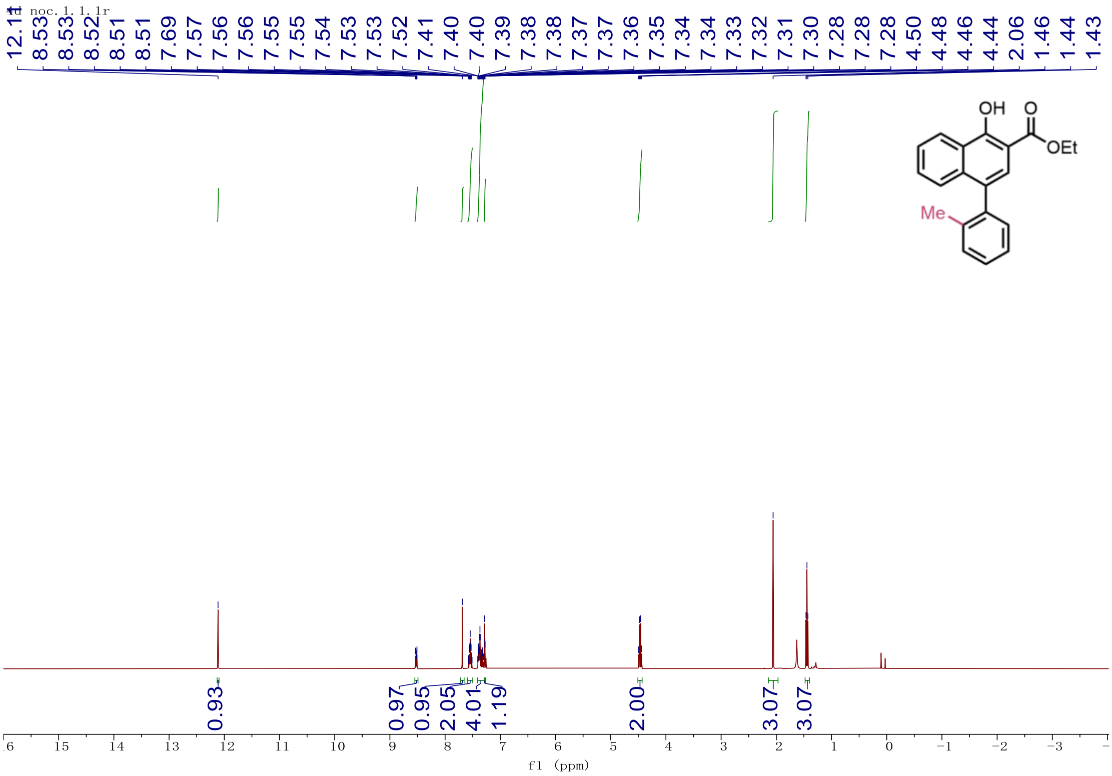
5a ^{1}H NMR



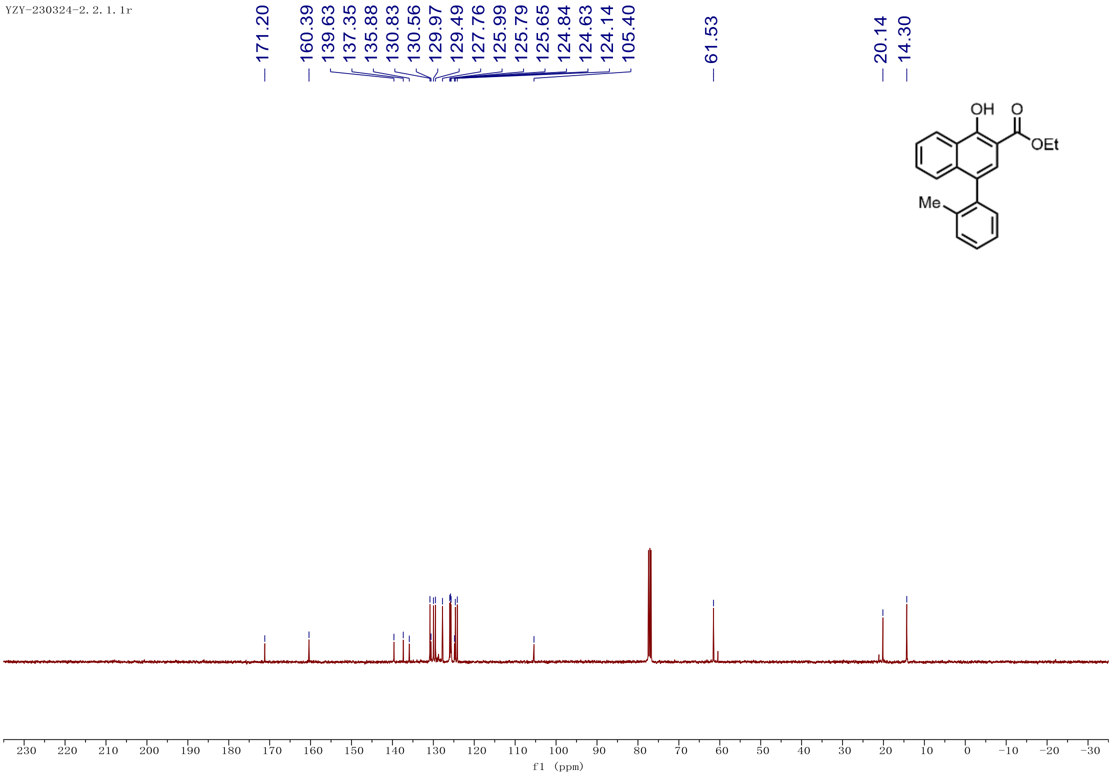
5a ^{13}C NMR



5b ^{1}H NMR

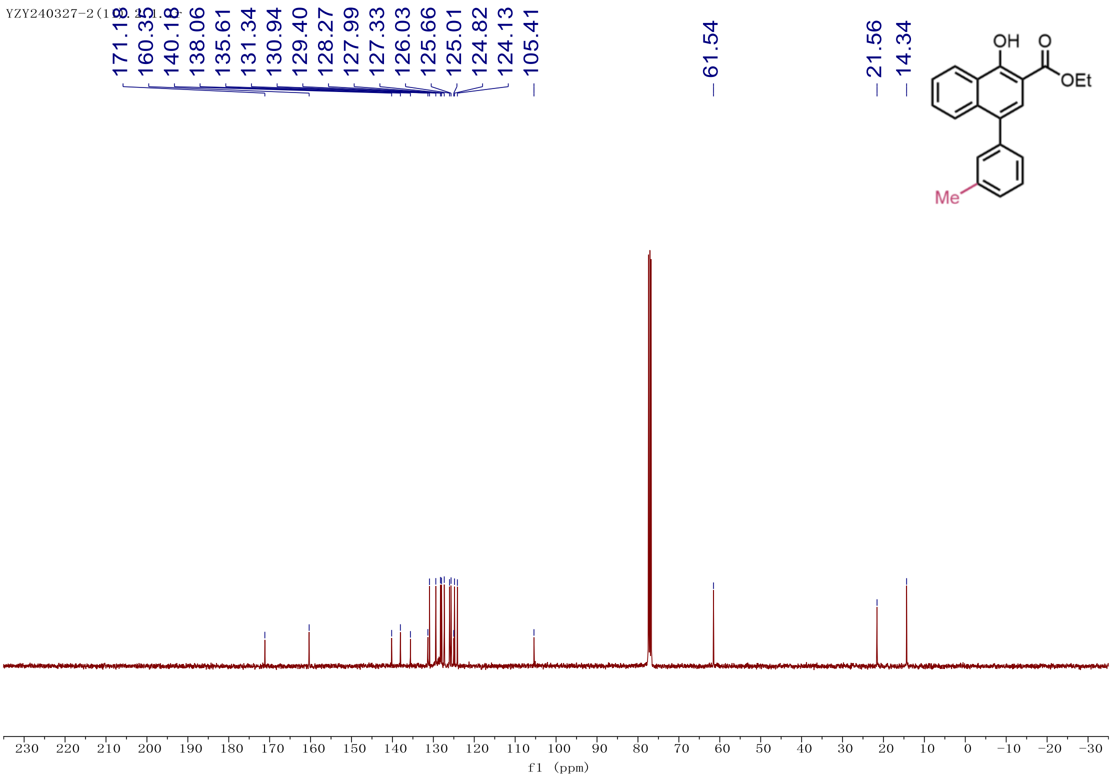


5b ^{13}C NMR



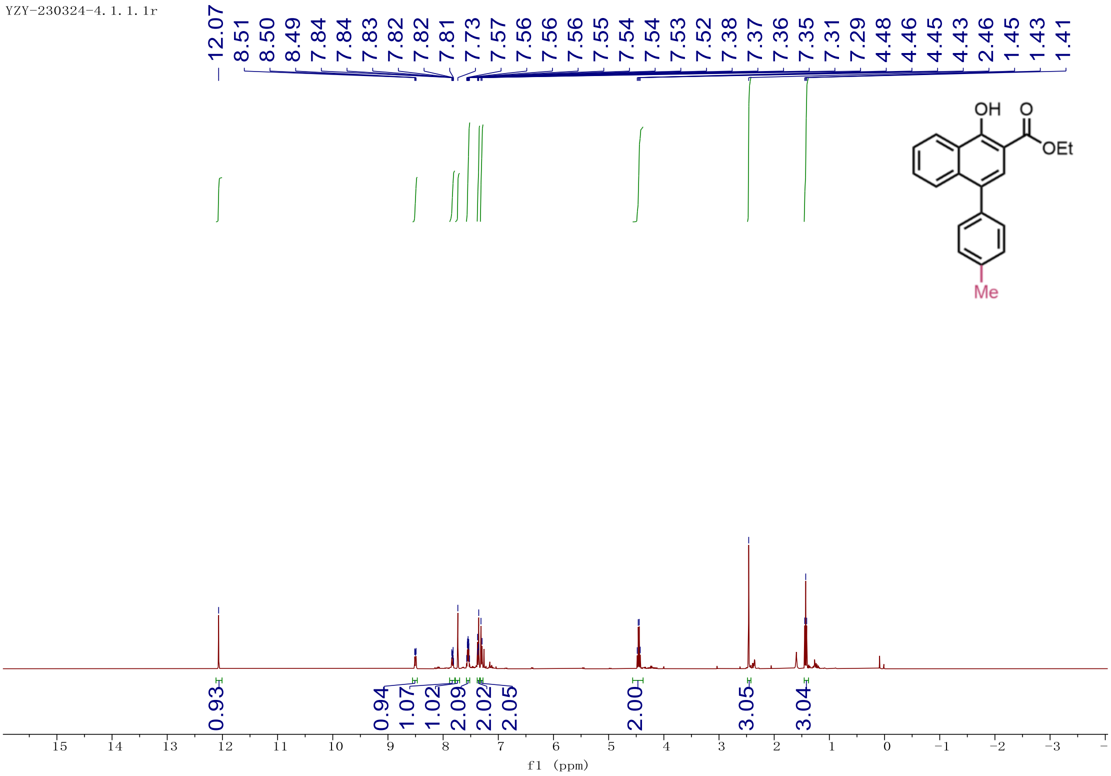
5c ^{1}H NMR

5c ^{13}C NMR



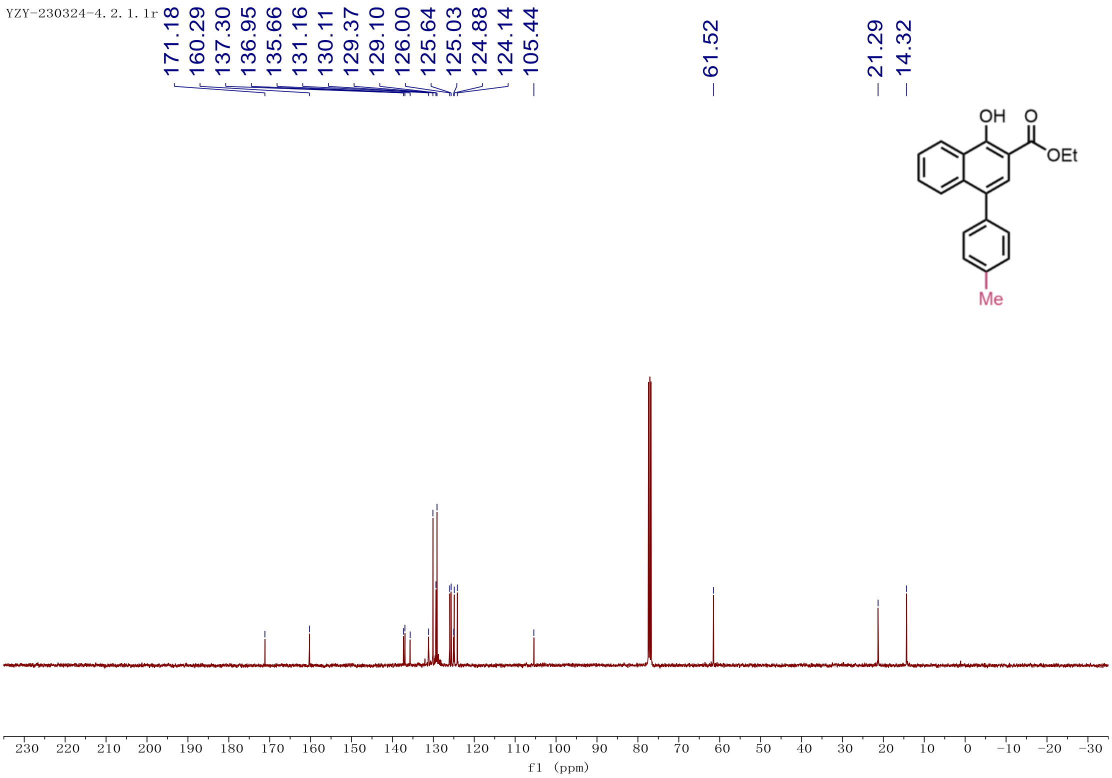
5d ^{1}H NMR

YZY-230324-4.1.1.1r



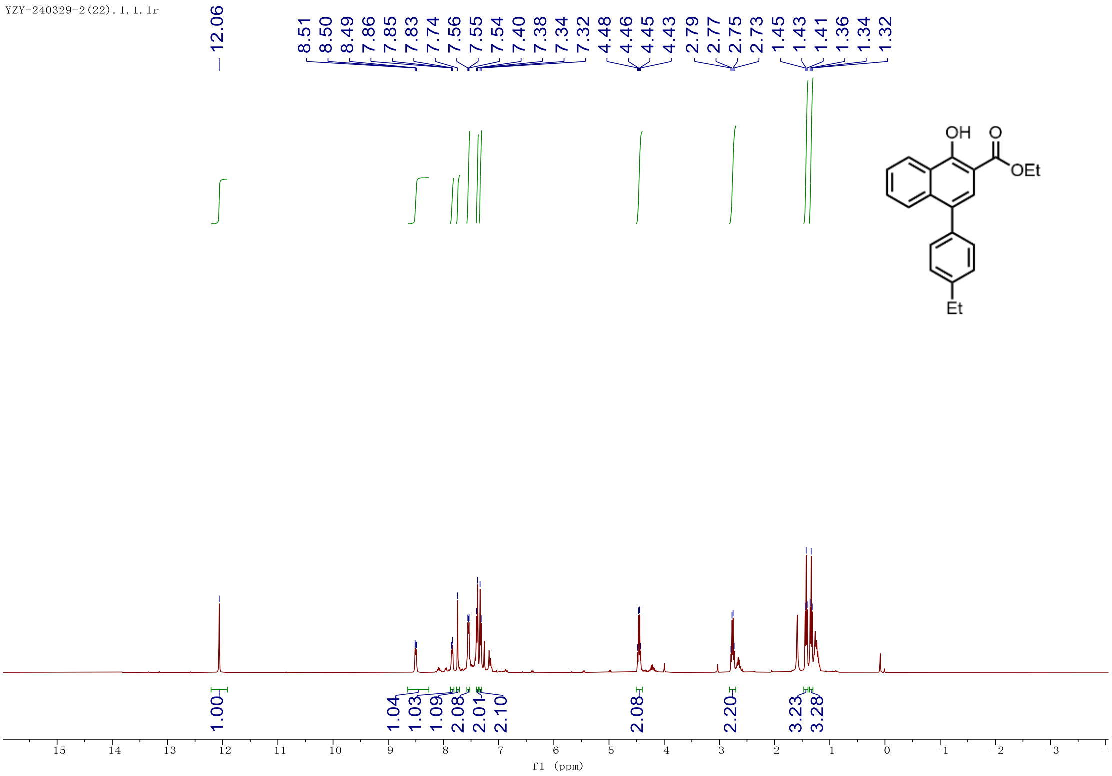
5d ^{13}C NMR

YZY-230324-4.2.1.1r



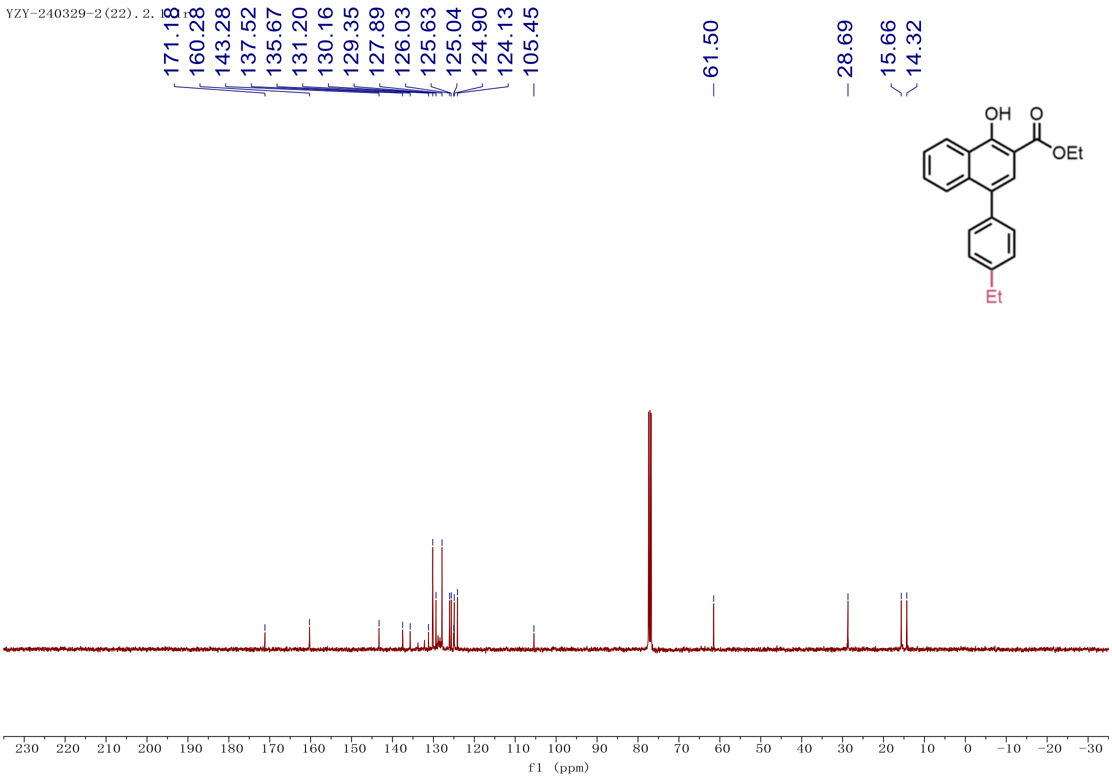
5e ^{1}H NMR

YZY-240329-2(22).1.1.1r

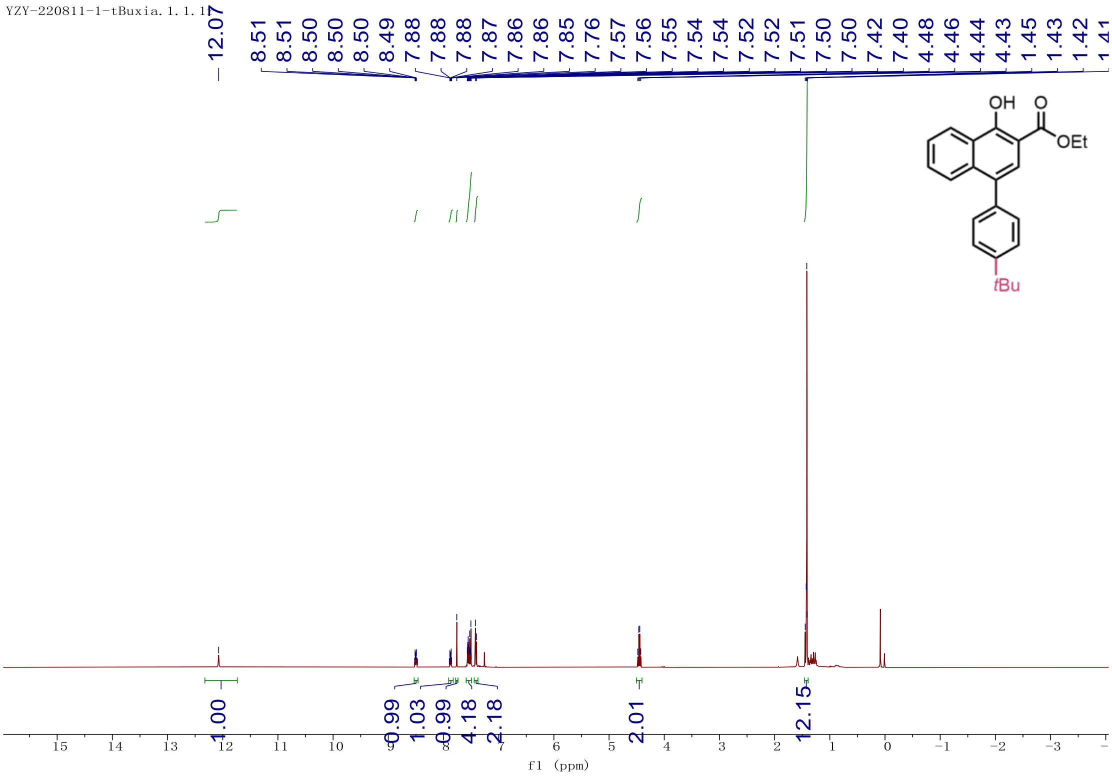


5e ^{13}C NMR

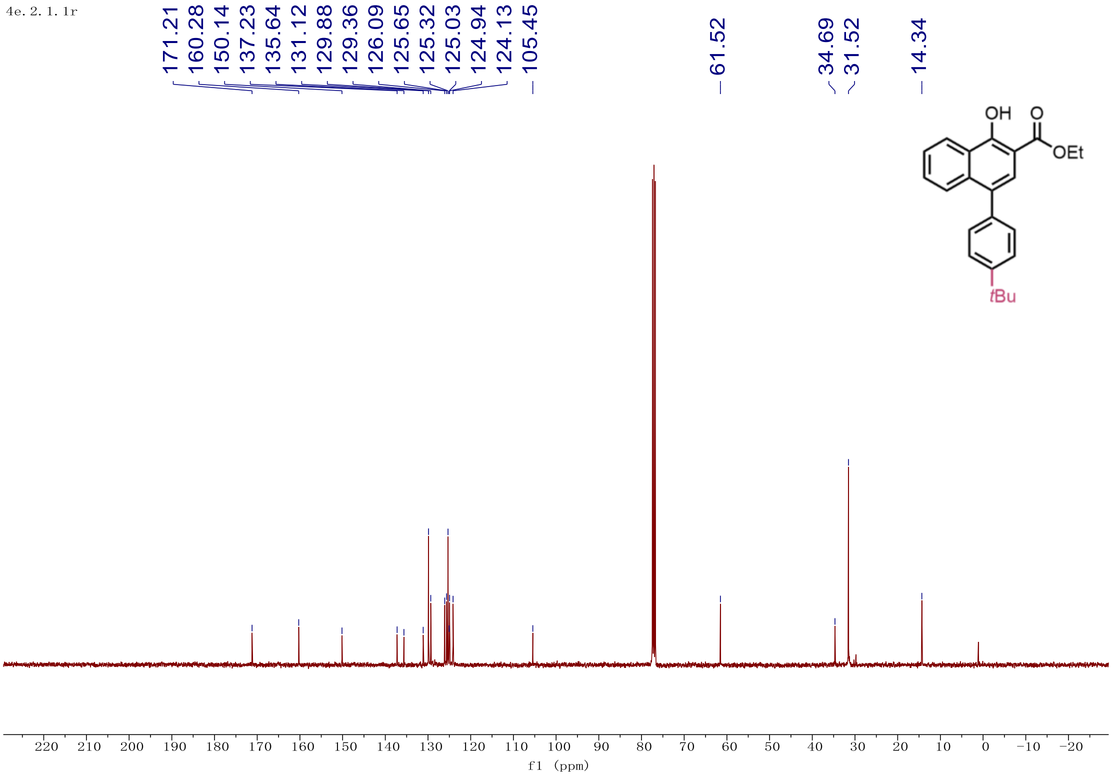
YZY-240329-2(22).2.1.1r



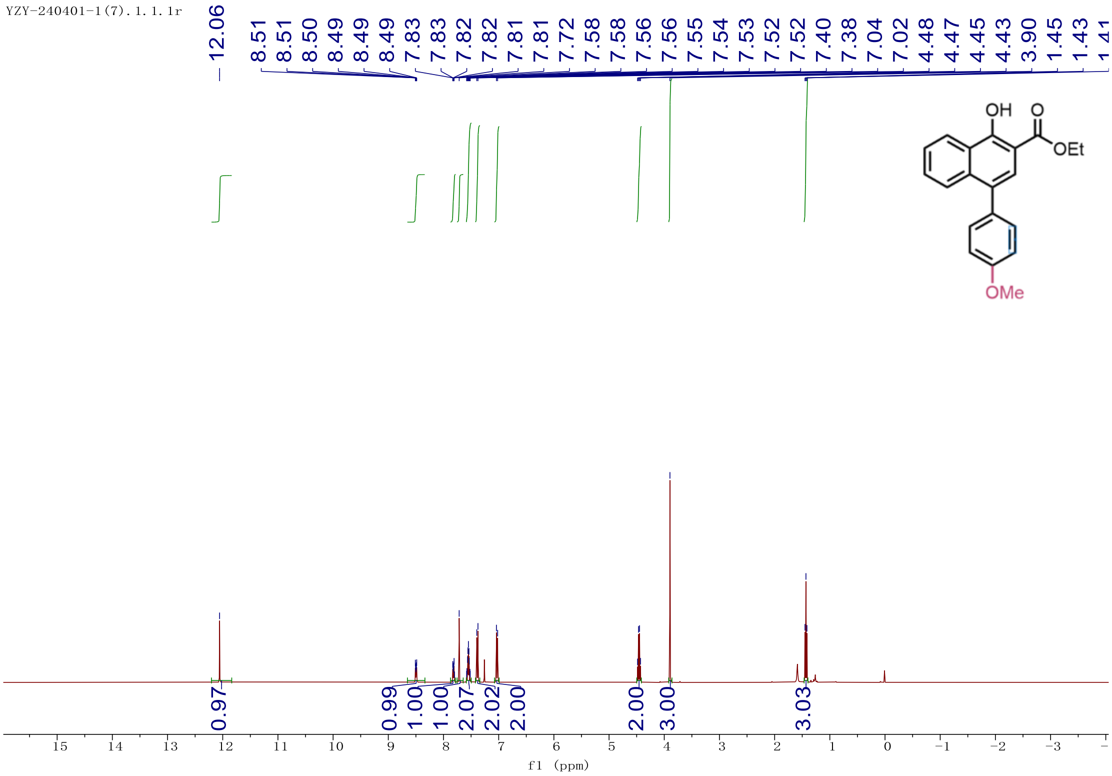
