Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Phosphine-catalyzed Formal Buchner [6+1] Annulation: De Novo Construction of Cycloheptatrienes

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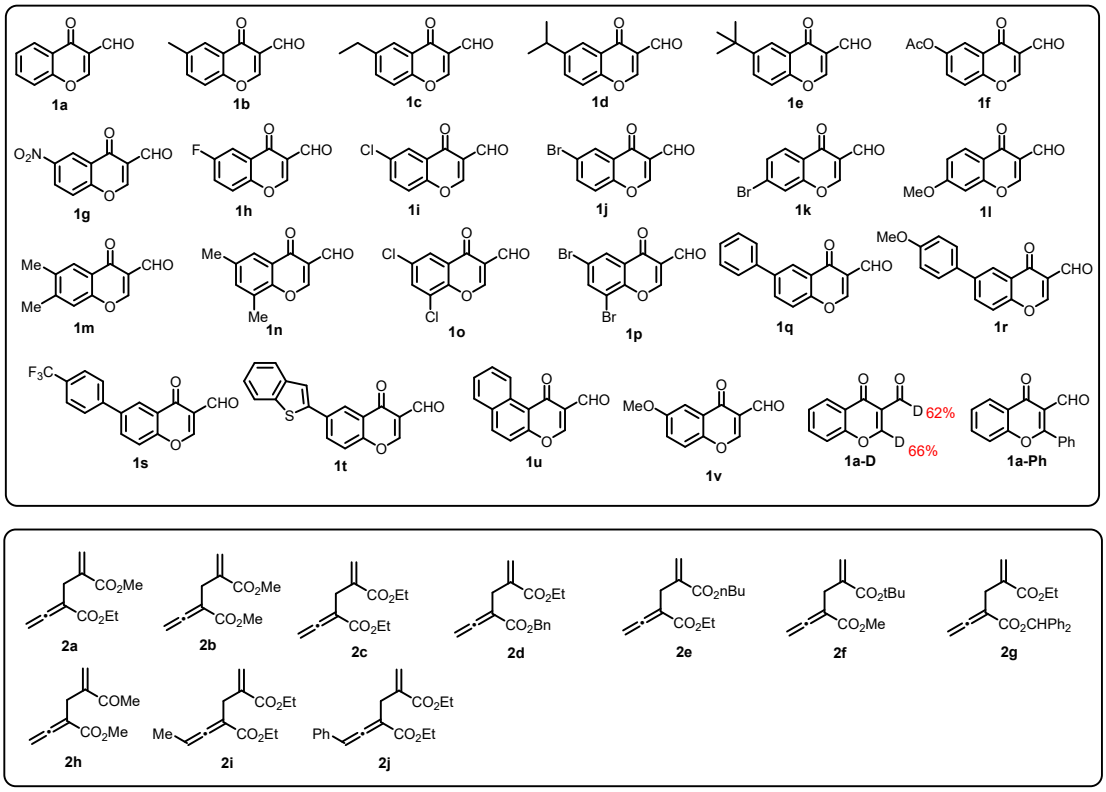
1. General Information

Commercial reagents and solvents were used as received without further purification, unless otherwise stated. Unless otherwise specified, reactions at 60 °C have been performed using the pre-heated water-bath or the pre-heated oil-bath maintained at 60 °C. Yields referred to isolated compounds through preparative TLC. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. And ^{19}F NMR were reported on a Bruker Avance (376 MHz) spectrometer. Chemical shifts for protons are reported in ppm and are referenced to the NMR solvent peak ($CDCl_3$: δ 7.26 ppm, D). Chemical shifts for carbons are reported in ppm and are referenced to the carbon resonances of the NMR solvent peak ($CDCl_3$: δ 77.06 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), brs (broad singlet) and m (multiplet). Enantiomeric excesses of the cycloheptatrienes products were determined by Agilent 6890 chiral-phase high performance liquid chromatography (HPLC) or LabAlliance PC2001, using chiralcel AD-H, OD-H, and ID-H. High resolution mass spectrometry (HRMS) were obtained on Q Exactive Focus or Agilent 6520 Q-TOF LC/MS with ESI resource. Melting points were measured on a RY-I apparatus and reported uncorrected.

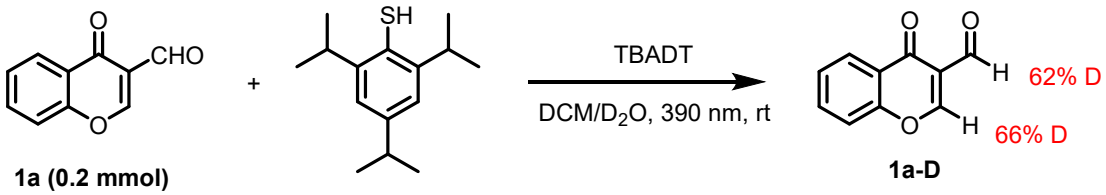
2. General Procedure of Starting Material

2.1. The substrates examined in this report.



The substituted 4-oxo-4H-chromene-3-carbaldehyde **1a-1v** [1], **1a-Ph** are known compounds, and their NMR data were identical with the literature. **1a-D** was prepared following the synthetic method according to the reported literature procedures [2]. The α-activated-allylic substituted allenoates **2a-2j** were prepared following the synthetic method according to the reported literature procedures [3].

2.2. General Procedure for substituted 3-formylchromones 1a-D:

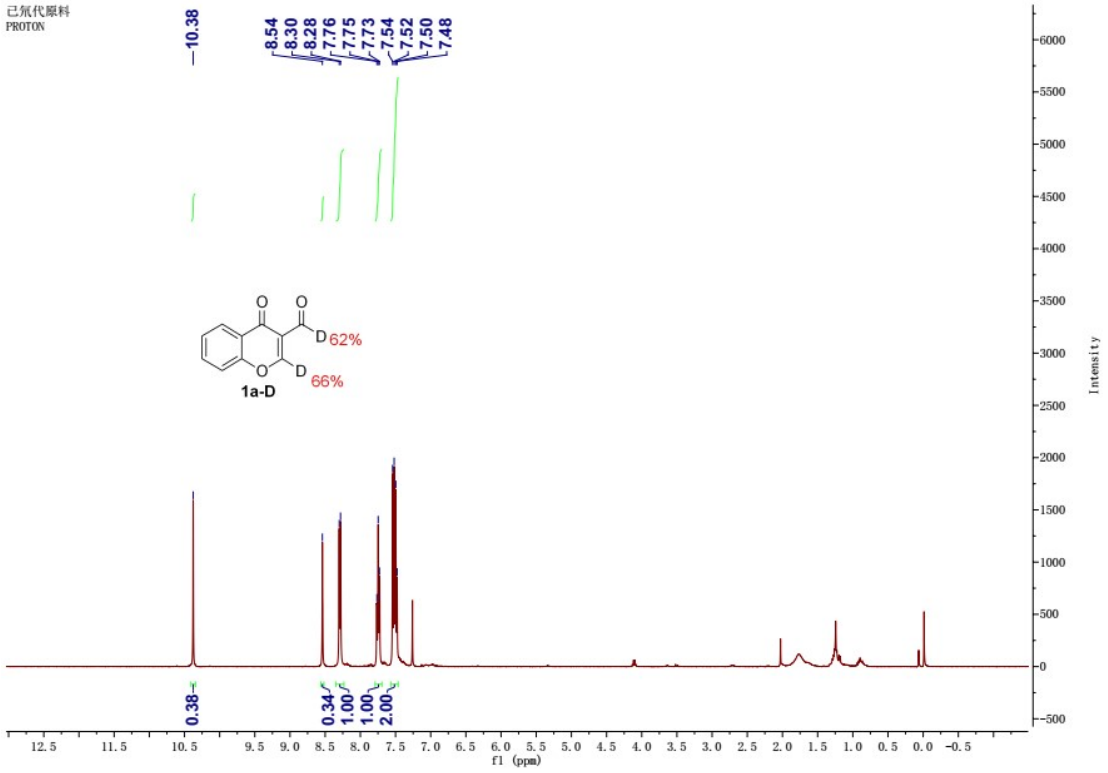


1a (0.2 mmol) **1a-D**

To a 10 mL glass vial was added TBADT (40.8 mg, 0.012 mmol, 4 mol %), aldehyde (0.3 mmol,
1.0 equiv), thiol (28 mg, 0.12 mmol, 40 mol %) and DCM/D_2O (1:1, v/v; 3.0 mL). The reaction mixture was degassed by bubbling with argon for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W 390 nm LED (approximately 2 cm away from the light source) at room temperature for 4 days. The reaction mixture was diluted with 10 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 ×20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography

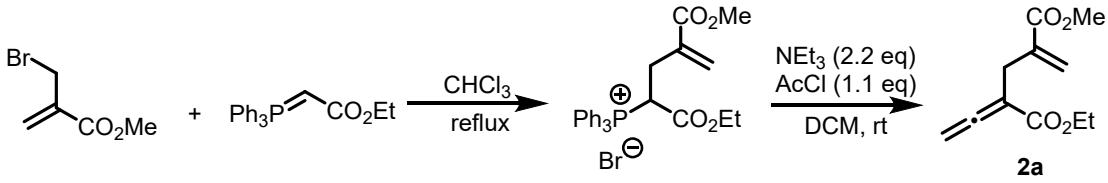
on silica gel using the indicated solvent system afforded the desired product as a white solid (27 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 0.38H), 8.54 (s, 0.34H), 8.29 (d, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 17.3, 8.2 Hz, 2H).



2.3. General Procedure for α-activated-allylic substituted allenoates 2a-2g:

Allenoates **2a-2f** were prepared according to the reported methods described in the literature[4]

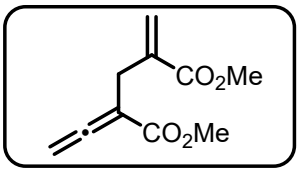


Allenoate 2a:

To a stirred solution of (carbethoxymethylene)triphenylphosphorane (20.89 g, 60 mmol) in chloroform (250 mL) was added 1.0 eq of methyl 2-(bromomethyl)acrylate (10.74 g, 60 mmol) in an oven-dried 500 mL glass vial at room temperature. The reaction mixture was refluxed until methyl 2-(bromomethyl)acrylate (monitored by TLC) was disappeared. The solvent was evaporated under reduced pressure. To the resulting phosphornium salt was added dichloromethane (300 mL) and 2.2 eq of triethylamine (17 mL, 132 mmol). After stirred for about 1 hr, 1.1 eq of acetyl chloride (5.4 mL, 66 mmol) was added dropwise over 30 min. Then the reaction mixture was allowed to be stirred overnight. The resulting mixture was poured into a Buchner funnel that was packed with silica gel and was washed with dichloromethane for several times. The combined filtrate was carefully concentrated and the residue was subjected to a flash column chromatography (petroleum ether : ethyl acetate = 20:1) to provide allenoate **2a** as a colorless oil (7.5 g, 60 mmol, 60% yield).

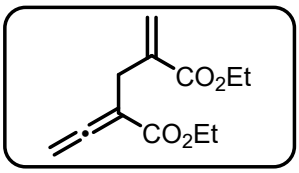
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 5.57 (s, 1H), 5.06 (t, J = 2.8 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 3.21 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.97, 166.83, 166.33, 137.16, 126.61, 98.09, 79.31, 60.96, 51.70, 30.81, 14.03;
HRMS (ESI): m/z calcd for $C_{11}H_{15}O_4$ ($[M+H]^+$): 211.0965; found: 211.0963.

Allenoate 2b:



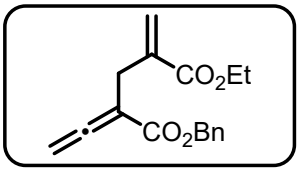
The general procedure outlined above was followed (30 mmol scale, using 1.0 eq of methyl (triphenylphosphoranylidene)acetate). Allenoate **2b** was formed as a colorless oil (3.3 g, 30 mmol, 56% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 1H), 5.59 (s, 1H), 5.10 (t, *J* = 2.7 Hz, 2H), 3.70 (s, 6H), 3.22 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.21, 166.91, 137.15, 126.81, 97.93, 79.50, 52.24, 51.83, 30.94.
HRMS (ESI): m/z calcd for $C_{10}H_{13}O_4$ ($[M+H]^+$): 197.0809; found: 197.0809.

Allenoate 2c:



The general procedure outlined above was followed (30 mmol scale, using 1.0 eq of ethyl 2-(bromomethyl)acrylate). Allenoate **2c** was formed as a colorless oil (4.5 g, 30 mmol, 67% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (s, 1H), 5.57 (s, 1H), 5.09 (t, J = 2.8 Hz, 2H), 4.17 (m, 4H), 3.24 (s, 2H), 1.25 (m, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.14, 166.47, 166.43, 144.87, 122.97, 97.45, 79.97, 61.42, 60.40, 31.29, 14.34, 14.32.
HRMS (ESI): m/z calcd for $C_{12}H_{17}O_4$ ($[M+H]^+$): 225.1121; found: 225.1120.

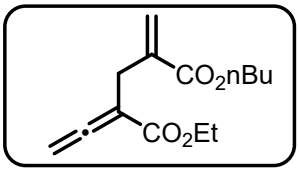
Allenoate 2d:



The general procedure outlined above was followed (using 30 mmol ethyl 2-(bromomethyl)acrylate and 1.0 eq benzyl 2-(triphenylphosphoranylidene)acetate). Allenoate **2d** was formed as a colorless oil (4.8 g, 30 mmol, 56% yield);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 6.24 (s, 1H), 5.61 (d, *J* = 0.9 Hz, 1H), 5.19 (s, 2H),

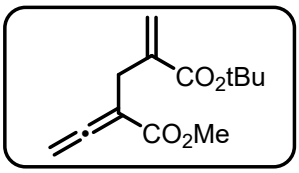
5.14 (t, *J* = 2.8 Hz, 2H), 4.23 – 4.16 (m, 2H), 3.29 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.43, 166.54, 166.44, 137.54, 136.01, 128.49, 128.08, 127.87, 126.63, 98.23, 79.71, 66.66, 60.75, 30.99, 14.19.
HRMS (ESI): m/z calcd for $C_{17}H_{19}O_4$ ($[M+H]^+$): 287.1278; found: 287.1274.

Allenoate 2e:



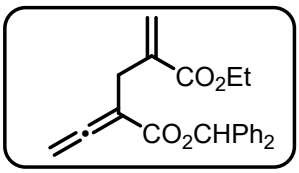
The general procedure outlined above was followed (30 mmol scale, using 1.0 eq of N-butyl 2-(bromomethyl)acrylate). Allenoate **2e** was formed as a colorless oil (4.26 g, 30 mmol, 56% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 1H), 5.56 (s, 1H), 5.08 (d, J = 1.2 Hz, 2H), 4.08-4.18 (m, 4H), 3.22 (s, 2H), 1.66 – 1.54 (m, 2H), 1.41 – 1.29 (m, 2H), 1.27 – 1.19 (m, 3H), 0.93 – 0.85 (m, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.07, 166.54, 166.47, 137.61, 126.39, 98.35, 79.42, 64.54, 61.05, 30.92, 30.59, 19.11, 14.15, 13.63;
HRMS (ESI): m/z calcd for $C_{14}H_{21}O_4$ ($[M+H]^+$): 253.1434; found: 253.1433.

Allenoate 2f:



The general procedure outlined above was followed (using 23.8 mmol methyl 2-(bromomethyl)acrylate and 1.0 eq methyl (triphenylphosphoranylidene)acetate). Allenoate **2f** was formed as a colorless oil (2.16 g, 23.8 mmol, 37% yield);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.48 (d, J = 1.3 Hz, 1H), 5.07 (t, J = 2.9 Hz, 2H), 3.69 (s, 3H), 3.18 (s, 2H), 1.42 (s, 9H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.08, 166.96, 165.58, 138.84, 125.58, 98.32, 80.52, 79.54, 52.17, 30.99, 27.91;
HRMS (ESI): m/z calcd for $C_{13}H_{18}O_4Na$($[M+Na]^+$): 261.1097; found: 261.1094.

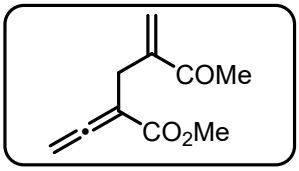
Allenoate 2g:



The general procedure outlined above was followed (using 40 mmol methyl 2-(bromomethyl)acrylate and 1.0 eq methyl (triphenylphosphoranylidene)acetate). Allenoate **2g** was formed as a colorless oil (4.14 g, 40 mmol, 29% yield);

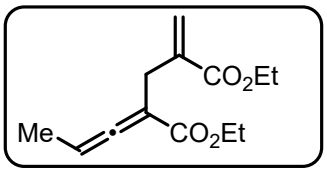
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 1.1 Hz, 3H), 7.36 (d, *J* = 1.0 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 2H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.30 (t, *J* = 1.7 Hz, 1H), 7.29 (t, *J* = 2.8 Hz, 1H), 6.94 (s, 1H), 6.25 (d, *J* = 0.5 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 5.24 (t, *J* = 2.8 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.62, 166.48, 165.55, 140.32, 137.46, 128.43, 127.80, 126.89, 126.60, 98.40, 79.67, 77.34, 60.70, 30.86, 14.13;
HRMS (ESI): m/z calcd for $C_{23}H_{22}O_4Na([M+Na]^+)$: 385.1410; found: 385.1413.

Allenoate 2h:



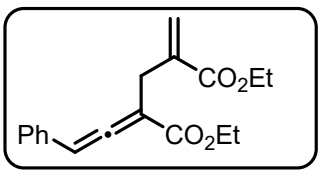
The general procedure outlined above was followed (using 40 mmol 3-(bromomethyl)but-3-en-2-one and 1.0 eq methyl (triphenylphosphoranylidene)acetate). Allenoate **2h** was formed as a colorless oil (0.7 g, 7.5 mmol, 52% yield);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.84 (s, 1H), 5.10 (t, *J* = 2.8 Hz, 2H), 3.73 (s, 3H), 3.22 (s, 2H), 2.32 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.40, 198.76, 167.09, 145.78, 126.62, 98.17, 79.37, 52.32, 30.03, 25.83;
HRMS (ESI): m/z calcd for $C_{10}H_{13}O_3$ ($[M+H]^+$): 181.0859; found: 181.0870.

Allenoate 2i:



The general procedure outlined above was followed (using 40 mmol 3-(bromomethyl)but-3-en-2-one and 1.0 eq ethyl (triphenylphosphoranylidene)acetate). Allenoate **2i** was formed as a colorless oil (0.75 g, 10 mmol, 32% yield);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 1H), 5.57 (s, 1H), 5.52 – 5.41 (m, 1H), 4.17 (qd, *J* = 7.1, 2.7 Hz, 4H), 3.31 – 3.16 (m, 2H), 1.69 (d, *J* = 7.3 Hz, 3H), 1.26 (dd, *J* = 15.7, 7.2 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 210.89, 166.98, 166.64, 138.17, 126.10, 98.17, 90.52, 60.92, 60.65, 31.47, 14.25, 14.21, 13.01;
HRMS (ESI): m/z calcd for $C_{13}H_{19}O_4$ ($[M+H]^+$): 239.1278; found: 239.1287.

Allenoate 2j:



The general procedure outlined above was followed (using 40 mmol 3-(bromomethyl)but-3-en-2-one and 1.0 eq ethyl (triphenylphosphoranylidene)acetate). Allenoate **2j** was formed as a colorless oil (7 g, 40 mmol, 58% yield);

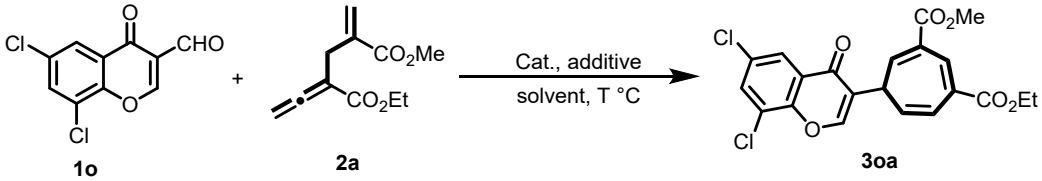
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (t, *J* = 2.6 Hz, 1H), 6.21 (s, 1H), 5.66 (s, 1H), 4.26 – 4.17 (m, 2H), 4.10 – 3.97 (m, 2H), 3.42 (ddd, *J* = 46.8, 15.9, 2.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.52, 166.42, 166.08, 137.63, 131.96, 128.68, 127.80, 127.36, 126.67, 102.54, 99.09, 61.25, 60.73, 31.69, 14.22, 14.02;

HRMS (ESI): m/z calcd for $C_{18}H_{21}O_4$ ($[M+H]^+$): 301.1434; found: 301.1432.

3. Optimization of Reaction Conditions

Table S1. Optimization of reaction conditions.[a]

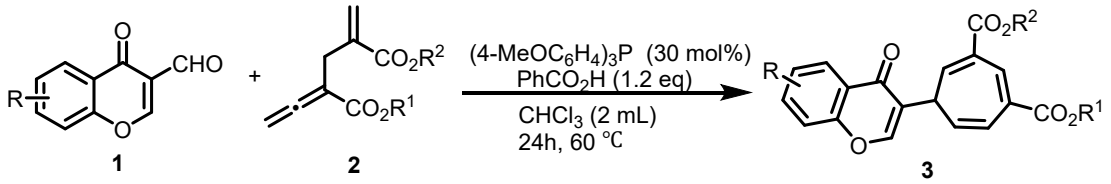


entry	cat.	additive	solvent	yield (%)[b]
1	PPh_3	-	toluene	32
2	$(4\text{-}MeOC_6H_4)_3P$	-	toluene	51
3	$(4\text{-}FC_6H_4)_3P$	-	toluene	trace
4	PCy_3	-	toluene	trace
5	$(4\text{-}MeOC_6H_4)_3P$	-	ClPh	51
6	$(4\text{-}MeOC_6H_4)_3P$	-	$CHCl_3$	59
7	$(4\text{-}MeOC_6H_4)_3P$	-	THF	NR
8	$(4\text{-}MeOC_6H_4)_3P$	Cs_2CO_3	$CHCl_3$	30
9	$(4\text{-}MeOC_6H_4)_3P$	$PhCO_2H$	$CHCl_3$	86
10	$(4\text{-}MeOC_6H_4)_3P$	4 Å MS	$CHCl_3$	50
11[c]	$(4\text{-}MeOC_6H_4)_3P$	$PhCO_2H$	$CHCl_3$	89
12[c,d]	$(4\text{-}MeOC_6H_4)_3P$	($PhCO_2H$	$CHCl_3$	92
13[c,d,e]	$(4\text{-}MeOC_6H_4)_3P$	(L)-N-Ts-Proline	$CHCl_3$	95
14	-	$PhCO_2H$	$CHCl_3$	20

[a]Reaction conditions, unless otherwise noted: 0.1 mmol **1o**, 0.2 mmol **2a**, 30 mol% Cat., 1.2 equiv. additive at 25 °C in solvent (2 mL) for 24 h. [b]Isoalted yield. [c]0.18 mmol 2a. [d]60 °C. [e](L)-*N*-Ts-Proline was used instead of $PhCO_2H$.

4. General Procedure of New Products 3

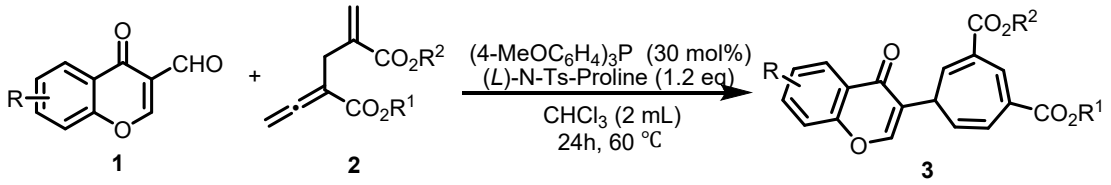
Procedure A:



1 2 3

To an oven-dried 10 mL glass vial was added substituted 4-oxo-4H-chromene-3-carbaldehyde **1** (0.1 mmol), allenoate **2** (0.18 mmol), $PhCO_2H$ (0.12 mmol), (p-$MeOC_6H_4)_3P$ (0.3 eq) and 2.0 mL of $CHCl_3$. The resulting mixture was stirred at 60 ºC for 24 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford **3.**

Procedure B:

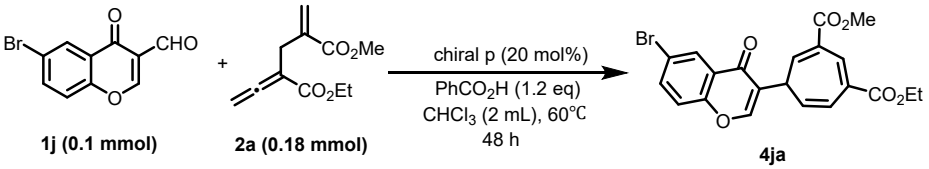


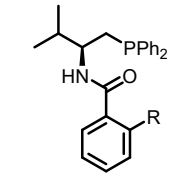
1 2 3

To an oven-dried 10 mL glass vial was added substituted 4-oxo-4H-chromene-3-carbaldehyde **1** (0.1 mmol), allenoate **2** (0.18 mmol), (*L*)-N-Ts-Proline (0.12 mmol), (p-$MeOC_6H_4)_3P$ (0.3 eq) and 2.0 mL of $CHCl_3$. The resulting mixture was stirred at 60 ºC for 24 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford **3.**

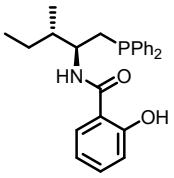
5. Primary Attempt on Asymmetric Edition in the Presence of Chiral Phosphine Catalysts

5.1. Primary attempt on asymmetric edition

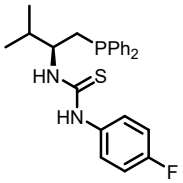




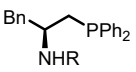
P1, R = H, 47%, -24% ee
P2, R = OH, 38%, -15% ee



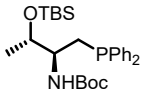
P3, 36%, -16% ee



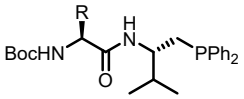
P4, trace



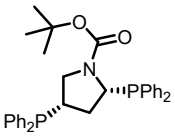
P5, R = Ts, trace
P6, R = Boc, 61%, -13% ee



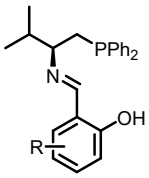
P7, 47 %, -37 % ee



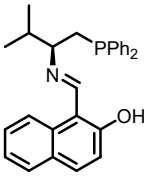
P8, R = isopropyl, 23%, -28% ee
P9, R = Bn, 9%, -38% ee



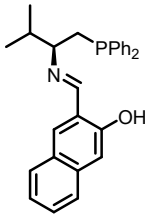
P10, 57%, 34% ee



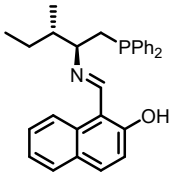
P11, R = H, 37%, 57.5% ee
P12, R = 3-Me, 50%, 65% ee
P13, R = 4-OMe, 48%, 63% ee



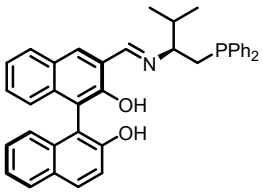
P14, 46%, 66% ee



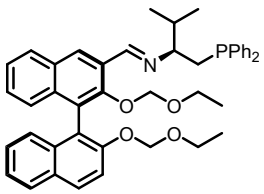
P15, 31%, 66% ee



P16, 47%, 66% ee



P17, 59%, 59.7% ee



P18, 30%, 17% ee

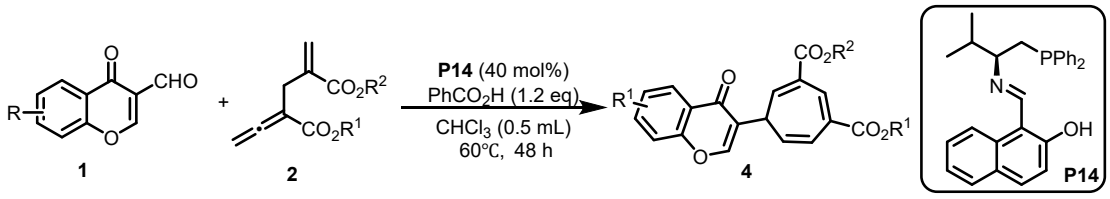
Table S2. Optimization of an asymmetric version of [6+1] annulation[a]

entry	Cat.	Solvent	Temp(℃)	Time	Yield(%)[b]	ee(%)[c]
1	**P14**(0.3 eq)	$CHCl_3$(2 mL)	60	48	34	65
2	**P14**(0.4 eq)	$CHCl_3$(2 mL)	60	48	49	65
3	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	60	48	57	66
4	**P14**(0.4 eq)	$CHCl_3$(1 mL)	60	48	45	66
5	**P14**(0.4 eq)	$CHCl_3$(3 mL)	60	48	38	66
6	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	0	48	-	-
7	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	50	48	48	42

8	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	70	12	12	46
9	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	80	12	48	66
10	**P14**(0.4 eq)	$CHCl_3$(0.5 mL)	90	12	39	66

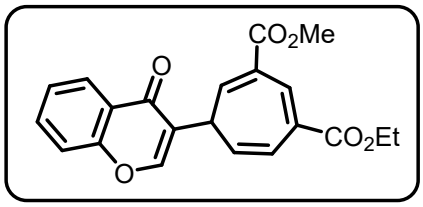
[a]Reaction conditions: **1** (0.1 mmol), **2** (0.18 mmol), $PhCO_2H$ (120 mol%) in $CHCl_3$ (x mL) at T °C; [b]Yields of isolated products; [c]ee was determined by chiral HPLC.

5.2. General Procedure for Enantioselective version of New Products 4



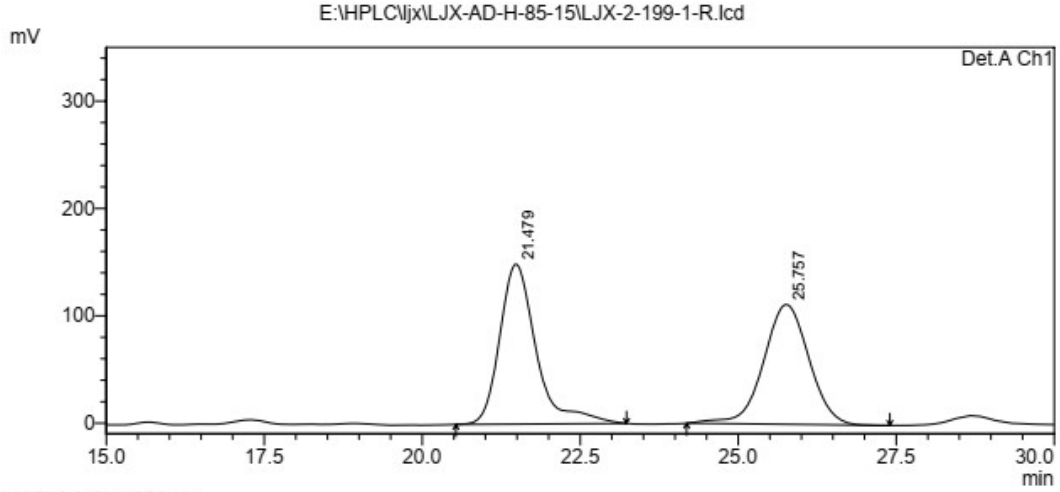
To an oven-dried 10 mL glass vial was added substituted 4-oxo-4H-chromene-3-carbaldehyde **1** (0.1 mmol), allenoate **2** (0.18 mmol), $PhCO_2H$ (0.12 mmol), **P14** (0.4 eq) and 0.5 mL of $CHCl_3$. The resulting mixture was stirred at 60 ºC for 48 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford **4.** The ee was determined chiral HPLC analysis of the isolated products.

Chiral product 4aa:



Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4aa** (21.3 mg, 55% yield) as a yellow oil. $[\alpha]^{25}_{D}$ = +13 (c = 0.5, $CHCl_3$). The ee value was 66%, t_R (major) = 21.528 min, t_R (minor) = 25.594 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85:10, flow rate = 1.0 mL/min).

<Chromatogram>

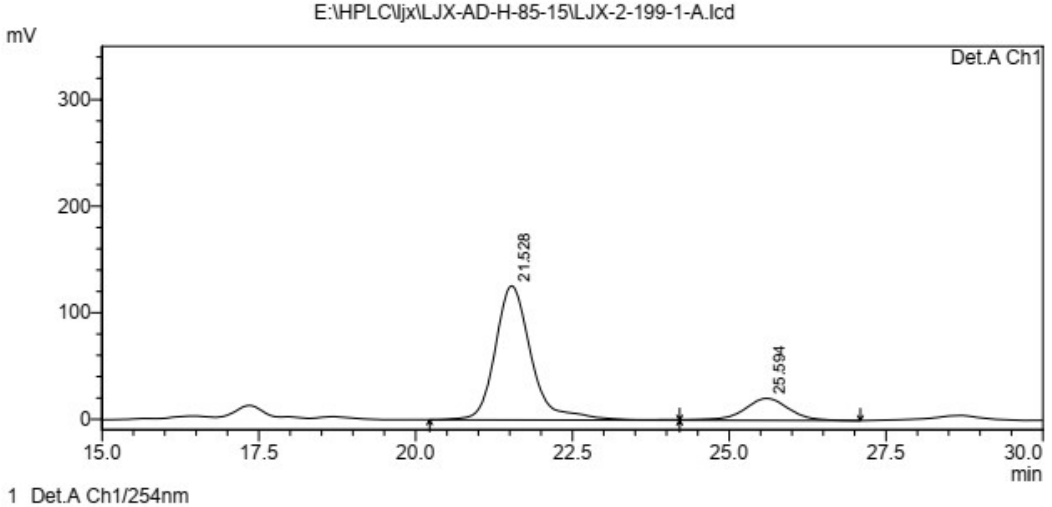


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.479	5974025	148879	51.728	57.158
2	25.757	5575005	111591	48.272	42.842
Total		11549030	260470	100.000	100.000



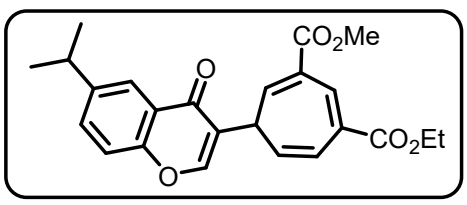
1 Det.A Ch1/254nm

PeakTable

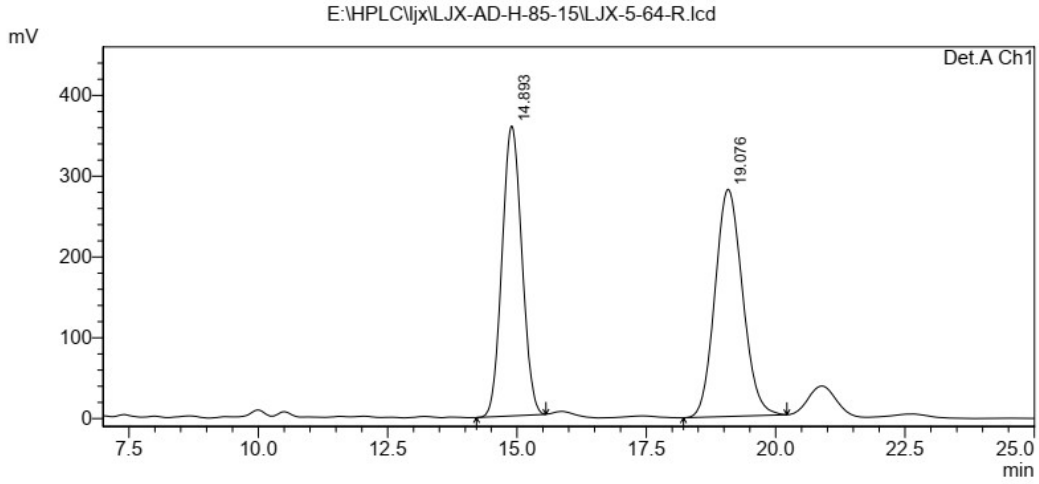
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.528	5022154	125820	83.124	85.884
2	25.594	1019613	20680	16.876	14.116
Total		6041768	146500	100.000	100.000

Chiral product 4da:



Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4da** (23.2 mg, 54% yield) as a yellow oil. $[\alpha]^{25}_{D}$ = +0.6 (c = 0.4, $CHCl_3$). The ee value was 51%, t_R (major) = 14.607 min, t_R (minor) = 18.604 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).

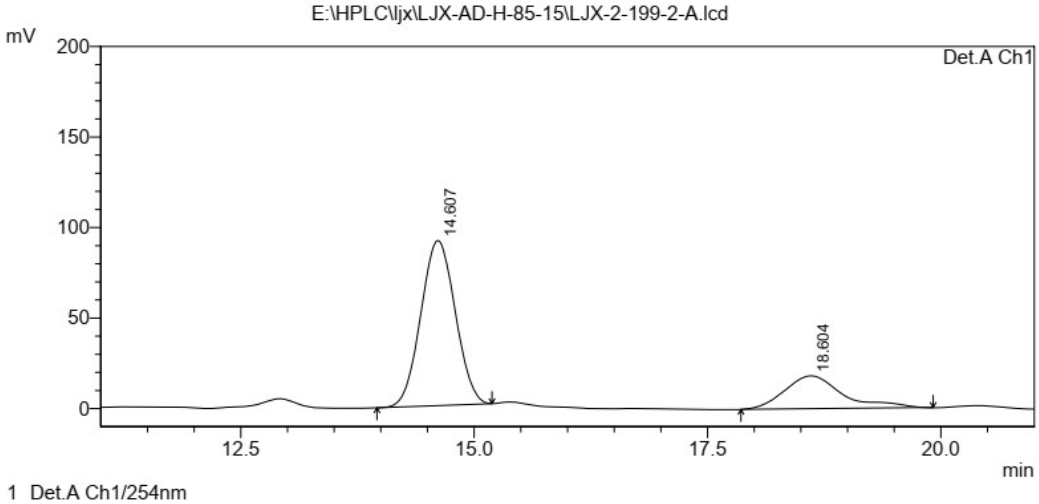


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.893	9549744	359044	47.844	56.070
2	19.076	10410357	281302	52.156	43.930
Total		19960102	640346	100.000	100.000



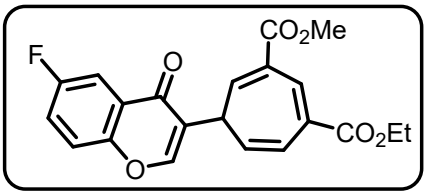
1 Det.A Ch1/254nm

PeakTable

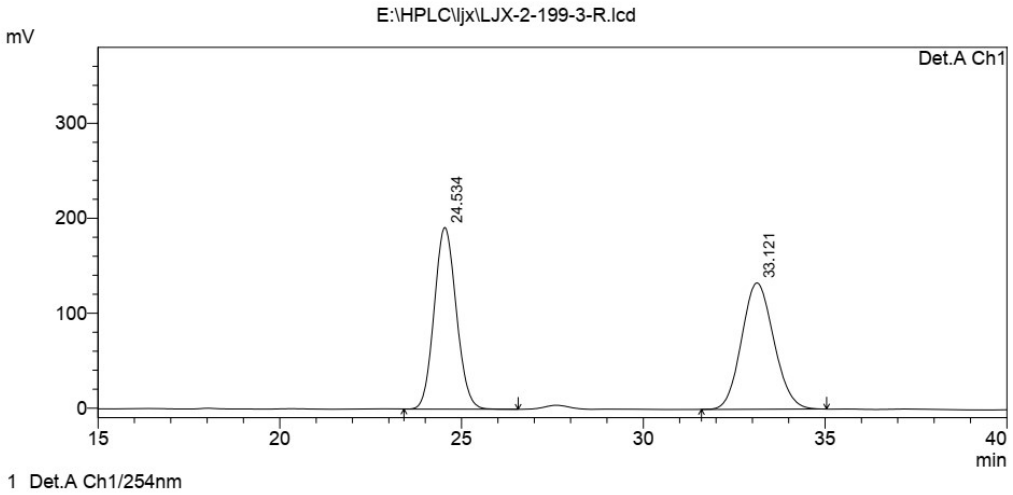
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.607	2342562	91186	74.987	83.399
2	18.604	781376	18151	25.013	16.601
Total		3123938	109337	100.000	100.000

Chiral product 4ha:



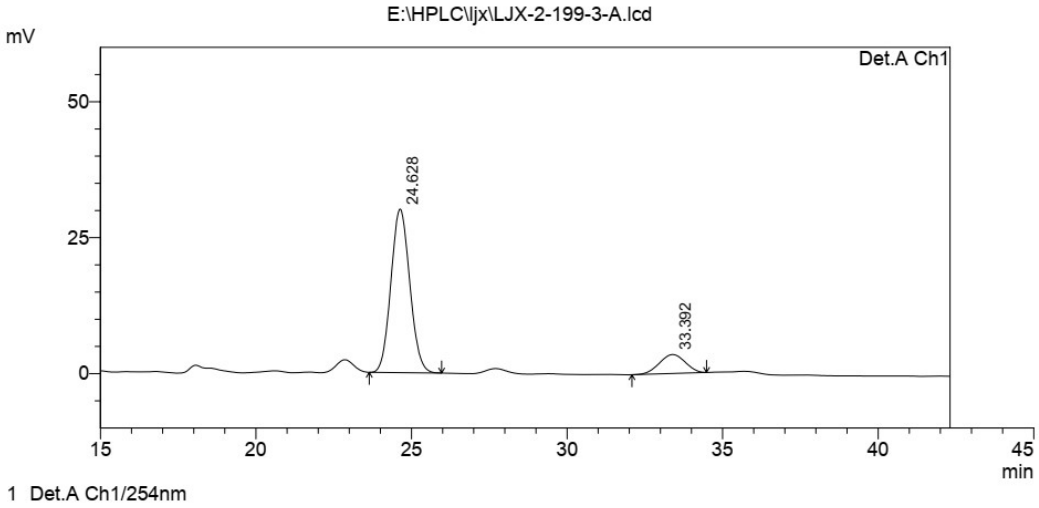
Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4ha** (23 mg, 68% yield) as a white solid. $[\alpha]^{25}_{D}$ = +4.3 (c = 0.7, $CHCl_3$). The ee value was 72.5%, t_R (major) = 24.628 min, t_R (minor) = 33.392 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.534	8078997	191312	49.632	58.975
2	33.121	8198640	133084	50.368	41.025
Total		16277637	324396	100.000	100.000

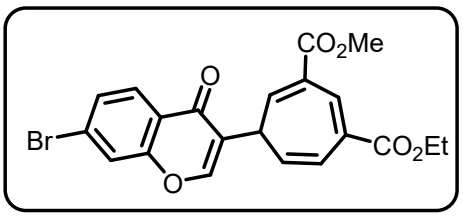


PeakTable

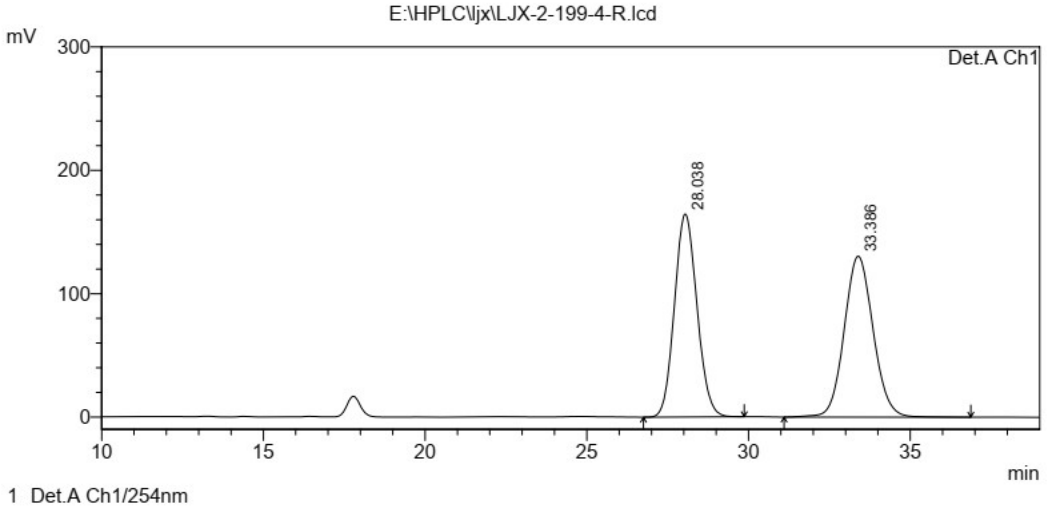
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.628	1268687	30091	86.294	89.625
2	33.392	201503	3483	13.706	10.375
Total		1470191	33574	100.000	100.000

Chiral product 4ka:



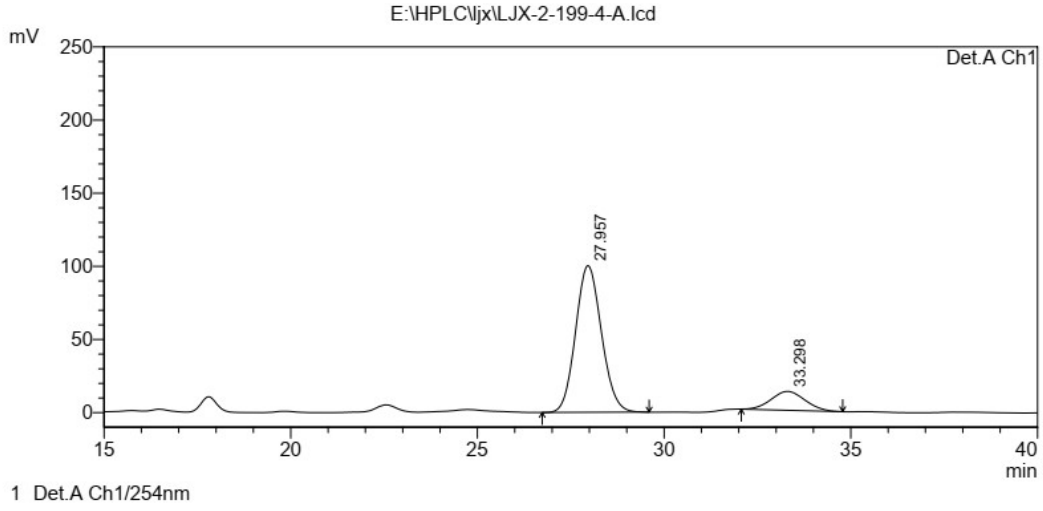
Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4ka** (28.2 mg, 61% yield) as a white solid. $[\alpha]_D^{25}$ = +0.8 (c = 1, $CHCl_3$). The ee value was 71%, t_R (major) = 27.957 min, t_R (minor) = 33.298 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.038	7950628	164425	49.460	55.756
2	33.386	8124376	130478	50.540	44.244
Total		16075004	294903	100.000	100.000

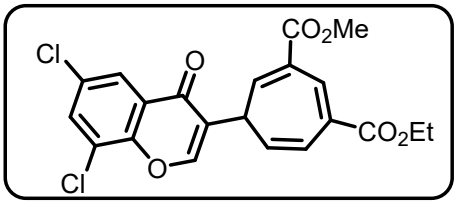


PeakTable

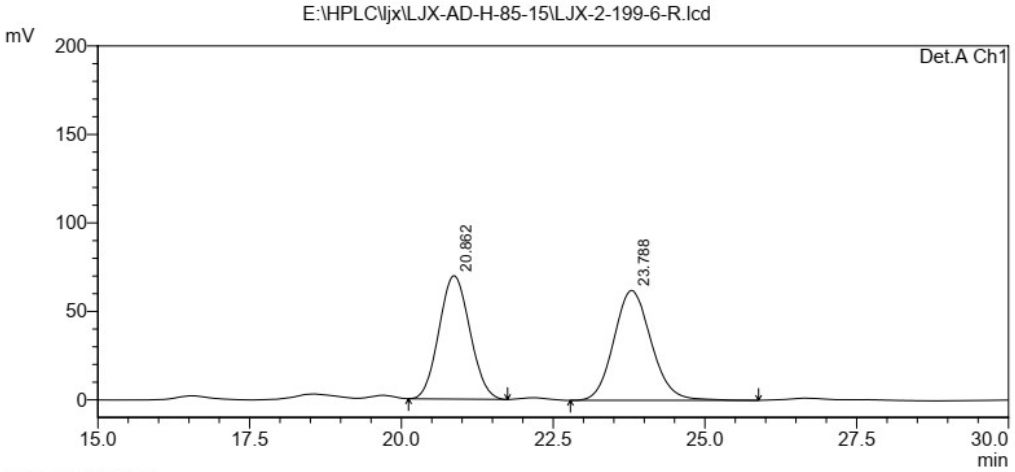
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.957	4833414	100308	85.512	88.577
2	33.298	818918	12936	14.488	11.423
Total		5652332	113244	100.000	100.000

Chiral product 4oa:



Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4oa** (27.4 mg, 60% yield) as a white solid. $[\alpha]^{25}_{D}$ = +6.7 (c = 0.9, $CHCl_3$). The ee value was 67%, t_R (major) = 20.773 min, t_R (minor) = 23.775 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).

