Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Enantioselective reduction of azaarene-based ketones via visible light-driven photoredox asymmetric catalysis

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Table of Contents

1. General information

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reactions mixtures were stirred in 10 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed *in vacuo* under ~30 mmHg and heated with a water bath at 30–35 ^{o}C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 ^{o}C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $Ce(SO_4)_2$ and phosphomolybdic acid solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained basified *silica gel* (with Et_3N) 200–300 mesh. Columns were packed as slurry of basified *silica gel* in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR) were recorded in $CDCl_3$ otherwise stated. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of carbon atoms (*n*) for a given resonance was indicated by *n*C. HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in CH_3CN (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]_{\lambda}^{T^{\circ}C}$ (*c* = g/100 mL, solvent). Melting points were determined on a melting point apparatus.

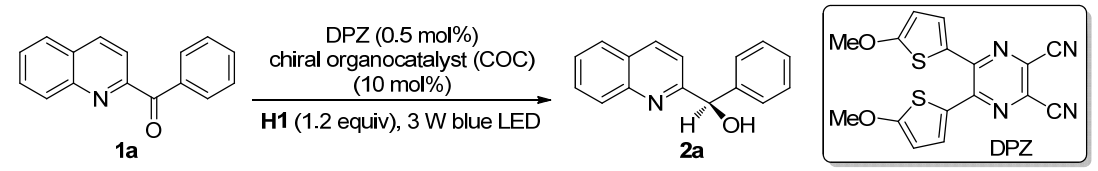
Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

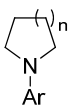
Materials

All commercial reagents were purchased with the highest purity grade. The syntheses of material **1**[1] has been previously reported. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous dichloromethane (DCM) was freshly distilled from CaH_2 and stored under N_2 atmosphere. Toluene, CPME and its derivatives were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a 0 ^oC freezer and light-sensitive compounds were protected with aluminium foil.

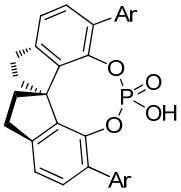
2. Optimization of reaction conditions

Table S1. Screening of the chiral organocatalyst (COC)[a]

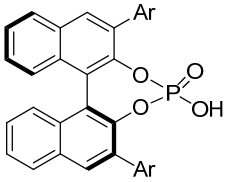




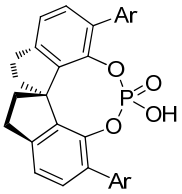
H1: n = 2, Ar = C_6H_5



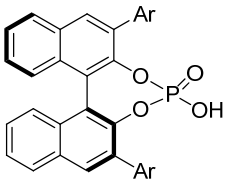
C1: Ar = 2-$CF_3C_6H_4$
C2: Ar = 2-$OMeC_6H_4$
C3: Ar = 9-phenanthrene
C4: Ar = 2,4,6-*i*$Pr_3C_6H_3$
C5: Ar = 2,4,6-$Me_3C_6H_3$



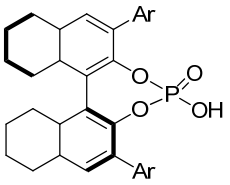
C6: Ar = 2,4,6-$Me_3C_6H_3$



C7: Ar = C_6H_5
C8: Ar = 2-MeC_6H_4
C9: Ar = 2-PhC_6H_4
C10: Ar = 2-OMe-3,5-F_2-C_6H_2
C11: Ar = 2,6-$Me_2C_6H_3$
C12: Ar = 2,6-*i*$Pr_2C_6H_3$
C13: Ar = 1-naphthyl
C14: Ar = 2-naphthyl
C15: Ar = 4-pyrenyl
C16: Ar = 3,5-$(C_6H_3)_2C_6H_3$
C17: Ar = 3,5-$(CF_3)_2C_6H_4$
C18: Ar = 9,9-Diphenyl-9H-fluoren-4-yl



C19: Ar = 1-naphthyl
C20: Ar = 2-naphthyl
C21: Ar = 3,5-$(C_6H_3)_2C_6H_3$
C22: Ar = 3,5-$(CF_3)_2C_6H_3$



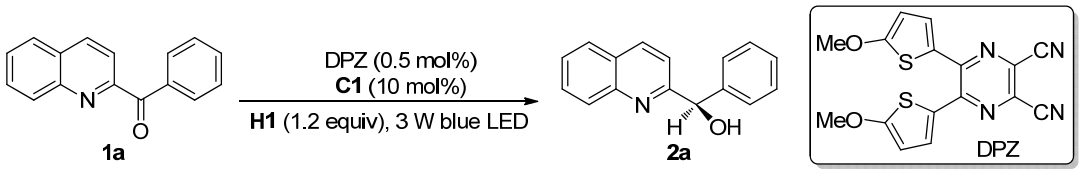
C23: Ar = 1-naphthyl
C24: Ar = 2-naphthyl
C25: Ar = 3,5-$(C_6H_3)_2C_6H_3$
C26: Ar = 3,5-$(CF_3)_2C_6H_3$

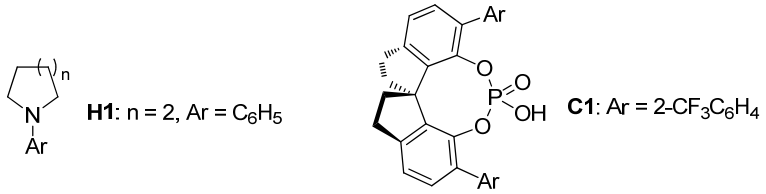
Entry	COC	Conv. (%)[b]	ee (%)[c]
1	--	middle	0
2	**C2**	good	14
3	**C3**	excellent	7
4	**C4**	excellent	–49
5	**C5**	excellent	60
6	**C6**	excellent	44
7	**C7**	excellent	24
8	**C8**	excellent	68
9	**C9**	excellent	69
10	**C10**	excellent	8
11	**C11**	good	25
12	**C12**	middle	–49
13	**C13**	excellent	41
14	**C14**	excellent	25
15	**C15**	excellent	8
16	**C16**	excellent	20
17	**C17**	excellent	20
18	**C17**	excellent	35
19	**C19**	good	36
20	**C29**	excellent	23
21	**C21**	excellent	12

22	**C22**	excellent	14
23	**C23**	good	–35
24	**C24**	excellent	–13
25	**C25**	excellent	–14
26	**C26**	excellent	–12
27	**C27**	excellent	74

[a]Reaction conditions: **1a** (0.05 mmol), **H** (0.06 mmol) in diethyl ether (1.0 mL) at 25 °C for 12 h. [b]Determined by TLC analysis: "excellent" for Conv. ≥ 90%, "good" for 90% > Conv. ≥ 70%, "middle" for 70% > Conv. ≥ 40%, "low" for Conv. < 40%. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S2. **Screening of the solvent**[a]

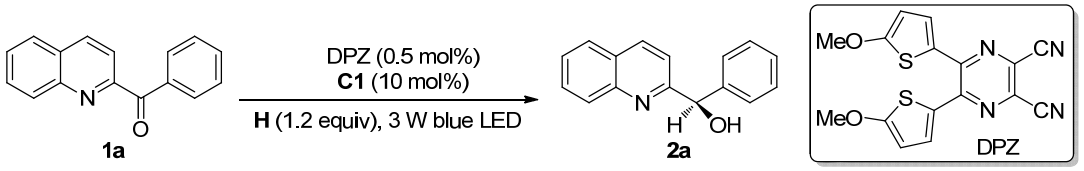


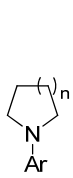


Entry	Solvent	Conv. (%)[b]	ee (%)[c]
1	Toluene	good	11
2	$CHCl_3$	0	N.P.
3	CH_2Cl_2	low	11
4	CH_3CN	excellent	N.D.
5	THF	excellent	74
6	Dioxane	good	47
7	DME	excellent	76
8	Anisole	good	56
9	nBu$_2$O	good	64
10	iPr$_2$O	good	66
11	CPME	excellent	79
12	MTBE	excellent	78

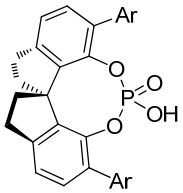
[a]Reaction conditions: **1a** (0.05 mmol), **H** (0.06 mmol) in 1.0 mL solvent at 25 °C for 12 h. [b] Determined by TLC analysis: "excellent" for Conv. ≥ 90%, "good" for 90% > Conv. ≥ 70%, "middle" for 70% > Conv. ≥ 40%, "low" for Conv. < 40%. [c]Determined by HPLC analysis on a chiral stationary phase. N.D. = not determined. N.P. = no product.

Table S3. **Screening of the reductant**[a]





H1: n = 2, Ar = C_6H_5
H2: n = 0, Ar = C_6H_5
H3: n = 1, Ar = C_6H_5
H4: n = 3, Ar = C_6H_5
H5: n = 2, Ar = 2-FC_6H_4
H6: n = 2, Ar = 2-MeC_6H_4
H7: n = 2, Ar = 3-MeC_6H_4
H8: n = 2, Ar = 4-MeC_6H_4
H9: n = 2, Ar = 2-*t*BuC_6H_4

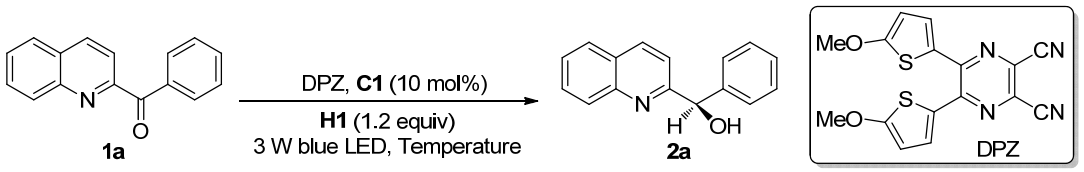


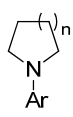
C1: Ar = 2-$CF_3C_6H_4$

entry	**H** (1.2 equiv)	Conv. (%)[b]	ee (%)[c]
1	Et_3N	low	64
2	DIPEA	middle	68
3	HZE	excellent	40
4	**H2**	excellent	55
5	**H3**	excellent	74
6	**H4**	excellent	69
7	**H5**	excellent	79
8	**H6**	excellent	78
9	**H7**	excellent	73
10	**H8**	excellent	70
11	**H9**	excellent	78

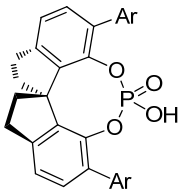
[a]Reaction conditions: **1a** (0.05 mmol), **H** (0.06 mmol) in 1.0 mL CPME at 25 °C for 12 h. [b]Determined by TLC analysis: "excellent" for Conv. ≥ 90%, "good" for 90% > Conv. ≥ 70%, "middle" for 70% > Conv. ≥ 40%, "low" for Conv. < 40%. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S4. **Screening of the amount of DPZ, Molecular Sieve, and temperature**[a]





H1: n = 2, Ar = C_6H_5



C1: Ar = 2-$CF_3C_6H_4$

entry	PC (mol%)	Molecular Sieve (25 mg)	Conv. (%)[b]	T (°C)	ee (%)[c]
1	DPZ (0.5)	--	excellent	10	82
2	DPZ (0.5)	--	good	0	83
3	DPZ (0.5)	--	good	-10	86
4	DPZ (0.5)	--	middle	-20	88
5	DPZ (0.5)	--	middle	-40	89
6	DPZ (0.5)	3 Å	good (93)[d]	-40	91
7	DPZ (0.5)	4 Å	middle	-40	90
8	DPZ (0.5)	5 Å	middle	-40	88
9	DPZ (1.0)	3 Å	good	-40	89
10	DPZ (0.2)	3 Å	middle	-40	91
11	DPZ (0.1)	3 Å	low	-40	91

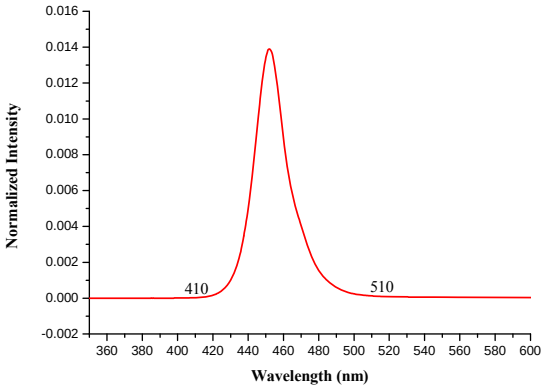
[a]Reaction conditions: **1a** (0.05 mmol), **H** (0.06 mmol) in 1.0 mL CPME for 48 h. [b]Determined by TLC analysis: "excellent" for Conv. ≥ 90%, "good" for 90% > Conv. ≥ 70%, "middle" for 70% > Conv. ≥ 40%, "low" for Conv. < 40%. [c]Determined by HPLC analysis on a chiral stationary phase. [d]0.10 mmol scale for 72 h, isolated yield based on the **1a**. N.P. = no product.

3. General experimental procedures

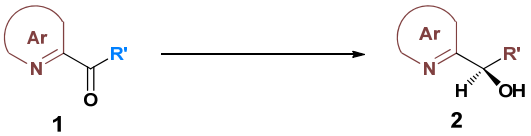
Reaction set-up

10 mL Schlenk tube is placed at the center of a stir plate. A 3 W blue LED lamp (HW-450-455LED-3W) is placed to one sidewall of reaction tube (at approximately 2 cm away from the light source). The transformations were conducted in a cryostat which allows a stable and certain temperature.

Side view Top View



Emission spectrum of the 3 W LED light.



For the preparation of 2a-zc: To a flame dried Schlenk tube was sequentially added **1a-zc** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C1** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), 3 Å MS (50 mg), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at –40 ^{o}C (the temperature was maintained in an incubator) for 30 min without light, then irradiated by a 3 W blue LED for another 72 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly loaded onto a short

silica gel column, followed by gradient elution with petroleum ether/ethyl acetate (20/1 to 4/1 ratio). Removing the solvent in *vacuo*, afforded products **2a**−**zc**.

For the preparation of 2zd: To a flame dried Schlenk tube was sequentially added **1zd** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C1** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), 3 Å MS (50 mg), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 25 ^{o}C with the irradiation by a 3 W blue LED for 24 h. The reaction was monitored by TLC. After completion of the reaction, the crude mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1 to 10/1 ratio). Removing the solvent in *vacuo*, afforded product **2zd**.

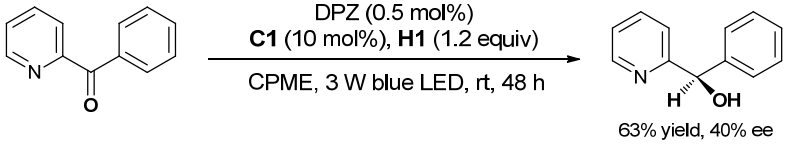
For the preparation of 2ze and 2zg: To a flame dried Schlenk tube was sequentially added **1ze/1zg** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C18/C26** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), 3 Å MS (50 mg), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at –40 ^{o}C (the temperature was maintained in an incubator) for 30 min without light, then irradiated by a 3 W blue LED for another 72 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1 to 10/1 ratio). Removing the solvent in *vacuo*, afforded product **2ze**/**2zg**.

For the preparation of 2zf: To a flame dried Schlenk tube was sequentially added **1zf** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C3** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 25 ^{o}C with the irradiation by a blue 3 W LED for 24 h. The reaction was monitored by TLC. After completion of the reaction, the crude mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (50/1 to 12/1 ratio). Removing the solvent in *vacuo*, afforded product **2zf**.

For the preparation of 2zj-l: To a flame dried Schlenk tube was sequentially added **1zj-l** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C2** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 25 ^{o}C with the irradiation by a 3 W blue LED for 15 h. The reaction was monitored by TLC. After

completion of the reaction, the crude mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (30/1 to 5/1 ratio). Removing the solvent in *vacuo*, afforded products **2zj-l**.

We also explored the reduction of phenyl(pyridin-2-yl)methanol with modified reaction conditions.



The procedures in detail are as follows:

To a flame dried Schlenk tube was sequentially added phenyl(pyridin-2-yl)methanone (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), **C1** (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), and degassed CPME (2.0 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 25 ^{o}C with the irradiation by a 3 W blue LED for 48 h. The reaction was monitored by TLC. After completion of the reaction, the crude mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (20/1 to 4/1 ratio). Removing the solvent in *vacuo*, afforded product phenyl(pyridin-2-yl)methanol in 63% yield with 40% ee.

