Supporting Information

Visible-Light-Induced Palladium-Catalyzed formal [3+3] Cyclization of 2-Iodophenols and Cyclopropenes

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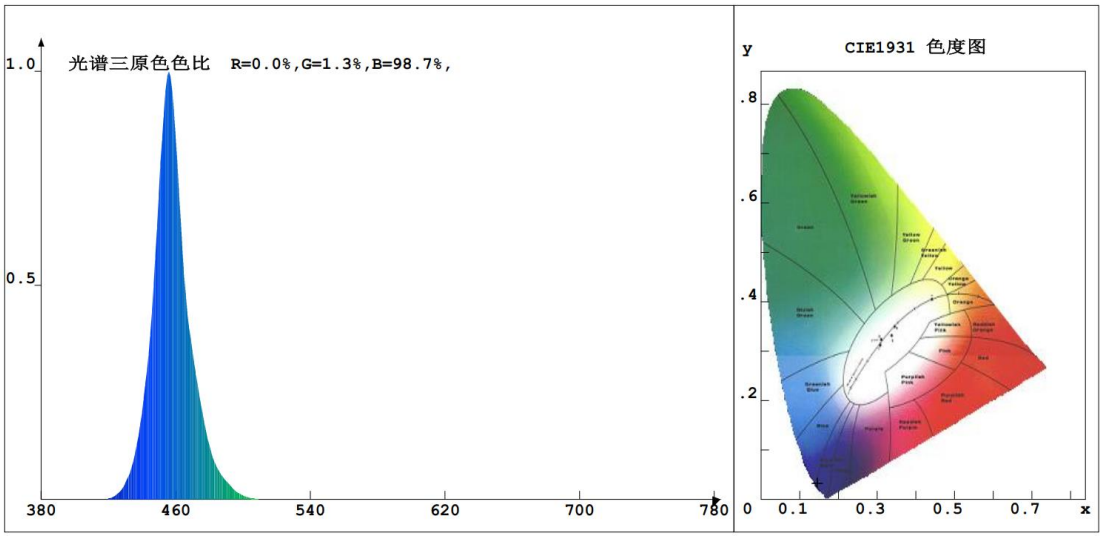
General Information

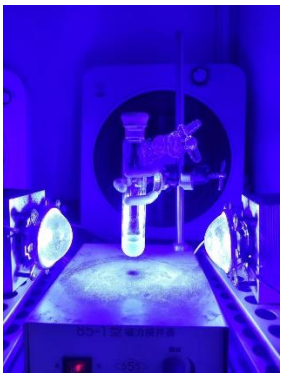
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere, reagents and solvents were obtained from commercial suppliers and were used without further purification. Pd catalysts and ligands are commercially available and purchased from Adamas unless otherwise state. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel GF-254. Column chromatography purifications were carried out using 200-300 mesh silica gel. Melting points were measured using open glass capillaries in a SGW® X-4A apparatus. ^{1}H and ^{13}C spectra were recorded on a 400 MHz JEOL (100 MHz for ^{13}C NMR) spectrometer at ambient temperature. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^{1}H NMR: δ 7.26; ^{13}C NMR: δ 77.0). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), m (multiplet) and br (broad). Infrared spectra were recorded on a Bruker V 70 and only major peaks were reported in cm^{-1}. HRMS were obtained on a WATERS I-Class VION IMS Q-Tof with an ESI source. Some compounds were visualized by exposure to UV-light or by dipping the plates in $KMnO_4$ stain followed by heating.

The Light Source and the Material of the Irradiation Vessel

Light Source purchased from XuSheng Electronic Technology.
Broadband source： λ = 455-460 nm
Spectral distribution and intensity：



Material of the irradiation vessel: borosilicate reaction tube
Distance from the light source to the irradiation vessel: 3.0 cm
Not use any filters

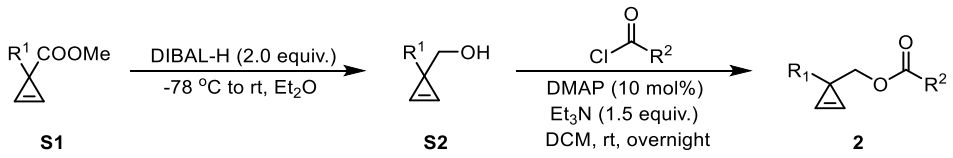


The setting-up reactions.

Starting Materials

2-Iodophenols **1** are commercially available unless otherwise state.

General procedures A for synthesis of cyclopropenes **2**

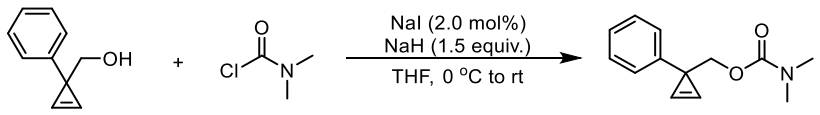


Compounds **S1** were prepared according to literature procedures.[1]. To a stirred at -78 °C solution of ester **S1** (25 mmol, 1.0 equiv.) in dry ether, DIBAL-H (1.0 M solution in hexane, 50 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred for 1 hour at -78 °C, then additionally for 1 h at room temperature. Then, the mixture was quenched with saturated NH_4Cl, diluted aqueous HCl, EtOAc and brine. Combined organic phases were washed with $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated in *vacuo*. The residue was purified by preparative column chromatography (EtOAc/petroleum ether = 1:3) to give alcohol **S2**.

To a stirred solution of alcohol **S2** (2.0 mmol, 1.0 equiv.), 4-(dimethylamino)pyridine (DMAP, 0.2 mmol, 10 mol%), and triethylamine (Et_3N, 3.0 mmol, 1.5 equiv.) in anhydrous CH_2Cl_2 (10 mL) was added acyl chloride (3.0 mmol, 1.5 equiv.). The mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the solution was quenched with water and extracted CH_2Cl_2. Combined organic phases were washed with diluted aqueous HCl, saturated $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated in *vacuo*. The residue was purified by preparative column chromatography (EtOAc/petroleum ether = 1:20) to give product **2**.

The compounds **2y**,[2] **2z**,[3] are known and were prepared according to corresponding literature.

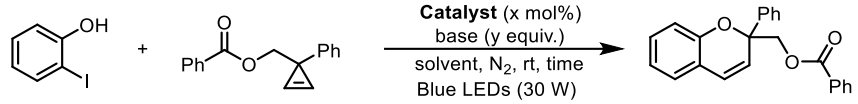
General procedures for synthesis of cyclopropenes **2ag**



This procedure was performed according to the known literature.[4] To a suspension of **S2a** (2 mmol, 1.0 equiv.) in dry THF (0.2 M) at 0°C was added NaH (1.5 equiv.) in one

portion. The reaction mixture was stirred at 0°C for 15 min before NaI (2.0 mol%) was added. Then carbamyl chloride (1.2 equiv.) was added dropwise. The mixture was allowed to stirred at room temperature, after a complete conversion (monitored by TLC), the mixture was diluted with sat. aq. NH_4Cl and extracted with EA. The combined organic phases were washed with brine, dried over Na_2SO_4 and then filtered. After removal of the solvent, the resulting residue was purified by flash chromatography to yield target product.

General Procedure for the Reaction of 1a with 2a



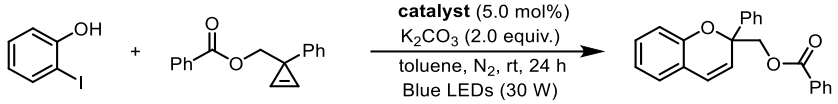
1a **2a** **3a**

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with 2-iodophenol **1a** (0.24 mmol, 1.2 equiv.), catalyst (5.0 mol%) and base (0.4 mmol, 2.0 equiv.) under N_2 atmosphere (glovebox). Subsequently, cyclopropene **2a** (0.2 mmol, 1.0 equiv.) and dry/degassed toluene were added via syringes. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of 2 * 30 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h with cooling by fan (vial temperature reached 35 ºC). After the reaction completed, the mixture was quenched with brine and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 40:1) to afford the desired product **3a** as colorless oil.

Detailed Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions

Catalysts[a]

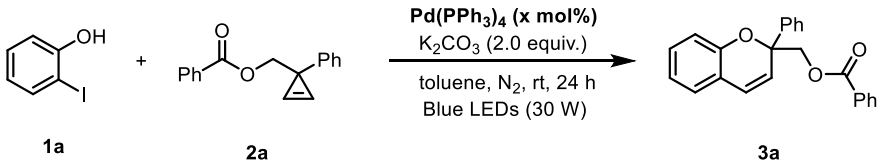


1a **2a** **3a**

Entry	**catalyst**	Yield (%)
1	$Pd_2(dba)_3$	8
2	$Pd(PPh_3)_4$	30
3	$Pd(^tBu_3P)_2$	0
4	$PdCl_2$	0
5	$Pd(OAc)_2$	15
6	$Pd(acac)_2$	0
7	$Pd(PhCN)_2Cl_2$	28
8	$Pd(MeCN)_2Cl_2$	16
9	$Pd(PPh_3)_2(OAc)_2$	25
10	$Pd(PPh_3)_2Cl_2$	27
11	$Fe(OAc)_2$	0
12	$Co(acac)_2$	0
13	$Ni(cod)_2$	0
14	$Cu(OAc)_2$	0

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv.), **2a** (0.2 mmol, 1.0 equiv.), **catalyst** (5.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with Blue LEDs (30 W) at room temperature for 24 h under N_2. Isolated yield.

Ratio of catalyst[a]

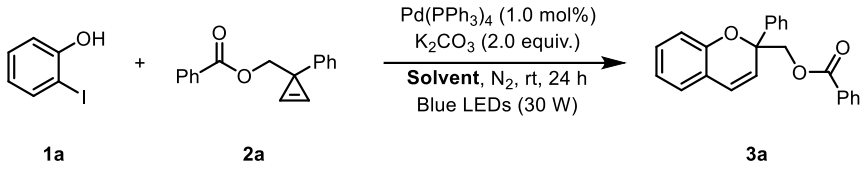


1a **2a** **3a**

Entry	**Pd(PPh3)4** (x mol%)	Yield (%)
1	0.5	22
2	1	46
3	2	40
4	5	30
5	10	18

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv.), **2a** (0.2 mmol, 1.0 equiv.), **Pd(PPh3)4** (x mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Solvent[a]

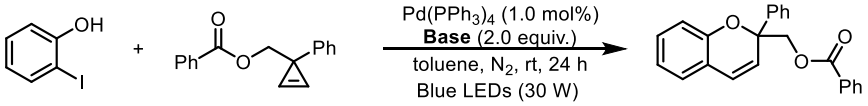


1a **2a** **3a**

Entry	**Solvent** (1.0 mL)	Yield (%)
1	MeCN	0
2	DCM	15
3	DCE	22
4	$CHCl_3$	43
5	THF	0
6	1, 4-Dioxane	< 5
7	DMF	0
8	DMSO	0
9	$PhCF_3$	20
10	toluene	46
11	Xylene	< 5
12	Ethylbenzene	18
13	PhCl	11
14	PhH	44
15	CH_3OH	0
16	EtOAc	0
17	CH_3NO_2	0
18	Acetone	0

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in **solvent** (2.0 mL) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Base[a]

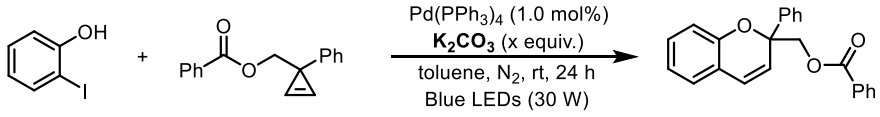


1a **2a** **3a**

Entry	**Base** (2.0 equiv.)	Yield (%)
1	Cs_2CO_3	0
2	Na_2CO_3	0
3	KOAc	14
4	Li_2CO_3	0
5	$NaHCO_3$	< 5
6	$KHCO_3$	10
7	K_3PO_4	8
8	^tBuOK	0
9	KOH	18
10	NaOH	0
11	K_2CO_3	46
12	$K_3PO_4 \cdot 3H_2O$	13
13	KH_2PO_4	0
14	KF	10
15	CsOPiv	0
16	PhCOONa	< 5
17	Et_3N	0
18	DIPEA	0
19	DABCO	25
20	2,4,6-Collidine	< 5
21	DBU	0

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and **Base** (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Ratio of base[a]

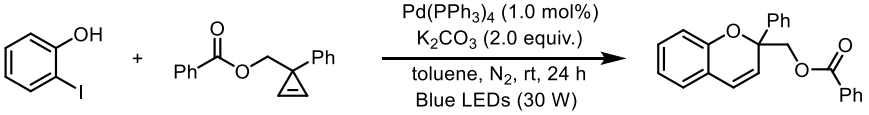


1a **2a** **3a**

Entry	**K_2CO_3** (x equiv.)	Yield (%)
1	1.0	31
2	1.5	37
3	2.0	46
4	2.5	14
5	3.0	35
6	5.0	23

[a]Reaction conditions: **1a** (0.24 mmol, 1.2 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and **K_2CO_3** (x equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Ratio of 1a:2a[a]

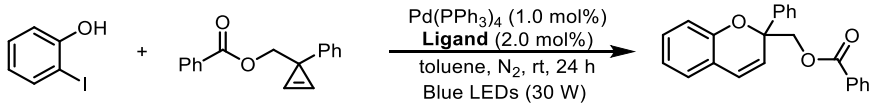


1a **2a** **3a**

Entry	**1a:2a**	Yield (%)
1	1:1.2	37
2	1:1.5	33
3	1:2.0	27
4	1:3.0	25
5	1.2:1	46
6	1.5:1	66
7	1.7:1	52
8	2.0:1	49

[a]Reaction conditions: **1a**:**2a** = x:y (0.2 mmol reaction scale), $Pd(PPh_3)_4$ (1.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Ligand[a]

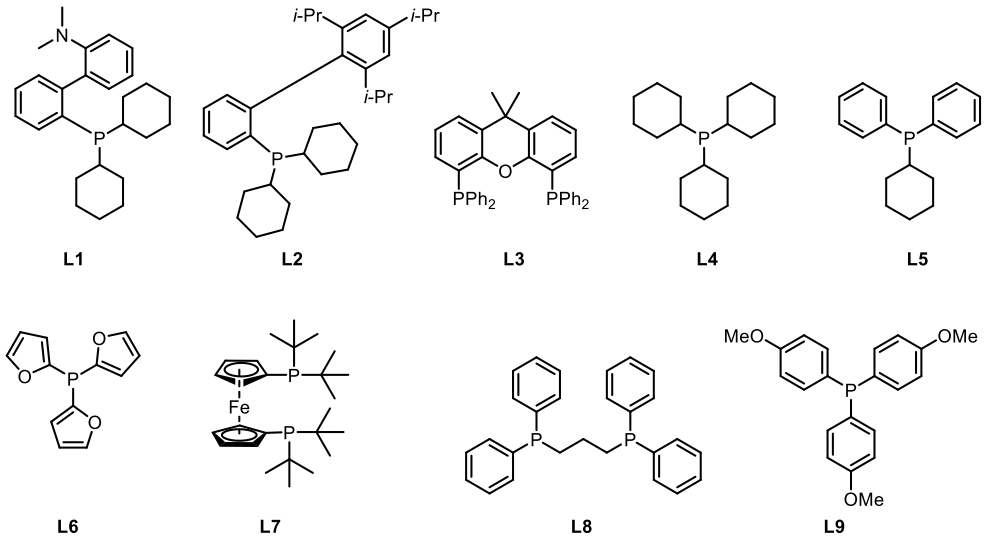


1a **2a** **3a**

Entry	**Ligand** (2.0 mol%)	Yield (%)
1	**L1**	< 5
2	**L2**	35
3	**L3**	25
4	**L4**	0
5	**L5**	0
6	**L6**	18
7	**L7**	0
8	**L8**	25
9	**L9**	44

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%), **Ligand** (2.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

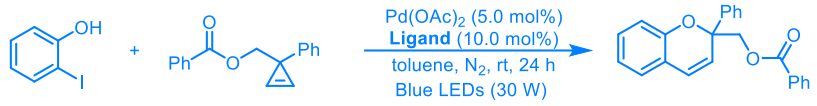
Ligand:



L1 **L2** **L3** **L4** **L5**

L6 **L7** **L8** **L9**

Asymmetric experiments[b]

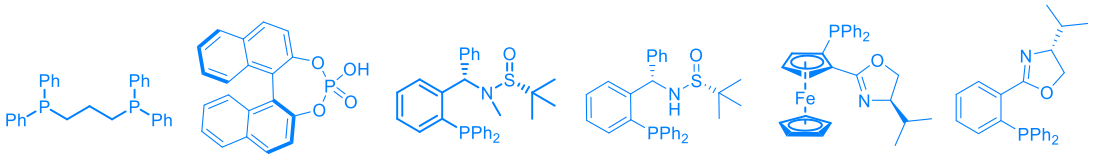


1a 2a 3a

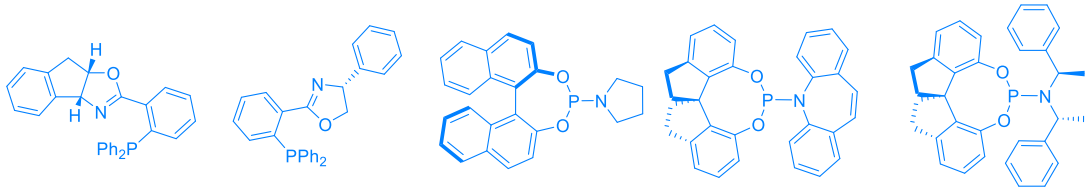
Entry	**Ligand** (10.0 mol%)	Yield (%)
1	**none**	15
2	**L1**	50
3	**L2**	15, 0% ee
4	**L3**	29, 0% ee
5	**L4**	19, 0% ee
6	**L5**	18, 0% ee
7	**L6**	trace
8	**L7**	trace
9	**L8**	trace
10	**L9**	trace
11	**L10**	trace
12	**L11**	trace

[b]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(OAc)_2$ (5.0 mol%), **Ligand** (10.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

Ligand:

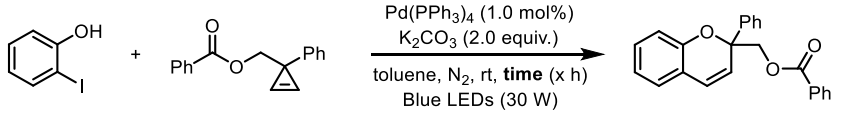


L1 50% | L2 15%, 0% ee | L3 29%, 0% ee | L4 19%, 0% ee | L5 18%, 0% ee | L6 trace



L7 trace | L8 trace | L9 trace | L10 trace | L11 trace

Time[a]

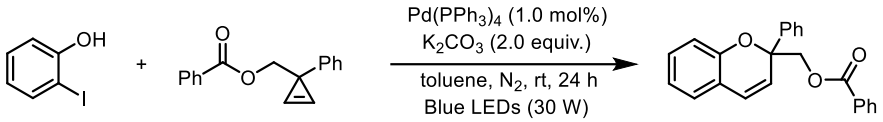


1a **2a** **3a**

Entry	**Time** (x h)	Yield (%)
1	6	trace
2	12	32
3	24	66
4	36	59

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for **x** h under N_2. Isolated yield.

Controlled experiments[a]

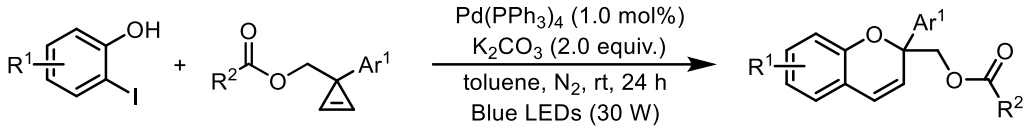


1a **2a** **3a**

Entry	**Reaction conditions**	Yield (%)[b]
1	none	66
2	without $Pd(PPh_3)_4$	0
3	without K_2CO_3	14
4	in the dark	0
5	in the air	0
6	in the dark, 80 ºC instead of rt	< 5

[a]Reaction conditions: **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL, dry) were irradiated with 30 W Blue LEDs at room temperature for 24 h under N_2. Isolated yield.

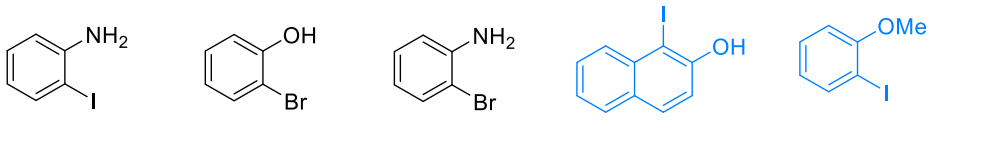
Representative Procedure for the Reaction of 1 with 2



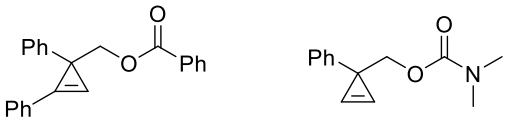
1 **2** **3 or 4**

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with 2-iodophenols **1** (0.3 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (1.0 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) under N_2 atmosphere (glovebox). Subsequently, cyclopropenes (CPEs) **2** (0.2 mmol, 1.0 equiv.) and dry/degassed toluene were added via syringes. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of 2 * 30 W blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 24 h with cooling by fan (vial temperature reached 35 °C). After the reaction completed, the mixture was quenched with brine and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography to the desired product **3** or **4**.

Unsuccessful substrates:



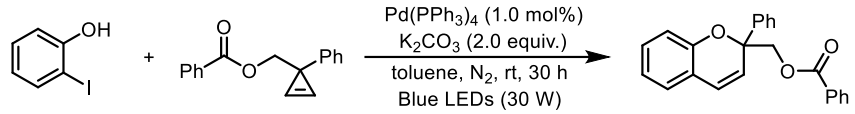
95% was recovered 97% was recovered



2af **2ag**

Large Scale Reaction and Synthetic Application

Large scale reaction



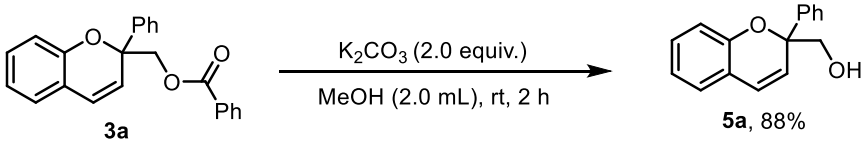
1a
(3.0 mmol)
660 mg

2a
(2.0 mmol)
500.6 mg

3a
397.2 mg, 61%

A 100 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with 2-iodophenol **1a** (3.0 mmol, 1.5 equiv.), catalyst (1.0 mol%) and K_2CO_3 (6.0 mmol, 2.0 equiv.) under N_2 atmosphere (glovebox). Subsequently, cyclopropene **2a** (2.0 mmol, 1.0 equiv.) and dry/degassed toluene were added via syringes. The tube was capped with a pressure screw cap. The reaction mixture was stirred under the irradiation of 2 * 30 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 30 h with cooling by fan (vial temperature reached 35 ^oC). After the reaction completed, the mixture was quenched with brine and extracted with EtOAc (3 × 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 1:40) for 61% yields to afford the desired product **3a** (397.2 mg) as colorless oil.

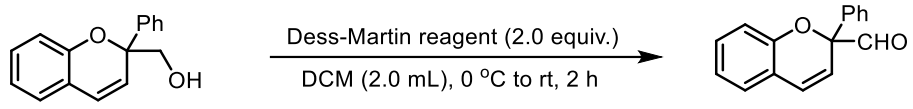
Synthetic application



3a

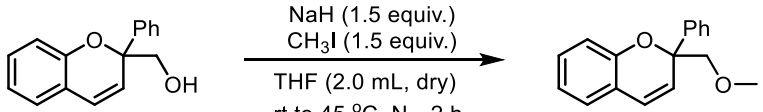
5a, 88%

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with **3a** (0.2 mmol, 1.0 equiv.), K_2CO_3 (0.4 mmol, 2.0 equiv.), MeOH (2.0 mL) under air atmosphere. The tube was capped with a pressure screw cap. The reaction mixture was stirred 2 h at room temperature. After the reaction completed, the mixture was concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 1:8) for 88% yields to afford **5a** as colorless oil.



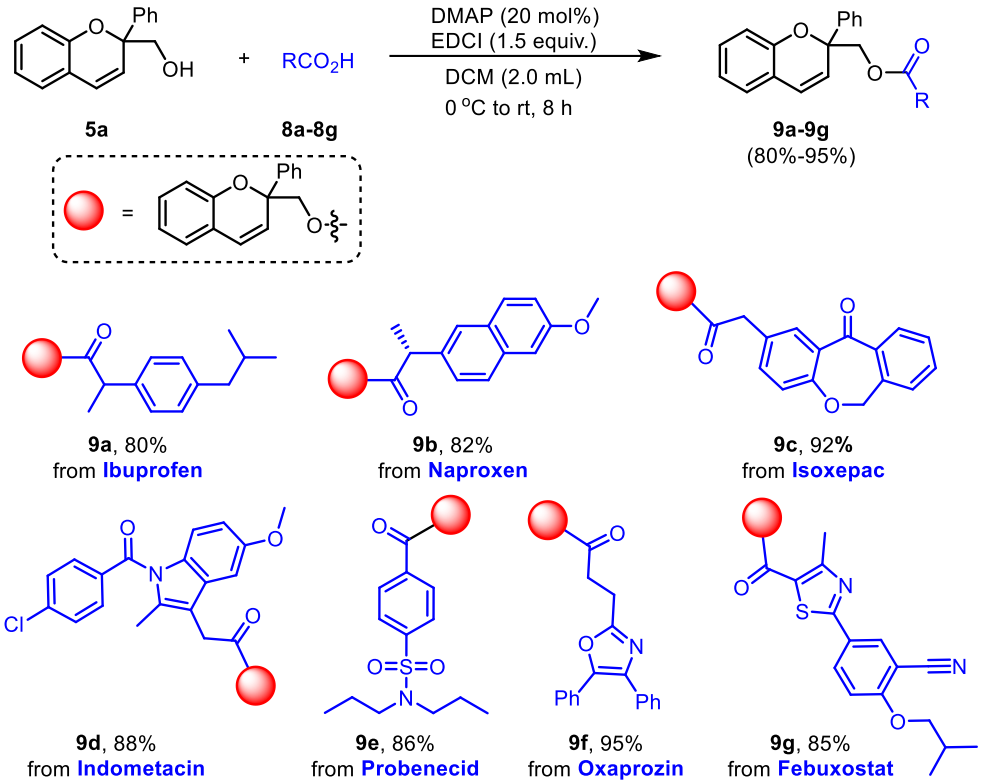
5a **6a**

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with **5a** (0.2 mmol, 1.0 equiv.) and DCM (2.0 mL) at 0 °C was added Dess-Martin reagent (0.4 mmol, 2.0 equiv.) in one portion. The tube was capped with a pressure screw cap. The reaction mixture was stirred 2 h at room temperature. After the reaction completed, the mixture was quenched with saturated sodium thiosulfate, brine and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 1:5) for 92% yields to afford the desired product **6a** as colorless oil.



5a **7a**

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with **5a** (0.2 mmol, 1.0 equiv.), THF (2.0 mL, dry) at N_2 atmosphere was added NaH (0.3 mmol, 1.5 equiv.) in one portion. The reaction was stirred at room temperature for 1h. Then, added CH_3I (0.3 mmol, 1.5 equiv.) in one portion and then warmed to 45 °C and stirred 2 h. After the reaction completed, the mixture was quenched with brine and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 1:20) for 88% yields to afford the desired product **7a** as yellow oil.

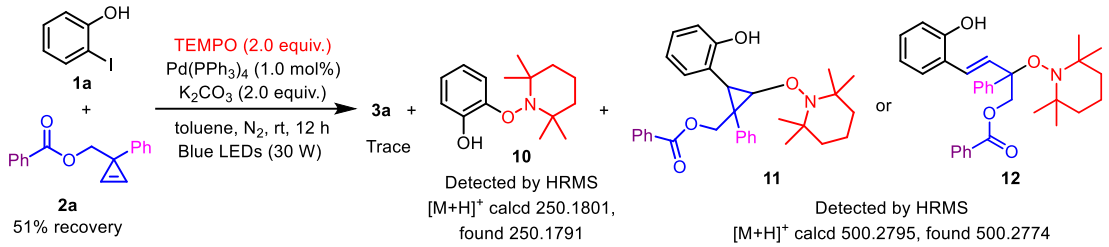


A 10 mL oven-dried reaction tube equipped with a magnetic stirrer was charged with **5a** (0.2 mmol, 1.0 equiv.), RCO_2H **8** (0.24 mmol, 1.2 equiv.) and DMAP (20 mol%) in DCM (2.0 mL, dry) at 0 °C was added EDCI (0.3 mmol, 1.5 equiv.) in one portion. The tube was capped with a pressure screw cap. A precipitate began to form almost immediately. The reaction was stirred at 0 °C for 10 min and then warmed to room temperature for overnight. After the reaction completed, the mixture was concentrated in *vacuo*. Purification of the crude product by flash chromatography (silica gel; EtOAc/petroleum ether = 1:10-1:5) to afford the desired products **9**.

Mechanistic Investigation

(1) Radical trapping experiments

(a) 2-Iodophenol **1a** (0.3 mmol, 1.5 equiv.), cyclopropene **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.), dry/degassed toluene (2.0 mL) under N_2 for 12 h, with the irradiation of 30 W Blue LEDs.



When TEMPO (2.0 equiv.) was subjected into the reaction of **1a** with **2a** under the standard conditions, only a trace amount of **3a** was observed, along with the TEMPO adducts **10, 11** or **12** were detected by HRMS (**10**: Calcd for $C_{15}H_{24}NO_2$ $[M+H]^+$: 250.1801, found: 250.1791; **11** , **12**: Calcd for $C_{32}H_{37}KNO_4$ $[M+K]^+$: 500.2795, found: 500.2774). In this case, 51% of **2a** was recovered. This results indicates that a radical intermediate might be involved in this transformation (**Figure S1** (a) and (b)).

(a) (b)

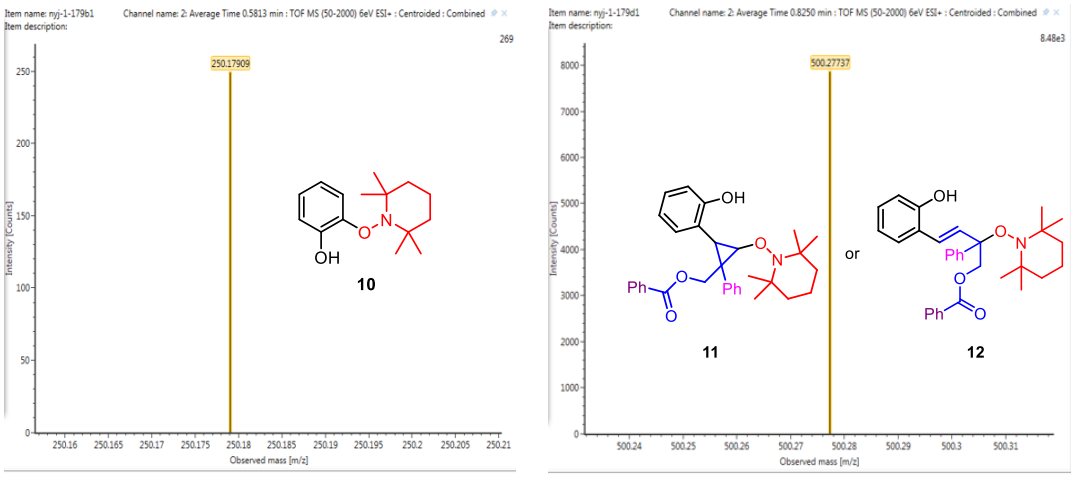
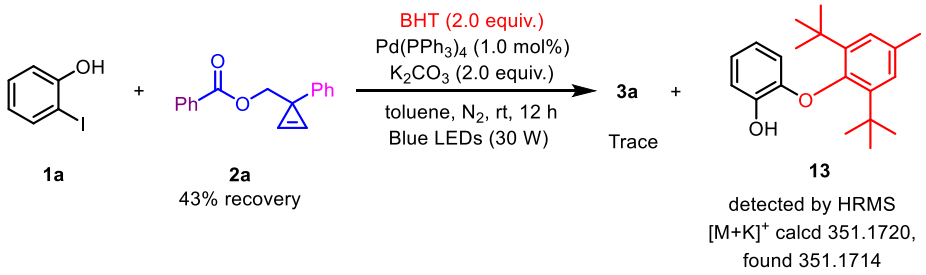


Figure S1. HRMS of TEMPO trapping experiments

(b) 2-Iodophenol **1a** (0.3 mmol, 1.5 equiv.), cyclopropene **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv.), BHT (0.4 mmol, 2.0 equiv.), dry/degassed toluene (2.0 mL) under N_2 for 12 h, with the irradiation of 30 W Blue LEDs.



1a **2a** 43% recovery **13** detected by HRMS $[M+K]^+$ calcd 351.1720, found 351.1714

When BHT (2.0 equiv.) was subjected into the reaction of **1a** with **2a** under the standard conditions, only a trace amount of **3a** was observed, along with the TEMPO adducts **13** were detected by HRMS (Calcd for $C_{21}H_{28}KO_2$ $[M+K]^+$: 351.1720, found: 351.1714. In this case, 43% of **2a** was recovered. These results support a radical pathway (**Figure S2**).

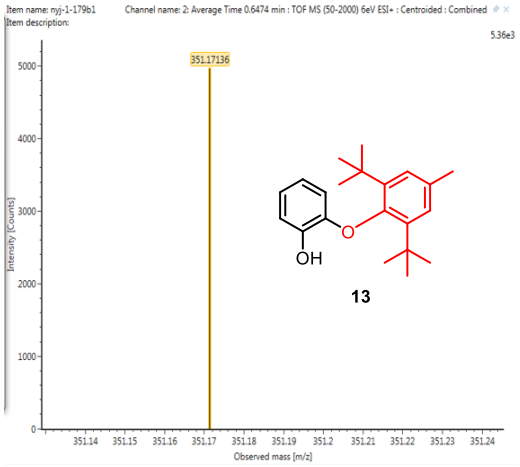
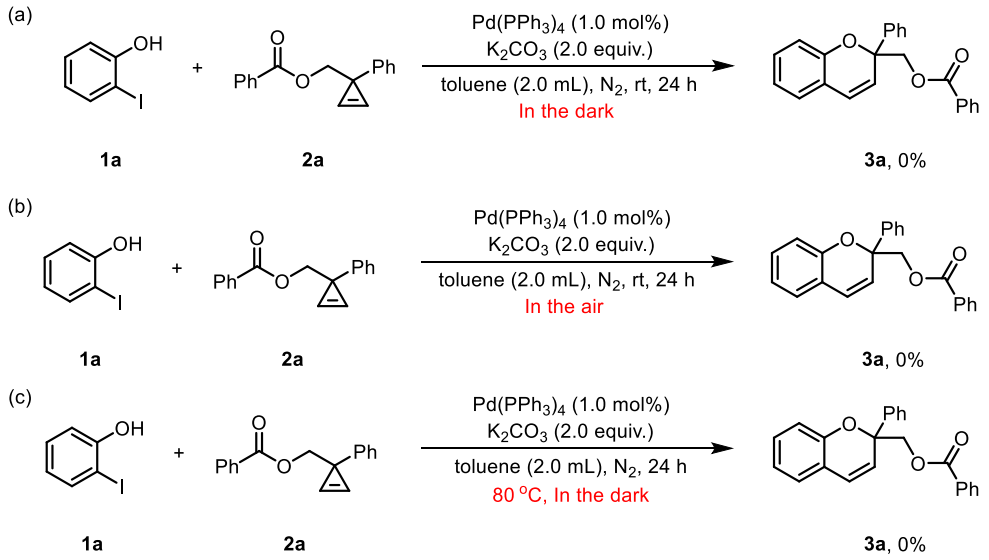


Figure S2. HRMS of BHT trapping experiments

(2) Control experiments

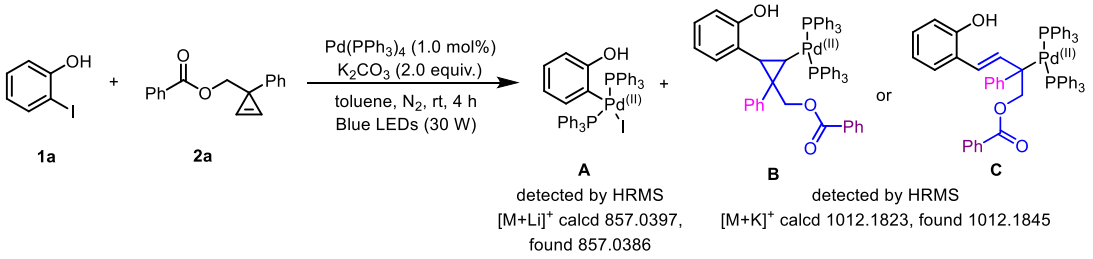
2-Iodophenol **1a** (0.3 mmol, 1.5 equiv.), cyclopropene **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv.), dry/degassed toluene (2.0 mL) under N_2 for 24 h, in the dark, air atmosphere and 80 °C instead of rt in the dark, conditions.



When the reaction of **1a** with **2a** under the dark and air conditions, **3a** was not observed, 82% of **2a** was recovered. When 80 °C instead of rt and in the dark, **3a** was not observed. The results indicate that blue light and nitrogen atmosphere are necessary.

(3) Mass spectrometry experiments

2-Iodophenol **1a** (0.3 mmol, 1.5 equiv.), cyclopropene **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv.), dry/degassed toluene (2.0 mL) under N_2 for 4 h, with the irradiation of 30 W Blue LEDs. After 4 h, 5.0 μL reaction mixture was picked up and dissolvent into 1.0 mL MeCN. The mixture was injected into the HRMS, then collected MS data.



detected by HRMS
$[M+Li]^+$ calcd 857.0397, found 857.0386

detected by HRMS
$[M+K]^+$ calcd 1012.1823, found 1012.1845

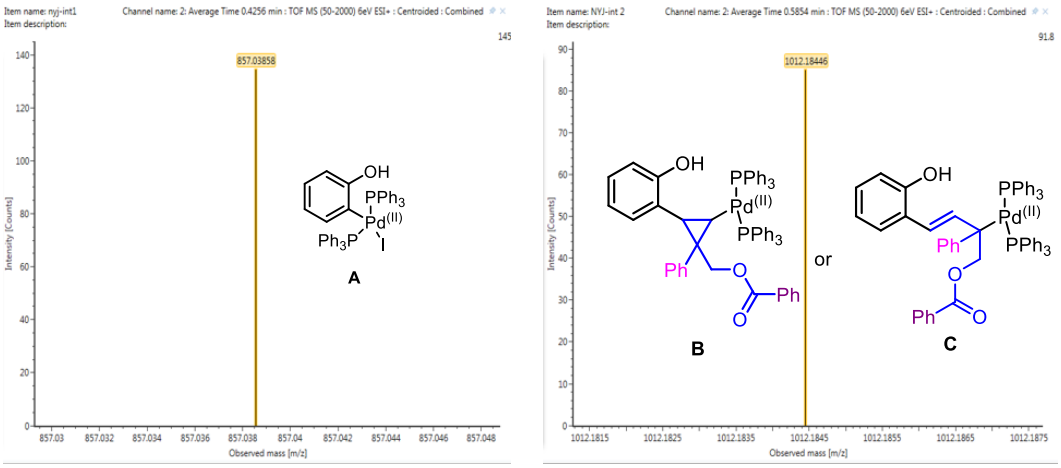


Figure S3. HRMS of intermediates

We successfully detected the intermediate **A** singnal (Calcd for $C_{42}H_{35}OILiP_2Pd^{(II)}$ $[M+Li]^+$:857.0397, found: 857.0386) and **B** or **C** singnal (Calcd for $C_{59}H_{49}O_3KP_2Pd^{(II)}$ $[M+K]^+$:1012.1823, found: 1012.1845). This result suggests that intermediate **A**, **B**, **C** was generated in the reaction (**Figure S3**).

(4) Stern-volmer fluorescence quenching experiments

To a solution of $Pd(PPh_3)_4$ in dry/degassed toluene (2×10^{-3} mol/L) in a quartz cuvette, different amounts of 2-iodophenol **1a** and cyclopropene **2a** were added, respectively, and the resulting changes in fluorescence intensity (concentration of **1a** and **2a**: 0.5×10^{-3} mol/L, 1.0×10^{-3} mol/L, 1.5×10^{-3} mol/L, 2.0×10^{-3} mol/L, 2.5×10^{-3} mol/L were collected. The emission intensity at 600 nm was collected with excited wavelength of 446 nm. The results are shown in **Figure S4**, **S5**.

(a) (b)

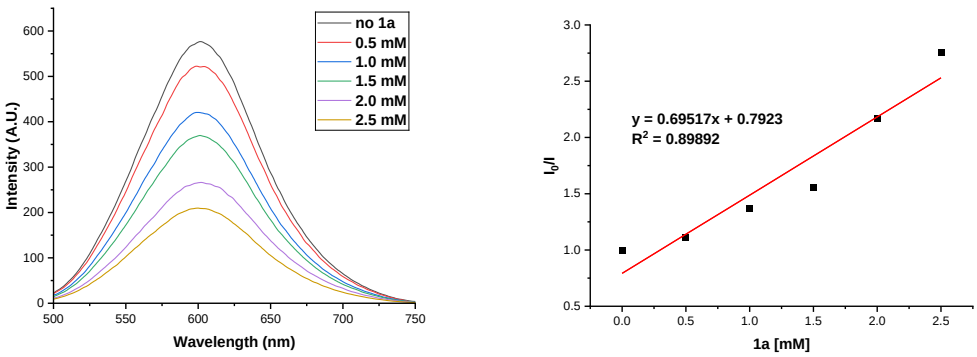


Figure S4 (a) The fluorescence emission spectra of $Pd(PPh_3)_4$ with different concentration of **1a** added. (b) The Stern–Volmer emission quenching studies of **1a**. I_0

is the inherent fluorescence intensity of $Pd(PPh_3)_4$. I is the fluorescence intensity of $Pd(PPh_3)_4$ in the presence of **1a**.

(a) (b)

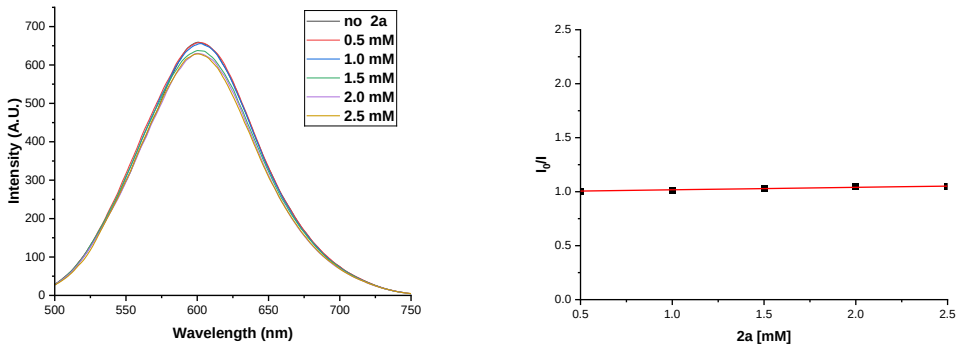


Figure S5 (a) The fluorescence emission spectra of $Pd(PPh_3)_4$ with different concentration of **2a** added. (b) The Stern–Volmer emission quenching studies of **2a**. I_0 is the inherent fluorescence intensity of $Pd(PPh_3)_4$. I is the fluorescence intensity of $Pd(PPh_3)_4$ in the presence of **2a**.

According to the results as well as the corresponding Stern-Volmer plots (**Figure S4, S5**), the substrate **1a** showed an obvious quenching effect to the fluorescence intensity of $Pd(PPh_3)_4$, where it presumably engages in SET event with the photoexcited Pd(0) complex. While the substrate **2a** did not show an obvious quenching effect to the fluorescence intensity of $Pd(PPh_3)_4$.

(5) UV-vis absorption experiments

UV-vis absorption experiments were performed using a spectrophotometer. The samples were measured in a 1.5 mL quartz cuvette fitted with a PTFE stopper. 2-iodophenol **1a**, cyclopropene **2a**, 2-iodophenol **1a** + cyclopropene **2a** and $Pd(PPh_3)_4$ were prepared as a 5 mM, 5 mM, 5 mM + 5 mM and 0.05 mM solution respectively in toluene for measurement (**Figure S6**).

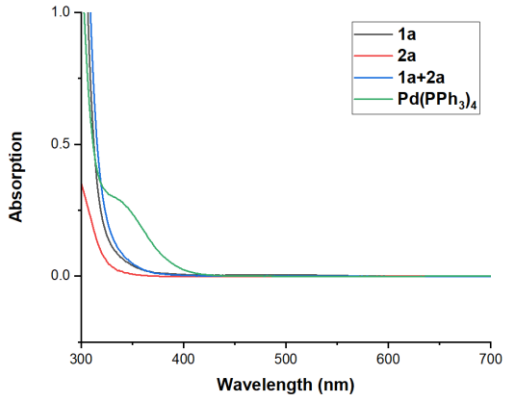


Figure S6. UV-vis absorption experiments

The measurement results show that only $Pd(PPh_3)_4$ absorbs light in the wavelength range of the light source, and the mixture of **1a** and **2a** showed no obvious change compared with **1a** and **2a** alone. These results indicate that EDA complex is unlikely to be formed between **1a** and **2a**.

(6) Cyclic voltammetry measurements

The cyclic voltammetry experiments were performed, and the redox potentials of **1a** and **2a** were determined separately. The data indicated that **1a** ($E_{red,\ 1/2}$ = -1.80 V vs SCE in MeCN), **2a** ($E_{red,\ 1/2}$ = -2.12 V vs SCE in MeCN) (**Figure S7**). The results indicates that **1a** is more easily reduced by the excited $Pd(PPh_3)_4$* ($E_{red,\ 1/2}$ = -2.51 V vs SCE in MeCN)[5]. Cyclic voltammetry was performed in a three-electrode cell (volume 10 mL; acetonitrile as solvent, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as the supporting electrolyte, **1a** (2.0 mM) and **2a** (2.0 mM) respectively as the tested compound) with glassy carbon (diameter 3.0 mm) as the working electrode, Pt wire as the auxiliary electrode, and SCE (saturated calomel electrode) as the reference electrode. The scan speed was 100 $mV \cdot s^{-1}$ under room temperature (25 °C). Unless otherwise noted, the initial potential was 0 V. The potential range investigated for **1a** is 0 to -2.8 V vs SCE, and for **2a** is -2.7 to 0 V vs SCE.

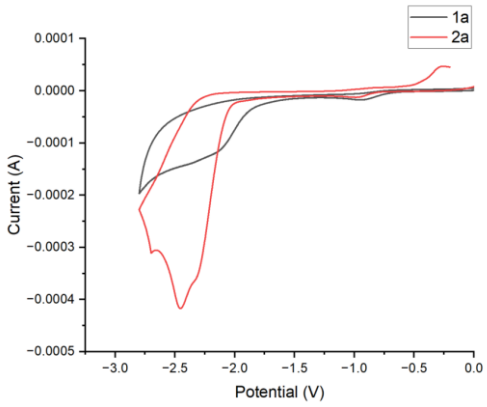


Figure S7. Cyclic voltammetry measurements

The polishing material and method:

Working electrode: The working electrode is a 3.0 mm diameter glassy carbon working electrode. Polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

Reference electrode: The reference electrode is SCE (saturated calomel electrode) that was washed with water and ethanol before measurements.

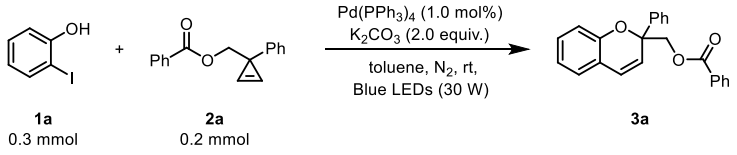
Counter electrode: The counter electrode is a platinum wire that was polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

The solvent deoxygenation method, if applicable:

When measuring the reduction potential of a substance, the measured solution undergoes deoxygenation operation. Deoxygenation method: The solution of interest was sparged with argon for 10 minutes before data collection.

(7) Light on-off experiments

To further examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness. The yield of **3a** was determined by crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard (**Figure S8**).



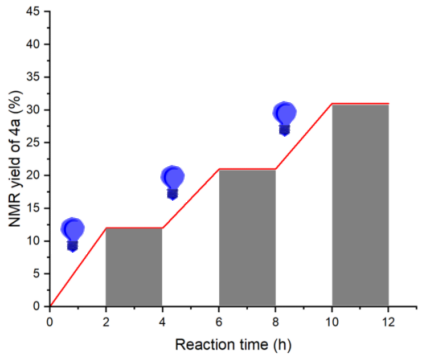
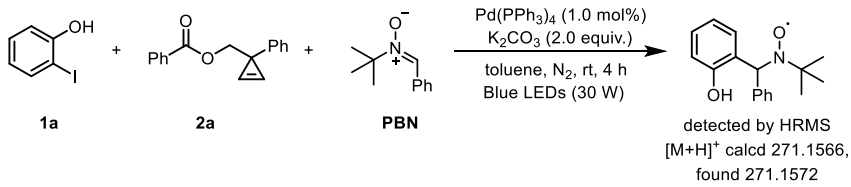


Figure S8. Light on-off experiments

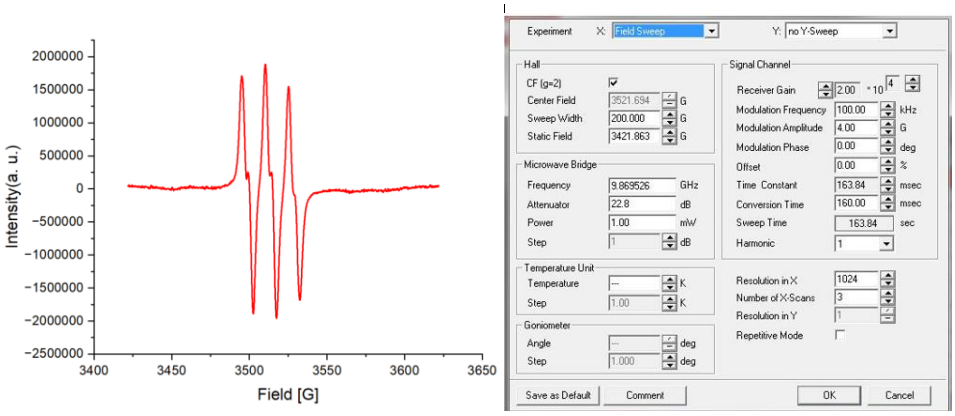
The results of light on-off experiments indicated that the reaction proceeded only under the irradiation of light, and the reaction maybe proceed by a catalytic process rather than by a radical chain process.

(8) EPR experiments

A 10 mL Shlenck tube containing a PTFE-coated stirring bar was charged with 2-iodophenol **1a** (0.3 mmol, 1.5 equiv.), cyclopropene **2a** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (1.0 mol%), K_2CO_3 (0.4 mmol, 2.0 equiv.), dry/degassed toluene (2.0 mL) and PBN (0.4 mmol, 2.0 equiv.) under N_2 for 12 h, with the irradiation of 30 W Blue LEDs. After 12 hours, Then, the resulting mixture was analyzed by EPR at room temperature. The experimental parameters are shown on the right in (**Figure S9-**(a)). The reaction mixture was concentrated under reduced pressure and directly used for HRMS analysis. HRMS: $C_{17}H_{21}NO_2$ $[M+H]^+$ calcd. for 271.1566, found 271.1572 (**Figure S9-**(b)).



(a) EPR



(b) HRMS

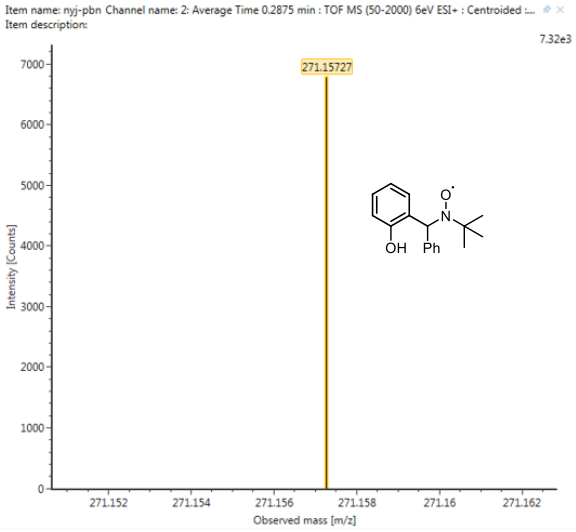
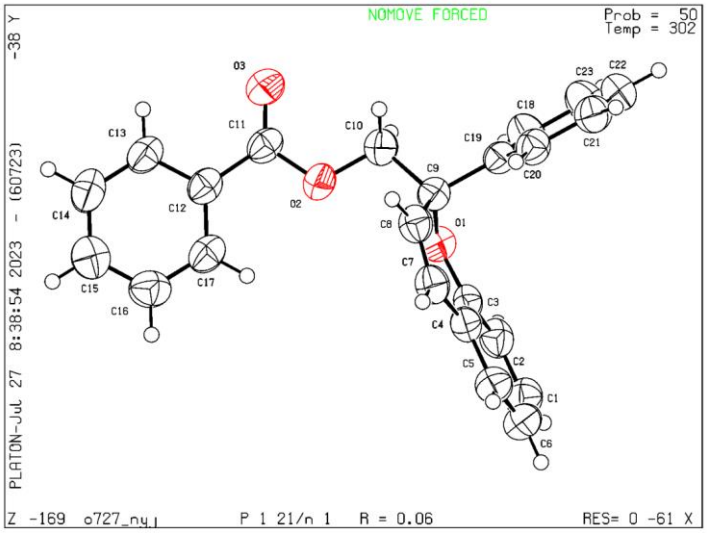


Figure S9. EPR experiments

X-ray crystallographic analysis of 3a

Preparation of the single crystals of **3a**: 30.0 mg of pure **3a** was dissolved in the combined solvents of EtOAc/petroleum ether (5.0 mL, v/v = 1:4) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing the slow solvent evaporation at room temperature. After about two days, several small crystals were observed at the bottom of the bottle. The crystals were collected and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3a** (CCDC: 2306968).



Empirical formula	$C_{23}H_{18}O_3$
Formula weight	342.37
Temperature/K	302.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3943(12)
b/Å	11.8944(14)
c/Å	17.744(2)
α/°	90
β/°	93.493(5)
γ/°	90
Volume/Å^3	1768.4(4)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	0.084
F(000)	720.0
Crystal size/mm^3	0.156 × 0.082 × 0.028
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.124 to 57.79
Index ranges	$-10 \leq h \leq 11$, $-16 \leq k \leq 13$, $-24 \leq l \leq 24$
Reflections collected	28856
Independent reflections	4638 [R_{int} = 0.1108, R_{sigma} = 0.0732]
Data/restraints/parameters	4638/12/235
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0563, wR_2 = 0.1381
Final R indexes [all data]	R_1 = 0.1254, wR_2 = 0.1765
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.17

Reference

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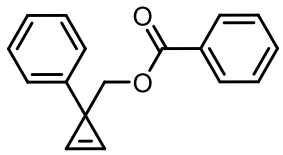
[3] M. Rubin and V. Gevorgyan, Catalytic Enantioselective Hydrostannation of Cyclopropenes, *J. Am. Chem. Soc.,* 2004, **126**, 3688−3689;

[4] J. Qu and Y. Chen, Catalytic Asymmetric Diarylation of Internal Acyclic Styrenes and Enamides, *J. Am. Chem. Soc.,* 2022, **144**, 8389–8398;

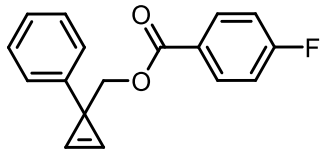
[5] C.-Y. He and X. Zhang, Visible-Light-Induced Palladium-Catalyzed Selective Defluoroarylation of Trifluoromethylarenes with Arylboronic Acids, *J. Am. Chem. Soc.,* 2021, **143**, 13971−13979.

Characterization of substrates 2 and Products 3, 4, 5a, 6a, 7a and 9a-g

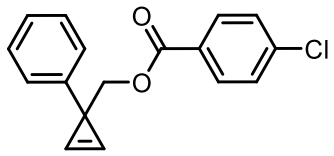
Characterization of Substrates 2



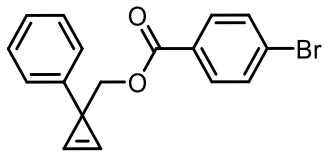
(1-phenylcycloprop-2-en-1-yl)methyl benzoate (2a) [3] pale yellow oil (72%, 360.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.2 Hz, 2H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.34-7.29 (m, 6H), 7.24-7.20 (m, 1H) 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 145.6, 132.8, 130.3, 129.6, 128.3, 128.1, 126.3, 125.8, 111.9, 71.6, 26.1 ppm.



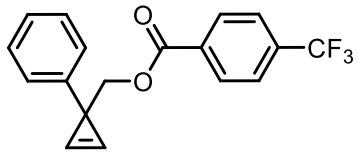
(1-phenylcycloprop-2-en-1-yl)methyl 4-fluorobenzoate (2b) colorless oil (80%, 429.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-8.01 (m, 2H), 7.34-7.27 (m, 6H), 7.23-7.19 (m, 1H), 7.12-7.06 (m, 2H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.7 (d, *J* = 252.0 Hz), 165.6, 145.5, 132.1 (d, *J* = 23.0 Hz), 128.2, 126.6 (d, *J* = 3.0 Hz), 126.2, 125.9, 115.4 (d, *J* = 22.0 Hz), 111.9, 71.8, 26.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.8 (s) ppm; HRMS (ESI) calcd for $C_{17}H_{13}LiFO_2$ $[M+Li]^+$ 275.1054, found 275.1037.



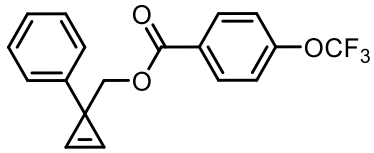
(1-phenylcycloprop-2-en-1-yl)methyl 4-chlorobenzoate (2c) colorless oil (83%, 472.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.94 (m, 2H), 7.41-7.38 (m, 2H), 7.34-7.26 (m, 6H), 7.21-7.19 (m, 1H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.7, 145.4, 139.2, 131.0, 128.8, 128.6, 128.2, 126.2, 125.9, 111.9, 71.9, 26.0 ppm; HRMS (ESI) calcd for $C_{17}H_{13}LiClO_2$ $[M+Li]^+$ 291.0758, found 291.0763.



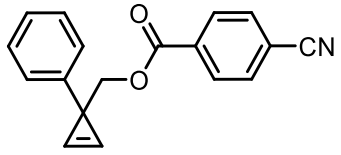
(1-phenylcycloprop-2-en-1-yl)methyl 4-bromobenzoate (2d) colorless oil (75%, 493.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.86 (m, 2H), 7.57-7.54 (m, 2H), 7.34-7.25 (m, 6H), 7.23-7.18 (m, 1H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.9, 145.4, 131.6, 131.1, 129.3, 128.2, 128.0, 126.2, 125.9, 111.9, 71.9, 26.1 ppm; HRMS (ESI) calcd for $C_{17}H_{13}KBrO_2$ $[M+K]^+$ 336.9730, found 366.9730.



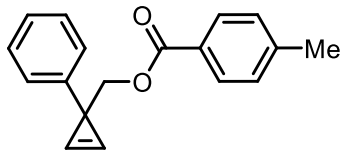
(1-phenylcycloprop-2-en-1-yl)methyl 4-(trifluoromethyl)benzoate (2e) colorless oil (70%, 445.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.35-7.27 (m, 6H), 7.24-7.20 (m, 1H), 4.82 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.4, 145.3, 134.3 (q, *J* = 32.0 Hz), 133.6, 130.0, 128.2, 126.2, 125.9, 125.4 (q, *J* = 3.0 Hz), 123.6 (q, *J* = 271.0 Hz), 112.0, 72.2, 26.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.3 (s) ppm; HRMS (ESI) calcd for $C_{18}H_{14}F_3O_2$ $[M+H]^+$ 319.0940, found 319.0928.



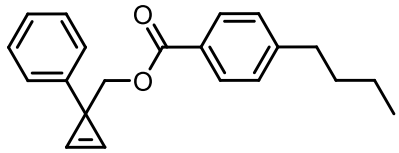
(1-phenylcycloprop-2-en-1-yl)methyl 4-(trifluoromethoxy)benzoate (2f) colorless oil (72%, 481.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.06 (m, 2H), 7.35-7.19 (m, 9H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.3, 152.5, 145.4, 131.5, 128.8, 128.2, 126.1, 125.9, 120.24 (q, *J* = 257.0 Hz), 120.19, 111.9, 72.0, 26.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -57.5 (s) ppm; HRMS (ESI) calcd for $C_{18}H_{17}NF_3O_3$ $[M+NH_4]^+$ 352.1155, found 352.1138.



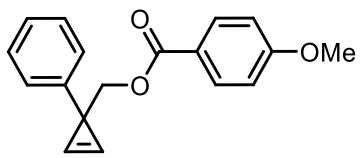
(1-phenylcycloprop-2-en-1-yl)methyl 4-cyanobenzoate (2g) colorless oil (67%, 368.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12-8.10 (m, 2H), 7.74-7.71 (m, 2H), 7.34-7.20 (m, 7H), 4.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.9, 145.1, 134.2, 132.2, 130.1, 128.2, 126.1, 126.0, 118.0, 116.3, 111.9, 72.5, 26.0 ppm; HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2$ $[M+NH_4]^+$ 293.1284, found 293.1291.



(1-phenylcycloprop-2-en-1-yl)methyl 4-methylbenzoate (2h) colorless oil (84%, 444.0 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93-7.91 (m, 2H), 7.34-7.27 (m, 6H), 7.23-7.18 (m, 3H), 4.76 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 145.7, 143.5, 129.6, 129.0, 128.1, 127.7, 126.2, 125.8, 111.9, 71.4, 26.1, 21.6 ppm; HRMS (ESI) calcd for $C_{18}H_{16}KO_2$ $[M+K]^+$ 303.0781, found 303.0782.

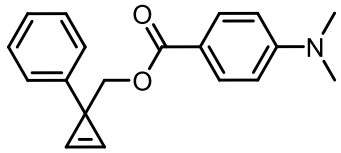


(1-phenylcycloprop-2-en-1-yl)methyl 4-butylbenzoate (2i) colorless oil (82%, 501.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.94 (m, 2H), 7.35-7.28 (m, 6H), 7.24-7.19 (m, 3H), 4.77 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.65-1.57 (m, 2H), 1.40-1.31 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 148.4, 145.7, 129.6, 128.4, 128.1, 127.8, 126.2, 125.7, 111.9, 71.4, 35.7, 33.3, 26.1, 22.3, 13.9 ppm; HRMS (ESI) calcd for $C_{21}H_{23}O_2$ $[M+H]^+$ 307.1692, found 307.1681.

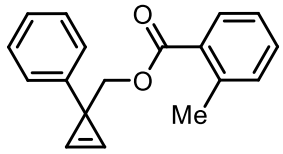


(1-phenylcycloprop-2-en-1-yl)methyl 4-methoxybenzoate (2j) colorless oil (86%, 482.1 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.97 (m, 2H), 7.35-7.28 (m, 6H), 7.23-7.19 (m, 1H), 6.93-6.89 (m, 2H), 4.75 (s,

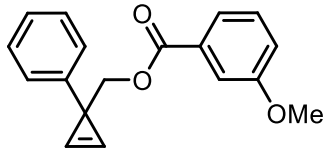
2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 163.2, 145.7, 131.6, 128.1, 126.2, 125.7, 122.8, 113.5, 112.0, 71.3, 55.3, 26.1 ppm; HRMS (ESI) calcd for $C_{18}H_{16}NaO_3$ $[M+Na]^+$ 303.0991, found 303.0974.



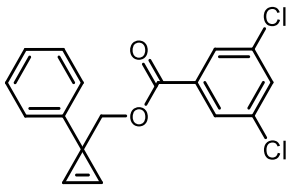
(1-phenylcycloprop-2-en-1-yl)methyl 4-(dimethylamino)benzoate (2k) pale yellow oil (72%, 442.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (m, 2H), 7.34-7.28 (m, 6H), 7.22-7.17 (m, 1H), 6.65-6.62 (m, 2H), 4.72 (s, 2H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 153.2, 146.0, 131.3, 128.1, 126.3, 125.6, 117.2, 112.0, 110.6, 70.7, 40.02, 26.2 ppm; HRMS (ESI) calcd for $C_{19}H_{19}LiNO_2$ $[M+Li]^+$ 316.1519, found 316.1509.



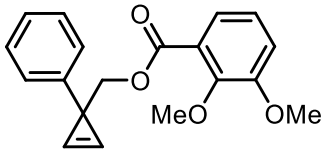
(1-phenylcycloprop-2-en-1-yl)methyl 2-methylbenzoate (2l) colorless oil (82%, 433.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.2 Hz, 1H), 7.41-7.28 (m, 7H), 7.24-7.20 (m, 3H), 4.77 (s, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 145.6, 140.0, 131.8, 131.6, 130.6, 129.8, 128.1, 126.2, 125.8, 125.6, 112.1, 71.5, 26.1, 21.8 ppm; HRMS (ESI) calcd for $C_{18}H_{16}KO_2$ $[M+K]^+$ 303.0781, found 303.0783.



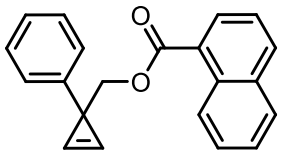
(1-phenylcycloprop-2-en-1-yl)methyl 3-methoxybenzoate (2m) colorless oil (74%, 414.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.61 (m, 1H), 7.56-7.54 (m, 1H), 7.35-7.28 (m, 7H), 7.23-7.19 (m, 1H), 7.11-7.08 (m, 1H), 4.78 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 159.5, 145.6, 131.7, 129.3, 128.1, 126.2, 125.8, 122.0, 119.3, 114.1, 112.0, 71.7, 55.4, 26.1 ppm; HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $[M+NH_4]^+$ 298.1437, found 298.1430.



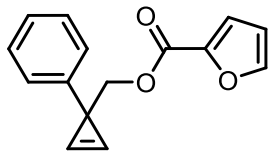
(1-phenylcycloprop-2-en-1-yl)methyl 3,5-dichlorobenzoate (2n) colorless oil (78%, 497.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 2.0 Hz, 2H), 7.53-7.52 (m, 1H), 7.35-7.30 (m, 4H), 7.27-7.20 (m, 3H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.3, 145.1, 135.2, 133.2, 132.7, 128.2, 128.0, 126.1, 126.0, 112.0, 72.4, 26.0 ppm; HRMS (ESI) calcd for $C_{17}H_{13}Cl_2O_2$ $[M+H]^+$ 319.0287, found 319.0292.



