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Supporting Information

Highly Enantioselective Addition of Aliphatic Aldehydes to 2-Hydroxychalcone Promoted by Cooperative Organocatalysts

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Table of Contents

1. General Information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction were conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvent were treated as follow: tetrahydrofuran and diethyl ether were distilled from sodium under argon atmosphere, dichloromethane and toluene was distilled distilled from calciumhydride under argon atmosphere. Anhydrous chloroform, acetonitrile, 1,2-dichloroethane, methanol and ethyl acetate were commercial available (Adamas, SafeDry, with molecular sieves).

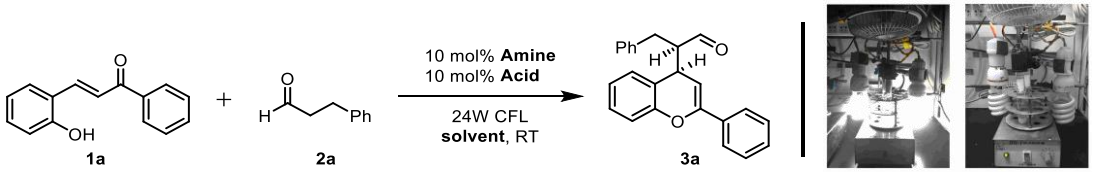
Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm, 200-400 mesh, Silicycle P60). NMR data including ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Coupling constants are given in Hz.

Low mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI).

Optical rotations were measured on a Anton Paar MCP 300 polarimeter and are reported as follows: $[\alpha]_D^{rt}$ (*c* in g per 100 mL, solvent).

2. Conditions Optimization for Enantioselective Construction of Flavonoids

2.1. General Procedure for the Model Reaction



A 10 mL Schlenk tube was charged with the *amine* (10 mol%), *acid* (10 mol%), *2-hydroxychalcone* ***1a*** (0.1 mmol), and *phenylpropyl aldehyde* ***2a*** (0.15 mmol) dissolved in solvent (1 mL). The vial was then sealed and positioned approximately 5 cm away from the light source. A household full spectrum 24 W compact fluorescent light (CFL) bulb was used for irradiating the reaction mixture. A fan was placed above the reaction apparatus for insuring the reaction temperature at RT. The reaction mixture was stirred at this condition until all *2-hydroxychalcone* ***1a*** was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:40, v/v) to afford the product.

2.2. The Screening of Solvents for the Model Reaction

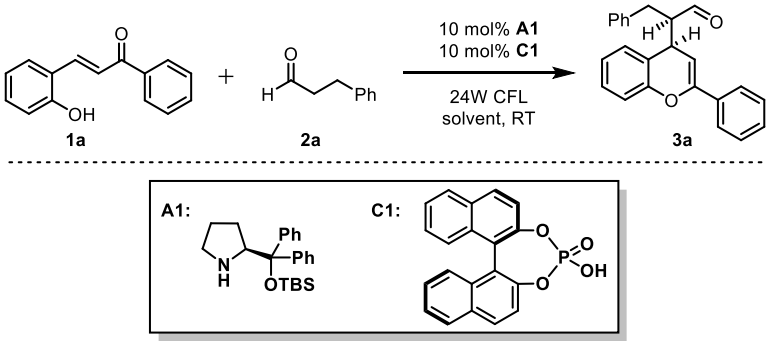


Table S1. The Screening of Solvents for the Model Reaction [a]

Entry	Solvent	Yield (%) [b]	*ee* (%) (major, minor) [c]	*dr* [c]
1	MTBE	86	83, 60	2: 1
2	DIPE	79	92, 83	2: 1
3	2-MeTHF	85	93, 89	2: 1
4	THF	71	93, 86	2: 1
5	Et_2O	71	94, 83	2: 1
6	CH_3CN	90	55, 27	2: 1
7	EtOAc	79	77, 55	2: 1
8	CH_2Cl_2	91	43, 17	2: 1
9	MeOH	18	15, 15	2: 1

[a] Conditions: A mixture of 2-hydroxylchalcone **1a** (0.1 mmol), aldehyde **2a** (0.1 mmol), **A1** (10 mol %) and **C1** (10 mol %) in **solvent** (1.0 mL) was irradiated by 24W CFL at RT for 24 h

[b] Isolated yield

[c] Determined by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 10.55 min, t_{minor} = 11.70 min)

2.3. The Screening of Amine & Acid Promoter for the Model Reaction

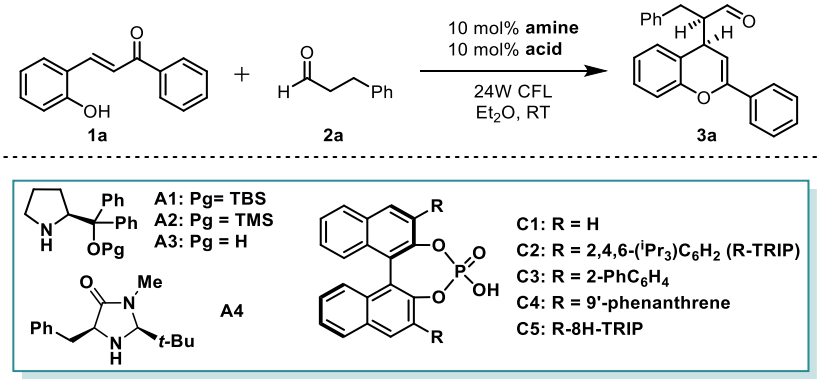


Table S2. The Screening of Amine & Acid for the Model Reaction [a]

Entry	Amine	Acid	Yield (%) [b]	*ee* (%) (major, minor) [c]	*dr* [c]
1	A1	(±)-CSA	35	28, 19	1: 1
2	A1	TFA	59	79, 58	1: 1
3	A1	TsOH	15	32, 21	1: 1
4	A1	C1	71	94, 83	2: 1
5 [d]	A1	C1	ND	NA	NA
6	A1	--	ND	NA	NA
7	--	C1	ND	NA	NA
8	A1	C2	74	95, 55	3: 1
9	A1	C3	91	79, 20	2.5: 1
10	A1	C4	74	68, -10	2: 1
11	A1	C5	72	95, 71	3: 1
12	A2	C2	82	95, 91	2: 1
13	A3	C2	29	-38, 12	2: 1
14	A4	C2	81	98, 53	12: 1
15	A4	(S)-C2	73	68, 41	3: 1

[a] Conditions: A mixture of 2-hydroxylchalcone **1a** (0.1 mmol), aldehyde **2a** (0.1 mmol), **amine catalyst** (10 mol %) and **Brϕnsted acid** (10 mol %) in Et_2O (1.0 mL) was irradiated by 24W CFL at RT for 24 h

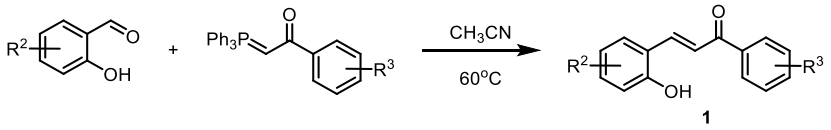
[b] Isolated yield

[c] Determined by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 10.55 min, t_{minor} = 11.70 min)

[d] Run in dark

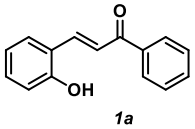
ND not detected, NA not assigned.

3. General Procedure for the Preparation of 2-Hydroxychalcones



General procedure A[1]:

The *salicylaldehyde* (1.0 equiv.) and *corresponding phosphorane* (1.2 equiv) were stirred in *CH_3CN* (0.25 M) at 60°C until all salicylaldehyde was consumed completely as judged by TLC. The reactions were cooled down to RT, concentrated *in vacuo* and purified by column chromatography (silica gel) to afford the corresponding *2-hydroxychalcones* ***1.***



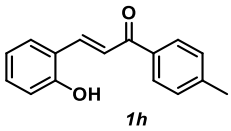
1a

This compound was prepared according to the general procedure A as a yellow solid (2.13 g, 95% yield in 10 mmol scale).

^{1}H NMR (500 MHz, MeOD): δ 8.11 (d, *J* = 15.8 Hz, 1H), 8.04-7.99 (m, 2H), 7.78 (d, *J* = 15.8 Hz, 1H), 7.67-7.63 (m, 1H), 7.62-7.57 (m, 1H), 7.54-7.49 (m, 2H), 7.27-7.21 (m, 1H), 6.90-6.85 (m, 2H).

^{13}C NMR (126 MHz, MeOD): δ 193.27, 158.86, 142.65, 139.65, 133.92, 133.06, 130.47, 129.73, 129.52, 123.09, 122.67, 120.86, 117.09.

HRMS (ESI): exact mass calcd for $C_{15}H_{13}O_2$: m/z 225.0910 $[M+H]^+$, found: m/z 225.0911.



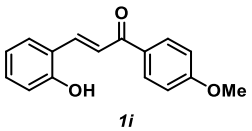
1h

This compound was prepared according to the general procedure A as a yellow solid (417 mg, 88% yield in 2 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.12 (s, 1H), 8.17 (d, *J* = 15.8 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 15.8 Hz, 1H), 7.82-7.79 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.25 (m, 1H), 7.02-6.98 (m, 1H), 6.95-6.90 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 189.83, 157.83, 144.11, 140.05, 136.97, 132.48, 130.11, 129.76, 129.34, 123.08, 122.58, 120.89, 117.10, 21.55.

HRMS (ESI): exact mass calcd for $C_{16}H_{15}O_2$: m/z 239.1067 $[M+H]^+$, found: m/z 239.1068.



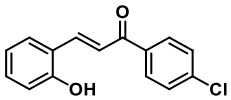
1i

This compound was prepared according to the general procedure A as a yellow solid (421 mg, 83% yield in 2 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.11 (s, 1H), 8.18-8.10 (m, 3H), 7.89 (d, *J* = 15.7 Hz, 1H), 7.82-7.78 (m, 1H), 7.30-7.25 (m, 1H), 7.09-7.04 (m, 2H), 7.01-6.97 (m, 1H), 6.95-6.90 (m, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 188.57, 164.31, 157.75, 139.54, 132.35, 132.30, 131.46, 129.70, 123.16, 122.42, 120.86, 117.06, 114.68, 55.93.

HRMS (ESI): exact mass calcd for $C_{16}H_{15}O_3$: m/z 255.1016 $[M+H]^+$, found: m/z 255.1017.



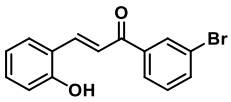
1j

This compound was prepared according to the general procedure A as a yellow solid (2.20 g, 85% yield in 10 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.16 (s, 1H), 8.19 (d, *J* = 15.8 Hz, 1H), 8.14-8.10 (m, 2H), 7.86 (d, *J* = 15.7 Hz, 1H), 7.82-7.79 (m, 1H), 7.60-7.56 (m, 2H), 7.31-7.27 (m, 1H), 7.02-6.98 (m, 1H), 6.95-6.90 (m, 1H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 189.22, 157.98, 140.98, 139.12, 138.07, 132.79, 130.97, 129.88, 129.67, 122.86, 122.09, 120.92, 117.14.

HRMS (ESI): exact mass calcd for $C_{15}H_{12}ClO_2$: m/z 259.0520 $[M+H]^+$, found: m/z 259.0522.



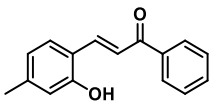
1k

This compound was prepared according to the general procedure A as a yellow solid (509 mg, 84% yield in 2 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.13 (s, 1H), 7.76 (d, *J* = 16.3 Hz, 1H), 7.73-7.70 (m, 1H), 7.69-7.66 (m, 1H), 7.54-7.48 (m, 2H), 7.46-7.42 (m, 1H), 7.31-7.26 (m, 1H), 7.23 (d, *J* = 16.3 Hz, 1H), 6.99-6.95 (m, 1H), 6.94-6.90 (m, 1H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 195.12, 157.80, 142.80, 142.72, 134.08, 133.10, 132.14, 129.94, 129.83, 128.47, 126.85, 122.39, 121.02, 119.69, 117.14.

HRMS (ESI): exact mass calcd for $C_{15}H_{12}O_2Br$: m/z 303.0015 $[M+H]^+$, found: m/z 303.0015.



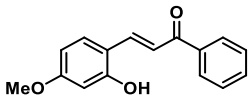
1l

This compound was prepared according to the general procedure A as a yellow solid (438 mg, 92% yield in 2 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.06 (s, 1H), 8.15 (d, *J* = 15.7 Hz, 1H), 8.11-8.08 (m, 2H), 7.83 (d, *J* = 15.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.64-7.60 (m, 1H), 7.57-7.52 (m, 2H), 6.83 (s, 1H), 6.78-6.74 (m, 1H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 190.37, 157.92, 143.39, 140.64, 139.65, 133.29, 129.81, 129.46, 129.12, 121.96, 121.46, 120.35, 117.60, 21.51.

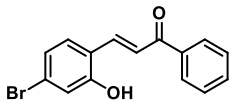
HRMS (ESI): exact mass calcd for $C_{16}H_{15}O_2$: m/z 239.1067 $[M+H]^+$, found: m/z 239.1068.



1m

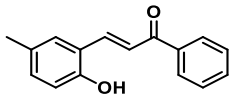
This compound was prepared according to the general procedure A as a yellow solid (477 mg, 94% yield in 2 mmol scale).

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.23 (s, 1H), 8.16-8.07 (m, 3H), 7.79-7.73 (m, 2H), 7.63-7.59 (m, 1H), 7.56-7.51 (m, 2H), 6.58-6.51 (m, 2H), 3.81 (s, 3H).
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 190.32, 164.05, 159.56, 140.68, 139.91, 133.24, 131.38, 129.51, 129.15, 119.97, 116.29, 107.56, 102.33, 55.80.
HRMS (ESI): exact mass calcd for $C_{16}H_{15}O_3$: m/z 255.1016 $[M+H]^+$, found: m/z 255.1016.



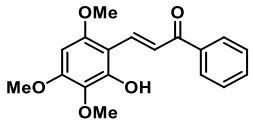
1n

This compound was prepared according to the general procedure A as a yellow solid (545 mg, 90% yield in 2 mmol scale).
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.64 (s, 1H), 8.13-8.06 (m, 3H), 7.91 (d, *J* = 15.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.21 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 1H).
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 190.22, 158.49, 139.32, 139.12, 133.59, 131.21, 129.56, 129.26, 125.29, 124.08, 123.16, 122.53, 120.00.
HRMS (ESI): exact mass calcd for $C_{15}H_{12}O_2Br$: m/z 303.0015 $[M+H]^+$, found: m/z 303.0015.



1o

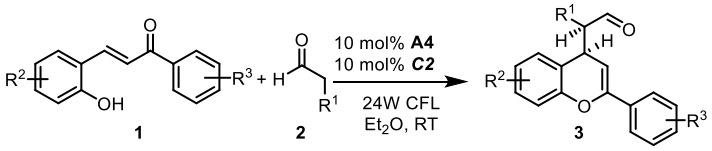
This compound was prepared according to the general procedure A as a yellow solid (443 mg, 93% yield in 2 mmol scale).
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.92 (s, 1H), 8.16 (d, *J* = 15.8 Hz, 1H), 8.12-8.06 (m, 1H), 7.87 (d, *J* = 15.8 Hz, 1H), 7.66-7.61 (m, 2H), 7.58-7.53 (m, 2H), 7.10 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 2.28 (s, 3H).
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 190.44, 155.92, 140.71, 139.66, 133.48, 133.45, 129.94, 129.92, 129.59, 129.27, 122.71, 122.29, 117.12, 20.53.
HRMS (ESI): exact mass calcd for $C_{16}H_{15}O_2$: m/z 239.1067 $[M+H]^+$, found: m/z 239.1066.



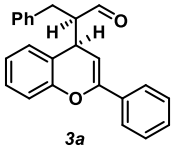
1p

The *corresponding salicylaldehyde* was prepared followed with a modification of *Kimpe's* method[2] and compound ***1p*** was prepared according to the general procedure A as a yellow solid (13.35 g, 85% yield in 50 mmol scale).
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.66 (s, 1H), 8.27 (d, *J* = 15.7 Hz, 1H), 8.07 (d, *J* = 15.9 Hz, 1H), 8.03-7.99 (m, 2H), 7.62-7.57 (m, 1H), 7.55-7.51 (m, 2H), 6.37 (s, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.77 (s, 3H).
^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ 191.06, 157.96, 156.03, 152.42, 140.23, 136.69, 132.96, 131.20, 129.41, 128.92, 122.20, 105.91, 89.35, 61.15, 56.43, 56.35.
HRMS (ESI): exact mass calcd for $C_{18}H_{19}O_5$: m/z 315.1227 $[M+H]^+$, found: m/z 315.1230.

4. Enantioselective Construction of Flavonoids



General procedure B: A 10 mL Schlenk tube was charged with the ***A4*** (10 mol%), ***C2*** (10 mol%), *2-hydroxychalcone **1*** (0.1 mmol), and *corresponding aldehyde **2*** (0.15 mmol) dissolved in *Et_2O* (1 mL). The vial was then sealed and positioned approximately 5 cm away from the light source. A household full spectrum 24 W compact fluorescent light (CFL) bulb was used for irradiating the reaction mixture. A fan was paced above the reaction apparatus for insuring the reaction temperature at RT. The reaction mixture was stirred at this condition until all *2-hydroxychalcone **1*** was consumed as judged by TLC. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford the product.



3a

This compound was prepared according to the general procedure B as a pale-yellow oil (27.5 mg, 81% yield, 98% *ee*, d.r. = 12: 1, in 0.1 mmol scale; 1.411 g, 83% yield, 98% *ee*, d.r. = 10: 1, in 5.0 mmol scale) and was isolated as a mixture of diastereoisomers. Spectral data for the main isomer is reported.

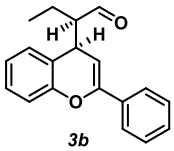
$[\alpha]_D^{25.0}$ = 19.3 (*c* 0.255, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 10.55 min, t_{minor} = 11.70 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.74-7.69 (m, 2H), 7.44-7.35 (m, 3H), 7.25-7.16 (m, 4H), 7.15-7.08 (m, 3H), 7.03-6.98 (m, 2H), 5.41 (d, *J* = 4.8 Hz, 1H), 4.36-4.32 (m, 1H), 3.10-3.01 (m, 2H), 2.75-2.67 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.43, 152.73, 151.07, 139.55, 133.97, 128.97, 128.59, 128.54, 128.37, 127.94, 126.33, 124.94, 124.14, 121.03, 117.07, 96.31, 61.54, 34.98, 31.21.

HRMS (ESI): exact mass calcd for $C_{24}H_{19}O_2$: m/z 339.1380 $[M-H]^-$, found: m/z 339.1380.



3b

This compound was prepared according to the general procedure B as a pale-yellow oil (25.0 mg, 90% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 8: 1). Spectral data for the main isomer is reported.

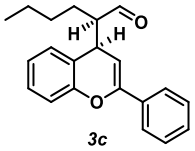
$[\alpha]_D^{23.6}$ = 82.8 (*c* 0.095, $CHCl_3$).

Enantiomeric excess was found to be 96% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 15.60 min, t_{minor} = 17.88 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (d, *J* = 1.9 Hz, 1H), 7.71-7.65 (m, 2H), 7.43-7.35 (m, 3H), 7.27-7.21 (m, 1H), 7.18-7.13 (m, 1H), 7.12-7.07 (m, 2H), 5.38 (d, *J* = 4.9 Hz, 1H), 4.24-4.19 (m, 1H), 2.61-2.54 (m, 1H), 1.86-1.74 (m, 1H), 1.52-1.43 (m, 1H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.46, 152.70, 150.87, 134.01, 128.86, 128.49, 128.14, 124.89, 123.94, 121.56, 116.90, 96.81, 61.55, 35.06, 18.49, 12.60.

HRMS (ESI): exact mass calcd for $C_{19}H_{17}O_2$: m/z 277.1223 $[M-H]^-$, found: m/z 277.1224.



3c

This compound was prepared according to the general procedure B as a pale-yellow oil (23.0 mg, 75% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 10: 1). Spectral data for the main isomer is reported.

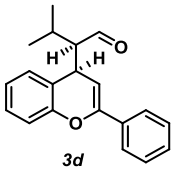
$[\alpha]_D^{23.8}$ = 74.1 (*c* 0.060, $CHCl_3$).

Enantiomeric excess was found to be 97% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 14.04 min, t_{minor} = 16.19 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.84 (d, *J* = 1.9 Hz, 1H), 7.70-7.67 (m, 2H), 7.42-7.34 (m, 3H), 7.26-7.21 (m, 1H), 7.17-7.13 (m, 1H), 7.11-7.07 (m, 2H), 5.37 (d, *J* = 4.9 Hz, 1H), 4.23-4.18 (m, 1H), 2.67-2.60 (m, 1H), 1.81-1.73 (m, 1H), 1.44-1.36 (m, 1H), 1.31-1.24 (m, 1H), 1.22-1.09 (m, 3H), 0.77 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.61, 152.69, 150.83, 134.04, 128.86, 128.50, 128.14, 128.11, 124.89, 123.93, 121.47, 116.90, 96.80, 59.68, 35.16, 30.15, 24.85, 22.73, 13.91.

HRMS (ESI): exact mass calcd for $C_{21}H_{21}O_2$: m/z 305.1536 $[M-H]^-$, found: m/z 305.1537.



3d

This compound was prepared according to the general procedure B as a pale-yellow oil (21.1 mg, 72% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 5: 1). Spectral data for the main isomer is reported.

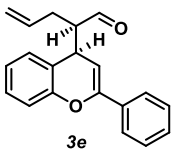
$[\alpha]_D^{24.2}$ = 84.6 (*c* 0. 250, $CHCl_3$).

Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 99:1, 214 nm, 0.7 mL/min, t_{major} = 18.41 min, t_{minor} = 24.69 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.79 (d, *J* = 3.1 Hz, 1H), 7.71-7.67 (m, 2H), 7.42-7.34 (m, 3H), 7.25-7.20 (m, 1H), 7.15-7.11 (m, 1H), 7.11-7.05 (m, 2H), 5.58 (d, *J* = 5.2 Hz, 1H), 4.22-4.17 (m, 1H), 2.51-2.46 (m, 1H), 2.28-2.19 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.08, 152.70, 150.54, 134.10, 128.81, 128.51, 128.47, 128.06, 124.90, 123.77, 122.34, 116.99, 98.48, 65.45, 33.75, 26.55, 22.21, 19.90.

HRMS (ESI): exact mass calcd for $C_{20}H_{19}O_2$: m/z 291.1380 $[M-H]^-$, found: m/z 291.1380.



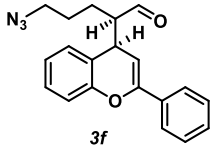
3e

This compound was prepared according to the general procedure B as a pale-yellow oil (24.1 mg, 83% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 11: 1). Spectral data for the main isomer is reported.

$[\alpha]_D^{25.0}$ = 80.0 (*c* 0.398, $CHCl_3$).

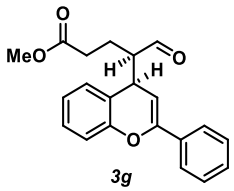
Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 15.93 min, t_{minor} = 17.46 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.85 (d, *J* = 1.4 Hz, 1H), 7.71-7.67 (m, 2H), 7.43-7.36 (m, 3H), 7.26-7.23 (m, 1H), 7.18-7.14 (m, 1H), 7.12-7.08 (m, 2H), 5.73-5.64 (m, 1H), 5.39 (d, *J* = 4.8 Hz, 1H), 5.02-4.94 (m, 2H), 4.31-4.26 (m, 1H), 2.80-2.75 (m, 1H), 2.56-2.48 (m, 1H), 2.23-2.16 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 203.94, 152.69, 151.00, 135.57, 133.91, 128.92, 128.51, 128.26, 128.06, 124.88, 124.02, 121.17, 117.06, 116.94, 96.47, 58.99, 34.70, 29.62.
HRMS (ESI): exact mass calcd for $C_{20}H_{17}O_2$: m/z 289.1223 $[M-H]^-$, found: m/z 289.1224.



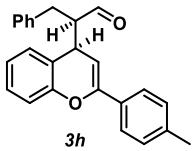
3f

This compound was prepared according to the general procedure B as a pale-yellow oil (20.6 mg, 63% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 6: 1). Spectral data for the main isomer is reported.
$[\alpha]_D^{25.0}$ = 14.6 (*c* 0.123, $CHCl_3$).
Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 12.56 min, t_{minor} = 13.72 min).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.71-7.66 (m, 2H), 7.43-7.36 (m, 3H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.13-7.09 (m, 2H), 5.32 (d, *J* = 4.8 Hz, 1H), 4.27 (t, *J* = 4.1 Hz, 1H), 3.14 (t, *J* = 6.7 Hz, 2H), 2.74-2.67 (m, 1H), 1.90-1.78 (m, 1H), 1.64-1.55 (m, 1H), 1.46-1.34 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 203.37, 152.59, 151.11, 133.79, 129.00, 128.52, 128.40, 127.96, 124.90, 124.13, 120.92, 117.07, 96.05, 59.41, 51.27, 34.93, 27.31, 22.20.
HRMS (ESI): exact mass calcd for $C_{20}H_{18}N_3O_2$: m/z 332.1405 $[M-H]^-$, found: m/z 332.1405.



3g

This compound was prepared according to the general procedure B as a pale-yellow oil (22.5 mg, 67% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 6: 1). Spectral data for the main isomer is reported.
$[\alpha]_D^{25.0}$ = 20.0 (*c* 0.088, $CHCl_3$).
Enantiomeric excess was found to be 96% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 19. 82 min, t_{minor} = 25. 07 min).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.69-7.65 (m, 2H), 7.42-7.35 (m, 3H), 7.27-7.23 (m, 1H), 7.19-7.16 (m, 1H), 7.13-7.08 (m, 2H), 5.30 (d, *J* = 4.7 Hz, 1H), 4.29 (t, *J* = 4.2 Hz, 1H), 3.56 (s, 3H), 2.84-2.80 (m, 1H), 2.34-2.17 (m, 2H), 2.14-2.04 (m, 1H), 1.74-1.66 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 203.20, 173.38, 152.52, 151.10, 133.79, 128.98, 128.49, 128.38, 128.05, 124.90, 124.06, 120.67, 117.08, 95.92, 58.62, 51.67, 34.81, 32.03, 20.34.
HRMS (ESI): exact mass calcd for $C_{21}H_{19}O_4$: m/z 335.1289 $[M-H]^-$, found: m/z 335.1290.



3h

This compound was prepared according to the general procedure B as a pale-yellow oil (30.4 mg, 86% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 17: 1). Spectral data for the main isomer is reported.

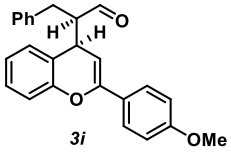
$[\alpha]_D^{25.0}$ = 4.3 (*c* 0.328, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 98:2, 214 nm, 0.7 mL/min, t_{minor} = 17.85 min, t_{major} = 20.09 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.25-7.18 (m, 6H), 7.15-7.09 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 2H), 5.36 (d, *J* = 4.8 Hz, 1H), 4.36-4.29 (m, 1H), 3.10-3.01 (m, 2H), 2.71 (q, *J* = 9.9 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.52, 152.78, 151.12, 139.62, 138.95, 131.20, 129.22, 128.97, 128.57, 128.31, 127.94, 126.30, 124.85, 124.05, 121.10, 117.06, 95.43, 61.60, 35.00, 31.17, 21.42.

HRMS (ESI): exact mass calcd for $C_{25}H_{21}O_2$: m/z 353.1547 $[M-H]^-$, found: m/z 353.1543.



3i

This compound was prepared according to the general procedure B as a pale-yellow oil (34.1 mg, 92% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 11: 1). Spectral data for the main isomer is reported.

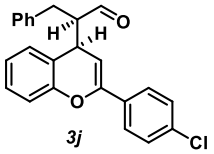
$[\alpha]_D^{24.1}$ = 7.8 (*c* 0.055, $CHCl_3$).

Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak IB-3 column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{minor} = 13.60 min, t_{major} = 14.13 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.67-7.62 (m, 2H), 7.25-7.16 (m, 4H), 7.14-7.06 (m, 3H), 7.02-6.98 (m, 2H), 6.96-6.91 (m, 2H), 5.27 (d, *J* = 4.7 Hz, 1H), 4.33-4.29 (m, 1H), 3.85 (s, 3H), 3.09-3.00 (m, 2H), 2.74-2.64 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.57, 160.28, 152.78, 150.87, 139.65, 128.97, 128.57, 128.30, 127.95, 126.65, 126.33, 126.30, 124.04, 121.13, 117.03, 113.91, 94.53, 61.63, 55.52, 34.99, 31.15.

HRMS (ESI): exact mass calcd for $C_{25}H_{21}O_3$: m/z 369.1496 $[M-H]^-$, found: m/z 369.1496.



3j

This compound was prepared according to the general procedure B as an off-white solid (32 mg, 85% yield, 98% *ee*, d.r. = 7: 1, in 0.1 mmol scale; 1.358 g, 91% yield, 96% *ee*, d.r. = 6: 1, in 5.0 mmol scale) and was isolated as a mixture of diastereoisomers. Spectral data for the main isomer is reported.

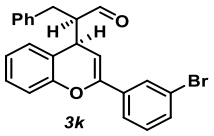
$[\alpha]_D^{25.0}$ = -2.0 (*c* 0.098, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{minor} = 23.32 min, t_{major} = 24.68 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.66-7.61 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.26 (m, 1H), 7.22-7.17 (m, 3H), 7.16-7.11 (m, 2H), 7.10-7.07 (m, 1H), 7.03-6.98 (m, 2H), 5.39 (d, *J* = 4.7 Hz, 1H), 4.35-4.30 (m, 1H), 3.10-2.98 (m, 2H), 2.73-2.67 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.30, 152.50, 150.05, 139.39, 134.77, 132.36, 128.93, 128.72, 128.61, 128.44, 127.92, 126.38, 126.19, 124.30, 120.86, 117.02, 96.76, 61.42, 34.79, 31.21.

HRMS (ESI): exact mass calcd for $C_{24}H_{18}ClO_2$: m/z 373.0990 $[M-H]^-$, found: m/z 373.0990.



3k

This compound was prepared according to the general procedure B as a pale-yellow oil (37.7 mg, 90% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 12: 1). Spectral data for the main isomer is reported.

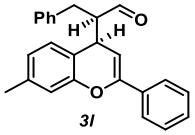
$[\alpha]_D^{25.0}$ = 35.5 (*c* 0.255, $CHCl_3$).

Enantiomeric excess was found to be 99% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 18.60 min, t_{minor} = 19.56 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.50-7.47 (m, 1H), 7.38-7.34 (m, 1H), 7.27-7.19 (m, 5H), 7.17-7.12 (m, 2H), 7.08-7.02 (m, 3H), 5.15 (d, *J* = 4.6 Hz, 1H), 4.33 (t, *J* = 4.1 Hz, 1H), 3.24 (dd, *J* = 14.2, 10.5 Hz, 1H), 3.12-3.05 (m, 1H), 2.84 (dd, *J* = 14.2, 3.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.48, 152.87, 151.48, 139.62, 136.20, 133.51, 131.02, 130.49, 129.00, 128.64, 128.43, 128.02, 127.45, 126.37, 124.28, 122.59, 120.80, 117.06, 101.45, 61.37, 35.24, 31.40.

HRMS (ESI): exact mass calcd for $C_{24}H_{18}BrO_2$: m/z 417.0485 $[M-H]^-$, found: m/z 417.0490.



3l

This compound was prepared according to the general procedure B as a pale-yellow oil (30.4 mg, 86% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 13: 1). Spectral data for the main isomer is reported.

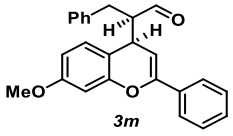
$[\alpha]_D^{25.0}$ = 7.7 (*c* 0.458, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H & IC column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 19.62 min, t_{minor} = 22.52 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.73-7.69 (m, 2H), 7.44-7.36 (m, 3H), 7.23-7.17 (m, 2H), 7.15-7.08 (m, 2H), 7.05-7.01 (m, 2H), 6.96-6.92 (m, 2H), 5.40 (d, *J* = 4.7 Hz, 1H), 4.31-4.28 (m, 1H), 3.08-3.00 (m, 2H), 2.75-2.67 (m, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.59, 152.55, 151.02, 139.68, 138.44, 134.09, 128.99, 128.90, 128.57, 128.52, 127.65, 126.27, 125.06, 124.92, 117.87, 117.42, 96.42, 61.53, 34.73, 31.20, 21.22.

HRMS (ESI): exact mass calcd for $C_{25}H_{21}O_2$: m/z 353.1547 $[M-H]^-$, found: m/z 353.1545.



3m

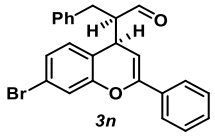
This compound was prepared according to the general procedure B as a pale-yellow oil (32.5 mg, 88% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 8: 1). Spectral data for the main isomer is reported.

$[\alpha]_D^{25.0}$ = −1.2 (*c* 0.318, $CHCl_3$).

Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{minor} = 19.12 min, t_{major} = 38.47 min).

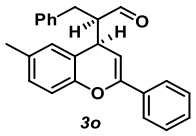
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.73-7.68 (m, 2H), 7.44-7.37 (m, 3H), 7.22-7.18 (m, 2H), 7.16-7.09 (m, 2H), 7.04-7.00 (m, 2H), 6.74-6.69 (m, 1H), 6.66-6.63 (m, 1H), 5.41 (d, *J* = 4.7 Hz, 1H), 4.30-4.25 (m, 1H), 3.84 (s, 3H), 3.07-3.00 (m, 2H), 2.74-2.67 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.61, 159.69, 153.44, 150.90, 139.69, 133.95, 128.97, 128.94, 128.58, 128.54, 128.52, 126.29, 124.92, 112.90, 111.21, 101.71, 96.72, 61.59, 55.61, 34.45, 31.15.
HRMS (ESI): exact mass calcd for $C_{25}H_{21}O_3$: m/z 369.1496 [M-H]$^-$, found: m/z 369.1497.



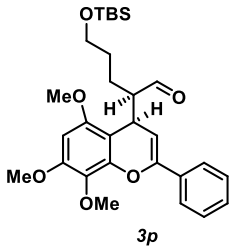
3n

This compound was prepared according to the general procedure B as a pale-yellow oil (29.7 mg, 71% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 4: 1). Spectral data for the main isomer is reported.
$[\alpha]_D^{25.0}$ = 1.2 (*c* 0.303, $CHCl_3$).
Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 98:2, 214 nm, 0.7 mL/min, t_{major} = 23.32 min, t_{minor} = 28.22 min).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.70-7.66 (m, 2H), 7.45-7.38 (m, 3H), 7.26-7.17 (m, 4H), 7.17-7.12 (m, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.03-6.99 (m, 2H), 5.42 (d, *J* = 4.8 Hz, 1H), 4.31-4.26 (m, 1H), 3.08-3.00 (m, 2H), 2.75-2.67 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 203.05, 153.26, 150.87, 139.07, 133.44, 129.21, 129.17, 128.93, 128.64, 128.60, 127.18, 126.43, 124.87, 121.13, 120.27, 120.25, 96.40, 61.22, 34.51, 31.28.
HRMS (ESI): exact mass calcd for $C_{24}H_{18}BrO_2$: m/z 417.0485 [M-H]$^-$, found: m/z 417.0488.



3o

This compound was prepared according to the general procedure B as a pale-yellow oil (29.4 mg, 83% yield in 0.1 mmol scale) and was isolated as a mixture of diastereoisomers (d.r. = 3.5: 1). Spectral data for the main isomer is reported.
$[\alpha]_D^{25.0}$ = 11.0 (*c* 0.223, $CHCl_3$).
Enantiomeric excess was found to be 92% by chiral HPLC (ChiralPak IB-3 & IC column, hexane/i-PrOH = 98:2, 214 nm, 0.7 mL/min, t_{major} = 21.52 min, t_{minor} = 23.77 min).
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.43-7.36 (m, 3H), 7.23-7.17 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.06-6.98 (m, 5H), 5.38 (d, *J* = 4.3 Hz, 1H), 4.31-4.28 (m, 1H), 3.11-3.01 (m, 2H), 2.71 (d, *J* = 12.0 Hz, 1H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 203.61, 151.11, 150.63, 139.66, 134.07, 133.52, 129.02, 128.96, 128.90, 128.55, 128.51, 128.10, 126.29, 124.92, 120.54, 116.78, 96.03, 61.40, 35.04, 31.12, 20.99.
HRMS (ESI): exact mass calcd for $C_{25}H_{21}O_2$: m/z 353.1547 [M-H]$^-$, found: m/z 353.1547.



3p

This compound was prepared according to the general procedure B as a pale-yellow oil (46.2 mg, 90% yield, 98% *ee*, d.r. = 21: 1, in 0.1 mmol scale; 4.874 g, 93% yield, 98% *ee*, d.r. > 40: 1, in 10.0 mmol scale) and was isolated as a mixture of diastereoisomers. Spectral data for the main isomer is reported.