4. Mechanism studies

Emission quenching experiments

Excitation spectrum was recorded on an EDINBURGH FLS 980 fluorescence spectrophotometer equipped with a monochromated 325 W Xe-arc excitation source and a visible detector (Hamamatsu R928P). DPZ solution was excited at 448 nm and the emission intensity at 544 nm was observed. A solution of DPZ (2.5×10^{-4} M) in MeCN was added to the appropriate amount of quencher in 5.0 mL volumetric flask under N_2. The solution was transferred to a 1.5 mL quartz cell and the emission spectrum of the sample was collected.

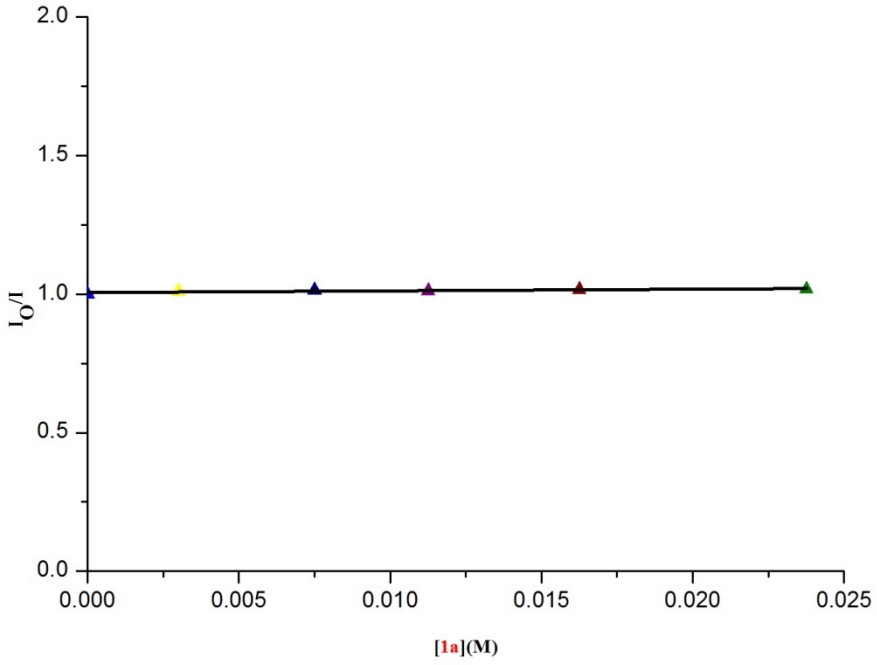


Fig. S1. Stern–Volmer quenching experiment of DPZ and **1a**. (No quenching observed.)

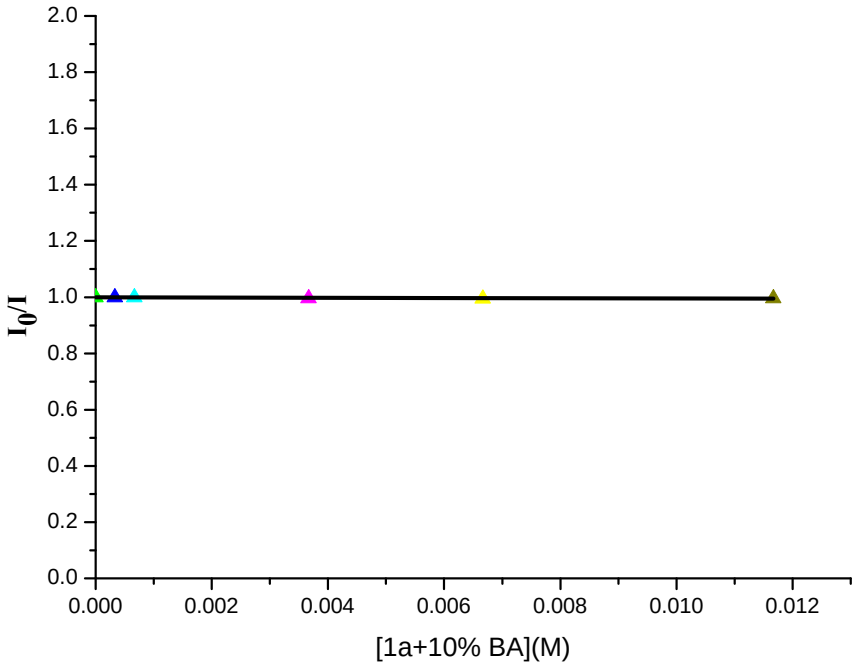


Fig. S2. Stern–Volmer quenching experiment of DPZ and [**1a**+10% ($(PhO)_2P(O)OH$)**]**. (No quenching observed.)

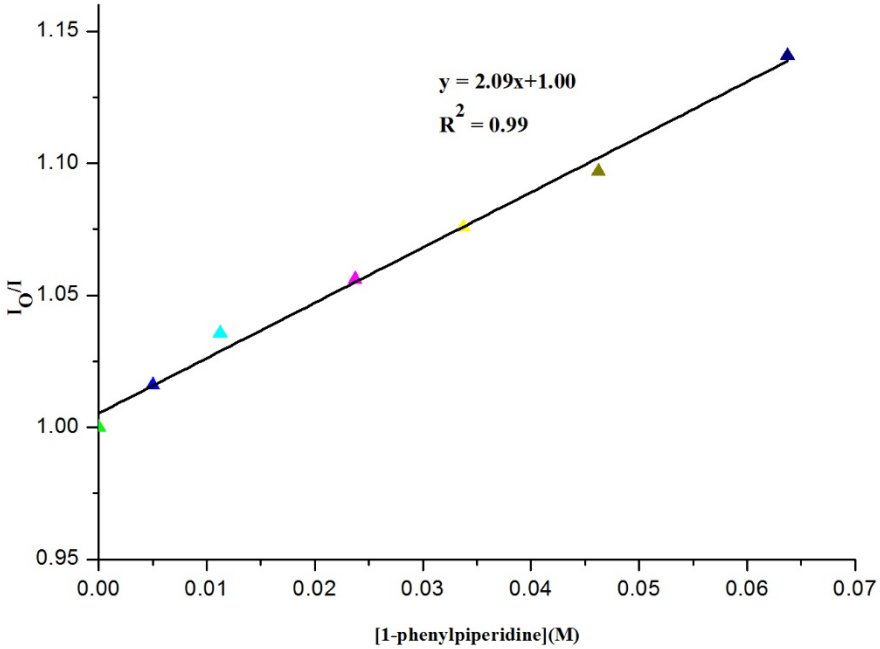


Fig. S3. Stern–Volmer quenching experiment of DPZ and **H1**. (Quenching observed.)

Electrochemistry. Cyclic voltammetry experiments were performed on a CHI600E Workstation. Measurements were performed for anhydrous acetonitrile solutions ([sample] =

1.0 mM, $[(NBu_4)PF_6]$ = 0.10 M) with a radium glassy carbon (working electrode) and platinum wire (counter electrode), and a Ag/AgCl reference electrode under N_2 at room temperature. The scan rate was 50 mV/s. Ferrocene (Cp_2Fe) was used as a reference.

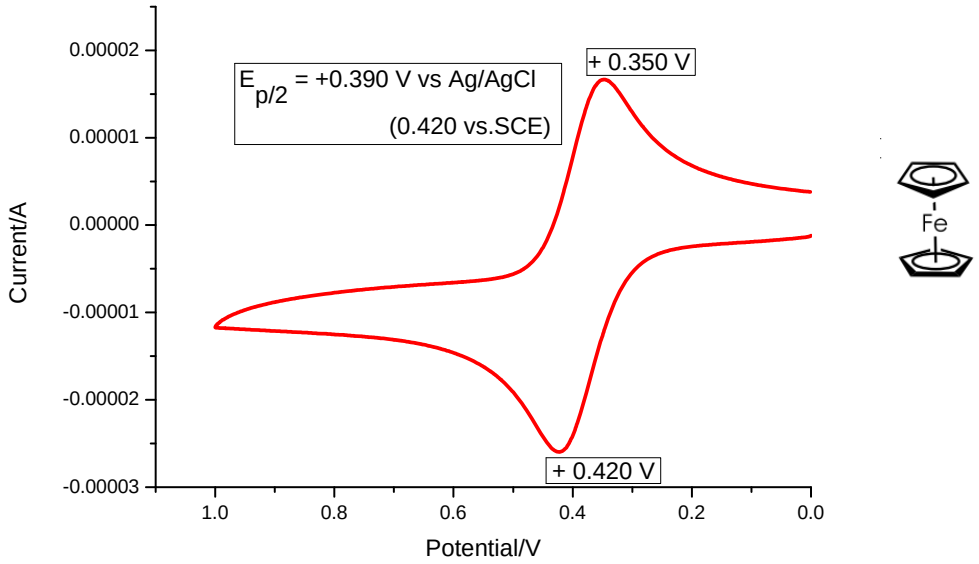


Fig. S4. Cyclic voltammogram of Ferrocene.

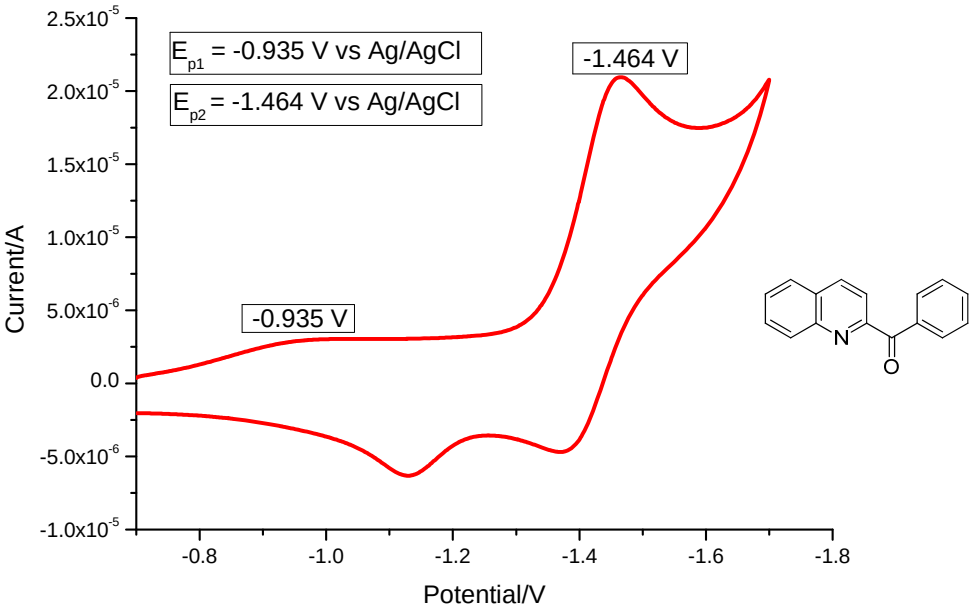


Fig. S5. Cyclic voltammogram of **1a**. Ferrocene (Cp_2Fe) was used as a reference. E_{p1} = −0.905 V versus SCE in CH_3CN, E_{p2} = −1.434 V versus SCE in CH_3CN.

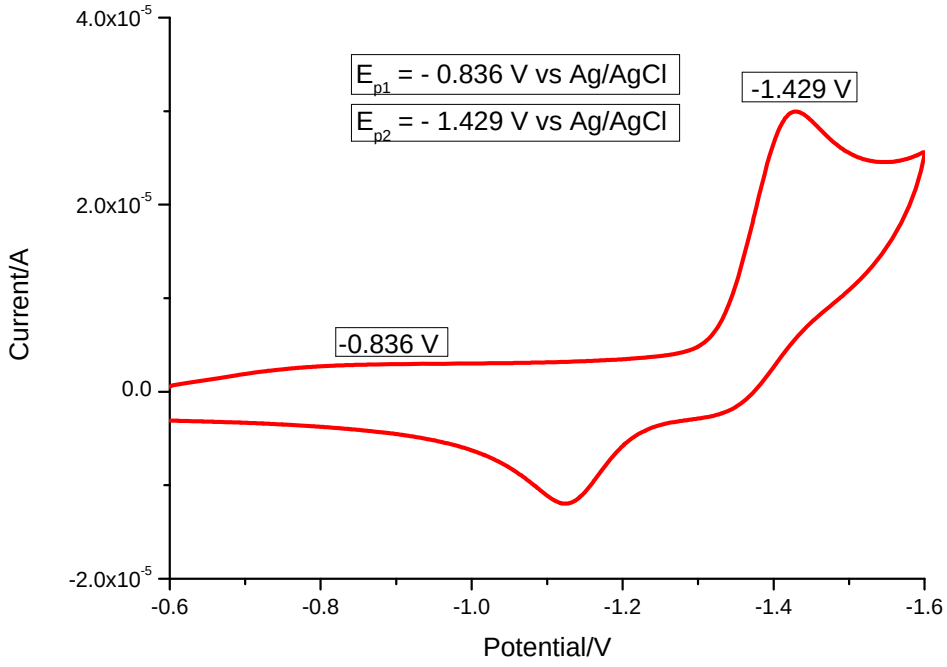


Fig. S6. Cyclic voltammogram of [**1a + 10% C1**]. Scan Rate: 50 mV/s. Ferrocene (Cp_2Fe) was used as a reference. E_{p1} = −0.806 V versus SCE in CH_3CN, E_{p2} = −1.399 V versus SCE in CH_3CN.

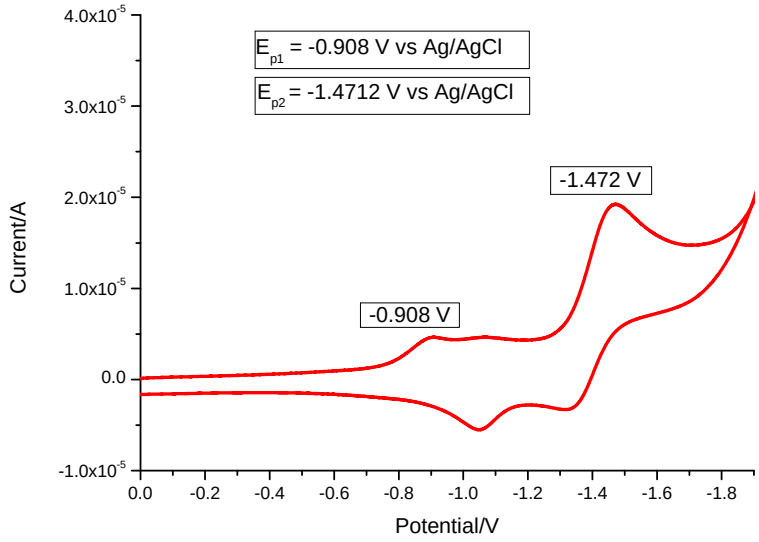


Fig. S7. Cyclic voltammogram of [**1a + 0.5% DPZ**]. Scan Rate: 50 mV/s. Ferrocene (Cp_2Fe) was used as a reference. E_{p1} = −0.878 V versus SCE in CH_3CN, E_{p2} = −1.442 V versus SCE in CH_3CN.

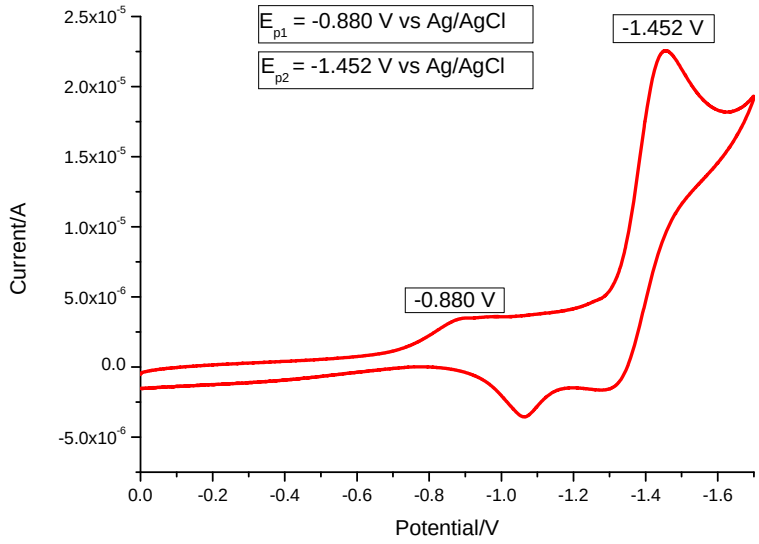


Fig. S8. Cyclic voltammogram of [**1a + 120% H1**]. Scan Rate: 50 mV/s. Ferrocene (Cp_2Fe) was used as a reference. E_{p1} = −0.850 V versus SCE in CH_3CN, E_{p2} = −1.422 V versus SCE in CH_3CN.

