

Electronic Supplementary Information for

**Asymmetric Double-Conjugate Addition of Alkenylboronic Acid to
Dienones Catalyzed by Chiral Diols**

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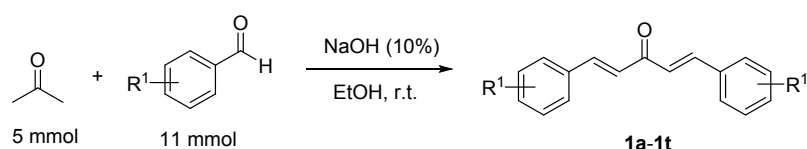
1. General information

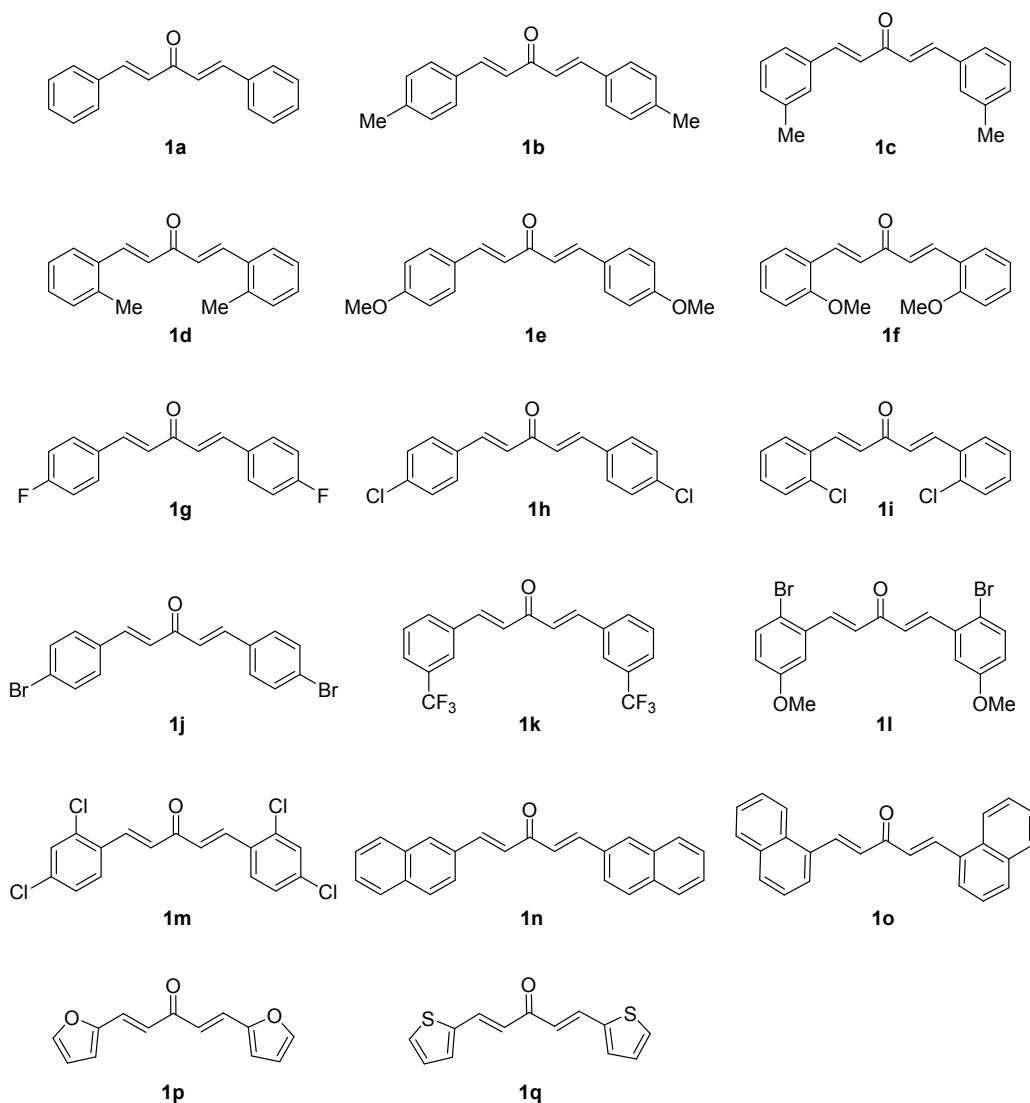
All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All the reactions that require heating were heated by oil bath. All solvents and reagents were obtained from commercial sources and purified according to established procedures before use. Flash chromatography (FC) was carried out using silica gel (300-400 mesh). HPLC analysis was performed on a Dionex UltiMate 3000, ThermoScientific. Chiral HPLC data for the products could be obtained using Chiralpak IB, Chiralpak ID, Chiralpak IE, Chiralpak IF, and Chiralpak IG column. These chiral columns were purchased from Daicel Chemical Industries Ltd. Optical rotations were measured on an Insmark polarimeter (IP-digi 300). ¹H NMR spectra were measured on a 400 MHz (Bruker, AVANCE NEO) or a 600 MHz spectrometer (Bruker, AVANCE III HD). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constants in hertz (Hz), integration. ¹³C NMR spectra were measured at 100 MHz (Bruker, AVANCE NEO) or 150 MHz (Bruker, AVANCE III HD). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 77.16). High-resolution mass spectra (HRMS) were recorded with a Bruker (Compact, TOF) mass spectrometer. All melting points were determined using a digital melting point apparatus (Shanghai INESA Physico-Optical Instrument Co., Ltd. SGW® X-4B) and were uncorrected. TLC was performed on glass-backed silica gel plate.

(*R*)-BINOL **Cat 1**, (*R*)-3,3'-Br₂-BINOL **Cat 2**, (*R*)-3,3'-I₂-BINOL **Cat 3**, (*R*)-3,3'-Ph₂-BINOL **Cat 4**, and **Cat 5** bearing two 3,5-bis(trifluoromethyl)phenyl groups were purchased from Daicel Chemical Industries Ltd. (*S,S*)-1,8,9,16-tetrahydroxytetraphenylene **Cat 6** [(*S,S*)-THTP] and (*S*)-1,16-dihydroxytetraphenylene **Cat 7** [(*S*)-DHTP] were prepared according to the literature.¹ Chiral ligand (*S*)-2,15-dichlorotetraphenylene-1,16-diol **Cat 8**, (*S*)-2,15-dibromotetraphenylene-1,16-diol **Cat 9** [(*S*)-2,15-Br₂-DHTP] and (*S*)-2,15-diphenyltetraphenylene-1,16-diol **Cat 10** [(*S*)-2,15-Ph₂-DHTP] were prepared according to the procedure previously reported.²

2. Preparation of starting materials

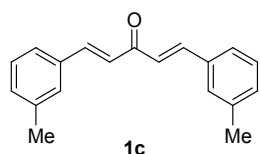
Symmetrical dienones **1a-1q** were prepared following the literature procedure^{3a} with starting acetone and appropriate aromatic aldehyde, using typical procedures for the aldol condensation.





Symmetrical dienones **1a-1b**,^{3a} **1d-1f**,^{3a} **1g**,^{3b} **1h-1j**,^{3a} **1m**,^{3c} **1n**,^{3d} **1o-1p**,^{3a} and **1q**^{3e} are known compounds. The ¹H NMR spectral data match those previously reported for these compounds. The ¹H NMR, ¹³C {¹H} NMR, ¹⁹F {¹H} NMR, HRMS spectra and the corresponding characterization data of starting materials **1c**, **1k**, and **1l** not reported previously are provided.

(1E,4E)-1,5-di-m-tolylpenta-1,4-dien-3-one (1c)



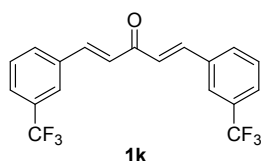
Yellow solid (686.5 mg, 52% yield); mp 66-67 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 16.0 Hz, 2H), 7.44-7.42 (m, 4H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 2H), 7.07 (d, *J* = 16.0 Hz, 2H), 2.40 (s, 6H);

¹³C {¹H} NMR (100 MHz, CDCl₃) δ 189.2, 143.6, 138.8, 134.9, 131.5, 129.2, 129.0, 125.8, 125.4, 21.5;

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{18}ONa$ 285.1250; Found 285.1236.

(1*E*,4*E*)-1,5-bis(3-(trifluoromethyl)phenyl)penta-1,4-dien-3-one (**1k**)



Yellow solid (256.4 mg, 14% yield); mp 114-115 °C;

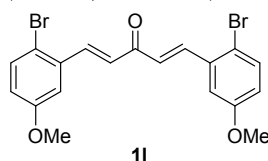
1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.79-7.75 (m, 4H), 7.68-7.67 (m, 2H), 7.58-7.54 (m, 2H), 7.14 (d, $J = 16.0$ Hz, 2H);

^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.2, 142.1, 135.6, 131.72 (q, $J = 33.0$ Hz), 131.73, 129.7, 127.1 (q, $J = 3.0$ Hz), 126.8, 124.9 (q, $J = 3.0$ Hz), 123.9 (q, $J = 271.0$ Hz);

^{19}F $\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -62.9;

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{12}F_6ONa$ 393.0685; Found 393.0674.

(1*E*,4*E*)-1,5-bis(2-bromo-5-methoxyphenyl)penta-1,4-dien-3-one (**1l**)



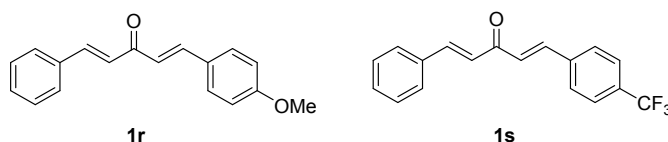
Yellow solid (699.2 mg, 31% yield); mp 129-131 °C;

1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, $J = 16.0$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.21 (d, $J = 3.2$ Hz, 2H), 7.00 (d, $J = 16.0$ Hz, 2H), 6.85 (dd, $J = 2.8, 8.8$ Hz, 2H); 3.85 (s, 6H);

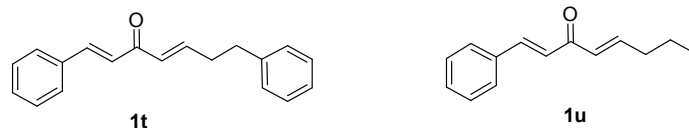
^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.9, 159.2, 142.3, 135.6, 134.3, 127.9, 117.9, 116.7, 112.9, 55.8;

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{16}Br_2O_3Na$ 472.9358; Found 472.9340.

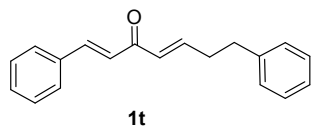
Unsymmetrical dienones **1r**^{4a} and **1s**^{4b} were prepared according to the literature procedures.^{4a}



Dienones **1t** and **1u**⁵ were synthesized according to the reported procedures.^{3a} The analytic data of the **1t** is provided below.



(1E,4E)-1,7-diphenylhepta-1,4-dien-3-one (**1t**)



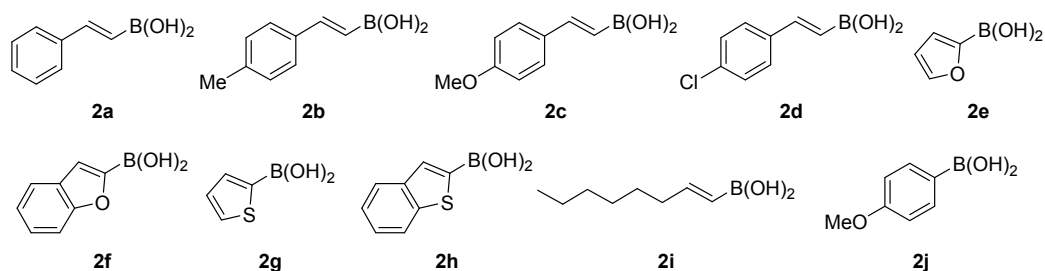
Yellow oil (308.8 mg, 65% yield);

^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 16.0$ Hz, 1H), 7.58-7.56 (m, 2H), 7.41-7.39 (m, 3H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 7.07-6.99 (m, 1H), 6.94 (d, $J = 16.0$ Hz, 1H), 6.48-6.43 (m, 1H), 2.84 (t, $J = 8.0$ Hz, 2H), 2.63-2.60 (m, 2H);

^{13}C $\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 189.1, 146.8, 143.1, 140.8, 134.8, 130.4, 129.7, 128.9, 128.5, 128.4, 128.3, 126.2, 124.9, 34.5, 34.4;

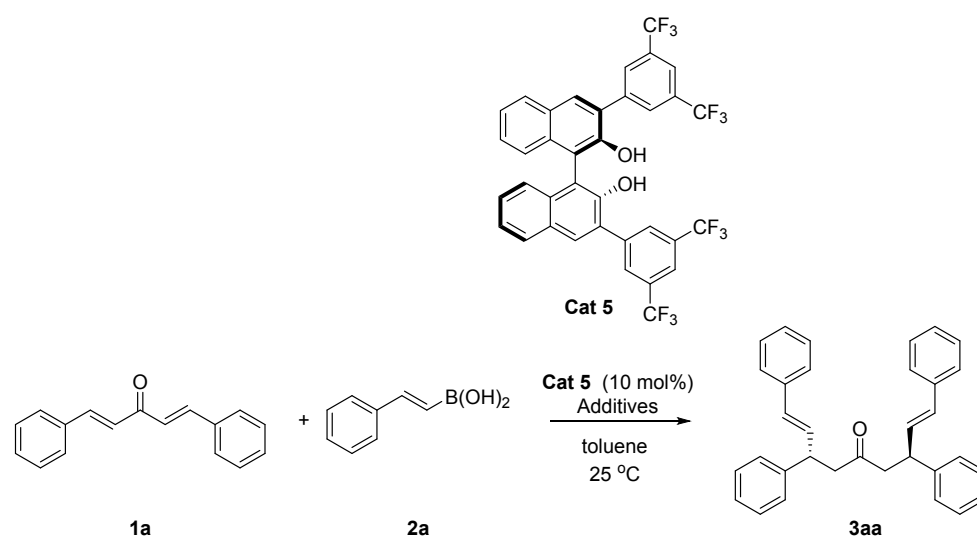
HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{ONa}$ 285.1250; Found 285.1241.

Boronic acid **2a-2j** were purchased from commercial suppliers and used without further purification.



3. Detailed Optimization of Reaction Conditions

Table S1. Screening of Additives.^a



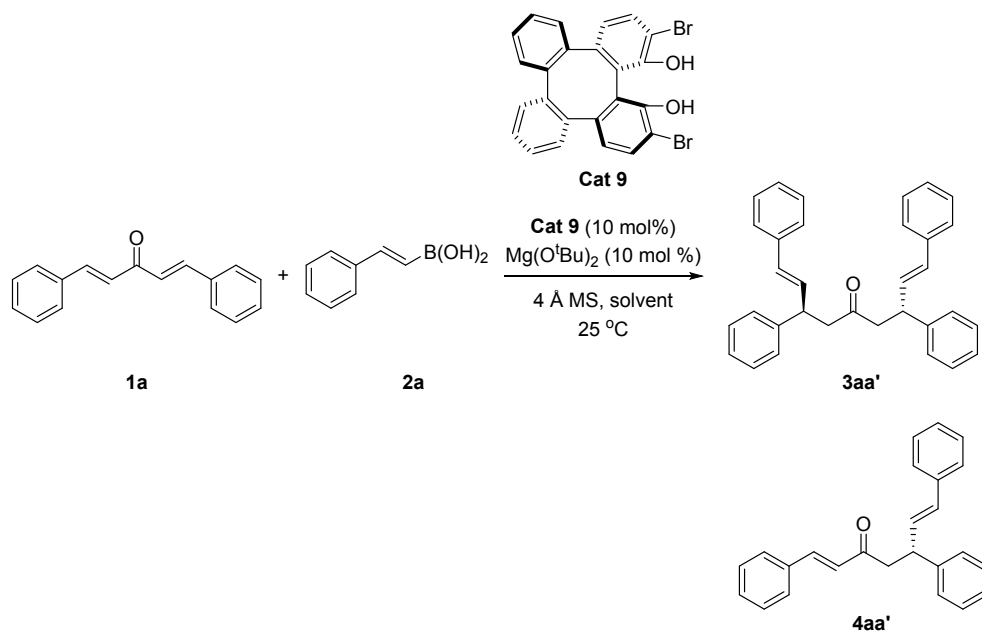
entry ^a	Additives	time (h)	yield (%) ^b	dl-/meso- ^c	ee (%) ^d
1	4 Å MS(100 mg), Mg(O ^t Bu) ₂ (0.1 eq)	24	94	94.8:5.2	>99
2	4 Å MS(100 mg)	24	91	95.5:4.5	>99
3	-	36	trace	-	-
4	4 Å MS(100 mg), LiO ^t Bu(0.1 eq)	24	96	94.2:5.8	>99
5	4 Å MS(100 mg), 1-Adamantanol (0.1 eq)	24	98	95.8:4.2	>99
6	4 Å MS(100 mg), 1-Adamantanol (1 eq)	48	72	96.1:3.9	>99
7	4 Å MS(100 mg), 1-Adamantanol (2 eq)	48	63	96.3:3.7	>99
8	4 Å MS(100 mg), MeOH (2 eq)	36	88	95.6:4.4	>99
9	4 Å MS(100 mg), HO ^t Bu (2 eq)	48	89	96.3:3.7	>99
10	4 Å MS(100 mg), HO ^t Bu (0.1 eq)	24	90	95.5:4.5	>99
11	4 Å MS(100 mg), ⁱ PrOH (2 eq)	48	79	96.3:3.7	>99
12	4 Å MS(100 mg), ⁱ PrOH (0.1 eq)	24	96	95.1:4.9	>99
13	4 Å MS(100 mg), HFIP (0.1 eq)	24	96	85.0:15.0	>99
14 ^e	4 Å MS(100 mg) 0 °C	48	66	96.0:4.0	>99
15	3 Å MS(100 mg)	24	98	95.5:4.5	>99

16	5 Å MS(100 mg)	24	97	95.8:4.2	>99
17 ^f	4 Å MS(100 mg)	36	89	92.9:7.1	>99

^aUnless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2a** (0.3 mmol), 10 mol% Cat **5** in a dry toluene (1.0 mL) at 25 °C under N₂. ^bIsolated yield. ^c*dl/meso* ratios were determined by chiral HPLC. ^dDetermined by HPLC on a chiral stationary phase. ^eAt 0 °C. ^fUsing 5 mol% Cat **5**.

In the optimization of the reaction conditions, we used other additives such as LiO^tBu, 1-Adamantanol, MeOH, HO^tBu, ⁱPrOH, HFIP and molecular sieves to improve the ratio of *dl/meso*, as shown in Table S1. In most cases, except for molecule sieves, the effect of other additives are not obvious.

Table S2. Screening of Solvent Using Cat 9 as Catalyst.^a



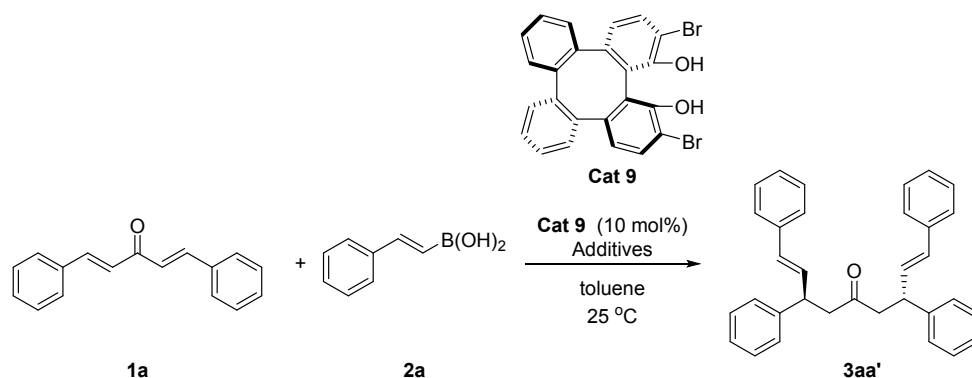
entry ^a	solvent	time	yield of 3aa' (%) ^b	3aa' <i>dl</i> -/ <i>meso</i> - ^c	ee of 3aa' (%) ^d	yield of 4aa' (%) ^b	ee of 4aa' (%) ^d
1 ^e	PhCF ₃	48	85	95.7:4.3	>99	-	-
2	PhCF ₃	24	87	95.9:4.1	>99	-	-
3	Toluene	24	92	96.3:3.7	>99	-	-
4	DCM	24	96	94:6	92	-	-
5	DCE	24	95	92.7:7.3	>99	-	-
6	<i>o</i> -xylene	24	84	96.2:3.8	>99	-	-
7	PhCl	24	88	94.4:5.6	>99	-	-
8	C ₆ HF ₅	48	84	93.4:6.6	>99	-	-

9	MTBE	24	87	96.2:3.8	>99	-	-
10	THF	48	-	-	-	36	62
11	MeCN	72	7	79.4:20.6	98	25	60
12	Et ₂ O	48	79	96.6:3.4	>99	-	-
13	CF ₃ CH ₂ OH	72	15	82.5:17.5	99	31	78

^aUnless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2a** (0.3 mmol), 10 mol% **Cat 9**, 10 mol% Mg(O^tBu)₂, 4 Å MS (100 mg) in a dry solvent (1.0 mL) at 25 °C under N₂. ^bIsolated yield. ^cdl/meso ratios were determined by chiral HPLC. ^dDetermined by HPLC on a chiral stationary phase. ^eUsing 2.0 eq of **2a**.

As shown in Table S2, the result in entry 3 was the best in terms of enantioselectivity and yield, and toluene was thus selected as the optimal solvent to further optimize the reaction conditions.

Table S3. Screening of Additives Using Cat 9 as Catalyst.^a



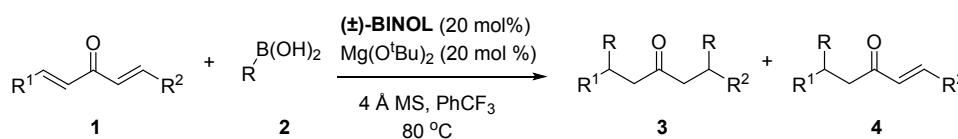
entry ^a	Additives	time (h)	yield of 3aa' (%) ^b	3aa' dl-/meso- ^c	ee of 3aa' (%) ^d
1	4 Å MS(100 mg), Mg(O ^t Bu) ₂ (0.1 eq)	24	92	96.3:3.7	>99
2	3 Å MS(100 mg), Mg(O ^t Bu) ₂ (0.1 eq)	18	91	95.8:4.2	>99
3	5 Å MS(100 mg), Mg(O ^t Bu) ₂ (0.1 eq)	20	90	94.8:5.2	>99
4	4 Å MS(100 mg)	12	94	96.2:3.8	>99
5	Mg(O ^t Bu) ₂ (0.1 eq)	28	trace	-	-
6	4 Å MS(100 mg), LiO ^t Bu(0.1 eq)	24	93	96.1:3.9	>99
7	4 Å MS(100 mg), HO ^t Bu(2 eq)	24	90	97.2:2.8	>99
8	4 Å MS(100 mg),	24	91	96.2:3.8	>99

MeOH (2 eq)					
9	4 Å MS(100 mg), <i>i</i> PrOH (2 eq)	24	85	97.1:2.9	>99
10	4 Å MS(100 mg), HFIP (2 eq)	24	93	71.2:28.8	95
11	4 Å MS(100 mg), 1-Adamantanol (2 eq)	24	91	97.2:2.8	>99
12	4 Å MS(100 mg), 1-Adamantanol (1 eq)	16	95	97.2:2.8	>99
13 ^e	4 Å MS(100 mg), 1-Adamantanol (1 eq)	23	96	96.6:3.4	>99
14 ^e	4 Å MS(100 mg)	24	92	96.1:3.9	>99

^aUnless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2a** (0.3 mmol), 10 mol% Cat **9**, 4 Å MS (100 mg) in a dry toluene (1.0 mL) at 25 °C under N₂. ^bIsolated yield. ^c*dl/meso* ratios were determined by chiral HPLC. ^dDetermined by HPLC on a chiral stationary phase. ^eUsing 5 mol% Cat **9**.

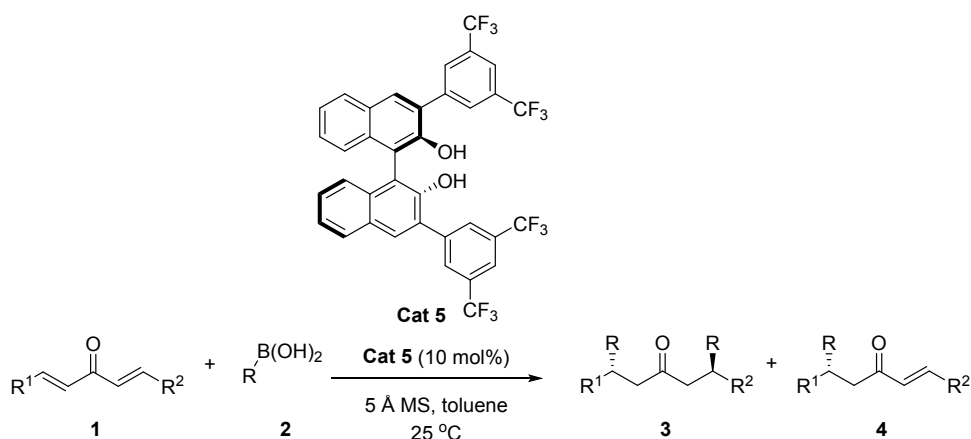
As shown in Table S3, the result in entry 14 was the best in terms of catalyst loading, enantioselectivity and yield, and was thus selected as the optimal conditions.

4. General procedures for the preparation of racemic products



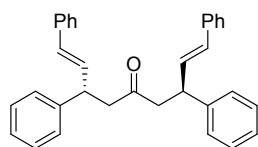
To a 10 mL Schlenk tube equipped with a stirring bar was added 4 Å MS (100 mg), and the tube was flamed-dried under high vacuum. After cooling to r.t., the tube was then backed-filled with nitrogen. Then boronic acid **2a–2i** (0.3 mmol, 3.0 equiv), Mg(O^tBu)₂ (0.02 mmol, 20 mol %), (±)-BINOL (0.02 mmol, 20 mol %), dienones **1a–1u** (0.1 mmol, 1.0 equiv), and dry PhCF₃ (1.0 mL) were successively added to the test tube under N₂. The tube was capped, sealed and allowed to stir at 80 °C in an oil bath for 24 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/DCM = 3:1–1:1) to give pure bis-adduct **3** (a mixture of the *dl*- and *meso*-isomers) and mono-adduct **4**.

5. General procedures for the catalytic asymmetric conjugate addition of boronic acid to dienones using Cat **5**



To a 10 mL Schlenk tube equipped with a stirring bar was added 5 Å MS (100 mg), and the tube was flamed-dried under high vacuum. After cooling to r.t., the tube was then backed-filled with nitrogen. Then boronic acid **2a-2i** (0.3 mmol, 3.0 equiv), **Cat 5** (0.01 mmol, 10 mol %), dienones **1a-1u** (0.1 mmol, 1.0 equiv), and dry toluene (1.0 mL) were successively added to the test tube under N₂. The tube was capped, sealed and allowed to stir at 25 °C for 24-72 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/DCM = 3:1-1:1) to give pure bis-adduct **3** (a mixture of the *dl*- and *meso*-isomers) and mono-adduct **4**.

(1E,3S,7S,8E)-1,3,7,9-tetraphenylnona-1,8-dien-5-one (**3aa**)⁶



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (42.8 mg, 97% yield); mp 102-103 °C;

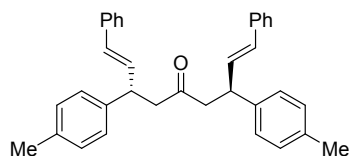
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) *t_R* (1) = 15.4 min, *t_R* (2) = 18.6 min, *t_R* (3) = 26.2 min, *dl*-/*meso*- = 95.8:4.2, >99% *ee*; [α]_D²⁵ = -8.2 (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.16 (m, 20H), 6.31-6.20 (m, 4H), 4.05 (q, *J* = 6.8 Hz, 2H), 2.89-2.85 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.9, 143.1, 137.2, 132.4, 130.1, 128.8, 128.6, 127.8, 127.4, 126.8, 126.4, 49.5, 43.8;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₃₀ONa 465.2189; Found 465.2168.

(1E,3S,7S,8E)-1,9-diphenyl-3,7-di-*p*-tolylnona-1,8-dien-5-one (**3ba**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (46.8 mg, 99% yield); mp 75-77 °C;

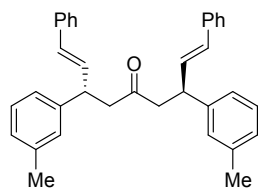
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) t_R (1) = 12.5 min, t_R (2) = 13.8 min, t_R (3) = 16.7 min, *dl*-/*meso*- = 97.0:3.0, >99% *ee*; $[\alpha]_D^{25} = -10.1$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 8H), 7.19-7.16 (m, 2H), 7.10-7.05 (m, 8H), 6.29-6.18 (m, 4H), 4.02 (q, *J* = 6.8 Hz, 2H), 2.91-2.79 (m, 4H), 2.29 (s, 6H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.1, 140.0, 137.3, 136.3, 132.7, 129.9, 129.5, 128.5, 127.6, 127.3, 126.4, 49.5, 43.4, 21.1;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₃₄ONa 493.2502; Found 493.2500.

(1E,3S,7S,8E)-1,9-diphenyl-3,7-di-*m*-tolylnona-1,8-dien-5-one (3ca)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (43.6 mg, 93% yield); mp 90-93 °C;

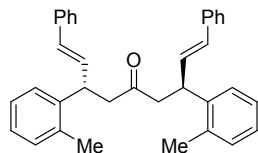
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) t_R (1) = 10.4 min, t_R (2) = 12.9 min, t_R (3) = 17.7 min, *dl*-/*meso*- = 95.5:4.5, >99% *ee*; $[\alpha]_D^{27} = -8.1$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.25-7.13 (m, 12H), 7.01-6.99 (m, 6H), 6.31-6.20 (m, 4H), 4.02 (q, *J* = 6.8 Hz, 2H), 2.88-2.85 (m, 4H), 2.29 (s, 6H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.0, 143.1, 138.4, 137.3, 132.6, 130.0, 128.7, 128.57, 128.55, 127.6, 127.3, 126.4, 124.7, 49.5, 43.7, 21.6;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₃₄ONa 493.2502; Found 493.2482.

(1E,3S,7S,8E)-1,9-diphenyl-3,7-di-*o*-tolylnona-1,8-dien-5-one (3da)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (43.1 mg, 92% yield); mp 91-93 °C;

HPLC (Daicel Chiralpak IG, hexane/*i*-PrOH = 95:5, flow rate 0.5 mL/min, λ =

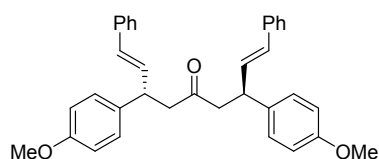
254 nm) t_R (1) = 19.6 min, t_R (2) = 20.3 min, t_R (3) = 22.1 min, *dl*-/*meso*- = 92.0:8.0, >99% *ee*; $[\alpha]_D^{26} = -5.5$ (c 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.24-7.21 (m, 8H), 7.19-7.09 (m, 10H), 6.23-6.12 (m, 4H), 4.32-4.27 (m, 2H), 2.91-2.88 (m, 4H), 2.34 (s, 6H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.1, 141.0, 137.3, 136.2, 132.1, 130.9, 130.0, 128.5, 127.3, 126.6, 126.43, 126.41, 126.35, 49.0, 39.2, 19.7;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₃₄ONa 493.2502; Found 493.2494.

(*1E,3S,7S,8E*)-3,7-bis(4-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ea**)⁶



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (47.9 mg, 95% yield); mp 144-147 °C;

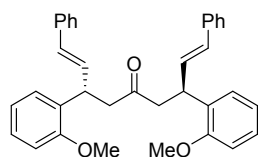
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 14.4 min, t_R (2) = 17.6 min, t_R (3) = 22.1 min, *dl*-/*meso*- = 97.3:2.7, >99% *ee*; $[\alpha]_D^{26} = -12.2$ (c 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.26-7.10 (m, 14H), 6.80 (d, *J* = 8.4 Hz, 4H), 6.28-6.19 (m, 4H), 4.03-3.98 (m, 2H), 3.75 (s, 6H), 2.90-2.78 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.3, 158.4, 137.3, 135.0, 132.8, 129.7, 128.8, 128.6, 127.3, 126.3, 114.2, 55.3, 49.6, 42.9;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₃₄O₃Na 525.2400; Found 525.2378.

(*1E,3S,7S,8E*)-3,7-bis(2-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one (**3fa**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (48.3 mg, 96% yield); mp 75-76 °C;

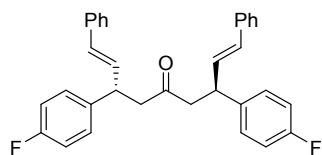
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) t_R (1) = 17.7 min, t_R (2) = 19.1 min, t_R (3) = 23.4 min, *dl*-/*meso*- = 95.6:4.4, >99% *ee*; $[\alpha]_D^{26} = -20.5$ (c 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.26-7.14 (m, 14H), 6.89-6.83 (m, 4H), 6.37-6.28 (m, 4H), 4.44 (q, *J* = 6.8 Hz, 2H), 3.79 (s, 6H), 2.96-2.86 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.9, 156.9, 137.6, 131.9, 131.5, 130.1, 128.5, 128.4, 127.7, 127.1, 126.4, 120.8, 111.0, 55.5, 48.1, 38.2;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₃₄O₃Na 525.2400; Found 525.2368.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(4-fluorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ga**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (46.0 mg, 96% yield); mp 68-69 °C;

HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R(1)$ = 7.6 min, $t_R(2)$ = 14.1 min, $t_R(3)$ = 18.3 min, *dl*-/*meso*- = 94.0:6.0, >99% *ee*; $[\alpha]_D^{27}$ = -6.9 (*c* 2.0, CHCl₃);

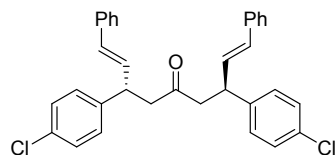
¹H NMR (400 MHz, CDCl₃) δ 7.28-7.10 (m, 14H), 6.95-6.91 (m, 4H), 6.31-6.16 (m, 4H), 4.04 (q, *J* = 6.8 Hz, 2H), 2.91-2.79 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.5, 161.7 (d, *J* = 244.0 Hz), 138.6 (d, *J* = 3.0 Hz), 137.0, 132.1, 130.3, 129.2 (d, *J* = 8.0 Hz), 128.6, 127.6, 126.3, 115.6 (d, *J* = 21.0 Hz), 49.5, 42.9;

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -116.1;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₂₈F₂ONa 501.2000; Found 501.1990.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(4-chlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ha**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (47.1 mg, 92% yield); mp 51-52 °C;

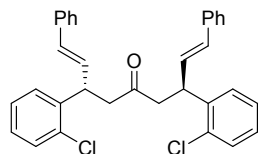
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R(1)$ = 9.7 min, $t_R(2)$ = 17.5 min, $t_R(3)$ = 24.9 min, *dl*-/*meso*- = 96.3:3.7, >99% *ee*; $[\alpha]_D^{23}$ = -8.5 (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.28-7.17 (m, 14H), 7.12-7.07 (m, 4H), 6.31-6.15 (m, 4H), 4.03 (q, *J* = 10.2 Hz, 2H), 2.93-2.77 (m, 4H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 206.2, 141.5, 137.0, 132.6, 131.8, 130.6, 129.2, 128.9, 128.7, 127.6, 126.4, 49.3, 43.1;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₂₈Cl₂ONa 533.1409; Found 533.1390.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(2-chlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ia**)



Eluent: hexane/DCM = 2:1-1:1; Colorless oil (46.9 mg, 92% yield);

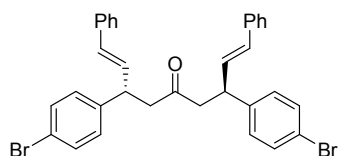
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 7.4 min, t_R (2) = 8.0 min, t_R (3) = 9.8 min, *dl*-/*meso*- = 92.6:7.4, >99% *ee*; $[\alpha]_D^{23} = -25.3$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.35-7.33 (m, 2H), 7.25-7.10 (m, 16H), 6.35-6.22 (m, 4H), 4.60 (q, *J* = 7.2 Hz, 2H), 2.97-2.96 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.9, 140.4, 137.1, 133.8, 131.1, 130.5, 130.2, 128.7, 128.6, 128.0, 127.5, 127.2, 126.5, 47.9, 40.3;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₂₈Cl₂ONa 533.1409; Found 533.1391.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(4-bromophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ja**)⁶



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (55.4 mg, 92% yield); mp 103-104 °C;

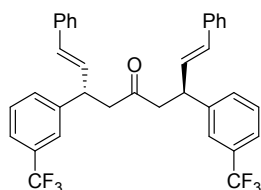
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 9.9 min, t_R (2) = 16.7 min, t_R (3) = 23.2 min, *dl*-/*meso*- = 96.5:3.5, >99% *ee*; $[\alpha]_D^{25} = -6.2$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.35 (m, 4H), 7.29-7.17 (m, 10H), 7.06-7.04 (m, 4H), 6.28-6.14 (m, 4H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.91-2.79 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.2, 141.9, 136.9, 131.9, 131.6, 130.6, 129.6, 128.7, 127.6, 126.4, 120.6, 49.2, 43.1;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₂₈Br₂ONa 621.0399; Found 621.0401.

(1*E*,3*S*,7*S*,8*E*)-1,9-diphenyl-3,7-bis(3-(trifluoromethyl)phenyl)nona-1,8-dien-5-one (**3ka**)



Eluent: hexane/DCM = 3:1-2:1; Colorless oil (27.8 mg, 48% yield);

HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 6.8 min, t_R (2) = 19.3 min, t_R (3) = 22.5 min, *dl*-/*meso*- = 91.5:8.5, >99% *ee*; $[\alpha]_D^{20} = -1.2$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.47-7.43 (m, 4H), 7.39-7.32 (m, 4H), 7.28-7.18 (m, 10H), 6.35-6.17 (m, 4H), 4.13 (q, *J* = 10.8 Hz, 2H), 3.01-2.83 (m, 4H);

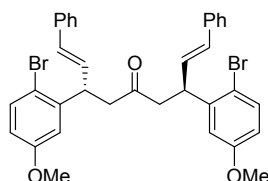
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 205.6, 144.0, 136.8, 131.3, 131.2, 131.1 (q, $J = 31.5$ Hz), 131.0, 129.3, 128.7, 127.7, 126.4, 124.4 (q, $J = 4.5$ Hz), 124.2 (q, $J = 271.5$ Hz), 123.8 (q, $J = 6.0$ Hz), 49.2, 43.5;

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -62.5;

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{28}\text{F}_6\text{ONa}$ 601.1937; Found 601.1922.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one

(3la)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (41.3 mg, 63% yield); mp 112-113 °C;

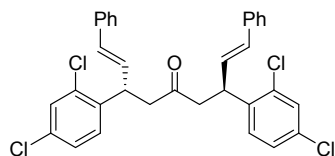
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, $\lambda = 254$ nm) t_R (1) = 12.2 min, t_R (2) = 13.3 min, t_R (3) = 23.0 min, *dl*-/*meso*- = 82.7:17.3, >99% *ee*; $[\alpha]_D^{20} = -2.7$ (*c* 2.0, CHCl_3);

^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 13.2$ Hz, 2H), 7.27-7.16 (m, 10H), 6.78 (d, $J = 4.2$ Hz, 2H), 6.63-6.61 (m, 2H), 6.38-6.19 (m, 4H), 4.54 (q, $J = 10.2$ Hz, 2H), 3.73 (s, 6H), 2.99-2.89 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 205.7, 159.2, 143.1, 137.0, 133.9, 131.2, 130.3, 128.6, 127.5, 126.5, 115.1, 114.9, 113.3, 55.6, 48.0, 42.6;

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{32}\text{Br}_2\text{O}_3\text{Na}$ 681.0610; Found 681.0610.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(2,4-dichlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ma**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (43.5 mg, 75% yield);

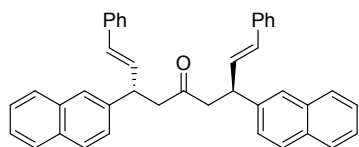
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, $\lambda = 254$ nm) t_R (1) = 13.0 min, t_R (2) = 18.7 min, t_R (3) = 27.9 min, *dl*-/*meso*- = 91.5:8.5, >99% *ee*; $[\alpha]_D^{27} = -17.2$ (*c* 2.0, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.35 (t, $J = 1.2$ Hz, 2H), 7.28-7.18 (m, 10H), 7.15-7.13 (m, 4H), 6.32-6.17 (m, 4H), 4.52 (q, $J = 6.8$ Hz, 2H), 2.99-2.89 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 205.4, 138.9, 136.8, 134.5, 133.0, 131.4, 129.9, 129.7, 129.5, 128.7, 127.7, 127.5, 126.4, 47.7, 39.8;

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{33}\text{H}_{26}\text{Cl}_4\text{ONa}$ 601.0630; Found 601.0613.

(1*E*,3*S*,7*S*,8*E*)-3,7-di(naphthalen-2-yl)-1,9-diphenylnona-1,8-dien-5-one (**3na**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (53.7 mg, 99% yield); mp 136-138 °C;

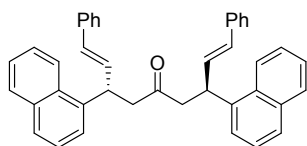
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 23.4 min, t_R (2) = 28.4 min, t_R (3) = 30.0 min, *dl*/*meso*- = 97.2:2.8, >99% *ee*; $[\alpha]_D^{20}$ = -14.2 (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.77-7.70 (m, 6H), 7.61 (s, 2H), 7.44-7.40 (m, 4H), 7.32-7.30 (m, 2H), 7.23-7.14 (m, 10H), 6.34-6.25 (m, 4H), 4.24-4.21 (m, 2H), 3.06-2.92 (m, 4H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 206.7, 140.5, 137.2, 133.7, 132.5, 132.3, 130.4, 128.6, 128.5, 127.9, 127.8, 127.4, 126.37, 126.31, 126.22, 126.17, 125.7, 49.4, 43.8;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₄₁H₃₄ONa 565.2502; Found 565.2487.

(1*E*,3*S*,7*S*,8*E*)-3,7-di(naphthalen-1-yl)-1,9-diphenylnona-1,8-dien-5-one (**3oa**)⁶



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (48.6 mg, 90% yield);

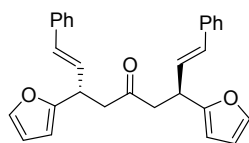
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 14.0 min, t_R (2) = 18.3 min, t_R (3) = 35.2 min, *dl*/*meso*- = 93.9:6.1, >99% *ee*; $[\alpha]_D^{27}$ = -43.7 (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 8.14-8.11 (m, 2H), 7.84-7.82 (m, 2H), 7.72-7.69 (m, 2H), 7.46-7.43 (m, 4H), 7.38-7.32 (m, 4H), 7.23-7.15 (m, 10H), 6.43-6.27 (m, 4H), 4.95 (q, *J* = 6.4 Hz, 2H), 3.18-3.02 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.9, 139.2, 137.2, 134.2, 132.0, 131.4, 130.7, 129.1, 128.6, 127.5, 127.4, 126.4, 125.8, 125.5, 124.4, 123.5, 49.2, 38.6;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₄₁H₃₄ONa 565.2502; Found 565.2481.

(1*E*,3*S*,7*S*,8*E*)-3,7-di(furan-2-yl)-1,9-diphenylnona-1,8-dien-5-one (**3pa**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (39.7 mg, 94% yield); mp 86-88 °C;

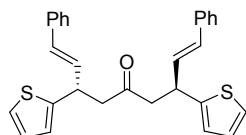
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R(1)$ = 8.5 min, $t_R(2)$ = 10.8 min, $t_R(3)$ = 11.7 min, *dl*-/*meso*- = 93.8:6.2, >99% *ee*; $[\alpha]_D^{24}$ = 26.6 (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.31-7.25 (m, 10H), 7.22-7.19 (m, 2H), 6.41 (d, J = 15.6 Hz, 2H), 6.28-6.24 (m, 2H), 6.20 (dd, J = 7.8, 15.6 Hz, 2H), 6.04-6.02 (m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.00 (dd, J = 6.6, 16.2 Hz, 2H), 2.83 (dd, J = 7.2, 16.8 Hz, 2H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 205.9, 155.8, 141.6, 137.1, 131.5, 129.3, 128.6, 127.6, 126.5, 110.4, 105.7, 47.1, 37.7;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₉H₂₆O₃Na 445.1774; Found 445.1765.

(1*E*,3*S*,7*S*,8*E*)-1,9-diphenyl-3,7-di(thiophen-2-yl)nona-1,8-dien-5-one (**3qa**)⁶



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (36.4 mg, 80% yield); mp 112-114 °C;

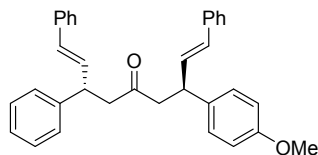
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R(1)$ = 8.7 min, $t_R(2)$ = 10.9 min, $t_R(3)$ = 14.2 min, *dl*-/*meso*- = 95.1:4.9, >99% *ee*; $[\alpha]_D^{23}$ = 7.3 (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.31-7.18 (m, 10H), 7.13-7.11 (m, 2H), 6.89-6.81 (m, 4H), 6.43-6.39 (m, 2H), 6.26-6.20 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 3.02-2.87 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.8, 146.8, 136.9, 131.6, 130.8, 128.6, 127.6, 127.0, 126.5, 124.2, 123.9, 50.3, 39.1;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₉H₂₆OS₂Na 477.1317; Found 477.1316.

(1*E*,3*S*,7*S*,8*E*)-3-(4-methoxyphenyl)-1,7,9-triphenylnona-1,8-dien-5-one (**3ra**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (40.3 mg, 85% yield); mp 70-71 °C;

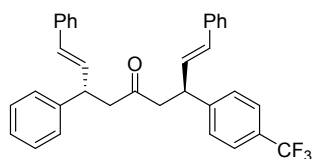
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R(1)$ = 10.6 min, $t_R(2)$ = 13.0 min, $t_R(3)$ = 16.2 min, $t_R(4)$ = 17.8 min, d.r. = 96.9:3.1, >99% *ee*; $[\alpha]_D^{27}$ = -12.3 (*c* 2.0, CHCl₃);

^1H NMR (600 MHz, CDCl_3) δ 7.28-7.22 (m, 10H), 7.20-7.15 (m, 5H), 7.12-7.09 (m, 2H), 6.81-6.78 (m, 2H), 6.31-6.19 (m, 4H), 4.08-3.98 (m, 2H), 3.75 (s, 3H), 2.91-2.80 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 207.1, 158.4, 143.1, 137.32, 137.28, 135.1, 132.9, 132.5, 130.2, 129.9, 128.81, 128.77, 128.6, 127.8, 127.40, 127.36, 126.8, 126.4, 114.2, 55.4, 49.6, 49.5, 43.8, 43.0;

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{32}\text{O}_2\text{Na}$ 495.2295; Found 495.2290.

(1*E*,3*S*,7*S*,8*E*)-1,3,9-triphenyl-7-(4-(trifluoromethyl)phenyl)nona-1,8-dien-5-one (**3sa**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (48.8 mg, 96% yield); mp 94-95 °C;

HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 10.4 min, t_R (2) = 14.7 min, t_R (3) = 17.3 min, t_R (4) = 21.5 min, d.r. = 94.7:5.3, >99% *ee*; $[\alpha]_D^{27} = -4.6$ (*c* 2.0, CHCl_3);

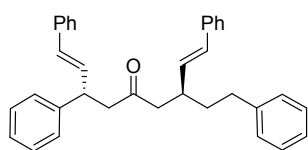
^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.29-7.16 (m, 17H), 6.32-6.16 (m, 4H), 4.12 (q, $J = 6.8$ Hz, 1H), 4.05 (q, $J = 7.2$ Hz, 1H), 2.96-2.84 (m, 4H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 206.3, 147.2, 142.9, 137.1, 136.9, 132.2, 131.4, 130.8, 130.3, 129.1, 128.9, 128.7, 128.6, 128.2, 127.72, 127.68, 127.5, 126.9, 126.4, 126.3, 125.7 (q, $J = 4.0$ Hz), 124.3 (q, $J = 270.0$ Hz), 49.3, 49.2, 44.0, 43.3;

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -62.4;

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{29}\text{F}_3\text{ONa}$ 533.2063; Found 533.2049.

(1*E*,3*S*,7*S*,8*E*)-3-phenethyl-1,7,9-triphenylnona-1,8-dien-5-one (**3ta**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (27.2 mg, 58% yield);

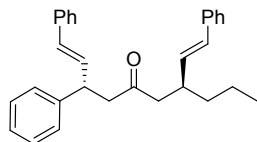
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 9.4 min, t_R (2) = 10.4 min, t_R (3) = 12.2 min, t_R (4) = 12.9 min, d.r. = 84.1:15.9, >99% *ee*; $[\alpha]_D^{18} = 1.4$ (*c* 0.5, CHCl_3);

^1H NMR (400 MHz, CDCl_3) mixture of diastereomers δ 7.31-7.10 (m, 20H), 6.38-6.24 (m, 3H), 6.00-5.94 (m, 1H), 4.06 (q, $J = 7.2$ Hz, 1H), 2.90-2.87 (m, 2H), 2.76-2.74 (m, 1H), 2.62-2.45 (m, 4H), 1.71-1.53 (m, 2H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) mixture of diastereomers δ 207.7, 143.13, 143.08, 142.2, 137.4, 137.2, 132.76, 132.75, 132.52, 132.50, 131.08, 131.05, 130.17,

130.12, 128.80, 128.79, 128.64, 128.59, 128.51, 128.47, 127.82, 127.77, 127.38, 127.35, 126.8, 126.4, 126.3, 125.9, 49.5, 49.4, 49.3, 43.9, 38.5, 38.4, 36.7, 33.7, 33.6;
HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₅H₃₄ONa 493.2502; Found 493.2484.

(3S,7S,E)-1,3-diphenyl-7-((*E*)-styryl)dec-1-en-5-one (**3ua**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (27.8 mg, 68% yield);

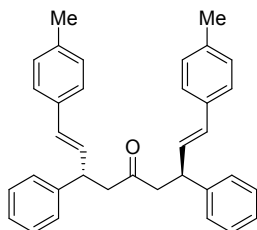
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 6.0 min, t_R (2) = 6.4 min, t_R (3) = 7.5 min, t_R (4) = 8.4 min, d.r. = 82.0:18.0, >99% *ee*; $[\alpha]_D^{21} = 12.1$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) mixture of diastereomers δ 7.30-7.15 (m, 15H), 6.37-6.25 (m, 3H), 5.96-5.90 (m, 1H), 4.08 (q, *J* = 6.8 Hz, 1H), 2.92-2.90 (m, 2H), 2.76-2.67 (m, 1H), 2.51-2.39 (m, 2H), 1.33-1.23 (m, 4H), 0.85-0.82 (m, 3H);

¹³C{¹H} NMR (150 MHz, CDCl₃) mixture of diastereomers δ 208.0, 143.2, 143.1, 137.5, 137.2, 133.34, 133.33, 132.6, 130.4, 130.3, 130.1, 128.79, 128.78, 128.6, 127.83, 127.79, 127.4, 127.2, 126.8, 126.3, 126.2, 49.54, 49.51, 49.46, 49.3, 43.9, 38.5, 37.3, 20.5, 20.4, 14.1;

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₀H₃₂ONa 431.2345; Found 431.2336.

(1E,3S,7S,8E)-3,7-diphenyl-1,9-di-*p*-tolylnona-1,8-dien-5-one (**3ab**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (41.1 mg, 87% yield);

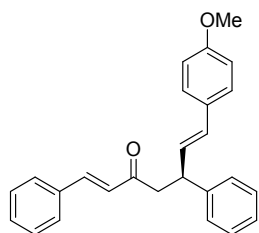
HPLC (Daicel Chiralpak IE, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 9.9 min, t_R (2) = 10.4 min, t_R (3) = 11.2 min, *dl*-/*meso*- = 95.3:4.7, >99% *ee*; $[\alpha]_D^{20} = -6.6$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.27-7.24 (m, 4H), 7.19-7.14 (m, 10H), 7.06-7.05 (m, 4H), 6.27-6.16 (m, 4H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.91-2.81 (m, 4H), 2.30 (s, 6H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 207.1, 143.2, 137.1, 134.4, 131.4, 130.0, 129.3, 128.8, 127.8, 126.7, 126.3, 49.5, 43.8, 21.3;

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₅H₃₄ONa 493.2502; Found 493.2491.

(S,1E,6E)-7-(4-methoxyphenyl)-1,5-diphenylhepta-1,6-dien-3-one (**4ac**)



Eluent: hexane/EA = 20:1–10:1; Colorless oil (17.1 mg, 47% yield);

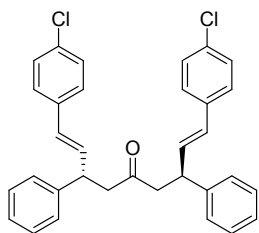
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (major) = 13.8 min, t_R (minor) = 16.6 min, 58% *ee*; $[\alpha]_D^{16} = -2.3$ (*c* 1.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.54–7.50 (m, 3H), 7.38–7.20 (m, 10H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 16.2 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 7.2, 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.22–3.14 (m, 2H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 198.4, 159.1, 143.6, 142.9, 134.6, 130.6, 130.5, 130.1, 129.6, 129.1, 128.8, 128.4, 127.9, 127.5, 126.7, 126.5, 114.0, 55.4, 47.0, 44.3;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₆H₂₄O₂Na 391.1669; Found 391.1669.

(1*E*,3*S*,7*S*,8*E*)-1,9-bis(4-chlorophenyl)-3,7-diphenylnona-1,8-dien-5-one (**3ad**)



Eluent: hexane/DCM = 3:1–1:1; Colorless solid (51.0 mg, 99% yield); mp 87–88 °C;

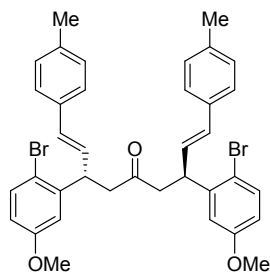
HPLC (Daicel Chiralpak IE, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 11.3 min, t_R (2) = 12.0 min, t_R (3) = 13.4 min, *dl*-/*meso*- = 93.6:6.4, >99% *ee*; $[\alpha]_D^{18} = -12.9$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.28–7.24 (m, 4H), 7.21–7.13 (m, 14H), 6.23–6.17 (m, 4H), 4.04 (q, *J* = 6.6 Hz, 2H), 2.91–2.82 (m, 4H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 206.7, 142.8, 135.6, 133.1, 133.0, 129.0, 128.9, 128.7, 127.7, 127.6, 126.9, 49.3, 43.7;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₂₈OCl₂Na 533.1409; Found 533.1409.

(1*E*,3*S*,7*S*,8*E*)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-di-*p*-tolylnona-1,8-dien-5-one (**31b**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (48.3 mg, 70% yield);

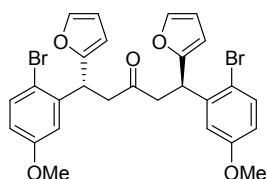
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 12.4 min, t_R (2) = 13.4 min, t_R (3) = 20.0 min, *dl*-/*meso*- = 88.5:11.5, >99% *ee*; $[\alpha]_D^{21} = -3.3$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.16-7.14 (m, 4H), 7.05-7.03 (m, 4H), 6.78-6.77 (m, 2H), 6.63-6.61 (m, 2H), 6.33-6.30 (m, 2H), 6.20-6.16 (m, 2H), 4.53-4.51 (m, 2H), 3.734-3.730 (m, 6H), 2.93-2.91 (m, 4H), 2.30 (s, 6H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 205.8, 159.2, 143.3, 137.3, 134.3, 133.9, 131.1, 129.3, 126.4, 115.1, 114.9, 113.4, 55.6, 48.1, 42.7, 21.3;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₇H₃₆Br₂O₃Na 709.0923; Found 709.0904.

(1R,5R)-1,5-bis(2-bromo-5-methoxyphenyl)-1,5-di(furan-2-yl)pentan-3-one (**31e**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (44.8 mg, 76% yield);

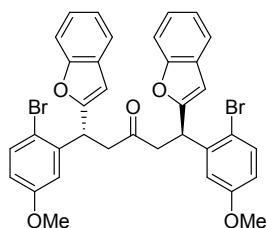
HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 220 nm) t_R (1) = 10.9 min, t_R (2) = 13.4 min, t_R (3) = 16.0 min, *dl*-/*meso*- = 73.0:27.0, 94% *ee*; $[\alpha]_D^{18} = -11.4$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.44-7.41 (m, 2H), 7.30-7.26 (m, 2H), 6.65-6.62 (m, 4H), 6.27-6.24 (m, 2H), 6.01-5.99 (m, 2H), 5.06-5.01 (m, 2H), 3.712-3.707 (d, 6H), 3.21-3.14 (m, 2H), 3.00-2.95 (m, 2H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 204.5, 159.2, 154.6, 142.0, 141.8, 133.8, 115.3, 114.5, 113.7, 110.4, 107.0, 55.5, 46.6, 39.5;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₇H₂₄Br₂O₅Na 608.9883; Found 608.9873.

(1R,5R)-1,5-di(benzofuran-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pentan-3-one (**31f**)



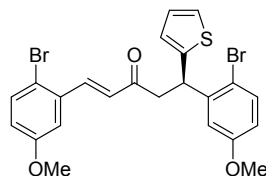
Eluent: hexane/DCM = 3:1-1:1; Colorless solid (54 mg, 79% yield); mp 70-72 °C; HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 8.1 min, t_R (2) = 9.2 min, t_R (3) = 10.3 min, *dl*-/*meso*- = 61.6:38.4, 91% *ee*; $[\alpha]_D^{19} = -7.8$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) mixture of diastereomers δ 7.46-7.33 (m, 6H), 7.22-7.13 (m, 4H), 6.74-6.73 (m, 2H), 6.66-6.62 (m, 2H), 6.34-6.33 (m, 2H), 5.22-5.18 (m, 2H), 3.68-3.67 (d, 6H), 3.38-3.30 (m, 2H), 3.15-3.09 (m, 2H);

¹³C {¹H} NMR (100 MHz, CDCl₃) mixture of diastereomers δ 204.10, 204.05, 159.3, 157.6, 157.55, 157.53, 154.9, 141.1, 141.0, 133.89, 133.87, 128.50, 128.48, 123.9, 122.8, 120.89, 120.86, 115.49, 115.45, 114.65, 114.64, 113.9, 113.8, 111.2, 104.2, 104.1, 55.5, 46.4, 39.9;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₂₈Br₂O₅Na 709.0196; Found 709.0189.

(R,E)-1,5-bis(2-bromo-5-methoxyphenyl)-5-(thiophen-2-yl)pent-1-en-3-one (**4lg**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (39.9mg, 74% yield);

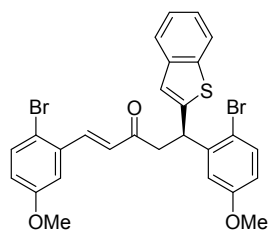
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (major) = 8.9 min, t_R (minor) = 13.4 min, 87.3% *ee*; $[\alpha]_D^{18} = -7.2$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 16.4 Hz, 2H), 7.47 (t, *J* = 8.8 Hz, 2H), 7.16-7.08 (m, 2H), 6.92-6.80 (m, 4H), 6.67-6.61 (m, 2H), 5.41 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.53-3.38 (m, 2H);

¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.8, 159.3, 159.2, 146.1, 143.7, 141.7, 135.1, 134.2, 133.9, 128.6, 126.9, 125.0, 124.3, 118.2, 116.6, 115.2, 114.9, 113.6, 112.6, 55.7, 55.6, 47.3, 40.9;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀Br₂O₃SNa 556.9392; Found 556.9386.

(R,E)-5-(benzo[*b*]thiophen-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pent-1-en-3-one

(4lh)

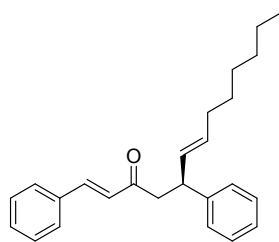
Eluent: hexane/DCM = 3:1-1:1; Colorless solid (52.9 mg, 90% yield); mp 90-91 °C;

HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (major) = 10.5 min, t_R (minor) = 18.0 min, 96% *ee*; $[\alpha]_D^{23} = -15.8$ (*c* 2.0, CHCl₃);

¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 16.2 Hz, 1H), 7.72-7.65 (m, 2H), 7.48 (dd, *J* = 2.4, 8.4 Hz, 2H), 7.30-7.24 (m, 2H), 7.12 (s, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 6.91 (d, *J* = 3.0 Hz, 1H), 6.81 (dd, *J* = 3.0, 9.0 Hz, 1H), 6.68-6.64 (m, 2H), 5.49-5.47 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.58 (dd, *J* = 7.8, 16.8 Hz, 1H), 3.46 (dd, *J* = 6.6, 16.8 Hz, 1H);

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 196.5, 159.2, 159.1, 146.8, 142.8, 141.7, 139.7, 135.0, 134.1, 133.9, 128.5, 124.3, 124.0, 123.3, 122.2, 121.6, 118.1, 116.5, 115.3, 114.9, 113.6, 112.5, 55.6, 55.5, 46.7, 41.5;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₇H₂₂Br₂O₃SNa 606.9549; Found 606.9540.

(*S*,1*E*,6*E*)-1,5-bis(2-bromo-5-methoxyphenyl)trideca-1,6-dien-3-one (4ai)

Eluent: hexane/DCM = 3:1-1:1; Colorless solid (25.3 mg, 73% yield); mp 43-44 °C;

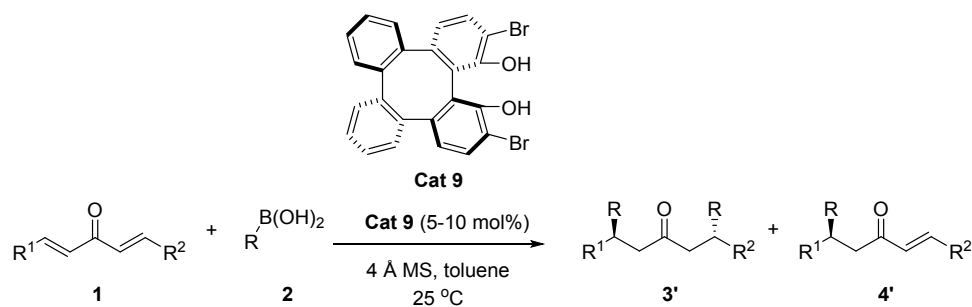
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) t_R (minor) = 6.4 min, t_R (major) = 6.8 min, 92% *ee*; $[\alpha]_D^{21} = 4.1$ (*c* 2.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.48 (m, 3H), 7.39-7.37 (m, 3H), 7.32-7.17 (m, 5H), 6.69 (d, *J* = 16.0 Hz, 1H), 5.63-5.43 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 1H), 3.11-2.98 (m, 2H), 1.98 (q, *J* = 6.8 Hz, 1H), 1.31-1.21 (m, 8H), 0.90-0.83 (m, 3H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 198.8, 144.2, 142.8, 134.7, 132.2, 131.3, 130.6, 129.1, 128.7, 128.4, 127.7, 126.6, 126.5, 47.3, 44.3, 32.7, 31.8, 29.4, 28.9, 22.7, 14.2;

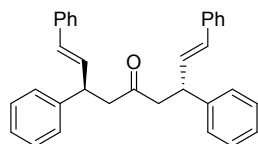
HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₅H₃₀ONa 369.2189; Found 369.2172.

6. General procedures for the catalytic asymmetric conjugate addition of boronic acid to dienones using Cat 9



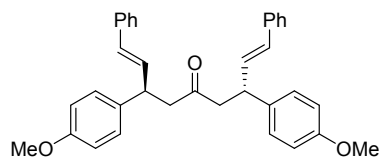
To a 10 mL Schlenk tube equipped with a stirring bar was added 4 Å MS (100 mg), and the tube was flamed-dried under high vacuum. After cooling to r.t., the tube was then backed-filled with nitrogen. Then boronic acid **2** (0.3 mmol, 3.0 equiv), **Cat 9** (0.005-0.01 mmol, 5-10 mol %), dienones **1** (0.1 mmol, 1.0 equiv), and dry toluene (1.0 mL) were successively added to the test tube under N₂. The tube was capped, sealed and allowed to stir at 25 °C for 24-48 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/DCM = 3:1-1:1) to give pure bis-adduct **3'** (a mixture of the *dl*- and *meso*-isomers) and mono-adduct **4'**.

