Supporting Information

N-Heterocyclic Carbene-Catalyzed Desymmetrization of Functionalized 1,4-Dienes via Stetter Reaction

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I. General Information.

Commercially available materials purchased from Alfa Aesar or Aldrich or Ouhe were used as received. Unless otherwise indicated, all reactions were carried out under argon atmosphere. Anhydrous THF and toluene were distilled from sodium and benzophenone, CH_2Cl_2, DMSO and DMF were distilled from CaH_2. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Ascend 400 (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Exactive Plus LC-MS spectrometer (Thermo Fisher Scientific). The determination of

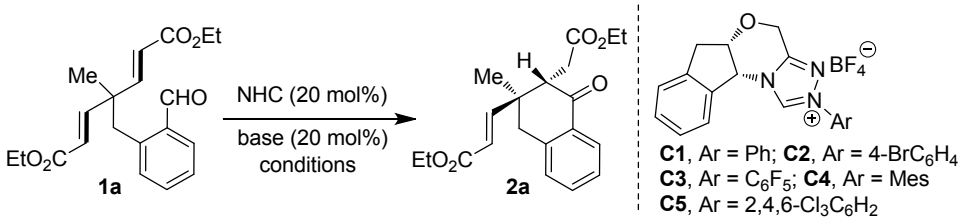
ee was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on SuperNova Rigaku Oxford X-ray diffraction meter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Starna scientific polarimeter (SGW-1) and are reported as follows: $[\alpha]^{rt}_D$ (*c* in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or potassium permanganate stain.

II. General procedures for 1,4-diloefin desymmetric reactions.

To a 10 mL Schlenk tube was added base (0.02 mmol), triazolium salt (0.02 mmol) and stirring bar. The flask was then evacuated and refilled with dry argon. The reaction mixture was then cooled to -25 °C. Anhydrous solvent (1 mL) was added. The mixture was stirred at -25 °C for 20 min. The diolefin (0.10 mmol) in solvent (1 mL) was added and the mixture was stirred for another 6 h. Then the mixture was quenched with saturated NH_4Cl aqueous, and extracted with ethyl acetate (2 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and filtered. The solvents were removed under reduced pressure, and the residue was purified via column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the product. Racemic products were synthesized via similar procedure using achiral precatalyst.

III. Reaction condition optimization.

1. Substrates with aromatic aldehyde groups



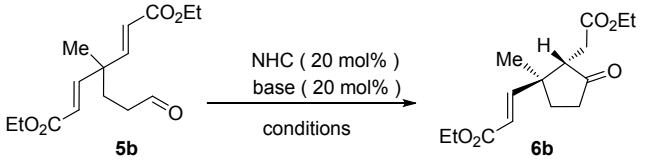
Entry[a]	NHC	Base	Solvent	T (°C)	Additive (mol %)	yield (%)	d.r.[b]	*ee*[c] (%)
1	**C1**	KHMDS	toluene	rt	-	0	-	-
2	**C2**	KHMDS	toluene	rt	-	0	-	-
3	**C3**	KHMDS	toluene	rt	-	65	4.2:1	87
4	**C4**	KHMDS	toluene	rt	-	49	5.2:1	99
5	**C5**	KHMDS	toluene	rt	-	93	4.3:1	99
6	**C5**	KO^{t}Bu	toluene	rt	-	100	4.5:1	99
7	**C5**	KOAc	toluene	rt	-	90	4.2:1	98
8	**C5**	K_2CO_3	toluene	rt	-	87	4.3:1	97
9	**C5**	KOH	toluene	rt	-	73	4.5:1	98
10	**C5**	NaOAc	toluene	rt	-	87	4.2:1	99

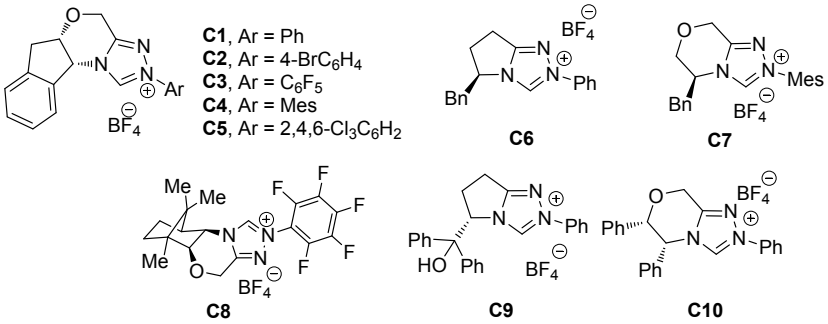
11	**C5**	Cs_2CO_3	toluene	rt	-	67	4.3:1	98
12	**C5**	NEt_3	toluene	rt	-	81	4.3:1	98
13	**C5**	DBU	toluene	rt	-	75	4.3:1	99
14	**C5**	$^{i}Pr_2NEt$	toluene	rt	-	23	4.2:1	98
15	**C5**	NaO^{t}Bu	toluene	rt	-	90	4.3:1	98
16	**C5**	LiO^{t}Bu	toluene	rt	-	15	3.0:1	98
17	**C5**	KO^{t}Bu	CH_2Cl_2	rt	-	100	3.6:1	99
18	**C5**	KO^{t}Bu	DCE	rt	-	99	3.8:1	99
19	**C5**	KO^{t}Bu	MeCN	rt	-	66	3.0:1	98
20	**C5**	KO^{t}Bu	THF	rt	-	100	4.4:1	98
21	**C5**	KO^{t}Bu	benzene	rt	-	100	3.7:1	98
22	**C5**	KO^{t}Bu	MeOH	rt	-	84	3.3:1	82
23	**C5**	KO^{t}Bu	1,4-dioxane	rt	-	100	4.2:1	98
24	**C5**	KO^{t}Bu	Et_2O	rt	-	100	4.2:1	99
25	**C5**	KO^{t}Bu	DMF	rt	-	71	3.2:1	93
26	**C5**	KO^{t}Bu	Mesitylene	rt	-	99	3.9:1	98
27	**C5**	KO^{t}Bu	TBME	rt	-	99.6	4.1:1	97
28	**C5**	KO^{t}Bu	Xylene	rt	-	98	4.1:1	98
29	**C5**	KO^{t}Bu	toluene	rt	$Ti(O^{i}Pr)_4$ (20)	97	4.3:1	98
30	**C5**	KO^{t}Bu	toluene	rt	LiCl (20]	96	4.3:1	98
31	**C5**	KO^{t}Bu	toluene	rt	$Mg(OTf)_2$ (20)	trace	-	-
32	**C5**	KO^{t}Bu	toluene	rt	HOAc (20)	100	4.1:1	97
33	**C5**	KO^{t}Bu	toluene	rt	$ZnCl_2$ (20)	trace	-	-
34	**C5**	KO^{t}Bu	toluene	rt	$SnCl_2$ (20)	54	4.0:1	96
35	**C5**	KO^{t}Bu	toluene	rt	$Mg(ClO_4)_2$ (20)	24	3.6:1	89
36	**C5**	NaOAc	toluene	rt	HOAc (20)	92	4.2:1	95
37	**C5**	NaOAc	toluene	rt	Picolinic acid (20)	0	-	-
38	**C5**	NaOAc	toluene	rt	L-Phenylalanine (20)	28	3.0:1	-
39	**C5**	NaOAc	toluene	rt	Citric acid monohydrate (20)	0	-	-
40	**C5**	KO^{t}Bu	toluene	rt	KCl (100)	84	4.1:1	98
41	**C5**	NaOAc	toluene	rt	Salicylic acid (100)	0	-	-
42	**C5**	NaOAc	toluene	rt	Picolinic acid (100)	22	2.7:1	-
43	**C5**	NaOAc	toluene	rt	L-Phenylalanine (100)	53	4.0:1	-
44	**C5**	NaOAc	toluene	rt	Citric acid monohydrate (100)	0	-	-

45	**C5**	KO^{t}Bu	toluene	0	-	100	5.7:1	99
46	**C5**	KO^{t}Bu	toluene	-20	-	90	6.7:1	99
47	**C5**	**KO^{t}Bu**	**toluene**	**-25**	**-**	**99**	**7.2:1**	**99**

[a] **1a** (0.1 mmol), 6 h. [b] Determined by ^{1}H NMR analysis of unpurified reaction mixtures. [c] Major diasteromer, determined by chiral-phase HPLC.

2. Substrate with aliphatic aldehyde group





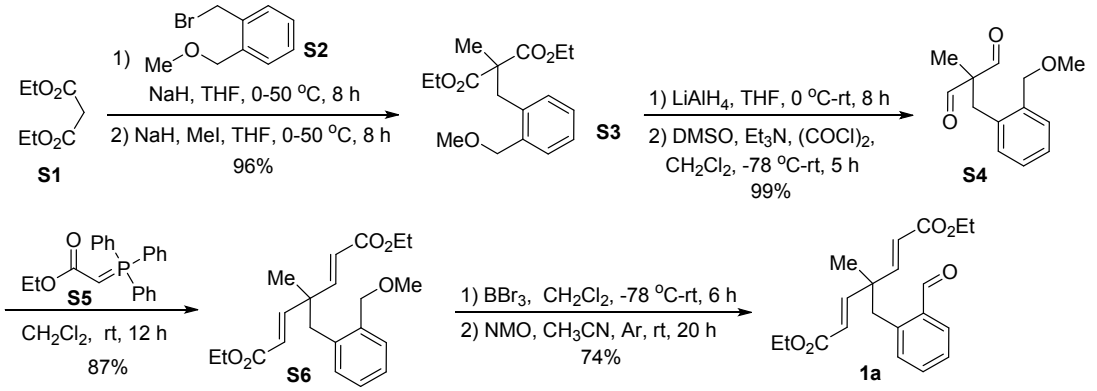
Entry[a]	NHC	Base	Solvent	Temp./time	Yield (%)	d.r.[b]	*ee*[c] (%)
1	**C1**	KO^{t}Bu	toluene	-25 ^{o}C/8 h; 25 ^{o}C/10 h	0	-	-
2	**C2**	KO^{t}Bu	toluene	-25 ^{o}C/12 h; 25 ^{o}C/12 h	0	-	-
3	**C3**	KO^{t}Bu	toluene	-25 ^{o}C/8 h; 25 ^{o}C/10 h; 70 ^{o}C/8 h	80	3.3:1	7
4	**C4**	KO^{t}Bu	toluene	-25 ^{o}C/12 h; 25 ^{o}C/6 h	71	4.7:1	19.0
5	**C5**	KO^{t}Bu	toluene	-25 ^{o}C/6 h	99	2.3:1	23.0
6	**C5**	KO^{t}Bu	THF	-25 ^{o}C/12 h	99	3.0:1	29.0
7	**C5**	KHMDS	THF	-25 ^{o}C/12 h; 25 ^{o}C/6 h	74	2.8:1	23.0
8	**C6**	KO^{t}Bu	toluene	-25 ^{o}C/12 h; 50 ^{o}C/12 h	64	36:1	31.0
9	**C6**	KHMDS	toluene	-25 ^{o}C/12 h; 50 ^{o}C/12 h	92	2.4:1	23.0
10	**C6**	KHMDS	toluene	25 ^{o}C/24 h	64	2.7:1	27.0
11	**C6**	KO^{t}Bu	toluene	25 ^{o}C/24 h	64	3.3:1	25.0
12	**C7**	**KO^{t}Bu**	**toluene**	**-25 ^{o}C/12 h; 25 ^{o}C/6 h**	**84**	**4.5:1**	**32.0**
13	**C8**	KO^{t}Bu	toluene	-25 ^{o}C/8 h; 25 ^{o}C/6 h; 70 ^{o}C/24 h	0	-	-
14	**C9**	KO^{t}Bu	toluene	-25 ^{o}C/8 h; 25 ^{o}C/6 h; 70 ^{o}C/10 h	80	2.0:1	22.0
15	**C10**	KO^{t}Bu	toluene	-25 ^{o}C/8 h; 25 ^{o}C/6 h; 70 ^{o}C/24 h	81	1.9:1	38.0

[a] **5b** (0.1 mmol). [b] Determined by ^{1}H NMR analysis of unpurified reaction mixtures. [c] Major diasteromer,

determined by chiral-phase HPLC.

IV. Procedures for substrates preparation

1. 1,4-diolefin with ester substitutent (**1a** as example)



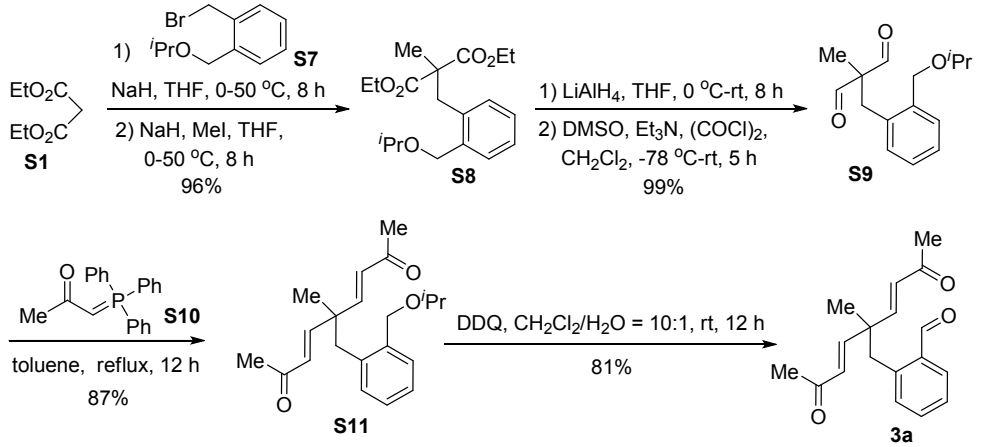
To a 200 mL flame dried round bottom flask charged with **S1** (5.9102 g, 0.0369 mol) and dry THF (90 ml) at 0 °C was added NaH (0.8856 g, 0.0369 mol) under argon. **S2** (6.6140 g, 0.0308 mol) in THF (15 mL) was added to the mixture after 1 h and the reaction was stirred at 50 °C for 8 h. Saturated NH_4Cl solution (25 mL) was added to quench the reaction. The mixture was washed with brine, dried over $MgSO_4$, concentrated in vacuum and was purified by flash column chromatography with petroleum ether/ethyl acetate (v/v = 10:1) to afford the yellow liquid product diethyl 2-(2-(methoxymethyl)benzyl)malonate (9.0511 g, 100% yield). To a solution of diethyl 2-(2-(methoxymethyl)benzyl)malonate (9.0511 g, 0.0308 mol) in THF (200 mL) was added NaH (0.8856 g, 1.2 eq) at 0 °C under argon. MeI (2.30 mL, 1.2 eq) was added to the mixture after 1 h and the reaction was stirred at 50 °C for 8 h. Saturated NH_4Cl solution (25 mL) was added to quench the reaction. The mixture was washed with brine, dried over $MgSO_4$, concentrated in vacuum and was purified by flash column chromatography with petroleum ether/ethyl acetate (v/v = 10:1) to afford yellow liquid product **S3** (9.0969 g, 96% yield).

To a suspension of $LiAlH_4$ (8.9572 g, 0.2360 mol) in THF (200 mL) at 0 °C was added a solution of **S3** (9.0969 g, 0.0295 mol) in THF (20 mL) dropwise under argon. The reaction mixture was stirred overnight at room temperature and quenched sequentially by adding H_2O (9 mL), 10% aqueous NaOH (18 mL), and then H_2O (27 mL) at 0 °C with caution. The mixture was stirred for another 1 h and then the white precipitate was filtrated off and the two layers were separated. The organic layer was washed with brine, dried over $MgSO_4$, concentrated in vacuum to afford the crude product 2-(2-(methoxymethyl)benzyl)-2-methylpropane-1,3-diol as a yellow oil (6.6168 g, 100% yield). A solution of dry DMSO (9.22 mL, 0.1298 mol) in dry CH_2Cl_2 (20 mL) was added dropwise at -78 °C to oxalyl chloride (8.18 mL, 0.0649 mol) in dry CH_2Cl_2 (300 mL). After stirring for 30 min at this temperature, 2-(2-(methoxymethyl)benzyl)-2-methylpropane-1,3-diol (6.6168 g, 0.0295 mol) in dry CH_2Cl_2 (40 mL) was added dropwise at a temperature of -78 to -70 °C. After stirring

for 90 min at -65 °C, the mixture was cooled to -78 °C again, Et_3N (28.74 mL, 0.2065 mol) was added slowly and the mixture was stirred for 30 min at this temperature. The reaction mixture was allowed to warm to room temperature over the course of 1 h. The reaction was terminated by addition of saturated NH_4Cl solution (25 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with 2M HCl and brine. The solution was dried over $MgSO_4$, concentrated in vacuum to afford the crude product **S4** as a yellow oil (6.4978 g, 100% yield).

The mixture of **S4 (**6.4978 g, 0.0295 mol**)** and **S5** (22.6095 g, 2.2 eq) in CH_2Cl_2 (200 mL) was stirred overnight at room temperature under argon. The mixture was concentrated and the residue was purified via silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 5:1) to afford product **S6** as a yellow oil (9.2454 g, 87% yield). A solution of **S6** (9.2454 g, 0.0257 mol) in 300 mL of CH_2Cl_2 cooled to -78 °C was treated with BBr_3 (24.31 mL, 10 eq) under argon. After 30 min the reaction was warmed to -12 °C and stirring was continued for 4 h. The reaction was quenched at -12 °C by addition of ether, warmed to room temperature and was stirred an additional 30 min followed by addition of water. The mixture was washed with brine, dried over $MgSO_4$, concentrated in vacuum and the residue was purified by flash column chromatography with petroleum ether/ethyl acetate (v/v = 10:1) to afford (2*E*,5*E*)-diethyl 4-(2-(hydroxymethyl)benzyl)-4-methylhepta-2,5-dienedioate as a yellow oil (8.8856 g, 100% yield). The mixture of (2*E*,5*E*)-diethyl 4-(2-(hydroxymethyl)benzyl)-4-methylhepta-2,5-dienedioate **(**8.8856 g, 0.0257 mol**)** and 4-Methylmorpholine N-oxide (NMO) (12.0196 g, 4 eq) in CH_3CN (300 mL) was stirred for 20 hours at room temperature under argon. The solvent was removed and the resulting residue was extracted with water and brine and the residue was purified via silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 5:1) to afford **1a** as a yellow oil (6.5371 g, 74% yield).

2. 1,4-diolefin with ketone substitutent (**3a** as example)



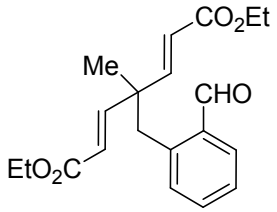
To a 200 mL flame dried round bottom flask charged with **S1** (5.3977 g, 0.0337 mol) and dry THF (90 ml) at 0 °C was added NaH (0.8088 g, 0.0337 mol) under argon. **S7** (6.8323 g, 0.0281 mol) in THF (15 mL) was added to the mixture after 1 h and the reaction was stirred at 50 °C for 8 h. Saturated NH_4Cl solution (25 mL) was added to

quench the reaction. The mixture was washed with brine, dried over $MgSO_4$, concentrated in vacuum and was purified by flash column chromatography with petroleum ether/ethyl acetate (v/v = 10:1) to afford the yellow liquid product diethyl 2-(2-(isopropoxymethyl)benzyl)malonate (9.0594 g, 100% yield). To a solution of diethyl 2-(2-(isopropoxymethyl)benzyl)malonate (9.0594 g, 0.0281 mol) in THF (200 mL) was added NaH (0.8088 g, 1.2 eq) at 0 ^oC under argon. MeI (2.10 mL, 1.2 eq) was added to the mixture after 1 h and the reaction was stirred at 50 ^oC for 8 h. Saturated NH_4Cl solution (25 mL) was added to quench the reaction. The mixture was washed with brine, dried over $MgSO_4$, concentrated in vacuum and was purified by flash column chromatography with petroleum ether/ethyl acetate (v/v = 10:1) to afford the yellow liquid product **S8** (9.0834 g, 96% yield).

To a suspension of $LiAlH_4$ (8.1982 g, 0.2160 mol) in THF (200 mL) at 0 ^oC was added a solution of **S8** (9.0834 g, 0.0270 mol) in THF (20 mL) dropwise under argon. The reaction mixture was stirred overnight at room temperature and quenched sequentially by adding H_2O (9 mL), 10% aqueous NaOH (18 mL), and then H_2O (27 mL) at 0 ^oC with caution. The mixture was stirred for another 1 h and then the white precipitate was filtrated off and the two layers were separated. The organic layer was washed with brine, dried over $MgSO_4$, concentrated in vacuum to afford the crude product 2-(2-(isopropoxymethyl)benzyl)-2-methylpropane-1,3-diol as a yellow oil (6.8135 g, 100% yield). A solution of dry DMSO (8.44 mL, 0.1188 mol) in dry CH_2Cl_2 (18 mL) was added dropwise at -78 ^oC to oxalyl chloride (7.49 mL, 0.0594 mol) in dry CH_2Cl_2 (300 mL). After stirring for 30 min at this temperature, 2-(2-(isopropoxymethyl)benzyl)-2-methylpropane-1,3-diol (6.8135 g, 0.0270 mol) in dry CH_2Cl_2 (36 mL) was added dropwise at a temperature of -78 to -70 ^oC. After stirring for 90 min at -65 ^oC, the mixture was cooled to -78 ^oC again, Et_3N (28.94 mL, 0.2079 mol) was added slowly and the mixture was stirred for 30 min at this temperature. The reaction mixture was allowed to warm to room temperature over the course of 1 h. The reaction was terminated by addition of saturated NH_4Cl solution (25 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with 2M HCl and brine. The solution was dried over $MgSO_4$, concentrated in vacuum to afford the crude product **S9** as a yellow oil (6.7046 g, 100% yield).

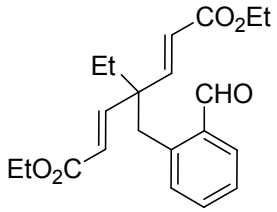
A mixture of **S9 (**6.7046 g, 0.0270 mol**)** and **S10** (18.9095 g, 2.2 eq) in toluene (150 mL) was refluxed overnight under argon. The mixture was concentrated and the residue was purified via silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 5:1) to afford product **S11** as a yellow oil (7.7185 g, 87% yield). The mixture of **S11 (**7.7185 g, 0.0235 mol**)** and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (10.6690 g, 2 eq) in CH_2Cl_2 (200 mL) and H_2O (20 mL) was stirred for 20 h at room temperature. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with water and brine and the residue was purified via silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 5:1) to afford **3a** as a yellow oil (5.4126 g, 81% yield).

V. Characterizations of new compounds.



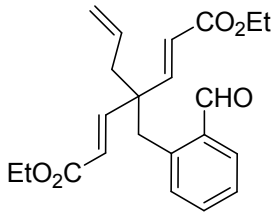
1a

(2*E*,5*E*)-diethyl 4-(2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.52-7.42 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 16.0 Hz, 2H), 5.70 (d, *J* = 16.0 Hz, 2H), 4.19 (q, *J* = 8.0 Hz, 4H), 3.42 (s, 2H), 1.28 (t, *J* = 8.0 Hz, 6H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 166.2, 151.9, 138.1, 135.0, 133.2, 133.1, 133.0, 127.6, 120.6, 60.5, 44.1, 41.1, 21.8, 14.2; HRMS (ESI, m/z): calcd. for $C_{20}H_{24}O_5H^+$ 345.1697, found 345.1690.



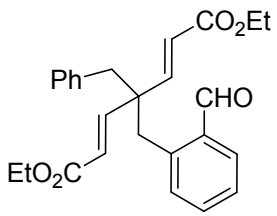
1b

(2*E*,5*E*)-diethyl 4-ethyl-4-(2-formylbenzyl)hepta-2,5-dienedioate (1b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.51-7.41 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 2H), 5.70 (d, *J* = 16.0 Hz, 2H), 4.19 (q, *J* = 8.0 Hz, 4H), 3.43 (s, 2H), 1.70 (q, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 8.0 Hz, 6H), 0.89 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 166.1, 150.7, 138.2, 135.1, 133.0, 132.8, 127.5, 122.0, 60.5, 47.6, 40.0, 29.3, 14.2, 8.9; HRMS (ESI, m/z): calcd. for $C_{21}H_{26}O_5H^+$ 359.1853, found 359.1850.



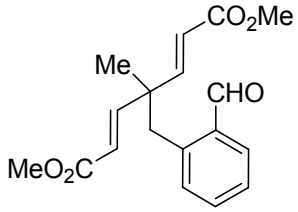
1c

(2*E*,5*E*)-diethyl 4-allyl-4-(2-formylbenzyl)hepta-2,5-dienedioate (1c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.52-7.43 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 2H), 5.75-5.71 (m, 3H), 5.17-5.12 (m, 2H), 4.19 (q, *J* = 6.0 Hz, 4H), 3.46 (s, 2H), 2.45 (d, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 164.9, 149.4, 137.0, 134.0, 132.1, 132.04, 132.02, 131.7, 126.6, 121.0, 118.4, 59.5, 45.7, 40.1, 38.6, 13.2; HRMS (ESI, m/z): calcd. for $C_{22}H_{26}O_5H^+$ 371.1853, found 371.1851.



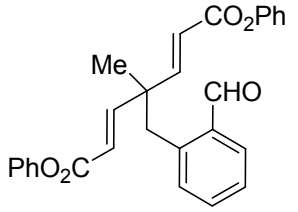
1d

(2*E*,5*E*)-diethyl 4-benzyl-4-(2-formylbenzyl)hepta-2,5-dienedioate (1d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (d, *J* = 2.8 Hz, 1H), 7.81-7.78 (m, 1H), 7.45-7.37 (m, 2H), 7.25-7.20 (m, 3H), 7.15-7.11 (m, 3H), 6.94 (dd, *J* = 2.0, 16.0 Hz, 2H), 5.73 (dd, *J* = 2.0, 16.0 Hz, 2H), 4.19-4.12 (m, 4H), 3.50 (d, *J* = 2.8 Hz, 2H), 3.01 (d, *J* = 2.8 Hz, 2H), 1.27-1.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 165.8, 150.8, 138.3, 135.7, 135.1, 133.2, 133.1, 132.8, 130.8, 128.2, 127.6, 126.9, 122.1, 60.5, 47.2, 45.4, 39.7, 14.2; HRMS (ESI, m/z): calcd. for $C_{26}H_{28}O_5H^+$ 421.2010, found 421.1997.



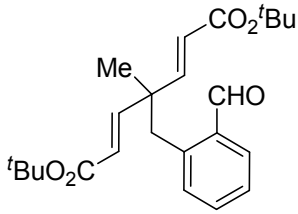
1e

(2*E*,5*E*)-dimethyl 4-(2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.53-7.43 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 2H), 5.69 (d, *J* = 16.0 Hz, 2H), 3.74 (s, 6H), 3.41 (s, 2H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 166.6, 152.2, 138.0, 135.0, 133.4, 133.2, 133.1, 127.6, 120.3, 51.7, 44.2, 41.1, 21.8; HRMS (ESI, m/z): calcd. for $C_{18}H_{20}O_5H^+$ 317.1389, found 317.1389.



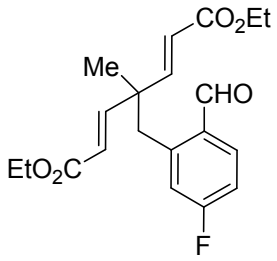
1f

(2*E*,5*E*)-diphenyl 4-(2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1f): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.58-7.37 (m, 6H), 7.25-7.12 (m, 9H), 5.94 (d, *J* = 16.0 Hz, 2H), 3.51 (s, 2H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 164.5, 153.8, 150.6, 137.8, 135.1, 133.7, 133.3, 133.2, 129.5, 127.9, 125.9, 121.6, 120.2, 44.7, 41.3, 21.8; HRMS (ESI, m/z): calcd. for $C_{28}H_{24}O_5Na^+$ 463.1516, found 463.1510.



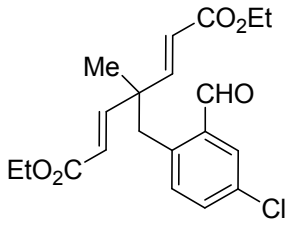
1g

(2*E*,5*E*)-di-tert-butyl 4-(2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1g): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.51-7.41 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 2H), 5.60 (d, *J* = 16.0 Hz, 2H), 3.37 (s, 2H), 1.48 (s, 18H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 165.5, 150.8, 138.4, 135.1, 133.3, 133.0, 132.4, 127.5, 122.2, 80.6, 43.8, 41.2, 28.1, 21.9; HRMS (ESI, m/z): calcd. for $C_{24}H_{32}O_5Na^+$ 423.2142, found 423.2137.



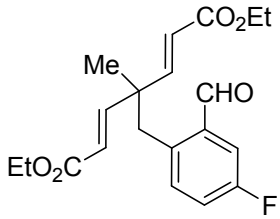
1h

(2*E*,5*E*)-diethyl 4-(5-fluoro-2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1h): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.48-7.45 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 2H), 5.70 (d, *J* = 16.0 Hz, 2H), 4.20 (q, *J* = 4.0 Hz, 4H), 3.35 (s, 2H), 1.29 (t, *J* = 8.0 Hz, 6H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 166.0, 151.4, 136.5, 136.2, 134.5, 133.9, 133.0, 132.0, 121.0, 60.6, 44.0, 40.6, 21.9, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 103.80; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}FO_5H^+$ 363.1602, found 363.1598.



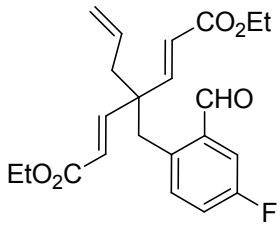
1i

(2*E*,5*E*)-diethyl 4-(4-chloro-2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1i): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.48-7.45 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 2H), 5.70 (d, *J* = 16.0 Hz, 2H), 4.22-4.17 (m, 4H), 3.35 (s, 2H), 1.29 (t, *J* = 8.0 Hz, 6H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 166.0, 151.3, 136.5, 136.2, 134.5, 133.9, 133.0, 132.0, 121.0, 60.6, 44.0, 40.6, 21.9, 14.2; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}ClO_5H^+$ 379.1307, found 379.1307.



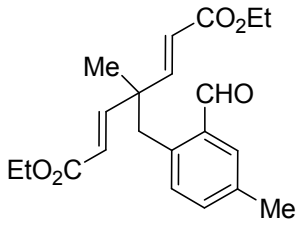
1j

(2*E*,5*E*)-diethyl 4-(4-fluoro-2-formylbenzyl)-4-methylhepta-2,5-dienedioate (1j): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (d, *J* = 4.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.24-7.14 (m, 2H), 6.96 (d, *J* = 16.0 Hz, 2H), 5.70 (d, *J* = 16.0 Hz, 2H), 4.22-4.17 (m, 4H), 3.34 (s, 2H), 1.29 (t, *J* = 8.0 Hz, 6H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 166.0, 161.9, 151.4, 136.5, 134.9, 134.0, 121.0, 120.3, 117.8, 60.6, 43.9, 40.5, 21.9, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 113.53; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}FO_5H^+$ 363.1602, found 363.1600.



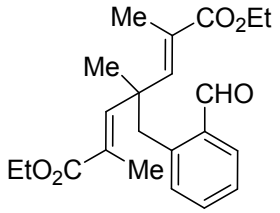
1k

(2*E*,5*E*)-diethyl 4-allyl-4-(4-fluoro-2-formylbenzyl)hepta-2,5-dienedioate (1k): Yellow solid. Mp 51-52 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 2H), 6.87 (d, *J* = 16.0 Hz, 2H), 5.76-5.30 (m, 3H), 5.18-5.12 (m, 2H), 4.20 (q, *J* = 8.0 Hz, 4H), 3.39 (s, 2H), 2.44 (d, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 165.8, 161.9, 150.0, 136.6, 134.7, 133.82, 132.5, 122.4, 120.3, 119.6, 117.8, 60.6, 46.6, 41.1, 39.0, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 113.47; HRMS (ESI, m/z): calcd. for $C_{22}H_{25}FO_5H^+$ 389.1759, found 389.1756.



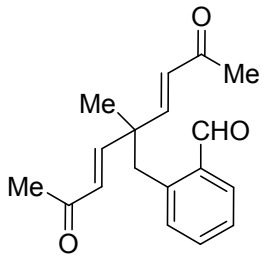
1l

(2*E*,5*E*)-diethyl 4-(2-formyl-4-methylbenzyl)-4-methylhepta-2,5-dienedioate (1l): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.61 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 2H), 5.69 (d, *J* = 16.0 Hz, 2H), 4.22-4.16 (m, 4H), 3.36 (s, 2H), 2.40 (s, 3H), 1.29 (t, *J* = 8.0 Hz, 6H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 166.2, 152.1, 137.4, 135.1, 134.8, 133.9, 133.4, 133.2, 120.5, 60.5, 44.1, 40.8, 21.8, 20.8, 14.2; HRMS (ESI, m/z): calcd. for $C_{21}H_{26}O_5H^+$ 359.1853, found 359.1851.



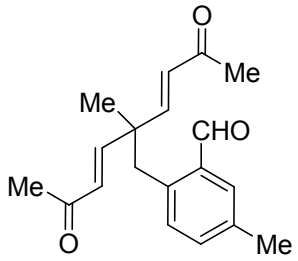
1m

(2*E*,5*E*)-diethyl 4-(2-formylbenzyl)-2,4,6-trimethylhepta-2,5-dienedioate (1m): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.53-7.42 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 2H), 4.19 (d, *J* = 4.0 Hz, 4H), 3.45 (s, 2H), 1.62 (s, 6H), 1.32-1.28 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 168.0, 146.3, 139.1, 135.3, 133.3, 133.0, 131.6, 129.3, 127.4, 60.7, 42.11, 42.05, 26.5, 14.4, 14.2; HRMS (ESI, m/z): calcd. for $C_{22}H_{28}O_5H^+$ 373.2010, found 373.2016.



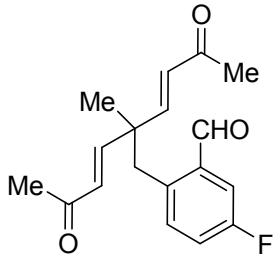
3a

2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxobut-1-en-1-yl)hex-3-en-1-yl)benzaldehyde (3a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40-7.30 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 2H), 5.76 (d, *J* = 16.0 Hz, 2H), 3.30 (s, 2H), 2.08 (s, 6H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 193.0, 150.8, 137.9, 134.9, 134.2, 133.3, 133.1, 129.4, 127.8, 44.3, 41.6, 27.4, 22.0; HRMS (ESI, m/z): calcd. for $C_{18}H_{20}O_3H^+$ 285.1485, found 285.1484.



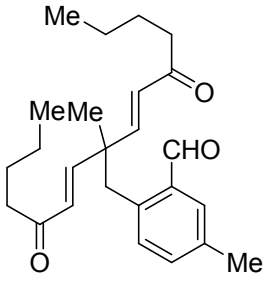
3b

5-methyl-2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxobut-1-en-1-yl)hex-3-en-1-yl)benzaldehyde (3b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.60 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 16.0 Hz, 2H), 5.91 (d, *J* = 16.0 Hz, 2H), 3.40 (s, 2H), 2.41 (s, 3H), 2.24 (s, 6H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 193.1, 151.0, 137.6, 134.9, 134.7, 134.4, 133.9, 133.3, 129.4, 44.3, 41.2, 27.2, 22.0, 20.8; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_3H^+$ 299.1642, found 299.1642.



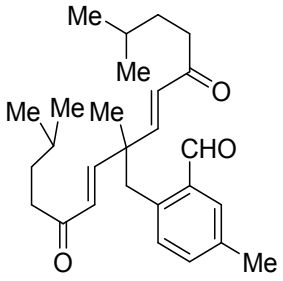
3c

5-fluoro-2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxobut-1-en-1-yl)hex-3-en-1-yl)benzaldehyde (3c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 0.8 Hz, 1H), 7.53 (dd, *J* = 4.0, 12.0 Hz, 1H), 7.26-7.15 (m, 2H), 6.81 (d, *J* = 16.0 Hz, 2H), 5.94 (d, *J* = 16.0 Hz, 2H), 3.39 (s, 2H), 2.24 (s, 6H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 191.0, 161.9, 150.3, 136.4, 135.0, 133.8, 129.6, 120.4, 118.6, 44.1, 40.7, 27.5, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ 113.14; HRMS (ESI, m/z): calcd. for $C_{18}H_{19}FO_3H^+$ 303.1391, found 303.1389.



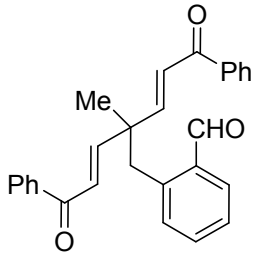
3d

5-methyl-2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxohept-1-en-1-yl)non-3-en-1-yl)benzaldehyde (3d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.59 (s, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 16.4 Hz, 2H), 5.93 (d, *J* = 16.4 Hz, 2H), 3.38 (s, 2H), 2.51 (t, *J* = 8.0 Hz, 4H), 2.40 (s, 3H), 1.61-1.53 (m, 4H), 1.36-1.30 (m, 4H), 1.21 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 192.9, 149.9, 137.5, 135.1, 134.8, 134.1, 133.9, 133.3, 128.5, 44.2, 41.1, 40.3, 26.1, 22.4, 22.0, 20.8, 13.9; HRMS (ESI, m/z): calcd. for $C_{25}H_{34}O_3Na^+$ 405.2400, found 405.2400.



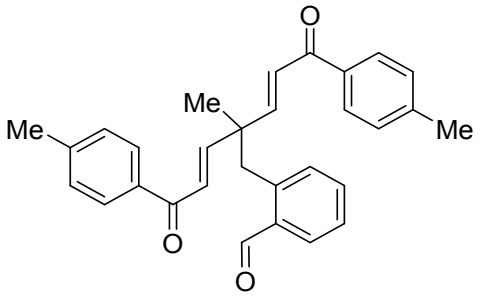
3e

2-((*E*)-2,8-dimethyl-2-((*E*)-6-methyl-3-oxohept-1-en-1-yl)-5-oxonon-3-en-1-yl)-5-methylbenzaldehyde (3e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.59 (s, 1H), 7.31-7.27 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 16.0 Hz, 2H), 5.93 (d, *J* = 16.0 Hz, 2H), 3.38 (s, 2H), 2.51 (t, *J* = 6.0 Hz, 4H), 2.40 (s, 3H), 1.60-1.45 (m, 6H), 1.34-1.21 (m, 8H), 0.91 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 192.9, 149.9, 137.5, 135.1, 134.8, 134.2, 133.9, 133.3, 128.4, 44.2, 41.2, 38.7, 32.8, 29.7, 27.8, 22.4, 22.1, 20.8; HRMS (ESI, m/z): calcd. for $C_{27}H_{38}O_3Na^+$ 433.2713, found 433.2712.



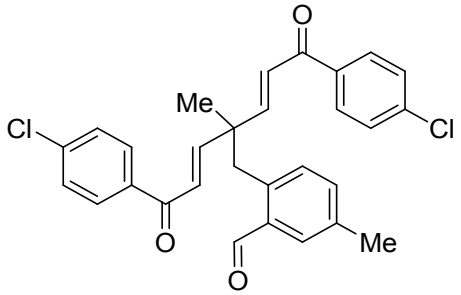
3f

2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)-5-phenylpent-3-en-1-yl)benzaldehyde (3f): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 4H), 7.82-7.79 (m, 1H), 7.59-7.54 (m, 2H), 7.51-7.44 (m, 6H), 7.23-7.16 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 2H), 3.55 (s, 2H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 190.1, 152.3, 138.2, 137.6, 135.1, 133.5, 133.4, 133.1, 133.06, 128.7, 128.6, 127.6, 124.4, 44.9, 41.4, 22.3; HRMS (ESI, m/z): calcd. for $C_{28}H_{24}O_3H^+$ 409.1798, found 409.1802.



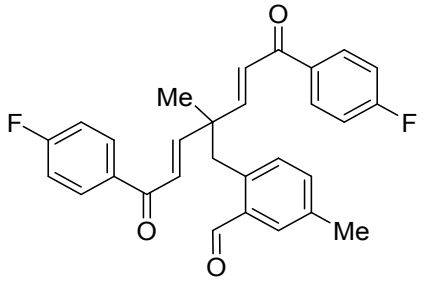
3g

2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxo-3-(p-tolyl)prop-1-en-1-yl)-5-(p-tolyl)pent-3-en-1-yl)benzaldehyde (3g): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 5H), 7.50-7.40 (m, 2H), 7.26-7.21 (m, 5H), 7.16 (d, *J* = 16.0 Hz, 2H), 6.80 (d, *J* = 16.0 Hz, 2H), 3.54 (s, 2H), 2.41 (s, 6H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 189.6, 151.9, 143.9, 138.3, 135.13, 135.05, 133.34, 133.25, 133.0, 129.3, 128.7, 127.5, 124.4, 44.8, 41.4, 22.4, 21.7; HRMS (ESI, m/z): calcd. for $C_{30}H_{28}O_3H^+$ 437.2111, found 437.2114.



3h

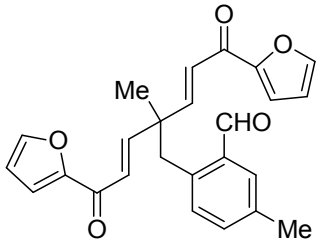
2-((*E*)-5-(4-chlorophenyl)-2-((*E*)-3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)-2-methyl-5-oxopent-3-en-1-yl)-5-methylbenzaldehyde (3h): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 4H), 7.59 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 16.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 2H), 3.50 (s, 2H), 2.38 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 188.7, 152.9, 139.4, 137.5, 135.8, 135.0, 134.9, 134.0, 133.9, 133.3, 130.0, 128.9, 123.8, 45.0, 41.1, 22.3, 20.8; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}Cl_2O_3H^+$ 491.1175, found 491.1179.



3i

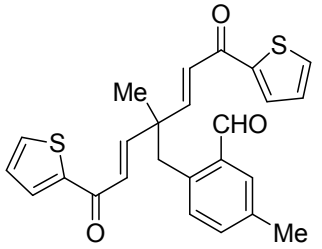
2-((*E*)-5-(4-fluorophenyl)-2-((*E*)-3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-2-methyl-5-oxopent-3-en-1-yl)-5-methylbenzaldehyde (3i): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.93 (m, 4H), 7.60 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20-7.09 (m, 7H), 6.77 (d, *J* = 16.0 Hz, 2H), 3.51 (s, 2H), 2.39 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 188.3, 165.7, 152.6, 137.5, 135.0, 134.9, 134.1, 133.93, 133.90, 133.3, 131.2, 123.9, 115.9, 115.7, 44.9, 41.1, 22.4, 20.8; ^{19}F NMR

(376 MHz, $CDCl_3$) δ 105.06; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}F_2O_3H^+$ 459.1766, found 459.1770.



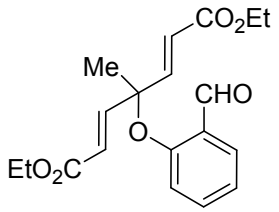
3j

2-((*E*)-5-(furan-2-yl)-2-((*E*)-3-(furan-2-yl)-3-oxoprop-1-en-1-yl)-2-methyl-5-oxopent-3-en-1-yl)-5-methylbenzaldehyde (3j): Yellow solid. Mp 181-182 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.63-7.59 (m, 3H), 7.29-7.23 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 2H), 6.56-6.55 (m, 2H), 3.49 (s, 2H), 2.37 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 177.6, 153.2, 151.8, 146.7, 137.4, 135.1, 134.9, 133.9, 133.7, 133.2, 123.5, 118.0, 112.5, 44.7, 41.0, 22.3, 20.8; HRMS (ESI, m/z): calcd. for $C_{25}H_{22}O_5H^+$ 403.1540, found 403.1549.



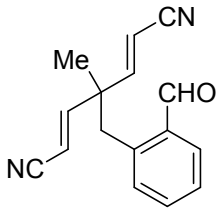
3k

5-methyl-2-((*E*)-2-methyl-5-oxo-2-((*E*)-3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)-5-(thiophen-2-yl)pent-3-en-1-yl)benzaldehyde (3k): Yellow solid. Mp 150-151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.71-7.59 (m, 5H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.21 (d, *J* = 16.0 Hz, 2H), 7.12-7.09 (m, 3H), 6.70 (d, *J* = 16.0 Hz, 2H), 3.49 (s, 2H), 2.36 (s, 3H), 1.36(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 181.7, 151.8, 144.9, 137.4, 135.1, 134.9, 134.2, 134.0, 133.9, 133.2, 132.3, 128.2, 123.9, 44.7, 41.1, 22.4, 20.8; HRMS (ESI, m/z): calcd. for $C_{25}H_{22}O_3S_2Na^+$ 457.0903, found 457.0904.



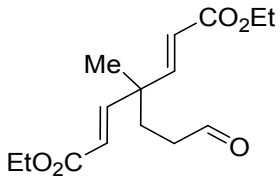
5a

(*2E,5E*)-diethyl 4-(2-formylphenoxy)-4-methylhepta-2,5-dienedioate (5a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.86 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.46-7.41 (m, 1H), 7.12-7.07 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.13 (d, *J* = 16.0 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 4H), 1.72 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 165.6, 157.4, 147.4, 135.1, 133.0, 128.8, 122.32, 122.27, 118.8, 80.5, 61.0, 25.7, 14.2; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_6H^+$ 347.1489, found 347.1488.



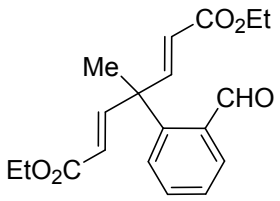
5b

(2*E*,5*E*)-4-(2-formylbenzyl)-4-methylhepta-2,5-dienedinitrile (5b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.60-7.52 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 2H), 5.22 (d, *J* = 16.0 Hz, 2H), 3.44 (s, 2H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 157.2, 136.4, 136.0, 134.8, 133.4, 133.3, 128.3, 116.7, 100.3, 46.3, 40.9, 21.1; HRMS (ESI, m/z): calcd. for $C_{16}H_{14}N_2ONa^+$ 273.0998, found 273.1004.



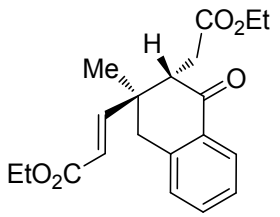
5c

(2*E*,5*E*)-diethyl 4-methyl-4-(3-oxopropyl)hepta-2,5-dienedioate (5c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 6.80 (d, *J* = 16.0 Hz, 2H), 5.73 (d, *J* = 16.0 Hz, 2H), 4.16-4.10 (m, 4H), 2.37 (t, *J* = 8.0 Hz, 2H), 1.83 (t, *J* = 8.0 Hz, 2H), 1.23 (t, *J* = 8.0 Hz, 6H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 165.2, 150.6, 120.0, 59.6, 40.9, 38.1, 30.4, 21.6, 13.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{22}O_5Na^+$ 305.1359, found 305.1364.



5d

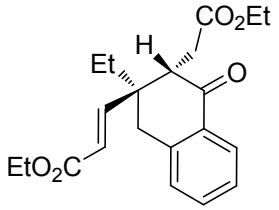
(*2E,5E*)-diethyl 4-(2-formylphenyl)-4-methylhepta-2,5-dienedioate (5d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.01 (d, *J* = 6.4 Hz, 1H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.40 (dd, *J* = 1.2, 16.0 Hz, 2H), 5.59 (dd, *J* = 1.2, 16.0 Hz, 2H), 4.20-4.15 (m, 4H), 1.73 (s, 3H), 1.29-1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 166.0, 153.7, 144.0, 134.0, 133.7, 131.3, 128.3, 127.8, 121.3, 60.8, 47.3, 28.1, 14.2; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_5Na^+$ 353.1359, found 353.1359.



2a

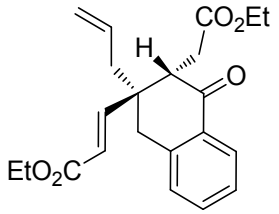
(*E*)-ethyl 3-((2*S*,3*S*)-3-(2-ethoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-

tetrahydronaphthalen-2-yl)acrylate (2a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 5.91 (d, *J* = 16.0 Hz, 1H), 4.26-4.16 (m, 4H), 3.41-3.36 (m, 2H), 2.81-2.72 (m, 2H), 2.22 (dd, *J* = 3.6, 16.4 Hz, 1H), 1.35-1.27 (m, 6H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 172.6, 166.3, 153.6, 140.2, 134.1, 131.4, 129.2, 127.2, 127.1, 120.7, 60.8, 60.7, 52.0, 43.1, 42.4, 30.7, 16.9, 14.24, 14.15; HRMS (ESI, m/z): calcd. for $C_{20}H_{24}O_5H^+$ 345.1697, found 345.1693; $[\alpha]_D^{26}$: 42.0 (c 2.2, $CHCl_3$); HPLC analysis: 99.5% *ee* (Chiralcel AD-H, 20:80 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 6.0 min, R_t (minor) = 5.4 min.



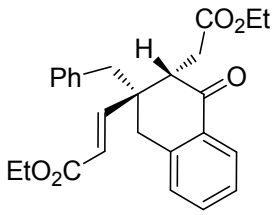
2b

(*E*)-ethyl 3-((2*S*,3*S*)-3-(2-ethoxy-2-oxoethyl)-2-ethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 9.8 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 5.94 (d, *J* = 16.0 Hz, 1H), 4.26-4.14 (m, 4H), 3.37-3.34 (m, 1H), 3.21 (d, *J* = 16.0 Hz, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 2.81-2.74 (m, 1H), 2.40-2.35 (m, 1H), 1.34-1.28 (m, 8H), 0.74 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 172.7, 166.3, 151.7, 139.8, 134.2, 131.7, 128.9, 127.2, 127.1, 121.7, 60.9, 60.7, 53.5, 45.7, 37.4, 30.1, 23.2, 14.3, 14.2, 8.6; HRMS (ESI, m/z): calcd. for $C_{21}H_{26}O_5H^+$ 359.1853, found 359.1846; $[\alpha]_D^{26}$: 20.5 (c 1.0, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel IA, Hexane, 1 mL/min), R_t (major) = 5.2 min, R_t (minor) = 4.8 min.



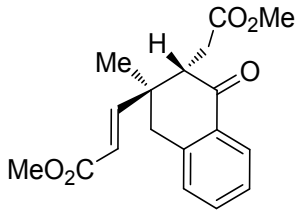
2c

(*E*)-ethyl 3-((2*S*,3*S*)-2-allyl-3-(2-ethoxy-2-oxoethyl)-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 5.65-5.54 (m, 1H), 5.00 (d, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 17.2 Hz, 1H), 4.26-4.17 (m, 4H), 3.41-3.37 (m, 1H), 3.22 (d, *J* = 16.4 Hz, 1H), 3.04 (d, *J* = 16.4 Hz, 1H), 2.85-2.79 (m, 1H), 2.43-2.37 (m, 1H), 2.30-2.24 (m, 1H), 2.07-2.02 (m, 1H), 1.31 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 172.6, 166.2, 151.4, 139.7, 134.2, 132.3, 131.7, 129.1, 127.2, 127.1, 121.8, 119.2, 60.9, 60.8, 53.0, 45.3, 38.3, 35.1, 30.2, 14.3, 14.2; HRMS (ESI, m/z): calcd. for $C_{22}H_{26}O_5H^+$ 371.1853, found 371.1849; $[\alpha]_D^{26}$: -15.7 (c 1.5, $CHCl_3$); HPLC analysis: 94% *ee* (Chiralcel IC, Hexane, 1 mL/min), R_t (major) = 9.0 min, R_t (minor) = 7.4 min.



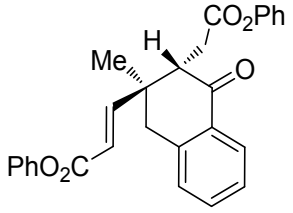
2d

(*E*)-ethyl 3-((2*S*,3*S*)-2-benzyl-3-(2-ethoxy-2-oxoethyl)-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.33-7.26 (m, 4H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 6.4 Hz, 2H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.25-4.18 (m, 2H), 4.11 (q, *J* = 6.8 Hz, 2H), 3.43 (dd, *J* = 4.0, 8.8 Hz, 1H), 3.10 (d, *J* = 16.8 Hz, 1H), 2.93-2.84 (m, 4H), 2.72-2.66 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 171.2, 164.7, 147.5, 139.1, 134.3, 133.2, 130.3, 129.6, 128.0, 127.2, 126.4, 126.1, 126.0, 121.9, 76.2, 60.0, 59.5, 51.6, 45.3, 43.6, 35.3, 29.8, 13.2, 13.1; HRMS (ESI, m/z): calcd. for $C_{26}H_{28}O_5H^+$ 421.2010, found 421.2005; $[\alpha]_D^{26}$: -31.1 (c 1.1, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel IC, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 10.5 min, R_t (minor) = 6.4 min.



2e

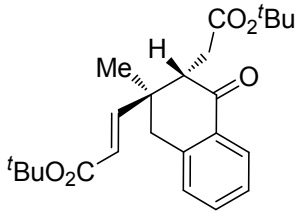
(*E*)-methyl 3-((2*S*,3*S*)-3-(2-methoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 16.0 Hz, 1H), 5.92 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.40-3.36 (m, 2H), 2.81-2.72 (m, 2H), 2.22 (dd, *J* = 3.2, 16.0 Hz, 1H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 173.1, 166.8, 153.9, 140.1, 134.2, 131.3, 129.2, 127.2, 127.1, 120.4, 52.1, 52.0, 51.8, 43.1, 42.3, 30.5, 16.8; HRMS (ESI, m/z): calcd. for $C_{18}H_{20}O_5H^+$ 317.1384, found 317.1381; $[\alpha]_D^{26}$: -15.4 (c 1.6, $CHCl_3$); HPLC analysis: 99% *ee* (Chiralcel IC, Hexane, 1 mL/min), R_t (major) = 13.4 min, R_t (minor) = 9.6 min.



2f

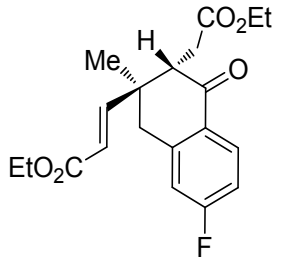
(*E*)-phenyl 3-((2*S*,3*S*)-2-methyl-4-oxo-3-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2f): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.42-7.32 (m, 5H), 7.29-7.12 (m, 8H), 6.18 (d, *J* = 16.0 Hz, 1H), 3.53 (dd, *J* = 3.6, 9.6 Hz, 1H), 3.46 (d, *J* = 16.4 Hz,

1H), 3.10-3.03 (m, 1H), 2.83 (d, *J* = 16.4 Hz, 1H), 2.53 (dd, *J* = 3.8, 16.6 Hz, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 171.2, 164.7, 155.6, 150.9, 150.6, 140.1, 134.3, 131.2, 129.5, 129.4, 129.3, 127.3, 127.2, 126.0, 125.8, 121.6, 121.5, 120.3, 52.3, 43.4, 42.3, 31.0, 17.0; HRMS (ESI, m/z): calcd. for $C_{28}H_{24}O_5H^+$ 441.1697, found 441.1695; $[\alpha]_D^{26}$: -14.6 (c 2.1, $CHCl_3$); HPLC analysis: 95% *ee* (Chiralcel IC, 10:90 *i*PrOH/Hexane, 1 mL/min), R_t (major) = 38.1 min, R_t (minor) = 27.5 min.



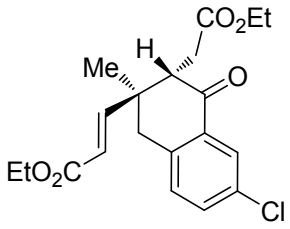
2g

(*E*)-tert-butyl 3-((2*S*,3*S*)-3-(2-(tert-butoxy)-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2g): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.52-7.47 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 1H), 5.82 (d, *J* = 16.0 Hz, 1H), 3.38-3.30 (m, 2H), 2.74-2.66 (m, 2H), 2.16 (dd, *J* = 3.2, 16.4 Hz, 1H), 1.51 (s, 9H), 1.48 (s, 9H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 171.8, 165.7, 152.7, 140.3, 133.9, 131.5, 129.1, 127.2, 126.9, 122.3, 80.8, 80.6, 52.1, 42.9, 42.6, 31.7, 28.2, 28.1, 17.1; HRMS (ESI, m/z): calcd. for $C_{24}H_{32}O_5H^+$ 401.2323, found 401.2323; $[\alpha]_D^{26}$: -83.2 (c 0.7, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 5:95 *i*PrOH/Hexane, 1 mL/min), R_t (major) = 6.3 min, R_t (minor) = 5.0 min.



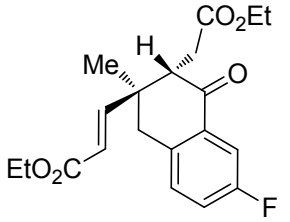
2h

(*E*)-ethyl 3-((2*S*,3*S*)-3-(2-ethoxy-2-oxoethyl)-7-fluoro-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2h): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.96 (m, 1H), 7.04-7.00 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.91 (d, *J* = 16.0 Hz, 1H), 4.26-4.16 (m, 4H), 3.38-3.14 (m, 2H), 2.80-2.70 (m, 2H), 2.22 (dd, *J* = 3.6, 16.4 Hz, 1H), 1.34-1.26 (m, 6H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 172.5, 166.2, 153.2, 143.2, 130.4, 128.0, 121.0, 115.6, 114.8, 60.9, 60.7, 51.9, 43.0, 42.4, 30.6, 16.9, 14.3, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 103.58; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}FO_5Na^+$ 385.1422, found 385.1423; $[\alpha]_D^{26}$: 8.6 (c 2.7, $CHCl_3$); HPLC analysis: 90% *ee* (Chiralcel IC, 3:97 *i*PrOH/Hexane, 1 mL/min), R_t (major) = 36.0 min, R_t (minor) = 34.3 min.



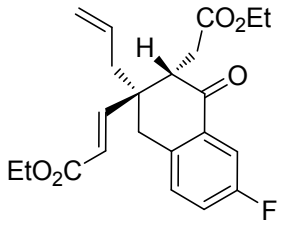
2i

(*E*)-ethyl 3-((2*S*,3*S*)-6-chloro-3-(2-ethoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2i): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.95 (m, 1H), 7.53-7.29 (m, 1H), 7.23-6.99 (m, 2H), 5.91 (dd, *J* = 0.8, 16.0 Hz, 1H), 4.26-4.16 (m, 4H), 3.38-3.30 (m, 2H), 2.79-2.70 (m, 2H), 2.25-2.19 (m, 1H), 1.34-1.27 (m, 6H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 172.4, 166.2, 153.2, 138.4, 134.0, 133.3, 132.6, 130.8, 127.0, 121.0, 77.2, 60.9, 60.8, 51.9, 43.0, 41.8, 30.5, 16.9, 14.3, 14.2; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}ClO_5Na^+$ 401.1126, found 401.1127; $[\alpha]_D^{26}$: -20.8 (c 1.9, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel AS-H, 1:99 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 24.3 min, R_t (minor) = 18.8 min.



2j

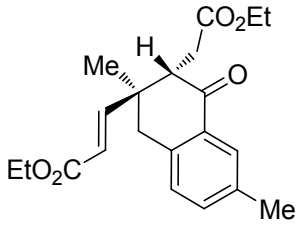
(*E*)-ethyl 3-((2*S*,3*S*)-3-(2-ethoxy-2-oxoethyl)-6-fluoro-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2j): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 6.0, 13.2 Hz, 1H), 7.23-7.20 (m, 2H), 7.03 (d, *J* = 16.0 Hz, 1H), 5.91 (d, *J* = 16.0 Hz, 1H), 4.26-4.17 (m, 4H), 3.38-3.31 (m, 2H), 2.80-2.71 (m, 2H), 2.22 (dd, *J* = 3.2, 16.4 Hz, 1H), 1.34-1.27 (m, 6H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 172.4, 166.2, 161.7, 153.3, 135.8, 133.0, 131.0, 121.5, 121.4, 113.2, 60.9, 60.7, 51.9, 43.1, 41.7, 30.6, 16.9, 14.2, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ 104.30; HRMS (ESI, m/z): calcd. for $C_{20}H_{23}FO_5Na^+$ 385.1422, found 385.1423; $[\alpha]_D^{26}$: -12.7 (c 2.9, $CHCl_3$); HPLC analysis: 94% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 9.3 min, R_t (minor) = 7.7 min.



2k

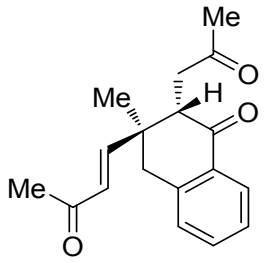
(*E*)-ethyl 3-((2*S*,3*S*)-2-allyl-3-(2-ethoxy-2-oxoethyl)-6-fluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2k): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 2.6, 9.0 Hz, 1H), 7.25-7.17 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 5.63-5.53 (m, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 4.76 (d, *J* = 17.2 Hz, 1H), 4.25-4.17 (m, 4H), 3.38 (dd, *J* = 3.6, 9.2 Hz, 1H), 3.16 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.84-2.78 (m, 1H), 2.40 (dd, *J* = 3.4, 16.2 Hz, 1H), 2.30-2.25 (m, 1H), 2.04-1.98 (m, 1H), 1.33-1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8,

172.4, 166.1, 151.0, 135.4, 133.3, 132.1, 130.9, 122.0, 121.5, 119.3, 113.3, 61.0, 60.8, 52.7, 45.4, 37.6, 35.1, 30.1, 14.23, 14.15; ^{19}F NMR (376 MHz, $CDCl_3$) δ 114.17; HRMS (ESI, m/z): calcd. for $C_{22}H_{25}FO_5Na^+$ 411.1578, found 411.1579; $[\alpha]_D^{26}$: 15.0 (c 5.0, $CHCl_3$); HPLC analysis: 93% *ee* (Chiralcel IC, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 13.4 min, R_t (minor) = 10.2 min.



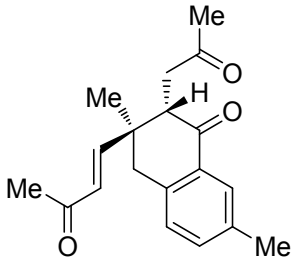
2l

(*E*)-ethyl 3-((2*S*,3*S*)-3-(2-ethoxy-2-oxoethyl)-2,6-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (2l): Yellow oil. ^{1}H NMR (400 MHz , $CDCl_3$) δ 7.81 (s, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.11-7.02 (m, 2H), 5.90 (d, *J* = 16.0 Hz, 1H), 4.25-4.16 (m, 4H), 3.38-3.31 (m, 2H), 2.79-2.68 (m, 2H), 2.36 (s, 3H), 2.20 (dd, *J* = 3.4, 16.2 Hz, 1H), 1.34-1.27 (m, 6H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 172.7, 166.4, 153.8, 137.3, 136.8, 135.0, 131.1, 129.1, 127.3, 120.6, 60.8, 60.7, 52.1, 43.2, 42.0, 30.7, 21.0, 16.9, 14.3, 14.2; HRMS (ESI, m/z): calcd. for $C_{21}H_{26}O_5Na^+$ 381.1673, found 381.1672; $[\alpha]_D^{26}$: -68.6 (c 0.7, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel AD-H, 5:95 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 13.3 min, R_t (minor) = 11.8 min.



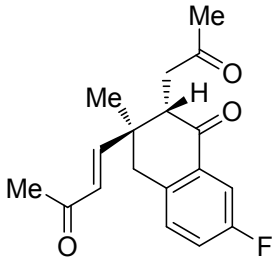
4a

(2*S*,3*S*)-3-methyl-3-((*E*)-3-oxobut-1-en-1-yl)-2-(2-oxopropyl)-3,4-dihydronaphthalen-1(2H)-one (4a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 16.4 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 3.52 (d, *J* = 8.0 Hz, 1H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.10-3.03 (m, 1H), 2.76 (d, *J* = 16.4 Hz, 1H), 2.29 (s, 6H), 2.12 (d, *J* = 17.2 Hz, 1H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 198.4, 196.8, 153.0, 140.2, 134.1, 131.3, 129.3, 129.2, 127.13, 127.09, 51.5, 43.1, 42.5, 38.9, 30.6, 27.3, 17.0; HRMS (ESI, m/z): calcd. for $C_{18}H_{20}O_3Na^+$ 307.1305, found 307.1305; $[\alpha]_D^{26}$: 74.1 (c 0.6, $CHCl_3$); HPLC analysis: 98% *ee* (Chiralcel AD-H, 30:70 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 4.1 min, R_t (minor) = 3.7 min.



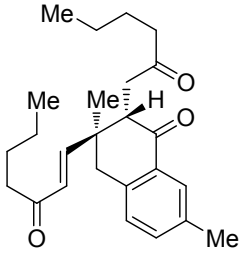
4b

(2*S*,3*S*)-3,7-dimethyl-3-((*E*)-3-oxobut-1-en-1-yl)-2-(2-oxopropyl)-3,4-dihydronaphthalen-1(2H)-one (4b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.35-7.30 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.12 (d, *J* = 16.0 Hz, 1H), 3.51 (dd, *J* = 3.4, 8.4 Hz, 1H), 3.33 (d, *J* = 16.4 Hz, 1H), 3.09-3.02 (m, 1H), 2.71 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H), 2.12 (dd, *J* = 3.2, 16.8 Hz, 1H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 198.5, 197.0, 153.2, 137.3, 136.8, 135.1, 131.1, 129.3, 129.1, 127.3, 51.5, 43.2, 42.1, 38.9, 30.6, 27.3, 21.0, 16.9; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_3H^+$ 299.1642, found 299.1642; $[\alpha]_D^{26}$: 70.3 (c 1.5, $CHCl_3$); HPLC analysis: 92% *ee* (Chiralcel AD-H, 5:95 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 14.3 min, R_t (minor) = 12.7 min.



4c

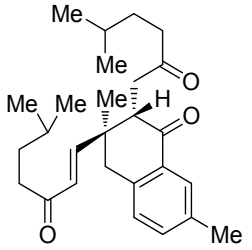
(2*S*,3*S*)-7-fluoro-3-methyl-3-((*E*)-3-oxobut-1-en-1-yl)-2-(2-oxopropyl)-3,4-dihydronaphthalen-1(2H)-one (4c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.24-7.21 (m, 2H), 6.82 (d, *J* = 16.4 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 3.51 (dd, *J* = 3.2, 8.4 Hz, 1H), 3.33 (d, *J* = 16.4 Hz, 1H), 3.08-3.02 (m, 1H), 2.74 (d, *J* = 16.4 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 2.13 (dd, *J* = 3.2, 17.2 Hz, 1H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 198.3, 195.9, 161.7, 152.6, 135.9, 132.9, 131.1, 129.5, 121.5, 113.2, 51.2, 43.2, 41.8, 38.8, 30.5, 27.4, 16.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ 114.21; HRMS (ESI, m/z): calcd. for $C_{18}H_{19}FO_3Na^+$ 325.1210, found 325.1216; $[\alpha]_D^{26}$: 31.9 (c 0.6, $CHCl_3$); HPLC analysis: 83% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 7.1 min, R_t (minor) = 6.7 min.



4d

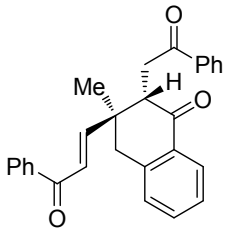
(2*S*,3*S*)-3,7-dimethyl-3-((*E*)-3-oxohept-1-en-1-yl)-2-(2-oxohexyl)-3,4-dihydronaphthalen-1(2H)-one (4d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 16.4 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 3.53 (dd, *J* = 3.2, 8.4 Hz, 1H), 3.32 (d, *J* = 16.4 Hz, 1H), 3.04-2.97 (m, 1H), 2.72-2.44 (m, 5H), 2.36 (s, 3H), 2.07 (dd, *J* = 3.0, 9.0 Hz, 1H), 1.62-1.60 (m, 4H), 1.38-1.32 (m, 4H), 1.00 (s, 3H), 0.95-0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 200.7, 197.3, 152.1, 137.3, 136.8, 135.0, 131.2, 129.1, 128.5, 127.3, 51.4, 43.2, 42.2, 40.1, 38.2, 29.7, 26.2, 25.9, 22.4, 21.0, 17.1, 13.9; HRMS (ESI, m/z): calcd. for $C_{25}H_{34}O_3Na^+$ 405.2400, found 405.2407; $[\alpha]_D^{26}$: -58.9 (c 0.6,

$CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 5.5 min, R_t (minor) = 4.9 min.



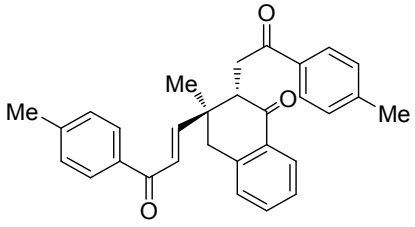
4e

(2*S*,3*S*)-3,7-dimethyl-2-(5-methyl-2-oxohexyl)-3-((*E*)-6-methyl-3-oxohept-1-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (4e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.14 (d, *J* = 16.0 Hz, 1H), 3.53 (dd, *J* = 2.8, 8.8 Hz, 1H), 3.32 (d, *J* = 16.4 Hz, 1H), 3.05-2.99 (m, 1H), 2.72-2.45 (m, 5H), 2.36 (s, 3H), 2.08 (dd, *J* = 3.0, 17.0 Hz, 1H), 1.60-1.47 (m, 6H), 1.01 (s, 3H), 0.91 (t, *J* = 5.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 200.8, 197.3, 152.0, 137.3, 136.8, 135.0, 131.1, 129.1, 128.4, 127.3, 51.4, 43.20, 42.19, 41.5, 38.5, 38.2, 32.9, 32.6, 27.8, 22.41, 22.37, 21.0, 17.1; HRMS (ESI, m/z): calcd. for $C_{27}H_{38}O_3Na^+$ 433.2713, found 433.2717; $[\alpha]_D^{26}$: 16.0 (c 1.2, $CHCl_3$); HPLC analysis: 90% *ee* (Chiralcel AD-H, 8:92 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 5.0 min, R_t (minor) = 4.5 min.