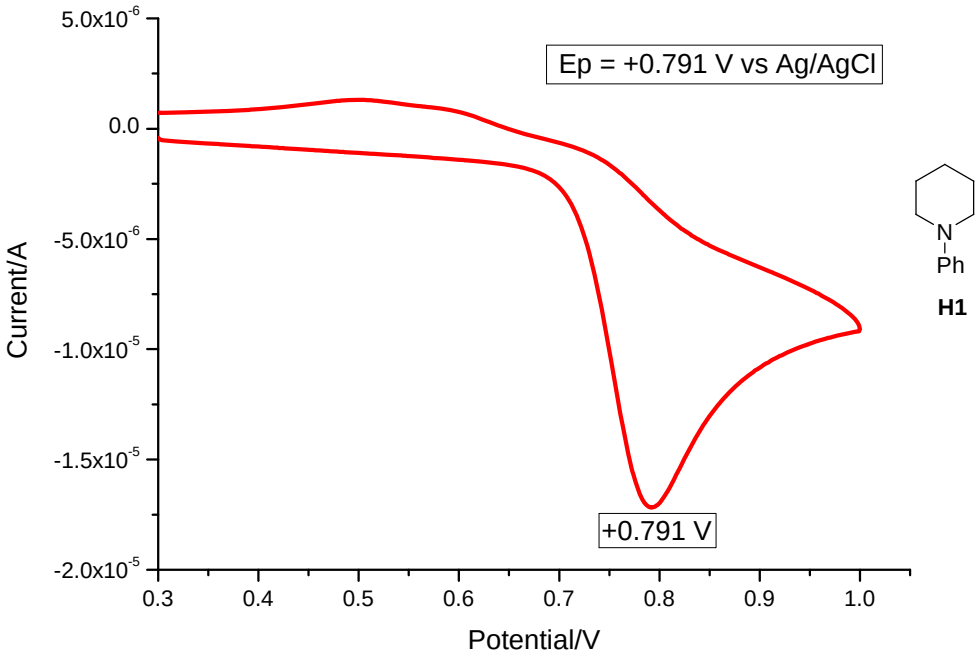


Fig. S9. Cyclic voltammogram of **H1**. Ferrocene (Cp_2Fe) was used as a reference. E_p = +0.821 V versus SCE in CH_3CN.

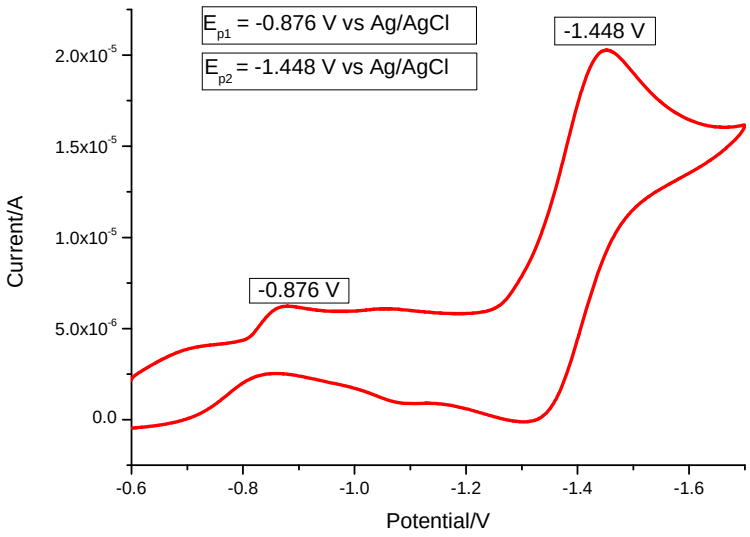
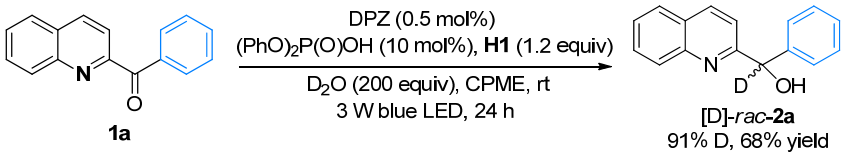
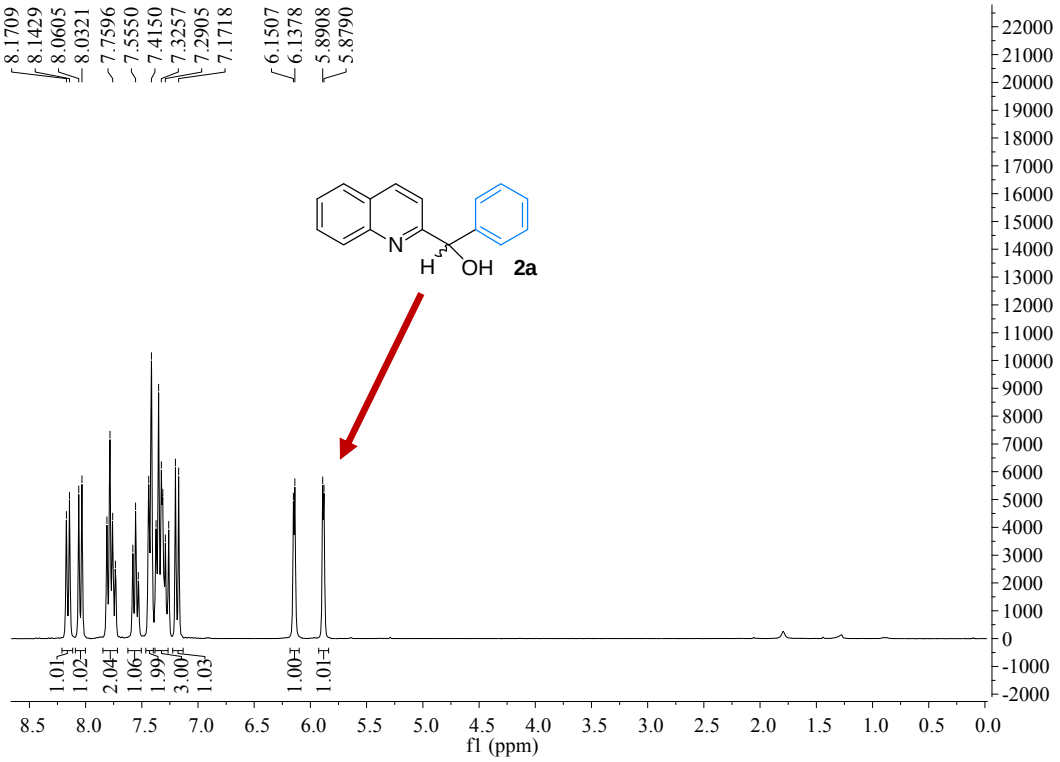


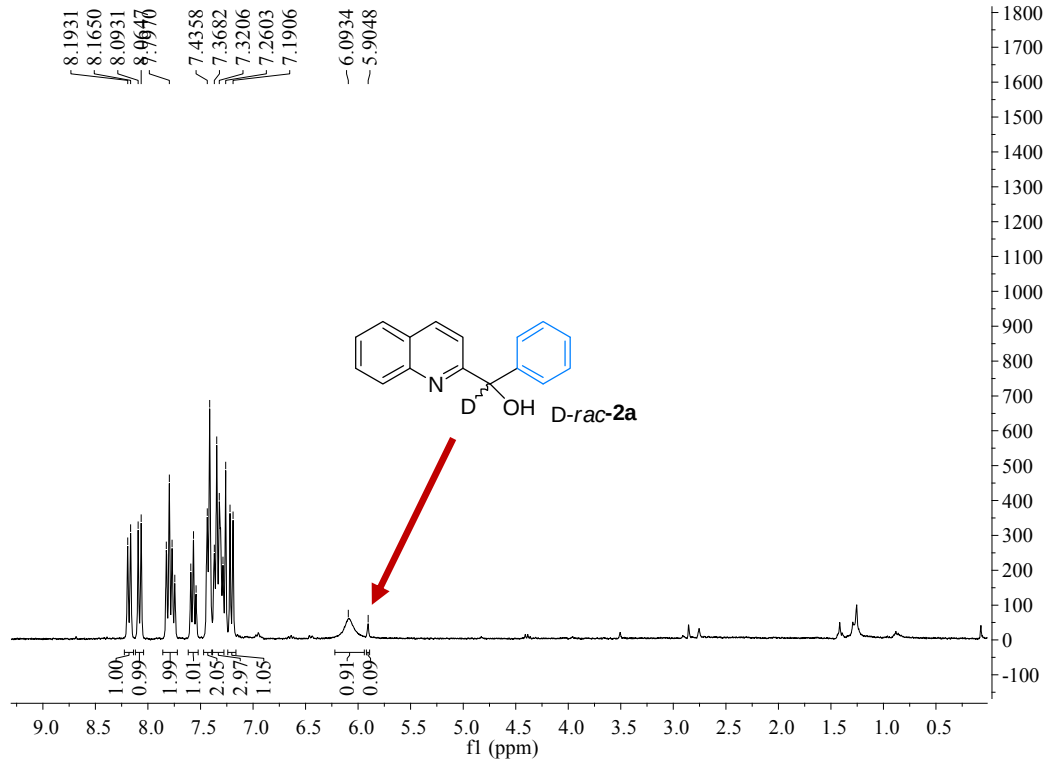
Fig. S10. Cyclic voltammogram of [**1a** + **10% C1** + **120% H1** + **0.5% DPZ**]. Scan Rate: 50 mV/s. Ferrocene (Cp_2Fe) was used as a reference. E_{p1} = −0.846 V versus SCE in CH_3CN, E_{p2} = −1.418 V versus SCE in CH_3CN.

Determination of the proton source



To a flame dried Schlenk tube was sequentially added **1a** (0.10 mmol, 1.0 equiv), DPZ (0.0005 mmol, 0.005 equiv), diphenyl phosphate (0.01 mmol, 0.1 equiv), **H1** (0.12 mmol, 1.2 equiv), D_2O (20 mmol, 200 equiv) and CPME (2 mL). Then degassed three times by freeze-pump-thaw method. The reaction mixture was irradiated by a 3 W blue LED for 24 hours at rt. The reaction mixture was directly loaded onto a short basified *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (20/1 to 4/1 ratio). Removing the solvent in *vacuo*, afforded [D]-*rac*-**2a** in 68% yield with 91% deuterium incorporation. The result suggests the protonation as a feasible process to form the product.


8.1709
8.1429
8.0605
8.0321
7.7596
7.5550
7.4150
7.3257
7.2905
7.1718
6.1507
6.1378
5.8908
5.8790
N
H
OH
2a
1.01
1.02
2.04
1.06
1.99
3.00
1.03
1.00
1.01
fl (ppm)


8.1931
8.1650
8.0931
7.4358
7.3682
7.3206
7.2603
7.1906
6.0934
5.9048
N
D
OH
D-rac-2a
1.00
0.99
1.99
1.01
2.05
2.97
1.05
0.91
0.09
fl (ppm)

5. Determination of the absolute configurations

Determination of the absolute configurations of 2zj

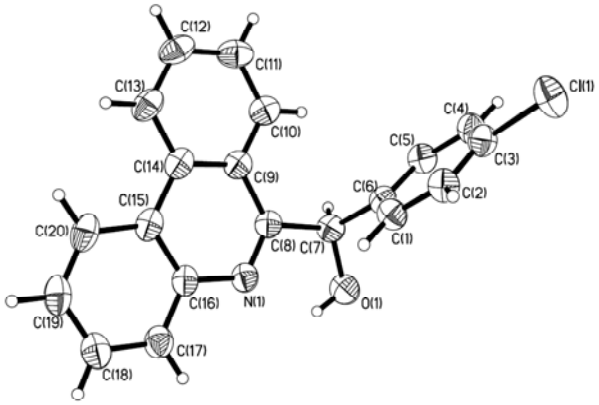


Fig. S19. Absolute configuration of **2zj** (CCDC 1920199)
Displacement ellipsoids are drawn at the 30% probability level.
(sovlent: ethyl acetate:*n*hexane = 1:3)

Table S6. Crystal data and structure refinement for qbk4cl.

Identification code	**qbk4cl**
Empirical formula	$C_{20}H_{14}ClNO$
Formula weight	319.77
Temperature/K	293(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	5.15285(17)
b/Å	11.3914(5)
c/Å	26.4345(10)
α/	90
β/	90
γ/	90
Volume/Å^3	1551.66(10)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	2.197

F(000)	664.0
Crystal size/mm^3	0.15 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.452 to 134.11
Index ranges	-3 ≤ h ≤ 6, -13 ≤ k ≤ 13, -31 ≤ l ≤ 31
Reflections collected	10220
Independent reflections	2755 [R_{int} 0.0644, R_{sigma} = 0.0422]
Data/restraints/parameters	2755/0/197
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0669, wR_2 = 0.1777
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.1906
Largest diff. peak/hole / e Å^{-3}	0.33/-0.24
Flack parameter	-0.026(17)

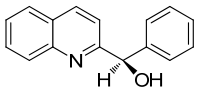
Experimental

The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

Crystal structure determination

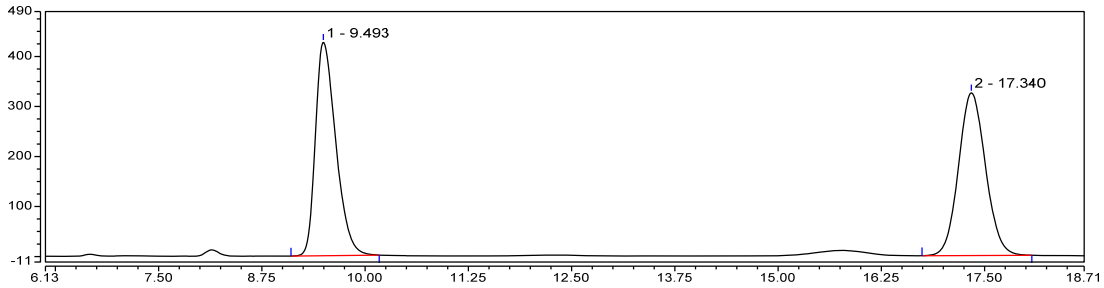
Crystal Data for $C_{20}H_{14}ClNO$ (*M* =319.77 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 5.15285(17) Å, *b* = 11.3914(5) Å, *c* = 26.4345(10) Å, *V* = 1551.66(10) Å^3, *Z* = 4, *T* = 293(2) K, μ(CuKα) = 2.197 mm^{-1}, *Dcalc* = 1.369 g/cm^3, 10220 reflections measured (8.452 ≤ 2Θ ≤ 134.11), 2755 unique (R_{int} = 0.0644, R_{sigma} = 0.0422) which were used in all calculations. The final R_1 was 0.0669 (I > 2σ(I)) and wR_2 was 0.1906 (all data).

6. Characterization of adducts

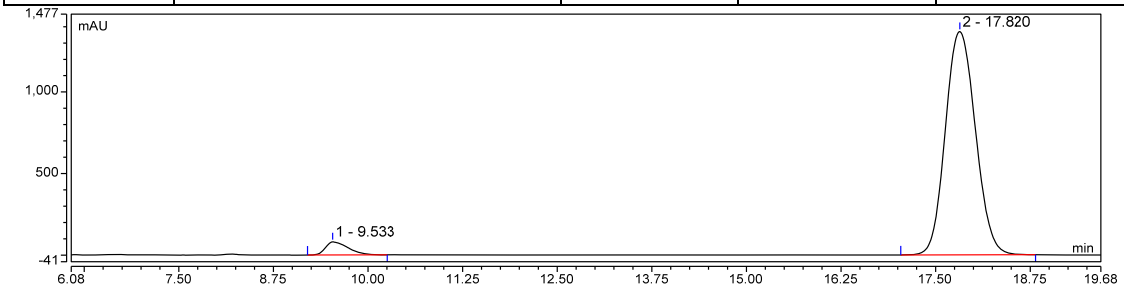


2a: white solid, Mp 59.2 – 60.4 °C, 21.9 mg, 93% yield, 92% ee, $[\alpha]_D^{22}$ – 88.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 14.7, 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.33 (dt, *J* = 8.5, 6.8 Hz, 3H), 7.19 (d, *J* = 8.5 Hz, 1H), 6.14 (d, *J* = 3.9 Hz, 1H), 5.88 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 145.9, 142.7, 137.0, 129.9, 128.8, 128.6, 128.0, 127.6, 127.4, 126.6, 119.2, 75.1; HRMS (ESI) m/z 258.0901 ($M+Na^+$), calc. for $C_{16}H_{13}NONa$ 258.0895.