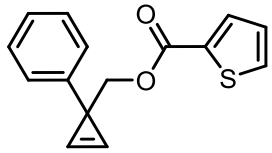
(1-phenylcycloprop-2-en-1-yl)methyl 2,3-dimethoxybenzoate (2o) colorless oil (70%, 434.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.33-7.28 (m, 6H), 7.22-7.17 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.74 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 152.9, 148.5, 145.7, 128.1, 126.3, 125.8, 123.6, 123.0, 112.1, 112.0, 110.2, 71.4, 55.99, 55.93, 26.2 ppm; HRMS (ESI) calcd for $C_{19}H_{19}O_4$ $[M+H]^+$ 311.1277, found 311.1288.



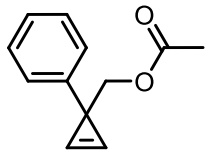
(1-phenylcycloprop-2-en-1-yl)methyl 1-naphthoate (2p) colorless oil (68%, 408.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 8.4 Hz, 1H), 8.21-8.19 (m, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.92-7.90 (m, 1H), 7.64-7.48 (m, 3H), 7.41-7.39 (m, 6H), 7.31-7.27 (m, 1H), 4.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.5, 145.5, 133.7, 133.1, 131.2, 130.1, 128.4, 128.1, 127.6, 127.3, 126.3, 126.1, 125.81, 125.76, 124.4, 112.1, 71.7, 26.2 ppm; HRMS (ESI) calcd for $C_{21}H_{16}O_2$ $[M]^+$ 300.1144, found 300.1151.



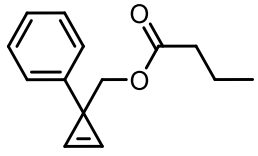
(1-phenylcycloprop-2-en-1-yl)methyl furan-2-carboxylate (2q) colorless oil (88%, 422.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.56 (m, 1H), 7.34-7.26 (m, 6H), 7.23-7.18 (m, 1H), 7.16-7.14 (m, 1H), 6.49-6.48 (m, 1H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.7, 146.2, 145.3, 144.6, 128.1, 126.1, 125.7, 117.8, 111.73, 111.66, 71.4, 25.9 ppm; HRMS (ESI) calcd for $C_{15}H_{12}NaO_3$ $[M+Na]^+$ 263.0678, found 263.0667.



(1-phenylcycloprop-2-en-1-yl)methyl thiophene-2-carboxylate (2r) colorless oil (83%, 425.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.54 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.34-7.27 (m, 6H), 7.23-7.18 (m, 1H), 7.10-7.08 (m, 1H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.2, 145.5, 134.0, 133.3, 132.3, 128.1, 127.7, 126.2, 125.8, 112.0, 71.8, 26.1 ppm; HRMS (ESI) calcd for $C_{15}H_{12}NaO_2S$ $[M+Na]^+$ 279.0450, found 279.0473.

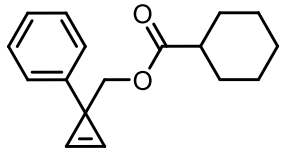


(1-phenylcycloprop-2-en-1-yl)methyl acetate (2s) colorless oil (75%, 282.3 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.33-7.28 (m, 2H), 7.24-7.18 (m, 5H), 4.53 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.2, 145.5, 128.1, 126.2, 125.8, 112.0, 71.1, 25.9, 21.0 ppm; HRMS (ESI) calcd for $C_{12}H_{13}O_2$ $[M+H]^+$ 189.0910, found 189.0921.

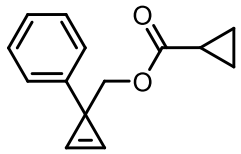


(1-phenylcycloprop-2-en-1-yl)methyl butyrate (2t) colorless oil (80%, 346.0 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.33-7.28 (m,

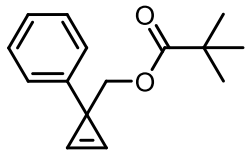
2H), 7.24-7.19 (m, 5H), 4.54 (s, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.68-1.59 (m, 3H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.7, 145.5, 128.1, 126.2, 125.7, 112.0, 70.8, 36.2, 25.9, 18.5, 13.6 ppm; HRMS (ESI) calcd for $C_{14}H_{20}NO_2$ $[M+NH_4]^+$ 234.1488, found 234.1484.



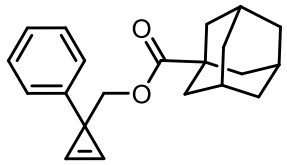
(1-phenylcycloprop-2-en-1-yl)methyl cyclohexanecarboxylate (2u) colorless oil (84%, 430.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.32-7.28 (m, 2H), 7.23-7.17 (m, 5H), 4.52 (s, 2H), 2.34-2.27 (m, 1H), 1.89-1.85 (m, 2H), 1.77-1.68 (m, 2H), 1.65-1.59 (m, 1H), 1.47-1.38 (m, 2H), 1.32-1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 176.4, 145.6, 128.0, 126.2, 125.7, 112.0, 70.5, 43.2, 29.0, 26.0, 25.7, 25.4 ppm; HRMS (ESI) calcd for $C_{17}H_{20}KO_2$ $[M+K]^+$ 295.1094, found 295.1093.



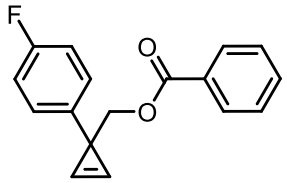
(1-phenylcycloprop-2-en-1-yl)methyl cyclopropanecarboxylate (2v) colorless oil (76%, 325.7 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.33-7.29 (m, 2H), 7.24-7.18 (m, 5H), 4.53 (s, 2H), 1.65-1.59 (m, 1H), 1.00-0.96 (m, 2H), 0.86-0.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.8, 145.5, 128.0, 126.1, 125.7, 111.8, 71.1, 25.9, 12.9, 8.34 ppm; HRMS (ESI) calcd for $C_{14}H_{14}NaO_2$ $[M+Na]^+$ 237.0886, found 237.0892.



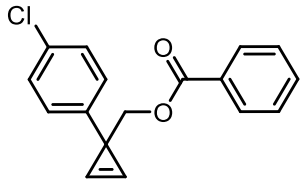
(1-phenylcycloprop-2-en-1-yl)methyl pivalate (2w) colorless oil (82%, 377.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.31-7.27 (m, 2H), 7.23-7.16 (m, 5H), 4.50 (s, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 178.5, 145.6, 128.0, 126.2, 125.7, 112.0, 70.5, 38.8, 27.2, 26.1ppm; HRMS (ESI) calcd for $C_{15}H_{18}LiO_2$ $[M+Li]^+$ 237.1461, found 237.1468.



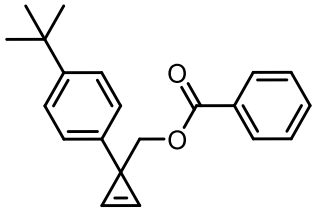
(1-phenylcycloprop-2-en-1-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (2x) colorless oil (85%, 524.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.28 (m, 2H), 7.23-7.17 (m, 5H), 4.51 (s, 2H), 2.01-1.99 (m, 3H), 1.87 (d, *J* = 2.8 Hz, 6H), 1.75-1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 177.6, 145.7, 128.0, 126.2, 125.7, 112.0, 70.2, 40.8, 38.8, 36.5, 27.9, 26.0 ppm; HRMS (ESI) calcd for $C_{21}H_{24}NaO_2$ $[M+Na]^+$ 331.1668, found 331.1668.



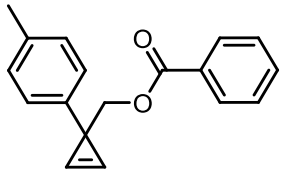
(1-(4-fluorophenyl)cycloprop-2-en-1-yl)methyl benzoate (2aa) colorless oil (74%, 397.0 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-8.02 (m, 2H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.31-7.21 (m, 2H), 7.02-6.97 (m, 2H) 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 162.2 (d, *J* = 242.0 Hz), 141.27 (d, *J* = 3.0 Hz), 132.9, 130.3, 129.6, 128.3, 127.4 (d, *J* = 7.0 Hz), 114.9 (d, *J* = 21.0 Hz), 112.4, 71.6, 25.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -117.4 (s) ppm; HRMS (ESI) calcd for $C_{17}H_{13}KFO_2$ $[M+K]^+$ 307.0531, found 307.0519.



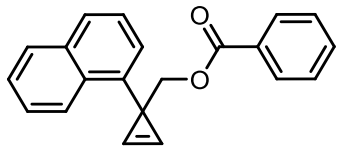
(1-(4-chlorophenyl)cycloprop-2-en-1-yl)methyl benzoate (2ab) colorless oil (78%, 444.1 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.2 Hz, 2H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.31-7.21 (m, 4H), 7.02-6.97 (m, 2H) 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 144.2, 132.9, 131.6, 130.2, 129.6, 128.3, 128.2, 127.6, 111.9, 71.4, 25.8 ppm; HRMS (ESI) calcd for $C_{17}H_{13}KClO_2$ $[M+K]^+$ 323.0235, found 323.0242.



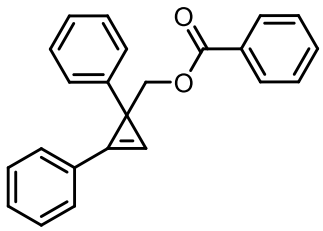
(1-(4-(tert-butyl)phenyl)cycloprop-2-en-1-yl)methyl benzoate (2ac) colorless oil (80%, 490.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 6.8 Hz, 2H), 7.57-7.53 (m, 1H), 7.45-7.41 (m, 2H), 7.37-7.34 (m, 2H), 7.27 (s, 2H), 7.24-7.22 (m, 2H), 4.78 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 148.6, 142.8, 132.8, 130.4, 129.6, 128.3, 125.8, 125.1, 111.8, 71.8, 34.3, 31.4, 25.7 ppm; HRMS (ESI) calcd for $C_{21}H_{22}NaO_2$ $[M+Na]^+$ 329.1512, found 329.1493.



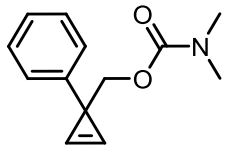
(1-(p-tolyl)cycloprop-2-en-1-yl)methyl benzoate (2ad) colorless oil (84%, 444.0 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.02 (m, 2H), 7.57-7.53 (m, 1H), 7.45-7.40 (m, 2H), 7.29 (s, 2H), 7.20-7.12 (m, 4H), 4.76 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 142.8, 135.5, 132.9, 130.5, 129.7, 129.0, 128.4, 126.3, 112.3, 71.9, 26.0, 21.0 ppm; HRMS (ESI) calcd for $C_{18}H_{16}O_2$ $[M]^+$ 264.1144, found 264.1146



(1-(naphthalen-1-yl)cycloprop-2-en-1-yl)methyl benzoate (2ae) pale yellow oil (72%, 432.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.4 Hz, 1H), 8.03-8.01 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 3H), 7.64-7.60 (m, 1H), 7.59-7.50 (m, 3H), 7.47-7.42 (m, 3H), 4.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 141.4, 134.0, 132.8, 131.4, 130.3, 129.5, 128.8, 128.3, 127.4, 126.03, 126.00, 125.8, 125.7, 124.5, 116.5, 71.3, 26.5 ppm; HRMS (ESI) calcd for $C_{21}H_{16}O_2$ $[M+K]^+$ 339.0781, found 339.0797.

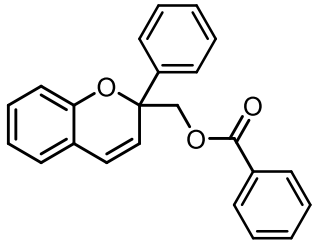


(1,2-diphenylcycloprop-2-en-1-yl)methyl benzoate (2af) coloress oil (78%, 509.2 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.57-7.53 (m, 1H),, 7.44-7.36 (m, 7H), 7.33-7.29 (m, 3H), 7.22-7.18 (m, 1H), 5.08 (dd, *J* = 11.6, 1.2 Hz, 1H), 4.86 (dd, *J* = 11.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 144.6, 132.8, 130.4, 129.74, 129.56, 129.48, 129.0, 128.3, 128.2, 126.7, 126.2, 125.7, 121.1, 104.6, 71.8, 29.0 ppm; HRMS (ESI) calcd for $C_{23}H_{18}O_2Na$ $[M+Na]^+$ 349.1199, found 349.1188.

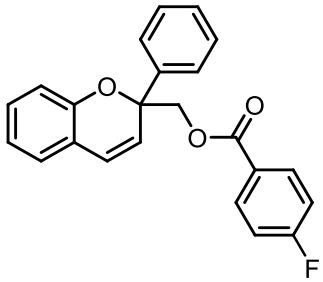


(1-phenylcycloprop-2-en-1-yl)methyl dimethylcarbamate (2ag) coloress oil (30%, 130.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.28 (m, 2H), 7.25-7.16 (m, 5H), 4.51 (s, 2H), 2.91 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.7, 145.9, 128.0, 126.2, 125.6, 111.9, 71.8, 36.4, 35.9, 26.2 ppm; HRMS (ESI) calcd for $C_{13}H_{15}NO_2K$ $[M+K]^+$ 256.0734, found 256.0738.

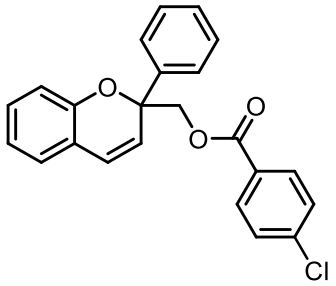
Characterization of Products 3, 4



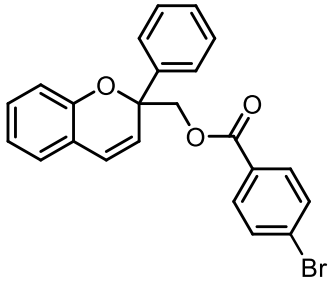
(2-phenyl-2*H*-chromen-2-yl)methyl benzoate (3a) colorless solid (66%, 45.2 mg); m.p.: 75.5-76.2 ºC; R_f = 0.4 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.84 (m, 2H), 7.62-7.59 (m, 2H), 7.55-7.50 (m, 1H), 7.41-7.28 (m, 5H), 7.19-7.14 (m, 1H), 7.00-6.97 (m, 2H), 6.89-6.85 (m, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 152.9, 141.5, 133.0, 129.69, 129.57, 129.6, 128.4, 128.2, 128.0, 126.7, 125.7, 125.4, 124.8, 121.2, 120.8, 116.3, 80.2, 70.2 ppm; HRMS (ESI) calcd for $C_{23}H_{22}NO_3$ $[M+NH_4]^+$ 360.1594, found 360.1591.



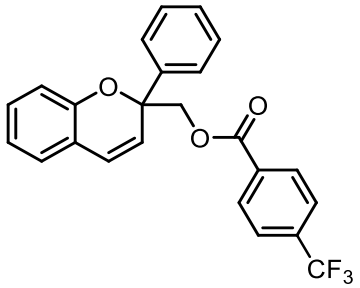
(2-phenyl-2*H*-chromen-2-yl)methyl 4-fluorobenzoate (3b) colorless oil (55%, 39.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 2H), 7.59-7.56 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.15 (td, *J* = 8.0, 2.0 Hz, 1H), 7.03-6.95 (m, 4H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.1 (d, *J* = 253.0 Hz), 165.3, 152.9, 141.4, 132.2 (d, *J* = 9.5 Hz), 129.6, 128.5, 128.0, 126.7, 126.0 (d, *J* = 2.8 Hz), 125.6, 125.4, 124.7, 121.2, 120.8, 116.2, 115.4, (d, *J* = 21.7 Hz), 80.2, 70.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.0 (s) ppm; HRMS (ESI) calcd for $C_{23}H_{17}NaFO_3$ $[M+Na]^+$ 383.1053, found 383.1046.



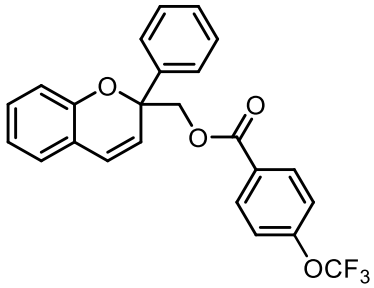
(2-phenyl-2*H*-chromen-2-yl)methyl 4-chlorobenzoate (3c) colorless oil (63%, 47.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75-7.71 (m, 2H), 7.59-7.56 (m, 2H), 7.40-7.36 (m, 2H), 7.33-7.30 (m, 3H), 7.16 (td, *J* = 8.0, 2.0 Hz, 1H), 6.99-6.95 (m, 2H), 6.86 (td, *J* = 7.2, 1.2 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.5, 153.1, 141.5, 140.0, 131.2, 130.0, 128.7, 128.6, 128.3, 128.1, 126.9, 125.7, 125.6, 124.8, 121.4, 120.9, 116.3, 80.3, 70.4 ppm; HRMS (ESI) calcd for $C_{23}H_{17}NaClO_3$ $[M+Na]^+$ 399.0758, found 399.0741.



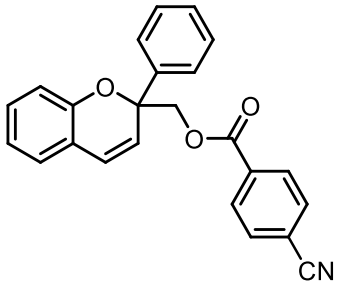
(2-phenyl-2*H*-chromen-2-yl)methyl 4-bromobenzoate (3d) pale yellow oil (57%, 48.0 mg); R_f = 0.6 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.50-7.47 (m, 2H), 7.40-7.37 (m, 2H), 7.32-7.28 (m, 1H), 7.16 (td, *J* = 8.0, 2.0 Hz, 1H), 6.99-6.96 (m, 1H), 6.87 (td, *J* = 7.2, 0.8 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.5, 152.9, 141.3, 131.6, 131.2, 130.0, 128.6, 128.5, 128.1, 128.0, 126.7, 125.6, 125.5, 124.7, 121.2, 120.7, 116.2, 80.2, 70.3 ppm; HRMS (ESI) calcd for $C_{23}H_{18}BrO_3$ $[M+H]^+$ 421.0433, found 421.0429.



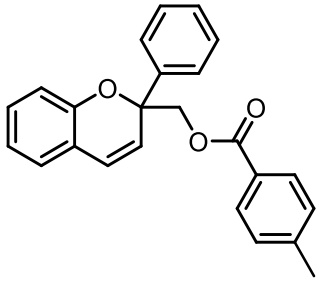
(2-phenyl-2*H*-chromen-2-yl)methyl 4-(trifluoromethyl)benzoate (3e) colorless oil (40%, 32.8 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 2H), 7.62-7.57 (m, 4H), 7.41-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.96 (m, 2H), 6.87 (td, *J* = 7.2, 2.0 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.1, 152.9, 141.2, 134.4 (q, *J* = 32.0 Hz), 133.0, 130.1, 129.7, 128.5, 128.1, 126.8, 125.6, 125.3 (q, *J* = 2.8 Hz), 124.6, 123.6 (q, *J* = 271.0 Hz), 122.2, 121.3, 120.7, 116.2, 80.2, 70.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.0 (s) ppm; HRMS (ESI) calcd for $C_{24}H_{17}NaF_3O_3$ $[M+Na]^+$ 433.1022, found 433.1018.



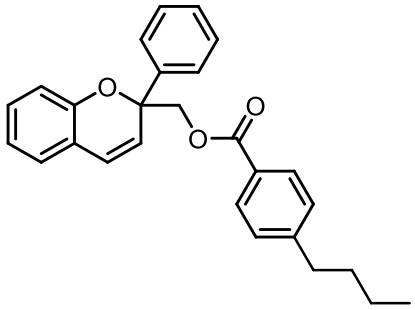
(2-phenyl-2*H*-chromen-2-yl)methyl 4-(trifluoromethoxy)benzoate (3f) colorless oil (42%, 35.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.83 (m, 2H), 7.59-7.57 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.28 (m, 1H), 7.18-7.14 (m, 3H), 6.99-6.95 (m, 2H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.1, 152.9, 152.6, 141.3, 131.7, 129.7, 128.5, 128.14, 128.06, 126.7, 125.6, 125.5, 124.7, 121.3, 120.7, 120.2 (q, *J* = 257.0 Hz), 120.1, 116.2, 80.2, 70.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -57.5 (s) ppm; HRMS (ESI) calcd for $C_{24}H_{21}NF_3O_4$ $[M+NH_4]^+$ 444.1417, found 444.1426.



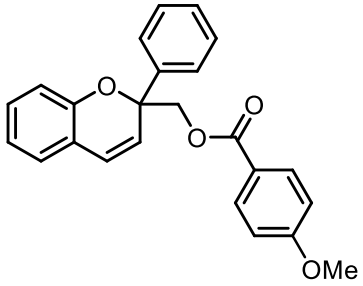
(2-phenyl-2*H*-chromen-2-yl)methyl 4-cyanobenzoate (3g) yellow oil (35%, 25.7 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.86 (m, 2H), 7.65-7.62 (m, 2H), 7.59-7.56 (m, 2H), 7.41-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.95 (m, 2H), 6.87 (td, *J* = 7.2, 0.8 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.6, 152.9, 141.1, 133.5, 132.1, 130.2, 129.7, 128.5, 128.1, 126.8, 125.6, 125.5, 124.5, 121.3, 120.6, 117.9, 116.3, 116.2, 80.1, 70.7 ppm; HRMS (ESI) calcd for $C_{24}H_{18}NO_3$ $[M+H]^+$ 368.1281, found 368.1256.



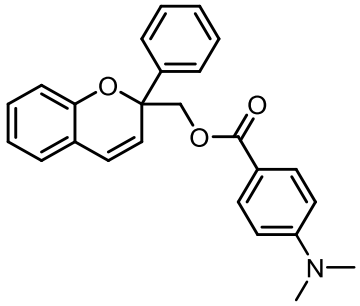
(2-phenyl-2*H*-chromen-2-yl)methyl 4-methylbenzoate (3h) colorless oil (44%, 31.4 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.39-7.36 (m, 2H), 7.31-7.27 (m, 1H), 7.18-7.14 (m, 3H), 6.98-6.96 (m, 2H), 6.88-6.84 (m, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 152.9, 143.7, 141.6, 129.7, 129.6, 129.0, 128.4, 128.0, 127.0, 126.7, 125.7, 125.3, 124.9, 121.2, 120.9, 116.3, 80.2, 69.9, 21,6 ppm; HRMS (ESI) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1485, found 357.1479.



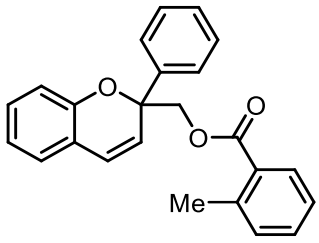
(2-phenyl-2*H*-chromen-2-yl)methyl 4-methylbenzoate (3i) colorless oil (43%, 34.3 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.52 (m, 2H), 7.61-7.58 (m, 2H), 7.41-7.36 (m, 2H), 7.32-7.28 (m, 1H), 7.19-7.14 (m, 3H), 7.00-6.97 (m, 2H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.39-1.30 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 152.9, 148.6, 141.6, 129.8, 129.5, 128.4, 128.3, 127.9, 127.2, 126.7, 125.7, 125.3, 124.9, 121.2, 120.9, 116.2, 80.2, 69.9, 35.7, 33.2, 11.3, 13.9 ppm; HRMS (ESI) calcd for $C_{27}H_{26}NaO_3$ $[M+Na]^+$ 421.1774, found 421.1784.



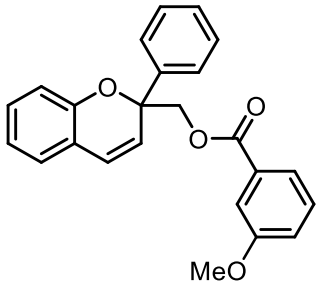
(2-phenyl-2*H*-chromen-2-yl)methyl 4-methoxybenzoate (3j) colorless oil (47%, 35.0 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81-7.79 (m, 2H), 7.60-7.58 (m, 2H), 7.39-7.35 (m, 2H), 7.30-7.28 (m, 1H), 7.17-7.13 (m, 1H), 6.98-6.95 (m, 2H), 6.87-6.80 (m, 3H), 6.58 (d, *J* = 10.0 Hz, 1H), 6.04 (d, *J* = 10.0 Hz, 1H), 4.76 (dd, *J* = 11.6, 1.2 Hz, 1H), 4.53 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 163.3, 152.9, 141.6, 131.7, 129.5, 128.4, 127.9, 126.7, 125.6, 125.3, 124.9, 122.1, 121.1, 120.8, 116.2, 113.5, 80.3, 70.0, 55.3 ppm; HRMS (ESI) calcd for $C_{24}H_{20}NaO_4$ $[M+Na]^+$ 395.1253, found 395.1270.



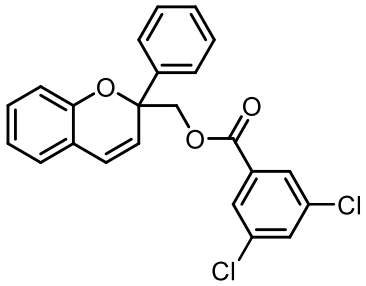
(2-phenyl-2*H*-chromen-2-yl)methyl 4-(dimethylamino)benzoate (3k) yellow oil (46%, 35.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76-7.72 (m, 2H), 7.61-7.58 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.16 (td, *J* = 8.0, 2.0 Hz, 1H), 6.99-6.97 (m, 2H), 6.86 (td, *J* = 7.2, 1.2 Hz, 1H), 6.60-6.55 (m, 3H), 6.08 (d, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 153.3, 153.0, 141.8, 131.4, 129.4, 128.3, 127.8, 126.6, 125.7, 125.2, 125.1, 121.1, 121.0, 116.4, 116.2, 110.6, 80.4, 69.4, 40.0 ppm; HRMS (ESI) calcd for $C_{25}H_{24}NO_3$ $[M+H]^+$ 386.1750, found 386.1761.



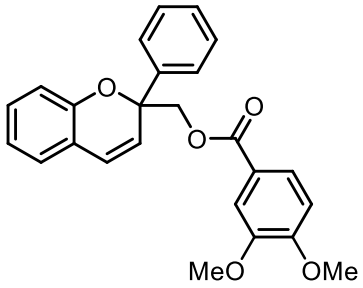
(2-phenyl-2*H*-chromen-2-yl)methyl 2-methylbenzoate (3l) colorless oil (48%, 34.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.60-7.58 (m, 2H), 7.40-7.34 (m, 3H), 7.32-7.27 (m, 1H), 7.21-7.13 (m, 3H), 7.00-6.97 (m, 2H), 6.86 (td, *J* = 7.2, 1.2 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 152.7, 141.6, 140.4, 132.0, 131.5, 130.8, 129.6, 129.1, 127.9, 126.7, 125.7, 125.6, 125.3, 125.0, 121.2, 120.8, 116.3, 80.3, 69.7, 21.8 ppm; HRMS (ESI) calcd for $C_{24}H_{21}O_3$ $[M+H]^+$ 357.1485 found 357.1467.



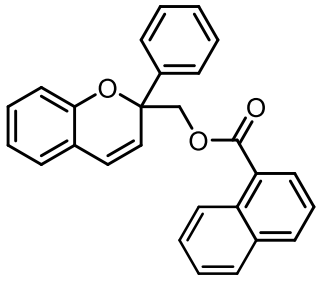
(2-phenyl-2*H*-chromen-2-yl)methyl 3-methoxybenzoate (3m) colorless oil (44%, 32.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.58 (m, 2H), 7.45-7.35 (m, 4H), 7.32-7.27 (m, 2H), 7.15 (td, *J* =7.6, 1.6 Hz, 1H), 7.07-7.04 (m, 1H), 6.98-6.95 (m, 2H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.1, 159.4, 152.8, 141.5, 131.0, 129.6, 129.3, 128.4, 128.0, 126.7, 124.6, 125.3, 124.7, 122.2, 121.2, 120.7, 119.8, 116.2, 113.8, 80.2, 70.1, 55.3 ppm; HRMS (ESI) calcd for $C_{24}H_{20}NaO_4$ $[M+Na]^+$ 395.1253, found 395.1260.



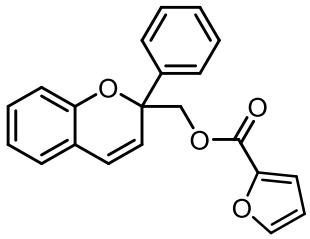
(2-phenyl-2*H*-chromen-2-yl)methyl 3,5-dichlorobenzoate (3n) colorless oil (48%, 39.5 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 2.0 Hz, 2H), 7.60-7.56 (m, 2H), 7.49-7.48 (m, 1H), 7.42-7.37 (m, 2H), 7.34-7.30 (m, 1H), 7.17 (td, *J* = 8.0, 2.0 Hz, 1H), 7.00-6.96 (m, 2H), 6.87 (td, *J* = 7.6, 1.2 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 152.9, 141.1, 135.1, 132.9, 132.5, 129.8, 128.5, 128.12, 128.05, 126.7, 125.7, 125.5, 124.4, 121.5, 120.6, 116.1, 80.1, 70.9 ppm; HRMS (ESI) calcd for $C_{23}H_{20}NCl_2O_3$ $[M+NH_4]^+$ 428.0814, found 428.0825.



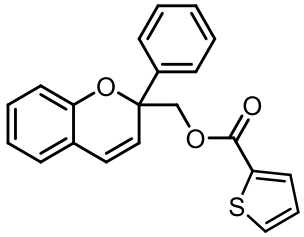
(2-phenyl-2*H*-chromen-2-yl)methyl 3,4-dimethoxybenzoate (3o) colorless oil (48%, 38.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 2H), 7.48 (td, *J* = 8.4 , 1.6 Hz, 1H), 7.41-7.35 (m, 3H), 7.31-7.27 (m, 1H), 7.15 (td, *J* = 7.6, 2.0 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.84 (td, *J* = 7.6, 1.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 153.0, 152.9, 148.4, 141.6, 129.6, 128.4, 127.9, 126.7, 125.6, 125.2, 124.8, 123.8, 122.2, 121.1, 120.6, 116.1, 111.9, 110.1, 80.4, 70.0, 55.9, 55.8 ppm; HRMS (ESI) calcd for $C_{25}H_{22}NaO_5$ $[M+Na]^+$ 425.1359, found 425.1348.



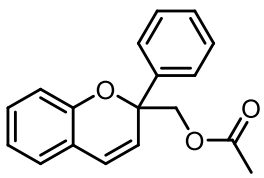
(2-phenyl-2*H*-chromen-2-yl)methyl 1-naphthoate (3p) colorless oil (47%, 36.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86-8.83 (m, 1H), 7.99-7.92 (m, 2H), 7.87-7.83 (m, 1H), 7.64-7.62 (m, 2H), 7.52-7.46 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 1H), 7.18 (td, *J* = 7.6, 1.6 Hz, 1H), 7.02-6.98 (m, 2H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.62 (d, *J* = 10.0 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 152.8, 141.6, 133.7, 133.5, 131.3, 130.6, 130.0, 128.5, 128.4, 128.0, 127.7, 126.8, 126.6, 126.1, 125.8, 125.7, 125.4, 124.9, 124.5, 121.3, 120.8, 116.3, 80.4, 70.0 ppm; HRMS (ESI) calcd for $C_{27}H_{20}LiO_3$ $[M+Li]^+$ 399.1567, found 399.1577.



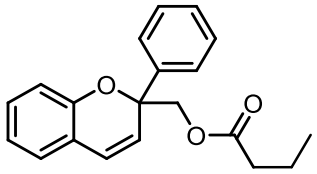
(2-phenyl-2*H*-chromen-2-yl)methyl furan-2-carboxylate (3q) colorless oil (51%, 33.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.54 (m, 3H), 7.40-7.33 (m, 2H), 7.31-7.27 (m, 1H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97(dd, *J* = 7.2, 1.2 Hz, 2H), 6.90-6.89 (m, 1H), 6.84 (td, *J* = 7.2, 0.8 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.42 (dd, *J* = 3.6, 2.0 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.3, 152.8, 146.6, 144.1, 141.3, 129.6, 128.4, 128.0, 126.7, 125.7, 125.5, 124.6, 121.2, 120.8, 118.3, 116.3, 111.7, 80.2, 69.7 ppm; HRMS (ESI) calcd for $C_{21}H_{16}NaO_4$ $[M+Na]^+$ 355.0940, found 355.0938.



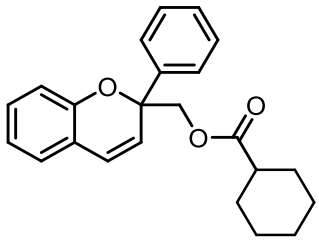
(2-phenyl-2*H*-chromen-2-yl)methyl thiophene-2-carboxylate (3r) colorless oil (53%, 36.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.57 (m, 3H), 7.52-7.50 (m, 1H), 7.39-7.36 (m, 2H), 7.31-7.27 (m, 1H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 7.04-7.02 (m, 1H), 6.98-6.96 (m, 2H), 6.85 (td, *J* = 7.2, 0.8 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 152.8, 141.4, 133.7, 133.3, 132.7, 129.6, 128.4, 128.0, 127.7, 126.7, 125.7, 125.4, 124.6, 121.2, 120.8, 116.2, 80.1, 70.0 ppm; HRMS (ESI) calcd for $C_{21}H_{16}NaO_3S$ $[M+Na]^+$ 371.0712, found 371.0724.



(2-phenyl-2*H*-chromen-2-yl)methyl acetate (3s) colorless oil (42%, 23.5 mg); R_f = 0.6 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.50 (m, 2H), 7.36-7.32 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.94 (m, 2H), 6.85 (td, *J* = 7.2, 1.2 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 152.6, 141.4, 129.6, 128.3, 127.9, 126.7, 125.7, 125.4, 124.9, 121.3, 120.9, 116.4, 80.2, 69.2, 20.8 ppm; HRMS (ESI) calcd for $C_{18}H_{16}LiO_3$ $[M+Li]^+$ 287.1254, found 287.1269.

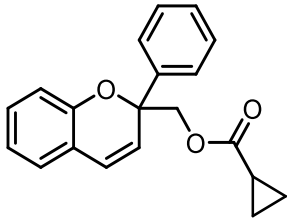


(2-phenyl-2*H*-chromen-2-yl)methyl butyrate (3t) colorless oil (45%, 27.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.50 (m, 2H), 7.37-7.32 (m, 2H), 7.29-7.25 (m, 1H), 7.15 (td, *J* = 8.0, 2.0 Hz, 1H), 6.99-6.95 (m, 2H), 6.87-6.83 (m, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.00 (d, *J* = 9.6 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 2.24 (t, *J* = 7.2 Hz, 2H), 1.61-1.51 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.8, 152.6, 141.5, 129.5, 128.3, 127.9, 126.6, 125.6, 125.2, 124.9, 121.2, 120.8, 116.3, 80.2, 68.9, 36.0, 18.3, 13.5 ppm; HRMS (ESI) calcd for $C_{20}H_{20}NaO_3$ $[M+Na]^+$ 331.1304, found 331.1311.

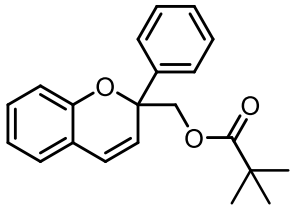


(2-phenyl-2*H*-chromen-2-yl)methyl cyclohexanecarboxylate (3u) colorless oil (54%, 37.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.50 (m, 2H), 7.37-7.32 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.94 (m, 2H), 6.84 (td, *J* = 7.6, 1.2 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 2.29-2.21 (m, 1H), 1.82-1.57 (m, 5H), 1.38-1.14 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 175.7, 152.7,

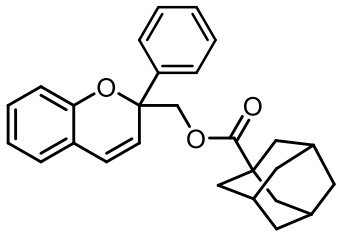
141.6, 129.5, 128.3, 127.8, 126.6, 125.6, 125.2, 124.9, 121.2, 120.8, 116.3, 80.3, 68.8, 43.0, 28.8 (d, J = 15.0Hz), 25.6, 25.2 (d, J = 15.0 Hz) ppm; HRMS (ESI) calcd for $C_{23}H_{24}KO_3$ $[M+K]^+$ 387.1357, found 387.1365.



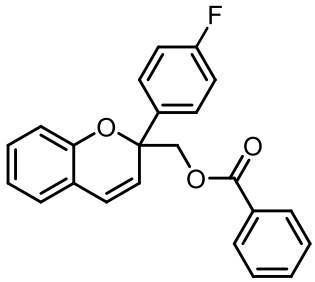
(2-phenyl-2*H*-chromen-2-yl)methyl cyclopropanecarboxylate (3v) colorless oil (54%, 33.1 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.50 (m, 2H), 7.37-7.32 (m, 2H), 7.29-7.25 (m, 1H), 7.15 (td, J = 8.0, 2.0 Hz, 1H), 6.99-6.95 (m, 2H), 6.85 (td, J = 7.2, 1.2 Hz, 1H), 6.59 (d, J = 10.0 Hz, 1H), 6.00 (d, J = 10.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 1.60-1.53 (m, 1H), 0.93-0.89 (m, 2H), 0.82-0.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.6, 152.7, 141.5, 129.5, 128.3, 127.9, 126.7, 125.7, 125.2, 124.9, 121.2, 120.9, 116.3, 80.2, 69.2, 12.9, 8.6 ppm; HRMS (ESI) calcd for $C_{20}H_{18}NaO_3$ $[M+Na]^+$ 329.1148, found 329.1157.



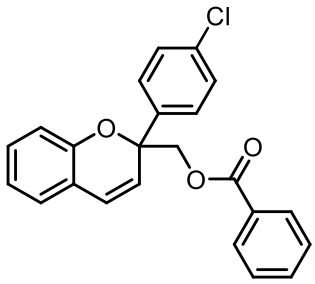
(2-phenyl-2*H*-chromen-2-yl)methyl pivalate (3w) colorless oil (40%, 25.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.37-7.33 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (td, J = 7.6, 1.6 Hz, 1H), 6.98-6.93 (m, 2H), 6.84 (td, J = 7.6, 1.2 Hz, 1H), 6.57 (d, J = 9.6 Hz, 1H), 5.97 (d, J = 9.6 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 4.38 (d, J = 11.6 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 178.1, 152.8, 141.6, 129.5, 128.3, 127.8, 126.6, 125.6, 125.0, 124.8, 121.1, 120.7, 116.1, 80.3, 69.1, 38.8, 27.0 ppm; HRMS (ESI) calcd for $C_{21}H_{22}NaO_3$ $[M+Na]^+$ 345.1461, found 345.1479.



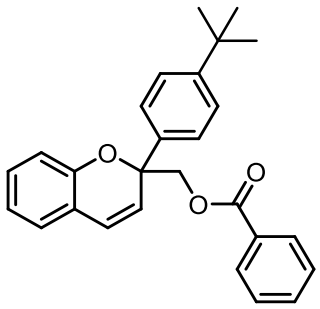
(2-phenyl-2*H*-chromen-2-yl)methyl pivalate (3x) colorless oil (47%, 37.6 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.50 (m, 2H), 7.37-7.33 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (td, *J* = 8.0, 2.0 Hz, 1H), 6.99-6.92 (m, 2H), 6.84 (td, *J* = 7.6, 1.6 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 1.94-1.91 (m, 3H), 1.73-1.72 (m, 5H), 1.69-1.59 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): 177.3, 152.9, 141.6, 129.5, 128.3, 127.8, 126.6, 125.6, 125.0, 124.9, 121.1, 120.8, 116.1, 80.3, 69.0, 40.7, 38.5, 36.7, 27.8 ppm; HRMS (ESI) calcd for $C_{27}H_{29}O_3$ $[M+H]^+$ 401.2111, found 401.2114.



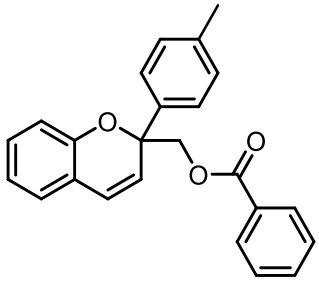
(2-(4-fluorophenyl)-2*H*-chromen-2-yl)methyl benzoate (3aa) colorless oil (51%, 36.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.85 (m, 2H), 7.59-7.50 (m, 3H), 7.39-7.35 (m, 2H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 7.08-7.00 (m, 2H), 6.99-6.95 (m, 2H), 6.87 (td, *J* = 7.2, 1.2 Hz, 1H), 6.62 (d, *J* = 7.2, 1.2 Hz, 1H), 6.04 (d, *J* = 10.0 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 162.3 (d, *J* = 245.0 Hz), 152.6, 137.2 (d, *J* = 3.0 Hz), 133.1, 129.7, 128.3, 127.64, 127.56, 126.8, 125.6, 124.5, 121.4, 120.8, 116.3, 115.4, 115.2, 79.8, 69.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.0 (s) ppm; HRMS (ESI) calcd for $C_{23}H_{18}FO_3$ $[M+H]^+$ 361.1234, found 361.1220.



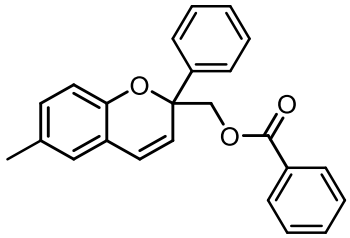
(2-(4-chlorophenyl)-2*H*-chromen-2-yl)methyl benzoate (3ab) colorless oil (48%, 36.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.84 (m, 2H), 7.54-7.51 (m, 3H), 7.39-7.33 (m, 4H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 7.00-6.95 (m, 2H), 6.87 (td, *J* = 7.2, 1.2 Hz, 1H), 6.62 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 152.6, 140.0, 133.9, 133.1, 129.8, 129.7, 129.6, 128.58, 128.3, 127.2, 126.8, 125.8, 124.3, 121.5, 120.8, 116.3, 79.7, 69.6 ppm; HRMS (ESI) calcd for $C_{23}H_{17}LiClO_3$ $[M+Li]^+$ 383.1020, found 383.1010.



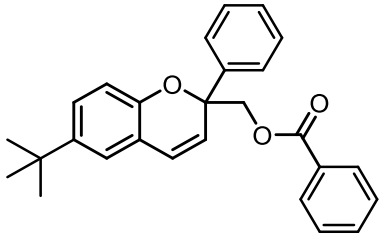
(2-(4-(tert-butyl)phenyl)-2*H*-chromen-2-yl)methyl benzoate (3ac) colorless oil (44%, 35.1 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.85 (m, 2H), 7.53-7.50 (m, 3H), 7.42-7.34 (m, 4H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H), 7.00-6.97 (m, 2H), 6.88-6.84 (m, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 153.1, 150.9, 138.5, 132.9, 129.8, 129.7, 129.5, 128.2, 126.7, 125.4, 125.3, 125.1, 125.0, 121.6, 120.8, 116.2, 80.2, 70.3, 34.5, 31.3 ppm; HRMS (ESI) calcd for $C_{27}H_{26}NaO_3$ $[M+Na]^+$ 421.1774, found 421.1772.



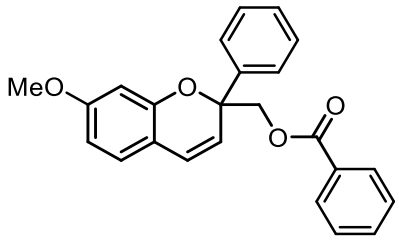
(2-(p-tolyl)-2*H*-chromen-2-yl)methyl benzoate (3ad) colorless oil (42%, 29.9 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.82 (m, 2H), 7.52-7.44 (m, 3H), 7.36-7.32 (m, 2H), 7.18-7.11 (m, 3H), 7.00-6.93 (m, 2H), 6.83 (td, *J* = 7.6, 1.2 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 153.0, 138.5, 137.8, 133.0, 129.8, 129.7, 129.5, 129.1, 128.2, 126.7, 125.6, 125.2, 125.0, 121.1, 120.9, 116.2, 80.1, 70.1, 21.1 ppm; HRMS (ESI) calcd for $C_{24}H_{20}NaO$ $[M+Na]^+$ 395.1253, found 395.1243. HRMS (ESI) calcd for $C_{24}H_{20}NaO_3$ $[M+H]^+$ 395.1044, found 395.1048.



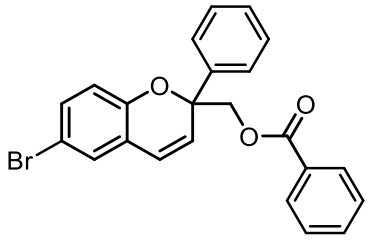
(6-methyl-2-phenyl-2*H*-chromen-2-yl)methyl benzoate (4a) colorless oil (62%, 44.2 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.85 (m, 2H), 7.60-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.39-7.34 (m, 4H), 7.31-7.28 (m, 1H), 6.98-6.95 (m, 1H), 6.89-6.87 (m, 1H), 6.80-6.79 (m, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 150.7, 141.6, 133.0, 130.4, 129.99, 129.77, 129.72, 128.4, 128.2, 127.9, 127.1, 125.7, 125.5, 125.0, 120.7, 116.0, 80.0, 70.0, 20.5 ppm; HRMS (ESI) calcd for $C_{24}H_{20}NaO_3$ $[M+Na]^+$ 379.1304, found 379.1312.



(6-(tert-butyl)-2-phenyl-2*H*-chromen-2-yl)methyl benzoate (4b) colorless oil (60%, 47.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.84 (m, 2H), 7.61-7.58 (m, 2H), 7.53-7.49 (m, 1H), 7.40-7.27 (m, 5H), 7.18 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.04 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 150.6, 144.0, 141.8, 132.9, 129.8, 129.7, 128.4, 128.2, 127.9, 126.5, 125.8, 125.7, 124.6, 123.7, 120.1, 115.6, 80.1, 70.2, 34.0, 31.5 ppm; HRMS (ESI) calcd for $C_{27}H_{26}LiO_3$ $[M+Li]^+$ 405.2036, found 405.2051.



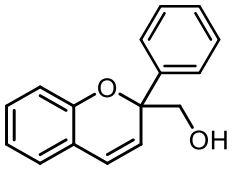
(7-methoxy-2-phenyl-2*H*-chromen-2-yl)methyl benzoate (4c) colorless oil (48%, 35.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.86 (m, 2H), 7.60-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.40-7.35 (m, 4H), 7.32-7.27 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.57-6.54 (m, 2H), 6.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.92 (d, *J* = 9.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 161.0, 154.1, 141.6, 133.0, 129.8, 129.7, 128.4, 128.2, 128.0, 127.4, 125.7, 125.0, 121.9, 114.2, 107.1, 102.1, 80.4, 70.0, 55.3 ppm; HRMS (ESI) calcd for $C_{24}H_{20}KO_4$ $[M+K]^+$ 411.0993, found 411.0973.



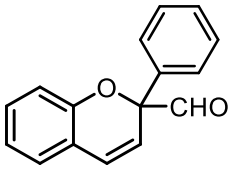
(6-bromo-2-phenyl-2*H*-chromen-2-yl)methyl benzoate (4d) colorless oil (52%, 43.8 mg); R_f = 0.5 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.81 (m, 2H), 7.56-7.51 (m, 3H), 7.41-7.36 (m, 4H), 7.34-7.29 (m, 1H), 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.10 (d, *J* = 10.0 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 152.1, 140.9, 133.1, 132.1, 129.7, 129.6, 129.2,

128.5, 128.3, 128.2, 126.2, 125.6, 124.4, 122.7, 118.0, 113.2, 80.6, 70.0 ppm; HRMS (ESI) calcd for $C_{23}H_{17}KBrO_3$ $[M+K]^+$ 458.9992, found 458.9973.

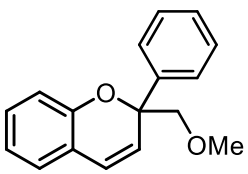
Characterization of 5a, 6a, 7a and 8a-g



(2-phenyl-2*H*-chromen-2-yl)methanol (5a) colorless oil (88%, 41.9 mg); R_f = 0.45 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.45 (m, 2H), 7.35-7.30 (m, 2H), 7.27-7.23 (m, 1H), 7.14 (td, *J* = 7.6, 1.6 Hz, 1H), 6.99-6.96 (m, 2H), 6.85 (td, *J* =7.6, 1.2 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.95 (d, *J* = 12.0 Hz, 1H), 3.84 (d, *J* = 12.0 Hz, 1H), 2.11 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.5, 141.8, 129.4, 128.3, 127.8, 126.8, 125.9, 125.6, 125.5, 121.5, 121.3, 116.4, 82.1, 70.0 ppm; HRMS (ESI) calcd for $C_{16}H_{14}O_2$ $[M]^+$ 238.0988, found 238.0979.

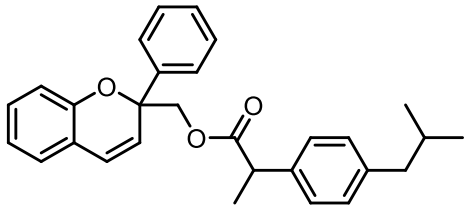


2-(2-phenyl-2*H*-chromen-2-yl)acetaldehyde (6a) colorless oil (92%, 43.5 mg); R_f = 0.35 (EtOAc/petroleum ether = 1:30); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 7.54-7.52 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.30 (m, 1H), 7.24-7.19 (m, 1H), 7.09 (d, *J* =8.0 Hz, 1H), 7.03 (td, *J* = 8.4, 1.6 Hz, 1H), 6.94-6.90 (m, 1H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.23 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 196.6, 152.0, 138.0, 130.0, 128.8, 128.6, 127.1, 126.1, 125.9, 122.1, 122.0, 121.0, 116.4, 84.7 ppm; HRMS (ESI) calcd for $C_{16}H_{13}O_2$ $[M+H]^+$ 237.0910, found 237.0916.

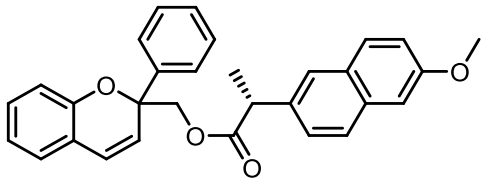


2-(methoxymethyl)-2-phenyl-2*H*-chromene (7a) yellow oil (88%, 44.4 mg); R_f =

0.45 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 1H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H), 6.98-6.96 (m, 2H), 6.83 (td, *J* = 7.6, 1.2 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 3.44 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 152.6, 142.4, 129.3, 128.1, 127.6, 126.6, 126.0, 125.8, 124.7, 121.3, 121.2, 116.5, 81.0, 79.1, 60.0 ppm; HRMS (ESI) calcd for $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1223, found 253.1233.

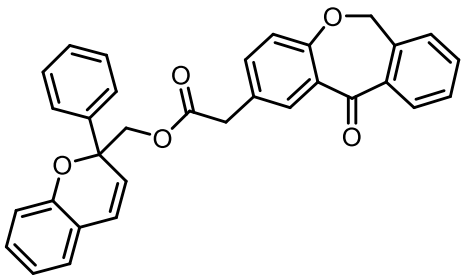


(2-phenyl-2*H*-chromen-2-yl)methyl 2-(4-isobutylphenyl)propanoate (9a) colorless oil (80%, 68.3 mg); R_f = 0.3 (EtOAc/petroleum ether = 1:20, d.r. = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.44 (m, 2H), 7.34-7.25 (m, 3H), 7.17-7.10 (m, 3H), 7.05-6.84 (m, 5H), 6.50 (d, *J* = 10.0 Hz, 0.8H), 6.45 (d, *J* = 10.0 Hz, 0.19H), 5.91-5.85 (m, 1H), 4.55-4.37 (m, 2H), 3.69-3.63 (m, 1H), 2.47-2.44 (m, 2H), 1.90-1.82 (m, 1H), 1.45-1.41 (m, 3H), 0.94-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3 (overlap, two isomers), 152.6 (overlap, two isomers), 140.5 (overlap, two isomers), 140.3 (overlap, two isomers), 137.2 (overlap, two isomers), 129.50, 129.45, 129.1 (overlap, two isomers), 128.2 (overlap, two isomers), 127.8 (overlap, two isomers), 127.28, 127.22, 126.6 (overlap, two isomers), 125.60, 125.57, 125.06, 125.01, 124.70, 124.57, 121.17 (overlap, two isomers), 120.72 (overlap, two isomers), 116.2 (overlap, two isomers), 80.1 (overlap, two isomers), 69.1 (overlap, two isomers), 45.03, 44.98, 30.1 (overlap, two isomers), 22.4 (overlap, two isomers), 18.1 (overlap, two isomers) ppm; HRMS (ESI) calcd for $C_{29}H_{30}KO_3$ $[M+K]^+$ 465.1826, found 465.1820.

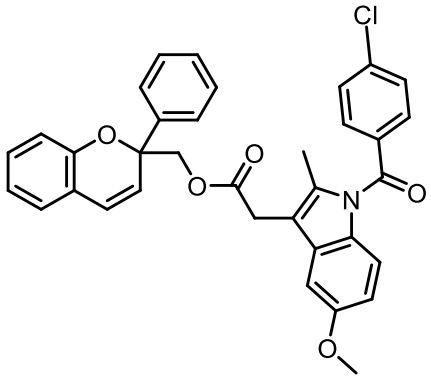


(2-phenyl-2*H*-chromen-2-yl)methyl (2R)-2-(6-methoxynaphthalen-2-

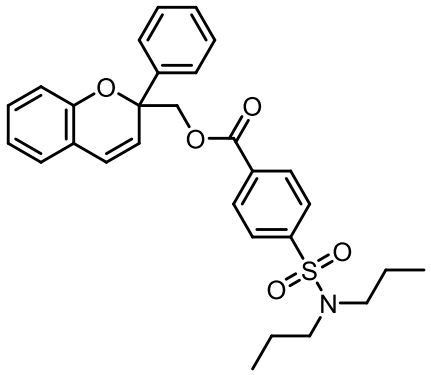
yl)propanoate (9b) colorless oil (82%, 73.9 mg, d.r. = 1:1); R_f = 0.5 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.57 (m, 3H), 7.43-7.39 (m, 2H), 7.33-7.21 (m, 4H), 7.16-7.08 (m, 3H), 6.92-6.79 (m, 3H), 6.43 (d, *J* = 10.0 Hz, 0.5 H), 6.31 (d, *J* = 10.0 Hz, 0.5 H), 5.83 (dd, *J* = 26.8, 9.6 Hz, 1H), 4.56-4.35 (m, 2H), 3.93 (d, *J* = 2.8 Hz, 3H), 3.81 (q, *J* = 7.2 Hz, 1H), 1.53-1.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.3 (overlap, two isomers), 157.67, 157.63, 152.69, 152.64, 141.6 (overlap, two isomers), 135.38, 135.30, 133.78, 133.74, 129.64, 129.58, 129.43, 129.41, 128.98, 128.94, 128.39, 128.37, 127.93, 127.92, 127.1 (overlap, two isomers), 126.77, 126.75, 126.5 (overlap, two isomers), 126.4 (overlap, two isomers), 126.25, 126.20, 125.70, 125.67, 125.18, 125.17, 124.8 (overlap, two isomers), 124.6 (overlap, two isomers), 121.31, 121.26, 128.82, 128.75, 118.93, 118.90, 116.34, 116.25, 105.6 (overlap, two isomers), 80.39, 80.36, 69.45, 69.37, 55.41, 55.40, 45.54, 45.44, 18.24, 18.07 ppm; HRMS (ESI) calcd for $C_{30}H_{30}NO_4$ $[M+NH_4]^+$ 468.2169, found 468.2163.



(2-phenyl-2*H*-chromen-2-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (9c) colorless oil (92%, 89.9 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 2.4 Hz, 1H), 7.90 (dd, *J* =7.6, 1.2 Hz, 1H), 7.56 (td, *J* =7.6, 1.6 Hz, 1H), 7.50-7.46 (m, 3H), 7.37-7.22 (m, 5H), 7.13 (td, *J* = 8.0, 1.6 Hz, 1H), 6.95-6.90 (m, 3H), 6.82 (td, *J* = 7.2, 1.2 Hz, 1H), 6.54 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 5.16 (s, 2H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.573-3.568 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 190.7, 171.0, 160.3, 152.5, 141.3, 140.4, 136.4, 135.5, 132.7, 132.4, 129.5, 129.4, 129.2, 128.3, 127.9, 127.7, 127.5, 126.7, 125.5, 125.3, 125.0, 124.6, 121.2, 120.9, 120.6, 116.2, 80.2, 73.5, 69.5, 40.0 ppm; HRMS (ESI) calcd for $C_{32}H_{24}KO_5$ $[M+K]^+$ 527.1255, found 527.1255.

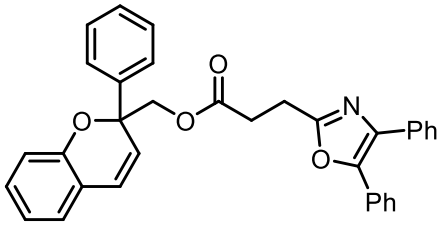


(2-phenyl-2*H*-chromen-2-yl)methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (9d) colorless oil (88%, 101.7 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:25); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.59 (m, 2H), 7.47-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.29-7.20 (m, 3H), 7.11 (td, *J* =7.6, 1.6 Hz, 1H), 6.93-6.91 (m, 3H), 6.85-6.81 (m, 2H), 6.68 (dd, *J* =9.2, 2.4 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 5.84 (d, *J* = 10.0 Hz, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.609-3.605 (m, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.4, 168.1, 156.0, 152.4, 141.2, 139.1, 135.8, 133.9, 131.0, 130.7, 130.5, 129.6, 129.0, 128.2, 127.8, 126.7, 125.5, 125.2, 124.5, 121.3, 120.6, 116.1, 114.9, 112.3, 111.6, 101.3, 80.2, 69.3, 55.6, 30.2, 13.2 ppm; HRMS (ESI) calcd for $C_{35}H_{29}ClNO_5$ $[M+H]^+$ 578.1728, found 578.1728.

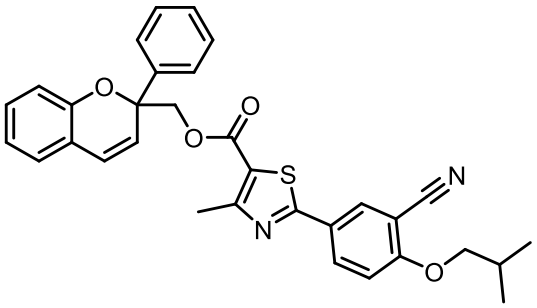


(2-phenyl-2*H*-chromen-2-yl)methyl 4-(N,N-dipropylsulfamoyl)benzoate (9e) colorless oil (86%, 86.9 mg); R_f = 0.3 (EtOAc/petroleum ether = 1:30); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.89 (m, 2H), 7.78-7.76 (m, 2H), 7.59-7.56 (m, 2H), 7.41-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.16 (td, *J* =8.0, 2.0 Hz, 1H), 6.99-6.95 (m, 2H), 6.86 (td, *J* = 8.0, 0.8 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 3.09-3.05 (m, 4H), 1.58-1.49 (m, 4H), 0.86 (t,

J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.8, 152.9, 144.2, 141.2, 133.0, 130.3, 129.7, 128.5, 128.1, 126.9, 126.7, 125.6, 124.6, 121.3, 120.7, 116.2, 80.2, 70.6, 49.9, 21.9, 11.1 ppm; HRMS (ESI) calcd for $C_{29}H_{32}NO_5S$ $[M+H]^+$ 506.1995, found 506.2001.



(2-phenyl-4a,5-dihydro-2H-chromen-2-yl)methyl 3-(4,5-diphenyloxazol-2-yl)propanoate (9f) colorless oil (95%, 97.6 mg); R_f = 0.4 (EtOAc/petroleum ether = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.61 (m, 2H), 7.58-7.55 (m, 2H), 7.51-7.48 (m, 2H), 7.39-7.30 (m, 8H), 7.28-7.24 (m, 1H), 7.12 (td, *J* =7.6, 1.6 Hz, 1H), 6.95-6.92 (m, 2H), 6.83 (td, *J* = 7.2, 1.6 Hz, 1H), 6.51 (d, *J* = 9.6 Hz, 1H), 5.97 (d, *J* = 9.6 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.11-3.07 (m, 2H), 2.93-2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 161.6, 152.5, 145.3, 141.4, 135.0, 132.4, 129.6, 129.0, 128.6, 128.5, 128.4, 128.3, 128.03, 127.94, 127.9, 126.7, 126.4, 125.6, 125.3, 124.7, 121.3, 120.8, 116.3, 60.1, 69.5, 31.0, 23.4 ppm; HRMS (ESI) calcd for $C_{34}H_{28}NO_4$ $[M+H]^+$ 514.2012, found 514.2013.

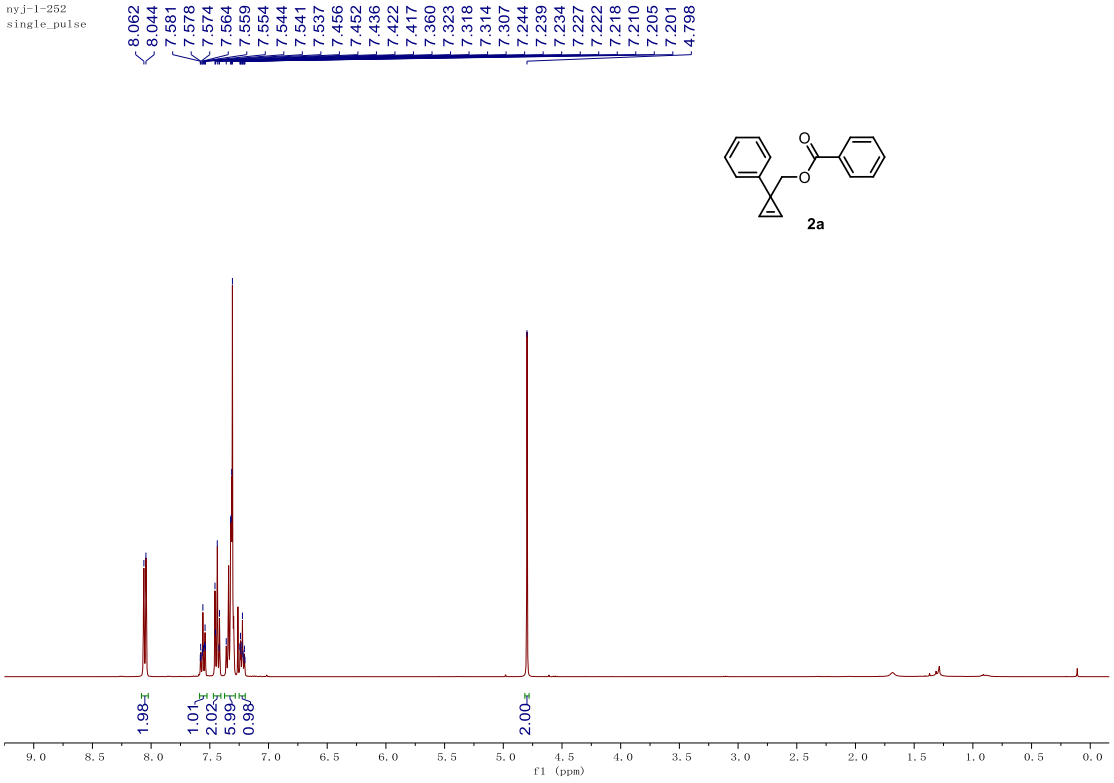


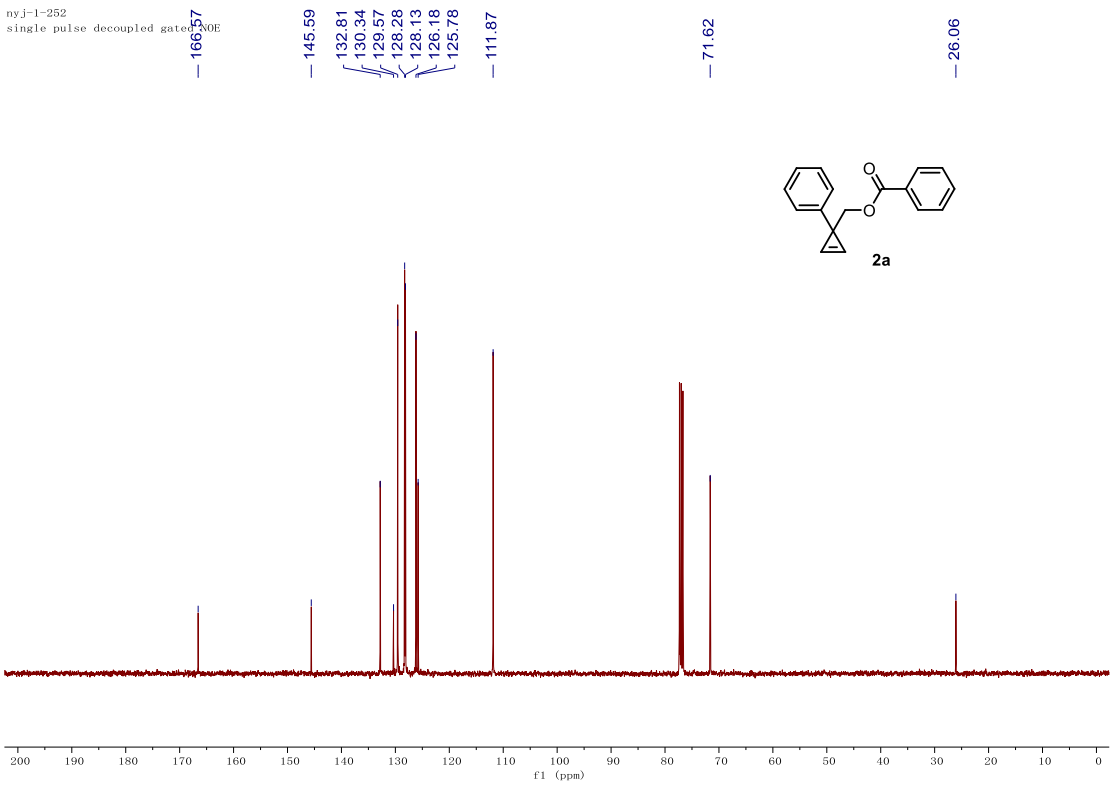
(2-phenyl-4a,5-dihydro-2H-chromen-2-yl)methyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (9g) pale yellow oil (85%, 91.2 mg); R_f = 0.6 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 2.0 Hz, 1H), 8.04 (dd, *J* =8.8, 2.0 Hz, 1H), 7.58-7.55 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.28 (m, 1H), 7.17 (td, *J* =7.6, 1.6 Hz, 1H), 7.00-6.96 (m, 3H), 6.87 (td, *J* =7.2, 1.2 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 3.88 (d, *J* = 6.4 Hz, 2H), 2.66 (s, 3H), 2.25-2.15 (m, 1H), 1.09 (d, *J* = 6.8

Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.7, 162.4, 161.6, 161.5, 152.9, 141.2, 132.5, 132.0, 129.7, 128.5, 128.1, 126.9, 125.9, 125.6, 125.5, 124.5, 121.5, 121.2, 120.6, 116.3, 115.4, 112.5, 102.9, 80.1, 75.6, 70.2, 28.1, 19.0, 17.4 ppm; HRMS (ESI) calcd for $C_{32}H_{29}N_2O_4S$ $[M+H]^+$ 537.1842, found 537.1841.

