Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Constructing Chiral Aza-quaternary Carbon Centres by Enantioselective Carbonylative Heck reaction of Allenes with *o*-Iodoanilines

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1. General information

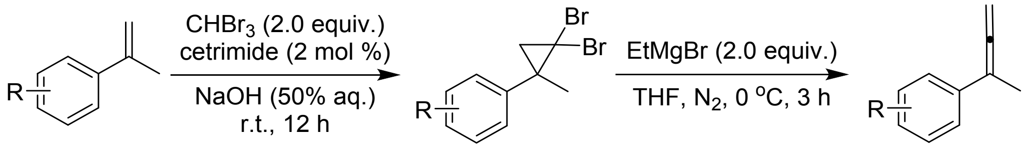
Unless otherwise stated, all experiments were carried out under N_2 atmosphere. Column chromatography was performed using 200-300 mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm).

All commercial reagents were purchased from Macklin, TCI, Sigma-Aldrich, Adamas-beta, J&K, Laajoo, 9-Ding chemistry, Alfa Aesar and Energy Chemical. Commercially available materials were used as received without further purification unless specified. Anhydrous DMAc was purchased from Energy Chemical and was used as received without further purification. (*R*)-BTFM-Garphos (97%) was purchased from Alfa Aesar and was used as received without further purification.

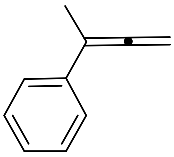
NMR spectra were recorded on Bruker AVANCE Ⅲ 500 MHz NMR spectrometer. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) as internal reference. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. HRMS were recorded on a Bruker Daltonics maXis Impact + 1290 infinity mass spectrometer at the Center for Mass Spectrometry, East China Normal University. The absolute configuration was determined by single crystal X-ray diffraction analysis on Rigaku XtaLAB PRO MM003-DS dual system with a Cu micro-focus source. Optical rotation was determined using $CHCl_3$ and as the solvent on INESA WZZ-3. Enantiomeric ratios were determined by chiral HPLC (SHIMADZU LC-20) with ^{n}hexane and ^{i}PrOH as solvents. Analytical and spectral data of all those known compounds are exactly consistent with the reported values.

2. Synthesis of allene substrates, 2-amino phenyl triflate and *N*-substituted 2-iodoanilines

All the allene substrates are known compounds and have been prepared according to methods reported in the previous literature.[S1,S2]

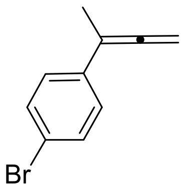


(3λ⁵-buta-2,3-dien-2-yl)benzene



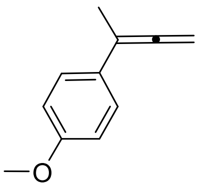
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.01 (q, *J* = 3.0 Hz, 2H), 2.09 (td, *J* = 3.0 Hz, 0.85 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.00, 136.72, 128.34, 126.58, 125.69, 99.82, 76.91, 16.71.

1-bromo-4-(3λ⁵-buta-2,3-dien-2-yl)benzene



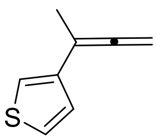
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.01 (q, *J* = 3.0 Hz, 2H), 2.06 (t, *J* = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.90, 135.77, 131.35, 127.28, 120.39, 99.12, 77.38, 16.59.

1-(3λ⁵-buta-2,3-dien-2-yl)-4-methoxybenzene



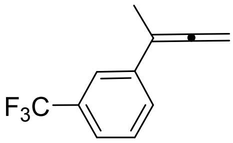
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.00 (q, *J* = 3.0 Hz, 2H), 3.80 (s, 3H), 2.08 (t, *J* = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.60, 158.46, 128.98, 126.77, 113.81, 99.31, 76.80, 55.30, 16.89.

3-(3λ⁵-buta-2,3-dien-2-yl)thiophene



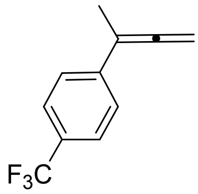
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 - 7.20 (m, 1H), 7.12 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.08 - 7.00 (m, 1H), 4.97 (q, *J* = 3.0 Hz, 2H), 2.07 (t, *J* = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.22, 138.87, 126.60, 125.42, 118.83, 96.36, 76.54, 17.21.

1-(3λ⁵-buta-2,3-dien-2-yl)-3-(trifluoromethyl)benzene



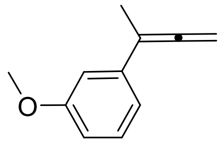
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 - 7.37 (m, 2H), 5.08 (q, *J* = 3.0 Hz, 2H), 2.10 (t, *J* = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.07, 137.80, 130.75 (q, $J_{C\text{-}F}$ = 31.25 Hz), 128.80, 128.68, 124.26 (q, $J_{C\text{-}F}$ = 271.25 Hz), 123.14 (q, $J_{C\text{-}F}$ = 3.75 Hz), 122.30 (q, $J_{C\text{-}F}$ = 3.75 Hz), 99.07, 77.70, 16.48. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.69.

1-(3λ⁵-buta-2,3-dien-2-yl)-4-(trifluoromethyl)benzene



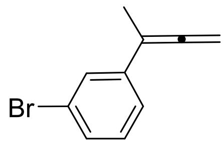
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 5.07 (q, J = 3.0 Hz, 2H), 2.10 (t, J = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.48, 140.64, 128.45 (q, $J_{C\text{-}F}$ = 31.25 Hz), 125.79, 125.18 (q, $J_{C\text{-}F}$ = 3.75 Hz), 123.30 (q, $J_{C\text{-}F}$ = 270.0 Hz), 99.15, 77.51, 16.48. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.40.

1-(3λ⁵-buta-2,3-dien-2-yl)-3-methoxybenzene



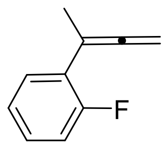
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 - 7.18 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.98 - 6.93 (m, 1H), 6.74 (dd, J = 8.0 Hz, 2.5 Hz, 1H), 5.01 (q, J = 3.0 Hz, 2H), 3.78 (s, 3H), 2.06 (t, J = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.06, 159.73, 138.32, 129.26, 118.27, 111.98, 111.58, 99.80, 76.99, 55.19, 16.76.

1-bromo-3-(3λ⁵-buta-2,3-dien-2-yl)benzene



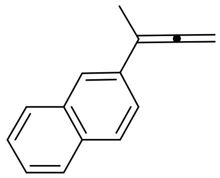
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 - 7.46 (m, 1H), 7.36 - 7.27 (m, 2H), 7.20 - 7.14 (m, 1H), 5.12 - 5.00 (m, 2H), 2.11 - 2.00 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.00, 139.15, 129.75, 129.44, 128.69, 124.20, 122.68, 98.97, 77.54, 16.55.

1-(3λ⁵-buta-2,3-dien-2-yl)-2-fluorobenzene

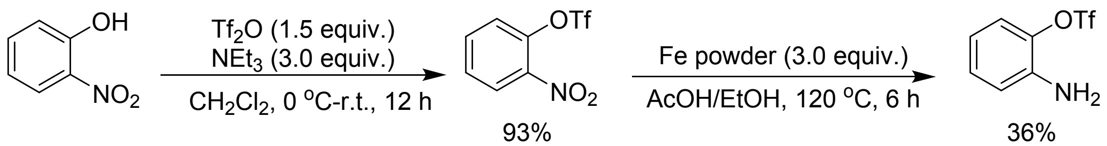


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.32 (m, 1H), 7.27 - 7.21 (m, 1H), 7.18 - 7.12 (m, 1H), 7.11 - 7.04 (m, 1H), 4.96 (q, J = 3.0 Hz, 2H), 2.18 (t, J = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.95 (d, $J_{C\text{-}F}$ = 1.25 Hz), 160.3 (d, $J_{C\text{-}F}$ = 247.5 Hz), 129.02 (d, $J_{C\text{-}F}$ = 3.75 Hz), 138.34 (d, $J_{C\text{-}F}$ = 8.75 Hz), 125.50 (d, $J_{C\text{-}F}$ = 12.5 Hz), 123.95 (d, $J_{C\text{-}F}$ = 3.75 Hz), 116.03 (d, $J_{C\text{-}F}$ = 22.5 Hz), 95.64, 74.95 (d, $J_{C\text{-}F}$ = 2.5 Hz), 18.72 (d, $J_{C\text{-}F}$ = 2.5 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -112.62.

2-(3λ⁵-buta-2,3-dien-2-yl)naphthalene



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 - 7.68 (m, 4H), 7.62 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.45 - 7.36 (m, 2H), 5.07 (q, J = 3.0 Hz, 2H), 2.19 (t, J = 3.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.74, 134.15, 133.69, 132.40, 128.04, 127.76, 127.65, 126.17, 125.70, 125.02, 123.39, 100.20, 77.35, 16.83.

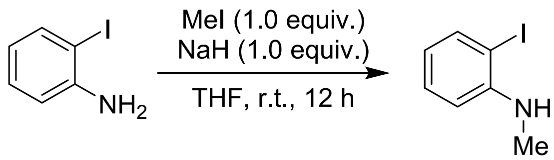


The procedure of preparing 2-amino phenyltriflate was according to the report of literature.[S3]

1st step: To an oven-dried 100 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, 2-nitrophenol (15.8 mmol, 1.0 equiv.), NEt_3 (31.6 mmol) and

20 mL anhydrous dichloromethane were added and then the CH_2Cl_2 solution was cooled in the ice bath. Afterwards, Tf_2O (23.7 mmol) was slowly added into the solution at 0 °C. Then, the reaction was gradually warmed up and stirred for 12 h to room temperature under N_2 atmosphere. Upon the completion of reaction, the reaction mixture was condensed under reduced pressure. 2-Nitro phenyl triflate was isolated by column chromatography on silica gel (PE/EA = 10:1, v/v) as a yellow oil (4.0 g, 93% yield).

2nd step: To an oven-dried 100 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, 2-nitro phenyl triflate (14.0 mmol, 1.0 equiv.), iron powder (42.0 mmol), glacial acetic acid (10.0 mL) and ethanol (20 mL) were successively added and stirred for 6 h under N_2 atmosphere in 120 °C oil bath. Upon completion of the reaction, the reaction mixture was filtrated through a short pad (ca. 2 cm thick) of silica gel. The filtrate was neutralized with saturated $NaHCO_3$ aqueous solution and extracted with ethyl acetate (50 mL × 3). The organic phase was dried over anhydrous Na_2SO_4 and condensed under reduced pressure. The product 2-amino phenyl triflate was obtained by column chromatography on silica gel (PE/EA = 10:1, v/v) as a yellow oil (1.2 g, 36% yield).

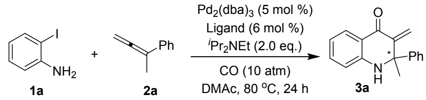


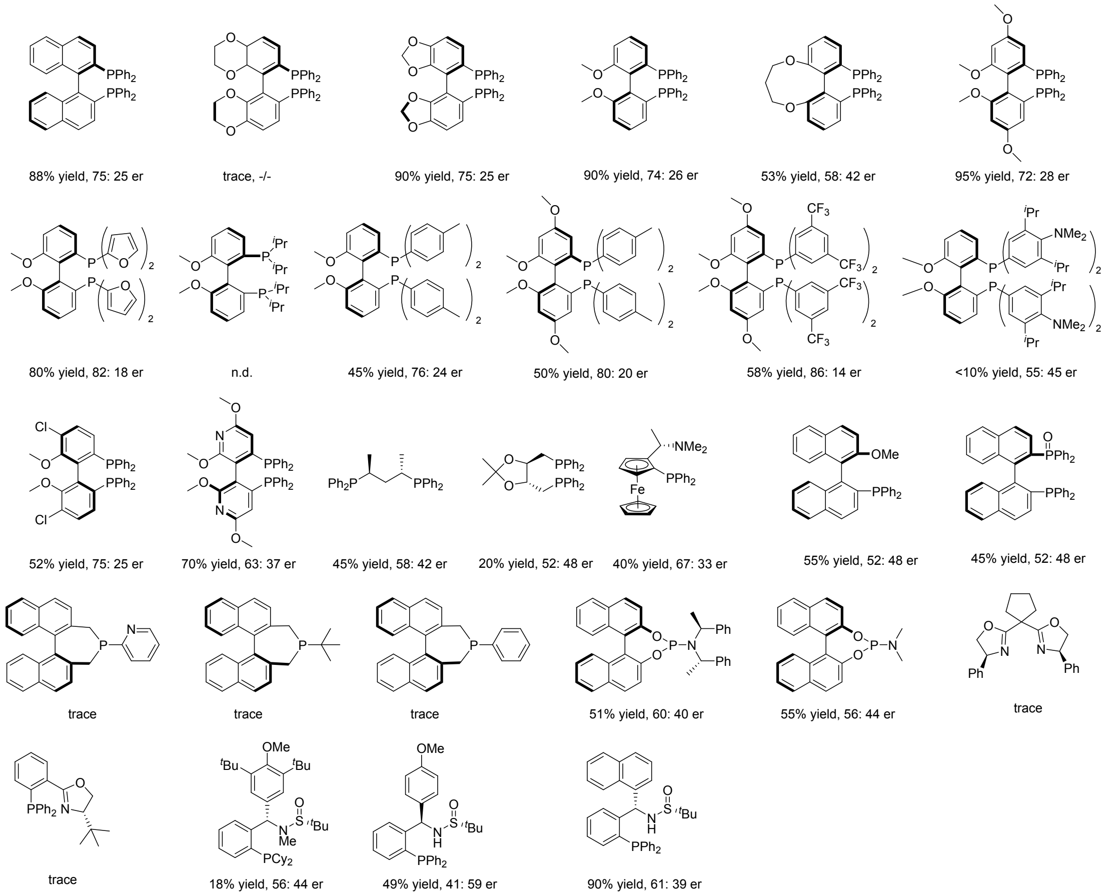
The procedure of preparing *N*-methyl 2-iodoaniline was according to the report of literature.[S4]

To an oven-dried 100 mL Schlenk tube charged with a PTFE-coated stirring bar, *o*-iodoaniline (20.0 mmol, 1.0 equiv.) and THF (20 mL) was subjected and the solution was cooled down to 0 °C in ice bath. Then, NaH (20.0 mmol, 60% dispersion in mineral oil) was portion-wise added into this cooling THF solution and the mixture was stirred for 0.5 h at 0 °C under N_2 atmosphere. Then, CH_3I (20.0 mmol, 1.0 equiv.) was dropped into the reaction system. The mixture was further stirred for 12 h at 0 °C to room temperature. Upon completion of the reaction, 50 mL saturated $NaHCO_3$ solution was slowly added into the reaction system under ice bath to work up the reaction. The mixture was extracted with ethyl acetate (50 mL × 3) and dried over anhydrous Na_2SO_4. The product 2-iodo-*N*-methylaniline was isolated by column chromatography on silica gel (PE/EA = 20:1, v/v) as a yellow oil 3.5 g in 75% yield.

3. Optimization of asymmetric carbonylative Heck reaction of 1a with 2a

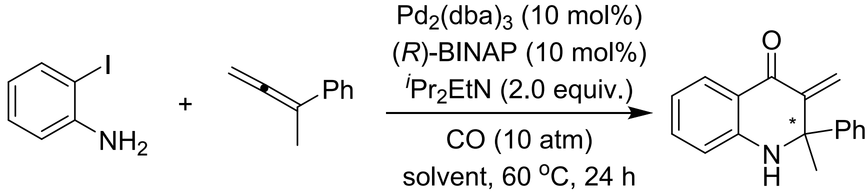
Table S1. Screening of chiral ligands





Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), ligand (0.012 mmol, 6 mol%), additive (0.4 mmol, 2.0 equiv.), CO (10 atm), DMAc (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (er) was determined by chiral HPLC.

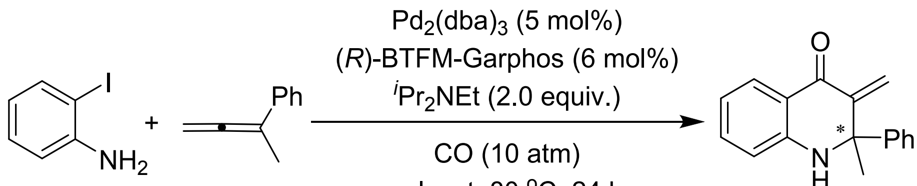
Table S2. Solvent screening with the employment of (*R*)-BINAP ligand



entry	solvent	yield (%)	er
1	toluene	38	72: 28
2	DMAc	77	76: 24
3	DCE	39	75: 25
4	DCM	41	72: 28
5	THF	57	74: 26
6	DMSO	<10	---
7	DMF	<10	---

Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (0.02 mmol, 10 mol%), (*R*)-BINAP (0.02 mmol, 10 mol%), $^i Pr_2NEt$ (0.4 mmol, 2,0 equiv.), CO (10 atm), solvent (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (er) was determined by chiral HPLC. DMAc = *N,N*-dimethylacetamide; DCE = 1,2-dichloroethane; DME = dimethoxyethane; THF = tetrahydrofuran; DMF = *N*,*N*-dimethylformamide

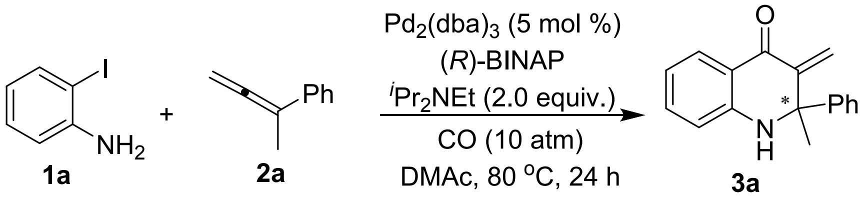
Table S3. Solvent screening with the employment of (*R*)-BTFM-Garphos



entry	solvent	yield (%)	er
1	toluene	trace	60: 40
2	DMAc	58	86: 14
3	DCE	trace	---
4	DME	trace	---
5	THF	25	86: 14
6	DMF	54	83: 17

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), (*R*)-BTFM-Garphos (0.012 mmol, 6 mol%), CO (10 atm), solvent (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (er) was determined by chiral HPLC. DMAc = *N,N*-dimethylacetamide; DCE = 1,2-dichloroethane; DME = dimethoxyethane; THF = tetrahydrofuran; DMF = N,N-dimethylformamide

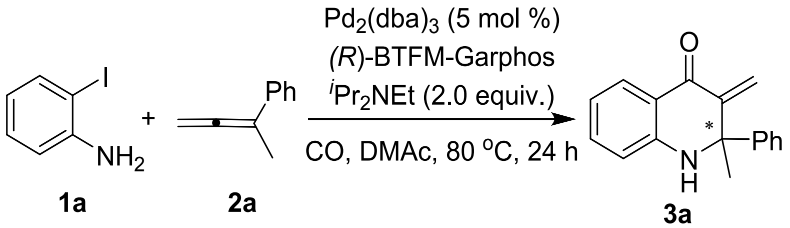
Table S4. Effects of the Pd/P molar ratio on yield and enantioselectivity by (*R*)-BINAP



(*R*)-BINAP (mol%)	0	2.5	5.0	6.0	7.0	8.0	10.0	12.0
yield (%)	16	60	88	86	<10	trace	trace	trace
e.r.	0	63: 37	75: 25	76: 24	78: 22	---	---	---

Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), $^i Pr_2NEt$ (0.4 mmol), CO (10 atm), DMAc (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (e.r.) was determined by chiral HPLC.

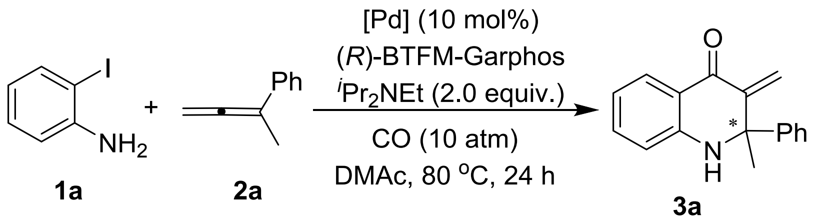
Table S5. Effects of the Pd/P molar ratio and CO pressure on yield and enantioselectivity by (*R*)-BTFM-Garphos



(*R*)-BTFM-Garphos (mol%)	6.0	6.0	6.0	7.5	10.0
CO (atm)	10	5	1	5	5
yield (%)	56	58	54	36	34
e.r.	87: 13	86: 14	87: 13	89: 11	90: 10

Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), $^i Pr_2NEt$ (0.4 mmol, 2.0 equiv.), CO, DMAc (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (e.r.) was determined by chiral HPLC.

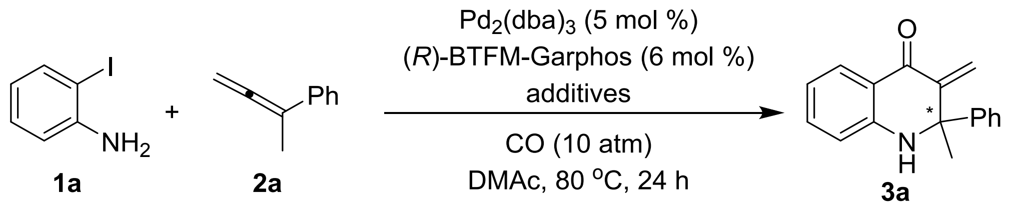
Table S6. The evaluation of different Pd sources and racemic background reaction.



[Pd]	(*R*)-BTFM-Garphos	conv. of **1a** (%)	conv. of **2a** (%)	yield of **3a** (%)	er
-/-	-	<5	<5	0	-
$Pd_2(dba)_3$	-	>99	>99	11	-
PdI_2	-	>99	>99	12	-
PdI_2	6 mol%	>99	>99	20	77: 23
PdI_2	10 mol%	>99	60	32	87: 13
10wt% Pd/C	-	>99	>99	13	-
10wt% Pd/C	6 mol%	>99	42	29	90: 10

Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), [Pd] (0.02 mmol, 5 mol%), ^{i}Pr$_2$NEt (0.4 mmol, 2.0 equiv.), CO (10 atm), DMAc (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (er) was determined by chiral HPLC.

Table S7. The effect of additives and substrate feeding manner on the product yield and enantioselectivity

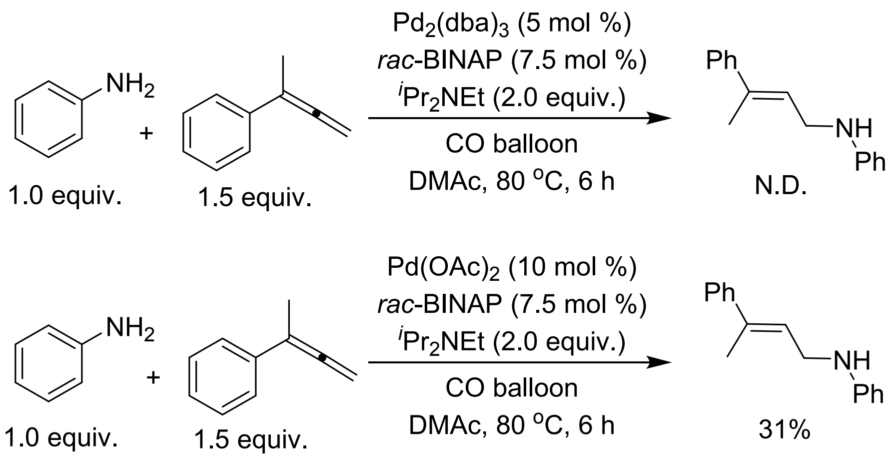


entry	Additives	Yield (%)	er
1	K_2CO_3 (2.0 equiv.)	N.D.	---
2	NEt_3 (2.0 equiv.)	<10	---
3	DBU (2.0 equiv.)	trace	---
4	DMAP (2.0 equiv.)	N.D.	---
5	K_2CO_3 (2.0 equiv.), PivOH (1.0 equiv.)	43	72: 28
6	^{i}Pr$_2$NEt (2.0 equiv.), CsOPiv (1.0 equiv.)	N.D.	---
7	^{i}Pr$_2$NEt (2.0 equiv.), $CsCO_3$ (1.0 equiv.)	trace	---
8	^{i}Pr$_2$NEt (2.0 equiv.), Ag_3PO_4 (33 mol %)	60	84: 16
9	^{i}Pr$_2$NEt (2.0 equiv.), Ag_2CO_3 (50 mol %)	trace	---
10	DABCO (2.0 equiv.)	trace	---
11[b]	^{i}Pr$_2$NEt (2.0 equiv.)	34	90: 10
12[a,b]	^{i}Pr$_2$NEt (2.0 equiv.)	50	89: 11
13[a,c]	^{i}Pr$_2$NEt (2.0 equiv.), AgOTf (1.0 equiv.)	95	85: 15
14[b]	^{i}Pr$_2$NEt (2.0 equiv.), $AgBF_4$ (1.0 equiv.)	29	92: 8

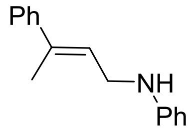
15[a,c]	^{i}Pr$_2$NEt (2.0 equiv.), $AgBF_4$ (1.0 equiv.)	96 (88)	89: 11
16[b,d]	^{i}Pr$_2$NEt (2.0 equiv.)	0	-
17[b,e]	^{i}Pr$_2$NEt (2.0 equiv.)	0	-

Unless otherwise noted, reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), Pd$_2$(dba)$_3$ (0.01 mmol， 5 mol%), ligand (0.012 mmol), additive (0.4 mmol), CO (10 atm), solvent (1.0 mL). Yield was determined by GC using decane as internal standard. Enantiomeric ratio (er) was determined by chiral HPLC. In the parentheses was isolated yield. [a]CO balloon (1 atm) instead of 10 atm CO, substrate **1a** was dissolved in 0.5 mL DMAc and fed into the reaction solution (0.5 mL DMAc) with programmable syringe pump in 6 h. [b](*R*)-BTFM-Garphos (0.02 mmol, 10 mol%). [c](*R*)-BTFM-Garphos (0.024 mmol). [d]2-bromoaniline (0.2 mmol, 1.0 equiv.) instead of **1a**. [e]2-amino phenyl triflate (0.2 mmol, 1.0 equiv.) instead of **1a**. DMAP = 4-dimethylaminopyridine; DBU = 1,8-Diazabicyclo(5.4.0)undec-7-ene.

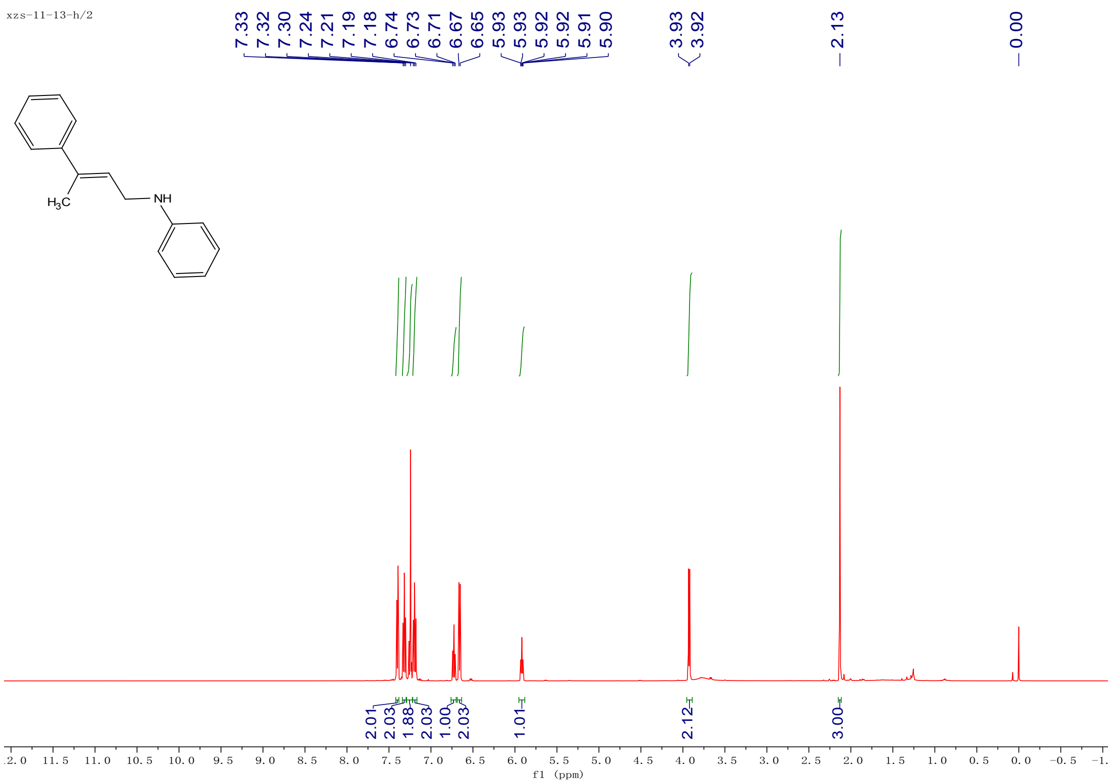
To elucidate the reaction mechanism, control experiments were carried out as follows:

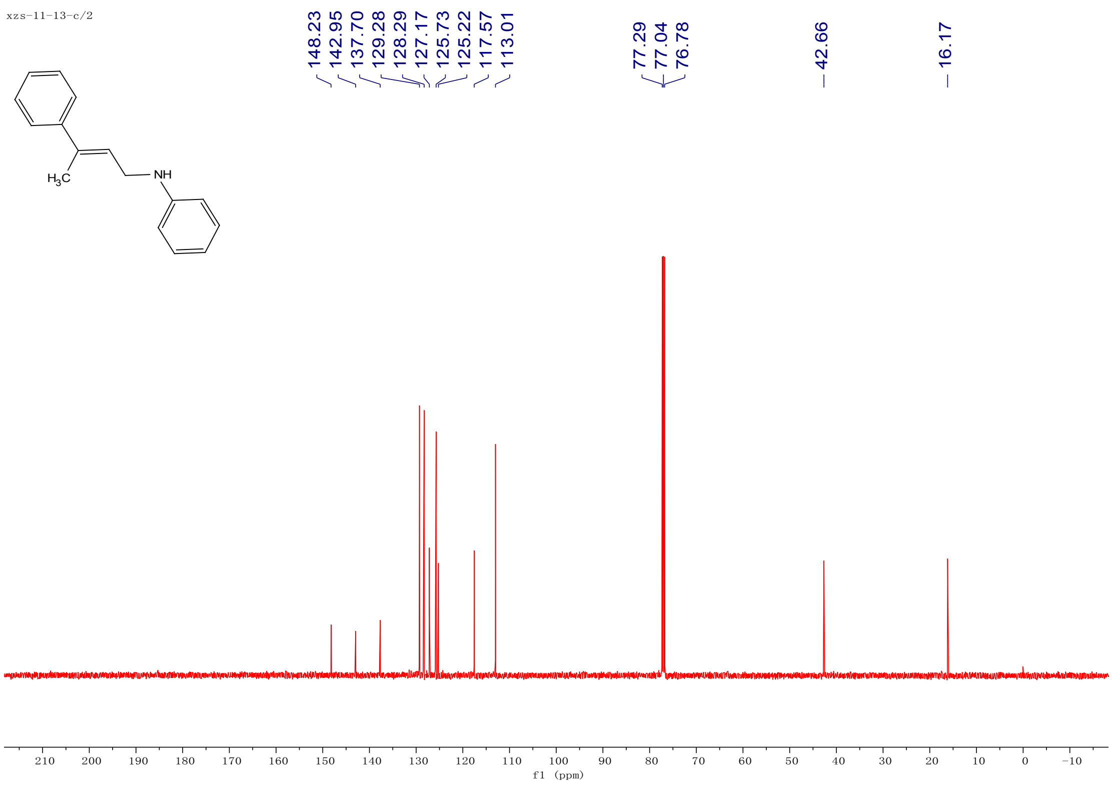


To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, aniline (0.2mmol, 1.0 equiv.), allene (0.3 mmol), the corresponding Pd complex (0.02 mmol Pd), *rac*-BINAP (0.015 mmol), ^{i}Pr$_2$NEt (0.4 mmol) and anhydrous DMAc (1.0 mL) were added and stirred for 24 h at 80 ^{o}C under CO atmosphere. Upon completion of the reaction, the pure product was isolated by column chromatography on silica gel (PE/EA = 10:1, v/v) as a yellow oil in 31% yield (13.9 mg).



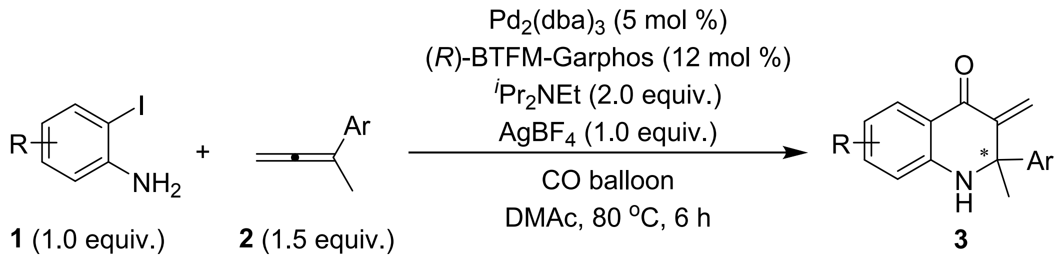
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 2H), 7.34 - 7.29 (m, 2H), 7.29 - 7.22 (m, 2H), 7.22 - 7.17 (m, 2H), 6.76 – 6.70 (m, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.96 - 5.88 (m, 1H), 3.92 (d, J = 6.5 Hz, 2H), 2.15 - 2.11 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.23, 142.95, 137.70, 129.28, 128.29, 127.17, 125.73, 125.22, 117.57, 113.01, 42.66, 16.17.





Using aniline instead of *o*-iodoaniline as the reaction substrate under otherwise identical reaction conditions, no conversion of aniline and allene was observed. Replacing Pd(0) pre-catalyst by $Pd(OAc)_2$ resulted in 31% yield of hydroamination product. Based on these results and the catalytic cycle proposed by Alper (F. Ye and H. Alper, Ionic-Liquid-Promoted Palladium-Catalyzed Multicomponent Cyclocarbonylation of o-Iodoanilines and Allenes To Form Methylene-2,3-dihydro-1H-quinolin-4-ones. *J. Org. Chem.*, **2007**, *72*, 3218-3222), the enantioselective carbonylative Heck reaction started with the oxidative addition of aryl halide to Pd(0) followed by CO addition to generate Pd(II)-benzoyl intermediates. The addition of acylpallladium intermediate to the allene can give a π-allylpalladium species, which was attacked by the amino group. Final reductive elimination of palladium-amino species gave the product and regenerated the catalyst. We have attempted to give an appropriate mechanistic pathway for the stereochemistry in the illustration manner, however we found it would provide misinformation to the readers due to the following reasons: (1) It is reasonable to envisage that the stereochemistry of carbonylative product should be determined by the elementary step of adding Pd-C bond of the Pd(II)-benzoyl intermediates to the internal C=C bond of allene. In this work, we found that the enantioselectivity of product is insensitive to the ratio of bis-phosphine ligand to Pd (details see Table S4 and S5). Moreover, in the afforded Pd(II)-benzoyl intermediate, the coordination of NH_2 group at the ortho position to Pd(II) center is also plausible since the probable formation of stable five-membered ring. Thus, the coordination mode of chiral bis-phosphine ligand (BINAP or BTFM-Garphos) with Pd center is rather hard to be elucidated, and the scenario of chiral bis-phosphine ligand acting as monodentate ligand for the coordination with Pd center cannot be completely excluded. (2) The outcomes indicate that adding silver salt is crucial the yield of product **1a** but has far less significant impact on the enantioselectivity. Empirically, adding silver salt is for removing the coordinative iodide anion from the reaction by forming insoluble salt of AgI. In our work, we cannot ensure whether the iodide anion is still coordinating with Pd(II) or not when the Pd-C bond of the Pd(II)-benzoyl intermediate is added on the internal C=C bond of allene. Therefore, in order to avoid conveying incorrect mechanism to the readers, we did not provide a mechanistic pathway for the stereochemistry.

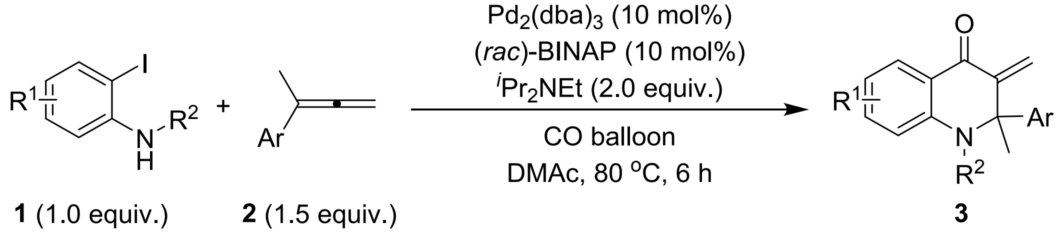
4. Enantioselective carbonylative Heck reaction of *o*-iodoanilines with allenes



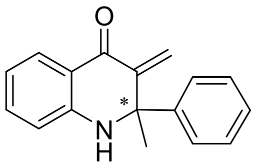
4.1 General procedure for enantioselective carbonylative Heck reaction

In a N_2-filled glove box, an oven-dried 10 mL Schlenk tube was charged with a PTFE-coated magnetic stirring bar, $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), (*R*)-BTFM-Garphos (28.5 mg, 0.024 mmol), DMAc (0.5 mL) and then the solution was stirred for 30 minutes. Then, the stirring was suspended and in the still state, allene **2** (0.3 mmol), ^{i}Pr$_2$NEt (0.4 mmol), $AgBF_4$ (0.2 mmol) were added. Afterwards, the Schlenk tube was moved out of the glove box. The tube was evacuated and backfilled with CO for three times via cannula in a well-ventilated fumehood. After being charged with CO balloon, the reaction was stirred and heated to 80 °C in oil bath. Substrate **1** dissolving in DMAc (0.5 mL) was slowly added into the reaction solution by programmed syringe pump in 6 h. Upon completion of the reaction, the reaction mixture was cooled down to room temperature in water bath and the excess CO was carefully released in a well-ventilated fume hood. Then, ethylenediaminetetraacetic acid tetrasodium salt hydrate ($EDTANa_4$, ca. 100 mg) was added for chelating and removing the palladium complexes, and afterwards the mixture was stirred for two minutes. The resulting mixture was filtrated through a short column (ca. 12 cm) packed with aluminium oxide (basic, pH 9~10) and eluted with ethyl acetate. The organic phase was washed with deionized water for 3 times and dried over anhydrous Na_2SO_4. The pure products were isolated by column chromatography on silica gel (PE/EA = 10:1, v/v). The enantiomeric ratio (er) was determined by chiral HPLC with a mobile phase system containing ^{n}hexane and ^{i}PrOH.

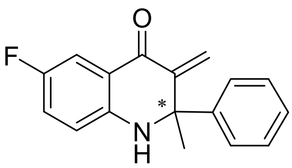
Note: Racemic carbonylative Heck reaction products were prepared using *rac*-BINAP instead of (*R*)-BTFM-Garphos.



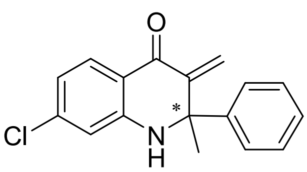
4.2 Characterization data of products bearing aza-quaternary carbon center



3a Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a yellow solid (43.9 mg, 88% yield). $[\alpha]_D^{25}$ = 95.167 (*c* = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.42 - 7.36 (m, 2H), 7.32 - 7.24 (m, 3H), 7.23 - 7.17 (m, 1H), 6.76 - 6.60 (m, 2H), 6.35 (s, 1H), 5.40 (s, 1H), 4.96 (br, 1H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.75, 149.94, 148.39, 144.22, 135.64, 128.52, 128.39, 127.47, 126.25, 121.28, 118.52, 118.26, 115.71, 62.29, 28.78. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{15}NNaO$ 272.1046, found 272.1043. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 240 nm, t_R = 6.1 min, t_R = 6.9 min) (89: 11 er). After recrystallization with petroleum ether/dichloromethane, 33.3 mg product was obtained in 66% yield with 99: 1 er

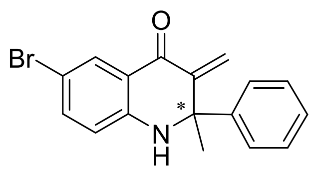


3b Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a yellow solid (48.6 mg, 90% yield). $[\alpha]_D^{25}$ = 41.445 (*c* = 0.3, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 9.0 Hz, 3.0 Hz,, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.25 (m, 2H), 7.24 - 7.17 (m, 1H), 7.06 (td, *J* = 8.6 Hz, 3.0 Hz, 1H), 6.68 (q, *J* = 4.0 Hz, 1H), 6.37 (s, 1H), 5.45 (s, 1H), 4.90 (br, 1H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.15 (d, $J_{C\text{-}F}$ = 2.25 Hz), 155.90 (d, $J_{C\text{-}F}$ = 237.5 Hz), 147.14 (d, $J_{C\text{-}F}$ = 147.5 Hz), 143.88, 128.57, 127.57, 126.19, 123.69 (d, $J_{C\text{-}F}$ = 25.0 Hz), 121.84, 118.87 (d, $J_{C\text{-}F}$ = 6.25 Hz), 117.23 (d, $J_{C\text{-}F}$ = 6.25 Hz), 113.04, 112.87, 62.40, 28.72. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -125.86. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}FNNaO$ 290.0952, found 290.0945. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 237 nm, t_R = 6.1 min, t_R = 7.1 min) (80: 20 er).

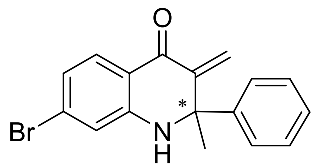


3c Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v:v) to provide the title compound as a light yellow solid (49.5 mg, 87% yield). $[\alpha]_D^{25}$ = 14.500 (*c* = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 10.0 Hz, 1H), 7.38 (d, *J* = 10.0 Hz, 2H), 7.34 -7.28 (m, 2H), 7.27 -7.22 (m, 1H), 6.73 (d, *J* = 1.5 Hz, 1H), 6.67 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.36 (s, 1H), 5.42 (s, 1H), 4.94 (br, 1H), 1.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.83, 150.27, 147.77, 143.74, 141.77, 130.03, 128.64, 127.68, 126.15, 121.80, 118.98, 117.03, 115.07, 62.42, 28.74. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{35}ClNNaO$ 306.0656, found 306.0649; $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{37}ClNNaO$ 308.0627, found 308.0635. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 243 nm, t_R = 5.6

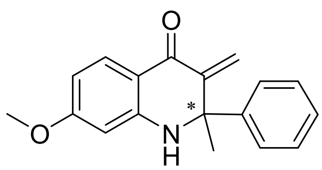
min, t_R = 6.3 min) (88: 12 er). After recrystallization with petroleum ether/dichloromethane, 24.4 mg product in 43% yield was obtained with 95: 1 er.



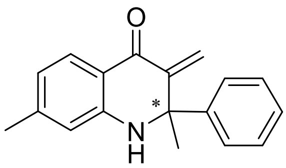
3d Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a yellow solid (53.0 mg, 80% yield). $[\alpha]_D^{25}$ = 88.667 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, J = 2.5 Hz, 1H), 7.39 - 7.33 (m, 3H), 7.32 - 7.26 (m, 2H), 7.25 - 7.20 (m, 1H), 6.63 (d, J = 10.0 Hz, 1H), 6.36 (s, 1H), 5.44 (s, 1H), 5.00 (br, 1H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.69, 148.66, 147.54, 143.68, 138.16, 130.64, 128.64, 127.67, 126.14, 122.00, 119.73, 117.64, 110.40, 62.28, 28.68. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{79}BrNNaO$ 350.0151, found 350.0146; $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{81}BrNNaO$ 352.0131, found 352.0130. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 244 nm, t_R = 6.7 min, t_R =7.8 min) (87: 13 er).