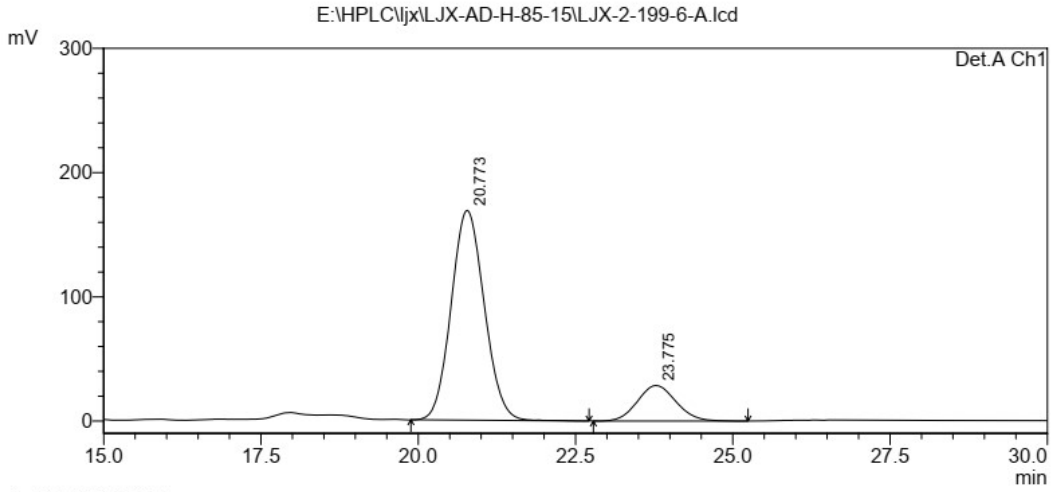


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.862	2468736	69759	48.099	52.892
2	23.788	2663927	62132	51.901	47.108
Total		5132664	131891	100.000	100.000



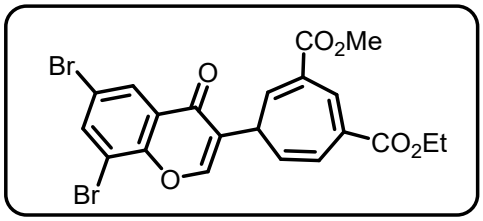
1 Det.A Ch1/254nm

PeakTable

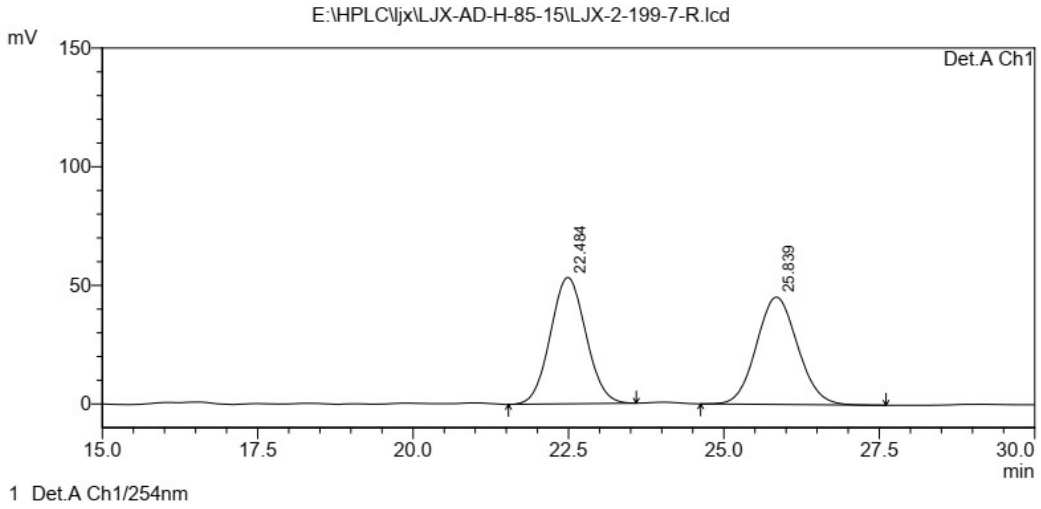
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.773	6176557	168831	83.496	85.504
2	23.775	1220905	28622	16.504	14.496
Total		7397462	197453	100.000	100.000

Chiral product 4pa:



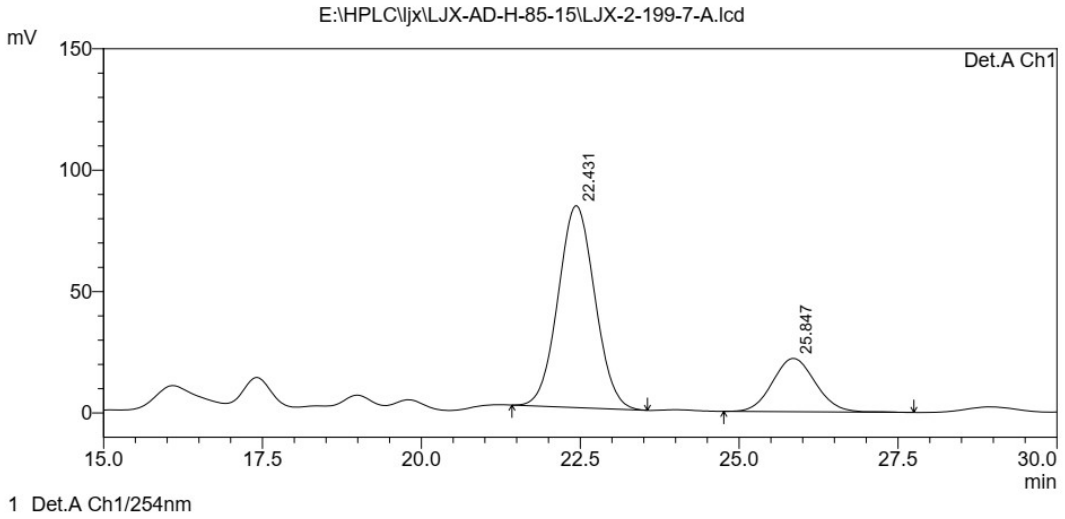
Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4pa** (37 mg, 69% yield) as a white solid. $[\alpha]^{25}_{D}$ = +6.8 (c = 1, $CHCl_3$). The ee value was 53%, t_R (major) = 22.431 min, t_R (minor) = 25.847 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.484	2115355	53260	50.319	54.075
2	25.839	2088548	45232	49.681	45.925
Total		4203903	98493	100.000	100.000

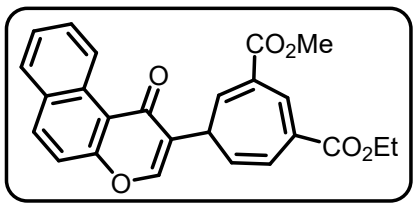


PeakTable

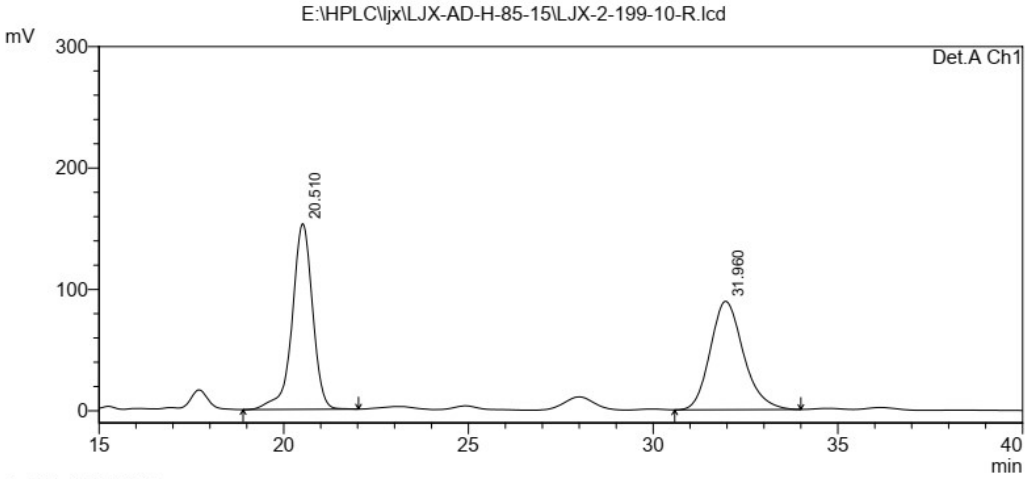
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.431	3350918	83150	76.424	79.083
2	25.847	1033747	21993	23.576	20.917
Total		4384665	105143	100.000	100.000

Chiral product 4ua:



Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4pa** (30 mg, 72% yield) as a white solid. $[\alpha]^{25}_{D}$ = +4.5 (c = 0.5, $CHCl_3$). The ee value was 63.5%, t_R (major) = 20.443 min, t_R (minor) = 32.097 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).

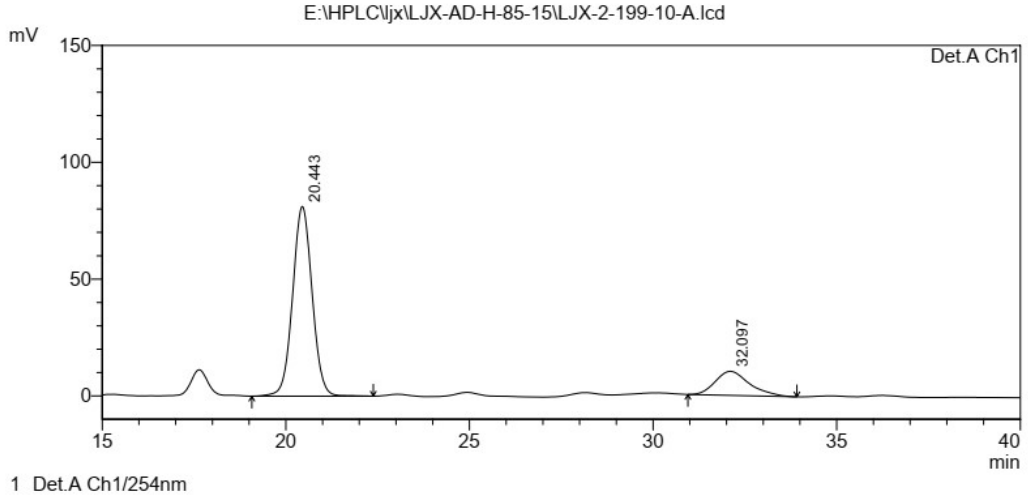


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.510	5871664	152957	51.249	63.130
2	31.960	5585388	89331	48.751	36.870
Total		11457052	242288	100.000	100.000



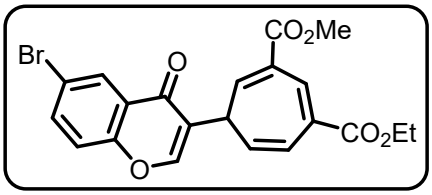
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

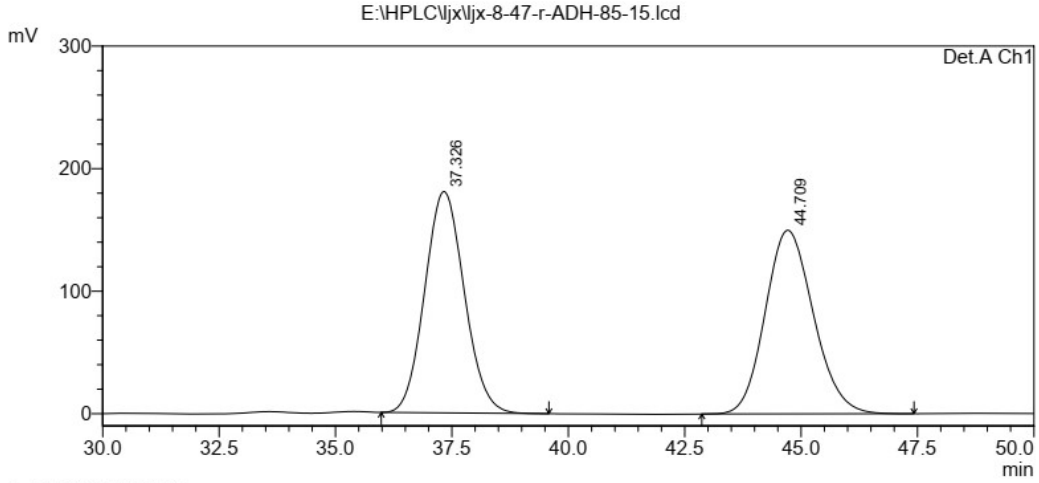
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.443	2996794	81169	81.756	88.726
2	32.097	668720	10313	18.244	11.274
Total		3665514	91482	100.000	100.000

Chiral product 4ja:



Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded

the compound **4ja** (25.3 mg, 57% yield) as a white solid. $[\alpha]^{25}_{D}$ = +15 (c = 0.5, $CHCl_3$). The ee value was 66%, t_R (major) = 28.286 min, t_R (minor) = 32.998 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).

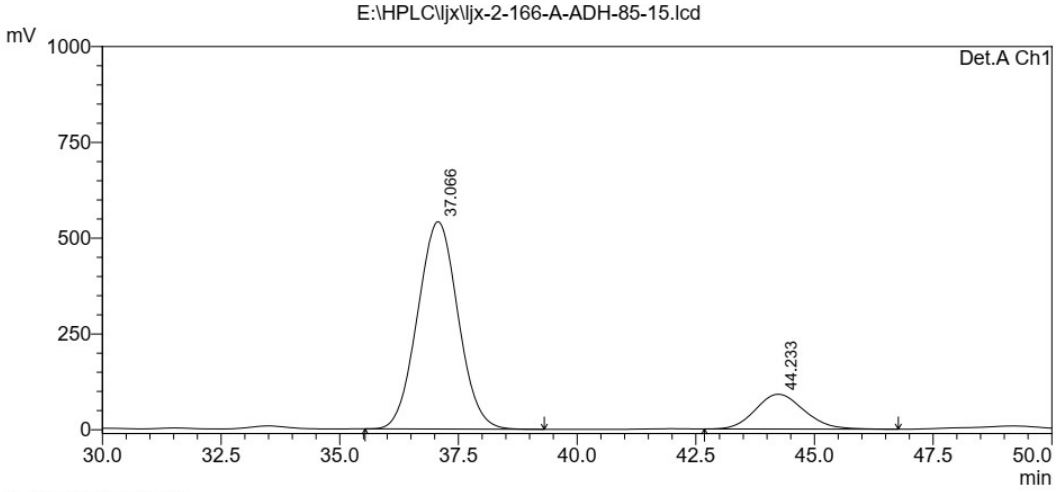


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.326	10690611	180685	49.738	54.664
2	44.709	10803129	149853	50.262	45.336
Total		21493740	330538	100.000	100.000



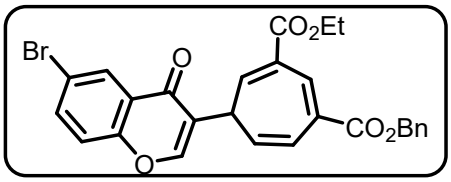
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.066	32114531	541250	83.183	85.606
2	44.233	6492403	91005	16.817	14.394
Total		38606935	632255	100.000	100.000

Chiral product 4jd:

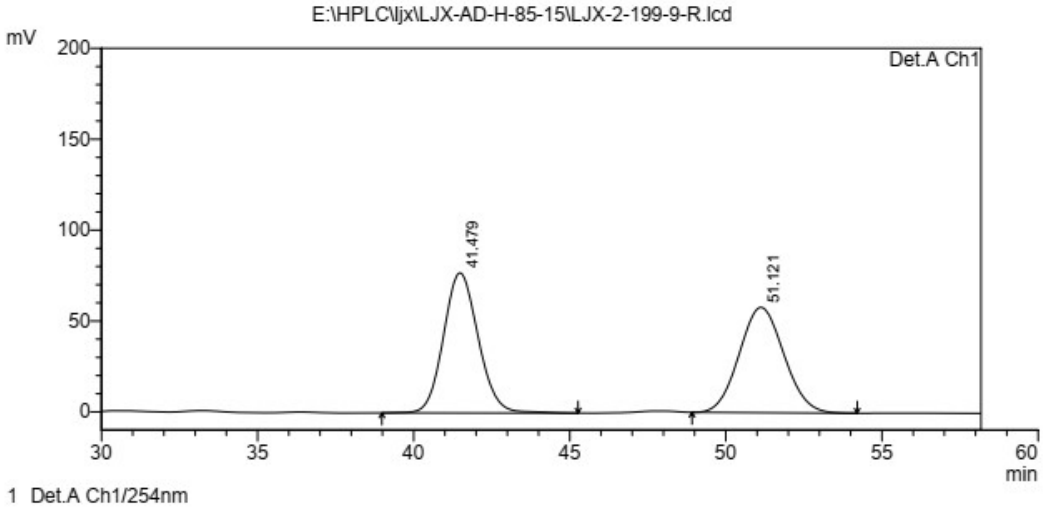


Purification by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) afforded the compound **4jd** (30 mg, 56% yield) as a white solid(m.p. 160-162°C). $[\alpha]_D^{25}$ = +6 (c = 0.5, $CHCl_3$). The ee value was 69.3%, t_R (major) = 37.958 min, t_R (minor) = 47.234 min (Chiralcel AD-H, λ = 220 nm, hexanes : *i*PrOH = 85 : 15, flow rate = 1.0 mL/min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.4 Hz, 1H), 8.27 (s, 1H), 7.84 (s, 1H), 7.77 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.40 (ddd, *J* = 16.3, 12.5, 4.9 Hz, 6H), 6.92 (d, *J* = 9.3 Hz, 1H), 6.54 (d, *J* = 6.4 Hz, 1H), 5.41 – 5.36 (m, 1H), 5.31 (dd, *J* = 24.9, 12.5 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.68, 166.48, 165.68, 155.09, 153.35, 136.93, 135.82, 134.35, 132.99, 130.13, 128.64, 128.62, 128.50, 128.35, 128.29, 126.13, 125.35, 122.95, 120.15, 118.85, 118.07, 67.07, 61.38, 36.75, 14.28.

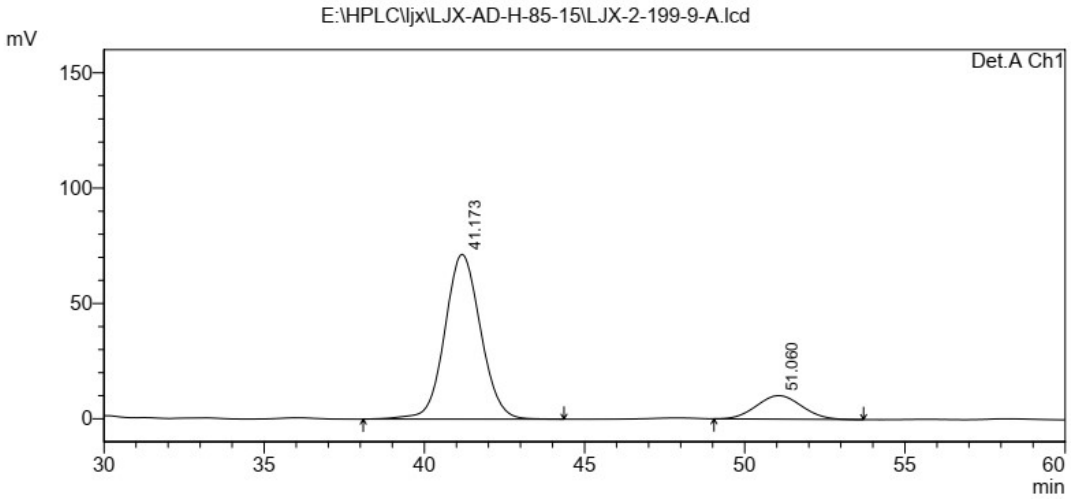
HRMS (ESI): m/z calcd for $C_{27}H_{22}BrO_6$ ($[M+H]^+$): 521.0594; found: 521.0592



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.479	5966084	77056	50.837	57.086
2	51.121	5769676	57927	49.163	42.914
Total		11735759	134983	100.000	100.000



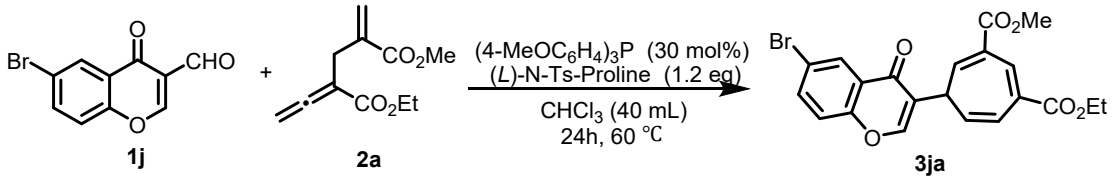
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.173	5559976	71421	84.683	87.486
2	51.060	1005632	10216	15.317	12.514
Total		6565609	81637	100.000	100.000

6. Scale-up Experiment of the New Product 3

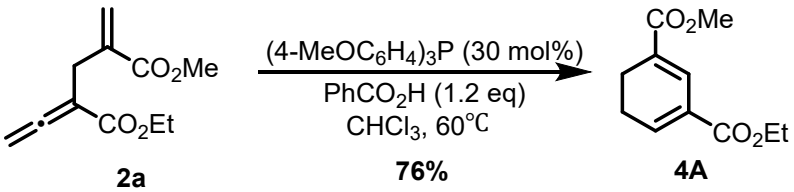


To an oven-dried 100 mL glass vial was added compound **1j** (2 mmol), allenoate **2a** (3.6 mmol), (*L*)-N-Ts-Proline (2.4 mmol), (*p*-$MeOC_6H_4)_3P$ (0.3 eq) and 40 mL of $CHCl_3$. The resulting mixture was stirred at 60 ºC for 24 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was subjected to a flash column chromatography (petroleum ether: ethyl acetate = 5:1) to provide **3ja** as a white solid (853 mg, 2 mmol, 96% yield)

7. Control and Deuterium-labeling Experiments

7.1. Control experiment

a) Cyclization of the allenoate under phosphine.

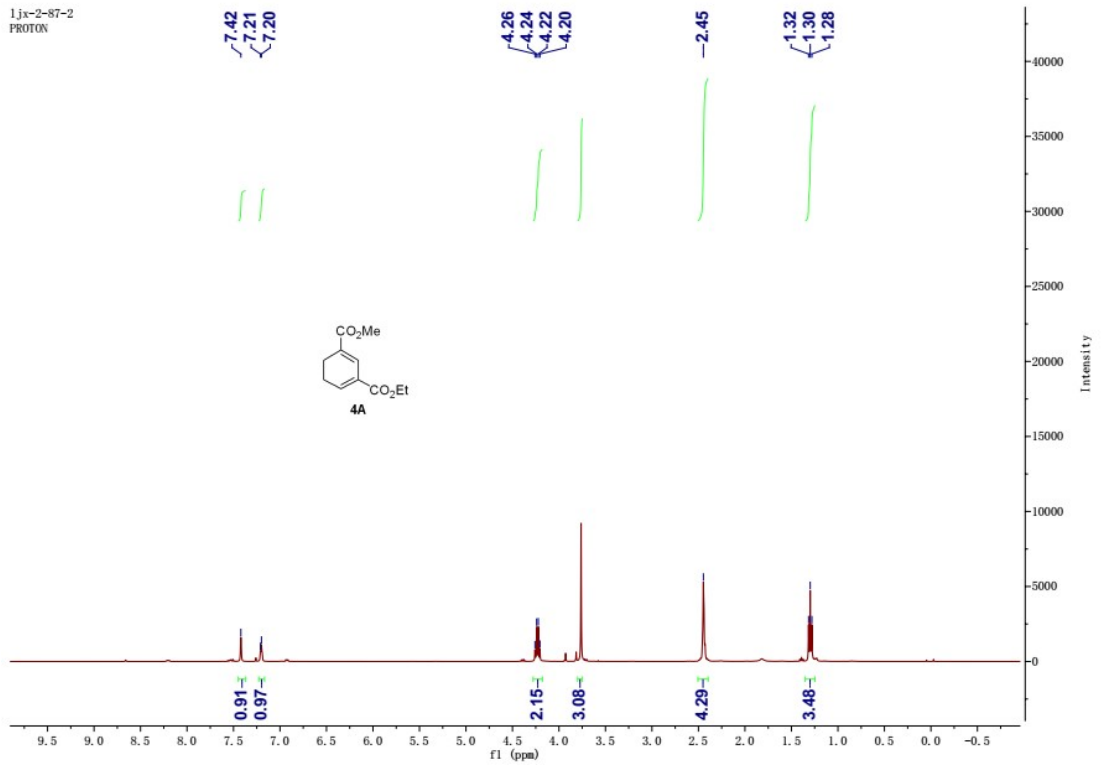


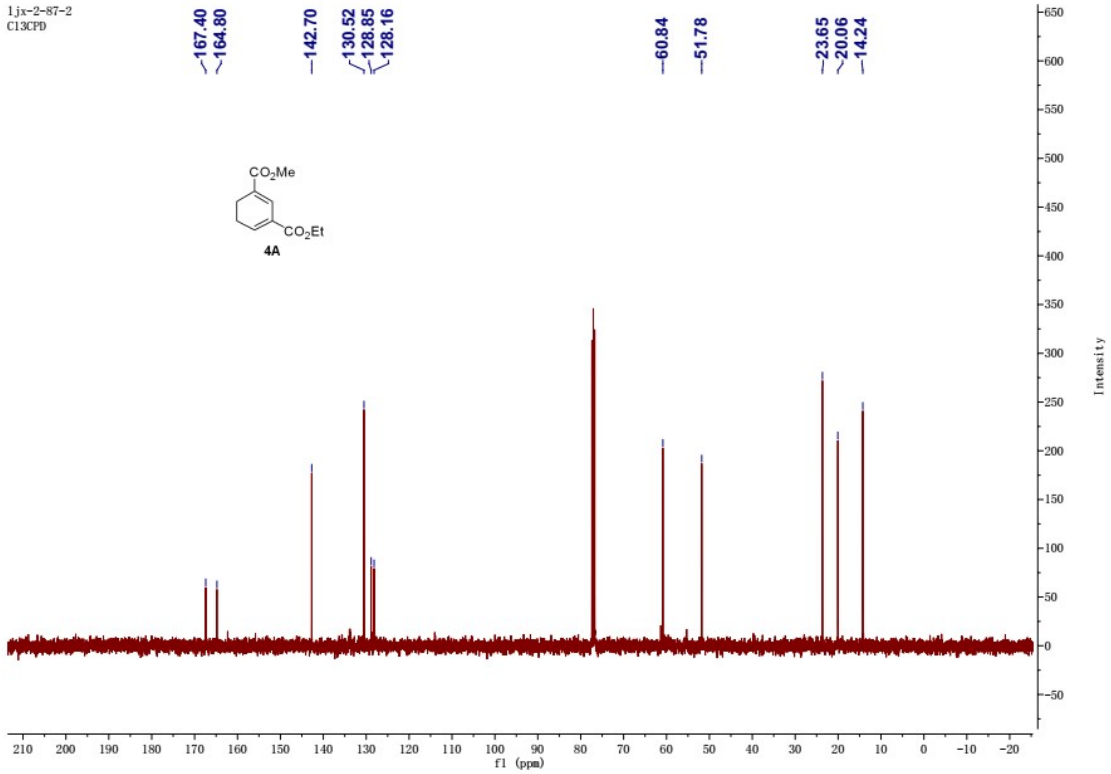
To an oven-dried 10 mL glass vial was added allenoate **2a** (0.18 mmol), $PhCO_2H$ (0.12 mmol), (*p*-$MeOC_6H_4)_3P$ (0.3 eq) and 2 mL of $CHCl_3$. The resulting mixture was stirred at 60 ºC for 24 hours until the complete consumption of the starting materials monitored by TLC. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford **4A** as colorless oil(28.6 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.23 – 7.17 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 2.45 (s, 4H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 164.80, 142.70, 130.52, 128.85, 128.16, 60.84, 51.78, 23.65, 20.06, 14.24.

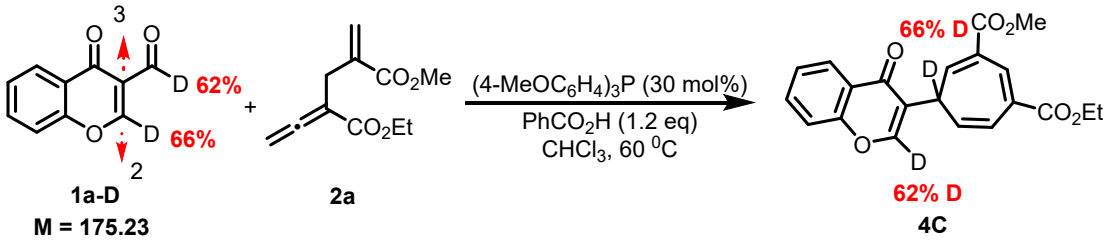
HRMS (ESI): m/z calcd for $C_{11}H_{15}O_4$ ($[M+H]^+$): 211.0965; found: 211.0963.





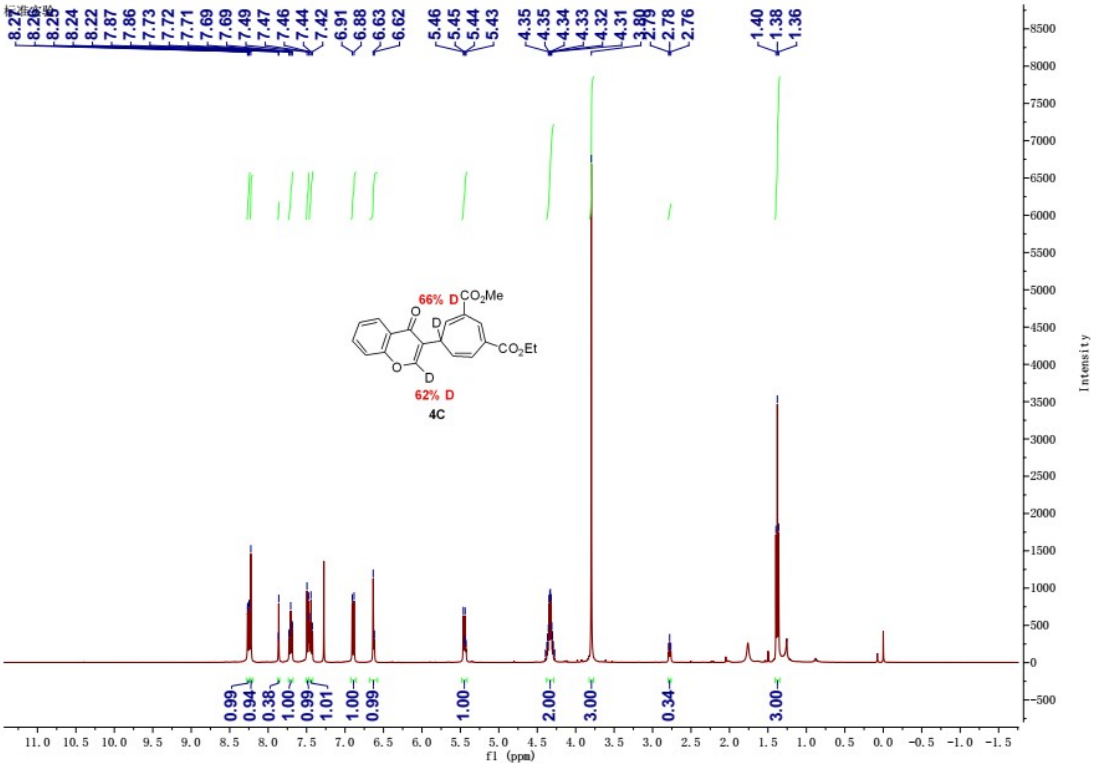
Under standard condition, cyclization product of allenoate **2a** confirmed our hypothesis that the newly-designed allenoate can work as C_6 synthon under proper conditions.

b) Reaction of deuterium-labeling substrate 1a-D under standard condition



Under the standard conditions, product **4C** was obtained as colorless oil (30.8 mg, 84% yield) with exchange value of deuterium labeling, suggesting that the reaction may undergo a ring opening and ring closing process. Therefore, the electronic property of substituted 3-formylchromones affected the reaction greatly.

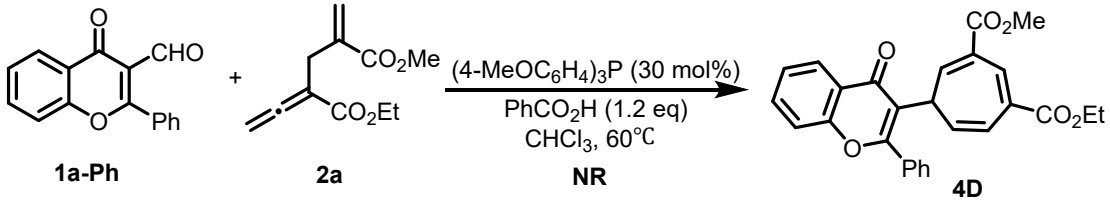
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.22 (s, 1H), 7.86 (d, *J* = 2.1 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 9.3 Hz, 1H), 6.63 (d, *J* = 6.4 Hz, 1H), 5.44 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.38 – 4.29 (m, 2H), 3.80 (s, 3H), 2.78 (t, *J* = 5.9 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

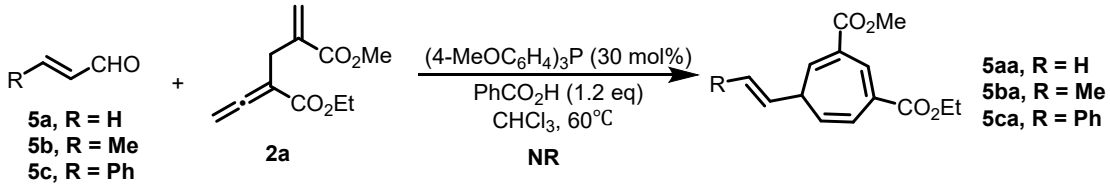


c) Substrates control experiments

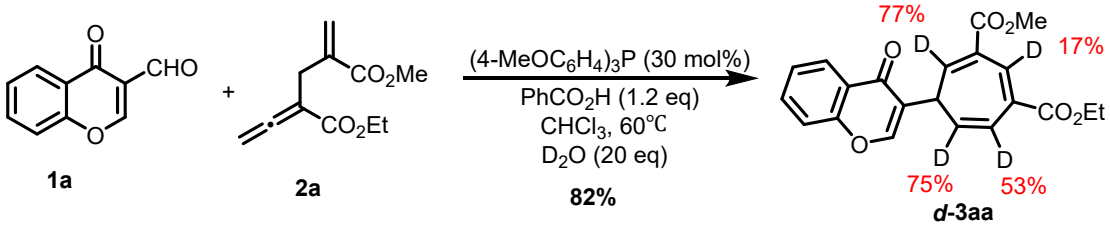
Under the standard conditions, no corresponding product was obtained when allenoate **2a** reacted with **1a-Ph**, suggesting that the steric phenyl could stop the Michael addition of zwitterion **A** to C2 of **1-a-Ph,**

which thus inhibited the reaction. This experiment also confirmed the existence of ring opening and ring closing process. Alkenyl-carbaldehyde substrates **5a-5b** could not undergo the process of ring opening and ring closing, which plays important role in the reaction, failed to give the desired products.



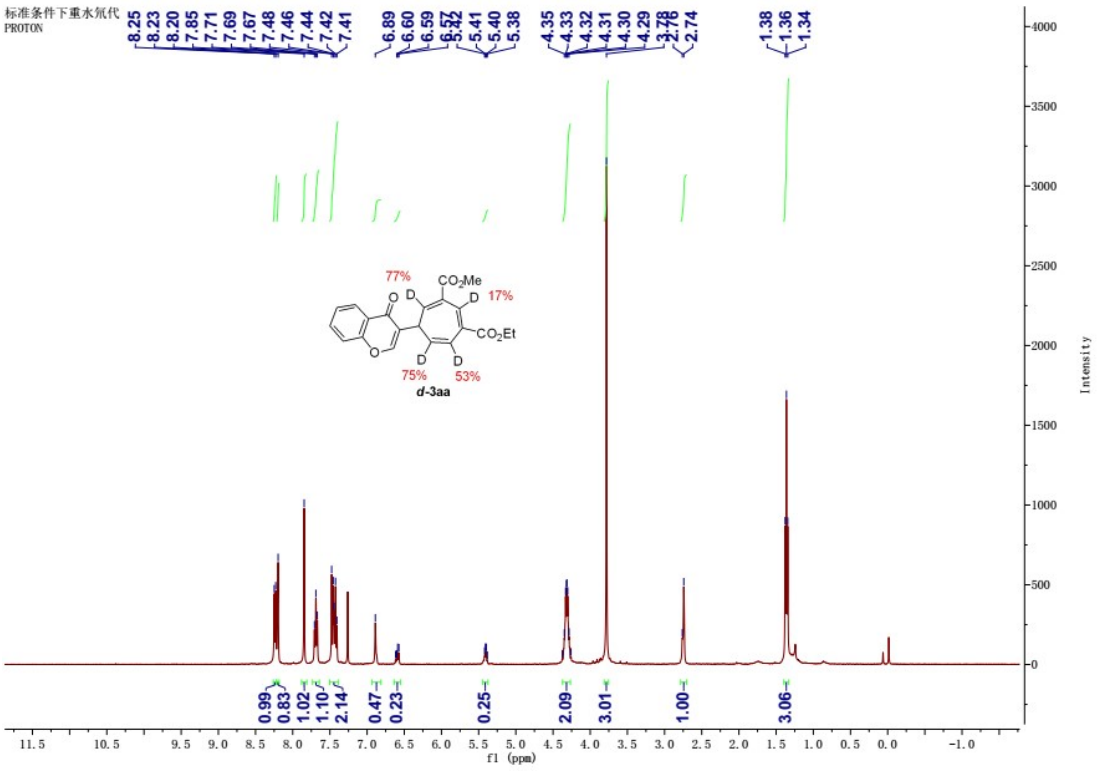


7.2. Deuterium-labeling reaction(d)



To an oven-dried 10 mL glass vial was added compound **1a** (0.1 mmol), allenoate **2** (0.18 mmol), $PhCO_2H$ (0.12 mmol), (p-$MeOC_6H_4)_3P$ (0.3 equiv) and 2.0 mL of $CHCl_3$. Then D_2O (2.0 mmol, 20.0 equiv) was added to the system. The resulting mixture was stirred at 60 ºC for 24 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford colorless oil ***d*-3aa** (30 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.9 Hz, 1H), 8.20 (s, 1H), 7.85 (s, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.50 – 7.39 (m, 2H), 6.89 (s, 1H), 6.59 (dd, J = 11.3, 6.4 Hz, 1H), 5.40 (dd, J = 9.7, 4.9 Hz, 1H), 4.37 – 4.27 (m, 2H), 3.78 (s, 3H), 2.75 (d, J = 7.8 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H).



During annulation reaction catalyzed by nucleophilic phosphine, there may be four position of the allenoate involving nucleophilic site or carbanion (intermediate **A**, **E**, **G**, **H, I, J,**), which would be deuterated in the present of D_2O (**Figure S1**). The nucleophilic addition of phosphine to allenoate formed zwitterion **A,** with its γ position 75% deuterated**.**

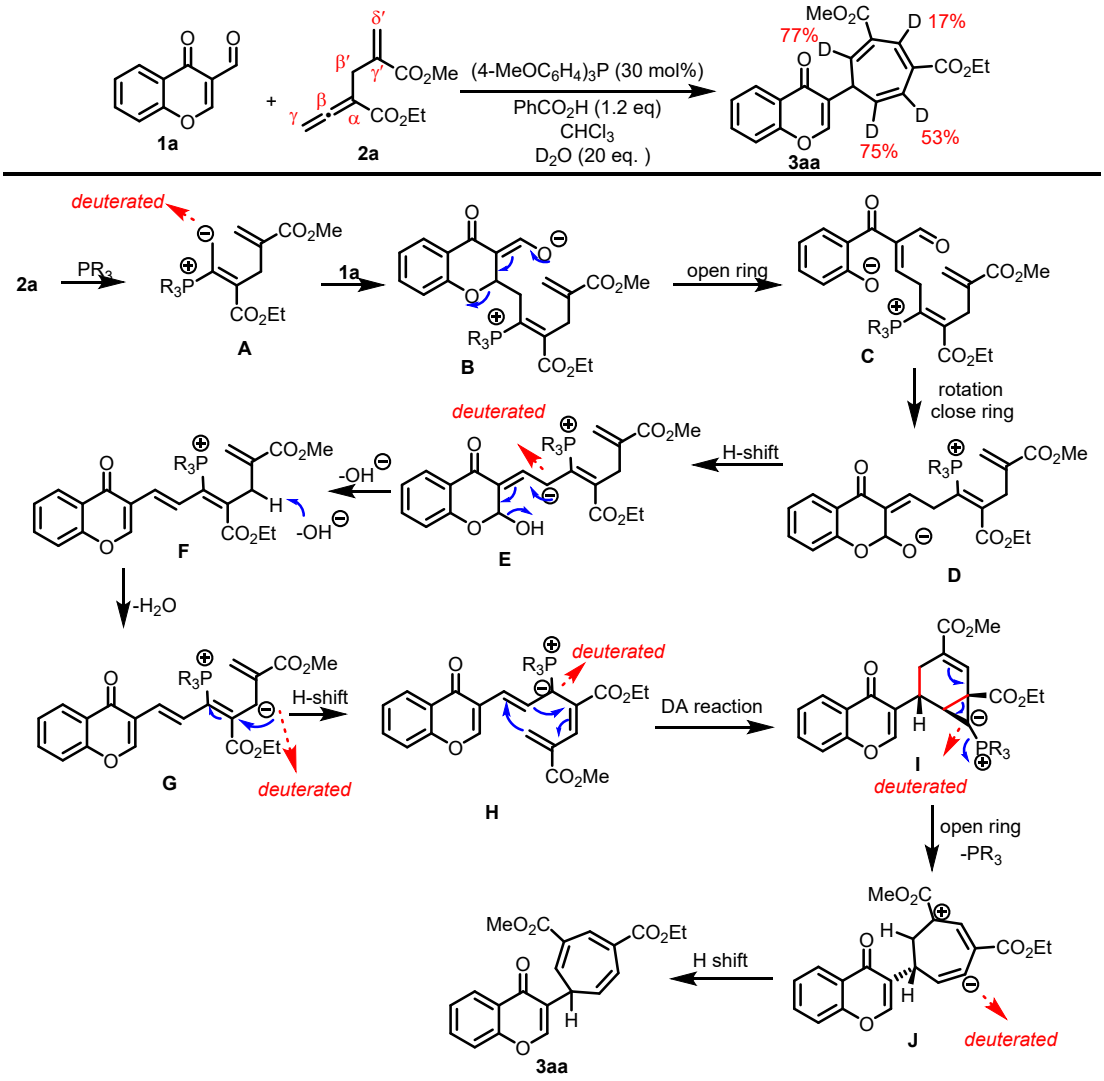
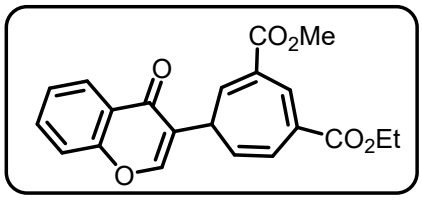


Figure S1. The exchange process of hydrogen and deuterium

8. Characterization Data of New Products 3

1-ethyl 3-methyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3aa).



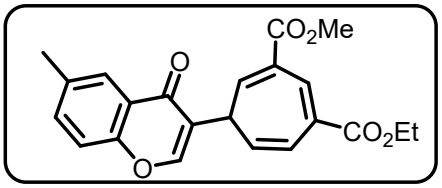
Yellow oil (34.9 mg, 95% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.21 (m, *J* = 10.5 Hz, 2H), 7.85 (s, 1H), 7.69 – 7.63 (m, 1H), 7.46 – 7.37 (m, 2H), 6.85 (d, *J* = 9.3 Hz, 1H), 6.59 (d, *J* = 6.4 Hz, 1H), 5.41 (dd, *J* = 9.1, 5.6 Hz, 1H), 4.29 (m, *J* = 7.7, 3.7 Hz, 2H), 3.75 (s, 3H), 2.73 (t, *J* = 5.9 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.75, 166.46, 166.04, 156.12, 153.06, 133.74, 133.67, 133.20, 131.46, 127.78, 125.71, 125.61, 125.19, 123.86, 122.48, 119.02, 117.99, 61.17, 52.07, 36.92, 14.13.

HRMS (ESI): m/z calcd for $C_{21}H_{19}NO_6$ ($[M+H]^+$): 367.1176; found: 367.1174

1-ethyl 3-methyl 5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ba).



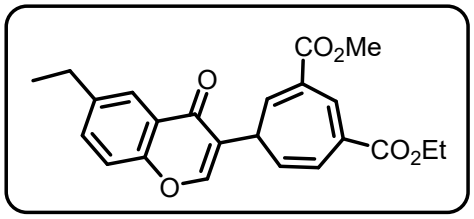
Yellow oil (28.1 mg, 74% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.00 (s, 1H), 7.82 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.60 (d, *J* = 6.2 Hz, 1H), 5.42 (dd, *J* = 8.7, 5.8 Hz, 1H), 4.31 (dd, *J* = 6.9, 4.6 Hz, 2H), 3.77 (s, 3H), 2.74 (t, *J* = 5.6 Hz, 1H), 2.45 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.98, 166.68, 166.26, 154.60, 153.08, 135.36, 135.16, 133.84, 133.37, 131.92, 127.91, 125.73, 125.14, 123.71, 122.43, 119.42, 117.89, 61.34, 52.22, 37.13, 20.97, 14.28.

