Supporting Information for

Asymmetric hydrogenation of 3-substituted 2*H*-1,4-benzoxazines with chiral cationic Ru-MsDPEN catalysts: remarkable counteranion effect

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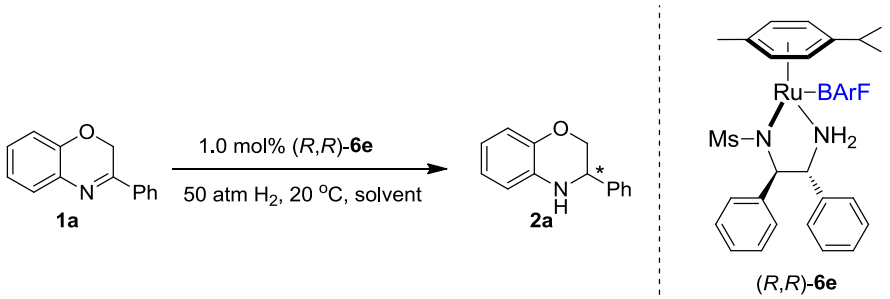
Contents

1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 300 Spectrometer (^{1}H 300 MHz and ^{13}C 75 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with PerkinElmer 341 polarimeter. High resolution MS (P-ESI HRMS) were obtained on Bruker Apex IV FTMS spectrometer. HPLC analyses were performed on a Varian Prostar 210 liquid chromatograph. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. All Ru-catalysts were prepared according to the published method.[1] 3-Substituted-2*H*-1,4-benzoxazines **1** and **3** were synthesized according to modified literature method.[2]

2. Optimization of conditions for asymmetric hydrogenation

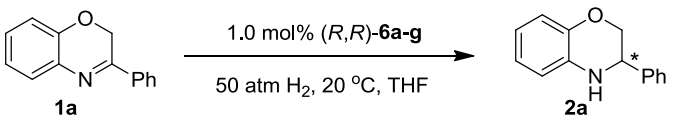
Table S1 Screening of the solvents for asymmetric hydrogenation of **1a** with (*R*,*R*)-**6e**[a]

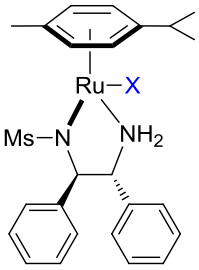


Entry	Solvent	Time (h)	Conv. (%)[b]	Ee (%)[c, d]
1	$ClCH_2CH_2Cl$	12	>95	19 (*S*)
2	CH_2Cl_2	12	>95	15 (*S*)
3	toluene	12	>95	9 (*S*)
4	MeOH	12	>95	55 (*R*)
5	EtOH	12	>95	57 (*R*)
6	*i*-PrOH	12	>95	67 (*R*)
7	**THF**	**12**	**>95**	**65 (*R*)**
8	MeOH/CH_2Cl_2 (1/1, *v*/*v*)	12	>95	45 (*R*)

[a] Reaction conditions: **1a** (0.1 mmol) in solvent (1 mL), (*R*,*R*)-**6e** (1.0 mol%), H_2 (50 atm), stirred at 20 °C for 12 h. [b] The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column. [d] The absolute configurations of the products were assigned by comparison of the optical rotations with those in the published literature.

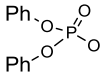
Table S2 Screening of the catalysts for asymmetric hydrogenation of **1a** in THF[a]





(*R*,*R*)-**6a-g**

X = OTf (**a**); BF_4 (**b**); PF_6 (**c**); SbF_6 (**d**); BArF (**e**);



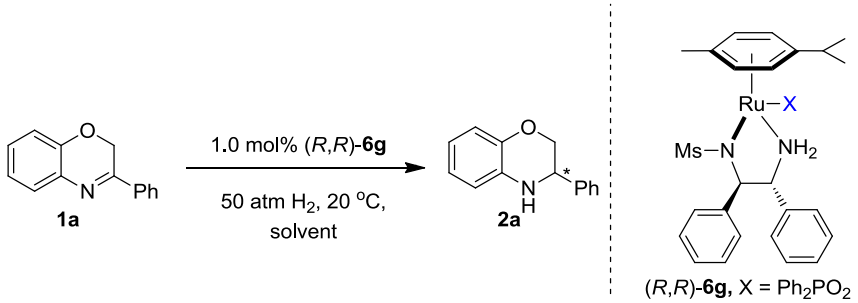
f

g

Entry	Catalyst	X	Conv. (%)[b]	Ee (%)[c, d]
1	(*R*,*R*)-**6a**	OTf	>95	8 (*S*)
2	(*R*,*R*)-**6b**	BF_4	>95	13 (*R*)
3	(*R*,*R*)-**6c**	PF_6	>95	47 (*R*)
4	(*R*,*R*)-**6d**	SbF_6	>95	55 (*R*)
5	(*R*,*R*)-**6e**	BArF	>95	65 (*R*)
6	(*R*,*R*)-**6f**	$(PhO)_2PO_2$	92	83 (*R*)
7	**(*R*,*R*)-6g**	**Ph_2PO_2**	**19**	**92 (*R*)**

[a] Reaction conditions: **1a** (0.1 mmol) in THF (1 mL), catalyst (1.0 mol%), H_2 (50 atm), stirred at 20 °C for 12 h. [b] The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column. [d] The absolute configurations of the products were assigned by comparison of the optical rotations with those in the published literature.

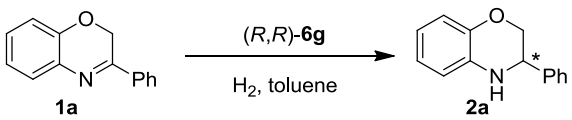
Table S3 Screening of the solvents for asymmetric hydrogenation of **1a** with (*R*,*R*)-**6g**[a]

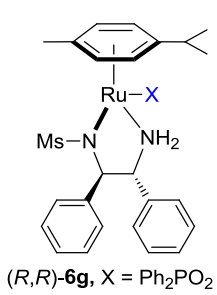


Entry	Solvent	Conv. (%)[b]	Ee (%)[c]
1	THF	19	92
2	CF_3CH_2OH	>95	35
3	CH_2Cl_2	32	82
4	$ClCH_2CH_2Cl$	57	88
5	**toluene**	**>95**	**94**

[a] Reaction conditions: **1a** (0.1 mmol) in solvent (1 mL), (*R*,*R*)-**6g** (1.0 mol%), H_2 (50 atm), stirred at 20 °C for 12 h. [b] The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column.

Table S4 Optimization of conditions for asymmetric hydrogenation of **1a** with (*R*,*R*)-**6g**[a]



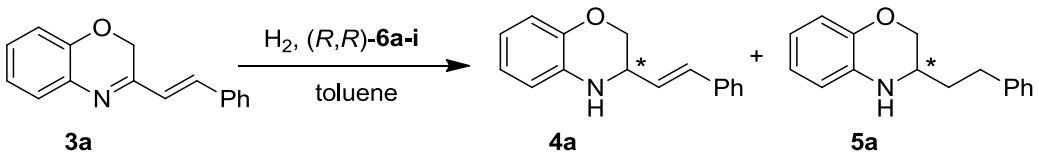


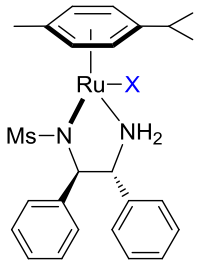
(*R*,*R*)-**6g**, X = Ph_2PO_2

Entry	S/C	H_2 (atm)	Temp. (^oC)	Time (h)	Conv. (%) [b]	Ee (%) [c]
1	100	10	20	12	74	94
2	100	50	20	12	>95	94
3	100	80	20	12	>95	94
4	**100**	**50**	**40**	**12**	**>95**	**94**
5	100	50	0	12	79	94
6	100	50	40	6	>95	94
7	200	50	40	6	>95	94
8	**500**	**50**	**40**	**24**	**>95**	**94**
9	1000	50	40	24	40	93
10	1000	50	40	72	73	93

[a] Reaction conditions: **1a** (0.1 mmol) in solvent (1 mL), (*R*,*R*)-**6g**. [b] The conversions were determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] The enantiomeric excesses were determined by chiral HPLC with a chiral OD-H column.

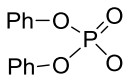
Table S5: Screening of the catalysts for asymmetric hydrogenation of **3a** in toluene[a]





(*R*,*R*)-**6a-i**

X = OTf (**a**); BF_4 (**b**); PF_6 (**c**);
SbF_6 (**d**); BArF (**e**);



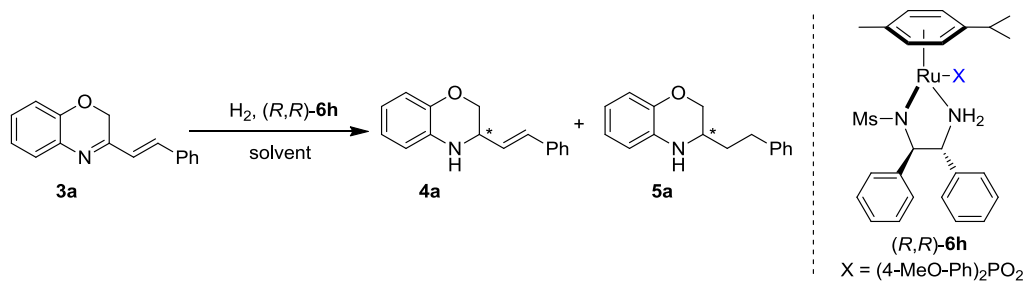
f

Ar = C_6H_5 (**g**);
Ar = 4-CH_3O-C_6H_4 (**h**);
Ar = 3,5-$(CH_3)_2C_6H_5$ (**i**).

Entry	Catalyst	X	Conv. (%)[b]	**4a**:**5a**[c]	Ee (%)[d] **4a**/**5a**
1	(*R*,*R*)-**6e**	BArF	>95	33:67	75/92
2	(*R*,*R*)-**6c**	PF_6	>95	70:30	8/14
3	(*R*,*R*)-**6a**	OTf	>95	89:11	47/ 0
4	(*R*,*R*)-**6f**	$(PhO)_2PO_2$	>95	91:9	75/nd
5	(*R*,*R*)-**6g**	Ph_2PO_2	>95	95:5	98/nd
6	(*R*,*R*)-**6h**	$(4\text{-MeO-Ph})_2PO_2$	>95	97:3	99/nd
7	(*R*,*R*)-**6i**	$(3,5\text{-Me}_2\text{-Ph})_2PO_2$	>95	96:4	98/nd
8[e]	**(*R*,*R*)-6h**	**$(4\text{-MeO-Ph})_2PO_2$**	**>95**	**97:3**	**99/nd**
9[f]	(*R*,*R*)-**6h**	$(4\text{-MeO-Ph})_2PO_2$	>95	97:3	98/nd

[a] Reaction conditions: **3a** (0.1 mmol) in toluene (1 mL), catalyst (1.0 mol%), H_2 (50 atm), stirred at 20 °C for 24 h. [b] The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] The product ratios of **4a**/**5a** were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] The enantiomeric excesses were determined by chiral HPLC. [e] 0.5 mol% catalyst was used. [f] 0.2 mol%c atalyst was used.

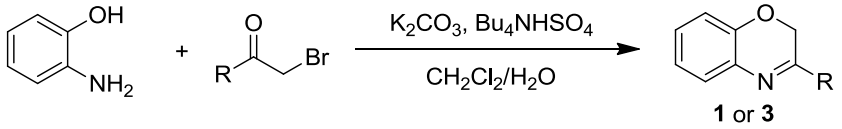
Table S6: Optimization of conditions for asymmetric hydrogenation of **3a**[a]



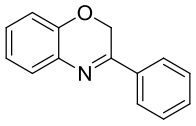
Entry	Solvent	H_2 (atm)	Temp. (^oC)	T (h)	Conv. (%)[b]	**4a**/**5a**[c]	Ee (%)[d] **4a**/**5a**
1	MeOH	50	20	12	>95	53:47	28/50
2	CH_2Cl_2	50	20	12	>95	97:3	95/nd
3	DCE	50	20	12	>95	97:3	94/nd
4	toluene	50	20	12	>95	98:2	99/nd
5	toluene	50	20	1.5	68	98:2	99/nd
6	toluene	10	20	1.5	30	96:4	99/nd
8	**toluene**	**80**	**20**	**1.5**	**>95**	**98:2**	**99/nd**
9	toluene	50	40	1.5	>95	97:3	99/nd

[a] Reaction conditions: **3a** (0.1 mmol) in toluene (1 mL), (*R*,*R*)-**6h** (0.5 mol %). [b] The conversions were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] The product ratios of **4a**/**5a** were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] The enantiomeric excesses were determined by chiral HPLC.

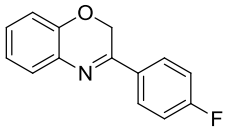
3. Synthesis of 3-substituted-2*H*-1,4-benzoxazines



General procedure:[3] To a solution of 2-aminophenol (1.09 g, 10 mmol) in dichloromethane (60 mL) was added 20% aqueous K_2CO_3 solution (40 mL) and *n*-Bu_4NHSO_4 (10 mg). Then a solution of substituted 2-bromoacetophenone or (*E*)-1-bromo-4-phenylbut-3-en-2-one (10 mmol) in dichloromethane (25 mL) was added dropwise to the reaction mixture over a period of 15 min. The reaction mixture was stirred at room temperature and monitored by TLC. After the consumption of the starting materials, the reaction mixture was washed by water (50 mL) and brine (50 mL), then the organic layer was seperated and dried by anhydrous Na_2SO_4. The solvent was removed on vacuum and the crude product was purified by column chromatography using dichloromethane as eluent to obtain the corresponding 3-substituted-2*H*-1,4-benzoxazines.

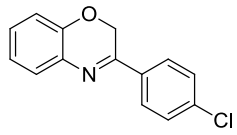


3-phenyl-2*H*-1,4-benzoxazine (1a): Yellow solid; 70% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.95-7.91 (m, 2H), 7.50-7.44 (m, 4H), 7.19-7.14 (m, 1H), 7.07-7.01 (m, 1H), 6.95-6.92 (m, 1H), 5.07 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.8, 146.5, 135.6, 133.9, 131.3, 128.9, 128.8, 127.9, 126.6, 122.5, 115.7, 63.0.

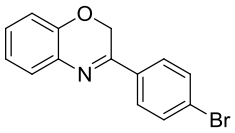


3-(4-fluorophenyl)-2*H*-1,4-benzoxazine (1b): Yellow solid; 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.95-7.89 (m, 2H),

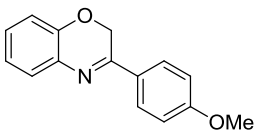
7.44-7.41 (m, 1H), 7.19-7.12 (m, 3H), 7.06-7.00 (m, 1H), 6.93-6.90 (m, 1H), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.4, 163.0, 157.5, 146.3, 133.9, 131.8, 131.8, 128.8, 128.8, 128.7, 127.9, 122.5, 116.1, 115.9, 115.7, 62.8.



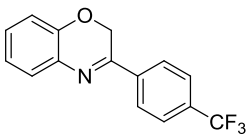
3-(4-chlorophenyl)-2*H*-1,4-benzoxazine (1c): Yellow solid; 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.88-7.85 (m, 2H), 7.46-7.41 (m, 3H), 7.19-7.14 (m, 1H), 7.06-7.01 (m, 1H), 6.93-6.90 (m, 1H), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.4, 146.3, 137.4, 133.9, 133.7, 129.2, 129.0, 128.0, 127.9, 122.6, 115.7, 62.8.



3-(4-bromophenyl)-2*H*-1,4-benzoxazine (1d): Yellow solid; 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.81-7.76 (m, 2H), 7.62-7.58 (m, 2H), 7.44-7.41 (m, 1H), 7.19-7.13 (m, 1H), 7.06-7.00 (m, 1H), 6.93-6.90 (m, 1H), 5.02 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.5, 146.4, 134.4, 133.7, 132.1, 129.1, 128.1, 128.0, 125.9, 122.6, 115.7, 62.7.

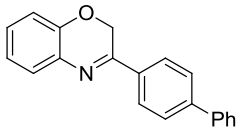


3-(4-methoxyphenyl)-2*H*-1,4-benzoxazine (1e): Yellow solid; 70% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.91-7.88 (m, 2H), 7.44-7.41 (m, 1H), 7.16-7.10 (m, 1H), 7.05-6.90 (m, 4H), 5.02 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.2, 158.3, 146.4, 134.0, 128.4, 128.2, 128.1, 127.6, 122.4, 115.6, 114.3, 62.8, 55.5.

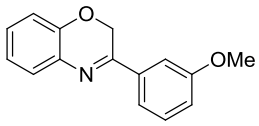


3-(4-trifluoromethylphenyl)-2*H*-1,4-benzoxazine (1f): Yellow solid; 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04-8.01 (m, 2H), 7.74-7.71 (m, 2H), 7.47-7.44 (m, 1H), 7.22-7.16 (m, 1H),

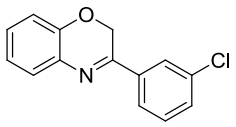
7.07-7.02 (m, 1H), 6.95-6.92 (m, 1H), 5.07 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.2, 146.4, 138.7, 133.7, 132.9, 132.5, 129.5, 128.3, 126.9, 125.9, 125.8, 122.7, 115.8, 62.9.



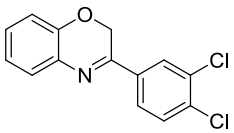
3-([1,1'-biphenyl]-4-yl)-2*H*-1,4-benzoxazine (1g): Yellow solid; 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.02-8.00 (m, 2H), 7.73-7.70 (m, 2H), 7.67-7.64 (m, 2H), 7.51-7.46 (m, 3H), 7.43-7.38 (m, 1H), 7.20-7.14 (m, 1H), 6.96-6.93 (m, 1H), 5.10 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.4, 146.5, 144.0, 140.2, 134.4, 134.0, 129.1, 128.8, 128.1, 128.0, 127.5, 127.3, 127.1, 122.5, 115.7, 63.0.



3-(3-methoxyphenyl)-2*H*-1,4-benzoxazine (1h): Yellow solid; 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.57-7.56 (m, 1H), 7.47-7.35 (m, 3H), 7.19-7.13 (m, 1H), 7.07-7.00 (m, 2H), 6.94-6.91 (m, 1H), 5.05 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.1, 158.6, 146.5, 137.0, 133.9, 129.8, 128.8, 128.0, 122.5, 119.0, 117.6, 115.7, 111.3, 63.1, 55.6.

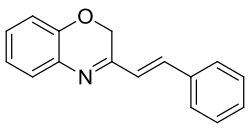


3-(3-chlorophenyl)-2*H*-1,4-benzoxazine (1i): Yellow solid; 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.96-7.95 (m, 1H), 7.76-7.73 (m, 1H), 7.48-7.38 (m, 3H), 7.20-7.14 (m, 1H), 7.06-7.01 (m, 1H), 6.94-6.90 (m, 1H), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.3, 146.4, 137.3, 135.2, 133.7, 131.2, 130.1, 129.2, 128.1, 126.7, 124.6, 122.6, 115.8, 62.9.

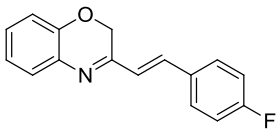


3-(3,4-dichlorophenyl)-2*H*-1,4-benzoxazine (1j): Yellow solid; 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04-8.03 (m,

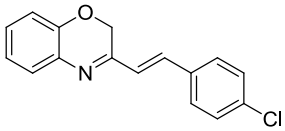
1H), 7.72-7.68 (m, 1H), 7.54-7.51 (m, 1H), 7.43-7.40 (m, 1H), 7.20-7.14 (m, 1H), 7.06-7.00 (m, 1H), 6.93-6.89 (m, 1H), 4.99 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 156.1, 146.3, 135.4, 135.3, 133.5, 133.5, 130.8, 129.4, 128.5, 128.1, 125.6, 122.7, 115.8, 62.6.



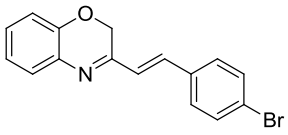
(*E*)-3-styryl-2*H*-1,4-benzoxazine (3a): Yellow solid; 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56-7.53 (m, 2H), 7.43-7.33 (m, 4H), 7.17-7.11 (m, 1H), 7.06-6.99 (m, 3H), 6.92-6.89 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.92 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.0, 146.7, 137.4, 135.6, 134.2, 129.8, 129.1, 128.9, 127.6, 126.9, 122.6, 115.8, 62.2.



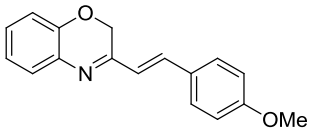
(*E*)-3-(4-fluorostyryl)-2*H*-1,4-benzoxazine (3b): Yellow solid; 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.54-7.49 (m, 2H), 7.36-7.33 (m, 1H), 7.16-6.95 (m, 6H), 6.91-6.88 (m, 1H), 4.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 165.2, 161.9, 158.8, 146.7, 135.9, 134.2, 131.9, 129.4, 129.3, 128.9, 127.7, 126.8, 122.6, 116.4, 116.1, 115.8, 62.2.



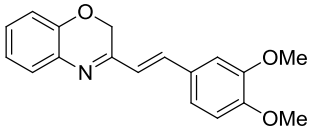
(*E*)-3-(4-chlorostyryl)-2*H*-1,4-benzoxazine (3c): Yellow solid; 80% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.44 (m, 2H), 7.37-7.33 (m, 3H), 7.16-7.11 (m, 1H), 7.05-6.99 (m, 3H), 6.93-6.88 (m, 1H), 4.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 158.7, 146.7, 135.8, 135.5, 134.2, 134.1, 129.4, 129.0, 128.7, 127.8, 127.6, 122.6, 115.8, 62.2.



(*E*)-3-(4-bromostyryl)-2*H*-1,4-benzoxazine (3d): Yellow solid; 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.54-7.50 (m, 2H), 7.41-7.34 (m, 3H), 7.17-7.11 (m, 1H), 7.04-6.98 (m, 3H), 6.91-6.88 (m, 1H), 4.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 158.7, 146.7, 135.8, 134.6, 134.2, 132.3, 129.0, 128.9, 127.8, 127.7, 123.8, 122.7, 115.8, 62.2. HRMS-ESI exact mass calcd. for $C_{16}H_{13}BrNO^{+}$ ($[M+H]^{+}$) requires m/z 314.01797, found m/z 314.01750.