5f ^{1}H NMR



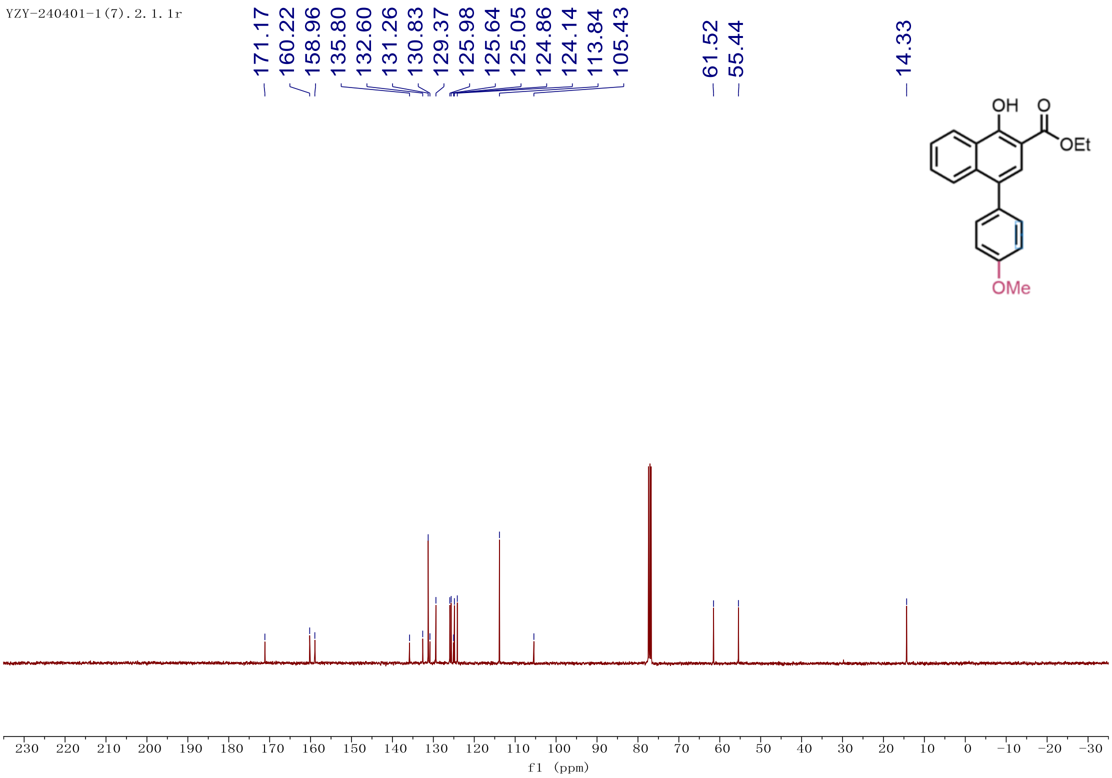
5f ^{13}C NMR



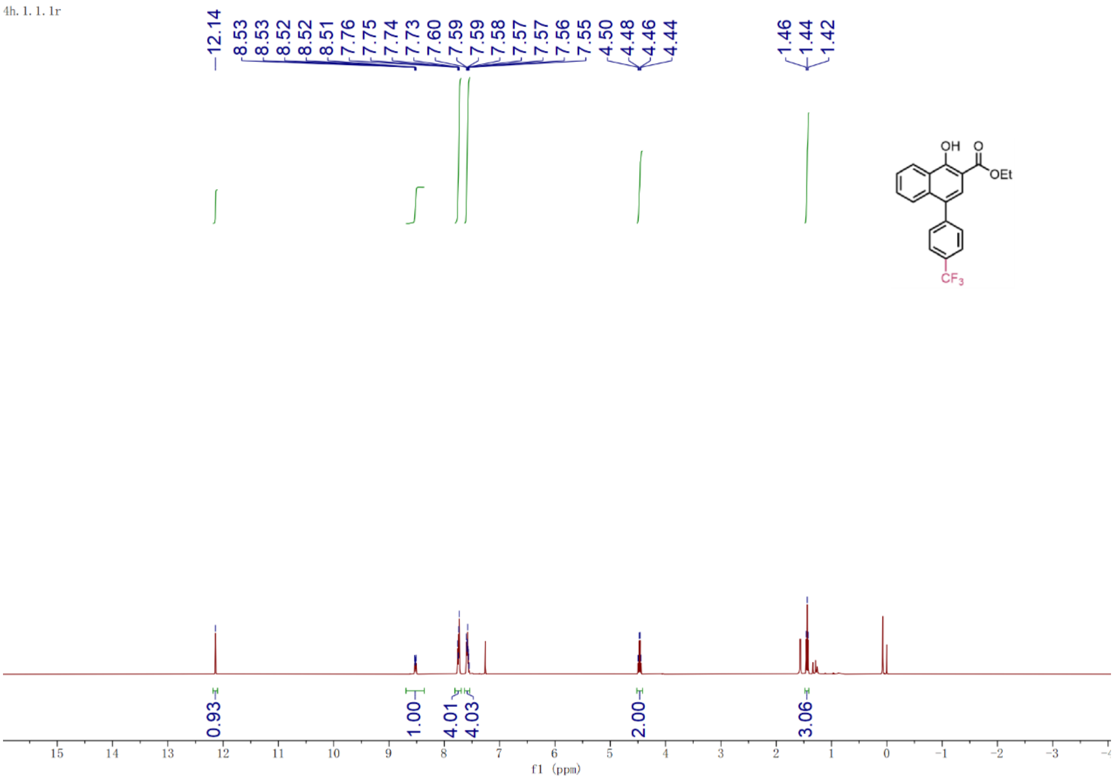
5g ^{1}H NMR



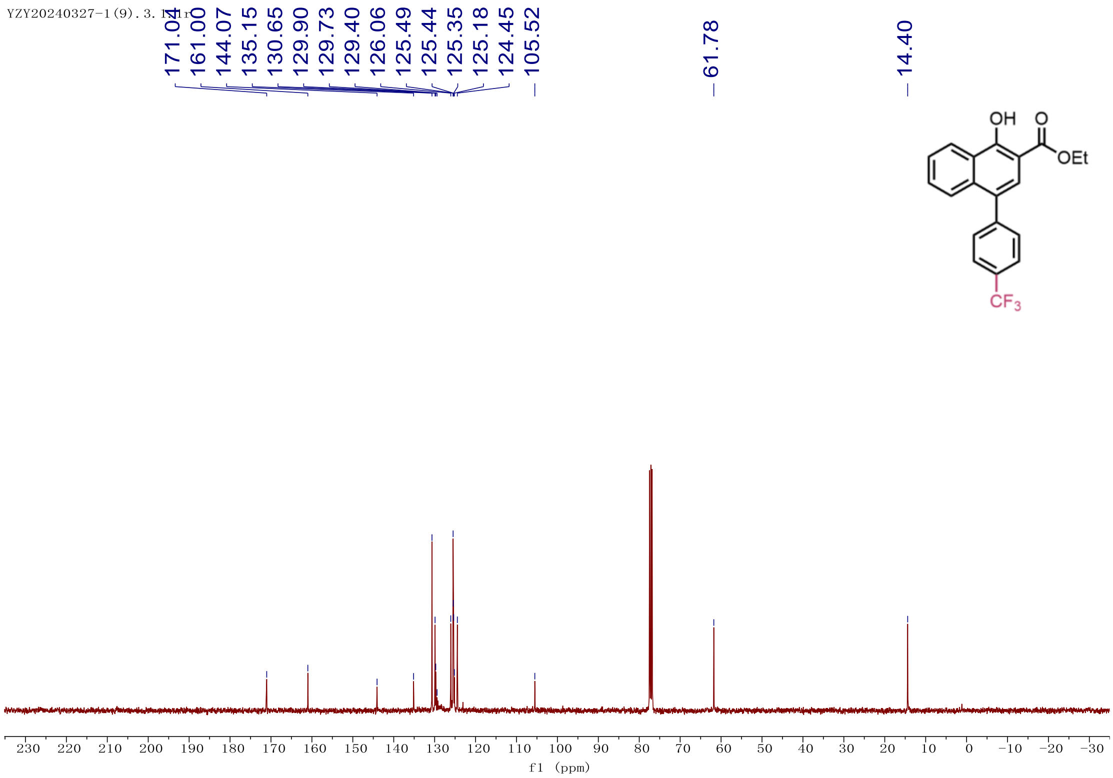
5g ^{13}C NMR



5h ^{1}H NMR

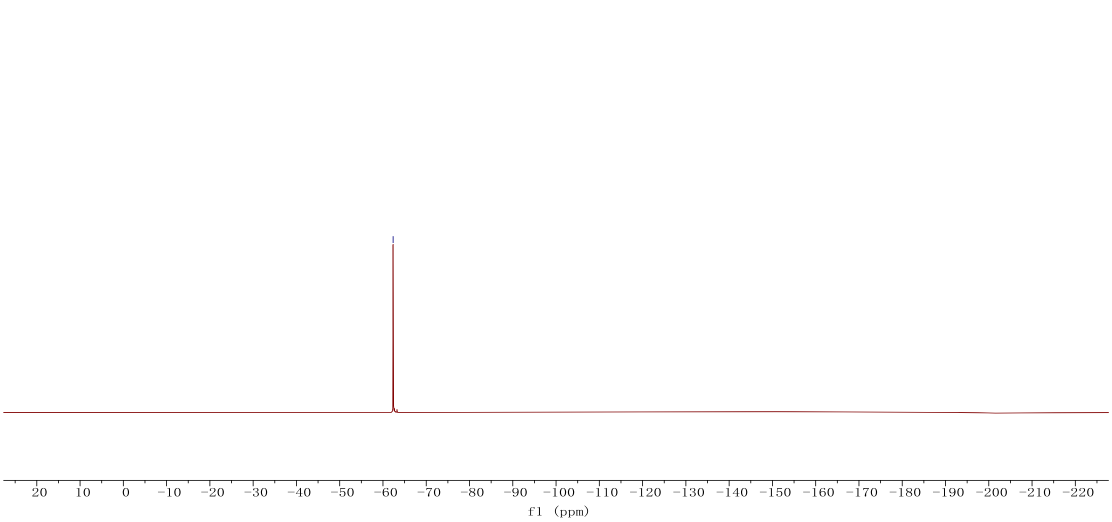


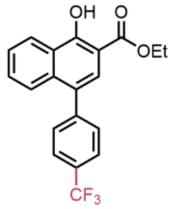
5h ^{13}C NMR



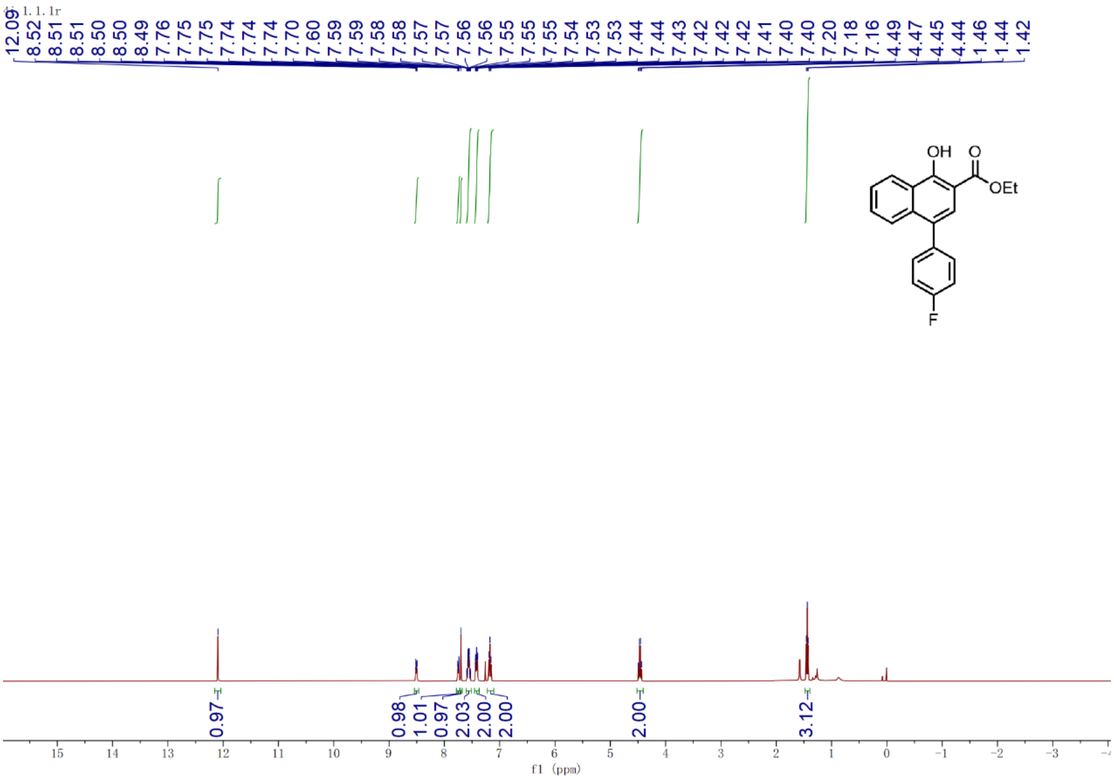
5h ^{19}F NMR

YZY20240327-1(9).2.1.1r

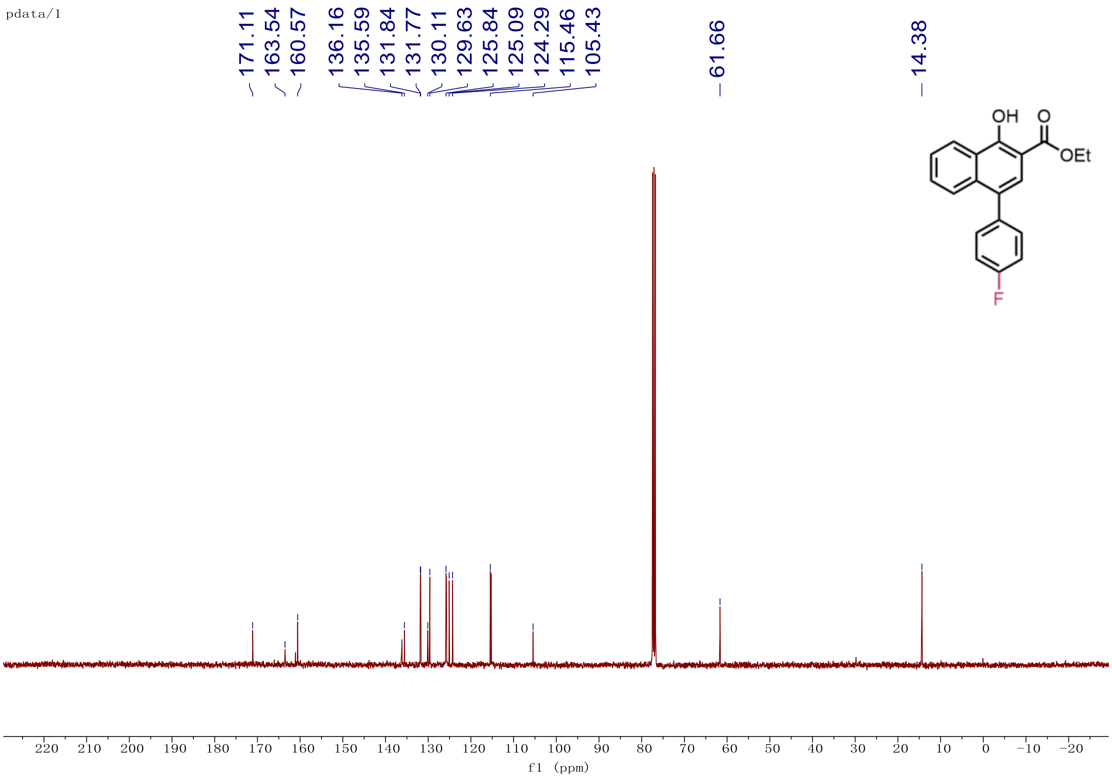




5i ^{1}H NMR

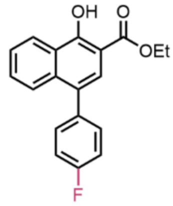


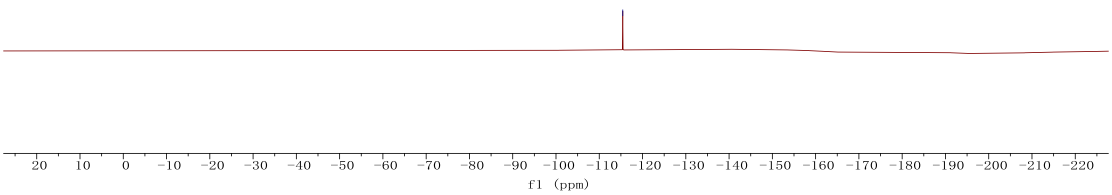
5i ^{13}C NMR



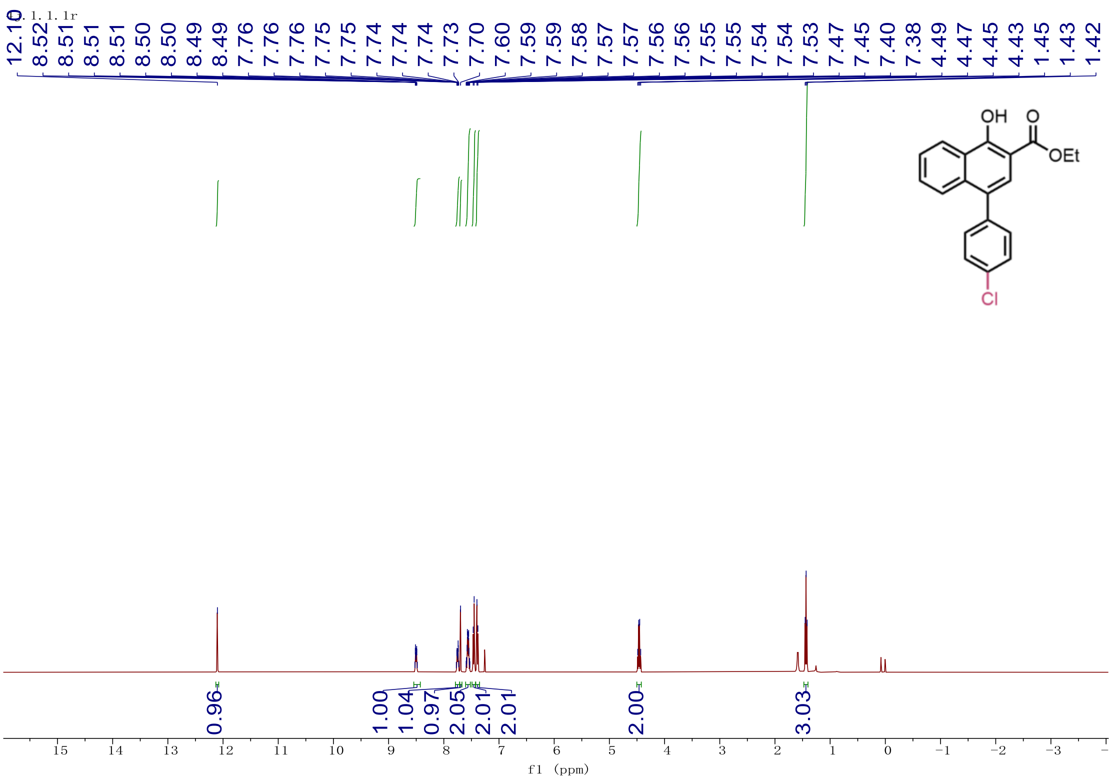
5i ^{19}F NMR

pdata/1

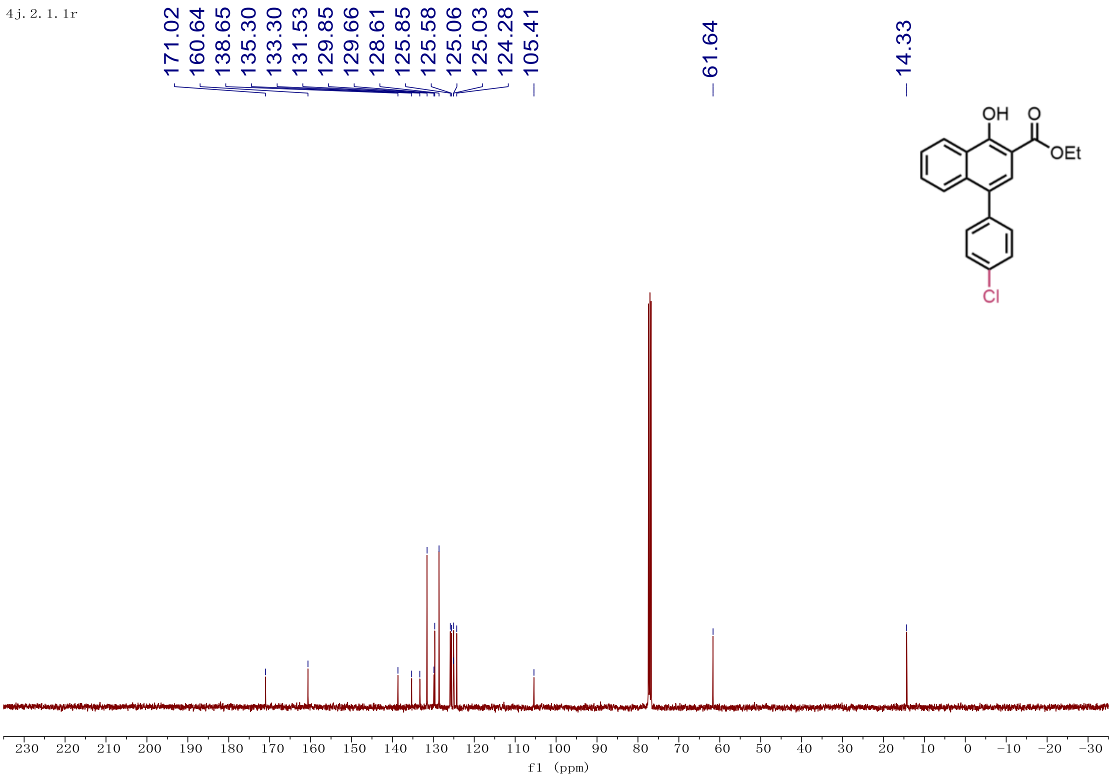