4f

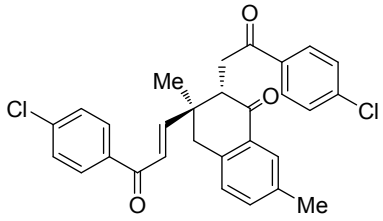
(2*S*,3*S*)-3-methyl-2-(2-oxo-2-phenylethyl)-3-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (4f): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J* = 7.6 Hz, 3H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.57-7.42 (m, 7H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.26-7.23 (m, 1H), 7.15 (d, *J* = 16.0 Hz, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 3.91 (dd, *J* = 2.2, 8.6 Hz, 1H), 3.78-3.72 (m, 1H), 3.49 (d, *J* = 16.4 Hz, 1H), 2.86 (d, *J* = 16.4 Hz, 1H), 2.64 (dd, *J* = 2.6, 17.0 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 197.1, 190.4, 154.3, 140.3, 137.6, 137.1, 134.1, 133.0, 131.5, 129.3, 128.7, 128.6, 128.2, 127.2, 127.1, 124.3, 51.6, 43.7, 42.7, 34.4, 17.8; HRMS (ESI, m/z): calcd. for $C_{28}H_{24}O_3H^+$ 409.1798, found 409.1802; $[\alpha]_D^{26}$: 47.6 (c 4.0, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel IC, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 15.9 min, R_t (minor) = 12.1 min.



4g

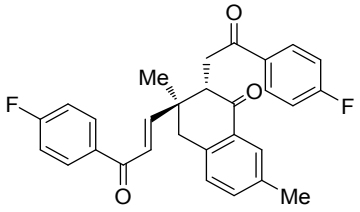
(2*S*,3*S*)-3-methyl-2-(2-oxo-2-(*p*-tolyl)ethyl)-3-((*E*)-3-oxo-3-(p-tolyl)prop-1-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (4g): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.99 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.58-7.50 (m, 1H), 7.33-7.17 (m, 6H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 3.89 (d, *J* = 7.6 Hz, 1H), 3.74-3.68 (m, 1H), 3.47 (d, *J* = 16.0 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 2.63 (d, *J* = 16.8 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 197.3, 190.0, 153.9, 143.9, 143.7, 140.3, 135.1, 134.6, 134.0, 131.6, 129.33, 129.27, 129.2, 128.7, 128.6, 128.4, 128.3, 127.2, 127.0, 124.2, 51.6, 43.7, 42.8, 34.2, 21.69, 21.65, 17.8; HRMS (ESI, m/z): calcd. for $C_{30}H_{28}O_3H^+$ 437.2111, found 437.2114; $[\alpha]_D^{26}$: 15.7 (c 1.2, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel AS-H, 4:96 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 39.3 min, R_t (minor) = 34.1 min.



4h

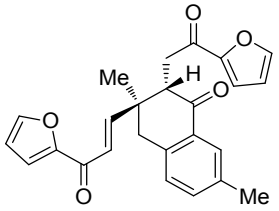
(2*S*,3*S*)-2-(2-(4-chlorophenyl)-2-oxoethyl)-3-((*E*)-3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)-3,7-dimethyl-3,4-dihydronaphthalen-1(2H)-one (4h): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.79 (s, 1H), 7.44-7.40 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.17-7.13 (m, 2H), 6.94 (d, *J* = 16.0 Hz, 1H), 3.86 (dd, *J* = 2.6, 8.2 Hz, 1H), 3.71-3.65 (m, 1H), 3.44 (d, *J* = 16.4 Hz, 1H), 2.82 (d, *J* = 16.4 Hz, 1H), 2.56 (dd, *J* = 2.8, 16.8 Hz, 1H), 2.36 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 197.2, 188.9, 154.9, 139.6, 137.3, 136.9, 135.8, 135.5, 135.2, 131.1, 129.9, 129.6, 129.2, 129.0, 128.9, 127.4, 123.6, 51.9, 43.8, 42.3, 34.3, 21.0, 17.7; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}Cl_2O_3Na^+$ 513.0995, found 513.0999; $[\alpha]_D^{26}$: -22.3 (c 0.7, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel OD-H, 5:95 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 19.4 min, R_t (minor) = 17.3 min.



4i

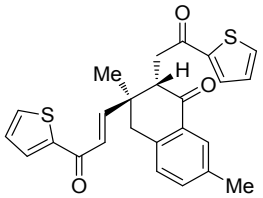
(2*S*,3*S*)-2-(2-(4-fluorophenyl)-2-oxoethyl)-3-((*E*)-3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-3,7-dimethyl-3,4-dihydronaphthalen-1(2H)-one (4i): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (q, *J* = 5.6 Hz, 2H), 7.94 (q, *J* = 5.6 Hz, 2H), 7.79 (s, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.17-7.09 (m, 6H), 6.96 (d, *J* = 15.6 Hz, 1H), 3.87 (dd, *J* = 2.6, 8.2 Hz, 1H), 3.73-3.66 (m, 1H), 3.44 (d, *J* = 16.4 Hz, 1H), 2.82 (d, *J* = 16.4 Hz, 1H), 2.58 (dd, *J* = 2.8, 16.8 Hz, 1H), 2.36 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 196.9, 188.6, 167.0, 164.5, 154.7, 137.1, 135.1, 133.7, 131.2, 131.1, 130.8, 129.2, 127.4, 123.7, 115.9, 115.7, 115.5, 51.8, 43.8, 42.4, 34.3, 21.0, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ 104.96, 105.53; HRMS (ESI, m/z): calcd. for $C_{29}H_{24}F_2O_3Na^+$ 481.1586, found 481.1584; $[\alpha]_D^{26}$: -13.7 (c 6.6, $CHCl_3$); HPLC analysis: 96% *ee* (Chiralcel IC, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 18.0

min, R_t (minor) = 16.8 min.



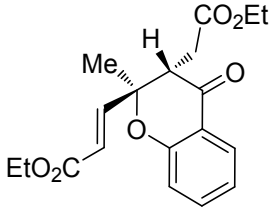
4j

(2*S*,3*S*)-2-(2-(furan-2-yl)-2-oxoethyl)-3-((*E*)-3-(furan-2-yl)-3-oxoprop-1-en-1-yl)-3,7-dimethyl-3,4-dihydronaphthalen-1(2H)-one (4j): Yellow solid. Mp 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.63 (s, 1H), 7.57 (s, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.29-7.21 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.60-6.50 (m, 2H), 3.80 (dd, *J* = 2.4, 9.2 Hz, 1H), 3.58-3.52 (m, 1H), 3.42 (d, *J* = 16.8 Hz, 1H), 2.80 (d, *J* = 16.4 Hz, 1H), 2.53 (dd, *J* = 2.6, 16.6 Hz, 1H), 2.36 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 187.4, 177.7, 153.6, 153.2, 152.7, 146.8, 146.1, 137.3, 136.8, 135.0, 131.2, 129.1, 127.4, 123.5, 118.1, 116.9, 112.6, 112.3, 51.3, 43.6, 42.3, 34.3, 21.0, 17.7; HRMS (ESI, m/z): calcd. for $C_{25}H_{22}O_5Na^+$ 425.1359, found 425.1366; $[\alpha]_D^{26}$: -37.0 (c 0.6, $CHCl_3$); HPLC analysis: 85% *ee* (Chiralcel AD-H, 40:60 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 5.1 min, R_t (minor) = 4.4 min.



4k

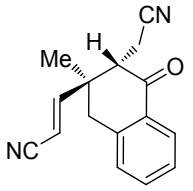
(2*S*,3*S*)-3,7-dimethyl-2-(2-oxo-2-(thiophen-2-yl)ethyl)-3-((*E*)-3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (4k): Yellow solid. Mp 150-151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.67 (d, *J* = 4.4 Hz, 1H), 7.62 (d, *J* = 4.8 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.21-7.11 (m, 5H), 6.90 (d, *J* = 15.6 Hz, 1H), 3.84 (d, *J* = 6.4 Hz, 1H), 3.65-3.58 (m, 1H), 3.42 (d, *J* = 16.4 Hz, 1H), 2.82 (d, *J* = 16.4 Hz, 1H), 2.66-2.62 (m, 1H), 2.36 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 191.0, 182.0, 153.5, 144.9, 144.0, 137.3, 136.8, 135.1, 134.3, 133.5, 132.3, 131.9, 131.2, 129.1, 128.3, 128.0, 127.4, 124.0, 51.5, 43.6, 42.4, 35.3, 29.7, 21.0, 17.9; HRMS (ESI, m/z): calcd. for $C_{25}H_{22}O_3S_2H^+$ 435.1083, found 435.1084; $[\alpha]_D^{26}$: 11.1 (c 1.6, $CHCl_3$); HPLC analysis: 92% *ee* (Chiralcel IA, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 17.3 min, R_t (minor) = 14.3 min.



6a

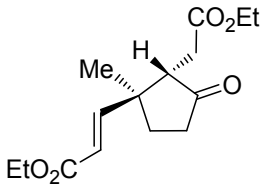
(*E*)-ethyl 3-((*2S,3S*)-3-(2-ethoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (6a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.05-6.97 (m, 3H), 6.22 (d, *J* = 16.0 Hz, 1H), 4.26-4.16 (m, 4H), 3.56-3.52 (m, 1H), 2.82-2.75 (m, 1H), 2.37 (dd, *J* = 4.4, 16.4 Hz,

1H), 1.41 (s, 3H), 1.31-1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 171.4, 165.8, 158.6, 147.4, 136.5, 126.9, 122.5, 121.5, 119.9, 118.2, 82.4, 61.2, 60.9, 50.4, 30.2, 18.8, 14.2, 14.1; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_6H^+$ 347.1489, found 347.1488; $[\alpha]_D^{26}$: 20.4 (c 2.5, $CHCl_3$); HPLC analysis: 88% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 6.9 min, R_t (minor) = 6.1 min.



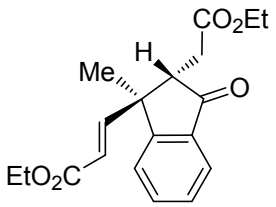
6b

(*E*)-3-((2*S*,3*S*)-3-(cyanomethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylonitrile (6b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.25-7.23 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 5.53 (d, *J* = 16.4 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 3.06 (t, *J* = 6.0 Hz, 1H), 2.90 (d, *J* = 6.8 Hz, 0.5H), 2.85 (d, *J* = 6.8 Hz, 0.5H), 2.79 (d, *J* = 16.4 Hz, 1H), 2.44 (d, *J* = 5.2 Hz, 0.5H), 2.40 (d, *J* = 5.2 Hz, 0.5H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 158.7, 139.1, 134.9, 130.6, 129.3, 127.72, 127.66, 118.4, 116.4, 101.1, 52.1, 44.6, 41.9, 15.9, 13.9; HRMS (ESI, m/z): calcd. for $C_{16}H_{14}N_2ONa^+$ 273.0998, found 273.0999; $[\alpha]_D^{26}$: -39.1 (c 1.0, $CHCl_3$); HPLC analysis: 76% *ee* (Chiralcel IA, Hexane, 0.5 mL/min), R_t (major) = 13.9 min, R_t (minor) = 12.4 min.



6c

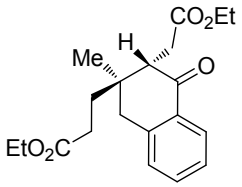
(*E*)-ethyl 3-((1*S*,2*S*)-2-(2-ethoxy-2-oxoethyl)-1-methyl-3-oxocyclopentyl)acrylate (6c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 16.0 Hz, 1H), 5.84 (d, *J* = 16.0 Hz, 1H), 4.24-4.10 (m, 4H), 2.83 (t, *J* = 6.6 Hz, 1H), 2.57-1.86 (m, 6H), 1.35-1.24 (m, 6H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 171.9, 166.4, 154.1, 120.0, 60.9, 60.6, 55.5, 44.3, 33.8, 29.2, 17.7, 14.3, 14.1; HRMS (ESI, m/z): calcd. for $C_{15}H_{22}O_5Na^+$ 305.1359, found 305.1361; $[\alpha]_D^{26}$: -87.6 (c 1.8, $CHCl_3$); HPLC analysis: 32% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 8.5 min, R_t (minor) = 8.0 min.



6d (2.1:1 dr)

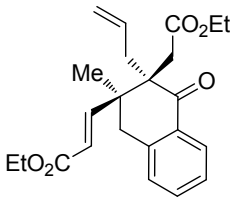
(*E*)-ethyl 3-((*1S,2S*)-2-(2-ethoxy-2-oxoethyl)-1-methyl-3-oxo-2,3-dihydro-1H-inden-1-yl)acrylate (6d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 6.8

Hz, 1H), 7.68-7.62 (m, 1H), 7.48-7.37(m, 2H), 7.16 (d, *J* = 16.0 Hz, 0.3H), 6.79 (d, *J* = 16.0 Hz, 0.7H), 5.96 (d, *J* = 16.0 Hz, 0.3H), 5.59 (d, *J* = 16.0 Hz, 0.7H), 4.23-4.14 (m, 4H), 3.30-3.26 (m, 0.3H), 3.26-3.15 (m, 0.7H), 2.97-2.86 (m, 1H), 2.48-2.36 (m, 1H), 1.71 (s, 3H), 1.32-1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 172.2, 165.9, 157.6, 151.1, 135.4, 128.6, 125.0, 124.1, 121.5, 120.6, 61.0, 60.6, 56.7, 47.8, 31.6, 24.8, 14.2; HRMS (ESI, m/z): calcd. for $C_{19}H_{22}O_5Na^+$ 353.1359, found 353.1359. $[\alpha]_D^{26}$: -35.9 (c 1.0, $CHCl_3$); HPLC analysis: 24% *ee* (Chiralcel AD-H, 3:97 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 11.4 min, R_t (minor) = 10.8 min; 14% *ee* (Chiralcel AD-H, 3:97 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 19.1 min, R_t (minor) = 13.5 min.



7a

ethyl 3-((2R,3S)-3-(2-ethoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propanoate (7a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.23-4.12 (m, 4H), 3.21-3.14 (m, 2H), 2.81-2.67 (m, 2H), 2.46-2.37 (m, 3H), 1.87-1.81 (m, 2H), 1.32-1.26 (m, 6H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 172.3, 172.0, 139.9, 132.8, 130.4, 128.3, 126.0, 125.7, 59.7, 59.6, 51.6, 39.8, 37.8, 34.8, 28.4, 27.8, 18.8, 13.19, 13.17; HRMS (ESI, m/z): calcd. for $C_{20}H_{26}O_5Na^+$ 369.1673, found 369.1673; $[\alpha]_D^{26}$: -13.0 (c 5.0, $CHCl_3$); HPLC analysis: 97% *ee* (Chiralcel AD-H, 5:95 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 11.0 min, R_t (minor) = 9.4 min.

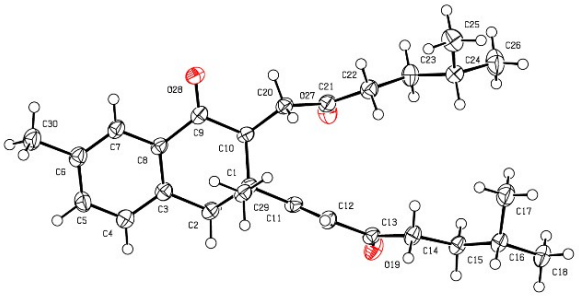


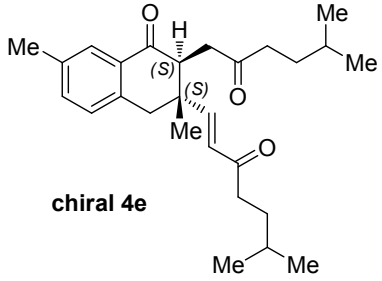
7b

(*E*)-ethyl 3-((2*S*,3*R*)-3-allyl-3-(2-ethoxy-2-oxoethyl)-2-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)acrylate (7b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.25-7.16 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 15.6 Hz, 1H), 6.09-5.99 (m, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.33-4.29(m, 2 H), 4.17-4.10 (m, 4H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.16 (d, *J* = 16.4 Hz, 1H), 2.90-2.80 (m, 2H), 1.26 (t, *J* = 6 Hz, 6H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 166.6, 152.3, 151.4, 134.5, 133.9, 130.1, 127.9, 126.8, 122.13, 122.09, 119.7, 116.9, 72.8, 60.8, 60.3, 41.5, 41.0, 32.3, 29.7, 22.1, 14.21, 14.15; HRMS (ESI, m/z): calcd. for $C_{23}H_{28}O_5H^+$ 385.2010, found 385.2021; $[\alpha]_D^{26}$: 18.3 (c 2.6, $CHCl_3$); HPLC analysis: 86% *ee* (Chiralcel AD-H, 10:90 ^{i}PrOH/Hexane, 1 mL/min), R_t (major) = 4.2 min, R_t (minor) = 3.7 min.

VI. Stereochemistry determination and X-Ray Crystallographic analysis.

Absolute configuration of Stetter products was determined via X-ray structure analysis of **4e**.

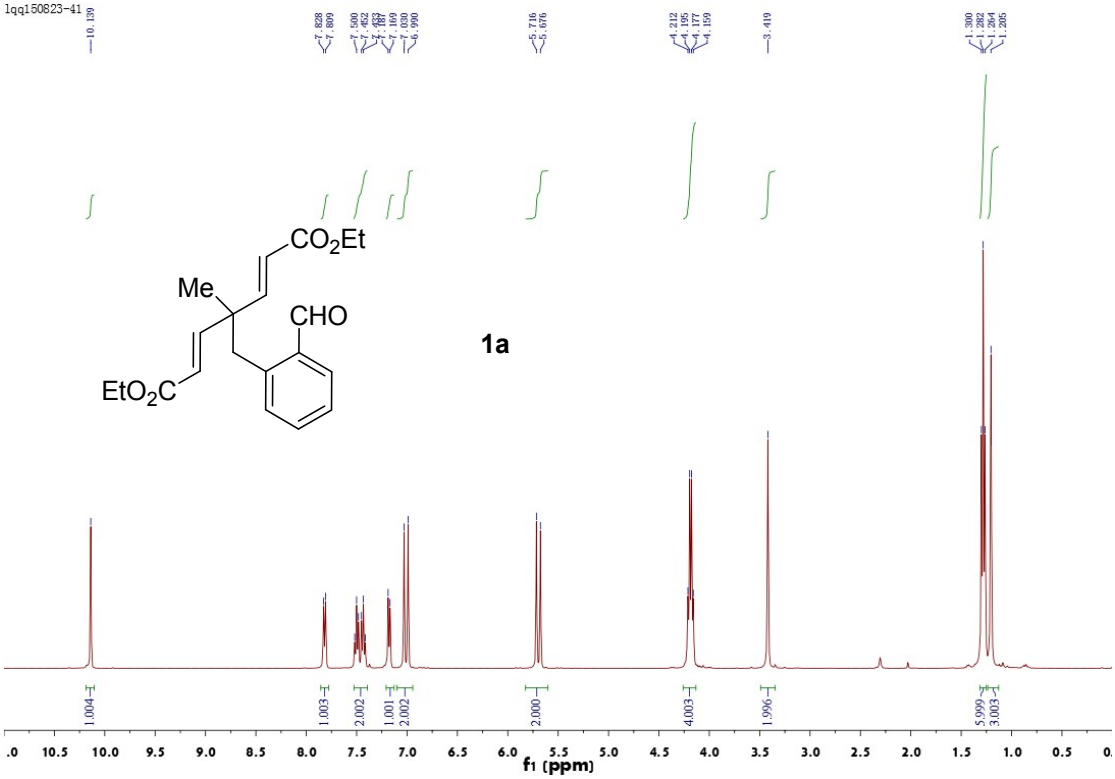


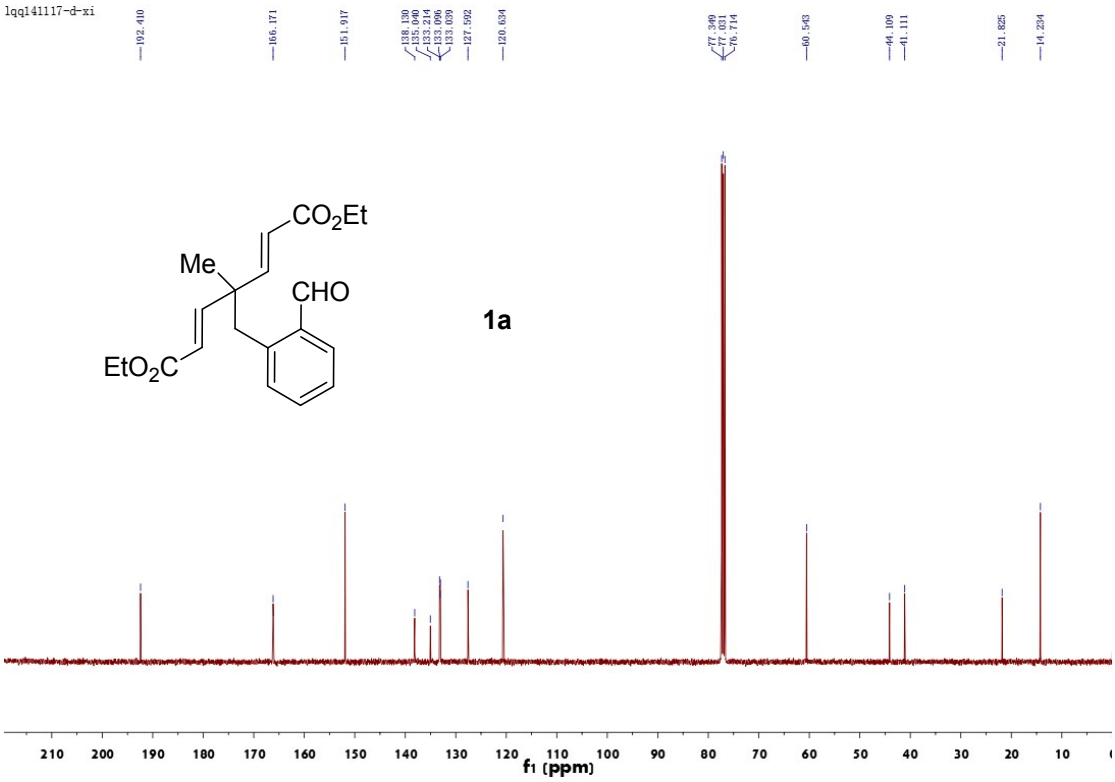


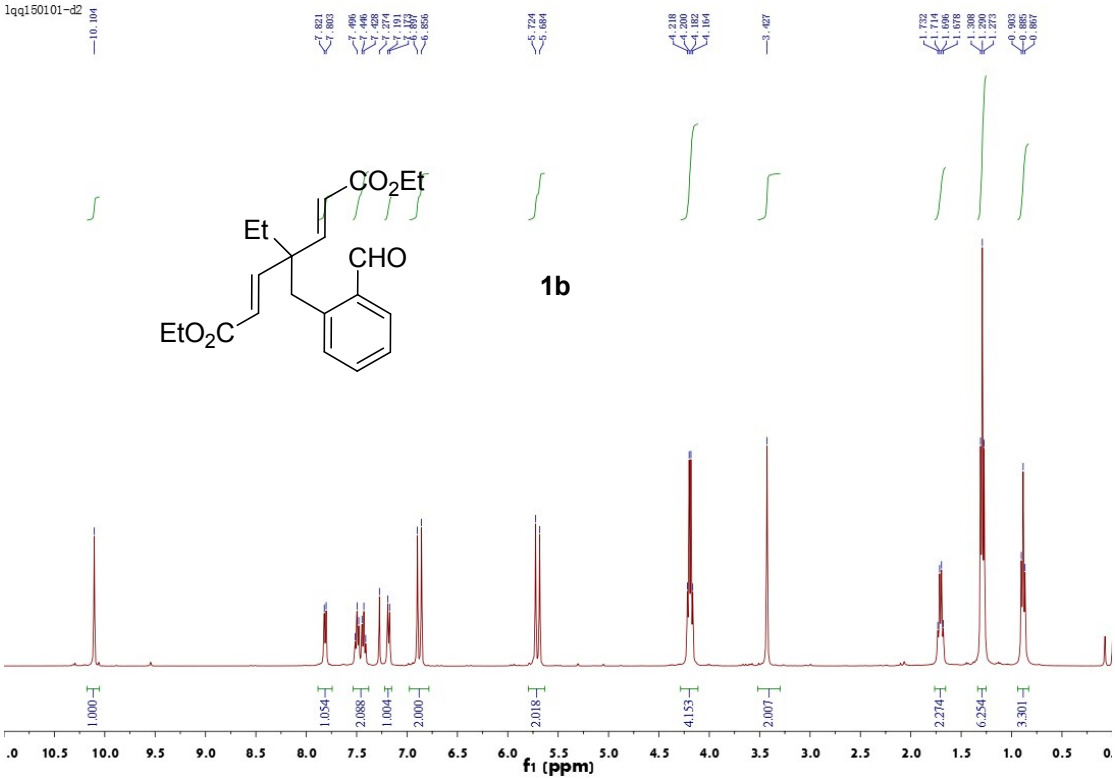
Crystallographic data of **(2*S*,3*S*)-3,7-dimethyl-2-(5-methyl-2-oxohexyl)-3-((*E*)-6-methyl-3-oxohept-1-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (4e):** $C_{27}H_{38}O_3$, monoclinic, space group $P2_1$, a = 5.8458(3) Å, b = 12.3784(6) Å, c = 16.7657(12) Å, V = 1201.22(12) Å^3, Z = 2, d = 1.135 g/cm^3, crystal dimensions 0.20 × 0.18 × 0.15 mm was used for measurements on an SuperNova Rigaku oxford X-ray diffraction meter with a mirror Cu Ka (λ= 1.54184 Å) radiation at 293 K (ω scans, 2θmax = 150.78º). The total number of independent reflections measured was 3204, of which 3024 were observed ($|F|^2 \geq 2\delta|F|^2$). Final indices ($|F|^2 \geq 2\delta|F|^2$): R_1 = 0.0457, ωR_2 = 0.1185, S = 1.044, (Δρ)min = -0.175 e/ Å^3, (Δρ)max = 0.228 e/ Å^3. Flack χ = -0.1(2).

The crystal structures were solved by direct methods using SHELXS-97 (Sheldrick, G.M. University of Gottingen: Gottingen, Germany, 1997) and expanded using difference Fourier techniques, refined by SHELXL-97 (Sheldrick, G. M. University of Gottingen, Germany, 1997) and full-matrix least-squares calulations. The absolute configuration was determined by anomalous dispersion effects in diffraction measurements on the crystal.

VII. NMR spectra of new compounds.






lqq150101-d2
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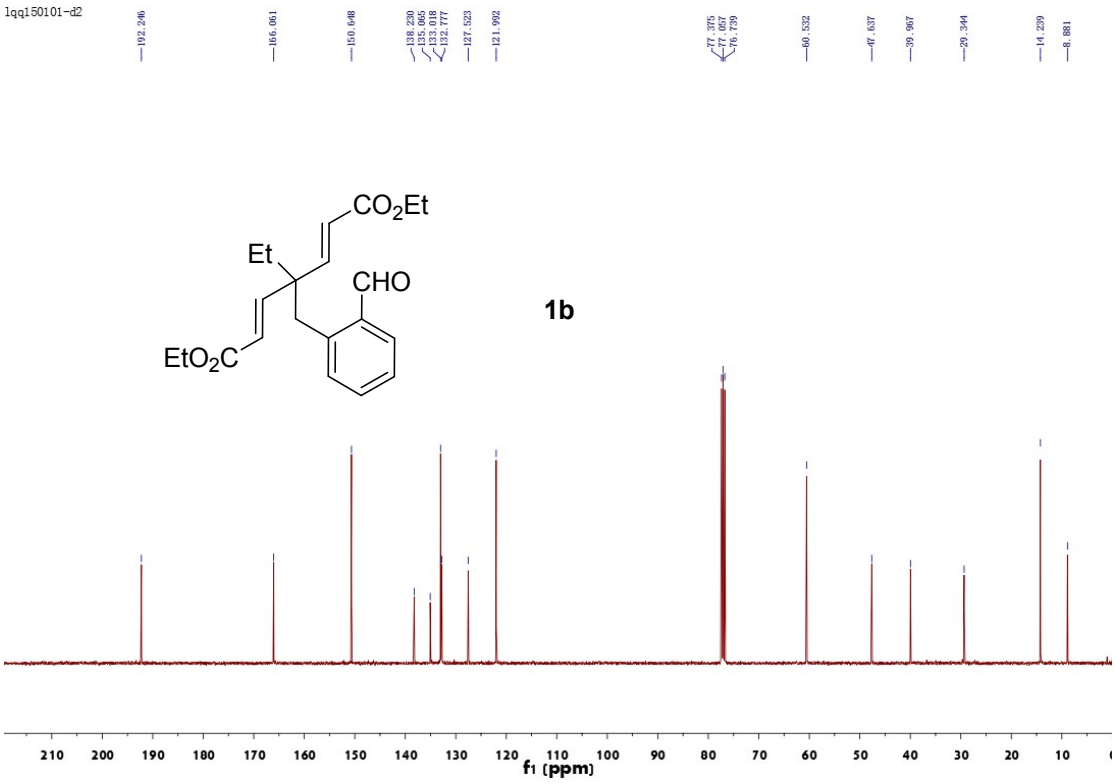
7.821
7.803
7.496
7.446
7.428
7.274
7.191
7.177
6.897
6.856
5.724
5.684
4.218
4.200
4.182
4.164
3.427
1.732
1.714
1.696
1.678
1.308
1.290
1.273
0.903
0.885
0.867
CO2Et
Et
CHO
EtO2C
1b
1.000
1.054
2.088
1.004
2.000
2.018
4.153
2.007
2.274
6.254
3.301
f1 (ppm)


lqq150101-d2
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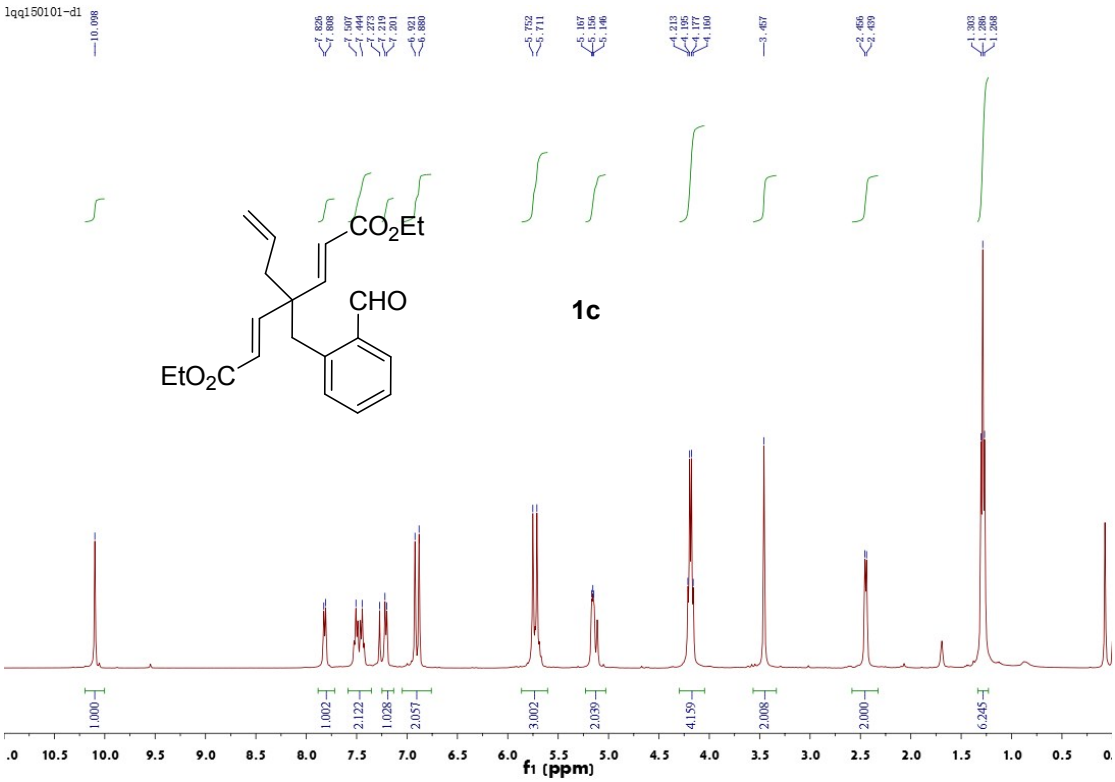
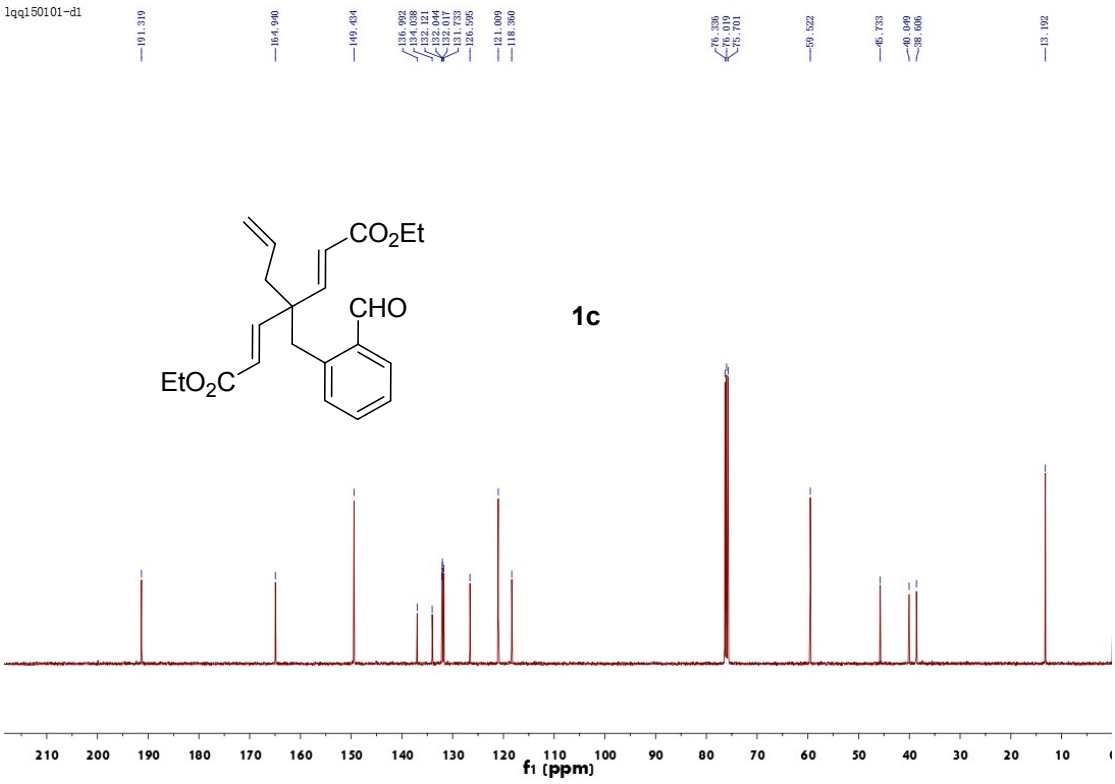
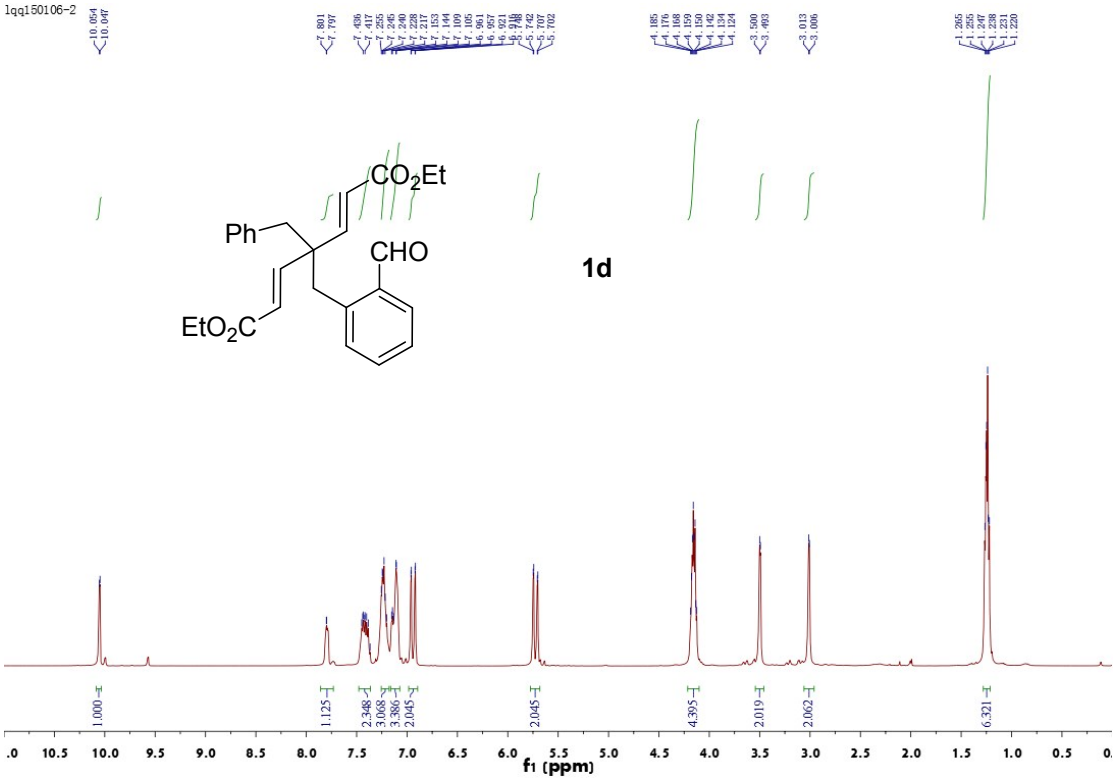
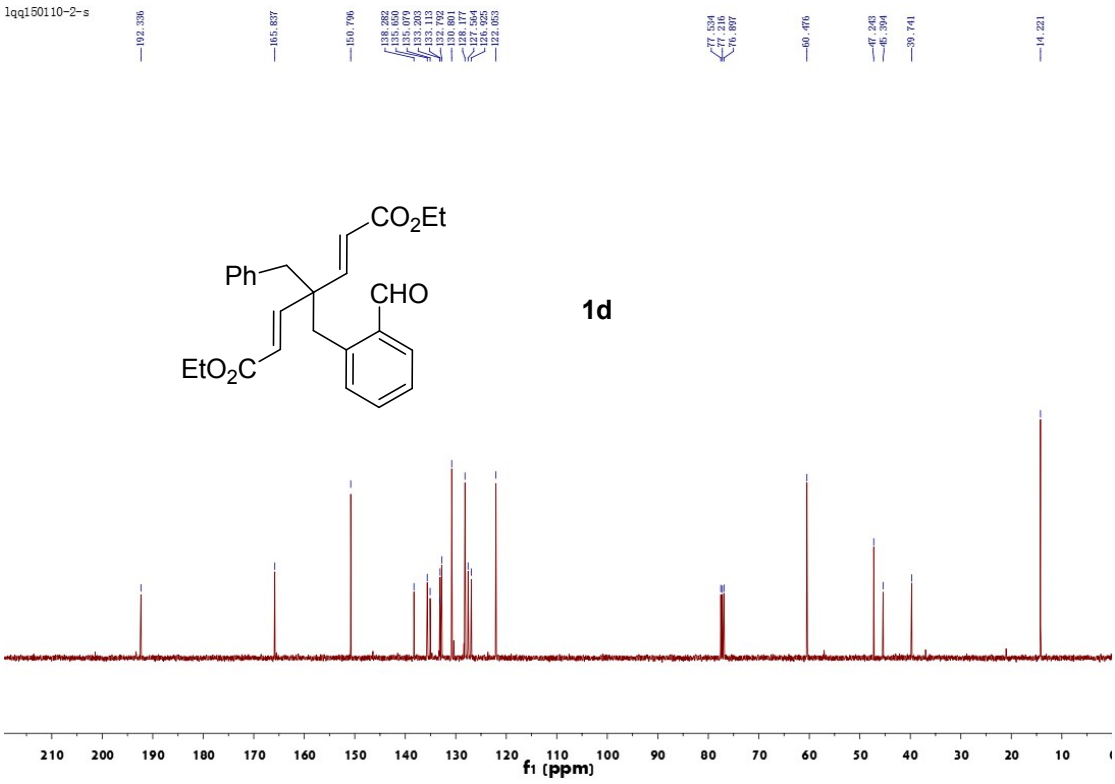
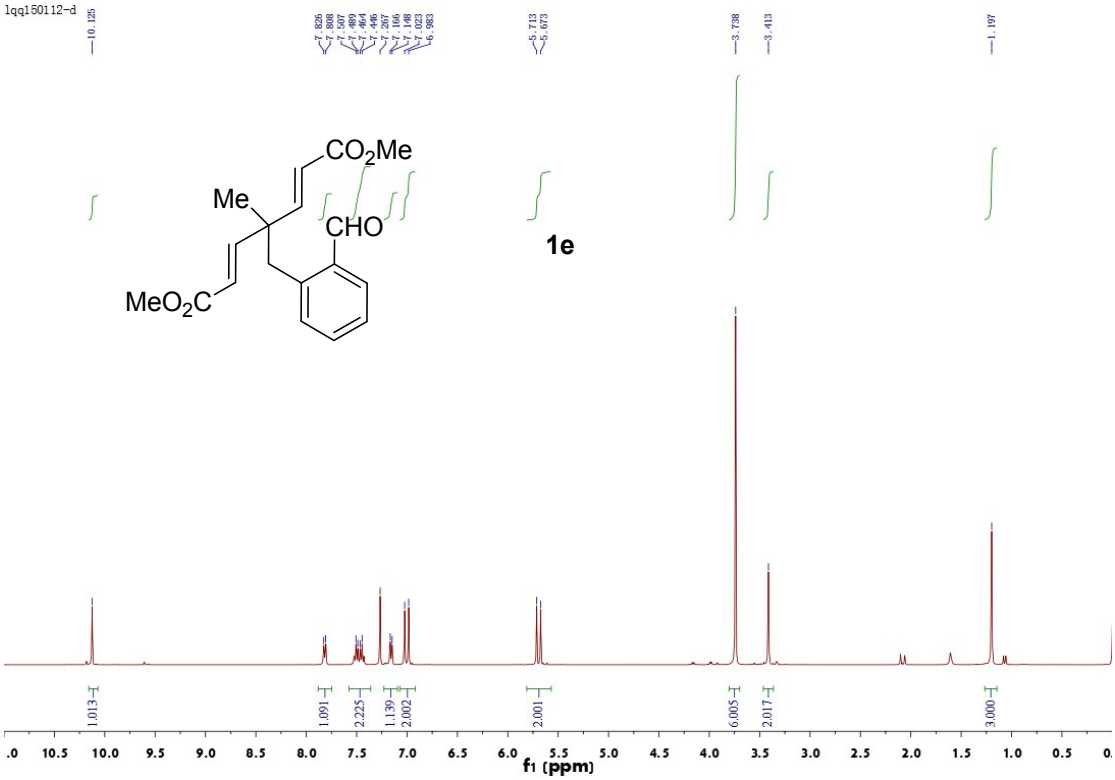
166.061
150.648
138.230
135.565
133.018
132.777
127.523
121.992
77.375
77.057
76.739
60.532
47.637
39.967
29.344
14.239
8.881
CO2Et
Et
CHO
EtO2C
1b
f1 (ppm)

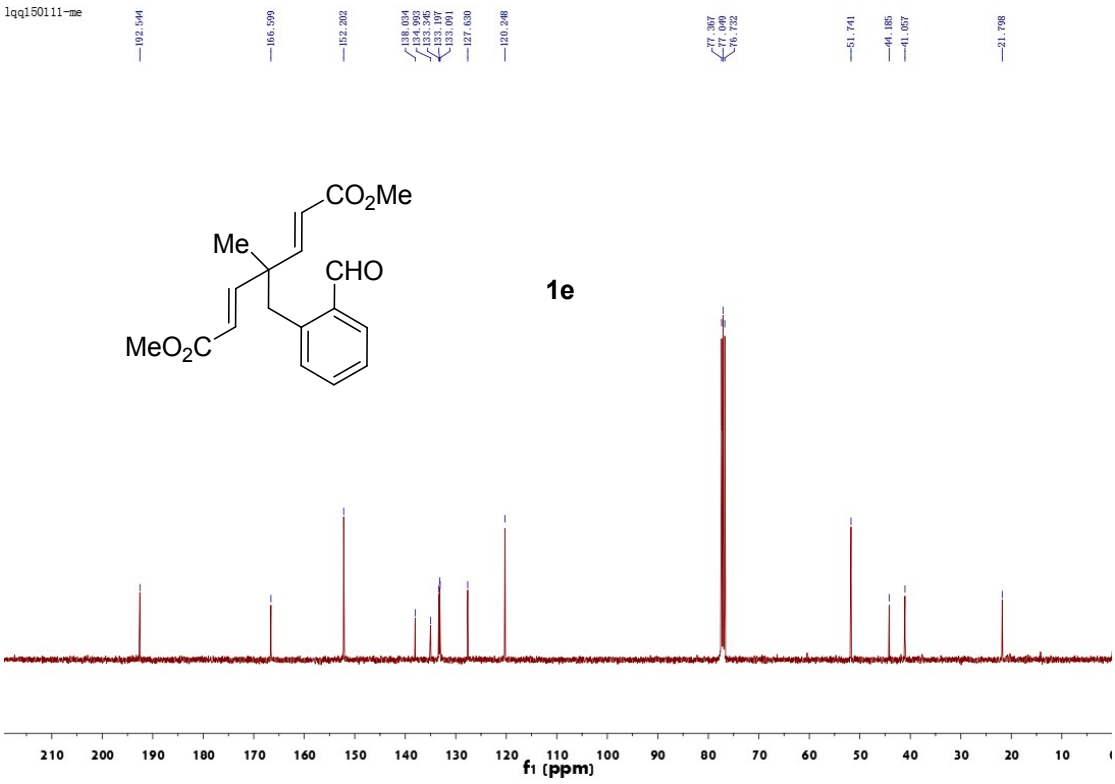

lqq150101-d1
10.098
7.826
7.808
7.507
7.444
7.273
7.219
7.201
6.921
6.880
5.752
5.711
5.167
5.156
5.146
4.213
4.195
4.177
4.160
3.457
2.456
2.439
1.303
1.286
1.268
CO2Et
CHO
EtO2C
1c
1.000
1.002
2.122
1.028
2.057
3.002
2.039
4.159
2.008
2.000
6.245
f1 (ppm)

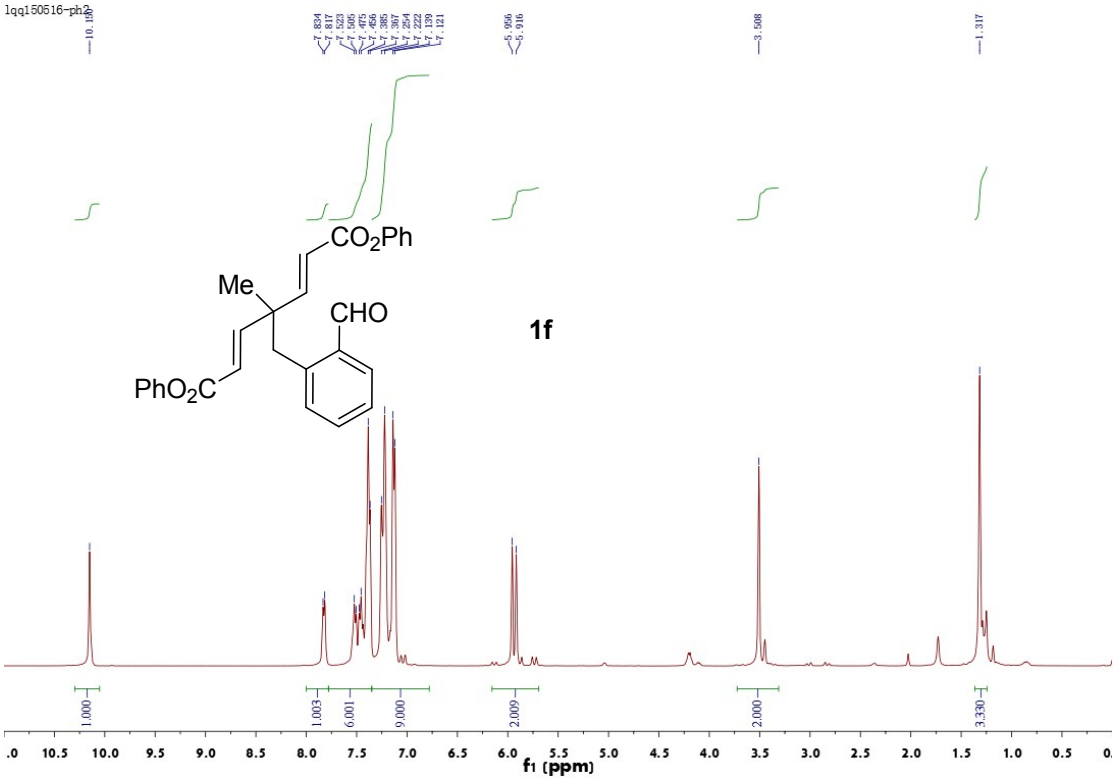

lqq150101-d1
191.319
164.940
149.404
136.992
134.038
132.121
132.044
132.017
131.733
126.595
121.009
118.360
76.336
76.019
75.701
59.522
45.733
40.049
38.606
13.192
CO2Et
CHO
EtO2C
1c
f1 (ppm)

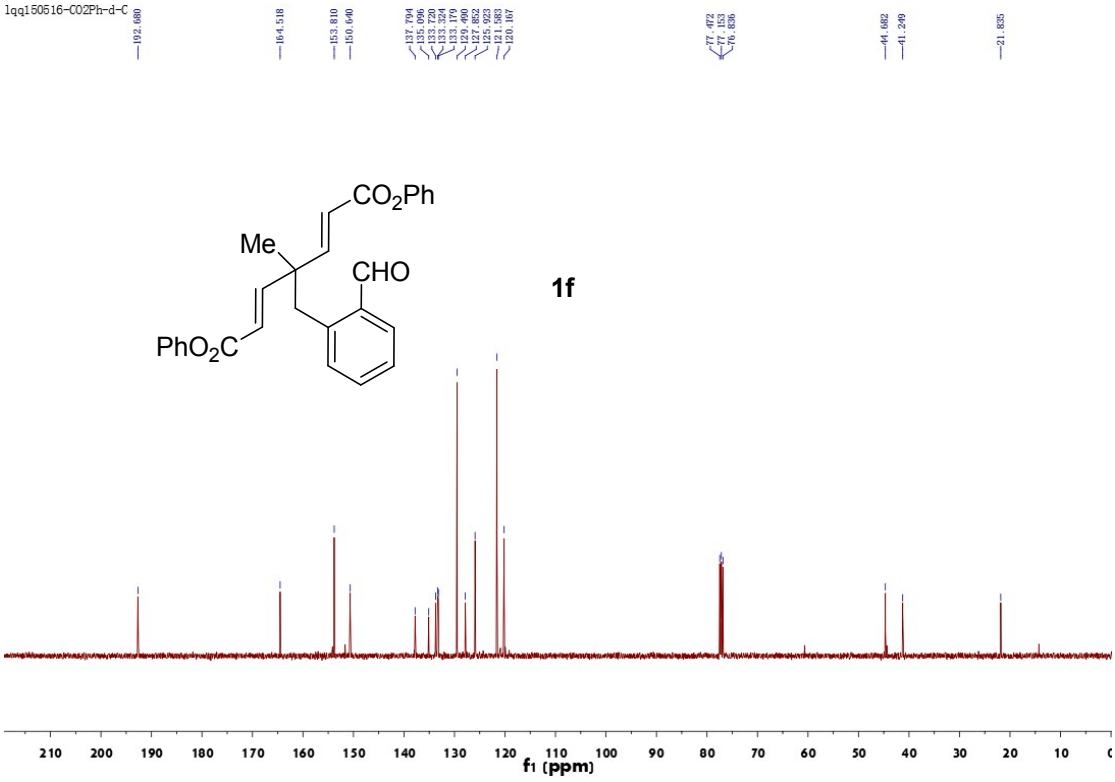

lqq150106-2
CO2Et
Ph
CHO
EtO2C
1d
f1 (ppm)

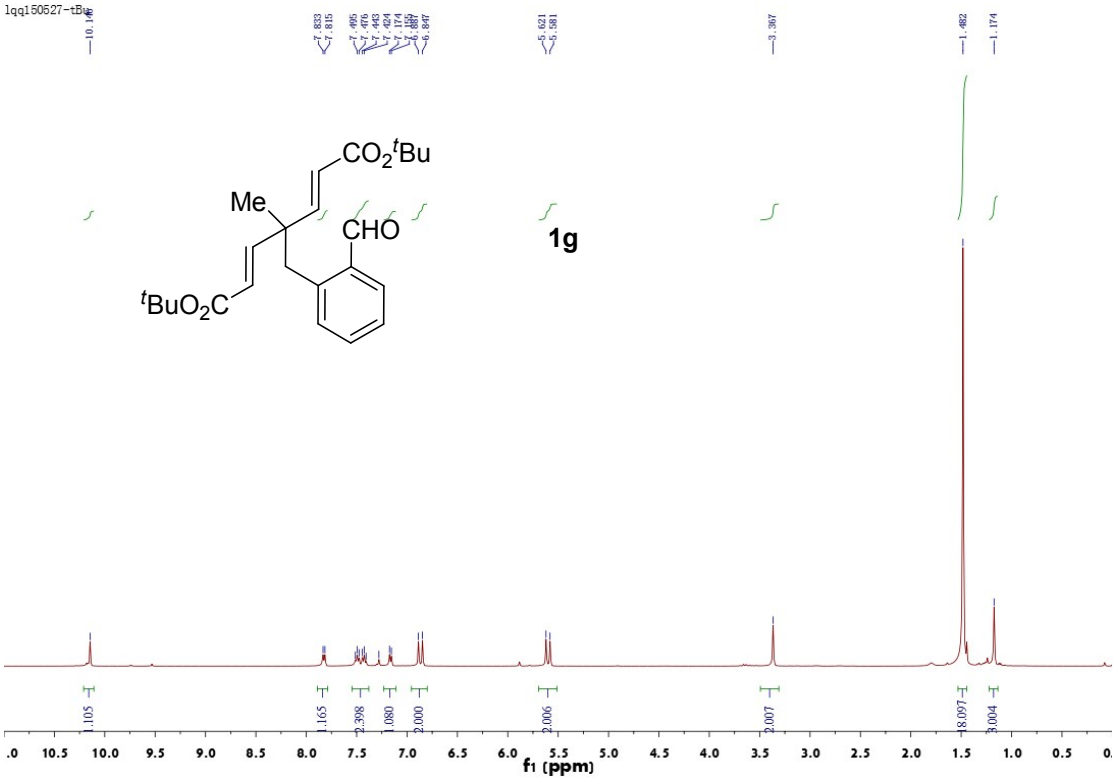

lqq150110-2-s
CO2Et
Ph
CHO
EtO2C
1d
f1 (ppm)


lqq150112-d
10.125
7.826
7.808
7.497
7.489
7.464
7.446
7.267
7.166
7.148
7.023
6.983
5.713
5.673
3.738
3.413
1.197
CO2Me
Me
CHO
MeO2C
1e
1.013
1.091
2.225
1.139
2.002
2.001
6.005
2.017
3.000
f1 (ppm)


lqq150111-me
192.544
166.599
152.202
138.034
134.993
133.345
133.197
133.091
127.630
120.248
77.367
77.049
76.732
51.741
44.185
41.057
21.798
CO2Me
Me
CHO
MeO2C
1e
f1 (ppm)


lqq150516-ph2
10.190
7.834
7.817
7.523
7.506
7.475
7.456
7.385
7.367
7.254
7.222
7.139
7.121
5.956
5.916
3.598
1.317
CO2Ph
Me
CHO
PhO2C
1f
1.000
1.003
6.001
9.000
2.009
2.000
3.330
f1 (ppm)


lqq150516-CO2Ph-d-C
192.680
164.518
153.810
150.640
137.794
135.796
133.720
133.324
133.179
130.490
127.852
125.923
121.583
120.167
77.472
77.153
76.836
44.662
41.249
21.835
CO2Ph
Me
CHO
PhO2C
1f
f1 (ppm)


lqq150527-tBu
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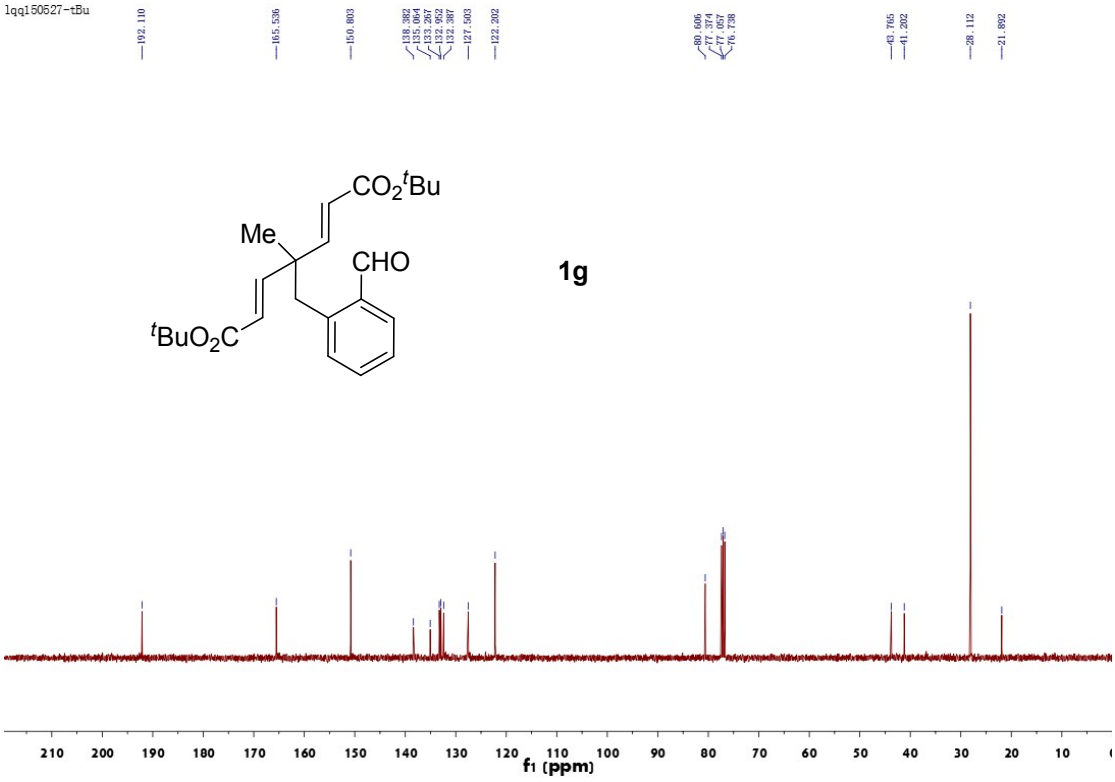
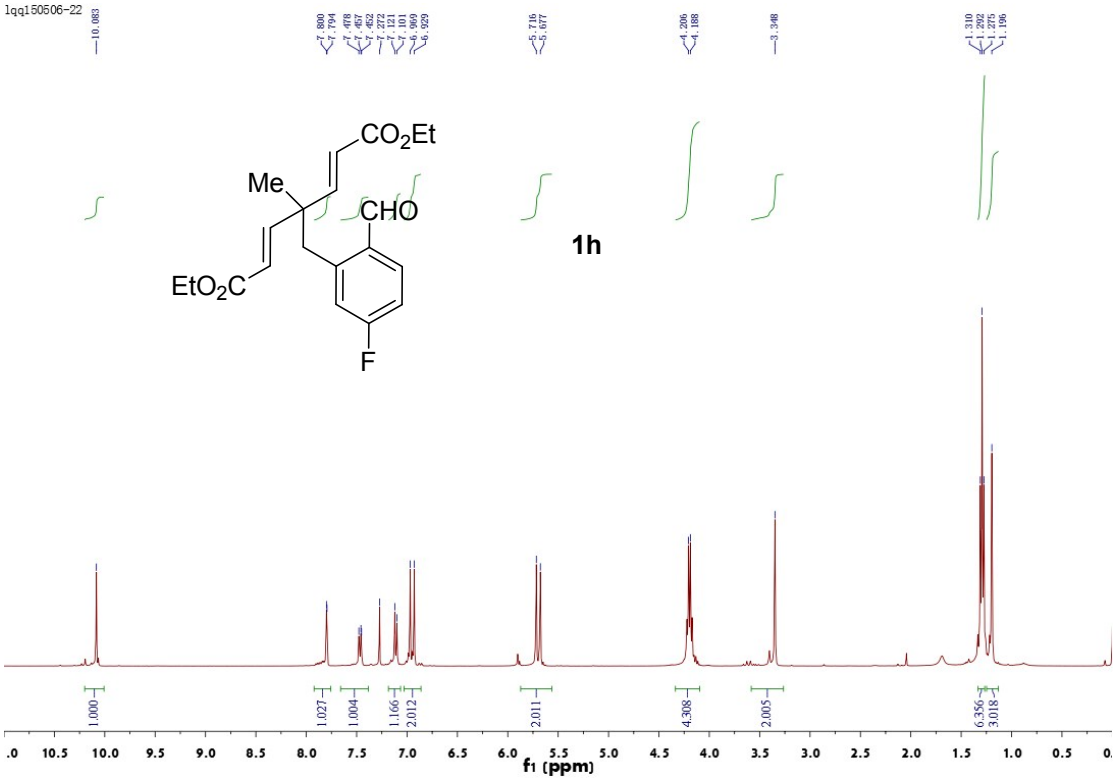
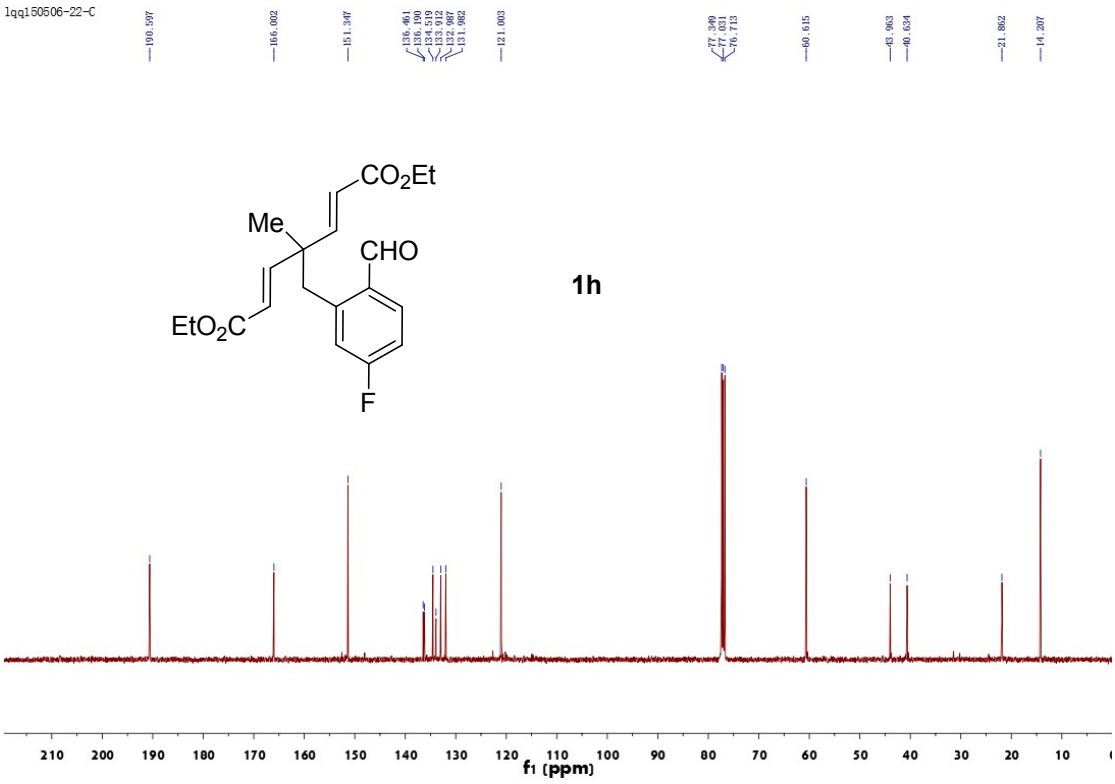
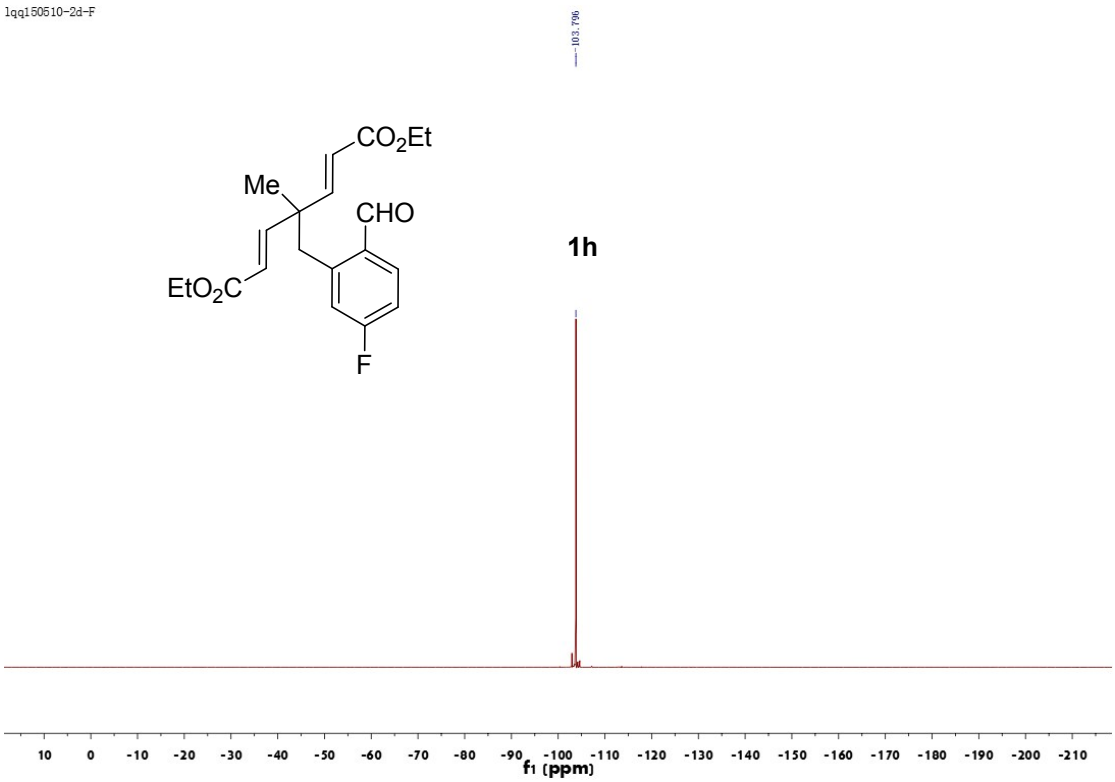
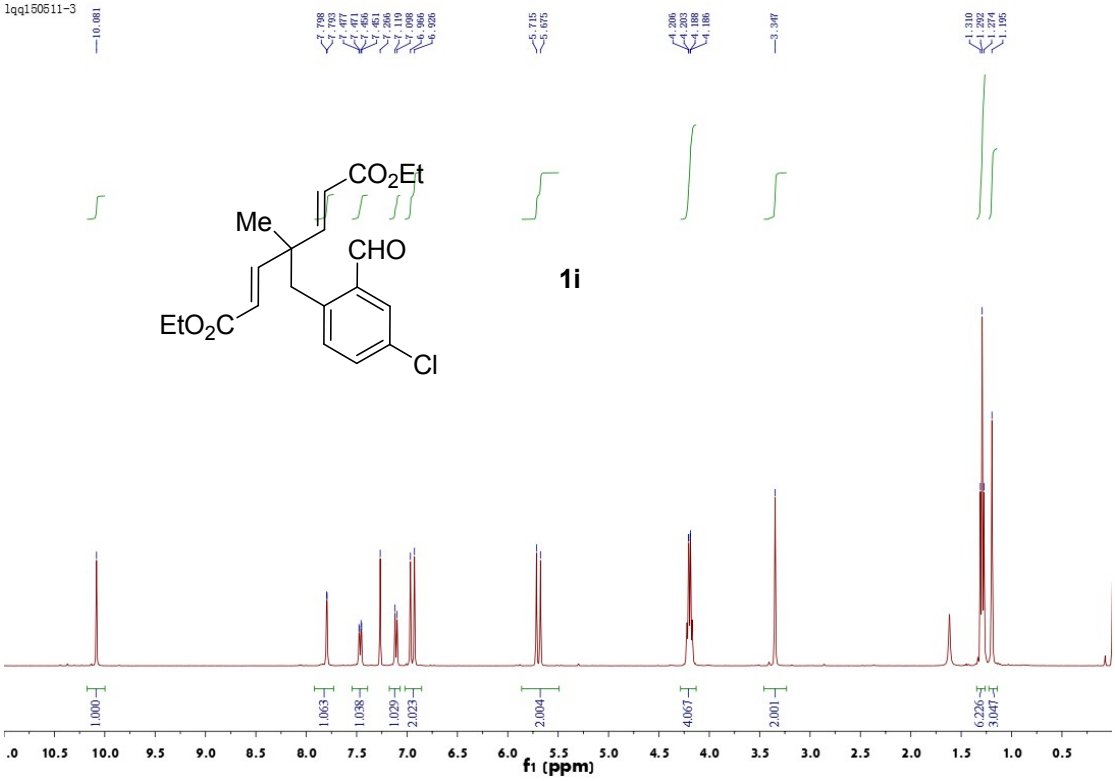
7.833
7.815
7.496
7.476
7.443
7.424
7.174
7.155
6.887
6.847
5.621
5.581
3.367
1.482
1.174
CO2tBu
Me
CHO
tBuO2C
1g
1.105
1.165
2.398
1.080
2.000
2.006
2.007
18.097
3.004
f1 (ppm)