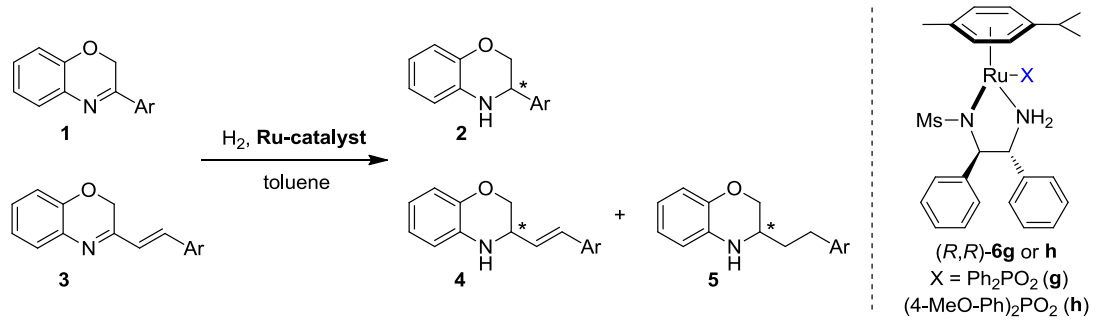


(*E*)-3-(4-methoxystyryl)-2*H*-1,4-benzoxazine (3e): Yellow solid; 78% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50-7.47 (m, 2H), 7.36-7.33 (m, 1H), 7.14-7.08 (m, 1H), 7.05-6.97 (m, 2H), 6.93-6.86 (m, 4H), 4.88 (s, 2H),3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.0, 159.2, 146.7, 137.0, 134.4, 129.1, 128.5, 128.3, 127.5, 124.8, 122.5, 115.7, 114.6, 62.2, 55.5. HRMS-ESI exact mass calcd. for $C_{17}H_{16}NO_2^{+}$ ($[M+H]^{+}$) requires m/z 266.11775, found m/z 266.11756.

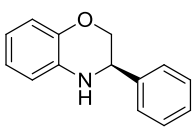


(*E*)-3-(3,4-dimethoxystyryl)-2*H*-1,4-benzoxazine (3f): Yellow solid; 73% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.35-7.31 (m, 1H), 7.14-6.97 (m, 5H), 6.92-6.85 (m, 3H), 4.89 (s, 2H), 3.91 (s, 3H) 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.1, 150.8, 149.5, 146.7, 137.2, 134.4, 128.6, 128.5, 127.5, 125.0, 122.6, 122.1, 115.7, 111.2, 108.8, 62.1, 56.1, 56.0. HRMS-ESI exact mass calcd. for $C_{18}H_{18}NO_3^{+}$ ($[M+H]^{+}$) requires m/z 296.12850, found m/z 296.12812.

4. Asymmetric hydrogenation of 3-substituted-2*H*-1,4-benzoxazines

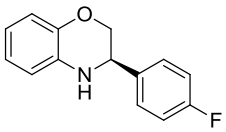


A 50 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ru-catalyst (0.001 mmol, 0.5 mol%) and the corresponding 3 -substituted-2*H*-1,4-benzoxazines (0.2 mmol) in toluene (2 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 40 ^{o}C for 12 h. Then the hydrogen gas was carefully released and the conversion was determined by ^{1}H NMR spectroscopy after the solvent was evaporated under reduced pressure. The reaction mixture was filtered through a short pad of silica eluted with DCM to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral OD-H column.

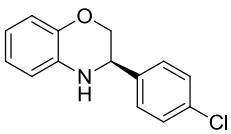


(*R*)-3-phenyl-3,4-dihydro-2*H*-1,4-benzoxazine (2a): known compound,[3] Yellow oil; 95% yield, 94% ee, $[\alpha]_D^{20}$ = -134.5 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$= -118.1 (*c* 1.0, $CHCl_3$) for 98% ee of (*R*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44-7.34 (m, 5H), 6.91-6.6.83 (m, 2H), 6.77-6.69 (m, 2H), 4.54-4.50 (dd, J_1 = 2.8 Hz, J_2 = 8.6 Hz, 1H), 4.34-4.29 (dd, J_1 = 2.9 Hz, J_2 =

10.7 Hz, 1H), 4.06-4.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.6, 139.2, 133.9, 128.9, 128.4, 127.3, 121.6, 119.1, 116.7, 115.6, 71.0, 54.3; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 9.9 min (major), (*S*) t_2 =13.7 min (minor).

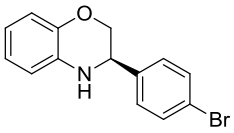


(*R*)-3-(4-fluorophenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2b): Yellow oil; 98% yield, 95% ee, $[\alpha]_D^{20}$ = -139.8 (*c* 1.0, $CHCl_3$), {Lit.[3] $[\alpha]_D^{20}$ = +74.8 (c 1.2, $CHCl_3$) for 88% ee of (*S*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41-7.36 (m, 2H),7.12-7.06 (m, 2H), 6.89-6.81 (m, 2H), 6.76-6.67 (m, 2H), 4.51-4.47 (dd, J_1 = 2.9 Hz, J_2 = 8.5 Hz, 1H), 4.29-4.24 (dd, J_1 = 3.0 Hz, J_2 =10.6 Hz, 1H), 4.04-3.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.4, 161.1, 143.6, 135.1, 135.0, 133.8, 129.0, 128.9, 121.7, 119.2, 116.7, 116.0, 115.7, 115.6, 71.0, 53.6; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 9.9 min (major), (*S*) t_2 =15.4 min (minor).

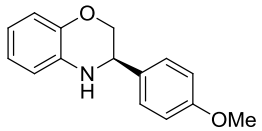


(*R*)-3-(4-chlorophenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2c): Yellow oil; 97% yield, 96% ee, $[\alpha]_D^{20}$ = -131.3 (*c* 1.0, $CHCl_3$), {Lit.[3] $[\alpha]_D^{20}$ = +59.1 (*c* 0.7, $CHCl_3$) for 90% ee of (*S*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39-7.32 (m, 4H), 6.87-6.80 (m, 2H), 6.74-6.67 (m, 2H),4.52-4.48 (dd, J_1 = 2.8 Hz, J_2 = 8.3 Hz, 1H), 4.28-4.24 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.00-3.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.6, 137.9, 134.2, 133.7, 129.2, 128.7, 121.7, 119.3, 116.8, 115.6, 70.9, 53.8; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 11.6 min

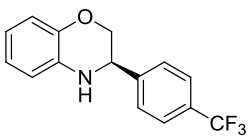
(major), (*S*) t_2 =20.4 min (minor).



(*R*)-3-(4-bromophenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2d): Yellow oil; 95% yield, 96% ee, $[\alpha]_D^{20}$ = -111.5 (*c* 1.0, $CHCl_3$), {Lit.[3] $[\alpha]_D^{20}$ = +89.5 (*c* 1.03, $CHCl_3$) for 89% ee of (*S*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55-7.50 (m, 2H), 7.30-7.27 (m, 2H), 6.89-6.81 (m, 2H), 6.76-6.67 (m, 2H), 4.48-4.45 (dd, J_1 = 2.9 Hz, J_2 = 8.3 Hz, 1H), 4.28-4.23 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.00-3.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.6, 138.3, 133.6, 132.0, 129.0, 122.3, 121.7, 119.3, 117.0, 115.6, 70.7, 53.7; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 12.6 min (major), (*S*) t_2 =22.5 min (minor).

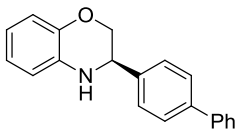


(*R*)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2e): Yellow oil; 96% yield, 98% ee, $[\alpha]_D^{20}$ = -126.5 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$ = -55.5 (*c* 1.0, $CHCl_3$) for 98% ee of (*R*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.35-7.31 (m, 2H), 6.96-6.92 (m, 2H), 6.89-6.80 (m, 2H), 6.75-6.66 (m, 2H), 4.47-4.43 (dd, J_1 = 2.8 Hz, J_2 = 8.6 Hz, 1H), 4.28-4.24 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.01-3.95 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.7, 143.6, 134.1, 131.2, 128.4, 121.5, 119.0, 116.4, 115.5, 114.3, 71.2, 55.4, 53.7; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 10.5 min (major), (*S*) t_2 =15.9 min (minor).

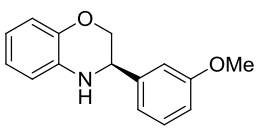


(*R*)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-1,4-benzo xazine (2f): Yellow oil; 97% yield, 92% ee, $[\alpha]_D^{20}$ = -122.8 (*c*

1.0, $CHCl_3$), {Lit.[3] $[\alpha]_D^{20}$ = +63.1 (*c* 1.48, $CHCl_3$) for 89% ee of (*S*)-enantiomer}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68-7.66 (m, 2H), 7.55-7.53 (m, 2H), 6.90-6.83 (m, 2H), 6.78-6.70 (m, 2H), 4.60-4.57 (dd, J_1 = 2.9 Hz, J_2 = 8.1 Hz, 1H), 4.32-4.28 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.04-3.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.6, 143.5, 133.5, 130.9, 130.4, 127.7, 125.9, 125.9, 125.8, 122.3, 121.9, 119.4, 116.9, 115.7, 70.6, 54.0; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 11.3 min (major), (*S*) t_2 =16.4 min (minor).

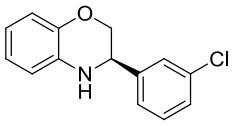


(*R*)-3-([1,1'-biphenyl]-4-yl)-3,4-dihydro-2*H*-1,4-benzoxazine (2g): Yellow oil; 95% yield, 97% ee, $[\alpha]_D^{20}$ = -129.2 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$ = -53.4 (*c* 1.0, $CHCl_3$) for 98% ee of (*R*)-enantiomer}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.67-7.63 (m, 4H), 7.53-7.48 (m, 4H), 7.44-7.39 (m, 1H), 6.95-6.86 (m, 2H), 6.80-6.71 (m, 2H), 4.59-4.55 (dd, J_1 = 2.9 Hz, J_2 = 8.5 Hz, 1H), 4.38-4.34 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.11-4.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)143.6, 141.4, 140.7, 138.3, 133.9, 129.0, 127.7, 127.6, 127.2, 121.6, 119.1, 116.7, 115.5, 71.0, 54.0; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*S*) t_1 = 17.7 min (major), (*R*) t_2 = 25.5 min (minor).

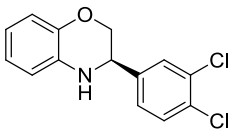


(*R*)-3-(3-methoxyphenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2h): Yellow oil; 95% yield, 90% ee, $[\alpha]_D^{20}$ = -129.8 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$ = +84.6 (*c* 0.87, $CHCl_3$) for 87% ee of (*S*)-enantiomer}; ^1H

NMR (300 MHz, $CDCl_3$): δ (ppm) 7.35-7.30 (m, 1H),7.02-6.99 (m, 2H), 6.92-6.82 (m, 3H), 6.76-6.68 (m, 2H), 4.50-4.46 (dd, J_1 = 2.9 Hz, J_2 = 8.6 Hz, 1H), 4.33-4.28 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 4.04-3.98 (m, 2H),3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.1, 143.6, 140.9, 133.9, 129.9, 121.6, 119.6, 119.0, 116.7, 115.5, 113.8, 112.8, 71.0, 55.4, 54.2; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 17.3 min (major), (*S*) t_2 =19.8 min (minor).

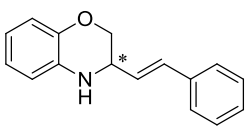


(*R*)-3-(3-chlorophenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2i): Yellow oil; 94% yield, 82% ee, $[\alpha]_D^{20}$ = -123.2 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$ = +71.0 (*c* 1.38, $CHCl_3$) for 88% ee of (*S*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (s, 1H),7.34-7.29 (m, 3H), 6.89-6.82 (m, 2H), 6.76-6.68 (m, 2H), 4.50-4.46 (dd, J_1 = 2.9 Hz, J_2 = 8.3 Hz, 1H), 4.30-4.26 (dd, J_1 = 2.9, J_2 = 10.7 Hz, 1H), 4.01-3.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.6, 141.4, 134.9, 133.6, 130.2, 128.6, 127.4, 125.5, 121.7, 119.3, 116.8, 115.6, 70.7, 53.9. HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 11.0 min (major), (*S*) t_2 = 15.3 min (minor).

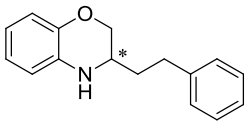


(*R*)-3-(3,4-dichlorophenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (2j): Yellow oil; 98% yield, 86% ee, $[\alpha]_D^{20}$ = -117.8 (*c* 1.0, $CHCl_3$), {Lit.[2] $[\alpha]_D^{20}$ = +52.9 (*c* 1.12, $CHCl_3$) for 92% ee of (*S*)-enantiomer}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.48-7.47 (m, 1H),7.44-7.41(m, 1H), 7.23-7.19 (m, 1H), 6.85-6.78 (m, 2H), 6.73-6.65 (m, 2H),4.45-4.41 (dd, J_1 = 2.9 Hz, J_2 = 8.2 Hz,

1H), 4.24-4.20 (dd, J_1 = 2.9 Hz, J_2 = 10.7 Hz, 1H), 3.95-3.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.5, 139.7, 133.3, 133.1, 132.4, 130.9, 129.2, 126.6, 121.8, 119.5, 116.8, 115.7, 70.5, 53.3; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*R*) t_1 = 14.0 min (major), (*S*) t_2 = 23.8 min (minor).

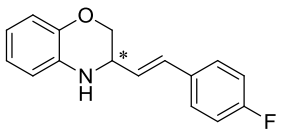


(-)-(*E*)-3-styryl-3,4-dihydro-2*H*-1,4-benzoxazine (4a): Yellow oil; 95% yield, 99% ee, $[\alpha]_D^{20}$ = -34.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41-7.24 (m, 5H), 6.84-6.64 (m, 5H), 6.23-6.15 (m, 1H), 4.32-4.28 (m, 1H), 4.17-4.12 (m, 1H), 4.02-3.96 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)143.7, 136.3, 133.1, 133.0, 128.8, 128.1, 126.6, 126.5, 121.7, 119.0, 116.7, 115.5, 69.1, 52.4; HPLC (AD-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), t_1 = 9.8 min (minor), t_2 =11.1 min (major).HRMS-ESI exact mass calcd. for $C_{16}H_{16}NO^+$ ($[M+H]^+$) requires m/z 238.12297, found m/z 238.12264.

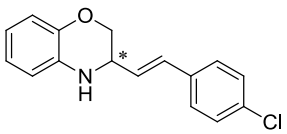


(*S*)-3-phenethyl-3,4-dihydro-2*H*-1,4-benzoxazine (5a): Yellow solid; m.p. 89-90 ^{o}C; yield 91%, 89% ee, $[\alpha]_D^{20}$ = +82.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.31-7.26 (m, 2H), 7.21-7.17 (m, 3H), 6.79-6.71 (m, 2H), 6.66-6.60 (m, 1H), 6.54-6.51 (m, 1H), 4.20-4.16 (m, 1H), 3.89-3.83 (m, 1H), 3.65 (b, 1H), 3.41-3.33 (m, 1H), 2.75-2.70 (m, 2H), 1.83-1.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)143.9, 141.2, 133.3, 128.7, 128.4, 126.3, 121.5, 118.8, 116.6, 115.6, 69.3, 49.3, 33.9, 32.0; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), (*S*) t_1 = 14.4 min (major),

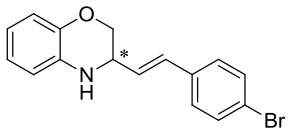
(*R*) t_2 =17.9 min (minor).



(-)-(*E*)-3-(4-fluorostyryl)-3,4-dihydro-2*H*-1,4-benzoxazine (3b): Yellow oil; 96% yield, 91% ee, $[\alpha]_D^{20}$ = -28.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38-7.34 (m, 2H), 7.05-6.99 (m, 2H), 6.85-6.78 (m, 2H), 6.72-6.64 (m, 3H), 6.14-6.06 (m, 1H), 4.31-4.27 (m, 1H), 4.15-4.10 (m, 1H), 4.02-3.96 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.3, 161.0, 143.7, 133.1, 132.5, 132.5, 131.8, 128.2, 128.1, 126.3, 126.3, 121.7, 119.1, 116.7, 115.8, 115.6, 69.1, 52.3; HPLC (AD-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), t_1 = 10.1 min (minor), t_2 =13.5 min (major).HRMS-ESI exact mass calcd. for $C_{16}H_{15}FNO^+$ ($[M+H]^+$) requires m/z 256.11359, found m/z 256.11322.

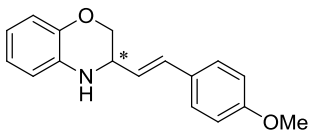


(-)-(*E*)-3-(4-chlorostyryl)-3,4-dihydro-2*H*-1,4-benzoxazine (3c): Yellow oil; 94% yield, 98% ee, $[\alpha]_D^{20}$ = -35.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33-7.28 (m, 4H), 6.85-6.78 (m, 2H), 6.73-6.64 (m, 3H), 6.21-6.13 (m, 1H), 4.31-4.27 (m, 1H), 4.16-4.10 (m, 1H), 4.02-3.96 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.7, 134.8, 133.8, 133.0, 131.7, 128.9, 127.8, 127.3, 121.7, 119.1, 116.7, 115.6, 69.0, 52.3; HPLC (AD-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), t_1 = 11.2 min (minor), t_2 = 15.4 min (major). HRMS-ESI exact mass calcd. for $C_{16}H_{15}ClNO^+$ ($[M+H]^+$) requires m/z 272.08405, found m/z 272.08367.

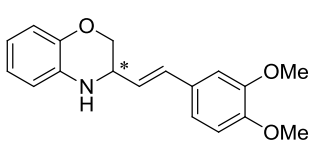


(-)-(*E*)-3-(4-bromostyryl)-3,4-dihydro-2*H*-1,4-benzoxazin

e (3d): Yellow oil; 93% yield, 98% ee, $[\alpha]_D^{20}$ = -32.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.24-7.14 (m, 4H), 6.83-6.75 (m, 2H), 6.70-6.56 (m, 3H), 6.17-6.09 (m, 1H), 4.27-4.22 (m, 1H), 4.10-4.04 (m, 1H), 3.98-3.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.7, 134.8, 133.8, 133.0, 131.7, 128.9, 127.8, 127.3, 121.7, 119.1, 116.7, 115.6, 69.0, 52.3; HPLC (AD-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), t_1 = 12.2 min (minor), t_2 =16.9 min (major).HRMS-ESI exact mass calcd. for $C_{16}H_{15}BrNO^+$ ($[M+H]^+$) requires m/z 316.03343, found m/z 316.03315.



(-)-(*E*)-3-(4-methoxystyryl)-3,4-dihydro-2*H*-1,4-benzoxazine (3e): Yellow oil; 95% yield, 97% ee, $[\alpha]_D^{20}$ = -38.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.24-7.14 (m, 4H), 6.83-6.75 (m, 2H), 6.70-6.56 (m, 3H), 6.17-6.09 (m, 1H), 4.27-4.22 (m, 1H), 4.10-4.04 (m, 1H), 3.98-3.92 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.7, 134.8, 133.8, 133.0, 131.7, 128.9, 127.8, 127.3, 121.7, 119.1, 116.7, 115.6, 69.0, 55.9, 52.3; HPLC (AD-H, elute: Hexane / *i*-PrOH = 90 / 10, detector: 254 nm, flow rate: 1 mL / min), t_1 = 14.1 min (minor), t_2 =17.6 min (major).HRMS-ESI exact mass calcd. for $C_{17}H_{18}NO_2^+$ ($[M+H]^+$) requires m/z 268.13377, found m/z 268.13321.



(-)-(*E*)-3-(3,4-dimethoxystyryl)-3,4-dihydro-2*H*-1,4-benzoxazine (3f): Yellow oil; 97% yield, 98% ee, $[\alpha]_D^{20}$ = -40.5 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.95-6.92 (m, 2H), 6.85-6.78 (m, 3H), 6.71-6.60 (m, 3H), 6.07-5.99 (m, 1H), 4.30-4.26 (m, 1H), 4.12-4.06 (m, 1H),

4.01-3.95 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)149.2, 149.1, 143.6, 133.2, 132.7, 129.3, 124.4, 121.6, 119.9, 118.9, 116.6, 115.5, 111.2, 108.8, 69.2, 55.9, 55.9, 52.4; HPLC (OD-H, elute: Hexane / *i*-PrOH = 80 / 20, detector: 254 nm, flow rate: 1 mL / min), t_1 = 28.2 min (major), t_2 =37.1 min (minor).HRMS-ESI exact mass calcd. for $C_{18}H_{20}NO_3^+$ ($[M+H]^+$) requires m/z 298.14425, found m/z 298.14377.

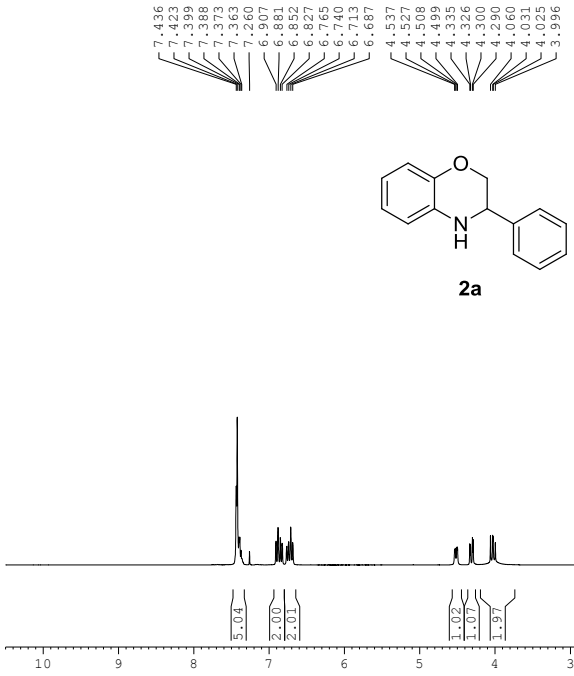
5. Reference

[1] G. Sabitha, A. V. S. Rao, *Synth. Commun.* **1987**, *17*, 341.