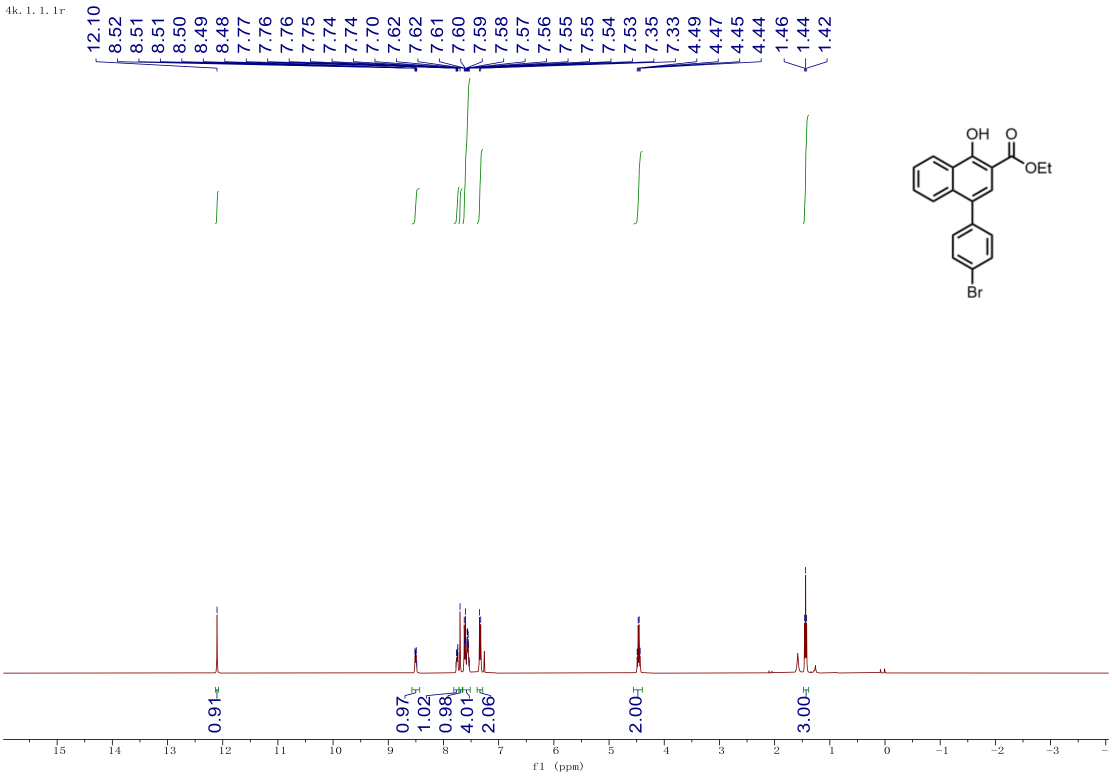
5j ^{1}H NMR



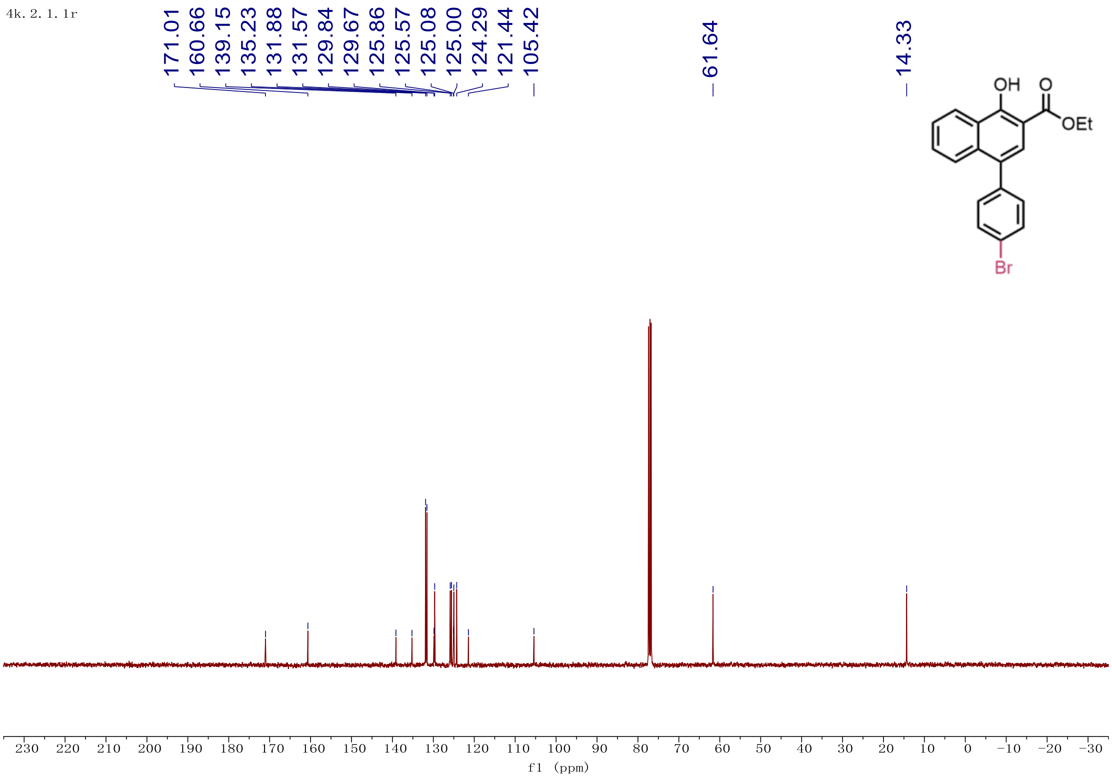
5j ^{13}C NMR



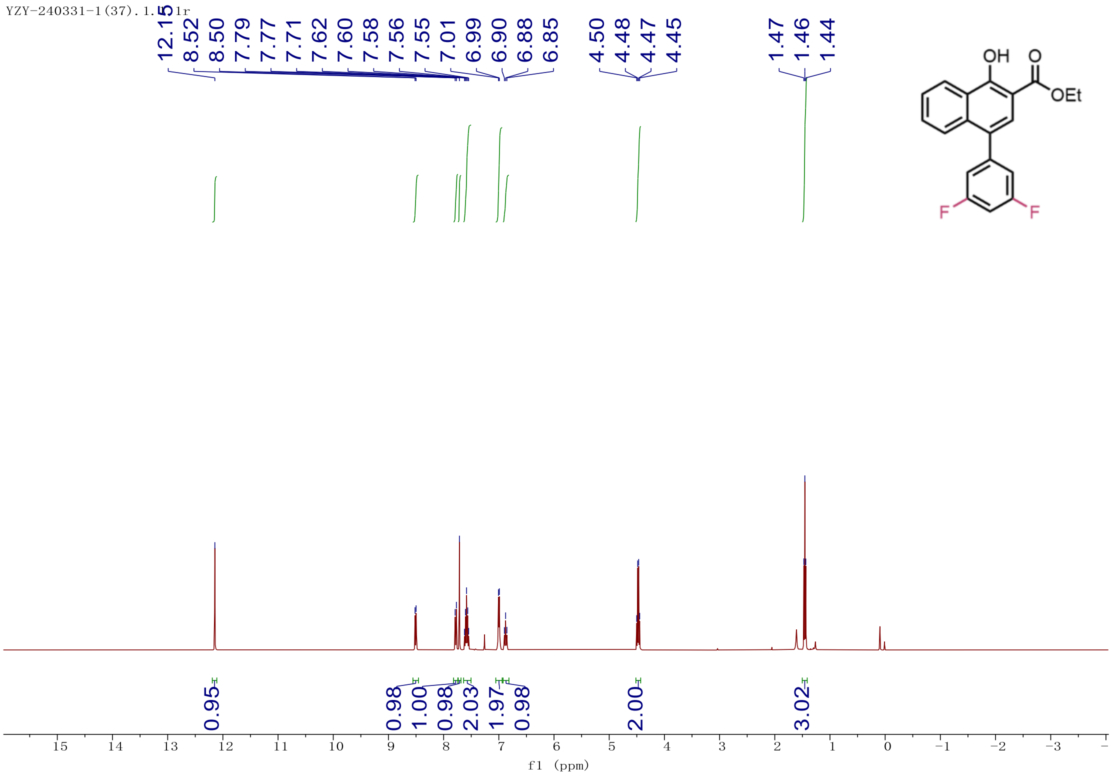
5k ¹H NMR



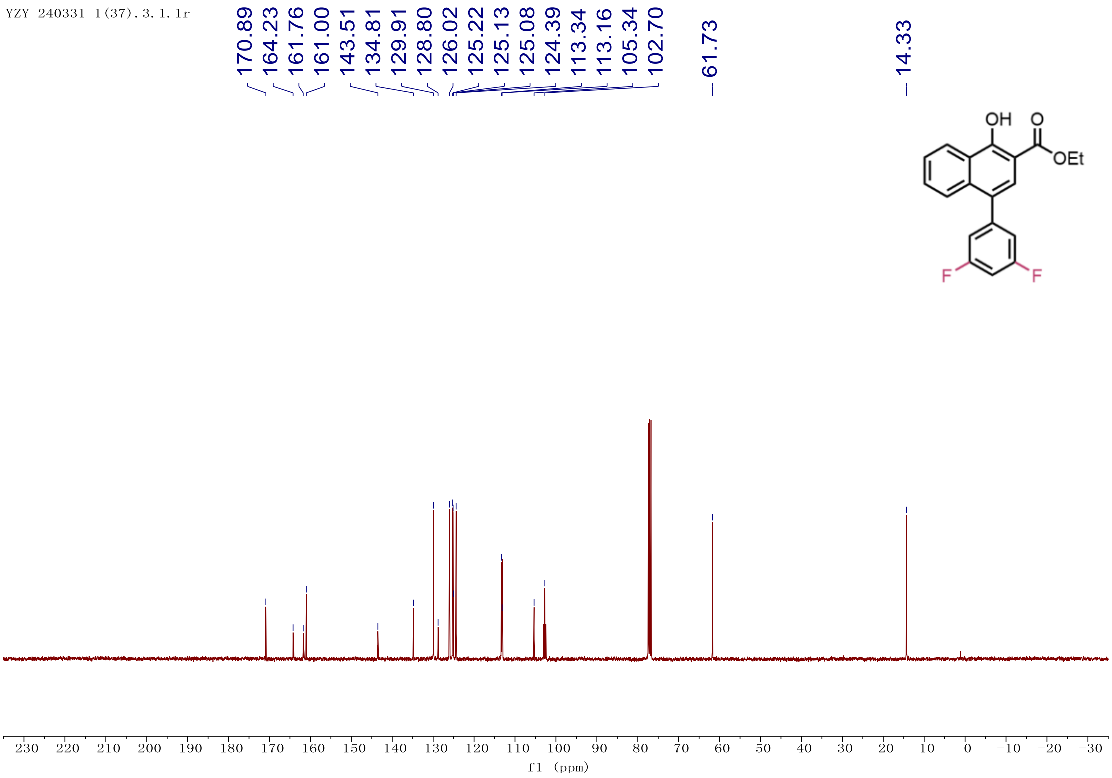
5k ¹³C NMR



5l ^{1}H NMR

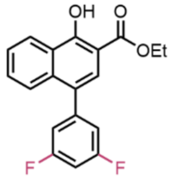


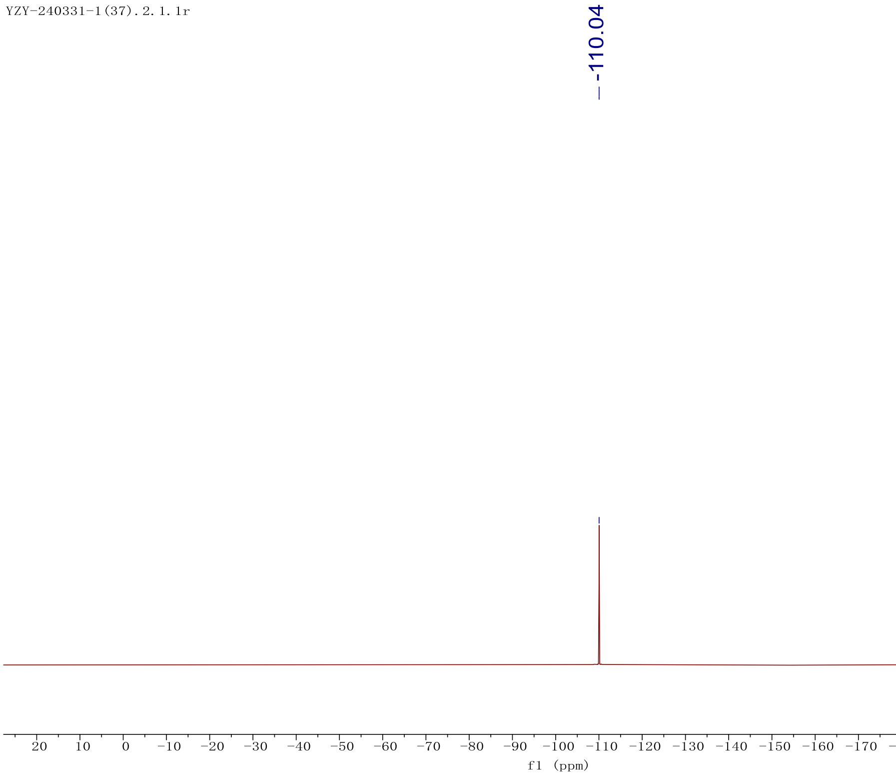
5l ^{13}C NMR



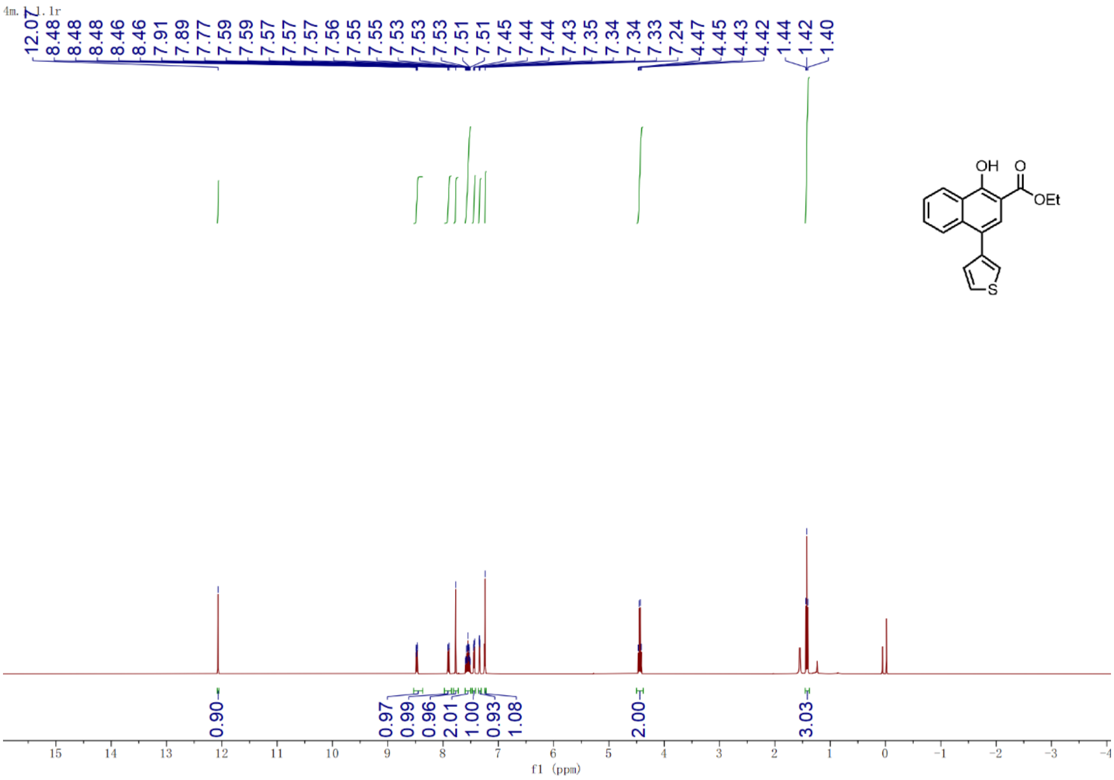
5l ^{19}F NMR

YZY-240331-1(37).2.1.1r

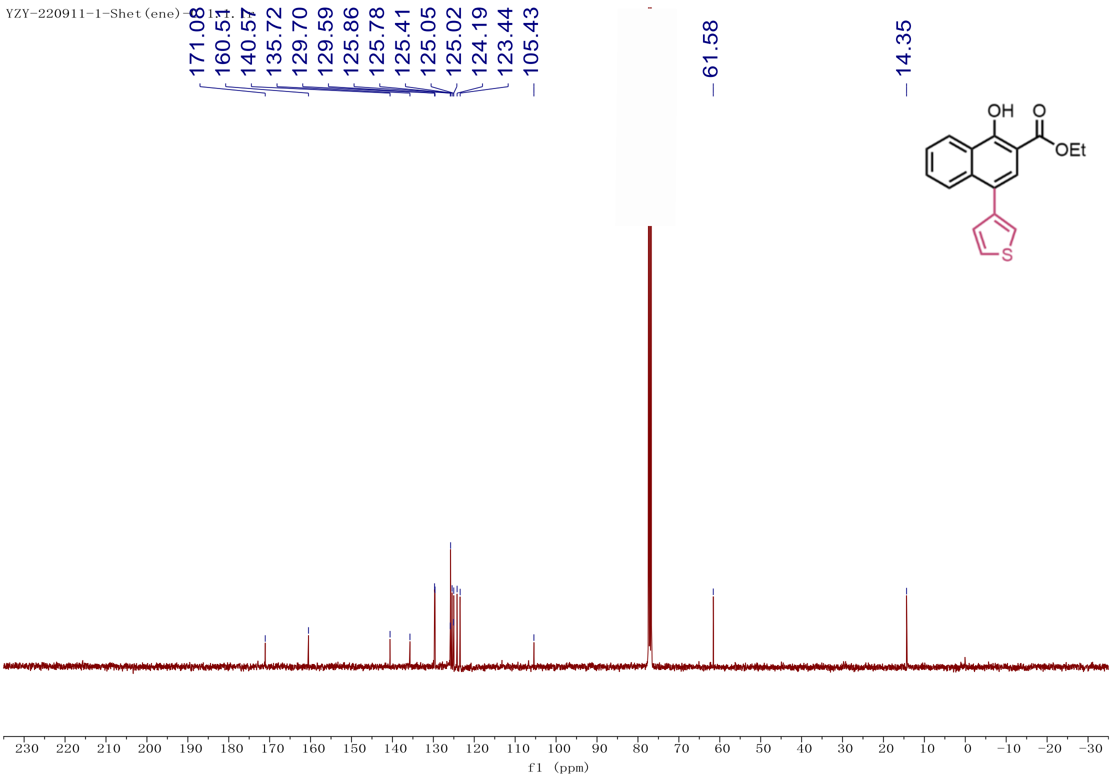




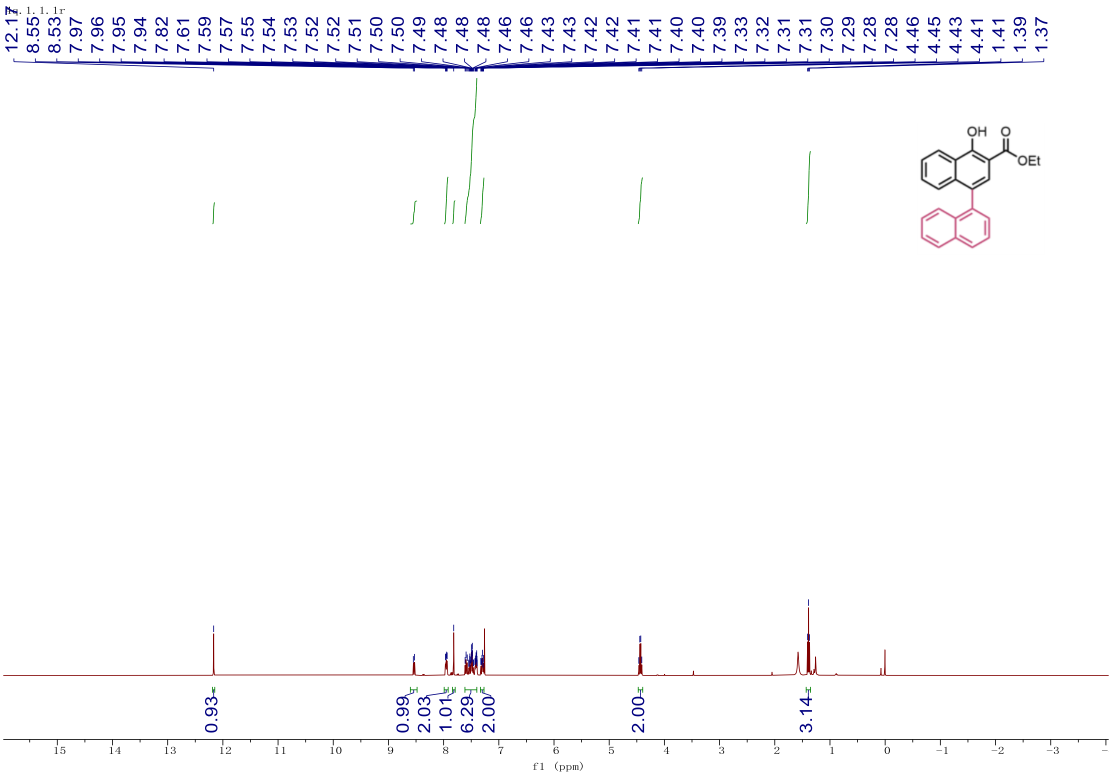
5m ^{1}H NMR



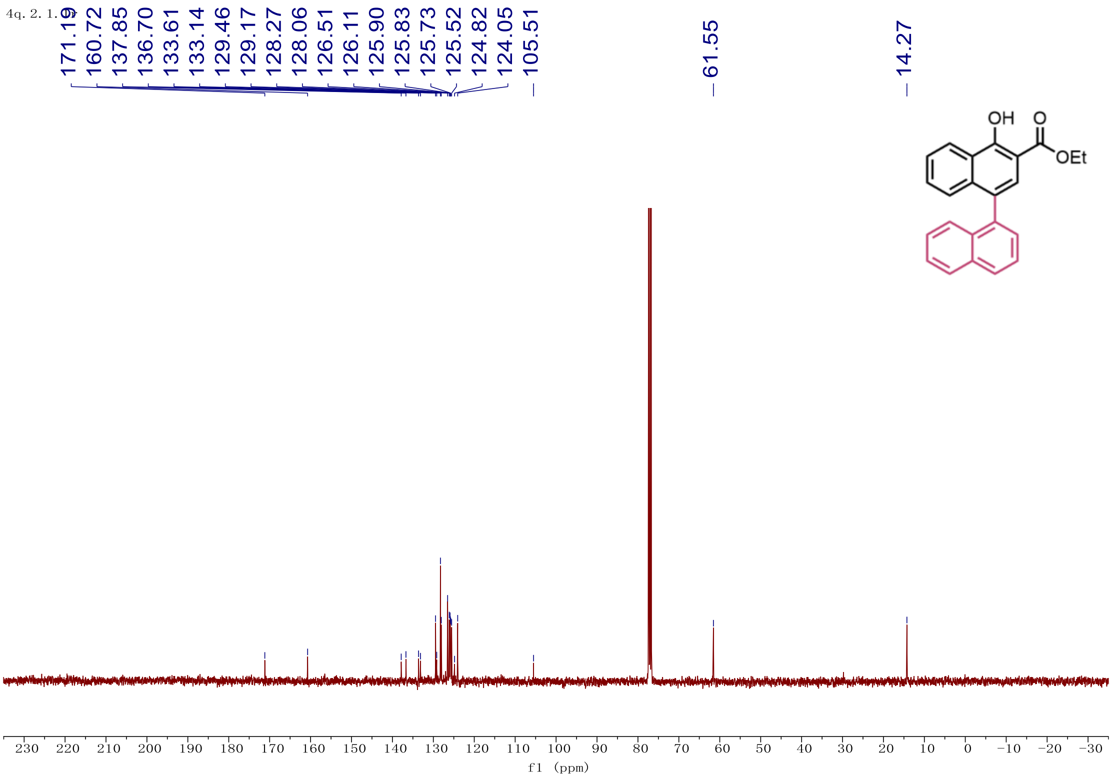
5m ^{13}C NMR



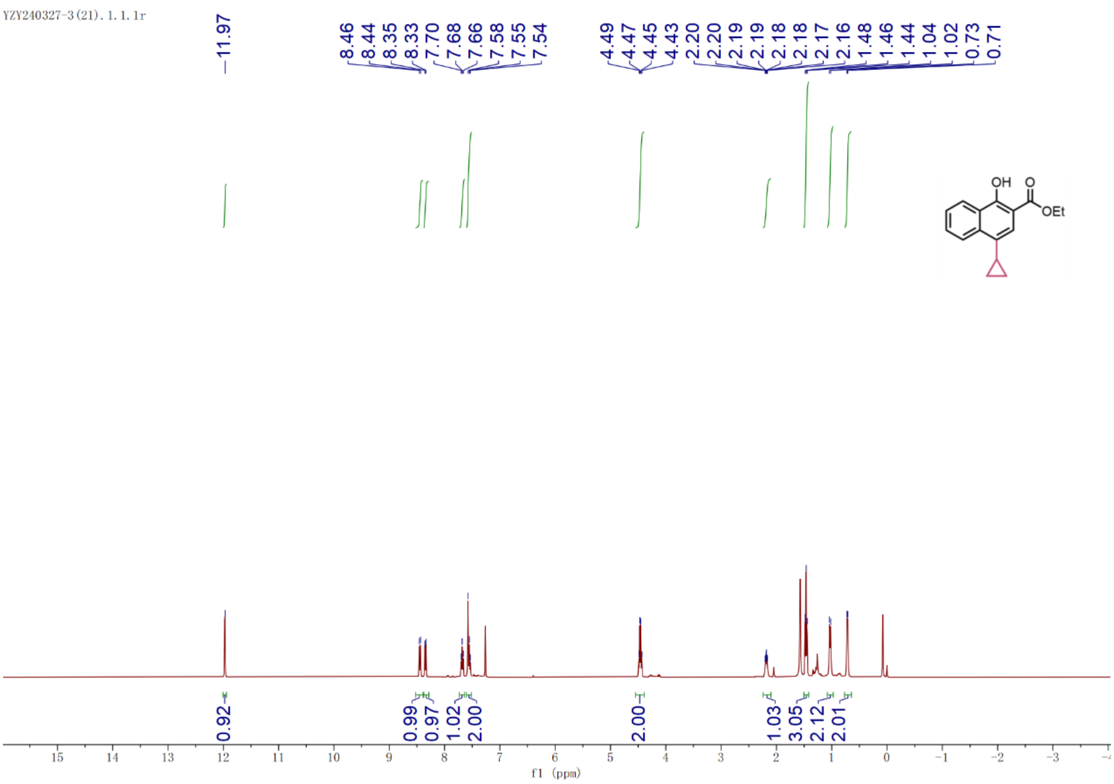
5n ^{1}H NMR