NOTE: The ***A4*** and ***C2*** could be could be recovered by column chromatography on silica gel (MeOH/CH2Cl2 = 1: 100) and these two organocatalysts could be further used without noticeable loss of reactivity.

$[\alpha]_D^{25.0}$ = 88.5 (*c* 0.265, $CHCl_3$).

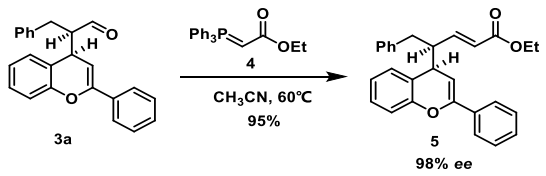
Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak OD-H column, hexane/i-PrOH = 9:1, 214 nm, 0.7 mL/min, t_{major} = 9.08 min, t_{minor} = 14.42 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.70 (d, *J* = 6.9 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.36-7.32 (m, 1H), 6.25 (s, 1H), 5.42 (d, *J* = 5.4 Hz, 1H), 4.31-4.27 (m, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.50-3.41 (m, 2H), 2.87-2.80 (m, 1H), 1.81-1.71 (m, 1H), 1.57-1.40 (m, 2H), 1.38-1.29 (m, 1H), 0.80 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 204.63, 152.41, 152.31, 150.57, 147.27, 133.90, 131.65, 128.75, 128.48, 124.81, 104.03, 97.40, 91.75, 62.91, 61.54, 57.17, 56.56, 55.72, 31.15, 30.77, 25.99, 21.36, 18.34, -5.25, -5.28.

HRMS (ESI): exact mass calcd for $C_{29}H_{39}O_6Si$: m/z 511.2510 $[M-H]^-$, found: m/z 511.2509.

5. Derivatization of Flavonoid 3a and 3p



The *aldehyde **3a*** (34.0 mg, 0.1 mmol, 1.0 equiv.) and *Ethyl (triphenylphosphoranylidene)acetate **4*** (52.2 mg, 0.15 mmol, 1.5 equiv.) were stirred in *CH_3CN* (1 mL) at 60℃ until all *aldehyde **3a*** was consumed completely as judged by TLC. The reactions were cooled down to room temperature, concentrated *in vacuo* and purified by flash column chromatography (ethyl acetate/petroleum ether = 1/40, v/v) to afford *unsaturated ester**5*** (38.8 mg, 95% yield) as a colorless oil.

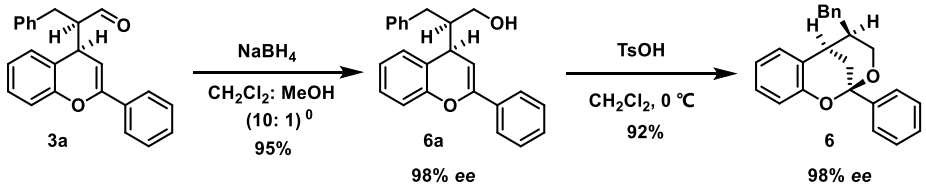
$[\alpha]_D^{25.0}$ = 86.0 (*c* 0.168, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H & OD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 16.29 min, t_{minor} = 18.12 min).

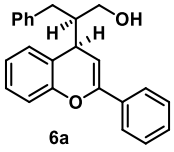
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.74 (m, 2H), 7.46-7.42 (m, 2H), 7.41-7.37 (m, 1H), 7.29-7.23 (m, 2H), 7.21-7.17 (m, 2H), 7.16-7.10 (m, 3H), 7.05-6.99 (m, 1H), 6.98-6.95 (m, 2H), 5.74 (dd, *J* = 15.7, 1.0 Hz, 1H), 5.56 (d, *J* = 4.9 Hz, 1H), 4.22-4.14 (m, 2H), 3.92 (t, *J* = 4.3 Hz, 1H), 2.95-2.89 (m, 1H), 2.79 (dd, *J* = 14.1, 3.6 Hz, 1H), 2.64 (dd, *J* = 14.1, 10.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.35, 152.67, 150.90, 149.28, 139.86, 134.21, 128.95, 128.83, 128.51, 128.34, 128.23, 128.17, 126.06, 124.95, 123.85, 123.13, 121.85, 116.84, 96.60, 60.40, 52.42, 39.85, 35.66, 14.35.

HRMS (ESI): exact mass calcd for $C_{28}H_{27}O_3$: m/z 411.1955 $[M+H]^+$, found: m/z 411.1954.



To a solution of *aldehyde **3a*** (170.0 mg, 0.5 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2/MeOH(10/1) 11 mL was added *$NaBH_4$* (38.0 mg, 1.0 mmol, 2.0 equiv.) portionwise at 0 ^oC. The resulting mixture was stirred until all *aldehyde **3a*** were consumed completely as judged by TLC. The reaction mixture was quenched with saturated $NaHCO_3$ carefully and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/40 to 1/20, v/v) to afford the *alcohol **6a*** (162.4 mg, 95%) as a colorless oil.



$[\alpha]_D^{25.0}$ = 5.2 (*c* 0.413, $CHCl_3$).

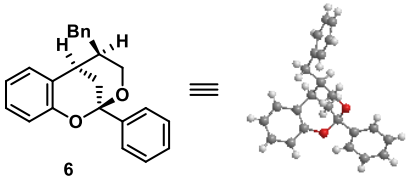
Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 80:20, 214 nm, 0.7 mL/min, t_{minor} = 5.89 min, t_{major} = 7.21 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.43-7.38 (m, 2H), 7.37-7.32 (m, 1H), 7.26-7.15 (m, 4H), 7.13-7.05 (m, 3H), 6.97 (d, *J* = 7.3 Hz, 2H), 5.59 (d, *J* = 4.8 Hz, 1H), 4.09-4.04 (m, 1H), 3.70-3.57 (m, 2H), 2.68-2.59 (m, 1H), 2.37 (t, *J* = 12.3 Hz, 1H), 2.28-2.18 (m, 1H), 1.32 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.84, 150.34, 140.84, 134.43, 128.93, 128.63, 128.49, 128.42, 128.27, 127.72, 125.99, 124.82, 123.79, 123.24, 116.65, 97.37, 62.89, 51.43, 35.47, 33.84.

HRMS (ESI): exact mass calcd for $C_{24}H_{23}O_2$: m/z 343.1693 $[M+H]^+$, found: m/z 343.1694.

To a solution of *alcohol* ***6a*** (68.4 mg, 0.2 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 2 mL was added *p-Toluenesulfonic acid* (34.4 mg, 0.2 mmol, 1.0 equiv.) portionwise at 0 °C. The resulting mixture was stirred until all *alcohol* ***6a*** were consumed completely as judged by TLC. The reaction mixture was quenched with saturated $NaHCO_3$ carefully and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/60, v/v) to afford ***6*** (62.7 mg, 92%) as a white solid.



6

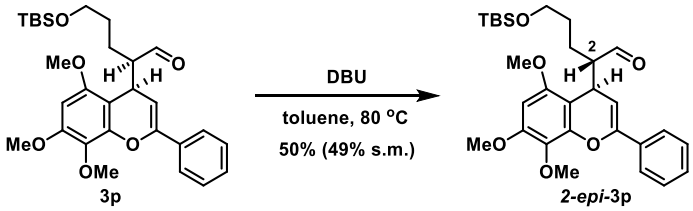
$[\alpha]_D^{25.0}$ = 13.6 (*c* 0.220, $CHCl_3$).

Enantiomeric excess was found to be 98% by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH = 95:5, 214 nm, 0.7 mL/min, t_{major} = 8.12 min, t_{minor} = 9.42 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.40-7.16 (m, 9H), 7.12-7.03 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 3.83-3.75 (m, 1H), 3.48 (t, *J* = 11.5 Hz, 1H), 3.14-3.06 (m, 1H), 2.58-2.49 (m, 2H), 2.30-2.20 (m, 2H), 2.12-2.04 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.26, 142.48, 139.35, 129.94, 129.03, 128.69, 128.50, 128.40, 128.24, 126.40, 125.47, 122.36, 120.31, 115.62, 98.22, 64.94, 41.08, 37.59, 36.33, 34.88.

HRMS (ESI): exact mass calcd for $C_{24}H_{23}O_2$: m/z 343.1693 $[M+H]^+$, found: m/z 343.1693.



To a solution of *aldehyde* ***3p*** (512 mg, 1.0 mmol, 1.0 equiv.) in anhydrous toluene 5 mL was added *DBU* (30.4 mg, 0.2 mmol, 0.2 equiv.) at 80 °C. The resulting mixture was stirred until the ratio of ***3p*** and ***2-epi-3p*** not changed anymore as judged by TLC. The reactions were cooled down to room temperature, concentrated *in vacuo* and purified by flash column chromatography (ethyl acetate/petroleum ether = 1/50 to 1/30, v/v) to afford ***3p*** (249 mg, 49%) as a colorless oil and (ethyl acetate/petroleum ether = 1/10, v/v) to afford ***2-epi-3p*** (254 mg, 50%) as a colorless oil.

$[\alpha]_D^{25.0}$ = 89.4 (*c* 0.413, $CHCl_3$).

Enantiomeric excess was found to be 95% by chiral HPLC (ChiralPak OD-H column, hexane/i-PrOH = 9:1, 214 nm, 0.7 mL/min, t_{major} = 10.76 min, t_{minor} = 19.26 min).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (d, *J* = 2.1 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.42-7.36 (m, 2H), 7.36-7.31 (m, 1H), 6.24 (s, 1H), 5.61 (d, *J* = 5.5 Hz, 1H), 4.12-4.09 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.78 (s, 3H), 3.65-3.55 (m, 2H), 2.60-2.56 (m, 1H), 1.73-1.64 (m, 1H), 1.63-1.50 (m, 3H), 0.86 (s, 9H), 0.01 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.49, 152.48, 152.31, 150.24, 146.91, 133.70, 131.48, 128.76, 128.43, 124.76, 103.53, 98.34, 91.47, 77.36, 62.87, 61.47, 57.38, 56.44, 55.37, 31.38, 30.79, 25.98, 21.71, 18.33, -5.25.

HRMS (ESI): exact mass calcd for $C_{29}H_{39}O_6Si$: m/z 511.2510 $[M-H]^-$, found: m/z 511.2508.

Table S4 The Condition Optimization for the Isomerization of Compound 3p

Entry	Conditions	Results
1	*t*-BuOK, *t*-BuOH, 40 ℃	Complex
2	K_2CO_3, MeOH, 40 ℃	32% (55% S.M.)
3	DBU, toluene, 40 ℃	48% (51% S.M.)
4	**DBU, toluene, 80 ℃**	**50% (49% S.M.)**
5	DBU, toluene, 120 ℃	46% (43% S.M.)
6	Basic Al_2O_3, toluene, 40 ℃	48% (45% S.M.)
7	Basic Al_2O_3, CH_2Cl_2, 40 ℃	47% (46% S.M.)
8	LDA, THF, -78 ℃ to rt	22% (58% S.M.)
9	LiHMDS, THF, -78 ℃ to rt	25% (51% S.M.)

6. X-ray Crystal Data for Compound 6

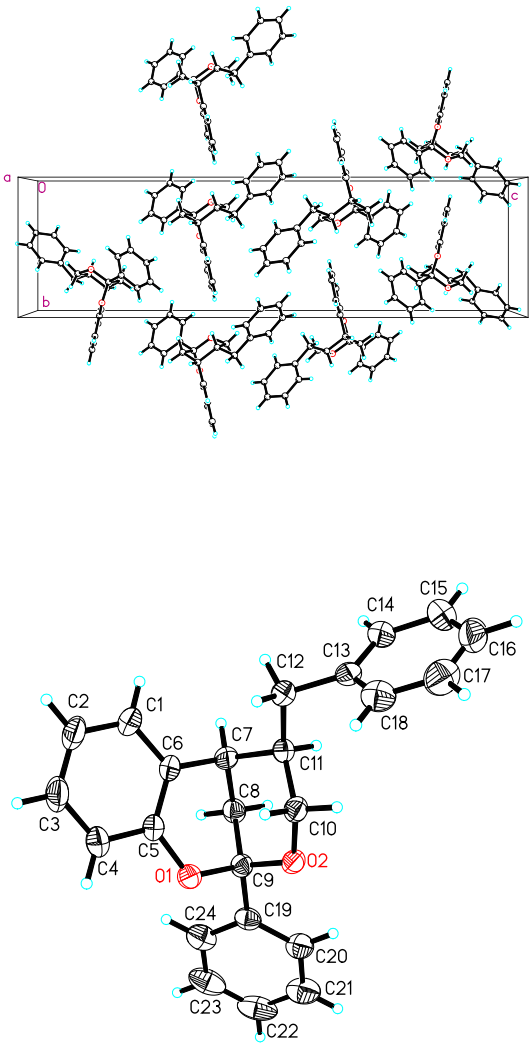


Figure S1. ORTEP of Compound 6

Table S5. Crystal data and structure refinement for compound 6

Identification code	11
Empirical formula	C24 H22 O2
Formula weight	342.42
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 6.87350(10) A alpha = 90 deg.
	b = 8.75670(10) A beta = 90 deg.
	c = 31.8081(4) A gamma = 90 deg.
Volume	1914.50(4) A^3
Z, Calculated density	4, 1.188 Mg/m^3
Absorption coefficient	0.581 mm^-1
F(000)	728
Crystal size	0.32 x 0.28 x 0.12 mm
Theta range for data collection	5.24 to 68.10 deg.
Limiting indices	-7<=h<=6, -9<=k<=10, -37<=l<=37
Reflections collected / unique	9180 / 3341 [R(int) = 0.0357]
Completeness to theta = 68.10	96.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7530 and 0.5067
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3341 / 0 / 236
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0935
R indices (all data)	R1 = 0.0401, wR2 = 0.0965
Absolute structure parameter	-0.1(2)
Extinction coefficient	0.0080(5)
Largest diff. peak and hole	0.114 and -0.131 e.A^-3

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for compound 6

	x	y	z	U(eq)
O(1)	4709(2)	9198(1)	1495(1)	56(1)
O(2)	4225(2)	6717(1)	1257(1)	50(1)
C(1)	11(3)	11014(2)	1281(1)	76(1)
C(2)	627(4)	12483(2)	1201(1)	90(1)
C(3)	2572(4)	12840(2)	1227(1)	83(1)
C(4)	3898(3)	11728(2)	1328(1)	67(1)
C(5)	3272(3)	10248(2)	1401(1)	53(1)
C(6)	1313(3)	9860(2)	1382(1)	56(1)
C(7)	716(2)	8251(2)	1485(1)	55(1)
C(8)	2150(2)	7644(2)	1807(1)	53(1)

C(9)	4162(2)	7666(2)	1613(1)	47(1)
C(10)	2821(2)	7077(2)	937(1)	53(1)
C(11)	758(2)	7180(2)	1102(1)	52(1)
C(12)	-664(3)	7639(2)	753(1)	65(1)
C(13)	-1060(3)	6370(2)	445(1)	55(1)
C(14)	-2560(3)	5373(2)	517(1)	68(1)
C(15)	-2957(4)	4208(3)	238(1)	91(1)
C(16)	-1842(5)	4020(3)	-113(1)	97(1)
C(17)	-333(4)	4978(3)	-183(1)	92(1)
C(18)	48(3)	6151(3)	87(1)	75(1)
C(19)	5717(2)	7125(2)	1914(1)	53(1)
C(20)	6595(3)	5721(2)	1873(1)	65(1)
C(21)	7980(3)	5236(3)	2158(1)	85(1)
C(22)	8488(3)	6142(4)	2490(1)	93(1)
C(23)	7589(3)	7534(4)	2540(1)	91(1)
C(24)	6215(3)	8032(3)	2253(1)	73(1)
H(1A)	-1310	10791	1267	91
H(2A)	-272	13232	1129	107
H(3A)	2988	13834	1176	99
H(4A)	5214	11967	1347	81
H(7A)	-594	8256	1606	66
H(8A)	2125	8277	2057	64
H(8B)	1802	6610	1886	64
H(10A)	2875	6300	720	63
H(10B)	3168	8045	809	63
H(11A)	384	6160	1200	63
H(12A)	-1883	7955	880	78
H(12B)	-135	8508	602	78
H(14A)	-3319	5483	757	82
H(15A)	-3990	3548	290	109
H(16A)	-2117	3240	-303	117
H(17A)	452	4837	-418	111
H(18A)	1072	6814	30	90
H(20A)	6252	5090	1650	78
H(21A)	8569	4288	2124	102
H(22A)	9431	5820	2680	112
H(23A)	7908	8146	2769	110
H(24A)	5626	8979	2288	88

Table S7. Bond lengths [A] and angles [deg] for compound 6

O(1)-C(5)	1.381(2)	O(2)-C(9)-C(19)	107.66(13)
O(1)-C(9)	1.444(2)	O(1)-C(9)-C(19)	105.80(13)
O(2)-C(9)	1.4044(19)	O(2)-C(9)-C(8)	110.41(13)

O(2)-C(10)	1.4378(19)	O(1)-C(9)-C(8)	110.84(14)
C(1)-C(2)	1.377(3)	C(19)-C(9)-C(8)	112.62(13)
C(1)-C(6)	1.388(3)	O(2)-C(10)-C(11)	113.37(14)
C(1)-H(1A)	0.9300	O(2)-C(10)-H(10A)	108.9
C(2)-C(3)	1.376(3)	C(11)-C(10)-H(10A)	108.9
C(2)-H(2A)	0.9300	O(2)-C(10)-H(10B)	108.9
C(3)-C(4)	1.372(3)	C(11)-C(10)-H(10B)	108.9
C(3)-H(3A)	0.9300	H(10A)-C(10)-H(10B)	107.7
C(4)-C(5)	1.386(2)	C(10)-C(11)-C(12)	111.22(15)
C(4)-H(4A)	0.9300	C(10)-C(11)-C(7)	109.16(14)
C(5)-C(6)	1.390(3)	C(12)-C(11)-C(7)	113.68(14)
C(6)-C(7)	1.504(2)	C(10)-C(11)-H(11A)	107.5
C(7)-C(8)	1.517(2)	C(12)-C(11)-H(11A)	107.5
C(7)-C(11)	1.536(2)	C(7)-C(11)-H(11A)	107.5
C(7)-H(7A)	0.9800	C(13)-C(12)-C(11)	113.16(14)
C(8)-C(9)	1.514(2)	C(13)-C(12)-H(12A)	108.9
C(8)-H(8A)	0.9700	C(11)-C(12)-H(12A)	108.9
C(8)-H(8B)	0.9700	C(13)-C(12)-H(12B)	108.9
C(9)-C(19)	1.512(2)	C(11)-C(12)-H(12B)	108.9
C(10)-C(11)	1.514(2)	H(12A)-C(12)-H(12B)	107.8
C(10)-H(10A)	0.9700	C(14)-C(13)-C(18)	117.65(19)
C(10)-H(10B)	0.9700	C(14)-C(13)-C(12)	119.79(18)
C(11)-C(12)	1.533(2)	C(18)-C(13)-C(12)	122.56(19)
C(11)-H(11A)	0.9800	C(13)-C(14)-C(15)	120.8(2)
C(12)-C(13)	1.507(3)	C(13)-C(14)-H(14A)	119.6
C(12)-H(12A)	0.9700	C(15)-C(14)-H(14A)	119.6
C(12)-H(12B)	0.9700	C(16)-C(15)-C(14)	120.3(2)
C(13)-C(14)	1.370(3)	C(16)-C(15)-H(15A)	119.8
C(13)-C(18)	1.382(3)	C(14)-C(15)-H(15A)	119.8
C(14)-C(15)	1.379(3)	C(17)-C(16)-C(15)	119.4(2)
C(14)-H(14A)	0.9300	C(17)-C(16)-H(16A)	120.3
C(15)-C(16)	1.365(4)	C(15)-C(16)-H(16A)	120.3
C(15)-H(15A)	0.9300	C(16)-C(17)-C(18)	120.6(2)
C(16)-C(17)	1.353(4)	C(16)-C(17)-H(17A)	119.7
C(16)-H(16A)	0.9300	C(18)-C(17)-H(17A)	119.7
C(17)-C(18)	1.366(3)	C(17)-C(18)-C(13)	121.2(2)
C(17)-H(17A)	0.9300	C(17)-C(18)-H(18A)	119.4
C(18)-H(18A)	0.9300	C(13)-C(18)-H(18A)	119.4
C(19)-C(20)	1.376(3)	C(20)-C(19)-C(24)	118.68(19)
C(20)-C(19)-C(9)	121.94(17)	C(21)-C(20)-H(20A)	119.5
C(24)-C(19)-C(9)	119.31(18)	C(22)-C(21)-C(20)	120.4(3)
C(19)-C(20)-C(21)	120.9(2)	C(22)-C(21)-H(21A)	119.8
C(19)-C(20)-H(20A)	119.5	C(20)-C(21)-H(21A)	119.8

C(21)-C(22)-C(23)	119.3(2)	C(24)-C(23)-H(23A)	119.7
C(21)-C(22)-H(22A)	120.4	C(19)-C(24)-C(23)	120.2(2)
C(23)-C(22)-H(22A)	120.4	C(19)-C(24)-H(24A)	119.9
C(22)-C(23)-C(24)	120.6(3)	C(23)-C(24)-H(24A)	119.9
C(22)-C(23)-H(23A)	119.7		

Table S8. Torsion angles [deg] for compound 6

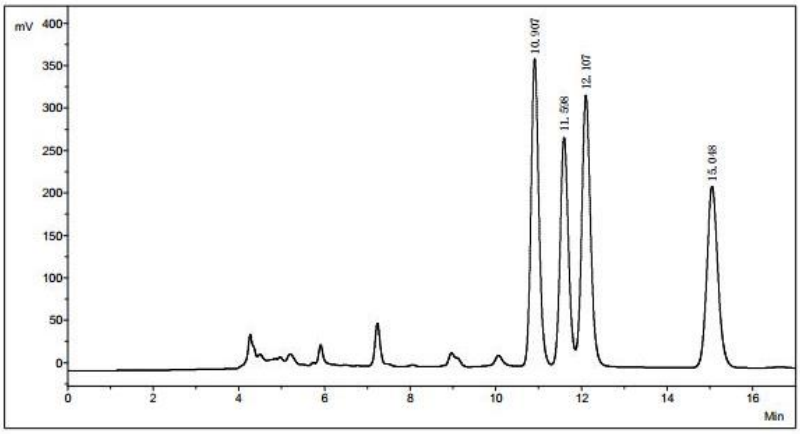
C(6)-C(1)-C(2)-C(3)	-1.1(4)
C(1)-C(2)-C(3)-C(4)	0.8(4)
C(2)-C(3)-C(4)-C(5)	0.3(4)
C(9)-O(1)-C(5)-C(4)	174.29(16)
C(9)-O(1)-C(5)-C(6)	-5.6(2)
C(3)-C(4)-C(5)-O(1)	179.02(19)
C(3)-C(4)-C(5)-C(6)	-1.1(3)
C(2)-C(1)-C(6)-C(5)	0.3(3)
C(2)-C(1)-C(6)-C(7)	178.1(2)
O(1)-C(5)-C(6)-C(1)	-179.37(17)
C(4)-C(5)-C(6)-C(1)	0.7(3)
O(1)-C(5)-C(6)-C(7)	2.8(3)
C(4)-C(5)-C(6)-C(7)	-177.11(18)
C(1)-C(6)-C(7)-C(8)	-146.89(19)
C(5)-C(6)-C(7)-C(8)	30.8(2)
C(1)-C(6)-C(7)-C(11)	94.0(2)
C(5)-C(6)-C(7)-C(11)	-88.2(2)
C(6)-C(7)-C(8)-C(9)	-60.74(18)
C(11)-C(7)-C(8)-C(9)	61.64(17)
C(10)-O(2)-C(9)-O(1)	-65.69(16)
C(10)-O(2)-C(9)-C(19)	179.81(13)
C(10)-O(2)-C(9)-C(8)	56.51(17)
C(5)-O(1)-C(9)-O(2)	95.67(16)
C(5)-O(1)-C(9)-C(19)	-148.64(14)
C(5)-O(1)-C(9)-C(8)	-26.3(2)
C(7)-C(8)-C(9)-O(2)	-61.37(18)
C(7)-C(8)-C(9)-O(1)	59.95(17)
C(7)-C(8)-C(9)-C(19)	178.26(14)
C(9)-O(2)-C(10)-C(11)	-52.27(18)
O(2)-C(10)-C(11)-C(12)	177.34(13)
O(2)-C(10)-C(11)-C(7)	51.12(19)
C(6)-C(7)-C(11)-C(10)	62.24(19)
C(8)-C(7)-C(11)-C(10)	-56.44(17)
C(6)-C(7)-C(11)-C(12)	-62.6(2)
C(8)-C(7)-C(11)-C(12)	178.76(14)
C(10)-C(11)-C(12)-C(13)	73.6(2)

C(7)-C(11)-C(12)-C(13)	-162.73(16)
C(11)-C(12)-C(13)-C(14)	89.7(2)
C(11)-C(12)-C(13)-C(18)	-89.7(2)
C(18)-C(13)-C(14)-C(15)	-0.9(3)
C(12)-C(13)-C(14)-C(15)	179.6(2)
C(13)-C(14)-C(15)-C(16)	0.8(4)
C(14)-C(15)-C(16)-C(17)	0.6(4)
C(15)-C(16)-C(17)-C(18)	-1.8(4)
C(16)-C(17)-C(18)-C(13)	1.6(4)
C(14)-C(13)-C(18)-C(17)	-0.3(3)
C(12)-C(13)-C(18)-C(17)	179.17(19)
O(2)-C(9)-C(19)-C(20)	-15.2(2)
O(1)-C(9)-C(19)-C(20)	-132.06(16)
C(8)-C(9)-C(19)-C(20)	106.72(18)
O(2)-C(9)-C(19)-C(24)	167.80(15)
O(1)-C(9)-C(19)-C(24)	50.97(19)
C(8)-C(9)-C(19)-C(24)	-70.3(2)
C(24)-C(19)-C(20)-C(21)	-1.4(3)
C(9)-C(19)-C(20)-C(21)	-178.41(17)
C(19)-C(20)-C(21)-C(22)	0.7(3)
C(20)-C(21)-C(22)-C(23)	0.8(3)
C(21)-C(22)-C(23)-C(24)	-1.4(3)
C(20)-C(19)-C(24)-C(23)	0.8(3)
C(9)-C(19)-C(24)-C(23)	177.85(16)
C(22)-C(23)-C(24)-C(19)	0.6(3)

7. HPLC Charts for Enantioenriched Flavonoids

HPLC Report

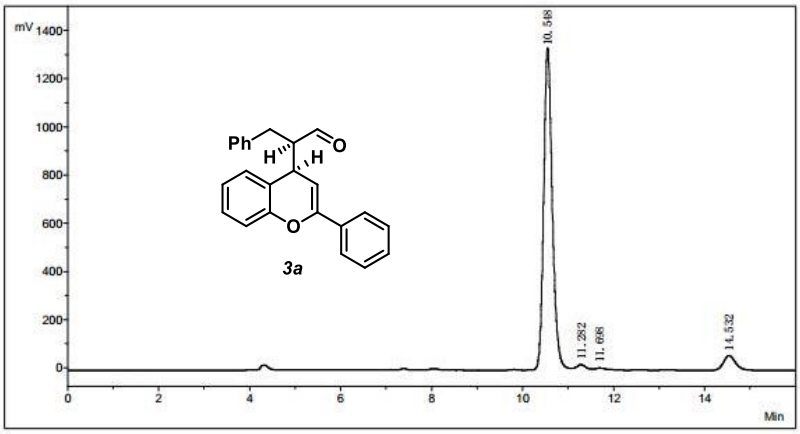
Sample Name:HJD-V-35 AD-H 214 955 0.7 Recording Time:2016.05.07 17:06



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		10.907	361842.1	4583935.2	27.9153
2	2		11.598	269666.2	3622589.9	22.0609
3	3		12.107	319724.9	4561087.6	27.7762
4	4		15.048	210421.0	3653237.4	22.2476
Total				1161654.1	16420850.2	100.0000

HPLC Report

Sample Name:HJD-V-94-1 AD-H 214 955 0.7 Recording Time:2016.10.10 22:15



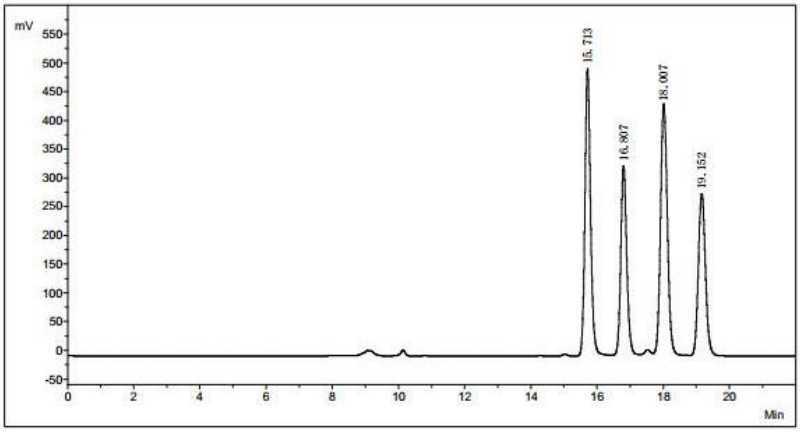
98% ee , dr = 11.92: 1

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		10.548	1336831.9	17691878.3	91.3483
2	2		11.282	23211.7	355327.7	1.8347
3	3		11.698	9141.2	174517.3	0.9011
4	4		14.532	61383.9	1145767.9	5.9159
Total				1430568.8	19367491.2	100.0000

Figure S2 HPLC Charts of Compound 3a

HPLC Report

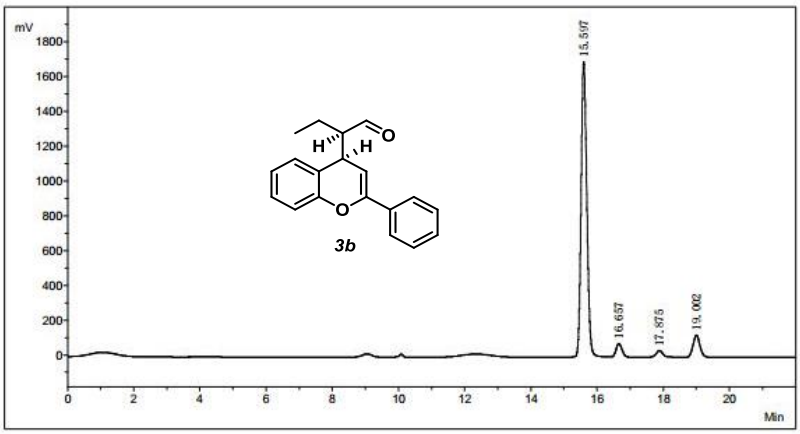
Sample Name:HJD-V-96-1 AD-H+IC 214 955 0.7 Recording Time:2016.10.19 21:03



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		15.713	496354.8	5864903.1	29.3217
2	2		16.807	327904.6	4095677.5	20.4764
3	3		18.007	428538.1	5976005.7	29.8771
4	4		19.152	278536.8	4065347.8	20.3248
Total				1531334.3	20001934.1	100.0000

HPLC Report

Sample Name:HJD-VI-1-1 AD-H+IC 214 955 0.7 Recording Time:2016.10.20 13:50



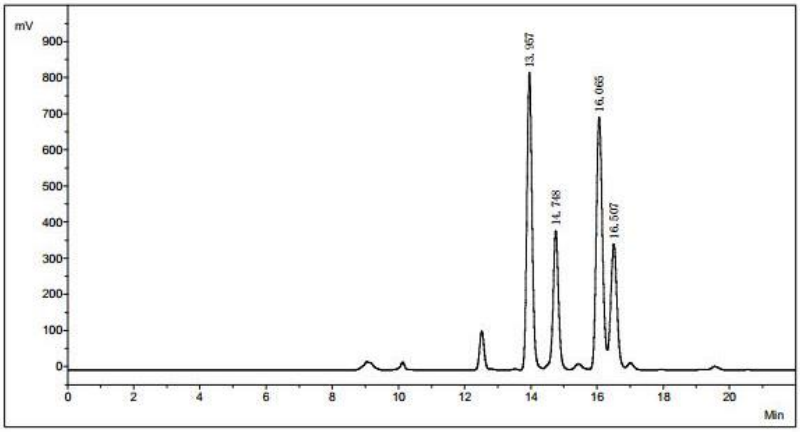
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		15.597	1694723.0	19930525.2	86.7424
2	2		16.657	75285.0	898347.6	3.9098
3	3		17.875	34837.8	447406.2	1.9472
4	4		19.002	122065.4	1700391.2	7.4005
Total				1926911.2	22976670.2	100.0000

96% ee , dr = 7.85: 1

Figure S3 HPLC Charts of Compound 3b

HPLC Report

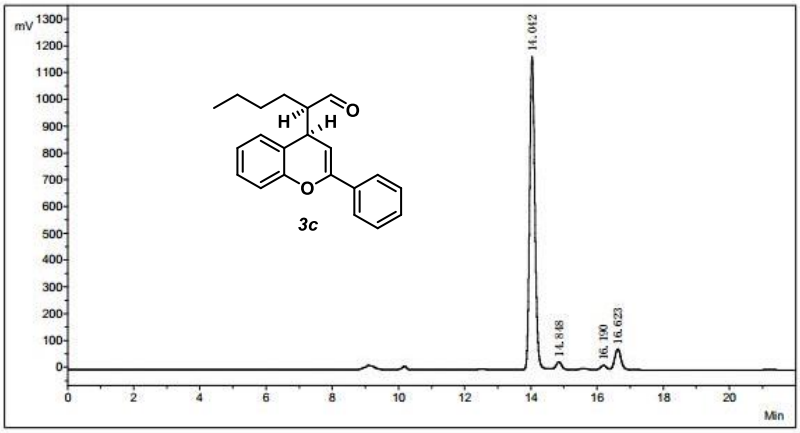
Sample Name:HJD-V-96-3 AD-H+IC 214 955 0.7 Recording Time:2016.10.19 21:26



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		13.957	819090.2	8687684.3	33.2112
2	2		14.748	382617.0	4408930.3	16.8544
3	3		16.065	695429.6	8646910.0	33.0554
4	4		16.507	342127.3	4415353.4	16.8790
Total				2239264.2	26158877.9	100.0000

HPLC Report

Sample Name:HJD-VI-1-3 AD-H+IC 214 955 0.7 Recording Time:2016.10.19 16:53



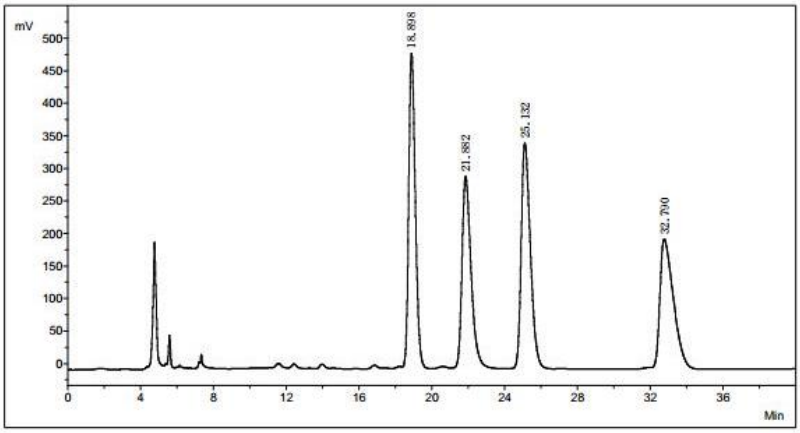
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		14.042	1166509.9	12470805.4	89.4385
2	2		14.848	26732.3	274152.2	1.9662
3	3		16.190	15686.4	192069.8	1.3775
4	4		16.623	77878.4	1006414.6	7.2178
Total				1286807.0	13943442.0	100.0000

97% ee, dr = 9.88: 1

Figure S4 HPLC Charts of Compound 3c

HPLC Report

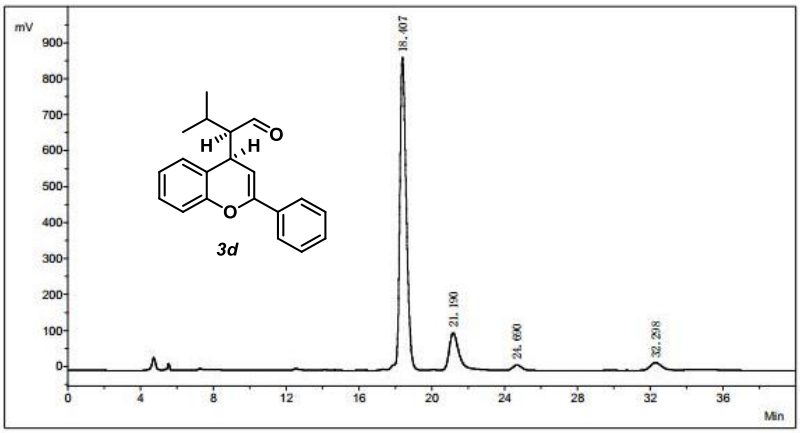
Sample Name:HJD-V-96-2 AD-H 214 991 0.7 Recording Time:2016.10.20 17:04