[2] M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem. Int. Ed.* **2006**, *45*, 6751.

[3] K. Gao, C-B. Yu, D-S. Wang, Y-G. Zhou, *Adv. Synth. Catal.* **2012**, *354*, 483.

6. Copy of NMR spectra of reduced products

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EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
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Time                  19.27
INSTRUM               spect
PROBHD   5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDC13
NS                        9
DS                        0
SWH                8992.806 Hz
FIDRES            0.137219 Hz
AQ                3.6438515 sec
RG                      128
DW                   55.600 usec
DE                    8.00 usec
TE                   295.9 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    10.80 usec
PL1                    3.00 dB
SFO1           300.1324010 MHz

F2 - Processing parameters
SI                    32768
SF             300.1300060 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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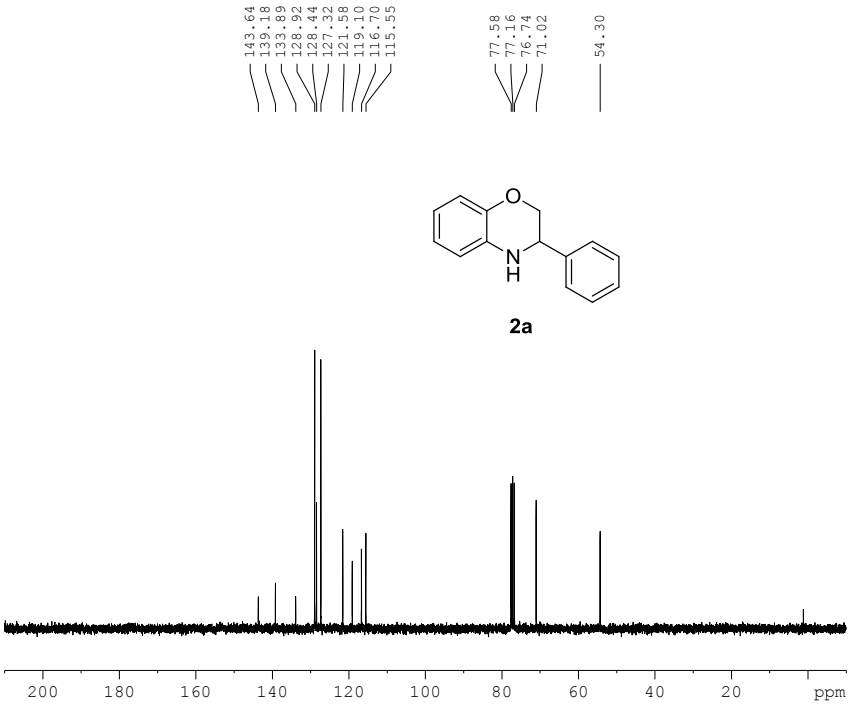


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Current Data Parameters
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EXPNO                        11
PROCNO                        1

F2 - Acquisition Parameters
Date_              20120328
Time                  19.30
INSTRUM               spect
PROBHD   5 mm DUL 13C-1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDC13
NS                       34
DS                        4
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                    1290.2
DW                   27.800 usec
DE                    6.50 usec
TE                   296.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    12.50 usec
PL1                    2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    3.00 dB
PL12                  22.33 dB
PL13                  23.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
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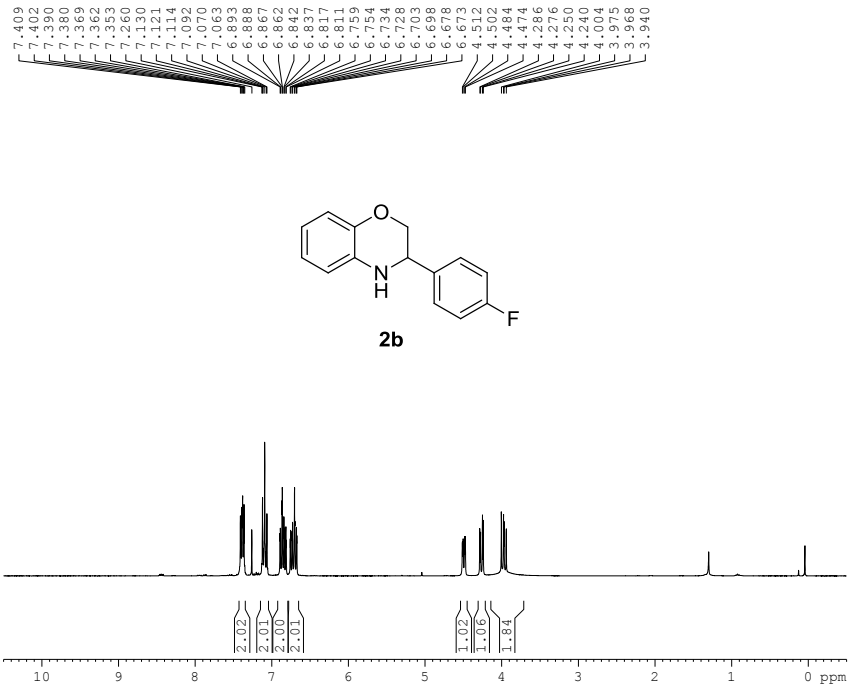


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Current Data Parameters
NAME            qj-hh149
EXPNO                101
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time                15.08
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      6
DS                      0
SWH              8992.806 Hz
FIDRES           0.137219 Hz
AQ               3.6438515 sec
RG                    128
DW                 55.600 usec
DE                  8.00 usec
TE                 297.4 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                  32768
SF           300.1300057 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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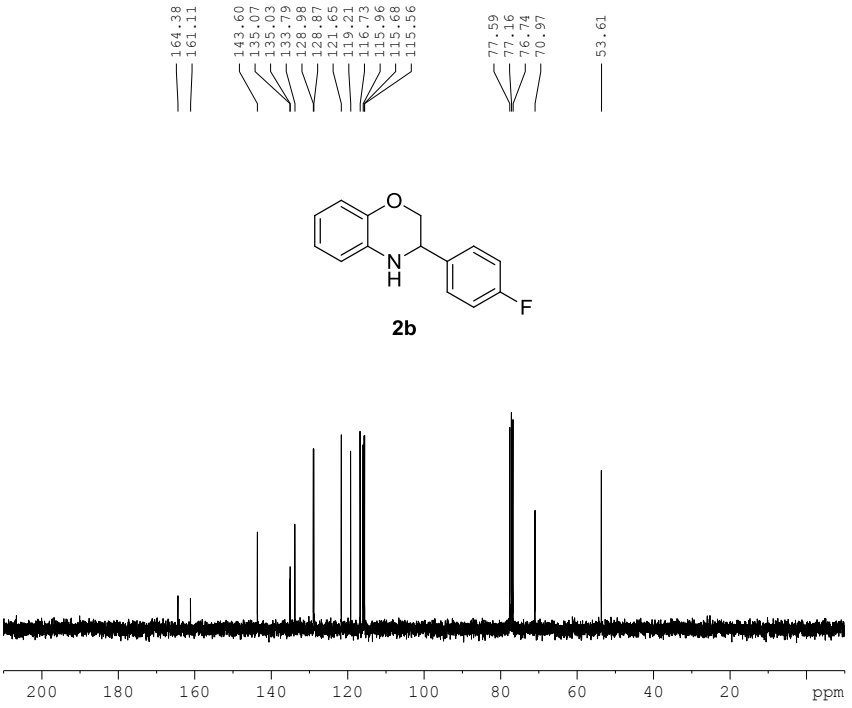


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Current Data Parameters
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EXPNO                102
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time                15.10
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     24
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   2298.8
DW                 27.800 usec
DE                   6.50 usec
TE                 297.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
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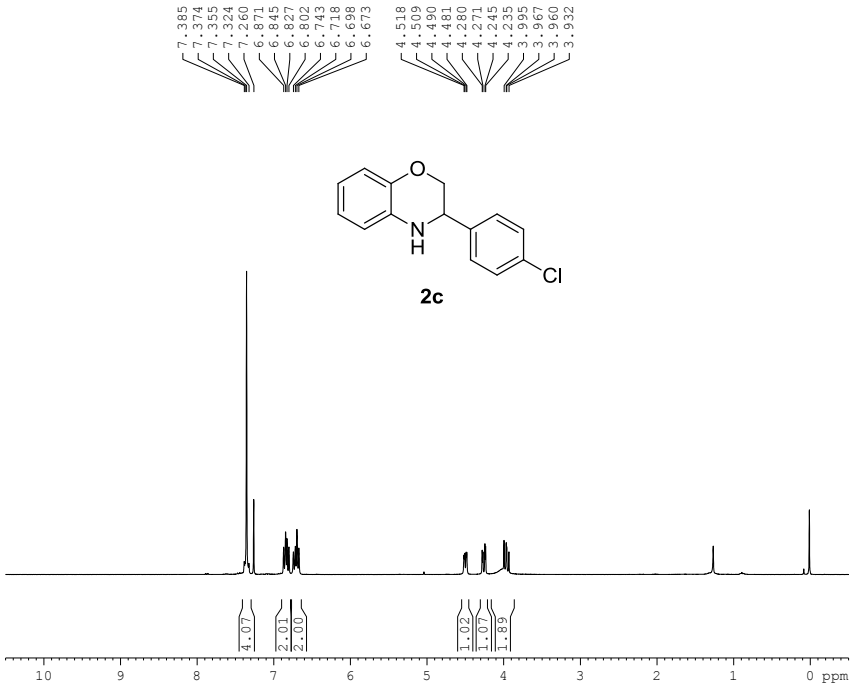


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Current Data Parameters
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EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.17
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   256
DW                55.600 usec
DE                 8.00 usec
TE                297.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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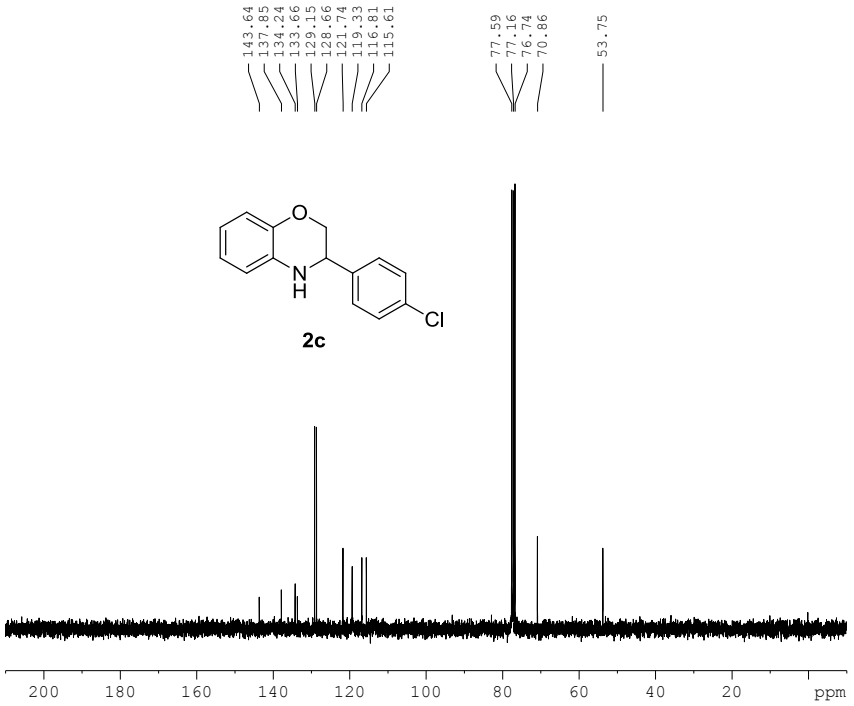


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Current Data Parameters
NAME            qj-hh149
EXPNO                 22
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.20
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    85
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                1625.5
DW                27.800 usec
DE                 6.50 usec
TE                297.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
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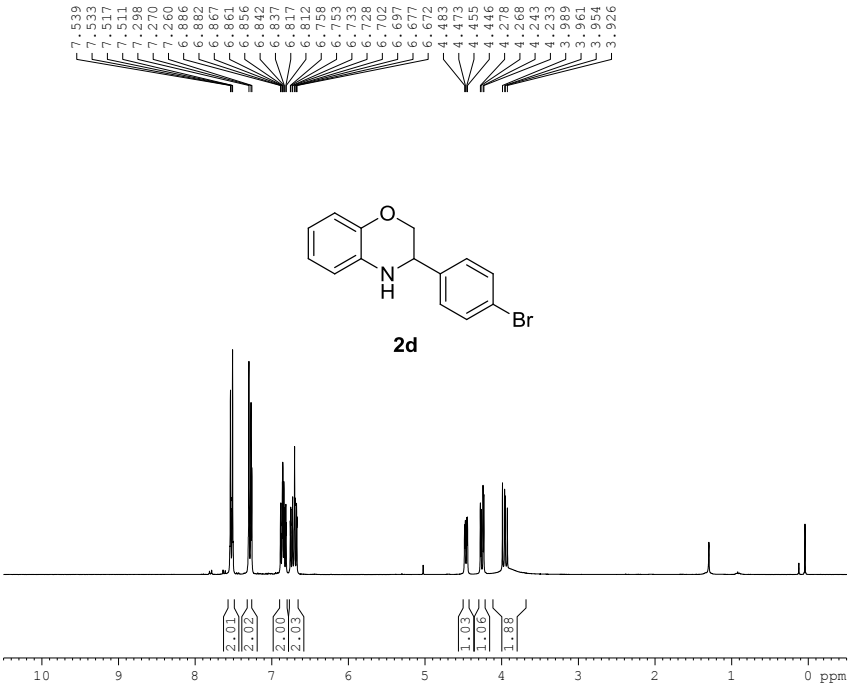


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Current Data Parameters
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EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.33
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                297.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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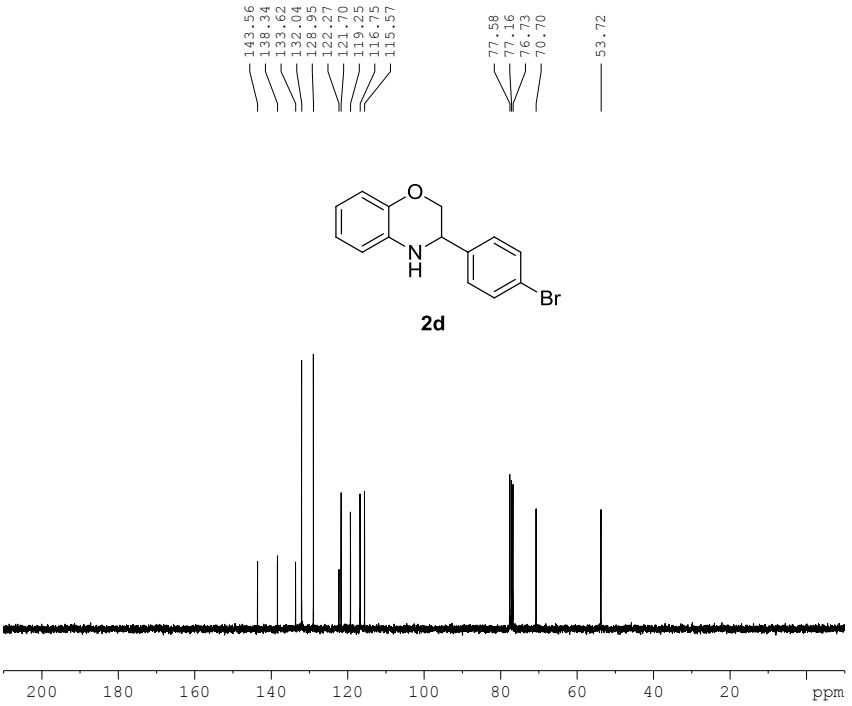


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Current Data Parameters
NAME            qj-hh149
EXPNO                 32
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.37
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    45
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                1149.4
DW                27.800 usec
DE                 6.50 usec
TE                297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
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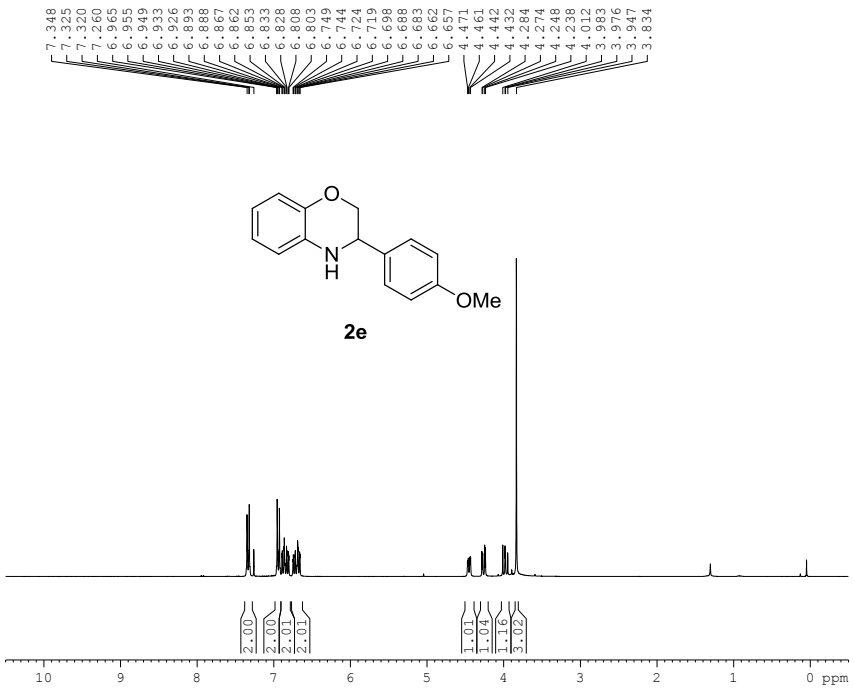


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EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.42
INSTRUM            spect
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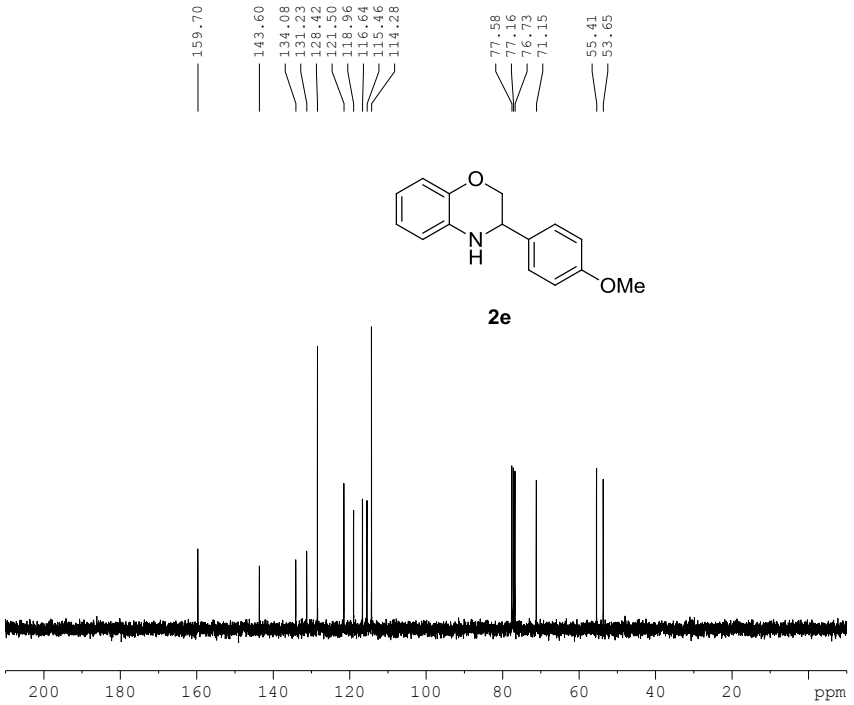
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                297.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



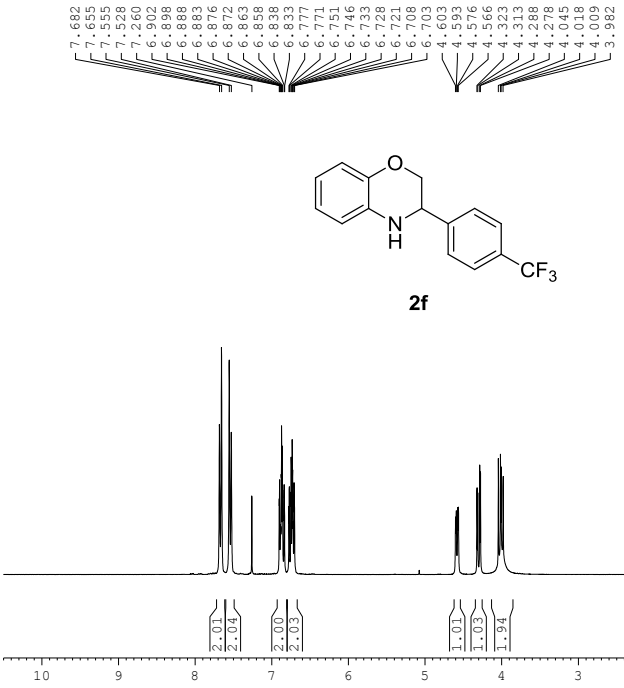

```
Current Data Parameters
NAME            qj-hh149
EXPNO                 42
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.46
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    22
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                   114
DW                27.800 usec
DE                 6.50 usec
TE                297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



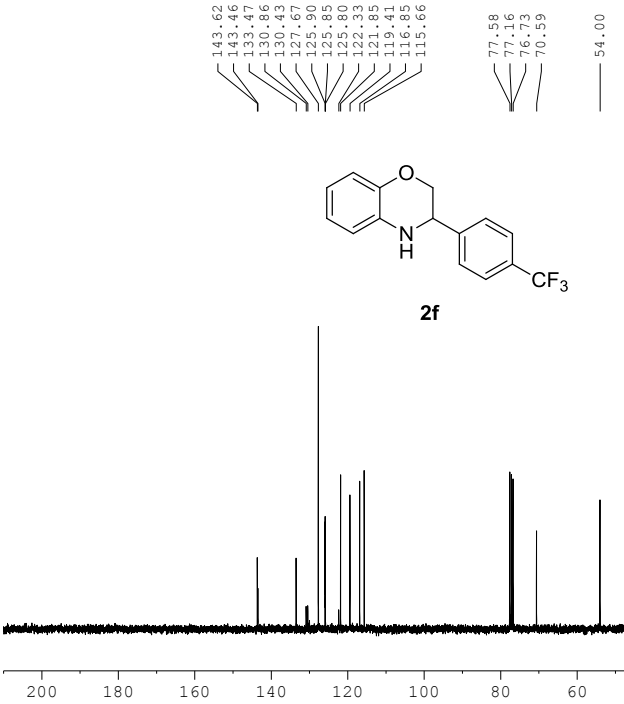
2f