(1*E*,3*R*,7*R*,8*E*)-1,3,7,9-tetraphenylnona-1,8-dien-5-one (**3aa'**)⁶



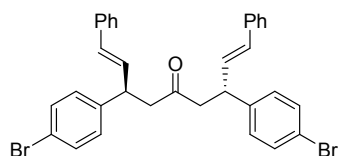
Eluent: hexane/DCM = 3:1-1:1; Colorless solid (40.7 mg, 92% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, λ = 254 nm) t_R (1) = 15.6 min, t_R (2) = 18.7 min, t_R (3) = 26.0 min, *dl*-/*meso*- = 96.1:3.9, >99% *ee*; $[\alpha]_D^{20}$ = 9.6 (*c* 2.0, CHCl₃);

(1*E*,3*R*,7*R*,8*E*)-3,7-bis(4-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ea'**)⁶



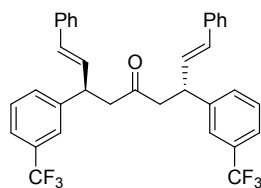
Eluent: hexane/DCM = 2:1-1:1; Colorless solid (49.8 mg, 99% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 14.4 min, t_R (2) = 17.8 min, t_R (3) = 21.6 min, *dl*-/*meso*- = 96.8:3.2, >99% *ee*; $[\alpha]_D^{19}$ = 11.4 (*c* 2.0, CHCl₃);

(1*E*,3*R*,7*R*,8*E*)-3,7-bis(4-bromophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ja'**)⁶



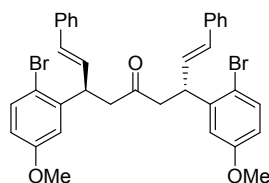
Eluent: hexane/DCM = 3:1-1:1; Colorless solid (57.7 mg, 96% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, $\lambda = 254$ nm) $t_R(1) = 9.8$ min, $t_R(2) = 16.2$ min, $t_R(3) = 22.3$ min, *dl*-/*meso*- = 97.0:3.0, >99% *ee*; $[\alpha]_D^{20} = 7.2$ (*c* 2.0, CHCl₃);

(*1E,3R,7R,8E*)-1,9-diphenyl-3,7-bis(3-(trifluoromethyl)phenyl)nona-1,8-dien-5-one
(**3ka'**)



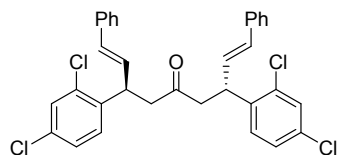
Eluent: hexane/DCM = 3:1-2:1; Colorless oil (56.1 mg, 97% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, $\lambda = 254$ nm) $t_R(1) = 6.5$ min, $t_R(2) = 19.3$ min, $t_R(3) = 21.9$ min, *dl*-/*meso*- = 96.0:4.0, >99% *ee*; $[\alpha]_D^{19} = 1.3$ (*c* 2.0, CHCl₃);

(*1E,3R,7R,8E*)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one
(**3la'**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (47.4 mg, 72% yield); HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, $\lambda = 254$ nm) $t_R(1) = 12.2$ min, $t_R(2) = 13.4$ min, $t_R(3) = 23.9$ min, *dl*-/*meso*- = 97.9:2.1, >99% *ee*; $[\alpha]_D^{19} = 7.3$ (*c* 2.0, CHCl₃);

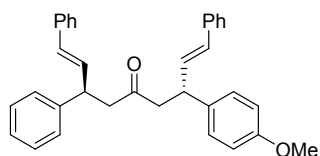
(*1E,3R,7R,8E*)-3,7-bis(2,4-dichlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ma'**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (53.7 mg, 92% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 0.8 mL/min, $\lambda = 254$ nm) $t_R(1) = 14.2$ min, $t_R(2) = 18.8$ min, $t_R(3) = 27.8$ min, *dl*-/*meso*- = 98.2:1.8, >99% *ee*; $[\alpha]_D^{19} = 19.8$

(*c* 2.0, CHCl₃);

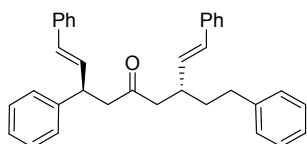
(1*E*,3*R*,7*R*,8*E*)-3-(4-methoxyphenyl)-1,7,9-triphenylnona-1,8-dien-5-one (**3ra'**)



Eluent: hexane/DCM = 2:1-1:1; Colorless solid (37.8 mg, 80% yield);

HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 10.6 min, t_R (2) = 12.7 min, t_R (3) = 16.9 min, t_R (4) = 18.2 min, d.r. = 97.4:2.6, >99% *ee*; $[\alpha]_D^{20}$ = 13.7 (*c* 2.0, CHCl₃);

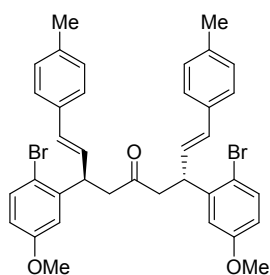
(1*E*,3*R*,7*R*,8*E*)-3-phenethyl-1,7,9-triphenylnona-1,8-dien-5-one (**3ta'**)



Eluent: hexane/DCM = 3:1-1:1; Colorless oil (46.6 mg, 99% yield);

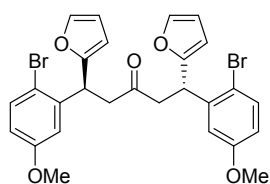
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 9.2 min, t_R (2) = 10.6 min, t_R (3) = 12.3 min, t_R (4) = 12.8 min, d.r. = 92.7:7.3, >99% *ee*; $[\alpha]_D^{20}$ = -0.4 (*c* 2.0, CHCl₃);

(1*E*,3*R*,7*R*,8*E*)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-di-*p*-tolylnona-1,8-dien-5-one (**3lb'**)



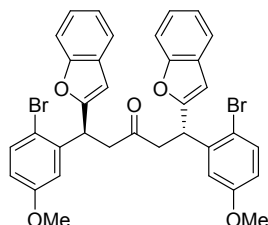
Eluent: hexane/DCM = 3:1-1:1; Colorless oil (68.8 mg, 99% yield); HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 12.3 min, t_R (2) = 13.3 min, t_R (3) = 20.1 min, *dl*-/*meso*- = 93.2:6.8, >99% *ee*; $[\alpha]_D^{19}$ = 5.1 (*c* 2.0, CHCl₃);

(1*S*,5*S*)-1,5-bis(2-bromo-5-methoxyphenyl)-1,5-di(furan-2-yl)pentan-3-one (**3lc'**)



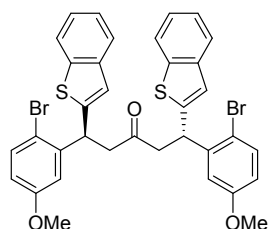
Eluent: hexane/DCM = 3:1-1:1; Colorless oil (49.8 mg, 85% yield); HPLC (Daicel Chiralpak ID, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, $\lambda = 220$ nm) t_R (1) = 10.8 min, t_R (2) = 13.2 min, t_R (3) = 16.5 min, *dl*-/*meso*- = 86.1:13.9, >99% *ee*; $[\alpha]_D^{23} = 13.7$ (*c* 2.0, CHCl₃);

(1*S*,5*S*)-1,5-di(benzofuran-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pentan-3-one (**31d'**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (59.1 mg, 86% yield); HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, $\lambda = 254$ nm) t_R (1) = 8.1 min, t_R (2) = 9.2 min, t_R (3) = 10.1 min, *dl*-/*meso*- = 83.8:16.2, >99% *ee*; $[\alpha]_D^{23} = 13.7$ (*c* 2.0, CHCl₃);

(1*S*,5*S*)-1,5-bis(benzo[*b*]thiophen-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pentan-3-one (**31f'**)



Eluent: hexane/DCM = 3:1-1:1; Colorless solid (40.3 mg, 56% yield); mp 88-90 °C;

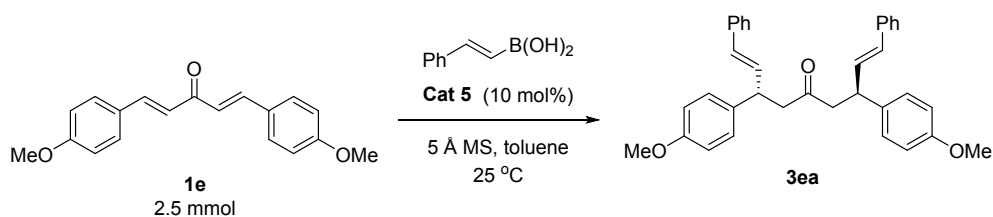
HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 85:15, flow rate 1.0 mL/min, $\lambda = 254$ nm) t_R (1) = 16.8 min, t_R (2) = 17.2 min, t_R (3) = 18.6 min, *dl*-/*meso*- = 92.0:8.0, >99% *ee*; $[\alpha]_D^{20} = -1.6$ (*c* 1.0, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.68-7.51 (m, 4H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.28-7.20 (m, 4H), 6.94 (s, 2H), 6.78 (d, *J* = 2.8 Hz, 2H), 6.63 (dd, *J* = 2.8, 8.8 Hz, 2H), 5.35-5.32 (m, 2H), 3.68 (s, 6H), 3.35-3.17 (m, 4H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 204.0, 159.3, 146.4, 142.7, 139.7, 139.4, 133.9, 124.3, 124.1, 123.4, 122.2, 121.7, 115.2, 114.8, 113.7, 55.5, 49.1, 41.2;

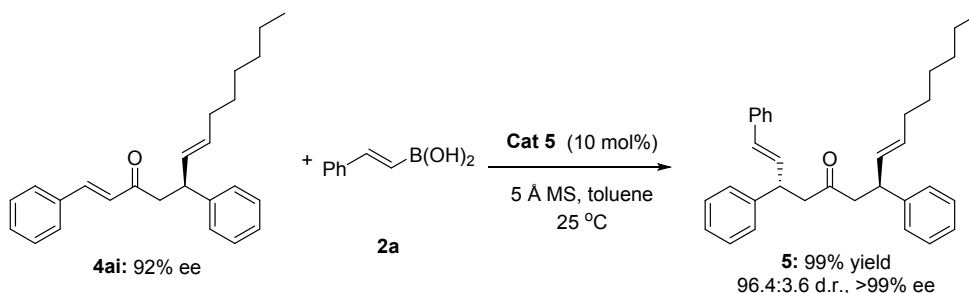
HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₅H₂₈Br₂O₃S₂Na 740.9739; Found 740.9728.

7. General procedures for scale-up reaction



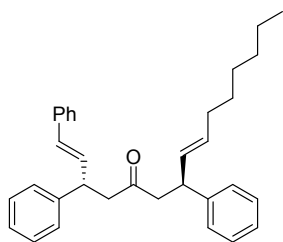
To a 100 mL Schlenk tube equipped with a stirring bar was added 5 Å MS (2.5 g), and the tube was flamed-dried under high vacuum. After cooling to r.t., the tube was then backed-filled with nitrogen. Then boronic acid **2a** (7.5 mmol, 3.0 equiv), **Cat 5** (0.25 mmol, 10 mol %), dienones **1e** (2.5 mmol, 1.0 equiv), and dry toluene (25.0 mL) were successively added to the test tube under N₂. The tube was capped, sealed and allowed to stir at 25 °C for 48 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/DCM = 2:1–1:1) to give pure bis-adduct **3ea** (a mixture of the *dl*- and *meso*-isomers). Colorless solid, 1.18 g, 94% yield, *dl*-/*meso*- = 96.4:3.6, >99% *ee* for *dl*- isomer.

8. General procedures for transformation of the product **4ag**



To a 10 mL Schlenk tube equipped with a stirring bar was added 5 Å MS (100 mg), and the tube was flamed-dried under high vacuum. After cooling to r.t., the tube was then backed-filled with nitrogen. Then boronic acid **2a** (0.2 mmol, 2.0 equiv), **Cat 5** (0.01 mmol, 10 mol %), mono-adduct **4ai** (0.1 mmol, 1.0 equiv), and dry toluene (1.0 mL) were successively added to the test tube under N₂. The tube was capped, sealed and allowed to stir at 25 °C for 24 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/DCM = 3:1–1:1) to give pure bis-adduct **5** (45.0 mg, 99% yield, 96.4:3.6 d.r., >99% *ee*).

(*1E,3S,7S,8E*)-1,3,7-triphenylpentadeca-1,8-dien-5-one (**5**)

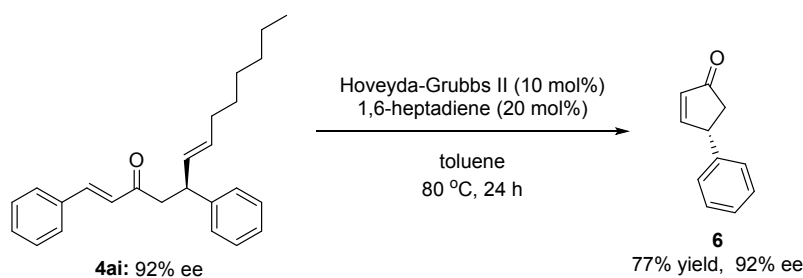


HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) t_R (1) = 5.3 min, t_R (2) = 5.7 min, t_R (3) = 6.3 min, t_R (4) = 8.5 min, d.r. = 96.4:3.6, >99% *ee*; $[\alpha]_D^{20} = -15.3$ (*c* 2.1, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 7.31-7.12 (m, 15H), 6.31-6.19 (m, 2H), 5.49-5.31 (m, 2H), 4.05 (q, *J* = 6.8 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 1H), 2.89-2.68 (m, 4H), 1.90 (q, *J* = 6.8 Hz, 2H), 1.30-1.88 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H);

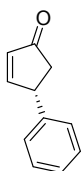
¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.2, 143.9, 143.2, 137.3, 132.6, 132.1, 131.1, 130.1, 128.8, 128.64, 128.56, 127.8, 127.6, 127.4, 126.7, 126.5, 126.4, 49.8, 49.4, 43.7, 32.6, 31.8, 29.4, 28.9, 22.7, 14.2;

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₃₃H₃₈ONa 473.2815; Found 473.2802.



Under an argon atmosphere, a 25 mL Schlenk tube equipped with a stirring bar was diene **4ai** (34.6 mg, 0.1 mmol, 92% *ee*), Hoveyda-Grubbs II catalyst (6.2 mg, 10 mol%), 1,6-heptadiene (2.7 μ L, 20 mol %), and dry toluene (2 mL) at room temperature. Then, the tube was capped, sealed and allowed to stir at 80 °C for 24 h. The reaction mixture was cooled to rt and purified by flash column chromatography on silica gel (eluent: petroleum ether/DCM = 3:1) to give cyclopentenone **5** (12.2 mg, 77% yield, 92% *ee*).

(*S*)-4-Phenyl-2-cyclopenten-1-one (**6**)⁶



HPLC (Daicel Chiralpak IF, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 220 nm) t_R (minor) = 11.1 min, t_R (major) = 11.7 min, 92% *ee*; $[\alpha]_D^{17} = -157.7$ (*c* 0.5, CHCl₃) [*lit.* $[\alpha]_D^{31} = -275$ (*c* 0.680, CHCl₃) for 87% *ee*];

^1H NMR (400 MHz, CDCl_3) δ 7.61-7.59 (m, 1H), 7.29-7.07 (m, 5H), 6.26-6.24 (m, 1H), 4.11-4.09 (m, 1H), 2.83 (dd, $J = 6.8, 18.8$ Hz, 1H), 2.26 (dd, $J = 2.4, 18.8$ Hz, 1H).

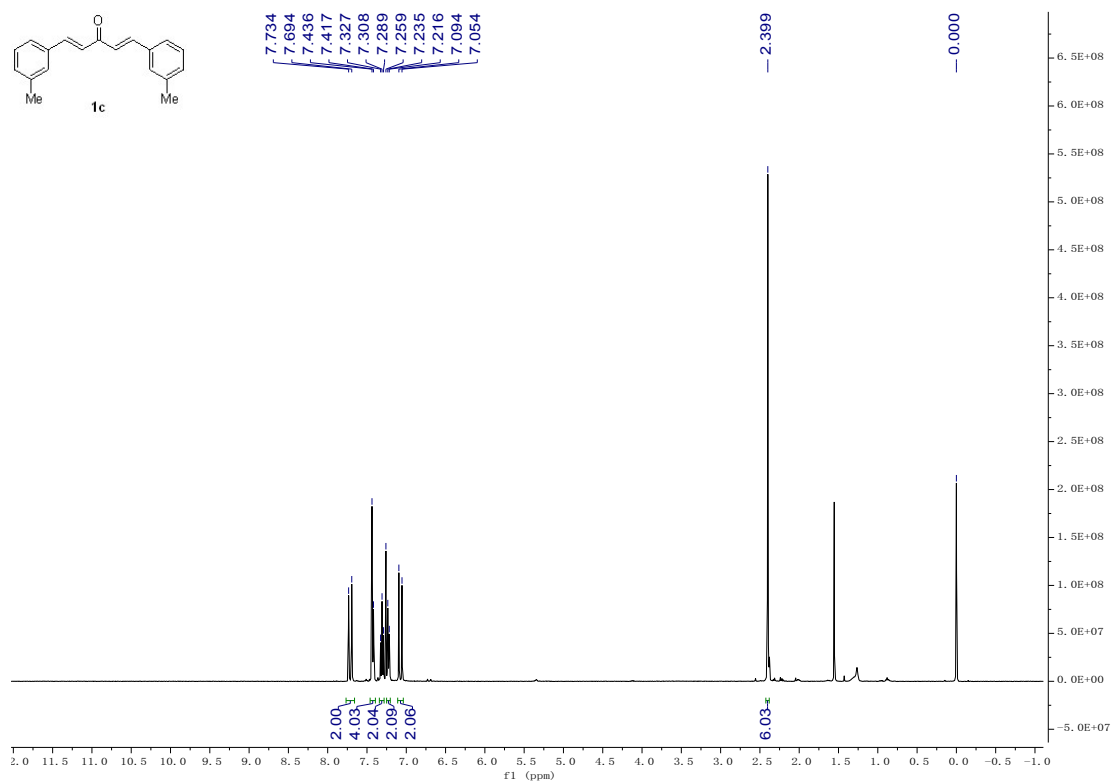
HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{10}\text{ONa}$ 181.0624; Found 181.0623.

9. References

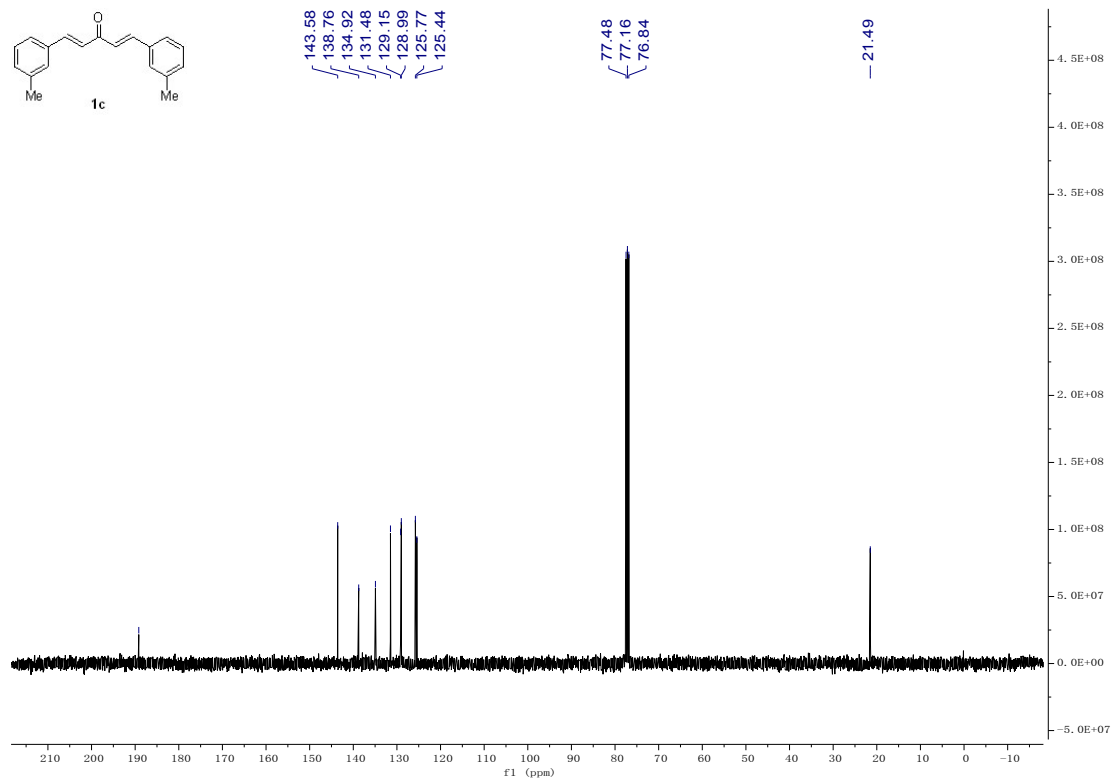
- [1] Chai, G.-L.; Han, J.-W.; Wong, H. N. C. *Synthesis* **2017**, *49*, 181–187.
- [2] Chai, G.-L.; Zhu, B.; Chang, J. *J. Org. Chem.* **2019**, *84*, 120–127.
- [3] (a) Ashtekar, K. D.; Ding, X.; Toma, E.; Sheng, W.; Gholami, H.; Rahn, C.; Reed, P.; Borhan, B. *Org. Lett.* **2016**, *18*, 3976–3979; (b) Daneshfar, Z.; Rostami, A. *RSC Adv.* **2015**, *5*, 104695–104707; (c) Aher, R. B.; Wanare, G.; Kawathekar, N.; Kumar, R. R.; Kaushik, N. K.; Sahal D.; Chauhan, V. S. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 3034–3036; (d) Horvath, K. L.; Newton, C. G.; Roper, K. A.; Ward, Jas S.; Sherburn, M. S. *Chem. Eur. J.* **2019**, *25*, 4072–4076; (e) Aguilera, E.; Varela, J.; Birriel, E.; Serna, E.; Torres, S.; Yaluff, G. *et al. ChemMedChem* **2016**, *11*, 1328–1338.
- [4] (a) Weber, M.; Frey, W.; Peters, R. *Chem. Eur. J.* **2013**, *19*, 8342–8351; (b) Mo, D.-L.; Pecak, W. H.; Zhao, M.; Wink, D. J.; Anderson, L. L. *Org. Lett.* **2014**, *16*, 3696–3699.
- [5] Ogiwara, Y.; Sakino, D.; Sakurai, Y.; Sakai, N. *Eur. J. Org. Chem.* **2017**, 4324–4327.
- [6] Sugiura, M.; Kinoshita, R.; Nakajima, M. *Org. Lett.* **2014**, *16*, 5172–5175.

10. Copies of ^1H , ^{13}C , and ^{19}F NMR spectra
(*1E,4E*)-1,5-di-*m*-tolylpenta-1,4-dien-3-one (**1c**)

^1H NMR (400 MHz, CDCl_3)

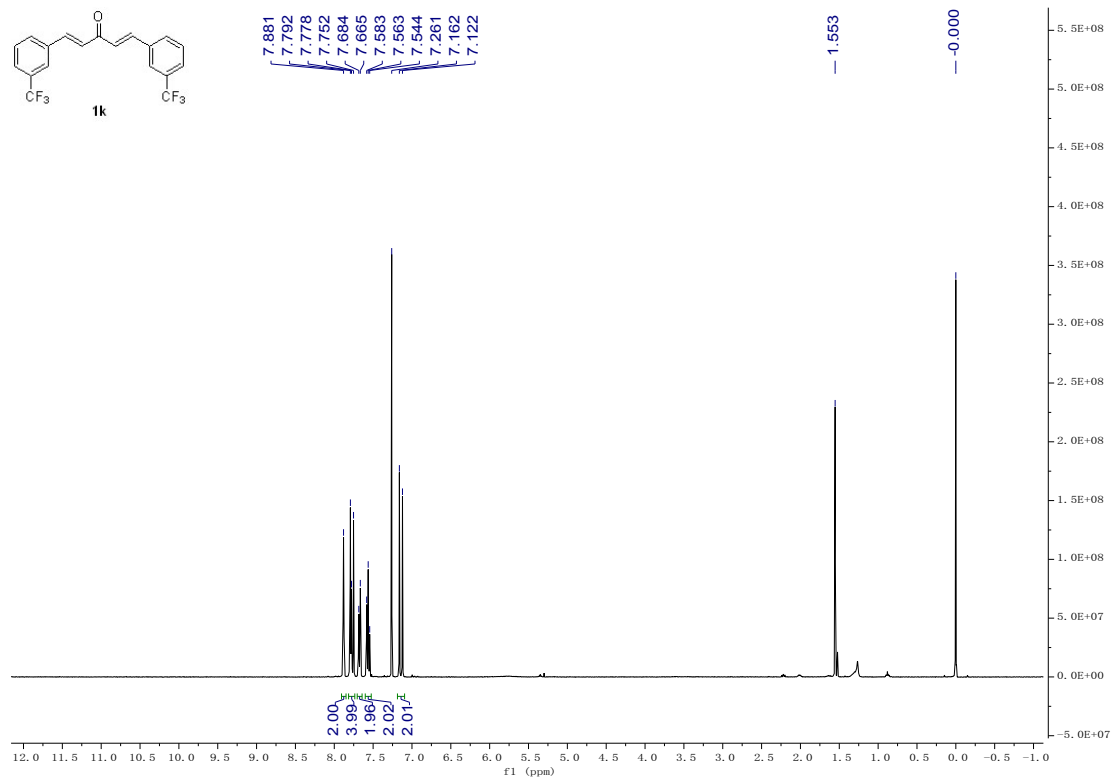


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

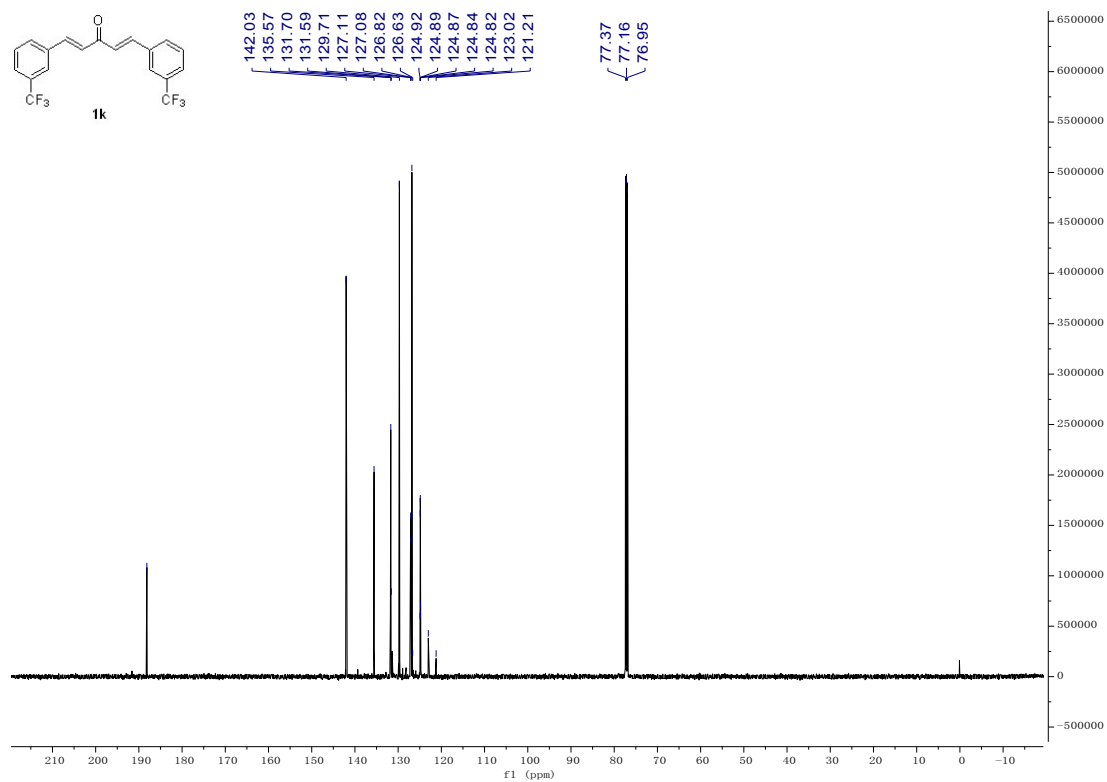


(1E,4E)-1,5-bis(3-(trifluoromethyl)phenyl)penta-1,4-dien-3-one (**1k**)

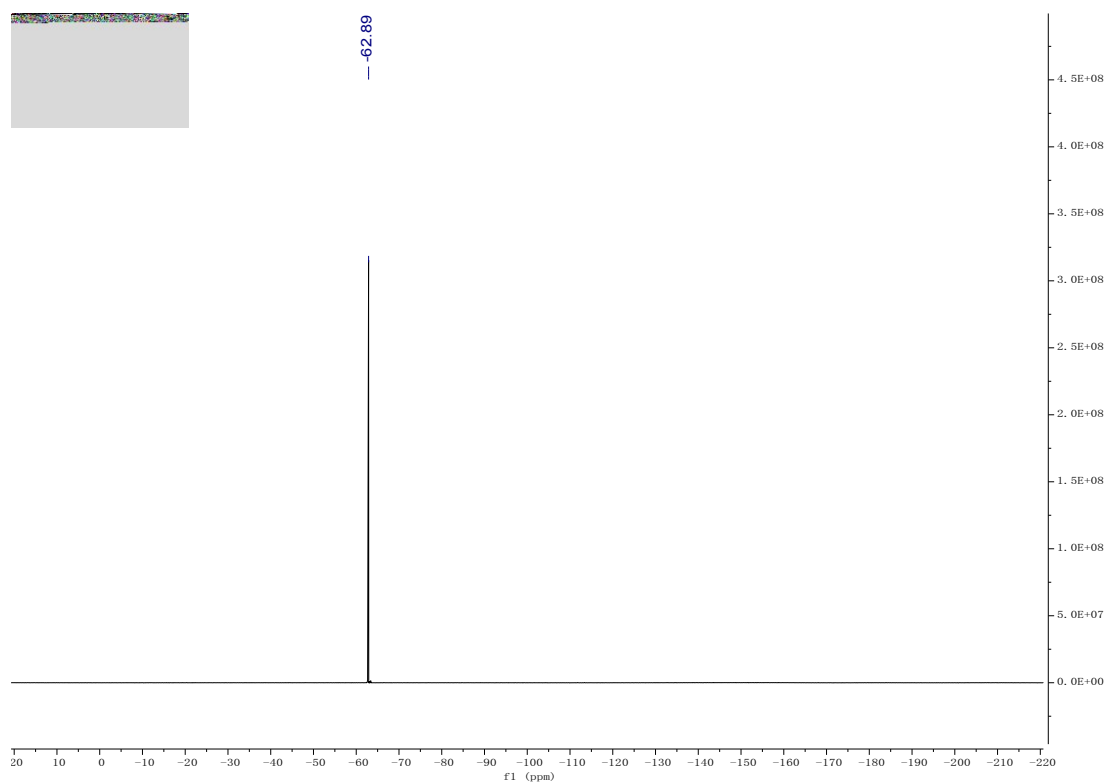
¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (150 MHz, CDCl₃)

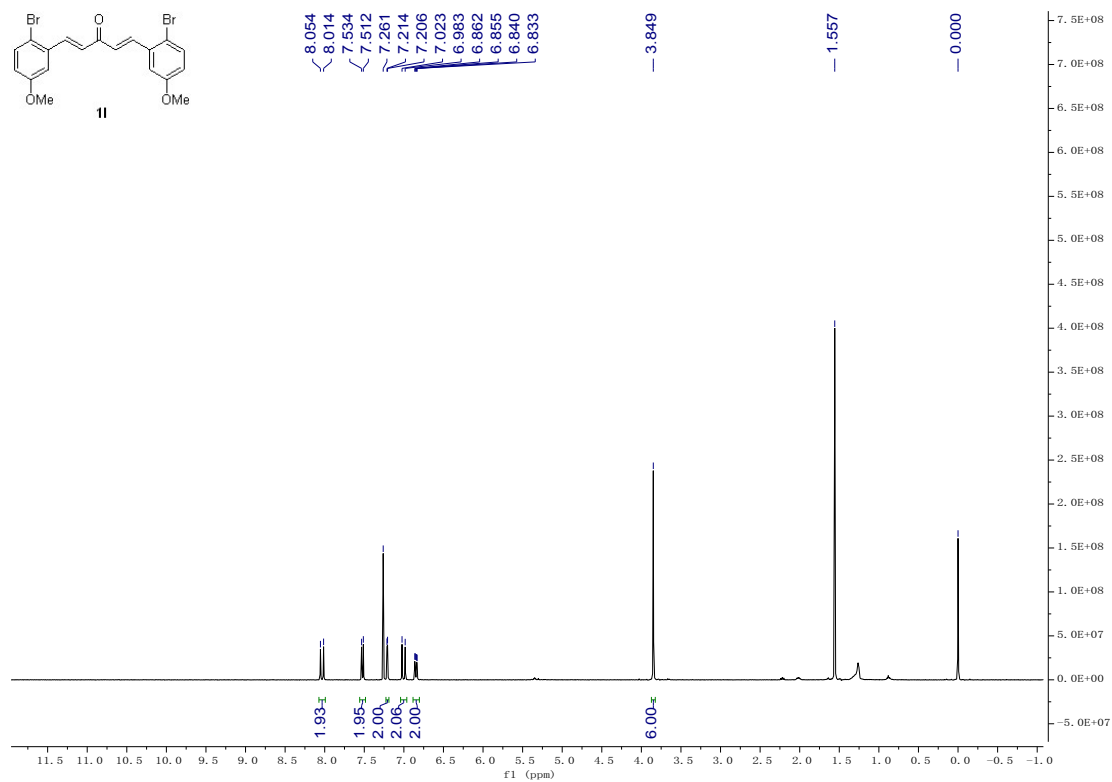


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

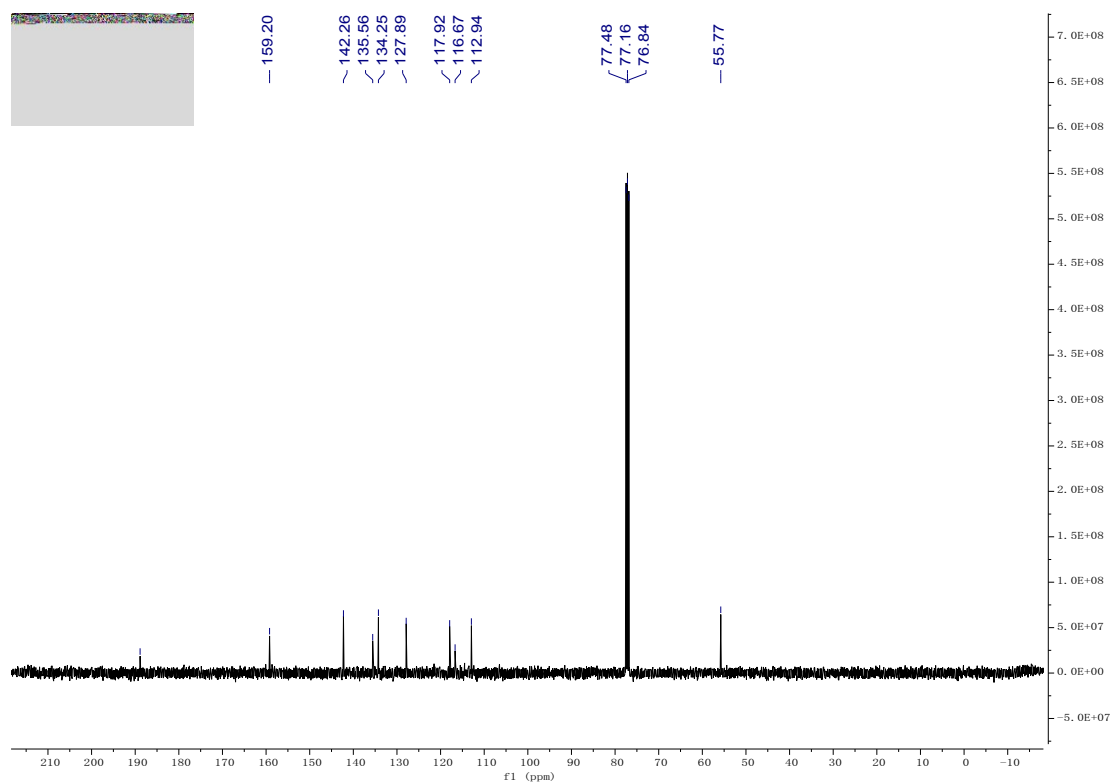


(1E,4E)-1,5-bis(2-bromo-5-methoxyphenyl)penta-1,4-dien-3-one (**11**)

^1H NMR (400 MHz, CDCl_3)

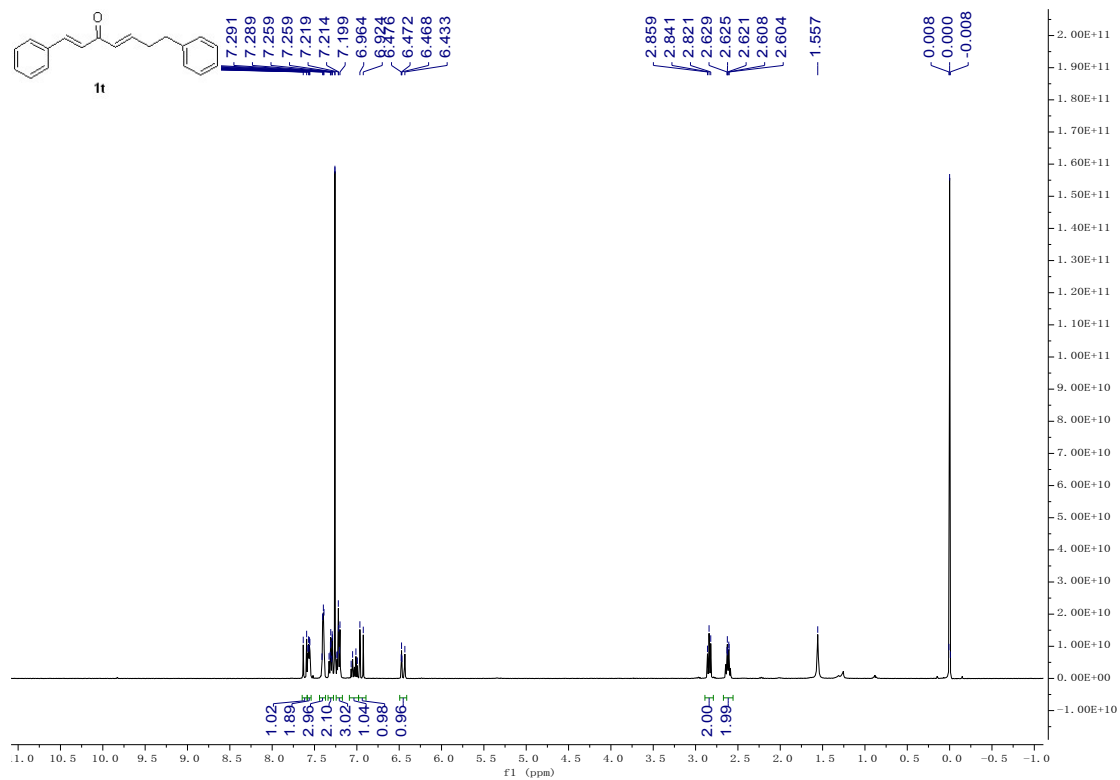


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

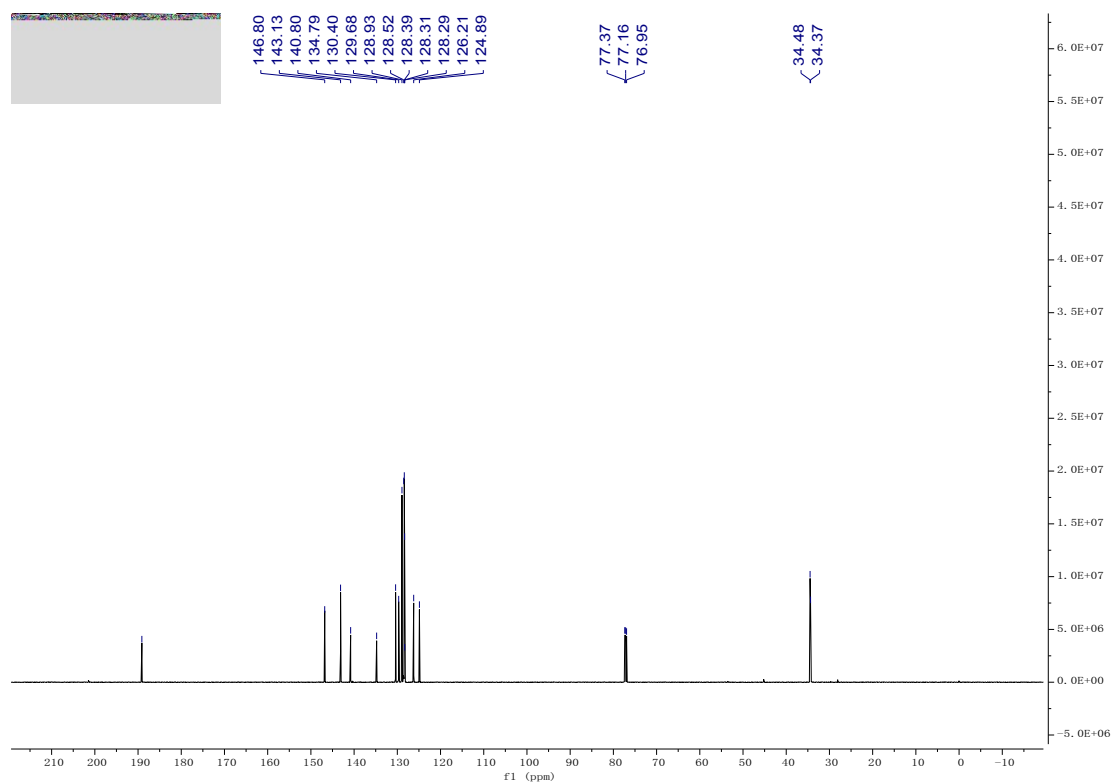


(1E,4E)-1,7-diphenylhepta-1,4-dien-3-one (**1t**)

^1H NMR (400 MHz, CDCl_3)

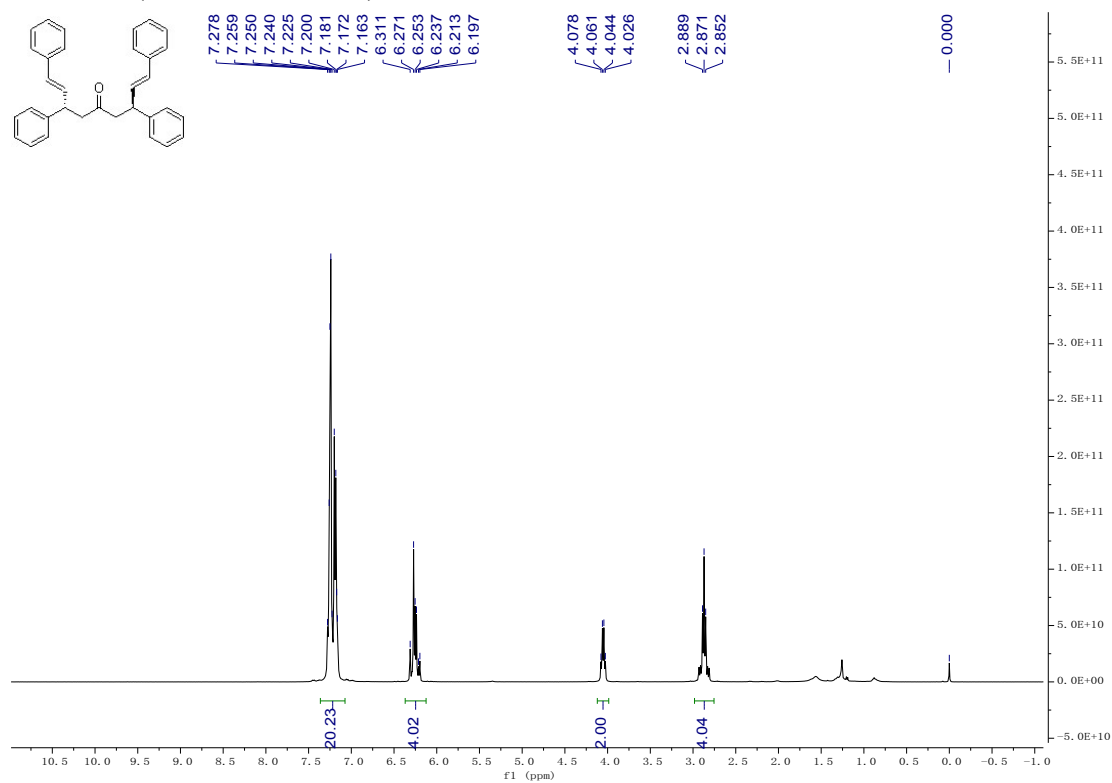


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

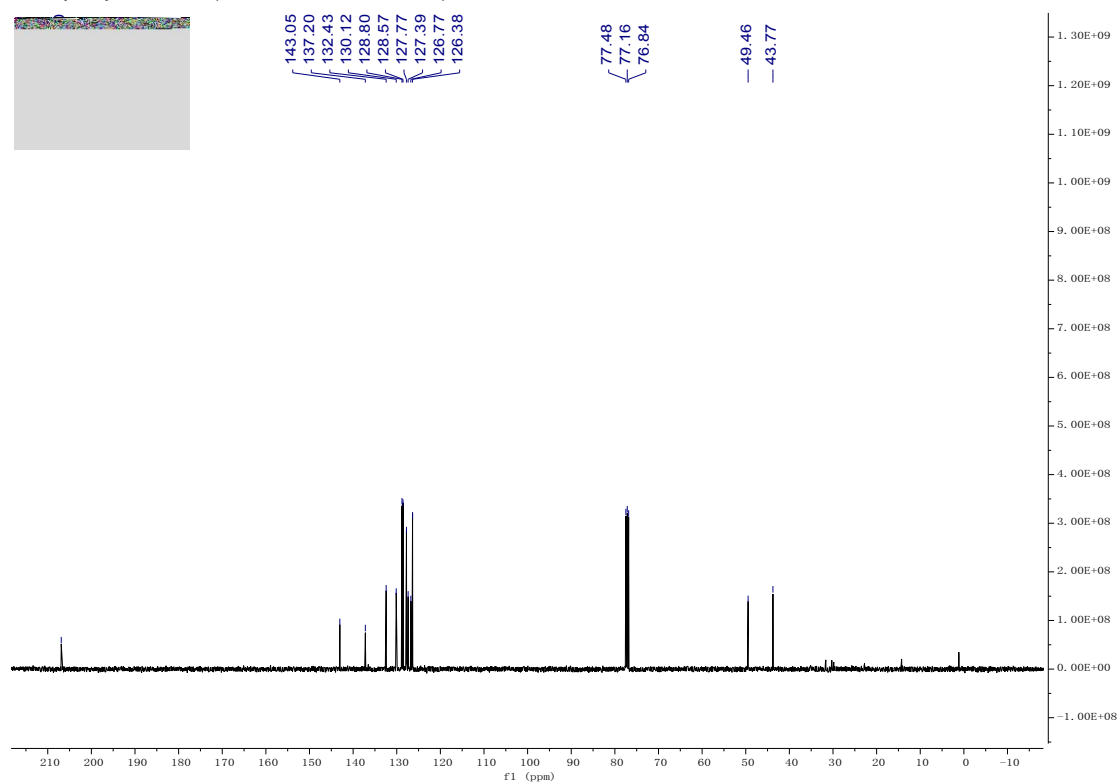


(1E,3S,7S,8E)-1,3,7,9-tetraphenylnona-1,8-dien-5-one (**3aa**)

^1H NMR (400 MHz, CDCl_3)

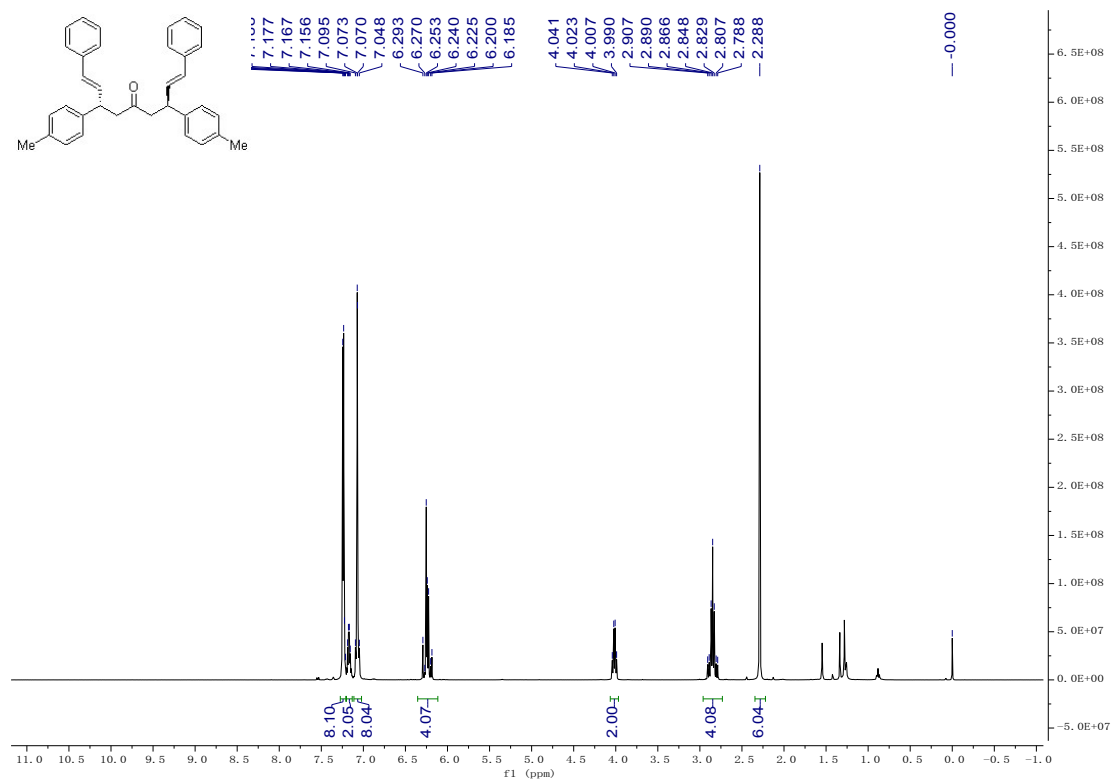


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

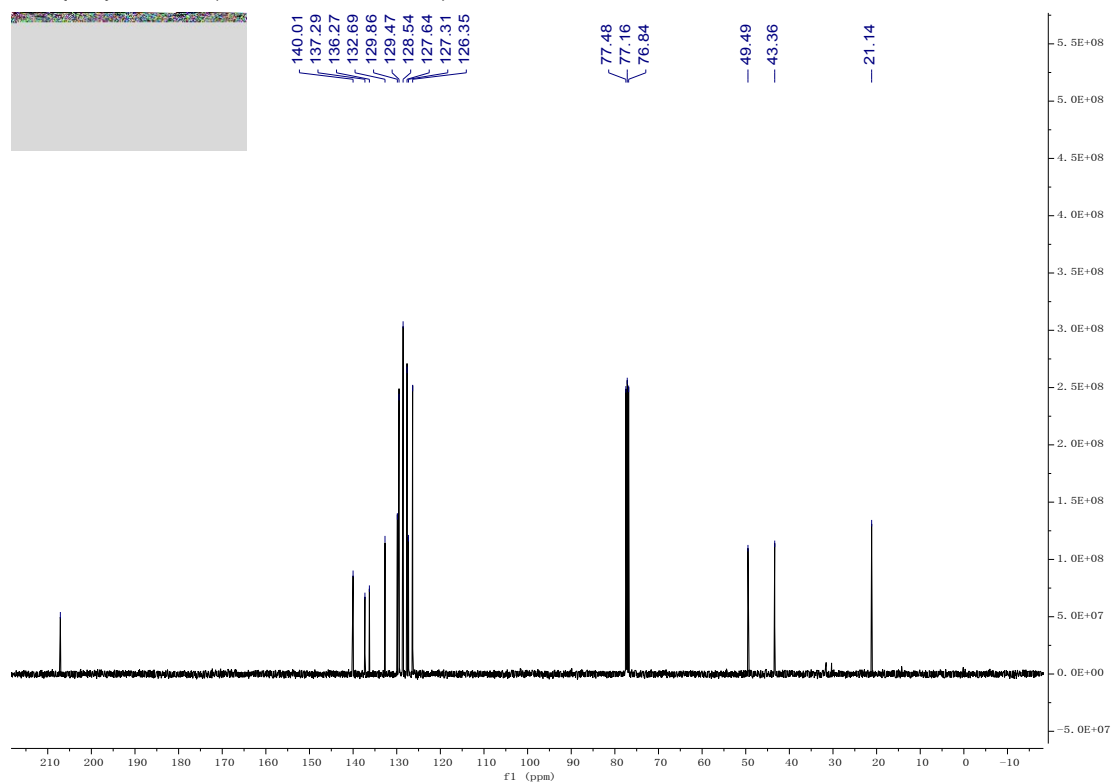


(1*E*,3*S*,7*S*,8*E*)-1,9-diphenyl-3,7-di-*p*-tolylnona-1,8-dien-5-one (**3ba**)

^1H NMR (400 MHz, CDCl_3)

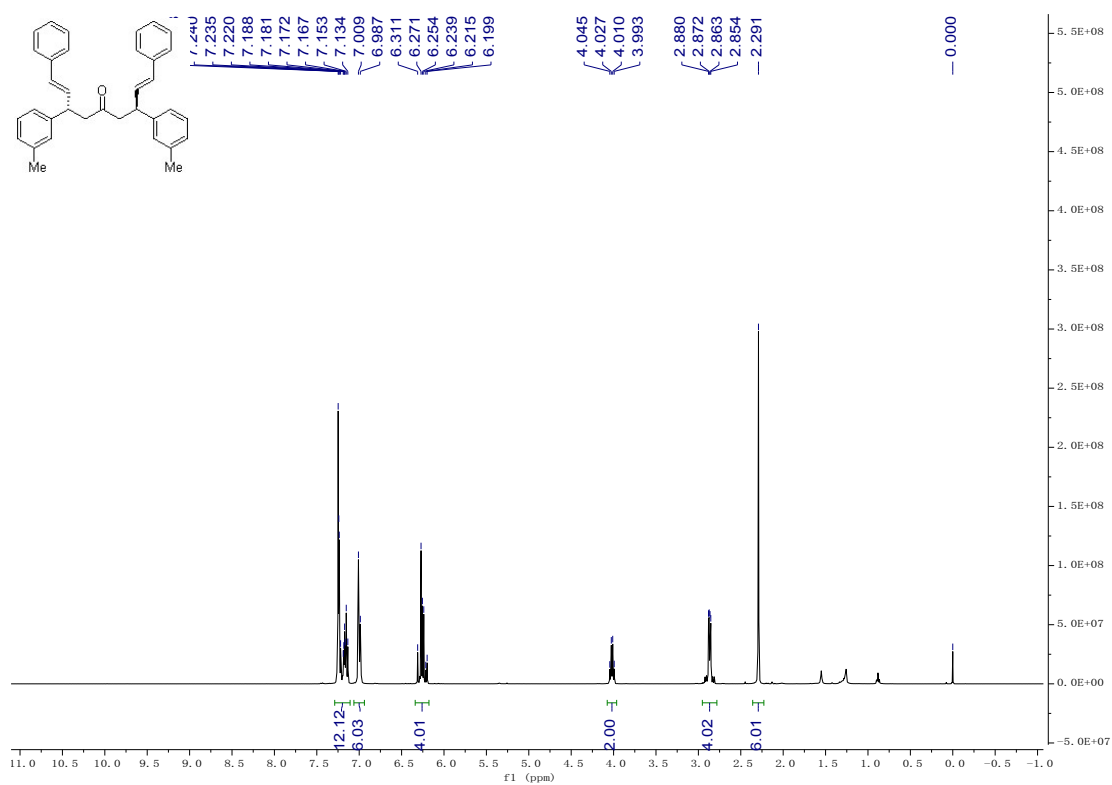


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

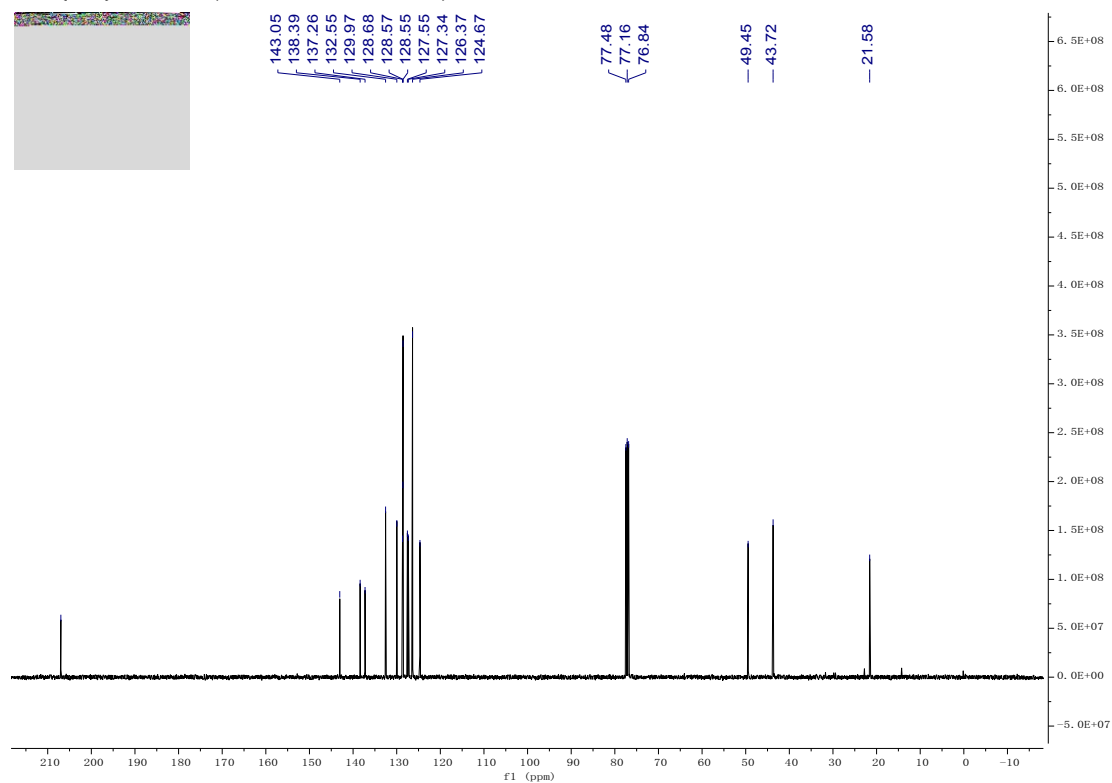


$(1E,3S,7S,8E)$ -1,9-diphenyl-3,7-di-*m*-tolylnona-1,8-dien-5-one (3ca)

^1H NMR (400 MHz, CDCl_3)

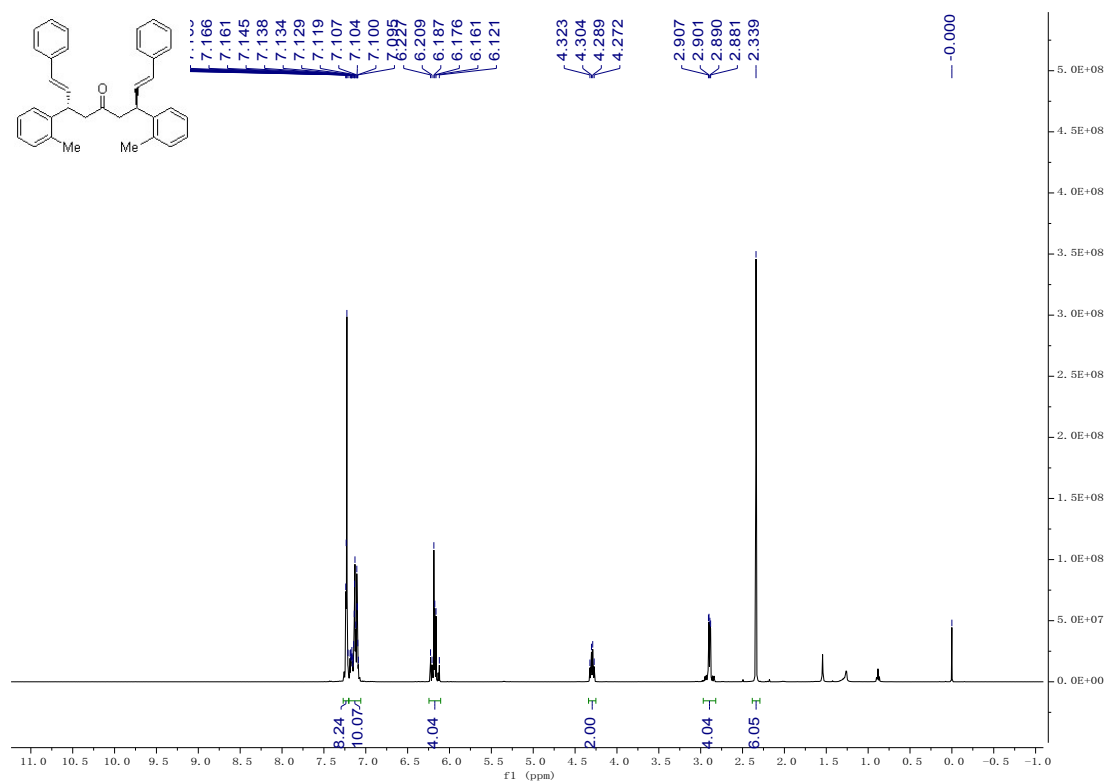


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

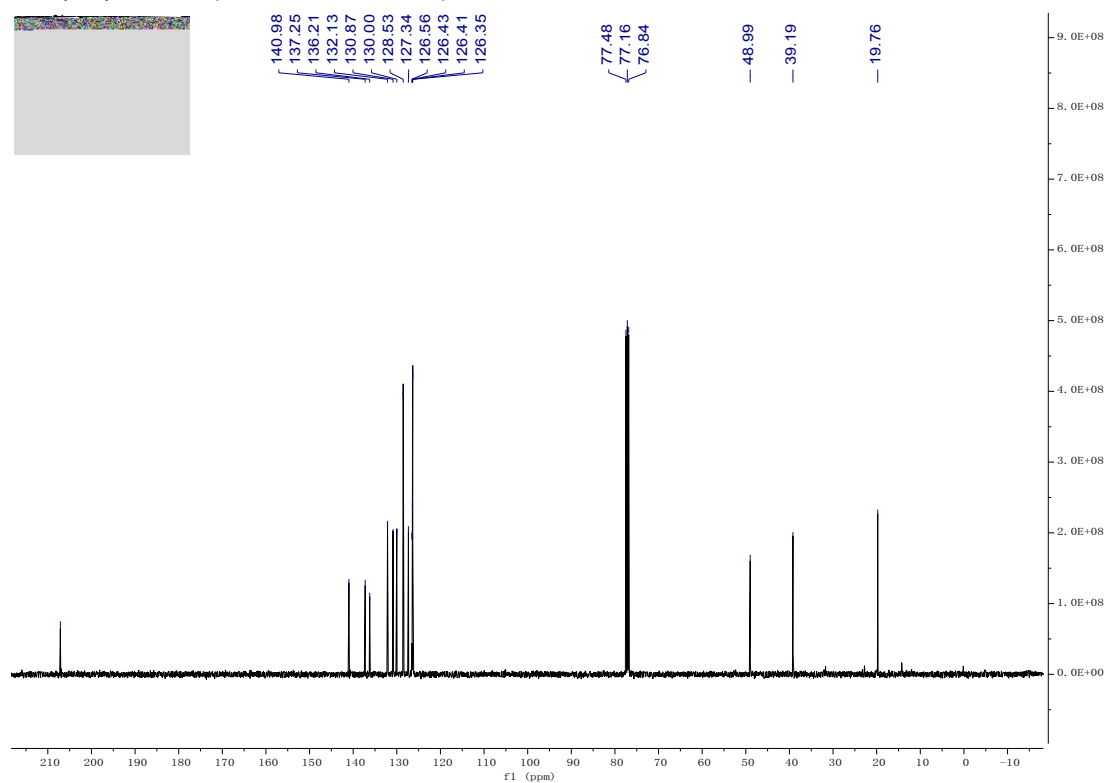


(1E,3S,7S,8E)-1,9-diphenyl-3,7-di-*o*-tolylnona-1,8-dien-5-one (**3da**)

^1H NMR (400 MHz, CDCl_3)

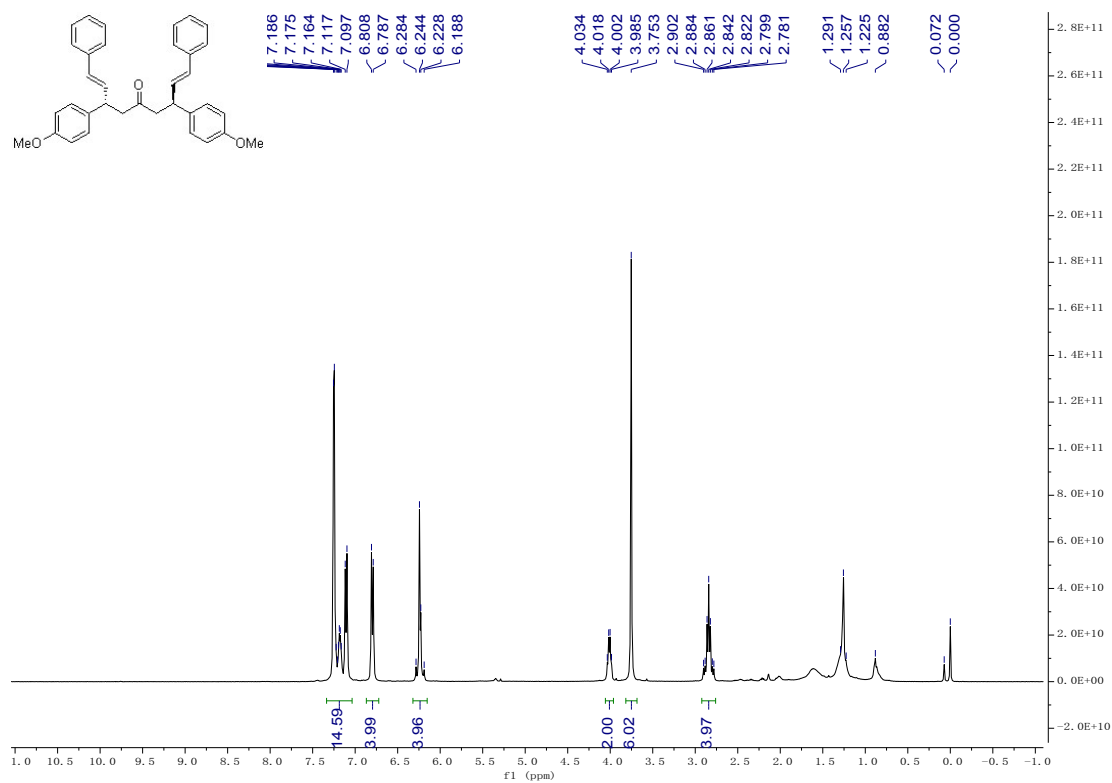


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

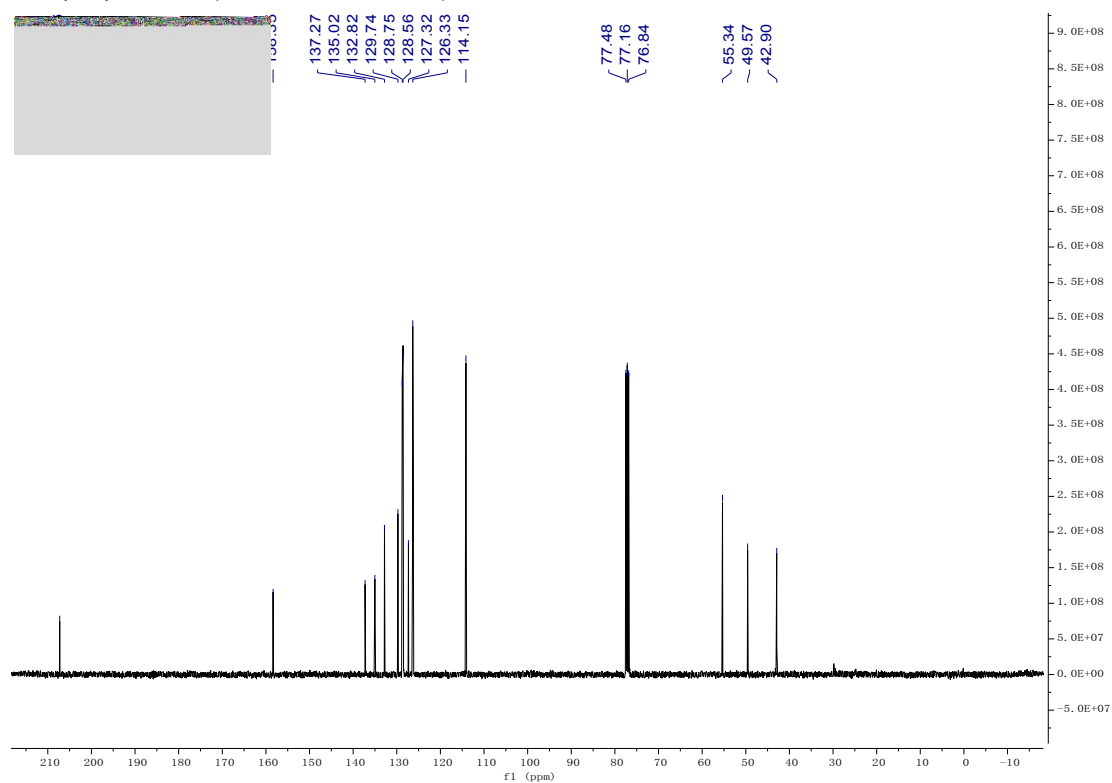


$(1E,3S,7S,8E)$ -3,7-bis(4-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one (3ea)

^1H NMR (400 MHz, CDCl_3)

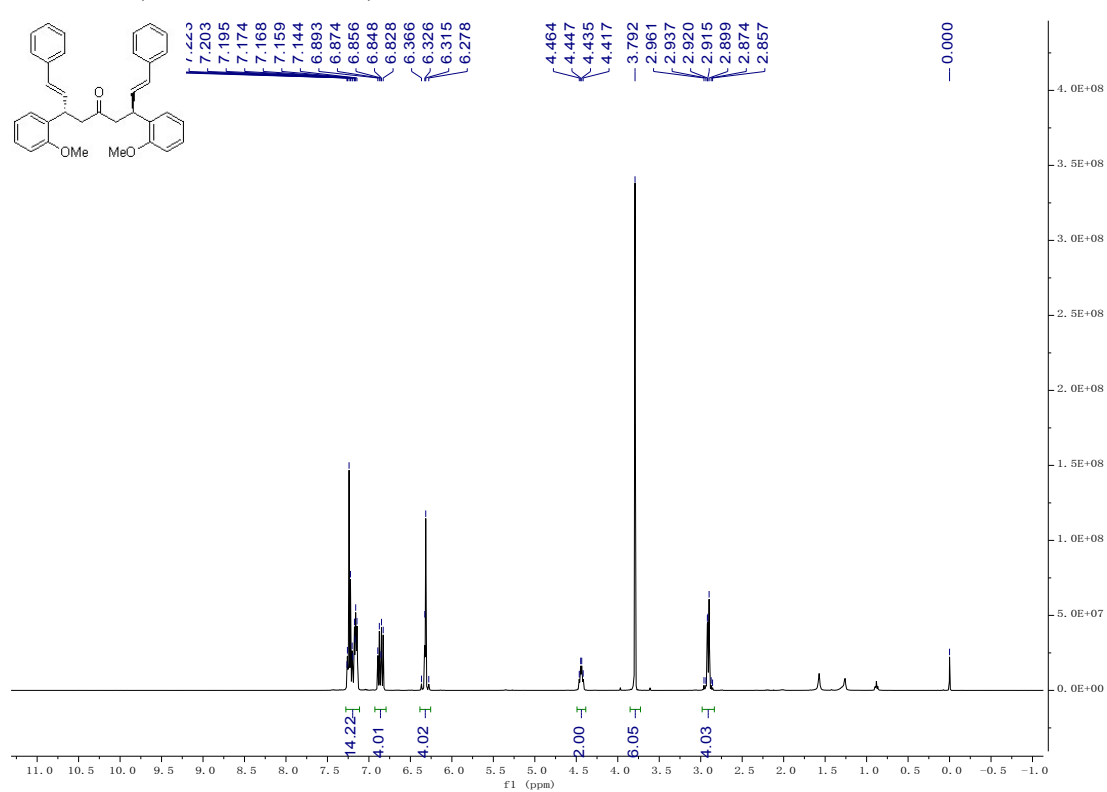


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

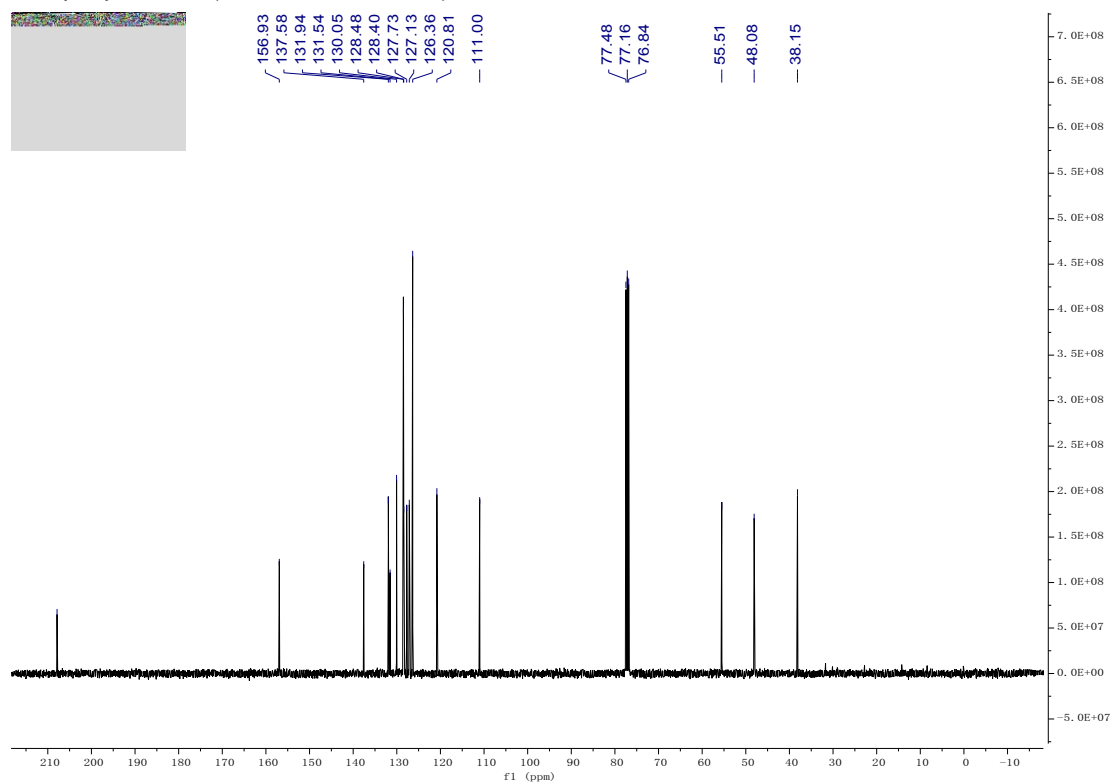


(1E,3S,7S,8E)-3,7-bis(2-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one (3fa)