lqq150527-tBu
192.110
165.536
150.803
138.382
135.064
133.267
132.652
132.387
127.603
122.202
80.606
77.374
77.057
76.738
63.765
41.202
28.112
21.892
CO2tBu
Me
CHO
tBuO2C
1g
f1 (ppm)


lqq150506-22
CO2Et
Me
CHO
EtO2C
F
1h
f1 (ppm)


lqq150506-22-C
CO2Et
Me
CHO
EtO2C
F
1h
f1 (ppm)


lqq150510-2d-F
-103.796
CO2Et
Me
CHO
EtO2C
F
1h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


lqq150511-3
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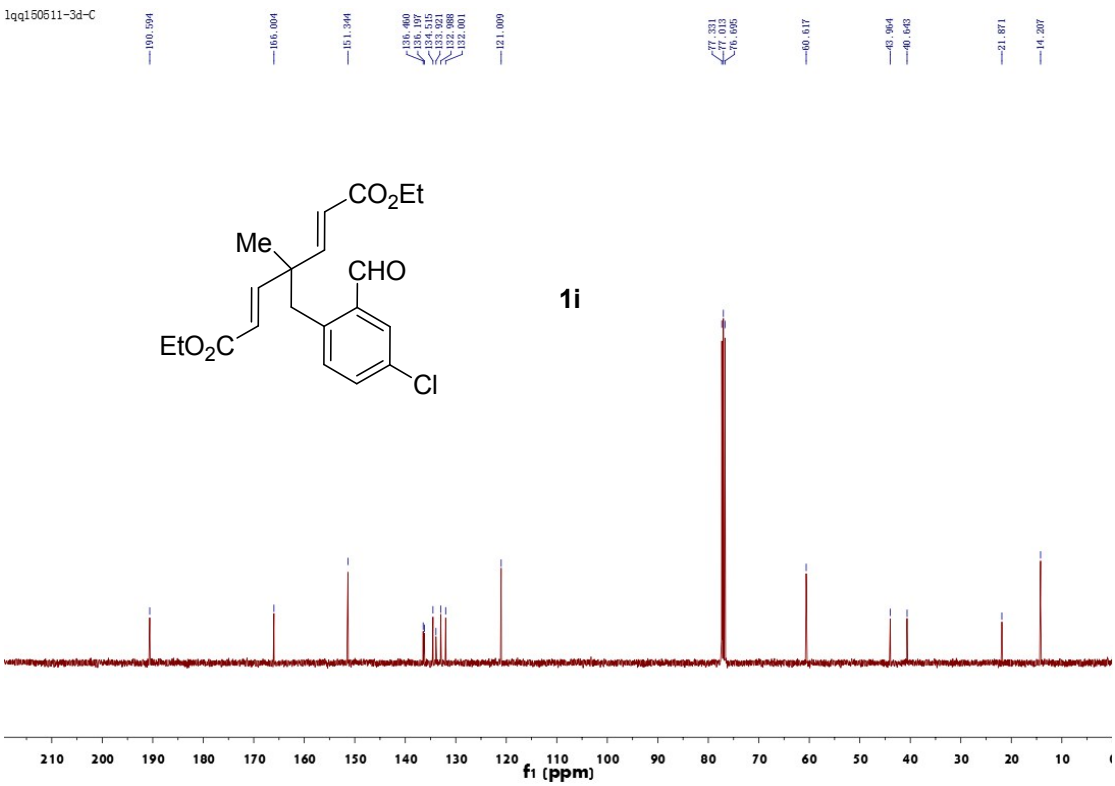
7.798
7.793
7.477
7.471
7.466
7.451
7.266
7.119
7.098
6.966
6.926
5.715
5.675
4.206
4.203
4.188
4.186
3.947
1.310
1.292
1.274
1.195
CO2Et
Me
CHO
EtO2C
Cl
1i
1.000
1.063
1.038
1.029
2.023
2.004
4.067
2.001
6.226
3.047
f1 (ppm)


lqq150511-3d-C
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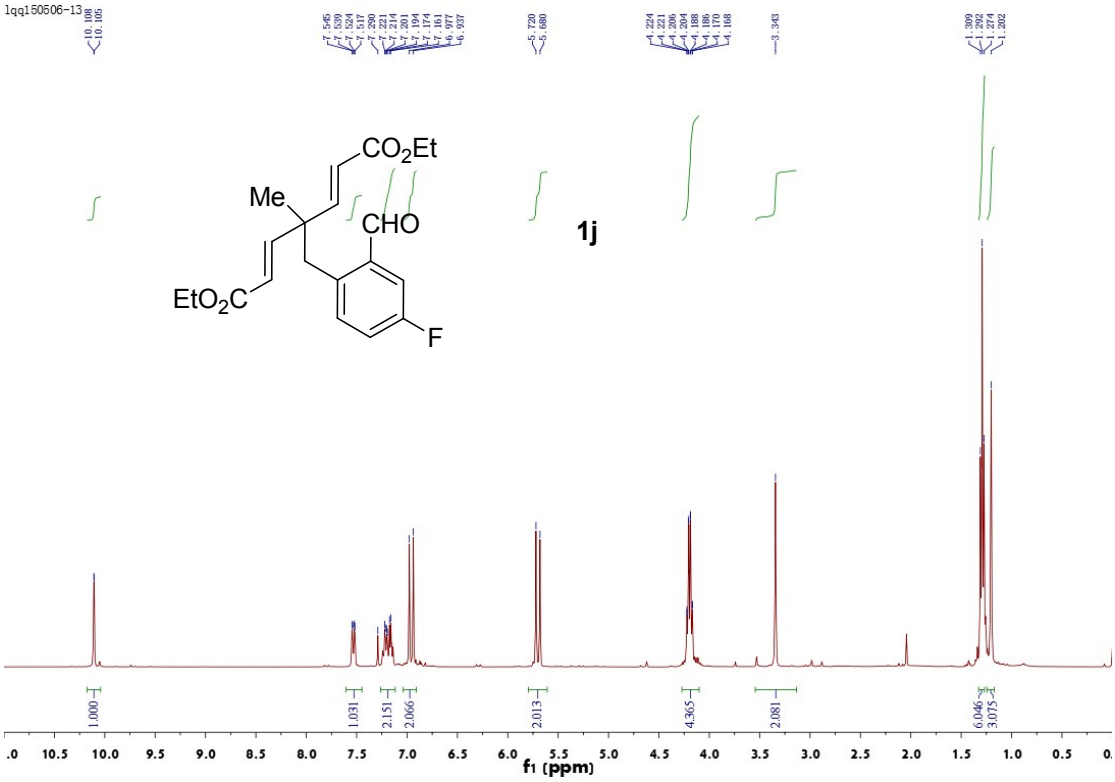
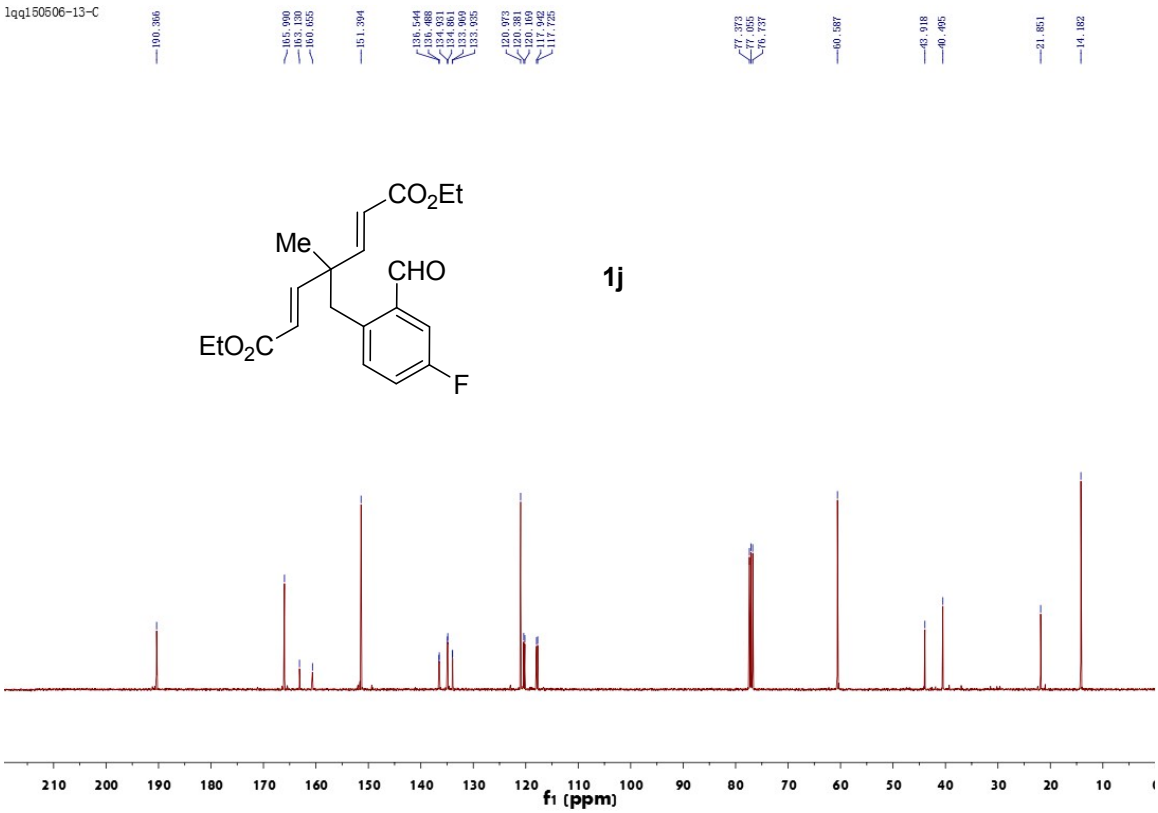
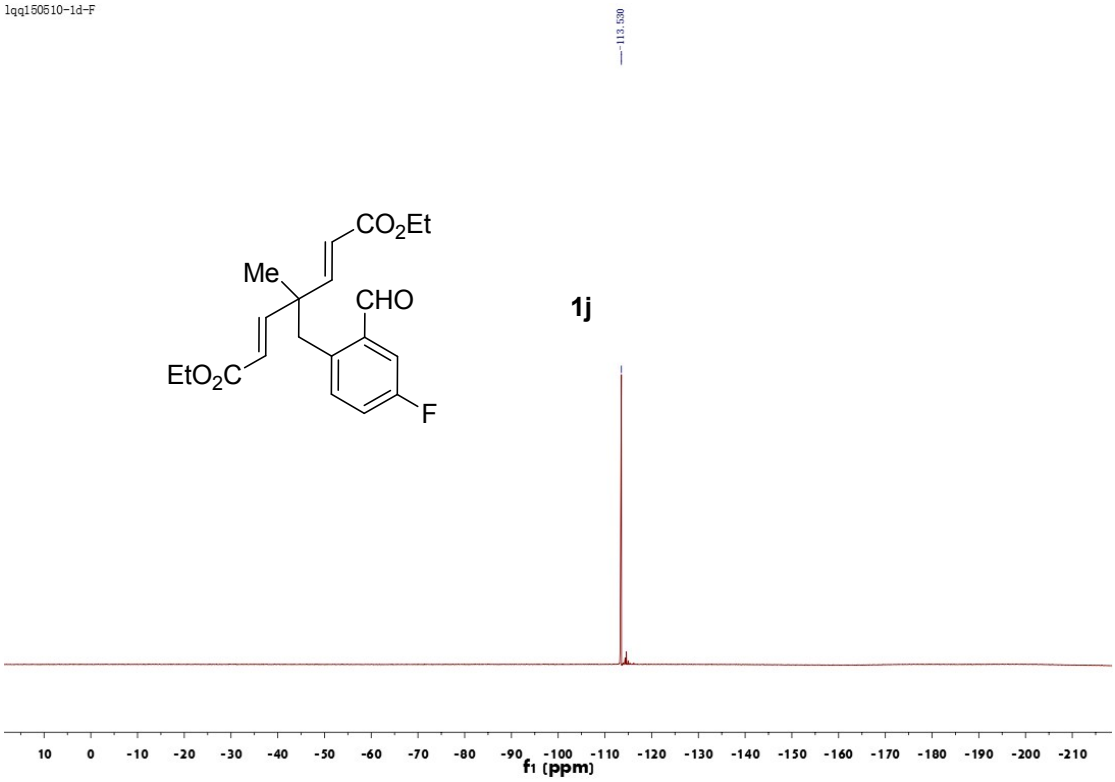
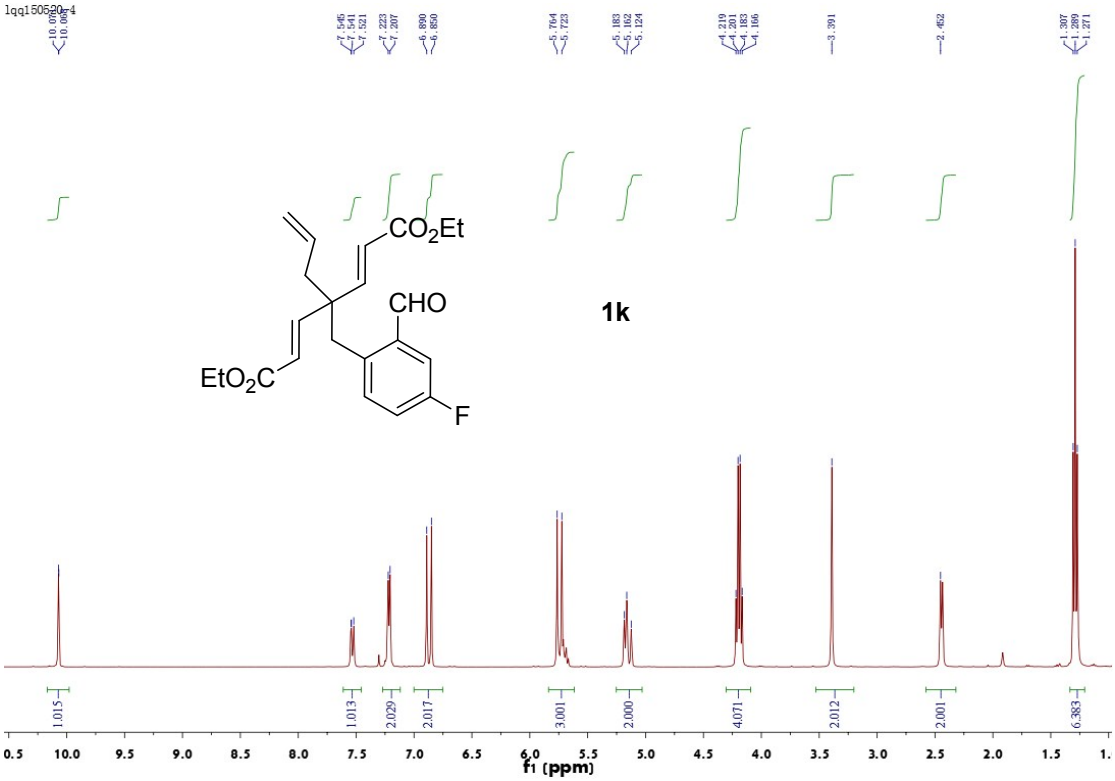
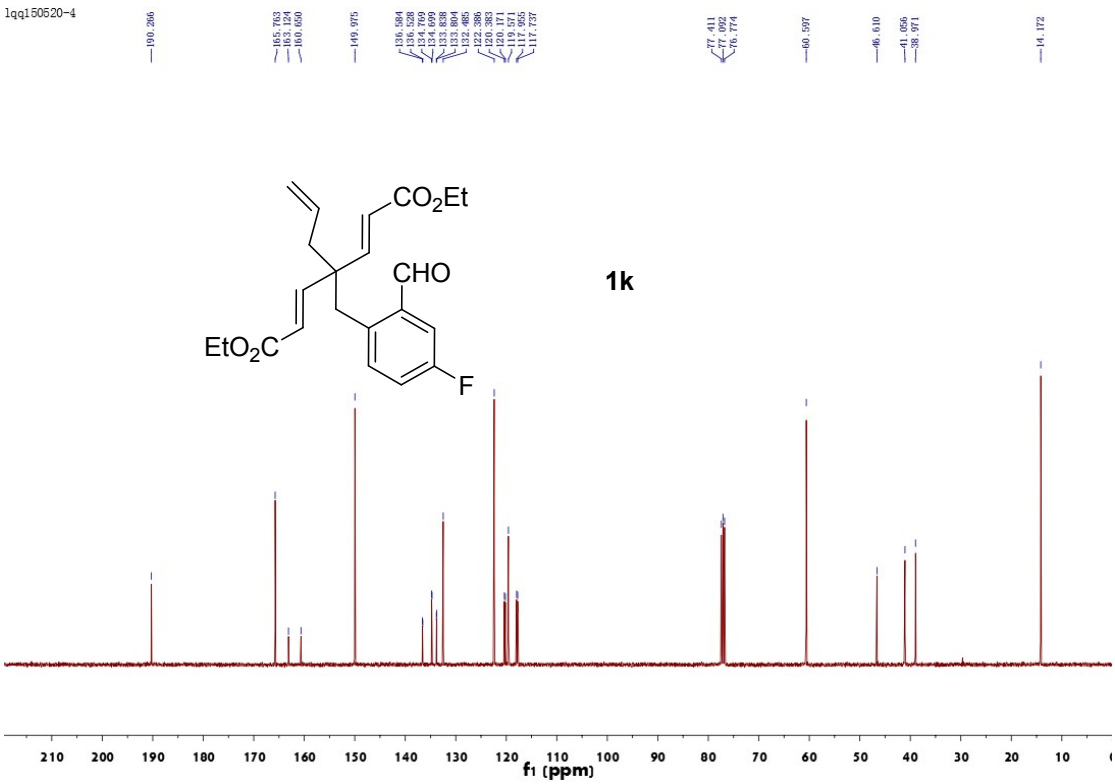
151.344
136.460
136.197
134.515
133.921
132.888
132.601
121.009
77.331
77.013
76.695
60.617
43.964
40.643
21.871
14.207
CO2Et
Me
CHO
EtO2C
Cl
1i
f1 (ppm)

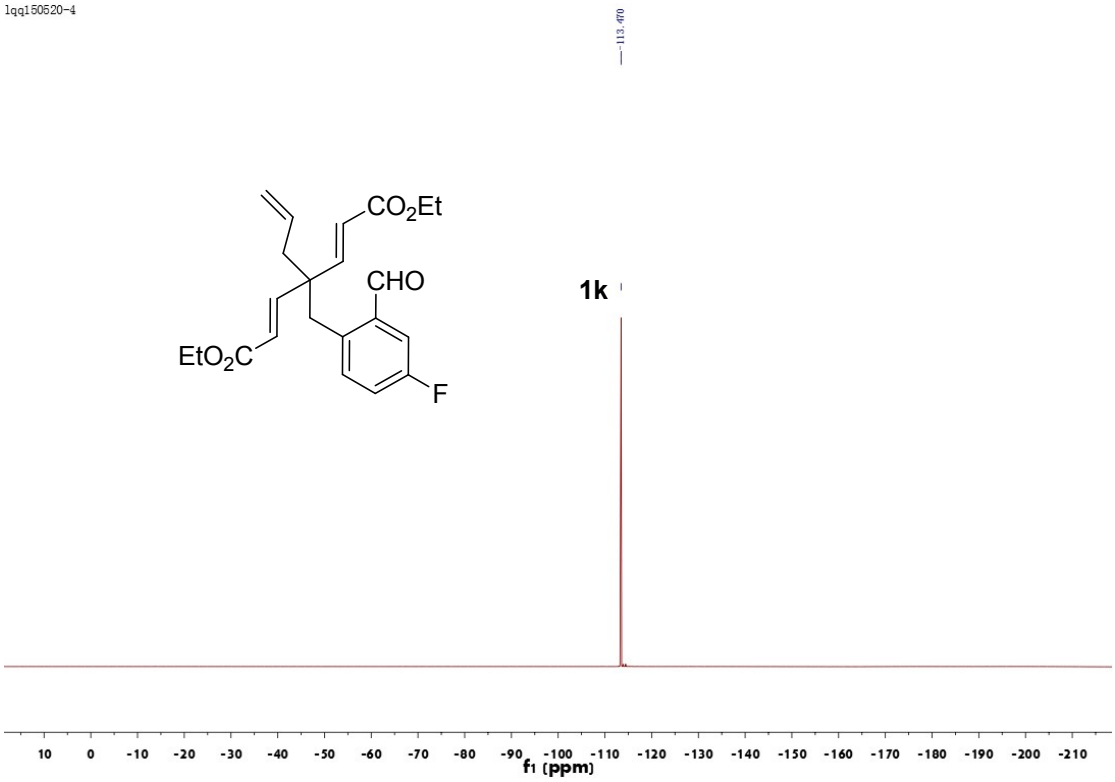

lqq150506-13
CO2Et
Me
CHO
EtO2C
F
1j
f1 (ppm)

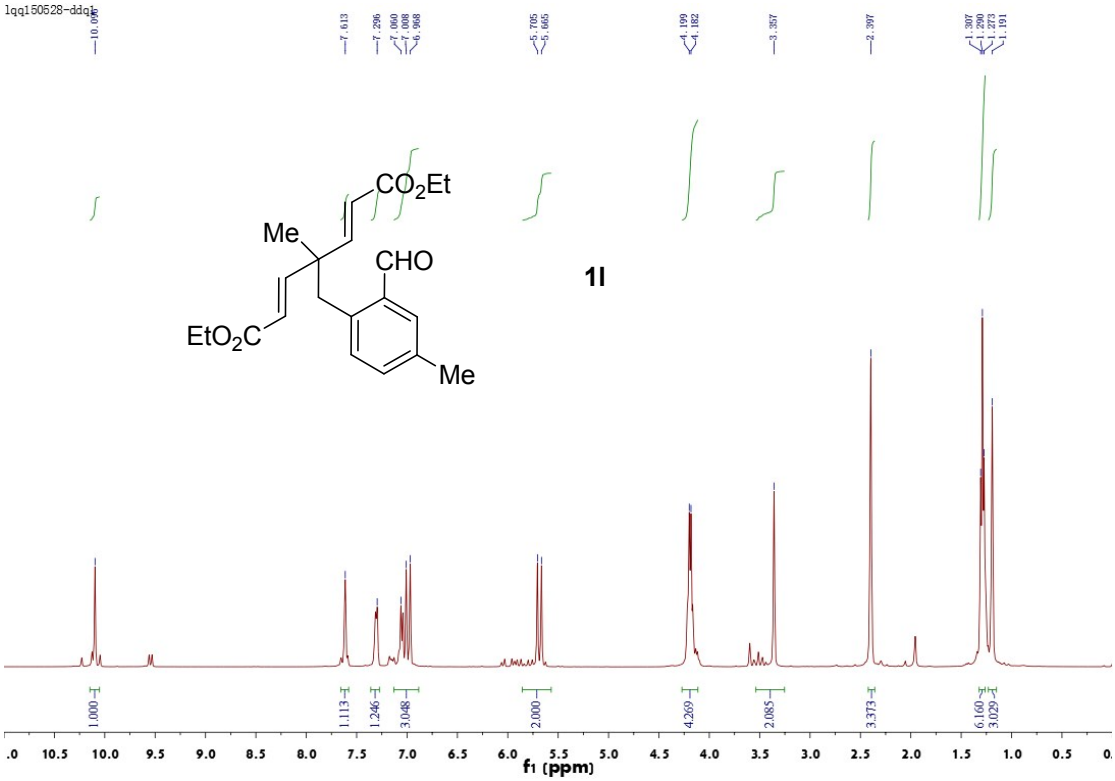

lqq150506-13-C
CO2Et
Me
CHO
EtO2C
F
1j
f1 (ppm)


lqq150510-1d-F
-113.530
CO2Et
Me
CHO
EtO2C
F
1j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


lqq150520-4
CO2Et
CHO
EtO2C
F
1k
f1 (ppm)


lqq150520-4
CO2Et
CHO
EtO2C
F
1k
f1 (ppm)


lqq150520-4
-113.470
CO2Et
CHO
1k
EtO2C
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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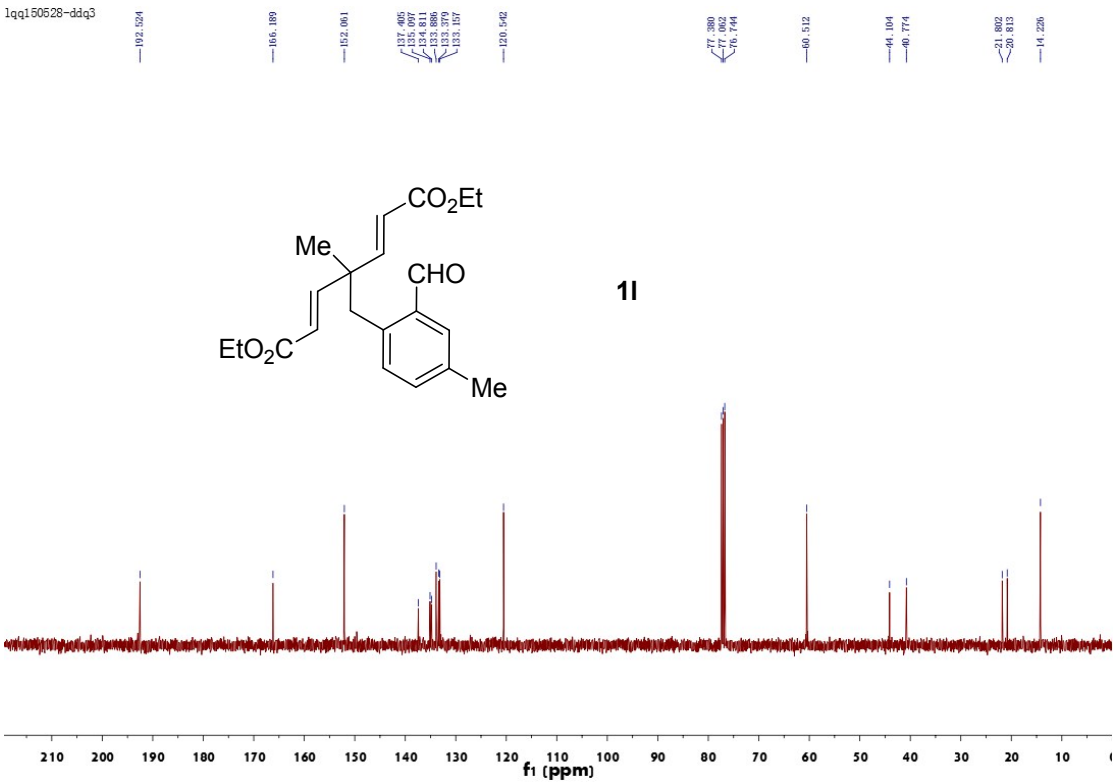
7.613
7.296
7.060
7.008
6.968
5.705
5.665
4.199
4.182
3.357
2.397
1.307
1.290
1.273
1.191
CO2Et
Me
CHO
EtO2C
Me
1l
1.000
1.113
1.246
3.048
2.000
4.269
2.085
3.373
6.160
3.029
f1 (ppm)


lqq150528-ddq3
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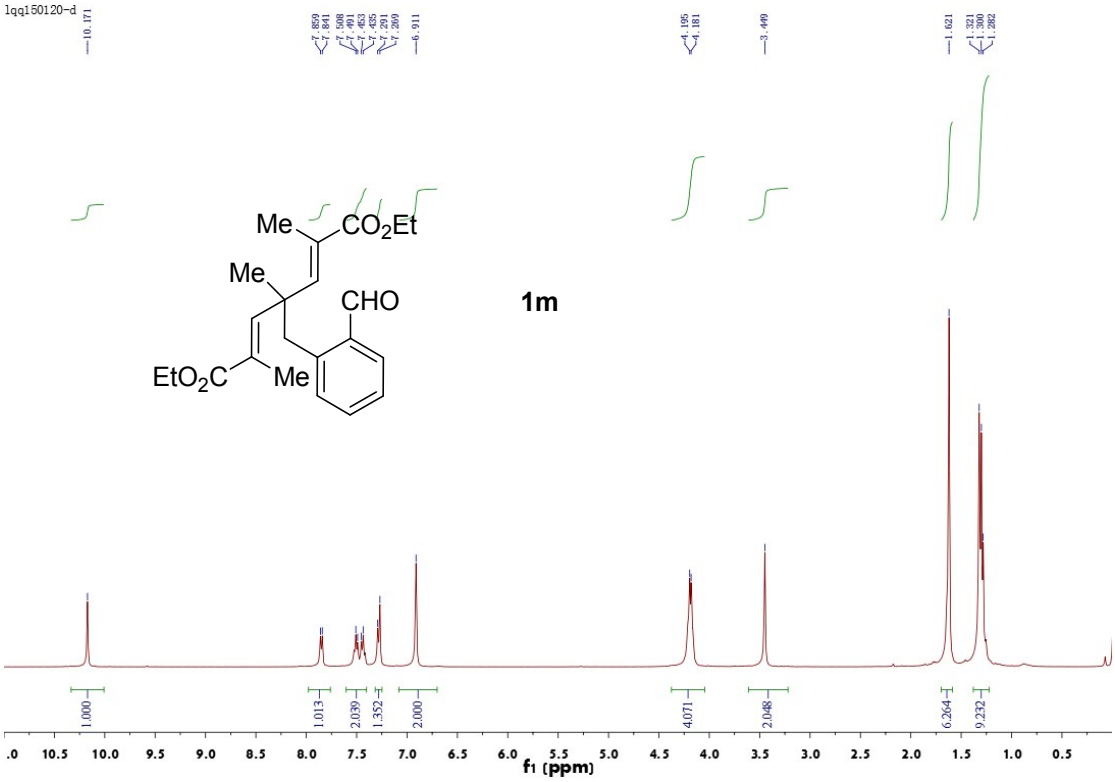
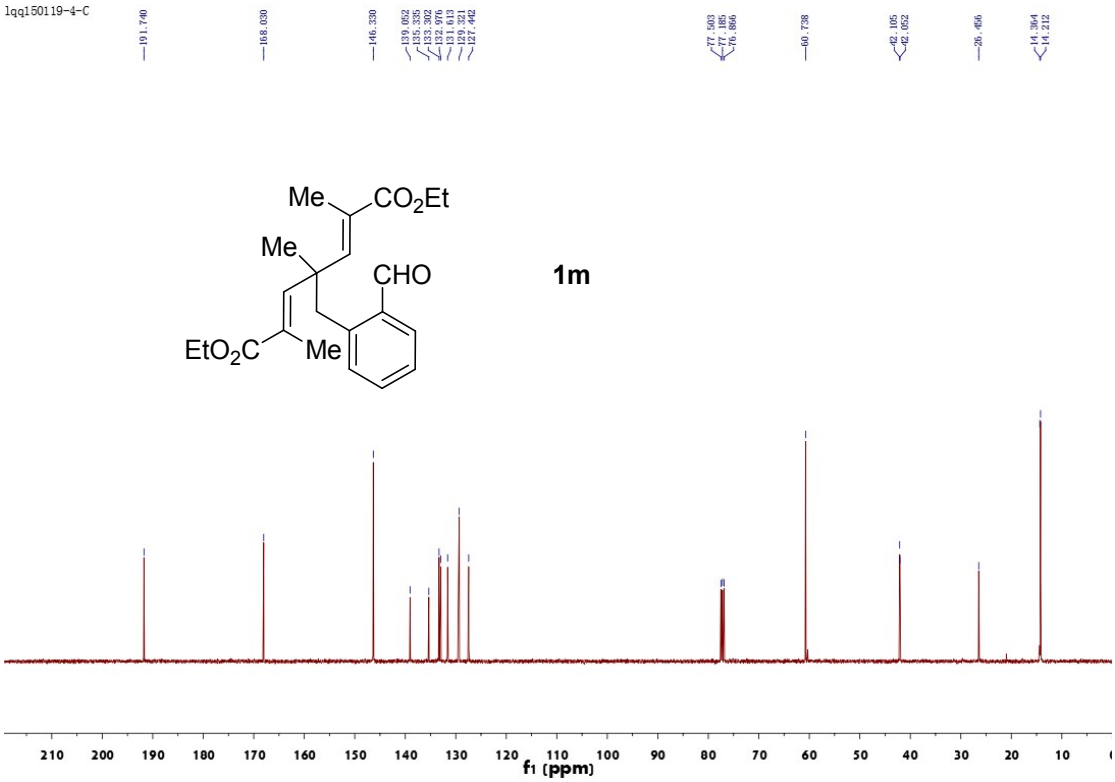
166.189
152.061
137.405
135.097
134.811
133.888
133.379
133.157
120.542
77.380
77.062
76.744
60.512
44.104
40.774
21.802
20.813
14.226
CO2Et
Me
CHO
EtO2C
Me
1l
f1 (ppm)


lqq150120-d
Me
CO2Et
Me
CHO
EtO2C
Me
1m
f1 (ppm)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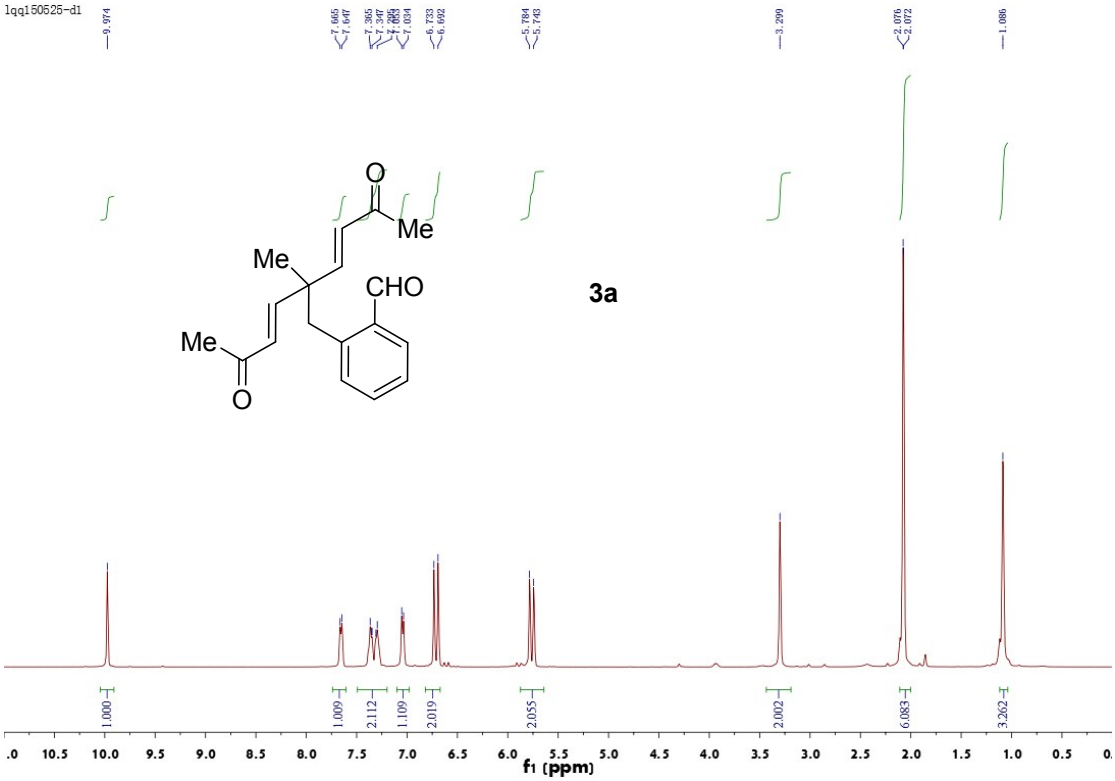
Me
CO2Et
Me
CHO
EtO2C
Me
1m
f1 (ppm)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9.974
7.665
7.647
7.365
7.347
7.283
7.263
7.034
6.733
6.692
5.784
5.743
3.299
2.076
2.072
1.086
O
Me
Me
CHO
Me
O
3a
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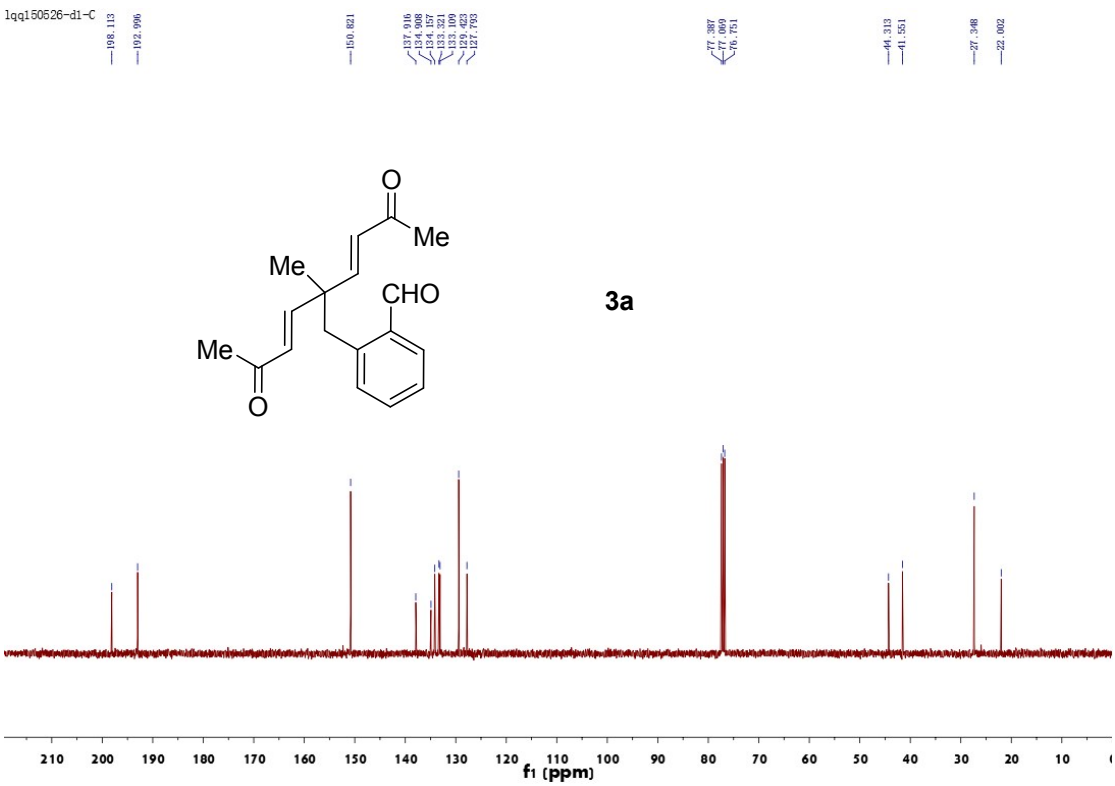
1.009
2.112
1.109
2.019
2.055
2.002
6.083
3.262
f1 (ppm)


lqq150526-d1-C
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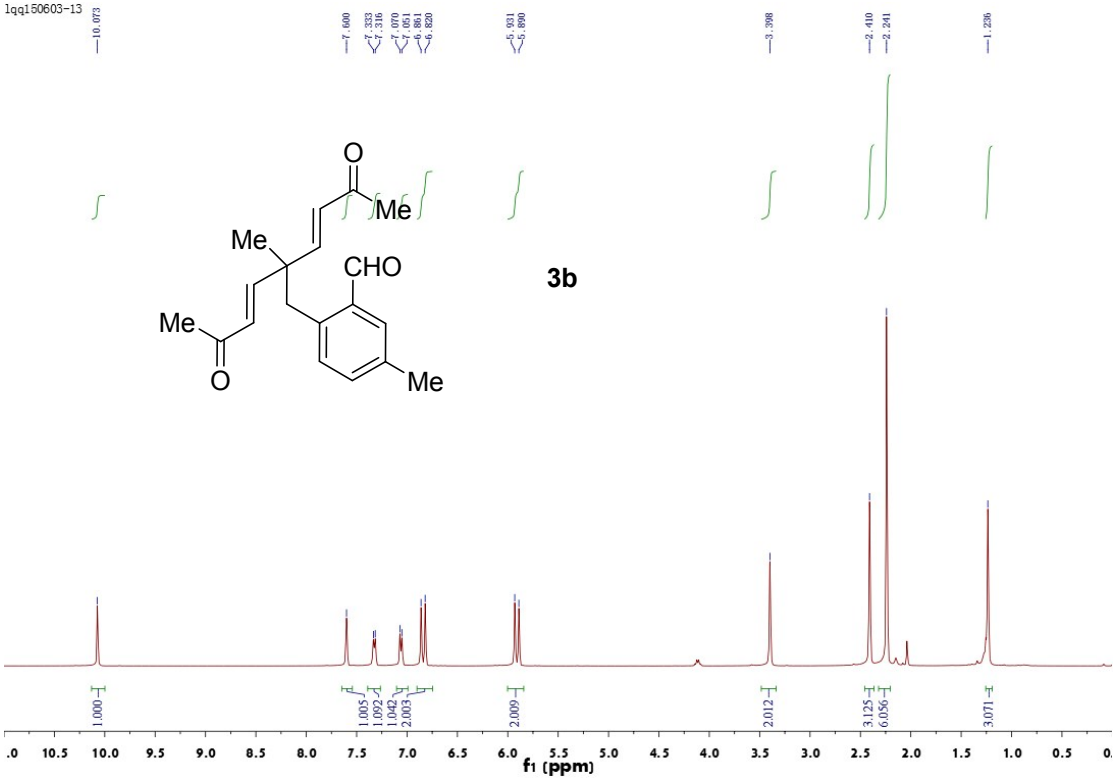
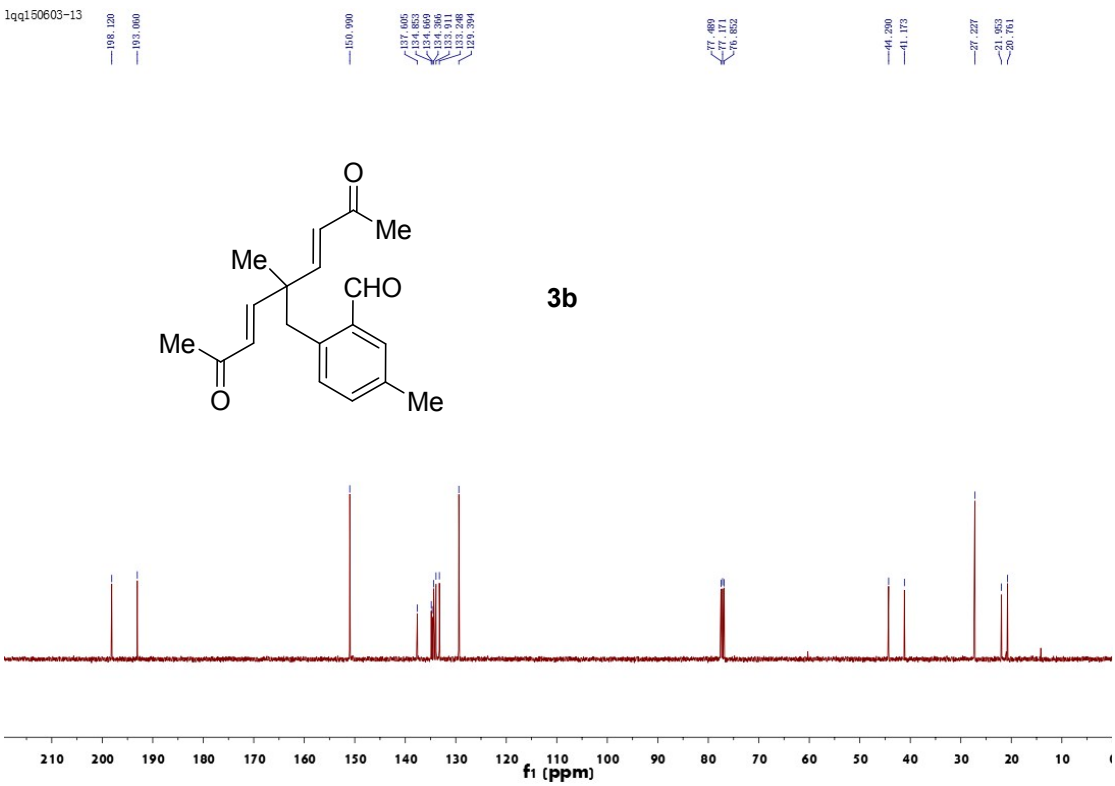
150.821
137.916
134.908
134.157
133.321
133.109
130.455
127.793
77.387
77.069
76.751
44.313
41.551
27.348
22.002
O
Me
Me
CHO
Me
O
3a
f1 (ppm)


lqq150603-13
10.073
7.600
7.333
7.316
7.070
7.051
6.861
6.820
5.931
5.890
3.398
2.410
2.241
1.236
O
Me
Me
CHO
Me
O
Me
3b
1.000
1.005
1.092
1.042
2.003
2.009
2.012
3.125
6.056
3.071
f1 (ppm)


lqq150603-13
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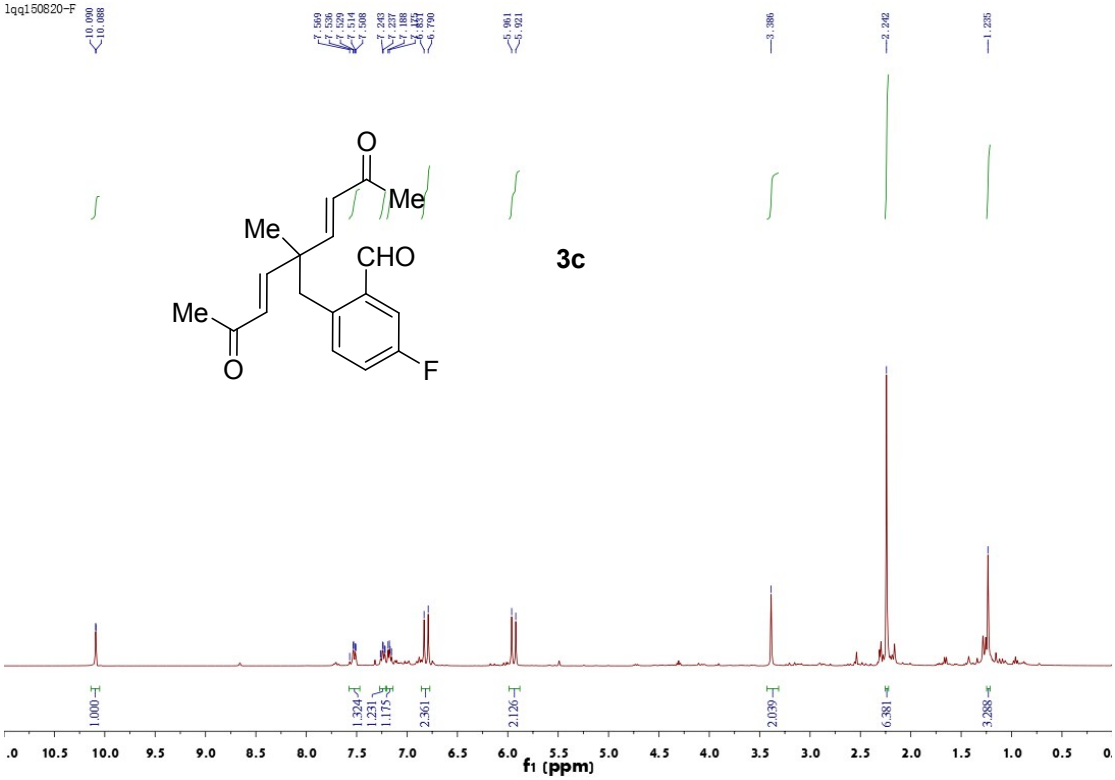
150.990
137.605
134.853
134.669
134.366
133.311
133.248
129.394
77.489
77.171
76.852
44.290
41.173
27.227
21.953
20.761
O
Me
Me
CHO
Me
O
Me
3b
f1 (ppm)


lqq150820-F
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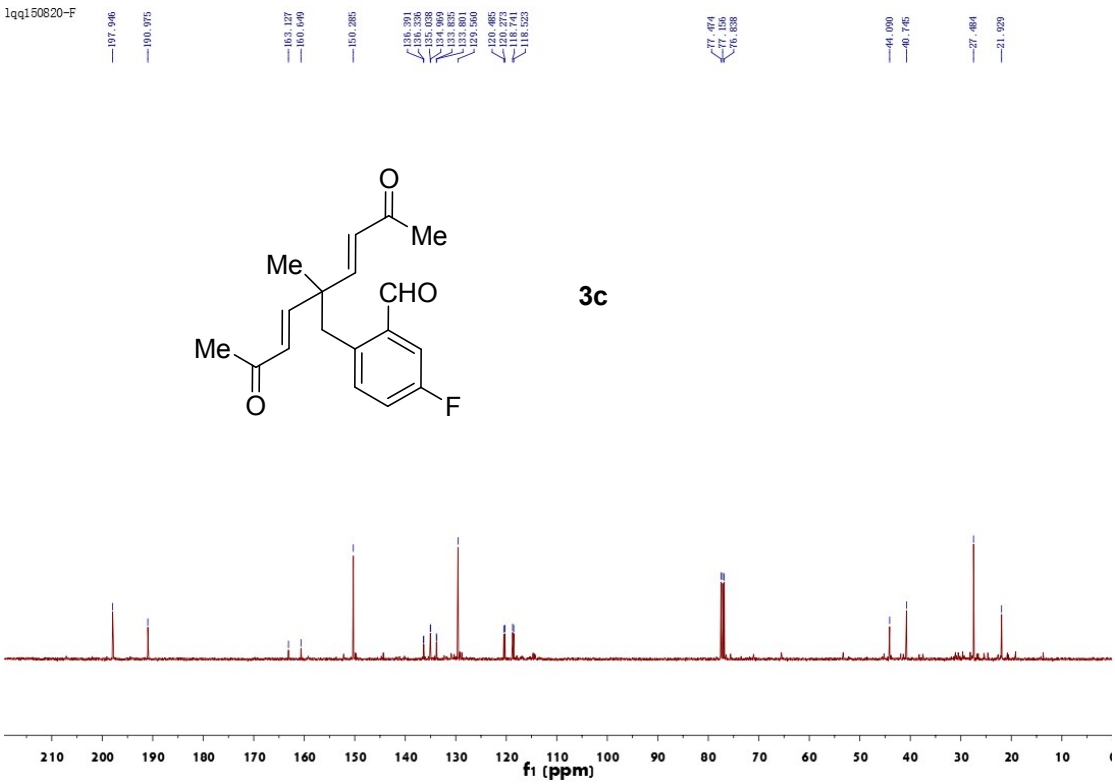
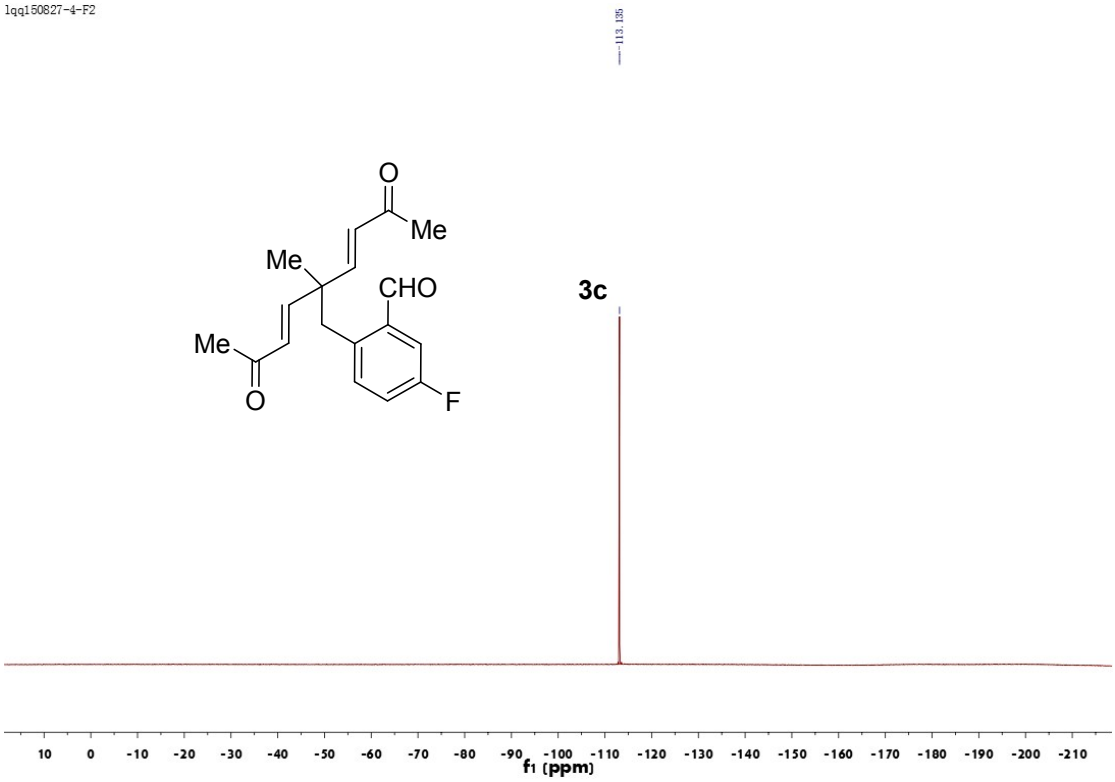
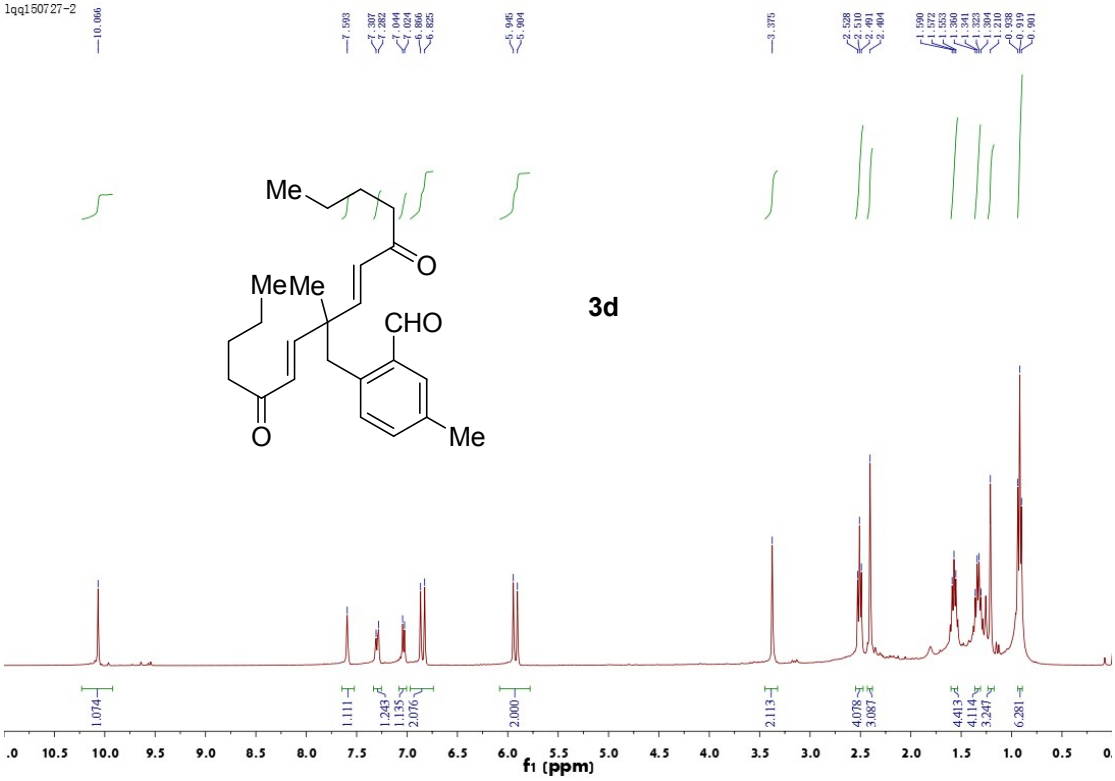
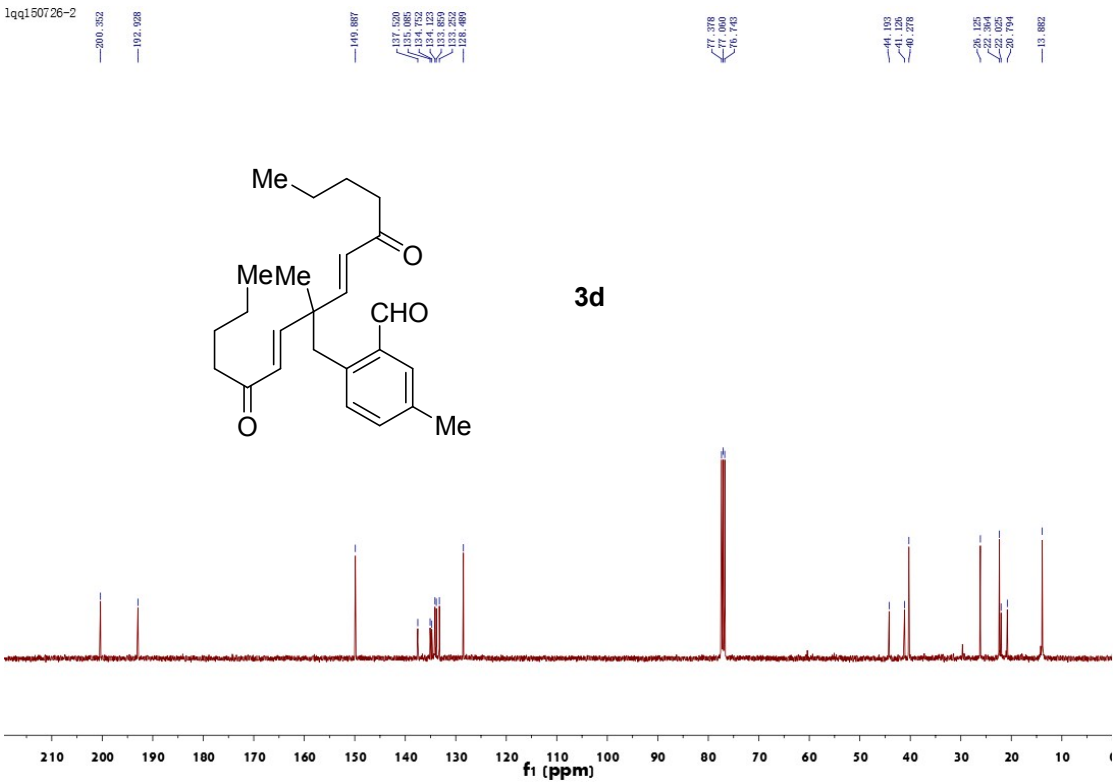
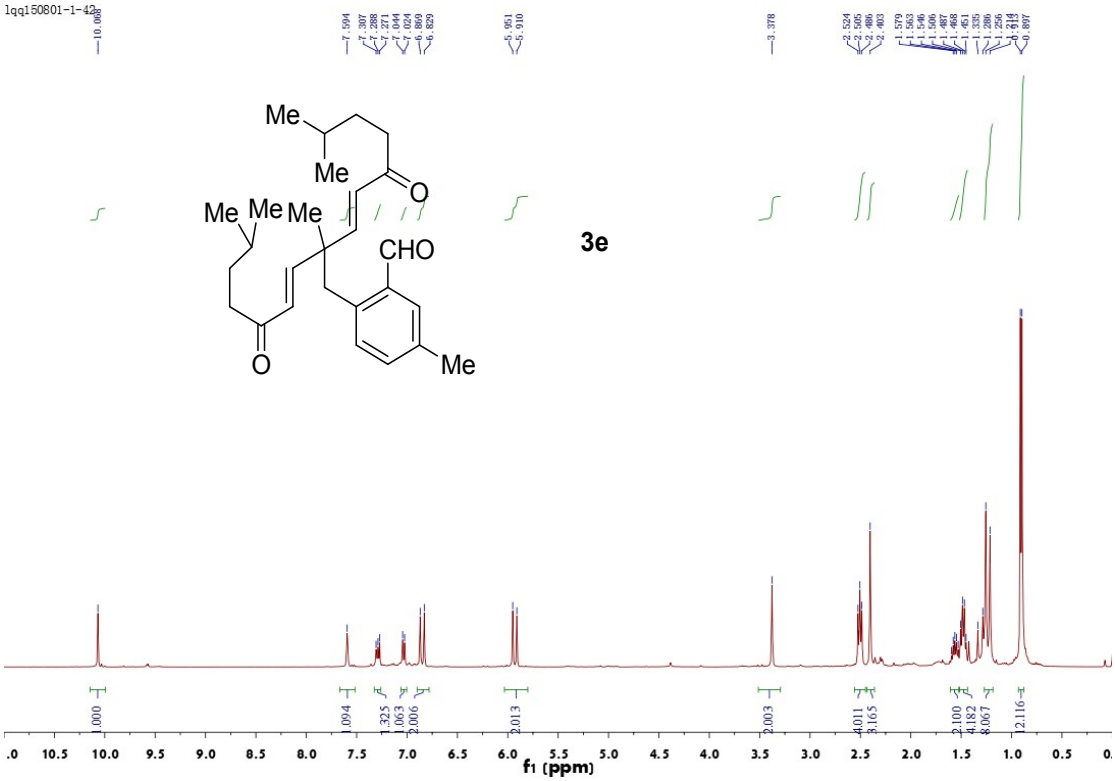
10.088
7.569
7.536
7.529
7.514
7.508
7.243
7.237
7.188
6.790
5.961
5.921
3.386
2.292
1.235
O
Me
Me
CHO
Me
O
F
3c
1.000
1.324
1.231
1.175
2.361
2.126
2.039
6.381
3.288
f1 (ppm)

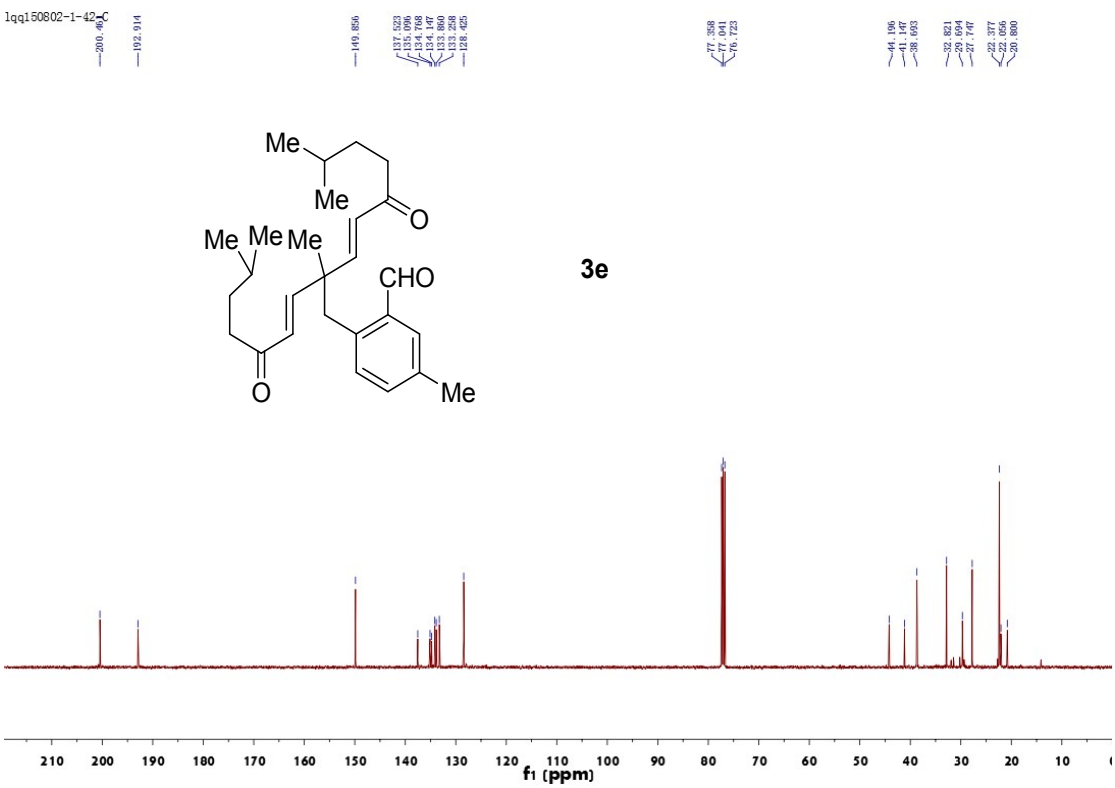

lqq150820-F
197.946
190.975
163.127
160.649
150.285
136.391
136.336
135.638
134.969
133.855
133.801
129.560
120.485
120.273
118.741
118.523
77.474
77.156
76.838
44.090
40.745
27.484
21.929
O
Me
Me
CHO
Me
O
F
3c
f1 (ppm)

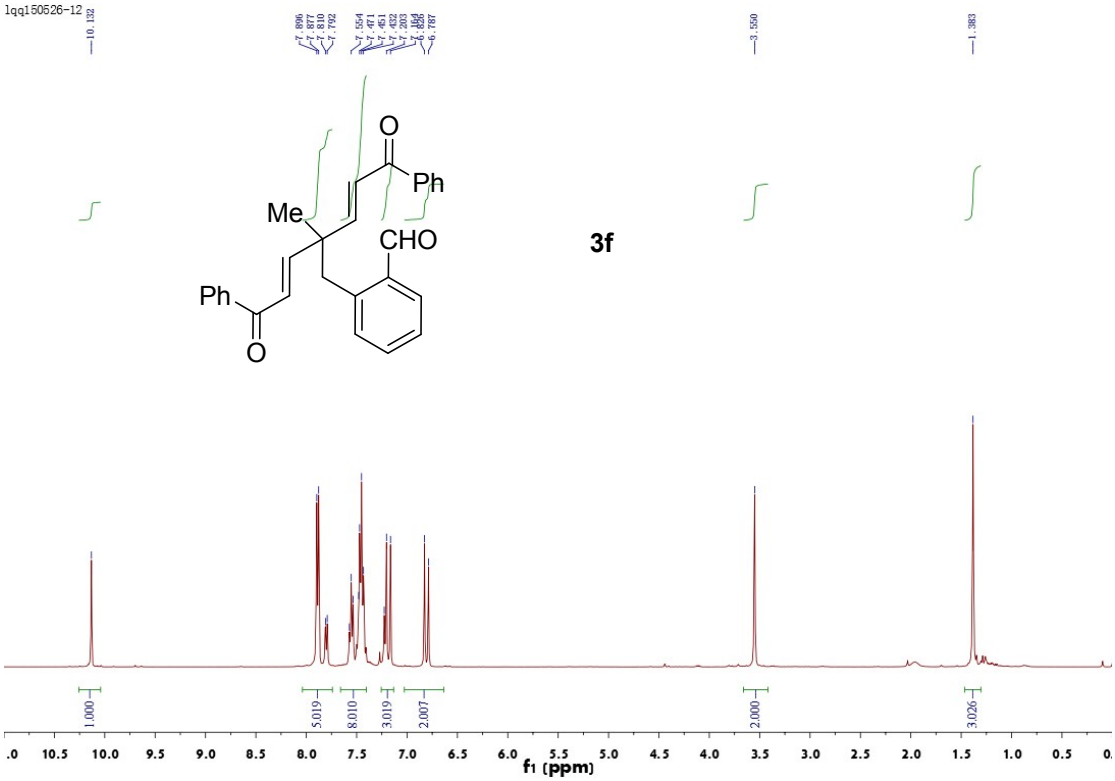

lqq150827-4-F2
-113.135
O
Me
Me
CHO
3c
Me
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

