Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Chemoselective tandem S_N2'/S_N2''/inter- or intramolecular Diels-Alder reaction of γ-vinyl MBH carbonates with phenols and *o*-hydroxychalcones

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Table of Contents:

General Information

Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers or purified by standard techniques.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (600 MHz) spectrometer. All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{19}F NMR spectra were recorded on a Bruker (600 MHz) spectrometer ($CFCl_3$ as outside standard and low field is positive).

Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light.

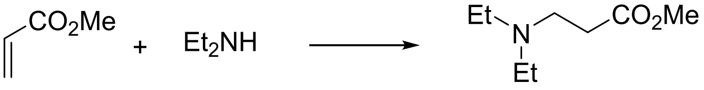
Melting points were determined on a SGW X-4 melting point and were uncorrected.

IR spectra were recorded on a Perkin-Elmer 983G instrument.

Mass spectra analysis was performed on Agilent technologies 5973N and Waters Synapt G2 Si.

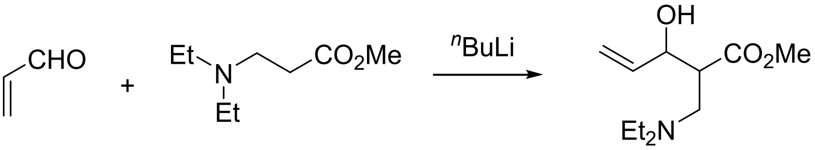
Vinyl MBH adducts were prepared according to the literature procedure[1,2] and stored at 4 °C prior to use. Phenols were purchased from commercial suppliers, and *orth*-hydroxychalcones were prepared following reported procedures.[3] All reactions were carried out employing oven dried glassware.

Procedure for the preparation of γ-vinyl MBH carbonate 1a and *o*-hydroxychalcone



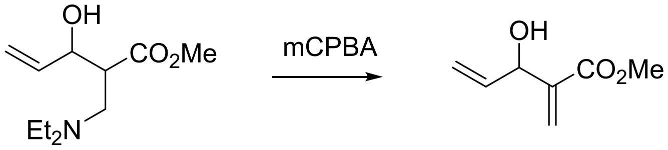
S1

S1: A mixture of methyl acrylate (17.1 mL, 190 mmol) and diethylamine (21.7 mL, 210 mmol) was stirred for 8 h. The crude was concentrated in vacuo to give **S1** as an oil (27.2 g, 90% yield); ^{1}H NMR ($CDCl_3$, 600MHz) δ 3.67 (s, 3H), 2.79 (t, *J* = 7.0 Hz, 2H), 2.51 (q, *J* = 6.9 Hz, 4H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 6.9 Hz, 6H).



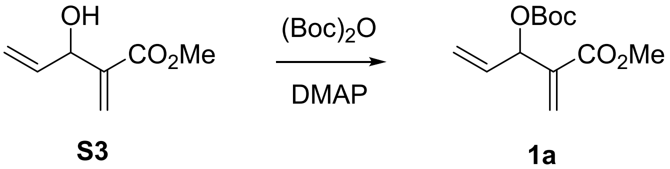
S1 **S2**

S2: To solution of diisopropylamine (21.9 mL, 156 mmol) in THF (200 mL) at –40 °C was added ^{n}BuLi (61.4 mL, 2.5 M in hexane, 154 mmol) and the reaction stirred for 15min. Methyl 3-(dimethylamino)propionate **S1** (21.0 g, 132 mmol) was then added dropwise and the reaction stirred for 30 min at –40 °C then warmed to RT for 30 min over which time a white precipitate formed. The reaction was then cooled back to –40 °C and acrolein (7.37 g, 132 mmol) was added dropwise as a solution in THF (60 mL) and the reaction stirred for 1 h. The reaction was quenched with NH_4Cl (150 mL) and diluted with EtOAc (300 mL). The aqueous layer was separated and extracted with EtOAc (3 × 200 mL), and the combined organic layers were dried (Mg_2SO_4), filtered and concentrated in vacuo to give **S2** (23.8 g, 84% yield, diastereomeric mixture, d.r. 1.7:1); R_f = 0.42 (EtOAc/MeOH, 90:10); data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 600MHz) δ 5.78 (ddd, *J* = 17.0, 11.1, 6.8 Hz, 1H), 5.26 (d, *J* = 18.0 Hz, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 4.40 (dd, *J* = 8.3, 7.8 Hz, 1H), 3.62 (s, 3H), 3.04 (dd, *J* = 12.4, 11.9 Hz, 2H), 2.70 (m, 4H), 2.41 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 6H). data for the minor diastereomer: ^{1}H NMR ($CDCl_3$, 600MHz) δ 5.88 (m, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 4.62 (m, 1H), 3.67 (s, 3H), 2.94 (dd, *J* = 11.6, 10.9 Hz, 1H), 2.66 (m, 4H), 2.43 (m, 2H), 1.02 (t, *J* = 6.9 Hz, 6H).

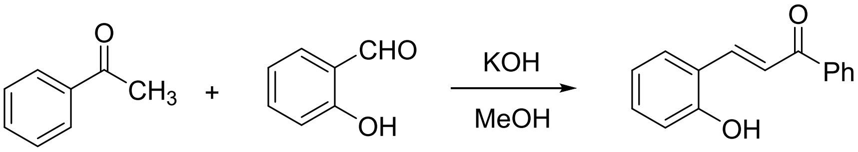


S2 **S3**

S3: To a stirred suspension of amine **S2** (23.2 g, 108 mmol) and $NaHCO_3$ (24.1 g, 287 mmol) in CH_2Cl_2 (500 mL) cooled to 0 °C was added a solution of mCPBA (43.5 g, 50% wt/wt, 126 mmol) in CH_2Cl_2 (250 mL). The reaction was then warmed to RT and stirred vigorously for 6 h. The mixture was concentrated in vacuo to approximately 40 mL and diluted with petroleum ether (150 mL) and sat. aq. $NaHCO_3$ (150 mL). The aqueous layer was separated and extracted with petroleum ether (2 × 150 mL). The combined organic layers were dried (Mg_2SO_4), filtered and concentrated in vacuo. Purification by flash column chromatography (eluent = petroleum ether/ethyl acetate = 10/1) gave **S3** as a colorless oil (9.2 g, 60% yield); R_f = 0.55 (petroleum ether/EtOAc, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 6.27 (s, 1H), 5.98 (ddd, J = 16.4, 10.0, 5.1 Hz, 1H), 5.85 (s, 1H), 5.35 (d, J = 16.6 Hz, 1H), 5.22 (d, J = 10.8 Hz, 1H), 4.95 (d, J = 5.5 Hz, 1H), 3.79 (s, 3H).

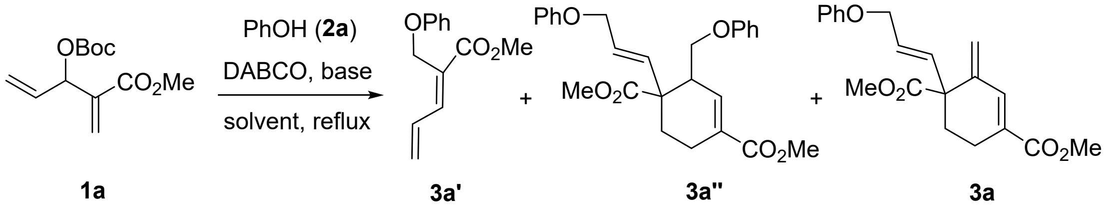


1a: A solution of Boc anhydride (12.6 ml, 55 mmol) in CH_2Cl_2 (100 mL) was added dropwise into a mixture of **S3** (7.1 g, 50 mmol) and DMAP (0.31g, 2.5 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The resulting solution was allowed to warm to room temperature. After stirring for 12h, the reaction mixture was cooled to 0 °C, and 1 N HCl (100 mL) was added. The organic layer was separated and washed sequentially with sat. aq. Na_2CO_3 and brine. The organic layer was concentrated to afford crude which were purified by flash column chromatography (eluent = petroleum ether/ethyl acetate = 20/1) gave **1a** as a colorless oil (6.8 g, 56% yield); R_f = 0.73 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 6.37 (s, 1H), 5.91 (s, 1H), 5.90 (m, 1H), 5.87 (m, 1H), 5.38 (d, J = 15.5 Hz, 1H), 5.26 (d, J = 8.8 Hz, 1H), 3.77 (s, 3H), 1.48 (s, 9H).



To a solution of various acetophenones (1.00 equiv) and salicylaldehyde (1.25 equiv) in ethanol (2.5 mL/mmol) was added dropwise potassium hydroxide 40% (3 equiv) at room temperature. After 24 h, the mixture was cooled with ice and neutralized carefully using 2 N hydrochloric acid. The crude mixture was extracted with ethyl acetate, washed with water and brine, and concentrated by rotary evaporator. The crude product were purified by recrystallisation with ethanol to give pure *o*-hydroxychalcones.

Table 1S. Condition survey for quadruple tandem reaction[a]



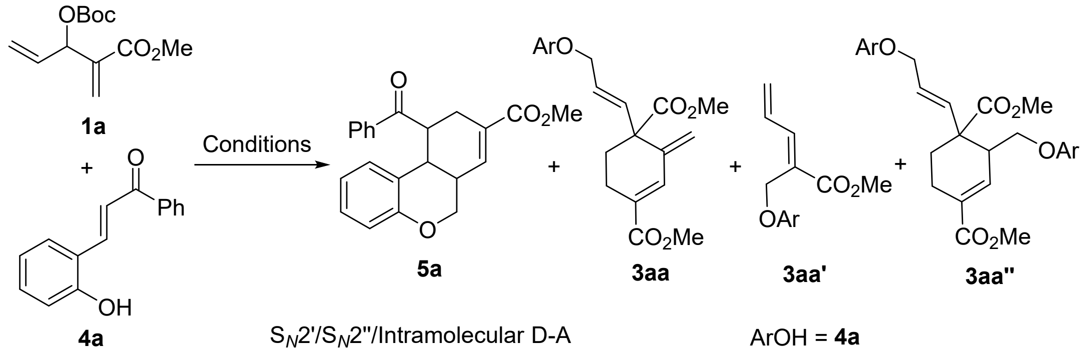
Entry	Base	Ratio of **1a**/**2a**	Solvent	**3a'**(%)[b]	**3a''**(%)[b]	**3a**(%)[b]
1[c]	K_2CO_3	2/1	toluene	-	-	28
2[c]	K_2CO_3	1/2	toluene	-	-	31
3[c]	K_2CO_3	1/1	toluene	-	-	47
4[c,d]	K_2CO_3	1/1	toluene	-	-	46
5[e]	K_2CO_3	1/1	toluene	-	-	48
6[f]	K_2CO_3	1/1	toluene	-	-	47
7	K_2CO_3	1/1	toluene	-	-	51
8	C_2CO_3	1/1	toluene	-	-	67
9	KOH	1/1	toluene	-	-	30
10	$LiOH·H_2O$	1/1	toluene	6	-	28
11	Et_3N	1/1	toluene	-	-	50
12	DBU	1/1	toluene	-	-	18
13	KOBu*t*	1/1	toluene	-	-	39
14	Cs_2CO_3	1/1	CH_2Cl_2	37	35	18
15	Cs_2CO_3	1/1	Acetone	14	-	8
16	Cs_2CO_3	1/1	Et_2O	46	trace	trace
17	Cs_2CO_3	1/1	THF	19	-	7
18	Cs_2CO_3	1/1	*n*-Hexane	15	-	6
19	Cs_2CO_3	1/1	Xylene	-	-	39
20	Cs_2CO_3	1/1	CH_3CN	trace	-	62

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol) and **2a** (0.1 mmol) in the presence of DABCO (0.2 mmol) and base (0.2mmol) in solvent (1 mL) for 24 h at reflux. [b] Yields of isolated products. [c] 0.1 mmol of DABCO and 0.1 mmol of base were employed. [d] 0.5 mL

solvent was employed. [e]0.1 mmol of DABCO and 0.2 mmol of base were employed. [f]0.2 mmol of DABCO and 0.1 mmol of base were employed.

With toluene as solvent at 109 °C, changing substrate ratio from 2/1 to 1/1 afforded the product **3a** in an increased yield of 47% with excellent chemoselectivity (Table 1S, entries 1-4). Increasing the amount of base or DABCO individually only gives similar yields (Entries 5-6). When the loading amount of both DABCO and base were increased to 2 equivalents, the yield of **3a** could be slightly improved to 51% (Entry 7). Screening of bases revealed that cesium carbonate worked best, affording **3a** in 67% yield (Entries 7-13). In solvent screening, toluene proved the best choice, and the solvents with lower boiling points generally gave lower yields and poor chemoselectivities (Entries 14-18). These results indicated that high temperature condition is beneficial to promoting the key S_N2'' addition step. However, conducting the reaction in xylene with higher temperature failed to achieve better results (Table 1S, entry 19). Except for toluene, acetonitrile also provided a comparable yield of 62% (Table 1S, entry 20).

Table 2S. Condition survey for the tandem intramolecualr D-A reaction[a]



Entry	Promoter	Solvent	Temp.(ºC)	Time(h)	**5a** (%)[b]	D.r.[c]	**3aa** (%)	**3aa'** (%)	**3aa''** (%)
1	PPh_3	Toluene	109	24	35	1/1.6	trace	trace	-
2[d]	DMAP	Toluene	109	24	49	1.4/1	42	trace	-
3	DABCO	Toluene	109	24	64	5.2/1	13	-	-
4	Cs_2CO_3	Toluene	109	24	54	6.5/1	trace	-	trace
5	CsF	Toluene	109	24	51	6/1	-	-	-
6	KOH	Toluene	109	24	27	8/1	-	-	-
7[e]	DABCO	Toluene	109	24	46	7.6/1	12	-	-
8[f]	DABCO	Toluene	109	24	61	4/1	10	-	trace

9[g]	DABCO	Toluene	109	24	50	12/1	7	-	-
10	DABCO	DCM	35	24	10	3/1	5	9	28
11	DABCO	THF	55	24	38	2.5/1	17	trace	18
12	DABCO	Hexane	55	24	trace	N.d.	trace	10	5
13	DABCO	Acetone	50	24	26	2.8/1	31	trace	trace
14	DABCO	CH_3CN	70	24	32	17/1	33	-	trace
15	DABCO	Xylene	120	24	51	14/1	trace	-	-
16	DABCO	Xylene	135	24	66	10/1	trace	-	-
17	DABCO	Xylene	135	3	73	2.5/1	trace	-	-
18	DABCO	Xylene	135	12	70	11/1	trace	-	-

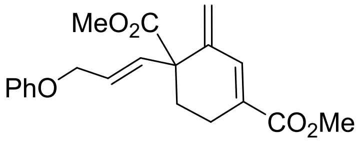
[a]Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol) and **4a** (0.1 mmol) in solvent for indicated time. [b]Yields of isolated products. [c]Determined by ^{1}H-NMR analysis of crude products. [d]Trace amount of other diastereomers was observed. [e]Two equivalent of DABCO was employed. [f]Two equivalents of *o*-hydroxychalcone was employed. [g]One equivalent of Cs_2CO_3 was added.

A variety of Lewis or Brønsted bases were examined for reaction optimization. Lewis base PPh_3 and DMAP both promoted the reaction to produce chromane **5a** smoothly, and DABCO provided superior outcomes in terms of product yield, diastereoselectivity and chemoselectivity (Table 2S, entris 1-3). In line with the observations in quadruple tandem reaction above developed, non-nucleophilic base also proved effective for the transformation giving tricyclic product **5a**, albeit with diminished yields (Table 2S, entries 4-6). Other efforts such as doubling the amount of **4a** or DABCO and using a combination of DABCO and Cs_2CO_3 all failed to provide better results (Table 2S, entries 7-9). The effects of solvent and temperature were also evaluated (Table 2S, entries 10-16). When conducting the reaction in xylenes at 135 °C, fewer dimerization by-products and better diastereoselectivity of the major product **5a** were observed. Furthermore, shortening the reaction time to 12 h also improved the reaction yield while maintaining good diastereoselectivity and excellent chemoselectivity (Table 2S, entries 17-18).

Procedure for the tandem reaction of γ-vinyl MBH adduct with phenol compound

To a stirred solution of γ-vinyl MBH adduct **1a** (0.1 mmol) and phenol **2** (0.1 mmol) in toluene (1 mL) was added 1,4-diazabicyclooctane(0.1 mmol, 11.2 mg) and Cs_2CO_3 (0.1 mmol, 32 mg) under an air atmosphere. Then the resulting mixture was vigorously stirred at 109 °C for 24 h. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1-20/1 as the eluent) to furnish the corresponding product.

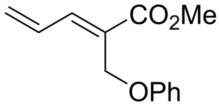
Dimethyl (*E*)-3-methylene-4-(3-phenoxyprop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3a)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), phenol **2a** (0.1 mmol, 9.4 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3a** (11.5 mg). 67% yield (eluent = petroleum ether/ethyl acetate = 20/1); Light yellow liquid; R_f = 0.55 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.27–7.25 (m, 2H), 7.23 (s, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 5.91 (dt, *J* = 15.8, 1.5 Hz, 1H), 5.60 (dt, *J* = 15.8, 5.3 Hz, 1H), 5.50 (s, 1H), 5.30 (s, 1H), 4.56 (dd, *J* = 5.3, 1.4 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.46–2.41 (m, 1H), 2.29– 2.25 (m, 2H), 1.81–1.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 158.5, 141.8, 137.3, 133.2, 129.7, 129.4, 127.3, 126.9, 122.3, 120.9, 114.9, 67.9, 52.9, 52.4, 51.8, 31.2, 21.3; HRMS (ESI): calcd. For $[M+H]^+$($C_{20}H_{23}O_5$) requires 343.1545, found 343.1540.

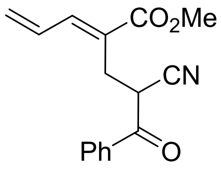
Diene **3a'** was preferentially prepared through the direct S_N2' addition of phenol **2a** to vinyl MBH carbonate **1a** in diethyl ether at room temperature (Table 1S, entry 16).

Methyl (E)-2-(phenoxymethyl)penta-2,4-dienoate (3a')



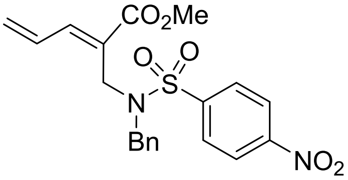
A mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), phenol **2a** (0.1 mmol, 9.4 mg), 1,4-diazabicyclooctane(0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and diethyl ether (1 mL) was stirred at 25 °C for 24 h to afford **3a'** (9.9 mg). **3a'** is a mixture of *E*- and *Z*-isomer, and can not be purified completely (molar ratio of *E*-/*Z*- isomer = 6.5/1). 46% yield (eluent = petroleum ether/ethyl acetate = 30/1); Colorless liquid; R_f = 0.7 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.44 (d, *J* = 12.1 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 6.96 (m, 3H), 6.81 (m, 1H), 5.71 (d, *J* = 15.9 Hz, 1H), 5.60 (d, *J* = 10.1 Hz, 1H), 4.86 (s, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.4, 158.6, 144.2, 131.6, 129.4, 127.7, 126.7, 121.1, 114.9, 61.9, 52.2; HRMS (ESI): calcd. For $[M+H]^+$($C_{13}H_5O_3$) requires 219.1021, found 219.1025.

Methyl (*E*)-2-(2-cyano-3-oxo-3-phenylpropyl)penta-2,4-dienoate (3ab')



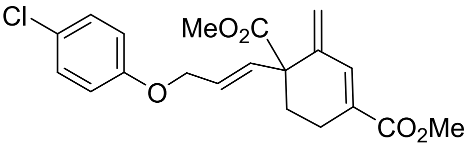
To a stirred solution of γ-vinyl MBH adduct **1a** (0.2 mmol, 48.4 mg) and 3-oxo-3-phenylpropanenitrile **2ab** (0.1 mmol, 14.5 mg) in CH_2Cl_2 (1 mL) was added 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg). Then the resulting mixture was vigorously stirred at 25 °C for 24h. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 as the eluent) to furnish the corresponding product **3ab'** (12.8 mg) as an inseparable mixture of *E*- and *Z*-isomer (ratio of *E*-/*Z*-isomer = 7/1). An O-alkyation product was formed concurrently, but failed to be purified completely. The Ratio of C-/O-alkylation product is 3.5/1 as determined by ^{1}H NMR analysis of crude product. 47% yield; Light yellow liquid; R_f = 0.65 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 11.8 Hz, 1H), 6.82 (ddd, *J* = 16.2, 11.1, 10.4 Hz, 1H), 5.73 (d, *J* = 16.2 Hz, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 4.87 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.82 (s, 3H), 3.08 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.04 (dd, *J* = 15.2, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 190.5, 167.7, 143.8, 134.7, 133.8, 131.2, 129.2, 129.0, 128.0, 125.1, 116.8, 52.3, 39.2, 28.0; HRMS (ESI): calcd. For $[M+H]^+(C_{16}H_6NO_3)$ requires 270.1130, found 270.1132.

Methyl (*E*)-2-(((N-benzyl-4-nitrophenyl)sulfonamido)methyl)penta-2,4-dienoate (3ac')



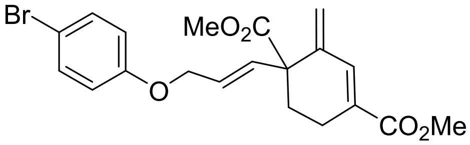
To a stirred solution of γ-vinyl MBH adduct **1a** (0.2 mmol, 48.4 mg) and *N*-benzyl-4-nitrobenzenesulfonamide **2ac** (0.1 mmol, 29.2 mg) in toluene (1 mL) was added 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg). Then the resulting mixture was vigorously stirred at 109 °C for 24h. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 as the eluent) to furnish the corresponding product **3ac'**(15.8 mg). **3ac'** is a mixture of *E*- and *Z*-isomer, and can not be purified completely (ratio of *E*-/*Z*- isomer = 4/1). 38% yield; Light yellow liquid; R_f = 0.6 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 8.31 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.31–7.28 (m, 5H), 7.06 (d, *J* = 11.4 Hz, 1H), 6.78 (ddd, *J* = 16.6, 11.4, 9.6 Hz, 1H), 5.61 (d, *J* = 16.4 Hz, 1H), 5.59 (d, *J* = 10.4 Hz, 1H), 4.51 (s, 2H), 4.20 (s, 2H), 3.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.3, 146.1, 144.3, 143.8, 135.9, 131.3, 128.7, 128.5, 128.3, 128.2, 127.9, 124.7, 124.2, 124.1, 52.7, 51.9, 43.5; HRMS (ESI): calcd. For $[M+H]^+(C_{20}H_{21}N_2O_6S)$ requires 417.1120, found 417.1123.

Dimethyl (*E*)-4-(3-(4-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3b)



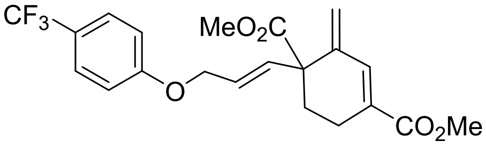
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 4-chlorophenol **2b** (0.1 mmol, 12.8 mg), 1,4-diazabicyclooctane(0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3b** (11.9 mg). **3b**, mixed with unreacted 4-chlorophenol **2b**, can not be purified completely. The yield was calculated based on discounted weight of product (molar ratio of **3b**/**2b** = 7.1/1). 60% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.42 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.23 (s, 1H), 7.21 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.90 (d, *J* = 15.9 Hz, 1H), 5.56 (dt, *J* = 15.8, 5.4 Hz, 1H), 5.50 (s, 1H), 5.28 (s, 1H), 4.52 (d, *J* = 5.3 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.45–2.42 (m, 1H), 2.28–2.21 (m, 2H), 1.81–1.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.9, 167.6, 157.0, 141.6, 137.4, 133.4, 129.4, 129.3, 127.0, 126.9, 125.8, 122.5, 116.7, 68.2, 53.0, 52.6, 52.0, 31.1, 21.3; HRMS (ESI): calcd. For $[M+H]^+$($C_{20}H_{22}ClO_5$) requires 377.1156, found 377.1152.

Dimethyl (*E*)-4-(3-(4-bromophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3c)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 4-bromophenol **2c** (0.1 mmol, 17.3 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3c** (13.8 mg). **3c**, mixed with unreacted 4-bromophenol **2c**, can not be purified completely. The yield was calculated based on discounted weight of product (molar ratio of **3c**/**2c** = 12/1). 63% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.42 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.35 (d, *J* = 9.2 Hz, 2H), 7.22 (s, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.89 (d, *J* = 15.9 Hz, 1H), 5.56 (dt, *J* = 15.8, 5.3 Hz, 1H), 5.50 (s, 1H), 5.28 (s, 1H), 4.52 (dd, *J* = 5.3, 1.2 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.46–2.42 (m, 1H), 2.29–2.20 (m, 2H), 1.82–1.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.8, 167.6, 157.5, 141.6, 137.4, 133.4, 132.2, 129.6, 127.0, 122.5, 117.2, 113.1, 68.1, 52.9, 52.6, 52.0, 31.1, 21.3; HRMS (ESI): calcd. For $[M+H]^+$($C_{20}H_{22}BrO_5$) requires 421.0651, found 421.0657.

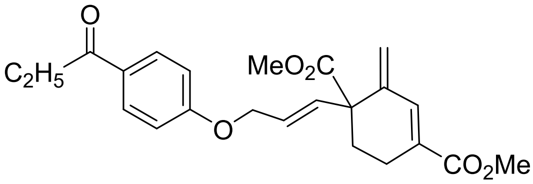
Dimethyl(*E*)-3-methylene-4-(3-(4-(trifluoromethyl)phenoxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3d)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2

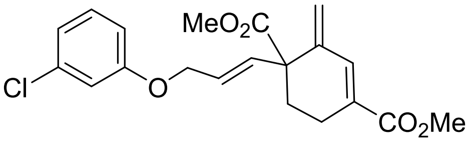
mg), 4-(trifluoromethyl)phenol **2d** (0.1 mmol, 16.2 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3d** (12.7 mg). 63% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.27 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.52 (d, *J* = 9.2 Hz, 2H), 7.23 (s, 1H), 6.94 (d, *J* = 9.2 Hz, 2H), 5.93 (d, *J* = 15.9 Hz, 1H), 5.58 (dt, *J* = 15.9, 5.2 Hz, 1H), 5.51 (s, 1H), 5.27 (s, 1H), 4.59 (dd, *J* = 5.1 Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.46–2.42 (m, 1H), 2.29–2.21 (m, 2H), 1.83–1.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 160.9, 141.6, 137.2, 133.8, 129.7, 126.8 (q, $^3J_{CF}$ = 4.2 Hz), 126.6, 124.4 (q, $^1J_{CF}$ = 270 Hz), 123.0 (q, $^2J_{CF}$ = 33.3 Hz), 114.8, 68.1, 52.9, 52.5, 51.8, 31.1, 21.3; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -61.5; HRMS (ESI): calcd. For $[M+H]^+(C_{21}H_{22}F_3O_5)$ requires 411.1419, found 411.1415.

Dimethyl(*E*)-3-methylene-4-(3-(4-propionylphenoxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3e)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), *para*-ethylketophenol **2e** (0.1 mmol, 15 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3e** (11.4 mg). 57% yield (eluent = petroleum ether/ethyl acetate = 5/1); Light yellow liquid; R_f = 0.33 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.23 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.93 (d, *J* = 15.9 Hz, 1H), 5.59 (dt, *J* = 15.8, 5.4 Hz, 1H), 5.50 (s, 1H), 5.28 (s, 1H), 4.61 (dd, *J* = 5.3, 1.7 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.95 (q, *J* = 7.1 Hz, 2H), 2.46–2.42 (m, 1H), 2.29–2.21 (m, 2H), 1.83–1.80 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 199.5 173.6, 167.4, 162.1, 141.6, 137.2, 133.7, 130.1, 129.7, 126.9, 126.6, 122.3, 114.4, 68.0, 52.9, 52.5, 51.9, 31.4, 31.1, 21.3, 8.4; HRMS (ESI): calcd. For $[M+H]^+(C_{23}H_{27}O_6)$ requires 399.1808, found 399.1805.

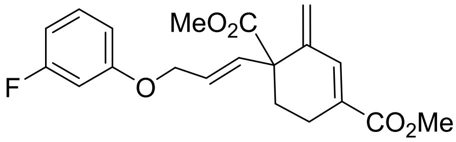
Dimethyl (*E*)-4-(3-(3-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3f)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 3-chlorophenol **2f** (0.1 mmol, 12.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3f** (11.9 mg). 63% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.34 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.23 (s, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.9, Hz, 1H), 6.88 (t, *J* = 2.2 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.91 (d, *J* = 15.8 Hz, 1H), 5.56 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.50 (s, 1H), 5.28 (s, 1H), 4.53 (dd, *J* = 5.2, 1.1

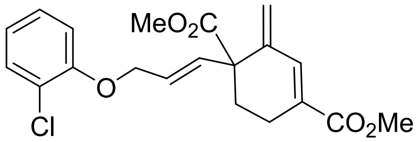
Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.47–2.42 (m, 1H), 2.29–2.21 (m, 2H), 1.82–1.78 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 159.1, 141.6, 137.2, 134.8, 133.6, 130.2, 129.7, 126.8, 122.3, 121.1, 115.3, 113.4, 68.1, 52.9, 52.5, 51.8, 31.1, 21.3; HRMS (ESI): calcd. For $[M+H]^+(C_{20}H_{22}ClO_5)$ requires 377.1156, found 377.1160.