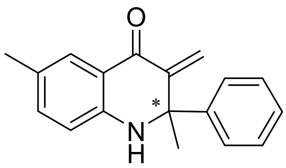
3e Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (53.6 mg, 81% yield). $[\alpha]_D^{25}$ = 22.833 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.26 - 7.20 (m, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 6.35 (s, 1H), 5.41 (s, 1H), 4.93 (br, 1H), 1.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.99, 150.27, 147.77, 143.72, 130.63, 129.97, 128.65, 127.69, 126.15, 121.82, 121.76, 118.14, 117.34, 62.41, 28.72. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{79}BrNNaO$ 350.0151, found 350.0151; $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{81}BrNNaO$ 352.0131, found 352.0127. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 245 nm, t_R = 5.8 min, t_R = 6.5 min) (88: 12 er).



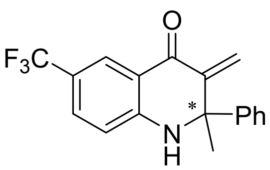
3f Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10:1, v: v) to provide the title compound as a light yellow solid (47.8 mg, 85% yield). $[\alpha]_D^{25}$ = -28.333 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 6.33 (s, 1H), 6.29 (dd, J = 9.0 Hz, 2.0 Hz, 1H), 6.13 (d, J = 2.5 Hz, 1H), 5.37 (s, 1H), 4.99 (br, 1H), 3.78 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.22, 165.86, 151.84, 148.41, 144.48, 130.67, 128.48, 127.43, 126.14, 120.69, 112.86, 107.13, 98.00, 62.40, 55.35, 28.87. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO_2$ 302.1151, found 302.1154. **HPLC** Chiralpak®OD-3 (*n*-hexane/*i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 241 nm, t_R = 7.3 min, t_R = 9.9 min) (90: 10 er). After recrystallization with petroleum ether/dichloromethane, 33.3 mg product in 62% yield was obtained with 95.5: 4.5 er.



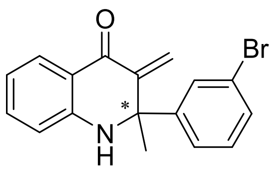
3g Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (45.2 mg, 85% yield). $[\alpha]_D^{25}$ = 33.000 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.0 Hz, 2H), 7.32 - 7.25 (m, 2H), 7.23 - 7.18 (m, 1H), 6.55 - 6.48 (m, 2H), 6.33 (s, 1H), 5.37 (s, 1H), 4.83 (br, 1H), 2.27, (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.25, 149.99, 148.53, 146.82, 144.41, 128.49, 128.39, 127.41, 126.22, 120.98, 120.00, 116.46, 115.61, 62.27, 28.83, 21.98. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO$ 286.1202, found 286.1202. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 242 nm, t_R = 5.7 min, t_R = 7.3 min) (86: 14 er).



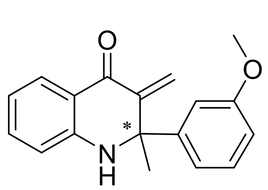
3h Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10:1, v: v) to provide the title compound as a light yellow solid (44.8 mg, 85% yield). $[\alpha]_D^{25}$ = 68.500 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.30 - 7.24 (m, 2H), 7.23 - 7.17 (m, 1H), 7.13 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.35 (s, 1H), 5.41 (s, 1H), 4.83 (br, 1H), 2.19 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.84, 148.56, 148.03, 144.37, 136.97, 128.48, 127.83, 127.54, 127.39, 126.22, 121.09, 118.44, 115.79, 62.32, 28.83, 20.29. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO$ 286.1202, found 286.1206. **HPLC** Chiralpak®OD-3 (n-hexane/i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 240 nm, t_R = 6.0 min, t_R = 6.7 min) (82: 18 er).



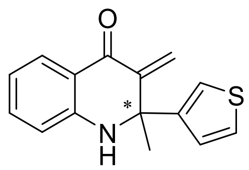
3i Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (30.0 mg, 47% yield). $[\alpha]_D^{25}$ = 63.000 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.50 (dd, J = 9.0 Hz, 2.0 Hz, 1H), 7.42 - 7.35 (m. 2H), 7.34 - 7.29 (m. 2H), 7.28 - 7.22 (m, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.38 (s, 1H), 5.44 (s, 1H), 5.18 (br, 1H), 1.82 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.79, 151.41, 147.38, 143.40, 131.73 (q, J_{C-F} = 3.25 Hz), 128.72, 127.85, 126.36 (q, J_{C-F} = 3.75 Hz), 126.12, 124.22 (q, J_{C-F} = 268.75 Hz), 122.34, 120.33 (q, J_{C-F} = 33.75 Hz), 117.42, 115.97, 62.32, 28.63. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -61.94. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{14}F_3NNaO$ 340.0920, found 340.0918. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 80 : 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 244 nm, t_R = 6.1 min, t_R = 7.1 min) (88: 12 er).



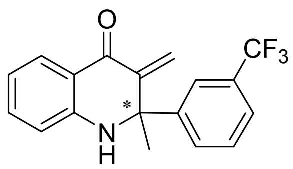
3j Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (25.2 mg, 38% yield). $[\alpha]_D^{25}$ = 87.000 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 1H), 7.58 - 7.52 (m, 1H), 7.40 - 7.29 (m, 3H), 7.15 (t, J = 8.0 Hz, 1H), 6.73 (t, J = 8.0 Hz, 2H), 6.38 (s, 1H), 5.44 (s, 1H), 4.87 (br, 1H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.33, 149.48, 147.67, 146.85, 135.81, 130.71, 130.08, 129.51, 128.45, 124.91, 122.87, 121.76, 118.63, 118.57, 115.68, 62.05. 28.77 **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{79}BrNNaO$ 350.0151, found 350.0153; $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{81}BrNNaO$ 352.0131, found 352.0137. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 239 nm, t_R = 6.3 min, t_R = 7.5 min) (90: 10 er).



3k Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (46.2 mg, 82% yield). $[\alpha]_D^{25}$ = 75.833 (c = 0.3, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.02 - 6.89 (m, 2H), 6.79 - 6.72 (m, 1H), 6.72 - 6.63 (m, 2H), 6.35 (s, 1H), 5.42 (s, 1H), 4.93 (br, 1H), 3.73 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.65, 159.69, 149.91, 148.23, 146.04, 135.63, 129.52, 128.39, 121.29, 118.69, 118.56, 118.29, 115.69, 112.76, 112.30, 62.28, 55.20, 28.74. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO_2$ 302.1151, found 302.1157. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 240 nm, t_R = 8.1 min, t_R =10.4 min) (82: 18 er).

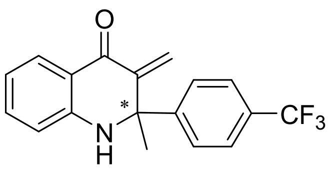


3l Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (36.5 mg, 71% yield). $[\alpha]_D^{25}$ = 68.677 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.33 - 7.27 (m, 1H), 7.27 - 7.23 (m, 1H), 7.18 - 7.10 (m, 1H), 7.05 (dd, J = 5.0 Hz, 1.0 Hz, 1H), 6.78 - 6.70 (m, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.30 (s, 1H), 5.30 (s, 1H), 4.79 (br, 1H), 1.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.45, 149.69, 148.12, 146.39, 135.65, 128.40, 126.60, 126.39, 122.08, 121.21, 118.38, 118.26, 115.70, 60.45, 28.32. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{15}H_{13}NNaOS$ 278.0610, found 278.0613. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 95: 5, flow rate = 1.0 mL/min, UV-vis detection at λ = 238 nm, t_R = 17.5 min, t_R = 18.5 min) (73: 27 er).

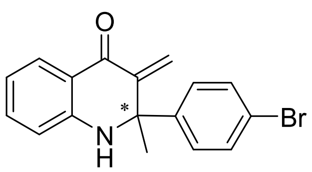


3m Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (33.0 mg, 52% yield). $[\alpha]_D^{25}$ = 74.833 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500

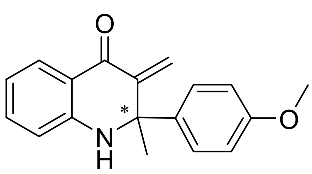
MHz, $CDCl_3$) δ 7.82 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.68 (s, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.36 - 7.30 (m, 1H), 6.79 - 6.68 (m, 2H), 6.39 (s, 1H), 5.42 (s, 1H), 4.99 (br, 1H), 1.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.26, 149.51, 147.77, 145.58, 135.89, 130.93 (q, J_{C-F} = 31.25 Hz), 129.83, 129.07, 128.43, 124.51 (q, J_{C-F} = 3.75 Hz),123.96 (q, J_{C-F} = 270.0 Hz), 122.96 (q, J_{C-F} = 3.75 Hz), 121.87, 118.71, 118.55, 115.71, 62.20, 28.66. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.53. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{14}F_3NNaO$ 340.0920, found 340.0919. **HPLC** Chiralpak®OD-3 (*n*-hexane/*i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 237 nm, t_R = 4.9 min, t_R = 5.3 min) (88: 12 er).



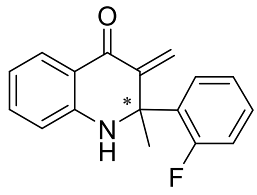
3n Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (39.6 mg, 62% yield). $[\alpha]_D^{25}$ = 109.170 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.56 - 7.46 (m, 4H), 7.36 - 7.29 (m, 1H), 6.80 - 6.68 (m, 2H), 6.39 (s, 1H), 5.49 (s, 1H), 5.01 (br, 1H), 1.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.50, 149.63, 148.50, 147.67, 135.91, 129.72 (q, J_{C-F} = 32.5 Hz), 128.41, 126.63, 125.52 (q, J_{C-F} = 3.75 Hz), 123.95 (q, J_{C-F} =271.25 Hz), 121.61, 118.66, 118.57, 115.71, 62.14, 28.67. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.56. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{14}F_3NNaO$ 340.0920, found 340.0919. **HPLC** Chiralpak®OD-3 (*n*-hexane/*i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 237 nm, t_R = 4.9 min, t_R = 5.6 min) (91: 9 er).



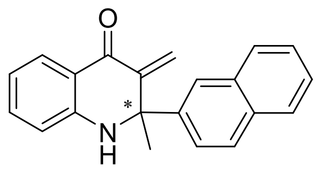
3o Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10:1, v: v) to provide the title compound as a light yellow solid (58.5 mg, 89% yield). $[\alpha]_D^{25}$ = 131.830 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.31(t, J = 7.5 Hz, 1H), 7.28 - 7.22 (m, 2H), 6.78 - 6.67 (m, 2H), 6.35 (s, 1H), 5.43 (s, 1H), 5.04 (br, 1H), 1.74 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.60, 149.72, 147.93, 143.46, 135.80, 131.62, 128.38, 128.09, 121.52, 121.38, 118.54, 118.52, 115.74, 61.98, 28.61. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{79}BrNNaO$ 350.0151, found 350.0148; $[M+Na]^+$ calcd. for $C_{17}H_{14}{}^{81}BrNNaO$ 352.0131, found 352.0130. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 238 nm, t_R = 5.7 min, t_R = 7.3 min) (81: 19 er).



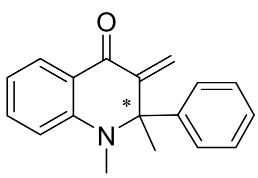
3p Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (51.0 mg, 91% yield.) $[\alpha]_D^{25}$ = 58.833 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 - 7.76 (m, 1H), 7.35 - 7.25 (m, 3H), 6.83 - 6.75 (m, 2H), 6.73 - 6.65 (m, 2H), 6.31 (s, 1H), 5.35 (s, 1H), 4.96 (br, 1H), 3.73 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.89, 158.83, 149.98, 148.69, 136.14, 135.60, 128.35, 127.54, 121.02, 118.45, 118.15, 115.74, 113.81, 61.90, 55.25, 28.71. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{18}H_{17}NNaO_2$ 302.1151, found 302.1147. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 238 nm, t_R = 6.4 min, t_R = 8.2 min) (79: 21 er).



3q Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10: 1, v: v) to provide the title compound as a light yellow solid (39.6 mg, 74% yield). $[\alpha]_D^{25}$ = 345.890 (c = 0.3, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.30 - 7.26 (m, 1H), 7.25 - 7.15 (m, 2H), 7.06 - 6.95 (m, 2H), 6.75 - 6.64 (m, 2H), 6.52 (s, 1H), 5.66 (s, 1H), 5.17 (br, 1H), 1.91(s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 184.10, 160.90 (d, J_{C-F} = 245.0 Hz), 149.97, 146.72, 135.57, 131.44 (d, J_{C-F} = 8.75 Hz), 129.57 (d, J_{C-F} = 8.75 Hz), 129.10 (d, J_{C-F} = 3.75 Hz), 128.15, 124.02 (d, J_{C-F} = 3.75 Hz), 122.12, 118.60, 118.35, 116.87 (d, J_{C-F} = 23.75 Hz), 115.72, 61.45 (d, J_{C-F} = 1.25 Hz), 26.63 (d, J_{C-F} = 3.1 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -114.22. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}FNNaO$ 290.0952, found 290.0948. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 237 nm, t_R = 5.2 min, t_R =5.7 min) (95: 5).



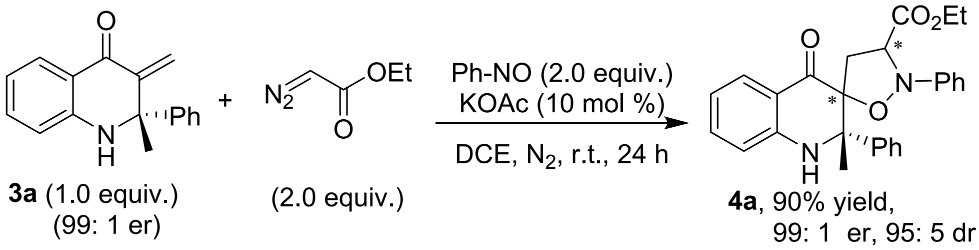
3r Following the general procedure, the crude product was purified by column chromatography (PE: EA = 10:1, v: v) to provide the title compound as a light yellow solid (48.5 mg, 80% yield. $[\alpha]_D^{25}$ = 164.830 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 - 7.78 (m, 2H), 7.78 - 7.70 (m, 3H), 7.52 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.47 - 7.38 (m, 2H), 7.35 - 7.27 (m, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.41 (s, 1H), 5.41 (s, 1H), 4.98 (br, 1H), 1.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.63, 149.85, 148.19, 141.55, 135.68, 132.94, 132.61, 128.48, 128.44, 128.18, 127.48, 126.34, 126.29, 125.21, 124.55, 121.76, 118.53, 118.37, 115.73, 62.43, 28.62. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{21}H_{17}NNaO$ 322.1202, found 322.1196. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 223 nm, t_R = 9.5 min, t_R =15.8 min) (79: 21 er).



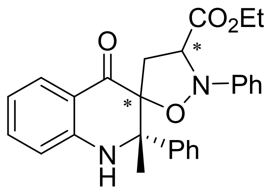
3s Following the general procedure, the crude product was purified by column chromatography (PE: EA = 20: 1, v: v) to provide the title compound as a yellow oil (7.9 mg, 15% yield). $[\alpha]_D^{25}$ = -298.75 (c = 0.16, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.47 - 7.41 (m, 3H), 7.40 - 7.36 (m, 2H), 7.35 - 7.30 (m, 1H), 6.82 - 6.71 (m, 2H), 6.26 (d, J = 1.0 Hz, 1H), 4.73 (d, J = 1.0 Hz, 1H), 2.68 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.31, 151.31, 150.43, 144.34, 136.12, 128.71, 128.47, 127.79, 127.68, 123.91, 118.35, 117.21, 113.69, 68.72, 34.62, 22.88. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for

$C_{18}H_{17}NNaO$ 286.1202, found 286.1196. **HPLC** Chiralpak®OD-3 (*n*-hexane: *i*-PrOH = 95: 5, flow rate = 1.0 mL/min, UV-vis detection at UV-vis detection at λ = 242 nm, t_R = 6.4 min, t_R = 6.7 min) (85: 14 er)

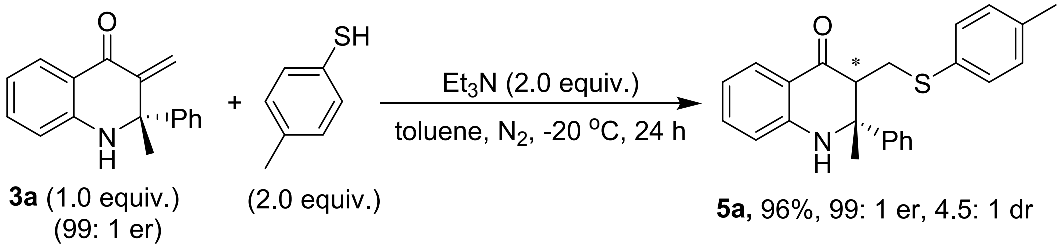
5. Further transformations of chiral product 3a to compounds containing a pair of vicinal chiral centers or multiple chiral centers.



To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, **3a** (0.2mmol, 1.0 equiv.), PhNO (0.4 mmol), KOAc (0.02 mmol), ethyl diazoacetate (0.4 mmol) and anhydrous 1,2-dichloroethane (2.0 mL) were added and stirred for 24 h at room temperature under N_2 atmosphere. Upon the completion of reaction monitored by TLC, the pure product was isolated by column chromatography on silica gel (PE: EA = 10: 1, v: v) as a yellow solid (80.2 mg, 90% yield, 99: 1 e.r., 95: 5 d.r).

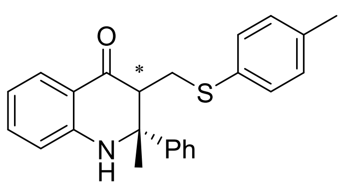


4a $[\alpha]_D^{25}$ = 132.63 (c = 0.2, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.0 Hz, 2H), 7.39 - 7.34 (m, 1H), 7.29 - 7.23 (m, 3H), 7.12 - 7.05 (m, 2H), 6.87 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.74 - 6.67 (m, 2H), 4.78 (s, 1H), 4.43 (t, J = 8.0 Hz, 1H), 4.23 - 4.12 (m, 2H), 3.03 - 2.90 (m, 1H), 2.90 - 2.79 (m, 1H), 1.89 (s, 3H), 1.23 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.86, 171.04, 150.51, 148.87, 140.80, 135.76, 128.61, 128.45, 128.37, 128.02, 126.82, 121.92, 117.76, 116.68, 114.82, 114.53, 87.24, 67.49, 63.00, 61.72, 36.13, 22.73, 14.09. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{27}H_{26}N_2NaO_4$ 465.1785, found 465.1787. **HPLC** Chiralpak®OD-3 (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 382 nm, t_R = 7.1 min, t_R = 21.2 min) (99: 1 e.r.). 95: 5 d.r. was determined by LC-MS.

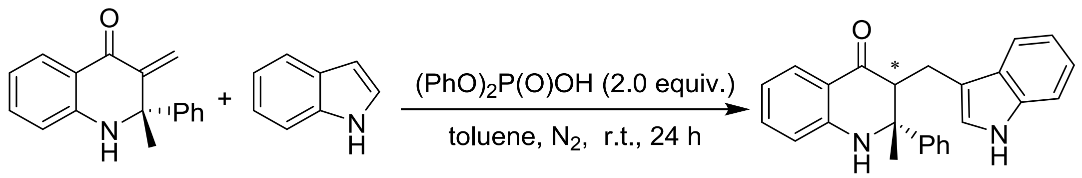


To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, **3a** (0.2 mmol, 1.0 equiv., 99: 1 er), p-toluenethiol (0.4 mmol, 2.0 equiv.), NEt_3 (0.4 mmol, 2.0 equiv.) and 2.0 mL anhydrous toluene were added and stirred for 24 h at -20 °C in thermostatic bath fulfilled with cooling EtOH under N_2 atmosphere. Upon completion of the reaction, the pure product was obtained by column chromatography on silica gel (PE/EA = 10: 1, v: v) as a light-yellow solid (72.0 mg, 96% yield), 99: 1

e.r. and 4.5: 1 d.r. were determined by chiral HPLC.

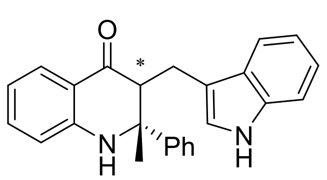


5a $[\alpha]_D^{25}$ = -87.083 (c = 0.4, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.0 Hz, 1.5 Hz, 0.2H), 7.74 (dd, J = 8.0 Hz, 1.5 Hz, 0.8H), 7.50 - 7.37 (m, 2H), 7.36 - 7.25 (m, 4H), 6.97 - 6.80 (m, 4H), 6.79 - 6.60 (m, 2H), 4.60 (br, 1H), 3.29 - 3.22 (m, 0.86H), 3.22 - 3.12 (m, 0.85H). 2.90 - 2.81 (m, 0.22H), 2.79 - 2.65 (m, 1.23H), 2.26 (s, 3H), 1.57 (s, 0.6H), 1.55 (s, 2.4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.64, 193.82, 148.77, 148.49, 143.91, 142.87, 136.06, 135.88, 135.46, 135.35, 132.54, 129.72, 129.63, 129.55, 128.86, 128.67, 127.92, 127.88, 127.77, 127.65, 126.40, 125.11, 118.39, 118.12, 117.70, 116.27, 115.36, 62.79, 62.15, 56.72, 56.69, 31.67, 29.68, 26.19, 21.02. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{24}H_{23}NNaOS$ 396.1393, found 396.1389. **HPLC** Chiralpak®AD-3 (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 369 nm, t_{R1} = 8.9 min, t_{R1} = 9.5 min; t_{R2} = 11.8 min, t_{R2} = 13.2 min) (99: 1 er, 4.5: 1 dr)



3a (1.0 equiv.) (99: 1 er)   (2.0 equiv.)   **6a,** 96%, 99: 1 er, 4.7: 1 dr

To an oven-dried 10 mL Schlenk tube charged with a stir bar, **3a** (0.2mmol, 1.0 equiv.), indole (0.4 mmol), $(PhO)_2P(O)OH$ (0.4 mmol, 2.0 equiv.) and 2.0 mL anhydrous toluene were added and stir for 24 h at room temperature under N_2 atmosphere. Upon completion of the reaction, the pure product was obtained by column chromatography on silica gel (PE: EA = 10:1, v: v) as a yellow solid (70.6 mg, 96% yield), 99: 1 er, 4.7: 1 dr were determined by chiral HPLC.



6a $[\alpha]_D^{25}$ = -121.33 (c = 0.4, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.80 (dd, J = 7.5 Hz, 1.5 Hz, 0.17H), 7.69 (dd, J = 7.5 Hz, 1.5 Hz, 0.89H), 7.65 - 7.55 (m, 2H), 7.49 - 7.27 (m, 4H), 7.24 - 7.19 (m, 1H), 7.12 - 7.03 (m, 1H), 6.97 - 6.77 (m, 3H), 6.73 - 6.55 (m, 2H), 4.59 (br, 1H), 3.35 - 3.27 (m, 0.85H), 3.24 - 3.14 (m, 0.86H), 2.92 - 2.42 (m, 1.44H), 1.65 (s, 2.4H), 1.64 (s, 0.6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ196.56, 195.68, 148.87, 145.00, 143.87, 135.94, 135.19, 128.86, 128.68, 127.77, 127.53, 127.18, 126.65, 125.24, 123.14, 121.54, 118.92, 118.45, 118.37, 117.50, 116.29, 115.21, 114.25, 112.60, 111.04, 62.91, 62.19, 58.78, 57.55, 26.35, 23.24, 20.60. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd. for $C_{25}H_{22}N_2NaO$ 389.1624, found 389.1625. **HPLC** Chiralpak®IC (n-hexane: i-PrOH = 80: 20, flow rate = 1.0 mL/min, UV-vis detection at λ = 370 nm, t_{R1} = 7.9 min, t_{R1} = 9.1 min; t_{R2} = 11.5 min, t_{R2} = 12.2 min) (99: 1 er, 4.7: 1 dr).

6. Determination of the absolute configuration of products 3a

To determine the absolute configuration of **3a**, the single crystals of product **3a** was cultivated in 25-mL vial by solvent diffusion method. Less-dense petroleum ether (10 mL) with poor solubility for **3a** was slowly dropwise added into the saturated dichloromethane solution (2 mL) of **3a** using pipette at 25 ^{o}C to form a distinct layer. With the diffusion of petroleum ether into the dichloromethane solution, the solvent mixture with lower solubility for **3a** was gradually formed under the ambient conditions. The crystals emerged in this solvent mixture, which were suitable for X-ray diffraction analysis.
The structure in Figure S1 display the (*S*)-configuration of **3a** (CCDC number: 2045084). The structure and supplementary crystallographic data for compound (*S*)-**3a** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

3a

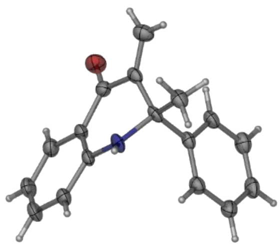


Figure S1

Table S8. Crystal data and structure refinement for exp_1230.

Identification code exp_1230
Empirical formula C51H45N3O3
Formula weight 747.90
Temperature/K 100.01(10)
Crystal system triclinic
Space group P1
a/Å 6.9249(6)
b/Å 12.8912(10)
c/Å 13.3715(12)
α/° 117.162(8)
β/° 100.783(7)
γ/° 96.082(7)
Volume/Å3 1017.97(17)
Z 1
ρcalcg/cm3 1.220
μ/mm-1 0.594
F(000) 396.0

Crystal size/mm3 0.42 × 0.26 × 0.12
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 7.71 to 134.152
Index ranges $-7 \leq h \leq 8$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$
Reflections collected 20412
Independent reflections 6625 [Rint = 0.1349, Rsigma = 0.1468]
Data/restraints/parameters 6625/3/518
Goodness-of-fit on F2 1.026
Final R indexes [I>=2σ (I)] R1 = 0.0769, wR2 =0.1859
Final R indexes [all data] R1 = 0.1051, wR2 = 0.2093
Largest diff. peak/hole / e Å-3 0.33/-0.31
Flack parameter 0.3(6)

7. Computational investigation of 1,3-dipolar cycloaddition of in-situ formed nitrone intermediate onto the alkene group of (*S*)-3a.

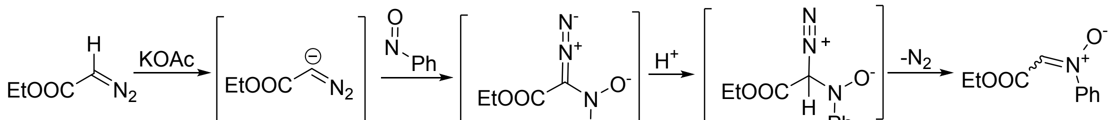
7.1 Computational methods

All DFT calculations were performed using Gaussian 16 program.[S5] Considering the applicability of hybrid meta-GGA functional M06-2X on thermochemistry, thermochemical kinetics, noncovalent interactions,[S6] geometries were optimized and characterized by frequency calculations to be local minima or transition states (**TS**) at the M06-2X/6-311+G(d) level in gas phase. Intrinsic reaction coordinate (IRC) calculations were also conducted to confirm that each transition state connects two relevant minima. The free energies (kcal/mol) at 298 K and 1 atm were generally used in the following discussions. Since the one-pot three-component 1,3-dipolar cycloaddition of ethyl 2-diazoacetate, nitrosobenzene with alkene (*R*)-**3a** employed 1,2-dichloroethane (DCE) as the solvent, the nonspecific solvation effects of DCE was considered by calculating single-point energies with the gas-phase optimized geometries in the SMD model[S7] at the level of M06-2X/6-311++G(2d,p). 3D structures were prepared by CYLview.[S8]

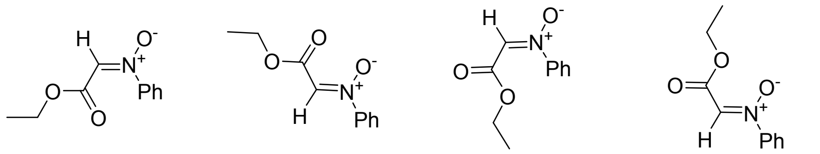
7.2 Discussion regarding the potential energy location of obtained 16 transition states for the 1,3-dipolar cycloaddition of nitrone intermediate with (*S*)-3a

According to the previous experimental study,[S9] the active nitrone intermediate 1-ethylcarboxy *N*-phenylmethanimine oxide (**A**) was in-situ formed in the reaction between ethyl 2-diazoacetate and nitrosobenzene promoted by KOAc (Figure S1). Following the hint from previous work[S10] and owing to the conjugation between ethylcarboxy group and C-N double bond, our DFT computation revealed that this reactive nitrone intermediate **A** possesses four plausible isomers **A**-(*E*)-*s*-cis, **A**-(*Z*)-*s*-cis, **A**-(*E*)-*s*-trans and **A**-(*Z*)-s-trans with different C-N double bond configuration and conformation. Although **A**-(*Z*)-*s*-cis is more stable than the other three isomers by 0.4~1.4 kcal/mol in the solvation of DCE, we still cannot completely exclude their isomerization between each other. Therefore, considering that the active nitrone intermediate **A** could be added on the alkene group of (*S*)-**3a** from either *Re*- or *Si* face of C-C double bond, we searched out all the 16 plausible transition states (**TS**) of this 1,3-dipolar cycloaddition between (*S*)-**3a** and **A** (Figure S2) and compared the location of their potential energy in the solvation of DCE. The potential energy location of $\mathbf{TS_{(S,R)}}$**-(*Z*)-*s*-trans** and $\mathbf{TS_{(S,R)}}$**-(*Z*)-*s*-cis** are much lower than the other fourteen transition stations by at least 1.1 kcal/mol (Table S8). And the corresponding energy barriers for the transformation of (*S*)-**3a** with nitrone intertmediate **A-(*Z*)-*s*-trans** or **A-(*Z*)-*s*-cis** to the product **4a** are both below 25.0 kcal/mol (Table S9). These two results well explained the observed good enantioselectivity and diastereoselectivity induced by the intervention of chiral aza-quaternary carbon center and also indicated that the obtained 1,3-cycloaddition product **4a** preferentially consisting of (*S*)-configuration oxa-quaternary carbon center and (*R*)-configuration aza-tertiary carbon center.

Figure S1. The in-situ formation of active nitrone intermediate **A** and the relative stability of its four isomers obtained by M06-2X-SCRF/6-311+G(2d,p)// M06-2X/6-311+G(d,p).

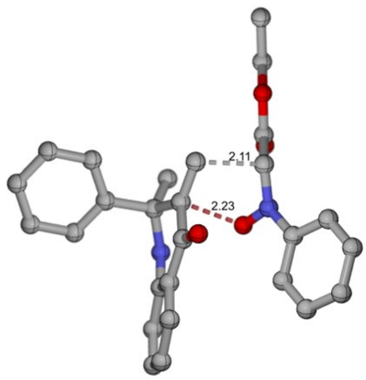


A

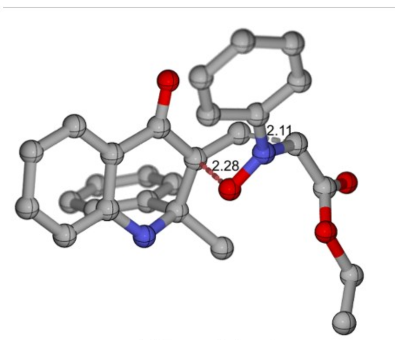


A-(*E*)-*s*-cis (0.9) **A-(*Z*)-*s*-cis** (0.0) **A-(*E*)-*s*-trans** (1.4) **A-(*Z*)-*s*-trans** (0.4)

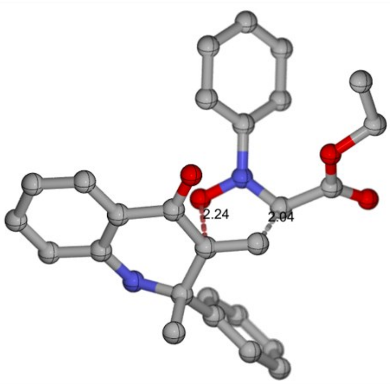
Figure S2. 3D structures of the 16 transition states respectively for the 1,3-dipolar cycloaddition between (*S*)-**3a** and nitrone intermediate **A** optimized at the level of M06-2X/6-311+G(d). The length of C-O and C-C bonds forming are marked in unit of Angstrom (Å).



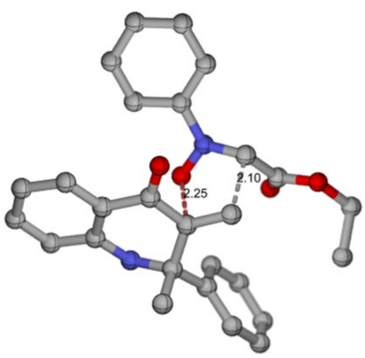
TS$_{(S,R)}$-(*Z*)-*s*-cis



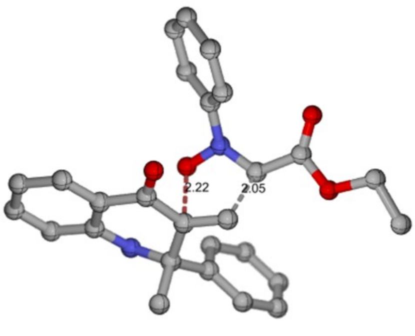
TS$_{(S,R)}$-(*Z*)-*s*-trans



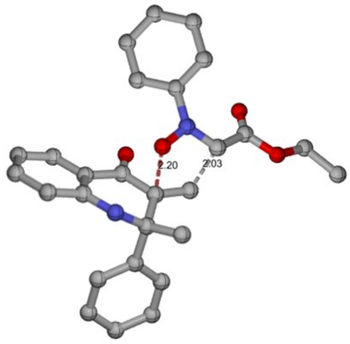
TS$_{(R,R)}$-(*E*)-*s*-trans



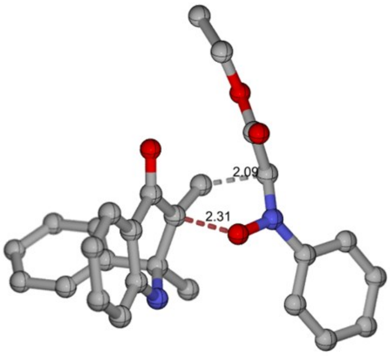
TS$_{(R,S)}$-(*Z*)-*s*-cis



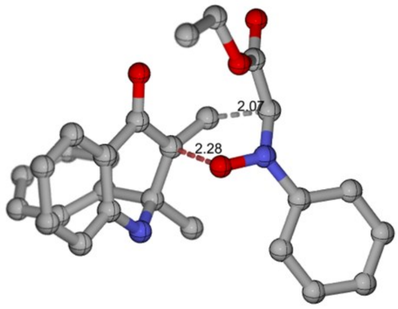
TS$_{(R,R)}$-(*E*)-*s*-cis



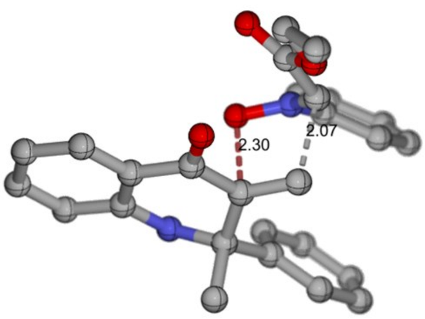
TS$_{(S,S)}$-(*E*)-*s*-cis



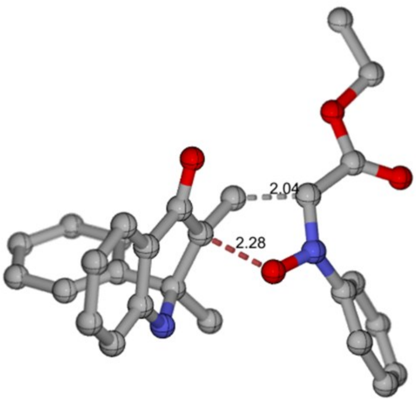
TS$_{(S,S)}$-(*Z*)-*s*-cis



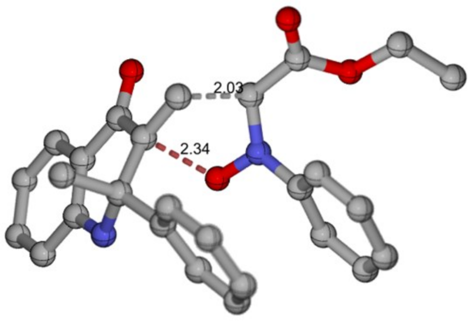
TS$_{(S,S)}$-(*Z*)-*s*-trans



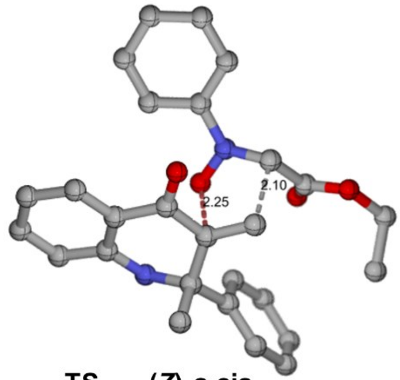
TS$_{(R,R)}$-(*Z*)-*s*-cis



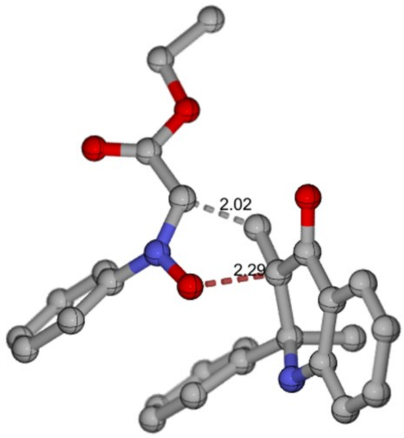
TS$_{(S,R)}$-(*E*)-*s*-cis



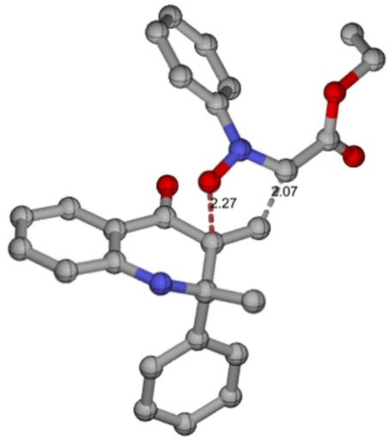
TS$_{(R,S)}$-(*E*)-*s*-trans



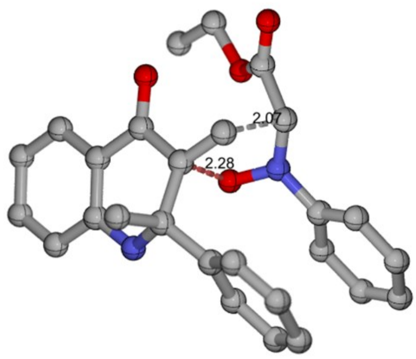
TS$_{(R,S)}$-(*Z*)-*s*-cis



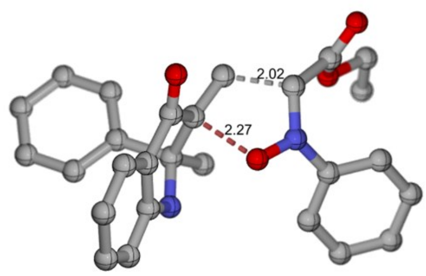
TS$_{(R,S)}$-(*E*)-*s*-cis



TS$_{(S,S)}$-(*E*)-*s*-trans



TS$_{(R,R)}$-(*Z*)-*s*-trans



TS$_{(S,R)}$-(*E*)-*s*-trans

Table S8. The relative potential energy location of 16 transition states for the 1,3-dipolar cycloaddition between nitrone intermediate **A** and (*S*)-**3a**

Transition state	Relative potential energy (kcal/mol)
TS$_{(S,R)}$-(*Z*)-*s*-trans	0.0
TS$_{(S,R)}$-(*Z*)-*s*-cis	0.2
TS$_{(R,R)}$-(*E*)-*s*-trans	1.3

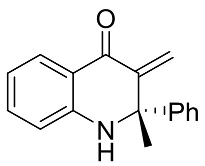
TS$_{(R,S)}$-(*Z*)-*s*-trans	1.9
TS$_{(R,R)}$-(*E*)-*s*-cis	2.3
TS$_{(S,S)}$-(*E*)-*s*-cis	2.8
TS$_{(S,S)}$-(*Z*)-*s*-cis	2.8
TS$_{(S,S)}$-(*Z*)-*s*-trans	3.4
TS$_{(R,R)}$-(*Z*)-*s*-cis	3.5
TS$_{(S,R)}$-(*E*)-*s*-cis	3.5
TS$_{(R,S)}$-(*E*)-*s*-trans	3.5
TS$_{(R,S)}$-(*Z*)-*s*-cis	3.6
TS$_{(R,S)}$-(*E*)-*s*-cis	3.6
TS$_{(S,S)}$-(*E*)-*s*-trans	4.0
TS$_{(R,R)}$-(*Z*)-*s*-trans	4.3
TS$_{(S,R)}$-(*E*)-*s*-trans	5.1

Table S9. The energy barriers corresponding to the obtained 16 transition states.

Initial state	Transition state	Energy barrier (kcal/mol)
(*R*)-3a + A-(*Z*)-*s*-trans	**TS$_{(S,R)}$-(*Z*)-*s*-trans**	23.8
(*R*)-3a + A-(*Z*)-*s*-cis	**TS$_{(S,R)}$-(*Z*)-*s*-cis**	24.4
(*R*)-3a + A-(*E*)-*s*-trans	**TS$_{(R,R)}$-(*E*)-*s*-trans**	24.0
(*R*)-3a + A-(*Z*)-*s*-trans	**TS$_{(R,S)}$-(*Z*)-*s*-trans**	25.7
(*R*)-3a + A-(*E*)-*s*-cis	**TS$_{(R,R)}$-(*E*)-*s*-cis**	25.6
(*R*)-3a + A-(*E*)-*s*-cis	**TS$_{(S,S)}$-(*E*)-*s*-cis**	26.1
(*R*)-3a + A-(*Z*)-*s*-cis	**TS$_{(S,S)}$-(*Z*)-*s*-cis**	26.9
(*R*)-3a + A-(*Z*)-*s*-trans	**TS$_{(S,S)}$-(*Z*)-*s*-trans**	27.2
(*R*)-3a + A-(*Z*)-*s*-cis	**TS$_{(R,R)}$-(*Z*)-*s*-cis**	27.7
(*R*)-3a + A-(*E*)-*s*-cis	**TS$_{(S,R)}$-(*E*)-*s*-cis**	26.8
(*R*)-3a + A-(*E*)-*s*-trans	**TS$_{(R,S)}$-(*E*)-*s*-trans**	26.3
(*R*)-3a + A-(*Z*)-*s*-cis	**TS$_{(R,S)}$-(*Z*)-*s*-cis**	27.8
(*R*)-3a + A-(*E*)-*s*-cis	**TS$_{(R,S)}$-(*E*)-*s*-cis**	27.7
(*R*)-3a + A-(*E*)-*s*-trans	**TS$_{(S,S)}$-(*E*)-*s*-trans**	26.8
(*R*)-3a + A-(*Z*)-*s*-trans	**TS$_{(R,R)}$-(*Z*)-*s*-trans**	28.1
(*R*)-3a + A-(*E*)-*s*-trans	**TS$_{(S,R)}$-(*E*)-*s*-trans**	27.9

7.3 Cartesian coordinate and electron energy of all structures

(*R*)-3a

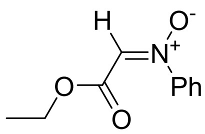


EE = -786.735272 a.u.