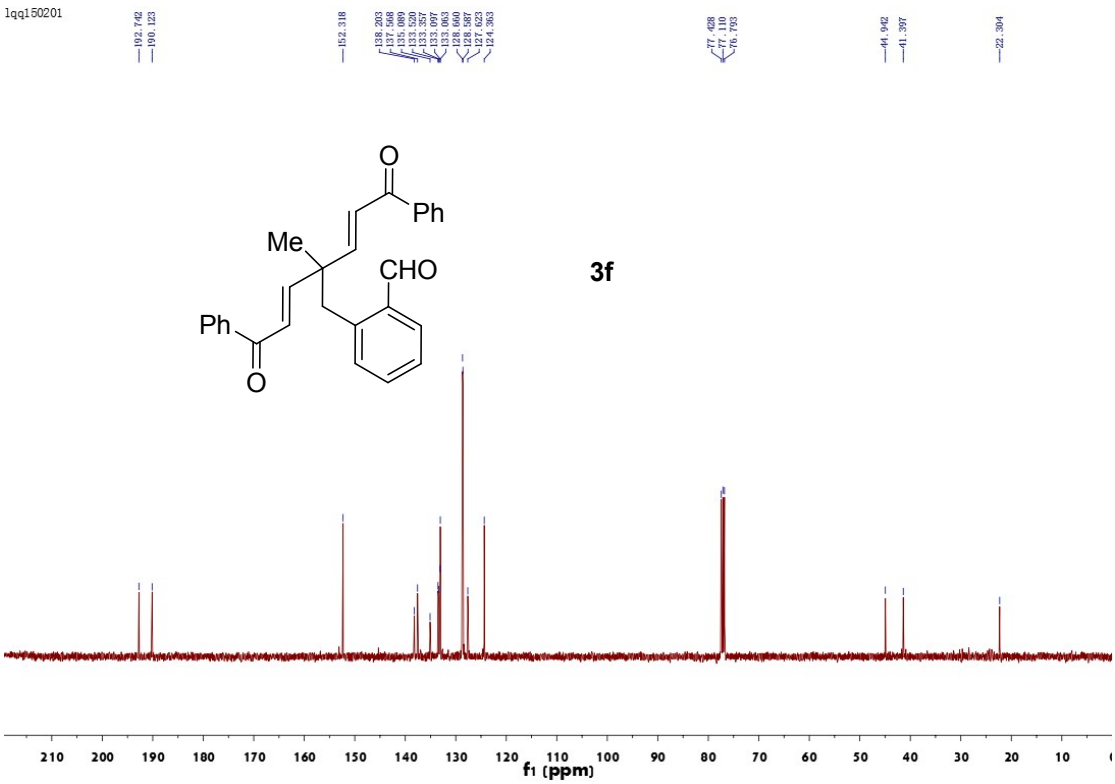

lqq150727-2
Me
O
MeMe
CHO
O
Me
3d
f1 (ppm)

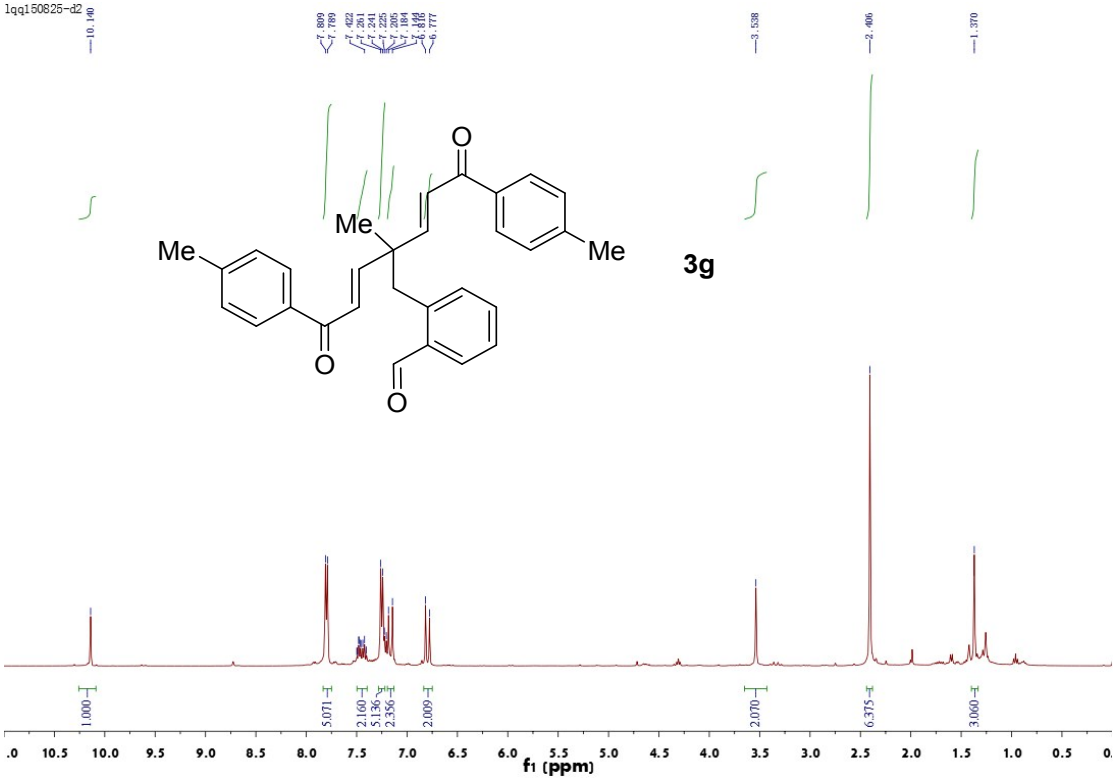

lqq150726-2
Me
O
MeMe
CHO
O
Me
3d
f1 (ppm)

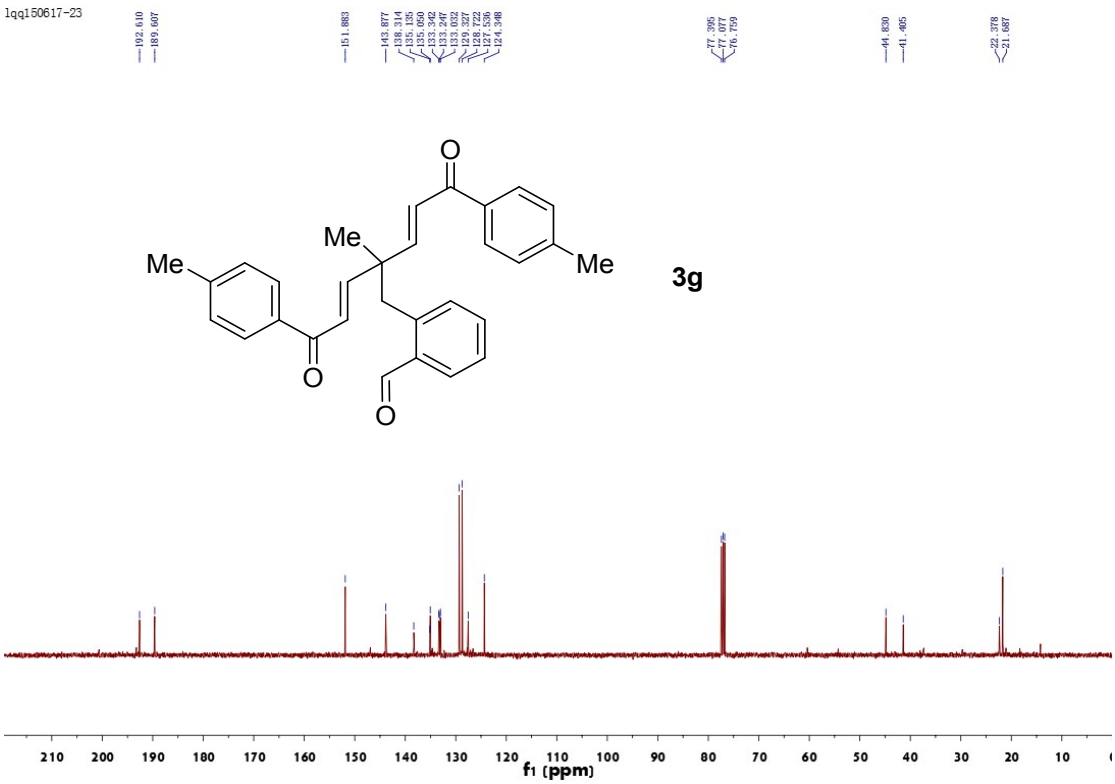

lqq150801-1-42
Me
Me
Me
Me
Me
O
CHO
O
Me
3e
f1 (ppm)

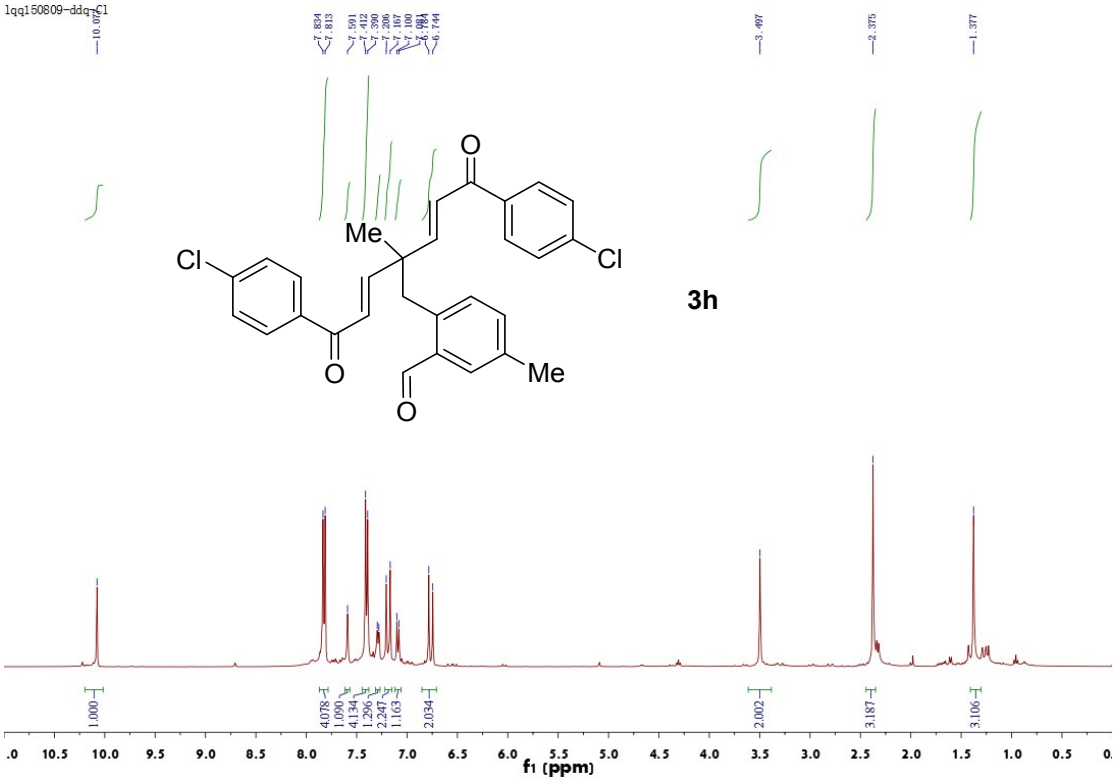

lqq150802-1-42-C
Me
Me
Me
Me
Me
O
CHO
O
Me
3e
f1 (ppm)

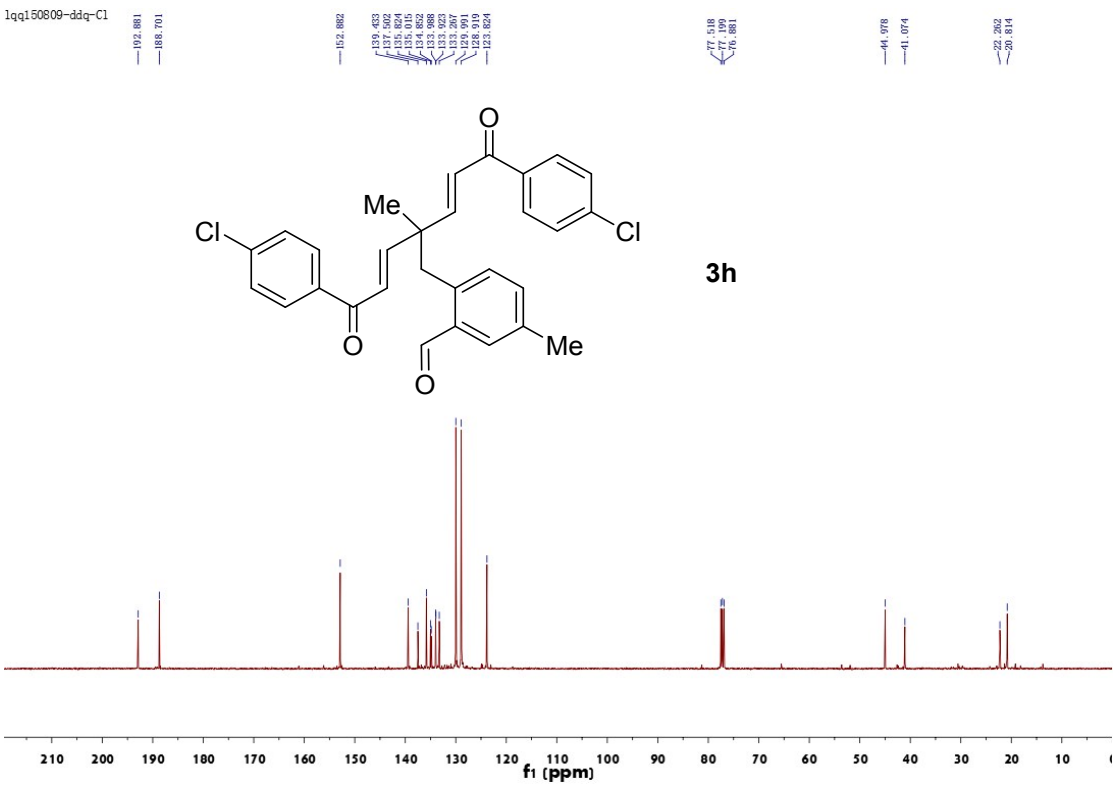

lqq150526-12
10.132
7.896
7.877
7.810
7.792
7.554
7.471
7.451
7.432
7.203
6.787
3.550
1.383
O
Ph
Me
CHO
Ph
O
3f
1.000
5.019
8.010
3.019
2.007
2.000
3.026
f1 (ppm)

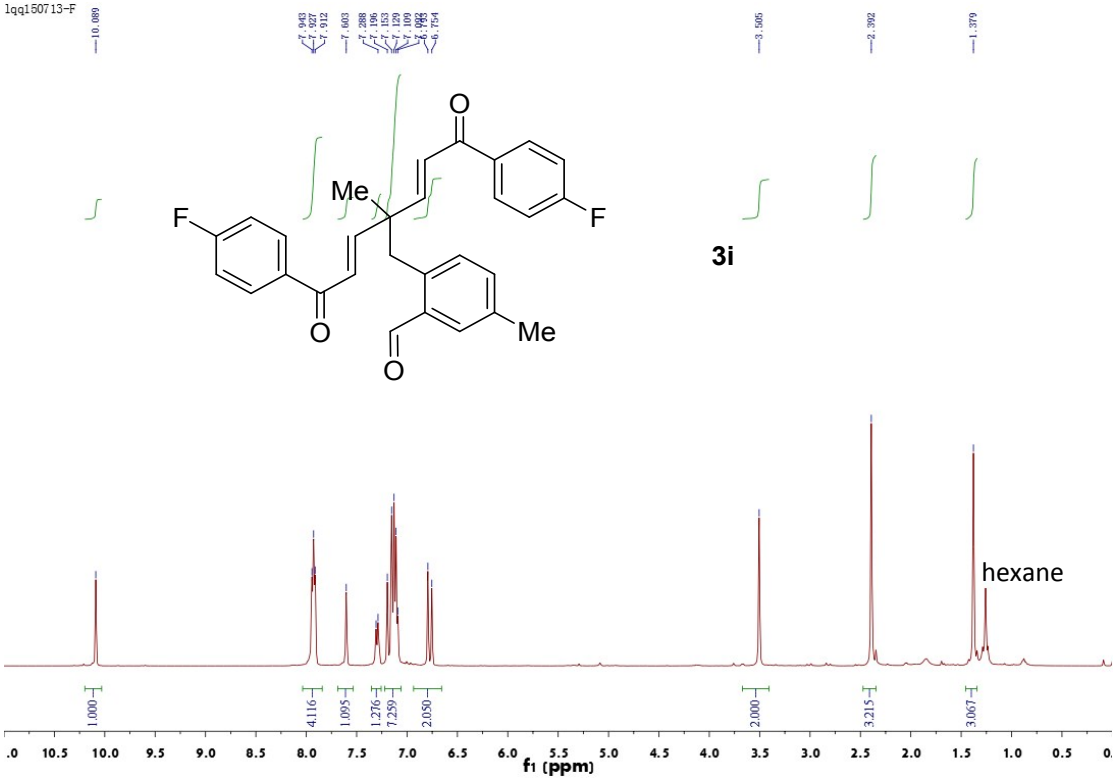

lqq150201
192.742
190.123
152.318
138.203
137.568
135.089
133.520
133.397
133.197
133.063
128.660
128.587
127.923
124.583
77.428
77.110
76.793
44.942
41.397
22.304
O
Ph
Me
CHO
Ph
O
3f
f1 (ppm)

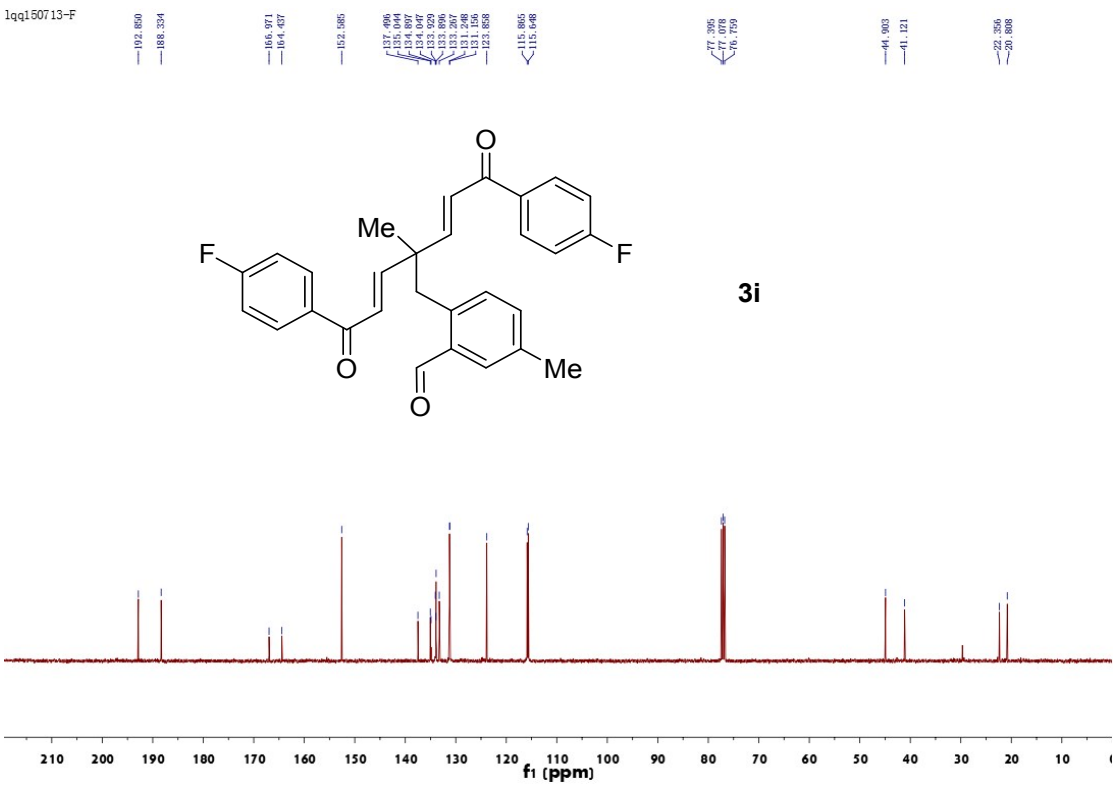

lqq150825-d2
10.140
7.809
7.789
7.422
7.261
7.241
7.225
7.205
7.184
6.777
3.538
2.406
1.370
Me
Me
Me
O
O
O
3g
1.000
5.071
2.160
5.136
2.356
2.009
2.070
6.375
3.060
f1 (ppm)

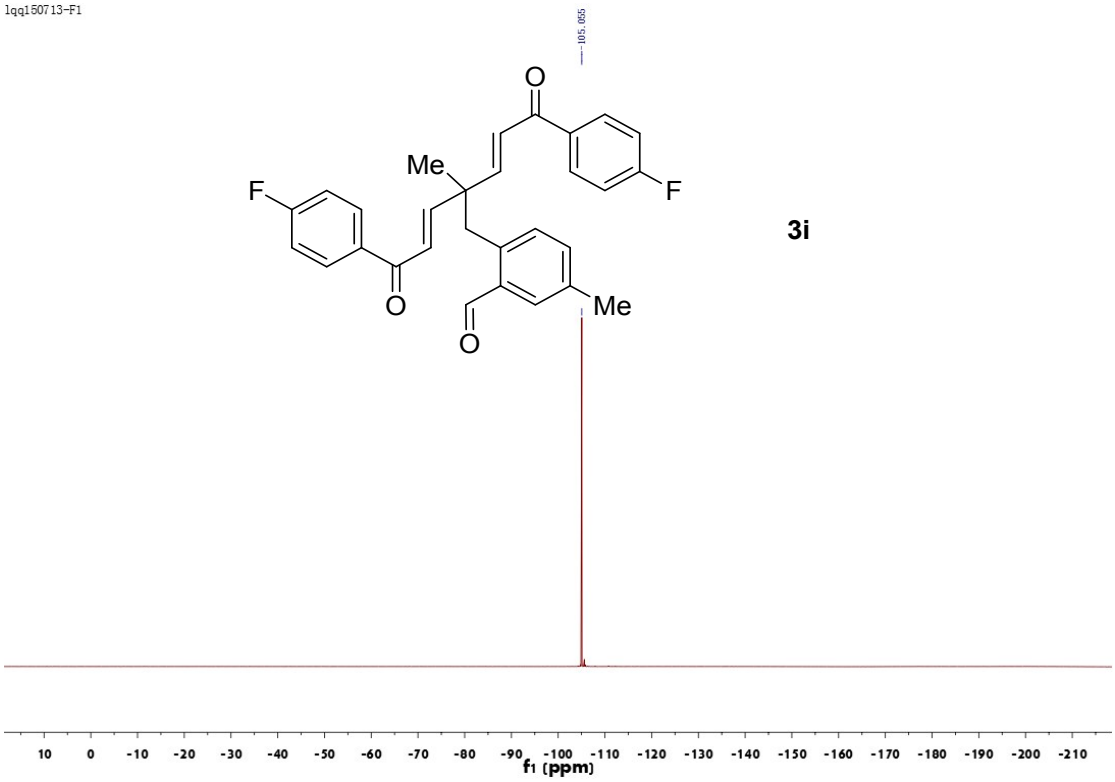

lqq150617-23
192.610
189.697
151.883
143.877
138.314
135.185
133.560
133.342
133.247
133.032
129.327
128.272
127.536
124.348
77.395
77.077
76.759
44.830
41.405
22.378
21.687
Me
Me
Me
O
O
O
3g
f1 (ppm)


lqq150809-ddq-C1
10.077
7.834
7.813
7.591
7.412
7.390
7.206
7.167
7.109
6.881
6.744
3.497
2.375
1.377
Cl
Me
O
O
Cl
Me
O
3h
1.000
4.078
1.090
4.134
1.296
2.247
1.163
2.034
2.002
3.187
3.106
f1 (ppm)

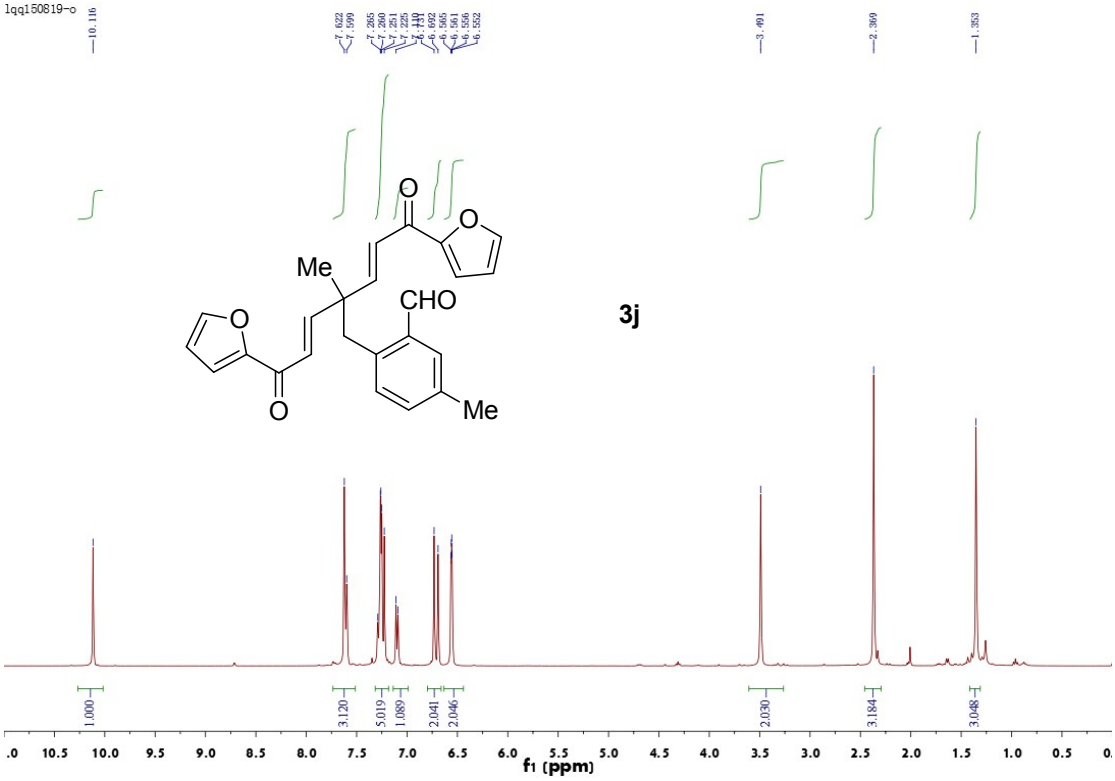

lqq150809-ddq-C1
192.881
188.701
152.882
139.433
137.502
135.824
135.616
134.852
133.988
133.923
133.267
130.991
128.919
123.824
77.518
77.199
76.881
44.978
41.074
22.262
20.814
Cl
Me
O
O
Cl
Me
O
3h
f1 (ppm)

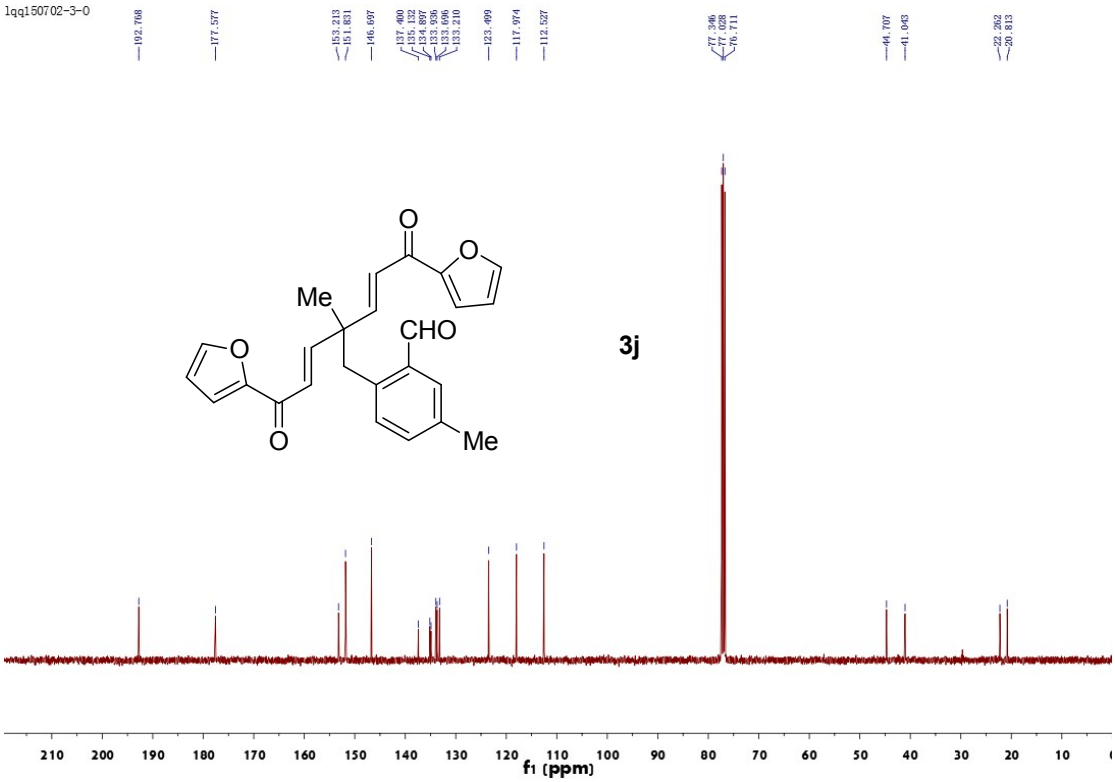

lqq150713-F
10.089
7.943
7.927
7.912
7.603
7.288
7.196
7.153
7.120
3.505
2.992
1.379
O
Me
F
F
O
Me
O
3i
hexane
1.000
4.116
1.095
1.276
7.259
2.050
2.000
3.215
3.067
f1 (ppm)

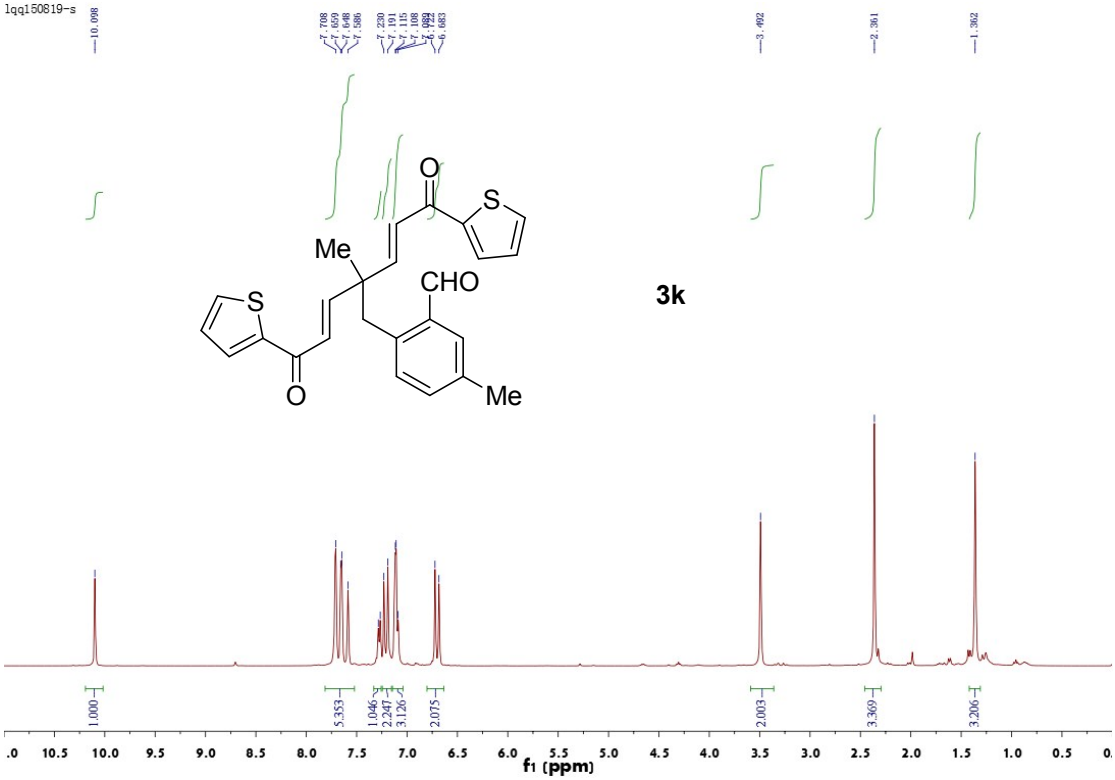

lqq150713-F
192.850
188.334
166.471
164.497
152.985
137.496
135.044
134.697
133.929
133.896
133.267
131.198
131.156
123.858
115.865
115.648
77.395
77.078
76.759
44.903
41.121
22.356
20.808
O
Me
F
F
O
Me
O
3i
f1 (ppm)

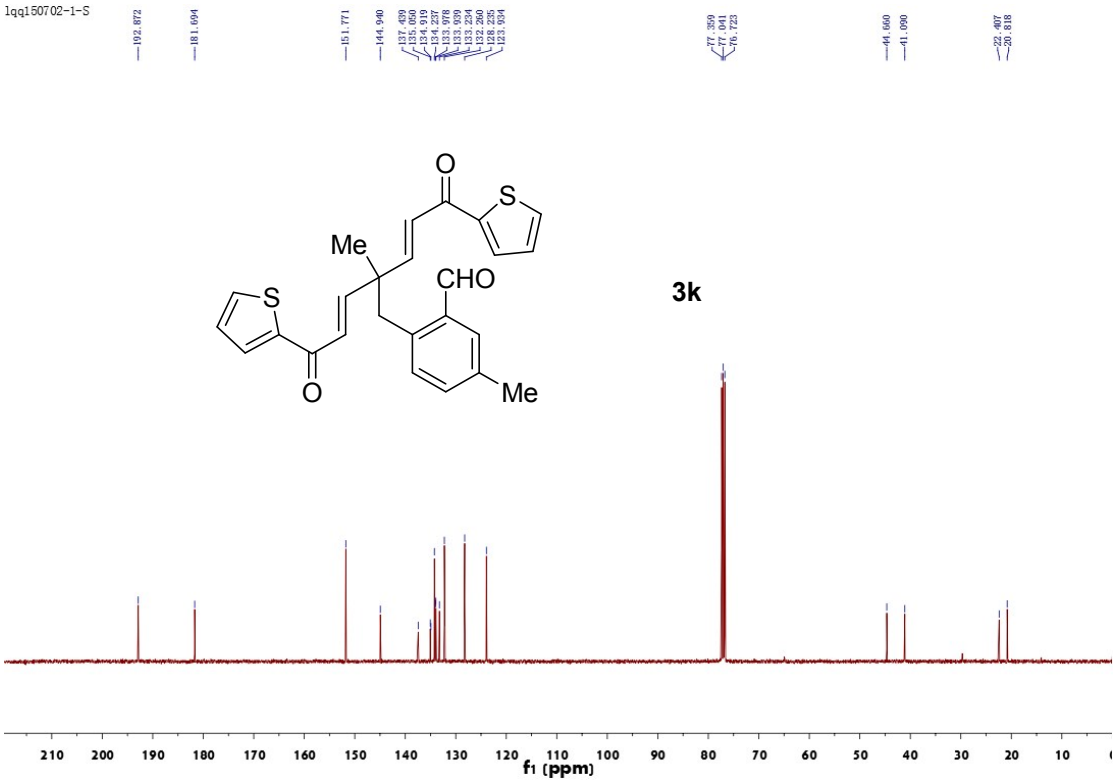

lqq150713-F1
-105.055
O
Me
F
F
O
Me
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

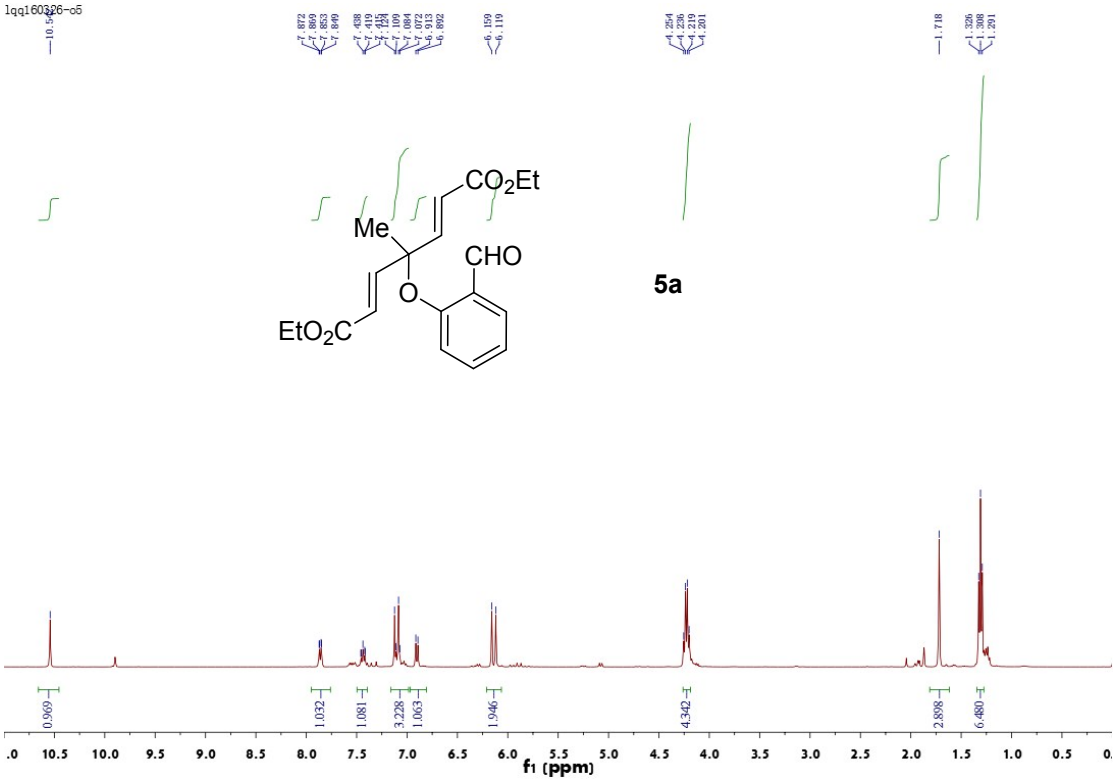
3i


lqq150819-o
10.116
7.622
7.599
7.365
7.280
7.251
7.225
7.119
7.092
6.692
6.565
6.561
6.556
6.552
3.491
2.369
1.353
O
O
Me
CHO
O
O
Me
3j
1.000
3.120
5.019
1.089
2.041
2.046
2.030
3.184
3.048
f1 (ppm)

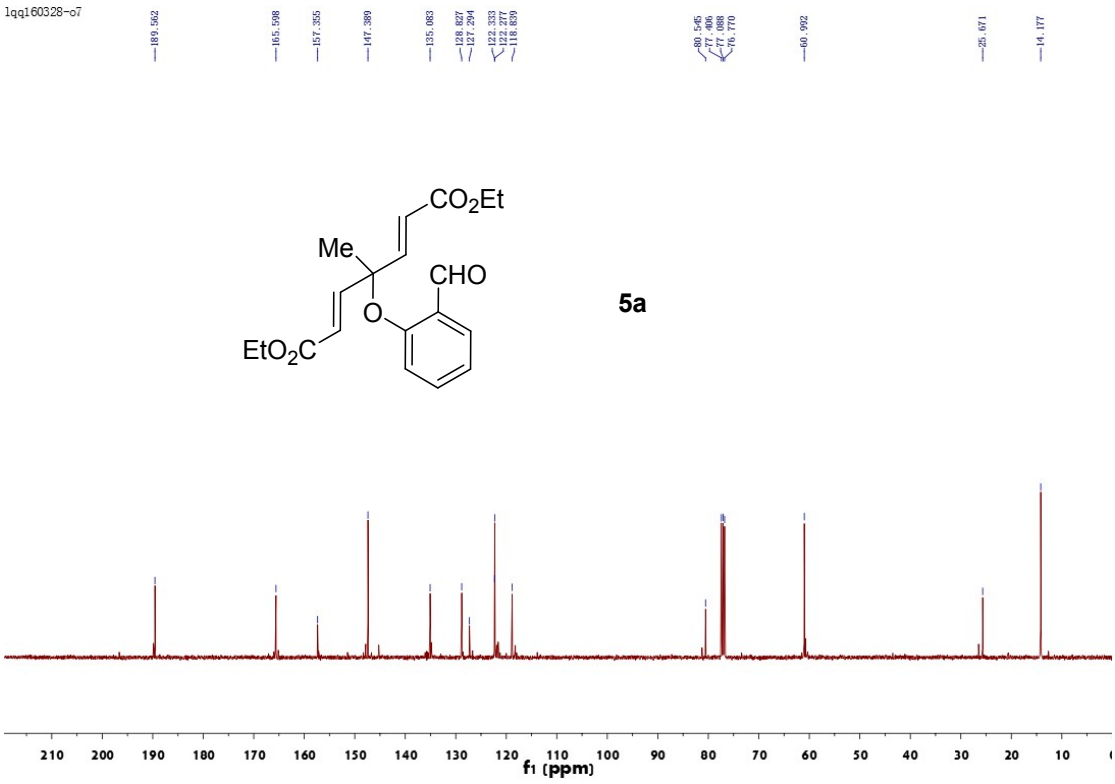

lqq150702-3-0
192.768
177.577
153.213
151.831
146.697
137.400
135.132
134.697
133.855
133.696
133.210
123.499
117.974
112.527
77.346
77.028
76.711
44.707
41.043
22.262
20.813
O
O
Me
CHO
O
O
Me
3j
f1 (ppm)


lqq150819-s
10.098
7.708
7.659
7.648
7.586
7.230
7.191
7.115
7.108
6.683
3.492
2.361
1.362
O
S
Me
CHO
S
O
Me
3k
1.000
5.353
1.046
2.247
3.126
2.075
2.003
3.369
3.206
f1 (ppm)

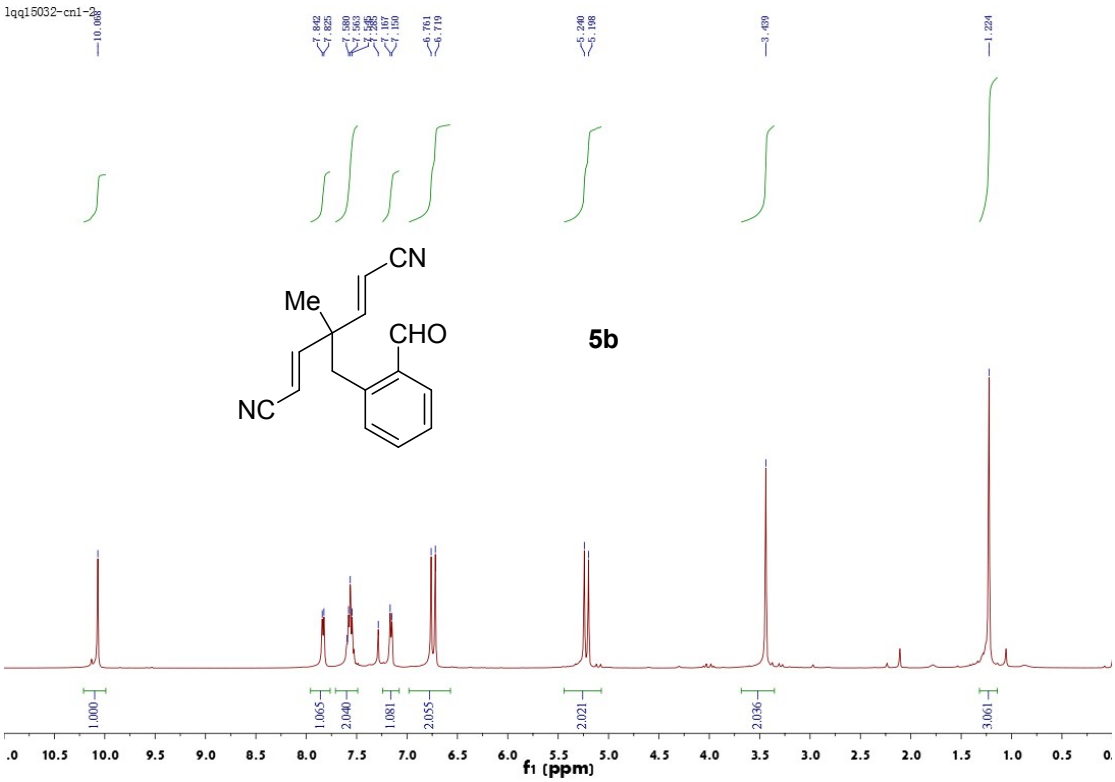

lqq150702-1-S
192.872
181.694
151.771
144.940
137.499
135.650
134.919
134.377
133.978
133.939
133.254
132.260
128.255
123.934
77.359
77.041
76.723
44.660
41.090
22.497
20.818
O
S
Me
CHO
S
O
Me
3k
f1 (ppm)

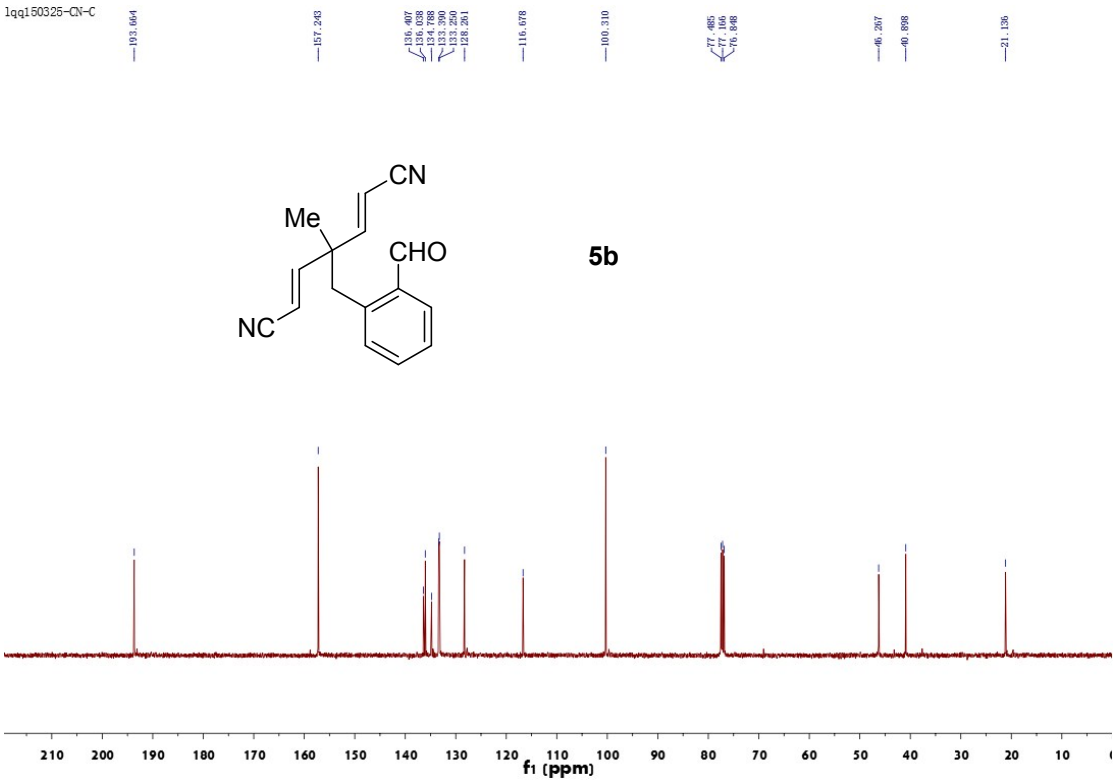

lqq160326-o5
10.545
7.872
7.869
7.855
7.849
7.438
7.419
7.414
7.124
7.109
7.094
7.072
6.913
6.892
6.159
6.119
4.254
4.236
4.219
4.201
1.718
1.326
1.308
1.291
CO2Et
Me
CHO
O
EtO2C
0.969
1.032
1.081
3.228
1.063
1.946
4.342
2.898
6.480
f1 (ppm)

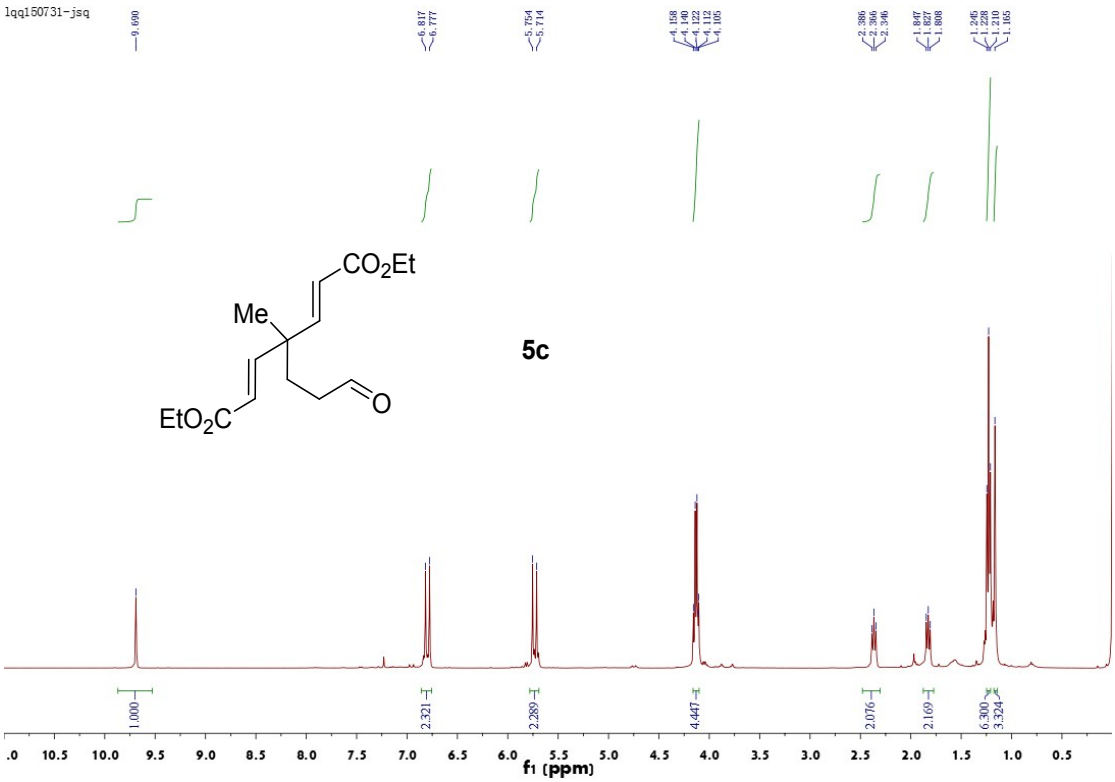
5a

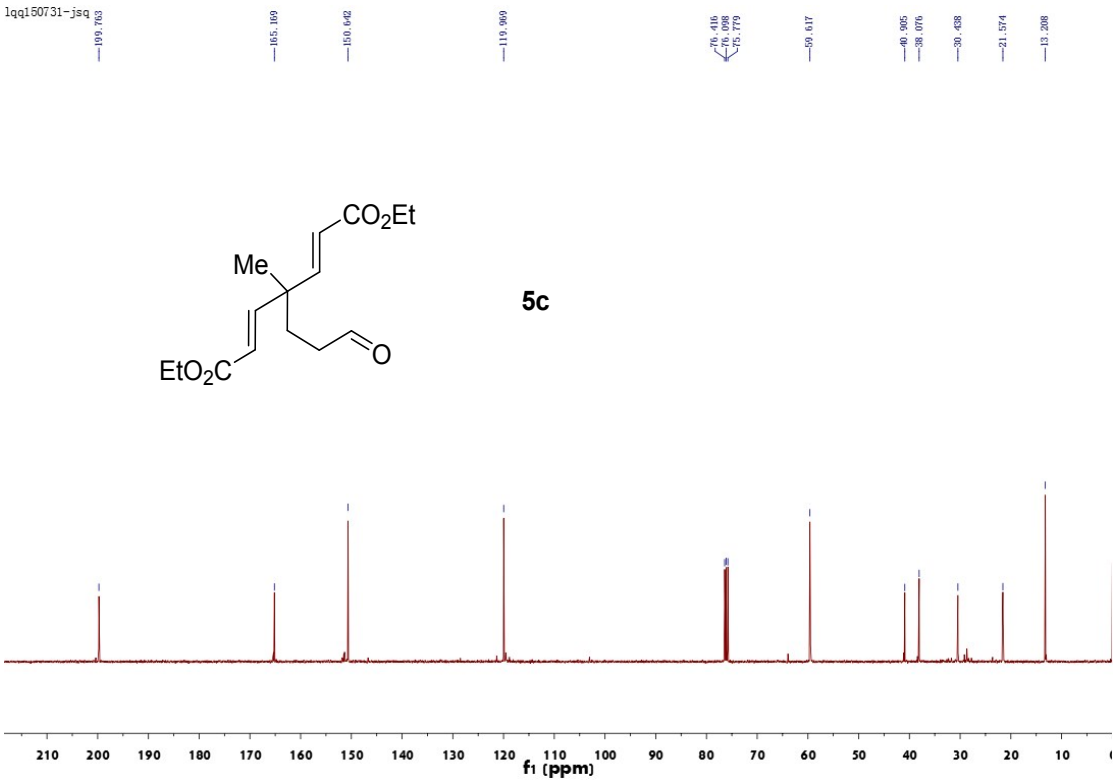

lqq160328-o7
189.562
165.598
157.355
147.389
135.083
128.827
127.294
122.333
122.277
118.839
80.545
77.406
77.088
76.770
60.992
25.671
14.177
CO2Et
Me
CHO
O
EtO2C
f1 (ppm)

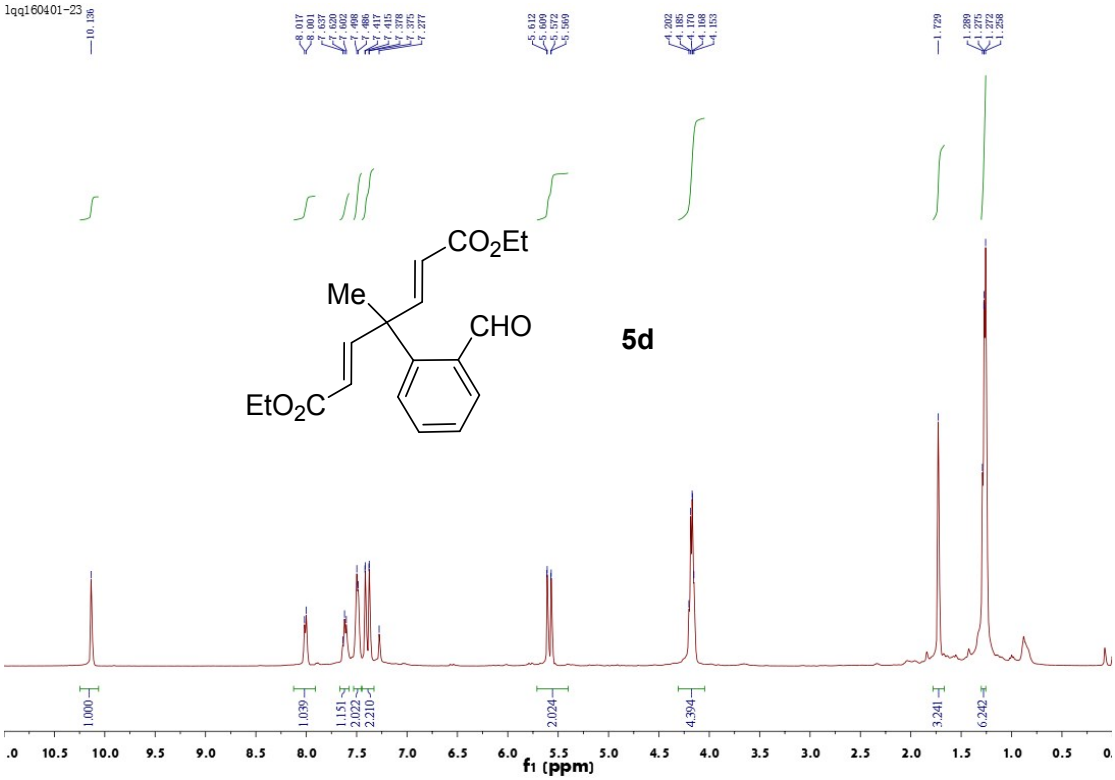
5a

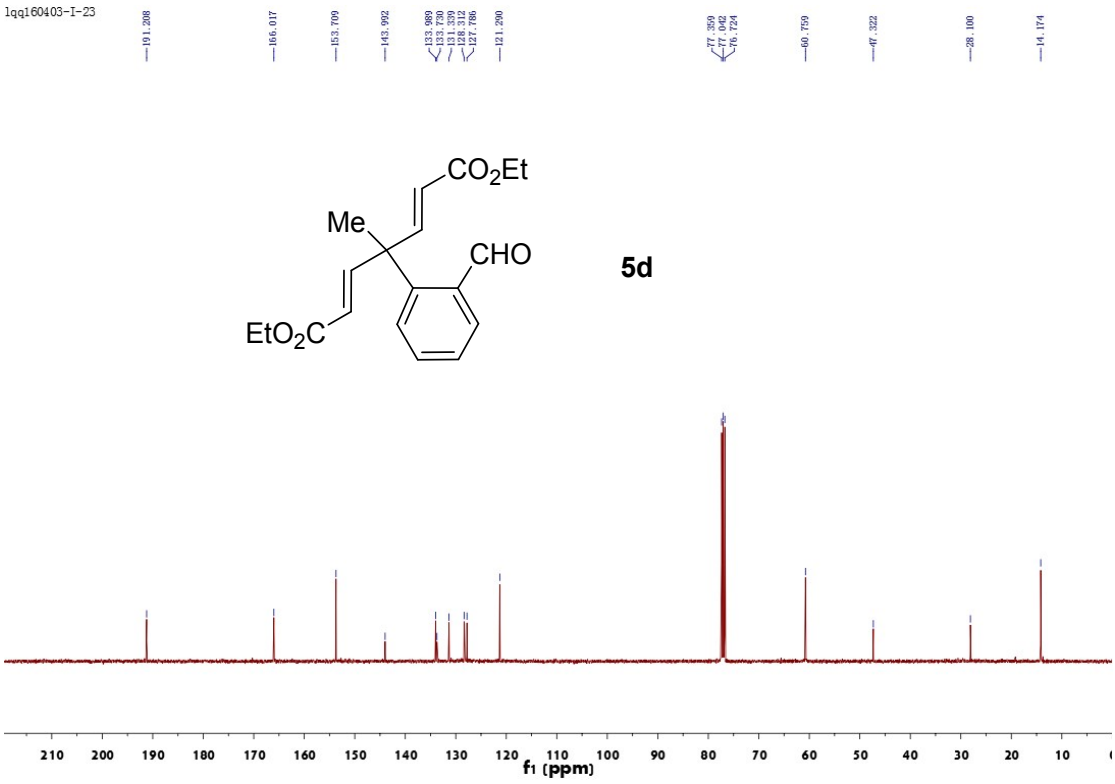

lqq15032-cn1-2
10.068
7.842
7.825
7.580
7.563
7.395
7.378
7.167
7.150
6.761
6.719
5.240
5.198
3.439
1.224
CN
Me
CHO
NC
5b
1.000
1.065
2.040
1.081
2.055
2.021
2.036
3.061
f1 (ppm)

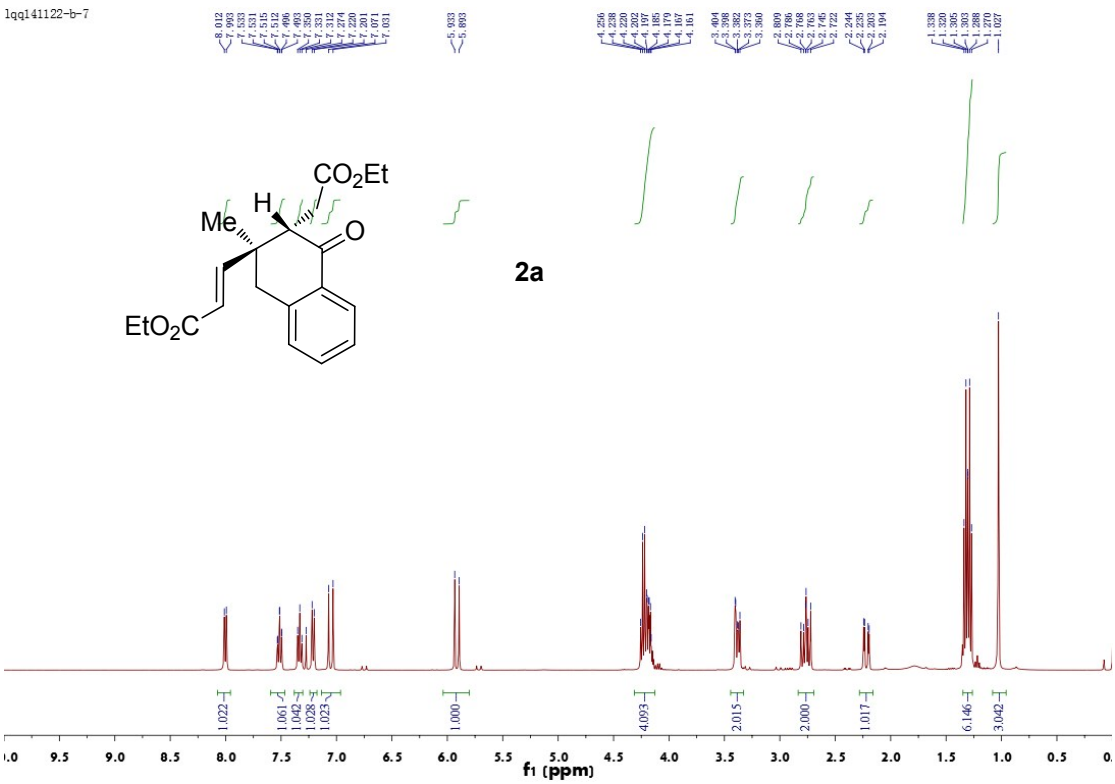

lqq150325-CN-C
193.664
157.243
136.407
136.038
134.788
133.390
133.250
128.261
116.678
100.310
77.485
77.166
76.848
46.267
40.898
21.136
CN
Me
CHO
NC
5b
f1 (ppm)

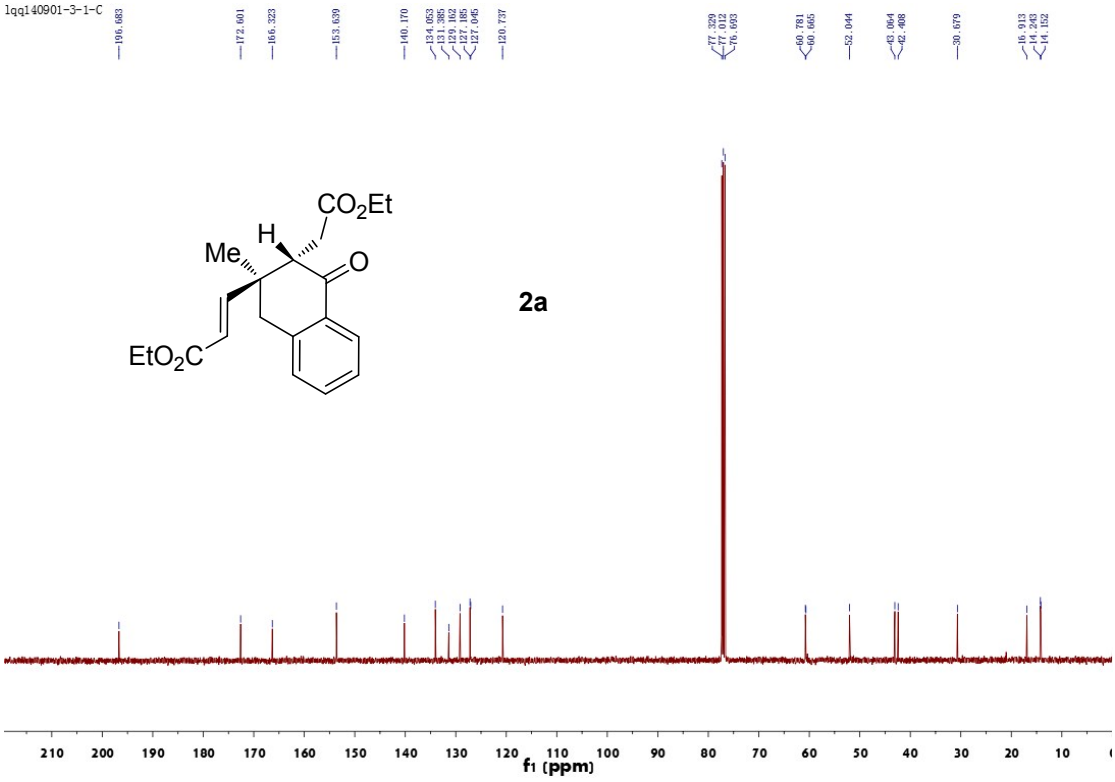

lqq150731-jsq
9.690
6.817
6.777
5.754
5.714
4.158
4.140
4.122
4.112
4.105
2.386
2.366
2.346
1.847
1.827
1.808
1.246
1.228
1.210
1.165
CO2Et
Me
EtO2C
O
5c
1.000
2.321
2.289
4.447
2.076
2.169
6.300
3.324
f1 (ppm)

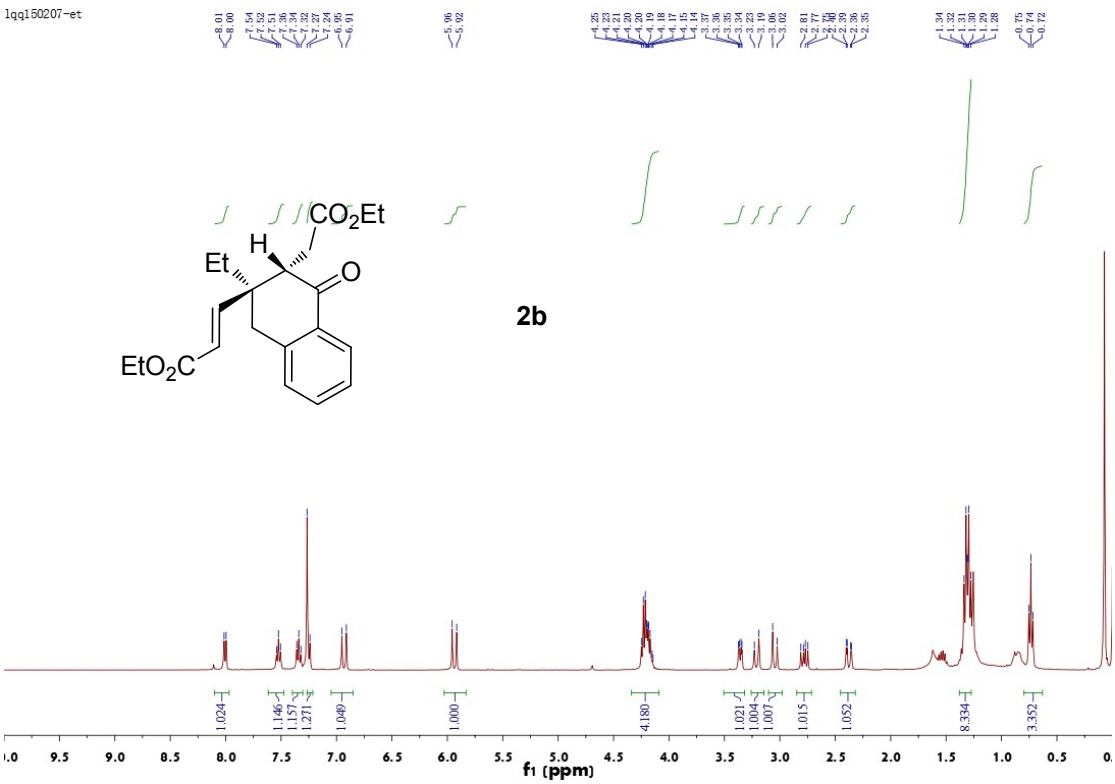

lqq150731-jsq
199.763
165.169
150.642
119.969
76.416
76.098
75.779
59.617
40.985
38.076
30.438
21.574
13.208
CO2Et
Me
EtO2C
O
5c
f1 (ppm)

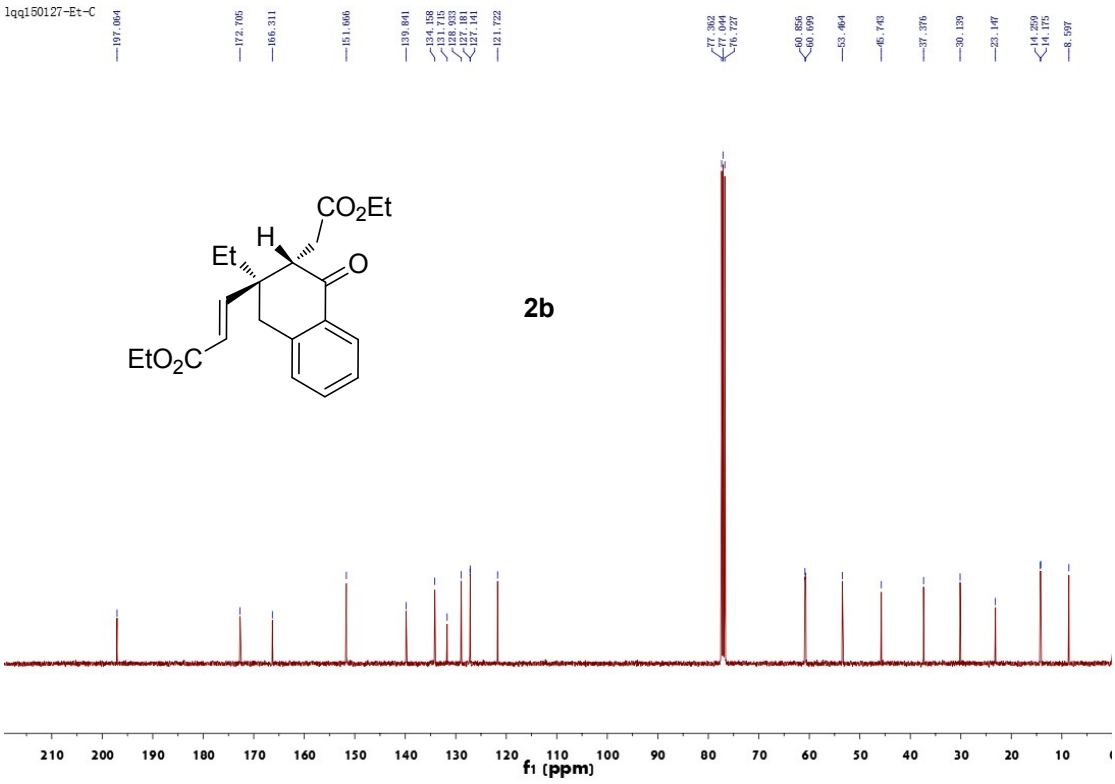

lqq160401-23
CO2Et
Me
CHO
EtO2C
5d
f1 (ppm)

