Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Efficient Synthesis of Chiral Cyclic Acetals by Metal and Brønsted Acid Co-Catalyzed Entioselective Four-component Cascade Reactions

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Contents pages

General Considerations:

All moisture sensitive reactions were performed under an argon atmosphere in a well-dried reaction flask. Dichloromethane (CH_2Cl_2), 1, 2-dichloroenthene [$(CH_2Cl)_2$] and chloroform ($CHCl_3$) were freshly distilled over calcium hydride, toluene from sodium benzophenone ketyl, respectively, prior to use. Solvents for the column chromatography were distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Brucker-400 MHz spectrometer. Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^1H NMR and deuteriochloroform (δ = 77.00 ppm) for ^{13}C NMR spectroscopy. HRMS spectra were recorded on a Bruker micrOTOF II instrument. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump) & Shimadzu (SPD-20AV UV-VIS Detector and LC-20AT Liquid Chromatograph Pump). Chiralpak IA and OD-H was purchased from Daicel Chemical Industries, LTD. The racemic standards used in HPLC studies were prepared according to the general procedure by using a racemic BINOL derivatived phosphoric acid catalyst.

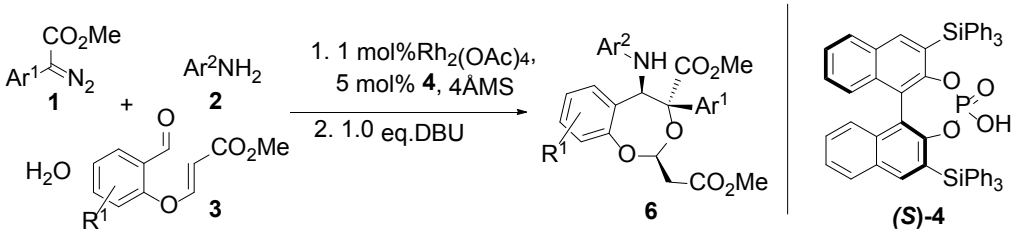
Synthesis of Substrates:

Various aryl diazo compounds **1** were prepared by the treatment of corresponding arylacetate with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in the presence of DBU following the general procedure.[1] Substrates **3** were synthesized following literature procedure.[2] Others were purchased from commercial suppliers and used without further purification.

References:

1. M. P. Doyle, M. A. McKervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, 1998.
2. D. H. T. Phan, B. Kim and V. M. Dong, *J. Am. Chem. Soc.* 2009, **131**, 15608.

General procedure for four-component reactions of aryldiazoacetates 1 with water, amines 2 and methyl 3-(2-formylphenoxy)propenoates 3:



To a stirred solution of $Rh_2(OAc)_4$ (3.3 mg, 1 mol%), the chiral phosphoric acid **4** (5.0 mol%), arylamine **2** (0.12 mmol), and methyl 3-(2-formylphenoxy)propenoates **3** (0.10 mmol, 1.0 eq), 4 Å MS (100 mg) in 1.5 mL dichloromethane (0.05% (w/w) water content) at room temperature for 30 min, then added diazo compounds **1**(0.15 mmol) in dichloromethane (0.5 ml) over 1 hour via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 0.5 h, then passed through a short flash column of silica gel, after removal of the solvent under reduced pressure，dichloromethane (2.0 mL) was added. This solution was transferred to a reaction tube containing a magnetic stirring bar, and the temperature of the solution was to room temperature, followed by the addition of DBU (0.10 mmol, 1.0 eq). The reaction was detected by TLC until **7** consumed up, and then subjected to ^{1}H NMR spectroscopic analysis after solvent removal to determine product diastereoselectivity. The crude reaction mixture was purified by column chromatography on silica gel (eluent light petroleum/EtOAc=20:1 to 5:1) to give the pure product **6**.

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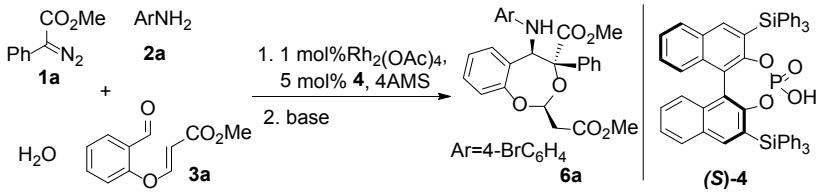
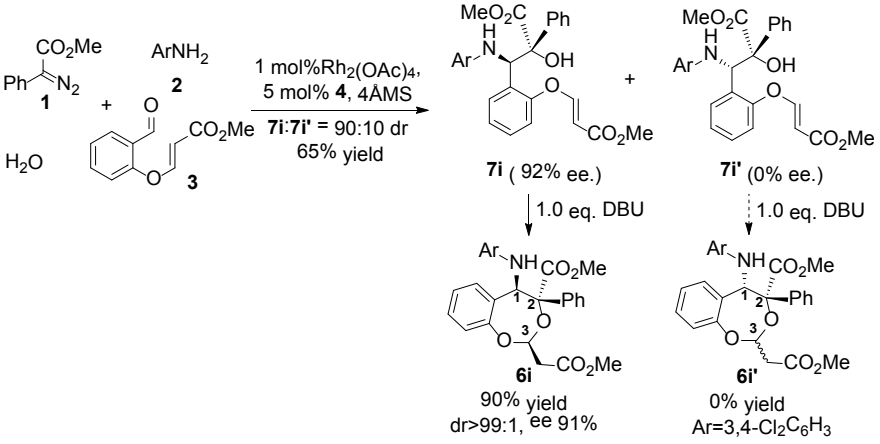
Table S1. Optimization for the four-component cascade reaction [a]



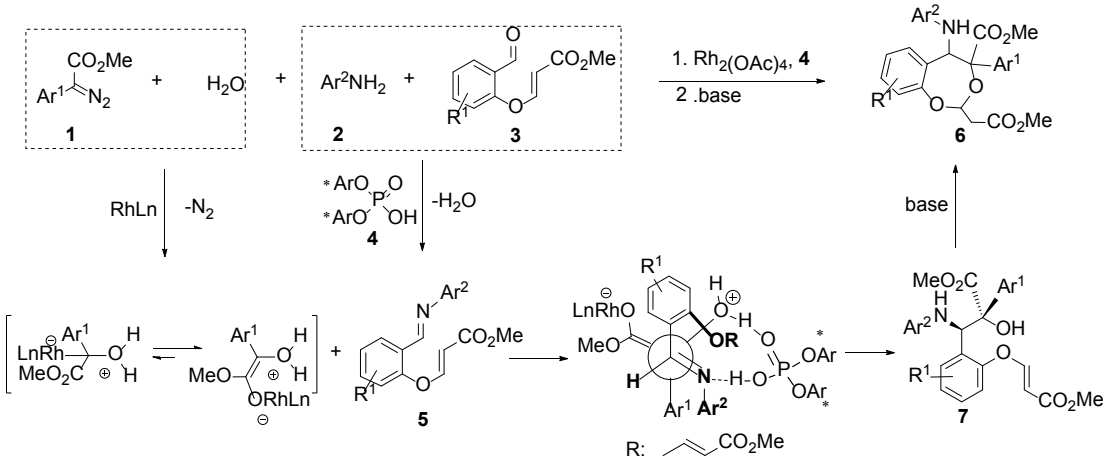
Entry	Solvent	*T* (°C)	Base (eqv.)	Yield(%) [b]	dr [c]	ee(%) [d]
1	DCM	25	DBU(0.2)	20	>99:1	91
2	DCM	25	piperidine(0.2)	<5	nd [e]	nd [e]
3	DCM	25	TEA(0.2)	<5	nd [e]	nd [e]
4	DCM	25	DIPEA(0.2)	<5	nd [e]	nd [e]
5	DCM	25	TFA	0	nd [e]	nd [e]
6	DCM	40	DBU(0.2)	35	>99:1	91
7	DCM	0	DBU(0.2)	10	>99:1	92
8	DCM	25	DBU(1.0)	45	>99:1	91
9	DCM	25	Na_2CO_3	0	nd [e]	nd [e]
10	DCM	25	K_2CO_3	0	nd [e]	nd [e]
11	DCM	25	NaOH	<5	nd [e]	nd [e]
12	$CHCl_3$	25	DBU(1.0)	47	>99:1	38
13	DCE	25	DBU(1.0)	35	>99:1	69
14	Toluene	25	DBU(1.0)	38	>99:1	80
15 [f]	DCM	25	DBU(1.0)	23	>99:1	91

[a] Reaction conditions: **1a**/H_2O/**2a**/**3a** was 1.5/0.5/1.2/1.0. [b] Isolated yield of **6a**. [c] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [d] Determined by chiral HPLC with IC column. [e] nd: not detected. [f] no 4 ÅMS added. DBU: 1, 8-diazabicyclo [5.4.0] undec-7-ene, TEA: triethylamine, DIPEA: *N*, *N*-diisopropylethylamine, TFA: trifluoroacetic acid.

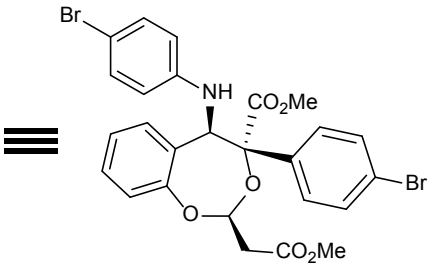
Scheme S1. Intramolecular oxy-Michael addition *via* DBU catalyzed.



Scheme S2. Proposed reaction pathway for the four-component cascade reactions



Crystal data of 6d (CCDC: 941071)



6d

Bond precision: C-C = 0.0050 A Wavelength=0.71073

Cell: a=11.8142(7) b=14.0221(8) c=15.3593(9)
alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2544.4(3)	2544.4(3)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C26 H23 Br2 N O6	?
Sum formula	C26 H23 Br2 N O6	C26 H23 Br2 N O6
Mr	605.25	605.27
Dx,g cm-3	1.580	1.580
Z	4	4
Mu (mm-1)	3.227	3.227
F000	1216.0	1216.0
F000'	1214.29	
h,k,lmax	14,16,18	14,16,18
Nref	2539[4478]	4478
Tmin,Tmax	0.281,0.559	0.344,0.594
Tmin'	0.237	

Correction method= MULTI-SCAN

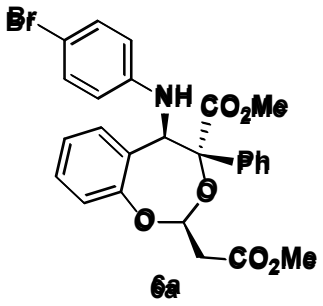
Data completeness= 1.76/1.00 Theta(max)= 25.010

R(reflections)= 0.0309(3826) wR2(reflections)= 0.0736(4478)

S = 1.025 Npar= 316

Characterization Data of Products:

(2S,4R,5R)-methyl5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6a)



6a

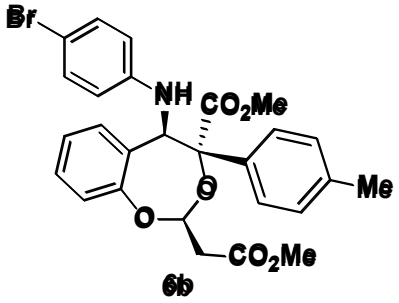
Yield: 45%; >95:5 dr; 91% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 12.7 min, t_{major} = 10.3 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2H), 7.37-7.22 (m, 3H), 7.23 – 7.13 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.8 Hz, 3H), 6.87 (d, J = 7.8 Hz, 1H), 6.33 (d, J = 7.9 Hz, 2H), 5.54 (s, 1H), 5.24 (d, J = 10.8 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 3.72 (s, 3H), 3.49 (s, 3H), 3.10 (qd, J = 15.3, 4.4 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.79, 168.26, 156.22, 144.30, 136.60, 130.87, 130.62, 129.67, 128.40, 127.45, 127.37, 124.41, 123.41, 120.44, 114.49, 108.38, 99.31, 83.36, 61.74, 51.63, 50.95, 40.42;

ESCI-HRMS Calcd. for $C_{26}H_{24}BrNNaO_6$, $[M+Na]^+$ 548.0664; Found: 548.0679.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4-p-tolyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate (6b)



6b

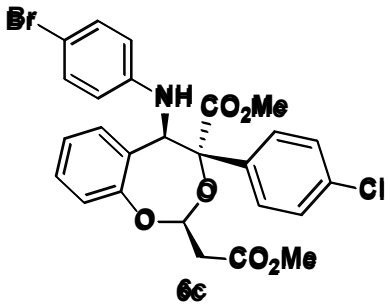
Yield: 43%; >95:5 dr; 95% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 8.7 min, t_{major} = 10.0 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 6.9 Hz, 1H), 7.19 (s, 1H), 7.08 (dd, J = 12.0, 8.4 Hz, 3H), 6.99 (dd, J = 11.4, 8.1 Hz, 3H), 6.86 (d, J = 7.8 Hz, 1H), 6.34 (d, J = 8.7 Hz, 2H), 5.65-5.43 (m, 1H), 5.23 (d, J = 10.8 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 3.72 (s, 3H), 3.49 (s, 3H), 3.09 (qd, J = 15.3, 5.5 Hz, 2H), 2.23 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.94, 168.29, 156.27, 144.39, 137.20, 133.73, 130.89, 130.64, 129.78, 128.36, 128.18, 124.36, 123.36, 120.45, 114.55, 108.37, 99.32, 83.32, 61.70, 51.56, 50.92, 40.47, 20.02;

ESCI-HRMS Calcd. for $C_{27}H_{26}BrNNaO_6$, $[M+Na]^+$ 562.0820; Found: 562.0836.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-4-(4-chlorophenyl)-2-(2-methoxy-2-oxoethyl)-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate (6c)



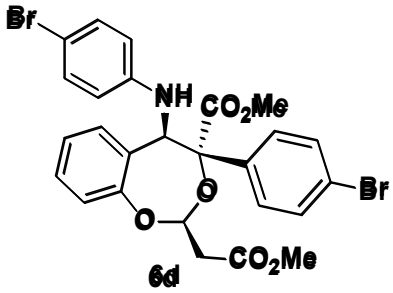
6c

Yield: 51%; >95:5 dr; 99% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 12.7 min, t_{major} = 10.5 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.3 Hz, 1H), 7.26-7.15 (m, 2H), 7.10 (m, 1H), 7.00 (m, 3H), 6.87 (d, J = 7.9 Hz, 1H), 6.33

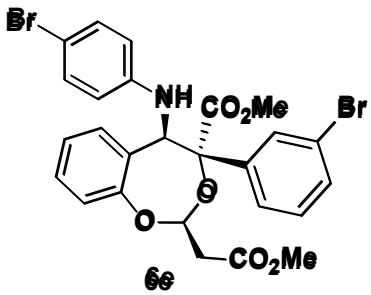
(d, *J* = 8.7 Hz, 2H), 5.52 (dd, *J* = 6.0, 5.0 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 3.09 (qd, *J* = 15.4, 5.5 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.53, 168.16, 156.19, 144.15, 135.33, 133.42, 130.85, 130.75, 129.41, 128.55, 127.63, 125.96, 123.51, 120.49, 114.60, 108.75, 99.32, 83.12, 61.89, 51.76, 50.97, 40.41;
ESCI-HRMS Calcd. for $C_{26}H_{23}BrClNNaO_6$, $[M+Na]^+$ 582.0272; Found: 582.0289.

(2S,4R,5R)-methyl 4-(4-bromophenyl)-5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate (6d)



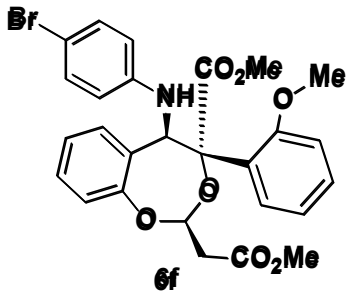
Yield: 47%; >95:5 dr; 96% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 13.4 min, t_{major} = 10.6 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.21-7.06 (m, 1H), 7.00 (m, 3H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 8.7 Hz, 2H), 5.52 (dd, *J* = 6.1, 4.9 Hz, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 3.72 (s, 3H), 3.51 (s, 3H), 3.09 (qd, *J* = 15.4, 5.5 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 168.15, 156.19, 144.14, 135.90, 130.86, 130.75, 130.60, 129.38, 128.56, 126.28, 123.52, 121.67, 120.49, 114.62, 108.78, 99.32, 83.16, 61.84, 51.77, 50.97, 40.41;
ESCI-HRMS Calcd. for $C_{26}H_{23}Br_2NNaO_6$, $[M+Na]^+$ 625.9775; Found: 625.9784.

(2S,4R,5R)-methyl 4-(3-bromophenyl)-5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6e)



Yield: 46%; >95:5 dr; 98% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 13.2 min, t_{major} = 10.6 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.32 (dd, *J* = 15.0, 7.7 Hz, 2H), 7.12 (dd, *J* = 18.2, 8.0 Hz, 2H), 7.00 (dd, *J* = 12.7, 8.1 Hz, 3H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.34 (d, *J* = 8.7 Hz, 2H), 5.57-5.44 (m, 1H), 5.17 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 11.1 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H), 3.11 (qd, *J* = 15.4, 5.5 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.37, 168.18, 156.15, 144.16, 138.98, 130.87, 130.71, 130.51, 129.37, 128.94, 128.56, 127.96, 123.55, 122.83, 121.70, 120.48, 114.71, 108.79, 99.36, 83.02, 62.19, 51.84, 51.01, 40.41;
ESCI-HRMS Calcd. for $C_{26}H_{23}Br_2NNaO_6$, $[M+Na]^+$ 625.9775; Found: 625.9784.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4-(2-methoxyphenyl)-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate (6f)



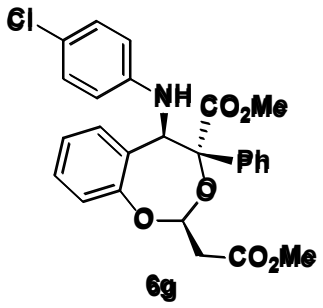
Yield: 38%; >95:5 dr; 95% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 8.1 min, t_{major} = 9.3 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.30-7.04 (m, 3H), 7.04-6.82 (m, 5H), 6.76 (d, J = 8.3 Hz, 1H), 6.18 (d, J = 7.9 Hz, 2H), 5.49 (d, J = 10.0 Hz, 1H), 5.37 (t, J = 5.4 Hz, 1H), 4.61 (d, J = 9.9 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.53 (s, 3H), 3.02 (qd, J = 15.4, 5.4 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.65, 168.15, 154.54, 154.36, 144.82, 131.12, 130.45, 128.49, 127.61, 127.49, 125.60, 123.25, 119.93, 114.20, 110.15, 107.80, 98.17, 81.80, 59.93, 54.63, 51.32, 50.92, 40.61;

ESCI-HRMS Calcd. for $C_{27}H_{26}BrNNaO_7$, $[M+Na]^+$ 578.0779; Found: 578.0785.

(2S,4R,5R)-methyl 5-(4-chlorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6g)



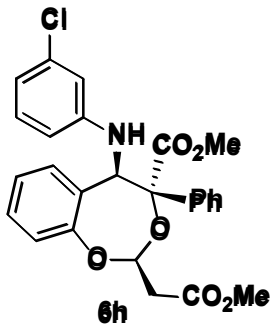
Yield: 46%; >95:5 dr; 90% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 12.0 min, t_{major} = 9.7 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 2H), 7.36-7.24 (m, 1H), 7.24-7.14 (m, 2H), 7.09 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.91-6.79 (m, 3H), 6.37 (d, J = 8.7 Hz, 2H), 5.54 (dd, J = 6.2, 4.9 Hz, 1H), 5.24 (d, J = 10.9 Hz, 1H), 4.80 (d, J = 10.9 Hz, 1H), 3.73 (s, 3H), 3.50 (s, 3H), 3.10 (qd, J = 15.4, 5.5 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 168.27, 156.25, 143.92, 136.67, 130.87, 129.78, 128.38, 127.77, 127.44, 127.36, 124.44, 123.40, 121.38, 120.44, 114.11, 99.34, 83.44, 62.08, 51.62, 50.94, 40.46;

ESCI-HRMS Calcd. for $C_{26}H_{24}ClNNaO_6$, $[M+Na]^+$ 504.1162; Found: 504.1184.

(2S,4R,5R)-methyl 5-(3-chlorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6h)

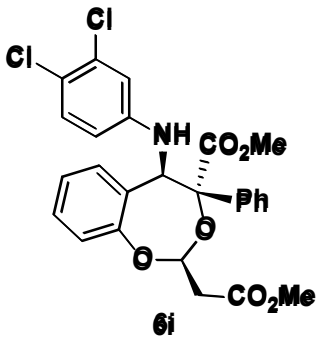


Yield: 42%; >95:5 dr; 90% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 9.7 min, t_{major} = 7.6 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.32-7.14 (m, 3H), 7.14-6.95 (m, 2H), 6.95-6.76 (m, 2H), 6.45 (d, J = 7.9 Hz, 2H), 6.31 (d, J = 8.5 Hz, 1H), 5.62-5.47 (m, 1H), 5.26 (d, J = 10.8 Hz, 1H), 4.89 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 3.11 (qd, J = 15.4, 5.5

Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.75, 168.27, 156.23, 146.40, 136.51, 133.57, 130.85, 129.61, 128.88, 128.42, 127.46, 127.39, 124.40, 123.47, 120.47, 116.58, 112.49, 111.04, 99.29, 98.94, 83.35, 61.49, 51.66, 50.97, 40.41;
ESCI-HRMS Calcd. for $C_{26}H_{24}ClNNaO_6$, $[M+Na]^+$ 504.1162; Found: 504.1145.

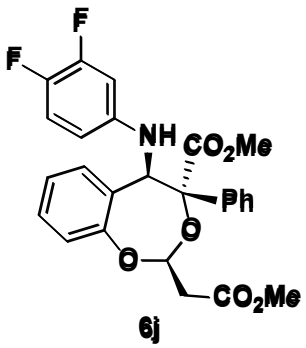
(2S,4R,5R)-methyl 5-(3,4-dichlorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6i)



6i

Yield: 52%; >95:5 dr; 92% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 20.3 min, t_{major} = 17.2 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 2H), 7.39-7.16 (m, 4H), 7.08 (dd, J = 31.2, 7.5 Hz, 2H), 6.91 (dd, J = 17.2, 8.3 Hz, 2H), 6.52 (s, 1H), 6.27 (d, J = 8.6 Hz, 1H), 5.54 (t, J = 5.2 Hz, 1H), 5.20 (d, J = 10.7 Hz, 1H), 4.90 (d, J = 10.7 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 3.10 (qd, J = 15.5, 5.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.64, 168.22, 156.19, 144.81, 136.42, 131.43, 130.81, 129.38, 129.31, 128.59, 127.51, 127.49, 124.35, 123.55, 120.55, 119.21, 113.97, 112.41, 99.34, 83.28, 61.85, 51.69, 50.98, 40.39;
ESCI-HRMS Calcd. for $C_{26}H_{23}Cl_2NNaO_6$, $[M+Na]^+$ 538.0781; Found: 538.0795.

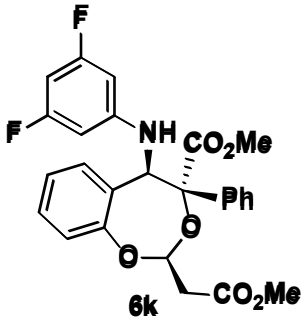
(2S,4R,5R)-methyl 5-(3,4-difluorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6j)



6j

Yield: 53%; >95:5 dr; 94% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 9.6 min, t_{major} = 12.0 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 2H), 7.36-7.21 (m, 4H), 7.06 (m, 2H), 6.89 (d, J = 7.8 Hz, 1H), 6.69 (q, J = 9.2 Hz, 1H), 6.32-6.15 (m, 1H), 6.09 (d, J = 8.6 Hz, 1H), 5.61-5.47 (m, 1H), 5.15 (d, J = 10.9 Hz, 1H), 4.75 (d, J = 10.9 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 3.11 (qd, J = 15.4, 5.5 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72, 168.24, 156.15, 136.55, 130.83, 129.56, 128.47, 127.47, 127.40, 124.35, 123.48, 120.45, 116.20, 116.02, 108.45, 101.86, 101.65, 99.32, 83.33, 62.77, 51.67, 50.97, 40.40;
ESCI-HRMS Calcd. for $C_{26}H_{23}F_2NNaO_6$, $[M+Na]^+$ 506.1371; Found: 506.1376.

(2S,4R,5R)-methyl 5-(3,5-difluorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6k)



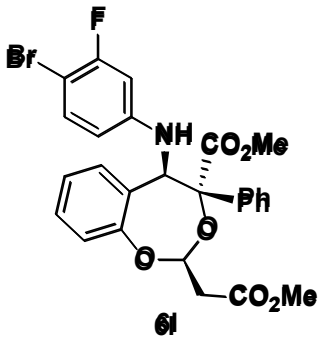
Yield: 43%; >95:5 dr; 93% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 9.4 min, t_{major} = 7.8 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ7.56 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.0 Hz, 1H), 7.32-7.17 (m, 5H), 7.13 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.92 (t, J = 10.8 Hz, 3H), 5.59-5.48 (m, 1H), 5.20 (d, J = 10.6 Hz, 1H), 5.05 (d, J = 10.6 Hz, 1H), 3.74 (s, 3H), 3.51 (s, 3H), 3.11 (qd, J = 15.5, 5.5 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.63, 168.21, 156.23, 146.39, 146.29, 136.43, 132.05, 130.81, 129.41, 128.59, 127.52, 124.36, 123.56, 120.55, 110.04, 100.58, 100.32, 99.35, 83.28, 61.82, 51.68, 50.96, 40.40;

ESCI-HRMS Calcd. for $C_{26}H_{23}F_2NNaO_6$, $[M+Na]^+$ 506.1371; Found: 506.1386.

(2S,4R,5R)-methyl 5-(4-bromo-3-fluorophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6l)



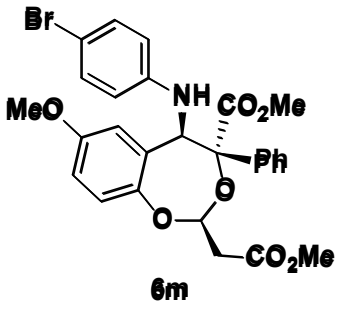
Yield: 41%; >95:5 dr; 88% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 13.2 min, t_{major} = 11.1 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.9 Hz, 2H), 7.38-7.16 (m, 4H), 7.08 (m, 2H), 6.91 (dd, J = 17.2, 8.3 Hz, 2H), 6.52 (s, 1H), 6.27 (d, J = 8.6 Hz, 1H), 5.54 (t, J = 5.2 Hz, 1H), 5.20 (d, J = 10.7 Hz, 1H), 4.90 (d, J = 10.7 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 3.10 (qd, J = 15.5, 5.4 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.64, 168.22, 156.19, 144.81, 136.42, 131.43, 130.81, 129.38, 129.31, 128.59, 127.51, 127.49, 124.35, 123.55, 120.55, 119.21, 113.97, 112.41, 99.34, 83.28, 61.85, 51.69, 50.98, 40.39;

ESCI-HRMS Calcd. for $C_{26}H_{23}BrFNNaO_6$, $[M+Na]^+$ 566.0573; Found: 566.0585.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-7-methoxy-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6l)

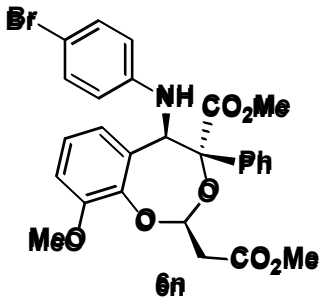


Yield: 47%; >95:5 dr; 76% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 15.6 min, t_{major} = 16.6 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.4 Hz, 2H), 7.27 (t, J = 7.1 Hz, 2H), 7.23-7.15 (m, 3H), 7.02 (d, J = 7.7 Hz, 2H), 6.89-6.73 (m, 2H), 6.60 (d, J = 8.7 Hz, 1H), 6.35 (d, J = 7.6 Hz, 2H), 5.51 (s, 1H), 5.17 (d, J = 10.9

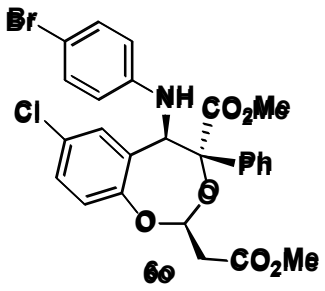
Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.52 (s, 3H), 3.07 (dd, *J* = 16.5, 11.5 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 168.34, 154.89, 149.97, 144.30, 136.70, 130.65, 127.44, 127.36, 124.41, 120.94, 116.56, 114.55, 112.41, 108.42, 99.52, 83.43, 61.78, 54.61, 51.66, 50.94, 40.35;
ESCI-HRMS Calcd. for $C_{27}H_{26}BrNNaO_7$, $[M+Na]^+$ 578.0772; Found: 578.0785.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-9-methoxy-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6m)



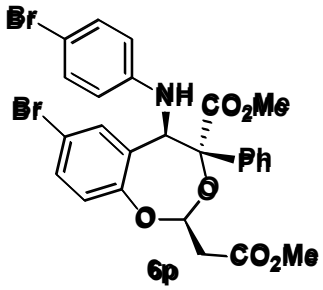
Yield: 45%; >95:5 dr; 98% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 12.5 min, t_{major} = 18.0 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.33-7.14 (m, 5H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 7.7 Hz, 2H), 5.54 (t, *J* = 4.9 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.51 (s, 3H), 3.14 (qd, *J* = 14.3, 5.1 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 168.10, 150.50, 145.23, 144.26, 136.65, 131.10, 130.58, 127.44, 127.36, 124.44, 123.55, 122.40, 114.53, 111.00, 108.32, 99.97, 83.29, 61.53, 54.87, 51.61, 51.01, 40.88;
ESCI-HRMS Calcd. for $C_{27}H_{26}BrNNaO_7$, $[M+Na]^+$ 578.0769; Found: 578.0785.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-7-chloro-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6o)



Yield: 51%; >95:5 dr; 98% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 9.4 min, t_{major} = 10.6 min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.12 (m, 6H), 7.04 (t, *J* = 9.1 Hz, 3H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 2H), 5.49 (s, 1H), 5.17 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 3.19 – 2.97 (m, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.57, 168.15, 154.76, 143.92, 136.21, 131.51, 130.78, 130.39, 128.61, 128.31, 127.52, 124.28, 121.83, 114.44, 108.76, 99.54, 83.38, 61.48, 51.83, 51.01, 40.22;
ESCI-HRMS Calcd. for $C_{26}H_{23}BrClNNaO_6$, $[M+Na]^+$ 582.0287; Found: 582.0289.