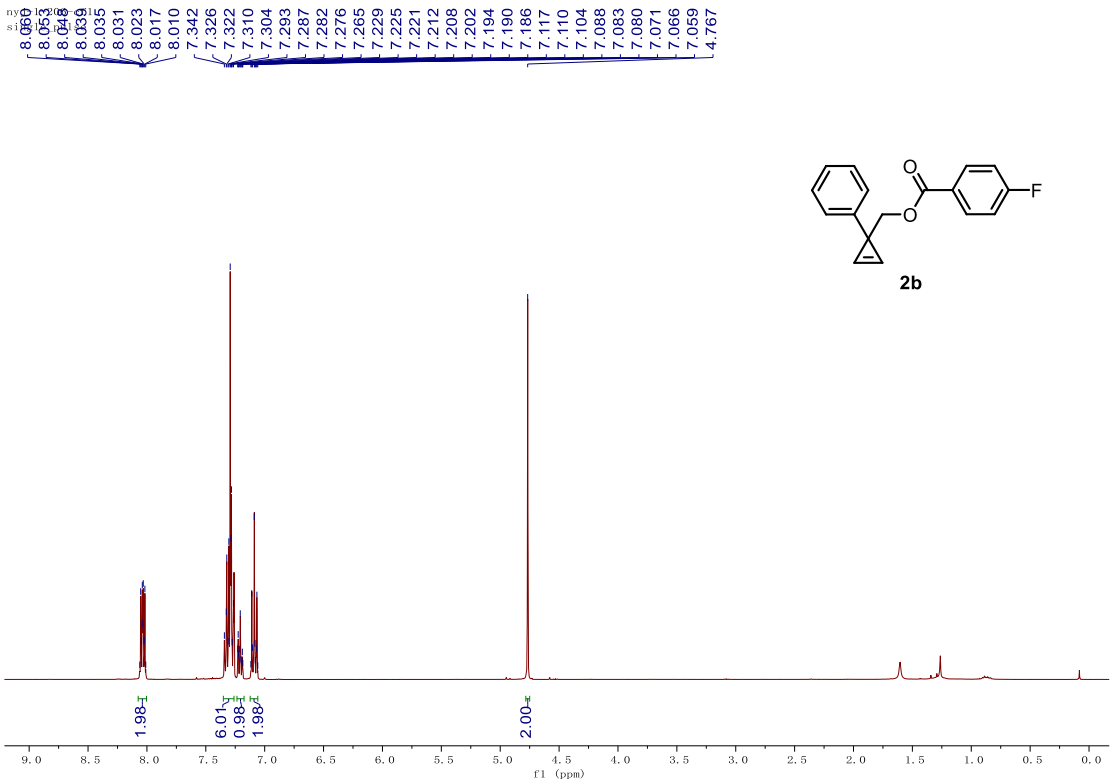
^{1}H NMR and ^{13}C NMR Spectra of Substrates 2, Products 3, 4, 5a, 6a, 7a and 9a-g

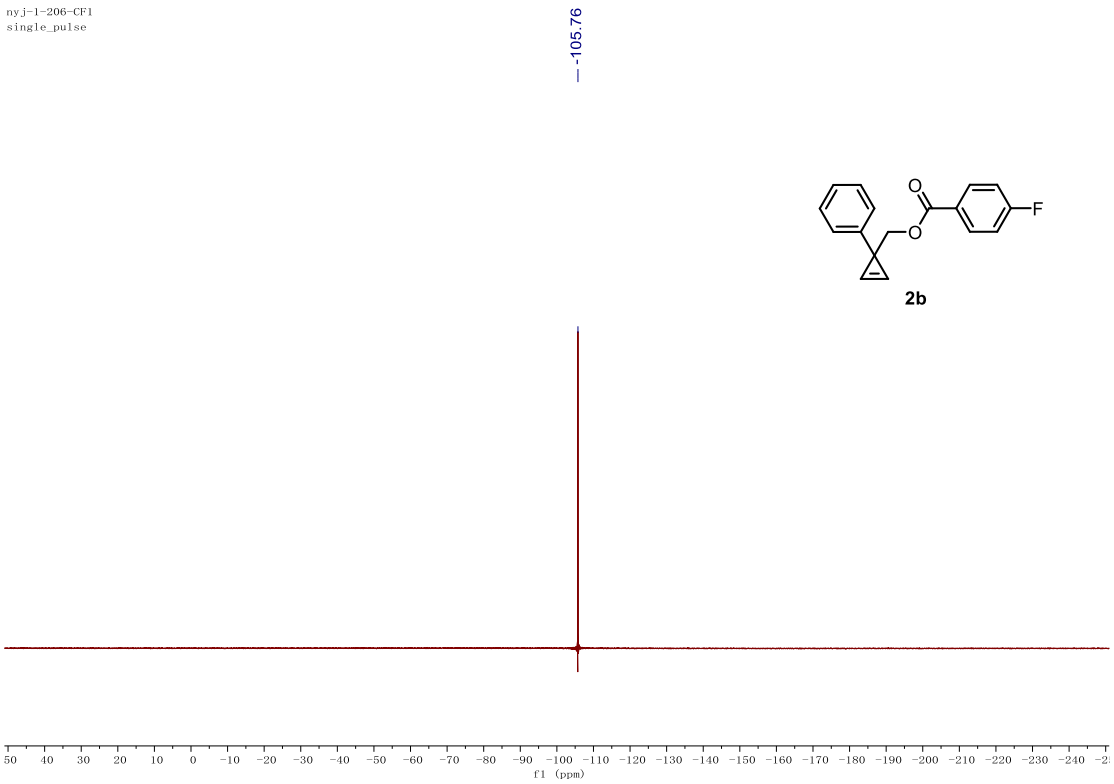
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2a**

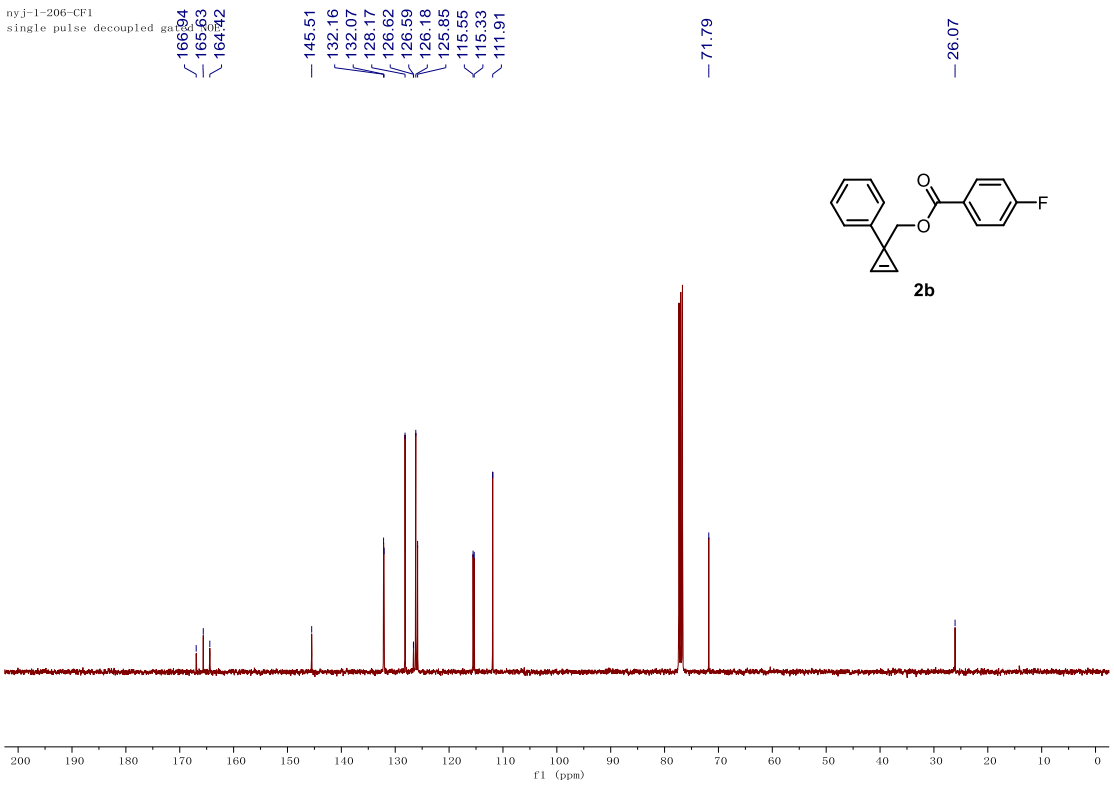




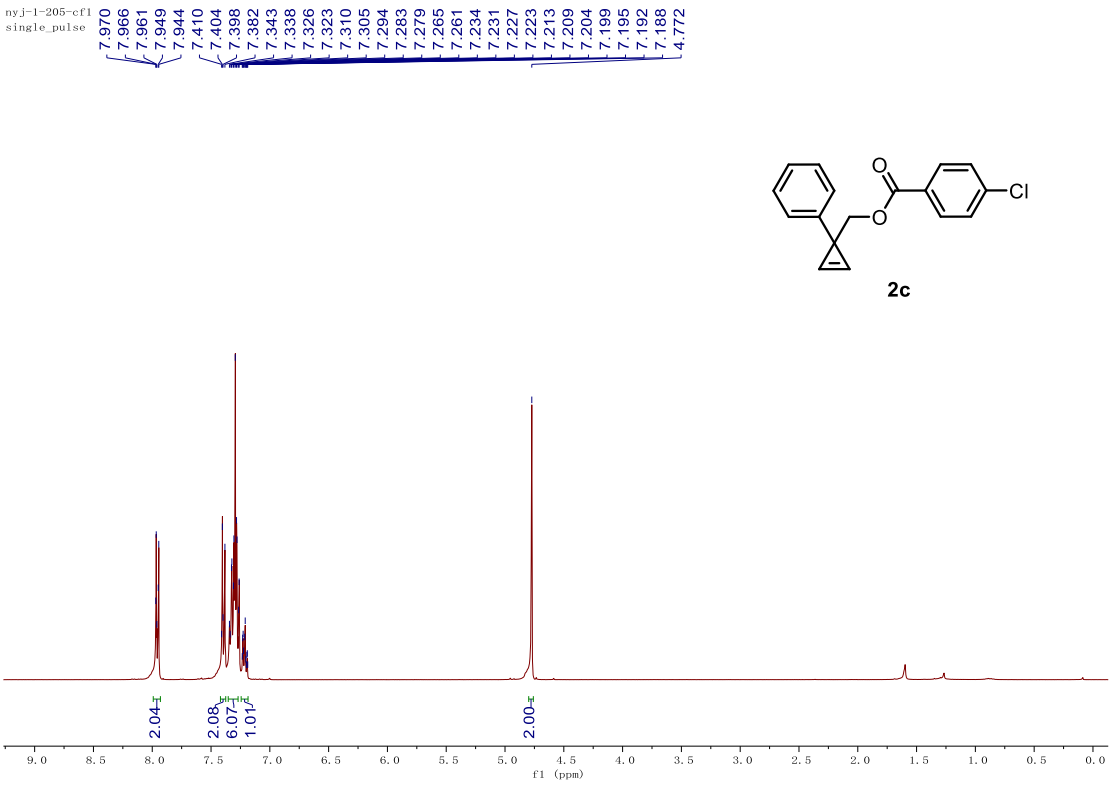
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2b**







^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2c**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7.343
7.338
7.326
7.323
7.310
7.305
7.294
7.283
7.279
7.265
7.261
7.234
7.231
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7.223
7.213
7.209
7.204
7.199
7.195
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O
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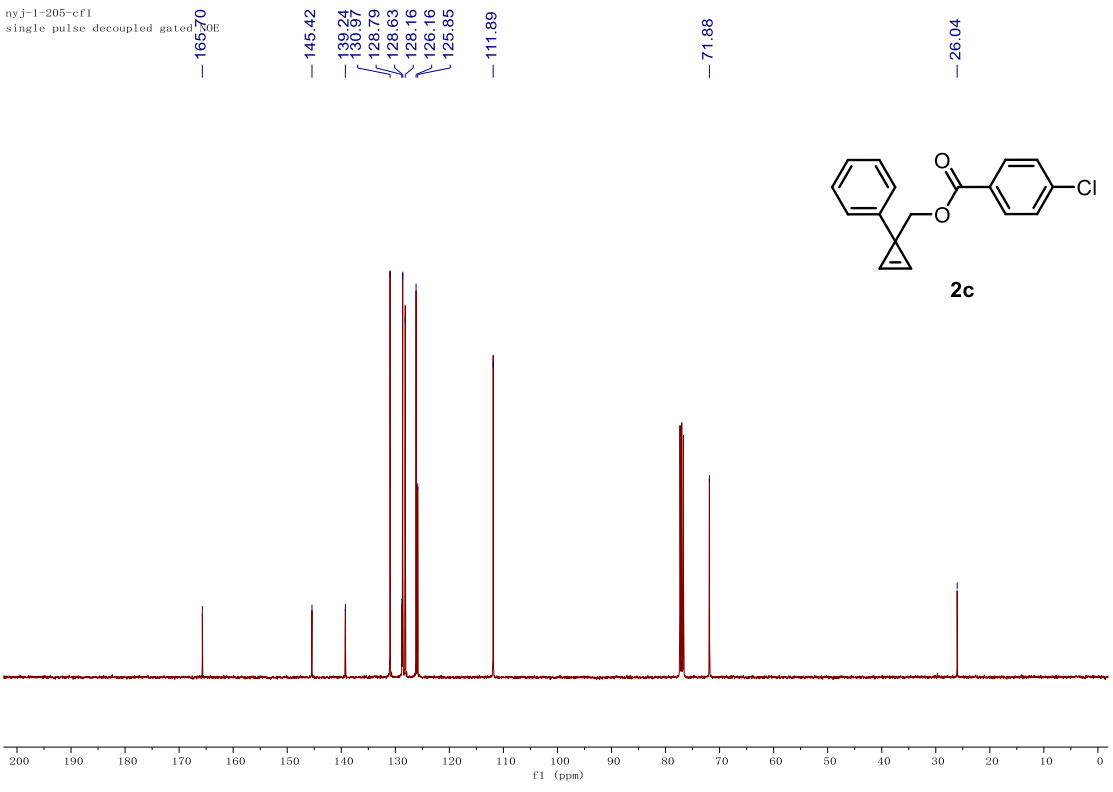
2.08
6.07
1.01
2.00
f1 (ppm)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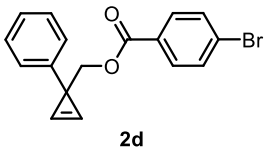
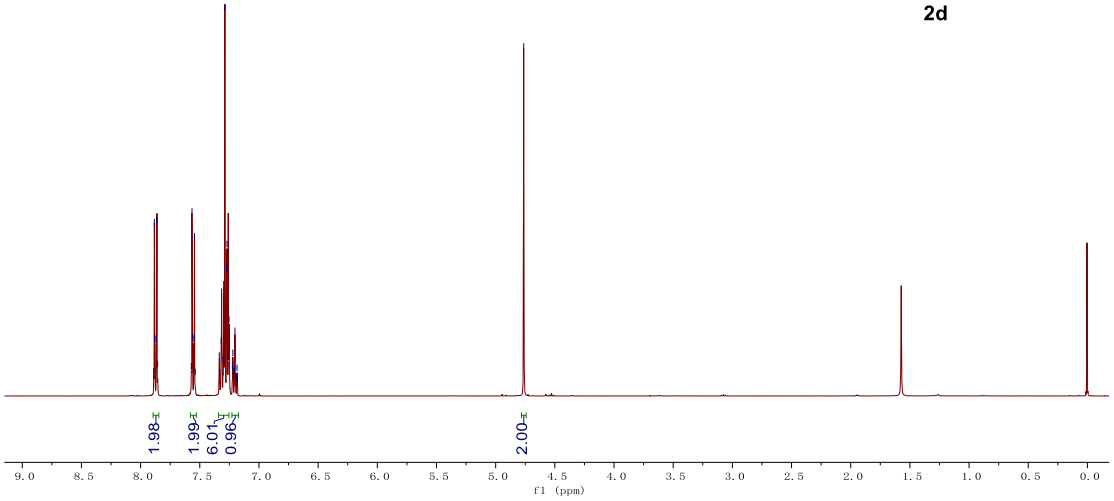
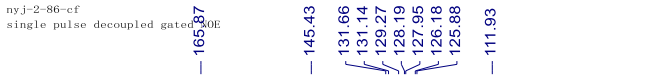
26.04
O
O
Cl
2c
f1 (ppm)

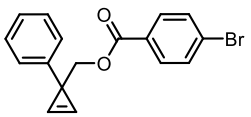
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2d**



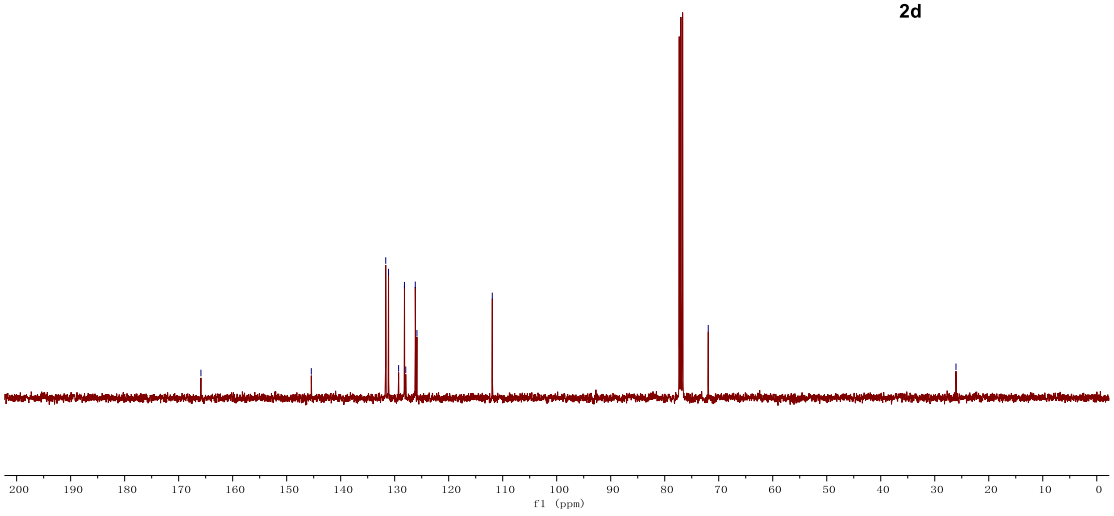
2d



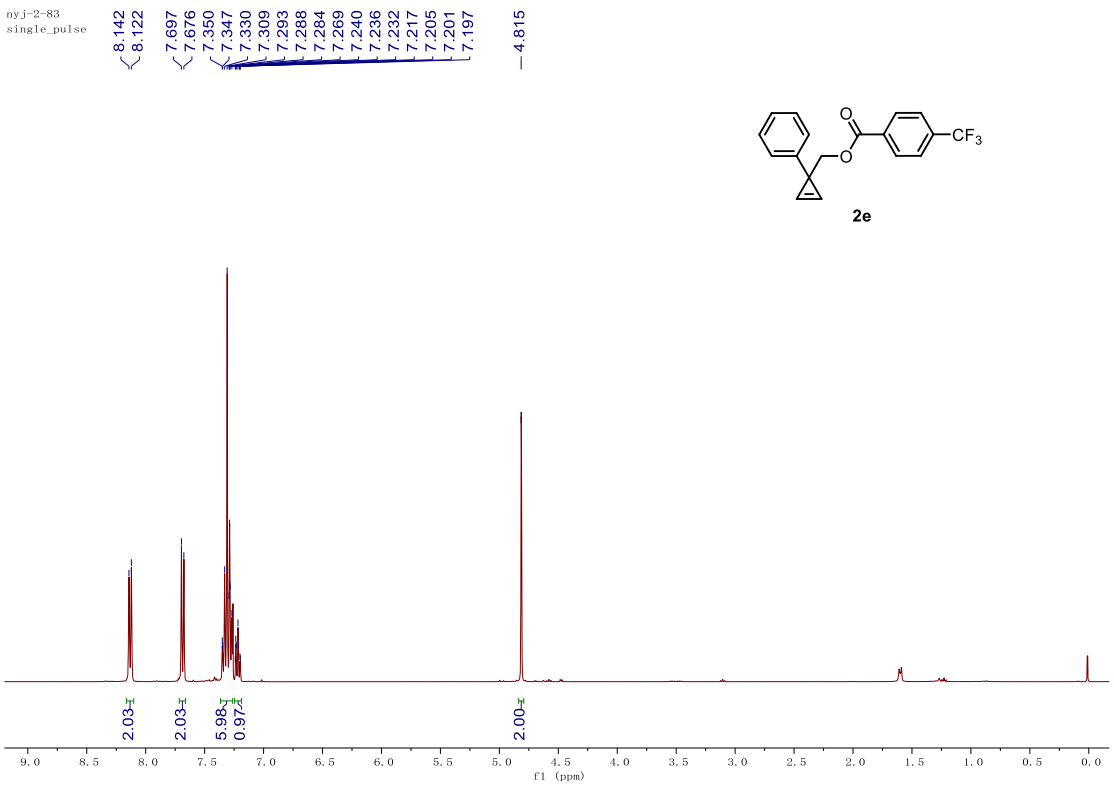


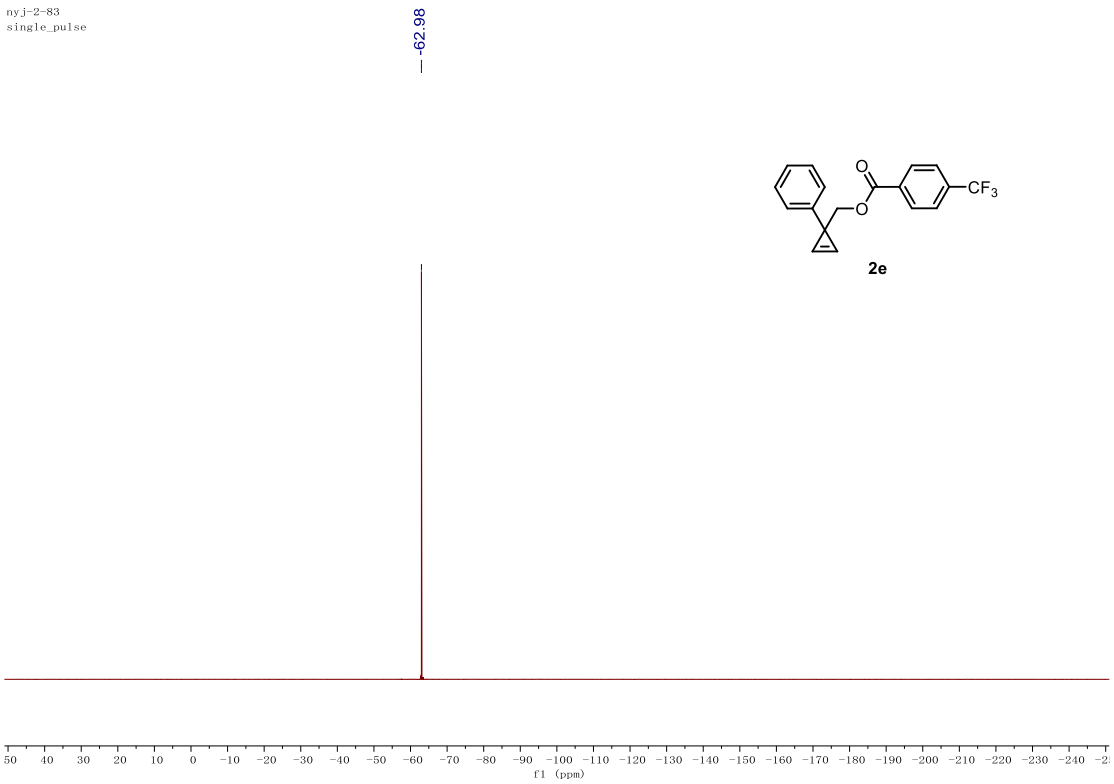


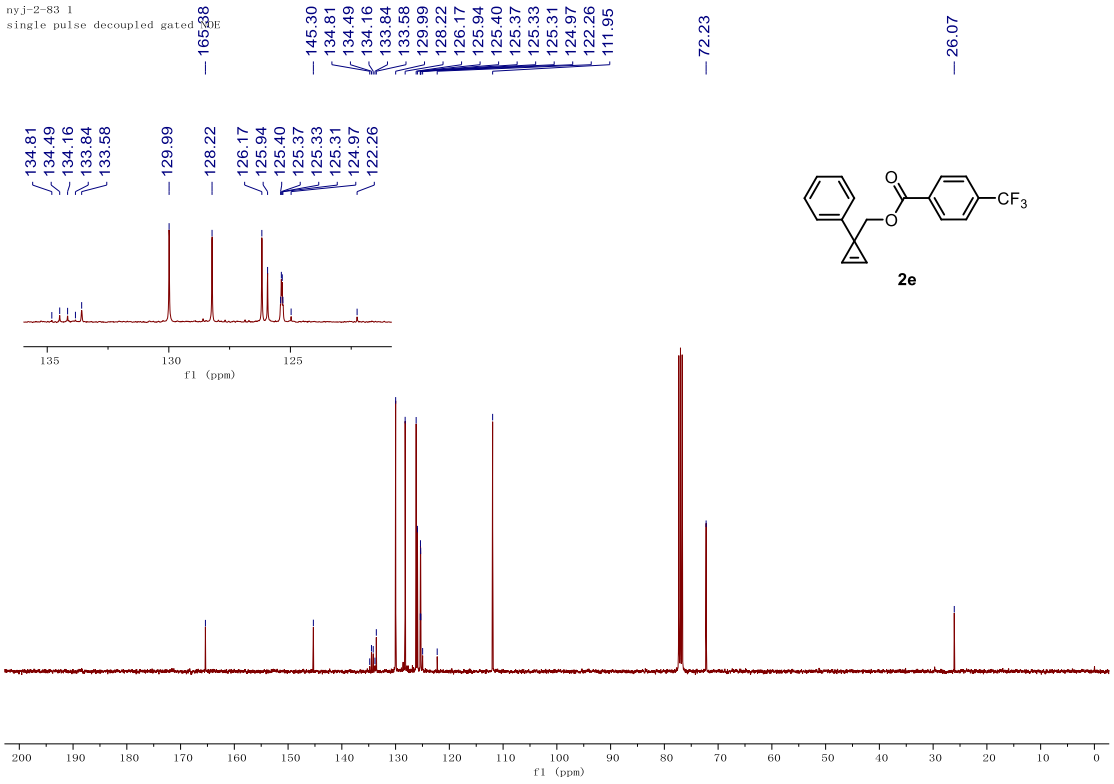
2d



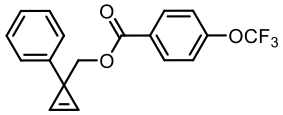
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2e**



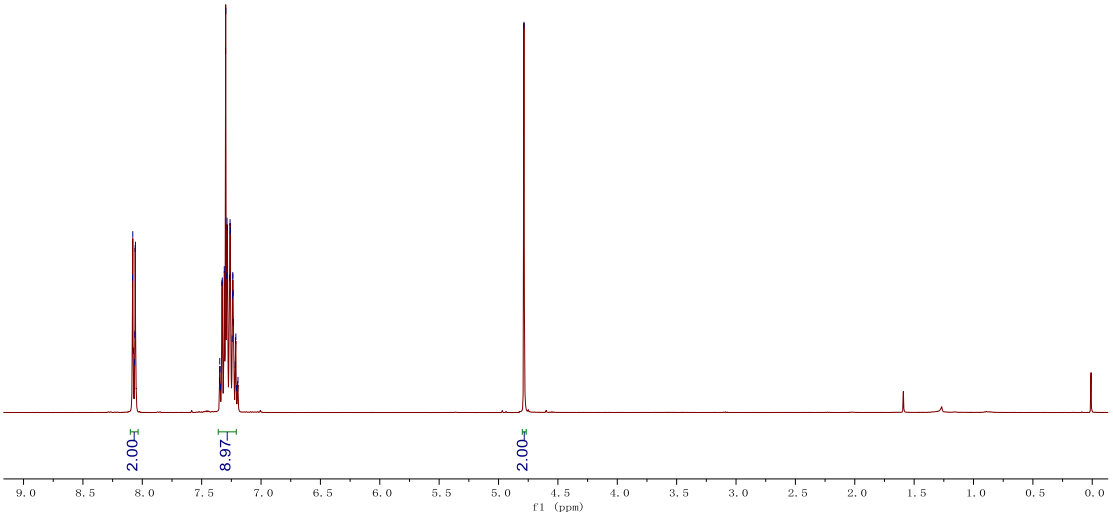




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2f**



2f



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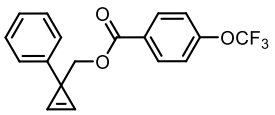
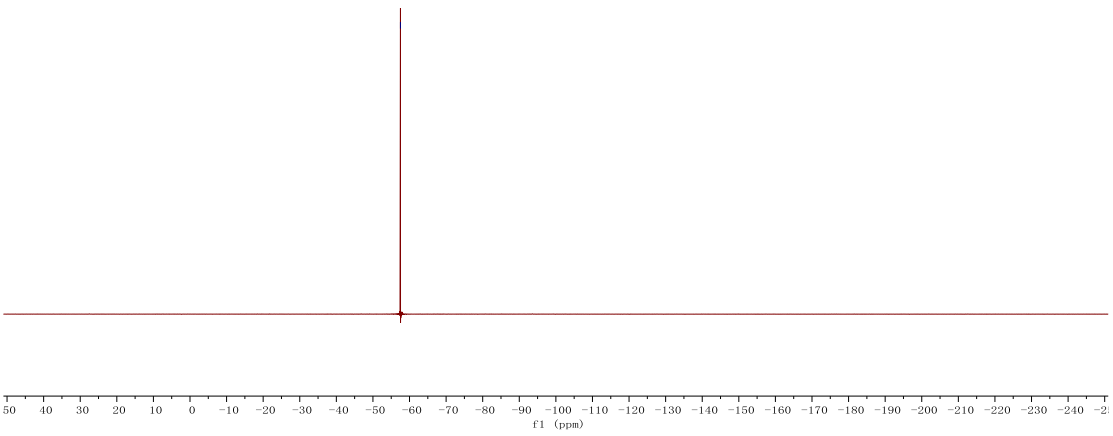
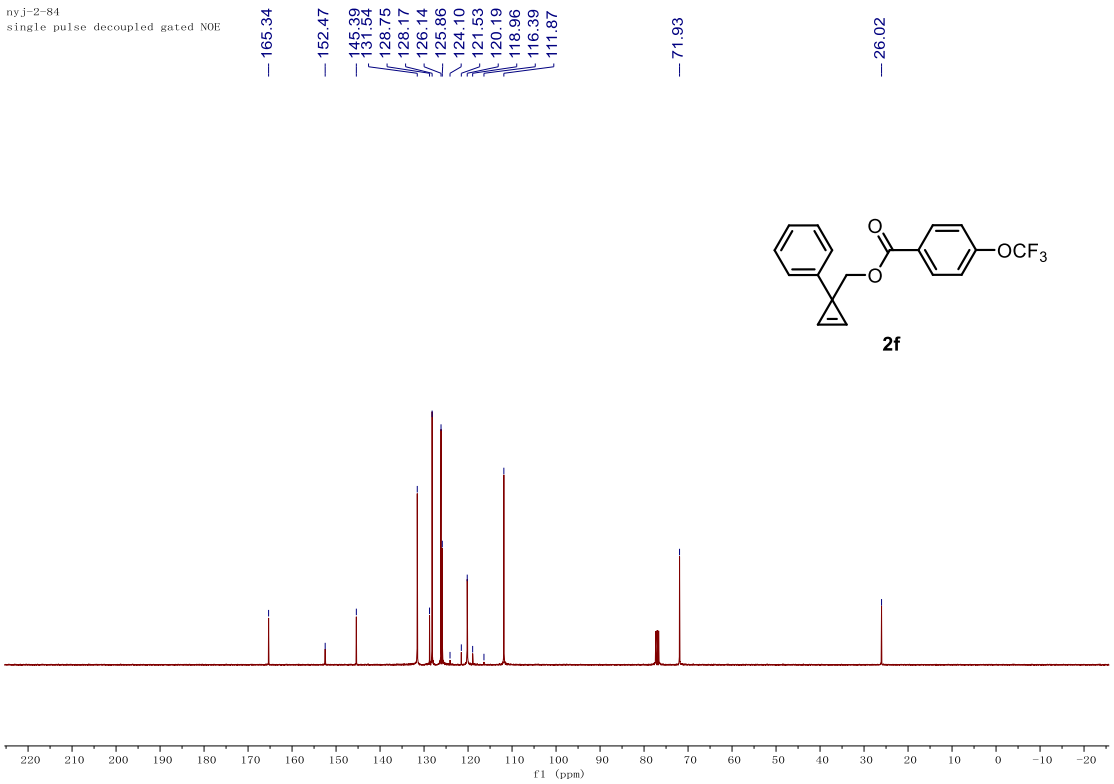
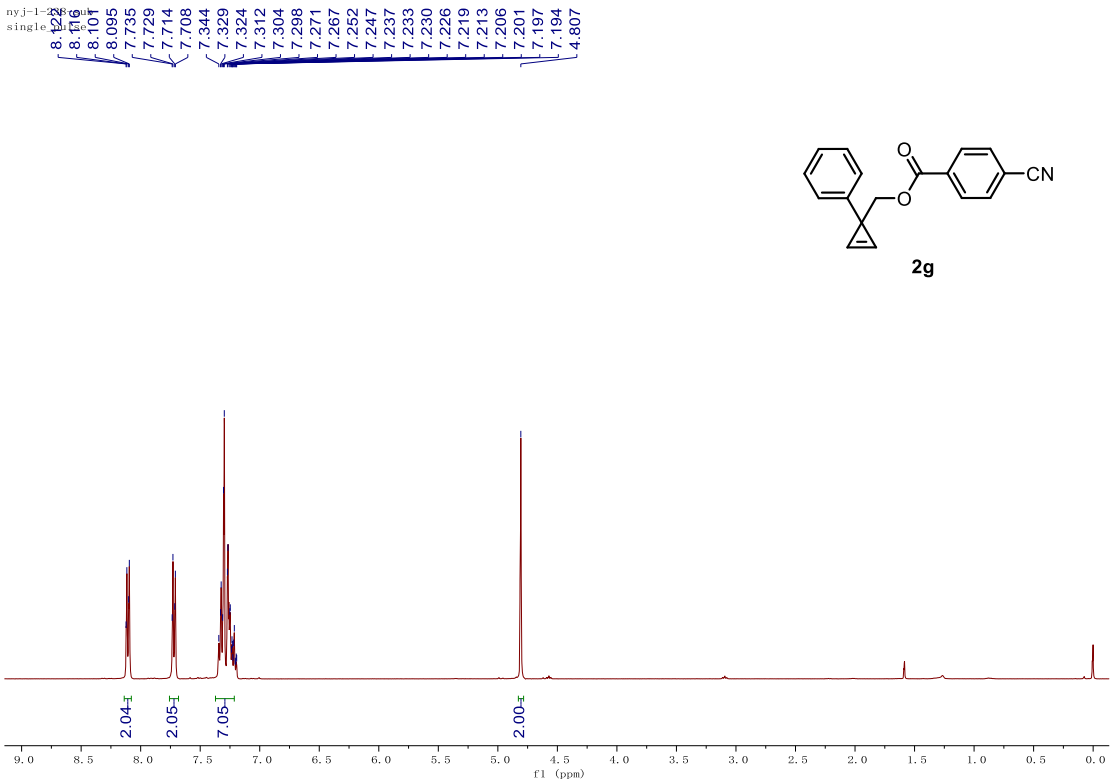


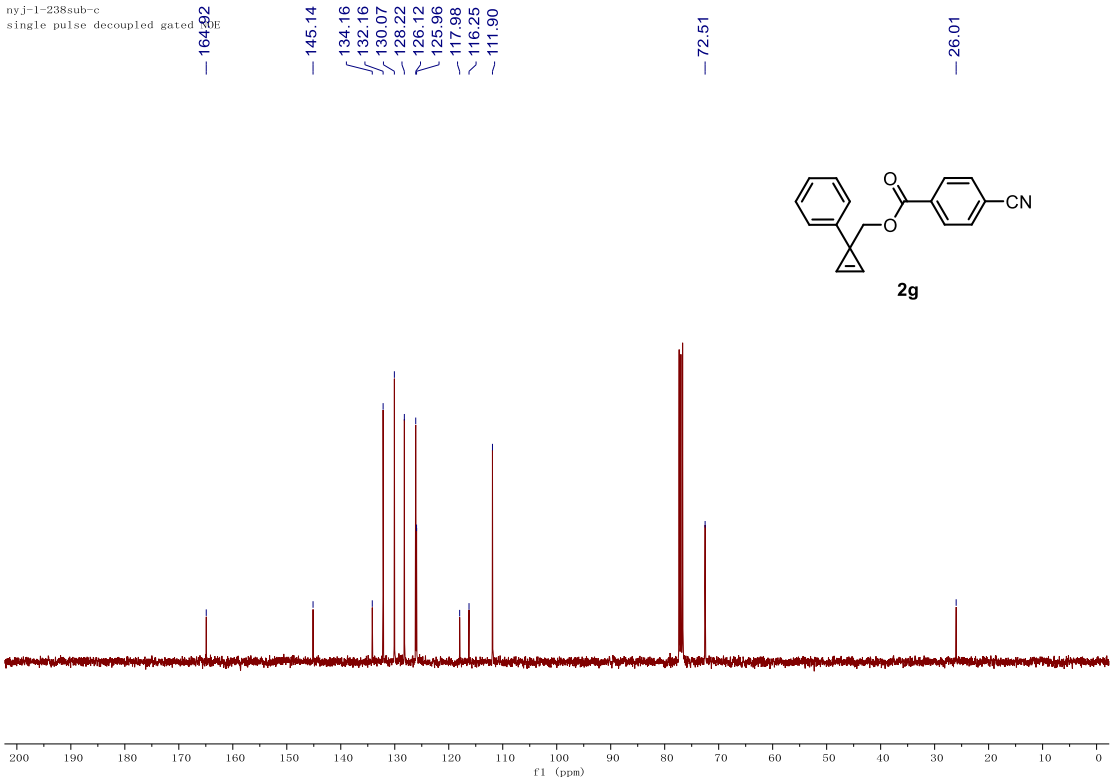
2f



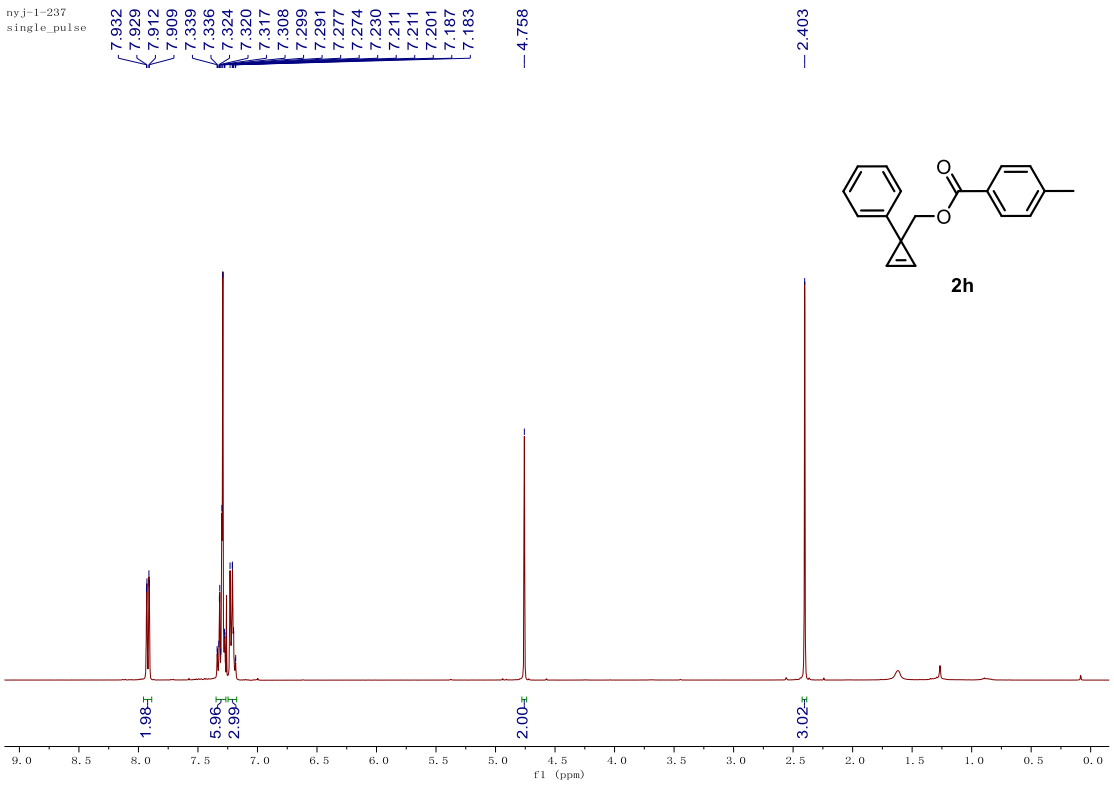


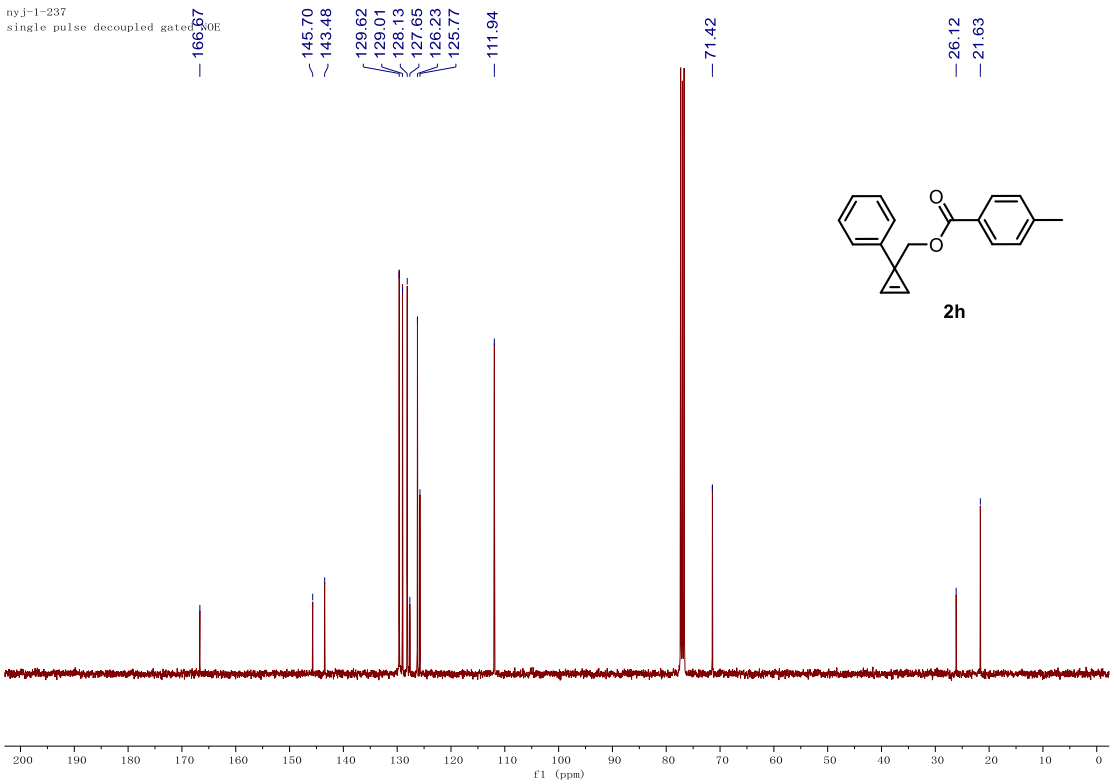
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2g**



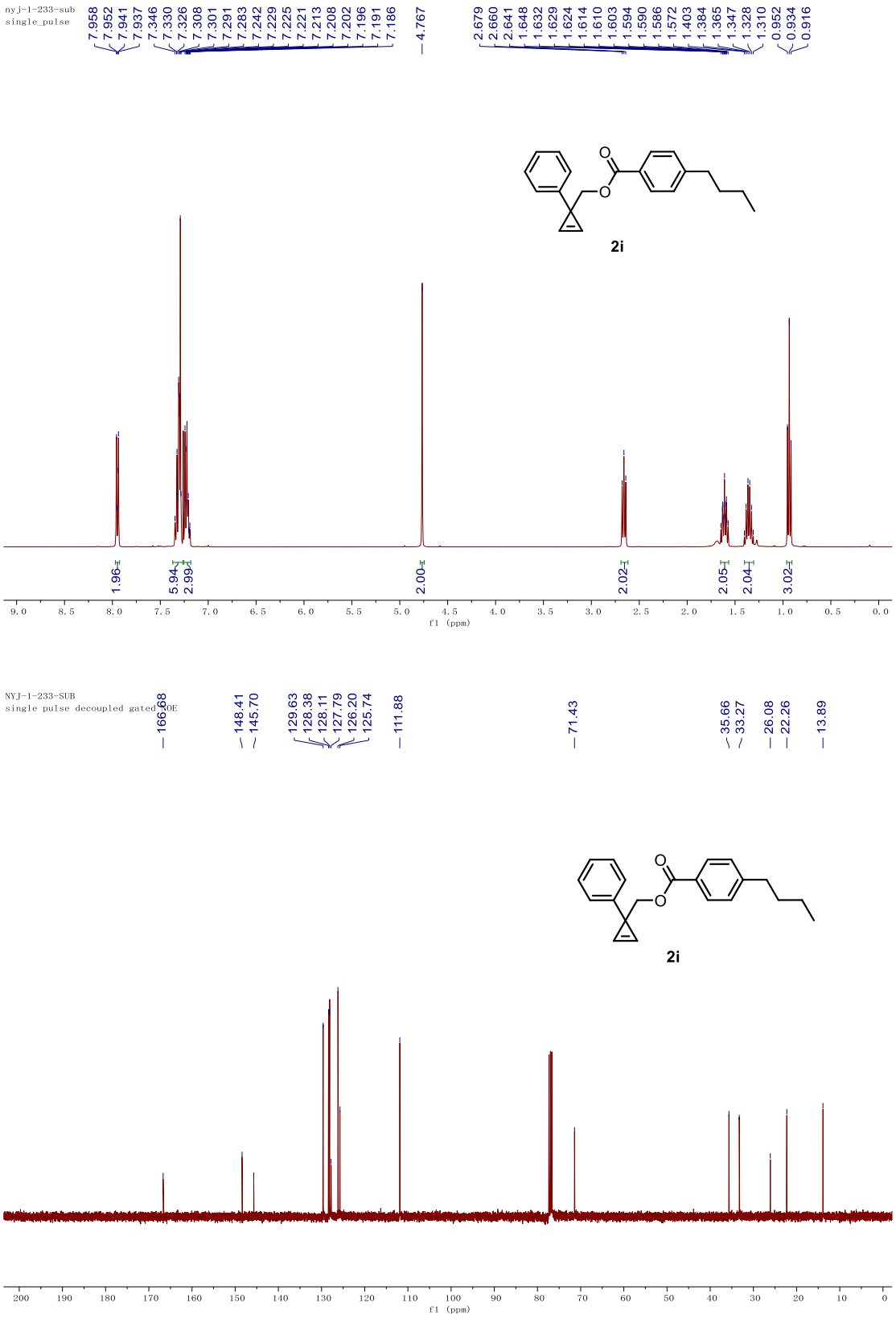


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2h**

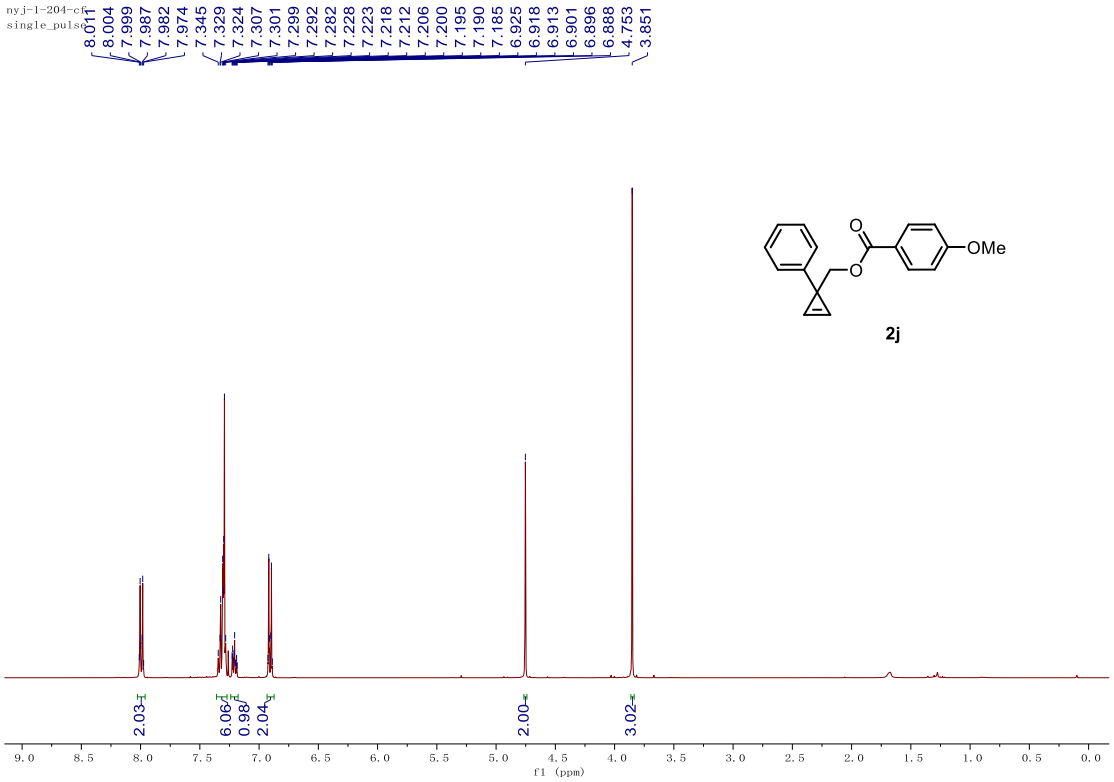


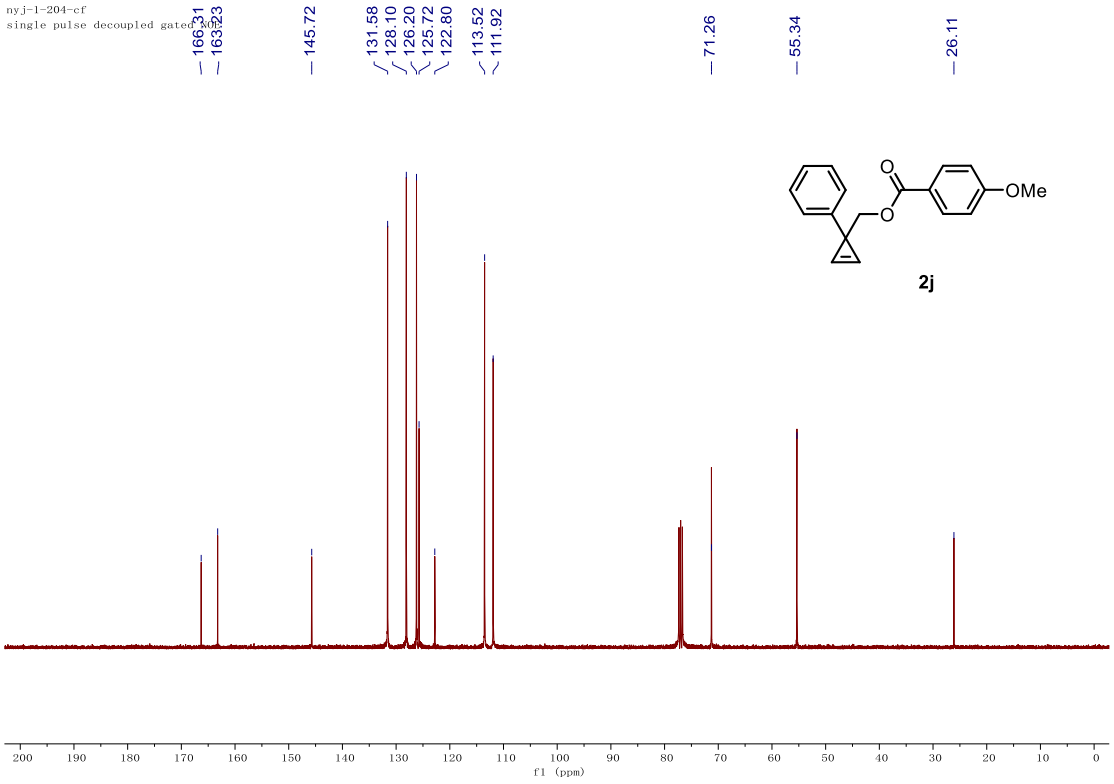


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2i**

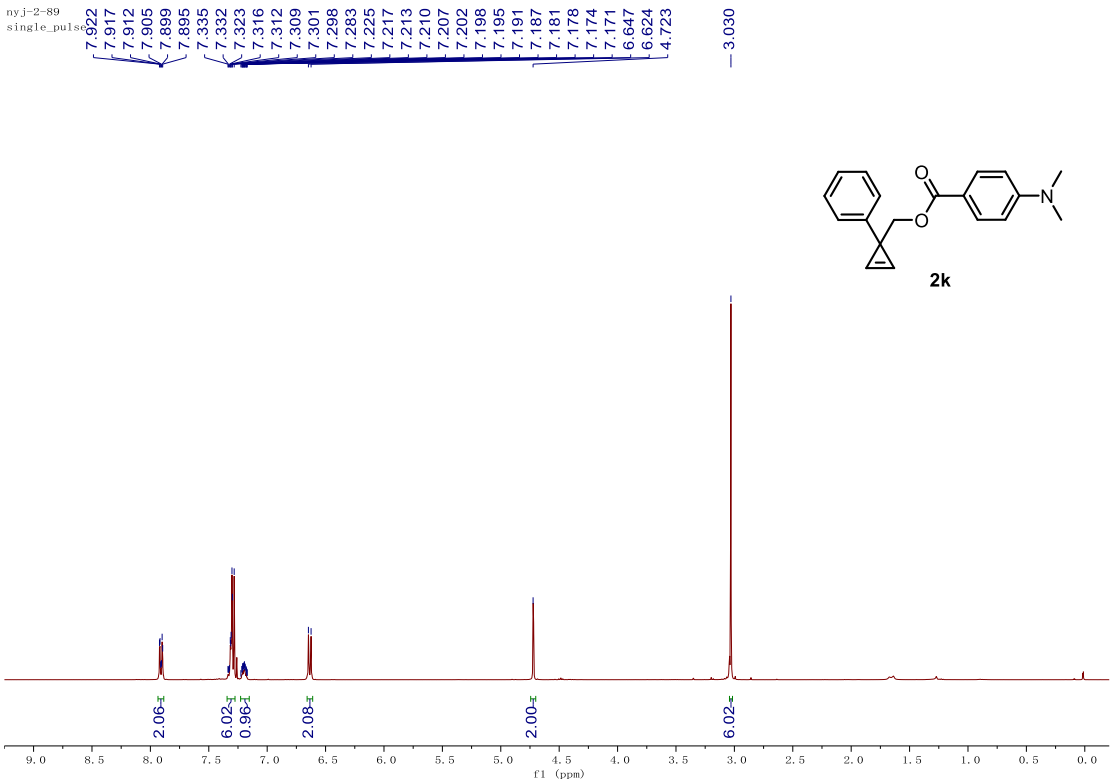


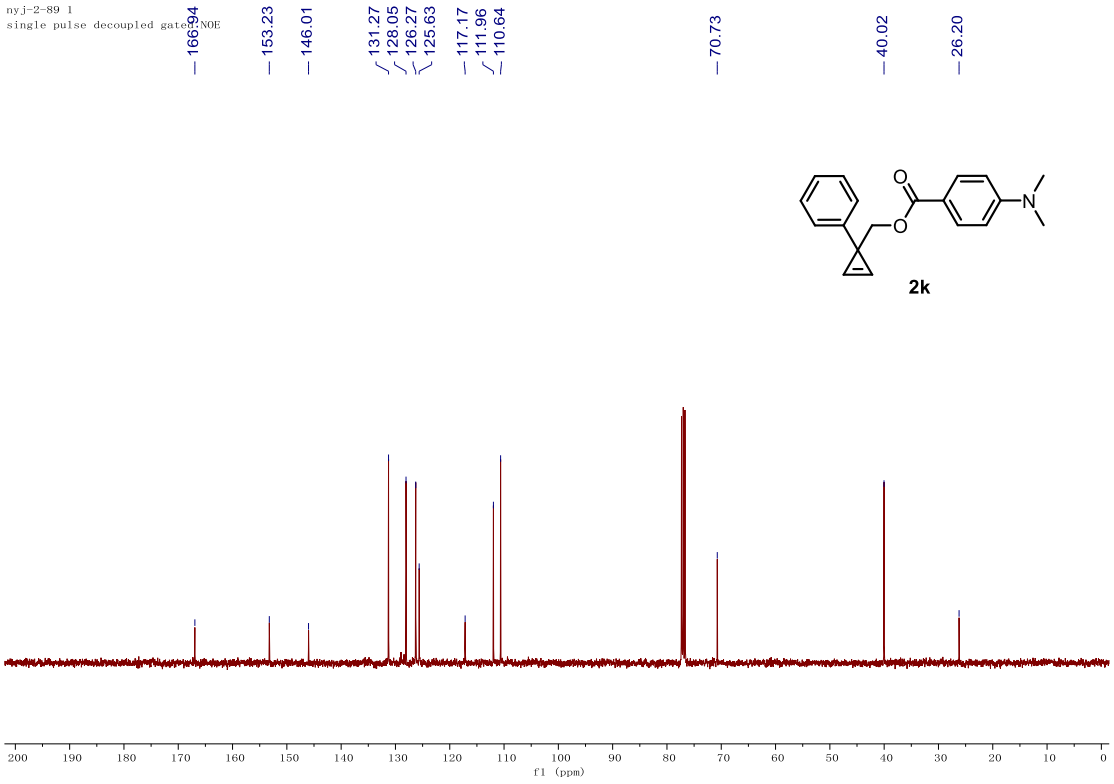
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2j**