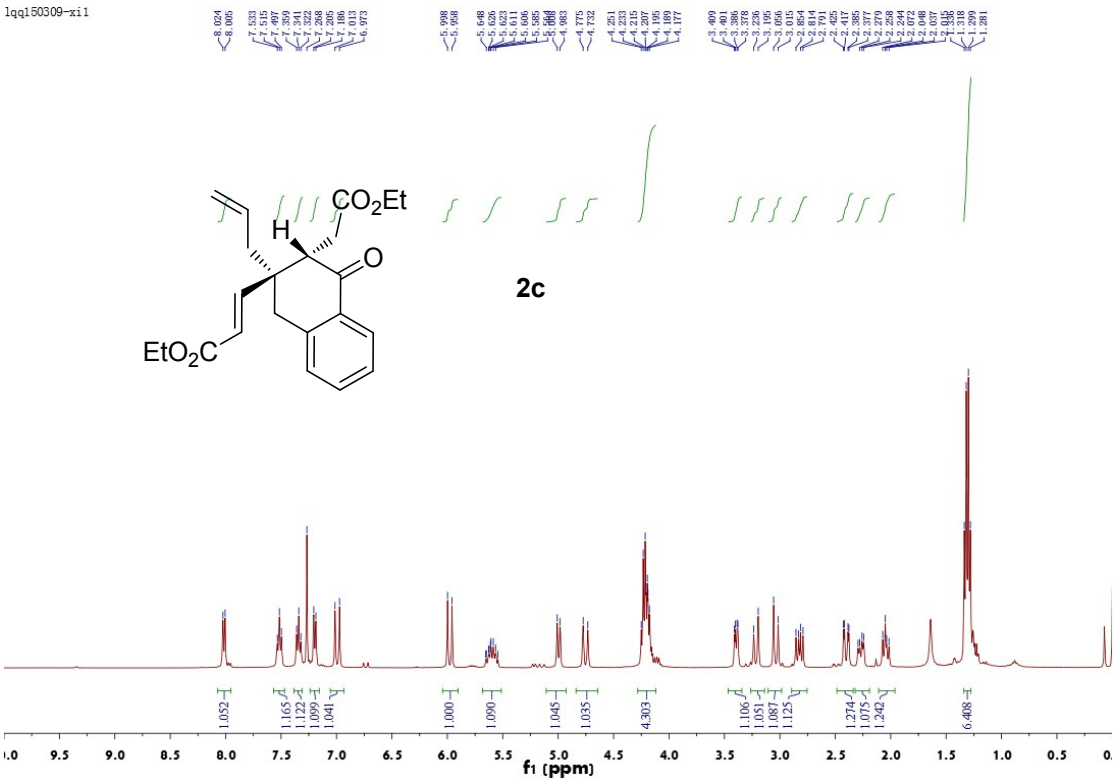

lqq160403-I-23
CO2Et
Me
CHO
EtO2C
5d
f1 (ppm)

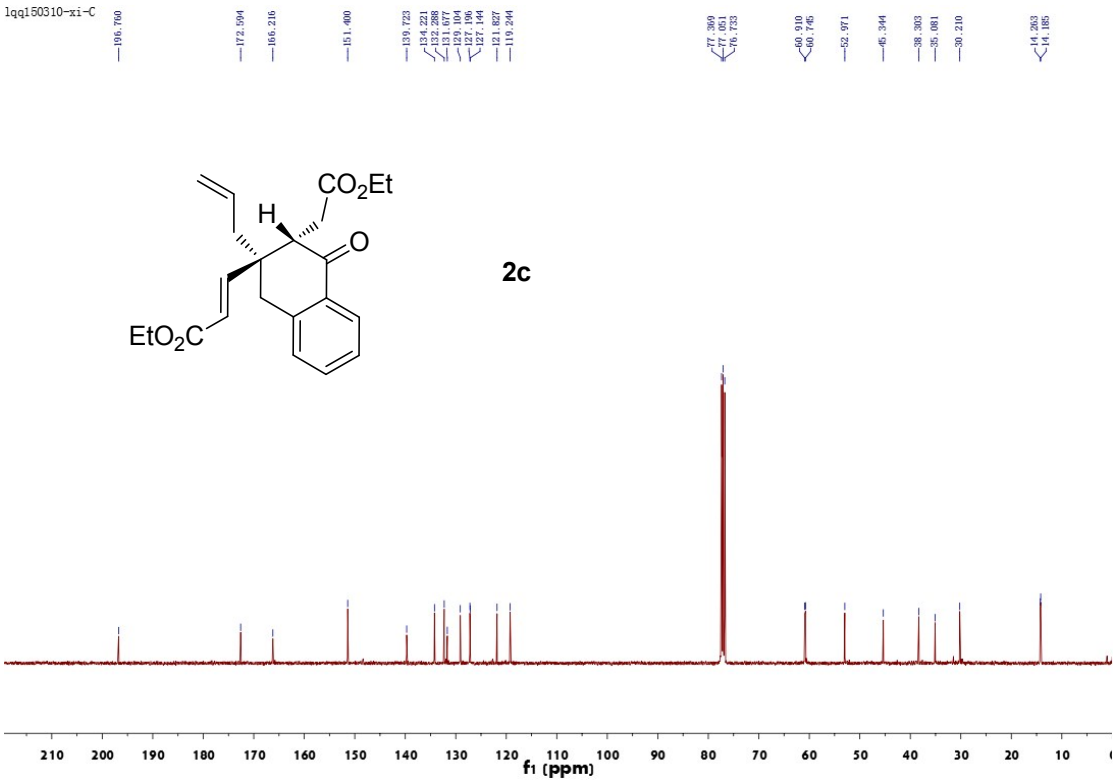

lqq141122-b-7
CO2Et
H
Me
O
EtO2C
2a
f1 (ppm)

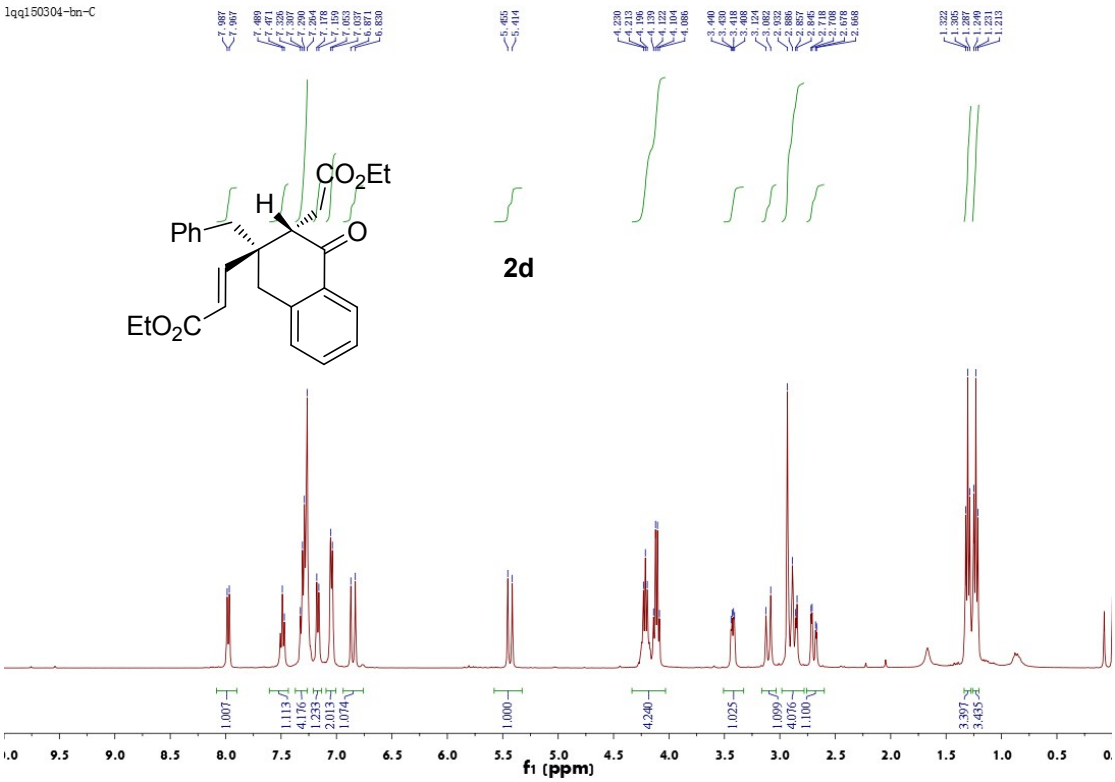

lqq140901-3-1-C
CO2Et
H
Me
O
EtO2C
2a
f1 (ppm)

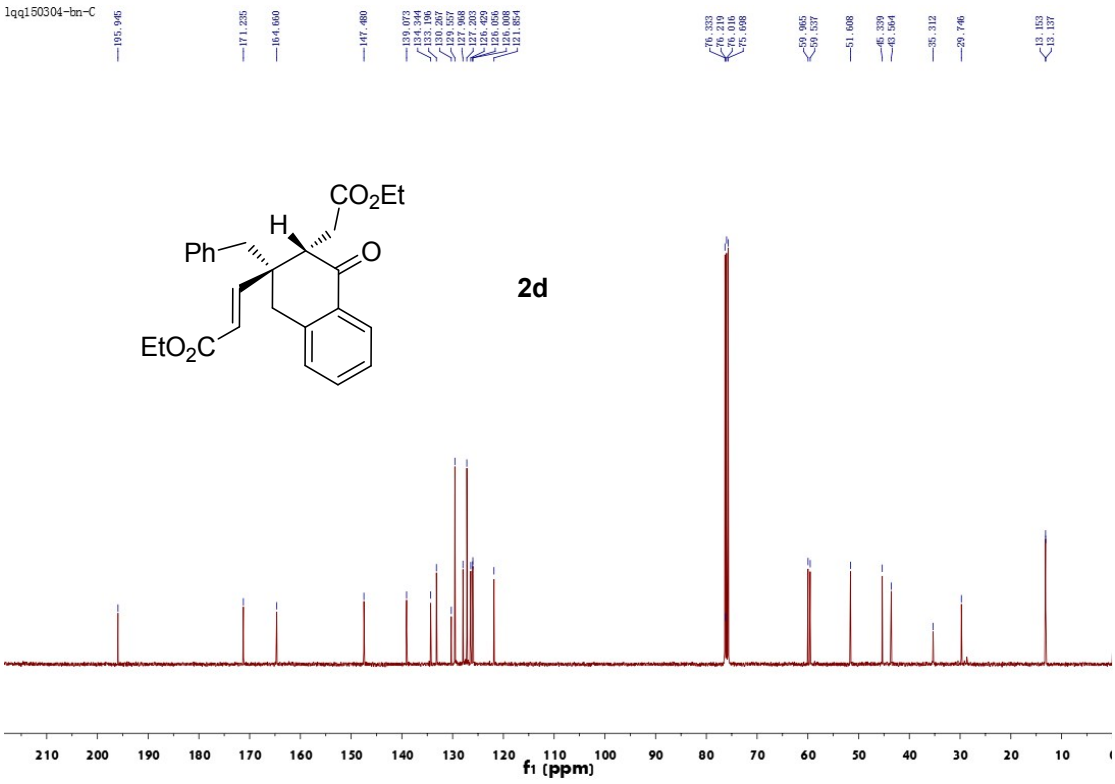

lqq150207-et
CO2Et
H
Et
O
EtO2C
2b
f1 (ppm)

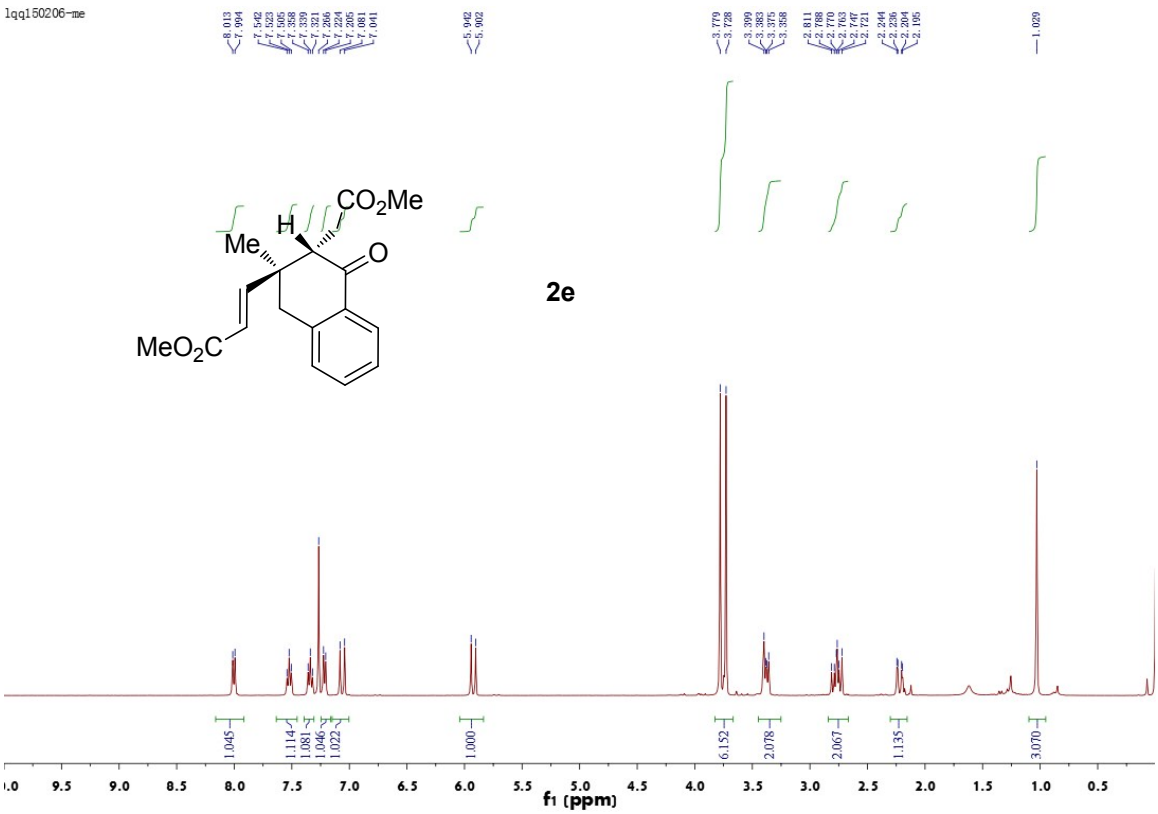

lqq150127-Et-C
CO2Et
H
Et
O
EtO2C
2b
f1 (ppm)

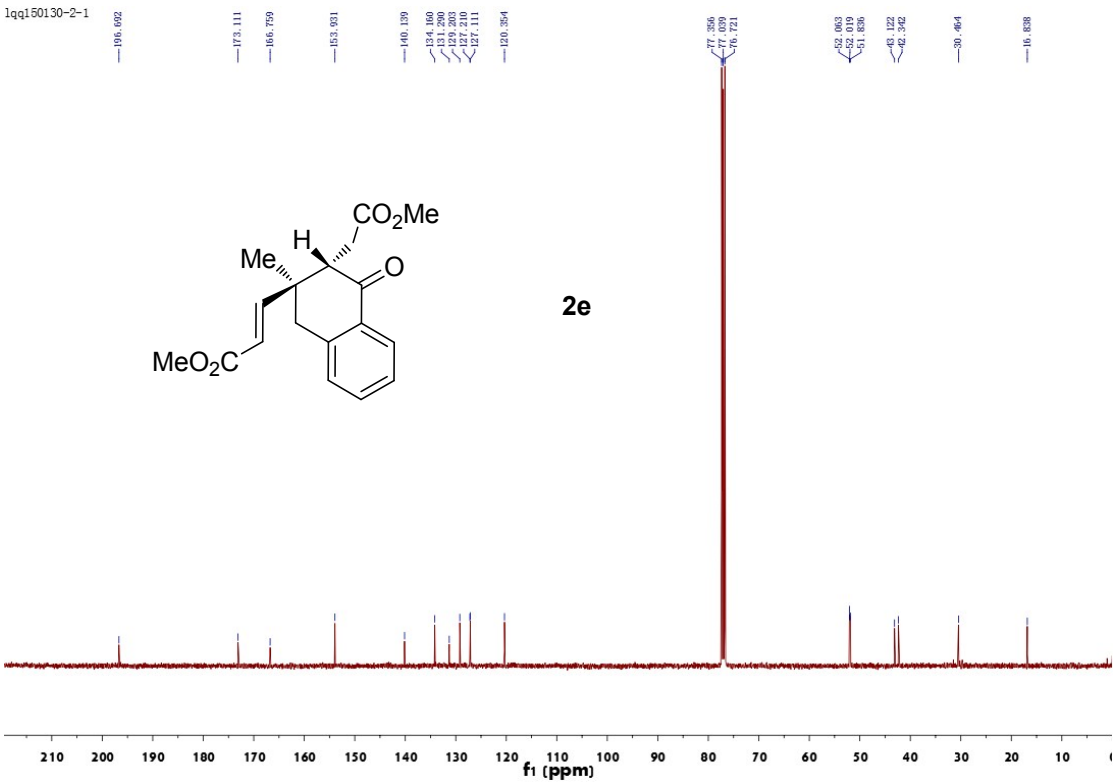

lqq150309-xi1
CO2Et
H
O
EtO2C
2c
f1 (ppm)

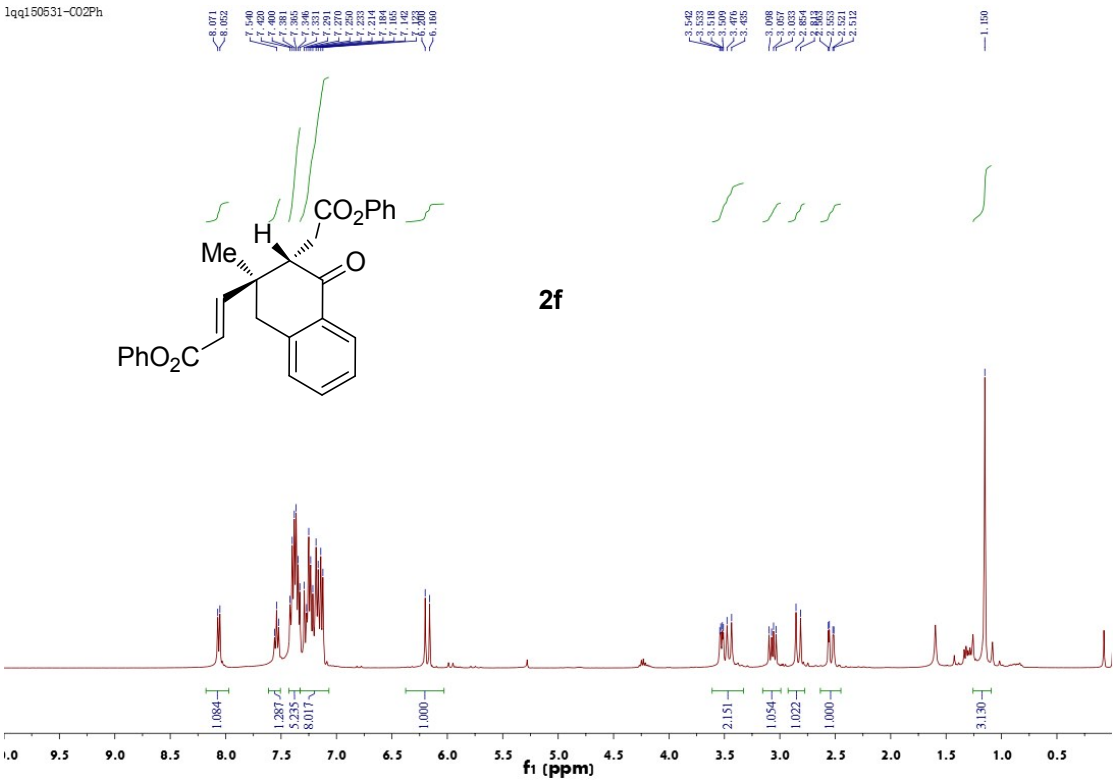

lqq150310-xi-C
CO2Et
H
O
EtO2C
2c
f1 (ppm)

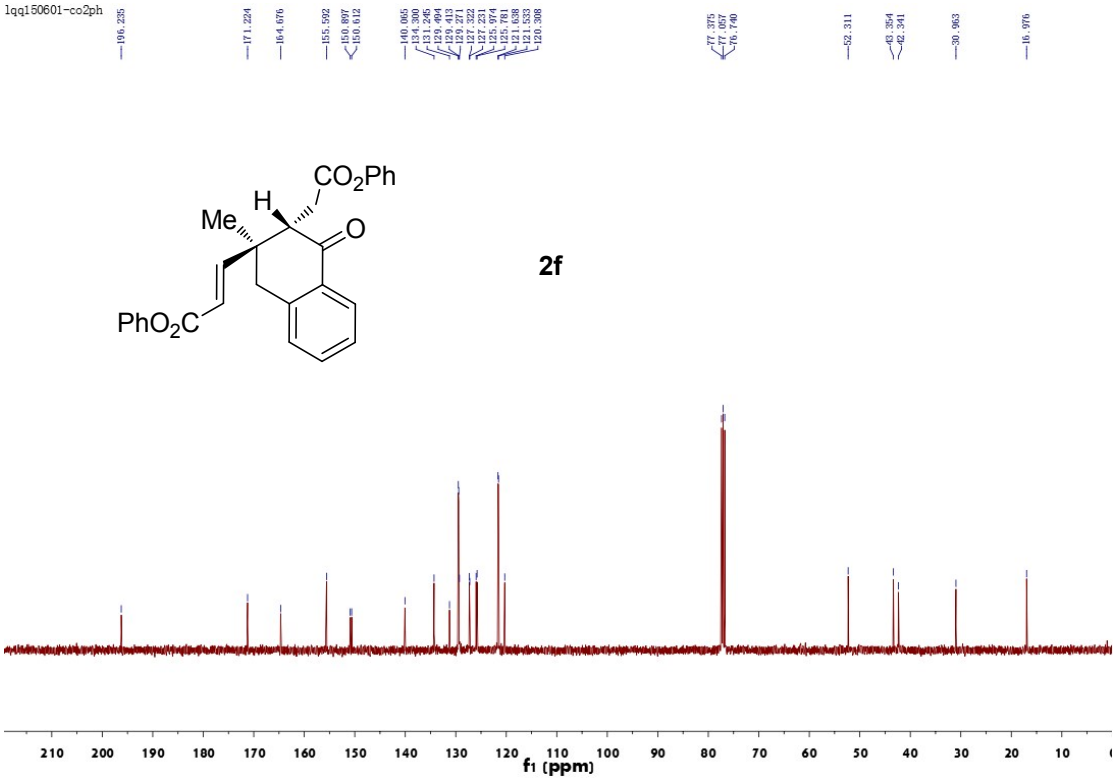

lqq150304-bn-C
CO2Et
H
Ph
O
EtO2C
2d
f1 (ppm)

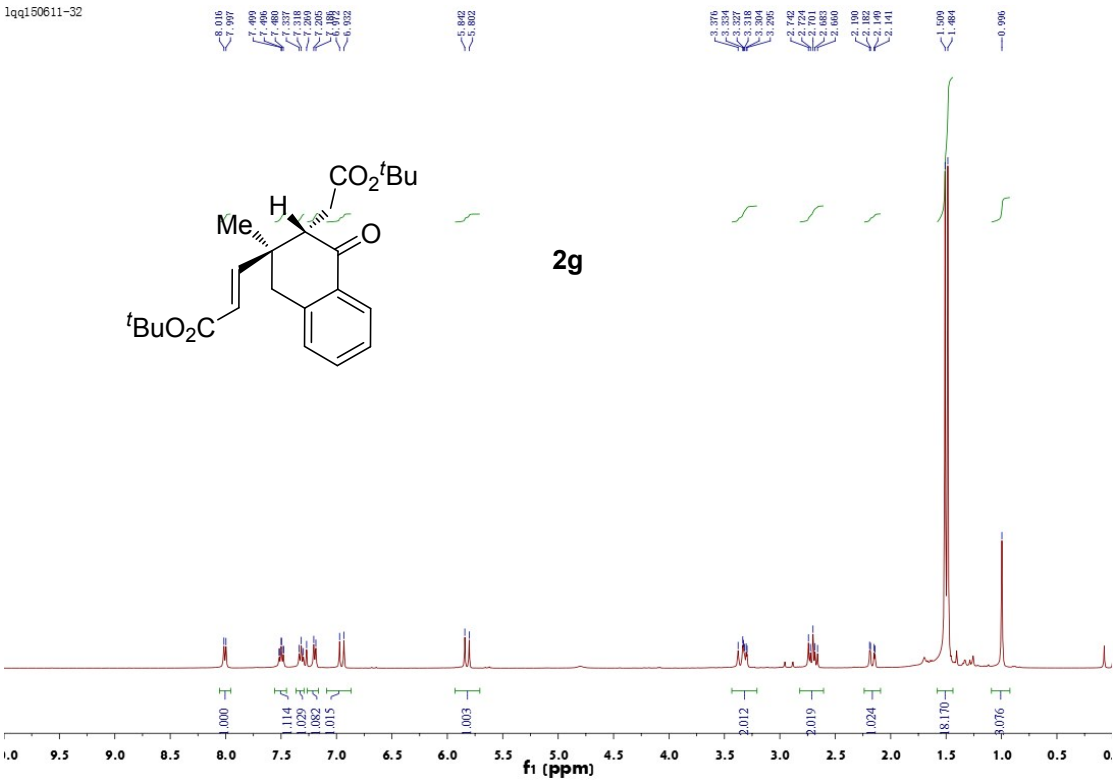

lqq150304-bn-C
CO2Et
H
Ph
O
EtO2C
2d
f1 (ppm)

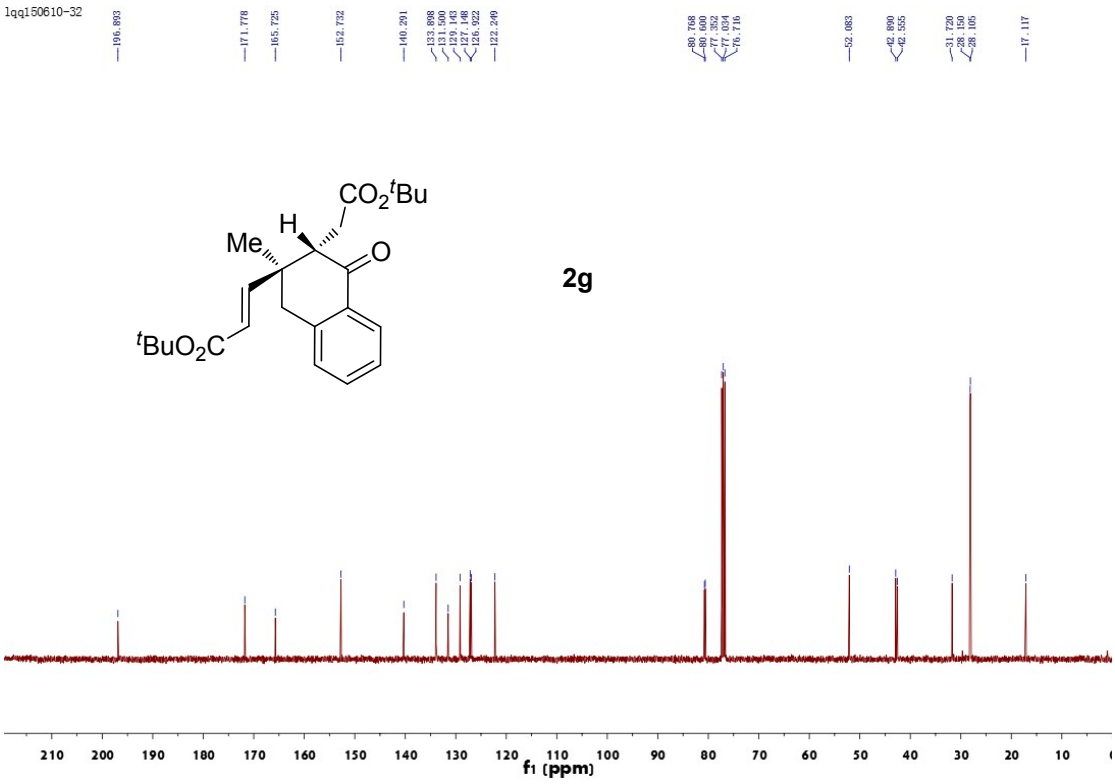

lqq150206-me
CO2Me
H
Me
O
MeO2C
2e
f1 (ppm)

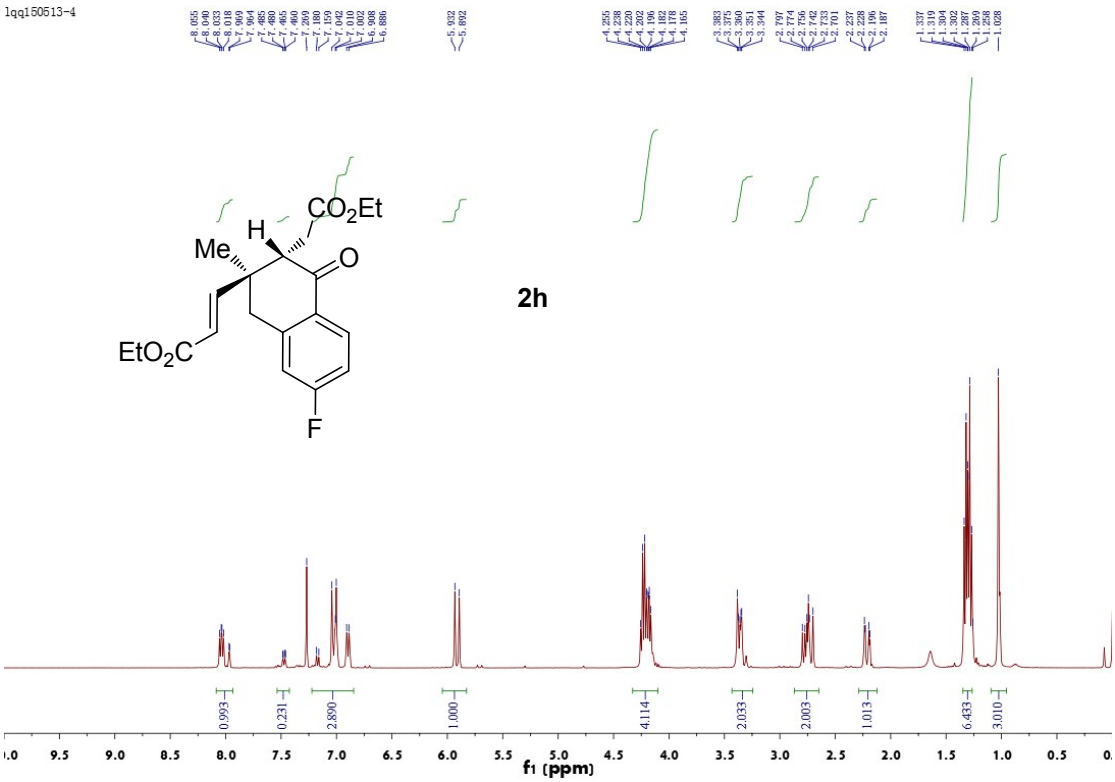

lqq150130-2-1
CO2Me
H
Me
O
MeO2C
2e
f1 (ppm)

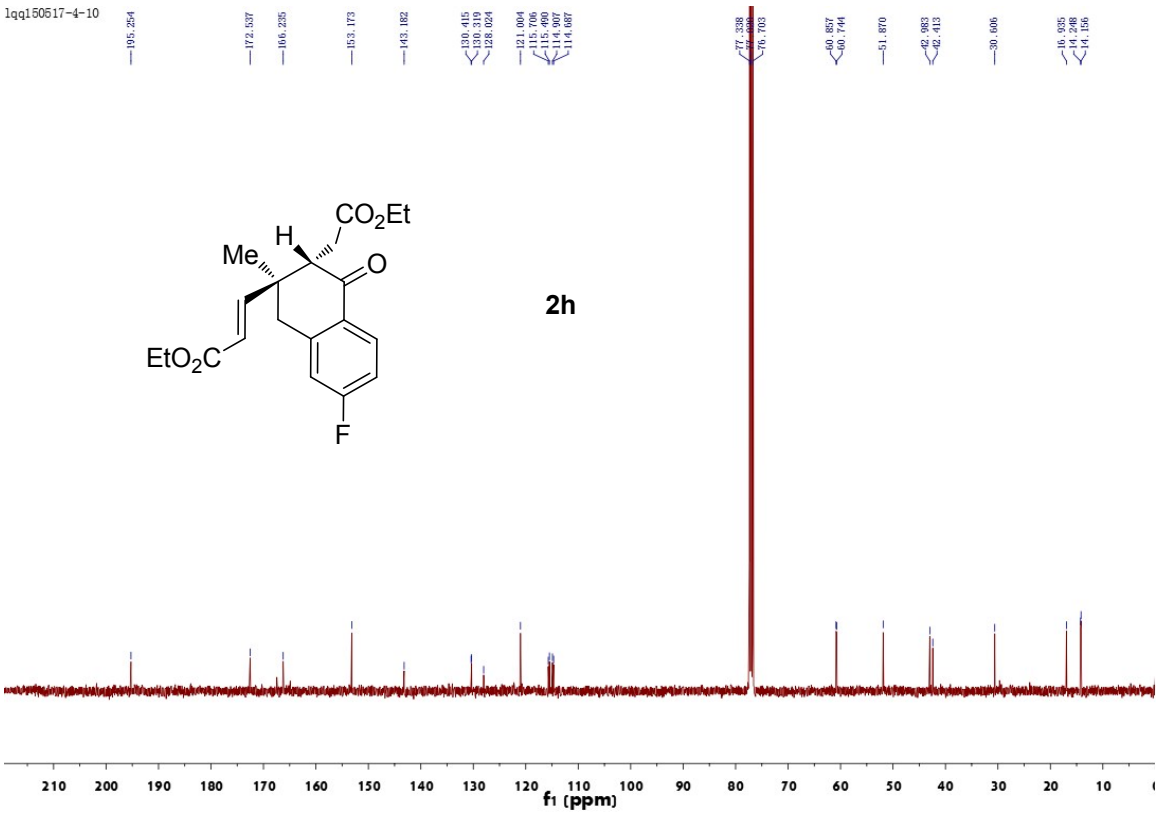

lqq150531-CO2Ph
CO2Ph
H
Me
O
PhO2C
2f
f1 (ppm)

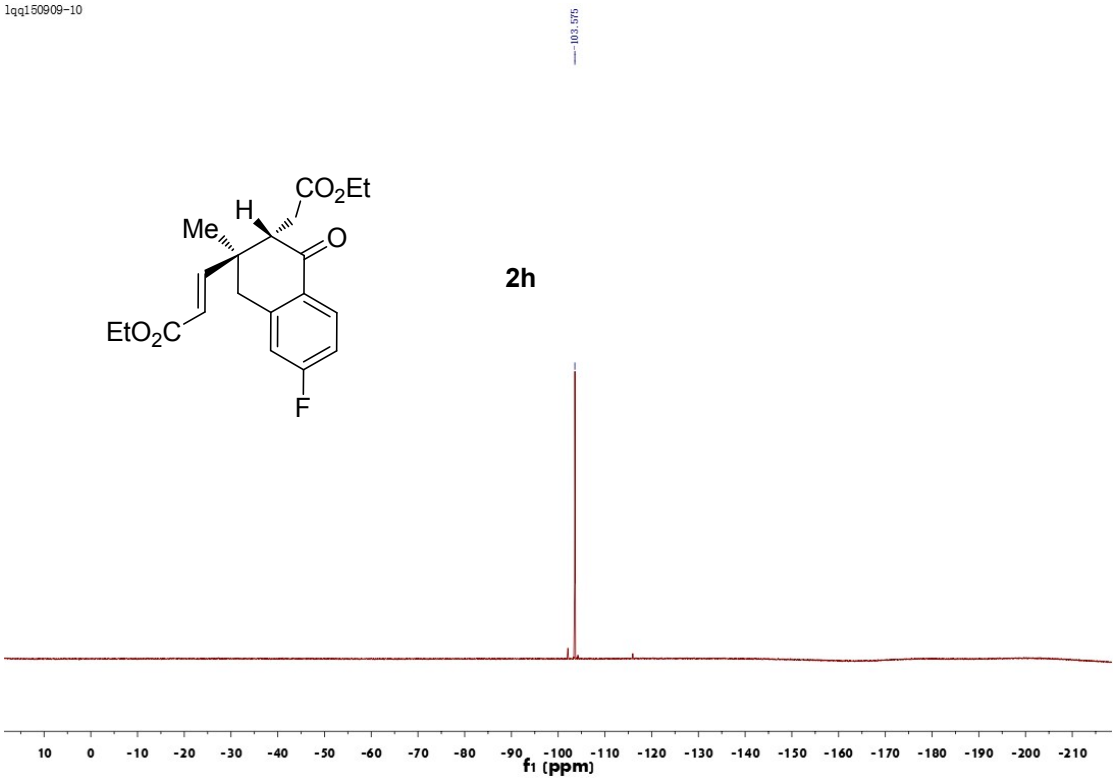

lqq150601-co2ph
CO2Ph
H
Me
O
PhO2C
2f
f1 (ppm)

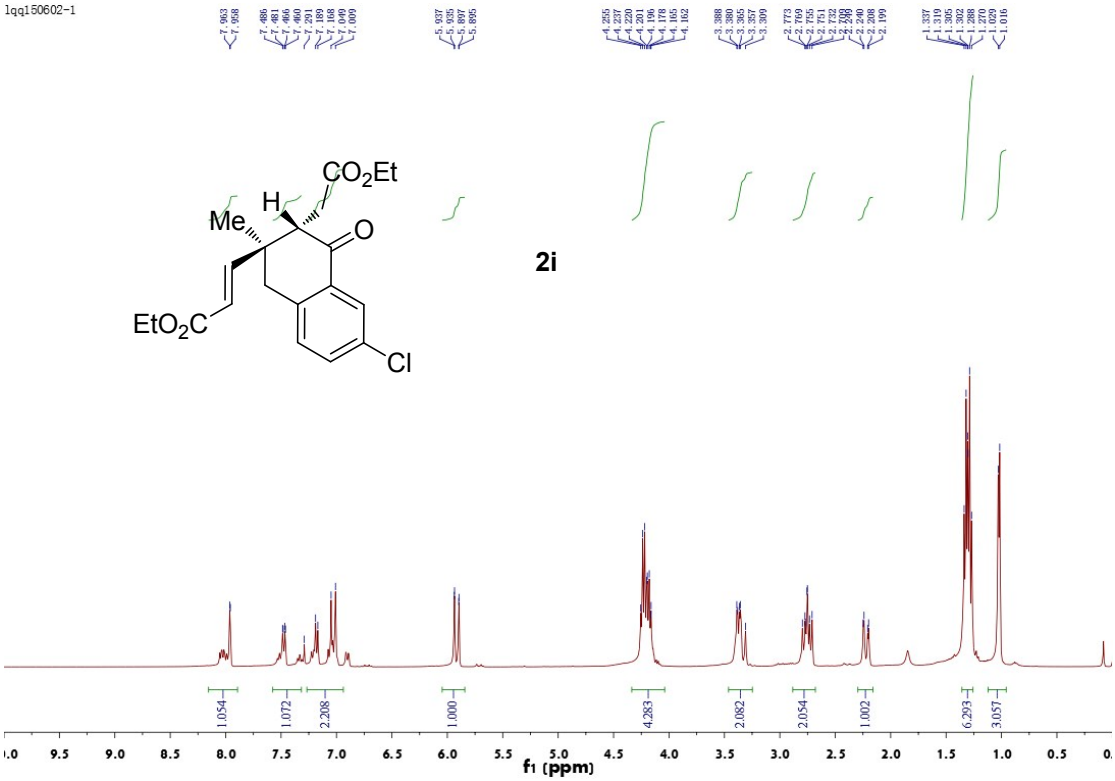

lqq150611-32
CO2tBu
H
Me
O
tBuO2C
2g
f1 (ppm)

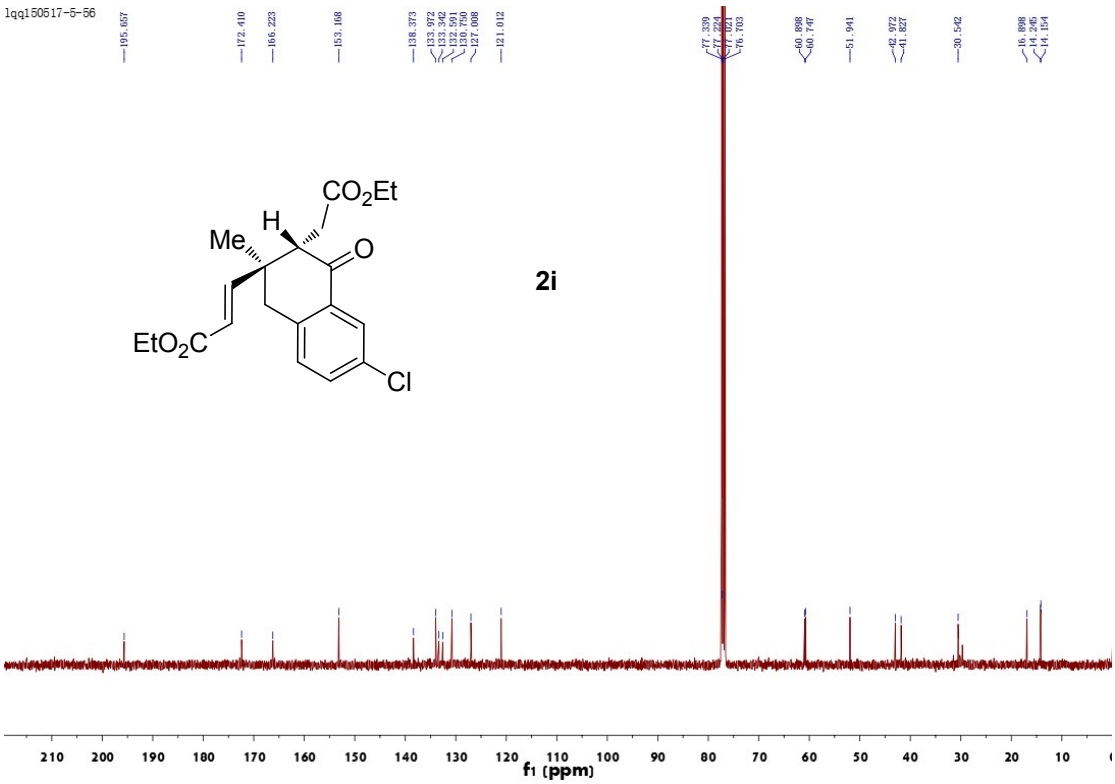

lqq150610-32
CO2tBu
H
Me
O
tBuO2C
2g
f1 (ppm)

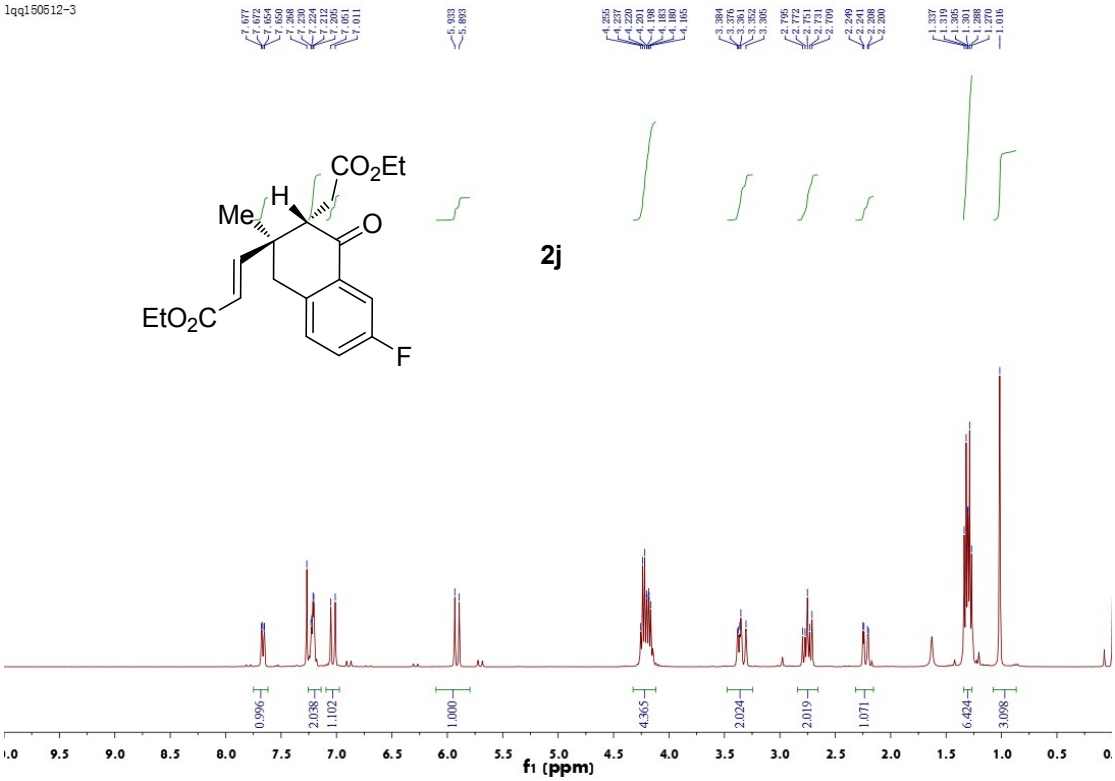

lqq150513-4
CO2Et
H
Me
O
EtO2C
F
2h
0.993
0.231
2.890
1.000
4.114
2.033
2.003
1.013
6.433
3.010
f1 (ppm)

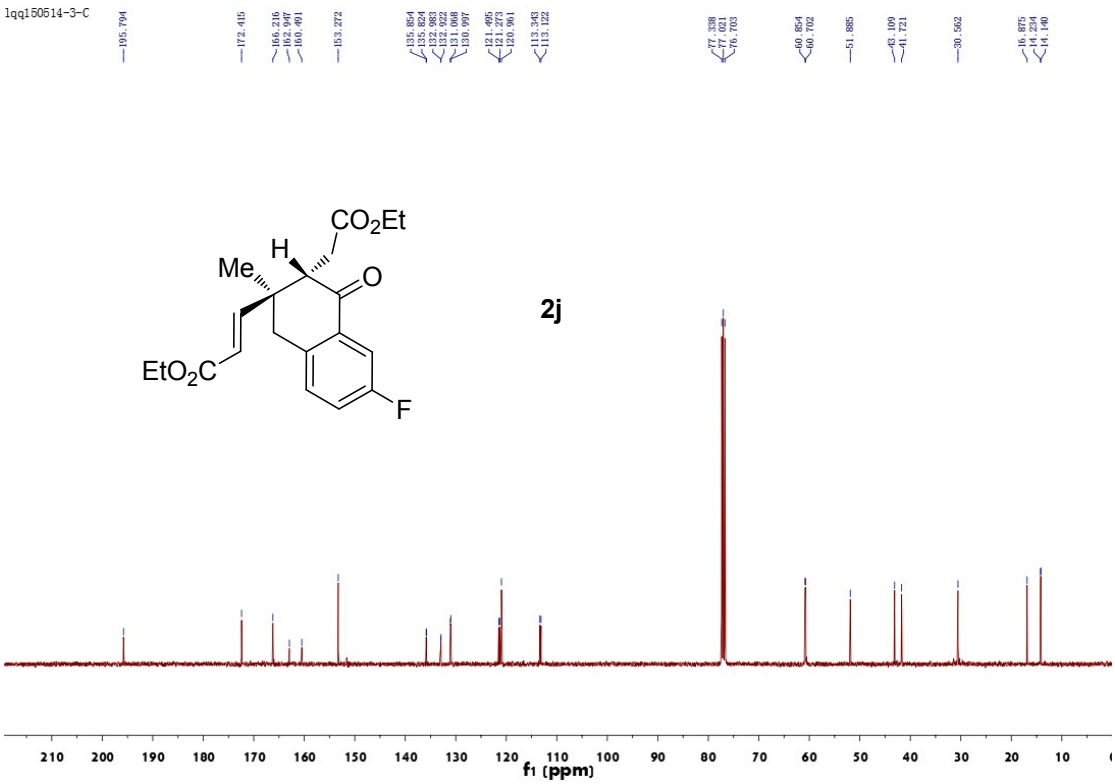

lqq150517-4-10
CO2Et
H
Me
O
EtO2C
F
2h
f1 (ppm)

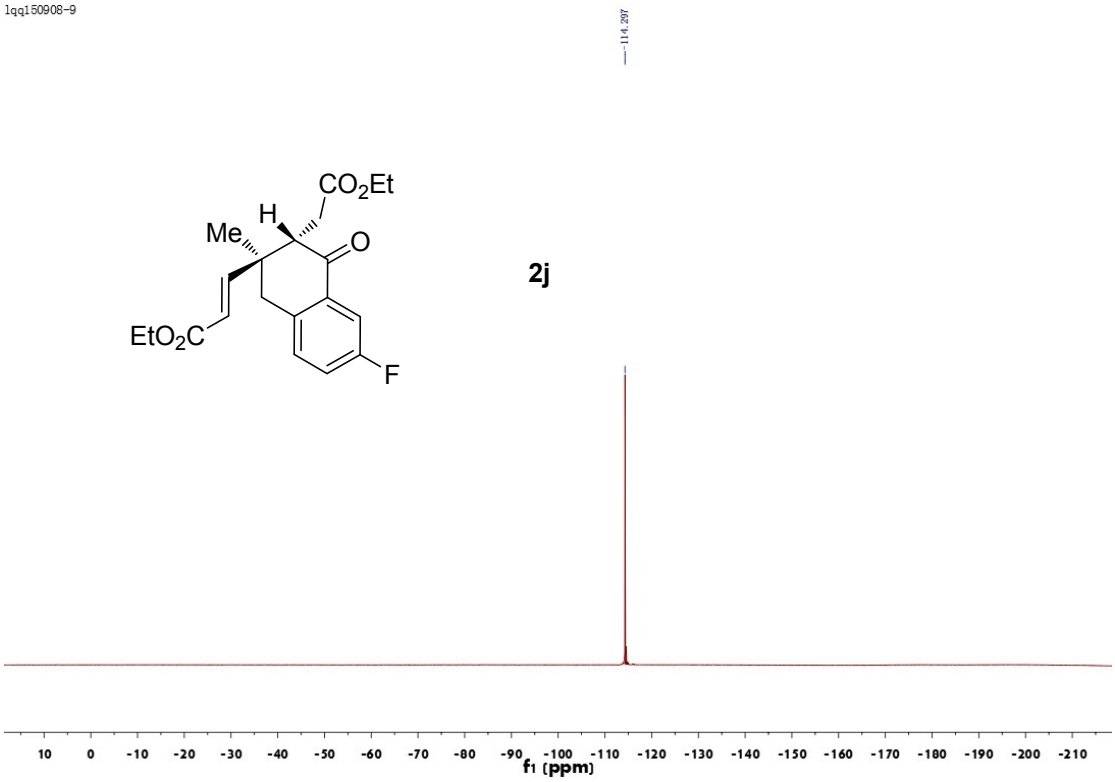

lqq150909-10
-103.575
CO2Et
H
Me
O
EtO2C
F
2h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

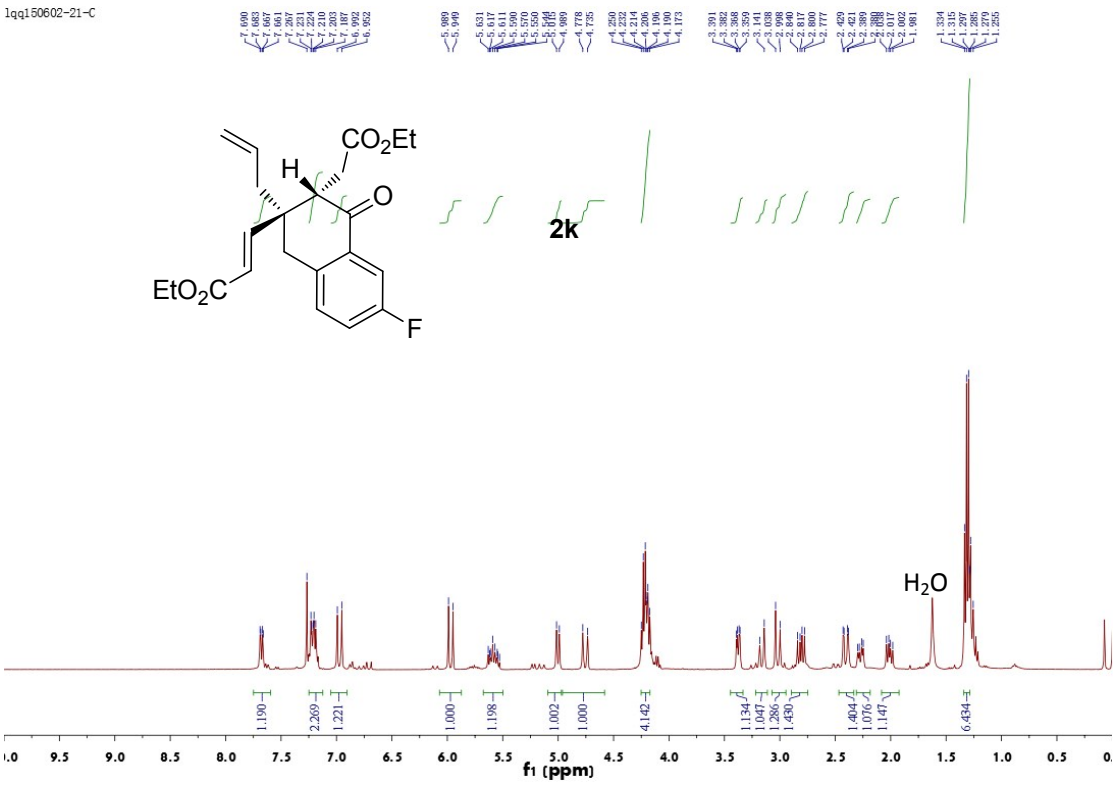

lqq150602-1
CO2Et
H
Me
O
EtO2C
Cl
2i
1.054
1.072
2.208
1.000
4.283
2.082
2.054
1.002
6.293
3.057
f1 (ppm)

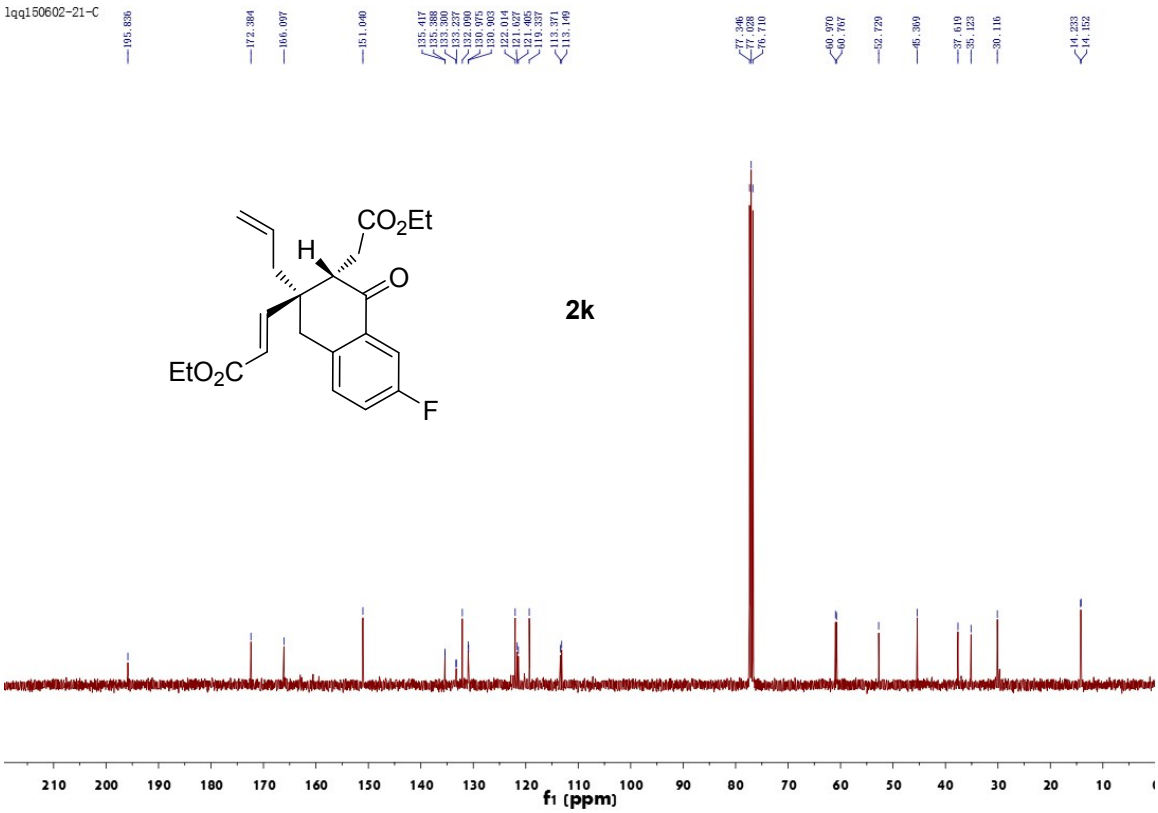

lqq150517-5-56
CO2Et
H
Me
O
EtO2C
Cl
2i
f1 (ppm)

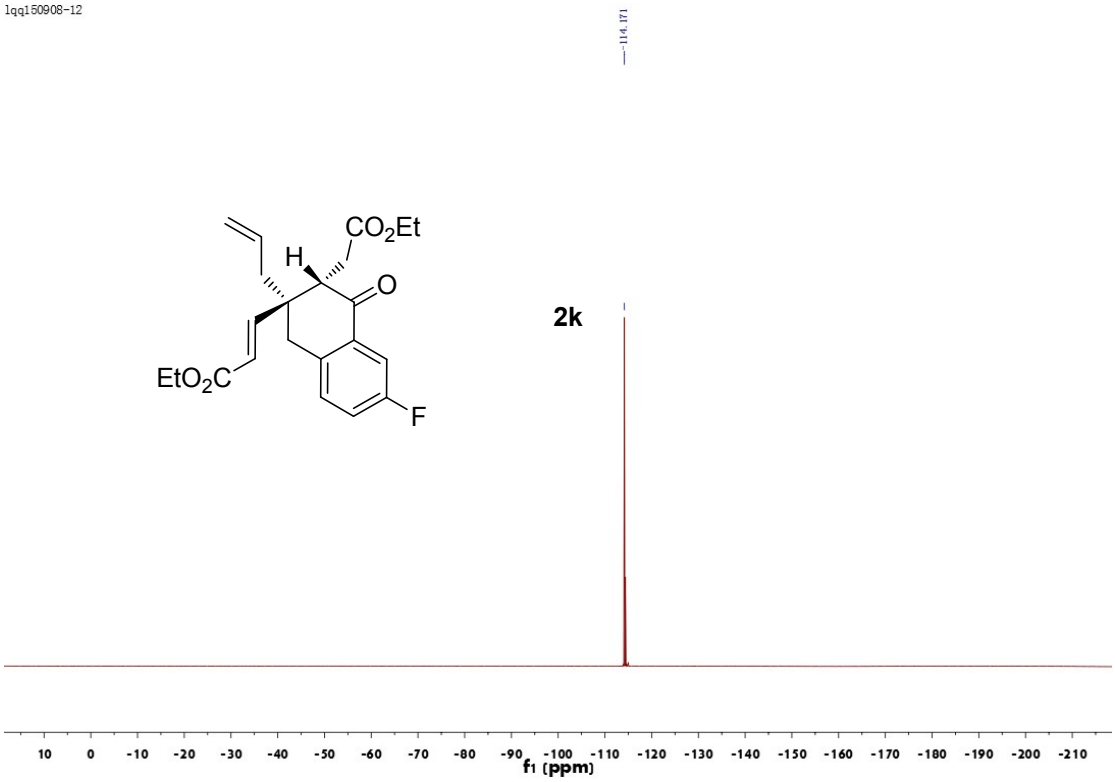

lqq150512-3
CO2Et
H
Me
O
EtO2C
F
2j
0.996
2.038
1.102
1.000
4.365
2.024
2.019
1.071
6.424
3.098
f1 (ppm)

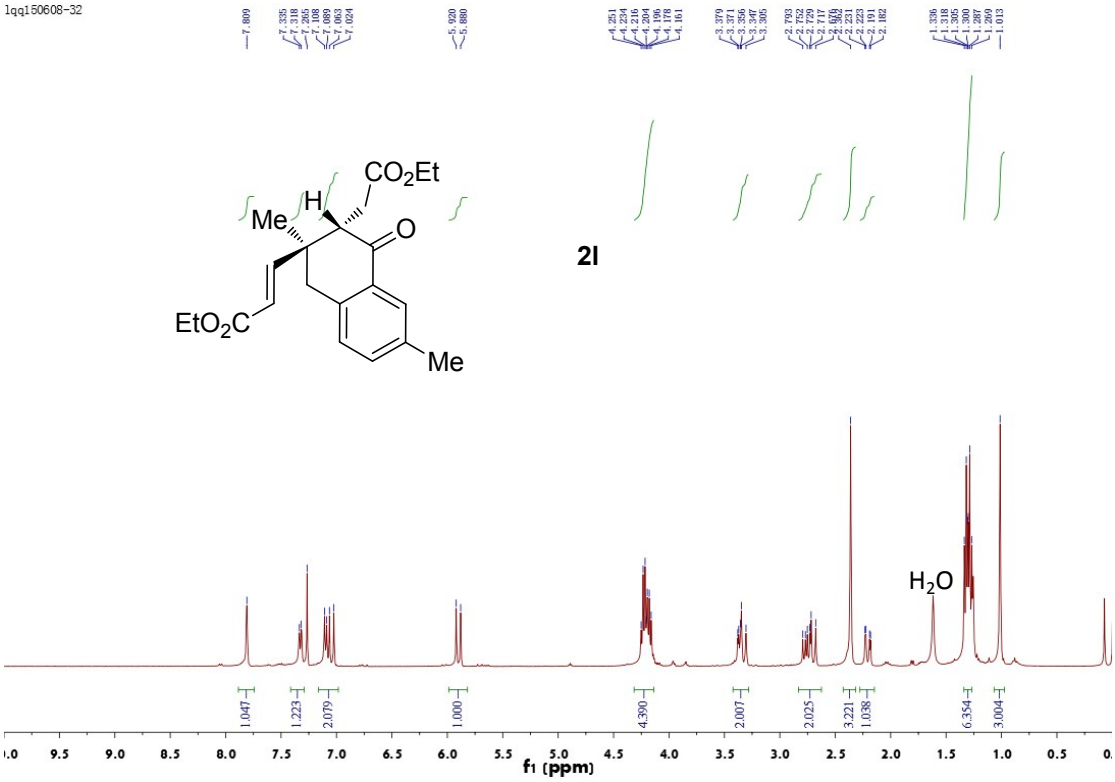

lqq150514-3-C
CO2Et
H
Me
O
EtO2C
F
2j
f1 (ppm)

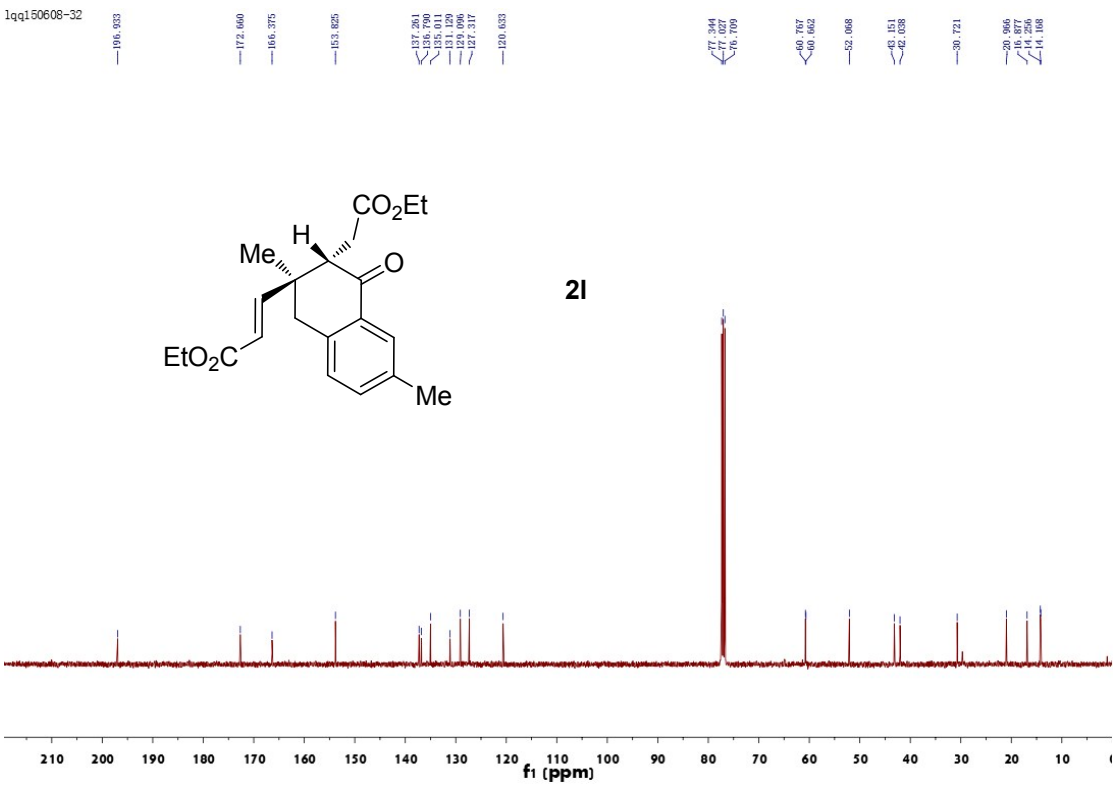

lqq150908-9
-114.297
CO2Et
H
Me
O
EtO2C
F
2j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

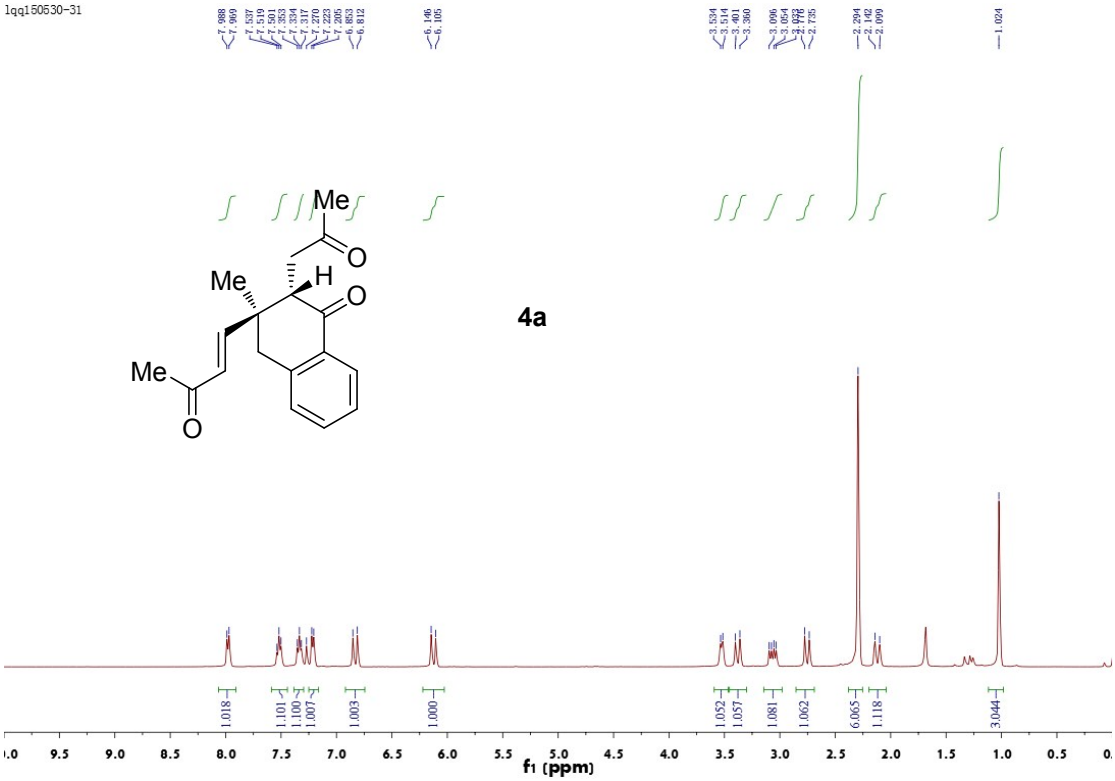

lqq150602-21-C
CO2Et
H
O
EtO2C
F
2k
H2O
f1 (ppm)