(2S,4R,5R)-methyl 7-bromo-5-(4-bromophenylamino)-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6p)



6p

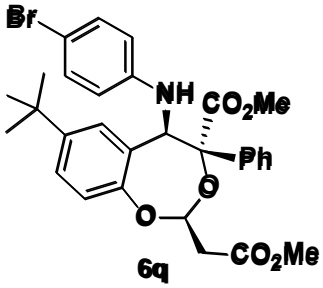
Yield: 53%; >95:5 dr; 97% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 9.7 min, t_{major} = 11.3 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 2H), 7.47 (s, 1H), 7.32-7.12 (m, 5H), 7.03 (d, J = 7.6 Hz, 2H), 6.76 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 7.7 Hz, 2H), 5.49 (s, 1H), 5.17 (d, J = 10.8 Hz, 1H), 4.79 (d, J = 10.8 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 3.18 – 2.98 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.54, 168.13, 155.29, 143.89, 136.18, 133.28, 131.95, 131.30, 130.79, 127.52, 124.27, 122.26, 116.30, 114.40, 108.75, 99.49, 83.37, 61.41, 51.84, 51.02, 40.22;

ESCI-HRMS Calcd. for $C_{26}H_{23}Br_2NNaO_6$, $[M+Na]^+$ 625.9767; Found: 625.9784.

(2S,4R,5R)-methyl 5-(4-bromophenylamino)-7-tert-butyl-2-(2-methoxy-2-oxoethyl)-4-phenyl-4,5-dihydrobenzo[d][1,3]dioxepine-4-carboxylate(6q)



6q

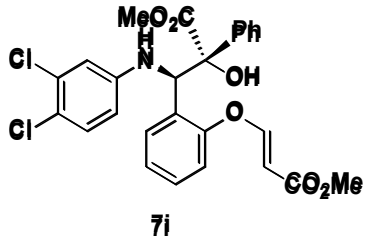
Yield: 42%; >95:5 dr; 97% ee; determined by HPLC (Daicel Chirapak OD-H, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 8.9 min, t_{major} = 10.4 min.);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.3 Hz, 2H), 7.36-7.14 (m, 4H), 7.04 (dd, J = 30.5, 8.1 Hz, 4H), 6.77 (d, J = 8.2 Hz, 1H), 6.35 (d, J = 7.7 Hz, 2H), 5.58 (s, 1H), 5.24 (d, J = 10.8 Hz, 1H), 4.86 (d, J = 10.7 Hz, 1H), 3.72 (s, 3H), 3.48 (s, 3H), 3.19-2.98 (m, 2H), 1.23 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.61, 168.31, 153.96, 145.91, 144.38, 136.67, 130.50, 128.68, 128.37, 127.42, 127.34, 124.92, 124.56, 119.60, 114.47, 108.19, 99.16, 83.28, 61.68, 51.45, 50.92, 40.43, 33.22, 30.34;

ESCI-HRMS Calcd. for $C_{30}H_{32}BrNNaO_6$, $[M+Na]^+$ 604.1294; Found: 604.1305.

(E)-methyl 3-(2-((1R,2R)-1-(3,4-dichlorophenylamino)-2-hydroxy-3-methoxy-3-oxo-2-phenylpropyl)phenoxy)acrylate(7i)



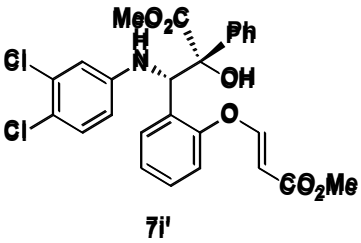
7i

Yield: 65%; 90:10; dr; 92% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t_{minor} = 8.6 min, t_{major} = 10.9 min.);

^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (d, J = 12.2 Hz, 1H), 7.69 (dd, J = 12.9, 7.8 Hz, 3H), 7.37 (t, J = 7.5 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.01 (dd, J = 14.7, 8.5 Hz, 3H), 6.54 (d, J = 2.6 Hz, 1H), 6.27 (dd, J = 8.8, 2.6 Hz, 1H), 5.84 (d, J

= 12.2 Hz, 1H), 5.65 (d, *J* = 9.3 Hz, 1H), 4.75 (d, *J* = 9.3 Hz, 1H), 4.18 (s, 1H), 3.78 (s, 3H), 3.56 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.22, 166.24, 157.73, 152.89, 144.77, 137.66, 131.64, 129.44, 128.92, 127.45, 127.39, 127.12, 125.11, 124.52, 119.22, 116.00, 113.44, 111.96, 102.06, 79.60, 53.62, 52.74, 50.50;
ESCI-HRMS Calcd. for $C_{26}H_{23}Cl_2NNaO_6$, $[M+Na]^+$ 538.0779; Found: 538.0795.

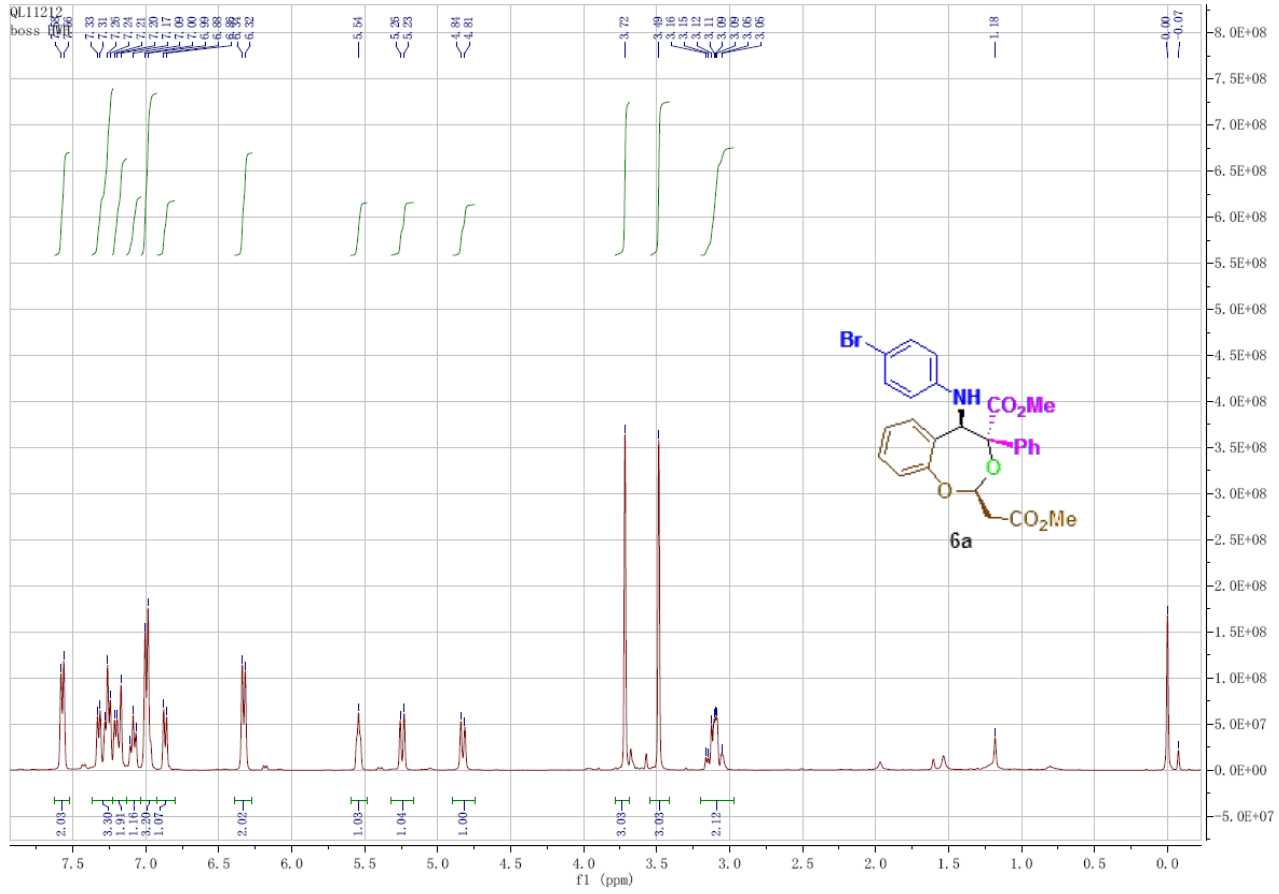
(E)-methyl 3-(2-((1S,2R)-1-(3,4-dichlorophenylamino)-2-hydroxy-3-methoxy-3-oxo-2-phenylpropyl)phenoxy)acrylate(7i')

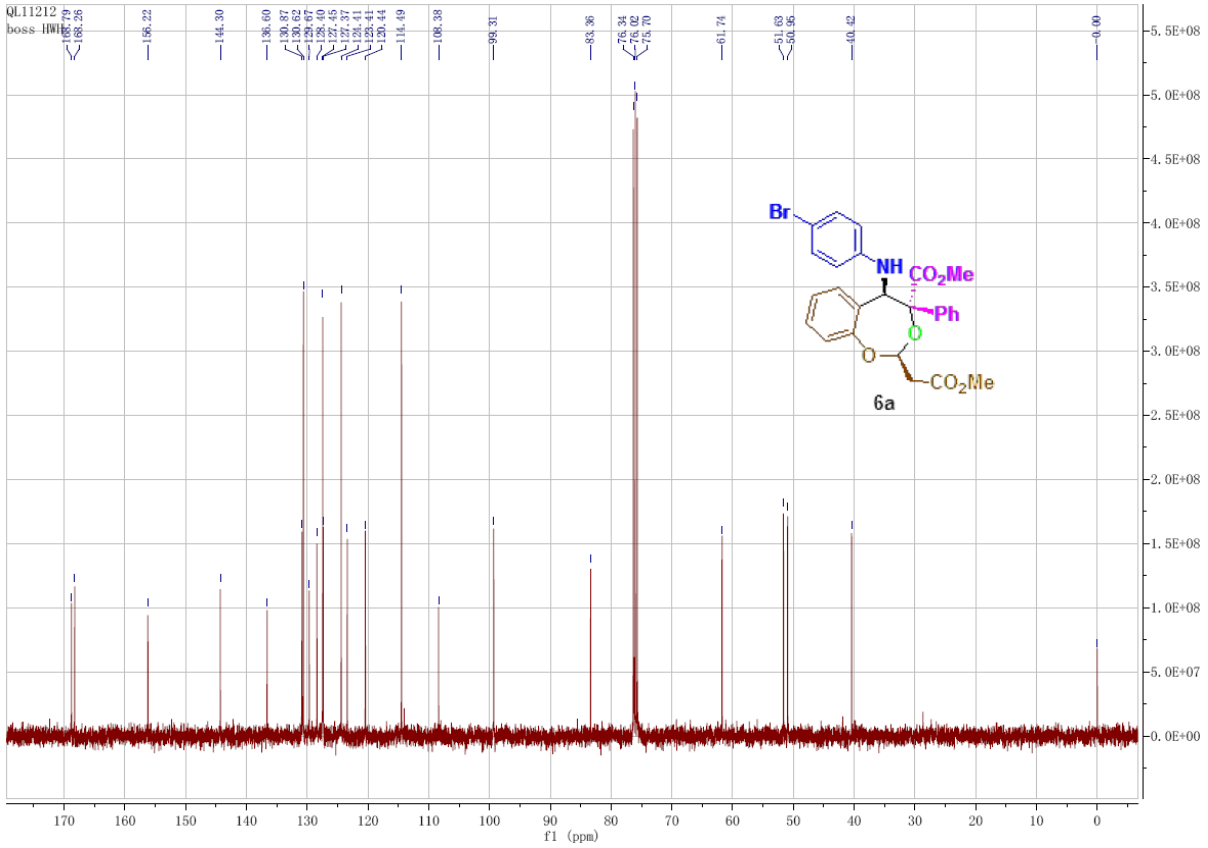


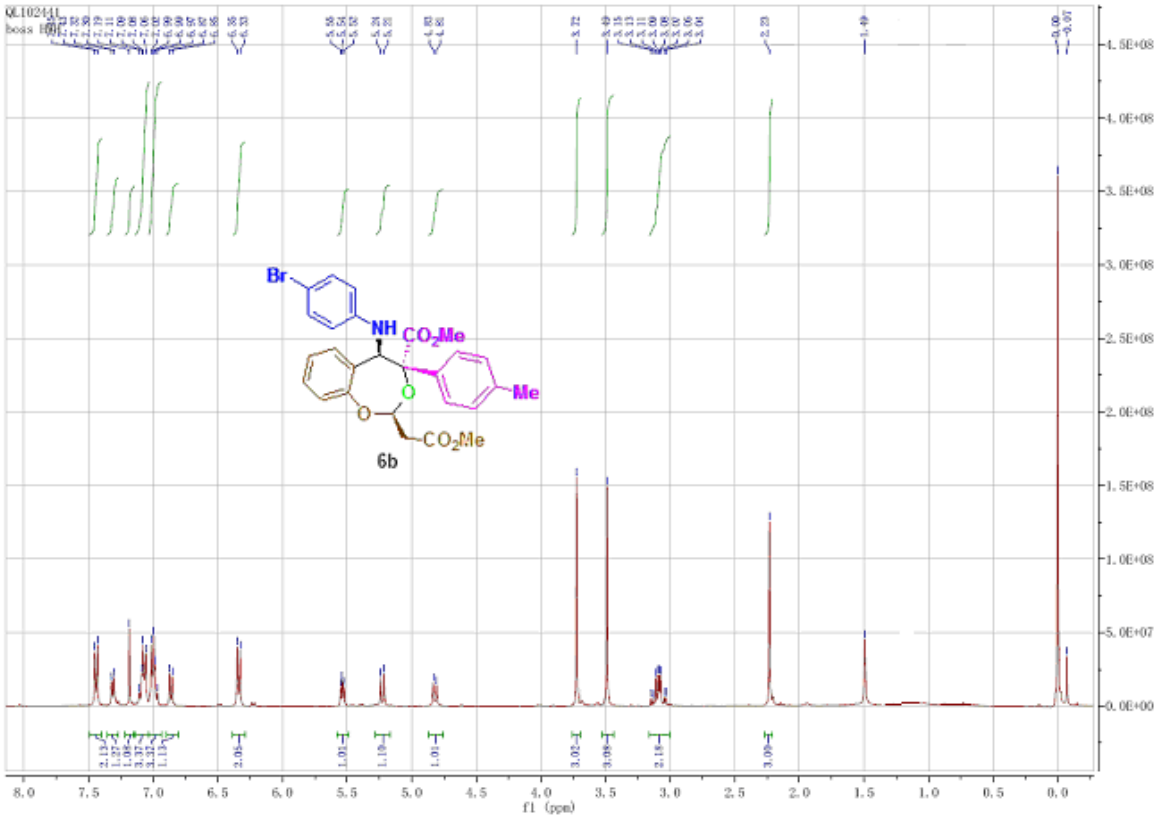
7i'

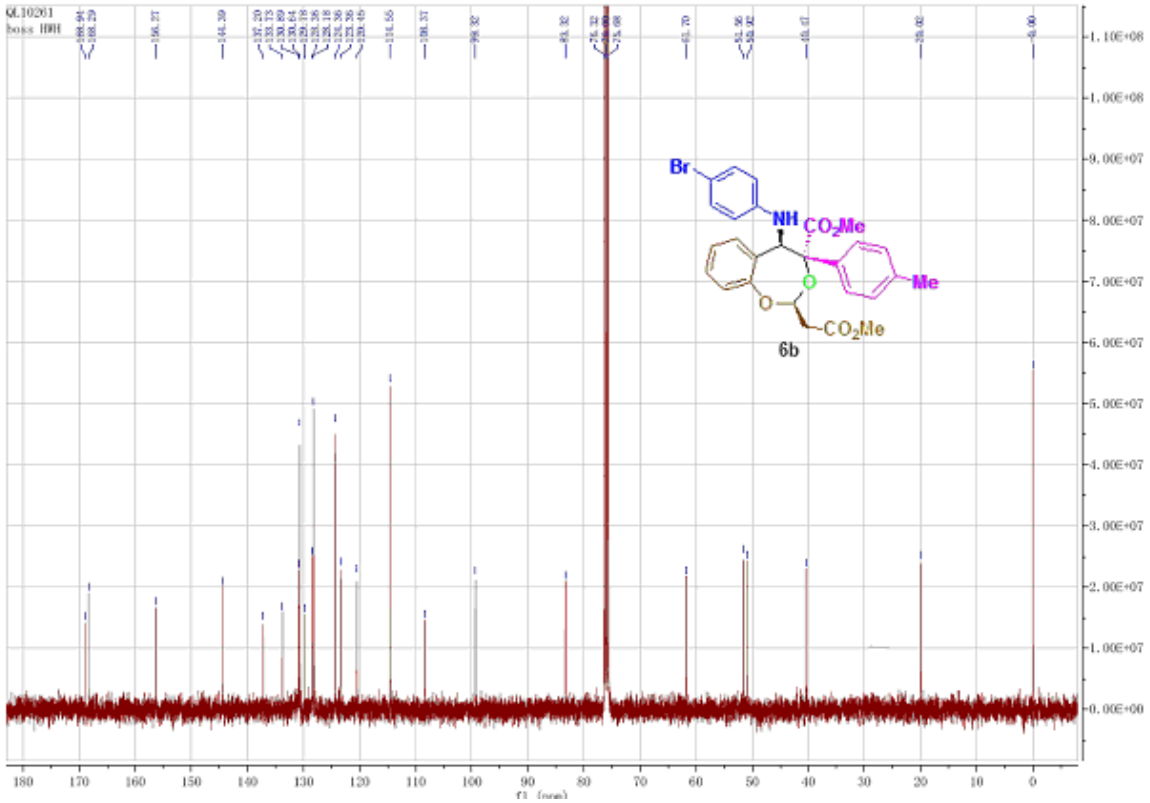
0% ee; determined by HPLC (Daicel Chirapak IC, flow rate 0.8 mL/min, hexane/isopropanol =50:10, 254 nm, Retention time: t = 10.9 min, t_{major} = 17.7 min.);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 – 7.24 (m, 3H), 7.03 (ddd, *J* = 23.6, 13.9, 5.0 Hz, 8H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.56 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.41 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.61 (d, *J* = 10.8 Hz, 1H), 5.55 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.07 (d, *J* = 0.7 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.34, 166.26, 157.78, 153.01, 144.67, 136.55, 131.75, 129.57, 128.43, 128.20, 127.20, 127.00, 126.27, 124.74, 123.83, 119.92, 115.37, 114.49, 112.68, 101.75, 80.47, 52.99, 52.40, 50.34;
ESCI-HRMS Calcd. for $C_{26}H_{23}Cl_2NNaO_6$, $[M+Na]^+$ 538.0779; Found: 538.0786.

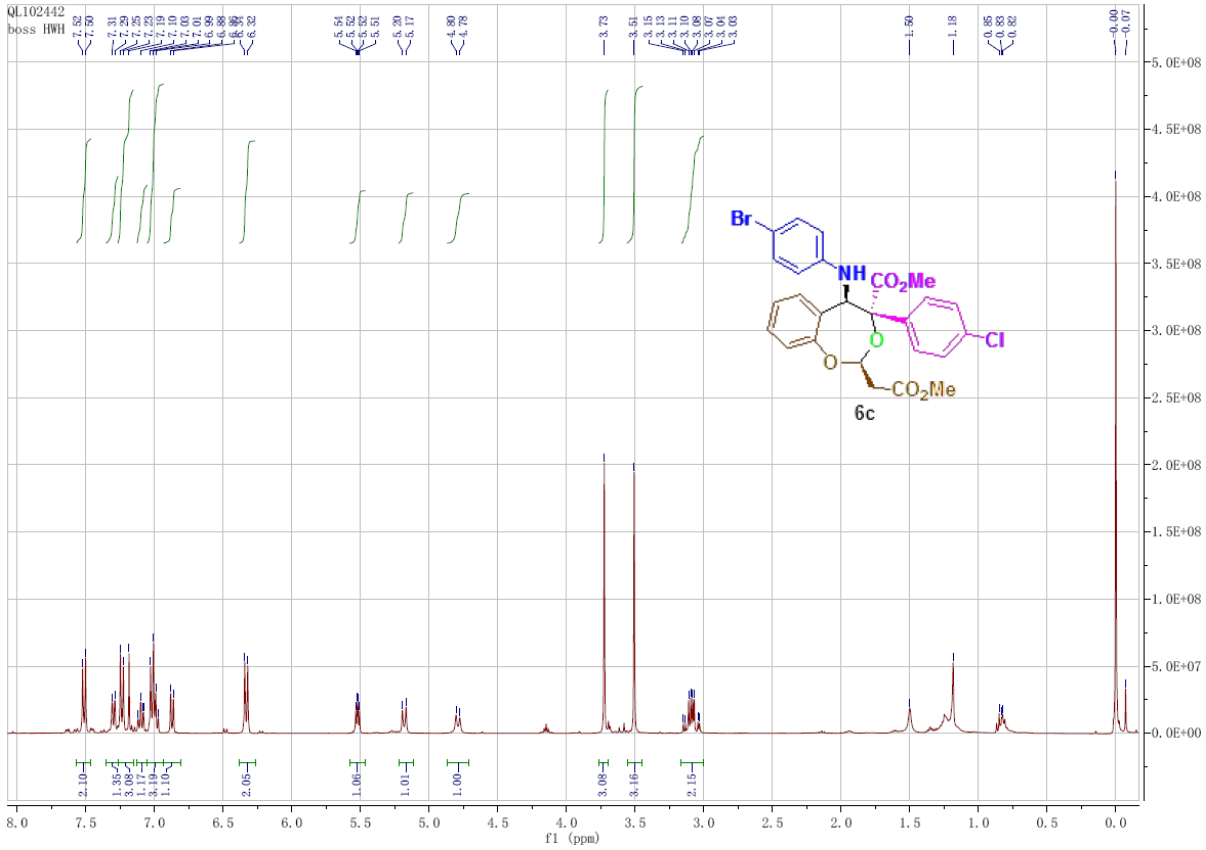
NMR spectra for the Compounds:

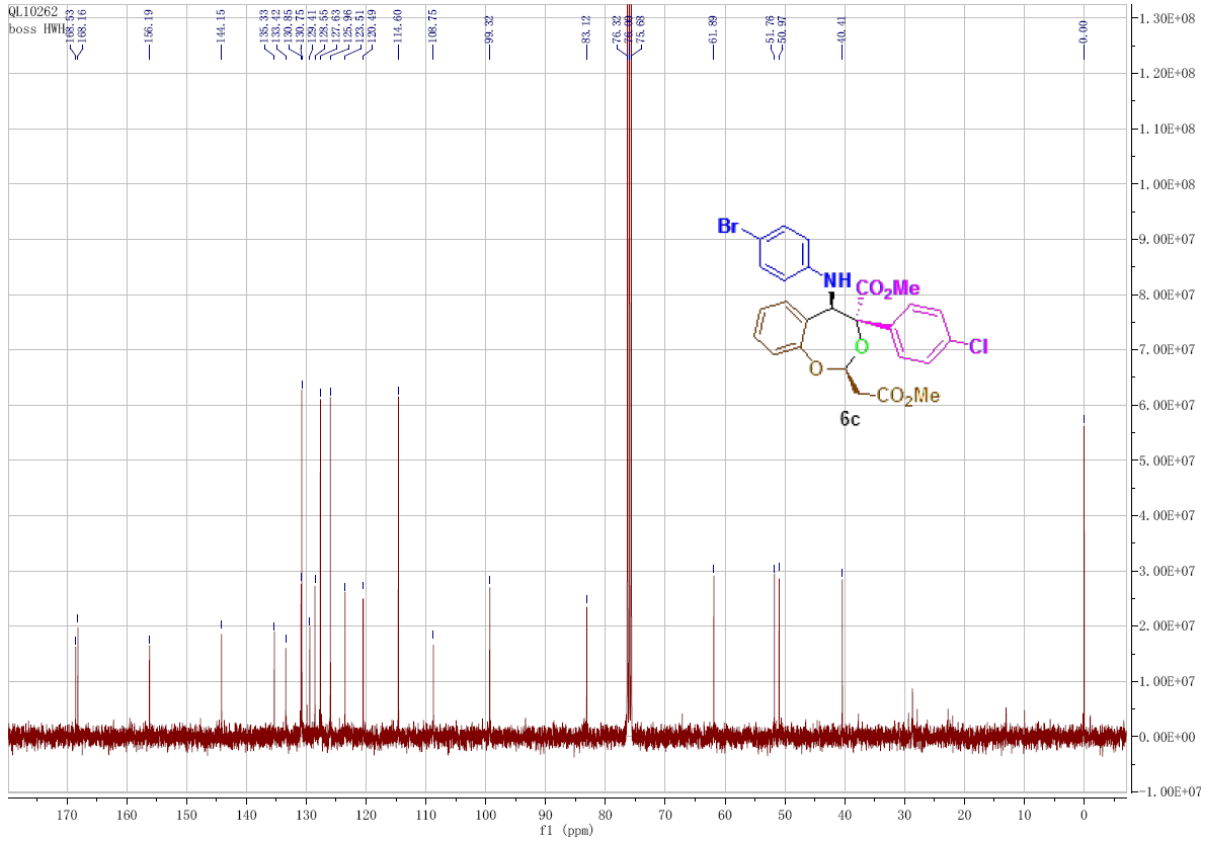





Br
NH
CO2Me
Me
O
O
CO2Me
6b
f1 (ppm)


Br
NH
CO2Me
Me
O
O
CO2Me
6b


QL102442
boss HWH
Br
NH
CO2Me
Cl
O
O
CO2Me
6c
f1 (ppm)