Dimethyl (*E*)-4-(3-(3-fluorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3g)



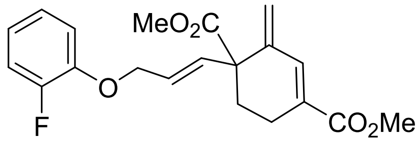
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 3-fluorophenol **2g** (0.1 mmol, 11.2 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3g** (9.2 mg). 51% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.37 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.23 (s, 1H), 7.19 (ddd, *J* = 8.4, 8.4, 6.8 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.64 (ddd, *J* = 8.4, 8.0, 1.8 Hz, 1H), 6.60 (ddd, *J* = 10.8, 2.3, 2.1 Hz, 1H), 5.91 (d, *J* = 15.8 Hz, 1H), 5.57 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.50 (s, 1H), 5.28 (s, 1H), 4.53 (dd, *J* = 5.2, 1.3 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.45–2.41 (m, 1H), 2.28–2.22 (m, 2H), 1.83–1.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 163.5 (d, $^1J_{CF}$ = 245 Hz), 159.8 (d, $^3J_{CF}$ = 10.5 Hz), 141.6, 137.3, 133.5, 130.1 (d, $^3J_{CF}$ = 10.3 Hz), 129.7, 126.8, 122.4, 110.6 (d, $^4J_{CF}$ = 3.6 Hz), 107.7 (d, $^2J_{CF}$ = 21.2 Hz), 102.6 (d, $^2J_{CF}$ = 24.4 Hz), 68.2, 52.9, 52.5, 51.9, 31.1, 21.3; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -111.7; HRMS (ESI): calcd. For $[M+H]^+(C_{20}H_{22}FO_5)$ requires 361.1451, found 361.1453.

Dimethyl (*E*)-4-(3-(2-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3h)



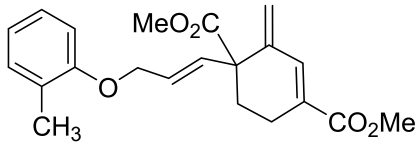
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 2-chlorophenol **2h** (0.1 mmol, 12.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3h** (12.3 mg). 65% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.33 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.34 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.22 (s, 1H), 7.17 (dd, *J* = 8.1, 6.7 Hz, 1H), 6.90–6.88 (m, 2H), 5.94 (d, *J* = 15.8 Hz, 1H), 5.60 (dt, *J* = 15.9, 5.1 Hz, 1H), 5.49 (s, 1H), 5.28 (s, 1H), 4.64 (d, *J* = 4.9 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 2.43–2.39 (m, 1H), 2.28–2.20 (m, 2H), 1.82–1.78 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 153.9, 141.7, 137.3, 133.6, 130.3, 129.7, 127.6, 126.9, 126.7, 122.3, 121.8, 114.4, 69.1, 52.9, 52.5, 51.8, 31.1, 21.4; HRMS (ESI): calcd. For $[M+H]^+(C_{20}H_{22}ClO_5)$ requires 377.1156, found 377.1161.

Dimethyl (*E*)-4-(3-(2-fluorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3i)



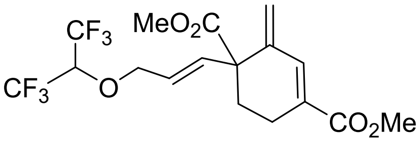
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 2-fluorophenol **2i** (0.1 mmol, 11.2 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3i** (9.9 mg). 55% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.28 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.21 (s, 1H), 7.05 (dd, *J* = 7.9, 7.8 Hz, 1H), 7.01 (m, 1H), 6.93 (m, 1H), 6.89 (m, 1H), 5.90 (d, *J* = 15.9 Hz, 1H), 5.59 (dt, *J* = 15.8, 5.4 Hz, 1H), 5.48 (s, 1H), 5.26 (s, 1H), 4.63 (d, *J* = 5.1 Hz, 2H), 3.75 (s, 3H), 3.70 (s, 3H), 2.43–2.39 (m, 1H), 2.27–2.17 (m, 2H), 1.80–1.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.6, 167.4, 154.6 (d, $^1J_{CF}$ = 243 Hz), 146.3 (d, $^2J_{CF}$ = 10.4 Hz), 141.6, 137.2, 133.9, 129.6, 126.9 (d, $^4J_{CF}$ = 2.0 Hz), 124.2 (d, $^3J_{CF}$ = 3.5 Hz), 122.4, 121.6 (d, $^3J_{CF}$ = 7.1 Hz), 116.3 (d, $^2J_{CF}$ = 17.3 Hz), 116.1, 69.6, 52.9, 52.5, 51.8, 31.1, 21.3; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -113.9; HRMS (ESI): calcd. For $[M+H]^+(C_{20}H_{22}FO_5)$ requires 361.1451, found 361.1457.

Dimethyl (*E*)-3-methylene-4-(3-(o-tolyloxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3j)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), *o*-cresol **2j** (0.1 mmol, 10.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 36 h to afford **3j** (9.9 mg). **3j**, mixed with unreacted *o*-cresol **2j**, can not be purified completely. The yield was calculated based on discounted weight of product (molar ratio of **3j**/**2j** = 6.3/1). 53% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.4 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.24 (s, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.11 (dd, *J* = 8.0, 7.7 Hz, 1H), 6.85 (dd, *J* = 7.8, 6.9 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.91 (dt, *J* = 15.9, 1.5 Hz, 1H), 5.60 (dt, *J* = 15.2, 4.9 Hz, 1H), 5.50 (s, 1H), 5.30 (s, 1H), 4.56 (d, *J* = 4.3 Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.46–2.41 (m, 1H), 2.30–2.25 (m, 2H), 2.22 (s, 3H), 1.82–1.77 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.7, 167.4, 156.6, 141.9, 137.3, 132.8, 130.7, 129.7, 127.6, 127.1, 126.6, 122.3, 120.6, 111.8, 68.0, 52.9, 52.4, 51.8, 31.2, 21.4, 16.2; HRMS (ESI): calcd. For $[M+H]^+(C_{21}H_{25}O_5)$ requires 357.1702, found 357.1706.

Dimethyl(*E*)-4-(3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3k)

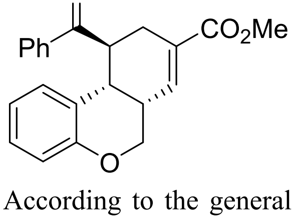


According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), 1,1,1,3,3,3-hexafluoropropan-2-ol **2k** (0.1 mmol, 16.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg), Cs_2CO_3 (0.1 mmol, 32 mg) and toluene (1 mL) was stirred at 109 °C for 24 h to afford **3k** (9.9 mg). 55% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.38 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.23 (s, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 5.52 (s, 1H), 5.46 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.24 (s, 1H), 4.37 (dd, *J* = 12.3, 6.7 Hz, 1H), 4.32 (dd, *J* = 12.3, 6.9 Hz, 1H), 4.14 (qq, *J* = 6.6, 6.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.48 (dt, *J* = 18.1, 5.1 Hz, 1H), 2.30–2.25 (m, 1H), 2.22–2.17 (m, 1H), 1.84 (dt, *J* = 13.4, 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.4, 167.2, 141.2, 137.5, 137.0, 129.7, 127.8 (q, $^1J_{CF}$ = 241 Hz), 126.0, 122.2, 73.8, 73.4 (q, $^2J_{CF}$ = 32.6 Hz), 53.1, 52.6, 51.9, 30.9, 21.2; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -73.8, -73.9; HRMS (ESI): calcd. For $[M+H]^+$($C_{17}H_{19}F_6O_5$) requires 417.1137, found 417.1141.

Procedure for the tandem reaction of γ-vinyl MBH adduct with *o*-hydroxychalcone

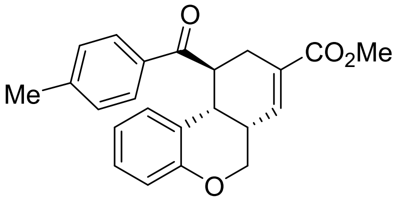
To a stirred solution of γ-vinyl MBH adduct **1a** (0.1 mmol) and *o*-hydroxychalcone **4** (0.1 mmol) in xylene (1 mL) was added 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) under an air atmosphere. Then the resulting mixture was vigorously stirred at 135 °C for 10 h. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1-10/1 as the eluent) to furnish the corresponding product.

(6a*S,10*S**,10a*S**)-**
methyl 10-benzoyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5a)



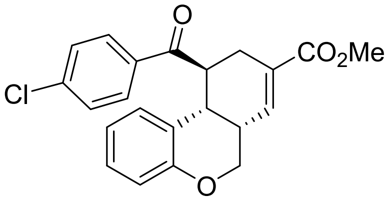
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), *o*-hydroxychalcone **4a** (0.1 mmol, 22.4 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5a** (24.3 mg). **5a**, mixed with trace amount of diastereoisomers, can not be purified completely. 70% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.35 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (td, *J* = 8.3, 1.4 Hz, 1H), 6.97 (dt, *J* = 4.0, 1.9 Hz, 1H), 6.78 (dd, *J* = 8.1, 1.1Hz, 1H), 6.71 (td, *J* = 8.4, 1.1 Hz, 1H), 4.26 (dd, *J* = 11.0, 3.3 Hz, 1H), 4.10 (dd, *J* = 11.1, 8.0 Hz, 1H), 4.04 (ddd, *J* = 10.0, 7.8, 7.5 Hz, 1H), 3.73 (s, 3H), 3.50 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.97 (m, 1H), 2.71 (ddt, *J* = 18.2, 8.0, 2.0 Hz, 1H), 2.48 (ddt, *J* = 18.3, 5.6, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.7, 166.6, 154.3, 137.0, 136.4, 133.1, 131.5, 129.8, 128.6, 128.3, 128.2, 121.7, 120.8, 117.0, 66.4, 51.9, 44.3, 34.9, 33.5, 26.1; HRMS (ESI): calcd. For $[M+H]^+$($C_{22}H_{21}O_4$) requires 349.1440, found 349.1443.

(6a*S**,10*S**,10a*S**)-methyl 10-(4-methylbenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5b)



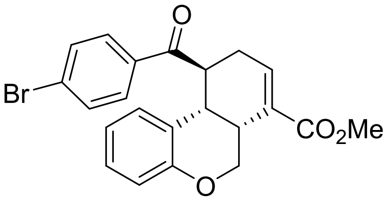
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(p-tolyl)prop-2-en-1-one **4b** (0.1 mmol, 23.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5b** (21.2 mg). **5b**, mixed with trace amount of diastereoisomers, can not be purified completely. 58% yield (eluent = petroleum ether/ethyl acetate = 8/1); Light yellow solid. m.p. = 90-93 °C; R_f = 0.4 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.03 (td, *J* = 8.2, 1.2 Hz, 1H), 6.96 (dt, *J* = 3.9, 1.8 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.70 (td, *J* = 7.0, 1.3 Hz, 1H), 4.25 (dd, *J* = 11.2, 2.7 Hz, 1H), 4.09 (dd, *J* = 11.2, 2.7 Hz, 1H), 4.01 (ddd, *J* = 13.1, 7.9, 5.5 Hz, 1H), 3.72 (s, 3H), 3.49 (dd, *J* = 7.9, 5.6 Hz, 1H), 2.96 (m, 1H), 2.69 (ddt, *J* = 18.1, 7.6, 2.1 Hz, 1H), 2.48–2.44 (m, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.2, 166.7, 154.2, 144.0, 136.4, 134.5, 131.5, 129.8, 129.3, 128.4, 128.1, 121.8, 120.7, 117.0, 66.4, 51.8, 44.1, 34.9, 33.5, 26.2, 21.6; HRMS (ESI): calcd. For $[M+H]^+$($C_{23}H_{23}O_4$) requires 363.1596, found 363.1591.

(6a*S**,10*S**,10a*S**)-methyl 10-(4-chlorobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5c)



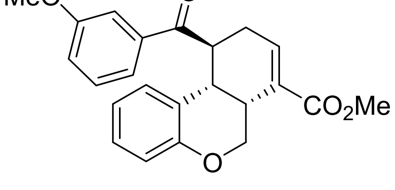
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-1-(4-chlorophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one **4c** (0.1 mmol, 25.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5c** (23.1 mg). **5c**, mixed with trace amount of diastereoisomers, can not be purified completely. 60% yield (eluent = petroleum ether/ethyl acetate = 8/1); Light yellow liquid; R_f = 0.4 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 6.7 Hz, 1H), 6.96 (dt, *J* = 3.9, 1.4 Hz, 1H), 6.78 (d, *J* = 7.3 Hz, 1H), 6.68 (td, *J* = 7.6, 1.1 Hz, 1H), 4.28 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.06 (dd, *J* = 11.3, 7.8 Hz, 1H), 3.93 (ddd, *J* = 13.1, 8.3, 4.9 Hz, 1H), 3.73 (s, 3H), 3.45 (dd, *J* = 8.3, 5.3 Hz, 1H), 2.98 (m, 1H), 2.70 (ddt, *J* = 17.9, 8.1, 2.2 Hz, 1H), 2.48 (dd, *J* = 8.0, 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 201.6, 166.6, 154.2, 139.6, 136.3, 135.4, 131.4, 129.8, 129.6, 128.9, 128.3, 121.4, 120.8, 117.1, 66.2, 51.9, 44.3, 35.2, 33.5, 26.4; HRMS (ESI): calcd. For $[M+H]^+(C_{22}H_{20}ClO_4)$ requires 383.1050, found 383.1053.

(6a*R**,10*S**,10a*S**)-methyl -10-(4-bromobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5d)



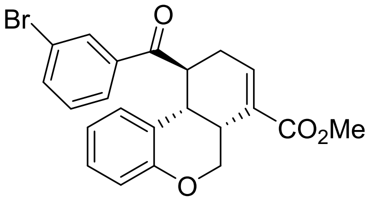
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-1-(4-bromophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one **4d** (0.1 mmol, 30.2 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5d** (22.3 mg). **5d**, mixed with trace amount of diastereoisomers, can not be purified completely. 52% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 141-146 °C; R_f = 0.45 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 9.2 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 5.8 Hz, 1H), 6.96 (dt, *J* = 4.4, 2.1 Hz, 1H), 6.79 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.68 (td, *J* = 7.9, 1.1 Hz, 1H), 4.28 (dd, *J* = 11.7, 3.1 Hz, 1H), 4.06 (dd, *J* = 12.2, 8.6 Hz, 1H), 3.93 (ddd, *J* = 13.2, 7.7, 4.9 Hz, 1H), 3.73 (s, 3H), 3.45 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.98 (m, 1H), 2.70 (ddt, *J* = 18.1, 7.8, 2.0 Hz, 1H), 2.48 (ddt, *J* = 18.4, 5.2, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 201.9, 166.6, 154.2, 136.3, 135.8, 131.9, 131.4, 129.8, 129.7, 128.4, 121.4, 120.8, 117.1, 66.2, 51.9, 44.3, 35.1, 33.5, 26.4; HRMS (ESI): calcd. For $[M+H]^+(C_{22}H_{20}BrO_4)$ requires 427.0545, found 427.0549.

(6a*R**,10*S**,10a*S**)-methyl -10-(3-methoxybenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5e)



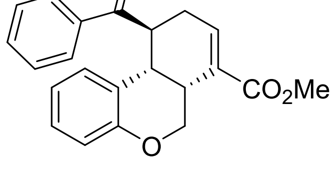
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(3-methoxyphenyl)prop-2-en-1-one **4e** (0.1 mmol, 25.4 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5e** (17.2 mg). **5e**, mixed with trace amount of diastereoisomers, can not be purified completely. 45% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.3 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.32 (m, 2H), 7.26 (t, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.05–7.03 (m, 2H), 6.96 (dt, *J* = 3.8, 1.9 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.72 (td, *J* = 7.8, 1.1 Hz, 1H), 4.26 (dd, *J* = 11.1, 3.1 Hz, 1H), 4.09 (dd, *J* = 11.1, 7.1 Hz, 1H), 4.00 (ddd, *J* = 12.8, 7.6, 5.2 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.50 (dd, *J* = 7.6, 6.2 Hz, 1H), 2.96 (m, 1H), 2.69 (ddt, *J* = 18.4, 7.0, 2.0 Hz, 1H), 2.47 (ddt, *J* = 18.0, 5.4, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.5, 166.6, 159.7, 154.2, 138.4, 136.4, 131.5, 129.7, 129.6, 128.2, 121.7, 120.8, 120.7, 119.6, 117.0, 112.5, 66.4, 55.4, 51.9, 44.5, 34.9, 33.5, 26.1; HRMS (ESI): calcd. For $[M+H]^+(C_{23}H_{23}O_5)$ requires 379.1545, found 379.1549.

(6a*R,10*S**,10a*S**)-methyl -10-(3-bromobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5f)**



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-1-(3-bromophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one **4f** (0.1 mmol, 30.2 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5f** (21.5 mg). **5f**, mixed with negligible amount of diastereoisomers, can not be purified completely. 50% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 157-160 °C; R_f = 0.4 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.90 (dd, *J* = 1.9, 1.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.61 (ddd, *J* = 6.6, 1.5, 1.4 Hz, 1H), 7.24 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.06 (d, *J* = 6.7 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.97 (dt, *J* = 2.8, 1.3 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.71 (td, *J* = 7.7, 1.1 Hz, 1H), 4.28 (dd, *J* = 11.6, 3.4 Hz, 1H), 4.08 (dd, *J* = 11.4, 8.2 Hz, 1H), 3.94 (ddd, *J* = 13.7, 8.6, 6.3 Hz, 1H), 3.73 (s, 3H), 3.47 (dd, *J* = 8.3, 5.8 Hz, 1H), 2.99 (s, 1H), 2.69 (ddt, *J* = 18.1, 7.5, 2.6 Hz, 1H), 2.48 (ddt, *J* = 17.7, 5.0, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 201.4, 166.6, 154.2, 138.8, 136.4, 135.9, 131.3, 131.2, 130.1, 129.7, 128.4, 126.7, 123.0, 121.4, 120.8, 117.1, 66.3, 51.9, 44.5, 35.0, 33.5, 26.2; HRMS (ESI): calcd. For $[M+H]^+(C_{22}H_{20}BrO_4)$ requires 427.0545, found 427.0550.

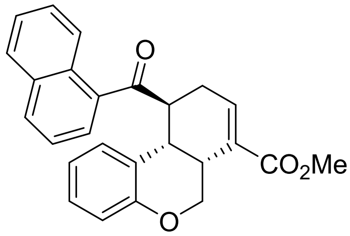
(6a*R,10*S**,10a*S**)-methyl -10-(2-methylbenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5g)**



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(*o*-tolyl)prop-2-en-1-one **4g** (0.1 mmol, 23.8 mg), 1,4-

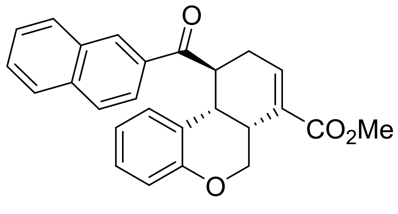
diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5g** (20.8 mg). **5g**, mixed with trace amount of diastereoisomers, can not be purified completely. 57% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 120-125 °C; $R_f = 0.43$ (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 6.3 Hz, 1H), 7.20 (d, *J* = 6.7 Hz, 1H), 7.14 (dd, *J* = 7.9, 7.5 Hz, 1H), 7.09 (dd, *J* = 7.4, 6.4 Hz, 1H), 6.95 (dt, *J* = 2.3, 1.6 Hz, 1H), 6.81 (m, 2H), 4.24 (dd, *J* = 11.1, 2.8 Hz, 1H), 4.09 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.86 (ddd, *J* = 13.1, 8.9, 7.0 Hz, 1H), 3.71 (s, 3H), 3.56 (dd, *J* = 7.8, 6.7 Hz, 1H), 2.97 (m, 1H), 2.62 (ddt, *J* = 17.8, 7.3, 2.4 Hz, 1H), 2.42 (s, 3H), 2.40 (ddt, *J* = 18.4, 5.0, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.3, 166.6, 154.4, 138.1, 137.9, 136.9, 131.9, 131.3, 131.2, 129.6, 128.2, 127.9, 125.7, 122.2, 121.0, 117.1, 66.6, 51.9, 47.7, 34.1, 33.3, 25.6, 20.9; HRMS (ESI): calcd. For $[M+H]^+(C_{23}H_{23}O_4)$ requires 363.1596, found 363.1592.

(6a*R**,10*S**,10a*S**)-methyl -10-(1-naphthoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5h)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(naphthalen-1-yl)prop-2-en-1-one **4h** (0.1 mmol, 27.4 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5h** (21.3 mg). **5h**, mixed with trace amount of diastereoisomers, can not be purified completely. 53% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.33 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 8.35 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 6.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.98 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 4.22 (dd, *J* = 11.3, 3.0 Hz, 1H), 4.09 (dd, *J* = 11.2, 7.8 Hz, 1H), 4.02 (ddd, *J* = 13.3, 7.0, 7.0 Hz, 1H), 3.71 (s, 3H), 3.64 (dd, *J* = 6.7, 6.4 Hz, 1H), 3.02 (m, 1H), 2.75 (dd, *J* = 17.7, 7.2 Hz, 1H), 2.48 (dd, *J* = 17.7, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1, 166.6, 154.4, 136.8, 136.2, 133.9, 132.5, 131.5, 130.3, 129.7, 128.5, 128.2, 128.0, 127.1, 126.6, 125.4, 124.3, 122.1, 121.0, 117.1, 66.6, 51.9, 48.6, 34.4, 33.4, 25.8; HRMS (ESI): calcd. For $[M+H]^+(C_{26}H_{23}O_4)$ requires 399.1596, found 399.1599.

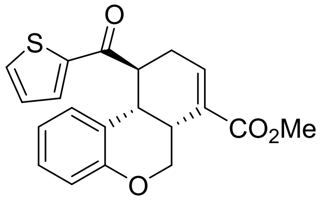
(6a*R**,10*S**,10a*S**)-methyl -10-(2-naphthoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5i)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2

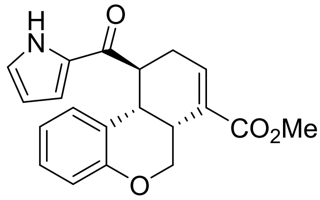
mg), (*E*)-3-(2-hydroxyphenyl)-1-(naphthalen-2-yl)prop-2-en-1-one **4i** (0.1 mmol, 27.4 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5i** (19.3 mg). **5i**, mixed with trace amount of diastereoisomers, can not be purified completely. 48% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.32 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 8.25 (s, 1H), 7.88 (dd, *J* = 8.1, 7.4 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.58 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.52 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.00 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.70 (dd, *J* = 7.7, 7.4 Hz, 1H), 4.29 (dd, *J* = 11.3, 3.2 Hz, 1H), 4.19 (ddd, *J* = 13.4, 7.7, 7.7 Hz, 1H), 4.15 (dd, *J* = 11.2, 7.9 Hz, 1H), 3.73 (s, 3H), 3.57 (dd, *J* = 8.1, 5.4 Hz, 1H), 3.01 (s, 1H), 2.77 (dd, *J* = 17.6, 6.8 Hz, 1H), 2.55 (dd, *J* = 18.2, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.6, 166.7, 154.3, 136.5, 135.5, 134.3, 132.4, 131.5, 129.9, 129.8, 129.6, 128.6, 128.5, 128.2, 127.7, 126.8, 124.0, 121.8, 120.8, 117.0, 66.4, 51.9, 44.4, 35.0, 33.5, 26.4; HRMS (ESI): calcd. For $[M+H]^+$($C_{26}H_{23}O_4$) requires 399.1596, found 399.1598.

(6a*R**,10*S**,10a*S**)-methyl -10-(thiophene-2-carbonyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5j)



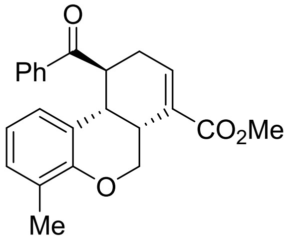
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one **4j** (0.1 mmol, 23 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5j** (17.8 mg). **5j**, mixed with trace amount of diastereoisomers, can not be purified completely. 50% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 106-110 ^{o}C; R_f = 0.34 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.58 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 3.1 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 6.9 Hz, 1H), 6.98 (m, 1H), 6.97 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.66 (dd, *J* = 8.1, 7.7 Hz, 1H), 4.29 (dd, *J* = 11.9, 3.5 Hz, 1H), 4.02 (dd, *J* = 11.3, 8.9 Hz, 1H), 3.75 (m, 1H), 3.74 (s, 3H), 3.43 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.01 (s, 1H), 2.75 (ddt, *J* = 18.2, 9.1, 2.2 Hz, 1H), 2.57 (dd, *J* = 18.1, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.0, 166.6, 154.0, 144.6, 136.1, 134.5, 132.2, 131.5, 130.3, 128.3, 128.2, 121.4, 120.6, 116.9, 65.9, 51.9, 46.2, 35.4, 33.8, 26.9; HRMS (ESI): calcd. For $[M+H]^+$($C_{20}H_{19}O_4S$) requires 355.1004, found 355.1009.

(6a*R**,10*S**,10a*S**)-methyl-10-(1*H*-pyrrole-2-carbonyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5k)



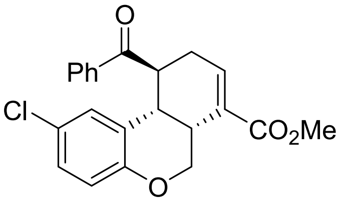
According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxyphenyl)-1-(1H-pyrrol-2-yl)prop-2-en-1-one **4k** (0.1 mmol, 21.3 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5k** (12.8 mg). **5k**, mixed with trace amount of diastereoisomers, can not be purified completely. 37% yield (eluent = petroleum ether/ethyl acetate = 2/1); Light green solid. m.p. = 140-143 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate, 65:35); ^{1}H NMR ($CDCl_3$, 600MHz) δ 9.48 (br, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.02 (td, *J* = 8.1, 0.8 Hz, 1H), 7.00 (m, 1H), 6.96 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.68– 6.66 (m, 2H), 6.15 (m, 1H), 4.27 (dd, *J* = 11.2, 3.7 Hz, 1H), 4.02 (dd, *J* = 11.2, 8.7 Hz, 1H), 3.74 (s, 3H), 3.63 (ddd, *J* = 17.3, 8.7, 5.1 Hz, 1H), 3.43 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.00 (m, 1H), 2.71 (ddt, *J* = 18.3, 8.1, 2.4 Hz, 1H), 2.53 (dd, *J* = 18.1, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 191.7, 166.8, 154.0, 136.2, 132.1, 131.7, 130.2, 128.1, 125.4, 121.8, 120.4, 116.9, 110.9, 66.0, 51.9, 44.7, 35.2, 33.7, 26.9; HRMS (ESI): calcd. For $[M+H]^+$($C_{20}H_{20}NO_4$) requires 338.1392, found 338.1397.

(6a*R,10*S**,10a*S**)-methyl -10-benzoyl-4-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5l)**



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxy-3-methylphenyl)-1-phenylprop-2-en-1-one **4l** (0.1 mmol, 23.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5l** (21.1 mg). **5l**, mixed with trace amount of diastereoisomers, can not be purified completely. 58% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 110-114 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.97 (m, 1H), 6.91 (d, *J* = 6.9 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 4.28 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.12 (dd, *J* = 11.1, 7.8 Hz, 1H), 4.05 (ddd, *J* = 13.6, 7.6, 7.2 Hz, 1H), 3.73 (s, 3H), 3.51 (dd, *J* = 7.1, 6.7 Hz, 1H), 2.94 (s, 1H), 2.69 (dd, *J* = 18.4, 7.0 Hz, 1H), 2.46 (dd, *J* = 18.0, 5.7 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.7, 166.7, 152.5, 137.0, 136.7, 133.1, 131.3, 129.3, 129.1, 128.6, 128.3, 127.2, 126.1, 121.1, 120.1, 66.6, 51.8, 44.4, 34.9, 33.4, 25.9, 16.2; HRMS (ESI): calcd. For $[M+H]^+$($C_{23}H_{23}O_4$) requires 363.1596, found 363.1591.

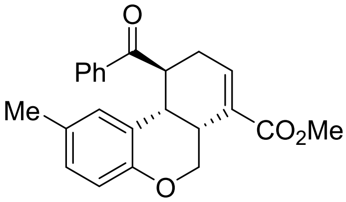
(6a*R,10*S**,10a*S**)-methyl -10-benzoyl-2-chloro-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5m)**



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2

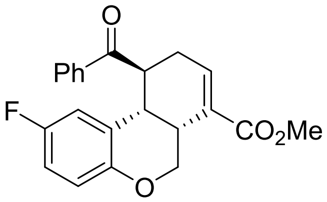
mg), (*E*)-3-(5-chloro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one **4m** (0.1 mmol, 25.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5m** (21.5 mg). **5m**, mixed with trace amount of diastereoisomers, can not be purified completely. 56% yield (eluent = petroleum ether/ethyl acetate = 8/1); Light yellow liquid; R$_f$ = 0.38 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR (CDCl$_3$, 600MHz) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 2.2 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.94 (m, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 4.23 (dd, *J* = 11.3, 3.2 Hz, 1H), 4.09 (dd, *J* = 11.8, 7.4 Hz, 1H), 4.01 (ddd, *J* = 13.9, 7.2, 6.9 Hz, 1H), 3.72 (s, 3H), 3.45 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.95 (m, 1H), 2.71 (ddt, *J* = 18.2, 7.3, 2.3 Hz, 1H), 2.48 (ddt, *J* = 18.2, 5.3, 1.7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 202.0, 166.5, 153.0, 136.7, 136.1, 133.3, 131.5, 129.2, 128.8, 128.2, 128.1, 125.5, 123.2, 118.4, 66.7, 51.9, 44.0, 34.6, 33.0, 25.7; HRMS (ESI): calcd. For [M+H]$^+$(C$_{22}$H$_{20}$ClO$_4$) requires 383.1050, found 383.1053.