```
Current Data Parameters
NAME            qj-hh149
EXPNO                 53
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.37
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                297.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300059 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



2f

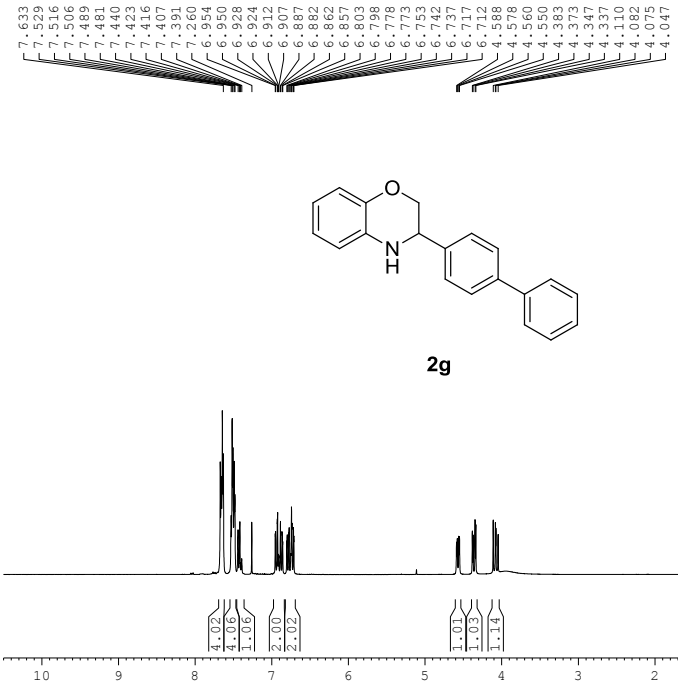
```
Current Data Parameters
NAME            qj-hh149
EXPNO                 54
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.39
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    50
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                1149.4
DW                27.800 usec
DE                 6.50 usec
TE                297.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



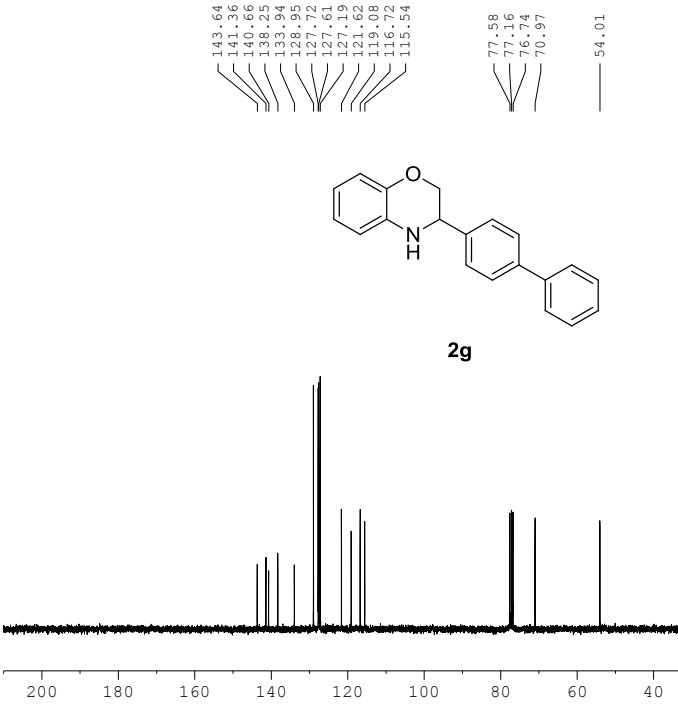
2g

```
Current Data Parameters
NAME            qj-hh149
EXPNO                 91
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.59
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    64
DW                55.600 usec
DE                 8.00 usec
TE                297.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



2g

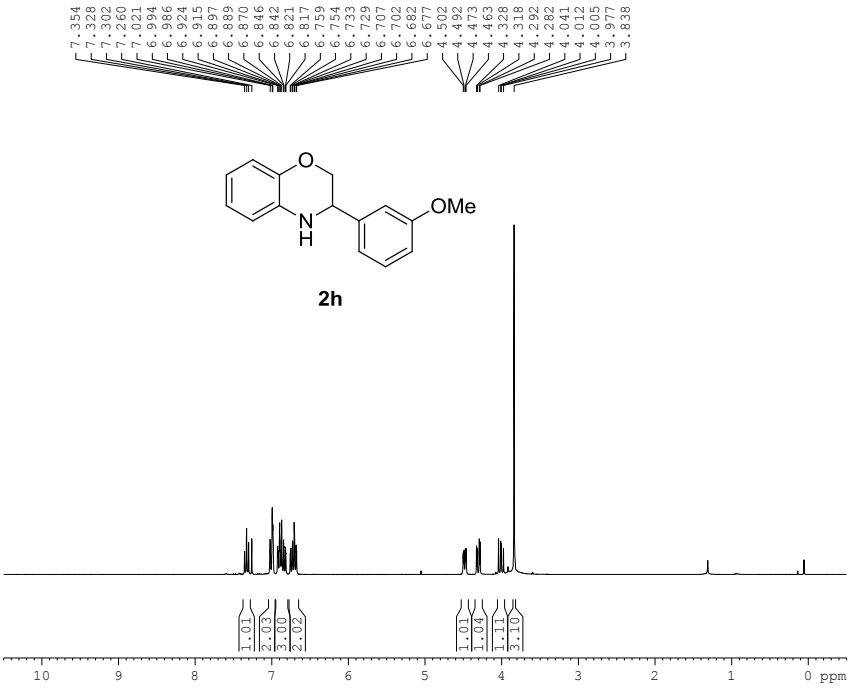
```
Current Data Parameters
NAME            qj-hh149
EXPNO                 92
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               15.01
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    54
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  1149.4
DW                27.800 usec
DE                 6.50 usec
TE                297.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

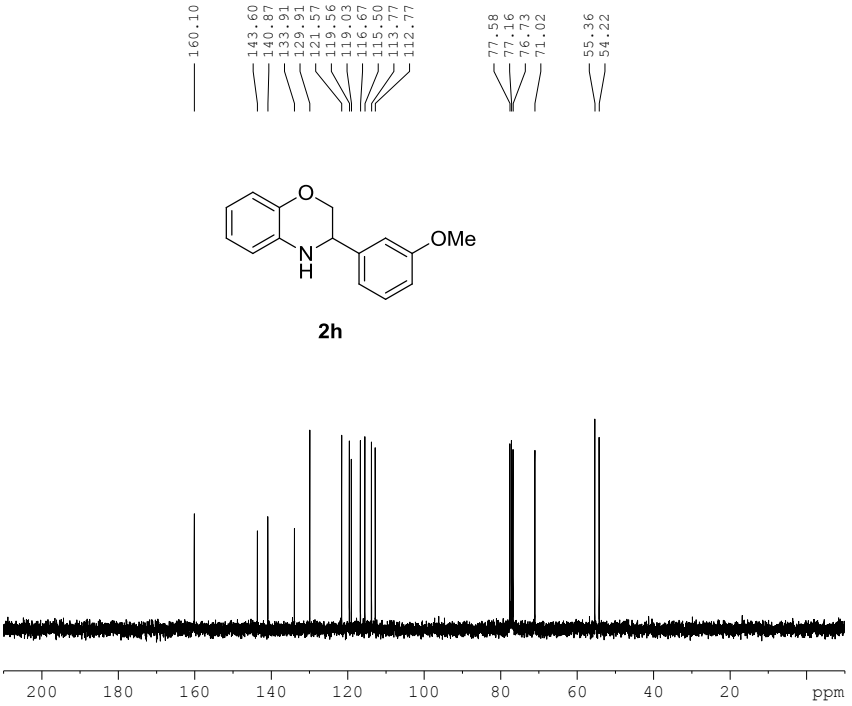



```
Current Data Parameters
NAME            qj-hh149
EXPNO                 61
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.51
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                    64
DW                55.600 usec
DE                 8.00 usec
TE                297.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



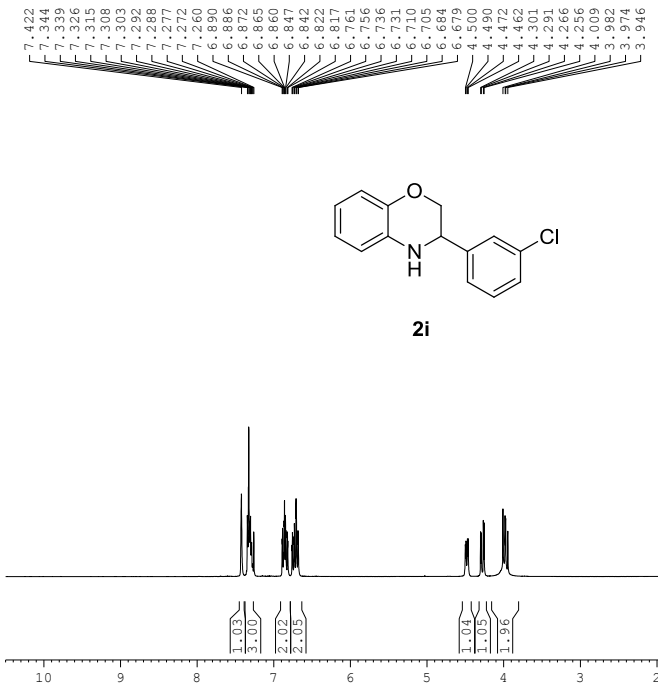

```
Current Data Parameters
NAME            qj-hh149
EXPNO                 62
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               14.54
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    27
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                 6.50 usec
TE                297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



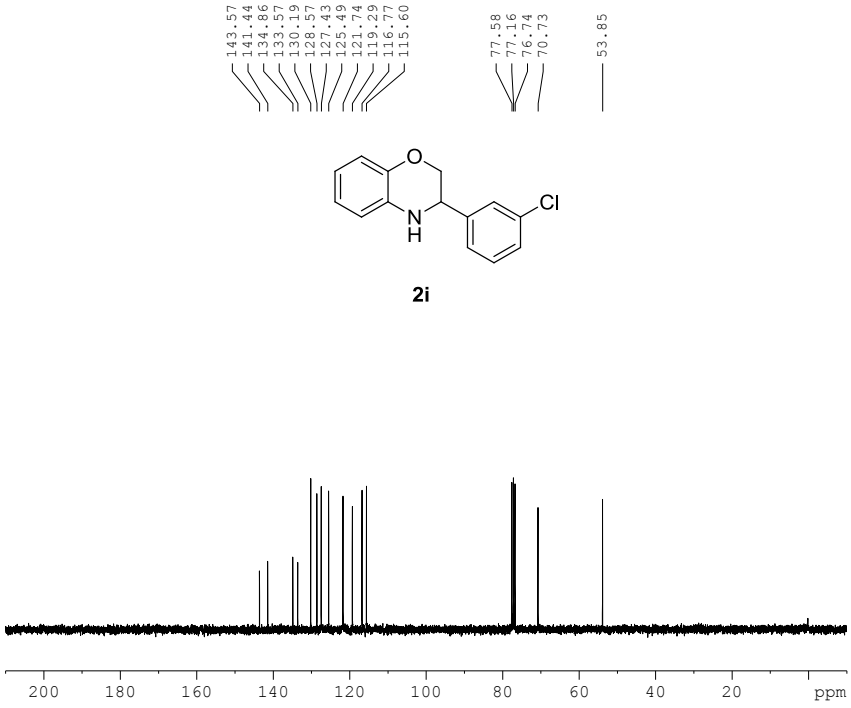
2i

Current Data Parameters
NAME qj-hh151
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120428
Time 21.01
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 90.5
DW 55.600 usec
DE 8.00 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 3.00 dB
SFO1 300.1324010 MHz

F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



2i

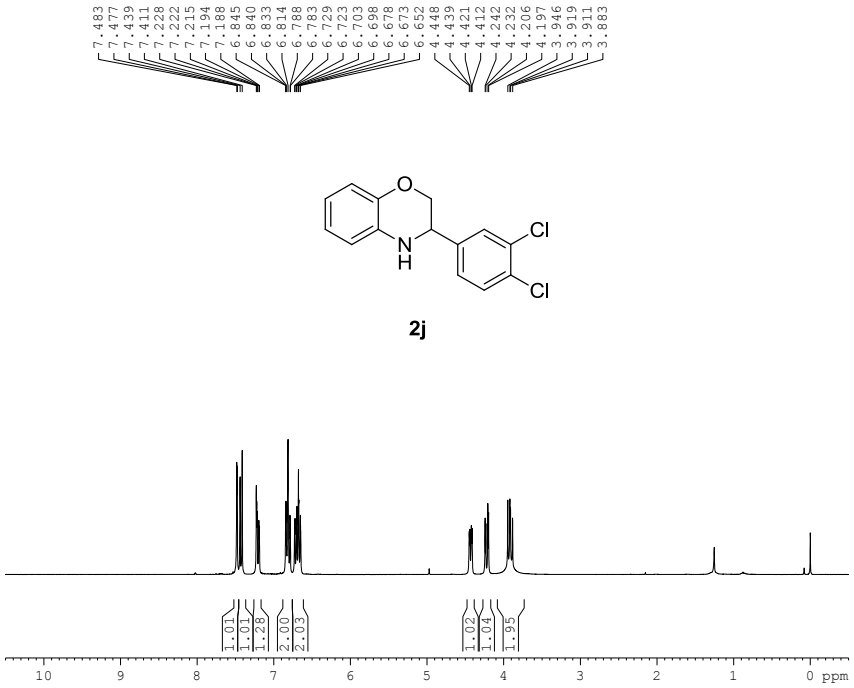
Current Data Parameters
NAME qj-hh151
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120428
Time 21.03
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgig30
TD 32768
SOLVENT CDCl3
NS 74
DS 0
SWH 18832.393 Hz
FIDRES 0.574719 Hz
AQ 0.8700404 sec
RG 11585.2
DW 26.550 usec
DE 8.00 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.33 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677438 MHz



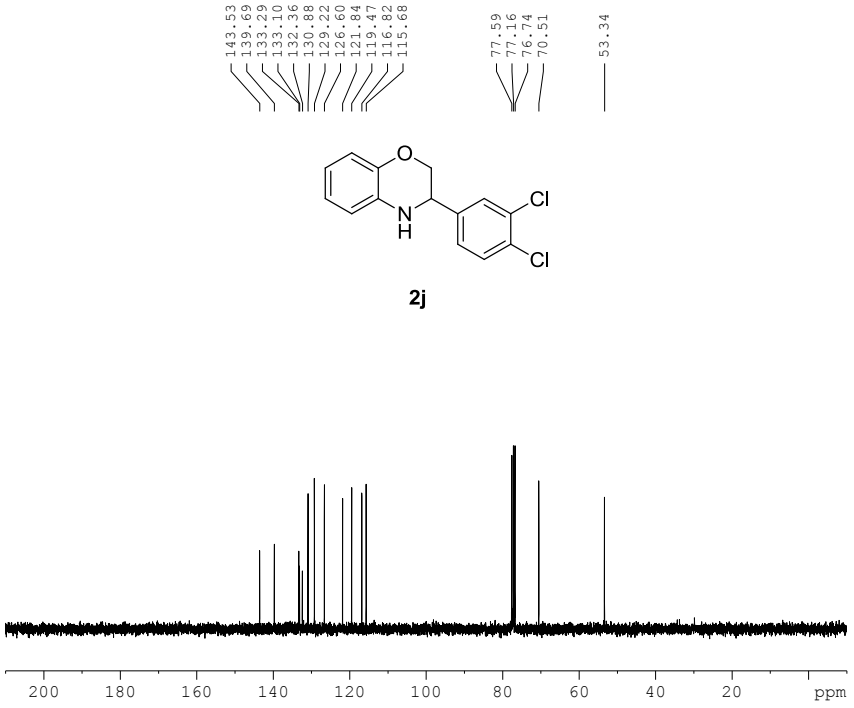
2j

```
Current Data Parameters
NAME            qj-hh149
EXPNO                 82
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.56
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    11
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                297.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300155 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



2j

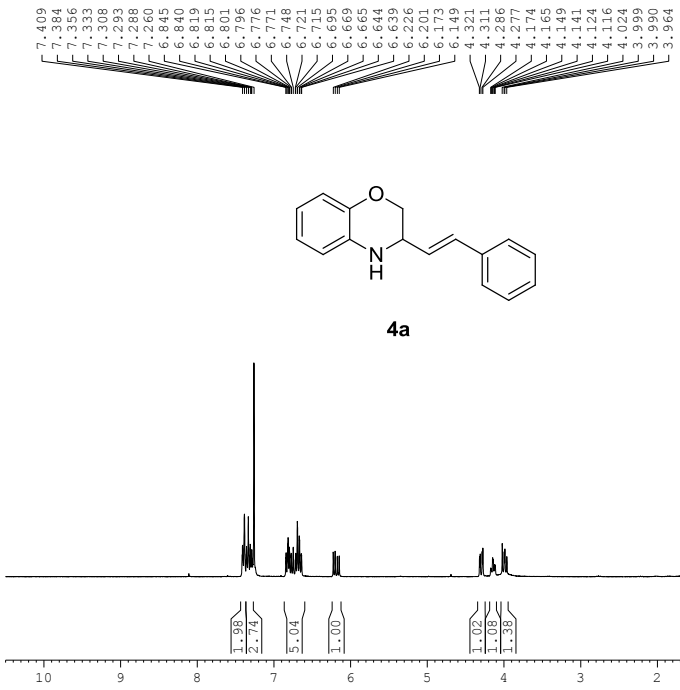
```
Current Data Parameters
NAME            qj-hh149
EXPNO                 83
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120411
Time               19.59
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                1290.2
DW                27.800 usec
DE                 6.50 usec
TE                297.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

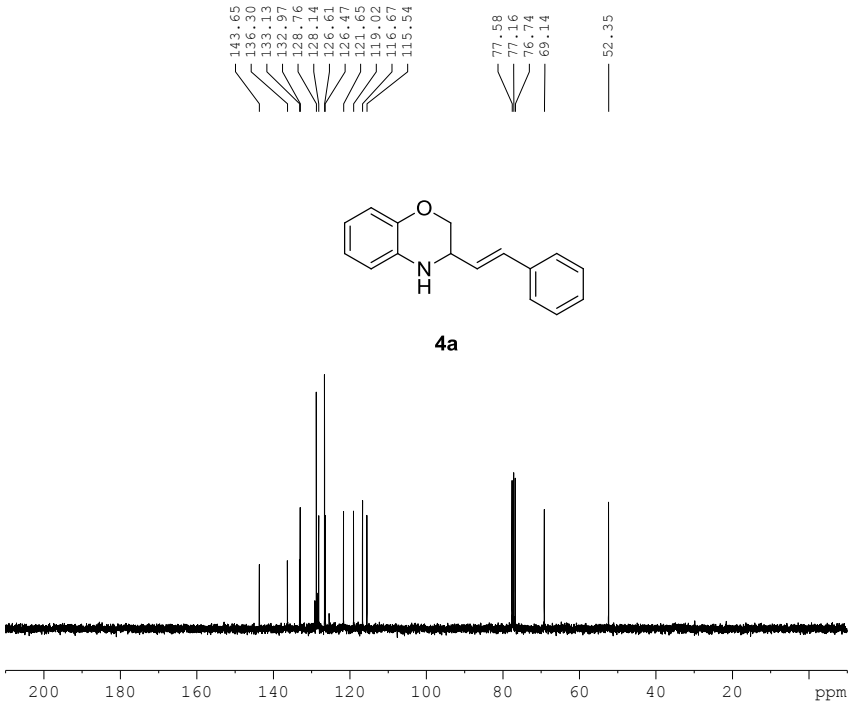



```
Current Data Parameters
NAME         qj-hh138-up
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120224
Time               15.11
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    11
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                 228.1
DW                55.600 usec
DE                 8.00 usec
TE                296.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



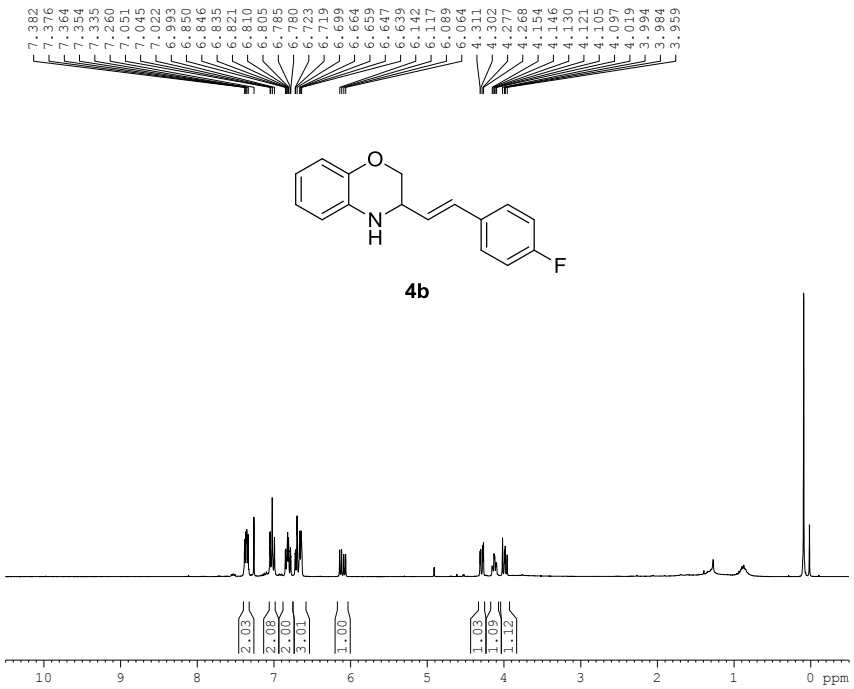

```
Current Data Parameters
NAME           qj-hh152
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20120417
Time               11.45
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    30
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 812.7
DW                27.800 usec
DE                 6.50 usec
TE                295.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



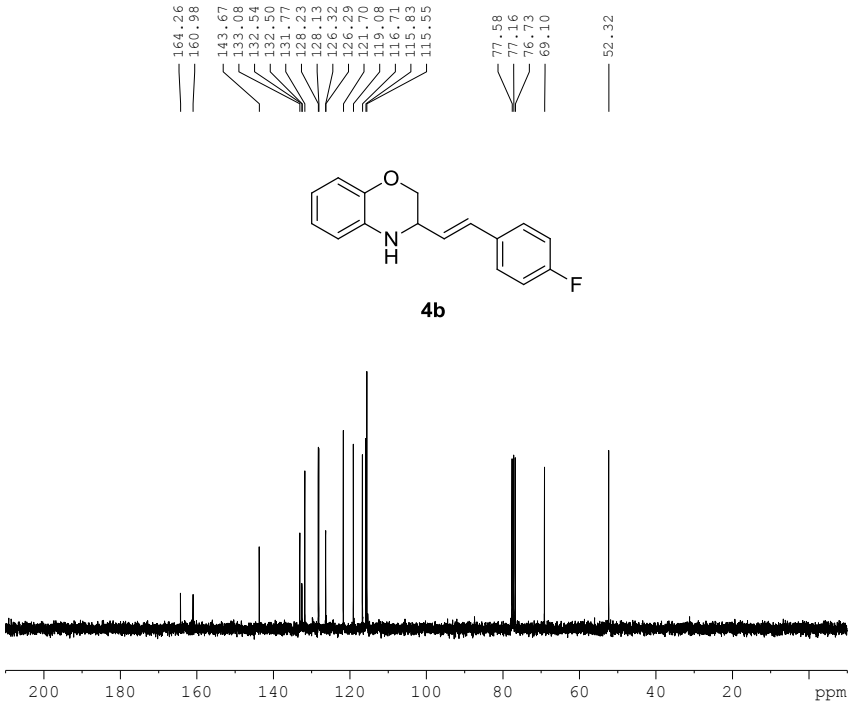
4b