^1H NMR (400 MHz, CDCl_3)

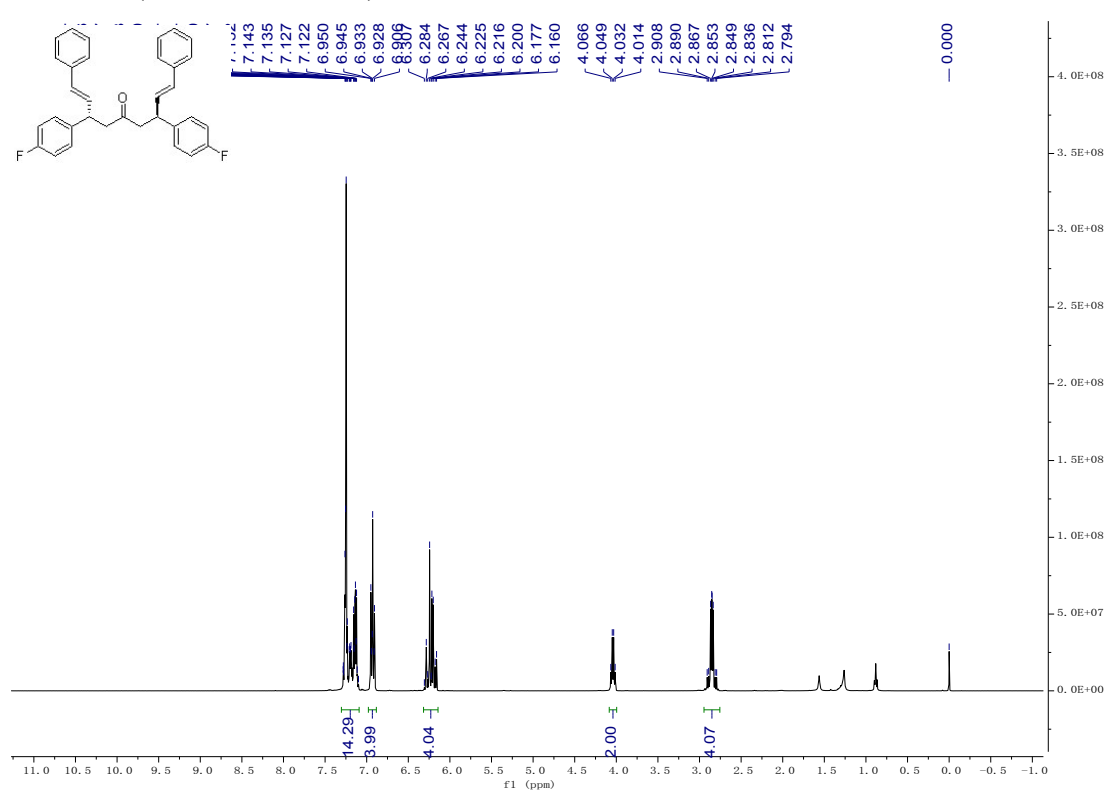


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

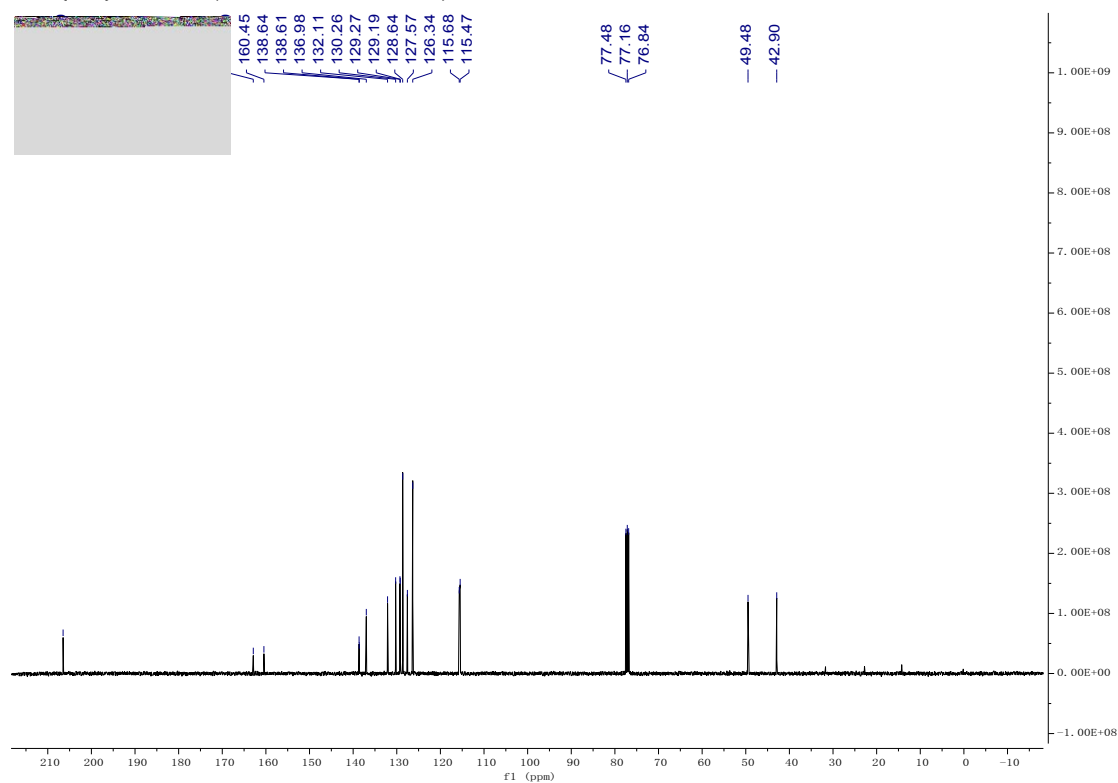


(1*E*,3*S*,7*S*,8*E*)-3,7-bis(4-fluorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ga**)

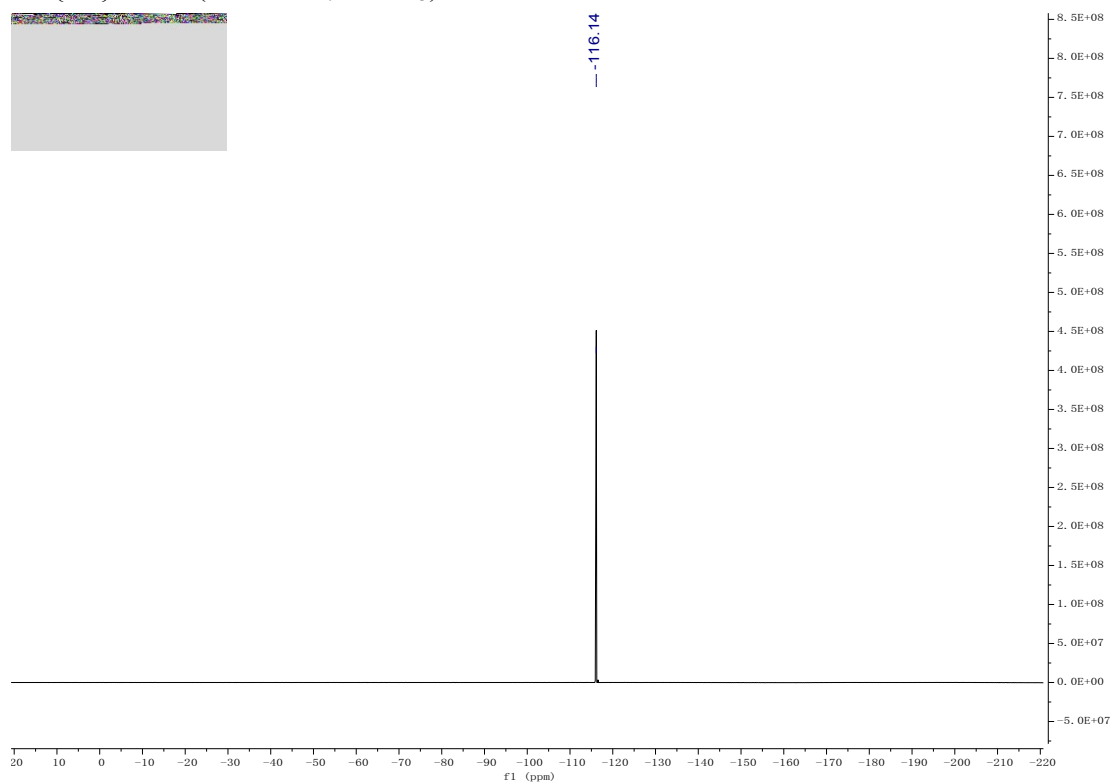
^1H NMR (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

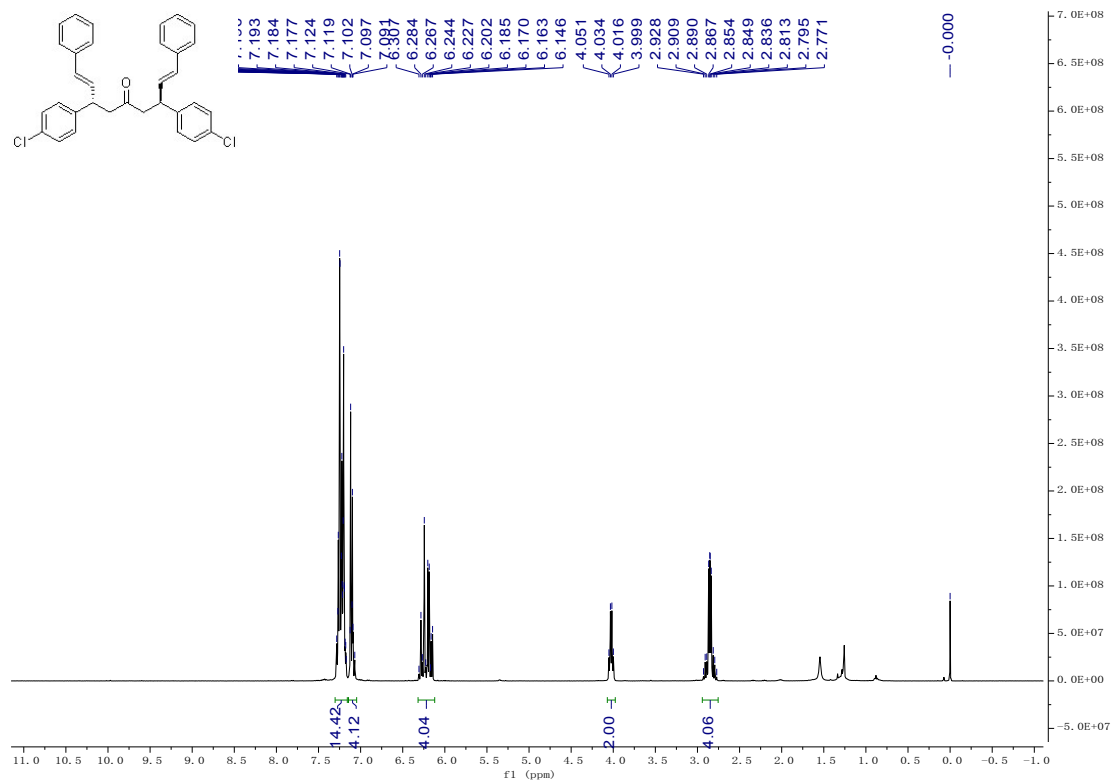


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

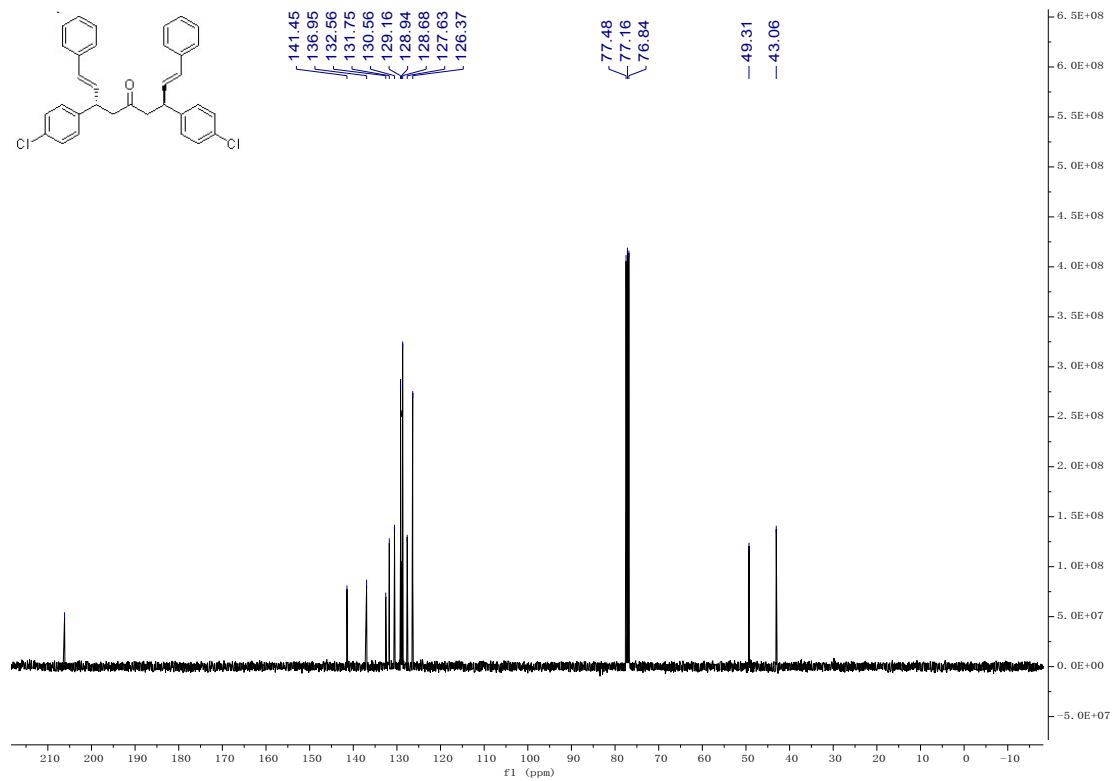


(1E,3S,7S,8E)-3,7-bis(4-chlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (3ha)

¹H NMR (600 MHz, CDCl₃)

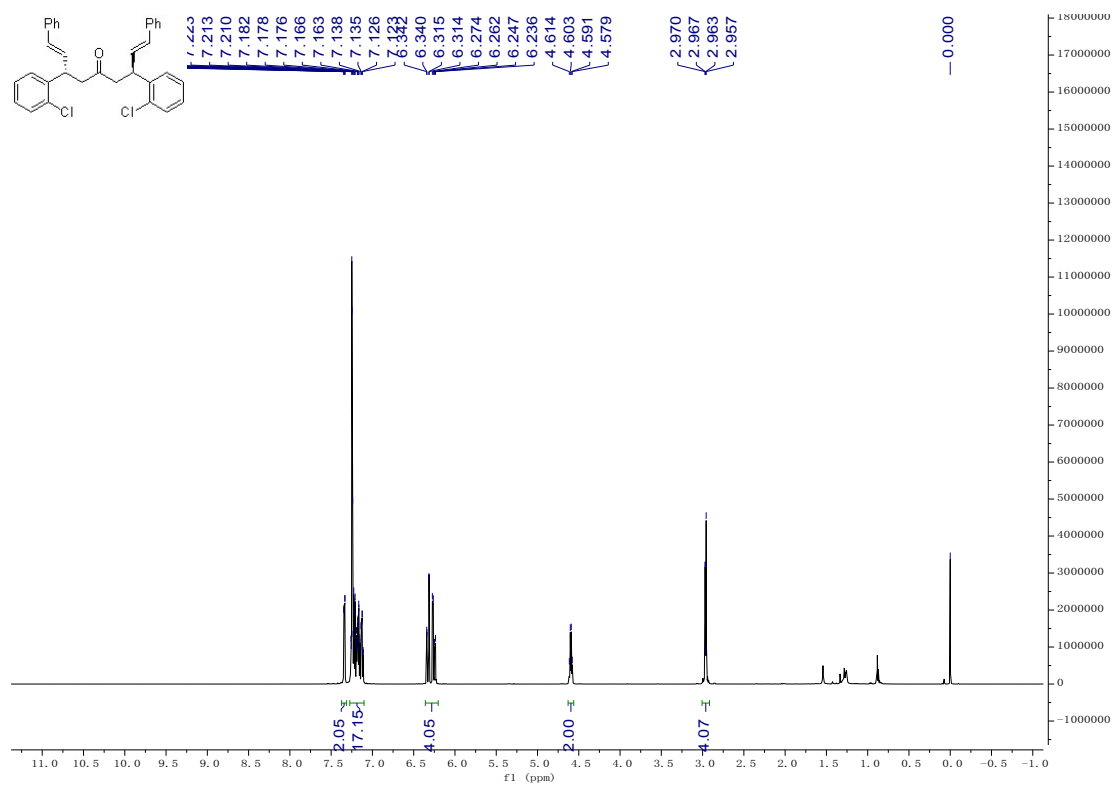


¹³C {¹H} NMR (150 MHz, CDCl₃)

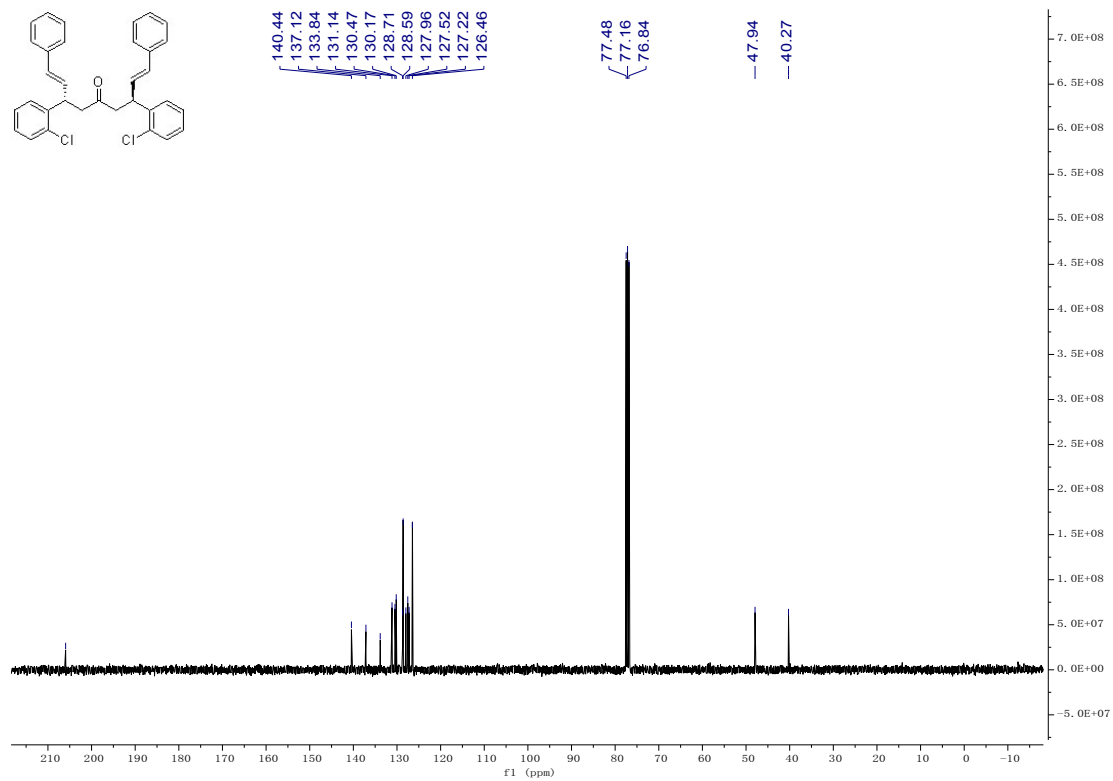


(1*E*,3*S*,7*S*,8*E*)-3,7-bis(2-chlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ia**)

^1H NMR (600 MHz, CDCl_3)

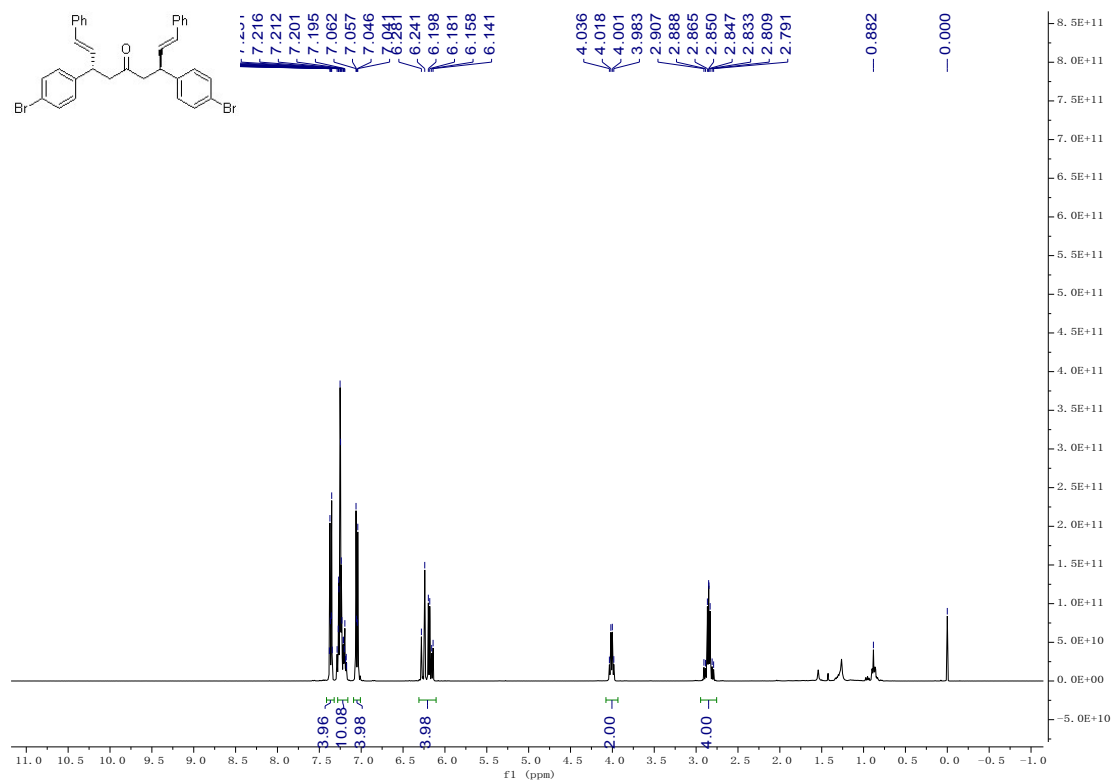


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

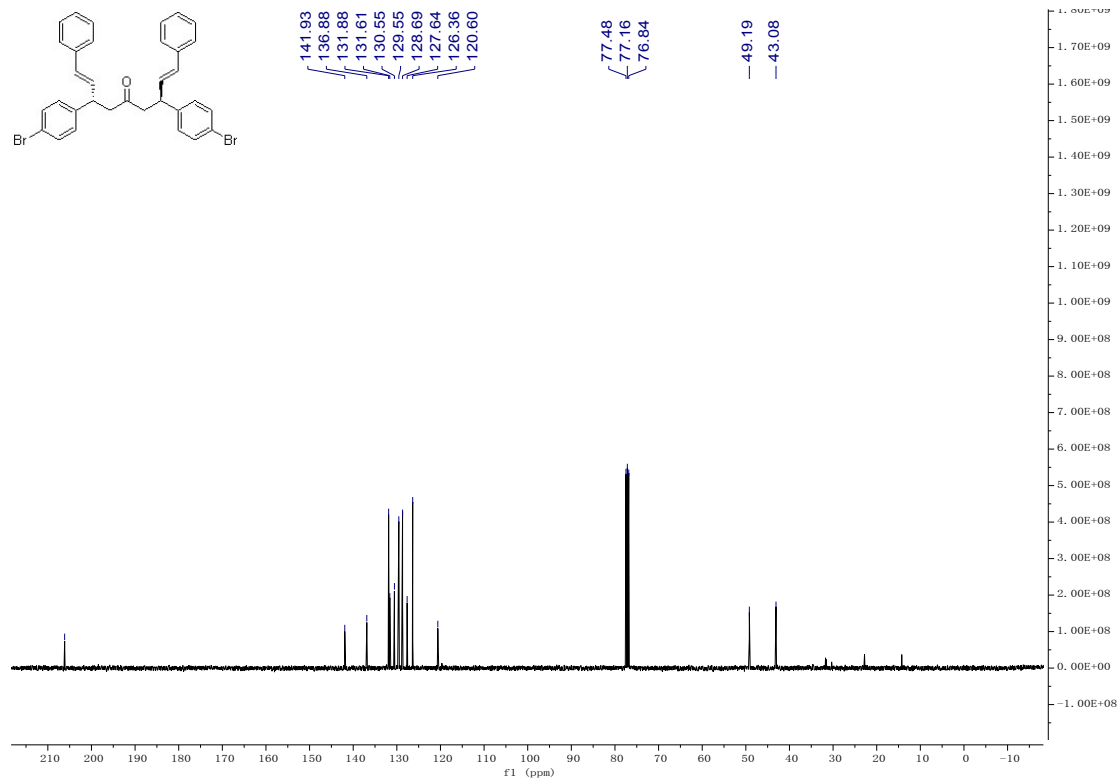


(1E,3S,7S,8E)-3,7-bis(4-bromophenyl)-1,9-diphenylnona-1,8-dien-5-one (**3ja**)

¹H NMR (400 MHz, CDCl₃)



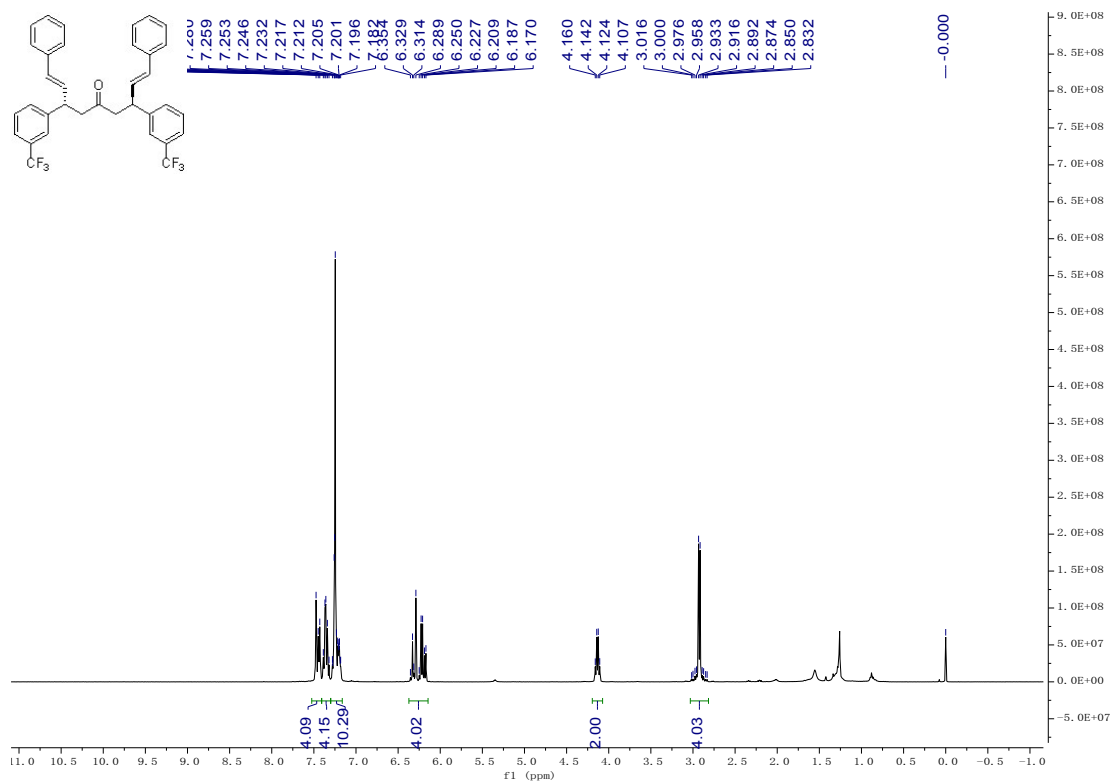
¹³C {¹H} NMR (100 MHz, CDCl₃) (n-hexane: 14.1, 22.7, 31.6.)



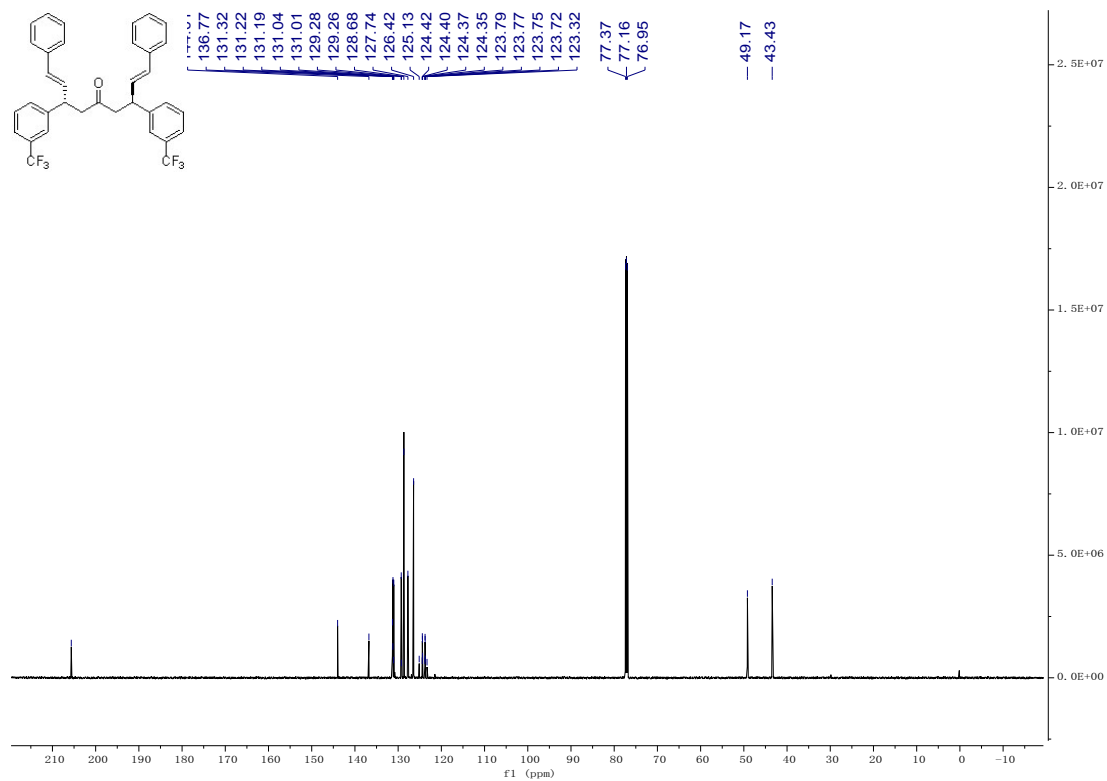
(1E,3S,7S,8E)-1,9-diphenyl-3,7-bis(3-(trifluoromethyl)phenyl)nona-1,8-dien-5-one

(3ka)

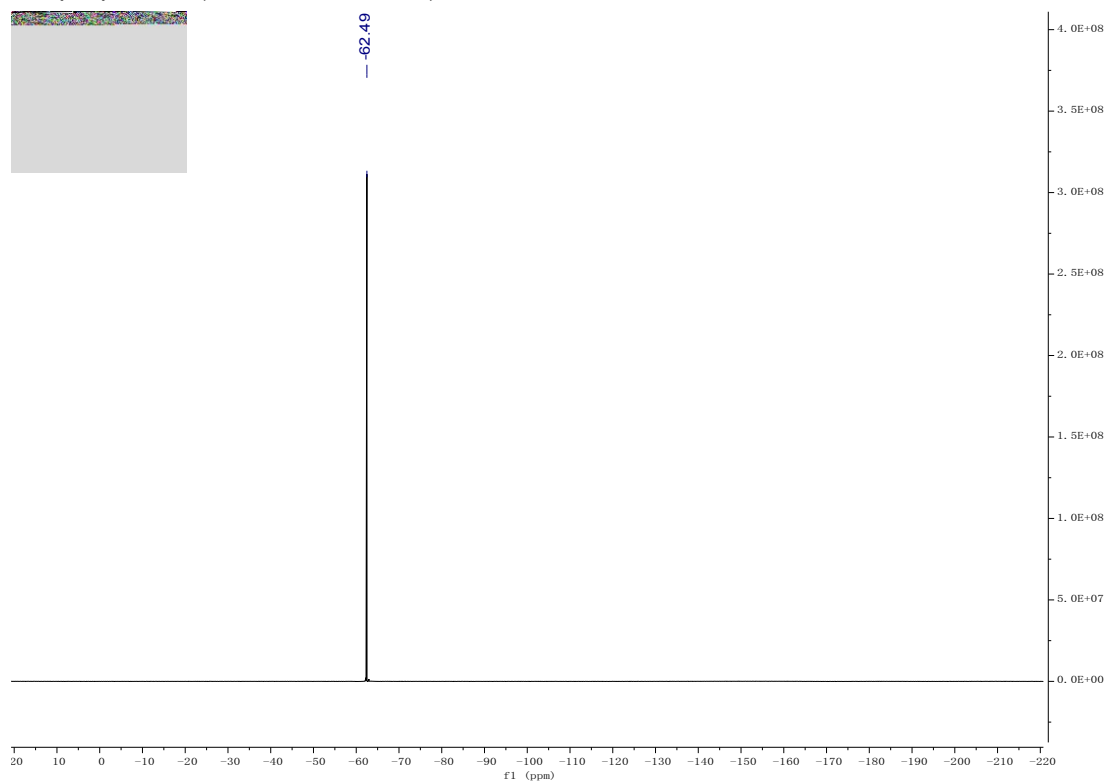
¹H NMR (600 MHz, CDCl₃)



¹³C {¹H} NMR (150 MHz, CDCl₃)

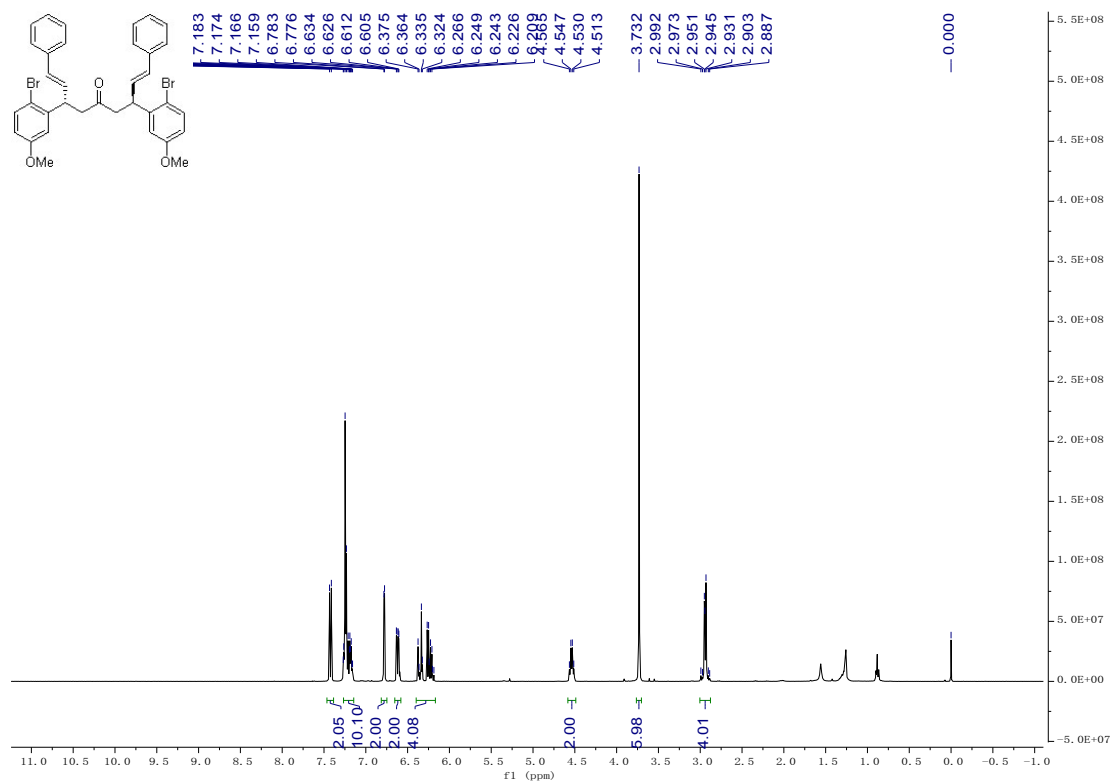


$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3)

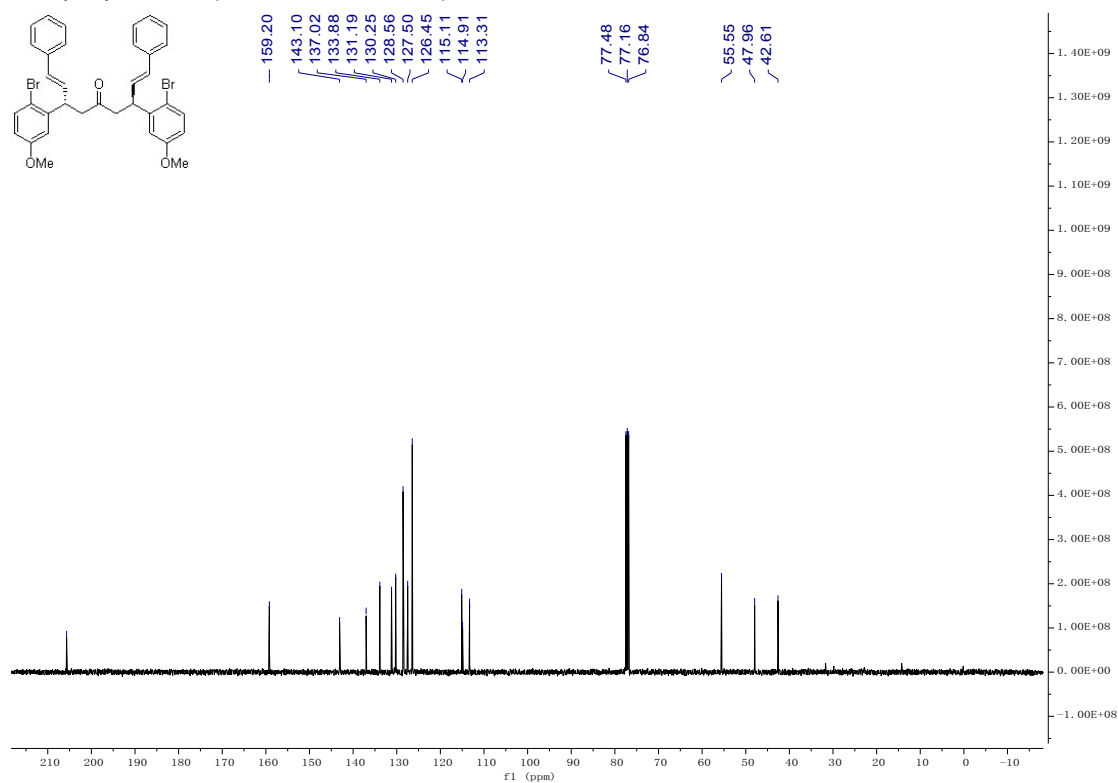


(1E,3S,7S,8E)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-diphenylnona-1,8-dien-5-one
(3la)

^1H NMR (600 MHz, CDCl_3)

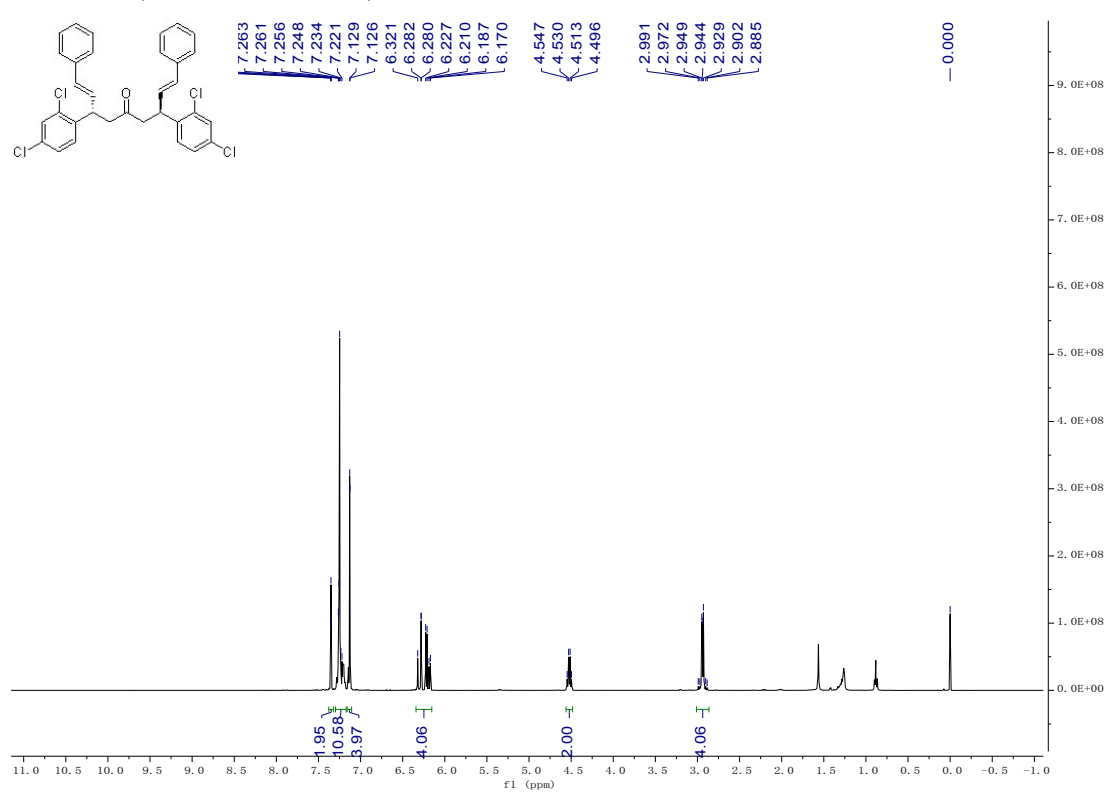


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

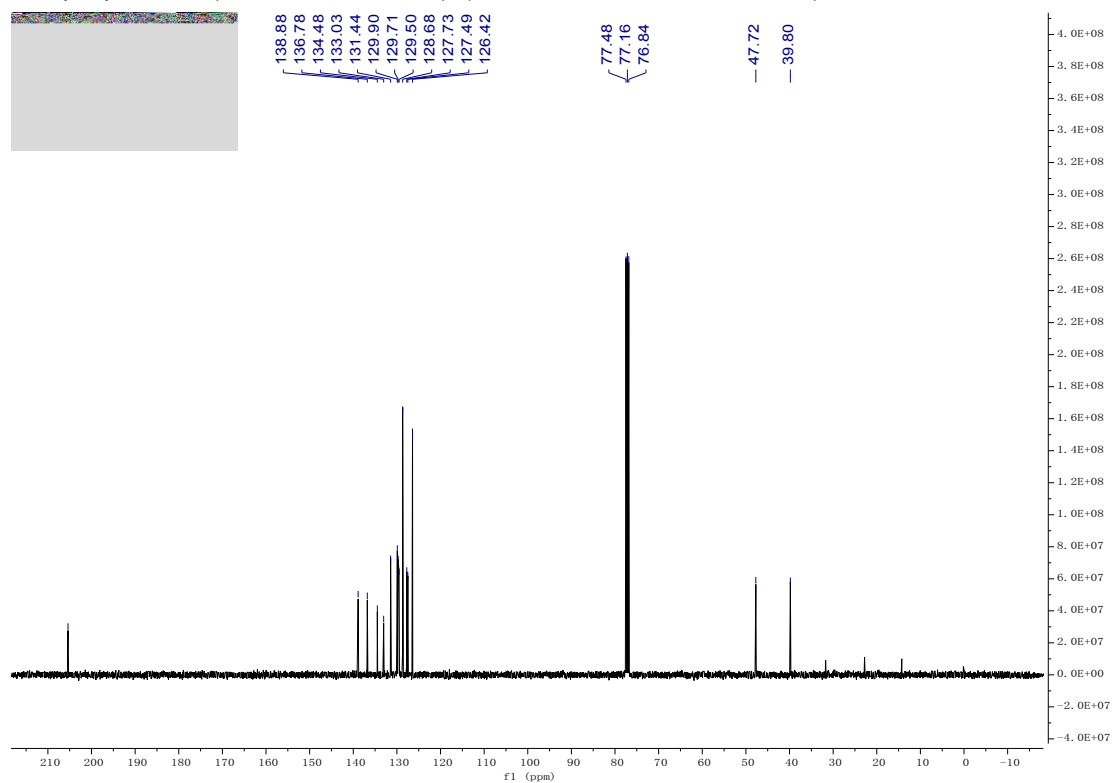


(1E,3S,7S,8E)-3,7-bis(2,4-dichlorophenyl)-1,9-diphenylnona-1,8-dien-5-one (3ma)

^1H NMR (400 MHz, CDCl_3)

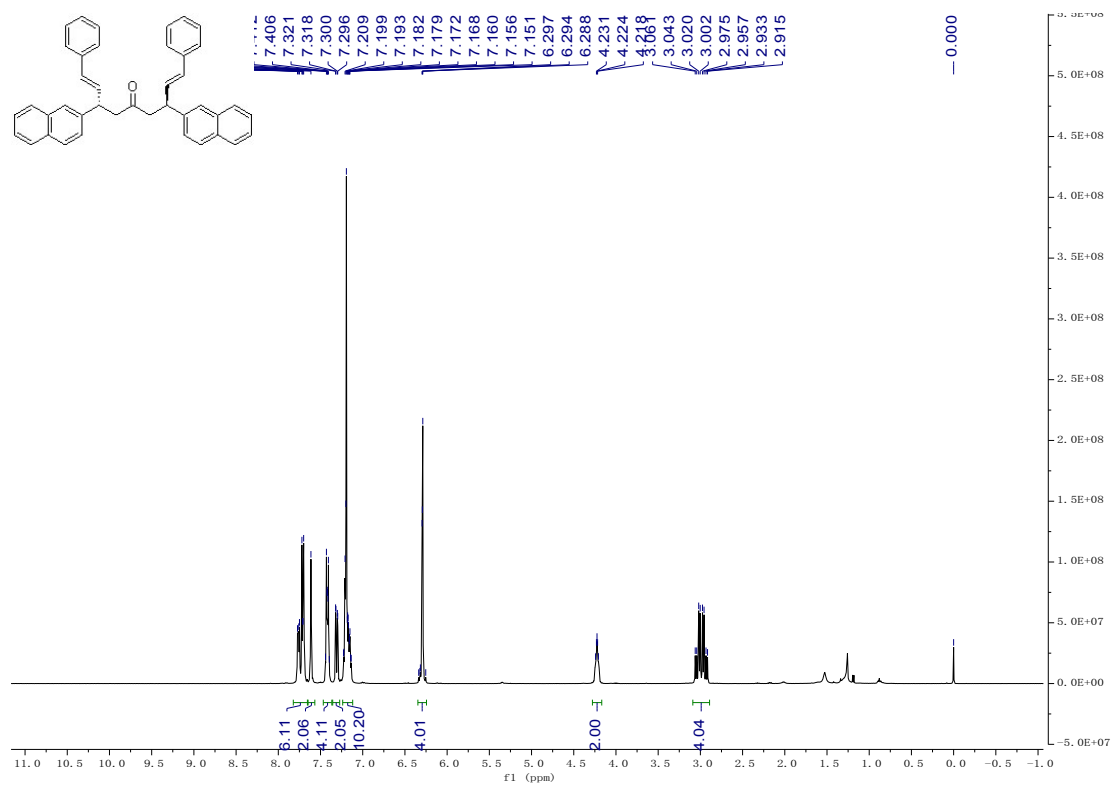


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) (n-hexane: 14.1, 22.7, 31.6.)

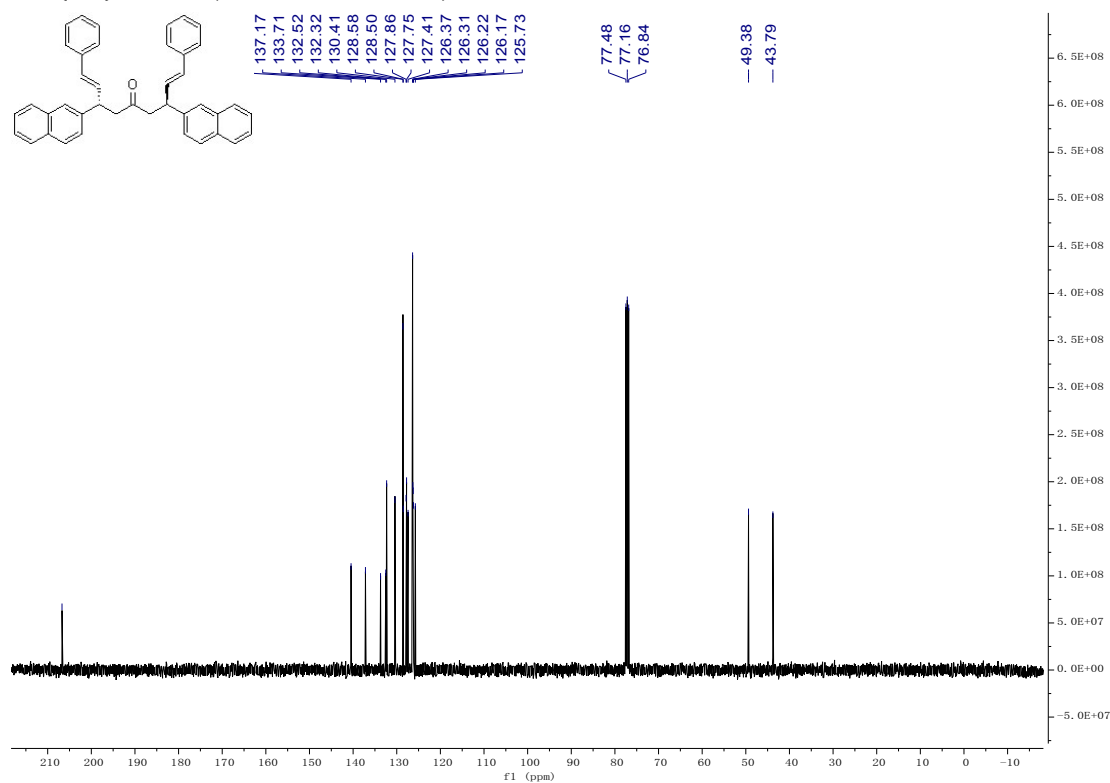


(1*E*,3*S*,7*S*,8*E*)-3,7-di(naphthalen-2-yl)-1,9-diphenylnona-1,8-dien-5-one (**3na**)

^1H NMR (600 MHz, CDCl_3)

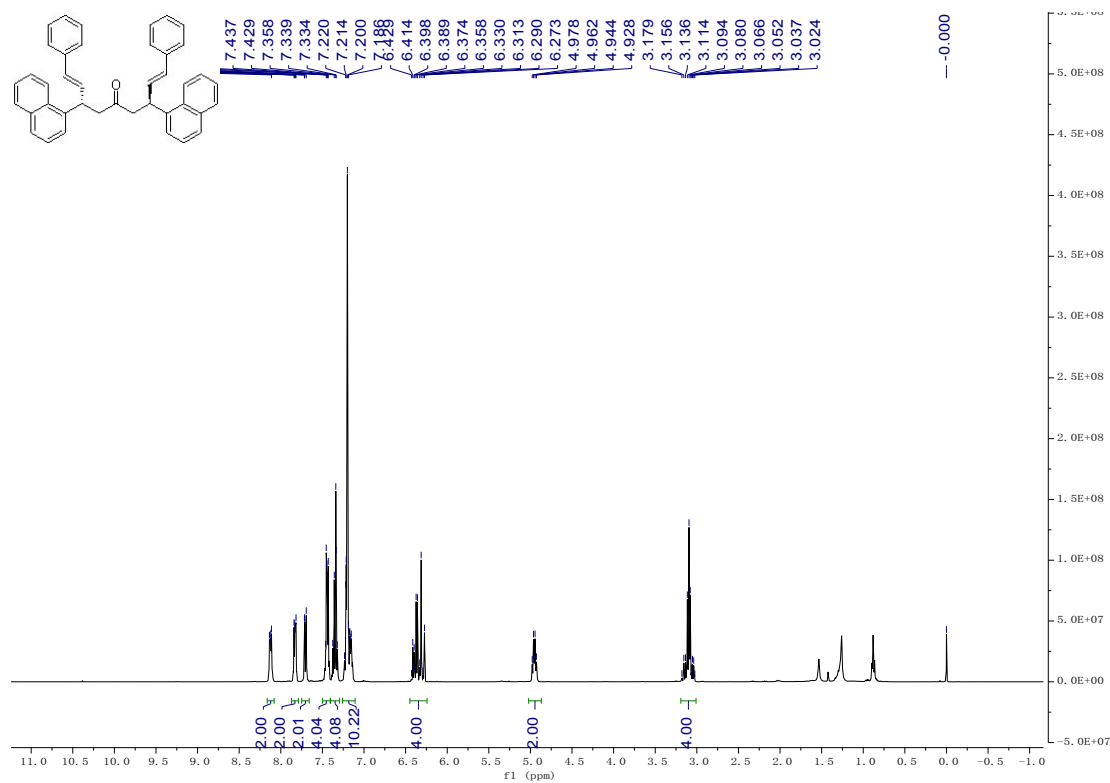


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

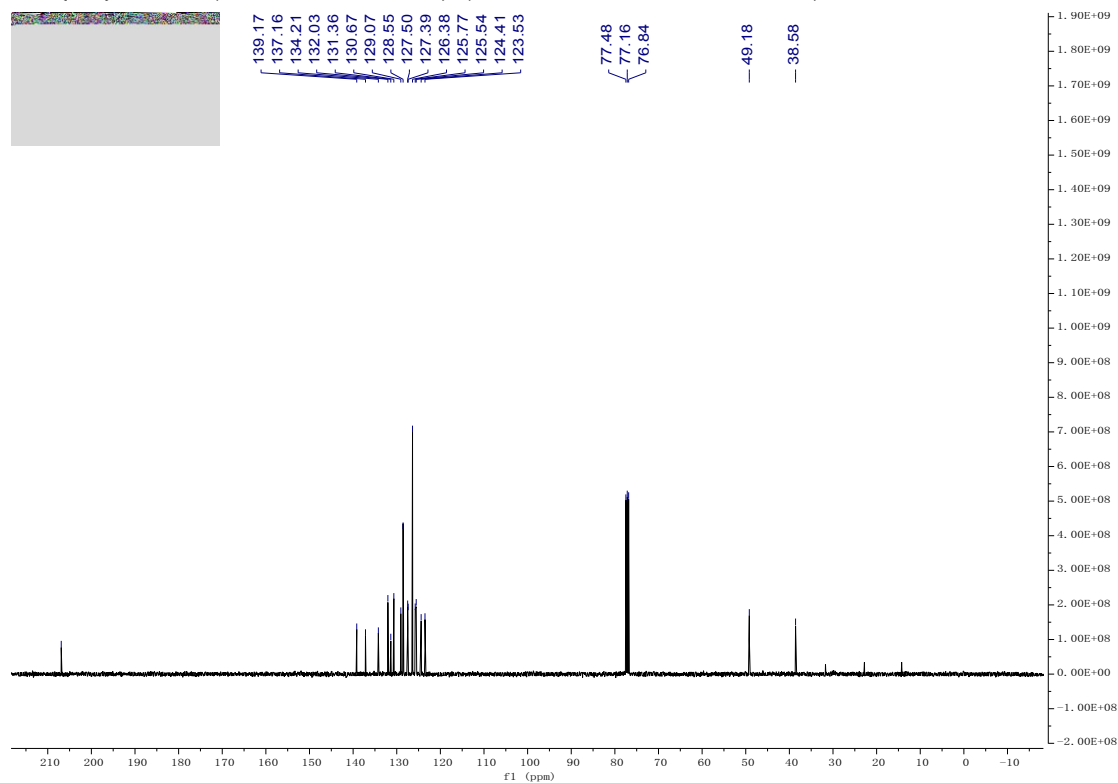


(1E,3S,7S,8E)-3,7-di(naphthalen-1-yl)-1,9-diphenylnona-1,8-dien-5-one (30a)

^1H NMR (400 MHz, CDCl_3)

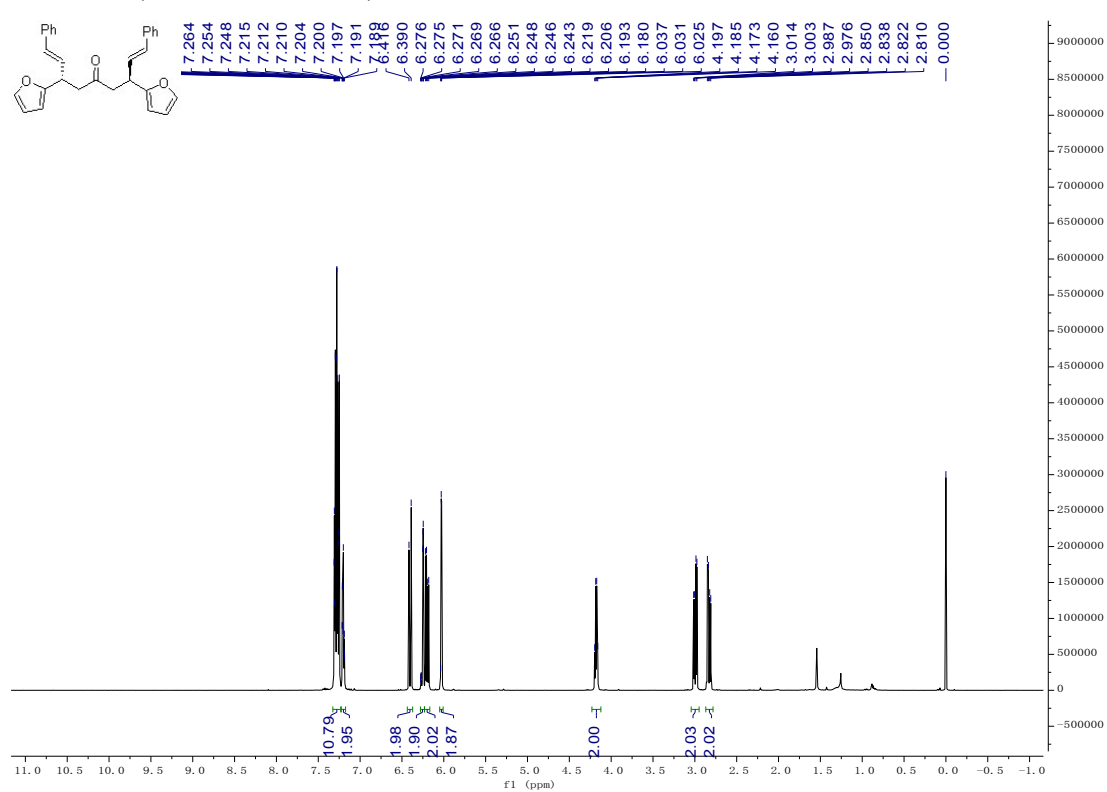


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) (n-hexane: 14.1, 22.7, 31.6.)