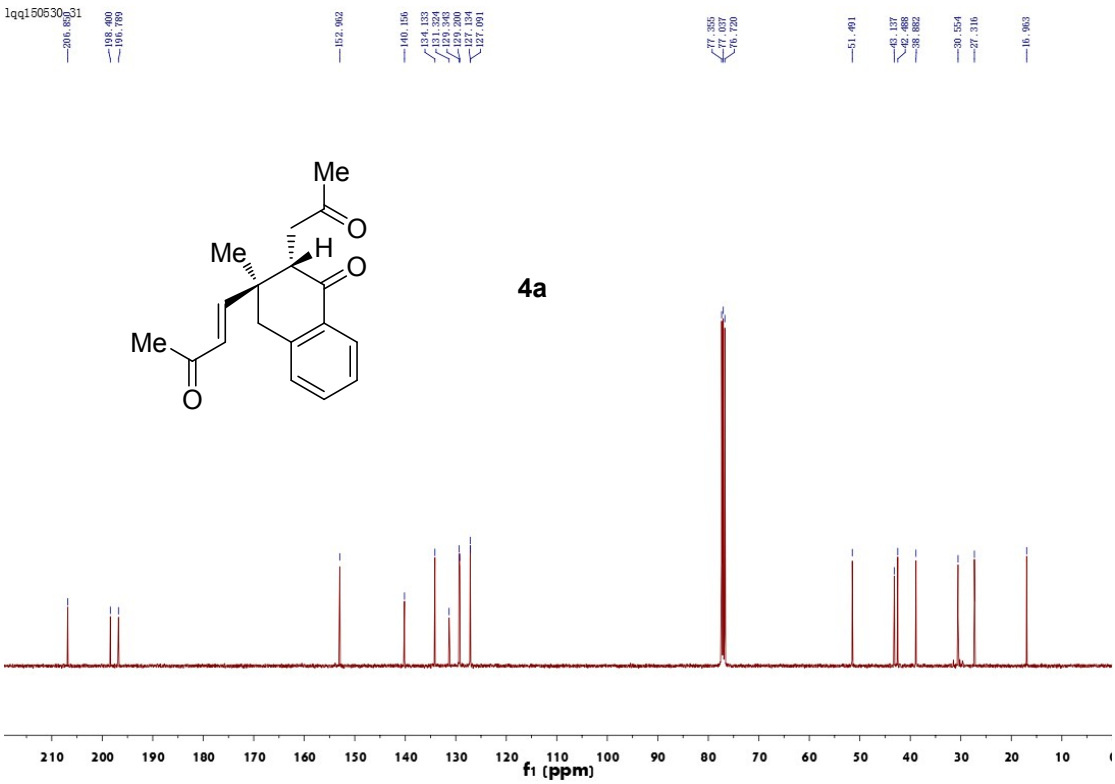

lqq150602-21-C
CO2Et
H
O
EtO2C
F
2k
f1 (ppm)

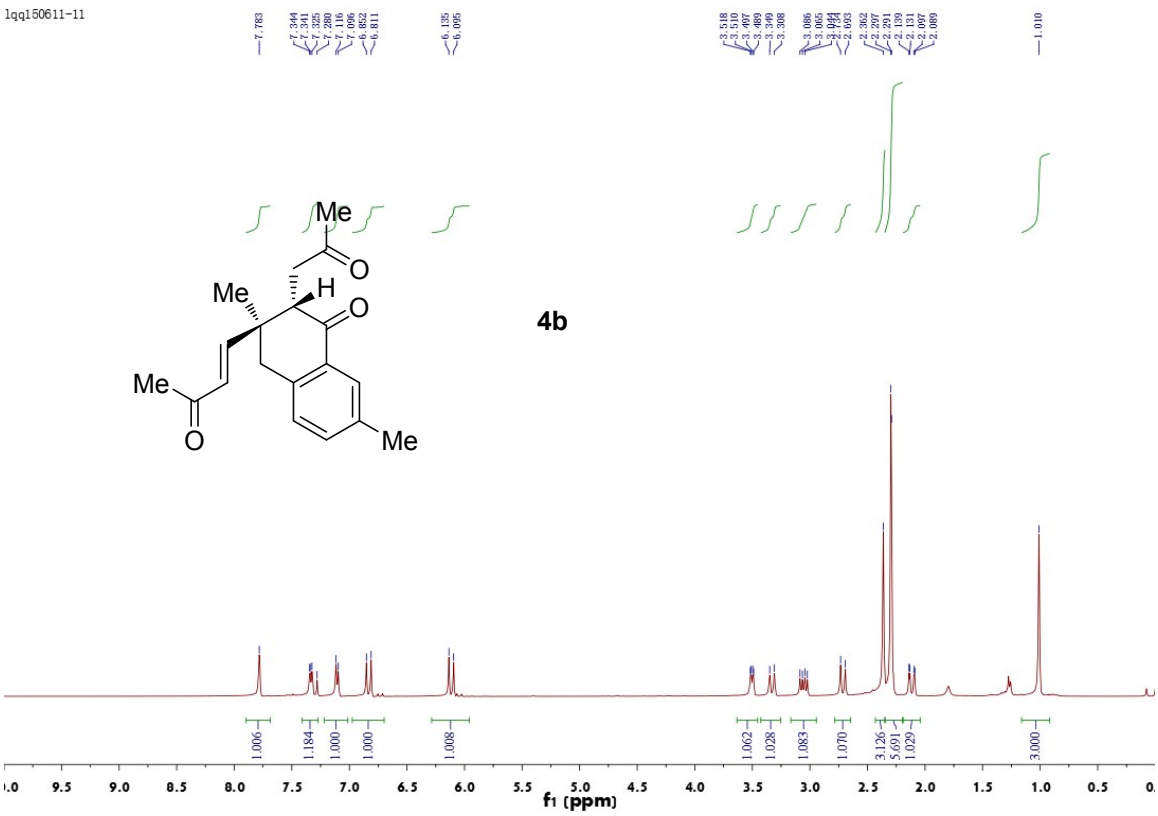

lqq150908-12
-114.171
CO2Et
H
O
EtO2C
F
2k
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

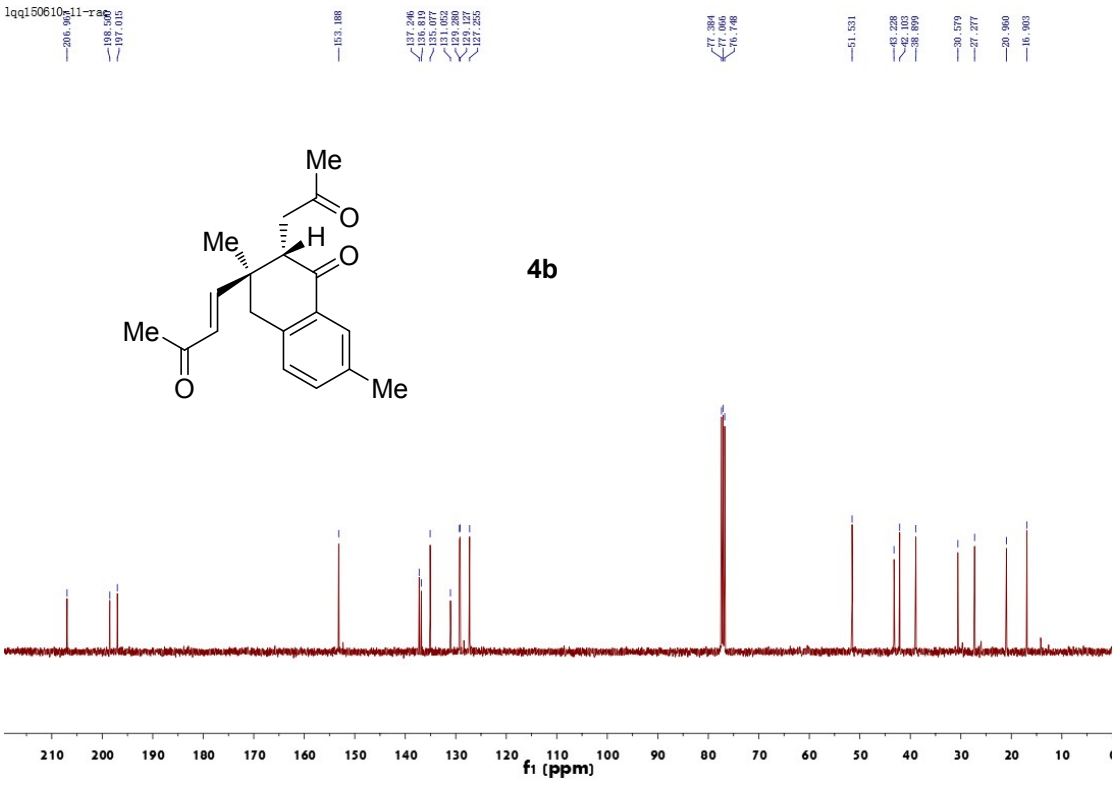

lqq150608-32
CO2Et
H
Me
O
EtO2C
Me
2l
H2O
1.047
1.223
2.079
1.000
4.390
2.007
2.025
3.221
1.038
6.354
3.004
f1 (ppm)

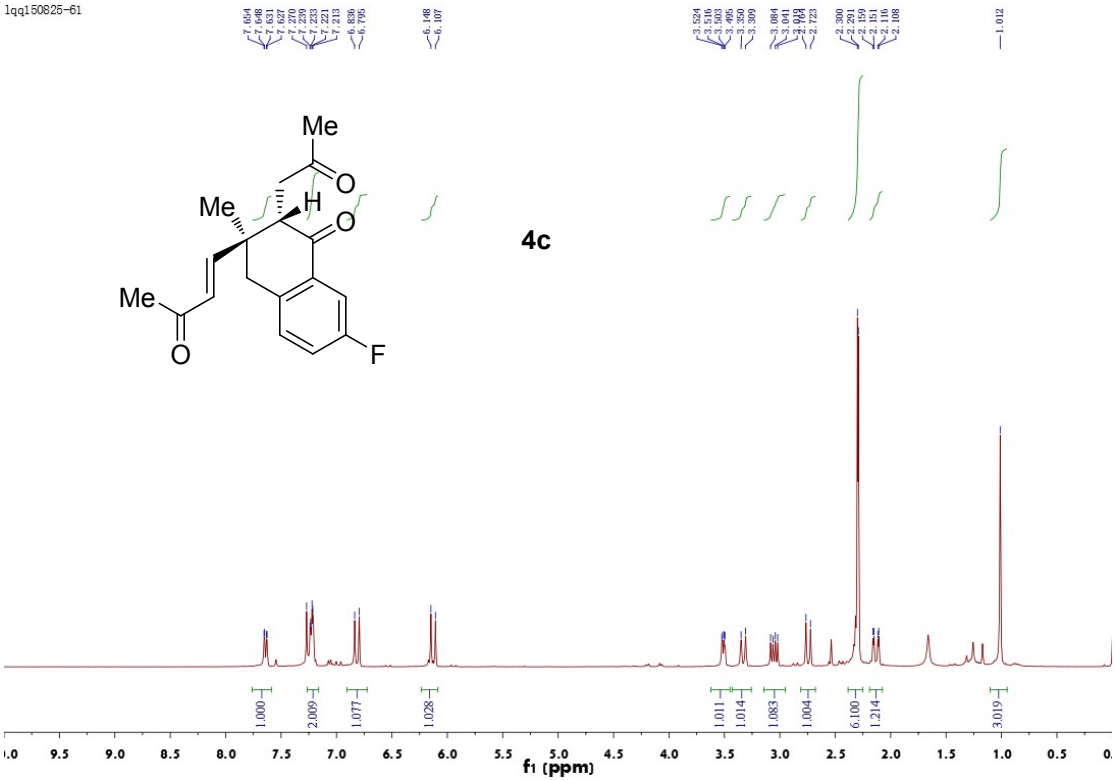

lqq150608-32
CO2Et
H
Me
O
EtO2C
Me
2l
f1 (ppm)

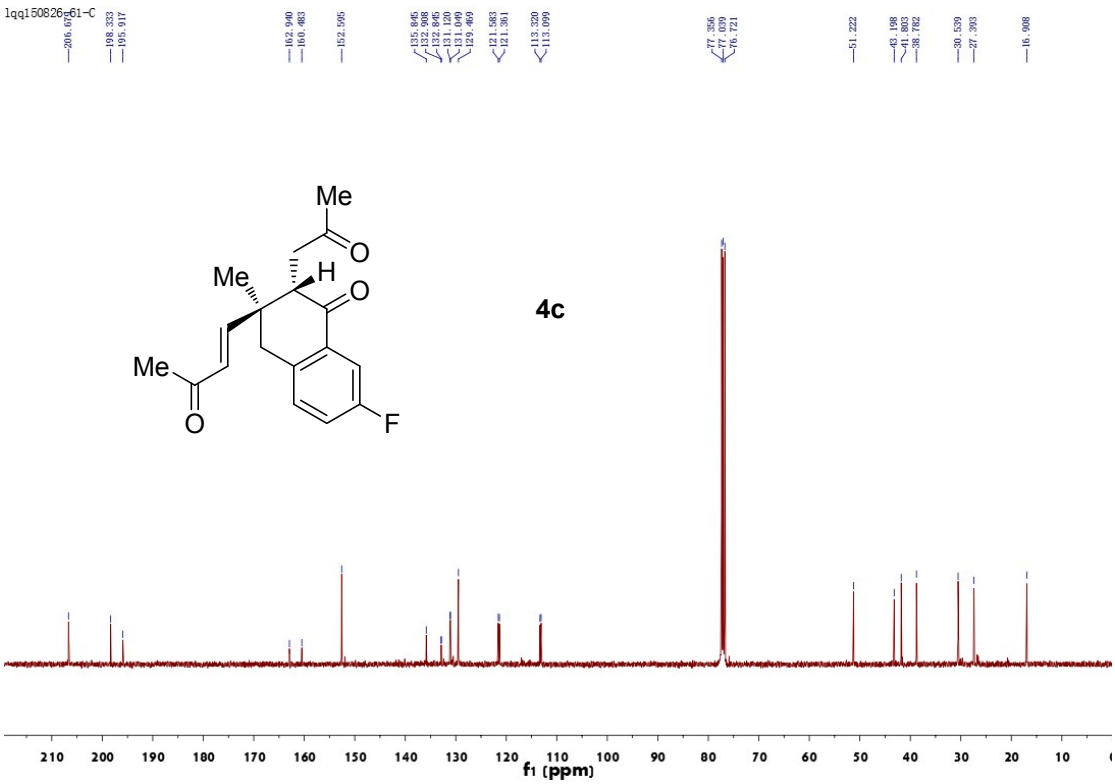

lqq150530-31
Me
O
Me
H
O
Me
O
4a
f1 (ppm)


lqq150530-31
Me
O
Me
H
O
Me
O
4a
f1 (ppm)

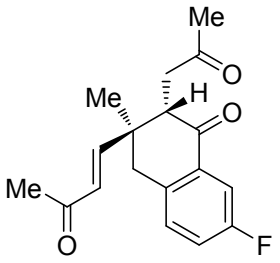

lqq150611-11
Me
O
Me
H
O
Me
O
Me
4b
f1 (ppm)


lqq150610-11-ra
Me
O
Me
H
O
Me
O
Me
4b
f1 (ppm)

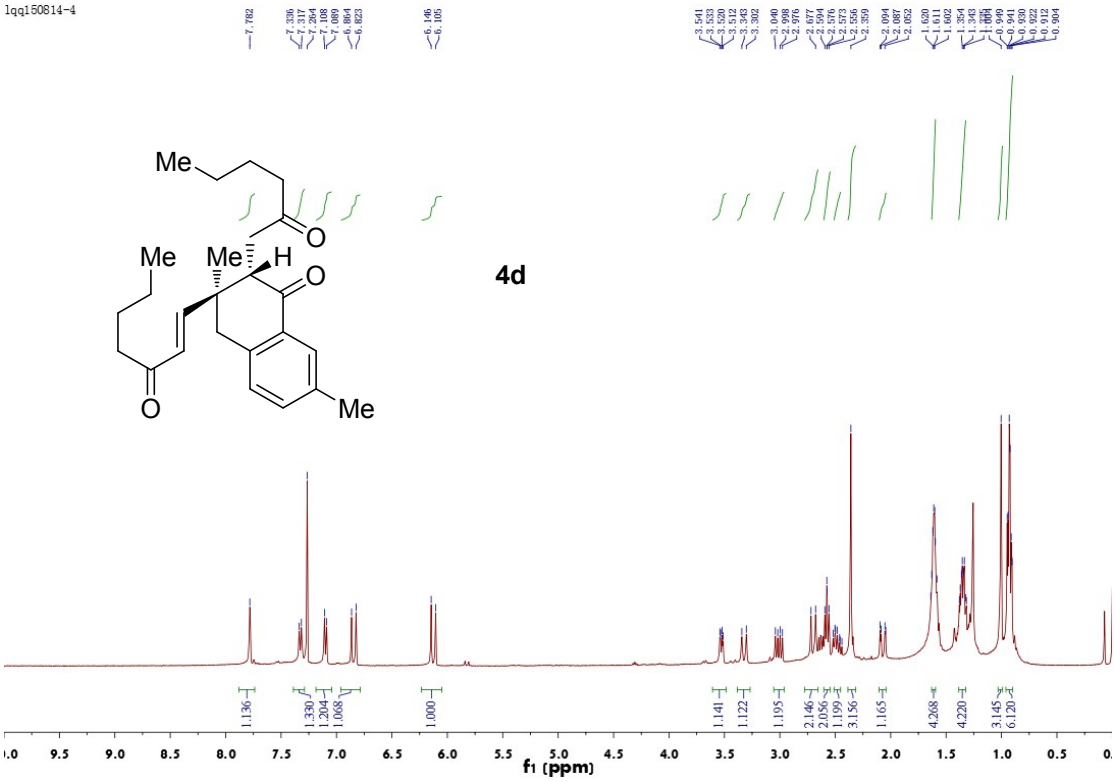

lqq150825-61
Me
O
Me
H
O
Me
O
F
4c
1.000
2.009
1.077
1.028
1.011
1.014
1.083
1.004
6.100
1.214
3.019
f1 (ppm)

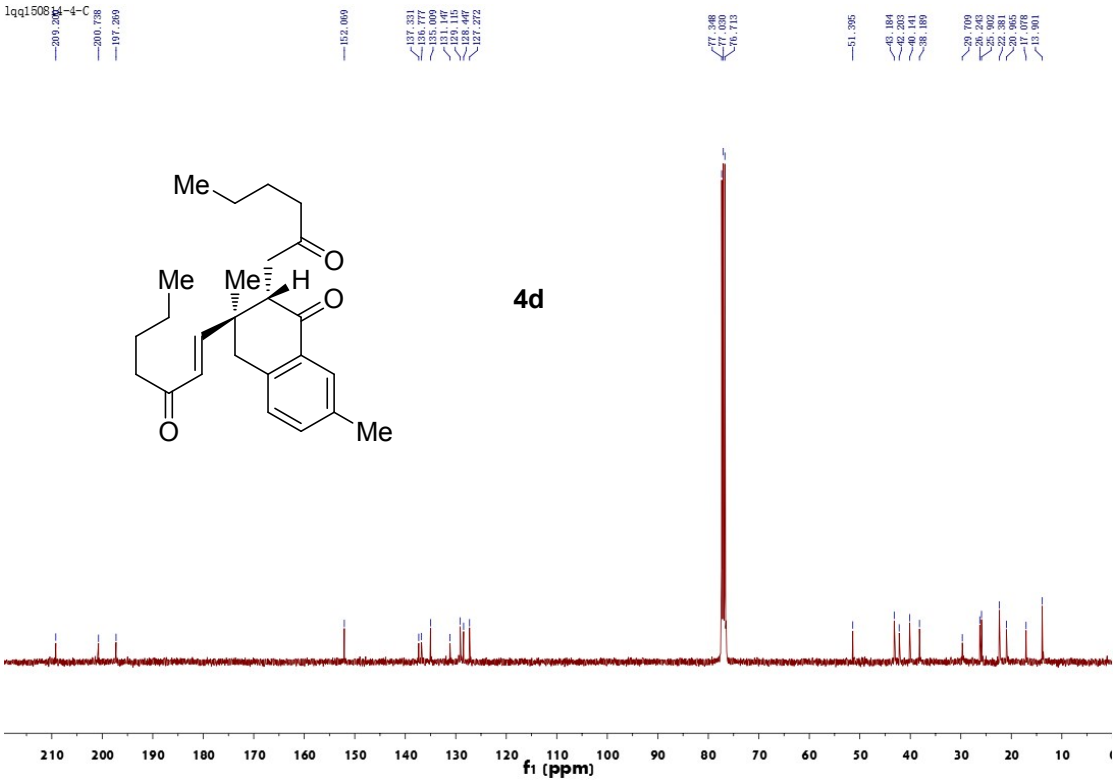

lqq150826-61-C
Me
O
Me
H
O
Me
O
F
4c
f1 (ppm)

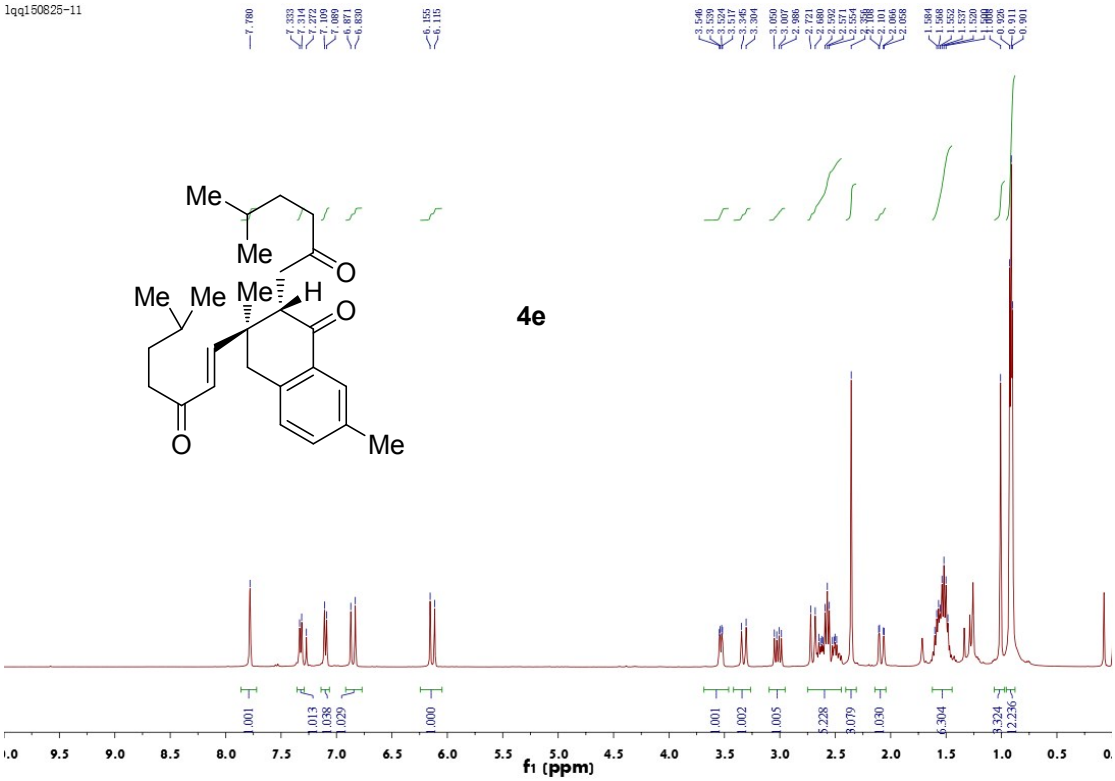
lqq150826-61-C

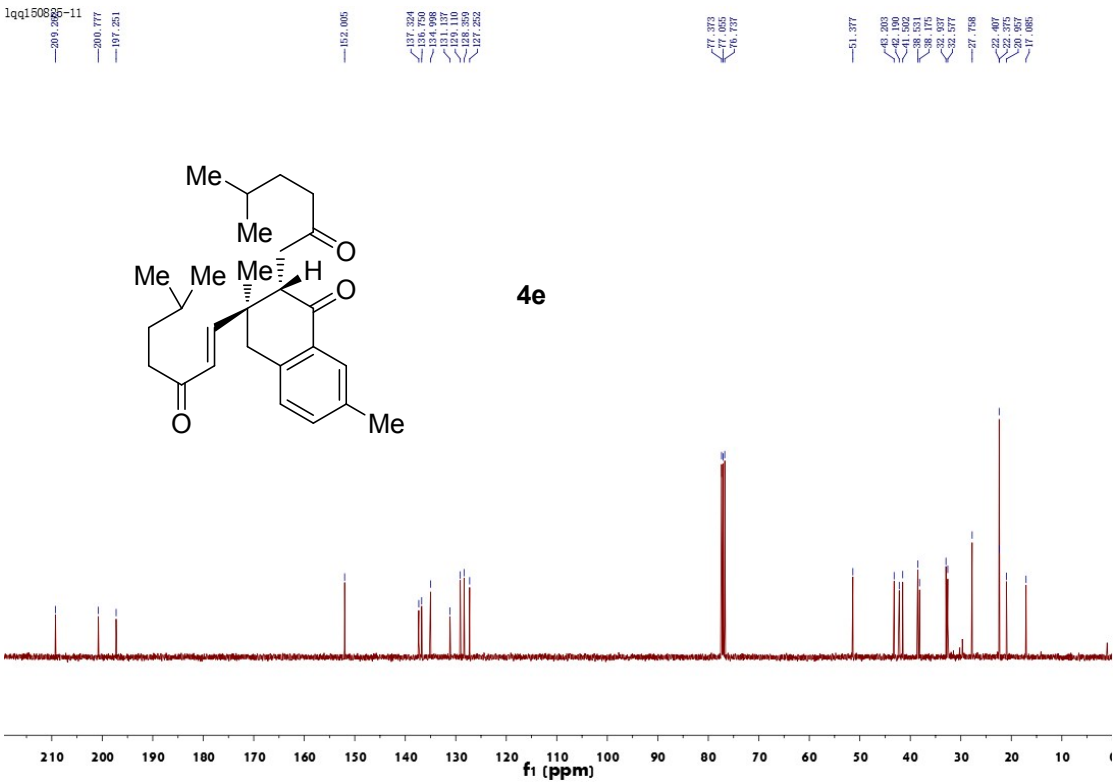


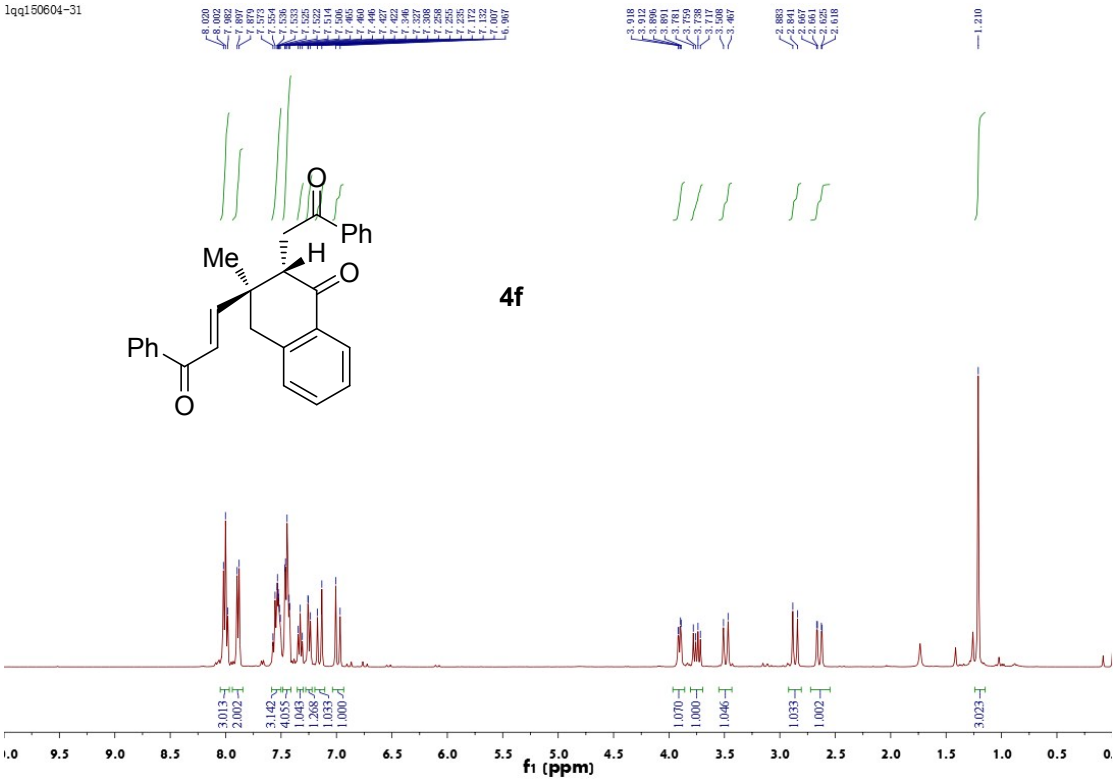
4c

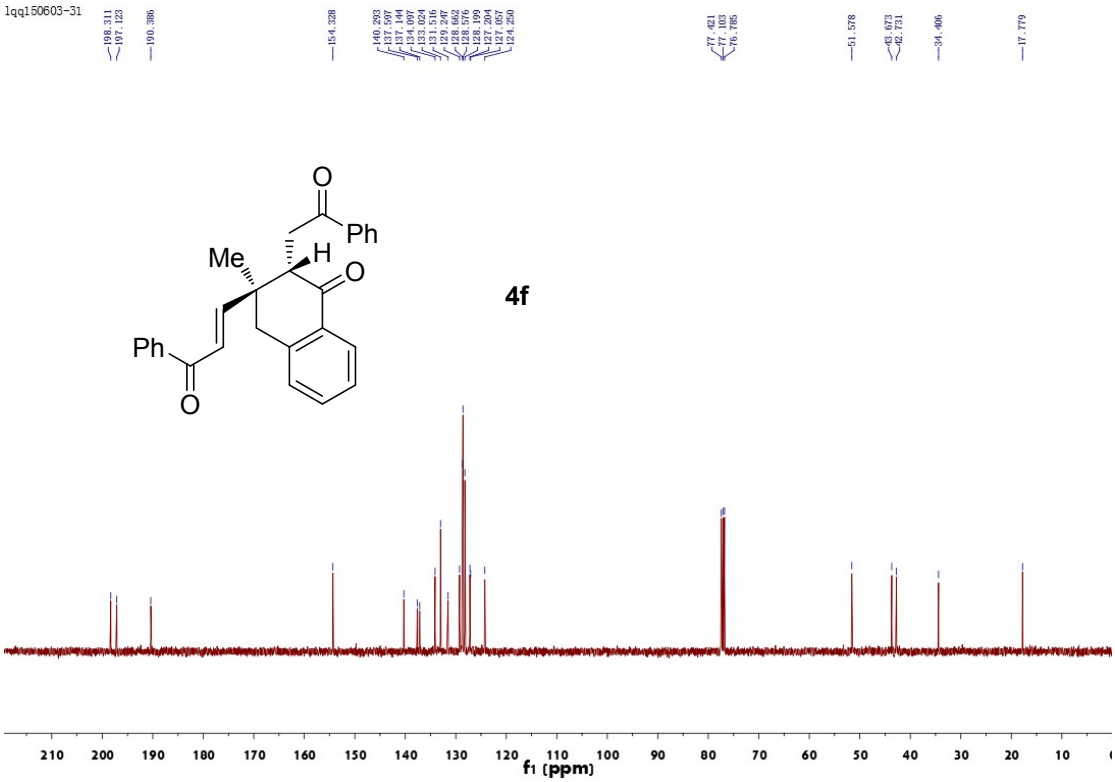

lqq150814-4
Me
Me
Me
H
O
O
O
Me
4d
f1 (ppm)

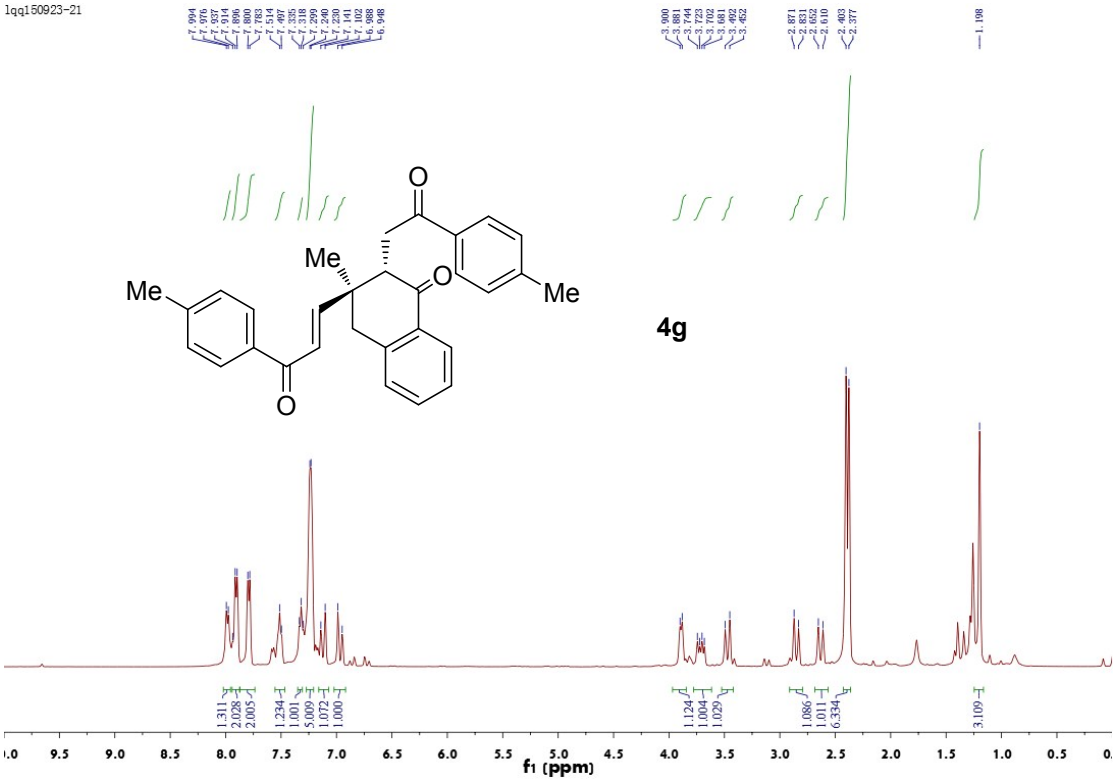

Me
Me
Me
H
O
O
O
Me
4d
f1 (ppm)

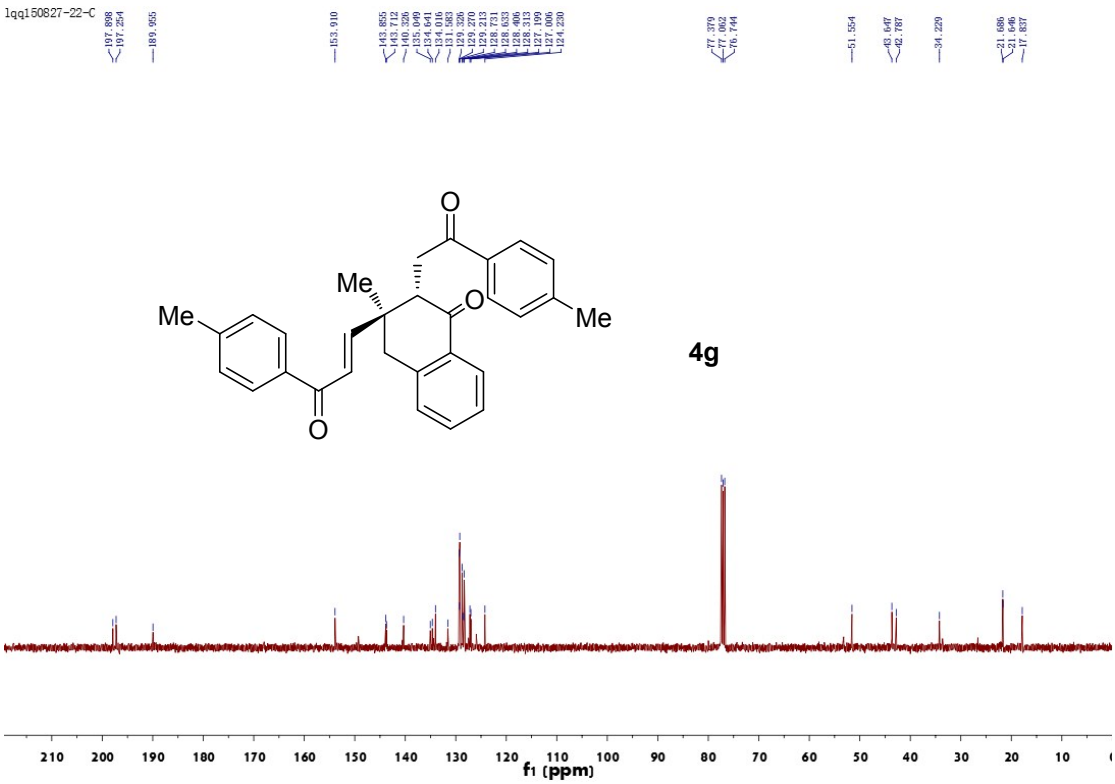

lqq150825-11
Me
Me
Me
Me
Me
H
O
O
O
Me
4e
f1 (ppm)

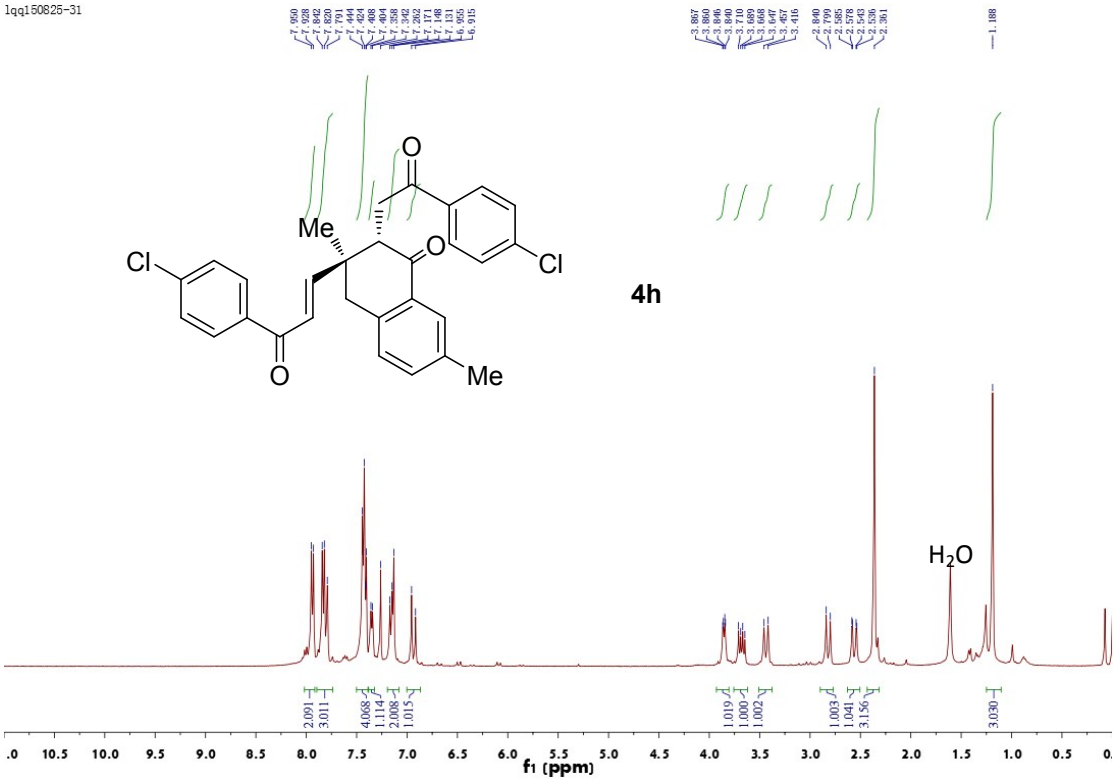

lqq150825-11
Me
Me
Me
Me
Me
H
O
O
O
Me
4e
f1 (ppm)

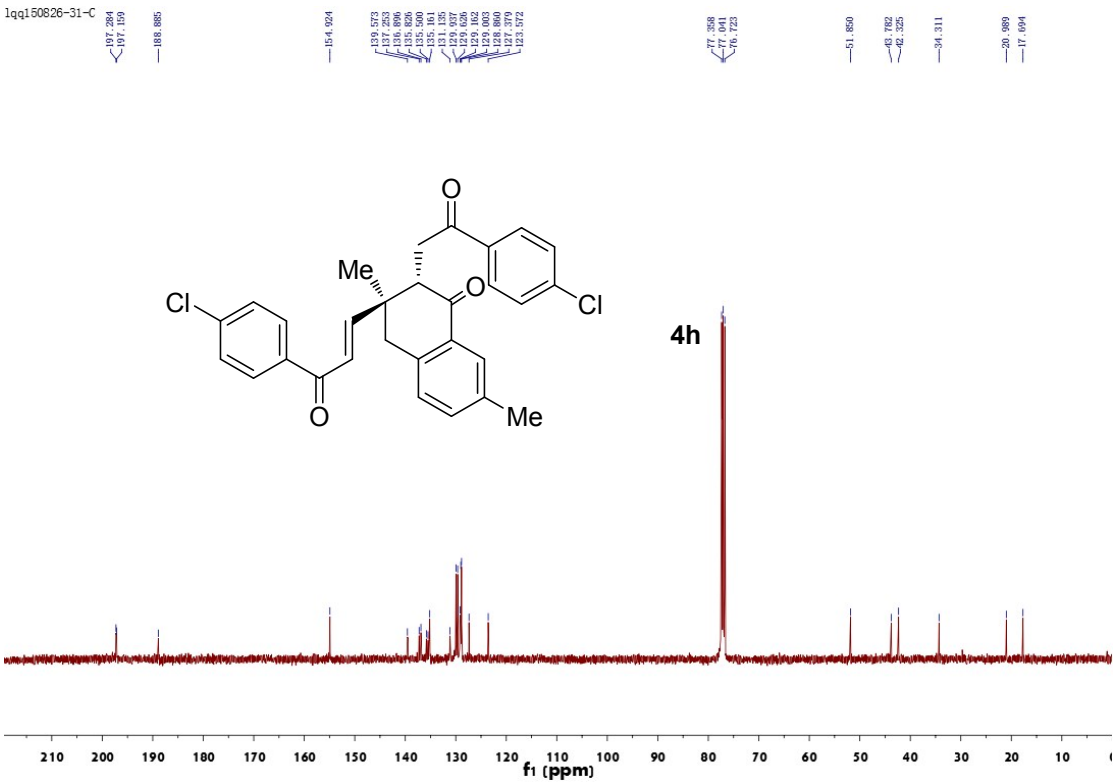

lqq150604-31
Me
H
O
Ph
O
Ph
O
4f
f1 (ppm)

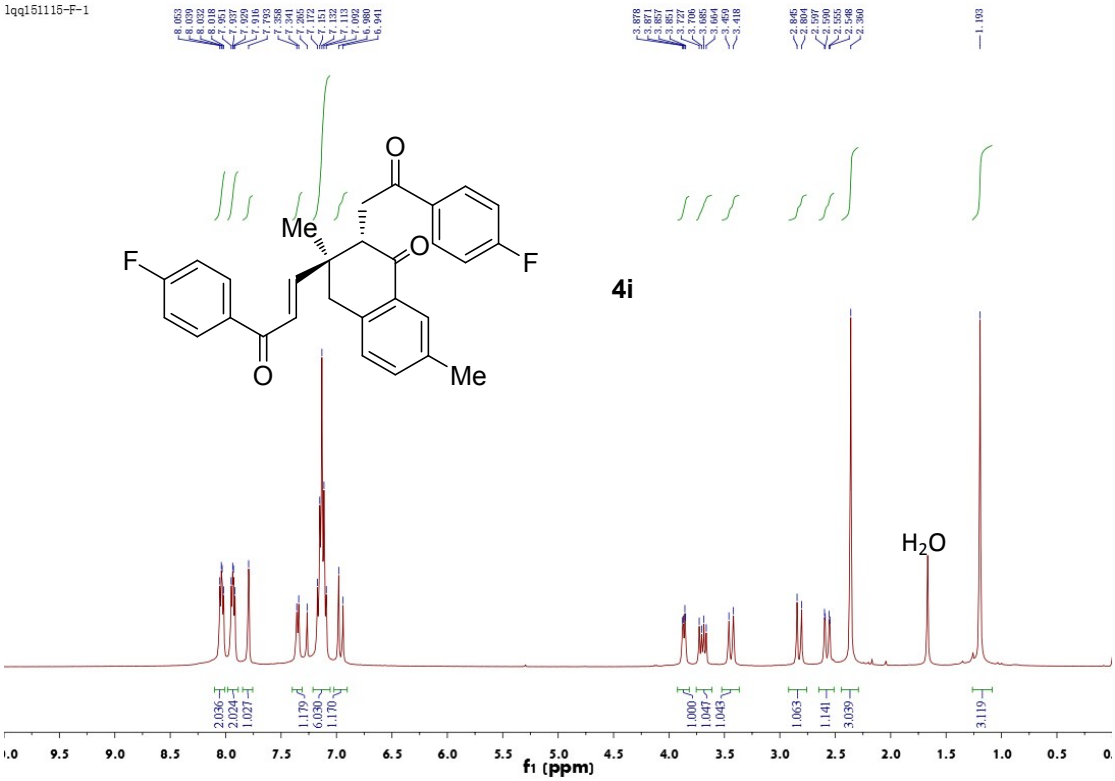

lqq150603-31
Me
H
O
Ph
O
Ph
O
4f
f1 (ppm)

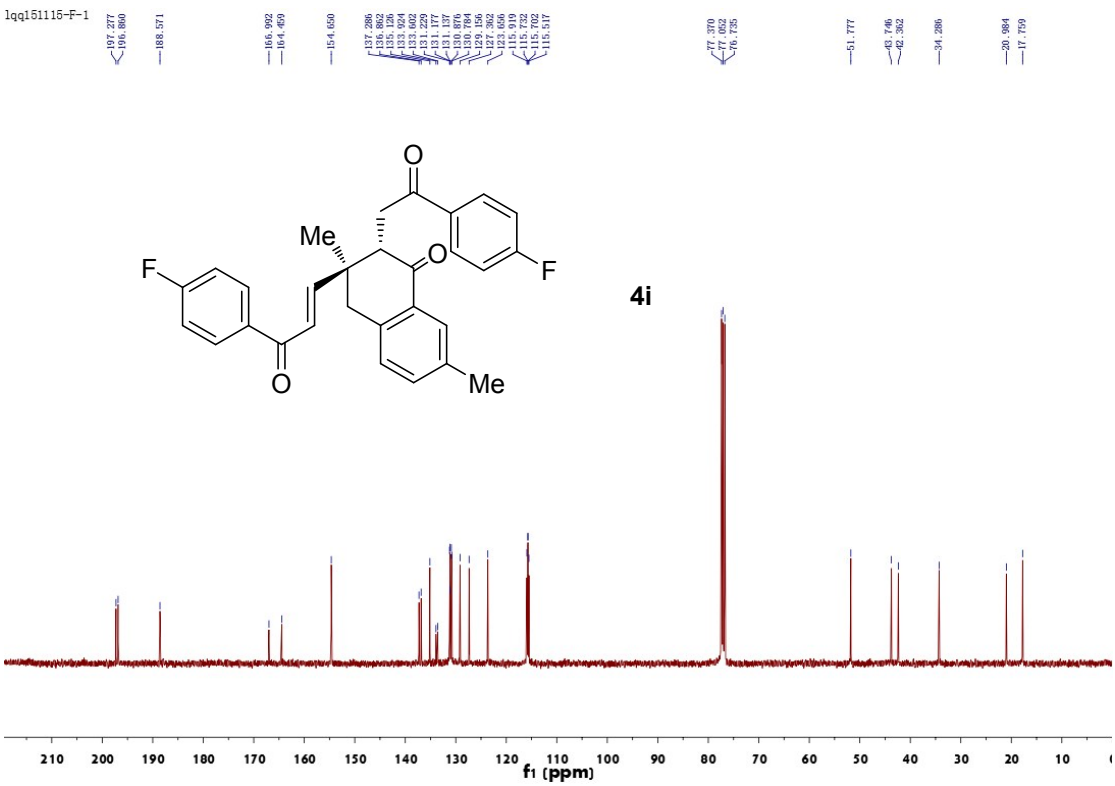

lqq150923-21
Me
Me
O
O
O
4g
f1 (ppm)

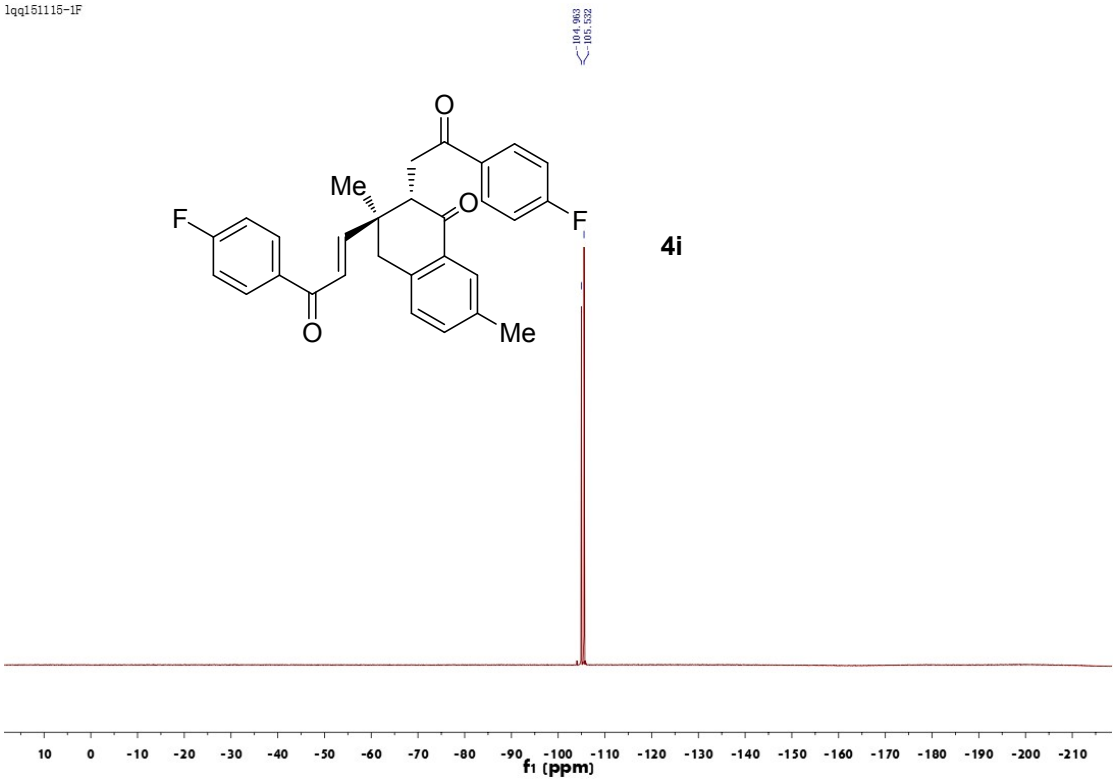

lqq150827-22-C
Me
Me
O
O
O
4g
f1 (ppm)

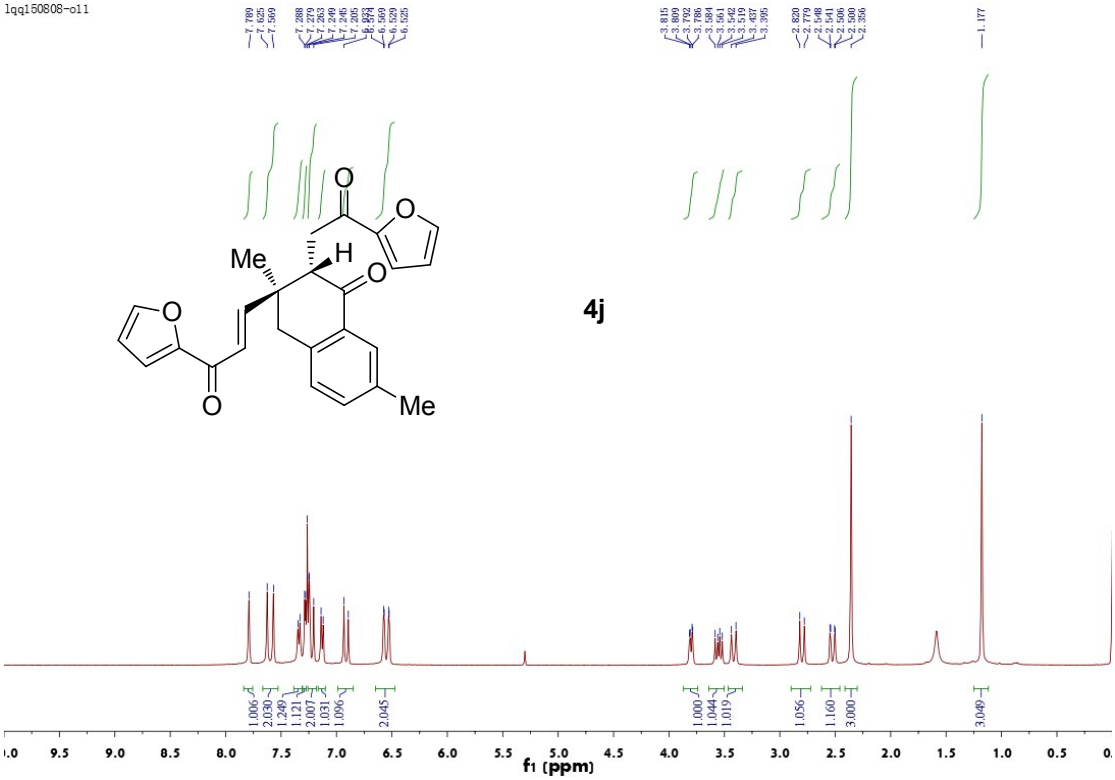

lqq150825-31
Me
Cl
O
O
Cl
Me
4h
H2O
f1 (ppm)

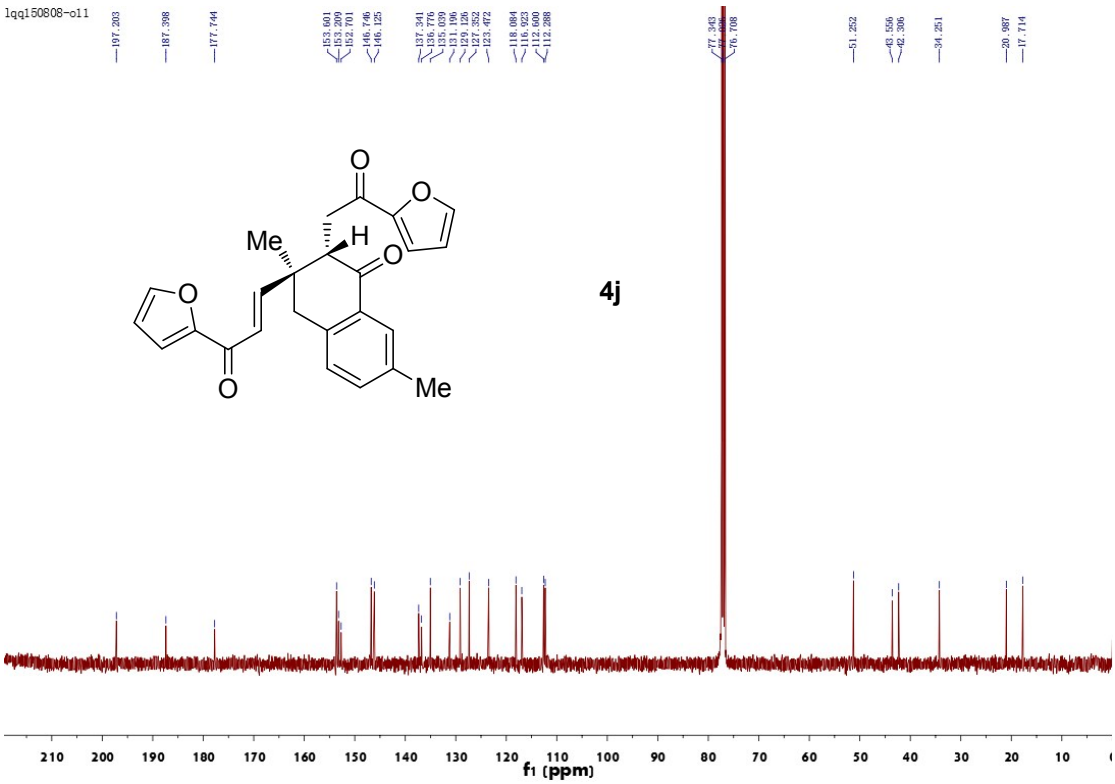

lqq150826-31-C
Me
Cl
O
O
Cl
Me
4h
f1 (ppm)

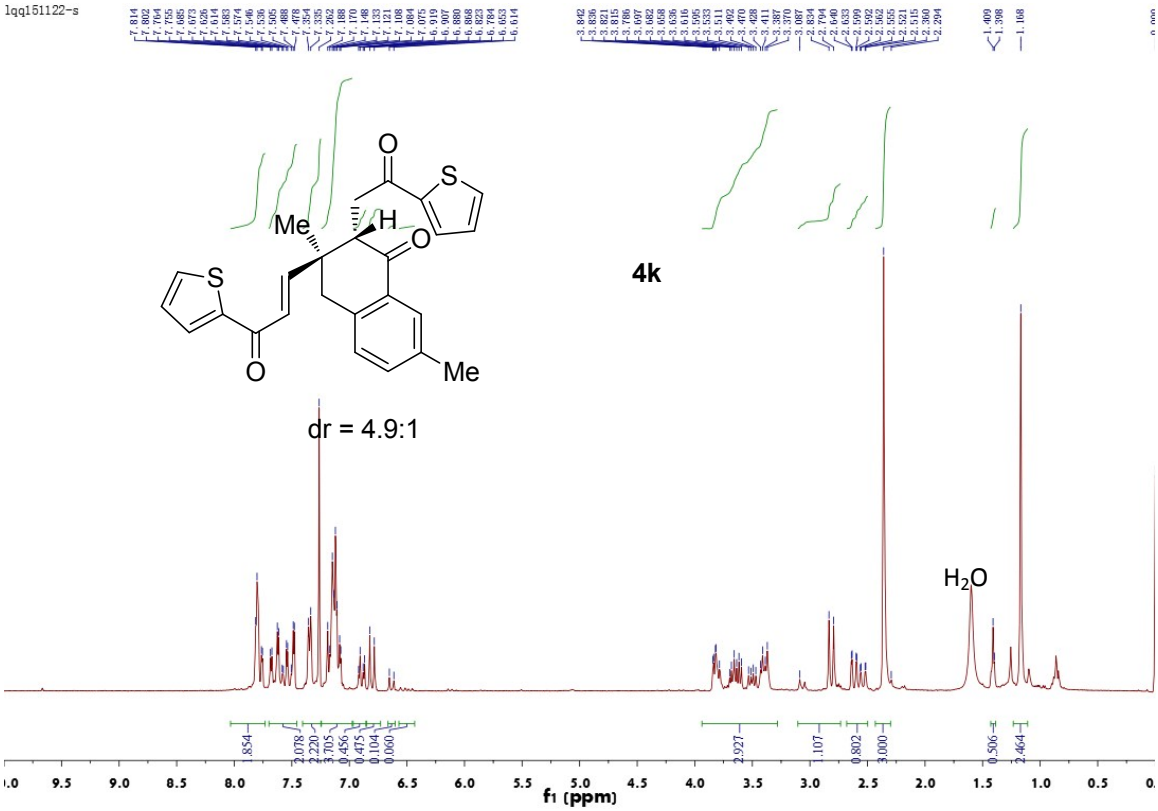

lqq151115-F-1
4i
H2O
f1 (ppm)

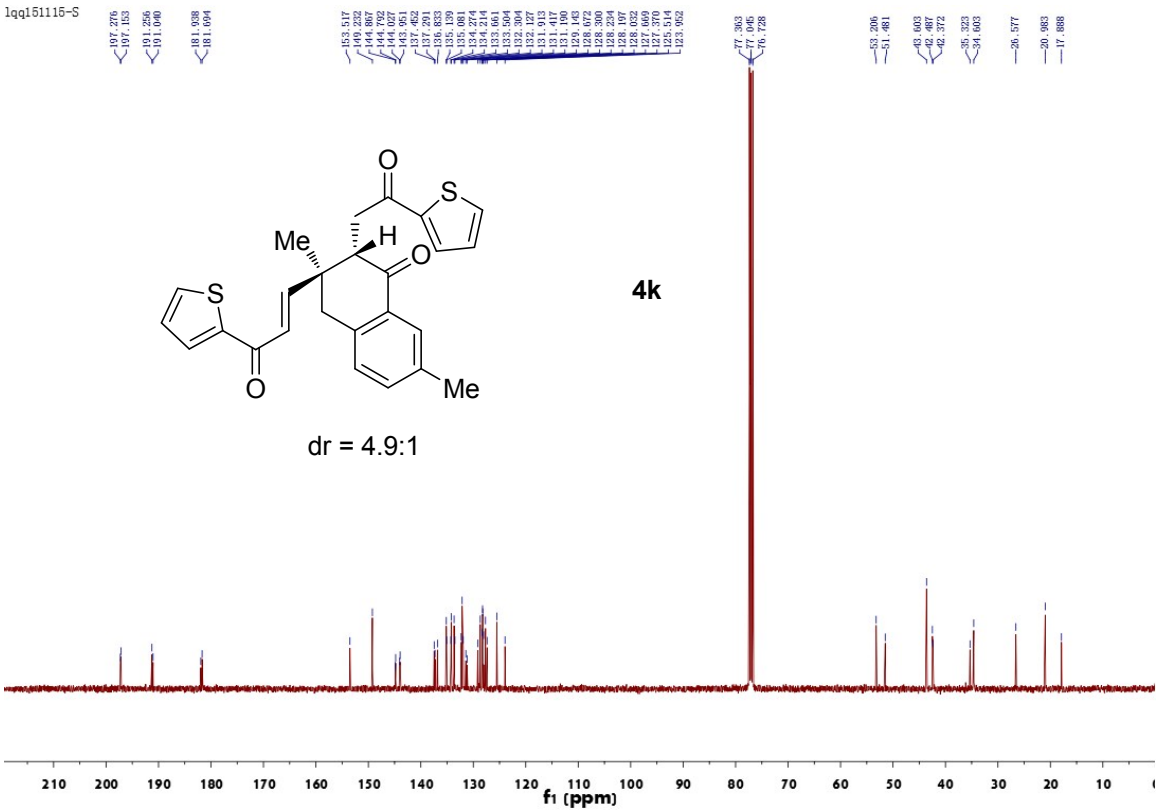

lqq151115-F-1
4i
f1 (ppm)

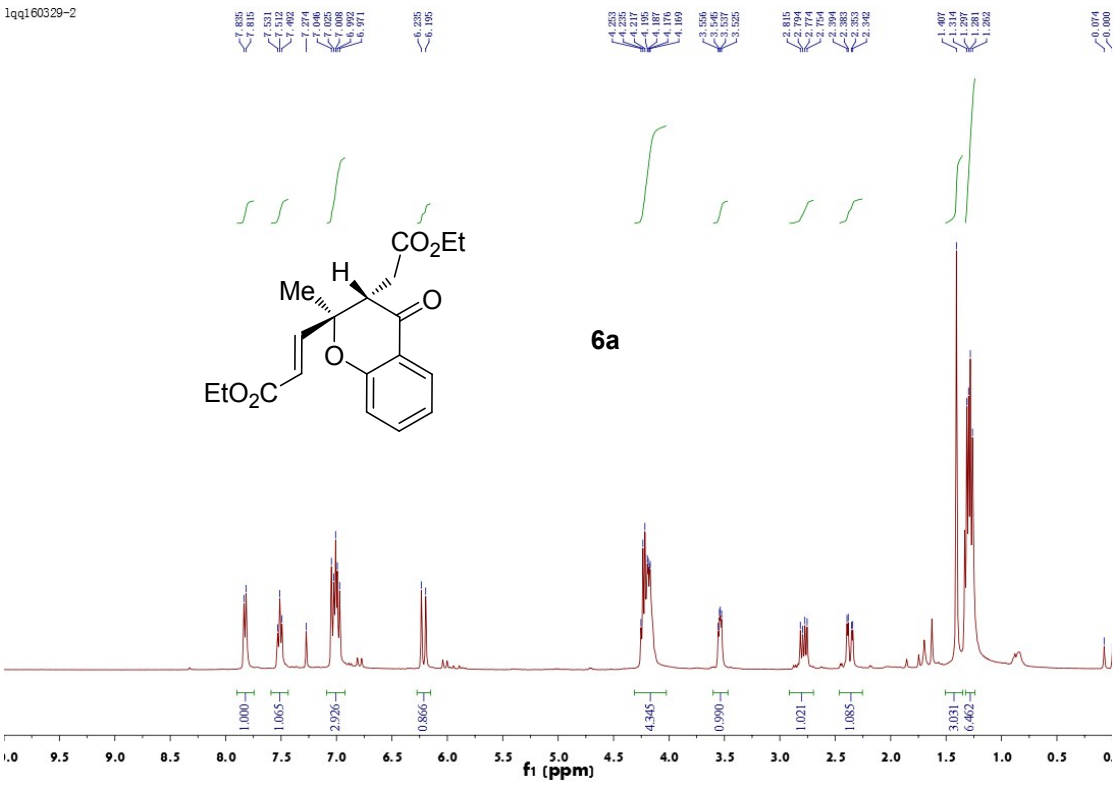

lqq151115-1F
104.963
105.532
O
Me
O
F
F
O
Me
4i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

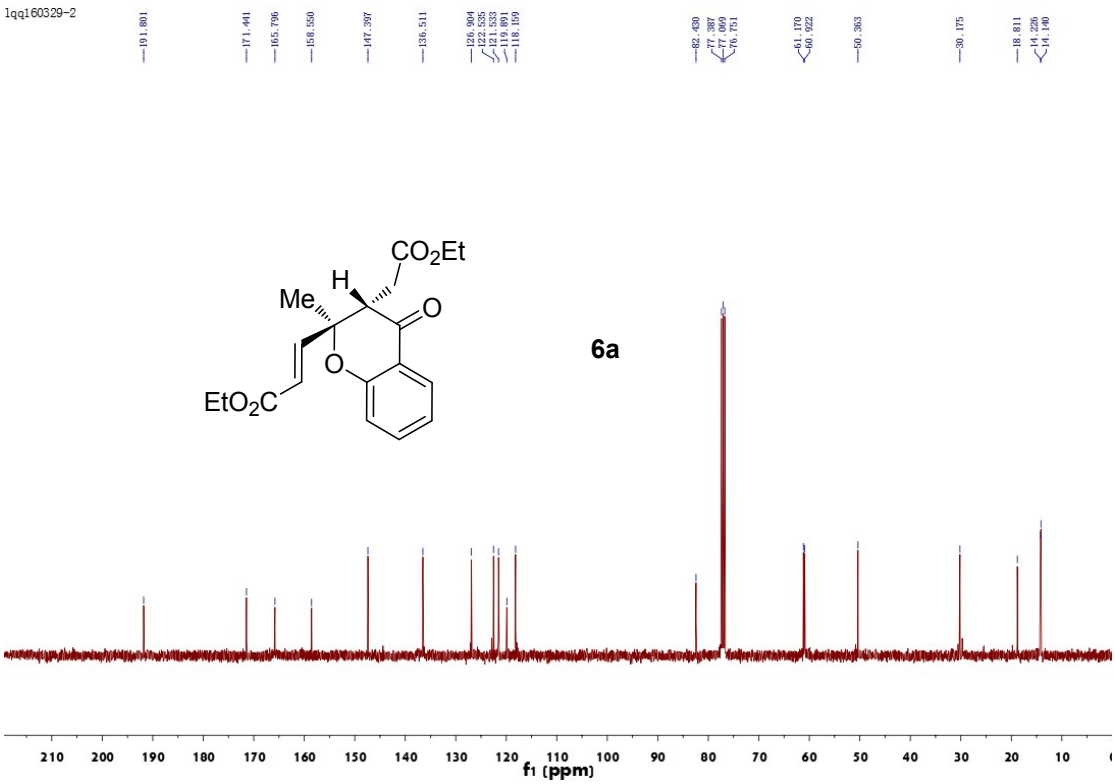

lqq150808-o11
Me
H
O
O
O
O
O
Me
4j
f1 (ppm)