```
Current Data Parameters
NAME      qj-hh156-2-up
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20120513
Time               9.37
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   15
DS                    0
SWH            8992.806 Hz
FIDRES        0.137219 Hz
AQ           3.6438515 sec
RG                  114
DW               55.600 usec
DE                8.00 usec
TE               298.8 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



4b

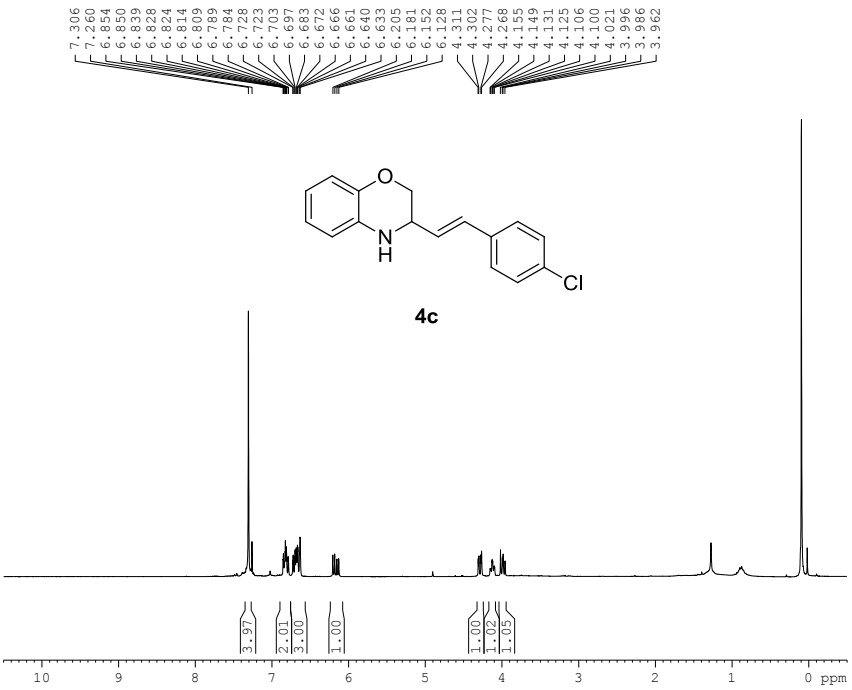
```
Current Data Parameters
NAME           qj-hh156
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_           20120511
Time              15.14
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   29
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG               2298.8
DW               27.800 usec
DE                6.50 usec
TE               298.7 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

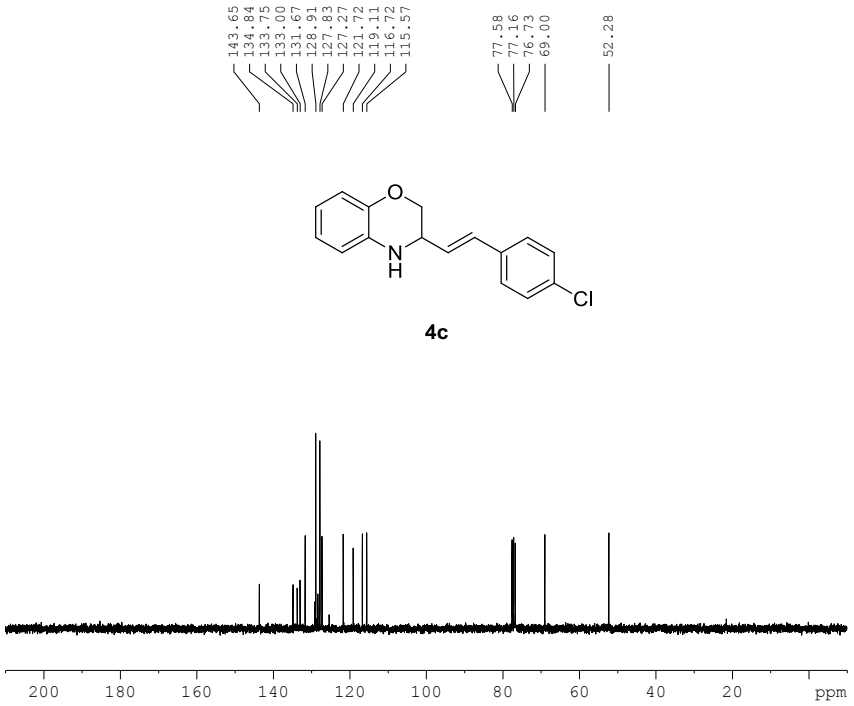



```
Current Data Parameters
NAME      qj-hh156-3-up
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_           20120513
Time                9.44
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    12
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                  71.8
DW                55.600 usec
DE                 8.00 usec
TE                298.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300062 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



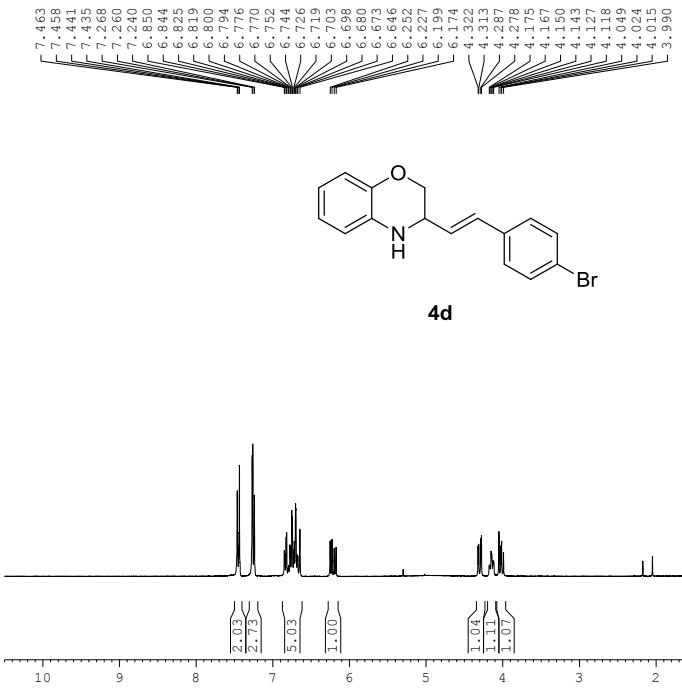

```
Current Data Parameters
NAME            qj-hh156
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120511
Time               15.22
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    18
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                 6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



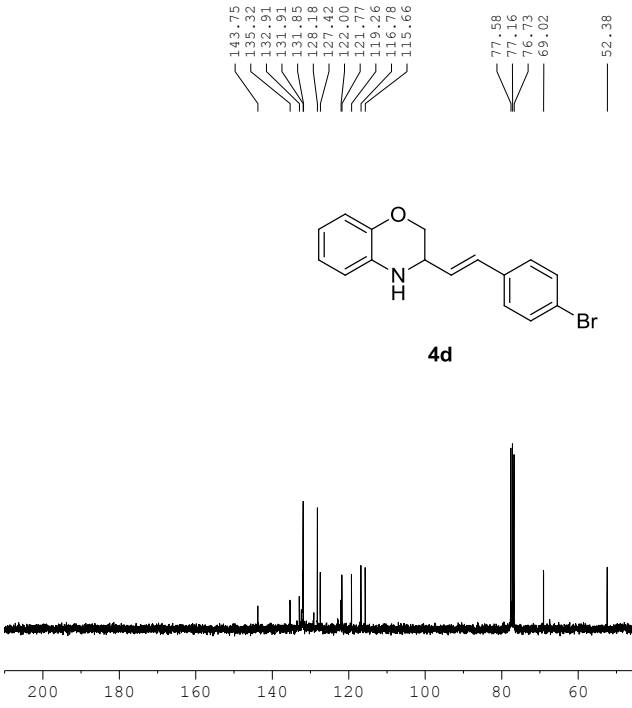
4d

```
Current Data Parameters
NAME            qj-hh-br
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120618
Time               11.16
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ            3.6438515 sec
RG                   512
DW                55.600 usec
DE                 8.00 usec
TE                300.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



4d

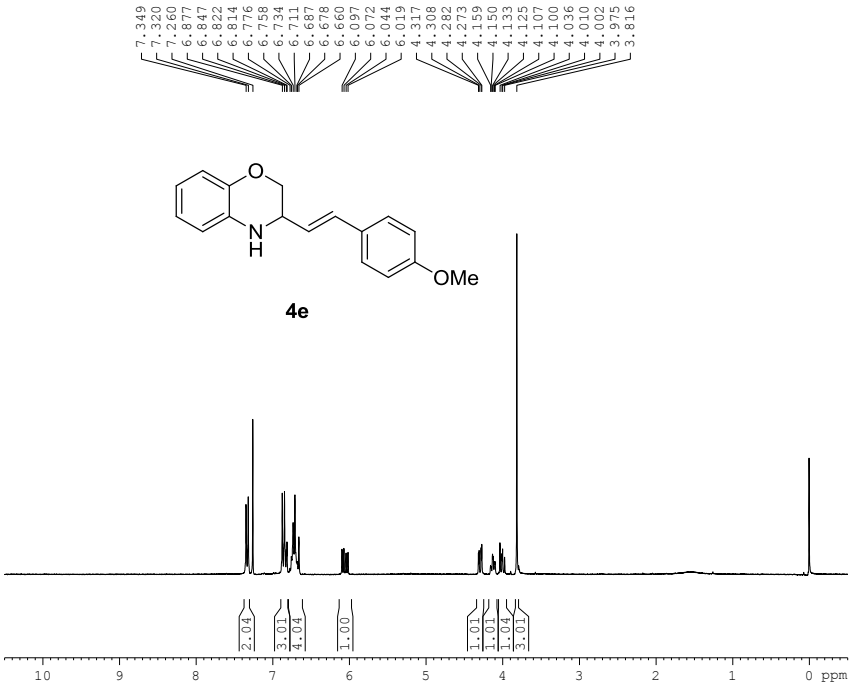
```
Current Data Parameters
NAME            qj-hh-br
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120619
Time               11.53
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   152
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                300.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```



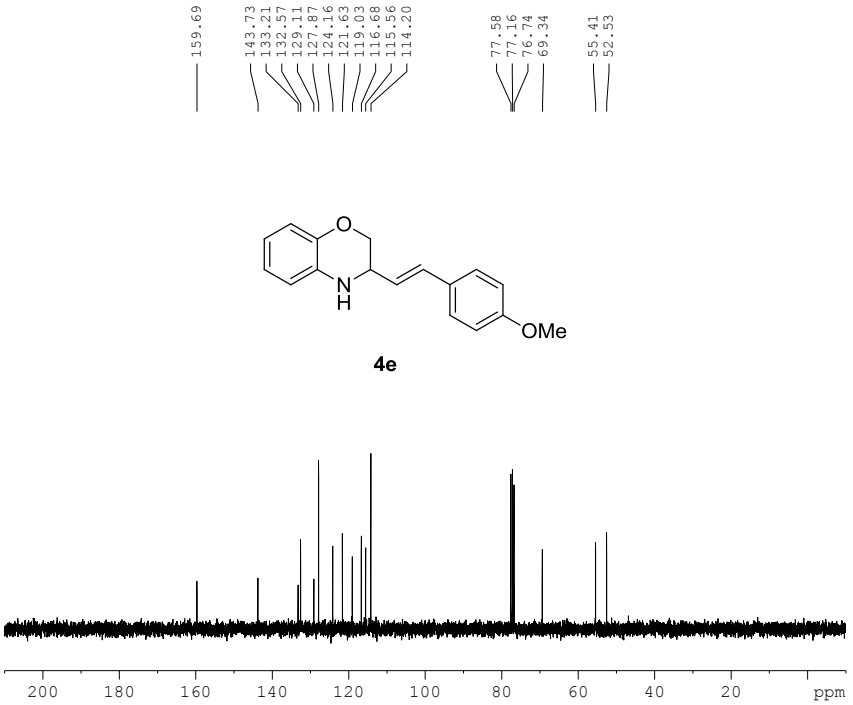
4e

```
Current Data Parameters
NAME          qj-hh-meo
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20120618
Time              11.21
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                574.7
DW               55.600 usec
DE                8.00 usec
TE                300.3 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



4e

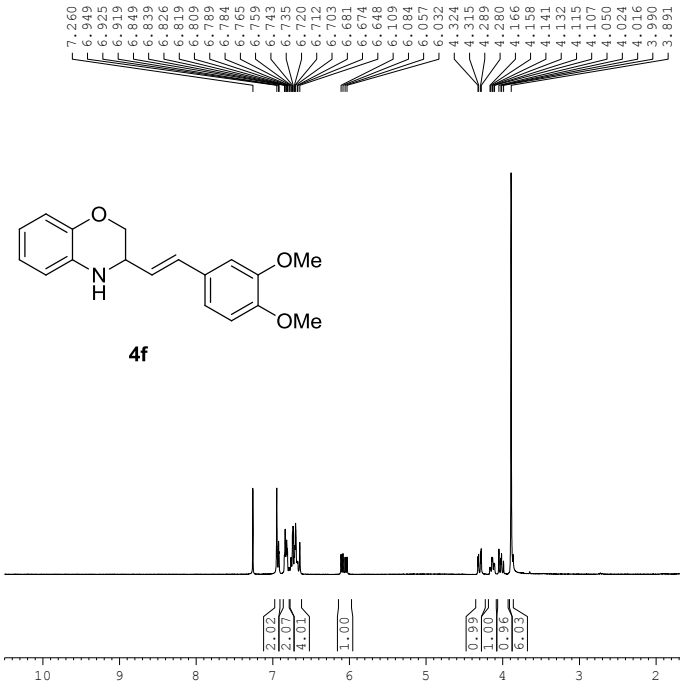
```
Current Data Parameters
NAME          qj-hh-meo
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20120619
Time              12.07
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   19
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                574.7
DW               27.800 usec
DE                6.50 usec
TE                300.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```



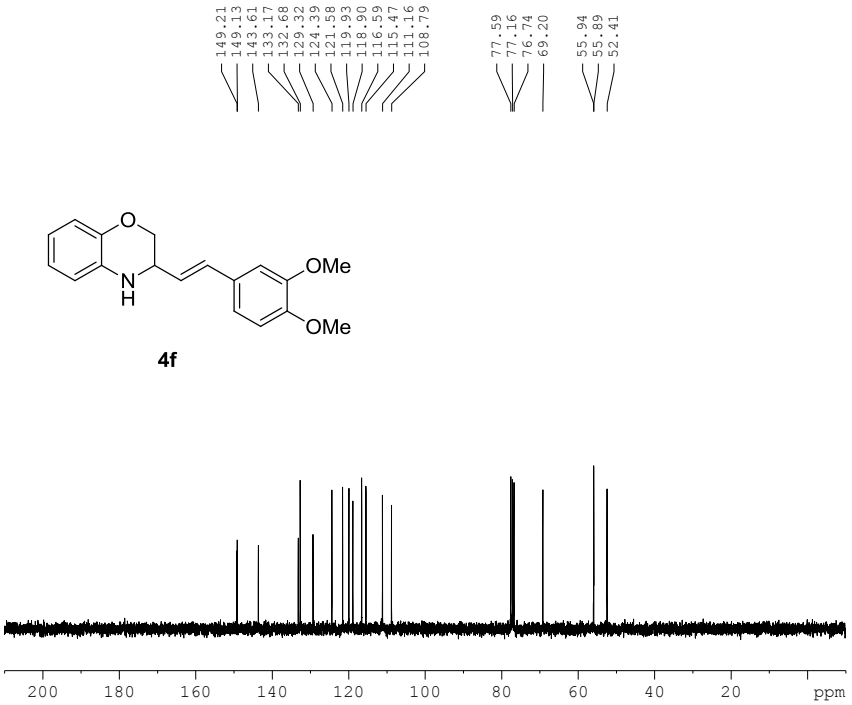
4f

```
Current Data Parameters
NAME         qj-hh-dimeo
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120618
Time               11.25
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                 456.1
DW                55.600 usec
DE                 8.00 usec
TE                 300.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



4f

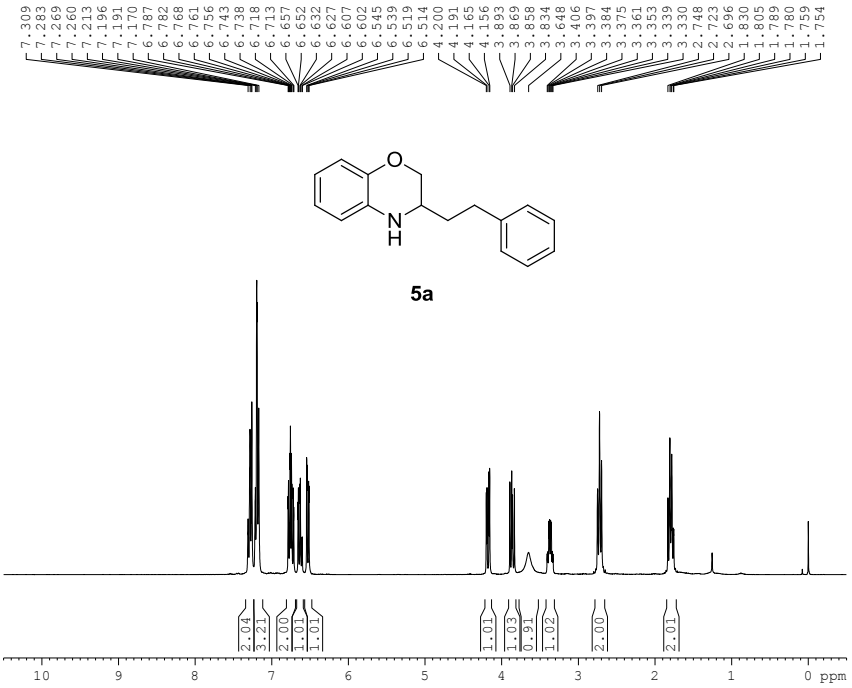
```
Current Data Parameters
NAME           qj-hh156
EXPNO                 41
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120511
Time               15.06
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    22
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                 6.50 usec
TE                 298.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
```