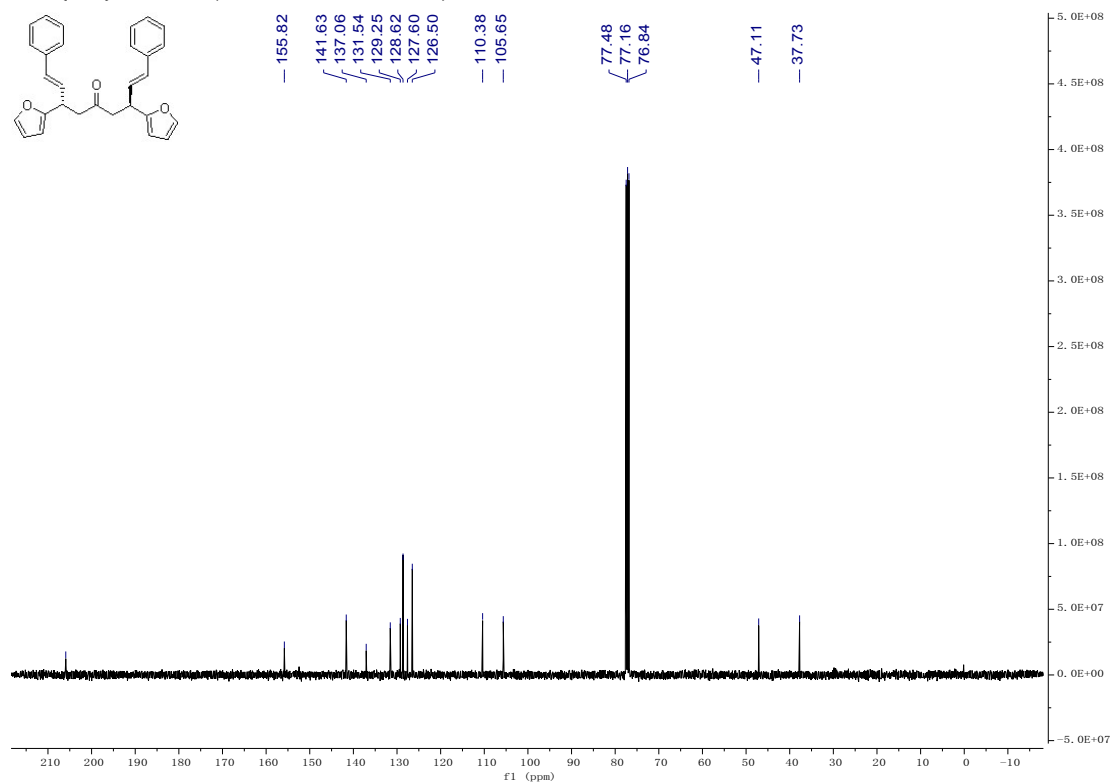


(1*E*,3*S*,7*S*,8*E*)-3,7-di(furan-2-yl)-1,9-diphenylnona-1,8-dien-5-one (**3pa**)

^1H NMR (600 MHz, CDCl_3)

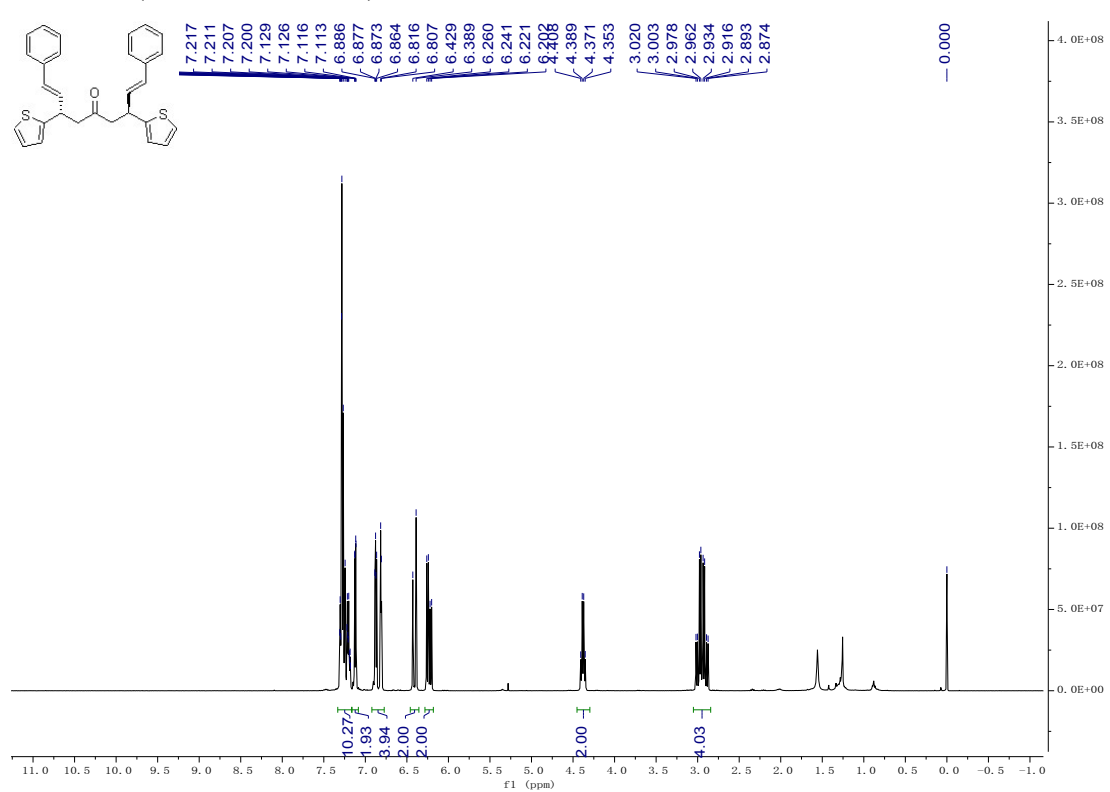


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

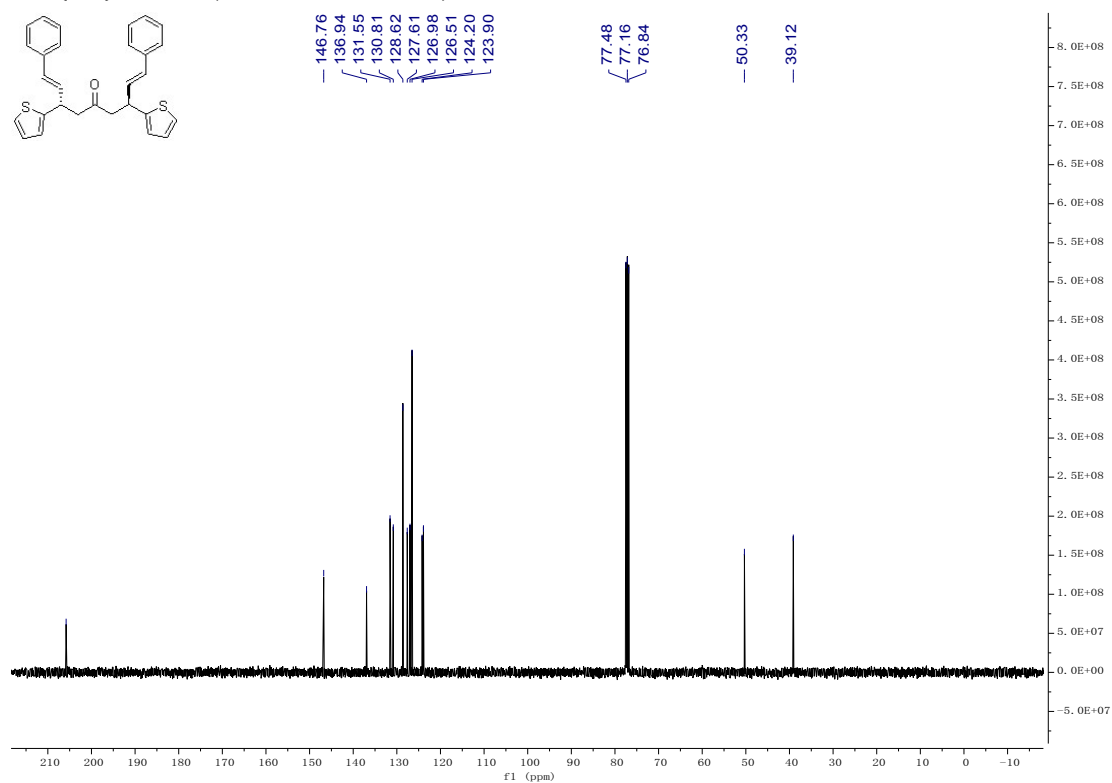


$(1E,3S,7S,8E)$ -1,9-diphenyl-3,7-di(thiophen-2-yl)nona-1,8-dien-5-one (**3qa**)

^1H NMR (400 MHz, CDCl_3)

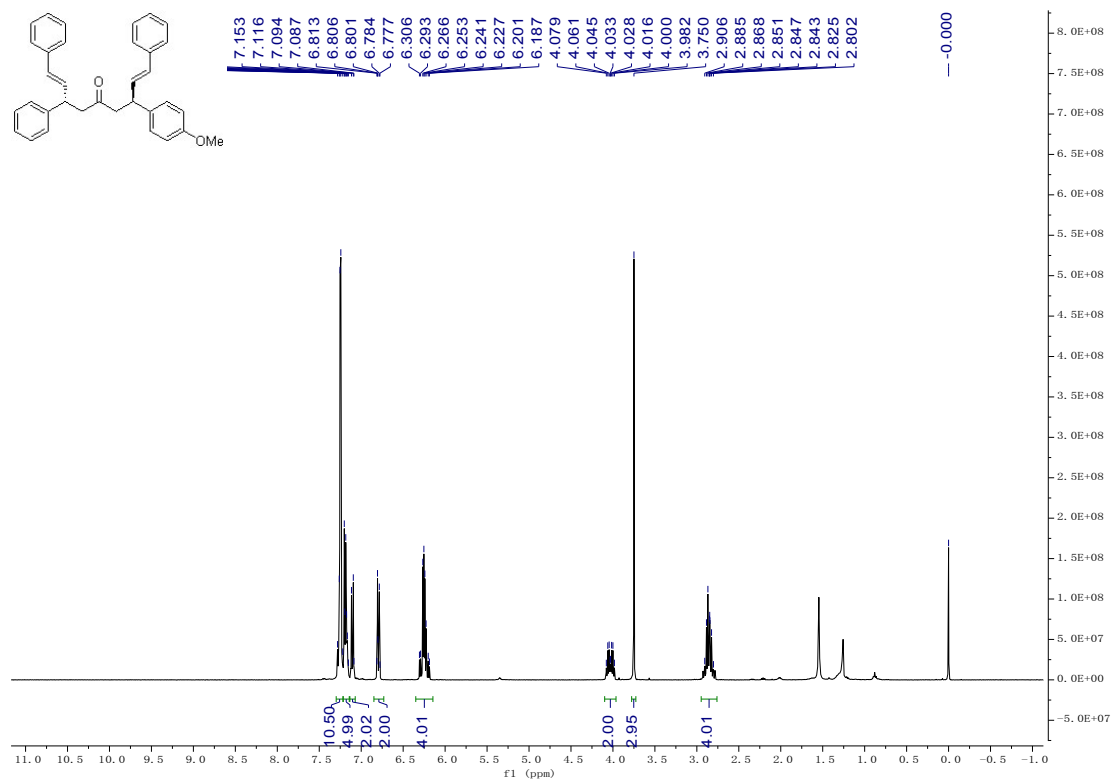


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

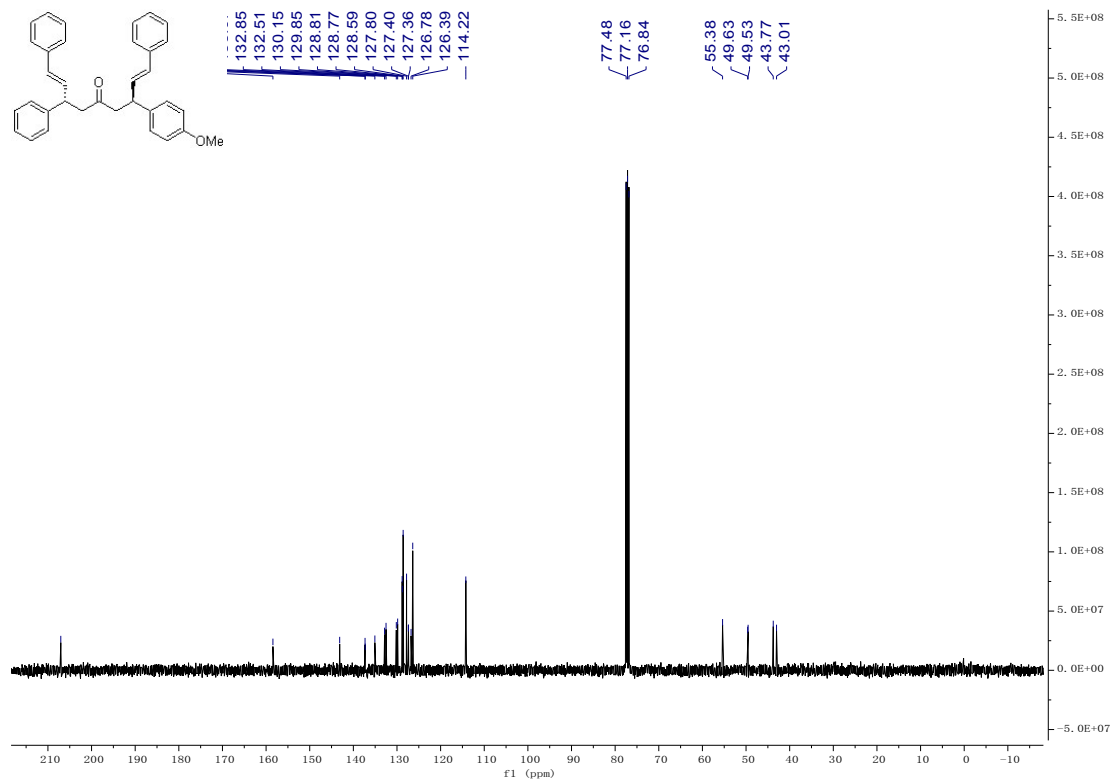


(1E,3S,7S,8E)-3-(4-methoxyphenyl)-1,7,9-triphenylnona-1,8-dien-5-one (**3ra**)

^1H NMR (600 MHz, CDCl_3)

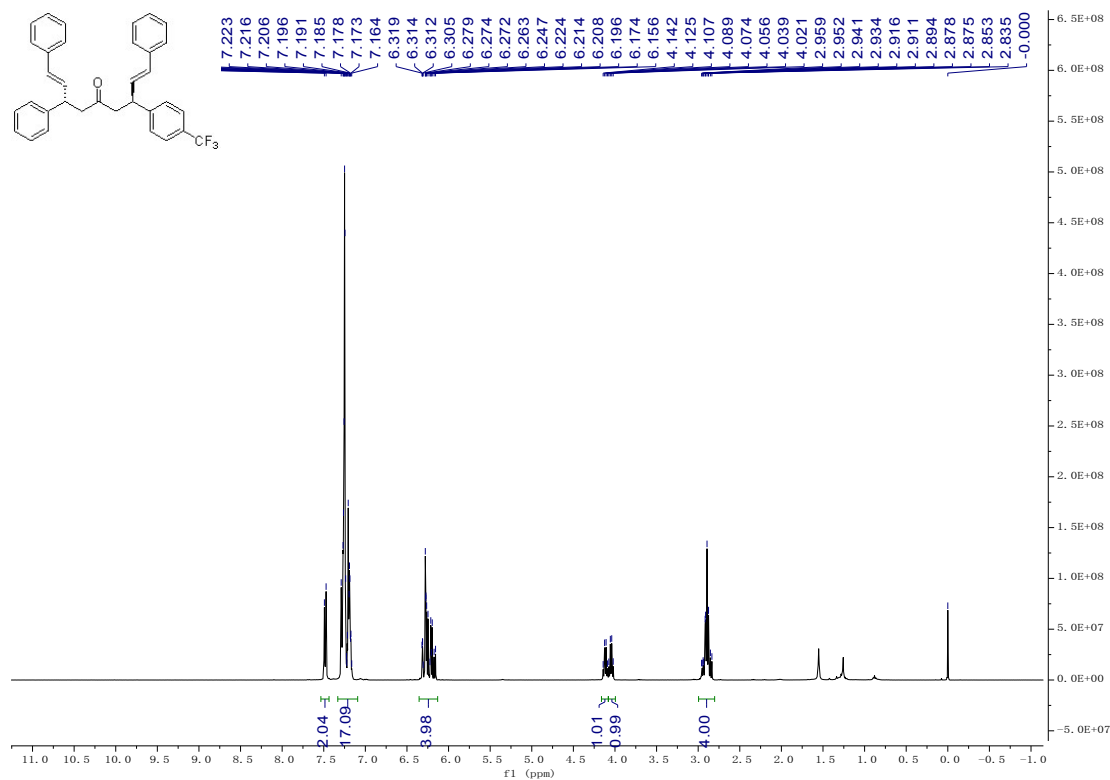


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

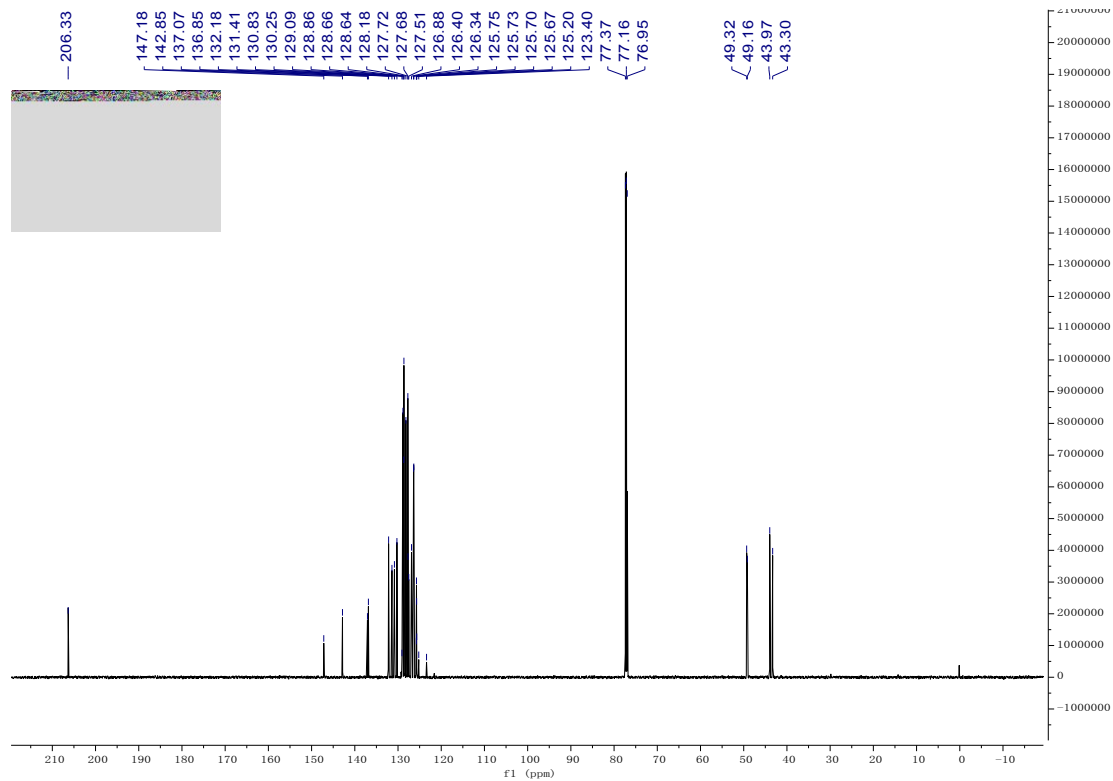


(1E,3S,7S,8E)-1,3,9-triphenyl-7-(4-(trifluoromethyl)phenyl)nona-1,8-dien-5-one (3sa)

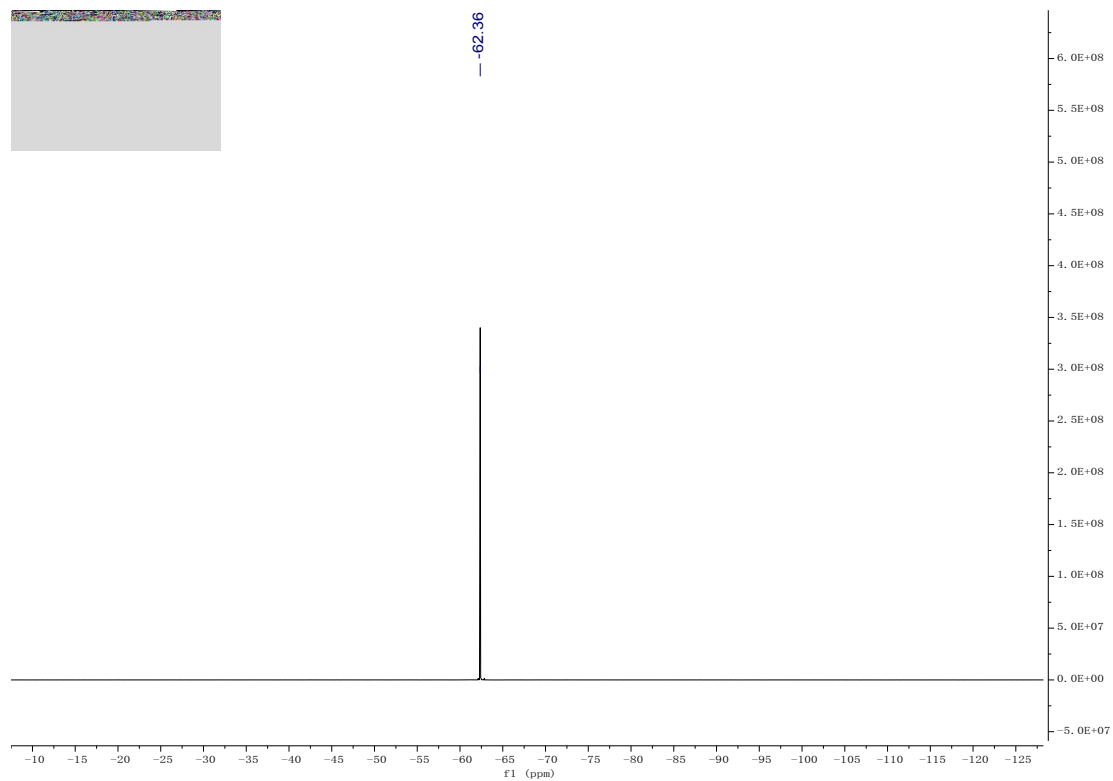
^1H NMR (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

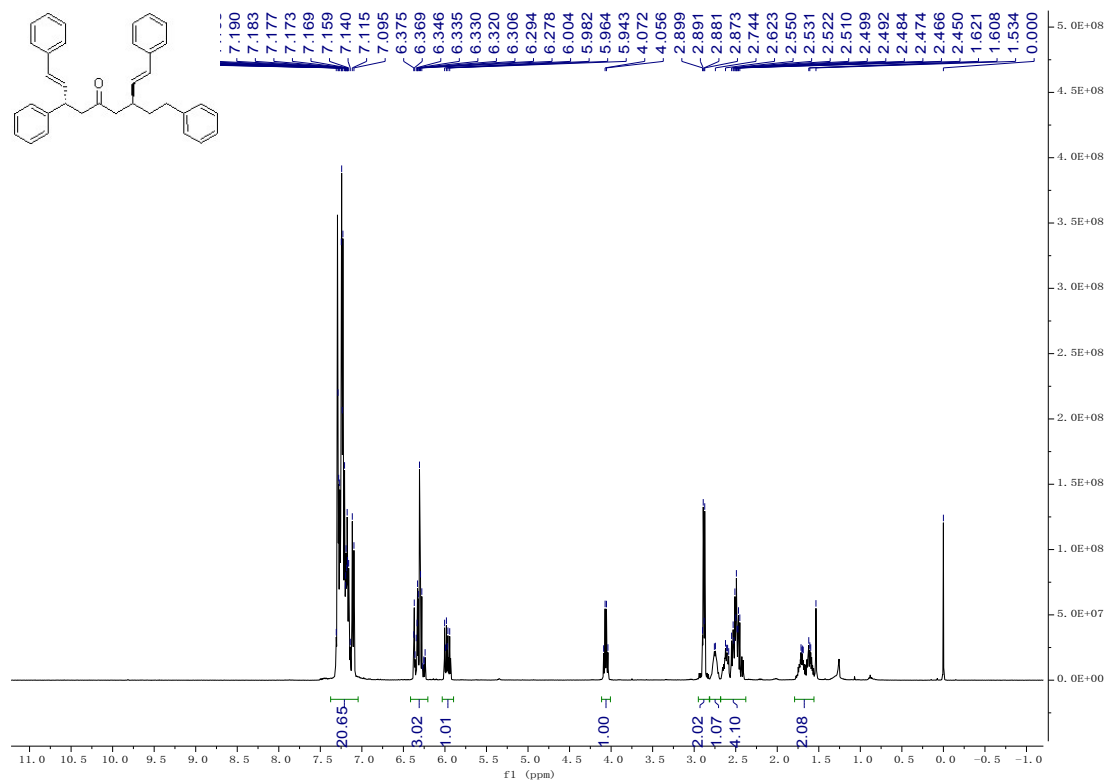


$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3)

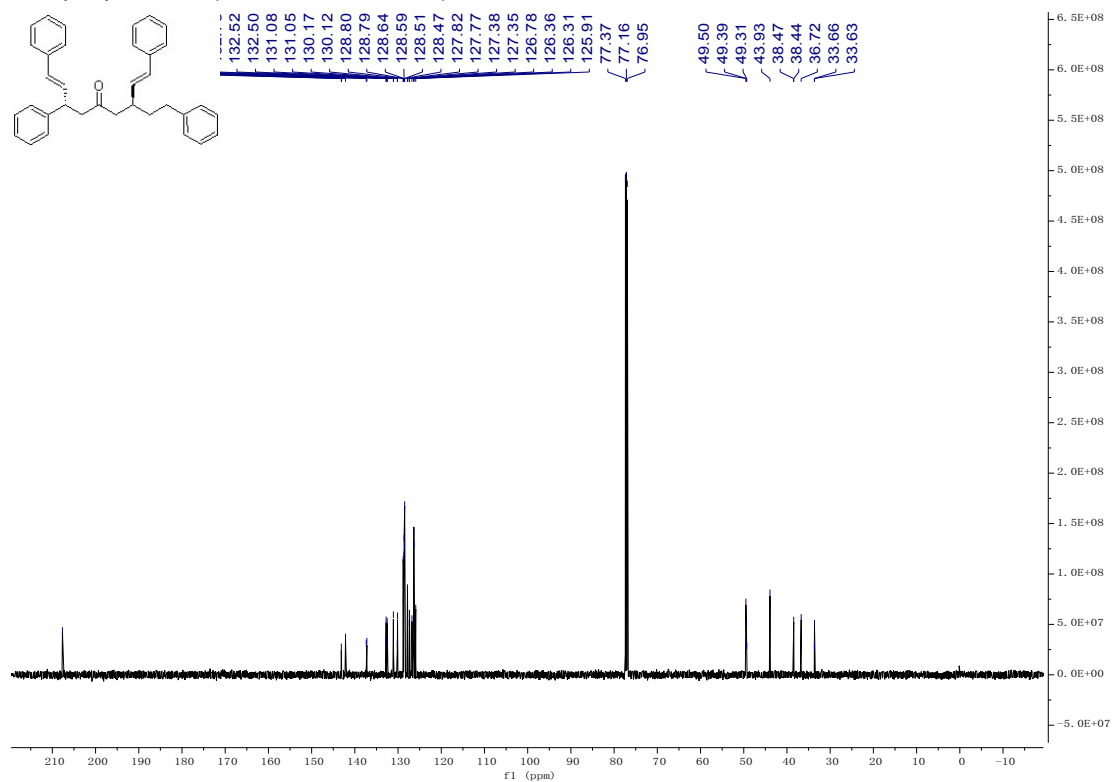


(1E,3S,7S,8E)-3-phenethyl-1,7,9-triphenylnona-1,8-dien-5-one (3ta)

¹H NMR (400 MHz, CDCl₃)

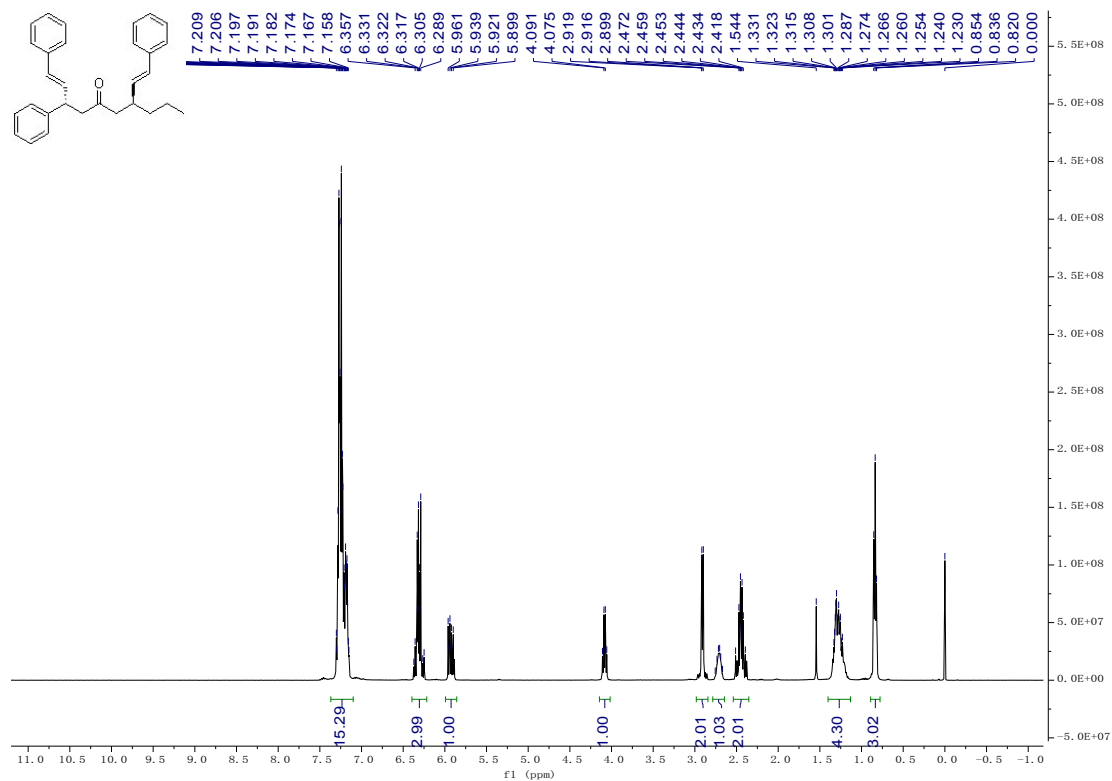


¹³C {¹H} NMR (150 MHz, CDCl₃)

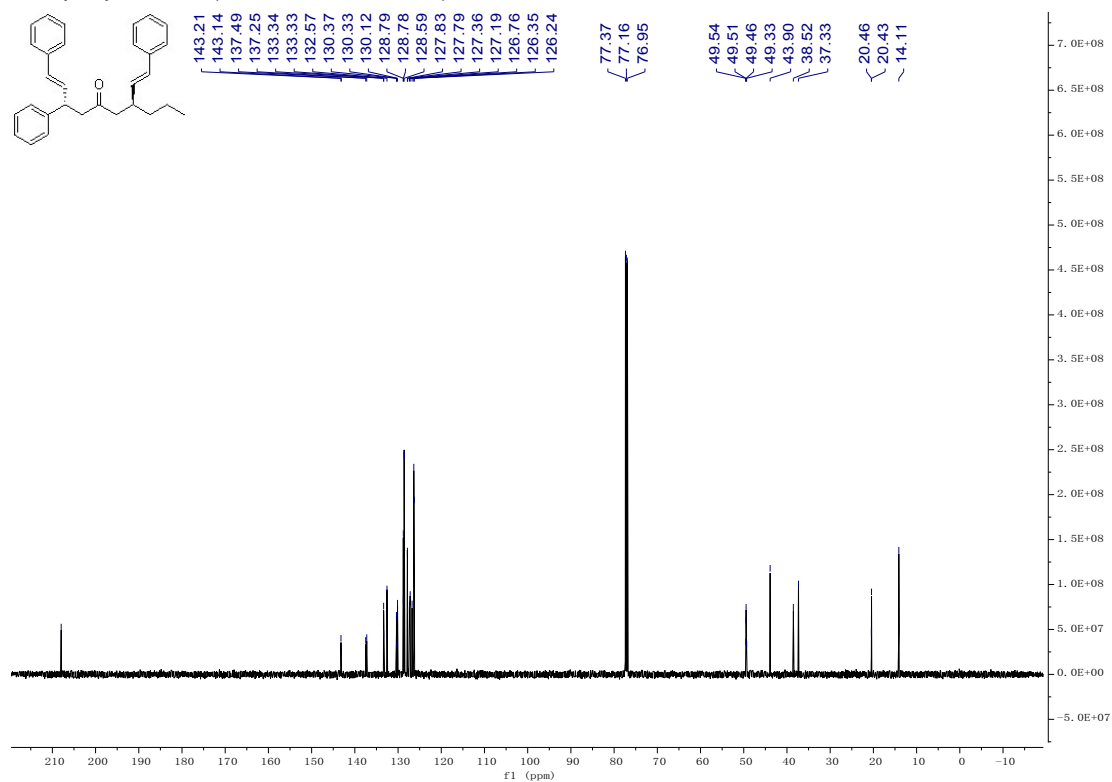


(3S,7S,E)-1,3-diphenyl-7-((*E*)-styryl)dec-1-en-5-one (**3ua**)

¹H NMR (400 MHz, CDCl₃)

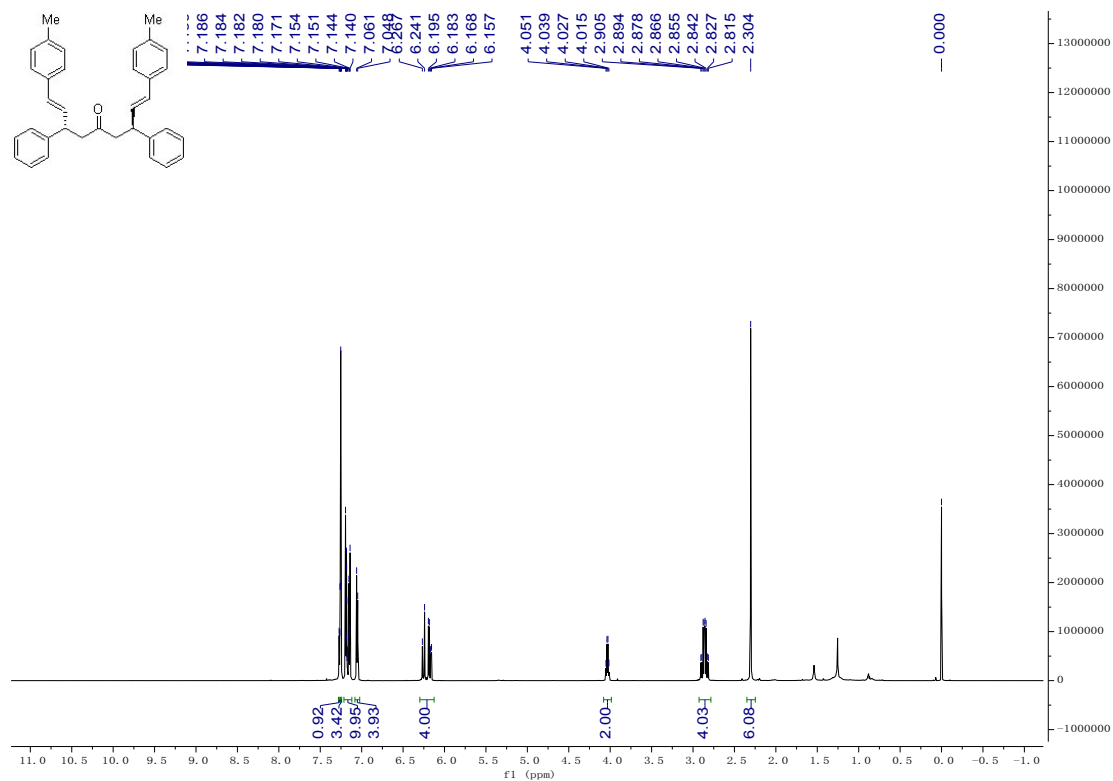


¹³C {¹H} NMR (150 MHz, CDCl₃)

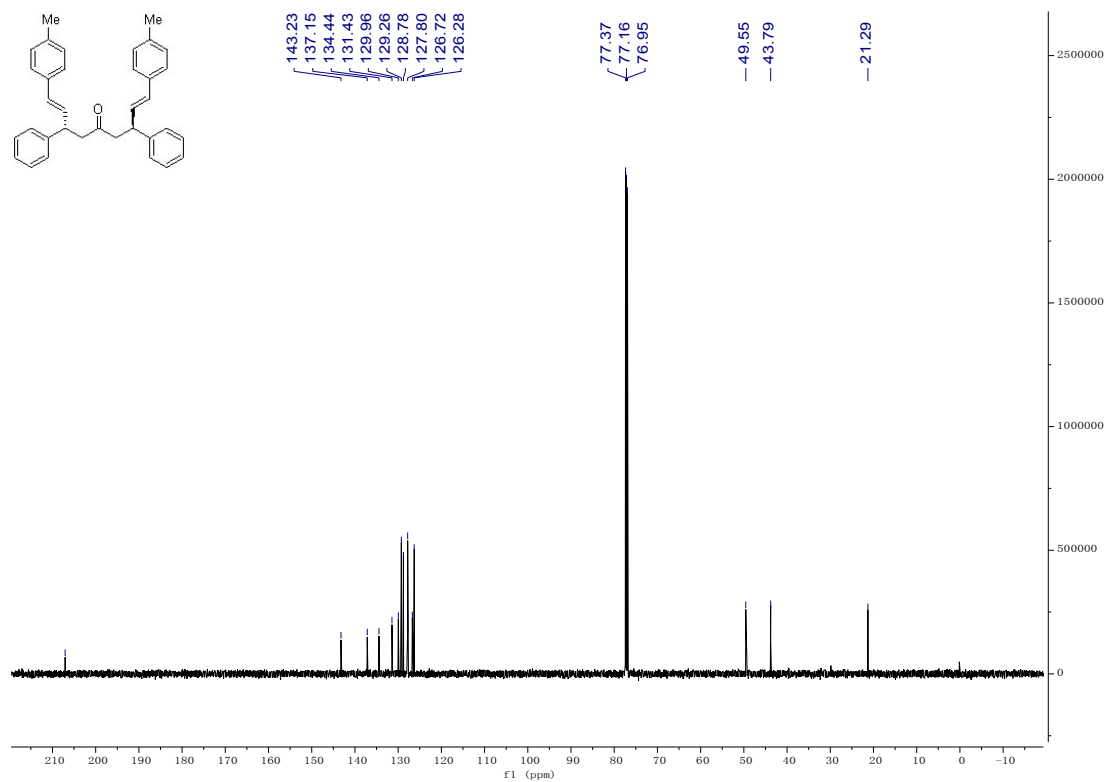


(1E,3S,7S,8E)-3,7-diphenyl-1,9-di-*p*-tolylnona-1,8-dien-5-one (**3ab**)

^1H NMR (600 MHz, CDCl_3)

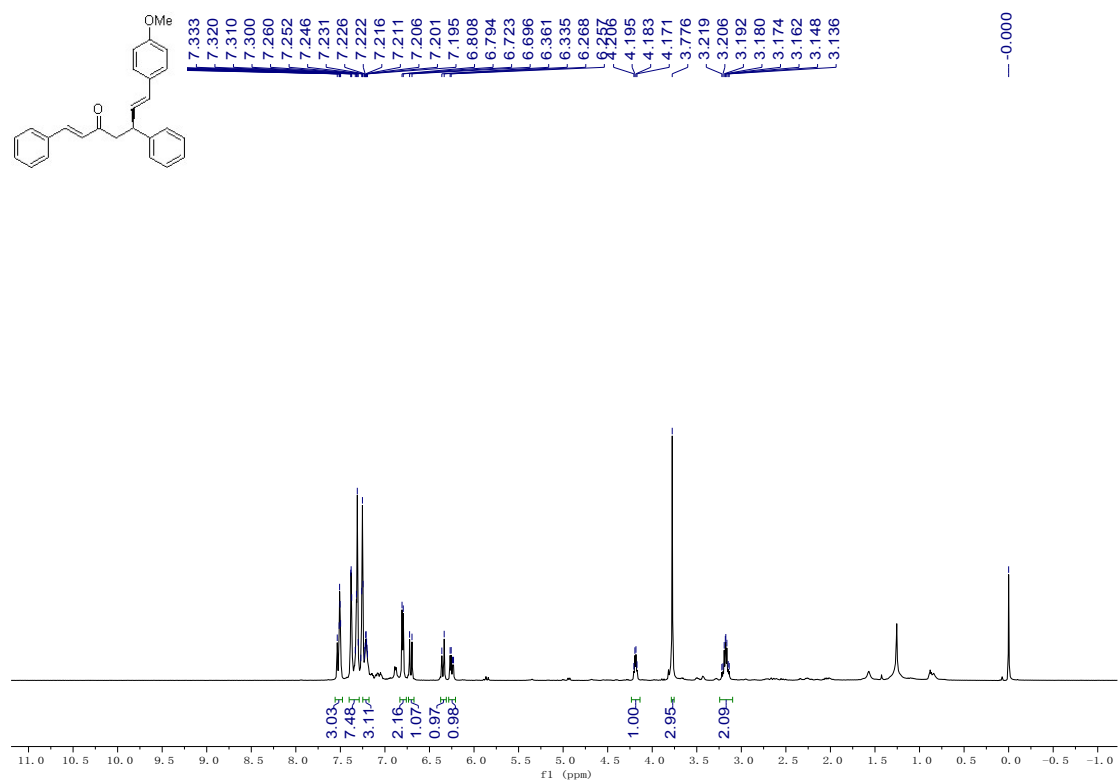


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

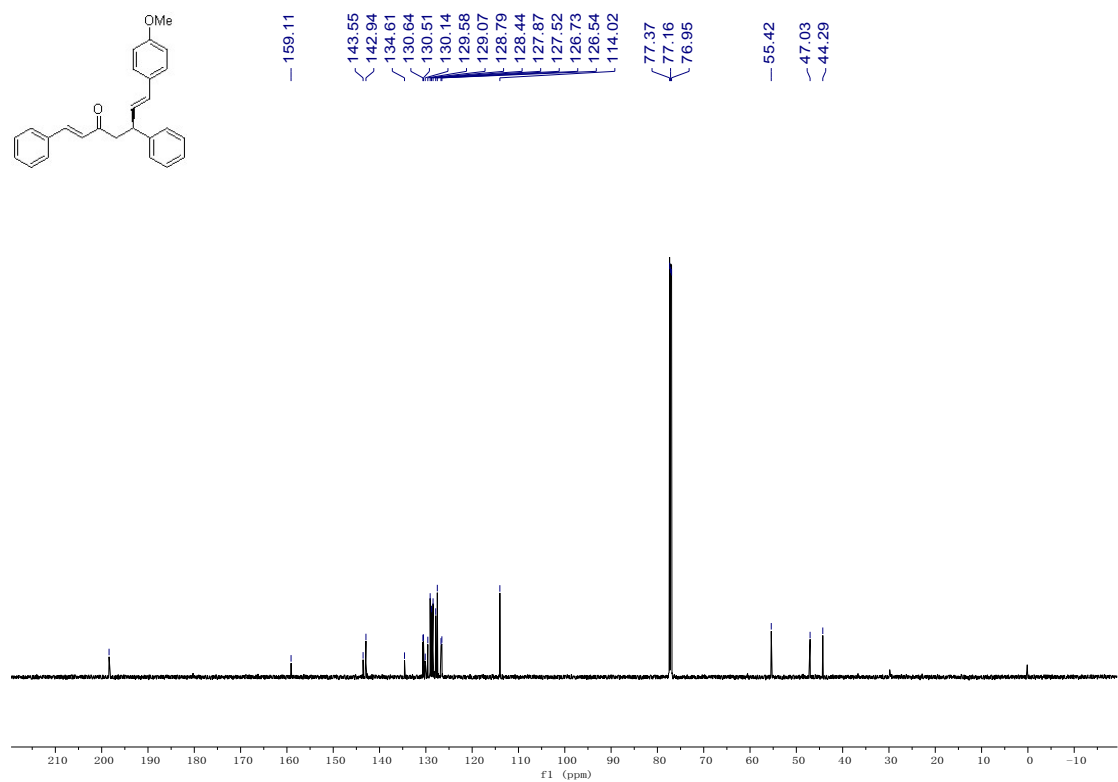


(S,1E,6E)-7-(4-methoxyphenyl)-1,5-diphenylhepta-1,6-dien-3-one (**4ac**)

^1H NMR (600 MHz, CDCl_3)

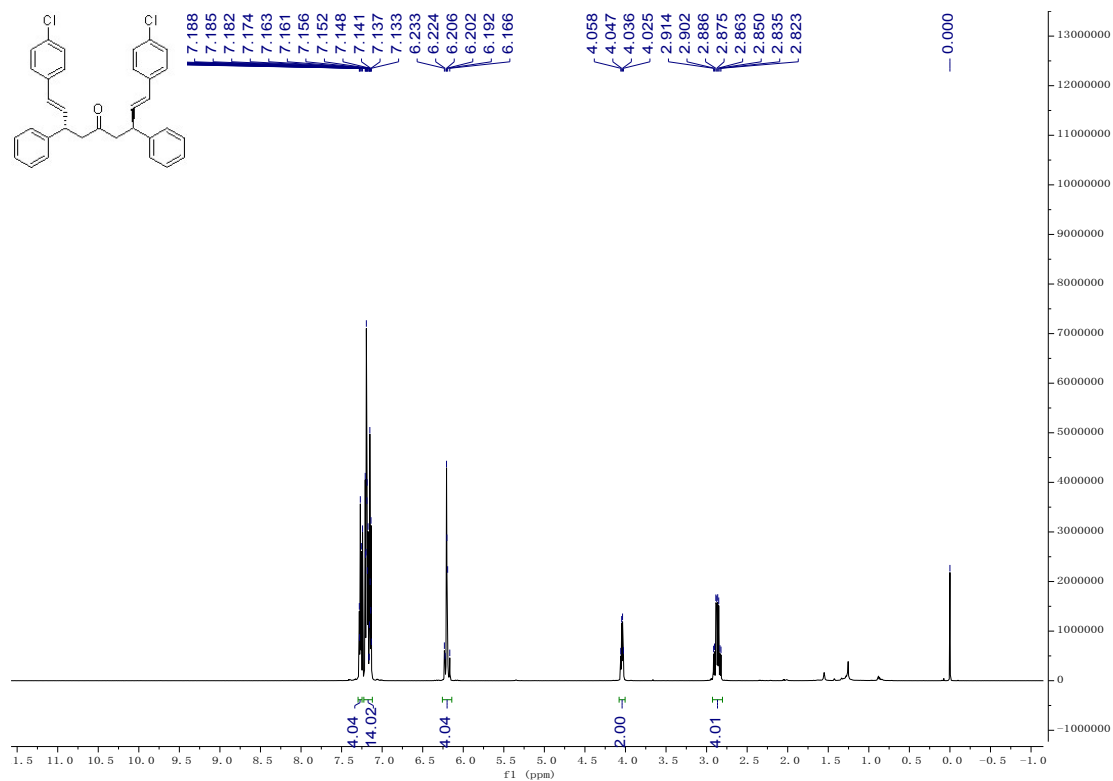


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

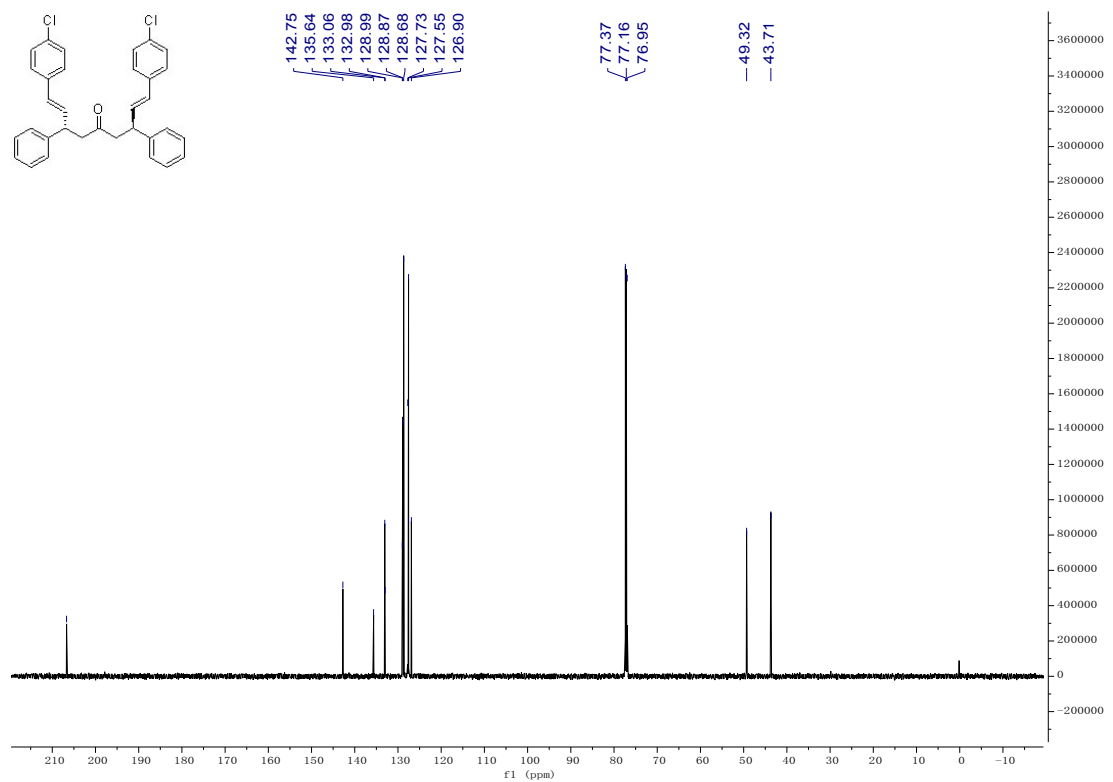


(1E,3S,7S,8E)-1,9-bis(4-chlorophenyl)-3,7-diphenylnona-1,8-dien-5-one (**3ad**)

¹H NMR (600 MHz, CDCl₃)



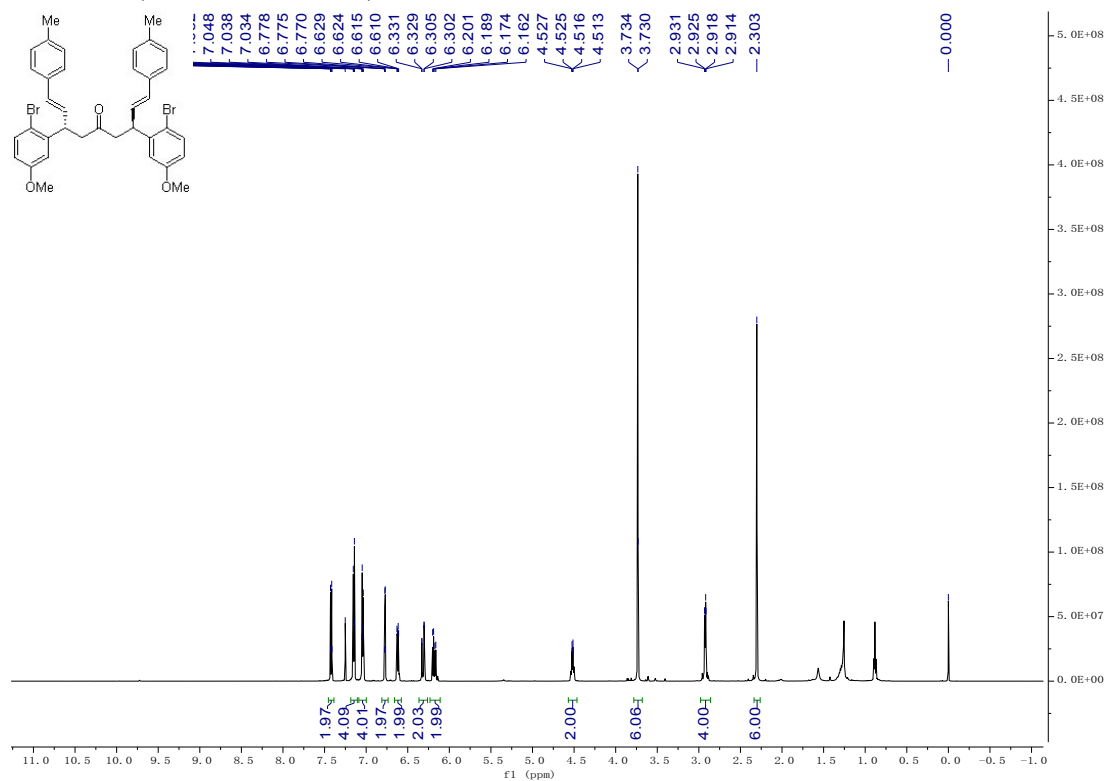
¹³C{¹H} NMR (150 MHz, CDCl₃)



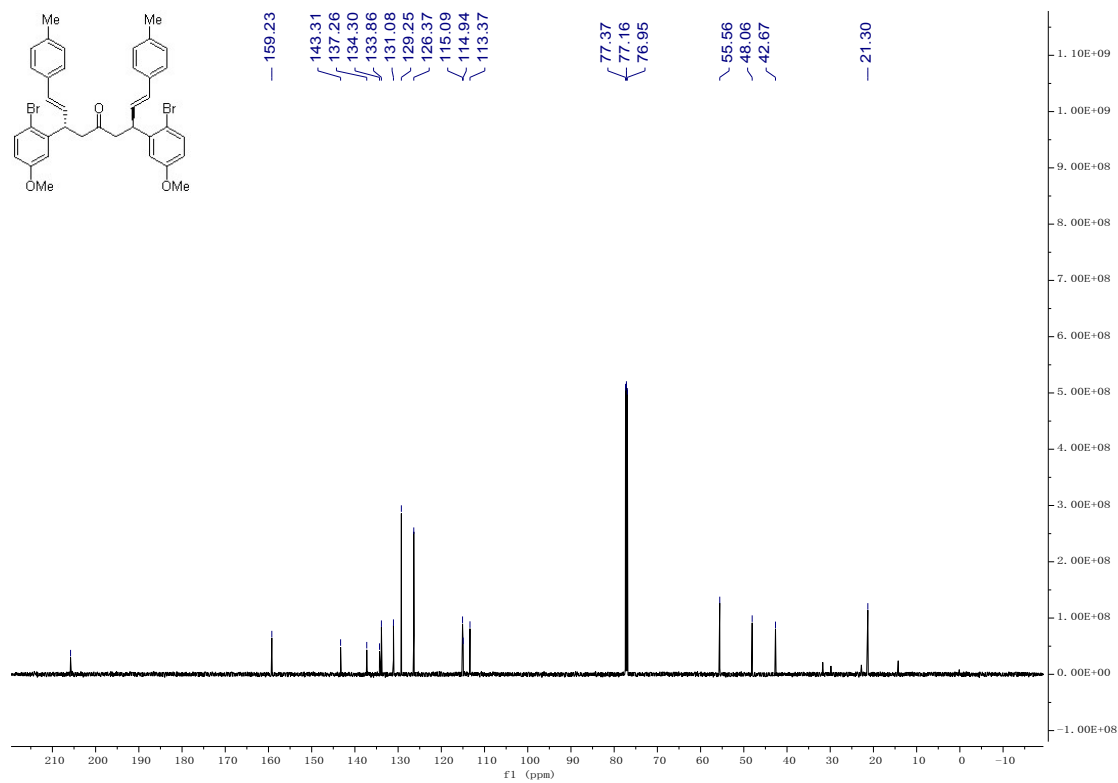
(1E,3S,7S,8E)-3,7-bis(2-bromo-5-methoxyphenyl)-1,9-di-p-tolylnona-1,8-dien-5-one

(31b)

¹H NMR (600 MHz, CDCl₃)

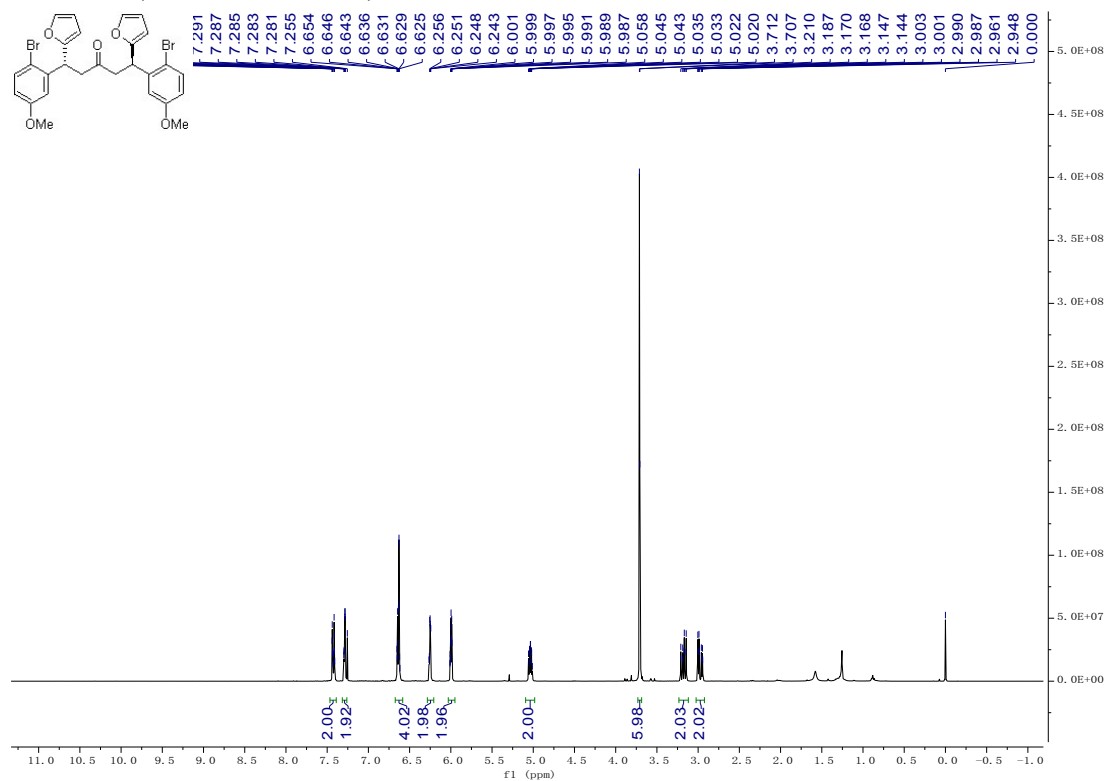


¹³C{¹H} NMR (150 MHz, CDCl₃) (n-hexane: 14.1, 22.7, 31.6)

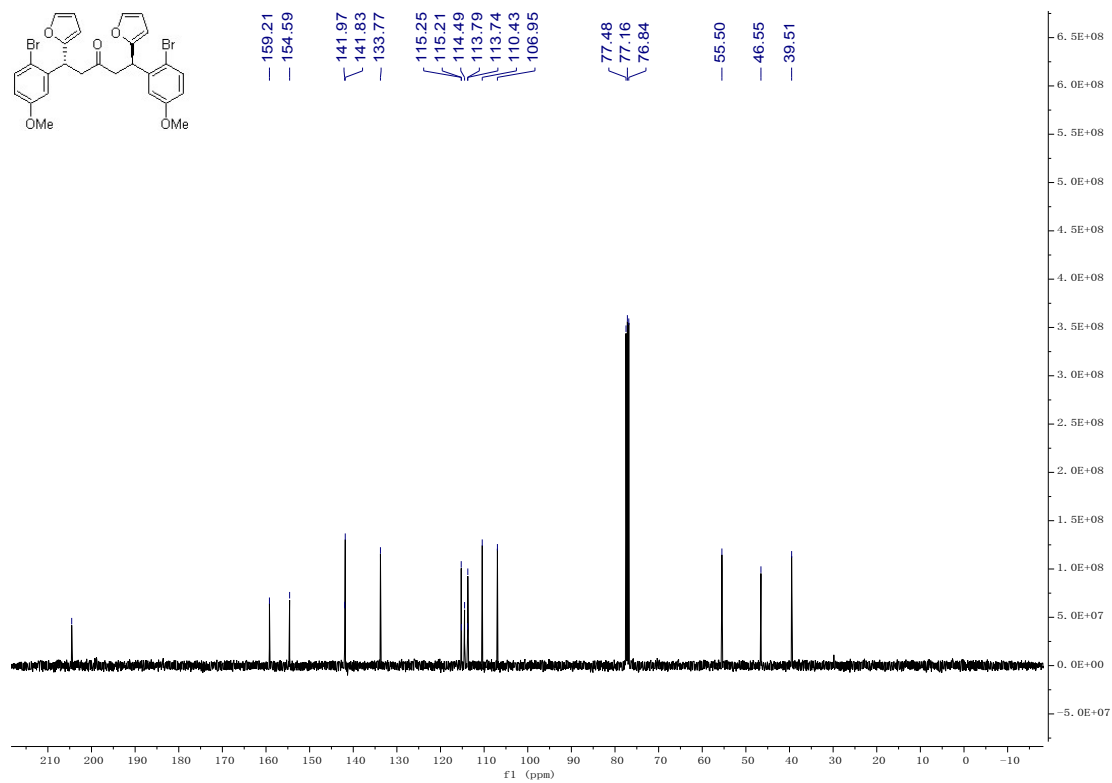


(2-Hydroxyphenyl)((1R,2R)-5-methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (**3le**)

¹H NMR (400 MHz, CDCl₃)

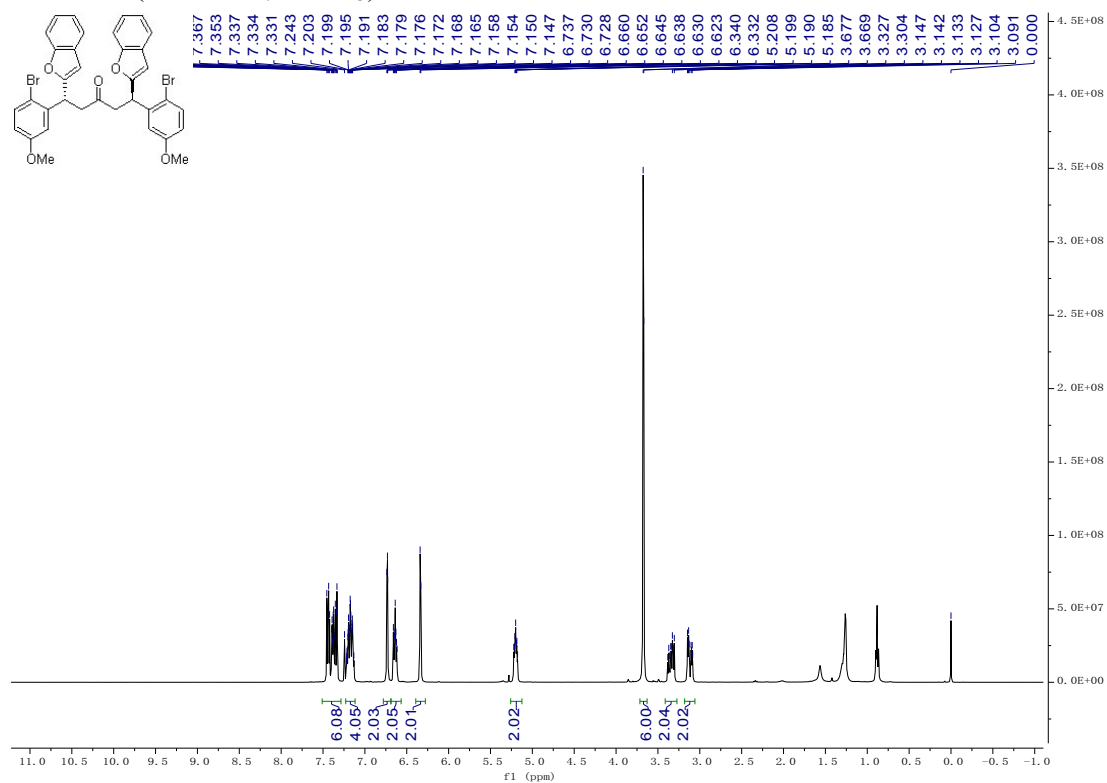


¹³C{¹H} NMR (100 MHz, CDCl₃)

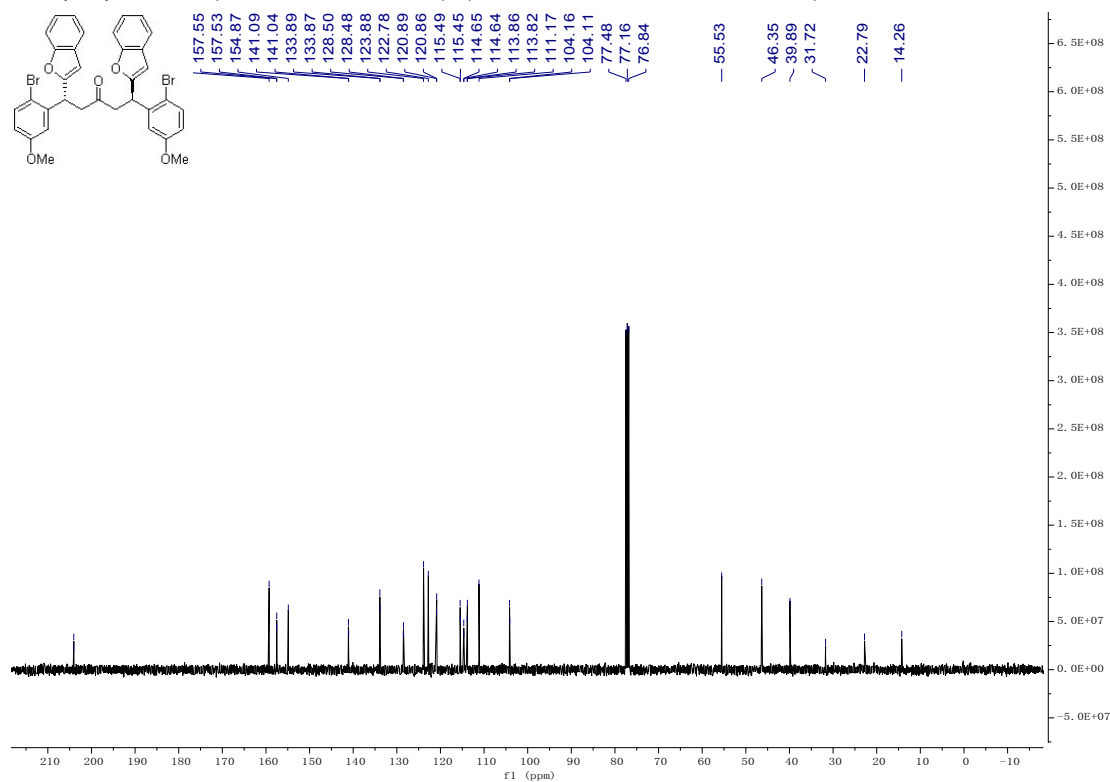


(1*R*,5*R*)-1,5-di(benzofuran-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pentan-3-one (**31f**)

¹H NMR (400 MHz, CDCl₃)

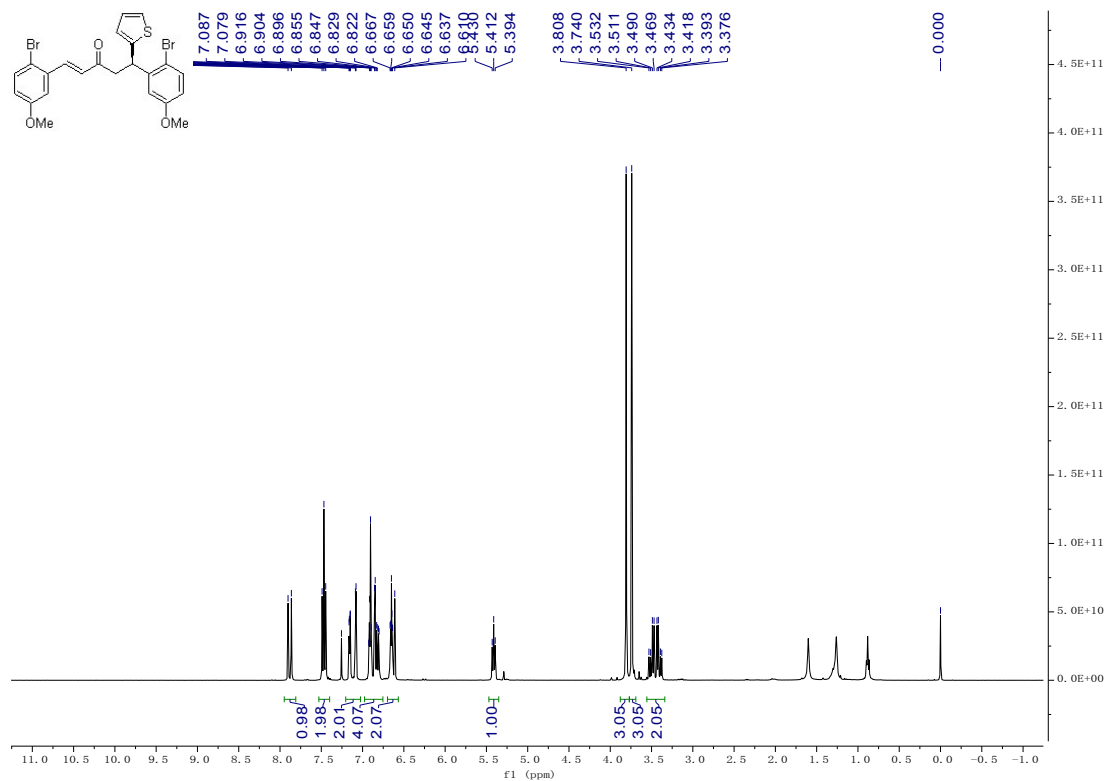


¹³C{¹H} NMR (100 MHz, CDCl₃) (n-hexane: 14.1, 22.7, 31.6.)