QL10262
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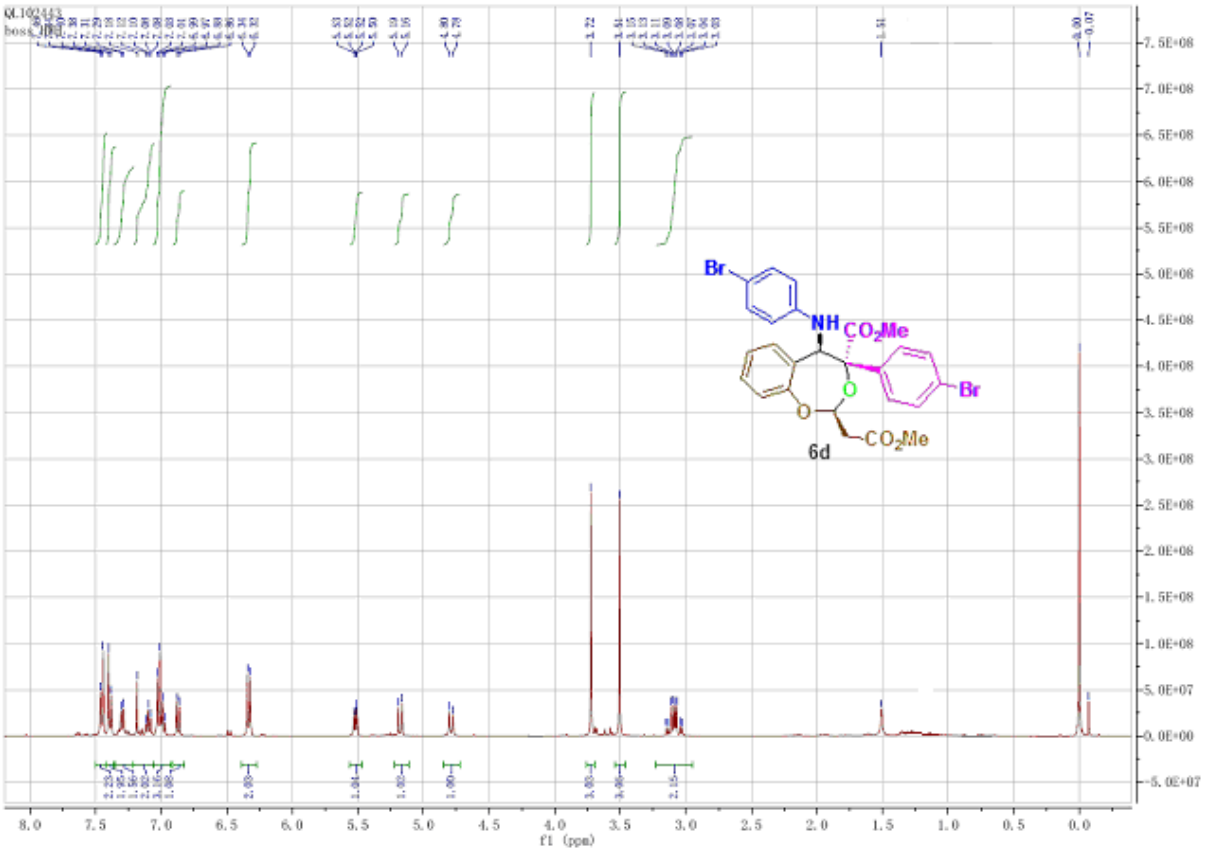
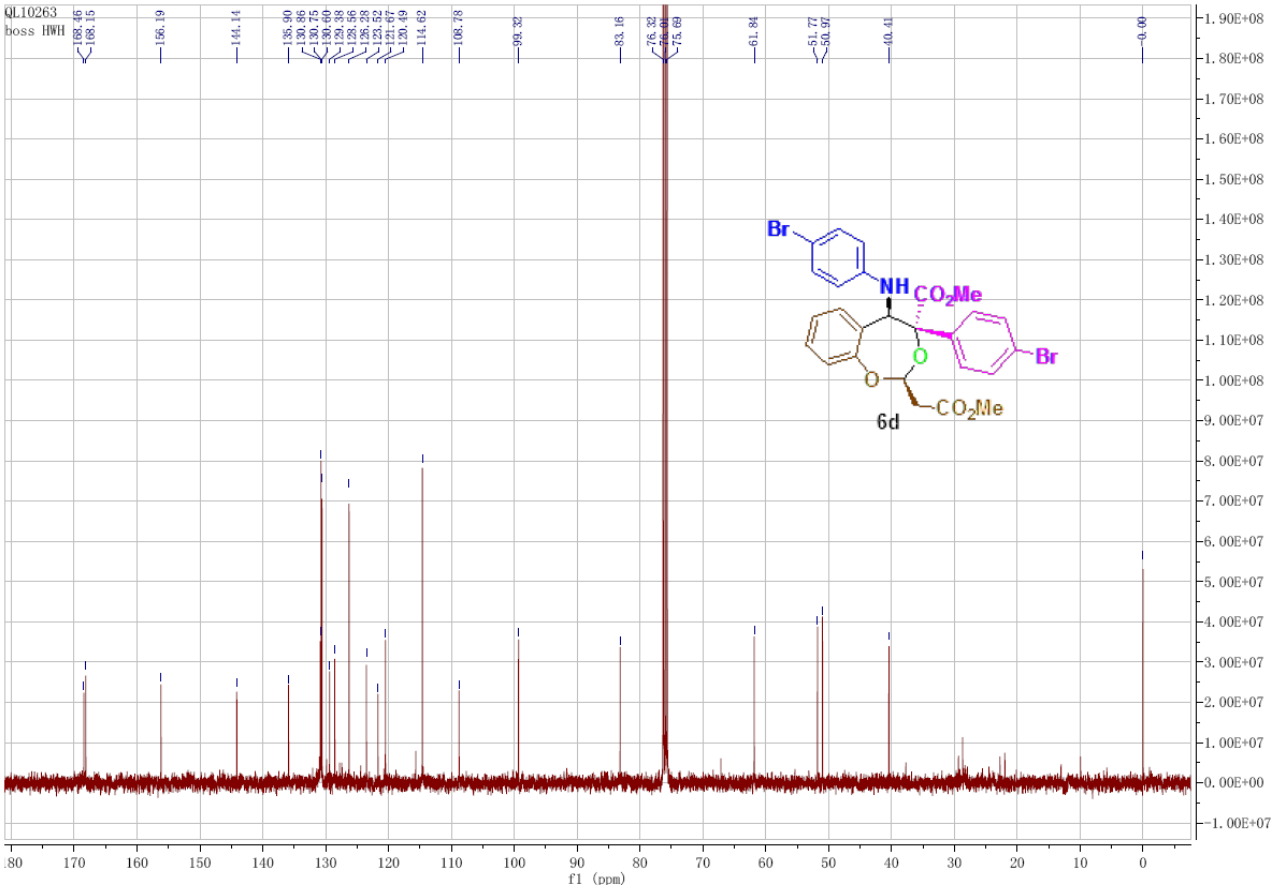
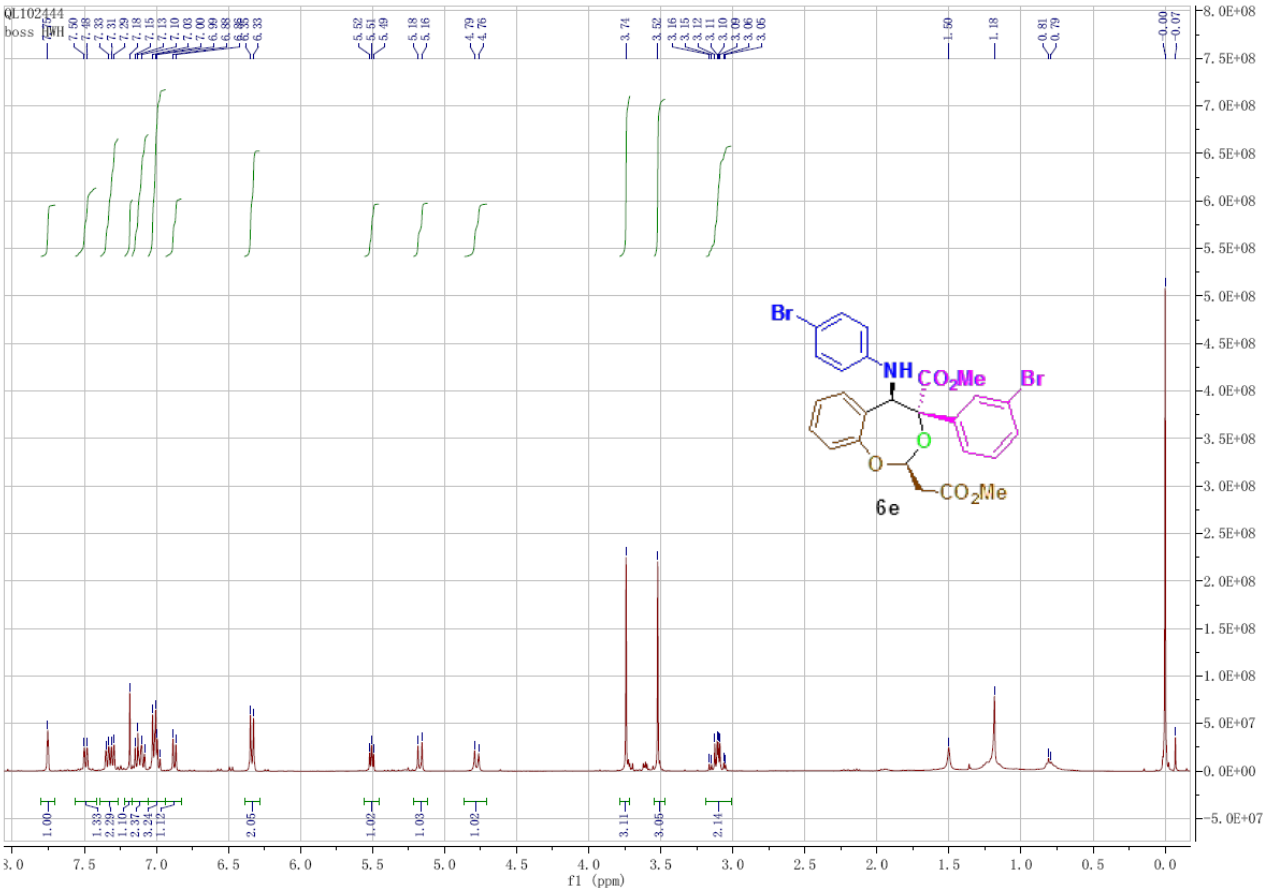
Br
NH
CO2Me
Cl
O
O
CO2Me
6c
f1 (ppm)


Br
NH
CO2Me
O
Br
O
CO2Me
6d
f1 (ppm)


QL10263
boss HWH
Br
NH
CO2Me
O
Br
O
CO2Me
6d
f1 (ppm)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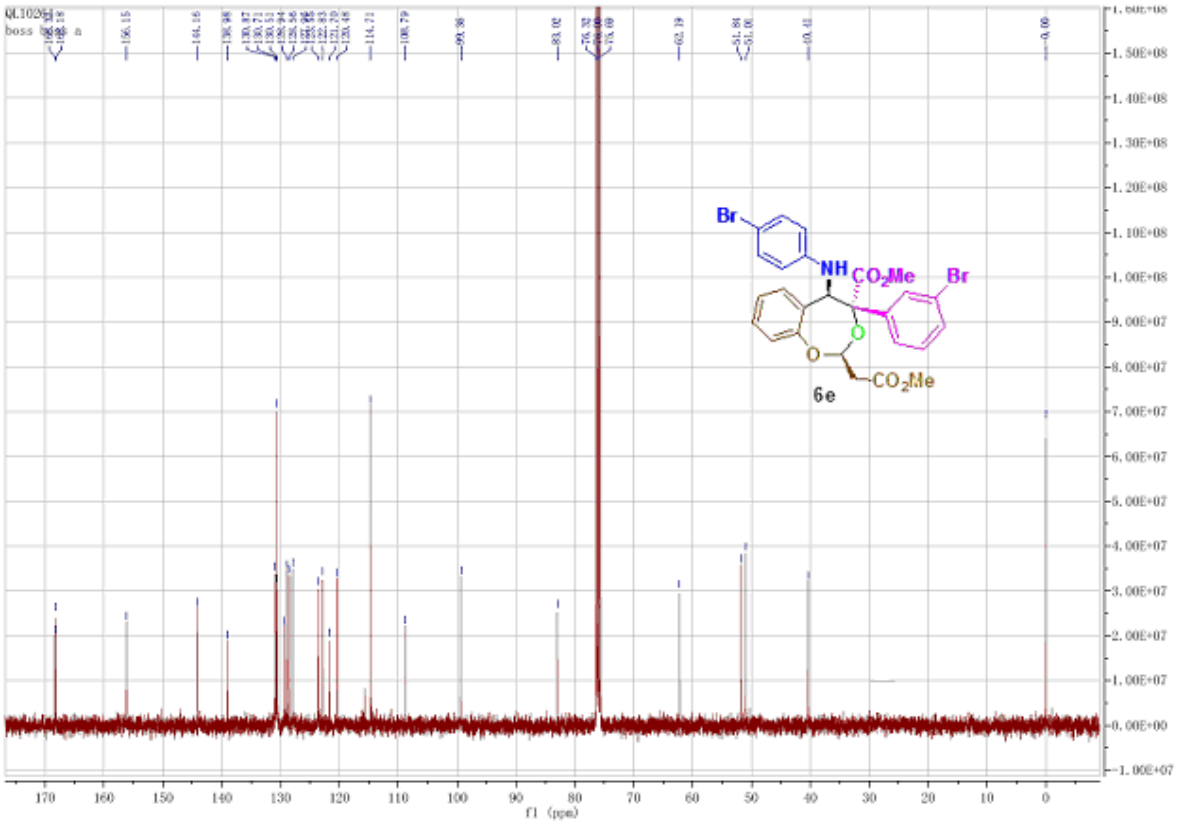
NH
CO2Me
Br
O
O
CO2Me
6e
f1 (ppm)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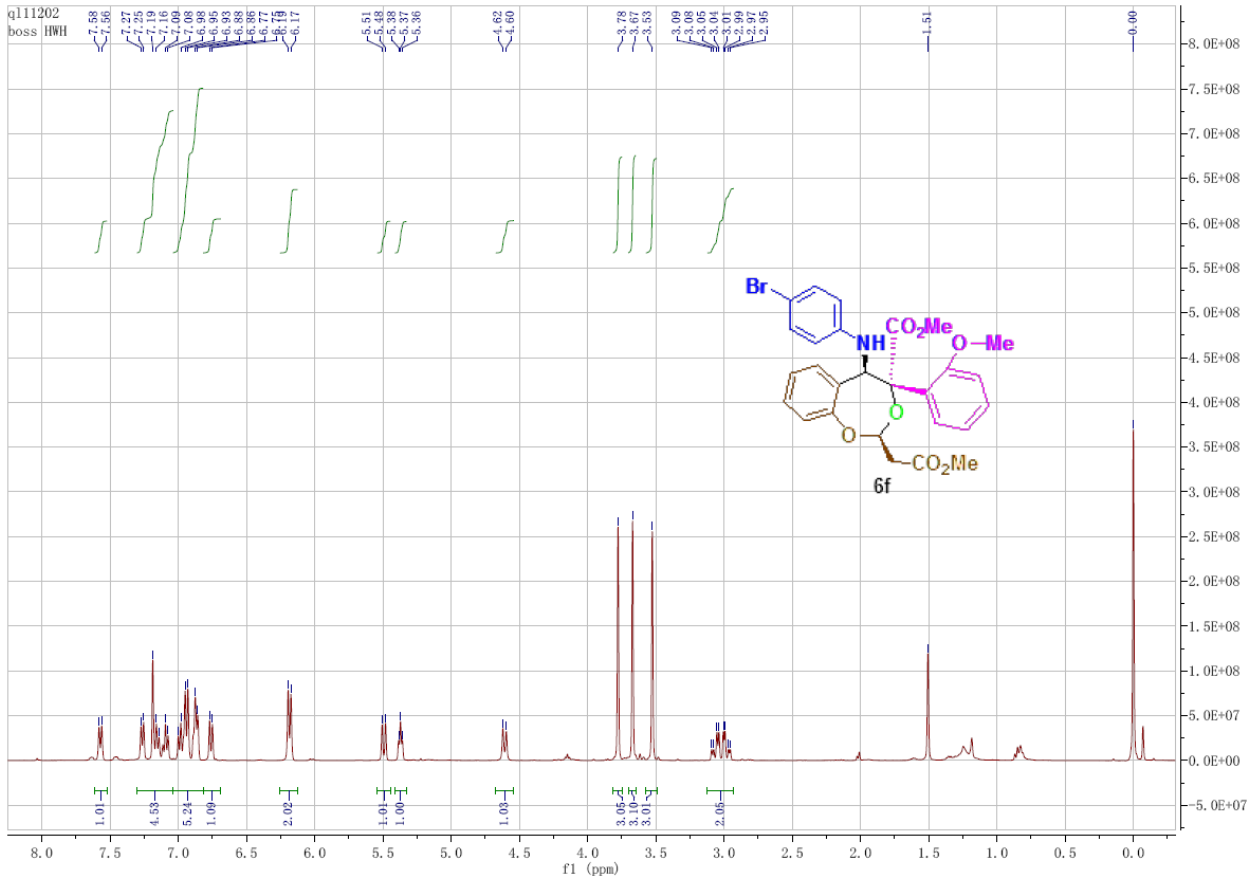
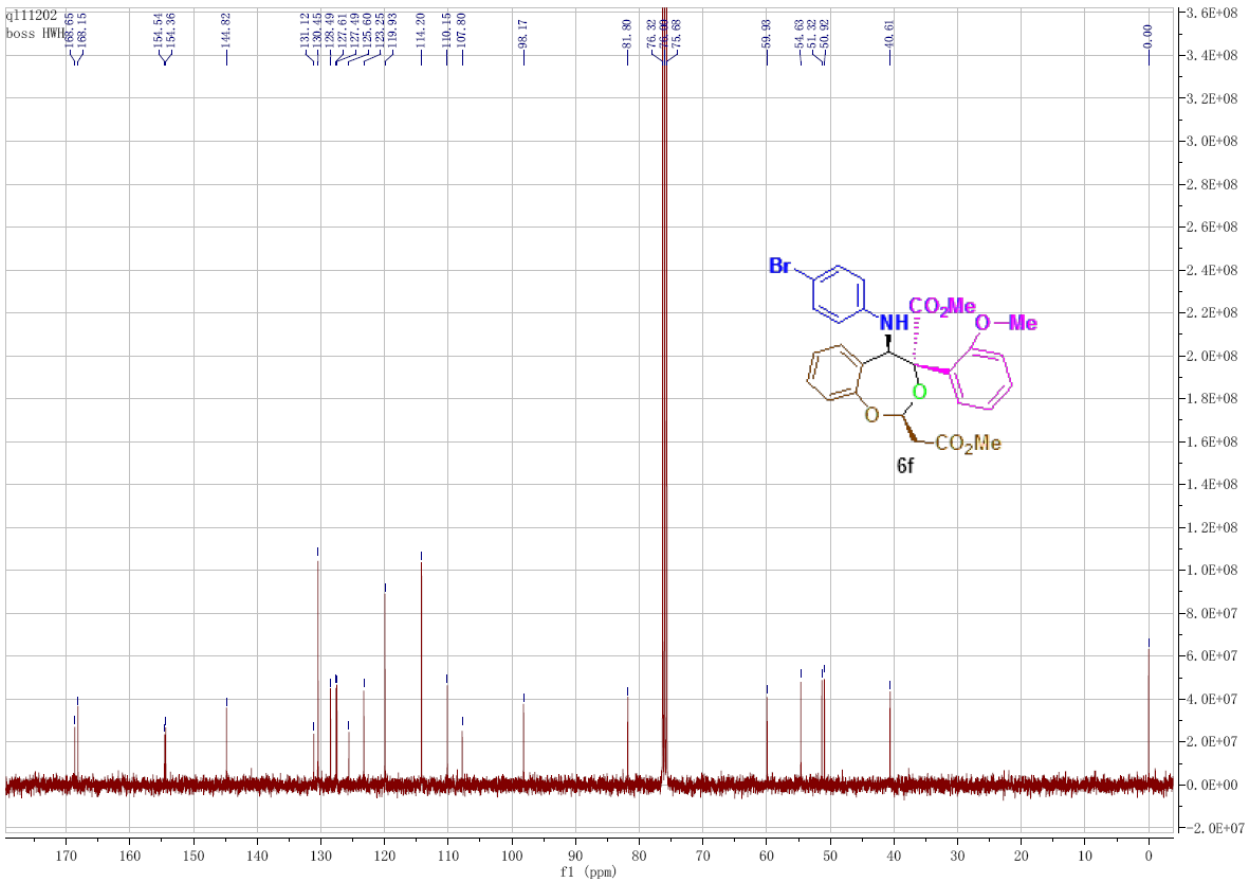
NH
CO2Me
Br
O
O
CO2Me
6e
f1 (ppm)


q111202
boss HWH
Br
NH
CO2Me
O—Me
O
O
CO2Me
6f
f1 (ppm)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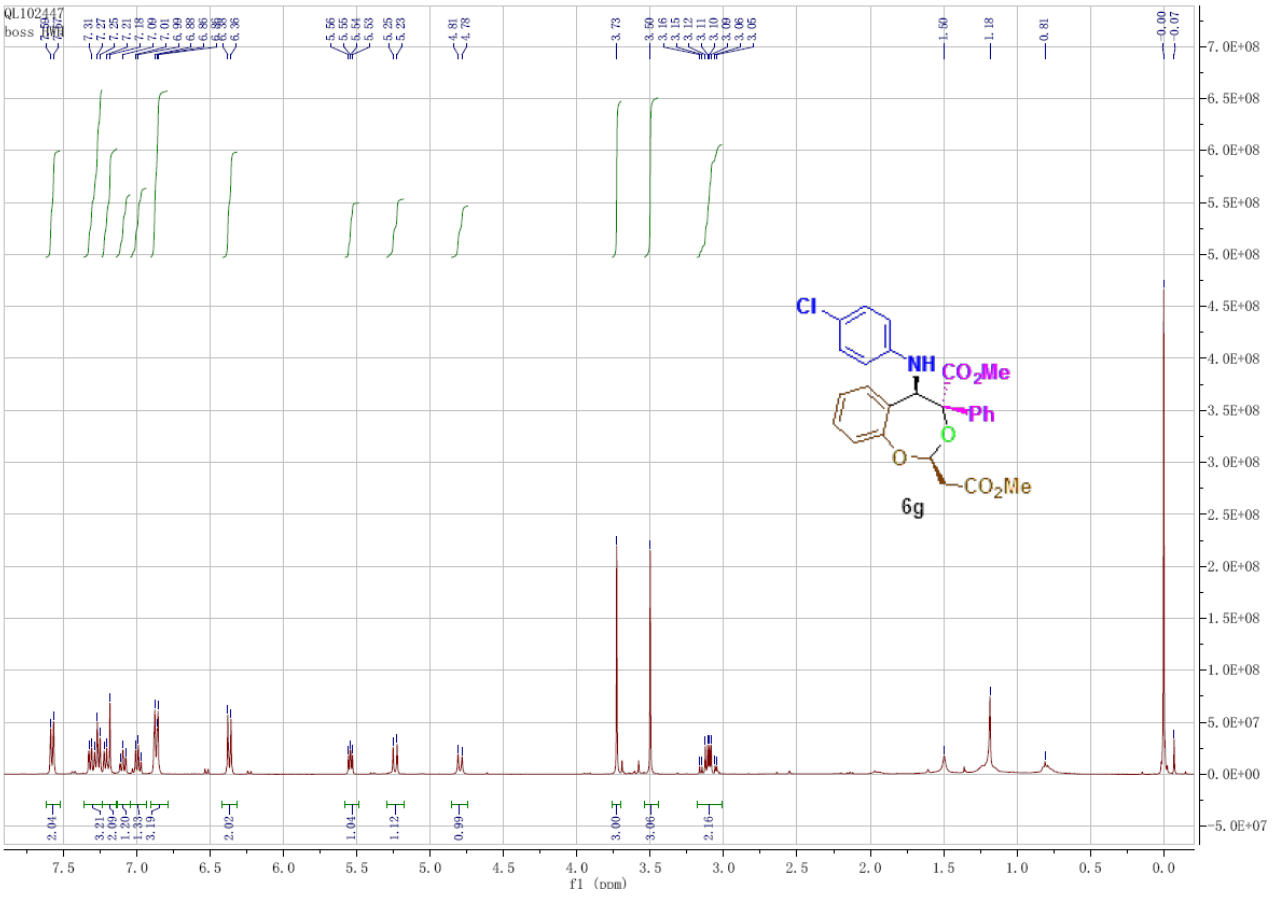
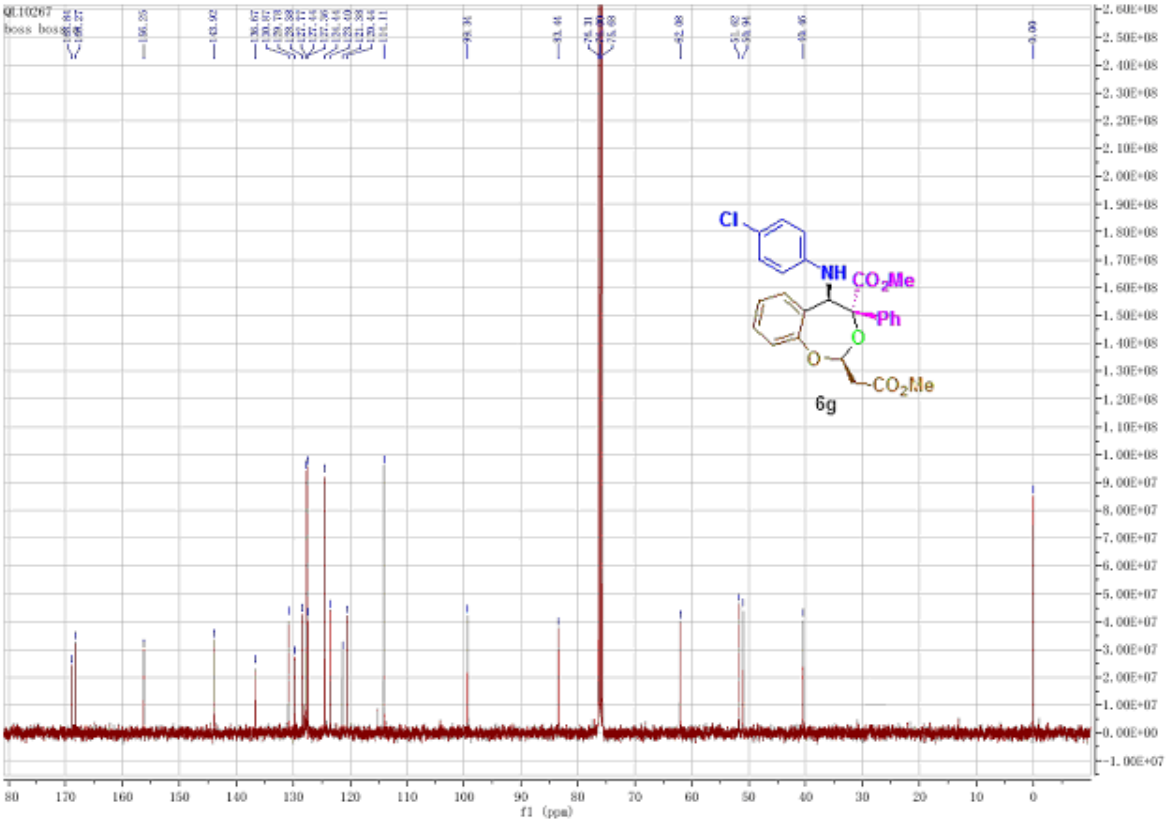
Br
NH
CO2Me
O—Me
O
O
CO2Me
6f
f1 (ppm)