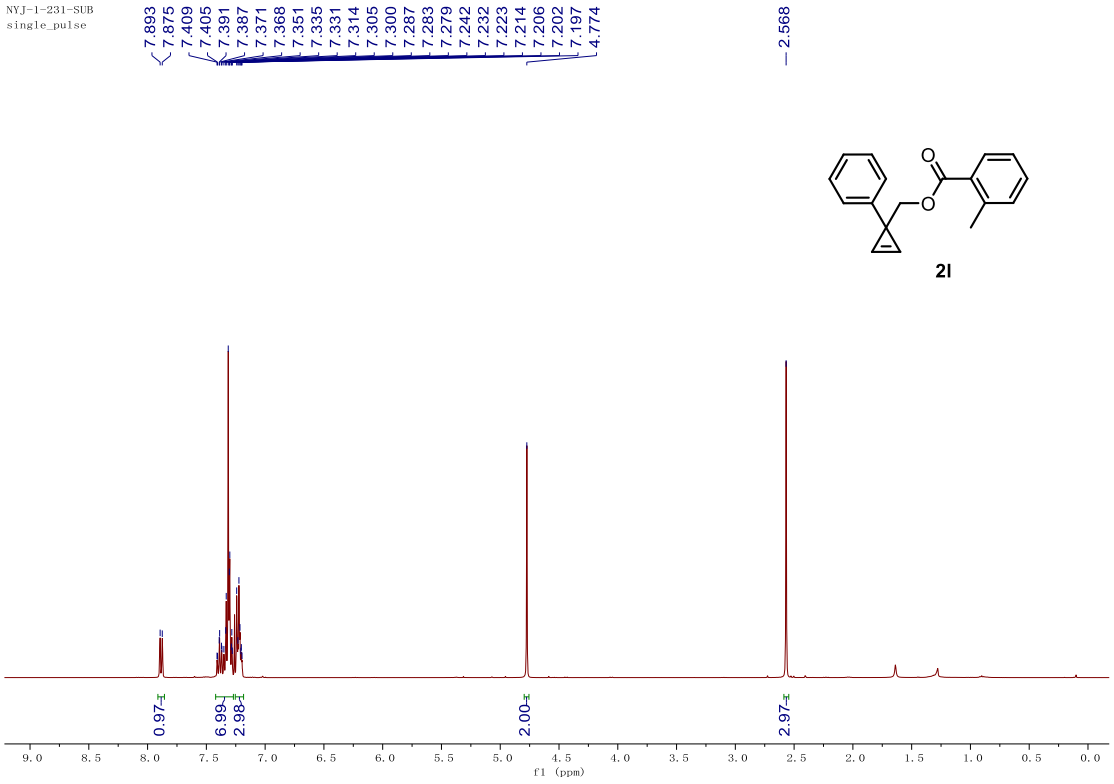


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2k**

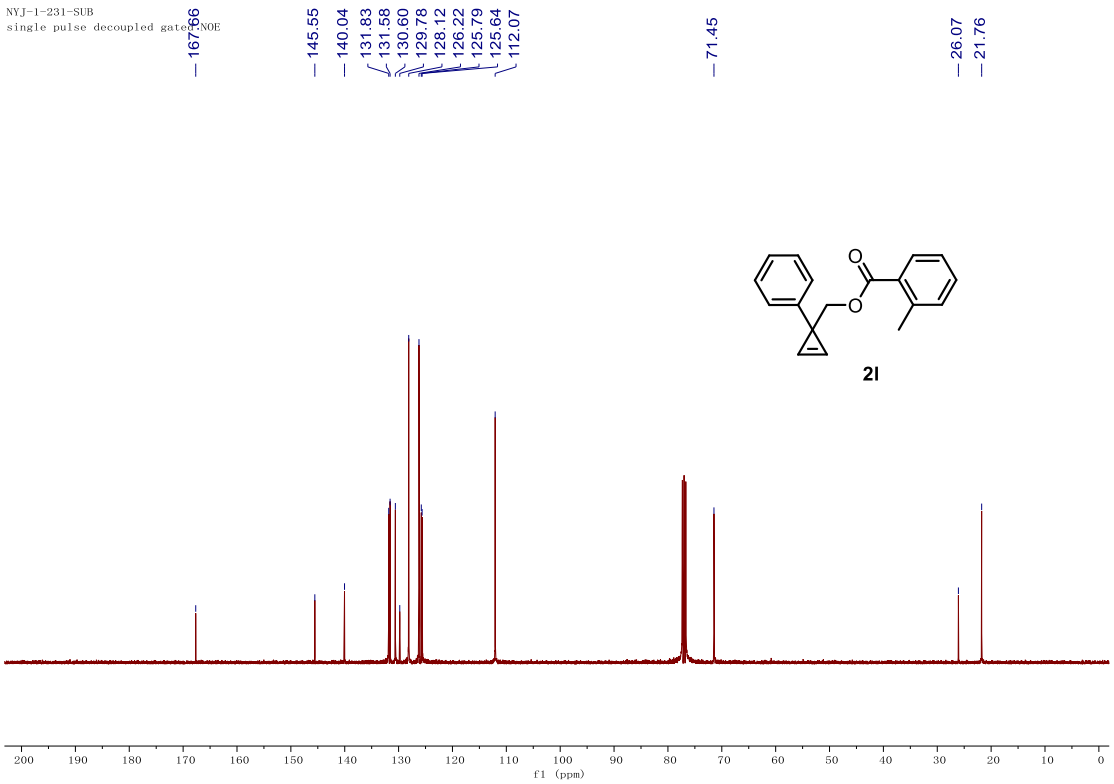




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2l**

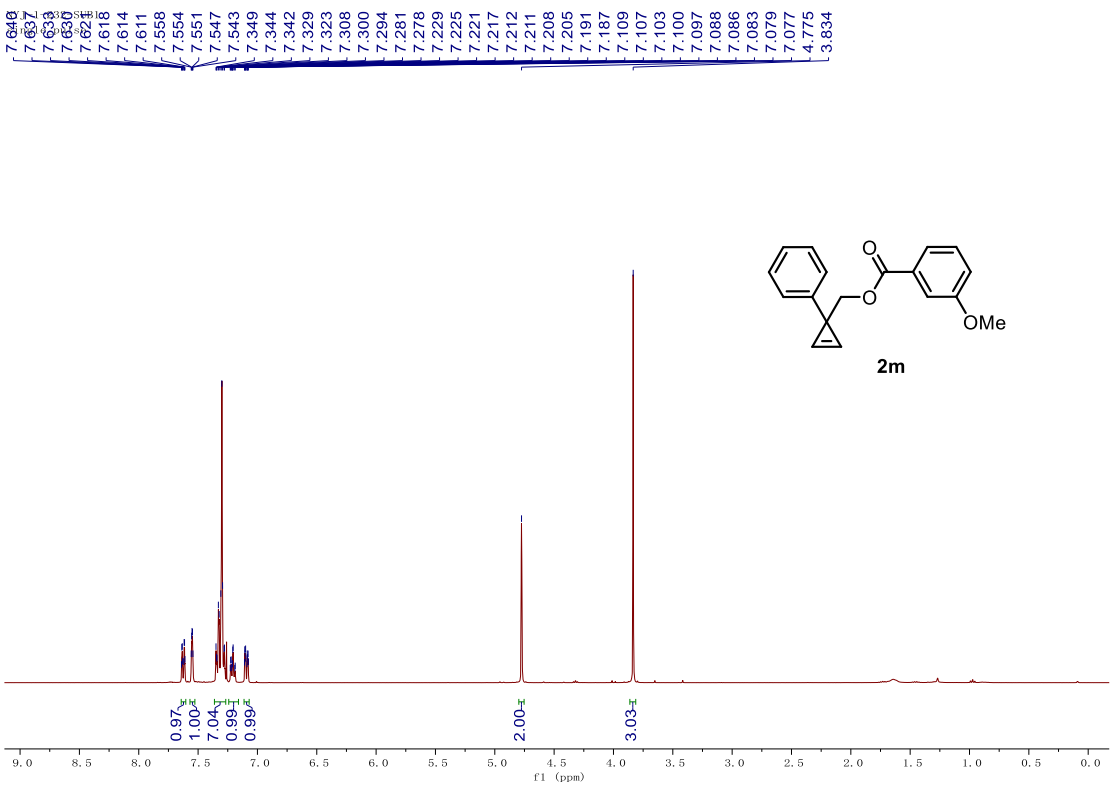


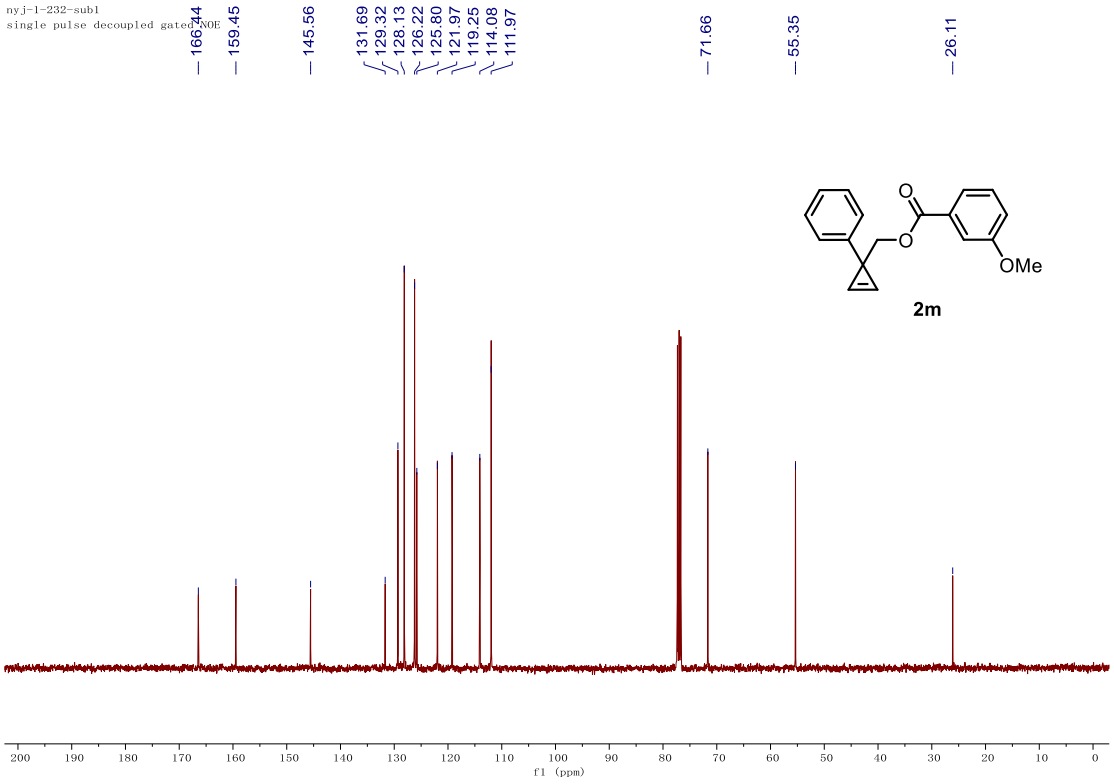
2l



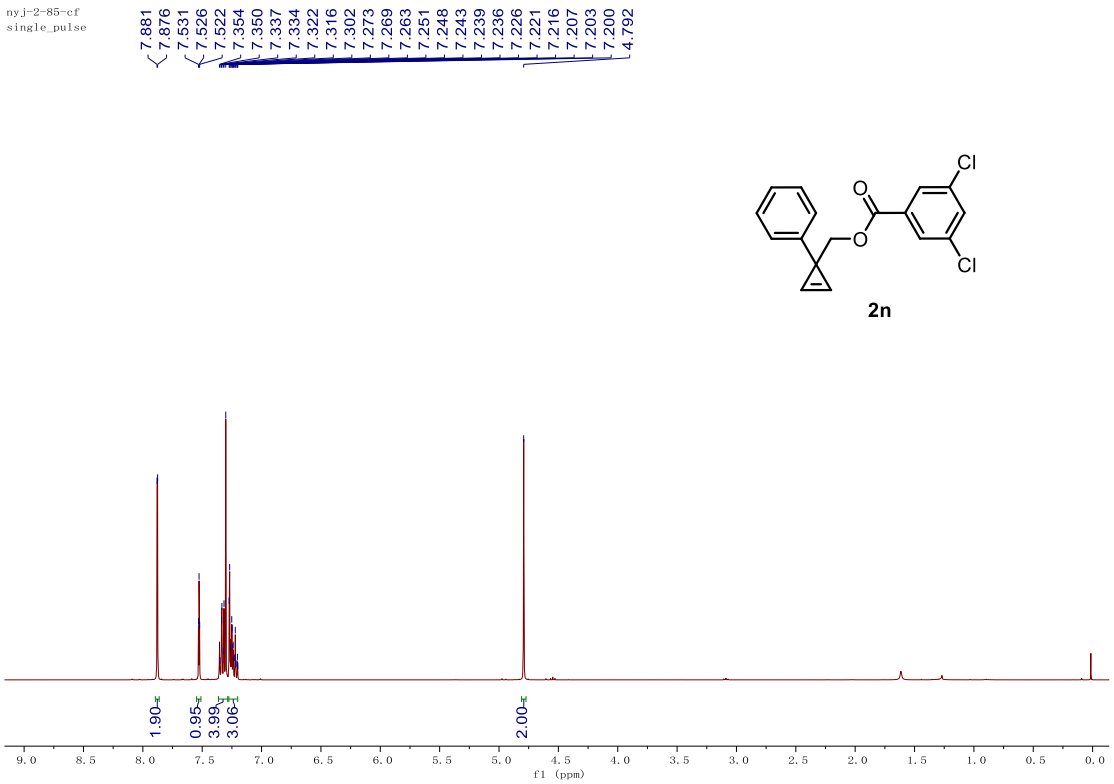
2l

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2m**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2n**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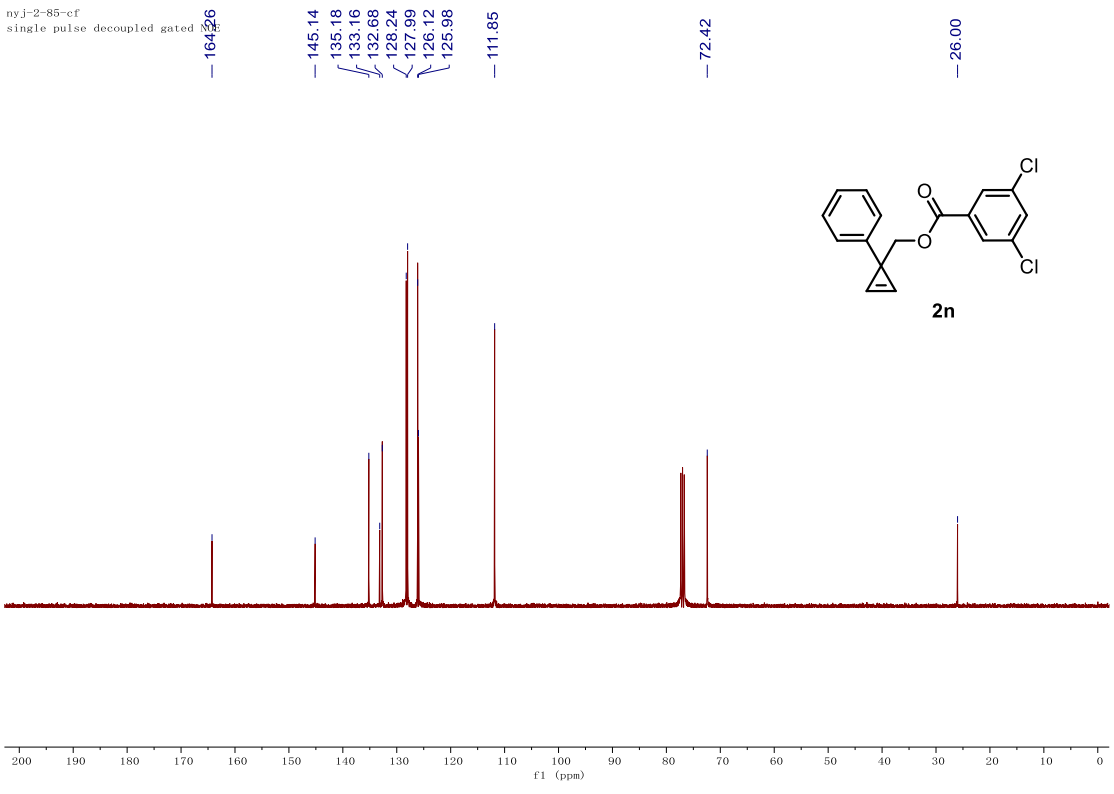
7.531
7.526
7.522
7.354
7.350
7.337
7.334
7.322
7.316
7.302
7.273
7.269
7.263
7.251
7.248
7.243
7.239
7.236
7.226
7.221
7.216
7.207
7.203
7.200
4.792
Cl
O
O
Cl
2n
1.90
0.95
3.99
3.06
2.00
f1 (ppm)


nyj-2-85-cf
single pulse decoupled gated
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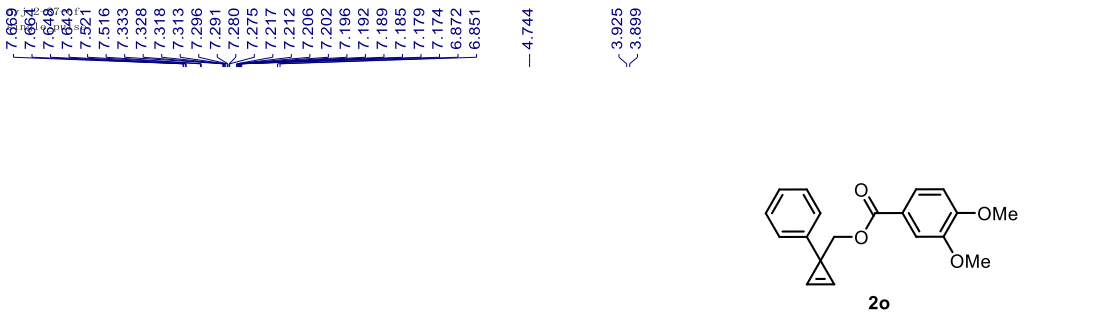
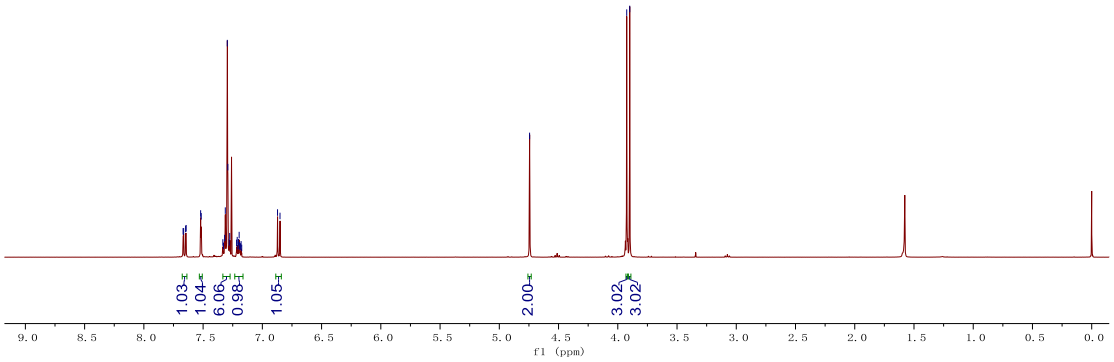
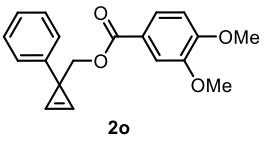
145.14
135.18
133.16
132.68
128.24
127.99
126.12
125.98
111.85
72.42
26.00
Cl
O
O
Cl
2n
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2o**

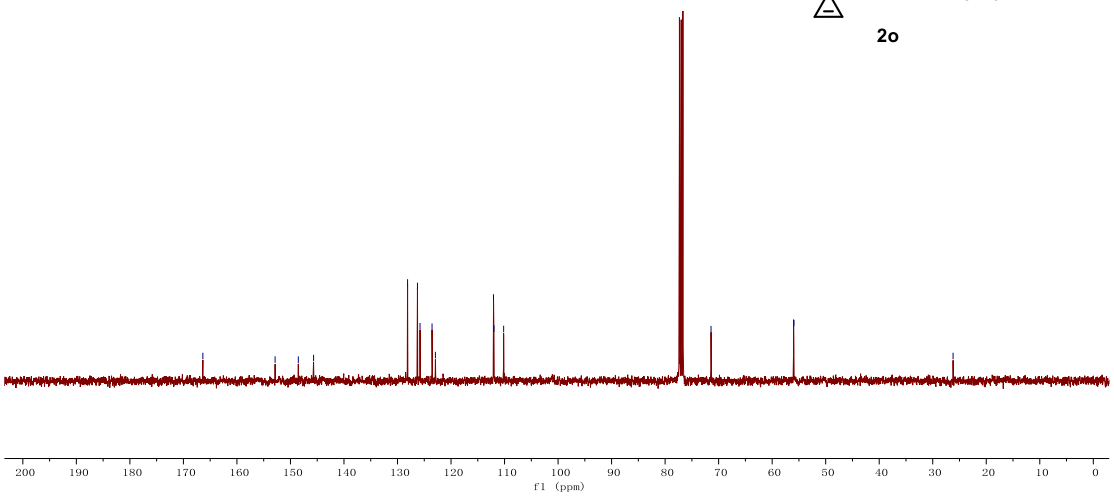


2o

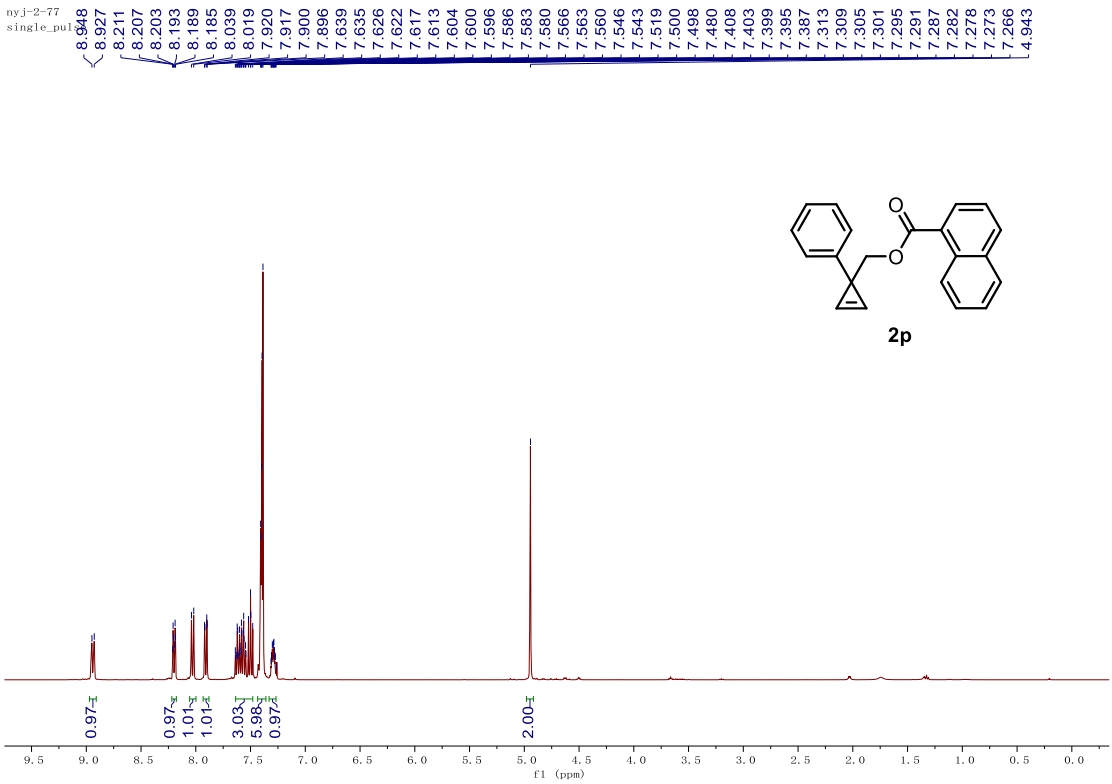


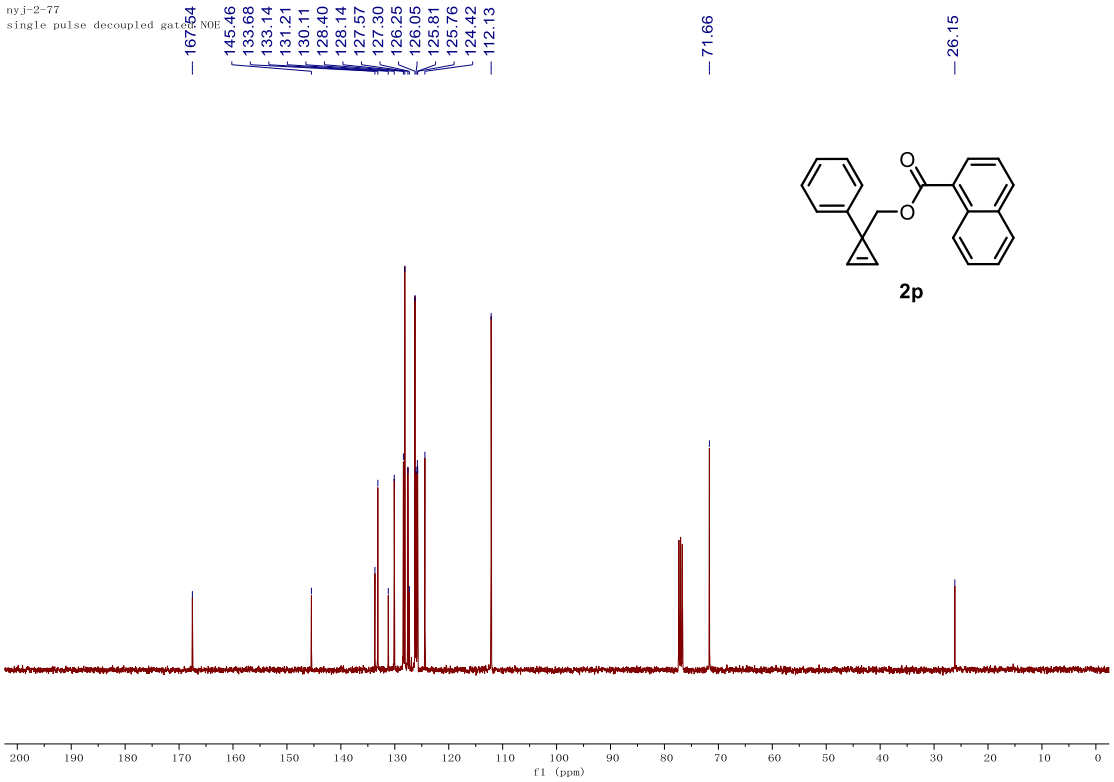


2o

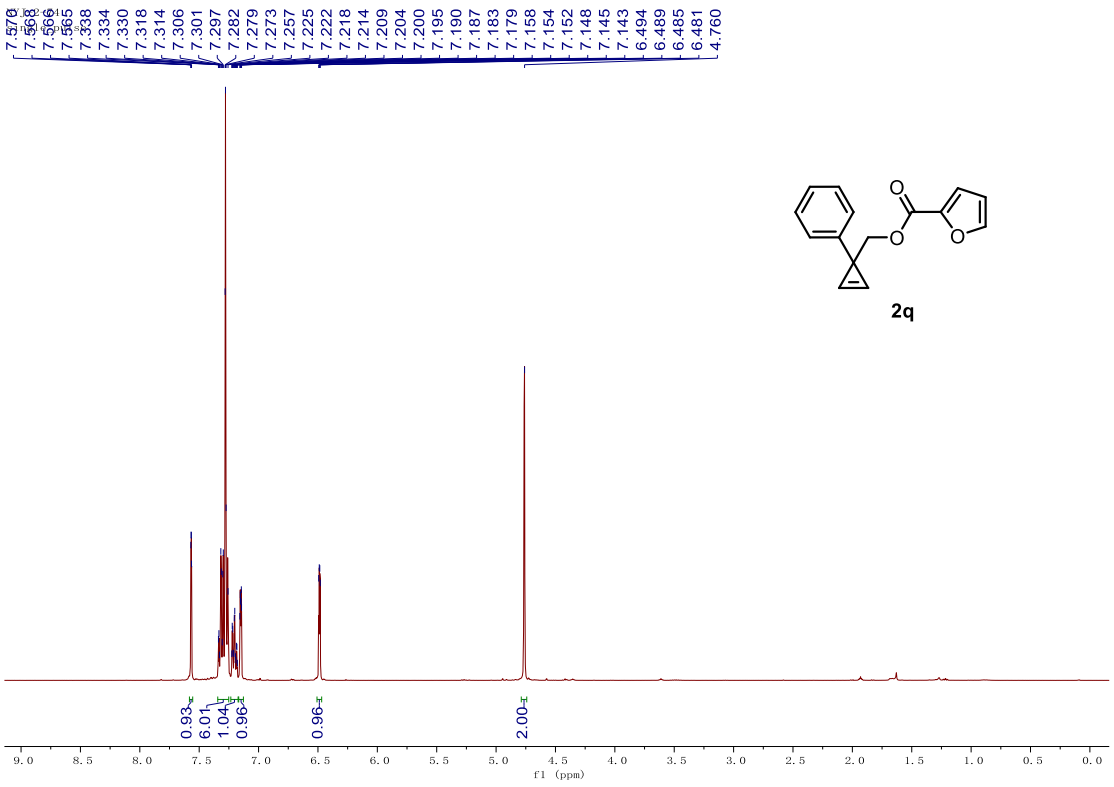


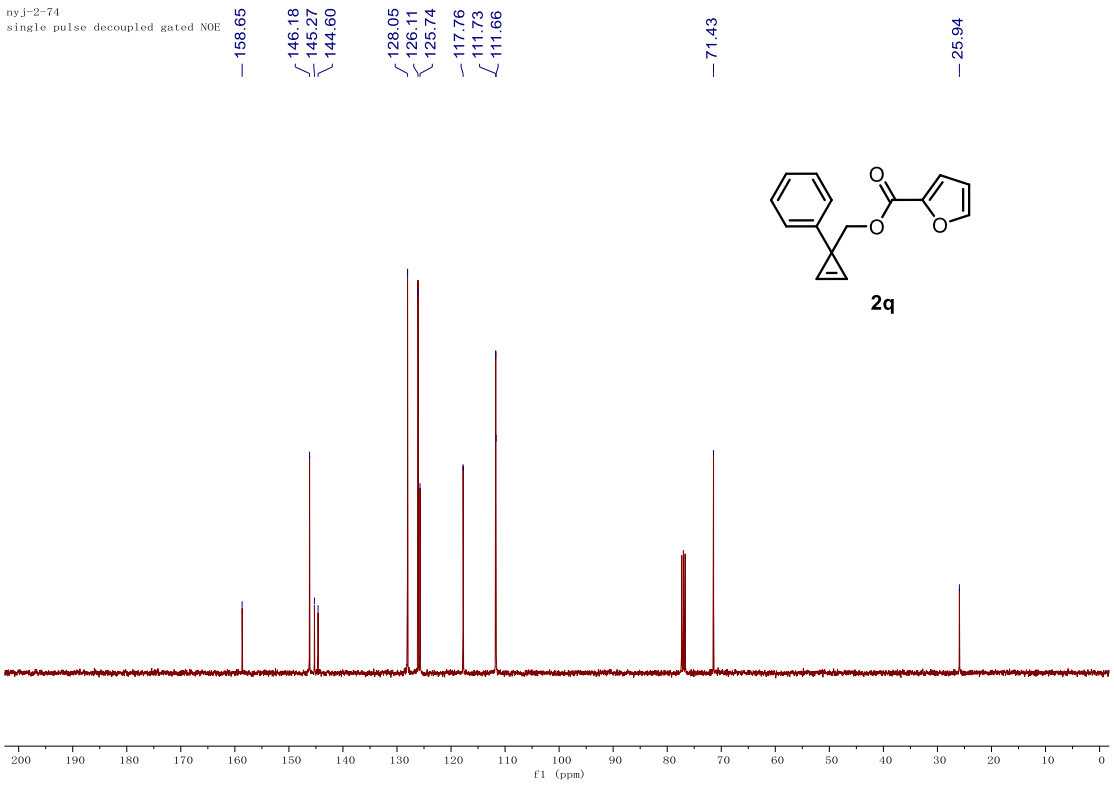
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2p**



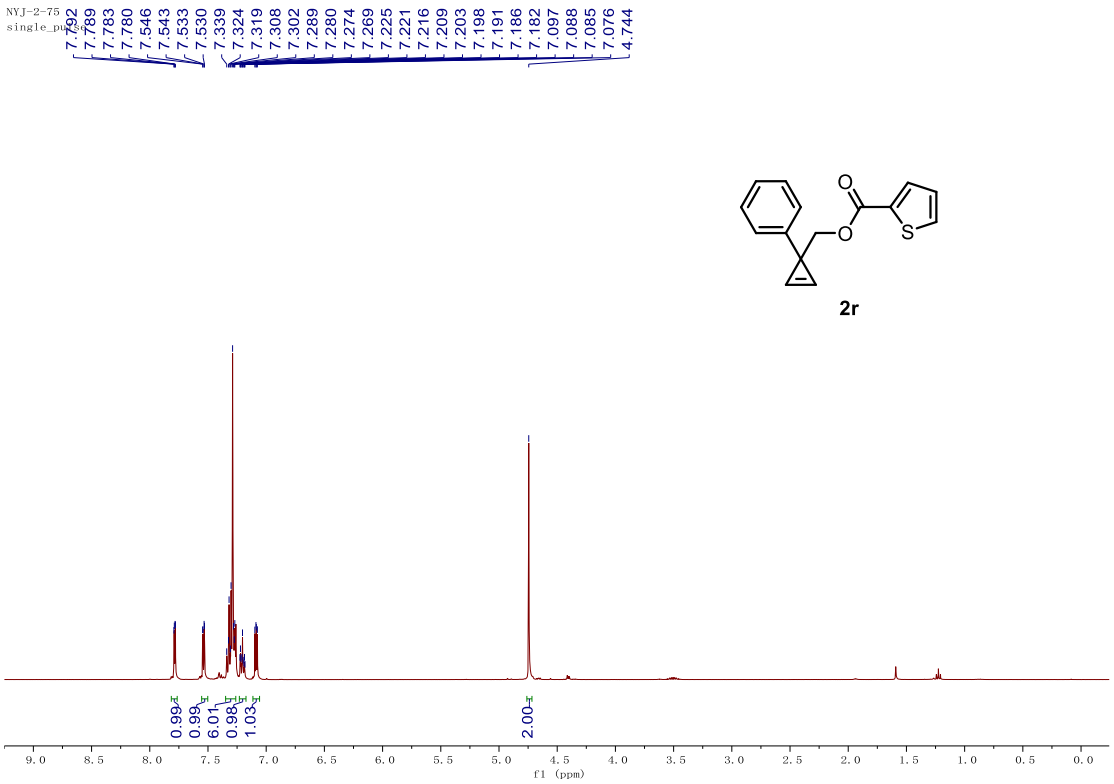


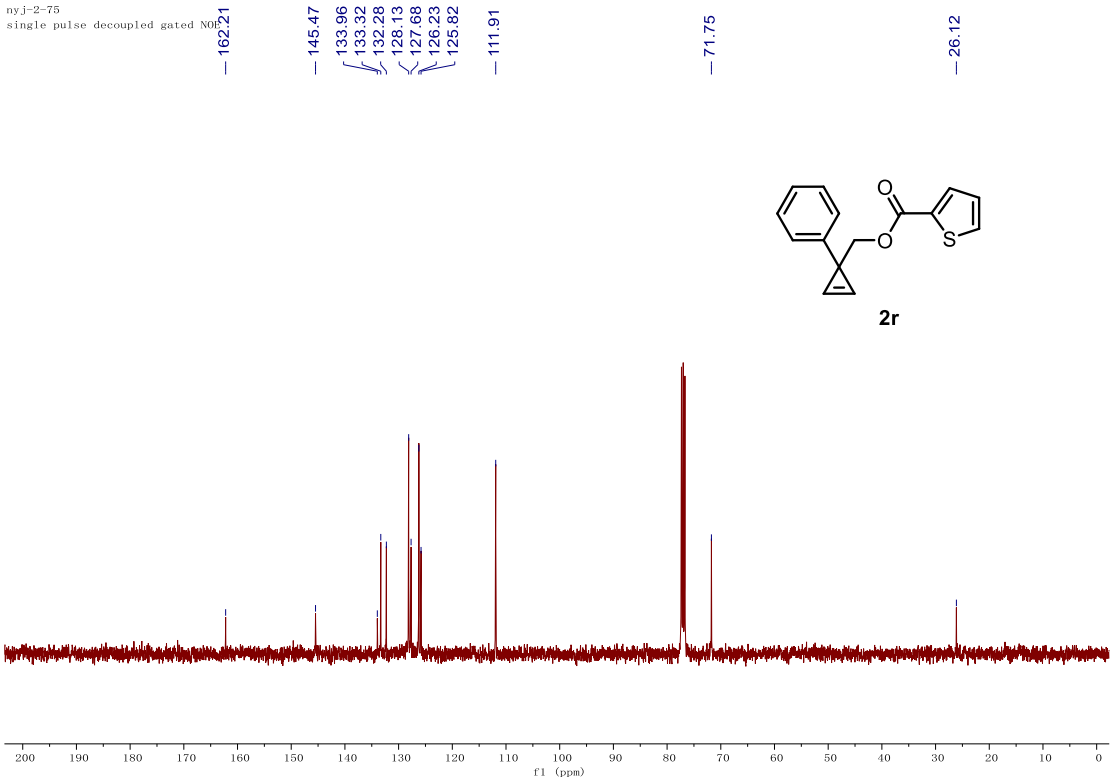
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2q**



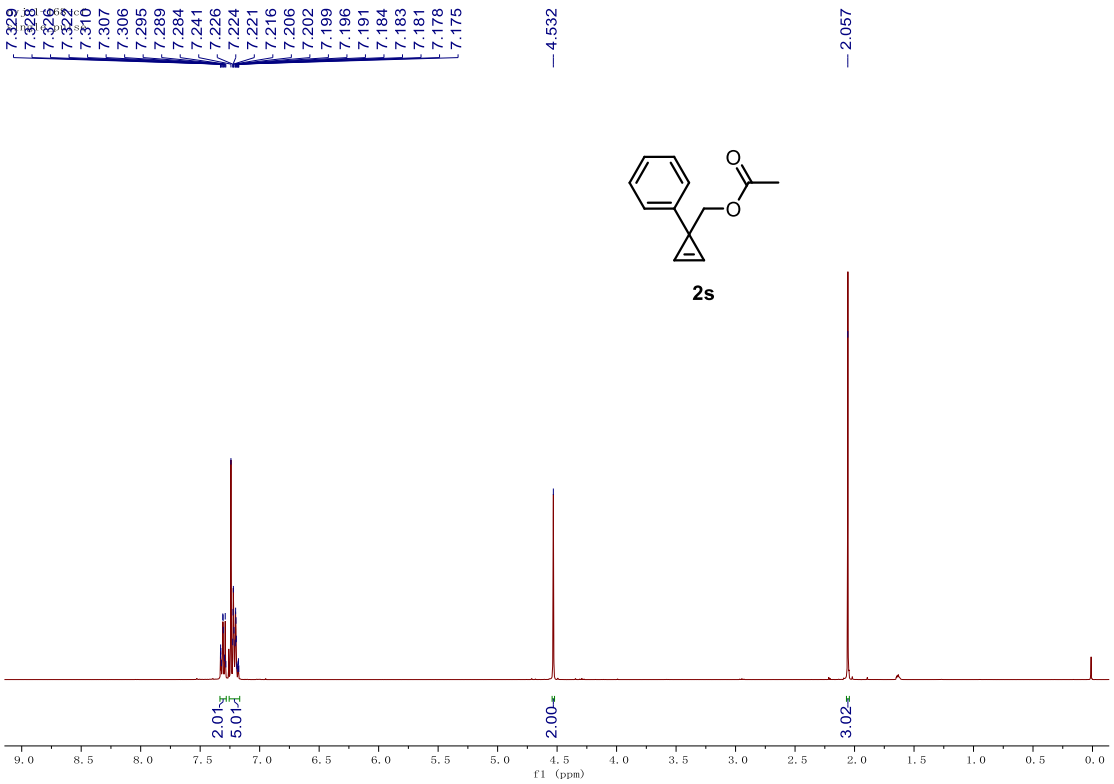


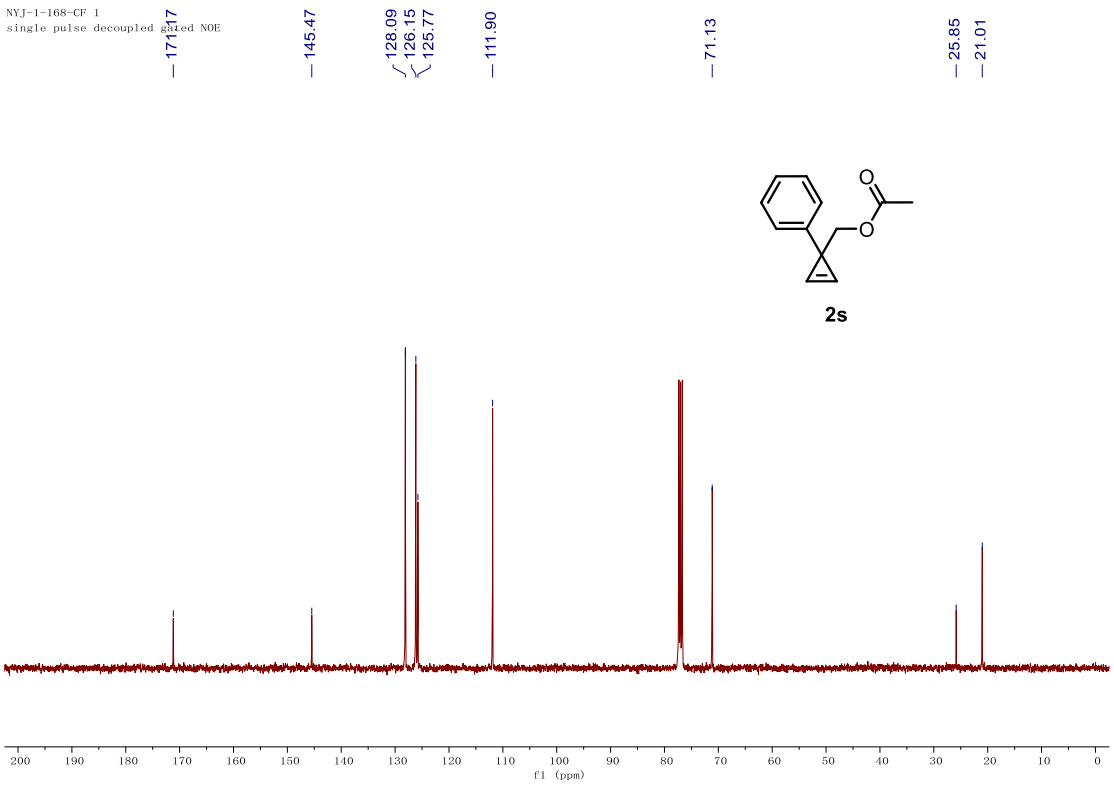
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2r**



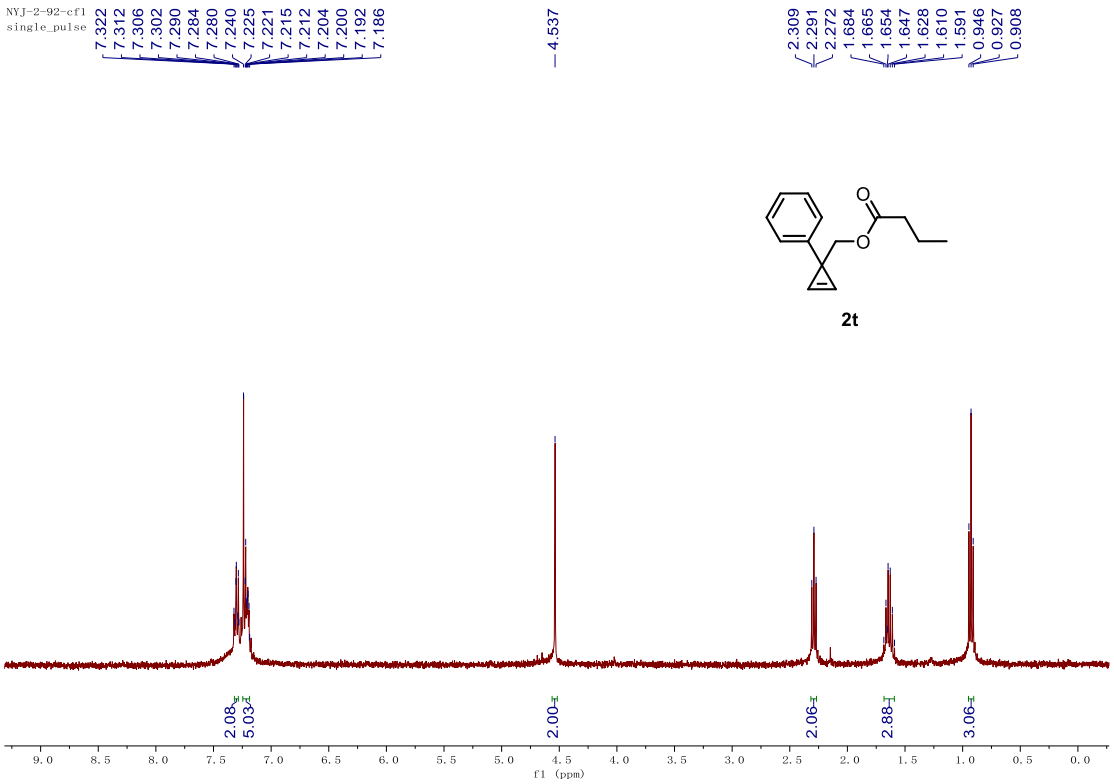


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2s**

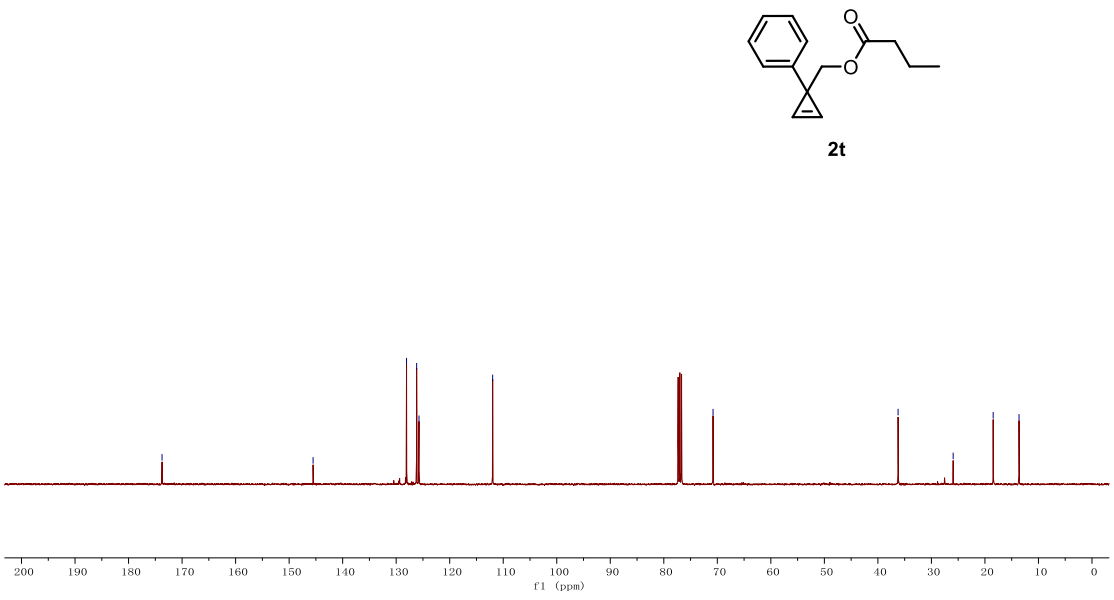




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2t**

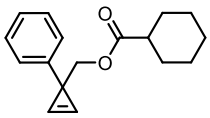


2t

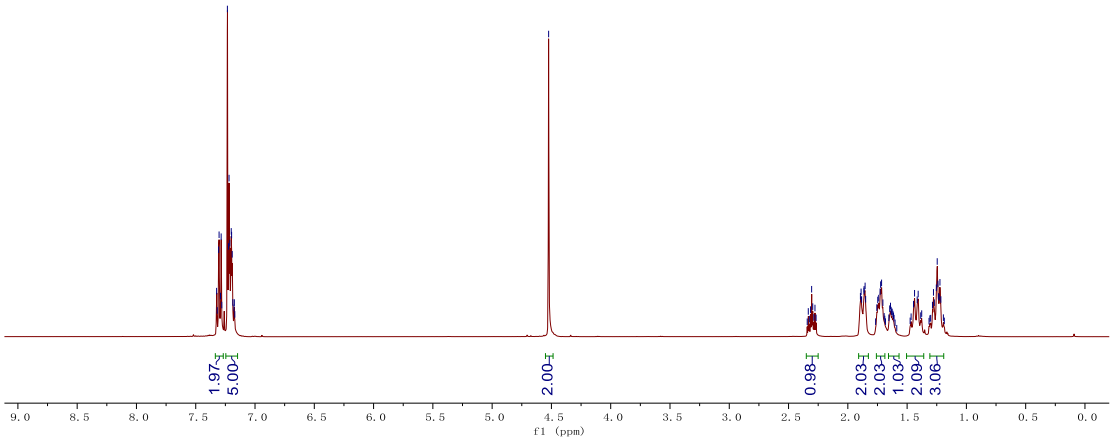


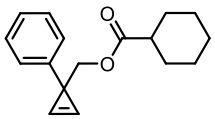
2t

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2u**



2u





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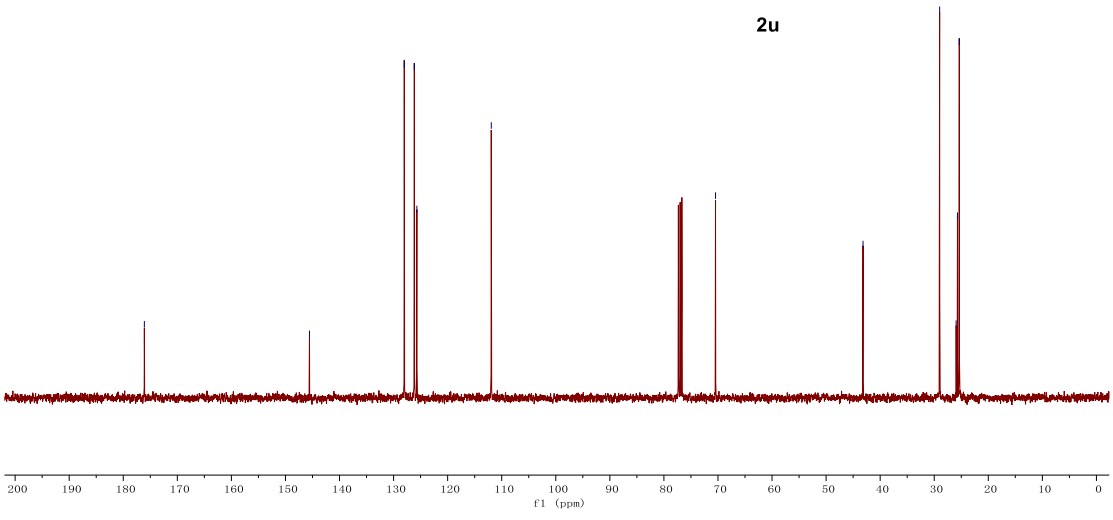
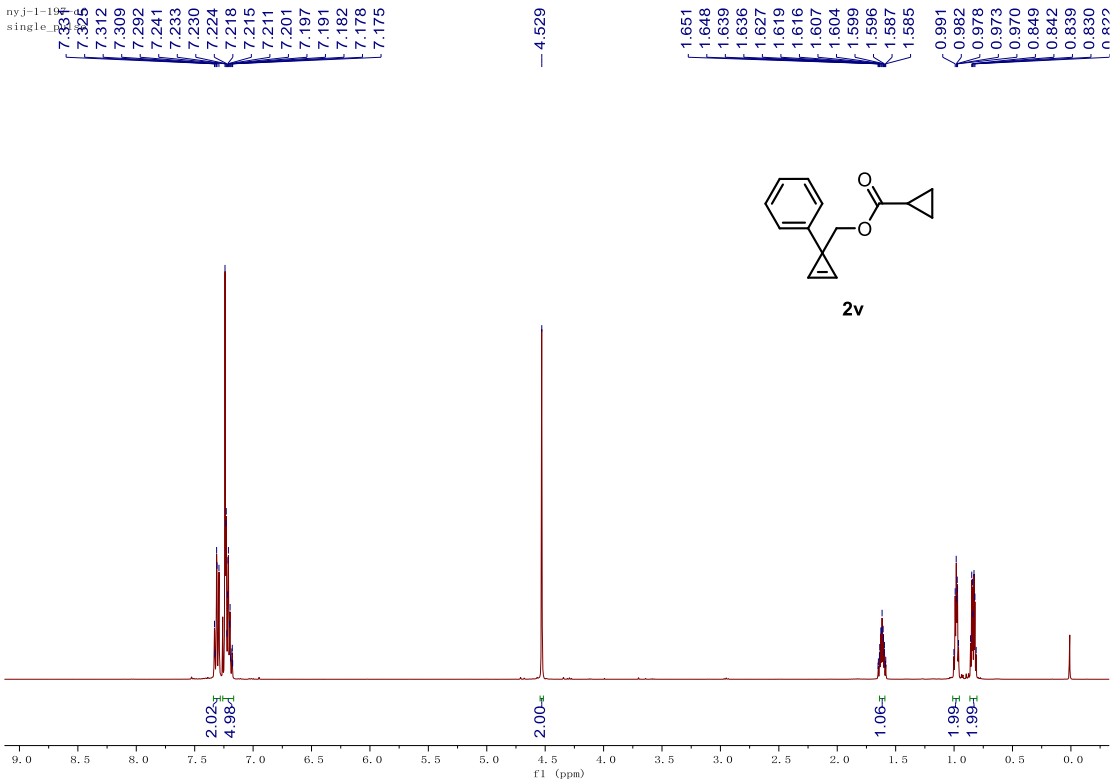
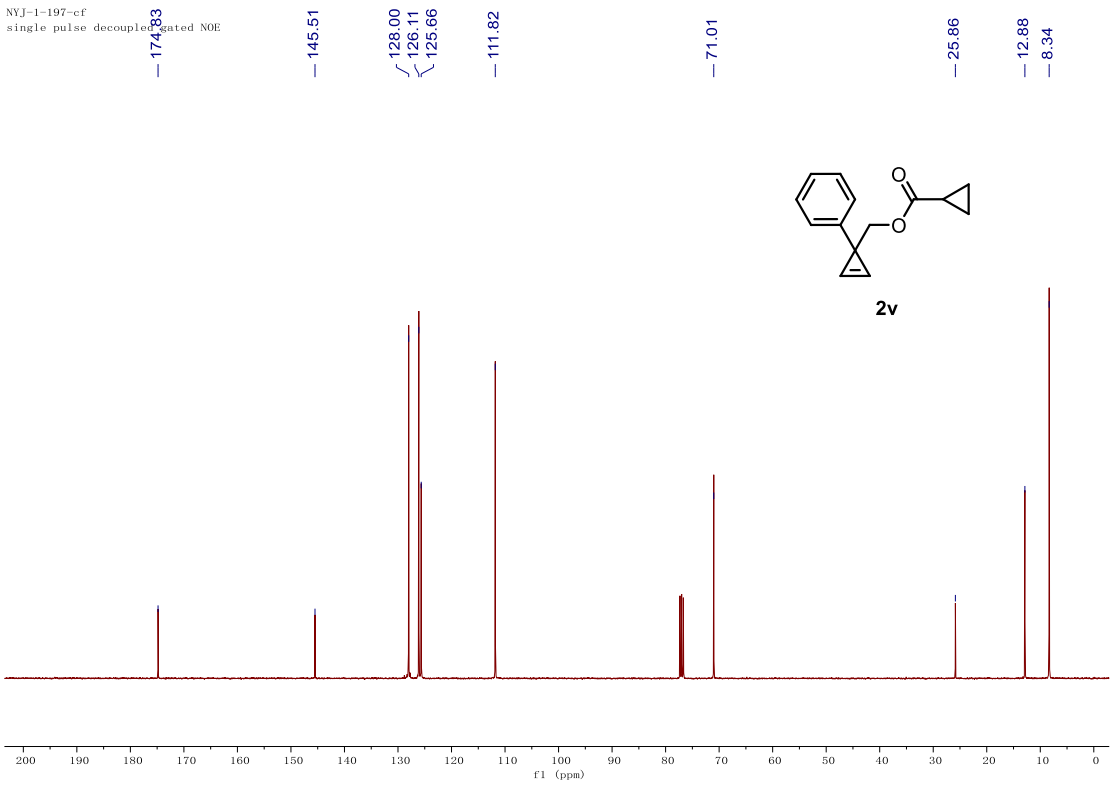
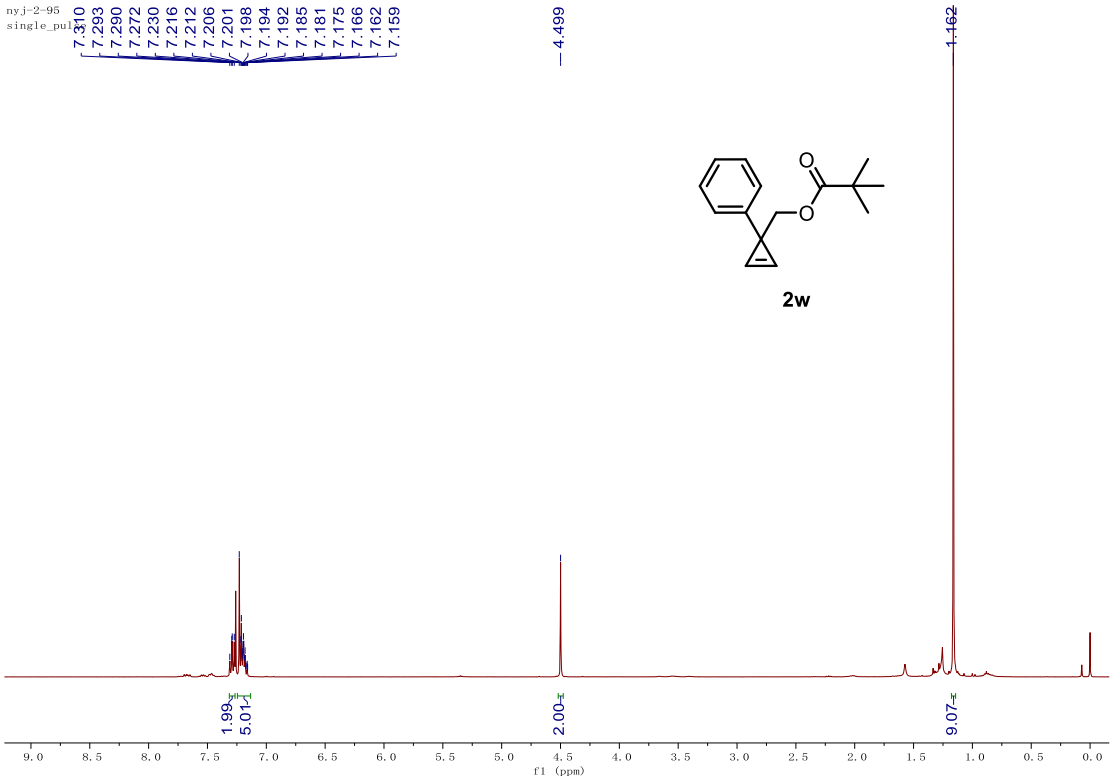


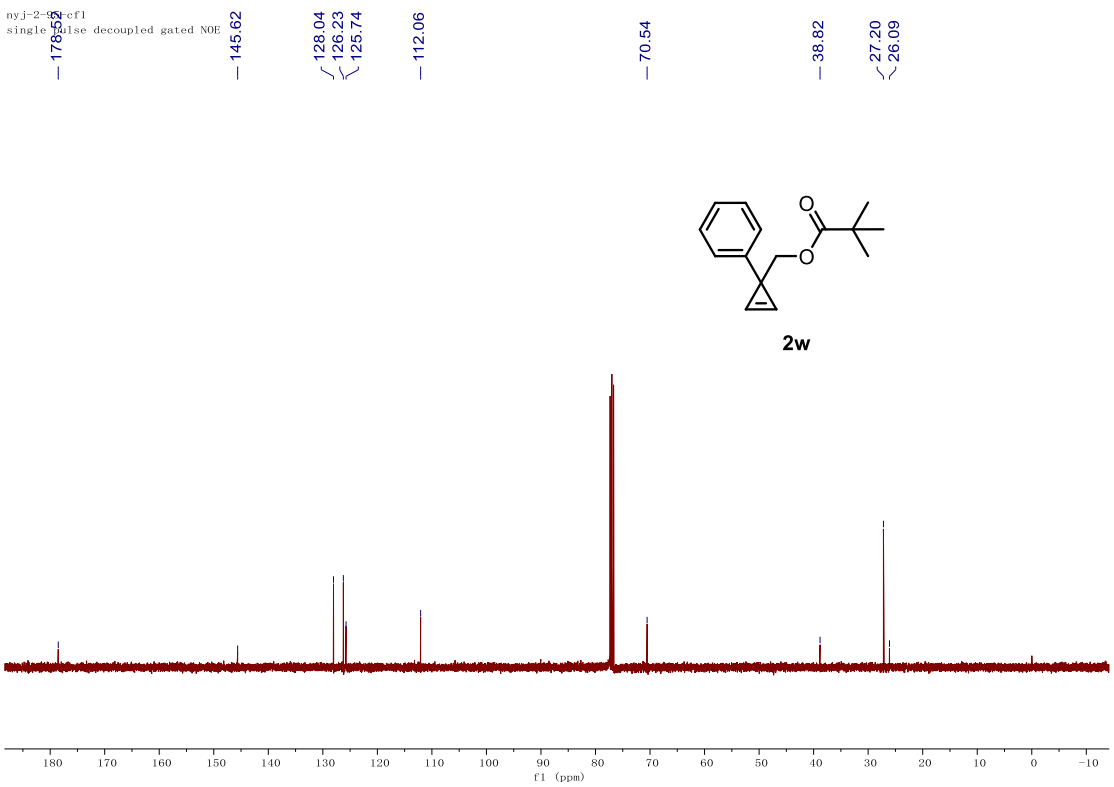
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2v**



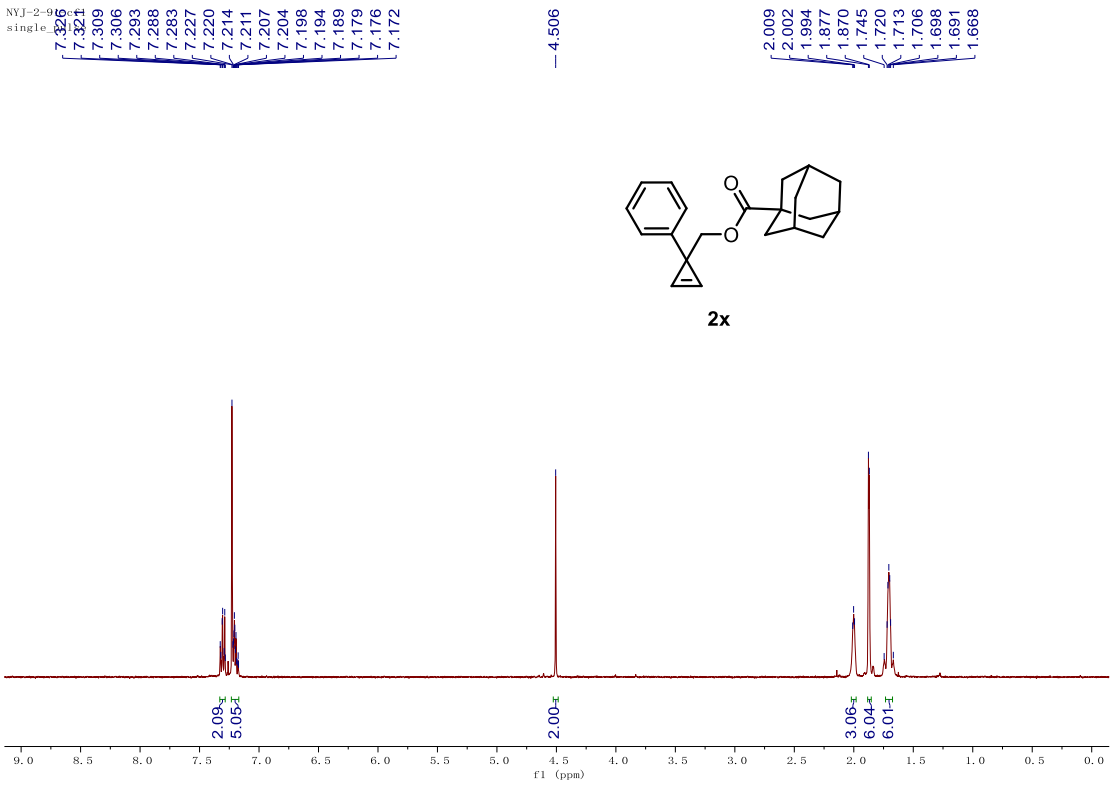


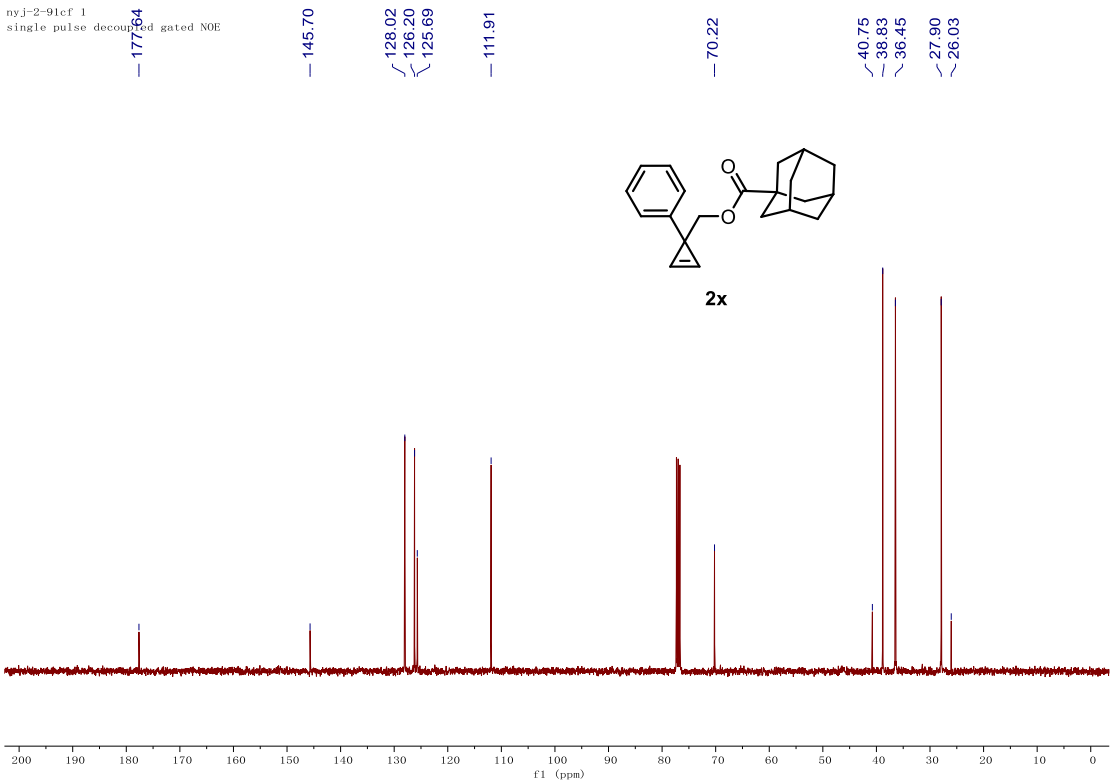
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2w**