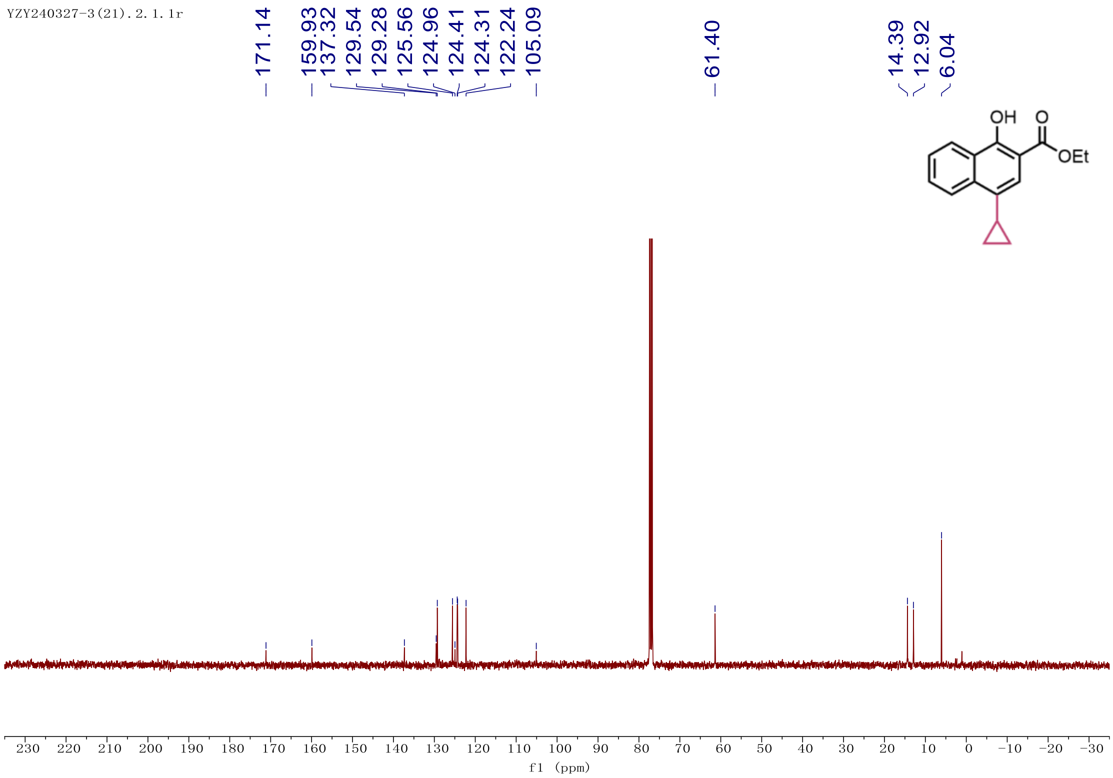
5n ^{13}C NMR



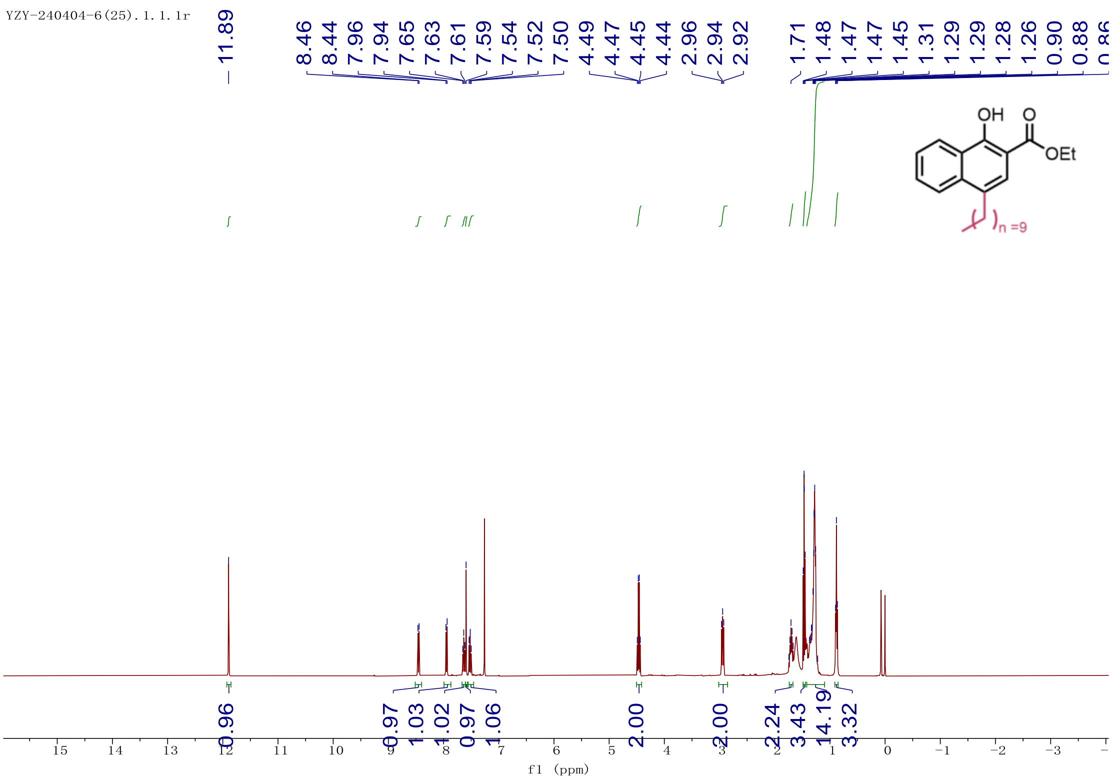
5o ^{1}H NMR



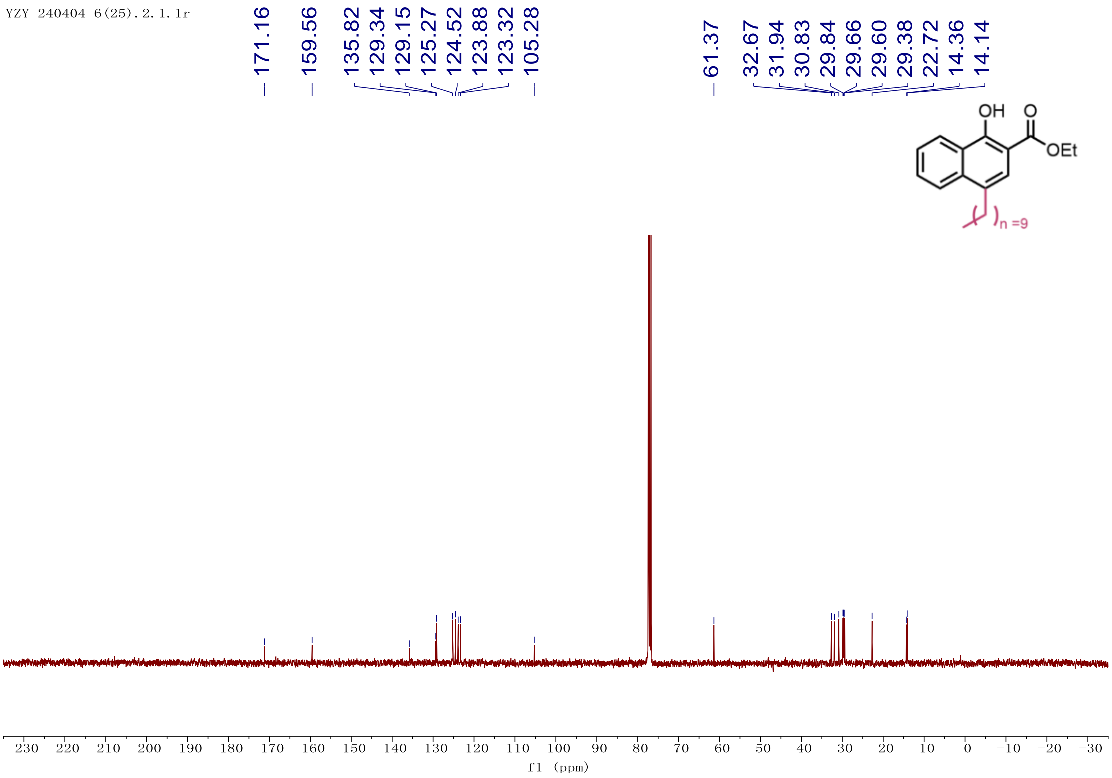
5o ^{13}C NMR



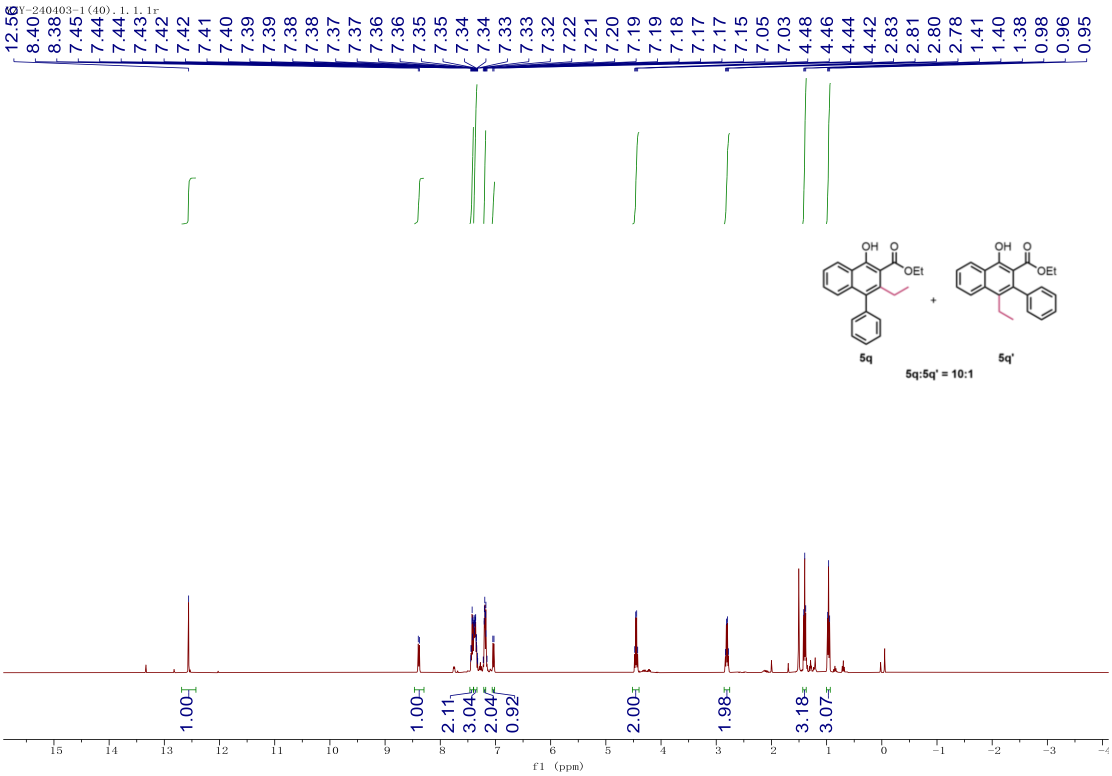
5p ^{1}H NMR



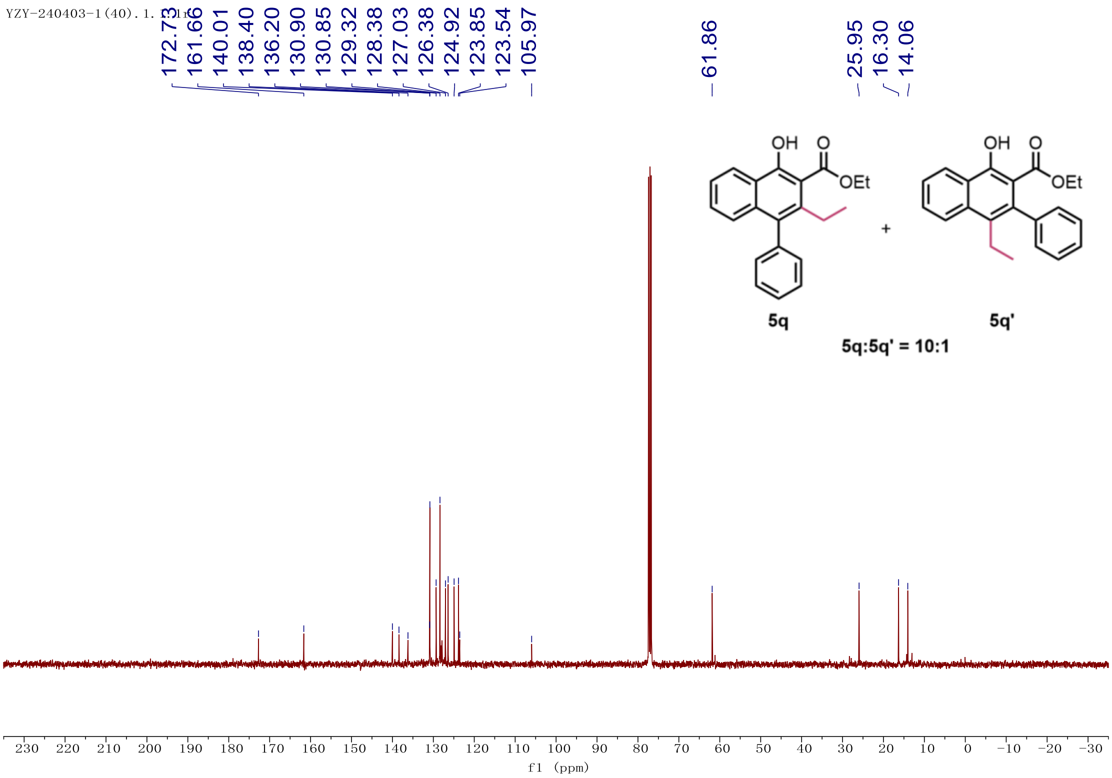
5p ^{13}C NMR



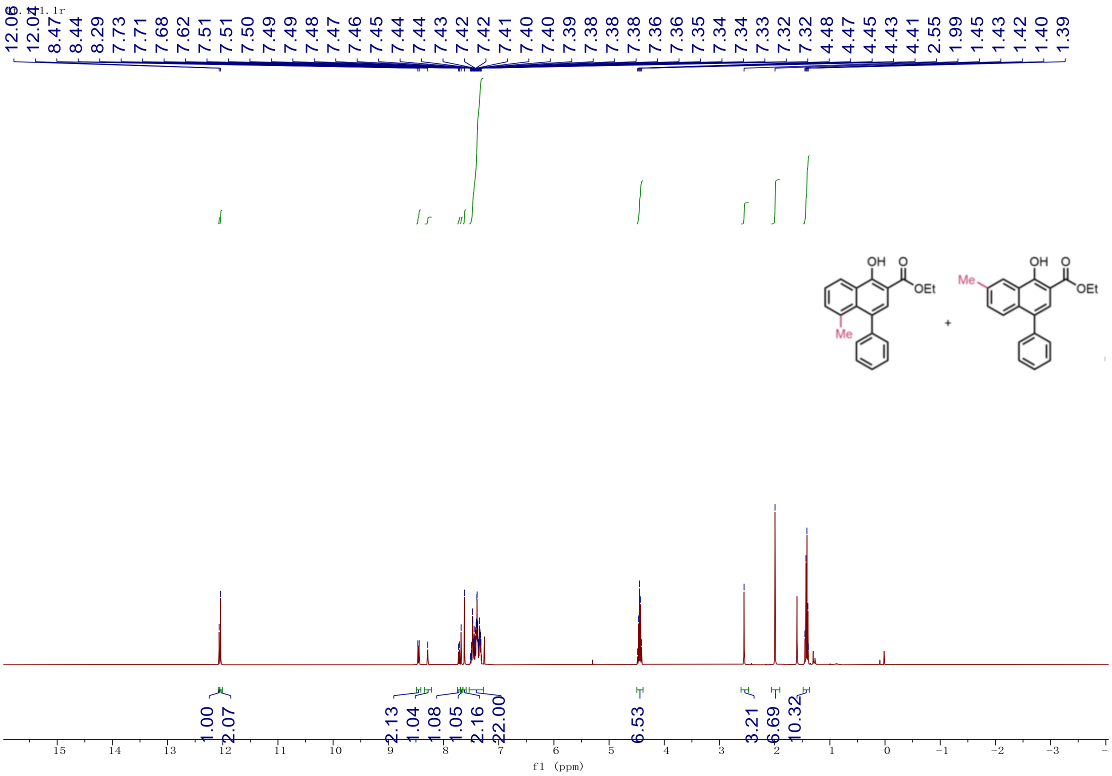
5q ^{1}H NMR



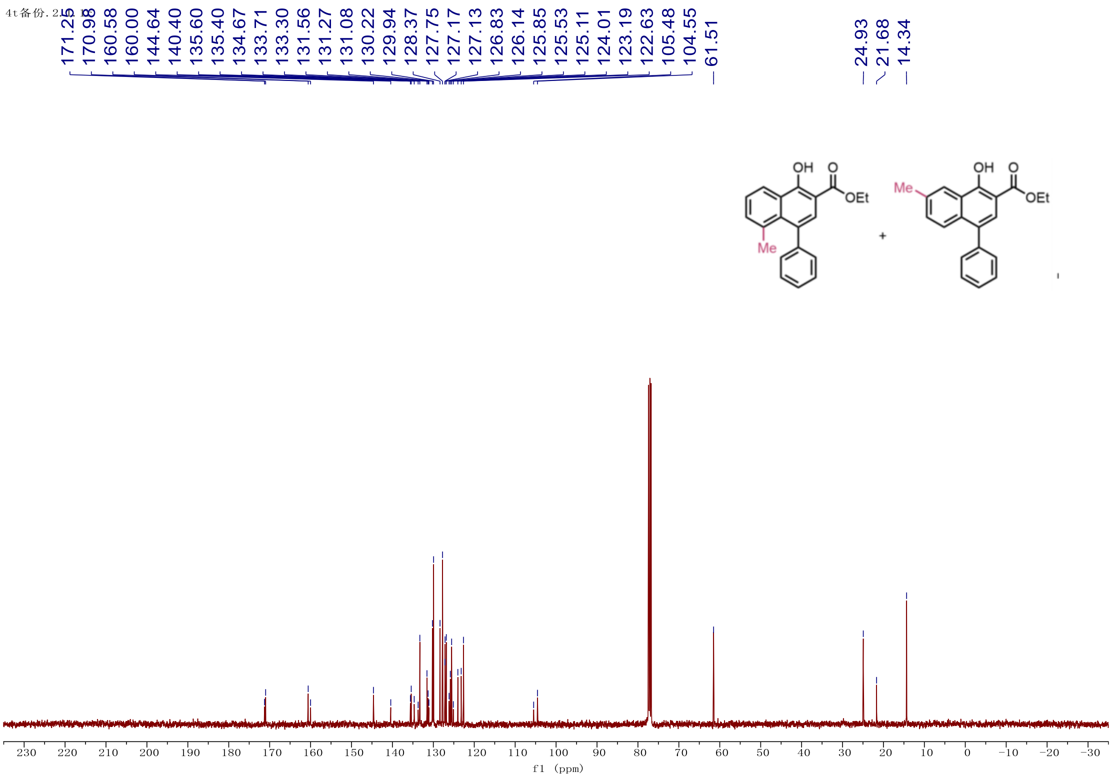
5q ^{13}C NMR



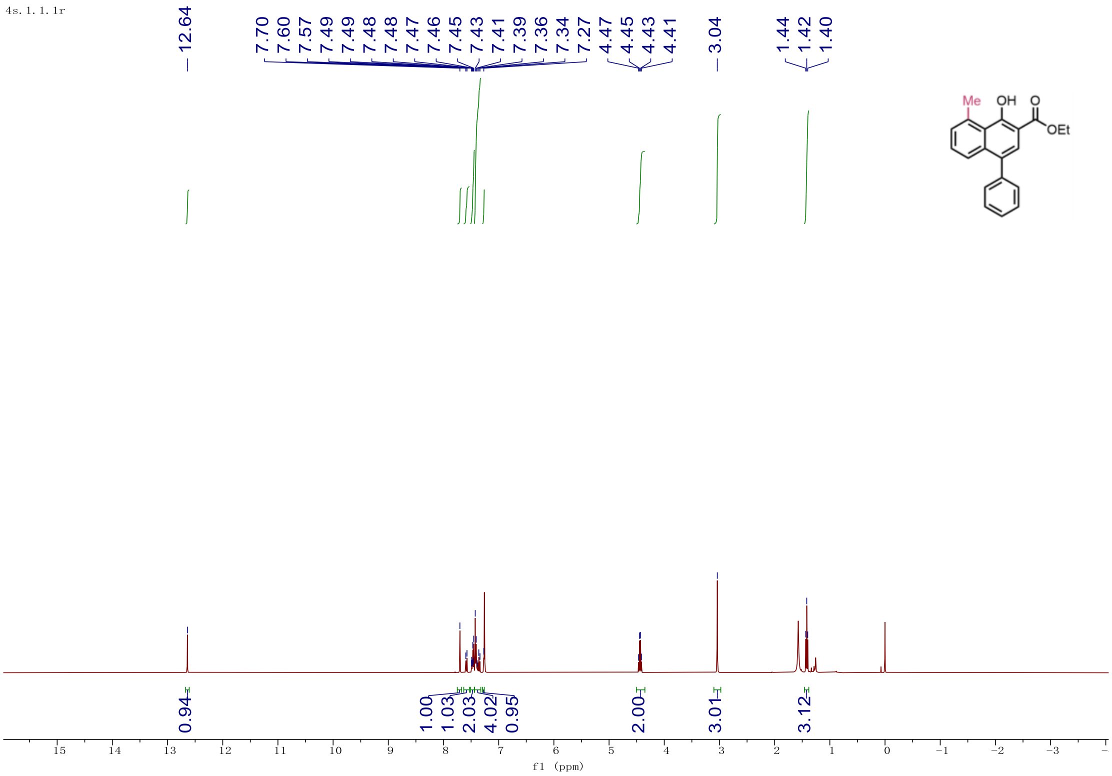
5r ^{1}H NMR



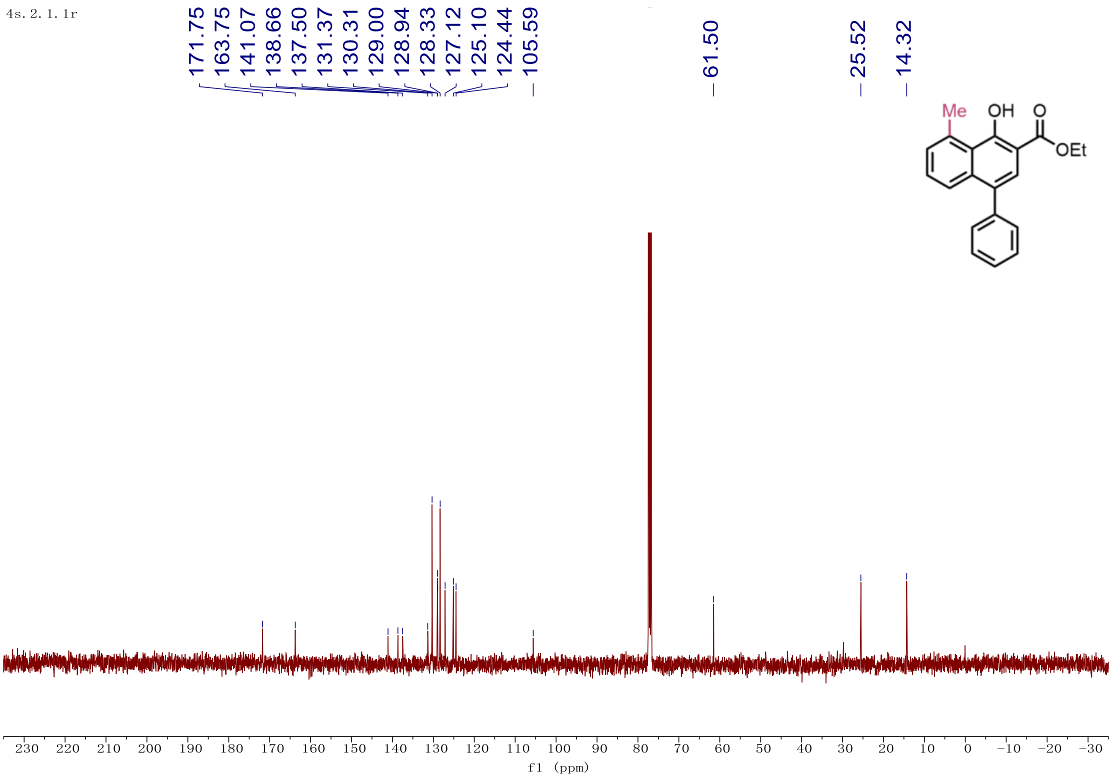
5r ^{13}C NMR



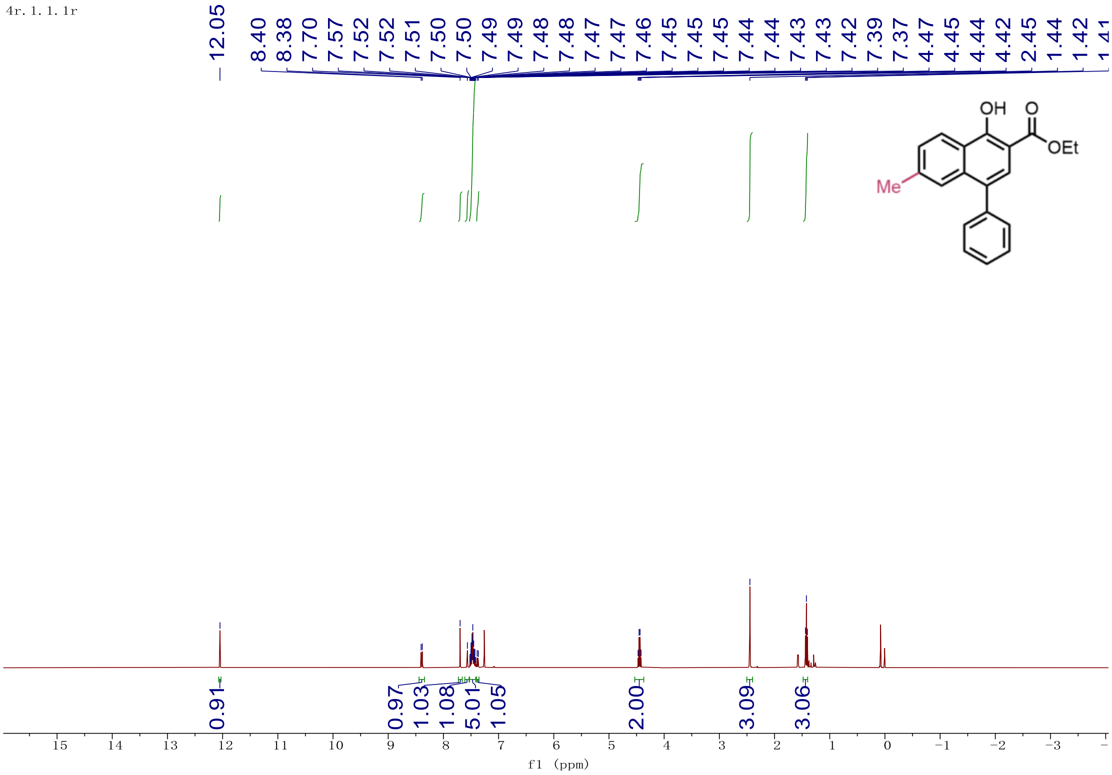
5s ^{1}H NMR



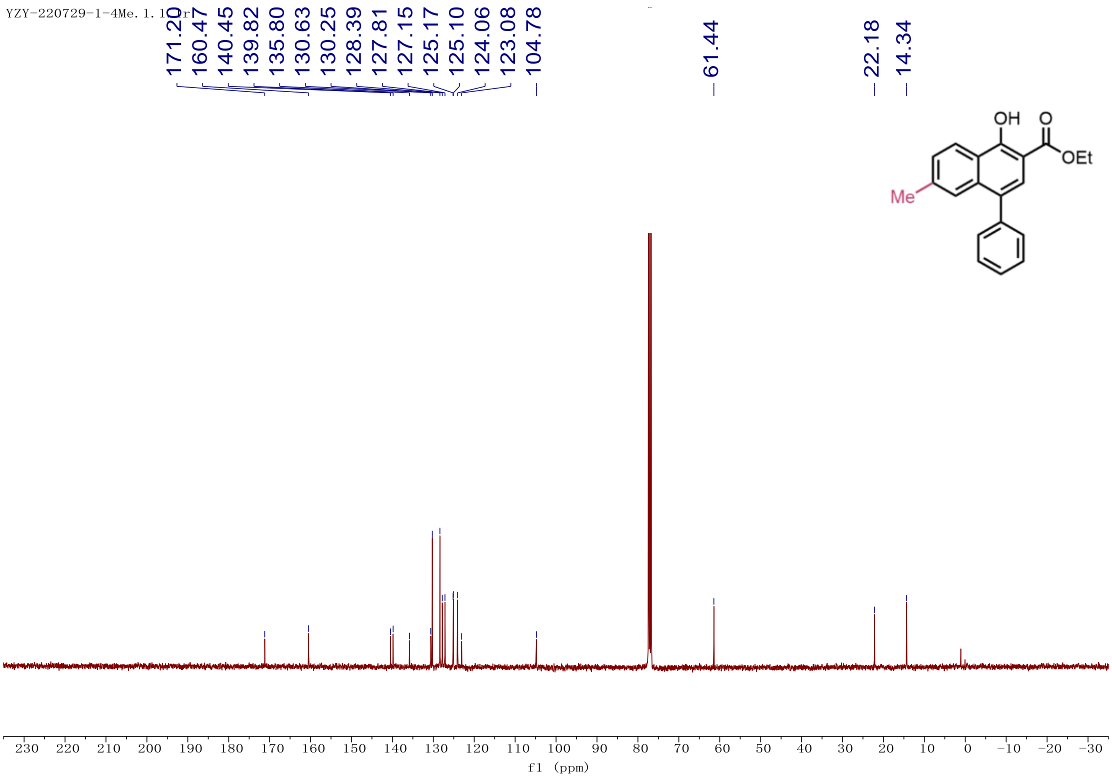
5s ^{13}C NMR



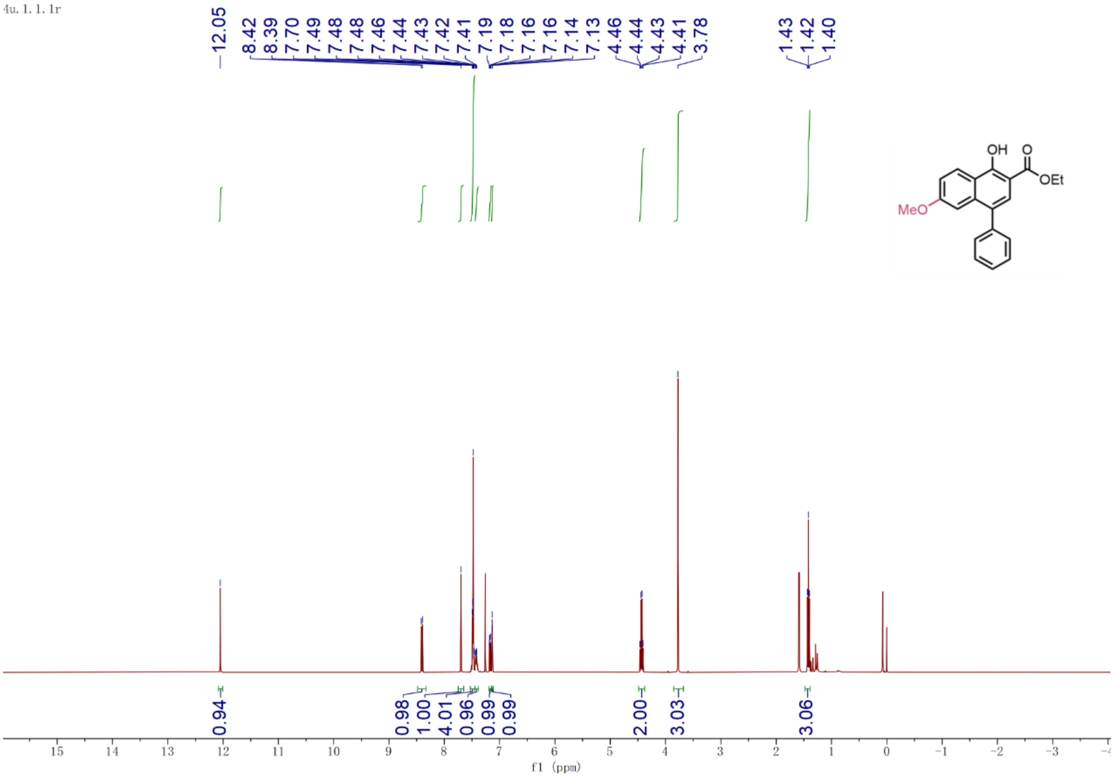