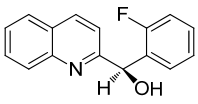
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 9.5 min (minor) and 17.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.493	122.1204	426.96	49.74
2	17.340	123.3960	325.30	50.26



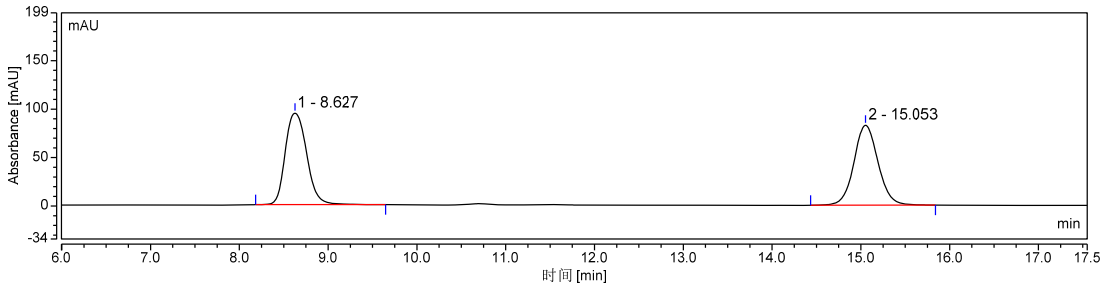
Entry	Retention Time	Area	Height	%Area
1	9.533	27.8260	80.68	4.22
2	17.820	631.2709	1368.70	95.78



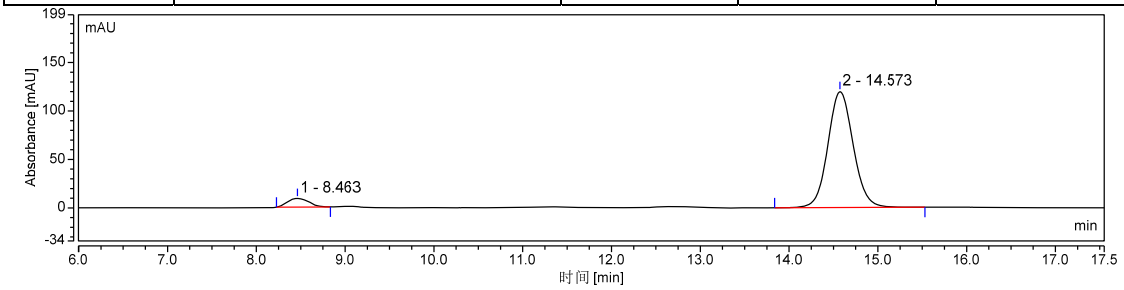
2b: colorless oil, 21.8 mg, 86% yield, 90% ee, $[\alpha]_D^{22}$ –235.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 16.6, 8.5 Hz, 2H), 7.78 (dd, *J* = 18.8, 7.8 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.28 (s, 1H), 6.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 160.4 (d, J = 246.2 Hz), 159.7, 145.9, 137.4, 130.0, 129.8, δ 129.4 (d, J = 8.3 Hz), 128.8 (d, J = 4.0 Hz), 128.7, 127.6, 127.6, 126.7, 124.5 (d, J = 3.5 Hz), 118.9 (d, J = 3.1 Hz), 115.5 (d, J = 21.9 Hz), 68.1 (d, J = 4.0 Hz); HRMS (ESI) m/z 276.0796 ($M+Na^+$), calc. for $C_{16}H_{12}FNONa$ 276.0801.

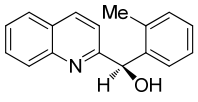
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.5 min (minor) and 14.6 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.627	26.4423	94.36	50.40
2	15.053	26.0221	82.48	49.60

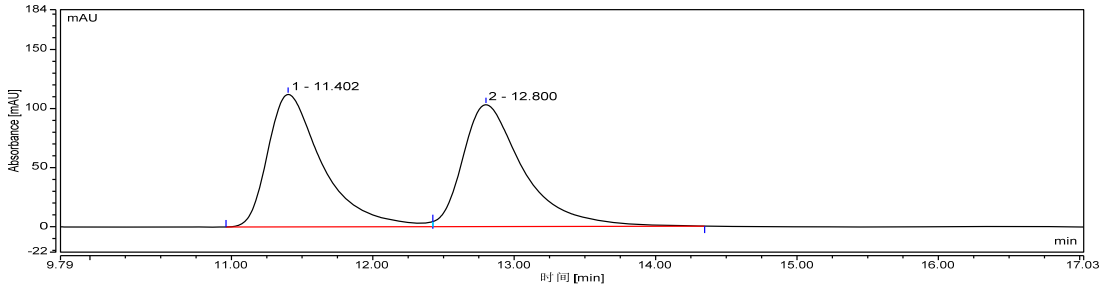


Entry	Retention Time	Area	Height	%Area
1	8.463	2.1477	8.22	5.15
2	14.573	39.5841	119.56	94.85

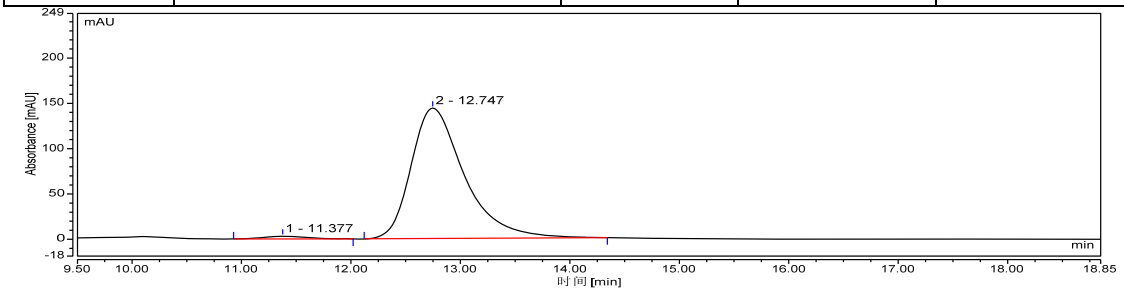


2c: white solid, Mp 82.1 – 83.7 °C, 20.2 mg, 81% yield, 97% ee, $[\alpha]_D^{22}$ +8.4 (c 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.79 (dd, J = 16.7, 7.9 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.24 – 7.13 (m, 4H), 7.08 (d, J = 8.5 Hz, 1H), 6.10 (s, 1H), 6.01 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 145.9, 140.2, 137.0, 136.6, 131.0, 129.9, 128.7, 128.7, 128.0, 127.6, 127.4, 126.6, 126.2, 119.1, 73., 19.5; HRMS (ESI) m/z 272.1040 ($M+Na^+$), calc. for $C_{17}H_{15}NONa$ 272.1051.

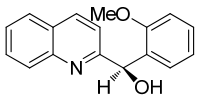
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.4 min (minor) and 12.7 min (major).



Entry	Retention Time	Area	Height	%Area
1	11.402	50.4517	112.20	49.09
2	12.800	52.3209	103.48	50.91

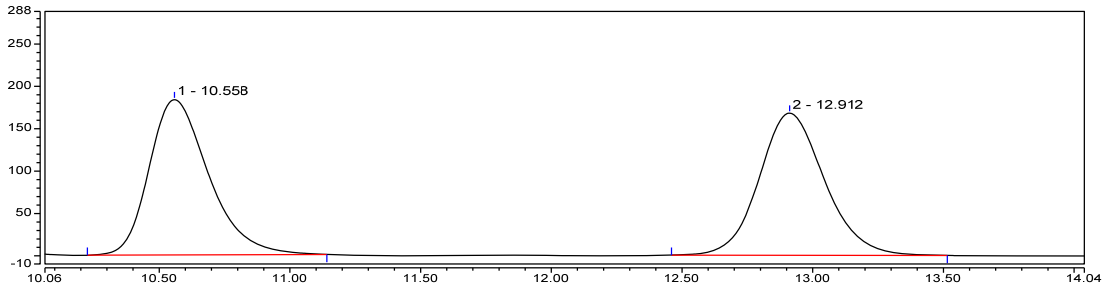


Entry	Retention Time	Area	Height	%Area
1	11.377	1.3977	2.98	1.69
2	12.747	81.1506	143.83	98.31

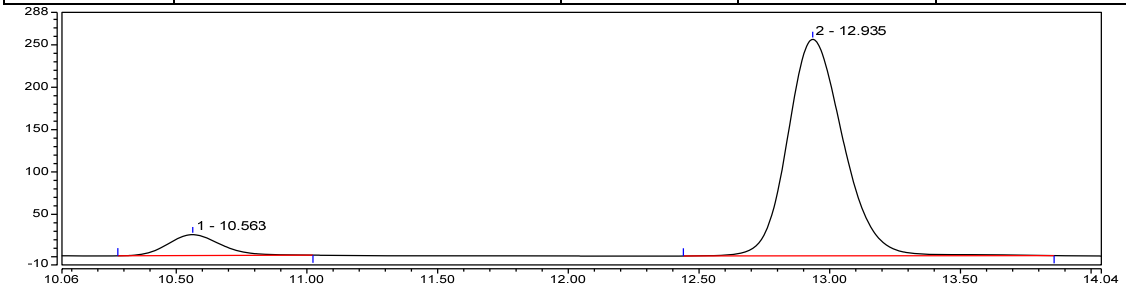


2d: white solid, Mp 120.6 – 121.8 °C, 18.8 mg, 71% yield, 83% ee, $[\alpha]_D^{22}$ +24.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 18.1, 7.8 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.13 (m, 3H), 6.83 (dd, *J* = 12.9, 7.8 Hz, 2H), 6.33 (d, *J* = 2.9 Hz, 1H), 5.96 (d, *J* = 3.7 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 156.7, 145.9, 136.8, 131.2, 129.6, 128.8, 128.7, 128.1, 127.5, 126.3, 120.9, 119.2, 110.7, 68.5, 55.5; HRMS (ESI) m/z 288.1006 ($M+Na^+$), calc. for $C_{17}H_{15}NO_2Na$ 288.1000.

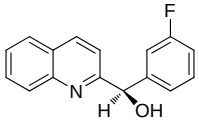
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.6 min (minor) and 12.9 min (major).



Entry	Retention Time	Area	Height	%Area
1	10.558	48.5202	183.23	49.87
2	12.912	48.7811	167.77	50.13

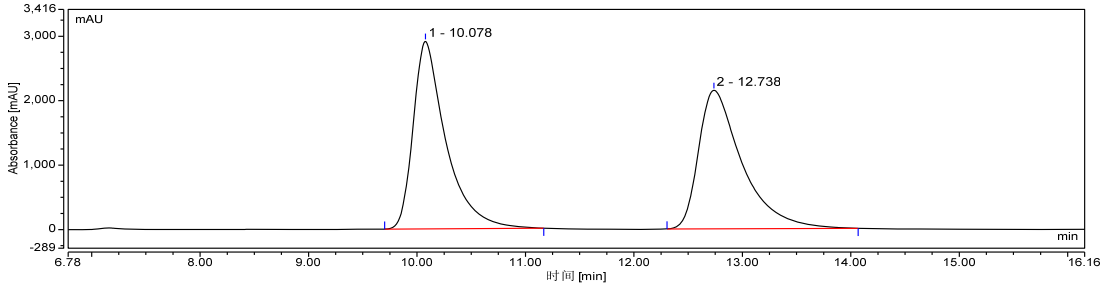


Entry	Retention Time	Area	Height	%Area
1	10.563	5.8003	24.66	8.42
2	12.935	63.0846	255.45	91.58

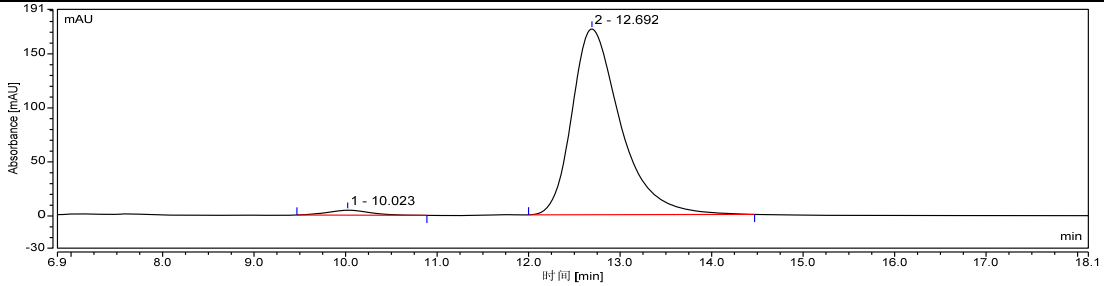


2e: white solid, Mp 93.9 – 94.8 °C, 23.5 mg, 93% yield, 95% ee, $[\alpha]_D^{22}$ −83.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 15.4, 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.00 (m, 4H), 6.94 – 6.84 (m, 1H), 6.12 (s, 1H), 5.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.5 Hz), 159.6, 145.9, 145.3 (d, *J* = 6.6 Hz), 137.2, 130.1, 130.0, 128.7, 127.6, 127.5, 126.7, 123.0 (d, *J* = 2.9 Hz), 119.0, 114.9 (d, *J* = 21.2 Hz), 114.1 (d, *J* = 21.8 Hz), 74.5 (d, *J* = 1.7 Hz); HRMS (ESI) m/z 276.0801 ($M+Na^+$), calc. for $C_{16}H_{12}FNONa$ 276.0801.

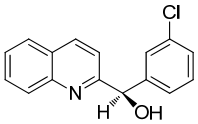
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.0 min (minor) and 12.7 min (major).



Entry	Retention Time	Area	Height	%Area
1	10.078	1034.9378	2915.88	50.22
2	12.738	1025.8774	2156.75	49.78

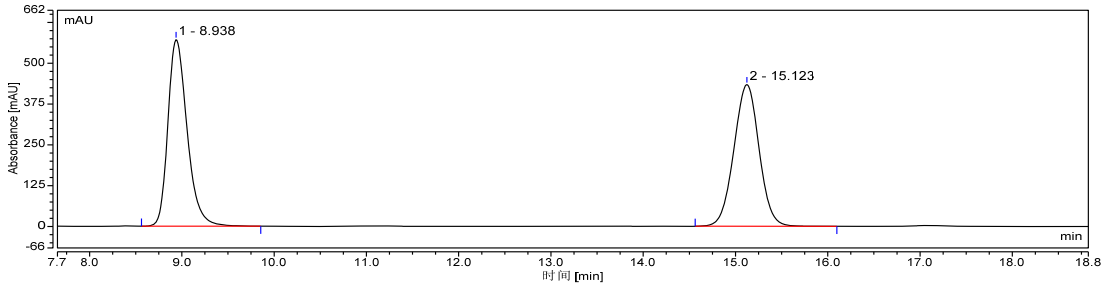


Entry	Retention Time	Area	Height	%Area
1	10.023	2.7309	4.75	2.46
2	12.692	108.1689	172.50	97.54

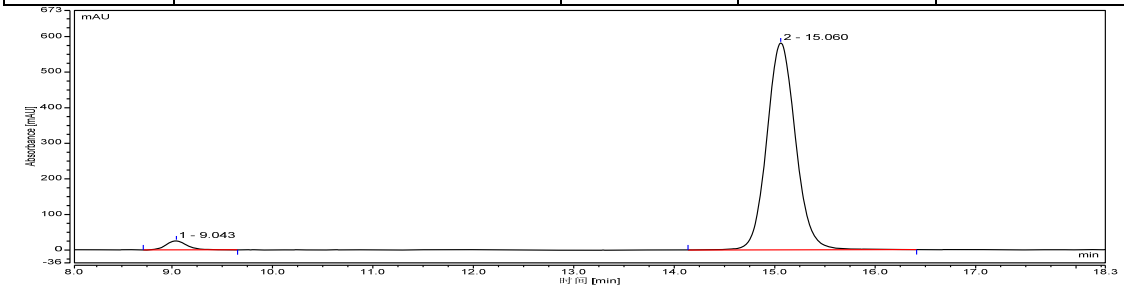


2f: white solid, Mp 83.9 – 85.1 °C, 23.7 mg, 88% yield, 94% ee, $[\alpha]_D^{22}$ −123.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 19.2, 8.5 Hz, 2H), 7.78 (dd, *J* = 16.4, 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.41 (s, 1H), 7.36 – 7.25 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.16 (s, 1H), 5.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.9, 144.8, 137.3, 134.5, 130.1, 129.9, 128.8, 128.2, 127.6, 127.5, 127.5, 126.8, 125.6, 119.0, 74.5; HRMS (ESI) m/z 292.0495 ($M+Na^+$), calc. for $C_{16}H_{12}ClNONa$ 292.0505.