(6a*R**,10*S**,10a*S**)-methyl -10-benzoyl-2-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5n)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(2-hydroxy-5-methylphenyl)-1-phenylprop-2-en-1-one **4n** (0.1 mmol, 23.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5n** (20.1 mg). **5n**, mixed with trace amount of diastereoisomers, can not be purified completely. 55% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow Liquid; R$_f$ = 0.4 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR (CDCl$_3$, 600MHz) δ 7.80 (d, *J* = 6.6 Hz, 2H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 6.95 (m, 1H), 6.89 (s, 1H), 6.81 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.21 (dd, *J* = 11.1, 2.7 Hz, 1H), 4.07 (dd, *J* = 11.1, 7.8 Hz, 1H), 4.03 (ddd, *J* = 13.0, 7.3, 5.8 Hz, 1H), 3.72 (s, 3H), 3.43 (dd, *J* = 8.2, 6.1 Hz, 1H), 2.93 (m, 1H), 2.73 (ddt, *J* = 18.3, 7.1, 1.8 Hz, 1H), 2.46 (ddt, *J* = 18.0, 5.5, 2.2 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 202.6, 166.7, 152.0, 137.1, 136.6, 133.1, 131.4, 129.9, 128.8, 128.6, 128.2, 121.2, 116.7, 66.5, 51.8, 44.1, 35.1, 33.6, 25.8, 20.4; HRMS (ESI): calcd. For [M+H]$^+$(C$_{23}$H$_{23}$O$_4$) requires 363.1596, found 363.1599.

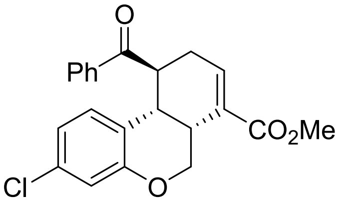
(6a*R**,10*S**,10a*S**)-methyl -10-benzoyl-2-fluoro-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5o)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(5-fluoro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one **4o** (0.1 mmol, 24.2 mg), 1,4-

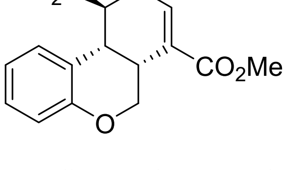
diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 12 h to afford **5o** (24.0 mg). **5o**, mixed with trace amount of diastereoisomers, can not be purified completely. 65% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.55 (petroleum ether/ethyl acetate, 85:15); ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.95 (m, 1H), 6.87 (dd, *J* = 9.8, 2.4 Hz, 1H), 6.74–6.70 (m, 2H), 4.22 (dd, *J* = 11.2, 3.0 Hz, 1H), 4.07 (dd, *J* = 11.8, 8.3 Hz, 1H), 4.00 (ddd, *J* = 13.3, 7.5, 7.2 Hz, 1H), 3.72 (s, 3H), 3.47 (dd, *J* = 7.3, 5.5 Hz, 1H), 2.96 (m, 1H), 2.69 (ddt, *J* = 18.2, 7.0, 1.8 Hz, 1H), 2.49 (ddt, *J* = 18.1, 5.7, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.2, 166.5, 156.8 (d, $^1J_{CF}$ = 239 Hz), 150.4 (d, $^4J_{CF}$ = 2.4 Hz), 136.7, 136.3, 133.3, 131.4, 128.7, 128.2, 122.9 (d, $^3J_{CF}$ = 8.3 Hz), 118.0 (d, $^3J_{CF}$ = 7.9 Hz), 115.6 (d, $^2J_{CF}$ = 24.9 Hz), 115.1 (d, $^2J_{CF}$ = 23.1 Hz), 66.6, 51.9, 44.1, 34.8, 33.1, 26.0; ^{19}F NMR ($CDCl_3$, 564 MHz) δ -123.0; HRMS (ESI): calcd. For $[M+H]^+$($C_{22}H_{20}FO_4$) requires 367.1346, found 367.1350.

(6a*R**,10*S**,10a*S**)-methyl -10-benzoyl-3-chloro-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5p)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), (*E*)-3-(4-chloro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one **4p** (0.1 mmol, 25.8 mg), 1,4-diazabicyclooctane (0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5p** (21.2 mg). **5p**, mixed with trace amount of diastereoisomers, can not be purified completely. 55% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow solid. m.p. = 107-109 °C; R_f = 0.37 (petroleum ether/ethyl acetate, 85:15); 1H NMR ($CDCl_3$, 600MHz) δ 7.78 (d, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H),7.04 (d, *J* = 8.5 Hz, 1H), 6.94 (m, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.26 (dd, *J* = 11.4, 2.7 Hz, 1H), 4.05 (dd, *J* = 11.4, 8.6 Hz, 1H), 3.97 (ddd, *J* = 13.7, 8.1, 5.4 Hz, 1H), 3.73 (s, 3H), 3.45 (dd, *J* = 8.6, 5.6 Hz, 1H), 2.96 (m, 1H), 2.67 (ddd, *J* = 18.3, 6.0, 1.8 Hz, 1H), 2.51 (dd, *J* = 18.2, 5.0 Hz, 1H);^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.5, 166.5, 154.9, 136.9, 135.9, 133.3, 133.2, 131.6, 131.0, 128.7, 128.2, 120.9, 120.3, 117.1, 66.4, 51.9, 44.1, 34.5, 33.2, 26.5; HRMS (ESI): calcd. For $[M+H]^+$($C_{22}H_{20}ClO_4$) requires 383.1050, found 383.1055.

(6a*R**,10*S**,10a*S**)-10-ethyl-7-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7,10-dicarboxylate (5q)



According to the general procedure, a mixture consisting of γ-vinyl adduct **1a** (0.1 mmol, 24.2 mg), ethyl (*E*)-3-(2-hydroxyphenyl)acrylate **4q** (0.1 mmol, 19.2 mg), 1,4-diazabicyclooctane

(0.1 mmol, 11.2 mg) and xylene (1 mL) was stirred at 135 °C for 10 h to afford **5q** (19.7 mg). **5q**, mixed with trace amount of diastereoisomers, can not be purified completely. 62% yield (eluent = petroleum ether/ethyl acetate = 10/1); Light yellow liquid; R_f = 0.6 (petroleum ether/ethyl acetate, 85:15); 1H NMR ($CDCl_3$, 600MHz) δ 7.13–7.10 (m, 2H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.85 (t, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.23 (dd, *J* = 11.1, 2.8 Hz, 1H), 4.15–4.11 (m, 2H), 4.00 (dd, *J* = 11.5, 7.6 Hz, 1H), 3.73 (s, 3H), 3.38 (dd, *J* = 7.6, 6.4 Hz, 1H), 2.98–2.95 (m, 2H), 2.70 (dd, *J* = 17.6, 6.6 Hz, 1H), 2.42 (dd, *J* = 18.3, 4.9 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 174.2, 166.6, 154.4, 136.7, 131.2, 129.0, 128.2, 121.7, 120.7, 117.1, 66.2, 60.8, 51.9, 43.6, 34.4, 33.2, 25.3, 14.1; HRMS (ESI): calcd. For $[M+H]^+$($C_{18}H_{21}O_5$) requires 317.1389, found 317.1393.

References

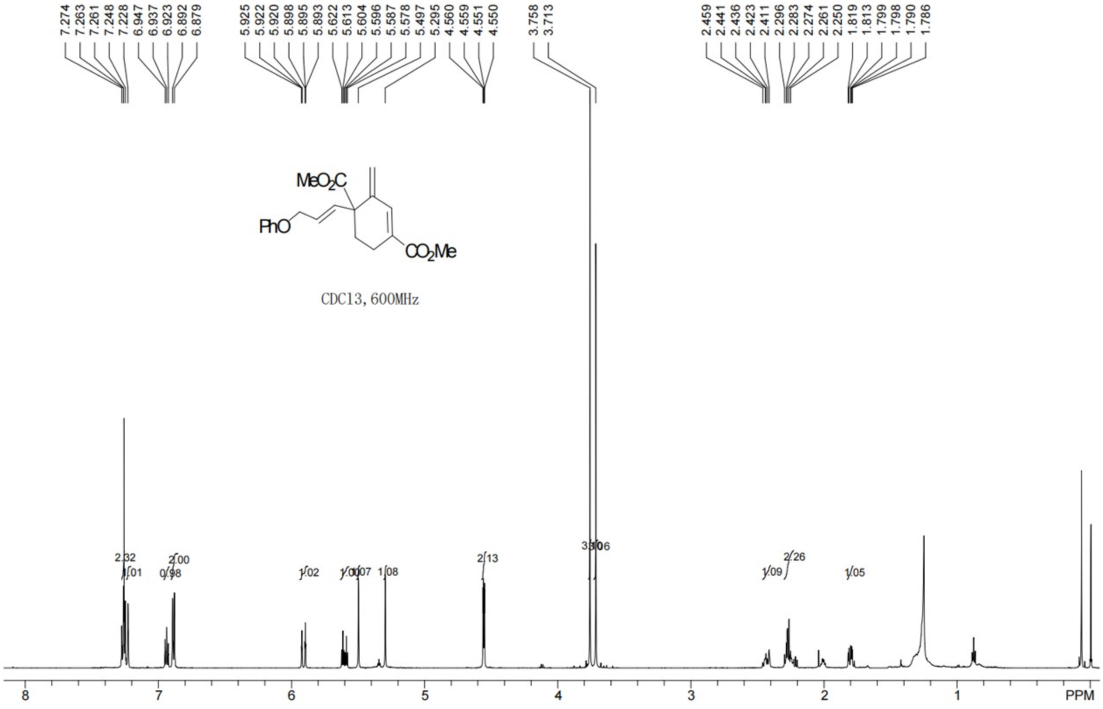
(1) Glaus, F.; Altmann, K.-H. *Angew. Chem. Int. Ed.* **2015**, *54*, 1937.

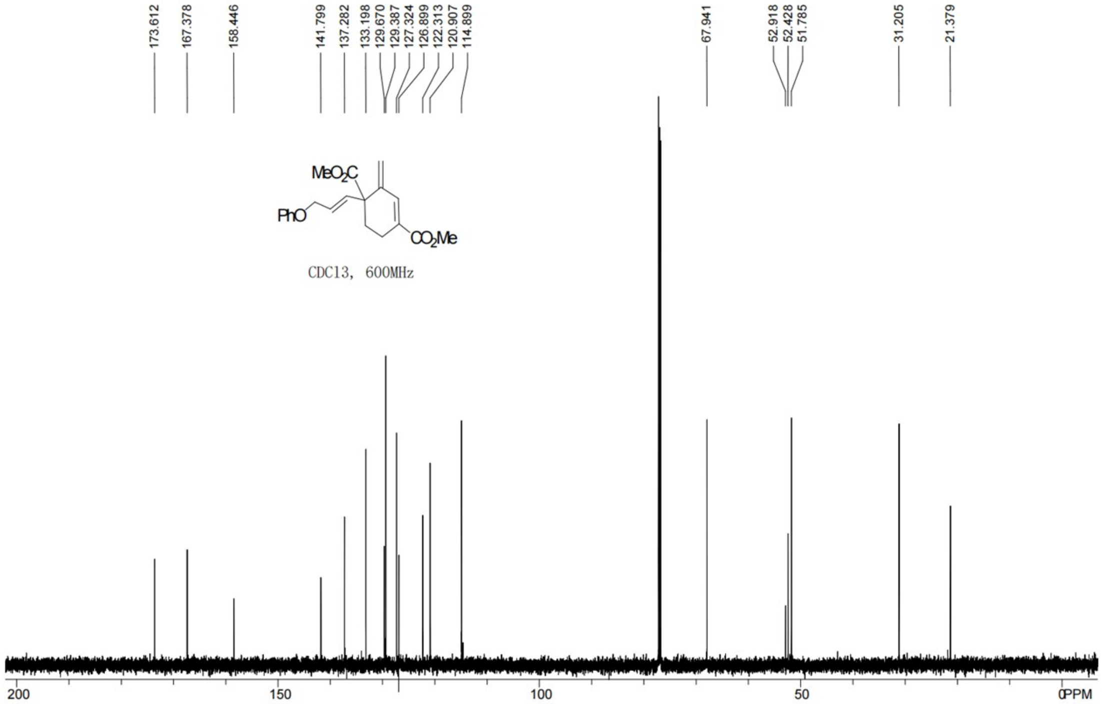
(2) Shephed, E. D.; Hallside, M. S.; Sutro, J. L.; Thompson, A.; Hutchings, M.; Burton, J. W. *Tetrahedron* **2020**, *76*, 130981.

(3) Rouh, H.; Liu, Y.; Katakam, N.; Pham, L.; Zhu, Y.-L.; Li, G. *J. Org. Chem.* **2018**, *83*, 15372.

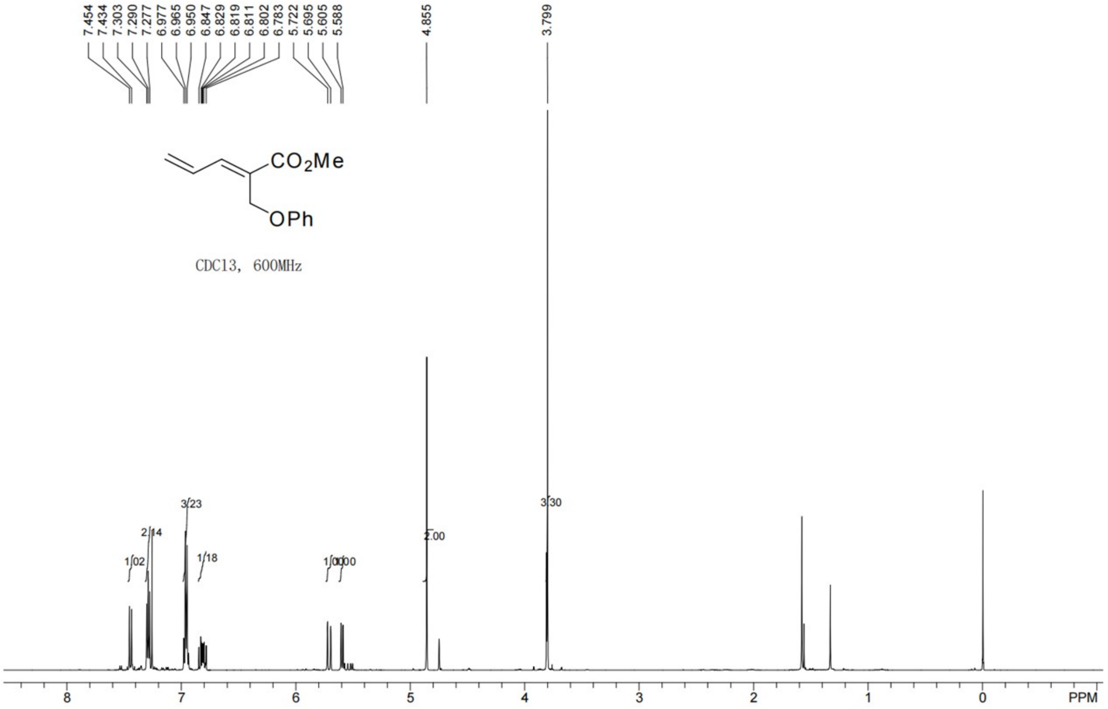
NMR spectra for compounds 3, 3a', 3ab' and 3ac'

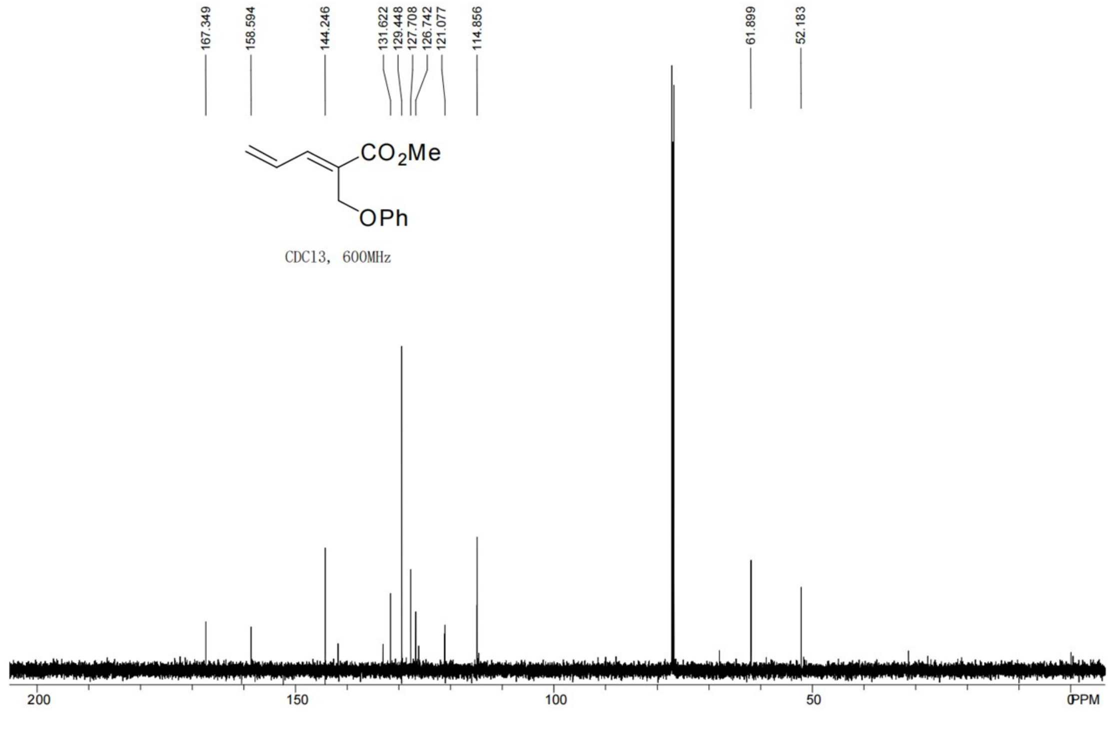
Dimethyl (*E*)-3-methylene-4-(3-phenoxyprop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3a)



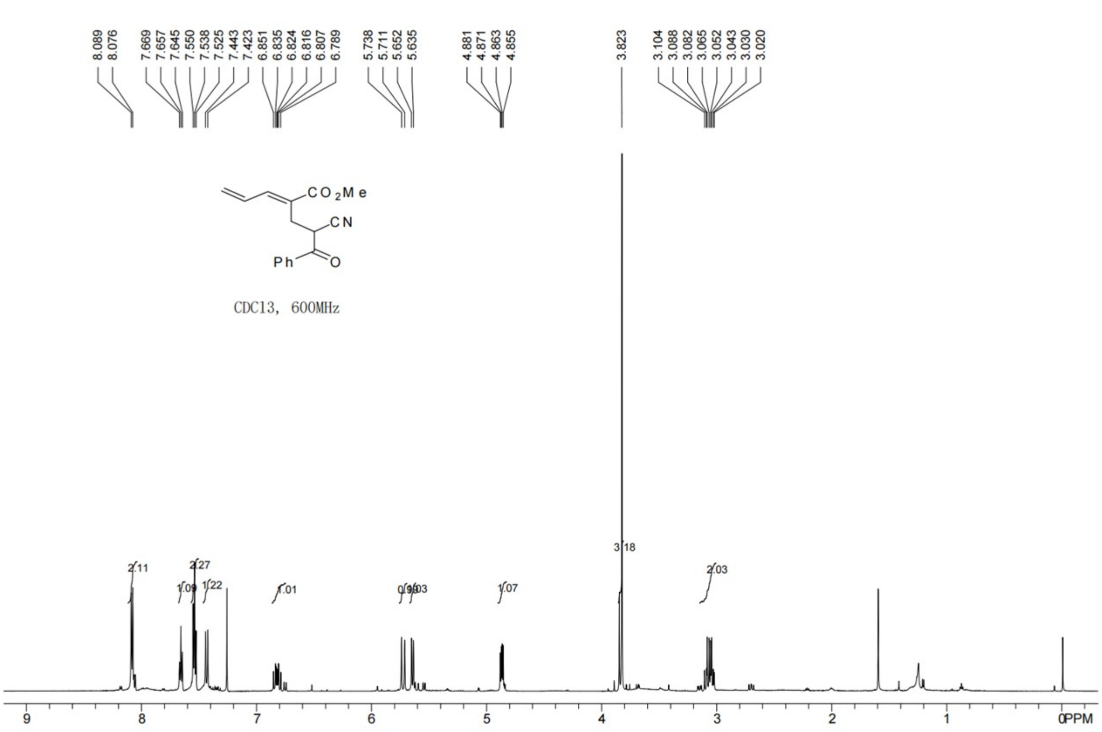


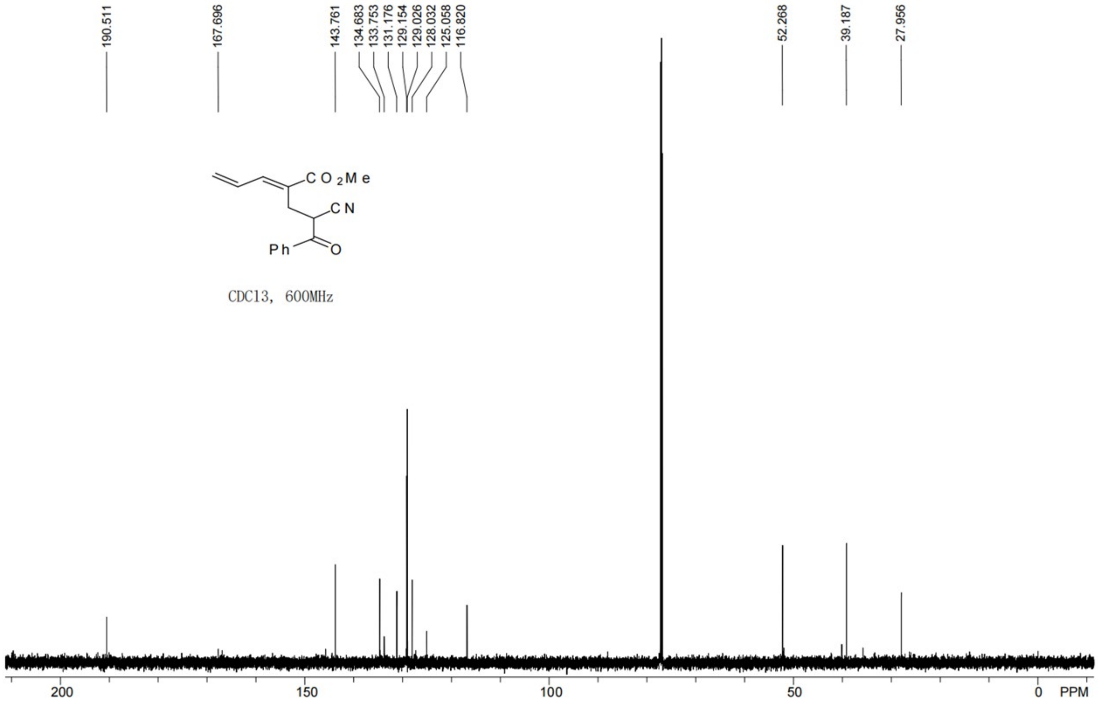
Methyl (E)-2-(phenoxymethyl)penta-2,4-dienoate (3a')



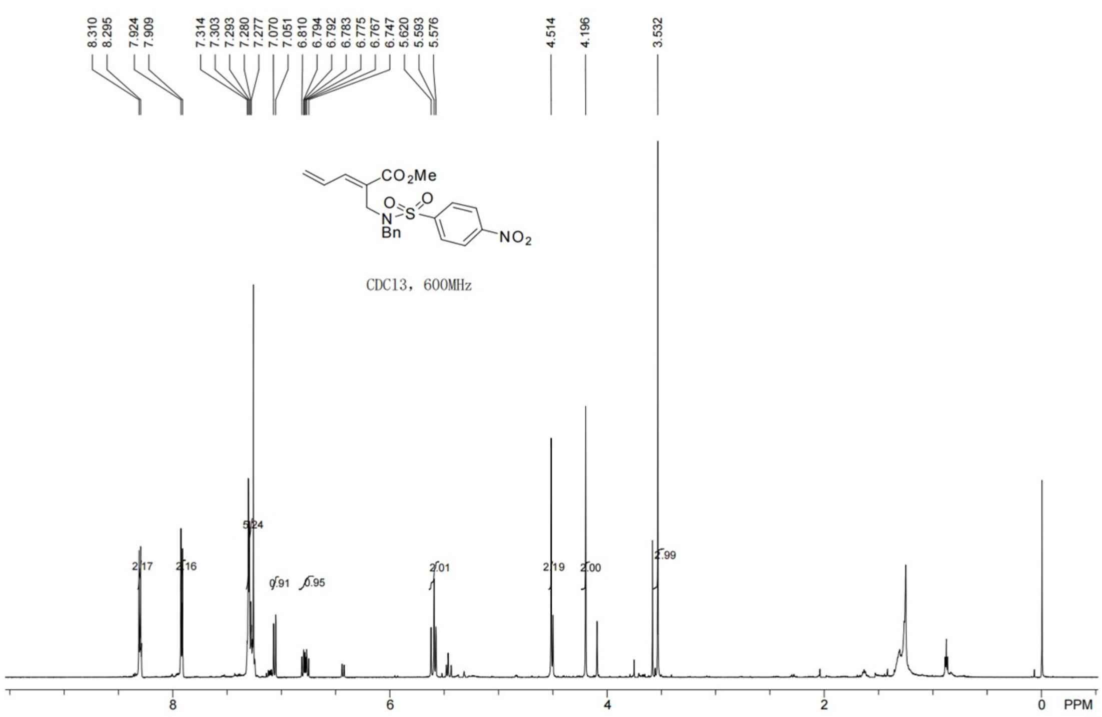


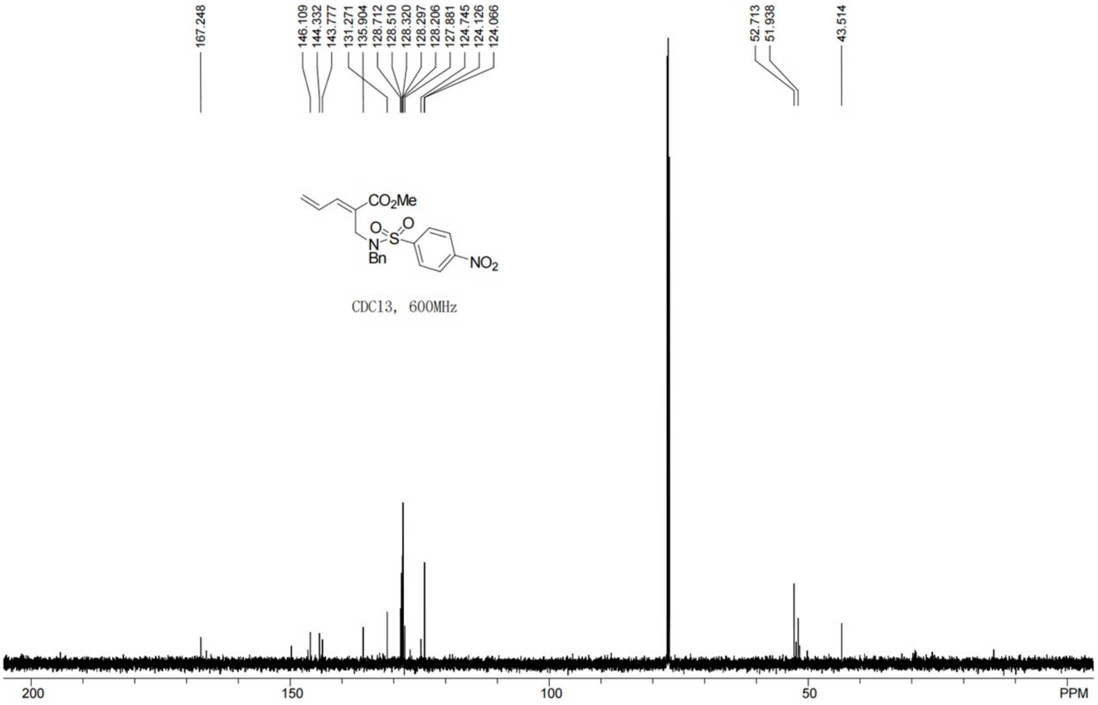
Methyl (*E*)-2-(2-cyano-3-oxo-3-phenylpropyl)penta-2,4-dienoate (3ab')