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		18.898	482741.8	12106686.7	27.1811
2	2		21.882	295144.3	10180238.5	22.8560
3	3		25.132	346659.7	12124210.7	27.2204
4	4		32.790	198119.7	10129727.5	22.7425
Total				1322665.5	44540863.5	100.0000

HPLC Report

Sample Name:HJD-VI-1-2 AD-H 214 991 0.7 Recording Time:2016.10.20 17:46



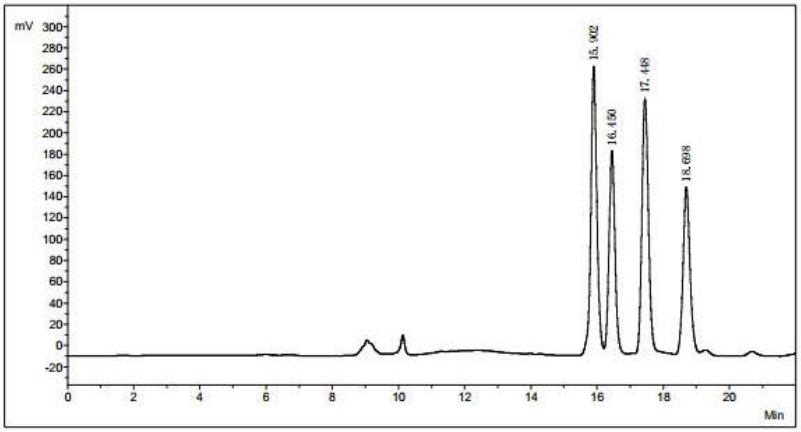
95% ee, dr = 4.56 :1

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	2		18.407	869193.7	21479032.6	80.1582
2	3		21.190	104422.3	3912226.5	14.6001
3	4		24.690	15056.4	495370.5	1.8487
4	5		32.298	21133.3	909176.5	3.3930
Total				1009805.8	26795806.2	100.0000

Figure S5 HPLC Charts of Compound 3d

HPLC Report

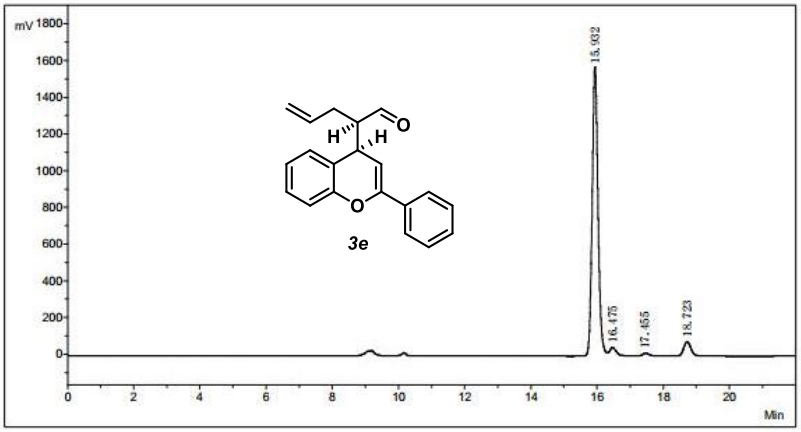
Sample Name:HJD-V-96-5 AD-H+IC 214 955 0.7 Recording Time:2016.10.19 20:39



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		15.902	266335.3	3239307.9	29.7237
2	2		16.450	186414.5	2207130.7	20.2525
3	3		17.448	238983.8	3183093.3	29.2078
4	4		18.698	156544.0	2268550.4	20.8161
Total				848277.6	10898082.4	100.0000

HPLC Report

Sample Name:HJD-VI-1-5 AD-H+IC 214 955 0.7 Recording Time:2016.10.19 17:16



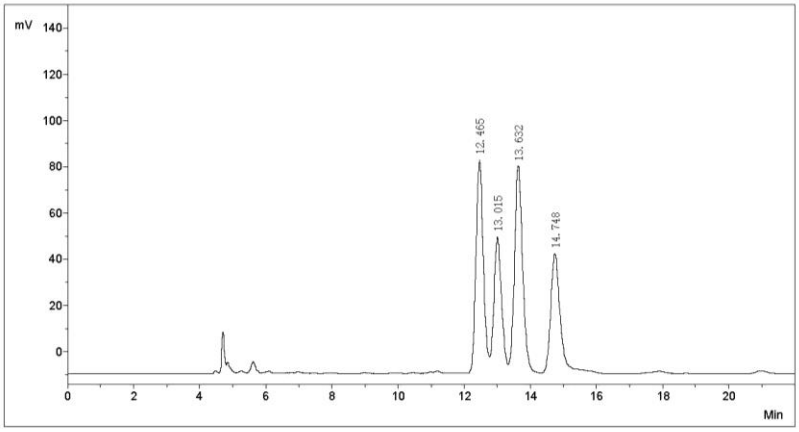
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		15.932	1565743.9	19379302.8	90.8743
2	2		16.475	44784.9	618213.9	2.8990
3	3		17.455	13984.9	179723.0	0.8428
4	4		18.723	78294.7	1148152.2	5.3840
Total				1702808.4	21325391.9	100.0000

98% ee , dr = 11.08: 1

Figure S6 HPLC Charts of Compound 3e

HPLC Report

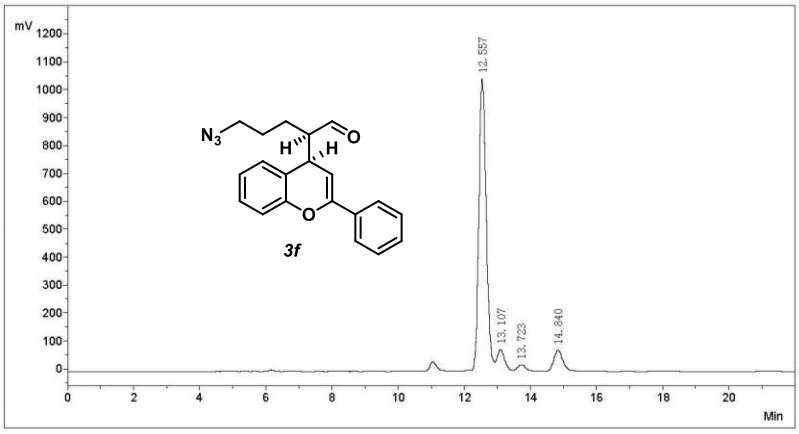
Sample Name:CL-I-63-2 IC 955 214 0.7 Recording Time:2018.03.03 21:07



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		12.465	91877.1	1396298.7	29.3700
2	2		13.015	57848.3	959966.4	20.1921
3	3		13.632	87799.4	1422272.2	29.9163
4	4		14.748	51087.9	975631.8	20.5216
Total				288612.7	4754169.1	100.0000

HPLC Report

Sample Name:CL-I-63-1 IC 955 214 0.7 Recording Time:2018.03.03 21:30



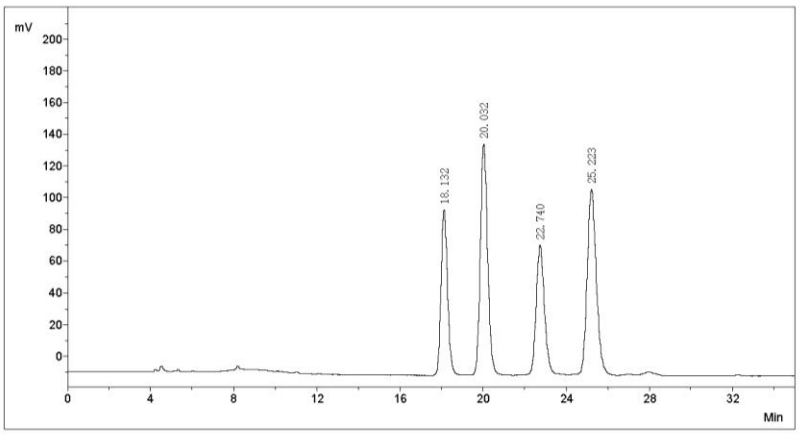
95% ee, dr = 6.17: 1

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		12.557	1047277.3	16092486.2	83.9289
2	2		13.107	76320.4	1264689.6	6.5959
3	3		13.723	23468.2	408483.8	2.1304
4	4		14.840	75575.7	1408299.6	7.3449
Total				1222641.5	19173959.2	100.0000

Figure S7 HPLC Charts of Compound 3f

HPLC Report

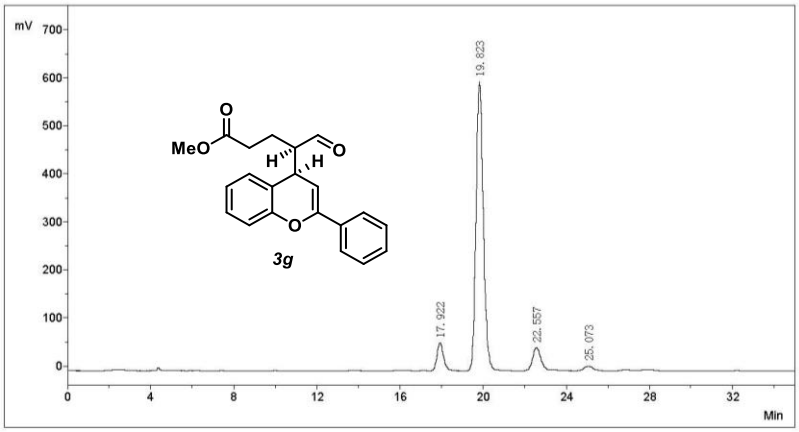
Sample Name:CL-I-72-2 AD-H 955 214 0.7 Recording Time:2018.03.07 16:02



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		18.132	104268.5	2251489.0	19.4421
2	2		20.032	145597.5	3527306.8	30.4591
3	3		22.740	81645.8	2254478.1	19.4679
4	4		25.223	116931.9	3547189.6	30.6308
Total				448443.7	11580463.6	100.0000

HPLC Report

Sample Name:CL-I-72-1 AD-H 955 214 0.7 Recording Time:2018.03.07 16:38



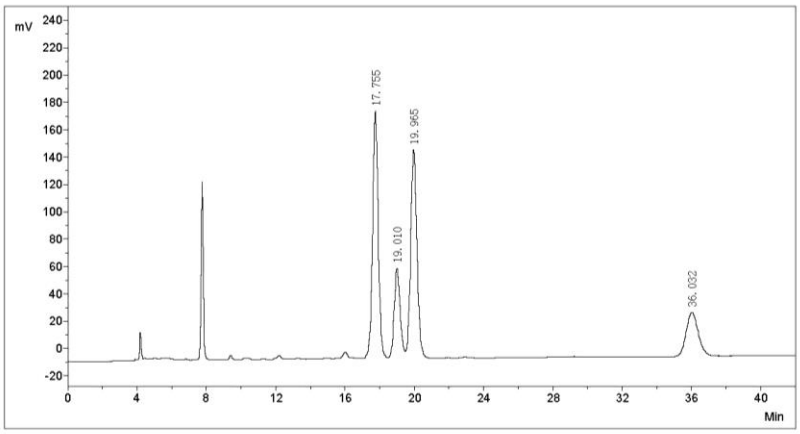
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		17.922	58170.2	1273450.2	7.2914
2	2		19.823	601515.1	14647672.5	83.8683
3	3		22.557	46859.3	1254261.0	7.1815
4	4		25.073	9871.6	289709.3	1.6588
Total				716416.3	17465093.0	100.0000

96% ee, dr = 5.91: 1

Figure S8 HPLC Charts of Compound 3g

HPLC Report

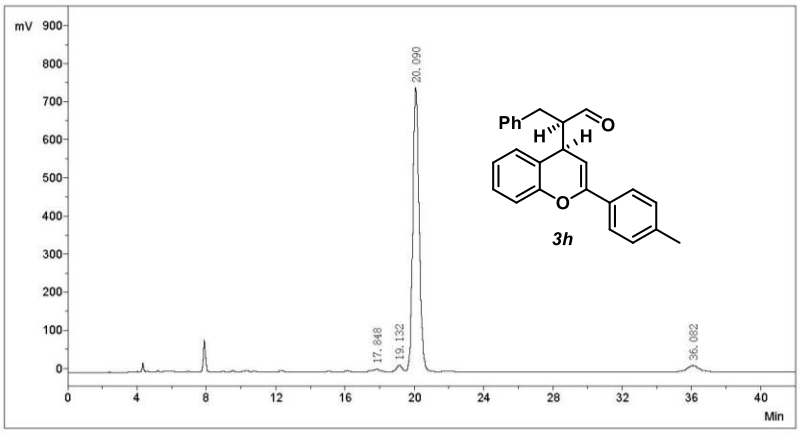
Sample Name:CL-I-49-2 AD-H 214 982 0.7 Recording Time:2018.01.26 18:30



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		17.755	177484.9	3855852.1	35.6040
2	2		19.010	65230.5	1564067.6	14.4422
3	3		19.965	151842.9	3848497.7	35.5361
4	4		36.032	32250.4	1561404.3	14.4176
Total				426808.7	10829821.7	100.0000

HPLC Report

Sample Name:CL-I-49-1 AD-H 214 982 0.7 Recording Time:2018.01.26 19:20



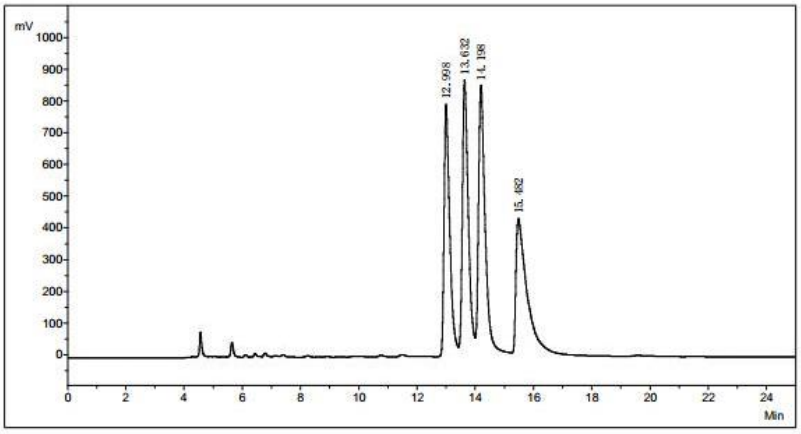
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		17.848	6466.1	216742.5	1.0648
2	2		19.132	16573.2	394070.3	1.9360
3	3		20.090	744263.0	19001745.2	93.3532
4	4		36.082	15702.7	742114.0	3.6459
Total				783005.0	20354672.0	100.0000

98% ee, dr = 16.92: 1

Figure S9 HPLC Charts of Compound 3h

HPLC Report

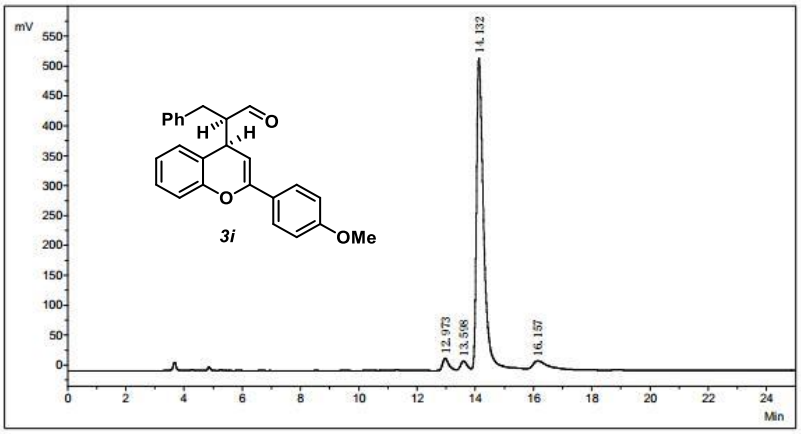
Sample Name:HJD-VI-17-2 IB-3 214 955 0.7 Recording Time:2016.11.17 21:16



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		12.998	793926.7	10817165.9	22.9221
2	2		13.632	868340.6	12760718.2	27.0406
3	3		14.198	848674.2	13014973.7	27.5794
4	4		15.482	423336.2	10598044.3	22.4578
Total				2934277.7	47190902.0	100.0000

HPLC Report

Sample Name:HJD-VI-17-1 IB-3 214 955 0.7 Recording Time:2016.11.21 21:36



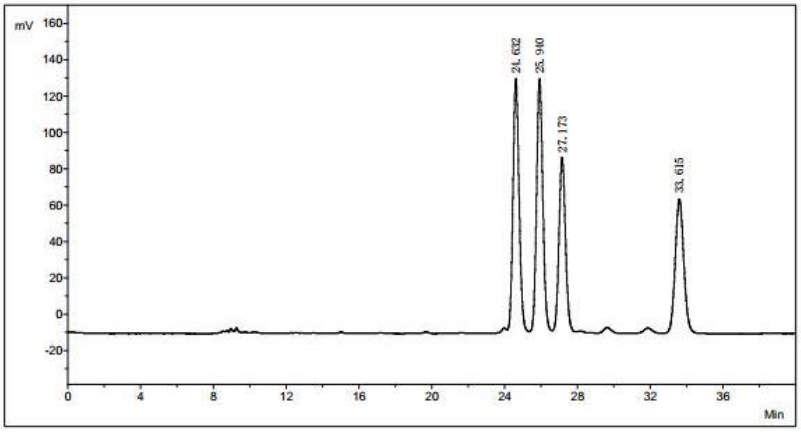
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		12.973	20306.0	309158.0	3.0688
2	2		13.598	15784.0	246067.6	2.4426
3	3		14.132	521499.4	8978980.9	89.1285
4	4		16.157	14964.4	539991.2	5.3601
Total				572553.8	10074197.7	100.0000

95% ee, dr = 10.86: 1

Figure S10 HPLC Charts of Compound 3i

HPLC Report

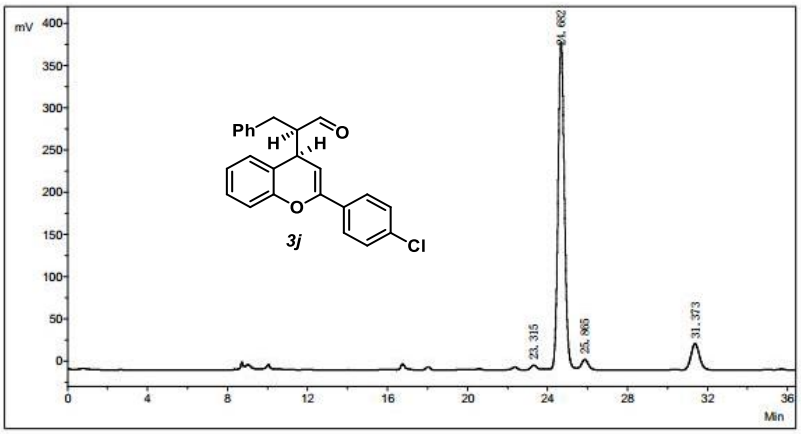
Sample Name:HJD-VI-6-1 AD-H+IC 214 955 0.7 Recording Time:2016.11.02 19:18



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		24.632	139360.3	3285220.6	29.0122
2	2		25.940	139033.9	3289314.4	29.0484
3	3		27.173	95985.0	2377212.3	20.9935
4	4		33.615	73422.2	2371821.9	20.9459
Total				447801.4	11323569.2	100.0000

HPLC Report

Sample Name:HJD-VI-3-1 AD-H+IC 214 955 0.7 Recording Time:2016.10.24 20:37



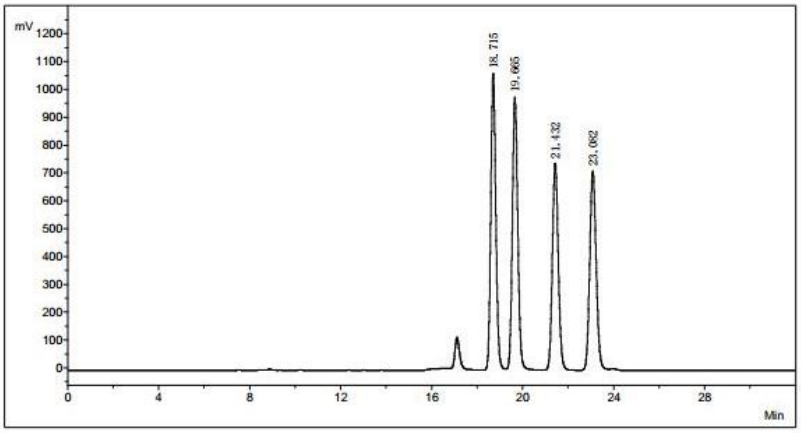
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		23.315	5132.3	96836.7	0.9780
2	2		24.682	388421.5	8586036.4	86.7131
3	3		25.865	12260.9	298301.3	3.0126
4	4		31.373	31187.1	920490.6	9.2963
Total				437001.8	9901665.1	100.0000

98% ee , dr = 7.13: 1

Figure S11 HPLC Charts of Compound 3j

HPLC Report

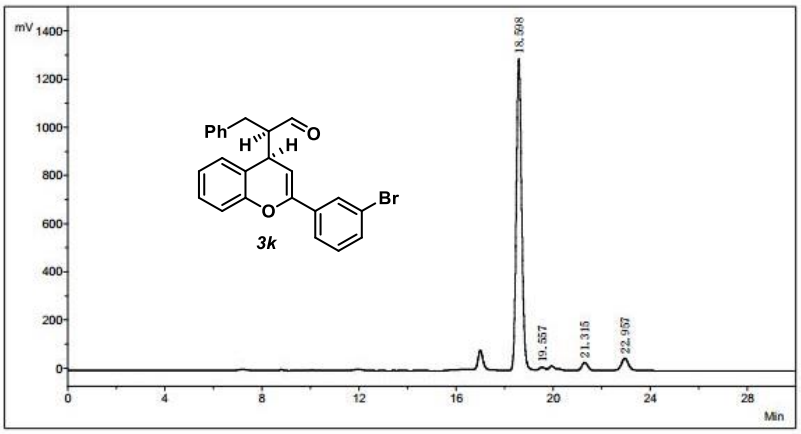
Sample Name:HJD-VI-6-2 AD-H+IC 214 955 0.7 Recording Time:2016.12.05 14:29



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		18.715	1054808.5	16001825.8	27.1351
2	2		19.665	977447.9	15983708.5	27.1044
3	3		21.432	743099.2	13437659.9	22.7869
4	4		23.082	705755.7	13547735.8	22.9736
Total				3481111.5	58970929.8	100.0000

HPLC Report

Sample Name:HJD-VI-3-2 AD-H+IC 214 955 0.7 Recording Time:2016.12.05 12:08



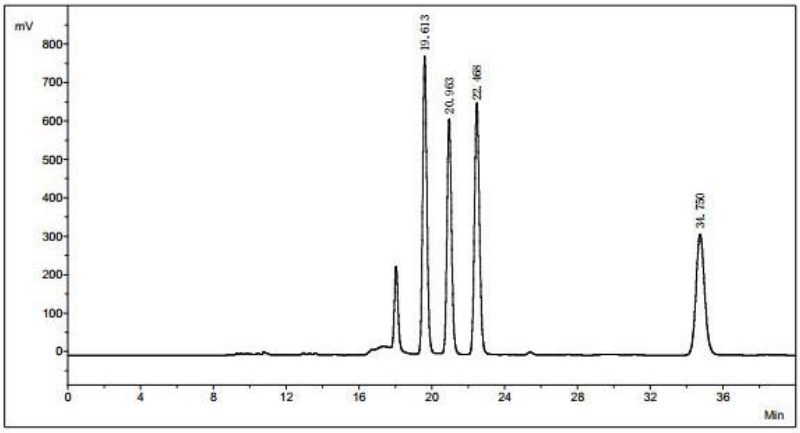
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		18.598	1292273.5	19877983.3	91.5711
2	2		19.557	9317.3	112813.5	0.5197
3	3		21.315	33949.7	604159.7	2.7832
4	4		22.957	51162.9	1112738.9	5.1260
Total				1386703.4	21707695.4	100.0000

99% ee, dr = 11.64: 1

Figure S12 HPLC Charts of Compound 3k

HPLC Report

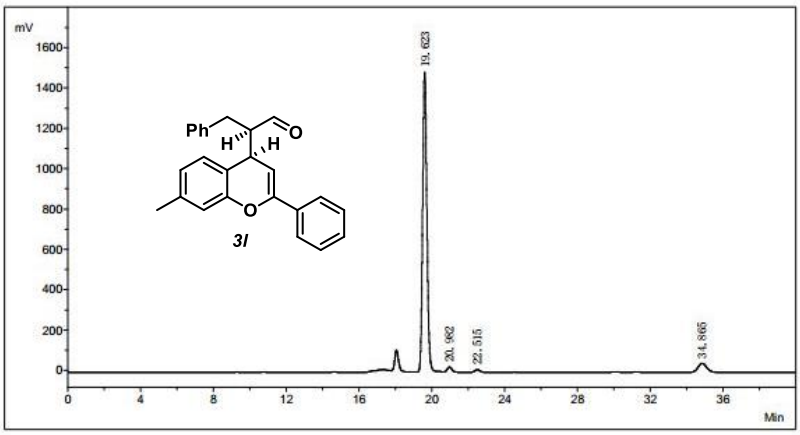
Sample Name:HJD-VI-6-4 AD-H+IC 214 955 0.7 Recording Time:2017.01.13 17:21



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		19.613	773445.7	12465771.9	27.3271
2	2		20.963	608682.0	10390783.1	22.7784
3	3		22.468	647668.2	12435328.1	27.2604
4	4		34.750	315139.1	10324923.8	22.6340
Total				2344934.9	45616806.9	100.0000

HPLC Report

Sample Name:HJD-VI-3-4 AD-H+IC 214 955 0.7 Recording Time:2017.01.13 18:44



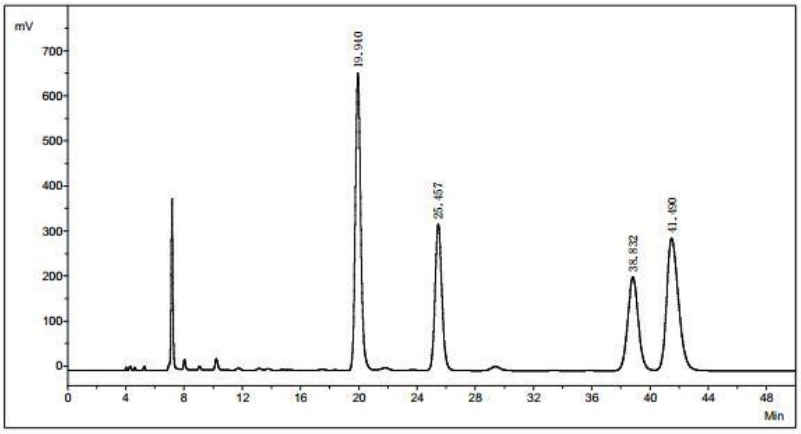
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		19.623	1484571.1	23972470.7	91.7082
2	2		20.982	24840.3	418060.4	1.5993
3	3		22.515	13191.7	246697.2	0.9438
4	4		34.865	44990.1	1502702.0	5.7487
Total				1567593.1	26139930.4	100.0000

98% ee , dr = 12.62: 1

Figure S13 HPLC Charts of Compound 3l

HPLC Report

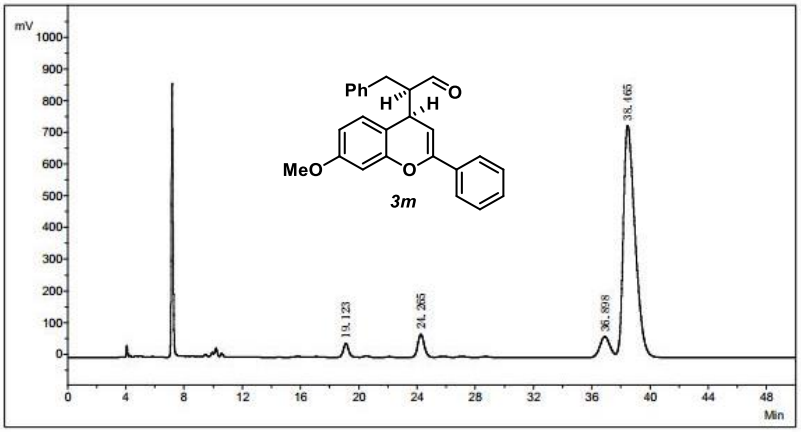
Sample Name:HJD-VI-44-2 AD-H 214 955 0.7 Recording Time:2017.03.09 10:55



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		19.940	656040.2	16630094.2	30.7018
2	2		25.457	324272.8	10536836.3	19.4527
3	3		38.832	207696.9	10474848.0	19.3382
4	4		41.490	294025.2	16524805.9	30.5074
Total				1482035.1	54166584.4	100.0000

HPLC Report

Sample Name:HJD-VI-44-1 AD-H 214 955 0.7 Recording Time:2017.03.08 16:04



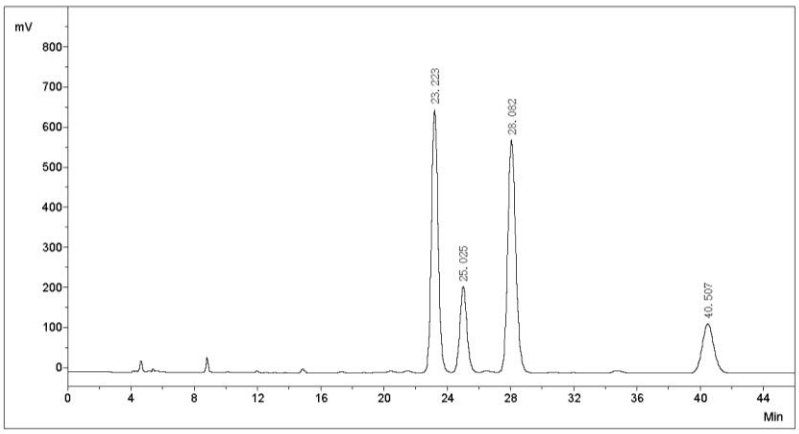
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		19.123	44393.9	1130060.0	2.3900
2	2		24.265	73170.2	2253500.6	4.7659
3	3		36.898	66201.1	3188644.8	6.7436
4	4		38.465	732442.7	40711558.1	86.1005
Total				916207.9	47283763.5	100.0000

95% ee, dr = 7.69: 1

Figure S14 HPLC Charts of Compound 3m

HPLC Report

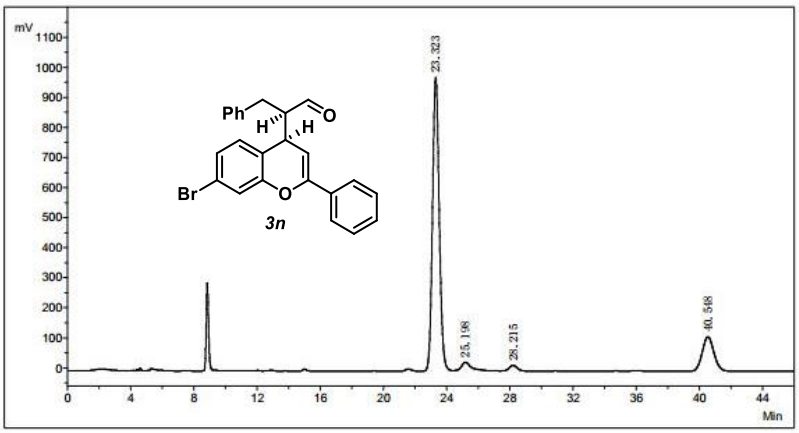
Sample Name:HJD-IX-1-2 AD-H 982 214 0.7 Recording Time:2017.12.29 23:16



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		23.223	655684.0	18969563.0	37.2481
2	2		25.025	212902.6	6547824.2	12.8571
3	3		28.082	564944.8	19059713.5	37.4251
4	4		40.507	123243.4	6350501.5	12.4697
Total				1556774.9	50927602.2	100.0000

HPLC Report

Sample Name:HJD-IX-1-1 AD-H 982 214 0.7 Recording Time:2017.12.30 00:02



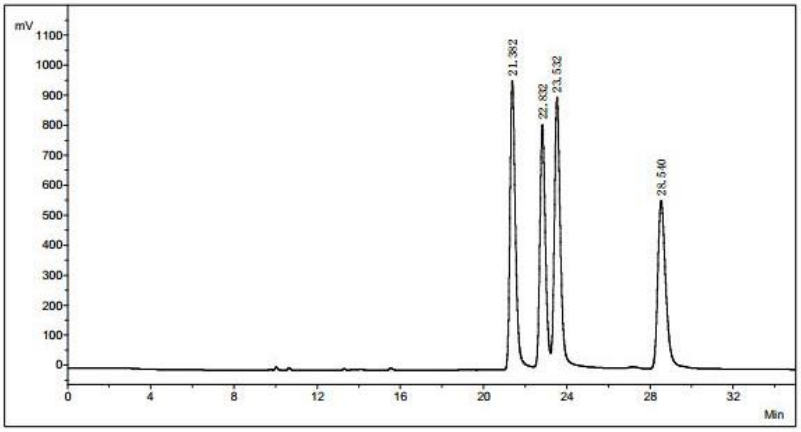
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		23.323	977324.0	28812477.3	78.1723
2	2		25.198	29718.1	1375167.7	3.7310
3	3		28.215	19060.0	672352.0	1.8242
4	4		40.548	115375.0	5997641.7	16.2725
Total				1141477.0	36857638.7	100.0000

95% ee, dr = 4.00: 1

Figure S15 HPLC Charts of Compound 3n

HPLC Report

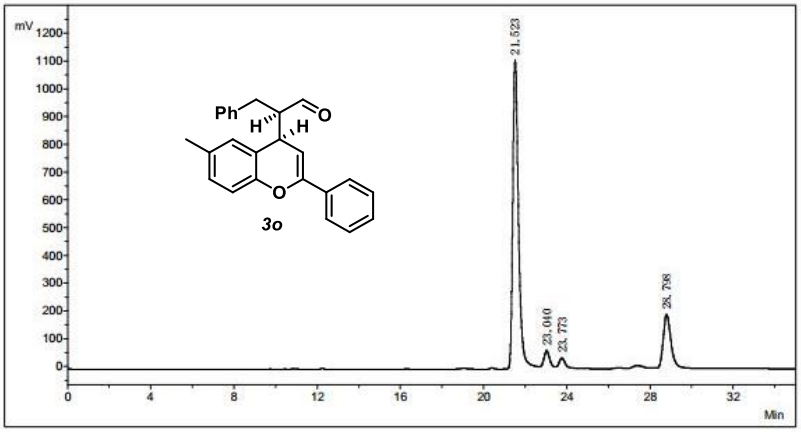
Sample Name:HJD-VI-41-2 IB-3+IC 214 982 0.7 Recording Time:2017.01.16 20:16



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		21.382	960530.5	17365626.9	27.1947
2	2		22.832	806141.4	14657356.7	22.9536
3	3		23.532	894323.9	17255693.1	27.0226
4	4		28.540	555699.0	14577898.1	22.8291
Total				3216694.8	63856574.8	100.0000

HPLC Report

Sample Name:HJD-VI-40-2 IB-3+IC 214 982 0.7 Recording Time:2017.01.16 20:52



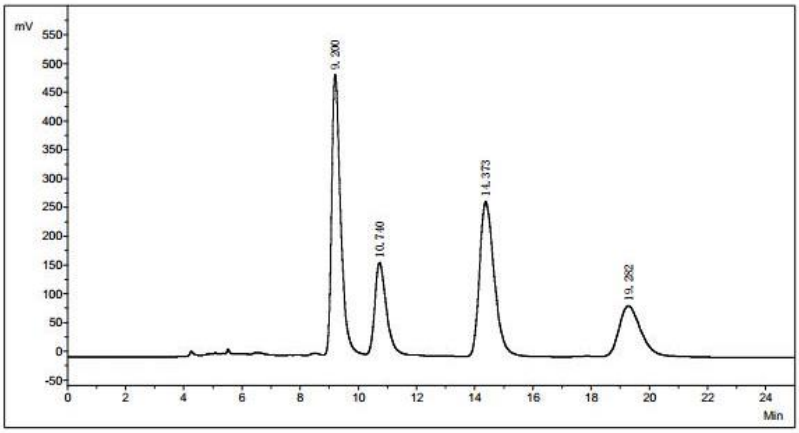
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		21.523	1112896.7	21281560.7	74.4858
2	2		23.040	65603.8	1381312.2	4.8346
3	3		23.773	39208.0	936261.8	3.2769
4	4		28.798	193819.6	4972152.3	17.4026
Total				1411528.0	28571287.0	100.0000