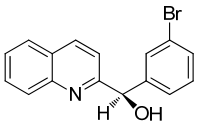
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.0 min (minor) and 15.1 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.938	137.8615	571.80	50.09
2	15.123	137.3843	434.08	49.91

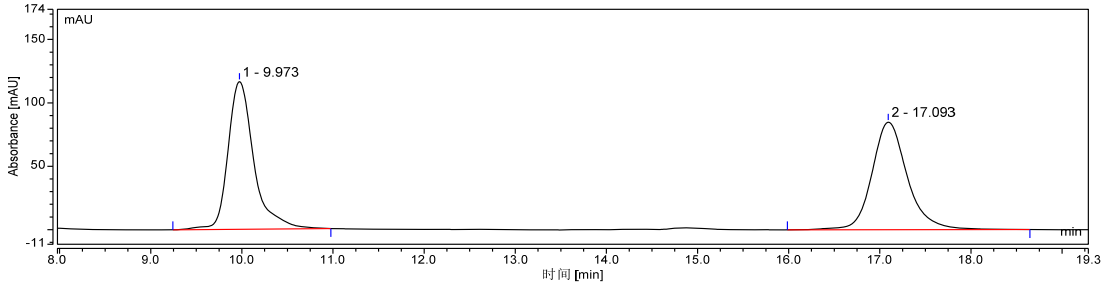


Entry	Retention Time	Area	Height	%Area
1	9.043	6.0046	25.17	3.02
2	15.060	193.0148	581.14	96.98

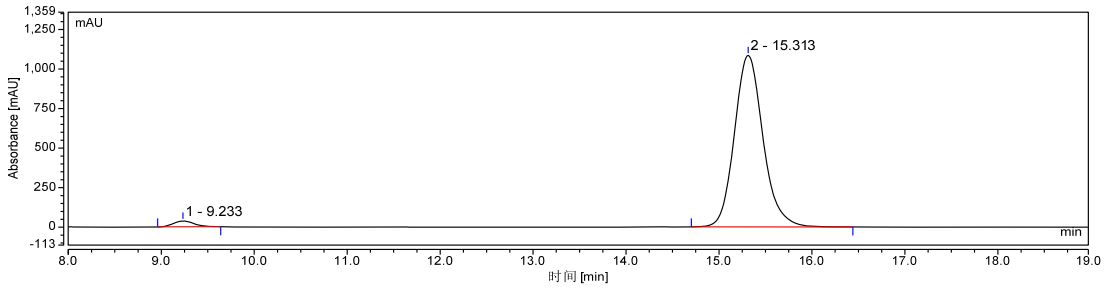


2g: white solid, Mp 115.4 – 117.2 °C, 28.8 mg, 92% yield, 95% ee, $[\alpha]_D^{22}$ −130.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 15.5, 7.6 Hz, 2H), 7.63 – 7.52 (m, 2H), 7.39 (dd, *J* = 14.3, 7.8 Hz, 2H), 7.25 – 7.15 (m, 2H), 6.20 (d, *J* = 3.1 Hz, 1H), 5.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.8, 145.0, 137.3, 131.0, 130.3, 130.2, 130.0, 128.7, 127.6, 127.5, 126.8, 126.0, 122.7, 119.0, 74.4; HRMS (ESI) m/z 335.9998 ($M+Na^+$), calc. for $C_{16}H_{12}BrNONa$ 336.0000.

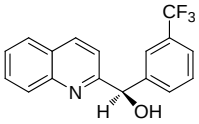
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 9.2 min (minor) and 15.3 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.973	38.2674	116.49	50.04
2	17.093	38.2118	84.80	49.96

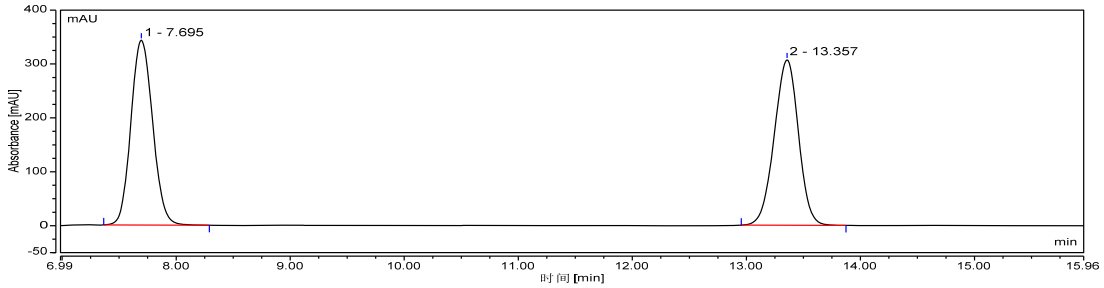


Entry	Retention Time	Area	Height	%Area
1	9.233	9.4314	36.86	2.38
2	15.313	386.2212	1084.72	97.62

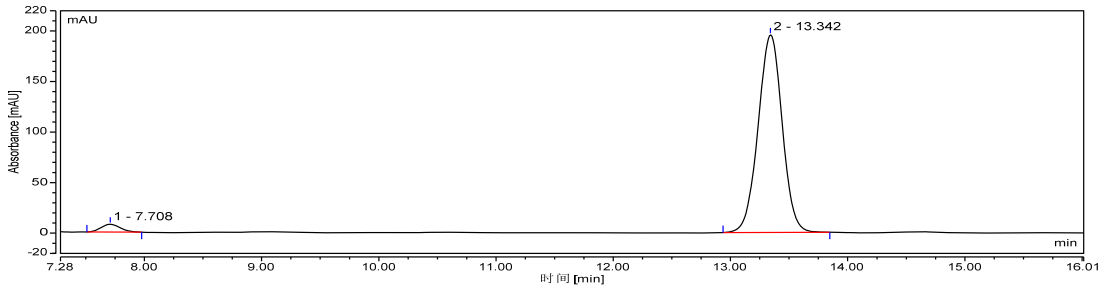


2h: white solid, Mp 79.2 – 80.8 °C, 30.0 mg, >99% yield, 94% ee, $[\alpha]_D^{22}$ −76.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 14.9, 8.1 Hz, 3H), 7.66 – 7.52 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.26 (s, 1H), 5.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 146.0, 143.8, 137.5, 131.0 (q, *J* = 30.1 Hz), 130.8, 130.2, 129.2, 128.8, 127.7, 127.6, 126.9, 124.9 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.4 Hz), 119.0, 74.7; HRMS (ESI) m/z 326.0767 ($M+Na^+$), calc. for $C_{17}H_{12}F_3NONa$ 326.0769.

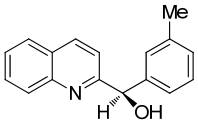
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.7 min (minor) and 13.3 min (major).



Entry	Retention Time	Area	Height	%Area
1	7.695	75.8652	343.28	50.01
2	13.357	75.8257	307.36	49.99

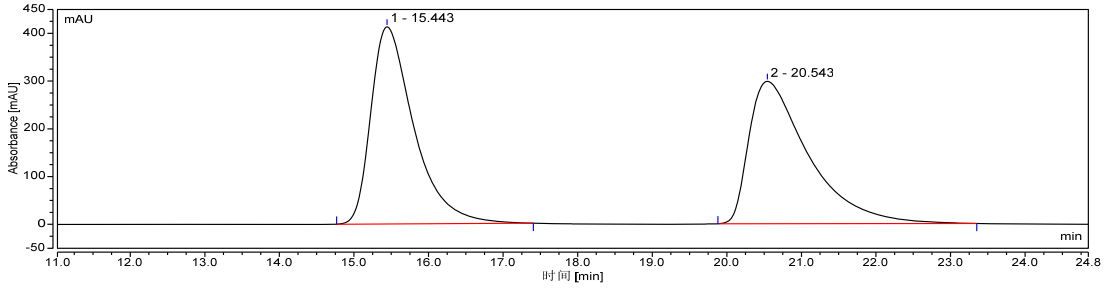


Entry	Retention Time	Area	Height	%Area
1	7.708	1.5527	7.86	3.20
2	13.342	46.9742	195.89	96.80

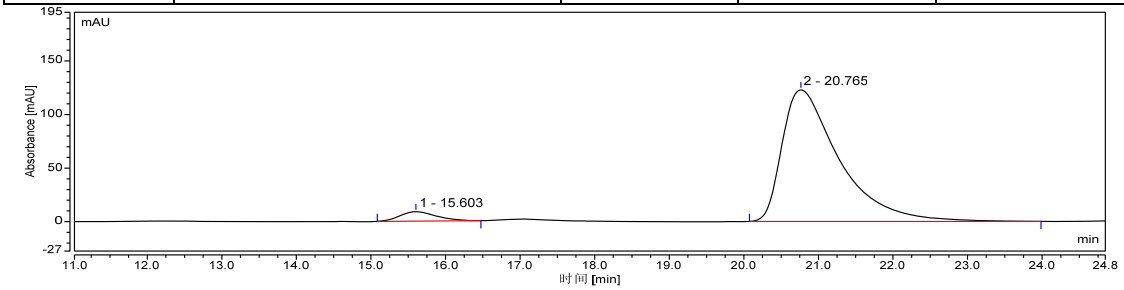


2i: white solid, Mp 82.2 – 83.8 °C, 20.4 mg, 82% yield, 91% ee, $[\alpha]_D^{22}$ −124.9 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 15.4, 7.5 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 3H), 6.11 (s, 1H), 5.86 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 145.8, 139.8, 137.7, 137.0, 129.9, 129.3, 128.7, 127.6, 127.4, 127.4, 126.6, 119.3, 74.9, 21.1; HRMS (ESI) m/z 272.1051 ($M+Na^+$), calc. for $C_{17}H_{15}NONa$ 272.1051.

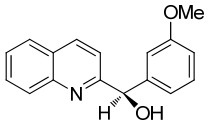
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.6 min (minor) and 20.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	15.443	279.3198	413.34	49.95
2	20.543	279.8474	298.99	50.05

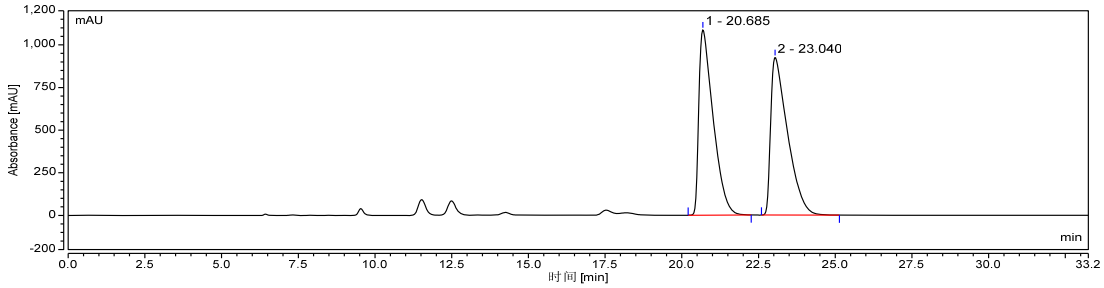


Entry	Retention Time	Area	Height	%Area
1	15.603	5.0897	8.90	4.48
2	20.765	108.6178	123.00	95.52

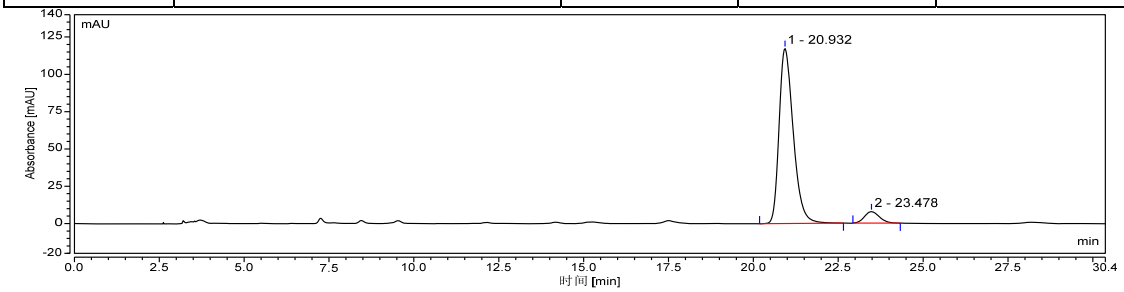


2j: white solid, Mp 125.6 – 126.8 °C, 20.4 mg, 77% yield, 88% ee, $[\alpha]_D^{22}$ −81.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.73 (dd, *J* = 14.7, 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.14 (m, 2H), 7.05 – 6.91 (m, 2H), 6.80 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.12 (s, 1H), 5.83 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 159.8, 145.9, 144.3, 137.0, 129.8, 129.6, 128.7, 127.5, 127.4, 126.5, 119.7, 119.1, 113.5, 112.6, 75.0, 55.1; HRMS (ESI) m/z 288.1008 ($M+Na^+$), calc. for $C_{17}H_{15}NO_2Na$ 288.1000.

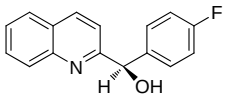
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.9 min (major) and 23.5 min (minor).



Entry	Retention Time	Area	Height	%Area
1	20.685	586.8982	1087.58	49.94
2	23.040	588.4198	924.89	50.06

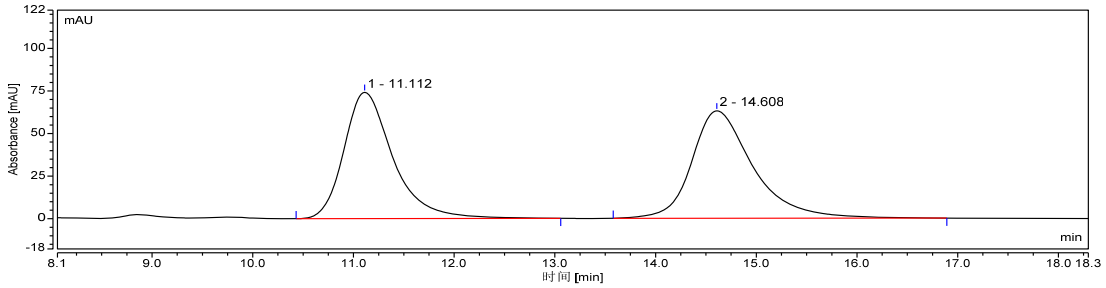


Entry	Retention Time	Area	Height	%Area
1	20.932	56.4126	117.36	93.90
2	23.478	3.6640	7.46	6.10

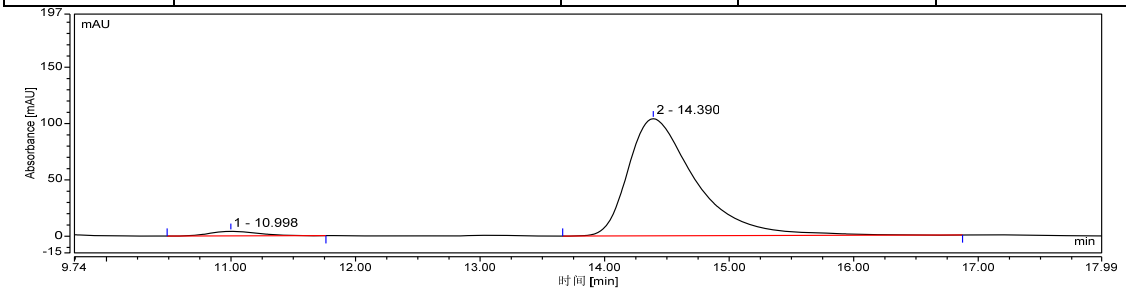


2k: white solid, Mp 74.1 – 75.2 °C, 24.3 mg, 96% yield, 94% ee, $[\alpha]_D^{22}$ −27.5 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.23 (s, 1H), 5.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.1 Hz), 160.3, 145.8, 138.5 (d, *J* = 3.1 Hz), 137.0, 129.8, 128.9 (d, *J* = 8.2 Hz), 128.6, 127.5, 127.3, 126.6, 118.9, 115.3 (d, *J* = 21.5 Hz), 74.4; HRMS (ESI) m/z 276.0795 ($M+Na^+$), calc. for $C_{16}H_{12}FNONa$ 276.0801.