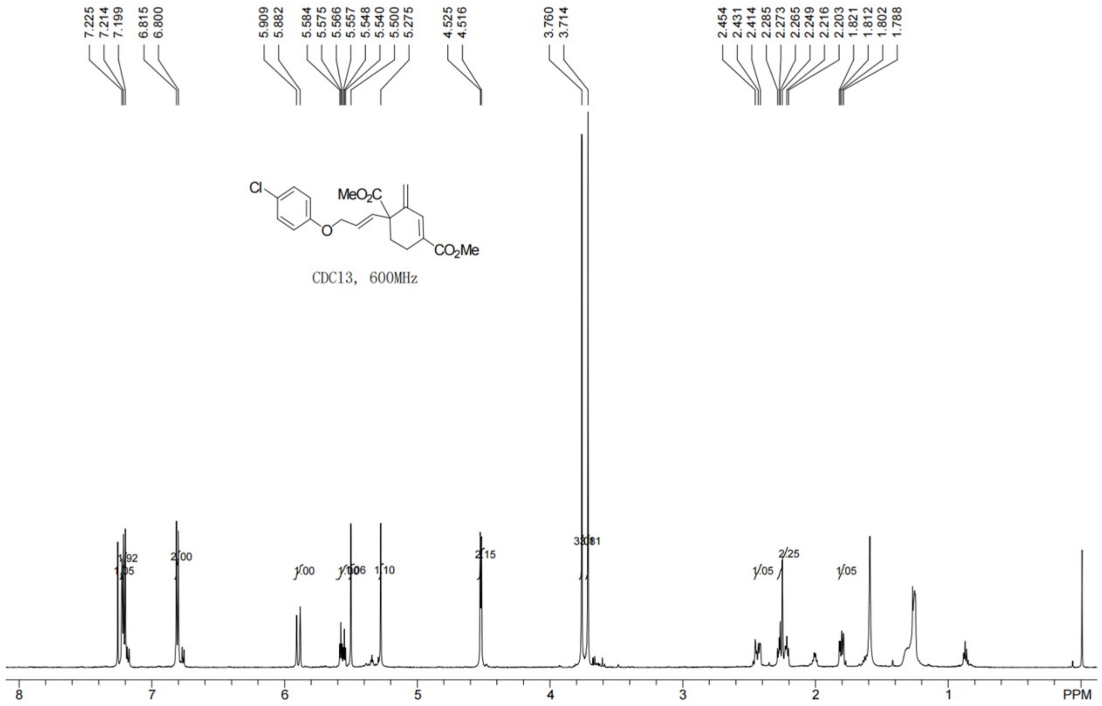


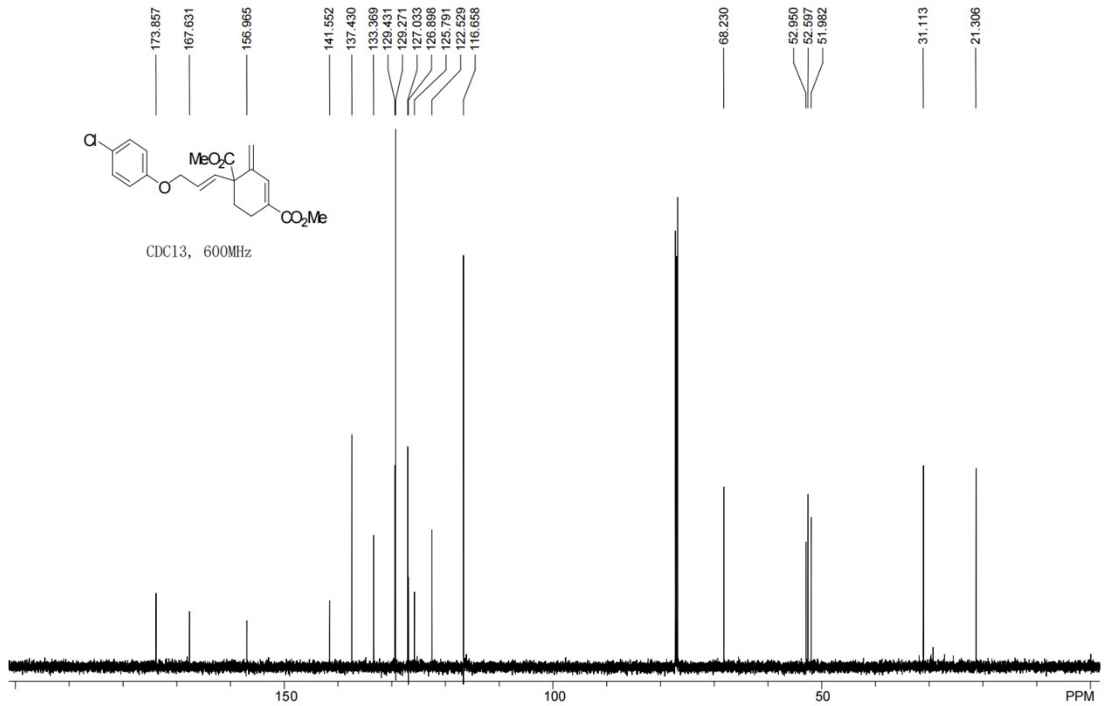
Methyl (*E*)-2-(((N-benzyl-4-nitrophenyl)sulfonamido)methyl)penta-2,4-dienoate (3ac')



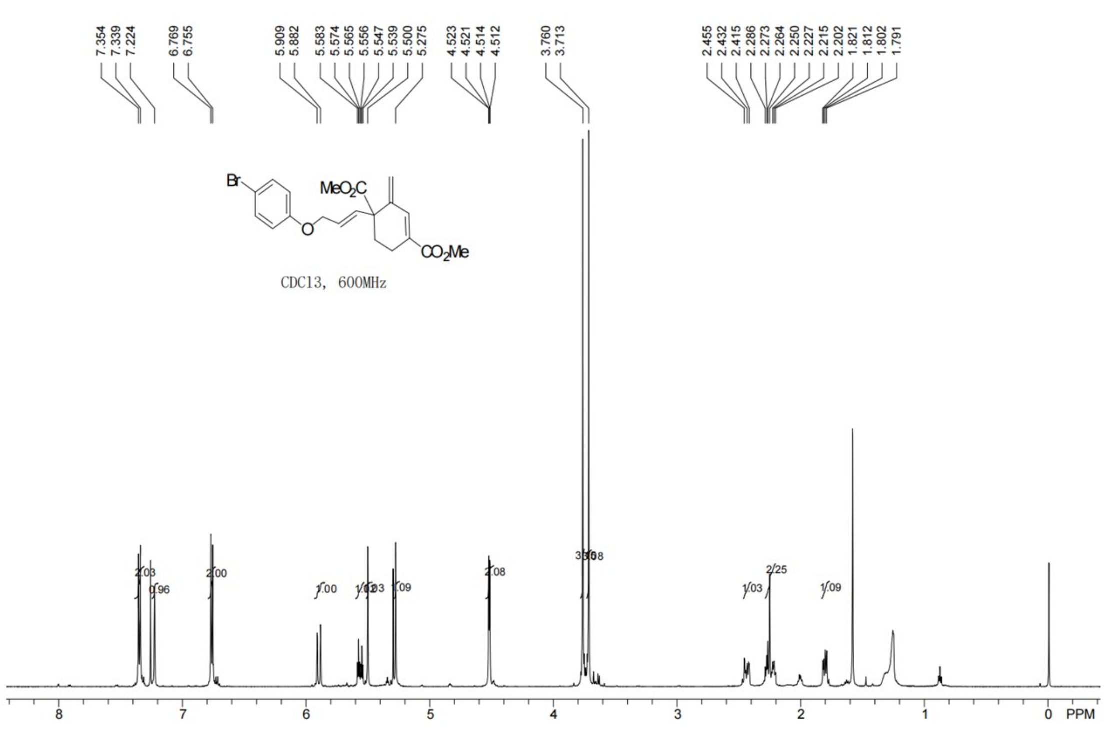


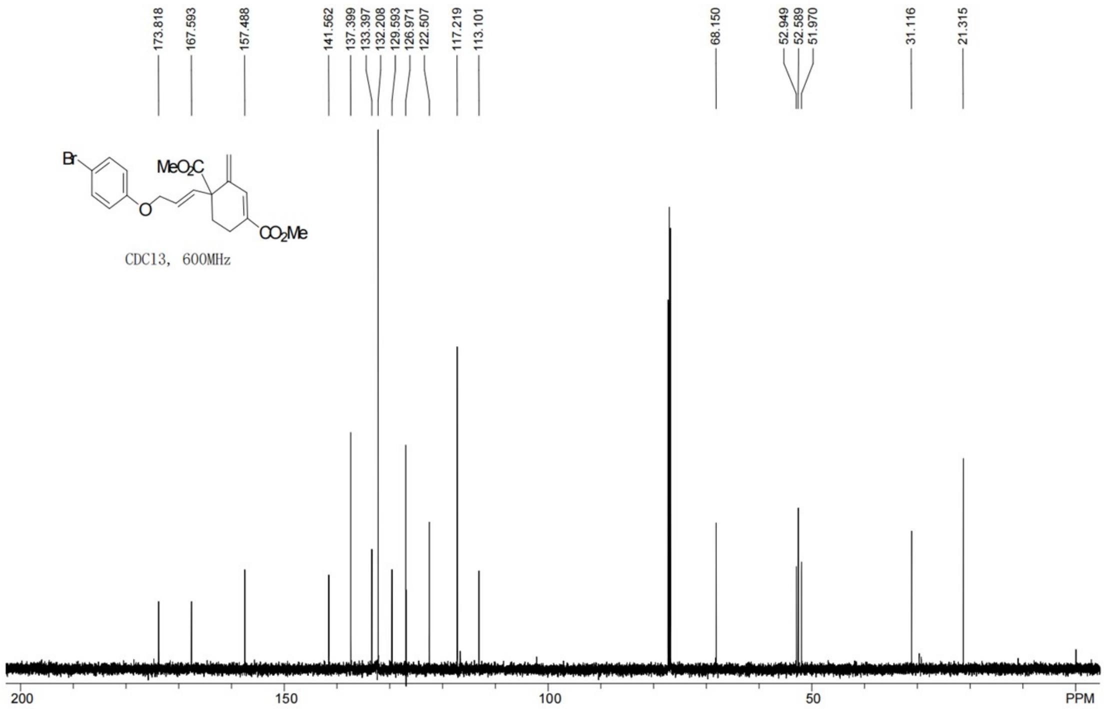
Dimethyl (*E*)-4-(3-(4-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3b)



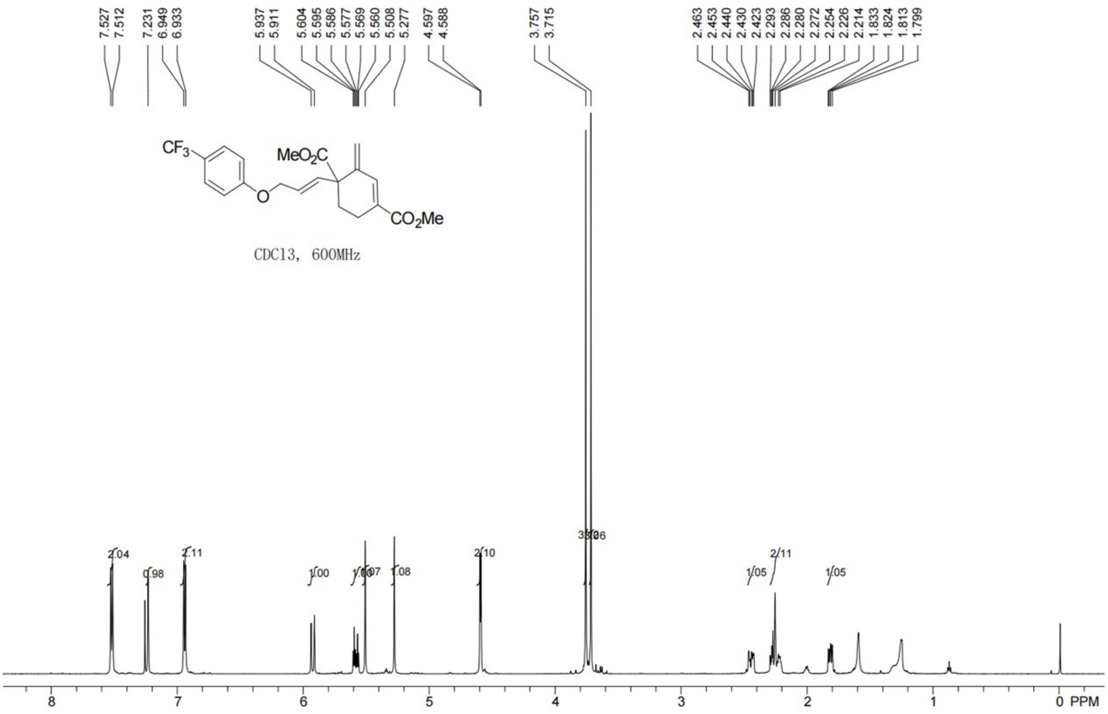


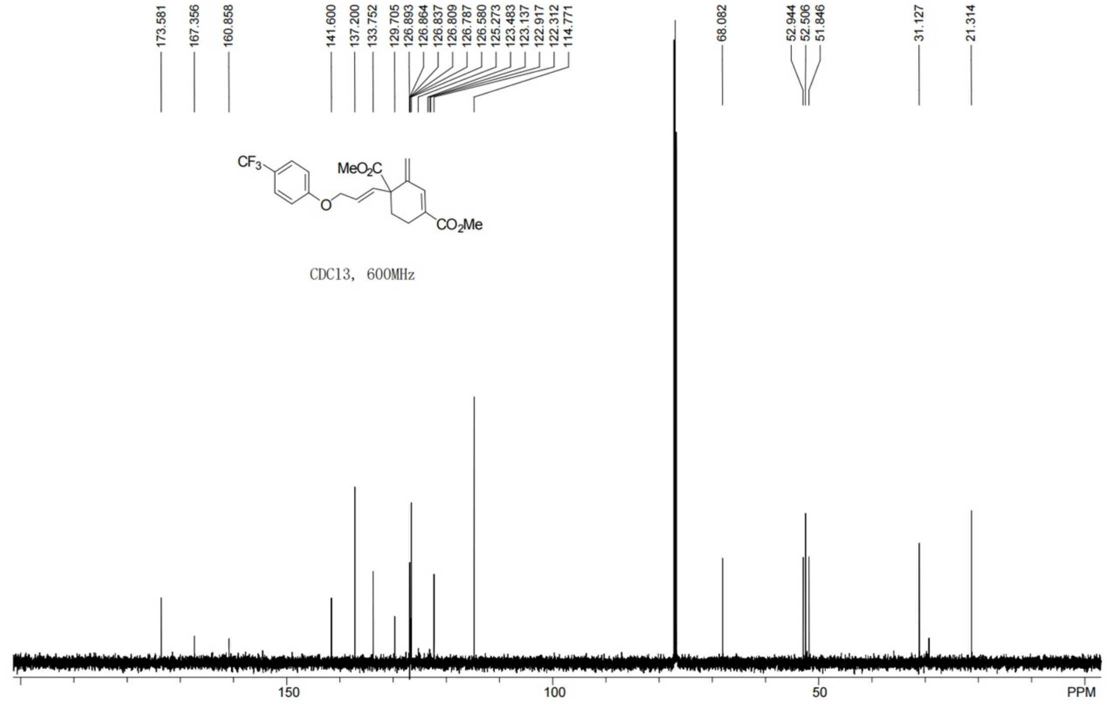
Dimethyl (*E*)-4-(3-(4-bromophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3c)



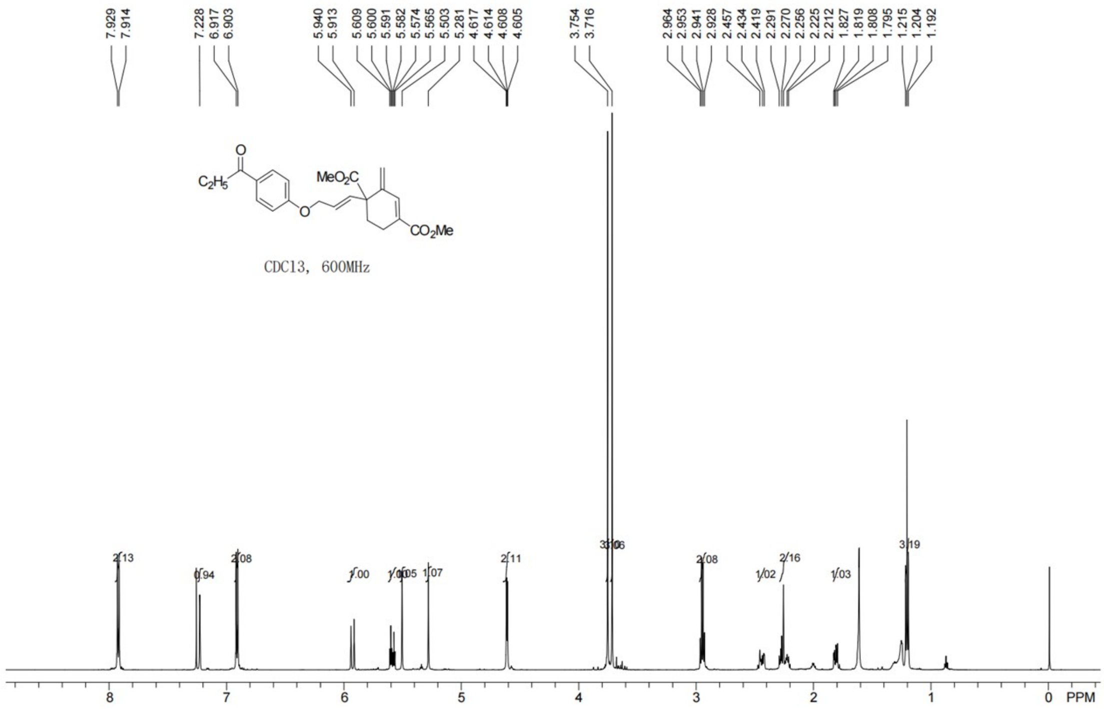


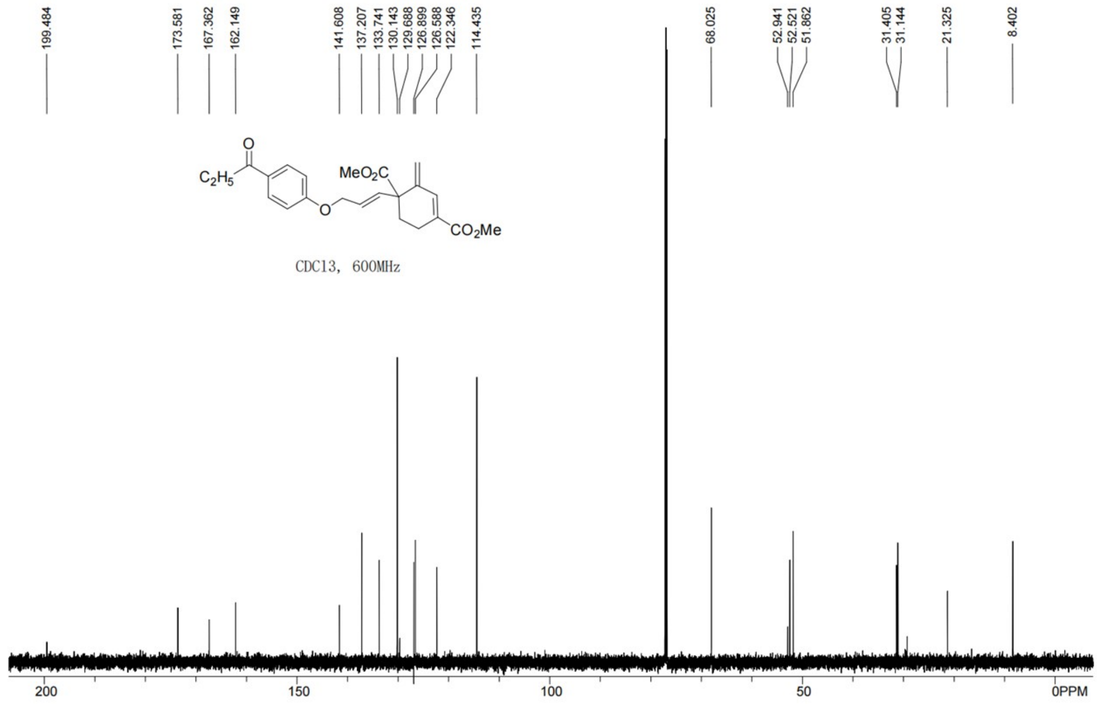
Dimethyl(*E*)-3-methylene-4-(3-(4-(trifluoromethyl)phenoxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3d)



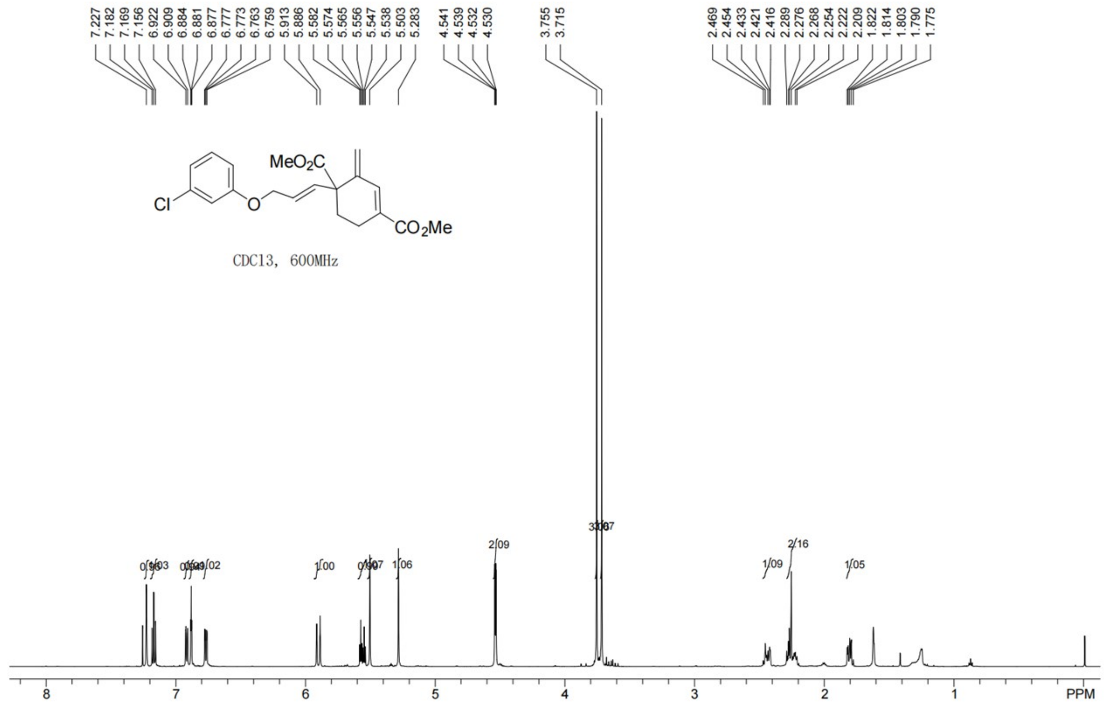


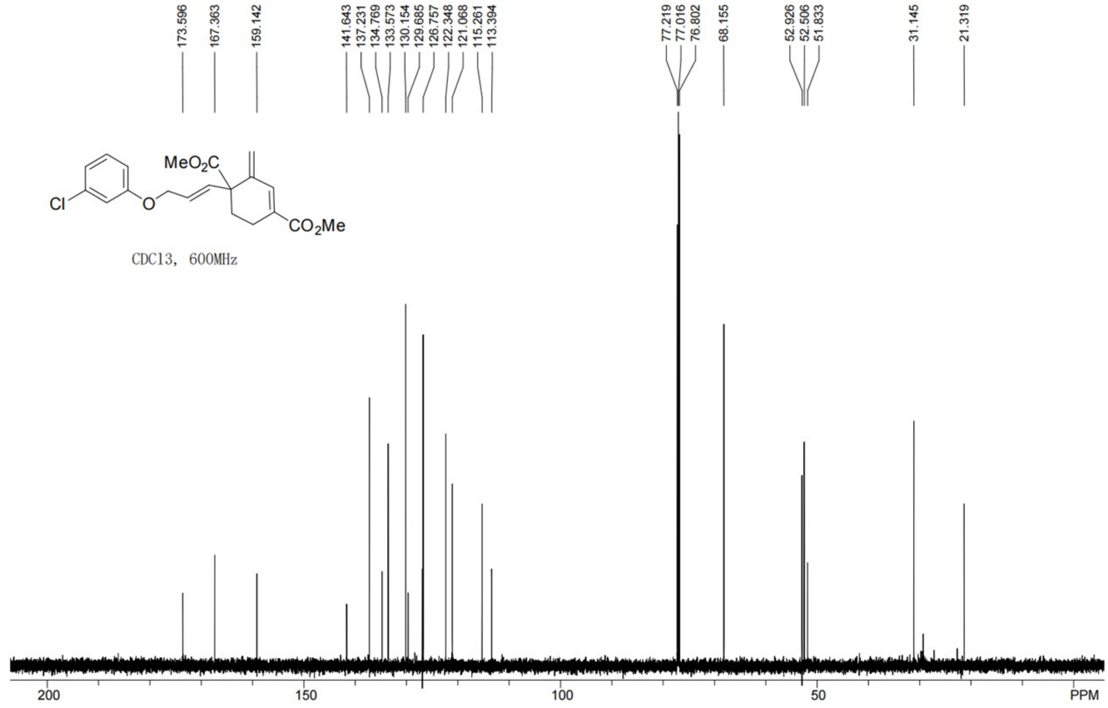
Dimethyl(*E*)-3-methylene-4-(3-(4-propionylphenoxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3e)



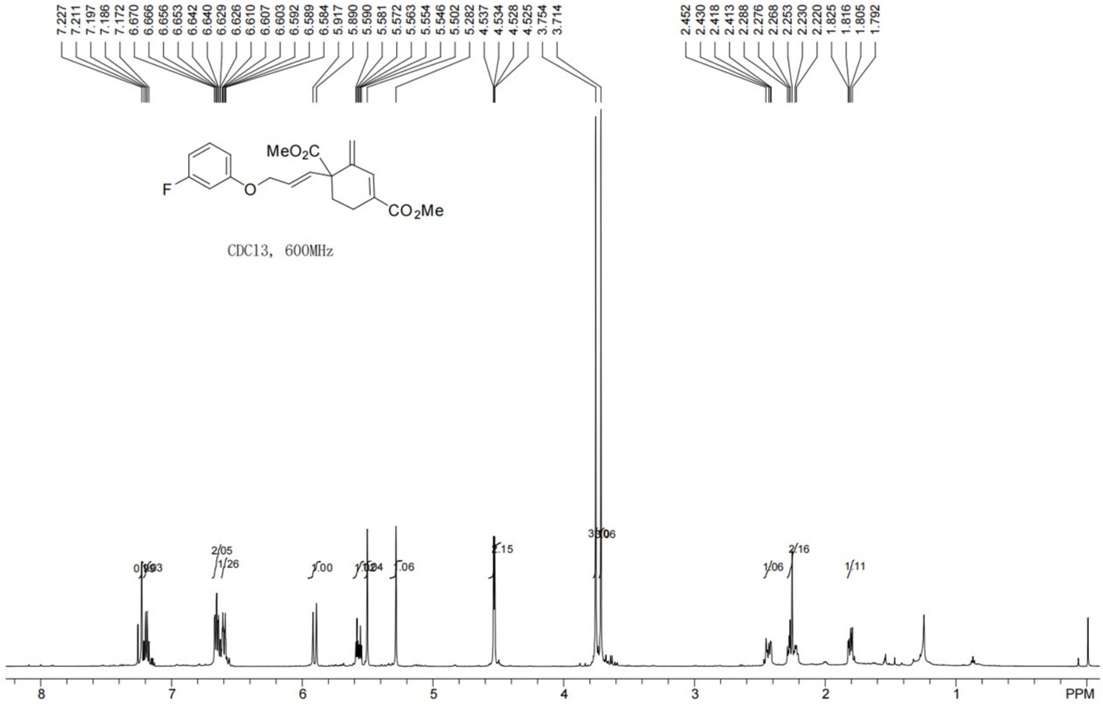


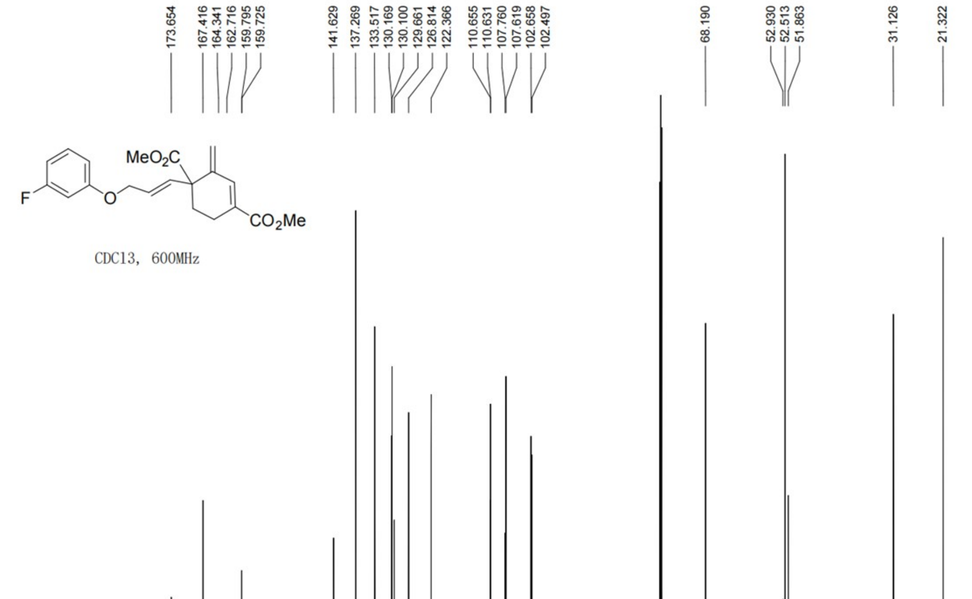
Dimethyl (*E*)-4-(3-(3-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3f)