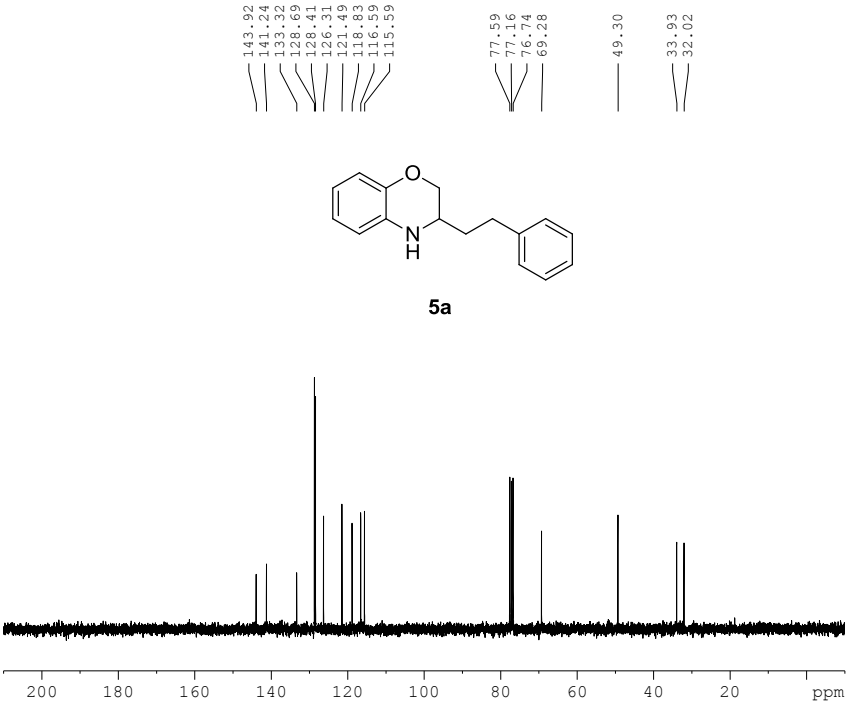



```
Current Data Parameters
NAME      qj-hh138-down
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20120428
Time               20.56
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    64
DW                55.600 usec
DE                 8.00 usec
TE                298.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.80 usec
PL1                 3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300268 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME      qj-hh138-down
EXPNO                20
PROCNO                1

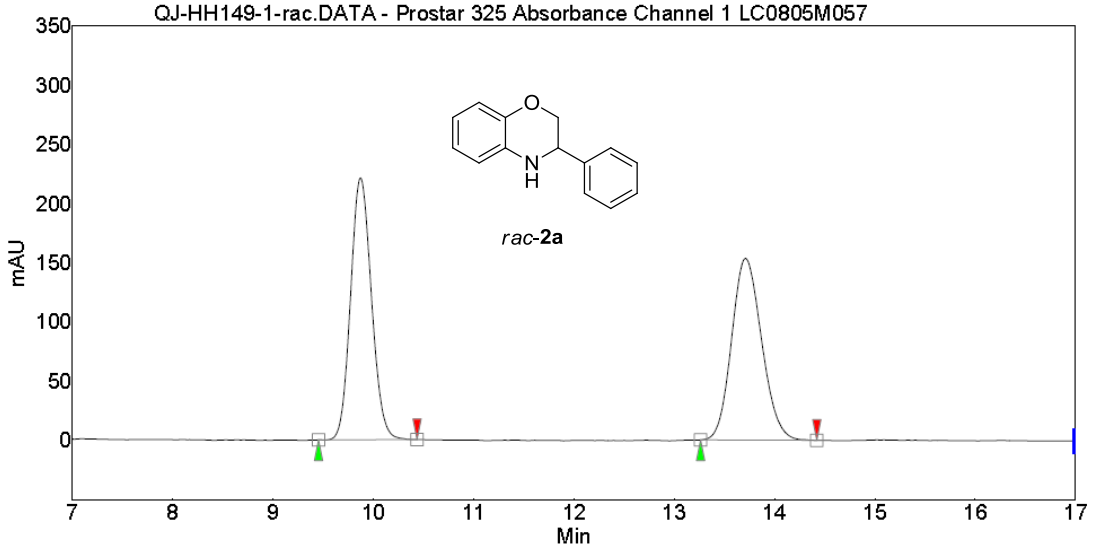
F2 - Acquisition Parameters
Date_           20120428
Time               20.54
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgig30
TD                 32768
SOLVENT            CDCl3
NS                    22
DS                     0
SWH            18832.393 Hz
FIDRES          0.574719 Hz
AQ             0.8700404 sec
RG                 13004
DW                26.550 usec
DE                 8.00 usec
TE                298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

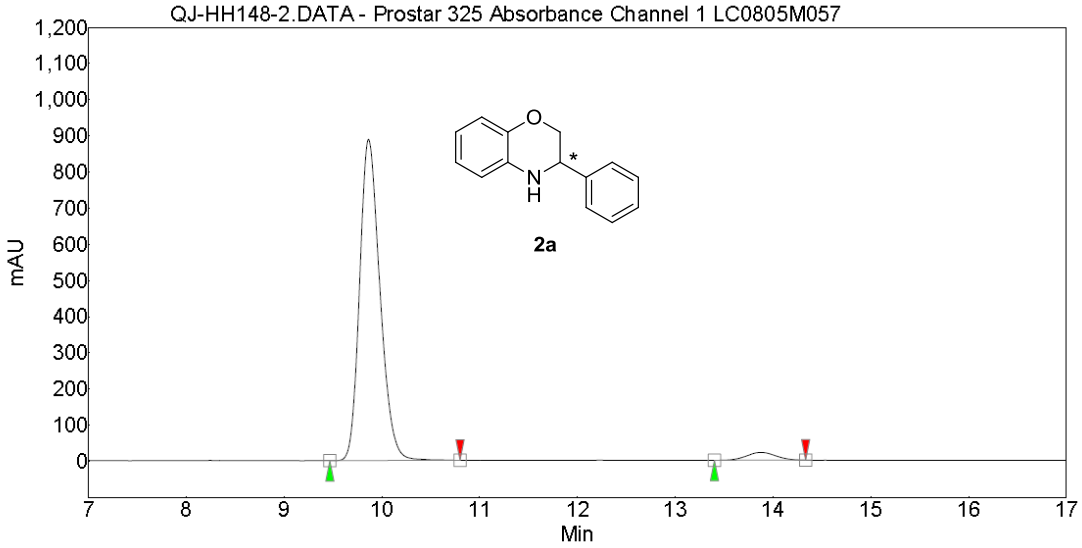
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.33 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677466 MHz
```

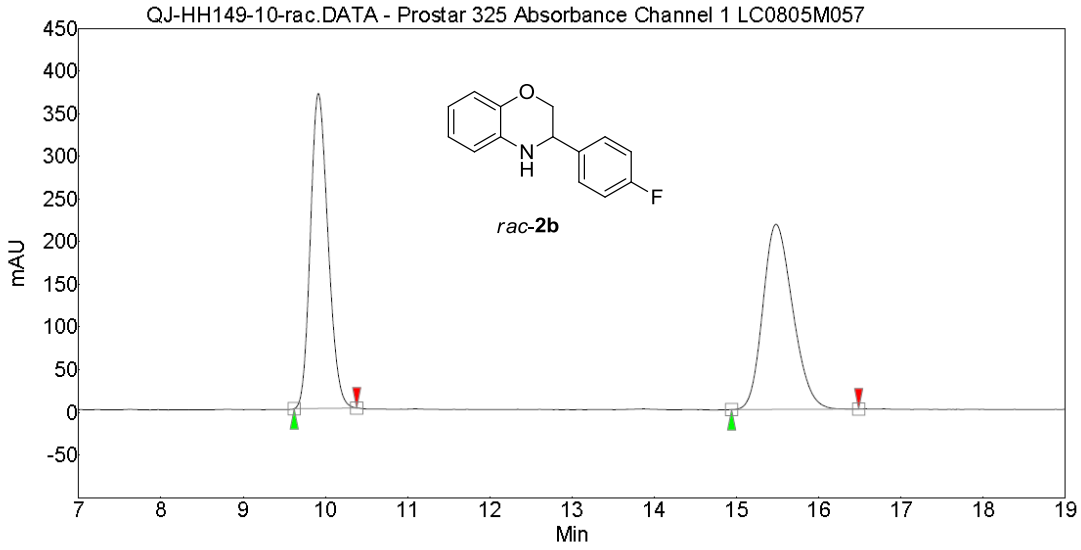
7. HPLC spectra of the reduced products



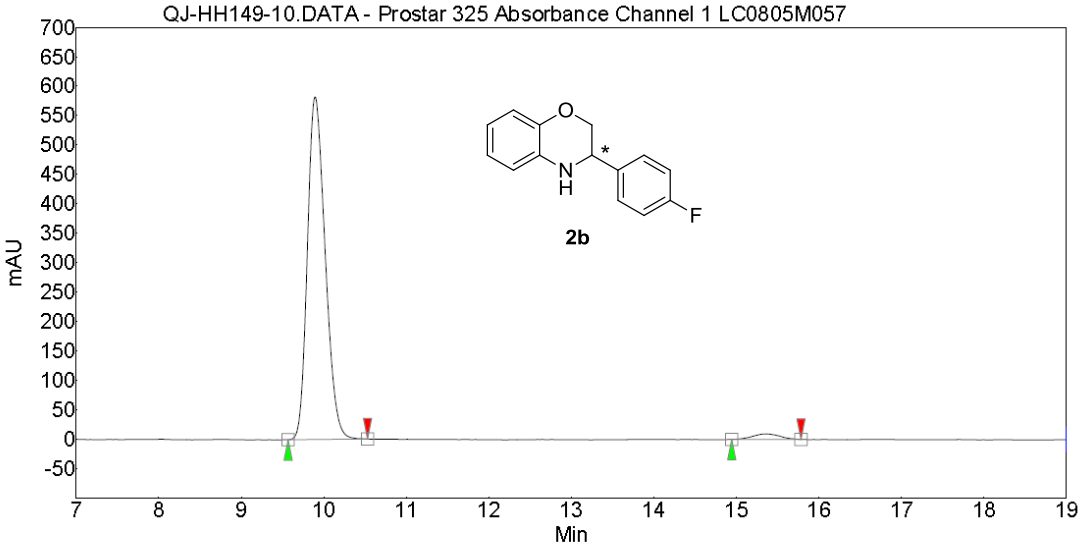
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.87	50.03	221.3	53.3	50.031
2	未知	13.71	49.97	153.5	53.3	49.969
Total			100.00	374.8	106.6	100.000



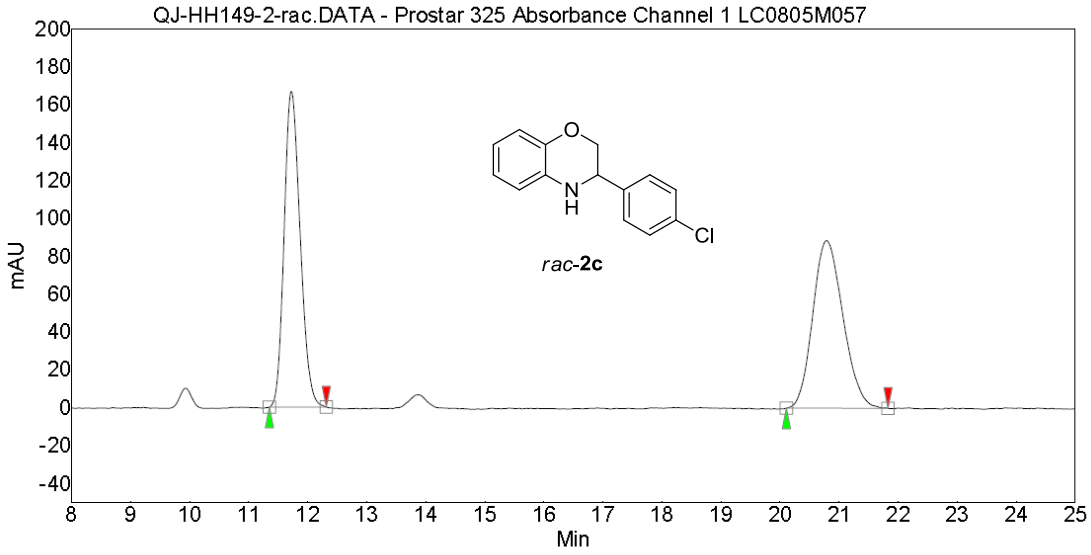
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	9.86	96.60	888.4	214.4	96.603
1	未知	13.87	3.40	21.7	7.5	3.397
Total			100.00	910.1	222.0	100.000



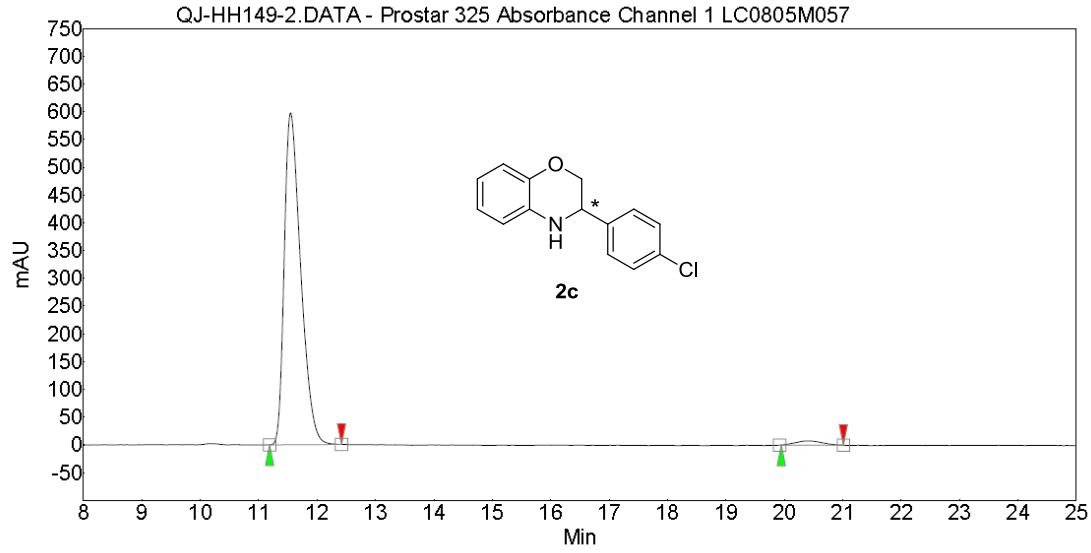
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	9.91	50.08	369.2	91.6	50.076
1	未知	15.48	49.92	217.0	91.3	49.924
Total			100.00	586.2	182.9	100.000



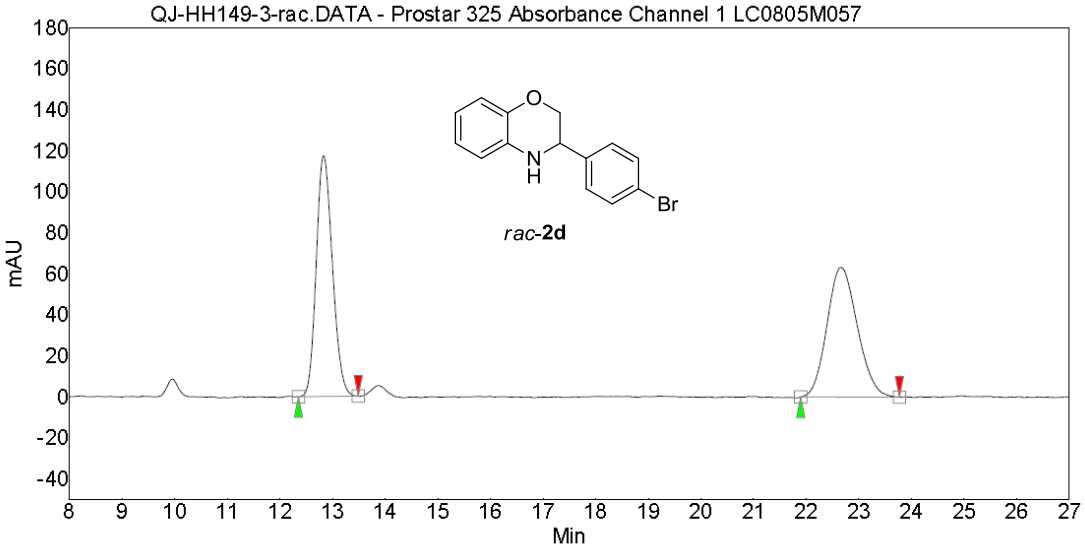
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.89	97.55	582.7	145.2	97.551
2	未知	15.37	2.45	9.5	3.6	2.449
Total			100.00	592.2	148.9	100.000



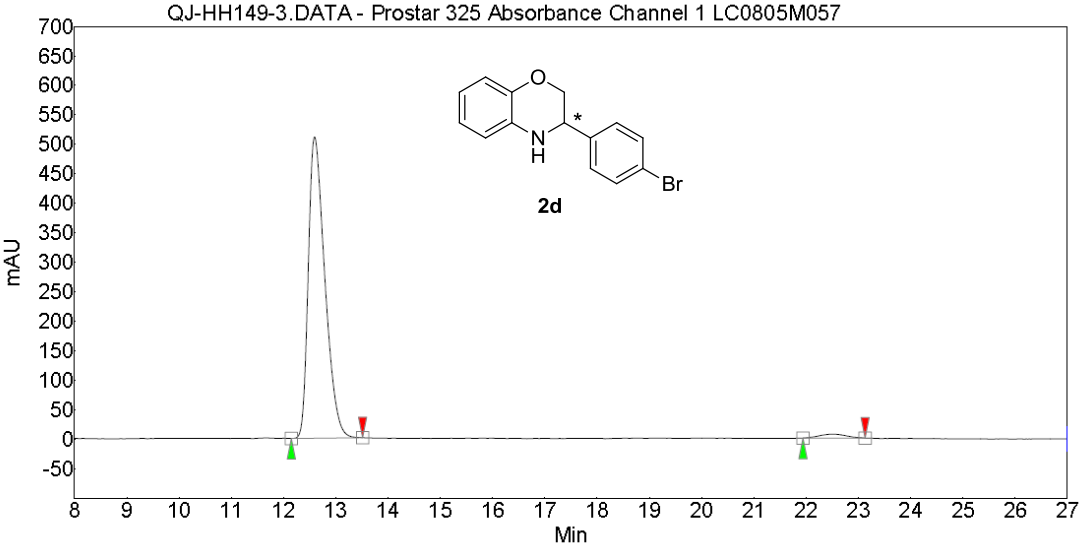
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	11.72	50.02	166.6	52.5	50.019
1	未知	20.79	49.98	88.5	52.5	49.981
Total			100.00	255.1	105.0	100.000



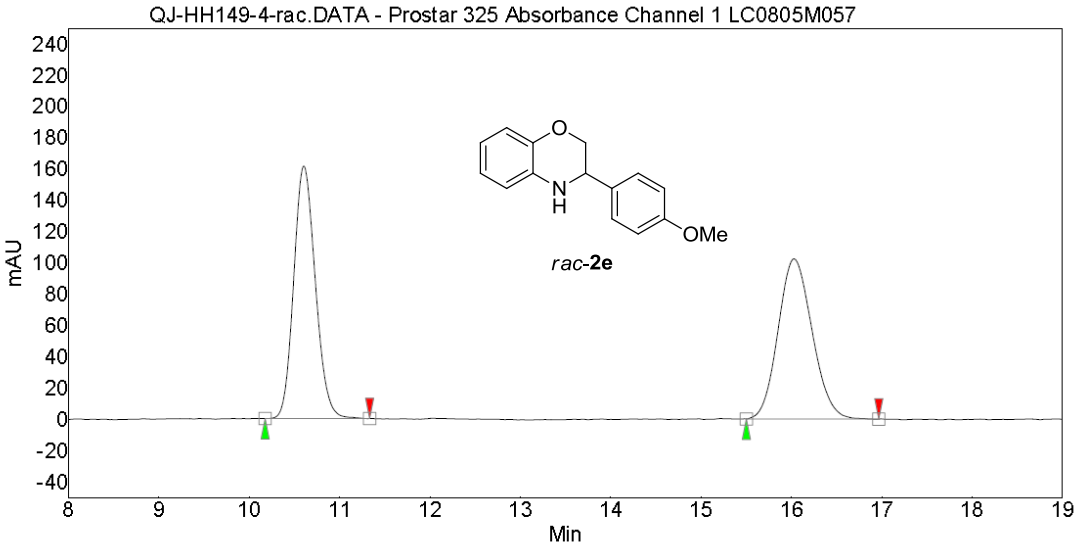
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	11.55	97.92	597.9	194.9	97.925
2	未知	20.43	2.08	7.8	4.1	2.075
Total			100.00	605.6	199.0	100.000



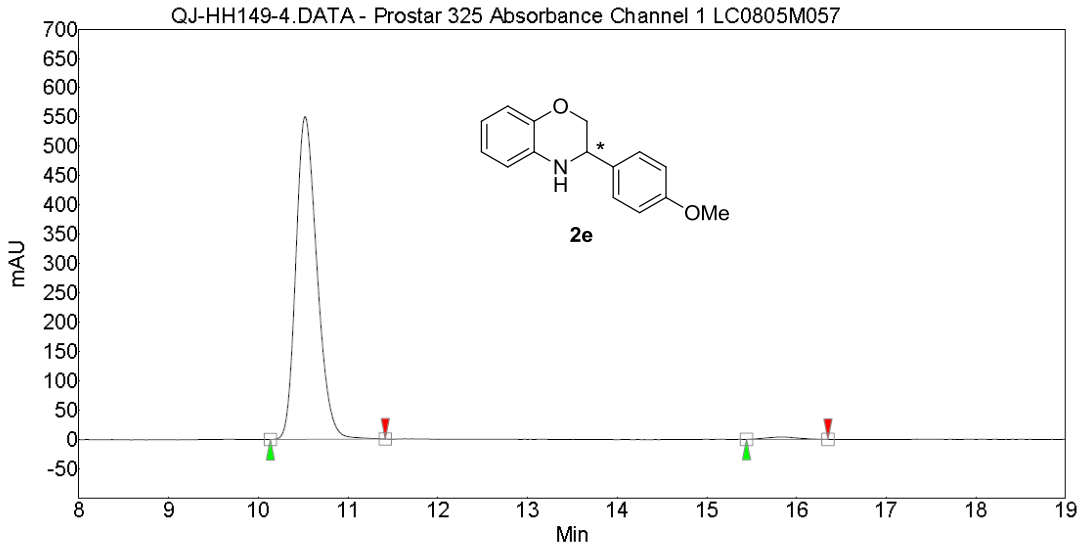
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.83	49.75	117.4	41.7	49.749
2	未知	22.65	50.25	63.2	42.2	50.251
Total			100.00	180.6	83.9	100.000



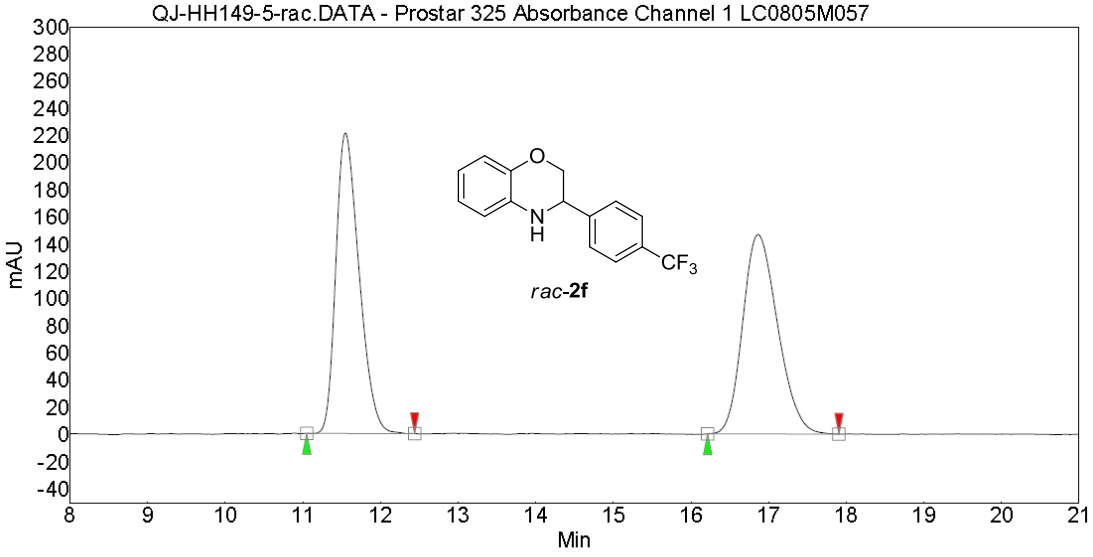
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.59	97.91	511.0	187.3	97.912
2	未知	22.54	2.09	6.7	4.0	2.088
Total			100.00	517.7	191.3	100.000