Thermal correction to free energy = 0.236726 a.u.
0 1

O	-0.99843400	1.96245200	-2.02192300
N	-0.51077400	0.27224200	1.63298600
C	-1.52599700	-0.20226700	0.81996900
C	-1.69178500	0.30865100	-0.47884000
C	1.51800600	-0.25891400	0.26979400
C	0.69707100	0.81903800	1.01294500
C	0.24112000	1.86129500	0.00547000
C	-2.42172400	-1.17801200	1.28365600
C	2.56976500	0.13298800	-0.56151200
C	-0.82789700	1.41266200	-0.95568700
C	1.27741900	-1.62041200	0.44281500
C	-2.72771000	-0.16581900	-1.28957500
C	-3.43991600	-1.63326300	0.46569400
C	-3.59921200	-1.13617100	-0.83252000
C	3.37061800	-0.81124000	-1.19131500
C	1.55667400	1.40650600	2.13107800
C	2.07697200	-2.56908900	-0.19025200
C	3.12699100	-2.16904600	-1.00652400
C	0.70587200	3.10252600	-0.09066600
H	-0.33585200	-0.28387900	2.45957400
H	-2.30683800	-1.57299400	2.28872200
H	2.75607200	1.18912600	-0.72863300
H	0.45316600	-1.95895800	1.05998000
H	-2.82482400	0.26020300	-2.28188000
H	-4.11992400	-2.39068000	0.84051600
H	-4.39772100	-1.50375800	-1.46506200
H	4.18051400	-0.48574600	-1.83453300
H	1.01454600	2.19578900	2.65452100
H	2.49207500	1.80568200	1.73854900
H	1.81649500	0.61884900	2.84325700
H	1.86933200	-3.62380000	-0.04830700
H	3.74599700	-2.90785800	-1.50262500
H	0.32879100	3.75370100	-0.87135600
H	1.45344200	3.50241900	0.58458100

A-(*E*)-*s*-cis



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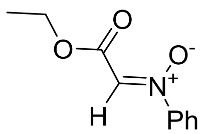
0 1

C	0.72836300	1.31303300	0.23502600
H	1.32491100	2.19695100	0.40589600
C	-1.53594300	0.42824300	0.11037400
C	-1.52185200	-0.61062300	1.02561600
C	-2.50461100	0.53878000	-0.87369900
C	-2.50569900	-1.58637700	0.93473600
H	-0.75821200	-0.65205400	1.79292000
C	-3.47181100	-0.45391900	-0.96642100
H	-2.49219700	1.39011100	-1.54292300
C	-3.47287900	-1.51312700	-0.06350400
H	-2.51552400	-2.40486800	1.64453700
H	-4.22985700	-0.39449100	-1.73830400
H	-4.23452900	-2.28117700	-0.13327600
O	-1.06917800	2.65894900	0.31991300
C	1.39738800	0.04591500	-0.09634600
O	0.90311000	-0.98468900	-0.47326300
O	2.72178200	0.22082400	0.05584500
C	3.54140400	-0.91023200	-0.27544300
C	4.97989900	-0.49914800	-0.06397600
H	3.34091700	-1.19548400	-1.31009900
H	3.25359500	-1.74894700	0.36187300
H	5.64344900	-1.33208000	-0.30292400
H	5.24003000	0.34329400	-0.70620700
H	5.15176700	-0.20867200	0.97330100
N	-0.56794400	1.51592300	0.21958200

A-(*Z*)-*s*-cis



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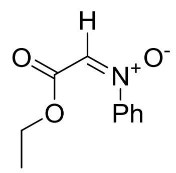
0 1

C	-0.56854100	-0.00332200	-0.02087800
H	-0.40402400	-1.03456200	-0.28426800
C	1.81016000	0.13079100	0.05084400
C	2.81597200	0.87577700	-0.54739100
C	2.04477500	-1.13312600	0.57379500
C	4.08275100	0.31871600	-0.65932600
H	2.59106500	1.87157900	-0.90721800
C	3.32125000	-1.67463900	0.46478400

H	1.25833600	-1.67324300	1.08692900
C	4.33625500	-0.95499500	-0.15652500
H	4.87542400	0.88339200	-1.13565100
H	3.52254900	-2.65514700	0.87967700
H	5.32897600	-1.38198300	-0.23886100
O	0.48636000	1.98434200	0.36136300
C	-1.94183000	0.50095600	0.10495700
O	-2.29709200	1.60919000	0.39196700
O	-2.79183900	-0.51734800	-0.15584700
C	-4.18533800	-0.19051800	-0.07091500
C	-4.96342700	-1.44417100	-0.39763400
H	-4.39838400	0.62053700	-0.77050800
H	-4.39883600	0.17656800	0.93525500
H	-6.03470000	-1.24171600	-0.34609700
H	-4.72789800	-1.79523300	-1.40333000
H	-4.72989300	-2.24095100	0.31005500
N	0.48940000	0.75835400	0.14912600

A-(*E*)-*s*-trans

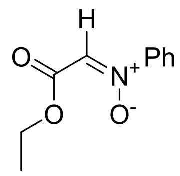


EE = -667.985883 a.u.
Thermal correction to free energy = 0.158894 a.u.
0 1

C	1.21025200	-1.80157300	0.02140900
H	1.75482700	-2.73451100	0.04586800
C	-0.97050900	-0.75688800	-0.05390500
C	-0.89538500	-0.05575000	-1.24743700
C	-1.90081600	-0.45498400	0.92576200
C	-1.76703400	1.00741900	-1.45045600
H	-0.17498000	-0.34490900	-2.00513300
C	-2.75601700	0.62052100	0.71826700
H	-1.94077500	-1.05510700	1.82635200
C	-2.68874500	1.35137400	-0.46514500
H	-1.73022300	1.56166300	-2.38098600
H	-3.48119400	0.88345400	1.47928500
H	-3.36510600	2.18311100	-0.62540400
O	-0.66902200	-2.97339700	0.45501100
C	1.97251000	-0.54871200	-0.14427700
O	3.01967000	-0.50671100	-0.73652900
O	1.41244400	0.49868300	0.46747000

C	1.99993000	1.78336800	0.21190300
C	1.09075300	2.80886200	0.84887800
H	2.08119700	1.91832900	-0.86934800
H	3.00889700	1.79882000	0.62845200
H	1.47077800	3.81494800	0.66295300
H	0.08345600	2.73283200	0.43424900
H	1.03158000	2.65608600	1.92738000
N	-0.08754700	-1.89787600	0.17124700

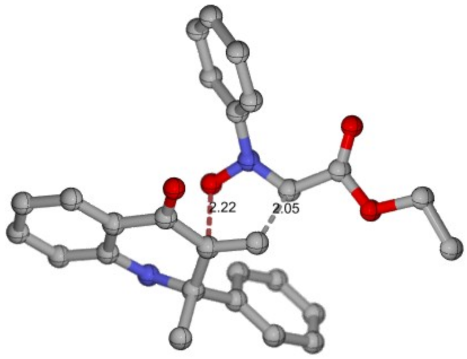
A-(*Z*)-*s*-trans



EE = -667.987560 a.u.
Thermal correction to free energy = 0.158979 a.u.
0 1

C	0.45020100	0.84025200	-0.26036100
H	-0.10060300	1.73335500	-0.50545600
C	-1.70653800	-0.12370900	0.02552500
C	-2.43309400	-1.18733400	-0.48981600
C	-2.32570100	0.98662300	0.58223800
C	-3.81959700	-1.11493800	-0.48199900
H	-1.90397300	-2.04718500	-0.87995700
C	-3.71547000	1.04098700	0.59388900
H	-1.73884200	1.78051700	1.02817700
C	-4.46136500	-0.00263100	0.05670600
H	-4.40049600	-1.93220300	-0.89282300
H	-4.21255400	1.89625400	1.03600600
H	-5.54405100	0.04526300	0.06779700
O	0.20390500	-1.38917000	0.20317800
C	1.91650500	0.96465300	-0.28371400
O	2.43192600	2.01661100	-0.57996400
O	2.58729600	-0.13147000	0.04933200
C	4.01891500	-0.00829700	0.04264400
C	4.57962600	-1.35315300	0.44169400
H	4.30505200	0.78394600	0.73763100
H	4.33826000	0.29486700	-0.95654500
H	5.67046600	-1.31363600	0.45095900
H	4.23383900	-1.63537600	1.43674200
H	4.26569700	-2.12528900	-0.26149800
N	-0.24552800	-0.24328600	-0.00031900

TS$_{(R,R)}$-(*E*)-*s*-cis

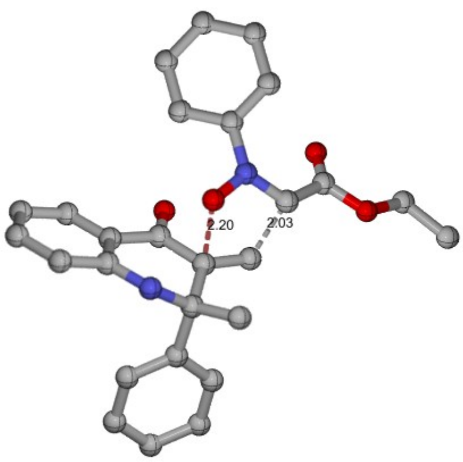


EE = -1454.706701 a.u.
Thermal correction to free energy = 0.423005 a.u.
0 1

O	1.42440500	1.34739700	-1.77305100
N	2.06476700	-2.06266500	0.35063400
C	3.15022000	-1.28074100	0.00549800
C	2.98145600	-0.11544100	-0.75978700
C	-0.26386500	-2.72511600	0.29547700
C	0.87407600	-2.08736400	-0.50393100
C	0.52047400	-0.65996300	-0.91758200
C	4.43941200	-1.61266900	0.45389300
C	-1.28241000	-3.44705500	-0.33077900
C	1.63128100	0.28791500	-1.20794100
C	-0.32635900	-2.55505100	1.68275900
C	4.08216800	0.69115900	-1.05962400
C	5.51645100	-0.80183900	0.14561300
C	5.34953200	0.35853000	-0.61760800
C	-2.34543500	-3.96855000	0.40234300
C	1.19068400	-2.88172800	-1.78982800
C	-1.38315700	-3.08378900	2.41616000
C	-2.40083300	-3.78766500	1.77905400
C	-0.74552600	-0.31526500	-1.36576800
H	2.30991900	-2.97915200	0.70414300
H	4.58140400	-2.51005400	1.04845600
H	-1.25878300	-3.61185900	-1.40155900
H	0.44936200	-1.98266900	2.17397200
H	3.90266600	1.58655400	-1.64408500
H	6.50367300	-1.07731900	0.50106900
H	6.20011200	0.98592200	-0.85434800
H	-3.12627500	-4.52220100	-0.10714600
H	2.08420300	-2.46429500	-2.25920500
H	0.37991000	-2.82167000	-2.51682800

H	1.37708600	-3.93264500	-1.55185800
H	-1.41342300	-2.93839000	3.49039300
H	-3.22586200	-4.19629600	2.35170400
H	-0.81134300	0.54767700	-2.01935200
H	-1.50437600	-1.07654800	-1.50470200
C	-1.59486600	0.46446200	0.32808900
H	-1.72734600	-0.54137000	0.70762800
C	-0.19301000	2.47915800	0.75773800
C	-0.51654000	3.24204100	-0.35504500
C	0.51575300	3.01750000	1.82354800
C	-0.13857600	4.57652200	-0.38594500
H	-1.02121400	2.79661100	-1.20184900
C	0.88841100	4.35518700	1.78359700
H	0.77258700	2.38286800	2.66280200
C	0.55744300	5.13657500	0.68180500
H	-0.37502900	5.17707200	-1.25630400
H	1.43818400	4.78416800	2.61316300
H	0.85028700	6.17979600	0.64869800
O	0.45264300	0.27516600	1.08996900
C	-2.87841500	1.17403300	0.04615100
O	-3.17457800	2.29835700	0.34002000
O	-3.70168400	0.32145900	-0.58027200
C	-5.01231400	0.82712500	-0.88418400
C	-5.77241200	-0.28277700	-1.57180700
H	-4.90721200	1.71047100	-1.51718400
H	-5.48882400	1.13955000	0.04710900
H	-6.78085800	0.05438100	-1.81768600
H	-5.27433800	-0.57937800	-2.49594000
H	-5.84971400	-1.15722500	-0.92418500
N	-0.51518700	1.07349400	0.84913400

TS$_{(S,S)}$-(*E*)-*s*-cis

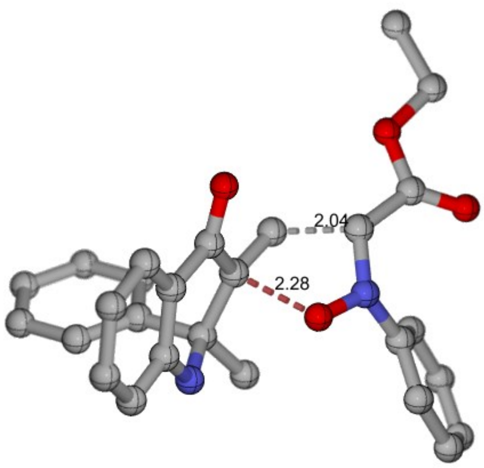


EE = -1454.704797 a.u.
Thermal correction to free energy = 0.420020 a.u.
0 1

O	0.11645400	0.87286400	1.90021100
N	2.21022300	0.36581300	-1.53456500
C	2.44788200	1.49048400	-0.78119000
C	1.81374600	1.66471000	0.46048600
C	2.84094200	-1.61754800	-0.17612700
C	1.71556400	-0.86730800	-0.93295600
C	0.60988800	-0.51643300	0.05576800
C	3.31089100	2.49863300	-1.24523400
C	2.59221000	-2.87408700	0.38564700
C	0.80792600	0.68208100	0.91556100
C	4.12362400	-1.08531400	-0.04852100
C	2.05850600	2.81396700	1.21758300
C	3.53835500	3.62817800	-0.48101100
C	2.92029800	3.79550000	0.76345400
C	3.59186600	-3.57958300	1.04173900
C	1.20065400	-1.73555000	-2.08515600
C	5.12776800	-1.78857000	0.61477700
C	4.86875900	-3.03802400	1.16006500
C	-0.39908000	-1.39085600	0.44157400
H	2.82408700	0.23125900	-2.32579500
H	3.79631500	2.38144500	-2.20956300
H	1.60380500	-3.31373500	0.32049400
H	4.35544700	-0.10884100	-0.45509400
H	1.54370300	2.90778300	2.16774200
H	4.21040600	4.39244700	-0.85659500
H	3.11238200	4.68126000	1.35630300
H	3.37187500	-4.55323700	1.46543900
H	0.42739400	-1.19216700	-2.62777800
H	0.80628900	-2.68921400	-1.73425200
H	2.02430600	-1.96285100	-2.76728900
H	6.11479500	-1.34877900	0.70521300
H	5.64978800	-3.58451700	1.67631100
H	-0.83125000	-1.21391700	1.42133900
H	-0.39640200	-2.42078900	0.10644300
C	-1.99331100	-0.82819400	-0.68729000
H	-1.67023000	-1.43415100	-1.52175100
C	-2.48990900	1.59921100	-0.32175300
C	-3.86907000	1.62187400	-0.49630200
C	-1.81661000	2.69041400	0.21488500
C	-4.59097200	2.72810100	-0.06982000
H	-4.37368300	0.78997100	-0.97161500

C	-2.54910400	3.79252500	0.63392900
H	-0.73894100	2.67273100	0.30147500
C	-3.93450300	3.81262400	0.50263700
H	-5.66685400	2.74559700	-0.19843200
H	-2.03028900	4.63992800	1.06658800
H	-4.49964600	4.67648100	0.83319200
O	-0.57564800	0.72125200	-1.32078400
C	-3.13504000	-1.36909900	0.10373500
O	-3.71174800	-0.83675500	1.00955500
O	-3.36398900	-2.63240000	-0.29130400
C	-4.35133800	-3.35024200	0.46854200
C	-4.43459500	-4.74590900	-0.10355300
H	-5.30118600	-2.81698300	0.39549700
H	-4.04986300	-3.34935900	1.51790600
H	-5.17978500	-5.32654000	0.44288800
H	-4.72402200	-4.71810200	-1.15491800
H	-3.47445900	-5.25737600	-0.02227200
N	-1.73259700	0.48882500	-0.83996500

TS$_{(S,R)}$-(*E*)-*s*-cis



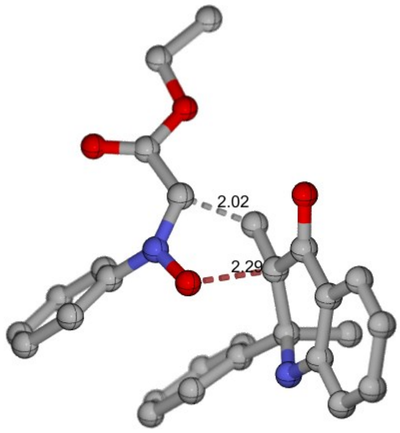
EE = -1454.703907 a.u.
Thermal correction to free energy = 0.420213 a.u.
0 1

O	0.65807900	1.66471700	-2.08356100
N	2.06900000	-1.37695700	0.20019700
C	2.70888100	-1.09060300	-0.98140800
C	2.31128900	0.00829400	-1.76158000
C	2.29010900	0.61165600	1.67424800
C	1.32928900	-0.35677400	0.93040300
C	0.51353000	0.47119700	-0.05373900
C	3.75801800	-1.90477200	-1.44522300

C	1.76895900	1.62468000	2.48507100
C	1.14638700	0.81479200	-1.35571900
C	3.67574600	0.48787600	1.58683500
C	2.96136200	0.28075000	-2.96928000
C	4.38983900	-1.61382000	-2.63911600
C	4.00233300	-0.51237200	-3.41207700
C	2.60277700	2.47580300	3.19716900
C	0.47760600	-1.09789700	1.96496600
C	4.51601400	1.34625400	2.29454100
C	3.98552300	2.34009300	3.10448700
C	-0.62721700	1.19429000	0.26913900
H	2.51656800	-2.06965300	0.78415800
H	4.06588100	-2.76305500	-0.85530100
H	0.69568900	1.76143300	2.55768000
H	4.12033600	-0.27142600	0.95544300
H	2.61297400	1.13059800	-3.54530200
H	5.19966500	-2.25184100	-2.97686000
H	4.50695200	-0.29334300	-4.34499900
H	2.17250000	3.25092400	3.82173800
H	-0.14810800	-1.83691900	1.46612000
H	-0.15172900	-0.42156100	2.54311900
H	1.13658900	-1.60683600	2.67402600
H	5.59069700	1.23372700	2.20355700
H	4.63938100	3.00725800	3.65454700
H	-0.75883700	2.15994500	-0.20608400
H	-1.07824000	1.08985900	1.25042300
C	-2.00227400	0.38508400	-1.00035500
H	-1.46245200	0.83104600	-1.83104500
C	-2.34176400	-1.80645400	0.09695600
C	-2.97434700	-1.35465700	1.24965900
C	-2.20192700	-3.16697500	-0.15667400
C	-3.48960600	-2.28219300	2.14652000
H	-3.05655100	-0.29681900	1.46140100
C	-2.72255300	-4.08510500	0.74502500
H	-1.67699300	-3.48210100	-1.04969500
C	-3.36860000	-3.64547700	1.89706500
H	-3.98111300	-1.93541900	3.04802100
H	-2.62257900	-5.14592100	0.54722500
H	-3.77329400	-4.36321900	2.60122300
O	-0.51571200	-1.22239500	-1.18479000
C	-3.38127400	0.92934600	-0.81038000
O	-4.39531800	0.30029500	-0.67843100
O	-3.32760900	2.26471900	-0.85672300
C	-4.59117000	2.94815300	-0.78413800

C	-4.30670900	4.42808200	-0.88758500
H	-5.07664700	2.68374200	0.15749600
H	-5.22497300	2.59013100	-1.59770900
H	-5.24164400	4.98925700	-0.84177600
H	-3.66610200	4.75907200	-0.06908600
H	-3.80995300	4.66133100	-1.83001500
N	-1.70683600	-0.91510000	-0.83721500

TS$_{(R,S)}$-A-(*E*)-*s*-cis

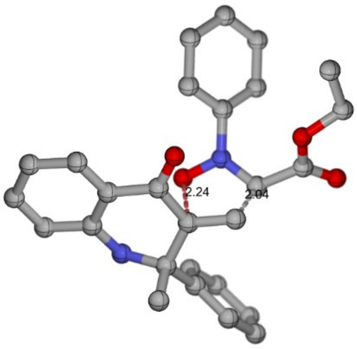


EE = -1454.705468 a.u.
Thermal correction to free energy = 0.421921 a.u.
0 1

O	1.65406500	-2.80176400	-0.08769600
N	2.58361900	1.13021800	0.33766000
C	3.54525200	0.27074700	-0.14454400
C	3.28763300	-1.10512500	-0.26032600
C	0.46169700	1.73094200	1.33144800
C	1.53623500	0.64594100	1.24144500
C	1.00622000	-0.69187000	0.73834700
C	4.79162600	0.76210400	-0.57271400
C	-0.33679700	1.87503400	2.46864000
C	1.97260700	-1.64209100	0.13094300
C	0.28374800	2.63215400	0.27798600
C	4.25849700	-1.95781300	-0.79652300
C	5.73822700	-0.09777400	-1.09504000
C	5.48268800	-1.46993600	-1.21034500
C	-1.27854000	2.89699900	2.55594300
C	2.17198700	0.38234700	2.62944900
C	-0.63792500	3.66807600	0.37479300
C	-1.42238600	3.80588600	1.51433800
C	-0.21510300	-1.23405800	1.11815300
H	2.93173900	2.04541600	0.59448800

H	5.00083200	1.82433800	-0.49108600
H	-0.22232100	1.19993100	3.30880000
H	0.86551900	2.50229900	-0.62645500
H	4.01144600	-3.01037400	-0.87728700
H	6.69402400	0.30181000	-1.41698900
H	6.23318400	-2.13428400	-1.62072000
H	-1.88592500	2.99022200	3.44967500
H	3.02290600	-0.29276300	2.51445700
H	1.46831800	-0.08954800	3.31583600
H	2.52238300	1.31975400	3.06927700
H	-0.75688000	4.35646800	-0.45450600
H	-2.14665000	4.61003700	1.58619200
H	-0.25240000	-2.30019100	1.31032000
H	-0.91400100	-0.62741200	1.68591700
C	-1.09942900	-1.52960700	-0.67258300
H	-0.35623500	-2.29409400	-0.88606000
C	-1.72002200	0.76155700	-1.33697600
C	-2.67599100	1.00297200	-0.35885700
C	-1.57088800	1.61456100	-2.42464400
C	-3.51870500	2.09821600	-0.49545900
H	-2.75641200	0.36006500	0.50916400
C	-2.41726700	2.70777000	-2.55031300
H	-0.79908800	1.40453600	-3.15519900
C	-3.39797500	2.94646700	-1.59107000
H	-4.26116700	2.29706000	0.26876400
H	-2.31572100	3.36950000	-3.40290700
H	-4.06121500	3.79805500	-1.69286400
O	0.42906400	-0.11906800	-1.39867700
C	-2.49809800	-2.05459700	-0.57735800
O	-3.44446000	-1.69707300	-1.22239600
O	-2.53254200	-3.05073300	0.31522900
C	-3.79166800	-3.73391300	0.44350000
C	-3.60687900	-4.82578200	1.47098000
H	-4.07245100	-4.12891500	-0.53473800
H	-4.55213200	-3.00904200	0.74082300
H	-4.54060700	-5.37611800	1.59922000
H	-2.83373200	-5.52724900	1.15527500
H	-3.31935800	-4.40645900	2.43613200
N	-0.81869400	-0.35724300	-1.26515700

$\mathbf{TS_{(R,R)}}$-(*E*)-*s*-trans



EE = -1454.708174 a.u.

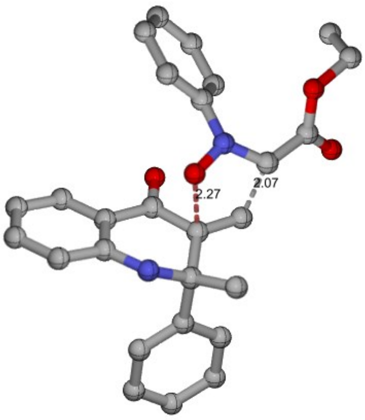
Thermal correction to free energy = 0.420923 a.u.

0 1

O	-0.05387800	-1.83438400	1.67176700
N	3.03980200	-0.16820000	-0.37257500
C	3.04271400	-1.53062500	-0.16251000
C	2.02092400	-2.14336000	0.58255600
C	2.21783400	2.09125500	-0.08938600
C	2.38939900	0.72969100	0.58622300
C	1.03843900	0.14360700	0.99012600
C	4.04243900	-2.34005400	-0.72829700
C	2.23695300	3.27905600	0.64501700
C	0.92109500	-1.32731600	1.13960000
C	1.99303200	2.16526700	-1.46830400
C	2.01330600	-3.53089400	0.75194400
C	4.01521100	-3.71086600	-0.55083100
C	3.00146900	-4.32193000	0.19537500
C	2.01717600	4.50689100	0.02568700
C	3.25645100	0.82129900	1.86067900
C	1.78282500	3.39257300	-2.08789200
C	1.78745500	4.56820700	-1.34339000
C	0.02053000	0.91949300	1.51670200
H	3.90896900	0.20348600	-0.73424900
H	4.83456000	-1.87844400	-1.30986600
H	2.42376900	3.26116100	1.71237600
H	1.96016700	1.24915400	-2.04312400
H	1.20552800	-3.96076700	1.33414600
H	4.79783200	-4.31626400	-0.99552400
H	2.99361900	-5.39621500	0.33301100
H	2.03048700	5.41514600	0.61768600
H	3.45424900	-0.18584400	2.23422500
H	2.75489300	1.37367600	2.65619000
H	4.21006900	1.30746300	1.63741900
H	1.60654800	3.42769000	-3.15729300
H	1.61672800	5.52353600	-1.82657200

H	-0.72352400	0.40646800	2.11519600
H	0.20711200	1.96078700	1.75786700
C	-1.14674200	1.33086400	-0.10699700
H	-0.50314100	2.13368400	-0.44527500
C	-2.07175200	-0.76746700	-1.03722000
C	-3.26727600	-0.29408500	-1.57105800
C	-1.86502800	-2.12410900	-0.82573800
C	-4.29499600	-1.18921800	-1.84111700
H	-3.38506700	0.76164900	-1.79359200
C	-2.89832000	-3.00949500	-1.10590200
H	-0.92131100	-2.46896900	-0.42583800
C	-4.11486700	-2.54829000	-1.60230400
H	-5.22763600	-0.82439900	-2.25599700
H	-2.75128600	-4.06827200	-0.92740000
H	-4.91486800	-3.24776800	-1.81605900
O	0.18521100	-0.16269400	-1.06130700
C	-2.48107000	1.75731800	0.42087400
O	-2.94981300	2.84810200	0.23247000
O	-3.05043300	0.79830100	1.14649700
C	-4.42861600	0.98571000	1.50529200
C	-4.92897900	-0.34735600	2.01104400
H	-4.97198500	1.31933700	0.61756800
H	-4.49169300	1.77597200	2.25616900
H	-5.98240500	-0.27221500	2.28699400
H	-4.82218100	-1.10808200	1.23512300
H	-4.36242200	-0.66720400	2.88642700
N	-1.01028000	0.17443300	-0.78829100

TS$_{(S,S)}$-(*E*)-*s*-trans



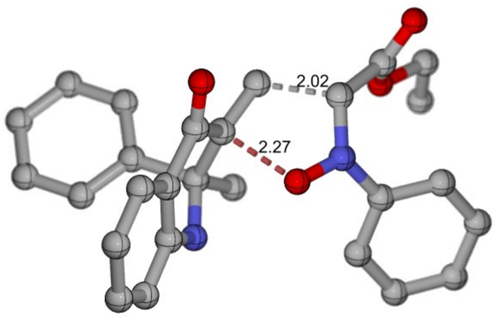
EE = -1454.704202 a.u.
Thermal correction to free energy = 0.421357 a.u.
0 1

O	-0.03808800	0.76645900	1.72556400

N	2.33615000	0.38558500	-1.53709800
C	2.37895600	1.56473400	-0.82795500
C	1.63674500	1.71253200	0.35460700
C	3.16051600	-1.42568200	-0.04603100
C	1.98510200	-0.87541300	-0.89369900
C	0.78778900	-0.64654000	0.02037600
C	3.14254000	2.65120200	-1.28748400
C	3.05144100	-2.67252900	0.57790000
C	0.74206100	0.62411500	0.80083200
C	4.35443200	-0.72035000	0.10221800
C	1.67356700	2.91840900	1.05792600
C	3.16789900	3.83620800	-0.57481500
C	2.43833000	3.98062100	0.61013100
C	4.10298300	-3.20334100	1.31268900
C	1.66398300	-1.85721500	-2.02514200
C	5.40969600	-1.24793400	0.84452700
C	5.29133200	-2.49093600	1.44972800
C	-0.11162500	-1.63343100	0.38350000
H	3.02738200	0.29741100	-2.26930400
H	3.71175900	2.55112200	-2.20704300
H	2.13143500	-3.24039000	0.50113200
H	4.47440500	0.25704300	-0.34830800
H	1.07551300	2.99183900	1.95934300
H	3.76710800	4.66172600	-0.94423500
H	2.46885700	4.91184000	1.16243500
H	3.99202200	-4.17371800	1.78383000
H	0.85985400	-1.44684200	-2.63671000
H	1.38275200	-2.84085400	-1.64885300
H	2.54970700	-1.99646400	-2.65082600
H	6.32489600	-0.67586200	0.94961500
H	6.11209600	-2.90080100	2.02731000
H	-0.64706600	-1.49395200	1.31601200
H	0.03043200	-2.66464800	0.08630600
C	-1.70866700	-1.30860400	-0.88599600
H	-1.17847000	-1.82882800	-1.67315200
C	-2.43218400	0.95732600	-0.24899600
C	-2.99756900	0.62304000	0.97513000
C	-2.58683800	2.22536200	-0.79409200
C	-3.75492600	1.57213400	1.64794800
H	-2.80287800	-0.33929300	1.43463500
C	-3.34570600	3.16700300	-0.11129200
H	-2.10335300	2.45768300	-1.73465200
C	-3.93623100	2.84118000	1.10590900
H	-4.18330000	1.32459800	2.61246500

H	-3.47259800	4.15817900	-0.53076500
H	-4.52295100	3.57966800	1.64004000
O	-0.52357800	0.44918300	-1.47820900
C	-2.94246200	-2.02289500	-0.41746900
O	-2.90061100	-2.99185300	0.29177800
O	-4.05149700	-1.50569500	-0.94191800
C	-5.29911300	-2.10534700	-0.53641200
C	-5.72882100	-1.59424300	0.82349900
H	-5.18415100	-3.18955400	-0.54309900
H	-5.99890600	-1.81139600	-1.31662200
H	-6.70714200	-2.00736200	1.07783600
H	-5.02095800	-1.89984500	1.59554300
H	-5.80178900	-0.50584400	0.81819100
N	-1.62669900	0.02346500	-0.99777000

TS$_{(S,R)}$-(*E*)-*s*-trans



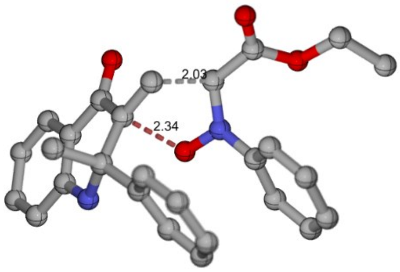
EE = -1454.702451 a.u.
Thermal correction to free energy = 0.421386 a.u.
0 1

O	-1.49112600	-0.16178500	2.83736500
N	-1.55049400	-0.77915900	-1.19902400
C	-2.38098100	-1.54269700	-0.38677900
C	-2.45619100	-1.30769700	0.99695800
C	-2.39557400	1.53199100	-0.78528100
C	-1.18248800	0.55980700	-0.74571700
C	-0.71459300	0.46766600	0.69747900
C	-3.14877700	-2.57848100	-0.93967000
C	-2.26032900	2.83005200	-0.28376600
C	-1.57887600	-0.29627200	1.63188700
C	-3.61833500	1.16878800	-1.34741200
C	-3.28940100	-2.09711500	1.79295800

C	-3.97331100	-3.34452500	-0.13497400
C	-4.05552700	-3.10717800	1.24031700
C	-3.30593400	3.74041000	-0.35478600
C	-0.10397000	1.10552800	-1.68636300
C	-4.67136800	2.07918800	-1.41715100
C	-4.52033300	3.36767600	-0.92441900
C	0.27658700	1.27583500	1.23544300
H	-1.80207400	-0.81203200	-2.17931500
H	-3.08987600	-2.77340400	-2.00670900
H	-1.32839900	3.13322500	0.18181500
H	-3.77748100	0.16538400	-1.72311800
H	-3.30550300	-1.89285000	2.85767400
H	-4.56152600	-4.13815500	-0.58312700
H	-4.70357700	-3.71213100	1.86261400
H	-3.17489000	4.74060200	0.04302500
H	0.84003200	0.57557300	-1.56031000
H	0.06631700	2.16819300	-1.51627000
H	-0.43605200	0.99692800	-2.72262500
H	-5.61465800	1.76985600	-1.85336500
H	-5.34105400	4.07403300	-0.97531100
H	0.14229700	1.58190200	2.26800000
H	0.79562400	1.98009800	0.59642500
C	1.76691100	0.01015500	1.72620700
H	1.32675100	-0.22432100	2.68829900
C	2.51588000	-1.29199000	-0.25966100
C	3.89305100	-1.30472600	-0.04826900
C	1.97405300	-1.69419400	-1.47636500
C	4.73753400	-1.64455200	-1.09671500
H	4.30294700	-1.09033200	0.93305900
C	2.83103500	-2.03263700	-2.51663100
H	0.89554800	-1.74046600	-1.57664400
C	4.21074500	-1.99580400	-2.33708300
H	5.80941600	-1.65811100	-0.93537800
H	2.41654000	-2.33667900	-3.47098500
H	4.87323300	-2.26730900	-3.15076100
O	0.45055500	-1.48270200	0.77095900
C	3.00700200	0.84827800	1.76373600
O	3.68302300	1.00388200	2.74350500
O	3.23746900	1.43369300	0.58469200
C	4.50821800	2.08505400	0.42900200
C	4.64909300	2.42102000	-1.03740200
H	5.28989000	1.40110800	0.76986700
H	4.53271700	2.96780000	1.07090700
H	5.61050900	2.90368600	-1.22117600

H	4.59321600	1.51208600	-1.63973800
H	3.85696000	3.09916600	-1.35847300
N	1.61606600	-0.97656000	0.81276600

$TS_{(R,S)}$-(*E*)-*s*-trans

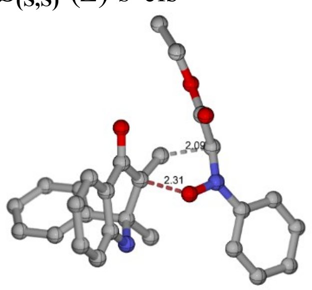


EE = -1454.706569 a.u.
Thermal correction to free energy = 0.422885 a.u.
0 1

O	-2.04736800	-2.70188100	-0.81978000
N	-2.65769600	1.17588200	0.21920900
C	-3.62408300	0.24638800	0.53494700
C	-3.48471300	-1.09652700	0.14794200
C	-0.63240200	1.97499700	-0.83558300
C	-1.79784400	0.99013400	-0.95277200
C	-1.34813100	-0.46371000	-1.03577700
C	-4.74849000	0.61649400	1.29406200
C	0.02680000	2.46469000	-1.96609200
C	-2.29220400	-1.52344700	-0.60484400
C	-0.22226100	2.43150000	0.41993100
C	-4.44944400	-2.03794400	0.52184700
C	-5.69263100	-0.32790900	1.64840300
C	-5.55446800	-1.66720400	1.26343600
C	1.06029600	3.38986300	-1.84640800
C	-2.63560200	1.27295800	-2.22453200
C	0.79283100	3.37419700	0.53904700
C	1.43834900	3.85784600	-0.59311700
C	-0.24922700	-0.88932400	-1.76271900
H	-2.94907100	2.13761200	0.34198100
H	-4.86535400	1.65124200	1.60146100
H	-0.26811200	2.13943800	-2.95696400
H	-0.69618000	2.02445100	1.30483100
H	-4.29426600	-3.06498400	0.21109600

H	-6.55395600	-0.02035500	2.23183800
H	-6.30166500	-2.39842200	1.54636600
H	1.55662800	3.75580400	-2.73861400
H	-3.52957900	0.64541700	-2.21349900
H	-2.08248900	1.04138700	-3.13518500
H	-2.94112600	2.32229300	-2.25150400
H	1.09234700	3.71550200	1.52390400
H	2.23485700	4.58806700	-0.49927700
H	-0.32527600	-1.83316800	-2.29048400
H	0.42483000	-0.16254000	-2.20449700
C	0.86327500	-1.81021400	-0.33993600
H	0.10898500	-2.59188900	-0.28224400
C	1.79907100	0.05319600	0.94203500
C	2.64161700	0.54922600	-0.04700000
C	1.91434600	0.47229700	2.26239000
C	3.63976000	1.45000300	0.30586900
H	2.50795600	0.26755500	-1.08598300
C	2.91309400	1.37501400	2.60225000
H	1.22461600	0.07933000	2.99948300
C	3.78359100	1.85834000	1.62796400
H	4.28996700	1.85106400	-0.46331700
H	3.01601100	1.69726500	3.63218700
H	4.56323700	2.56199800	1.89680100
O	-0.40195100	-0.69331200	1.09444600
C	2.19325600	-2.22399500	-0.89830300
O	2.39848400	-2.39760600	-2.06868700
O	3.09918300	-2.39294000	0.06351100
C	4.45751700	-2.59763100	-0.36261800
C	5.32686900	-2.42964100	0.86157800
H	4.68909700	-1.86111300	-1.13557000
H	4.53916900	-3.59107200	-0.80769400
H	6.37775800	-2.55572600	0.59507600
H	5.19089800	-1.43293600	1.28609000
H	5.07259400	-3.16810900	1.62295500
N	0.77431000	-0.91442600	0.65262700

TS$_{(S,S)}$-(*Z*)-*s*-cis

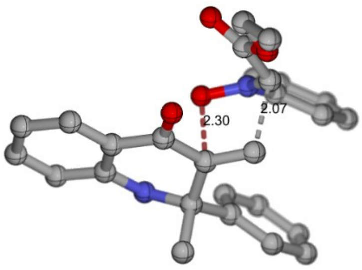


EE = -1454.705868 a.u.
Thermal correction to free energy = 0.421019 a.u.
0 1

O	-0.74966100	2.30020900	0.43926900
N	-1.15168800	-1.76140500	0.61464200
C	-1.66919800	-0.98896800	1.64201300
C	-1.60938100	0.41510100	1.59271500
C	-2.37936300	-0.91344900	-1.38364900
C	-1.00085000	-1.16161400	-0.70627700
C	-0.32631400	0.19259800	-0.55070300
C	-2.25450500	-1.60202300	2.76109600
C	-2.43688800	-0.25219200	-2.61389100
C	-0.91121300	1.09341000	0.47934700
C	-3.57199500	-1.37012500	-0.82537900
C	-2.12902300	1.17173200	2.64647500
C	-2.76922500	-0.83407900	3.78950400
C	-2.71528700	0.56274300	3.74008900
C	-3.64412100	-0.06718700	-3.27395100
C	-0.21780100	-2.13922500	-1.58370800
C	-4.78637500	-1.18163100	-1.48302800
C	-4.82834800	-0.53325300	-2.70935900
C	0.54270100	0.74683300	-1.47004400
H	-1.50088300	-2.71098100	0.59316000
H	-2.29843900	-2.68618200	2.81130500
H	-1.52652700	0.13653500	-3.05852700
H	-3.57594700	-1.86345200	0.13906600
H	-2.04547700	2.25034800	2.57741900
H	-3.21932200	-1.32776500	4.64418000
H	-3.11837200	1.15532900	4.55216000
H	-3.66150500	0.44893900	-4.22748400
H	0.79876600	-2.26948700	-1.21520500
H	-0.18394200	-1.80300900	-2.61962300
H	-0.72119100	-3.11008900	-1.58083500
H	-5.70154800	-1.53970300	-1.02470800
H	-5.77361000	-0.38450700	-3.21881900
H	0.49817200	1.81732100	-1.63071100
H	0.88612500	0.15342100	-2.31122300
C	2.33222000	0.98272300	-0.42123900
H	3.08559700	0.99840700	-1.19818600
C	3.02839600	-1.30640600	0.06522200
C	2.54427400	-2.51419800	0.56335900
C	4.23998400	-1.25279300	-0.62146500
C	3.26411800	-3.67935700	0.33520200
H	1.61011700	-2.51026300	1.11154200

C	4.94523300	-2.42852900	-0.84747900
H	4.65721300	-0.30953000	-0.95073900
C	4.46020400	-3.64416000	-0.37569300
H	2.88813600	-4.62076400	0.71905500
H	5.88787700	-2.38784400	-1.38068900
H	5.01983500	-4.55601300	-0.54818200
O	1.24629700	-0.23323800	1.08440100
C	2.09861600	2.30451400	0.26790100
O	2.15480500	2.47309500	1.44963600
O	1.91776000	3.27157800	-0.63586100
C	1.55218100	4.55441000	-0.09394100
C	1.14151300	5.42758300	-1.25590800
H	2.40871400	4.95888800	0.44971100
H	0.73453700	4.39565600	0.60992900
H	0.86148300	6.41875300	-0.89454400
H	1.95770500	5.54087300	-1.97157800
H	0.28168600	4.99474700	-1.76962200
N	2.26595500	-0.12109700	0.34112100

TS$_{(R,R)}$- (*Z*)-*s*-cis



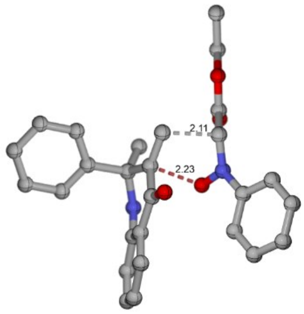
EE = -1454.706701 a.u.
Thermal correction to free energy = 0.423005 a.u.
0 1

O	-2.92496400	-0.58571400	-0.60162300
N	-0.30700900	2.49590700	-0.07564200
C	-1.59983400	2.62781300	0.38043700
C	-2.53880700	1.59725800	0.20892000
C	1.52942000	1.39552500	-1.20978000
C	0.01010700	1.56043300	-1.15710400
C	-0.73786400	0.24891000	-0.93572600
C	-1.99541300	3.79473900	1.05925200
C	2.17746900	1.00166300	-2.38448600
C	-2.14938800	0.34647200	-0.46502600
C	2.31134000	1.67407600	-0.08663900
C	-3.83496700	1.73864400	0.71736600
C	-3.28079700	3.91511100	1.54952700

C	-4.21679800	2.88635400	1.38309500
C	3.56382600	0.89265600	-2.43518300
C	-0.51658200	2.15681200	-2.48777200
C	3.69863000	1.59145600	-0.14342400
C	4.33123700	1.19923200	-1.31668300
C	-0.36033700	-0.96233000	-1.48652500
H	0.19797700	3.37017100	-0.15024300
H	-1.27773300	4.59757000	1.19795300
H	1.60565500	0.78698400	-3.27981800
H	1.82036100	1.93902800	0.84191600
H	-4.52172000	0.91233100	0.57394600
H	-3.56439800	4.82356800	2.07026000
H	-5.22108100	2.99085600	1.77484600
H	4.04310700	0.58501200	-3.35820800
H	-1.57817400	2.39239000	-2.38522800
H	-0.41343600	1.45595600	-3.31654100
H	0.02589900	3.07427600	-2.73029600
H	4.28360500	1.81654900	0.74138100
H	5.41264200	1.12805800	-1.35850700
H	-1.14561400	-1.63158200	-1.81740400
H	0.59022200	-1.04362900	-2.00317500
C	0.01802500	-2.15802700	0.16344400
H	0.64797000	-2.97489500	-0.16832500
C	2.03965800	-1.21372200	1.11865500
C	2.50381100	-0.63933800	2.29843100
C	2.91921400	-1.75725000	0.18907900
C	3.86613300	-0.63922200	2.56131400
H	1.78697400	-0.21118800	2.98837700
C	4.28268500	-1.74543500	0.46277800
H	2.55991900	-2.15196600	-0.75400200
C	4.75866600	-1.19690800	1.64814100
H	4.23226900	-0.20712100	3.48570100
H	4.97415500	-2.15258300	-0.26598000
H	5.82232200	-1.19574000	1.85706900
O	-0.05225900	-0.19325000	1.21929300
C	-1.37592500	-2.58753800	0.54533000
O	-1.89786300	-2.36109600	1.59620100
O	-1.89310000	-3.35148100	-0.42108700
C	-3.26401500	-3.74176700	-0.22477400
C	-3.73510700	-4.37630600	-1.51207000
H	-3.83233600	-2.84517600	0.02415400
H	-3.31083000	-4.43169600	0.62074700
H	-4.77303900	-4.69834700	-1.40954700
H	-3.67808100	-3.65832400	-2.33166900

H	-3.12874900	-5.24739500	-1.76645900
N	0.61576300	-1.23114400	0.92325900

TS$_{(S,R)}$-(*Z*)-*s*-cis



EE = -1454.709694 a.u.