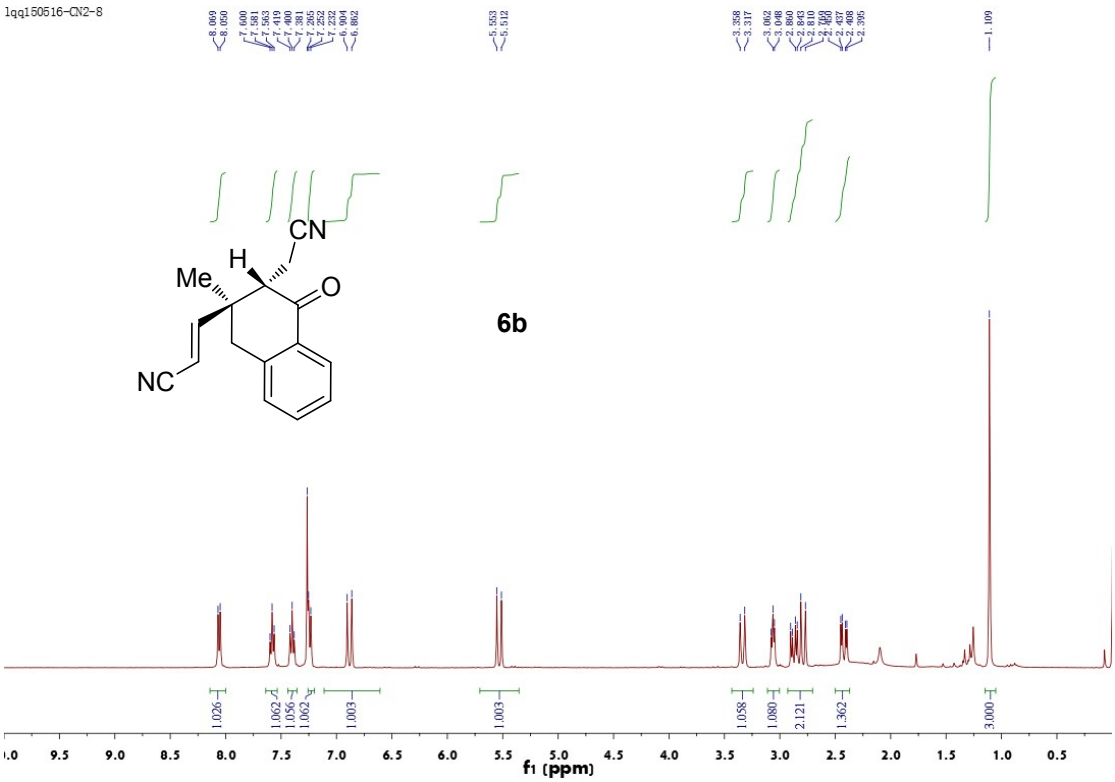

lqq150808-o11
Me
H
O
O
O
O
O
Me
4j
f1 (ppm)

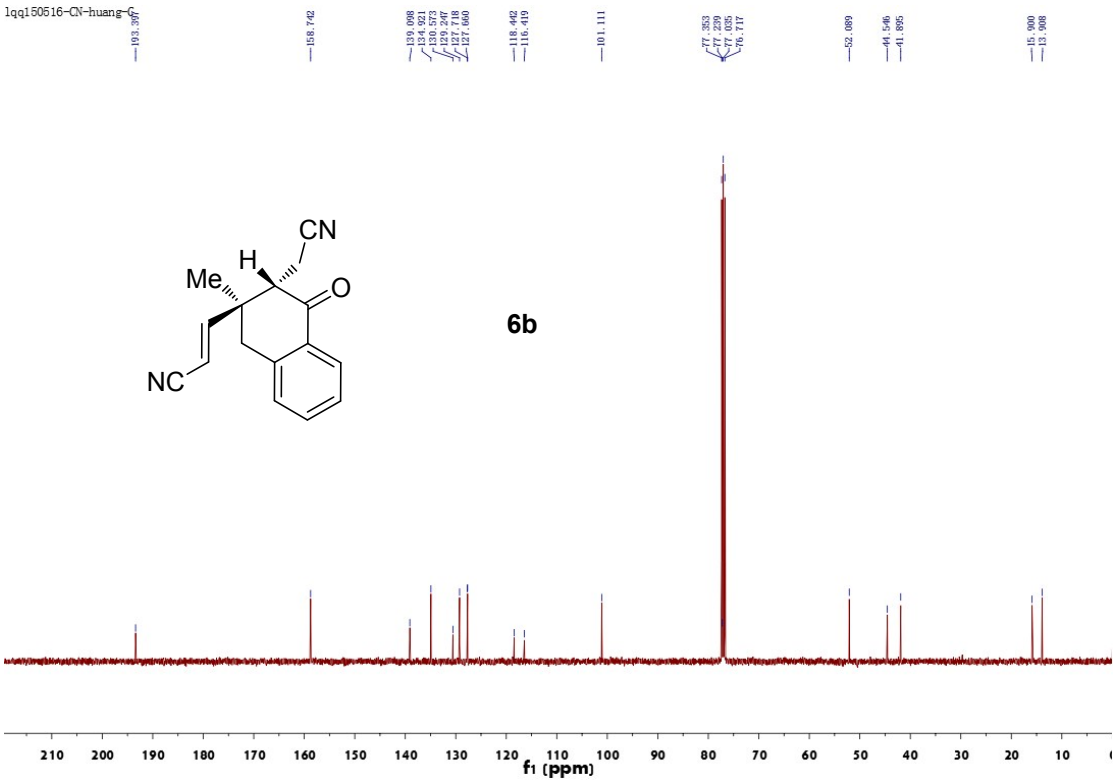

lqq151122-s
Me
H
O
S
O
S
O
Me
4k
dr = 4.9:1
H2O
f1 (ppm)

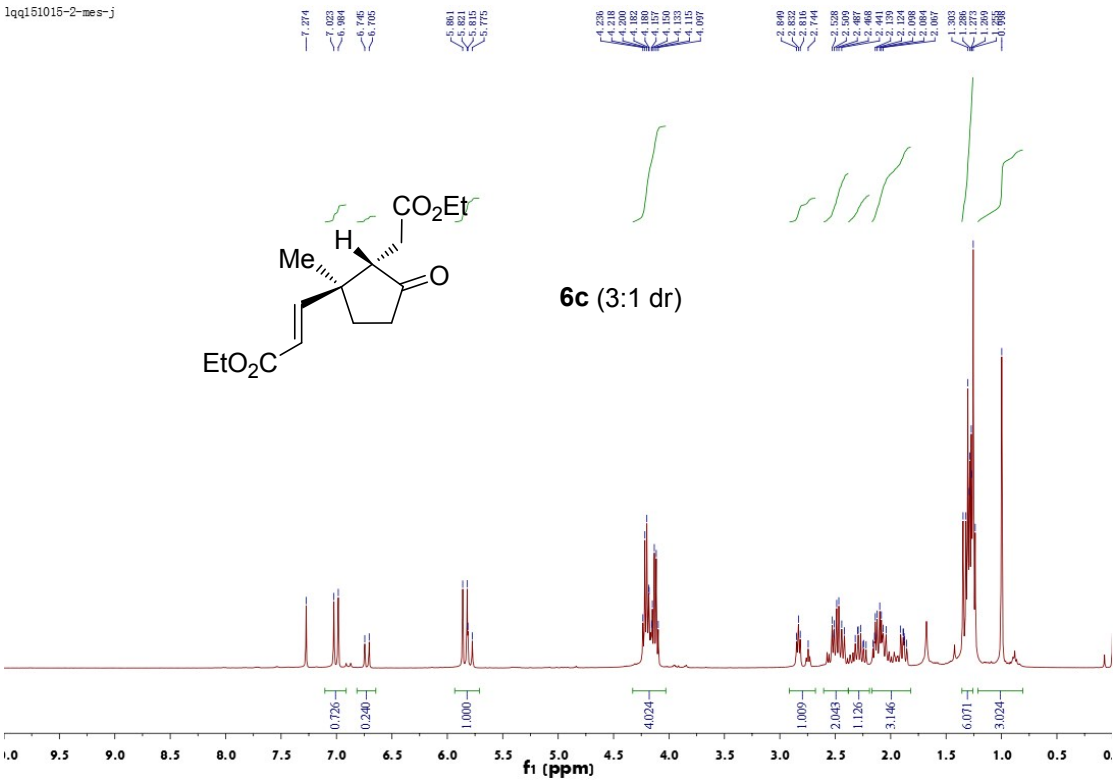

lqq151115-S
Me
H
O
S
O
S
O
Me
4k
dr = 4.9:1
f1 (ppm)

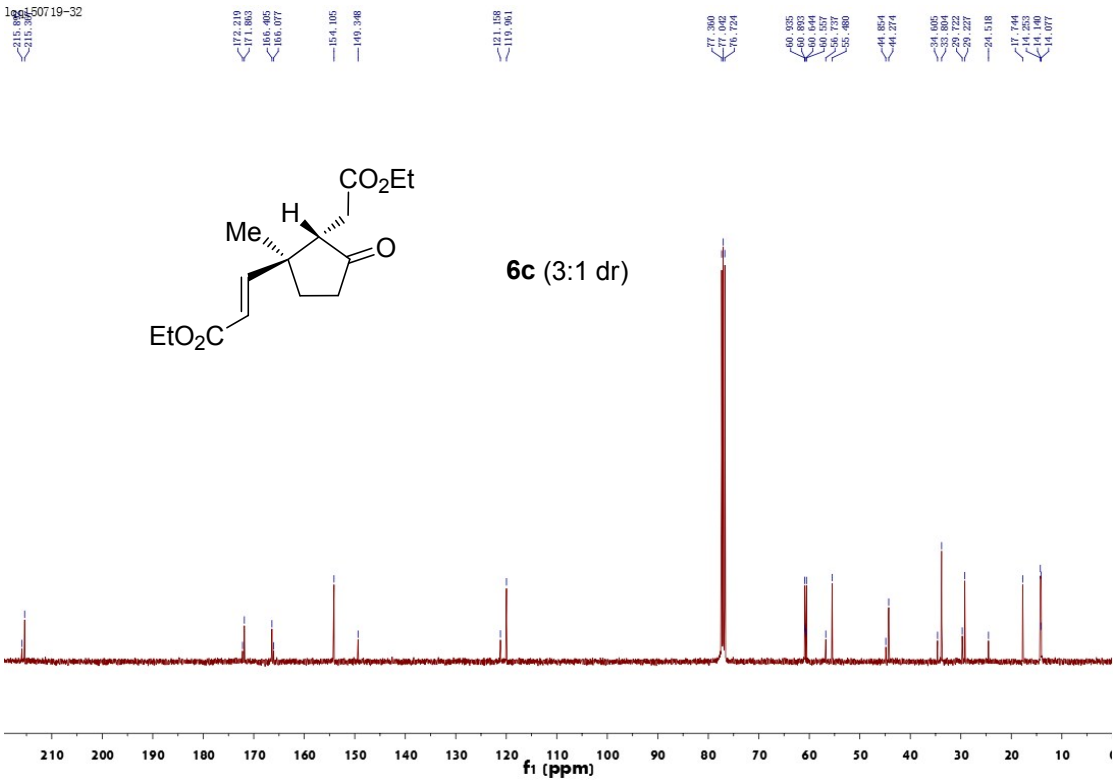

lqq160329-2
CO2Et
H
Me
O
O
EtO2C
6a
1.000
1.065
2.926
0.866
4.345
0.990
1.021
1.085
3.031
6.462
f1 (ppm)

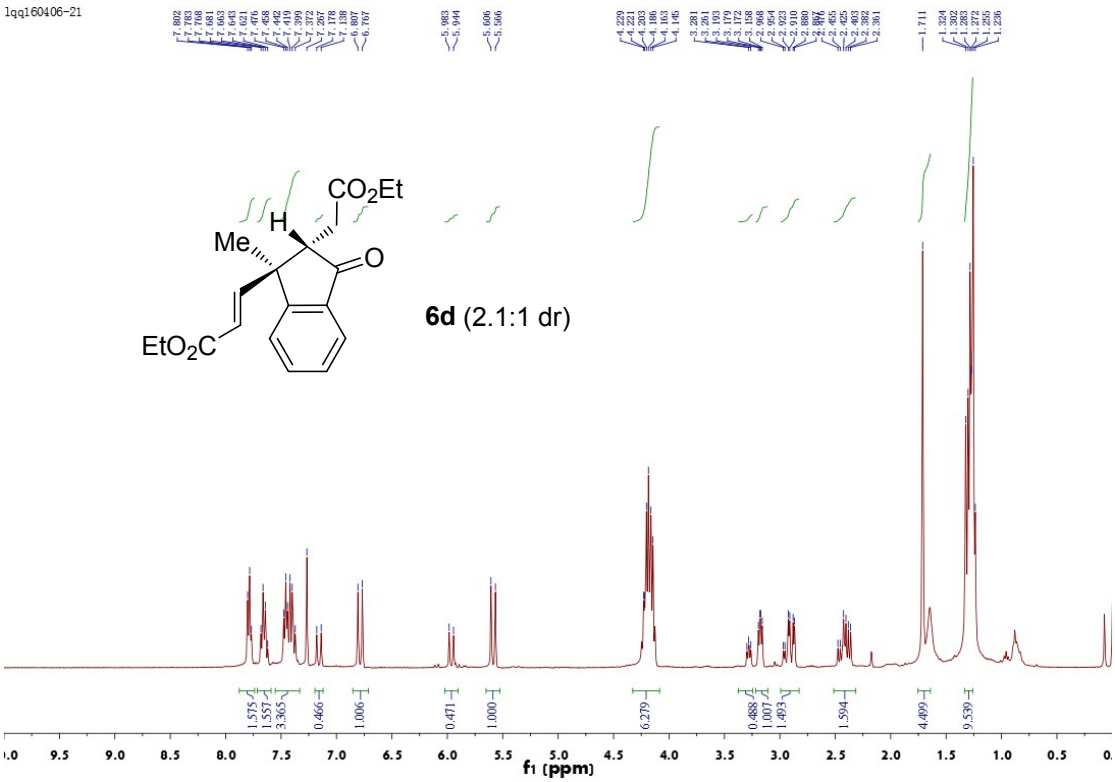

lqq160329-2
CO2Et
H
Me
O
O
EtO2C
6a
f1 (ppm)

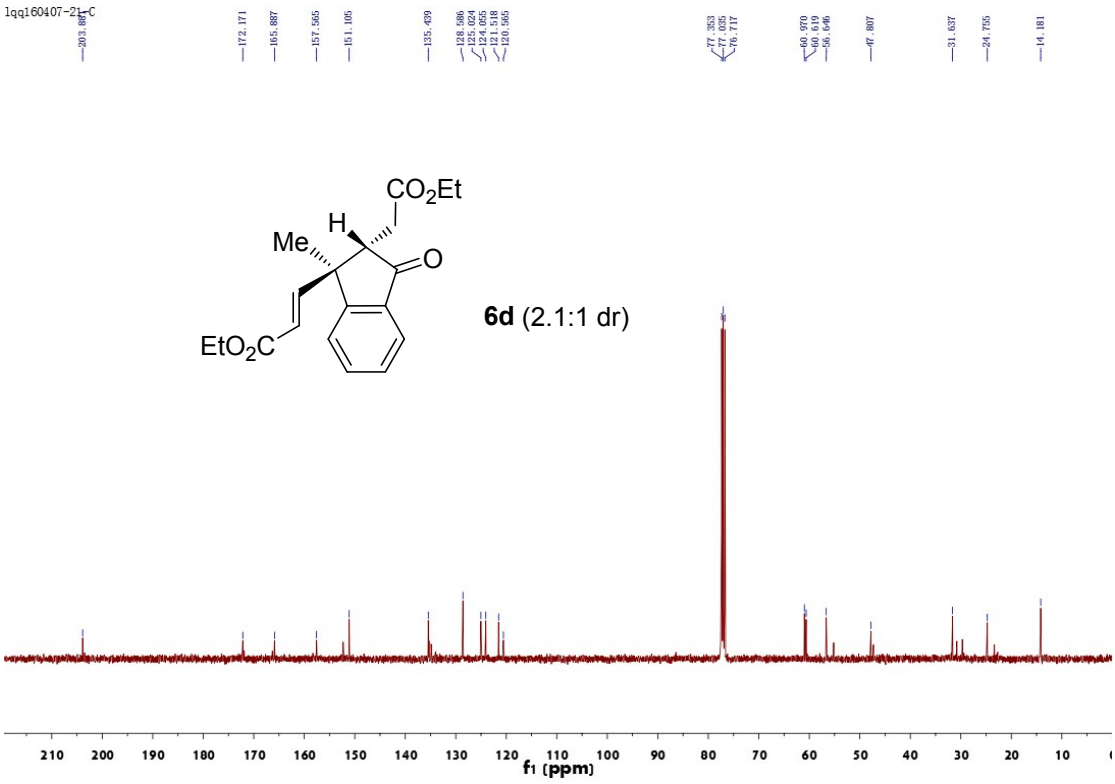

lqq150516-CN2-8
CN
H
Me
O
NC
6b
f1 (ppm)


lqq150516-CN-huang-C
CN
H
Me
O
NC
6b
f1 (ppm)


lqq151015-2-mes-j
CO2Et
H
Me
O
EtO2C
6c (3:1 dr)
f1 (ppm)


lqq150719-32
CO2Et
H
Me
O
EtO2C
6c (3:1 dr)
f1 (ppm)


lqq160406-21
CO2Et
H
Me
O
EtO2C
6d (2.1:1 dr)
f1 (ppm)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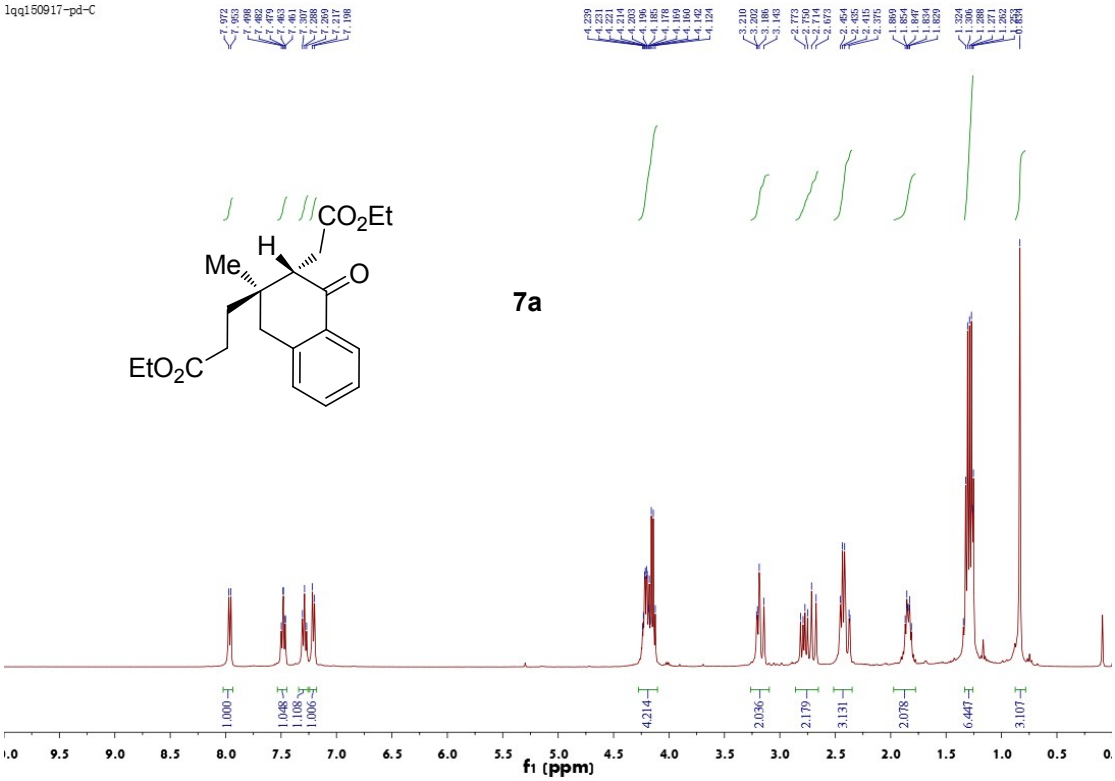
CO2Et
H
Me
O
EtO2C
6d (2.1:1 dr)
f1 (ppm)


lqq150917-pd-C
CO2Et
H
Me
O
EtO2C
7a
1.000
1.048
1.108
1.006
4.214
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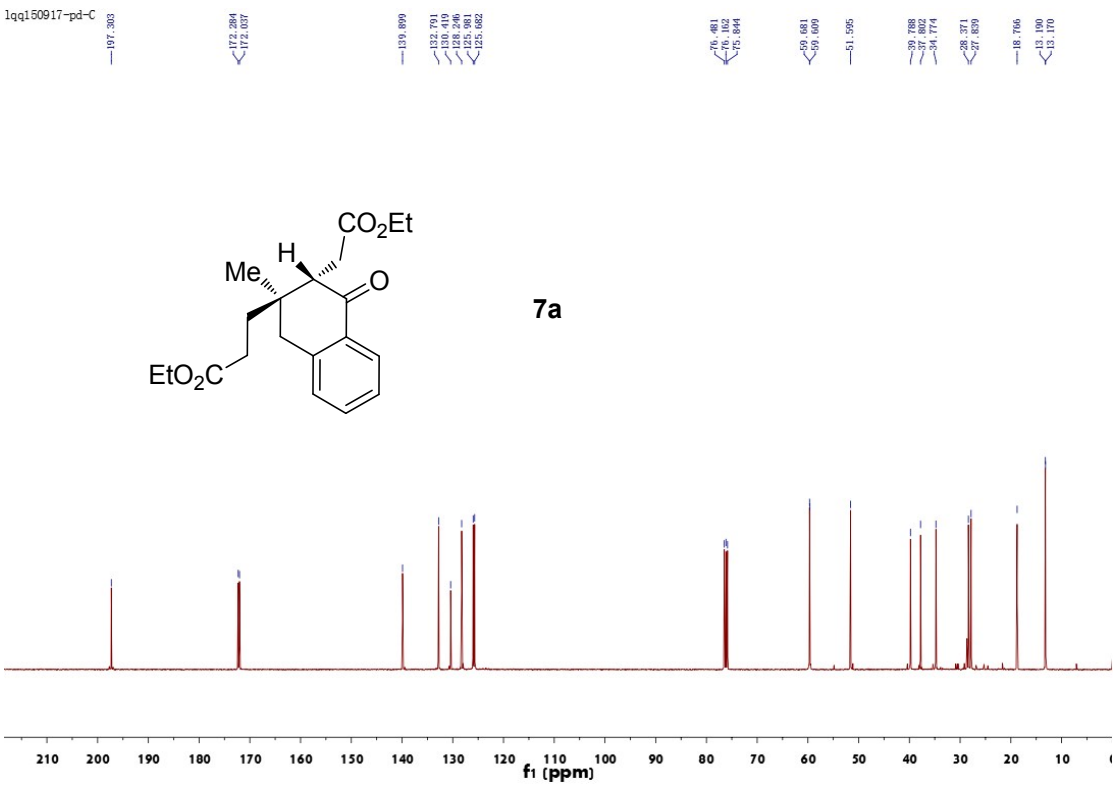
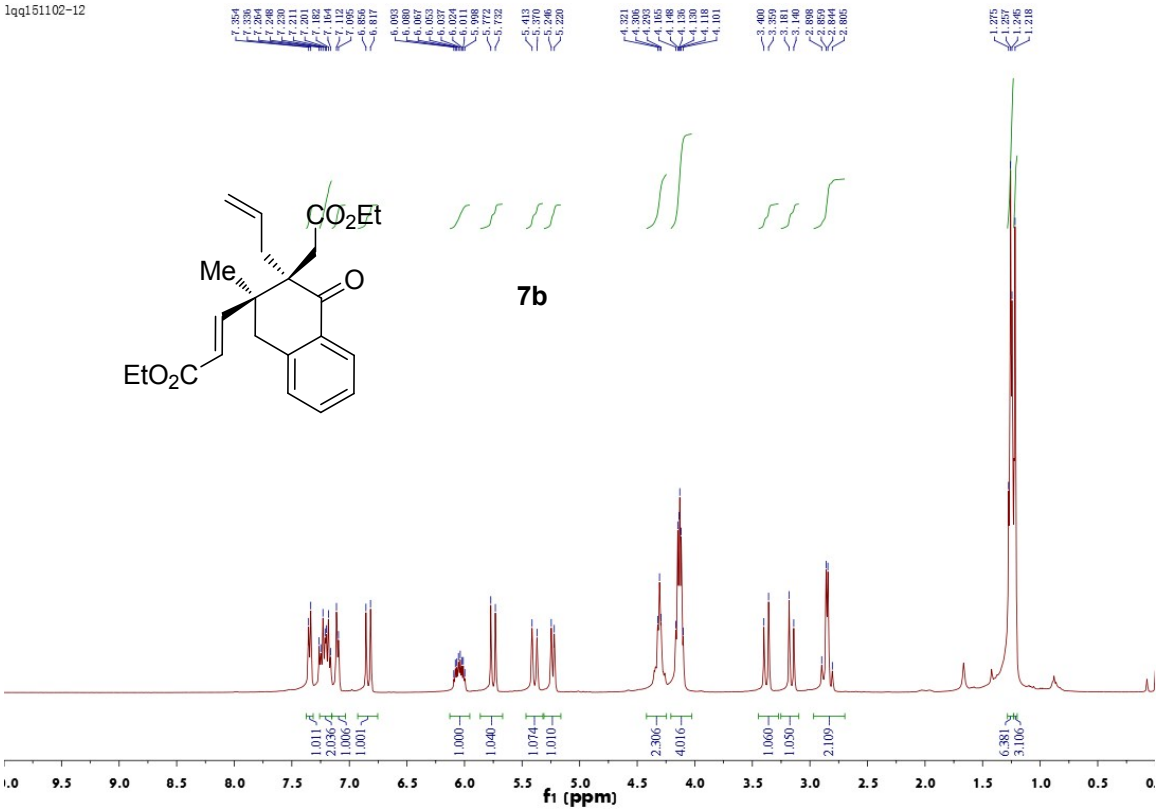
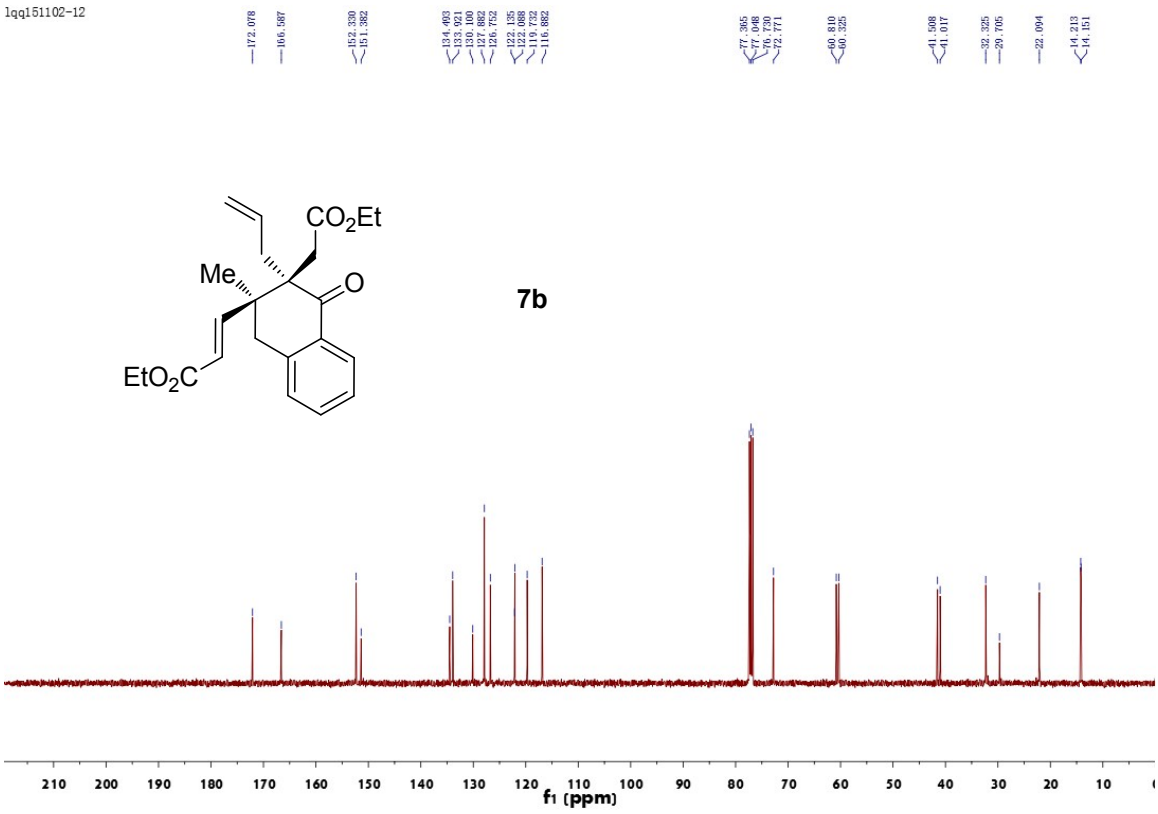
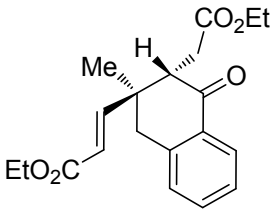
2.179
3.131
2.078
6.447
3.107
f1 (ppm)


lqq150917-pd-C
197.303
172.284
172.037
139.899
132.791
130.419
128.246
125.981
125.682
76.481
76.162
75.844
59.681
59.609
51.595
39.788
37.802
34.774
28.371
27.839
18.766
13.190
13.170
CO2Et
H
Me
O
EtO2C
7a
f1 (ppm)


lqq151102-12
CO2Et
Me
O
EtO2C
7b
f1 (ppm)


lqq151102-12
CO2Et
Me
O
EtO2C
7b
f1 (ppm)

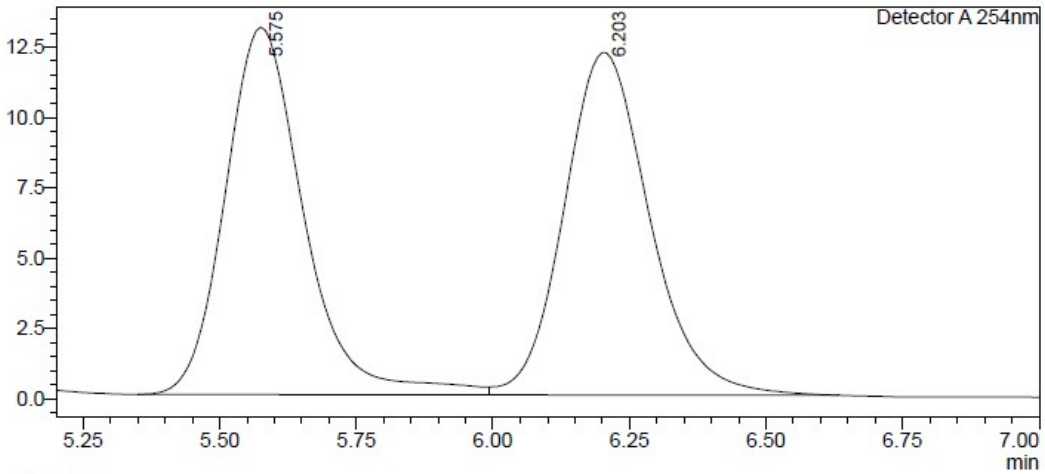
VIII. HPLC spectra for *ee* determination.



2a

<Chromatogram>

mV



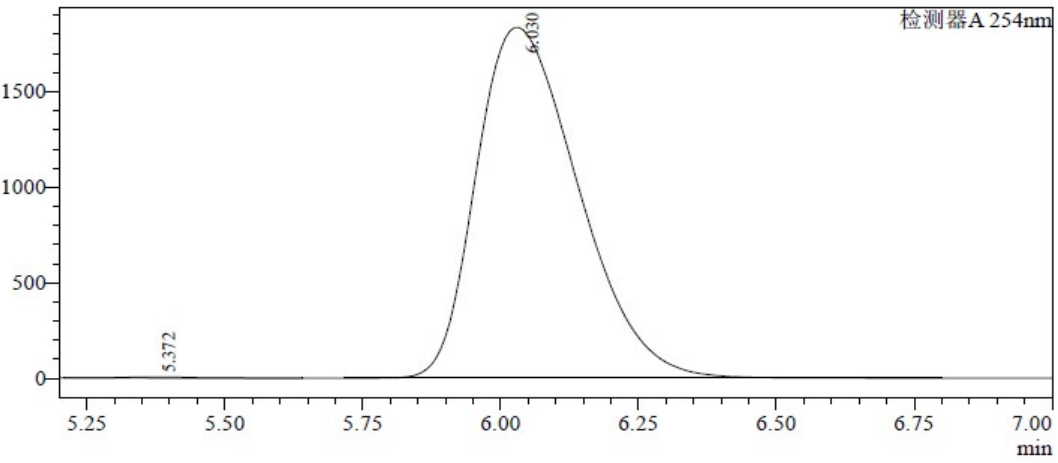
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.575	131289	13059	49.696			
2	6.203	132898	12170	50.304		V	
Total		264187	25229				

<Chromatogram>

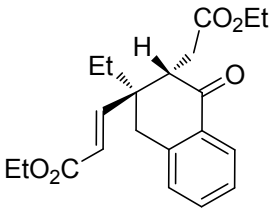
mV



<Peak Table>

检测器A 254nm

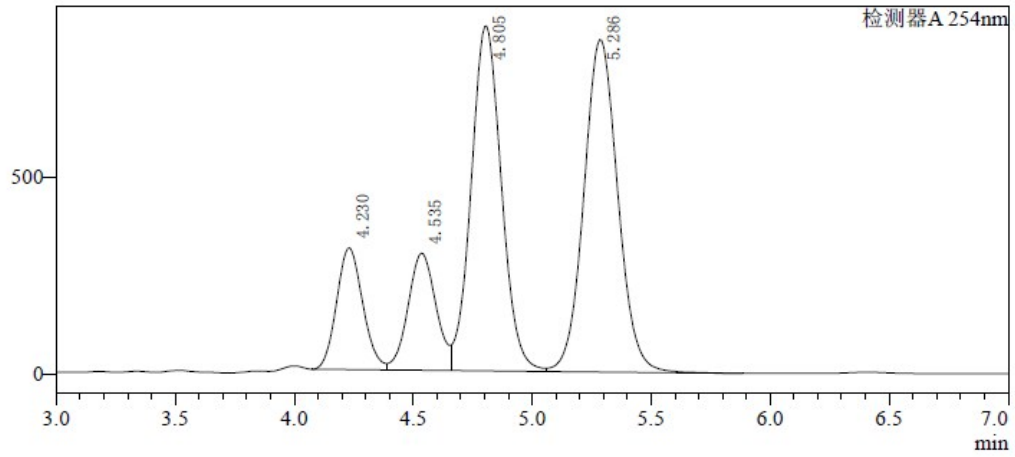
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.372	55958	5738	0.236			
2	6.030	23661082	1835790	99.764		M	
Total		23717039	1841528				



2b

<Chromatogram>

mV



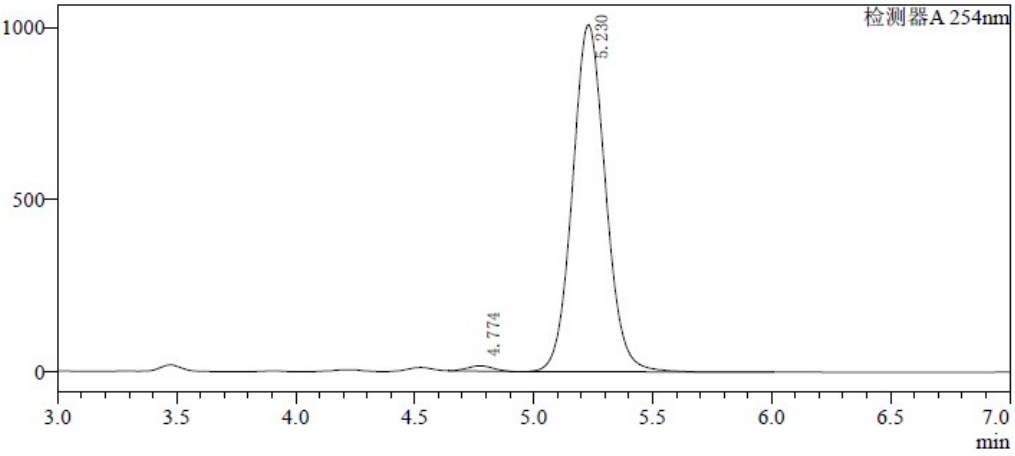
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.230	2372475	308568	11.350			
2	4.535	2443120	297250	11.688		V	
3	4.805	7733920	874910	36.999		V	
4	5.286	8353543	842958	39.963		V	
Total		20903057	2323686				

<Chromatogram>

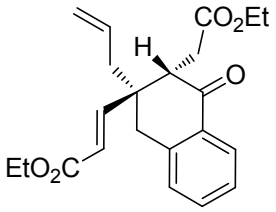
mV



<Peak Table>

检测器A 254nm

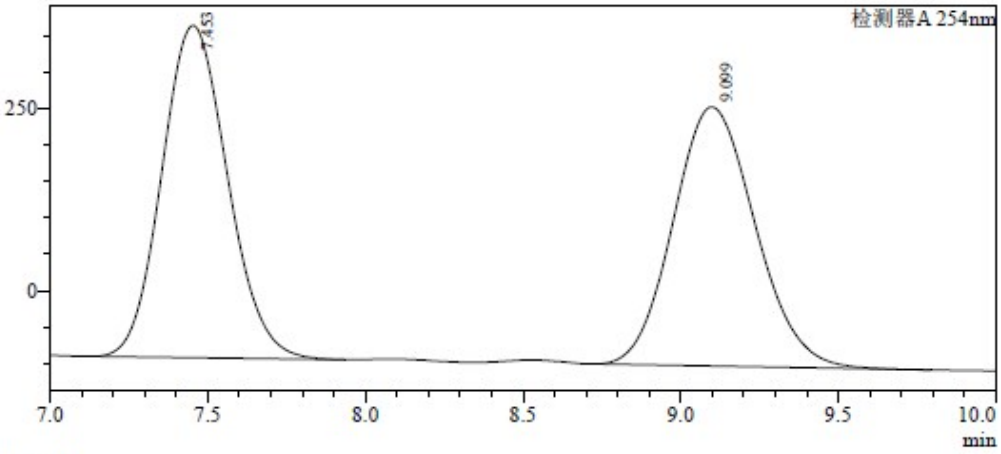
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.774	113799	15149	1.155			
2	5.230	9741990	1007158	98.845			
Total		9855788	1022307				



2c

<Chromatogram>

mV



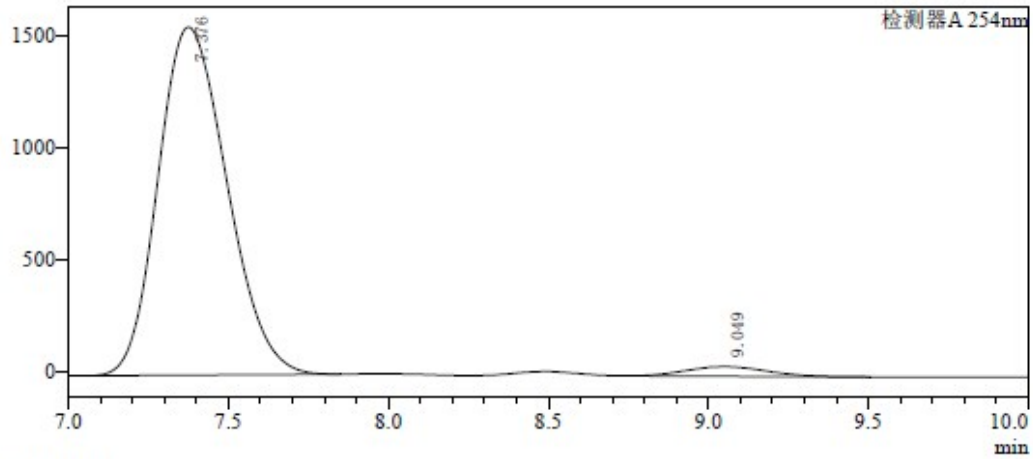
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.453	6625856	457093	50.678			
2	9.099	6448601	356622	49.322			
Total		13074457	813715				

<Chromatogram>

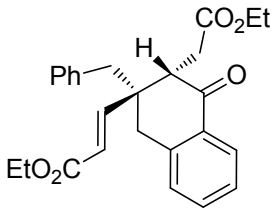
mV



<Peak Table>

检测器A 254nm

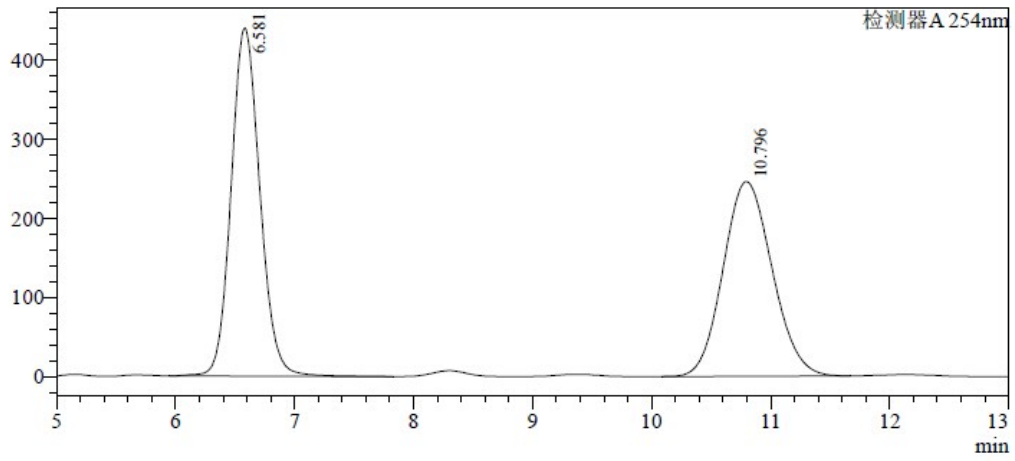
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.376	23287122	1556459	96.847			
2	9.049	758182	43548	3.153			
Total		24045304	1600007				



2d

<Chromatogram>

mV



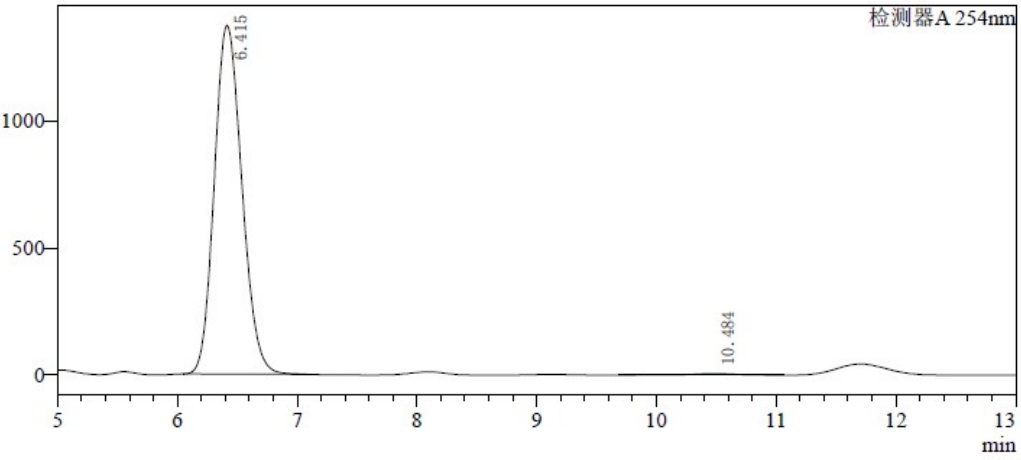
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.581	7407401	439926	51.238			
2	10.796	7049505	246037	48.762			
Total		14456906	685963				

<Chromatogram>

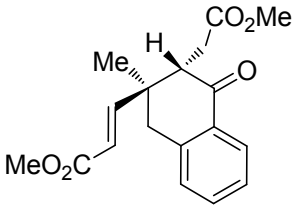
mV



<Peak Table>

检测器A 254nm

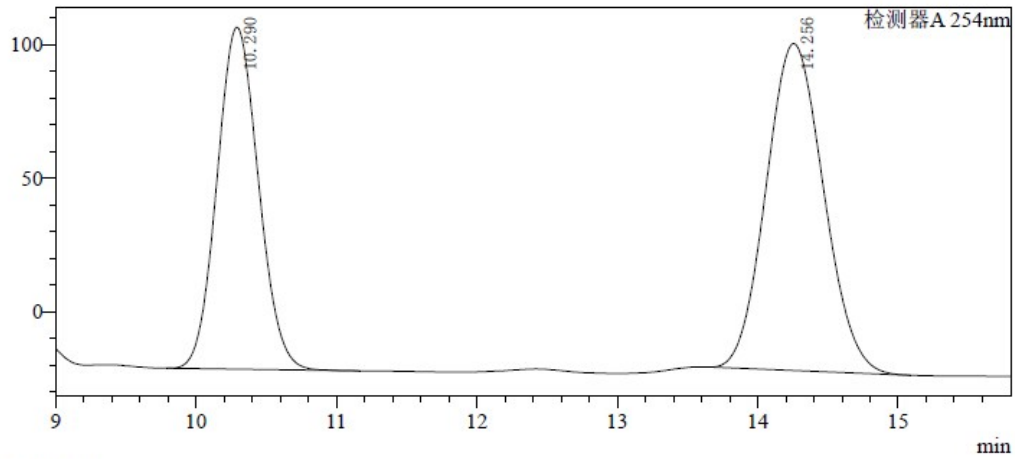
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.415	21981411	1372266	99.212		M	
2	10.484	174670	5431	0.788			
Total		22156081	1377696				



2e

<Chromatogram>

mV



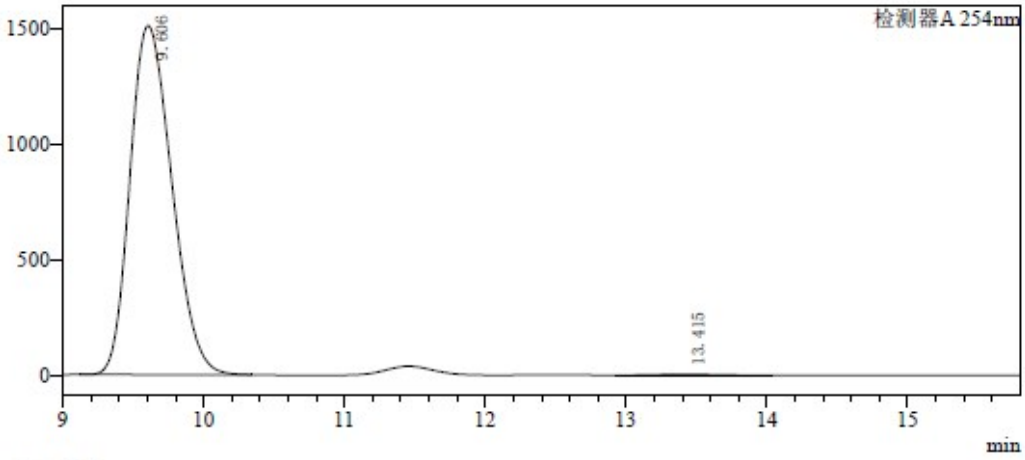
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.290	2629043	127816	43.045			
2	14.256	3478665	122150	56.955			
Total		6107708	249965				

<Chromatogram>

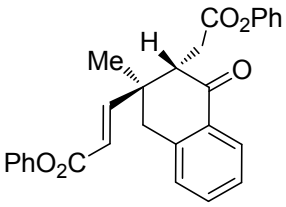
mV



<Peak Table>

检测器A 254nm

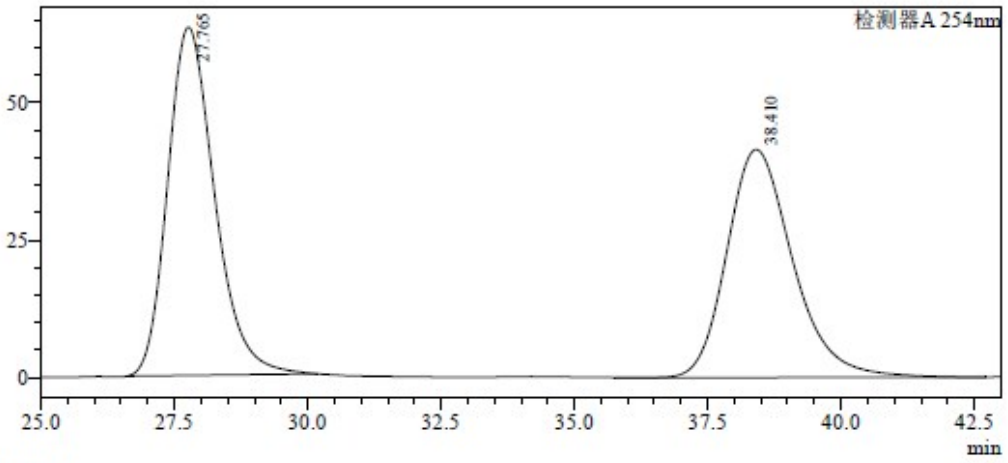
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.606	31238850	1510877	99.631		M	
2	13.415	115778	4416	0.369			
Total		31354628	1515293				



2f

<Chromatogram>

mV



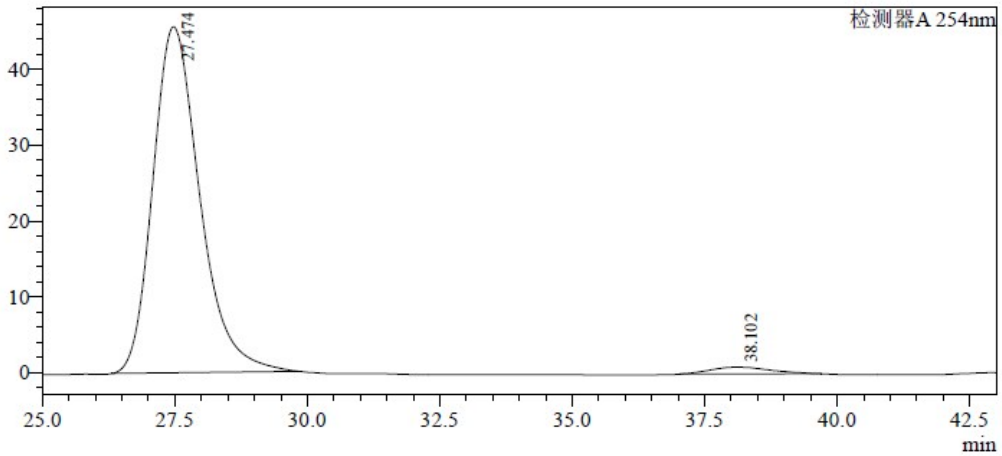
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.765	3878118	63319	52.151			
2	38.410	3558213	41442	47.849		M	
Total		7436332	104761				

<Chromatogram>

mV

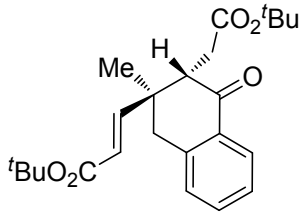


<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.474	2810429	45640	97.533		M	
2	38.102	71092	904	2.467		M	
Total		2881521	46544				

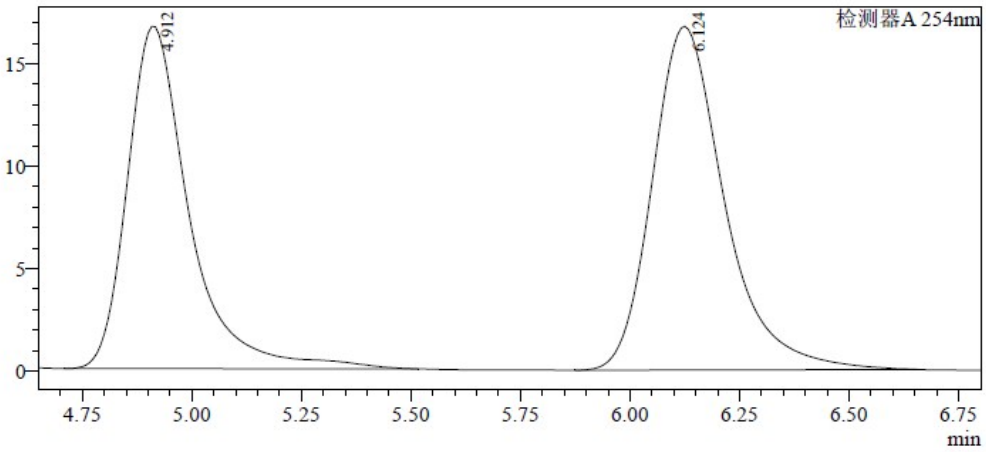
6b



2g

<Chromatogram>

mV



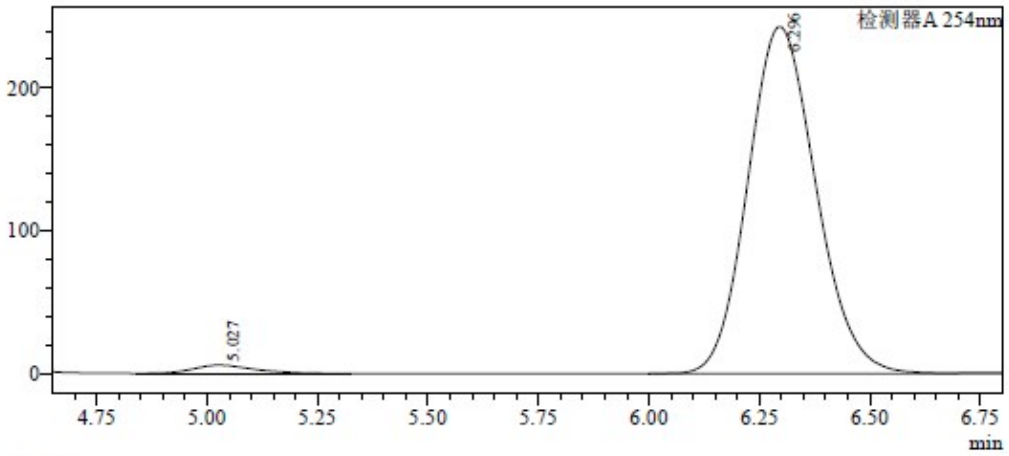
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.912	164249	16704	46.037			
2	6.124	192530	16766	53.963			
Total		356779	33470				

<Chromatogram>

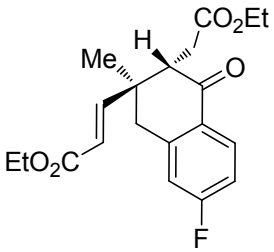
mV



<Peak Table>

检测器A 254nm

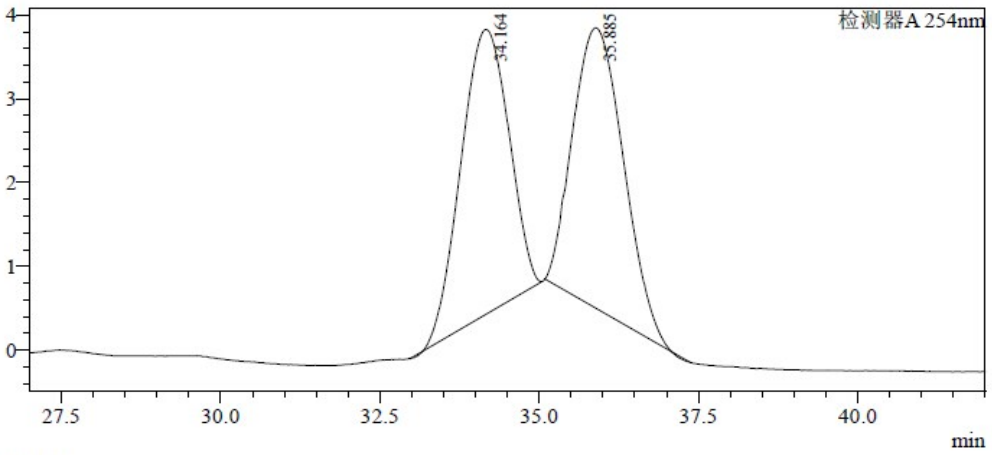
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.027	55504	5847	2.087			
2	6.296	2603693	242729	97.913			
Total		2659197	248575				



2h

<Chromatogram>

mV



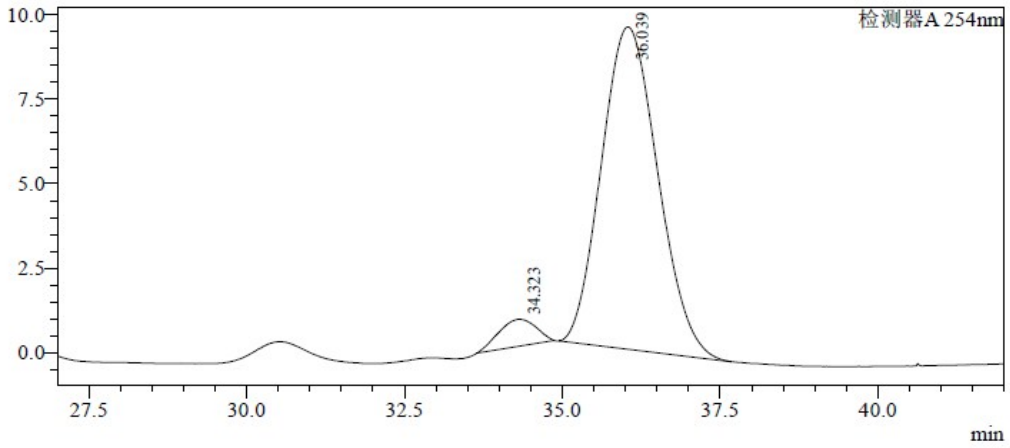
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.164	178728	3401	49.029		M	
2	35.885	185805	3348	50.971		M	
Total		364533	6749				

<Chromatogram>

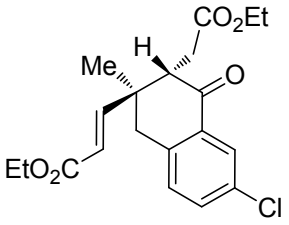
mV



<Peak Table>

检测器A 254nm

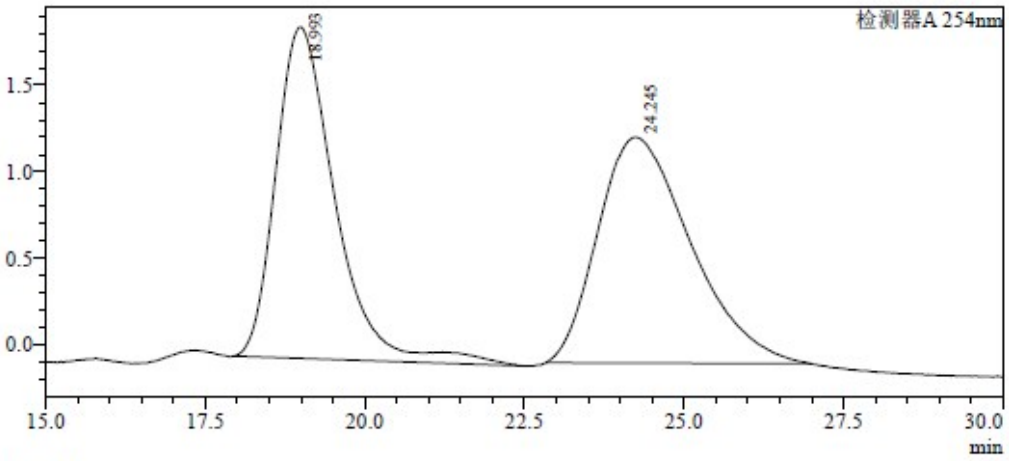
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.323	32969	795	5.260		M	
2	36.039	593778	9527	94.740		M	
Total		626747	10322				



2i

<Chromatogram>

mV



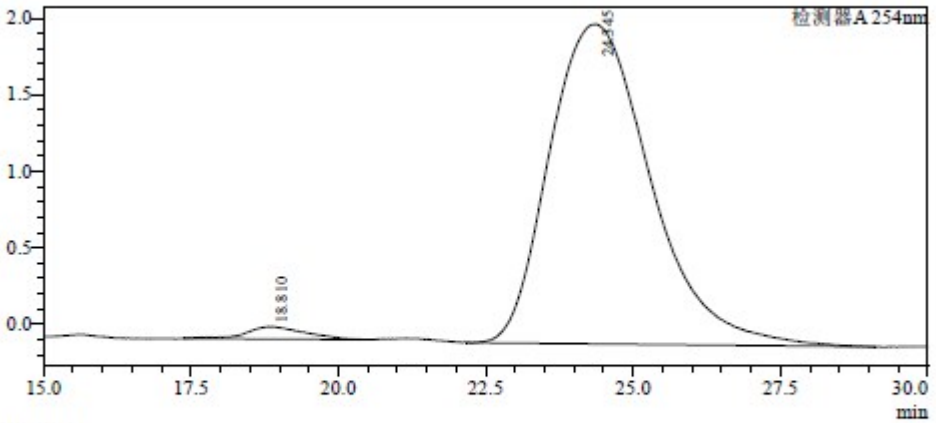
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.993	123557	1912	48.353		M	
2	24.245	131977	1303	51.647		M	
Total		255534	3215				

<Chromatogram>

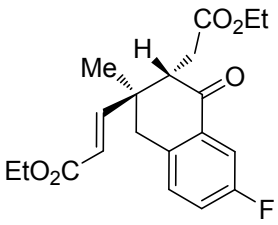
mV



<Peak Table>

检测器A 254nm

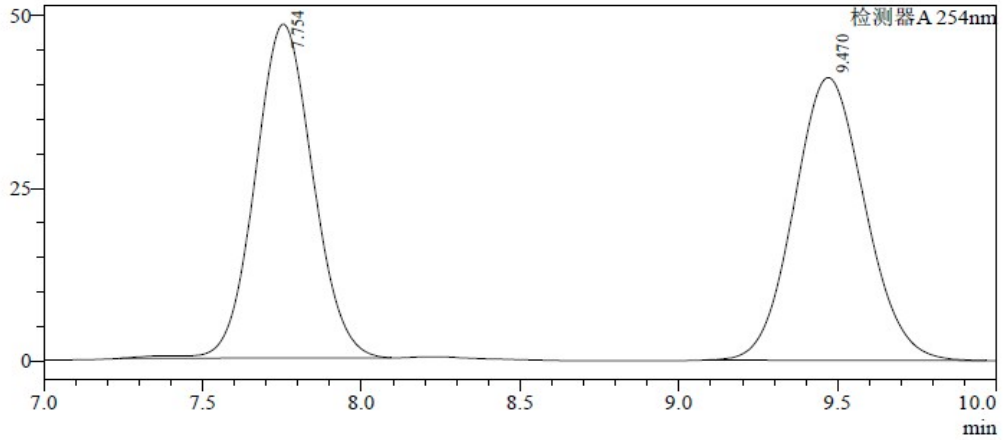
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.810	5597	80	2.195		M	
2	24.345	249375	2087	97.805		M	
Total		254971	2167				



2j

<Chromatogram>

mV



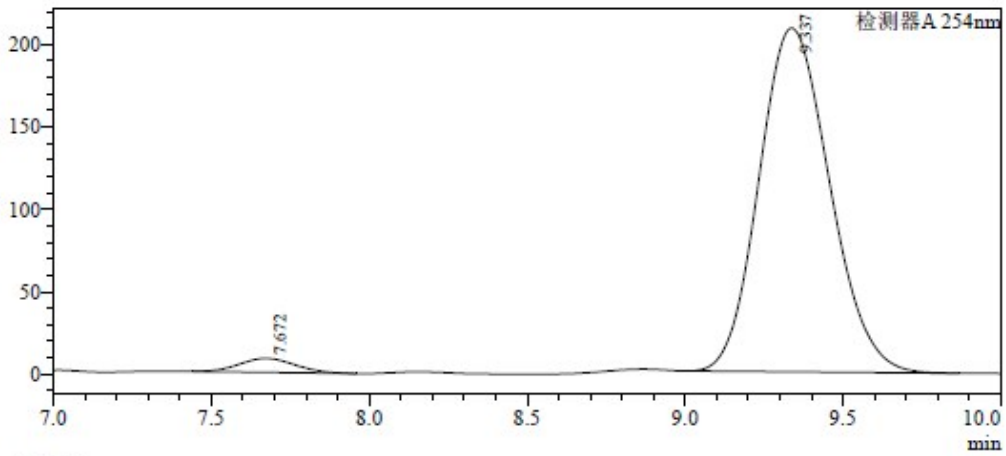
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.754	612402	48275	49.059		M	
2	9.470	635905	40905	50.941			
Total		1248307	89180				

<Chromatogram>

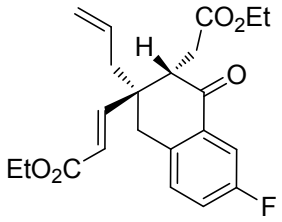
mV



<Peak Table>

检测器A 254nm

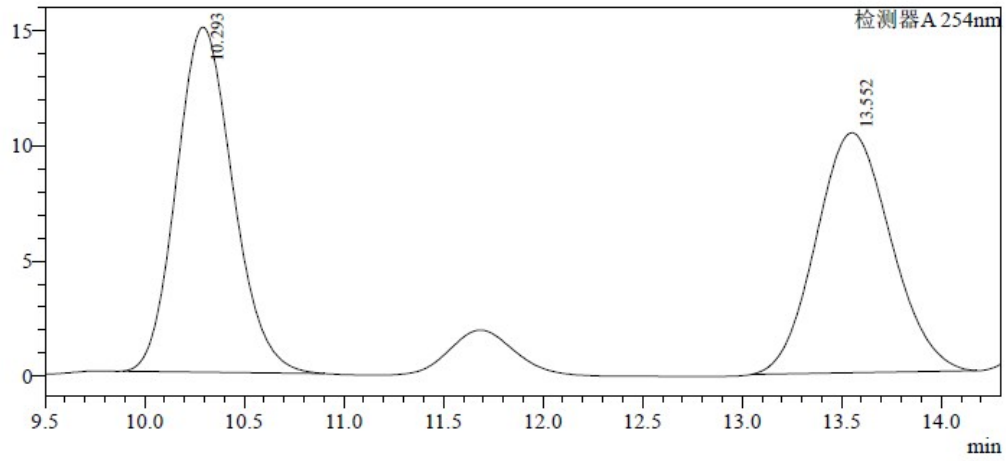
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.672	105093	8491	3.141			
2	9.337	3240891	208303	96.859			
Total		3345985	216794				



2k

<Chromatogram>

mV



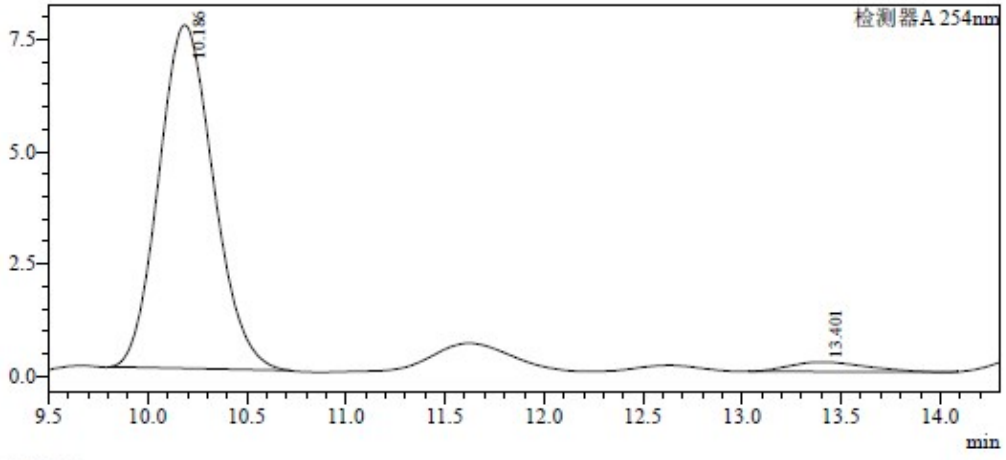
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.293	296114	14982	52.071			
2	13.552	272562	10419	47.929			
Total		568677	25401				

<Chromatogram>

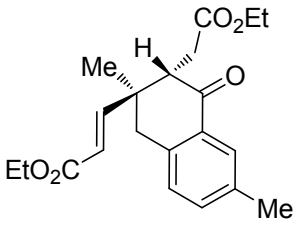
mV



<Peak Table>

检测器A 254nm

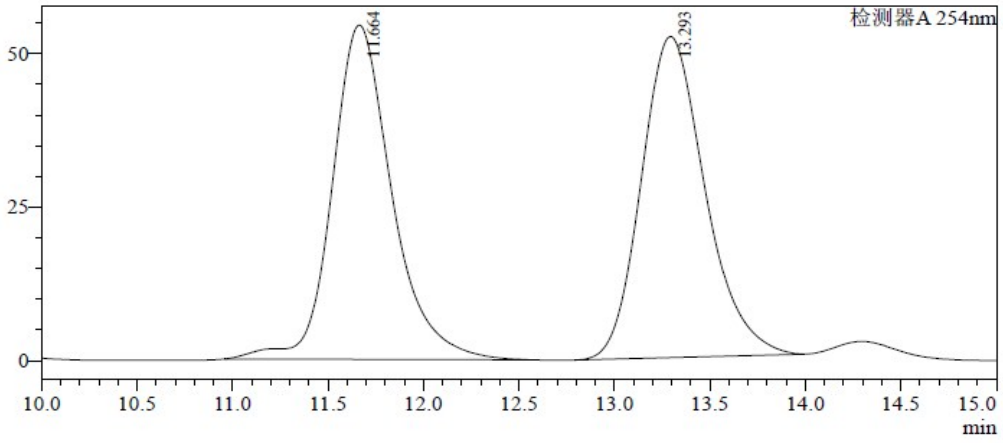
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.186	147154	7653	96.346			
2	13.401	5581	216	3.654		M	
Total		152735	7869				