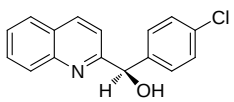
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.0 min (minor) and 14.4 min (major).



Entry	Retention Time	Area	Height	%Area
1	11.112	41.8234	74.14	49.66
2	14.608	42.3953	62.27	50.34



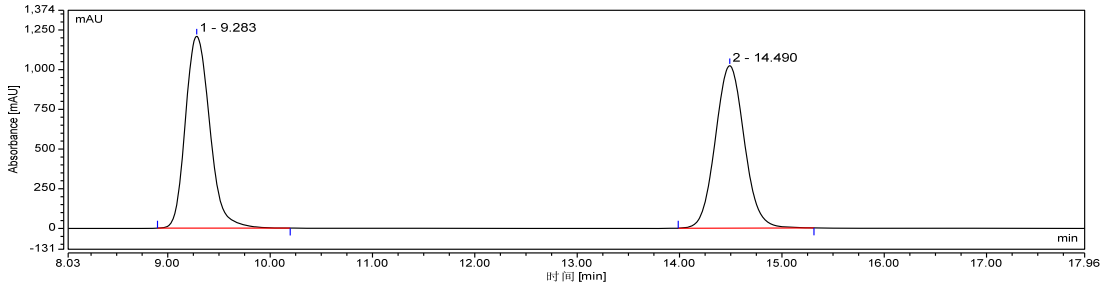
Entry	Retention Time	Area	Height	%Area
1	10.998	1.8127	4.09	2.72
2	14.390	64.9014	103.93	97.28



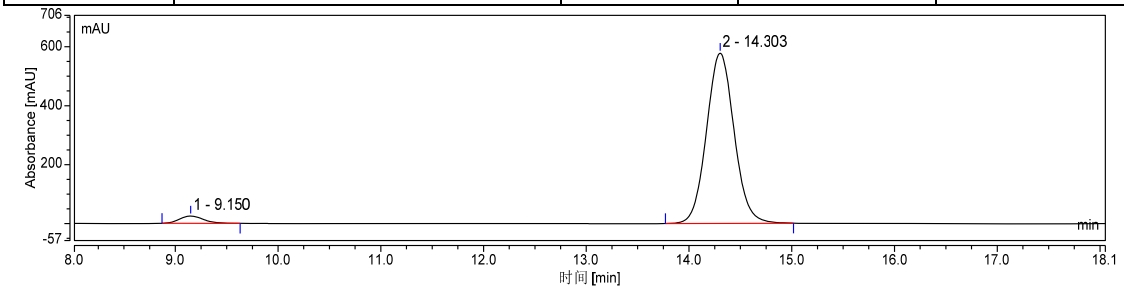
2l: white solid, Mp 105.7 – 106.8 °C, 26.4 mg, 98% yield, 93% ee, $[\alpha]_D^{22}$ −11.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 15.3, 7.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.33 (q, *J* = 8.5 Hz, 4H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.18 (d, *J* = 2.8 Hz, 1H), 5.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 145.9, 141.2, 137.2, 133.7, 130.0, 128.7,

128.7, 127.6, 127.4, 126.7, 119.0, 74.4; HRMS (ESI) m/z 292.0512 ($M+Na^+$), calc. for $C_{16}H_{12}ClNONa$ 292.0505.

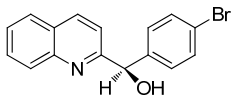
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 9.2 min (minor) and 14.3 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.283	333.6183	1207.95	49.91
2	14.490	334.8675	1021.66	50.09

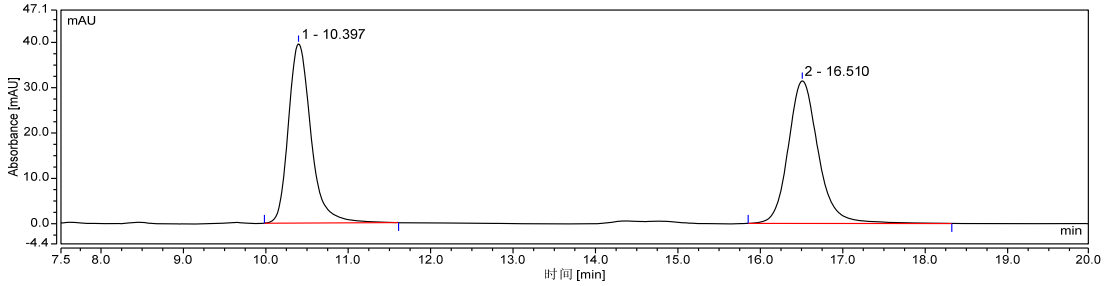


Entry	Retention Time	Area	Height	%Area
1	9.150	6.6336	24.63	3.55
2	14.303	180.1893	577.52	96.45

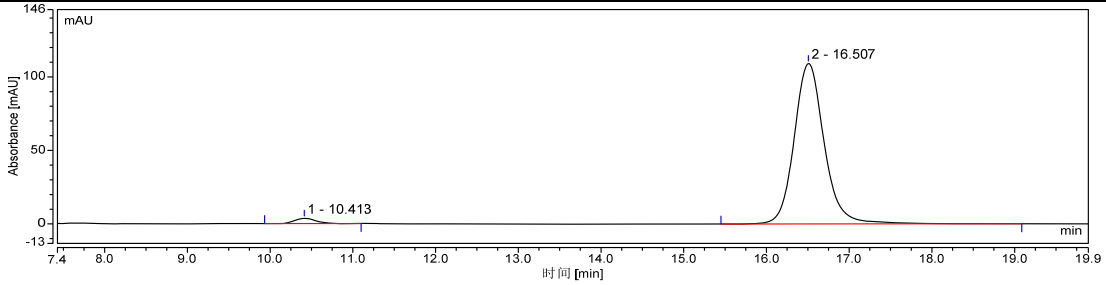


2m: white solid, Mp 108.9 – 109.8 °C, 29.4 mg, 94% yield, 96% ee, $[\alpha]_D^{22}$ −107.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 15.6, 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.18 (s, 1H), 5.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 145.9, 141.8, 137.2, 131.7, 130.0, 129.0, 128.7, 127.6, 127.4, 126.7, 121.9, 119.0, 74.5; HRMS (ESI) m/z 336.0002 ($M+Na^+$), calc. for $C_{16}H_{12}BrNONa$ 336.0000.

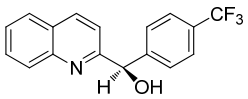
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.4 min (minor) and 16.5 min (major).



Entry	Retention Time	Area	Height	%Area
1	10.397	24.0338	40.13	49.92
2	16.510	24.1108	33.36	50.08

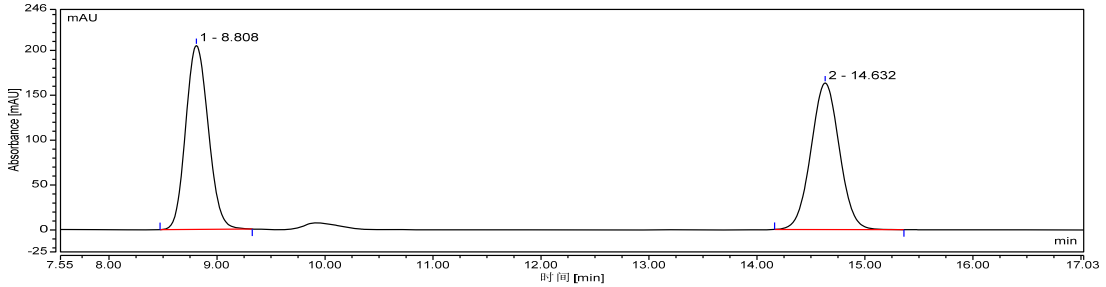


Entry	Retention Time	Area	Height	%Area
1	10.413	1.0166	3.53	2.16
2	16.507	46.0037	109.15	97.84

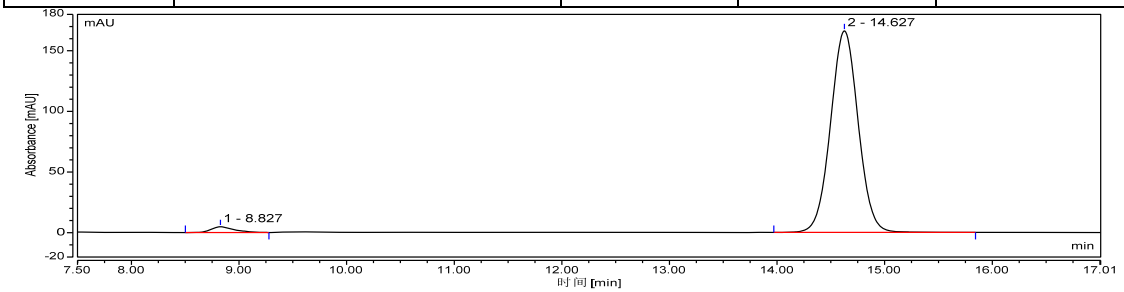


2n: white solid, Mp 120.3 – 121.8 °C, 29.7 mg, 98% yield, 95% ee, $[\alpha]_D^{22}$ −143.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 20.2, 8.5 Hz, 2H), 7.79 (dd, *J* = 15.1, 7.7 Hz, 2H), 7.58 (q, *J* = 8.2 Hz, 5H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.21 (s, 1H), 5.94 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 146.7, 146.0, 137.4, 130.1, 130.1 (q, *J* = 32.4 Hz), 128.7, 127.6, 127.6, 127.5, 126.9, 125.6 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz), 118.9, 74.6; HRMS (ESI) m/z 326.0766 ($M+Na^+$), calc. for $C_{17}H_{12}F_3NONa$ 326.0769.

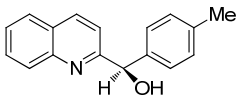
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.8 min (minor) and 14.6 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.808	49.7134	204.83	49.97
2	14.632	49.7646	163.21	50.03

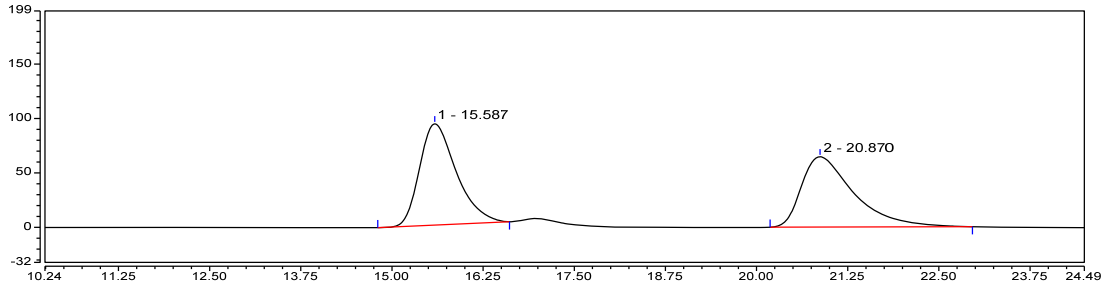


Entry	Retention Time	Area	Height	%Area
1	8.827	1.1684	4.77	2.30
2	14.627	49.5512	166.22	97.70

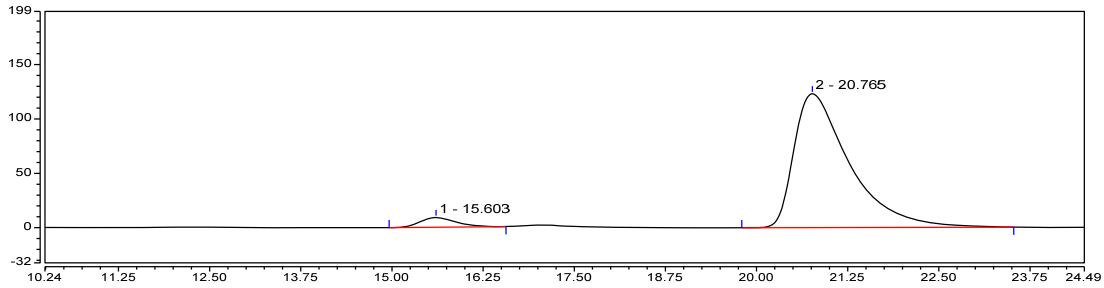


2o: white solid, Mp 67.2 – 68.8 °C, 21.9 mg, 88% yield, 91% ee, $[\alpha]_D^{22}$ −114.5 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 15.8, 8.1 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 12.3 Hz, 4H), 7.02 (s, 1H), 6.05 (s, 1H), 5.75 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 145.9, 142.6, 138.3, 137.0, 129.9, 128.8, 128.5, 128.0, 127.6, 126.6, 124.6, 119.3, 75.1, 21.4; HRMS (ESI) m/z 272.1044 ($M+Na^+$), calc. for $C_{17}H_{15}NONa$ 272.1051.

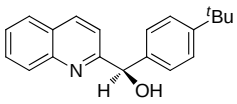
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.6 min (minor) and 20.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	15.587	54.3776	93.09	50.24
2	20.870	53.8486	64.64	49.76

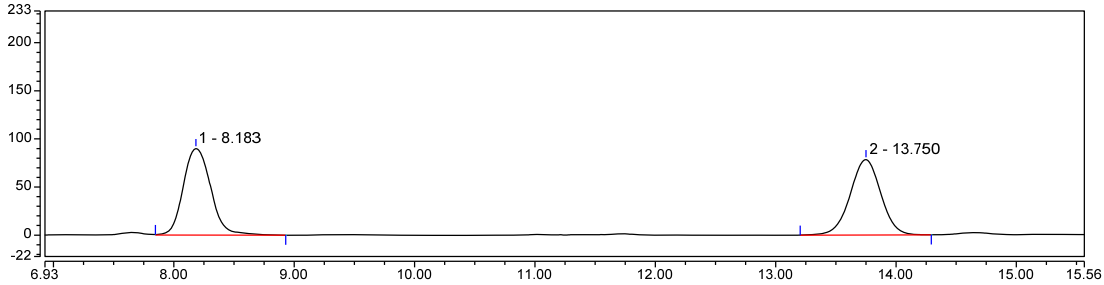


Entry	Retention Time	Area	Height	%Area
1	15.603	5.0858	8.90	4.48
2	20.765	108.4811	122.96	95.52

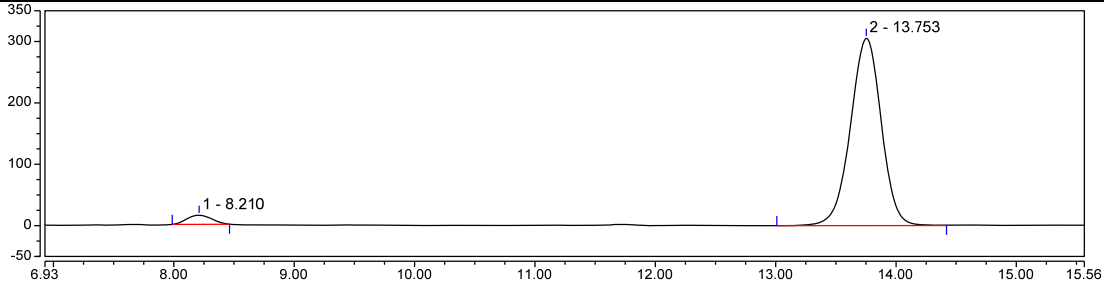


2p: white solid, Mp 83.7 – 85.2 °C, 24.7 mg, 85% yield, 93% ee, $[\alpha]_D^{22}$ −125.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.55 (dd, *J* = 11.1, 3.9 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.08 (s, 1H), 5.90 (s, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 150.7, 145.9, 139.7, 136.8, 129.7, 128.7, 127.5, 127.4, 127.0, 126.4, 125.5, 119.3, 74.9, 34.4, 31.2; HRMS (ESI) m/z 314.1513 ($M+Na^+$), calc. for $C_{20}H_{21}NONa$ 314.1521.