HRMS (ESI): m/z calcd for $C_{22}H_{21}O_6$ ($[M+H]^+$): 381.1333; found: 381.1328

1-ethyl 3-methyl 5-(6-ethyl-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ca).



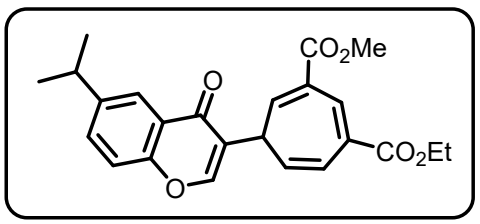
Yellow oil (29.2 mg, 74% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.05 (s, 1H), 7.83 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 6.87 (d, *J* = 9.2 Hz, 1H), 6.63 (d, *J* = 6.2 Hz, 1H), 5.44 (dd, *J* = 8.8, 5.7 Hz, 1H), 4.32 (dd, *J* = 6.9, 4.7 Hz, 2H), 3.78 (s, 3H), 2.74-2.79 (m, *J* = 14.8, 7.3 Hz, 3H), 1.37 (m, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.11, 166.71, 166.29, 154.77, 153.09, 141.72, 134.19, 133.89, 133.41, 132.06, 127.94, 125.73, 123.97, 123.85, 122.43, 119.54, 118.02, 61.36, 52.25, 37.23, 28.40, 15.53, 14.31.

HRMS (ESI): m/z calcd for $C_{23}H_{23}O_6$ ($[M+H]^+$): 395.1489; found: 395.1486

1-ethyl 3-methyl 5-(6-isopropyl-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3da).



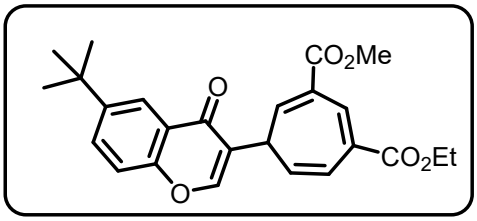
Yellow oil (25.7 mg, 63% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.82 (s, 1H), 7.34 – 7.29 (m, 2H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.63 (d, *J* = 6.4 Hz, 1H), 5.44 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.39 – 4.28 (m, 2H), 3.79 (s, 3H), 3.05 (m, *J* = 6.9 Hz, 1H), 2.76 (t, *J* = 6.0 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.83, 166.69, 166.28, 156.66, 156.13, 152.95, 133.85, 133.38, 131.82, 127.95, 125.81, 125.76, 124.52, 122.52, 122.15, 119.37, 115.19, 61.34, 52.22, 50.00, 37.11, 34.38, 23.57, 14.30.

HRMS (ESI): m/z calcd for $C_{24}H_{25}O_6$ ($[M+H]^+$): 409.1646; found: 409.1643

1-ethyl 3-methyl 5-(6-(tert-butyl)-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ea).



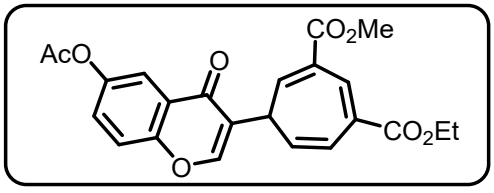
Yellow oil (27.5 mg, 65% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 7.82 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.65 (d, *J* = 6.3 Hz, 1H), 5.46 (dd, *J* = 8.9, 5.7 Hz, 1H), 4.32 (dd, *J* = 6.9, 4.3 Hz, 2H), 3.78 (s, 3H), 2.75 (t, *J* = 5.7 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.46, 166.86, 166.44, 154.66, 153.22, 148.86, 134.00, 133.81, 133.49, 132.12, 132.04, 130.29, 128.58, 128.02, 125.83, 123.51, 122.48, 121.65, 119.57, 117.89, 61.49, 52.37, 37.41, 35.01, 31.40, 14.40.

HRMS (ESI): m/z calcd for $C_{25}H_{27}O_6$ ($[M+H]^+$): 423.1802; found: 423.1801

1-ethyl 3-methyl 5-(6-acetoxy-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3fa).



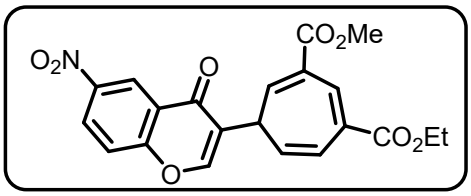
Yellow oil (27.4 mg, 65% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.92 (d, *J* = 2.7 Hz, 1H), 7.85 (s, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.43 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.59 (t, *J* = 7.9 Hz, 1H), 5.40 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.41 – 4.24 (m, 2H), 3.79 (s, 3H), 2.77 (t, *J* = 6.0 Hz, 1H), 2.34 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.30, 169.29, 166.65, 166.23, 153.84, 153.29, 147.70, 133.84, 133.42, 130.88, 128.21, 128.10, 126.02, 124.77, 122.38, 119.56, 118.59, 117.93, 61.40, 52.28, 36.87, 21.02, 14.30.

HRMS (ESI): m/z calcd for $C_{23}H_{21}O_8$ ($[M+H]^+$): 425.1231; found: 425.1233

1-ethyl 3-methyl 5-(6-nitro-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ga).



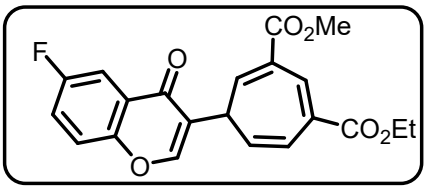
White solid (30.3 mg, 74% yield, m.p. 178-181 °C) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.7 Hz, 1H), 8.52 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.19 (s, 1H), 7.90 (d, *J* = 0.4 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 1H), 6.51 (d, *J* = 6.6 Hz, 1H), 5.35 (dd, *J* = 9.3, 5.7 Hz, 1H), 4.40 – 4.22 (m, 2H), 3.80 (s, 3H), 2.84 (t, *J* = 6.1 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.58, 166.46, 166.09, 159.05, 153.48, 144.88, 133.73, 133.35, 128.36, 128.22, 126.66, 124.01, 123.60, 122.80, 120.04, 116.42, 116.33, 61.47, 52.37, 36.17, 14.29.

HRMS (ESI): m/z calcd for $C_{21}H_{18}NO_8$ ($[M+H]^+$): 412.1027; found: 412.1022.

1-ethyl 3-methyl 5-(6-fluoro-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ha).



White solid (37.5 mg, 98% yield, m.p. 138-140 °C) according to procedure B.

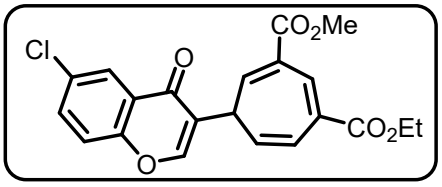
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.86 (s, 1H), 7.83 (m, *J* = 8.2, 2.6, 1.5 Hz, 1H), 7.47 (dd, *J* = 9.2, 4.2 Hz, 1H), 7.44 – 7.36 (m, 1H), 6.86 (d, *J* = 9.3 Hz, 1H), 6.55 (d, *J* = 6.4 Hz, 1H), 5.38 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.76 (s, 3H), 2.74 (t, *J* = 5.9 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.19, 166.57, 166.16, 159.57 (d, *J* = 247.2 Hz), 153.42, 152.54, 133.79, 133.36, 130.75, 128.05, 125.99, 125.14 (d, *J* = 7.5 Hz), 122.24 (d, *J* = 25.6 Hz), 122.08, 120.36 (d, *J* = 8.1 Hz), 118.44, 110.65 (d, *J* = 23.7 Hz), 61.37, 52.26, 36.80, 14.28.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.60.

HRMS (ESI): m/z calcd for $C_{21}H_{18}FO_6$ ($[M+H]^+$): 385.1082; found: 385.1079

1-ethyl 3-methyl 5-(6-chloro-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ia).

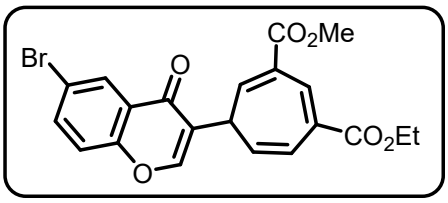


White solid (39 mg, 98% yield, m.p. 160-163 °C) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.17 (d, *J* = 2.5 Hz, 1H), 7.84 (s, 1H), 7.62 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.54 (d, *J* = 6.5 Hz, 1H), 5.37 (dd, *J* = 9.2, 5.6 Hz, 1H), 4.39 – 4.23 (m, 2H), 3.78 (s, 3H), 2.77 (t, *J* = 6.0 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

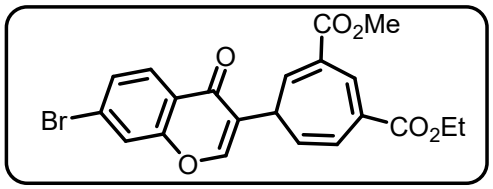
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.78, 166.56, 166.16, 154.63, 153.32, 134.15, 133.78, 133.37, 131.35, 130.28, 128.12, 126.14, 125.32, 124.94, 122.82, 119.92, 118.03, 61.38, 52.27, 36.70, 14.28.
HRMS (ESI): m/z calcd for $C_{21}H_{18}ClO_6$ ([M+H]$^+$): 401.0786; found: 401.0784

1-ethyl 3-methyl 5-(6-bromo-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ja).



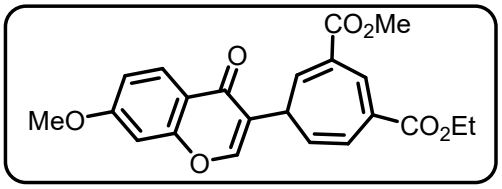
White solid (42.5 mg, 96% yield, m.p. 150-152 °C) according to procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.4 Hz, 1H), 8.18 (s, 1H), 7.84 (s, 1H), 7.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.54 (d, *J* = 6.5 Hz, 1H), 5.36 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.38 – 4.25 (m, 2H), 3.77 (s, 3H), 2.75 (t, *J* = 6.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.59, 166.51, 166.11, 155.00, 153.31, 136.85, 133.75, 133.32, 130.43, 128.47, 128.04, 126.06, 125.24, 122.86, 120.12, 118.76, 118.13, 61.35, 52.25, 36.71, 14.26.
HRMS (ESI): m/z calcd for $C_{21}H_{18}BrO_6$ ([M+H]$^+$): 445.0281; found: 445.0279

1-ethyl 3-methyl 5-(7-bromo-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ka).



White solid (44.1 mg, 99% yield, m.p. 128-130 °C) according to procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.81 (s, 1H), 7.65 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.55 (d, *J* = 6.4 Hz, 1H), 5.37 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.36 – 4.25 (m, 2H), 3.78 (s, 3H), 2.76 (t, *J* = 5.9 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.47, 166.80, 166.40, 156.55, 153.34, 134.02, 133.60, 130.57, 129.28, 128.47, 128.34, 127.61, 126.35, 123.35, 123.15, 121.48, 118.32, 61.62, 52.51, 36.97, 14.53.
HRMS (ESI): m/z calcd for $C_{21}H_{18}BrO_6$ ([M+H]$^+$): 445.0281; found: 445.0277

1-ethyl 3-methyl 5-(7-methoxy-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3la).



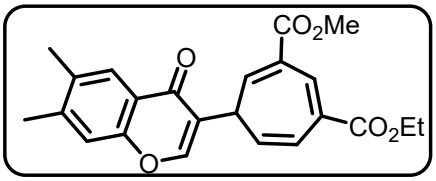
Yellow oil (29.8 mg, 75% yield) according to procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.77 (s, 1H), 6.99 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.43 (dd, *J* =

9.3, 5.5 Hz, 1H), 4.40 – 4.23 (m, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 2.74 (t, *J* = 6.0 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.53, 166.99, 166.58, 164.52, 158.41, 152.93, 134.14, 133.67, 132.21, 128.20, 127.61, 126.00, 122.80, 119.75, 118.30, 115.12, 100.43, 61.63, 56.15, 52.51, 37.37, 14.58.

HRMS (ESI): m/z calcd for $C_{22}H_{21}O_7$ ($[M+H]^+$): 397.1282; found: 397.1277

1-ethyl 3-methyl 5-(6,7-dimethyl-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ma).



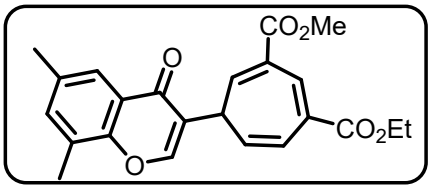
Yellow oil (25 mg, 63% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.96 (s, 1H), 7.79 (s, 1H), 7.23 (s, 1H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.43 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.38 – 4.26 (m, 2H), 3.78 (s, 3H), 2.73 (t, *J* = 6.0 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.91, 166.76, 166.34, 154.94, 152.85, 144.48, 134.76, 133.88, 133.39, 132.24, 127.89, 125.69, 125.44, 122.36, 121.96, 119.69, 118.20, 61.37, 52.25, 37.22, 20.50, 19.39, 14.31.

HRMS (ESI): m/z calcd for $C_{23}H_{23}O_6$ ($[M+H]^+$): 395.1489; found: 395.1488

1-ethyl 3-methyl 5-(6,8-dimethyl-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3na).



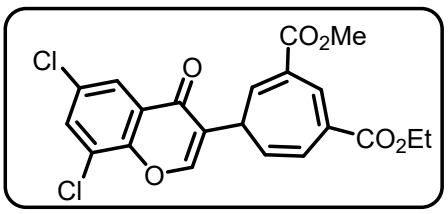
Yellow oil (33.6 mg, 85% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.87 (s, 1H), 7.85 (d, *J* = 1.3 Hz, 1H), 7.34 (s, 1H), 6.87 (d, *J* = 9.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.43 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.38 – 4.24 (m, 2H), 3.78 (s, 3H), 2.76 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.34, 166.74, 166.30, 153.21, 152.87, 136.16, 134.81, 133.89, 133.39, 132.23, 127.93, 127.28, 125.70, 123.69, 122.74, 122.20, 119.70, 61.36, 52.24, 37.17, 20.95, 15.45, 14.31.

HRMS (ESI): m/z calcd for $C_{23}H_{23}O_6$ ($[M+H]^+$): 395.1489; found: 395.1486

1-ethyl 3-methyl 5-(6,8-dichloro-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3oa).



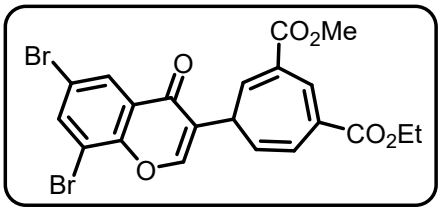
White solid (41.4 mg, 95% yield, m.p. 131-133 °C) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 (s, 1H), 7.92 (s, 1H), 7.74 (s, 1H), 6.91 (d, *J* = 9.2 Hz, 1H), 6.53 (d, *J* = 6.1 Hz, 1H), 5.43 – 5.28 (m, 1H), 4.33 (dd, *J* = 6.3, 4.6 Hz, 2H), 3.80 (s, 3H), 2.82 (t, *J* = 5.6 Hz, 1H), 1.37 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.18, 166.48, 166.08, 153.21, 150.67, 134.04, 133.76, 133.35, 131.08, 129.21, 128.28, 126.45, 125.70, 124.42, 124.07, 123.17, 117.07, 61.44, 52.33, 36.35, 14.28.

HRMS (ESI): m/z calcd for $C_{21}H_{17}Cl_2O_6$ ($[M+H]^+$): 435.0397; found: 435.0393

1-ethyl 3-methyl 5-(6,8-dibromo-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3pa).



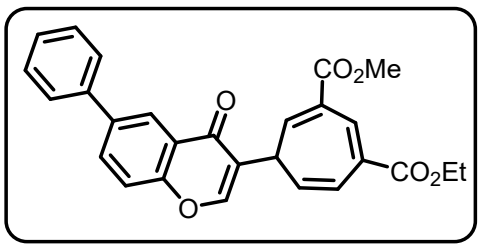
White solid (40 mg, 77% yield, m.p. 128-131 °C) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (t, *J* = 2.4 Hz, 1H), 8.16 (s, 1H), 7.99 (t, *J* = 2.1 Hz, 1H), 7.92 (s, 1H), 6.89 (d, *J* = 9.3 Hz, 1H), 6.48 (d, *J* = 6.1 Hz, 1H), 5.32 (dd, *J* = 9.2, 5.7 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.77 (d, *J* = 1.3 Hz, 3H), 2.80 (t, *J* = 6.0 Hz, 1H), 1.35 (td, *J* = 7.1, 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.01, 166.40, 166.00, 153.30, 151.91, 139.52, 133.68, 133.26, 128.89, 128.22, 127.92, 126.43, 125.90, 123.13, 118.62, 116.80, 112.88, 76.74, 61.37, 52.27, 36.23, 14.25.

HRMS (ESI): m/z calcd for $C_{21}H_{17}Br_2O_6$ ($[M+H]^+$): 522.9386; found: 522.9382

1-ethyl 3-methyl 5-(4-oxo-6-phenyl-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3qa).

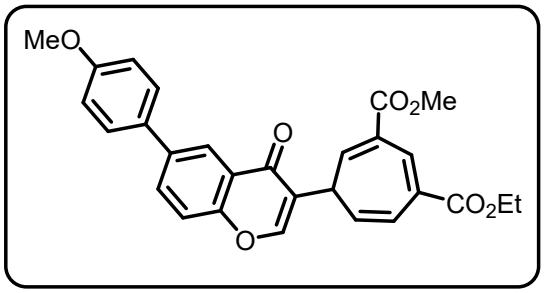


Yellow oil (41.2 mg, 93% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.2 Hz, 1H), 8.23 (s, 1H), 7.93 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.86 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 9.3 Hz, 1H), 6.63 (d, *J* = 6.4 Hz, 1H), 5.44 (dd, *J* = 9.3, 5.6 Hz, 1H), 4.38 – 4.28 (m, 2H), 3.79 (s, 3H), 2.79 (t, *J* = 6.0 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

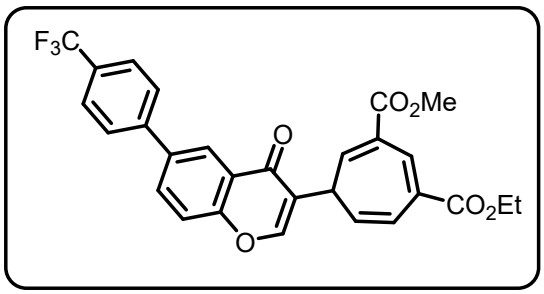
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.89, 166.60, 166.19, 155.64, 153.13, 139.14, 138.47, 133.80, 133.33, 132.74, 131.32, 128.98, 127.95, 127.89, 127.11, 125.85, 124.11, 123.61, 122.64, 118.89, 118.62, 61.32, 52.21, 36.97, 14.26.
HRMS (ESI): m/z calcd for $C_{27}H_{23}O_6$ ([M+H]$^+$): 443.1489; found: 443.1484

1-ethyl 3-methyl 5-(6-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ra).



White solid (40.7 mg, 86% yield, m.p. 78-81 °C) according to procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.2 Hz, 1H), 8.22 (s, 1H), 7.85 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 9.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.43 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.32 (dtt, *J* = 10.8, 7.4, 3.7 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 2.78 (t, *J* = 5.9 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.01, 166.65, 166.25, 159.62, 155.32, 153.13, 138.18, 133.82, 133.35, 132.41, 131.64, 130.12, 128.42, 128.22, 127.98, 125.90, 124.13, 122.88, 122.58, 118.55, 114.45, 61.34, 55.35, 52.23, 36.97, 14.28.
HRMS (ESI): m/z calcd for $C_{28}H_{25}O_7$ ([M+H]$^+$): 473.1595; found: 473.1593

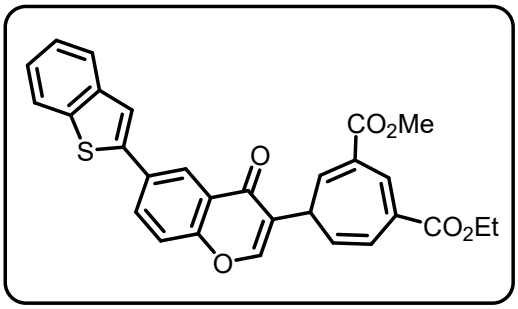
1-ethyl 3-methyl 5-(4-oxo-6-(4-(trifluoromethyl)phenyl)-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3sa).



White solid (31 mg, 61% yield, m.p. 160-163 °C) according to procedure A
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.2 Hz, 1H), 8.22 (s, 1H), 7.93 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 1H), 7.75 (q, *J* = 8.6 Hz, 4H), 7.59 (d, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 9.3 Hz, 1H), 6.61 (d, *J* = 6.5 Hz, 1H), 5.43 (dd, *J* = 9.2, 5.6 Hz, 1H), 4.41 – 4.26 (m, 2H), 3.80 (s, 3H), 2.82 (t, *J* = 6.0 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.84, 166.67, 166.27, 156.17, 153.30, 142.74, 137.06, 133.87, 133.43, 132.77, 130.98, δ 130.04 (q, *J* = 32.8 Hz), 128.11, 127.53, 126.04 (m, *J* = 6.3, 2.3 Hz), 124.15 (d, *J* = 272.0 Hz), 124.30, 122.93, 119.08, 118.60, 61.44, 52.34, 36.93, 14.33.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49.

HRMS (ESI): m/z calcd for $C_{28}H_{22}F_3O_6$ ([M+H]$^+$): 511.1363; found: 511.1363

1-ethyl 3-methyl 5-(6-(benzo[b]thiophen-2-yl)-4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ta)



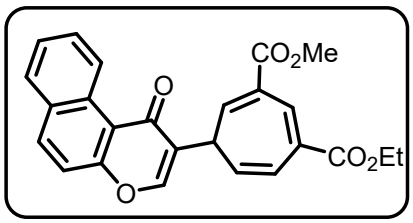
White solid (33.4 mg, 67% yield, m.p. 133-135 °C) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.3 Hz, 1H), 8.23 (s, 1H), 8.02 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.84 (d, *J* = 4.9 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.31 (m, 2H), 6.91 (d, *J* = 9.3 Hz, 1H), 6.63 (d, *J* = 6.4 Hz, 1H), 5.44 (dd, *J* = 9.2, 5.6 Hz, 1H), 4.40 – 4.26 (m, 2H), 3.81 (s, 3H), 2.80 (t, *J* = 5.9 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.64, 166.65, 166.24, 155.89, 153.15, 141.99, 140.49, 139.66, 133.83, 133.37, 131.80, 130.14, 128.45, 128.03, 126.00, 124.81, 124.75, 124.22, 123.84, 122.99, 122.77, 122.32, 120.62, 118.93, 118.47, 61.39, 52.28, 36.93, 14.30.

HRMS (ESI): m/z calcd for $C_{29}H_{23}O_6S_8$ ([M+H]$^+$): 499.1210; found: 499.1212

1-ethyl 3-methyl 5-(1-oxo-1H-benzo[f]chromen-2-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ua).



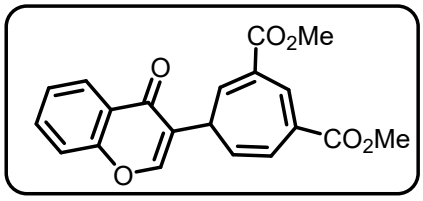
Yellow solid (31.1 mg, 75% yield) according to procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (d, *J* = 8.6 Hz, 1H), 8.24 (s, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.91 (d, *J* = 9.9 Hz, 2H), 7.75 (m, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 6.91 (d, *J* = 9.3 Hz, 1H), 6.70 (d, *J* = 6.4 Hz, 1H), 5.51 (dd, *J* = 9.3, 5.5 Hz, 1H), 4.38 – 4.29 (m, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 5.9 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.44, 166.65, 166.24, 157.57, 150.68, 135.72, 133.85, 133.38, 132.30, 130.56, 130.39, 129.35, 128.37, 128.25, 127.91, 127.00, 126.73, 125.69, 125.08, 119.70, 117.44, 61.30, 52.20, 37.13, 14.27.

HRMS (ESI): m/z calcd for $C_{25}H_{21}O_6$ ([M+H]$^+$): 417.1333; found: 417.1327

dimethyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ab).



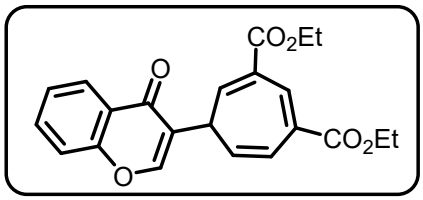
Yellow oil (33.7 mg, 96% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.21 (s, 1H), 7.85 (s, 1H), 7.74 – 7.63 (m, 1H), 7.48 – 7.39 (m, 2H), 6.86 (d, *J* = 9.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.44 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 2.77 (t, *J* = 5.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.97, 167.16, 166.22, 156.35, 153.19, 134.08, 133.94, 133.08, 131.86, 128.03, 125.97, 125.81, 125.41, 124.09, 122.65, 119.38, 118.18, 52.41, 52.29, 37.12.

HRMS (ESI): m/z calcd for $C_{20}H_{17}O_6$ ($[M+H]^+$): 353.1020; found: 353.1017

diethyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ac).



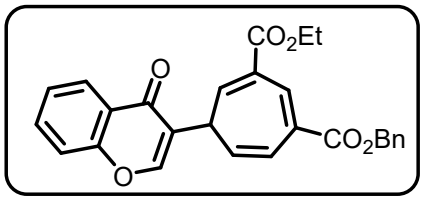
Yellow oil (36 mg, 95% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.1 Hz, 1H), 8.22 (s, 1H), 7.85 (s, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.37 (m, 2H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.58 (d, *J* = 6.3 Hz, 1H), 5.43 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.37 – 4.20 (m, 4H), 2.76 (t, *J* = 5.8 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.92, 166.69, 165.78, 156.31, 153.18, 133.95, 133.88, 133.30, 131.19, 128.34, 125.93, 125.80, 125.35, 124.05, 122.75, 119.06, 118.14, 61.31, 61.25, 37.02, 14.27.

HRMS (ESI): m/z calcd for $C_{22}H_{21}O_6$ ($[M+H]^+$): 381.1333; found: 381.1330

1-benzyl 3-ethyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ad).



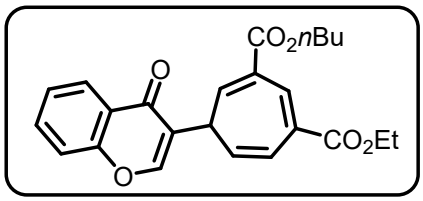
Yellow oil (42.3 mg, 96% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.30 (m, 7H), 6.91 (d, *J* = 9.3 Hz, 1H), 6.59 (d, *J* = 6.4 Hz, 1H), 5.43 (dd, *J* = 9.1, 5.6 Hz, 1H), 5.31 (q, *J* = 12.4 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 5.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.91, 166.51, 165.70, 156.31, 153.19, 135.84, 134.35, 133.88, 132.96, 131.15, 128.59, 128.34, 128.28, 128.23, 125.93, 125.80, 125.36, 124.05, 122.68, 118.95, 118.14, 66.98, 61.27, 37.01, 14.25.

HRMS (ESI): m/z calcd for $C_{27}H_{23}O_6$ ($[M+H]^+$): 443.1489; found: 443.1489

3-butyl 1-ethyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ae).



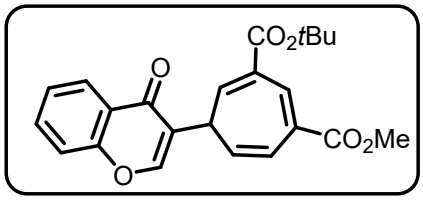
Yellow oil (35.3 mg, 87% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 1H), 8.22 (s, 1H), 7.85 (s, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.51 – 7.37 (m, 2H), 6.88 (d, *J* = 9.3 Hz, 1H), 6.56 (d, *J* = 6.4 Hz, 1H), 5.42 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.31 (q, *J* = 6.9 Hz, 2H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 5.9 Hz, 1H), 1.72 – 1.59 (m, 2H), 1.38 (dt, *J* = 21.5, 7.3 Hz, 5H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.90, 166.69, 165.86, 156.32, 153.16, 133.95, 133.87, 133.25, 130.77, 128.41, 125.96, 125.91, 125.35, 124.08, 122.77, 118.74, 118.15, 65.16, 61.31, 36.90, 30.66, 19.17, 14.27, 13.74.

HRMS (ESI): m/z calcd for $C_{24}H_{25}O_6$ ($[M+H]^+$): 409.1646; found: 409.1647

3-(tert-butyl) 1-methyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3af).



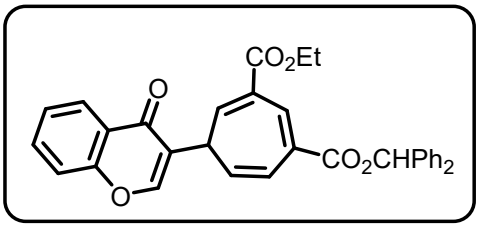
White solid (37.1 mg, 94% yield, m.p. 131-133 °C) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 8.20 (s, 1H), 7.84 (s, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.36 (m, 2H), 6.85 (d, *J* = 9.2 Hz, 1H), 6.49 (d, *J* = 6.2 Hz, 1H), 5.44 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.84 (s, 3H), 2.75 (t, *J* = 5.7 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.88, 167.26, 164.89, 156.31, 153.16, 134.43, 133.85, 132.69, 130.98, 129.74, 125.97, 125.59, 125.32, 124.08, 122.88, 119.57, 118.14, 81.64, 52.31, 36.93, 28.10.

HRMS (ESI): m/z calcd for $C_{23}H_{23}O_6$ ($[M+H]^+$): 395.1489; found: 395.1486

1-benzhydryl 3-ethyl 5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1,3-dicarboxylate (3ag).



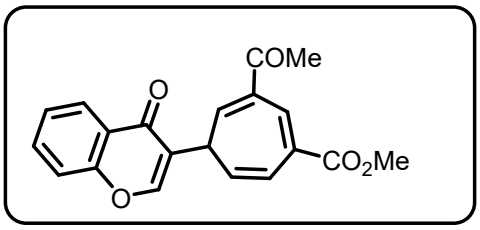
Yellow oil (50.5 mg, 97% yield) according to procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.26 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.85 (s, 1H), 7.69 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 5H), 7.39 – 7.33 (m, 4H), 7.30 (dd, *J* = 8.2, 6.1 Hz, 2H), 7.07 (s, 1H), 6.98 (d, *J* = 9.3 Hz, 1H), 6.61 (d, *J* = 6.4 Hz, 1H), 5.46 (dd, *J* = 9.2, 5.6 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.92, 165.67, 165.64, 156.29, 153.25, 140.12, 140.10, 134.51, 133.89, 132.94, 131.09, 128.57, 128.30, 128.01, 127.96, 127.17, 127.04, 125.91, 125.80, 125.37, 124.04, 122.62, 118.74, 118.14, 77.75, 61.27, 36.98, 14.24.

HRMS (ESI): m/z calcd for $C_{33}H_{26}O_6Na$ ($[M+Na]^+$): 541.1622; found: 541.1620.

methyl 3-acetyl-5-(4-oxo-4H-chromen-3-yl)cyclohepta-1,3,6-triene-1-carboxylate (3ah).



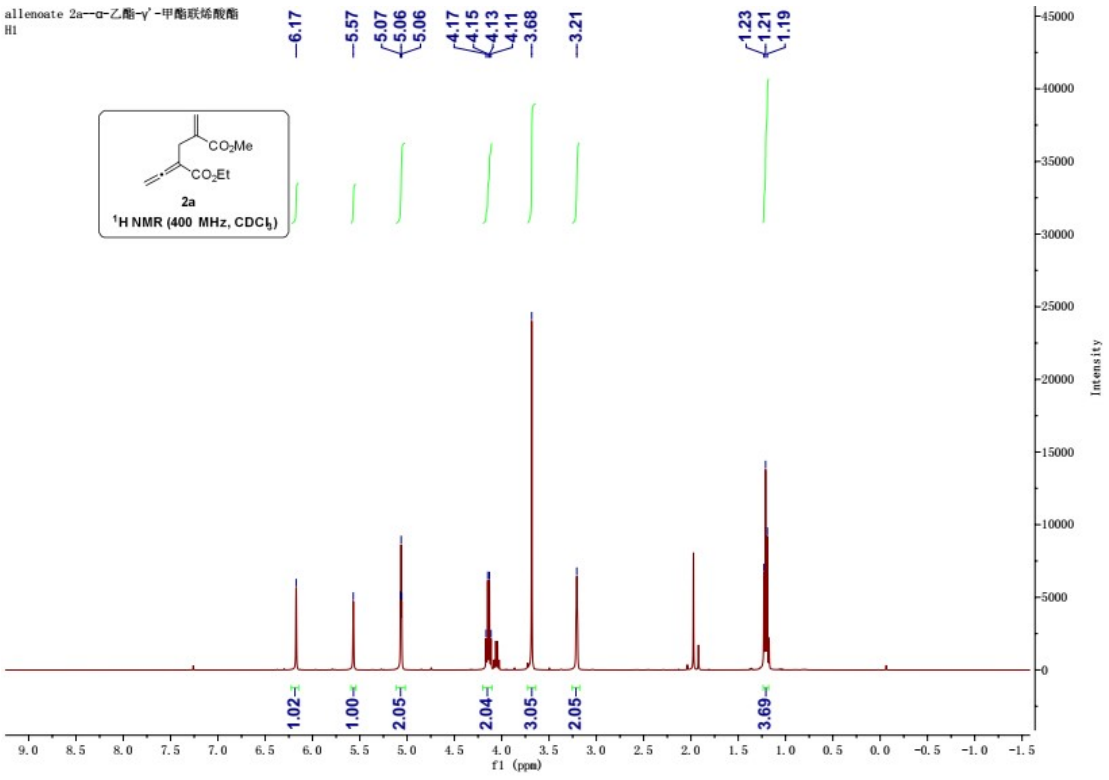
Yellow oil (33 mg, 99% yield) according to procedure A.

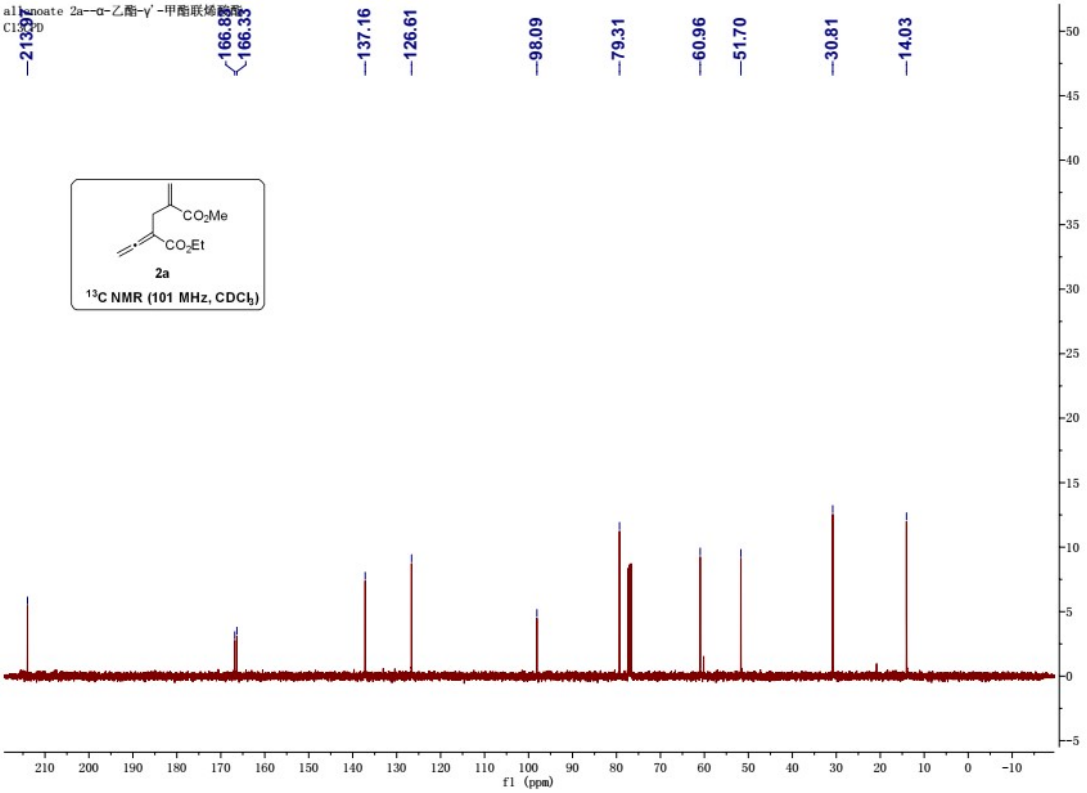
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 8.17 (s, 1H), 7.84 (s, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.14 (d, *J* = 5.9 Hz, 1H), 5.20 – 5.12 (m, 1H), 3.84 (s, 3H), 2.55 (t, *J* = 5.7 Hz, 1H), 2.41 (s, 3H).

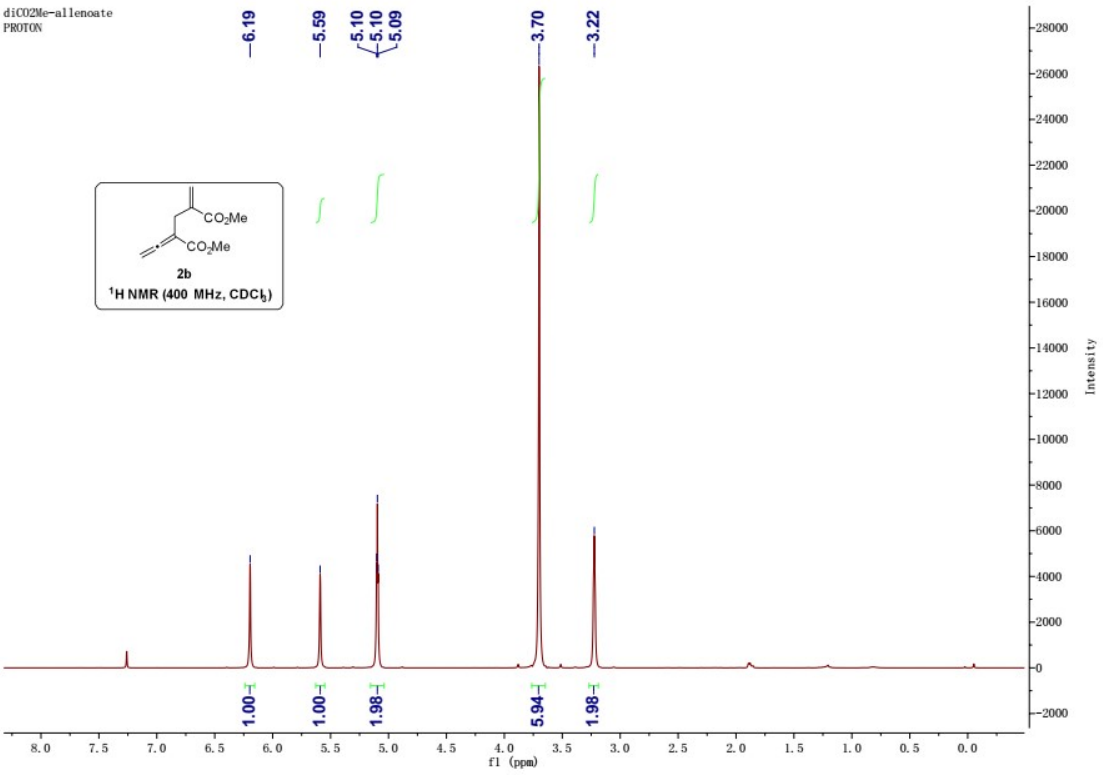
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.31, 177.18, 166.97, 156.32, 153.37, 136.03, 133.99, 133.00, 132.02, 130.11, 128.43, 128.02, 125.85, 125.45, 124.00, 122.34, 118.20, 52.36, 35.61, 26.44.

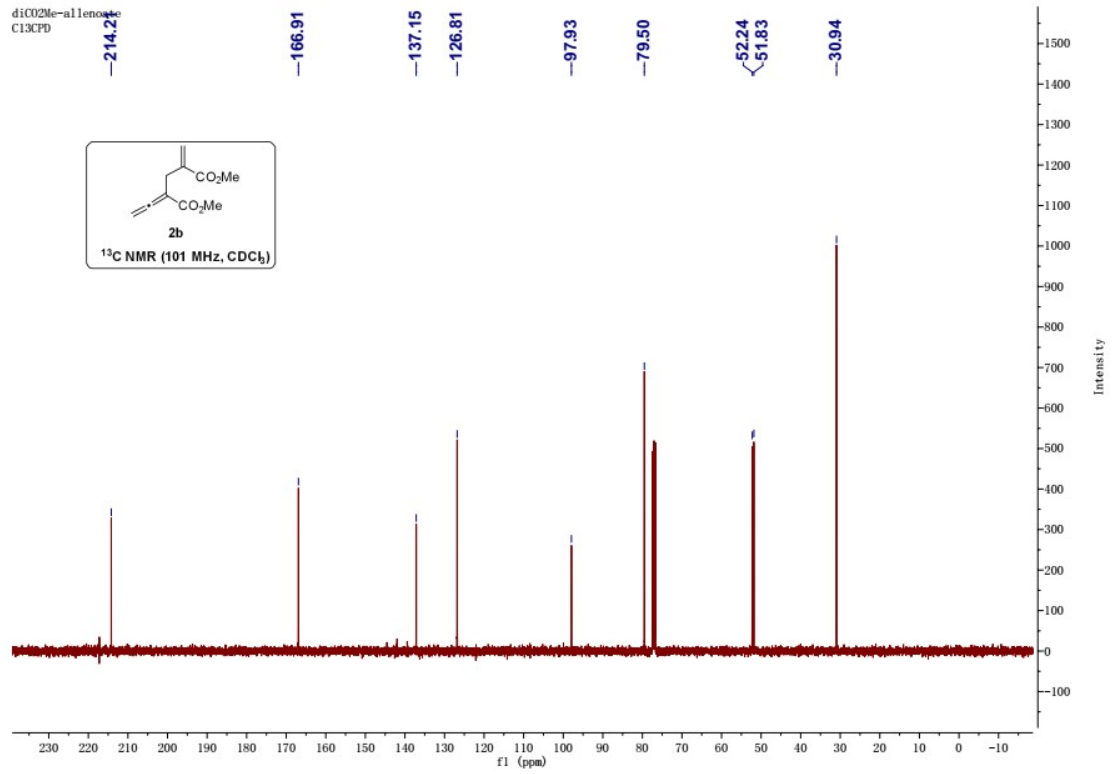
HRMS (ESI): m/z calcd for $C_{20}H_{17}O_5Na$ ([M+H]$^+$): 337.1071; found: 337.1074.