QL102447
boss
Cl
NH
CO2Me
Ph
O
O
CO2Me
6g
f1 (ppm)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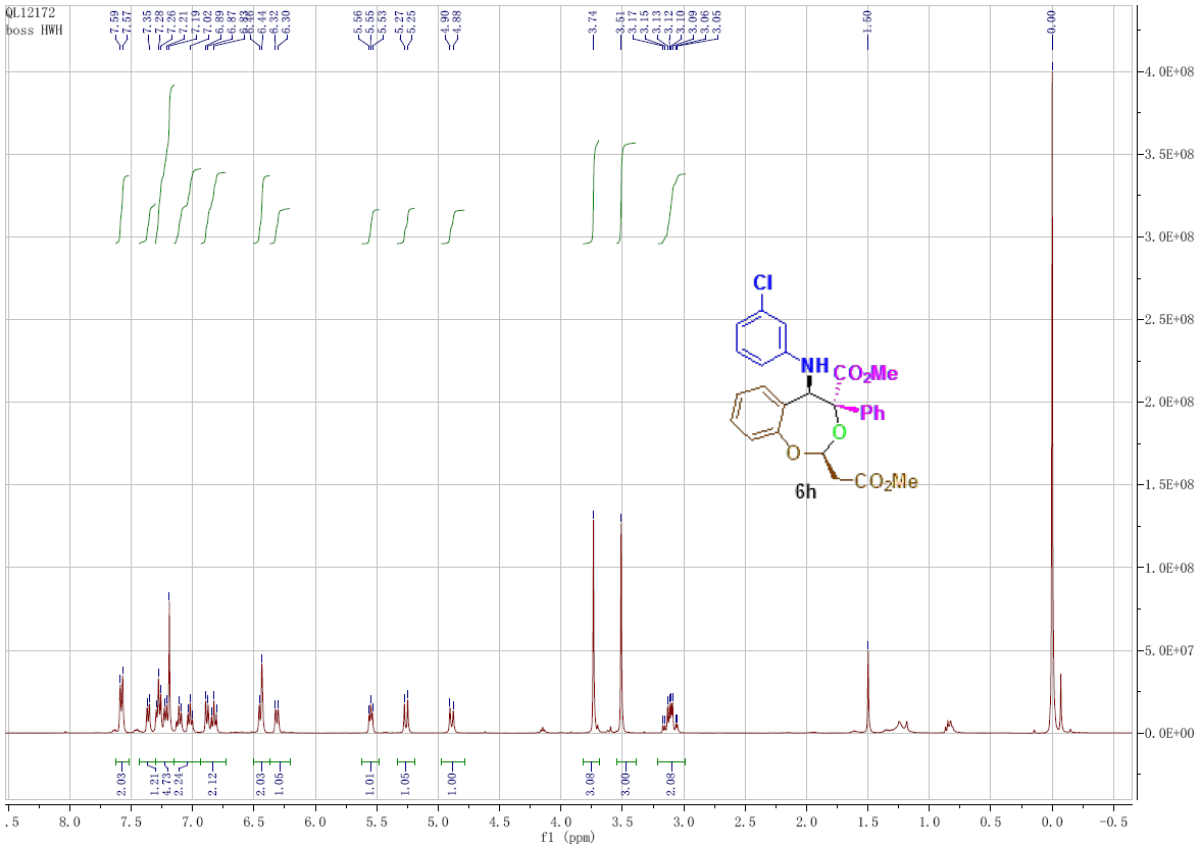
boss boss
Cl
NH
CO2Me
Ph
O
O
CO2Me
6g
f1 (ppm)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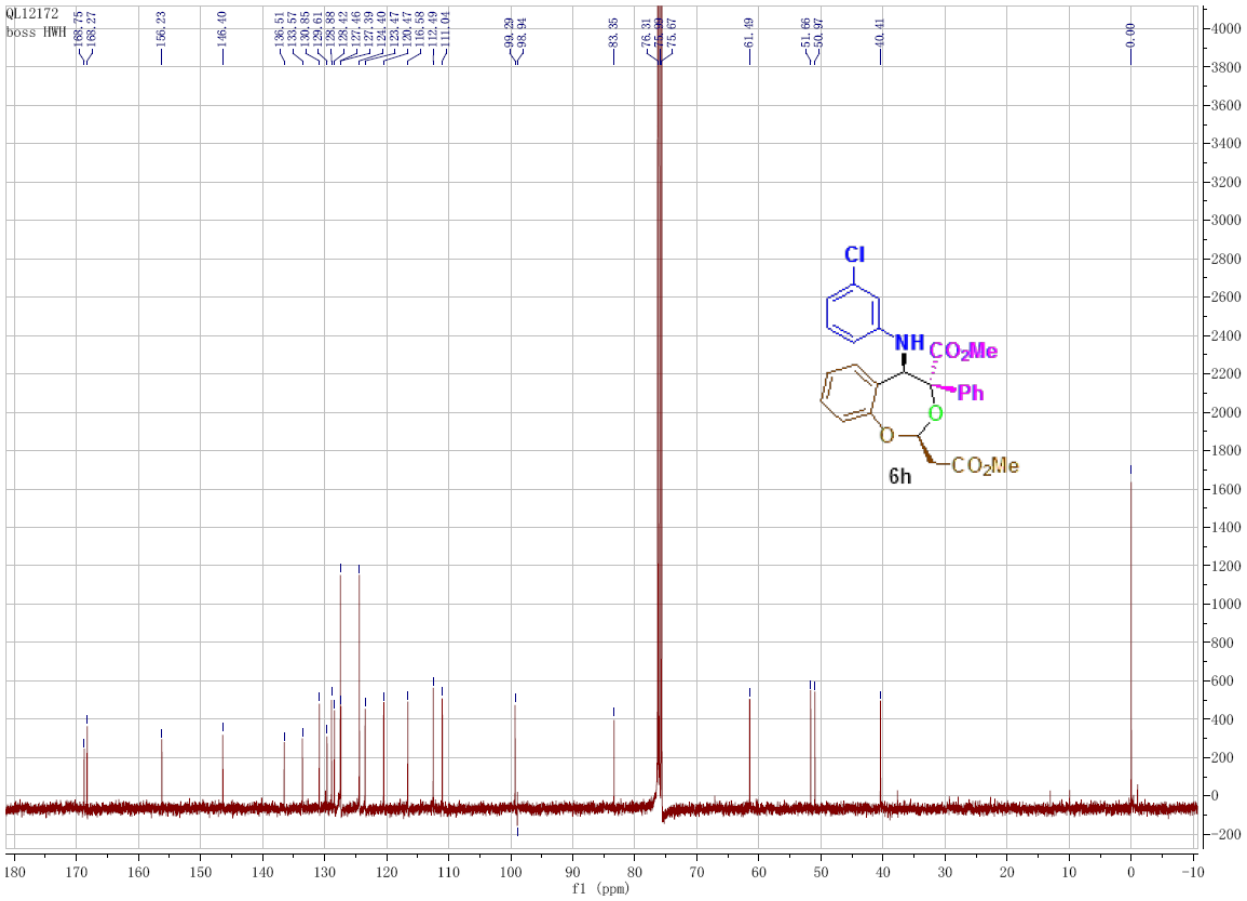
Cl
NH
CO2Me
Ph
O
O
CO2Me
6h
f1 (ppm)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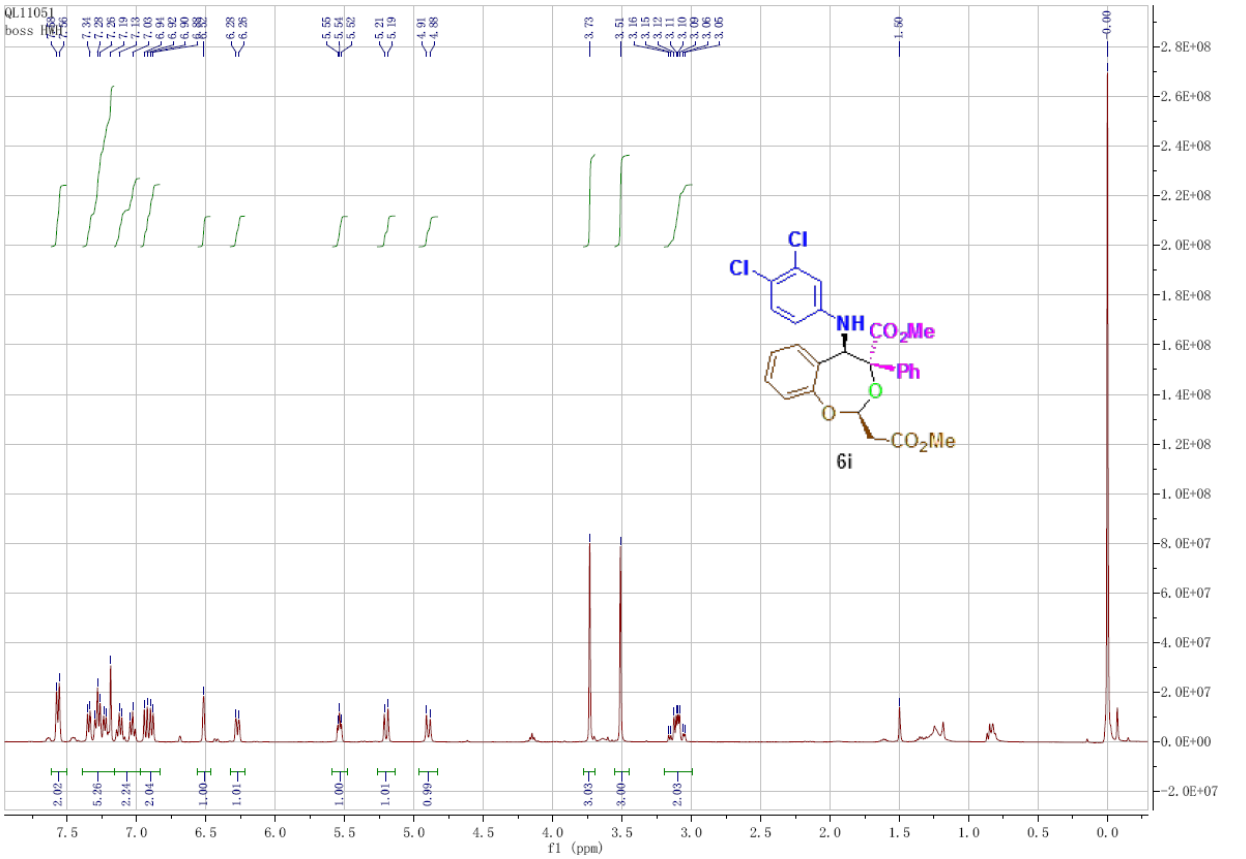
boss HWH
Cl
NH
CO2Me
Ph
O
O
CO2Me
6h
f1 (ppm)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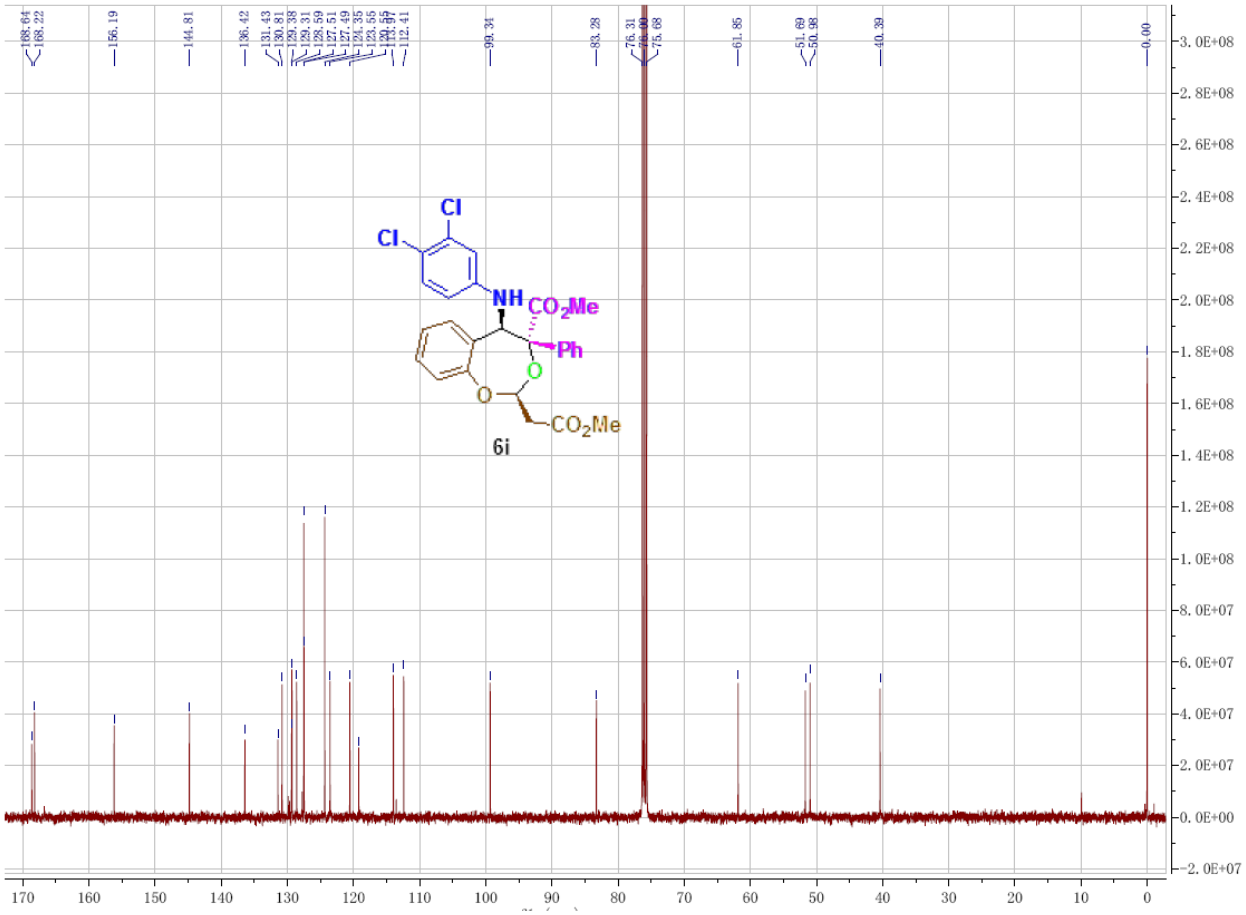
Cl
Cl
NH
CO2Me
Ph
O
O
CO2Me
6i
f1 (ppm)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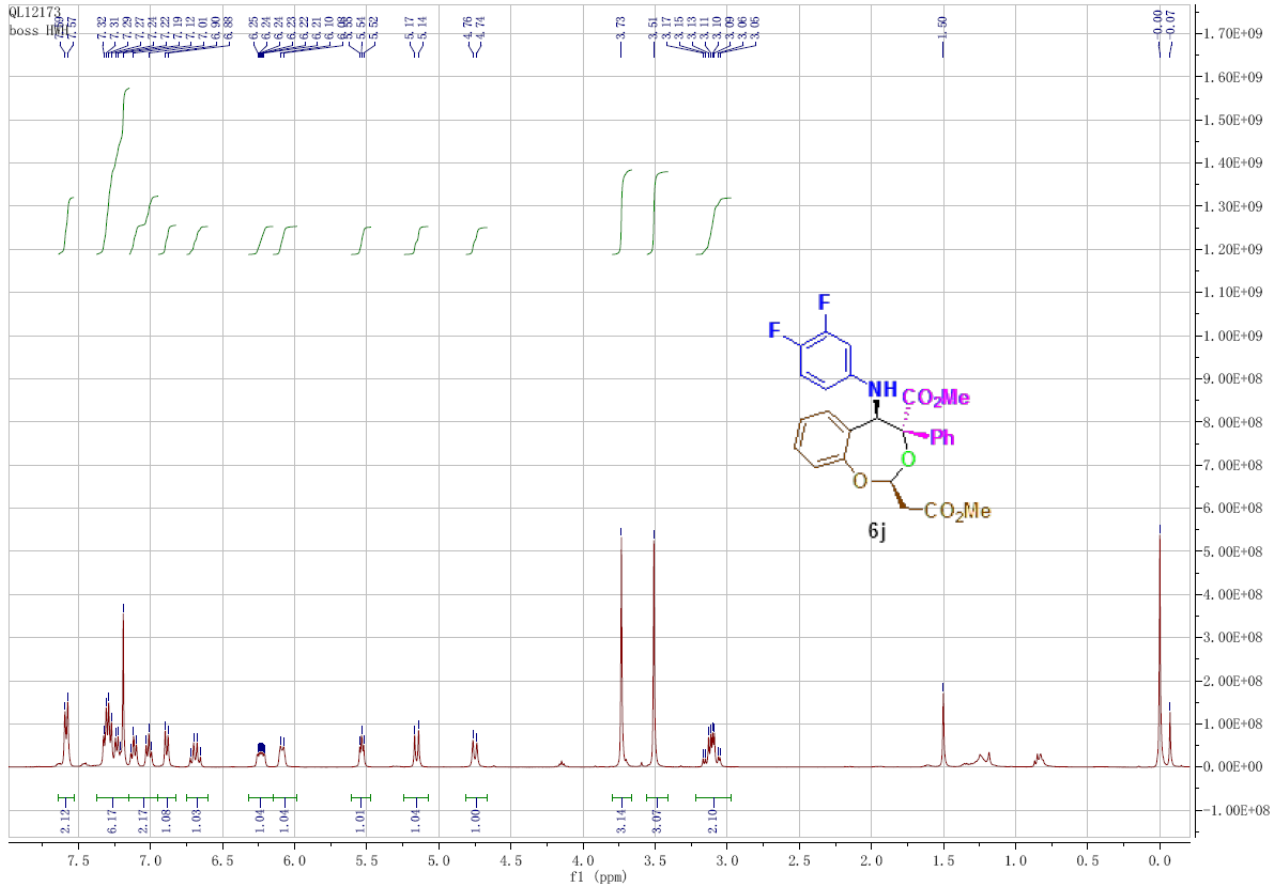
Cl
NH
CO2Me
Ph
O
O
CO2Me
6i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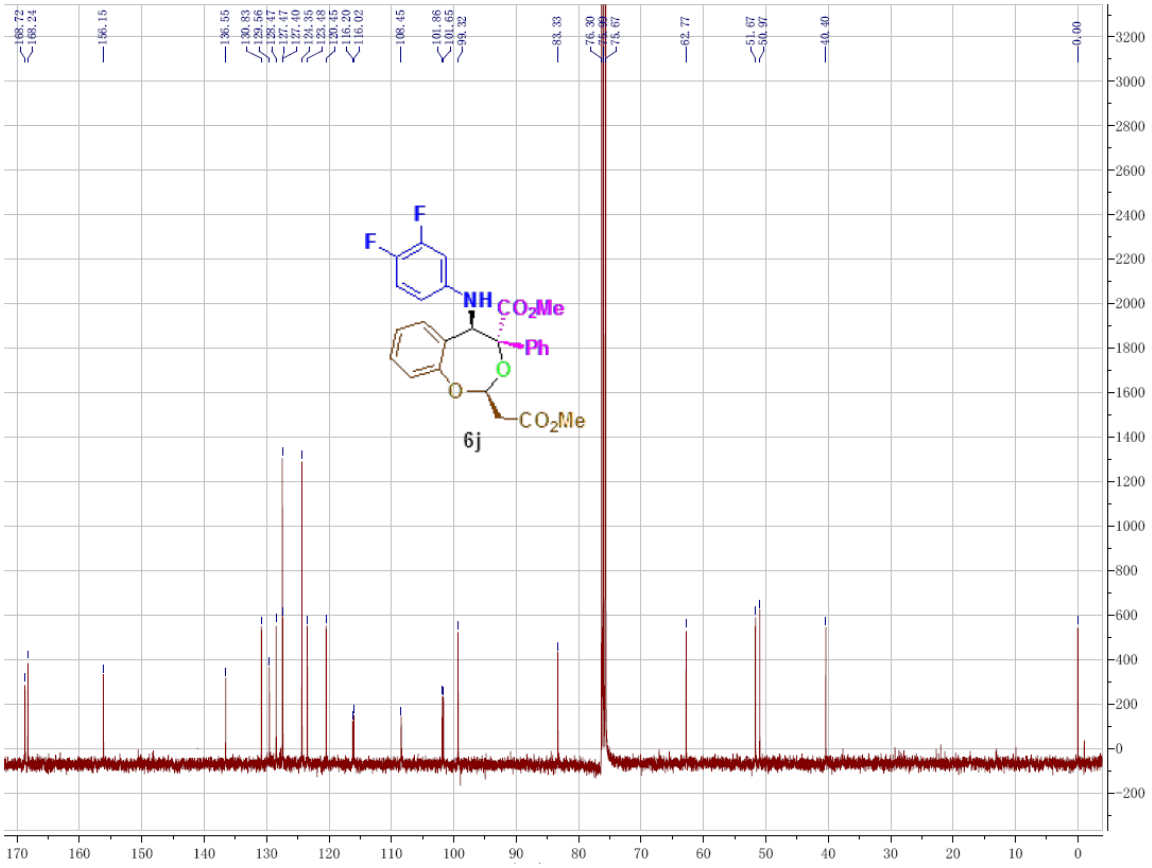
boss H1
F
F
NH
CO2Me
Ph
O
O
CO2Me
6j
f1 (ppm)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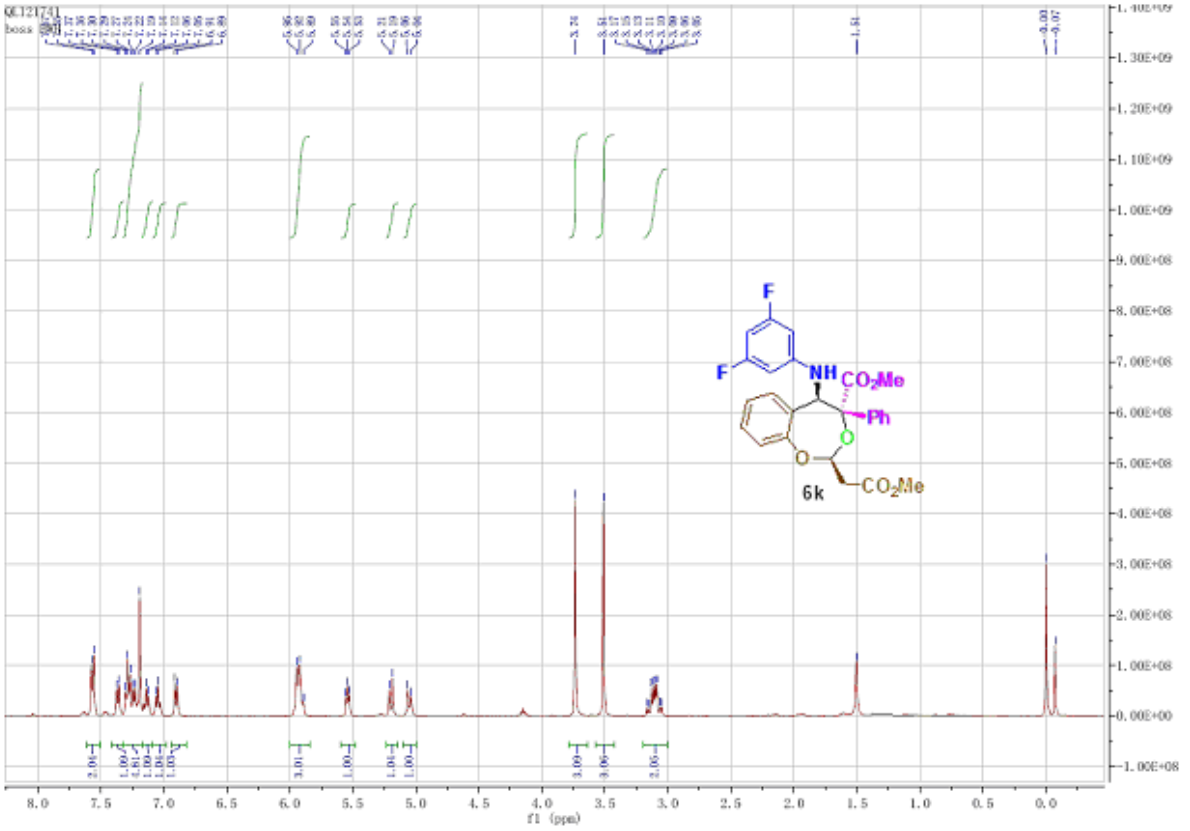
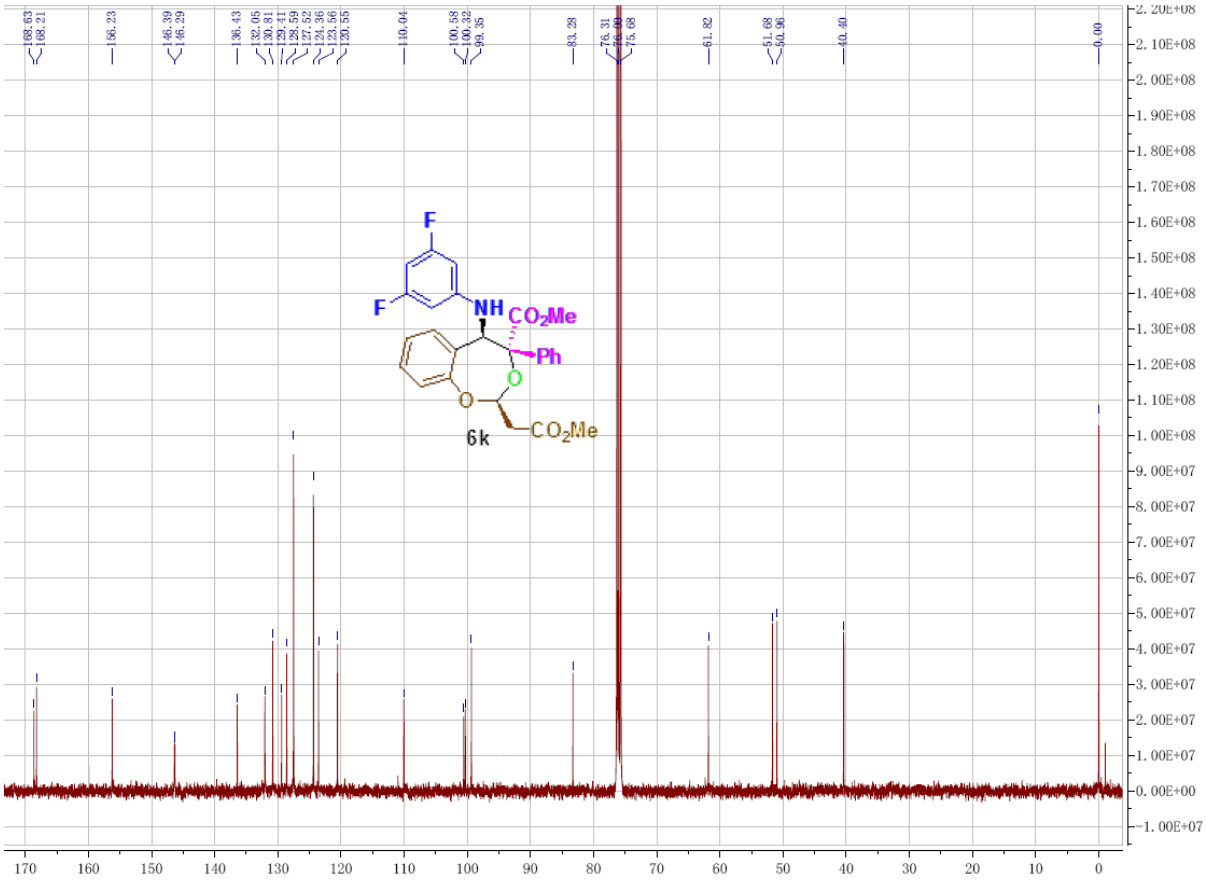
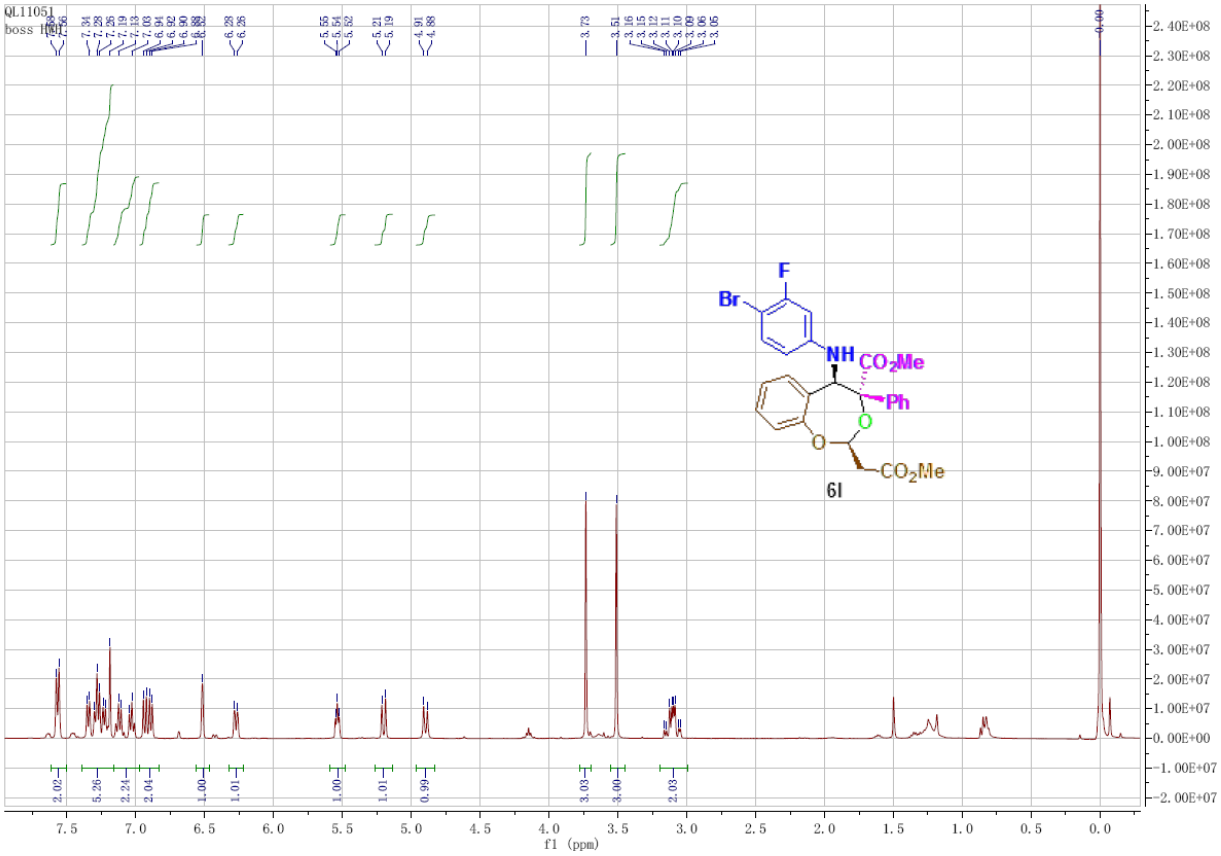
F
NH
CO2Me
Ph
O
O
CO2Me
6j


F
F
NH
CO2Me
Ph
O
O
CO2Me
6k
f1 (ppm)


F
F
NH
CO2Me
Ph
O
O
CO2Me
6k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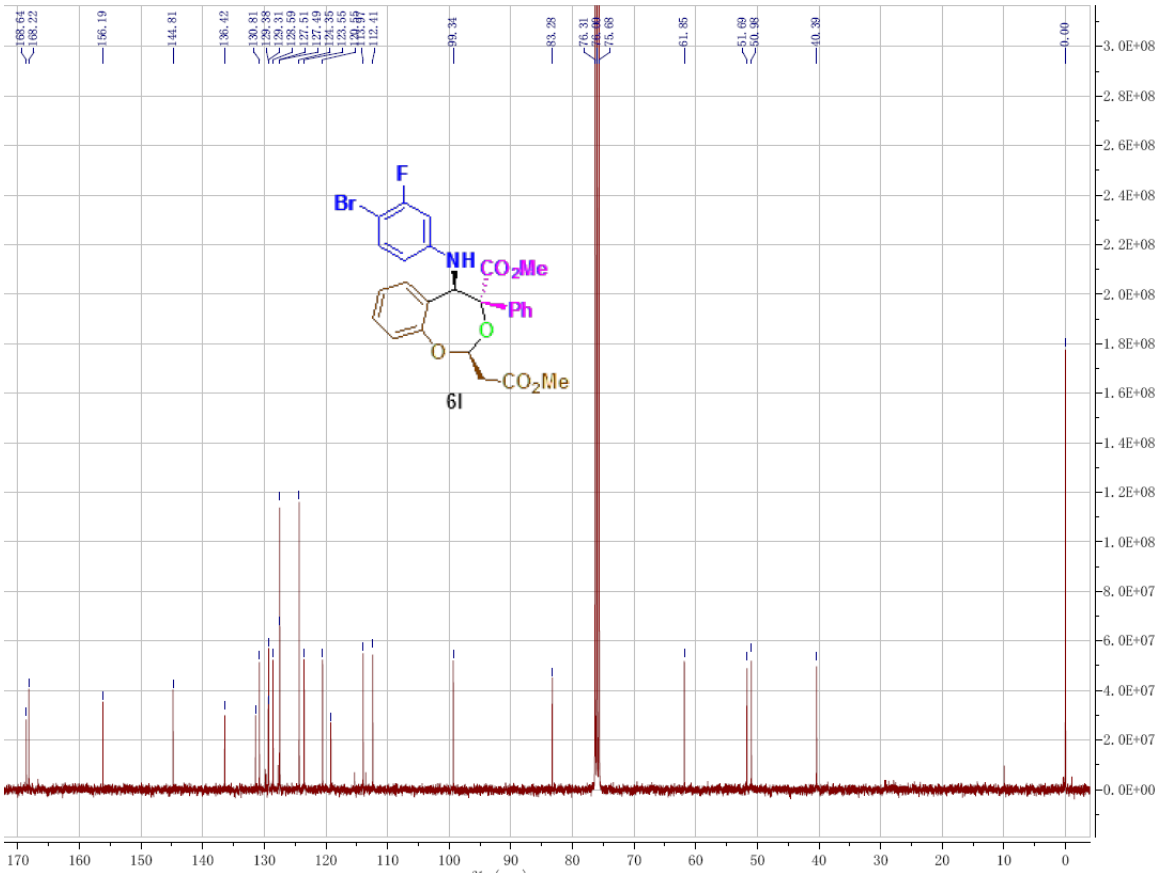
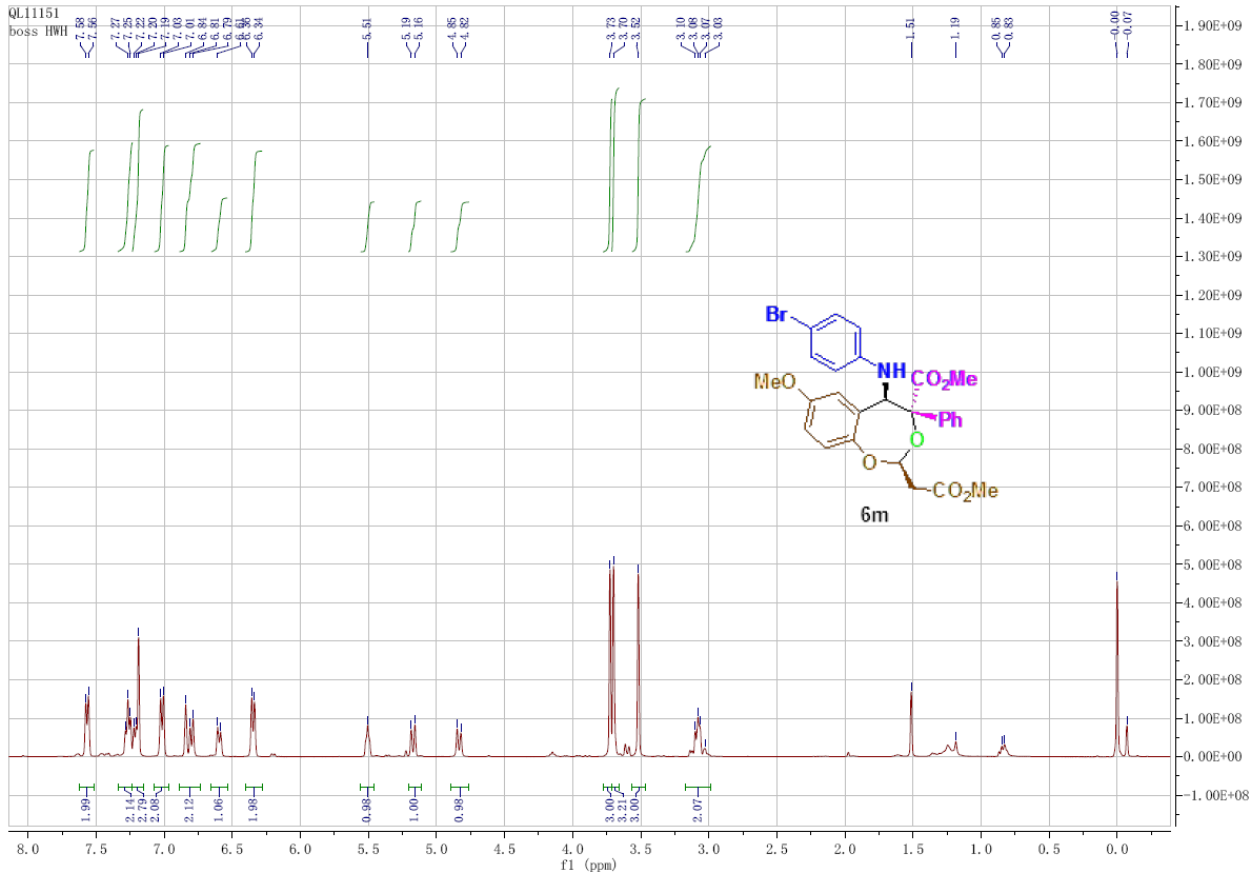
boss 1H
F
Br
NH
CO2Me
Ph
O
O
CO2Me
6l
f1 (ppm)