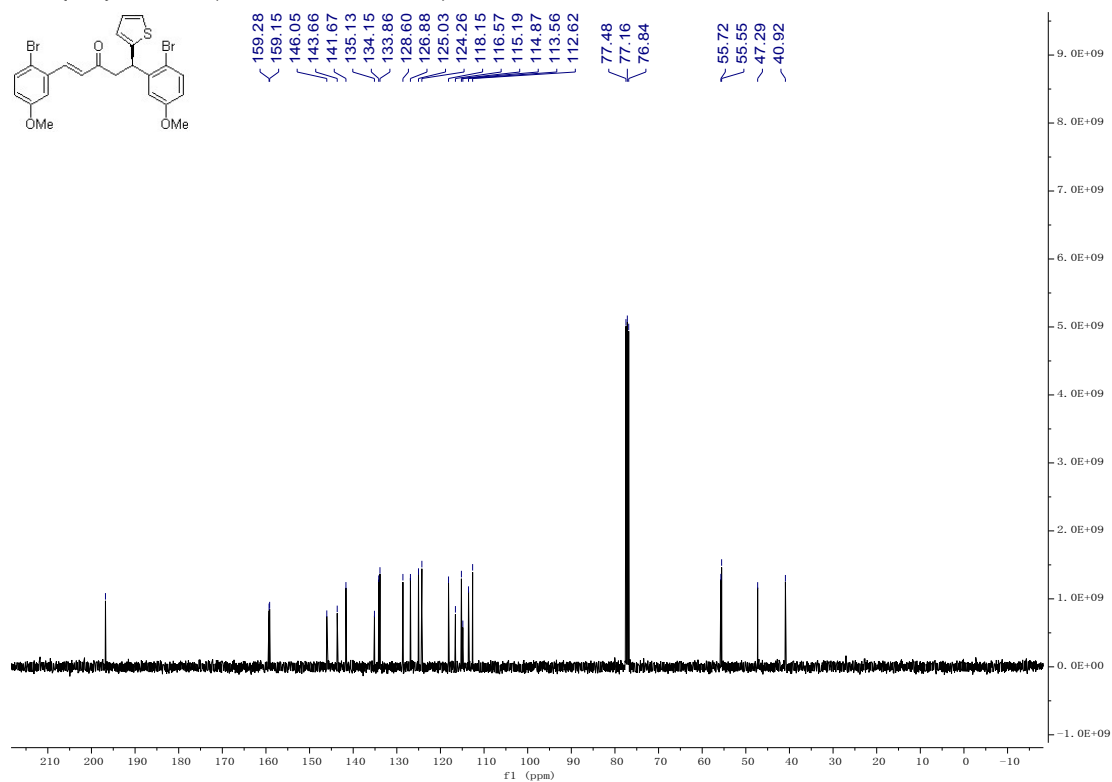


(R,E)-1,5-bis(2-bromo-5-methoxyphenyl)-5-(thiophen-2-yl)pent-1-en-3-one (**4lg**)

¹H NMR (400 MHz, CDCl₃)

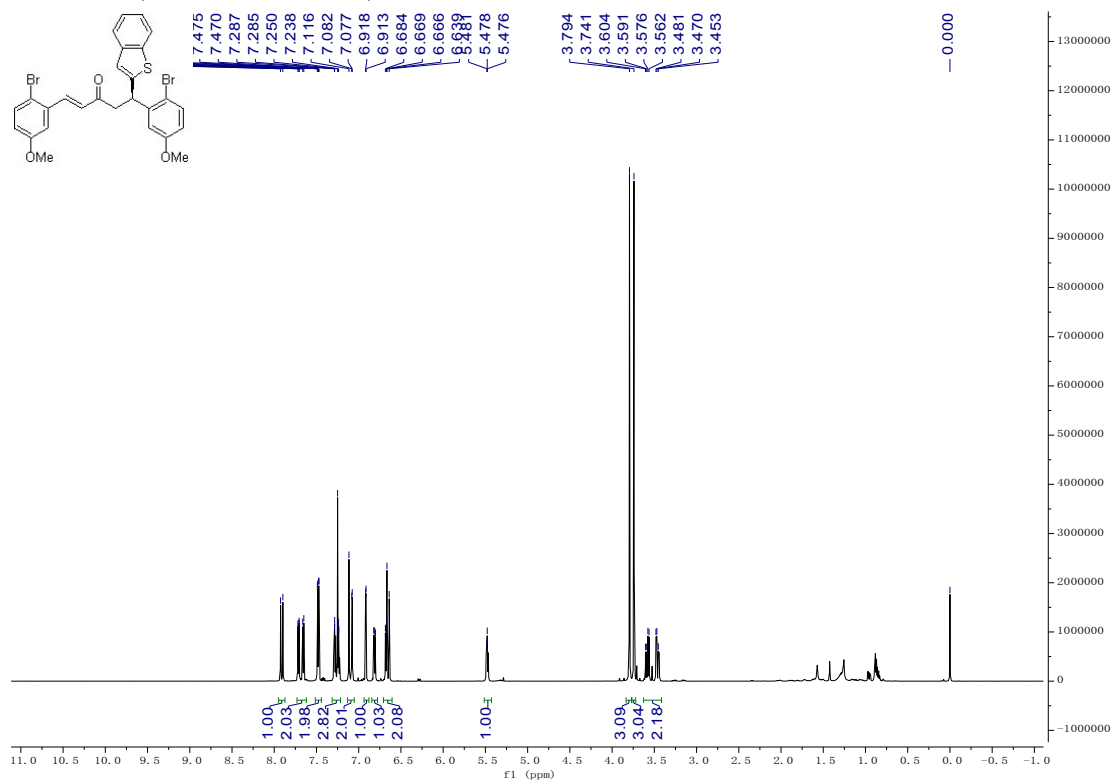


¹³C {¹H} NMR (100 MHz, CDCl₃)

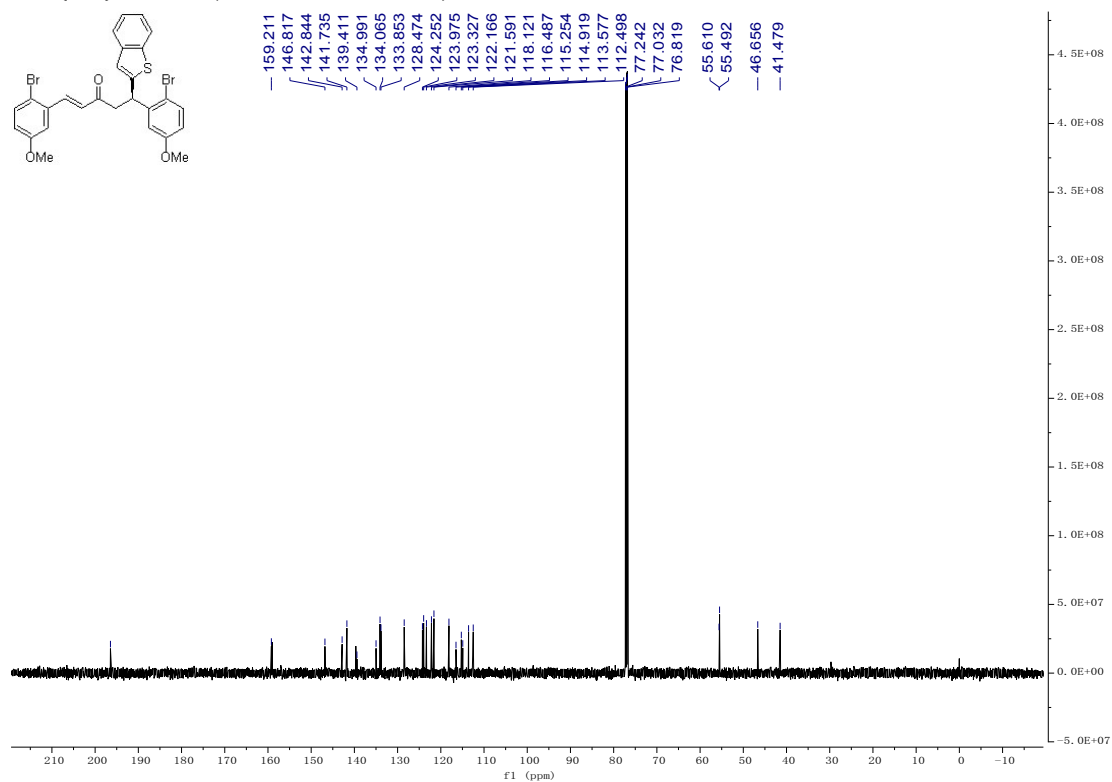


(R,E)-5-(benzo[*b*]thiophen-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pent-1-en-3-one
(4h)

¹H NMR (600 MHz, CDCl₃)

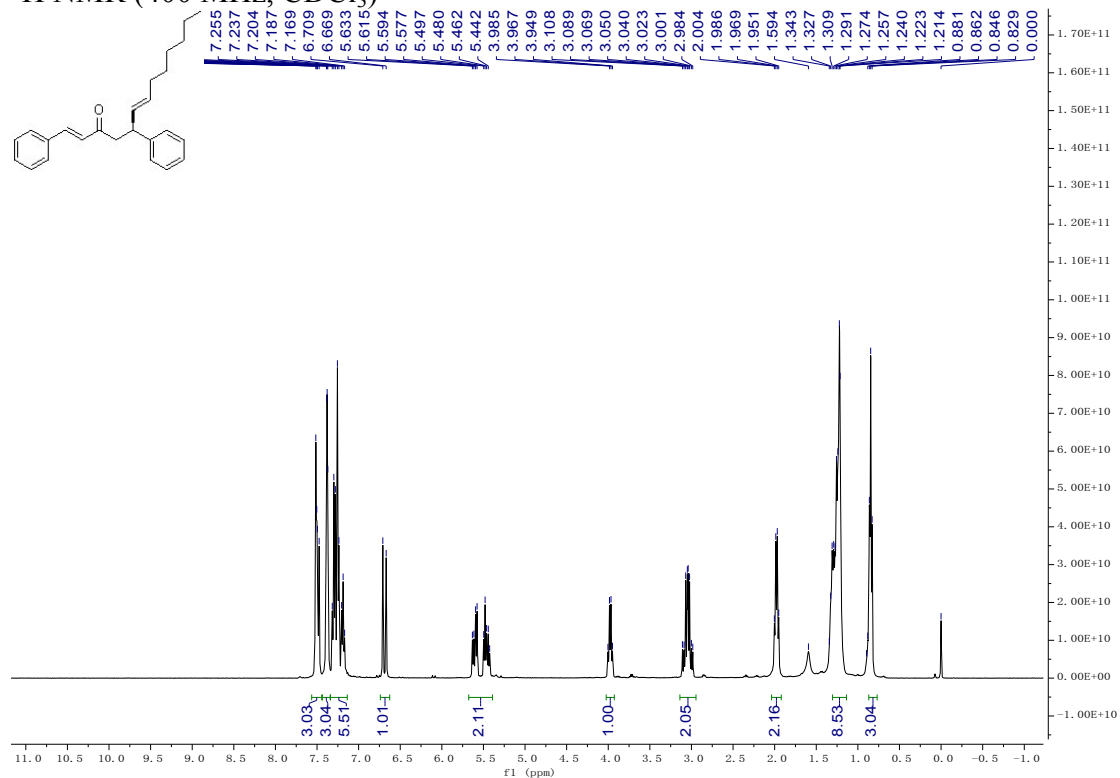


¹³C {¹H} NMR (150 MHz, CDCl₃)

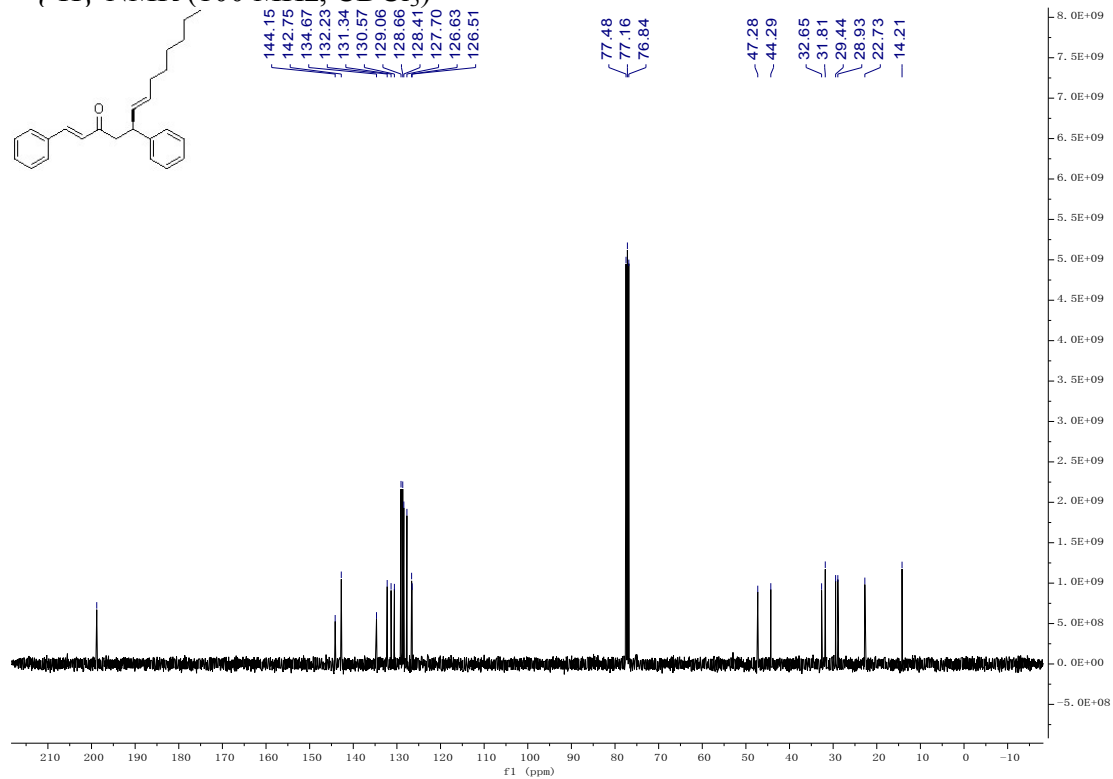


(S,1E,6E)-1,5-diphenyltrideca-1,6-dien-3-one (**4ai**)

^1H NMR (400 MHz, CDCl_3)

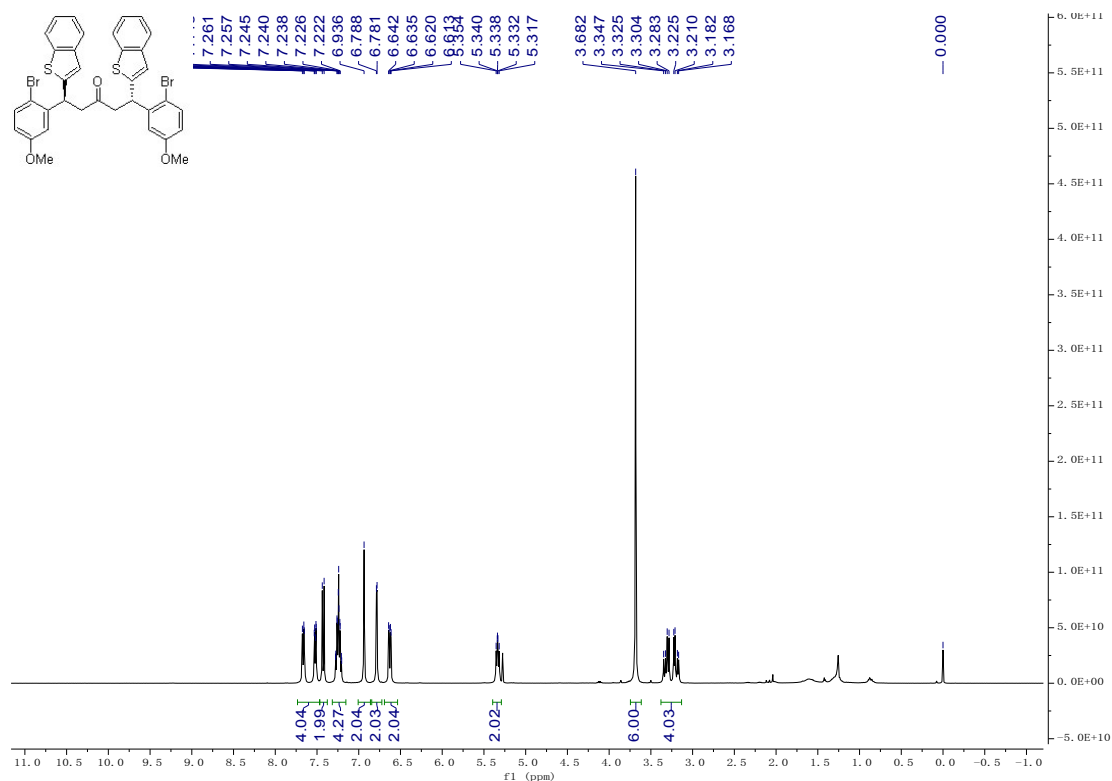


$^{13}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

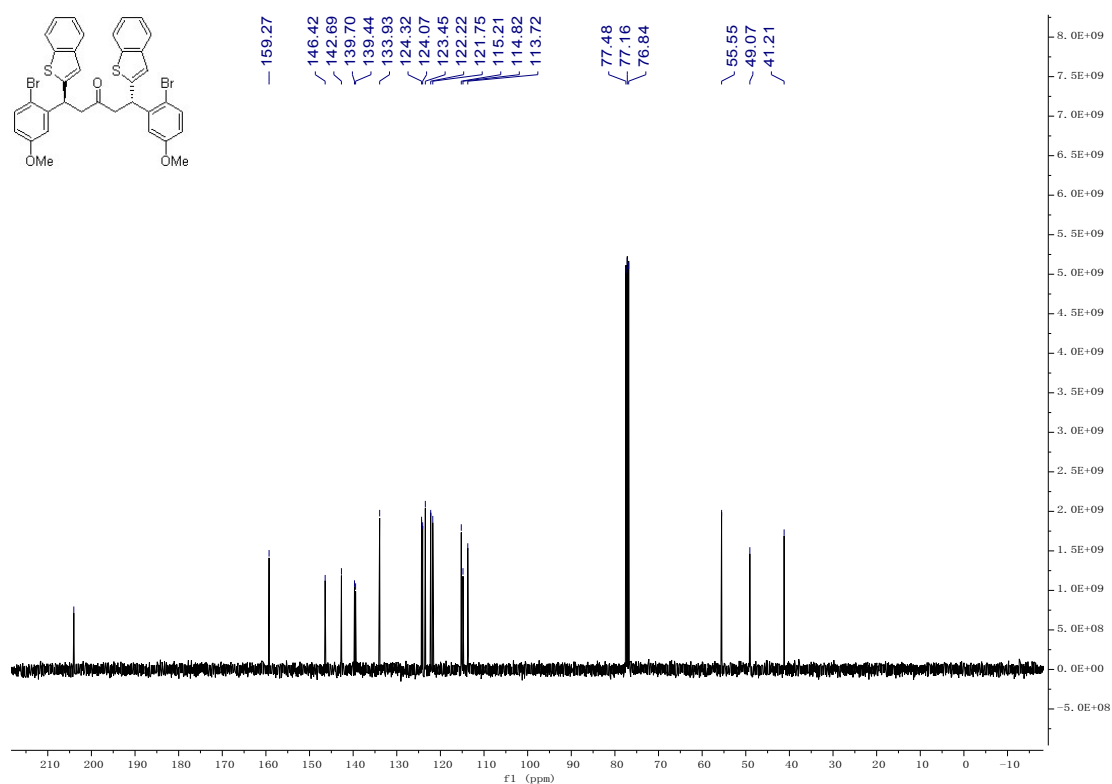


(1S,5S)-1,5-bis(benzo[b]thiophen-2-yl)-1,5-bis(2-bromo-5-methoxyphenyl)pentan-3-one (3lh')

^1H NMR (400 MHz, CDCl_3)

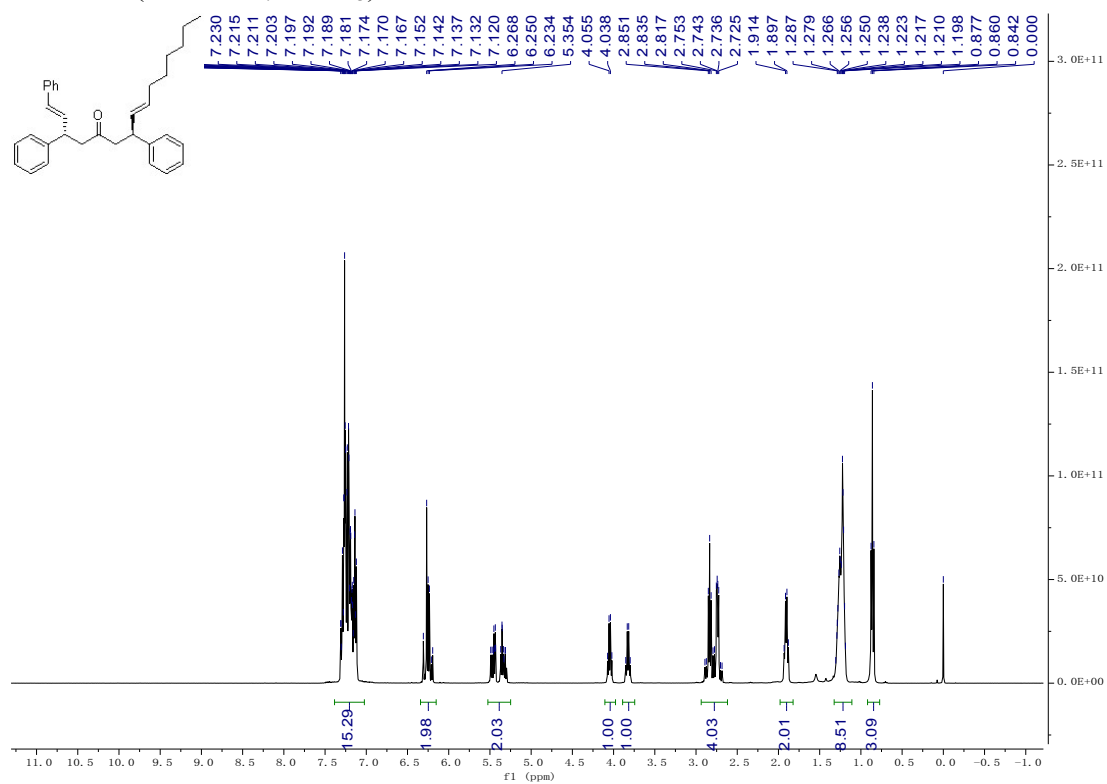


$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3)

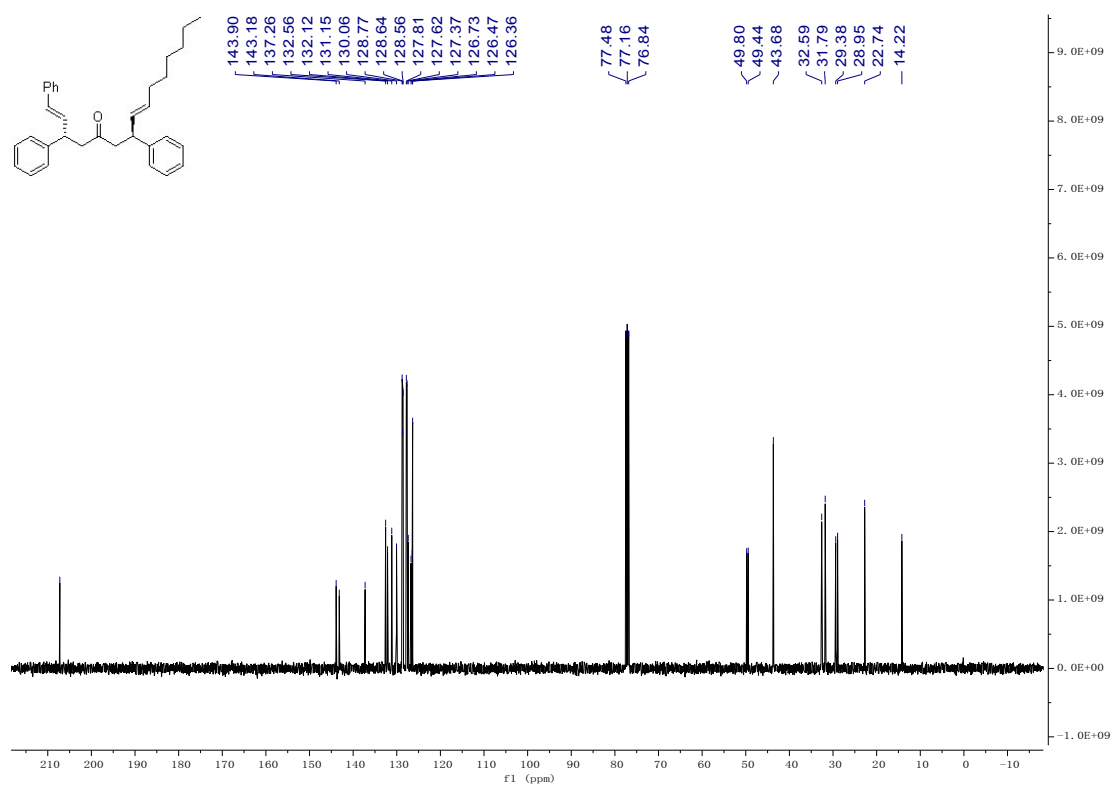


(1E,3S,7S,8E)-1,3,7-triphenylpentadeca-1,8-dien-5-one (**5**)

¹H NMR (400 MHz, CDCl₃)

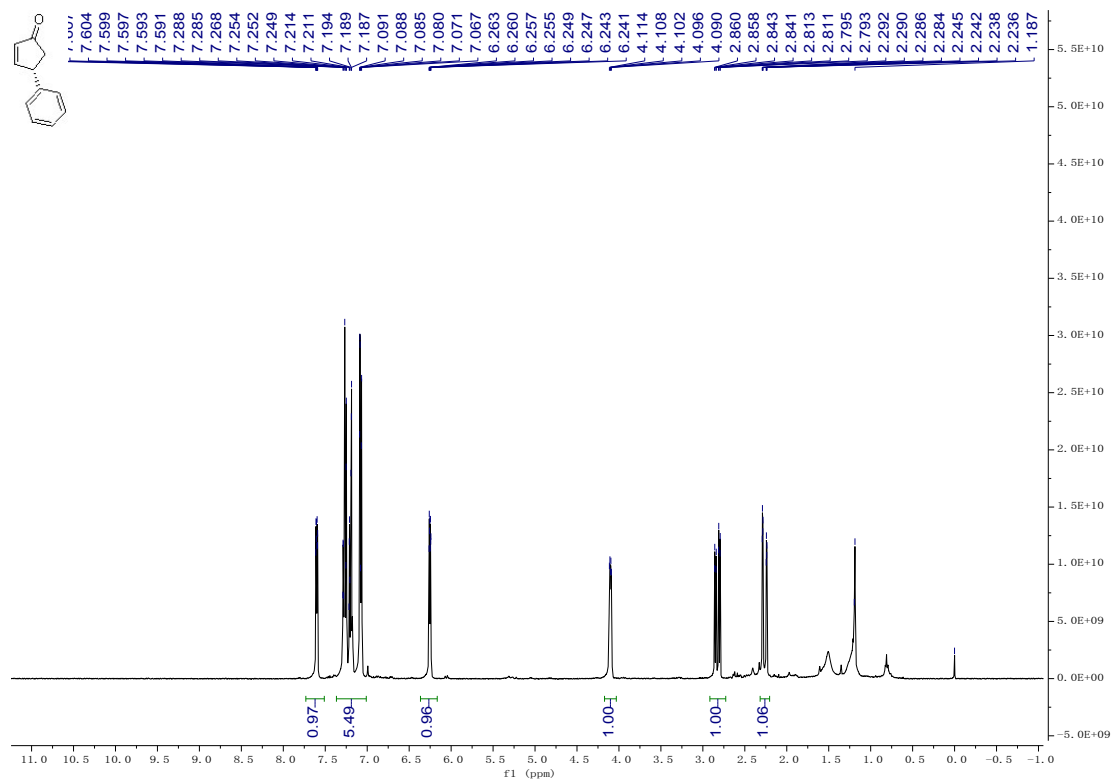


¹³C{¹H} NMR (150 MHz, CDCl₃)



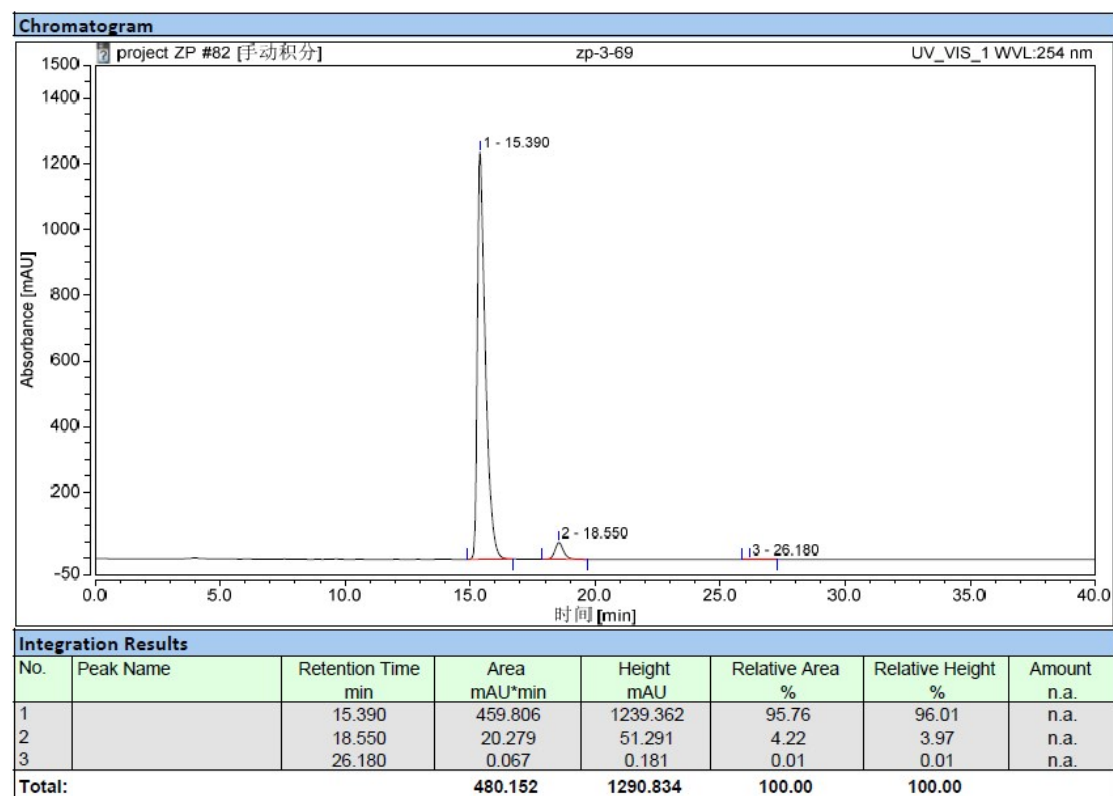
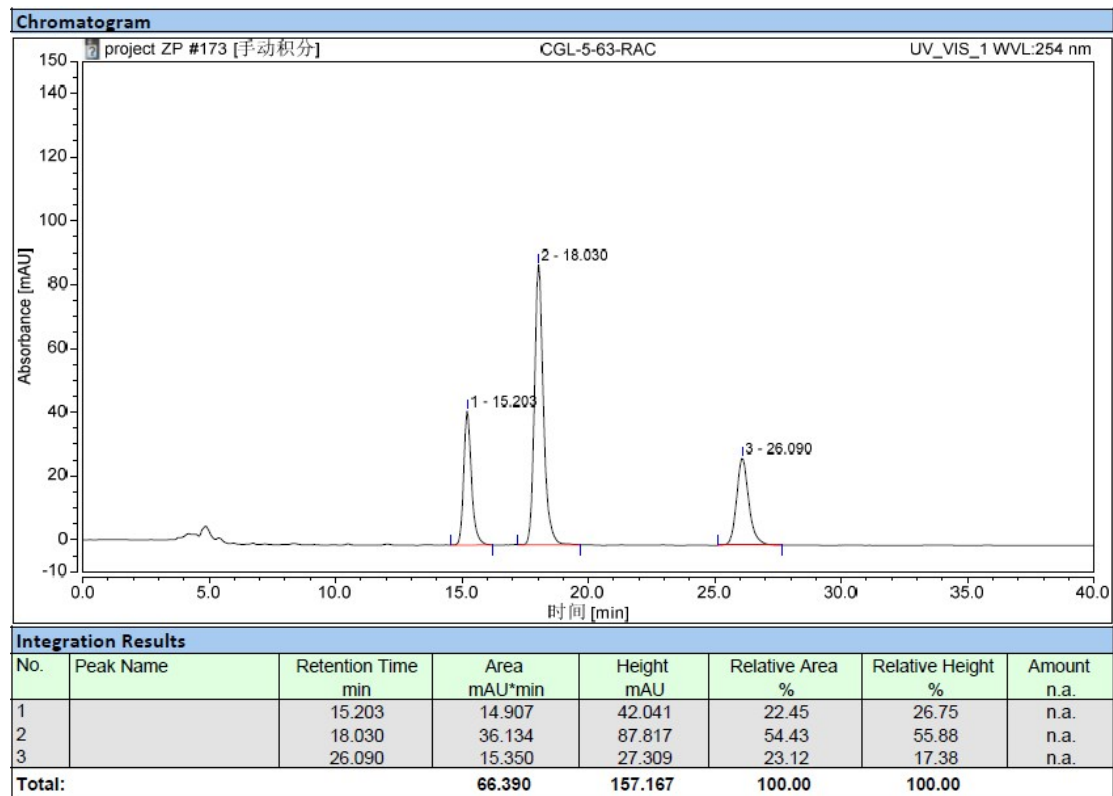
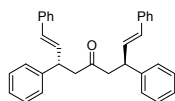
(S)-4-Phenyl-2-cyclopenten-1-one (**6**)

¹H NMR (400 MHz, CDCl₃)

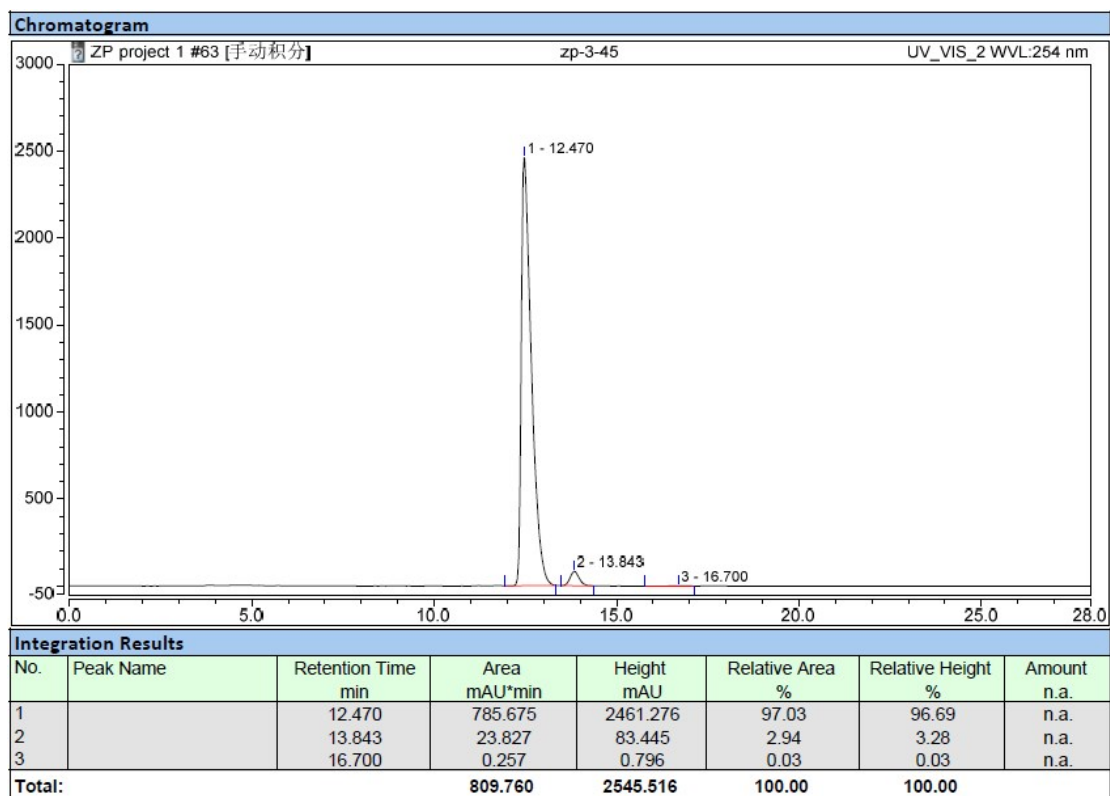
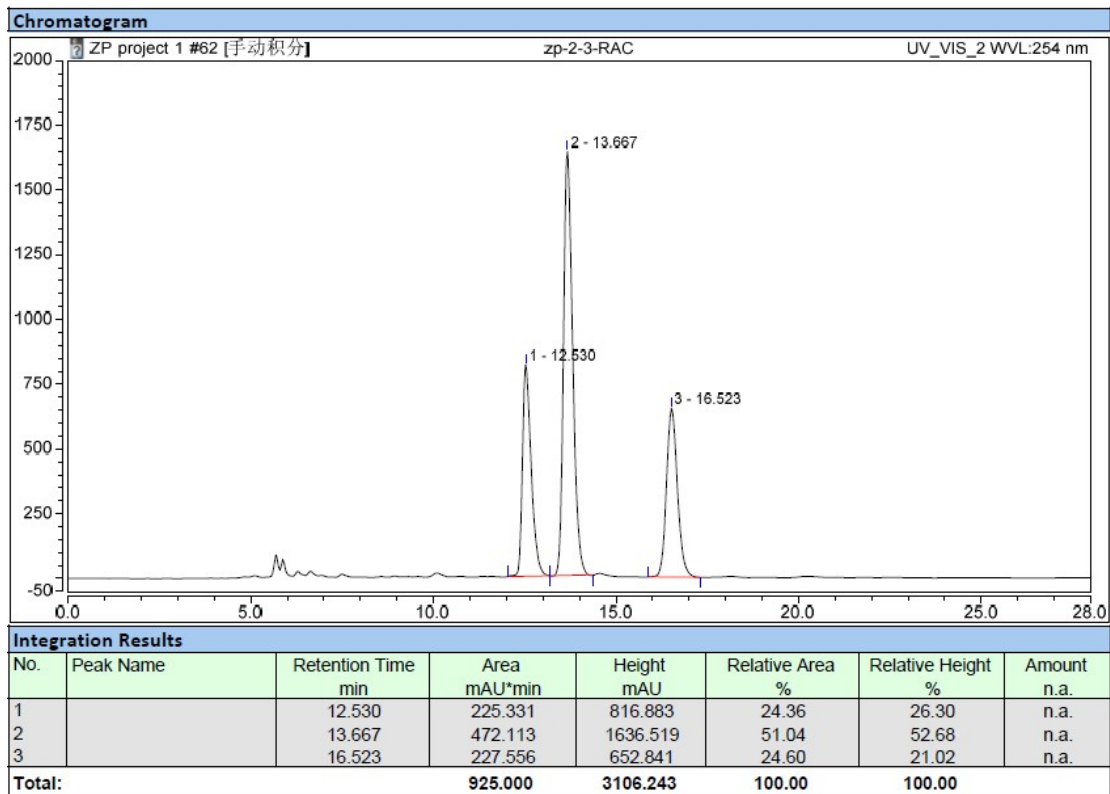
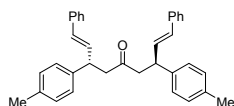


11. HPLC traces of optically active compounds

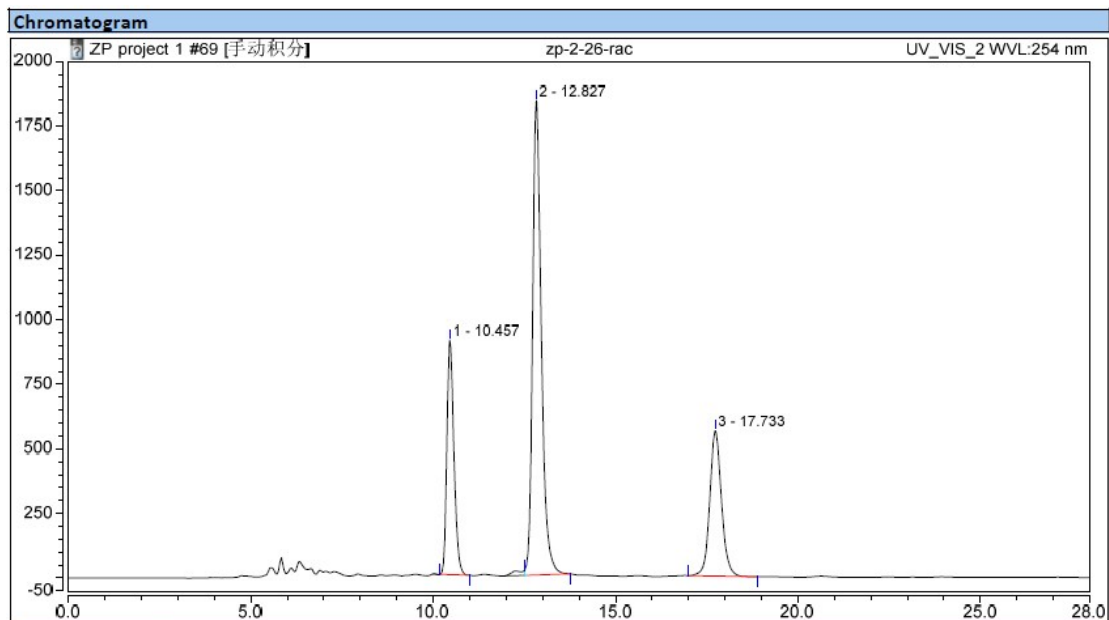
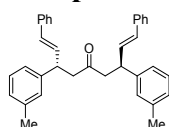
Compound 3aa



Compound 3ba

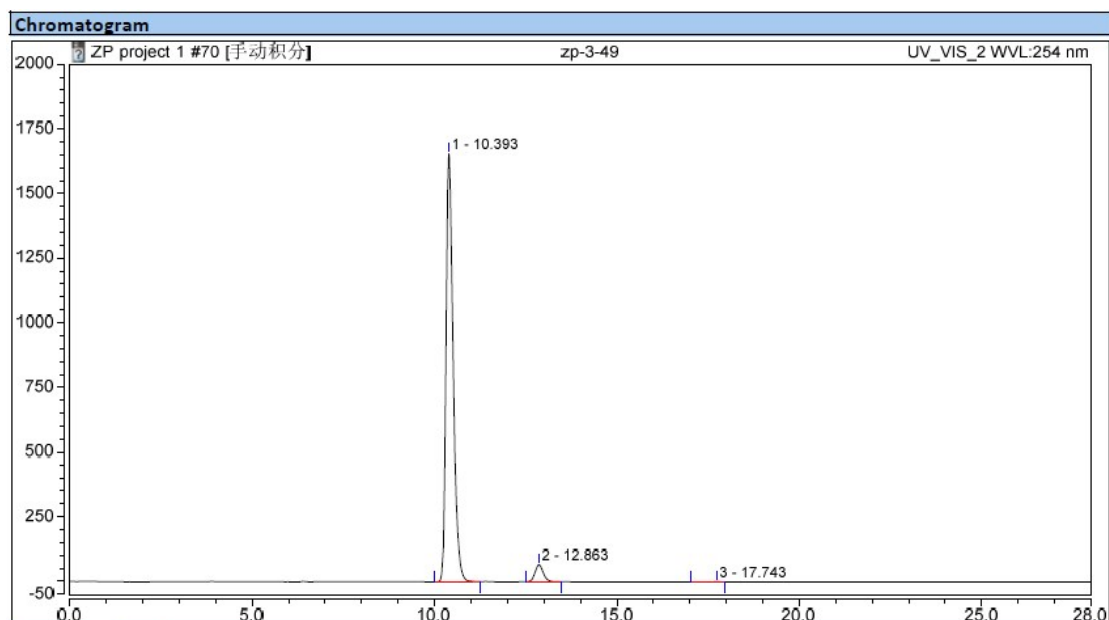


Compound 3ca



Integration Results

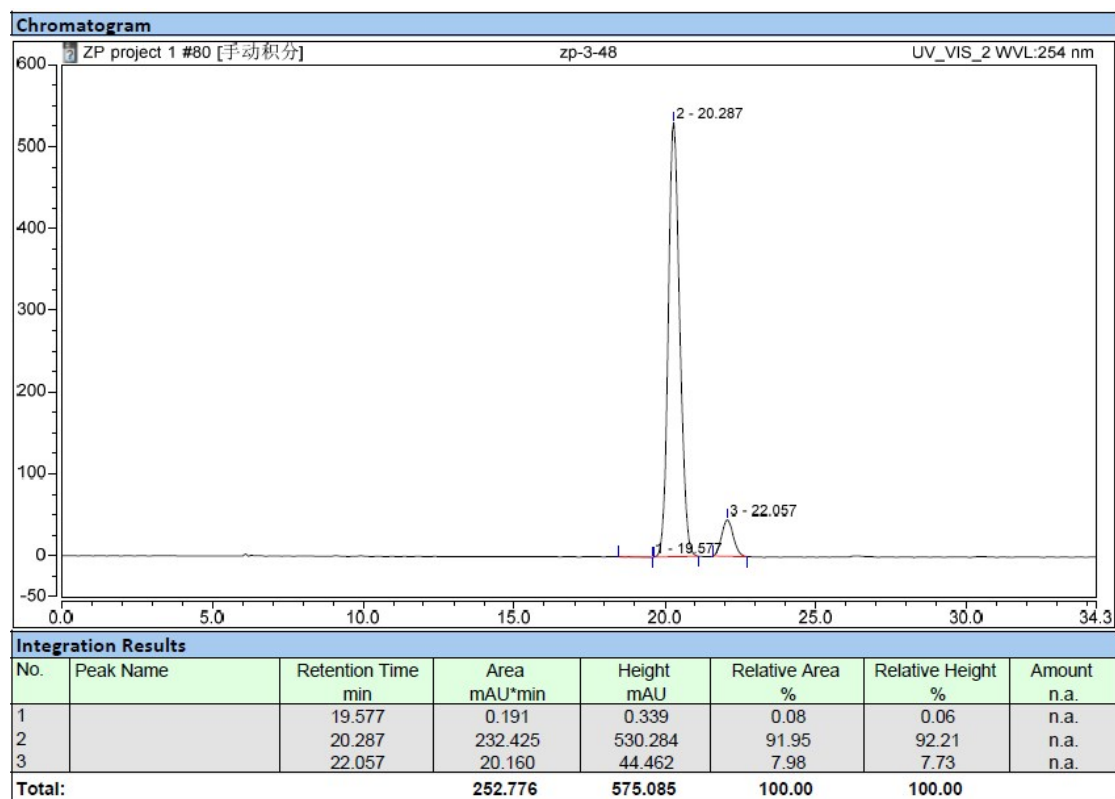
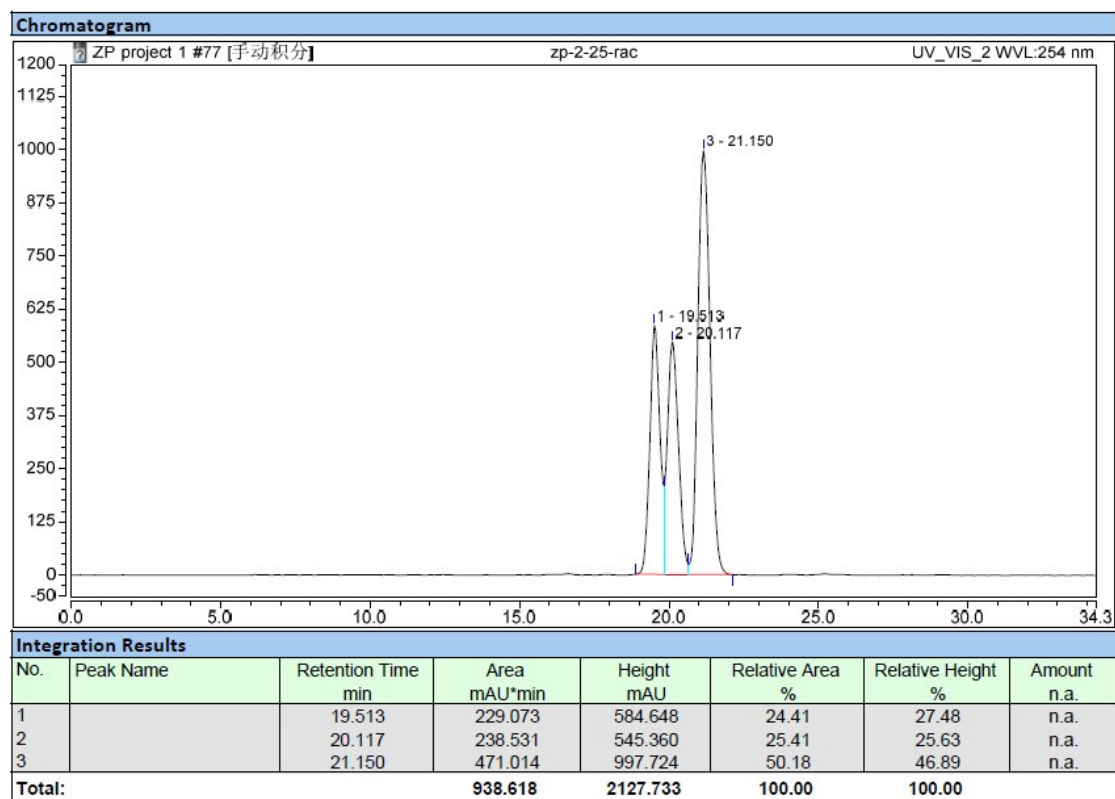
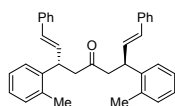
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.457	200.363	908.762	21.84	27.47	n.a.
2		12.827	507.706	1836.402	55.35	55.52	n.a.
3		17.733	209.220	562.660	22.81	17.01	n.a.
Total:			917.290	3307.825	100.00	100.00	



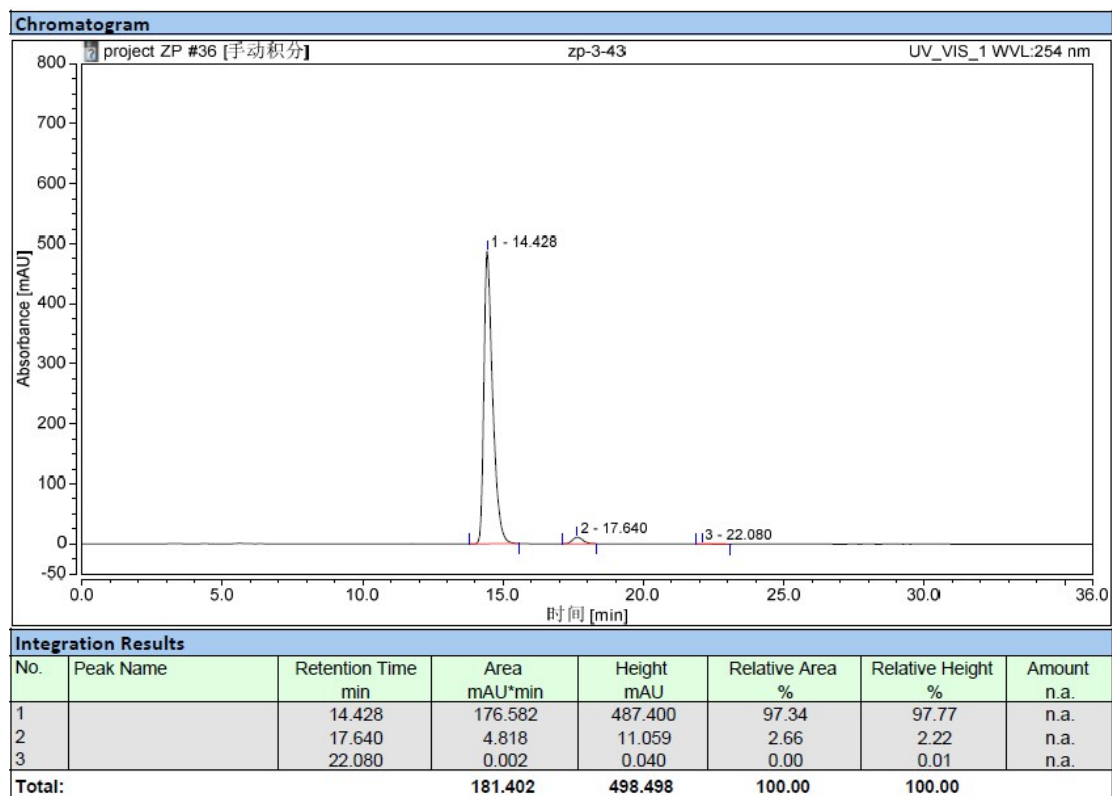
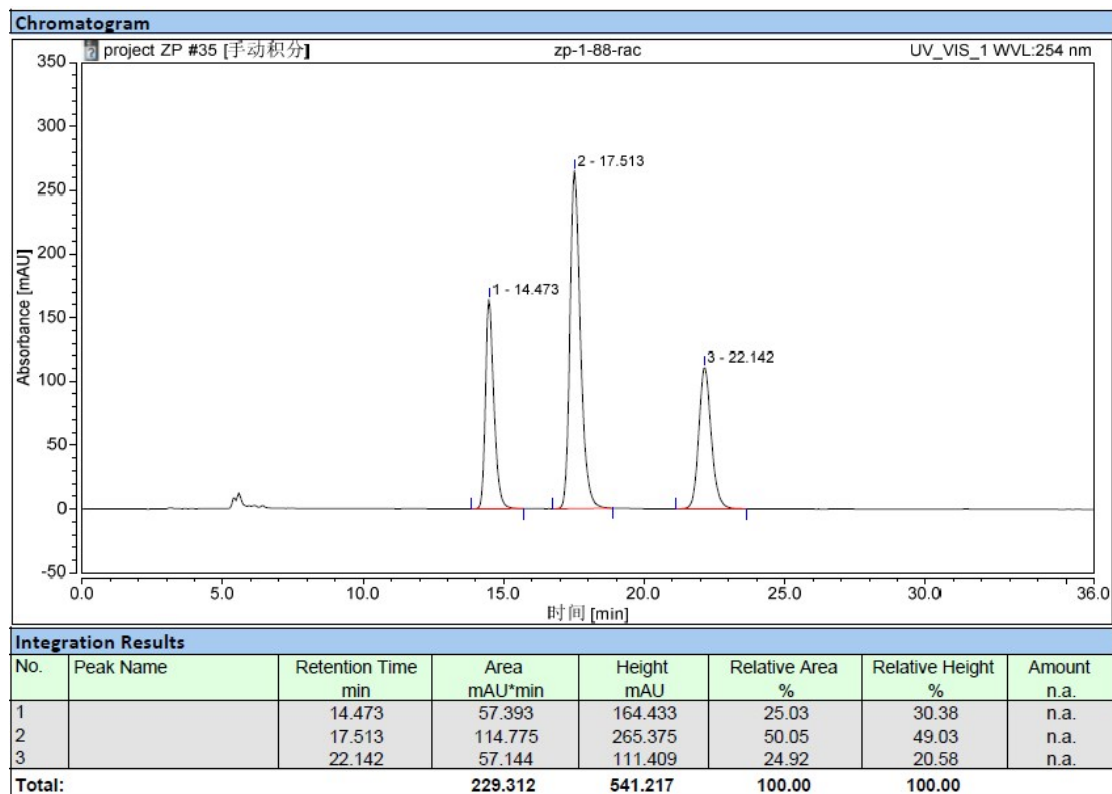
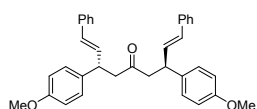
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.393	370.388	1655.885	95.51	96.11	n.a.
2		12.863	17.316	66.639	4.47	3.87	n.a.
3		17.743	0.083	0.410	0.02	0.02	n.a.
Total:			387.787	1722.934	100.00	100.00	

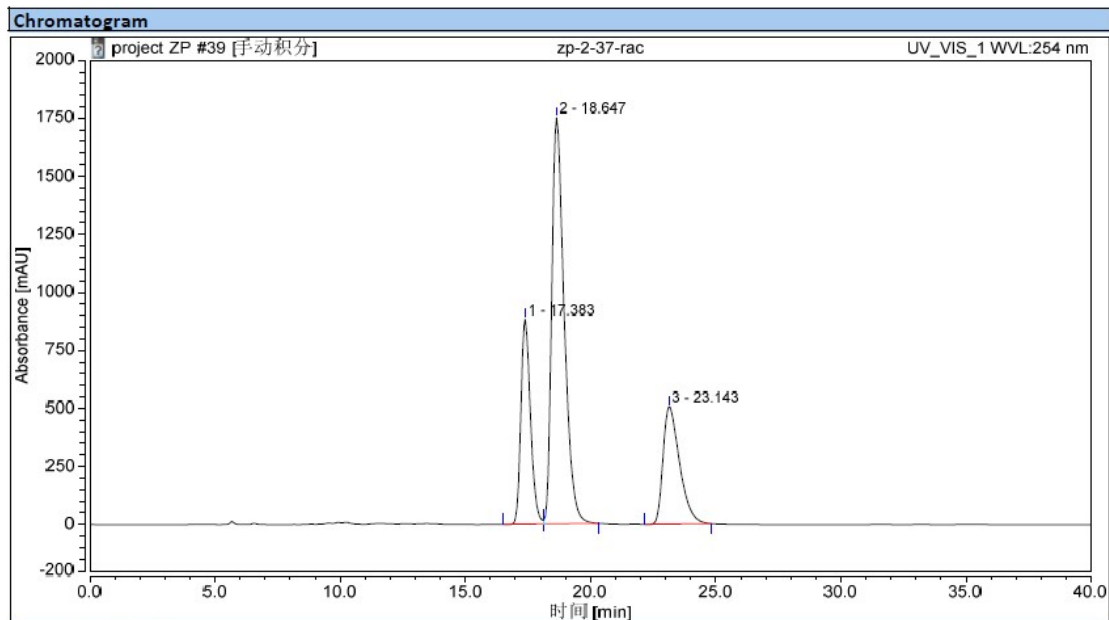
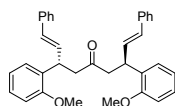
Compound 3da



Compound 3ea

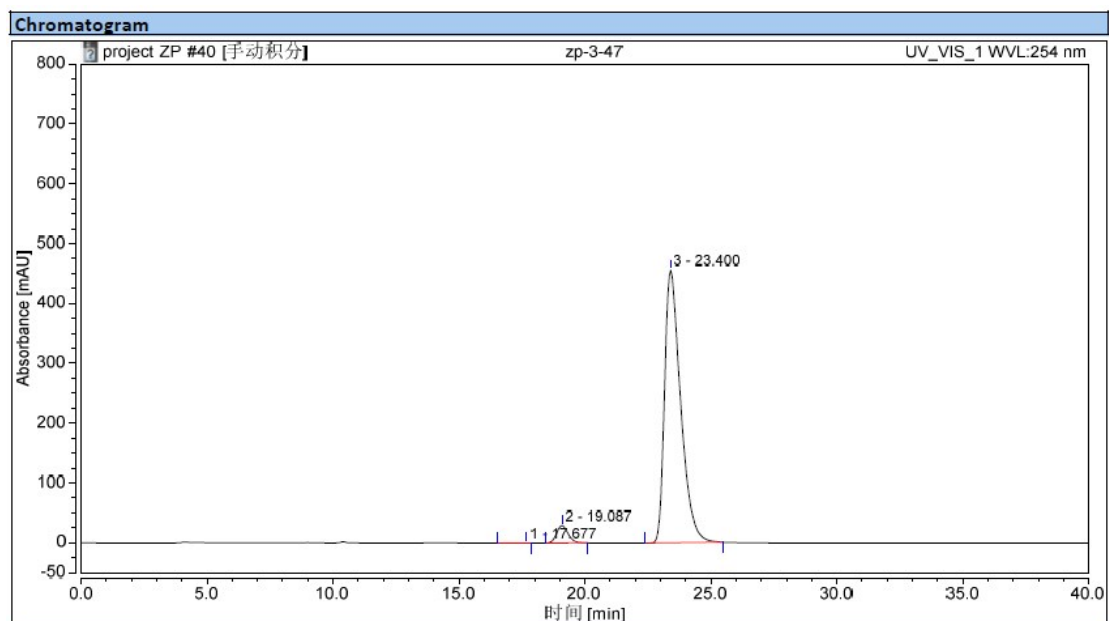


Compound 3fa



Integration Results

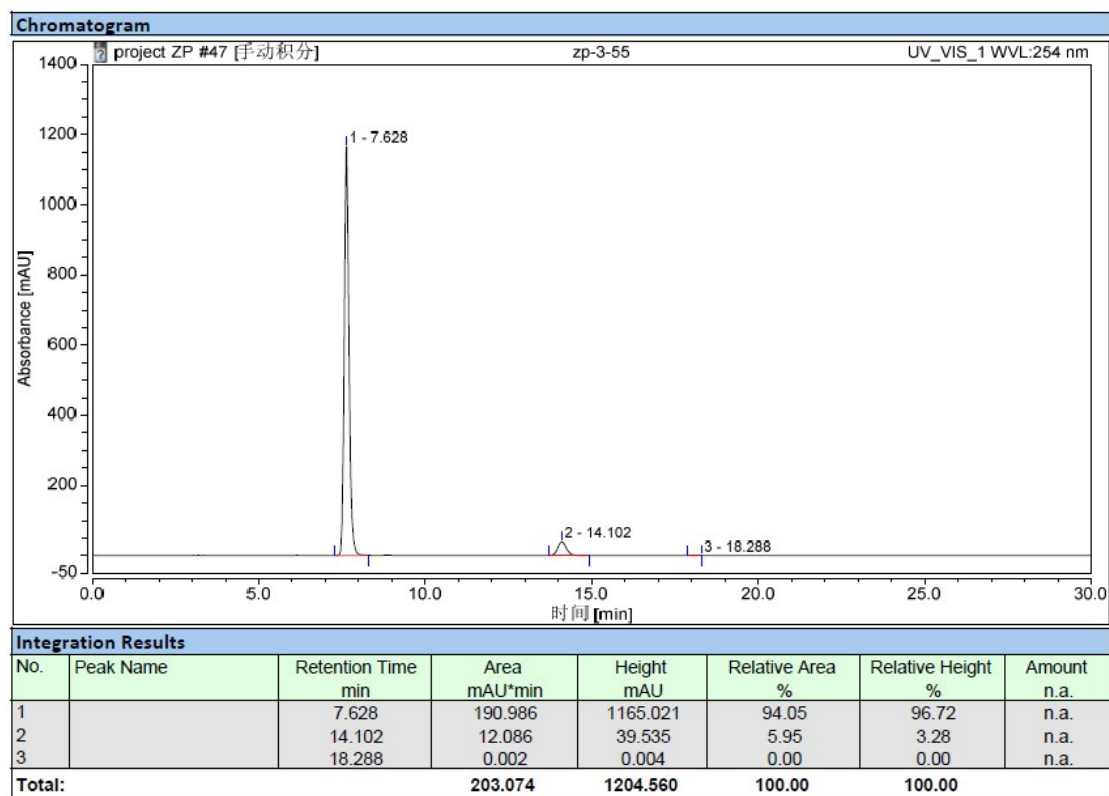
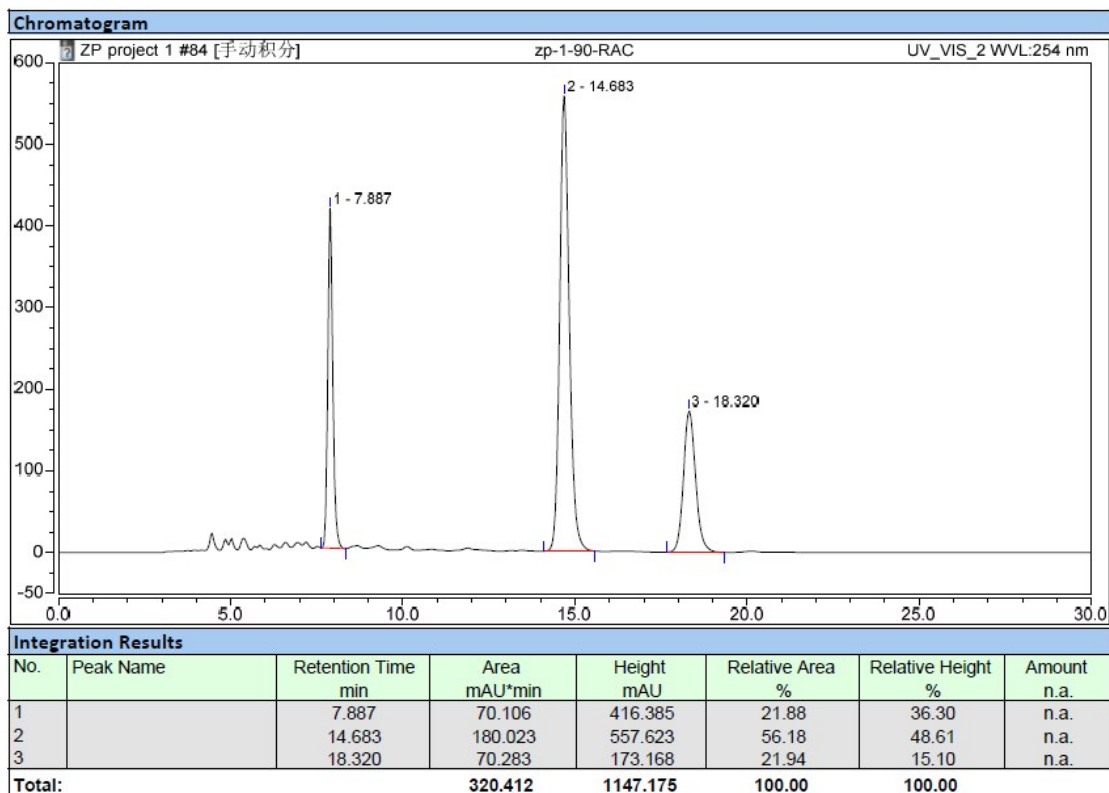
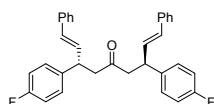
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.383	389.181	881.319	21.84	28.09	n.a.
2		18.647	1005.087	1749.433	56.42	55.76	n.a.
3		23.143	387.307	506.473	21.74	16.14	n.a.
Total:			1781.576	3137.225	100.00	100.00	



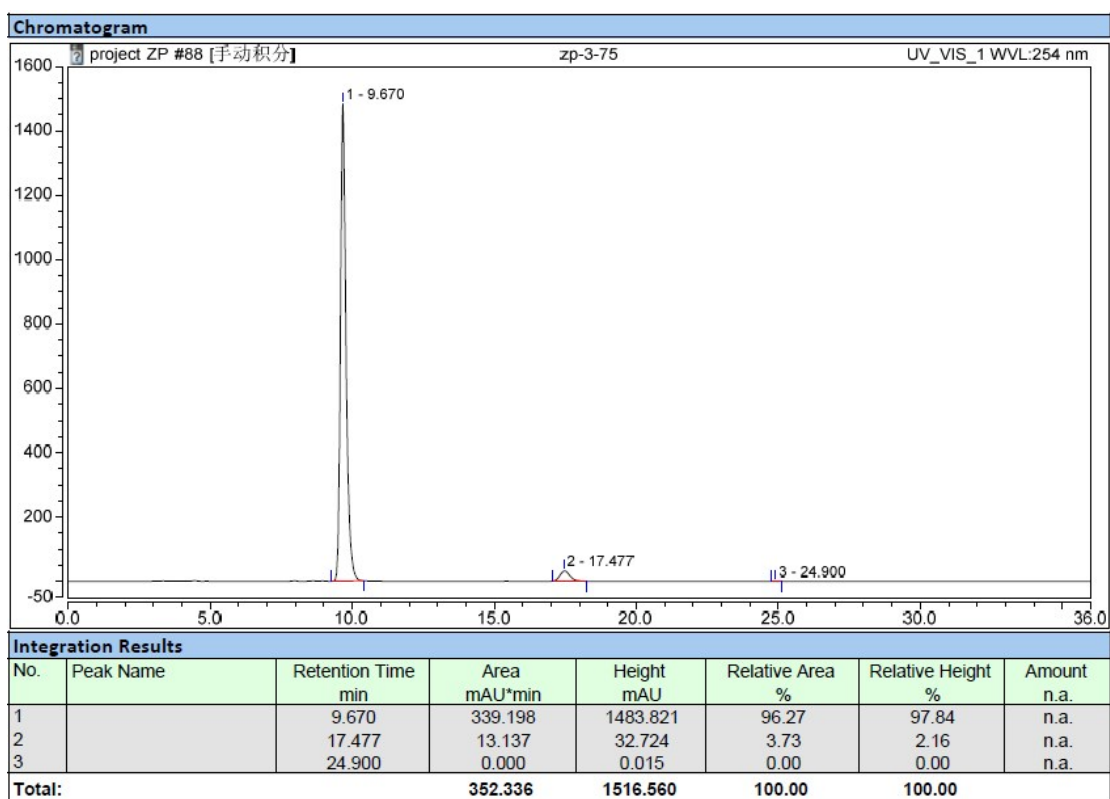
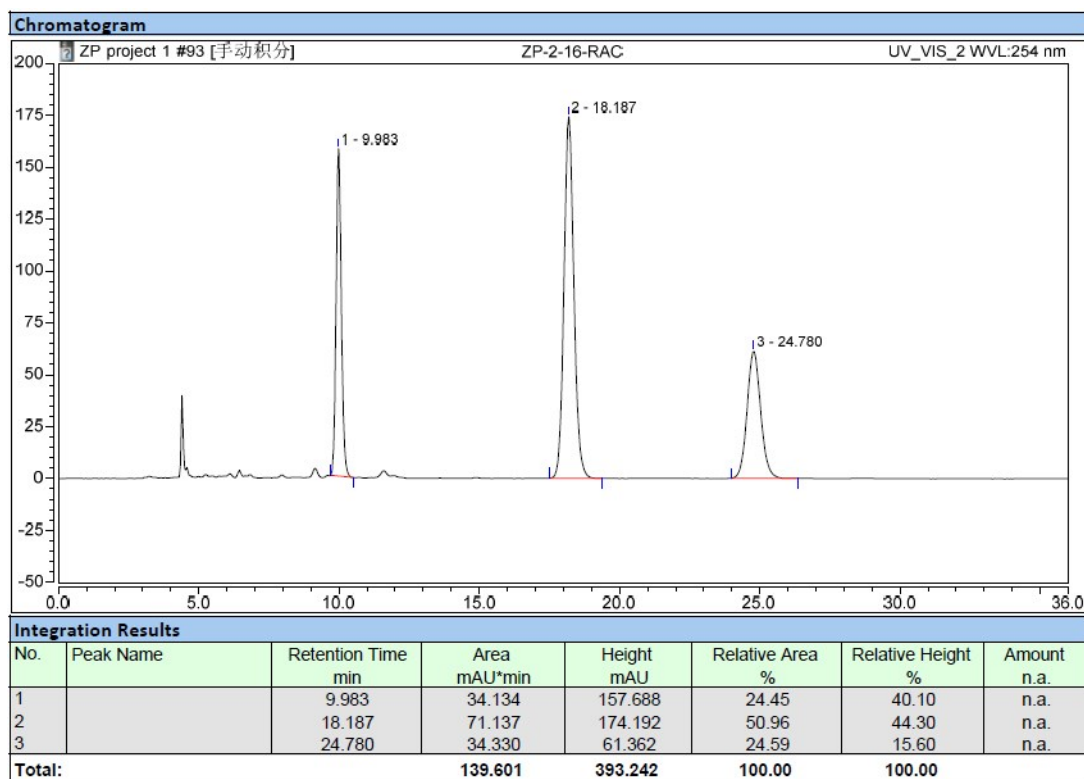
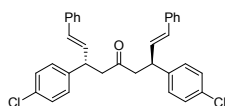
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.677	0.004	0.093	0.00	0.02	n.a.
2		19.087	15.421	29.164	4.39	6.02	n.a.
3		23.400	335.562	455.341	95.61	93.96	n.a.
Total:			350.988	484.598	100.00	100.00	

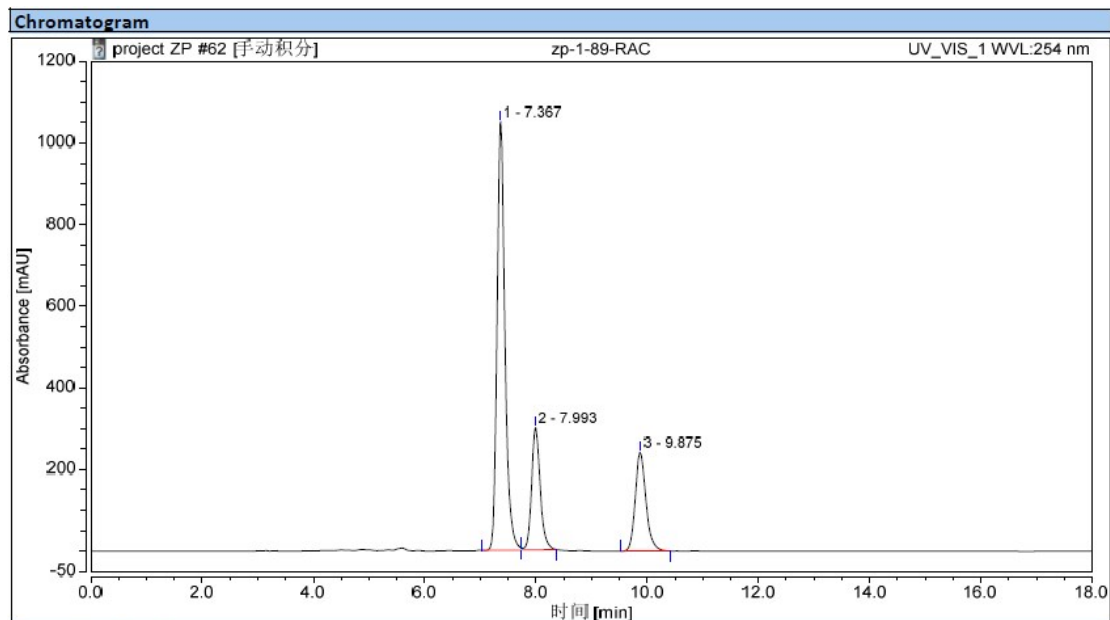
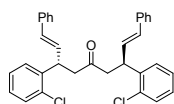
Compound 3ga