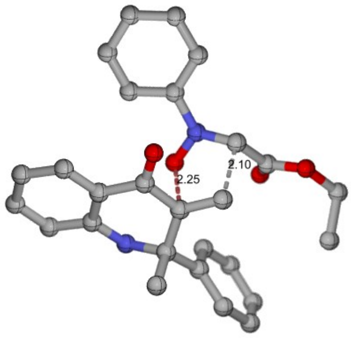
Thermal correction to free energy = 0.420764 a.u.

0 1

O	-0.06236700	1.22426600	1.89533900
N	1.78996800	0.16812200	-1.53769100
C	2.04715600	1.41079300	-1.01879800
C	1.52569900	1.77987300	0.23386200
C	2.65582900	-1.49787800	0.08598000
C	1.42358400	-0.95588900	-0.68487700
C	0.39333100	-0.47725400	0.32875100
C	2.80310600	2.35490600	-1.73826200
C	2.51409100	-2.58153000	0.95793900
C	0.59344000	0.87048600	0.92992000
C	3.92941000	-0.95802500	-0.08765200
C	1.77300400	3.05550100	0.74992900
C	3.03820600	3.60936300	-1.20817000
C	2.53253900	3.97190300	0.04677800
C	3.60819900	-3.11624800	1.62455100
C	0.87438700	-2.04782900	-1.60496300
C	5.02929700	-1.48867900	0.58437500
C	4.87552600	-2.57004200	1.44026800
C	-0.52955500	-1.28736800	0.96809500
H	2.28560300	-0.07707000	-2.38269800
H	3.19812700	2.08798500	-2.71390400
H	1.53488500	-3.01390200	1.12966300
H	4.07955000	-0.10818500	-0.74192500
H	1.33390000	3.30154000	1.71065100
H	3.62694000	4.32049700	-1.77789600
H	2.72971900	4.95626400	0.45326100
H	3.47020100	-3.95849700	2.29357300

H	0.00233300	-1.67445400	-2.13987300
H	0.59973600	-2.94301400	-1.04564800
H	1.65016900	-2.34441500	-2.31671100
H	6.00823200	-1.04631400	0.43630800
H	5.73090700	-2.98216000	1.96344800
H	-0.82692600	-0.99953700	1.96979100
H	-0.57845300	-2.34642400	0.74654500
C	-2.38553300	-0.69943800	0.16554700
H	-3.07087500	-0.62531000	0.99869500
C	-2.51420000	1.74316200	0.04896400
C	-1.74200300	2.87408300	-0.19837200
C	-3.76438800	1.84872500	0.65012700
C	-2.20748800	4.11296400	0.21377300
H	-0.78616400	2.76899000	-0.69442800
C	-4.21675100	3.09769400	1.06167800
H	-4.40000400	0.98114800	0.77665600
C	-3.43980700	4.23060000	0.85279800
H	-1.59828000	4.99185500	0.03670100
H	-5.18836400	3.18116400	1.53452300
H	-3.79744100	5.20195600	1.17385100
O	-0.99645300	0.44285100	-1.14646300
C	-2.56027900	-1.90675900	-0.68711800
O	-2.34395500	-2.00229100	-1.86192300
O	-3.04182300	-2.90936100	0.07048800
C	-3.26251300	-4.15328200	-0.61347500
C	-3.79073300	-5.13878000	0.40268900
H	-2.31790500	-4.48070000	-1.05426300
H	-3.96737800	-3.98367700	-1.42961900
H	-3.97178100	-6.10356800	-0.07431700
H	-3.07417500	-5.28449600	1.21229500
H	-4.72953700	-4.78659700	0.83230900
N	-2.01961900	0.46571700	-0.40267200

TS$_{(R,S)}$-(*Z*)-*s*-cis

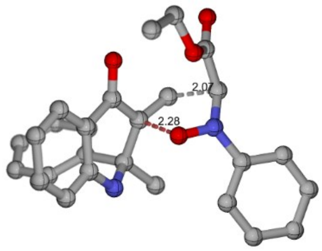


EE = -1454.707671 a.u.
Thermal correction to free energy = 0.424184 a.u.
0 1

O	1.92183600	0.23937700	-1.90996700
N	0.06177500	-2.43508800	0.49842500
C	1.41180200	-2.58402400	0.28072600
C	2.08739700	-1.73901400	-0.61848600
C	-2.16620800	-1.60320800	0.08939200
C	-0.78914000	-1.83121400	-0.53558600
C	-0.10992200	-0.56331600	-1.03808000
C	2.15565000	-3.54782300	0.98520100
C	-3.34544900	-2.01120200	-0.54033600
C	1.35521600	-0.63564000	-1.27494200
C	-2.25191600	-1.03142400	1.36201600
C	3.46749300	-1.86691600	-0.80276900
C	3.51890900	-3.65879400	0.78747500
C	4.19045000	-2.82257400	-0.11346200
C	-4.57660900	-1.88131600	0.09765800
C	-0.86323400	-2.78789600	-1.74826300
C	-3.48247100	-0.89580500	1.99527000
C	-4.64755600	-1.33308300	1.37299700
C	-0.77103100	0.50009000	-1.62579500
H	-0.38417100	-3.18694000	1.00688500
H	1.64844200	-4.20070500	1.68867800
H	-3.31918600	-2.45338100	-1.52847200
H	-1.34882700	-0.68034100	1.84409100
H	3.94736900	-1.17961800	-1.49121300
H	4.07233900	-4.41042800	1.34027400
H	5.25857100	-2.92309800	-0.26249700
H	-5.47788200	-2.21469300	-0.40500100
H	0.14427200	-3.01048800	-2.10420000
H	-1.41568900	-2.34113000	-2.57641200
H	-1.34216400	-3.72728300	-1.46149600
H	-3.52595200	-0.43598000	2.97593800
H	-5.60505900	-1.23511300	1.87285200
H	-0.27414900	1.00621500	-2.44540400
H	-1.85682000	0.50512000	-1.63894100
C	-0.33703000	2.12692300	-0.37090900
H	-0.03100400	2.93658200	-1.01963900
C	1.98593200	2.09884200	0.41804400
C	2.25417900	3.42719300	0.10399500
C	3.00132200	1.24611100	0.84081000
C	3.56634200	3.88534100	0.15388500
H	1.45793100	4.11468000	-0.15238700

C	4.30368300	1.71800200	0.89045500
H	2.76250700	0.22549900	1.10892300
C	4.59487800	3.03416600	0.53859600
H	3.77726800	4.91859600	-0.09619200
H	5.09666300	1.04856500	1.20376200
H	5.61526500	3.39713300	0.57839400
O	0.40777900	0.45363700	0.89767600
C	-1.71484900	2.25278300	0.17955500
O	-2.08831800	1.89381200	1.25967700
O	-2.48196800	2.88965400	-0.72330800
C	-3.88180000	2.98228000	-0.40730100
C	-4.56879900	1.66645700	-0.70968600
H	-4.25012400	3.79348900	-1.03365400
H	-3.98978300	3.25958100	0.64170200
H	-5.63197900	1.72744900	-0.46699500
H	-4.47226200	1.41381700	-1.76775700
H	-4.13336900	0.86408900	-0.11232900
N	0.63532800	1.59322000	0.39381800

TS$_{(S,S)}$-(*Z*)-*s*-trans



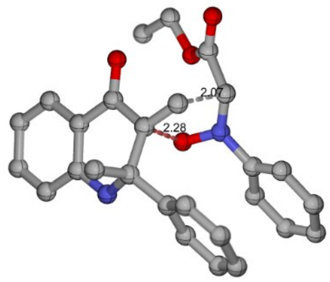
EE = -1454.706623 a.u.
Thermal correction to free energy = 0.422859 a.u.
0 1

O	-0.72524800	2.16595600	-1.09015400
N	-1.08546200	-1.12860900	1.29317300
C	-1.54542800	0.09306400	1.75904100
C	-1.51610800	1.23412200	0.93825300
C	-2.49116800	-1.46566000	-0.73994100
C	-1.05637000	-1.35481500	-0.14917100
C	-0.38231100	-0.16219500	-0.81241200
C	-2.04146900	0.21291600	3.06671300
C	-2.66625400	-1.55178700	-2.12407600
C	-0.89147500	1.17501800	-0.40320700
C	-3.62229800	-1.53273500	0.07199700

C	-1.99699600	2.45298900	1.42405700
C	-2.50971900	1.42953500	3.52849000
C	-2.49964200	2.56191100	2.70737000
C	-3.92857900	-1.71313200	-2.67928300
C	-0.34172400	-2.68242300	-0.40641100
C	-4.89108800	-1.69074600	-0.48228000
C	-5.05026700	-1.78375600	-1.85790100
C	0.40260800	-0.24405400	-1.94969300
H	-1.42018300	-1.92442400	1.82142400
H	-2.05715900	-0.66083300	3.71181800
H	-1.80611800	-1.47847600	-2.78140100
H	-3.53542400	-1.44473400	1.14822000
H	-1.96029300	3.30799300	0.75783300
H	-2.89304700	1.49919400	4.54084700
H	-2.87636000	3.50848400	3.07514500
H	-4.03720300	-1.77519100	-3.75635800
H	0.70725800	-2.62890700	-0.11743700
H	-0.41118900	-2.97146100	-1.45469300
H	-0.82721500	-3.47220500	0.17370600
H	-5.75613600	-1.73265400	0.17021300
H	-6.03787000	-1.90253400	-2.28880300
H	0.34070600	0.56361000	-2.67075700
H	0.65060900	-1.21807700	-2.35803400
C	2.28568700	0.38758900	-1.35131300
H	2.96554300	-0.13318800	-2.01232000
C	2.98998400	-1.19321600	0.36522200
C	2.50816200	-1.88457500	1.47475200
C	4.17656500	-1.57823900	-0.25609900
C	3.20315300	-2.99534600	1.93447900
H	1.59416400	-1.54007800	1.94312800
C	4.85691400	-2.69572000	0.21215200
H	4.59343700	-1.00178800	-1.07244200
C	4.37255400	-3.40998800	1.30322900
H	2.82862400	-3.53886000	2.79432900
H	5.77993300	-2.99605800	-0.26984800
H	4.91231700	-4.27571600	1.66873100
O	1.29253000	0.35572600	0.64735600
C	2.13759500	1.84302200	-1.69968100
O	2.12243200	2.20473600	-2.84746500
O	2.09146200	2.63259700	-0.64374800
C	1.73487600	4.00482000	-0.89399400
C	1.35182300	4.59830300	0.44082100
H	0.90210100	4.01112700	-1.59716600
H	2.58909100	4.50790500	-1.35283300

H	1.03847700	5.63626700	0.31234800
H	0.52476800	4.03124000	0.87093300
H	2.19022700	4.57271900	1.13872200
N	2.25937200	-0.03494600	-0.07172800

TS$_{(R,R)}$- (*Z*)-*s*-trans

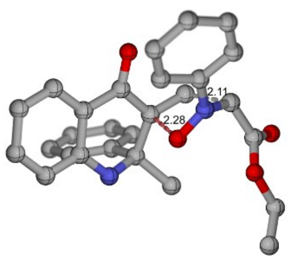


EE = -1454.706892 a.u.
Thermal correction to free energy = 0.424502 a.u.
0 1

O	2.69317800	0.65704400	-1.40490000
N	0.52546000	-2.29721200	0.37242600
C	1.87451500	-2.20756900	0.63103000
C	2.66444800	-1.22391600	0.01475000
C	-1.55262900	-1.73057900	-0.73300300
C	-0.03014000	-1.76688100	-0.87596400
C	0.59099600	-0.40471900	-1.17772900
C	2.48268400	-3.08655700	1.54600300
C	-2.38945600	-1.76016300	-1.85277100
C	2.05080100	-0.25408000	-0.91154800
C	-2.14473000	-1.71307900	0.53195800
C	4.03007000	-1.13690300	0.30910200
C	3.83077300	-2.97989000	1.82576200
C	4.62207100	-2.00386800	1.20638400
C	-3.77384100	-1.77439900	-1.71175900
C	0.38098000	-2.71247100	-2.03349300
C	-3.52747600	-1.75512300	0.67513800
C	-4.34847600	-1.78439600	-0.44546200
C	0.01567500	0.53507200	-2.01641800
H	0.11029100	-3.18033700	0.64227900
H	1.88038500	-3.84859900	2.03110800
H	-1.96834000	-1.78734200	-2.85103900
H	-1.51124200	-1.64891300	1.40820100
H	4.60324400	-0.36639300	-0.19480200
H	4.27961800	-3.66903300	2.53315600
H	5.67983900	-1.93419500	1.42836700

H	-4.40133500	-1.79702200	-2.59604400
H	1.46653100	-2.83322100	-2.03711800
H	0.09129700	-2.31355800	-3.00581800
H	-0.08238800	-3.69353700	-1.90078500
H	-3.96182300	-1.74463700	1.66860100
H	-5.42696400	-1.81040000	-0.33398900
H	0.67468700	1.11992700	-2.64855000
H	-0.98684000	0.36954400	-2.39643800
C	-0.33402600	2.16500900	-0.78486100
H	-1.13244700	2.74592500	-1.22869200
C	-2.02937900	1.41395500	0.77848200
C	-2.22568300	1.19616800	2.13917400
C	-3.10748400	1.56985300	-0.08589800
C	-3.51855100	1.16683500	2.64218600
H	-1.36079200	1.05932800	2.77655500
C	-4.39799100	1.53442200	0.43099400
H	-2.95738100	1.67923100	-1.15331900
C	-4.60790800	1.34311600	1.79183000
H	-3.67589000	1.01206300	3.70358500
H	-5.24156800	1.63921900	-0.24157000
H	-5.61663900	1.32216700	2.18809900
O	0.17135600	0.65703400	0.79705700
C	0.99287400	2.85701100	-0.93838000
O	1.26549400	3.44085600	-1.95382500
O	1.73589400	2.81749200	0.15233900
C	3.08044900	3.31307500	0.01861700
C	3.85544800	2.77993000	1.20047500
H	3.04605600	4.40478000	-0.00657700
H	3.47945900	2.95167800	-0.92875500
H	4.89688700	3.10263700	1.14118500
H	3.43484800	3.13822800	2.14145400
H	3.82502700	1.68897500	1.20094100
N	-0.66488600	1.48792100	0.32571800

TS$_{(S,R)}$-(*Z*)-*s*-trans



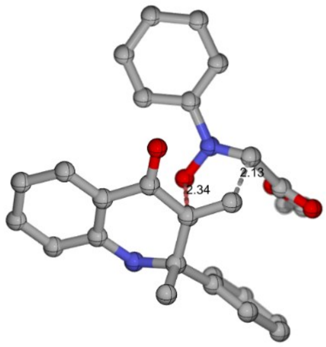
EE = -1454.710376 a.u.

Thermal correction to free energy = 0.421130 a.u.
0 1

O	0.35961300	1.65603900	-1.80320900
N	-1.55653300	0.24514800	1.47483400
C	-1.38723800	1.60203100	1.34827000
C	-0.81152000	2.14588500	0.18793700
C	-3.00558400	-0.58195200	-0.36646400
C	-1.61702100	-0.64256800	0.31777300
C	-0.56339800	-0.21149900	-0.69382900
C	-1.75664600	2.47323500	2.38917500
C	-3.31754400	-1.47714600	-1.39485700
C	-0.30532800	1.24551600	-0.86767500
C	-3.97787500	0.33997700	0.01974100
C	-0.62461200	3.52685700	0.07752100
C	-1.56532000	3.83599600	2.25907000
C	-1.00214700	4.37983200	1.09823500
C	-4.56267300	-1.45982500	-2.00841800
C	-1.35922900	-2.05564900	0.85170000
C	-5.22664600	0.36375800	-0.59941800
C	-5.52609300	-0.53570400	-1.61259200
C	-0.02219200	-1.03834800	-1.65801100
H	-2.12244100	-0.05263700	2.25742800
H	-2.19212900	2.06420700	3.29597200
H	-2.58156100	-2.19854200	-1.73077100
H	-3.77197500	1.05979800	0.80228800
H	-0.16655900	3.89908300	-0.83251400
H	-1.86077300	4.49000700	3.07260400
H	-0.86355500	5.45000800	1.00580600
H	-4.77989700	-2.16795000	-2.80039500
H	-0.40979300	-2.05571500	1.38626300
H	-1.33229300	-2.80004000	0.05508600
H	-2.16443300	-2.34074400	1.53463300
H	-5.96319600	1.09476000	-0.28471900
H	-6.49750200	-0.51751200	-2.09347300
H	0.35742100	-0.55240000	-2.54949800
H	-0.34552400	-2.06345700	-1.77740300
C	1.90459100	-1.50707800	-0.93598000
H	2.51531900	-1.54427000	-1.82828900
C	3.03366100	0.60135400	-0.42686200
C	2.79116300	1.87358400	0.08199300
C	4.19364000	0.32524500	-1.14344400
C	3.70089200	2.88689100	-0.17566700
H	1.89218800	2.05512100	0.65667600
C	5.09441900	1.35343000	-1.39985100

H	4.41821000	-0.68070700	-1.47626100
C	4.84939200	2.63545700	-0.92345800
H	3.50676400	3.88248700	0.20624100
H	5.99696000	1.14195800	-1.96125800
H	5.55507600	3.43338800	-1.12311200
O	1.20087800	-0.22990000	0.74569800
C	1.58523100	-2.85790800	-0.37449800
O	1.21805300	-3.77552300	-1.06267500
O	1.81813100	-2.94944000	0.93073700
C	1.49716000	-4.21255300	1.53773400
C	1.71380200	-4.05624800	3.02449200
H	2.13467400	-4.98342200	1.10048200
H	0.46065200	-4.45849300	1.29459700
H	1.47371400	-4.99019500	3.53571600
H	2.75185100	-3.80083400	3.24073100
H	1.07588600	-3.26684500	3.42480900
N	2.09113500	-0.44827300	-0.12794100

TS$_{(R,S)}$-(*Z*)-*s*-trans



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Thermal correction to free energy = 0.422562 a.u.
0 1

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N	-0.06690900	-2.41807700	-0.65498900
C	-1.43805300	-2.53678300	-0.68932100
C	-2.24316200	-1.80704200	0.20209400
C	2.05899900	-1.67645800	0.23190400
C	0.61575600	-2.03359100	0.58627000
C	-0.13193300	-0.87796600	1.23418600
C	-2.06519100	-3.35073500	-1.64956000
C	3.10910200	-1.92111100	1.11888500
C	-1.61508900	-0.87695100	1.16334600
C	2.35592800	-1.12155700	-1.01715100

C	-3.63655100	-1.89442400	0.12389300
C	-3.44391000	-3.42583000	-1.70860400
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C	4.42546800	-1.64275300	0.76381200
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C	3.67488900	-0.87611000	-1.38308800
C	4.71543300	-1.13678800	-0.49656500
C	0.43869100	0.01204600	2.11284300
H	0.43266300	-3.12440300	-1.18014600
H	-1.45514100	-3.91632000	-2.34714300
H	2.91357400	-2.34183000	2.09780300
H	1.54509700	-0.88957100	-1.69648000
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H	-5.32584800	-2.77117400	-0.87289000
H	5.22377200	-1.83688800	1.47109500
H	-0.48731000	-3.53449100	1.69676400
H	0.93168400	-2.95042600	2.55955700
H	1.12995300	-4.06647200	1.18942500
H	3.89107700	-0.47628900	-2.36843400
H	5.74284700	-0.94259200	-0.78489900
H	-0.21774600	0.46068100	2.84930700
H	1.49292900	-0.04300500	2.35731600
C	0.52320100	1.83515200	1.01859400
H	0.26269500	2.58250400	1.75741600
C	-1.66205900	2.28096400	0.00877500
C	-1.78238700	3.58120100	0.48690400
C	-2.72911200	1.64712300	-0.62037100
C	-3.00737700	4.23225900	0.38352600
H	-0.93175500	4.10202800	0.90882500
C	-3.94141000	2.31036400	-0.72341300
H	-2.60010000	0.64302600	-1.00322500
C	-4.08957000	3.59950900	-0.21515100
H	-3.10513400	5.24415700	0.75910800
H	-4.77876400	1.81309500	-1.19928900
H	-5.04122200	4.11161200	-0.29716200
O	-0.24278400	0.54415000	-0.62063200
C	1.98547500	1.83745800	0.66313000
O	2.86660700	1.69754800	1.46778600
O	2.17270400	2.17321400	-0.61129000
C	3.53374900	2.41825400	-1.00434400
C	3.52974400	2.61907400	-2.50156800
H	4.14587000	1.57140400	-0.69685400
H	3.88846300	3.30334500	-0.47017500

H	4.54836300	2.77789500	-2.86086400
H	3.11524600	1.74332300	-3.00329400
H	2.92701800	3.48517800	-2.77830400
N	-0.39806600	1.58862500	0.07787800

8. References

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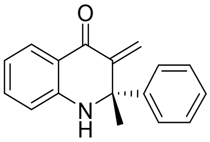
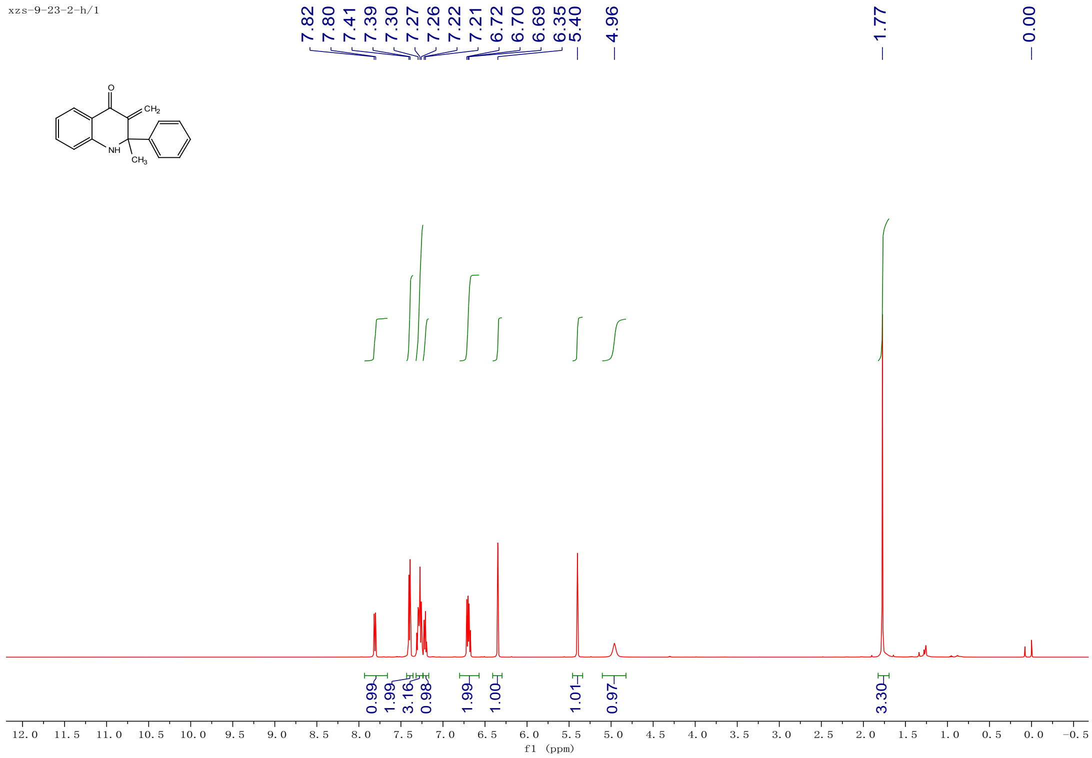
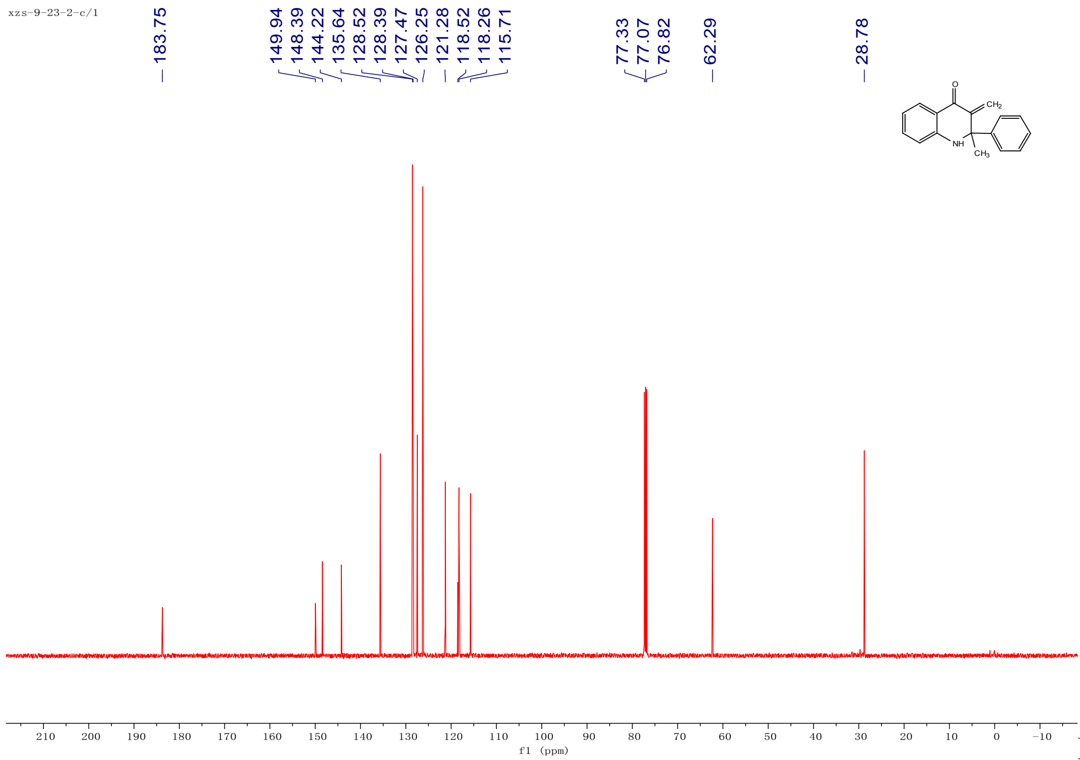
9. Copies of NMR spectra and HPLC charts



3a





H

PLC chart of racemic product **3a**

2020/8/31 16:10:41 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-33	Injection Volume	: 20 uL
Sample Type	: 未知		
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Date Processed	: 2020/7/1 19:27:36	Modified by	: System Administrator

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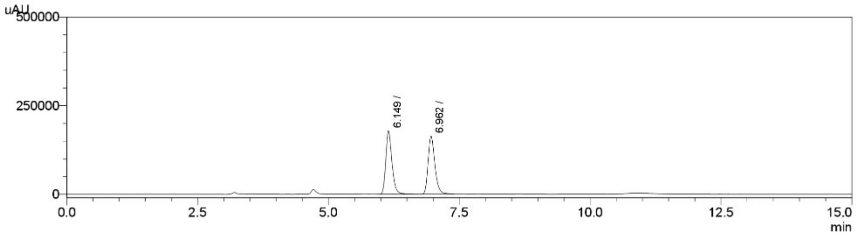

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.149	1461652	50.139	178361	0.000	M	
2	6.962	1453541	49.861	163035	0.000	M	
总计		2915193	100.000	341396			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-23-rac.lcd

HPLC chart of chiral product **3a**

2020/8/31 18:15:18 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 20 uL
Sample Type	: 未知		
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Date Processed	: 2020/8/31 18:14:27	Modified by	: System Administrator

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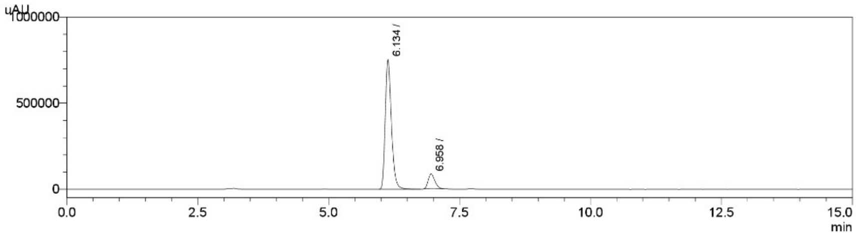

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.134	6172609	88.908	755439	0.000	M	
2	6.958	770093	11.092	87296	0.000	M	
总计		6942702	100.000	842734			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-23.lcd

HPLC chart of chiral product **3a** (after recrystallization)

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/29 13:36:08	Acquired by	: System Administrator
Date Processed	: 2020/7/29 13:52:38	Modified by	: System Administrator

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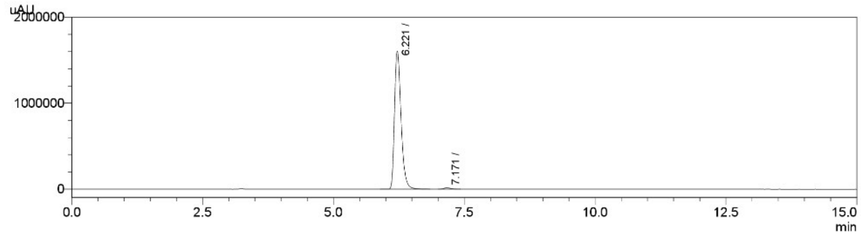

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.221	13962940	99.070	1607341	0.000	M	
2	7.171	131108	0.930	14250	0.000	M	
总计		14094048	100.000	1621591			

HPLC chart of chiral product **3a** (1.0 mmol scale)

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/8 15:29:12	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:57:03	Modified by	: System Administrator

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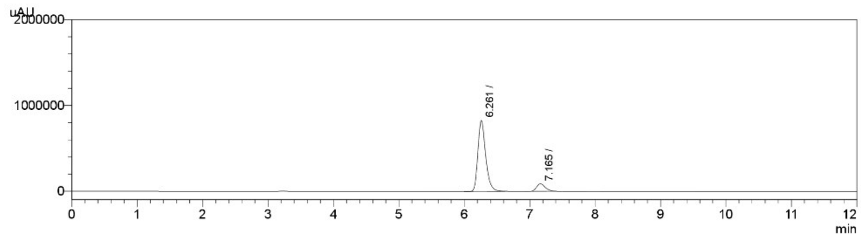

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.261	6848519	89.350	830111	0.000	M	
2	7.165	816288	10.650	87942	0.000	M	
总计		7664807	100.000	918053			

HPLC chart of chiral product **3a** (1.0 mmol scale, after recrystallization)

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/15 20:09:48	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:57:50	Modified by	: System Administrator

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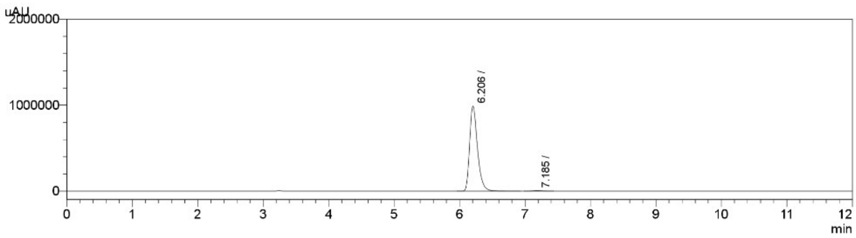
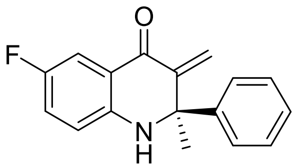
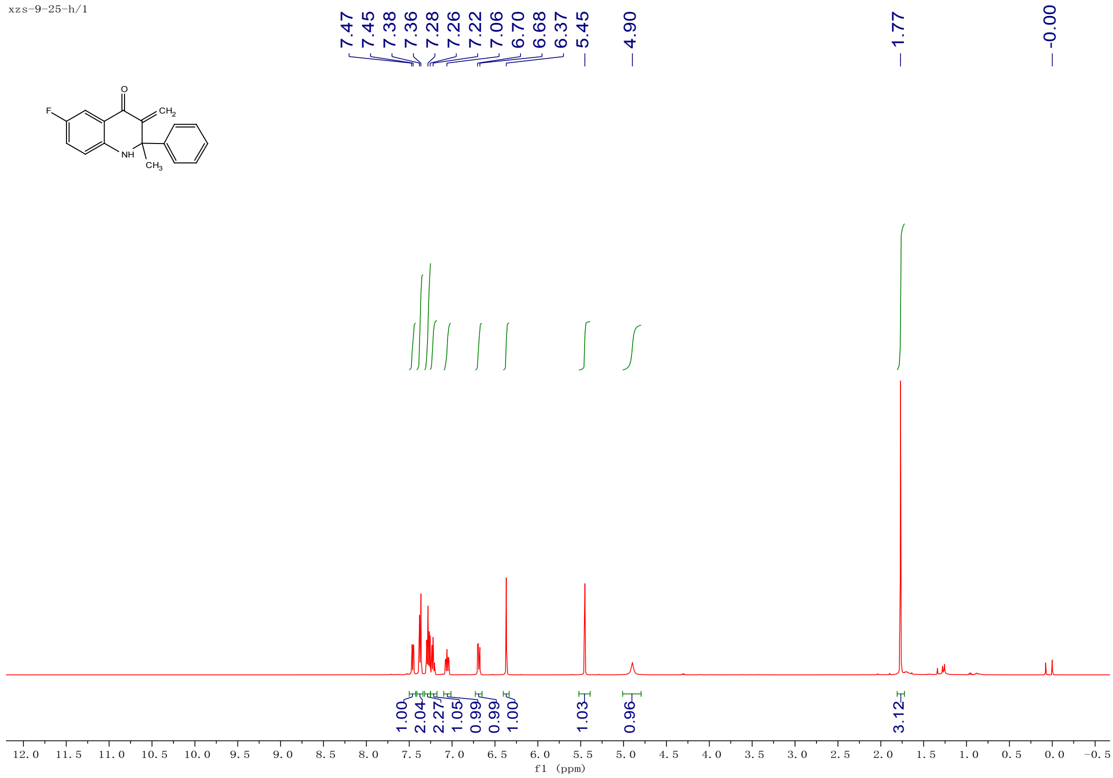


PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.206	8280344	99.176	991777	0.000	M	
2	7.185	68786	0.824	7397	0.000	M	
总计		8349131	100.000	999174			



3b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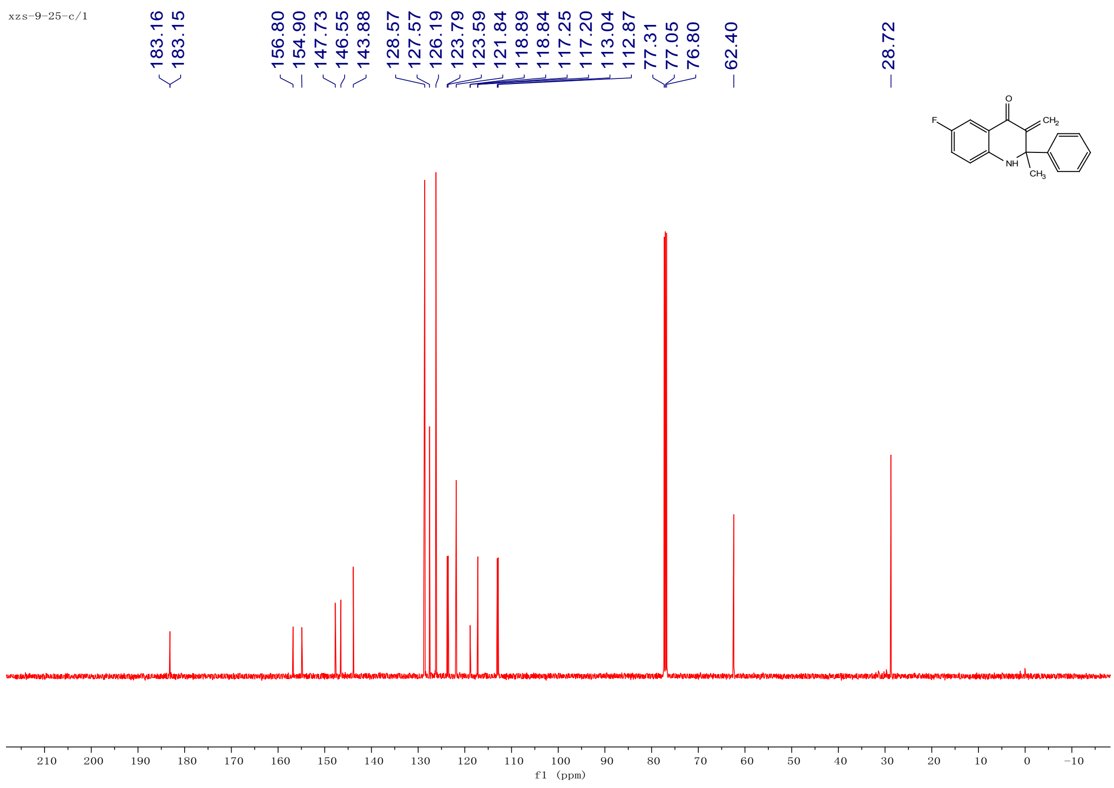
7.45
7.38
7.36
7.28
7.26
7.22
7.06
6.70
6.68
6.37
5.45
4.90
1.77
-0.00
1.00
2.04
2.27
1.05
0.99
0.99
1.00
1.03
0.96
3.12
f1 (ppm)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146.55
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128.57
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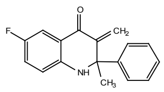
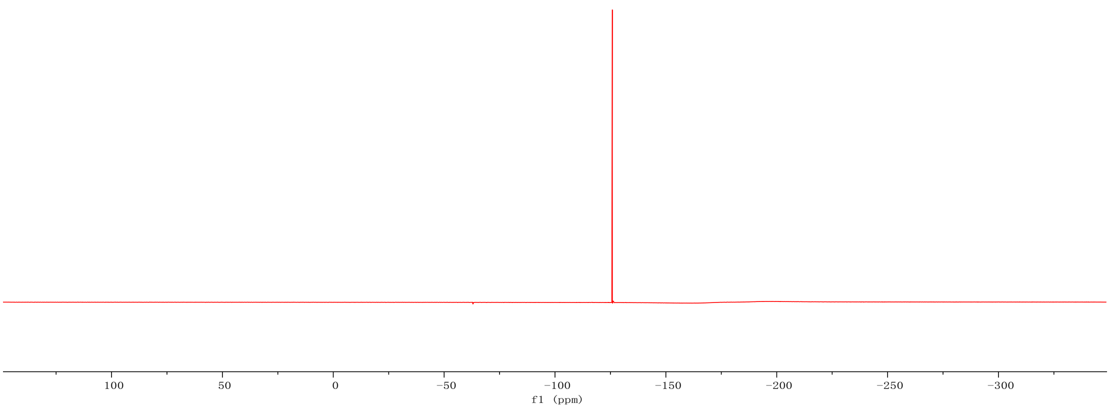
126.19
123.79
123.59
121.84
118.89
118.84
117.25
117.20
113.04
112.87
77.31
77.05
76.80
62.40
28.72
f1 (ppm)

xzs-9-25-f/1





HPLC chart of racemic product **3b**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 10 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/6 19:08:11	Acquired by	: System Administrator
Date Processed	: 2020/7/6 20:43:21	Modified by	: System Administrator

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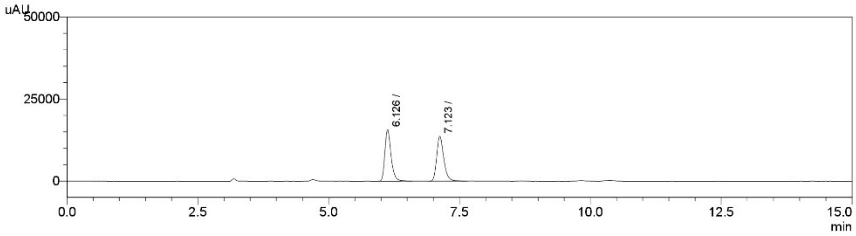

PDA Ch1 237nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.126	129346	50.102	15711	0.000		
2	7.123	128819	49.898	13738	0.000		
总计		258164	100.000	29449			

HPLC chart of chiral product **3b**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/6 18:52:39	Acquired by	: System Administrator
Date Processed	: 2020/7/6 20:44:25	Modified by	: System Administrator

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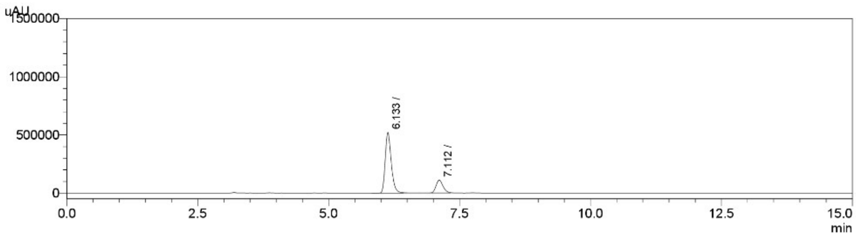
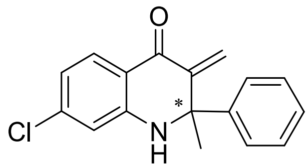
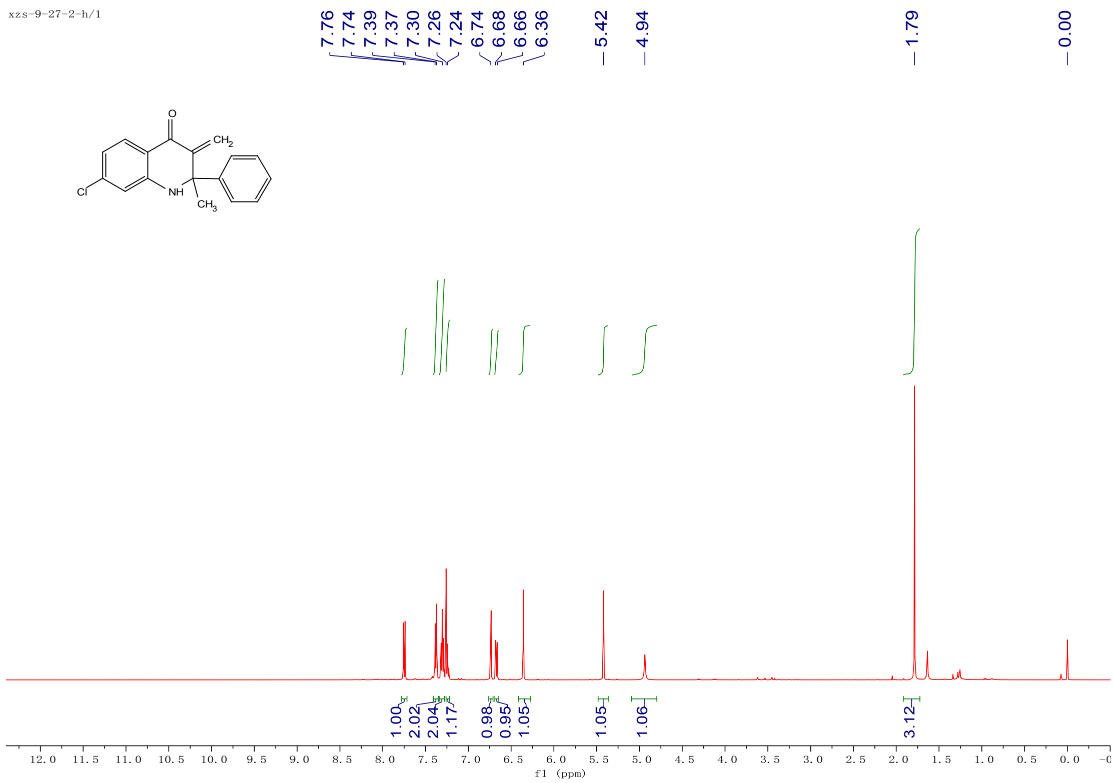