5t ^{1}H NMR



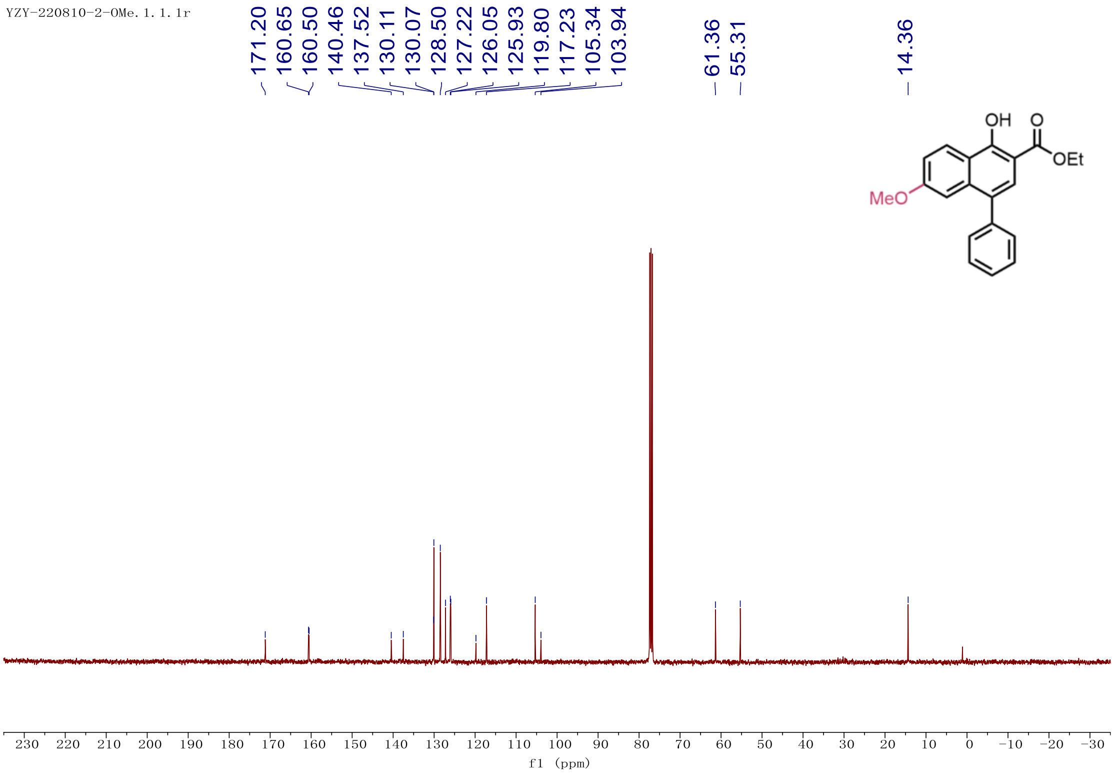
5t ^{13}C NMR



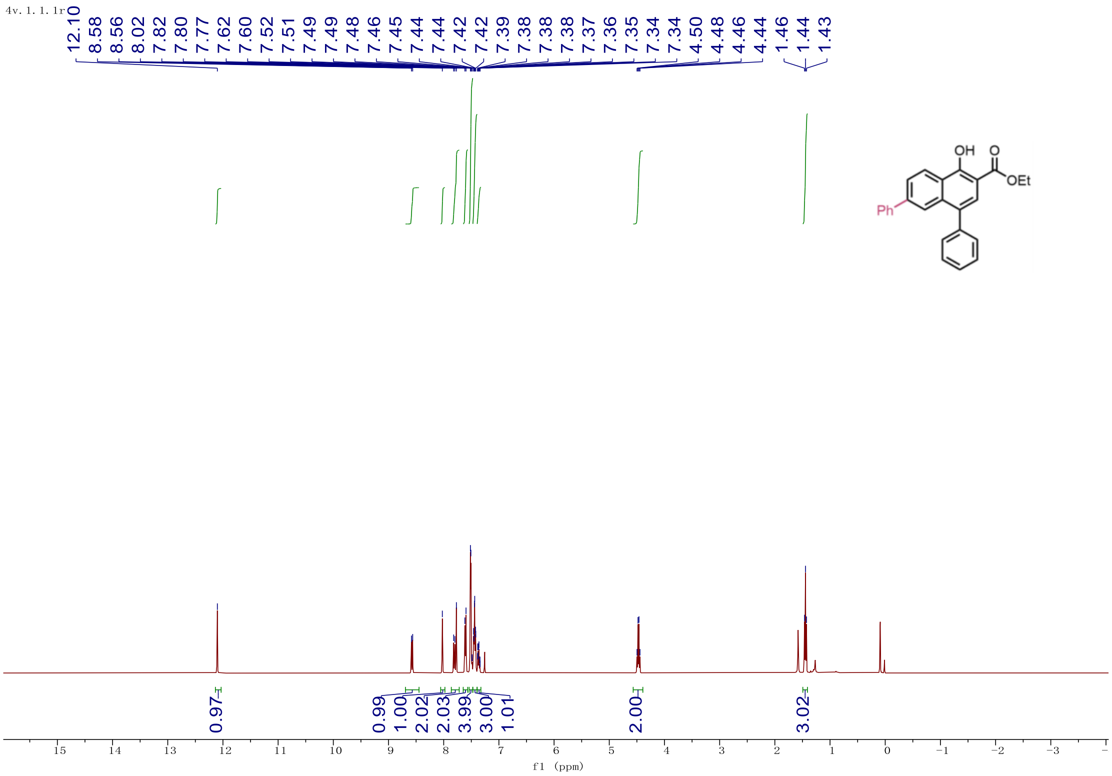
5u ^{1}H NMR



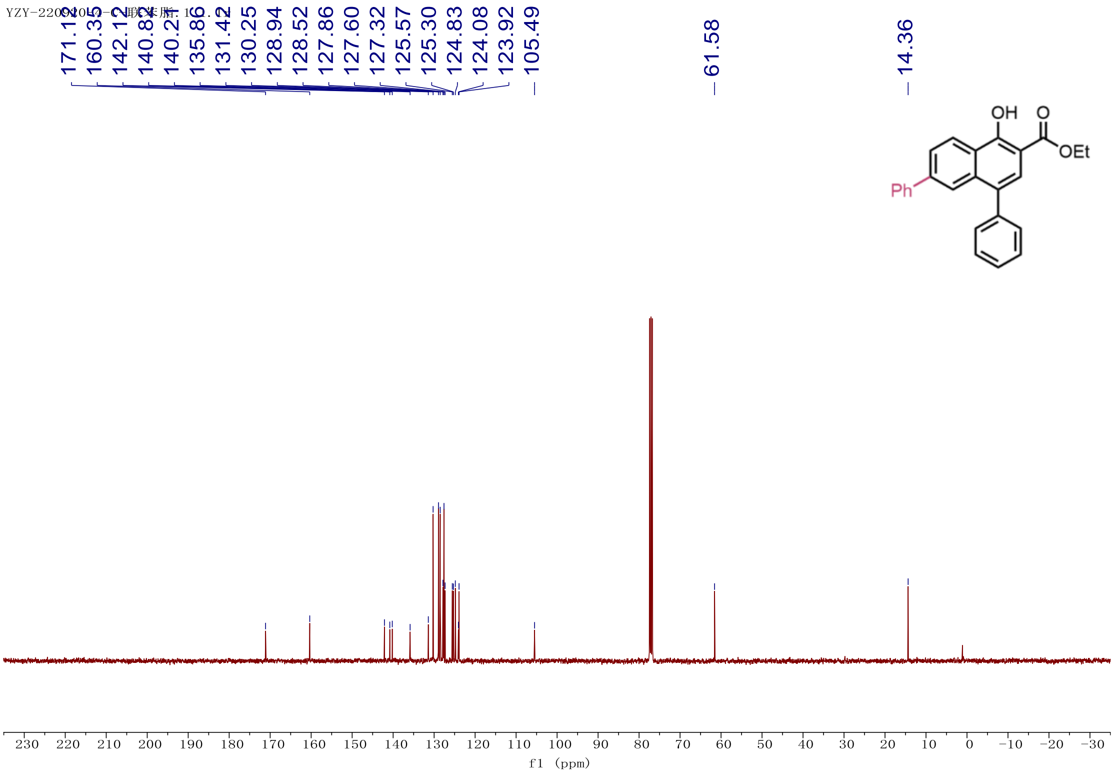
5u ^{13}C NMR



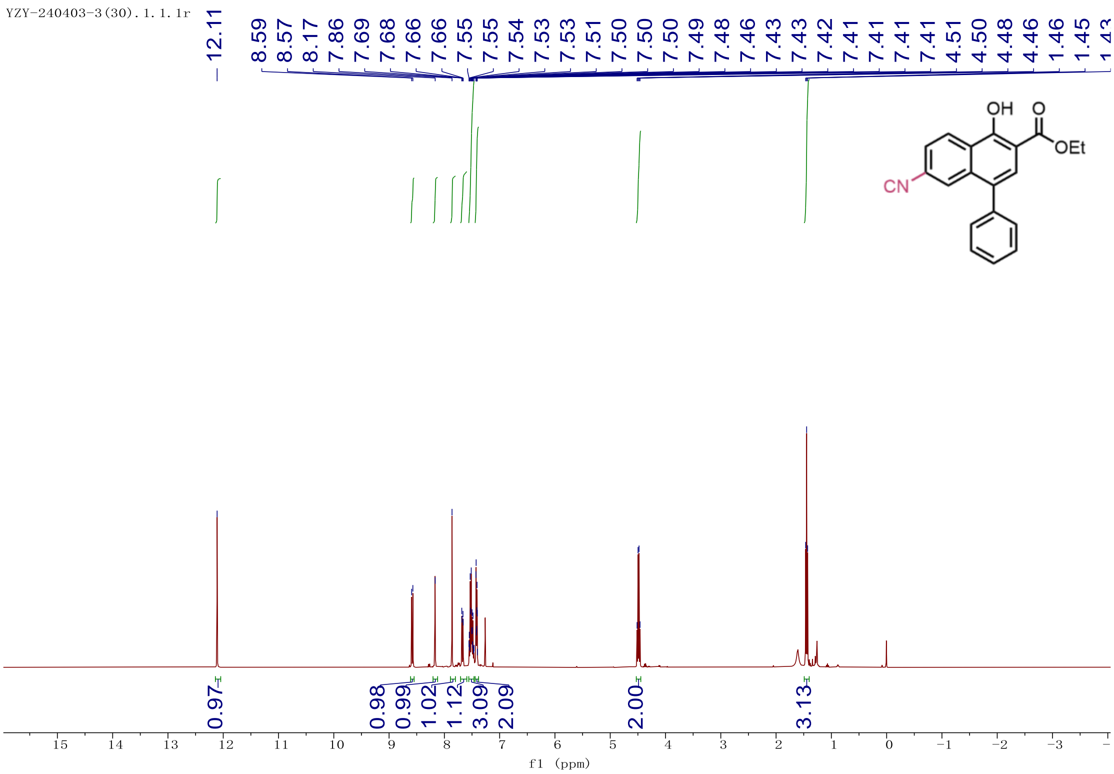
5v ^{1}H NMR



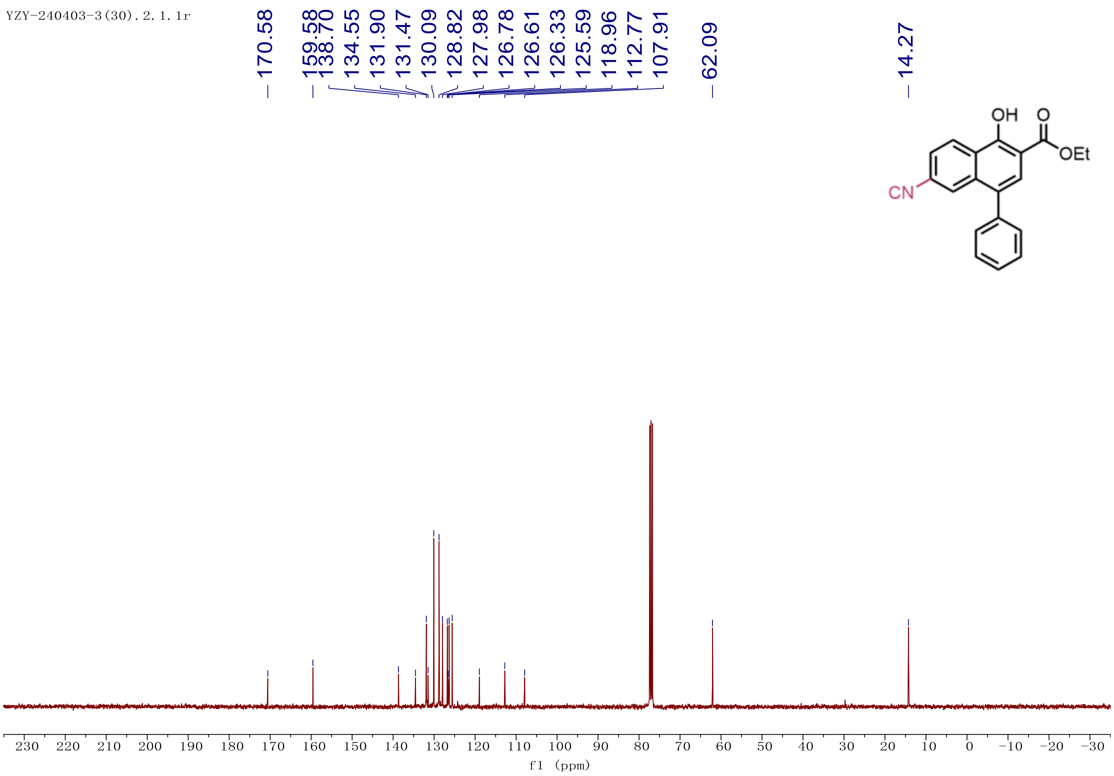
5v ^{13}C NMR



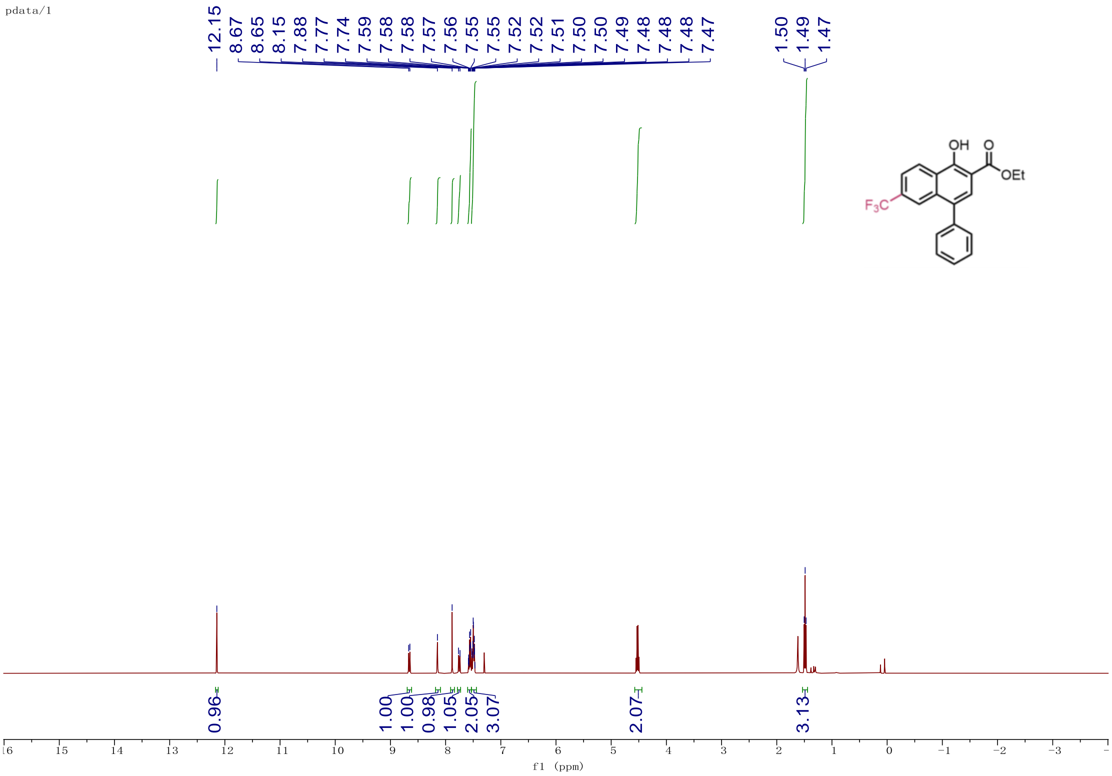
5w ¹H NMR



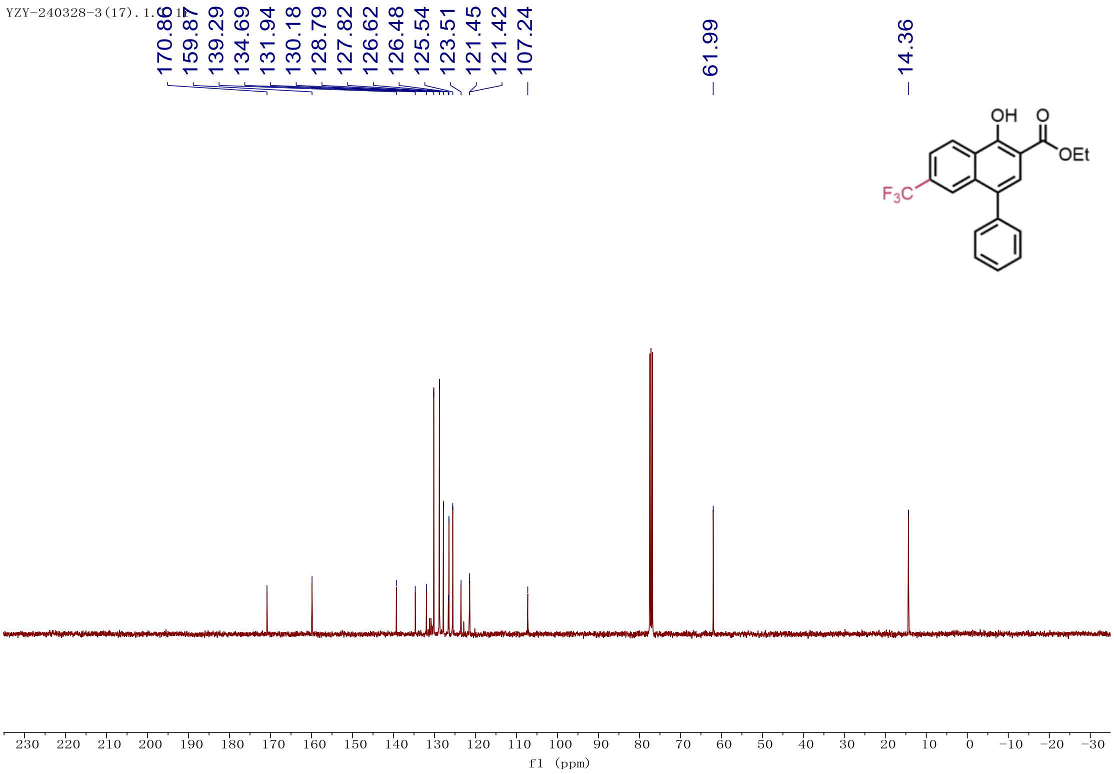
5w ¹³C NMR



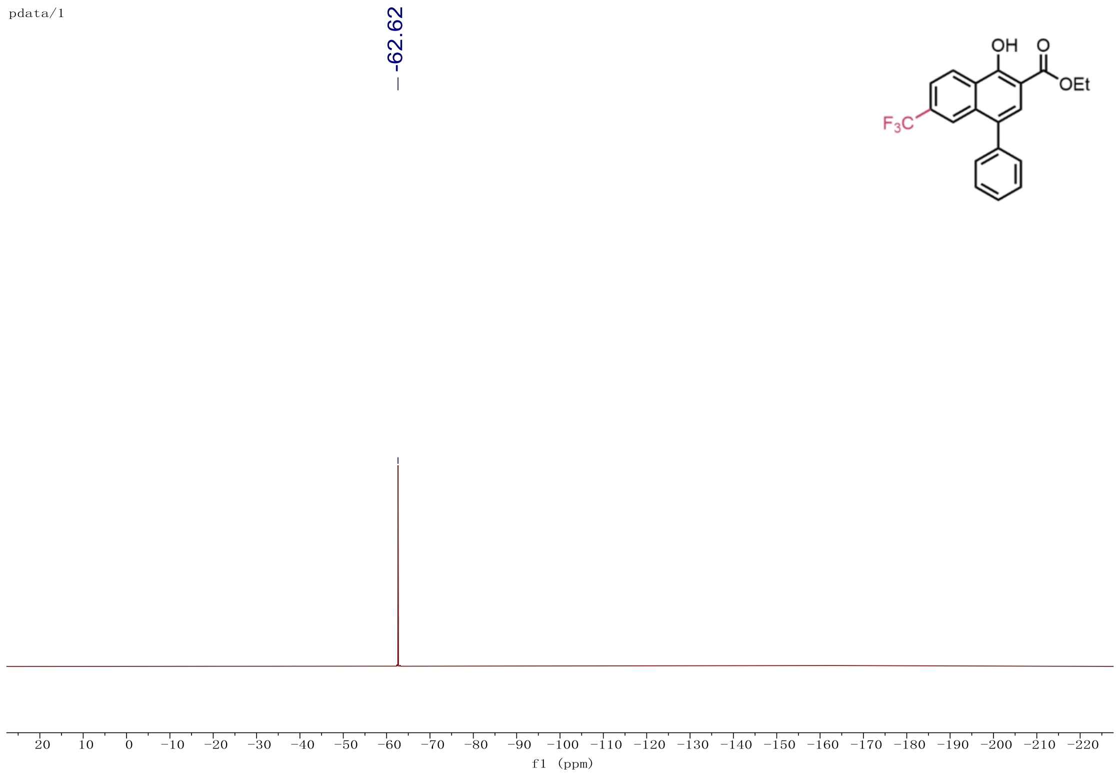
5x ¹H NMR



5x ¹³C NMR

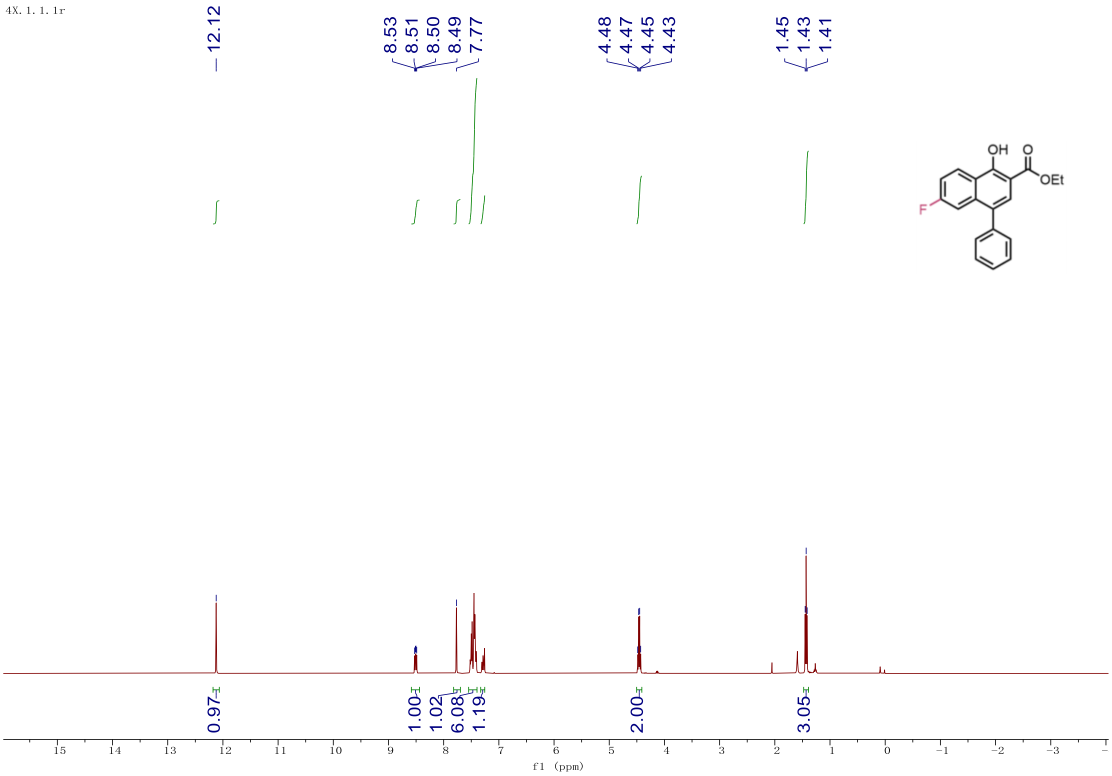


5x ^{19}F NMR

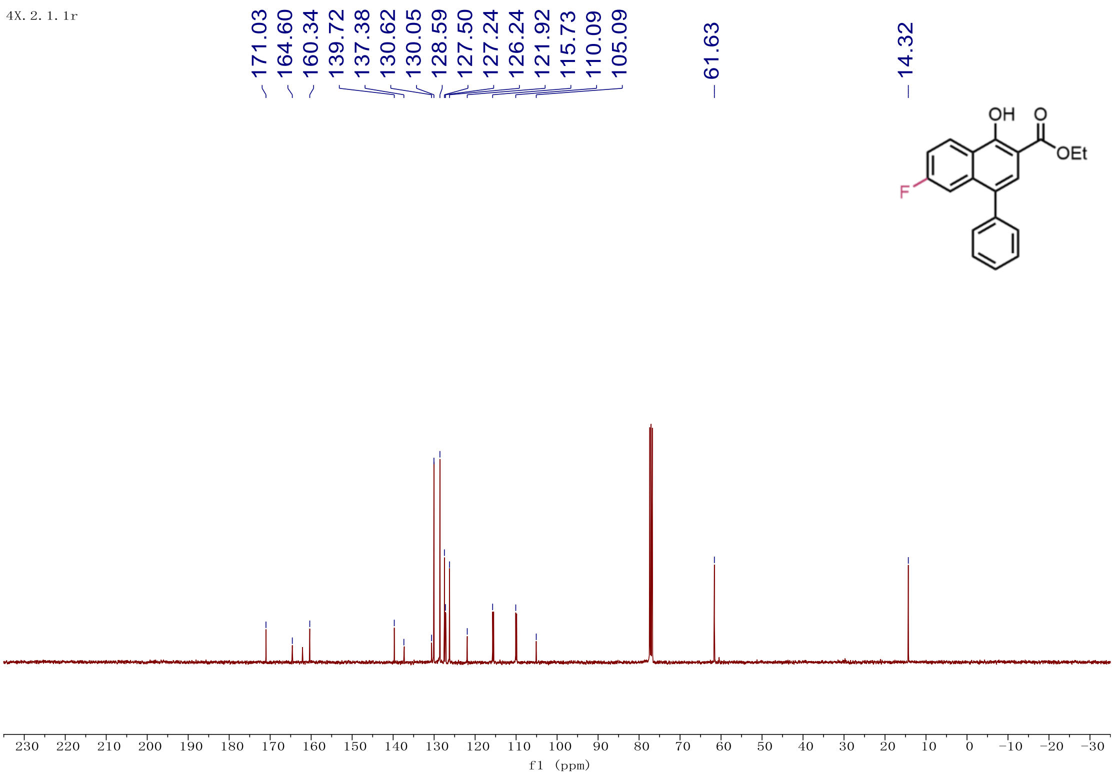


pdata/1
-62.62
OH
O
OEt
F_3C
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