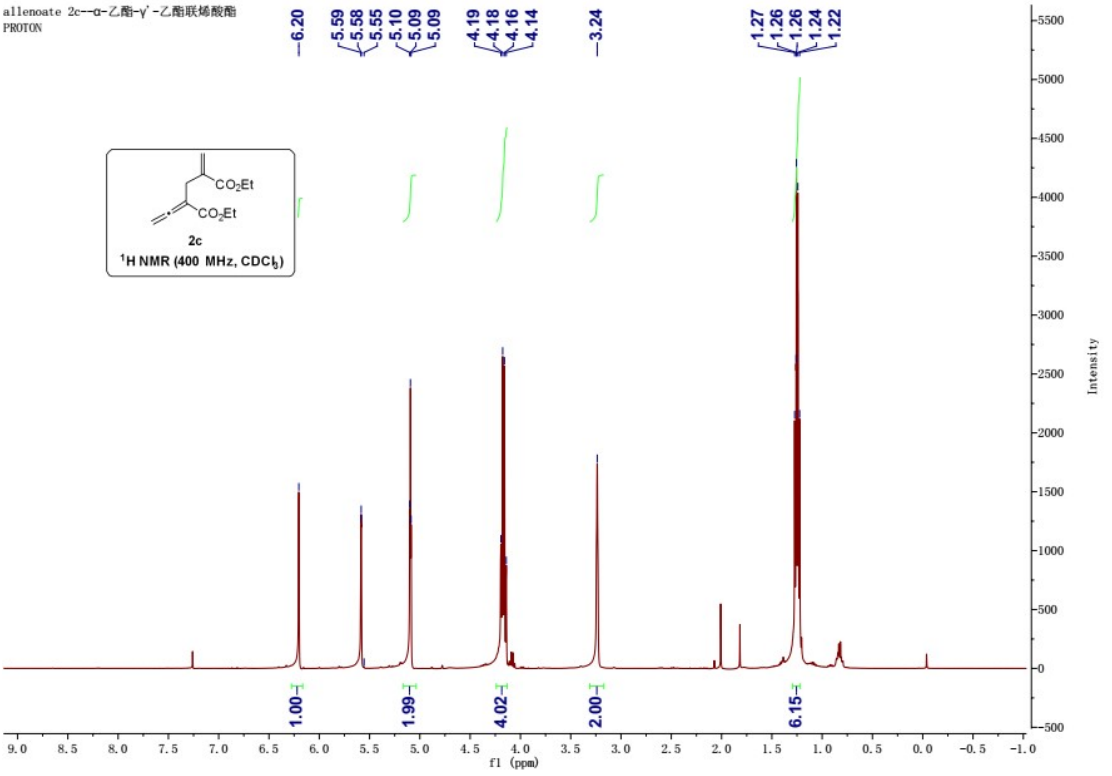
9. Spectra

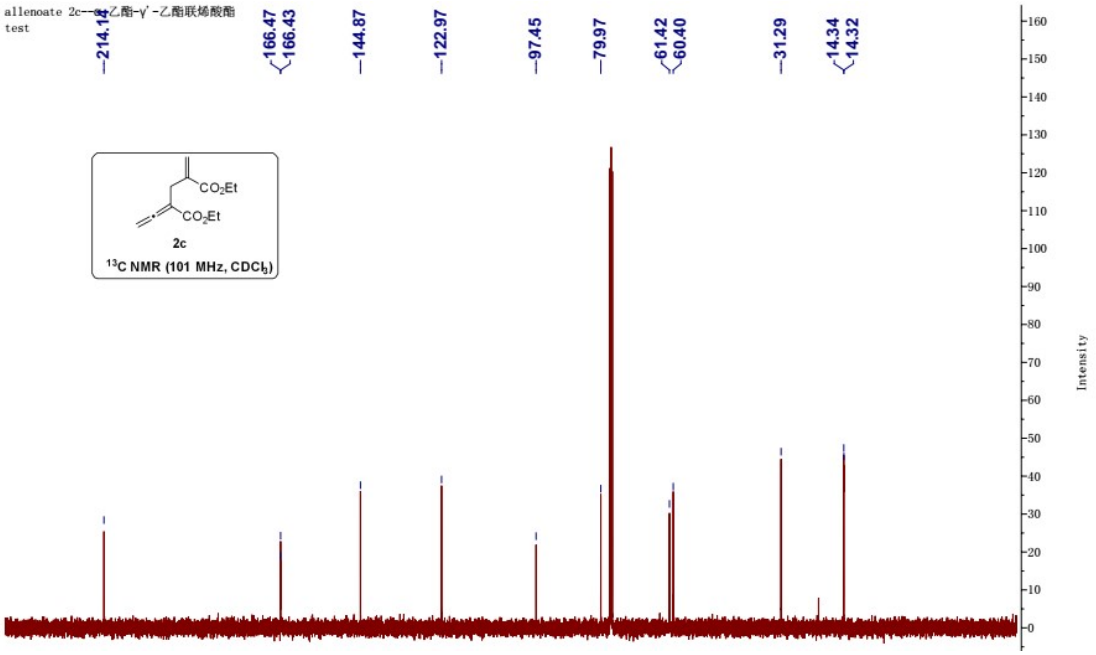


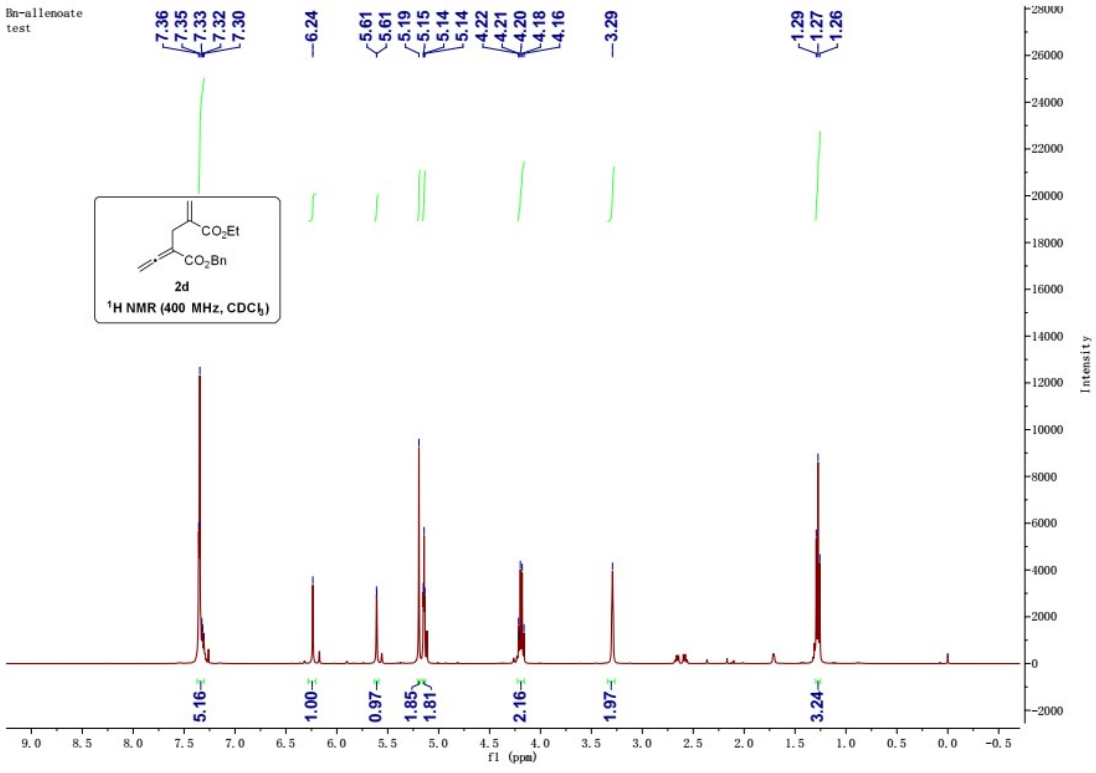

allenoate 2a--α-乙酯-γ'-甲酯联烯酸酯
C13CPD
213.97
166.85
166.33
137.16
126.61
98.09
79.31
60.96
51.70
30.81
14.03
CO2Me
CO2Et
2a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

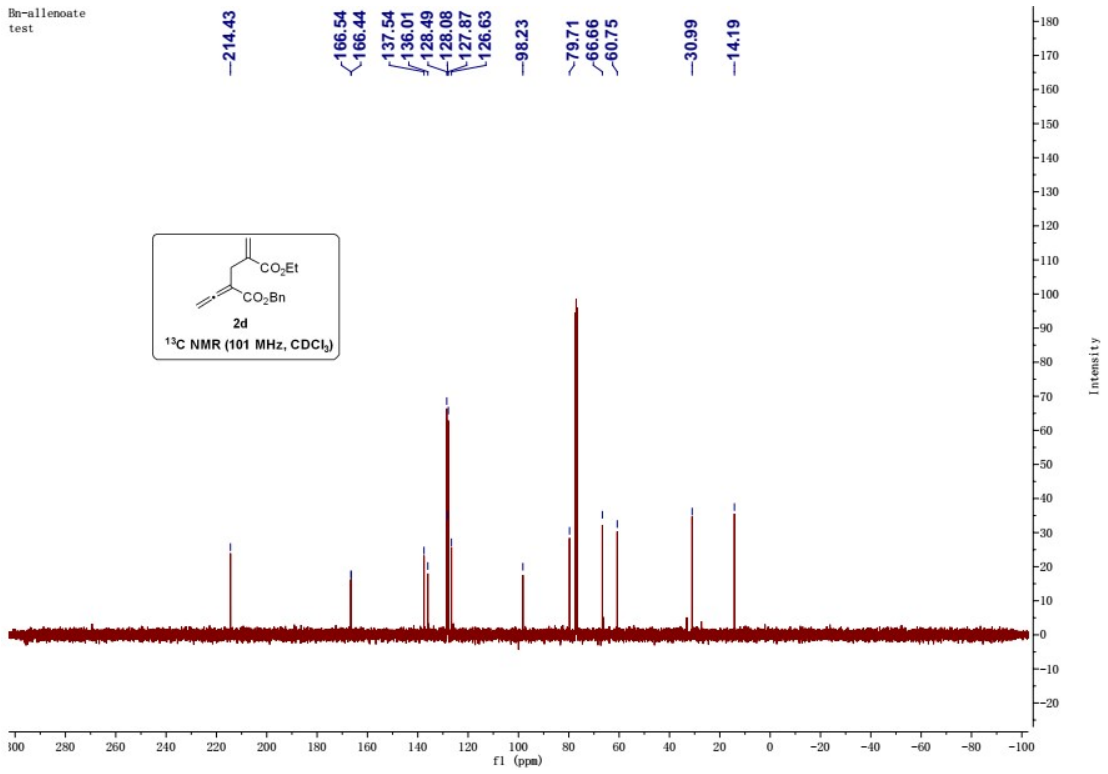

diCO2Me-allenoate
PROTON
6.19
5.59
5.10
5.10
5.09
3.70
3.22
CO2Me
CO2Me
2b
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.98
5.94
1.98
f1 (ppm)
Intensity

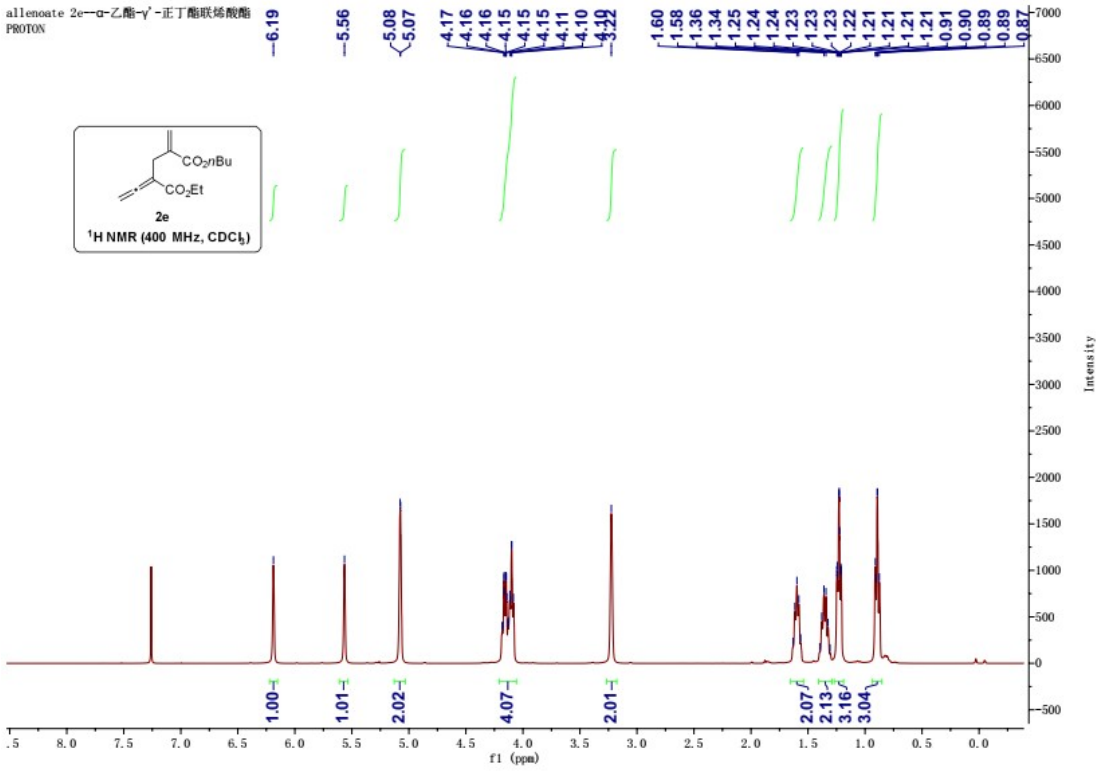

diCO2Me-allenoate
C13CPD
214.24
166.91
137.15
126.81
97.93
79.50
52.24
51.83
30.94
CO2Me
CO2Me
2b
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

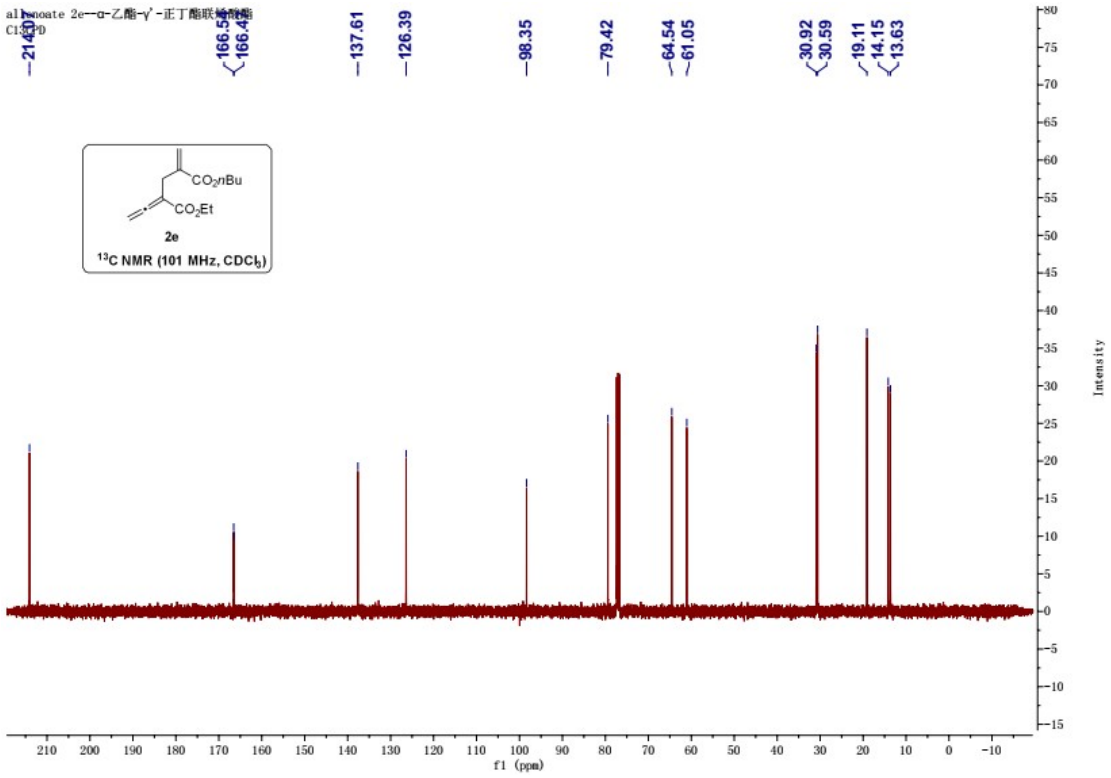

allenoate 2c--α-乙酯-γ'-乙酯联烯酸酯
PROTON
6.20
5.59
5.58
5.55
5.10
5.09
5.09
4.19
4.18
4.16
4.14
3.24
1.27
1.26
1.26
1.24
1.22
CO2Et
CO2Et
2c
1H NMR (400 MHz, CDCl3)
1.00
1.99
4.02
2.00
6.15
Intensity
f1 (ppm)

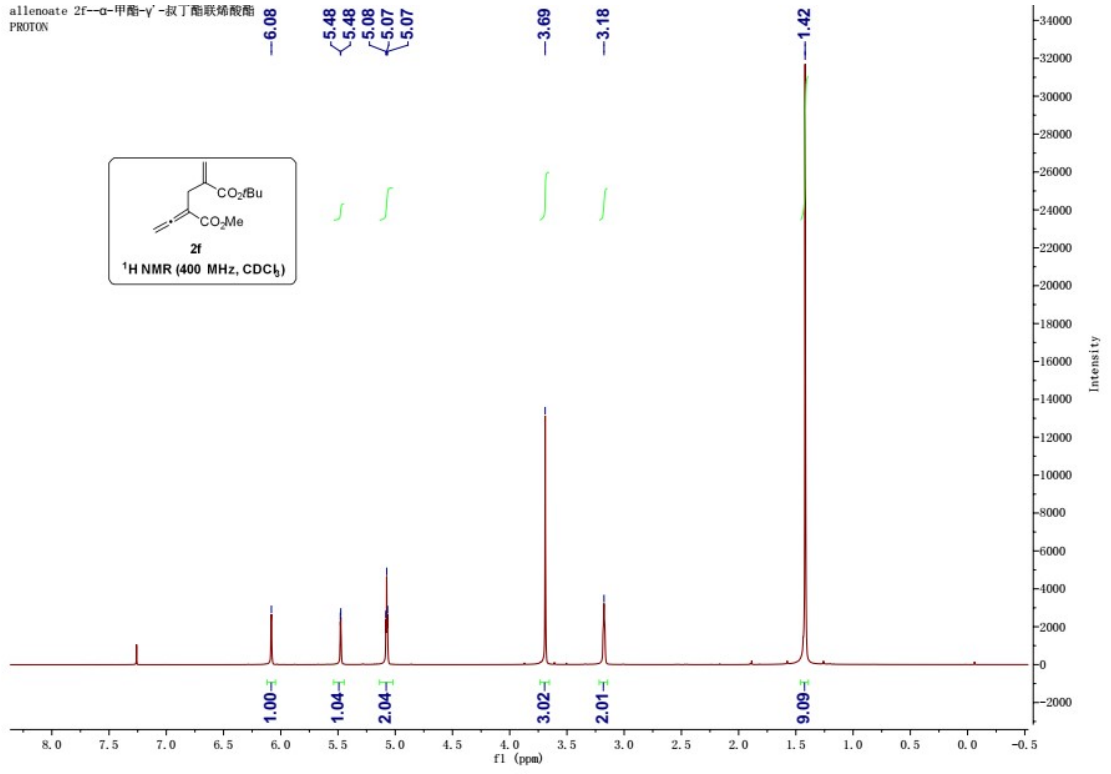

allenoate 2c
test
214.14
166.47
166.43
144.87
122.97
97.45
79.97
61.42
60.40
31.29
14.34
14.32
CO2Et
CO2Et
2c
13C NMR (101 MHz, CDCl3)
Intensity

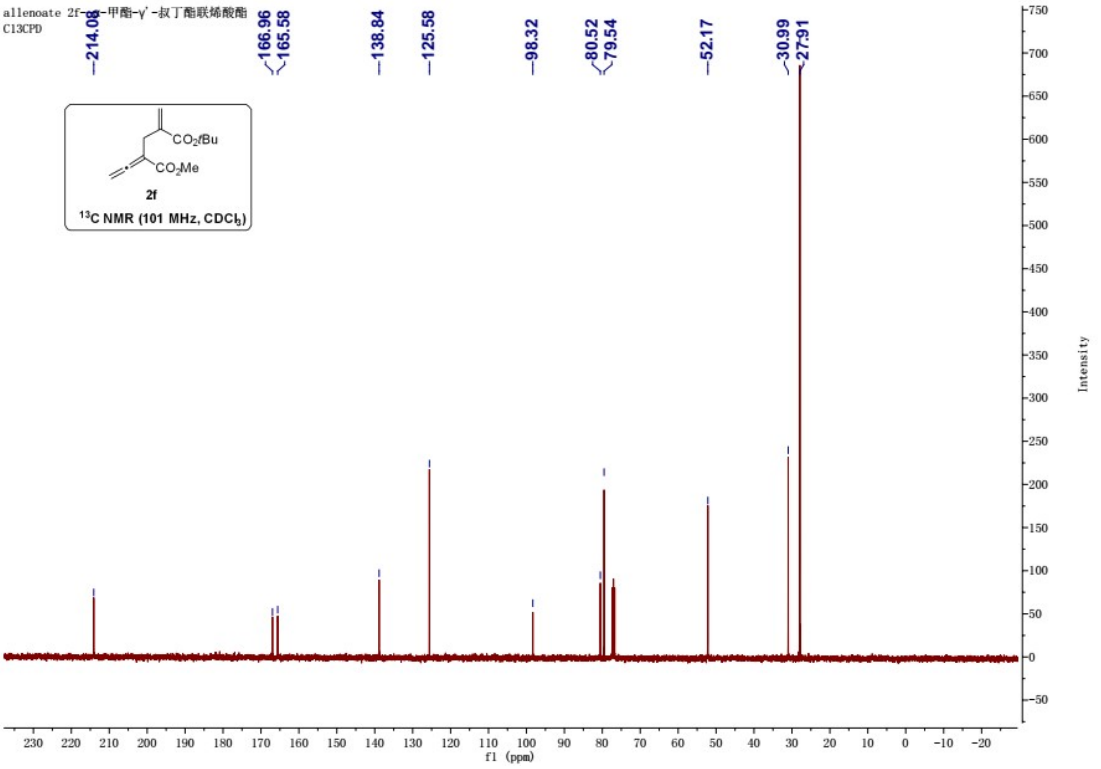

Bn-allenoate
test
7.36
7.35
7.33
7.32
7.30
6.24
5.61
5.61
5.19
5.15
5.14
5.14
4.22
4.21
4.20
4.18
4.16
3.29
1.29
1.27
1.26
CO2Et
CO2Bn
2d
1H NMR (400 MHz, CDCl3)
5.16
1.00
0.97
1.85
1.81
2.16
1.97
3.24
f1 (ppm)
Intensity

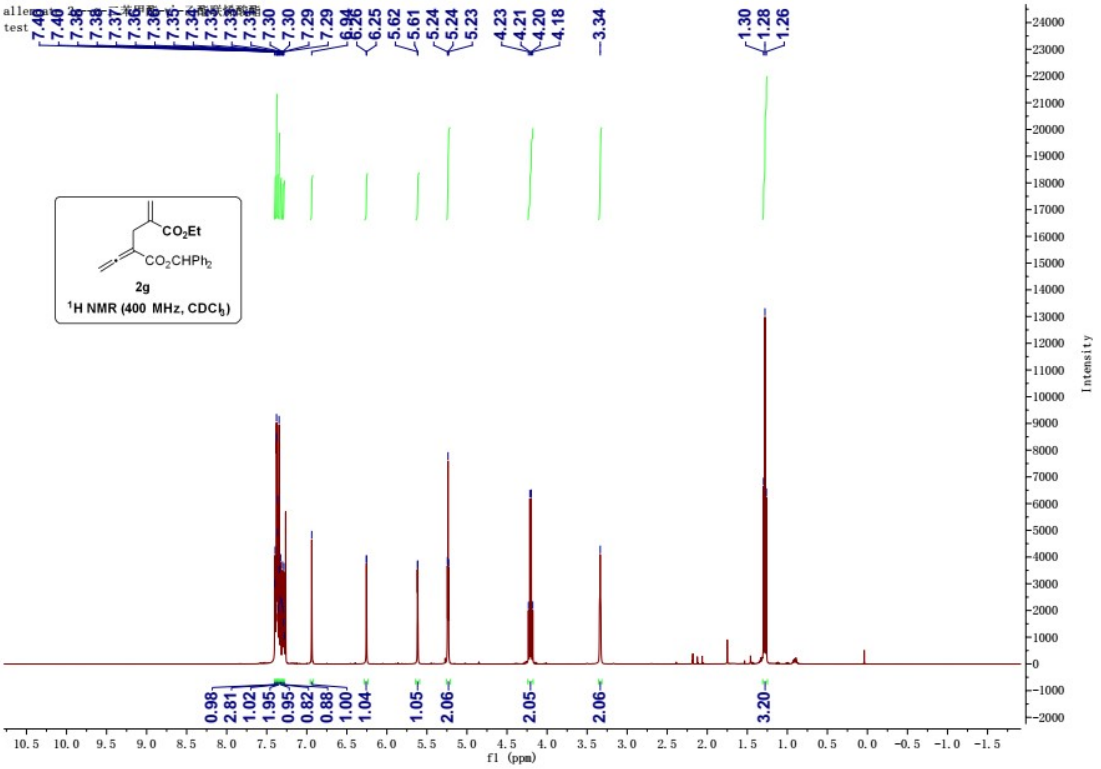

Bn-allenoate
test
214.43
166.54
166.44
137.54
136.01
128.49
128.08
127.87
126.63
98.23
79.71
66.66
60.75
30.99
14.19
CO2Et
CO2Bn
2d
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

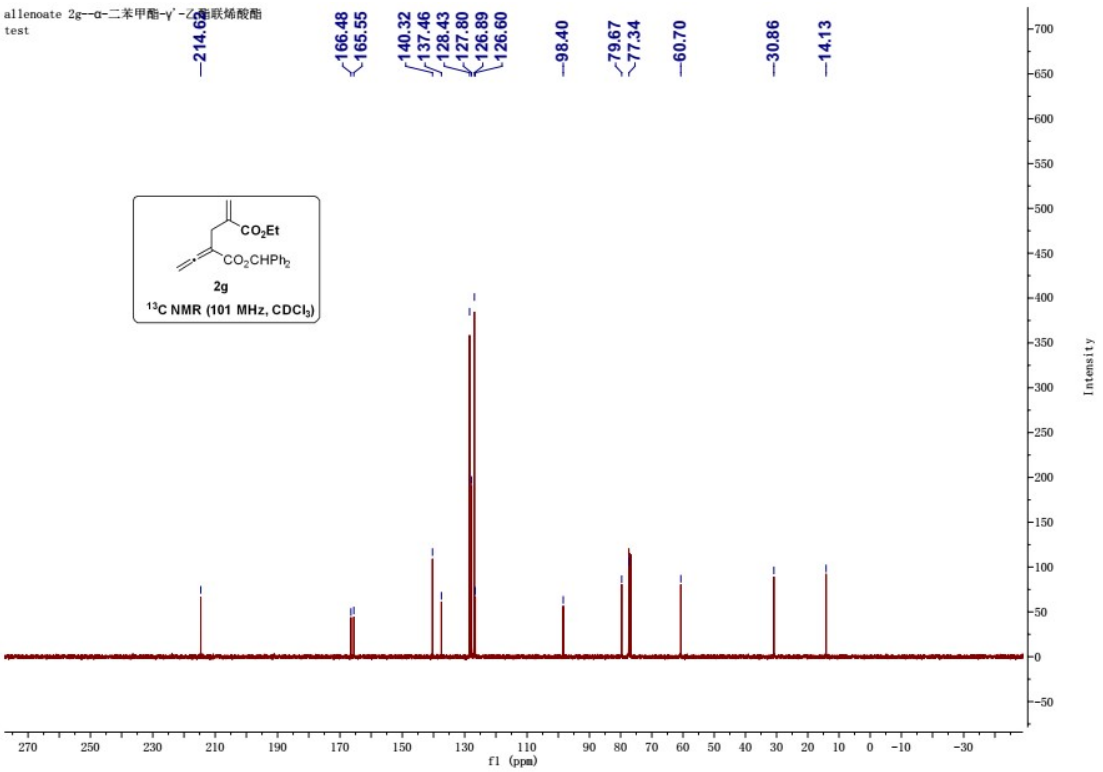

allenoate 2e—α-乙酯-γ'-正丁酯联烯酸酯
PROTON
6.19
5.56
5.08
5.07
4.17
4.16
4.16
4.15
4.15
4.15
4.11
4.10
3.22
1.60
1.58
1.36
1.34
1.25
1.24
1.24
1.23
1.23
1.23
1.22
1.21
1.21
1.21
1.21
0.91
0.90
0.89
0.89
0.87
CO2nBu
CO2Et
2e
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.02
4.07
2.01
2.07
2.13
3.16
3.04
Intensity
f1 (ppm)

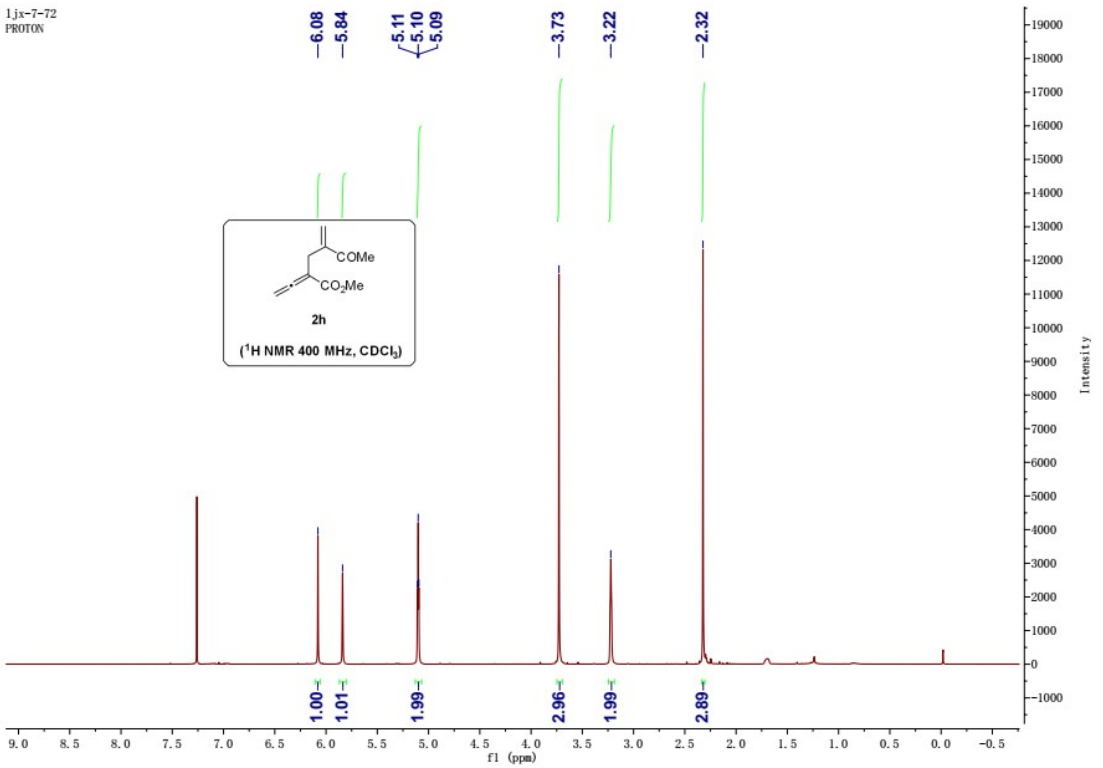

allenoate 2e--α-乙酯-γ'-正丁酯联烯酸酯
C13CPD
214.90
166.53
166.42
137.61
126.39
98.35
79.42
64.54
61.05
30.92
30.59
19.11
14.15
13.63
CO2nBu
CO2Et
2e
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

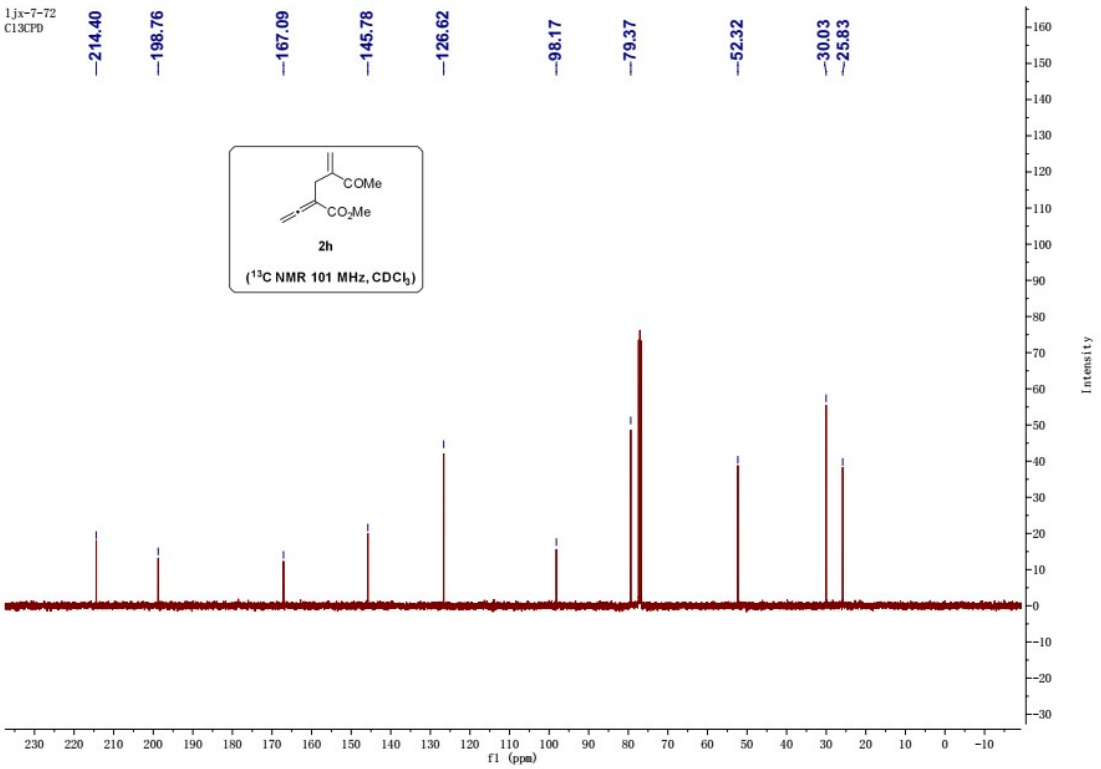

allenoate 2f--α-甲酯-γ'-叔丁酯联烯酸酯
PROTON
6.08
5.48
5.48
5.08
5.07
5.07
3.69
3.18
1.42
CO2tBu
CO2Me
2f
1H NMR (400 MHz, CDCl3)
1.00
1.04
2.04
3.02
2.01
9.09
Intensity
f1 (ppm)

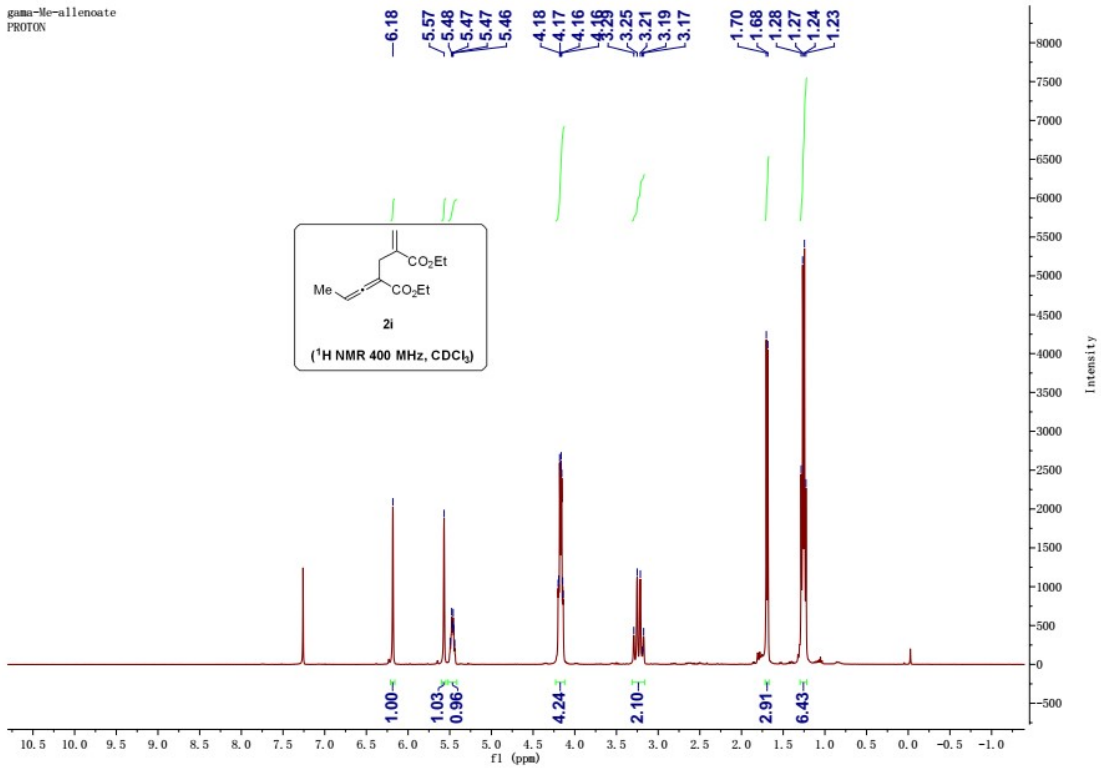

allenoate 2f-α-甲酯-γ'-叔丁酯联烯酸酯
C13CPD
214.08
166.96
165.58
138.84
125.58
98.32
80.52
79.54
52.17
30.99
27.91
CO2tBu
CO2Me
2f
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

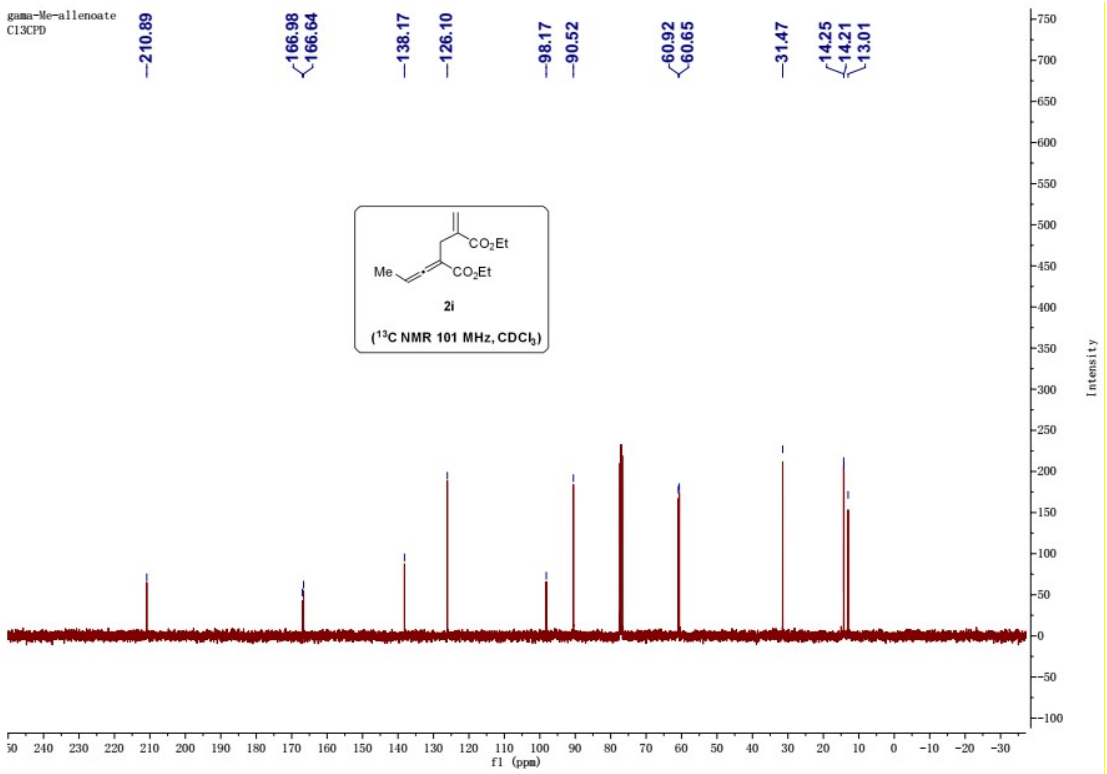

test
7.40
7.38
7.37
7.30
7.29
6.25
5.62
5.61
5.24
5.23
4.23
4.21
4.20
4.18
3.34
1.30
1.28
1.26
CO2Et
CO2CHPh2
2g
1H NMR (400 MHz, CDCl3)
0.98
2.81
1.02
1.95
0.95
0.82
0.88
1.00
1.04
1.05
2.06
2.05
2.06
3.20
f1 (ppm)
Intensity

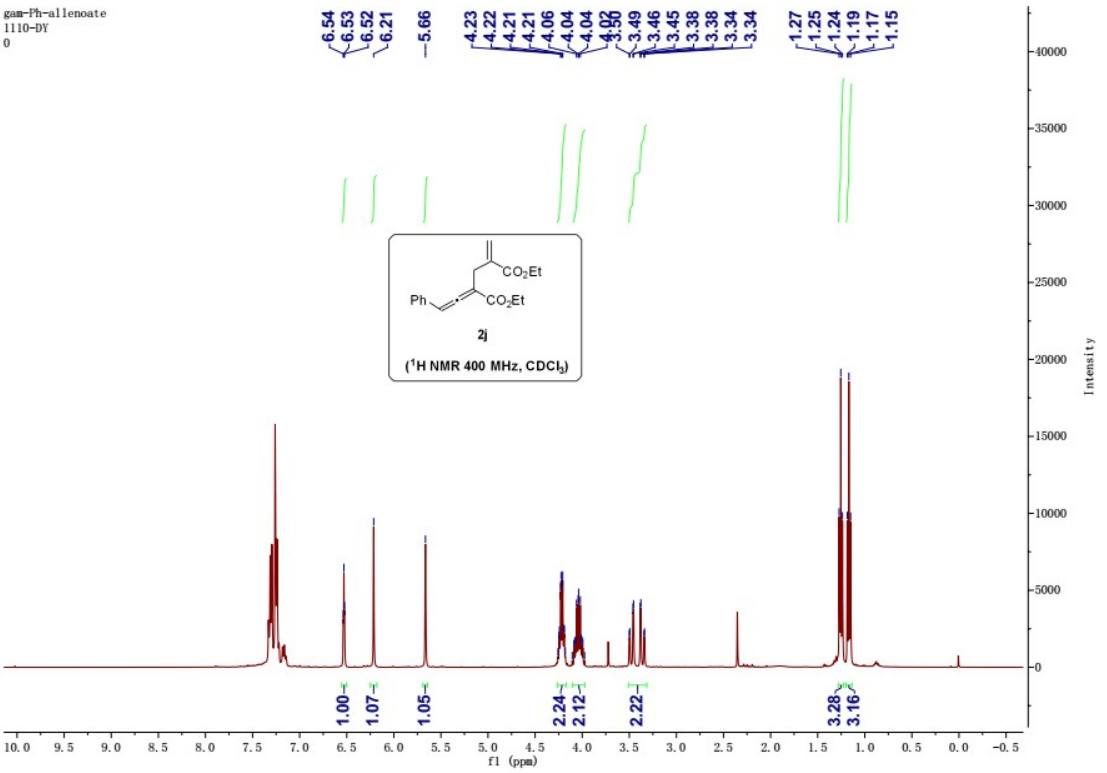

allenoate 2g--α-二苯甲酯-γ'-乙酯联烯酸酯
test
214.62
166.48
165.55
140.32
137.46
128.43
127.80
126.89
126.60
98.40
79.67
77.34
60.70
30.86
14.13
CO2Et
CO2CHPh2
2g
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

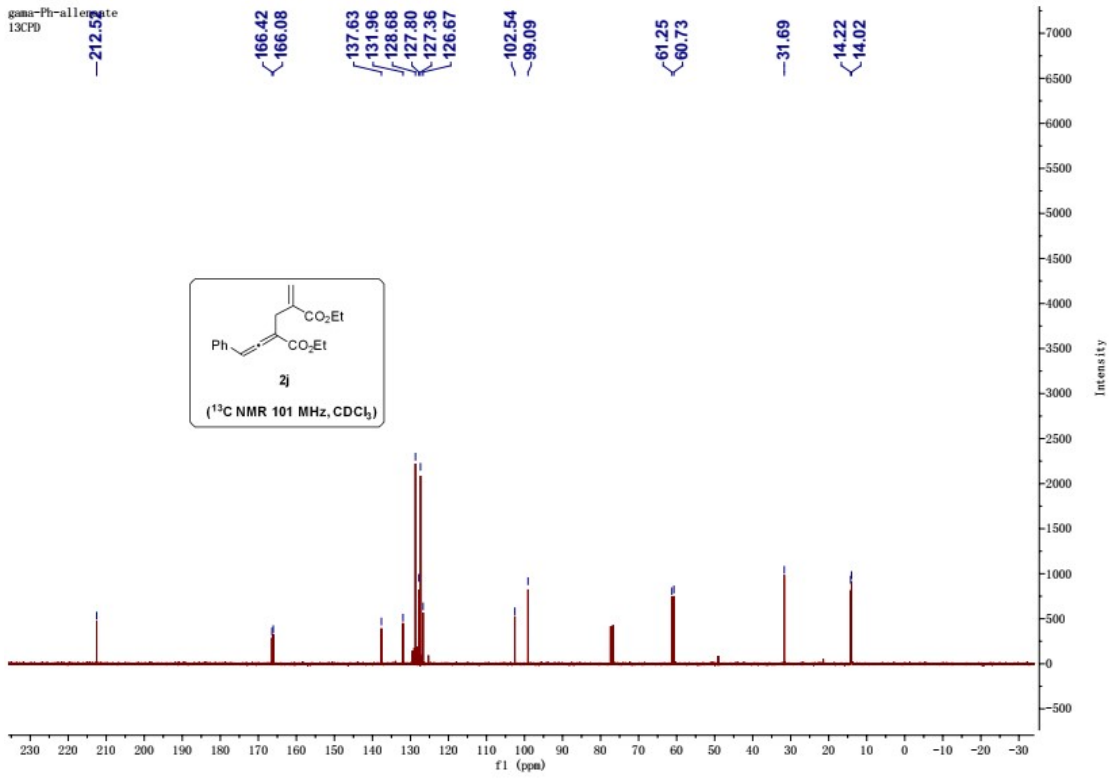

ljx-7-72
PROTON
6.08
5.84
5.11
5.10
5.09
3.73
3.22
2.32
COMe
CO2Me
2h
(1H NMR 400 MHz, CDCl3)
1.00
1.01
1.99
2.96
1.99
2.89
Intensity
f1 (ppm)

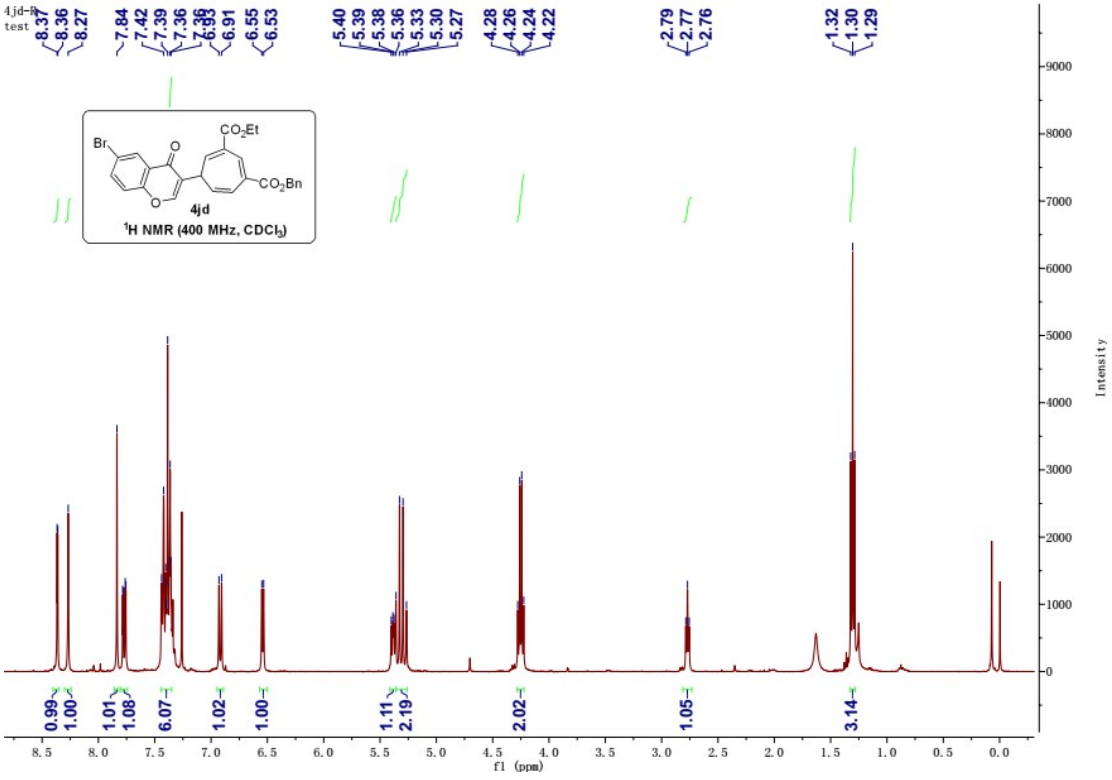

ljx-7-72
C13CPD
214.40
198.76
167.09
145.78
126.62
98.17
79.37
52.32
30.03
25.83
COMe
CO2Me
2h
(13C NMR 101 MHz, CDCl3)
Intensity
f1 (ppm)