PDA Ch1 237nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.133	4175449	80.064	522996	0.000	M	
2	7.112	1039692	19.936	111387	0.000	M	
总计		5215141	100.000	634383			



3c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7.30
7.26
7.24
6.74
6.68
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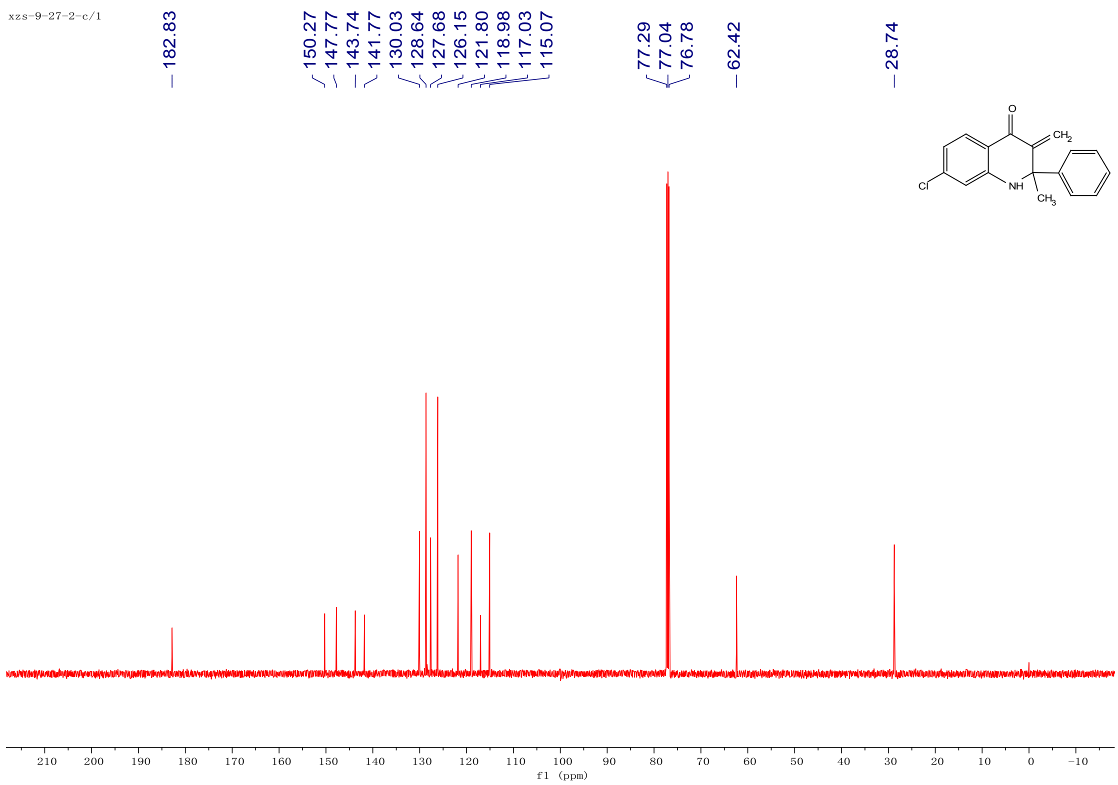
6.36
5.42
4.94
1.79
0.00
O
CH2
Cl
NH
CH3
1.00
2.02
2.04
1.17
0.98
0.95
1.05
1.05
1.06
3.12
f1 (ppm)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141.77
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126.15
121.80
118.98
117.03
115.07
77.29
77.04
76.78
62.42
28.74
O
CH2
Cl
NH
CH3
f1 (ppm)

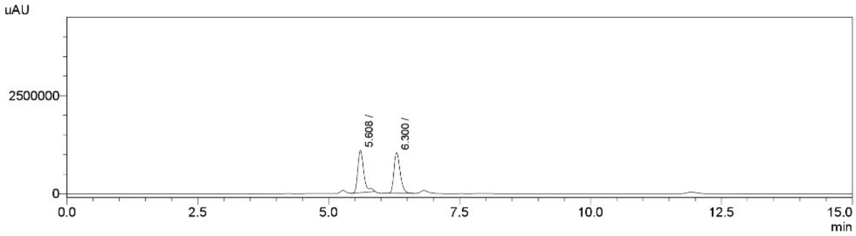
HPLC chart of racemic product **3c**

2020/8/31 16:18:36 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/3 19:05:16	Acquired by	: System Administrator
Date Processed	: 2020/7/3 19:25:00	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-27-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 243nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.608	8642608	50.284	1084419	0.000	M	
2	6.300	8545098	49.716	1034042	0.000	M	
总计		17187707	100.000	2118460			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-27-rac.lcd

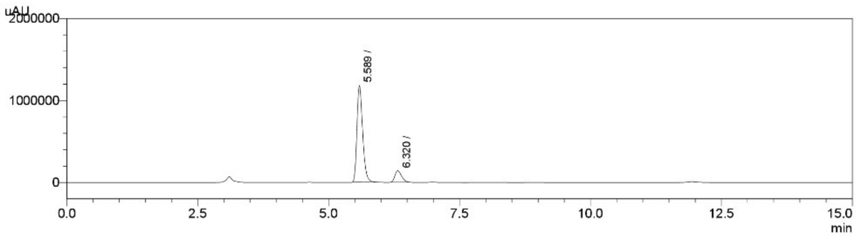
HPLC chart of chiral product **3c**

2020/8/31 18:22:44 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/3 18:49:43	Acquired by	: System Administrator
Date Processed	: 2020/8/31 18:21:53	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-27.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 243nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.589	8929833	87.873	1179402	0.000	M	
2	6.320	1232376	12.127	140856	0.000	M	
总计		10162208	100.000	1320258			

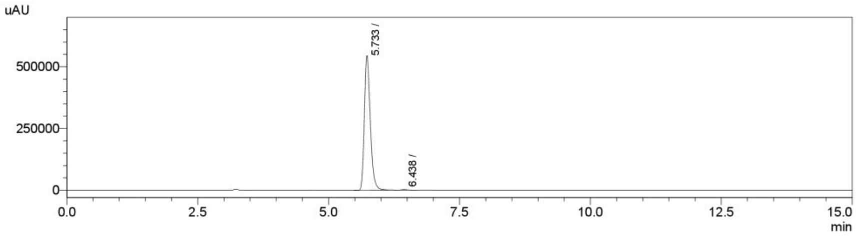
E:\XZS\xzs-1OD-3-80-20-15MIN-9-27.lcd

HPLC chart of chiral product **3c** (after recrystallization)

==== Shimadzu LabSolutions Analysis Report ====

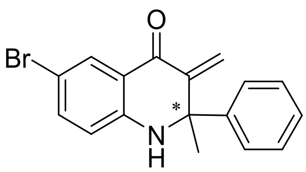
Sample Name	:	Sample ID	:
Vial#	: 1-35	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/5 14:15:13	Acquired by	: System Administrator
Date Processed	: 2020/11/3 13:52:40	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-27-chongjiejing-2.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

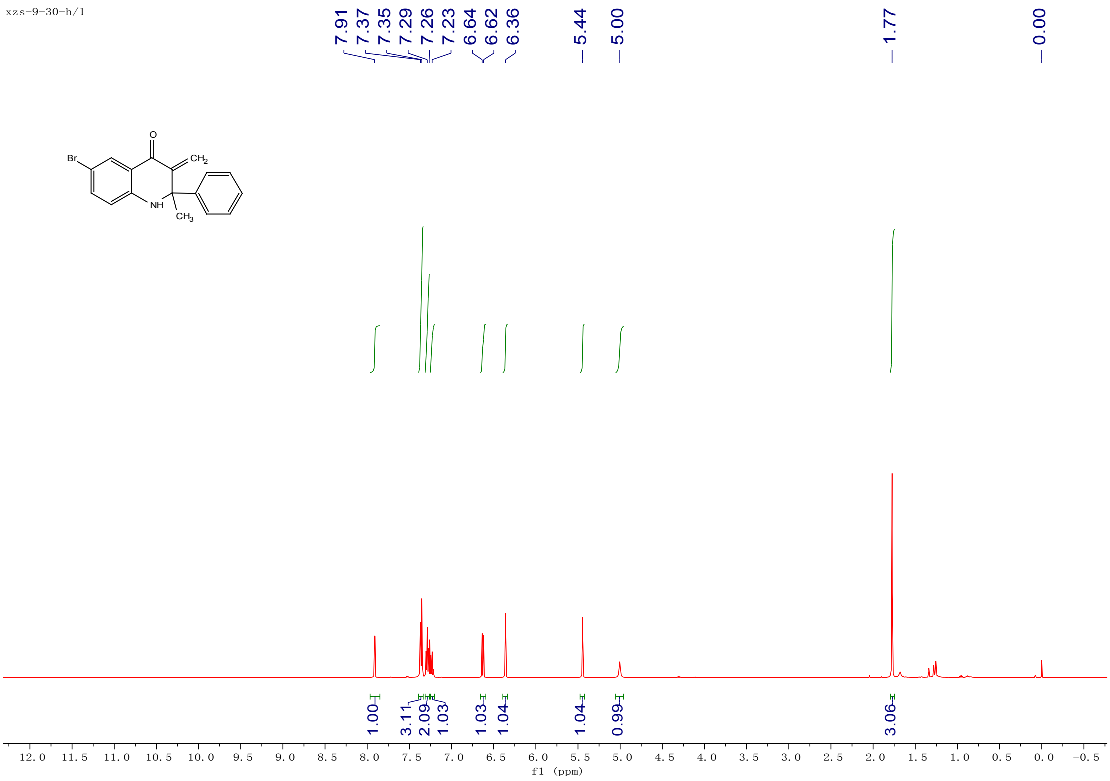


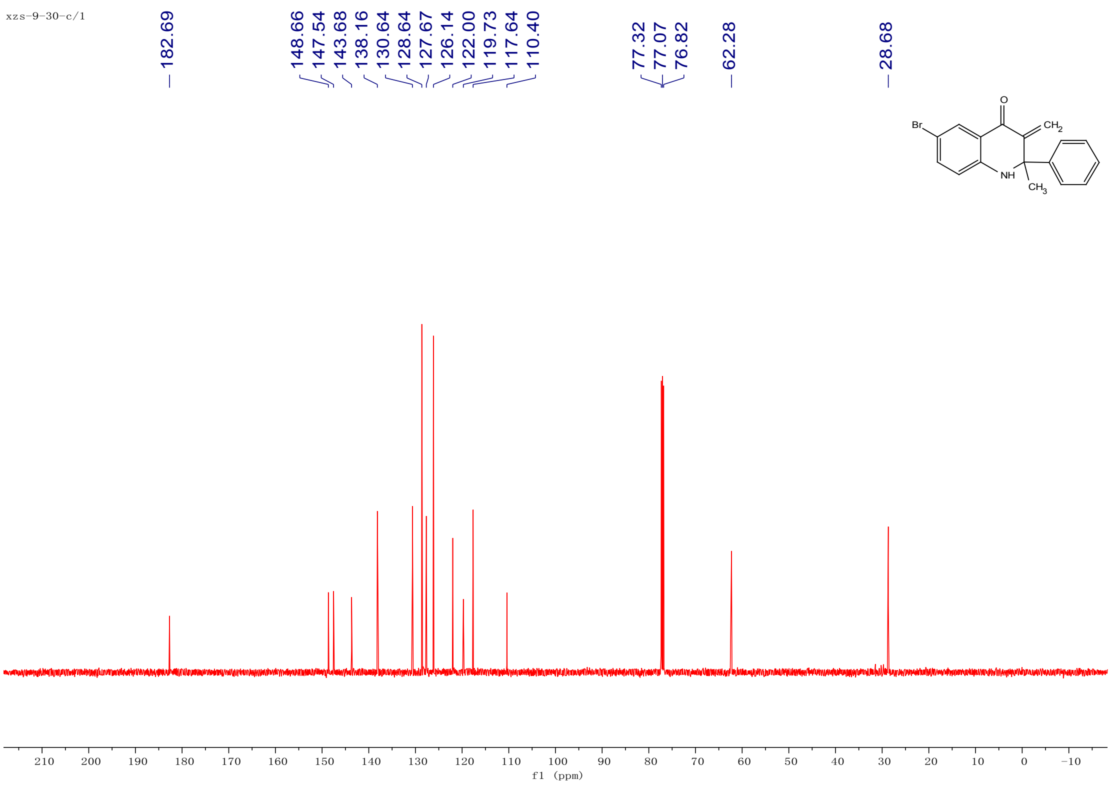
PDA Ch1 243nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.733	4319475	99.570	544887	0.000	M	
2	6.438	18643	0.430	2103	0.000	V M	
总计		4338118	100.000	546991			


O
Br
*
N
H

3d


xzs-9-30-h/1
7.91
7.37
7.35
7.29
7.26
7.23
6.64
6.62
6.36
5.44
5.00
1.77
0.00
1.00
3.11
2.09
1.03
1.03
1.04
1.04
0.99
3.06
f1 (ppm)

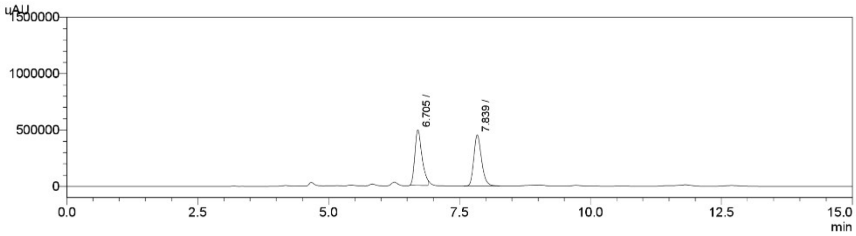

xzs-9-30-c/1
182.69
148.66
147.54
143.68
138.16
130.64
128.64
127.67
126.14
122.00
119.73
117.64
110.40
77.32
77.07
76.82
62.28
28.68
f1 (ppm)

HPLC chart of racemic product **3d**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/4 18:12:17	Acquired by	: System Administrator
Date Processed	: 2020/7/4 18:32:25	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-30-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 244nm

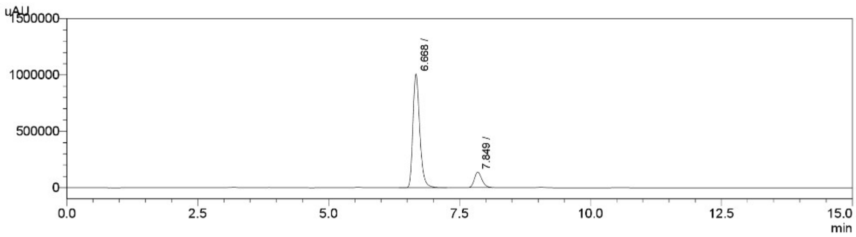
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.705	4704087	50.311	493015	0.000	M	
2	7.839	4645919	49.689	453701	0.000	M	
总计		9350006	100.000	946716			

HPLC chart of chiral product **3d**

==== Shimadzu LabSolutions Analysis Report ====

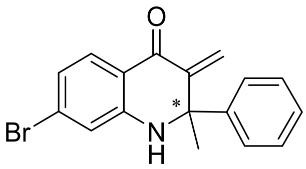
Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/4 18:29:45	Acquired by	: System Administrator
Date Processed	: 2020/7/4 18:47:03	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-30.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

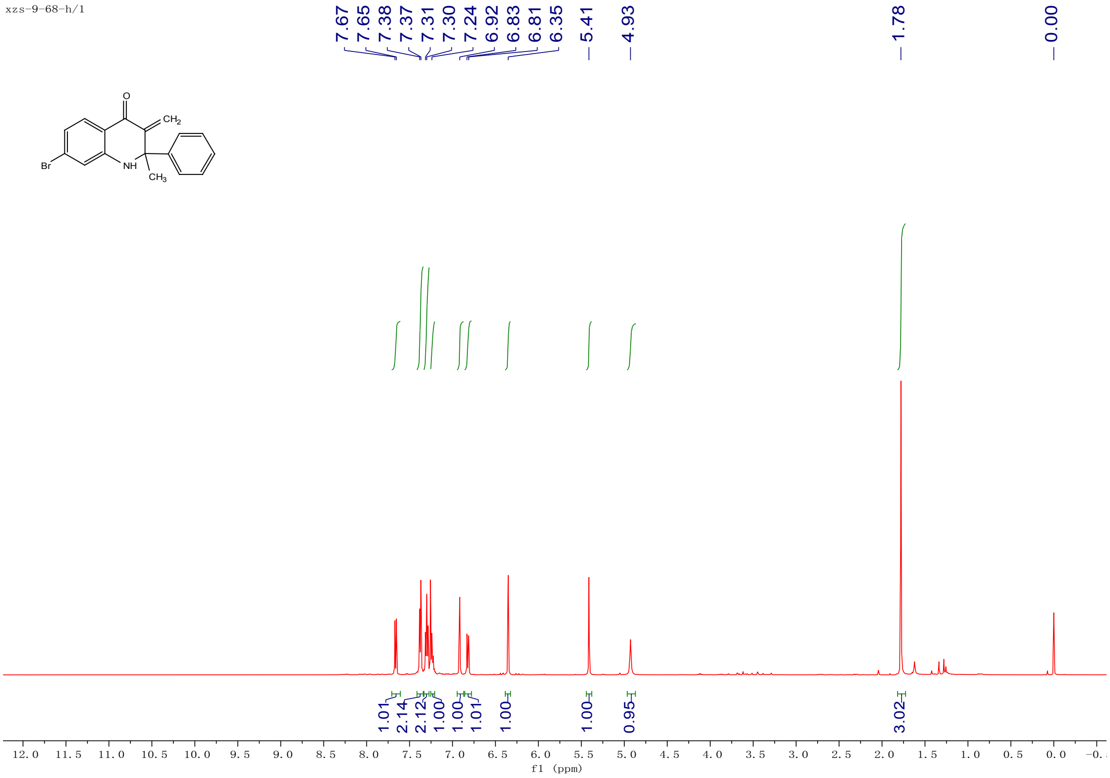


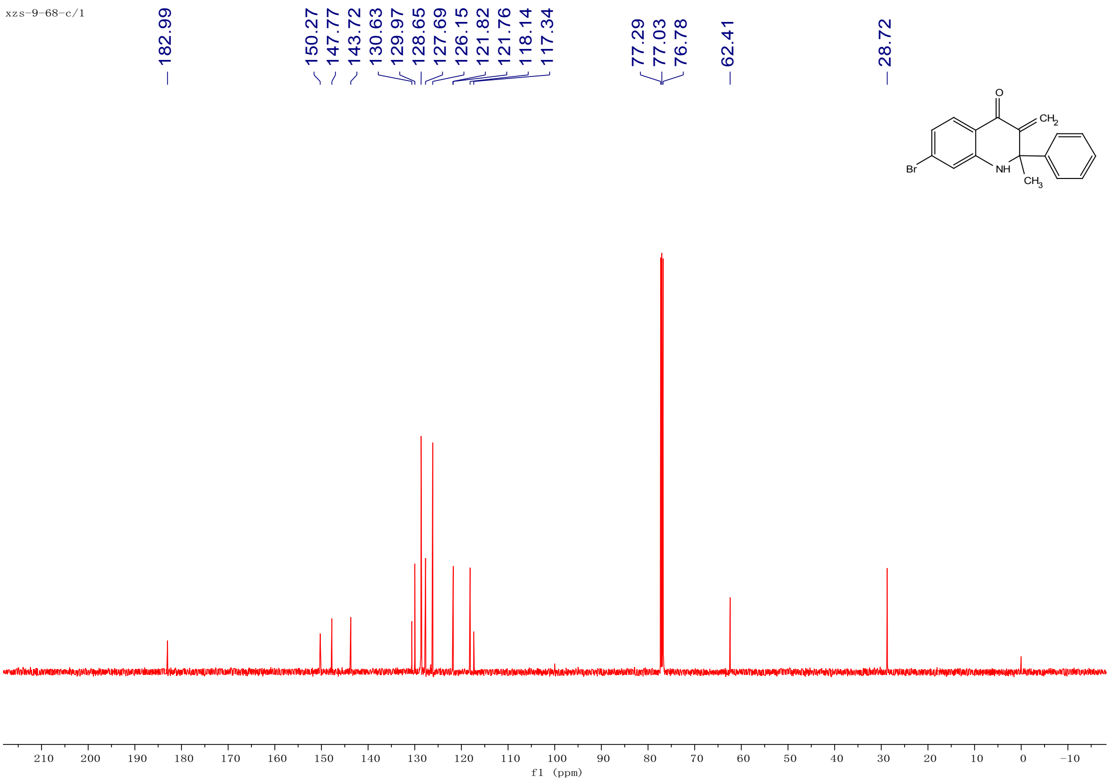
PDA Ch1 244nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.668	9147186	87.086	1010579	0.000	M	
2	7.849	1356432	12.914	137155	0.000	M	
总计		10503618	100.000	1147734			


O
Br
N
H
*

3e


xzs-9-68-h/1
7.67
7.65
7.38
7.37
7.31
7.30
7.24
6.92
6.83
6.81
6.35
5.41
4.93
1.78
0.00
O
CH2
Br
NH
CH3
1.01
2.14
2.12
1.00
1.00
1.01
1.00
1.00
0.95
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


xzs-9-68-c/1
182.99
150.27
147.77
143.72
130.63
129.97
128.65
127.69
126.15
121.82
121.76
118.14
117.34
77.29
77.03
76.78
62.41
28.72
O
CH2
Br
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

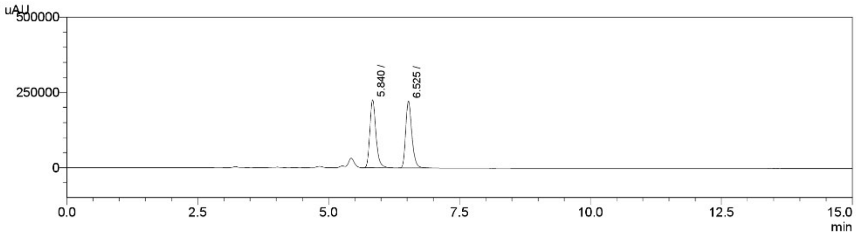
HPLC chart of racemic product **3e**

2020/8/31 16:24:22 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/17 19:57:54	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:42:40	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-68-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 245nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.840	1803816	49.918	225085	0.000	M	
2	6.525	1809733	50.082	222196	0.000	M	
总计		3613549	100.000	447282			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-68-rac.lcd

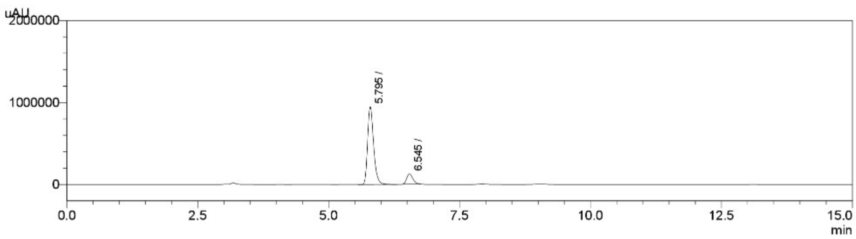
HPLC chart of chiral product **3e**

2020/8/31 18:23:46 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/17 18:46:33	Acquired by	: System Administrator
Date Processed	: 2020/8/31 18:04:01	Modified by	: System Administrator

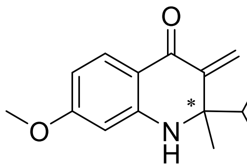
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-68.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



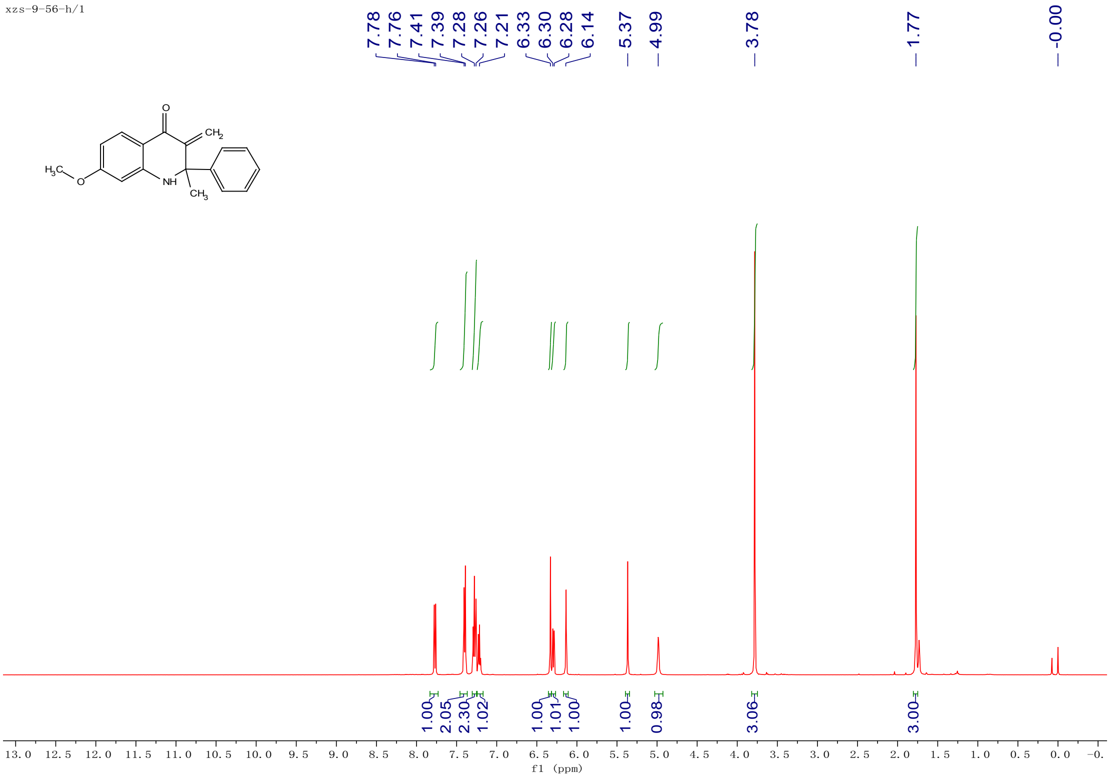
PDA Ch1 245nm

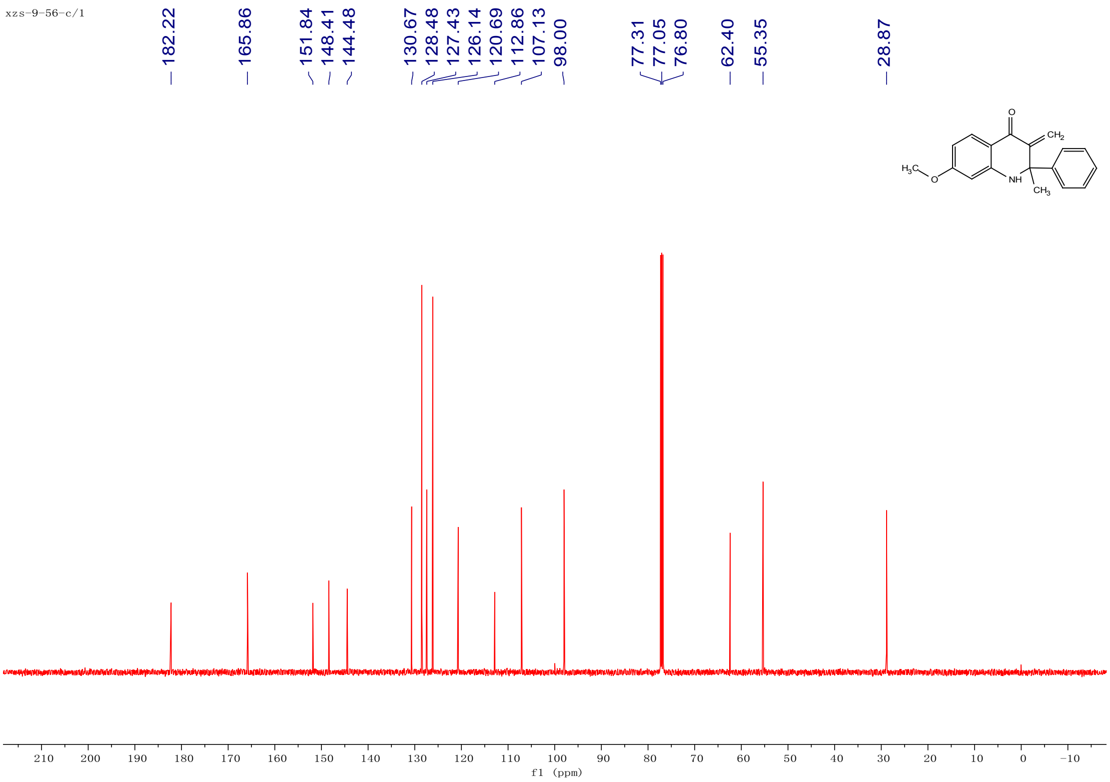
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.795	7556118	88.116	951470	0.000	M	
2	6.545	1019045	11.884	125107	0.000	M	
总计		8575163	100.000	1076577			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-68.lcd



3f


xzs-9-56-h/1
7.78
7.76
7.41
7.39
7.28
7.26
7.21
6.33
6.30
6.28
6.14
5.37
4.99
3.78
1.77
-0.00
1.00
2.05
2.30
1.02
1.00
1.01
1.00
1.00
0.98
3.06
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


xzs-9-56-c/1
182.22
165.86
151.84
148.41
144.48
130.67
128.48
127.43
126.14
120.69
112.86
107.13
98.00
77.31
77.05
76.80
62.40
55.35
28.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

HPLC chart of racemic product **3f**

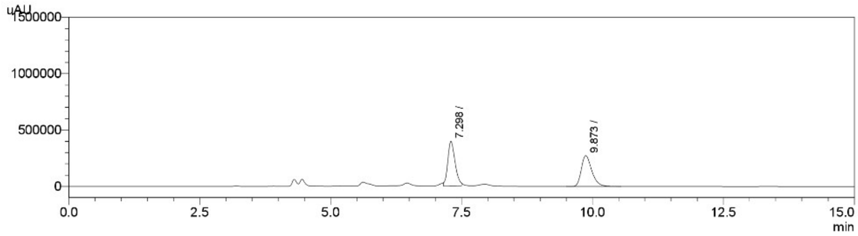
2020/8/31 16:23:00 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name :
Vial# : 1-31
Sample Type : 未知
Date Acquired : 2020/7/14 19:19:23
Date Processed : 2020/7/14 19:42:33

Sample ID :
Injection Volume : 20 uL
Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-56-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 241nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.298	3816382	50.166	396371	0.000	M	
2	9.873	3791066	49.834	272854	0.000	M	
总计		7607448	100.000	669226			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-56-rac.lcd

HPLC chart of chiral product **3f**

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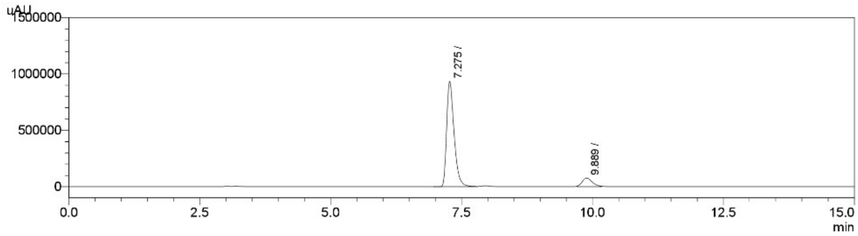
==== Shimadzu LabSolutions Analysis Report ====

Sample Name :
Vial# : 1-32
Sample Type : 未知
Date Acquired : 2020/7/14 19:34:56
Date Processed : 2020/7/14 19:53:34

Sample ID :
Injection Volume : 20 uL
Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-56.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 241nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.275	9238422	90.013	936385	0.000	M	
2	9.889	1024999	9.987	76105	0.000	M	
总计		10263421	100.000	1012491			

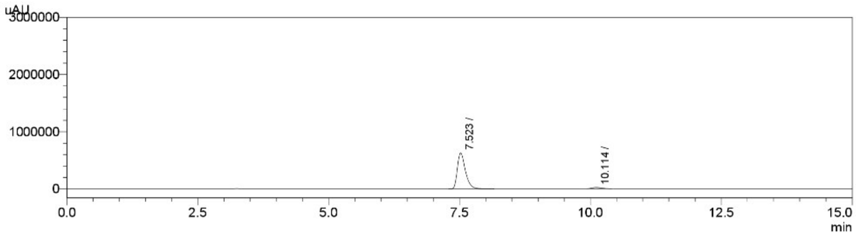
E:\XZS\xzs-1OD-3-80-20-15MIN-9-56.lcd

HPLC chart of chiral product **3f** (after recrystallization)

==== Shimadzu LabSolutions Analysis Report ====

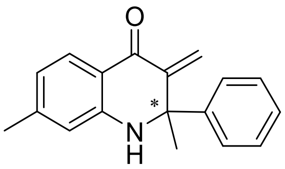
Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/9/1 19:47:25	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:03:08	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-56-cjj.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

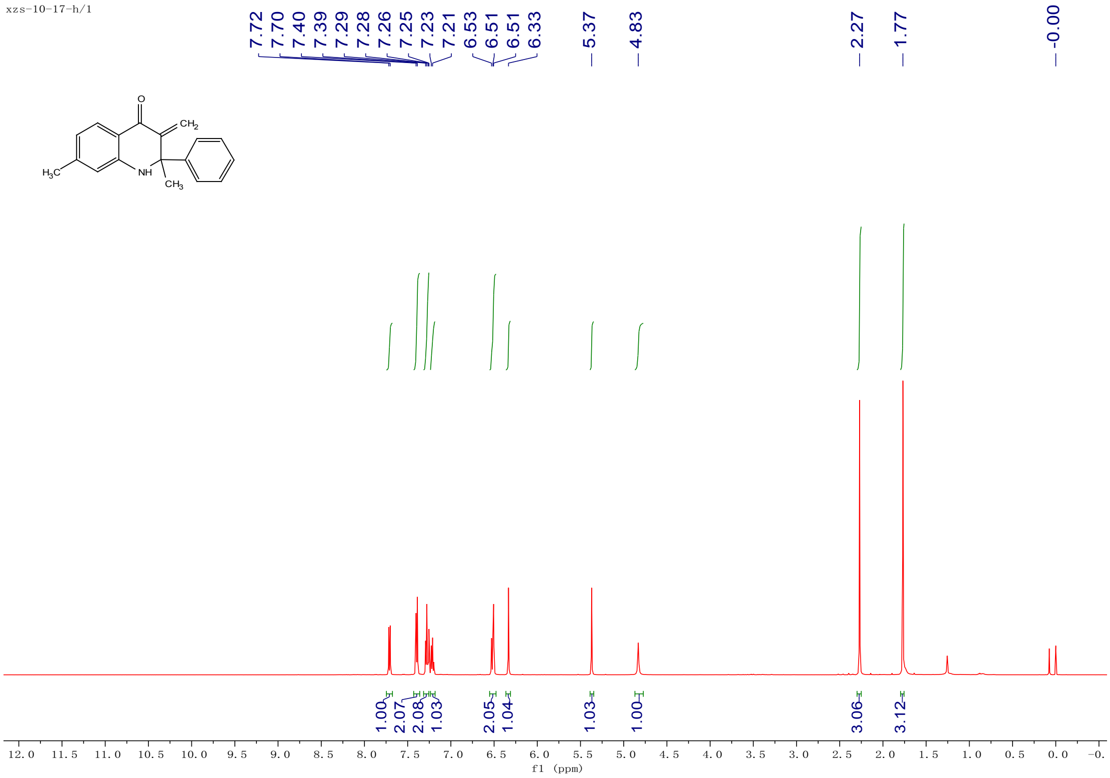


PDA Ch1 241nm

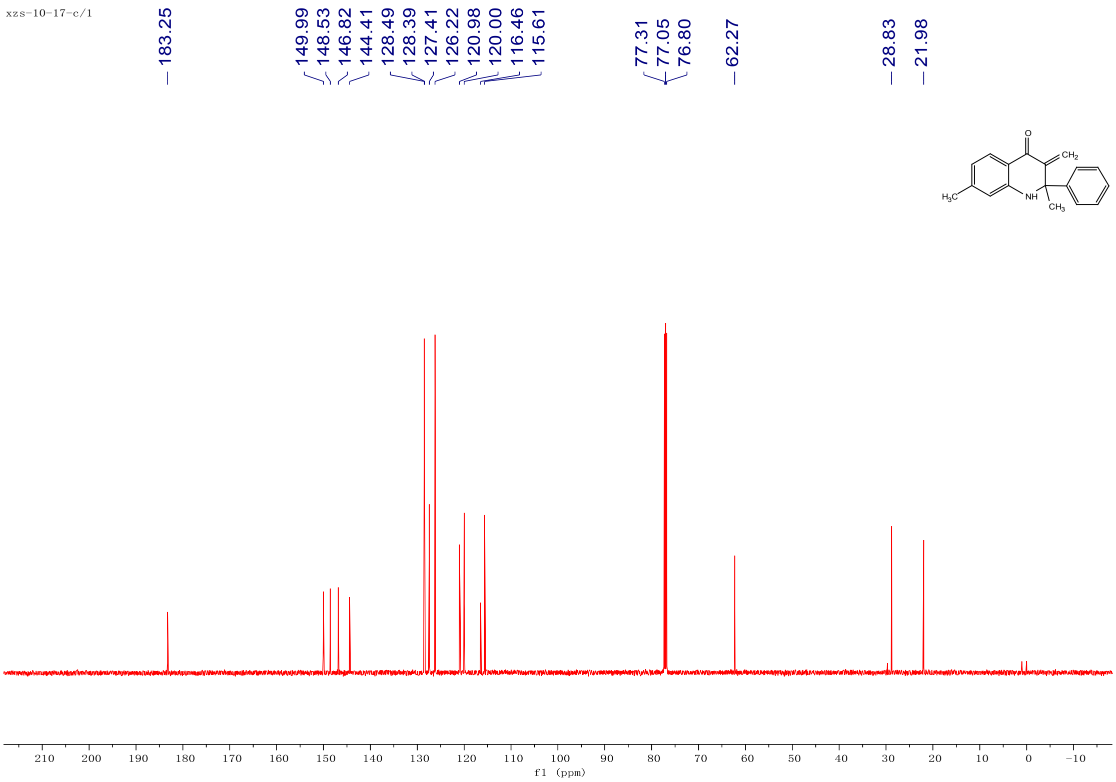
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.523	6686232	95.651	631653	0.000	M	
2	10.114	304010	4.349	23298	0.000	M	
总计		6990242	100.000	654950			



3g



xzs-10-17-h/1
7.72
7.70
7.40
7.39
7.29
7.28
7.26
7.25
7.23
7.21
6.53
6.51
6.51
6.33
5.37
4.83
2.27
1.77
-0.00
1.00
2.07
2.08
1.03
2.05
1.04
1.03
1.00
3.06
3.12
f1 (ppm)



xzs-10-17-c/1
183.25
149.99
148.53
146.82
144.41
128.49
128.39
127.41
126.22
120.98
120.00
116.46
115.61
77.31
77.05
76.80
62.27
28.83
21.98
f1 (ppm)

HPLC chart of racemic product **3g**

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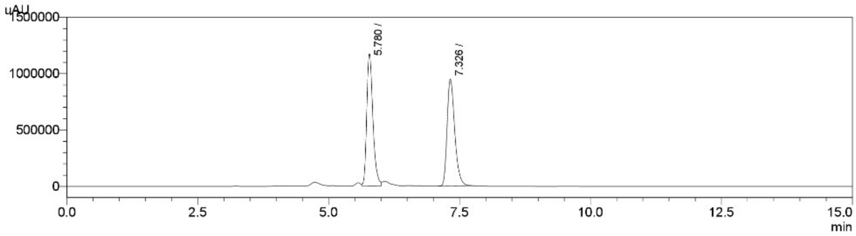
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/28 19:15:13	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:45:50	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-17-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 242nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.780	9561472	49.836	1174724	0.000	M	
2	7.326	9624551	50.164	950108	0.000	M	
总计		19186022	100.000	2124832			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-17-rac.lcd

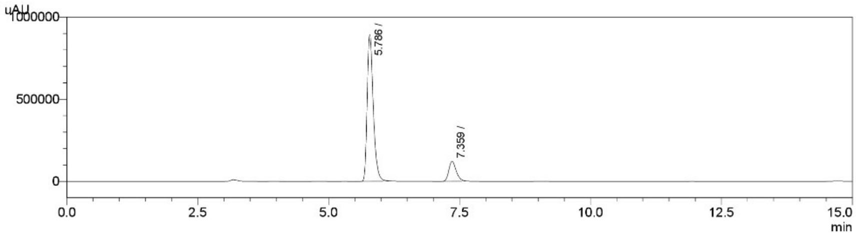
HPLC chart of chiral product **3g**

2020/8/31 18:25:04 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/28 19:30:45	Acquired by	: System Administrator
Date Processed	: 2020/8/31 18:08:41	Modified by	: System Administrator

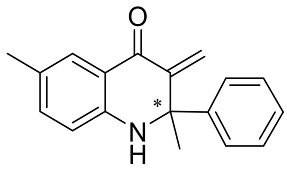
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-17.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 242nm

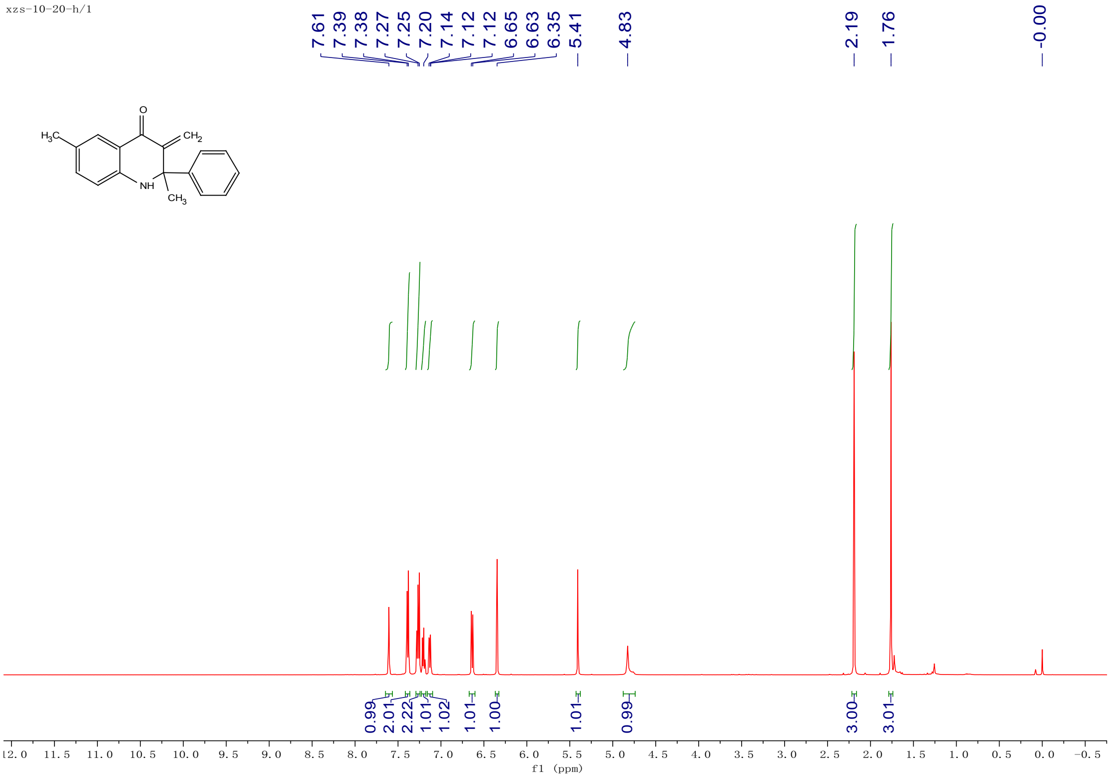
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.786	7193376	85.828	891541	0.000	M	
2	7.359	1187813	14.172	121505	0.000	M	
总计		8381189	100.000	1013046			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-17.lcd