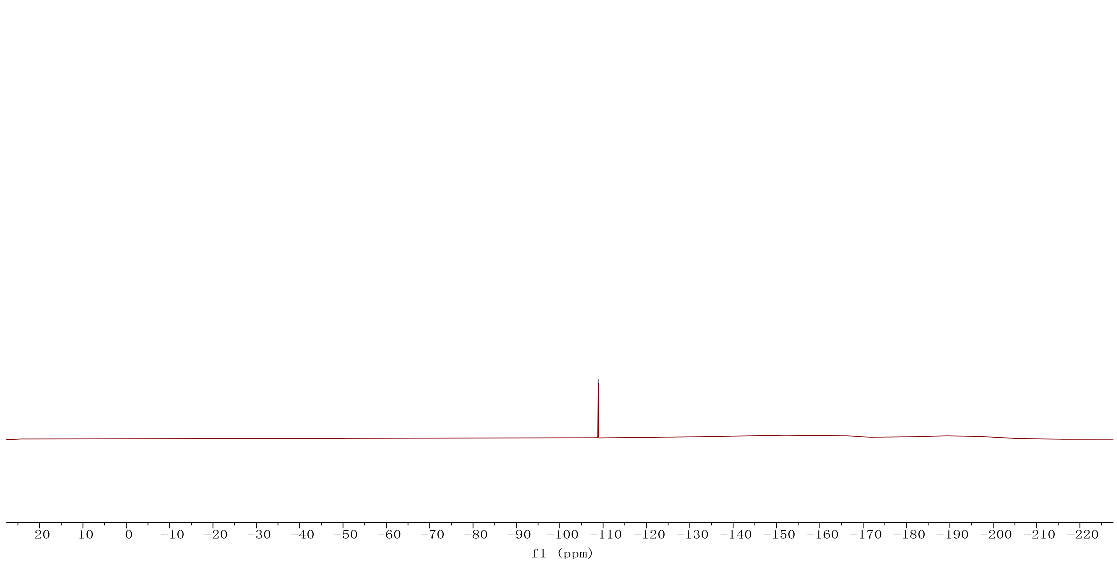
5y ^{1}H NMR

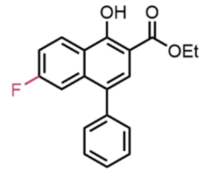


5y ^{13}C NMR

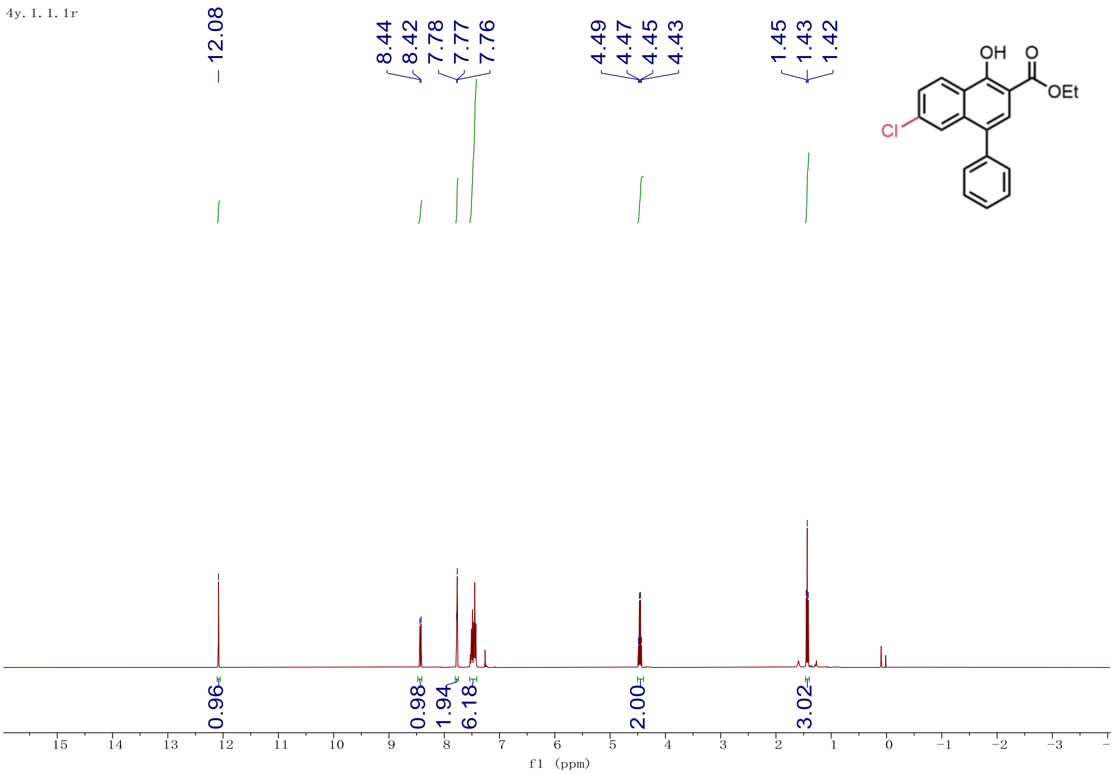


5y ^{19}F NMR

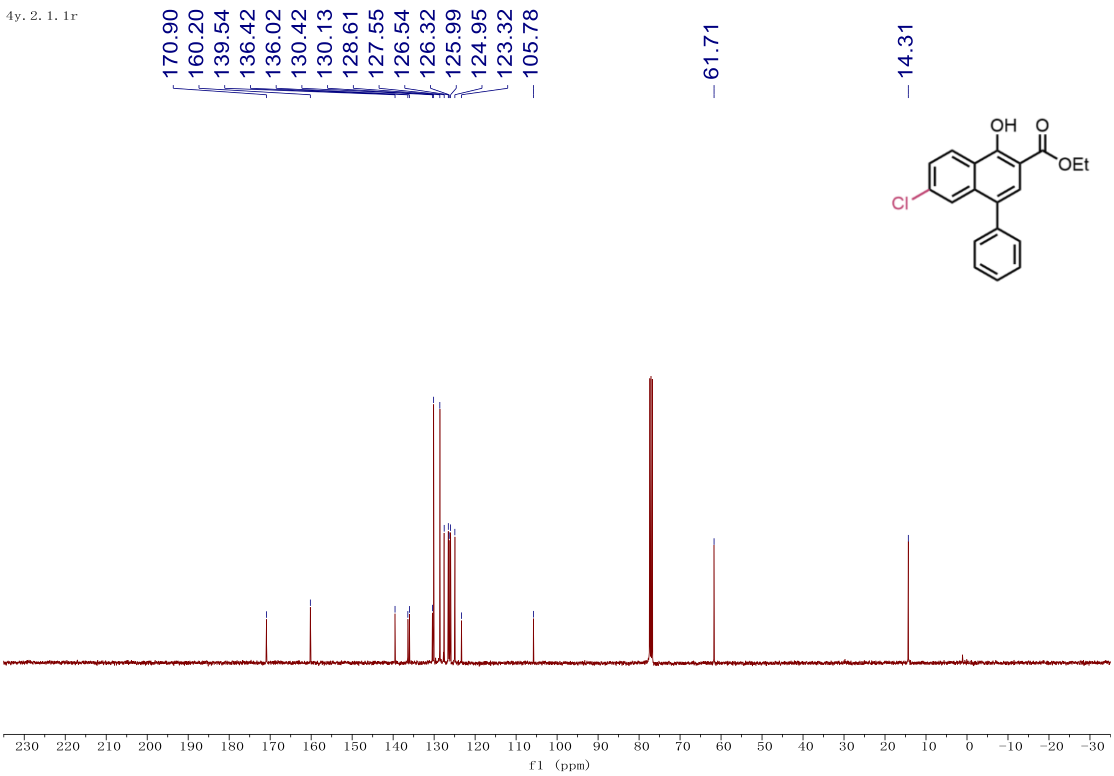

pdata/1
-108.85
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


OH
O
OEt
F

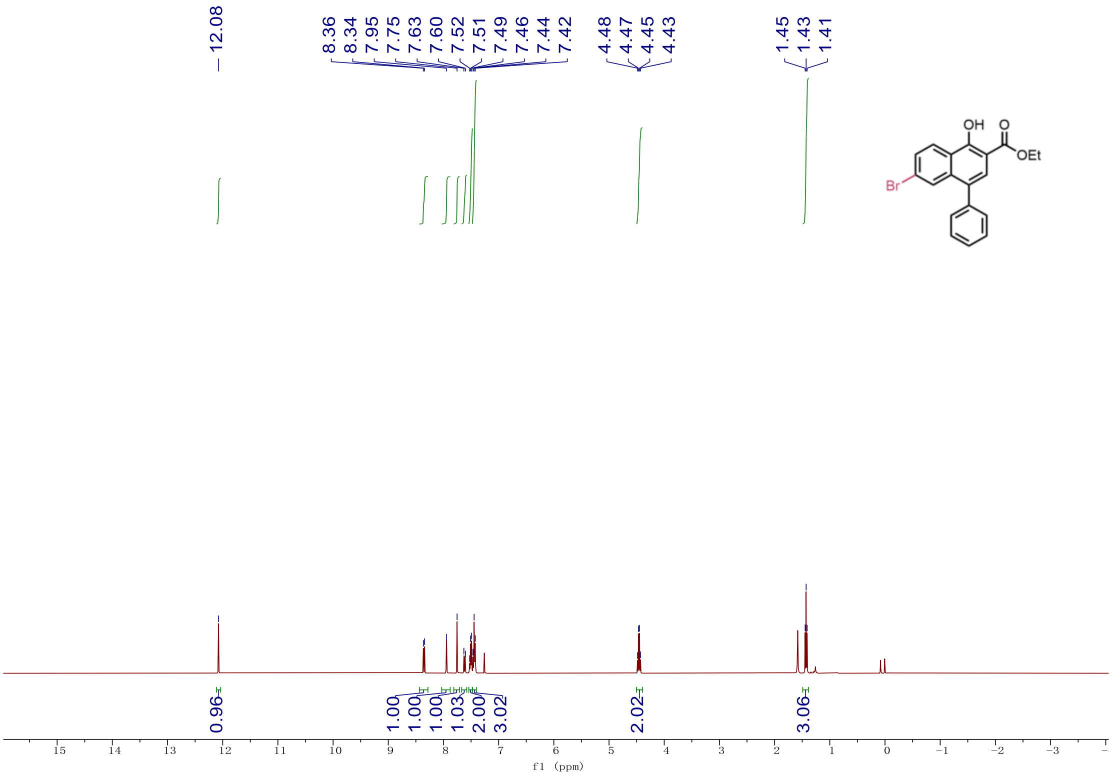
5z ^{1}H NMR



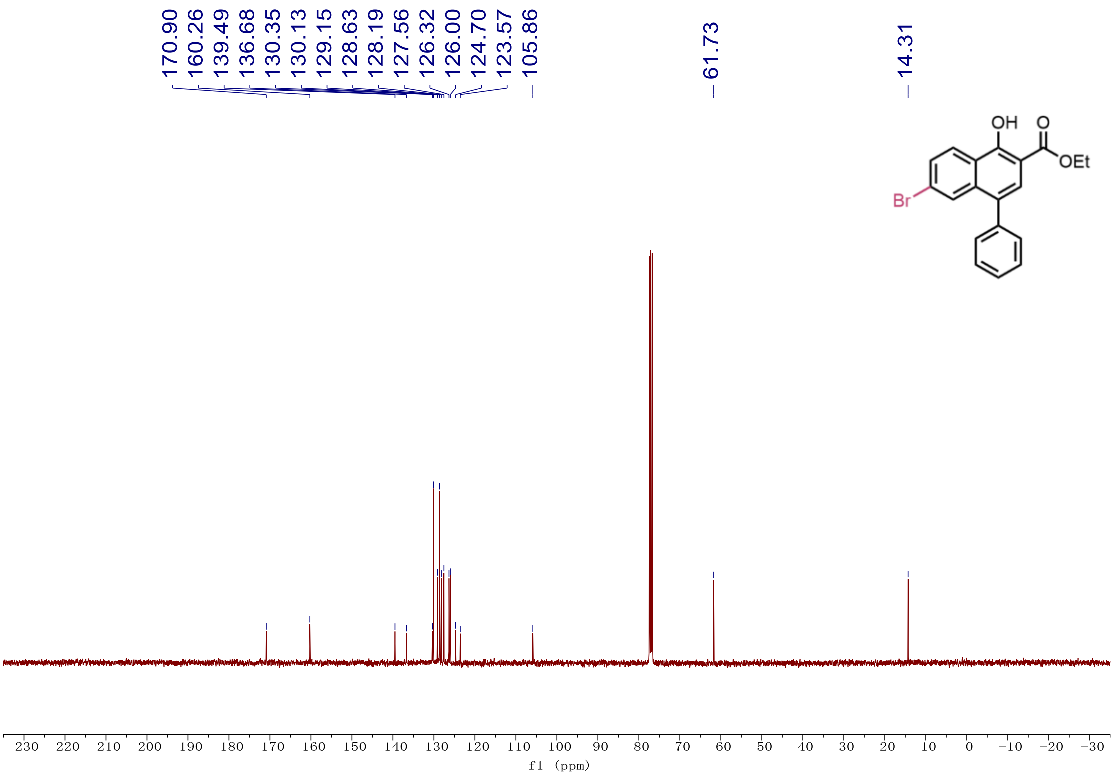
5z ^{13}C NMR



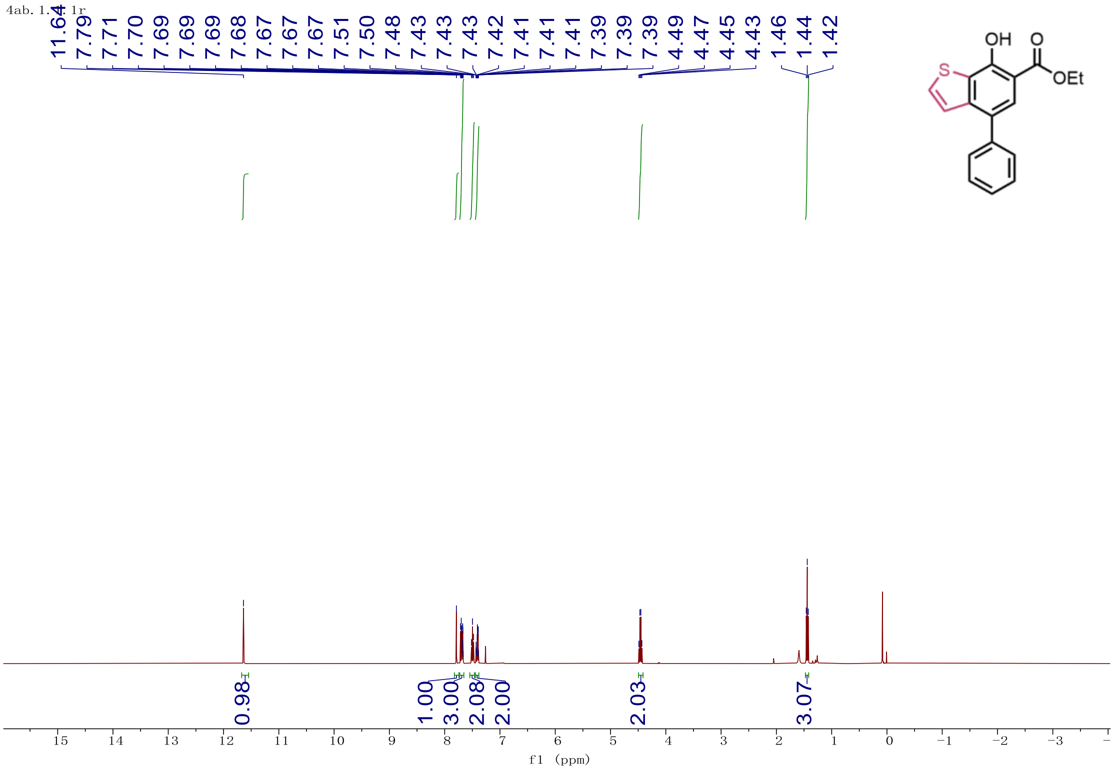
5aa ^{1}H NMR



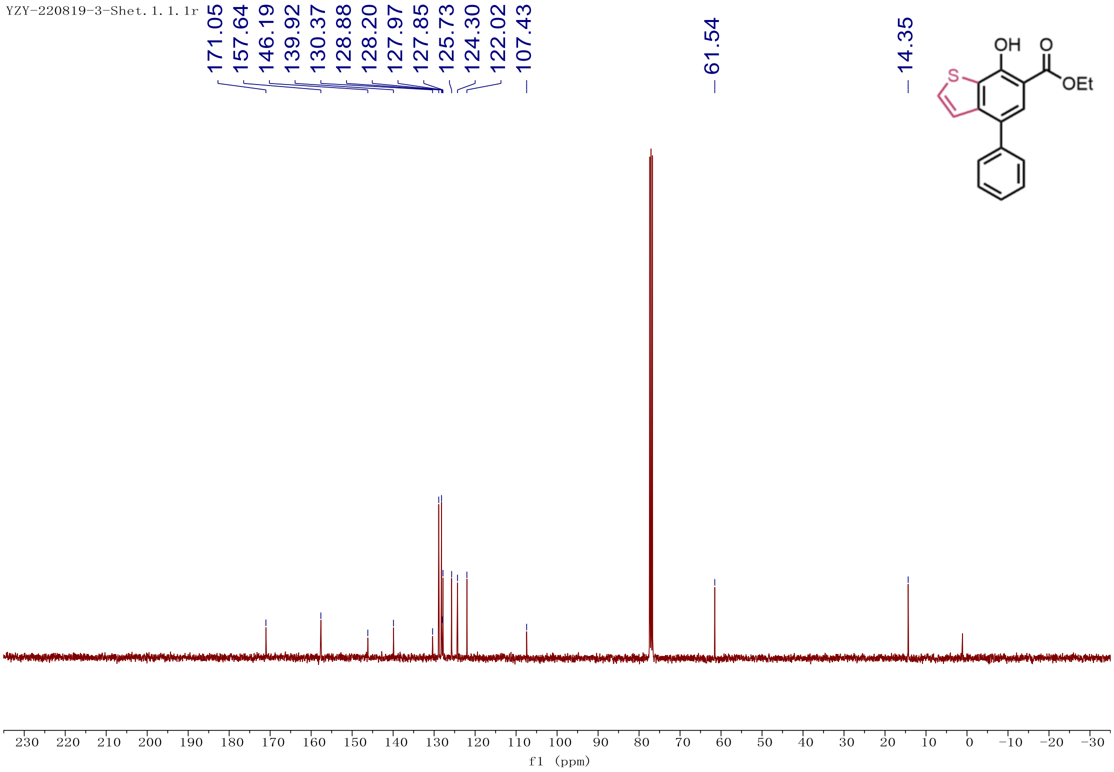
5aa ^{13}C NMR



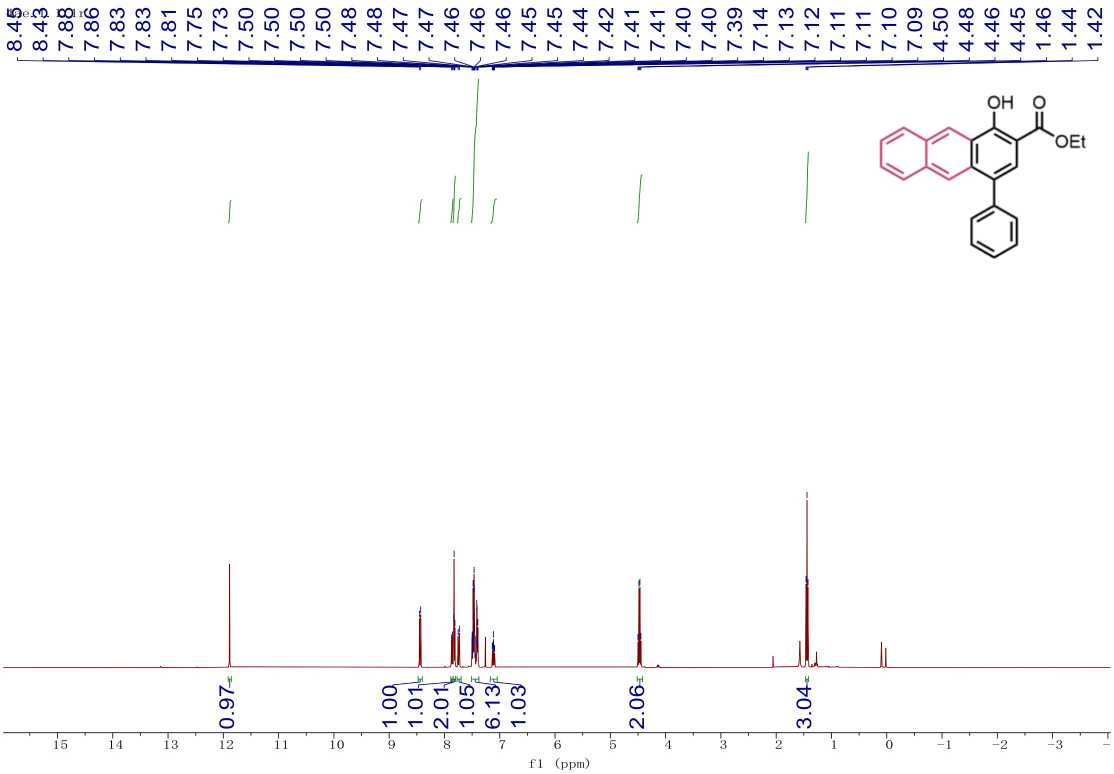
5ab ^{1}H NMR



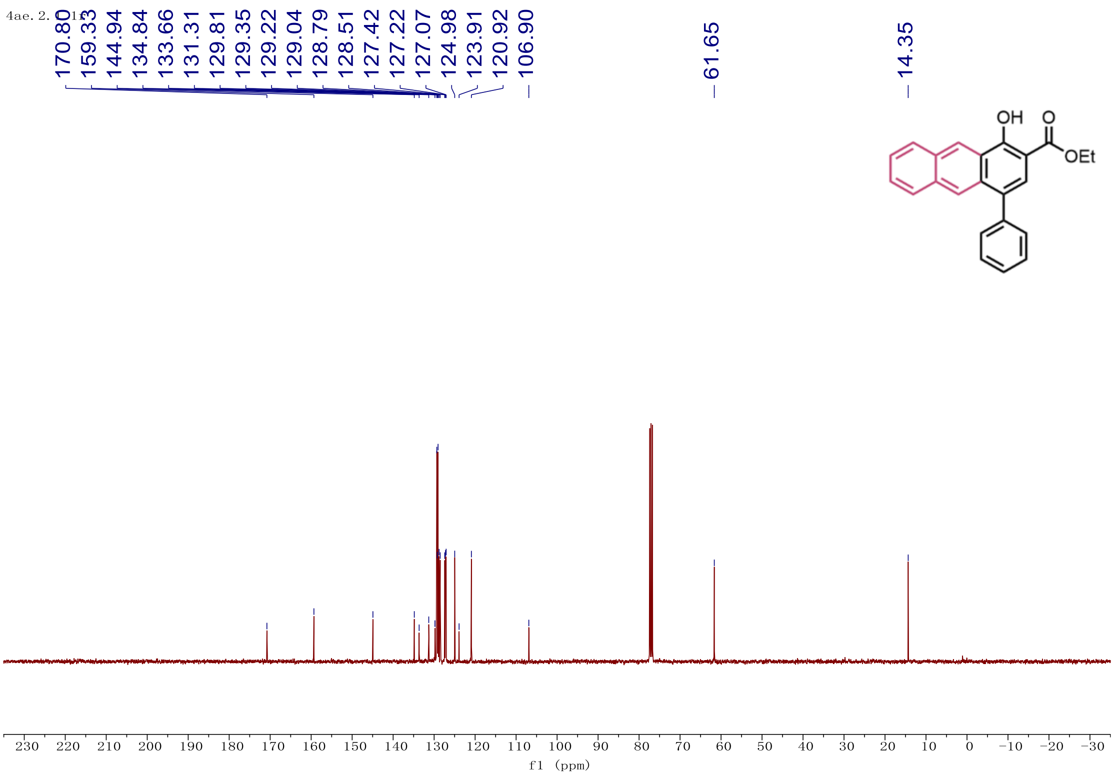
5ab ^{13}C NMR



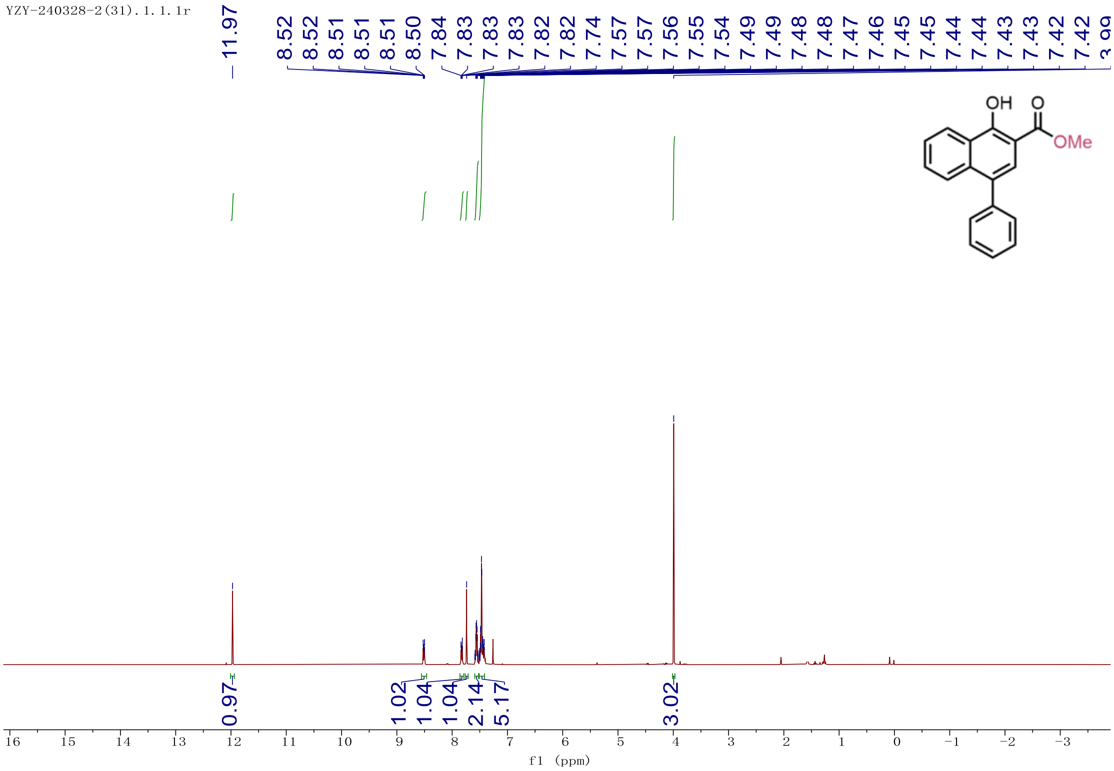
5ac ^{1}H NMR



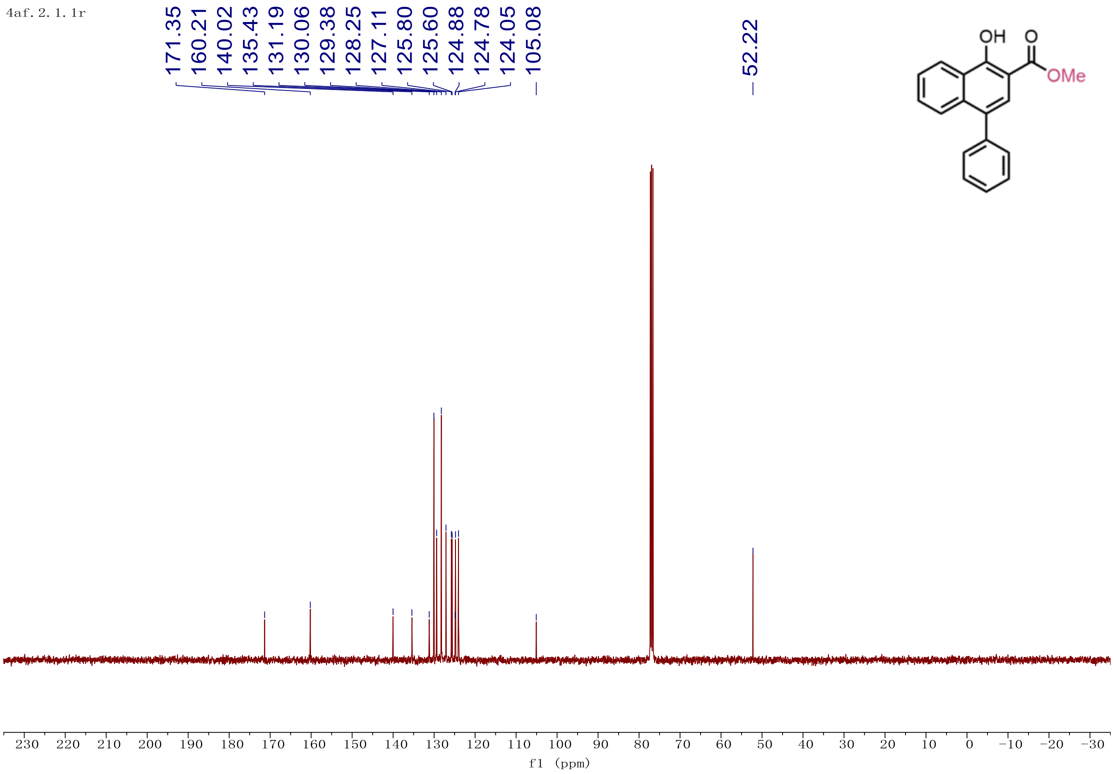
5ac ^{13}C NMR



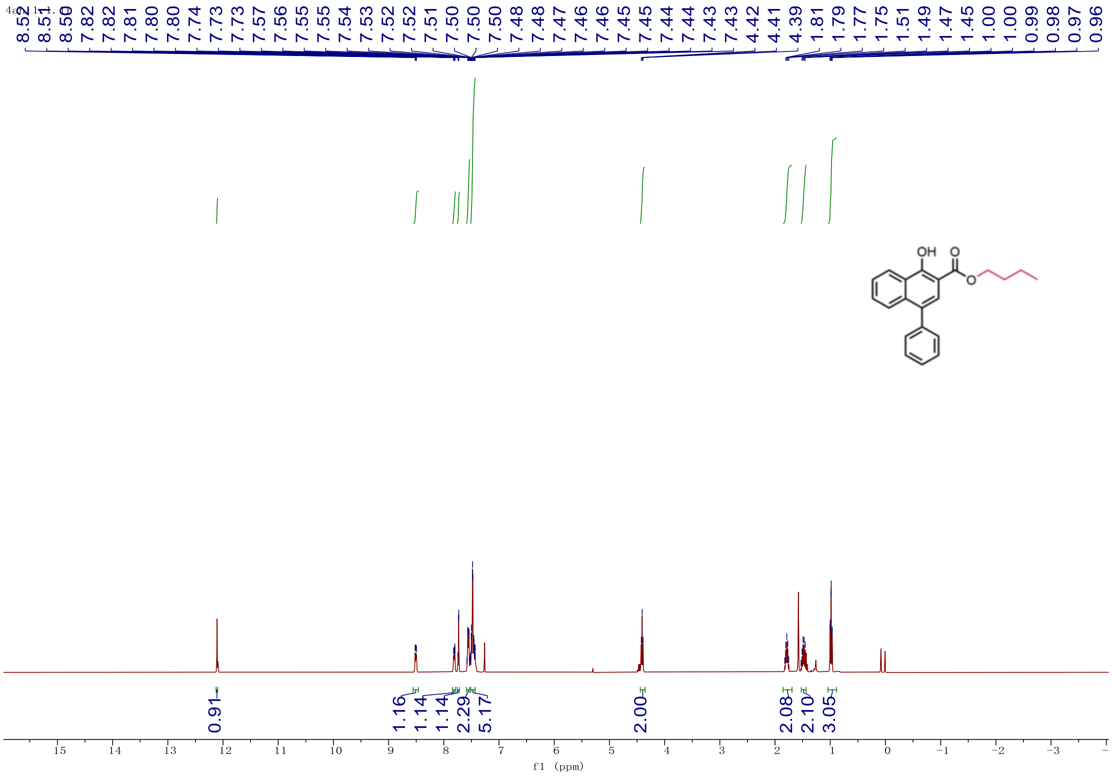
5ad ^{1}H NMR



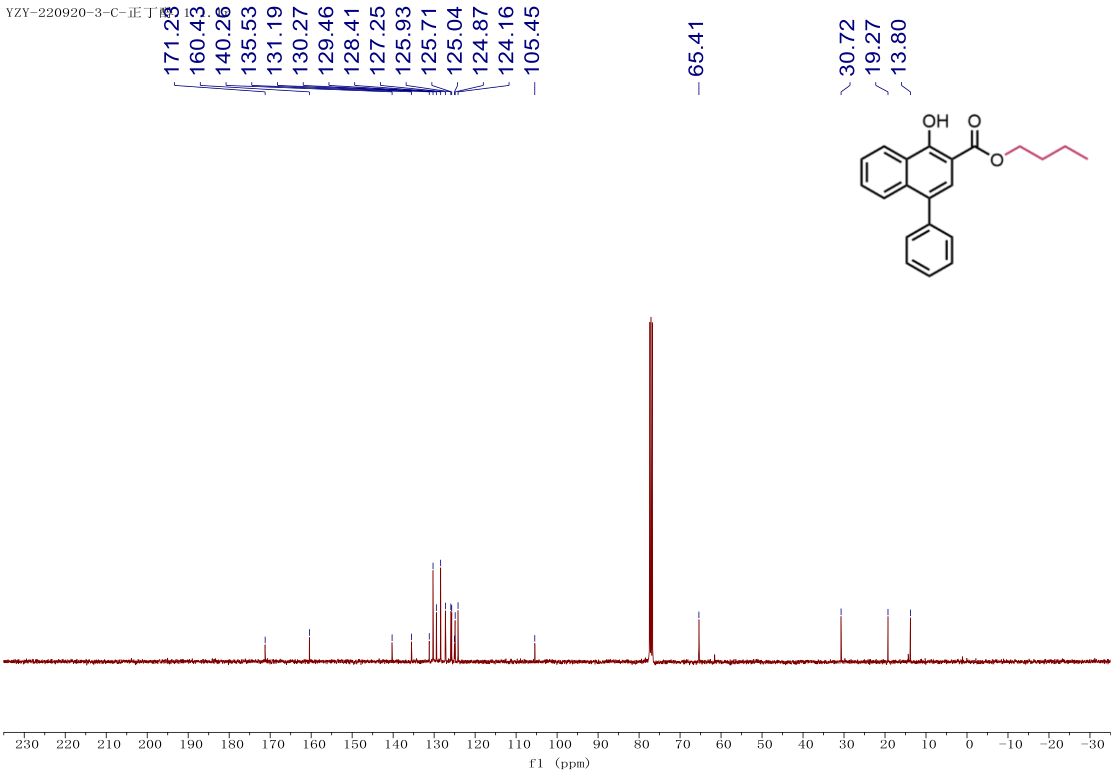
5ad ^{13}C NMR



5ae ^{1}H NMR

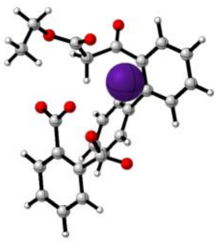


5ae ^{13}C NMR



7. Cartesian coordinates of optimized structure

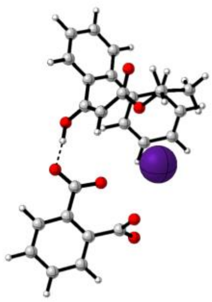
INT1



C	-3.21833600	-0.66923400	-0.95128200
C	-3.02725400	-0.87825900	0.42824500
C	-4.06955300	-0.59032800	1.32066400
C	-5.29823800	-0.12354600	0.85542600
C	-5.48306000	0.09920900	-0.51391800
C	-4.44133400	-0.15716200	-1.40666500
C	-1.70436700	-1.26876400	1.03020800
C	-2.15751600	-0.95184700	-1.98635300
O	-0.75542200	-1.69278200	0.25018800
O	-1.48523000	-1.14305700	2.24318000
O	-2.01248500	-0.19641500	-2.96285700
O	-1.44558200	-2.01956100	-1.82009800
C	-1.22608600	3.59989700	2.16315300
C	-0.04580300	3.32984300	1.46886700
C	-0.07530500	2.61232300	0.25901000
C	-1.31659100	2.19210400	-0.24991900
C	-2.49520600	2.46382000	0.44632300
C	-2.45359300	3.16361100	1.65538600
C	1.18106800	2.32966900	-0.48144200
C	1.22976600	2.57936500	-1.86809600
C	2.40871500	2.41525400	-2.59672200
C	3.58399700	2.01508700	-1.94599200
C	3.55583000	1.76253500	-0.57478400
C	2.36269500	1.88475700	0.16049100
C	2.44768300	1.48568400	1.61019100
C	1.42651900	0.50981700	2.20048300
O	3.39600300	1.84610100	2.29012300
C	1.94115200	-0.90967100	2.05423200
O	1.76597300	-1.62149500	3.16235400
O	2.44411100	-1.34322900	1.02358900
C	2.02801900	-3.05279500	3.10435200
C	0.80866100	-3.79136600	2.57345600
H	0.45864600	0.53607600	1.69323000

H	-3.88724700	-0.72294700	2.38233600
H	-6.10269500	0.08042100	1.55738300
H	-6.43275000	0.47711800	-0.88419700
H	-4.55809300	0.03420000	-2.46895000
H	-1.18561400	4.15380200	3.09744100
H	0.90242900	3.69435800	1.85597600
H	-1.36418200	1.62854900	-1.17833300
H	-3.44148600	2.10709900	0.05218300
H	-3.37262500	3.36366000	2.19978000
H	0.33299400	2.93638300	-2.36667900
H	2.41632700	2.62651500	-3.66321400
H	4.51315500	1.91096000	-2.50049300
H	4.45242100	1.44436800	-0.05117500
H	1.26735100	0.74486400	3.25387800
H	2.91652600	-3.22322100	2.48983400
H	2.24717400	-3.31761100	4.14118200
H	0.99790500	-4.87197700	2.59451700
H	-0.07022500	-3.56921500	3.18563700
H	0.58049000	-3.48686300	1.54848700
Cs	1.42362500	-1.40878300	-1.87204600

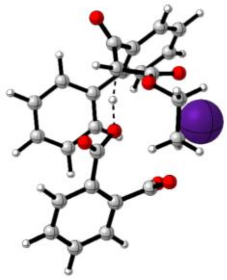
INT2



C	-4.69591900	0.37888200	-0.09702700
C	-3.95309500	1.57658200	-0.01528300
C	-4.63934400	2.78456000	0.12032600
C	-6.03718000	2.81175800	0.16359900
C	-6.77087100	1.62172400	0.07377800
C	-6.10261000	0.40600000	-0.05509500
C	-2.43520700	1.55058800	-0.09834700
C	-4.05304800	-0.95537900	-0.20130900
O	-1.90998300	0.43141500	-0.33879300
O	-1.83193700	2.64522400	0.08073800
O	-3.96044000	-1.58329200	-1.29624600
O	-3.71423200	-1.63536000	0.80994900
C	1.42907200	-0.82205400	-3.08285900
C	1.94896400	0.24403100	-2.34253500

C	3.01822700	0.04315500	-1.44994300
C	3.52216800	-1.25940500	-1.28559300
C	2.99777500	-2.32876700	-2.01968200
C	1.95756900	-2.11160700	-2.93274200
C	3.66597500	1.19525100	-0.76362500
C	5.04364700	1.39862900	-0.93925500
C	5.69229100	2.48932700	-0.35870800
C	4.96363600	3.40535400	0.40399000
C	3.59509500	3.21069700	0.59356800
C	2.94590400	2.10598000	0.03185200
C	1.49576600	1.91497000	0.33419700
C	1.02373800	0.98766200	1.22349600
C	1.87314600	0.07987700	1.97031400
O	1.09272600	-0.90173400	2.57790400
O	3.08865300	0.07531000	2.08920800
C	1.79170100	-1.82301400	3.44168800
C	2.39554800	-2.98426600	2.65891700
H	-4.05465100	3.69633800	0.18638100
H	-6.55577600	3.76152500	0.26571100
H	-7.85665100	1.64282200	0.10558000
H	-6.65979100	-0.52459700	-0.12041500
H	0.61932400	-0.64137300	-3.78586500
H	1.54005300	1.24278500	-2.46608300
H	4.32956300	-1.42446000	-0.57701800
H	3.41230600	-3.32620000	-1.89084300
H	1.57050600	-2.93502900	-3.52913100
H	5.60331100	0.70227100	-1.55881600
H	6.75938200	2.62847800	-0.51208900
H	5.45752900	4.26254900	0.85387700
H	3.02192000	3.90465800	1.20210700
H	-0.04728200	0.91061800	1.37093000
H	2.57103400	-1.28121700	3.98469700
H	1.03267000	-2.16807900	4.14994100
H	2.94428500	-3.65048000	3.33571300
H	1.61743400	-3.58312100	2.16746600
H	3.09172500	-2.60863500	1.90325400
Cs	-0.54608000	-2.05532500	-0.10653000
O	0.72049800	2.75137800	-0.33910700
H	-0.28246300	2.64730100	-0.13777900

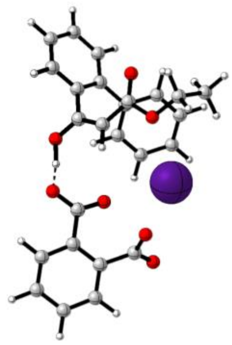
TS1



C	-3.07809100	-0.71034100	-0.87870300
C	-3.12307300	-0.34879400	0.48541900
C	-4.30528300	0.17081100	1.03294300
C	-5.44692800	0.30631800	0.24703100
C	-5.40933900	-0.05626700	-1.10908300
C	-4.23524100	-0.55942200	-1.66197500
C	-1.92549700	-0.37645500	1.40262000
C	-1.84873400	-1.28353300	-1.53756300
O	-0.82213300	-0.03268800	0.75861900
O	-2.01017700	-0.58236500	2.60406600
O	-1.40799400	-0.70689900	-2.56834200
O	-1.34947900	-2.32020300	-1.01230300
C	-1.37357500	3.73124800	1.28659500
C	-0.05627600	3.34723400	1.02305900
C	0.25702000	2.62473700	-0.14151400
C	-0.77723400	2.31762200	-1.04493500
C	-2.08976300	2.70265600	-0.78028800
C	-2.39440400	3.40631700	0.38909100
C	1.64932800	2.18518700	-0.42664900
C	2.17272200	2.37197800	-1.72351100
C	3.47768100	1.99905900	-2.04852400
C	4.30696200	1.43791100	-1.06936000
C	3.81500500	1.25724500	0.22378900
C	2.49481500	1.60510800	0.54894100
C	2.07128600	1.37159200	1.97944500
C	1.15847800	0.24512000	2.36887300
O	2.51985100	2.08499100	2.86796800
C	1.61794400	-1.14982000	2.12117200
O	1.11152200	-1.98451700	3.03165100
O	2.30168600	-1.50343500	1.16217500
C	1.12339200	-3.41190200	2.74672100
C	-0.15562400	-3.78971100	2.01307900
H	0.11659900	0.20949600	1.57226400
H	-4.31144400	0.44991100	2.08189400
H	-6.36573600	0.68624500	0.68621100

H	-6.29585600	0.05769800	-1.72790700
H	-4.18834900	-0.82861300	-2.71300600
H	-1.59850100	4.28508000	2.19437600
H	0.73090200	3.62766100	1.71599100
H	-0.57928300	1.70976600	-1.92314600
H	-2.87874400	2.41398900	-1.46883600
H	-3.42168700	3.68952900	0.60266100
H	1.54424700	2.84583600	-2.47267500
H	3.85423000	2.17076700	-3.05405600
H	5.33091800	1.16008400	-1.30511400
H	4.44810600	0.82154800	0.99122700
H	0.73750500	0.38558800	3.36380100
H	2.02386800	-3.65499500	2.17629700
H	1.18192800	-3.87883600	3.73249400
H	-0.17786500	-4.87377300	1.84508900
H	-1.03126600	-3.50688700	2.60546300
H	-0.23700700	-3.28872800	1.04315400
Cs	1.46941400	-1.46334200	-1.77048900

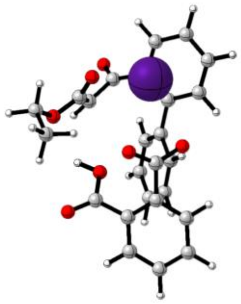
TS2



C	-4.58299400	0.43652200	-0.00822900
C	-3.82212400	1.62964500	0.00124700
C	-4.49132600	2.85738100	-0.00879700
C	-5.88764600	2.91158500	-0.04550200
C	-6.63857600	1.72882800	-0.06868100
C	-5.98818500	0.49781100	-0.04710100
C	-2.31175600	1.60009500	-0.04729100
C	-3.96447100	-0.91712800	0.08362000
O	-1.73637500	0.56668000	-0.44042500
O	-1.72588900	2.68617900	0.31429300
O	-3.98972400	-1.70182700	-0.90487300
O	-3.47746200	-1.31970100	1.17655600
C	1.33405100	-0.70751500	-3.00387300
C	1.86271200	0.33846000	-2.24196900
C	2.96983700	0.12437200	-1.40023800

C	3.50080700	-1.17389400	-1.30330800
C	2.96532600	-2.22421600	-2.05520900
C	1.88960700	-1.99138900	-2.92220000
C	3.62483500	1.26410100	-0.70140400
C	4.99199300	1.49455700	-0.91595600
C	5.64061900	2.58504000	-0.33398700
C	4.92068100	3.47781000	0.46404600
C	3.56070300	3.26063700	0.68735200
C	2.91466500	2.15046000	0.13130800
C	1.47444500	1.93882000	0.47479400
C	1.04209600	0.88687500	1.27821500
C	1.91548700	-0.09681800	1.88537700
O	1.16351900	-1.14919300	2.39407600
O	3.13468300	-0.09207300	1.97605200
C	1.89278600	-2.14803200	3.14090000
C	2.51115600	-3.20022300	2.22675000
H	-3.89930800	3.76627200	0.00824400