F
Br
NH
CO2Me
Ph
O
O
CO2Me
6l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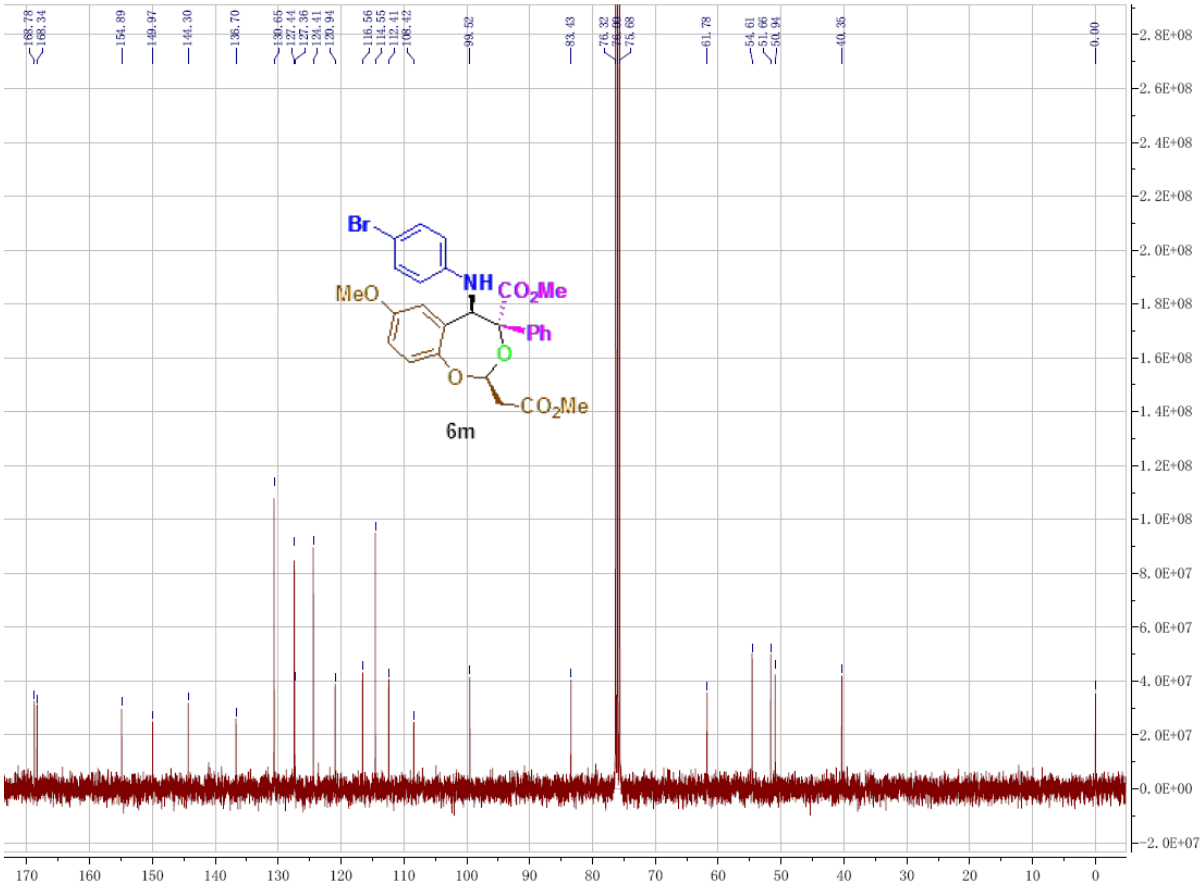
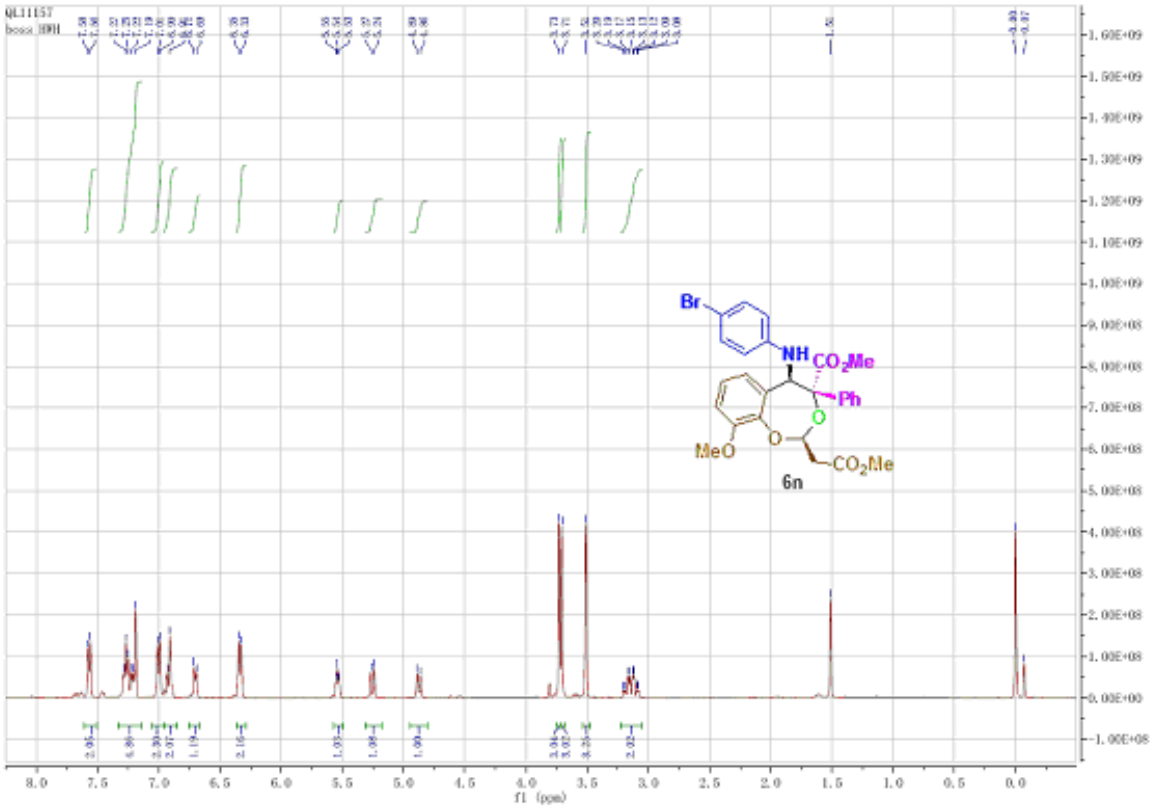
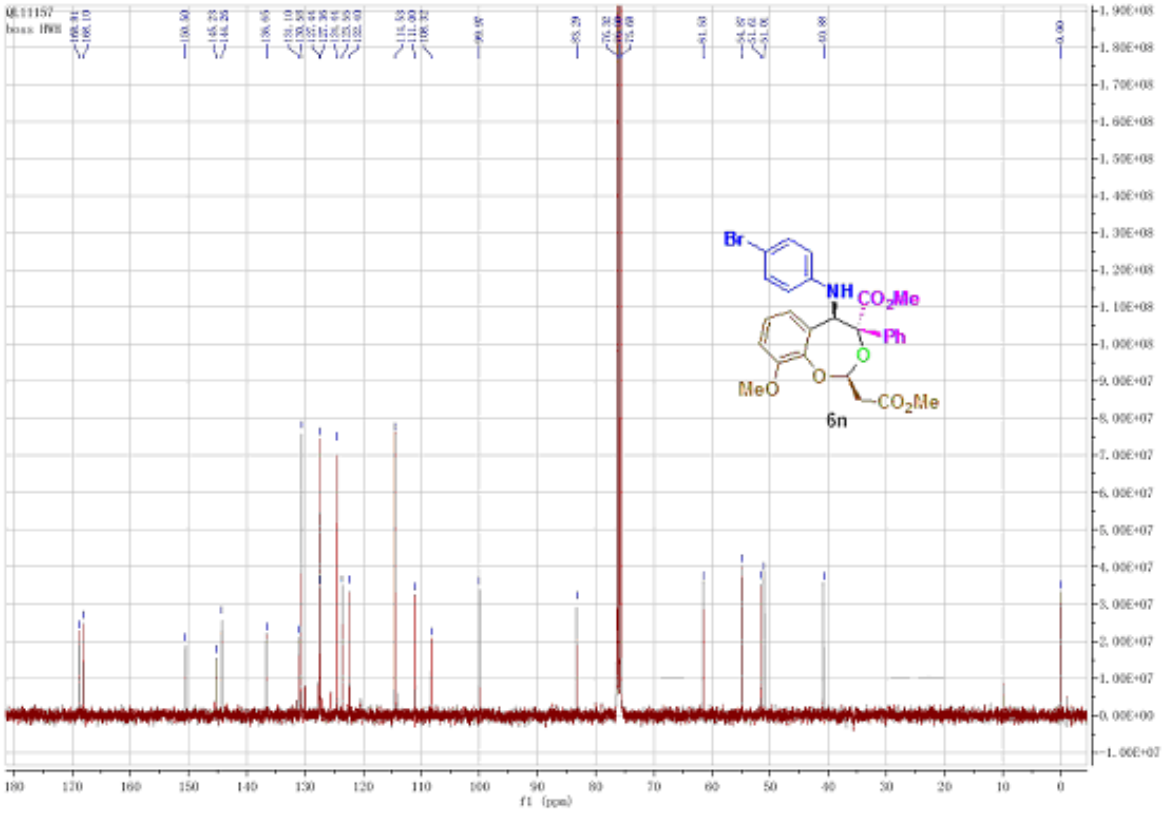
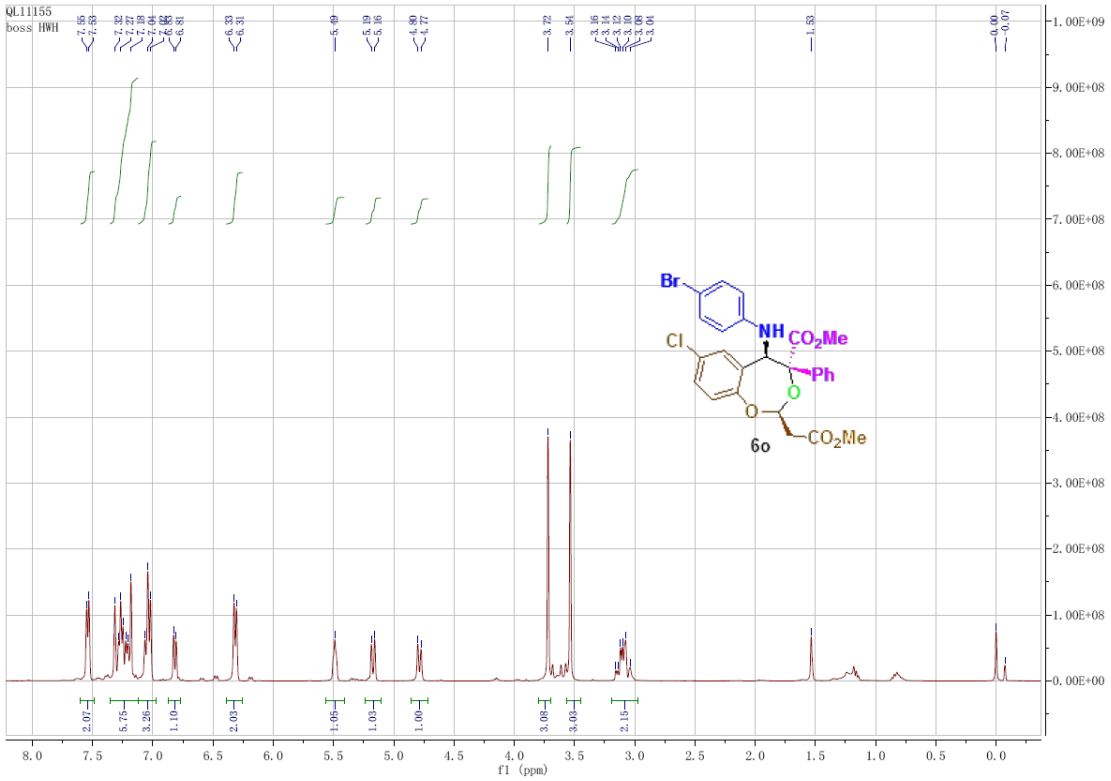
boss HWH
Br
NH
CO2Me
MeO
Ph
O
O
CO2Me
6m
f1 (ppm)


Br
NH
CO2Me
MeO
Ph
O
O
CO2Me
6m


Br
NH
CO2Me
Ph
O
MeO
O
CO2Me
6n
f1 (ppm)


Br
NH
CO2Me
Ph
O
MeO
O
CO2Me
6n
f1 (ppm)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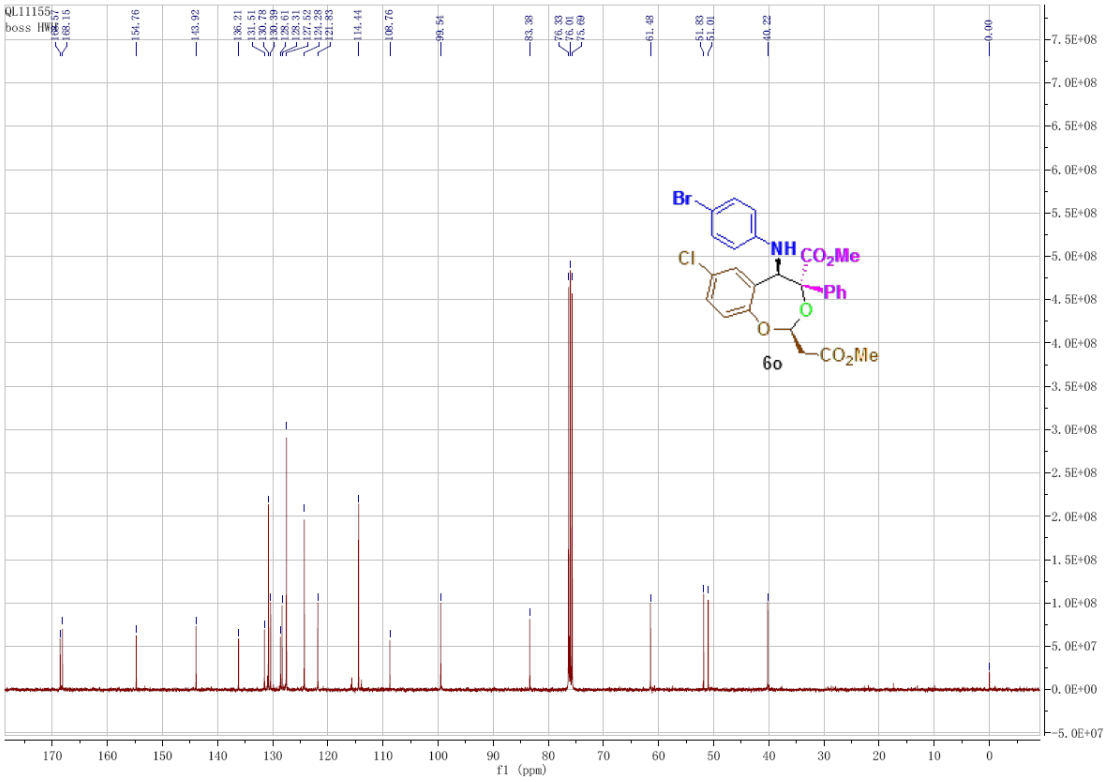
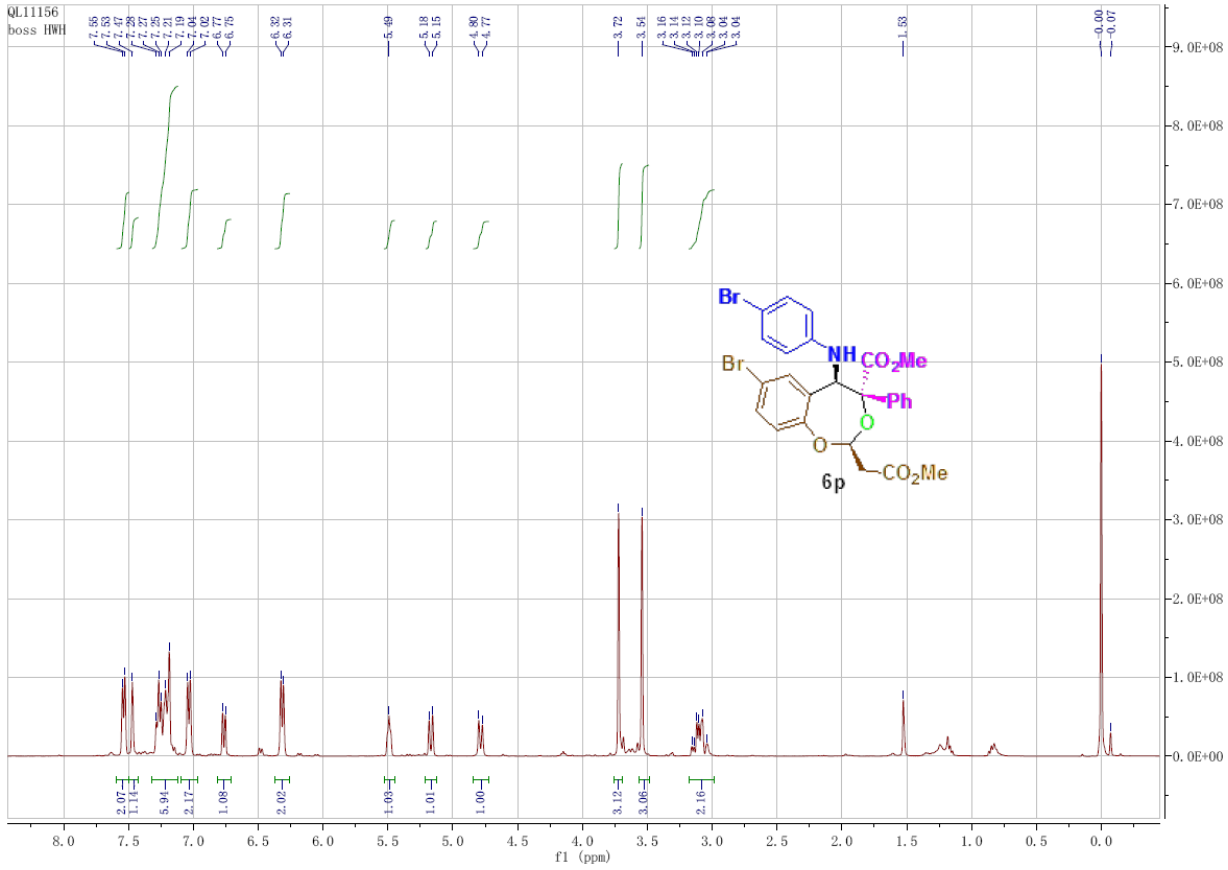
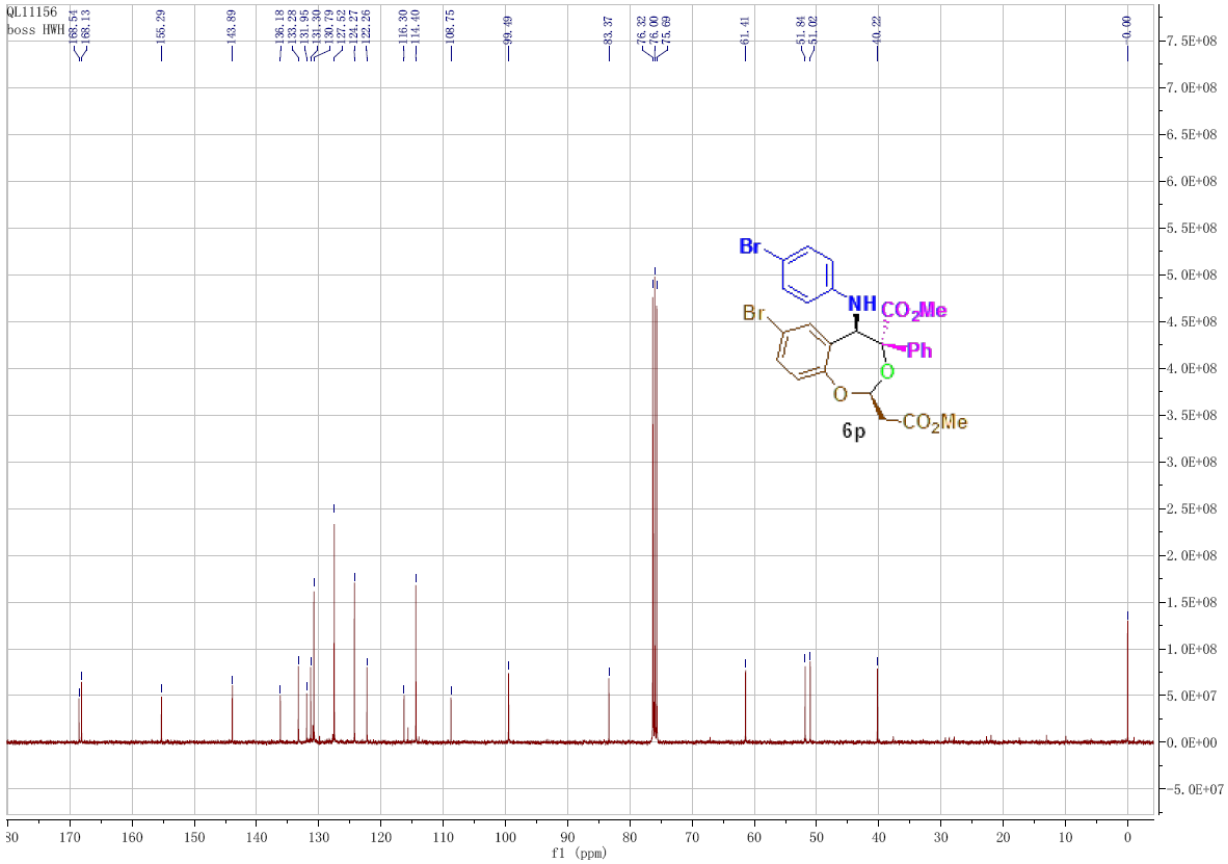
boss HWH
Br
NH
CO2Me
Cl
Ph
O
O
CO2Me
6o
f1 (ppm)


QL11155
boss HWH
Br
NH
CO2Me
Cl
Ph
O
O
CO2Me
6o
f1 (ppm)


QL11156
boss HWH
Br
NH
CO2Me
Br
Ph
O
O
CO2Me
6p
f1 (ppm)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Br
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CO2Me
Br
Ph
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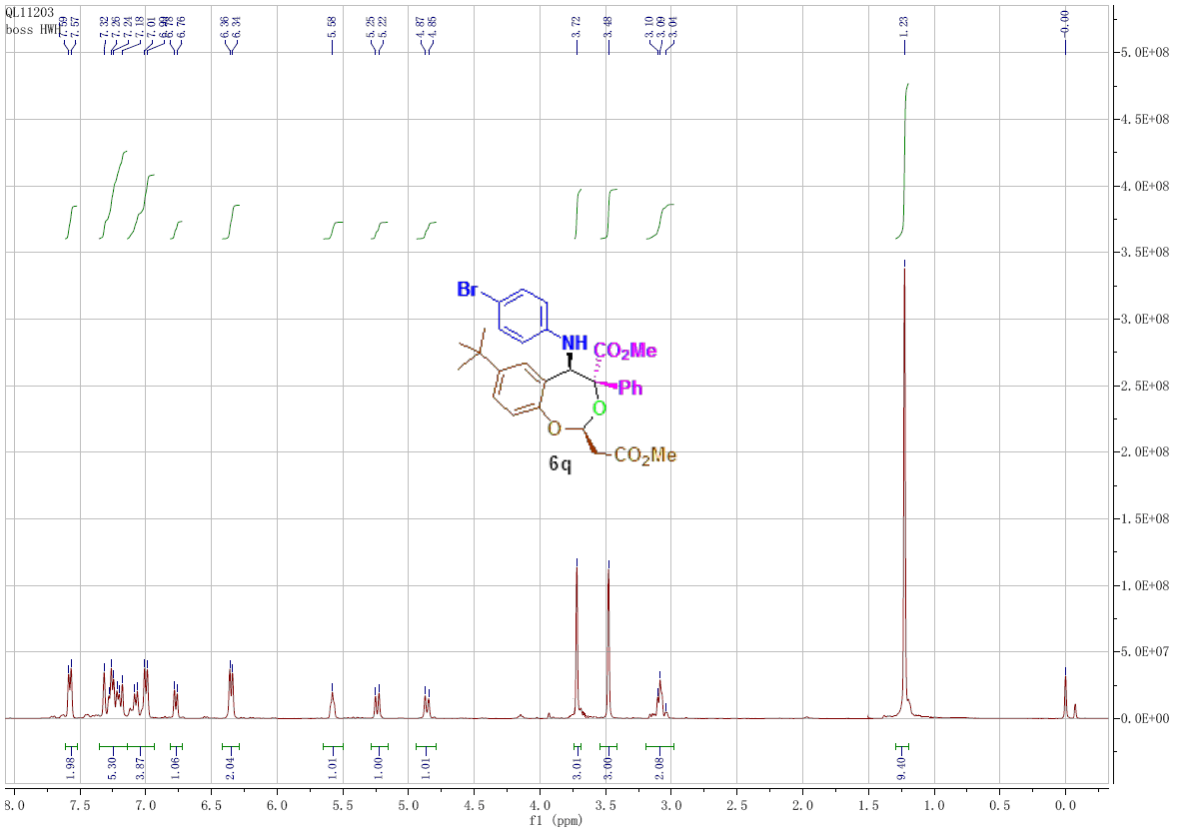
O
CO2Me
6p
f1 (ppm)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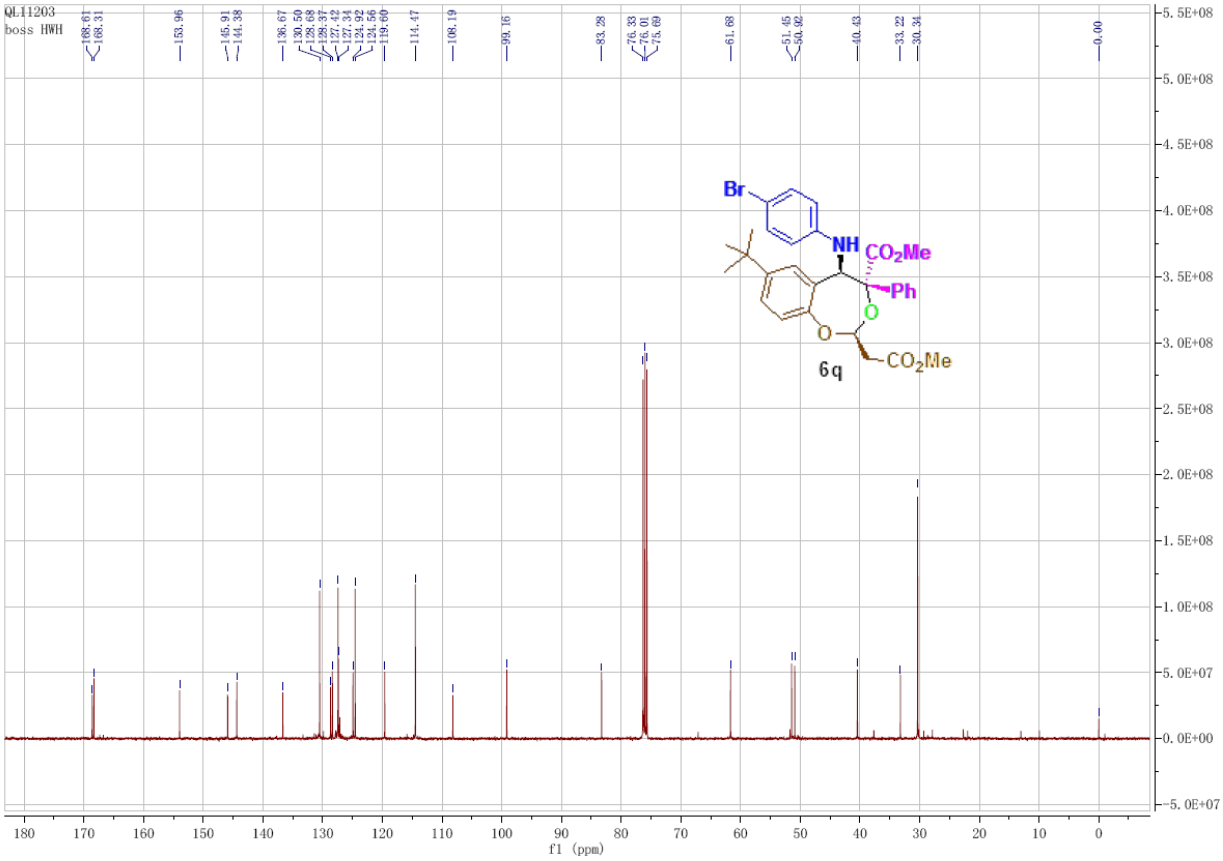
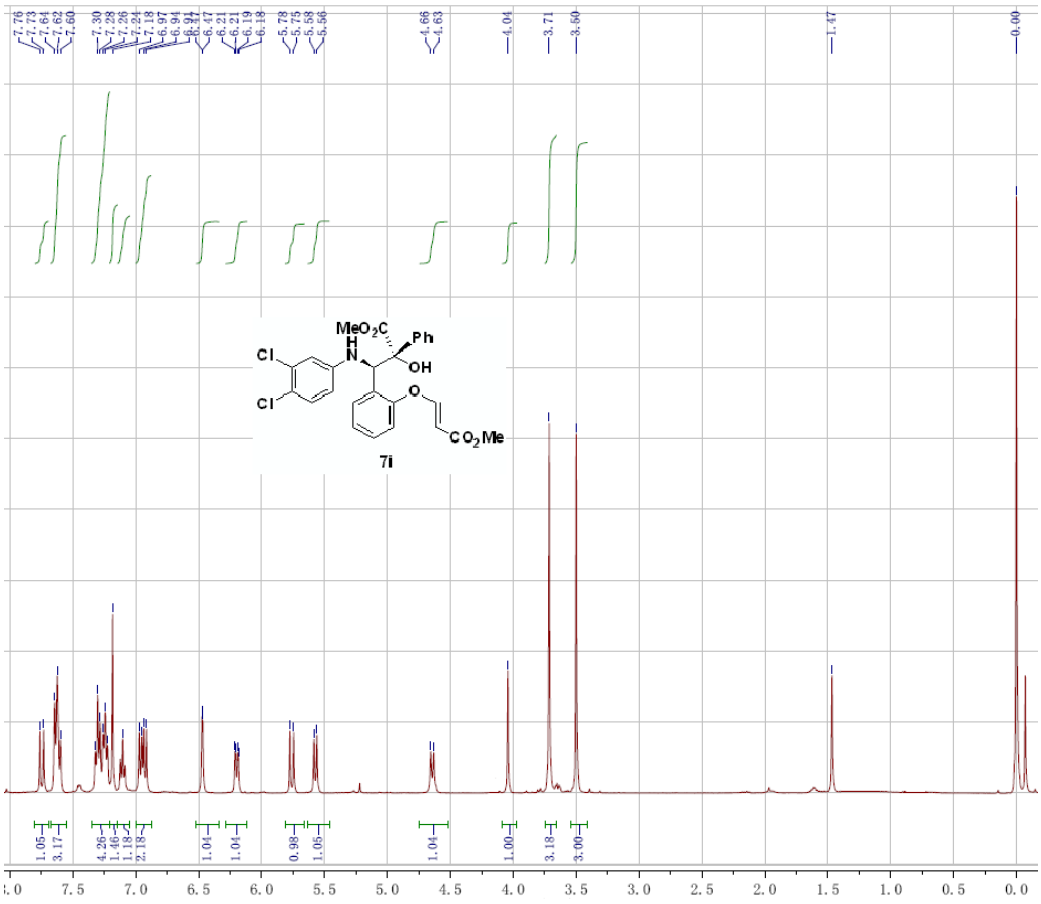
Br
NH
CO2Me
Ph
O
O
CO2Me
6q
f1 (ppm)