Compound 3ha

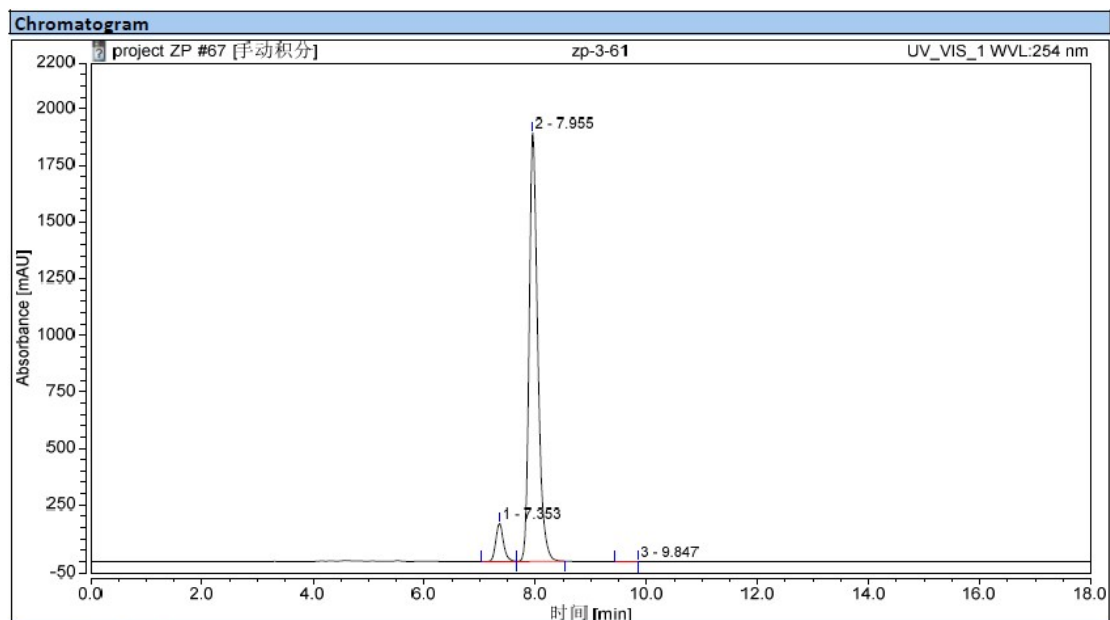


Compound 3ia



Integration Results

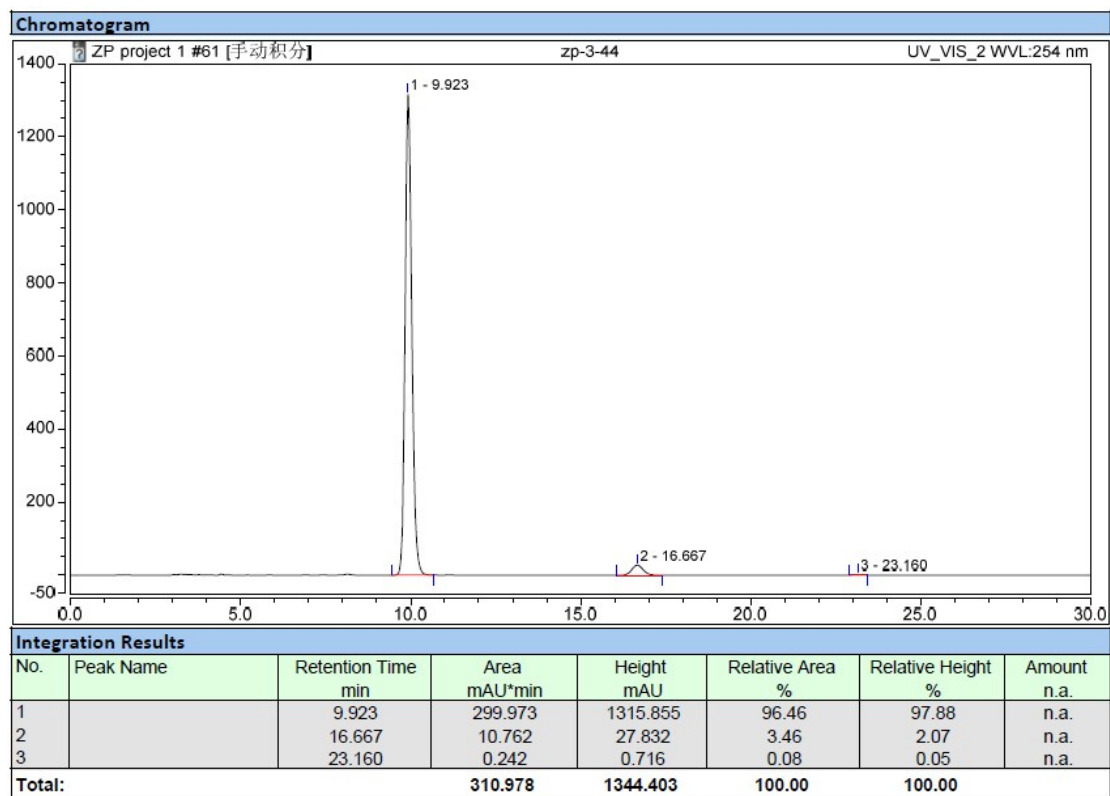
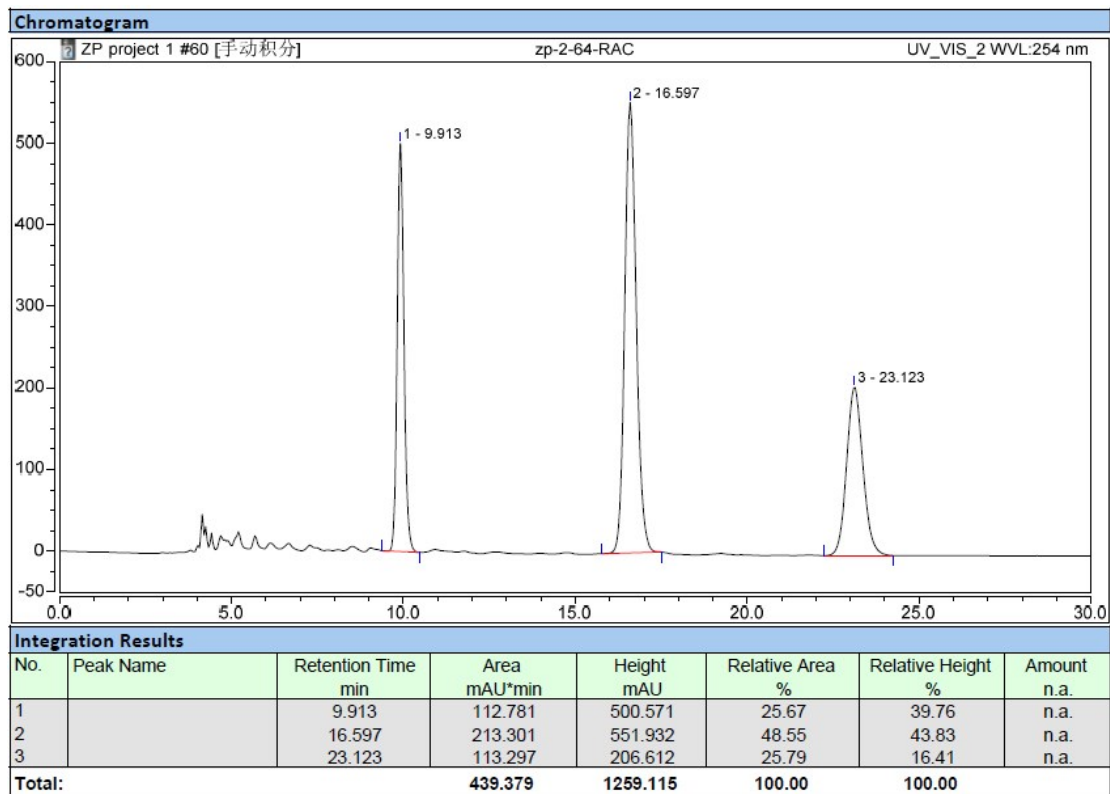
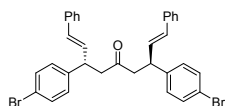
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.367	172.102	1050.097	61.54	65.96	n.a.
2		7.993	53.777	299.323	19.23	18.80	n.a.
3		9.875	53.771	242.672	19.23	15.24	n.a.
Total:			279.650	1592.092	100.00	100.00	



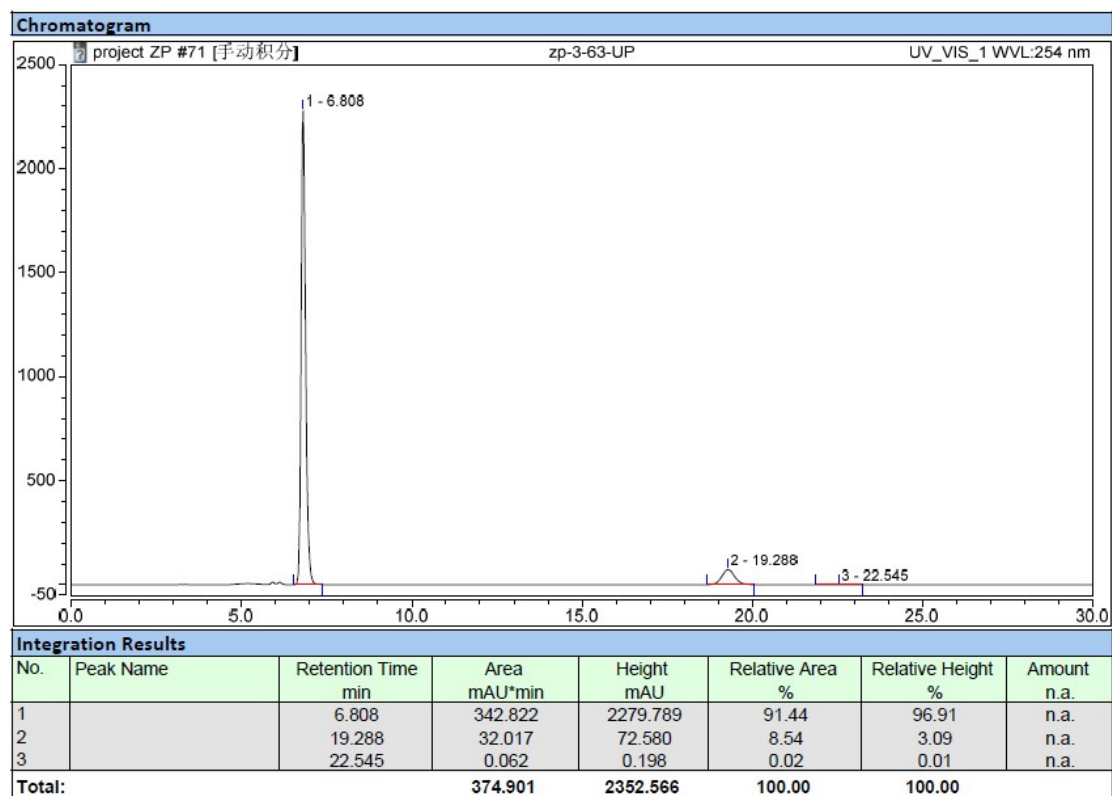
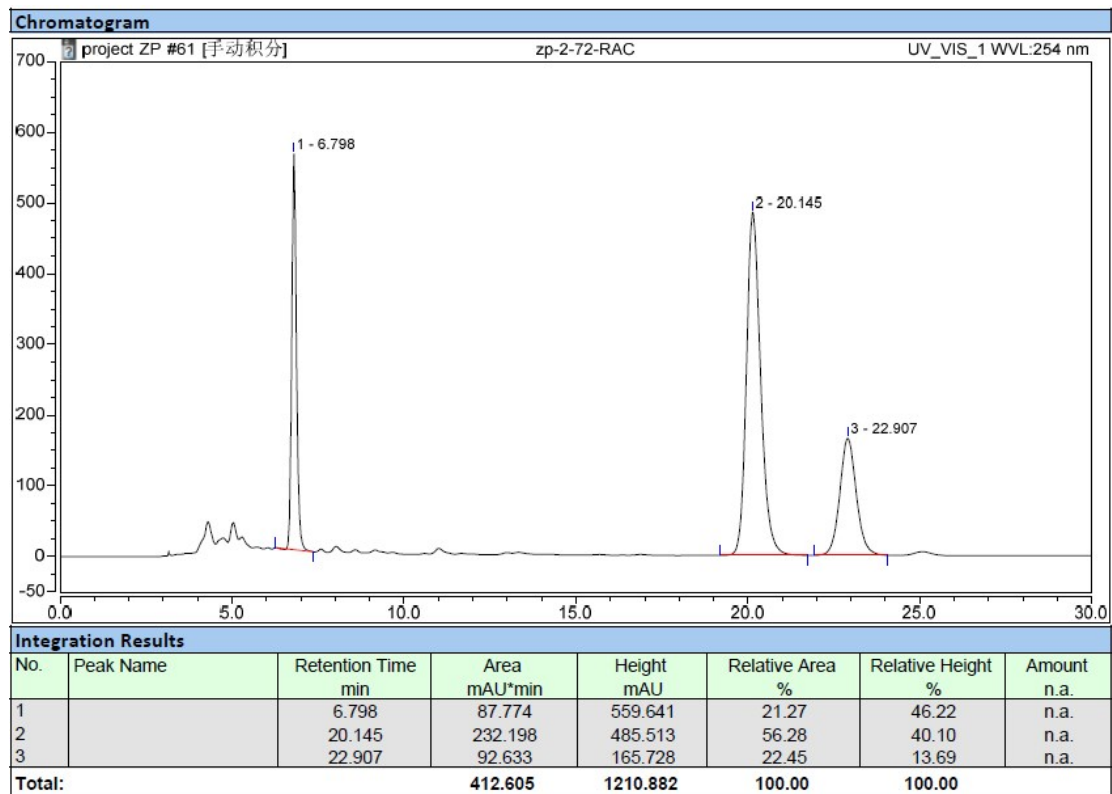
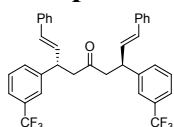
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.353	26.976	169.315	7.36	8.22	n.a.
2		7.955	339.701	1891.332	92.64	91.78	n.a.
3		9.847	0.003	0.007	0.00	0.00	n.a.
Total:			366.680	2060.654	100.00	100.00	

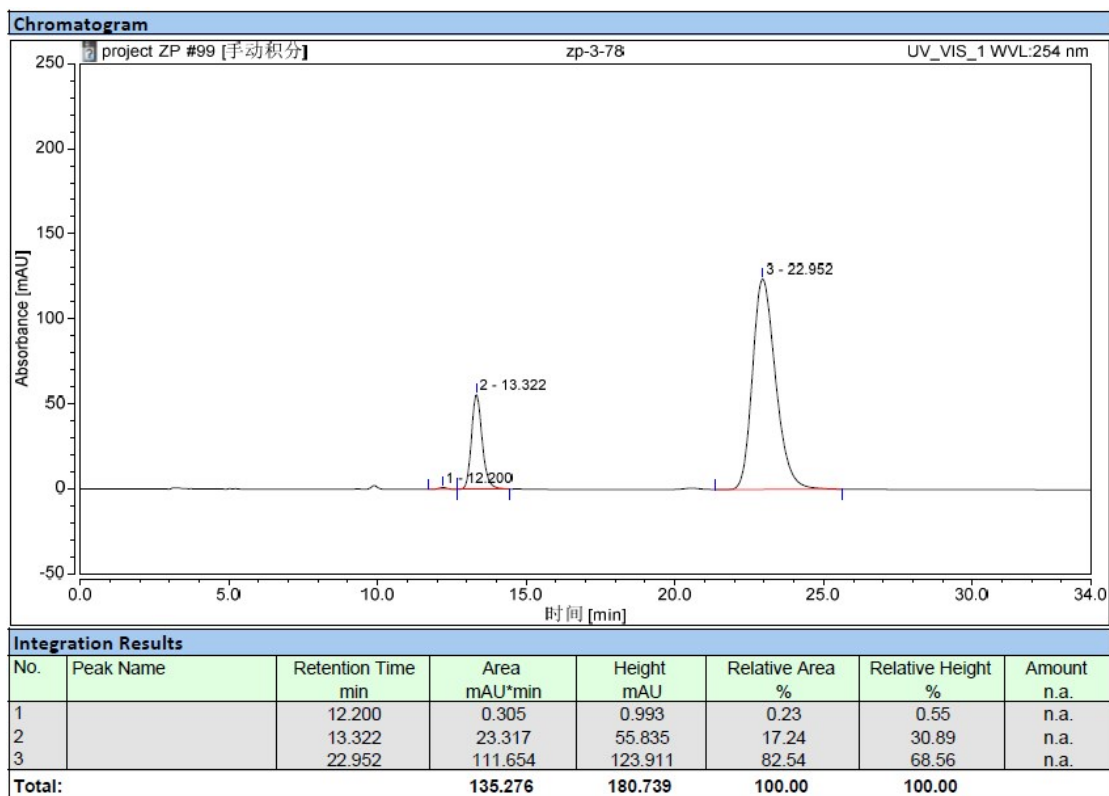
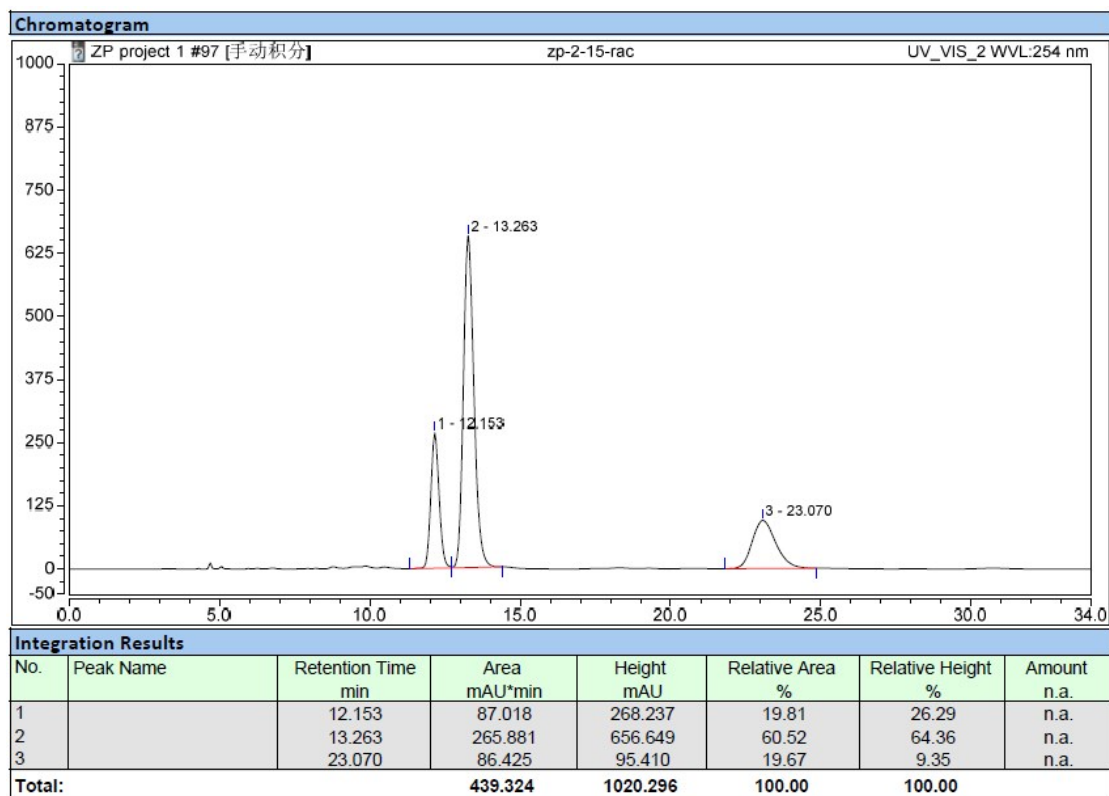
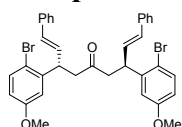
Compound 3ja



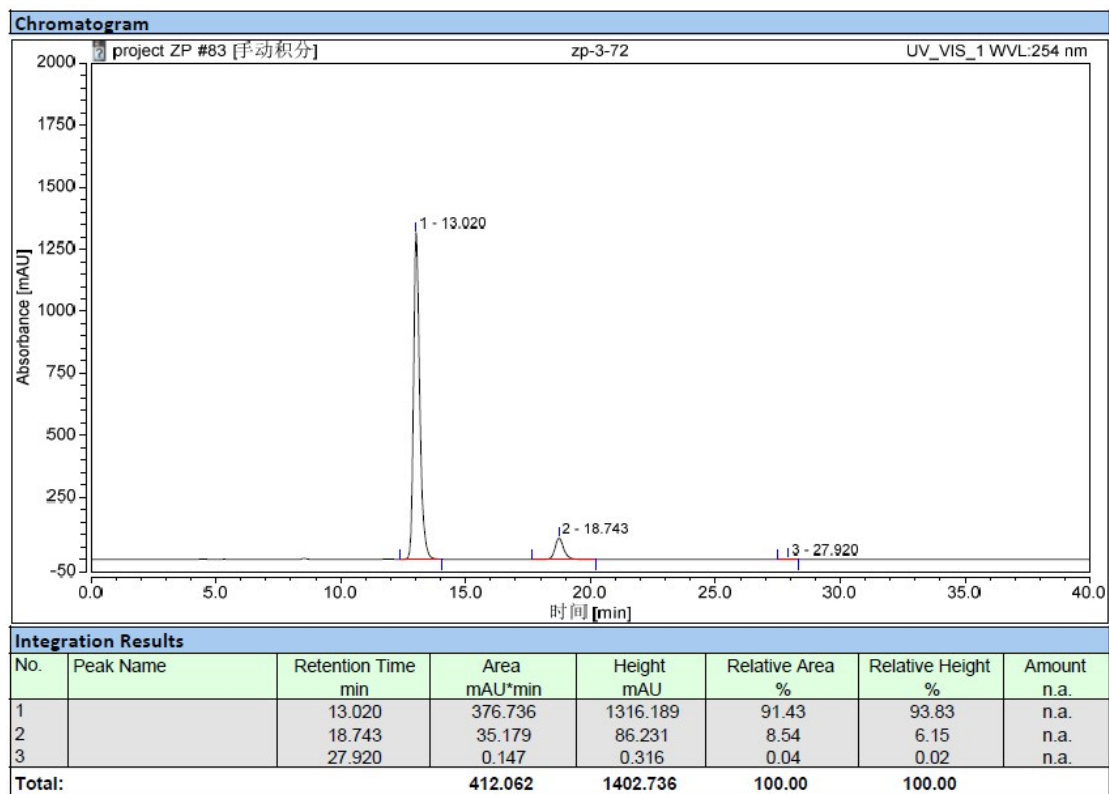
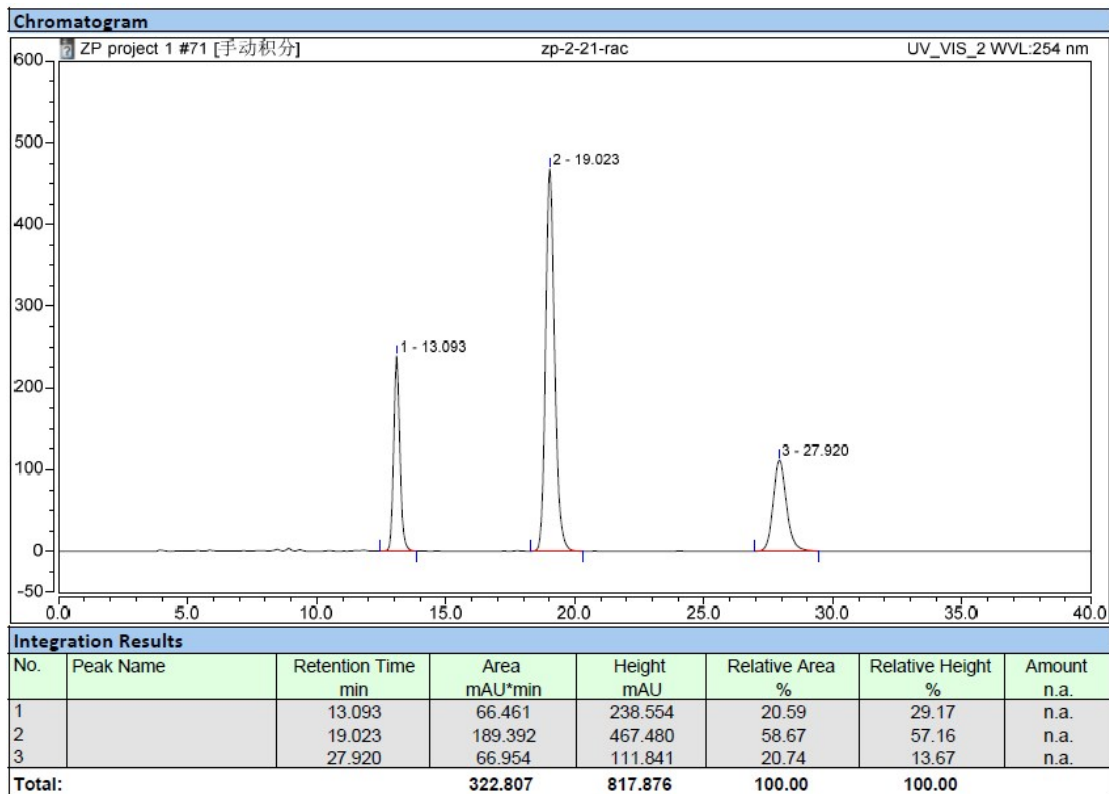
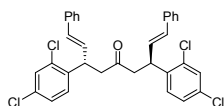
Compound 3ka



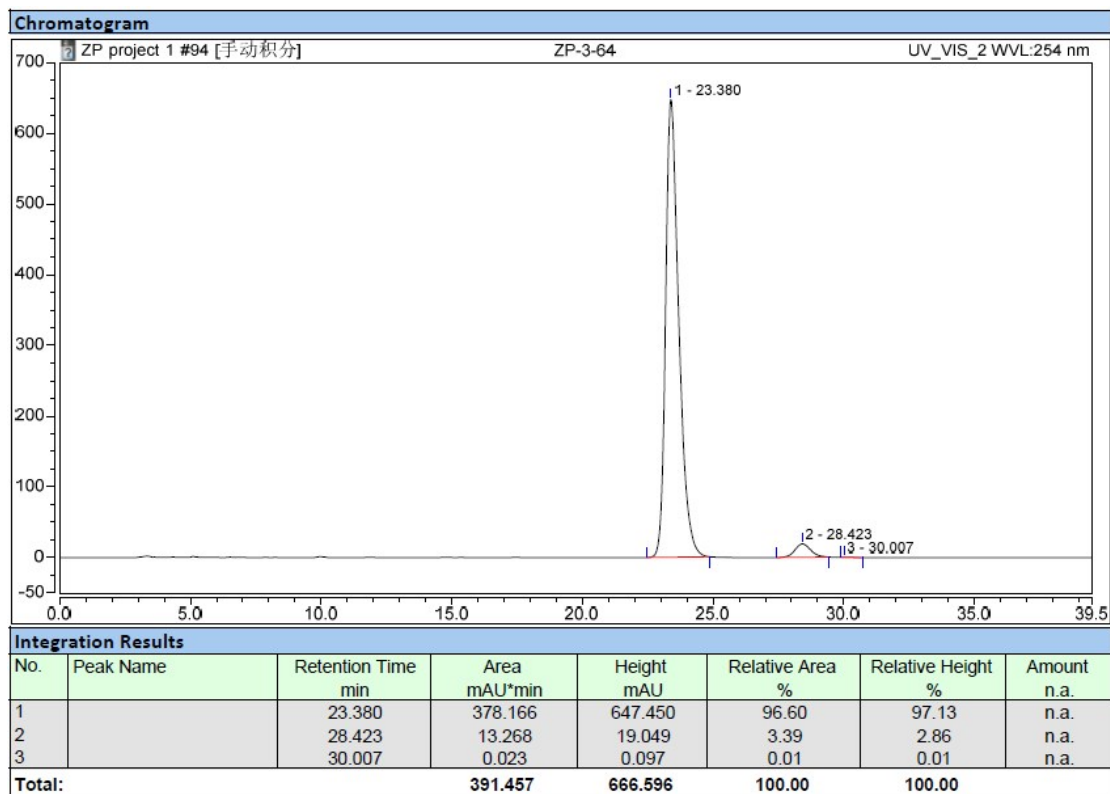
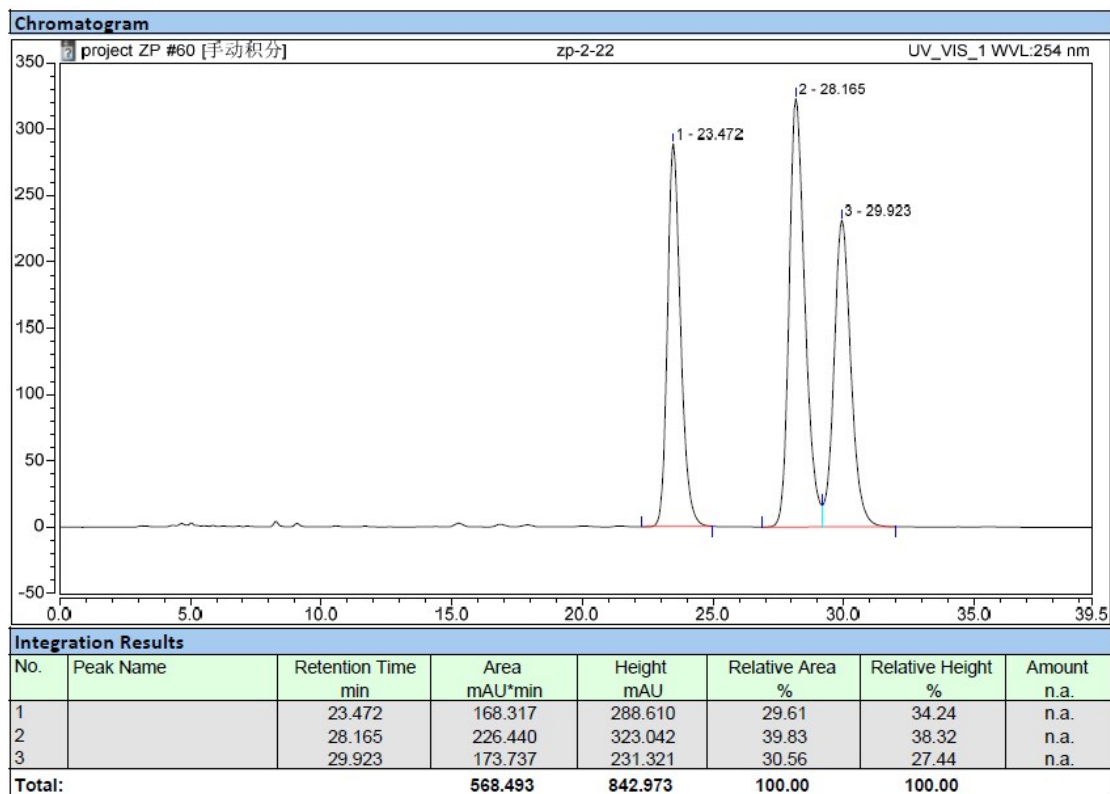
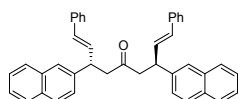
Compound 3la



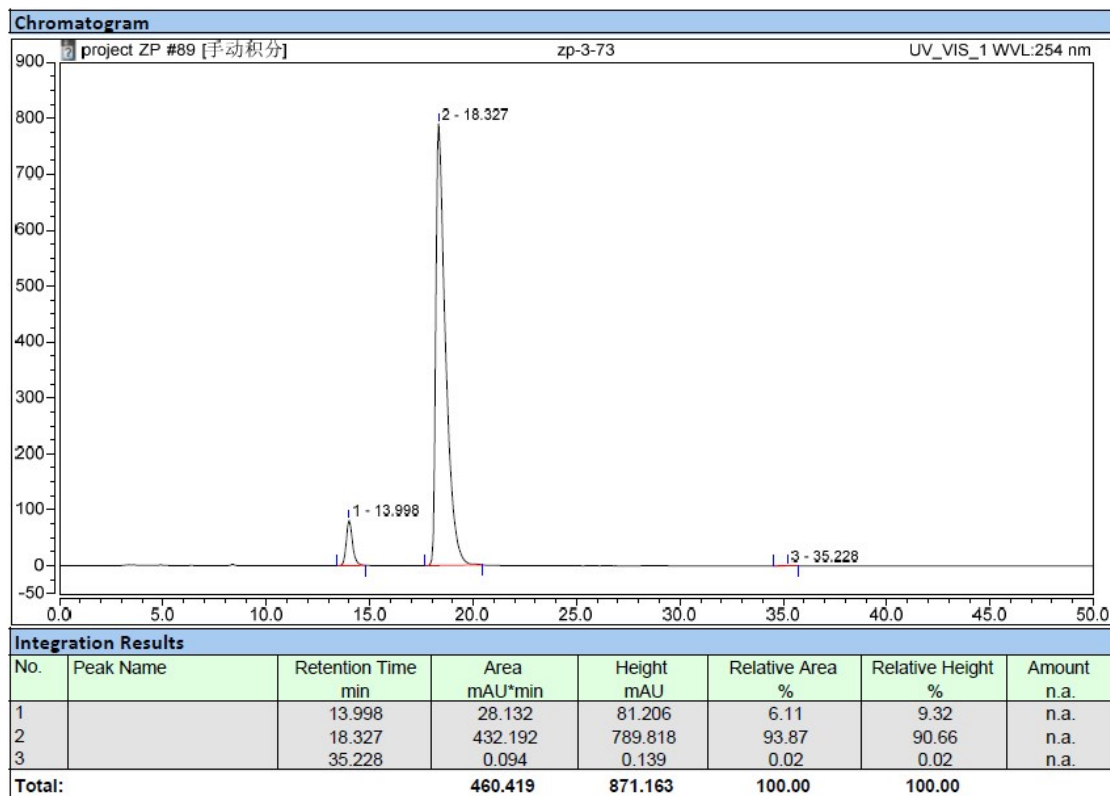
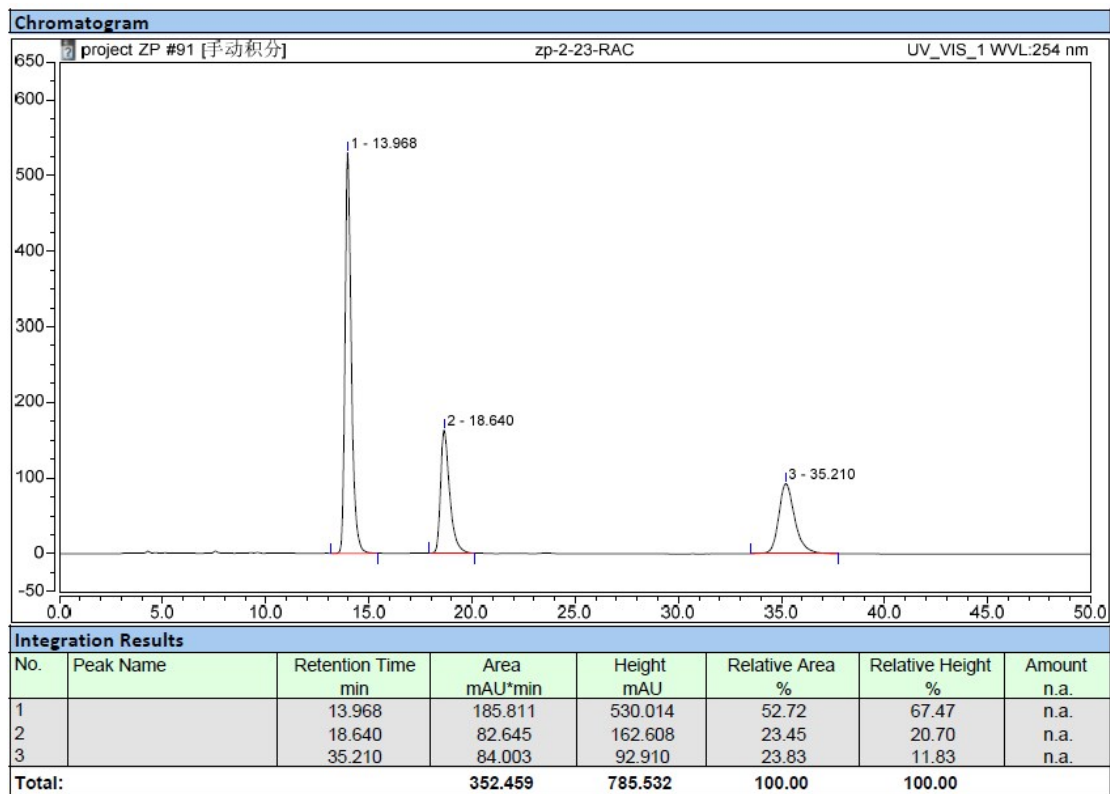
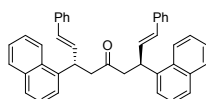
Compound 3ma



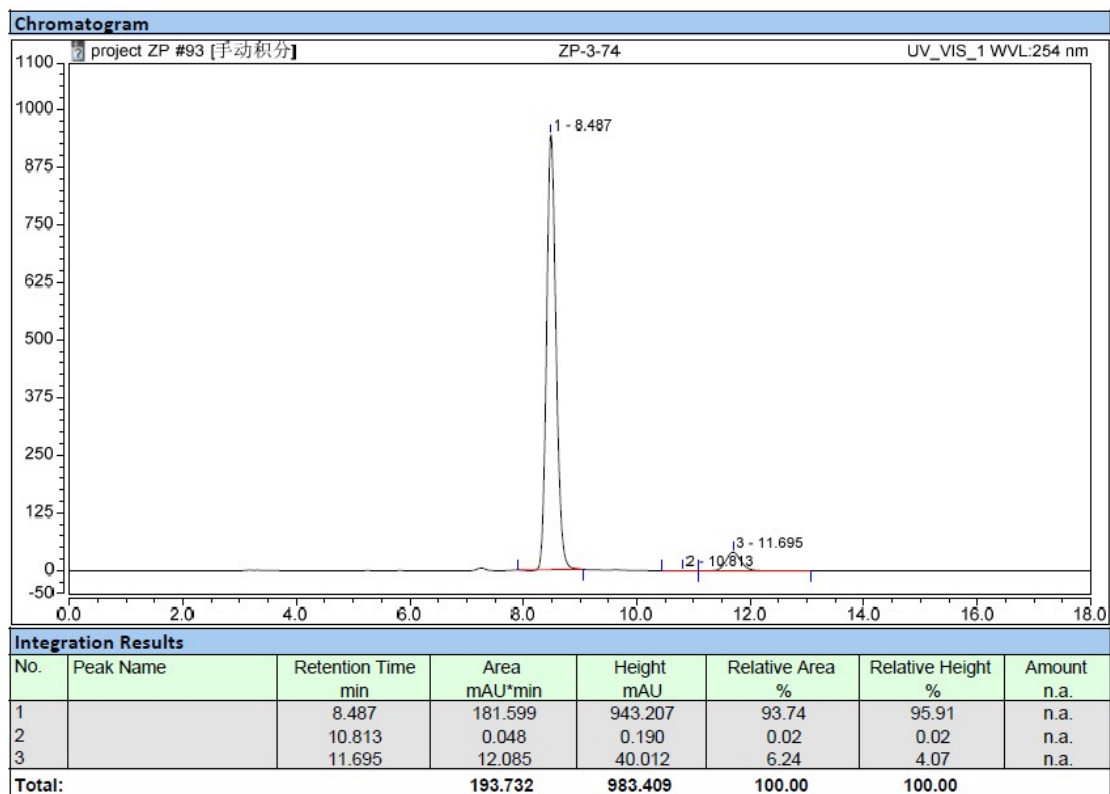
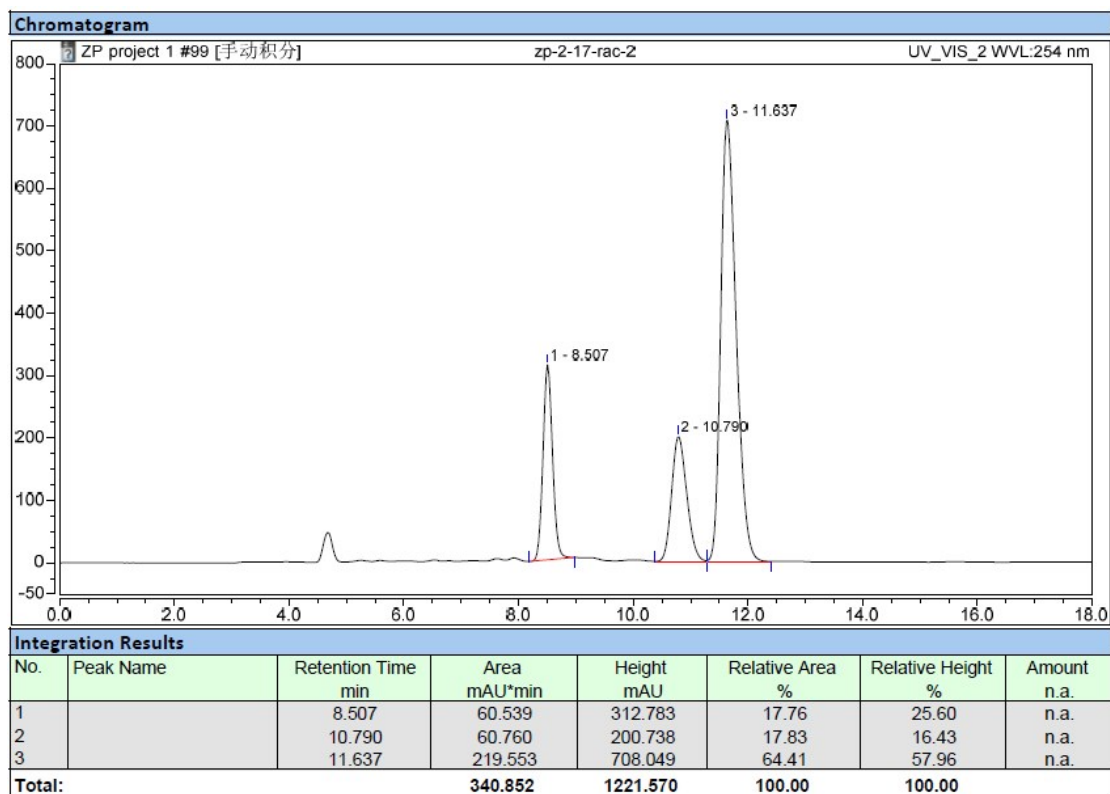
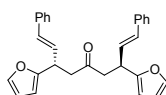
Compound 3na



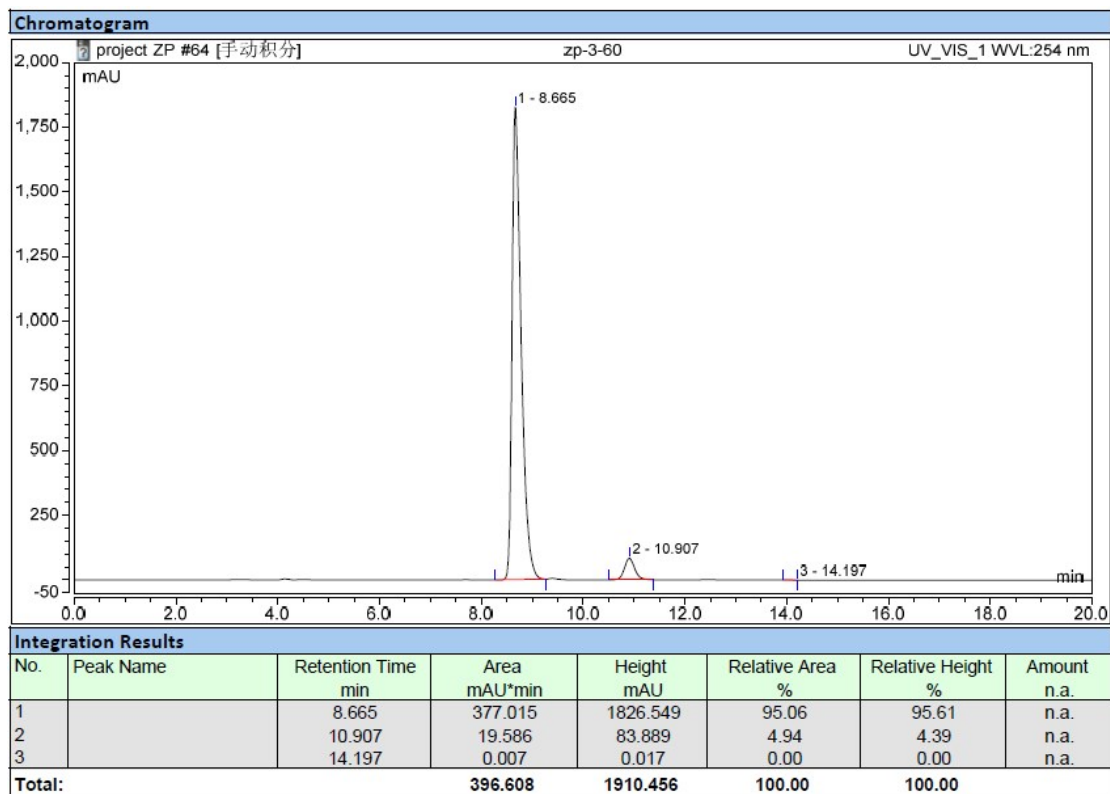
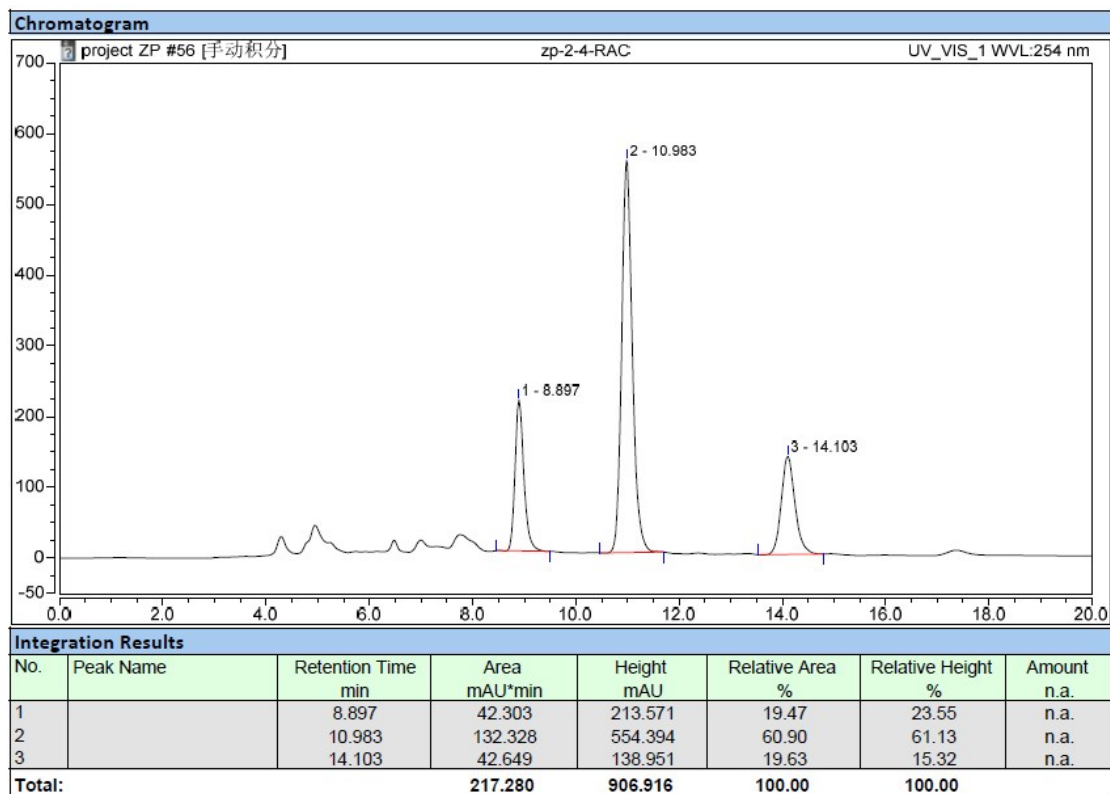
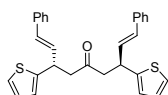
Compound 30a



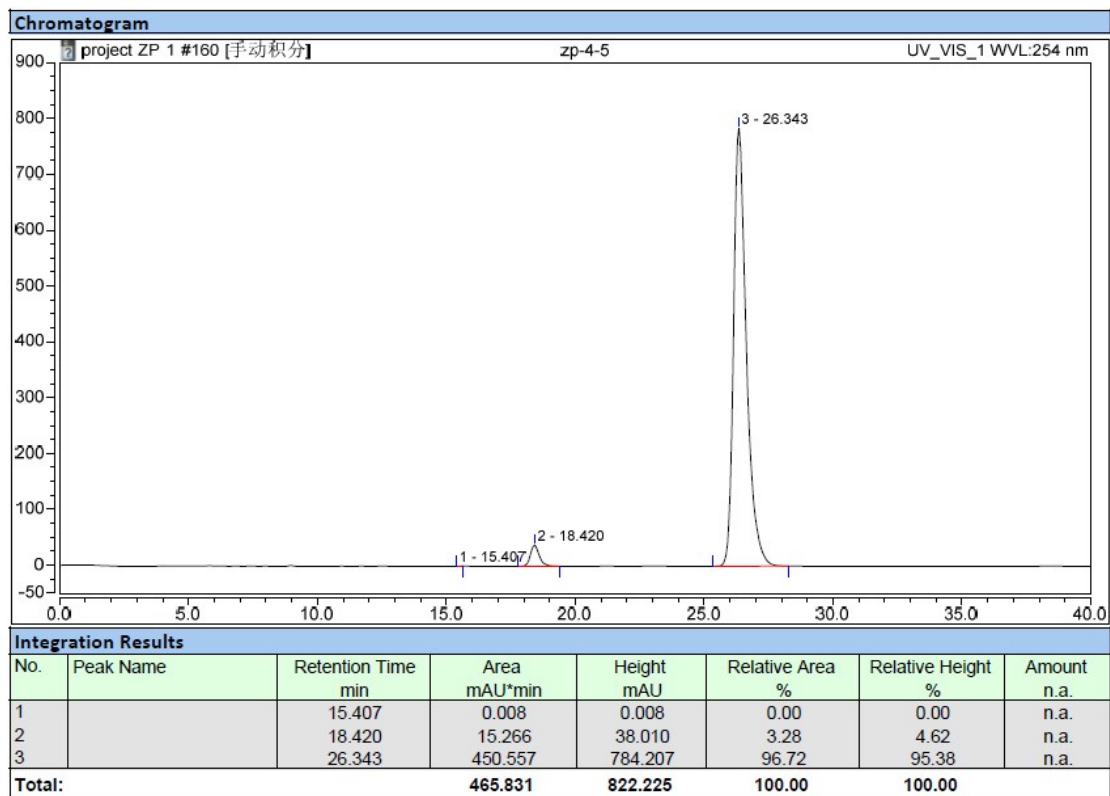
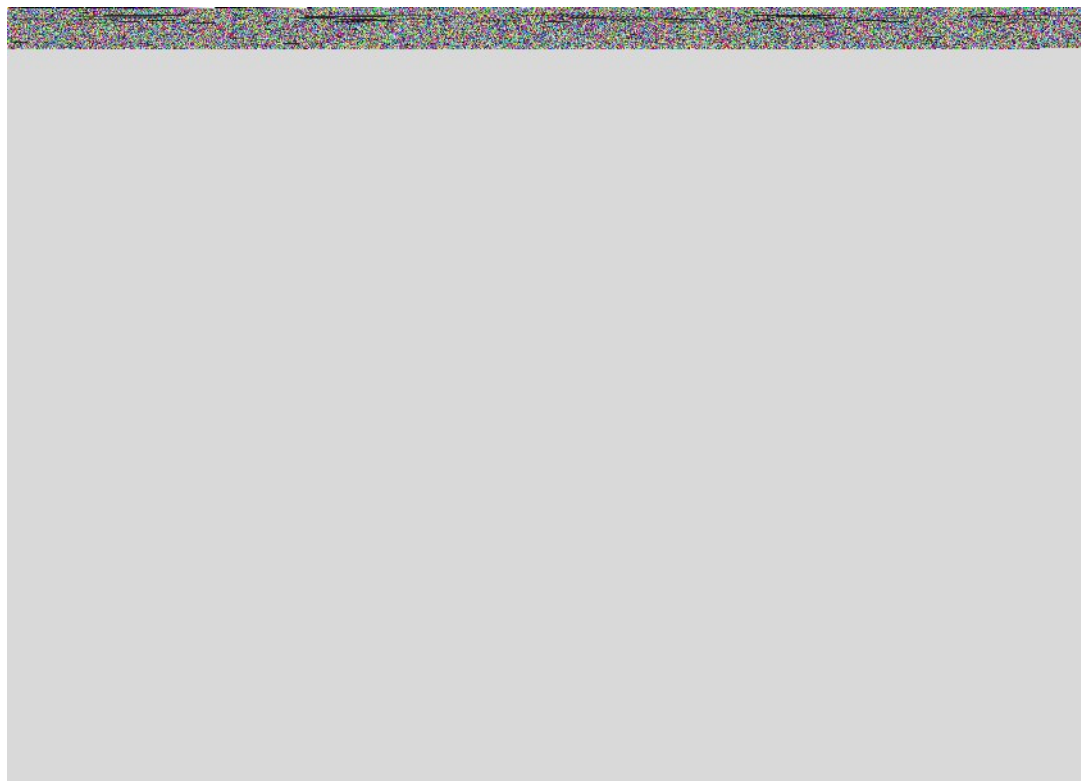
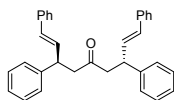
Compound 3pa



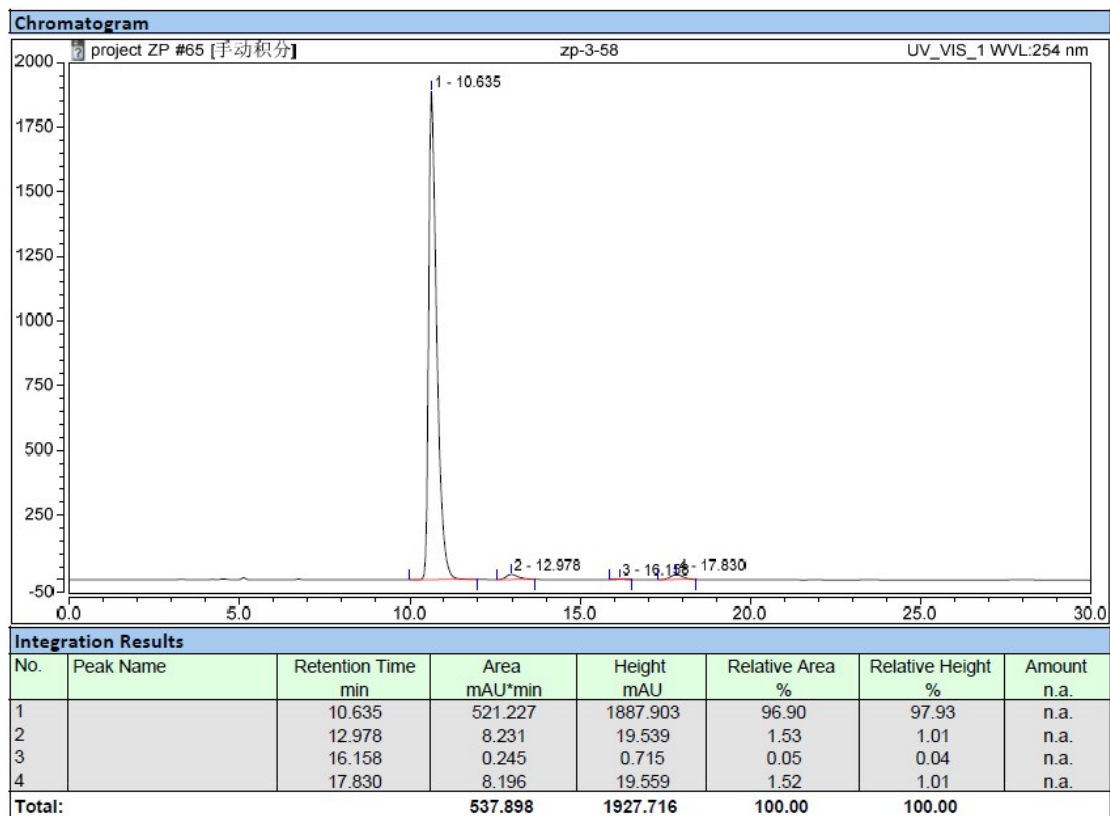
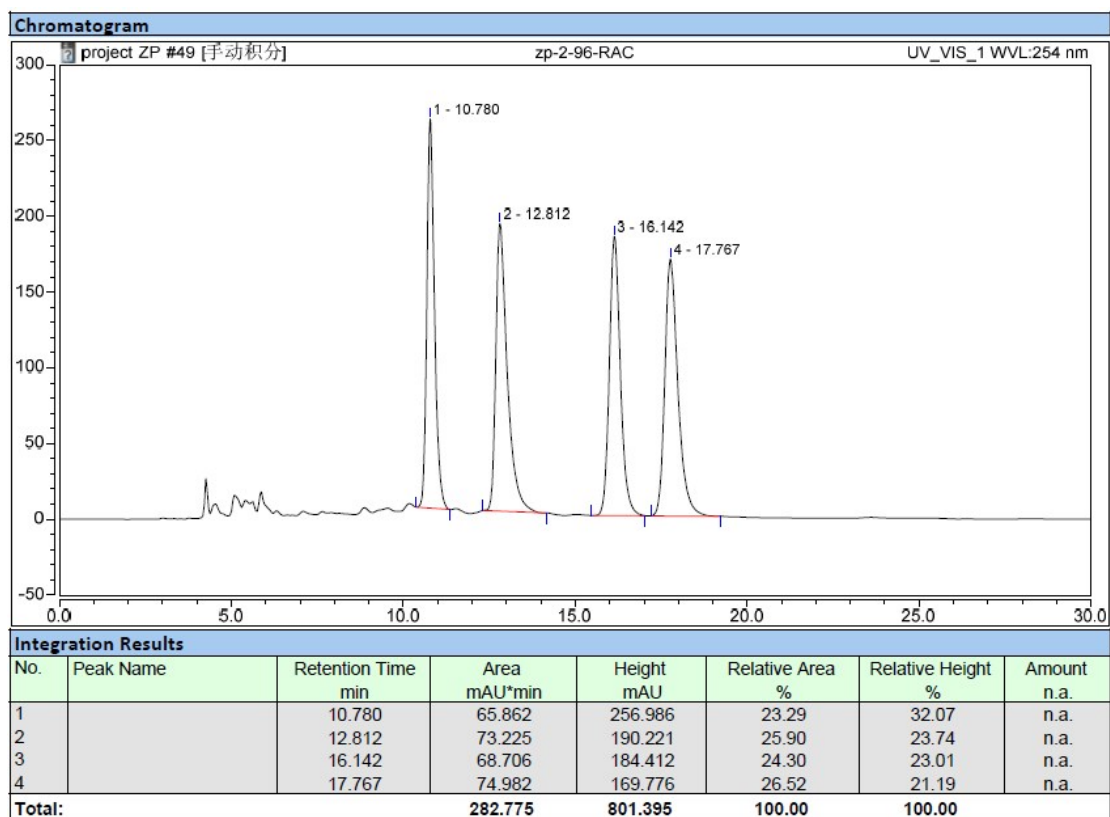
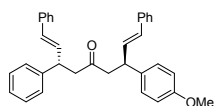
Compound 3qa



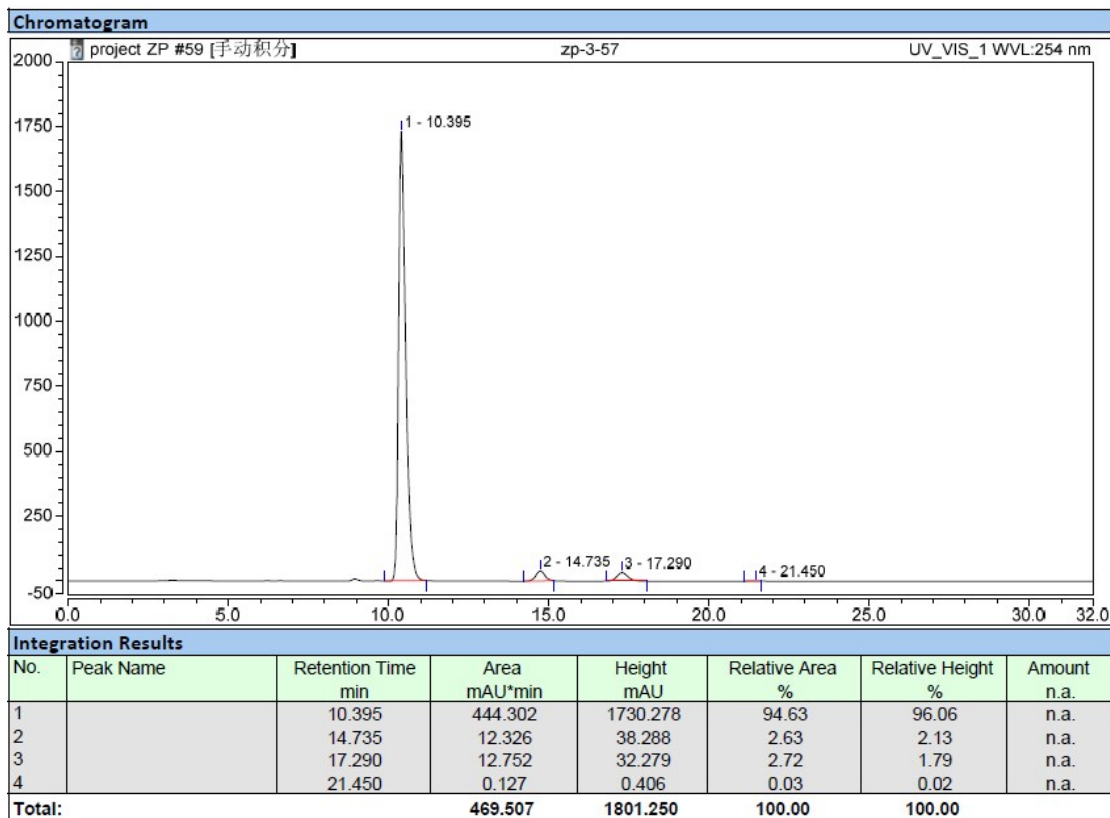
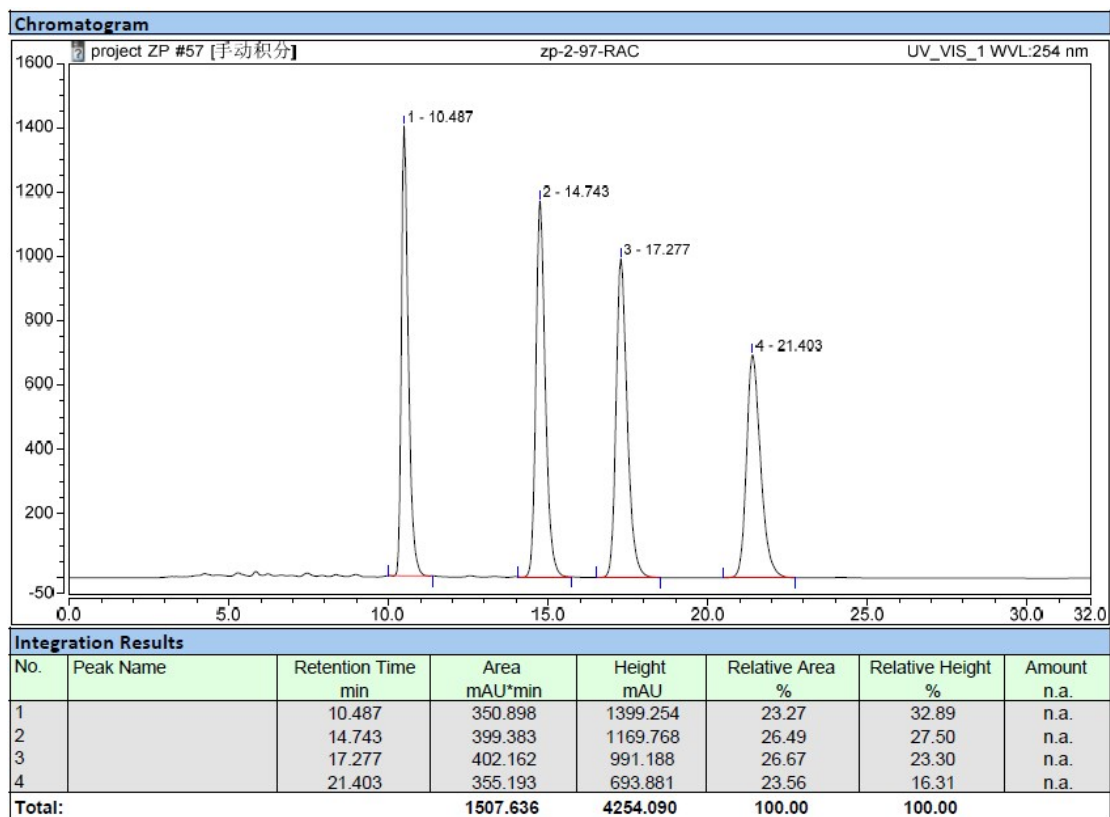
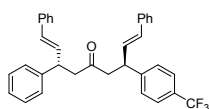
Compound 3aa'(using (S)-3,3'-(3,5-(CF₃)₂-C₆H₃)₂-BINOL)



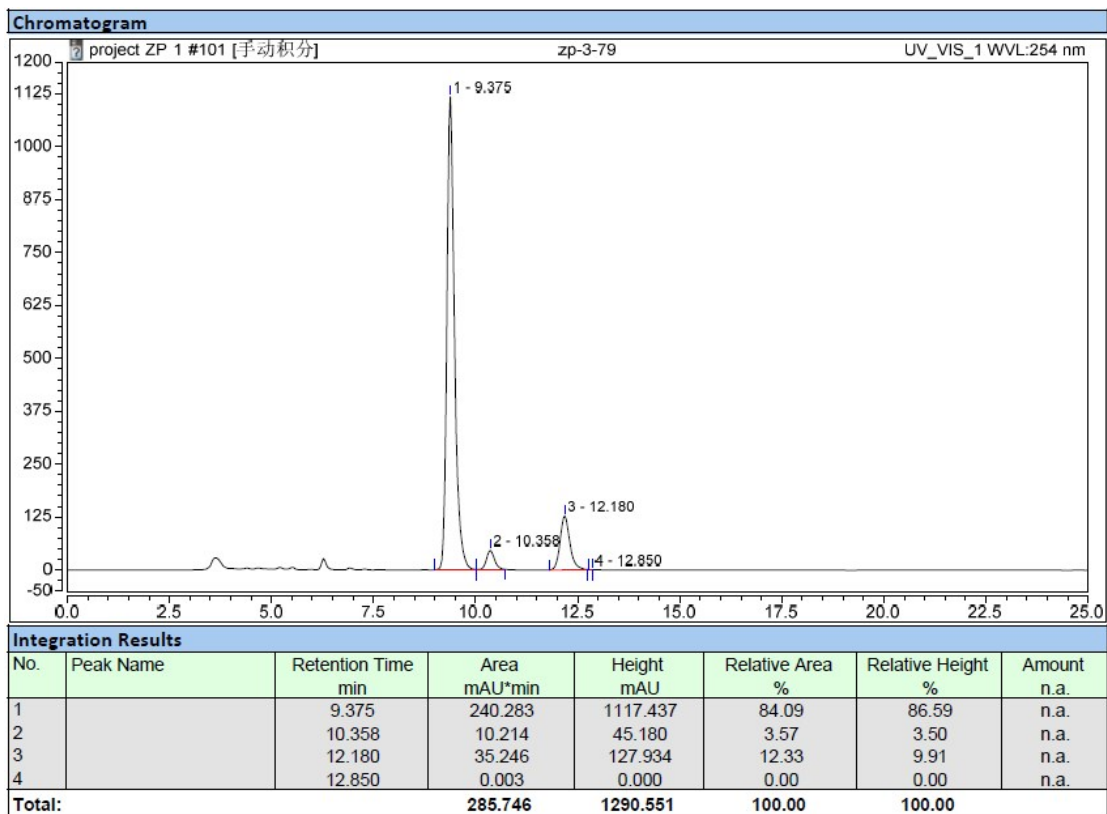
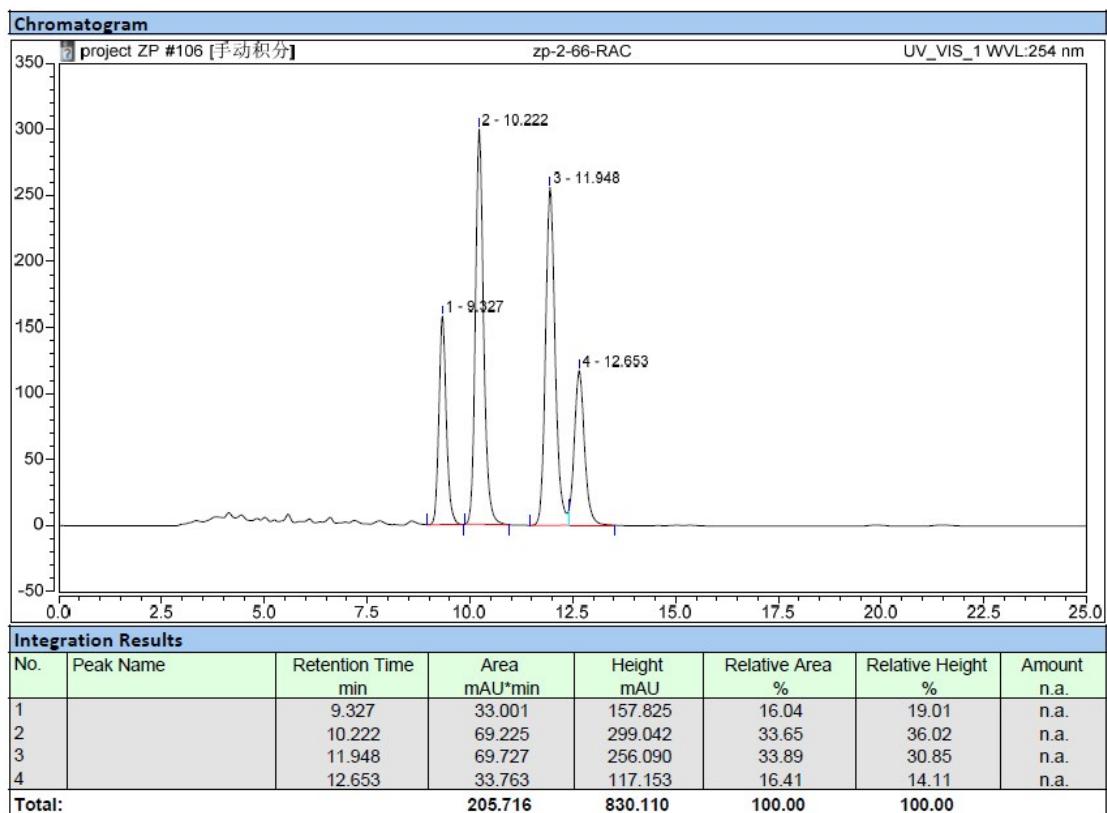
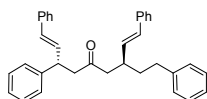
Compound 3ra