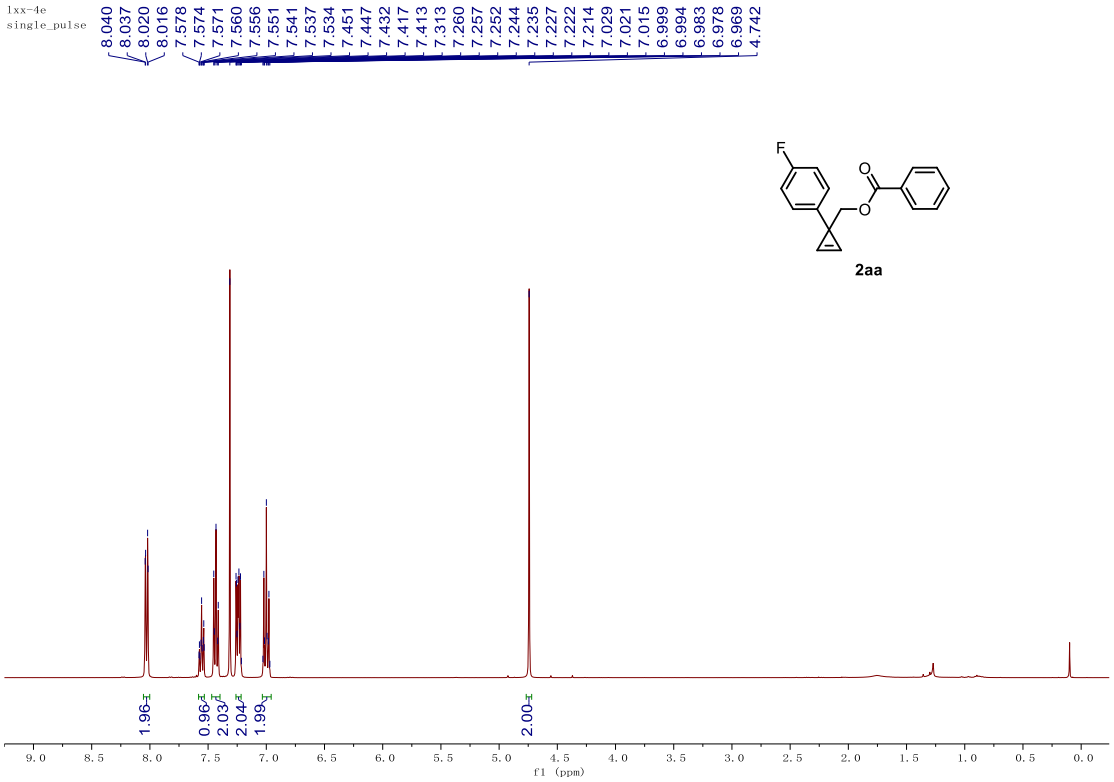


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2x**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2aa**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7.313
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7.244
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7.222
7.214
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7.015
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6.994
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6.978
6.969
4.742
F
O
O
2aa
1.96
0.96
2.03
2.04
1.99
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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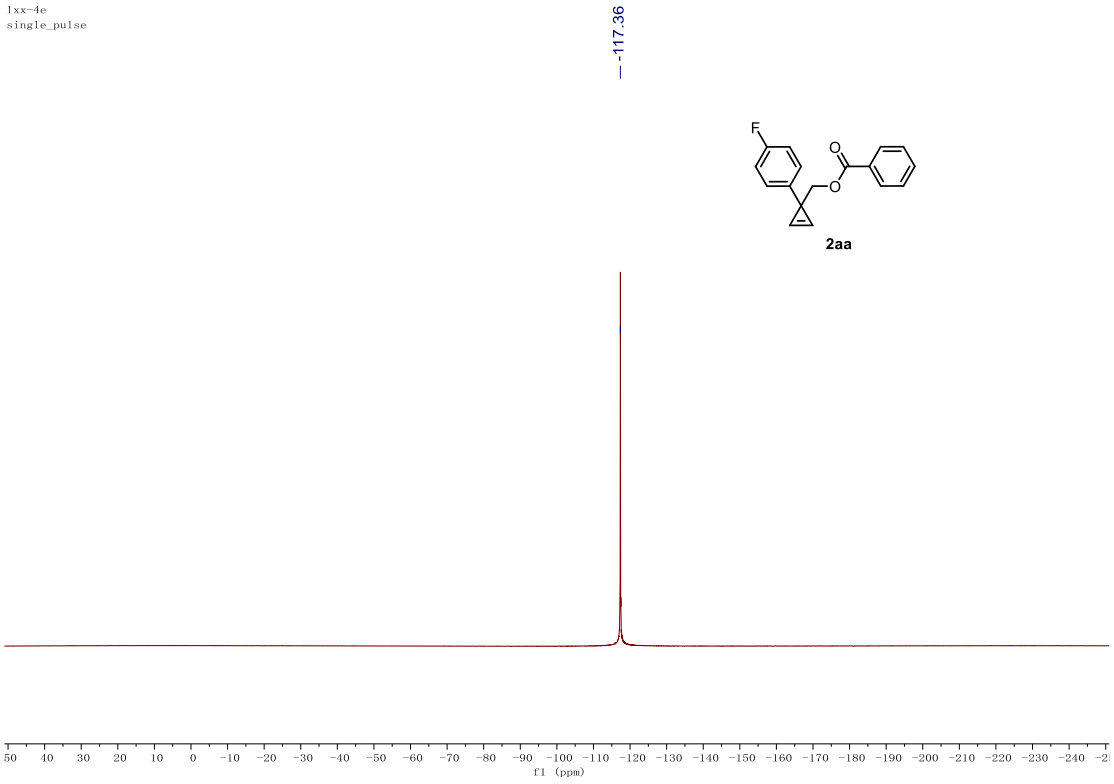
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


lxx-4e
single_pulse
-117.36
F
O
O
2aa
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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-150
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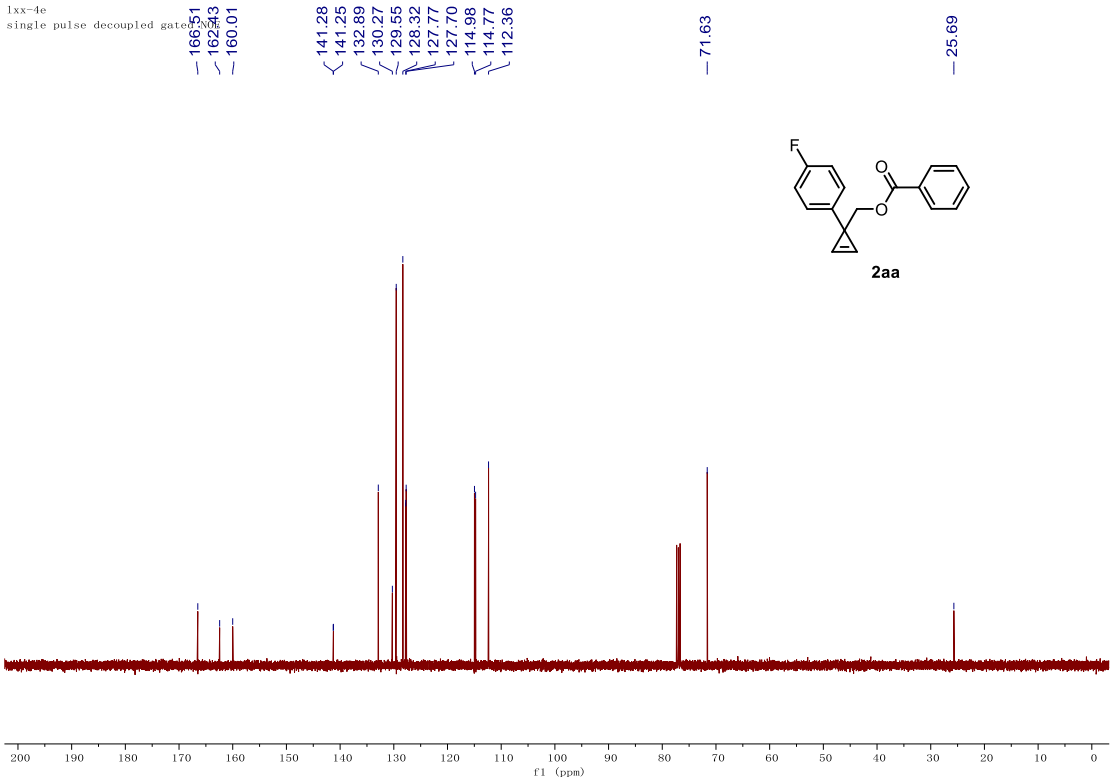
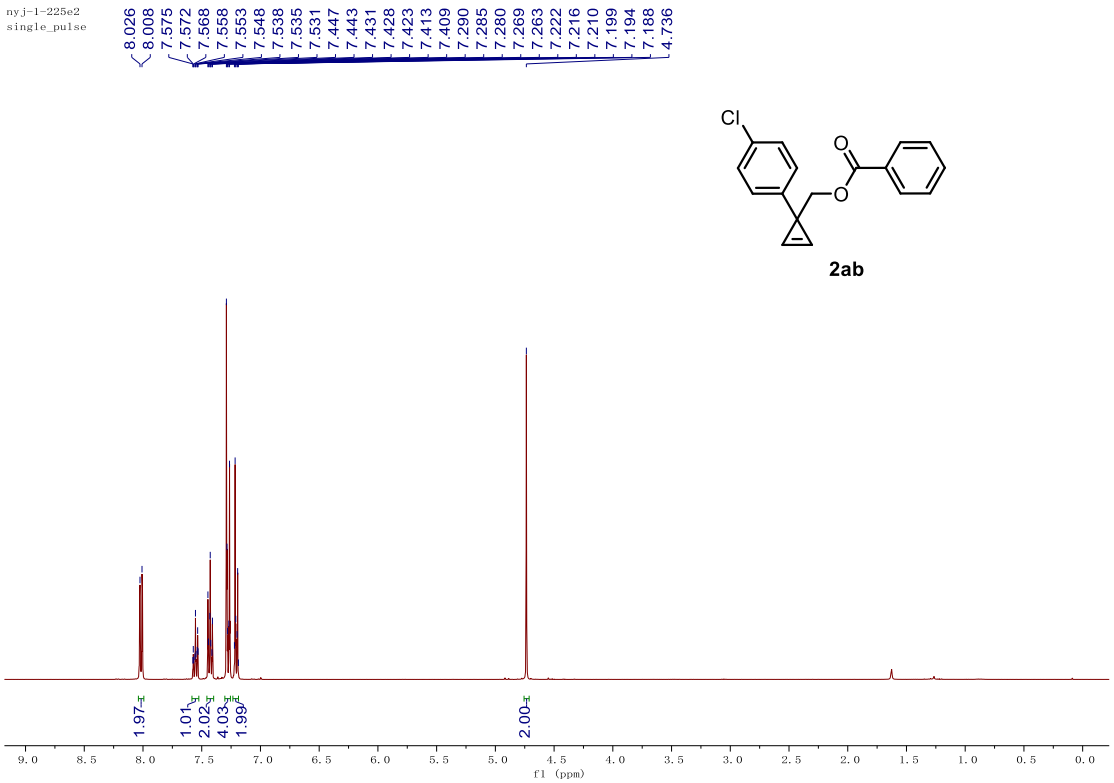
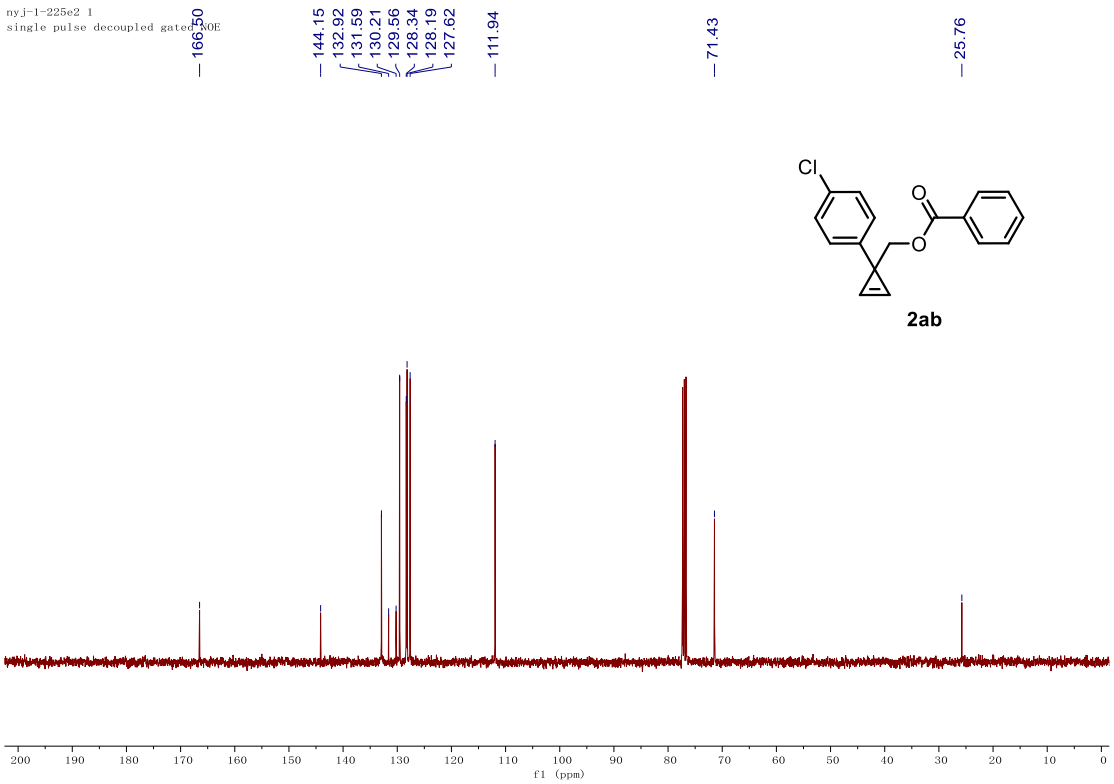
-240
f1 (ppm)

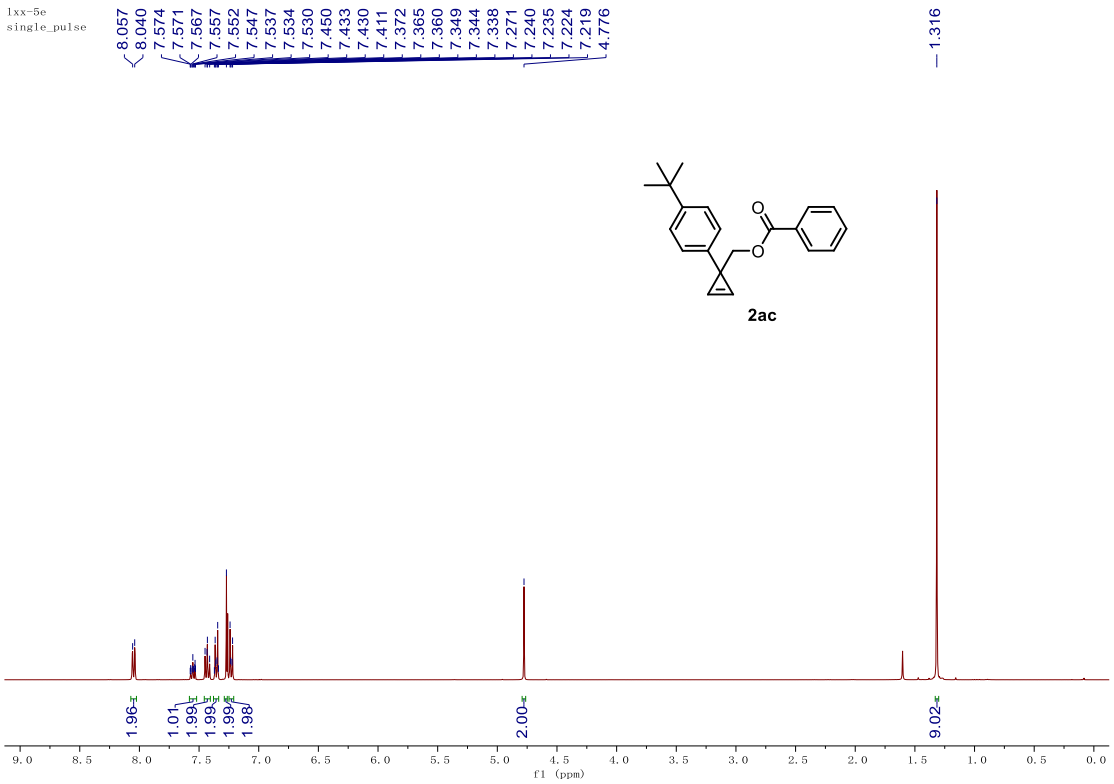


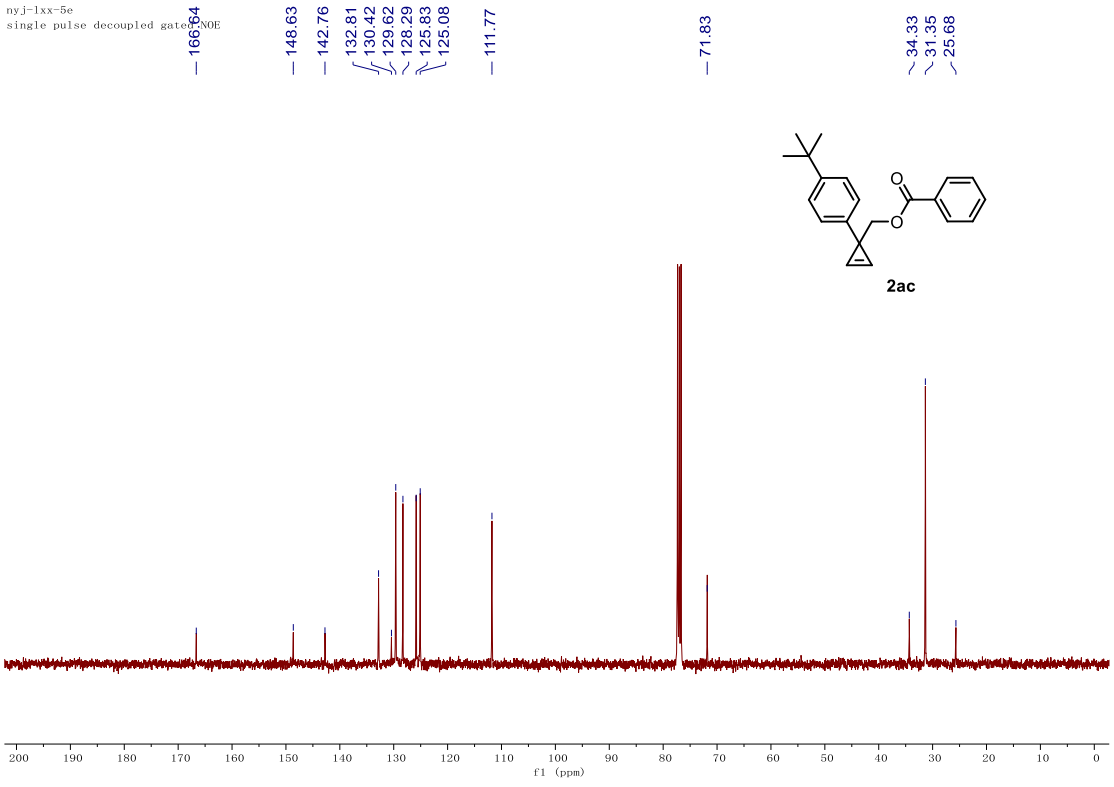
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2ab**



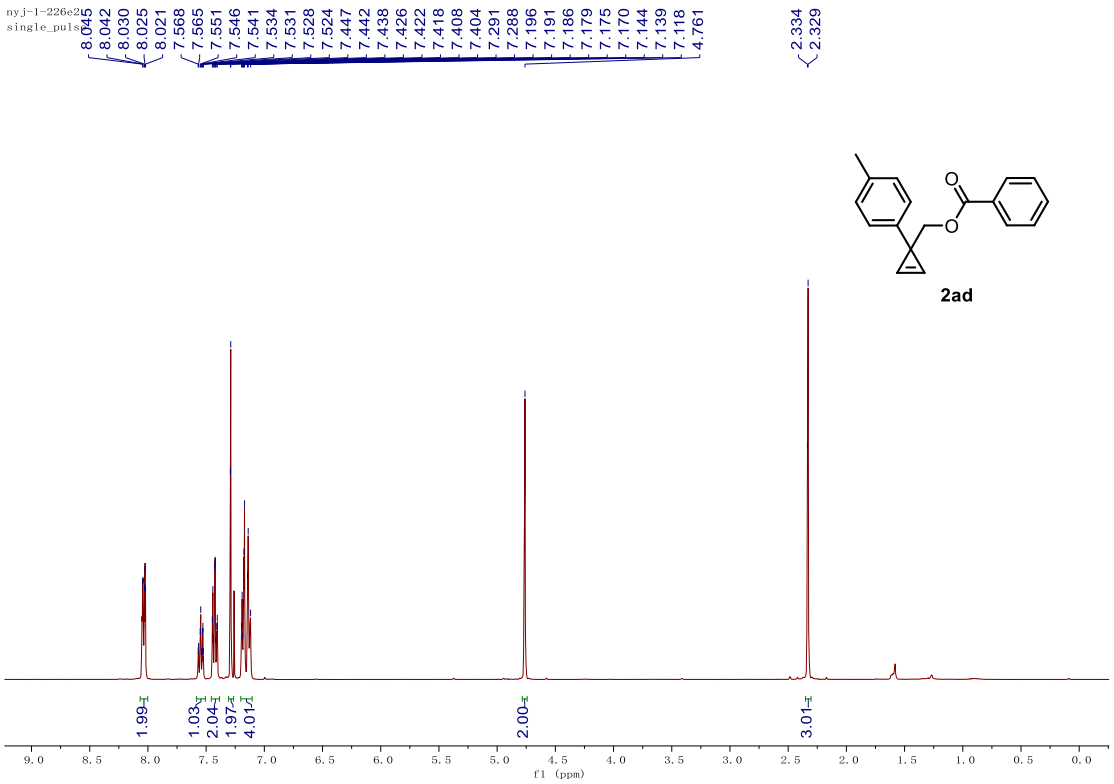


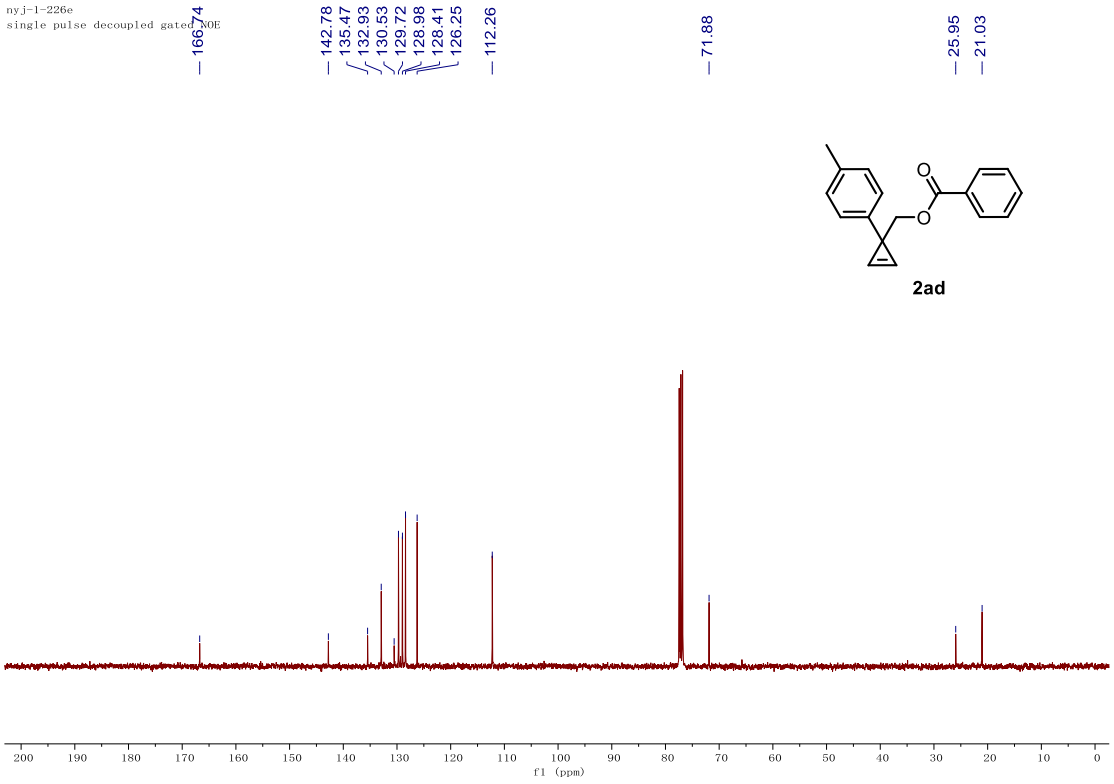
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2ac**



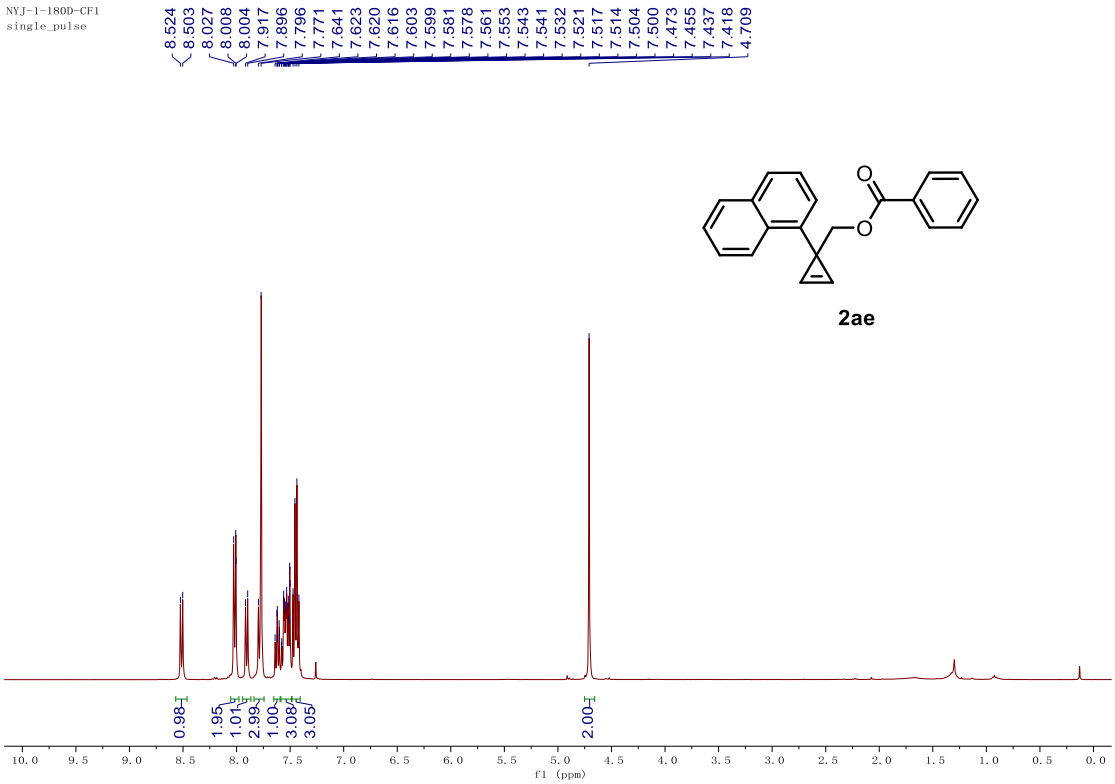


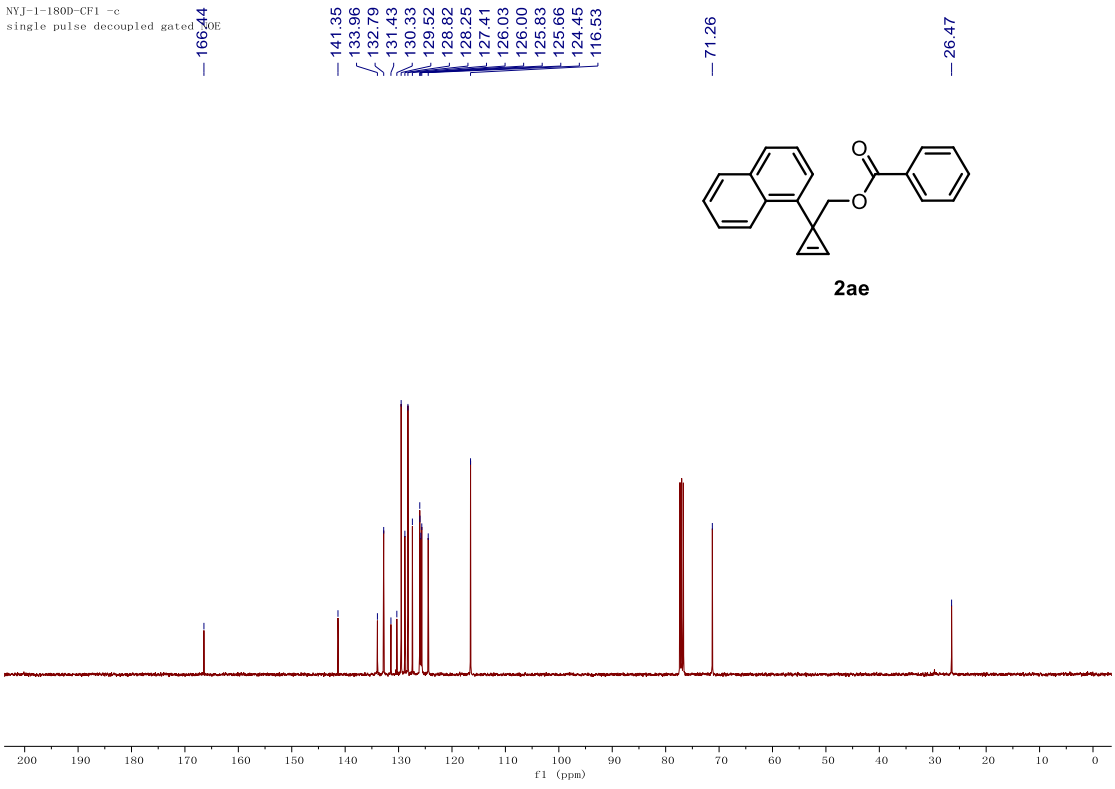
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2ad**



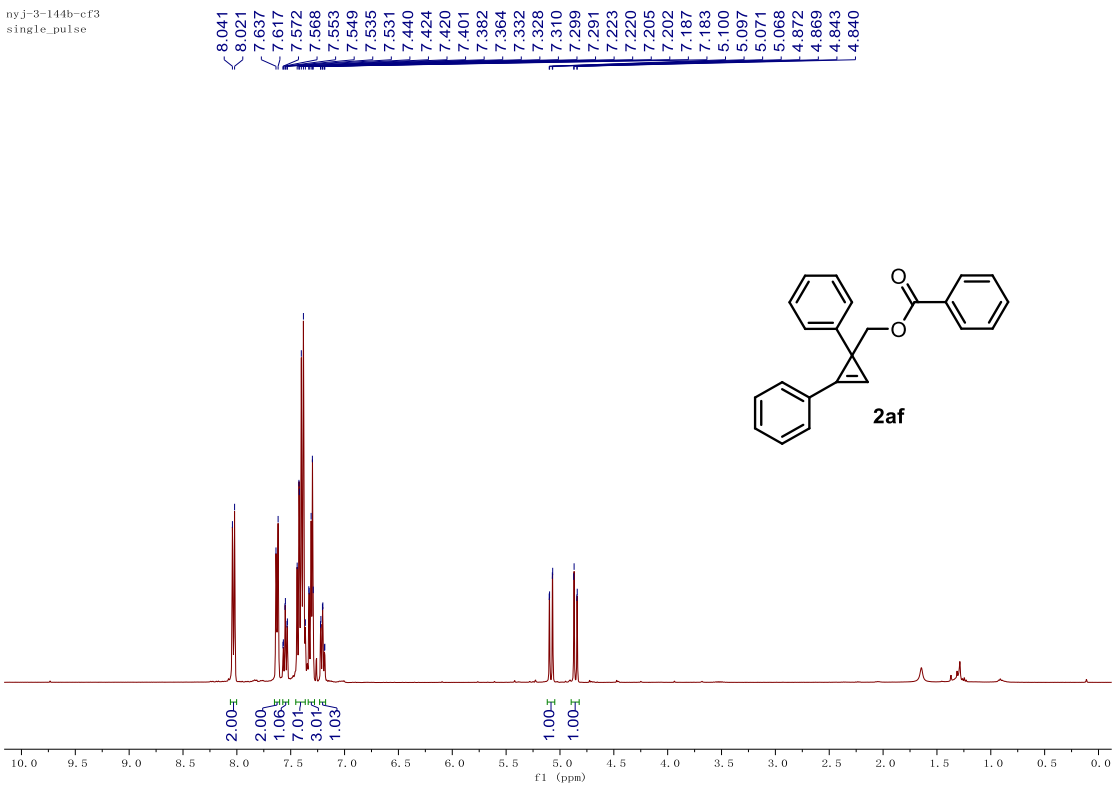


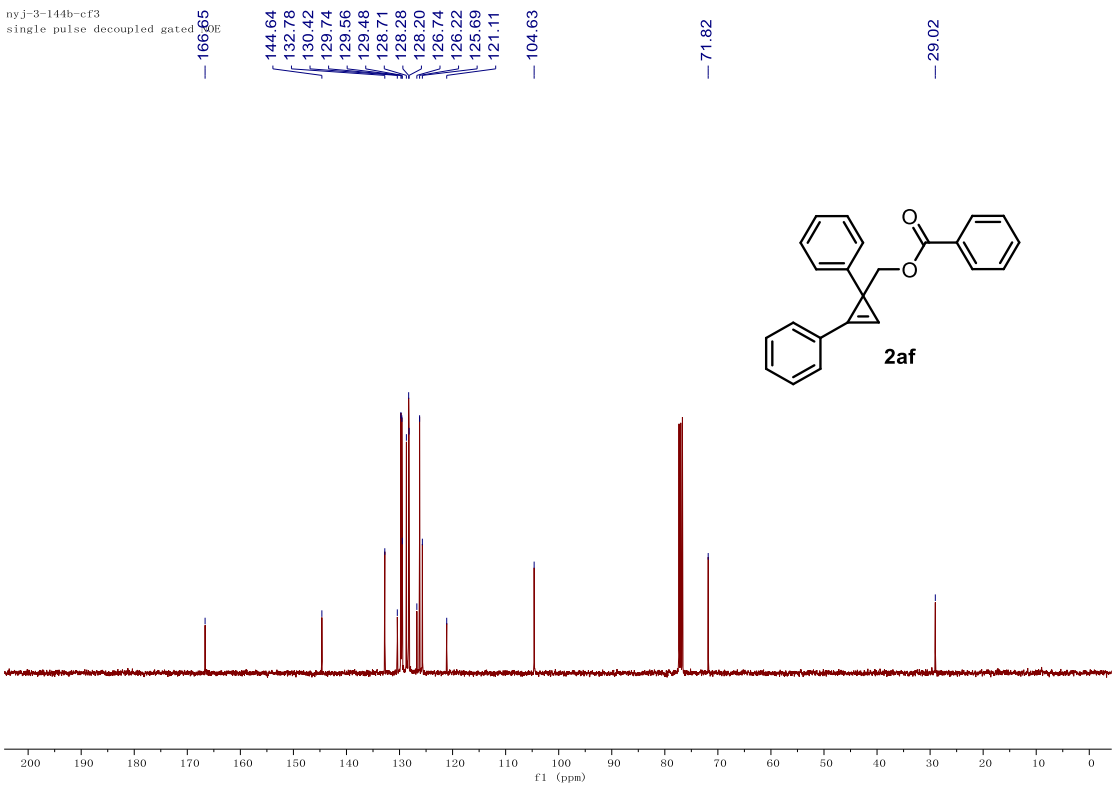
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2ae**



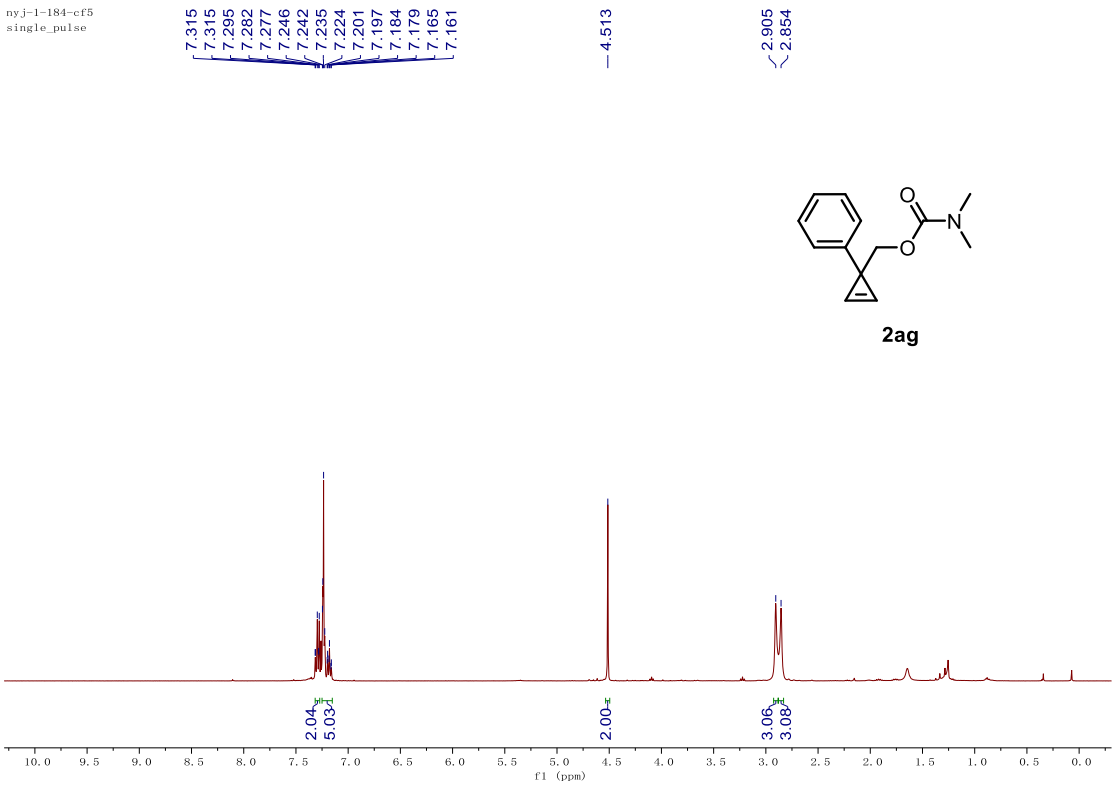


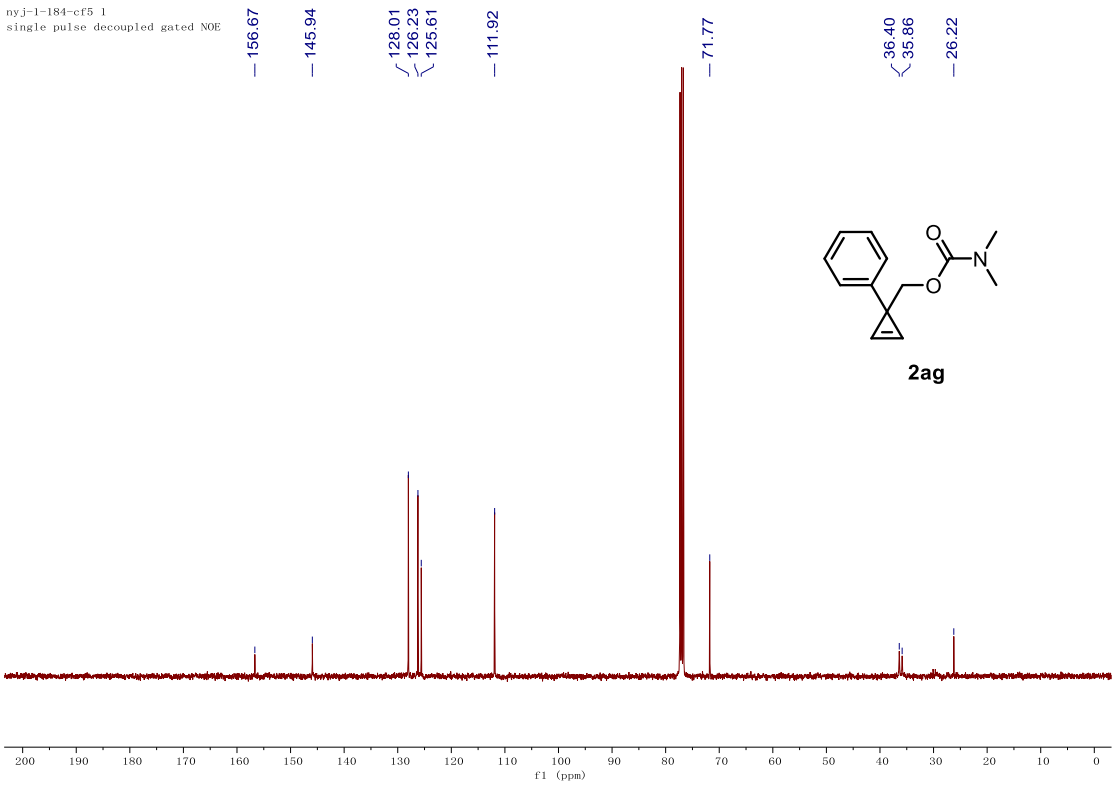
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2af**





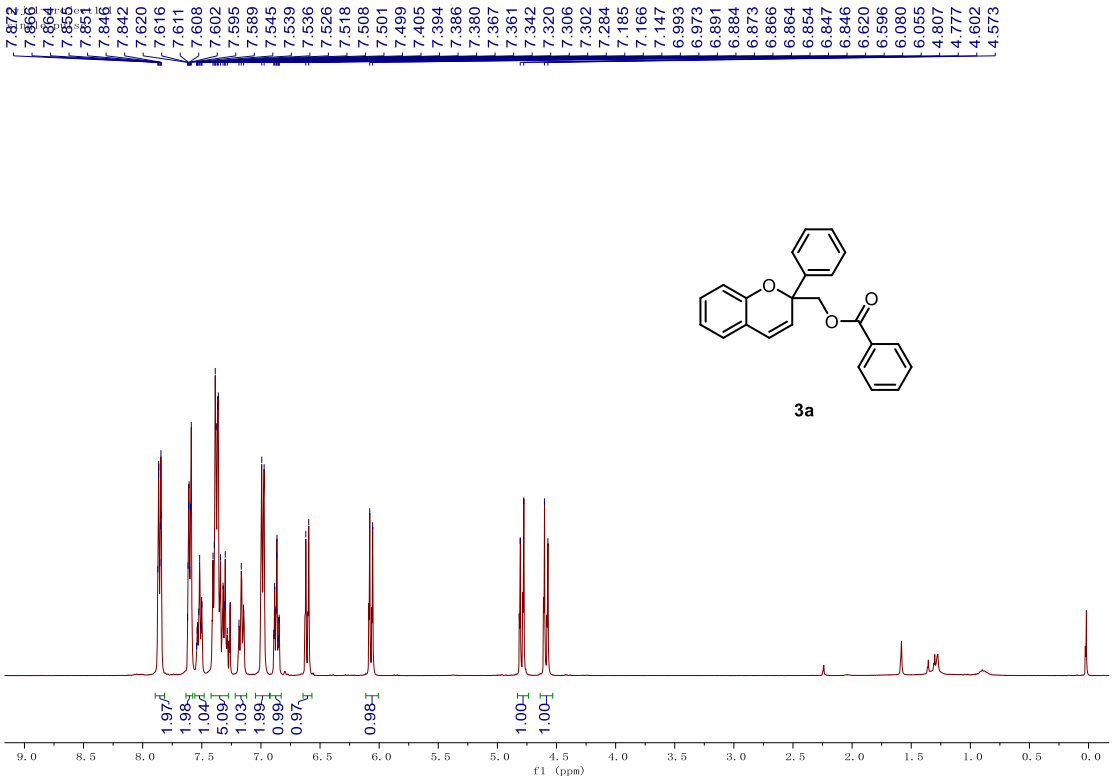
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2ag**

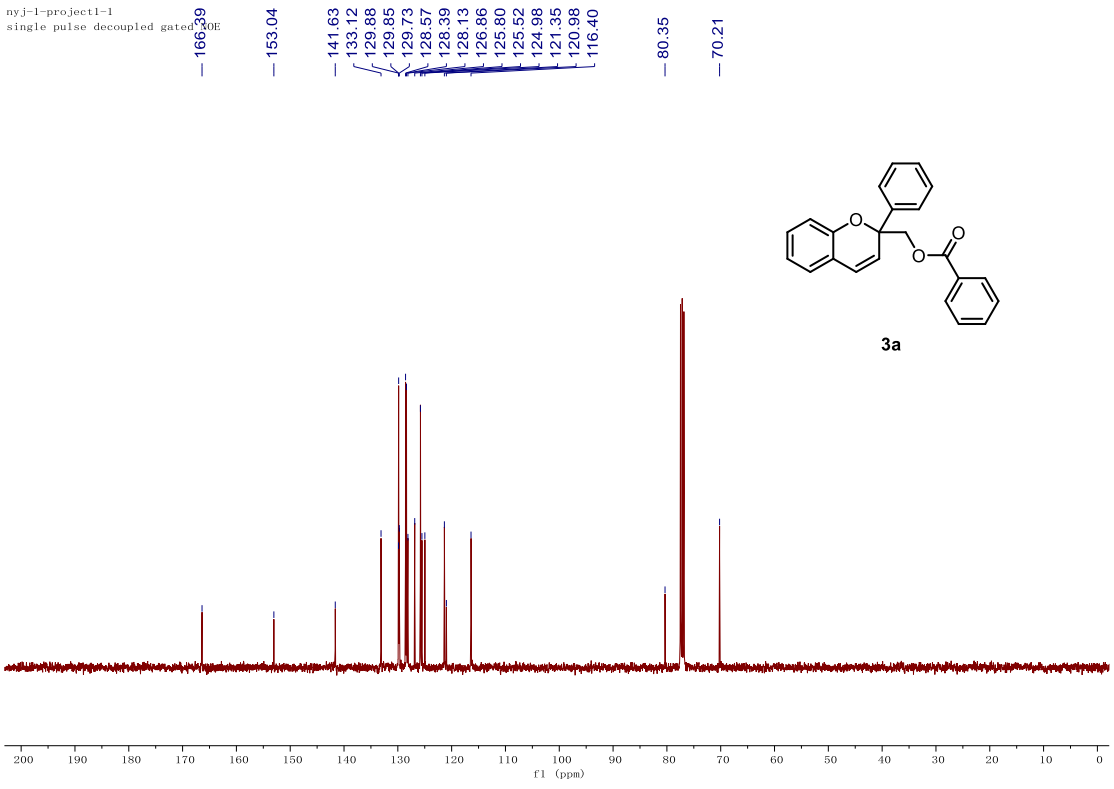

nyj-1-184-cf5
single_pulse
7.315
7.315
7.295
7.282
7.277
7.246
7.242
7.235
7.224
7.201
7.197
7.184
7.179
7.165
7.161
4.513
2.905
2.854
2ag
2.04
5.03
2.00
3.06
3.08
f1 (ppm)


nyj-1-184-cf5 1
single pulse decoupled gated NOE
156.67
145.94
128.01
126.23
125.61
111.92
71.77
36.40
35.86
26.22
2ag
f1 (ppm)

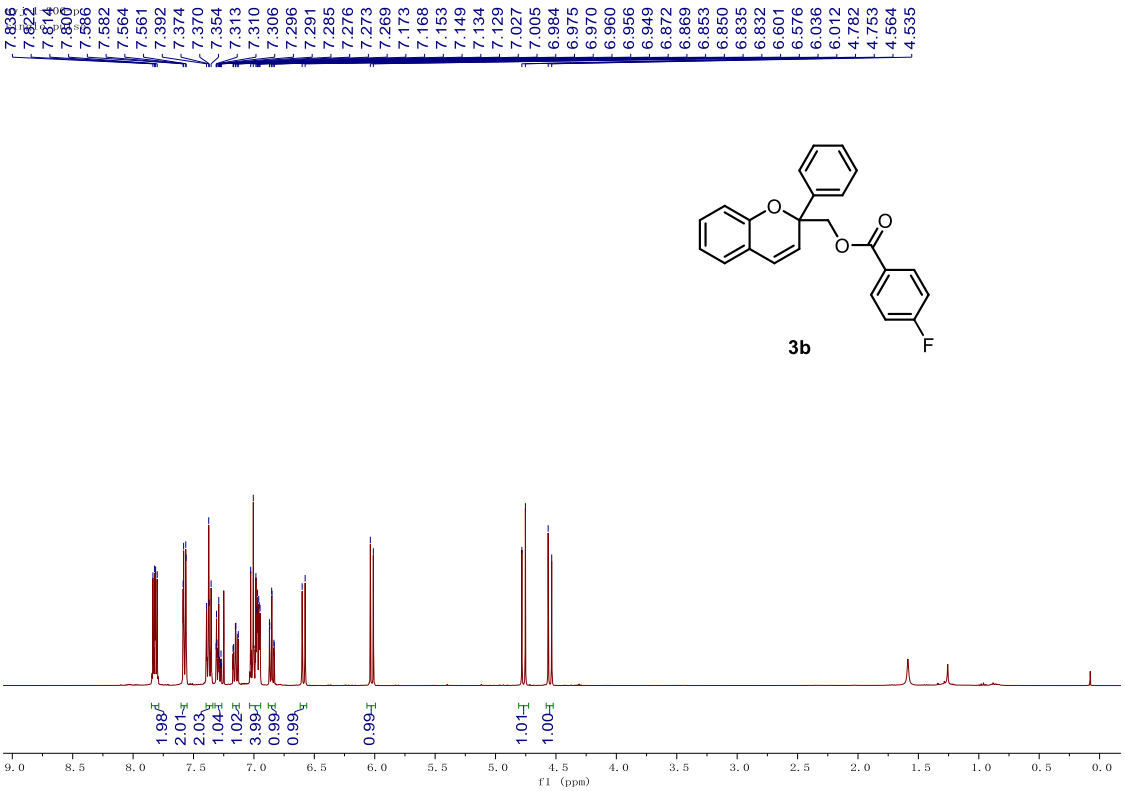
^{1}H NMR and ^{13}C NMR Spectra of Products **3** and **4**

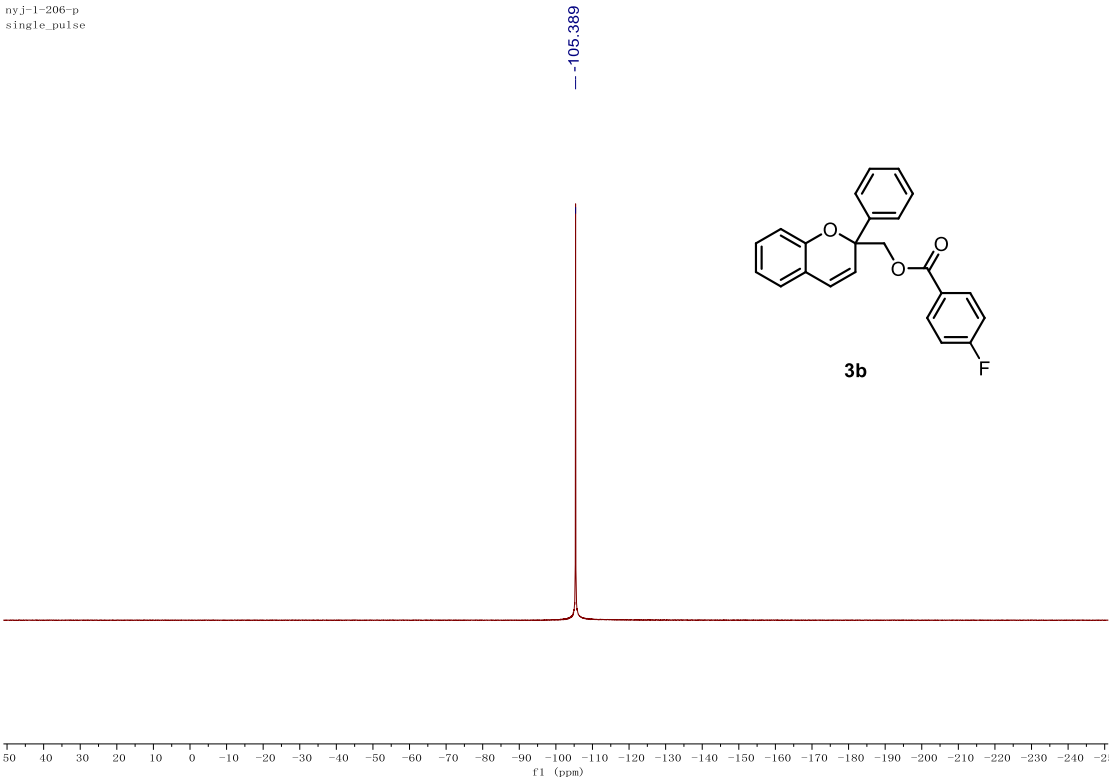
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3a**

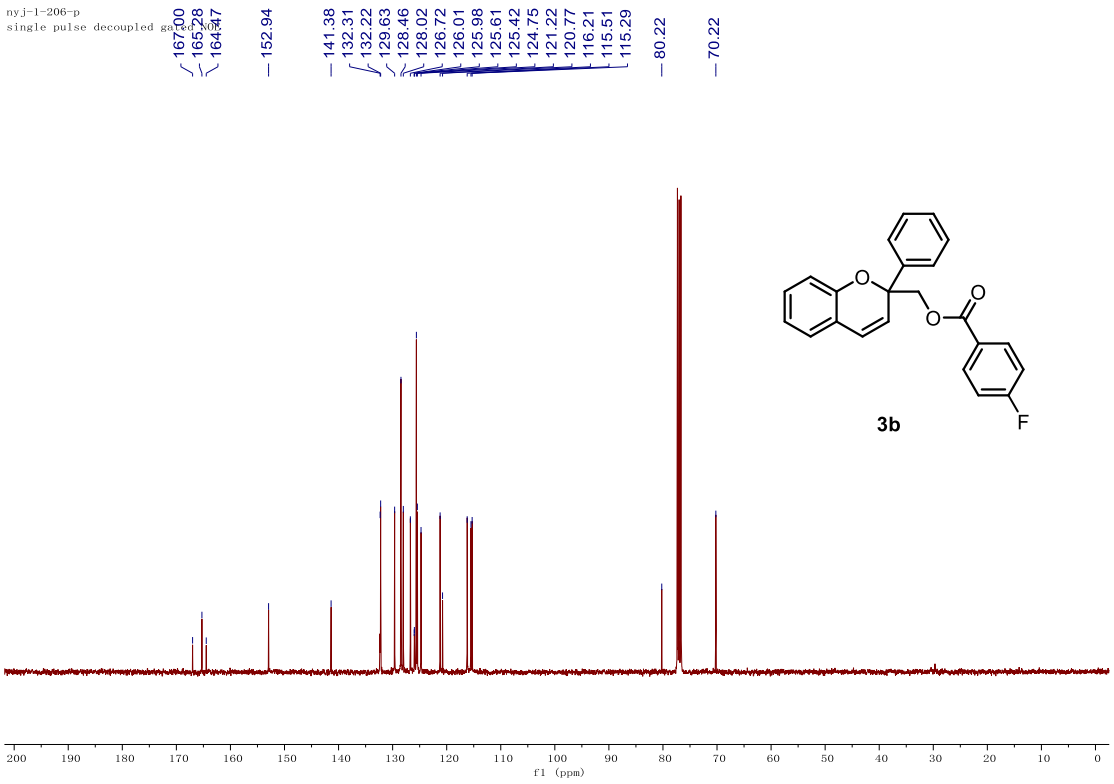




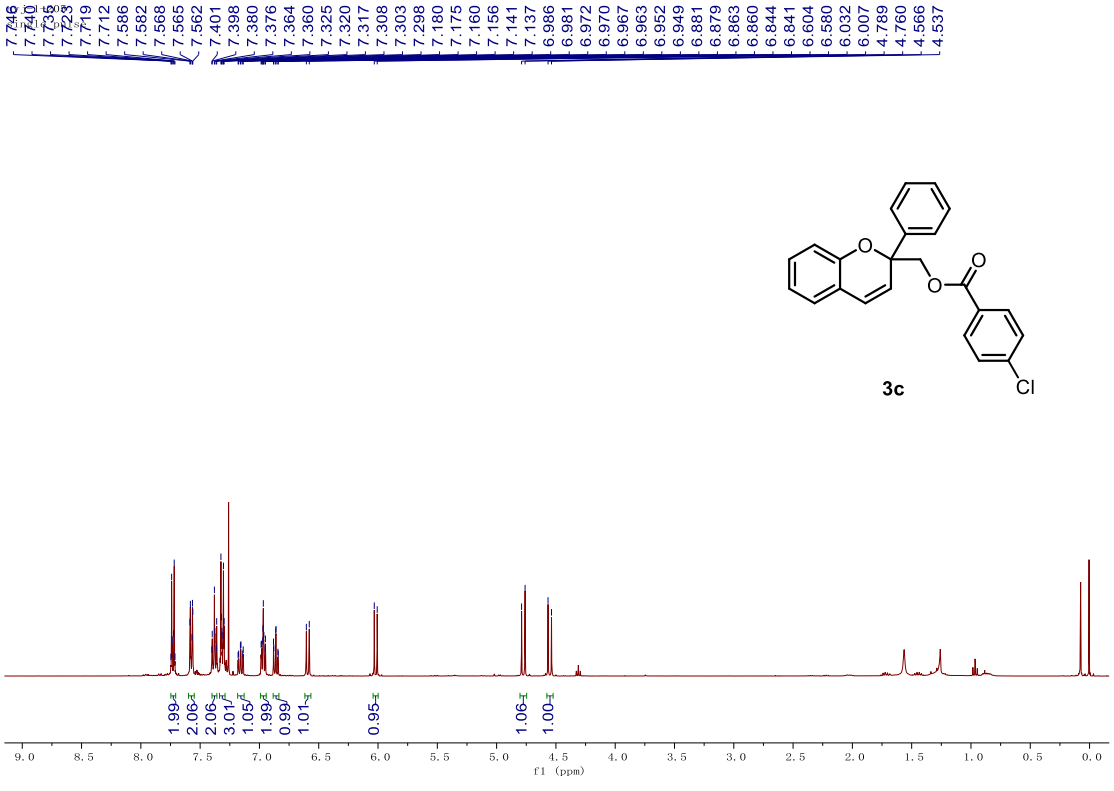
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3b**

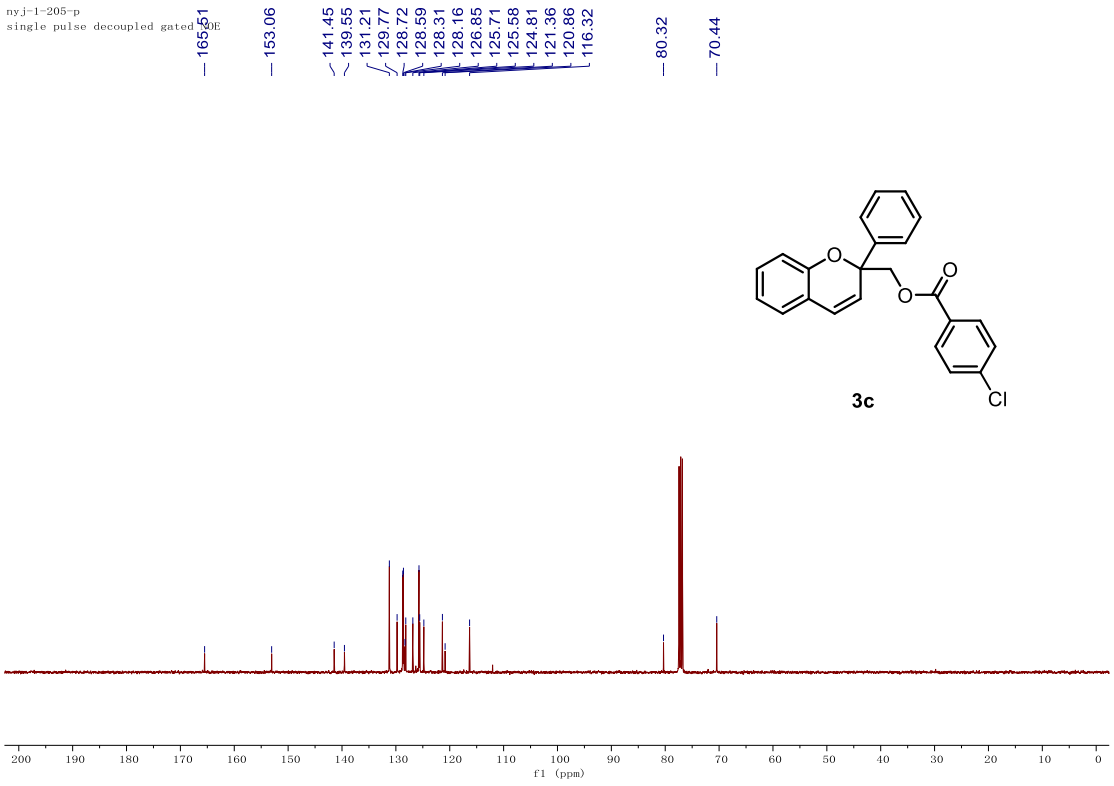




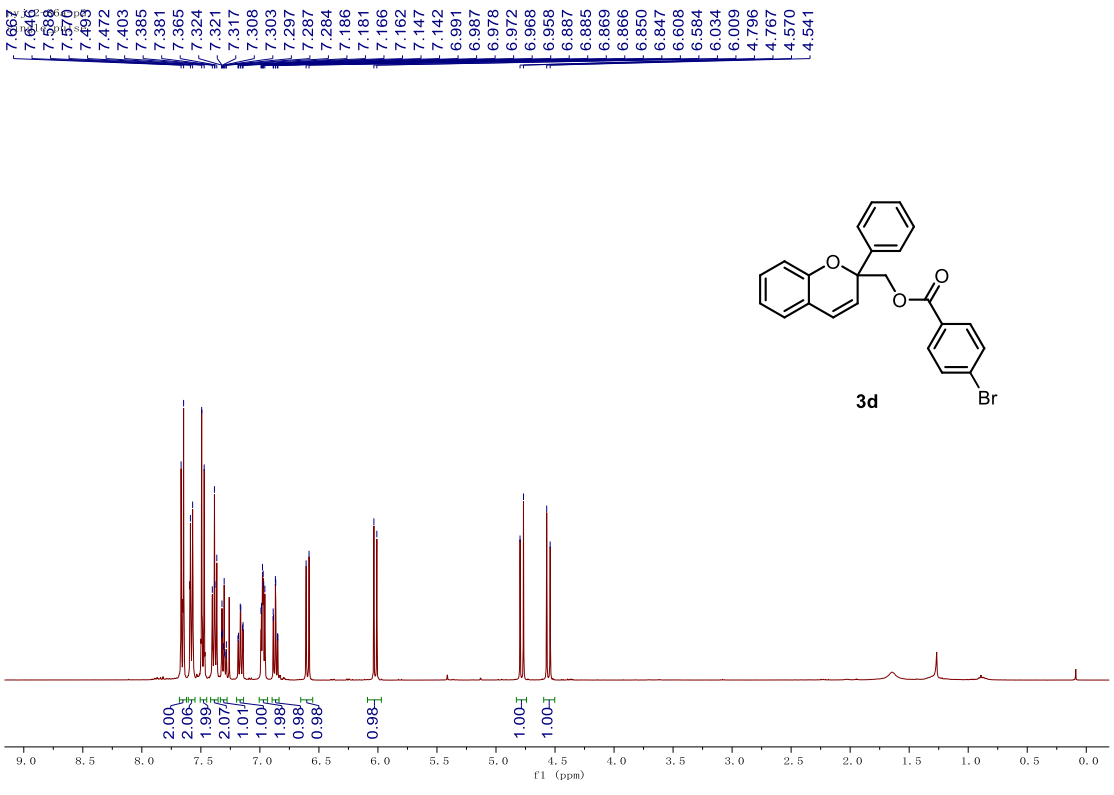


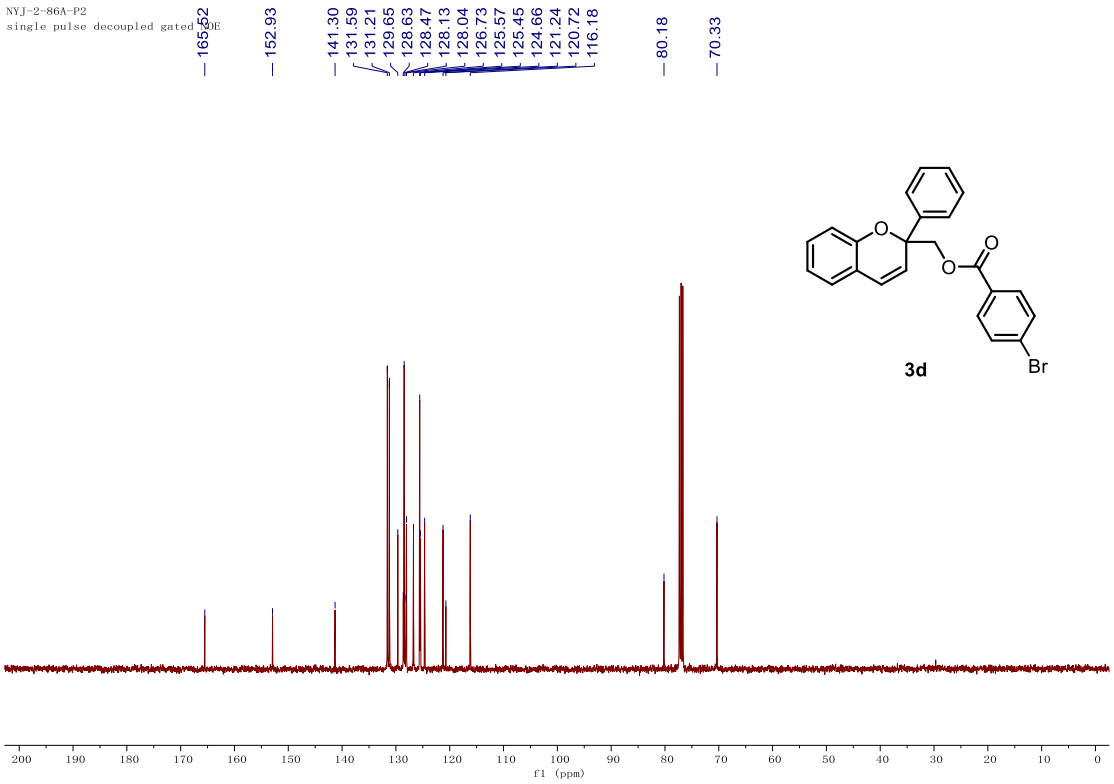
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3c**



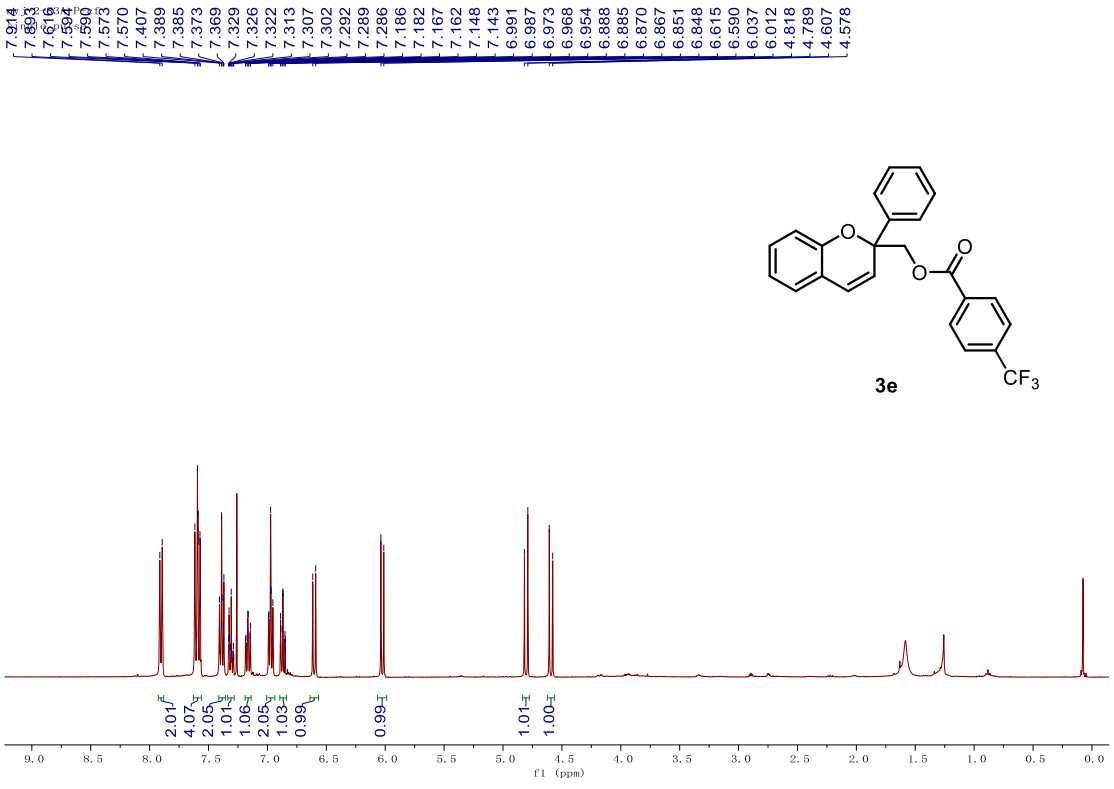


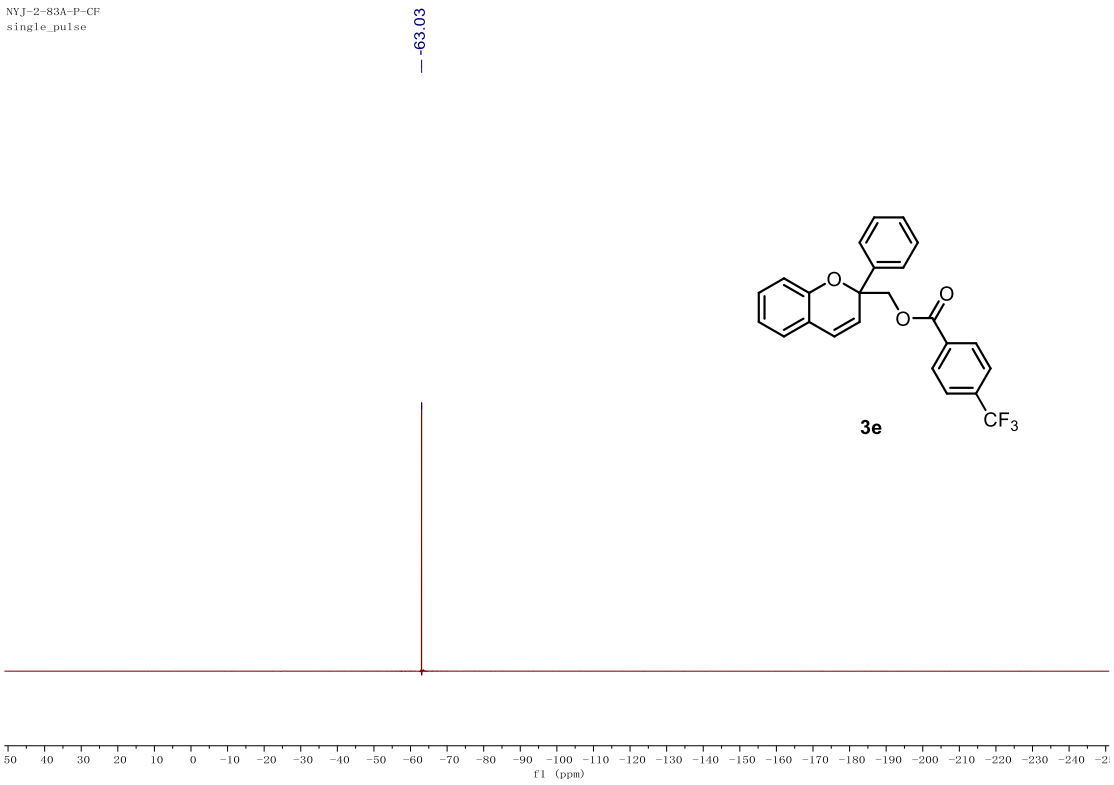
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3d**