92% ee, dr = 3.50: 1

Figure S16 HPLC Charts of Compound 3o

HPLC Report

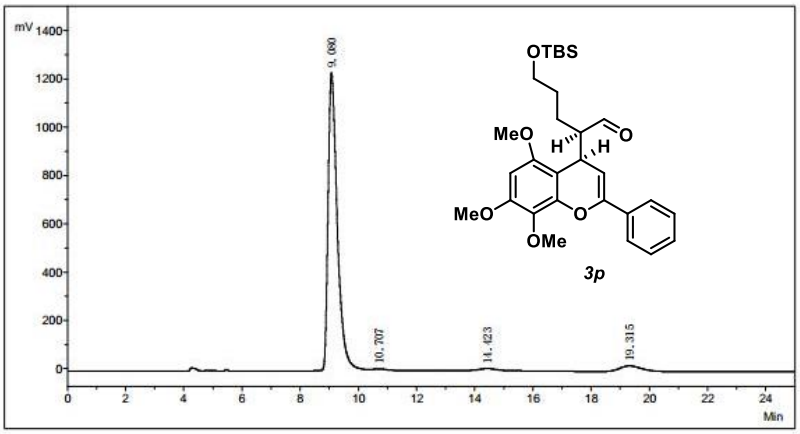
Sample Name:HJD-VI-43-2 OD-H 214 91 0.7 Recording Time:2017.02.08 15:00



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		9.200	470915.2	9413352.5	34.0786
2	2		10.740	160268.4	4393328.5	15.9049
3	3		14.373	268907.8	9428918.0	34.1350
4	4		19.282	87294.2	4386837.7	15.8814
Total				987385.5	27622436.7	100.0000

HPLC Report

Sample Name:HJD-VI-43-3 OD-H 214 91 0.7 Recording Time:2017.02.08 10:41



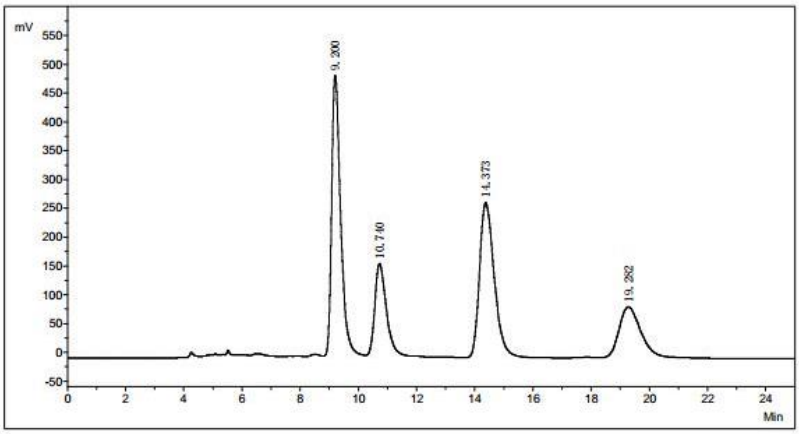
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		9.080	1228008.4	26557842.3	94.3630
2	2		10.707	3705.4	72695.6	0.2583
3	3		14.423	8291.5	311094.9	1.1054
4	4		19.315	23315.0	1202716.9	4.2734
Total				1263320.4	28144349.7	100.0000

98% ee, dr = 21.08: 1

Figure S17 HPLC Charts of Compound 3p

HPLC Report

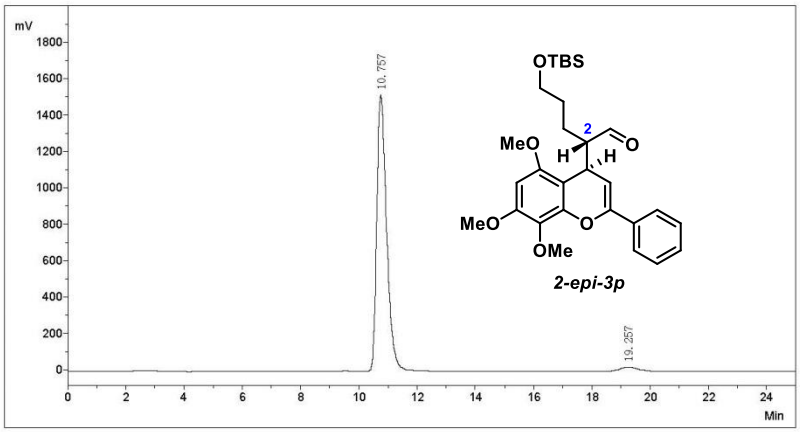
Sample Name:HJD-VI-43-2 OD-H 214 91 0.7 Recording Time:2017.02.08 15:00



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		9.200	470915.2	9413352.5	34.0786
2	2		10.740	160268.4	4393328.5	15.9049
3	3		14.373	268907.8	9428918.0	34.1350
4	4		19.282	87294.2	4386837.7	15.8814
Total				987385.5	27622436.7	100.0000

HPLC Report

Sample Name:CL-I-75 OD-H 91 214 0.7 Recording Time:2019.01.11 14:55



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		10.757	1519596.2	35696707.3	97.3714
2	2		19.257	21973.7	963658.9	2.6286
Total				1541569.8	36660366.2	100.0000

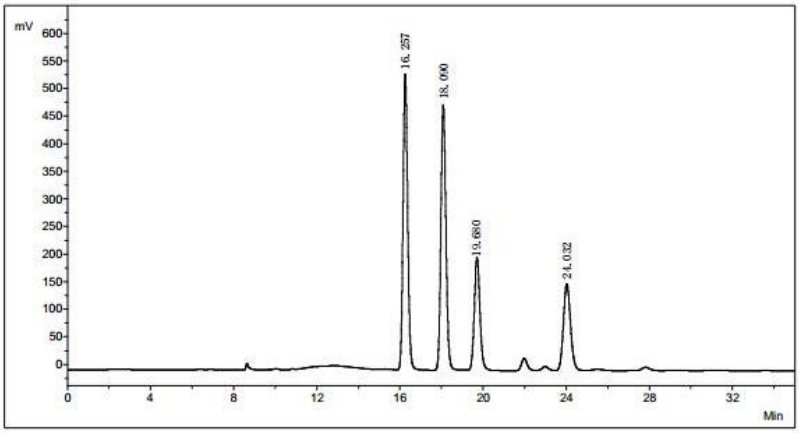
95% ee

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

Figure S18 HPLC Charts of Compound 2-epi-3p

HPLC Report

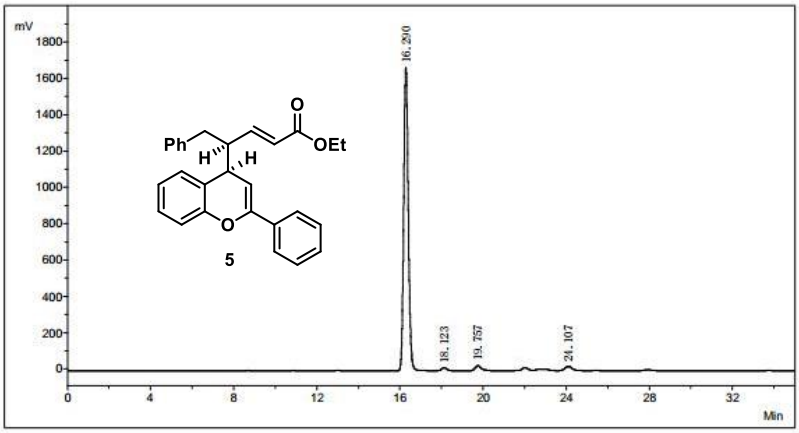
Sample Name:HJD-VII-61-2 AD-H+OD-H 214 955 0.7Recording Time:2017.06.30 14:37



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		16.257	532510.6	8025044.2	34.1544
2	2		18.090	480579.5	8022779.2	34.1448
3	3		19.680	195129.9	3741402.1	15.9233
4	4		24.032	156759.4	3707133.1	15.7775
Total				1364979.3	23496358.6	100.0000

HPLC Report

Sample Name:HJD-VII-61-1 AD-H+OD-H 214 955 0.7Recording Time:2017.06.30 15:24



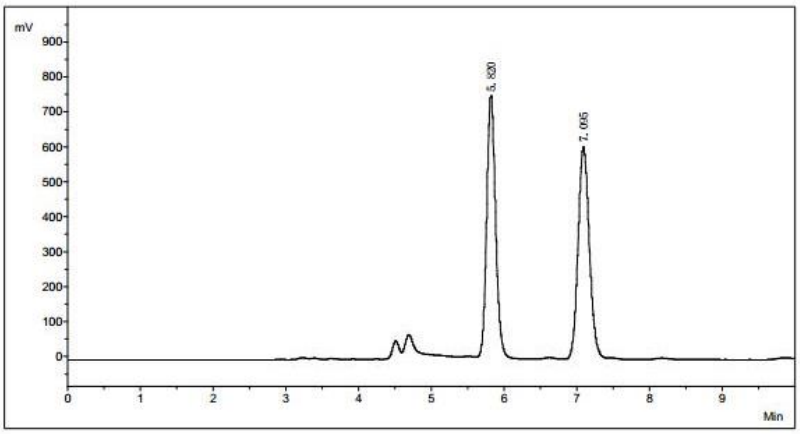
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		16.290	1667265.3	25338566.0	94.5499
2	2		18.123	16498.9	281977.9	1.0522
3	3		19.757	28289.2	600395.6	2.2404
4	4		24.107	23427.7	578214.4	2.1576
Total				1735481.1	26799153.9	100.0000

98% ee, dr = 21.73: 1

Figure S19 HPLC Charts of Compound 5

HPLC Report

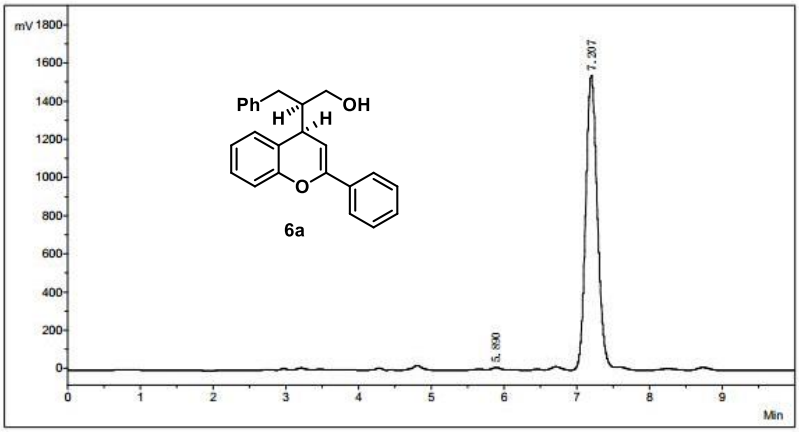
Sample Name:HJD-VII-62-2 AD-H 8020 214 1.0 Recording Time:2017.12.29 17:28



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		5.820	744922.7	6324099.8	49.4047
2	2		7.095	605478.6	6476514.5	50.5953
Total				1350401.3	12800614.3	100.0000

HPLC Report

Sample Name:HJD-VII-62-1 AD-H 8020 214 1.0 Recording Time:2017.12.29 11:11



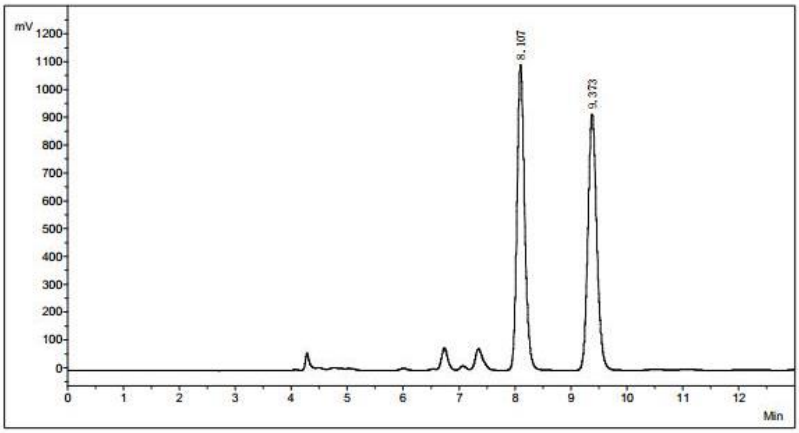
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		5.890	13245.9	99062.5	0.6070
2	2		7.207	1509996.1	16220100.6	99.3930
Total				1523242.0	16319163.1	100.0000

98% ee

Figure S20 HPLC Charts of Compound 6a

HPLC Report

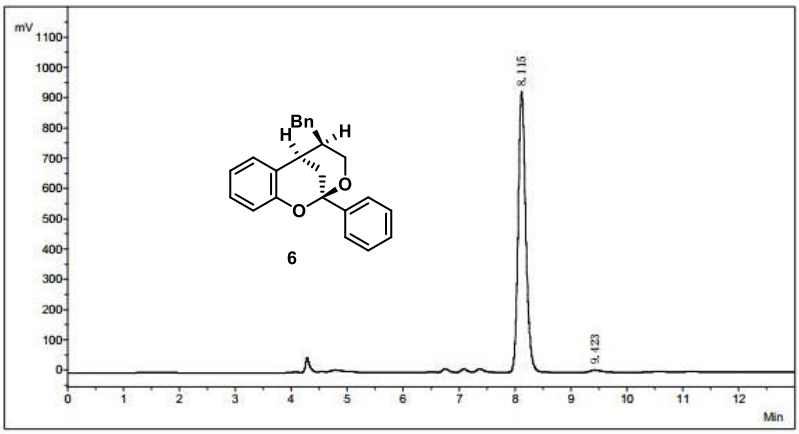
Sample Name:HJD-VII-63-2 AD-H 955 214 0.7 Recording Time:2017.12.29 22:08



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		8.107	1098587.1	10438605.3	50.6238
2	2		9.373	919144.4	10181365.5	49.3762
Total				2017731.5	20619970.8	100.0000

HPLC Report

Sample Name:HJD-VII-63-1 AD-H 955 214 0.7 Recording Time:2017.12.29 22:23



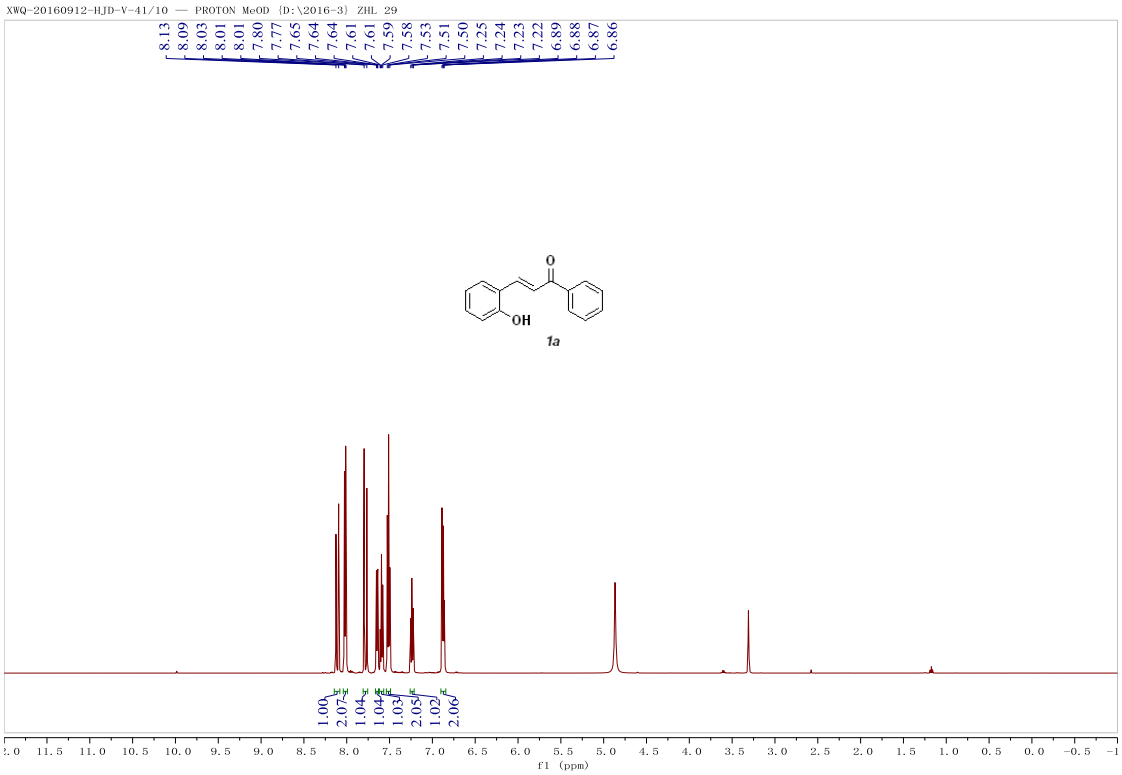
6

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	Conc
1	1		8.115	927207.1	8781296.7	98.9056
2	2		9.423	7206.0	97170.1	1.0944
Total				934413.1	8878466.8	100.0000

98% ee

Figure S21 HPLC Charts of Compound 6

8. ^{1}H & ^{13}C NMR Data for Substrate Scope and Derivatization



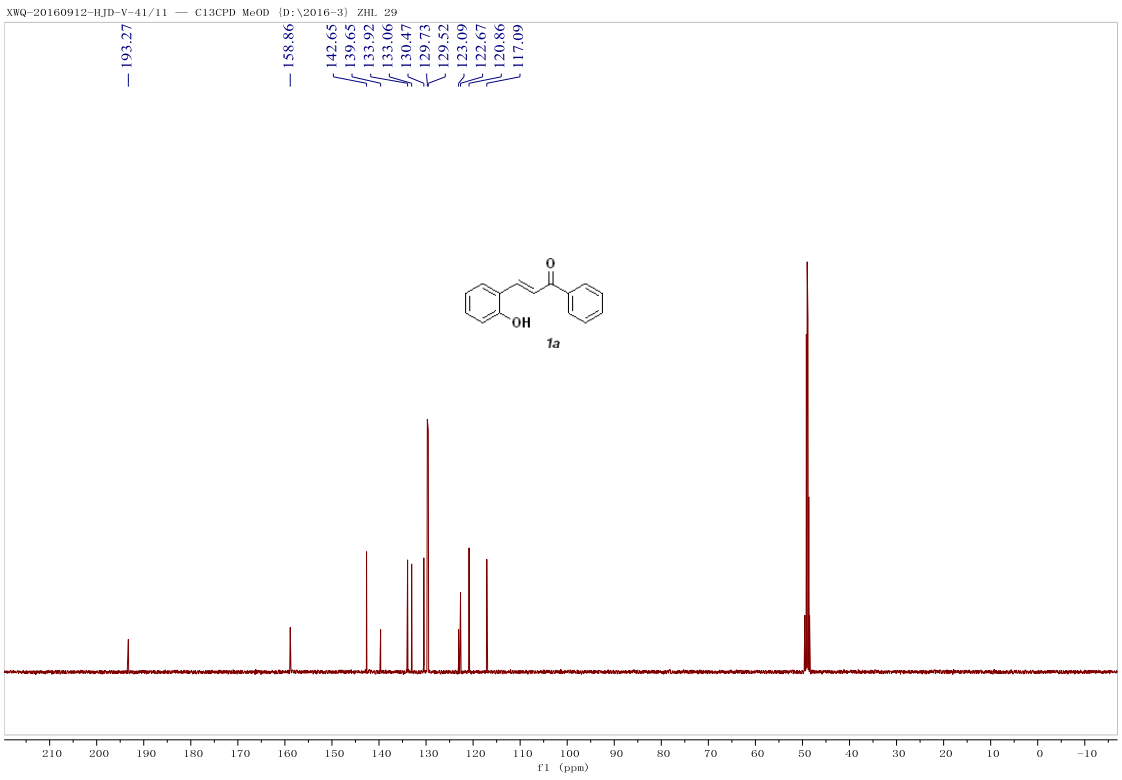
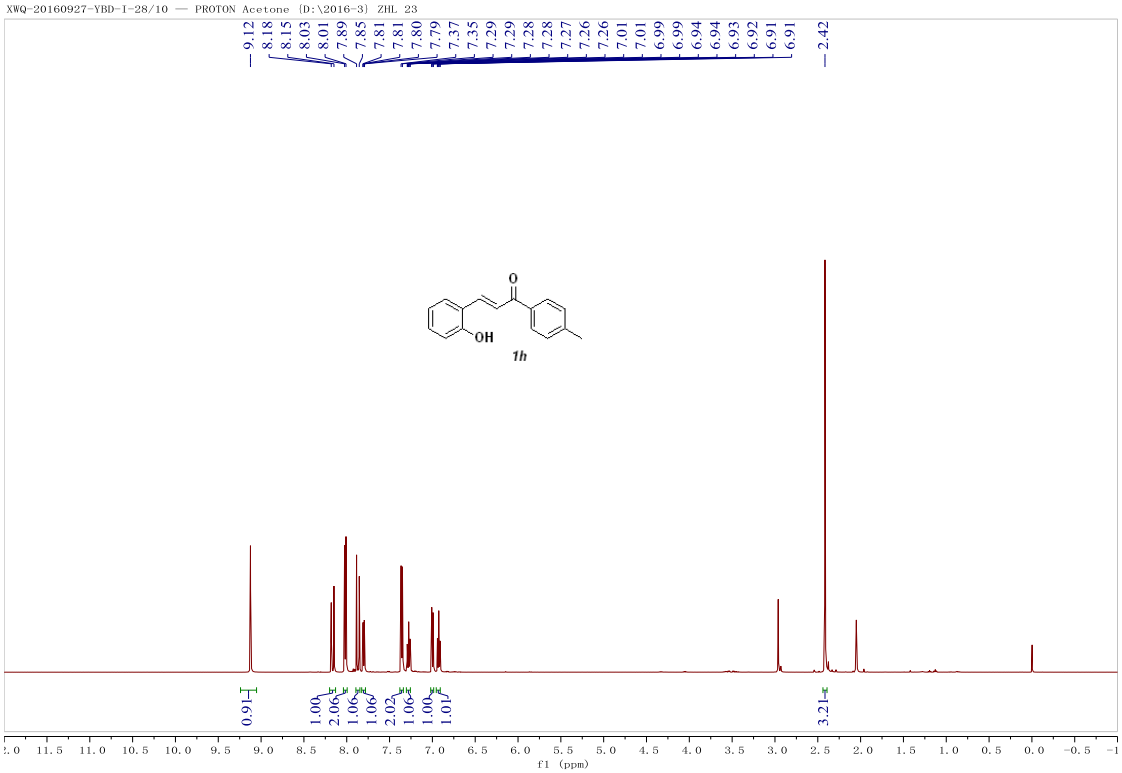


Figure S22 ^{1}H and ^{13}C NMR Spectrum of Compound 1a



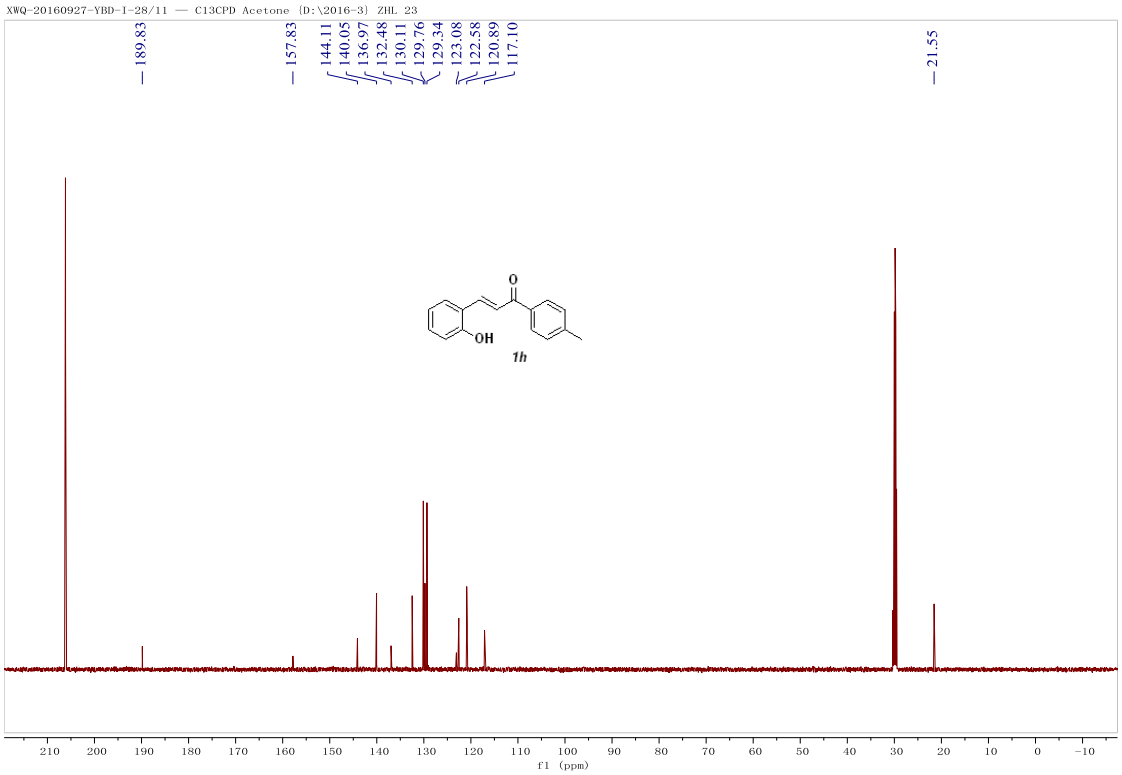
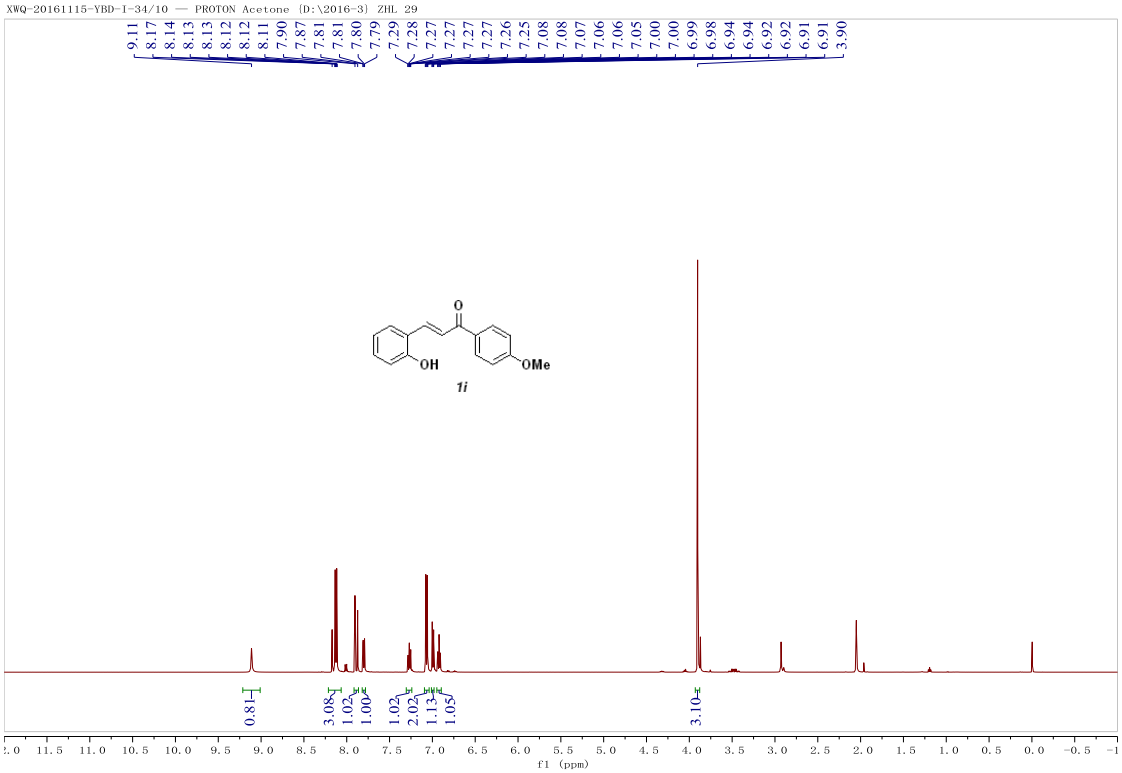


Figure S23 ^{1}H and ^{13}C NMR Spectrum of Compound 1h



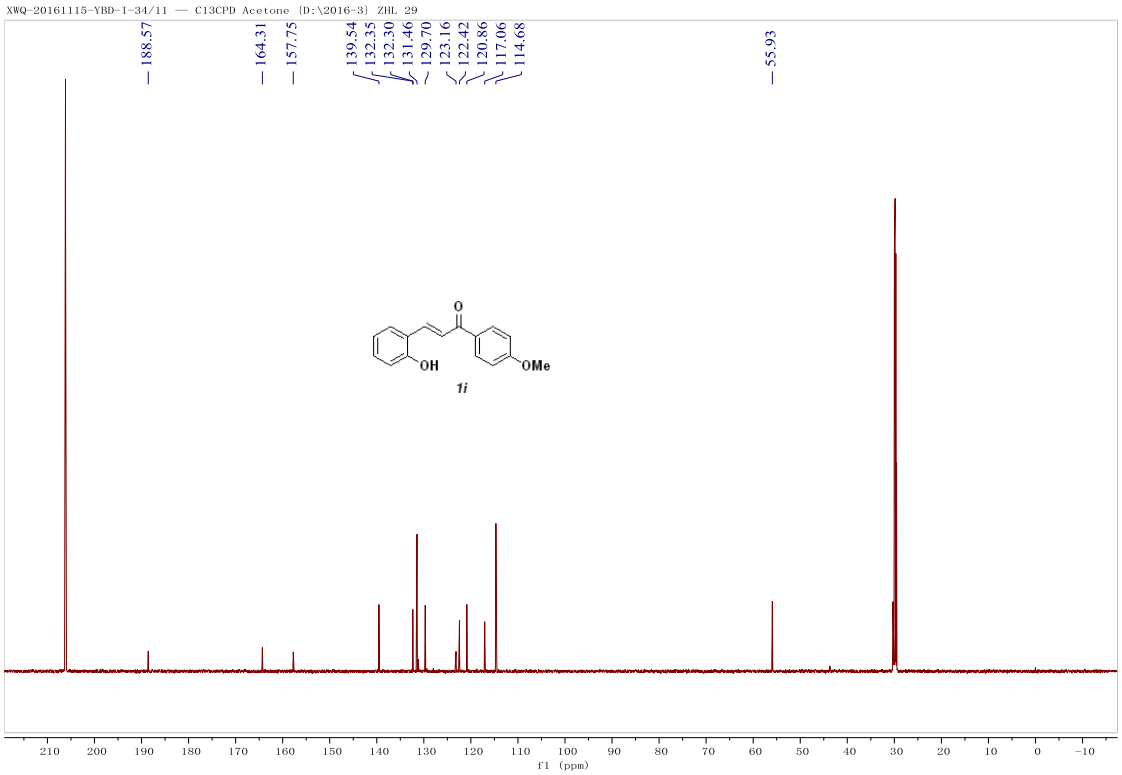
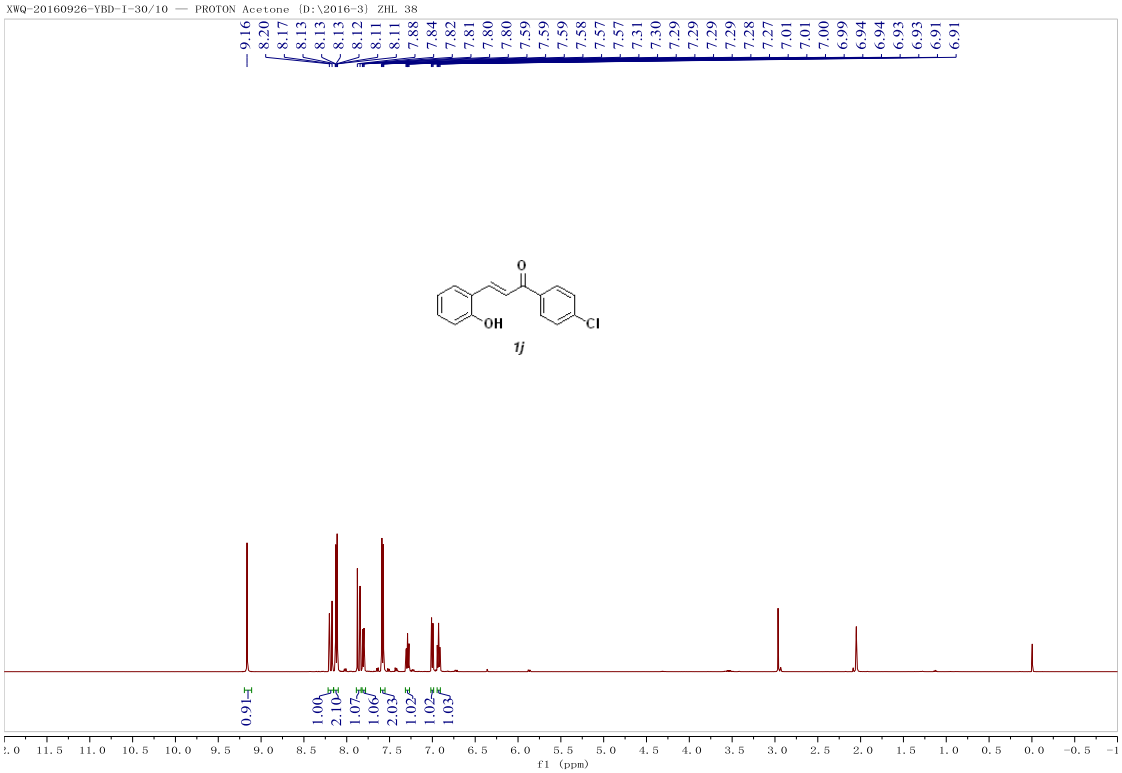