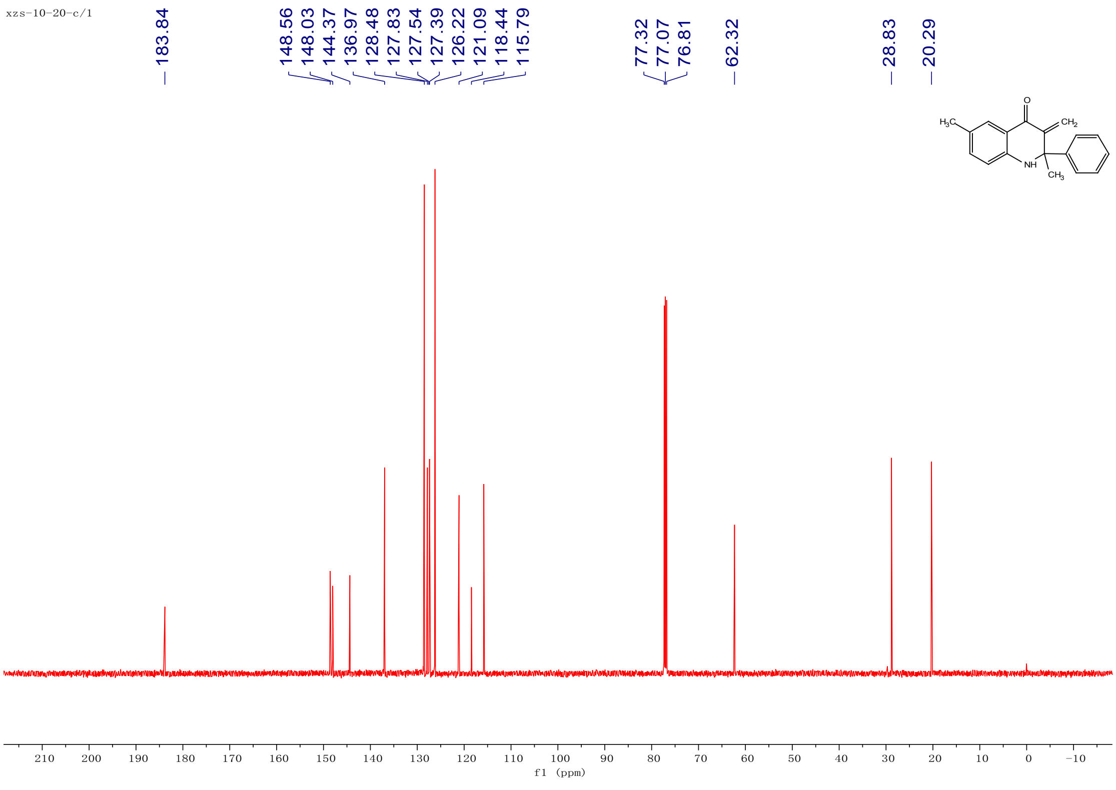


3h

xzs-10-20-h/1



xzs-10-20-c/1



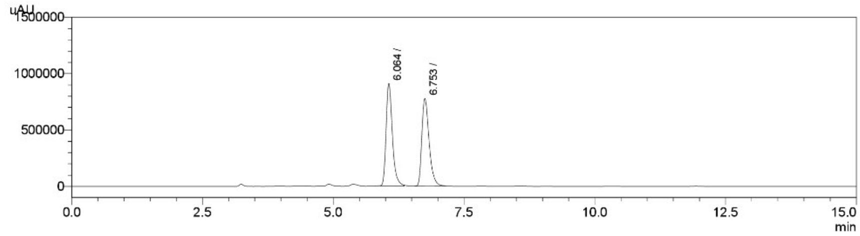
HPLC chart of racemic product **3h**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name :
Vial# : 1-16
Sample Type : 未知
Date Acquired : 2020/7/29 18:49:19
Date Processed : 2020/7/31 20:32:23

Sample ID :
Injection Volume : 15 uL
Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-20-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.064	7569861	50.241	909402	0.000	M	
2	6.753	7497312	49.759	777722	0.000	M	
总计		15067172	100.000	1687124			

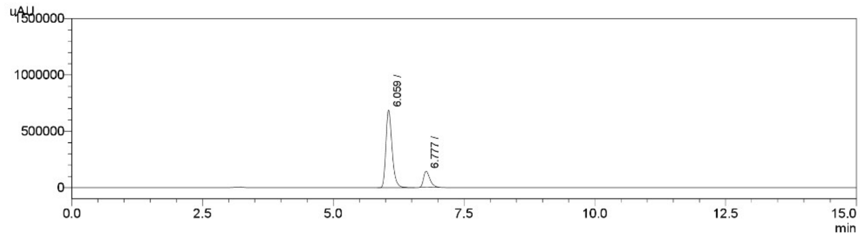
HPLC chart of chiral product **3h**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name :
Vial# : 1-17
Sample Type : 未知
Date Acquired : 2020/7/29 19:04:53
Date Processed : 2020/7/31 20:33:24

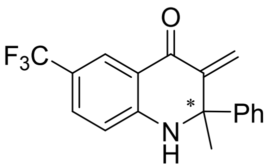
Sample ID :
Injection Volume : 20 uL
Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-20.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

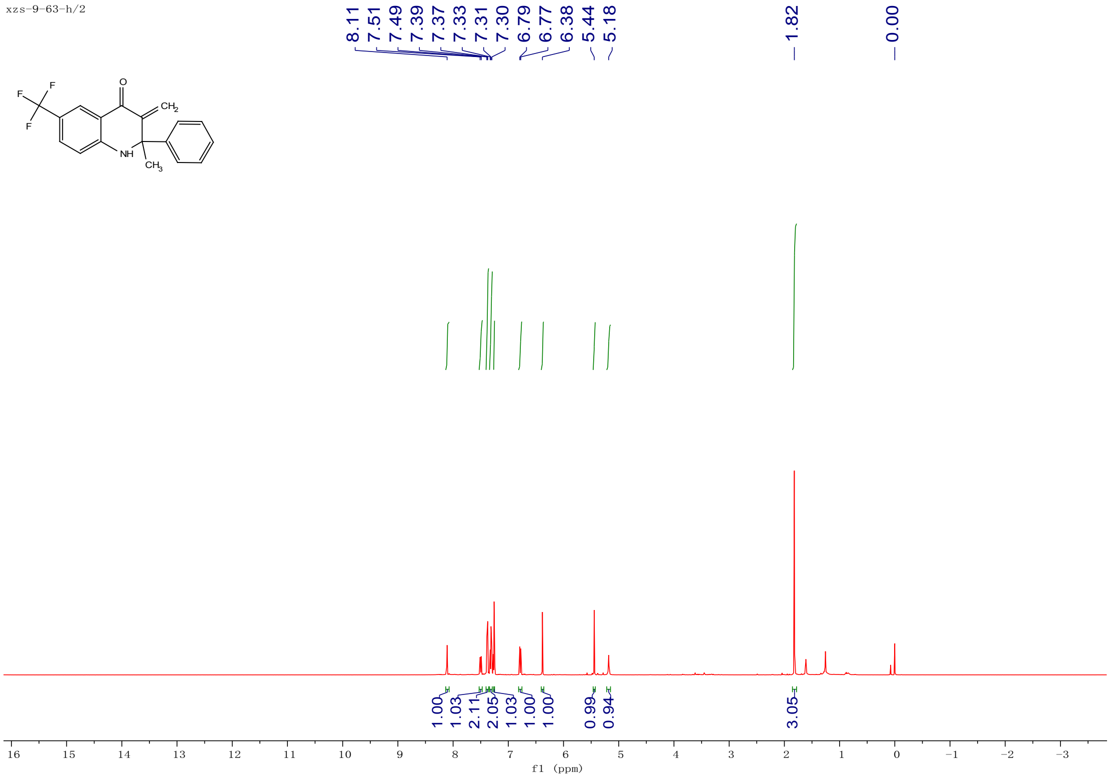


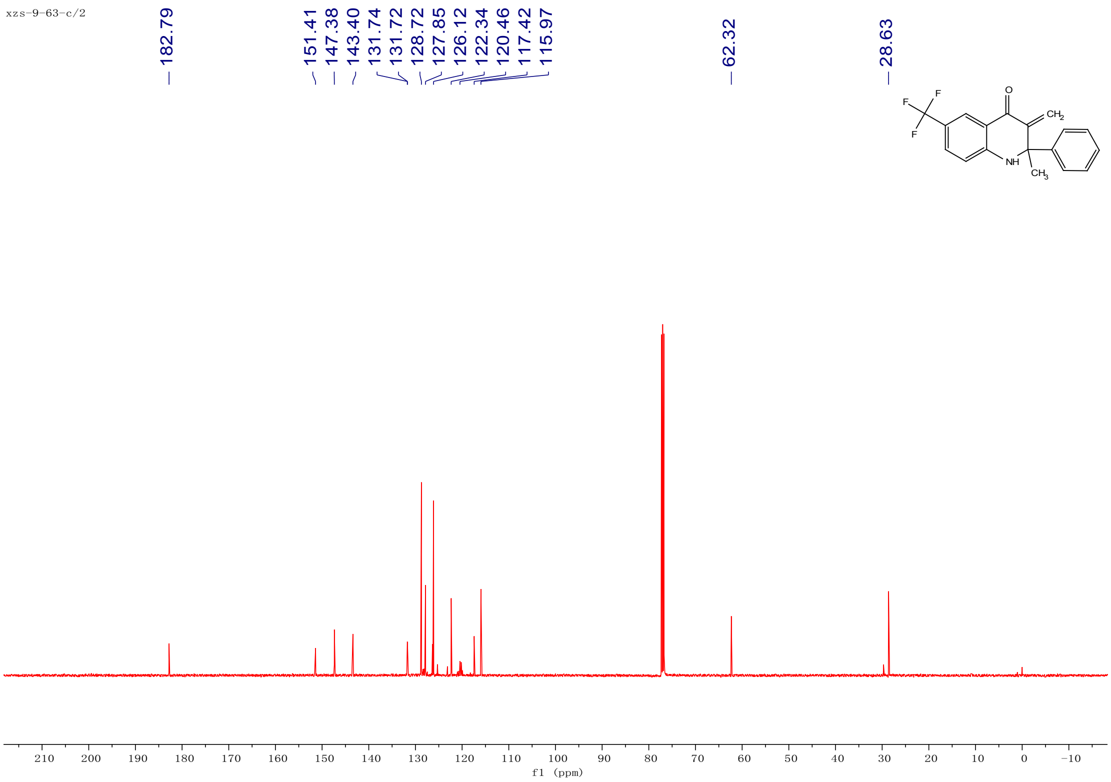
PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.059	5631708	82.294	690985	0.000	M	
2	6.777	1211720	17.706	143489	0.000	M	
总计		6843429	100.000	834474			

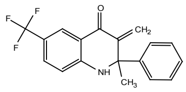

F3C
O
N
H
Ph
*

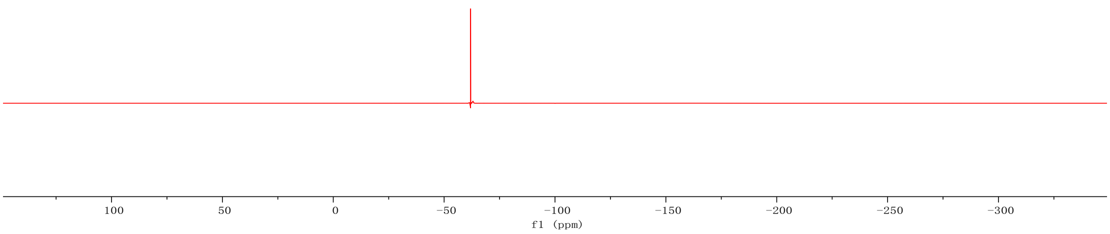
3i


xzs-9-63-h/2
8.11
7.51
7.49
7.39
7.37
7.33
7.31
7.30
6.79
6.77
6.38
5.44
5.18
1.82
0.00
1.00
1.03
2.11
2.05
1.03
1.00
1.00
0.99
0.94
3.05
f1 (ppm)


xzs-9-63-c/2
182.79
151.41
147.38
143.40
131.74
131.72
128.72
127.85
126.12
122.34
120.46
117.42
115.97
62.32
28.63
f1 (ppm)

xzs-9-63-f/2





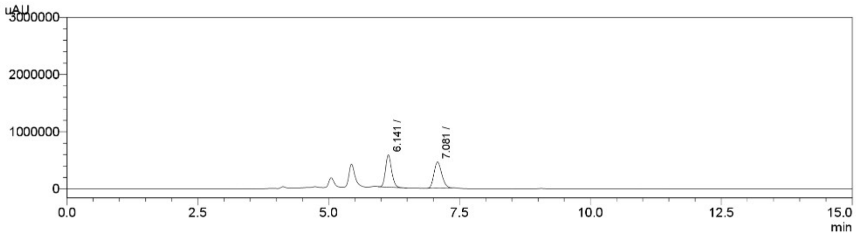
HPLC chart of racemic product **3i**

2020/9/28 20:18:38 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/16 17:41:39	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:05:02	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-63-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 244nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.141	4579826	49.221	566283	0.000	M	
2	7.081	4724811	50.779	457922	0.000	M	
总计		9304637	100.000	1024204			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-63-rac.lcd

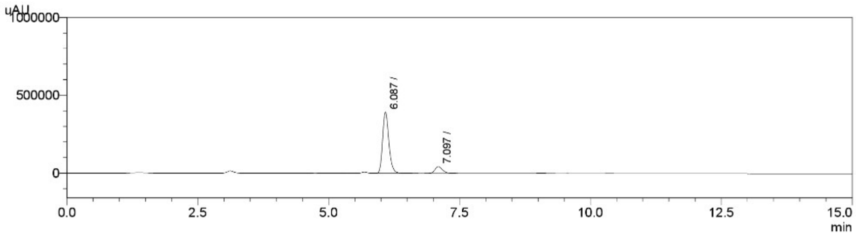
HPLC chart of chiral product **3i**

2020/9/28 20:19:27 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/16 17:57:11	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:06:17	Modified by	: System Administrator

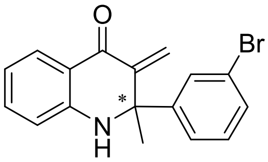
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-63.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



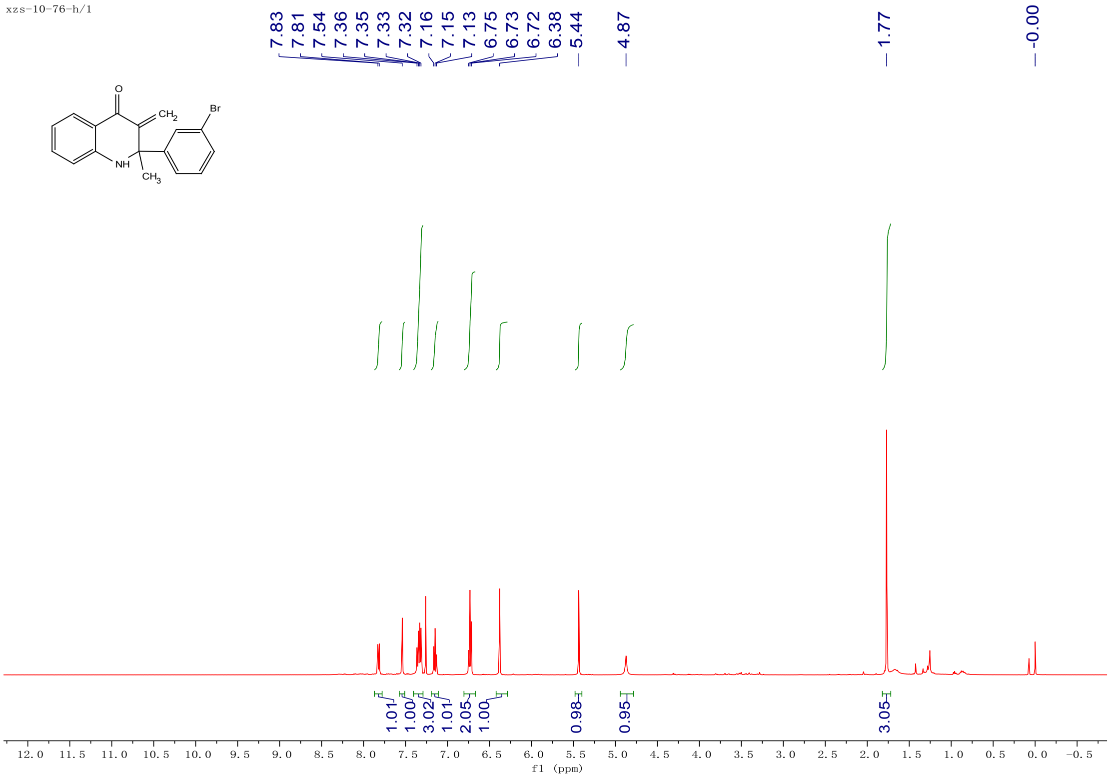
PDA Ch1 244nm

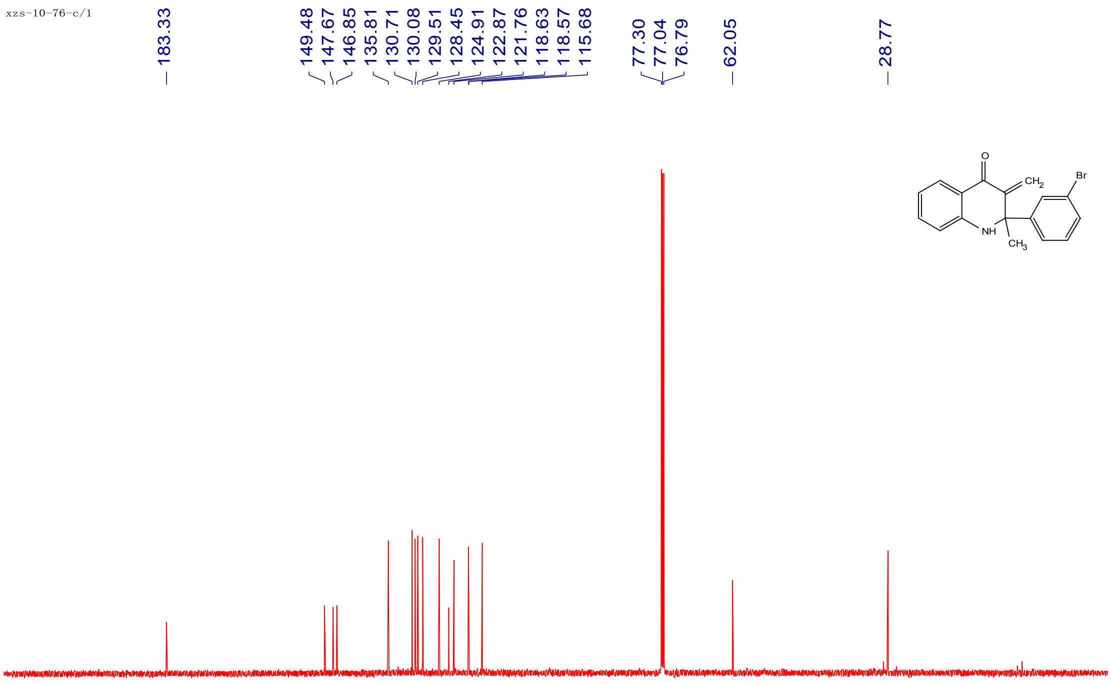
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.087	3276892	88.134	393515	0.000	M	
2	7.097	441178	11.866	43264	0.000	M	
总计		3718070	100.000	436779			

E:\XZS\xzs-1OD-3-80-20-15MIN-9-63.lcd


O
Br
*
N
H

3j


xzs-10-76-h/1
7.83
7.81
7.54
7.36
7.35
7.33
7.32
7.16
7.15
7.13
6.75
6.73
6.72
6.38
5.44
4.87
1.77
-0.00
O
CH2
Br
NH
CH3
1.01
1.00
3.02
1.01
2.05
1.00
0.98
0.95
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


xzs-10-76-c/1
183.33
149.48
147.67
146.85
135.81
130.71
130.08
129.51
128.45
124.91
122.87
121.76
118.63
118.57
115.68
77.30
77.04
76.79
62.05
28.77
O
CH2
Br
NH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

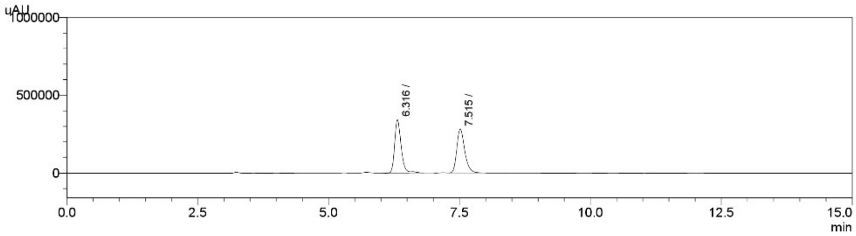
HPLC chart of racemic product **3j**

2020/9/28 20:20:44 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/27 18:20:41	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:11:17	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-76-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 239nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.316	2937247	50.053	343233	0.000	M	
2	7.515	2930986	49.947	281035	0.000	M	
总计		5868233	100.000	624268			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-76-rac.lcd

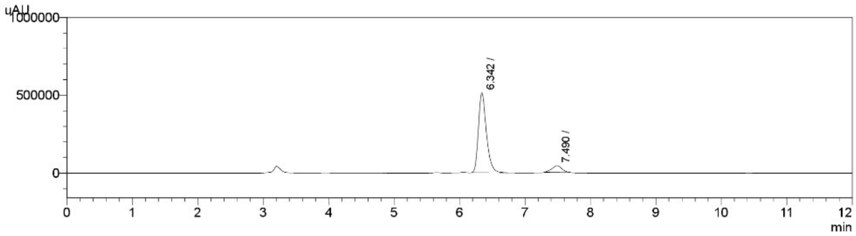
HPLC chart of chiral product **3j**

2020/9/28 20:21:49 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 40 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/25 20:24:00	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:08:34	Modified by	: System Administrator

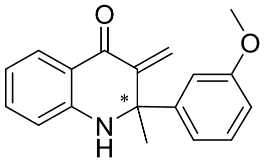
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-76.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



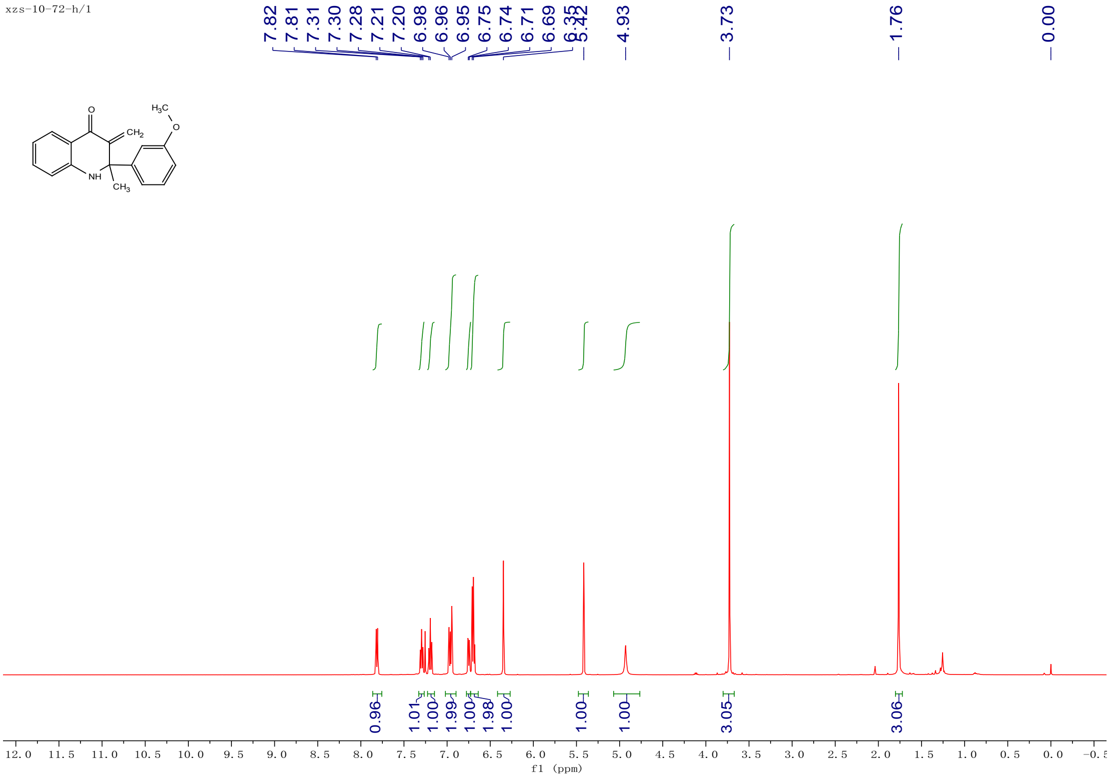
PDA Ch1 239nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.342	4342453	90.204	513103	0.000	M	
2	7.490	471565	9.796	43501	0.000	M	
总计		4814018	100.000	556604			

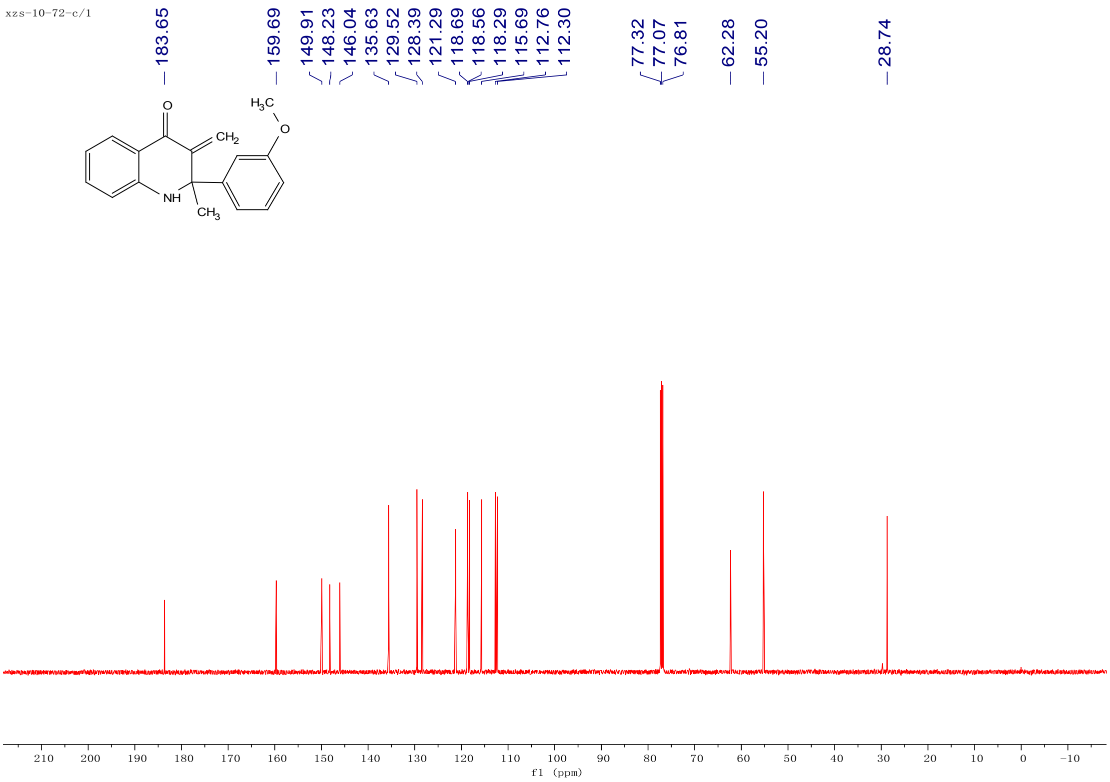
E:\XZS\xzs-1OD-3-80-20-15MIN-10-76.lcd



3k



xzs-10-72-h/1
7.82
7.81
7.31
7.30
7.28
7.21
7.20
6.98
6.96
6.95
6.75
6.74
6.71
6.69
6.35
5.42
4.93
3.73
1.76
0.00
0.96
1.01
1.00
1.99
1.00
1.98
1.00
1.00
1.00
3.05
3.06
f1 (ppm)



xzs-10-72-c/1
183.65
159.69
149.91
148.23
146.04
135.63
129.52
128.39
121.29
118.69
118.56
118.29
115.69
112.76
112.30
77.32
77.07
76.81
62.28
55.20
28.74
f1 (ppm)

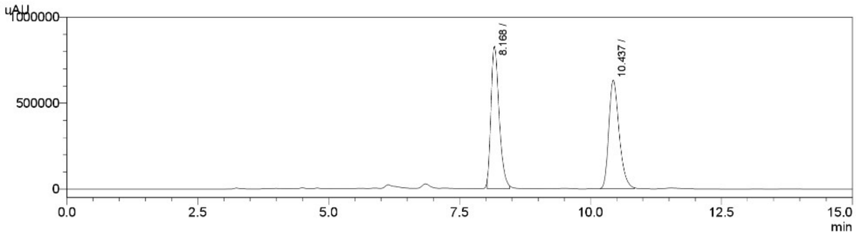
HPLC chart of racemic product **3k**

2020/8/31 16:35:32 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/22 19:55:37	Acquired by	: System Administrator
Date Processed	: 2020/8/28 19:36:16	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-72-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	8.168	8994747	50.750	830011	0.000	M	
2	10.437	8728735	49.250	631786	0.000	M	
总计		17723482	100.000	1461797			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-72-rac.lcd

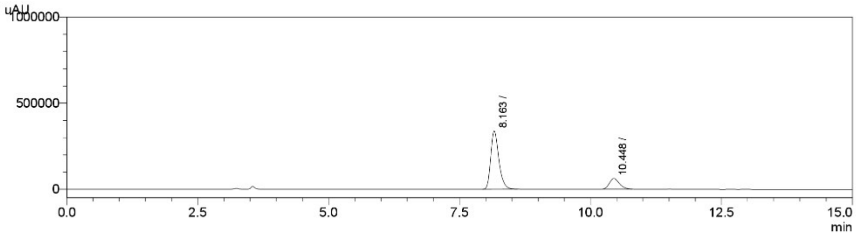
HPLC chart of chiral product **3k**

2020/8/31 16:36:06 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/22 19:40:04	Acquired by	: System Administrator
Date Processed	: 2020/8/28 19:37:07	Modified by	: System Administrator

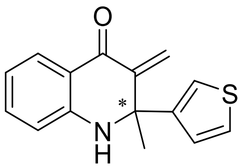
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-72.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



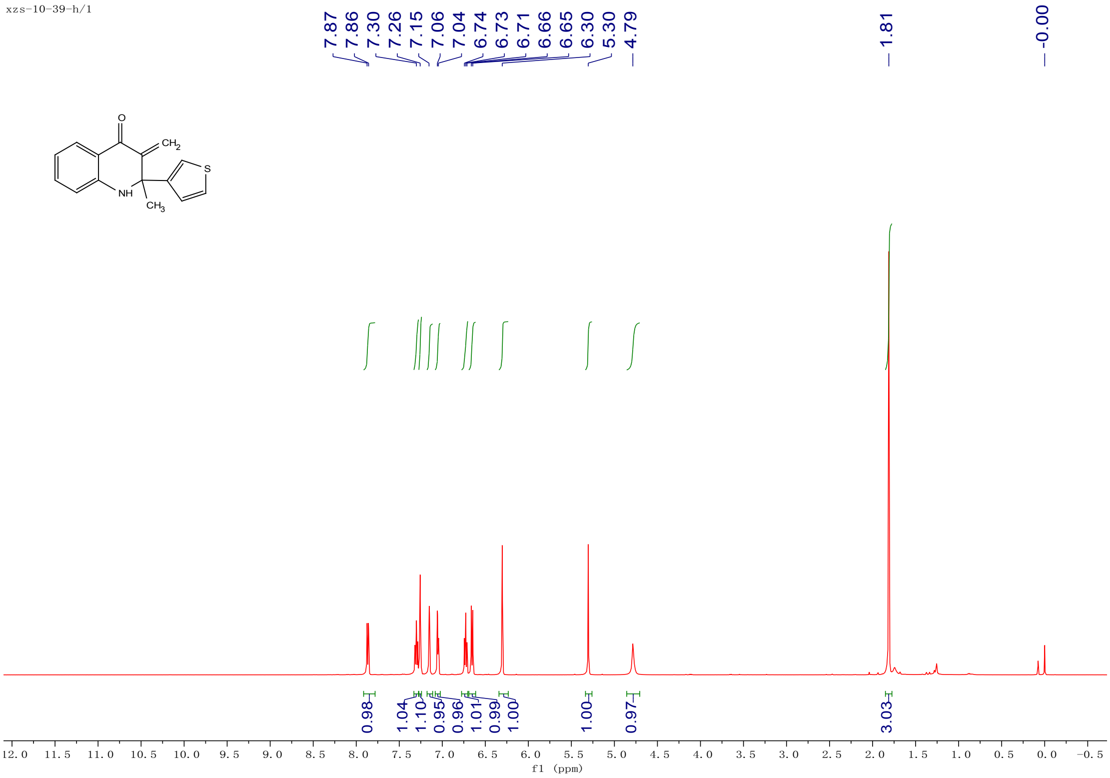
PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	8.163	3646209	81.952	338096	0.000	M	
2	10.448	802967	18.048	61356	0.000	M	
总计		4449176	100.000	399453			

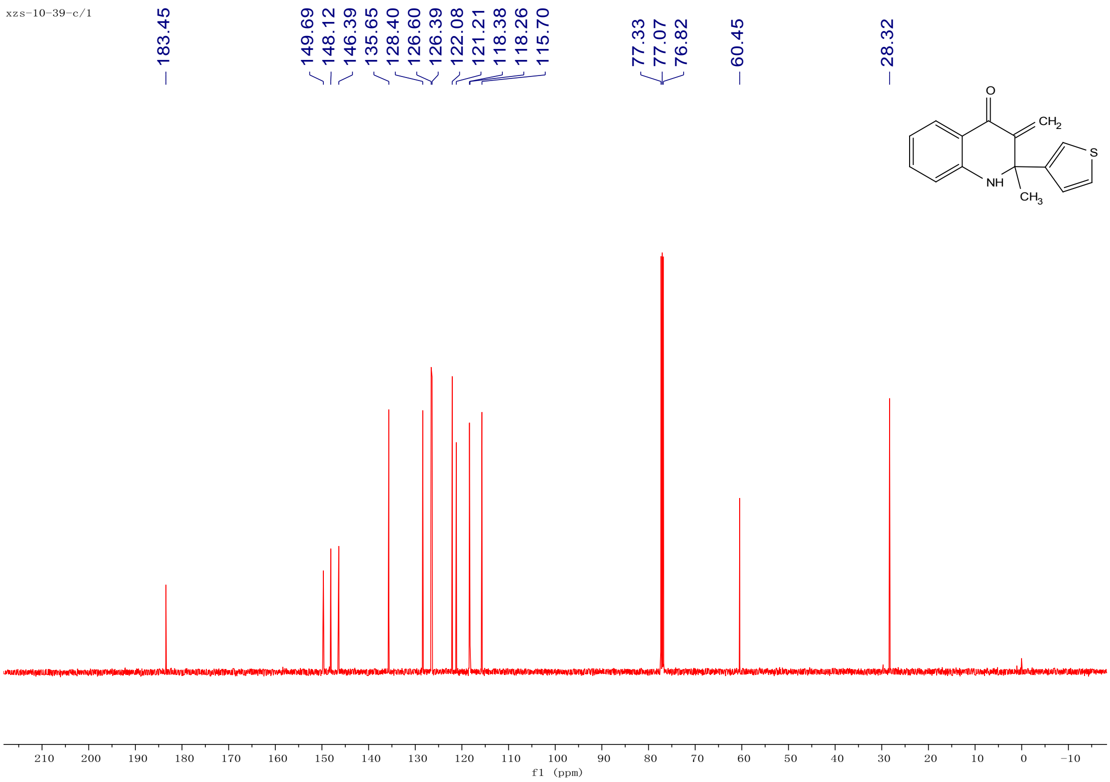
E:\XZS\xzs-1OD-3-80-20-15MIN-10-72.lcd



3l



xzs-10-39-h/1
7.87
7.86
7.30
7.26
7.15
7.06
7.04
6.74
6.73
6.71
6.66
6.65
6.30
5.30
4.79
1.81
-0.00
O
CH2
NH
CH3
S
0.98
1.04
1.10
0.95
0.96
1.01
0.99
1.00
1.00
0.97
3.03
f1 (ppm)



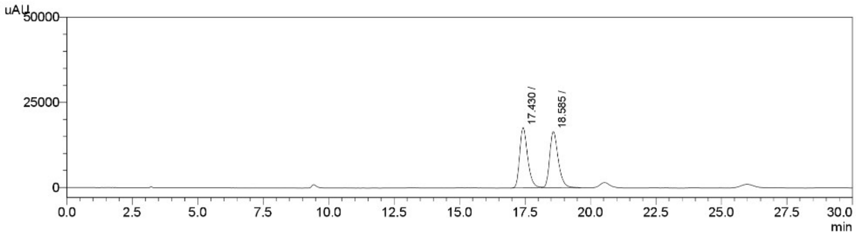
xzs-10-39-c/1
183.45
149.69
148.12
146.39
135.65
128.40
126.60
126.39
122.08
121.21
118.38
118.26
115.70
77.33
77.07
76.82
60.45
28.32
O
CH2
NH
CH3
S
f1 (ppm)

HPLC chart of racemic product **3l**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 10 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/6 19:48:40	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:48:42	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-95-5-40MIN-10-39-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-95-5-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 238nm

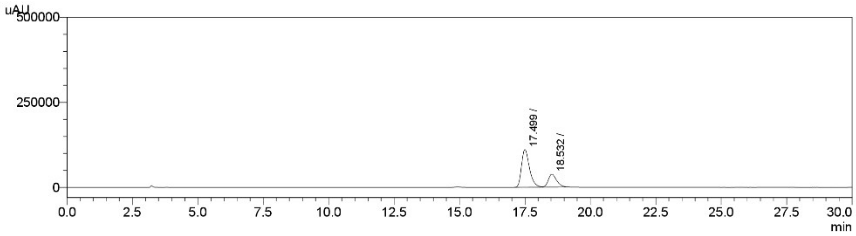
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	17.430	377223	50.103	17729	0.000	M	
2	18.585	375667	49.897	16564	0.000	V M	
总计		752889	100.000	34293			

HPLC chart of chiral product **3l**

==== Shimadzu LabSolutions Analysis Report ====

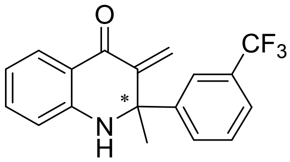
Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/6 20:29:13	Acquired by	: System Administrator
Date Processed	: 2020/8/31 18:10:06	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-95-5-40MIN-10-39.lcd
Method Filename : D:\XZS\XZS-1OD-3-95-5-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

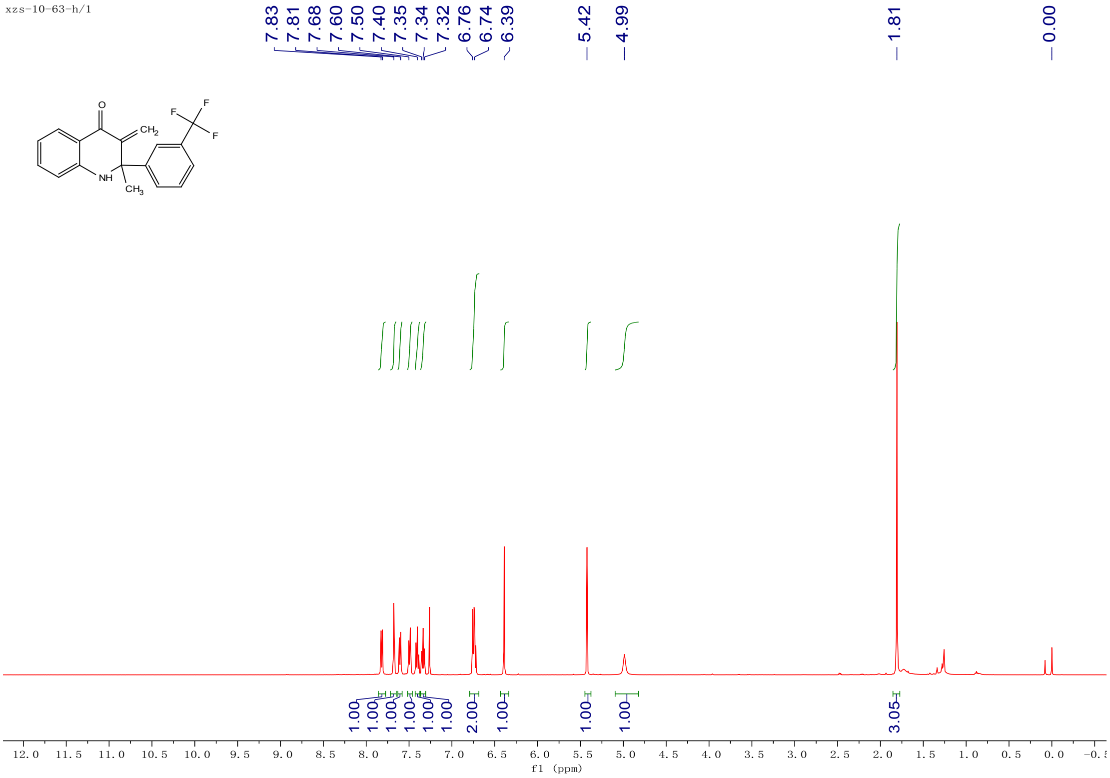


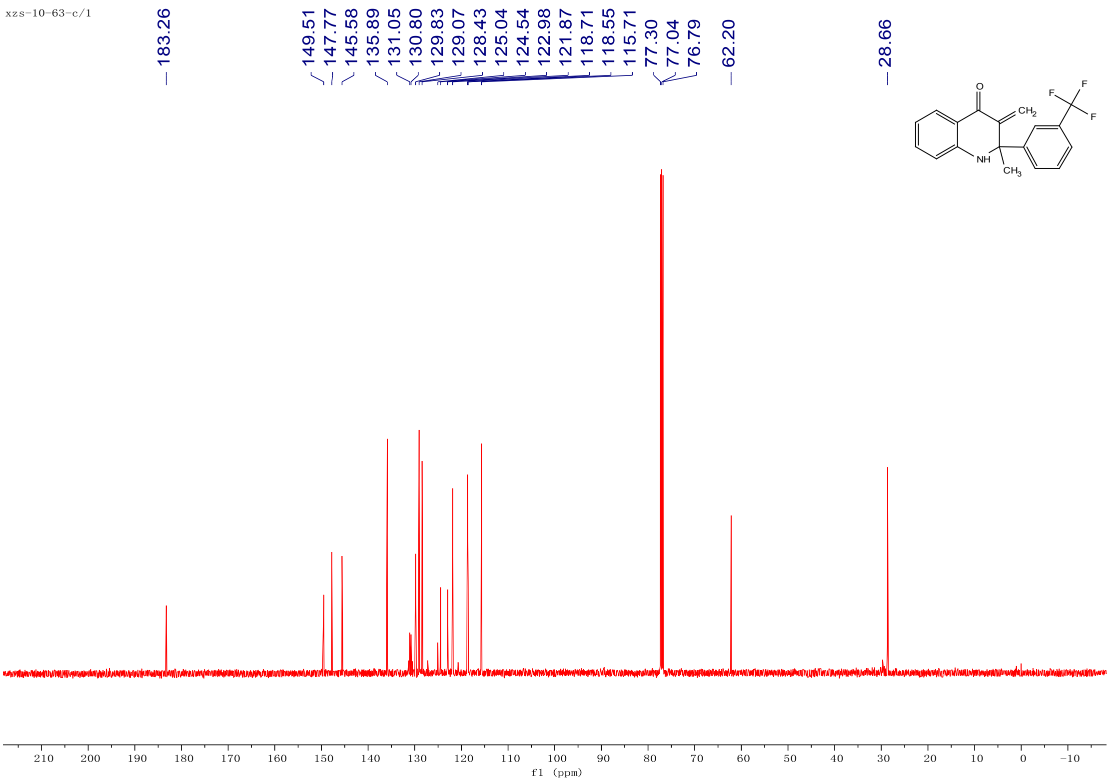
PDA Ch1 238nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	17.499	2360082	73.480	111061	0.000	M	
2	18.532	851800	26.520	38126	0.000	V M	
总计		3211883	100.000	149187			