H	-6.39007200	3.87523700	-0.05701300
H	-7.72397400	1.76942900	-0.09978100
H	-6.55787200	-0.42715700	-0.05576900
H	0.49588100	-0.51425000	-3.66920300
H	1.43178500	1.33304300	-2.31391600
H	4.33535000	-1.35062900	-0.63024000
H	3.39854600	-3.21886200	-1.97713700
H	1.49575500	-2.79887300	-3.53590200
H	5.54300000	0.82119900	-1.56776100
H	6.70037000	2.74387700	-0.51617600
H	5.41438100	4.33579800	0.91252800
H	2.99223100	3.93950600	1.31677900
H	-0.02020300	0.79693400	1.47036300
H	2.66672200	-1.65296000	3.73402100
H	1.14875700	-2.58543400	3.81289300
H	3.07840400	-3.92673700	2.82114400
H	1.74126300	-3.75509300	1.67510000
H	3.19140600	-2.72844200	1.51225600
Cs	-0.70612300	-2.14598100	-0.19392300
O	0.67177300	2.83096800	-0.01154700
H	-0.47821000	2.69513700	0.17310100

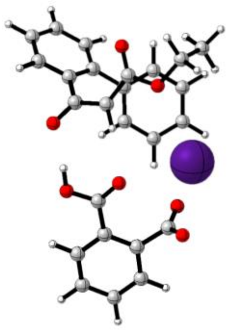
INT3



C	-2.98719400	-0.72548700	-0.96365600
C	-3.55491100	-0.24350700	0.23105200
C	-4.83660000	0.32527600	0.22386800
C	-5.55068300	0.45179400	-0.96832800
C	-4.98019100	0.00303800	-2.16391300
C	-3.71020500	-0.57798000	-2.15454900
C	-2.84253000	-0.22281500	1.54301700
C	-1.65076400	-1.45322900	-1.01769000
O	-1.58487000	0.26583100	1.46067600
O	-3.35990000	-0.50916600	2.60894700
O	-0.93873600	-1.24583500	-2.04778200
O	-1.36162700	-2.21210900	-0.05129400
C	-0.69214100	4.25867600	0.35747200
C	0.49295400	3.59272200	0.03729300
C	0.46824100	2.41181400	-0.73261900
C	-0.77008700	1.93257400	-1.19480800
C	-1.95014200	2.60582700	-0.88016400
C	-1.91768200	3.76553800	-0.09942100
C	1.73011600	1.72152000	-1.10963600
C	1.89872300	1.25761000	-2.42974300
C	3.10187100	0.69239500	-2.85400900
C	4.18481400	0.59088400	-1.96942200
C	4.04093500	1.04559000	-0.65924200
C	2.81992000	1.58001000	-0.21783100
C	2.73970200	1.99689500	1.21628000
C	1.69002300	1.47324800	2.12028300
O	3.58377900	2.73428700	1.72397000
C	1.50224000	0.04064100	2.30503600
O	0.64784100	-0.23374100	3.31486500
O	2.10065200	-0.82224000	1.66319600
C	0.57890500	-1.61731100	3.80061200
C	-0.61079800	-2.36504300	3.22352900
H	-1.19354100	0.22471800	2.35493400
H	-5.25626400	0.68005200	1.16085900
H	-6.54071600	0.90042700	-0.96381500

H	-5.52513900	0.10084800	-3.09984500
H	-3.25343900	-0.93240300	-3.07345600
H	-0.65302400	5.17104900	0.94726000
H	1.44238600	4.01977100	0.34853400
H	-0.81559400	1.00648300	-1.76107600
H	-2.89827300	2.20486900	-1.22588300
H	-2.84136700	4.28199900	0.14909400
H	1.07741700	1.36543600	-3.13147600
H	3.20259300	0.35526700	-3.88294800
H	5.13227400	0.17468600	-2.30198100
H	4.86468800	0.97604500	0.04539100
H	1.27443700	2.15405300	2.85481700
H	1.52707600	-2.10223800	3.55639300
H	0.49908100	-1.50008100	4.88427300
H	-0.58352100	-3.39909100	3.59061000
H	-1.55742900	-1.91957800	3.54268500
H	-0.60222800	-2.38218600	2.12993700
Cs	1.54247900	-2.37164400	-0.89755300

INT4

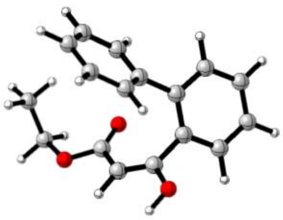


C	4.12598000	0.91952500	0.36143700
C	3.38605000	1.92171000	-0.30584400
C	3.91621800	3.22440100	-0.41610300
C	5.16295800	3.53525800	0.11643400
C	5.89945100	2.54019500	0.77155600
C	5.38293900	1.25103500	0.88696800
C	2.06342800	1.63208200	-0.91664400
C	3.63913500	-0.50605100	0.57074500
O	1.57324200	0.51388300	-1.06944300
O	1.40872000	2.73970200	-1.31187900
O	2.80629700	-0.68858700	1.50418700
O	4.11449100	-1.37908400	-0.20272300
C	-0.17764700	0.00475100	2.14085500
C	-1.08593100	0.85702900	1.50424700
C	-2.46875400	0.57417800	1.49062200

C	-2.92074800	-0.58737200	2.14110000
C	-2.01856400	-1.43816300	2.78187600
C	-0.64722100	-1.14604400	2.78144400
C	-3.42809500	1.49184500	0.82428400
C	-4.58951300	1.89888700	1.49859000
C	-5.47072900	2.81838300	0.92803700
C	-5.19502600	3.37289200	-0.32646500
C	-4.04261500	2.98820600	-1.00848600
C	-3.17755700	2.03209400	-0.45853600
C	-1.99662900	1.62249700	-1.26637100
C	-1.59387600	0.22438000	-1.39413000
C	-2.50229800	-0.91641000	-1.31689700
O	-1.80503000	-2.09408100	-1.36754200
O	-3.71892700	-0.86690100	-1.25503600
C	-2.59689800	-3.31225900	-1.37094300
C	-3.01343900	-3.71359300	0.03627500
H	3.34171700	3.98626800	-0.93090200
H	5.55979300	4.54227400	0.01974500
H	6.87652200	2.77090900	1.18990600
H	5.95534100	0.47676100	1.39038800
H	0.88950800	0.21353800	2.11693300
H	-0.71997800	1.77216300	1.04668200
H	-3.97938100	-0.83186900	2.11731400
H	-2.38569500	-2.33363600	3.27796600
H	0.05722200	-1.80282800	3.28640000
H	-4.78198900	1.51310400	2.49605500
H	-6.36269900	3.11757700	1.47230000
H	-5.87270000	4.09844300	-0.76758400
H	-3.80938000	3.40283600	-1.98465400
H	-0.55857700	0.06564700	-1.67574200
H	-3.46715900	-3.16191800	-2.01568700
H	-1.93863700	-4.05636300	-1.82901900
H	-3.54300100	-4.67324400	0.00353100
H	-2.14224100	-3.81937500	0.69225300
H	-3.67716100	-2.96068800	0.46753200
Cs	1.37541500	-2.51119400	-0.44339300
O	-1.31886500	2.46984100	-1.87592400
H	0.52749300	2.50114500	-1.68421900

Polarity matching

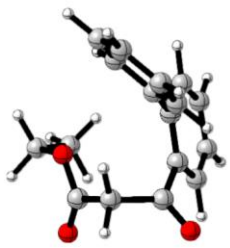
1a’



C	-1.16169900	2.54803400	1.69951100
C	-0.01455600	1.82729100	1.36078900
C	0.23237000	1.45773300	0.02846700
C	-0.69508300	1.83049300	-0.95768400
C	-1.84210800	2.55185600	-0.62011800
C	-2.08067100	2.91206700	0.70997300
C	1.46247000	0.71086800	-0.34555200
C	2.28681600	1.21702300	-1.36245400
C	3.47046400	0.57501200	-1.72829500
C	3.86363600	-0.59145000	-1.06731100
C	3.05716600	-1.11010000	-0.05497400
C	1.85218000	-0.48426200	0.29582600
C	1.02621600	-1.13733900	1.34267200
C	-0.22296300	-1.64292300	1.21603600
C	-0.99475800	-1.67324800	-0.02890300
O	-2.25255200	-2.13531000	0.22469000
O	-0.61662700	-1.35391000	-1.14392400
C	-3.16597900	-2.17760200	-0.89605900
C	-3.79086700	-0.81087600	-1.14390200
H	-1.33476800	2.83028700	2.73514000
H	0.70403900	1.55712300	2.13050400
H	-0.52809000	1.51746700	-1.98427300
H	-2.55551100	2.82297000	-1.39455600
H	-2.97443200	3.47222900	0.97307600
H	1.99835900	2.14178800	-1.85497900
H	4.08961500	0.99248500	-2.51823100
H	4.78764500	-1.09492600	-1.33834800
H	3.34514700	-2.02311300	0.45843700
H	-0.72215700	-2.05419800	2.09046400
H	-2.63016800	-2.53579700	-1.78017500
H	-3.91602100	-2.91675200	-0.60215900
H	-4.51665200	-0.87573800	-1.96423800
H	-4.30975200	-0.45435200	-0.24716400
H	-3.02119500	-0.08244300	-1.41298500
O	1.70662100	-1.21044400	2.52490600

H	1.18862200	-1.71518700	3.17599300

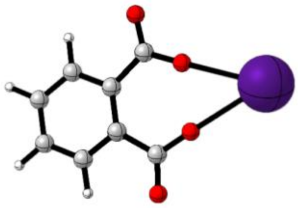
1a



C	-3.74003200	0.12274500	0.72903000
C	-2.48260200	0.73113000	0.74222800
C	-1.59694600	0.56789000	-0.33689500
C	-2.00451000	-0.20772500	-1.43419400
C	-3.26109900	-0.81575300	-1.44799400
C	-4.13238600	-0.65474600	-0.36506800
C	-0.25911500	1.21488200	-0.32034200
C	0.12655400	2.02797800	-1.39825700
C	1.34516700	2.70883800	-1.39368000
C	2.19803500	2.60686800	-0.29089400
C	1.82884700	1.80901900	0.79166600
C	0.62147900	1.09390400	0.77719400
C	0.39023400	0.16820900	1.94213100
C	0.13859800	-1.32135500	1.64991200
O	0.50053200	0.56127600	3.08986200
C	1.21748100	-1.86051800	0.72693000
O	0.80849900	-1.86760500	-0.55762000
O	2.32300500	-2.20095700	1.09650500
C	1.79995500	-2.19938800	-1.56603600
C	2.67772000	-0.99531700	-1.87720400
H	-0.84324100	-1.44798600	1.18739100
H	-4.41339300	0.26044300	1.57107100
H	-2.18522900	1.34433900	1.58922000
H	-1.31645000	-0.35895900	-2.26127700
H	-3.55637100	-1.42446100	-2.29886500
H	-5.10946000	-1.13063400	-0.37487200
H	-0.55732500	2.14587300	-2.23490300
H	1.61894500	3.33130900	-2.24169200
H	3.14319600	3.14251600	-0.27410200
H	2.48328900	1.70884700	1.65271200
H	0.18125700	-1.85018000	2.60350600
H	2.39013500	-3.05109400	-1.21598000
H	1.20261400	-2.50128200	-2.42984700

H	3.35866300	-1.23711300	-2.70233100
H	2.06662500	-0.13431800	-2.16652900
H	3.27618300	-0.71898400	-1.00463400

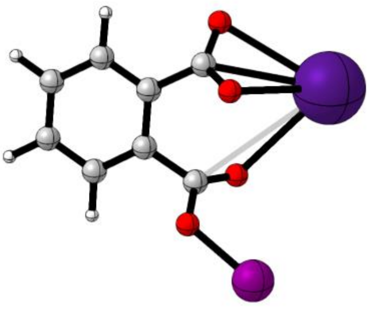
TDRA-1



C	-4.55142700	-0.69876900	0.00006100
C	-4.55142800	0.69876700	0.00004000
C	-3.34004800	1.38587100	0.00000500
C	-2.10828700	0.70804100	-0.00000900
C	-2.10828600	-0.70804200	0.00001000
C	-3.34004700	-1.38587300	0.00004300
C	-0.89236300	-1.61200000	-0.00000400
O	-1.01796500	-2.84272100	-0.00001600
O	0.29344000	-1.08417200	0.00001000
C	-0.89236600	1.61200000	-0.00004400
O	0.29343800	1.08417400	-0.00002100
O	-1.01796800	2.84272100	-0.00008900
H	-5.48781100	-1.25111500	0.00008900
H	-5.48781200	1.25111200	0.00005200
H	-3.31880300	2.47048800	-0.00001400
H	-3.31880100	-2.47048900	0.00005400
Cs	2.90747600	0.00000000	0.00000200