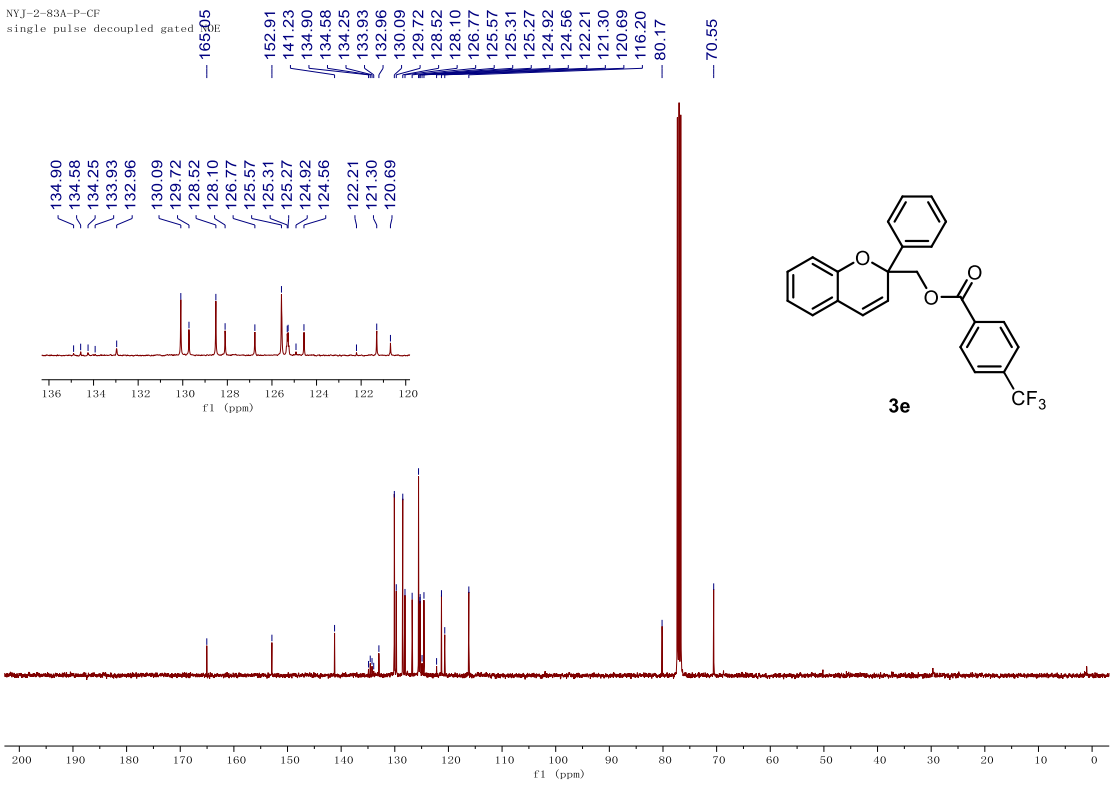




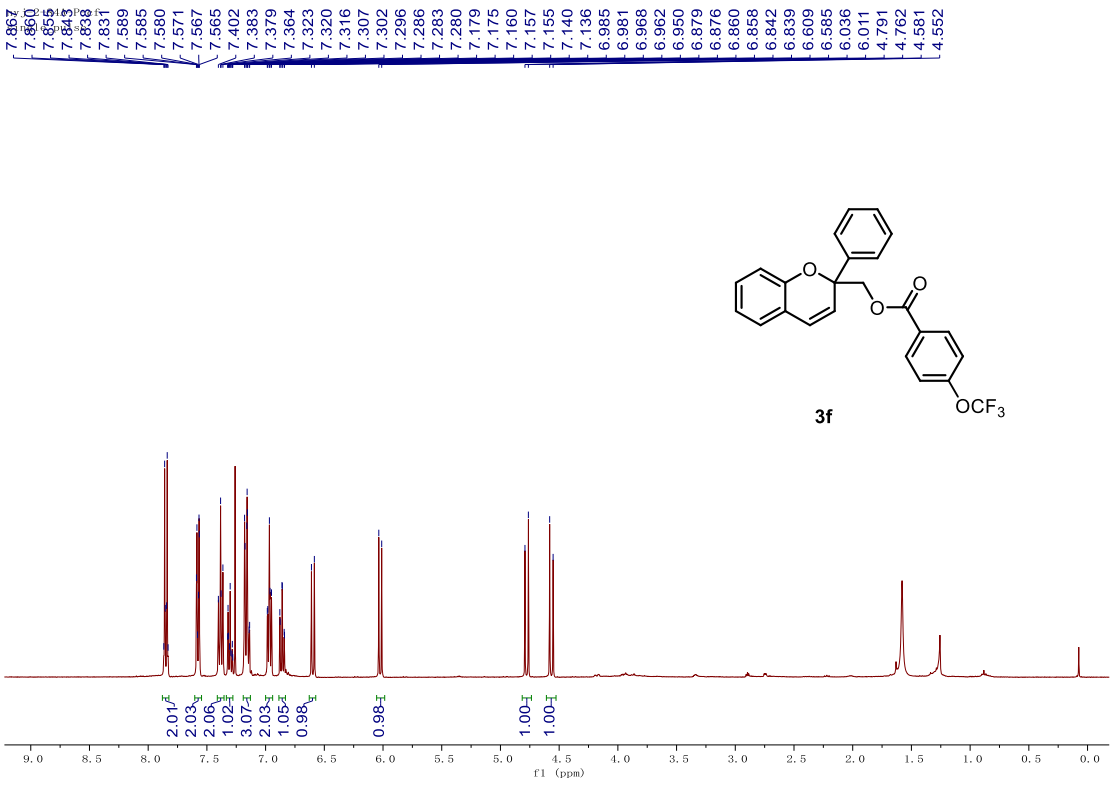
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3e**

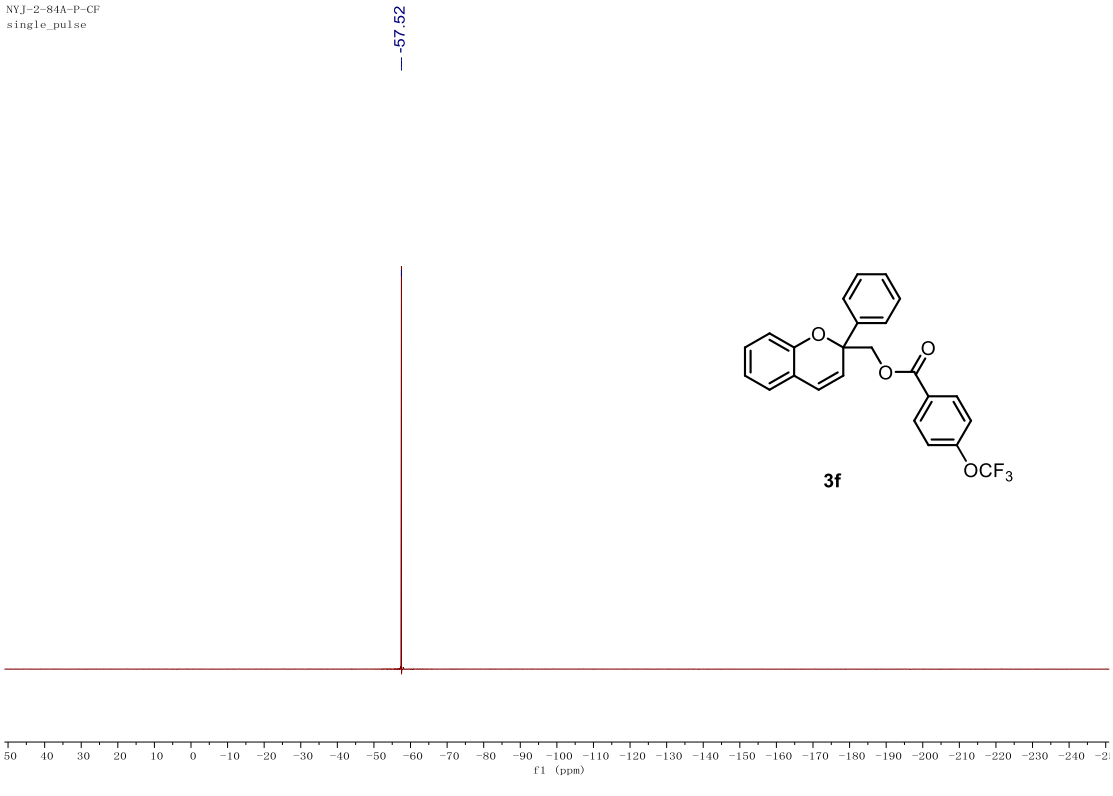


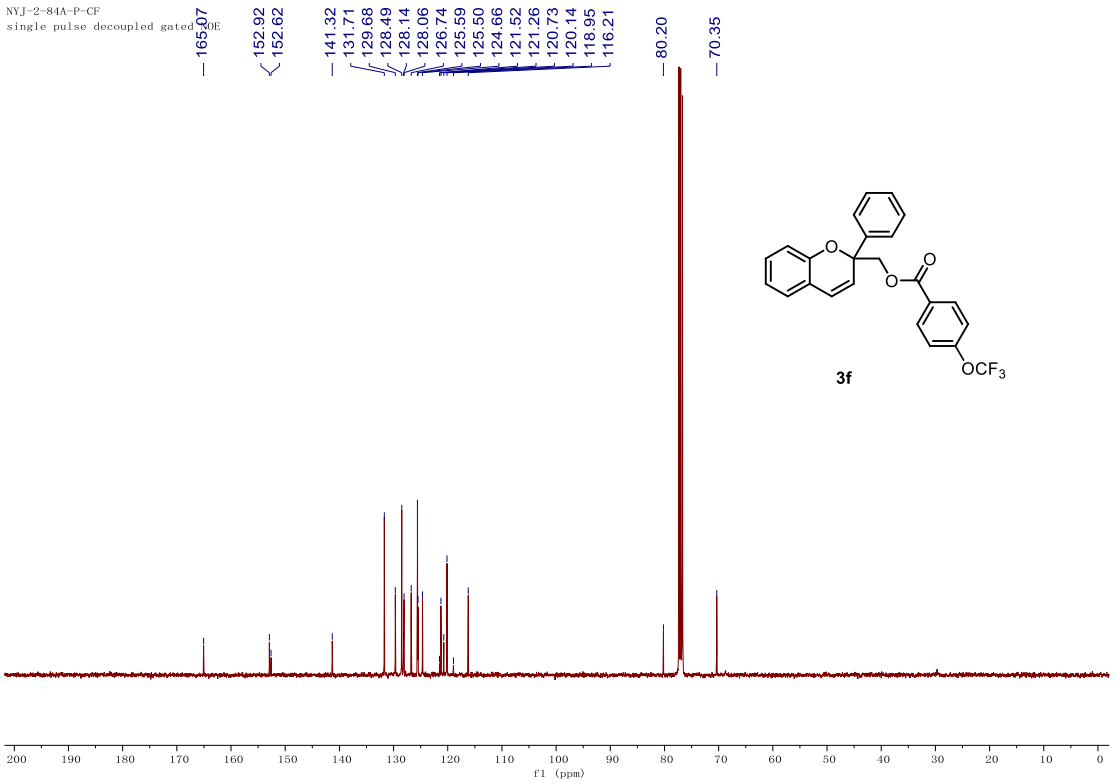

NYJ-2-83A-P-CF
single_pulse
-63.03
3e
CF3
f1 (ppm)


NYJ-2-83A-P-CF
single pulse decoupled gated DE
165.05
152.91
141.23
134.90
134.58
134.25
133.93
132.96
130.09
129.72
128.52
128.10
126.77
125.57
125.31
125.27
124.92
124.56
122.21
121.30
120.69
116.20
80.17
70.55
3e
CF3
f1 (ppm)

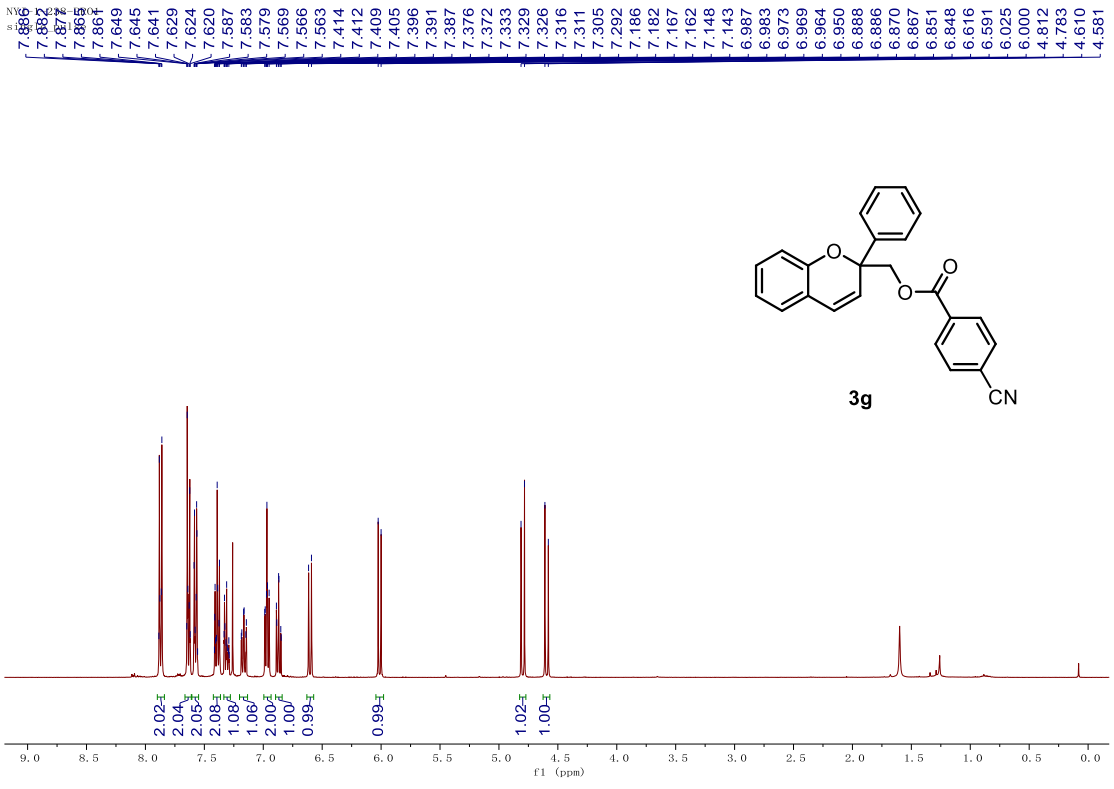
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3f**

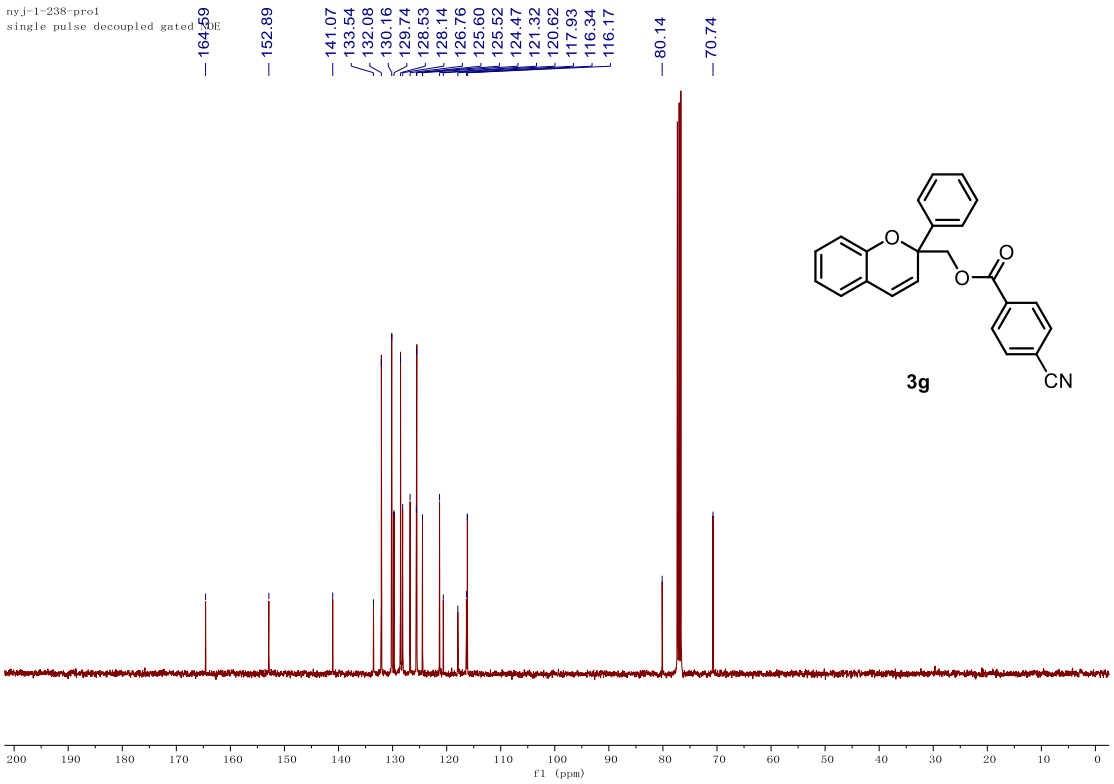




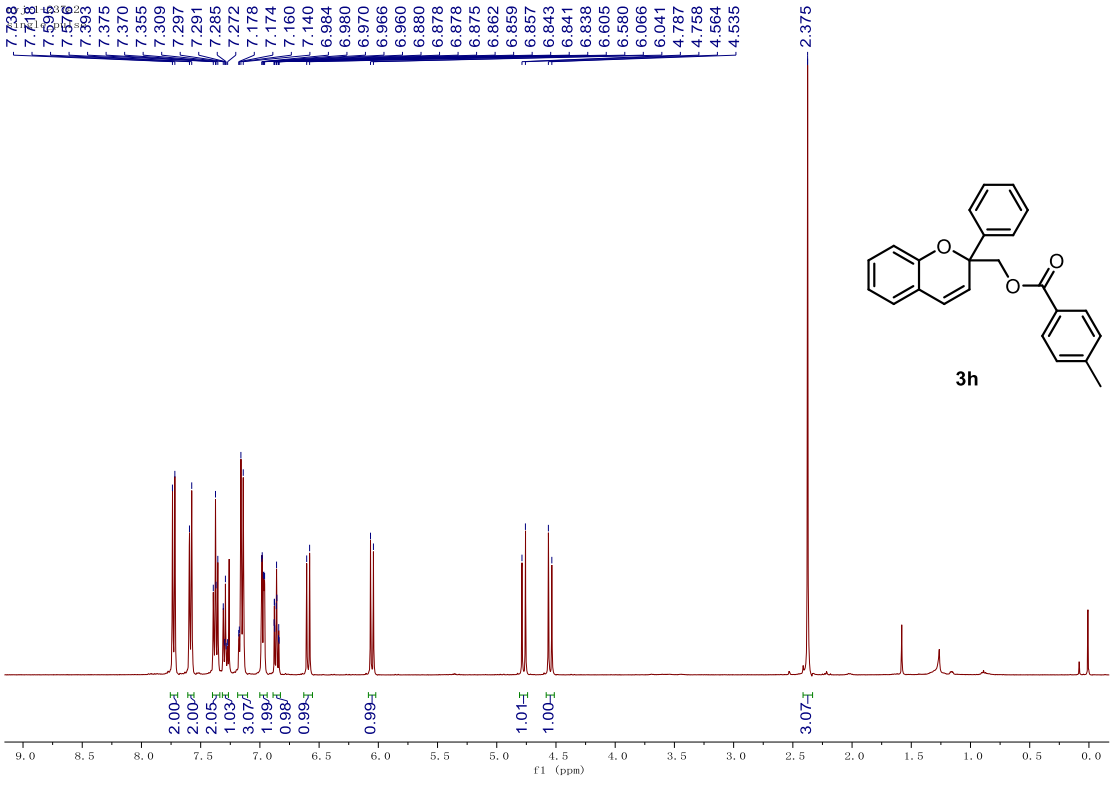


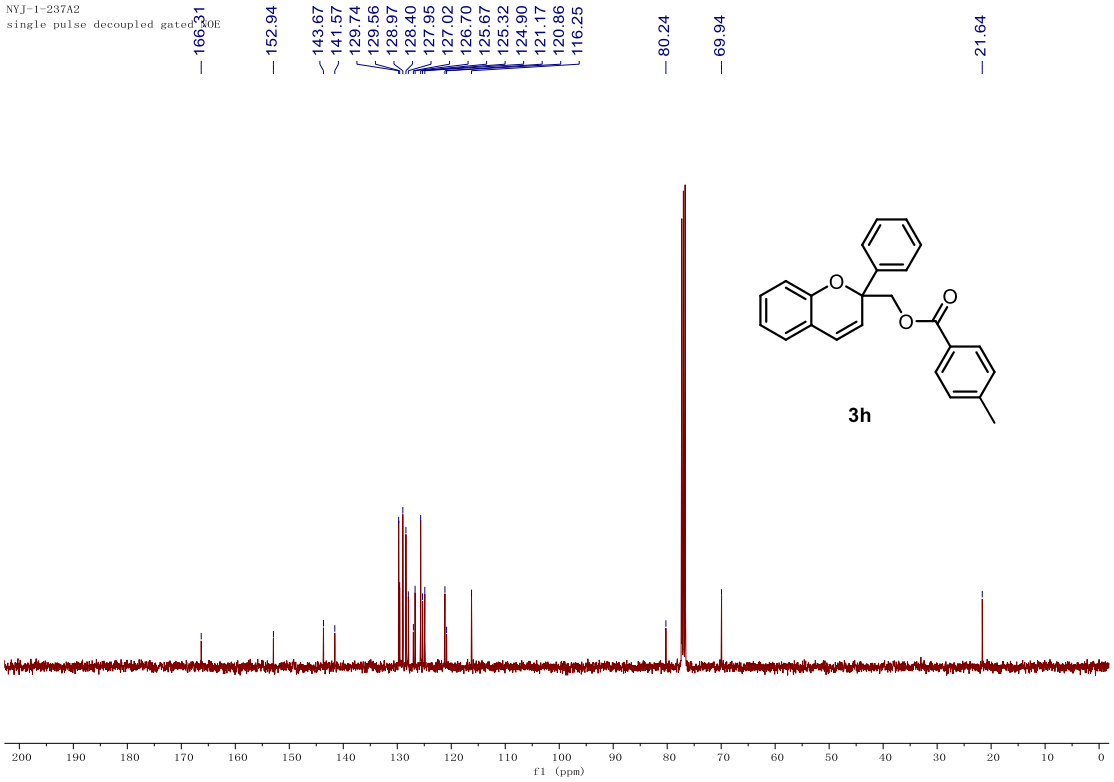
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3g**



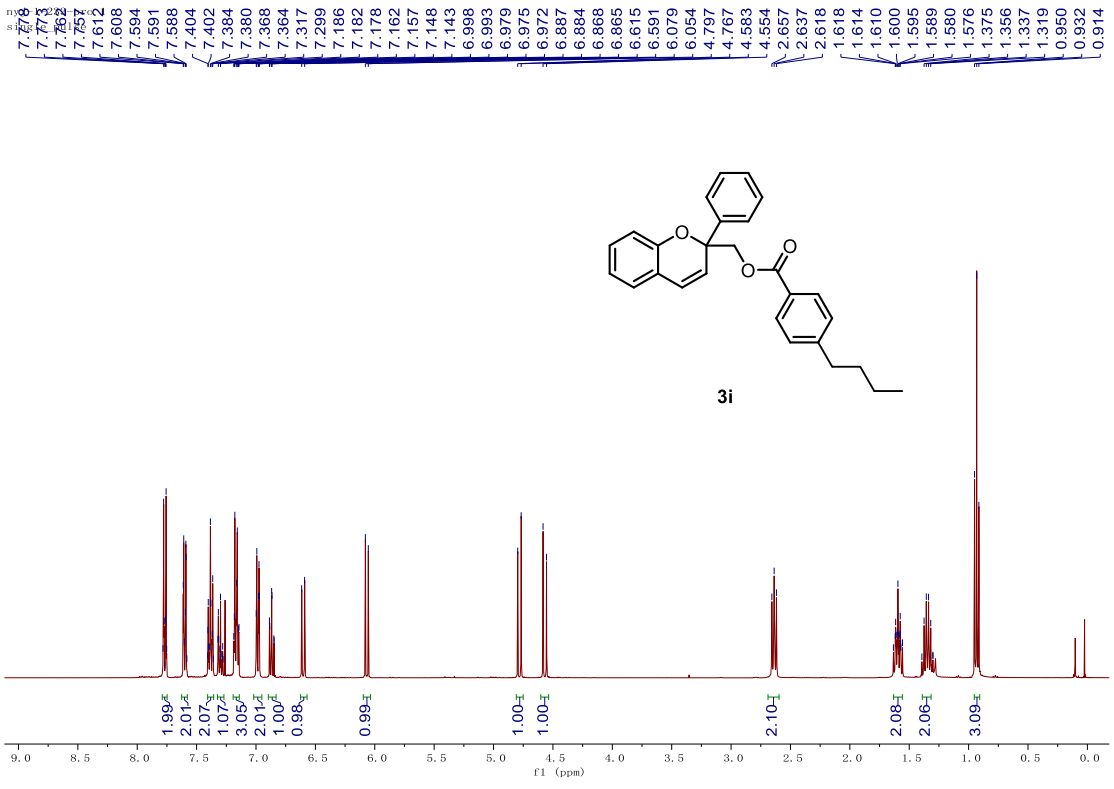


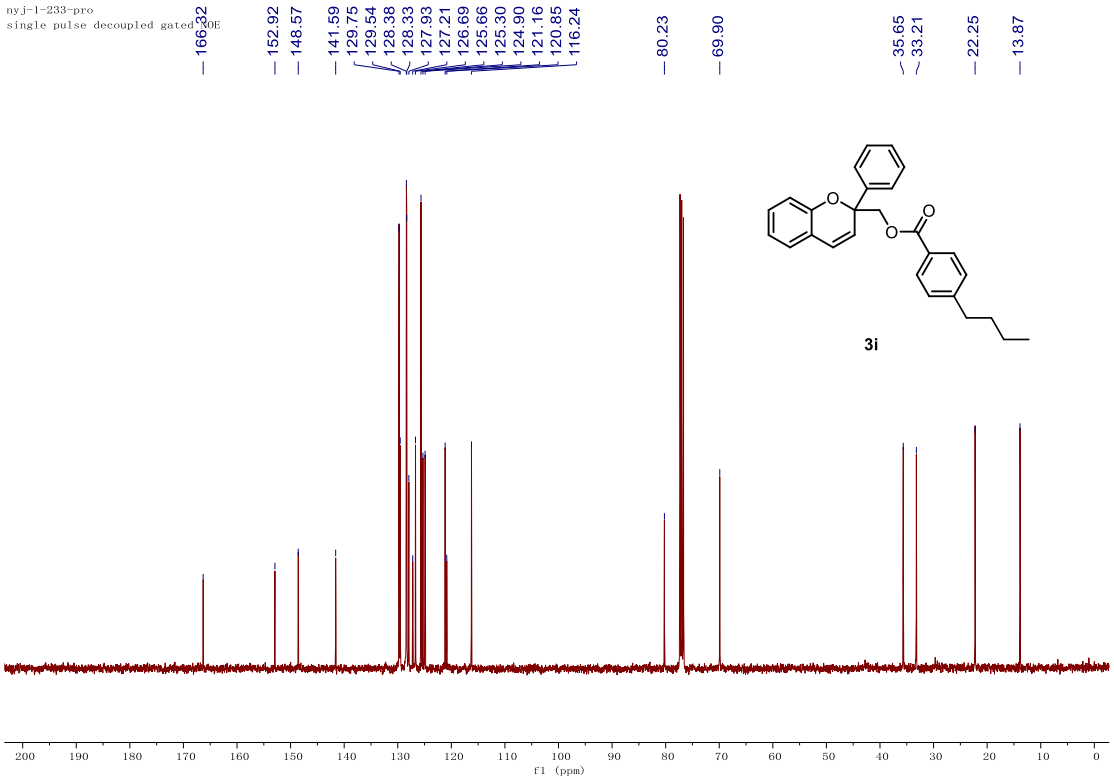
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3h**



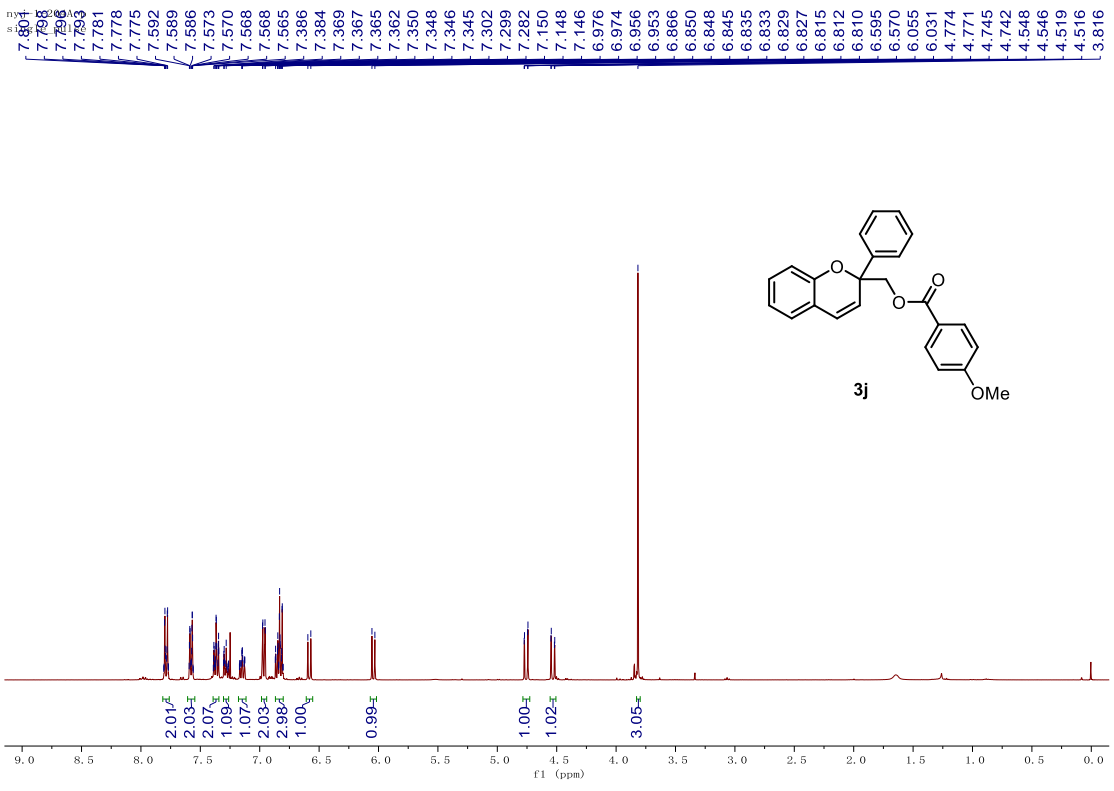


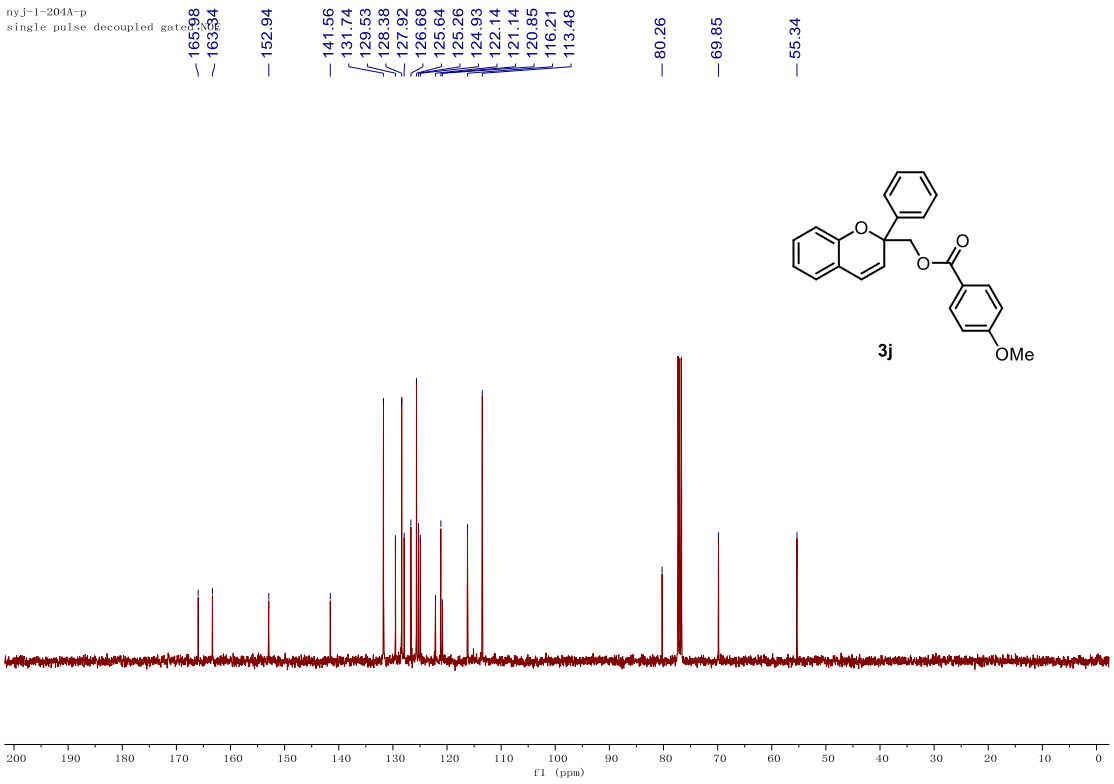
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3i**



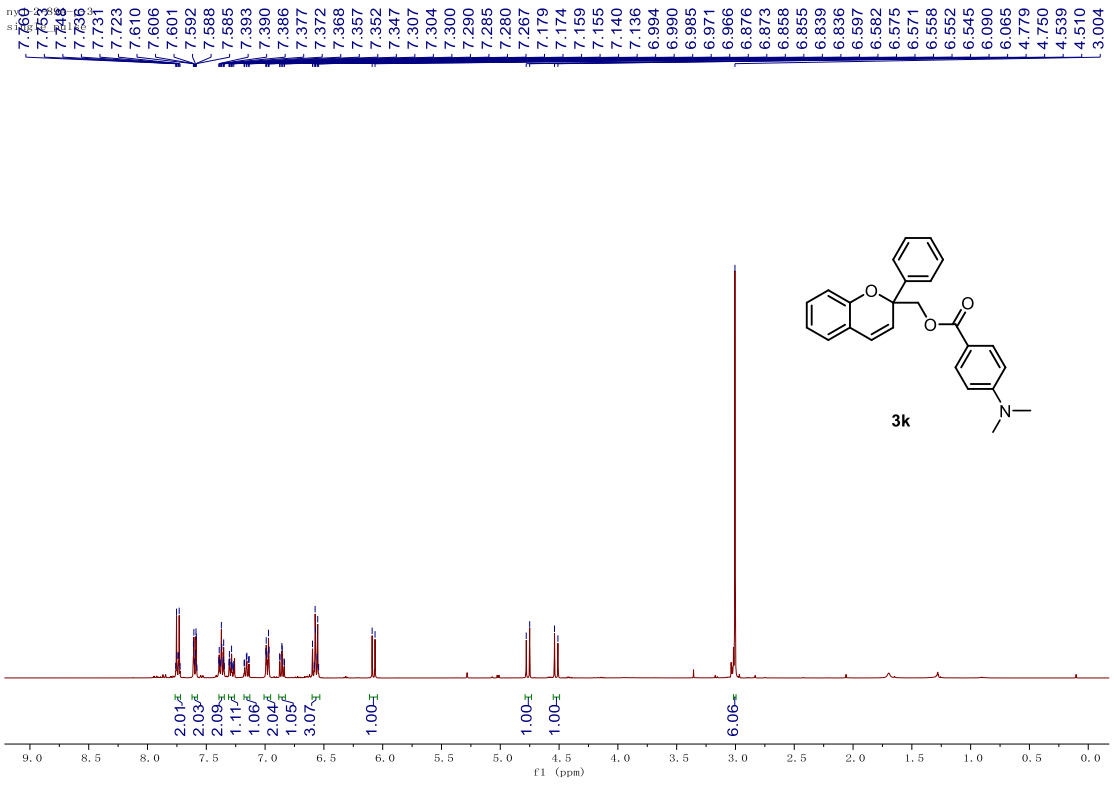


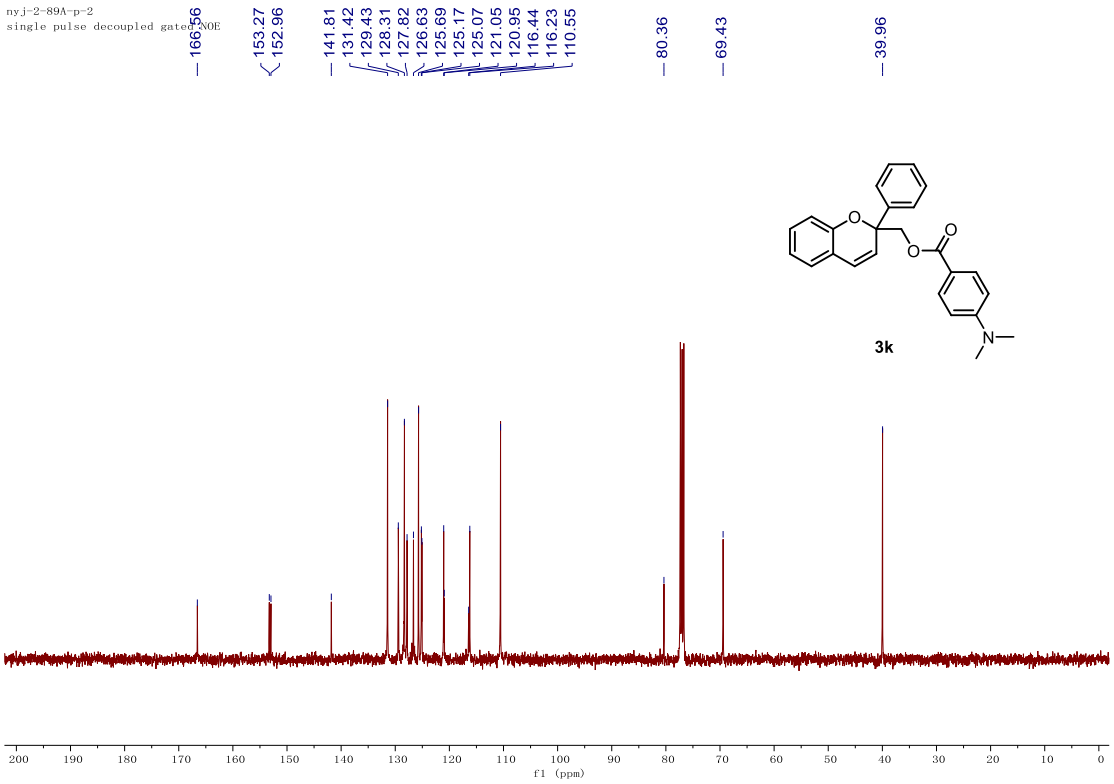
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3j**



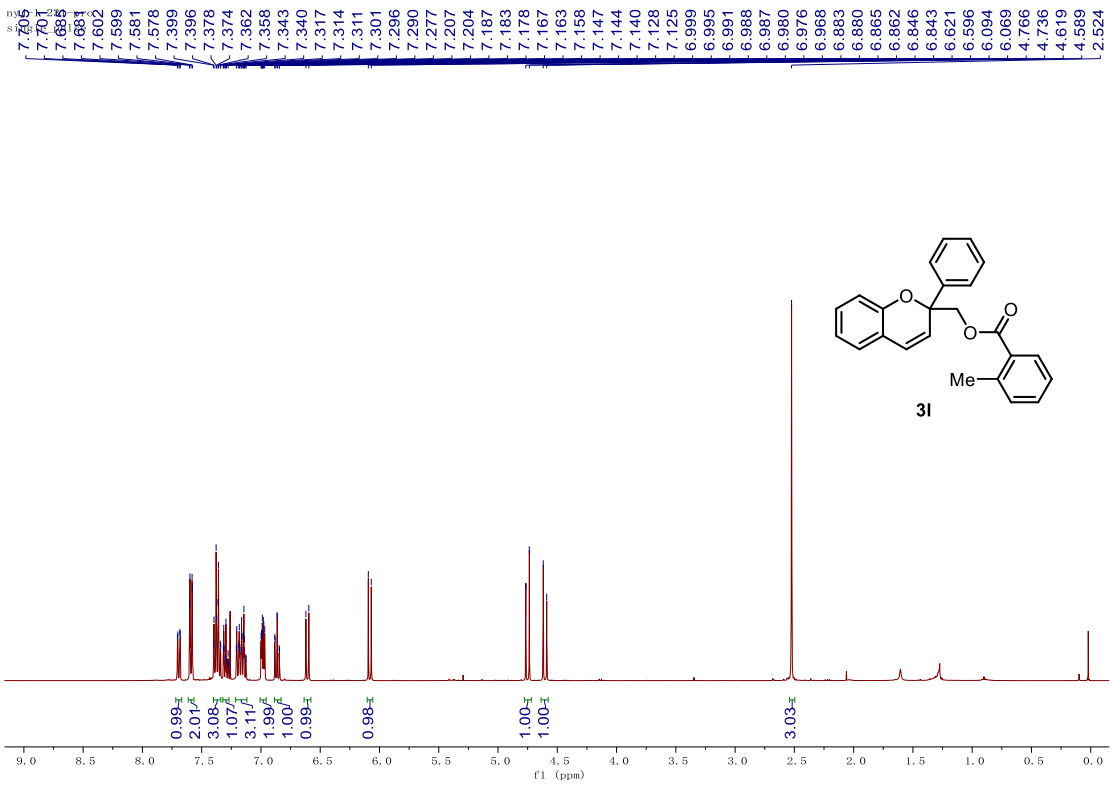


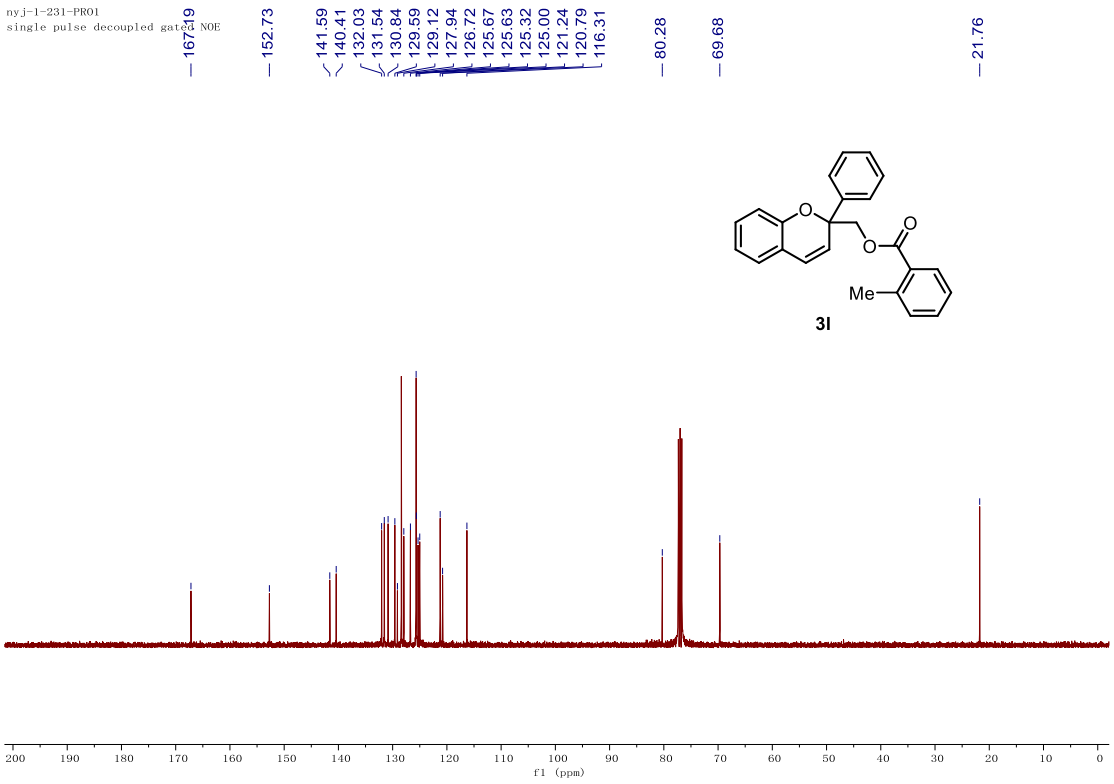
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3k**



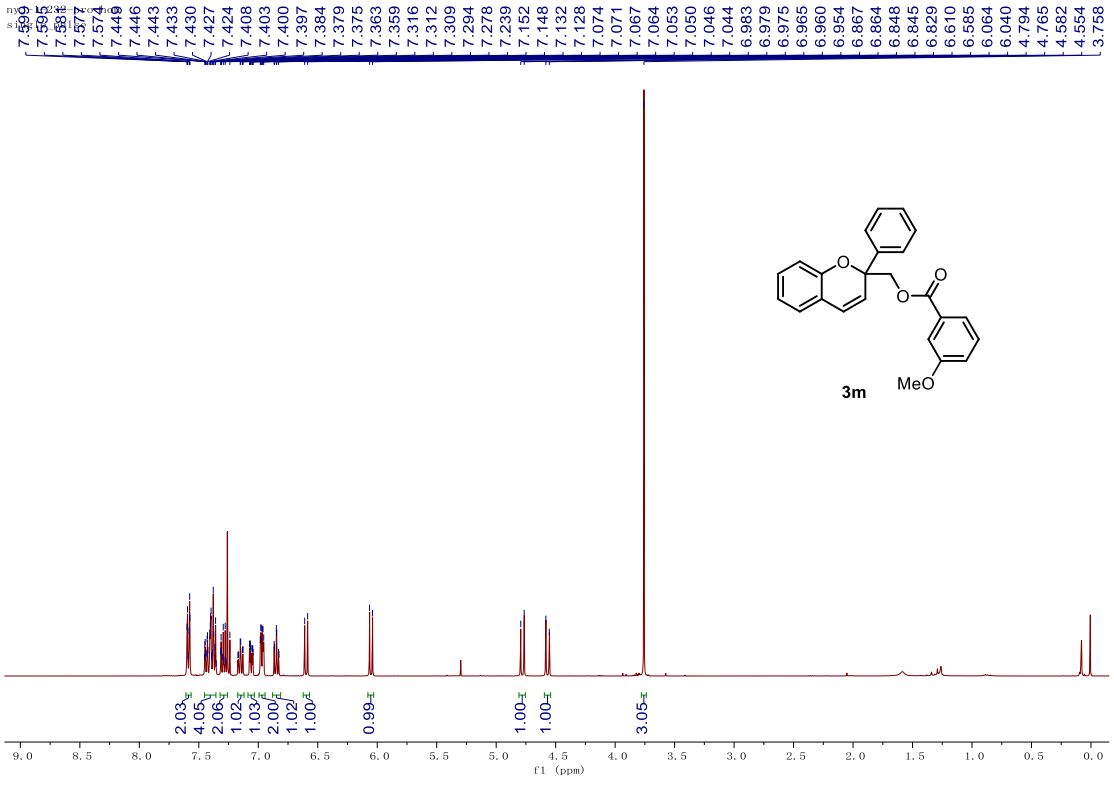


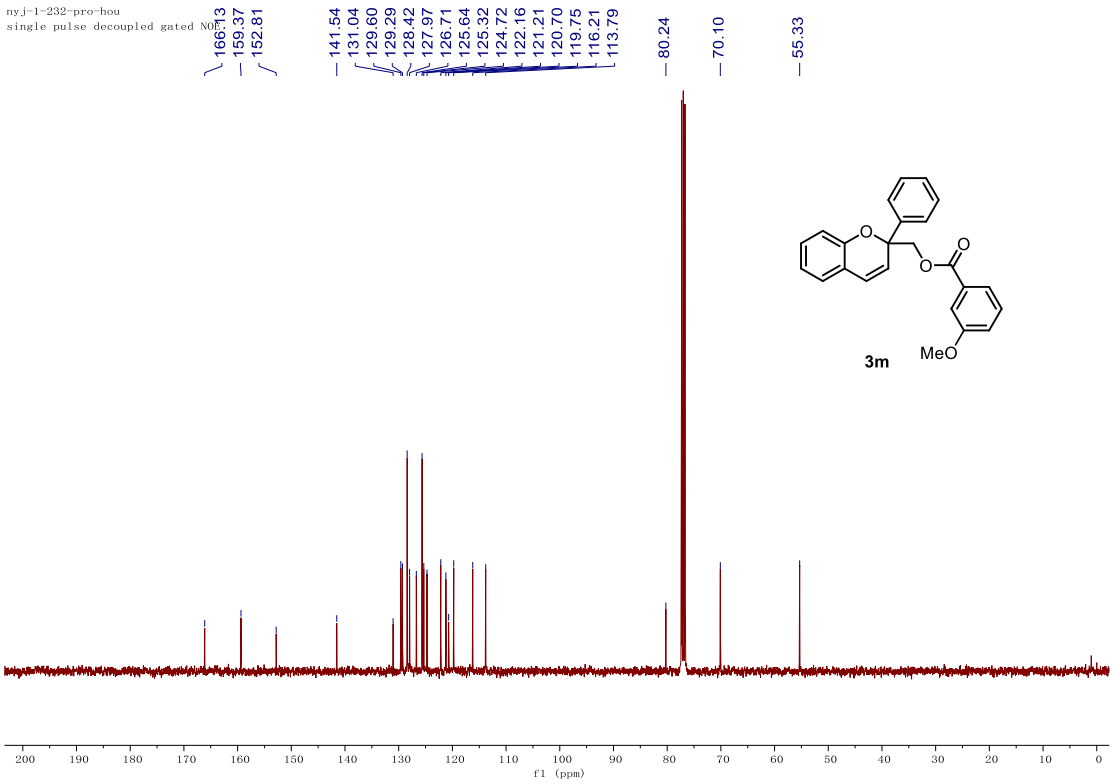
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3l**



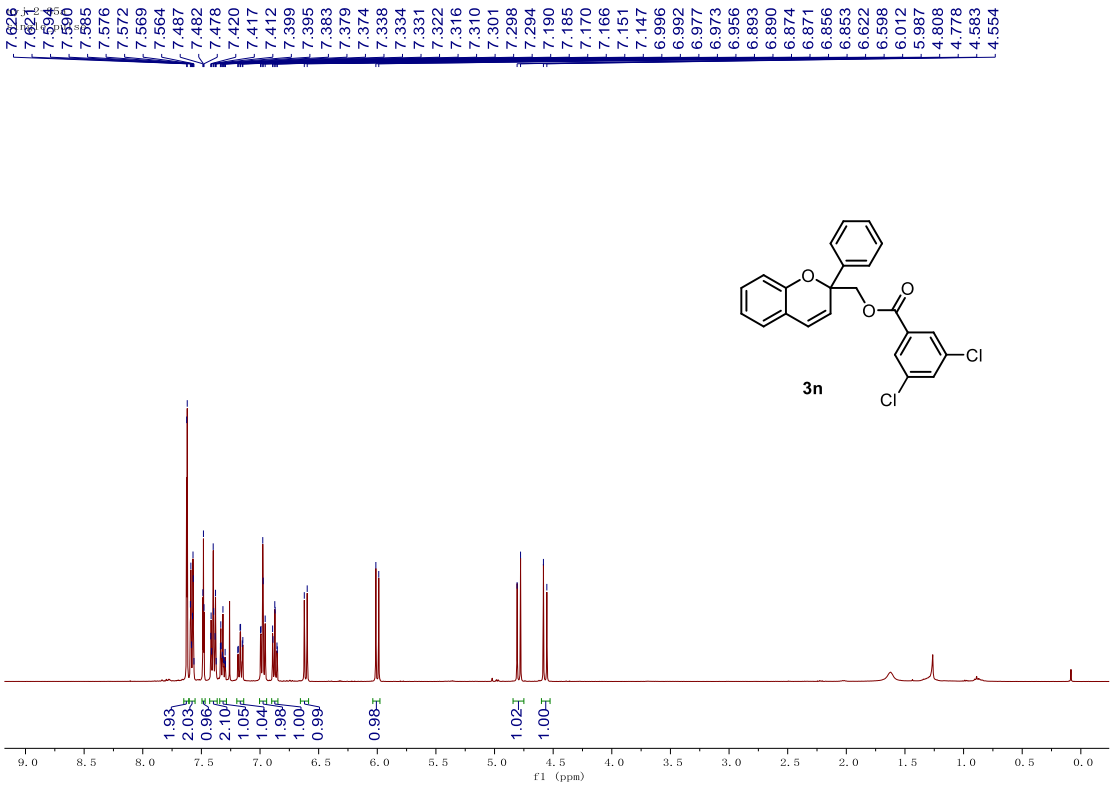


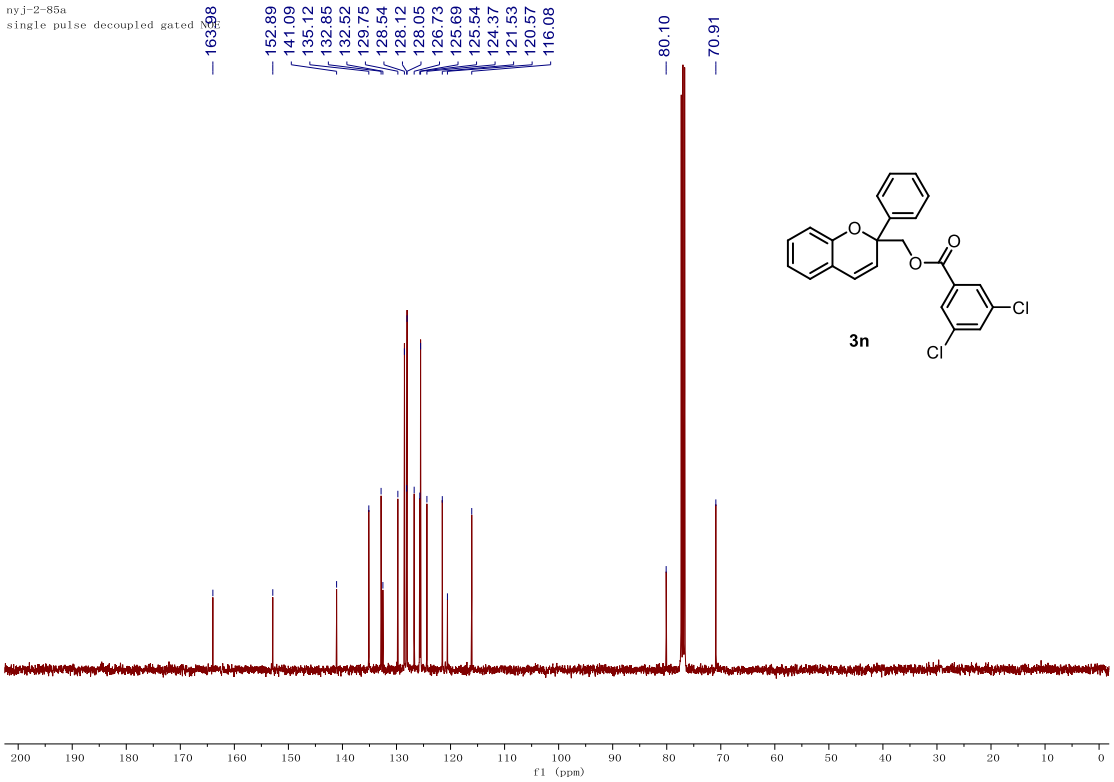
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3m**



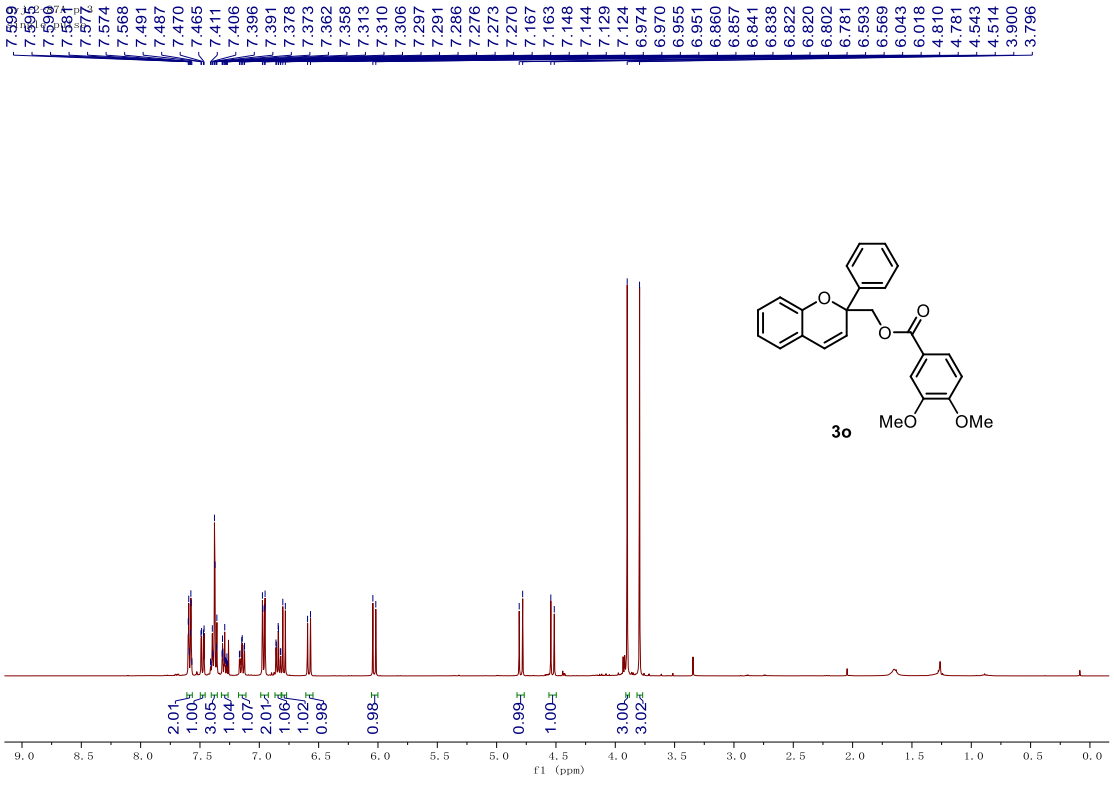


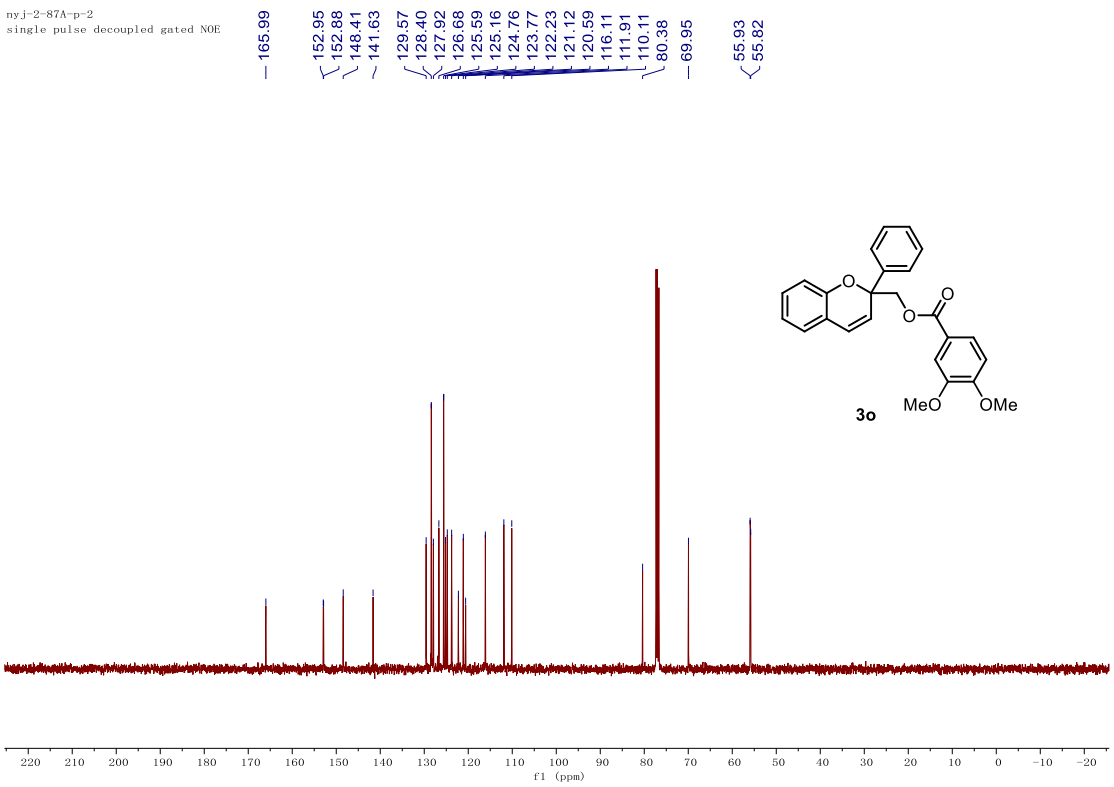
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3n**



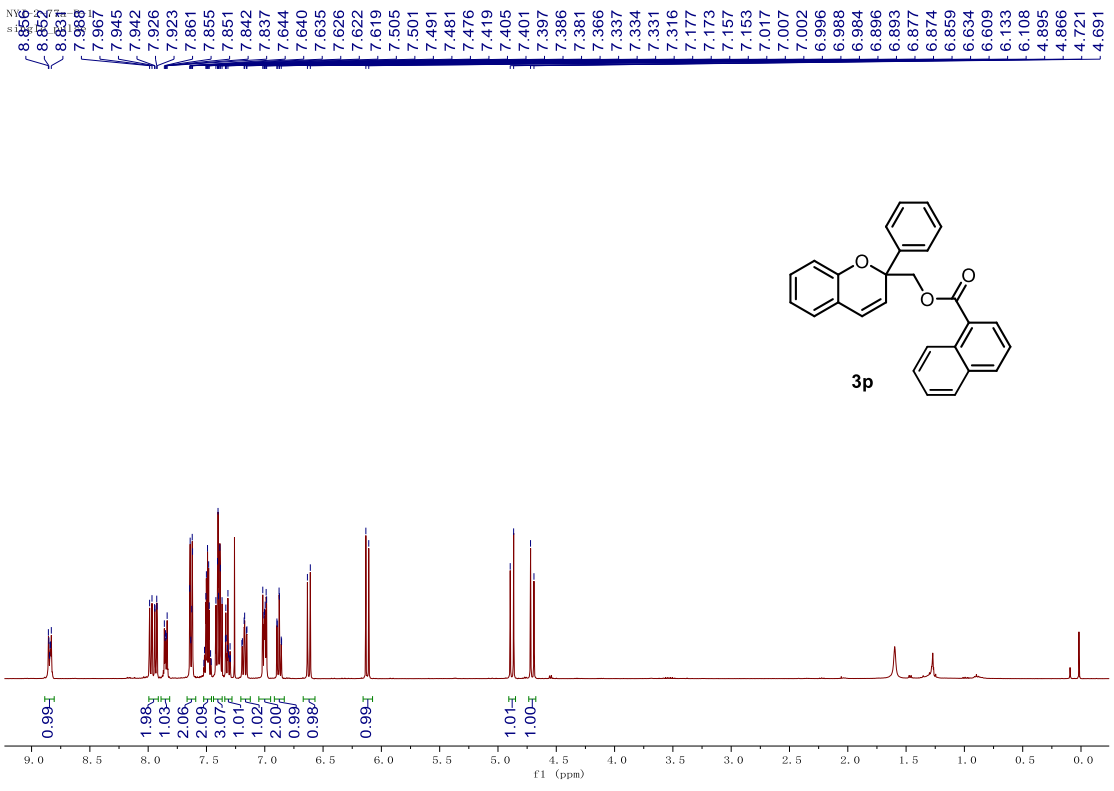


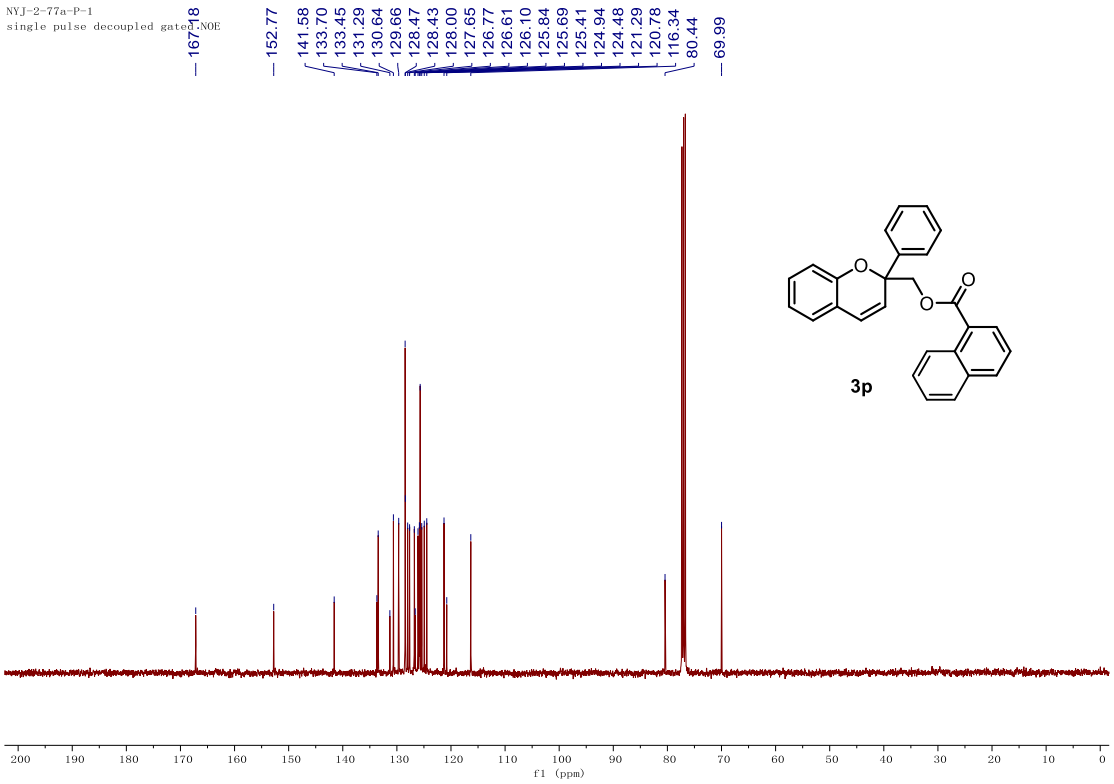
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3o**