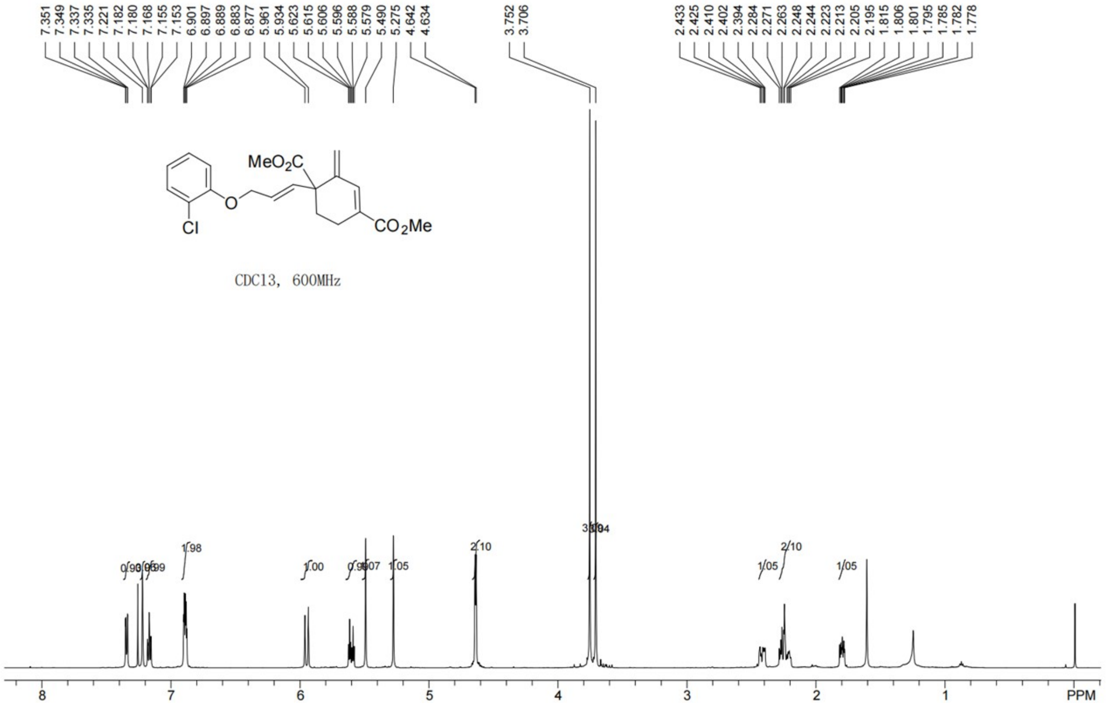


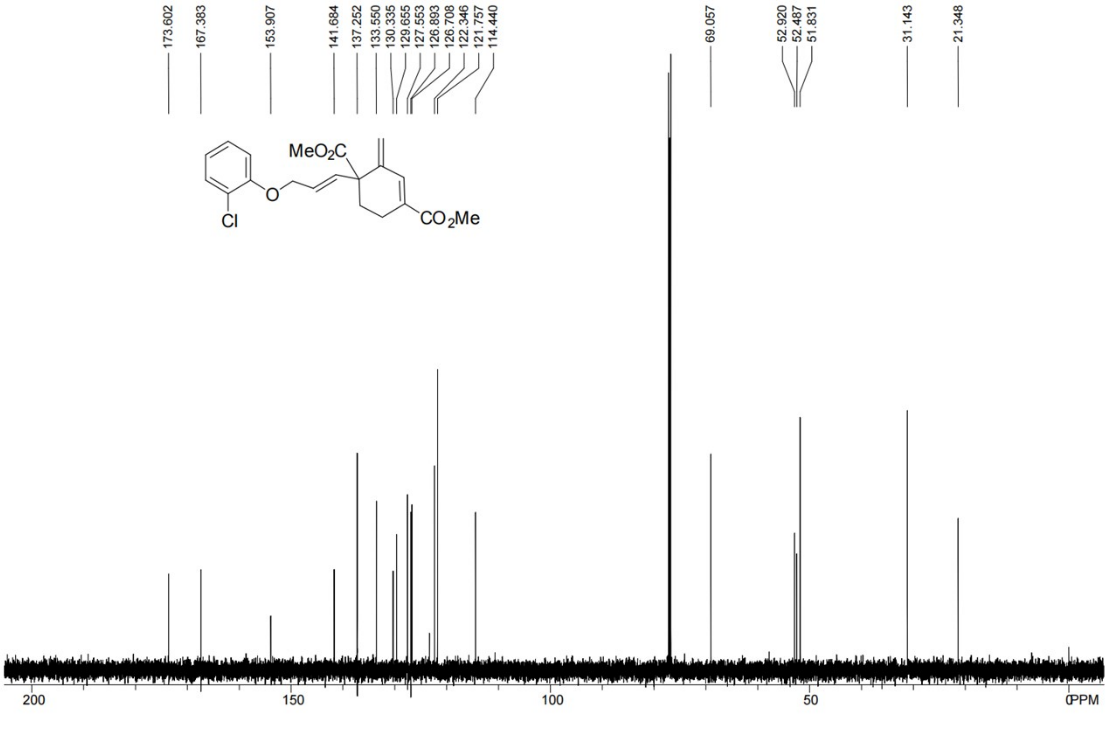
Dimethyl (*E*)-4-(3-(3-fluorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3g)



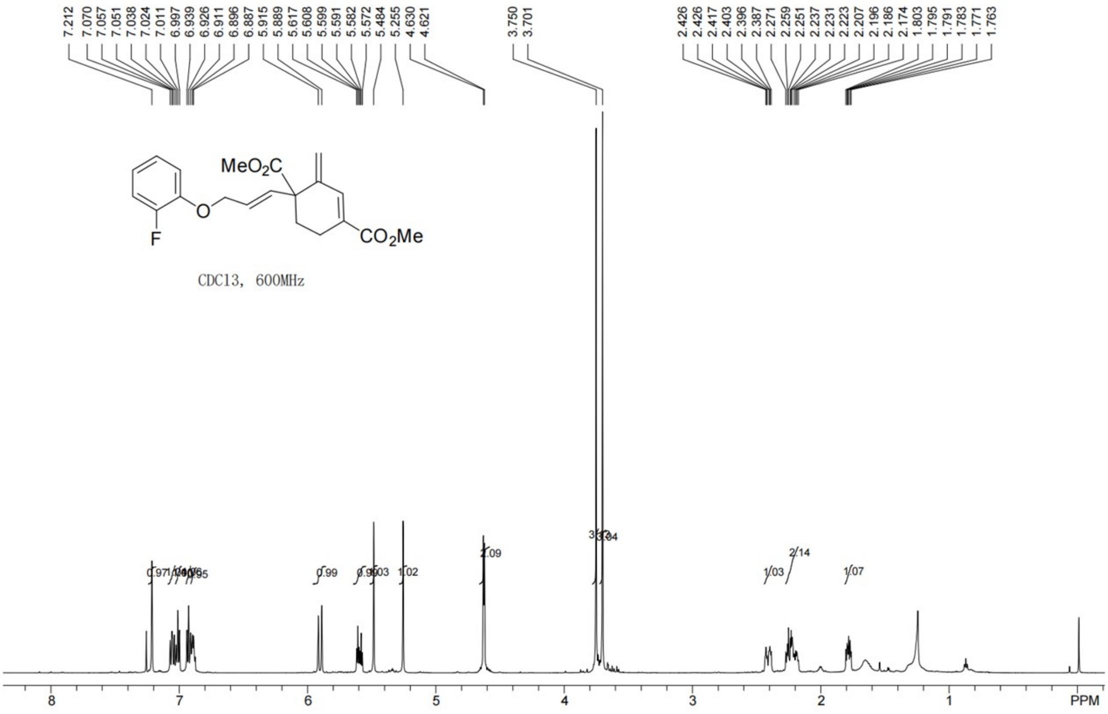


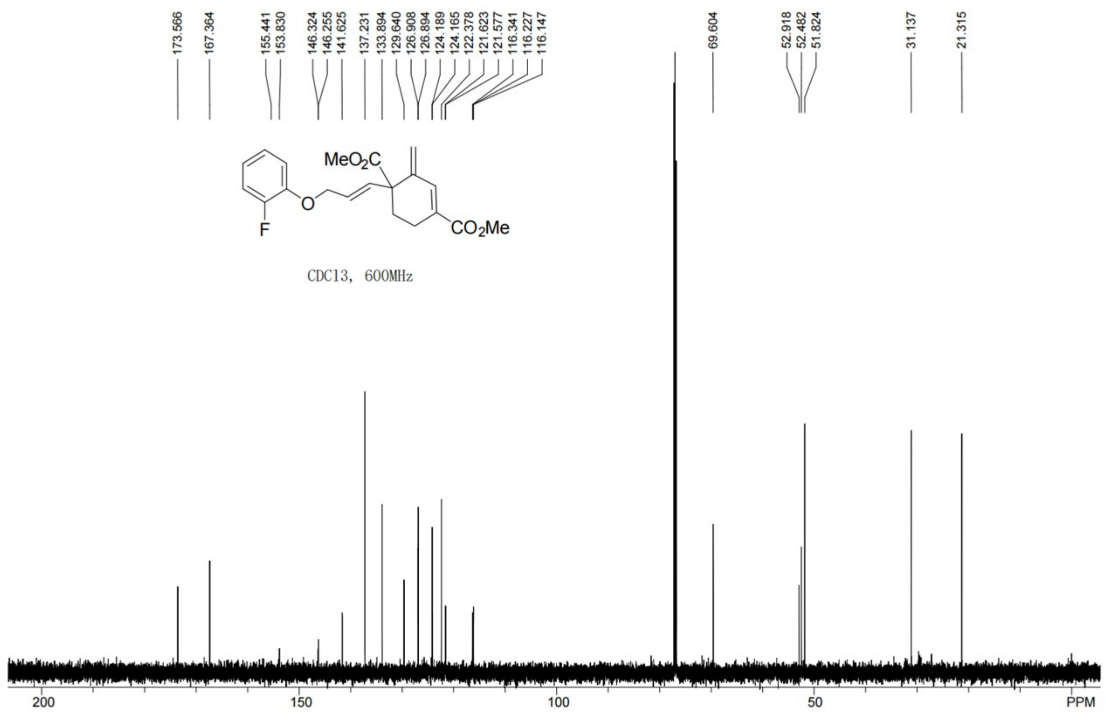
Dimethyl (*E*)-4-(3-(2-chlorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3h)



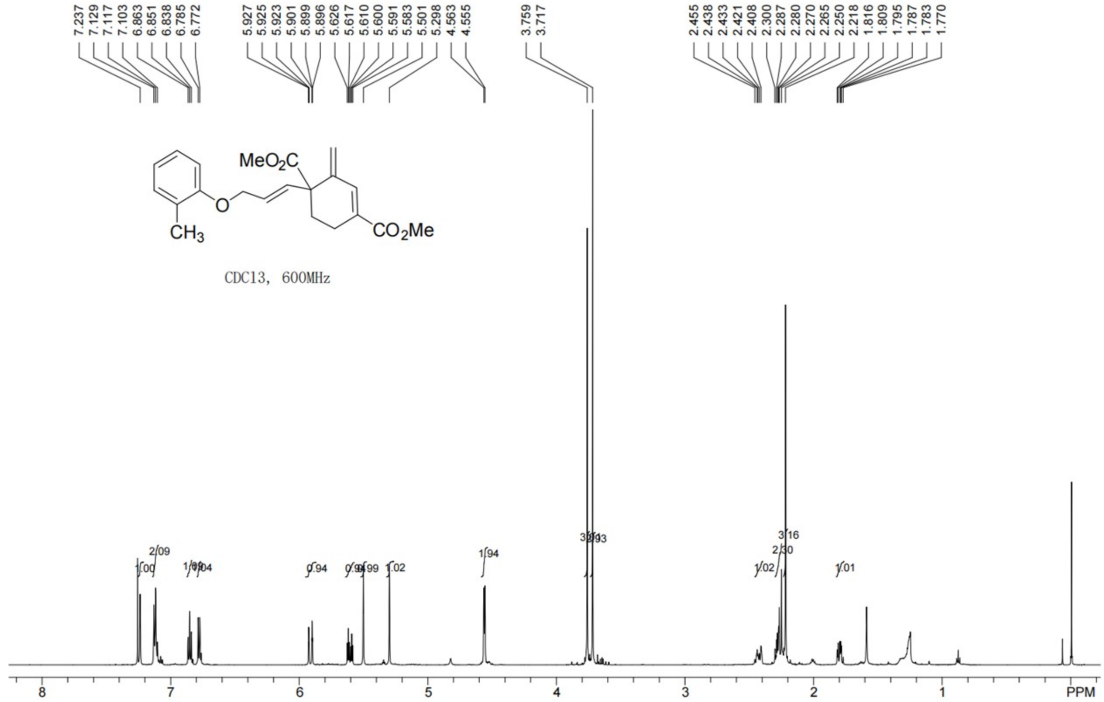


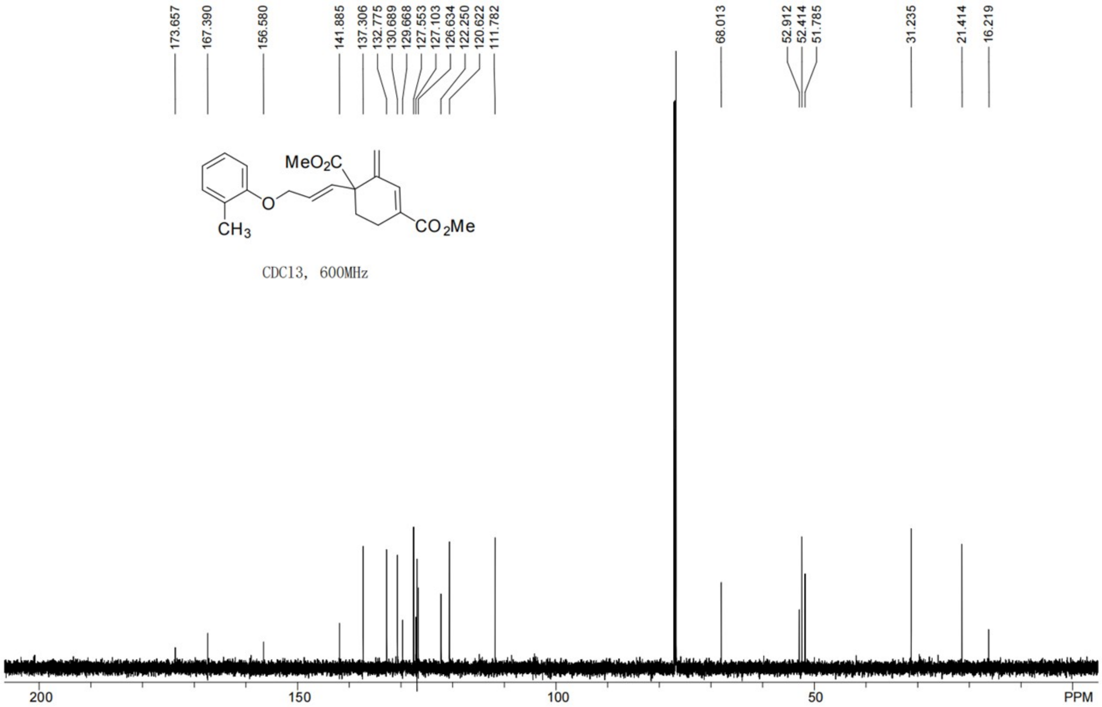
Dimethyl (*E*)-4-(3-(2-fluorophenoxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3i)



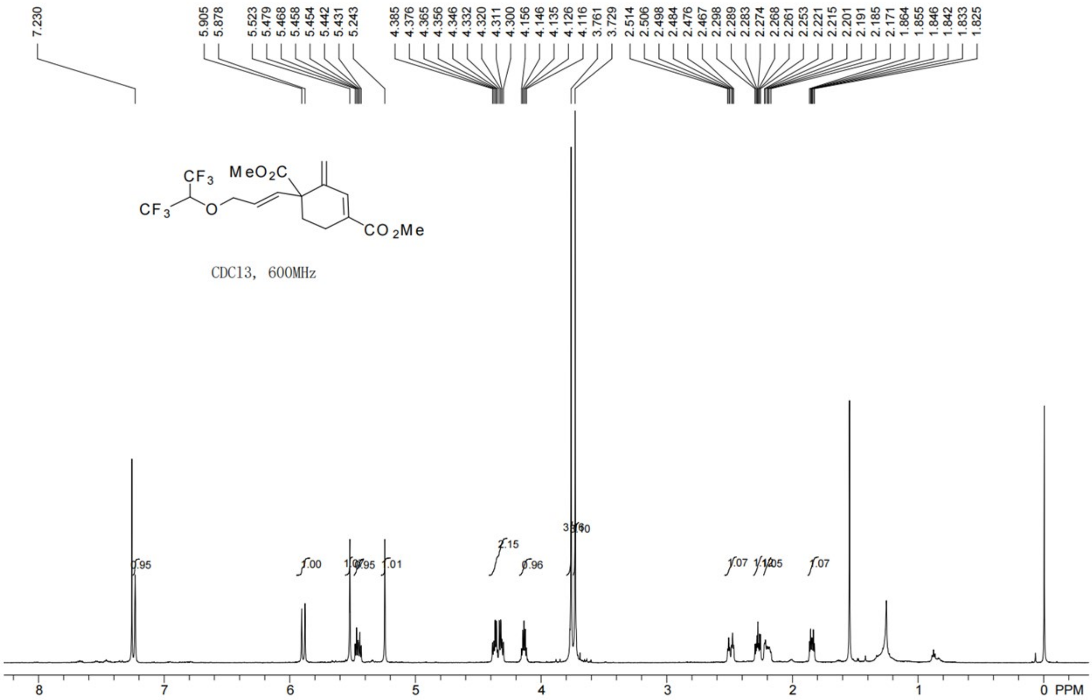


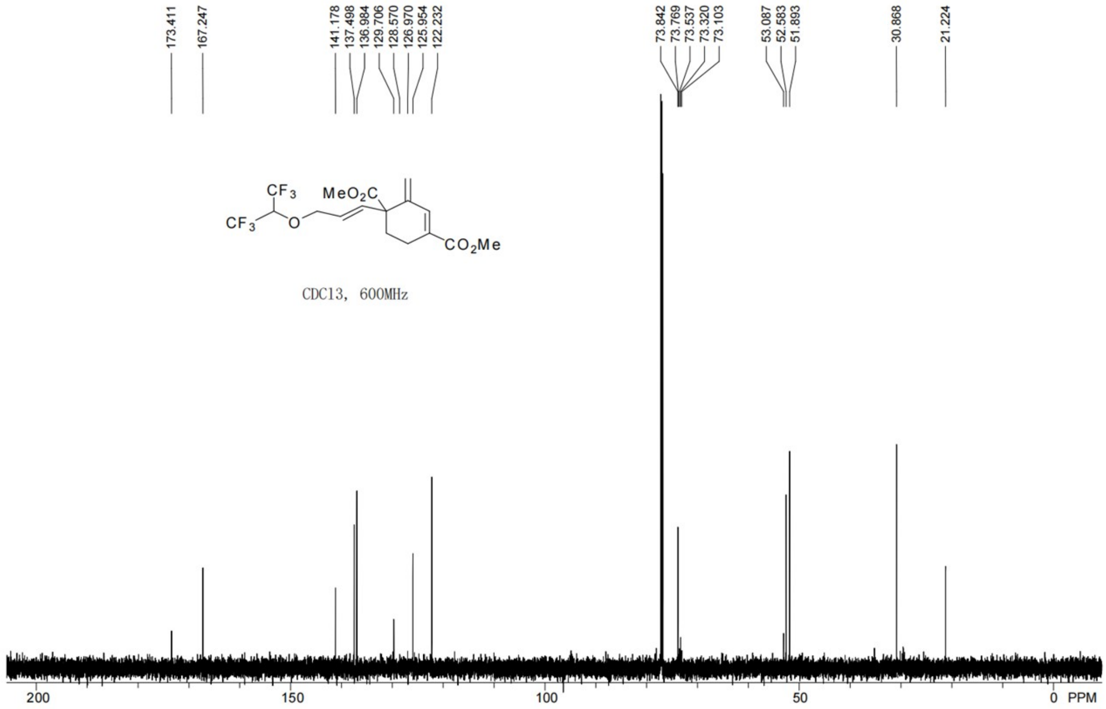
Dimethyl (*E*)-3-methylene-4-(3-(o-tolyloxy)prop-1-en-1-yl)cyclohex-1-ene-1,4-dicarboxylate (3j)





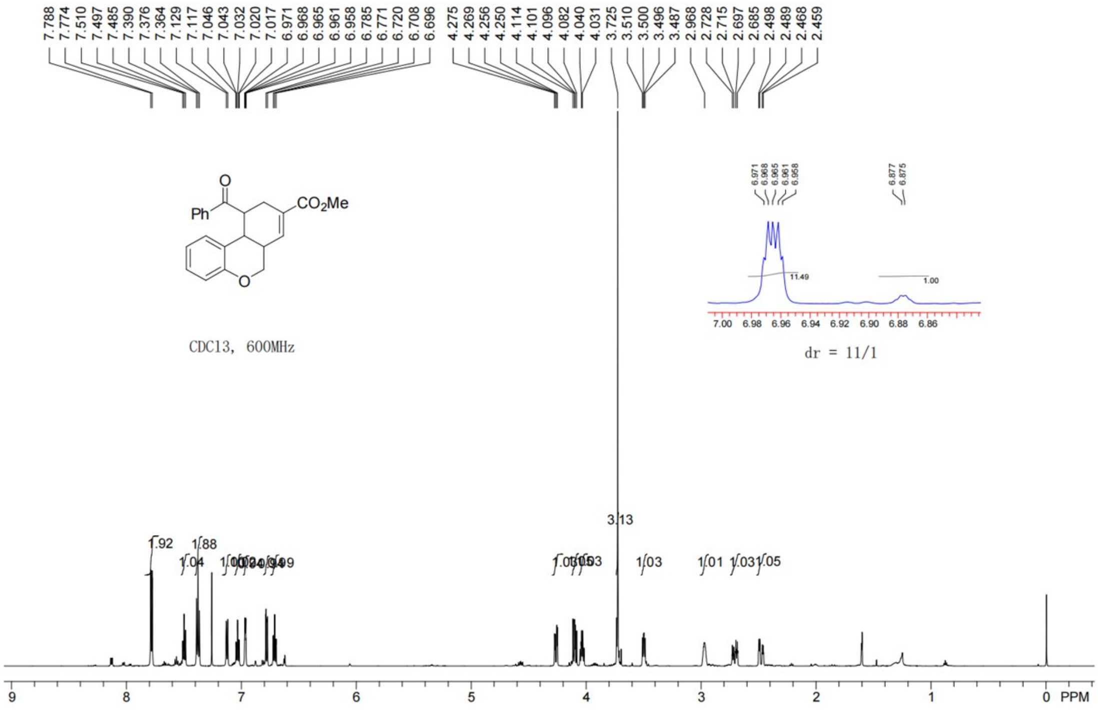
Dimethyl(*E*)-4-(3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)prop-1-en-1-yl)-3-methylenecyclohex-1-ene-1,4-dicarboxylate (3k)

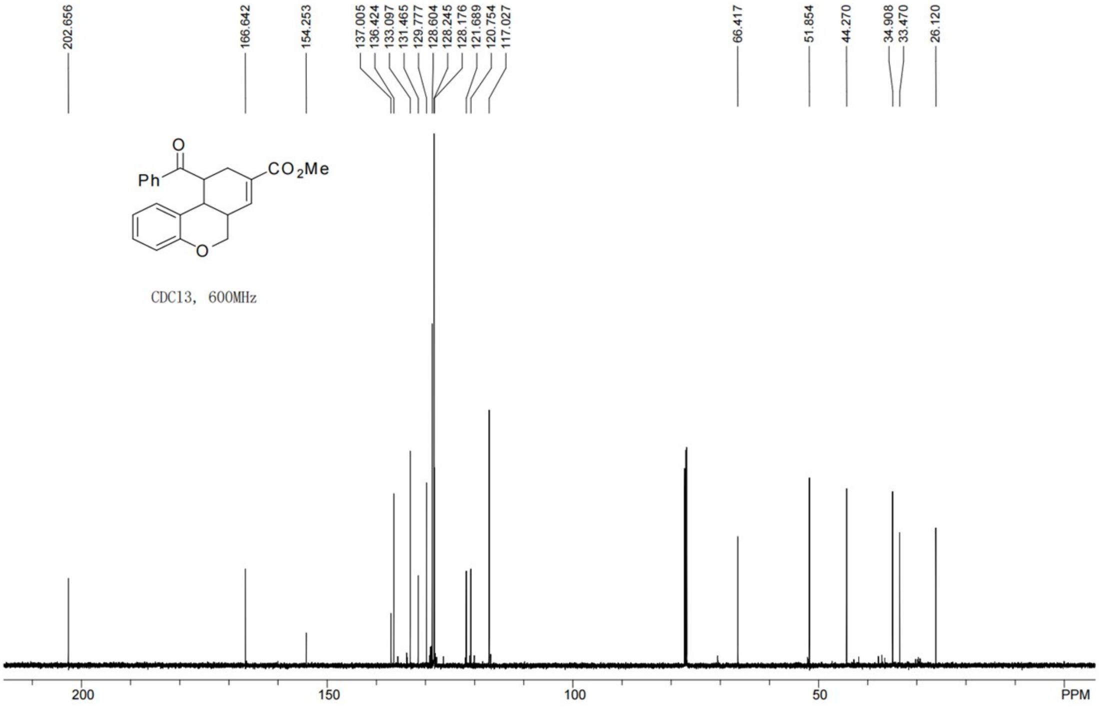




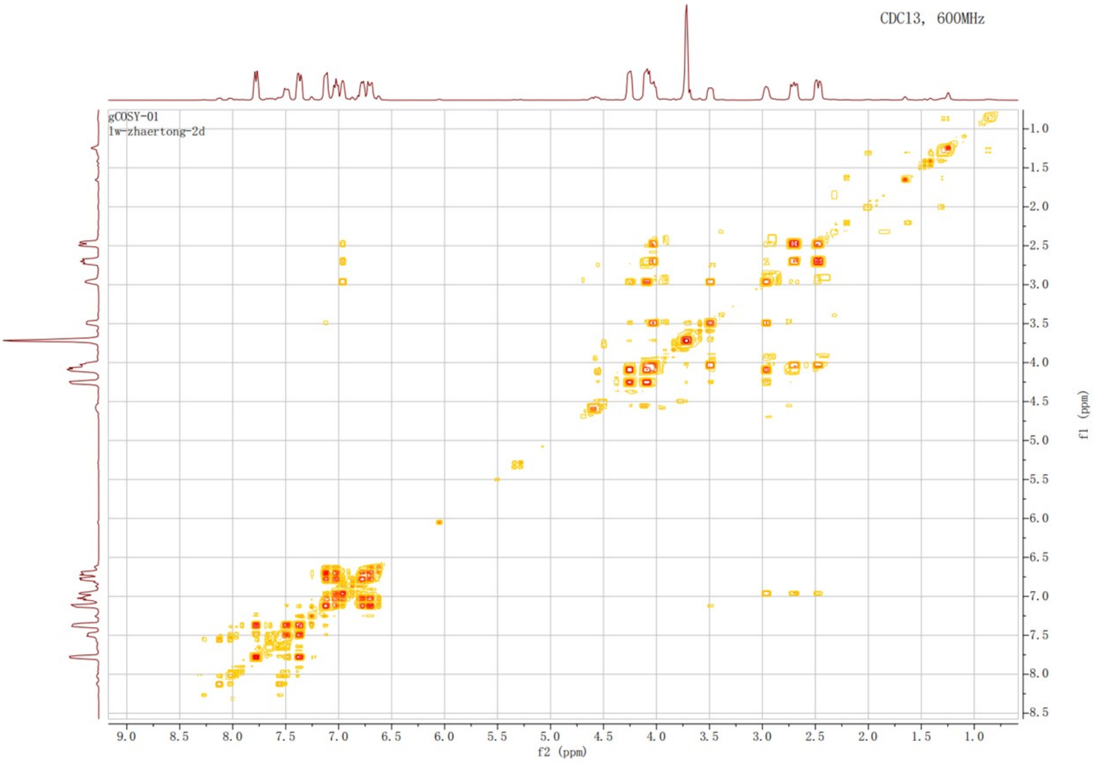
NMR spectra for compounds 5

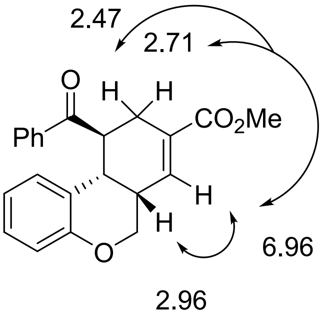
(6a*S,10*S**,10a*S**)-**
methyl 10-benzoyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5a)