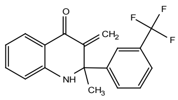

O
CF3
N
H
*

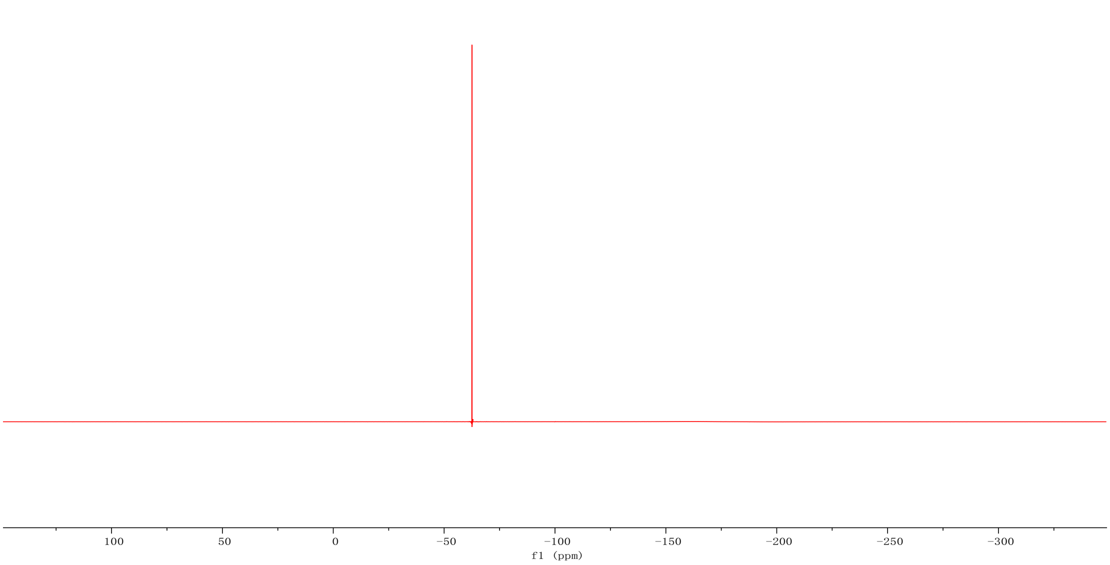
3m


xzs-10-63-h/1
7.83
7.81
7.68
7.60
7.50
7.40
7.35
7.34
7.32
6.76
6.74
6.39
5.42
4.99
1.81
0.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
3.05
f1 (ppm)


xzs-10-63-c/1
183.26
149.51
147.77
145.58
135.89
131.05
130.80
129.83
129.07
128.43
125.04
124.54
122.98
121.87
118.71
118.55
115.71
77.30
77.04
76.79
62.20
28.66
f1 (ppm)

xzs-10-63-f/1





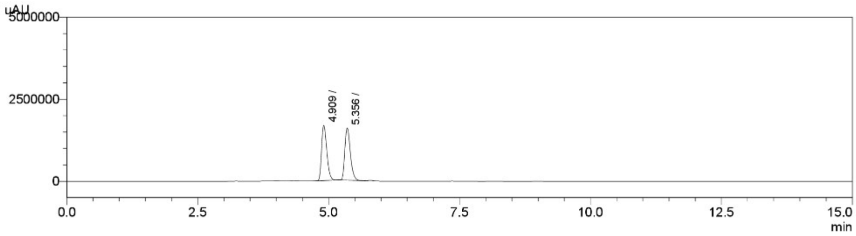
HPLC chart of racemic product **3m**

2020/8/31 16:41:50 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-1	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/18 19:20:49	Acquired by	: System Administrator
Date Processed	: 2020/8/21 19:57:43	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-63-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 237nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	4.909	11694401	49.916	1688349	0.000	M	
2	5.356	11733672	50.084	1594982	0.000	M	
总计		23428073	100.000	3283331			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-63-rac.lcd

HPLC chart of chiral product **3m**

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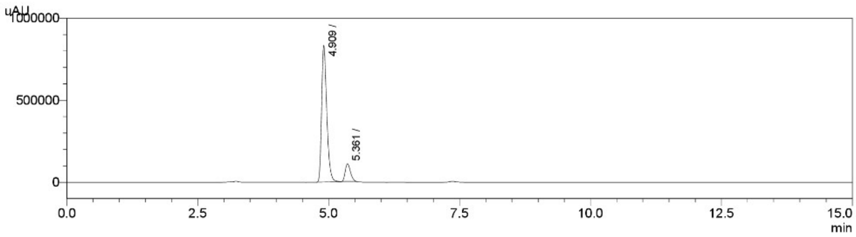
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-2	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/18 19:36:23	Acquired by	: System Administrator
Date Processed	: 2020/8/21 20:00:12	Modified by	: System Administrator

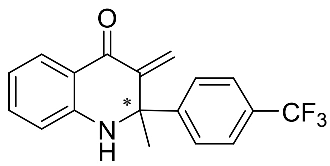
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-63.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



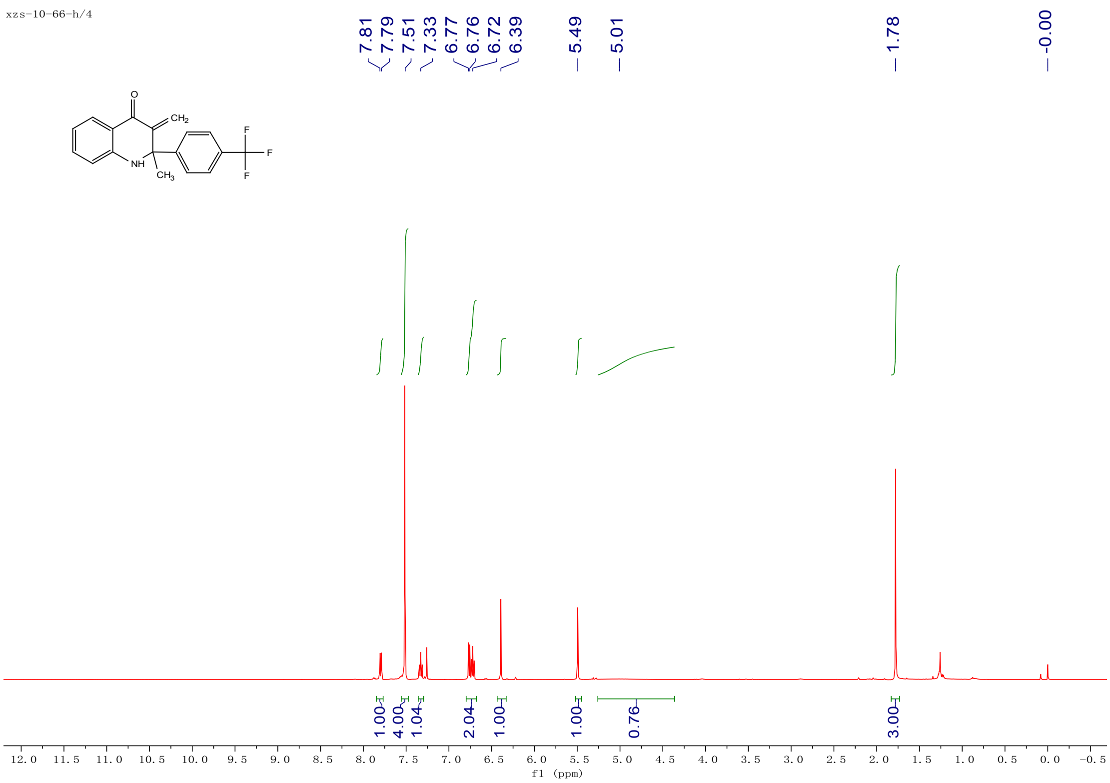
PDA Ch1 237nm

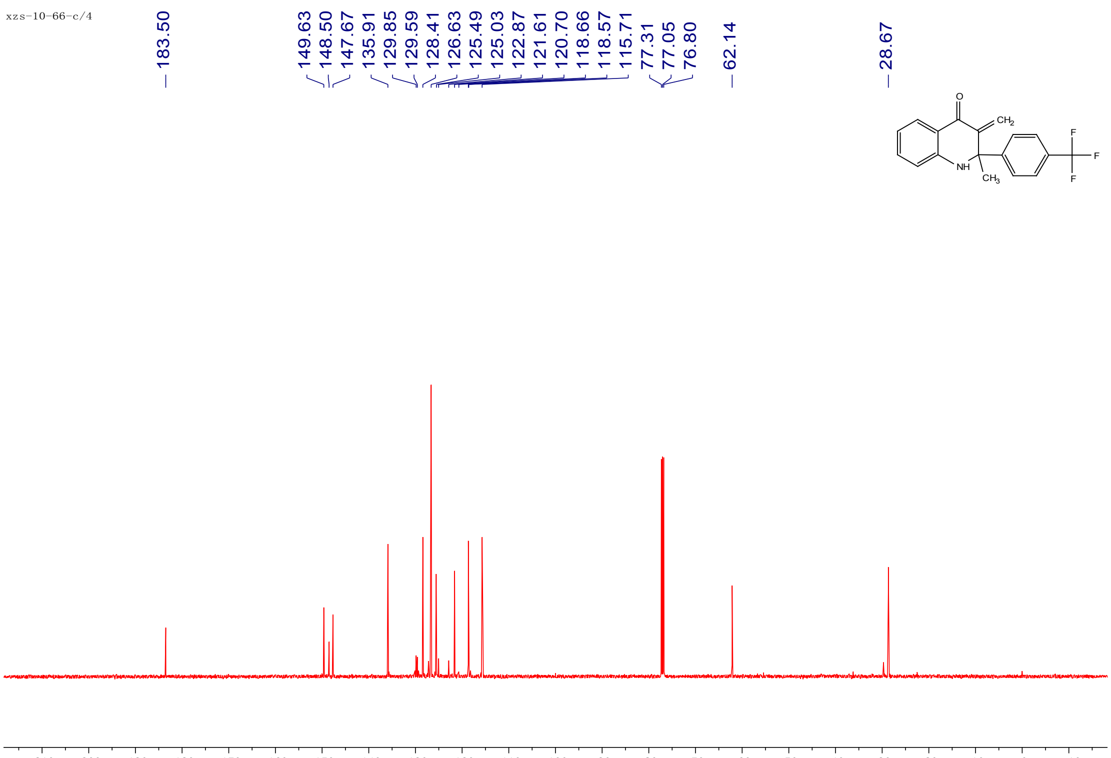
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	4.909	5685905	88.549	834837	0.000	M	
2	5.361	735294	11.451	107225	0.000	M	
总计		6421199	100.000	942062			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-63.lcd

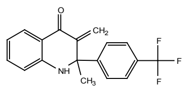

O
N
H
*
CF3

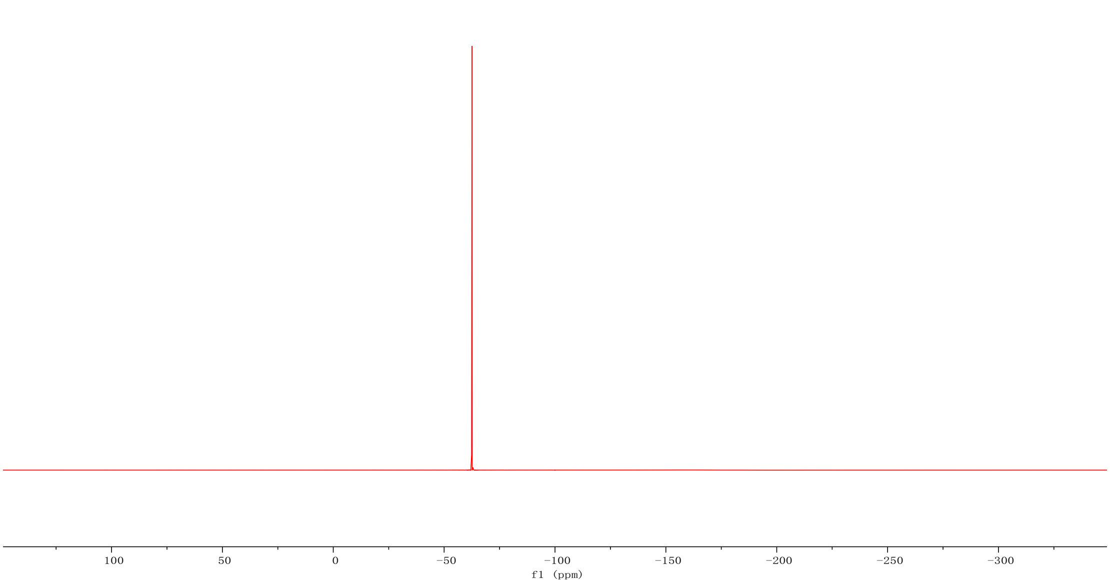
3n


xzs-10-66-h/4
7.81
7.79
7.51
7.33
6.77
6.76
6.72
6.39
5.49
5.01
1.78
-0.00
1.00
4.00
1.04
2.04
1.00
1.00
0.76
3.00
f1 (ppm)


xzs-10-66-c/4
183.50
149.63
148.50
147.67
135.91
129.85
129.59
128.41
126.63
125.49
125.03
122.87
121.61
120.70
118.66
118.57
115.71
77.31
77.05
76.80
62.14
28.67
f1 (ppm)

xzs-10-66-f/4



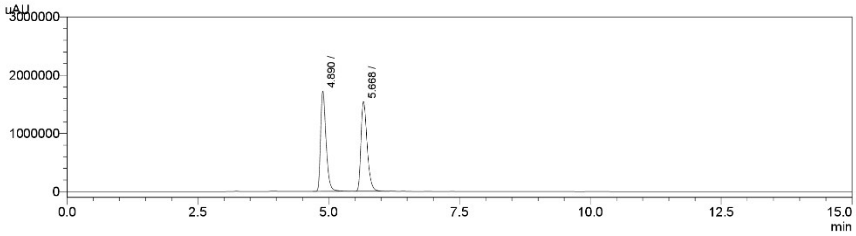


HPLC chart of racemic product **3n**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-1	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/20 20:26:00	Acquired by	: System Administrator
Date Processed	: 2020/8/21 20:00:43	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-66-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 237nm

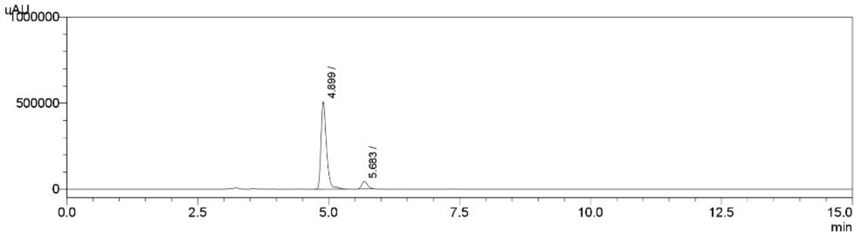
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	4.890	12549313	49.867	1722766	0.000	M	
2	5.668	12616402	50.133	1544189	0.000	M	
总计		25165714	100.000	3266955			

HPLC chart of chiral product **3n**

==== Shimadzu LabSolutions Analysis Report ====

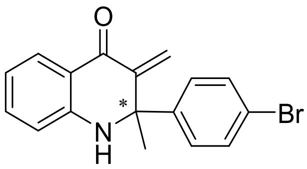
Sample Name	:	Sample ID	:
Vial#	: 1-2	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/20 20:41:32	Acquired by	: System Administrator
Date Processed	: 2020/8/21 20:02:03	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-66.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

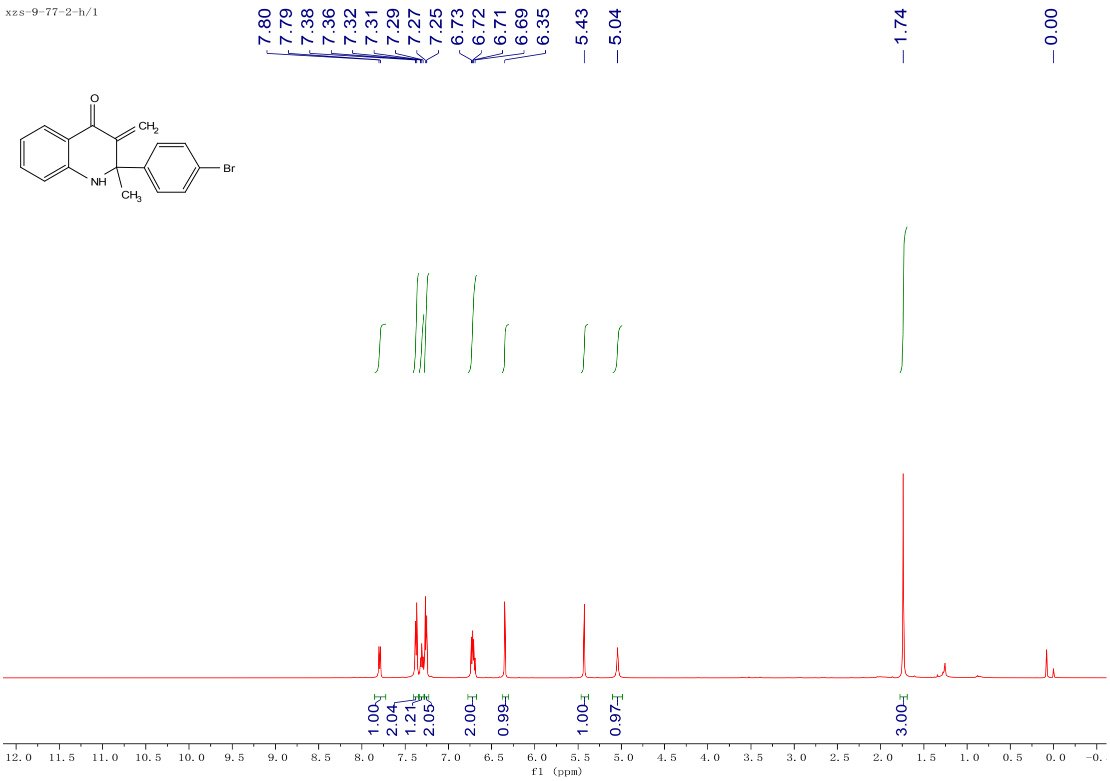


PDA Ch1 237nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	4.899	3704394	91.541	509052	0.000	M	
2	5.683	342318	8.459	45108	0.000	M	
总计		4046712	100.000	554160			



3o



xzs-9-77-2-h/1
7.80
7.79
7.38
7.36
7.32
7.31
7.29
7.27
7.25
6.73
6.72
6.71
6.69
6.35
5.43
5.04
1.74
0.00
O
CH2
NH
CH3
Br
1.00
2.04
1.21
2.05
2.00
0.99
1.00
0.97
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

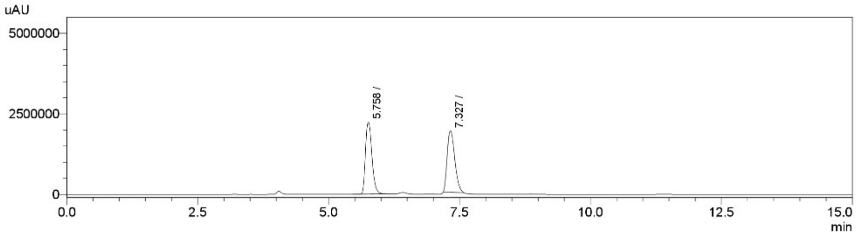
xzs-9-77-2-c/1
183.60
149.72
147.93
143.46
135.80
131.62
128.38
128.09
121.52
121.38
118.54
118.52
115.74
77.33
77.08
76.83
61.98
28.61
O
CH2
NH
CH3
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

HPLC chart of racemic product **3o**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/20 20:36:12	Acquired by	: System Administrator
Date Processed	: 2020/7/20 20:56:04	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-77-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.2cb.lcb



PDA Ch1 238nm

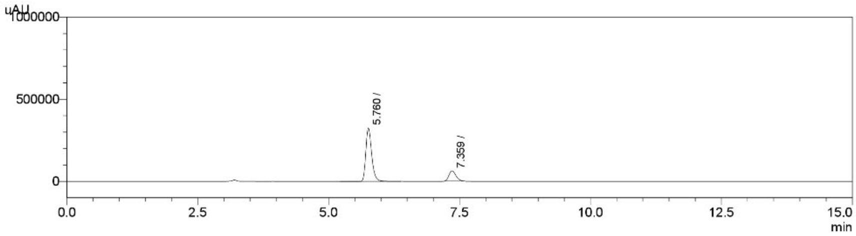
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.758	19123250	49.958	2238404	0.000	M	
2	7.327	19155080	50.042	1911867	0.000	M	
总计		38278330	100.000	4150271			

HPLC chart of chiral product **3o**

==== Shimadzu LabSolutions Analysis Report ====

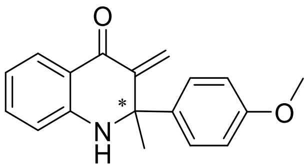
Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/20 20:20:39	Acquired by	: System Administrator
Date Processed	: 2020/8/31 18:05:53	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-9-77.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.2cb.lcb

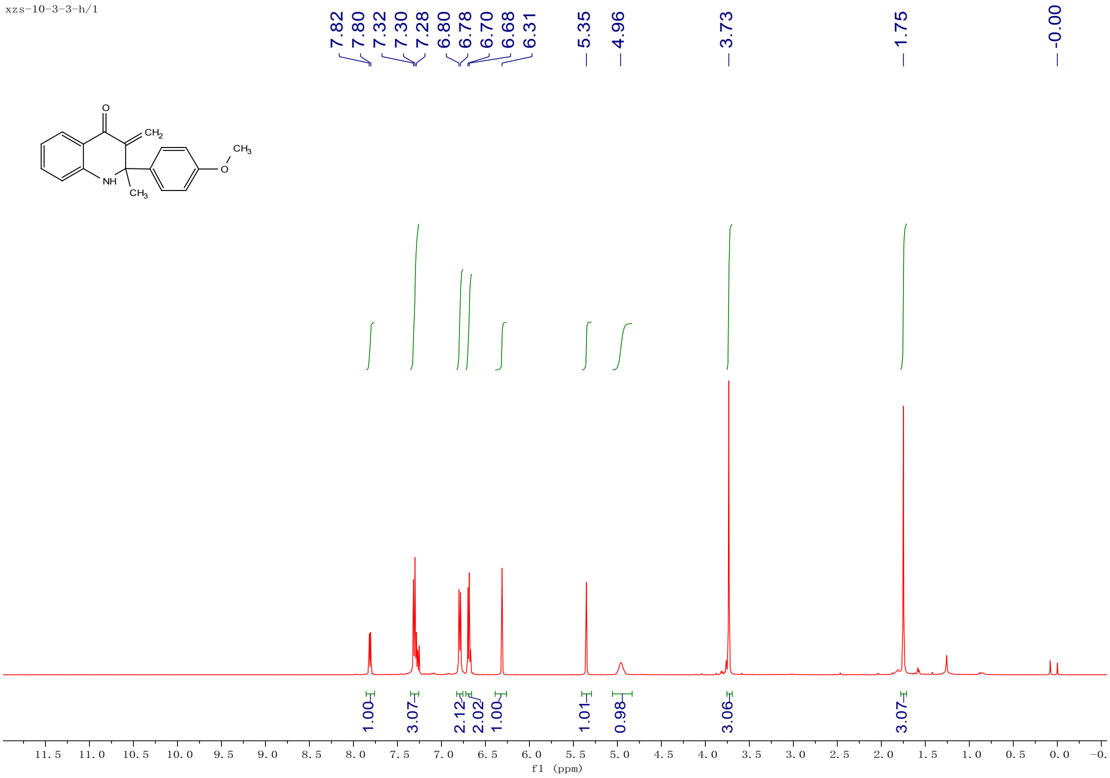


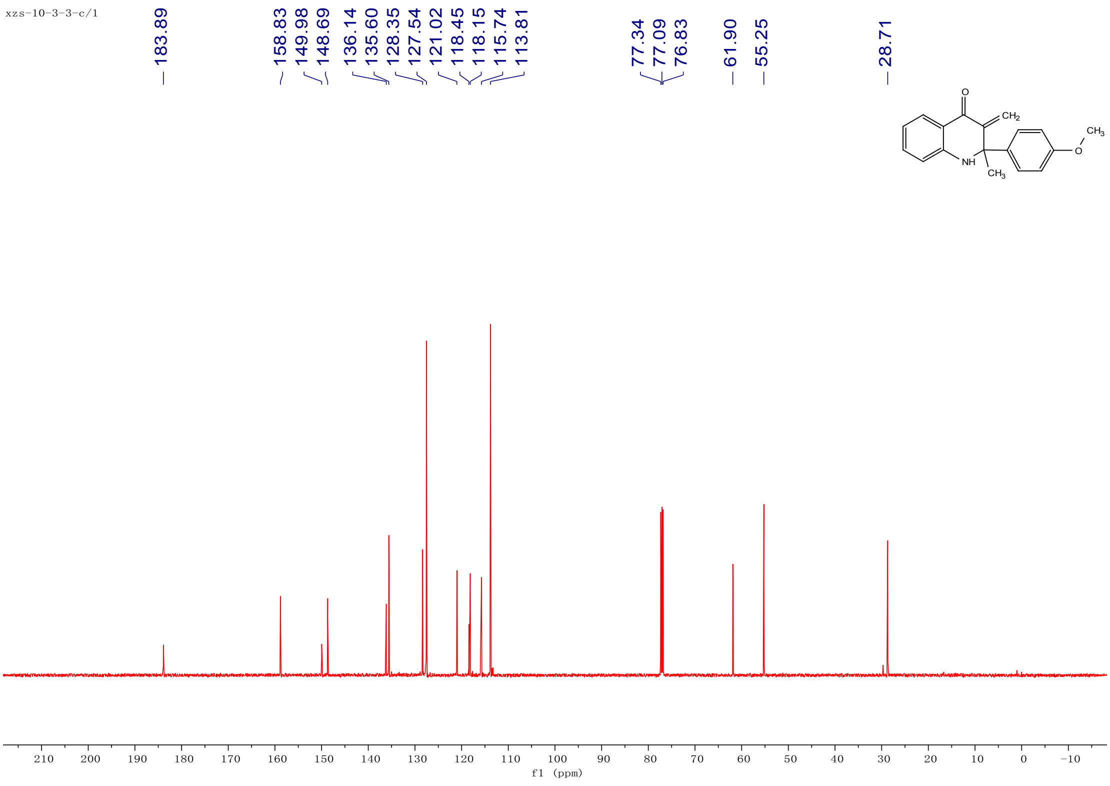
PDA Ch1 238nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.760	2528763	81.217	326312	0.000	M	
2	7.359	584838	18.783	63137	0.000	M	
总计		3113601	100.000	389449			



3p


xzs-10-3-3-h/1
7.82
7.80
7.32
7.30
7.28
6.80
6.78
6.70
6.68
6.31
5.35
4.96
3.73
1.75
-0.00
1.00
3.07
2.12
2.02
1.00
1.01
0.98
3.06
3.07
f1 (ppm)


xzs-10-3-3-c/1
183.89
158.83
149.98
148.69
136.14
135.60
128.35
127.54
121.02
118.45
118.15
115.74
113.81
77.34
77.09
76.83
61.90
55.25
28.71
f1 (ppm)

HPLC chart of racemic product **3p**

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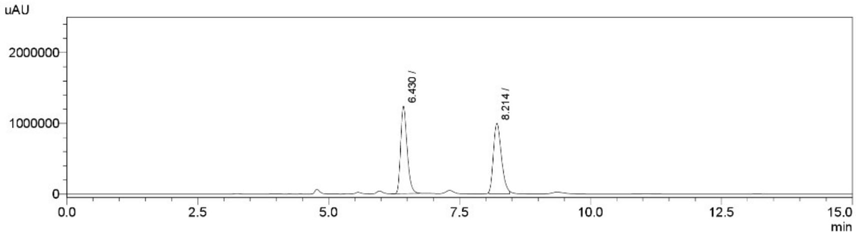
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-31	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/22 19:01:56	Acquired by	: System Administrator
Date Processed	: 2020/7/22 19:20:50	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-3-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 238nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.430	10629410	49.976	1239146	0.000	M	
2	8.214	10639689	50.024	1000378	0.000	M	
总计		21269099	100.000	2239525			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-3-rac.lcd

HPLC chart of chiral product **3p**

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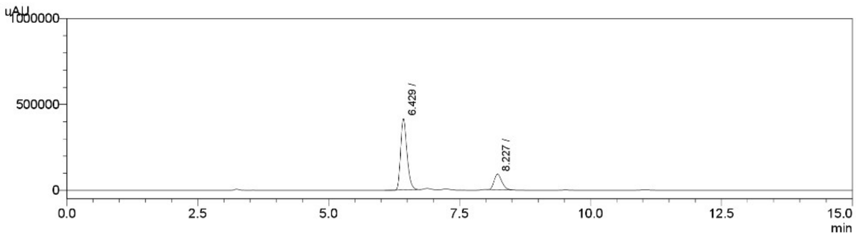
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-32	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/22 19:19:27	Acquired by	: System Administrator
Date Processed	: 2020/7/22 20:09:33	Modified by	: System Administrator

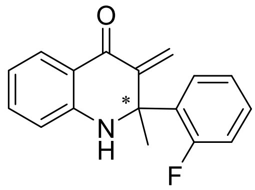
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-3.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



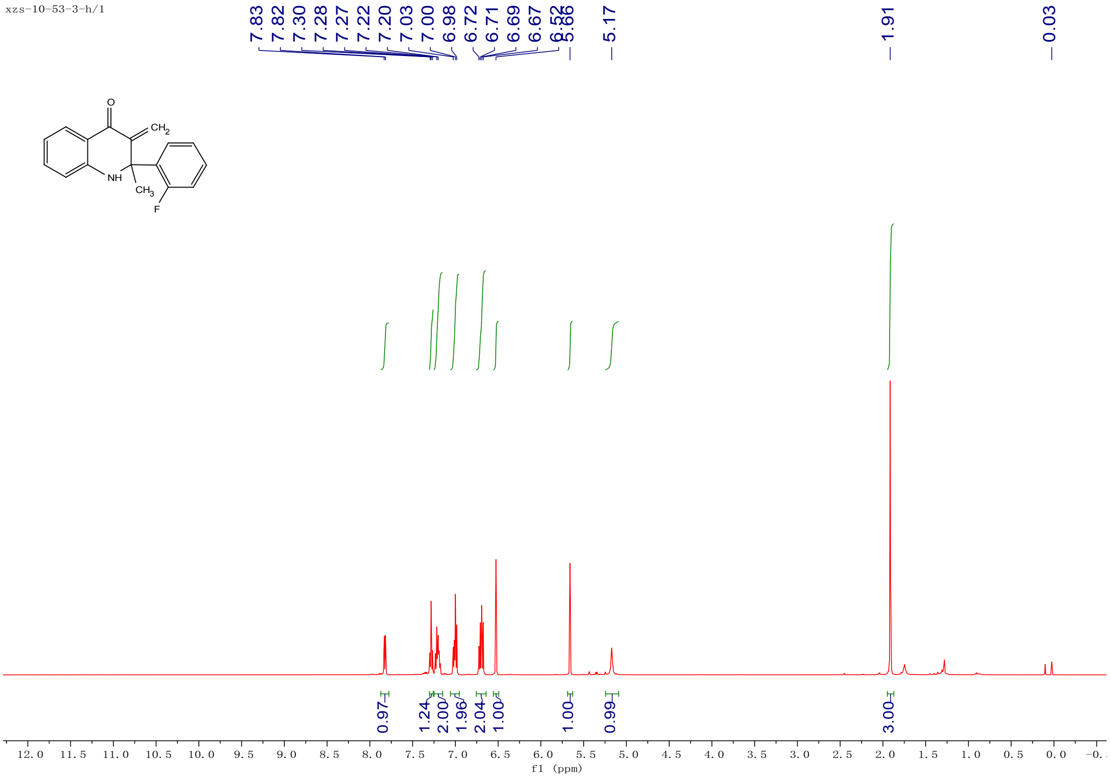
PDA Ch1 238nm

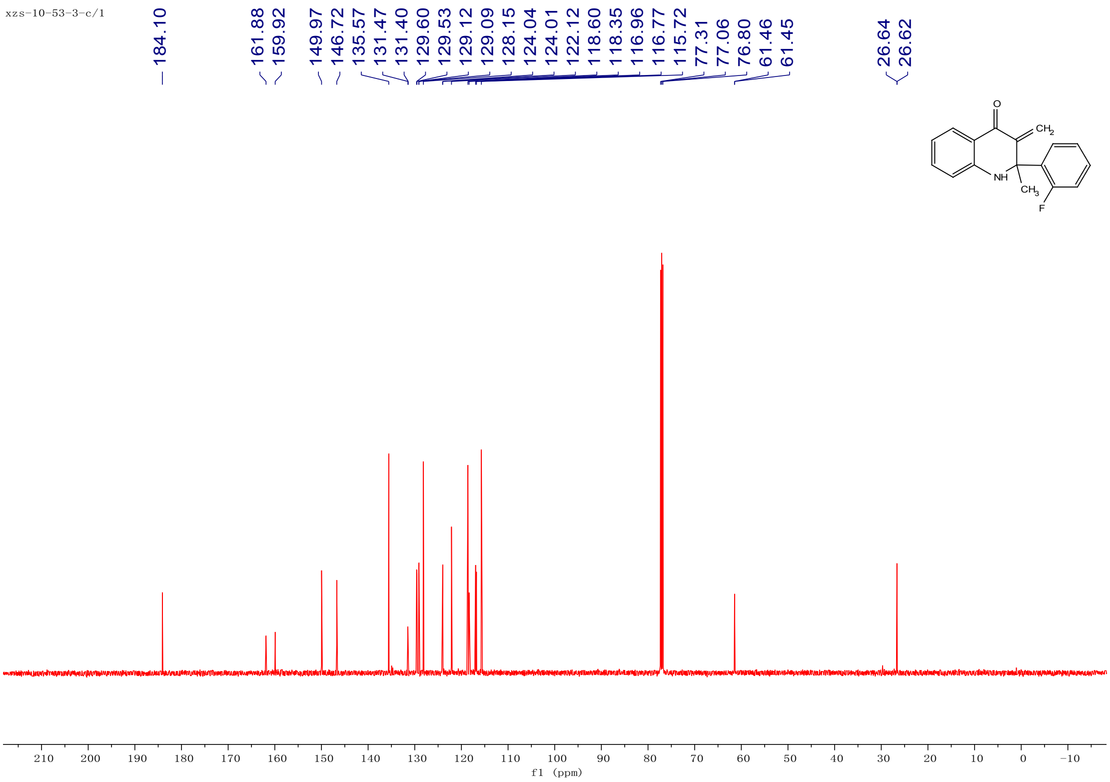
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.429	3497285	79.104	416237	0.000	M	
2	8.227	923815	20.896	90968	0.000	M	
总计		4421100	100.000	507205			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-3.lcd

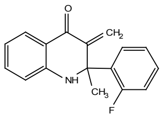

O
N
H
F
*

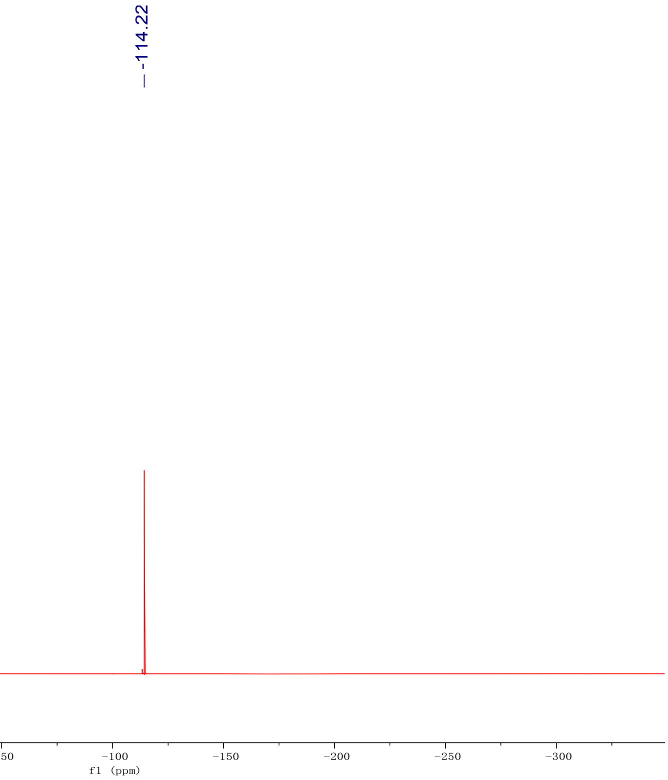
3q


xzs-10-53-3-h/1
7.83
7.82
7.30
7.28
7.27
7.22
7.20
7.03
7.00
6.98
6.72
6.71
6.69
6.67
6.52
5.66
5.17
1.91
0.03
O
CH2
NH
CH3
F
0.97
1.24
2.00
1.96
2.04
1.00
1.00
0.99
3.00
f1 (ppm)


xzs-10-53-3-c/1
184.10
161.88
159.92
149.97
146.72
135.57
131.47
131.40
129.60
129.53
129.12
129.09
128.15
124.04
124.01
122.12
118.60
118.35
116.96
116.77
115.72
77.31
77.06
76.80
61.46
61.45
26.64
26.62
O
CH2
NH
CH3
F
f1 (ppm)

xzs-10-53-3-f/2





HPLC chart of racemic product **3q**

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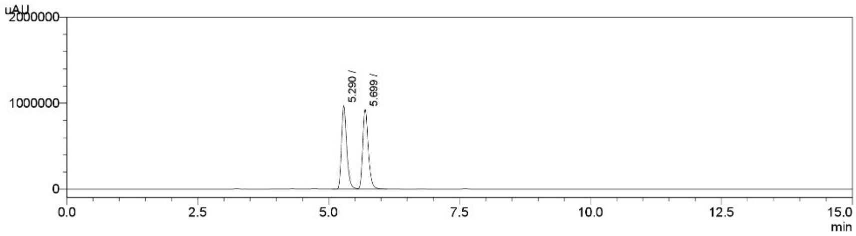
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/13 20:20:46	Acquired by	: System Administrator
Date Processed	: 2020/8/21 19:54:58	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-53-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 237nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.290	6745407	49.727	971565	0.000	M	
2	5.699	6819534	50.273	928483	0.000	V M	
总计		13564942	100.000	1900048			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-53-rac.lcd

HPLC chart of chiral product **3q**

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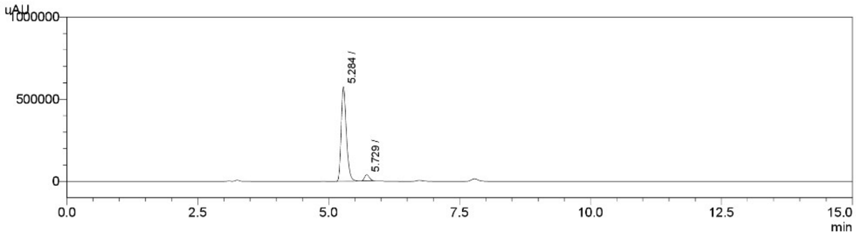
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/14 14:10:00	Acquired by	: System Administrator
Date Processed	: 2020/8/21 19:56:59	Modified by	: System Administrator

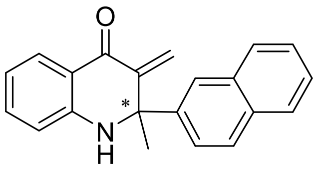
Data Filename : E:\XZS\xzs-1OD-3-80-20-15MIN-10-53.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-15-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