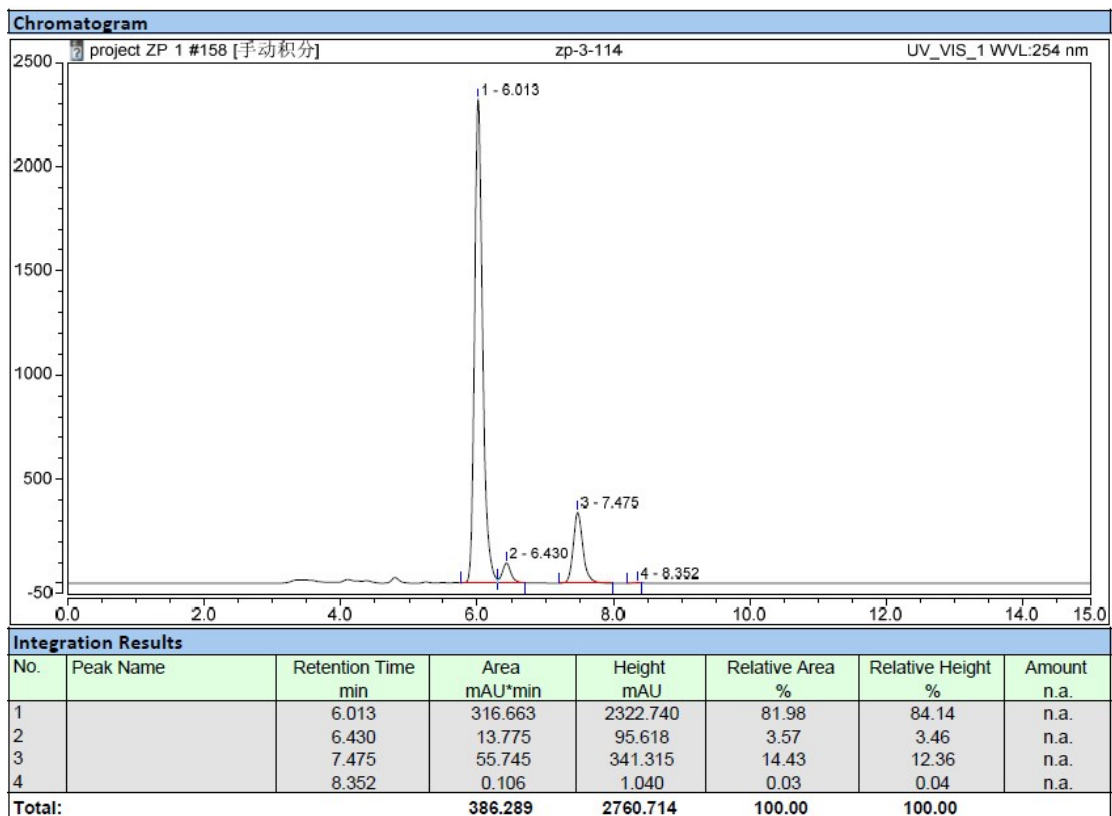
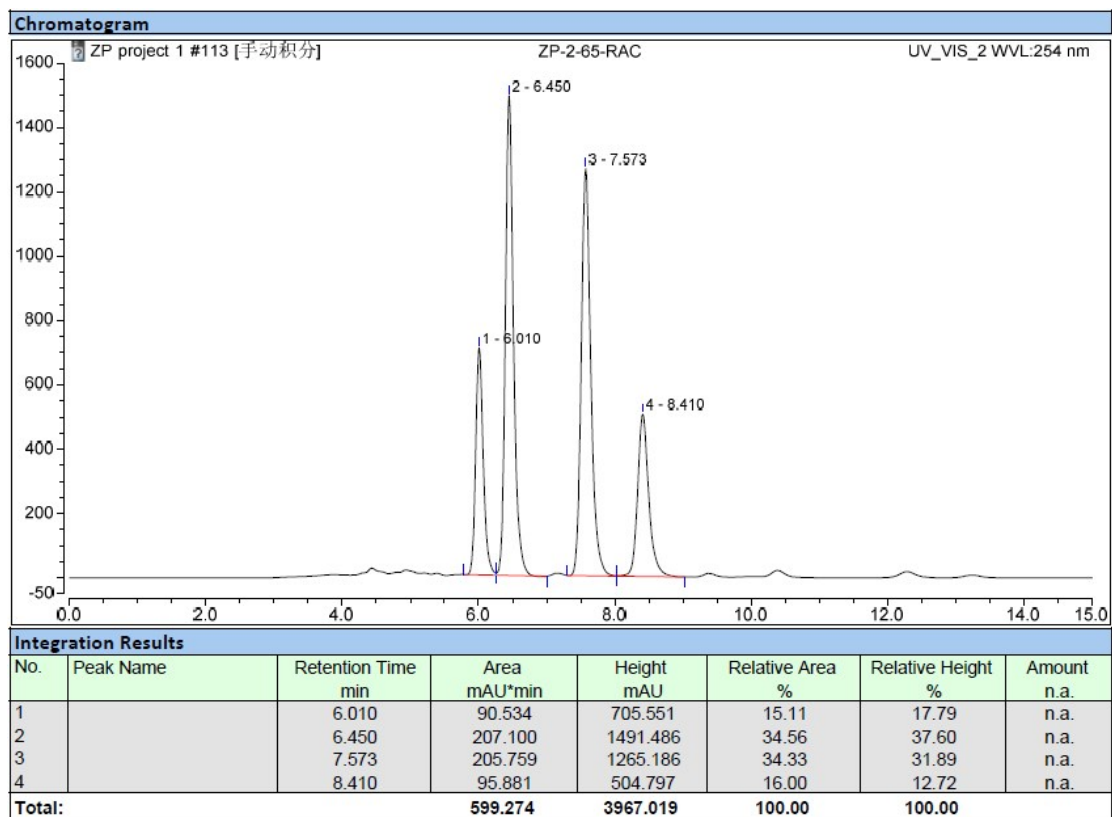
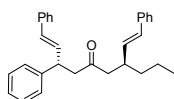
Compound 3sa



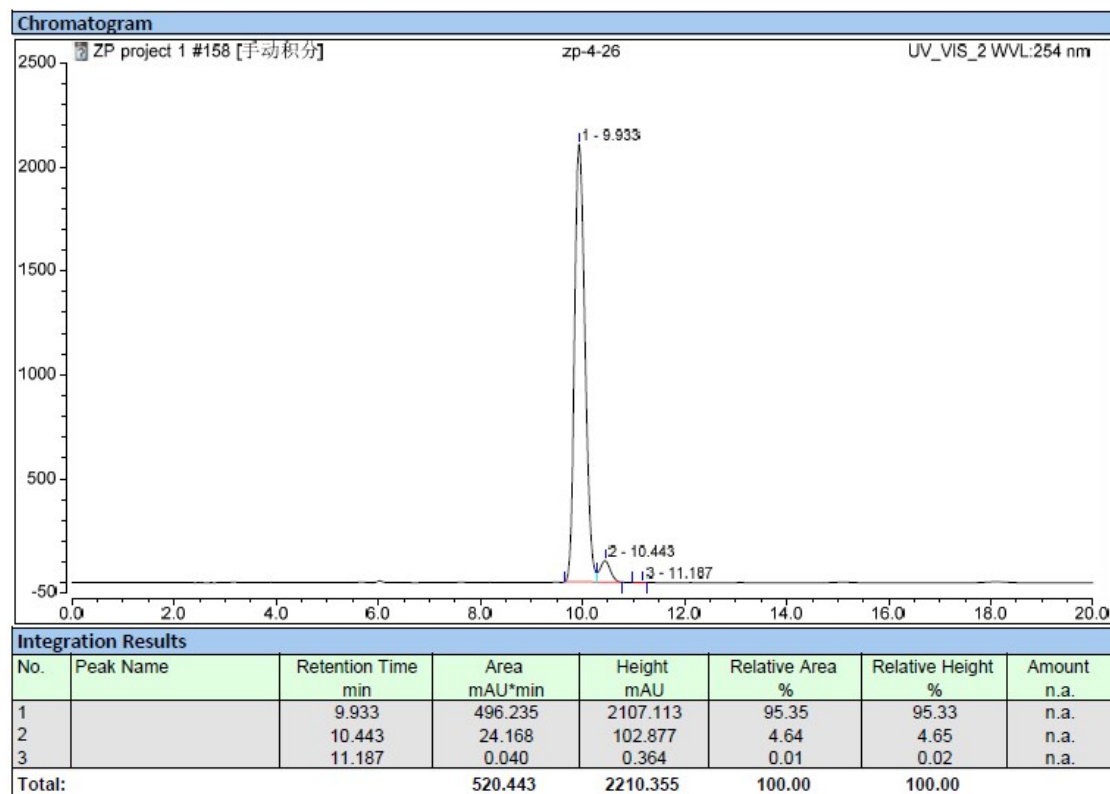
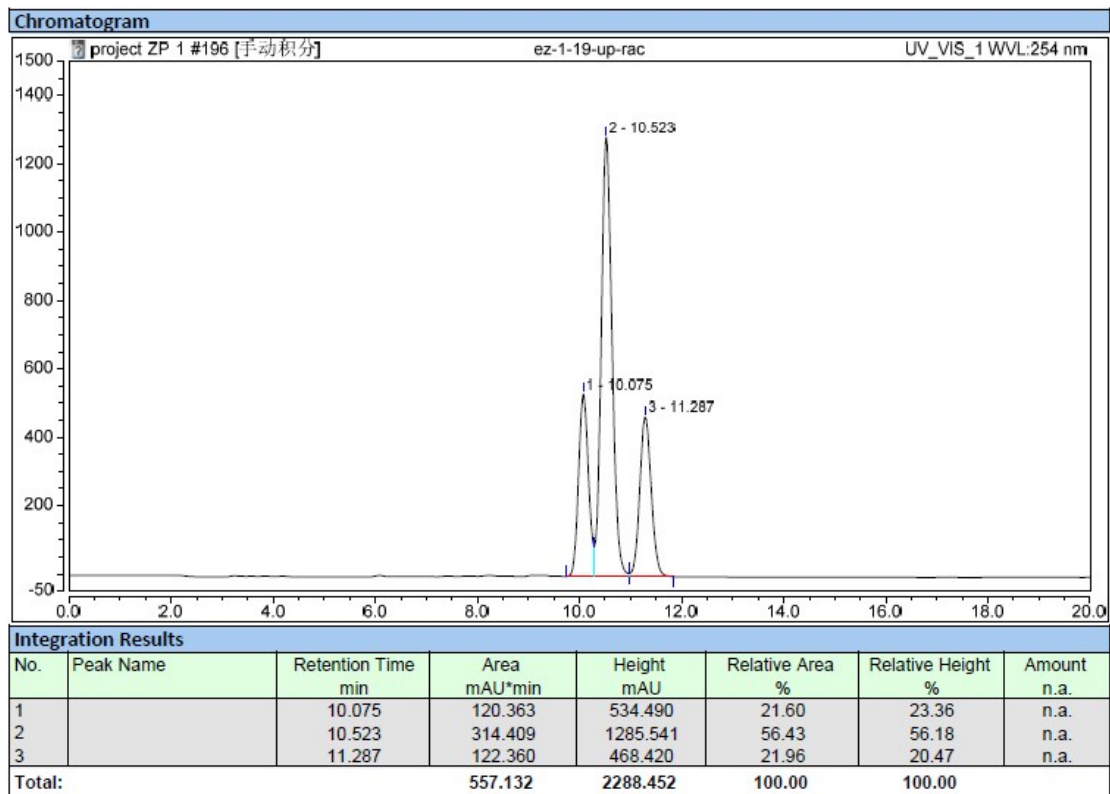
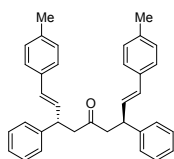
Compound 3ta



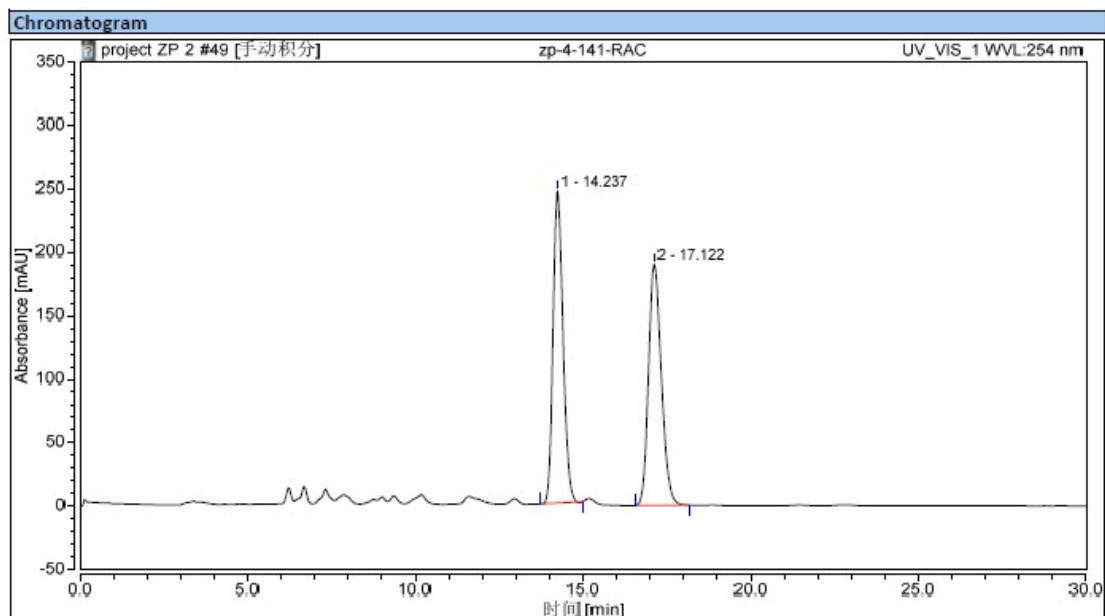
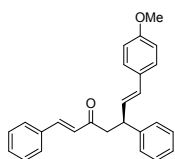
Compound 3ua



Compound 3ab

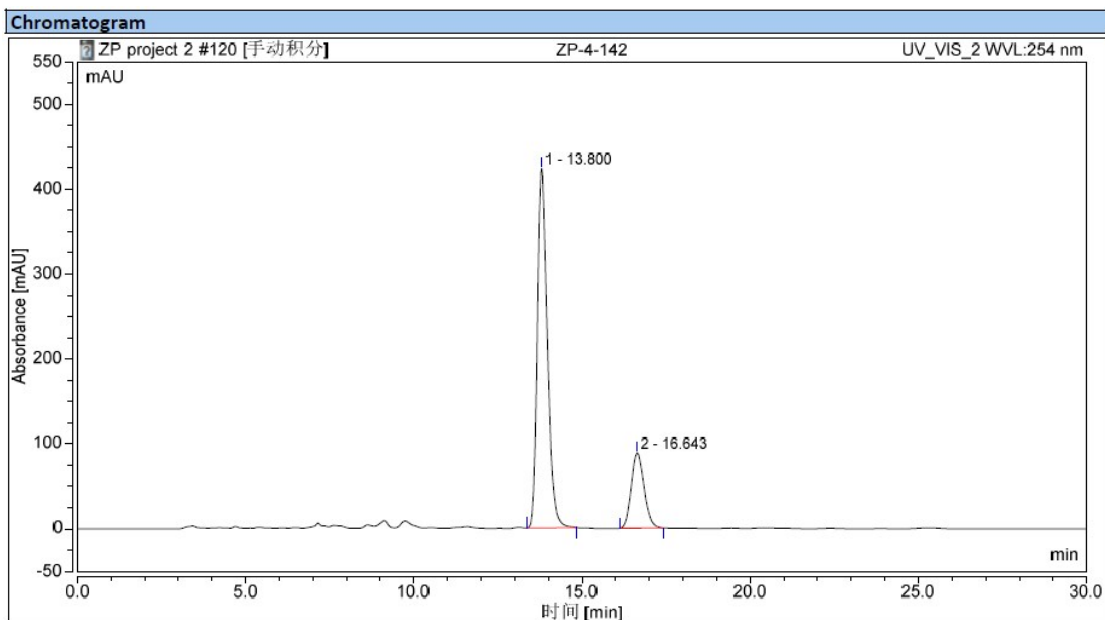


Compound 4ac



Integration Results

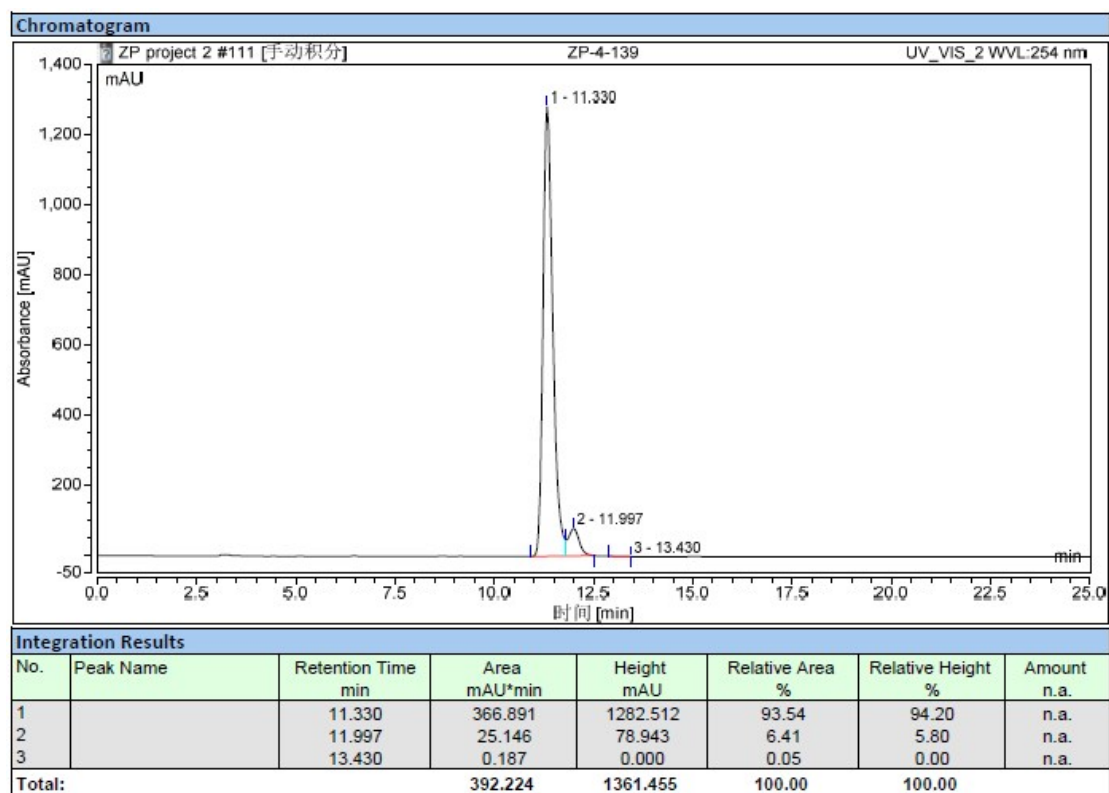
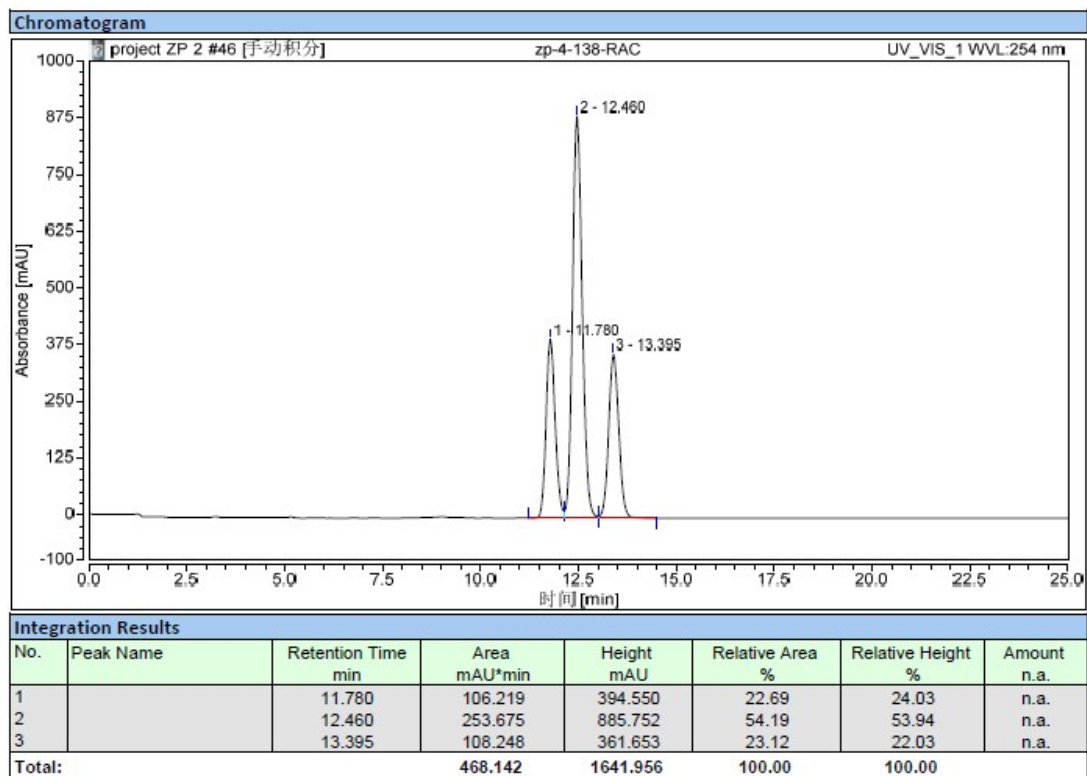
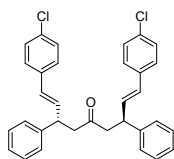
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.237	84.199	246.089	50.04	56.39	n.a.
2		17.122	84.069	190.296	49.96	43.61	n.a.
Total:			168.268	436.385	100.00	100.00	



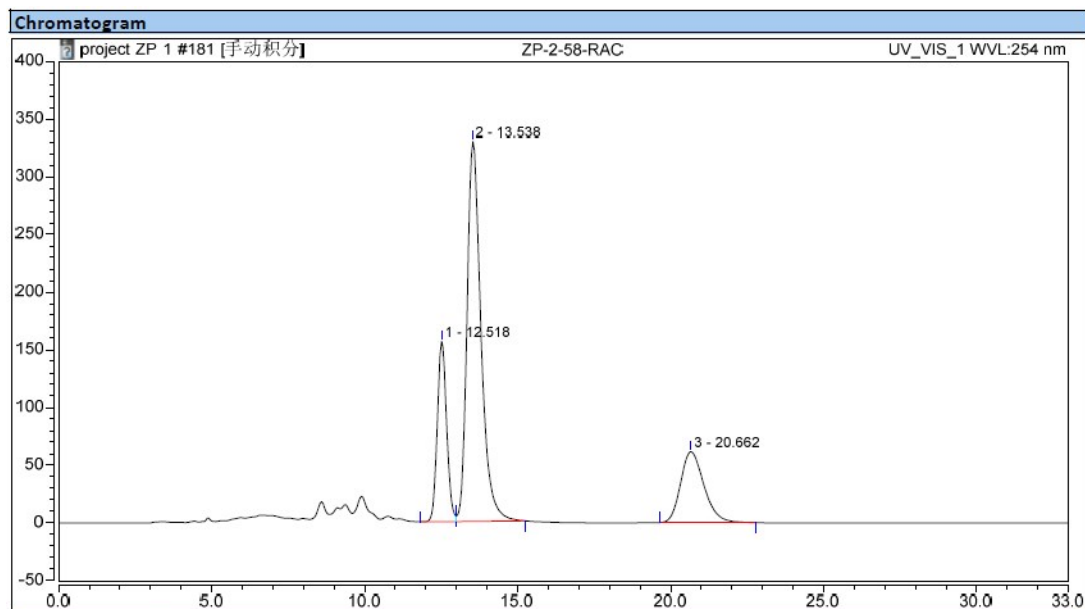
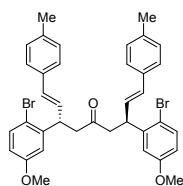
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.800	145.774	423.370	78.89	82.65	n.a.
2		16.643	38.996	88.866	21.11	17.35	n.a.
Total:			184.770	512.236	100.00	100.00	

Compound 3ad

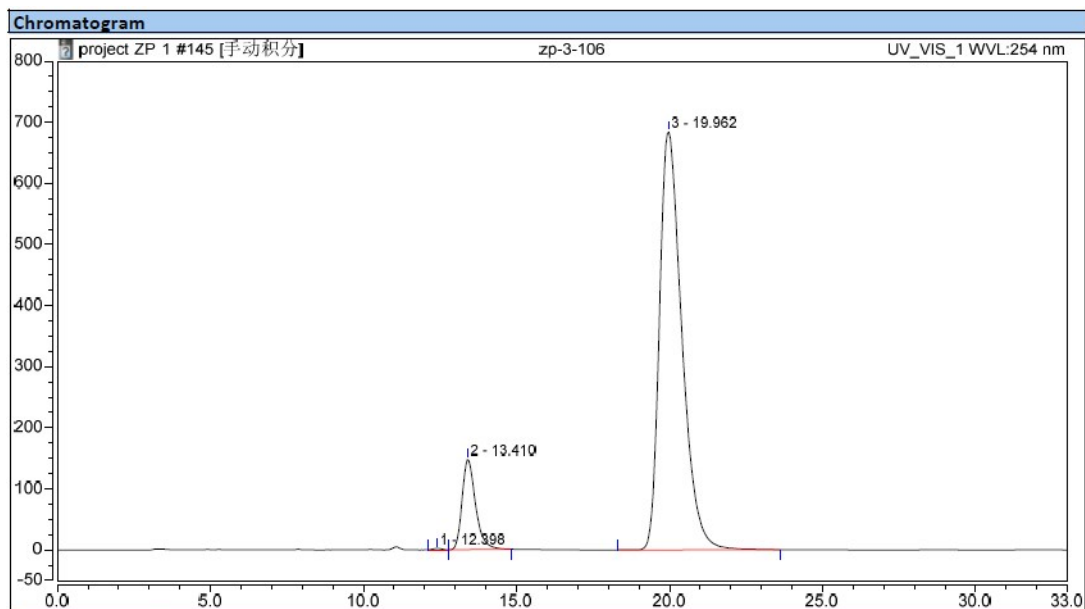


Compound 3lb



Integration Results

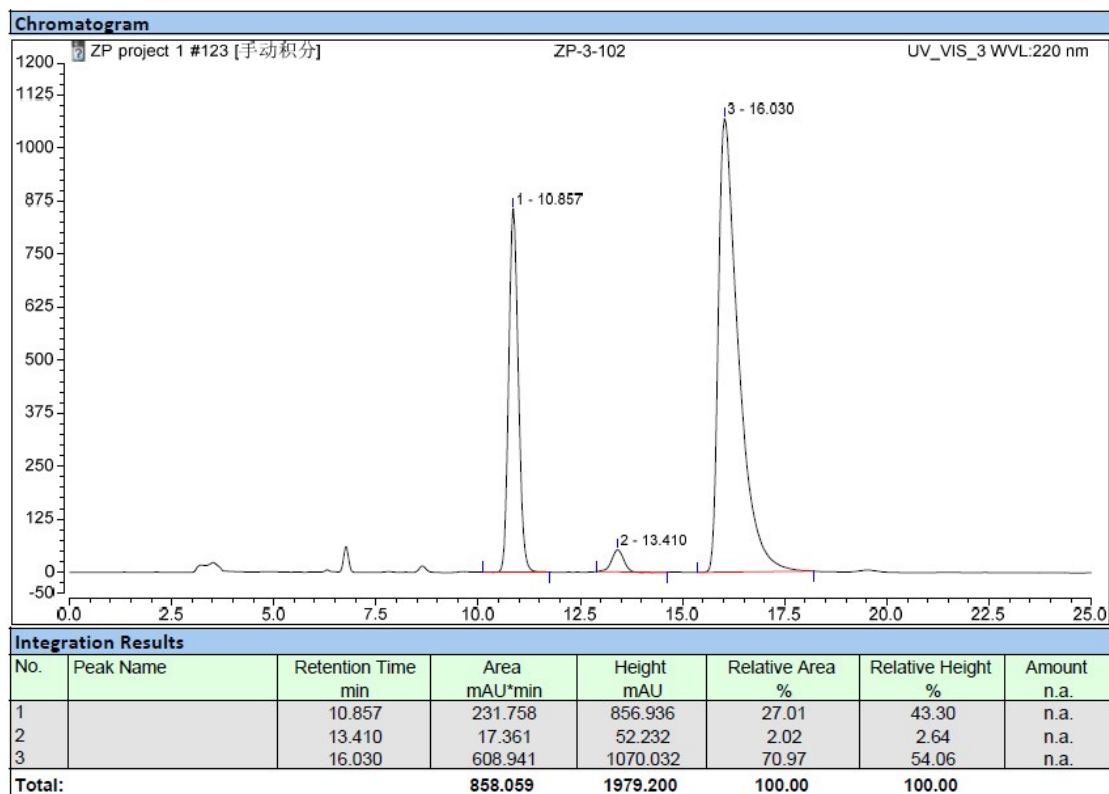
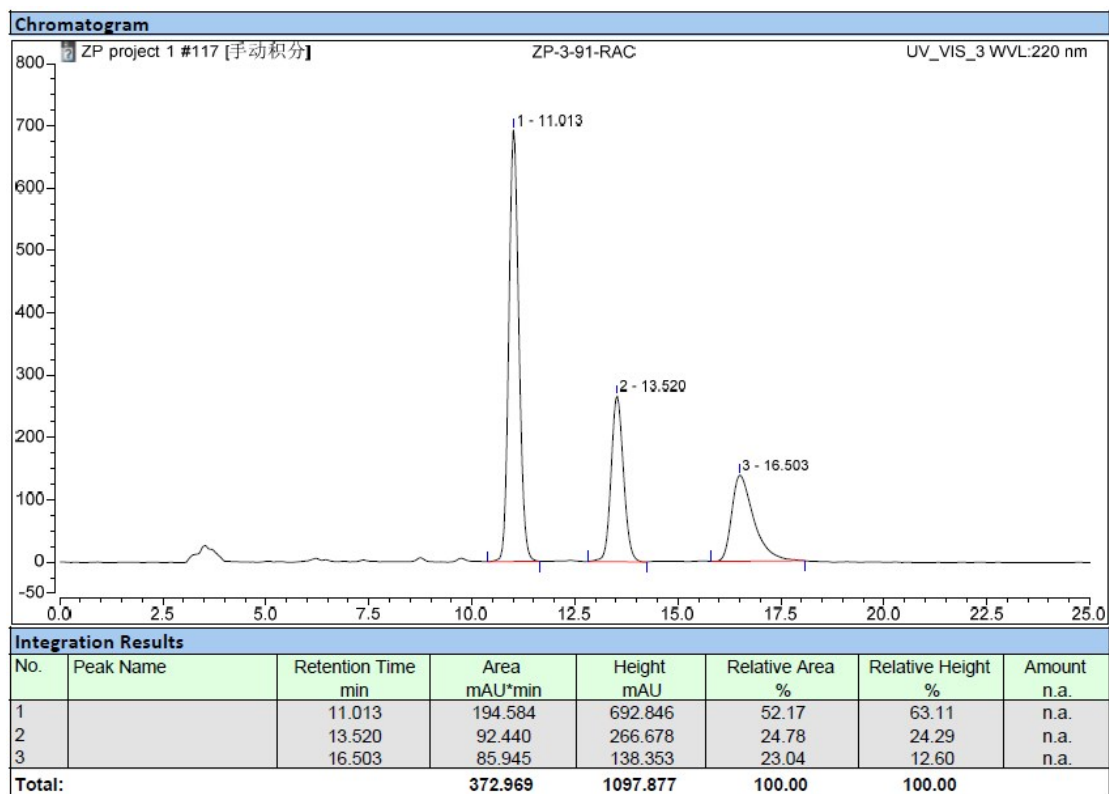
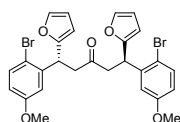
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.518	55.334	156.224	19.58	28.57	n.a.
2		13.538	173.117	329.234	61.24	60.21	n.a.
3		20.662	54.218	61.396	19.18	11.23	n.a.
Total:			282.669	546.854	100.00	100.00	



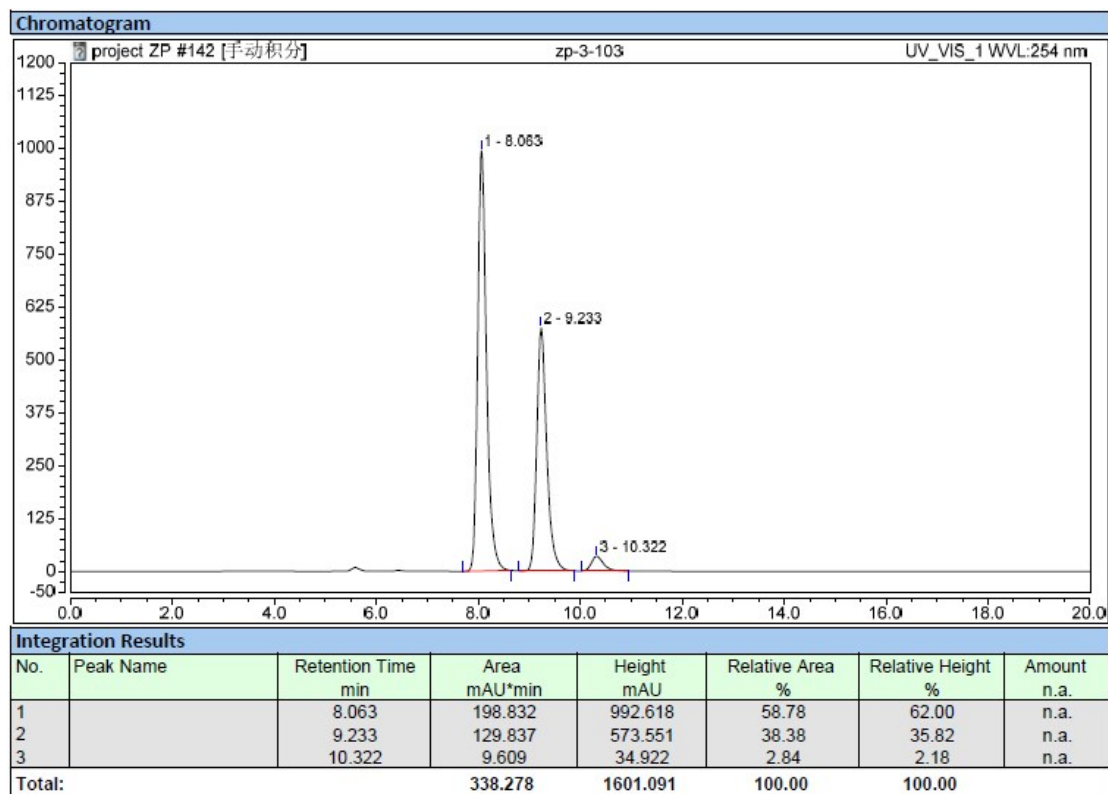
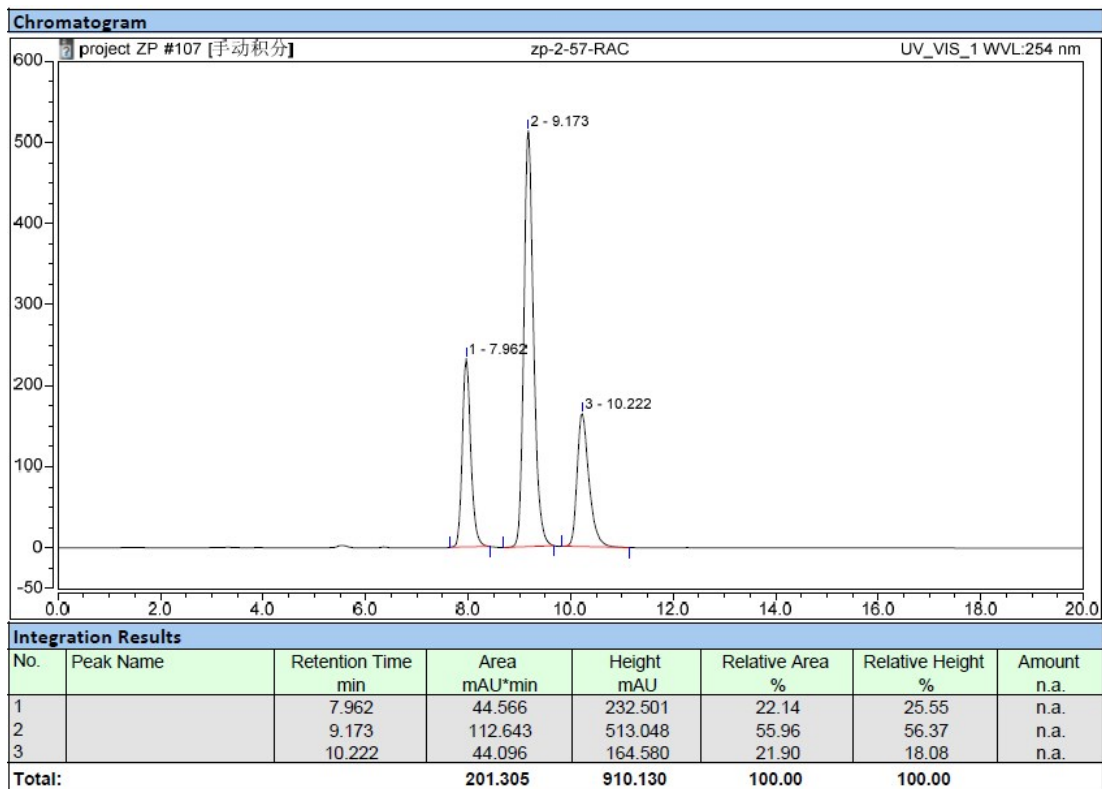
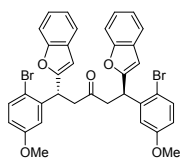
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		12.398	0.698	2.217	0.11	0.27	n.a.
2		13.410	75.003	147.730	11.45	17.69	n.a.
3		19.962	579.249	685.064	88.44	82.04	n.a.
Total:			654.950	835.011	100.00	100.00	

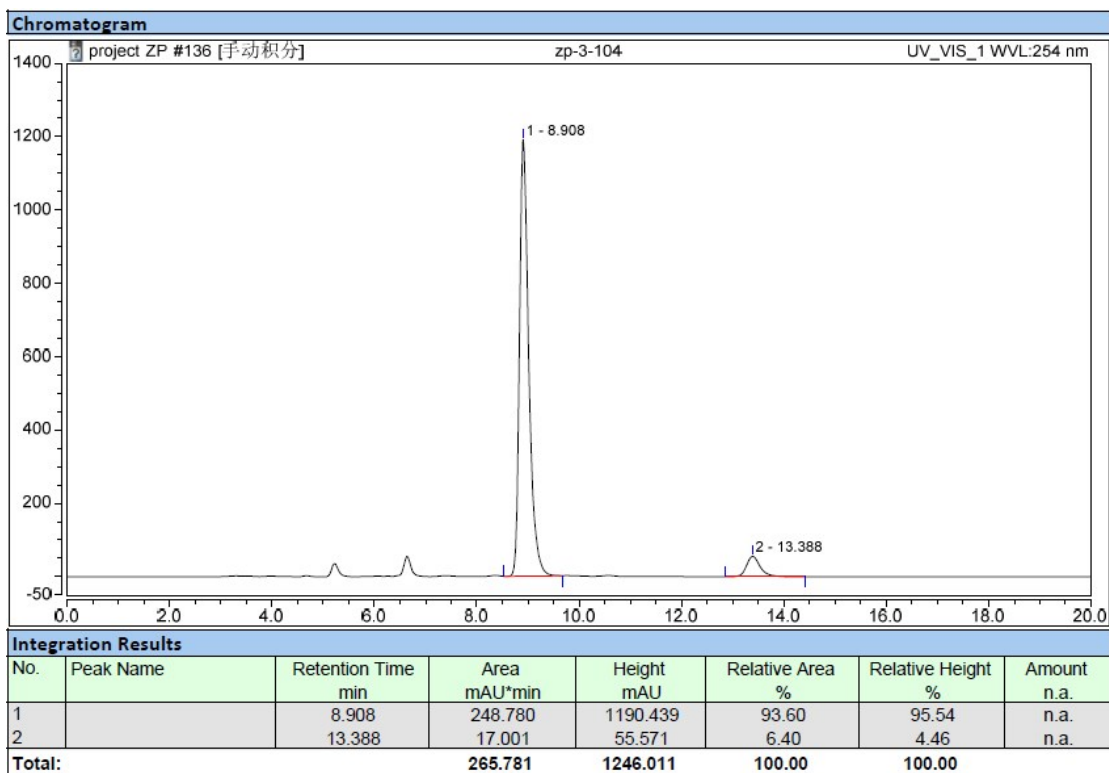
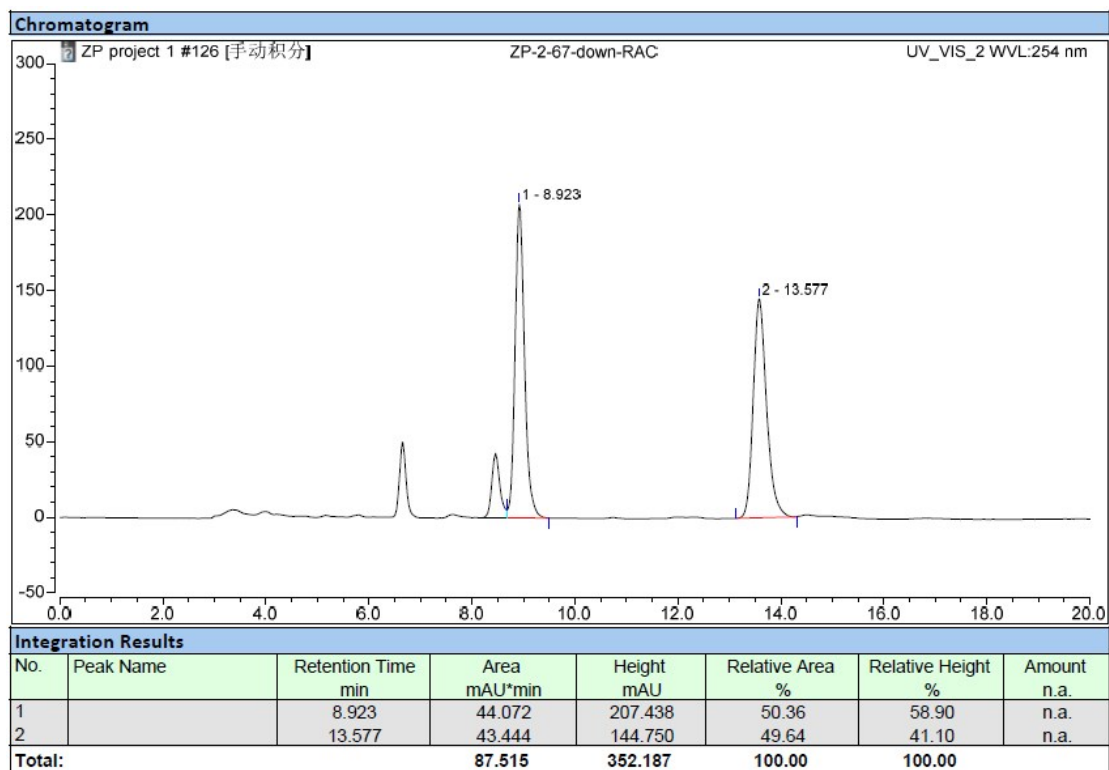
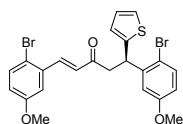
Compound 3le



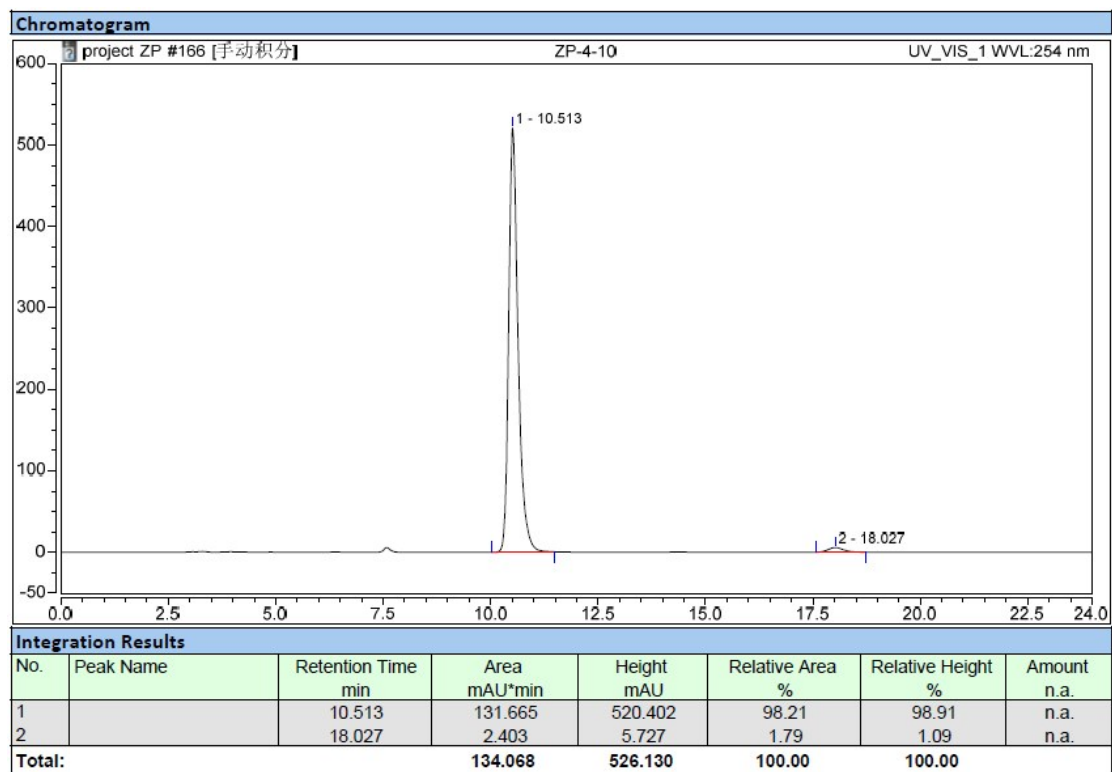
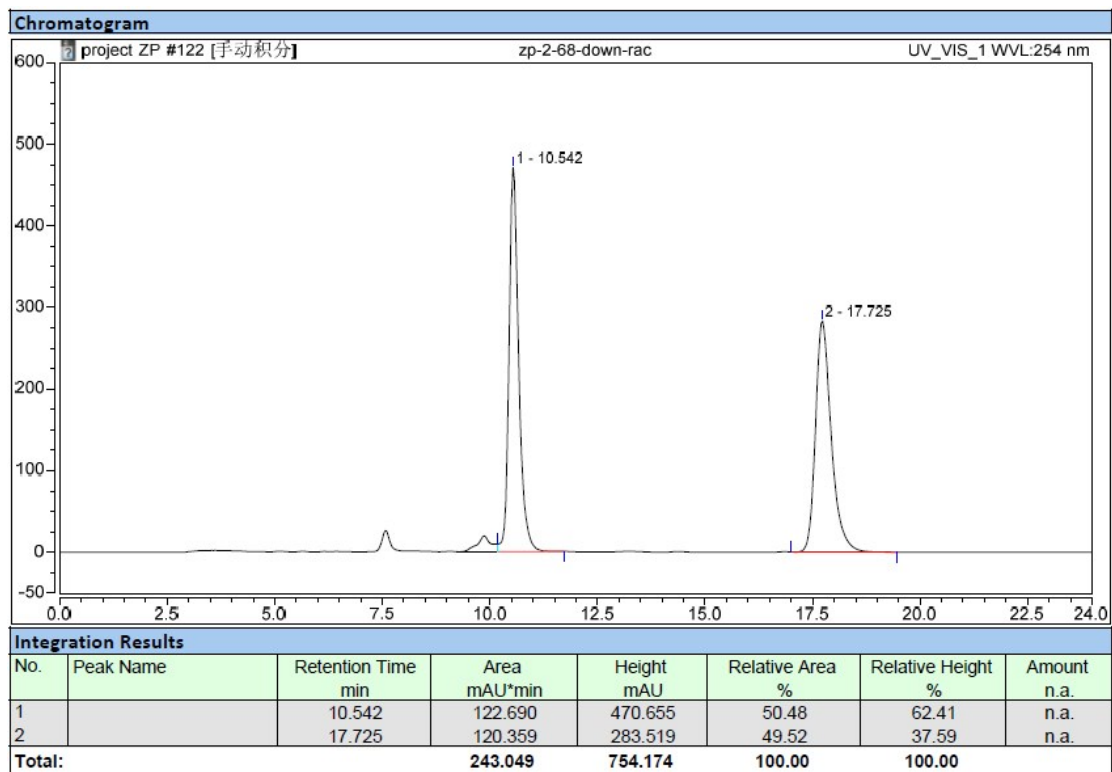
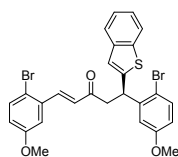
Compound 3lf



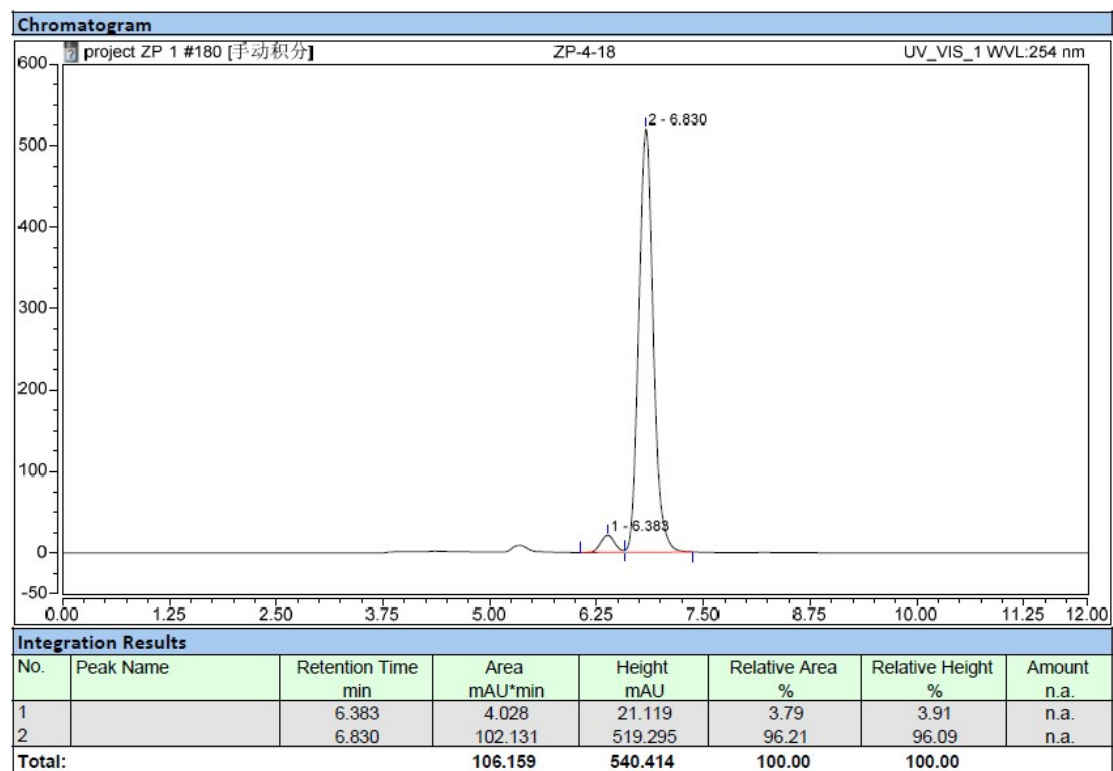
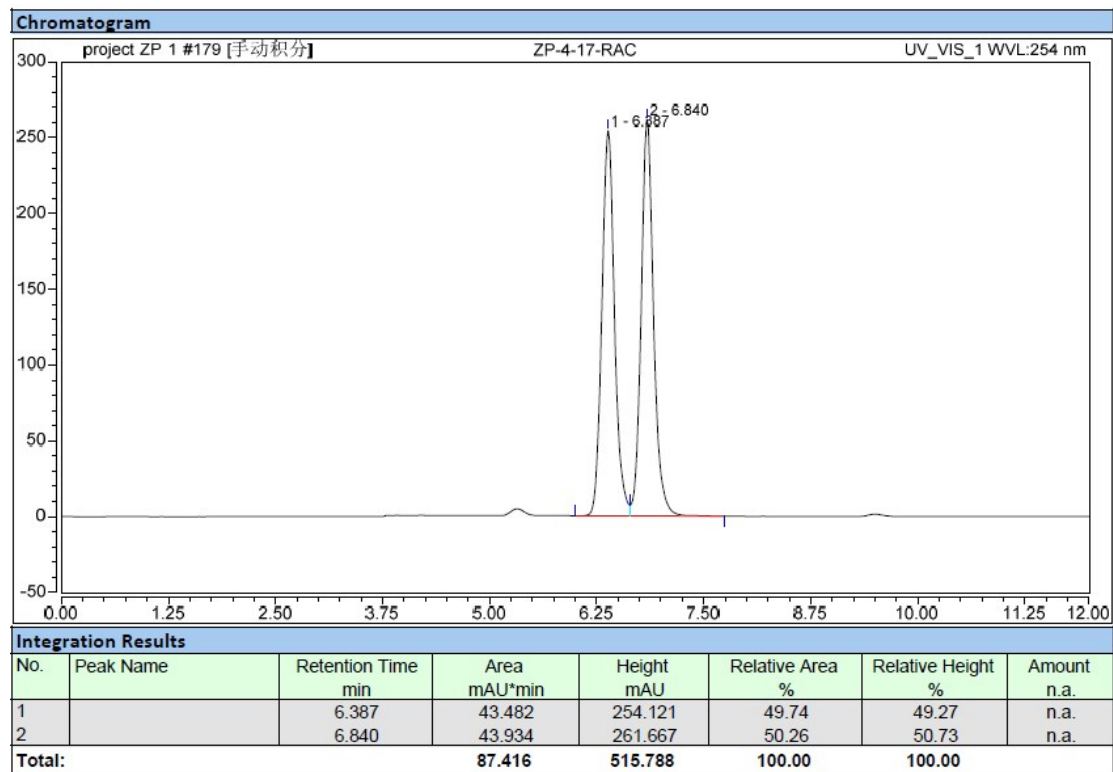
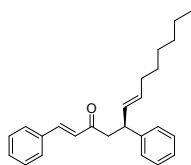
Compound 4lg



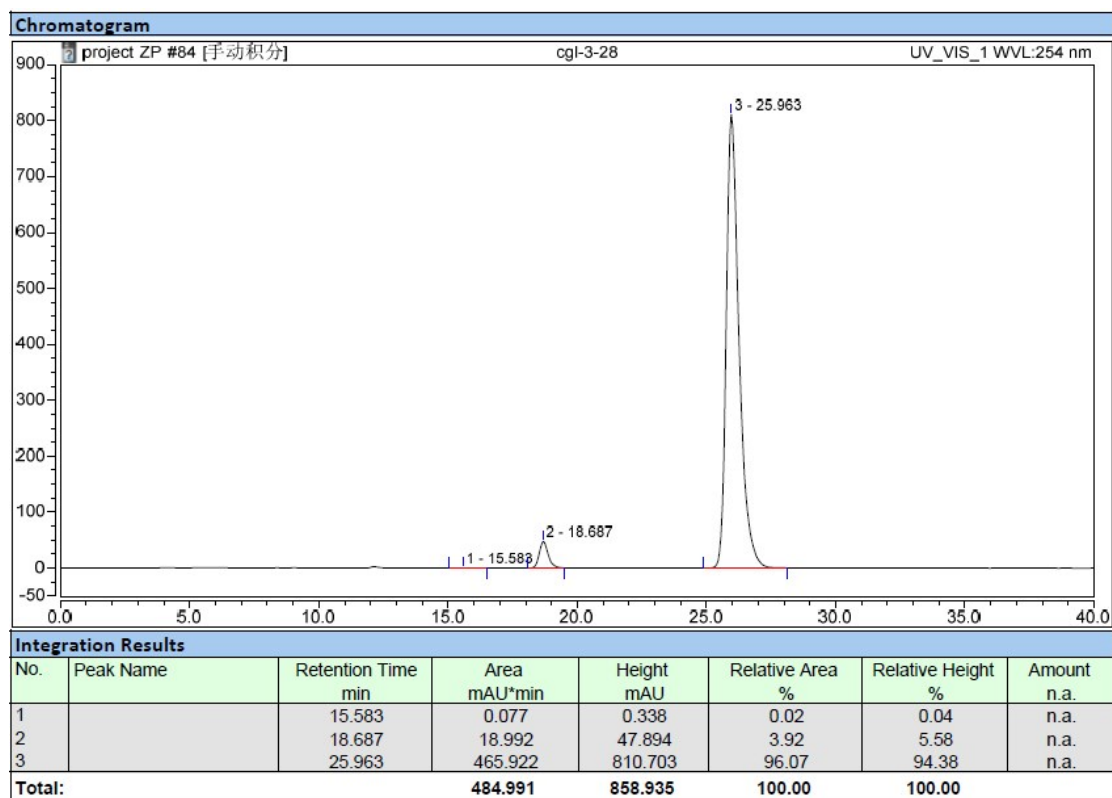
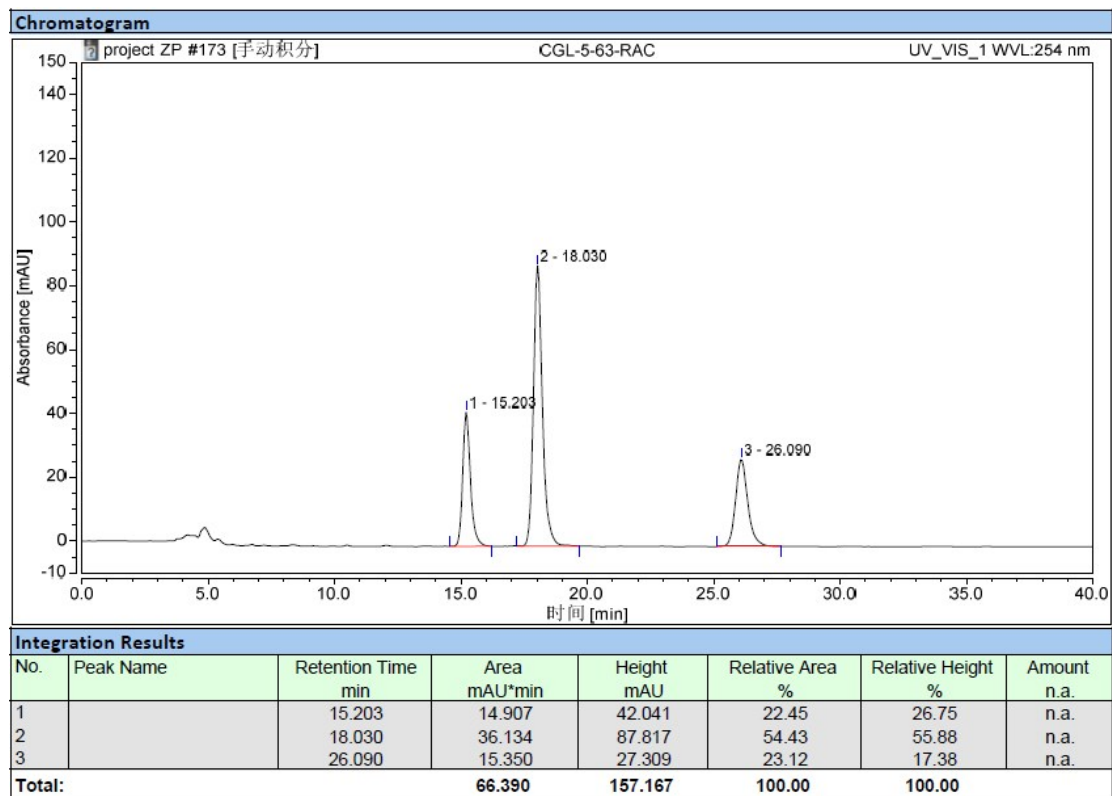
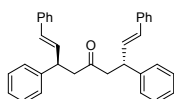
Compound 4h



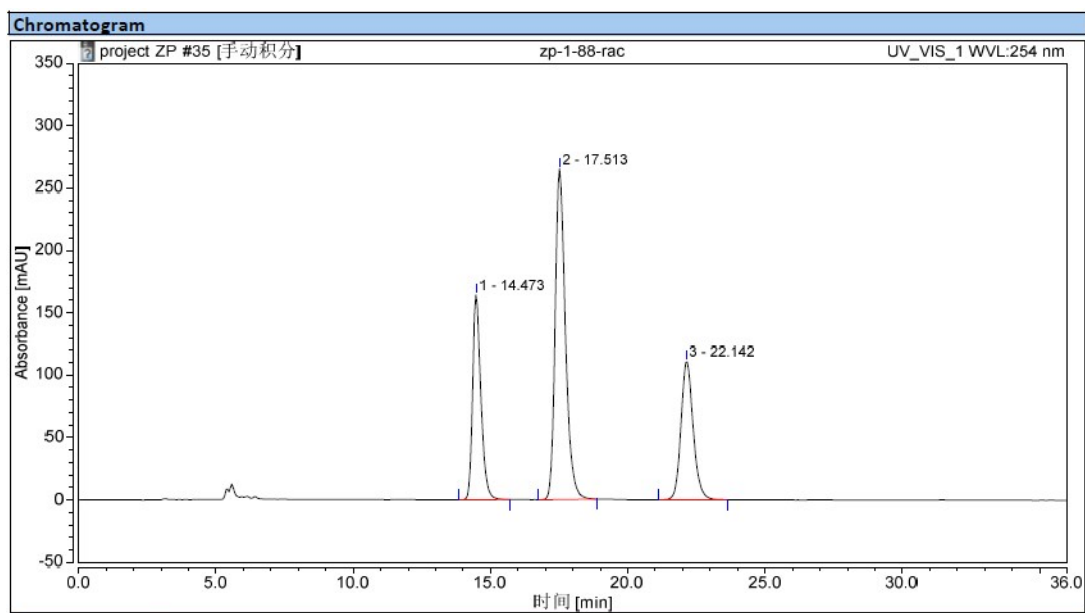
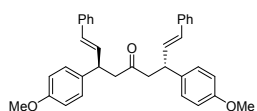
Compound 4ai



Compound 3aa'

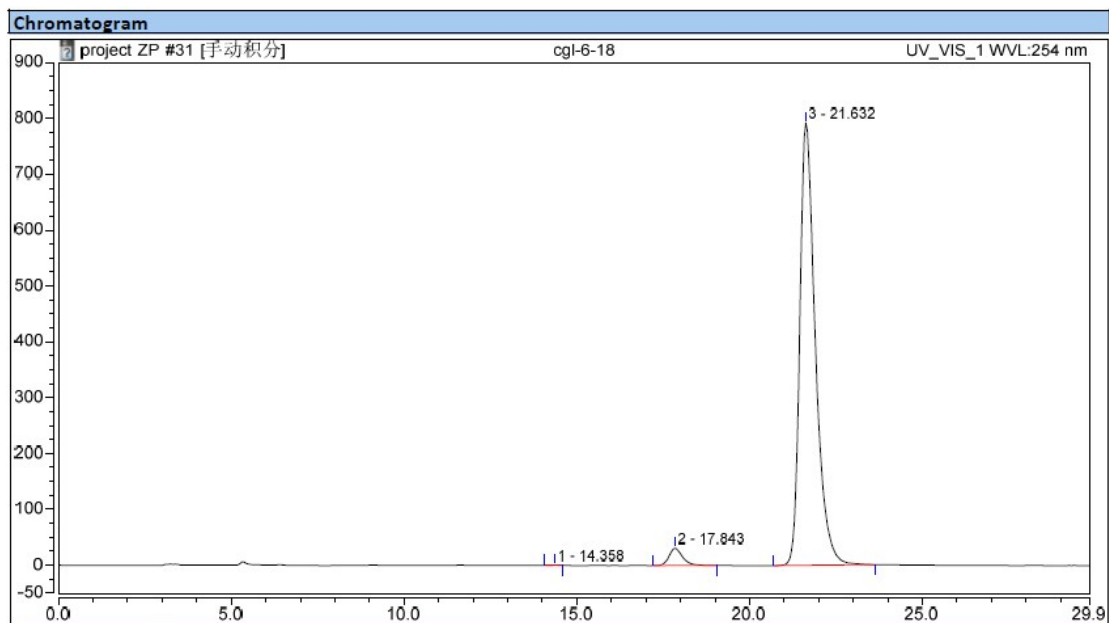


Compound 3ea'