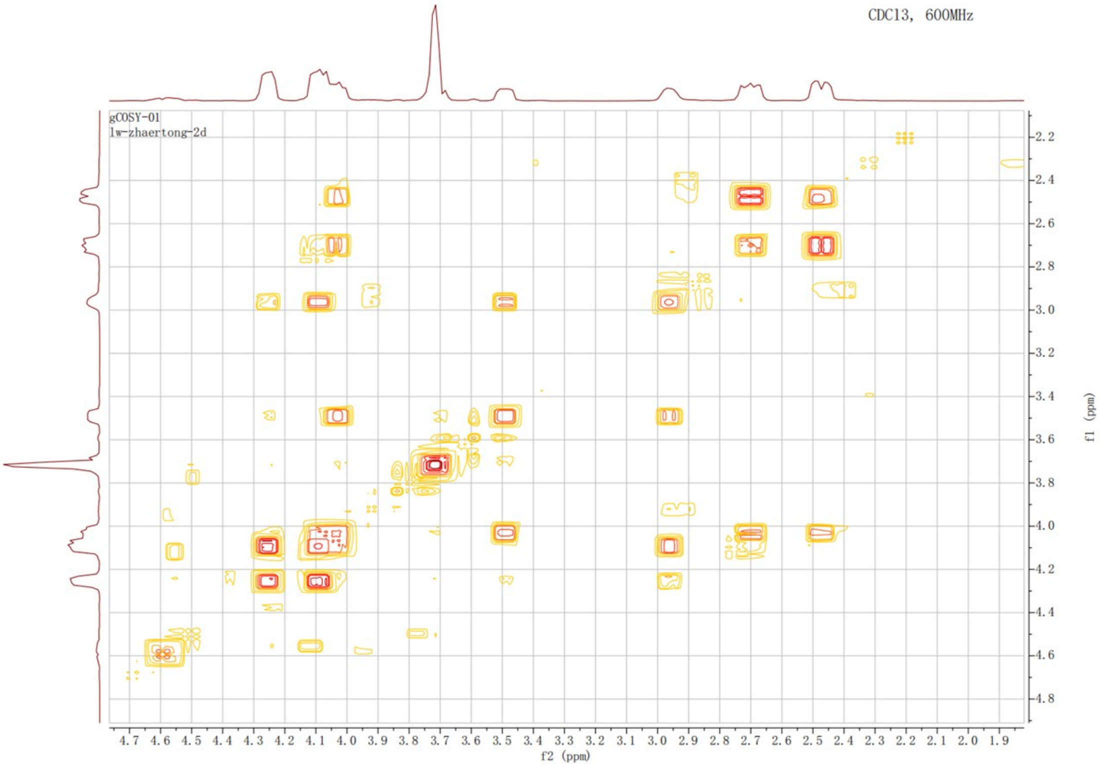


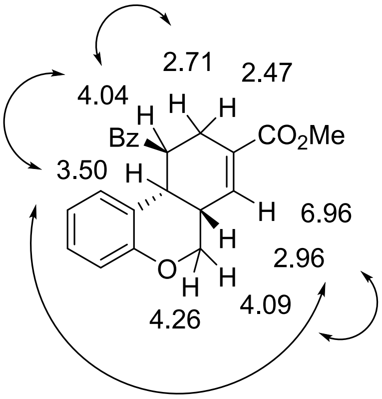
^1H-^1H COSY


CDCl3, 600MHz
gCOSY-01
lw-zhaertong-2d
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
8.5

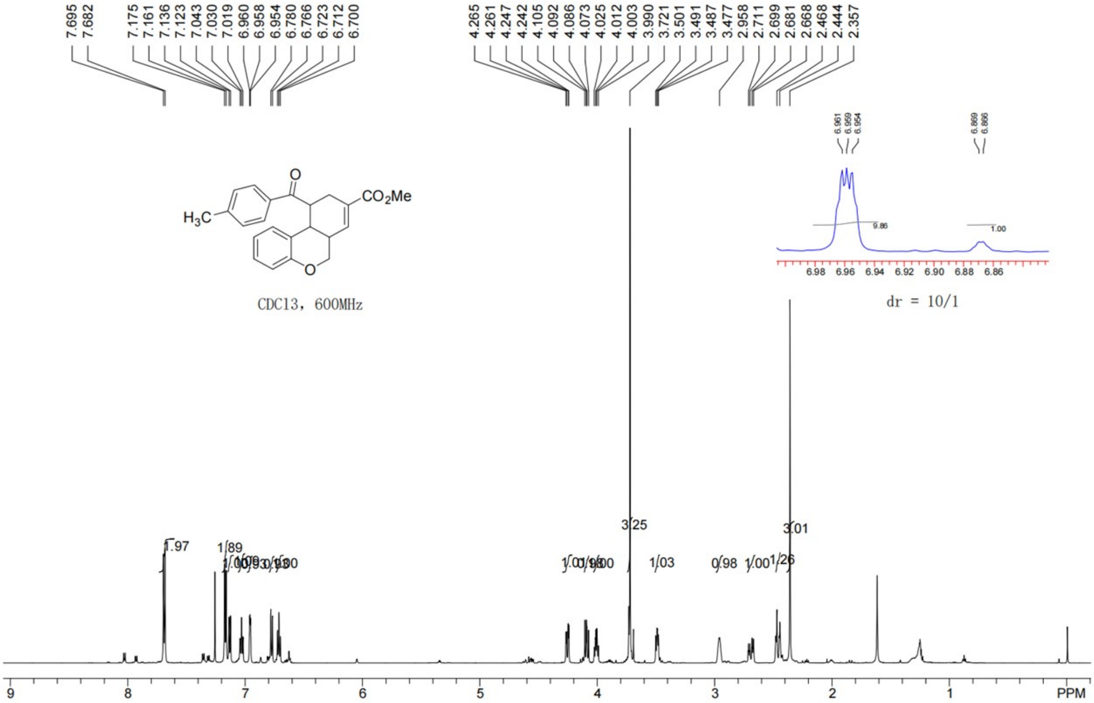

2.47
2.71
O
Ph
H
H
CO2Me
H
H
O
6.96
2.96

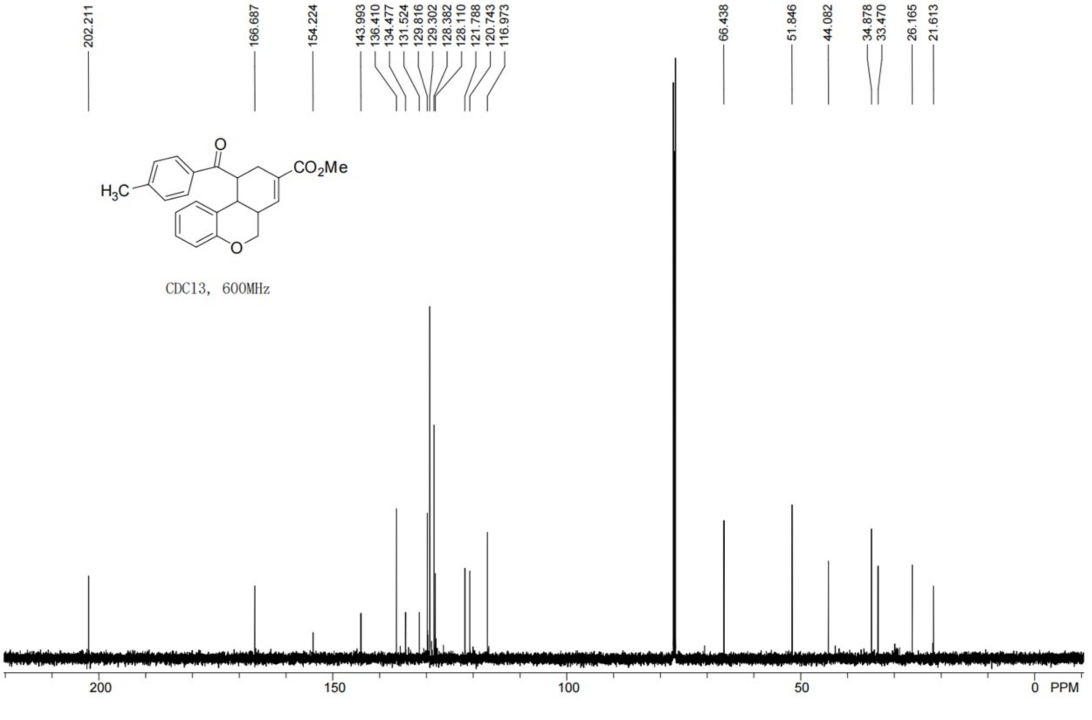
^{1}H-^{1}H COSY


CDCl3, 600MHz
gCOSY-01
lw-zhaertong-2d
4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
f2 (ppm)
2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8
f1 (ppm)

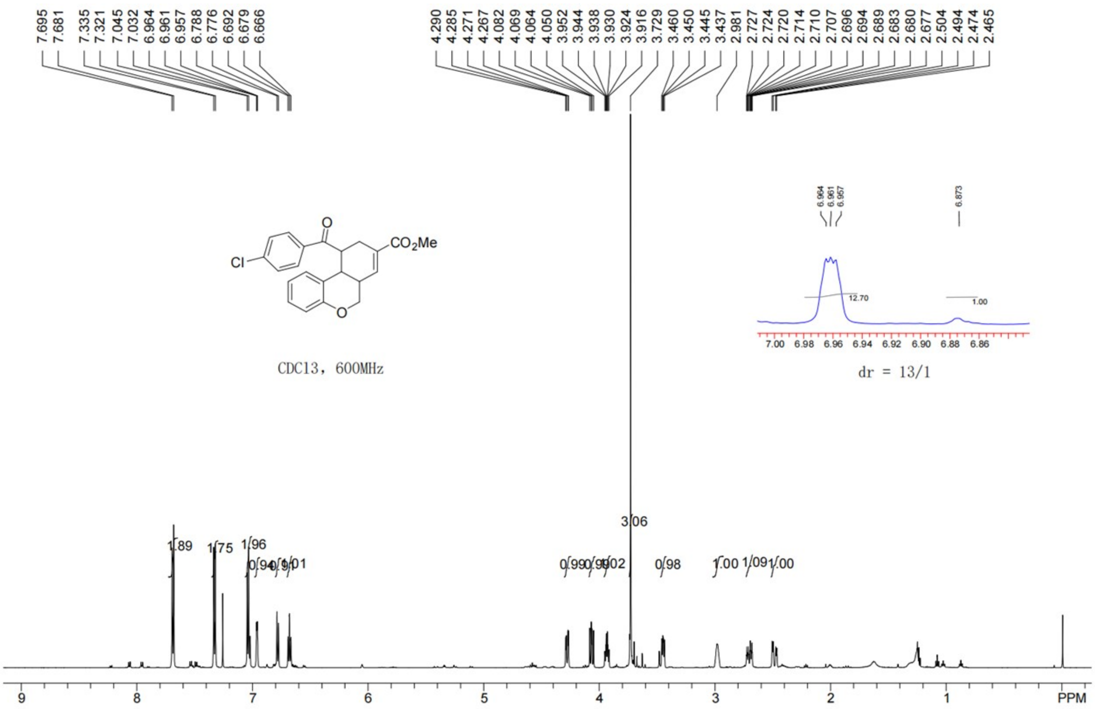

2.71
2.47
4.04
H
H
H
Bz
CO2Me
3.50
H
H
6.96
H
2.96
O
H
H
4.09
4.26

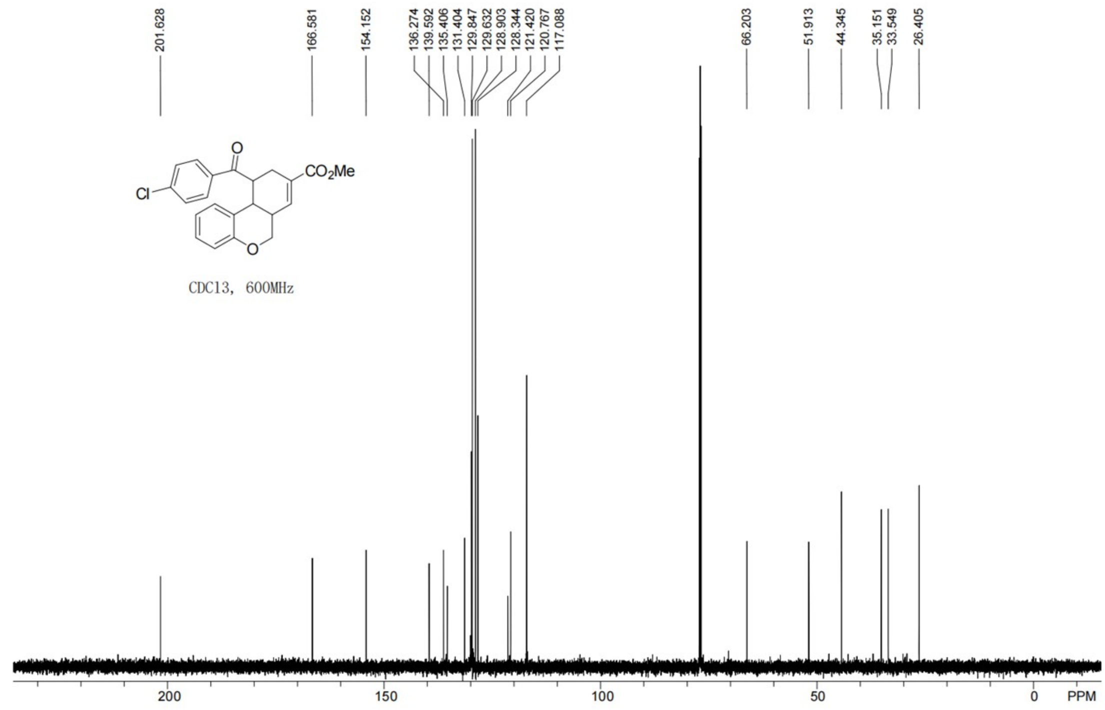
(6a*S**,10*S**,10a*S**)-methyl 10-(4-methylbenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5b)



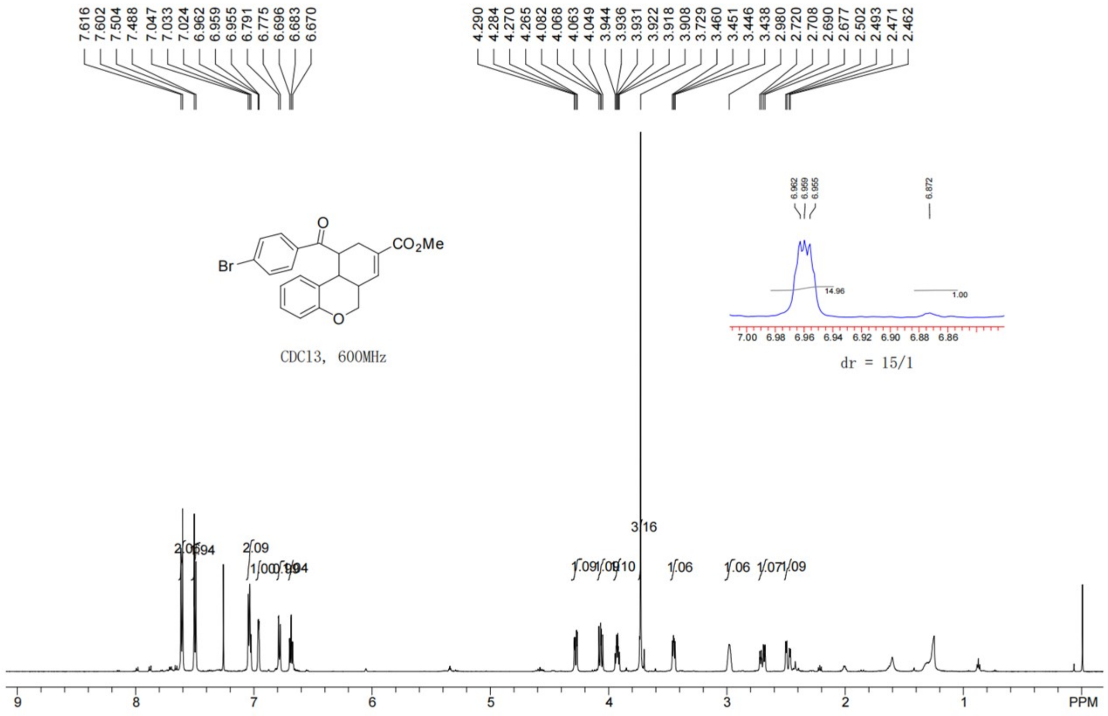


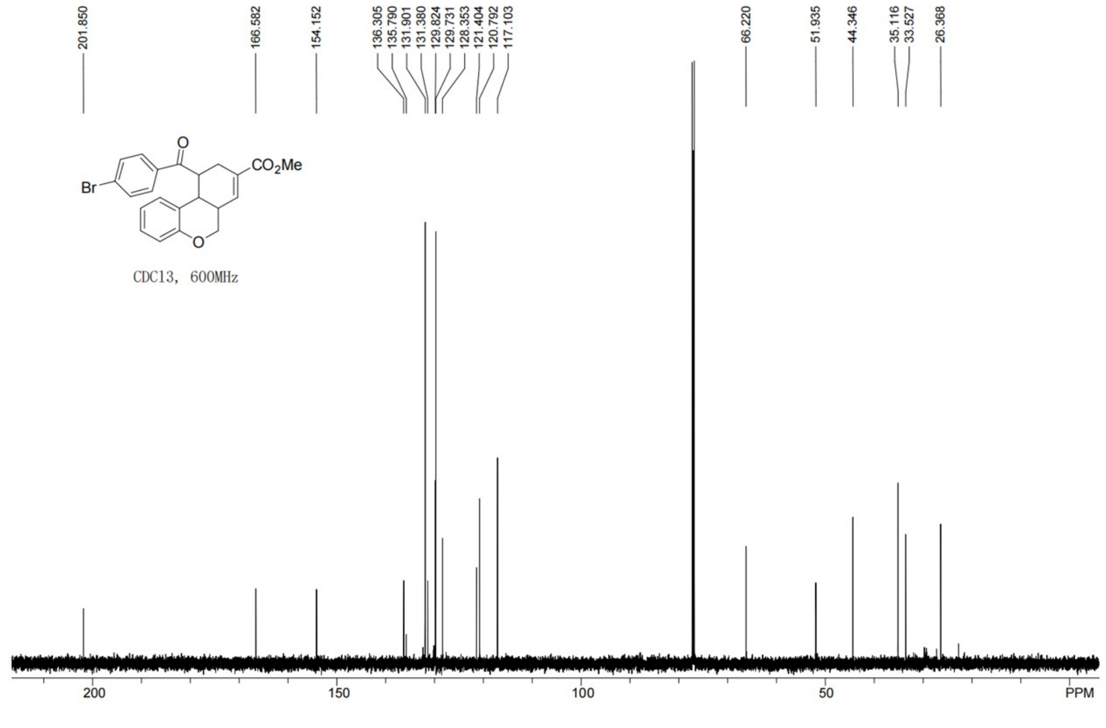
(6a*S,10*S**,10a*S**)-methyl 10-(4-chlorobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-8-carboxylate (5c)**



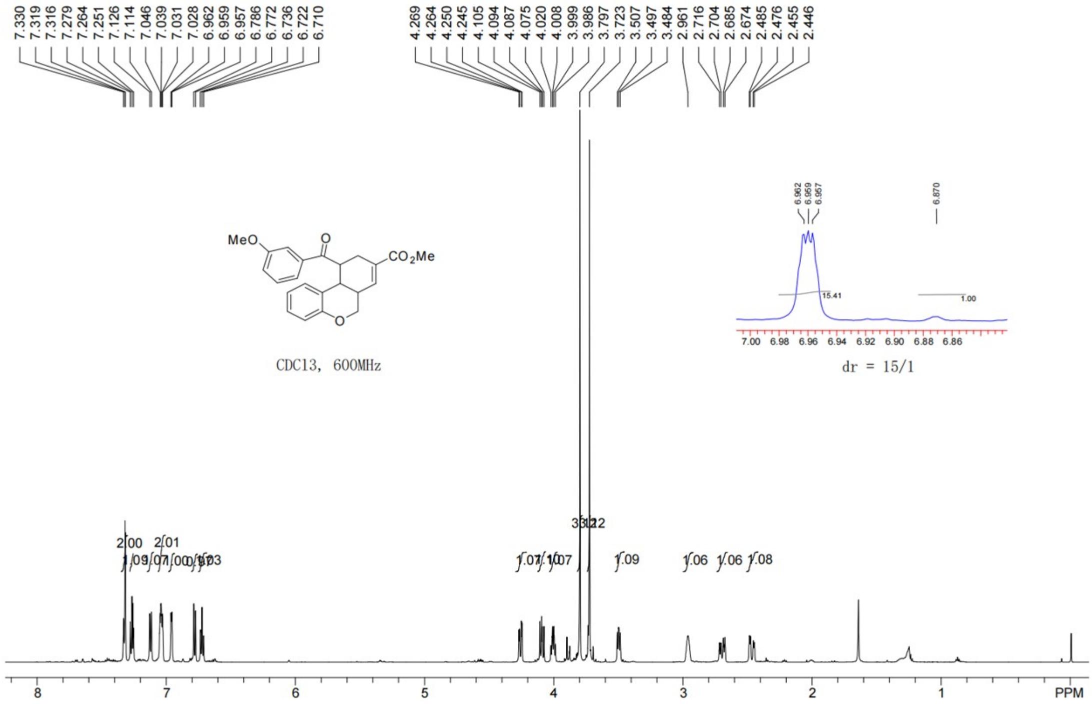


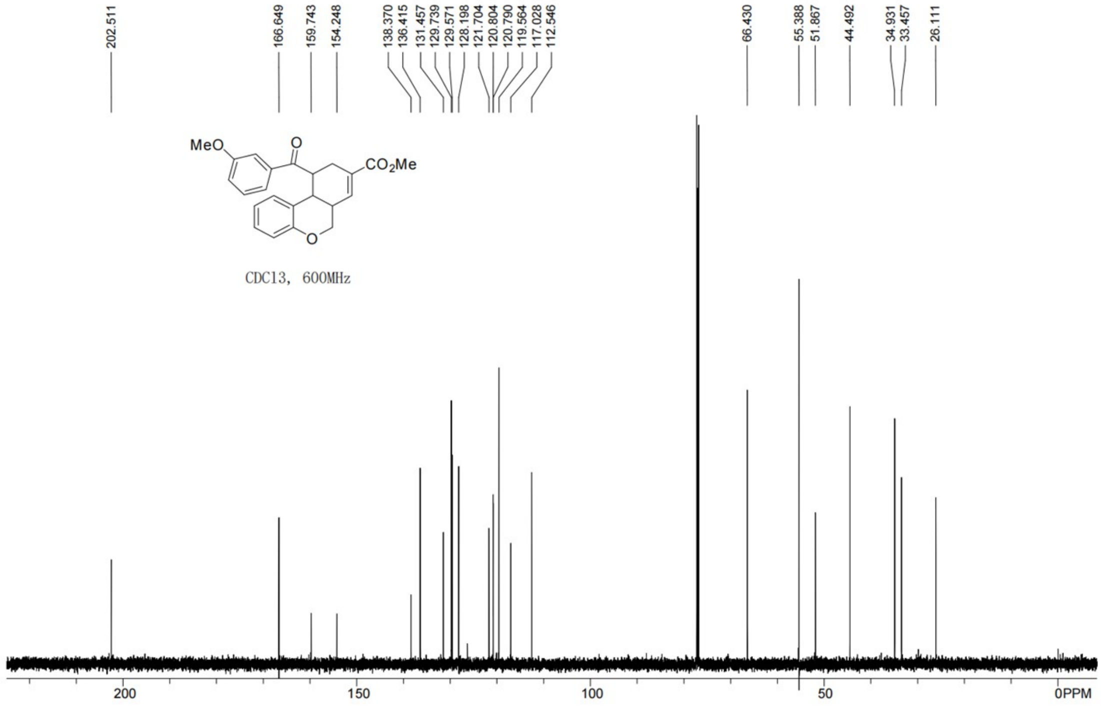
(6a*R,10*S**,10a*S**)-methyl -10-(4-bromobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5d)**



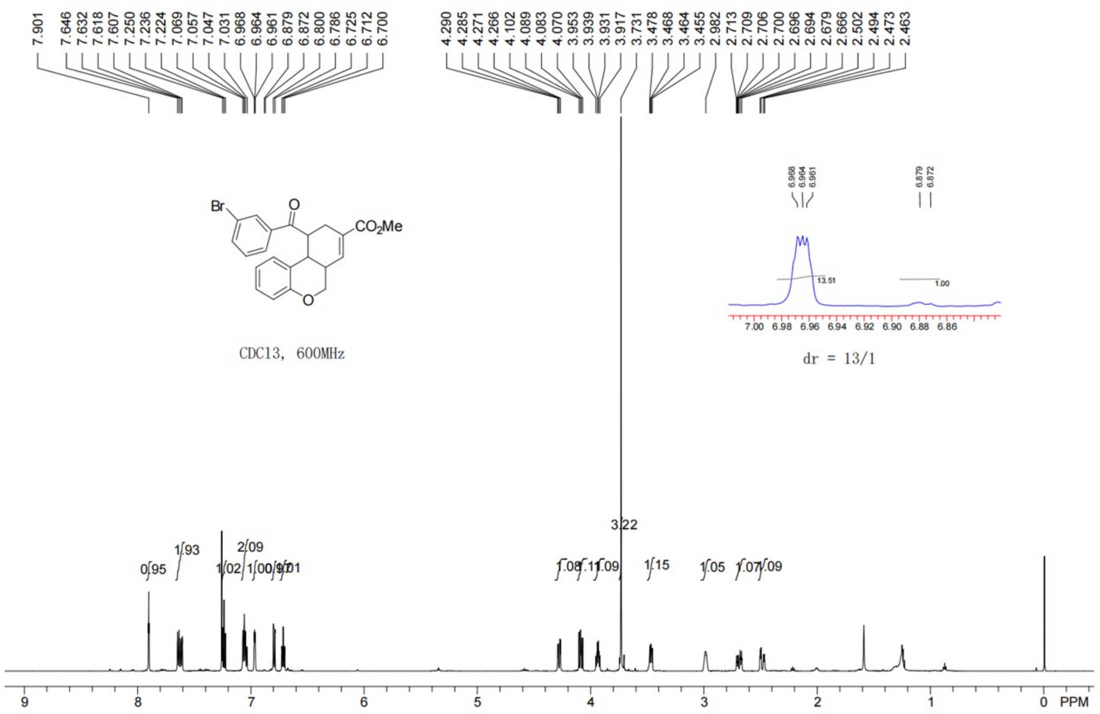


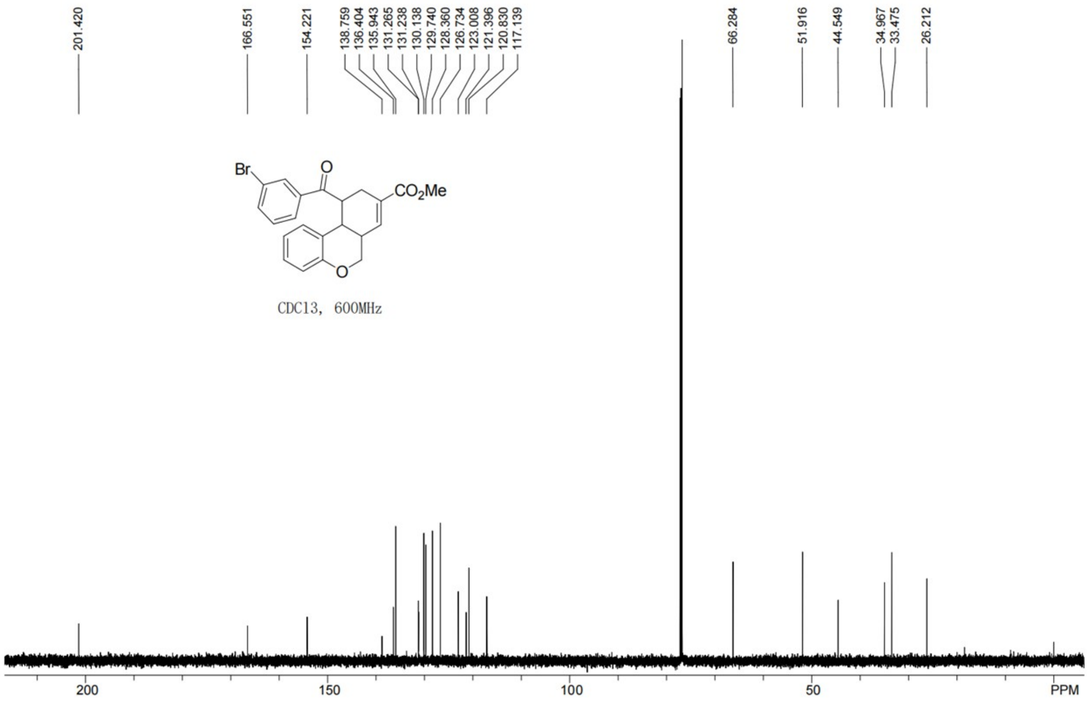
(6a*R,10*S**,10a*S**)-methyl -10-(3-methoxybenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5e)**