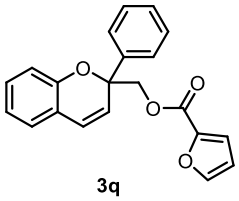


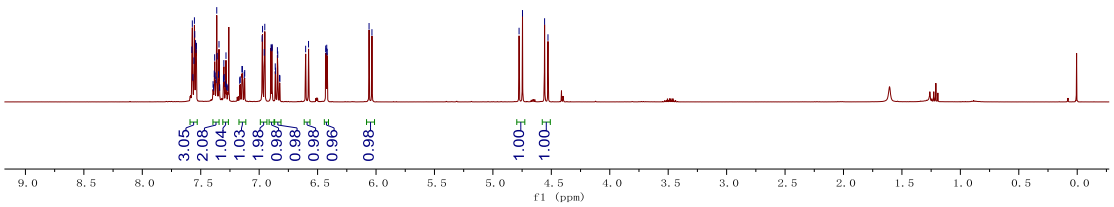
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3p**

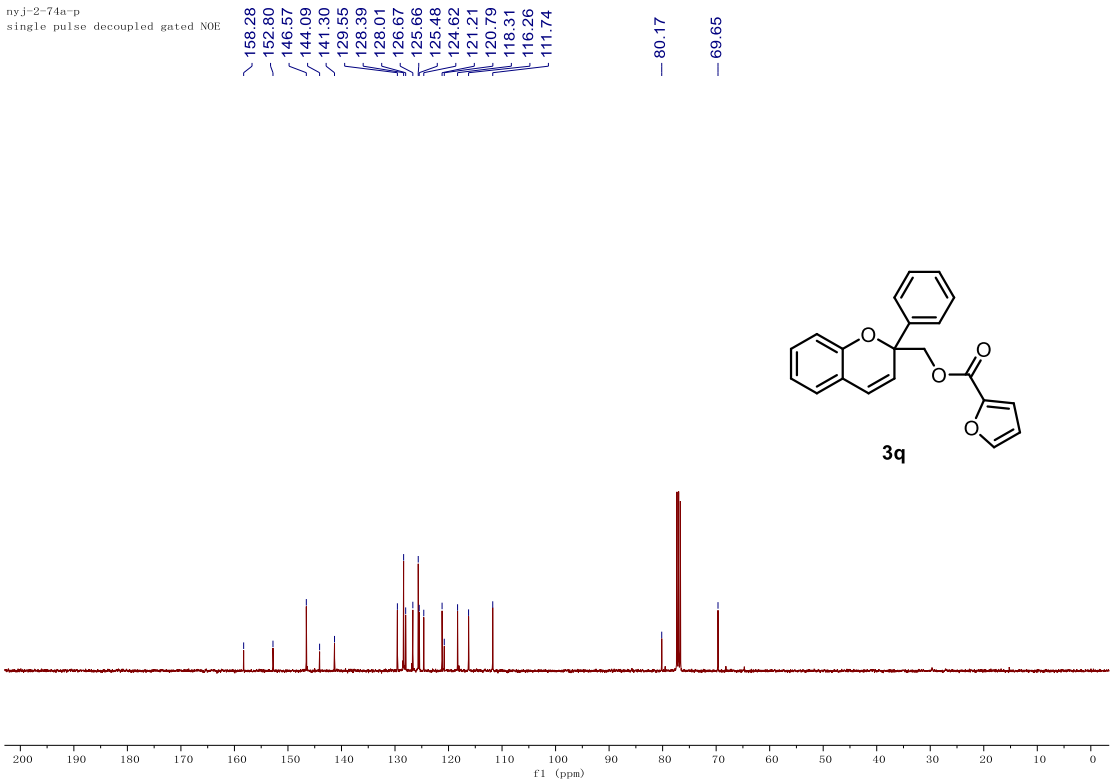




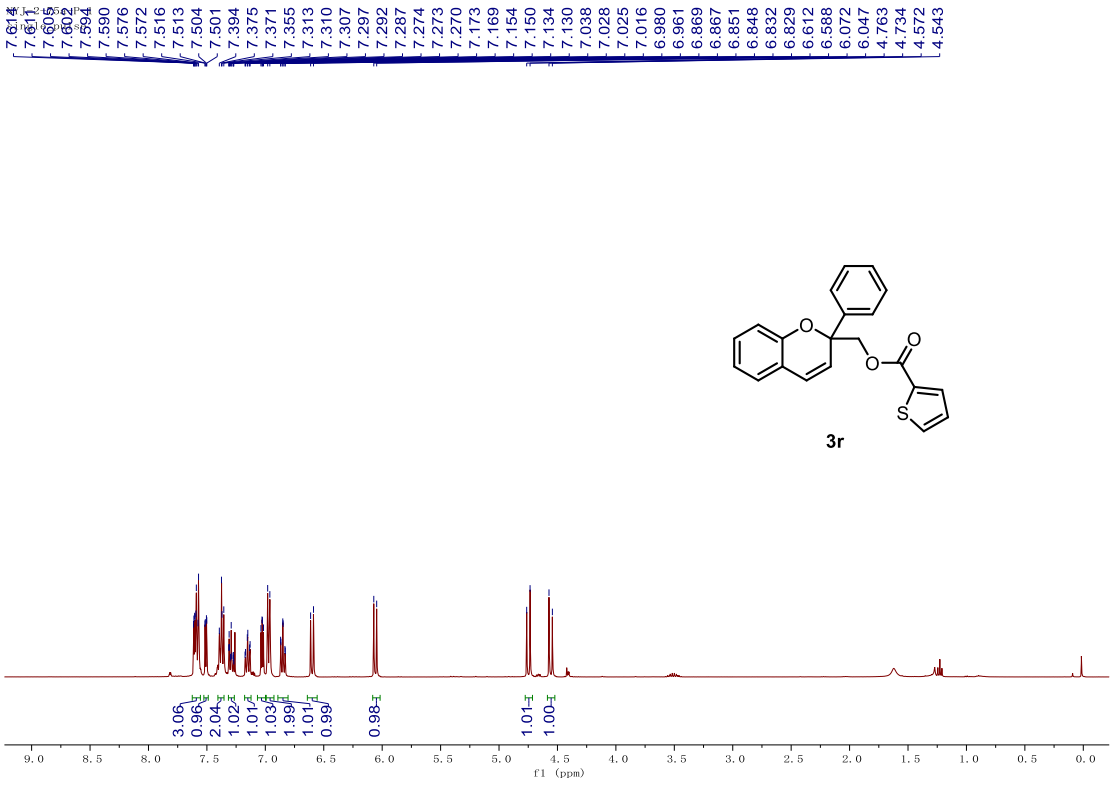
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3q**

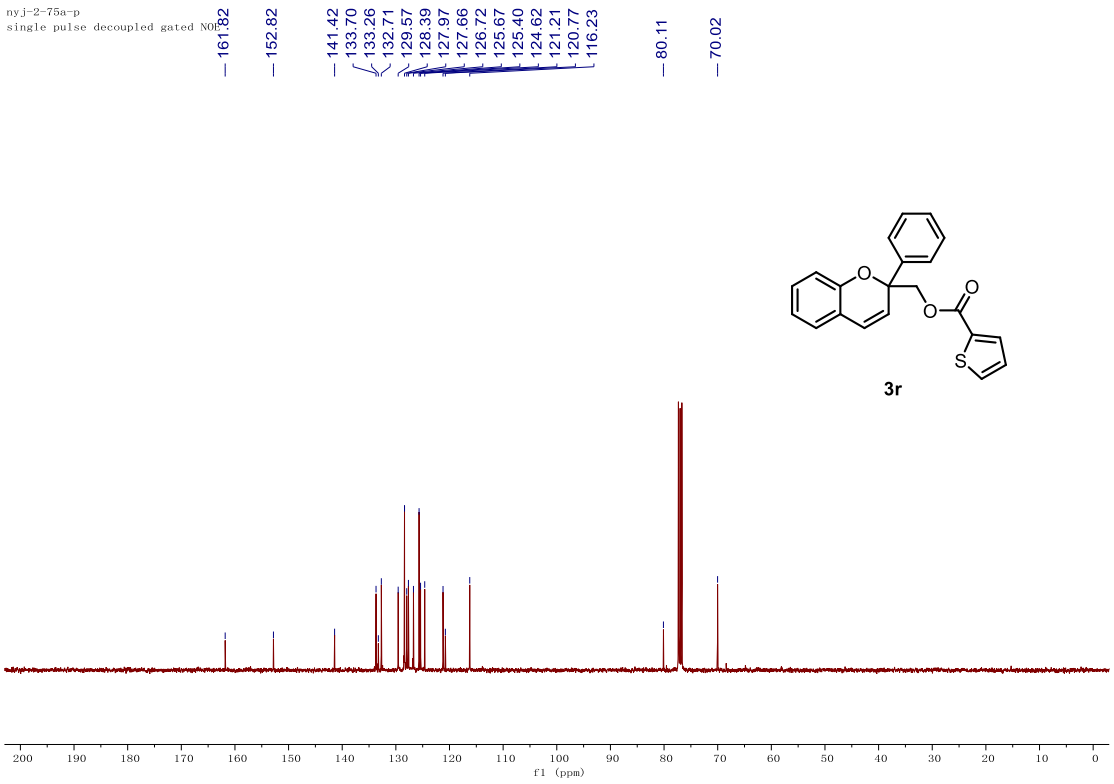




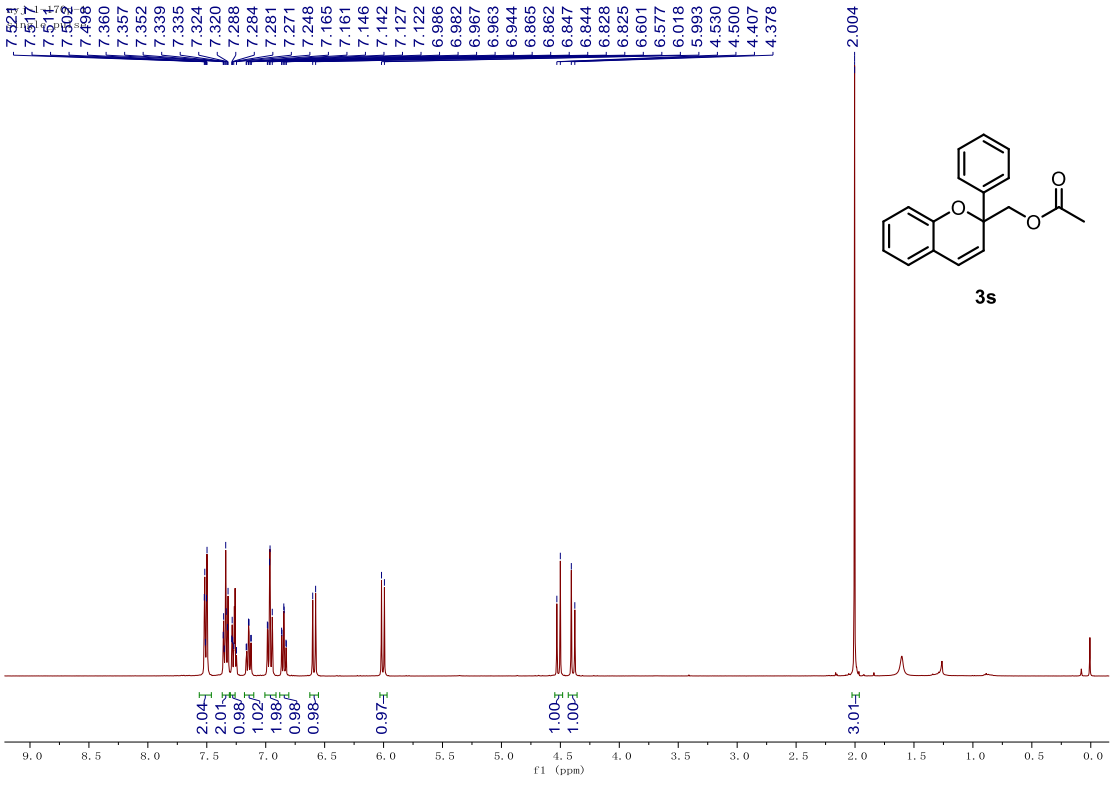


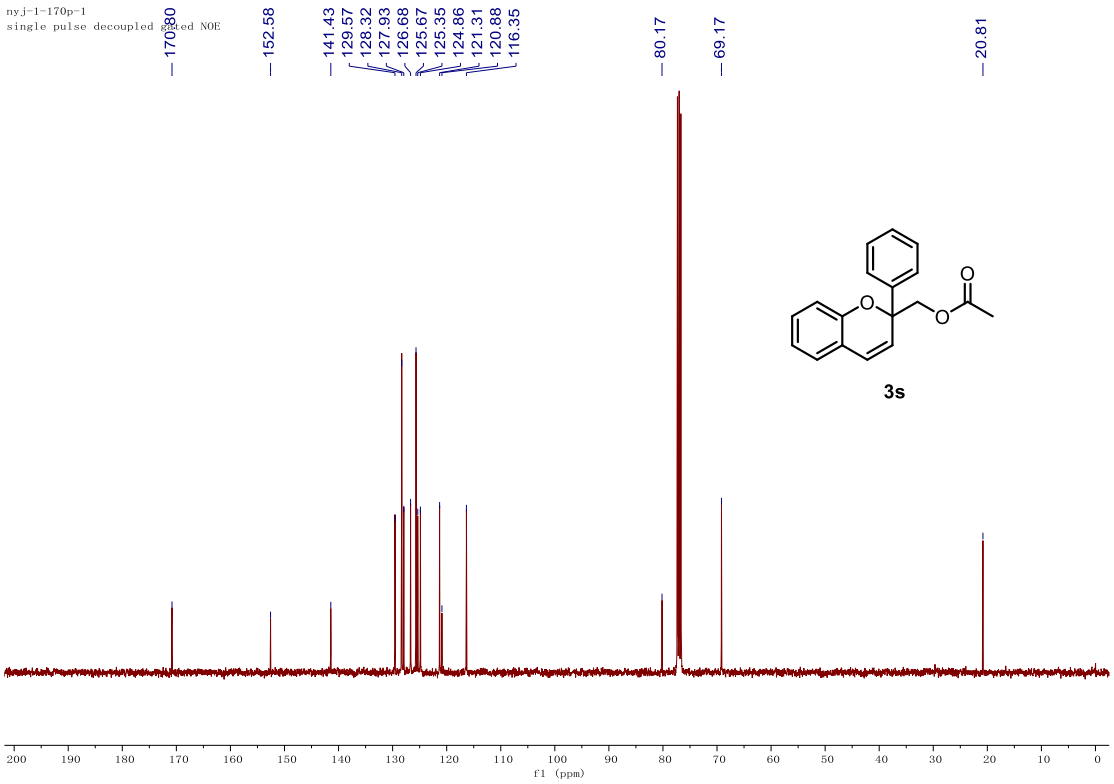
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3r**



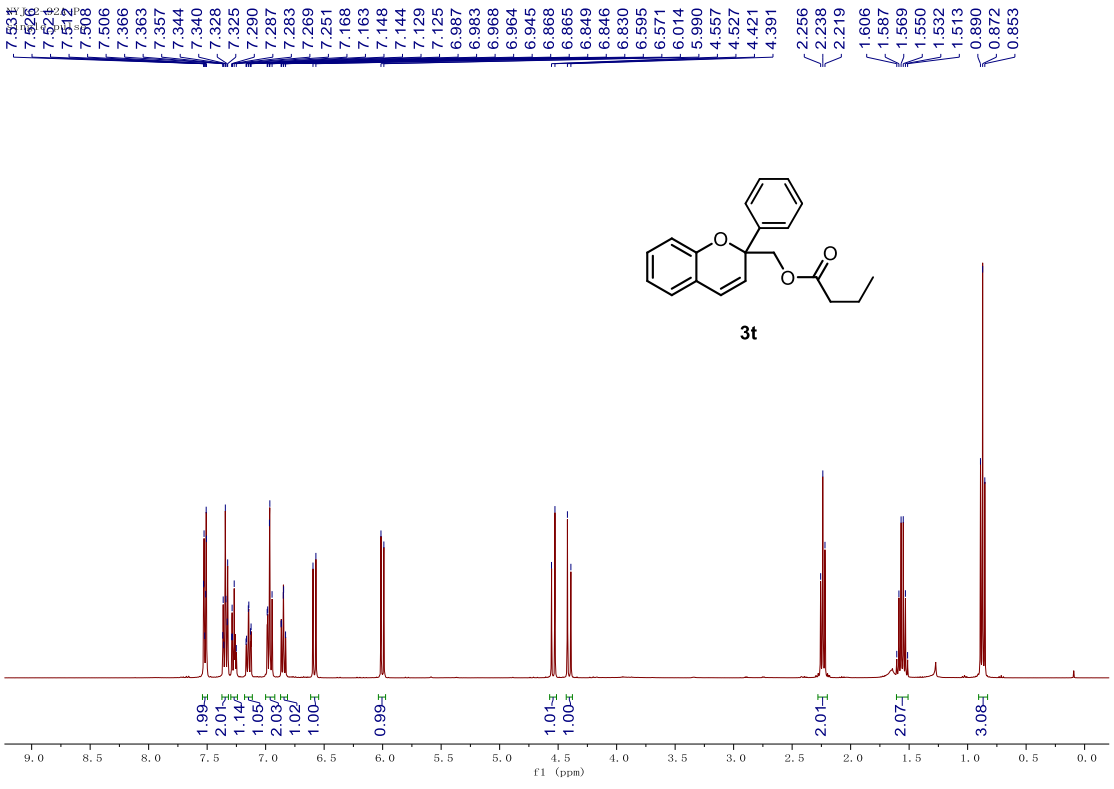


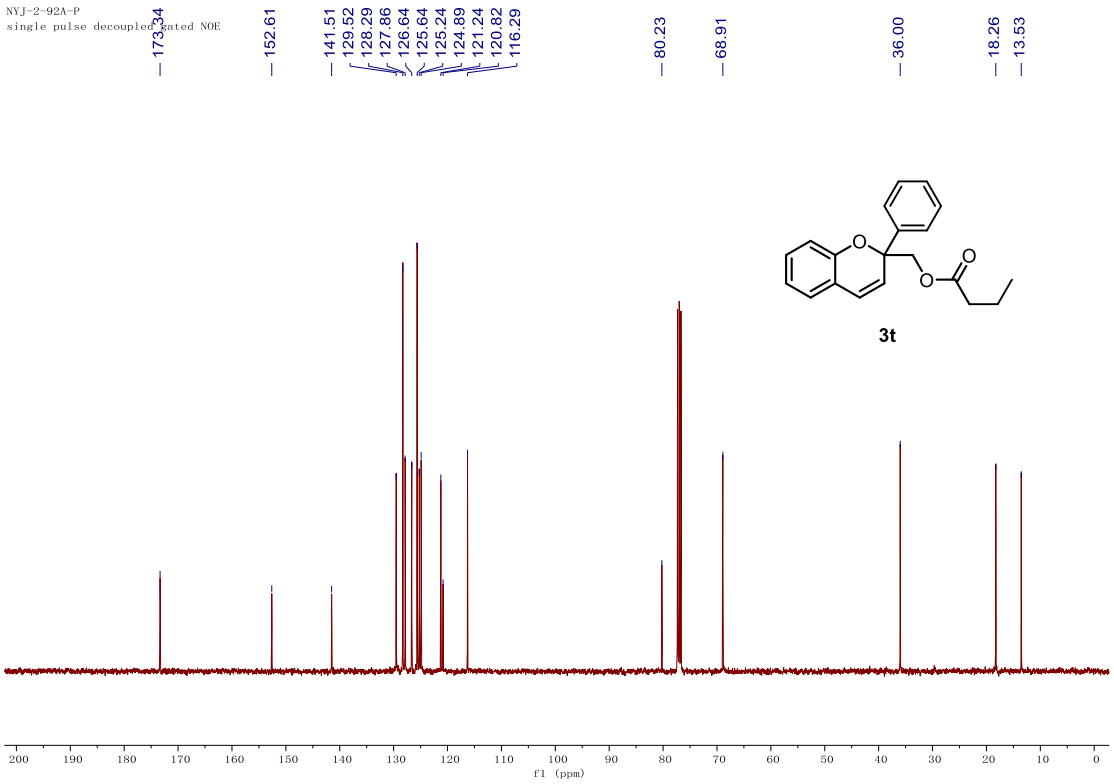
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3s**



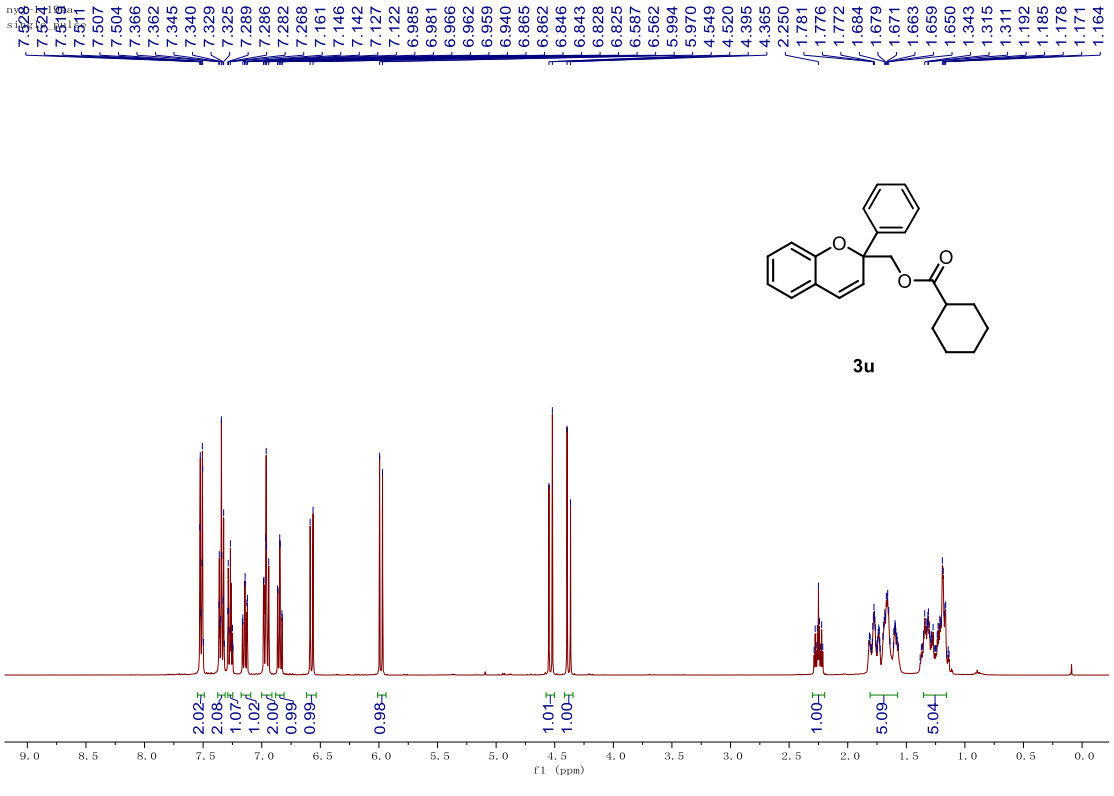


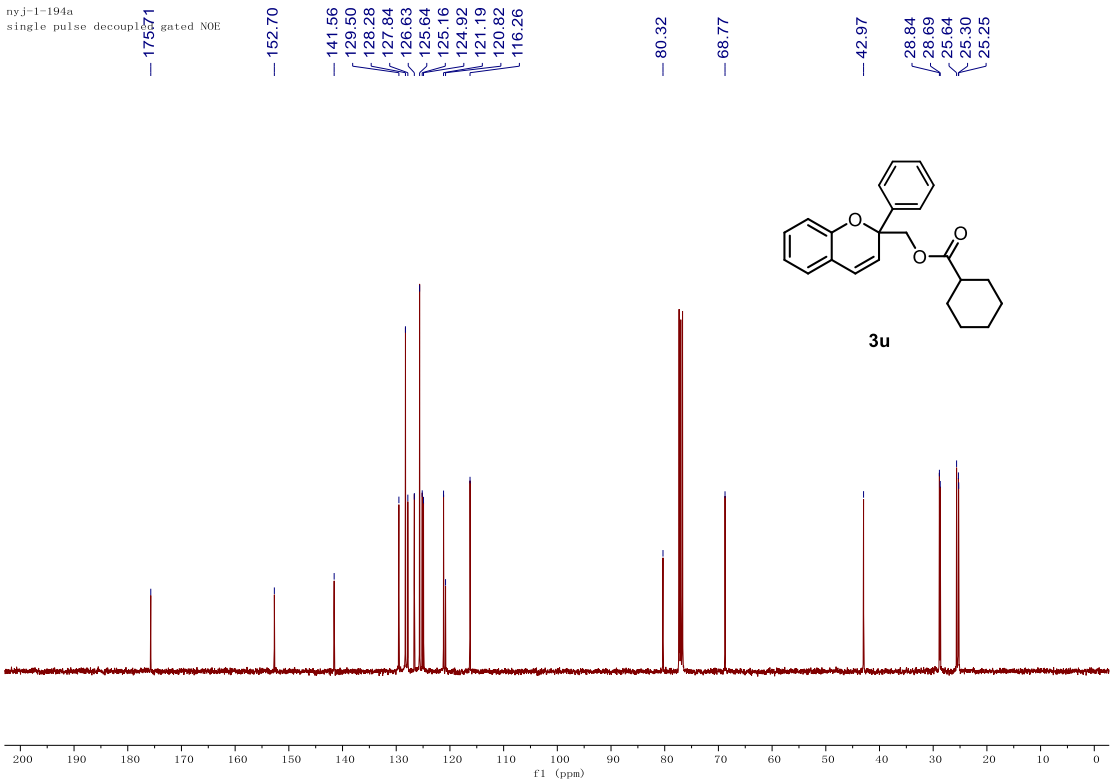
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3t**



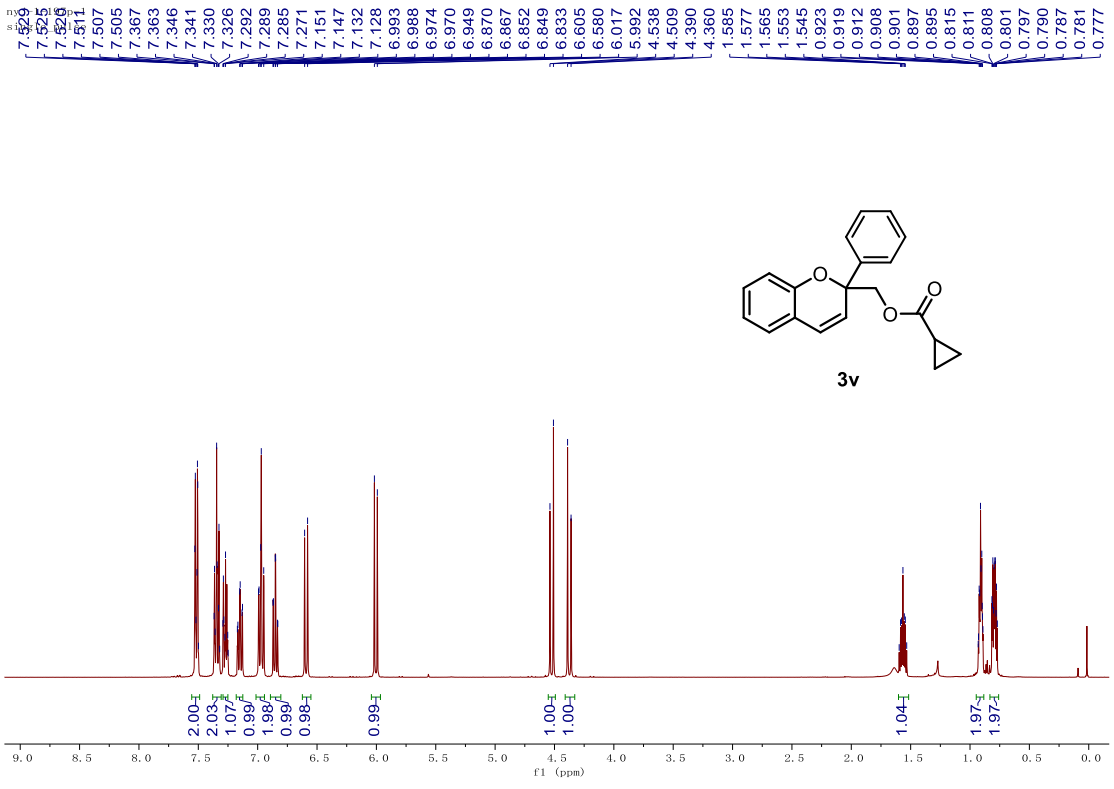


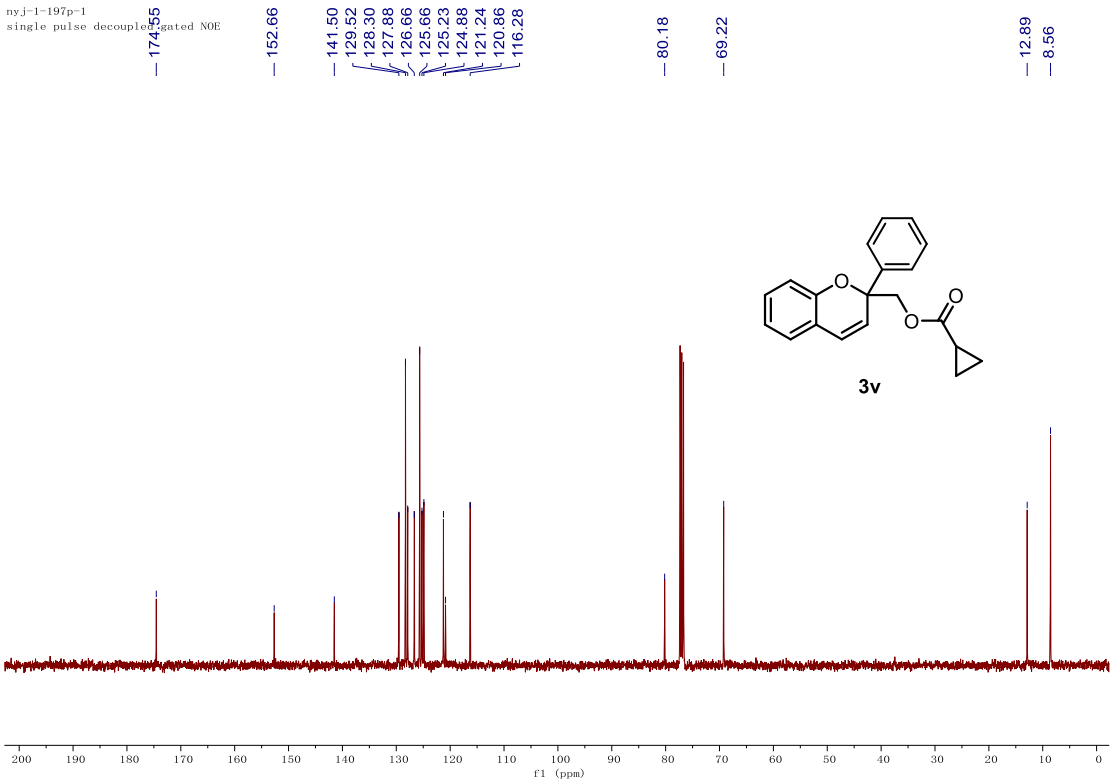
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3u**



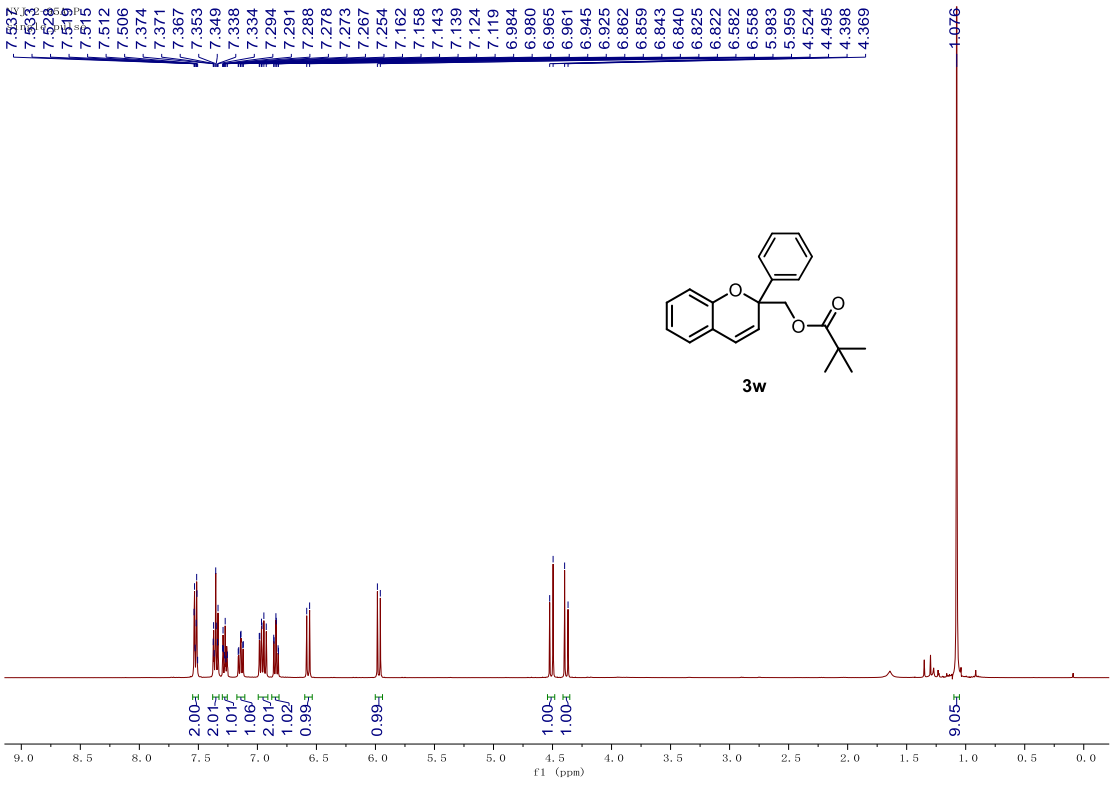


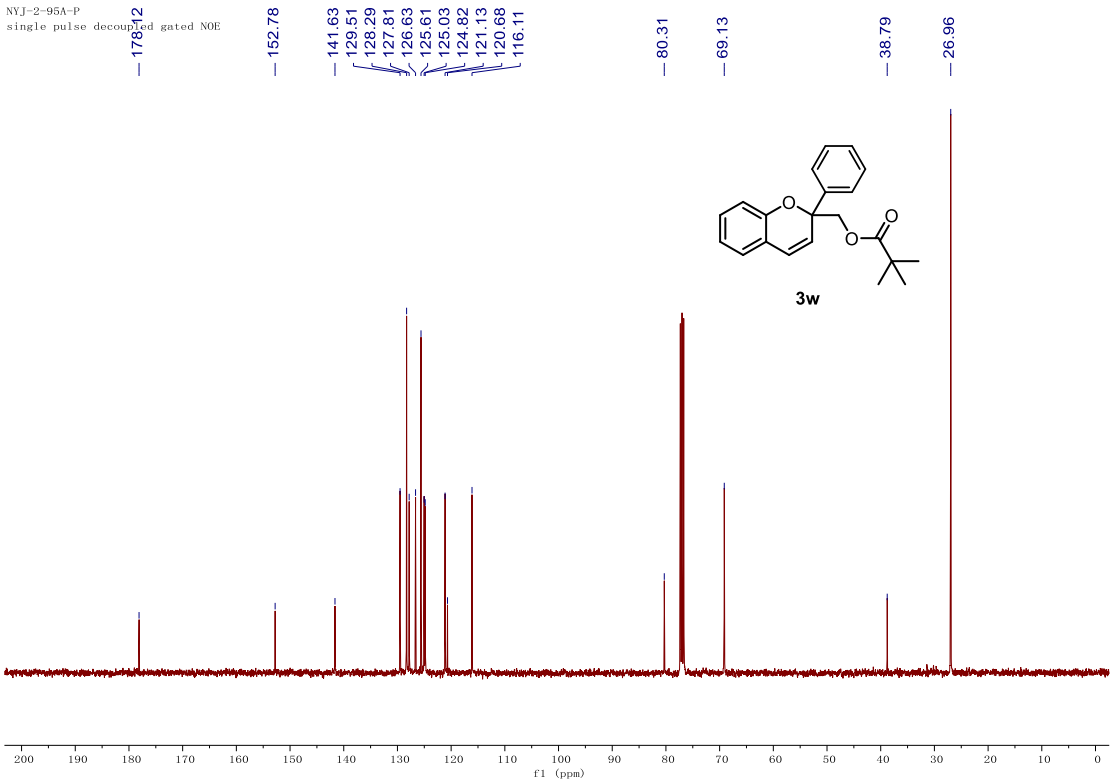
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3v**



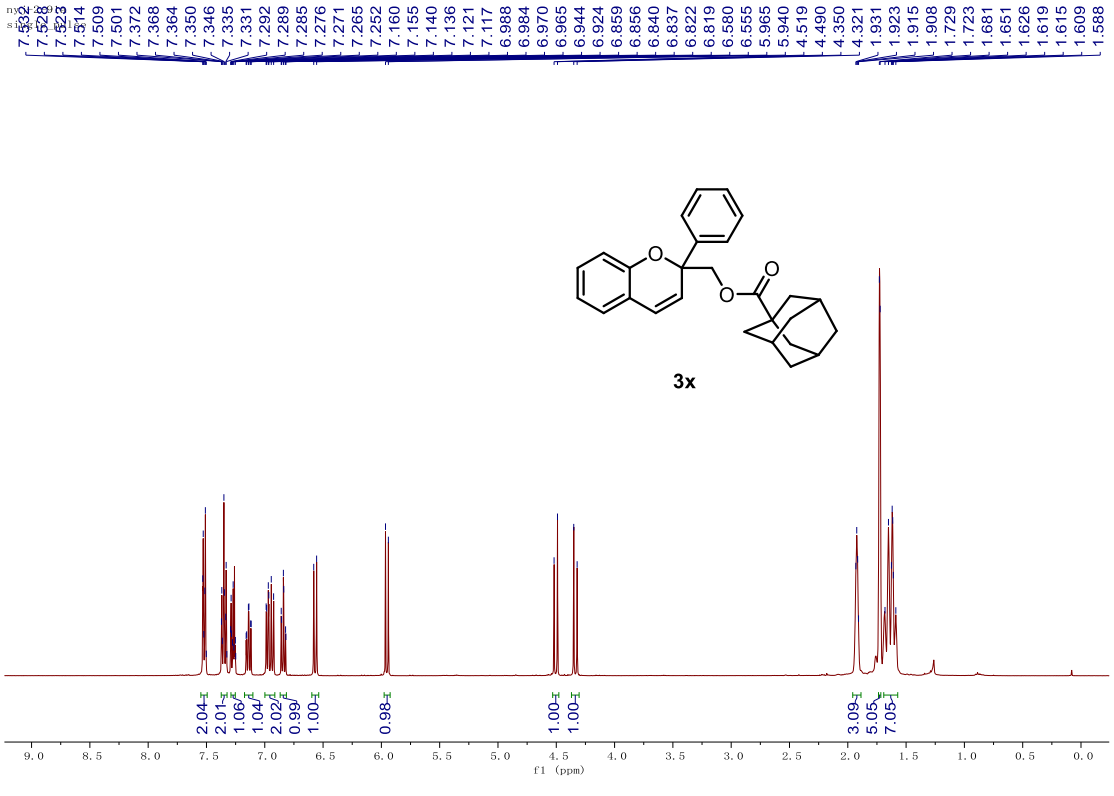


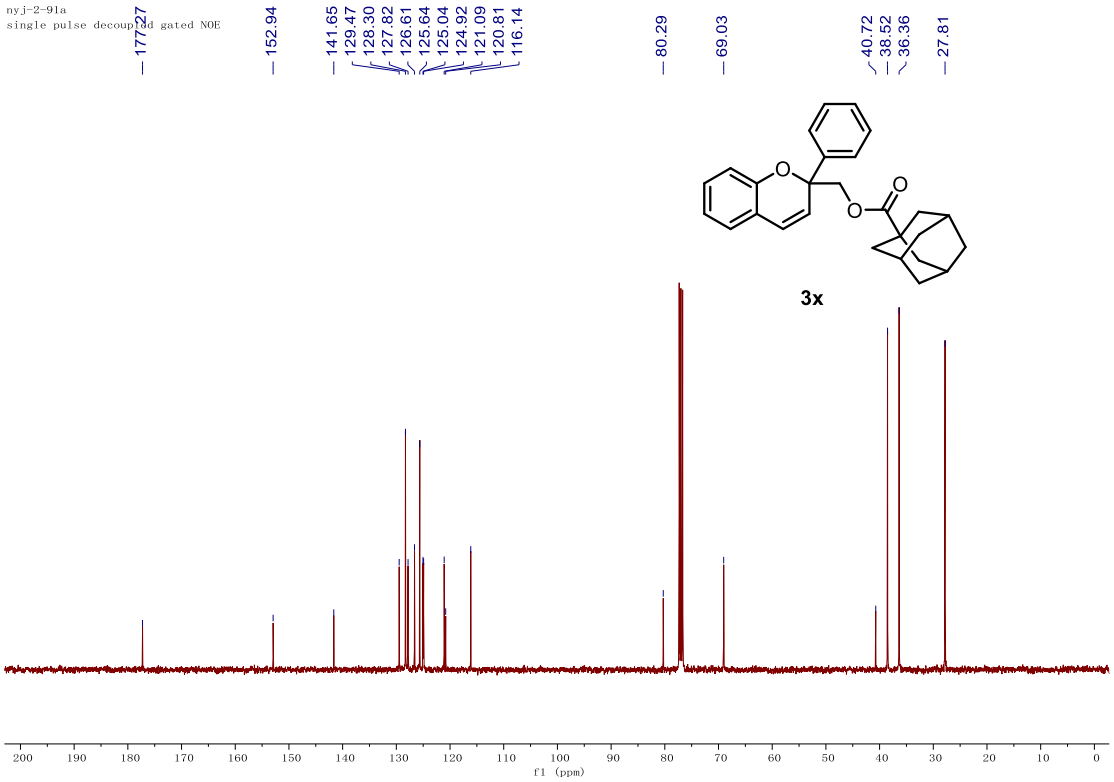
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3w**



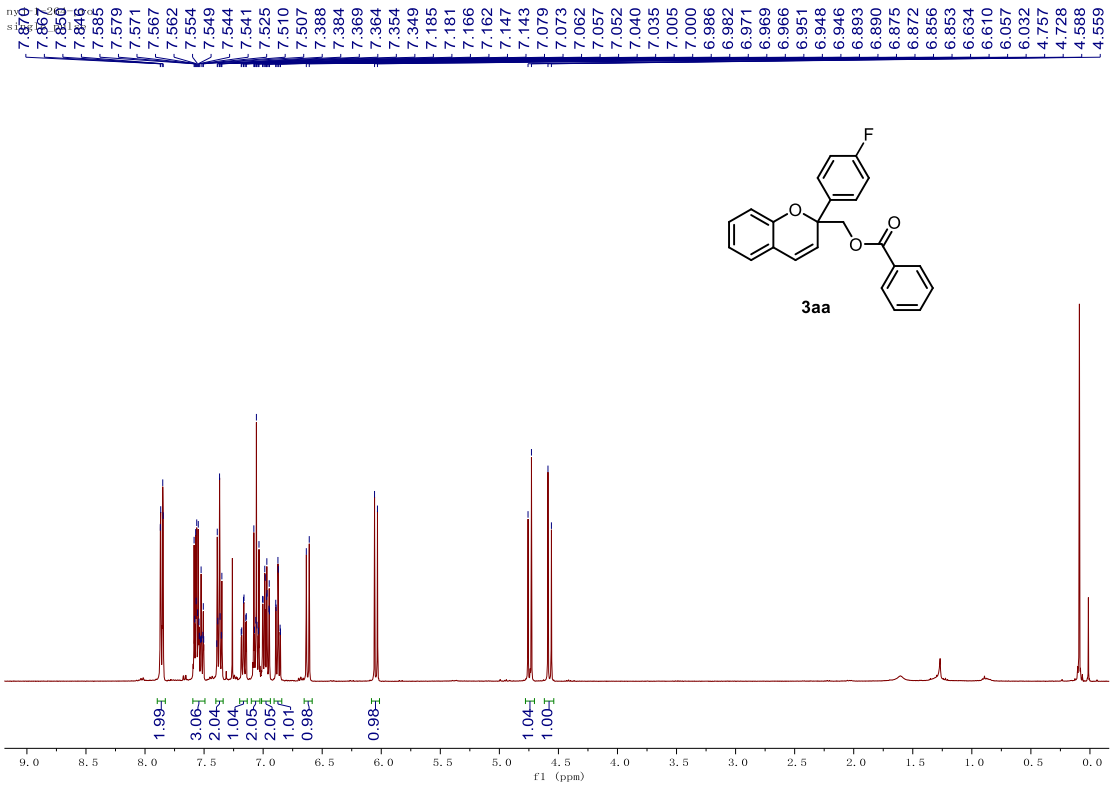


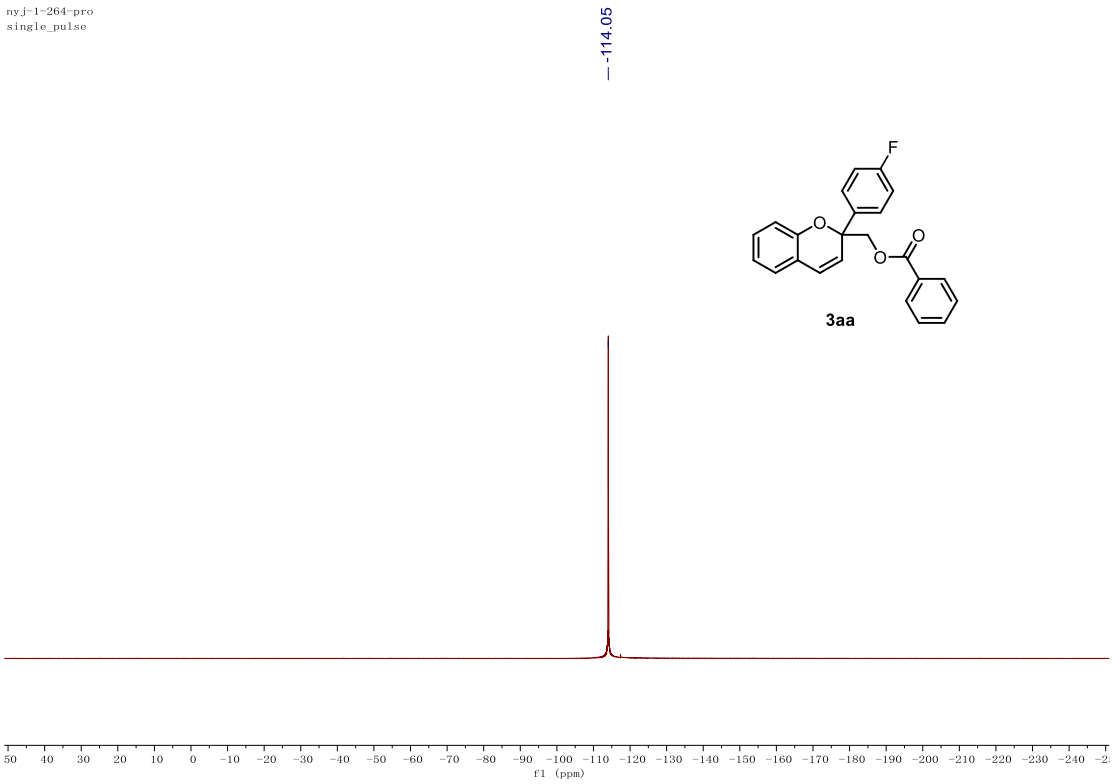
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3x**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3aa**

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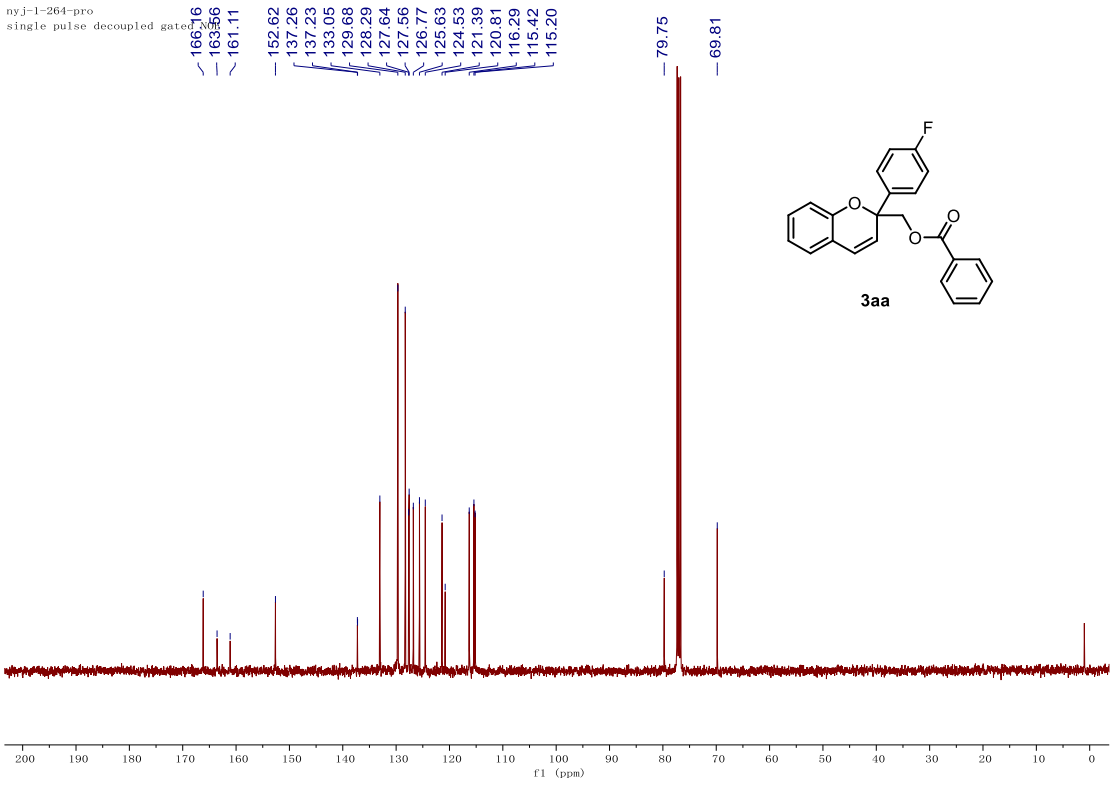
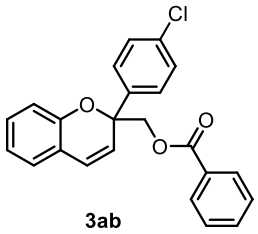
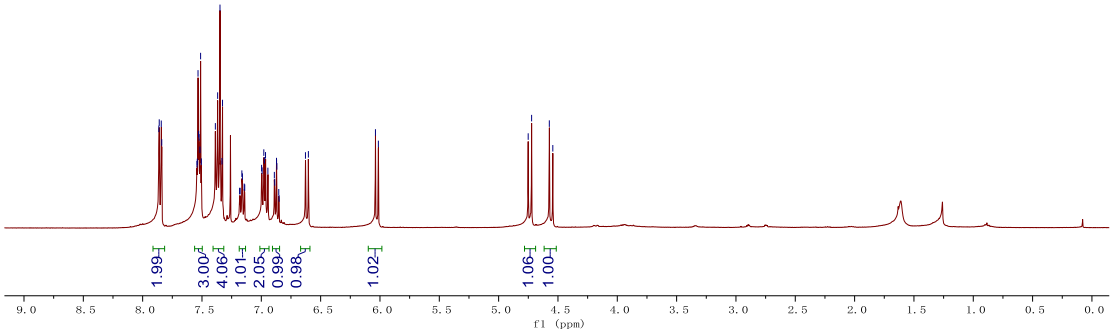
single_pulse
-114.05
F
O
O
O
3aa
f1 (ppm)

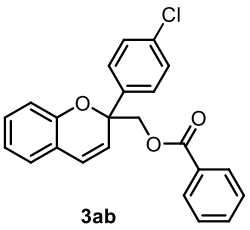

nyj-1-264-pro
single pulse decoupled gated NOE
166.16
163.56
161.11
152.62
137.26
137.23
133.05
129.68
128.29
127.64
127.56
126.77
125.63
124.53
121.39
120.81
116.29
115.42
115.20
79.75
69.81
F
O
O
O
3aa
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ab**

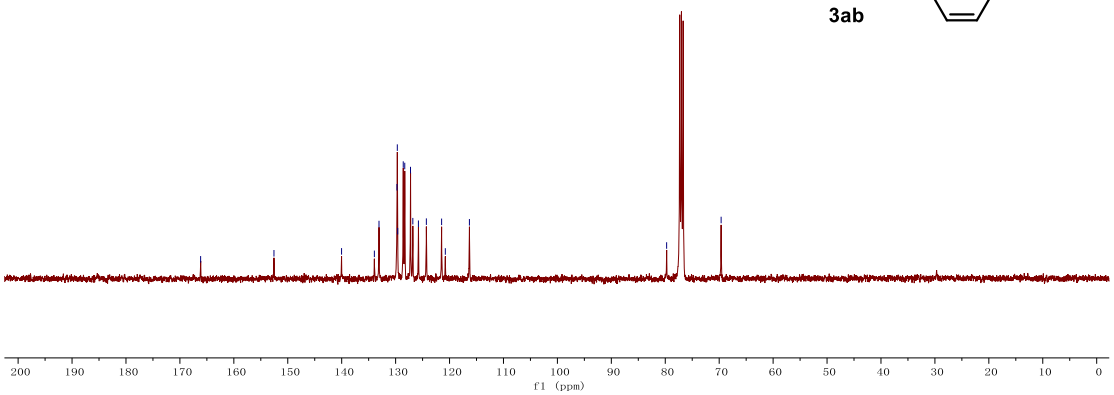


3ab

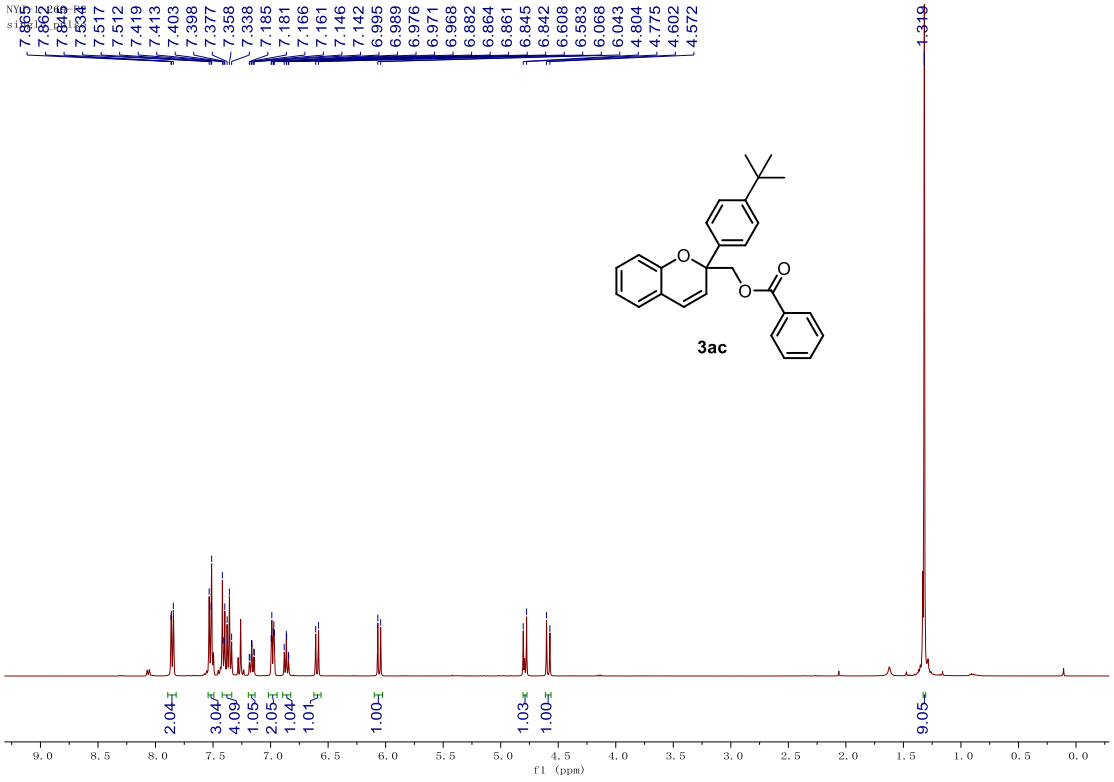


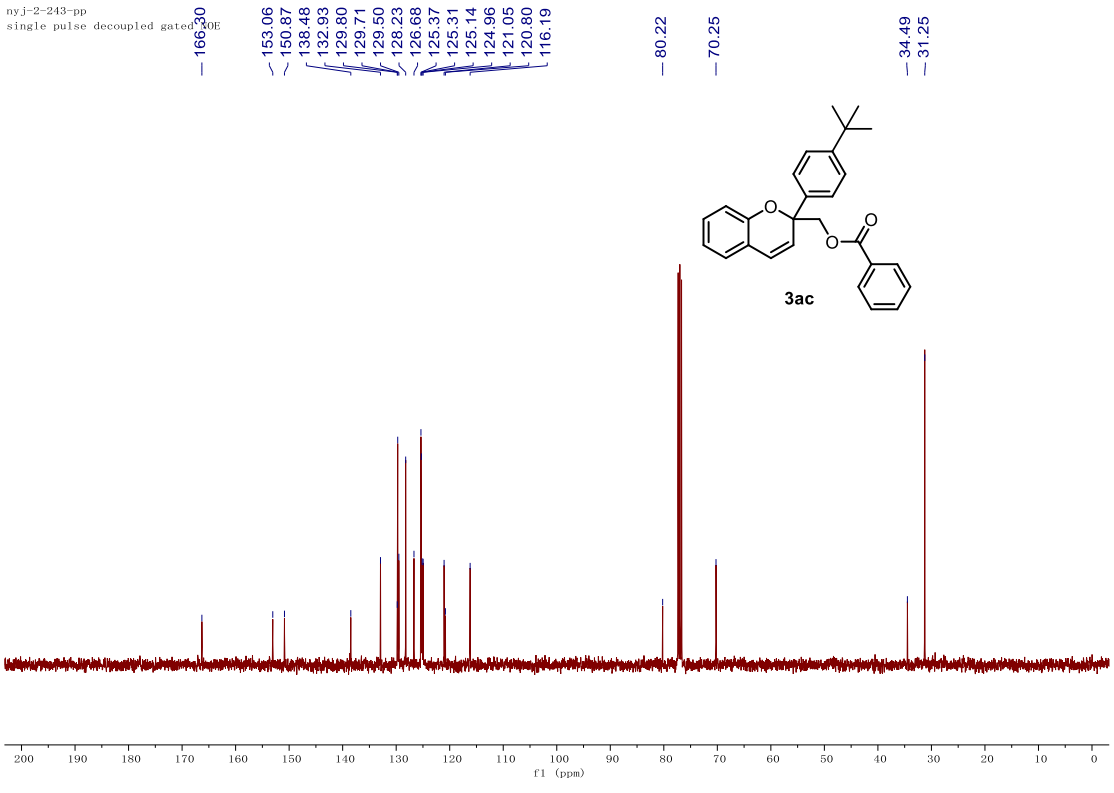


3ab

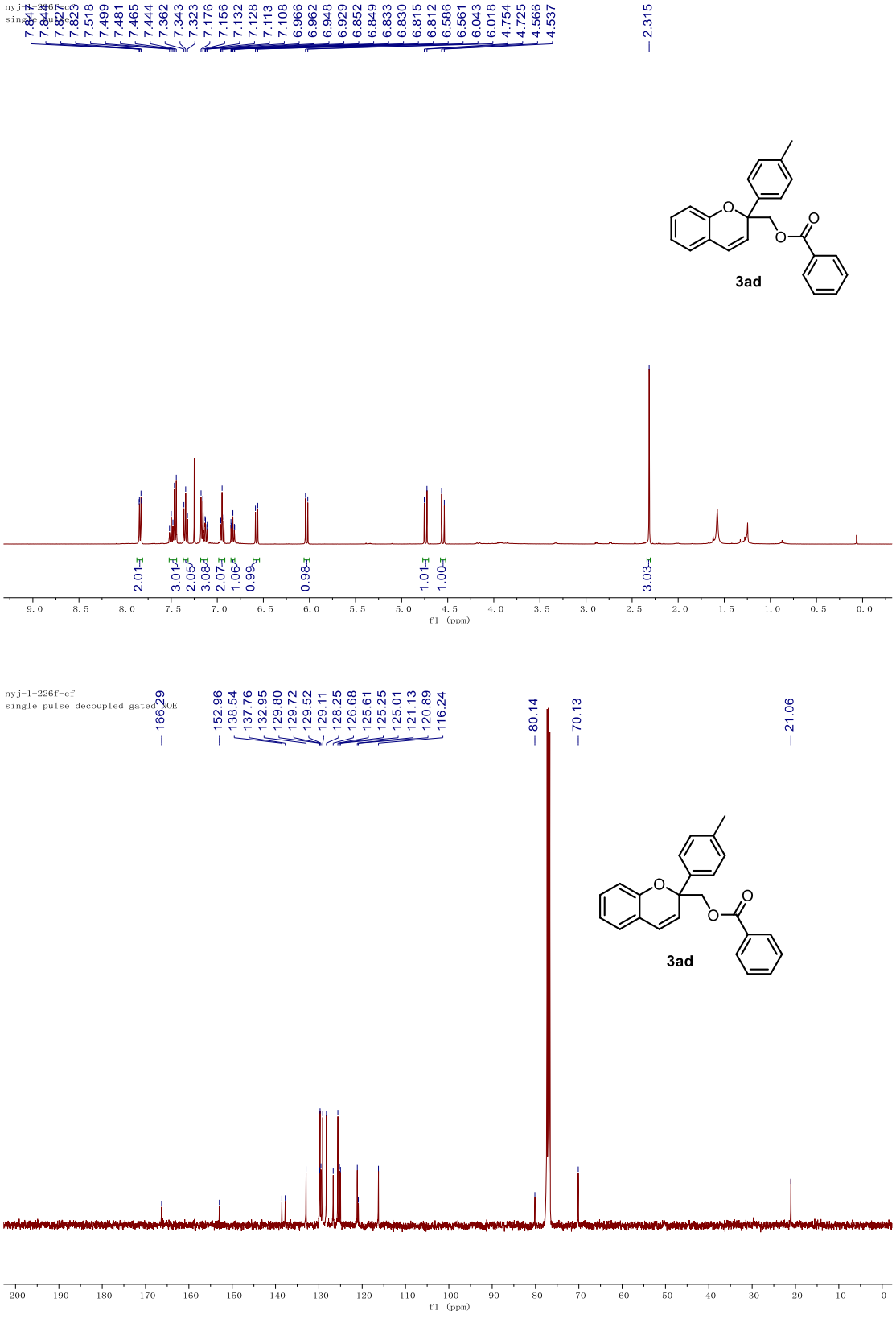


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ac**

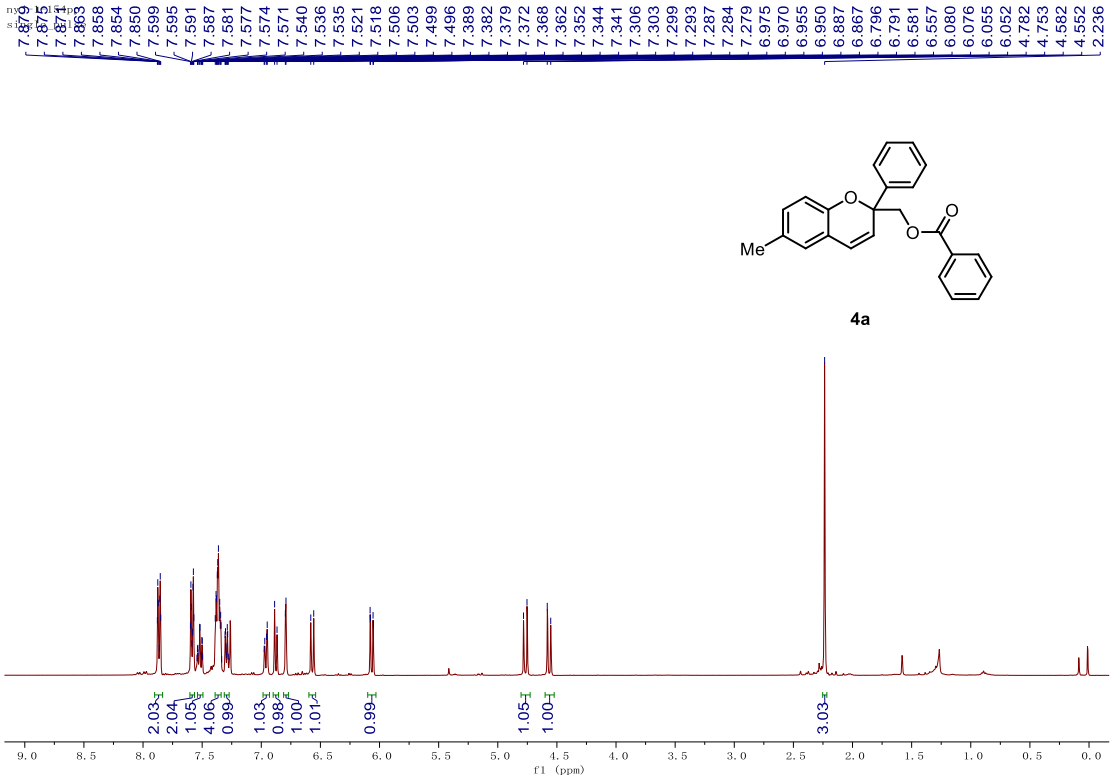


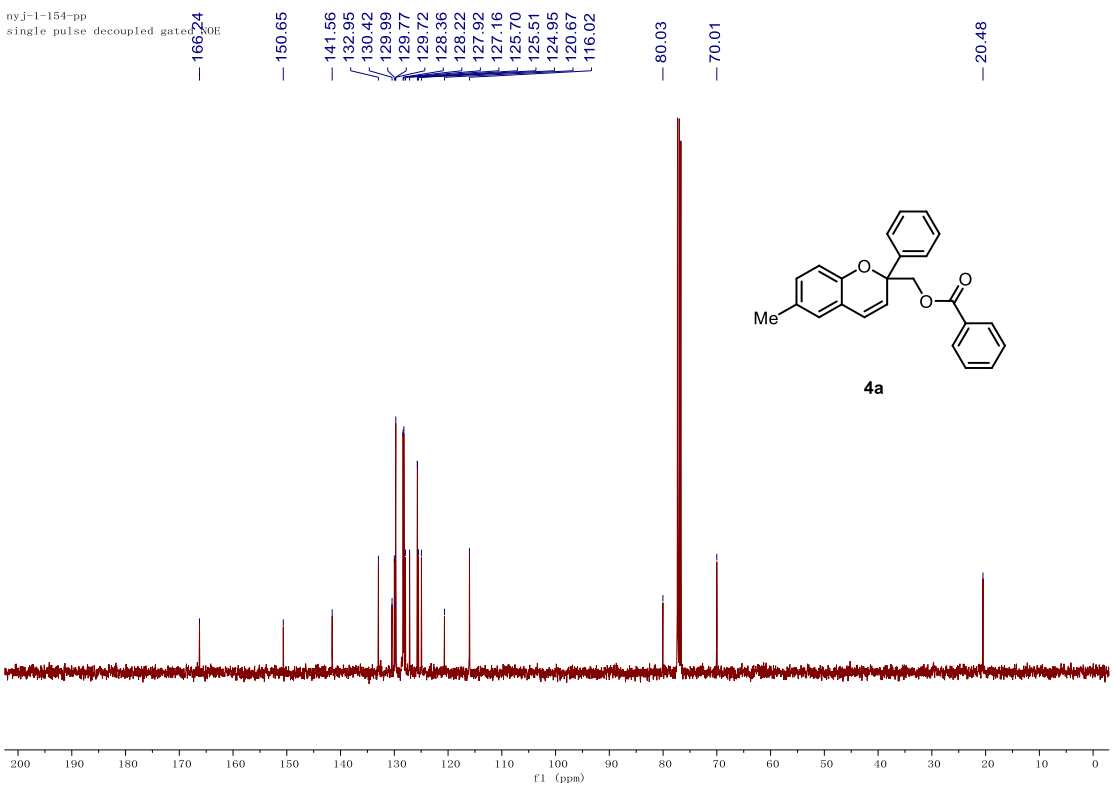


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3ad**

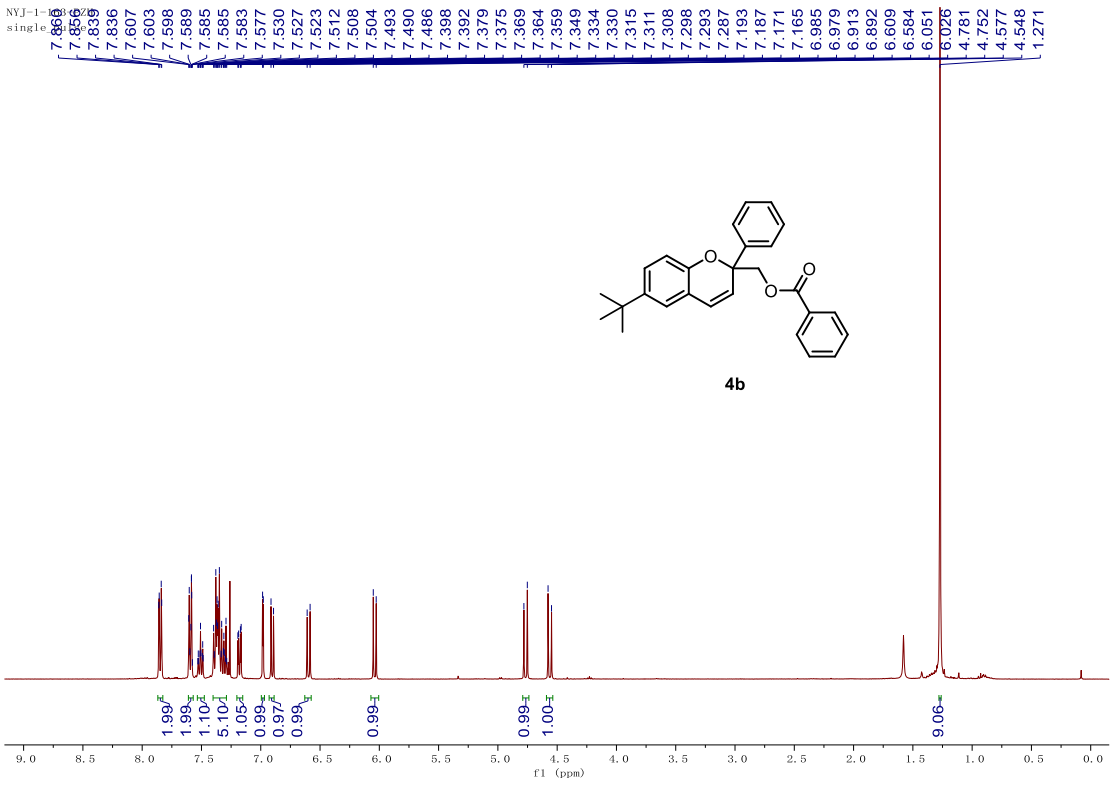


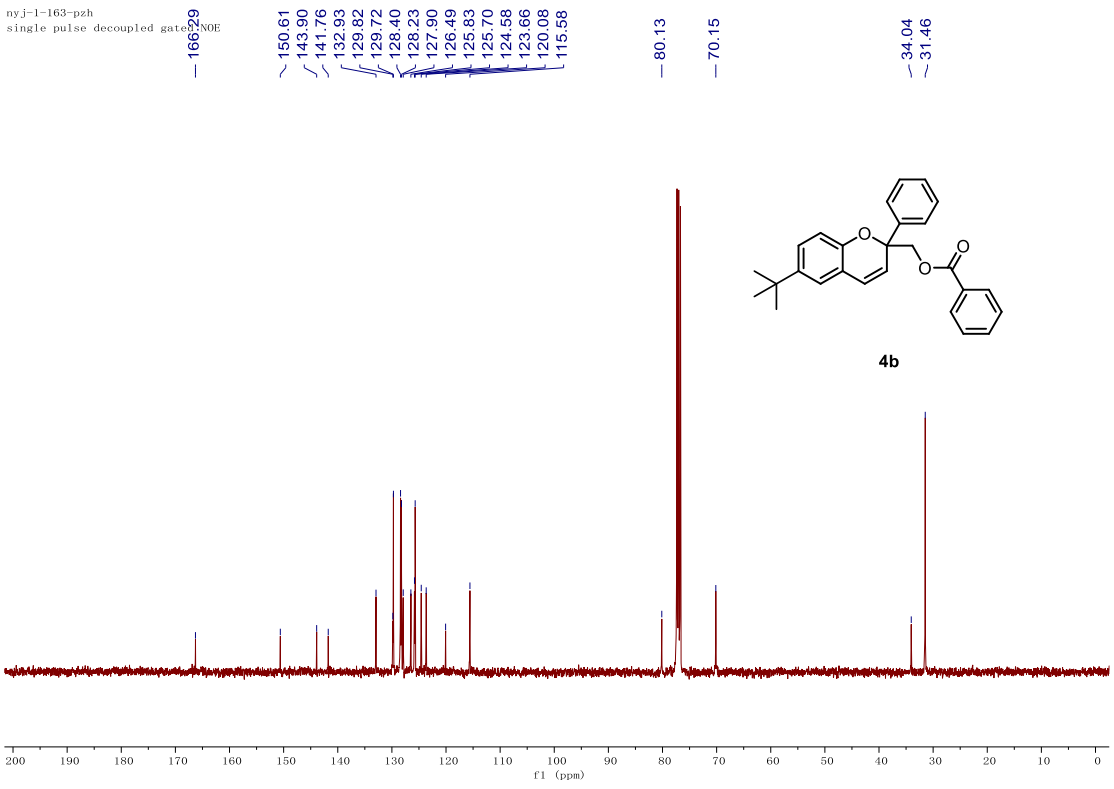
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4a**