Integration Results

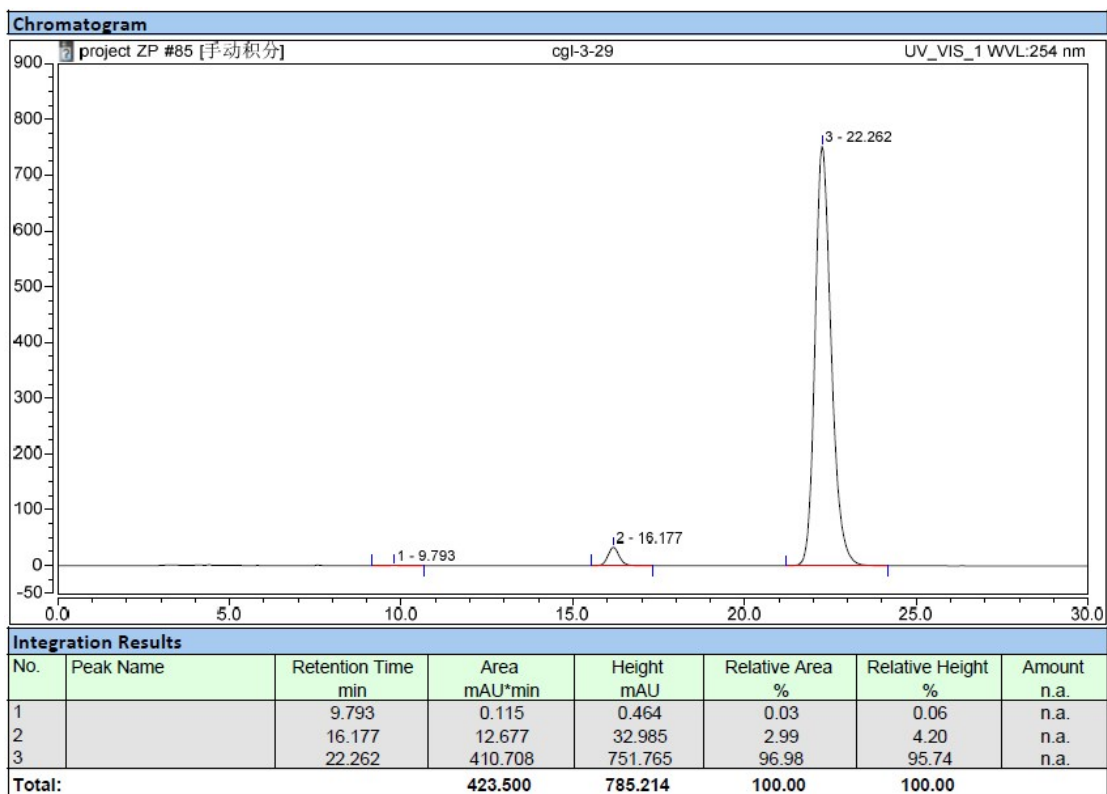
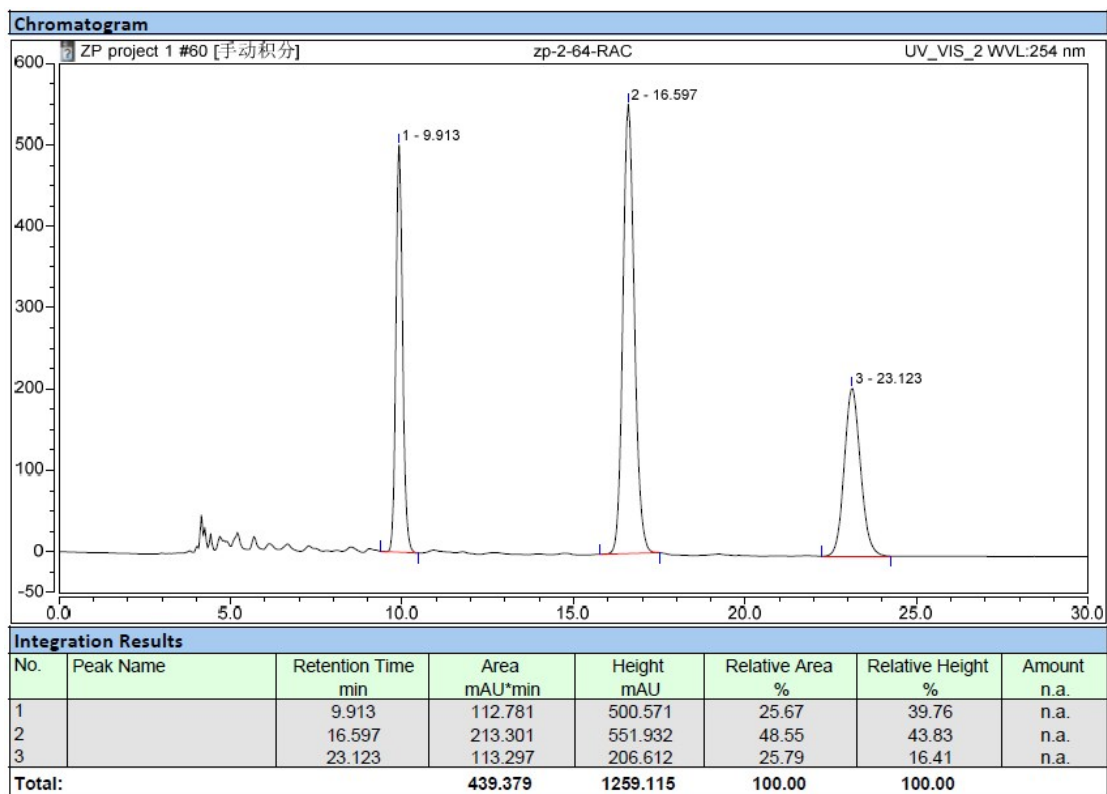
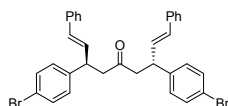
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.473	57.393	164.433	25.03	30.38	n.a.
2		17.513	114.775	265.375	50.05	49.03	n.a.
3		22.142	57.144	111.409	24.92	20.58	n.a.
Total:			229.312	541.217	100.00	100.00	



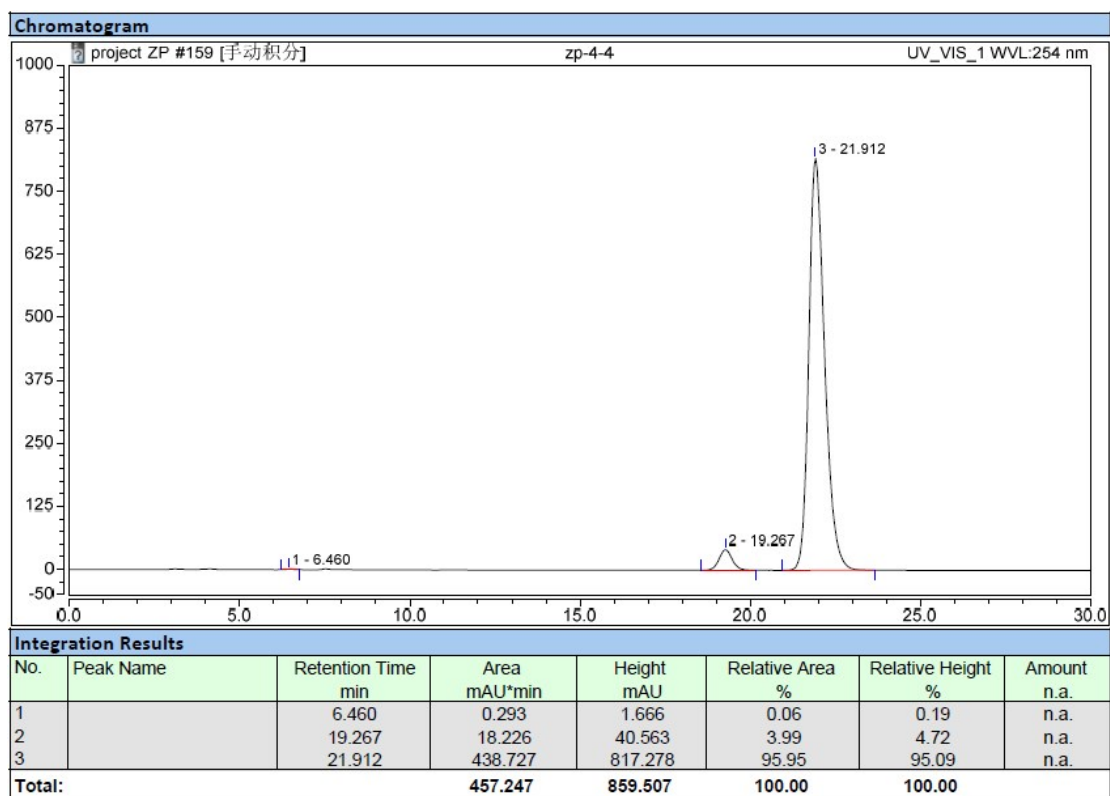
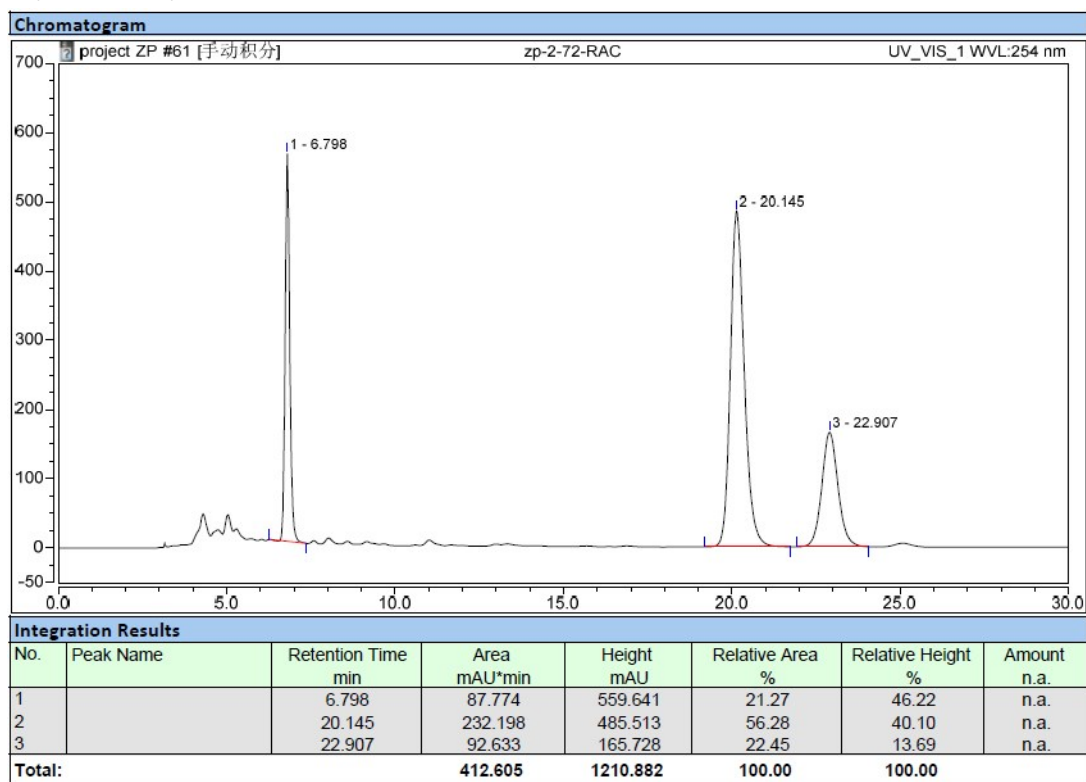
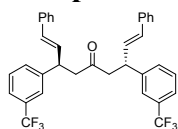
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.358	0.083	0.282	0.02	0.03	n.a.
2		17.843	13.697	30.739	3.21	3.73	n.a.
3		21.632	413.360	792.357	96.77	96.23	n.a.
Total:			427.140	823.379	100.00	100.00	

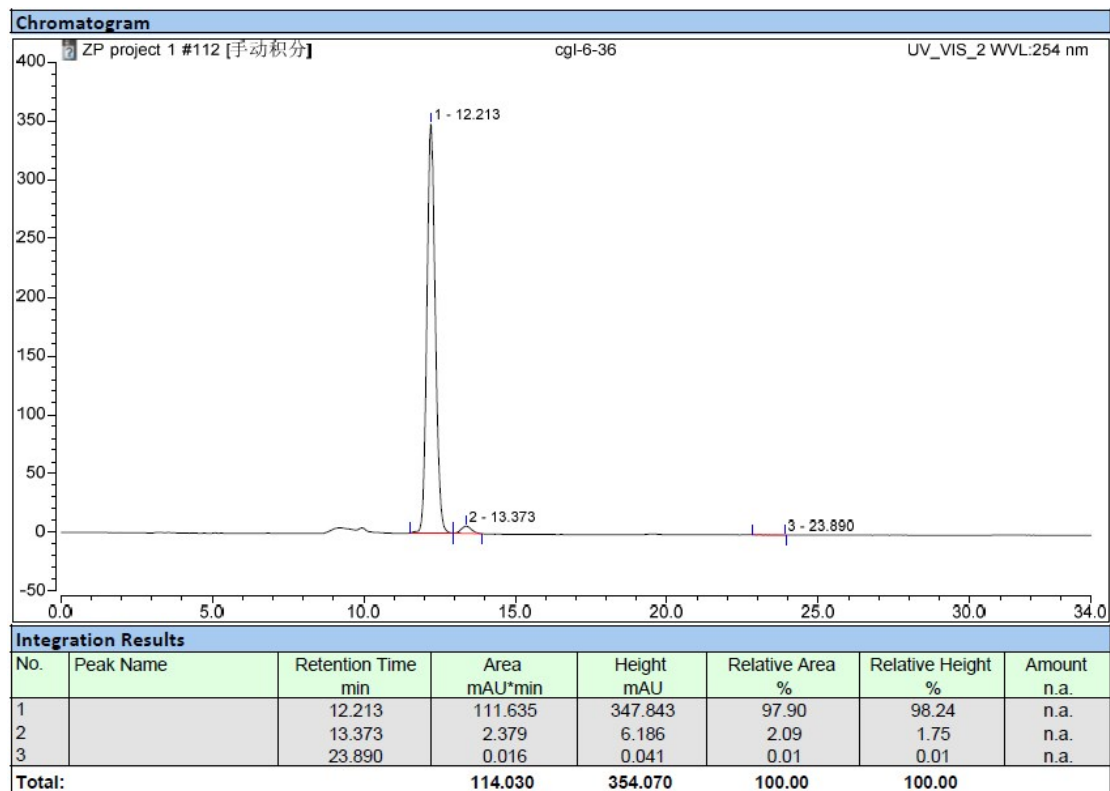
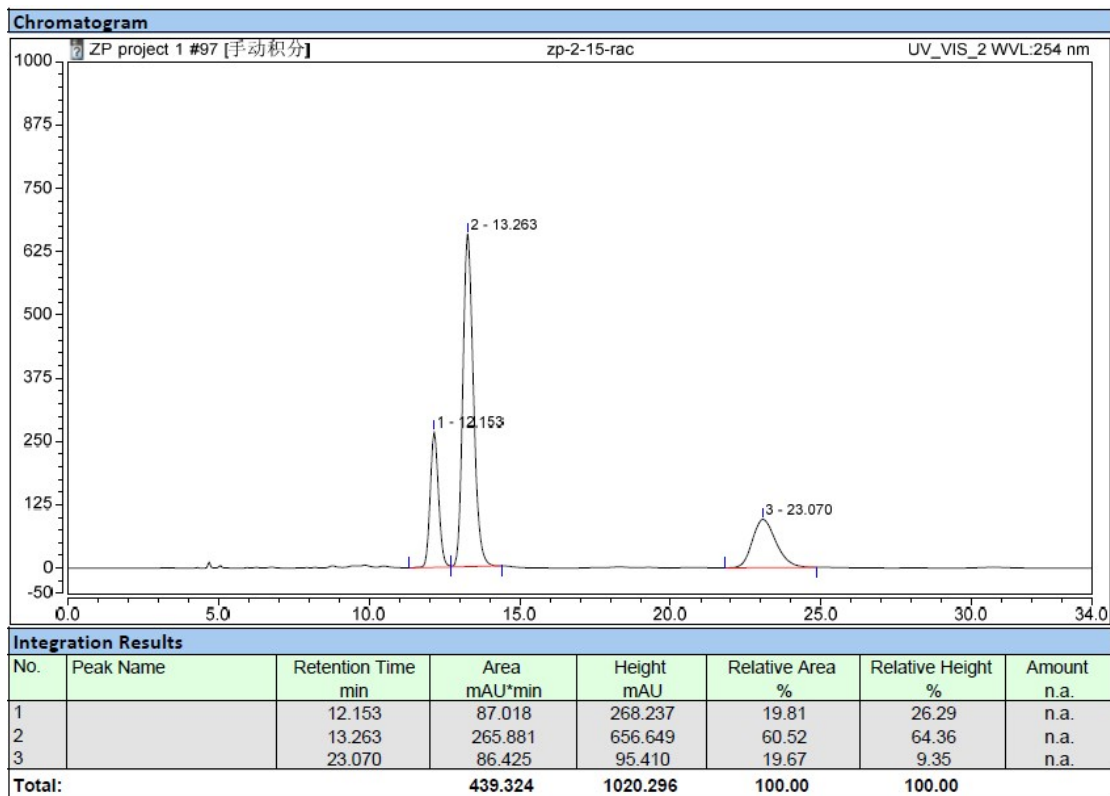
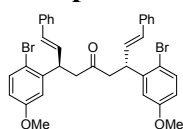
Compound 3ja'



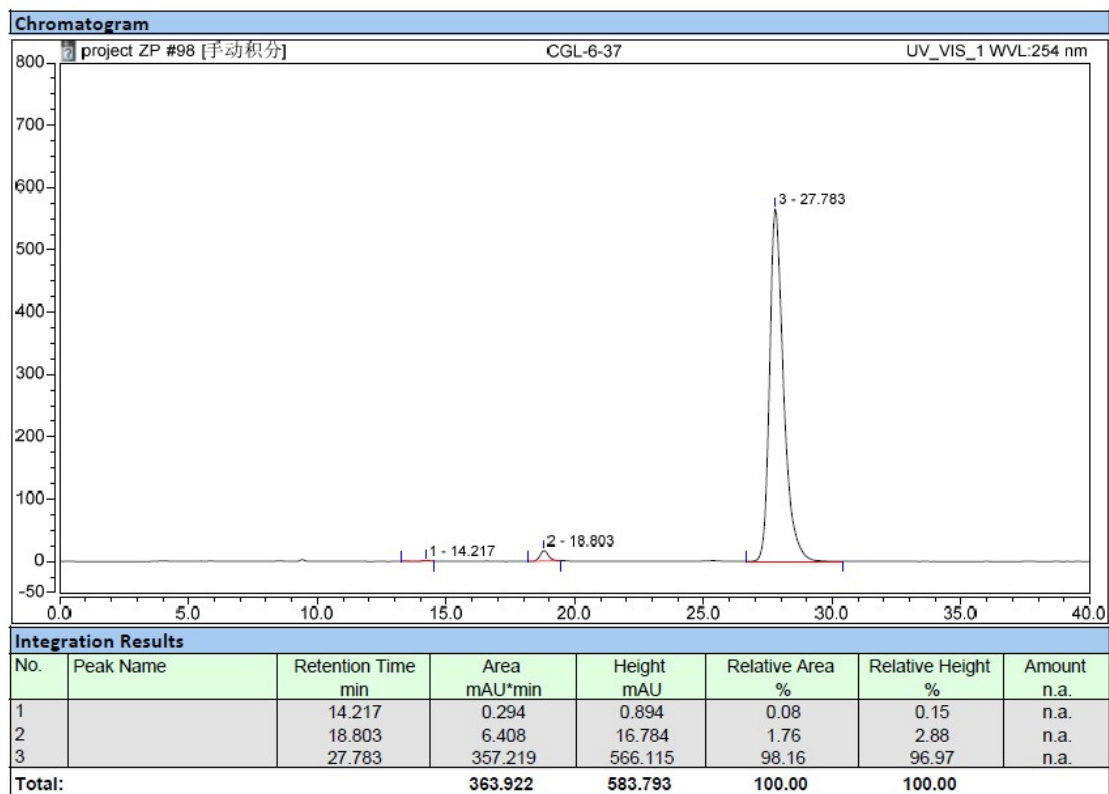
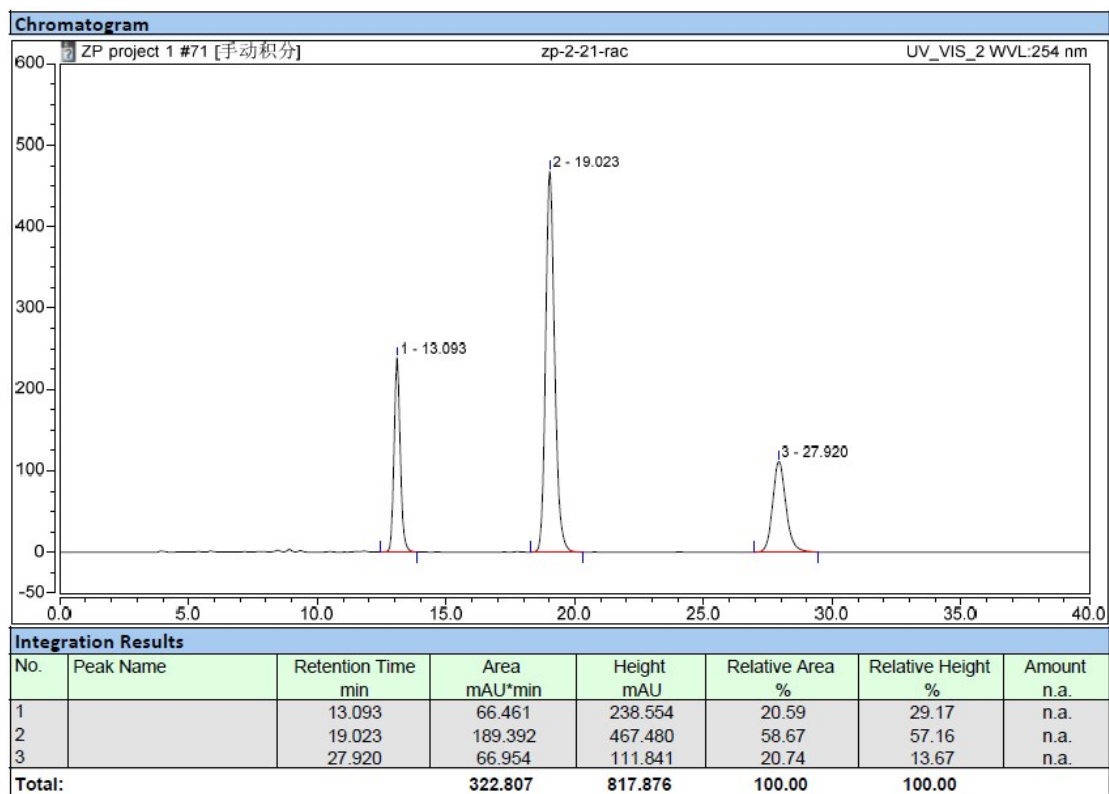
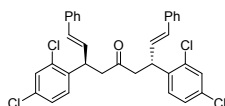
Compound 3ka'



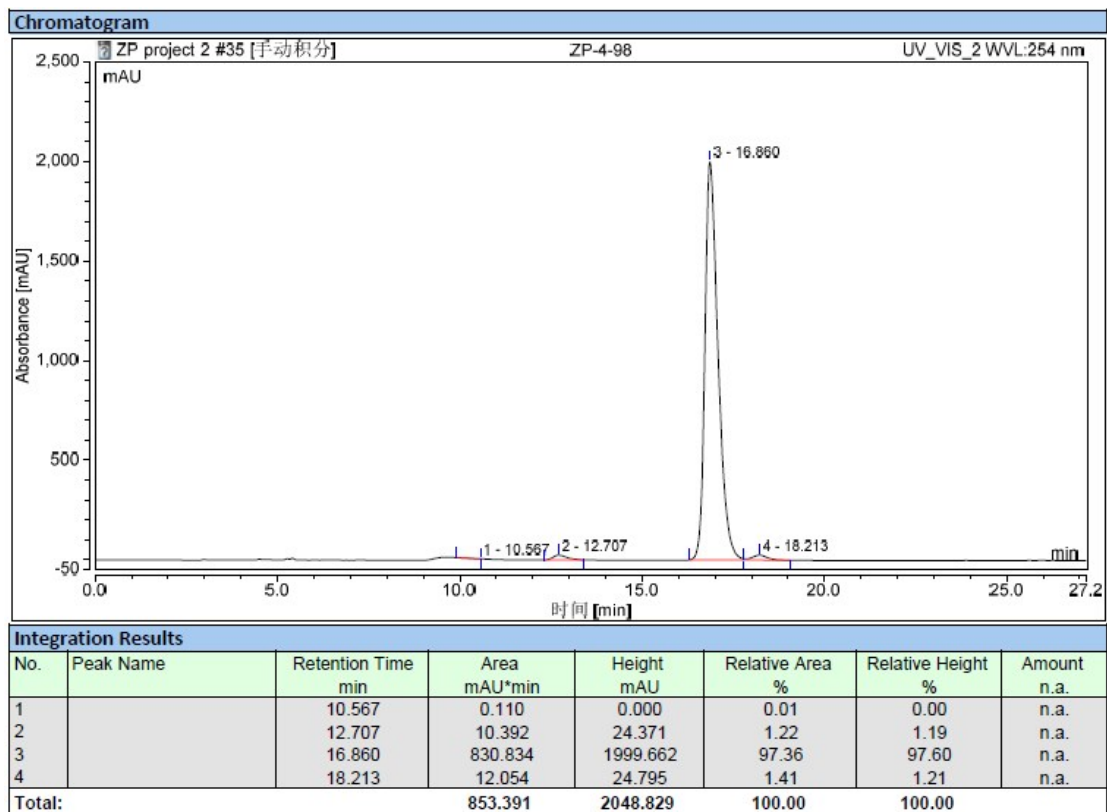
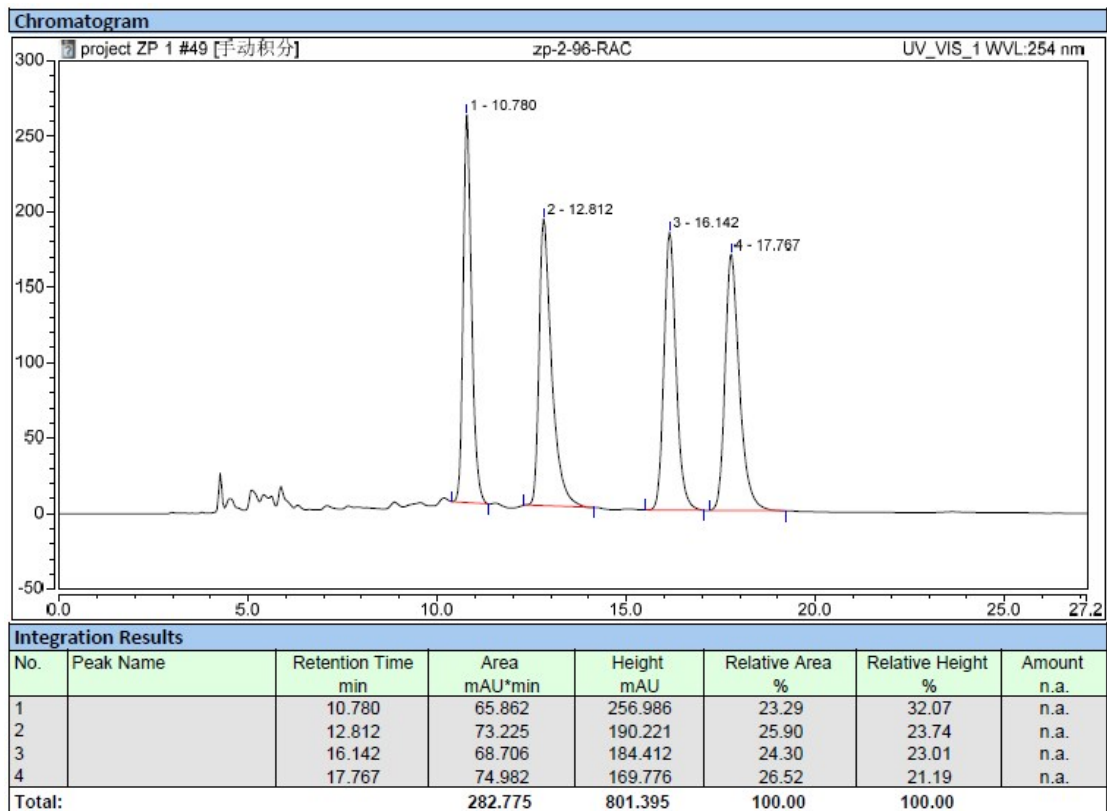
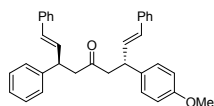
Compound 3la'



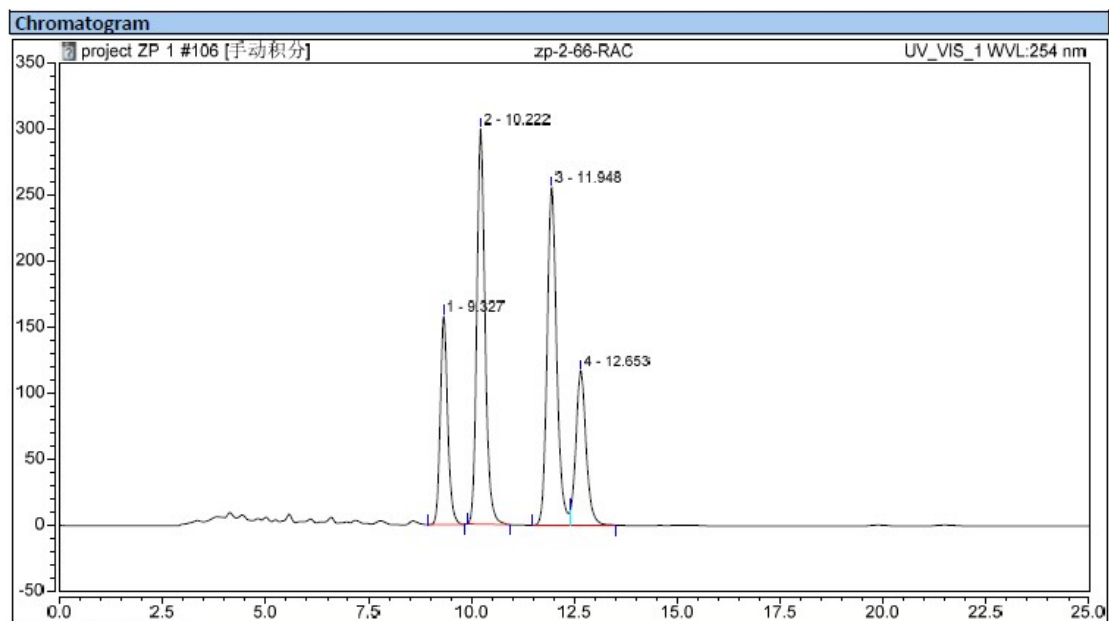
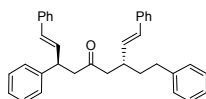
Compound 3ma'



Compound 3ra'

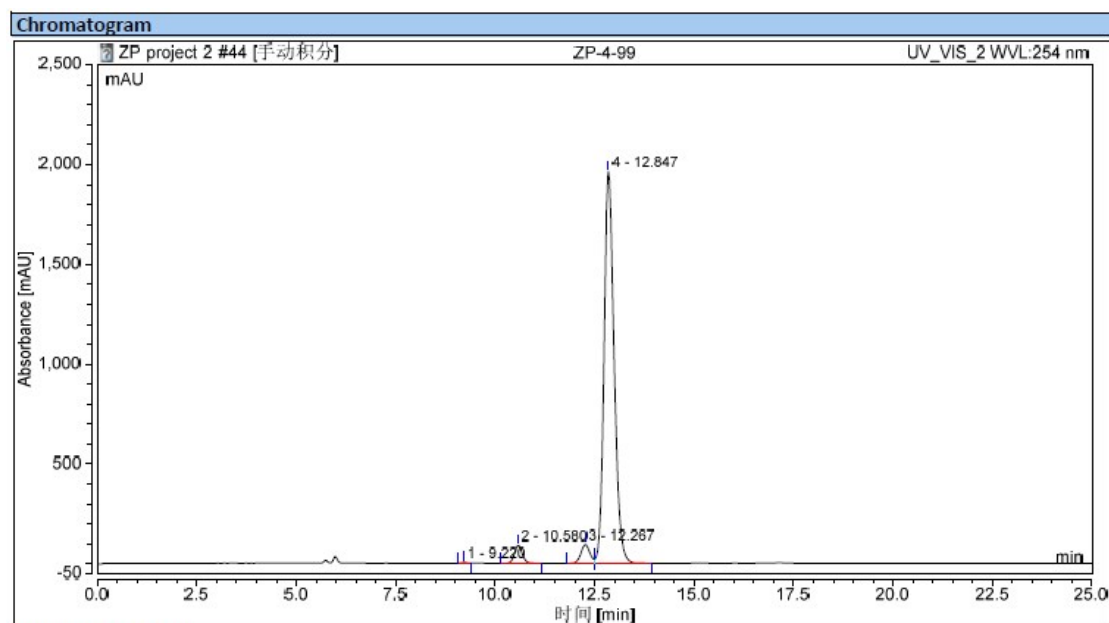


Compound 3ta'



Integration Results

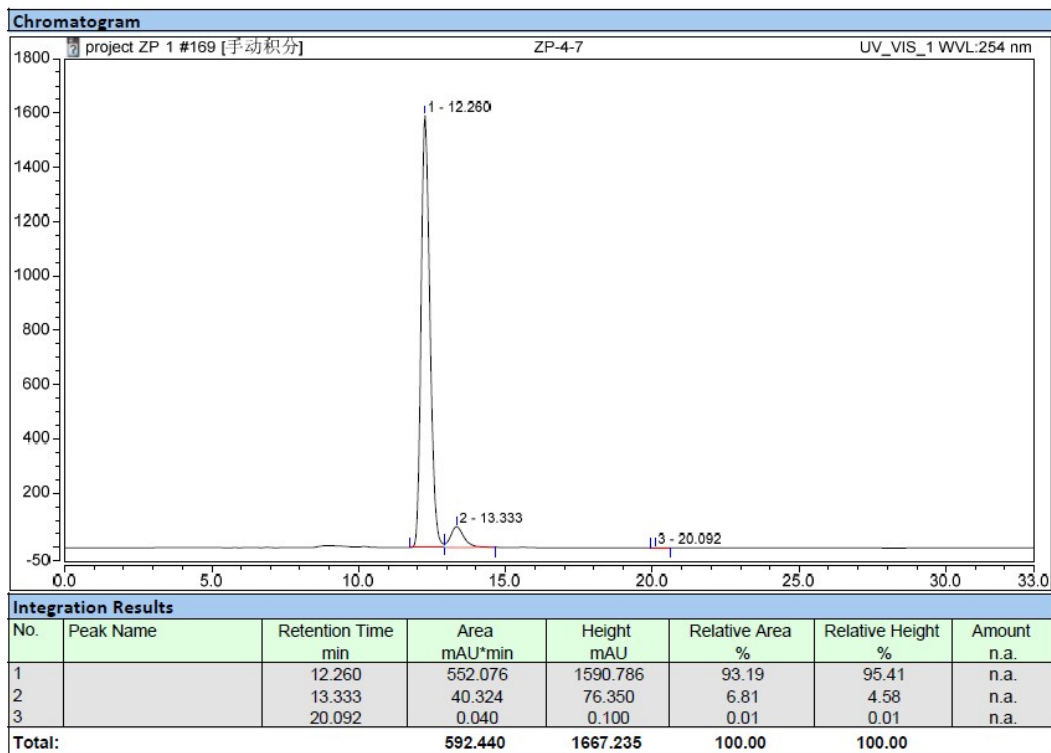
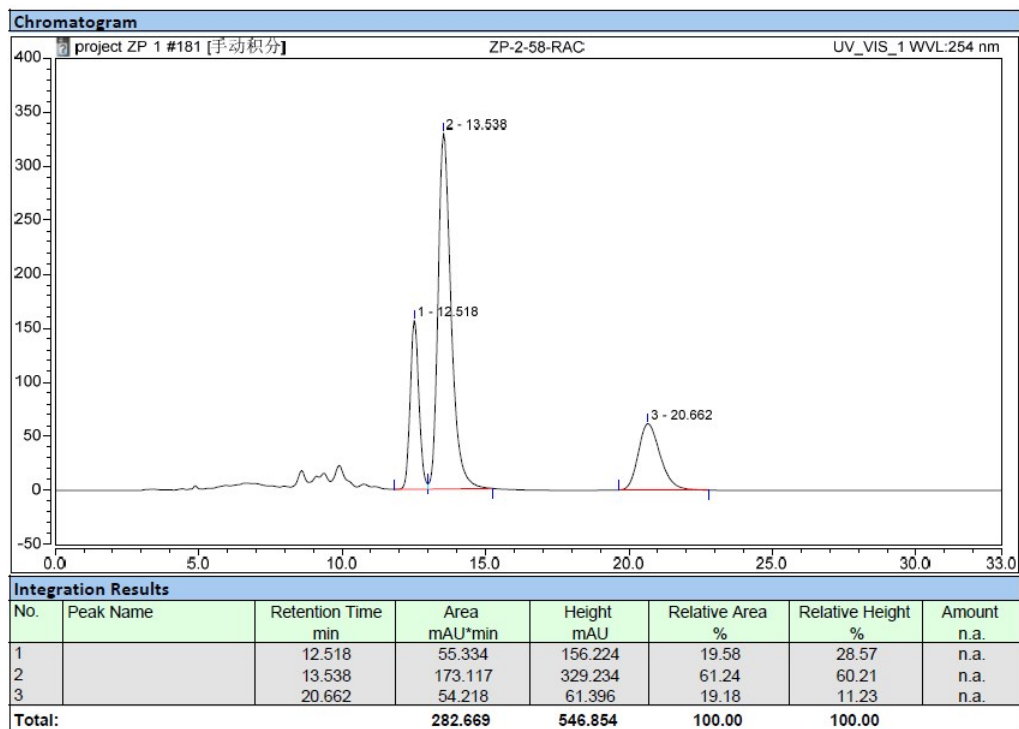
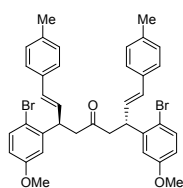
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.327	33.001	157.825	16.04	19.01	n.a.
2		10.222	69.225	299.042	33.65	36.02	n.a.
3		11.948	69.727	256.090	33.89	30.85	n.a.
4		12.653	33.763	117.153	16.41	14.11	n.a.
Total:			205.716	830.110	100.00	100.00	



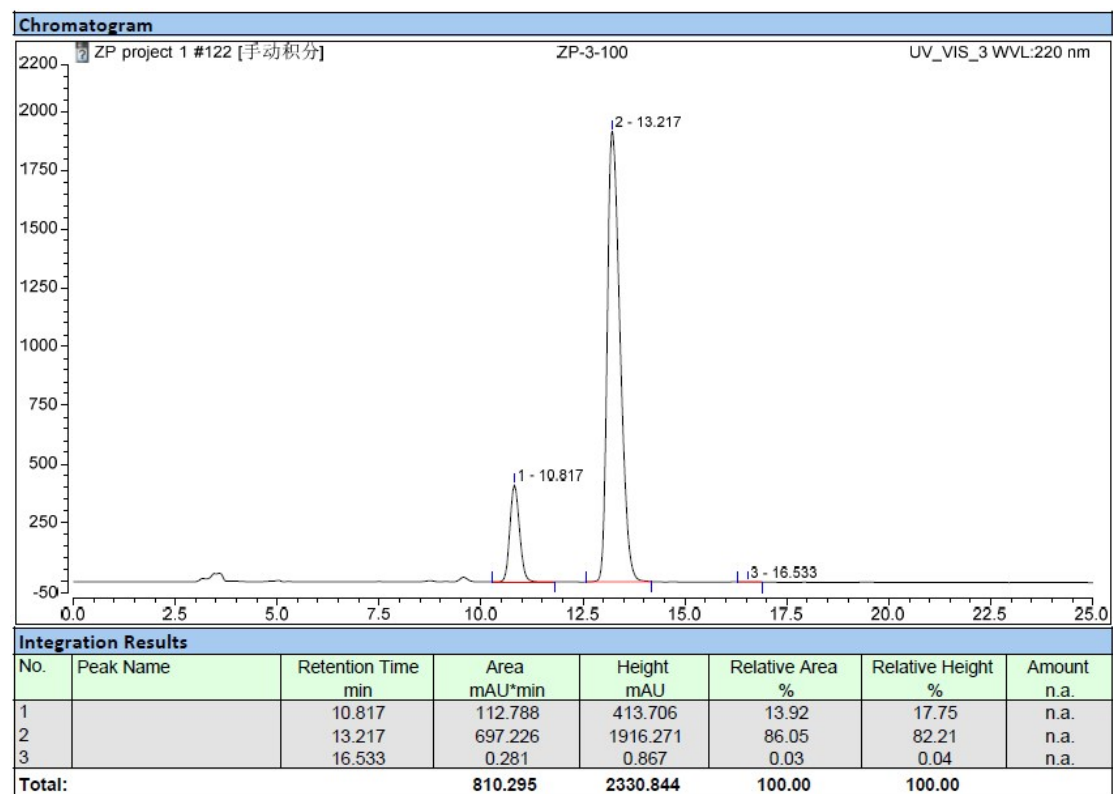
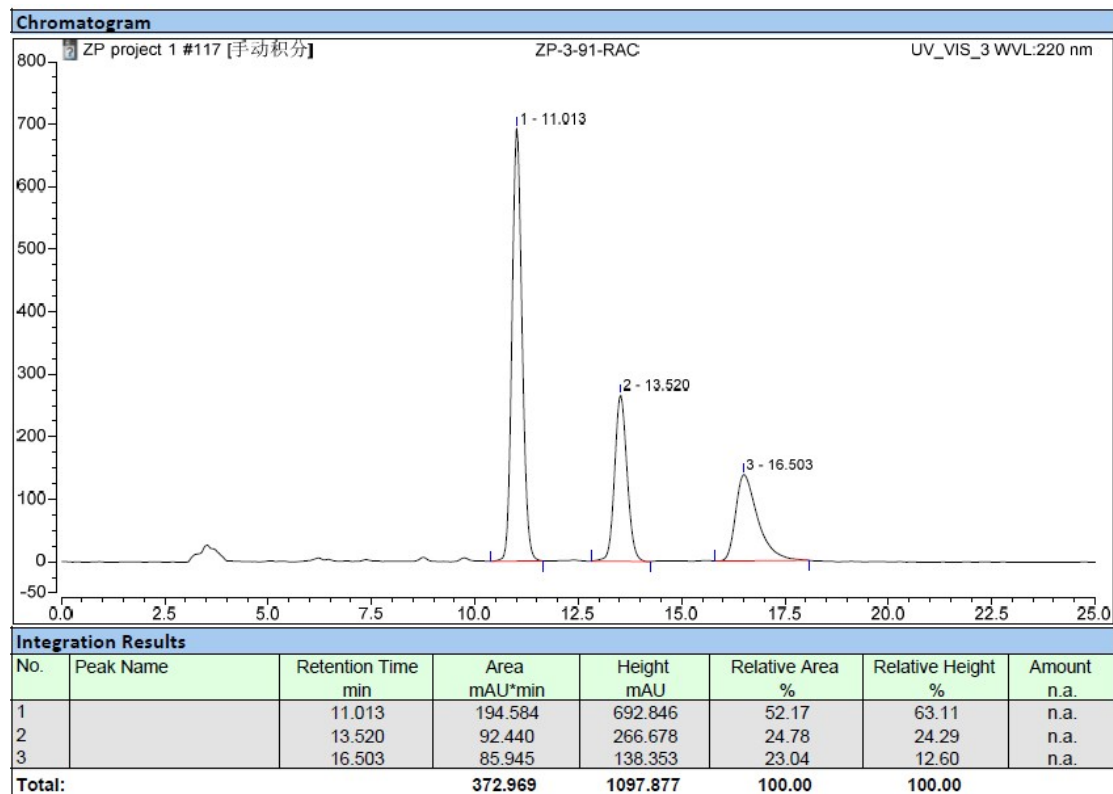
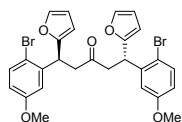
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.220	0.674	4.199	0.11	0.20	n.a.
2		10.580	20.602	90.588	3.32	4.21	n.a.
3		12.267	24.753	94.785	3.99	4.40	n.a.
4		12.847	574.501	1962.314	92.58	91.19	n.a.
Total:			620.529	2151.885	100.00	100.00	

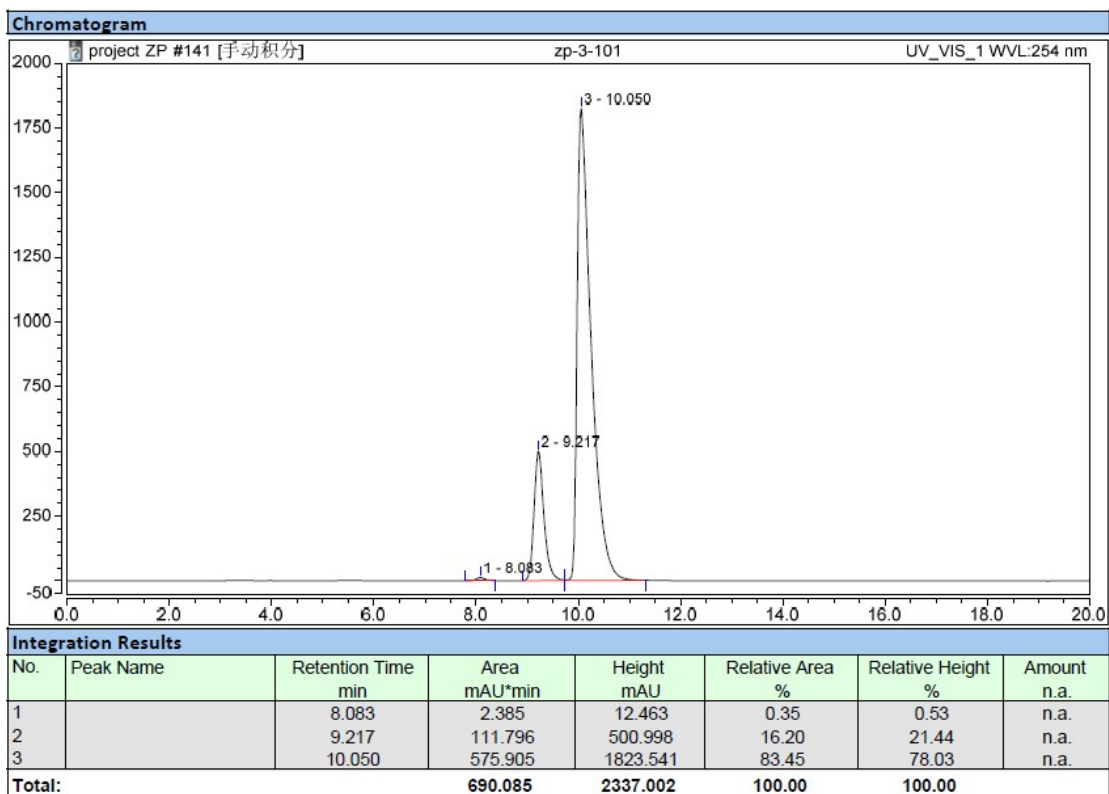
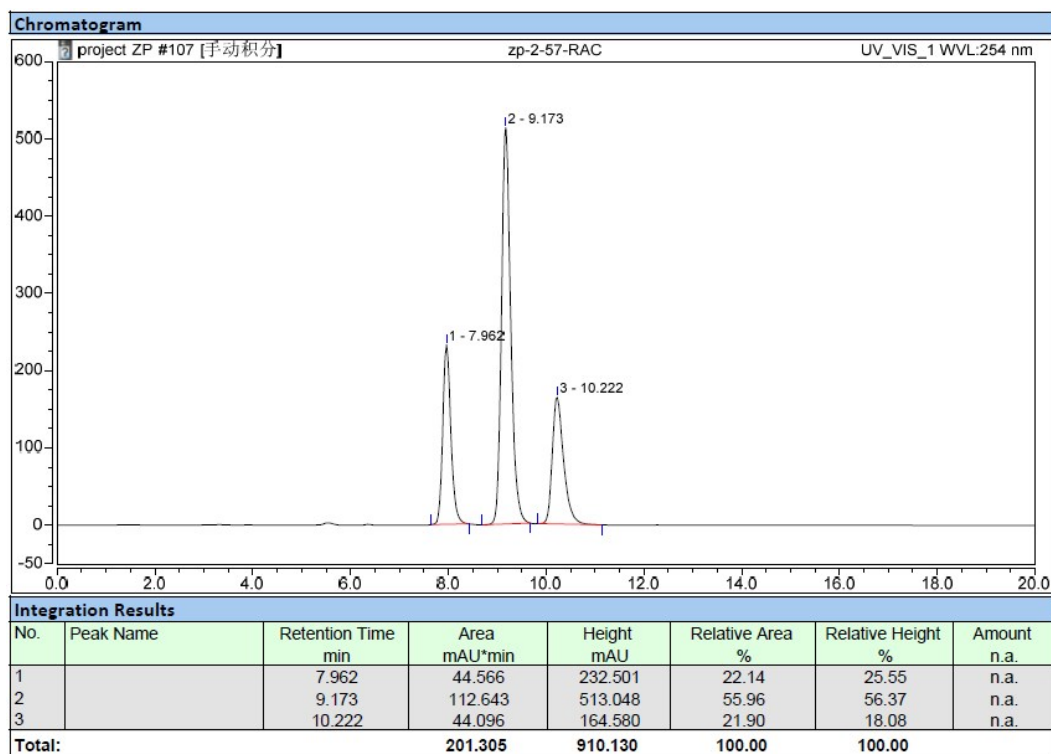
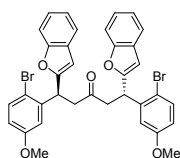
Compound 3b'



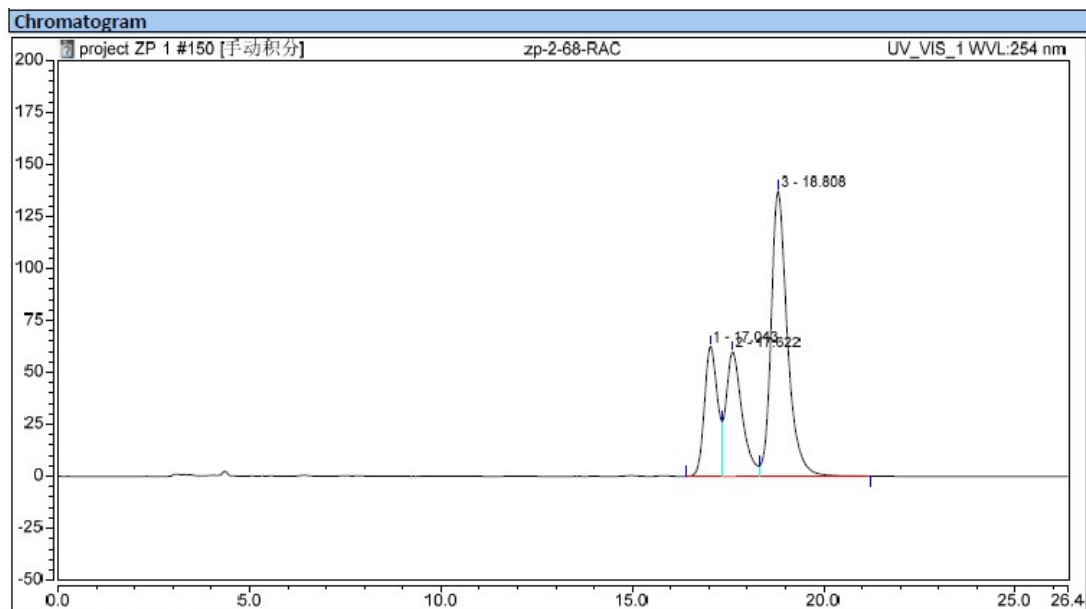
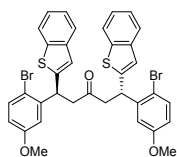
Compound 3le'



Compound 3lf

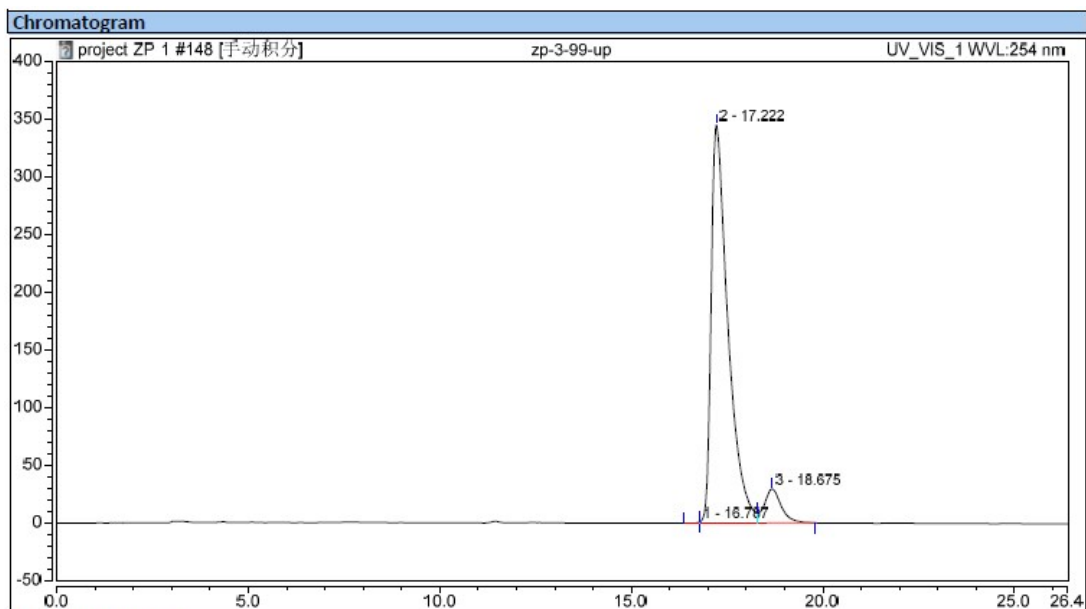


Compound 3h'



Integration Results

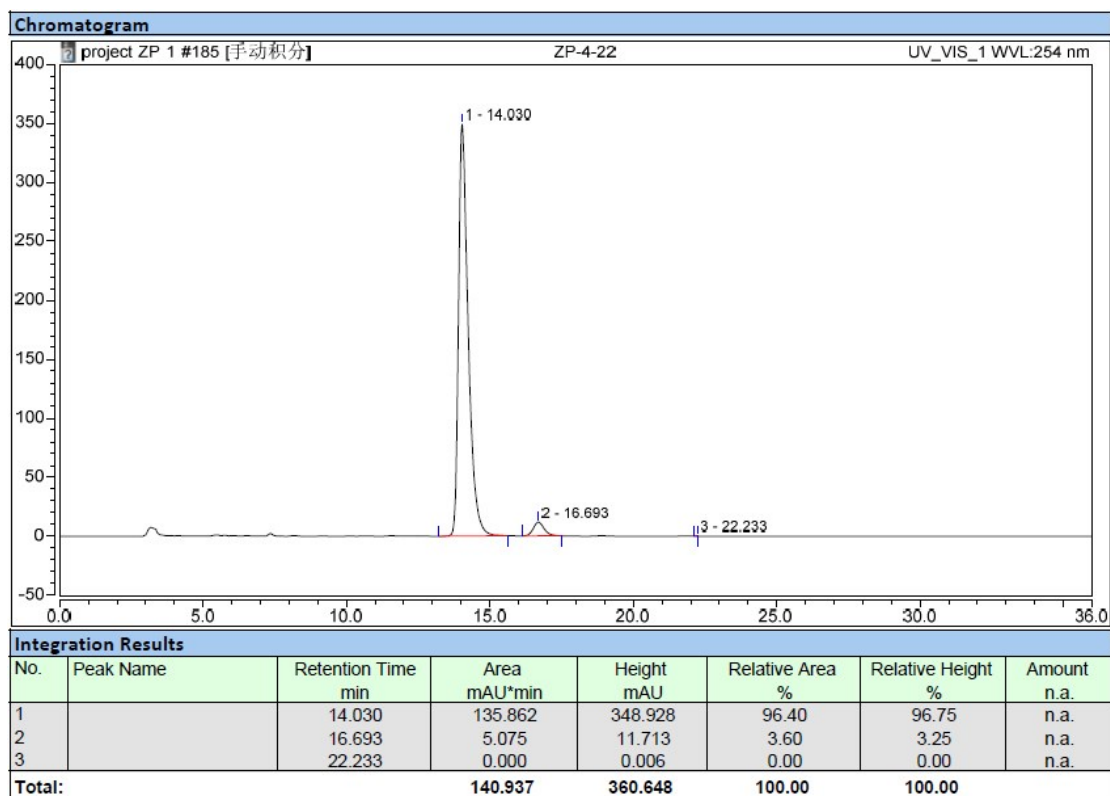
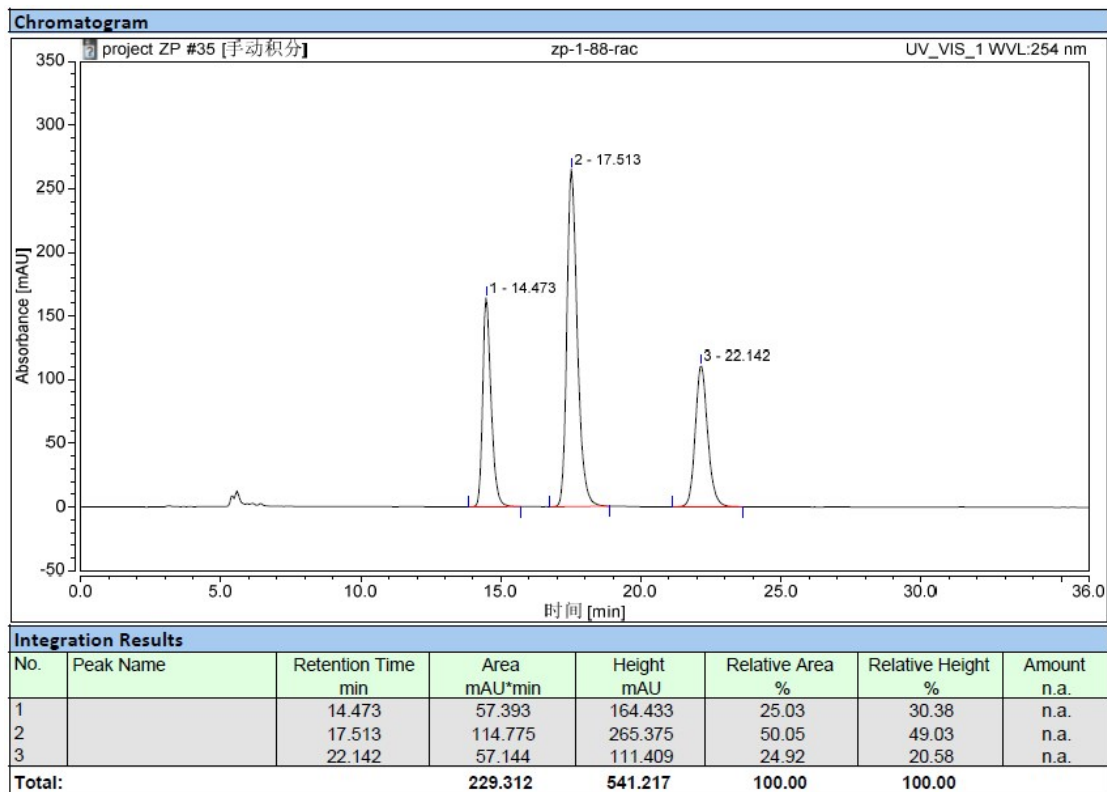
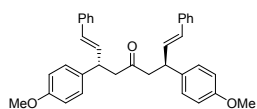
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.043	24.923	62.553	20.46	24.07	n.a.
2		17.622	29.211	60.004	23.98	23.09	n.a.
3		18.808	67.666	137.287	55.55	52.83	n.a.
Total:			121.800	259.844	100.00	100.00	



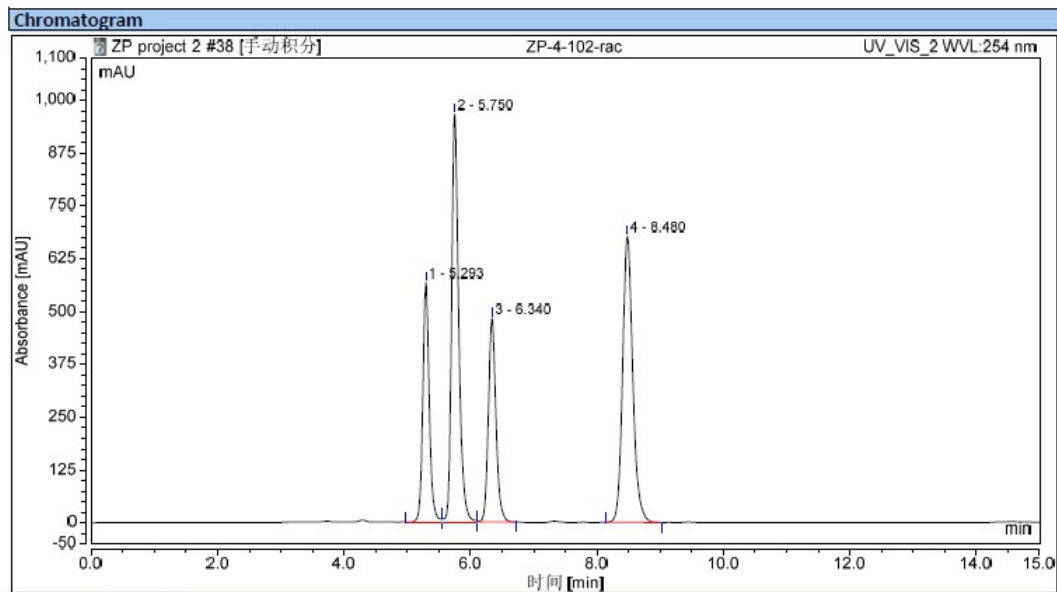
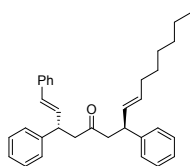
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		16.787	0.060	1.006	0.03	0.27	n.a.
2		17.222	175.453	344.923	91.97	91.86	n.a.
3		18.675	15.259	29.561	8.00	7.87	n.a.
Total:			190.772	375.489	100.00	100.00	

Compound 3ea (scale-up version)

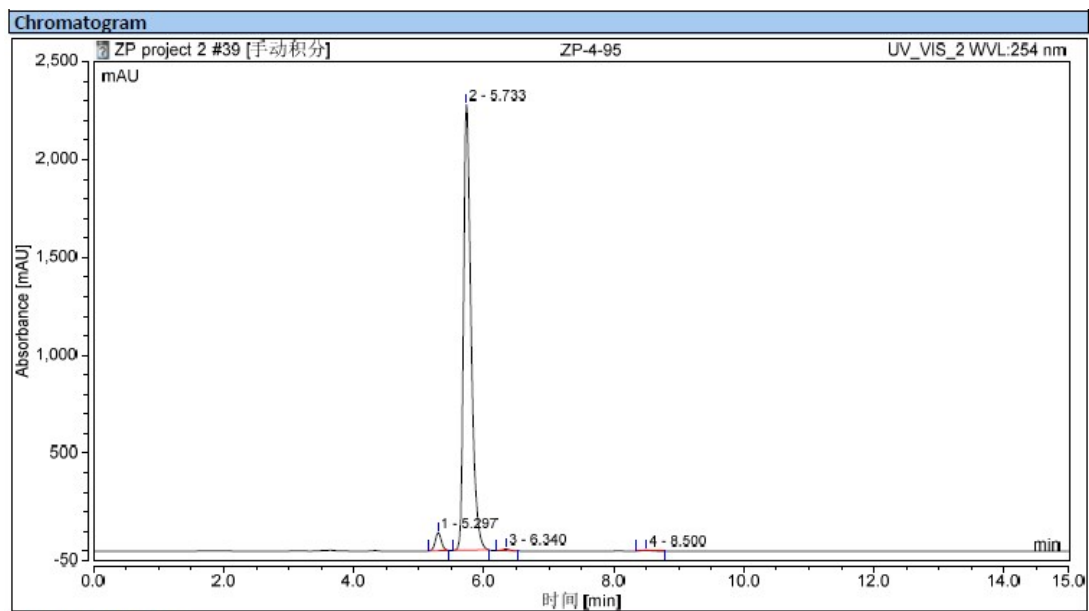


Compound 5



Integration Results

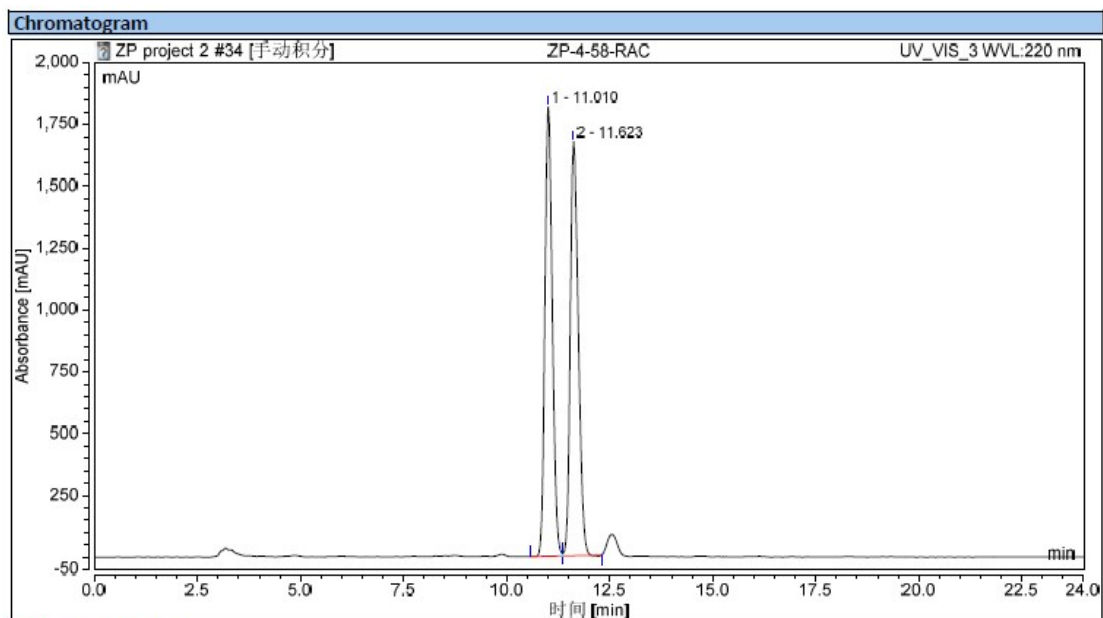
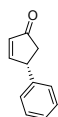
No.	Peak Name	Retention Time [min]	Area [mAU*min]	Height [mAU]	Relative Area [%]	Relative Height [%]	Amount [n.a.]
1		5.293	66.985	566.590	17.41	21.05	n.a.
2		5.750	125.988	965.472	32.75	35.87	n.a.
3		6.340	66.137	482.209	17.19	17.92	n.a.
4		8.480	125.612	677.166	32.65	25.16	n.a.
Total:			384.721	2691.437	100.00	100.00	



Integration Results

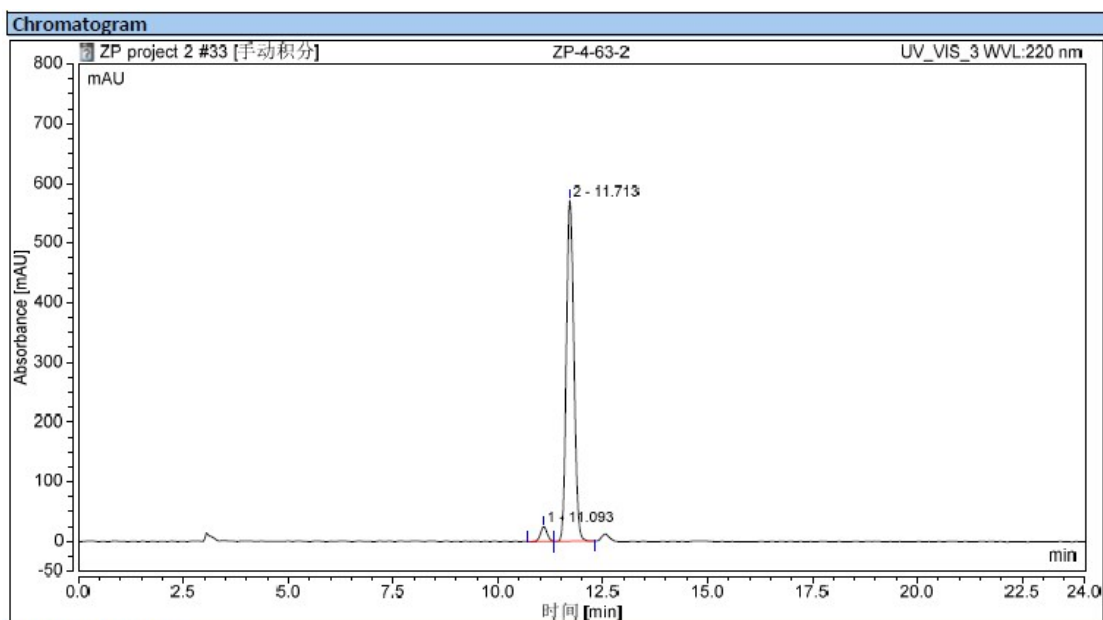
No.	Peak Name	Retention Time [min]	Area [mAU*min]	Height [mAU]	Relative Area [%]	Relative Height [%]	Amount [n.a.]
1		5.297	10.185	93.102	3.20	3.91	n.a.
2		5.733	306.013	2276.318	96.27	95.57	n.a.
3		6.340	1.132	9.147	0.36	0.38	n.a.
4		8.500	0.524	3.226	0.16	0.14	n.a.
Total:			317.854	2381.793	100.00	100.00	

Compound 6



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.010	380.334	1818.009	49.88	52.05	n.a.
2		11.623	382.219	1675.121	50.12	47.95	n.a.
Total:			762.554	3493.130	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.093	4.527	25.236	3.68	4.23	n.a.
2		11.713	118.554	570.880	96.32	95.77	n.a.
Total:			123.081	596.117	100.00	100.00	