2l

<Chromatogram>

mV



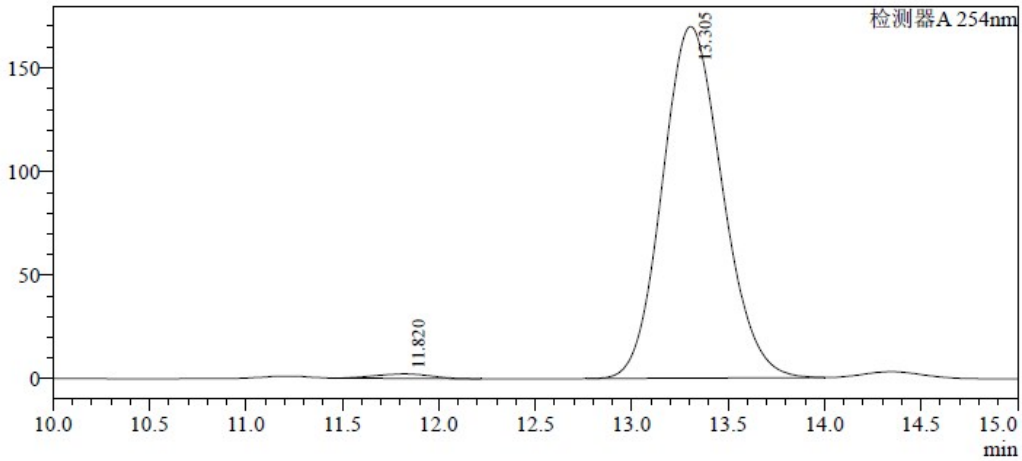
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.664	1183716	54406	49.378		M	
2	13.293	1213547	52257	50.622			
Total		2397264	106663				

<Chromatogram>

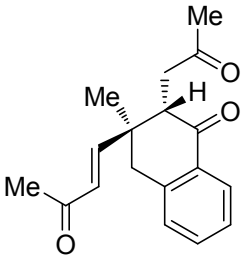
mV



<Peak Table>

检测器A 254nm

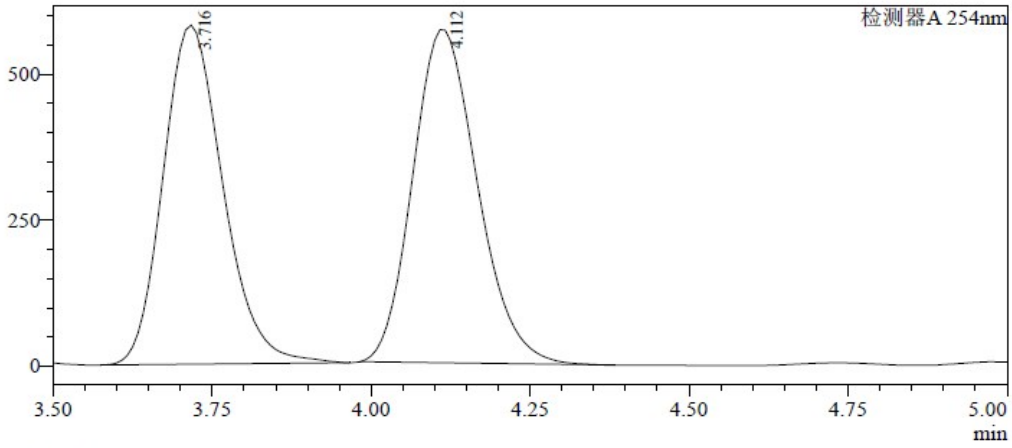
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.820	43133	2193	1.162			
2	13.305	3668838	169559	98.838			
Total		3711971	171752				



4a

<Chromatogram>

mV



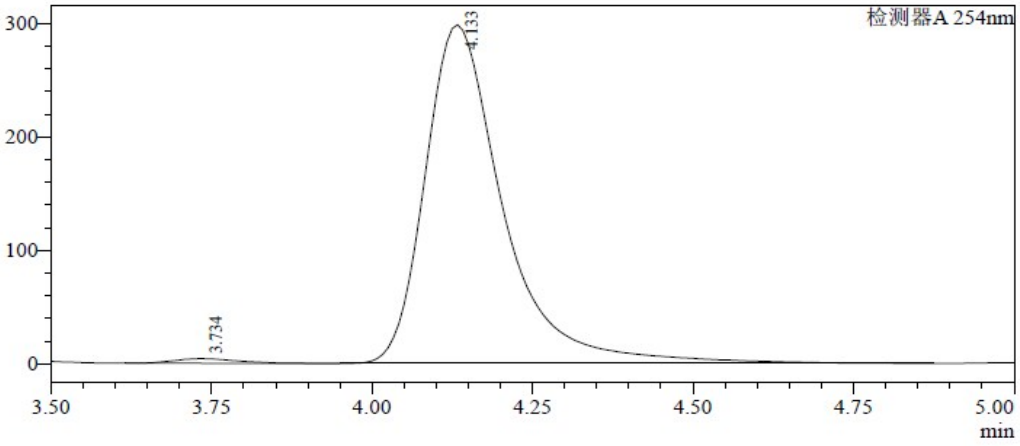
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.716	3794588	580518	48.472			
2	4.112	4033785	569690	51.528		M	
Total		7828373	1150208				

<Chromatogram>

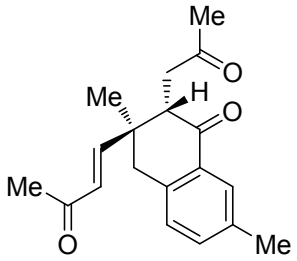
mV



<Peak Table>

检测器A 254nm

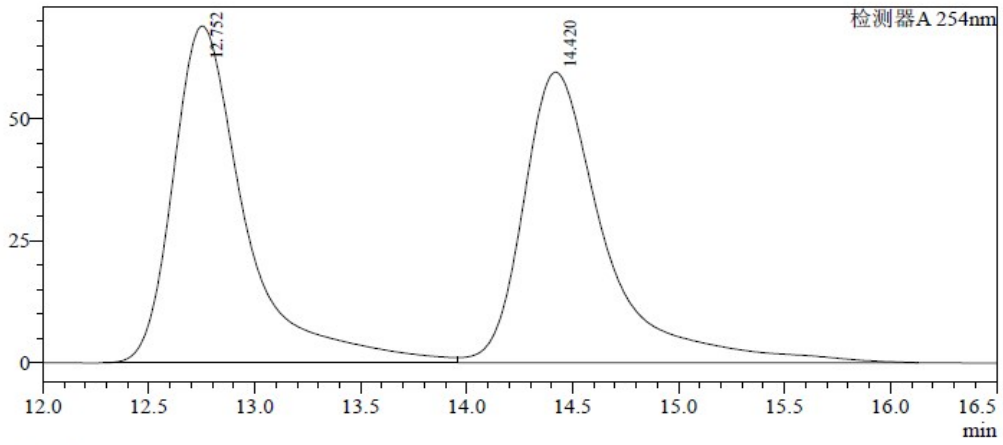
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.734	28377	4126	1.110			
2	4.133	2528279	298650	98.890			
Total		2556656	302776				



4b

<Chromatogram>

mV



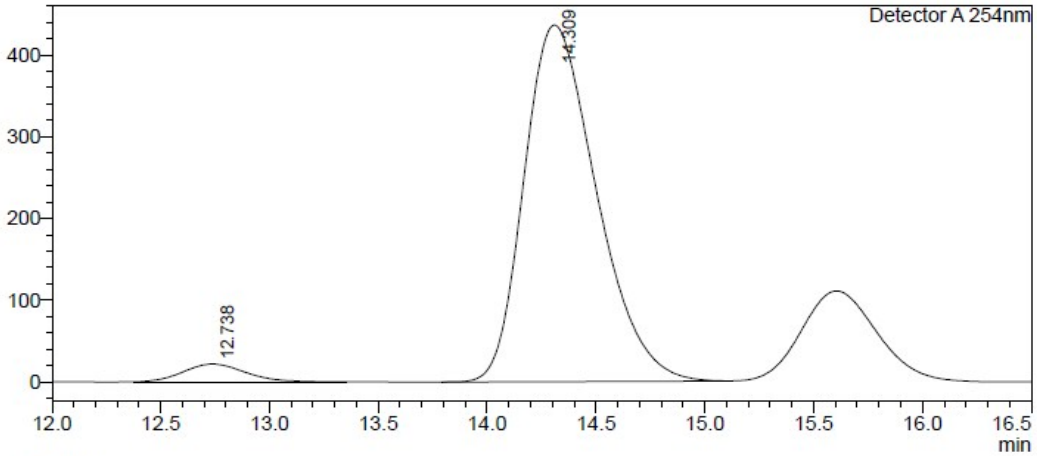
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.752	1642431	69004	50.672			
2	14.420	1598843	59482	49.328		V	
Total		3241273	128487				

<Chromatogram>

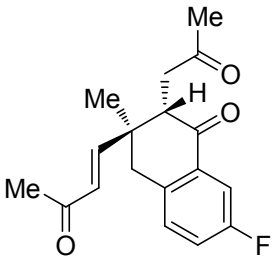
mV



<Peak Table>

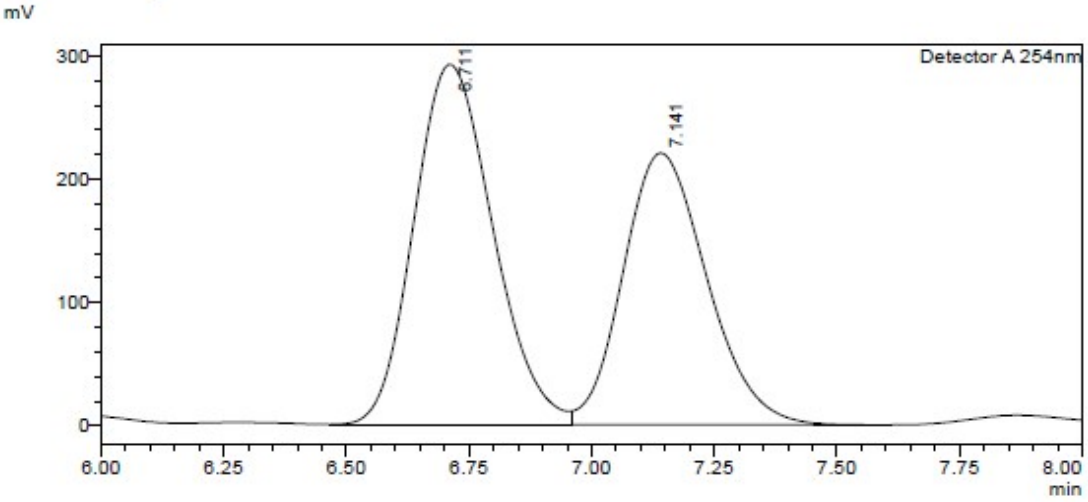
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.738	428193	21617	4.071		M	
2	14.309	10090143	436123	95.929			
Total		10518336	457740				



4c

<Chromatogram>

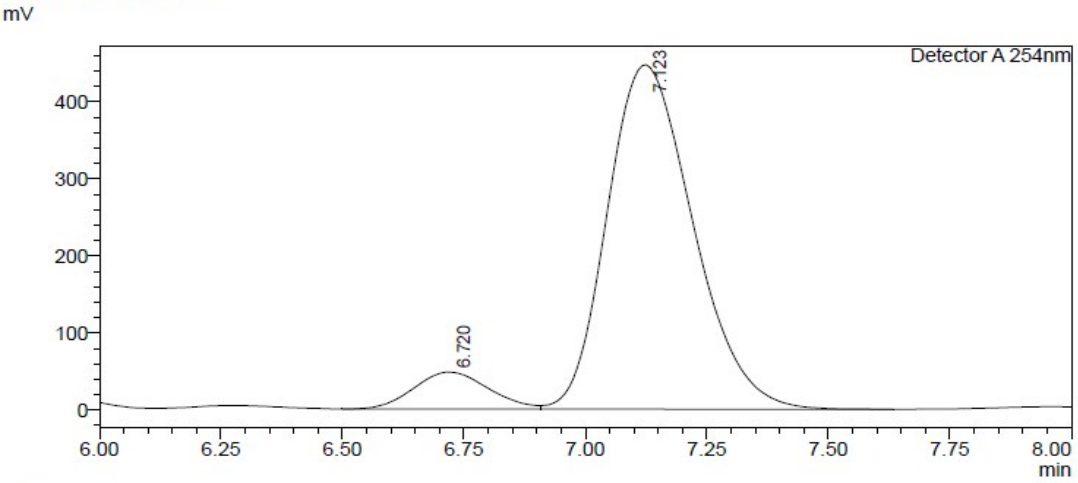


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.711	3273752	292160	55.564			
2	7.141	2618139	220542	44.436		V	
Total		5891891	512702				

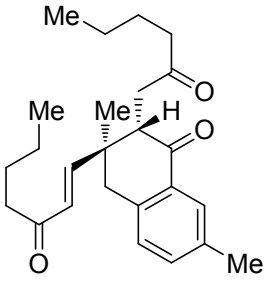
<Chromatogram>



<Peak Table>

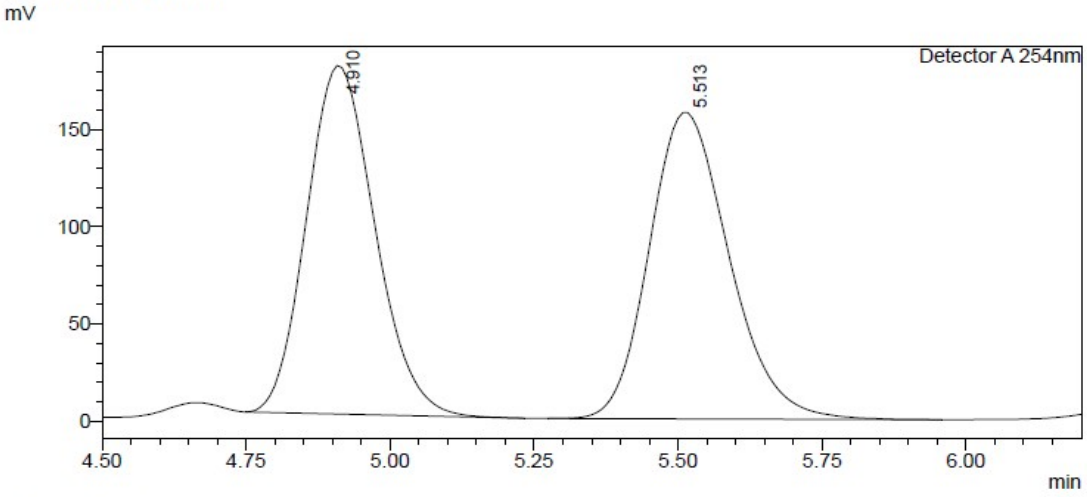
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.720	512529	47929	8.551			
2	7.123	5481114	447017	91.449		V	
Total		5993642	494946				



4d

<Chromatogram>

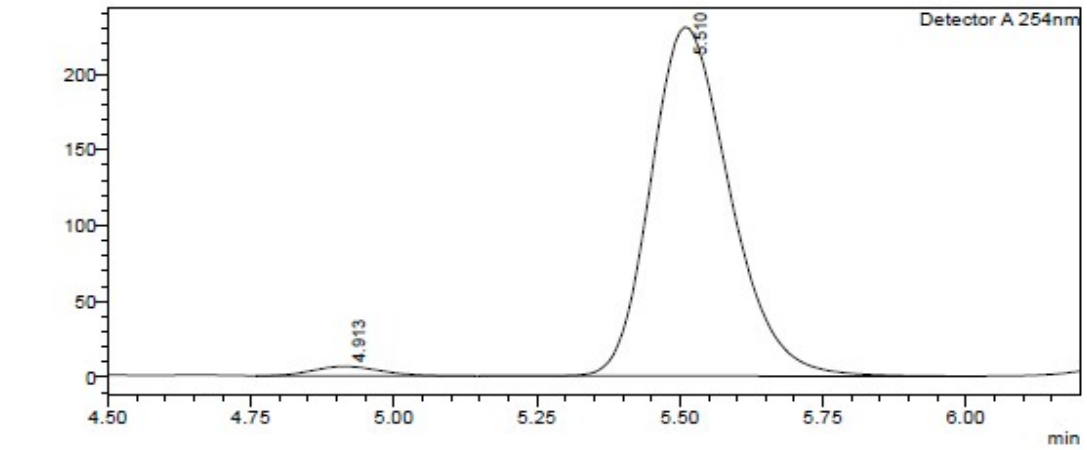


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.910	1479221	179196	49.246			
2	5.513	1524498	157473	50.754			
Total		3003718	336669				

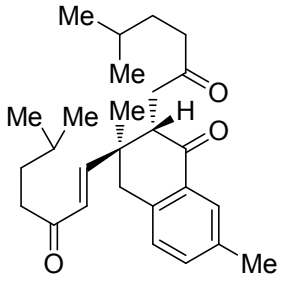
<Chromatogram>



<Peak Table>

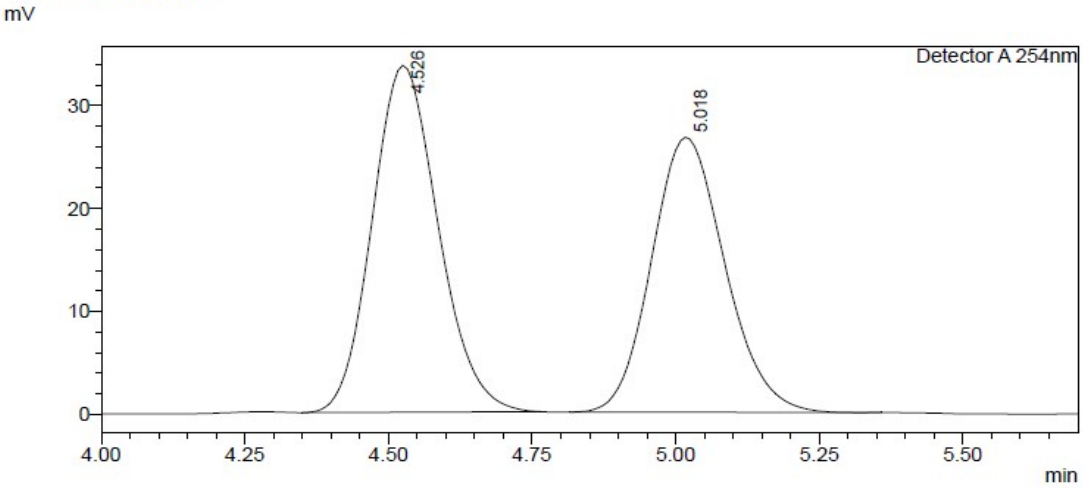
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.913	50717	6203	2.232			
2	5.510	2221604	230571	97.768			
Total		2272321	236774				



4e

<Chromatogram>

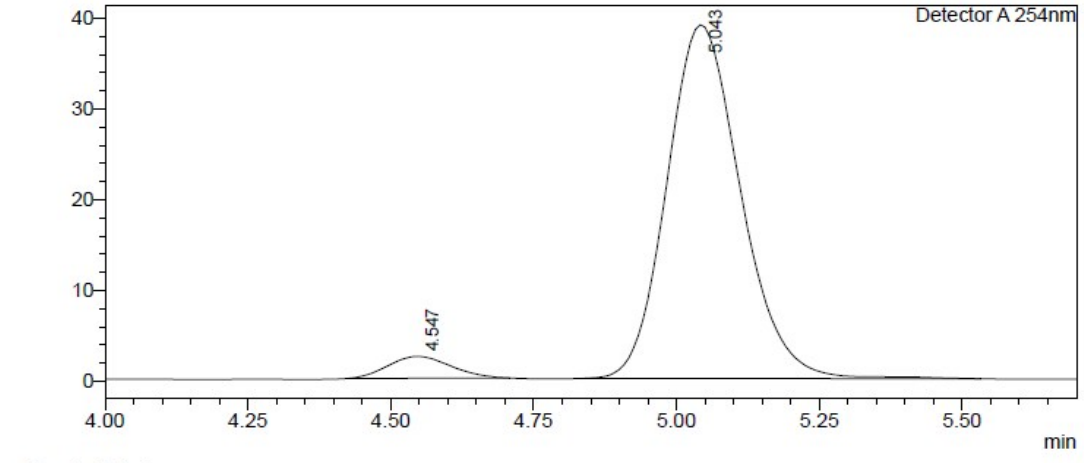


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.526	269508	33721	53.197		M	
2	5.018	237112	26744	46.803		M	
Total		506620	60466				

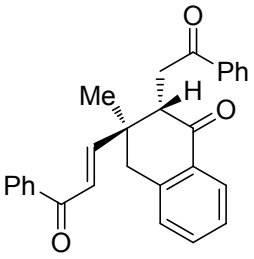
<Chromatogram>



<Peak Table>

Detector A 254nm

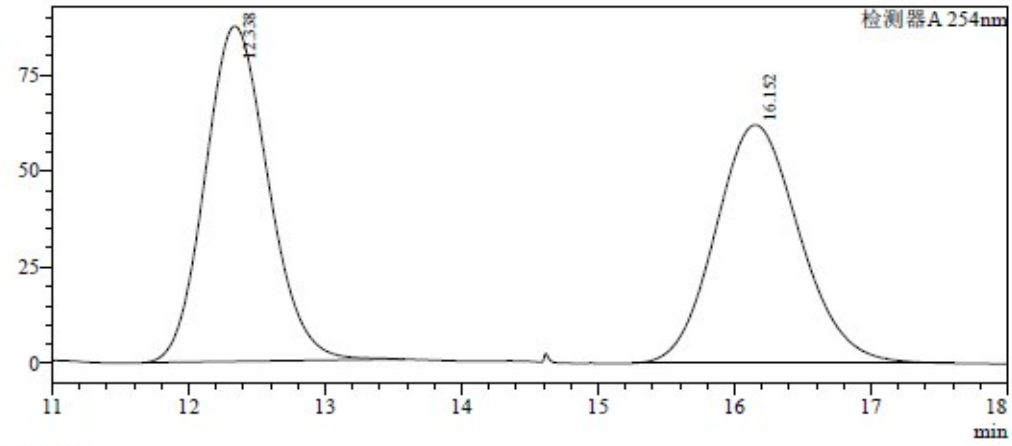
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.547	18421	2413	4.997		M	
2	5.043	350231	38983	95.003		M	
Total		368652	41395				



4f

<Chromatogram>

mV



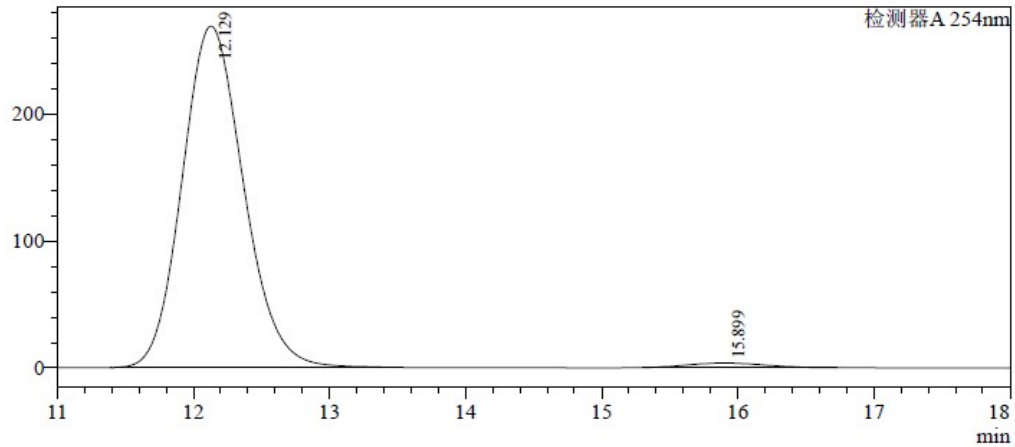
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.338	2804235	87185	51.309		M	
2	16.152	2661119	61964	48.691			
Total		5465354	149150				

<Chromatogram>

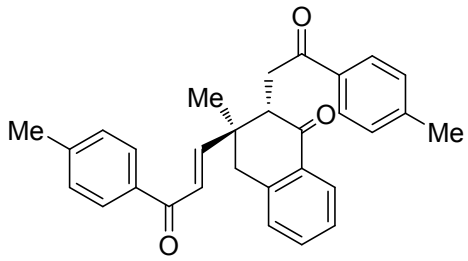
mV



<Peak Table>

检测器A 254nm

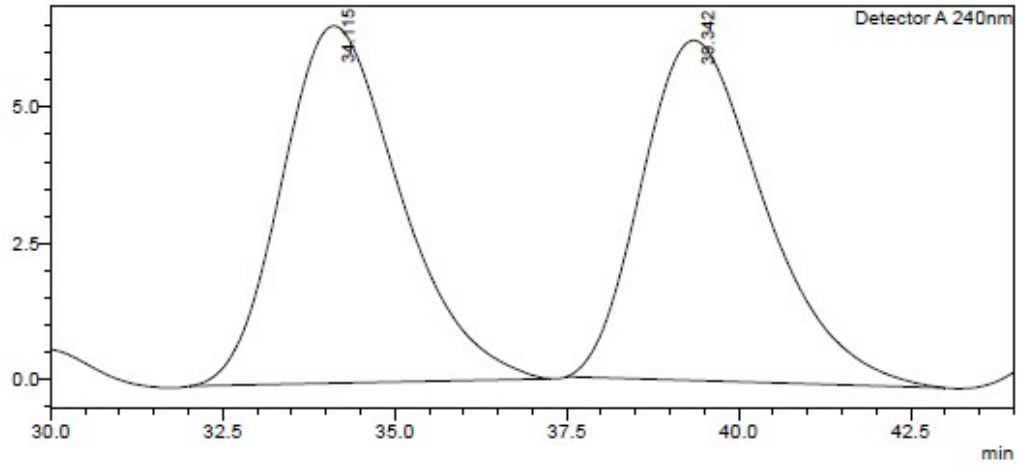
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.129	8422370	269094	98.332			
2	15.899	142910	3654	1.668			
Total		8565279	272747				



4g

<Chromatogram>

mV



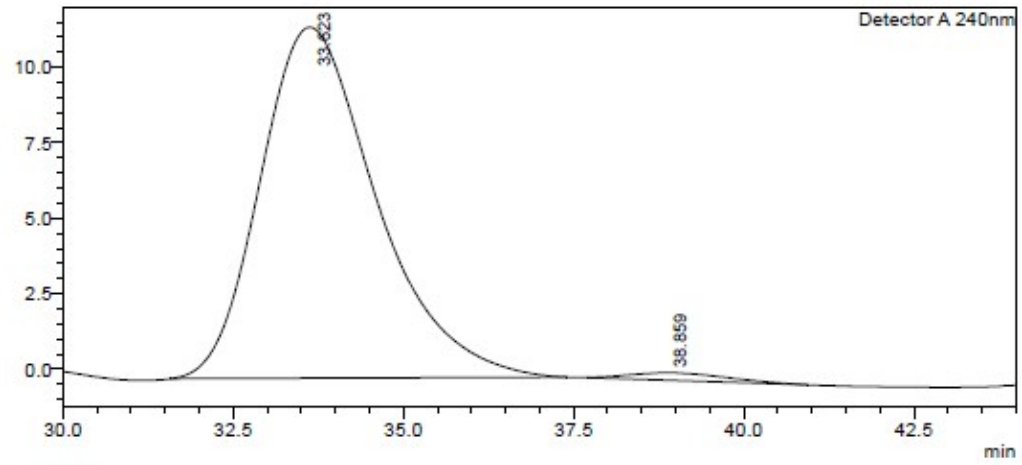
<Peak Table>

Detector A 240nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.115	782742	6554	50.265		M	
2	39.342	774494	6237	49.735		M	
Total		1557237	12791				

<Chromatogram>

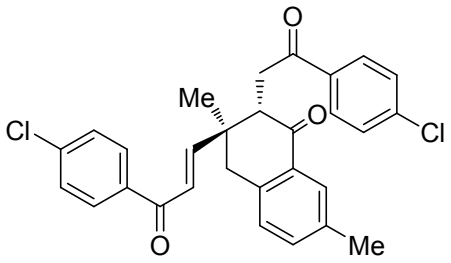
mV



<Peak Table>

Detector A 240nm

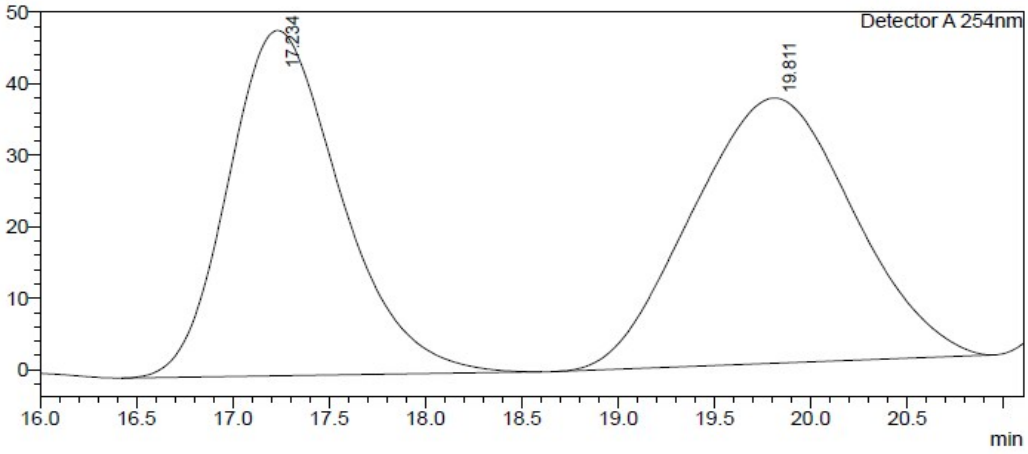
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.623	1376382	11629	98.268		M	
2	38.859	24265	241	1.732		M	
Total		1400647	11870				



4h

<Chromatogram>

mV



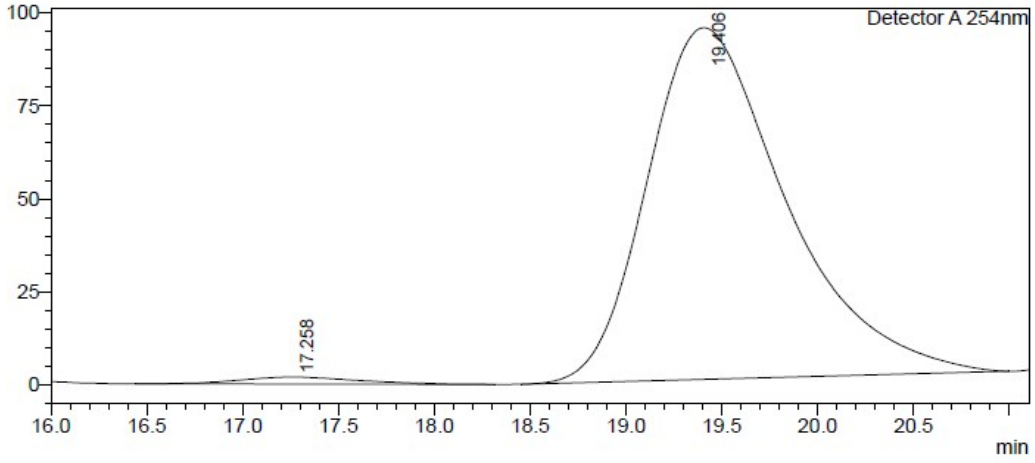
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.234	1958245	48283	47.618			
2	19.811	2154148	37090	52.382			
Total		4112394	85373				

<Chromatogram>

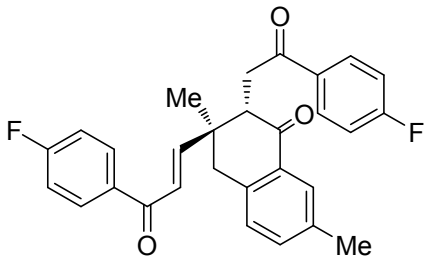
mV



<Peak Table>

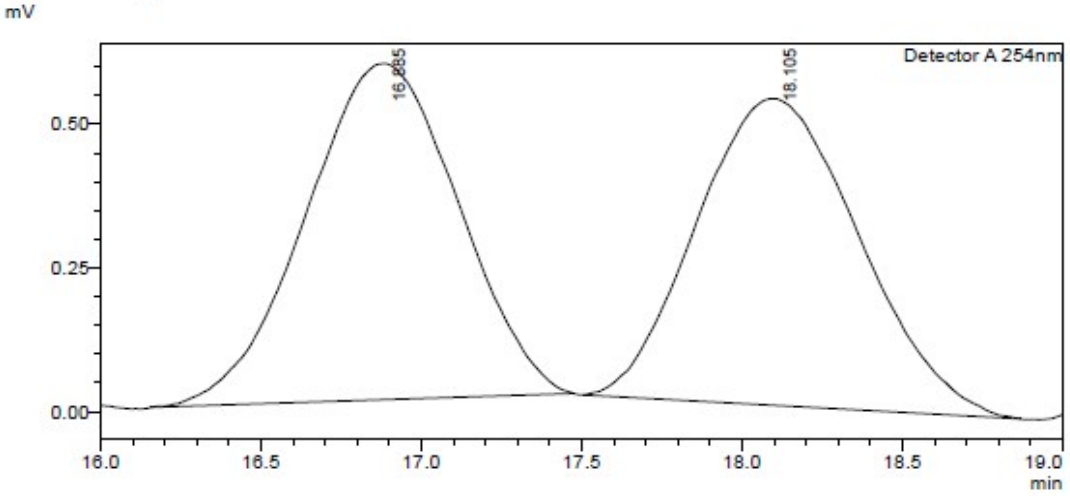
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.258	81129	1852	1.680			
2	19.406	4749386	94385	98.320			
Total		4830516	96237				



4i

<Chromatogram>

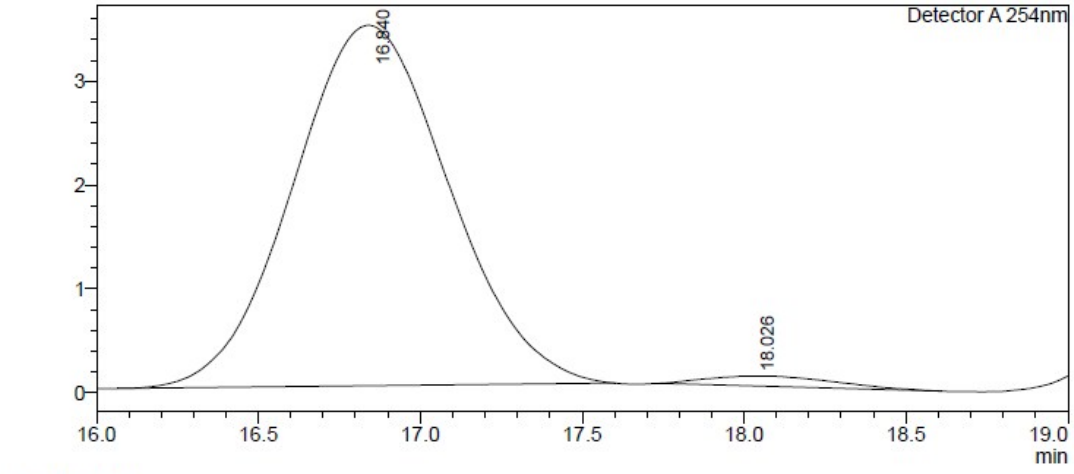


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.885	19326	585	50.763		M	
2	18.105	18745	534	49.237		M	
Total		38071	1119				

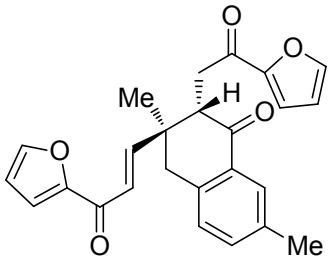
<Chromatogram>



<Peak Table>

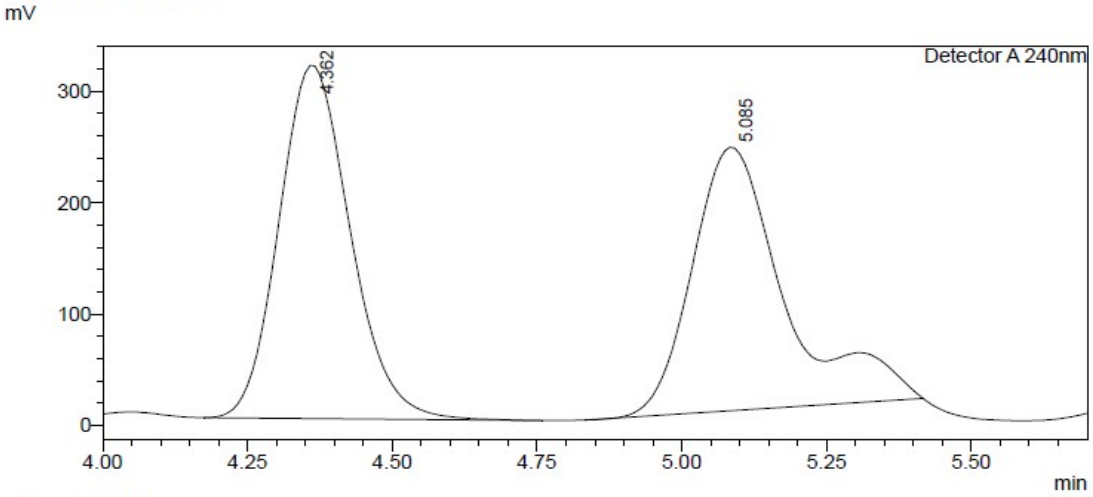
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.840	116256	3471	97.809		M	
2	18.026	2604	94	2.191		M	
Total		118860	3566				



4j

<Chromatogram>

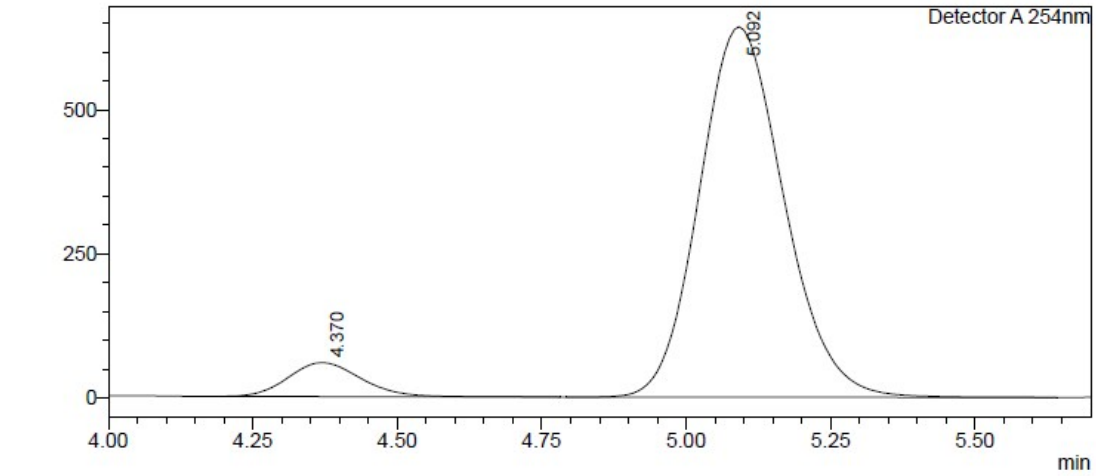


<Peak Table>

Detector A 240nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.362	2716808	316916	50.822			
2	5.085	2628873	236590	49.178		M	
Total		5345680	553506				

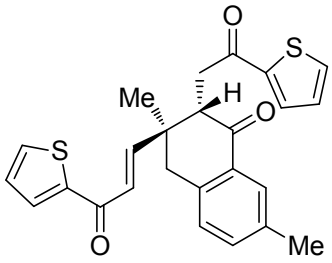
<Chromatogram>



<Peak Table>

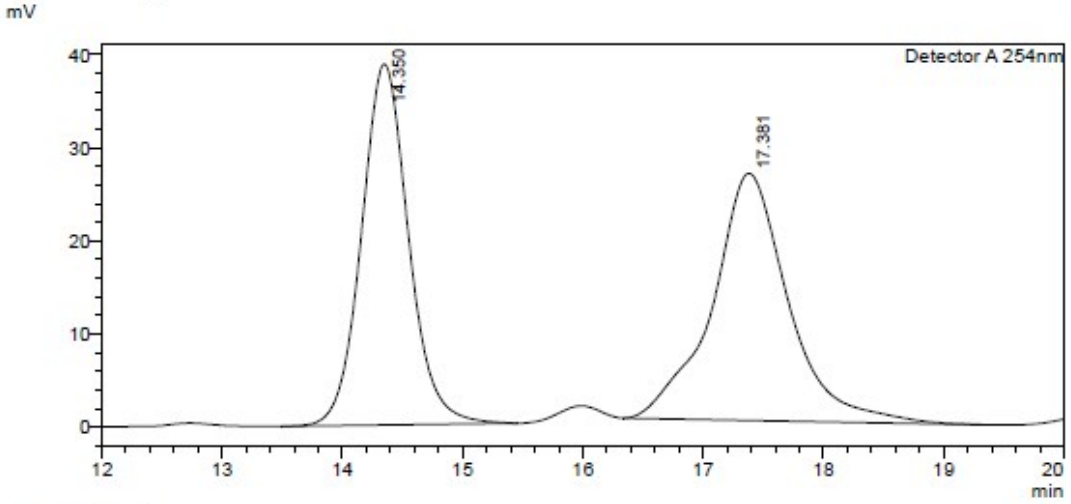
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.370	522350	59104	7.383			
2	5.092	6552819	642590	92.617			
Total		7075169	701693				



4k

<Chromatogram>

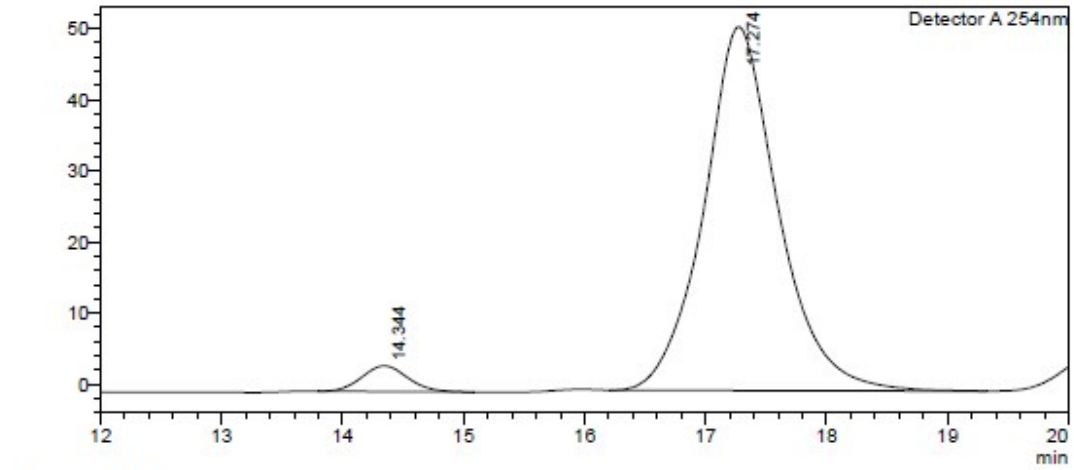


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.350	1056020	38755	47.397			
2	17.381	1171993	26524	52.603			
Total		2228012	65279				

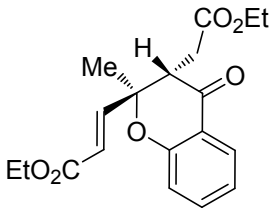
<Chromatogram>



<Peak Table>

Detector A 254nm

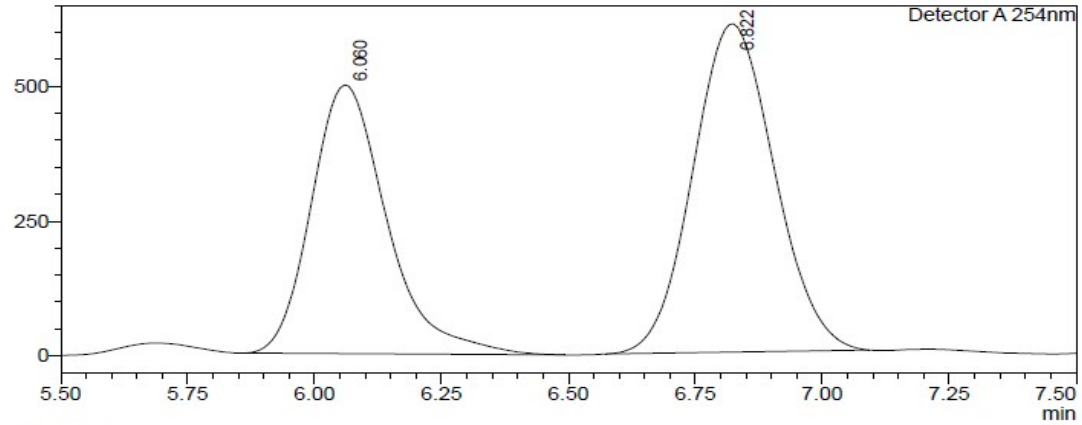
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.344	95616	3622	4.193			
2	17.274	2184860	51175	95.807			
Total		2280476	54797				



6a

<Chromatogram>

mV



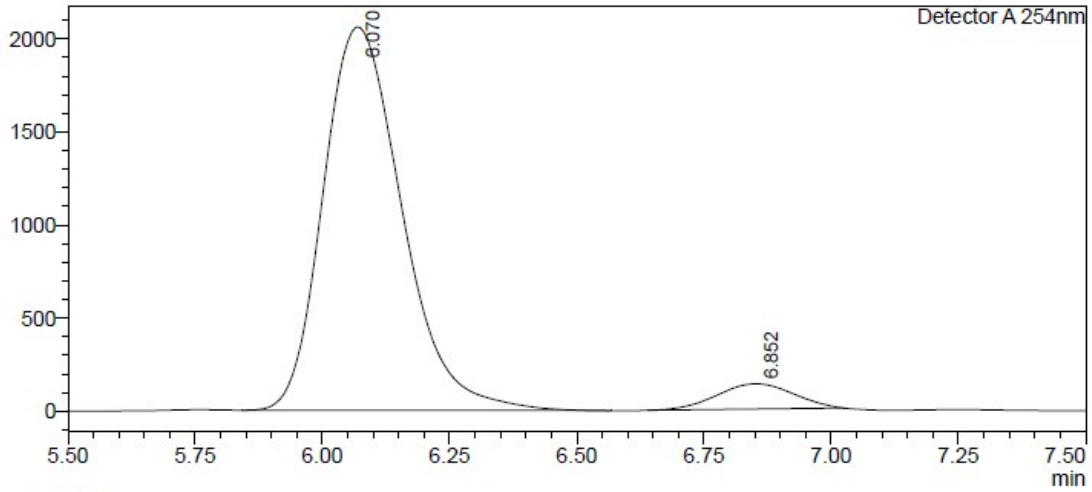
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.060	5155930	498327	43.143		M	
2	6.822	6794916	608918	56.857		M	
Total		11950846	1107245				

<Chromatogram>

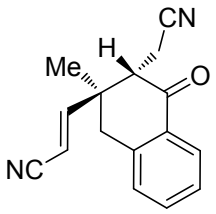
mV



<Peak Table>

Detector A 254nm

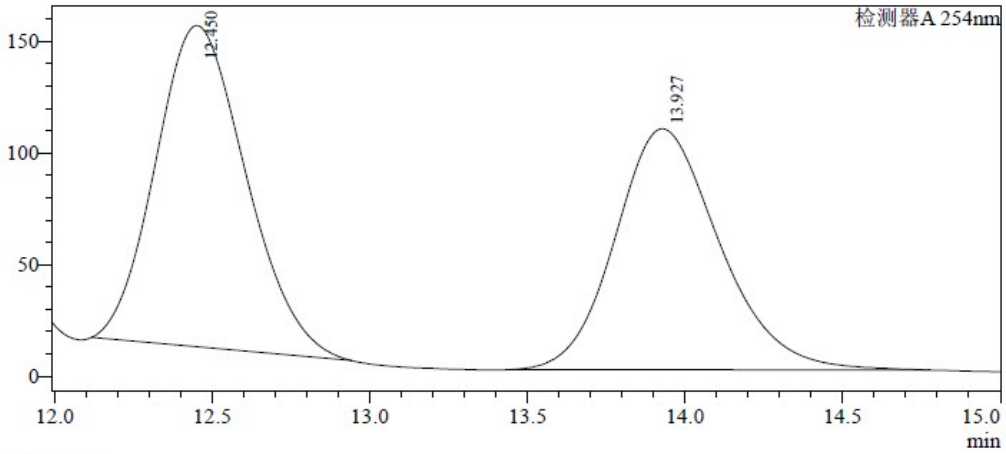
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.070	22191555	2060182	93.989			
2	6.852	1419205	135720	6.011		M	
Total		23610760	2195902				



6b

<Chromatogram>

mV



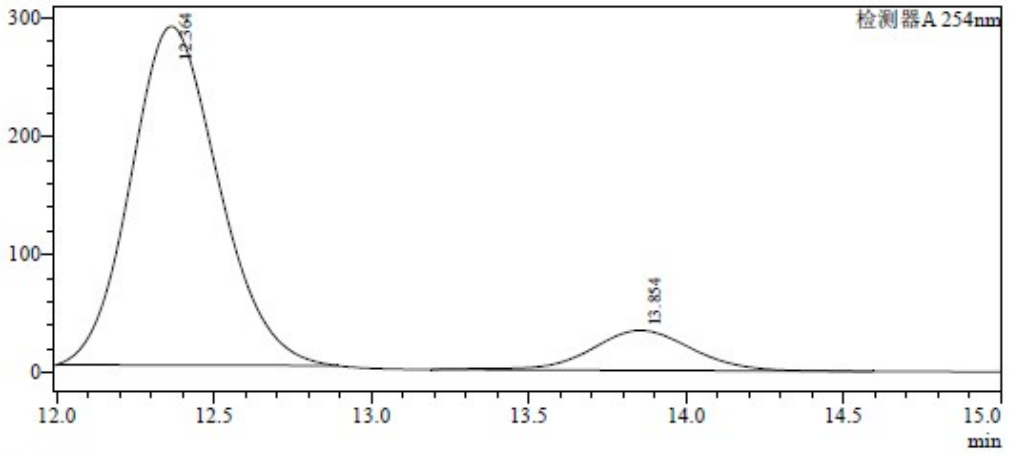
<Peak Table>

检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.450	2873611	144031	53.497		M	
2	13.927	2497945	108033	46.503		M	
Total		5371556	252064				

<Chromatogram>

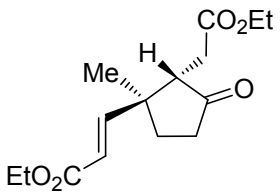
mV



<Peak Table>

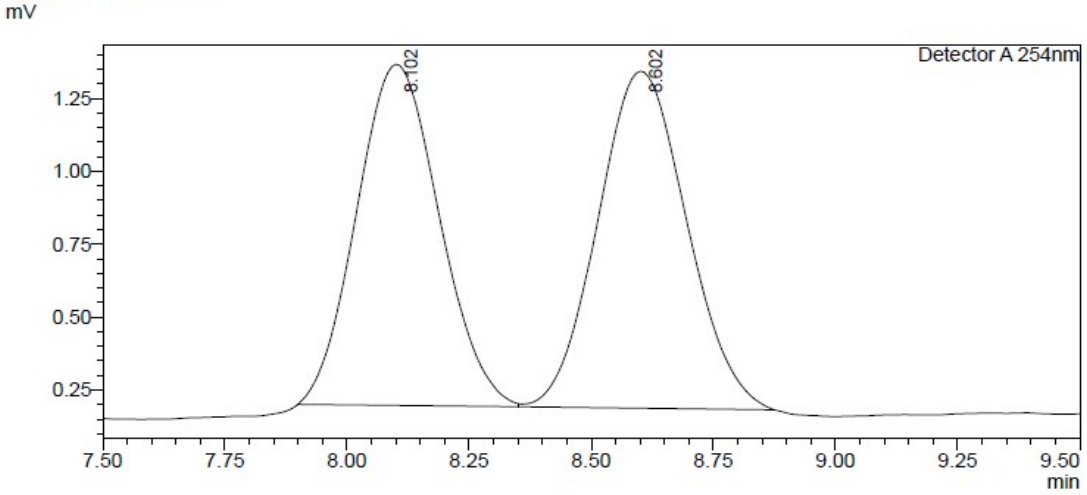
检测器A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.364	5579044	287026	88.118		M	
2	13.854	752325	33778	11.882		M	
Total		6331369	320804				



6c

<Chromatogram>

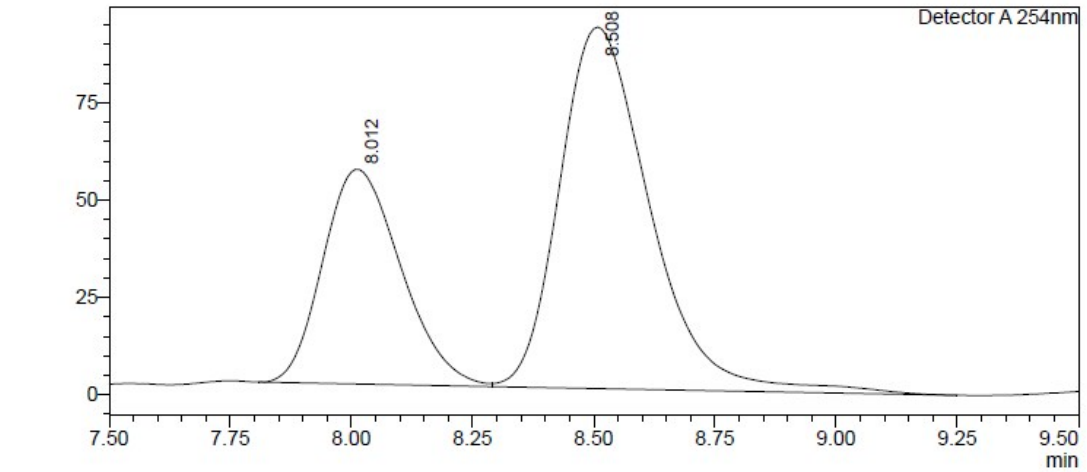


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.102	13750	1169	48.533			
2	8.602	14582	1155	51.467		V	
Total		28332	2324				

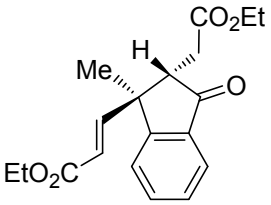
<Chromatogram>



<Peak Table>

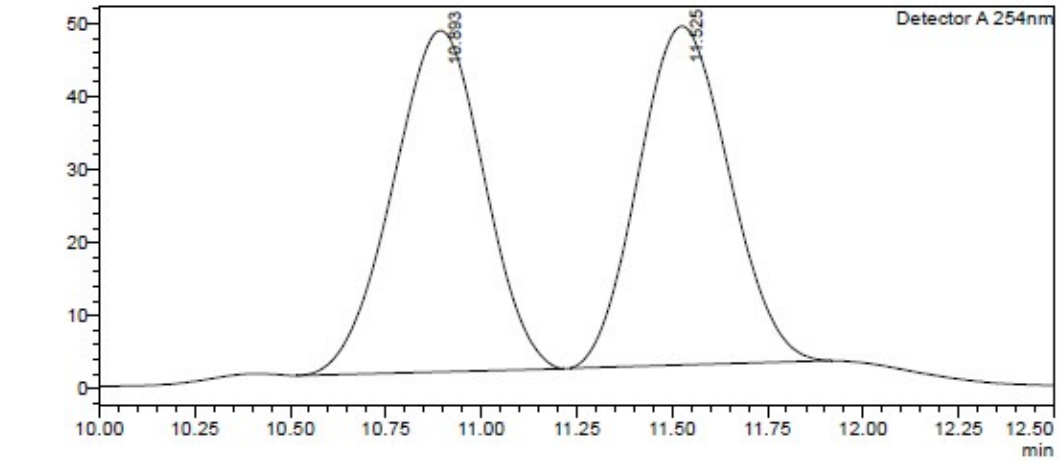
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.012	619469	55158	33.954			
2	8.508	1204993	92882	66.046		V	
Total		1824462	148039				



6d (major)

<Chromatogram>

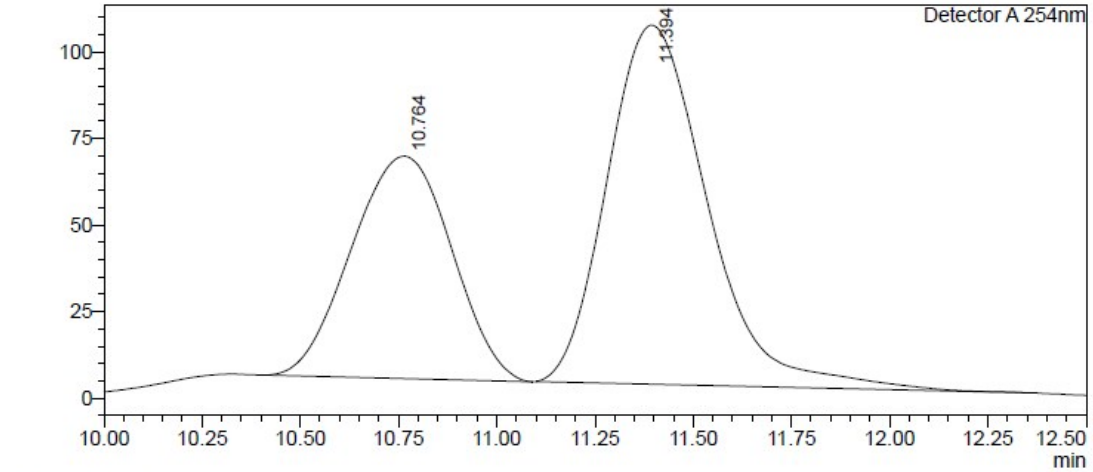


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.893	775107	46726	50.389			
2	11.525	763133	46357	49.611		M	
Total		1538240	93084				

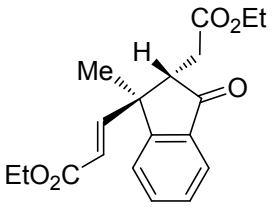
<Chromatogram>



<Peak Table>

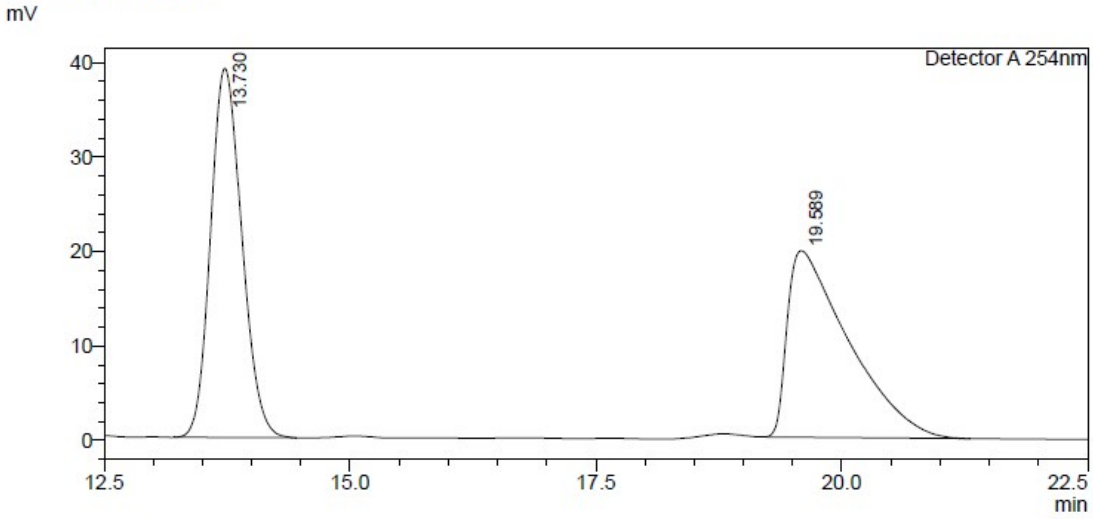
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.764	1138630	64231	38.197			
2	11.394	1842330	103678	61.803		M	
Total		2980959	167909				



6d (minor)

<Chromatogram>

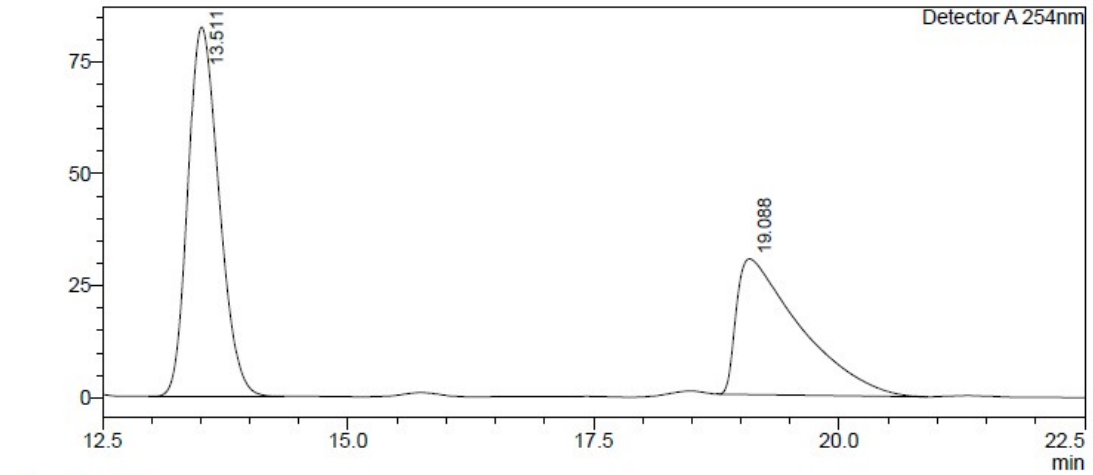


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.730	865591	39095	50.242		M	
2	19.589	857245	19759	49.758		M	
Total		1722836	58853				

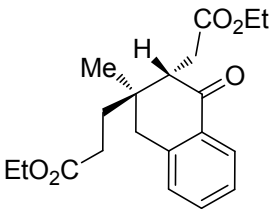
<Chromatogram>



<Peak Table>

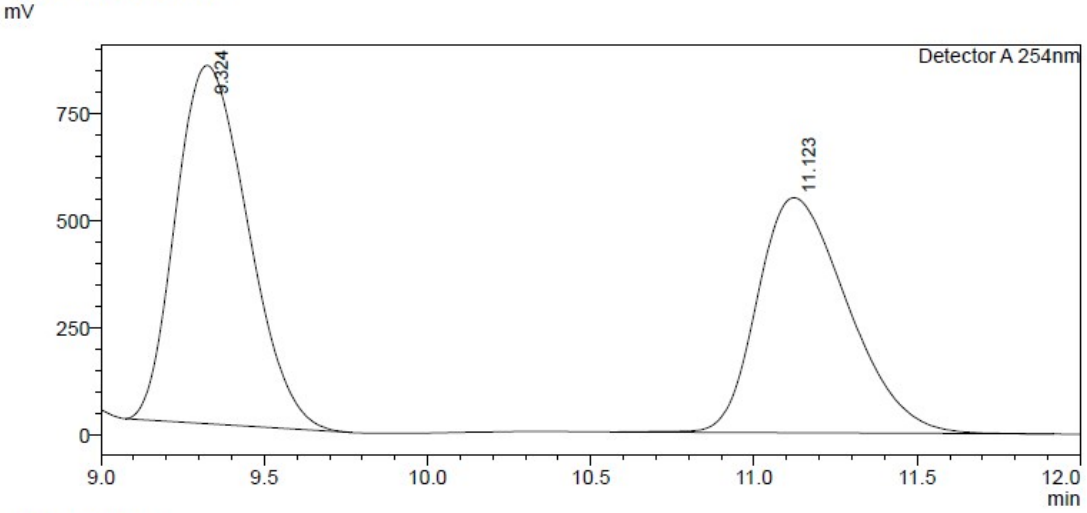
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.511	1818496	82326	57.157			
2	19.088	1363100	30274	42.843			
Total		3181596	112600				



7a

<Chromatogram>

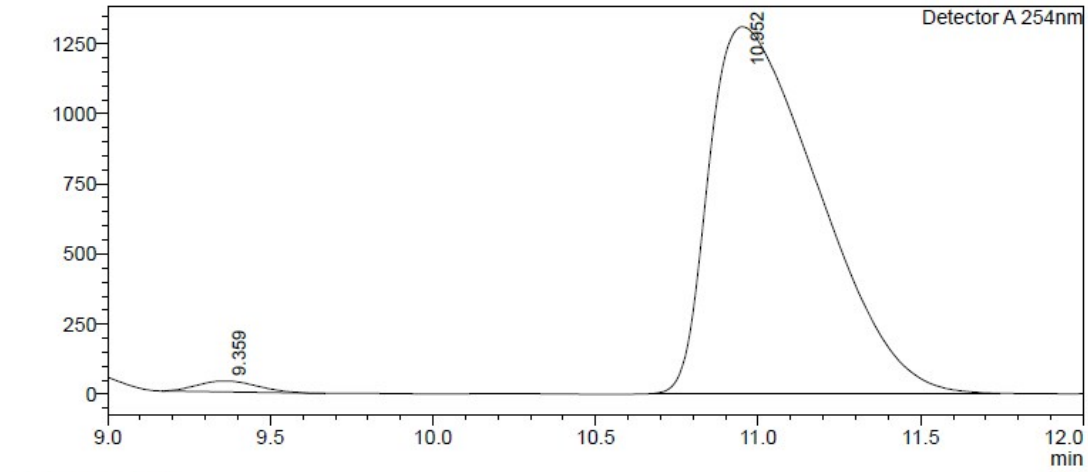


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.324	12869975	836849	54.923			
2	11.123	10562880	549048	45.077			
Total		23432855	1385896				

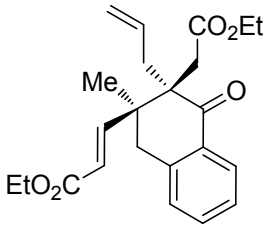
<Chromatogram>



<Peak Table>

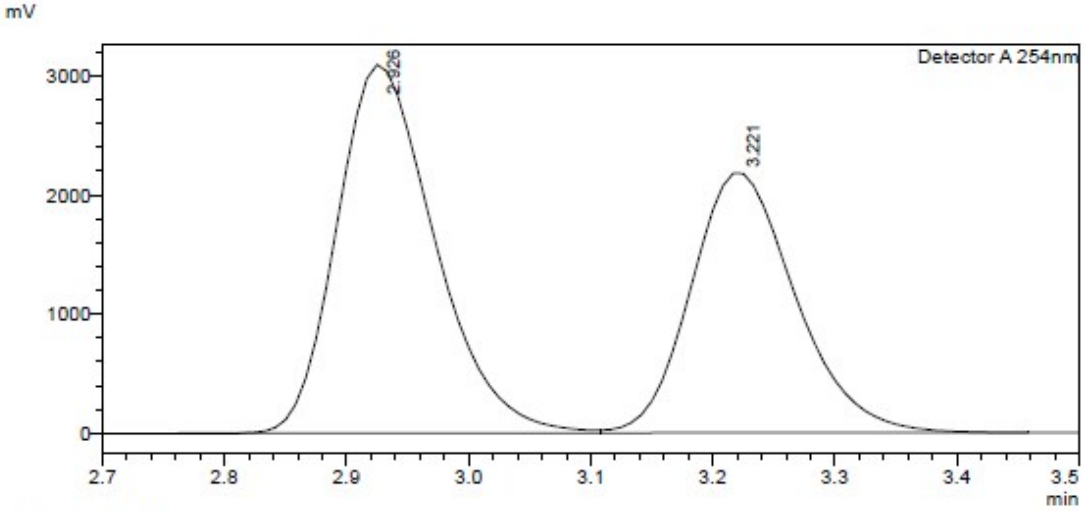
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.359	494528	39099	1.598		M	
2	10.952	30461534	1307778	98.402		M	
Total		30956062	1346877				



7b

<Chromatogram>

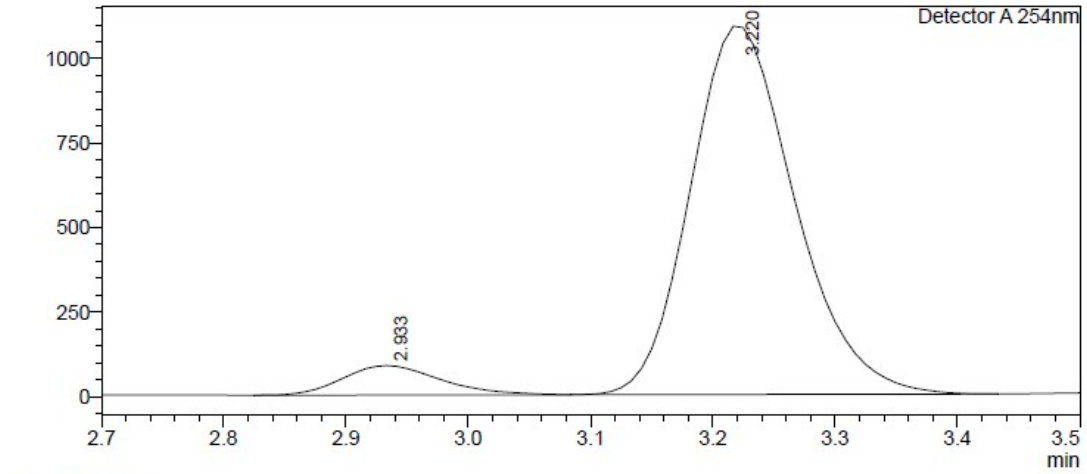


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.926	17231603	3089230	57.029			
2	3.221	12984088	2176790	42.971		V	
Total		30215692	5266020				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	2.933	483430	87249	6.957			
2	3.220	6464936	1089406	93.043		V	
Total		6948366	1176655				