Figure S24 ^{1}H and ^{13}C NMR Spectrum of Compound 1i



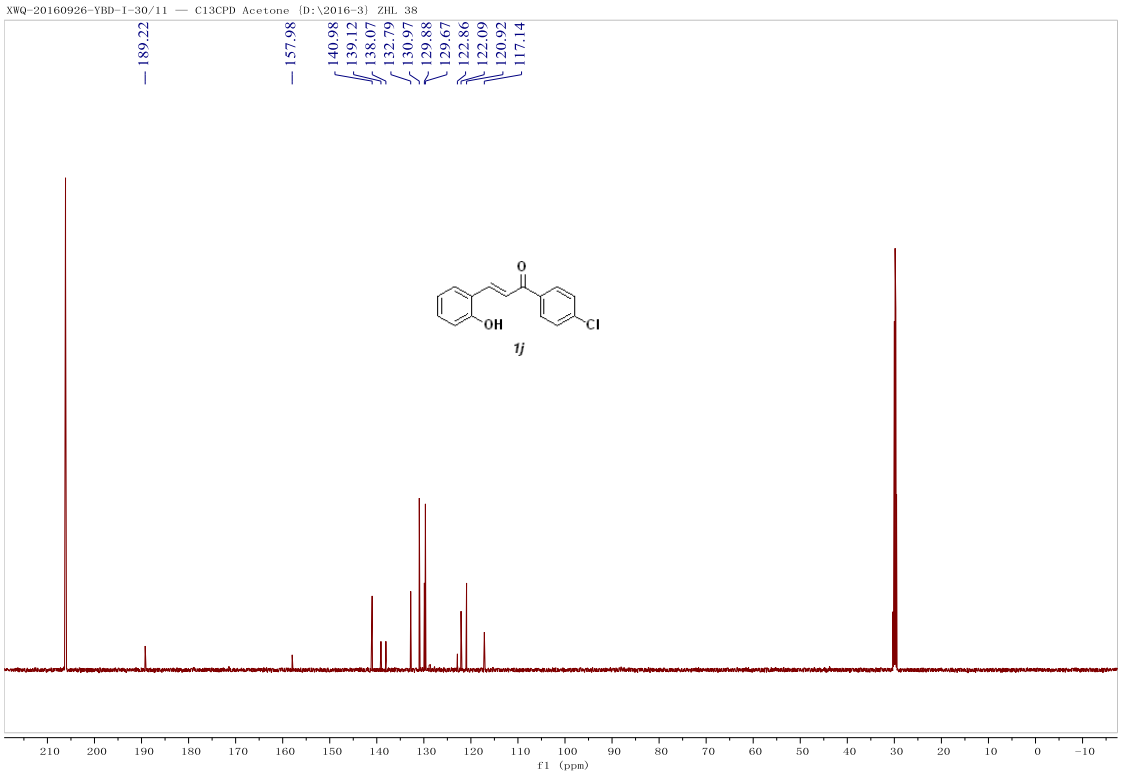
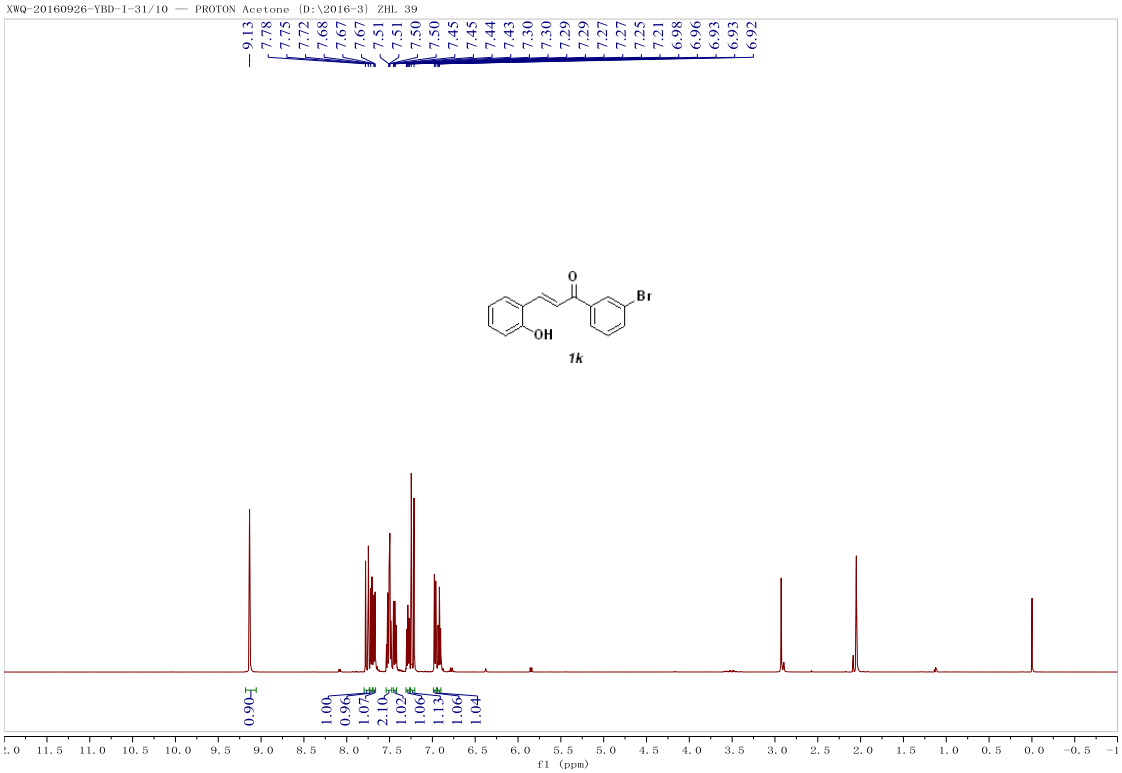


Figure S25 ^{1}H and ^{13}C NMR Spectrum of Compound 1j



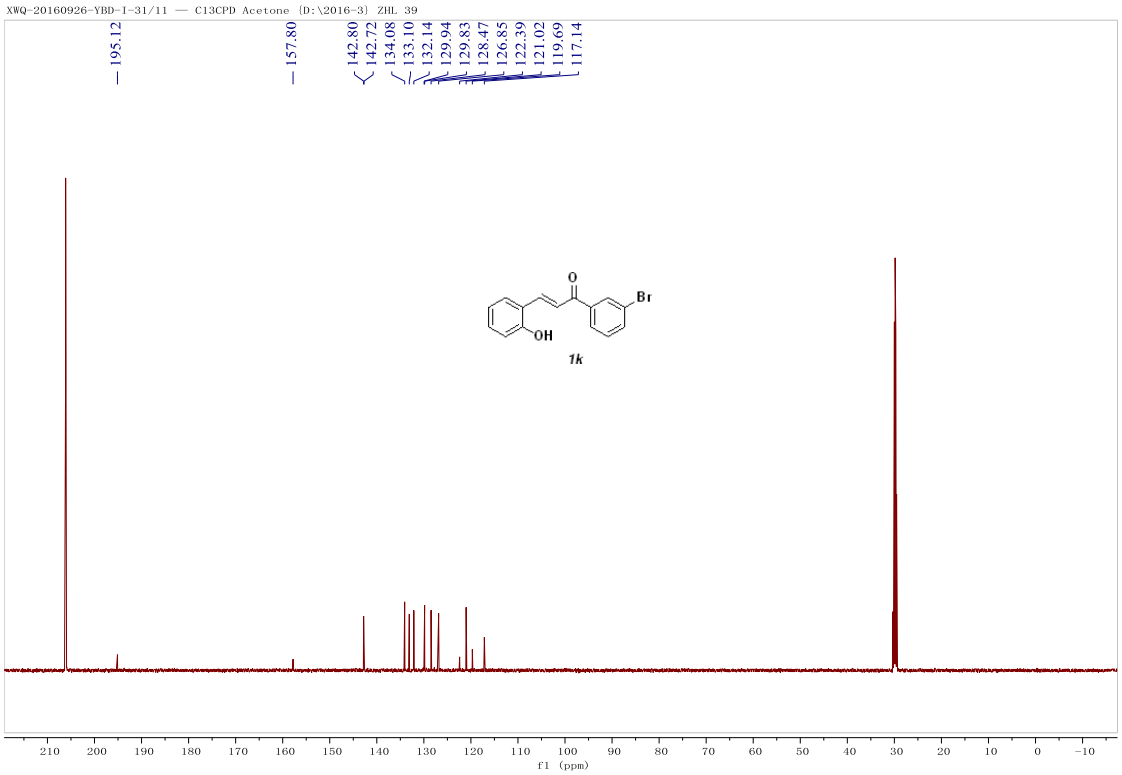
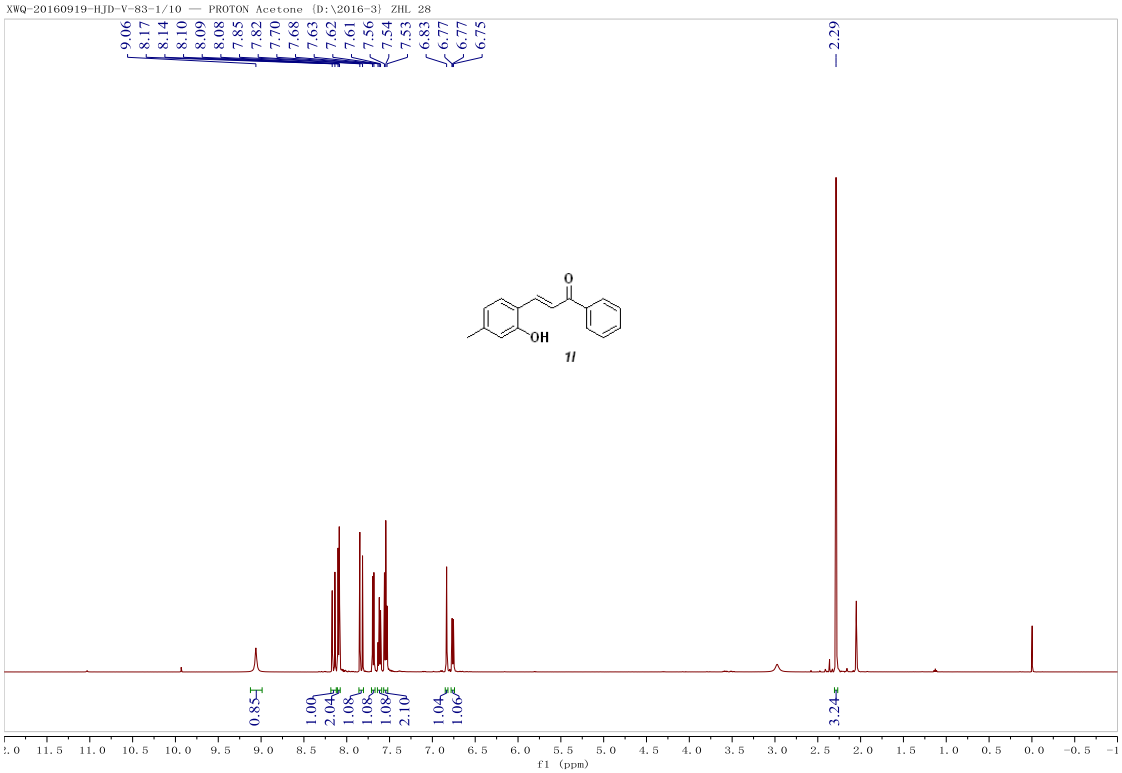


Figure S26 ^{1}H and ^{13}C NMR Spectrum of Compound 1k



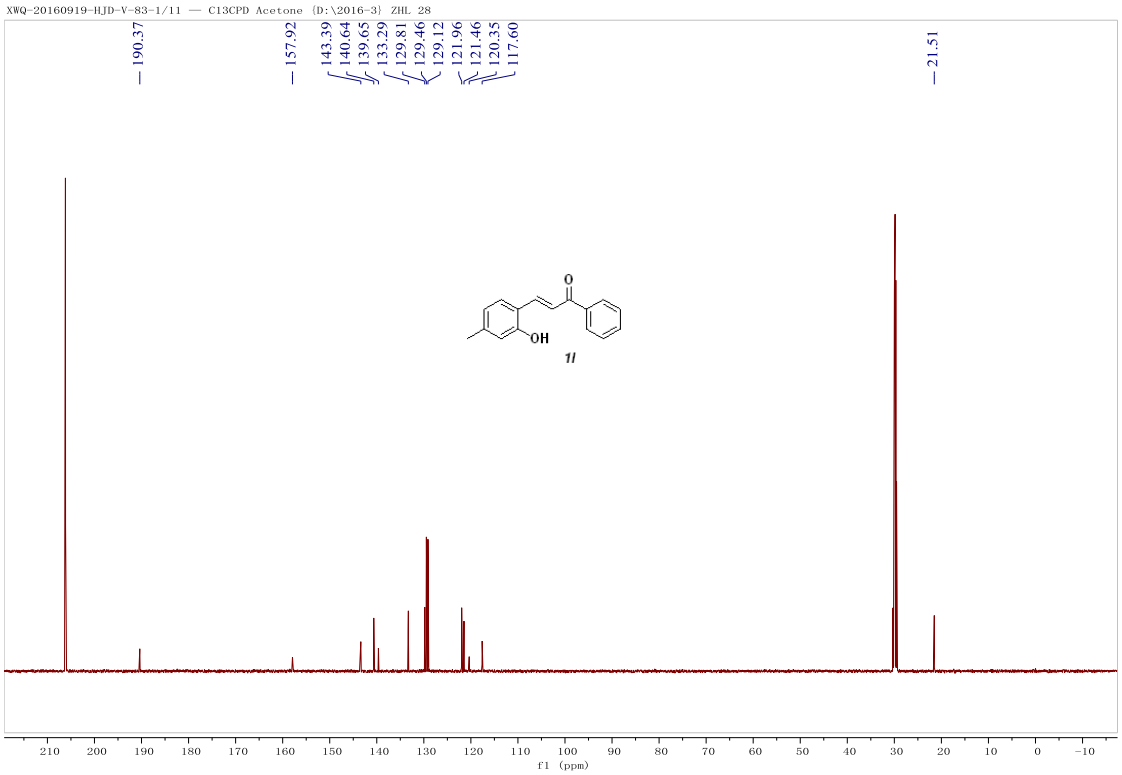
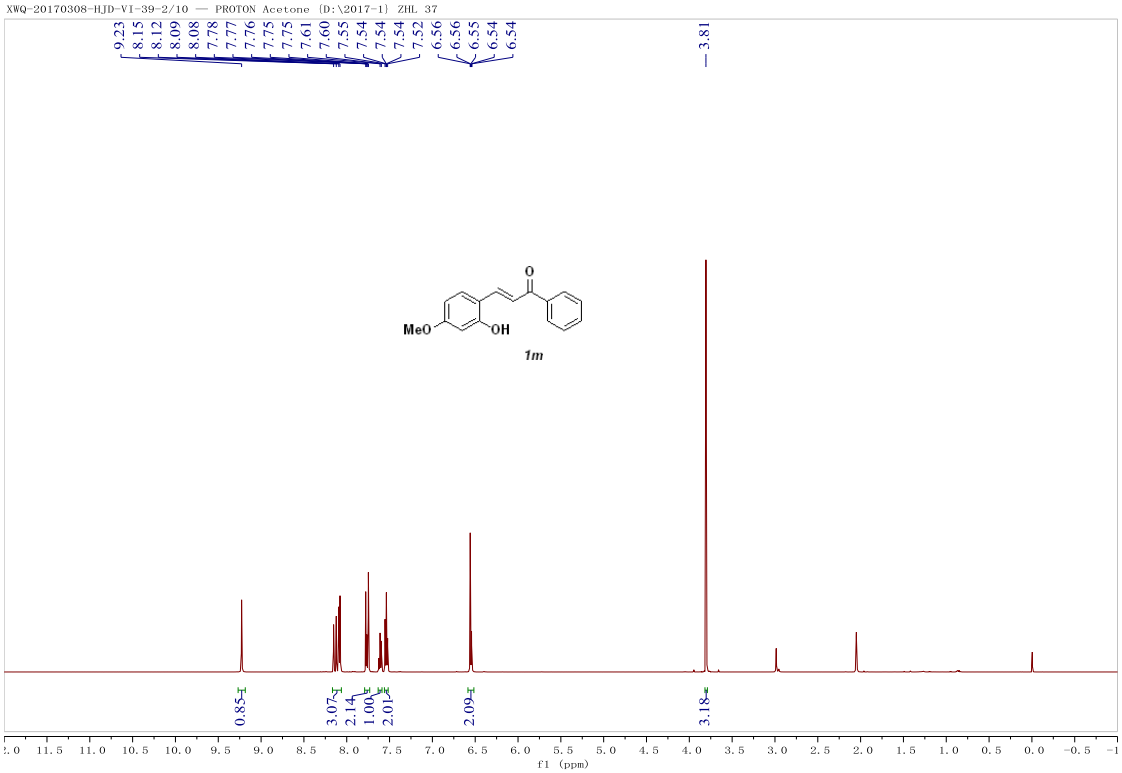


Figure S27 ^{1}H and ^{13}C NMR Spectrum of Compound 1l



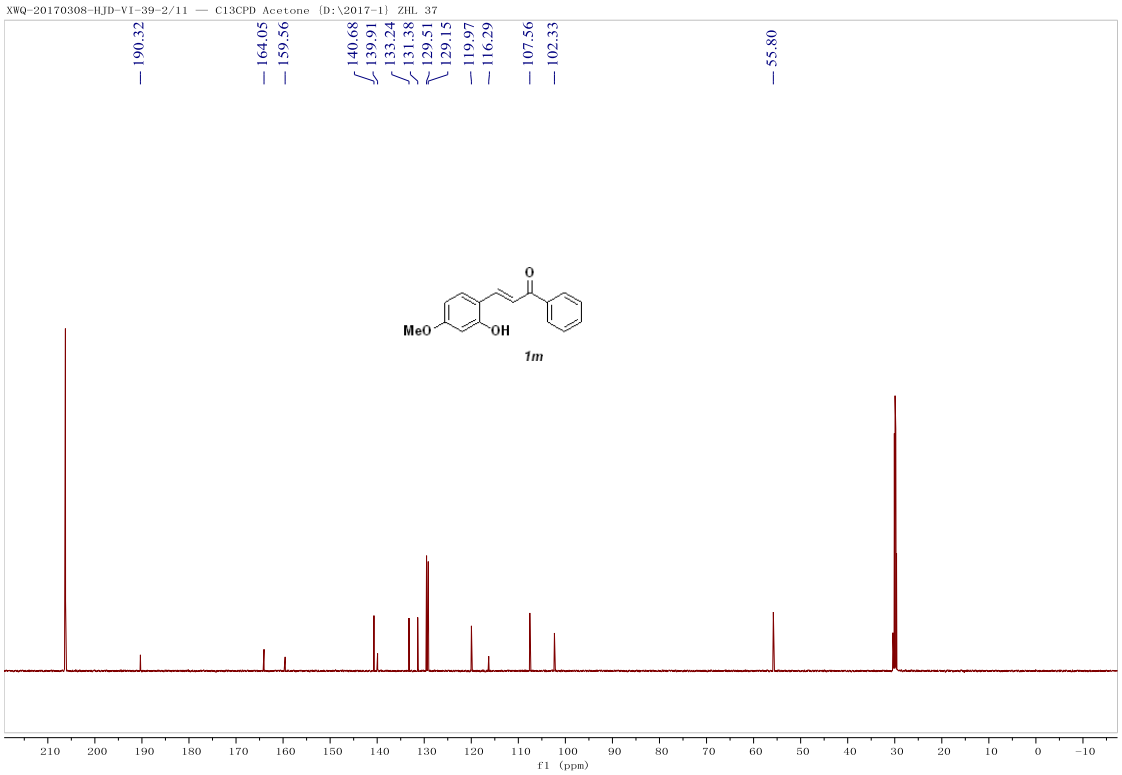
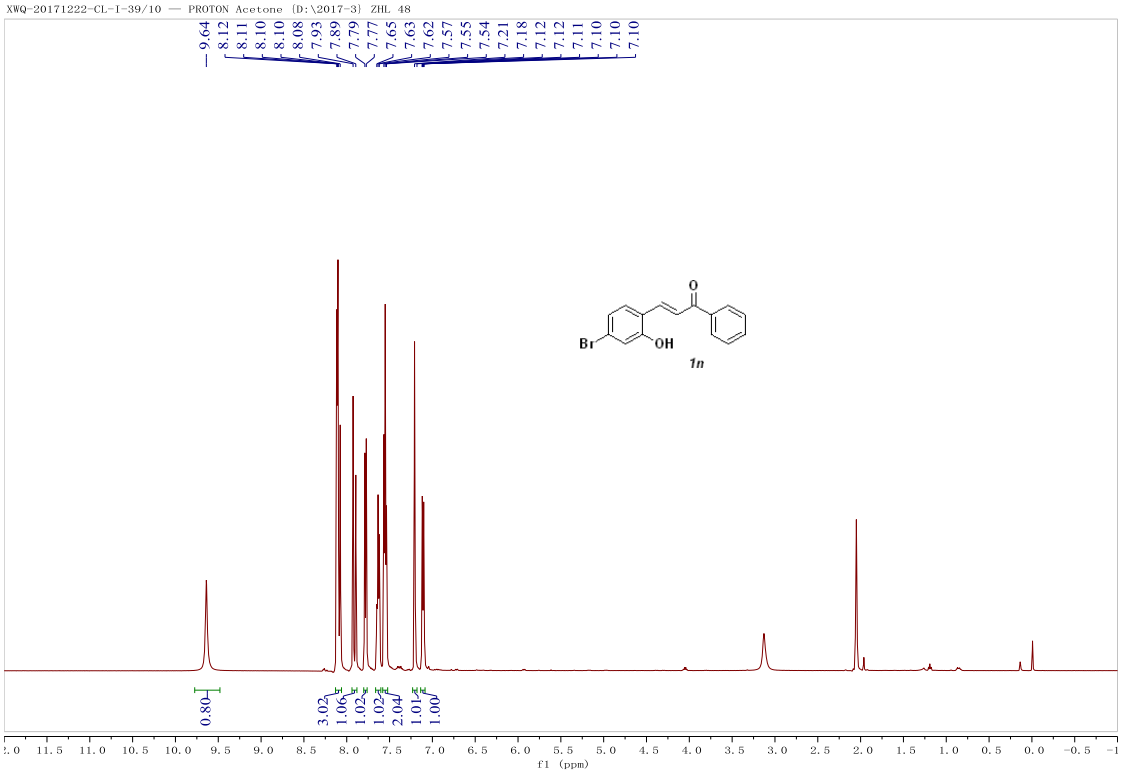


Figure S28 ^{1}H and ^{13}C NMR Spectrum of Compound 1m



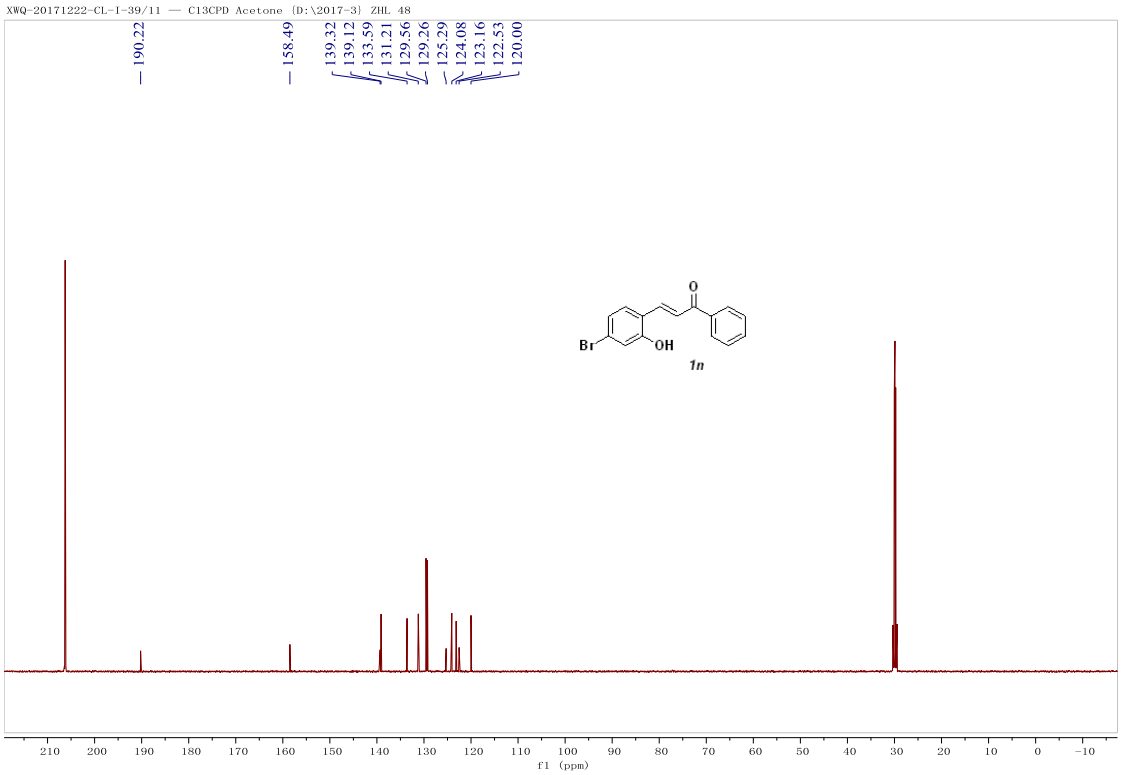
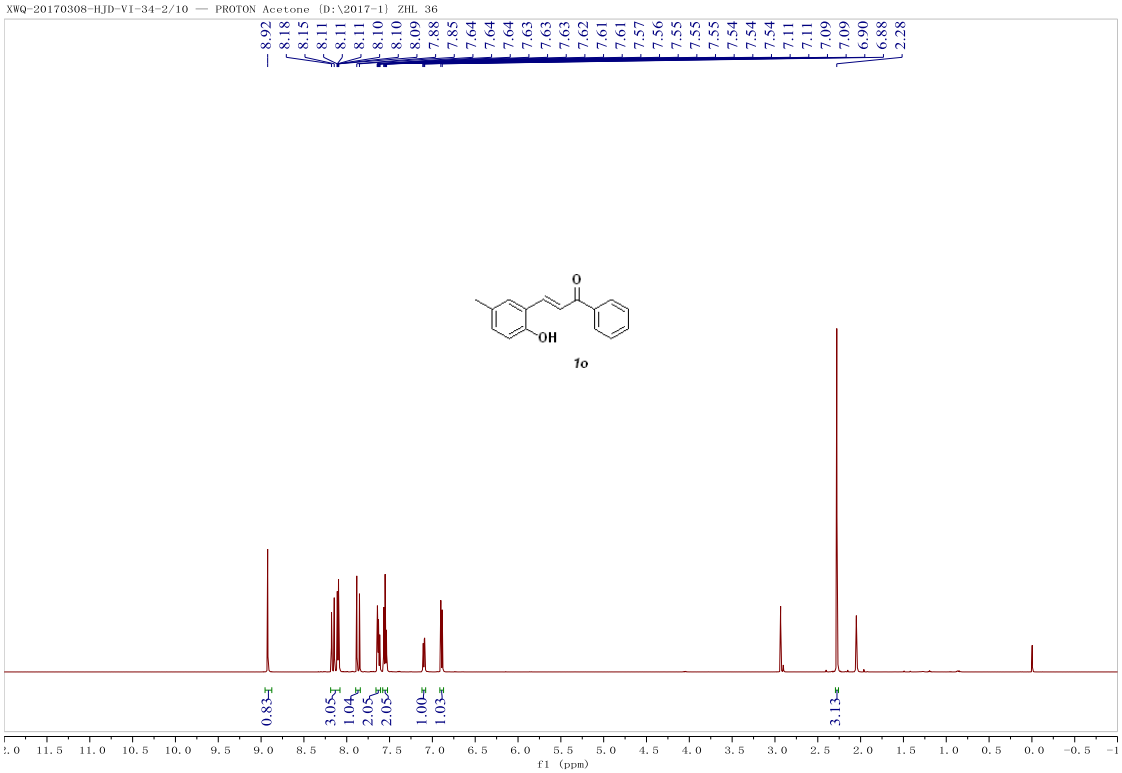


Figure S29 ^{1}H and ^{13}C NMR Spectrum of Compound 1n



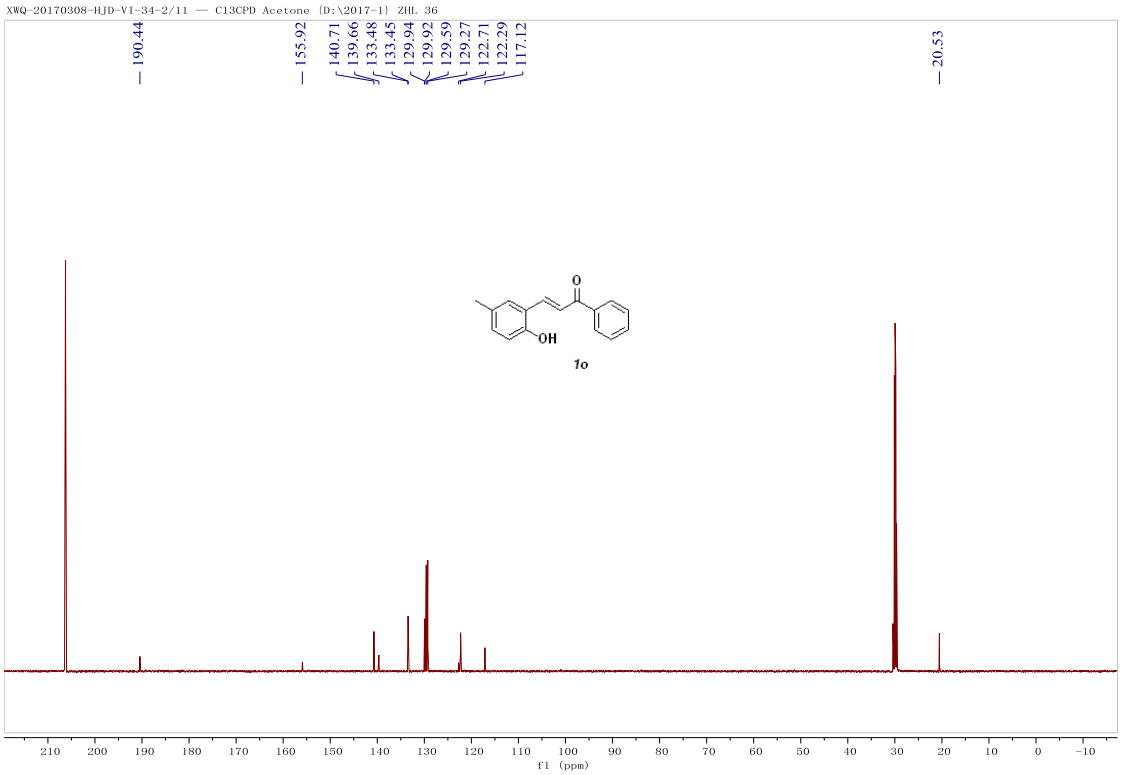
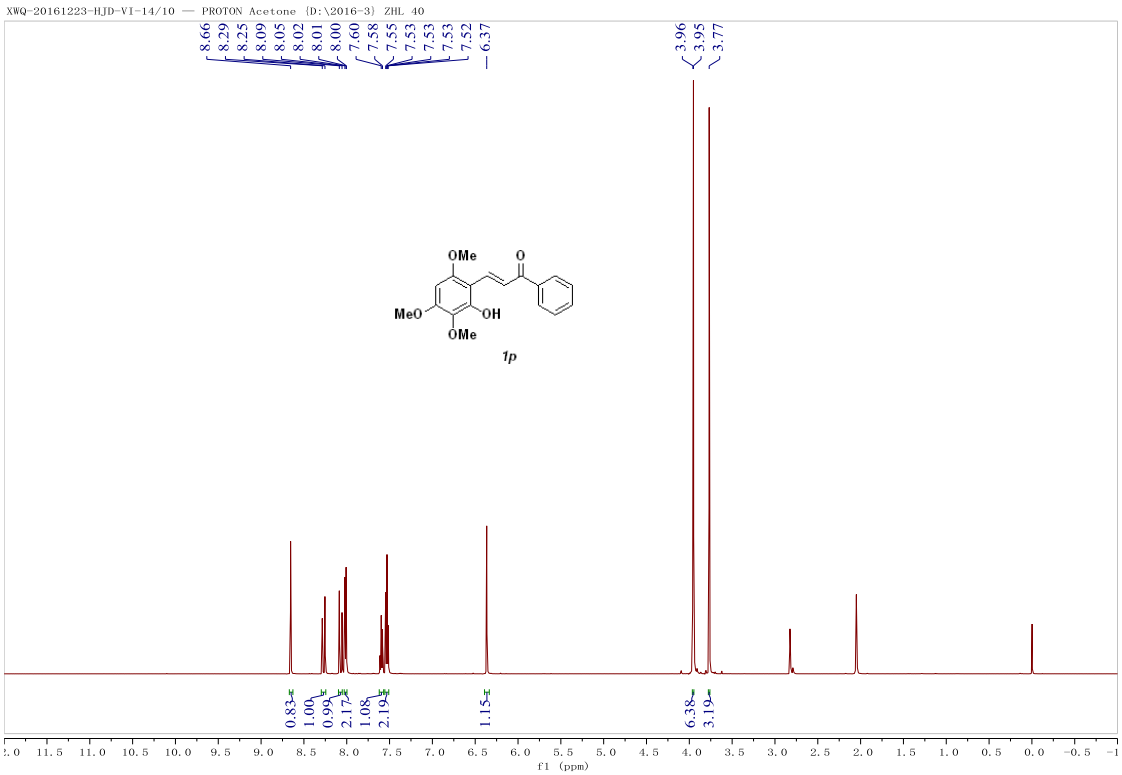


Figure S30 ^{1}H and ^{13}C NMR Spectrum of Compound 1o



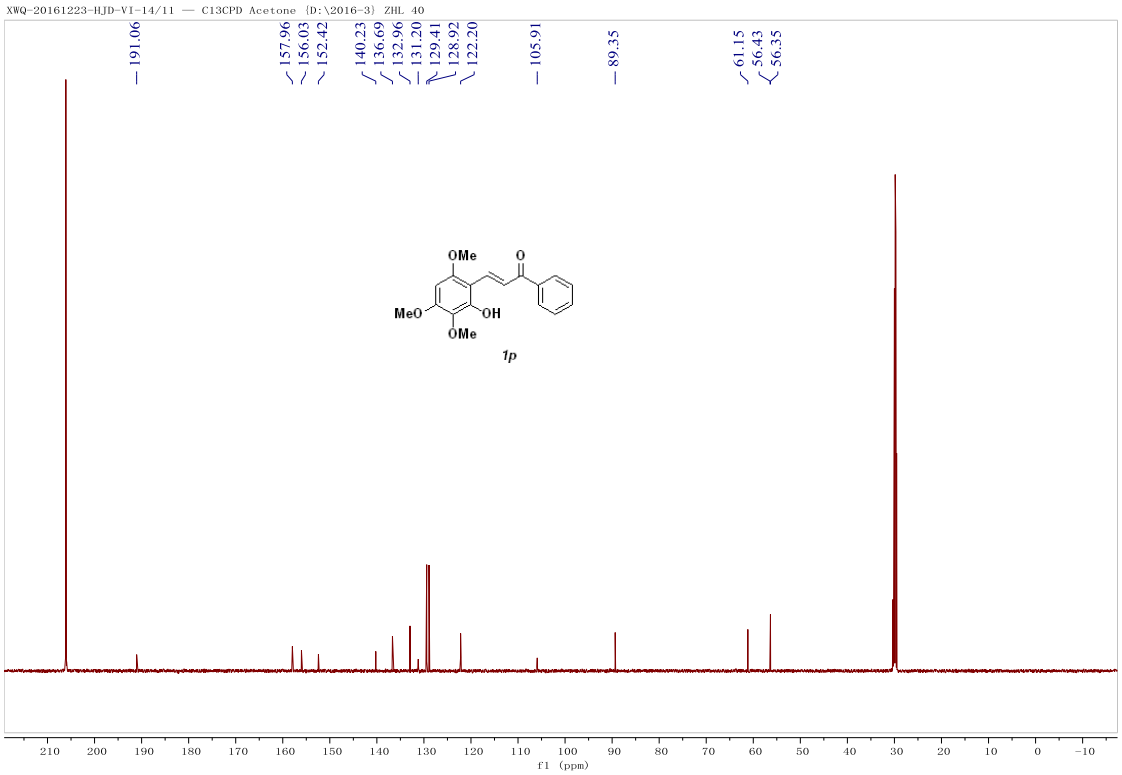
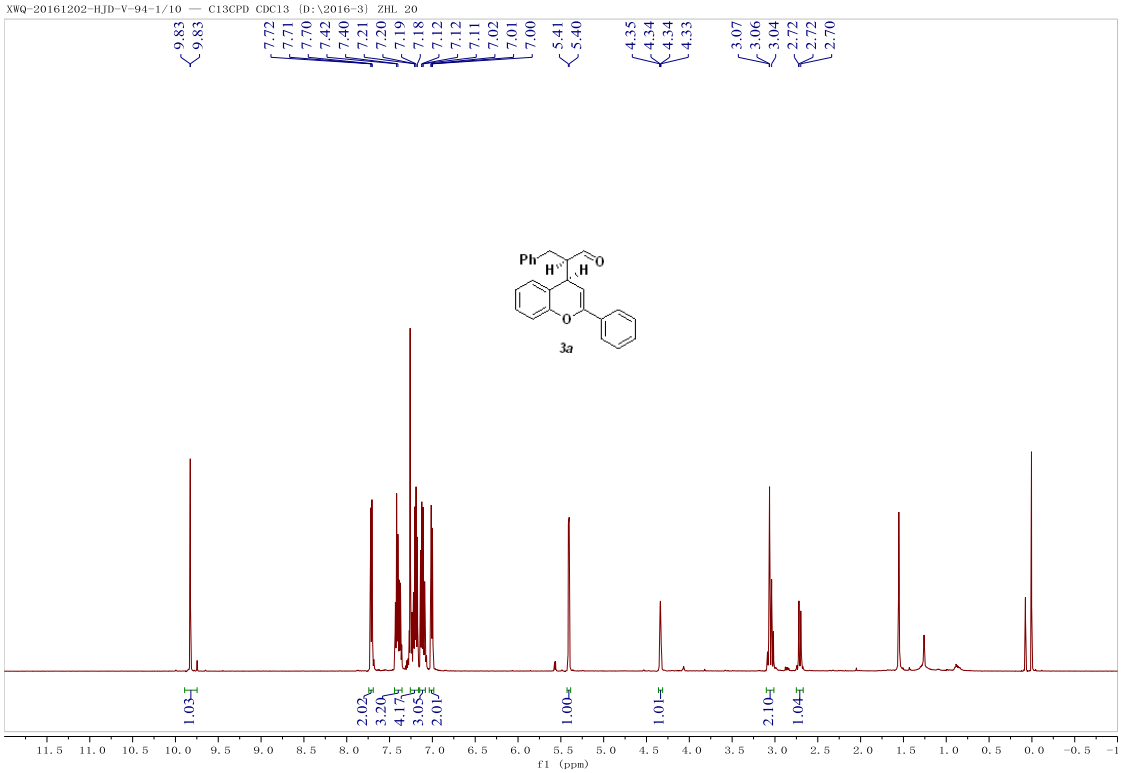