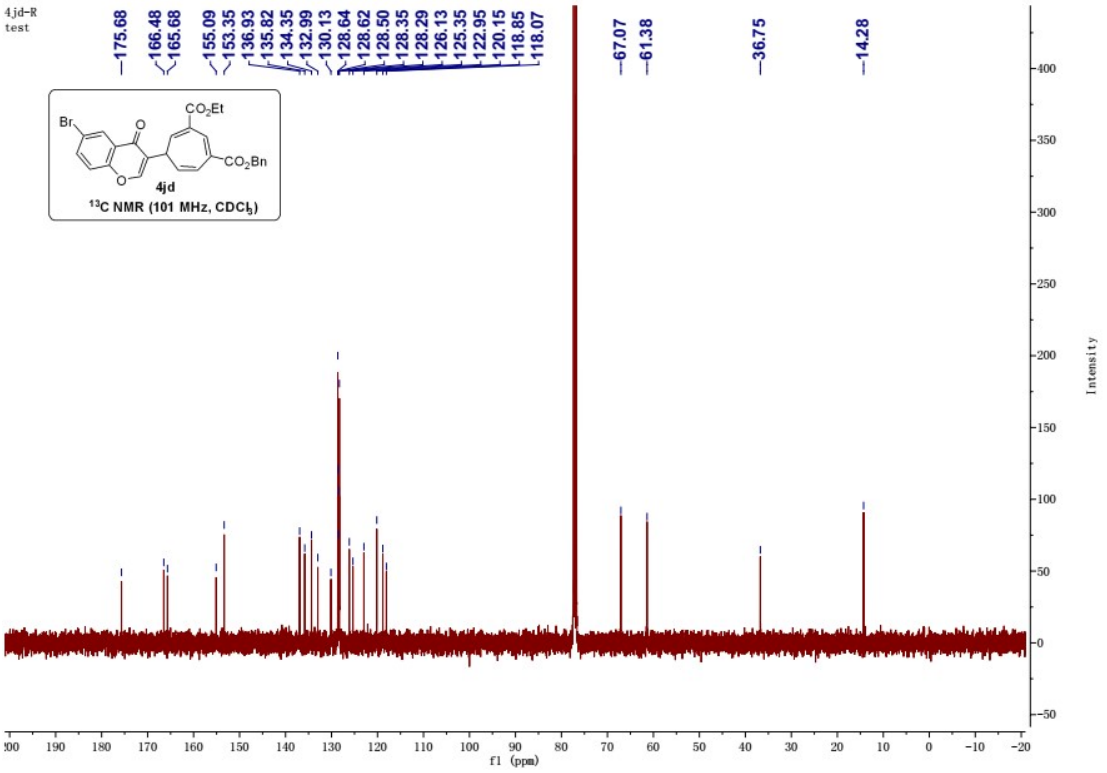

gama-Me-allenoate
PROTON
6.18
5.57
5.48
5.47
5.47
5.46
4.18
4.17
4.16
3.25
3.21
3.19
3.17
1.70
1.68
1.28
1.27
1.24
1.23
CO2Et
Me
CO2Et
2i
(1H NMR 400 MHz, CDCl3)
1.00
1.03
0.96
4.24
2.10
2.91
6.43
Intensity
f1 (ppm)

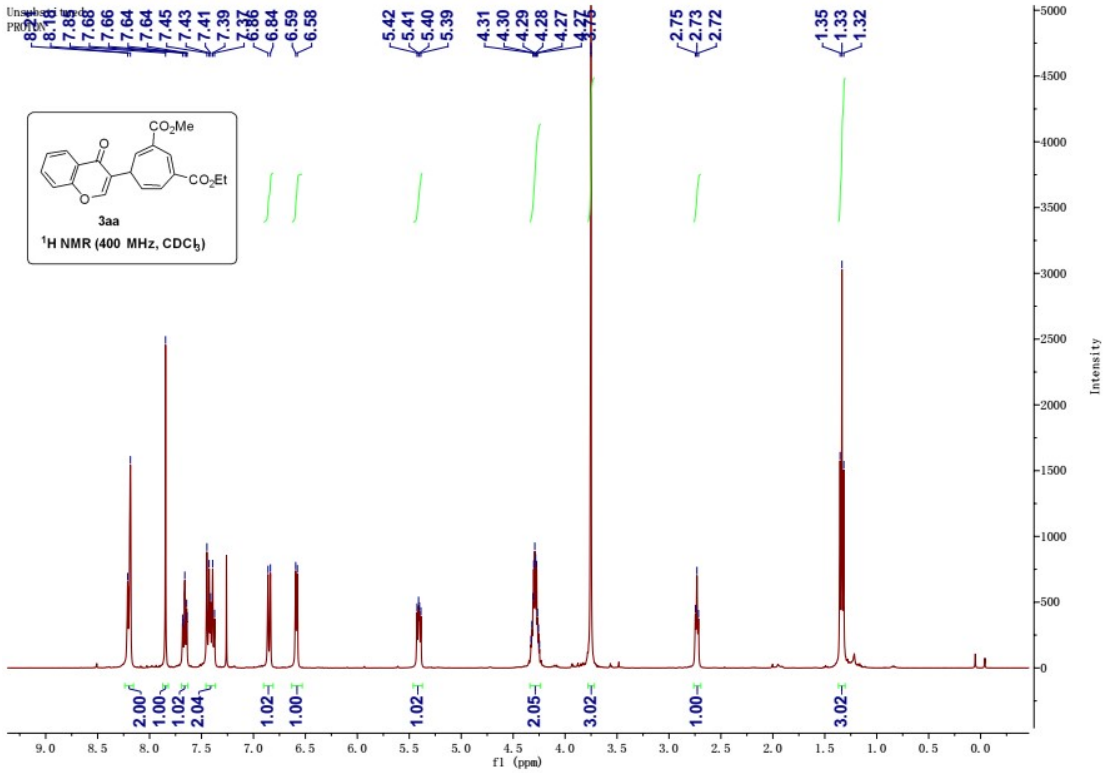

gama-Me-allenoate
C13CPD
210.89
166.98
166.64
138.17
126.10
98.17
90.52
60.92
60.65
31.47
14.25
14.21
13.01
CO2Et
Me
CO2Et
2i
(13C NMR 101 MHz, CDCl3)
Intensity
f1 (ppm)

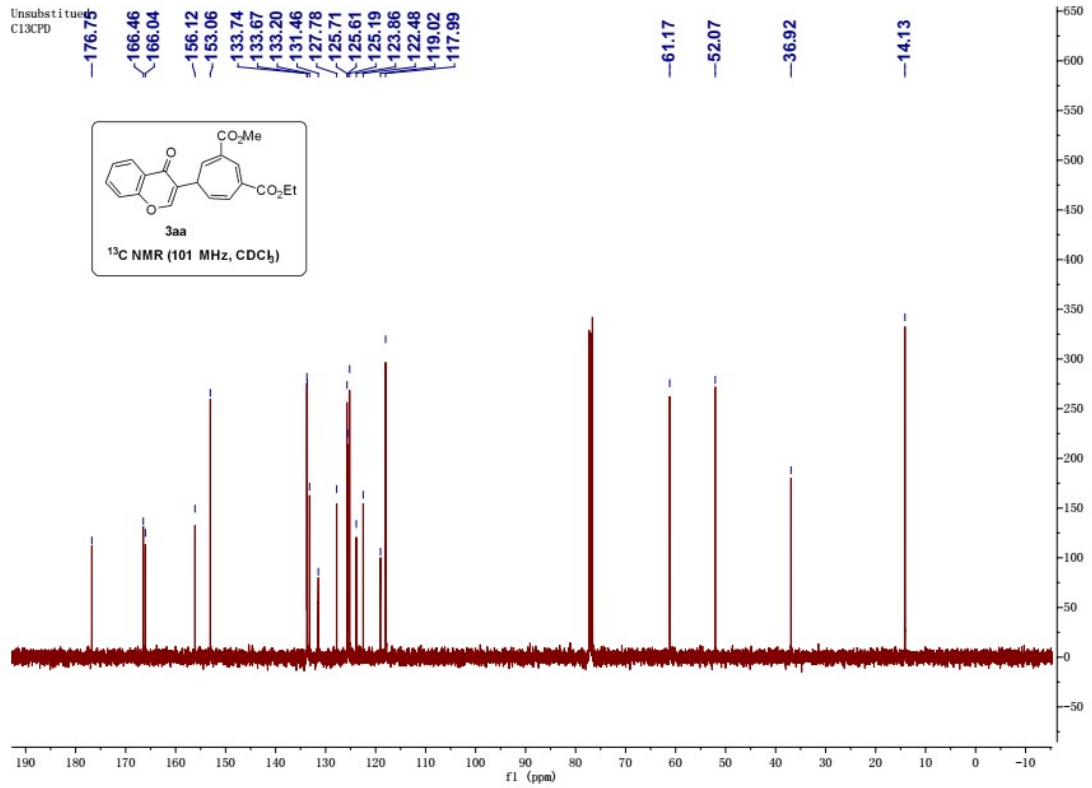

gam-Ph-allenoate
1110-DY
0
6.54
6.53
6.52
6.21
5.66
4.23
4.22
4.21
4.21
4.06
4.04
4.04
3.49
3.46
3.45
3.38
3.38
3.34
3.34
1.27
1.25
1.24
1.19
1.17
1.15
CO2Et
Ph
CO2Et
2j
(1H NMR 400 MHz, CDCl3)
1.00
1.07
1.05
2.24
2.12
2.22
3.28
3.16
Intensity
f1 (ppm)

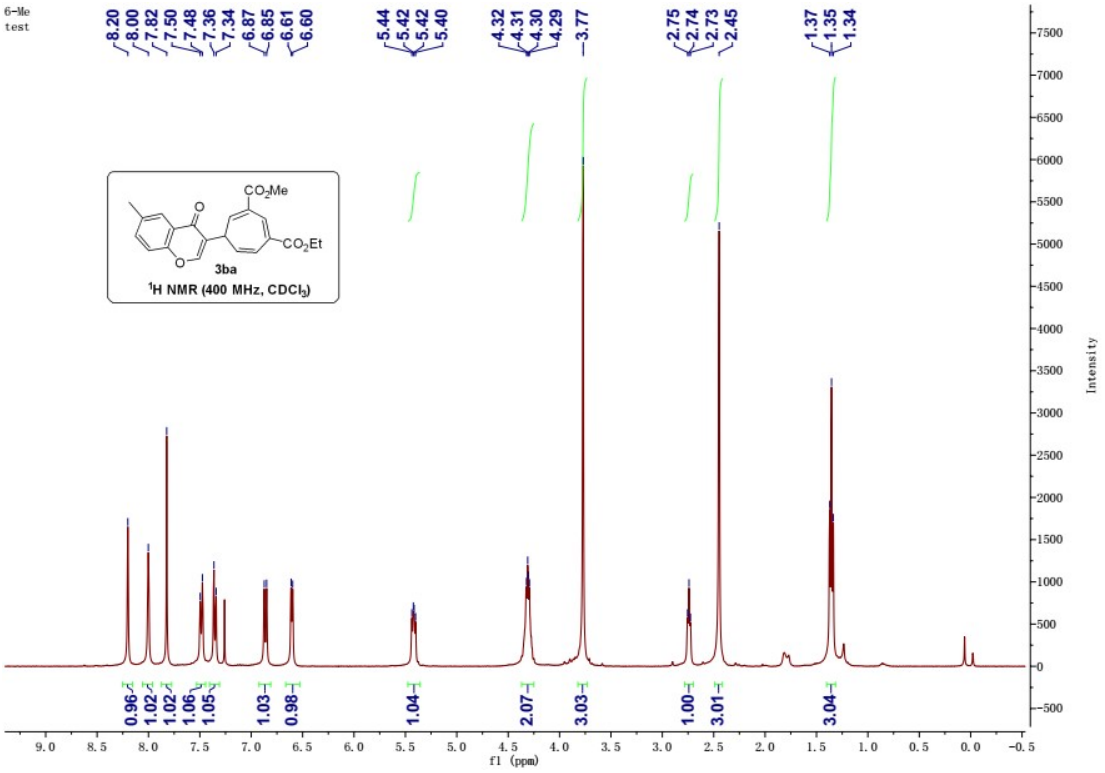

gama-Ph-allenate
13CPD
212.52
166.42
166.08
137.63
131.96
128.68
127.80
127.36
126.67
102.54
99.09
61.25
60.73
31.69
14.22
14.02
CO2Et
Ph
CO2Et
2j
(13C NMR 101 MHz, CDCl3)
Intensity
f1 (ppm)

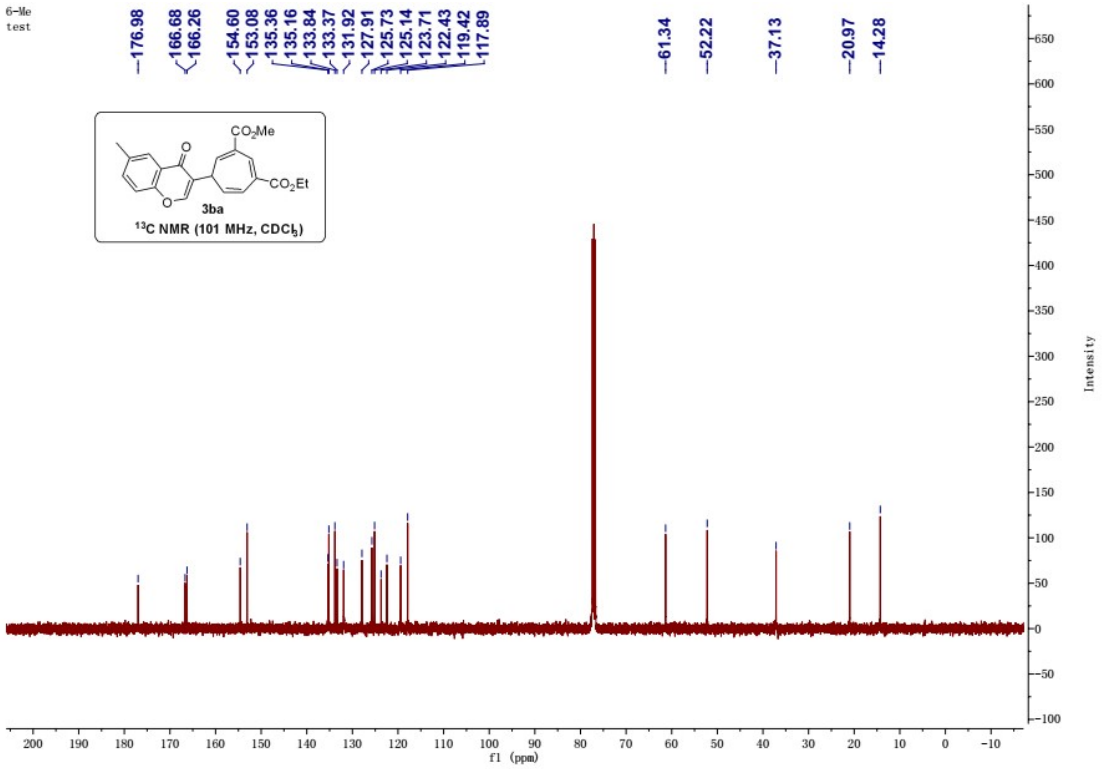

4jd-H
test
8.37
8.36
8.27
7.84
7.42
7.39
7.36
6.91
6.55
6.53
5.40
5.39
5.38
5.36
5.33
5.30
5.27
4.28
4.26
4.24
4.22
2.79
2.77
2.76
1.32
1.30
1.29
Br
CO2Et
CO2Bn
4jd
1H NMR (400 MHz, CDCl3)
0.99
1.00
1.01
1.08
6.07
1.02
1.00
1.11
2.19
2.02
1.05
3.14
Intensity
f1 (ppm)

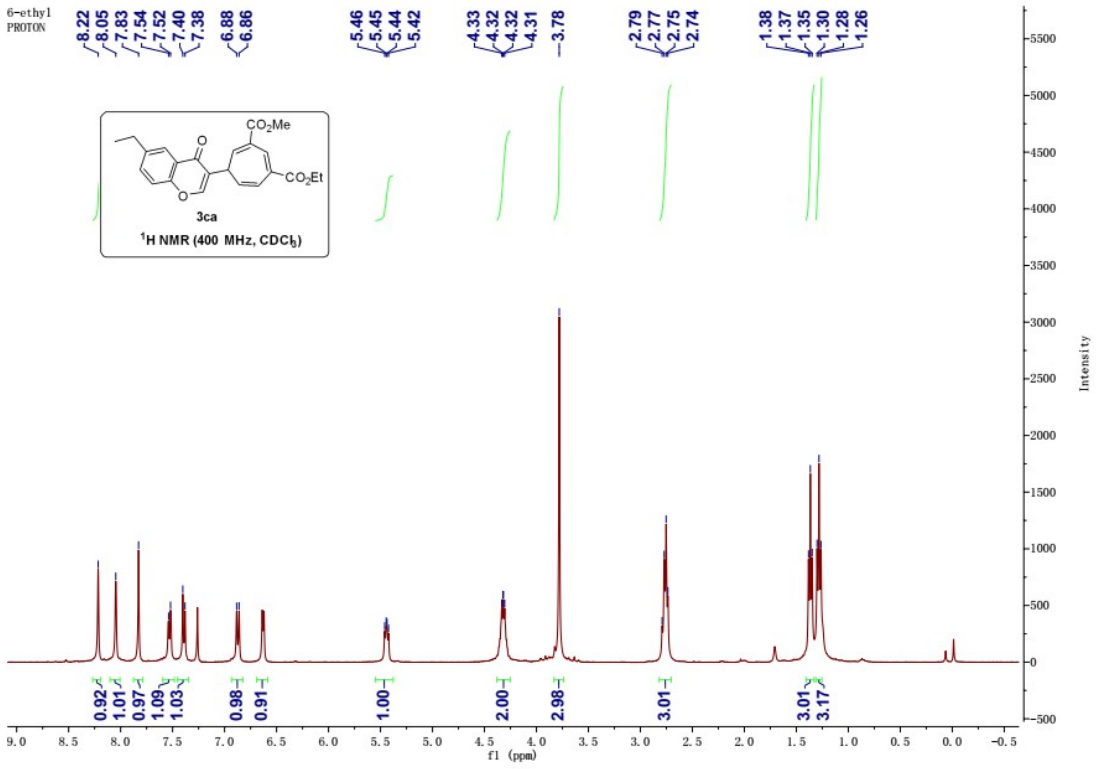

4jd-R
test
175.68
166.48
165.68
155.09
153.35
136.93
135.82
134.35
132.99
130.13
128.64
128.62
128.50
128.35
128.29
126.13
125.35
122.95
120.15
118.85
118.07
67.07
61.38
36.75
14.28
Br
CO2Et
CO2Bn
4jd
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

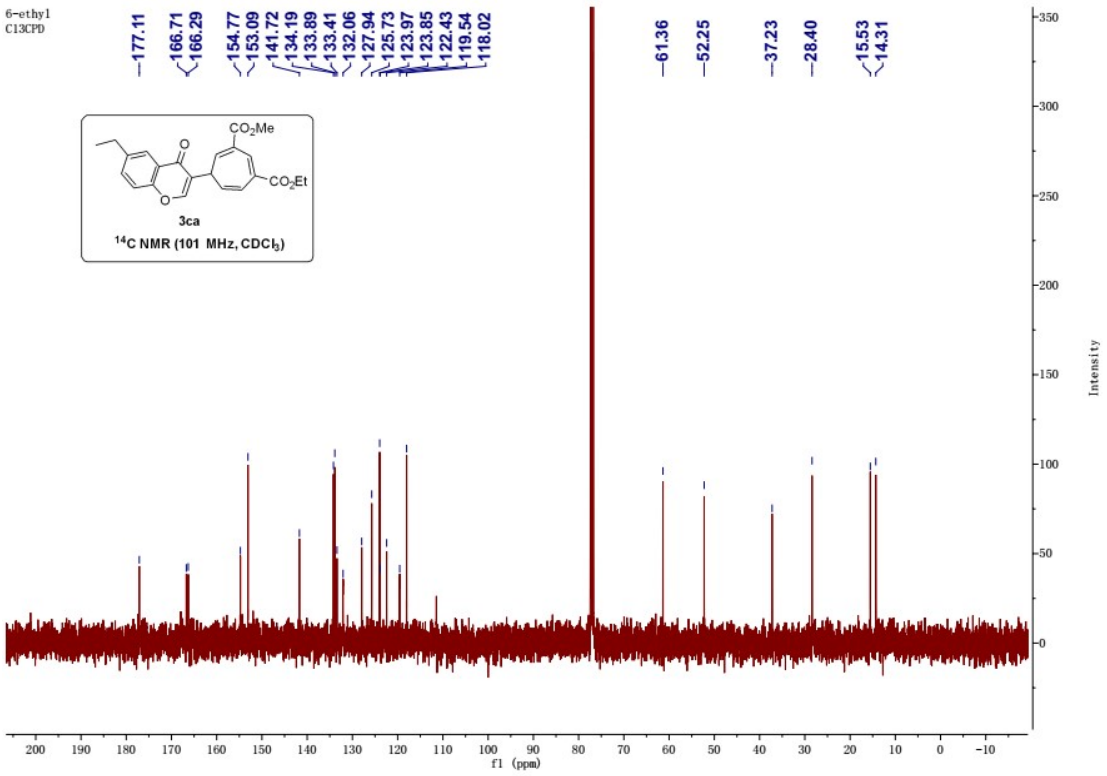

8.18
7.85
7.68
7.66
7.64
7.64
7.45
7.43
7.41
7.39
6.86
6.84
6.59
6.58
5.42
5.41
5.40
5.39
4.31
4.30
4.29
4.28
4.27
3.75
2.75
2.73
2.72
1.35
1.33
1.32
CO2Me
CO2Et
3aa
1H NMR (400 MHz, CDCl3)
2.00
1.00
1.02
2.04
1.02
1.00
1.02
2.05
3.02
1.00
3.02
Intensity
f1 (ppm)

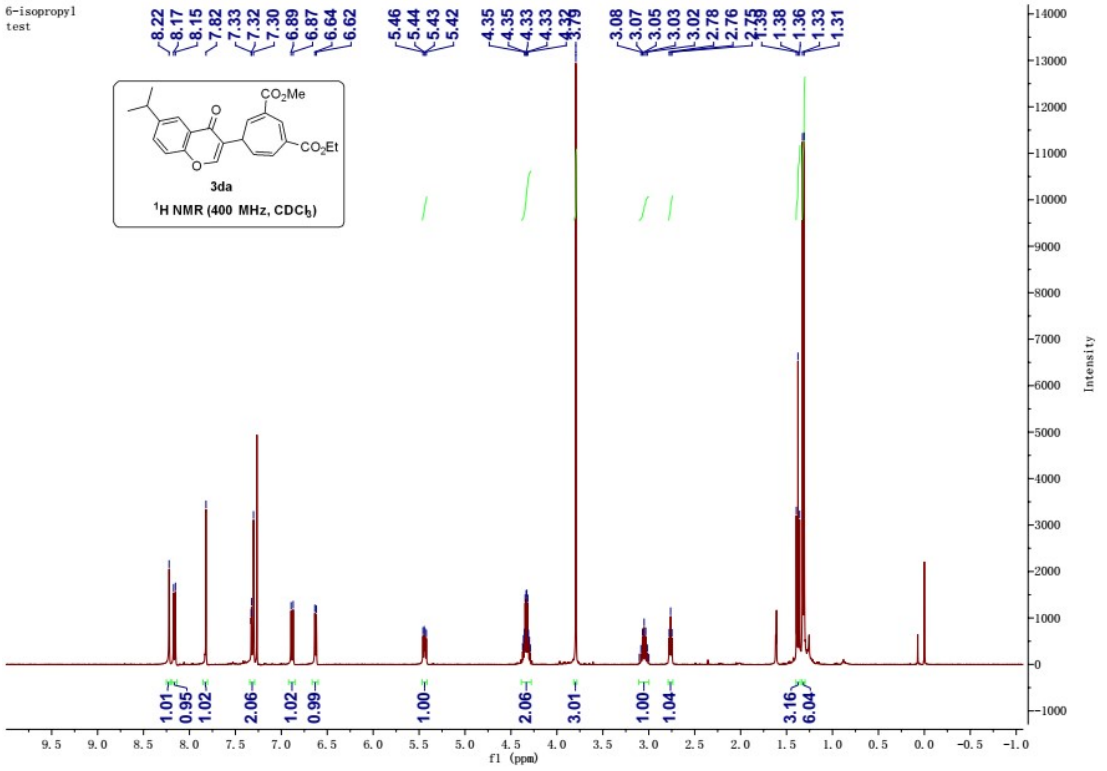

Unsubstituted
C13CPD
176.75
166.46
166.04
156.12
153.06
133.74
133.67
133.20
131.46
127.78
125.71
125.61
125.19
123.86
122.48
119.02
117.99
61.17
52.07
36.92
14.13
CO2Me
CO2Et
3aa
13C NMR (101 MHz, CDCl3)
f1 (ppm)

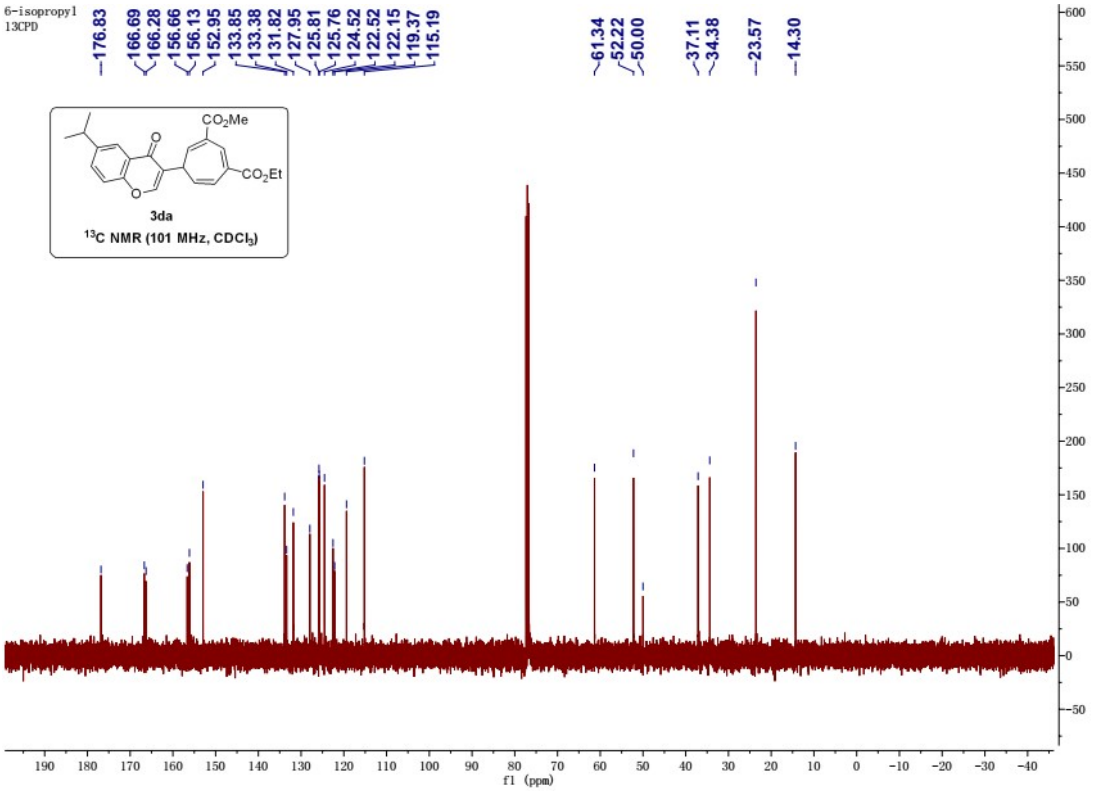

6-Me
test
8.20
8.00
7.82
7.50
7.48
7.36
7.34
6.87
6.85
6.61
6.60
5.44
5.42
5.42
5.40
4.32
4.31
4.30
4.29
3.77
2.75
2.74
2.73
2.45
1.37
1.35
1.34
CO2Me
CO2Et
3ba
1H NMR (400 MHz, CDCl3)
0.96
1.02
1.02
1.06
1.05
1.03
0.98
1.04
2.07
3.03
1.00
3.01
3.04
f1 (ppm)
Intensity

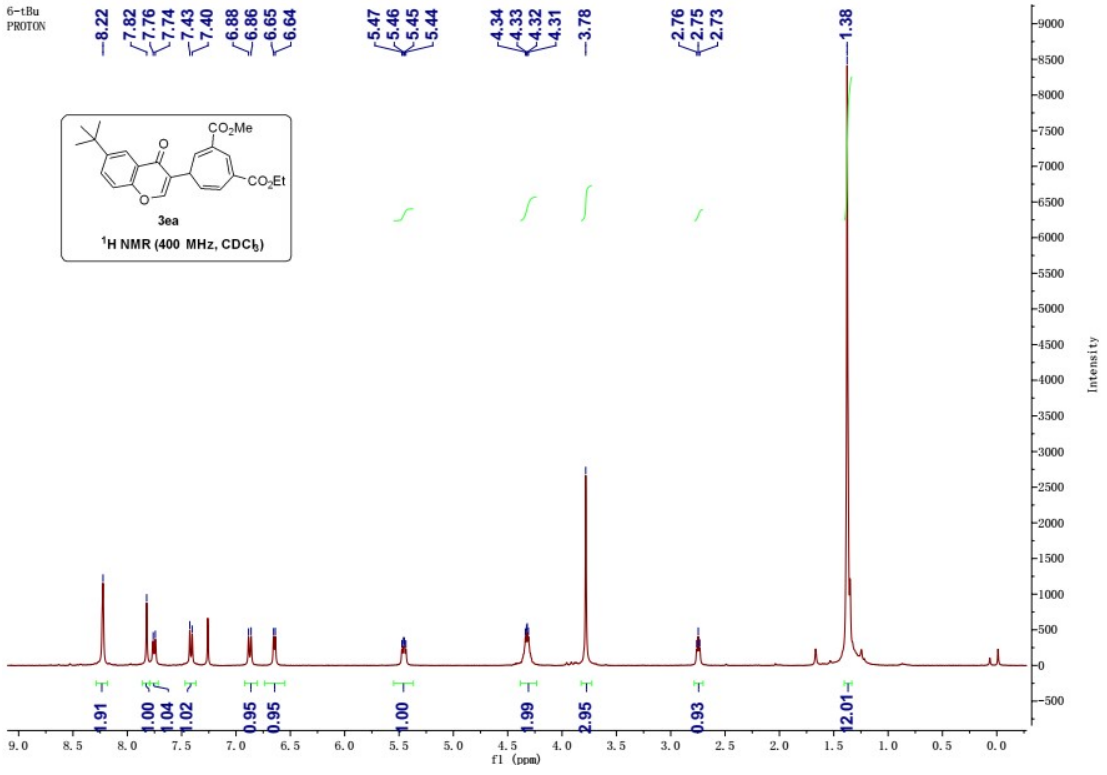

6-Me
test
176.98
166.68
166.26
154.60
153.08
135.36
135.16
133.84
133.37
131.92
127.91
125.73
125.14
123.71
122.43
119.42
117.89
61.34
52.22
37.13
20.97
14.28
CO2Me
CO2Et
3ba
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

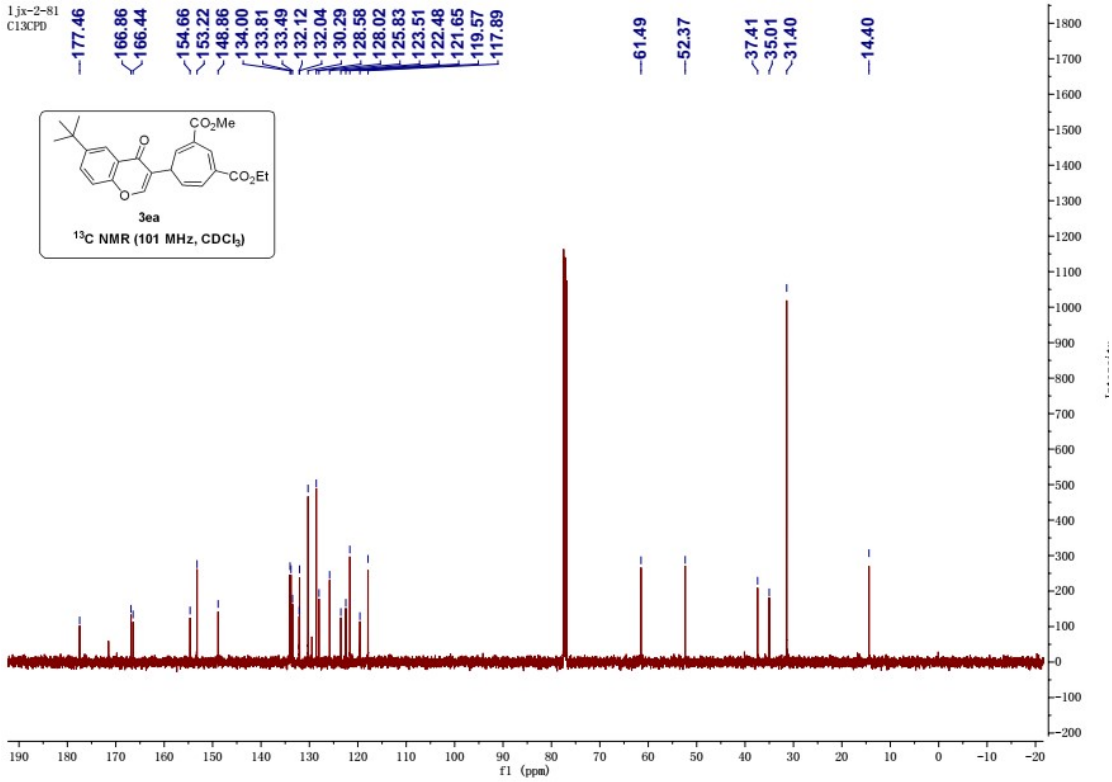

6-ethyl
PROTON
8.22
8.05
7.83
7.54
7.52
7.40
7.38
6.88
6.86
5.46
5.45
5.44
5.42
4.33
4.32
4.32
4.31
3.78
2.79
2.77
2.75
2.74
1.38
1.37
1.35
1.30
1.28
1.26
CO2Me
CO2Et
3ca
1H NMR (400 MHz, CDCl3)
0.92
1.01
0.97
1.09
1.03
0.98
0.91
1.00
2.00
2.98
3.01
3.01
3.17
Intensity
f1 (ppm)

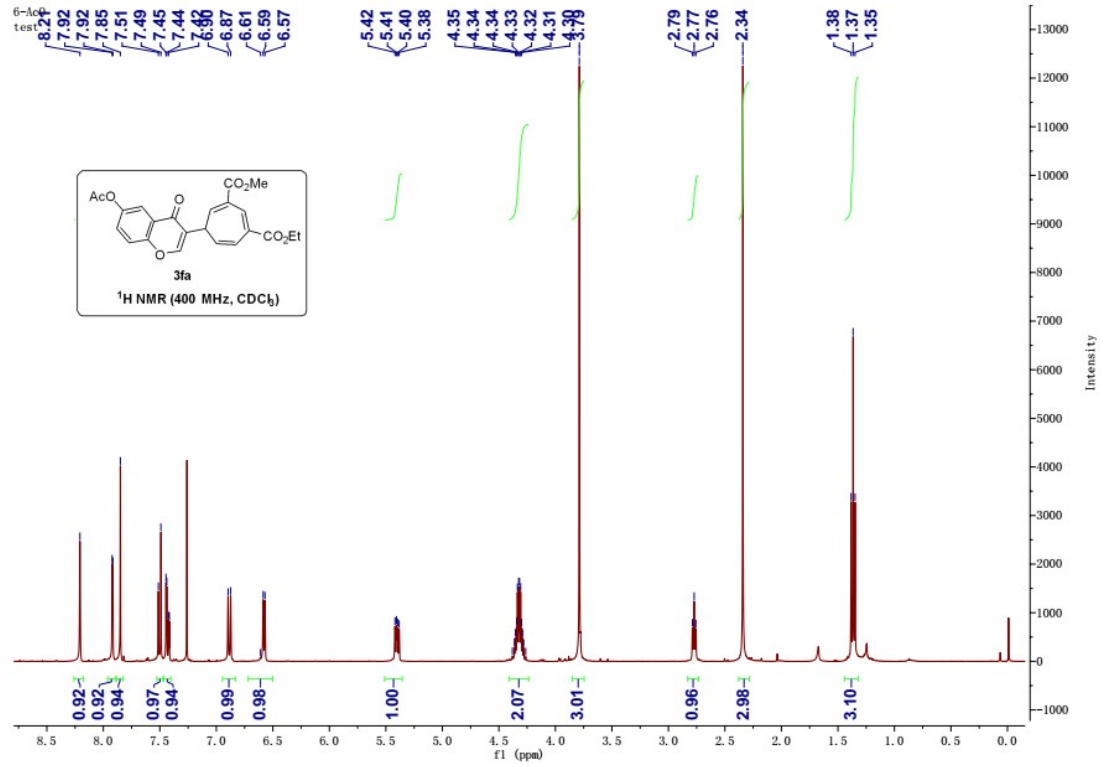

6-ethyl
C13CPD
177.11
166.71
166.29
154.77
153.09
141.72
134.19
133.89
133.41
132.06
127.94
125.73
123.97
123.85
122.43
119.54
118.02
61.36
52.25
37.23
28.40
15.53
14.31
CO2Me
CO2Et
3ca
14C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

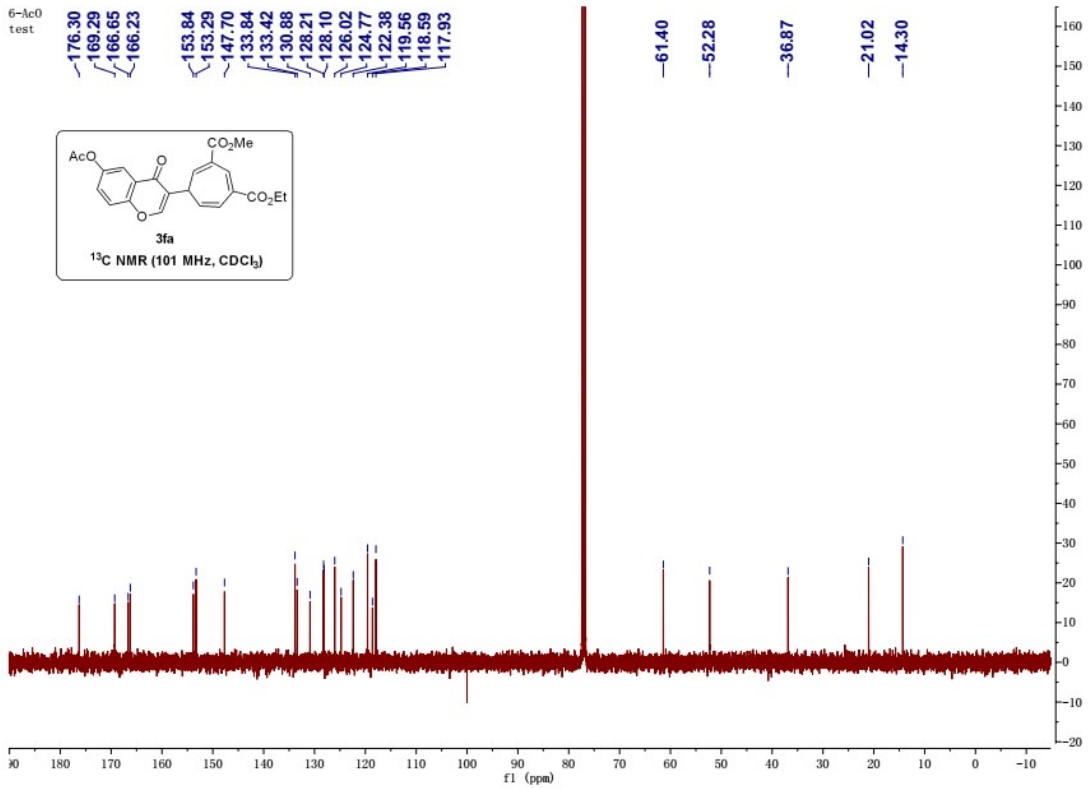

6-isopropyl
test
8.22
8.17
8.15
7.82
7.33
7.32
7.30
6.89
6.87
6.64
6.62
5.46
5.44
5.43
5.42
4.35
4.35
4.33
4.33
3.79
3.08
3.07
3.05
3.03
3.02
2.78
2.76
1.38
1.36
1.33
1.31
CO2Me
CO2Et
3da
1H NMR (400 MHz, CDCl3)
1.01
0.95
1.02
2.06
1.02
0.99
1.00
2.06
3.01
1.00
1.04
3.16
6.04
Intensity
f1 (ppm)

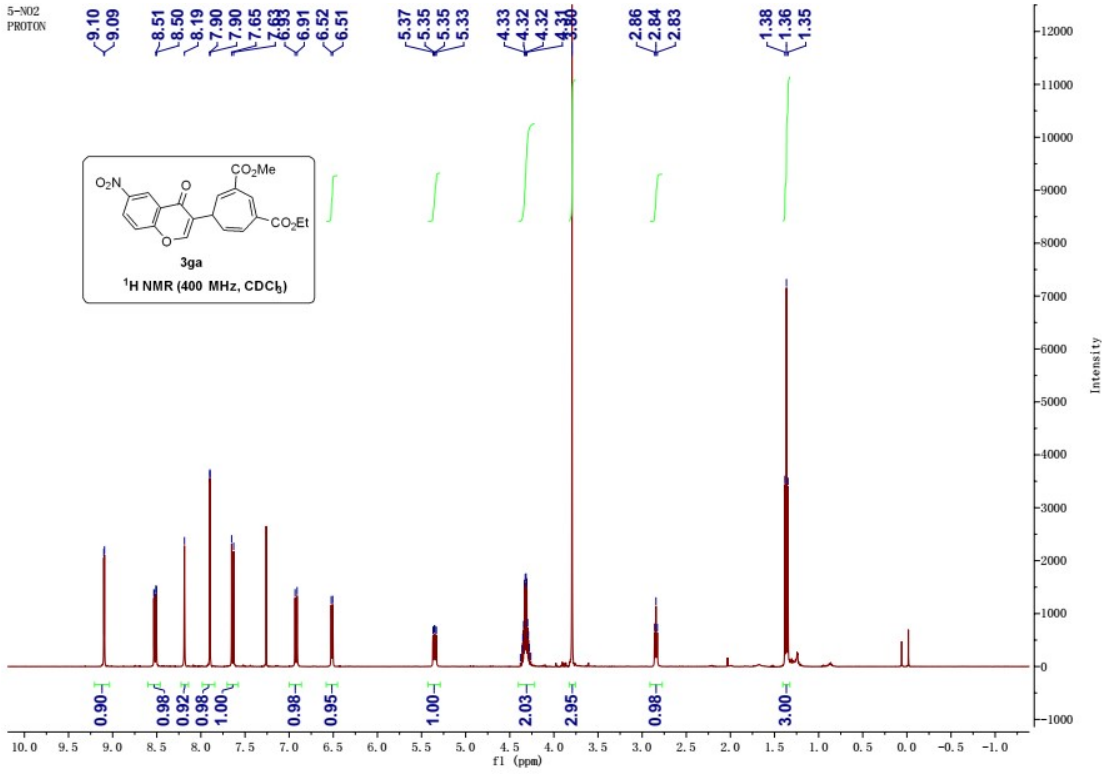

6-isopropyl
13CPD
176.83
166.69
166.28
156.66
156.13
152.95
133.85
133.38
131.82
127.95
125.81
125.76
124.52
122.52
122.15
119.37
115.19
61.34
52.22
50.00
37.11
34.38
23.57
14.30
CO2Me
CO2Et
3da
13C NMR (101 MHz, CDCl3)
f1 (ppm)

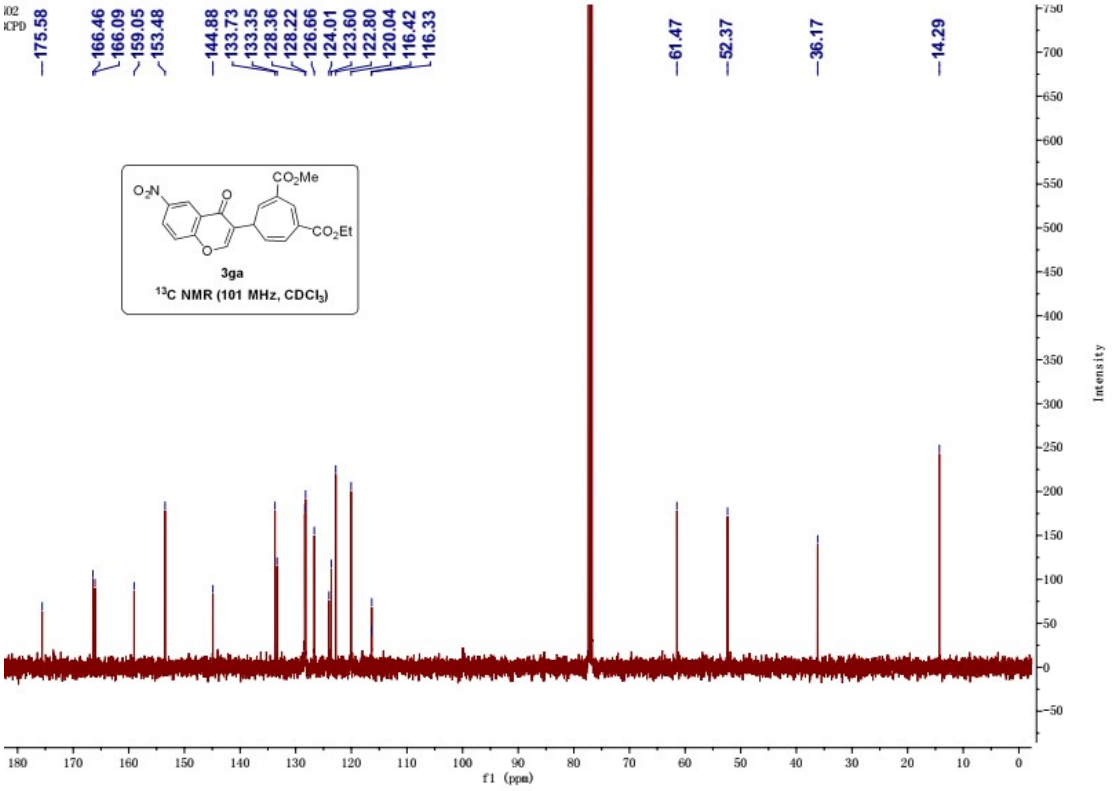

6-tBu
PROTON
8.22
7.82
7.76
7.74
7.43
7.40
6.88
6.86
6.65
6.64
5.47
5.46
5.45
5.44
4.34
4.33
4.32
4.31
3.78
2.76
2.75
2.73
1.38
CO2Me
CO2Et
3ea
1H NMR (400 MHz, CDCl3)
1.91
1.00
1.04
1.02
0.95
0.95
1.00
1.99
2.95
0.93
12.01
f1 (ppm)
Intensity