The details of the BDEs

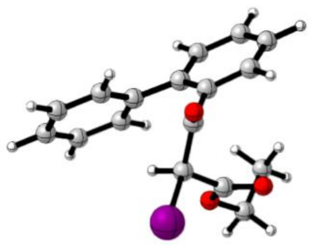
BCTC-1



C	2.14572900	0.39346300	0.76889300
O	1.24876800	-0.15789600	1.47265600
O	3.22629000	-0.12251800	0.37609600
C	-0.45618800	0.97874900	-0.38555600
O	-0.29010000	-0.02081200	-1.06317800

C	1.82038500	1.79632200	0.27782100
C	2.77057100	2.82031400	0.31165100
C	2.43622900	4.11940000	-0.08221800
C	1.14512600	4.40807600	-0.53771100
C	0.18935600	3.39175300	-0.60034100
C	0.53302800	2.09204800	-0.20690400
H	3.77230500	2.58067700	0.65621400
H	3.18280800	4.90838200	-0.03286400
H	0.88309700	5.41701700	-0.84483800
H	-0.81342400	3.59844800	-0.96300800
Cs	1.37299900	-2.53581800	-0.21324000
O	-1.59251100	1.28238400	0.26663600
I	-3.14688100	-0.09216200	0.13625000

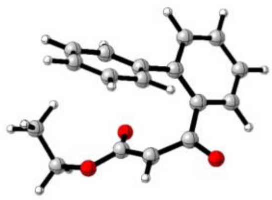
IM-1



C	-0.53261600	3.74408600	-0.43960200
C	-0.97089500	2.52102700	-0.95222100
C	-1.71512000	1.63556400	-0.15258400
C	-2.02275800	2.01088400	1.16567500
C	-1.58560200	3.23422100	1.67726100
C	-0.83634800	4.10349100	0.87718700
C	-2.16323500	0.32421000	-0.69066000
C	-3.51624500	-0.04056000	-0.59094000
C	-3.98573800	-1.23606900	-1.13554200
C	-3.10900700	-2.08743400	-1.81599100
C	-1.76353900	-1.74195200	-1.92952200
C	-1.28064000	-0.55567600	-1.35609700
C	0.21214400	-0.35353300	-1.42100400
C	0.88013400	-0.20392400	-0.03970100
O	0.82377200	-0.40525900	-2.46575600
C	0.48351500	-1.38903600	0.83165200
O	-0.02177200	-0.96529700	2.00357000
O	0.56752600	-2.54913600	0.48844000
C	-0.58293000	-1.98330100	2.87813900
C	-1.99943600	-2.33194300	2.44320600
H	0.55397700	0.71943000	0.43499500
H	0.04411300	4.41547600	-1.07017600

H	-0.74159200	2.25030700	-1.97966700
H	-2.57747100	1.32319700	1.79852400
H	-1.81870100	3.50325600	2.70426400
H	-0.49099500	5.05288600	1.27758900
H	-4.20743800	0.64230100	-0.10383800
H	-5.03746400	-1.49449300	-1.04350600
H	-3.46941800	-3.01573400	-2.25043200
H	-1.06280900	-2.40138900	-2.43231800
H	0.07227000	-2.85851600	2.86668100
H	-0.55980700	-1.52104900	3.86749500
H	-2.43274500	-3.05974300	3.13963500
H	-2.63285400	-1.43844600	2.43462000
H	-1.99985800	-2.76840900	1.44012400
I	3.06291500	-0.03569600	-0.13942600

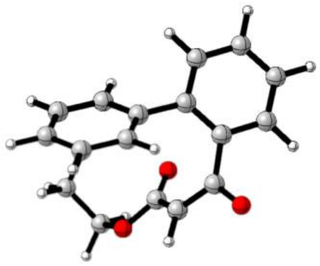
1a’



C	-1.34326800	2.20547500	1.84881700
C	-0.13822700	1.60631900	1.47141900
C	0.15744500	1.37407200	0.11473000
C	-0.78247400	1.76865300	-0.85239600
C	-1.98340900	2.37094200	-0.47573400
C	-2.27061900	2.58874700	0.87670700
C	1.44182100	0.74815900	-0.29425600
C	2.21114800	1.35703300	-1.29835400
C	3.44969200	0.83803700	-1.67736000
C	3.95768300	-0.29735400	-1.03866300
C	3.21140200	-0.91042300	-0.03411600
C	1.94936600	-0.41601000	0.32566300
C	1.20259400	-1.17804300	1.37506400
C	-0.22351400	-1.48006600	1.25412000
C	-0.96213500	-1.62569400	-0.00316000
O	-2.27454300	-1.85358600	0.24819600
O	-0.47766800	-1.58608800	-1.12428500
C	-3.13554000	-2.07052000	-0.89796800
C	-3.55867300	-0.75458800	-1.53509300
H	-1.55064200	2.37910600	2.90151000
H	0.59255400	1.34151400	2.23084800
H	-0.57905300	1.56738200	-1.90047300

H	-2.70342600	2.65796200	-1.23786700
H	-3.20820100	3.05476000	1.16831600
H	1.84107800	2.26607400	-1.76508600
H	4.02399100	1.32967000	-2.45841500
H	4.92573300	-0.70141700	-1.32195800
H	3.58538400	-1.79476300	0.47304400
H	-0.72916800	-1.75706500	2.17322100
H	-2.61165100	-2.71005100	-1.61492000
H	-3.99005800	-2.61136100	-0.48414900
H	-4.27695300	-0.95044400	-2.34069200
H	-4.03179400	-0.10165400	-0.79411100
H	-2.69347500	-0.23573300	-1.95495100
O	1.79045200	-1.62062700	2.37223200

1a

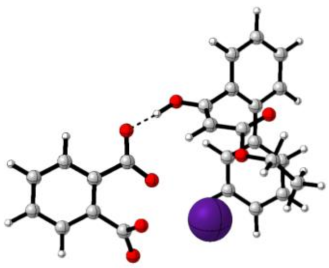


C	-1.34360100	2.20439400	1.84946400
C	-0.13848200	1.60548100	1.47190500
C	0.15727600	1.37380600	0.11513900
C	-0.78265700	1.76860900	-0.85189300
C	-1.98363900	2.37068300	-0.47506500
C	-2.27091800	2.58796300	0.87745200
C	1.44179300	0.74825000	-0.29400900
C	2.21103500	1.35759900	-1.29787800
C	3.44971300	0.83900100	-1.67700000
C	3.95790800	-0.29648600	-1.03865500
C	3.21170300	-0.91003000	-0.03434100
C	1.94953400	-0.41603400	0.32557000
C	1.20284200	-1.17859300	1.37459100
C	-0.22312500	-1.48098300	1.25337400
O	1.79074500	-1.62153000	2.37162000
C	-0.96197200	-1.62560000	-0.00386800
O	-2.27428300	-1.85377000	0.24752800
O	-0.47767000	-1.58495400	-1.12502500
C	-3.13546800	-2.07003500	-0.89860300
C	-3.55914300	-0.75372900	-1.53458000
H	-0.72851400	-1.75909000	2.17228100
H	-1.55101800	2.37766500	2.90220700

H	0.59225400	1.34040500	2.23127500
H	-0.57913600	1.56775700	-1.90003000
H	-2.70366700	2.65791600	-1.23710600
H	-3.20852900	3.05385200	1.16917600
H	1.84078700	2.26669700	-1.76435800
H	4.02393300	1.33100100	-2.45788200
H	4.92608900	-0.70021700	-1.32198500
H	3.58583500	-1.79447500	0.47253200
H	-2.61151500	-2.70875500	-1.61623900
H	-3.98971200	-2.61151600	-0.48505700
H	-4.27749600	-0.94917800	-2.34020200
H	-4.03228400	-0.10150100	-0.79299600
H	-2.69415800	-0.23431300	-1.95422400

Spin Population Analyses

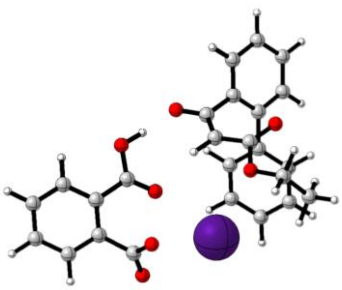
TS-20 (TDRA-1+1a')



C	-4.55751600	0.57701400	-0.00941500
C	-3.78616800	1.76130000	0.00759800
C	-4.44627100	2.99126700	-0.00700800
C	-5.84205200	3.05210900	-0.05344800
C	-6.60361200	1.87445100	-0.07875600
C	-5.96416500	0.63910500	-0.05292300
C	-2.26810900	1.71583100	-0.01925100
C	-3.94339700	-0.76706900	0.07942200
O	-1.73449300	0.64579700	-0.40860200
O	-1.67963200	2.77445000	0.34319600
O	-3.96601400	-1.58414900	-0.88363400
O	-3.47398700	-1.21602300	1.16411400
C	1.40465500	-0.62076500	-2.98403900
C	1.94996500	0.41802400	-2.22423300
C	3.05411300	0.18833800	-1.38280100
C	3.56374400	-1.11778600	-1.28372300
C	3.01210100	-2.16143700	-2.03424600
C	1.94016400	-1.91358400	-2.90124300
C	3.72627200	1.31804600	-0.68174300
C	5.09339000	1.53936800	-0.90630900

C	5.75494600	2.62172400	-0.32340000
C	5.05031700	3.51311800	0.48953200
C	3.69272800	3.30022900	0.72837900
C	3.03430600	2.20028500	0.16838000
C	1.59622300	2.00340100	0.50607500
C	1.12450900	0.98309300	1.29025800
C	1.97569400	-0.01583500	1.90453000
O	1.20225500	-1.06323000	2.40447800
O	3.19292200	-0.03895100	2.00601600
C	1.91524200	-2.07008200	3.15454800
C	2.53115900	-3.12839900	2.24514500
H	-3.84383500	3.89325500	0.01819600
H	-6.33961900	4.01834400	-0.06862800
H	-7.68824500	1.92419400	-0.11435800
H	-6.53986100	-0.28220900	-0.06062100
H	0.56934100	-0.41515900	-3.64947600
H	1.53269400	1.41857200	-2.29431500
H	4.39514400	-1.30655300	-0.61001400
H	3.43078100	-3.16228800	-1.95501500
H	1.53489500	-2.71538100	-3.51524700
H	5.63389200	0.86653200	-1.56748900
H	6.81365100	2.77513900	-0.51640900
H	5.55433200	4.36530100	0.93777100
H	3.13444900	3.97608300	1.36996500
H	0.05621900	0.90493100	1.45315100
H	2.69026500	-1.58486400	3.75430800
H	1.16285200	-2.50186600	3.82143700
H	3.08961500	-3.85908000	2.84298700
H	1.76072600	-3.67844900	1.68878000
H	3.21874500	-2.66143100	1.53463500
Cs	-0.64888300	-2.03862600	-0.18298600
O	0.83180500	2.93871300	-0.03100500
H	-0.17558900	2.81778300	0.15933600

TS+50 (TDRA-1+1a')



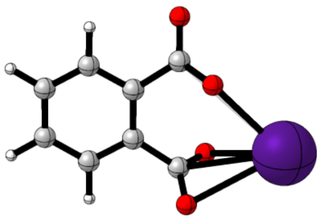
C	-4.51614800	0.50987600	-0.01619400

C	-3.80755300	1.73255000	-0.01670000
C	-4.51103700	2.94953100	-0.03432300
C	-5.90379500	2.96557200	-0.06249500
C	-6.60839300	1.75561200	-0.07350500
C	-5.91827100	0.54369600	-0.05288600
C	-2.32012900	1.76248400	-0.04137300
C	-3.83255000	-0.83871200	0.08352200
O	-1.60656400	0.82358600	-0.39278400
O	-1.81011500	2.93515900	0.34308000
O	-3.82877500	-1.57198000	-0.94209200
O	-3.31701200	-1.14109700	1.19525400
C	1.40492800	-0.60564500	-2.95119300
C	1.96750900	0.42551300	-2.19246600
C	3.08101100	0.18412600	-1.36560300
C	3.58321000	-1.12694100	-1.28014600
C	3.01356200	-2.16126500	-2.02772800
C	1.93244800	-1.90086500	-2.88025500
C	3.77559900	1.30751600	-0.67781200
C	5.14741600	1.49977800	-0.89985400
C	5.82609600	2.58105900	-0.33448200
C	5.13494200	3.50798400	0.45016000
C	3.76956700	3.33583100	0.67437900
C	3.09591200	2.23239800	0.13792300
C	1.64847600	2.08636400	0.48578700
C	1.16644200	0.97545700	1.26288100
C	2.00290300	-0.03435000	1.90207200
O	1.22727000	-1.06106200	2.37892800
O	3.21686900	-0.01135800	2.03444500
C	1.91148400	-2.08337100	3.14761700
C	2.54281600	-3.13521100	2.24440400
H	-3.95370800	3.87976600	-0.03309800
H	-6.43602500	3.91287100	-0.07900900
H	-7.69545400	1.75812400	-0.09771800
H	-6.46259300	-0.39645800	-0.06158500
H	0.56310500	-0.39125000	-3.60493500
H	1.56370500	1.43127500	-2.26707900
H	4.42515900	-1.32594000	-0.62247700
H	3.42427700	-3.16584300	-1.95840300
H	1.51104800	-2.69746500	-3.48936100
H	5.67845200	0.80558100	-1.54612400
H	6.88921400	2.70742100	-0.52151800
H	5.65430400	4.35839300	0.88328700
H	3.21760700	4.04395200	1.28593000
H	0.09558000	0.92257200	1.42362700

H	2.66769300	-1.60253600	3.77402100
H	1.13041900	-2.50789800	3.78314000
H	3.06880600	-3.87954500	2.85383600
H	1.78415300	-3.66503600	1.65573900
H	3.26294600	-2.67292900	1.56348200
Cs	-0.74225300	-2.05806700	-0.18794400
O	0.85946100	2.99227100	0.13278800
H	-0.81459200	2.91744000	0.26149500

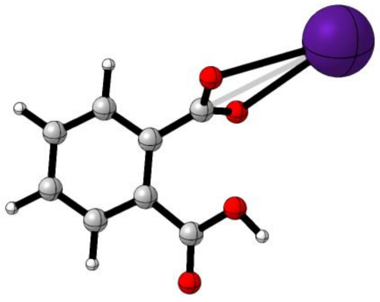
Asynchronicity Factor

TDRA-1^{-}



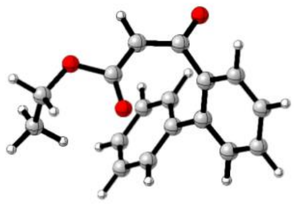
C	-4.06884400	-1.23567000	0.20270500
C	-4.35037800	0.13310000	0.27965600
C	-3.30649100	1.05540900	0.17125900
C	-1.97292800	0.65035200	-0.00365000
C	-1.69503000	-0.73294200	-0.09633200
C	-2.74893400	-1.65373300	0.01613400
C	-0.30637800	-1.29793700	-0.36474100
O	0.22046900	-1.01873400	-1.48124300
O	0.22211600	-2.00132100	0.54884900
C	-0.90343100	1.75948600	-0.02230500
O	0.19766700	1.48630700	0.55712600
O	-1.22353800	2.84545700	-0.55883300
H	-4.86876500	-1.97093700	0.28570900
H	-5.37370000	0.47900600	0.42270200
H	-3.50293500	2.12351500	0.21304300
H	-2.51539100	-2.71511600	-0.04008800
Cs	2.49166500	-0.00870100	0.09991100

TDRA-1H^{+}



H	0.88691900	2.98437200	0.48113100
C	0.43553400	-0.55955200	-0.01457100
O	-0.25937100	-0.89976500	0.98298200
O	-0.18656000	-0.21742100	-1.05423800
C	2.35012800	1.87295900	0.05340600
O	1.06222100	2.02409600	0.45411100
O	3.07256600	2.81098100	-0.19878000
C	1.91109500	-0.66963100	0.01866100
C	2.43294000	-1.98315200	0.02108400
C	3.80757100	-2.19299200	-0.01753100
C	4.67405600	-1.09380600	-0.06506100
C	4.16448300	0.21387900	-0.05902000
C	2.79072500	0.44359900	-0.00442400
H	1.74817200	-2.82546500	0.04408800
H	4.20354600	-3.20377400	-0.01601900
H	5.74825700	-1.24860500	-0.10205000
H	4.83292400	1.06825200	-0.08702800
Cs	-3.31508900	-0.04919500	-0.02523600

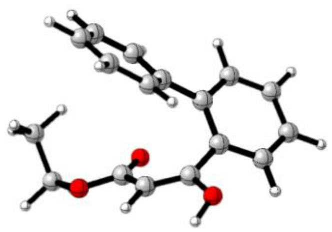
1a'•-



C	-1.17343100	2.60772900	1.59370900
C	-0.04108600	1.83912400	1.31474100
C	0.25891300	1.45792900	-0.00443200
C	-0.61499400	1.85355500	-1.03078200
C	-1.74846300	2.62152500	-0.75261800
C	-2.03137700	3.00567200	0.56234600
C	1.48046100	0.67142500	-0.32333700
C	2.32149200	1.11760500	-1.35739600
C	3.47964500	0.42069000	-1.70644100

C	3.82000200	-0.74042200	-1.00503800
C	2.99699300	-1.18469800	0.03131000
C	1.82078500	-0.50625200	0.37457100
C	1.01028400	-1.05514600	1.53900400
C	-0.27292500	-1.59726200	1.32909200
C	-0.95185100	-1.70020700	0.08616900
O	-2.24874500	-2.22845000	0.27390100
O	-0.58519200	-1.40196900	-1.05787500
C	-3.08736000	-2.24372800	-0.87794000
C	-3.72455800	-0.87691800	-1.12838200
H	-1.39167700	2.88587200	2.62278300
H	0.61225700	1.51587000	2.12026500
H	-0.42173300	1.51146500	-2.04348500
H	-2.42254400	2.90098700	-1.56024100
H	-2.91870500	3.59612600	0.78276800
H	2.06409800	2.03448000	-1.88425100
H	4.11381900	0.78675300	-2.51191400
H	4.72122100	-1.29442800	-1.26249300
H	3.25408300	-2.08078100	0.59054700
H	-0.80171800	-1.93542600	2.21490400
H	-2.51313800	-2.56040400	-1.75679200
H	-3.85502800	-2.99801400	-0.66262300
H	-4.39770700	-0.91751700	-1.99739200
H	-4.30162400	-0.55487800	-0.25275400
H	-2.94468100	-0.13391100	-1.31874700
O	1.57742300	-0.98207000	2.66547100

1a’H$^+$

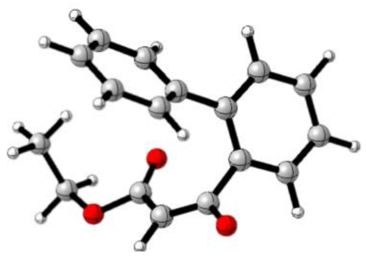


C	-1.33659800	2.09351100	1.95712600
C	-0.17242200	1.47752500	1.50475500
C	0.10239100	1.37128200	0.10709800
C	-0.82852000	1.92286600	-0.80878700
C	-1.99384500	2.51228000	-0.35121700
C	-2.25265000	2.60423600	1.03548600
C	1.33026100	0.74743800	-0.37027100
C	2.03617400	1.32675500	-1.44844300
C	3.30107800	0.87674700	-1.79239200

C	3.90319100	-0.17656900	-1.07395400
C	3.21973400	-0.79187800	-0.02842700
C	1.91857900	-0.38494000	0.29561600
C	1.17021900	-1.17230000	1.27928100
C	-0.12678400	-1.61608500	1.14368000
C	-0.89436700	-1.61338000	-0.12333800
O	-2.13848500	-2.05256400	0.11001600
O	-0.45930200	-1.28698800	-1.21613400
C	-3.04119700	-2.15955200	-1.03440800
C	-3.68249900	-0.81706700	-1.34815700
H	-1.51979300	2.18886000	3.02286200
H	0.57011700	1.14568400	2.22250500
H	-0.65639600	1.81674600	-1.87469100
H	-2.72064700	2.89702200	-1.06040700
H	-3.16325400	3.08461900	1.38169200
H	1.61347400	2.18380800	-1.96204000
H	3.84265500	1.35560800	-2.60265900
H	4.89328400	-0.52539100	-1.35146400
H	3.66331000	-1.62868600	0.50025600
H	-0.60573700	-2.10898800	1.98616200
H	-2.47467000	-2.54849100	-1.88463000
H	-3.77636100	-2.89825000	-0.71115100
H	-4.41146300	-0.94253200	-2.15672300
H	-4.20568000	-0.42236700	-0.47057100
H	-2.92856200	-0.09412600	-1.67192900
O	1.90915400	-1.48097000	2.36171800
H	1.47231300	-2.14455300	2.92609800

BDFE

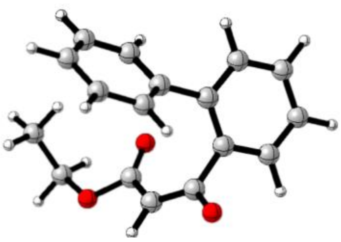
1a'$^{\cdot-}$



C	-1.17319300	2.60764600	1.59404700
C	-0.04084000	1.83909500	1.31496500
C	0.25892300	1.45771400	-0.00419500
C	-0.61519500	1.85312400	-1.03044300
C	-1.74868500	2.62102200	-0.75217100
C	-2.03136900	3.00535900	0.56278500
C	1.48055200	0.67140600	-0.32324600
C	2.32142400	1.11786500	-1.35730300

C	3.47966000	0.42117200	-1.70655700
C	3.82026900	-0.73996000	-1.00532700
C	2.99735600	-1.18456000	0.03098000
C	1.82103200	-0.50641500	0.37436900
C	1.01060400	-1.05573800	1.53870000
C	-0.27294200	-1.59720600	1.32895000
C	-0.95210400	-1.69986700	0.08612500
O	-2.24917800	-2.22768100	0.27406100
O	-0.58548700	-1.40172400	-1.05795600
C	-3.08774600	-2.24334400	-0.87783900
C	-3.72489400	-0.87661400	-1.12877700
H	-1.39126300	2.88594600	2.62311500
H	0.61268200	1.51598600	2.12040700
H	-0.42207000	1.51095100	-2.04314800
H	-2.42292700	2.90032100	-1.55971700
H	-2.91869200	3.59578700	0.78330200
H	2.06381500	2.03474100	-1.88405700
H	4.11368400	0.78746400	-2.51204800
H	4.72154900	-1.29380400	-1.26291600
H	3.25467000	-2.08065300	0.59009000
H	-0.80165400	-1.93546400	2.21477000
H	-2.51346300	-2.56031700	-1.75654800
H	-3.85541400	-2.99756800	-0.66229900
H	-4.39807000	-0.91752900	-1.99776200
H	-4.30194000	-0.55420700	-0.25327500
H	-2.94496800	-0.13373700	-1.31945900
O	1.57803400	-0.98335900	2.66503900

1a$^-$



C	-1.17305700	2.60794200	1.59390700
C	-0.04076800	1.83929000	1.31487700
C	0.25902800	1.45786700	-0.00426600
C	-0.61494100	1.85346800	-1.03056000
C	-1.74836000	2.62149700	-0.75234600
C	-2.03113000	3.00577400	0.56260500
C	1.48051600	0.67135700	-0.32330400
C	2.32139300	1.11760000	-1.35745500
C	3.47950400	0.42072400	-1.70671000

C	3.82002200	-0.74038700	-1.00538400
C	2.99714500	-1.18475000	0.03104100
C	1.82091700	-0.50642600	0.37443300
C	1.01056100	-1.05555500	1.53888700
C	-0.27305900	-1.59695800	1.32917200
O	1.57805200	-0.98317400	2.66517600
C	-0.95207300	-1.69985000	0.08628800
O	-2.24922600	-2.22774100	0.27421900
O	-0.58537600	-1.40192000	-1.05779200
C	-3.08779200	-2.24360900	-0.87771500
C	-3.72508200	-0.87698800	-1.12885800
H	-0.80179900	-1.93507900	2.21501500
H	-1.39117200	2.88620000	2.62297700
H	0.61266200	1.51610400	2.12035800
H	-0.42177000	1.51135700	-2.04327700
H	-2.42249800	2.90091200	-1.55993700
H	-2.91843100	3.59625300	0.78307800
H	2.06389100	2.03446700	-1.88428100
H	4.11351700	0.78684600	-2.51228900
H	4.72122000	-1.29435900	-1.26298600
H	3.25436100	-2.08082700	0.59022400
H	-2.51351000	-2.56069100	-1.75638600
H	-3.85540400	-2.99785500	-0.66205500
H	-4.39808800	-0.91801200	-1.99797600
H	-4.30231500	-0.55457100	-0.25348700
H	-2.94521000	-0.13404200	-1.31947900

8. References

(1) Guo, J.-D.; Yang, X.-L.; Chen, B.; Tung, C.-H.; Wu, L.-Z. N-Iodosuccinimide and dioxygen in an air-enabled synthesis of 10-phenanthrenols under sunlight. *Green Chem.* **2021**, *23*, 7193-7198.
(2) Jiang, Y.-T.; Yu, Z.-Z.; Zhang, Y.-K.; Wang, B. N-Bromosuccinimide-Induced C-H Bond Functionalization: An Intramolecular Cycloaromatization of Electron Withdrawing Group Substituted 1-Biphenyl-2-ylethanone for the Synthesis of 10-Phenanthrenol. *Org. Lett.* **2018**, *20*, 3728-3731.
(3) Yang, X.-L.; Guo, J.-D.; Xiao, H.; Feng, K.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Photoredox Catalysis of Aromatic beta-Ketoesters for in Situ Production of Transient and Persistent Radicals for Organic Transformation. *Angew. Chem. Int. Ed.* **2020**, *59*, 5365-5370.
(4) Yuan, C.; Axelrod, A.; Varela, M.; Danysh, L.; Siegel, D. Synthesis and reaction of phthaloyl peroxide derivatives, potential organocatalysts for the stereospecific dihydroxylation of alkenes. *Tetrahedron Letters* **2011**, *52*, 2540-2542.
(5) Griffith, J. C.; Jones, K. M.; Picon, S.; Rawling, M. J.; Kariuki, B. M.; Campbell, M.; Tomkinson, N. C. O. Alkene Syn Dihydroxylation with Malonoyl Peroxides. *J. Am. Chem. Soc.* **2010**, *132*, 14409-14411.
(6) Gan, S.; Yin, J.; Yu, Z.; Song, L.; Shi, L. A one-pot and two-stage Baeyer–Villiger reaction using 2,2′-diperoxyphenic acid under biomolecule-compatible conditions. *Green Chemistry* **2022**, *24*, 2232-2239.
(7) Yang, Q.; Li, Y.; Yang, J.-D.; Liu, Y.; Zhang, L.; Luo, S.; Cheng, J.-P. Holistic Prediction of the pKa in Diverse Solvents Based on a Machine-Learning Approach. *Angew. Chem. Int. Ed.* **2020**, *59*, 19282-19291.
(8) Trail, D.; Boehnke, P.; Savage, P. S.; Liu, M.-C.; Miller, M. L.; Bindeman, I. Origin and significance of Si and O isotope heterogeneities in Phanerozoic, Archean, and Hadean zircon. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 10287-10292.