Figure S31 ^{1}H and ^{13}C NMR Spectrum of Compound 1p



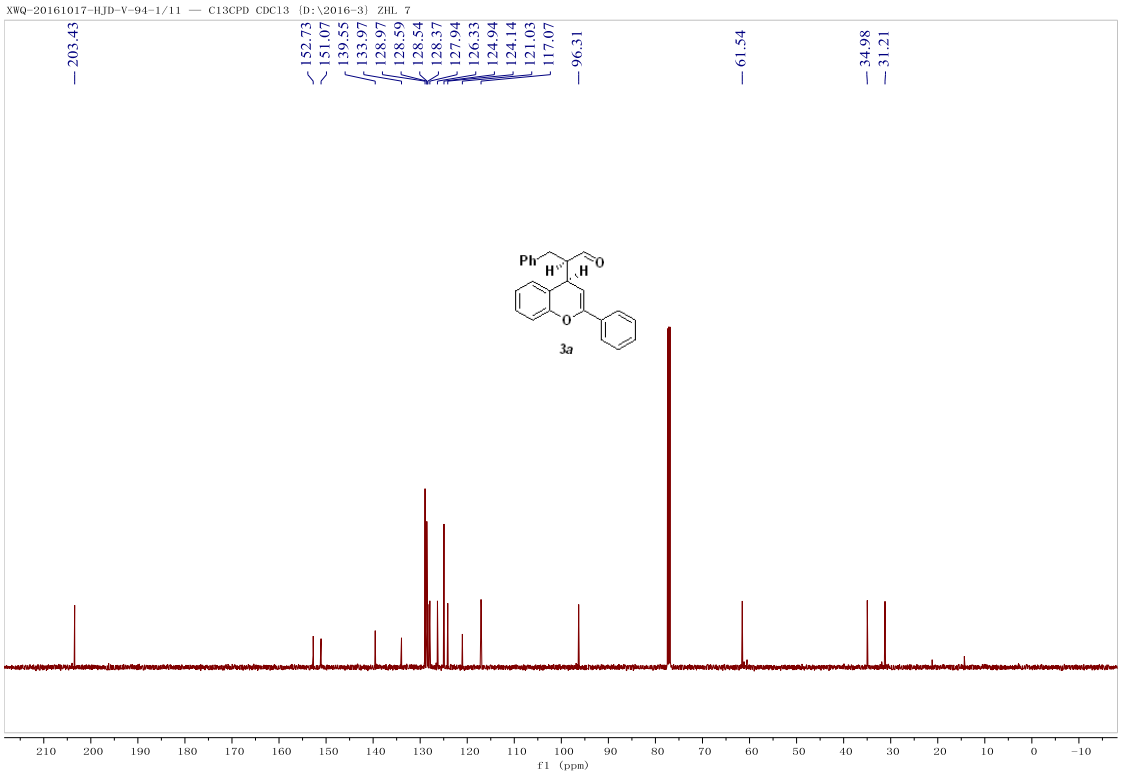
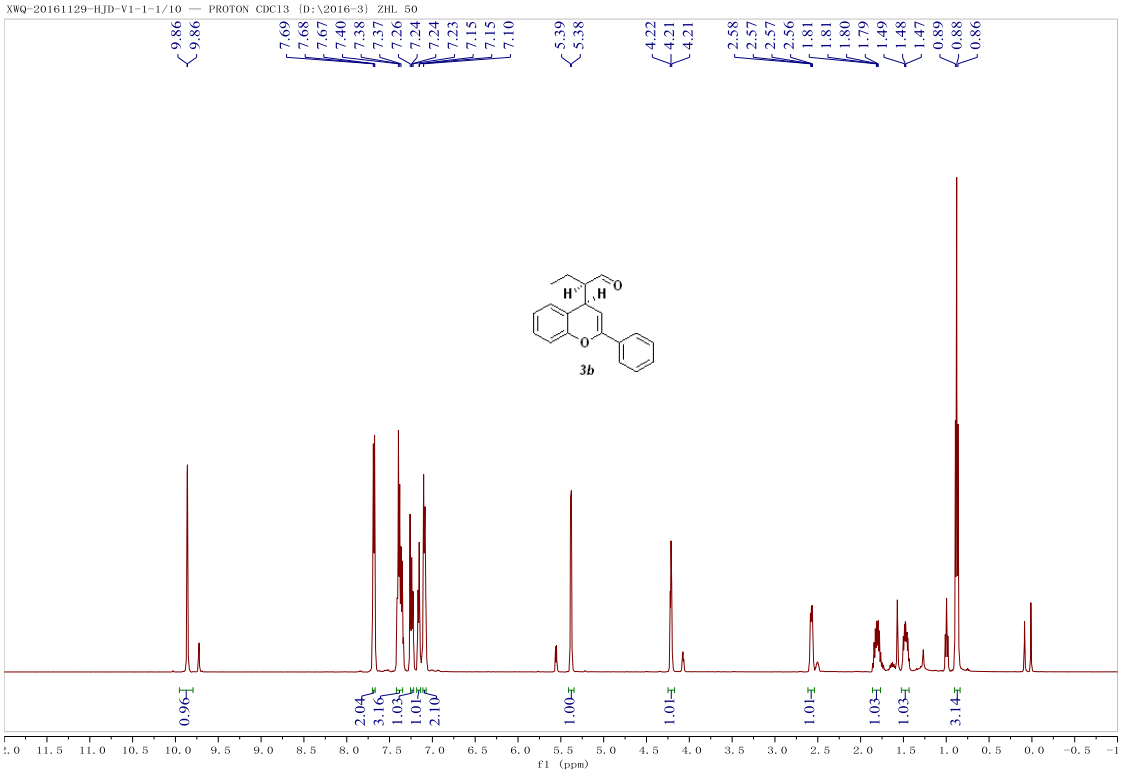


Figure S32 ^{1}H and ^{13}C NMR Spectrum of Compound 3a



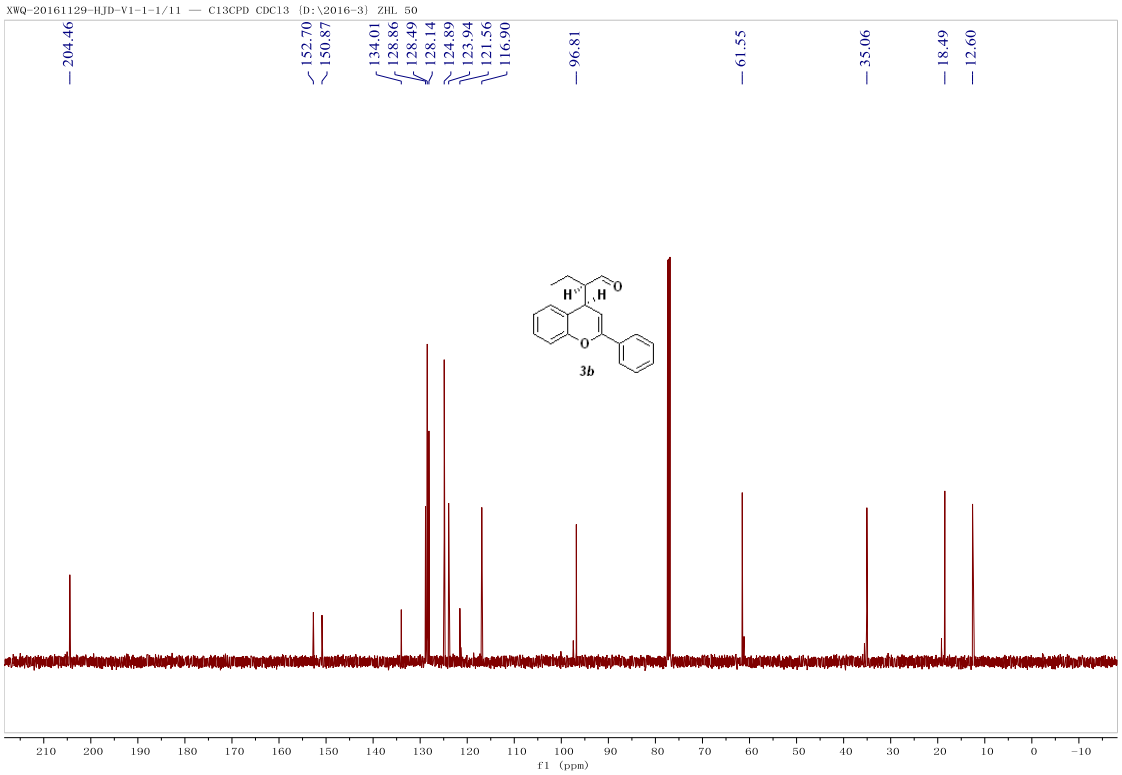
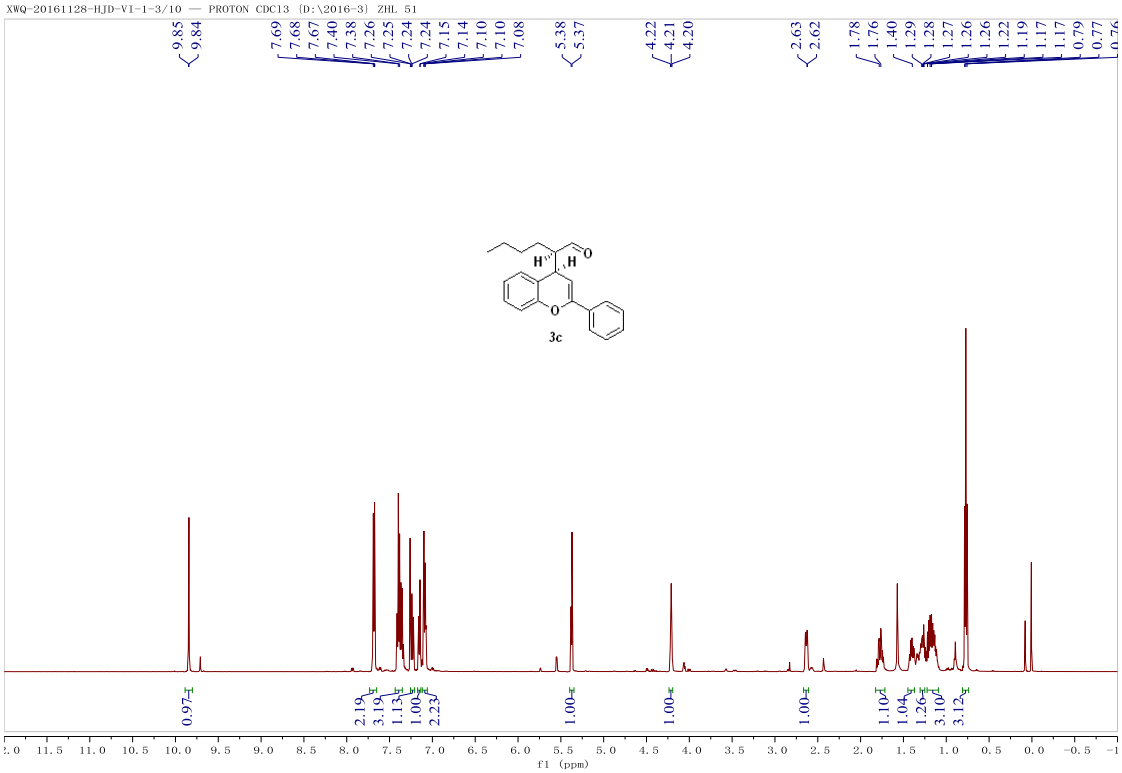


Figure S33 ^{1}H and ^{13}C NMR Spectrum of Compound 3b



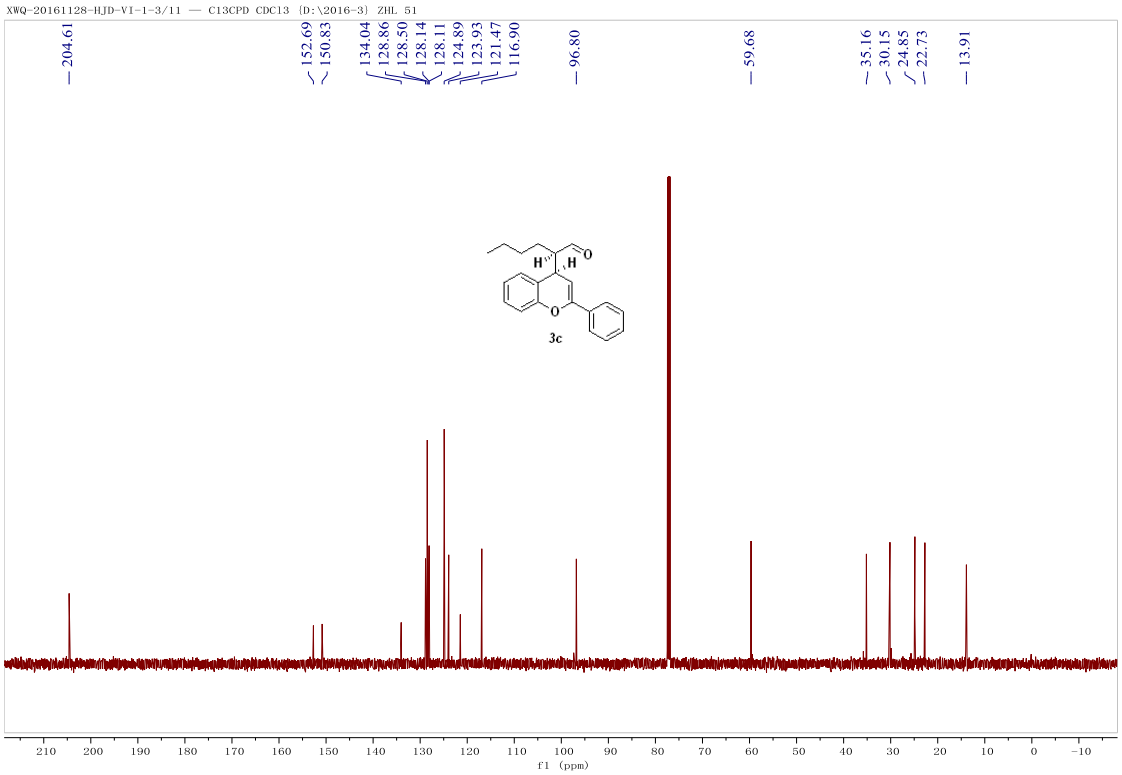
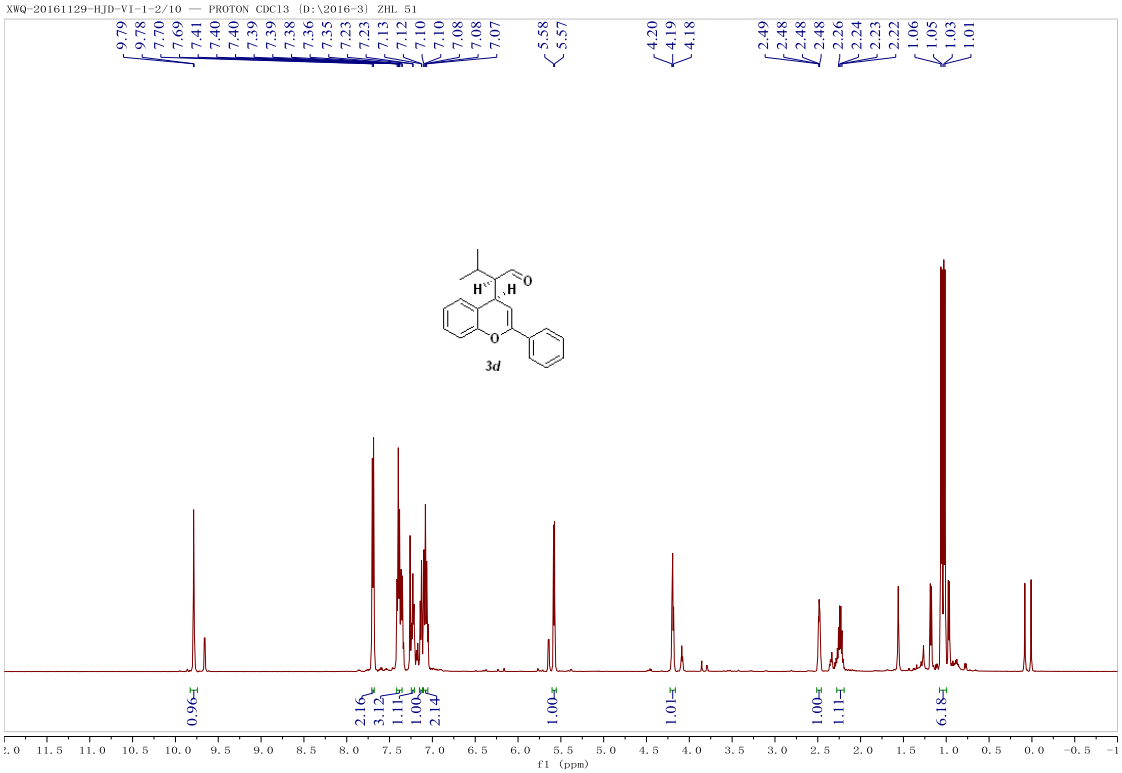


Figure S34 ^{1}H and ^{13}C NMR Spectrum of Compound 3c



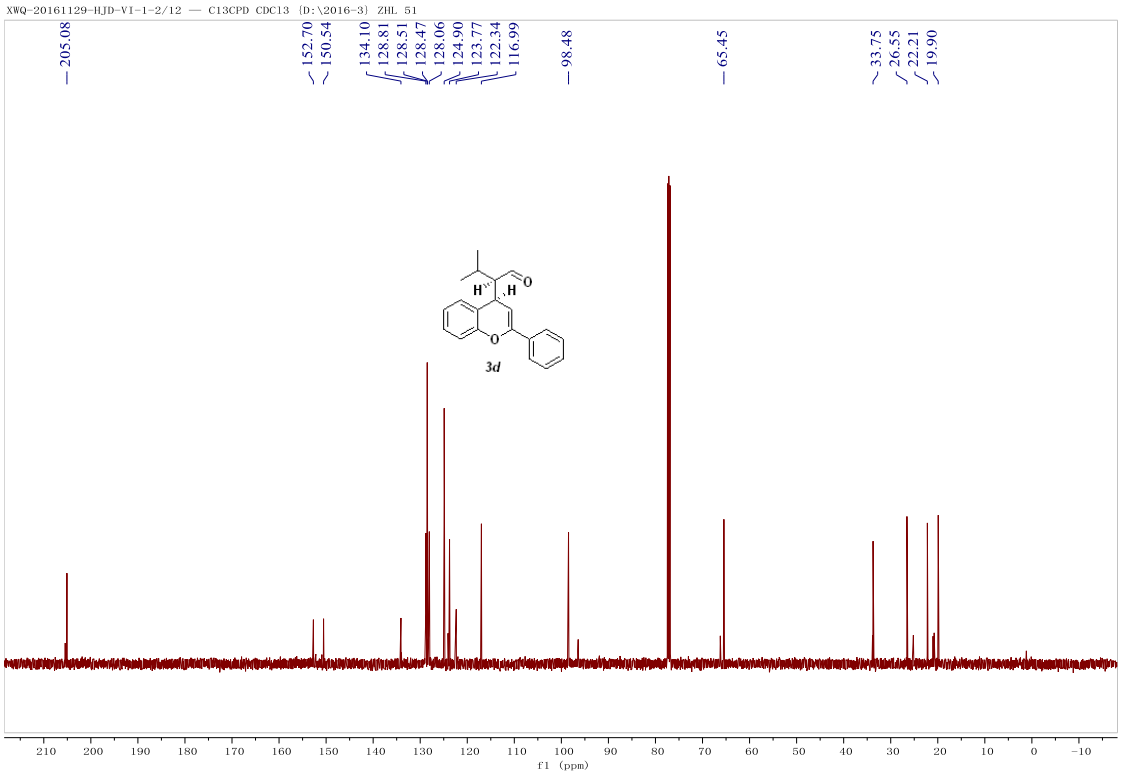
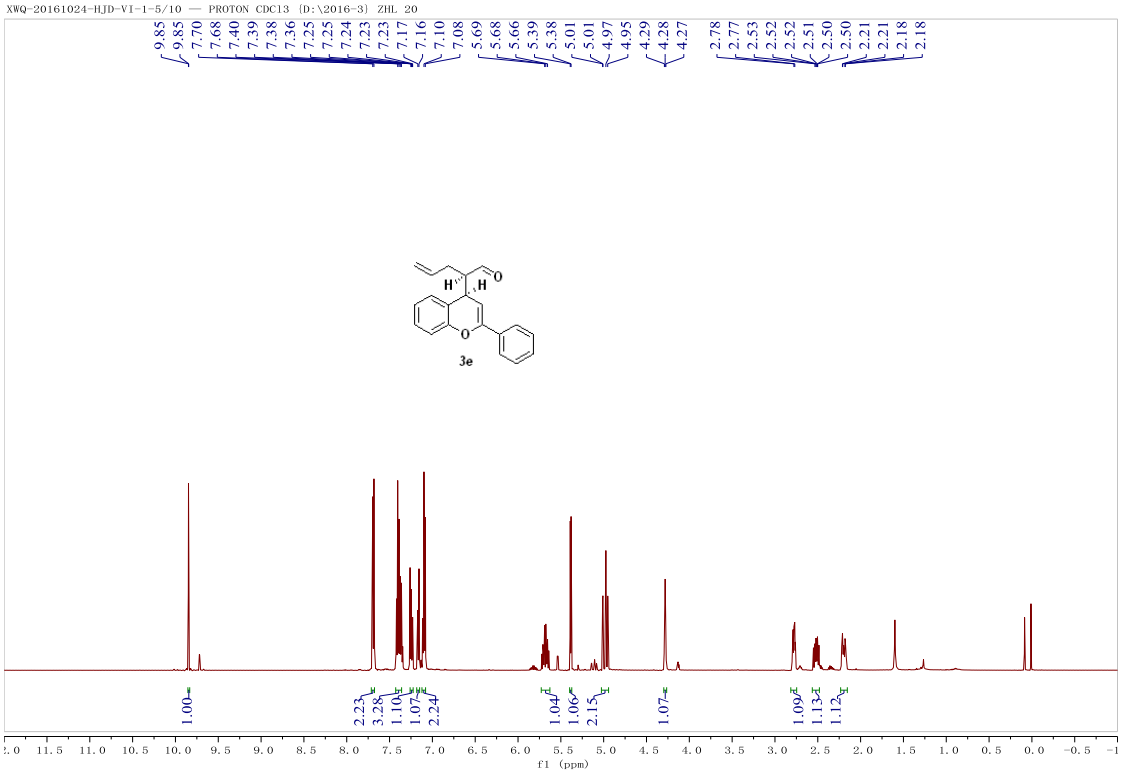


Figure S35 ^{1}H and ^{13}C NMR Spectrum of Compound 3d



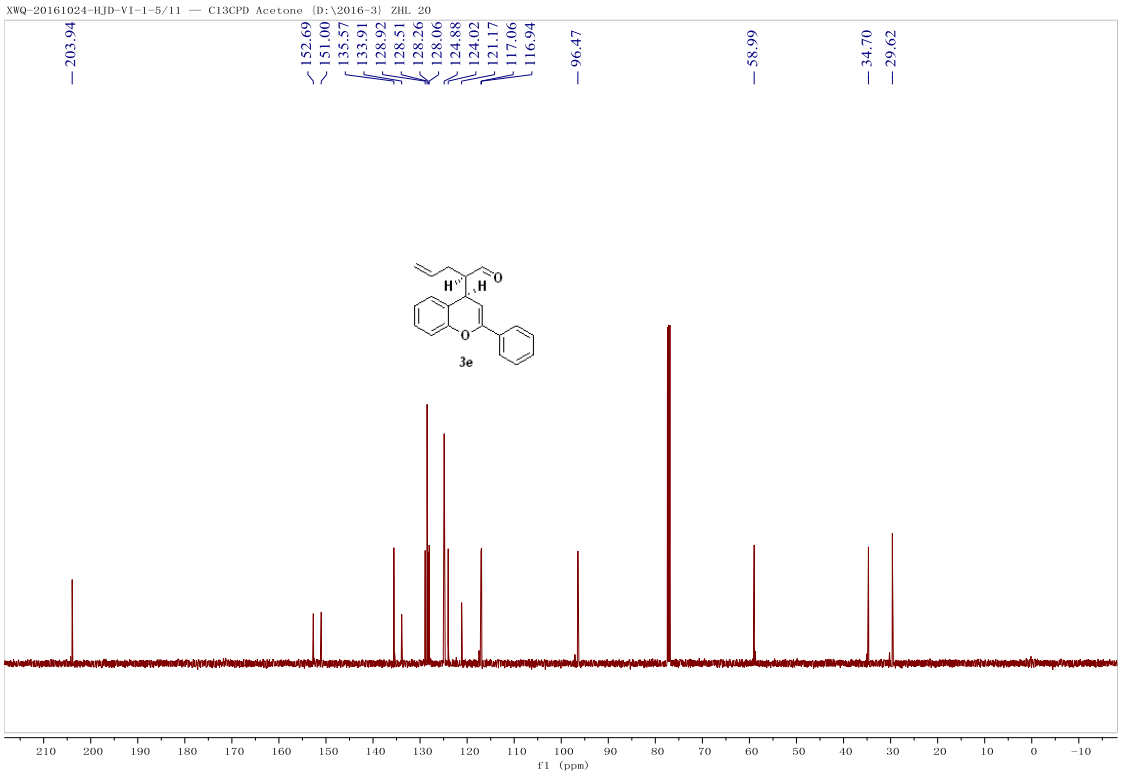
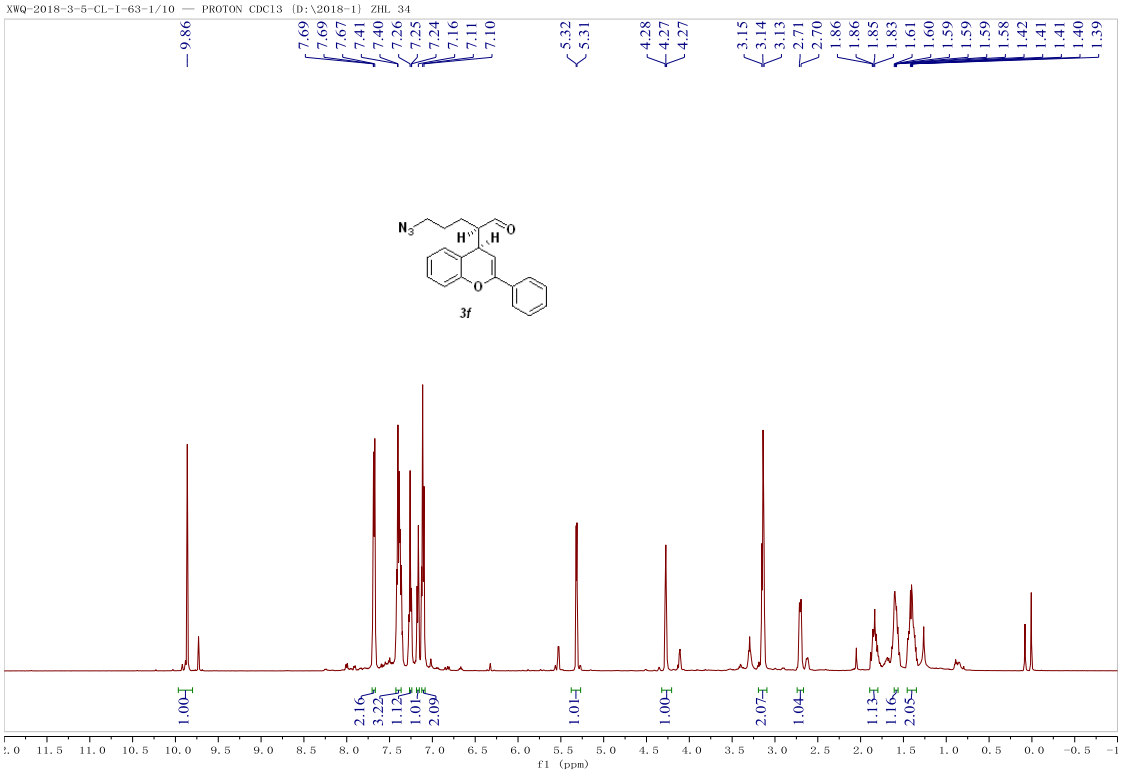


Figure S36 ^{1}H and ^{13}C NMR Spectrum of Compound 3e



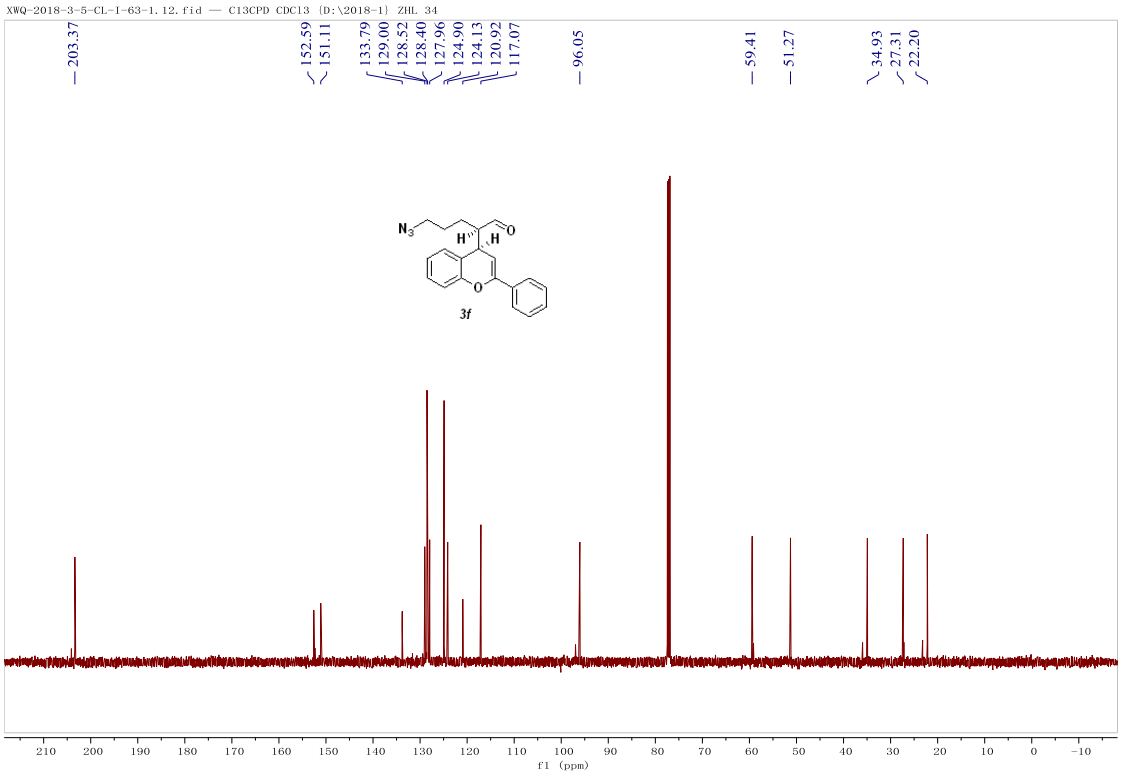
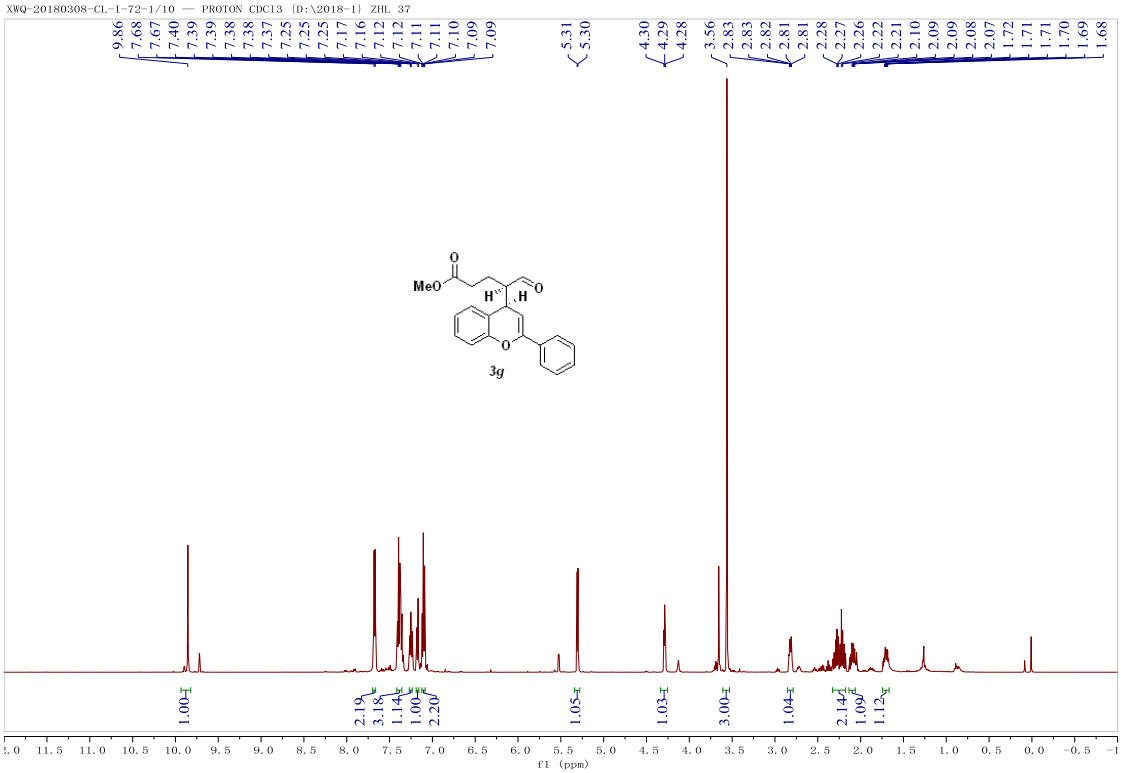


Figure S37 ^{1}H and ^{13}C NMR Spectrum of Compound 3f



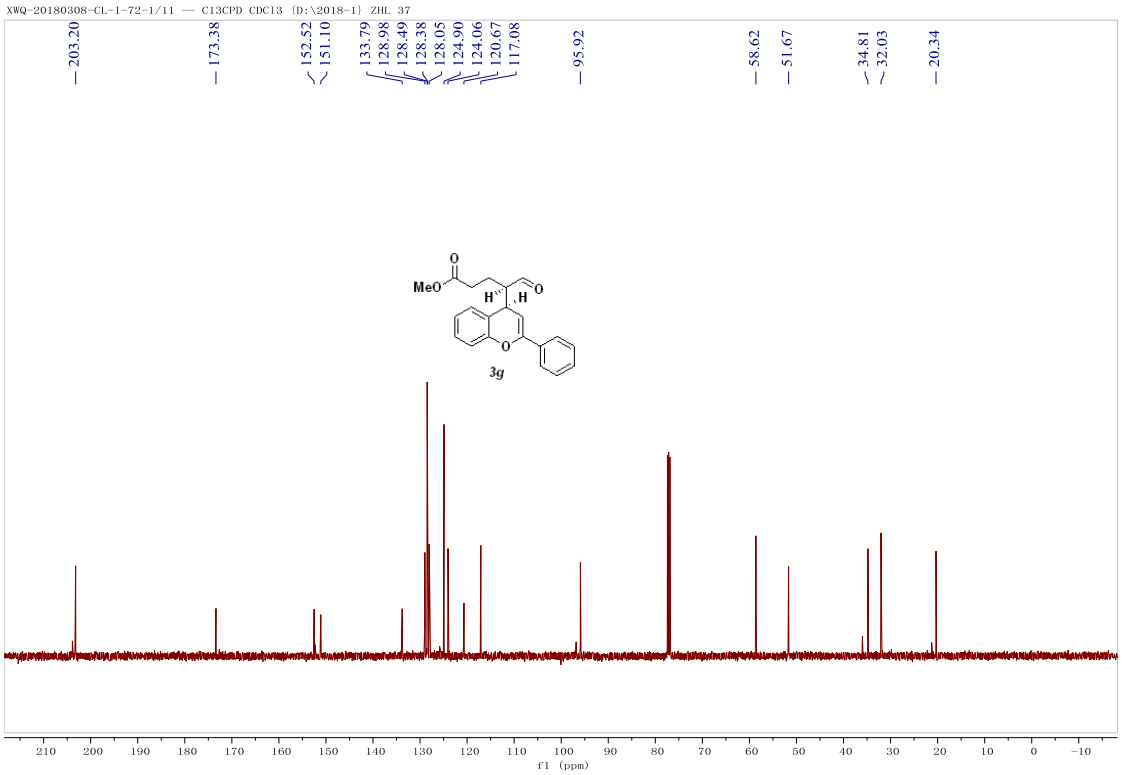
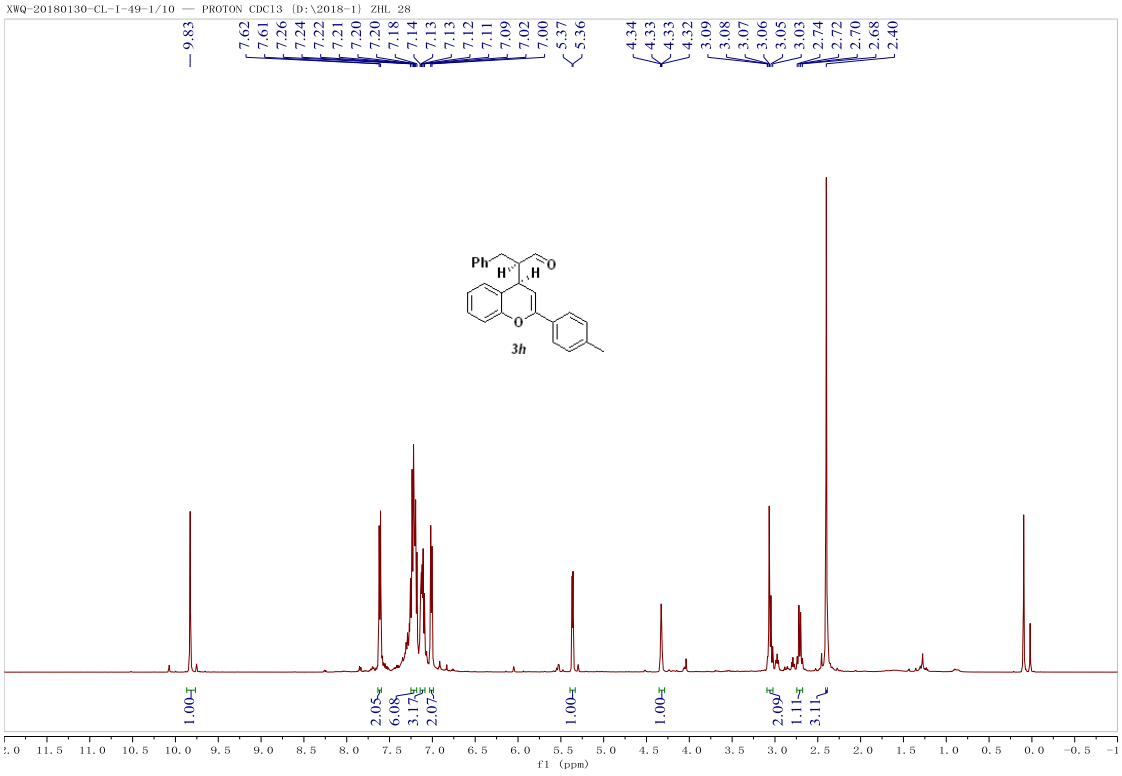