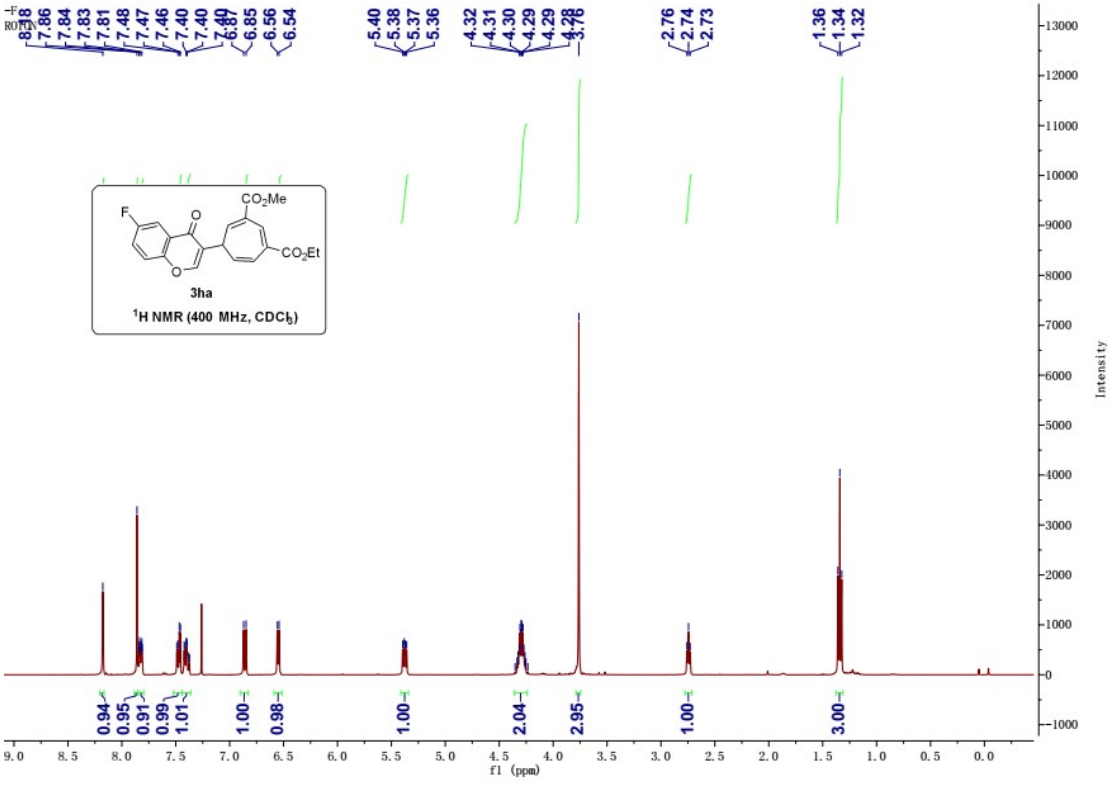

1jx-2-81
C13CPD
177.46
166.86
166.44
154.66
153.22
148.86
134.00
133.81
133.49
132.12
132.04
130.29
128.58
128.02
125.83
123.51
122.48
121.65
119.57
117.89
61.49
52.37
37.41
35.01
31.40
14.40
CO2Me
CO2Et
3ea
13C NMR (101 MHz, CDCl3)
f1 (ppm)

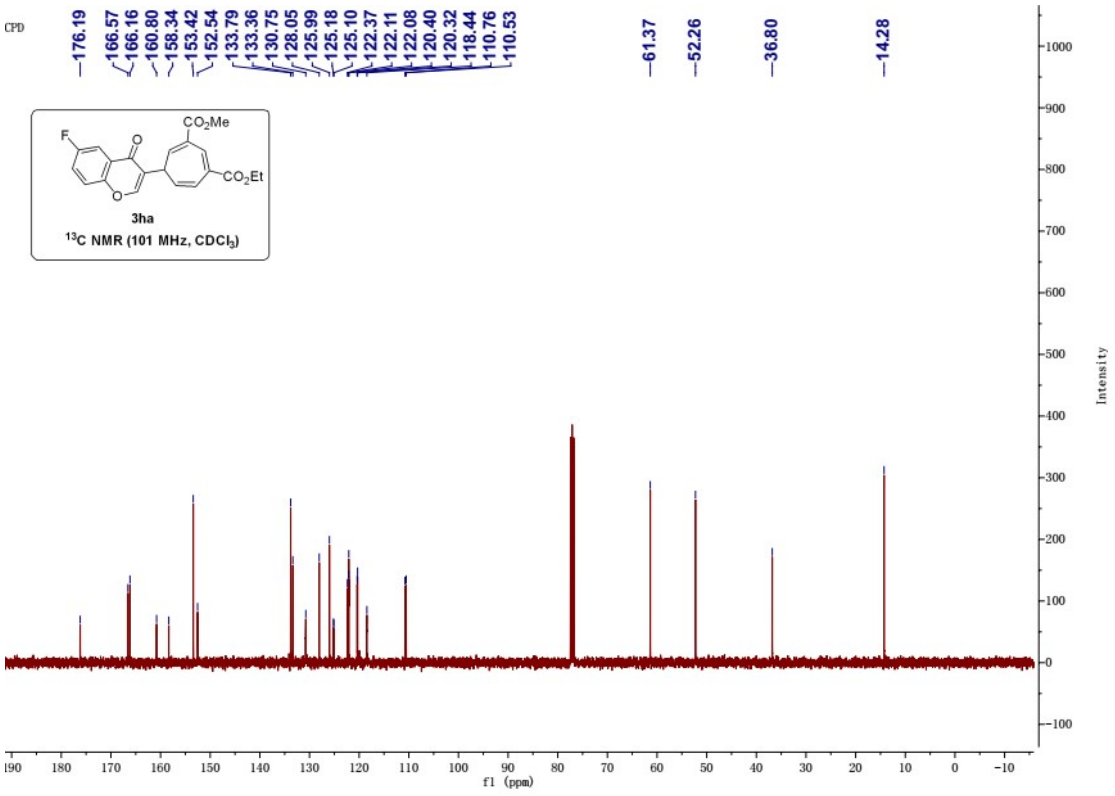

8.21
7.92
7.92
7.85
7.51
7.49
7.45
7.44
6.87
6.61
6.59
6.57
5.42
5.41
5.40
5.38
4.35
4.34
4.34
4.33
4.32
4.31
3.79
2.79
2.77
2.76
2.34
1.38
1.37
1.35
AcO
CO2Me
CO2Et
3fa
1H NMR (400 MHz, CDCl3)
0.92
0.92
0.94
0.97
0.94
0.99
0.98
1.00
2.07
3.01
0.96
2.98
3.10
f1 (ppm)
Intensity

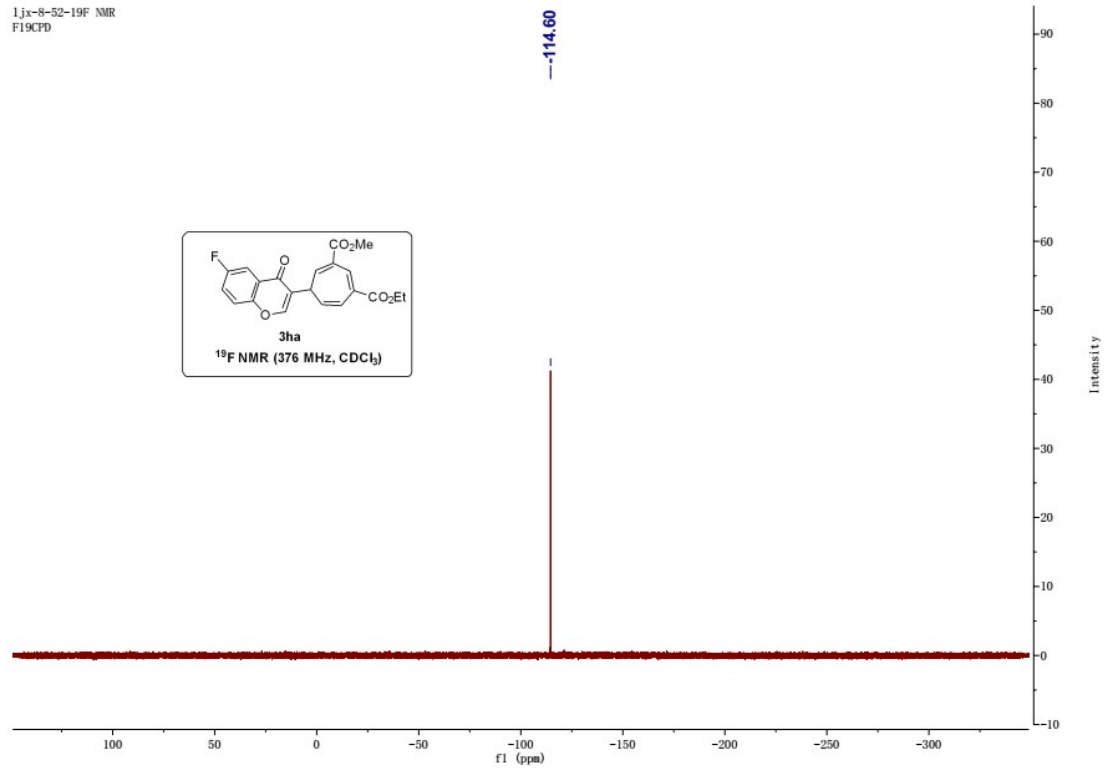

6-Ac0
test
176.30
169.29
166.65
166.23
153.84
153.29
147.70
133.84
133.42
130.88
128.21
128.10
126.02
124.77
122.38
119.56
118.59
117.93
61.40
52.28
36.87
21.02
14.30
AcO
CO2Me
CO2Et
3fa
13C NMR (101 MHz, CDCl3)
f1 (ppm)

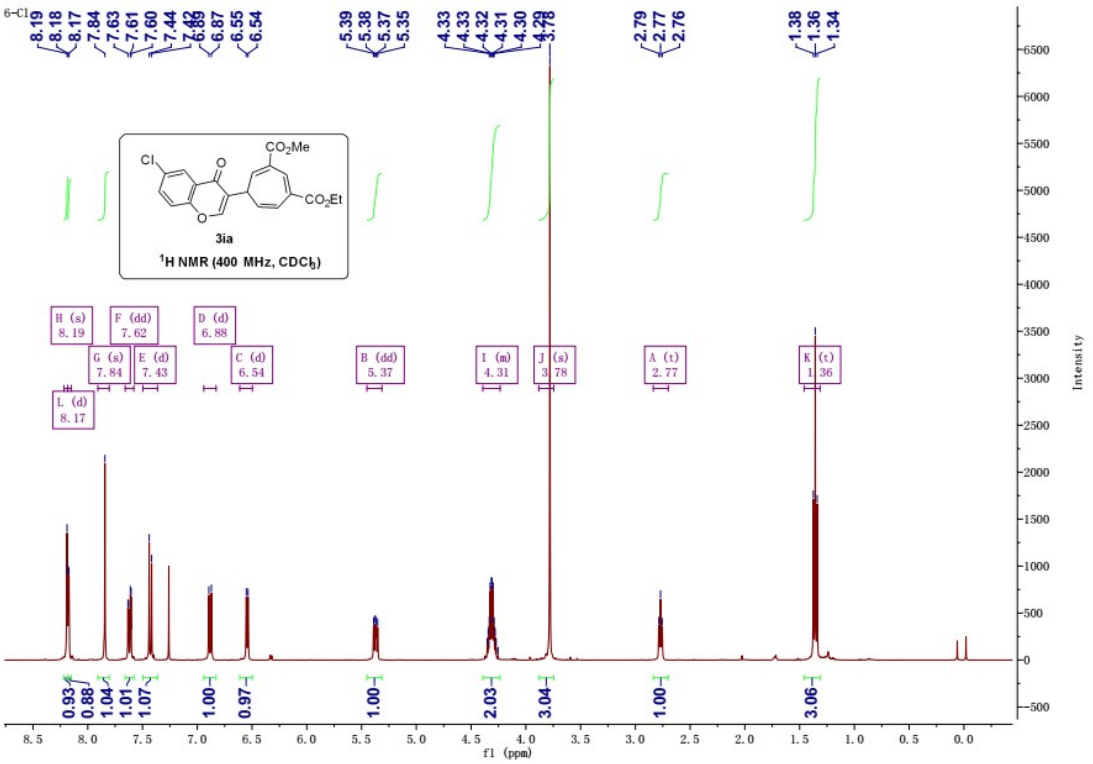

5-N02
PROTON
9.10
9.09
8.51
8.50
8.19
7.90
7.90
7.65
7.63
6.93
6.91
6.52
6.51
5.37
5.35
5.35
5.33
4.33
4.32
4.32
4.31
3.80
2.86
2.84
2.83
1.38
1.36
1.35
O2N
CO2Me
CO2Et
3ga
1H NMR (400 MHz, CDCl3)
0.90
0.98
0.92
0.98
1.00
0.98
0.95
1.00
2.03
2.95
0.98
3.00
f1 (ppm)
Intensity

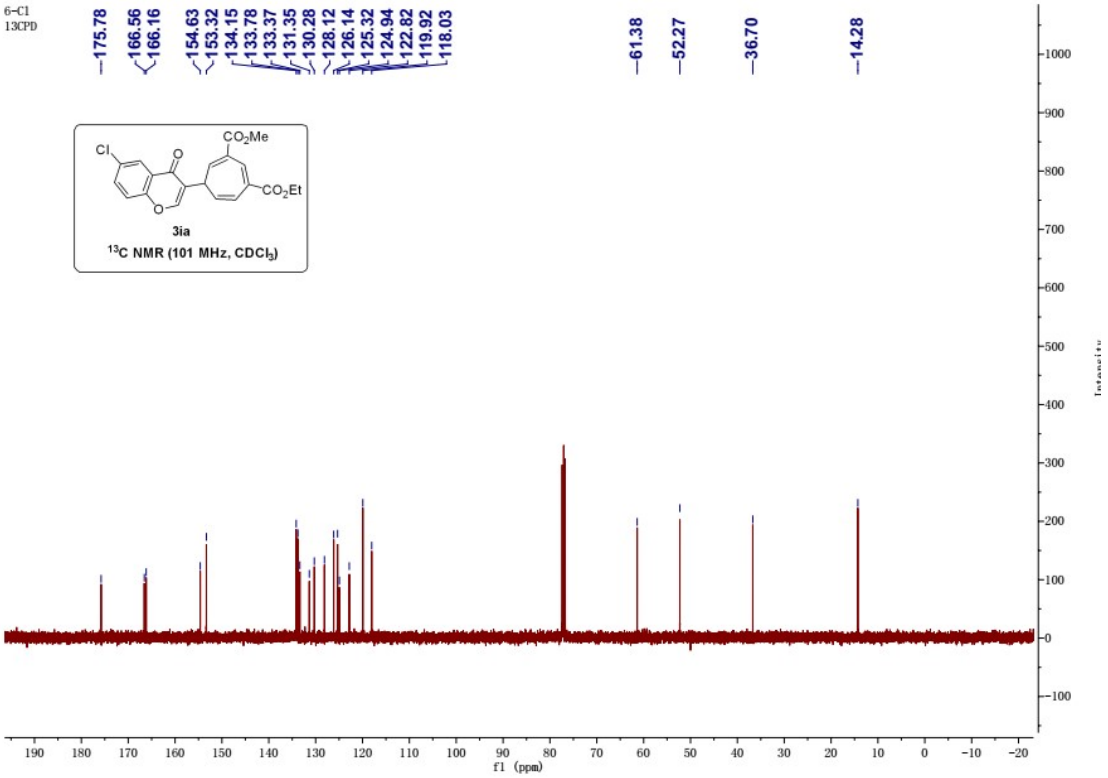

175.58
166.46
166.09
159.05
153.48
144.88
133.73
133.35
128.36
128.22
126.66
124.01
123.60
122.80
120.04
116.42
116.33
61.47
52.37
36.17
14.29
3ga
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

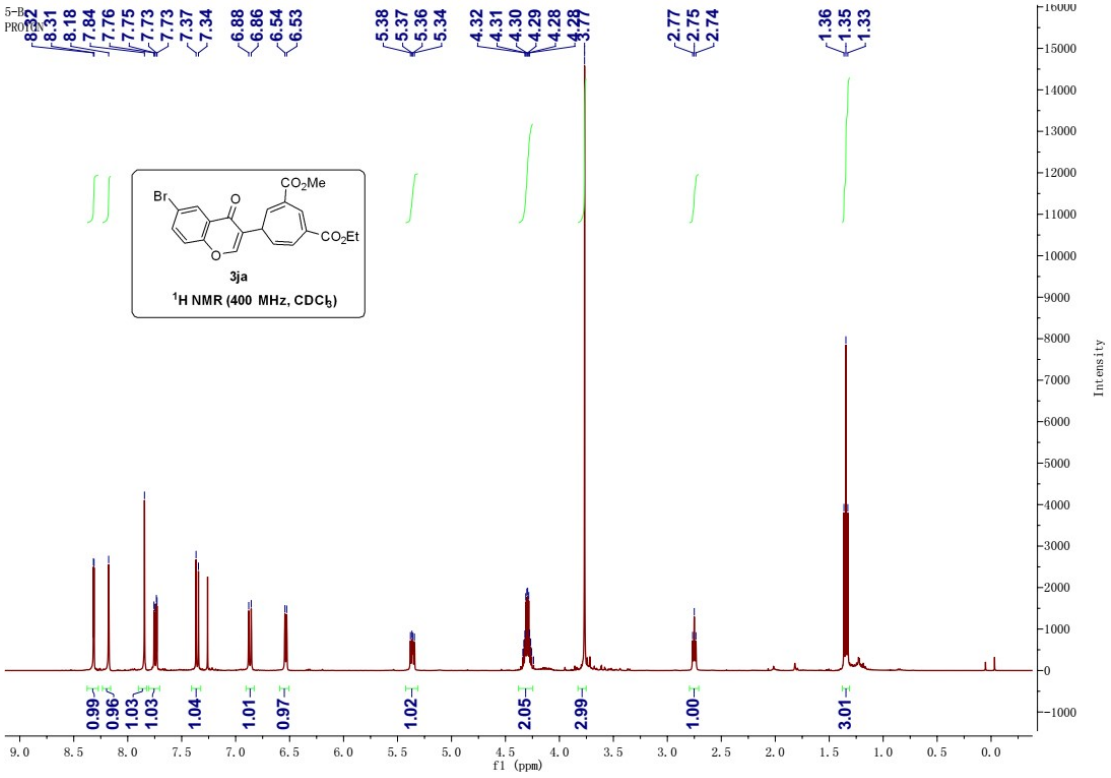

7.86
7.84
7.83
7.81
7.48
7.47
7.46
7.40
6.85
6.56
6.54
5.40
5.38
5.37
5.36
4.32
4.31
4.30
4.29
4.29
2.76
2.74
2.73
1.36
1.34
1.32
3ha
1H NMR (400 MHz, CDCl3)
0.94
0.95
0.91
0.99
1.01
1.00
0.98
1.00
2.04
2.95
1.00
3.00
f1 (ppm)
Intensity

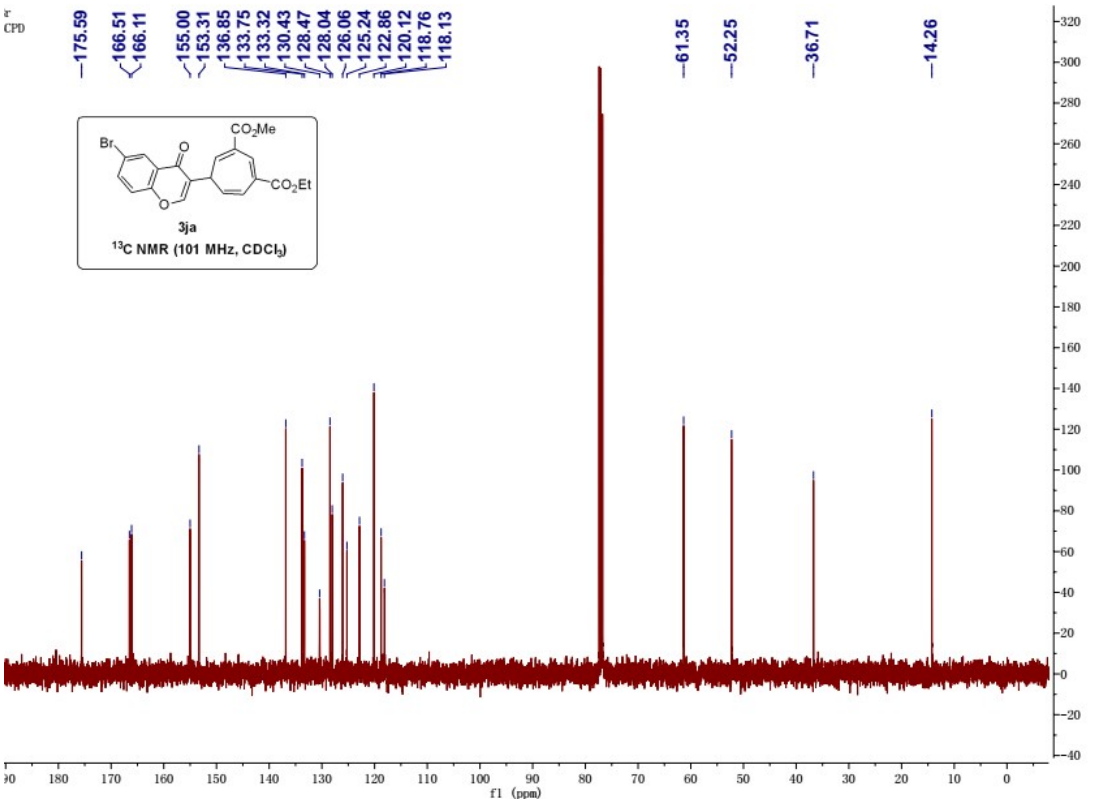

CPD
176.19
166.57
166.16
160.80
158.34
153.42
152.54
133.79
133.36
130.75
128.05
125.99
125.18
125.10
122.37
122.11
122.08
120.40
120.32
118.44
110.76
110.53
61.37
52.26
36.80
14.28
CO2Me
CO2Et
F
O
3ha
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

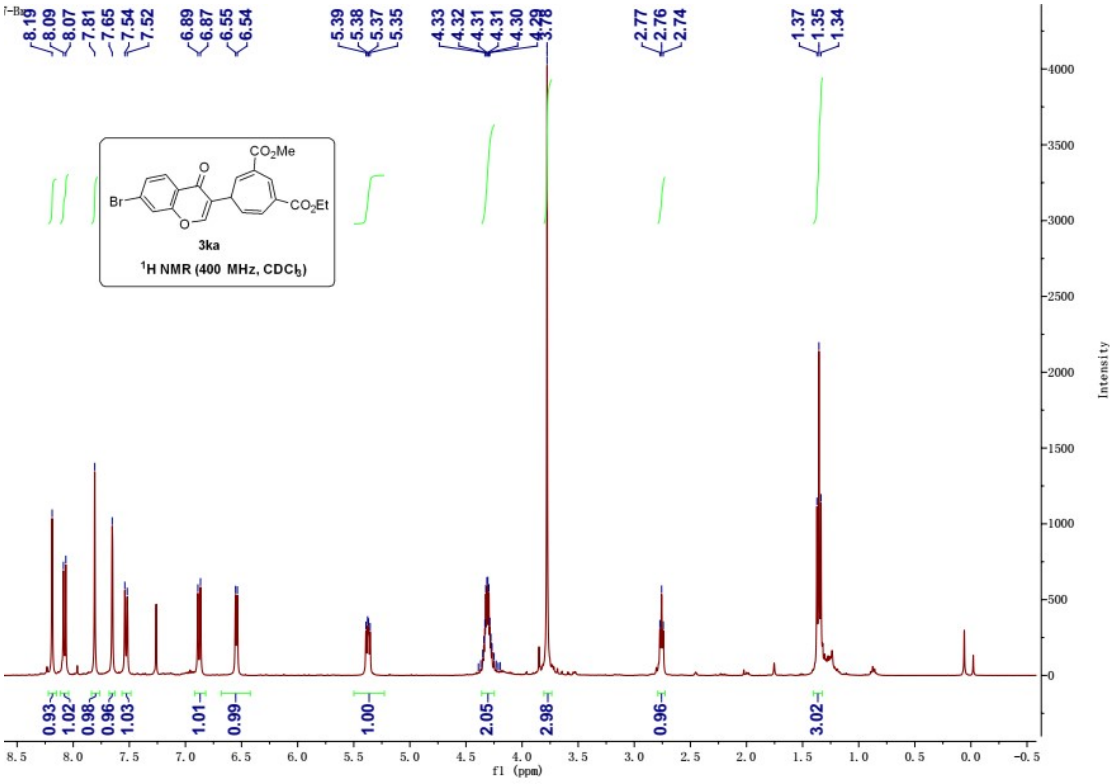

ljx-8-52-19F NMR
F19CPD
114.60
CO2Me
CO2Et
F
O
3ha
19F NMR (376 MHz, CDCl3)
Intensity
f1 (ppm)

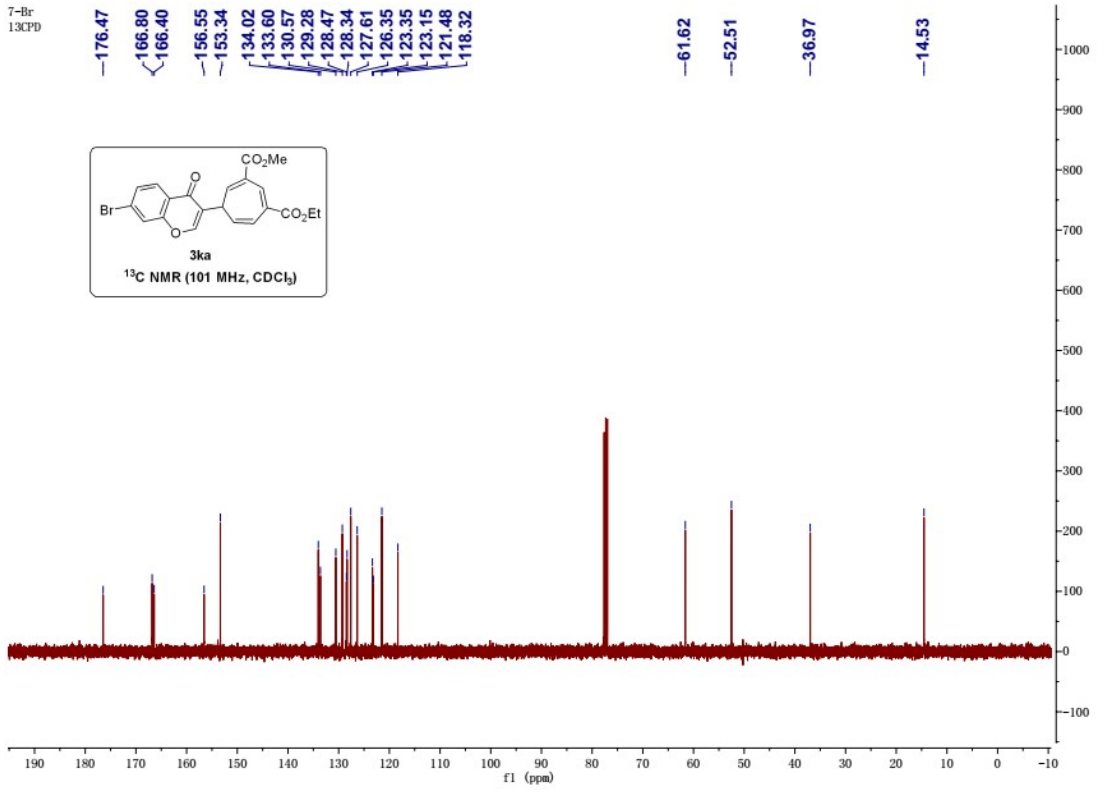

6-Cl
3ia
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity

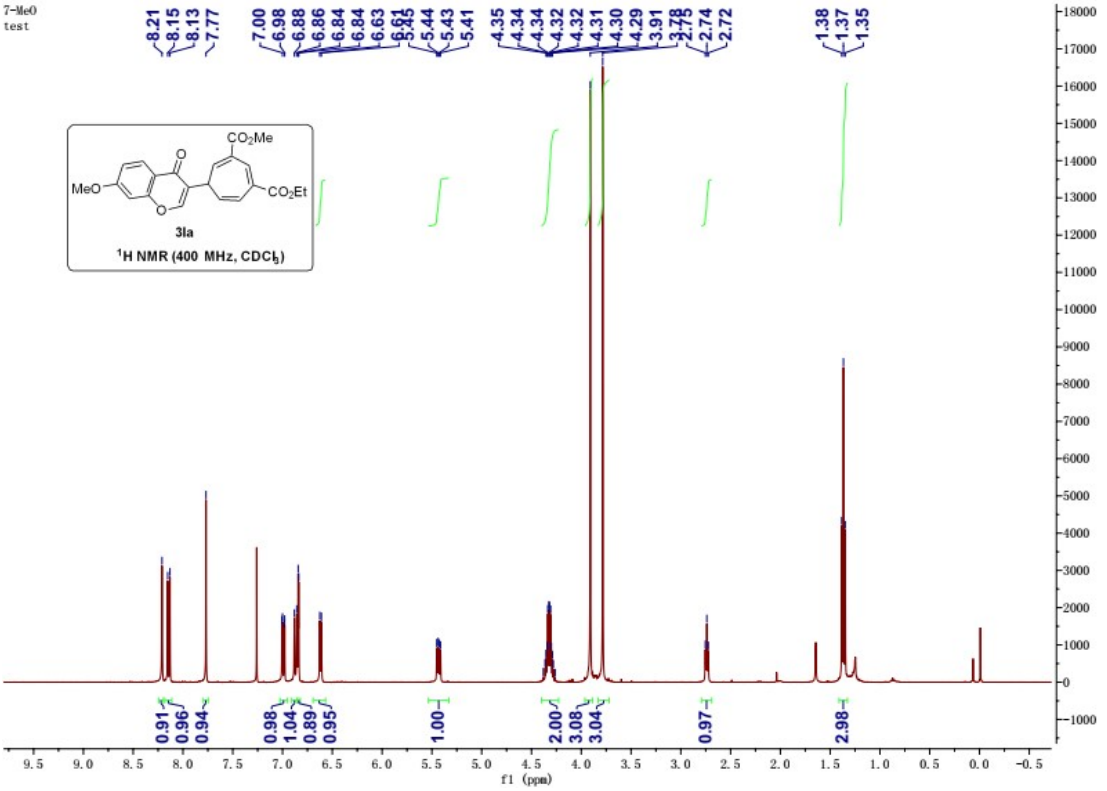

6-Cl
13CPD
3ia
13C NMR (101 MHz, CDCl3)
f1 (ppm)

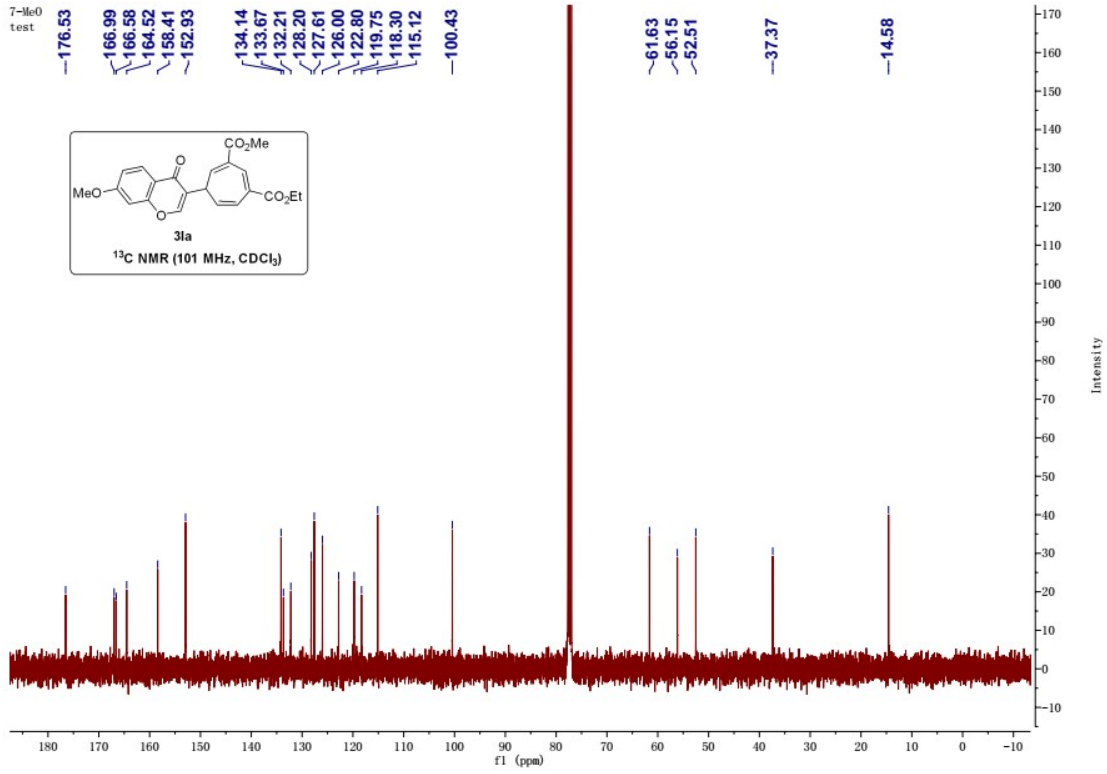

8.32
8.31
8.18
7.84
7.76
7.75
7.73
7.73
7.37
7.34
6.88
6.86
6.54
6.53
5.38
5.37
5.36
5.34
4.32
4.31
4.30
4.29
4.28
4.27
2.77
2.75
2.74
1.36
1.35
1.33
Br
O
CO2Me
CO2Et
3ja
1H NMR (400 MHz, CDCl3)
0.99
0.96
1.03
1.03
1.04
1.01
0.97
1.02
2.05
2.99
1.00
3.01
f1 (ppm)
Intensity

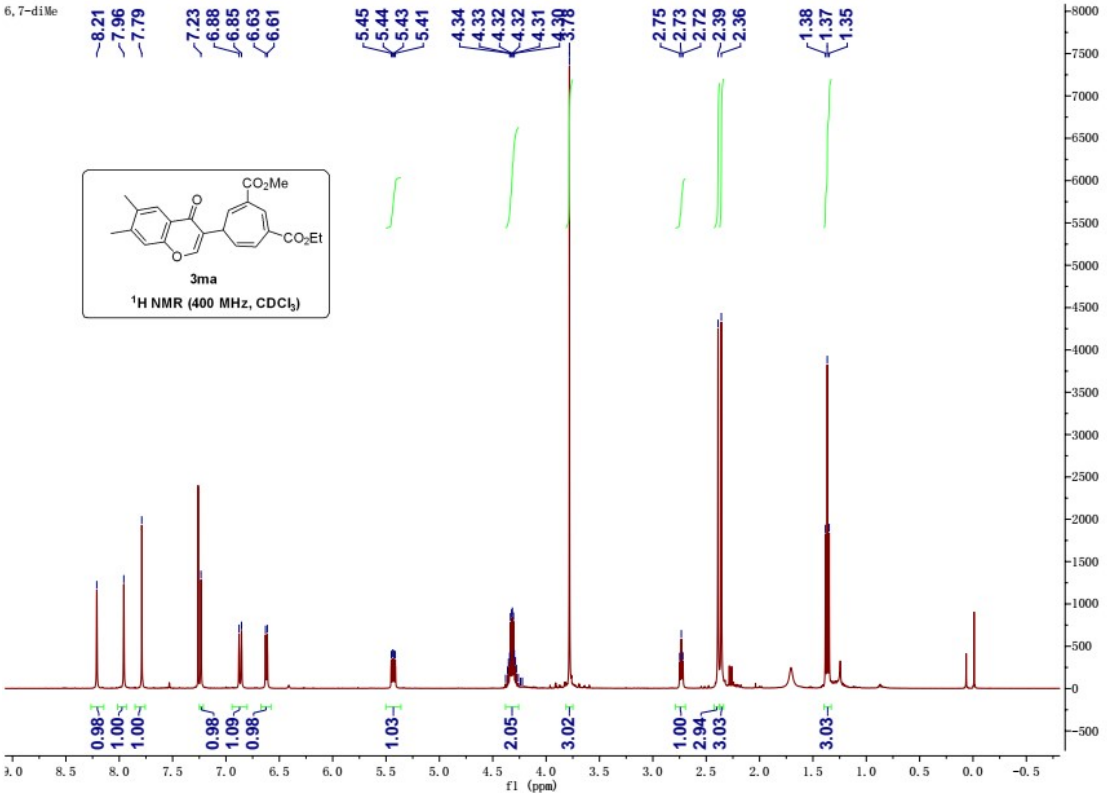

CPD
175.59
166.51
166.11
155.00
153.31
136.85
133.75
133.32
130.43
128.47
128.04
126.06
125.24
122.86
120.12
118.76
118.13
61.35
52.25
36.71
14.26
Br
O
CO2Me
CO2Et
3ja
13C NMR (101 MHz, CDCl3)
f1 (ppm)

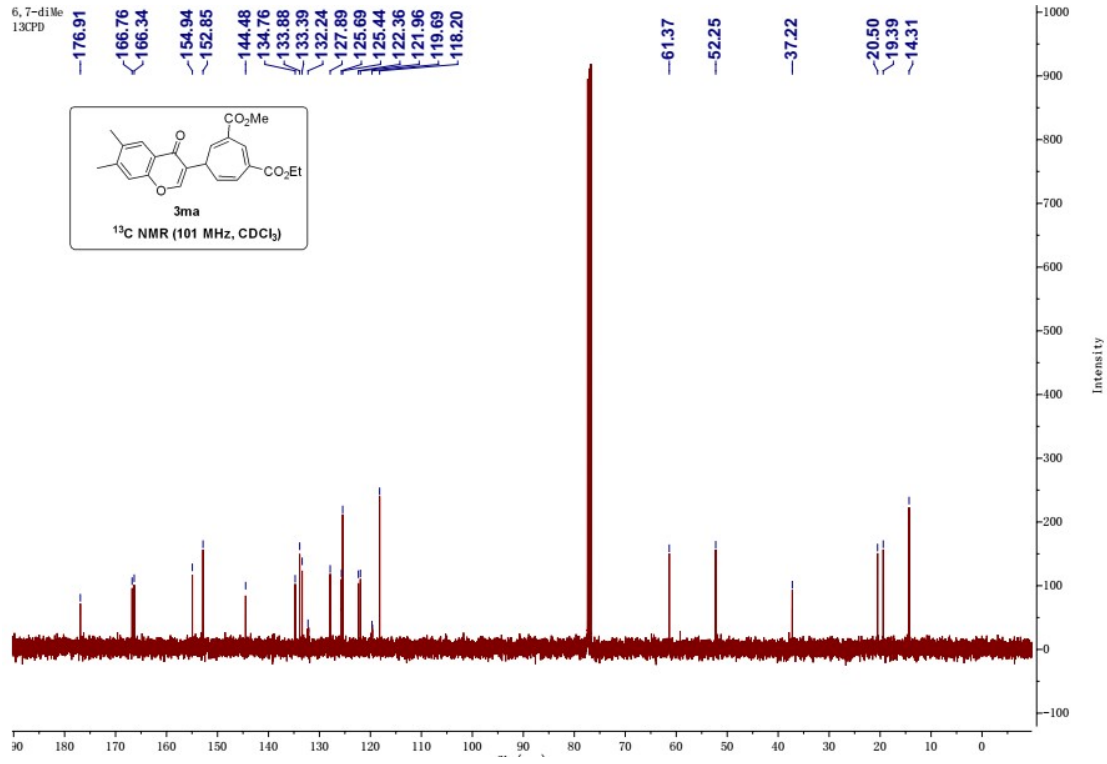

8.19
8.09
8.07
7.81
7.65
7.54
7.52
6.89
6.87
6.55
6.54
5.39
5.38
5.37
5.35
4.33
4.32
4.31
4.31
4.30
3.78
2.77
2.76
2.74
1.37
1.35
1.34
CO2Me
Br
CO2Et
3ka
1H NMR (400 MHz, CDCl3)
0.93
1.02
0.98
0.96
1.03
1.01
0.99
1.00
2.05
2.98
0.96
3.02
f1 (ppm)
Intensity

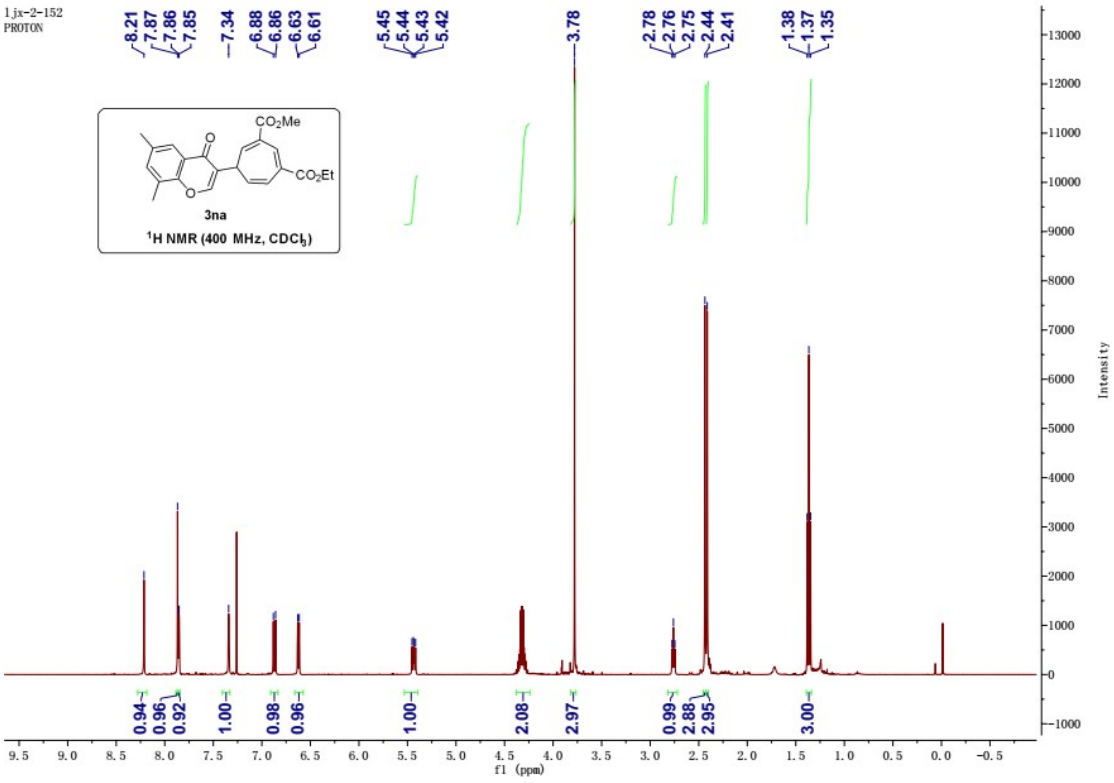

7-Br
13CPD
176.47
166.80
166.40
156.55
153.34
134.02
133.60
130.57
129.28
128.47
128.34
127.61
126.35
123.35
123.15
121.48
118.32
61.62
52.51
36.97
14.53
CO2Me
Br
CO2Et
3ka
13C NMR (101 MHz, CDCl3)
f1 (ppm)

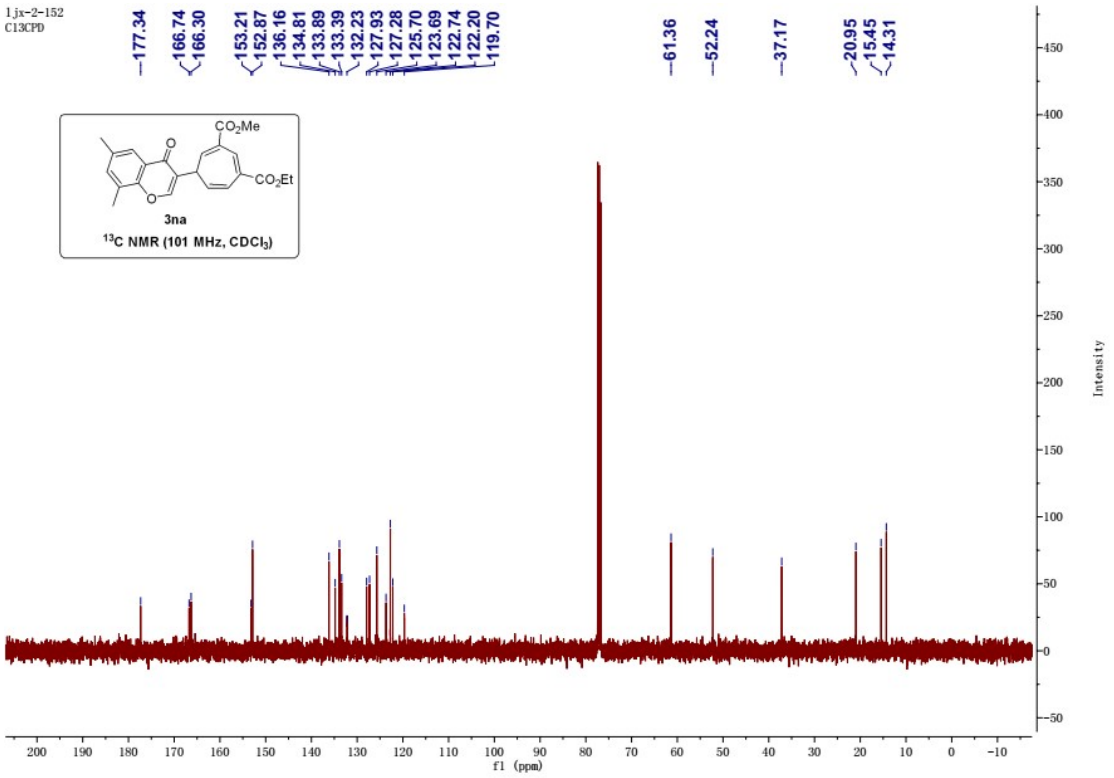

7-MeO
test
8.21
8.15
8.13
7.77
7.00
6.98
6.88
6.86
6.84
6.84
6.63
6.61
5.45
5.44
5.43
5.41
4.35
4.34
4.34
4.32
4.32
4.31
4.30
4.29
3.91
3.78
2.75
2.74
2.72
1.38
1.37
1.35
CO2Me
MeO
CO2Et
3la
1H NMR (400 MHz, CDCl3)
0.91
0.96
0.94
0.98
1.04
0.89
0.95
1.00
2.00
3.08
3.04
0.97
2.98
f1 (ppm)

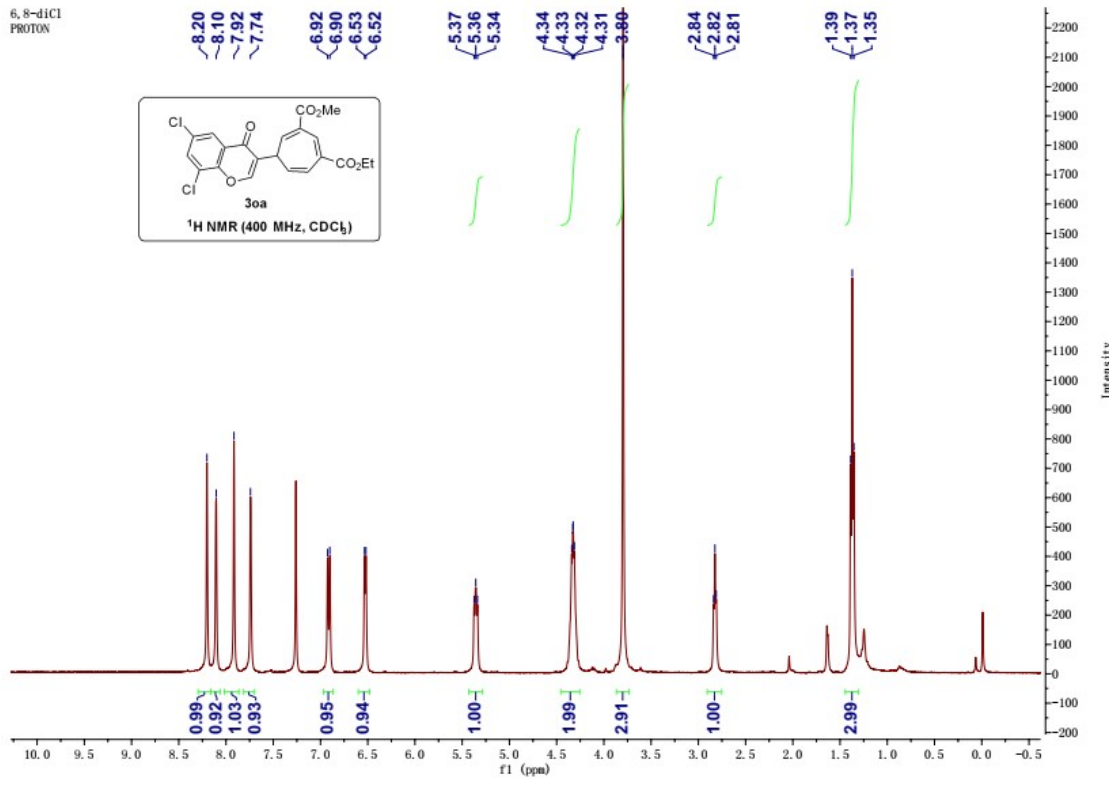

7-MeO
test
176.53
166.99
166.58
164.52
158.41
152.93
134.14
133.67
132.21
128.20
127.61
126.00
122.80
119.75
118.30
115.12
100.43
61.63
56.15
52.51
37.37
14.58
CO2Me
MeO
CO2Et
3la
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