QL11203
boss HWH
Br
NH
CO2Me
Ph
O
O
CO2Me
6q
f1 (ppm)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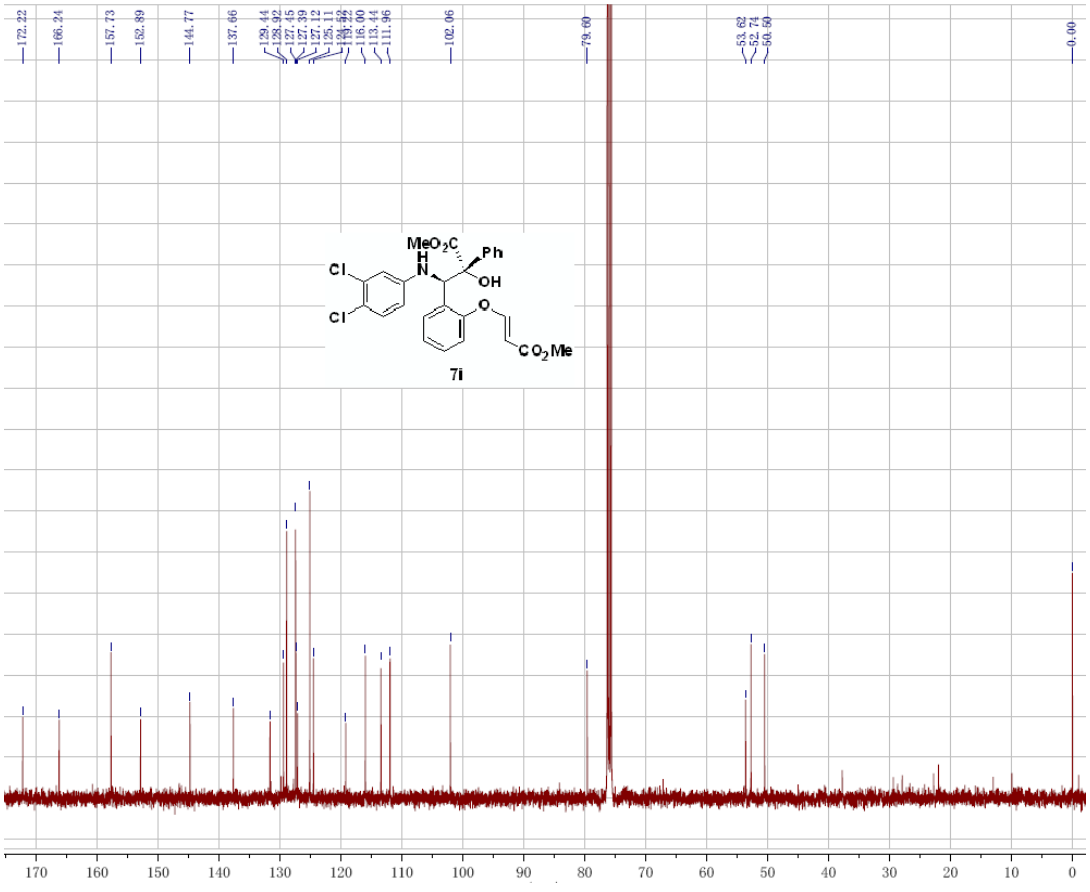
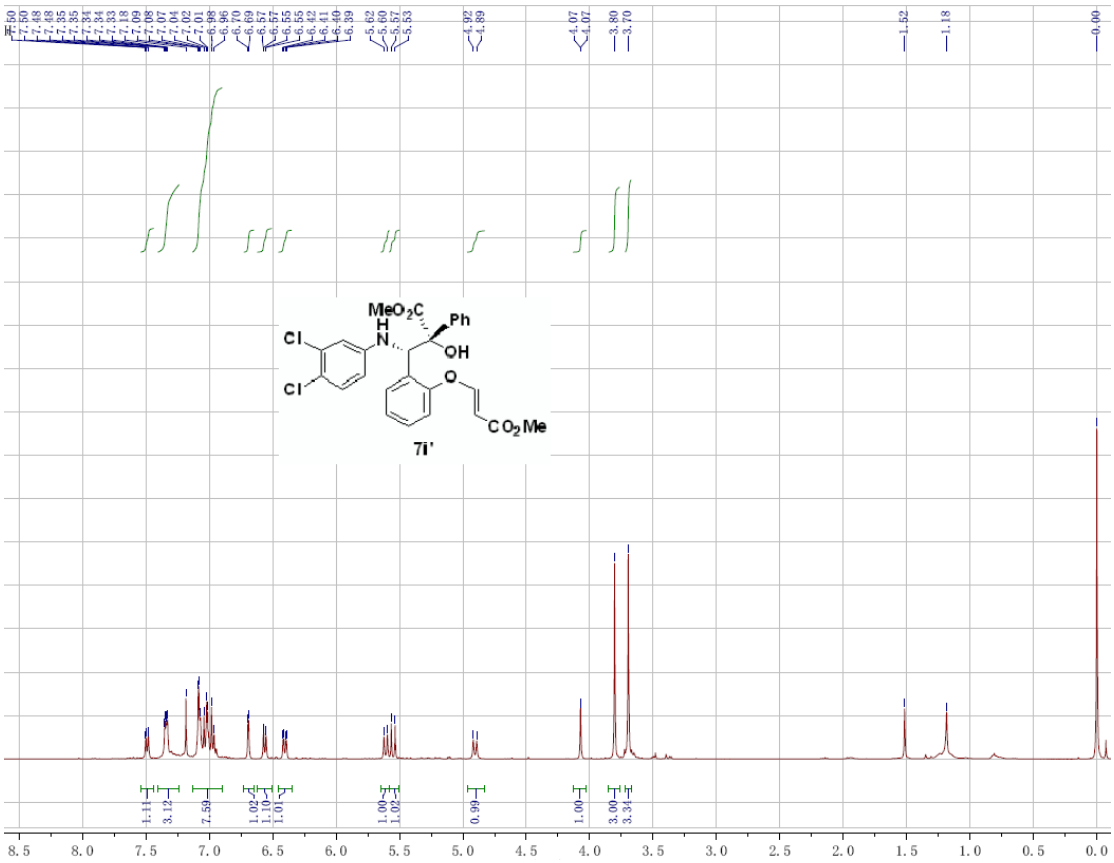
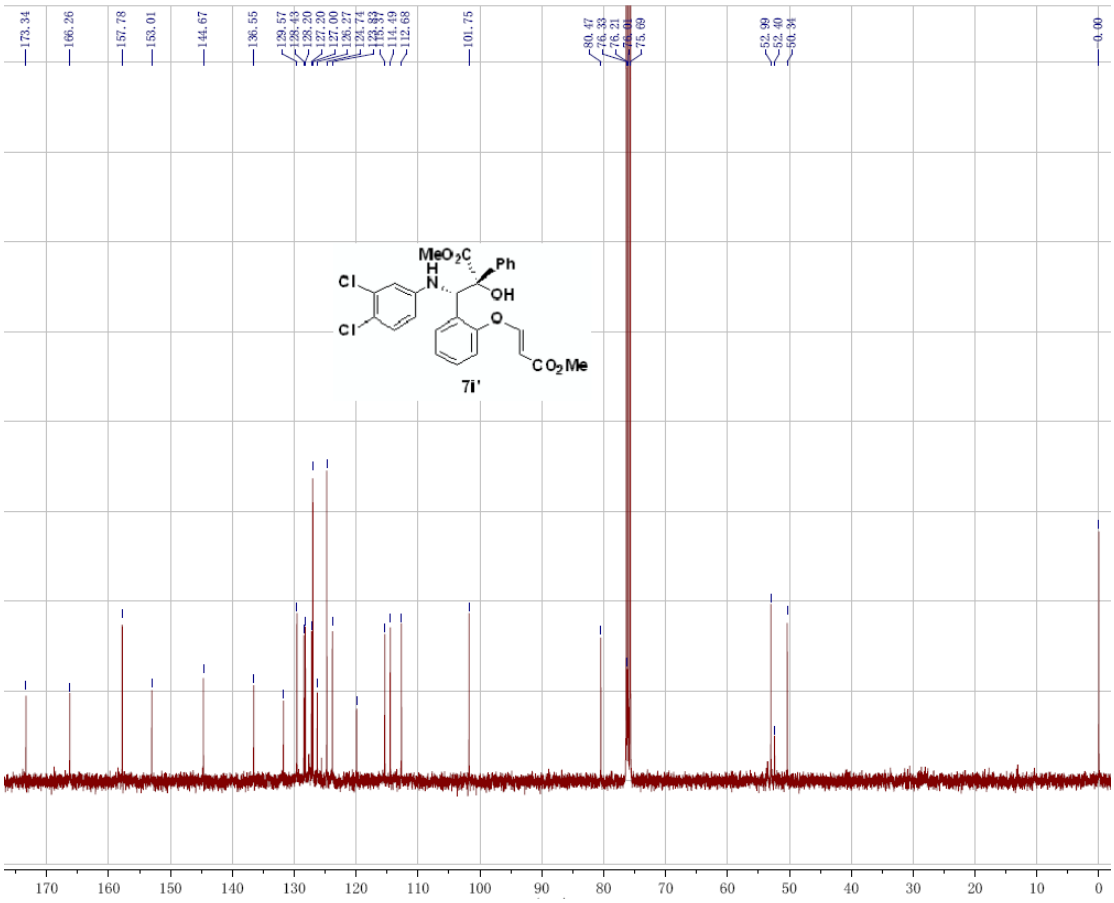
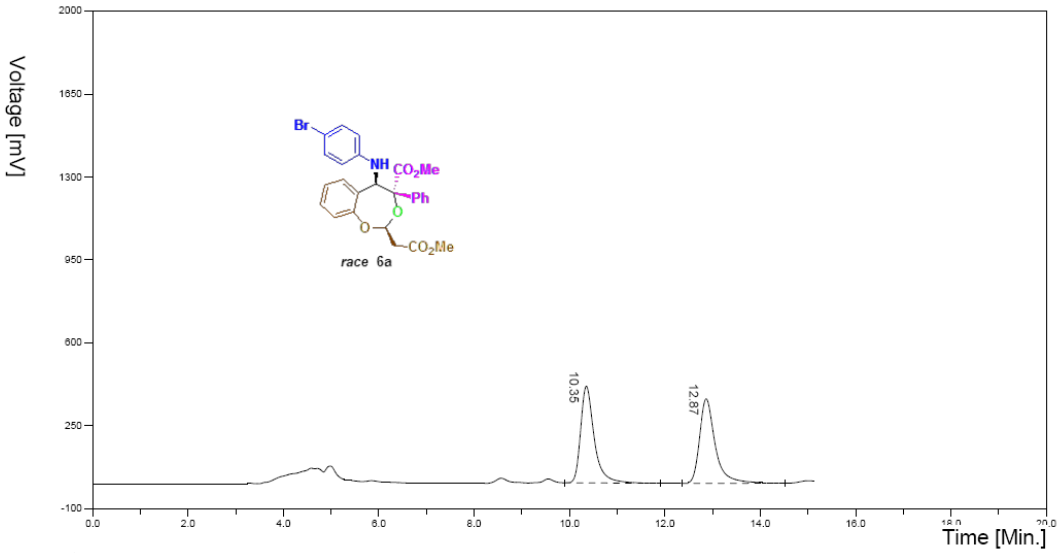
7.73
7.64
7.62
7.60
7.30
7.28
7.26
7.24
7.18
6.97
6.94
6.47
6.21
6.19
6.18
5.78
5.75
5.68
5.66
4.66
4.63
4.04
3.71
3.50
1.47
0.00
MeO2C
Ph
OH
Cl
Cl
O
CO2Me
7i
1.05
3.17
4.26
1.46
1.18
2.18
1.04
1.04
0.98
1.05
1.04
1.00
3.18
3.00


172.22
166.24
157.73
152.89
144.77
137.66
129.44
128.92
127.45
127.39
127.12
125.11
116.00
113.44
111.96
102.06
79.69
53.62
52.74
50.69
0.00
MeO2C
Ph
OH
Cl
Cl
O
CO2Me
7i


MeO2C
H
N
Ph
OH
Cl
Cl
O
CO2Me
7i'

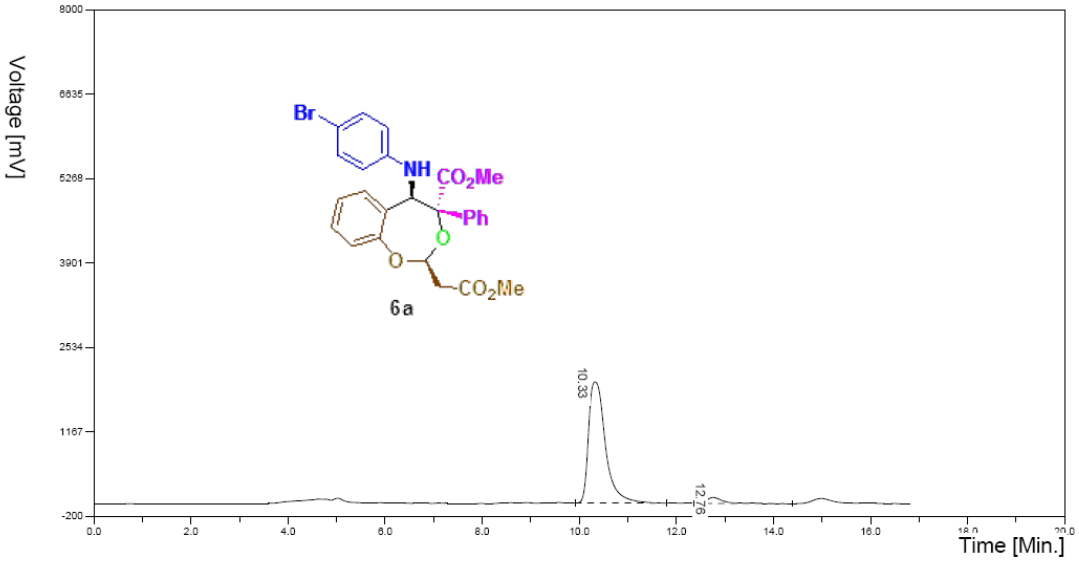

MeO2C
H
N
Ph
OH
Cl
Cl
O
CO2Me
7i'

Chiral HPLC analysis figures of the products



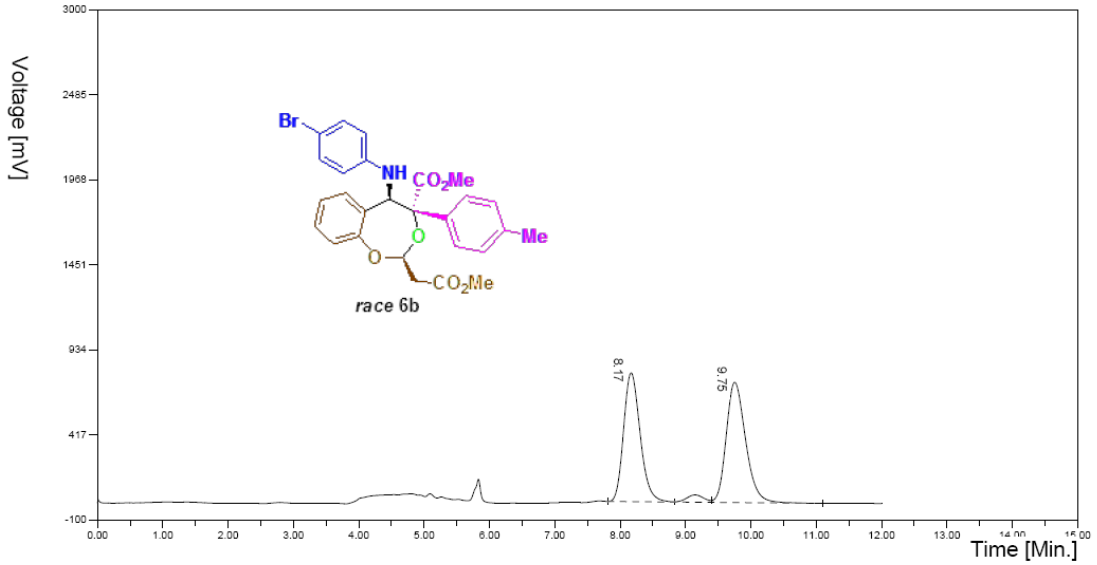
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.35	8094.44	49.8230
2	12.87	8151.97	50.1770
合计		16246.41	100



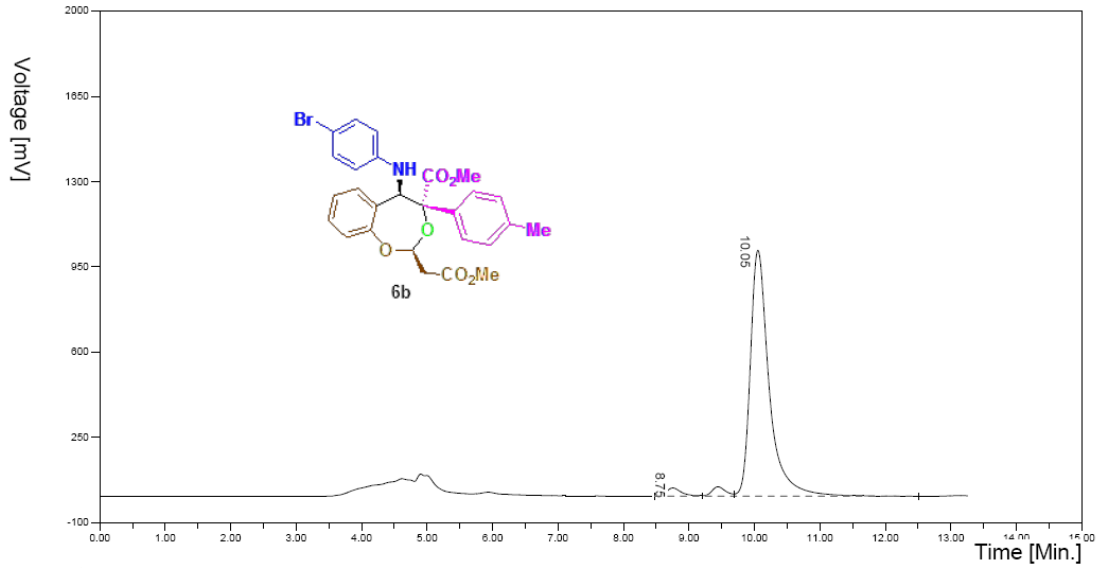
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.33	47377.29	95.4981
2	12.76	2233.43	4.5019
合计		49610.72	100



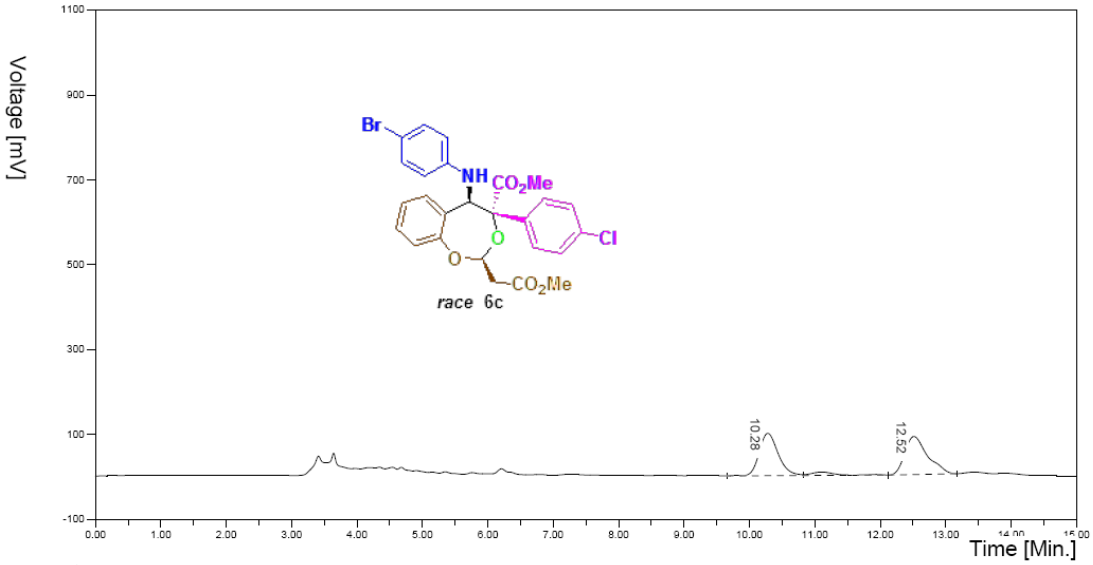
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.17	13767.55	47.7755
2	9.75	15049.62	52.2245
合计		28817.17	100



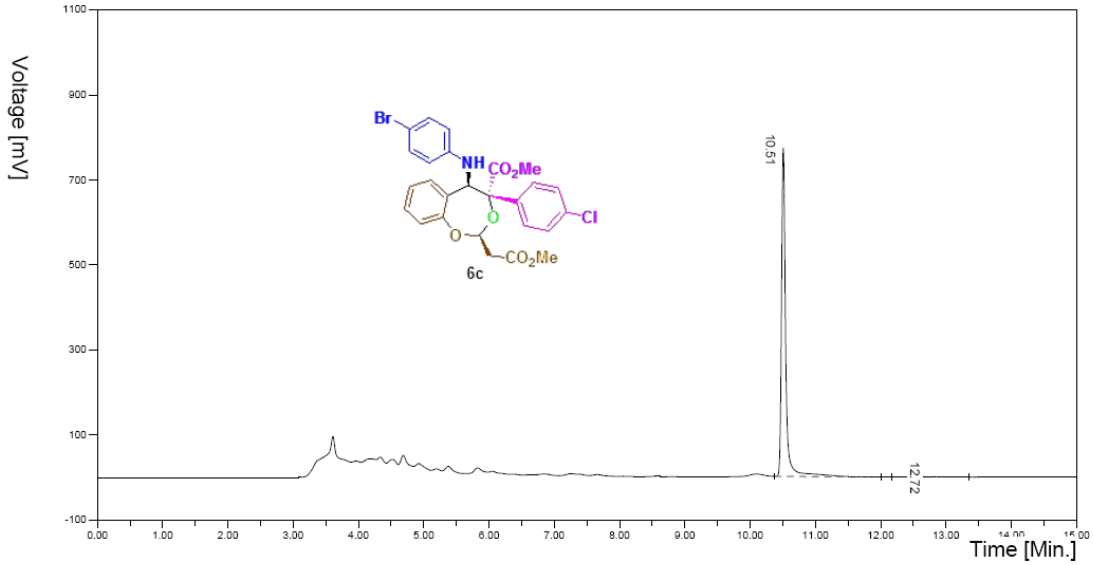
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.75	523.13	2.5198
2	10.05	20237.58	97.4802
合计		20760.70	100



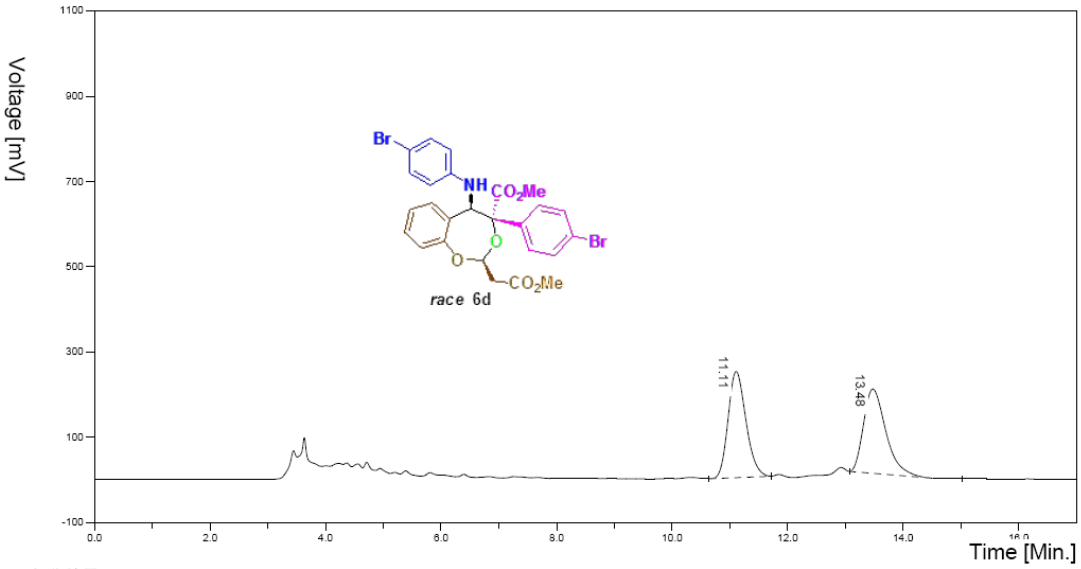
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.28	1972.72	48.2678
2	12.52	2114.31	51.7322
合计		4087.03	100



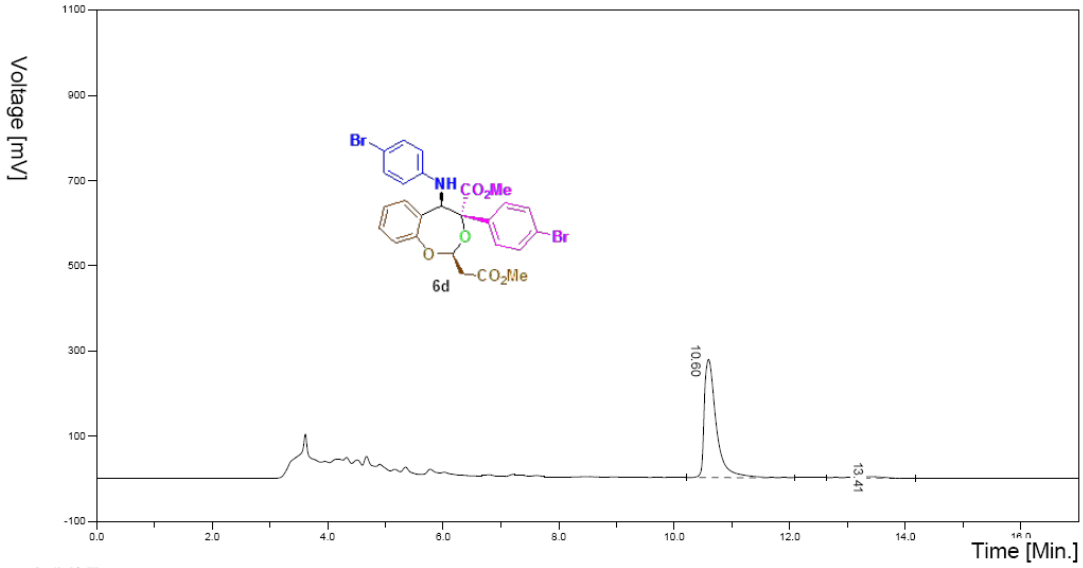
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.51	3450.05	99.4383
2	12.72	19.49	0.5617
合计		3469.54	100



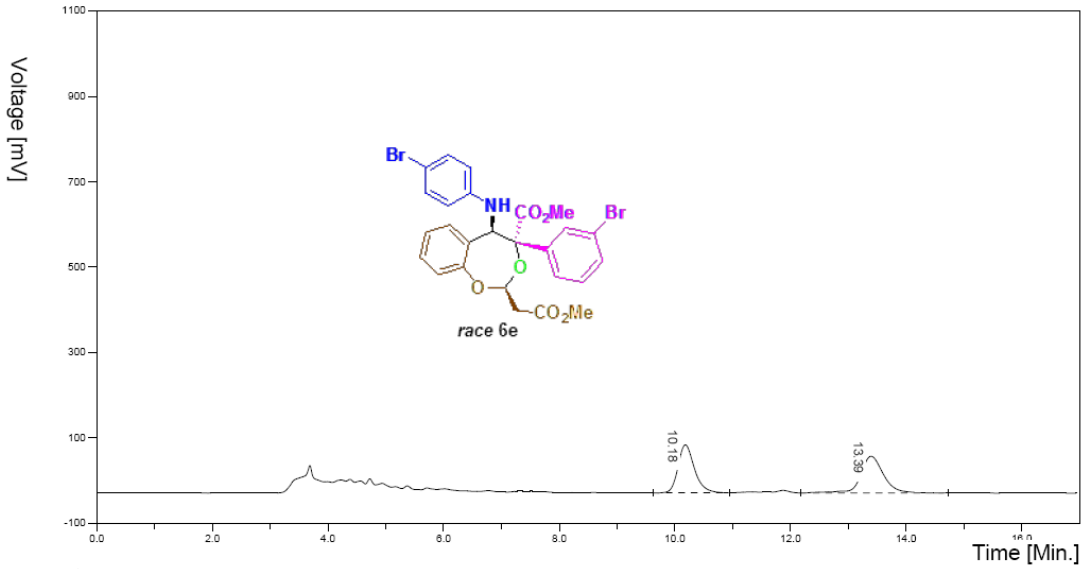
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	11.11	5345.64	51.0118
2	13.48	5133.58	48.9882
合计		10479.22	100