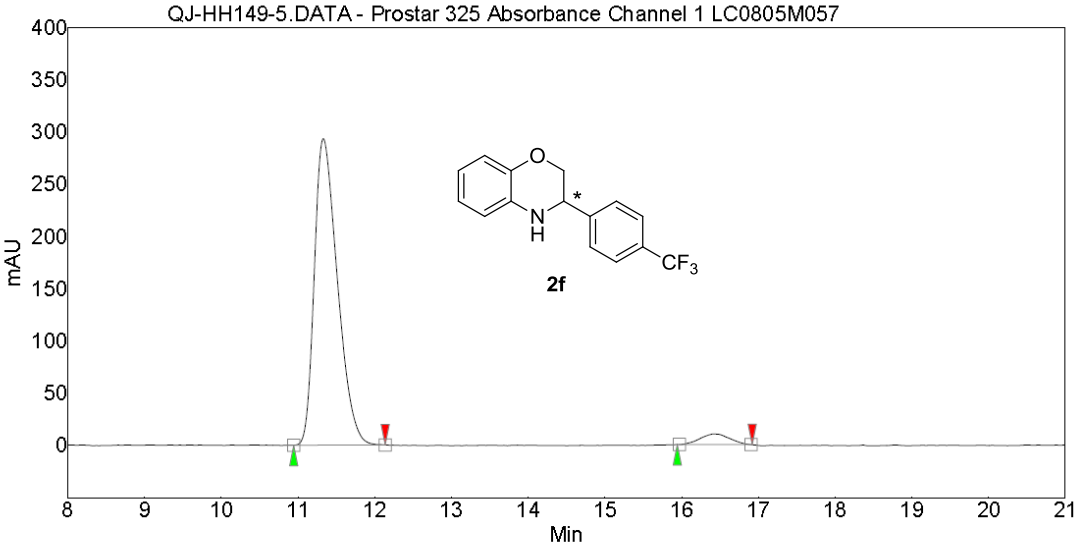
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.60	50.07	161.3	44.8	50.068
2	未知	16.03	49.93	102.4	44.7	49.932
Total			100.00	263.7	89.4	100.000



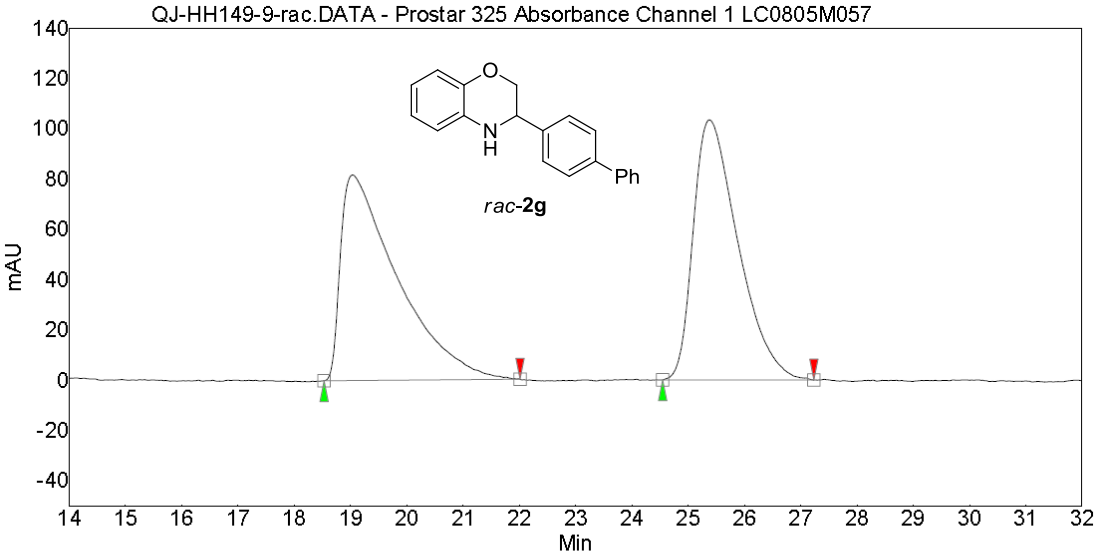
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.52	98.92	550.9	150.4	98.920
2	未知	15.85	1.08	4.0	1.6	1.080
Total			100.00	554.9	152.1	100.000



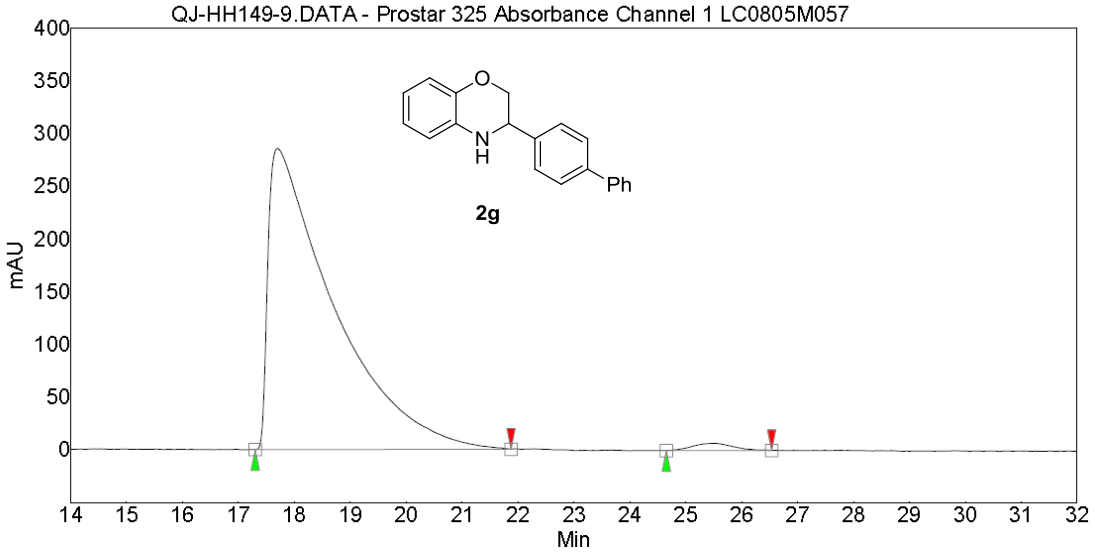
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	11.55	50.06	221.0	76.7	50.060
2	未知	16.87	49.94	146.7	76.5	49.940
Total			100.00	367.6	153.2	100.000



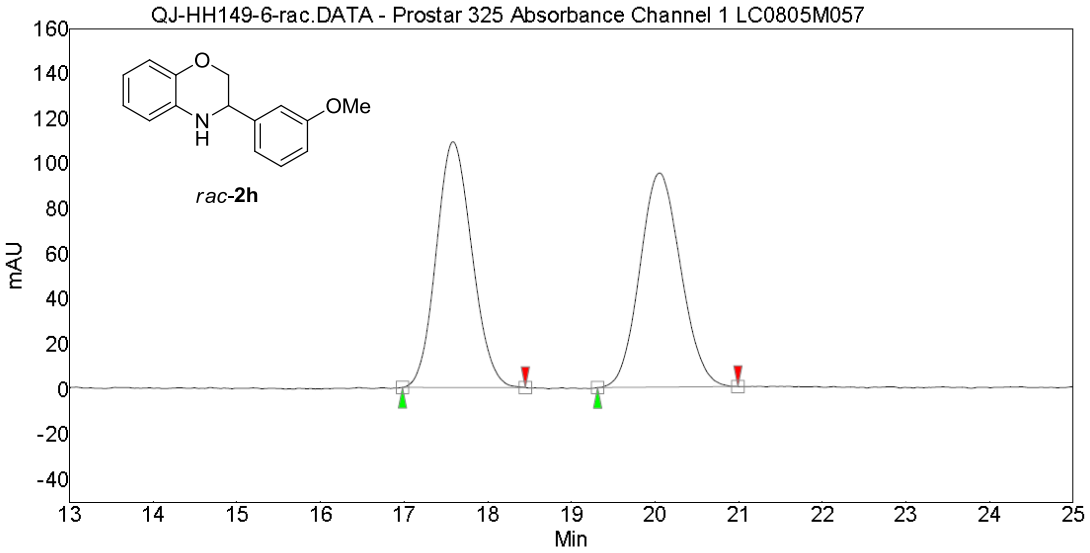
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	11.33	95.82	293.1	102.1	95.816
2	未知	16.42	4.18	10.1	4.5	4.184
Total			100.00	303.2	106.6	100.000



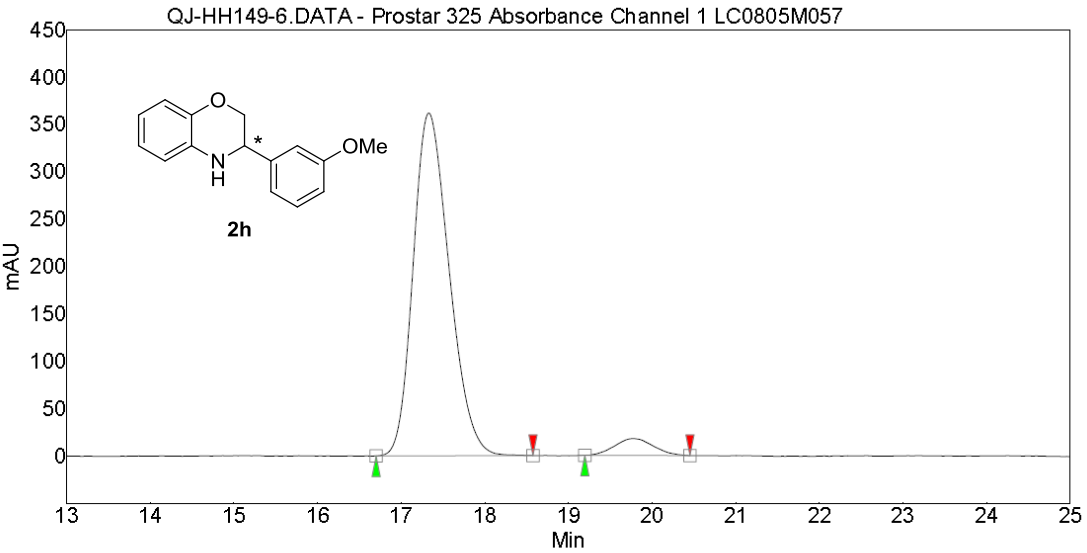
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	19.03	50.03	81.7	95.4	50.027
1	未知	25.37	49.97	103.4	95.3	49.973
Total			100.00	185.1	190.7	100.000



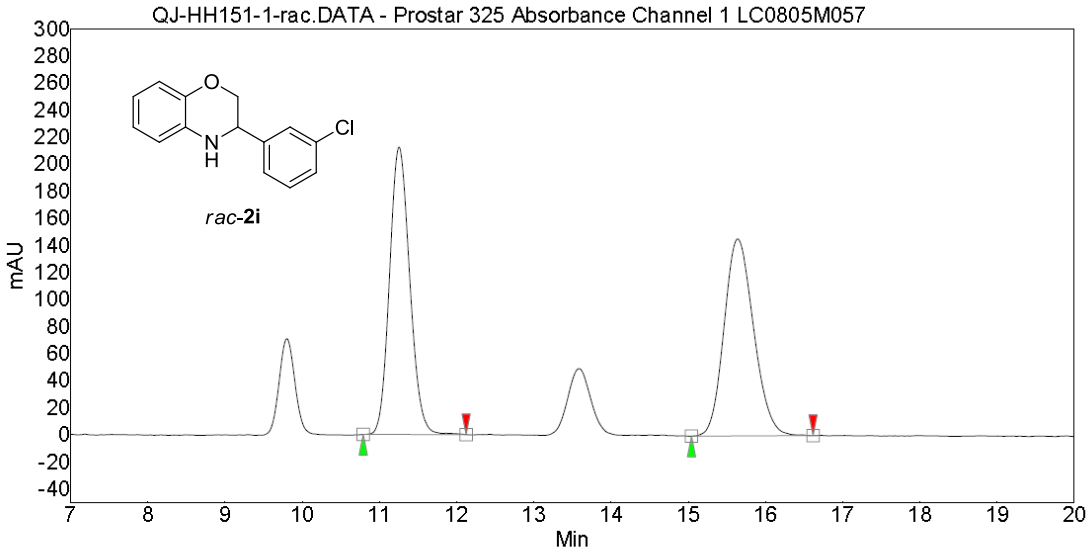
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	17.70	98.50	285.3	385.1	98.504
1	未知	25.49	1.50	6.9	5.8	1.496
Total			100.00	292.3	391.0	100.000



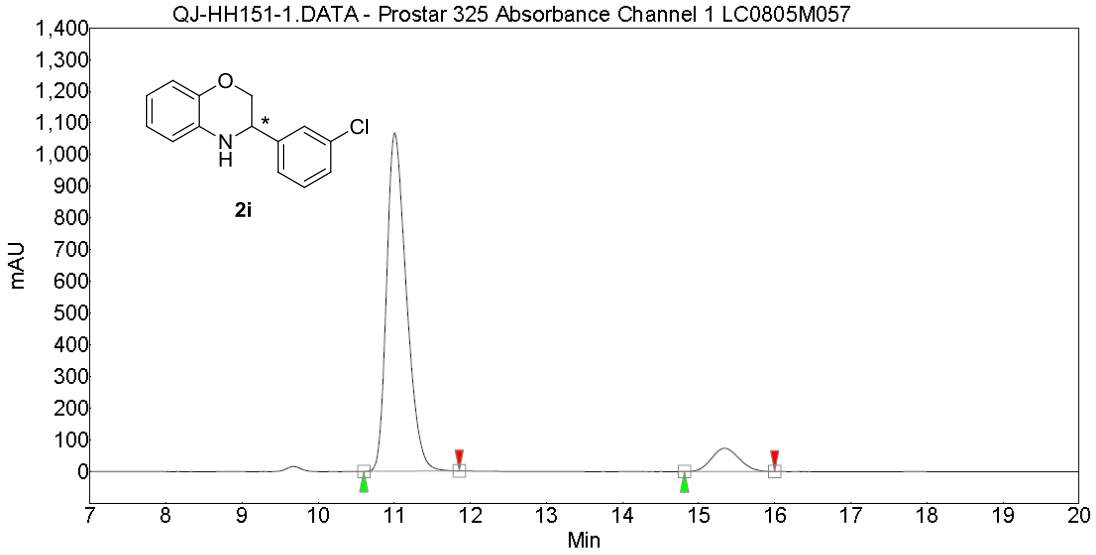
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	17.59	49.96	108.9	53.9	49.963
1	未知	20.05	50.04	94.9	54.0	50.037
Total			100.00	203.9	107.9	100.000



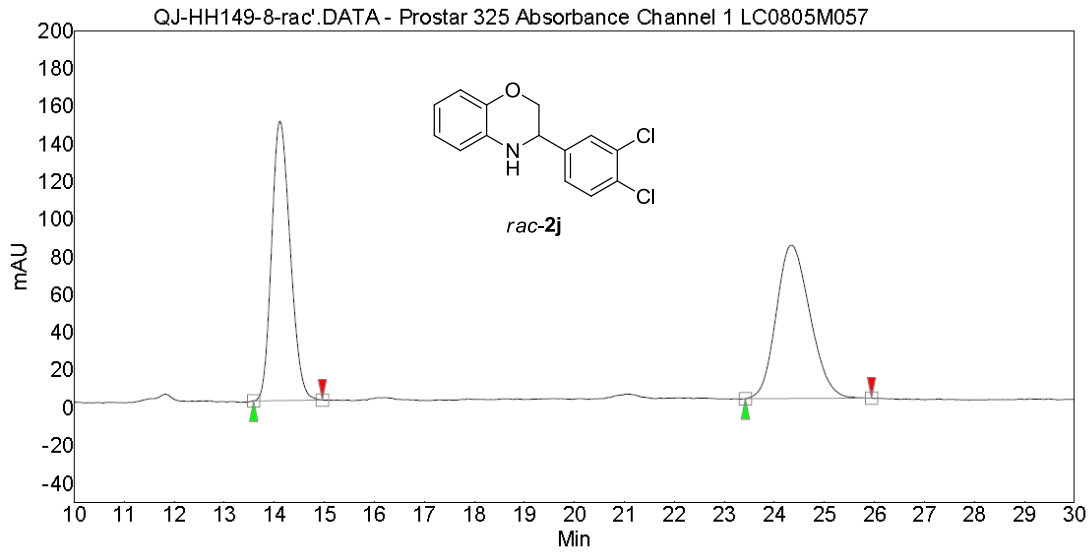
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	17.33	94.99	361.7	180.5	94.988
1	未知	19.77	5.01	17.8	9.5	5.012
Total			100.00	379.5	190.0	100.000



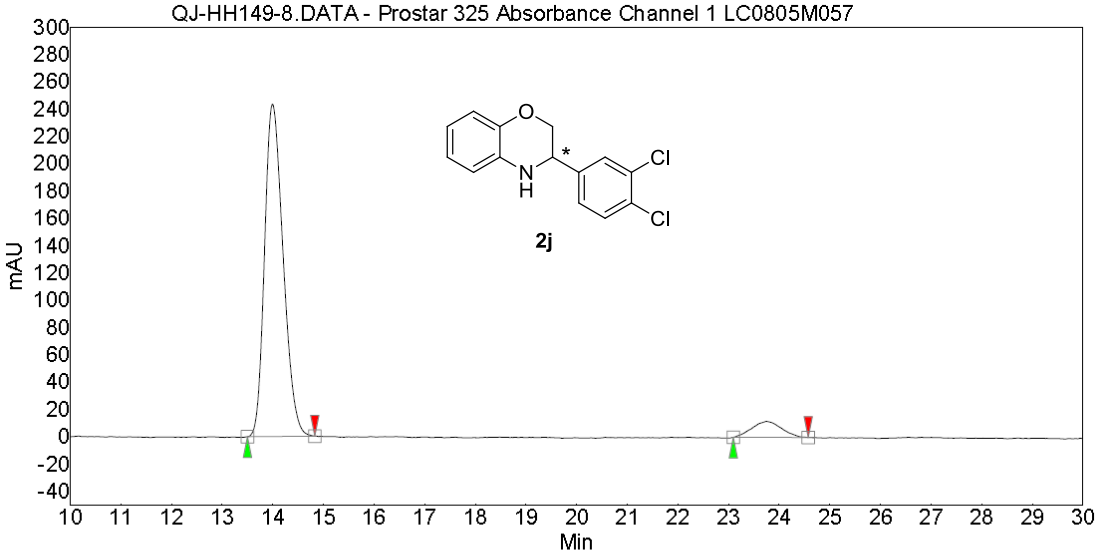
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	11.25	49.99	212.3	64.6	49.993
1	未知	15.64	50.01	145.6	64.6	50.007
Total			100.00	357.9	129.2	100.000



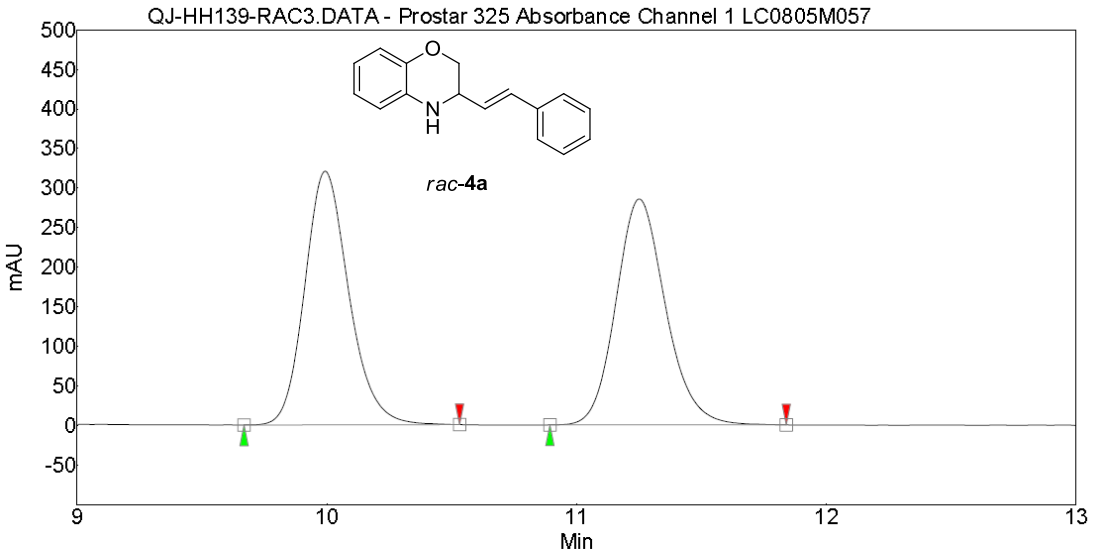
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	11.01	91.21	1067.5	320.7	91.210
2	未知	15.34	8.79	73.4	30.9	8.790
Total			100.00	1140.9	351.6	100.000



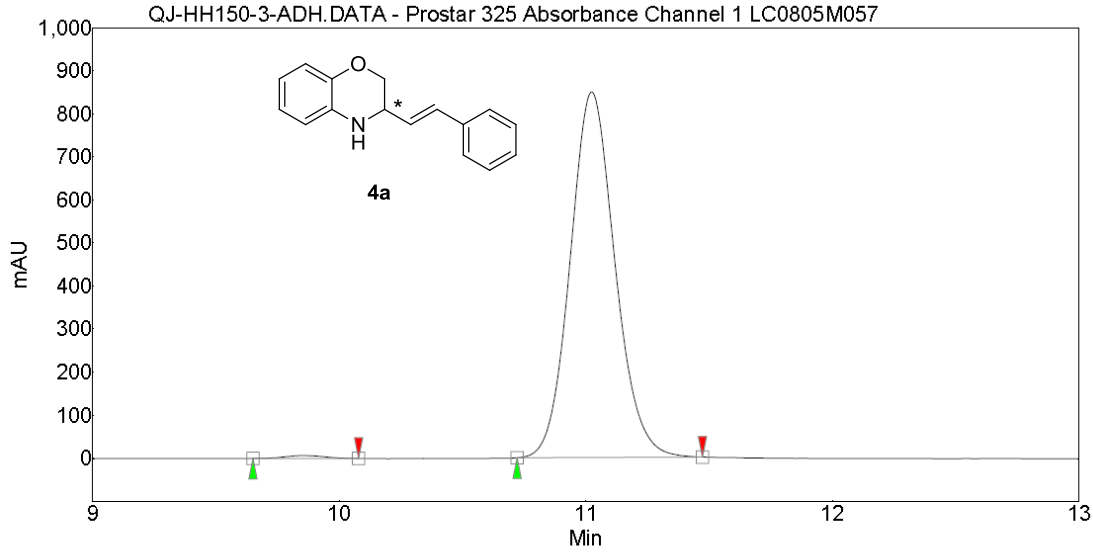
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	14.11	50.08	148.1	63.8	50.079
2	未知	24.34	49.92	81.3	63.6	49.921
Total			100.00	229.4	127.4	100.000