Figure S38 ^{1}H and ^{13}C NMR Spectrum of Compound 3g



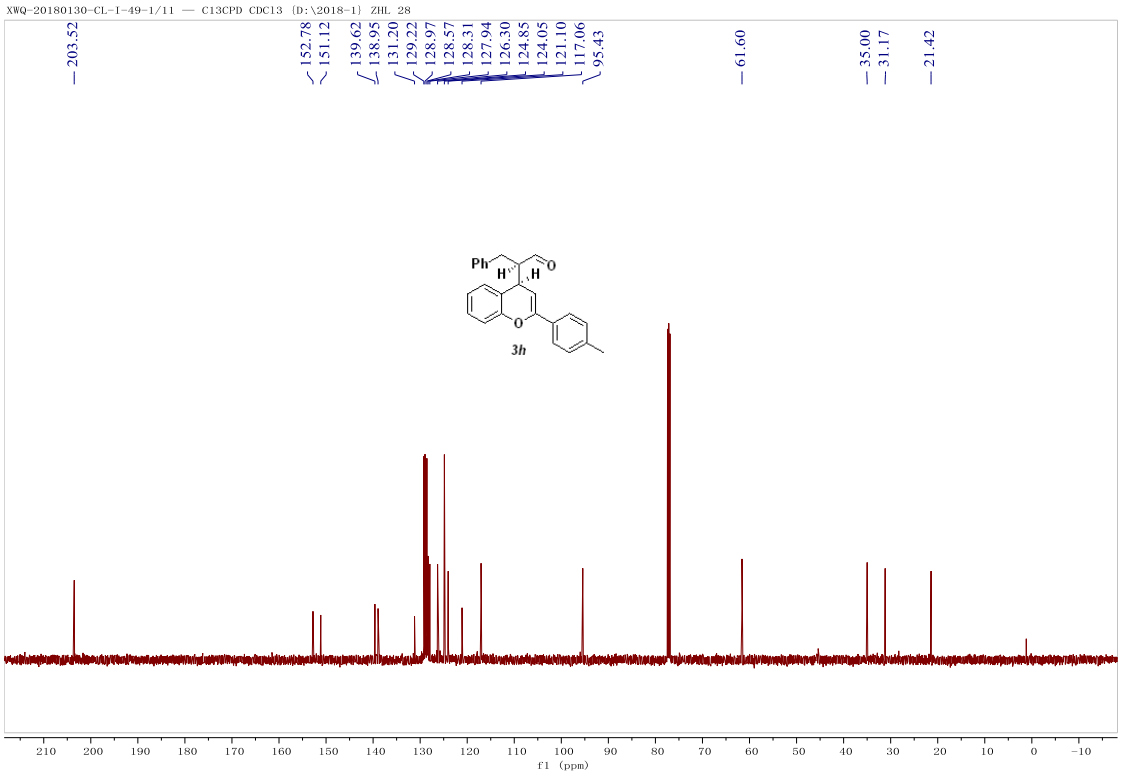
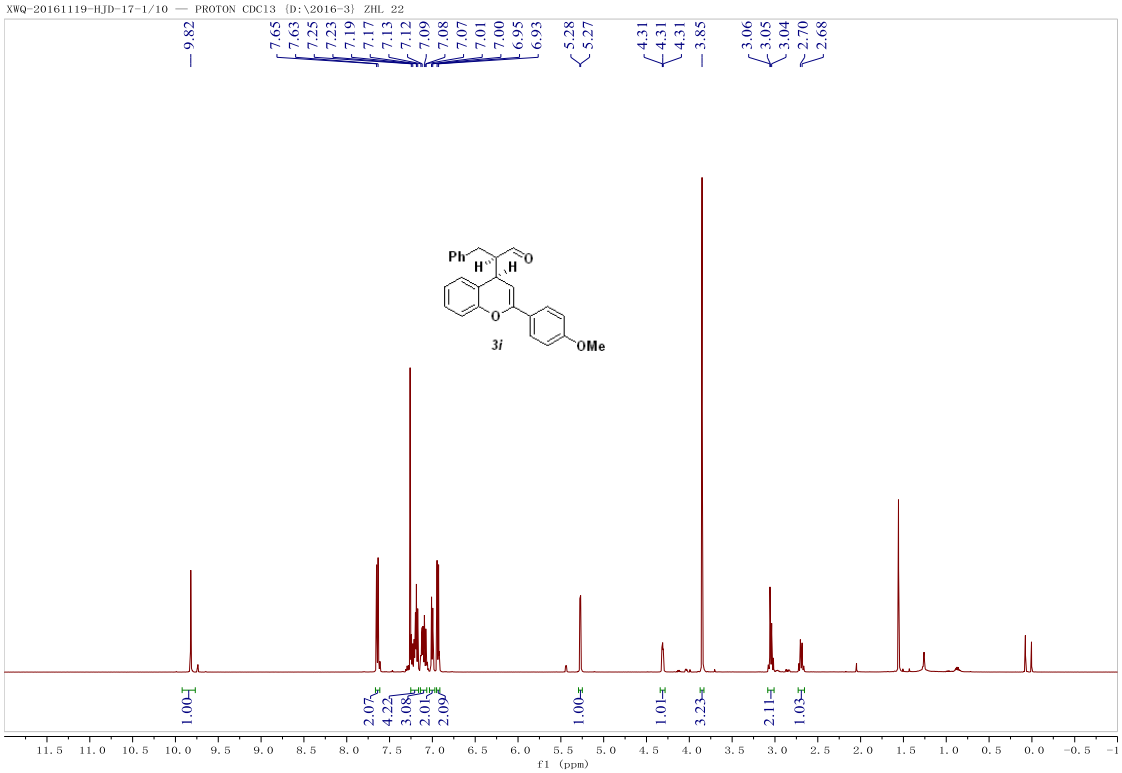


Figure S39 ^{1}H and ^{13}C NMR Spectrum of Compound 3h



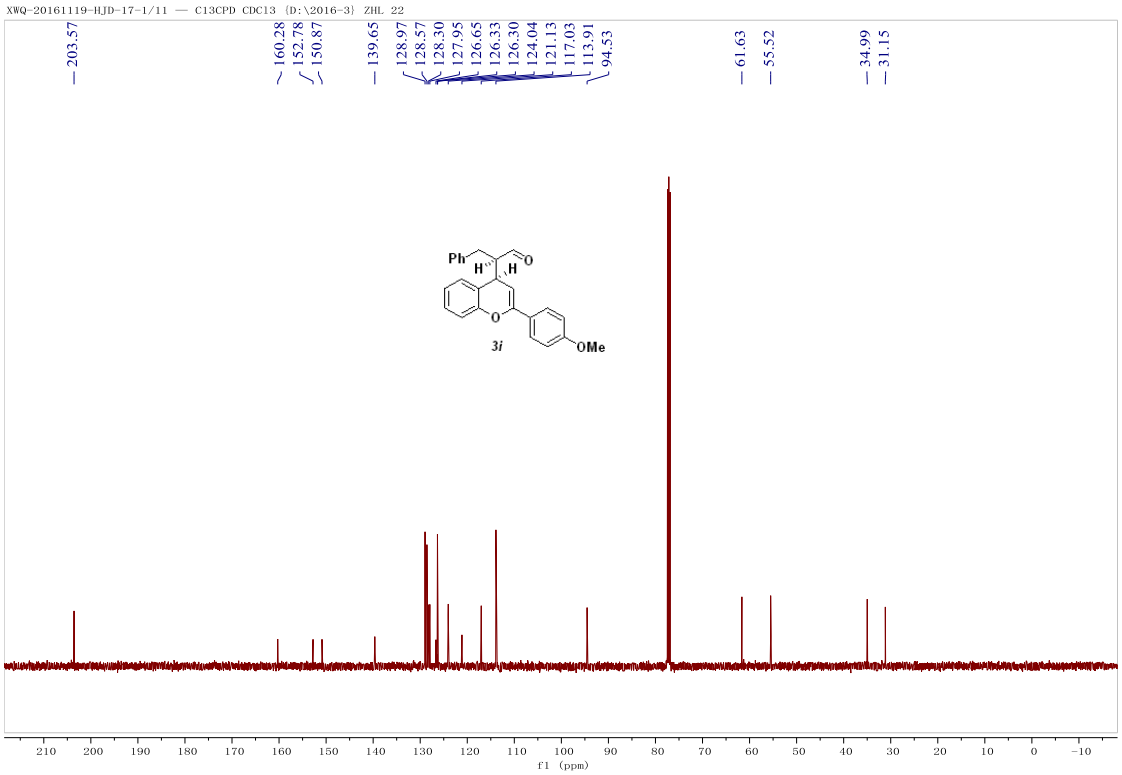
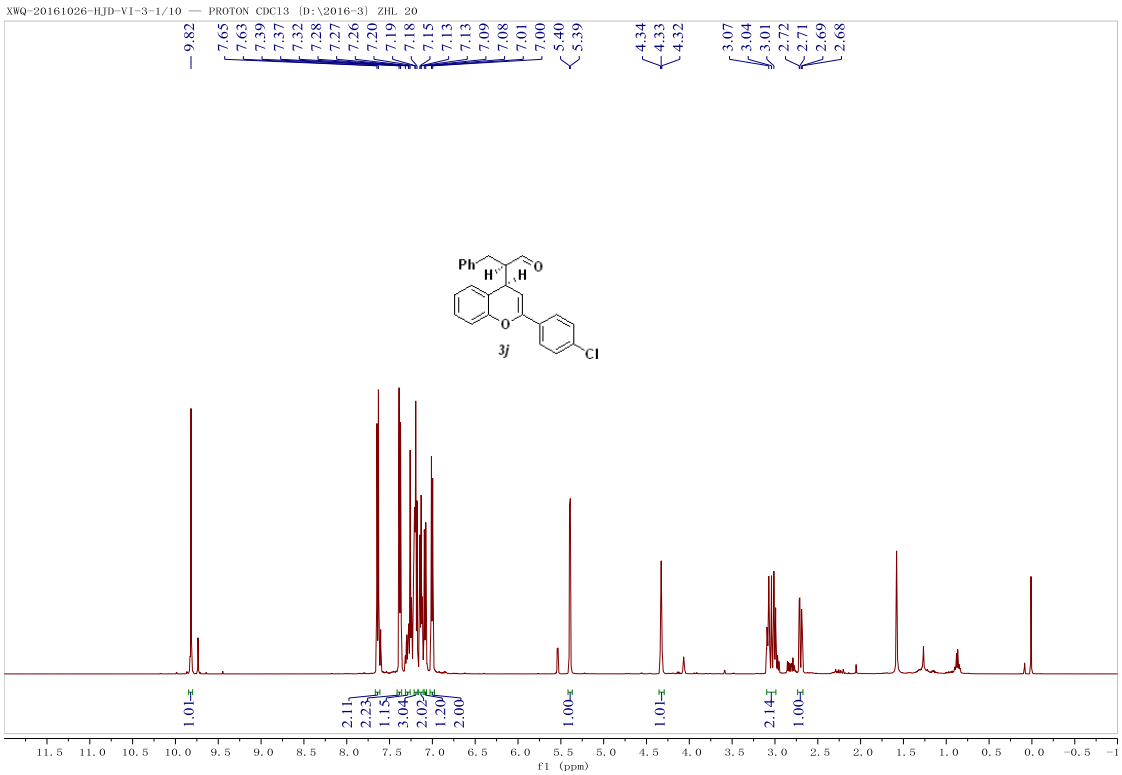


Figure S40 ^{1}H and ^{13}C NMR Spectrum of Compound 3i



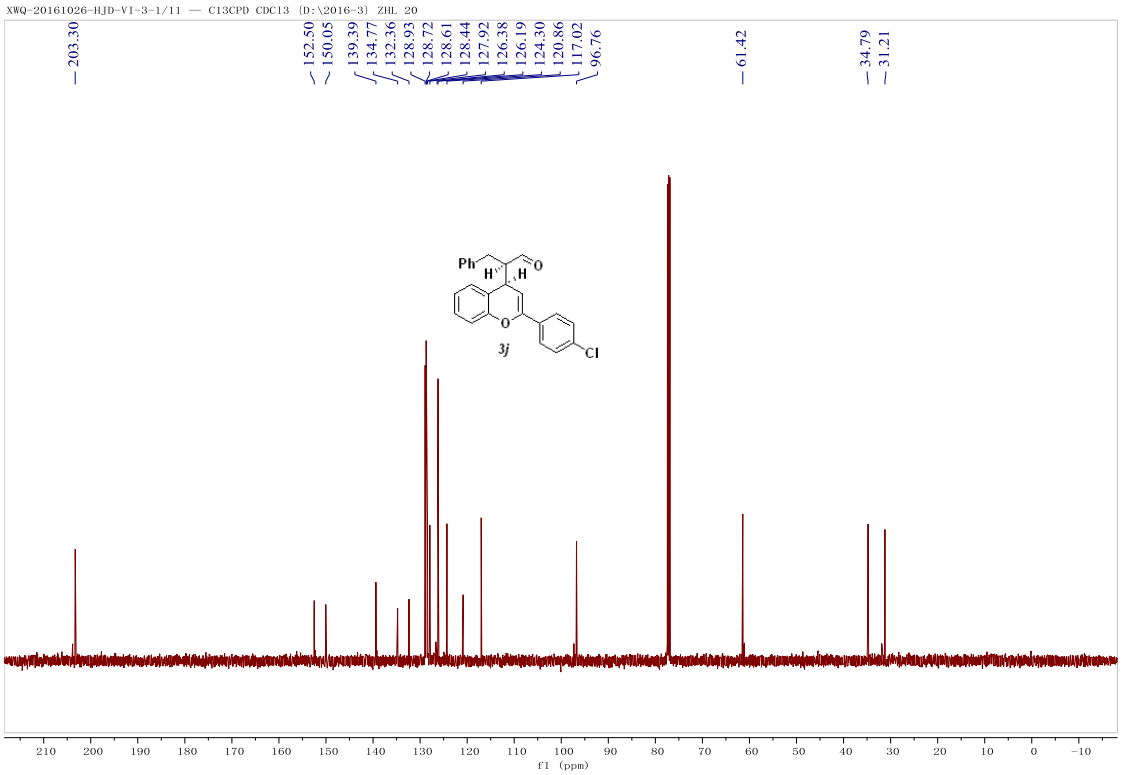
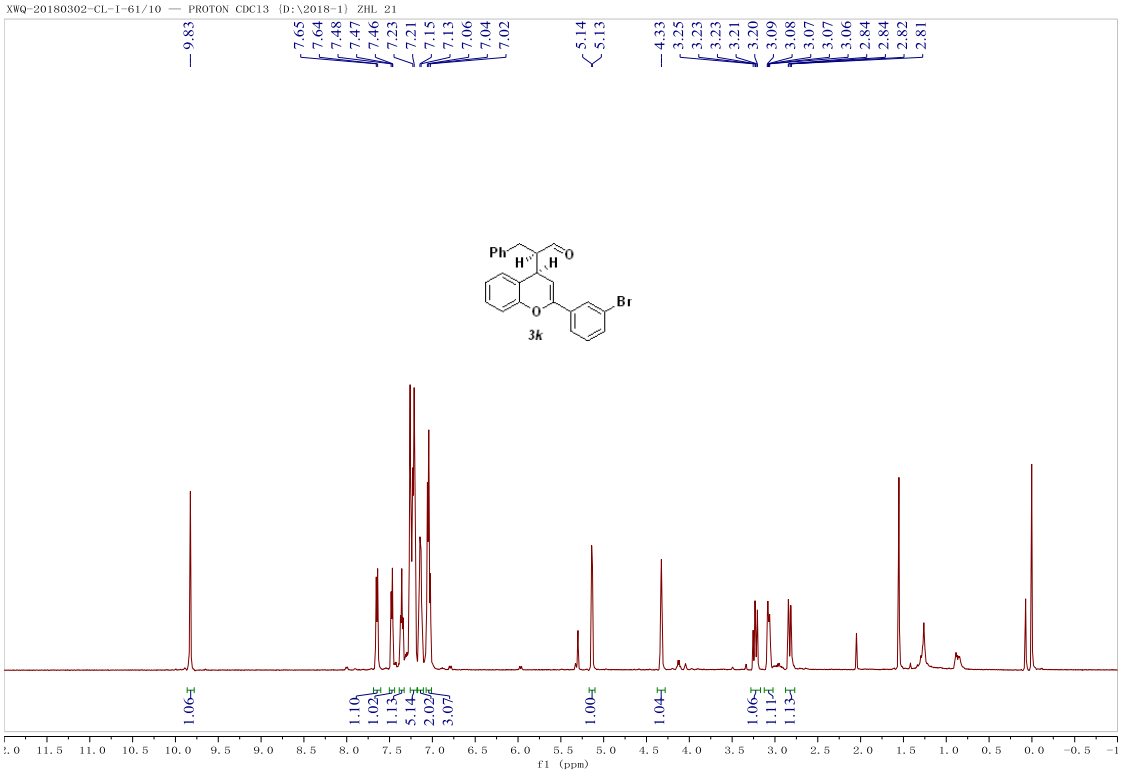


Figure S41 ^{1}H and ^{13}C NMR Spectrum of Compound 3j



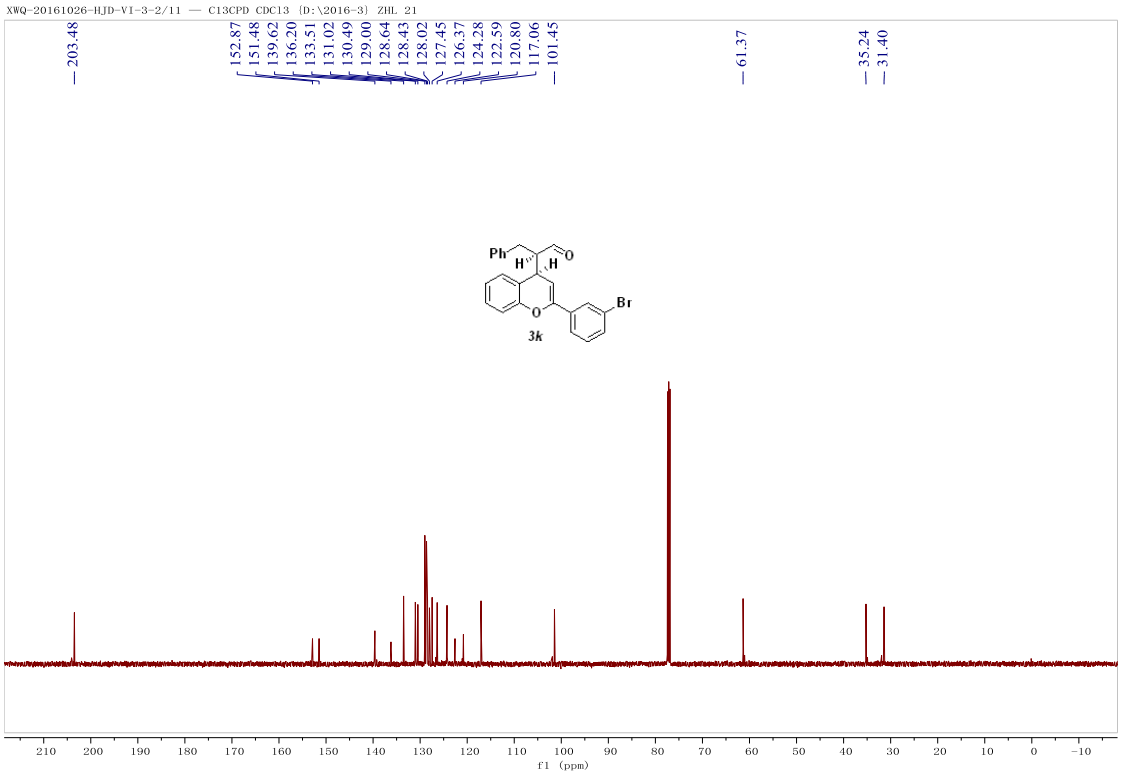
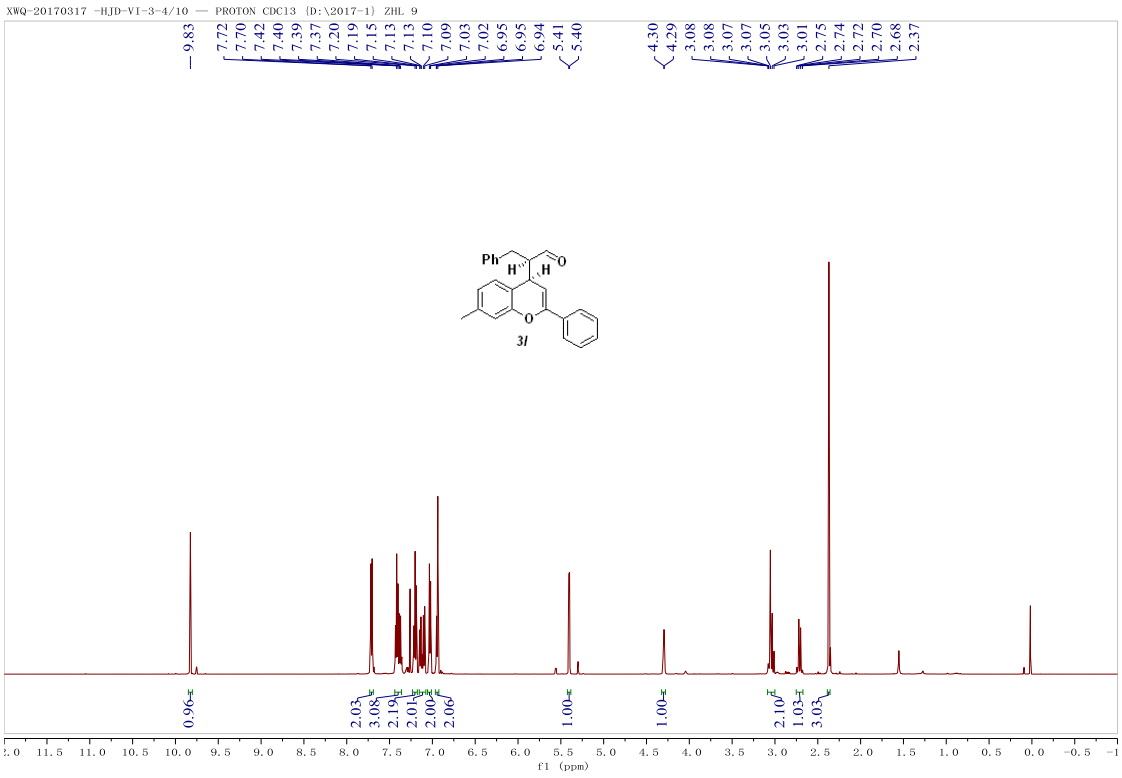


Figure S42 ^{1}H and ^{13}C NMR Spectrum of Compound 3k



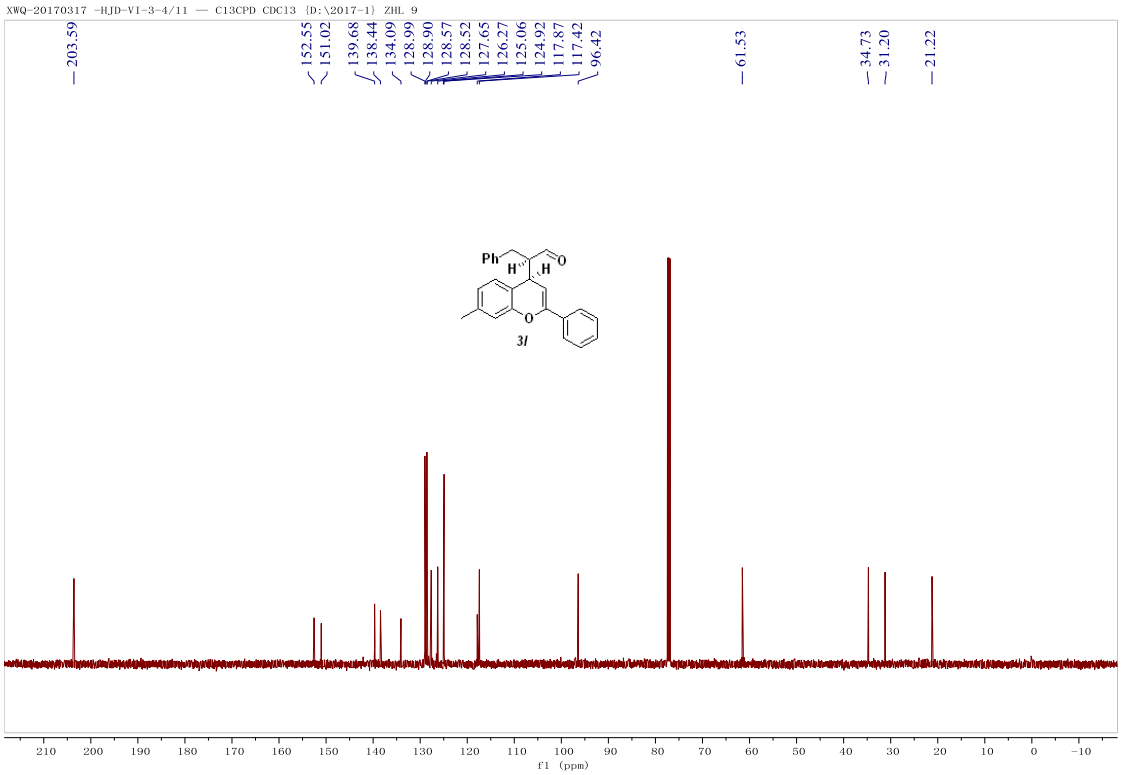
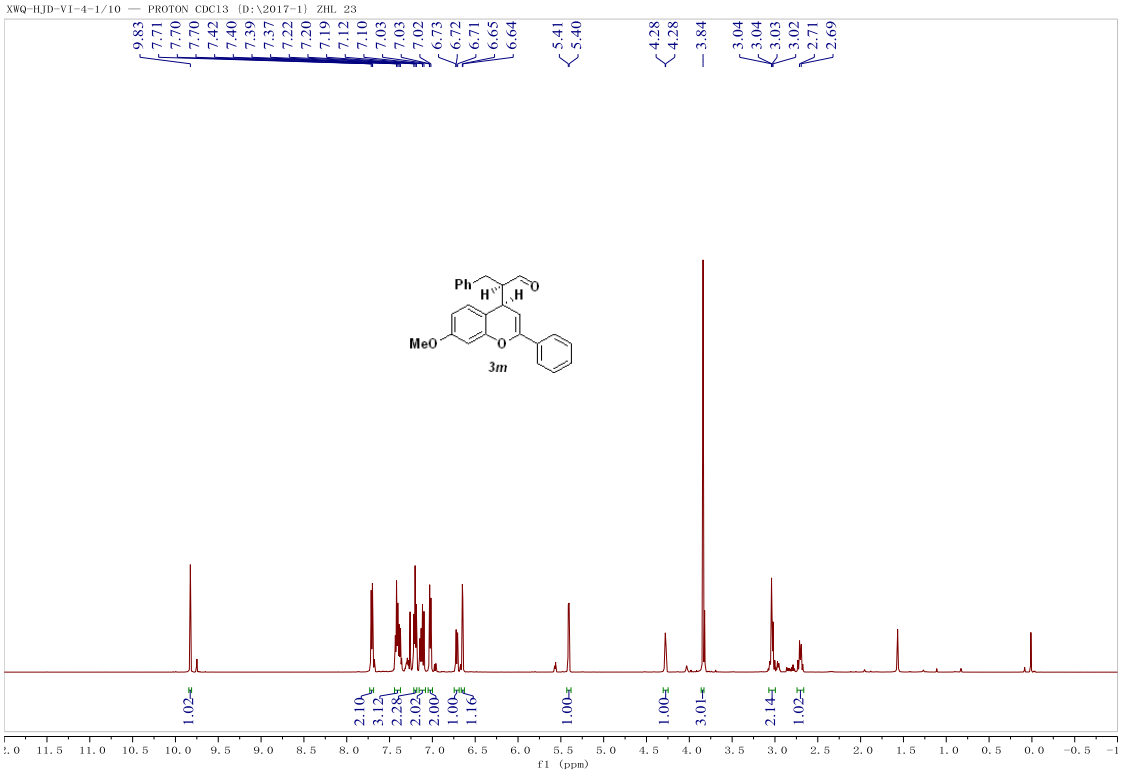


Figure S43 ^{1}H and ^{13}C NMR Spectrum of Compound 3l



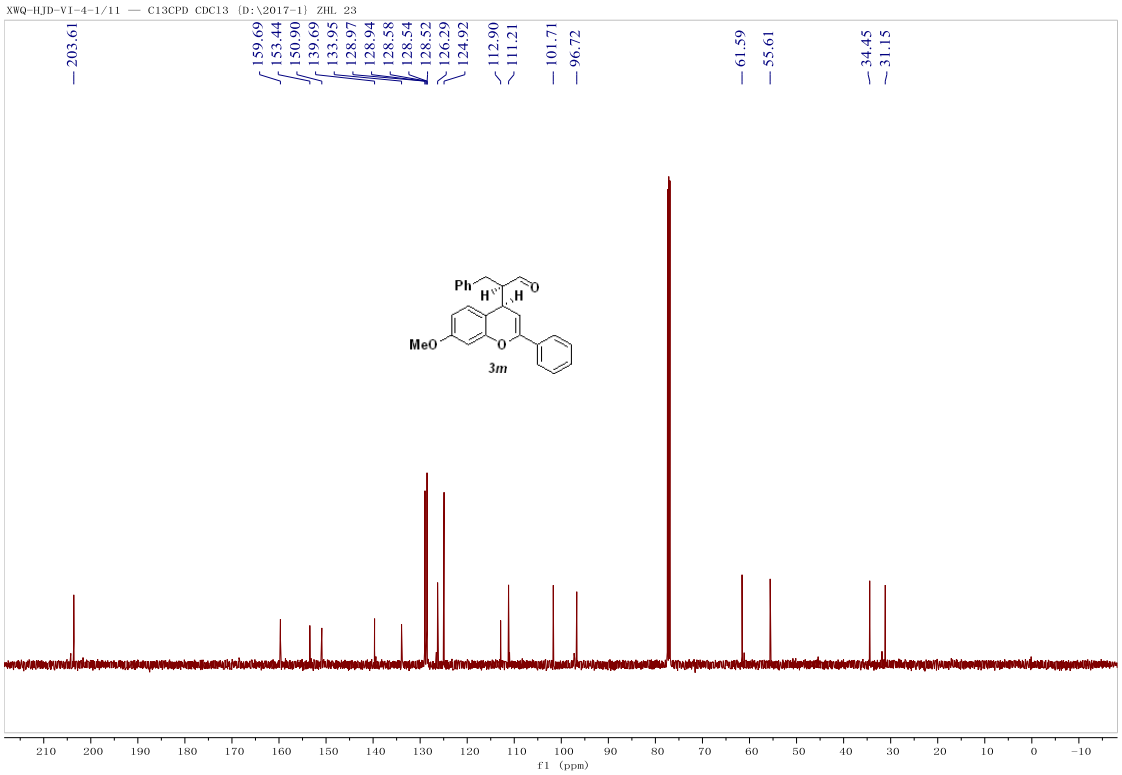
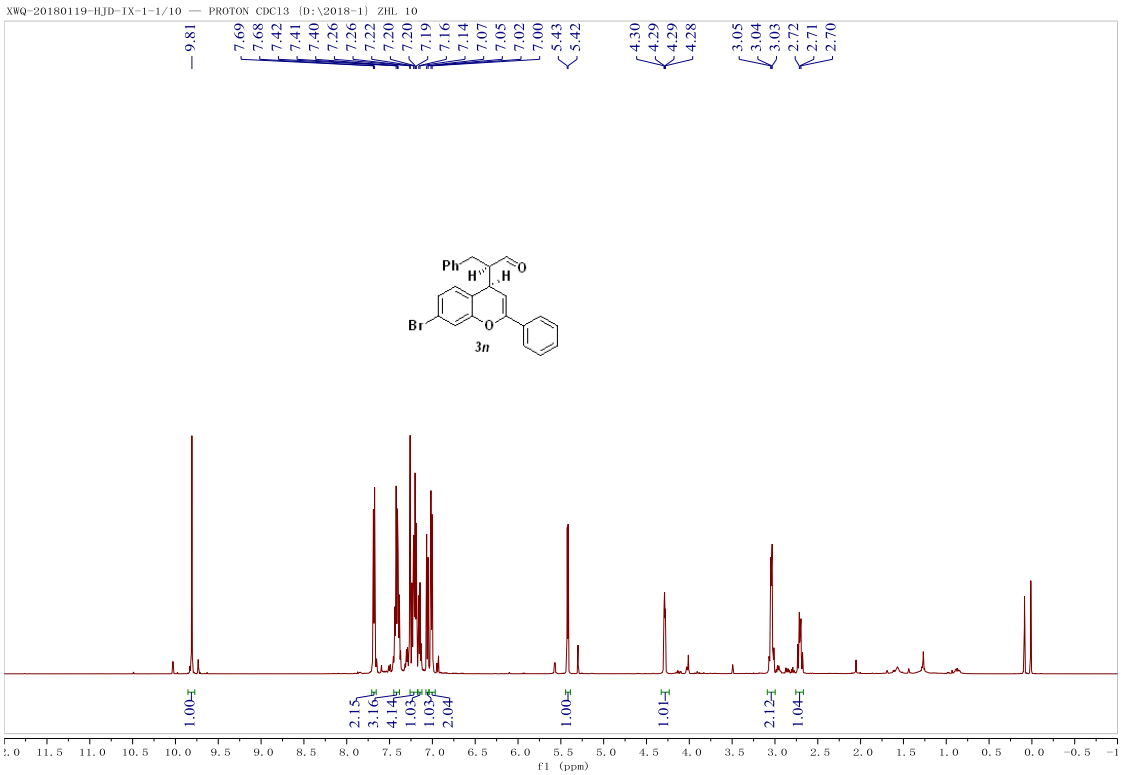