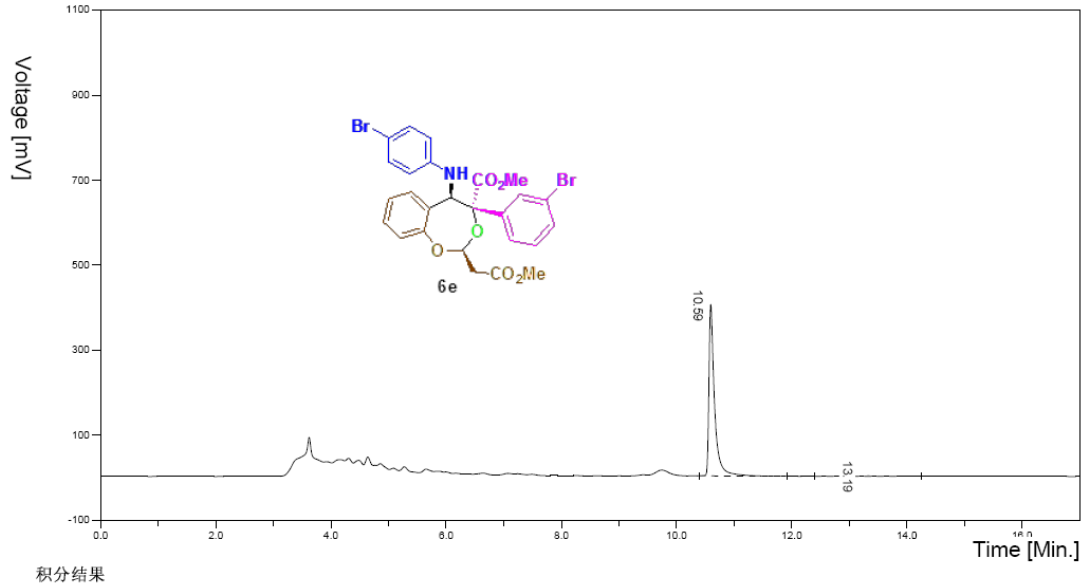
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.60	4010.70	97.7829
2	13.41	90.94	2.2171
合计		4101.64	100



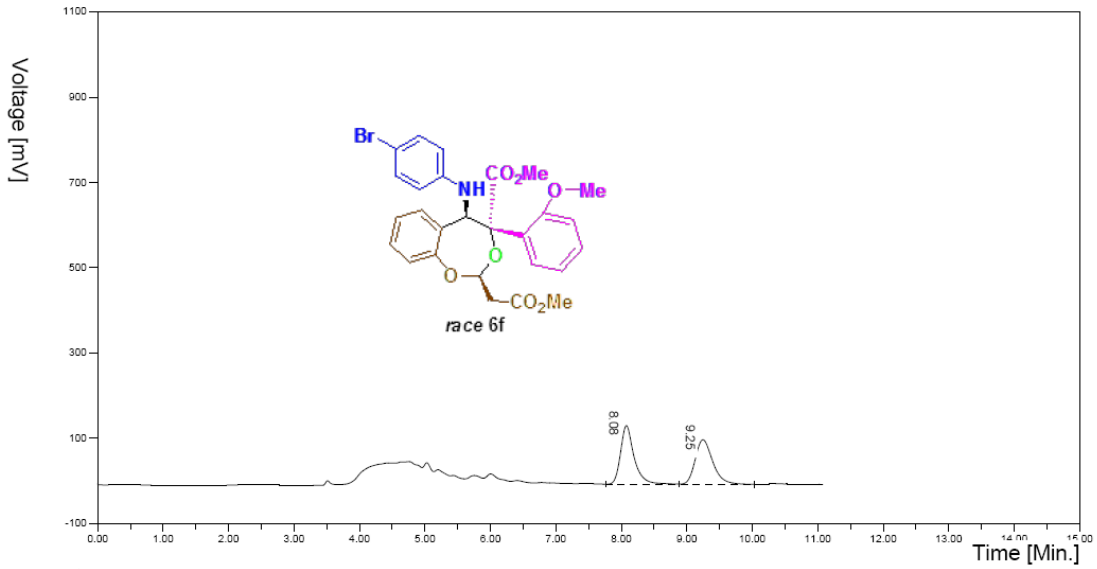
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.18	2216.05	48.3512
2	13.39	2367.19	51.6488
合计		4583.23	100



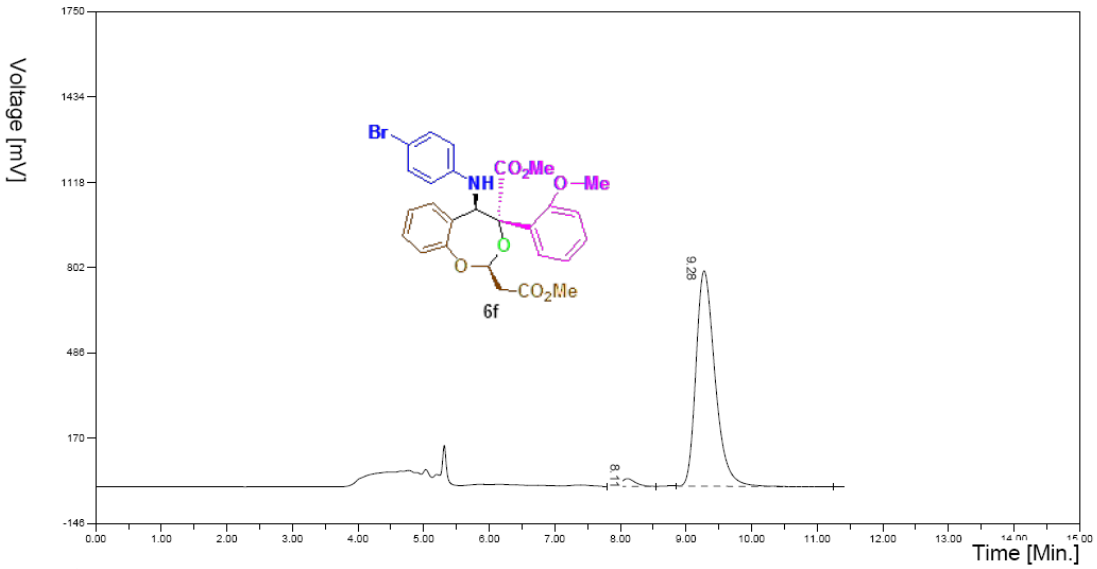
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.59	2732.24	98.9667
2	13.19	28.53	1.0333
合计		2760.77	100



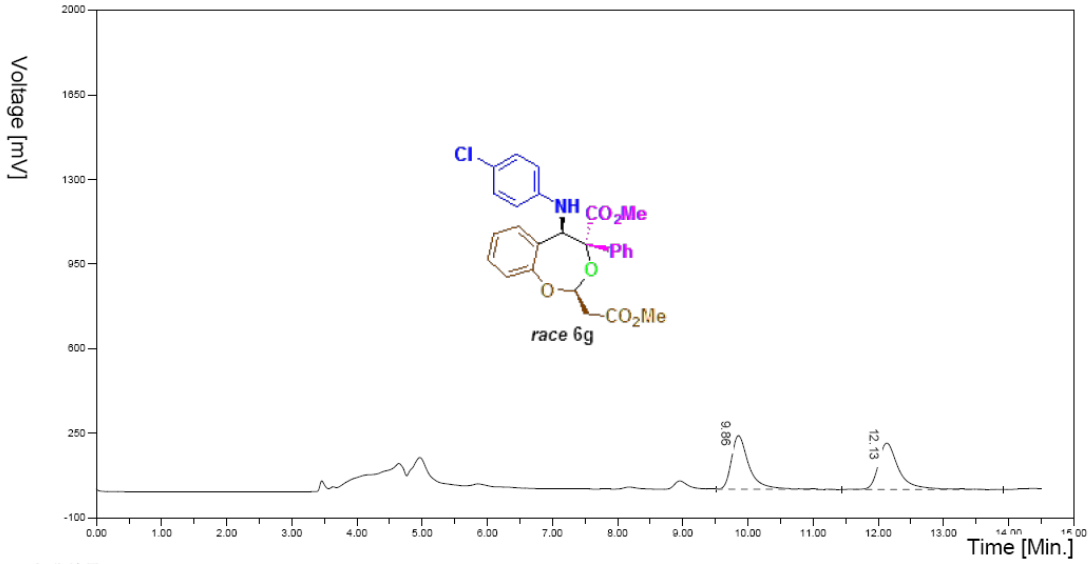
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.08	1969.18	50.5320
2	9.25	1927.72	49.4680
合计		3896.90	100



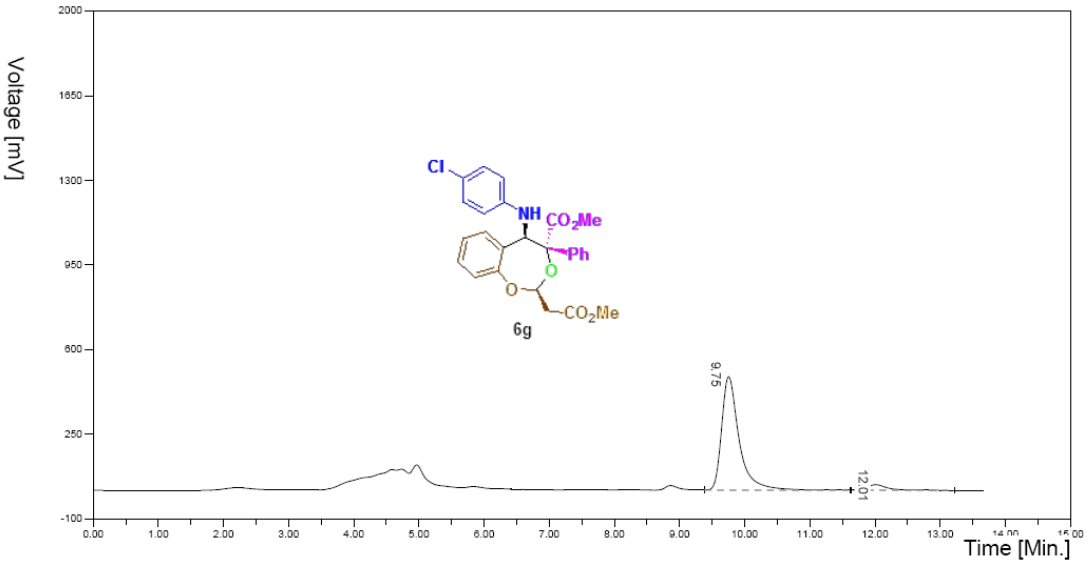
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.11	425.86	2.5756
2	9.28	16108.69	97.4244
合计		16534.56	100



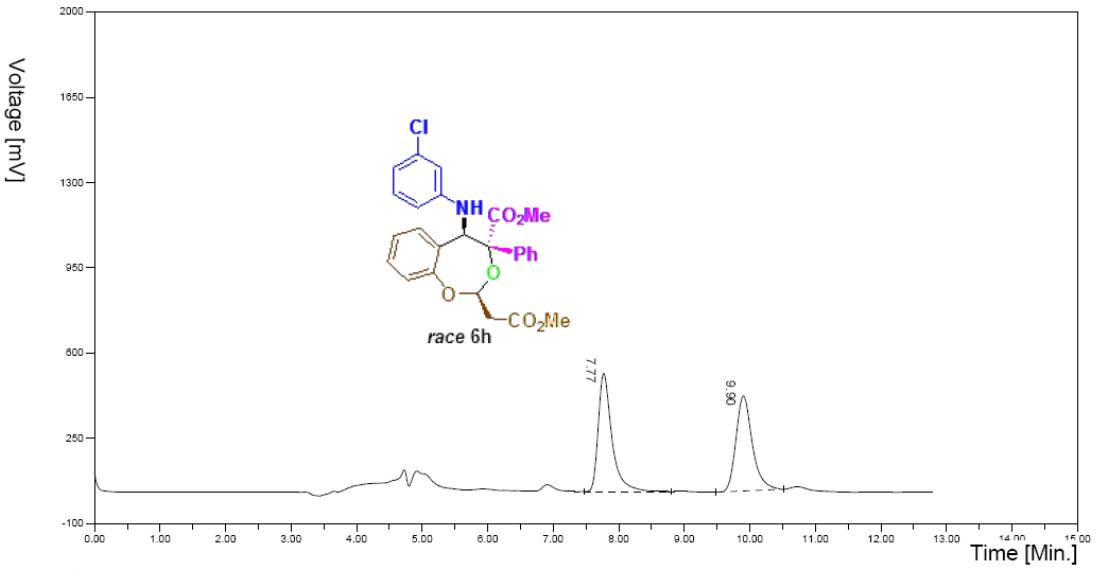
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.86	4092.84	49.8202
2	12.13	4122.38	50.1798
合计		8215.22	100



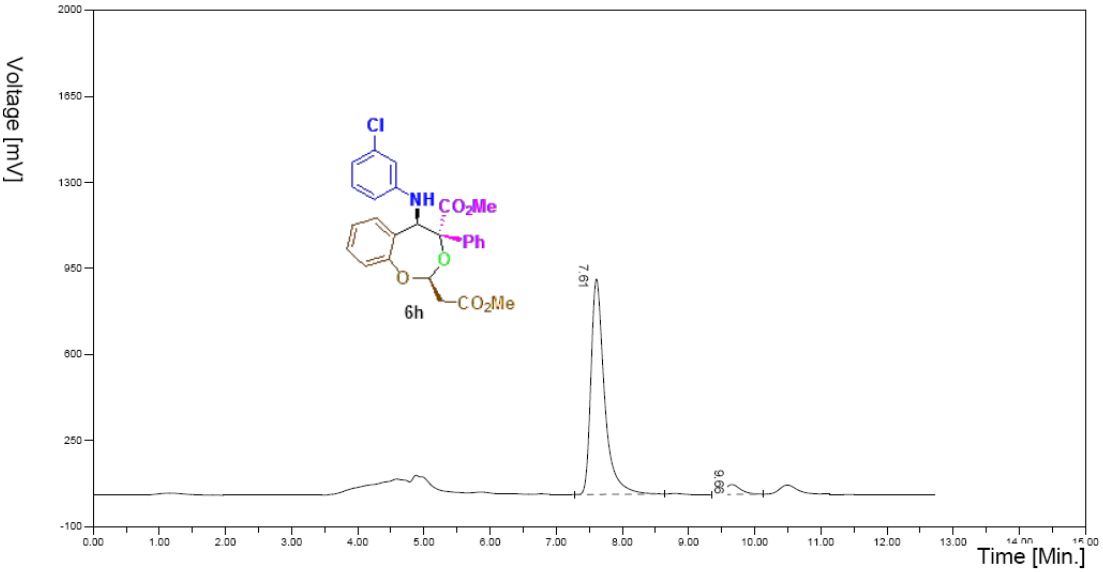
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.75	8738.85	94.7629
2	12.01	482.95	5.2371
合计		9221.80	100



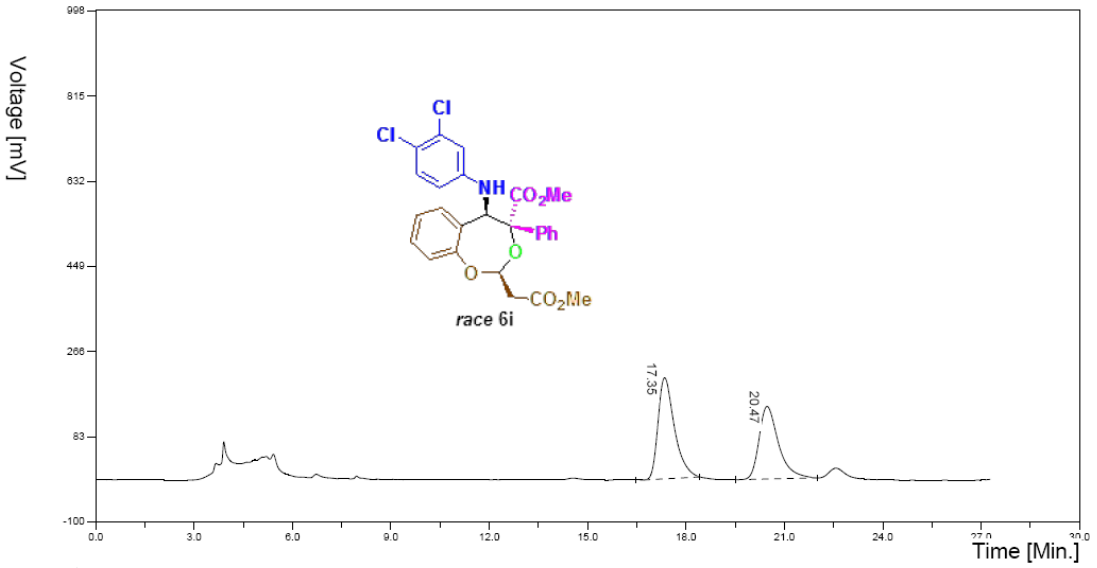
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	7.77	7035.74	50.9997
2	9.90	6759.91	49.0003
合计		13795.65	100



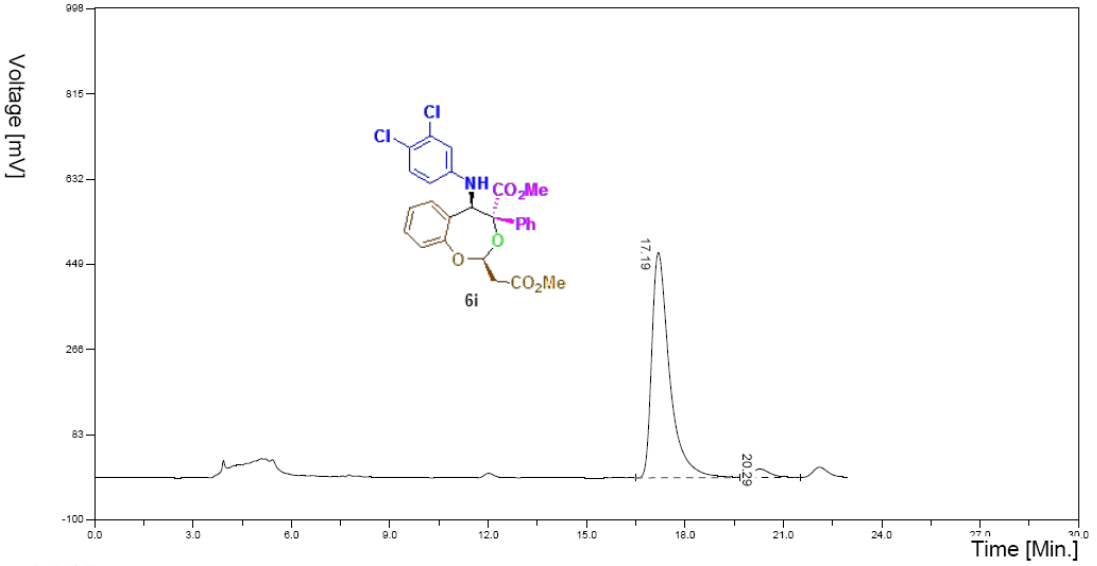
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	7.61	12469.24	95.0751
2	9.66	645.91	4.9249
合计		13115.15	100



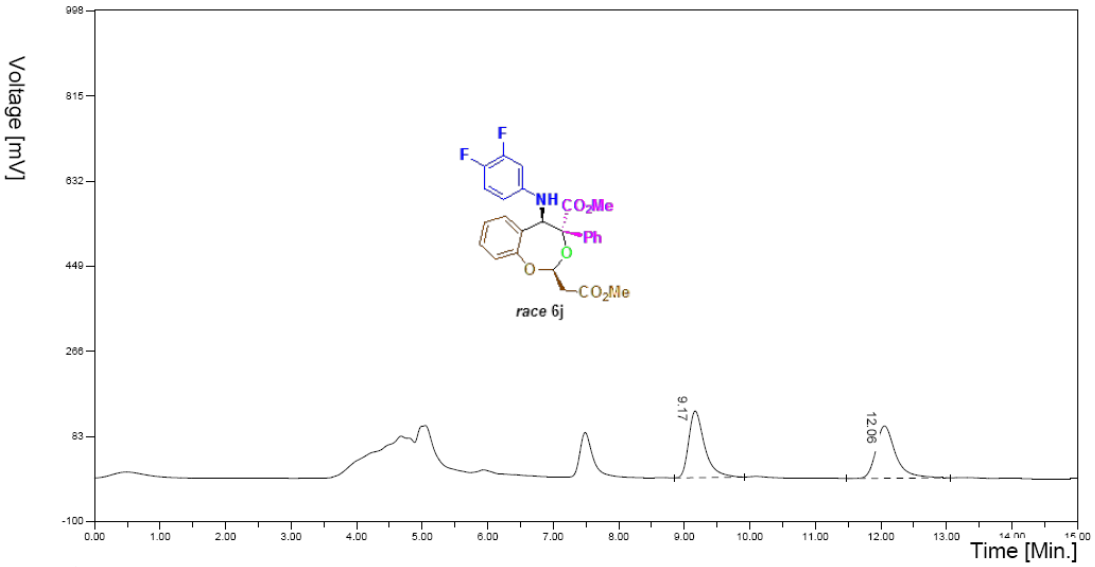
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	17.35	7512.95	53.8483
2	20.47	6439.12	46.1517
合计		13952.07	100



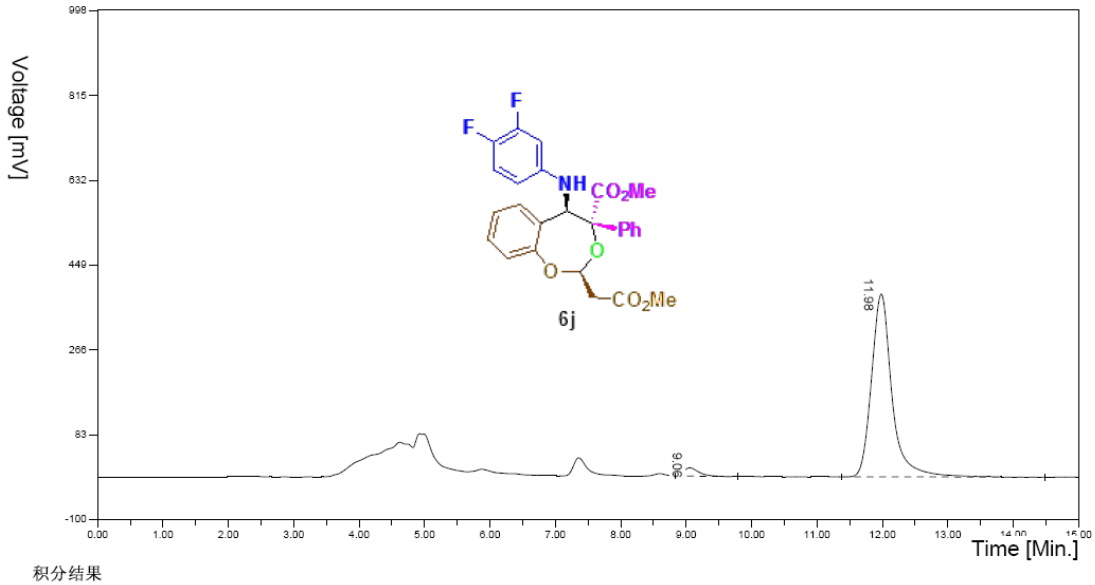
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	17.19	18241.64	96.2344
2	20.29	713.79	3.7656
合计		18955.43	100



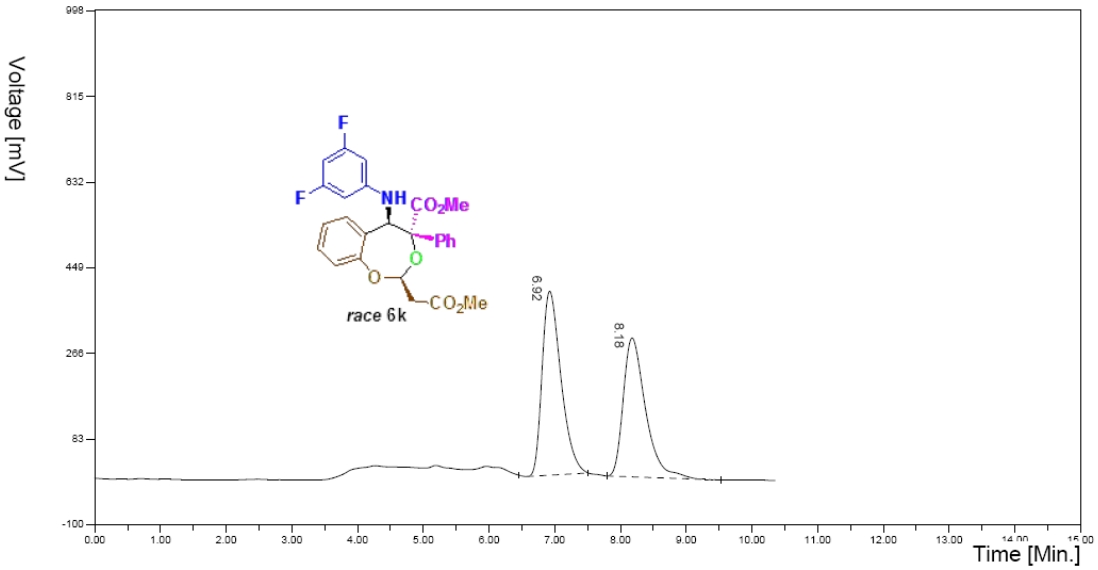
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.17	2423.57	50.7897
2	12.06	2348.20	49.2103
合计		4771.76	100



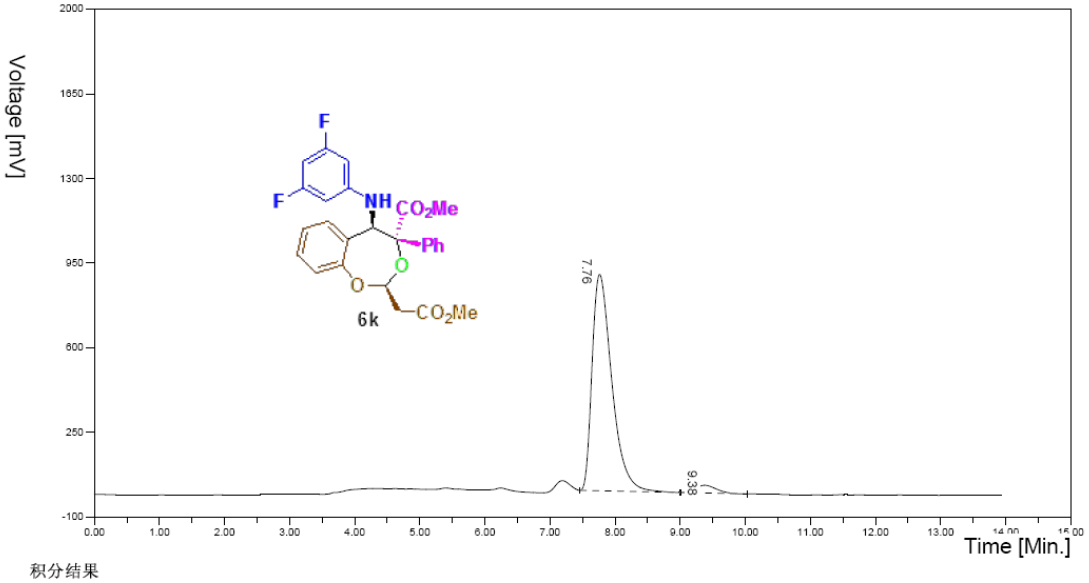
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.06	283.27	3.1836
2	11.98	8614.37	96.8164
合计		8897.64	100



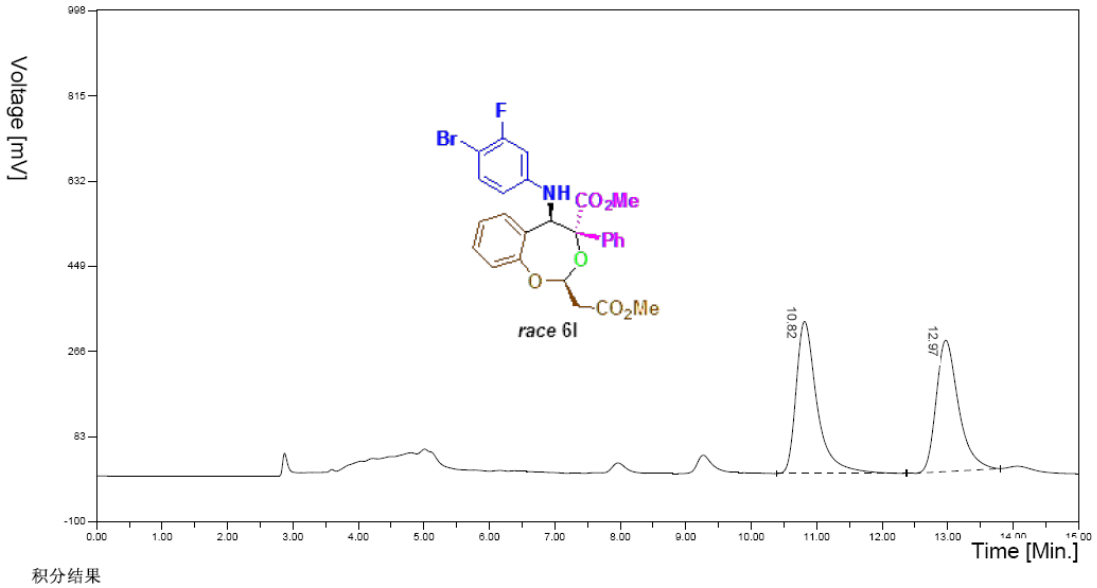
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	6.92	7752.94	52.6970
2	8.18	6959.36	47.3030
合计		14712.30	100



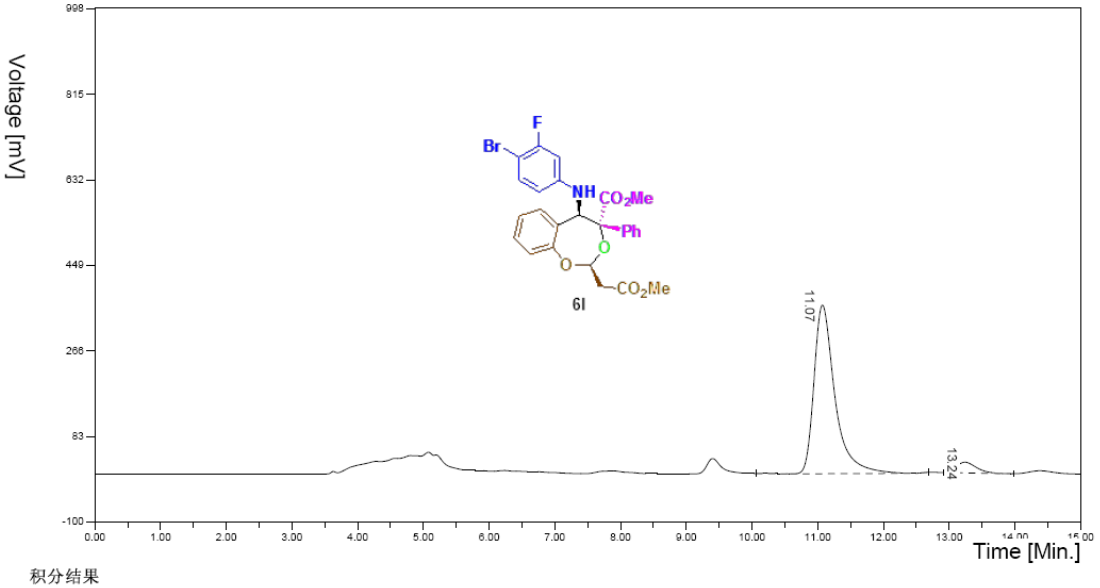
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	7.76	18795.30	96.3368
2	9.38	714.68	3.6632
合计		19509.98	100