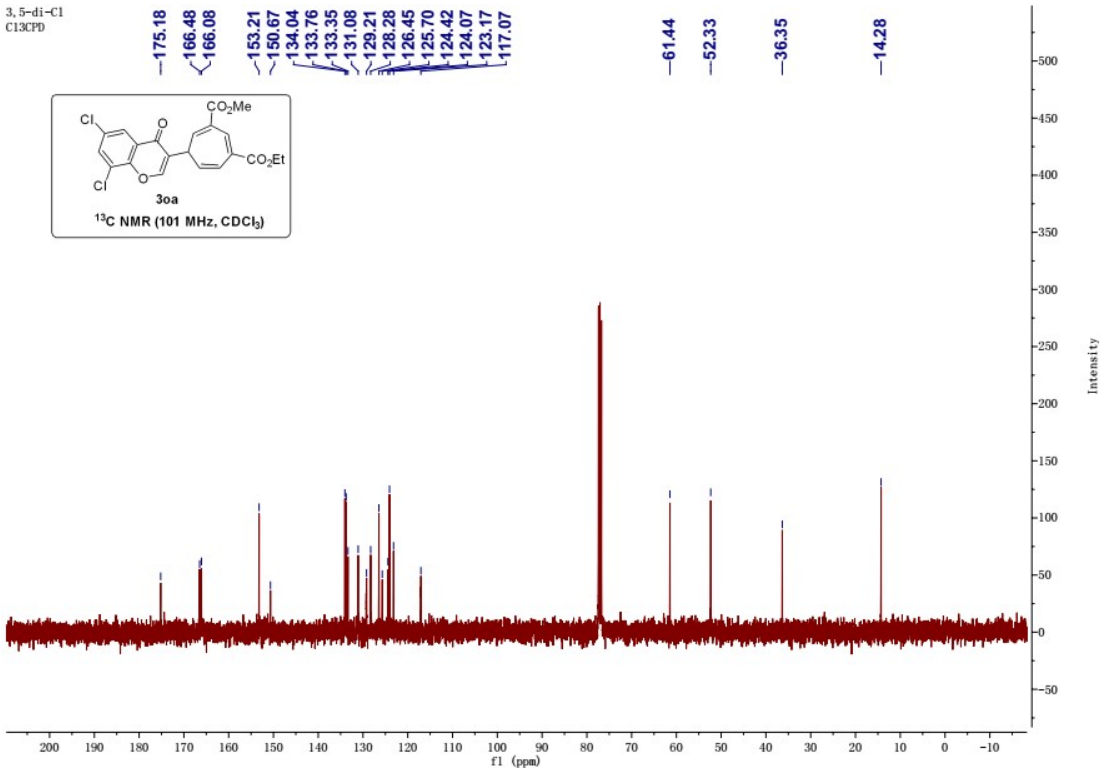

6,7-diMe
8.21
7.96
7.79
7.23
6.88
6.85
6.63
6.61
5.45
5.44
5.43
5.41
4.34
4.33
4.32
4.32
4.31
4.30
4.18
2.75
2.73
2.72
2.39
2.36
1.38
1.37
1.35
CO2Me
CO2Et
3ma
1H NMR (400 MHz, CDCl3)
0.98
1.00
1.00
0.98
1.09
0.98
1.03
2.05
3.02
1.00
2.94
3.03
3.03
f1 (ppm)

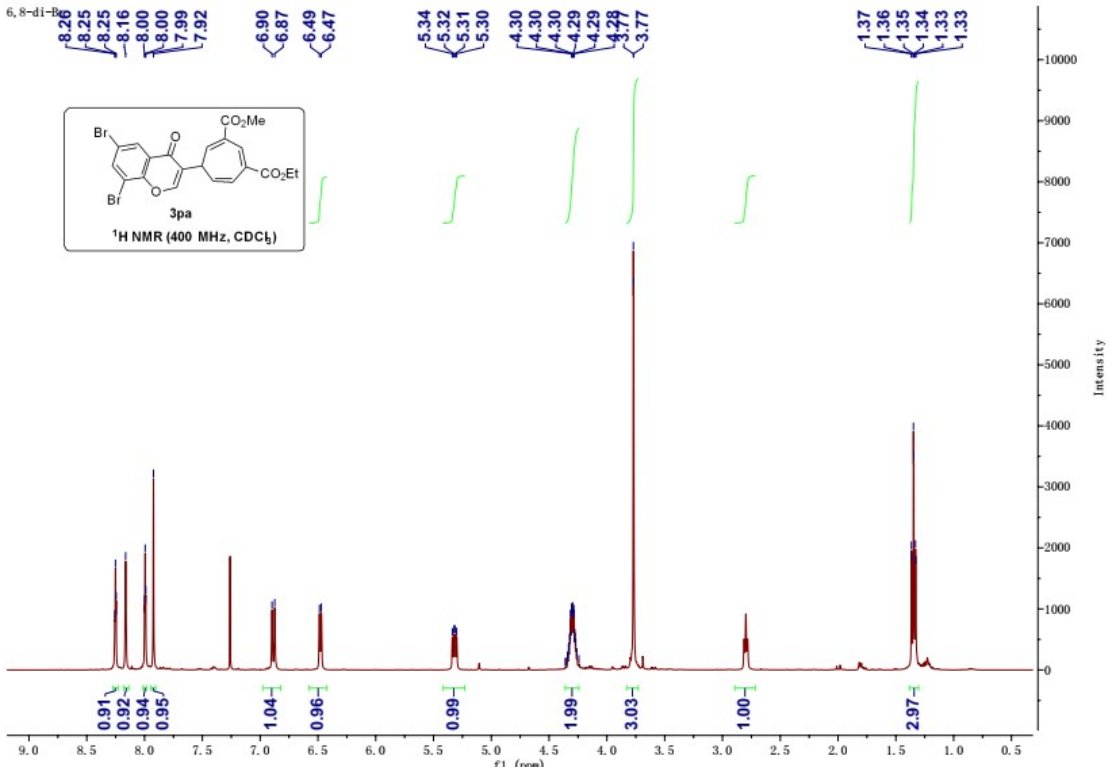

6,7-diMe
13CPD
176.91
166.76
166.34
154.94
152.85
144.48
134.76
133.88
133.39
132.24
127.89
125.69
125.44
122.36
121.96
119.69
118.20
61.37
52.25
37.22
20.50
19.39
14.31
CO2Me
CO2Et
3ma
13C NMR (101 MHz, CDCl3)
Intensity

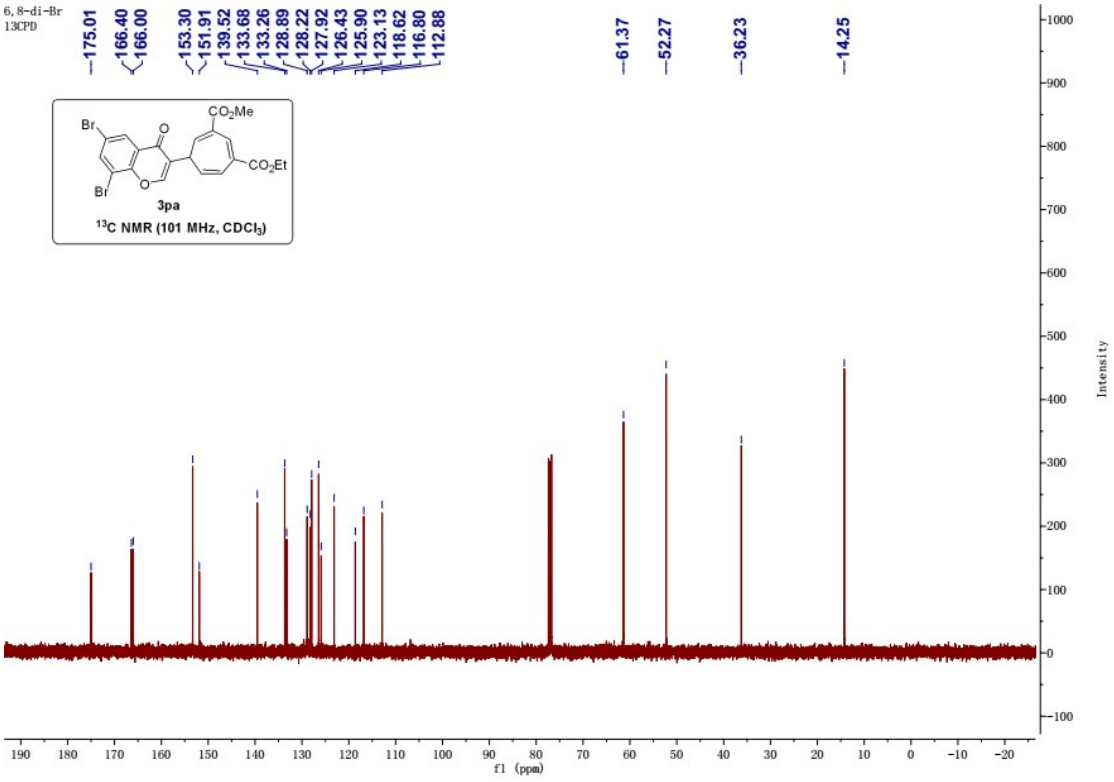

1jx-2-152
PROTON
8.21
7.87
7.86
7.85
7.34
6.88
6.86
6.63
6.61
5.45
5.44
5.43
5.42
3.78
2.78
2.76
2.75
2.44
2.41
1.38
1.37
1.35
CO2Me
CO2Et
3na
1H NMR (400 MHz, CDCl3)
0.94
0.96
0.92
1.00
0.98
0.96
1.00
2.08
2.97
0.99
2.88
2.95
3.00
f1 (ppm)
Intensity

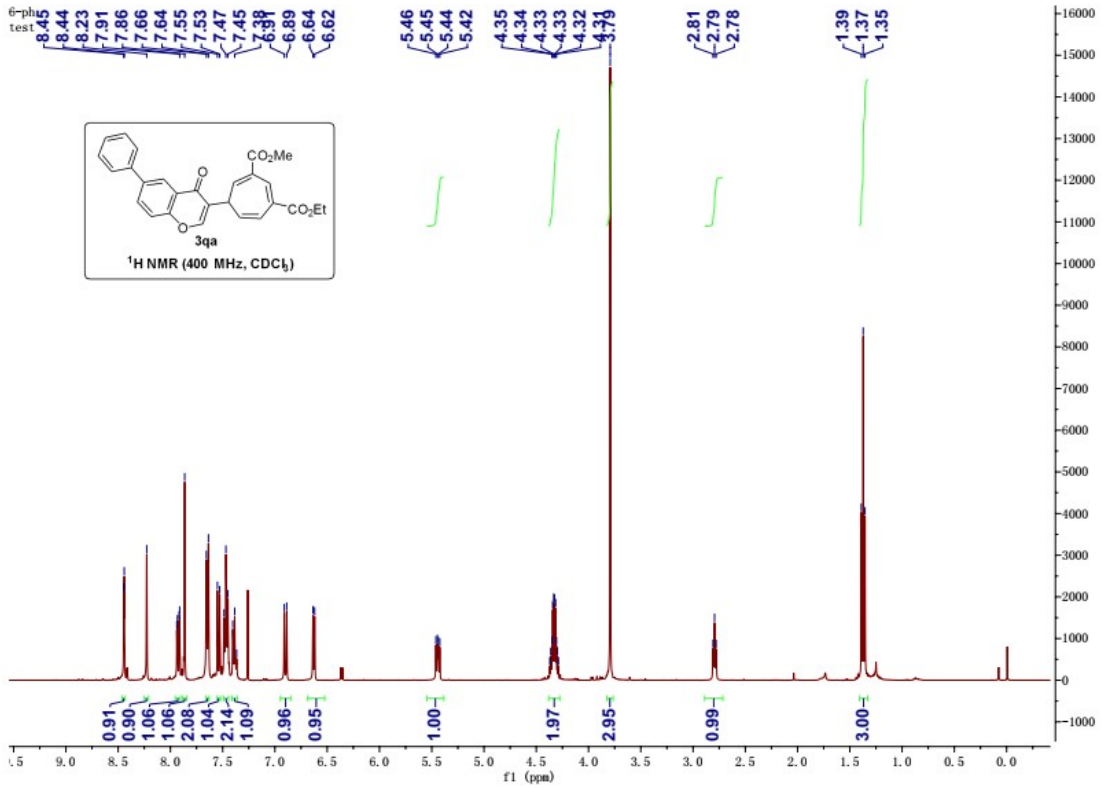

1jx-2-152
C13CPD
177.34
166.74
166.30
153.21
152.87
136.16
134.81
133.89
133.39
132.23
127.93
127.28
125.70
123.69
122.74
122.20
119.70
61.36
52.24
37.17
20.95
15.45
14.31
CO2Me
CO2Et
3na
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

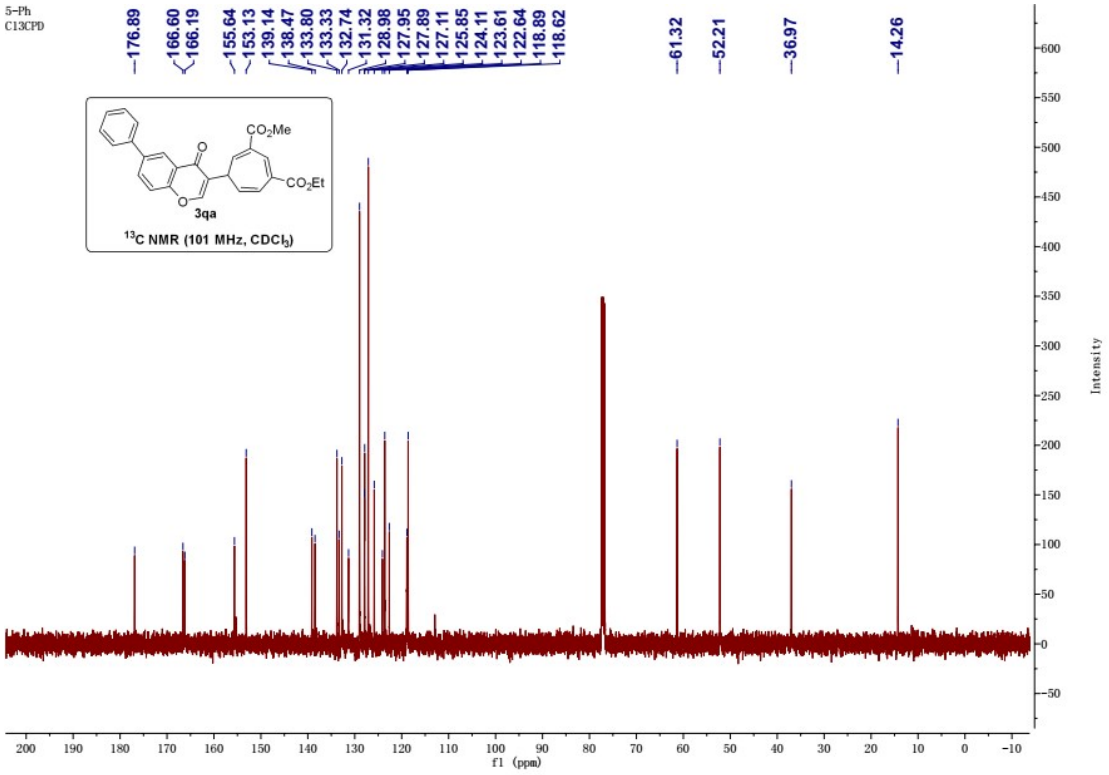

6,8-diCl
PROTON
8.20
8.10
7.92
7.74
6.92
6.90
6.53
6.52
5.37
5.36
5.34
4.34
4.33
4.32
4.31
3.80
2.84
2.82
2.81
1.39
1.37
1.35
Cl
O
CO2Me
CO2Et
Cl
O
3oa
1H NMR (400 MHz, CDCl3)
0.99
0.92
1.03
0.93
0.95
0.94
1.00
1.99
2.91
1.00
2.99
f1 (ppm)
Intensity

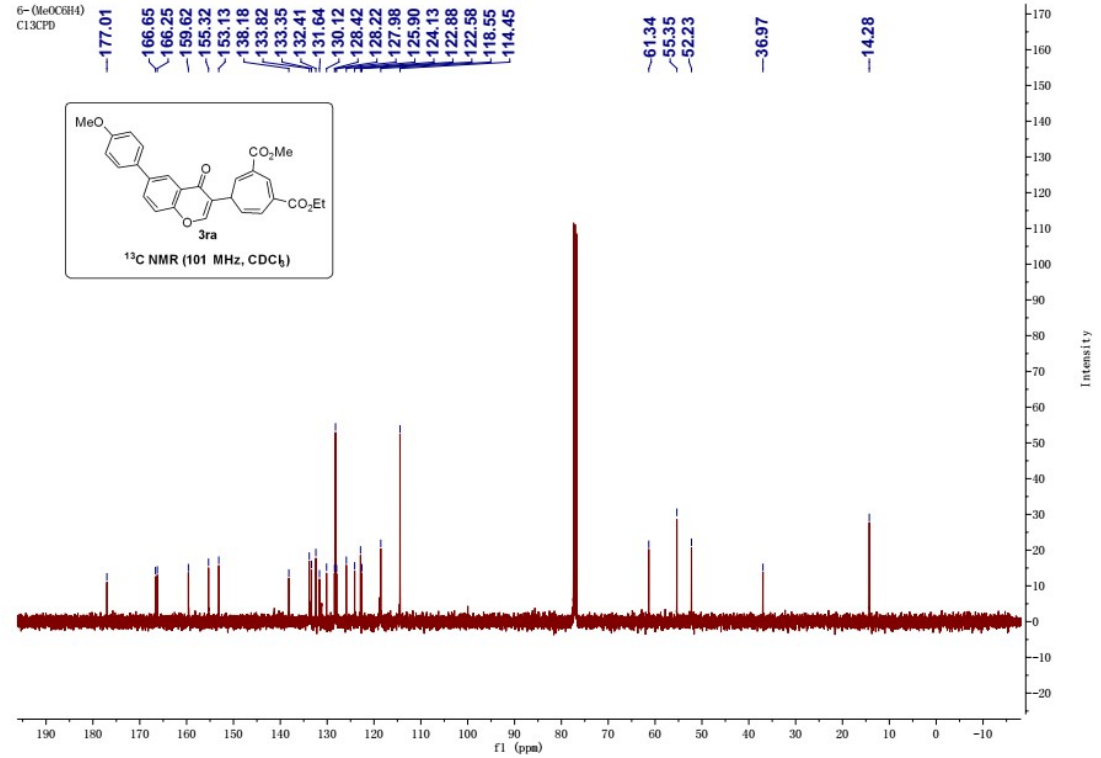

3,5-di-Cl
C13CPD
175.18
166.48
166.08
153.21
150.67
134.04
133.76
133.35
131.08
129.21
128.28
126.45
125.70
124.42
124.07
123.17
117.07
61.44
52.33
36.35
14.28
Cl
O
CO2Me
CO2Et
Cl
O
3oa
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

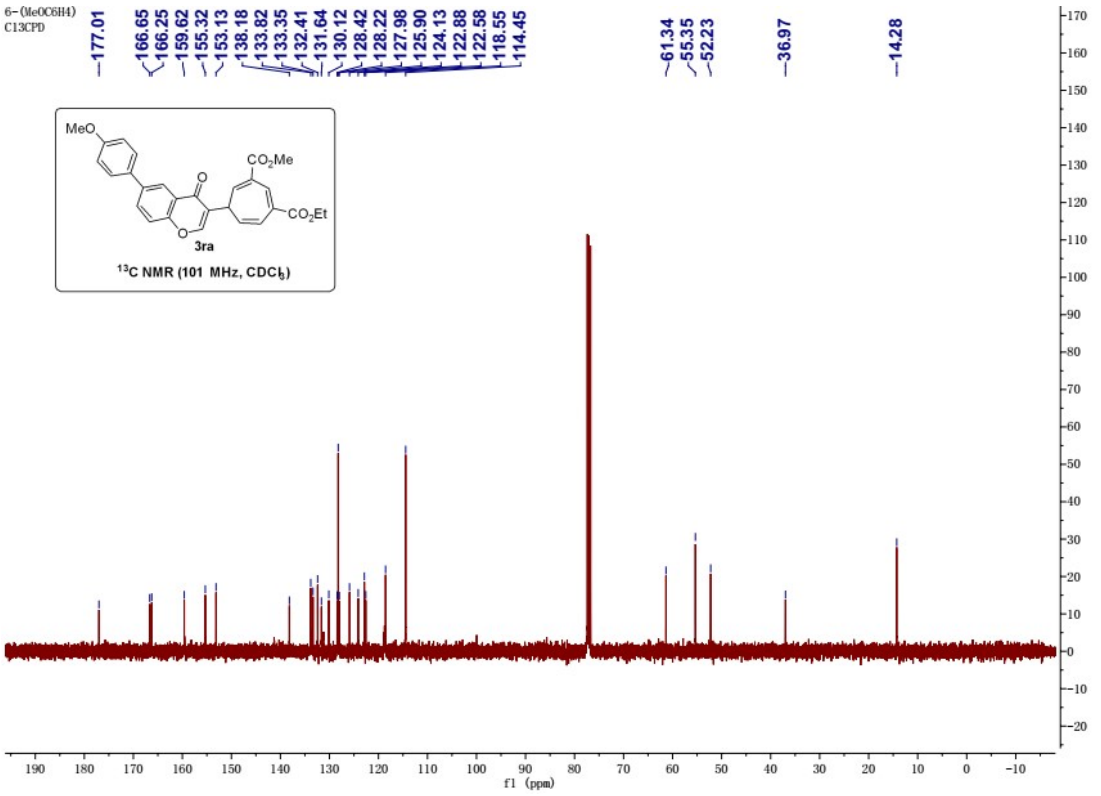

6,8-di-Br
8.26
8.25
8.25
8.16
8.00
8.00
7.99
7.92
6.90
6.87
6.49
6.47
5.34
5.32
5.31
5.30
4.30
4.30
4.30
4.29
4.29
4.28
3.77
3.77
1.37
1.36
1.35
1.34
1.33
1.33
Br
O
CO2Me
CO2Et
Br
3pa
1H NMR (400 MHz, CDCl3)
0.91
0.92
0.94
0.95
1.04
0.96
0.99
1.99
3.03
1.00
2.97
Intensity
f1 (ppm)

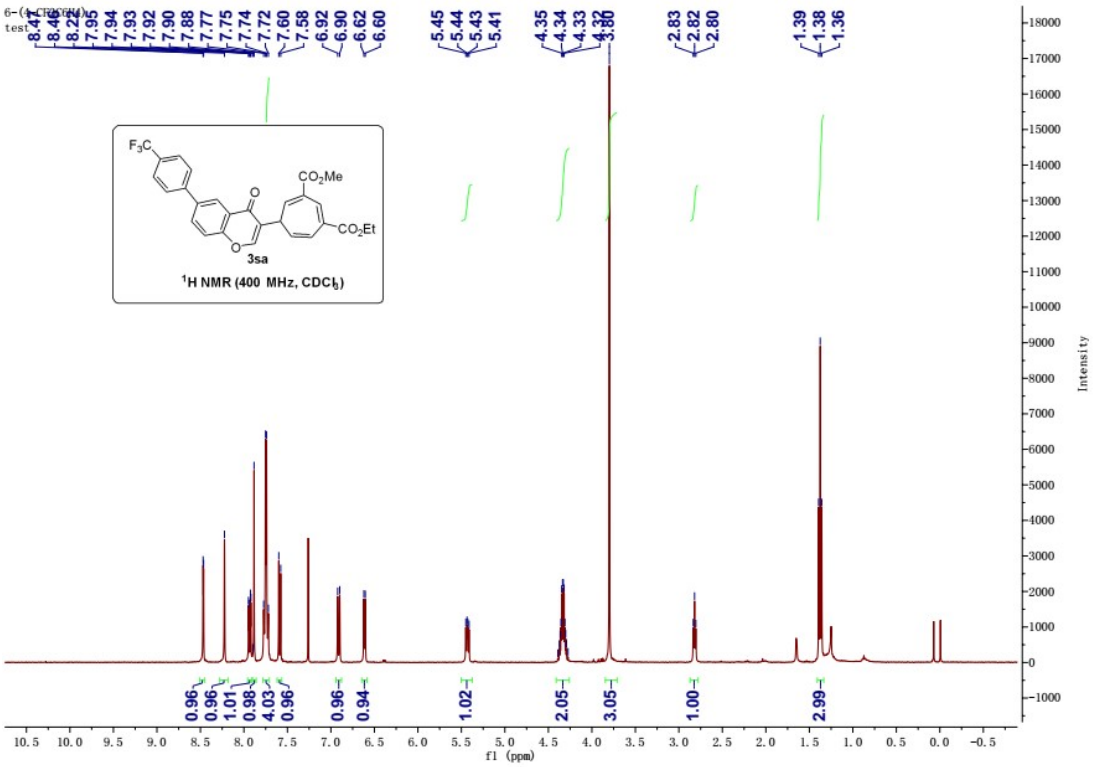

6,8-di-Br
13CPD
175.01
166.40
166.00
153.30
151.91
139.52
133.68
133.26
128.89
128.22
127.92
126.43
125.90
123.13
118.62
116.80
112.88
61.37
52.27
36.23
14.25
Br
O
CO2Me
CO2Et
Br
3pa
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

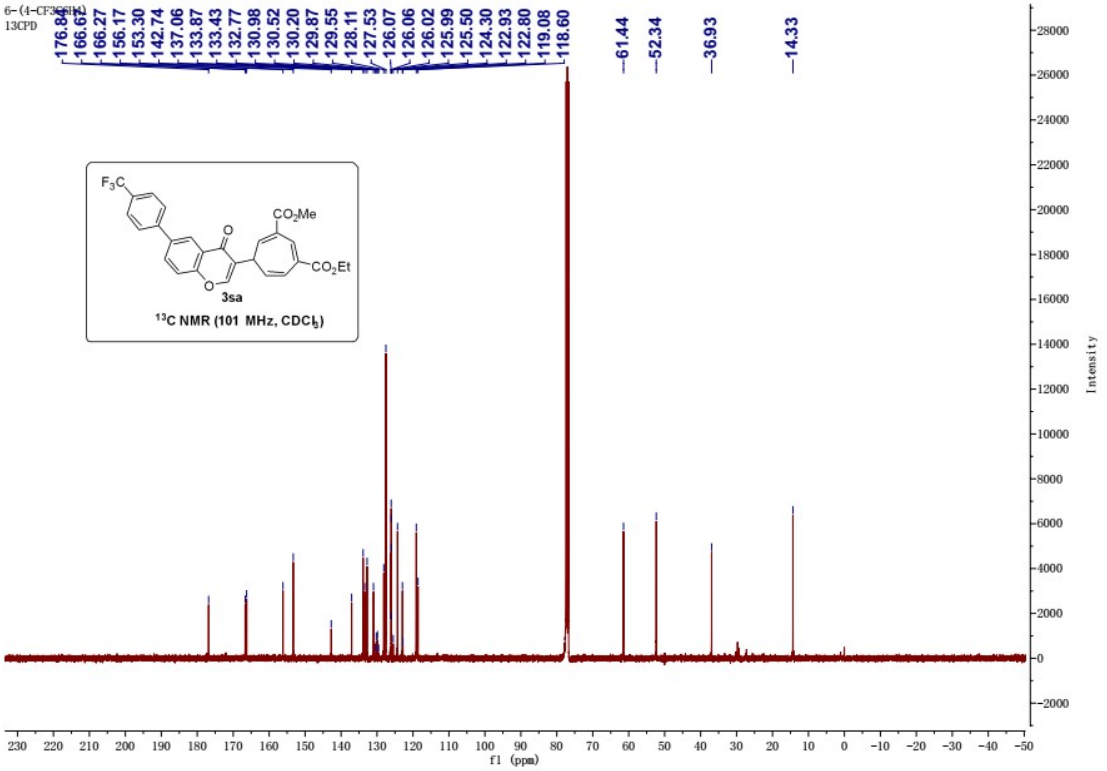

6-ph
test
8.45
8.44
8.23
7.91
7.86
7.66
7.64
7.55
7.53
7.47
7.45
7.38
6.91
6.89
6.64
6.62
5.46
5.45
5.44
5.42
4.35
4.34
4.33
4.32
4.31
3.79
2.81
2.79
2.78
1.39
1.37
1.35
CO2Me
CO2Et
3qa
1H NMR (400 MHz, CDCl3)
0.91
0.90
1.06
1.06
2.08
1.04
2.14
1.09
0.96
0.95
1.00
1.97
2.95
0.99
3.00
f1 (ppm)

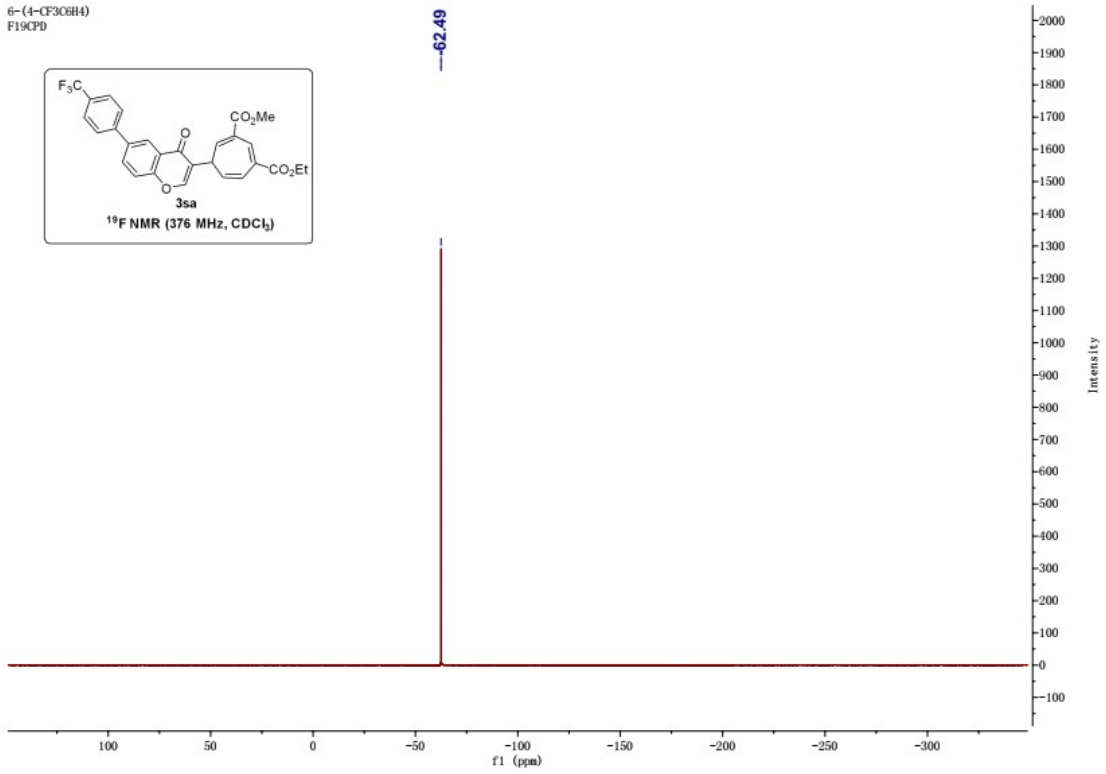

5-Ph
C13CPD
176.89
166.60
166.19
155.64
153.13
139.14
138.47
133.80
133.33
132.74
131.32
128.98
127.95
127.89
127.11
125.85
124.11
123.61
122.64
118.89
118.62
61.32
52.21
36.97
14.26
CO2Me
CO2Et
3qa
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

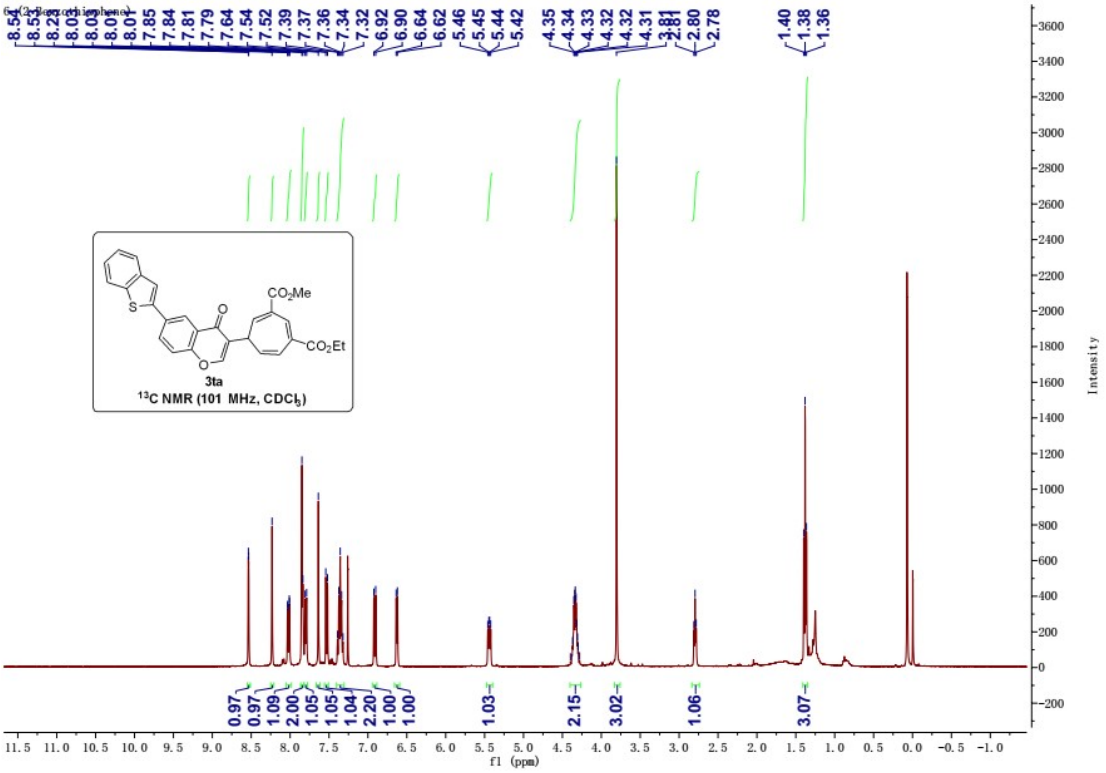

6-(MeOC6H4)
C13CPD
177.01
166.65
166.25
159.62
155.32
153.13
138.18
133.82
133.35
132.41
131.64
130.12
128.42
128.22
127.98
125.90
124.13
122.88
122.58
118.55
114.45
61.34
55.35
52.23
36.97
14.28
MeO
CO2Me
CO2Et
3ra
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

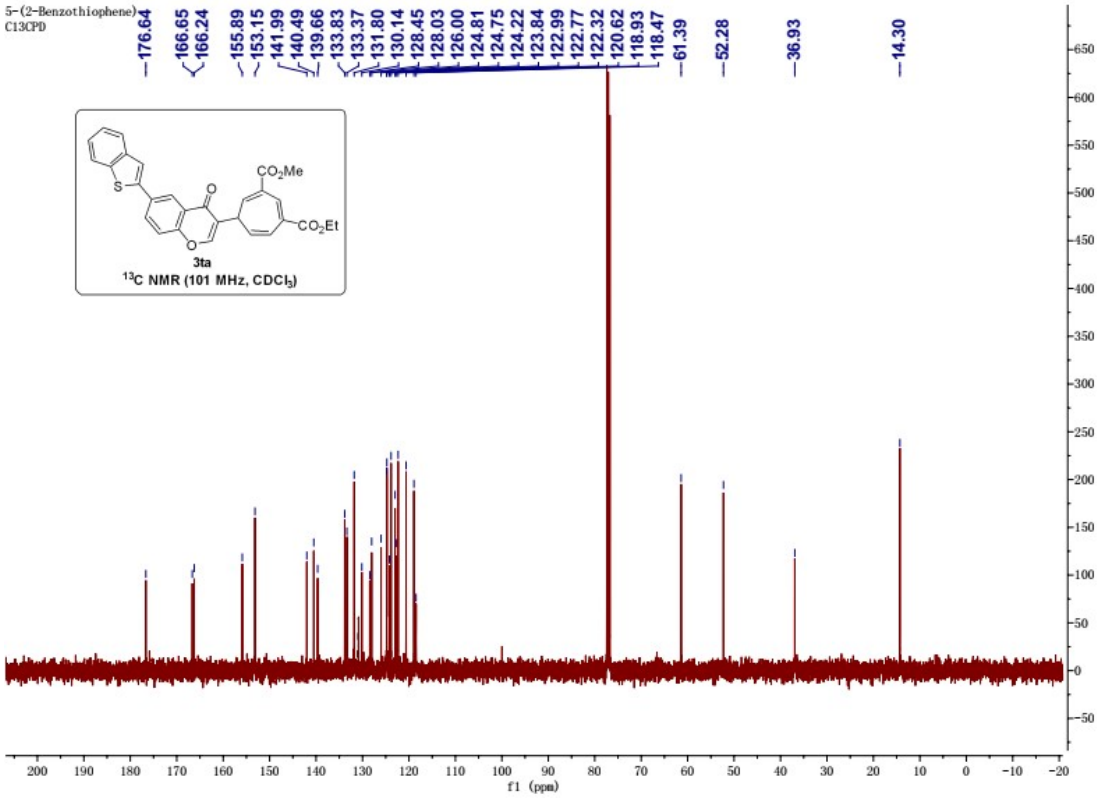

6-(MeOC6H4)
C13CPD
177.01
166.65
166.25
159.62
155.32
153.13
138.18
133.82
133.35
132.41
131.64
130.12
128.42
128.22
127.98
125.90
124.13
122.88
122.58
118.55
114.45
61.34
55.35
52.23
36.97
14.28
MeO
CO2Me
CO2Et
3ra
13C NMR (101 MHz, CDCl3)
f1 (ppm)

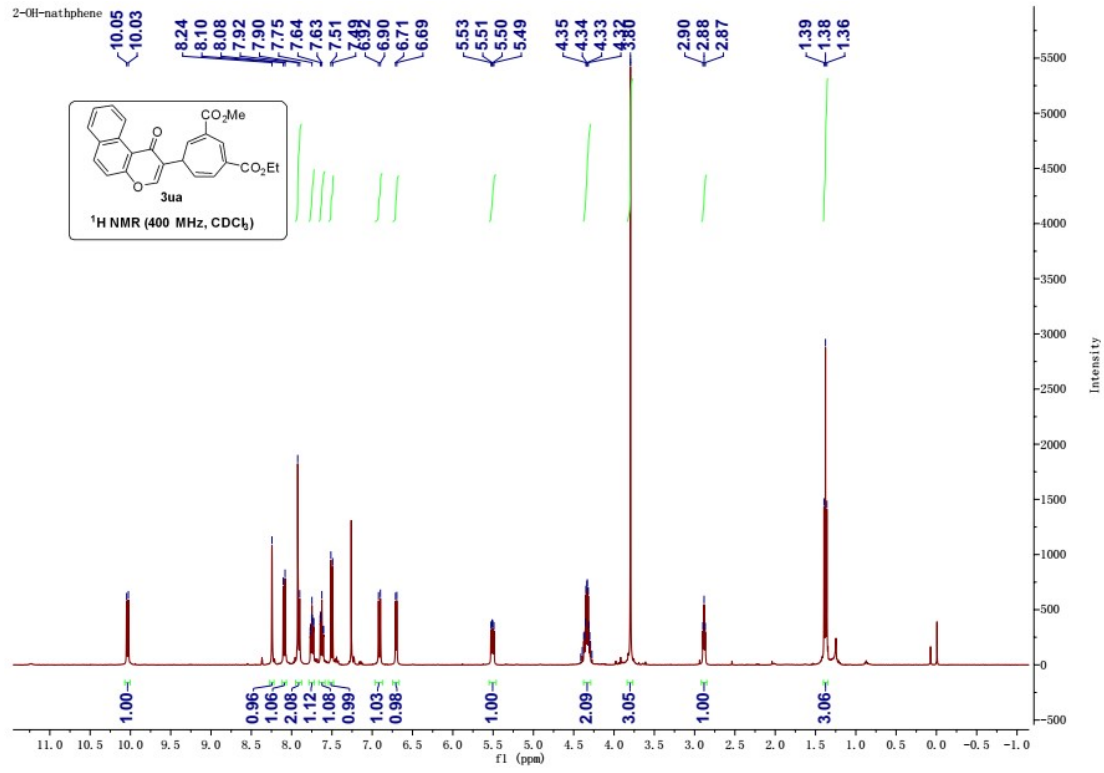

3sa
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

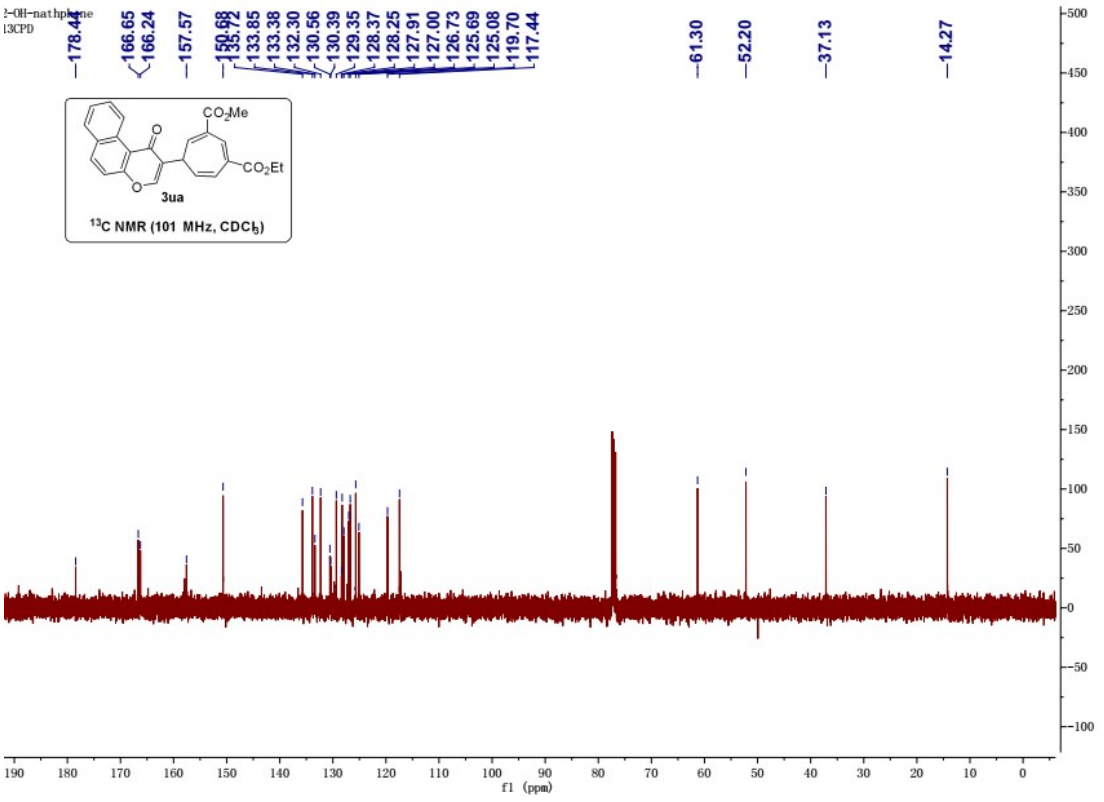

3sa
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

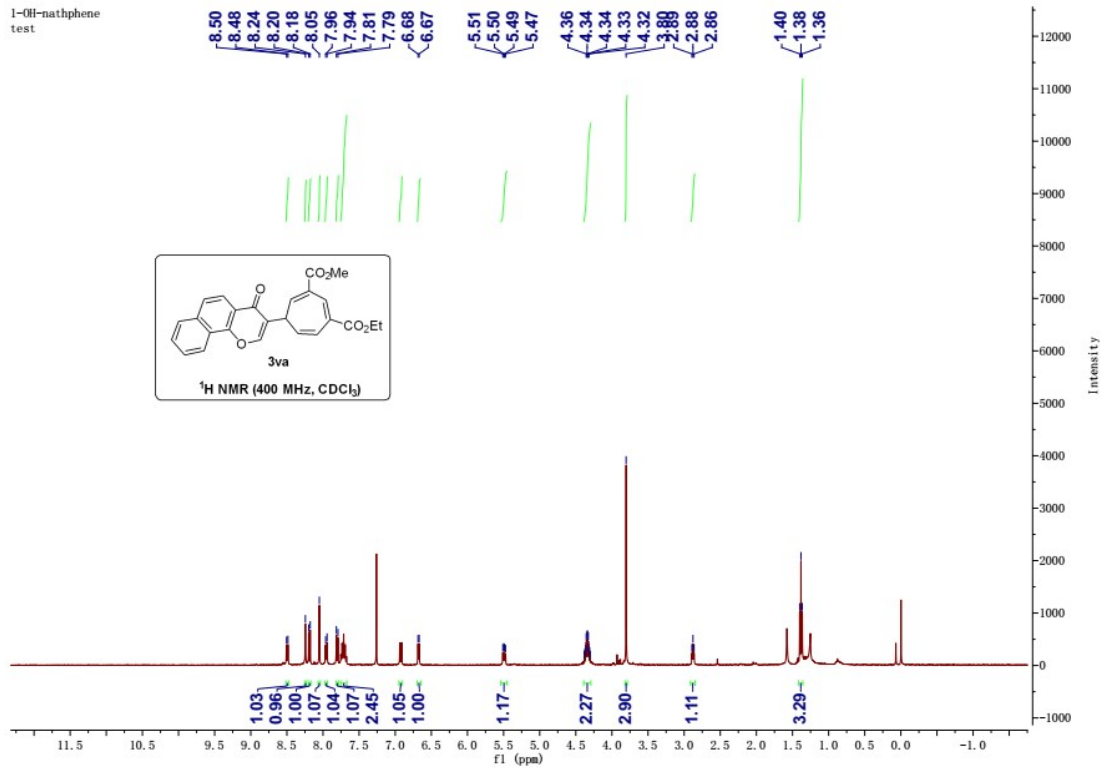

6-(4-CF3C6H4)
F19CPD
-62.49
3sa
19F NMR (376 MHz, CDCl3)
f1 (ppm)
Intensity


3ta
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


5-(2-Benzothiophene)
C13CPD
176.64
166.65
166.24
155.89
153.15
141.99
140.49
139.66
133.83
133.37
131.80
130.14
128.45
128.03
126.00
124.81
124.75
124.22
123.84
122.99
122.77
122.32
120.62
118.93
118.47
61.39
52.28
36.93
14.30
CO2Me
CO2Et
3ta
13C NMR (101 MHz, CDCl3)
f1 (ppm)