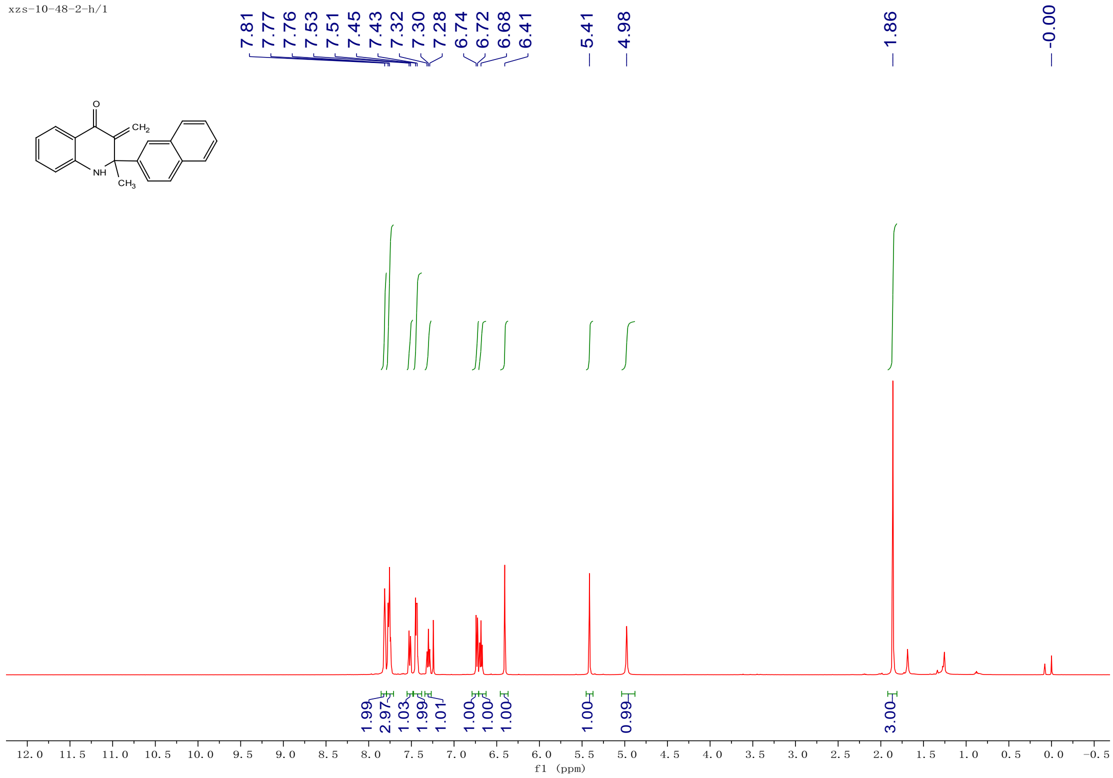
PDA Ch1 237nm

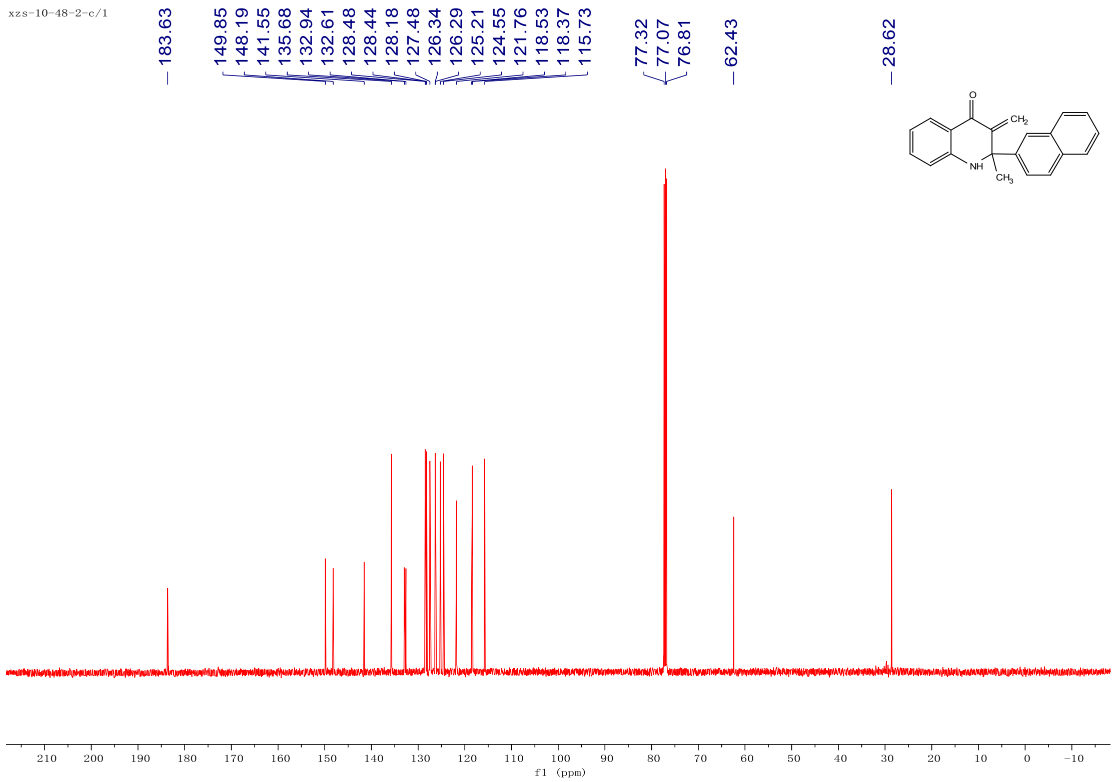
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	5.284	3978405	94.527	576481	0.000	M	
2	5.729	230329	5.473	35768	0.000	M	
总计		4208734	100.000	612248			

E:\XZS\xzs-1OD-3-80-20-15MIN-10-53.lcd


O
*
N
H

3r


xzs-10-48-2-h/1
7.81 7.77 7.76 7.53 7.51 7.45 7.43 7.32 7.30 7.28 6.74 6.72 6.68 6.41
5.41
4.98
1.86
-0.00
O
CH_2
NH
CH_3
1.99 2.97 1.03 1.99 1.01 1.00 1.00 1.00 1.00 0.99 3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

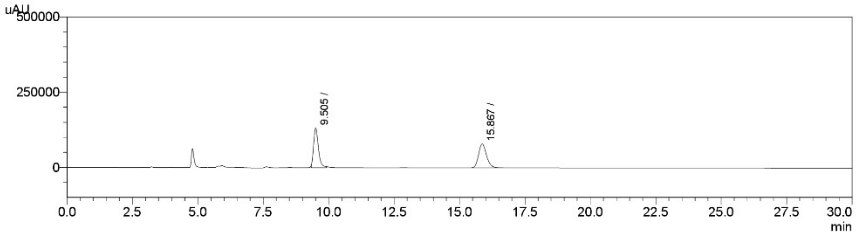

xzs-10-48-2-c/1
183.63
149.85 148.19 141.55 135.68 132.94 132.61 128.48 128.44 128.18 127.48 126.34 126.29 125.21 124.55 121.76 118.53 118.37 115.73
77.32 77.07 76.81
62.43
28.62
O
CH_2
NH
CH_3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

HPLC chart of racemic product **3r**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 10 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/11 20:25:45	Acquired by	: System Administrator
Date Processed	: 2020/8/14 19:59:23	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-40MIN-10-48-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 223nm

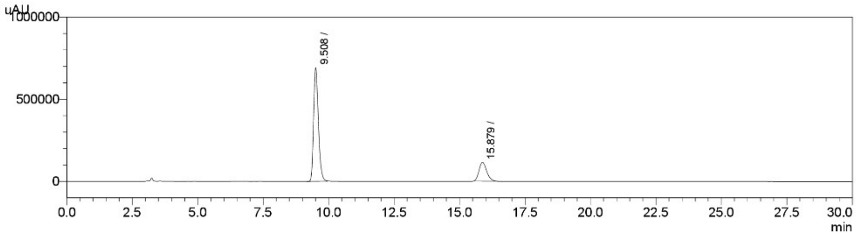
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	9.505	1698654	50.348	132325	0.000	M	
2	15.867	1675189	49.652	79423	0.000	M	
总计		3373843	100.000	211749			

HPLC chart of chiral product **3r**

==== Shimadzu LabSolutions Analysis Report ====

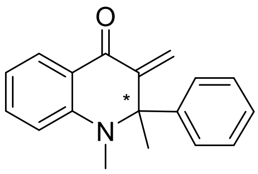
Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/8/11 20:57:38	Acquired by	: System Administrator
Date Processed	: 2020/8/14 19:57:51	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-40MIN-10-48.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

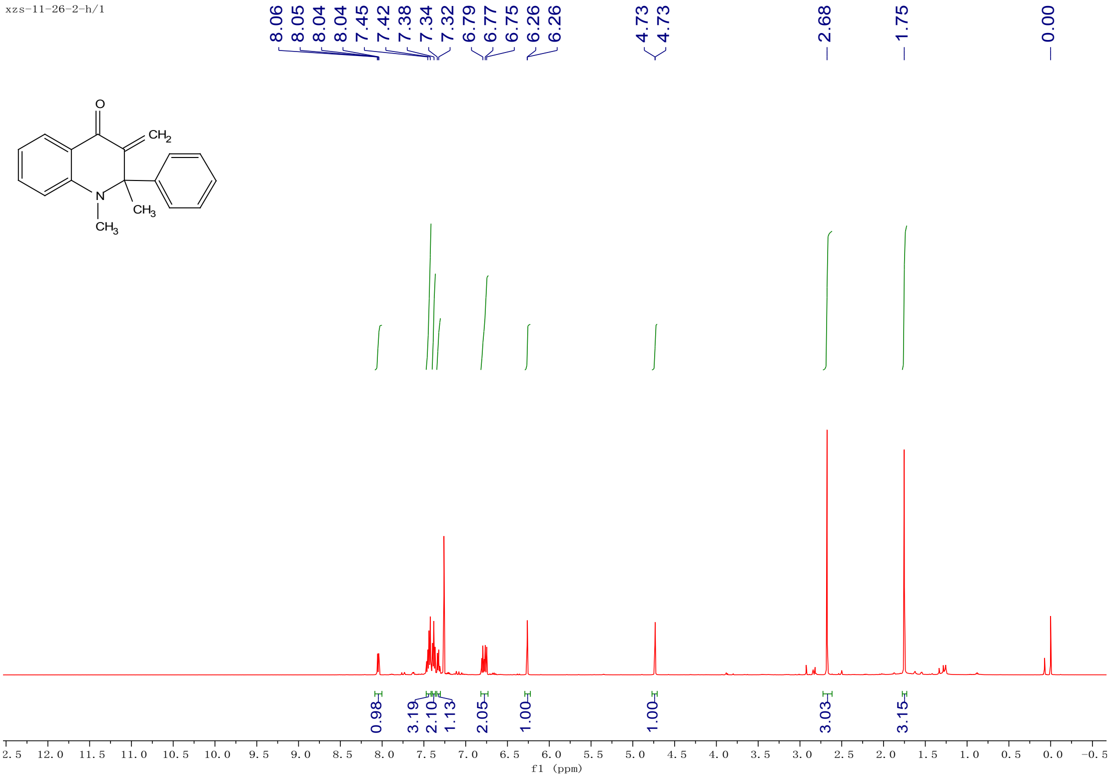


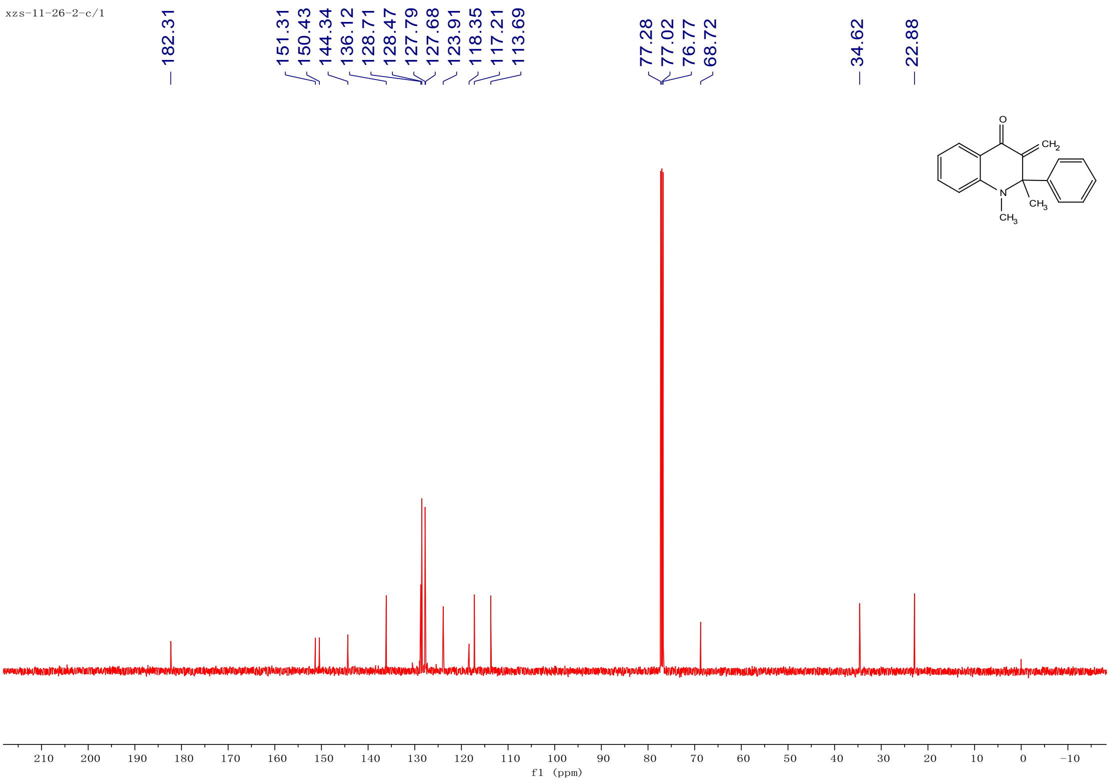
PDA Ch1 223nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	9.508	8809967	78.909	692632	0.000	M	
2	15.879	2354685	21.091	114468	0.000	M	
总计		11164651	100.000	807100			



3s


xzs-11-26-2-h/1
8.06
8.05
8.04
8.04
7.45
7.42
7.38
7.34
7.32
6.79
6.77
6.75
6.26
6.26
4.73
4.73
2.68
1.75
0.00
CH2
CH3
CH3
0.98
3.19
2.10
1.13
2.05
1.00
1.00
3.03
3.15
f1 (ppm)

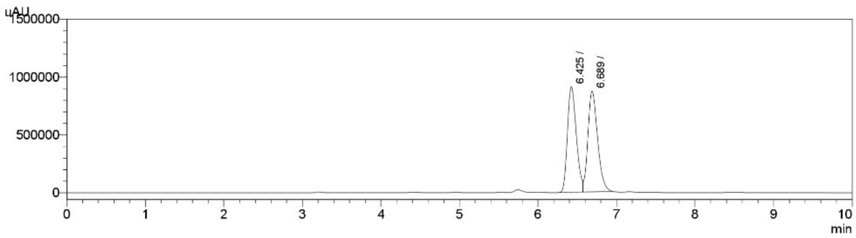

xzs-11-26-2-c/1
182.31
151.31
150.43
144.34
136.12
128.71
128.47
127.79
127.68
123.91
118.35
117.21
113.69
77.28
77.02
76.77
68.72
34.62
22.88
CH2
CH3
CH3
f1 (ppm)

HPLC chart of racemic product **3s**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-1	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/10/27 14:11:28	Acquired by	: System Administrator
Date Processed	: 2020/10/27 14:34:18	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-95-5-40MIN-11-26-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-95-5-40-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 242nm

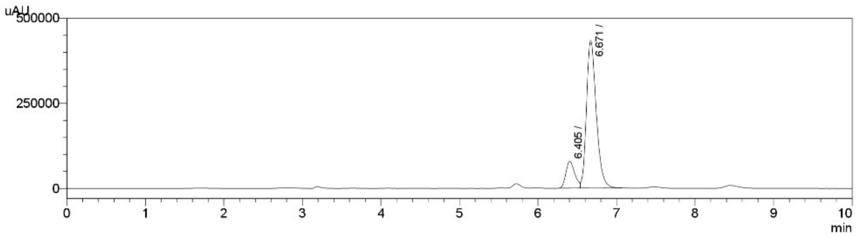
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.425	7186263	49.128	914185	0.000	M	
2	6.689	7441319	50.872	872100	0.000	V M	
总计		14627581	100.000	1786285			

HPLC chart of chiral product **3s**

==== Shimadzu LabSolutions Analysis Report ====

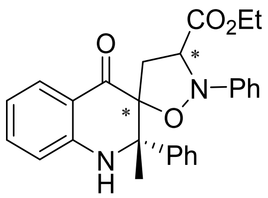
Sample Name	:	Sample ID	:
Vial#	: 1-2	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/10/27 14:22:10	Acquired by	: System Administrator
Date Processed	: 2020/10/27 14:35:08	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-95-5-40MIN-11-26.lcd
Method Filename : D:\XZS\XZS-1OD-3-95-5-40-MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

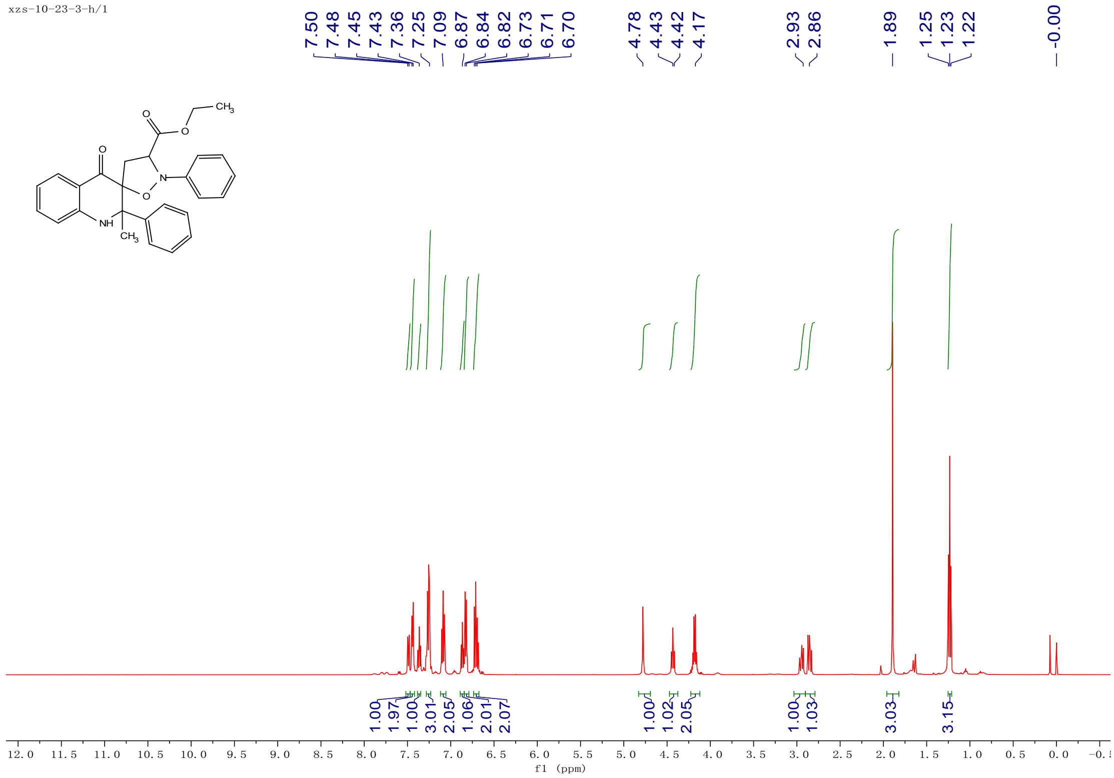


PDA Ch1 242nm

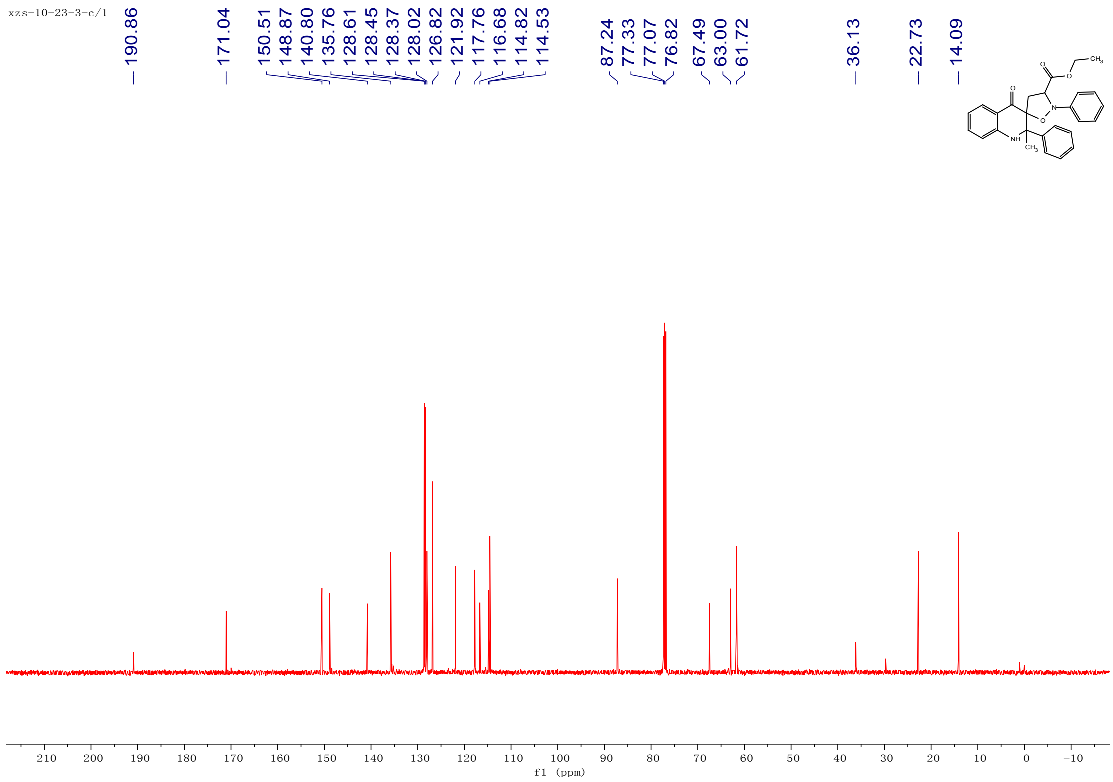
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	6.405	630957	14.442	78975	0.000	M	
2	6.671	3737970	85.558	434228	0.000	V M	
总计		4368927	100.000	513203			



4a



xzs-10-23-3-h/1
7.50
7.48
7.45
7.43
7.36
7.25
7.09
6.87
6.84
6.82
6.73
6.71
6.70
4.78
4.43
4.42
4.17
2.93
2.86
1.89
1.25
1.23
1.22
-0.00
1.00
1.97
1.00
3.01
2.05
1.06
2.01
2.07
1.00
1.02
2.05
1.00
1.03
3.03
3.15
f1 (ppm)



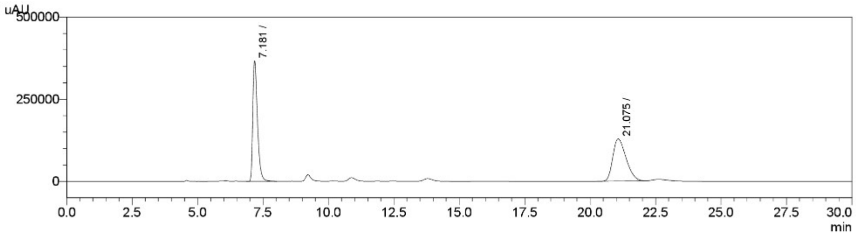
xzs-10-23-3-c/1
190.86
171.04
150.51
148.87
140.80
135.76
128.61
128.45
128.37
128.02
126.82
121.92
117.76
116.68
114.82
114.53
87.24
77.33
77.07
76.82
67.49
63.00
61.72
36.13
22.73
14.09
f1 (ppm)

HPLC chart of racemic product **4a**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/31 19:48:07	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:55:14	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-1OD-3-80-20-40MIN-10-23-rac.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 382nm

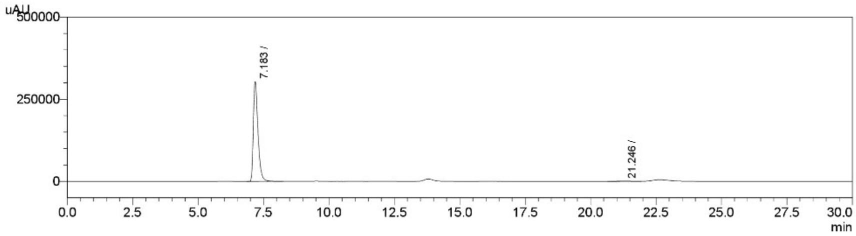
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.181	4543789	49.974	367112	0.000	M	
2	21.075	4548489	50.026	128636	0.000	M	
总计		9092278	100.000	495747			

HPLC chart of chiral product **4a**

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/7/31 20:20:07	Acquired by	: System Administrator
Date Processed	: 2020/8/31 15:55:52	Modified by	: System Administrator

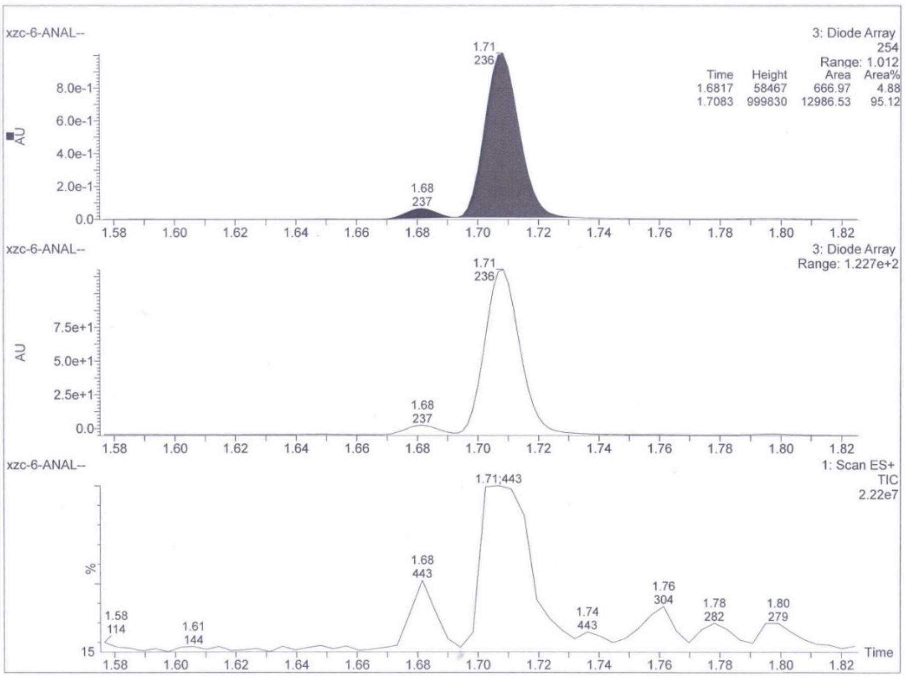
Data Filename : E:\XZS\xzs-1OD-3-80-20-40MIN-10-23.lcd
Method Filename : D:\XZS\XZS-1OD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb

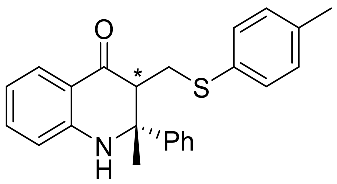


PDA Ch1 382nm

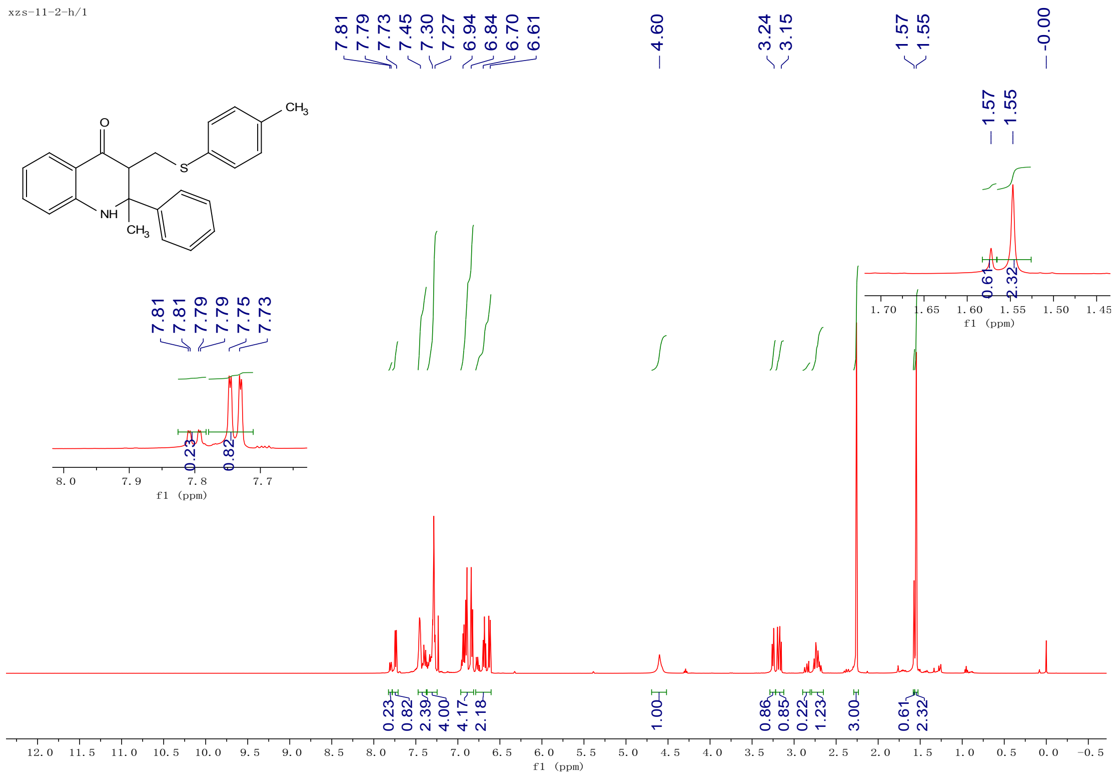
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.183	3748509	99.183	304225	0.000		
2	21.246	30869	0.817	960	0.000	M	
总计		3779378	100.000	305185			

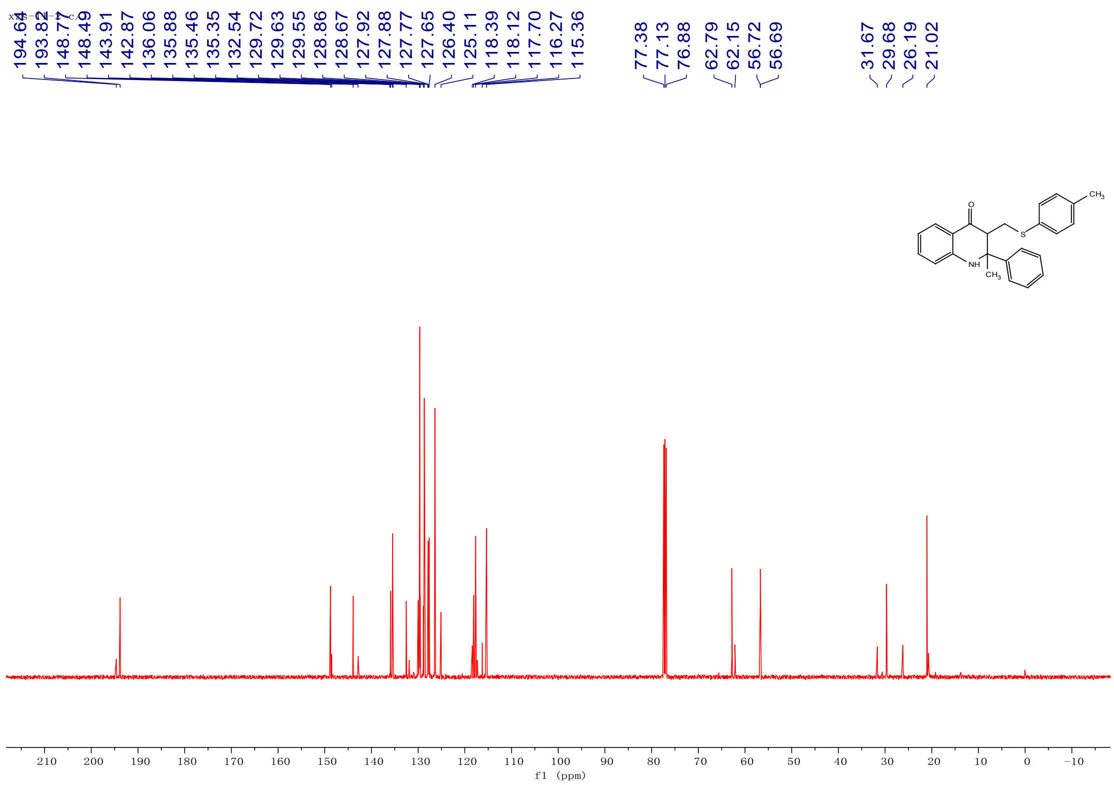
LC-MS chart of Chiral Product **4a**




O
S
N
H
Ph
*

5a


xzs-11-2-h/1
7.81
7.79
7.73
7.45
7.30
7.27
6.94
6.84
6.70
6.61
4.60
3.24
3.15
1.57
1.55
-0.00
0.23
0.82
2.39
4.00
4.17
2.18
1.00
0.86
0.85
0.22
1.23
3.00
0.61
2.32
f1 (ppm)


194.64
193.82
148.77
148.49
143.91
142.87
136.06
135.88
135.46
135.35
132.54
129.72
129.63
129.55
128.86
128.67
127.92
127.88
127.77
127.65
126.40
125.11
118.39
118.12
117.70
116.27
115.36
77.38
77.13
76.88
62.79
62.15
56.72
56.69
31.67
29.68
26.19
21.02
f1 (ppm)

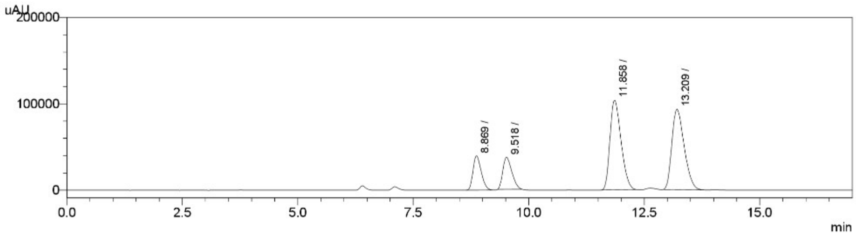
HPLC chart of racemic product **5a**

2020/9/3 19:05:35 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/9/2 20:48:43	Acquired by	: System Administrator
Date Processed	: 2020/9/2 21:21:57	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-4AD-3-80-20-40MIN-11-2-rac.lcd
Method Filename : D:\XZS\XZS-4AD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 369nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	8.869	488885	10.956	39523	0.000	M	
2	9.518	505517	11.329	37203	0.000	M	
3	11.858	1733771	38.854	103758	0.000	M	
4	13.209	1734056	38.861	93076	0.000	M	
总计		4462228	100.000	273560			

E:\XZS\xzs-4AD-3-80-20-40MIN-11-2-rac.lcd

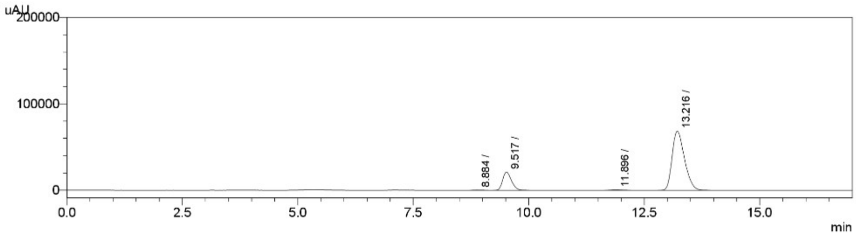
HPLC chart of chiral product **5a**

2020/9/3 19:06:43 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/9/2 21:07:42	Acquired by	: System Administrator
Date Processed	: 2020/9/3 19:01:15	Modified by	: System Administrator

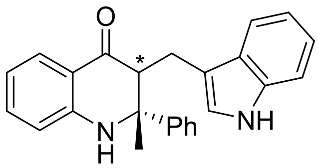
Data Filename : E:\XZS\xzs-4AD-3-80-20-40MIN-11-2.lcd
Method Filename : D:\XZS\XZS-4AD-3-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



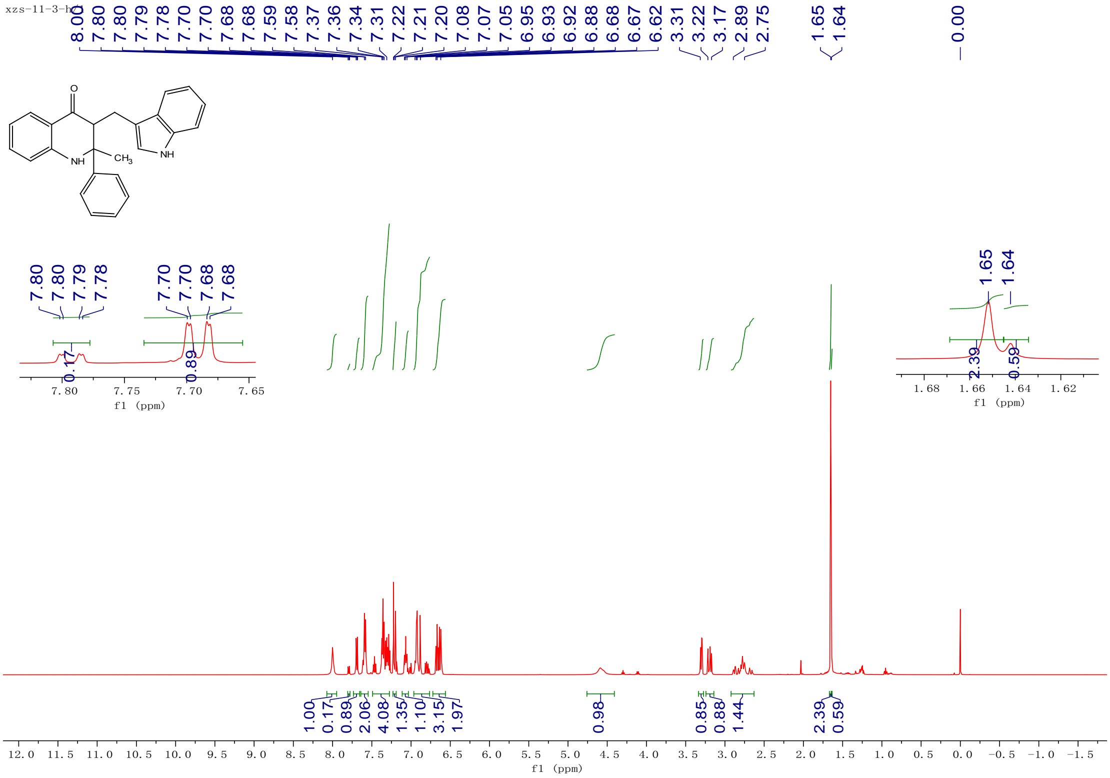
PDA Ch1 369nm

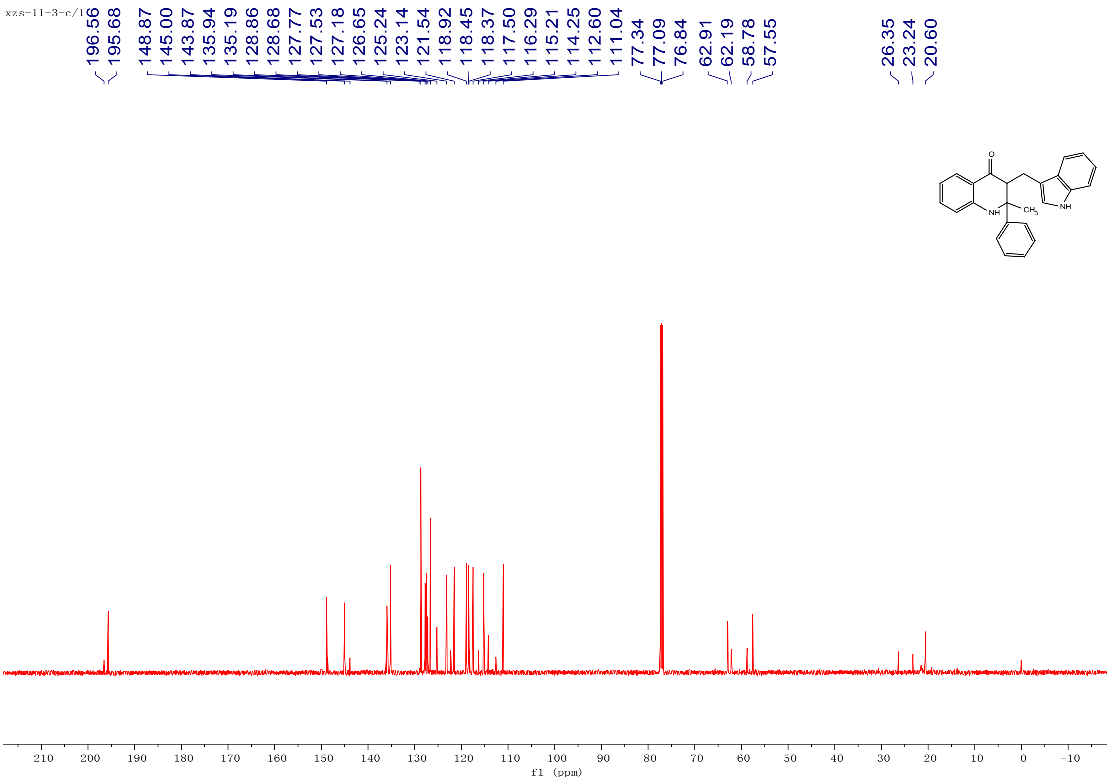
Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	8.884	2694	0.172	238	0.000		
2	9.517	279263	17.818	21291	0.000		
3	11.896	8501	0.542	551	0.000		
4	13.216	1276848	81.468	68635	0.000		
总计		1567307	100.000	90714			

E:\XZS\xzs-4AD-3-80-20-40MIN-11-2.lcd


O
*
NH
N
H
Ph

6a


xzs-11-3-h
8.00
7.80
7.80
7.79
7.78
7.70
7.70
7.68
7.68
7.59
7.58
7.37
7.36
7.34
7.31
7.22
7.21
7.20
7.08
7.07
7.05
6.95
6.93
6.92
6.88
6.68
6.67
6.62
3.31
3.22
3.17
2.89
2.75
1.65
1.64
0.00
O
NH
CH3
NH
0.17
0.89
1.00
0.17
0.89
2.06
4.08
1.35
1.10
3.15
1.97
0.98
0.85
0.88
1.44
2.39
0.59
f1 (ppm)


xzs-11-3-c/1
196.56
195.68
148.87
145.00
143.87
135.94
135.19
128.86
128.68
127.77
127.53
127.18
126.65
125.24
123.14
121.54
118.92
118.45
118.37
117.50
116.29
115.21
114.25
112.60
111.04
77.34
77.09
76.84
62.91
62.19
58.78
57.55
26.35
23.24
20.60
O
NH
CH3
NH
f1 (ppm)

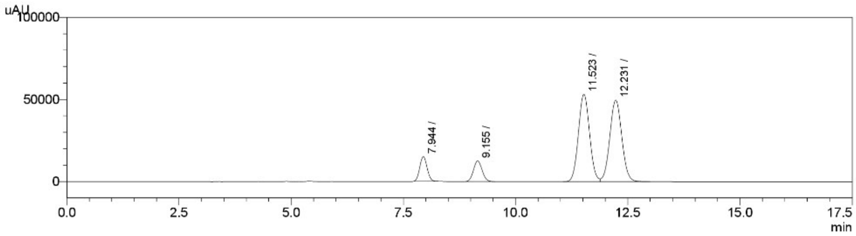
HPLC chart of racemic product **6a**

2020/9/28 20:29:53 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-16	Injection Volume	: 15 uL
Sample Type	: 未知		
Date Acquired	: 2020/9/4 10:13:33	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:14:05	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-5IC-80-20-40MIN-11-3-rac.lcd
Method Filename : D:\XZS\XZS-5IC-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 370nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.944	169726	7.772	15061	0.000	M	
2	9.155	168108	7.697	12615	0.000	M	
3	11.523	920991	42.171	53190	0.000		
4	12.231	925117	42.360	49694	0.000	V	
总计		2183942	100.000	130560			

E:\XZS\xzs-5IC-80-20-40MIN-11-3-rac.lcd

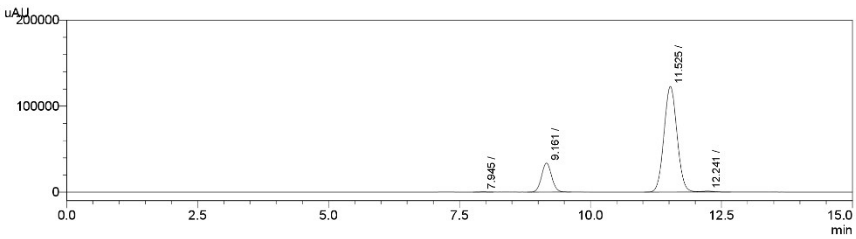
HPLC chart of chiral product **6a**

2020/9/28 20:30:57 Page 1 / 1

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	:	Sample ID	:
Vial#	: 1-17	Injection Volume	: 20 uL
Sample Type	: 未知		
Date Acquired	: 2020/9/4 10:33:09	Acquired by	: System Administrator
Date Processed	: 2020/9/28 20:14:36	Modified by	: System Administrator

Data Filename : E:\XZS\xzs-5IC-80-20-40MIN-11-3.lcd
Method Filename : D:\XZS\XZS-5IC-80-20-40MIN.lcm
Batch Filename : C:\LabSolutions\Data\Project1\12.lcb



PDA Ch1 370nm

Peak#	Ret. Time	Area	Area%	Height	Conc.	Mark	ID#
1	7.945	3362	0.129	312	0.000		
2	9.161	451698	17.359	33712	0.000		
3	11.525	2128799	81.812	122850	0.000		
4	12.241	18197	0.699	961	0.000	V	
总计		2602056	100.000	157835			

E:\XZS\xzs-5IC-80-20-40MIN-11-3.lcd