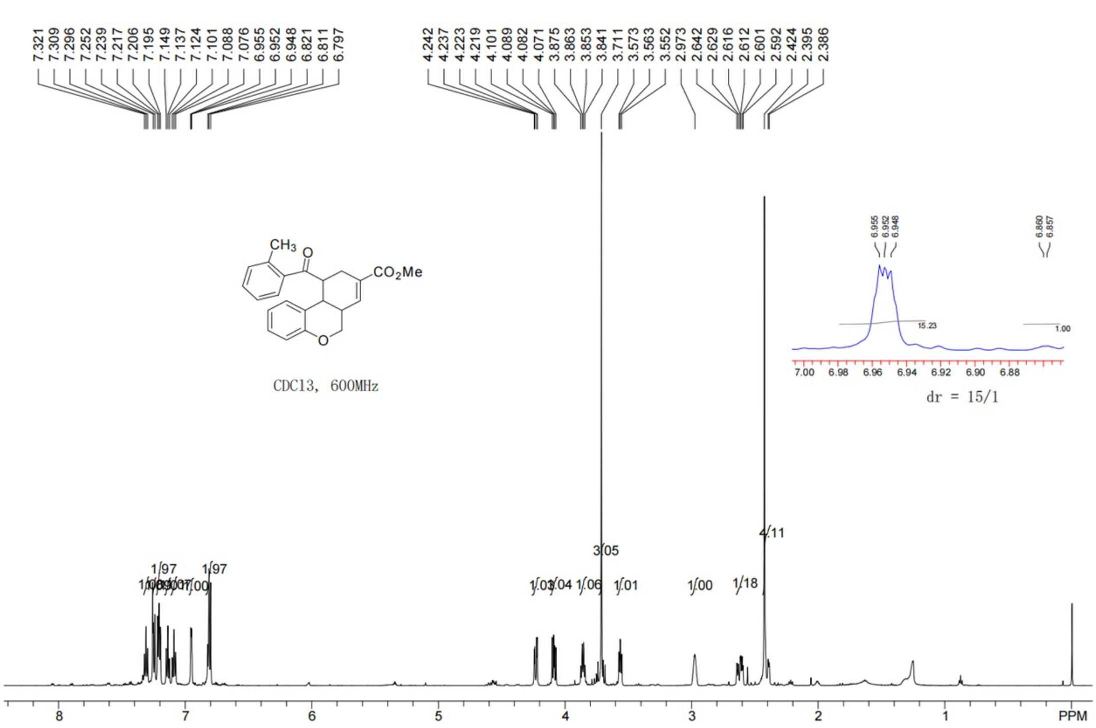


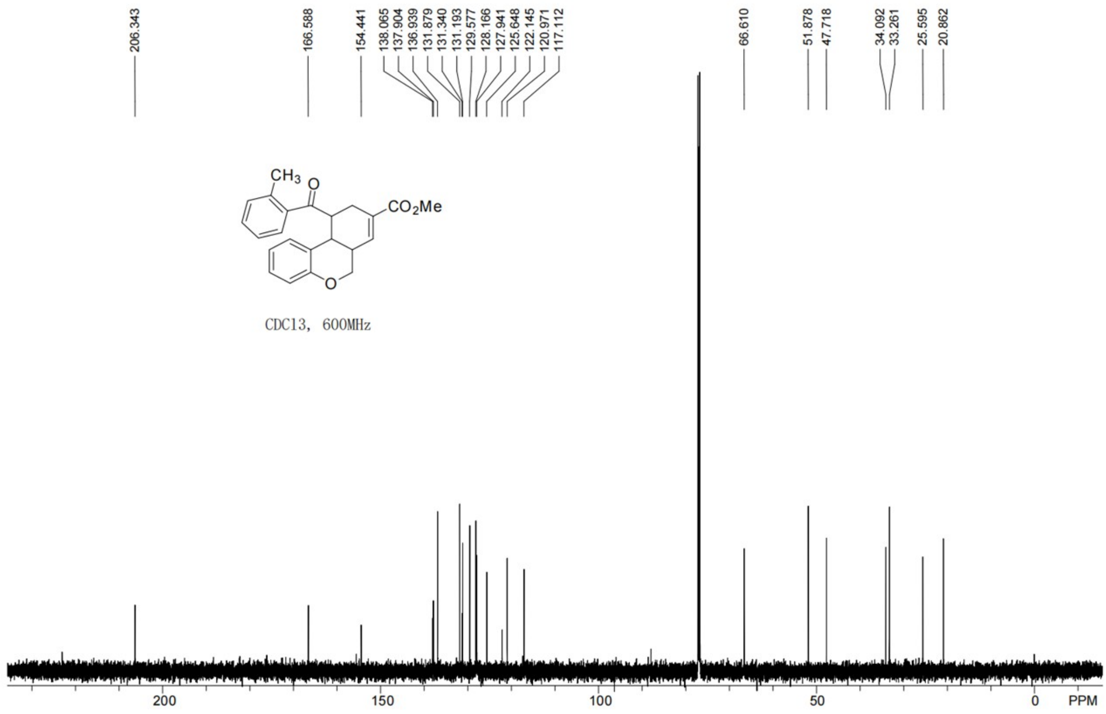
(6a*R,10*S**,10a*S**)-methyl -10-(3-bromobenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5f)**



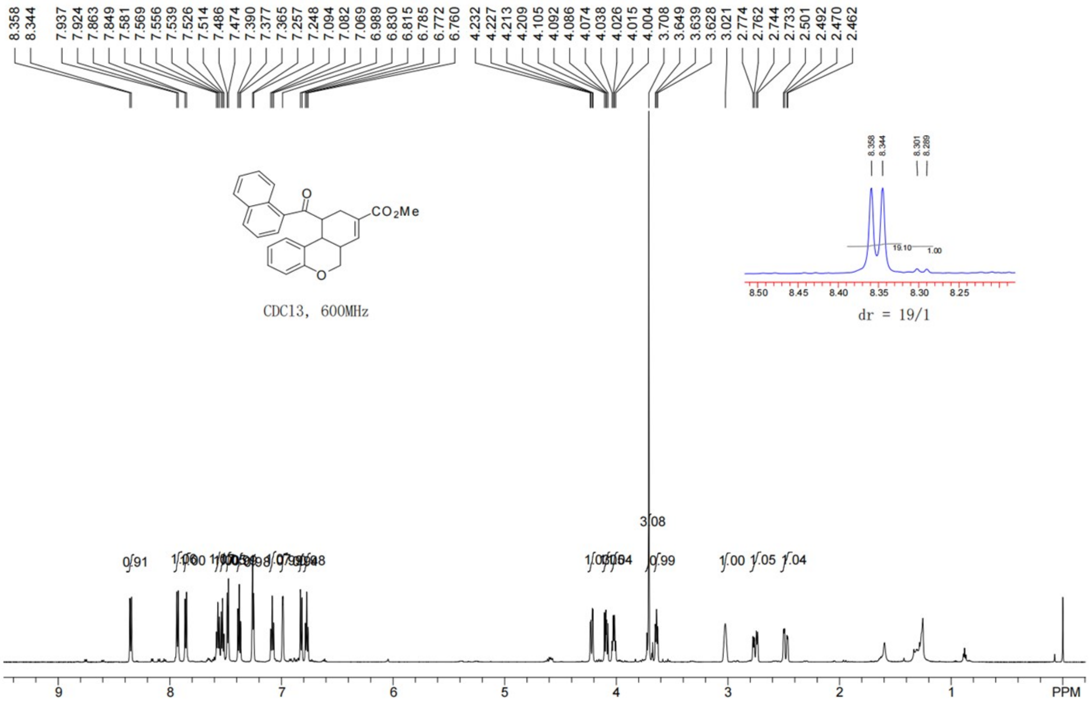


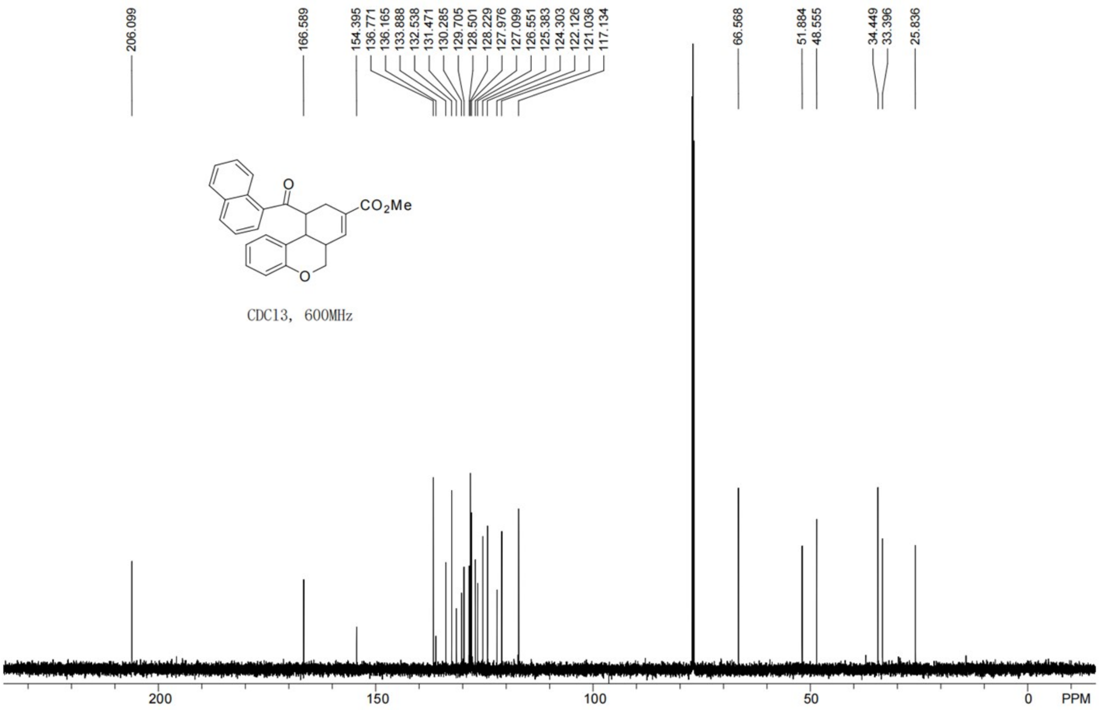
(6a*R,10*S**,10a*S**)-methyl -10-(2-methylbenzoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5g)**



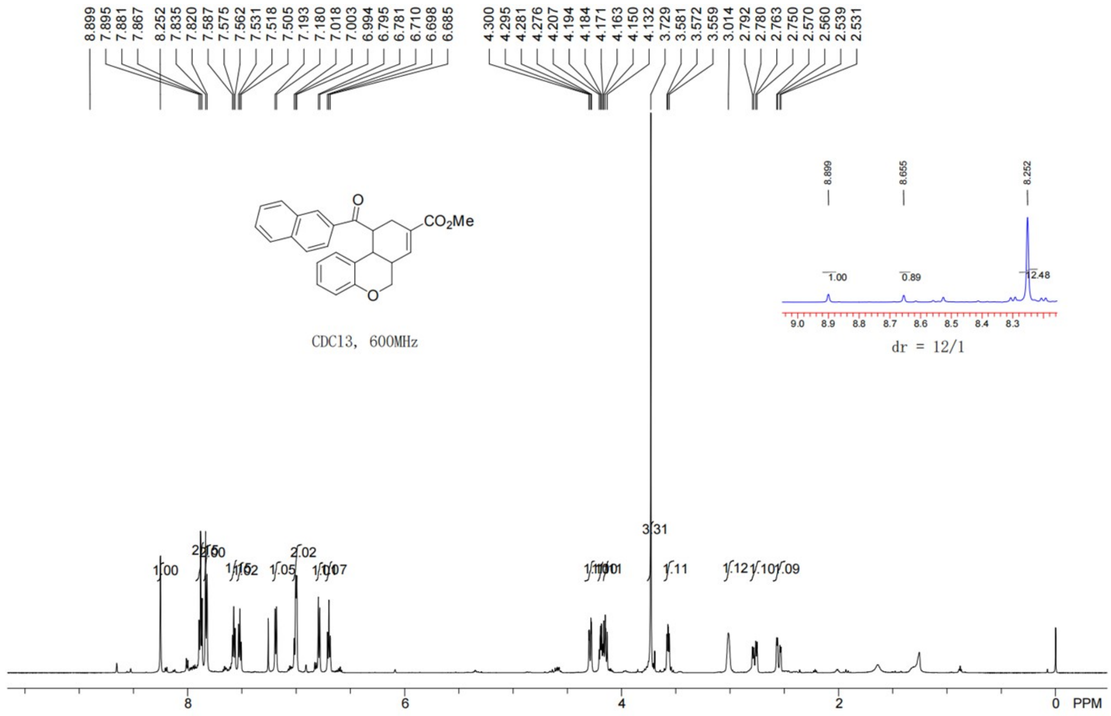


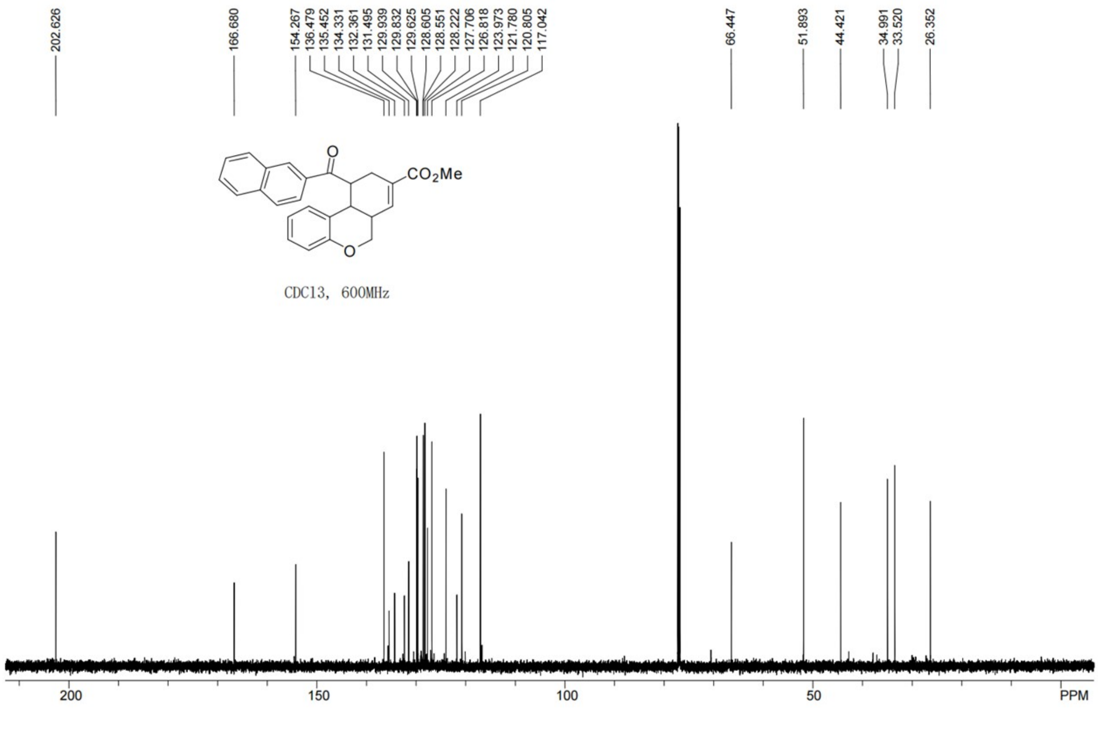
(6a*R,10*S**,10a*S**)-methyl -10-(1-naphthoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5h)**



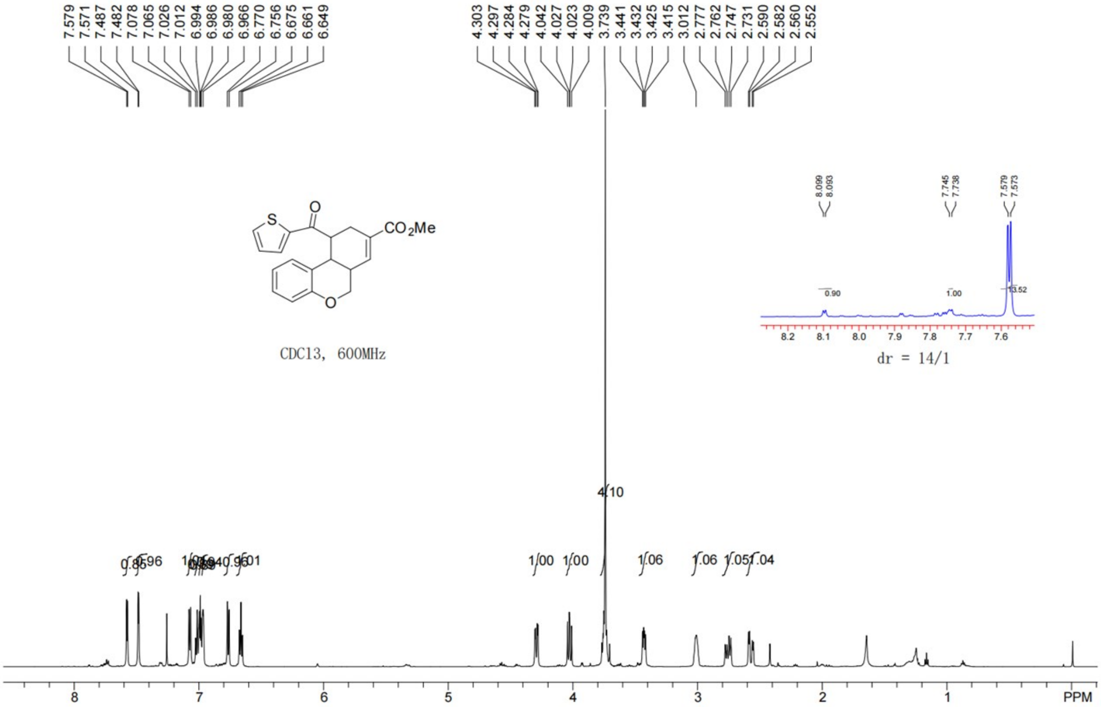


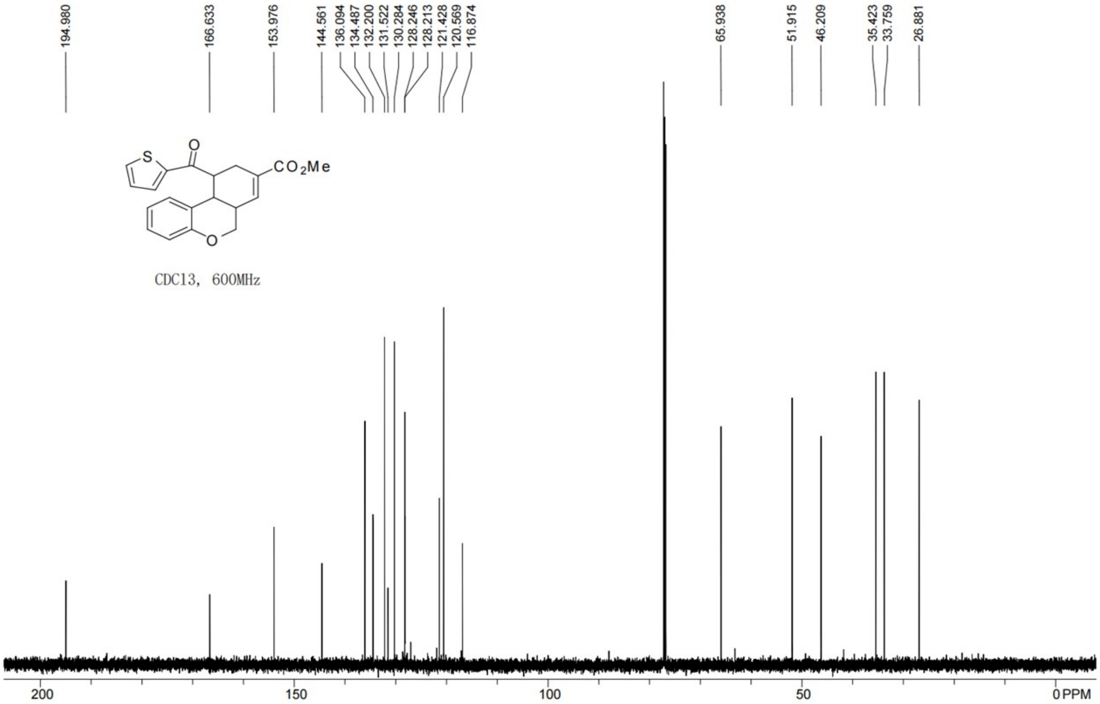
(6a*R,10*S**,10a*S**)-methyl -10-(2-naphthoyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5i)**



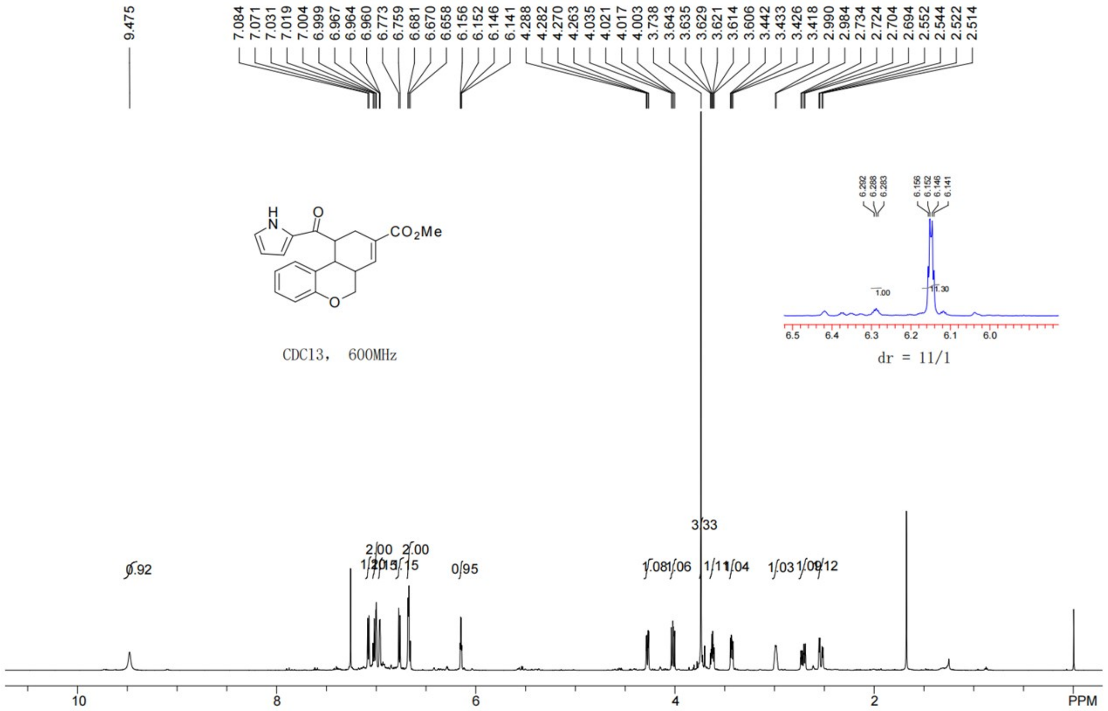


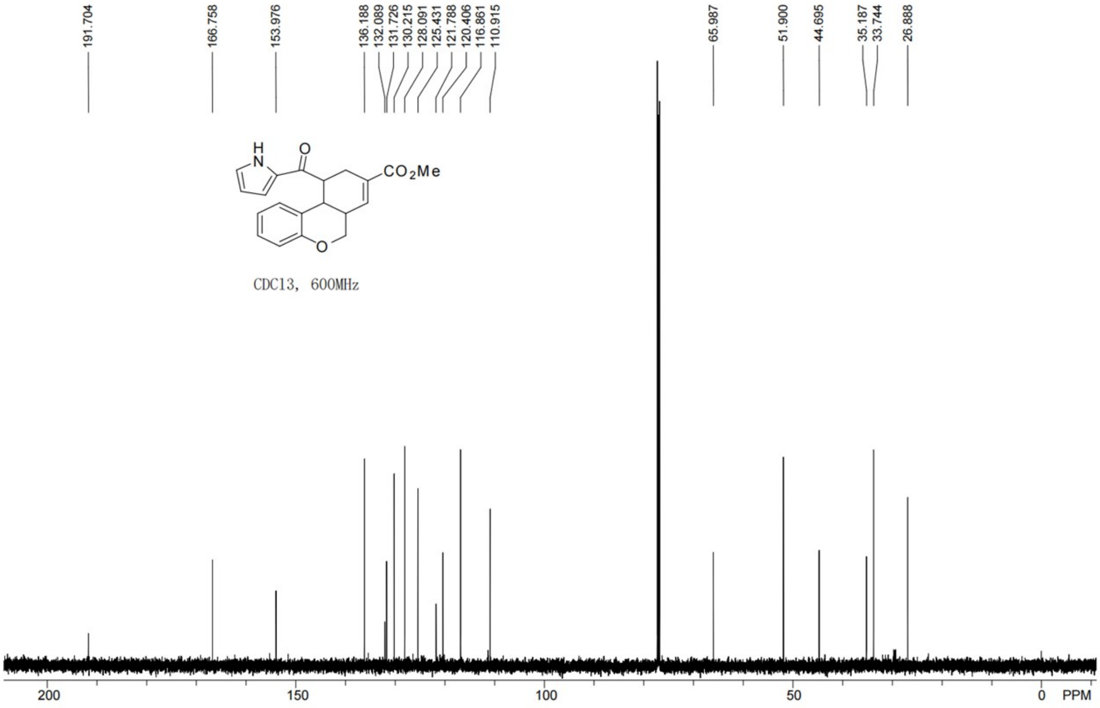
(6a*R,10*S**,10a*S**)-methyl -10-(thiophene-2-carbonyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5j)**



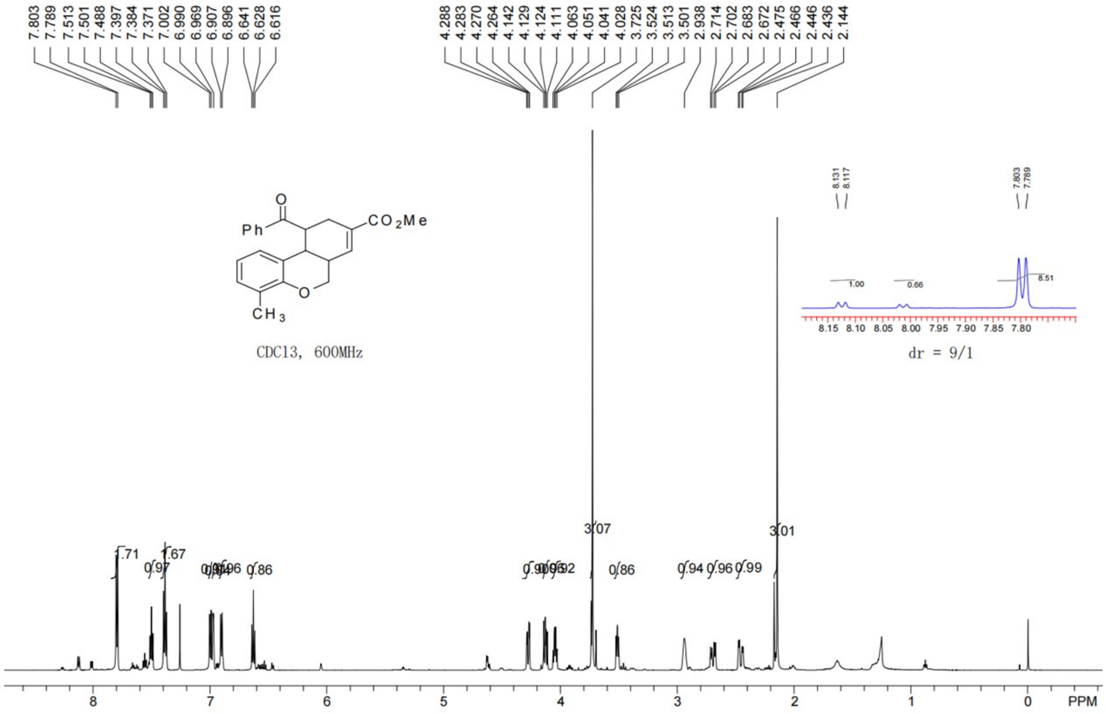


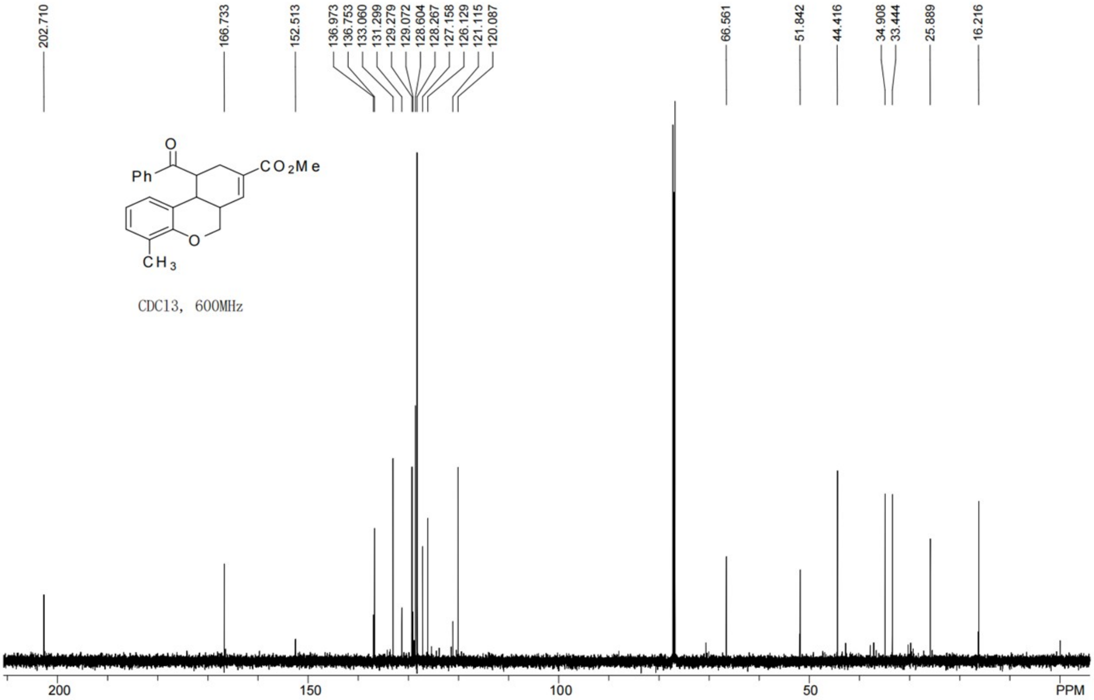
(6a*R**,10*S**,10a*S**)-methyl-10-(1*H*-pyrrole-2-carbonyl)-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5k)