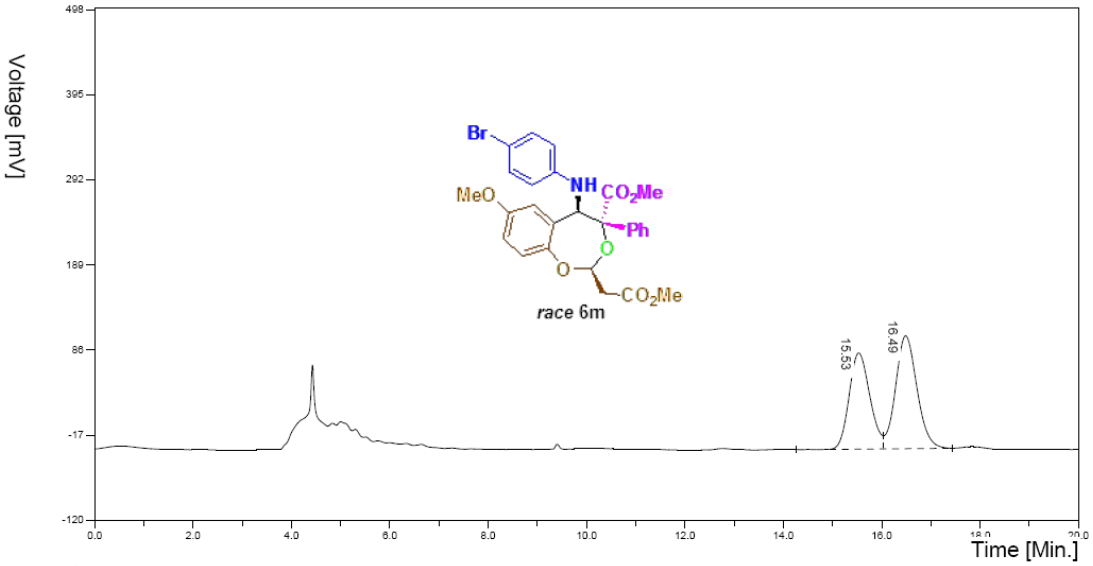
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.82	6939.82	51.9418
2	12.97	6420.96	48.0582
合计		13360.78	100



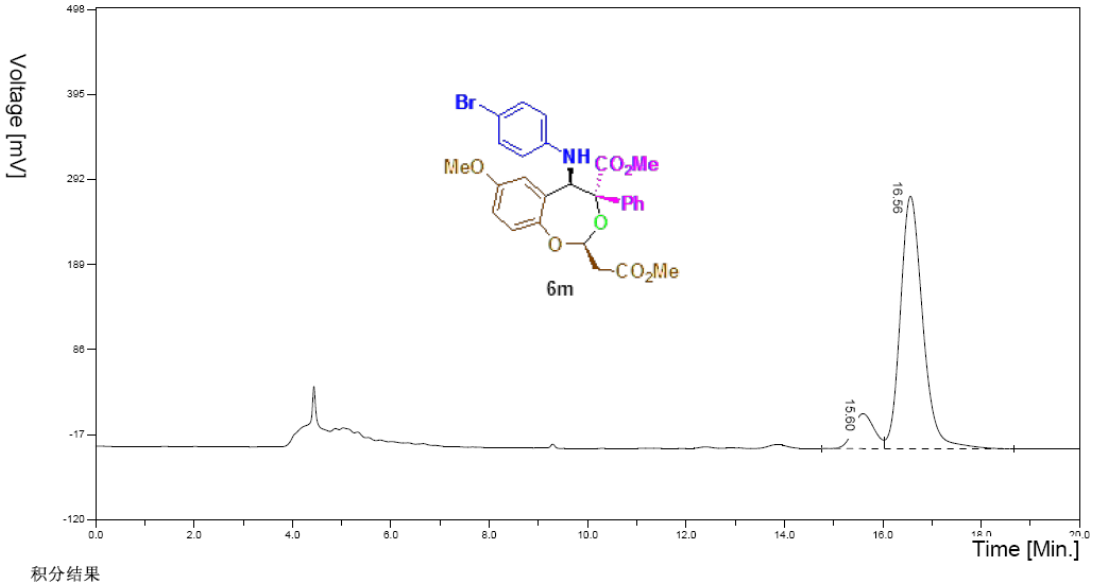
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	11.07	7766.95	94.1366
2	13.24	483.77	5.8634
合计		8250.72	100



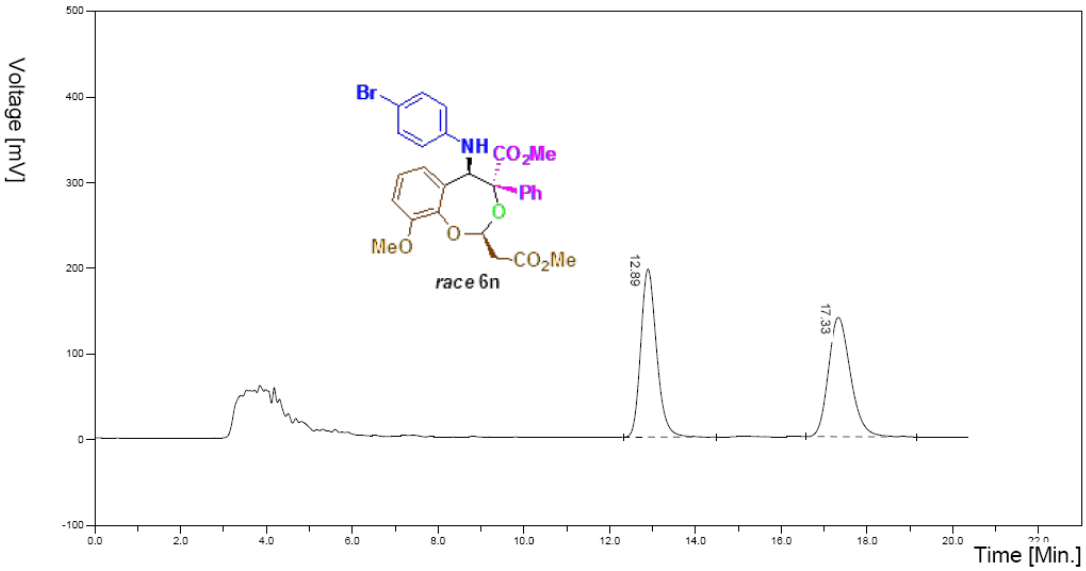
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	15.53	3402.00	45.1583
2	16.49	4131.50	54.8417
合计		7533.50	100



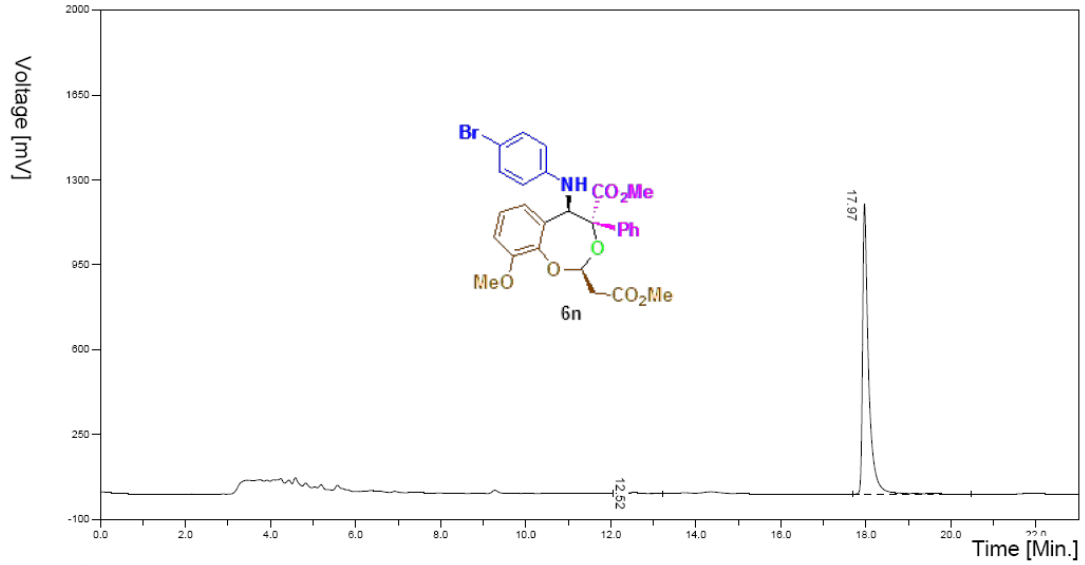
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	15.60	1263.52	11.5381
2	16.56	9687.28	88.4619
合计		10950.80	100



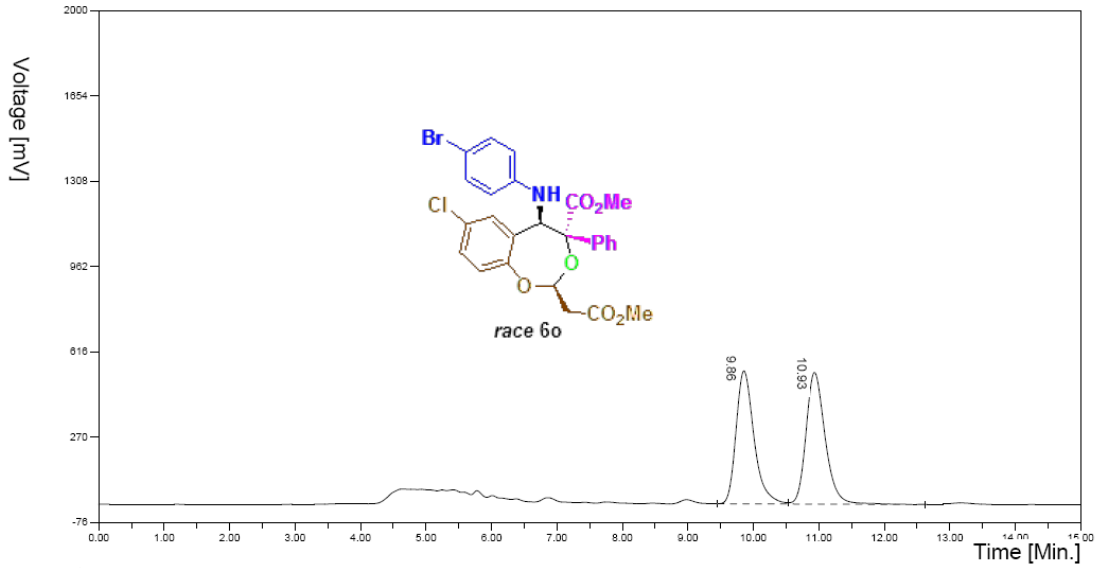
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	12.89	5041.34	50.3360
2	17.33	4974.05	49.6640
合计		10015.39	100



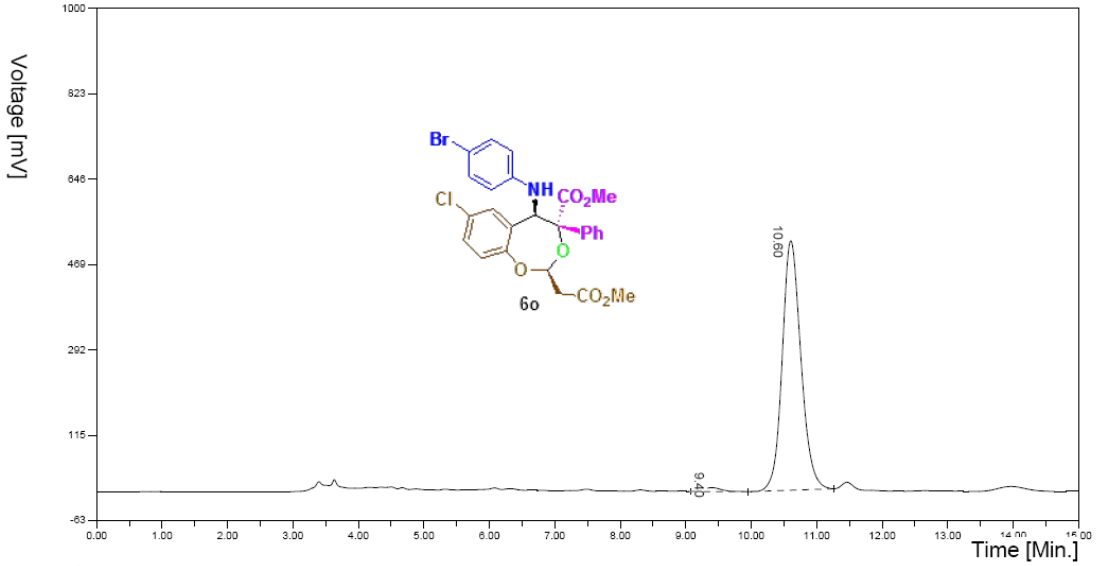
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	12.52	113.33	0.9657
2	17.97	11621.48	99.0343
合计		11734.81	100



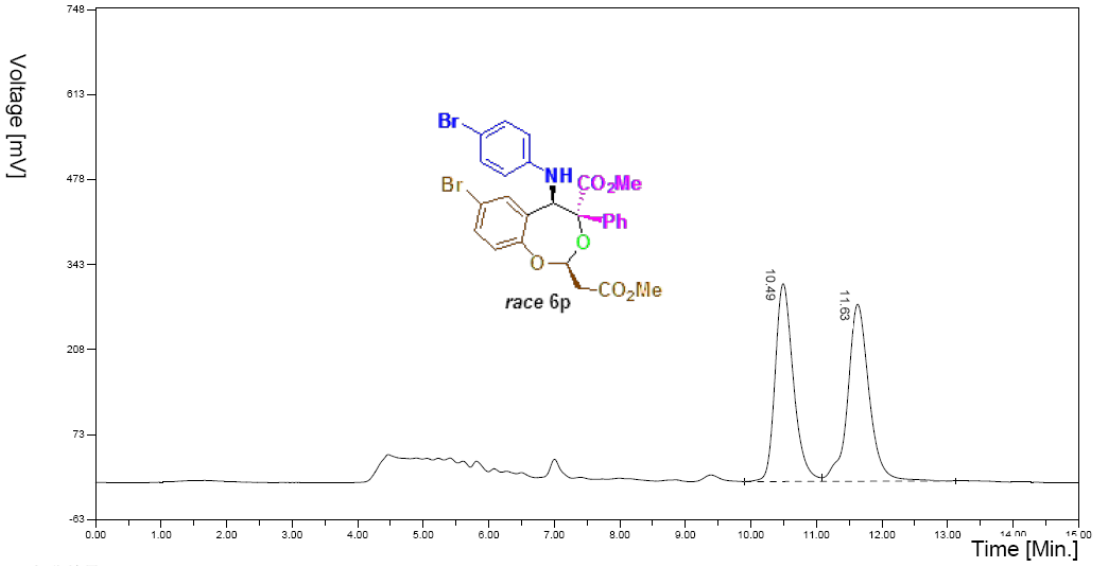
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.86	10290.33	48.7097
2	10.93	10835.51	51.2903
合计		21125.84	100



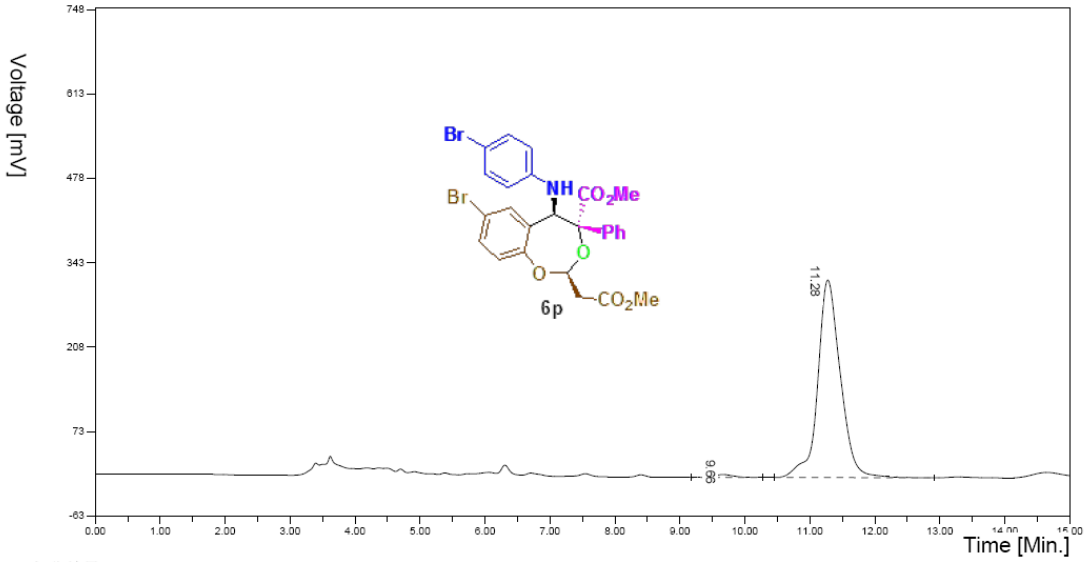
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.40	83.34	0.8123
2	10.60	10176.01	99.1877
合计		10259.35	100



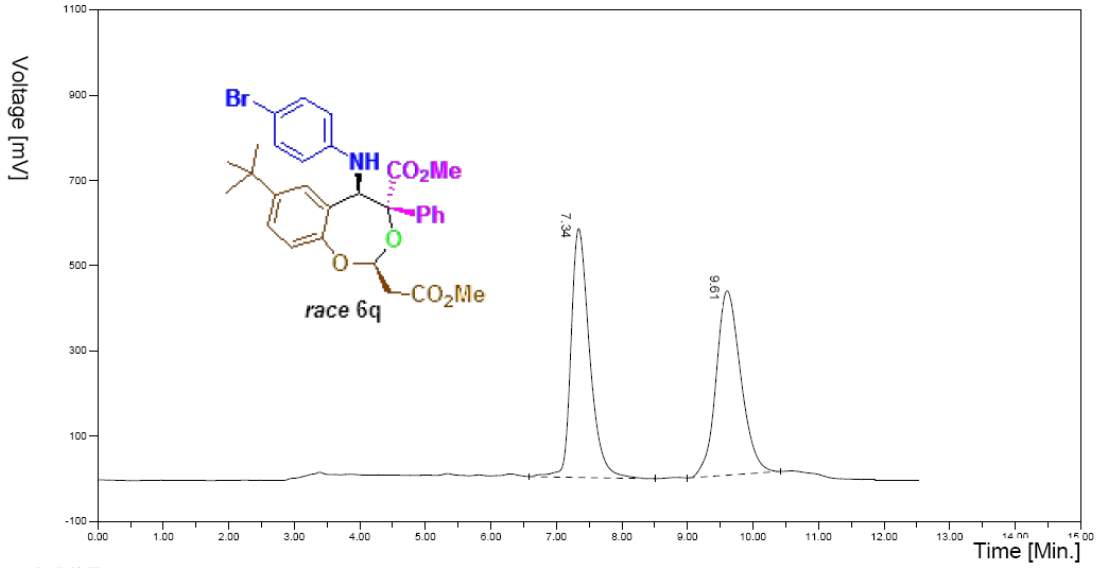
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.49	6089.71	48.7819
2	11.63	6393.82	51.2181
合计		12483.53	100



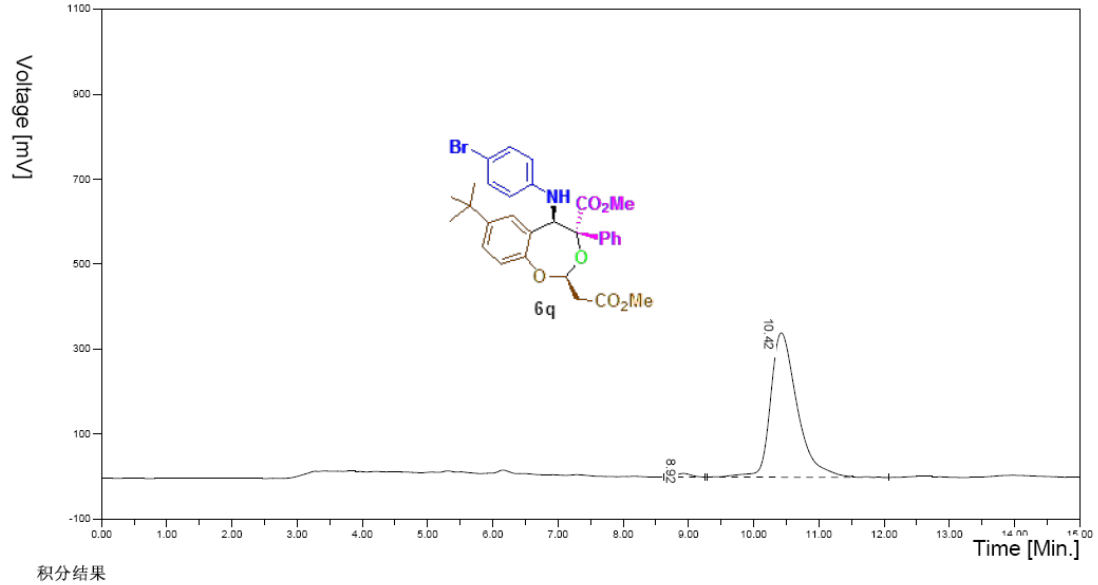
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	9.66	84.13	1.0849
2	11.28	7670.81	98.9151
合计		7754.94	100



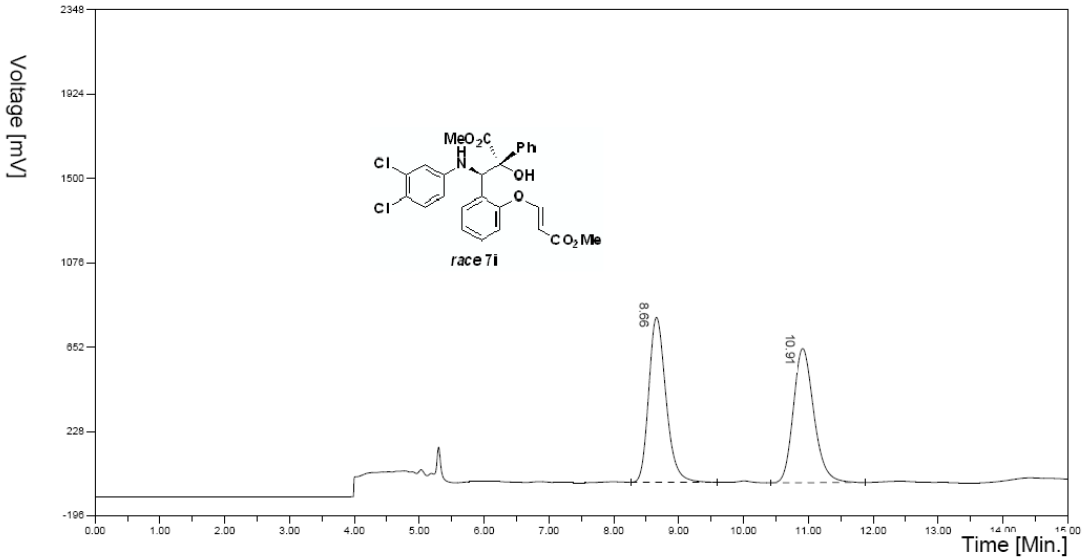
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	7.34	11525.21	50.4126
2	9.61	11336.56	49.5874
合计		22861.77	100



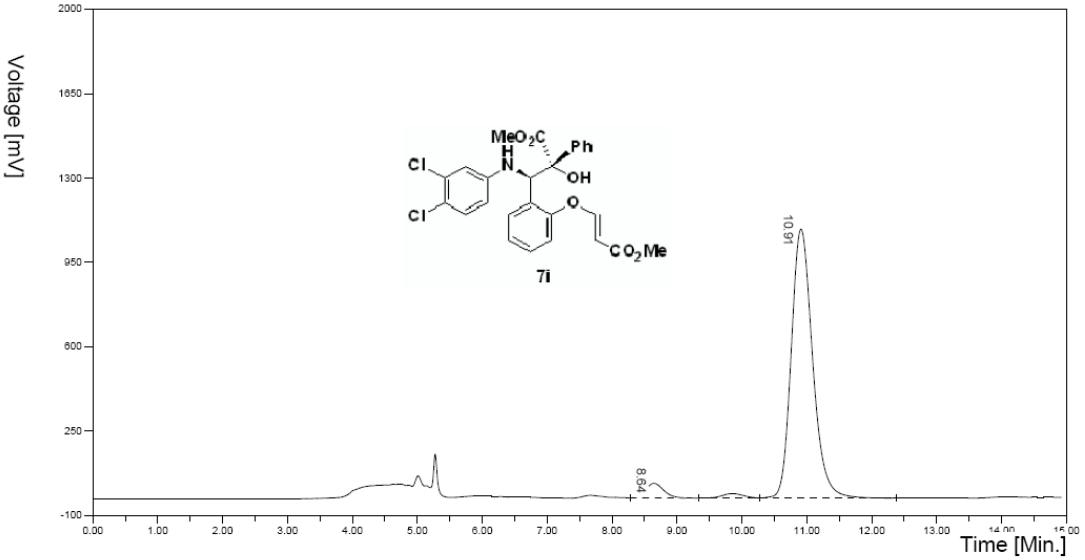
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.92	129.06	1.3156
2	10.42	9680.85	98.6844
合计		9809.91	100



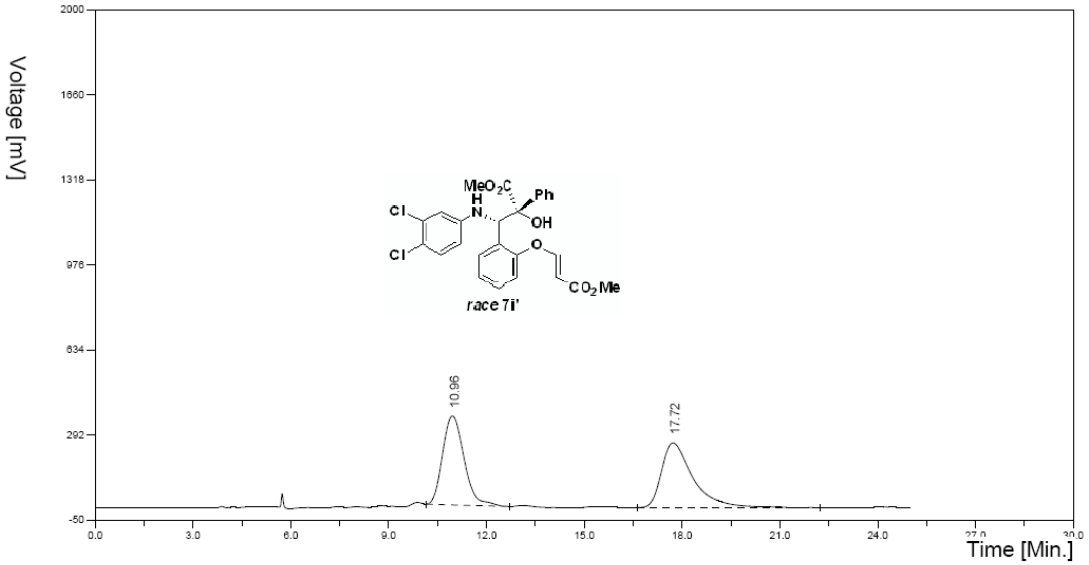
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.66	15304.23	50.7736
2	10.91	14837.89	49.2264
合计		30142.11	100



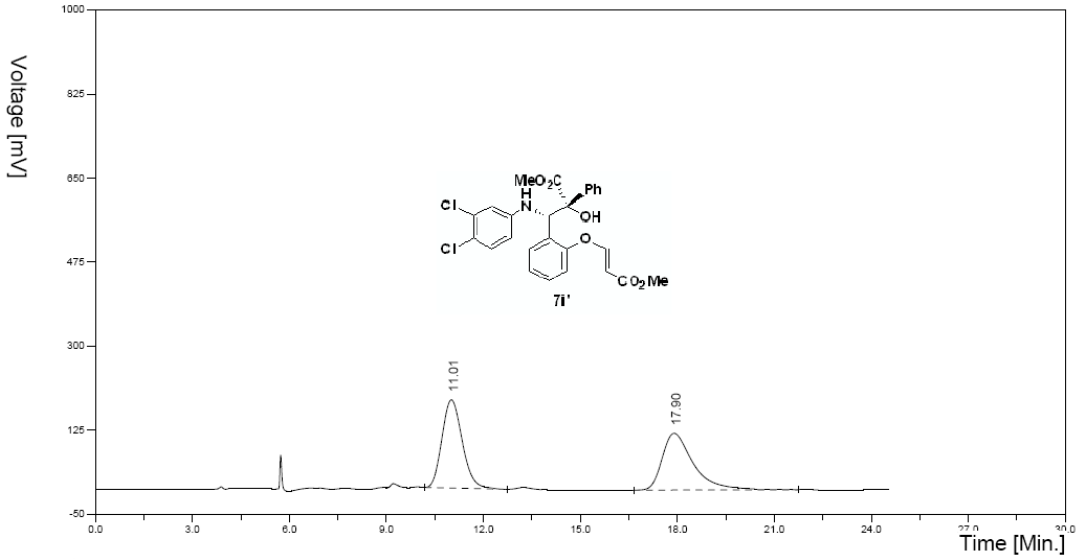
积分结果

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	8.64	1134.55	4.2701
2	10.91	25435.05	95.7299
合计		26569.60	100



组分表

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	10.96	16373.15	48.7081
2	17.72	17241.68	51.2919
合计		33614.83	100



组分表

#	保留时间(min)	峰面积(mv.sec)	面积百分比(%)
1	11.01	8012.69	50.3741
2	17.90	7893.67	49.6259
合计		15906.36	100