Figure S44 ^{1}H and ^{13}C NMR Spectrum of Compound 3m



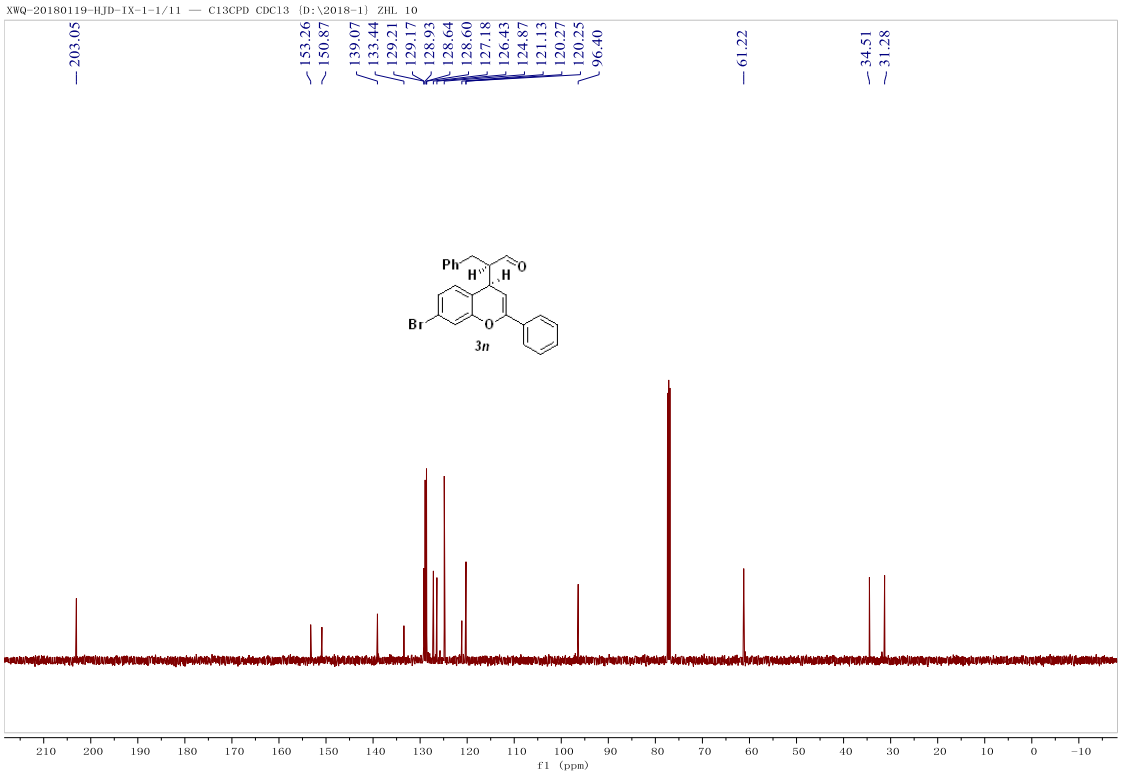
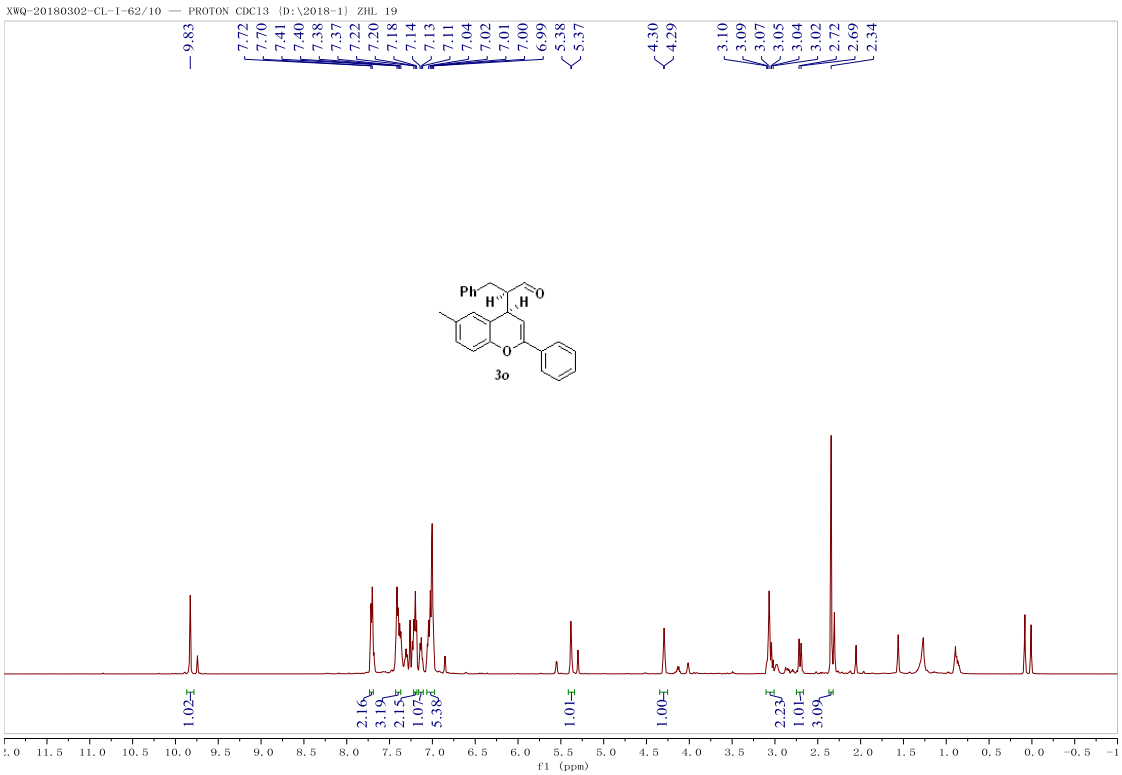


Figure S45 ^{1}H and ^{13}C NMR Spectrum of Compound 3n



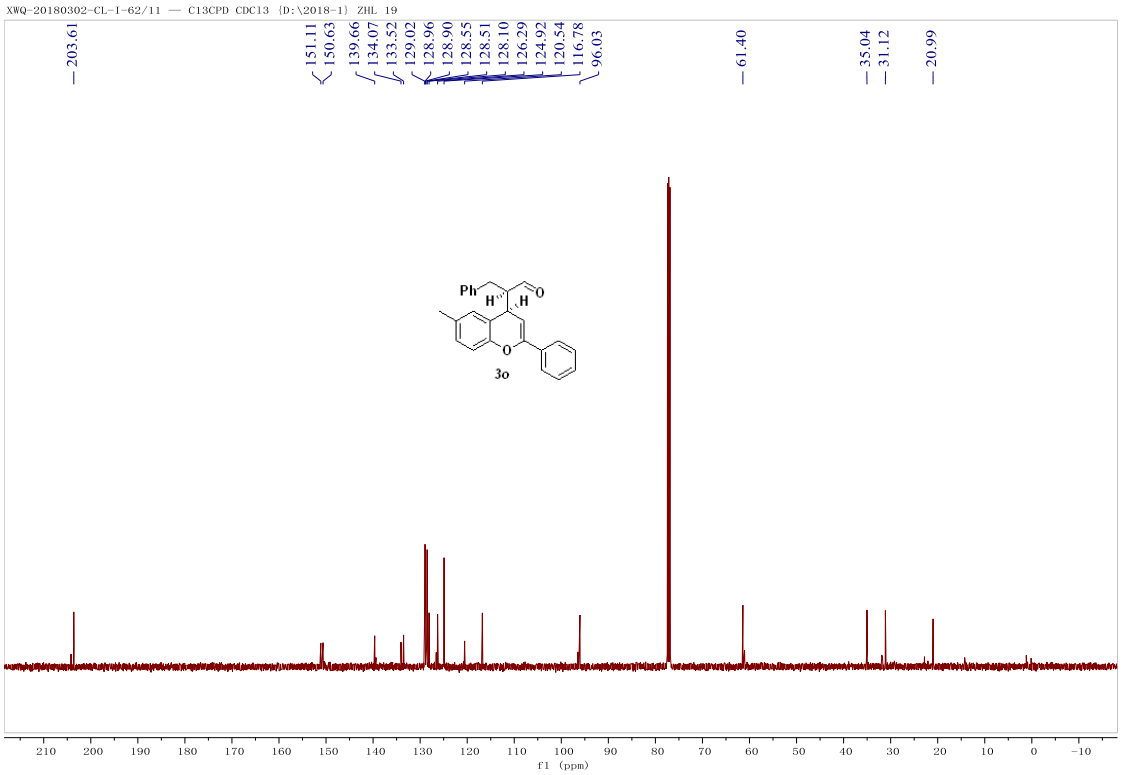
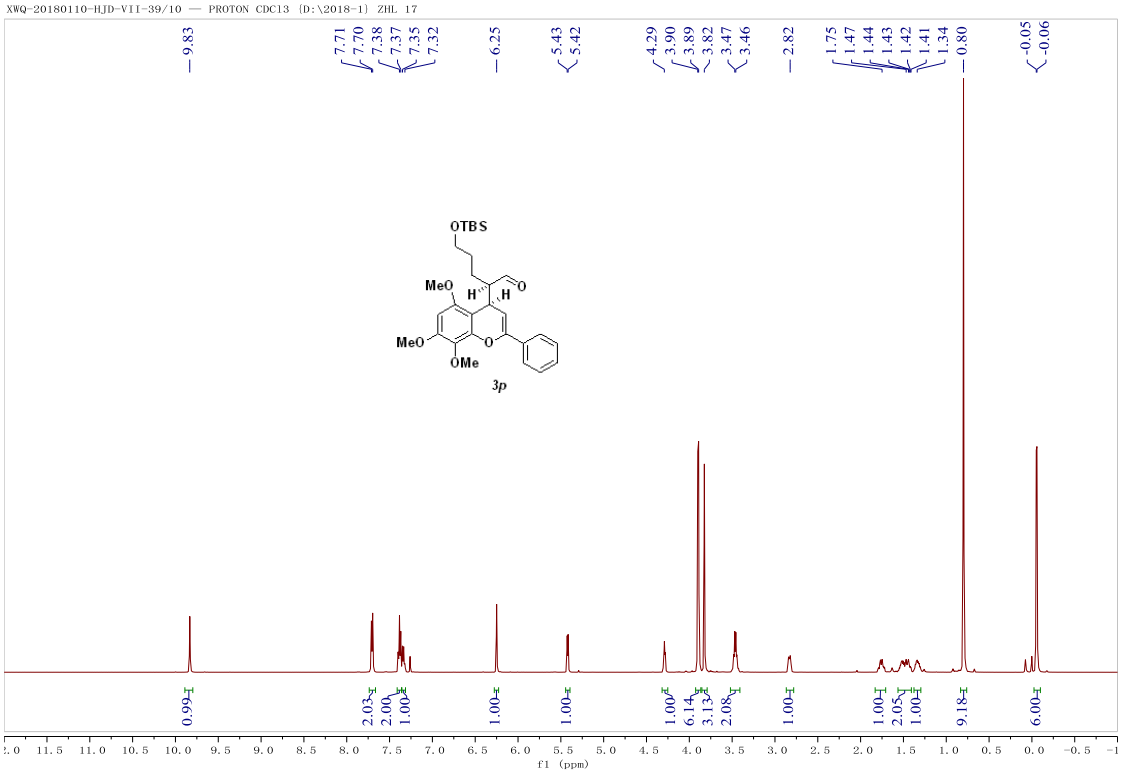


Figure S46 ^{1}H and ^{13}C NMR Spectrum of Compound 3o



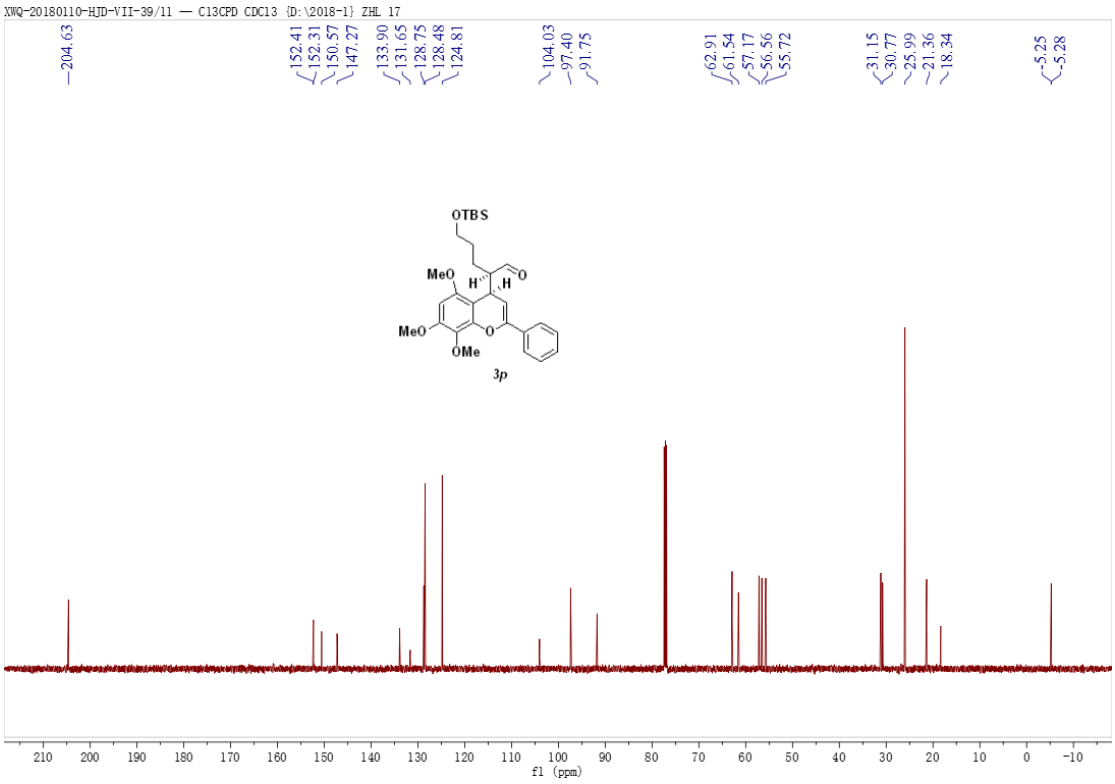
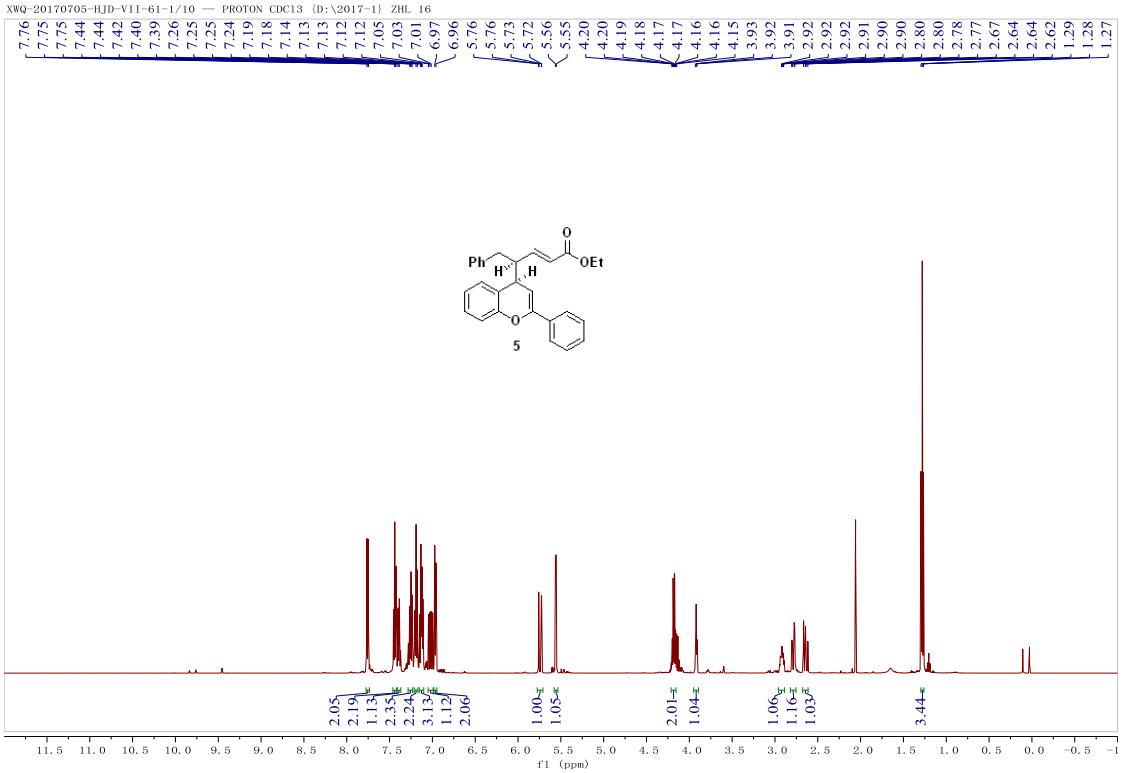


Figure S47 ^{1}H and ^{13}C NMR Spectrum of Compound 3p



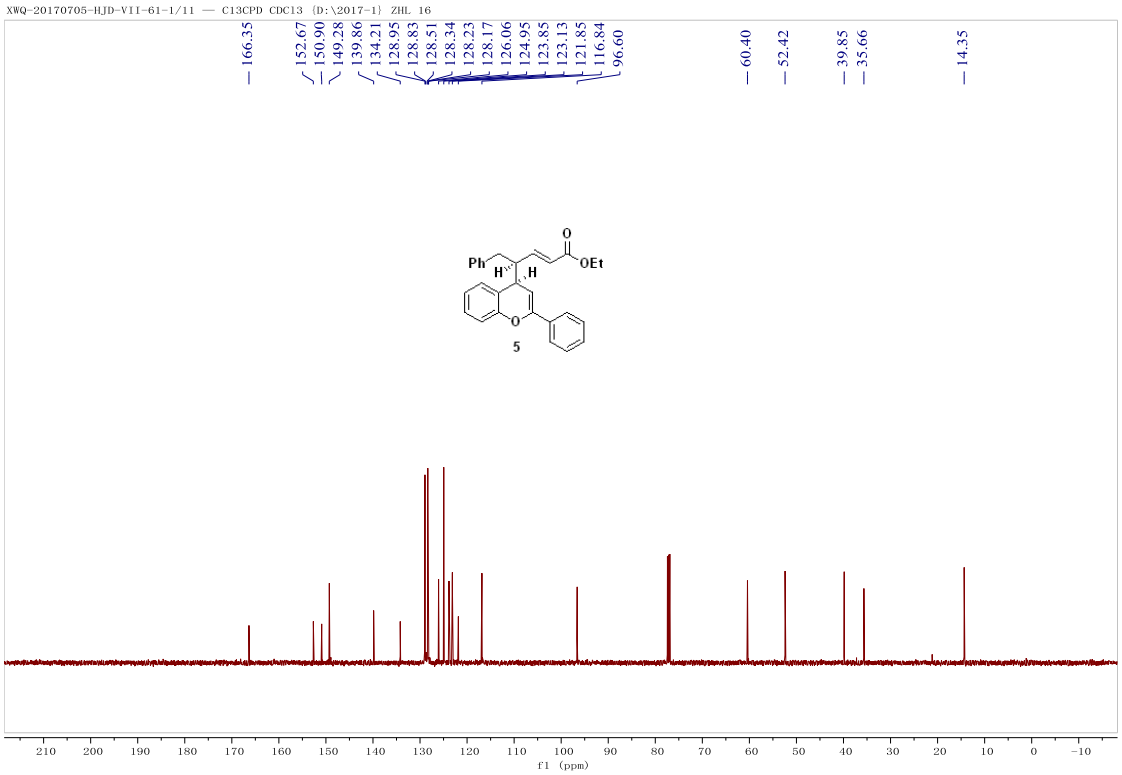
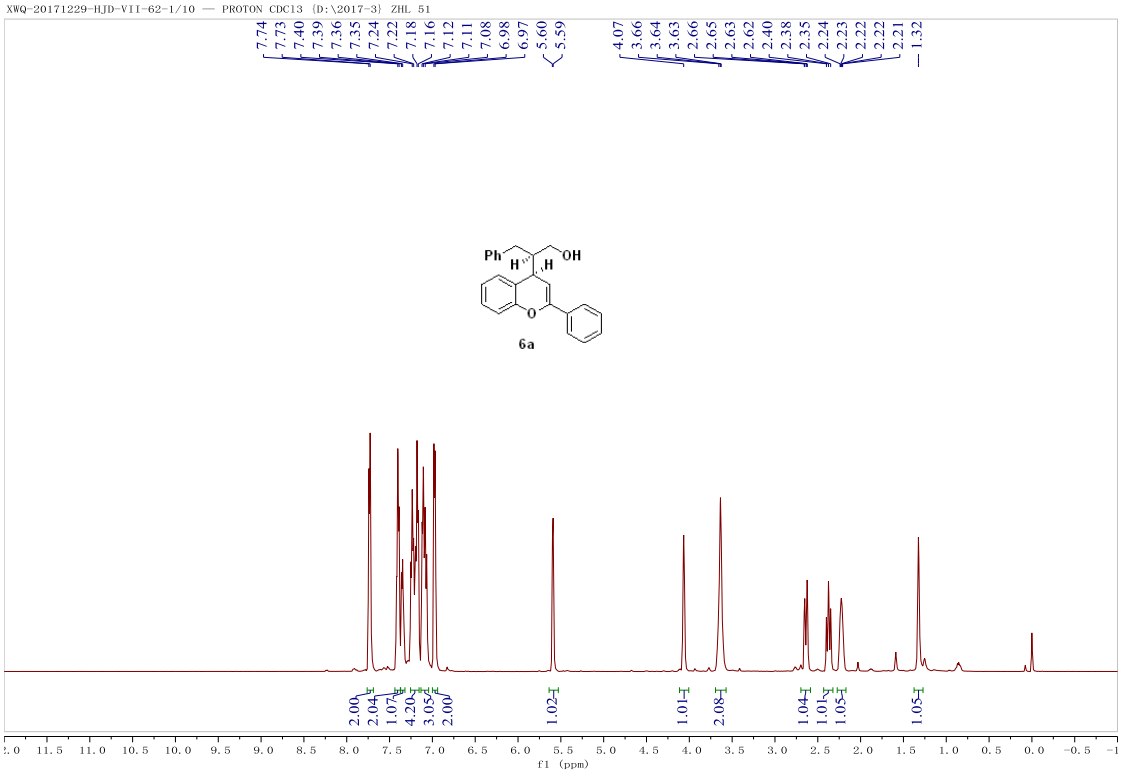


Figure S48 ^{1}H and ^{13}C NMR Spectrum of Compound 5



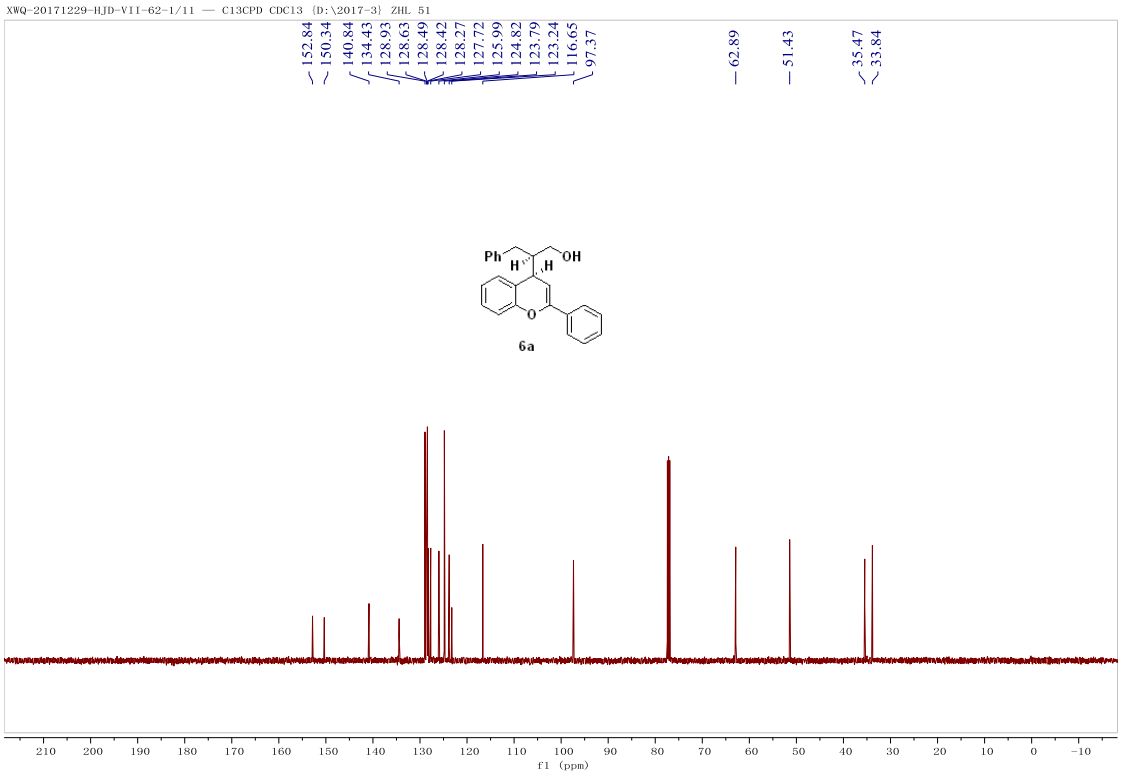
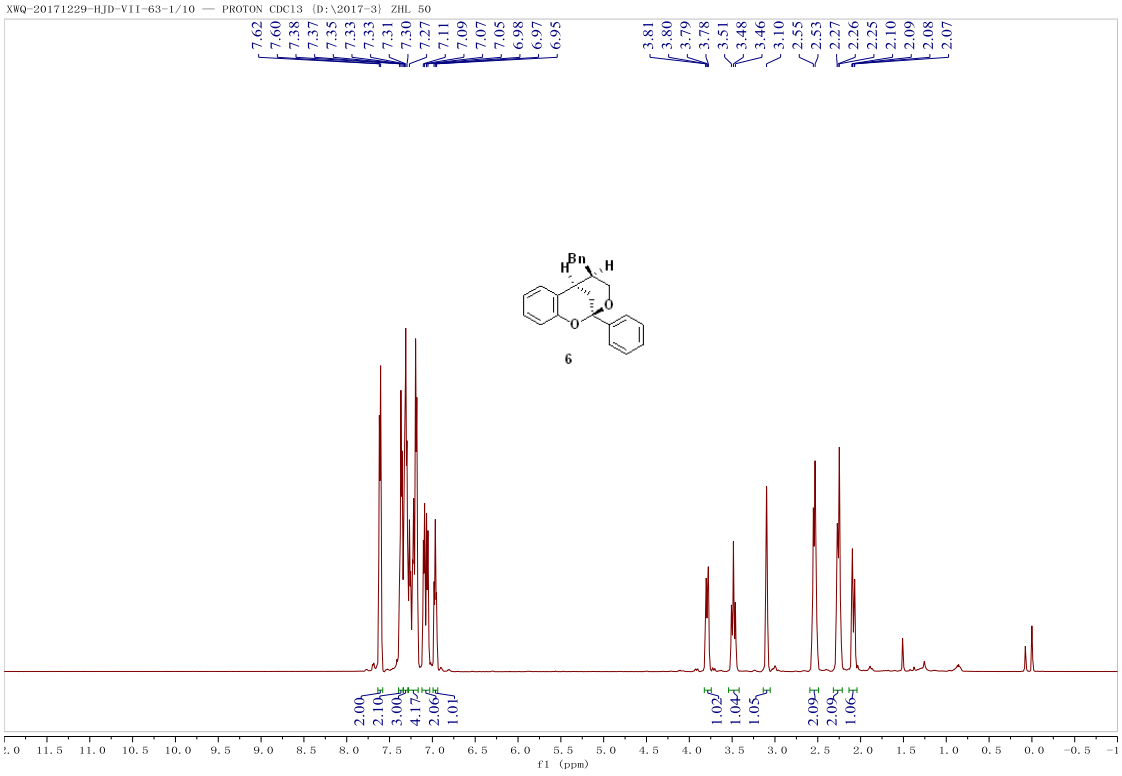


Figure S49 ^{1}H and ^{13}C NMR Spectrum of Compound 6a



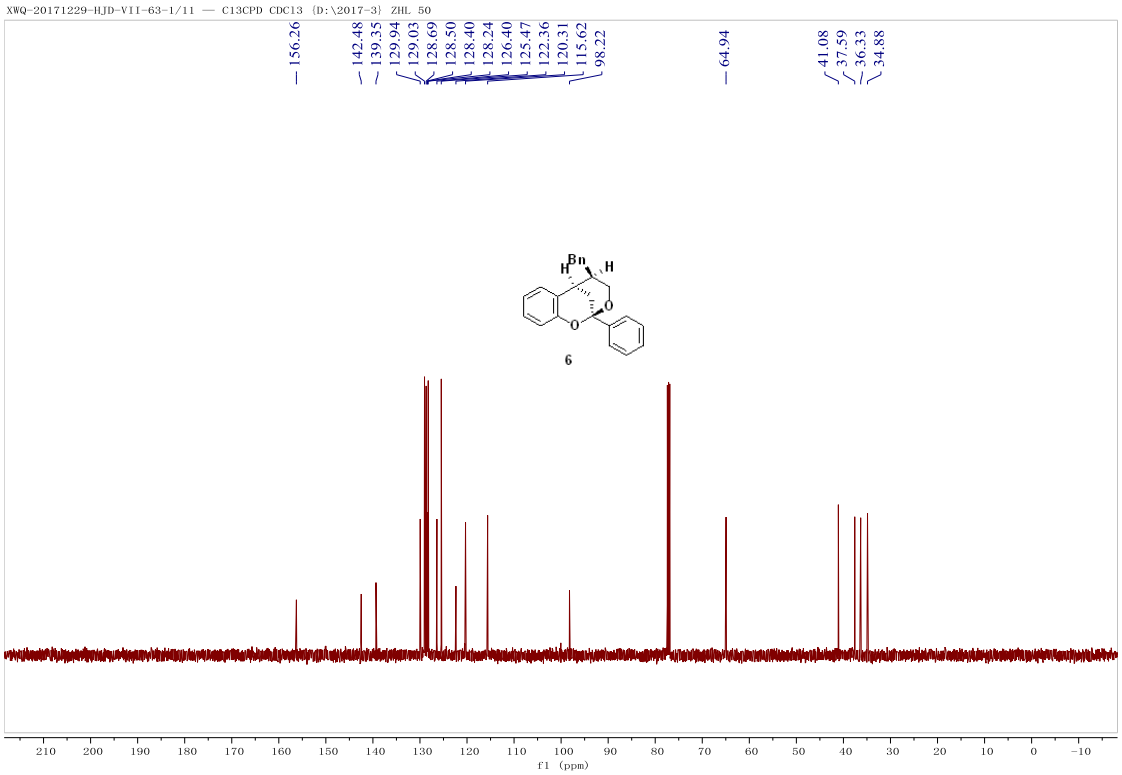
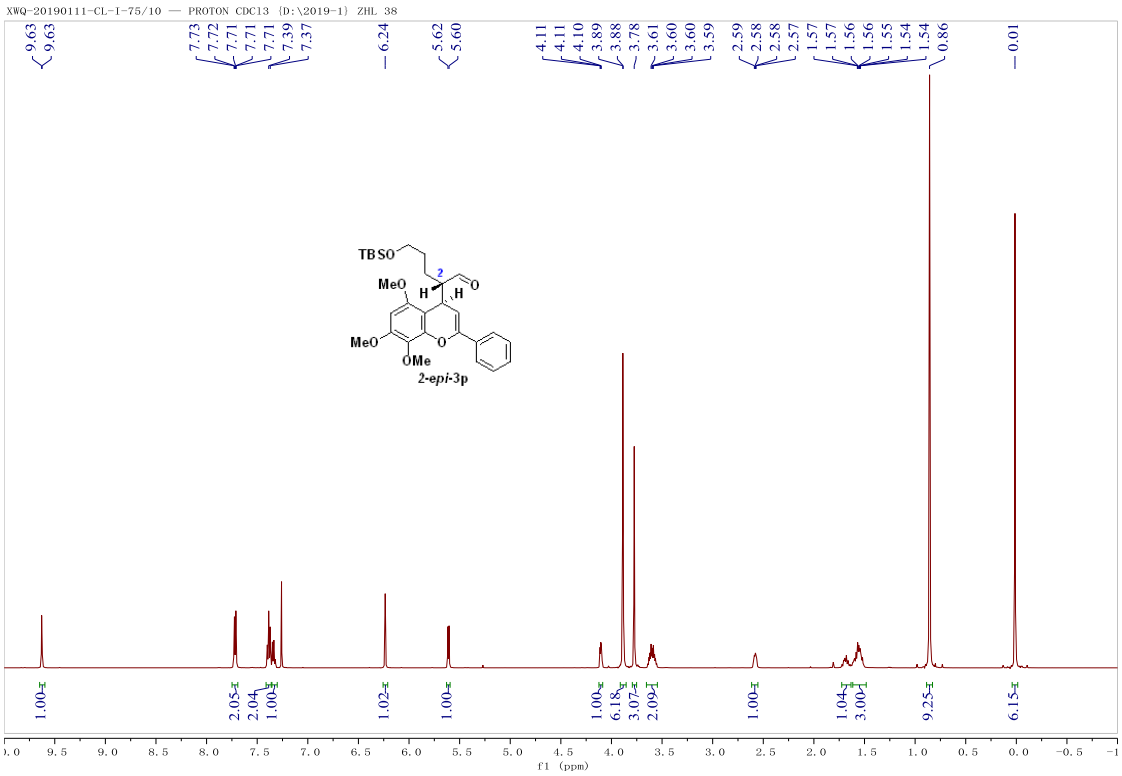


Figure S50 ^{1}H and ^{13}C NMR Spectrum of Compound 6



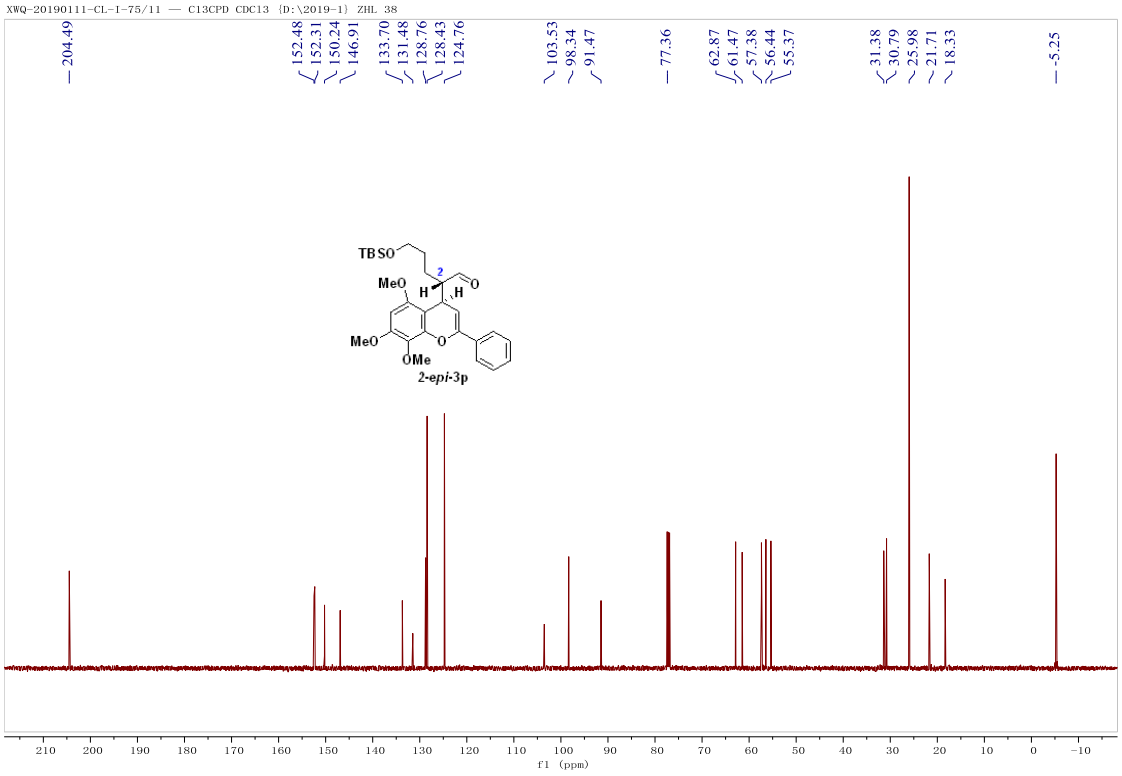


Figure S51 ^{1}H and ^{13}C NMR Spectrum of Compound *2-epi*-3p

9. References

1. Barrios Antúnez, D. J., Greenhalgh, M. D., Fallan, C., Slawin, A. M. Z. & Smith, A. D. Enantioselective synthesis of 2,3-disubstituted trans-2,3-dihydrobenzofurans using a Brønsted base/thiourea bifunctional catalyst. *Org Biomol Chem* **14**, 7268-7274 (2016).

2. Maes, D. *et al.* Total synthesis of naturally occurring 5,6,7- and 5,7,8-trioxygenated coumarins. *Tetrahedron* **64**, 4438-4443 (2008).

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