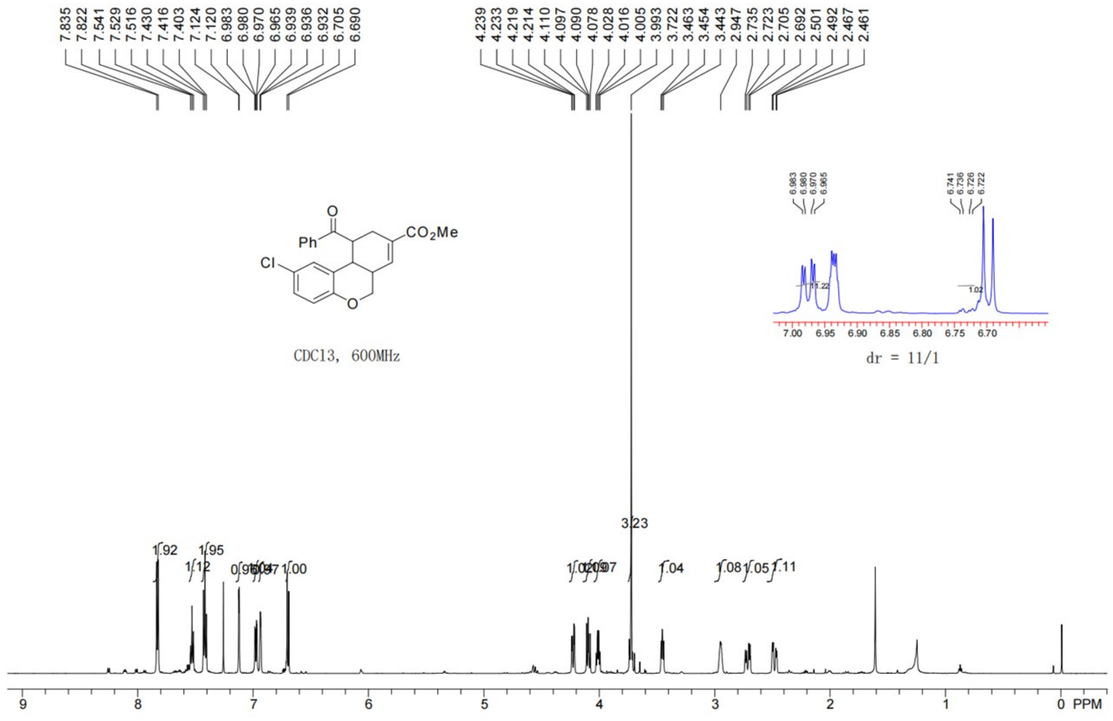


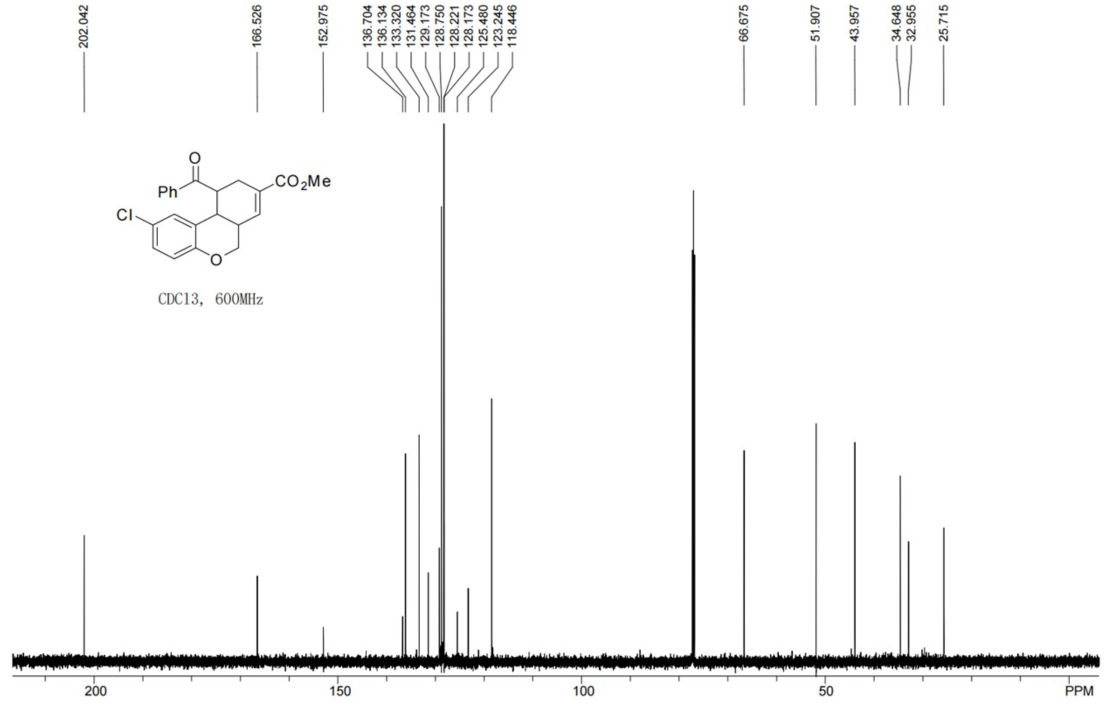
(6a*R,10*S**,10a*S**)-methyl -10-benzoyl-4-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5l)**



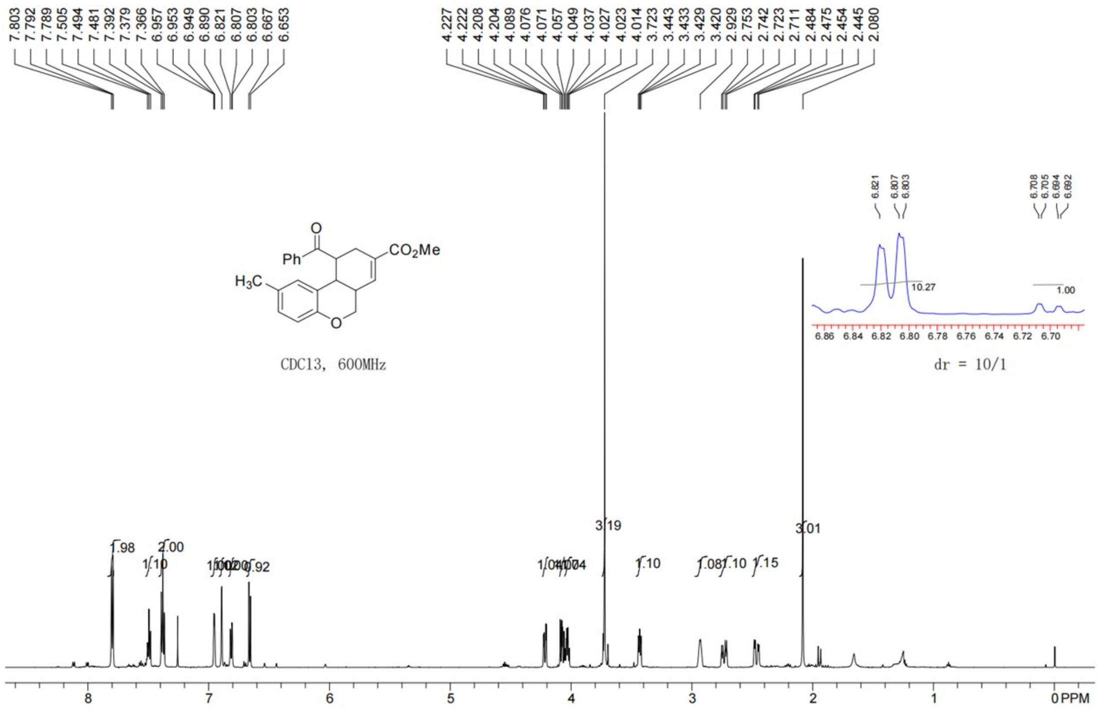


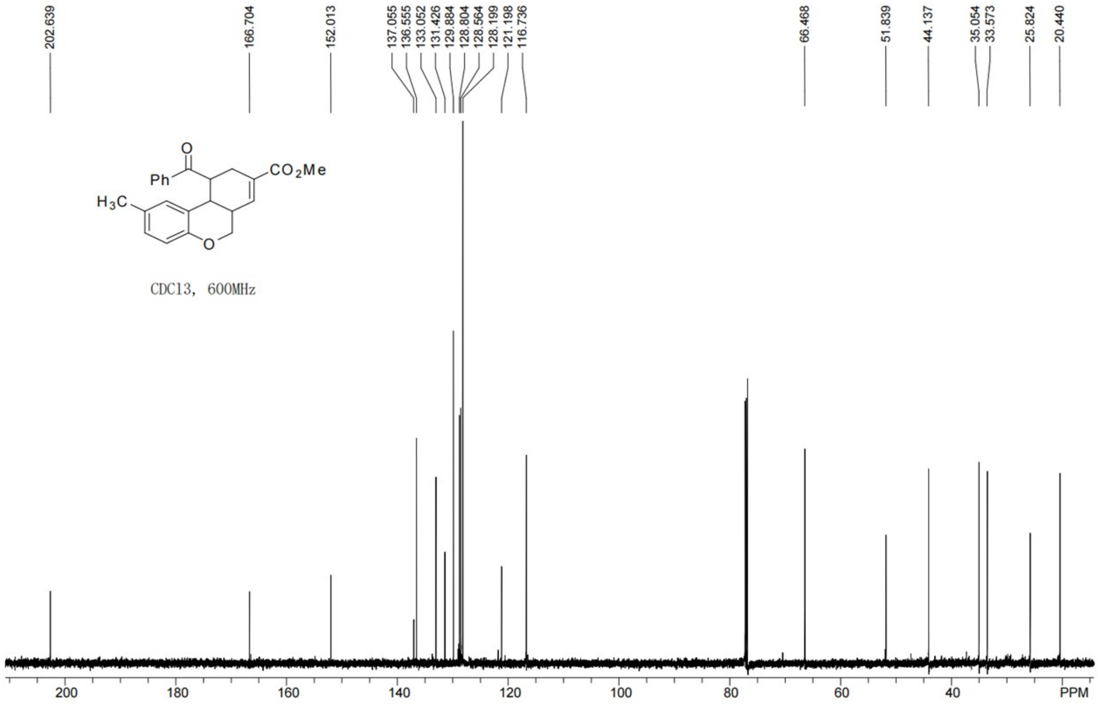
(6a*R**,10*S**,10a*S**)-methyl -10-benzoyl-2-chloro-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5m)



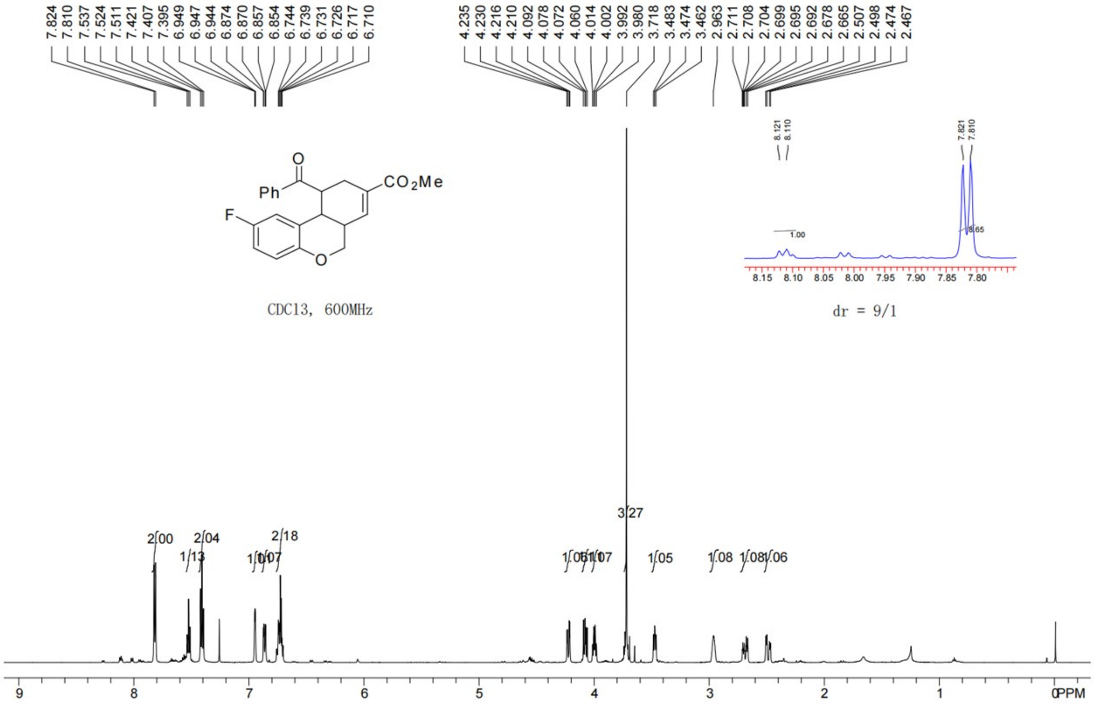


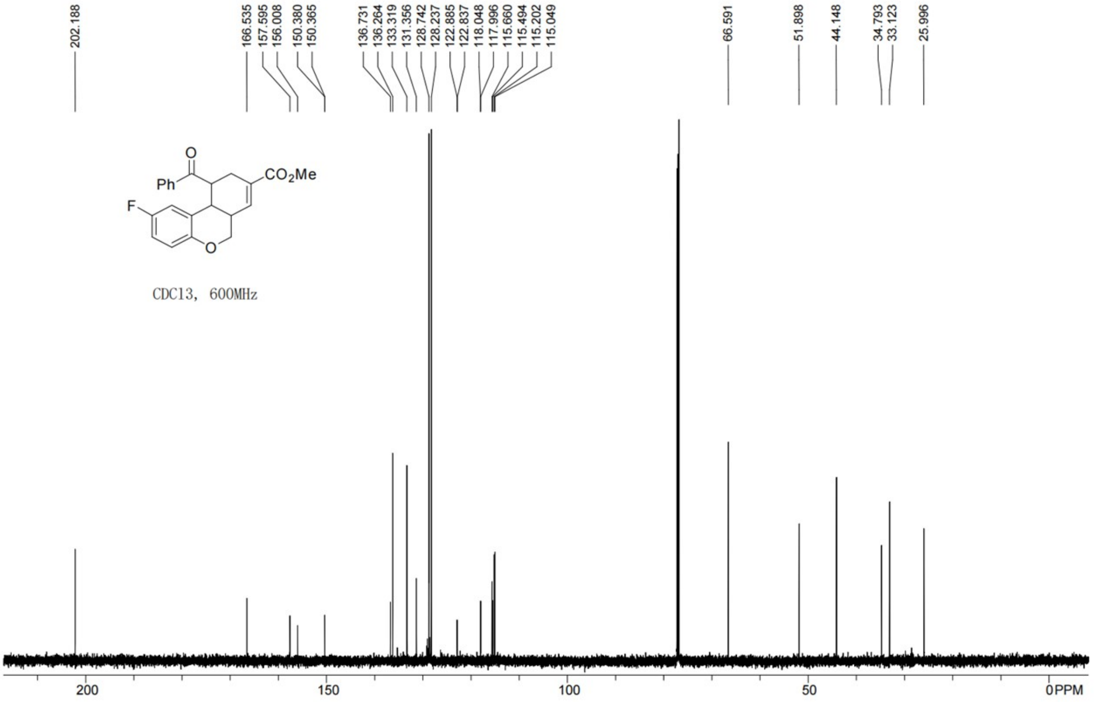
(6a*R,10*S**,10a*S**)-methyl -10-benzoyl-2-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5n)**



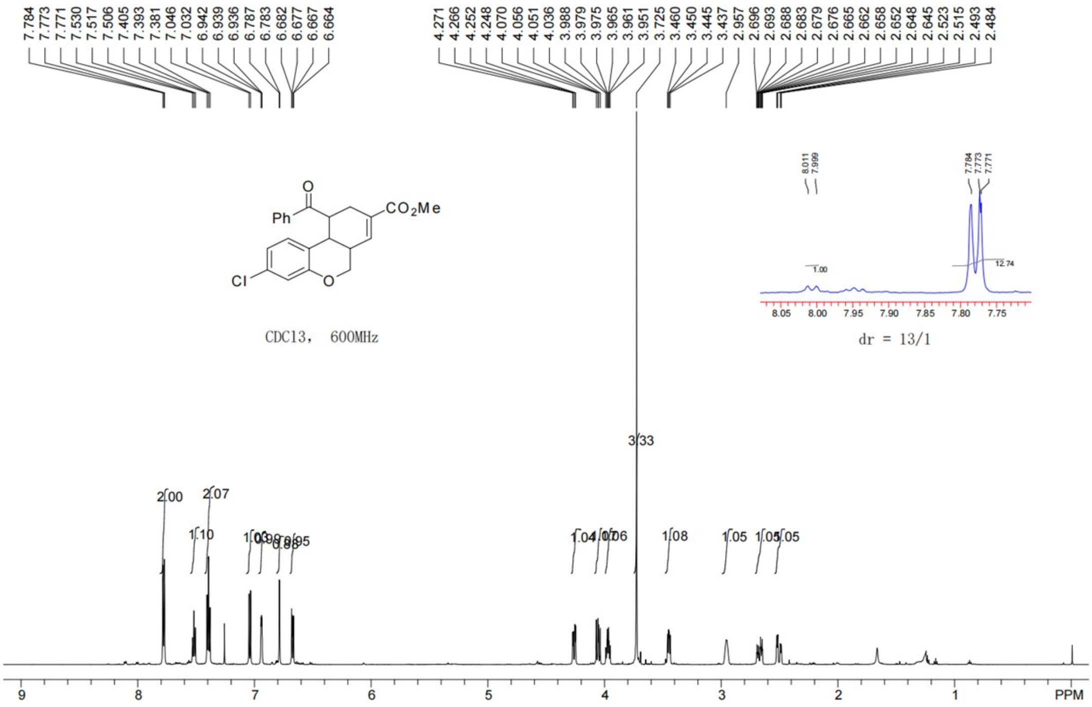


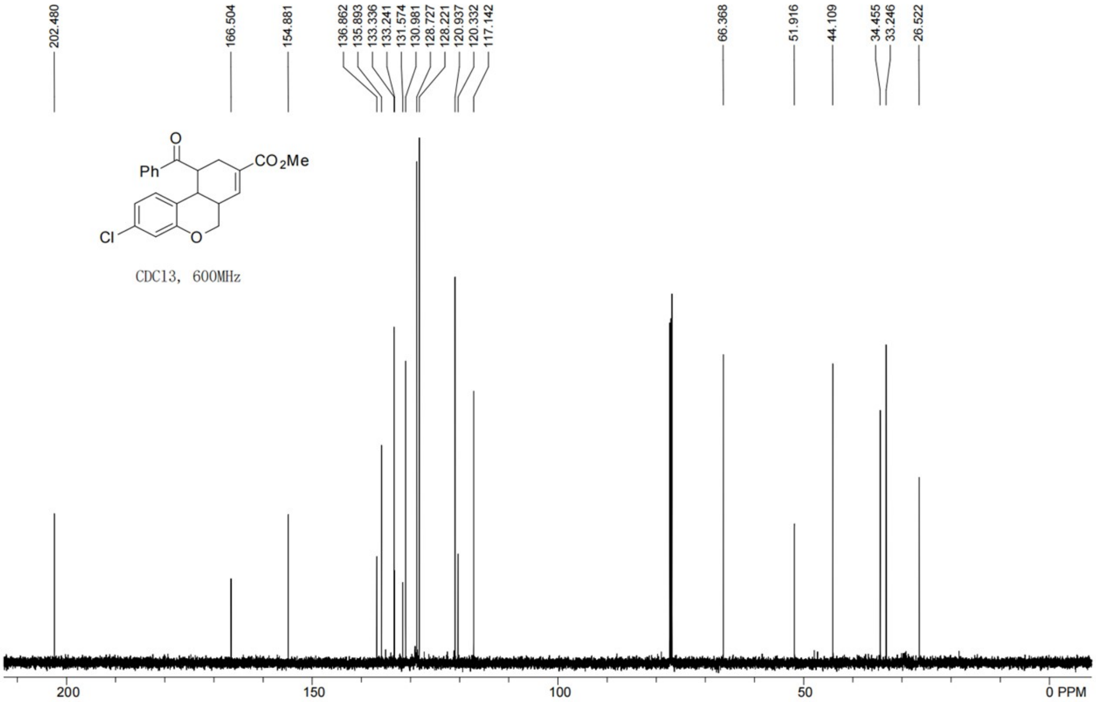
(6aR*,10S*,10aS*)-methyl -10-benzoyl-2-fluoro-6a,9,10,10a-tetrahydro-6H-benzo[c]chromene-7-carboxylate (5o)



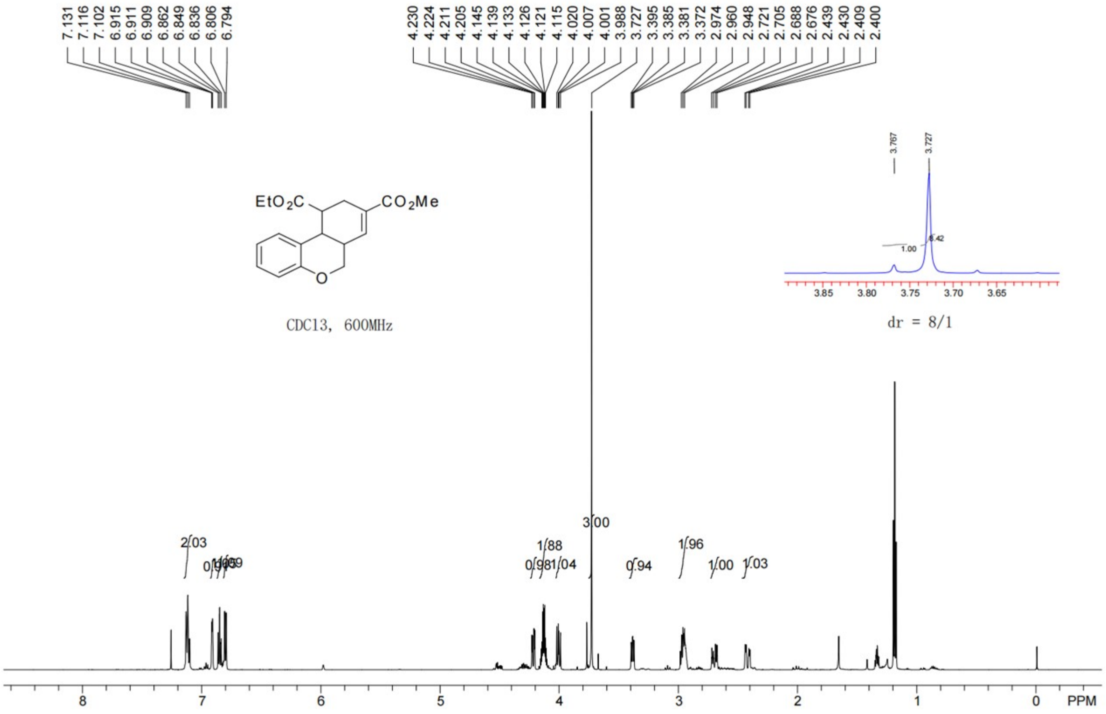


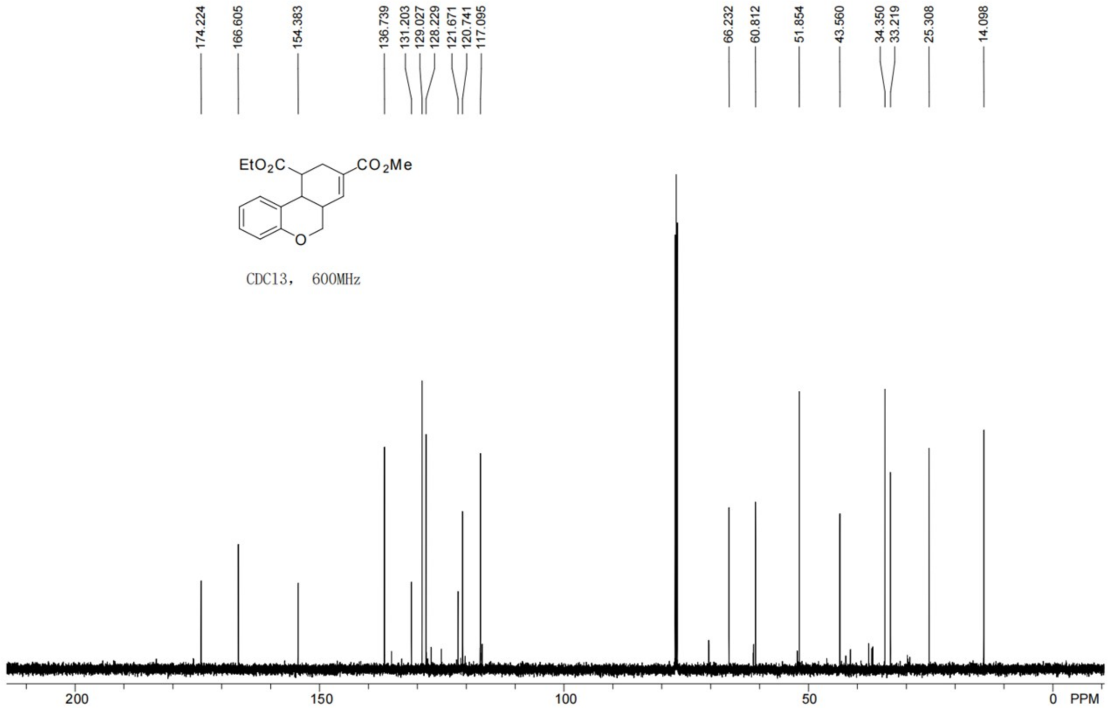
(6a*R,10*S**,10a*S**)-methyl -10-benzoyl-3-chloro-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7-carboxylate (5p)**





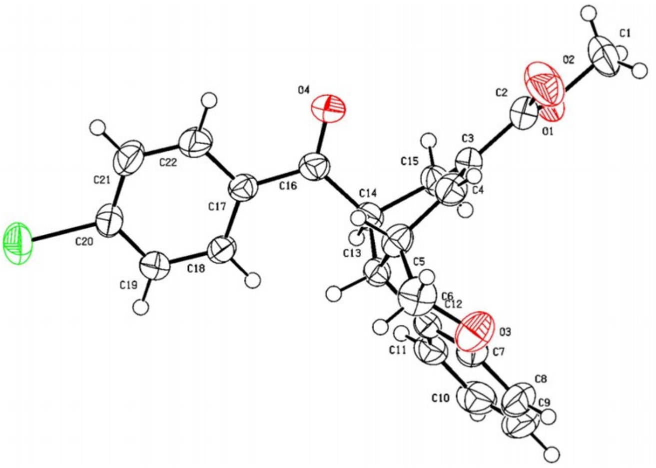
(6a*R**,10*S**,10a*S**)-10-ethyl-7-methyl-6a,9,10,10a-tetrahydro-6*H*-benzo[c]chromene-7,10-dicarboxylate (5q)

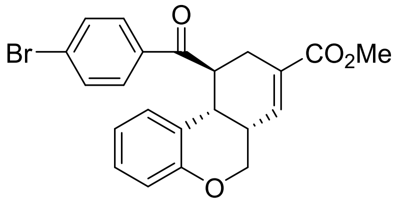




X-ray crystal structure for methyl 10-(4-bromobenzoyl)-6a,9,10,10a-tetrahydro-6H-benzo[c]chromene-8-carboxylate (5d)

$C_{22}H_{19}BrO_4$, MW = 427.28, Space group P b c a, Hall group -P 2ac 2ab, Cell a = 11.7751(17) Å, b = 15.553(2) Å, c = 20.306(3) Å, α = 90°, β = 90°, γ = 90°, V = 3718.9(9) Å^3, R (reflections) = 0.0408 (3090), wR2 (reflections) = 0.1123 (4351), T = 293 K, Z = 8, Mu (mm-1) = 2.236, F000 = 1744.0, h k lmax = 15 20 26, Nref = 4351, Tmin = 0.449, Tmax = 0.746, Data completeness = 0.997, Theta (max) = 27.703, S = 1.028, Npar = 246. Further information is contained in the CIF file.





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