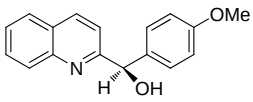
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.2 min (minor) and 13.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.183	23.9126	89.90	50.78
2	13.750	23.1737	78.34	49.22

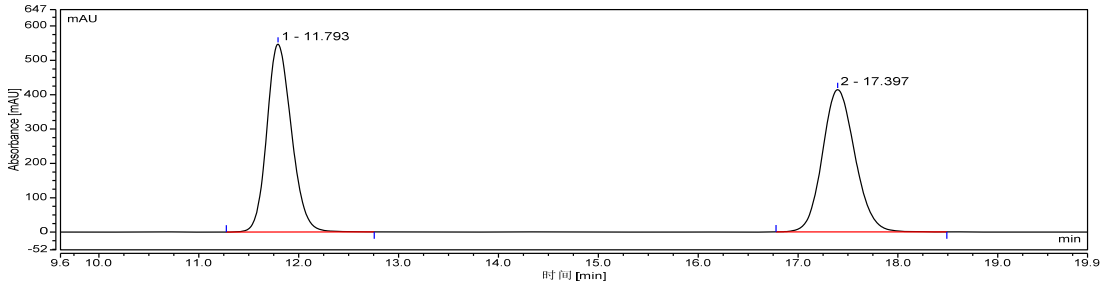


Entry	Retention Time	Area	Height	%Area
1	8.210	3.5132	14.63	3.73
2	13.753	90.7328	305.04	96.27

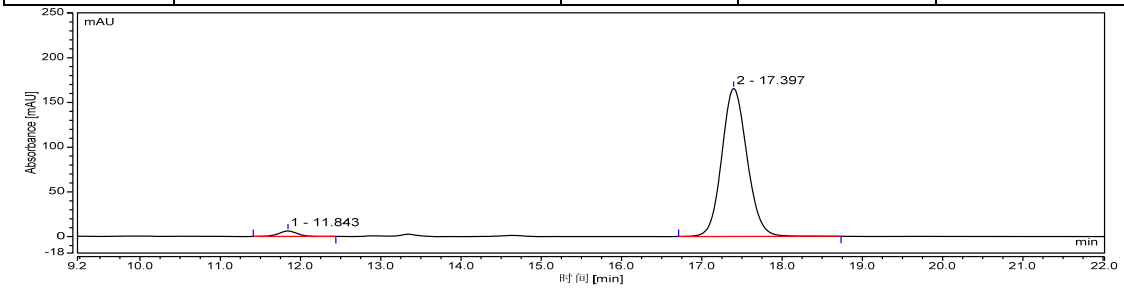


2q: white solid, Mp 65.1 – 65.9 °C, 21.5 mg, 81% yield, 95% ee, $[\alpha]_D^{22}$ −84.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.11 (s, 1H), 5.85 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 159.2, 145.8, 136.8, 134.9, 129.8, 128.6, 128.6, 127.5, 127.3, 126.4, 119.2, 113.9, 74.6, 55.1; HRMS (ESI) m/z 266.1182 ($M+H^+$), calc. for $C_{17}H_{16}NO_2$ 266.1181.

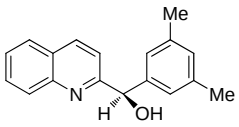
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.8 min (minor) and 17.4 min (major).



Entry	Retention Time	Area	Height	%Area
1	11.793	156.1545	546.47	49.99
2	17.397	156.2224	413.99	50.01

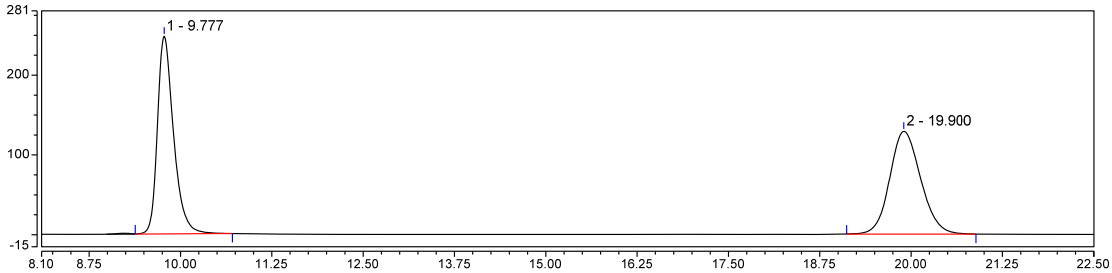


Entry	Retention Time	Area	Height	%Area
1	11.843	1.6445	6.10	2.66
2	17.397	60.2922	165.38	97.34

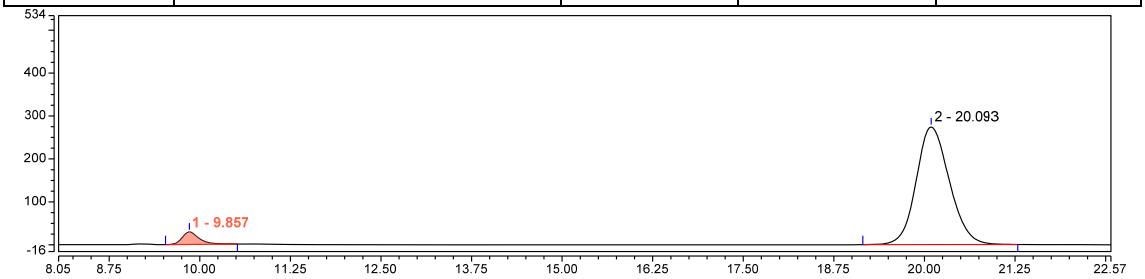


2r: white solid, Mp 82.2 – 83.6 °C, 20.8 mg, 79% yield, 90% ee, $[\alpha]_D^{22}$ −158.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 15.9, 7.7 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.03 (s, 2H), 6.93 (s, 1H), 6.10 (d, *J* = 3.4 Hz, 1H), 5.81 (d, *J* = 2.8 Hz, 1H), 2.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 145.9, 142.6, 138.1, 136.9, 129.8, 129.6, 128.8, 127.6, 127.4, 126.5, 125.2, 119.3, 75.2, 21.2; HRMS (ESI) m/z 286.1194 ($M+Na^+$), calc. for $C_{18}H_{17}NONa$ 286.1208.

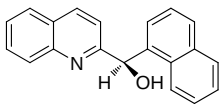
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.9 min (minor) and 20.1 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.777	63.4811	248.02	50.07
2	19.900	63.2995	128.94	49.93



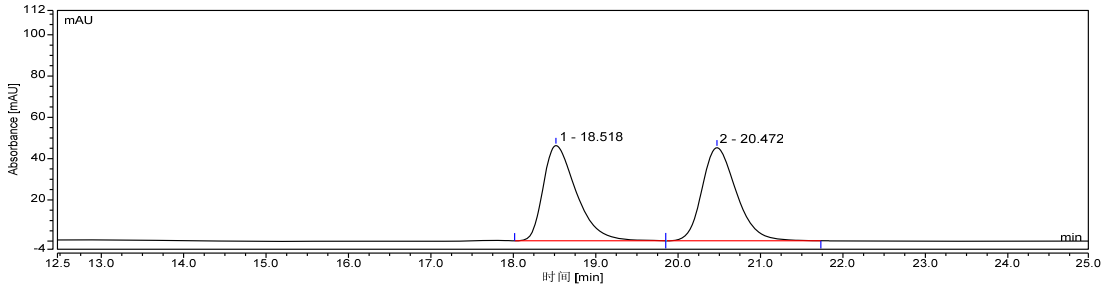
Entry	Retention Time	Area	Height	%Area
1	9.857	7.7457	28.96	5.05
2	20.093	145.6684	274.08	94.95



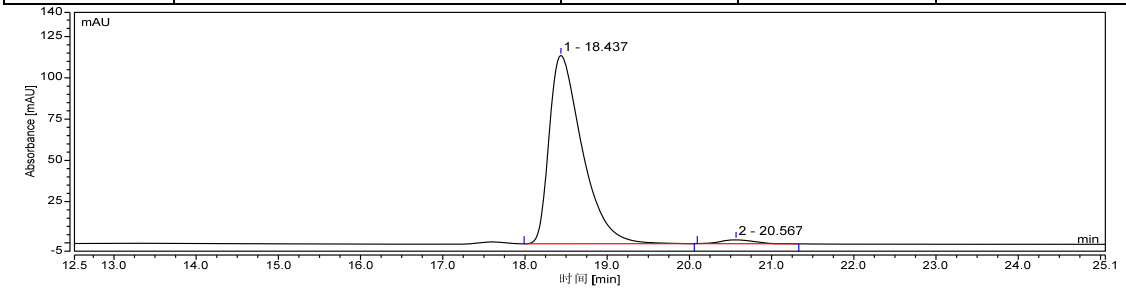
2s: white solid, Mp 167.5 – 168.5 °C, 21.7 mg, 76% yield, 96% ee, $[\alpha]_D^{22}$ −122.5 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (t, *J* = 7.1 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.75 (m, 4H), 7.62 – 7.37 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.53 (s, 1H), 6.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 146.1, 137.7, 137.1, 134.3, 131.5, 130.0, 129.0, 128.8, 128.7, 127.6, 127.5, 127.0, 126.7,

126.3, 125.6, 125.3, 124.3, 119.1, 73.9; HRMS (ESI) m/z 286.1219 ($M+H^+$), calc. for $C_{20}H_{16}NO$ 286.1232.

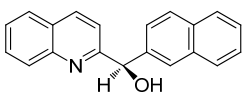
The ee was determined by HPLC analysis: CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.4 min (major) and 20.6 min (minor).



Entry	Retention Time	Area	Height	%Area
1	18.518	21.4431	46.13	49.66
2	20.472	21.7393	45.08	50.34

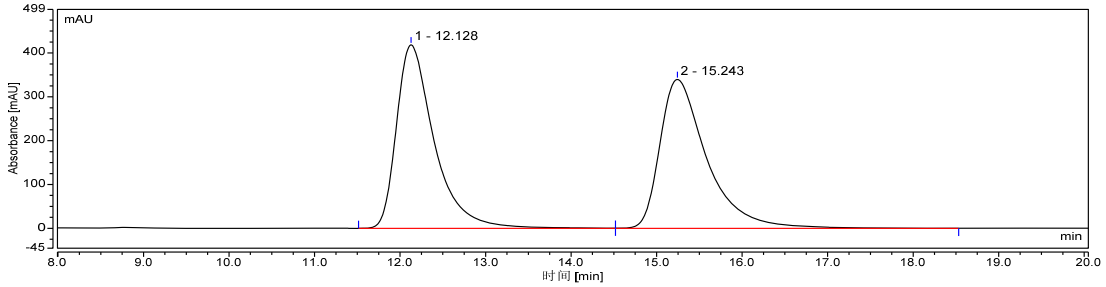


Entry	Retention Time	Area	Height	%Area
1	18.437	52.9129	114.04	97.91
2	20.567	1.1302	2.45	2.09

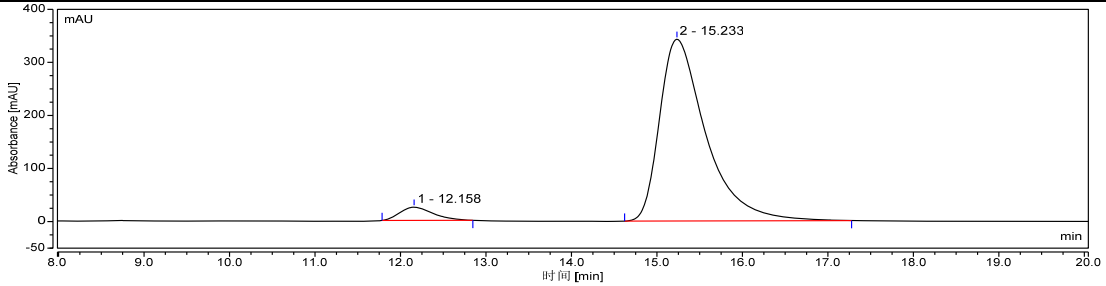


2t: white solid, Mp 131.8 – 132.5 °C, 27.6 mg, 97% yield, 90% ee, $[\alpha]_D^{22}$ −77.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.89 – 7.73 (m, 5H), 7.62 – 7.40 (m, 4H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.23 (s, 1H), 6.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 146.0, 140.1, 137.0, 133.3, 133.2, 130.0, 128.8, 128.6, 128.0, 127.7, 127.6, 127.5, 126.7, 126.7, 126.2, 126.0, 125.0, 119.3, 75.3; HRMS (ESI) m/z 308.1058 ($M+Na^+$), calc. for $C_{20}H_{15}NONa$ 308.1051.

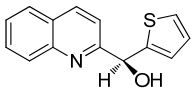
The ee was determined by HPLC analysis: CHIRALCEL OZ–H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 94/6; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.2 min (minor) and 15.2 min (major).



Entry	Retention Time	Area	Height	%Area
1	12.128	213.9403	418.38	49.81
2	15.243	215.5344	339.48	50.19

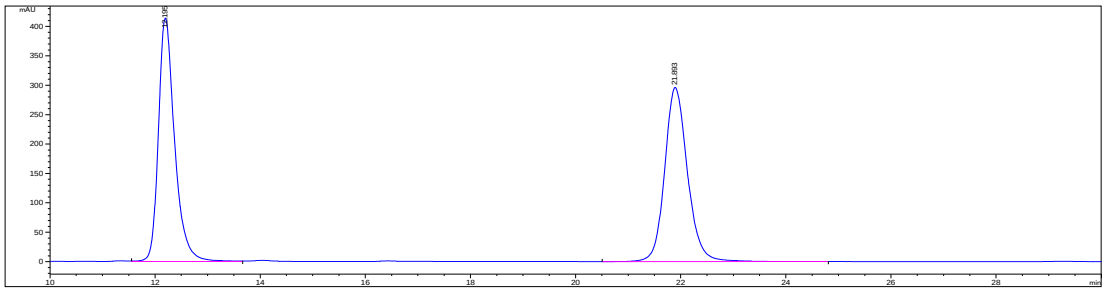


Entry	Retention Time	Area	Height	%Area
1	12.158	11.2472	24.87	4.91
2	15.233	217.9318	343.19	95.09

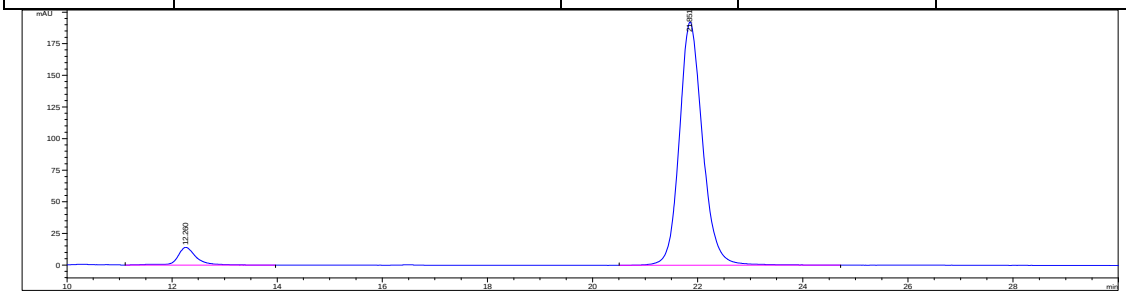


2u: white solid, Mp 118.1 – 118.8 °C, 23.9 mg, 98% yield, 90% ee, $[\alpha]_D^{22}$ −16.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.88 – 7.72 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 6.98 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.18 (s, 1H), 6.10 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 146.7, 145.8, 137.4, 130.1, 128.7, 127.6, 127.6, 126.9, 126.6, 125.9, 125.6, 119.0, 70.8; HRMS (ESI) m/z 264.0464 ($M+Na^+$), calc. for $C_{14}H_{11}NOSNa$ 264.0459.