2-OH-nathphene
10.05
10.03
8.24
8.10
8.08
7.92
7.90
7.75
7.64
7.63
7.51
6.90
6.71
6.69
5.53
5.51
5.50
5.49
4.35
4.34
4.33
2.90
2.88
2.87
1.39
1.38
1.36
CO2Me
CO2Et
3ua
1H NMR (400 MHz, CDCl3)
1.00
0.96
1.06
2.08
1.12
1.08
0.99
1.03
0.98
1.00
2.09
3.05
1.00
3.06
Intensity
f1 (ppm)


2-OH-nathphene
13CPD
178.44
166.65
166.24
157.57
150.68
135.72
133.85
133.38
132.30
130.56
130.39
129.35
128.37
128.25
127.91
127.00
126.73
125.69
125.08
119.70
117.44
61.30
52.20
37.13
14.27
CO2Me
CO2Et
3ua
13C NMR (101 MHz, CDCl3)
f1 (ppm)


1-OH-nathphene
test
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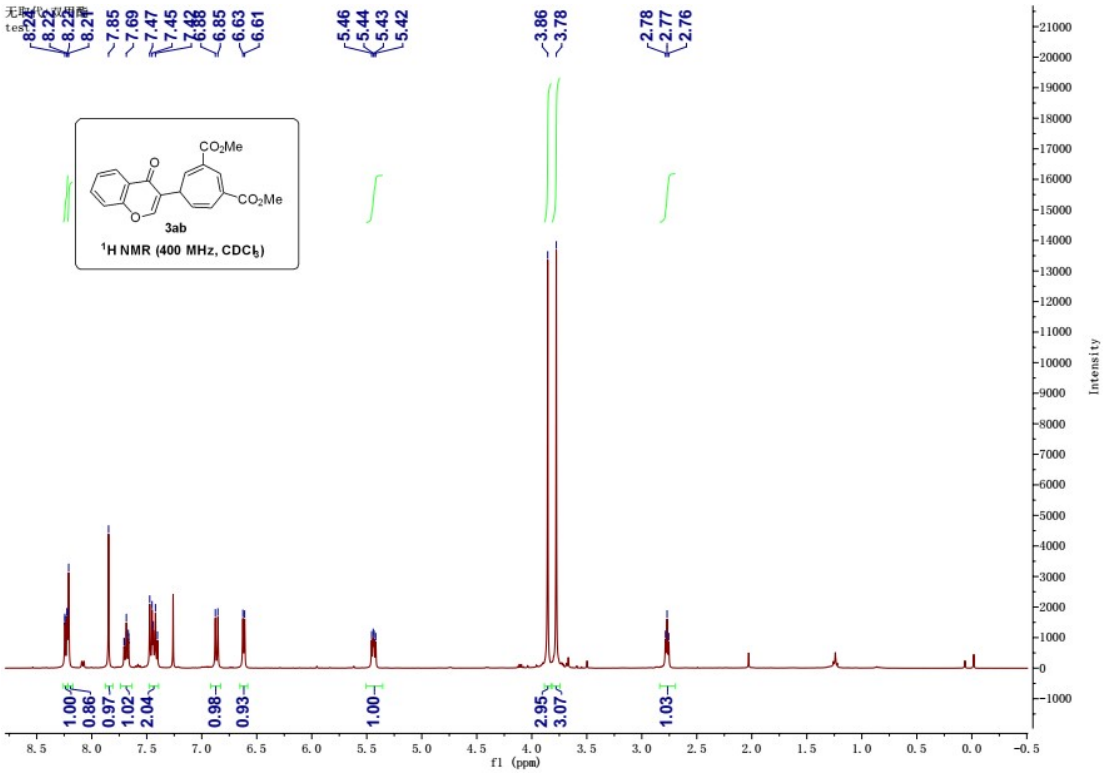
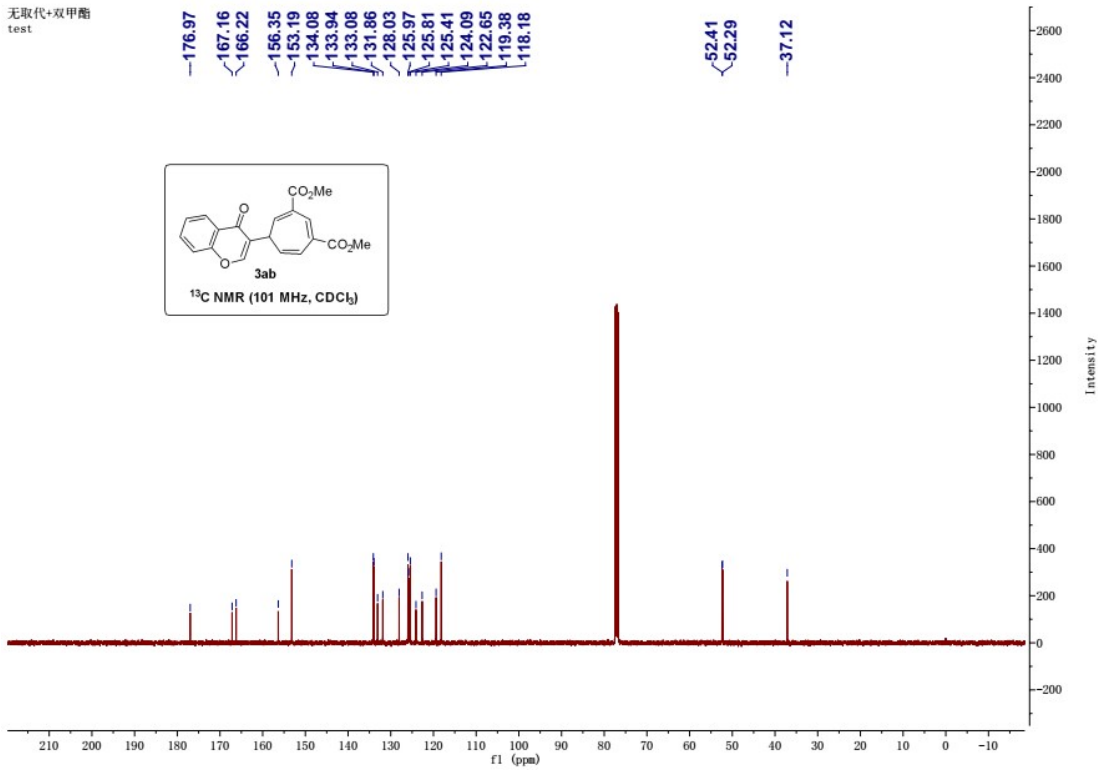
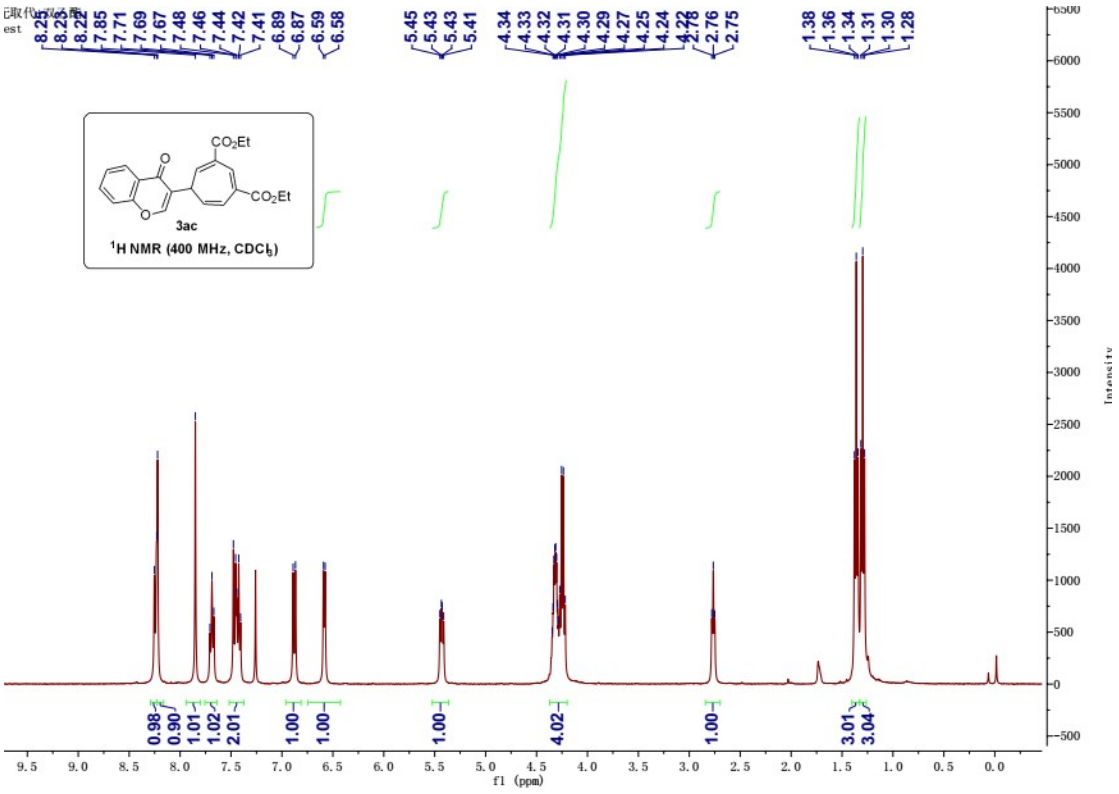
8.48
8.24
8.20
8.18
8.05
7.96
7.94
7.81
7.79
6.68
6.67
5.51
5.50
5.49
5.47
4.36
4.34
4.34
4.33
4.32
2.89
2.88
2.86
1.40
1.38
1.36
CO2Me
CO2Et
3va
1H NMR (400 MHz, CDCl3)
1.03
0.96
1.00
1.07
1.04
1.07
2.45
1.05
1.00
1.17
2.27
2.90
1.11
3.29
f1 (ppm)
Intensity


无取代双甲酯
test
8.24
8.22
8.21
7.85
7.69
7.47
7.45
6.88
6.85
6.63
6.61
5.46
5.44
5.43
5.42
3.86
3.78
2.78
2.77
2.76
CO2Me
CO2Me
O
O
3ab
1H NMR (400 MHz, CDCl3)
1.00
0.86
0.97
1.02
2.04
0.98
0.93
1.00
2.95
3.07
1.03
f1 (ppm)
Intensity


无取代+双甲酯
test
176.97
167.16
166.22
156.35
153.19
134.08
133.94
133.08
131.86
128.03
125.97
125.81
125.41
124.09
122.65
119.38
118.18
52.41
52.29
37.12
CO2Me
CO2Me
O
O
3ab
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity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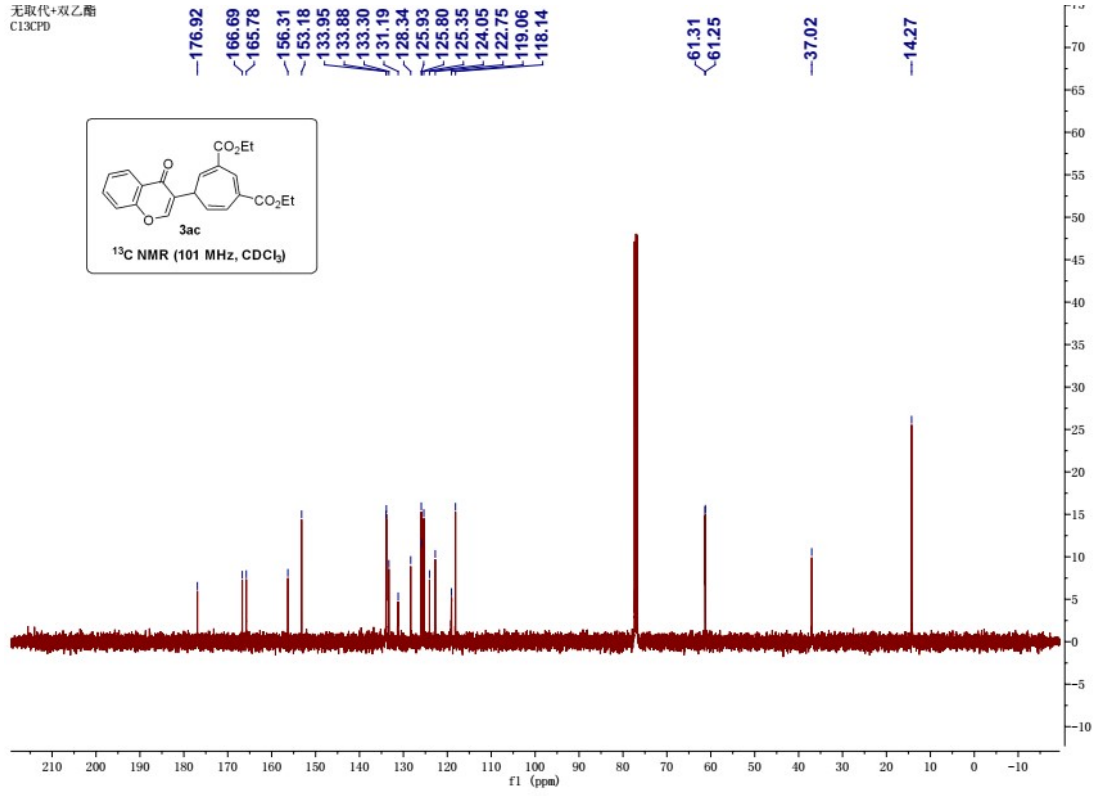
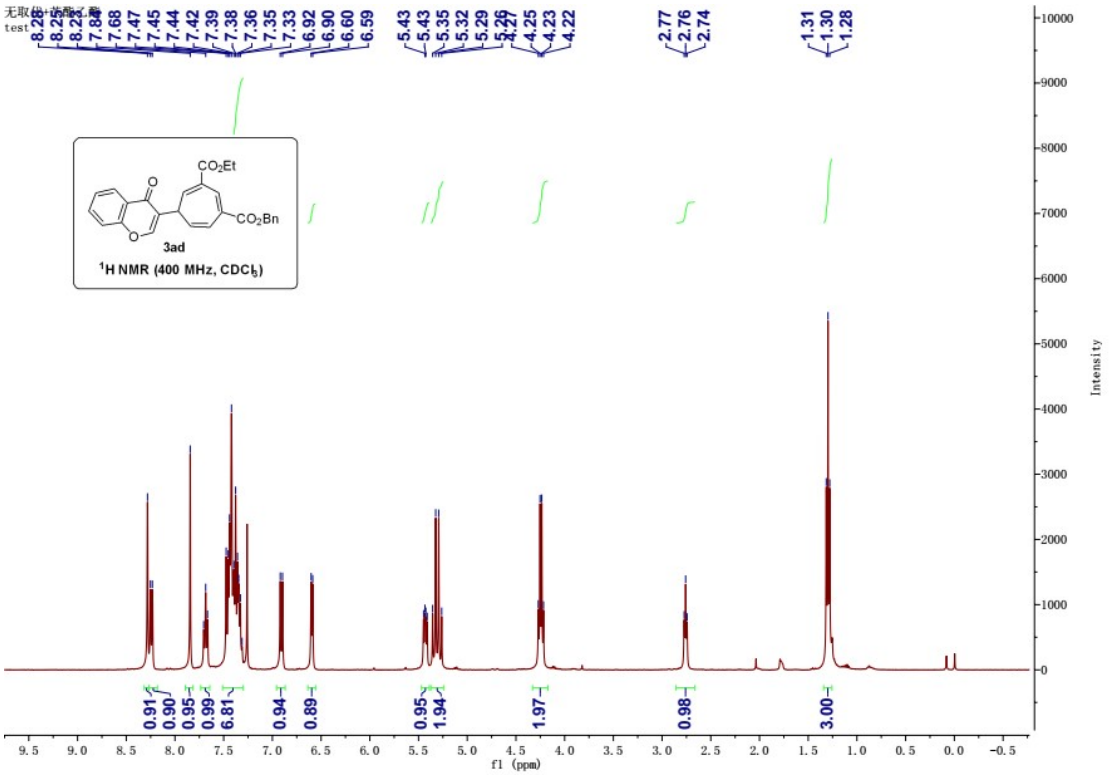
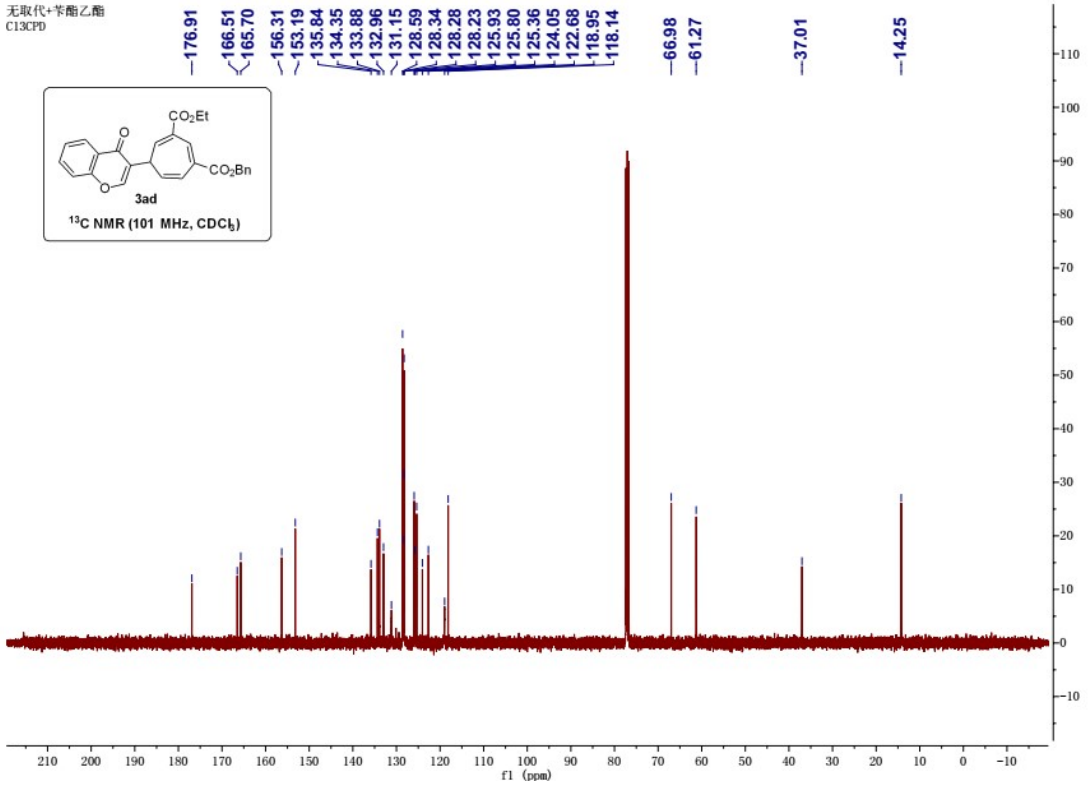
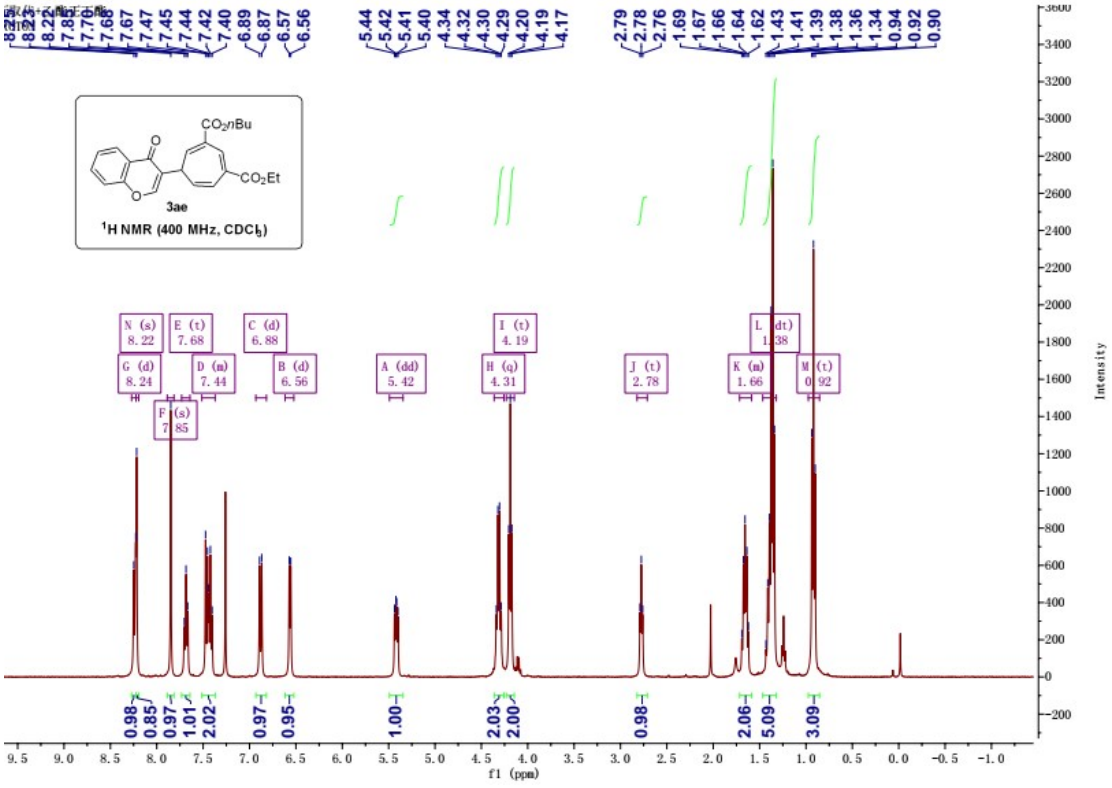
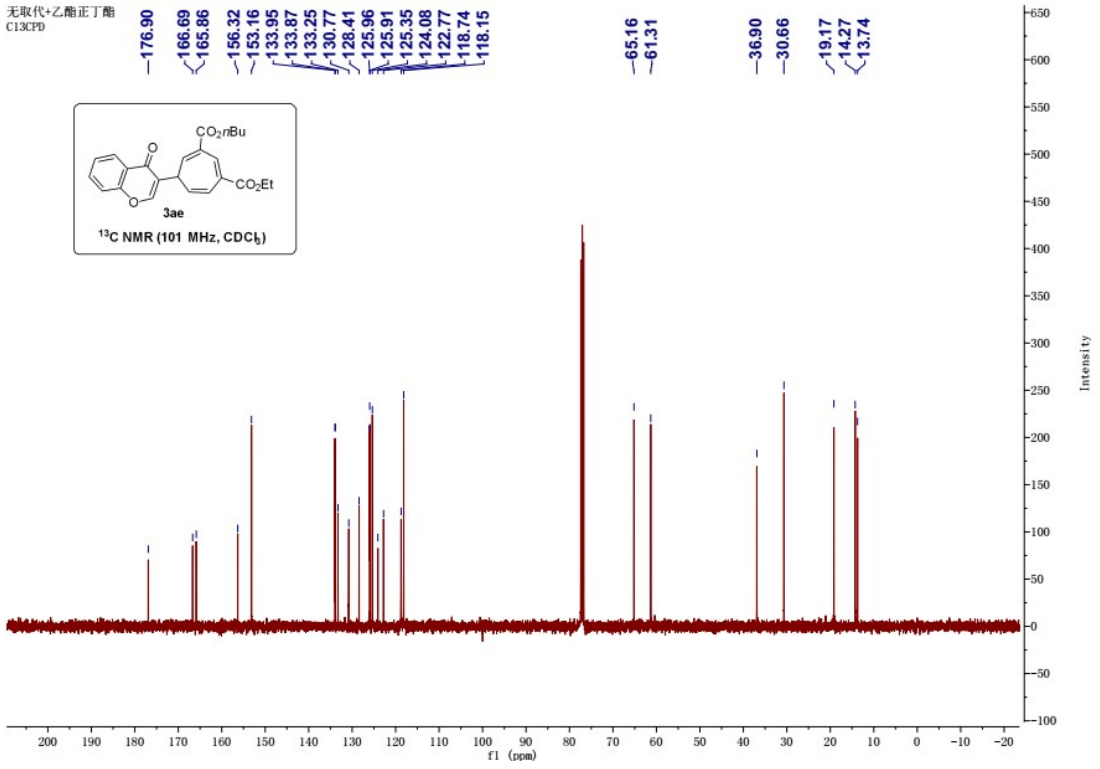
8.23
8.22
7.85
7.71
7.69
7.67
7.48
7.46
7.44
7.42
7.41
6.89
6.87
6.59
6.58
5.45
5.43
5.43
5.41
4.34
4.33
4.32
4.31
4.30
4.29
4.27
4.25
4.24
2.78
2.76
2.75
1.38
1.36
1.34
1.31
1.30
1.28
CO2Et
CO2Et
3ac
1H NMR (400 MHz, CDCl3)
0.98
0.90
1.01
1.02
2.01
1.00
1.00
1.00
4.02
1.00
3.01
3.04
f1 (ppm)
Intensity

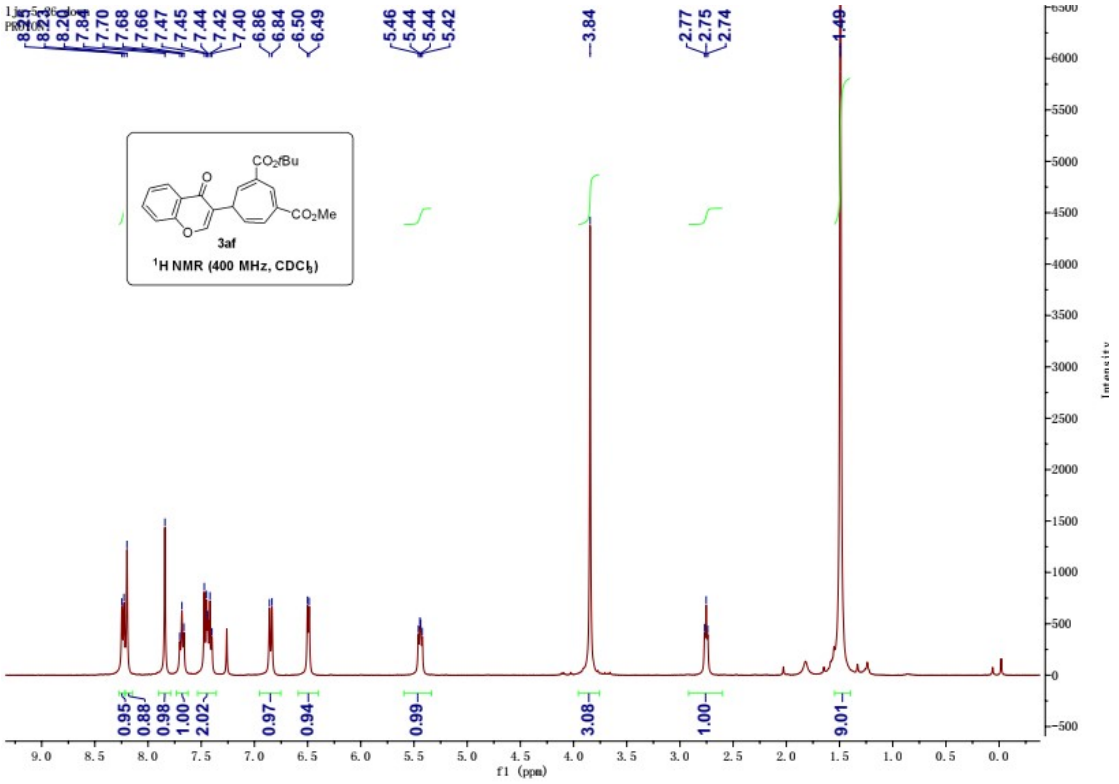

无取代+双乙酯
C13CPD
176.92
166.69
165.78
156.31
153.18
133.95
133.88
133.30
131.19
128.34
125.93
125.80
125.35
124.05
122.75
119.06
118.14
61.31
61.25
37.02
14.27
CO2Et
CO2Et
3ac
13C NMR (101 MHz, CDCl3)
f1 (ppm)

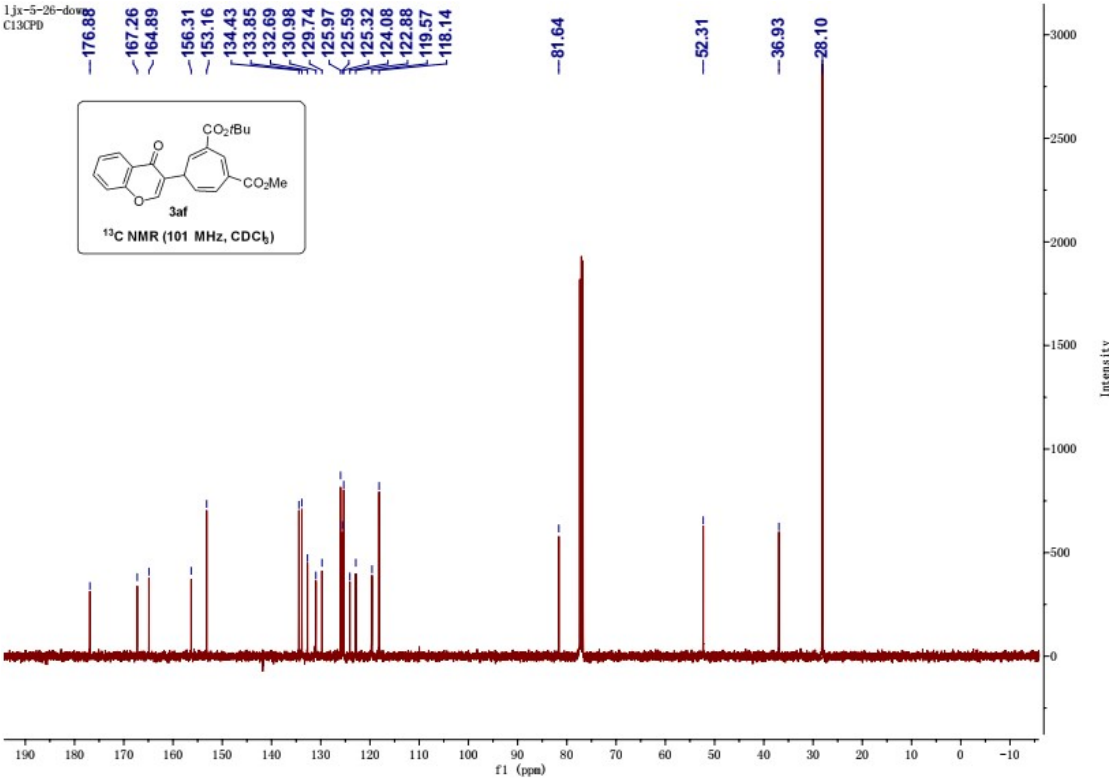

test
8.28
8.25
8.23
7.84
7.68
7.47
7.45
7.44
7.42
7.39
7.38
7.36
7.35
7.33
6.92
6.90
6.60
6.59
5.43
5.43
5.35
5.32
5.29
5.26
4.25
4.23
4.22
2.77
2.76
2.74
1.31
1.30
1.28
CO2Et
CO2Bn
3ad
1H NMR (400 MHz, CDCl3)
Intensity
0.91
0.90
0.95
0.99
6.81
0.94
0.89
0.95
1.94
1.97
0.98
3.00
f1 (ppm)

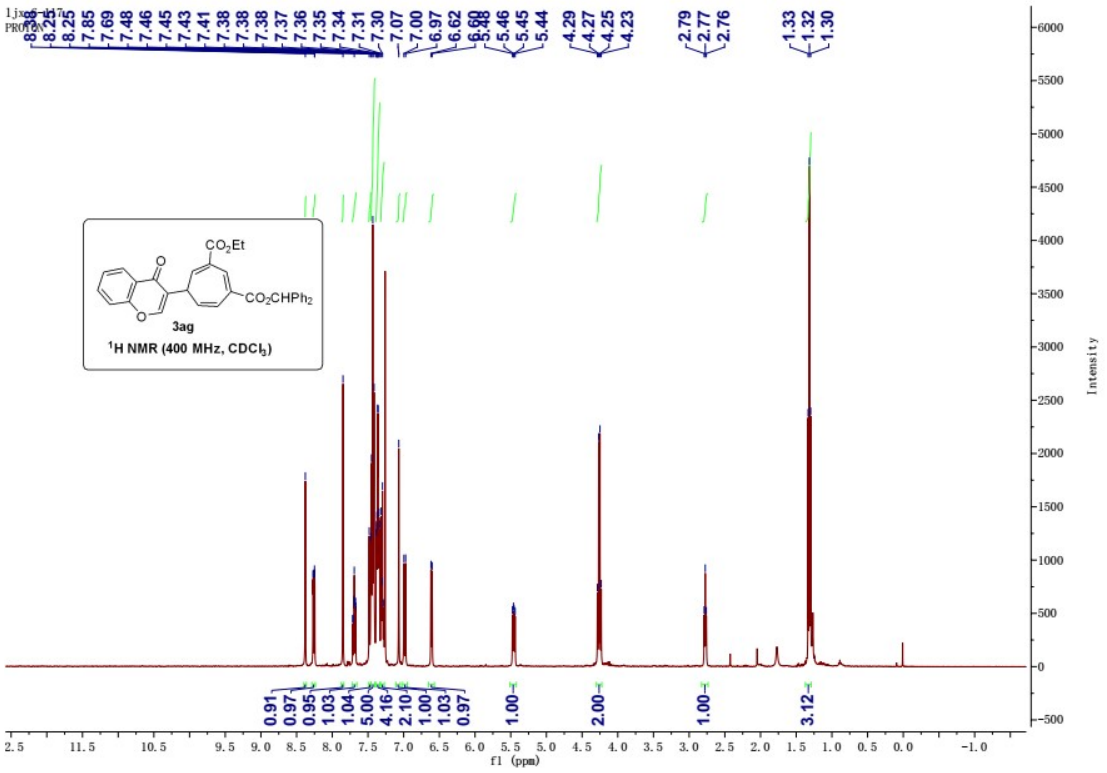

无取代+苄酯乙酯
C13CPD
176.91
166.51
165.70
156.31
153.19
135.84
134.35
133.88
132.96
131.15
128.59
128.34
128.28
128.23
125.93
125.80
125.36
124.05
122.68
118.95
118.14
66.98
61.27
37.01
14.25
CO2Et
CO2Bn
3ad
13C NMR (101 MHz, CDCl3)
f1 (ppm)

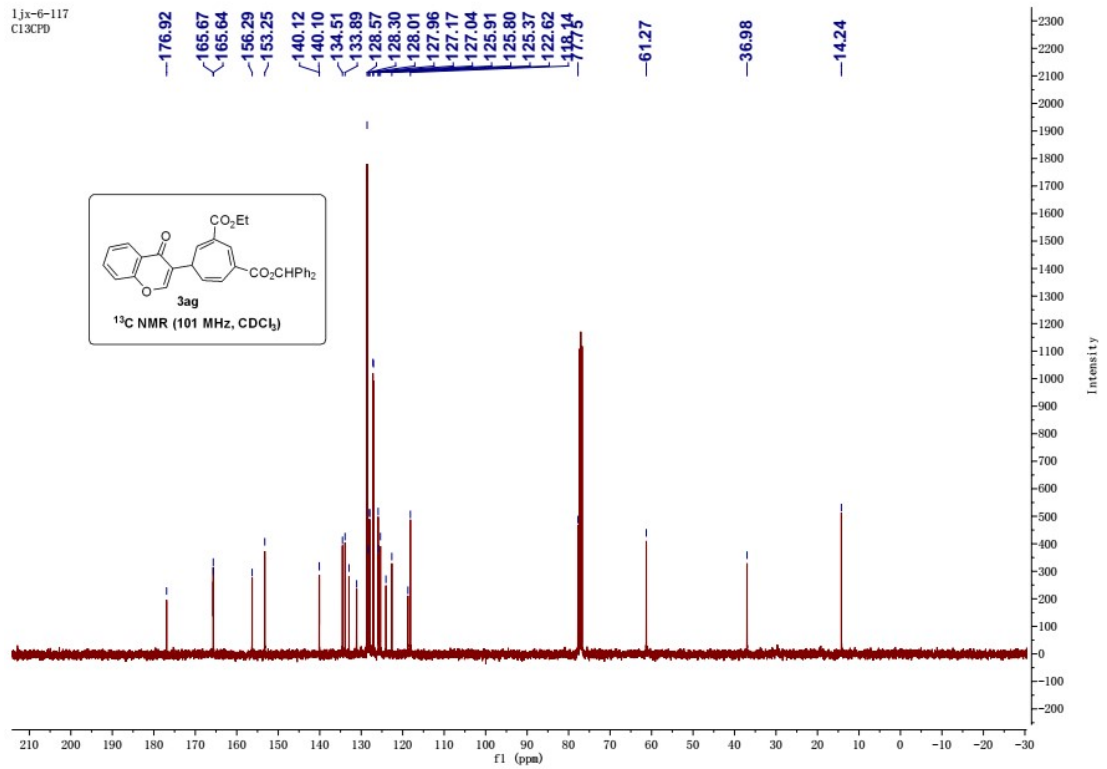

3ae
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

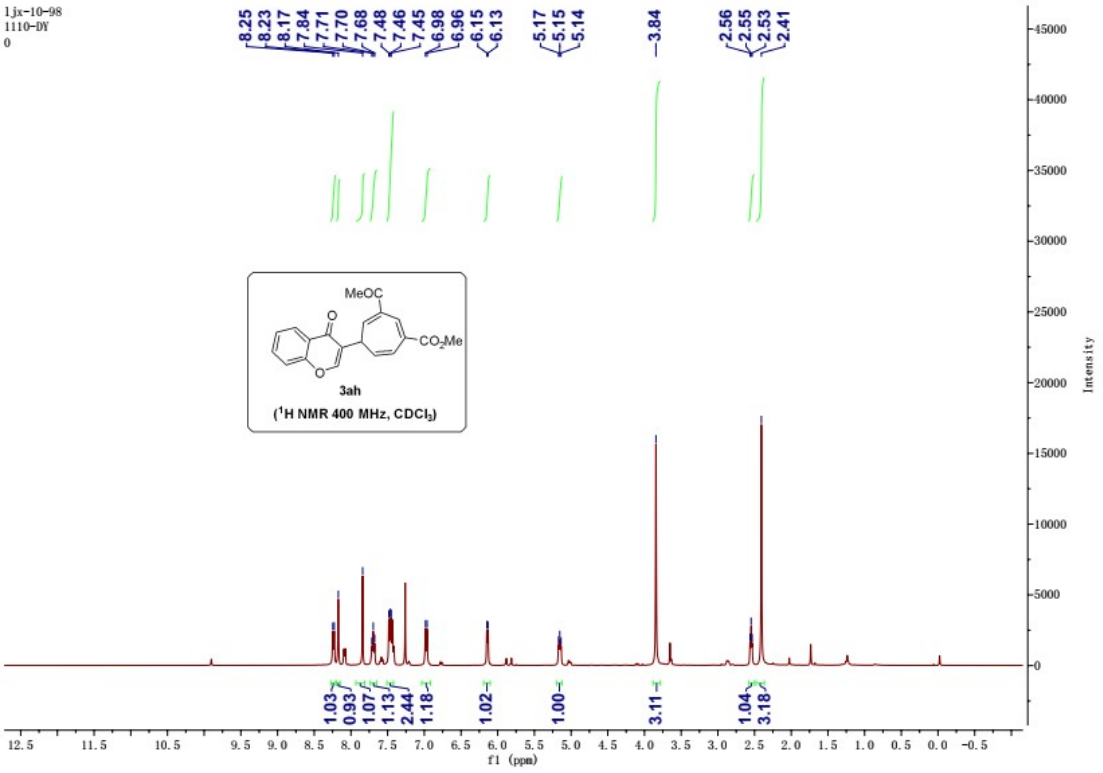

无取代+乙酯正丁酯
C13CPD
3ae
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

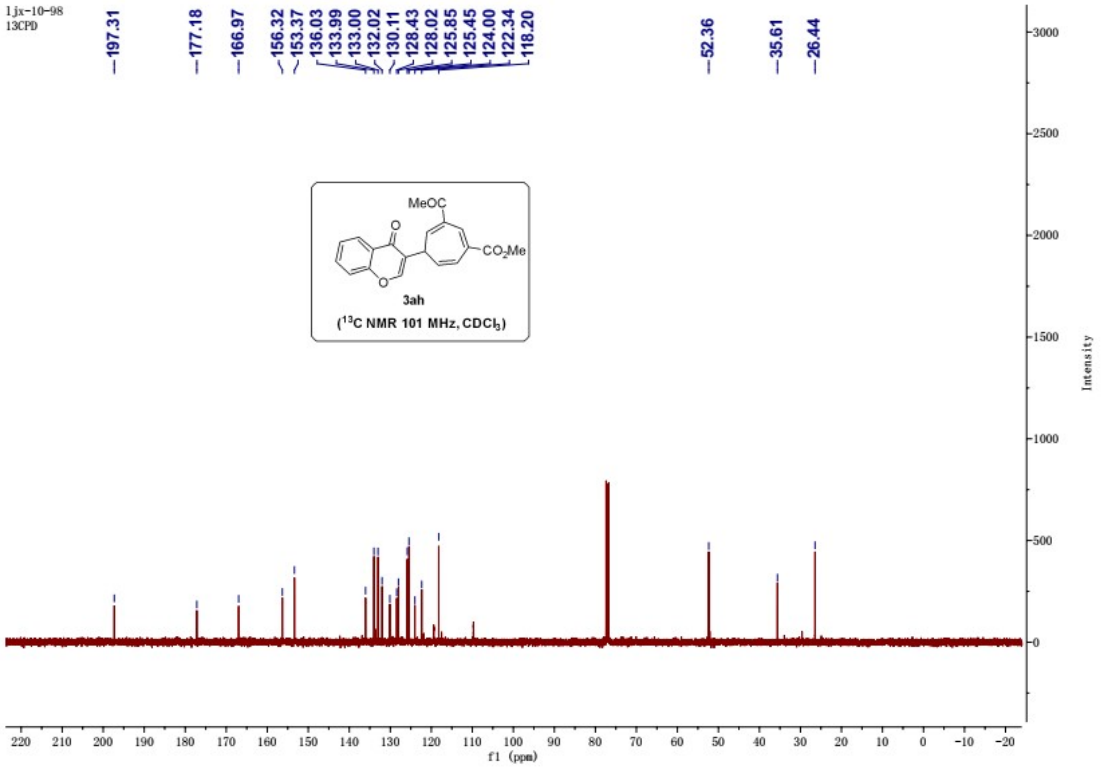

8.24
8.22
8.20
7.84
7.70
7.68
7.66
7.47
7.45
7.44
7.42
7.40
6.86
6.84
6.50
6.49
5.46
5.44
5.44
5.42
3.84
2.77
2.75
2.74
1.49
CO2tBu
CO2Me
3af
1H NMR (400 MHz, CDCl3)
0.95
0.88
0.98
1.00
2.02
0.97
0.94
0.99
3.08
1.00
9.01
f1 (ppm)
Intensity


176.88
167.26
164.89
156.31
153.16
134.43
133.85
132.69
130.98
129.74
125.97
125.59
125.32
124.08
122.88
119.57
118.14
81.64
52.31
36.93
28.10
CO2tBu
CO2Me
3af
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


3ag
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity


1jx-6-117
C13CPD
3ag
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity


ljx-10-98
1110-DY
0
8.25
8.23
8.17
7.84
7.71
7.70
7.68
7.48
7.46
7.45
6.98
6.96
6.15
6.13
5.17
5.15
5.14
3.84
2.56
2.55
2.53
2.41
MeOC
O
CO2Me
O
3ah
(1H NMR 400 MHz, CDCl3)
Intensity
1.03
0.93
1.07
1.13
2.44
1.18
1.02
1.00
3.11
1.04
3.18
f1 (ppm)


ljx-10-98
13CPD
197.31
177.18
166.97
156.32
153.37
136.03
133.99
133.00
132.02
130.11
128.43
128.02
125.85
125.45
124.00
122.34
118.20
52.36
35.61
26.44
MeOC
O
CO2Me
O
3ah
(13C NMR 101 MHz, CDCl3)
Intensity
f1 (ppm)

10. X-Ray Crystallography Data of 3sa

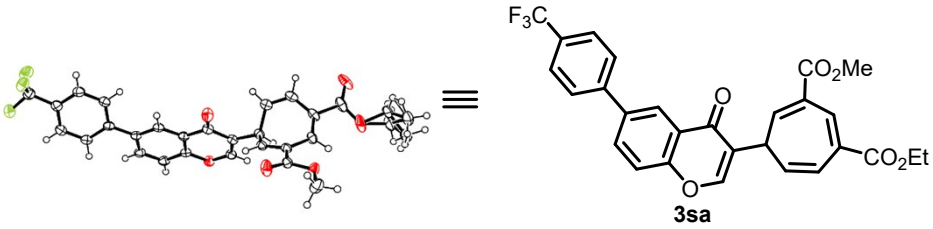


Figure S2. ORTEP diagram of 3**sa** (CCDC: 2008499). Thermal ellipsoids are shown at the 50% probability level. A colorless block crystal of **3sa** for X-ray diffraction was obtained by slowly volatilizing a solution of **3sa** in hexane/ ethyl acetate (5:1). The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer.

Table S3 Crystal data and structure refinement for 3sa.

Identification code	3sa
Empirical formula	$C_{28}H_{21}F_3O_6$
Formula weight	510.45
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.8322(6)
b/Å	13.7887(4)
c/Å	10.6237(4)
α/°	90
β/°	92.720(4)
γ/°	90
Volume/Å^3	2316.60(14)
Z	4
ρ_{calc}g/cm^3	1.464
μ/mm^{-1}	0.118
F(000)	1056.0
Crystal size/mm^3	0.2 × 0.18 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.918 to 52.736
Index ranges	-19 ≤ h ≤ 19, -17 ≤ k ≤ 17, -13 ≤ l ≤ 13
Reflections collected	24452
Independent reflections	4734 [R_{int} = 0.0453, R_{sigma} = 0.0289]
Data/restraints/parameters	4734/64/356
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1189
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1281
Largest diff. peak/hole / e Å^{-3}	0.45/-0.53

11. References

[1] J. R**.** Zimmerman, O. Johntony, D. Steigerwald, C. Criss, B. J. Myers, D. H. Kinder, *Org. Lett.* 2015, **17**, 3256.

[2] J.-Y. Dong, X.-C. Wang, Z. Wang, H.-J. Song, Y.-X. Liu, Q.-M. Wang, *Chem Sci* 2019, **11**, 1026.

[3] X.-F. Zhu, J. Lan, O. Kwon, *J. Am. Chem. Soc.* 2003, **125**, 4716.