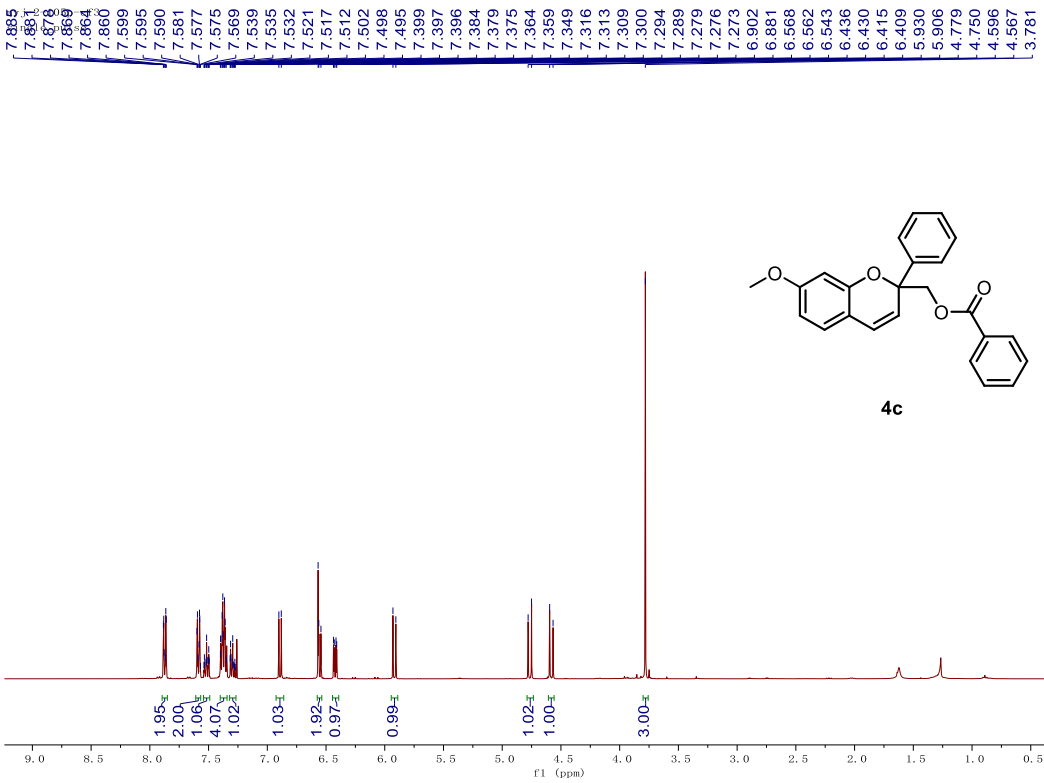


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4b**

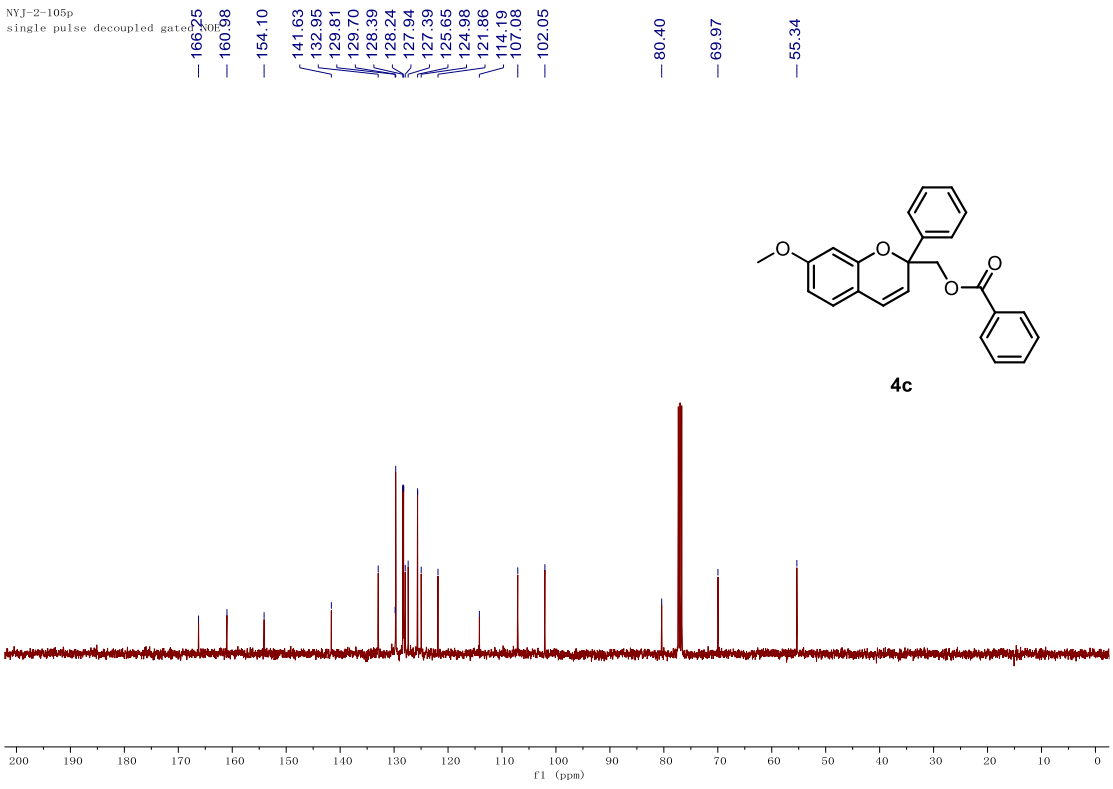




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4c**

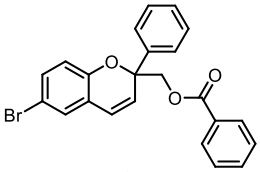


4c

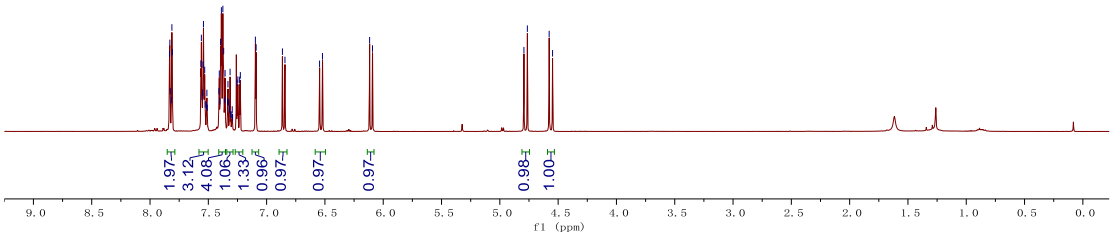


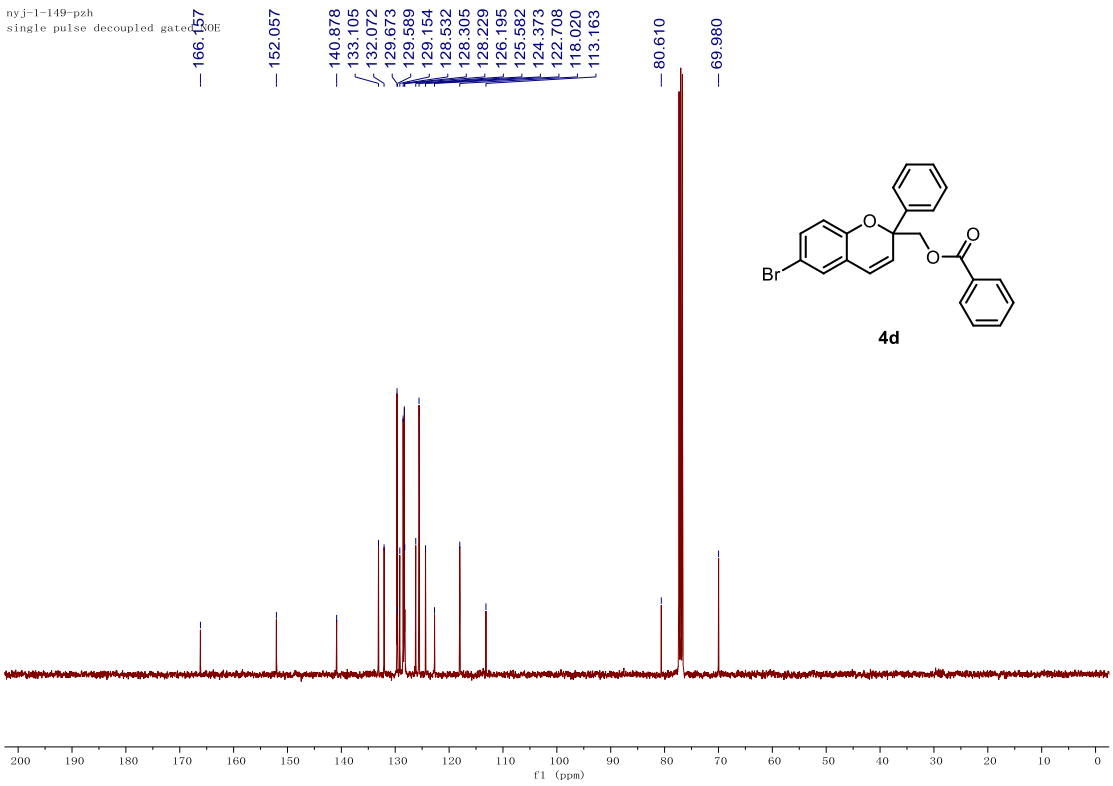
4c

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4d**



4d

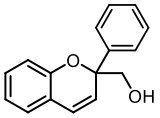




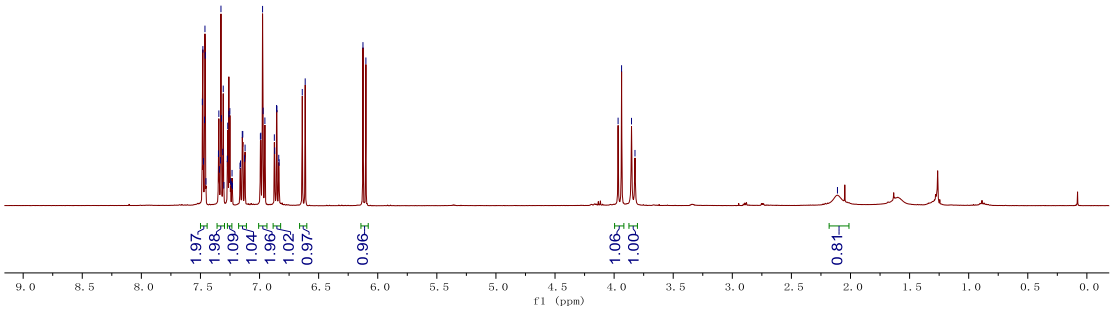
4d

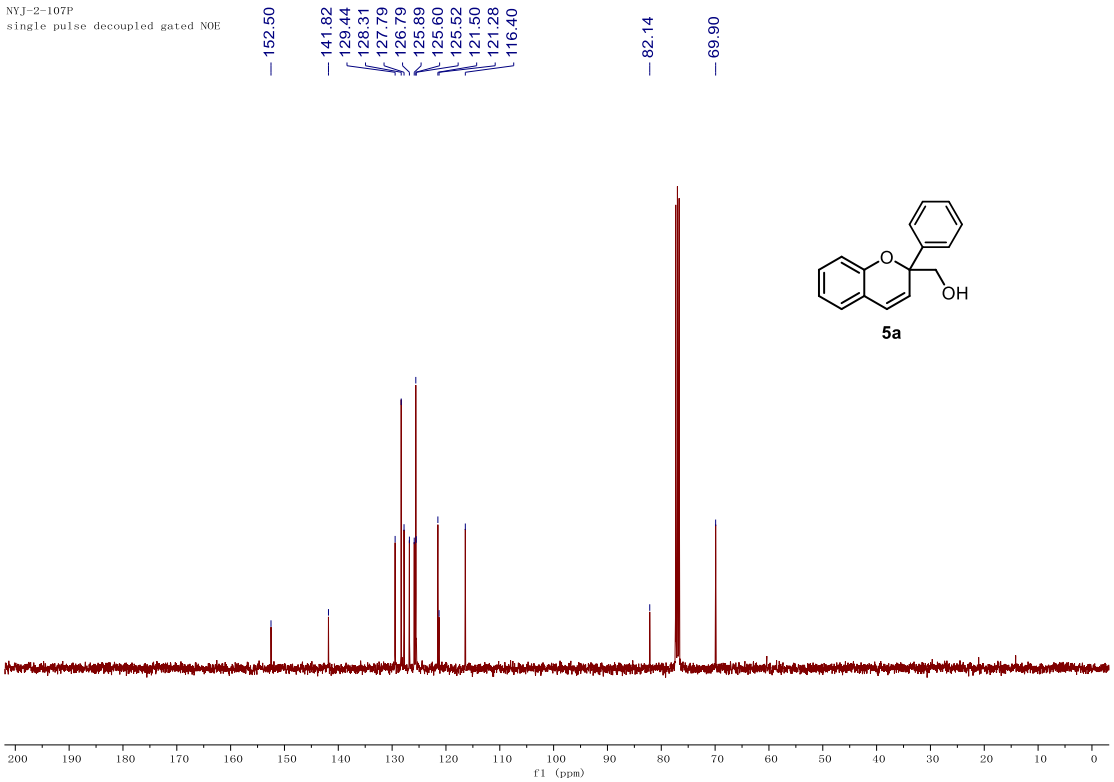
^{1}H NMR and ^{13}C NMR Spectra of Derivatizations **5a**, **6a**, **7a**, **8a-8g**

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5a**



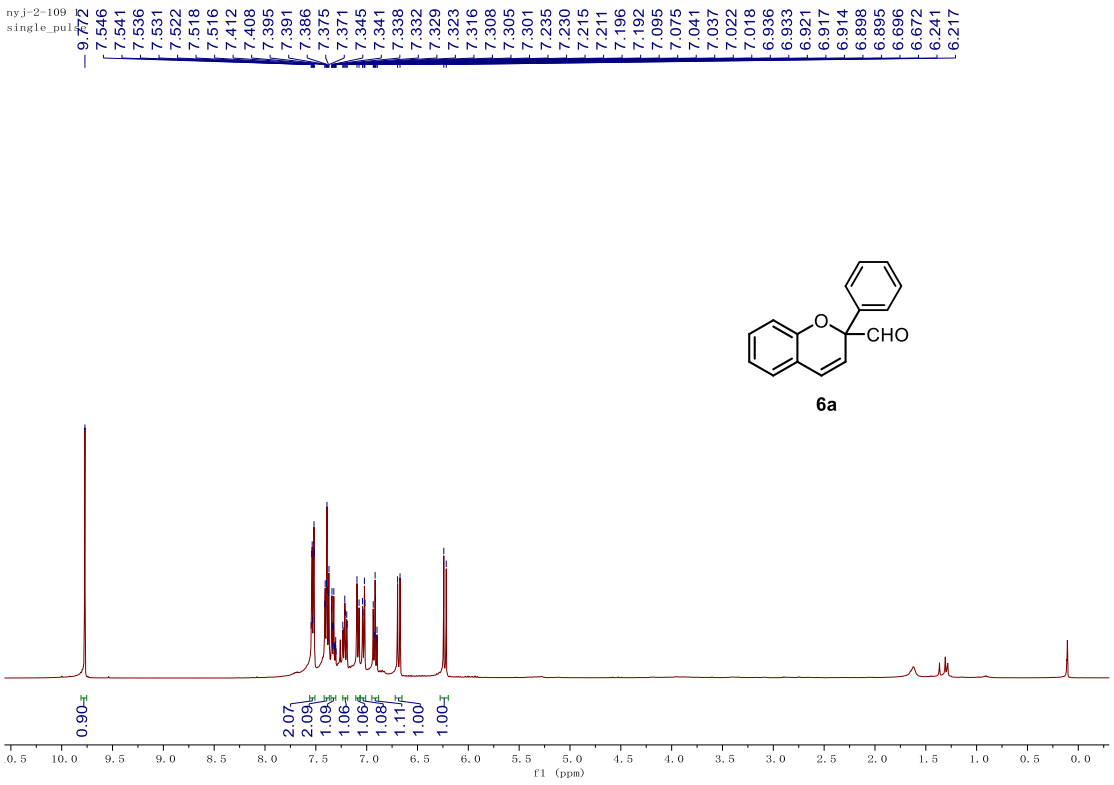
5a

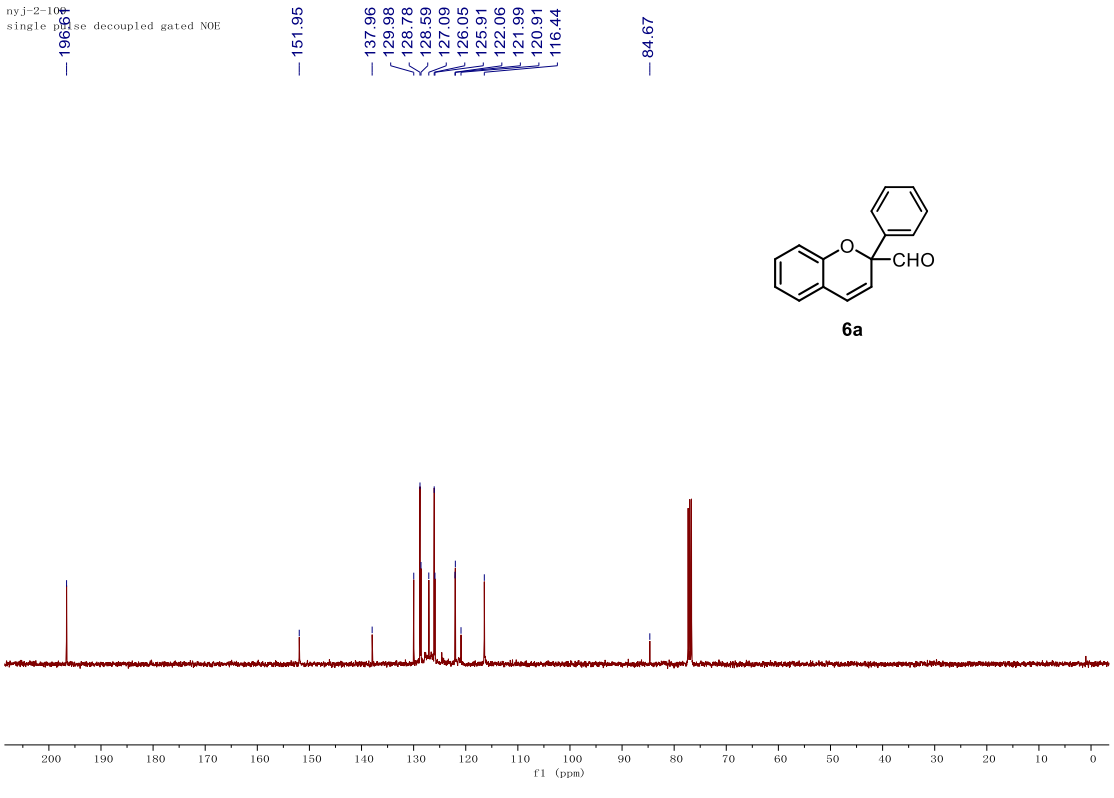




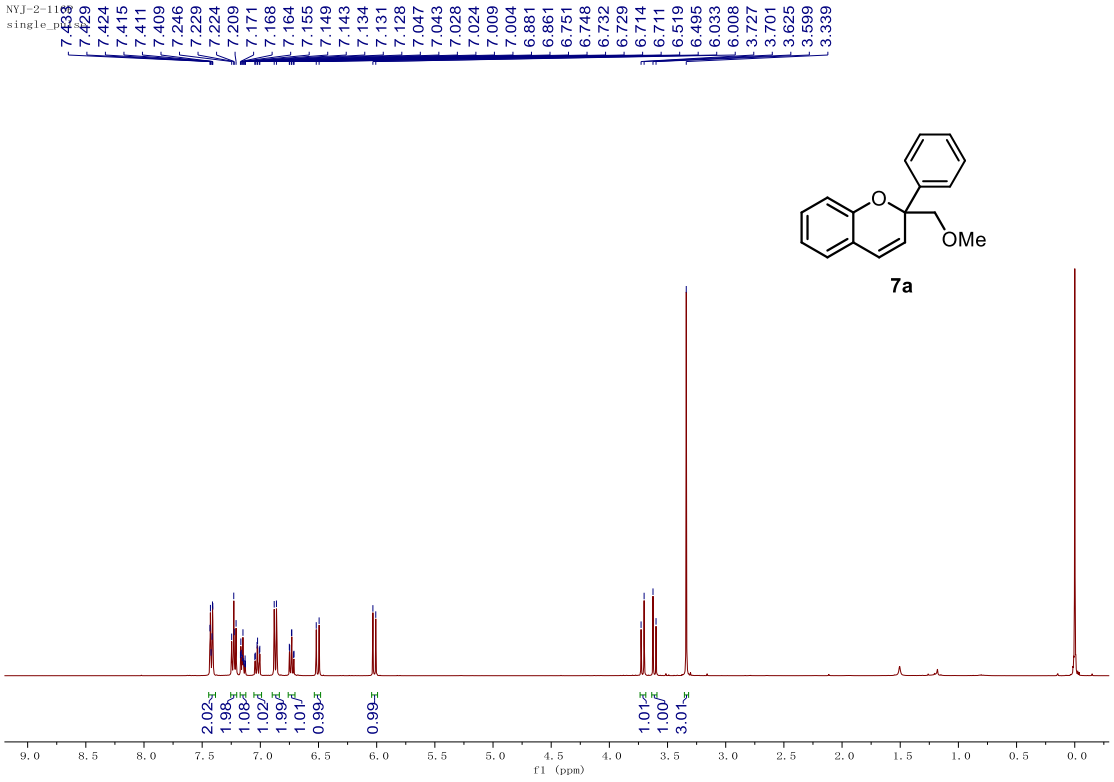
5a

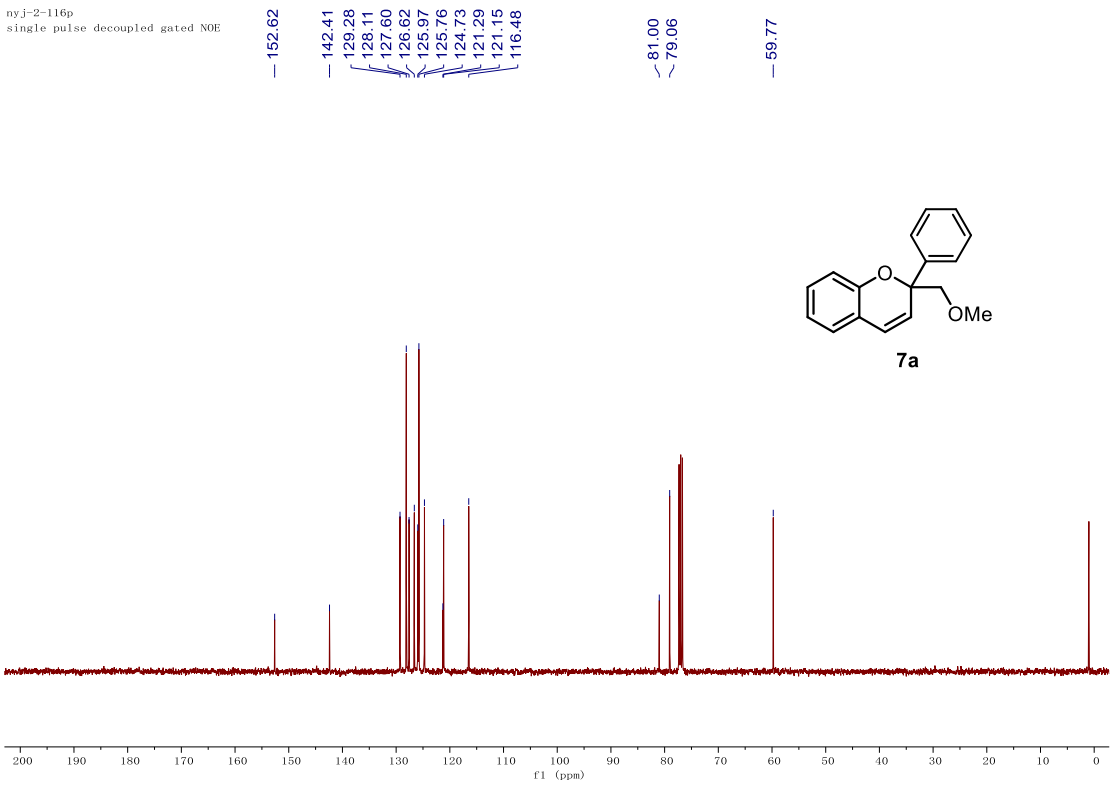
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **6a**



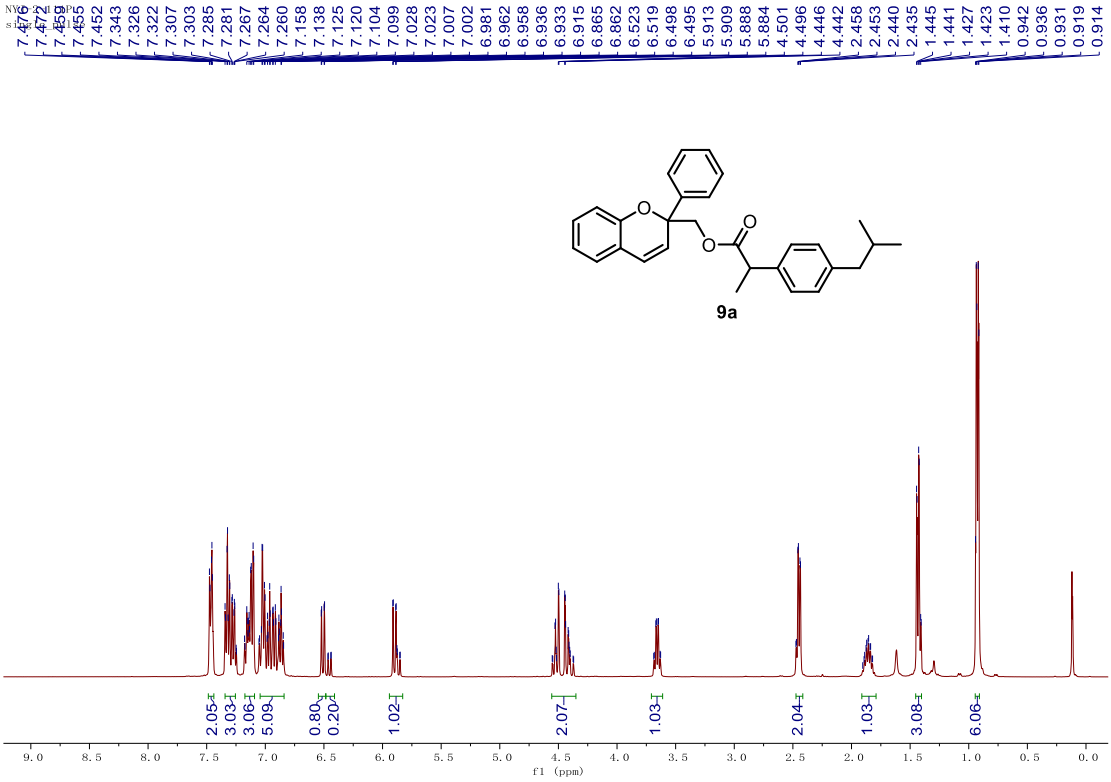


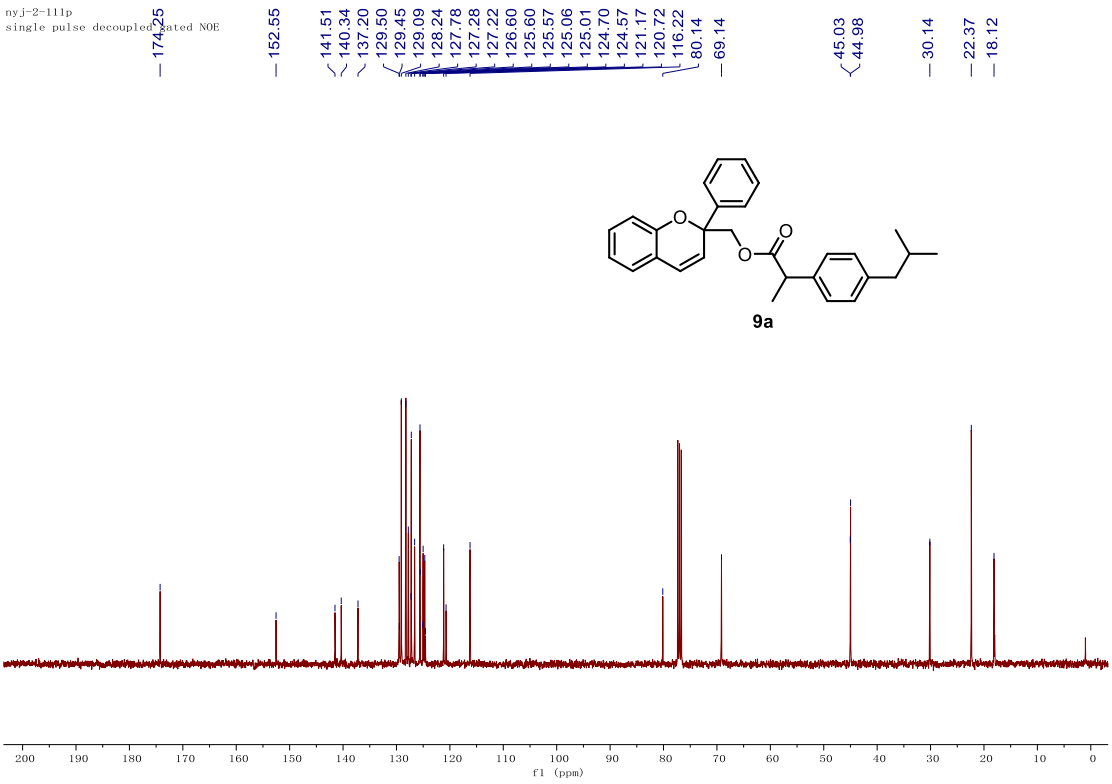
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **7a**



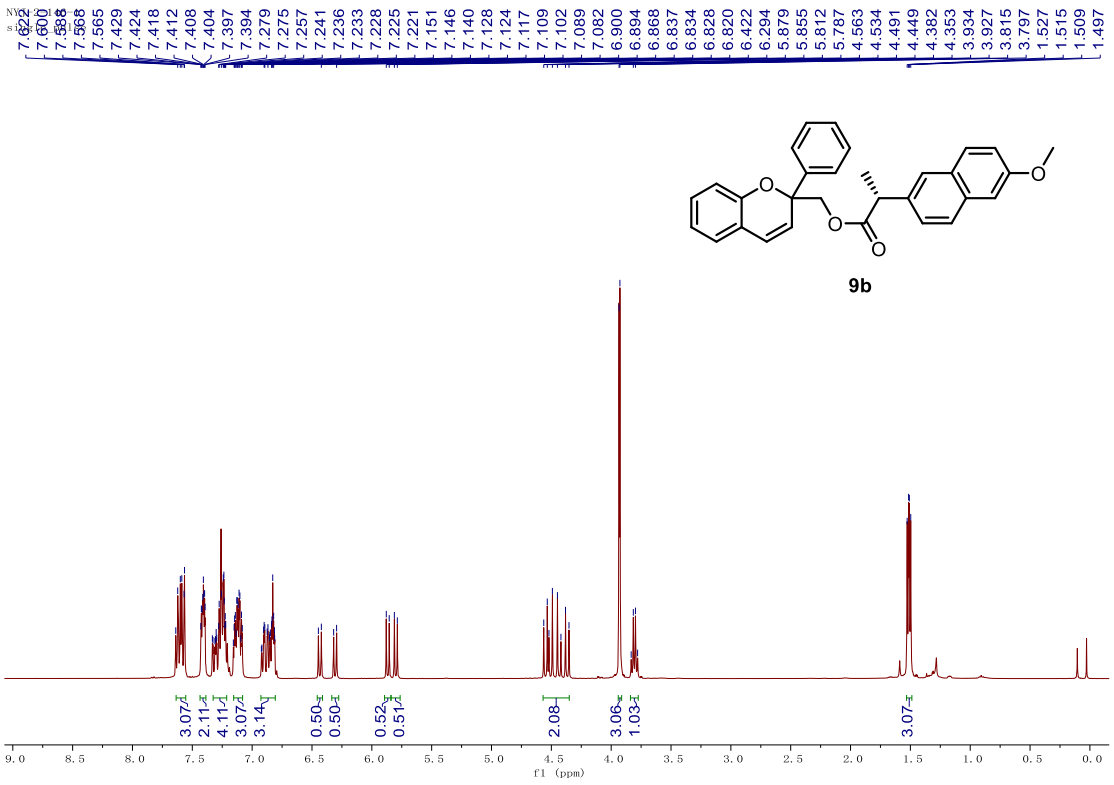


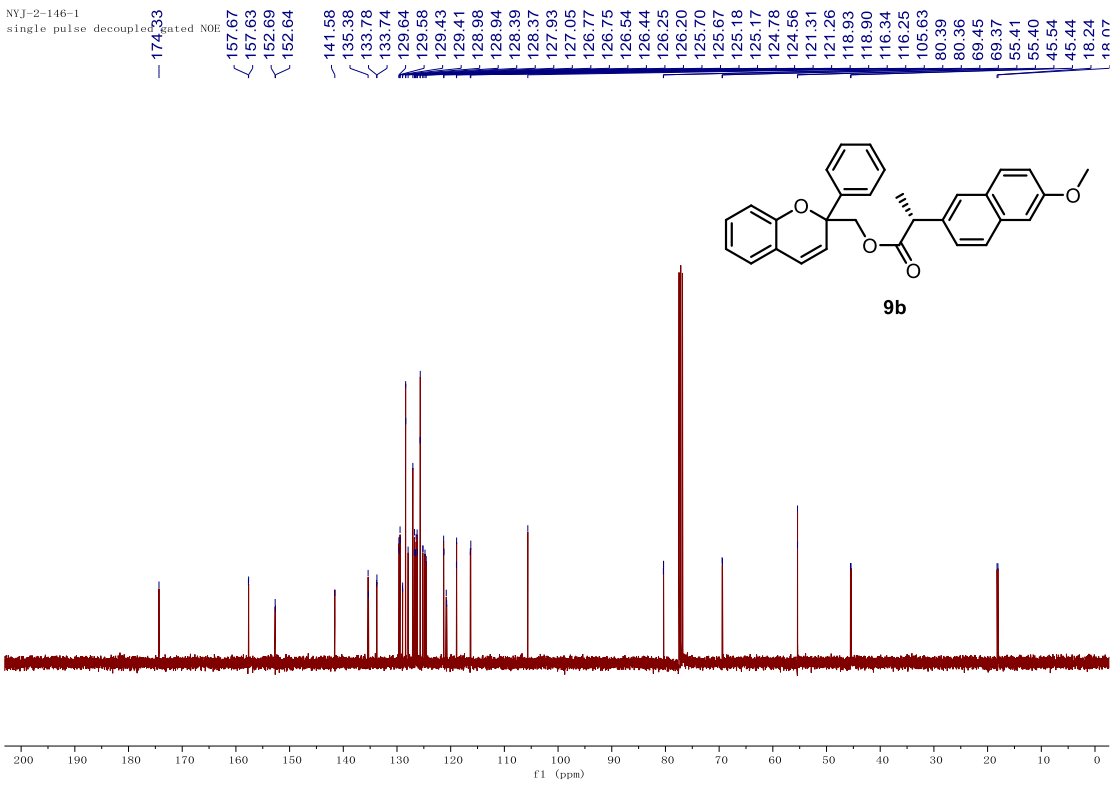
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9a**



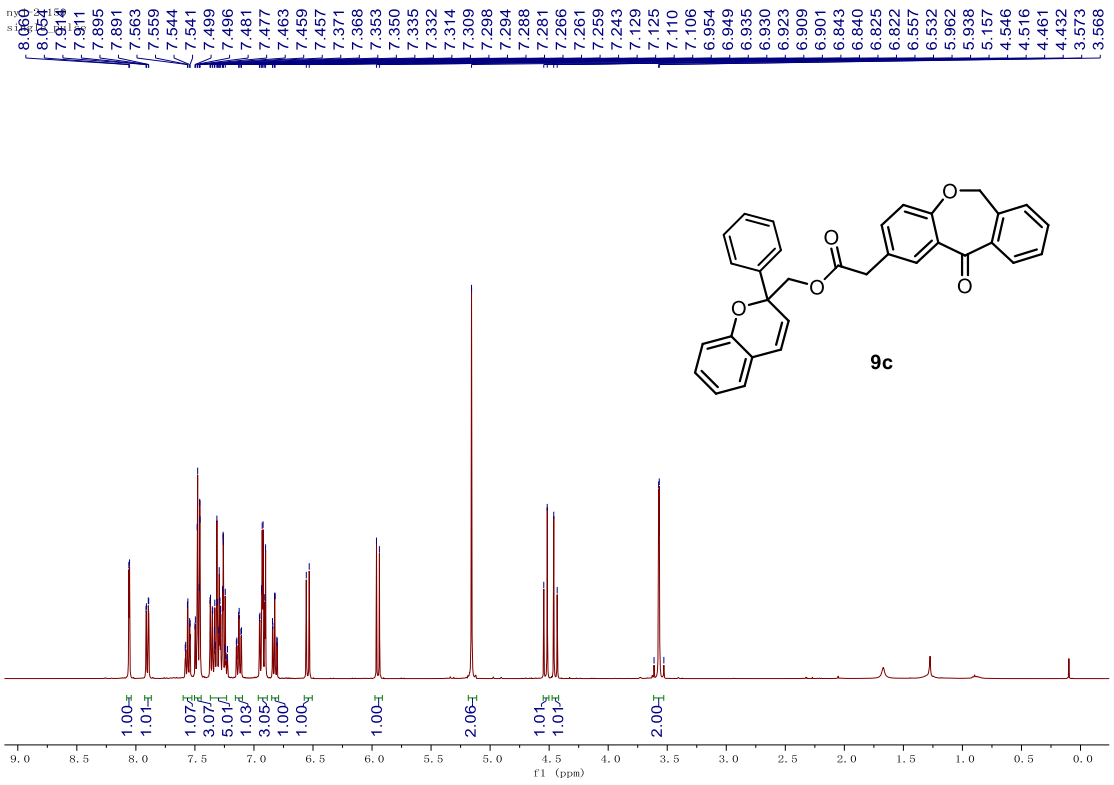


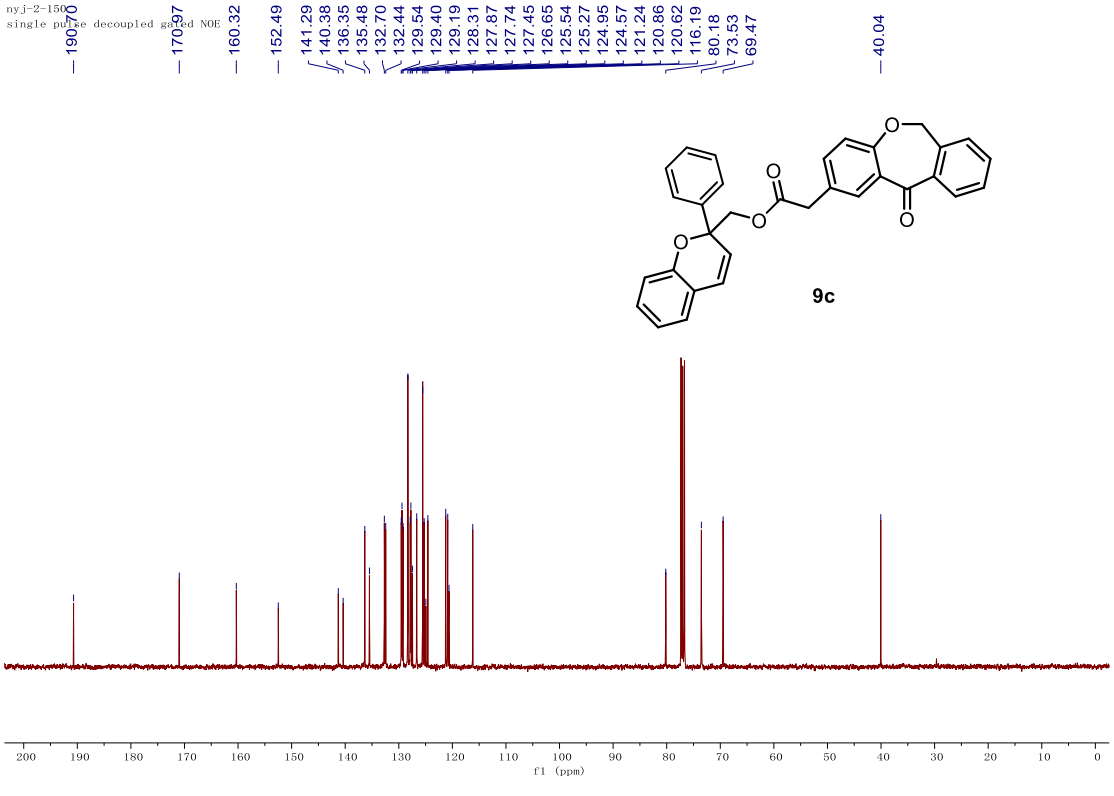
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9b**



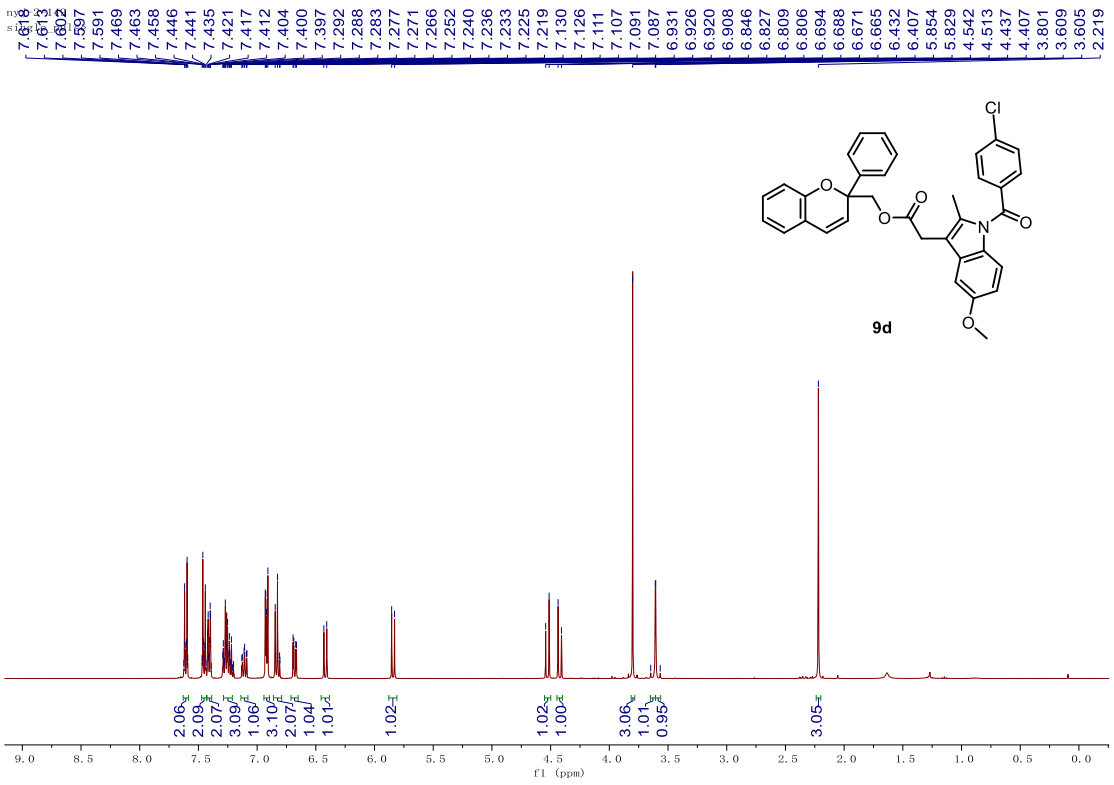


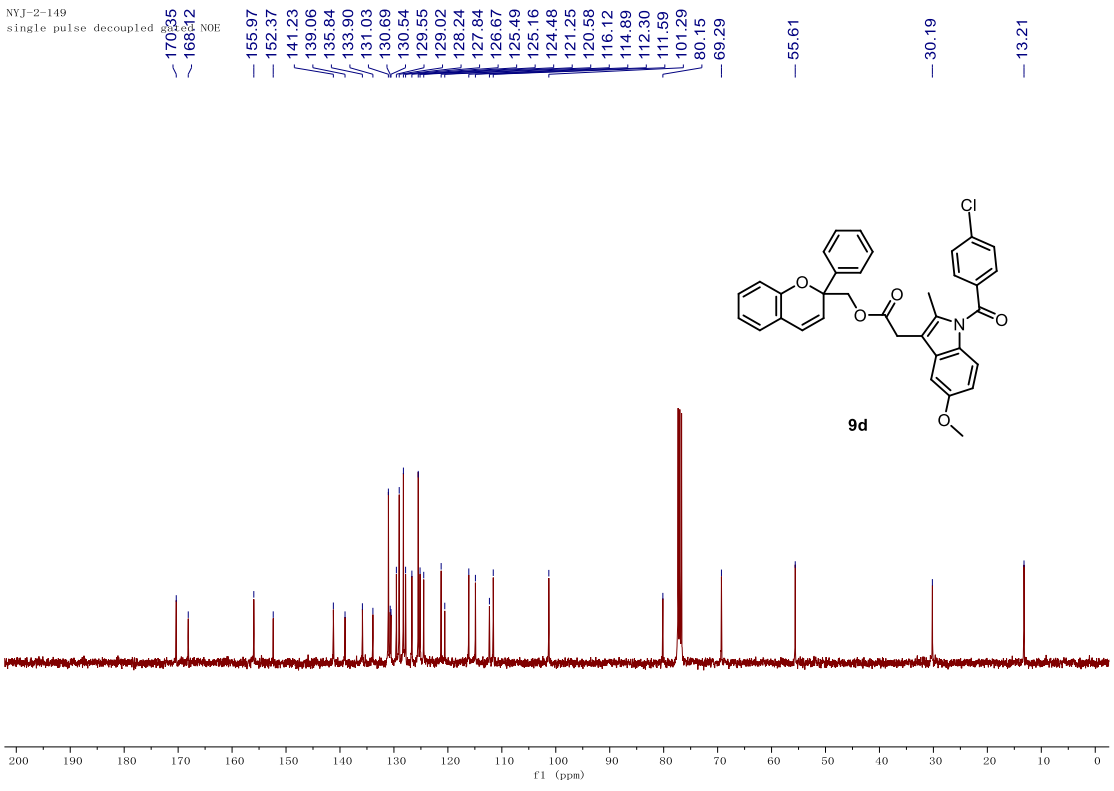
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9c**



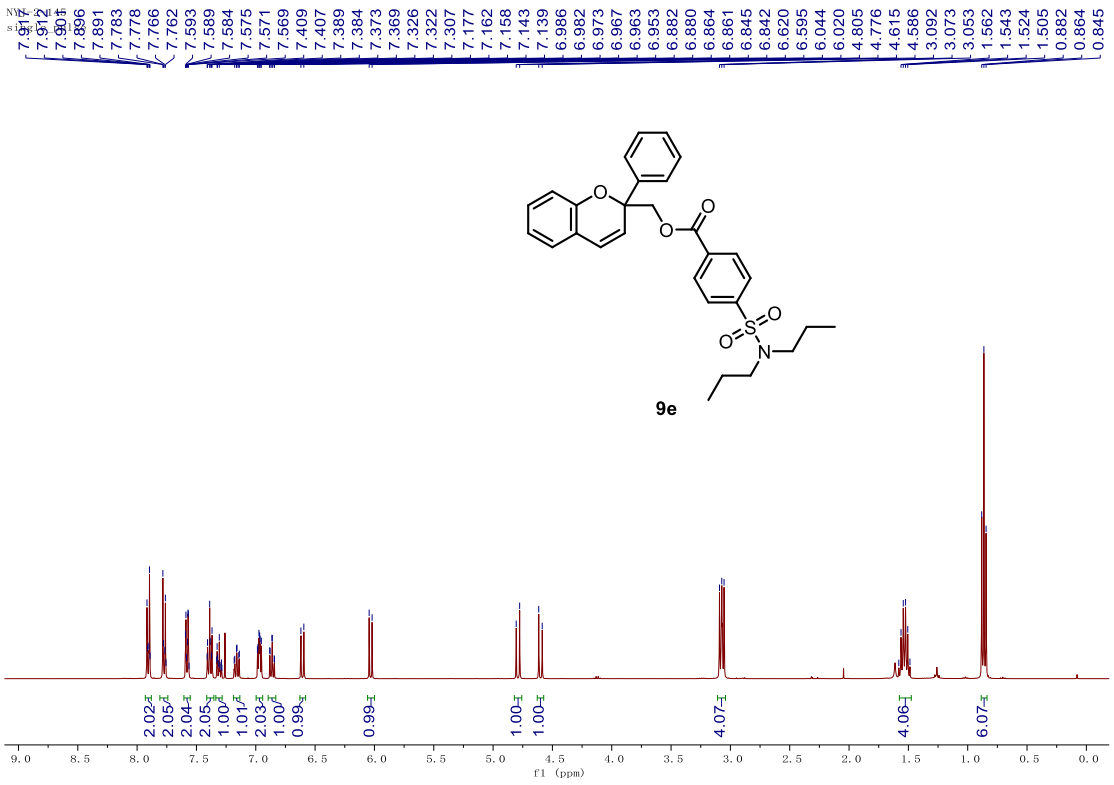


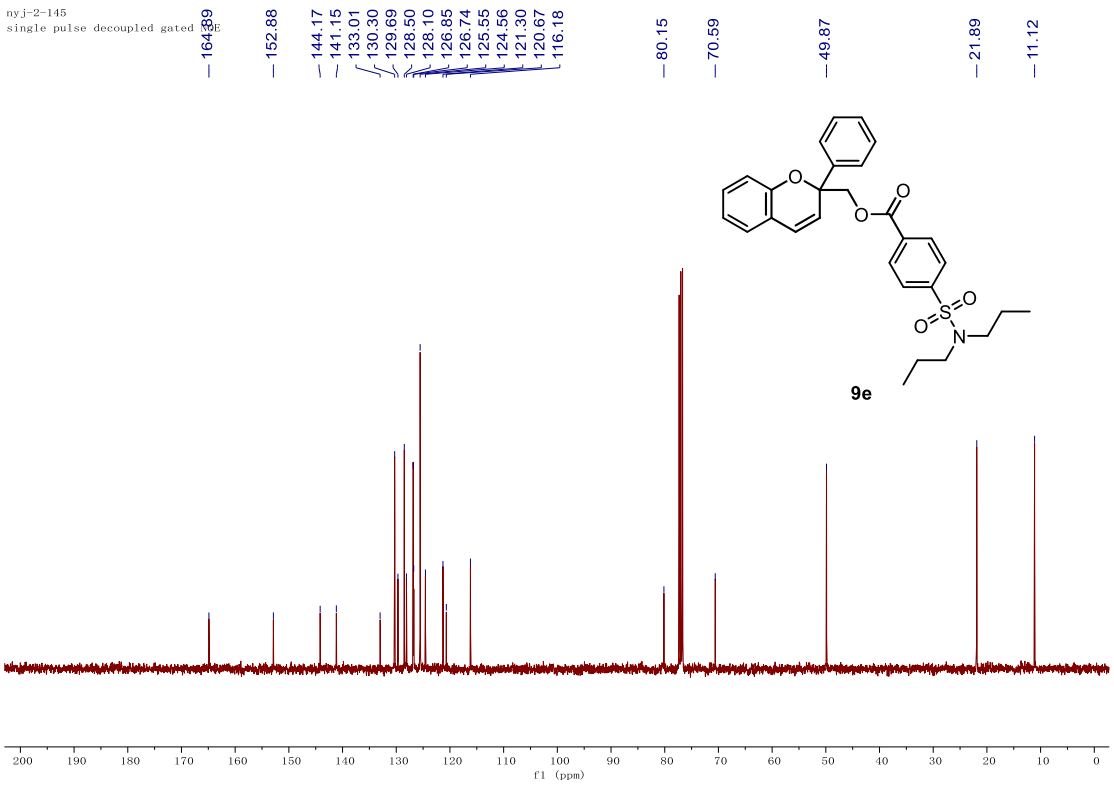
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9d**



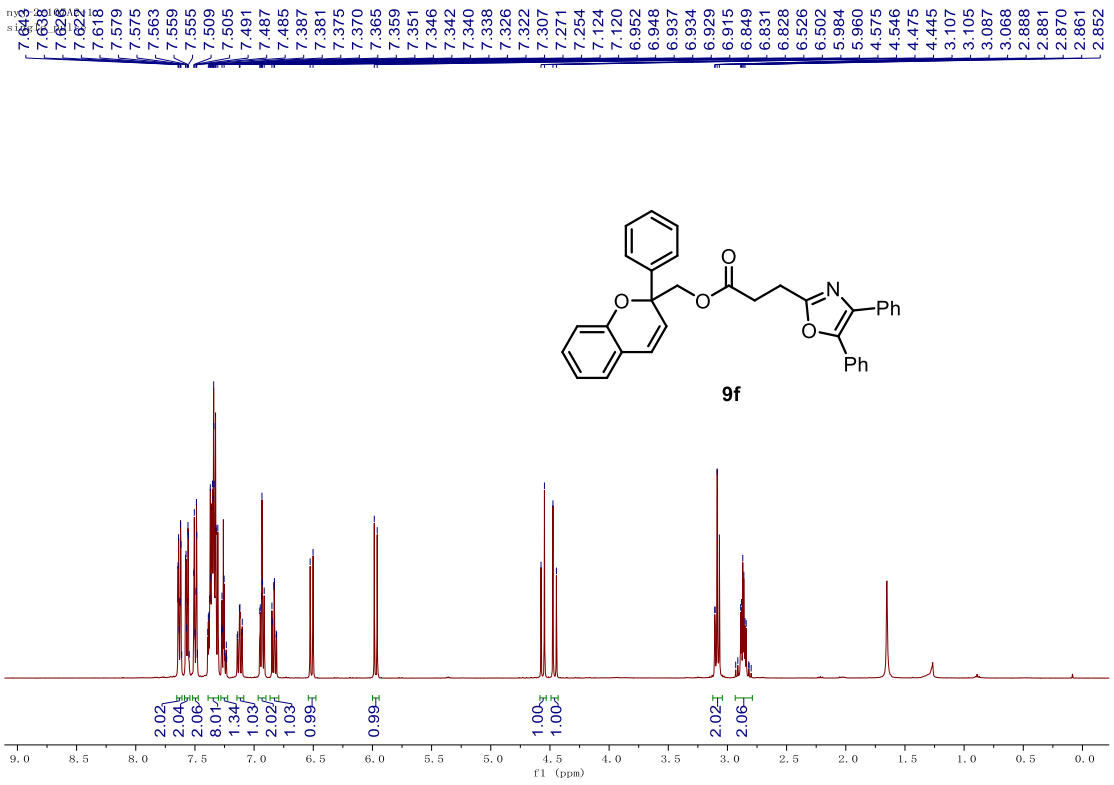


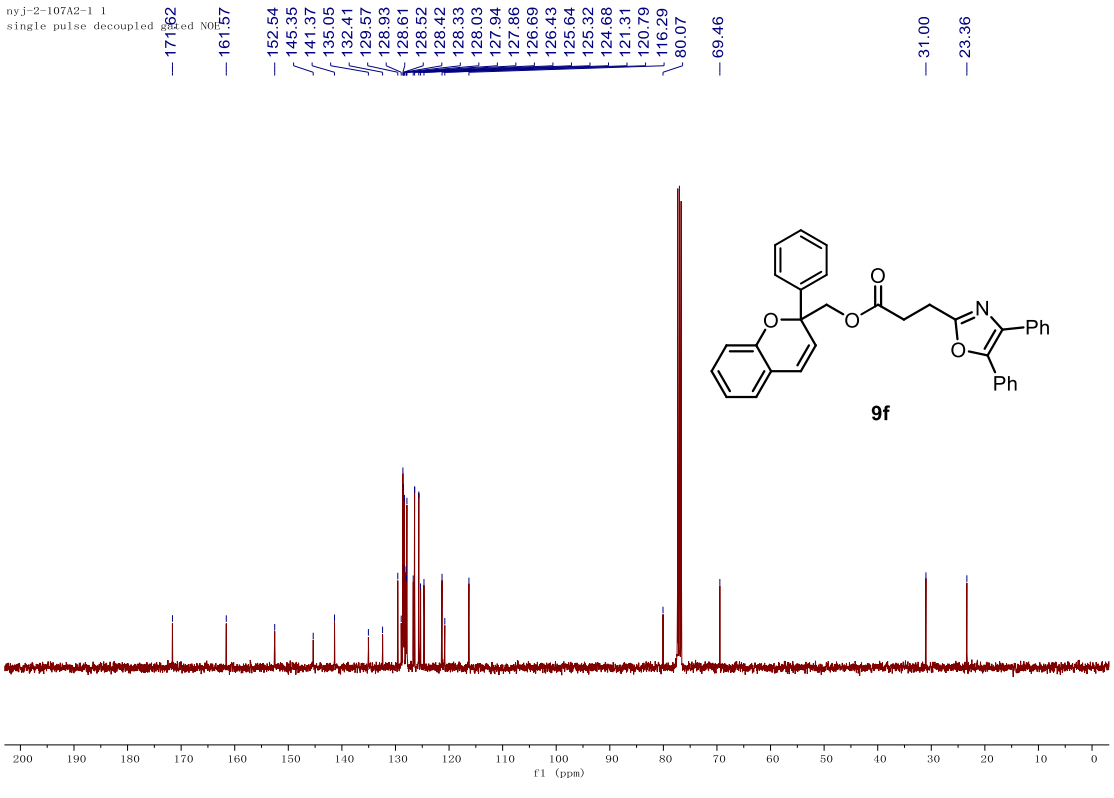
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9e**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9f**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **9g**