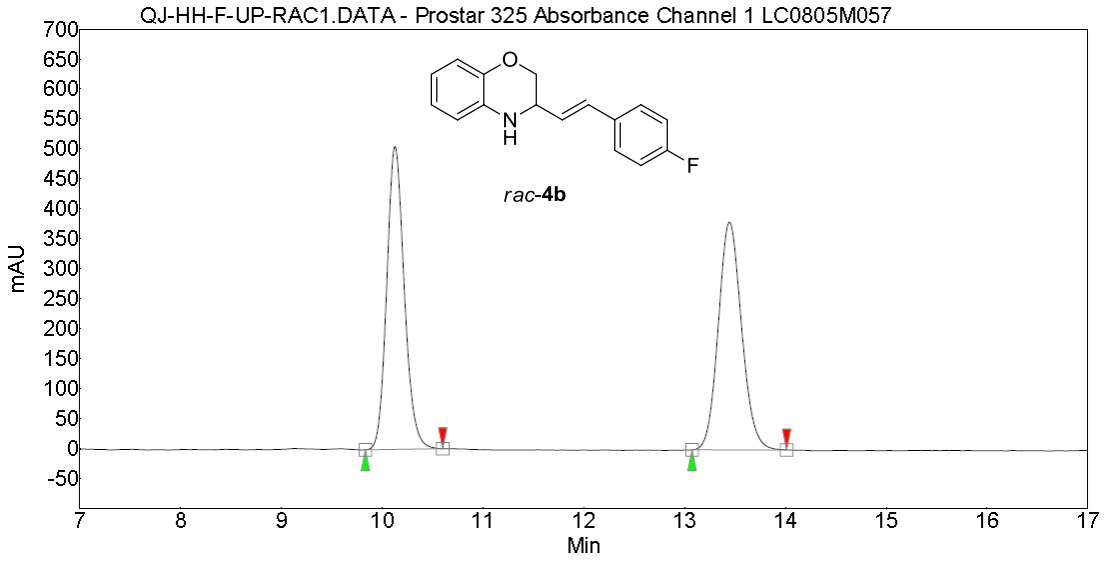
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	13.99	92.93	243.4	103.4	92.927
2	未知	23.75	7.07	11.7	7.9	7.073
Total			100.00	255.1	111.3	100.000



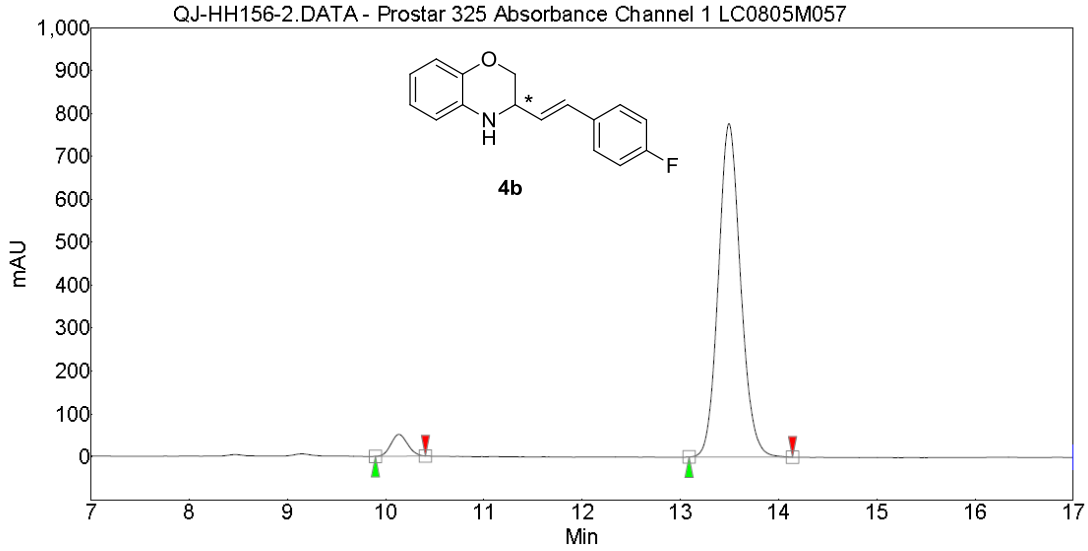
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.99	49.99	320.6	65.7	49.987
2	未知	11.25	50.01	285.5	65.7	50.013
Total			100.00	606.2	131.4	100.000



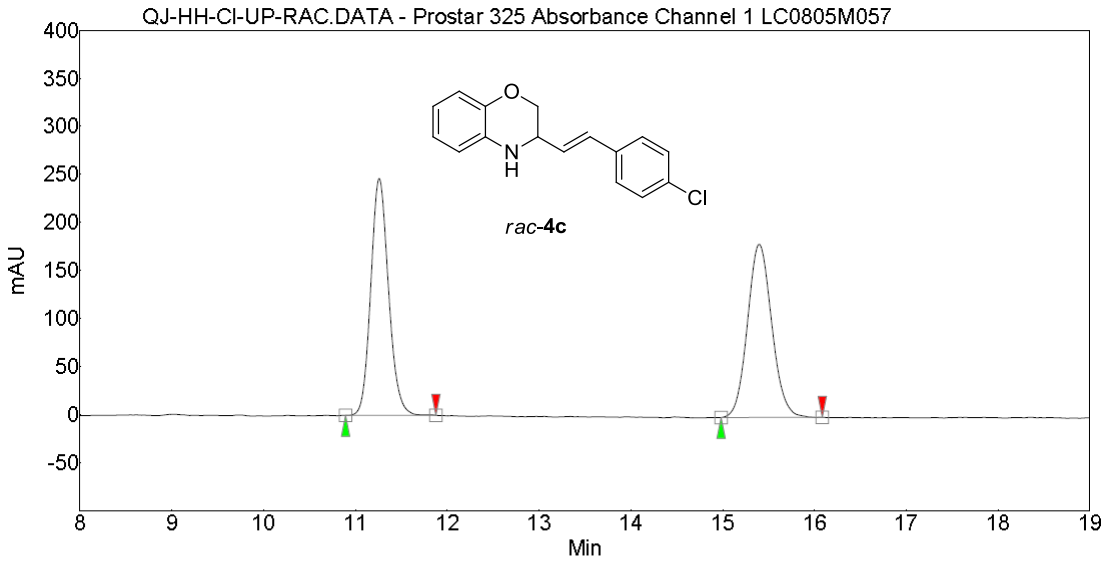
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.85	0.67	6.6	1.2	0.666
2	未知	11.02	99.33	849.0	178.5	99.334
Total			100.00	855.6	179.7	100.000



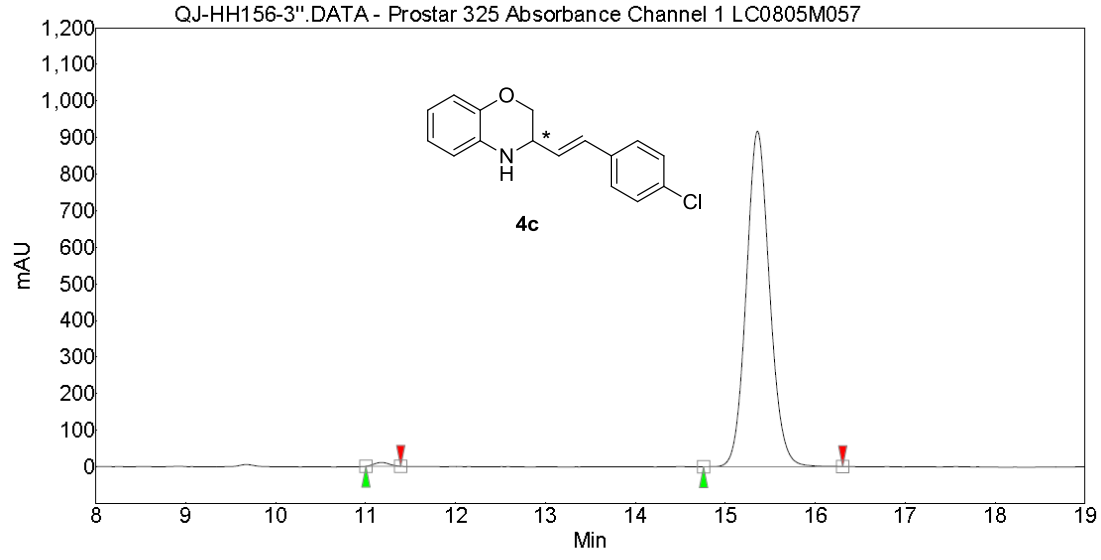
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.13	50.02	505.9	102.1	50.023
2	未知	13.45	49.98	380.2	102.0	49.977
Total			100.00	886.2	204.2	100.000



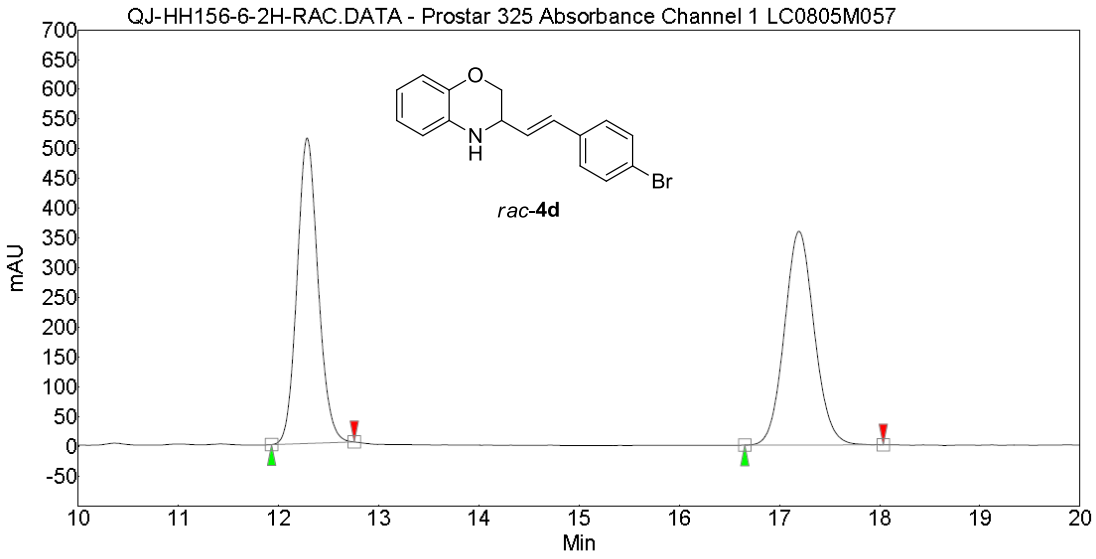
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.13	4.68	50.8	10.0	4.680
2	未知	13.49	95.32	776.9	203.9	95.320
Total			100.00	827.6	213.9	100.000



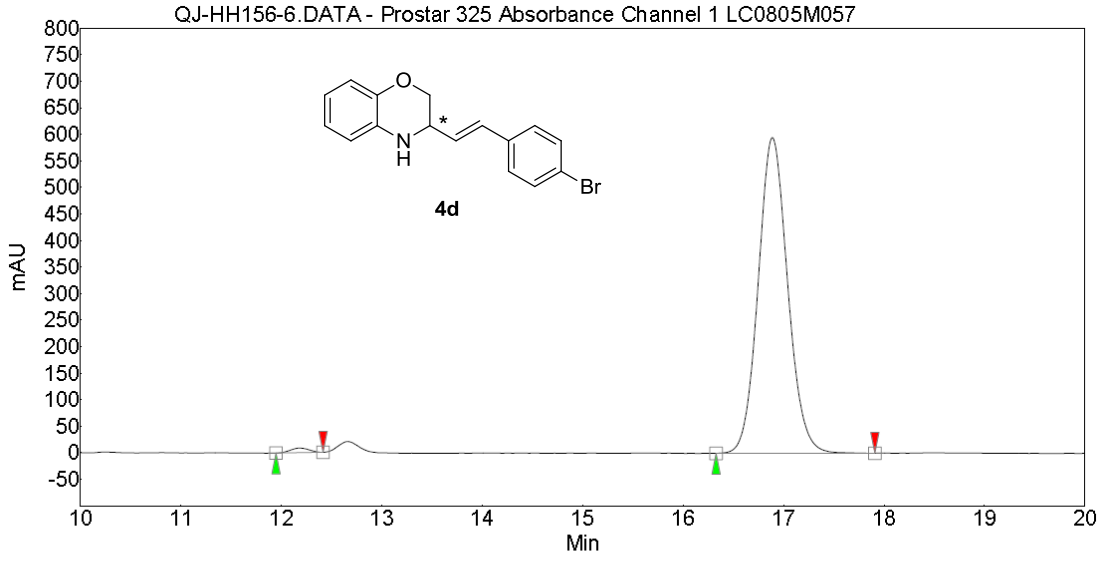
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	11.26	50.05	246.6	55.4	50.054
2	未知	15.40	49.95	180.2	55.3	49.946
Total			100.00	426.8	110.6	100.000



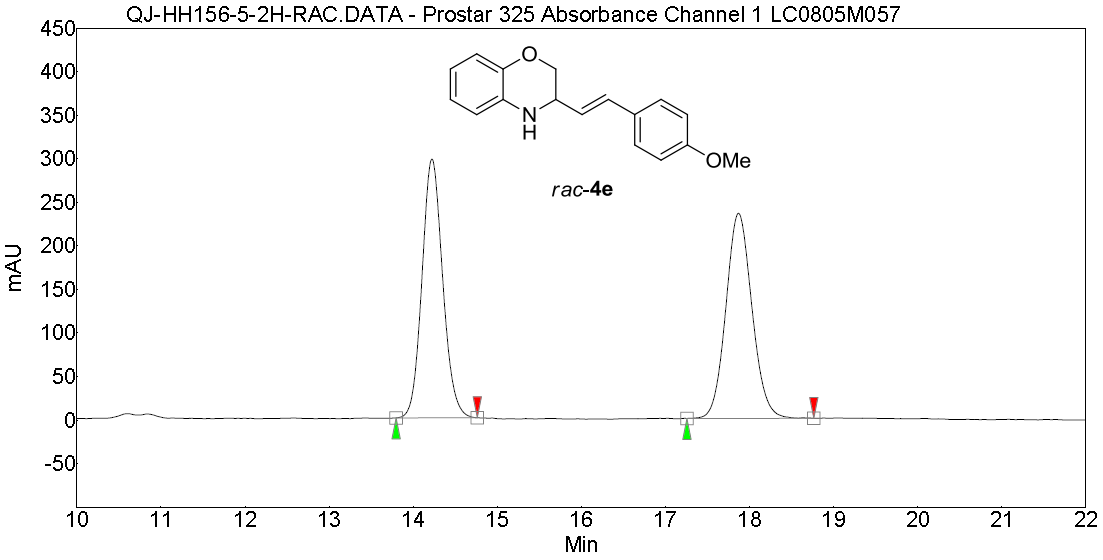
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	11.17	0.74	10.7	2.1	0.743
1	未知	15.36	99.26	917.5	276.1	99.257
Total			100.00	928.2	278.1	100.000



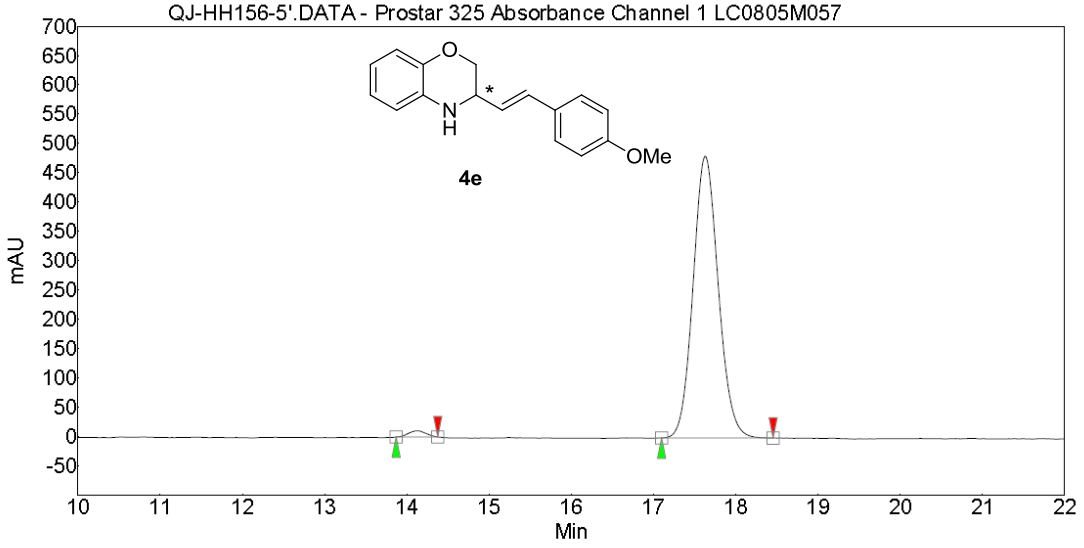
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	12.29	50.15	513.3	125.0	50.153
1	未知	17.19	49.85	359.2	124.2	49.847
Total			100.00	872.5	249.2	100.000



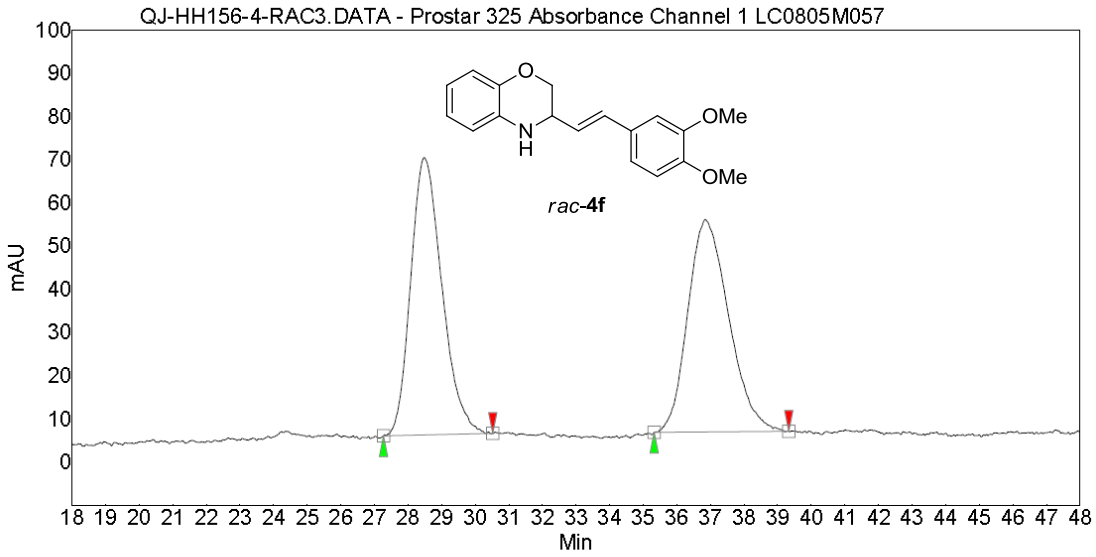
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	12.18	0.90	8.6	1.8	0.904
1	未知	16.89	99.10	594.7	202.2	99.096
Total			100.00	603.3	204.0	100.000



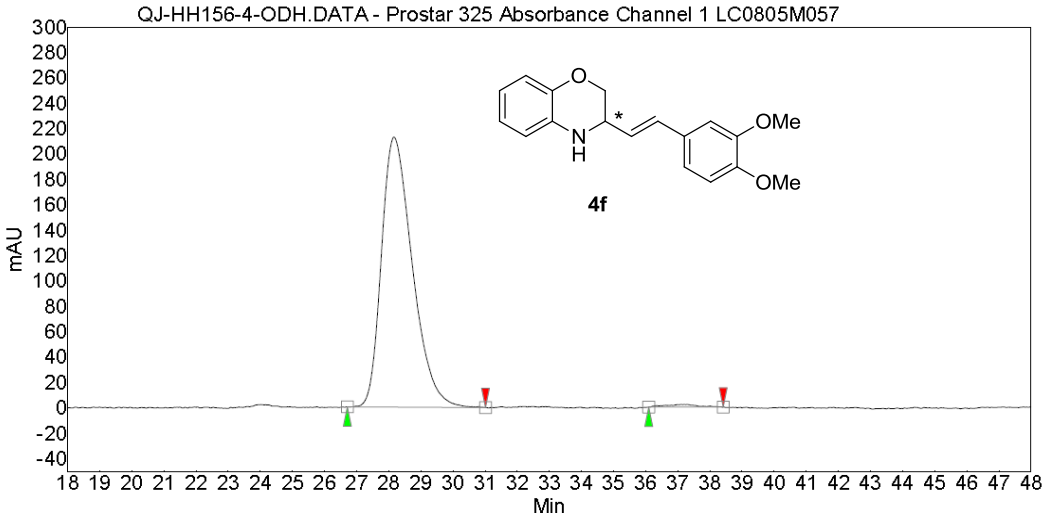
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	14.22	50.07	297.1	84.8	50.069
2	未知	17.87	49.93	235.4	84.5	49.931
Total			100.00	532.5	169.3	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	14.13	1.48	10.6	2.6	1.476
1	未知	17.63	98.52	480.9	170.6	98.524
Total			100.00	491.5	173.2	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	28.49	49.97	64.2	69.2	49.972
2	未知	36.85	50.03	49.2	69.3	50.028
Total			100.00	113.4	138.5	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	28.16	98.93	212.7	236.6	98.931
2	未知	37.10	1.07	2.2	2.6	1.069
Total			100.00	214.9	239.2	100.000