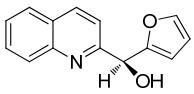
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.3 min (minor) and 21.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	12.195	8852.8	413.8	49.781
2	21.893	8930.6	296.1	50.219

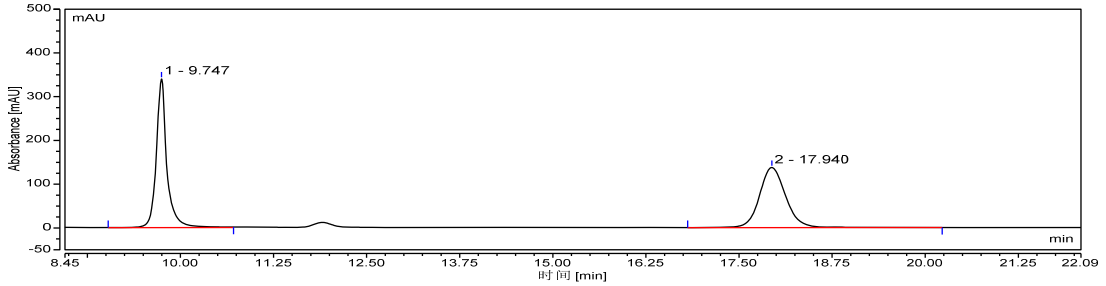


Entry	Retention Time	Area	Height	%Area
1	12.260	299.9	13.9	4.841
2	21.851	5894.7	192.4	95.159

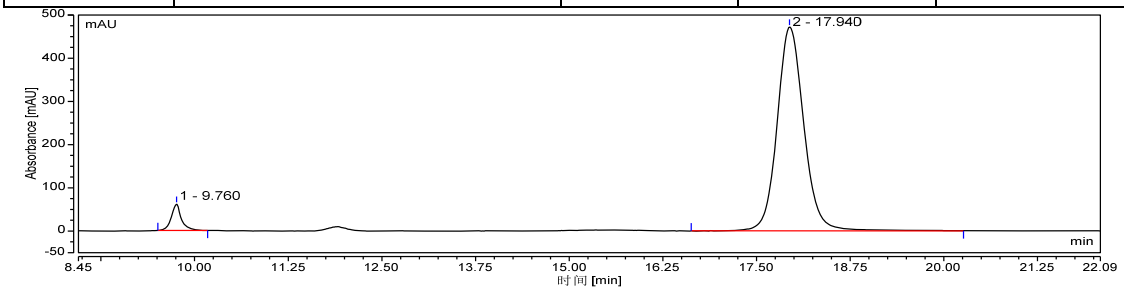


2v: yellow solid, Mp 84.2 – 84.6 °C, 17.1 mg, 76% yield, 91% ee, $[\alpha]_D^{22}$ +78.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.69 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.42 – 7.28 (m, 2H), 6.34 (s, 2H), 5.96 (s, 1H), 5.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 154.7, 146.1, 142.8, 137.2, 130.0, 128.8, 127.7, 127.6, 126.8, 118.9, 110.3, 108.0, 68.6; HRMS (ESI) m/z 226.0857 ($M+H^+$), calc. for $C_{14}H_{12}NO_2$ 226.0868.

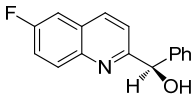
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 9.8 min (minor) and 17.9 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.747	56.3419	339.61	50.12
2	17.940	56.0624	137.26	49.88

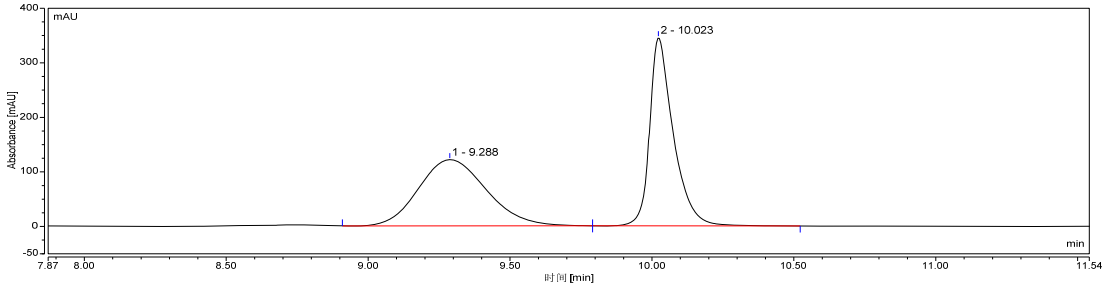


Entry	Retention Time	Area	Height	%Area
1	9.760	9.3841	60.55	4.59
2	17.940	195.2839	471.82	95.41

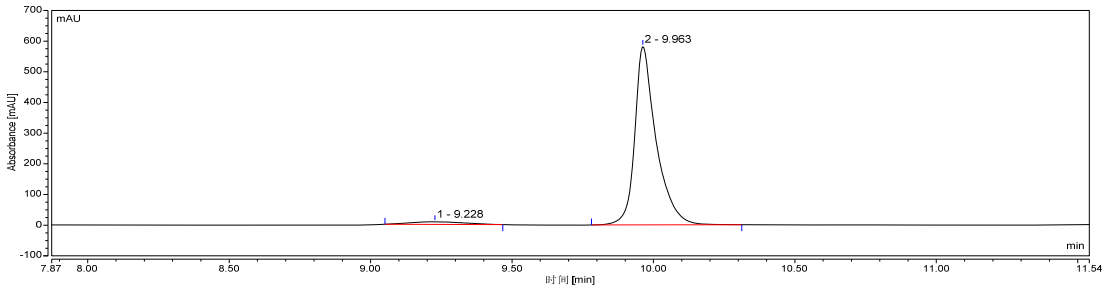


2w: white solid, Mp 126.3 – 127.8 °C, 20.5 mg, 81% yield, 93% ee, $[\alpha]_D^{22}$ −112.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 9.1, 5.3 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.58 (td, *J* = 8.9, 2.7 Hz, 1H), 7.47 (dd, *J* = 6.5, 4.8 Hz, 3H), 7.38 (m, 3H), 7.30 (d, *J* = 7.0 Hz, 1H), 6.05–5.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (d, *J* = 248.2 Hz), 160.0 (d, *J* = 2.6 Hz), 142.9, 142.5, 136.5 (d, *J* = 5.1 Hz), 131.1 (d, *J* = 9.0 Hz), 128.7, 128.1 (d, *J* = 10.0 Hz), 128.1, 127.4, 120.1, 120.1 (d, *J* = 25.5 Hz), 110.8 (d, *J* = 21.8 Hz), 75.1; HRMS (ESI) m/z 254.0981 ($M+H^+$), calc. for $C_{16}H_{13}FNO$ 254.0981.

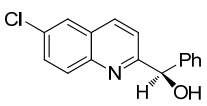
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.2 min (minor) and 10.0 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.288	33.6752	121.40	50.21
2	10.023	33.3970	345.08	49.79

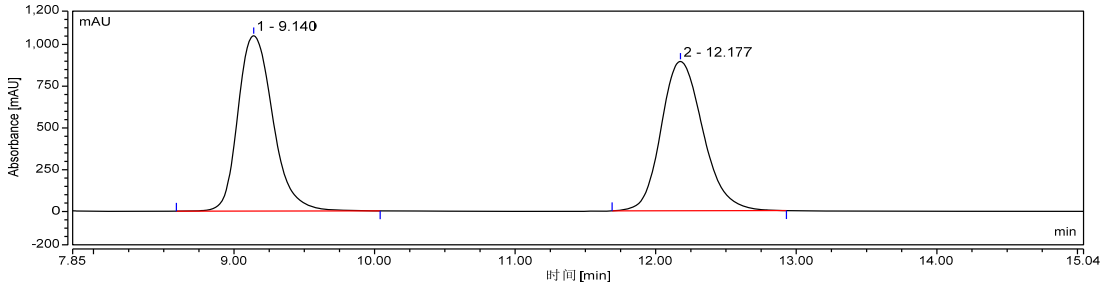


Entry	Retention Time	Area	Height	%Area
1	9.228	1.9593	8.64	3.70
2	9.963	51.0475	581.83	96.30

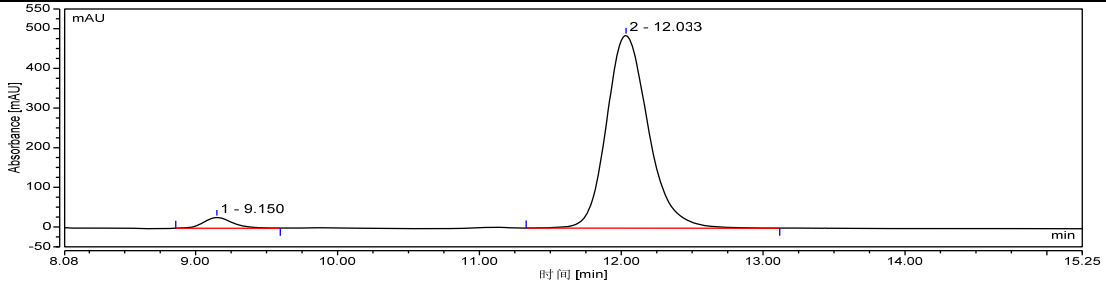


2x: white solid, Mp 81.9 – 82.9 °C, 23.7 mg, 88% yield, 93% ee, $[\alpha]_D^{22}$ −26.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.69 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.34 (tt, *J* = 13.2, 5.4 Hz, 5H), 7.22 (d, *J* = 8.6 Hz, 1H), 5.87 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 144.4, 142.4, 136.1, 132.4, 130.8, 130.4, 128.7, 128.1, 128.1, 127.4, 126.3, 120.2, 75.2; HRMS (ESI) m/z 270.0695 ($M+H^+$), calc. for $C_{16}H_{13}ClNO$ 270.0686.

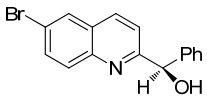
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 9.2 min (minor) and 12.0 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.140	302.5506	1049.59	49.53
2	12.177	308.3333	894.04	50.47

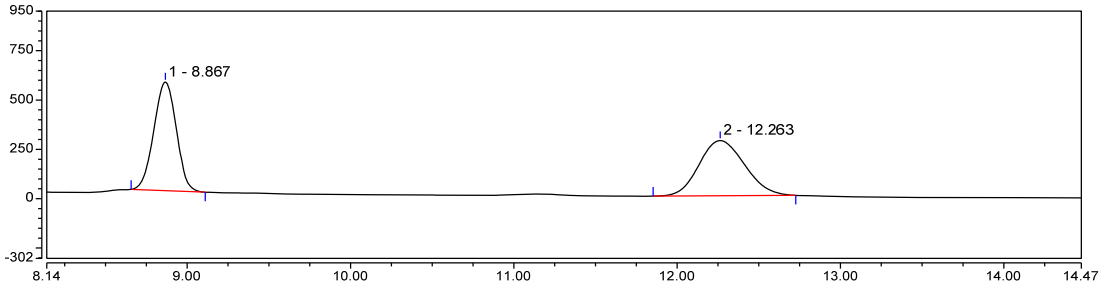


Entry	Retention Time	Area	Height	%Area
1	9.150	6.4377	26.93	3.73
2	12.033	165.9802	485.67	96.27

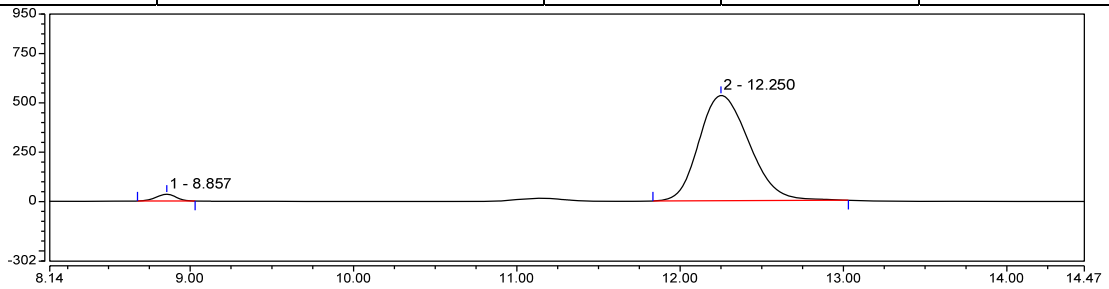


2y: white solid, Mp 97.6 – 99.2 °C, 29.1 mg, 93% yield, 95% ee, $[\alpha]_D^{22}$ −41.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.90 (m, 3H), 7.81 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.35 (ddd, *J* = 23.7, 10.7, 6.8 Hz, 5H), 7.21 (d, *J* = 8.6 Hz, 1H), 5.86 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 144.6, 142.4, 136.0, 133.4, 130.5, 129.6, 128.7, 128.6, 128.1, 127.4, 120.4, 120.2, 75.2; HRMS (ESI) m/z 314.0180 ($M+H^+$), calc. for $C_{16}H_{13}BrNO$ 314.0181.

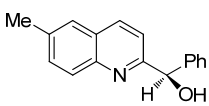
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 8.8 min (minor) and 12.2 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.867	87.7239	549.79	49.25
2	12.263	90.3805	279.50	50.75



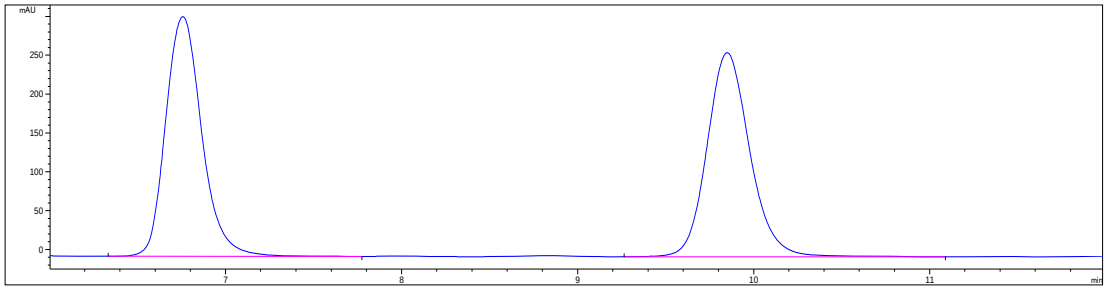
Entry	Retention Time	Area	Height	%Area
1	8.857	4.8913	34.41	2.52
2	12.250	189.3481	532.81	97.48



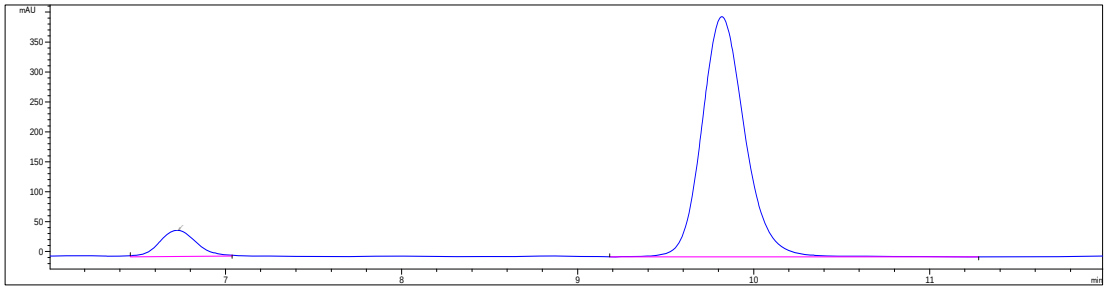
2za: white solid, Mp 122.3 – 124.8 °C, 22.7 mg, 91% yield, 83% ee, $[\alpha]_D^{22}$ −171.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz,

1H), 7.96 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 10.8 Hz, 2H), 7.41 (d, J = 7.3 Hz, 2H), 7.32 (dt, J = 8.4, 6.8 Hz, 3H), 7.14 (d, J = 8.5 Hz, 1H), 6.12 (s, 1H), 5.86 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 144.4, 142.9, 136.5, 136.4, 132.1, 128.6, 128.4, 127.9, 127.5, 127.4, 126.5, 119.2, 75.0, 21.5; HRMS (ESI) m/z 272.1043 ($M+Na^+$), calc. for $C_{17}H_{15}NONa$ 272.1051.

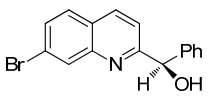
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.7 min (minor) and 9.8 min (major).



Entry	Retention Time	Area	Height	%Area
1	6.759	4403.9	308.5	49.876
2	9.851	4425.7	262.5	50.124

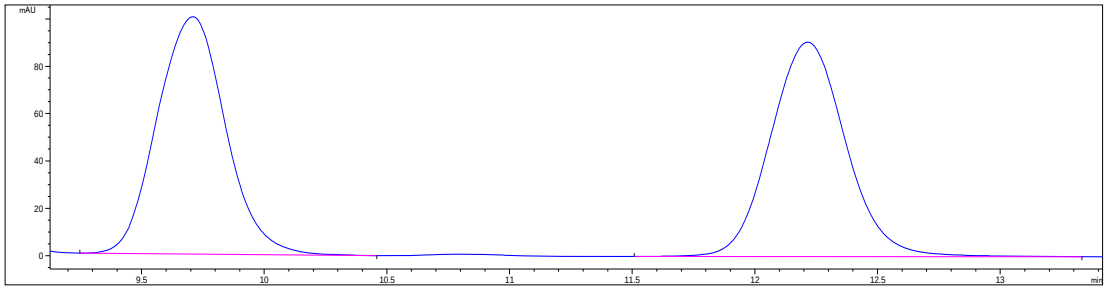


Entry	Retention Time	Area	Height	%Area
1	6.73	633.1	43.8	8.544
2	9.821	6776.1	401	91.456

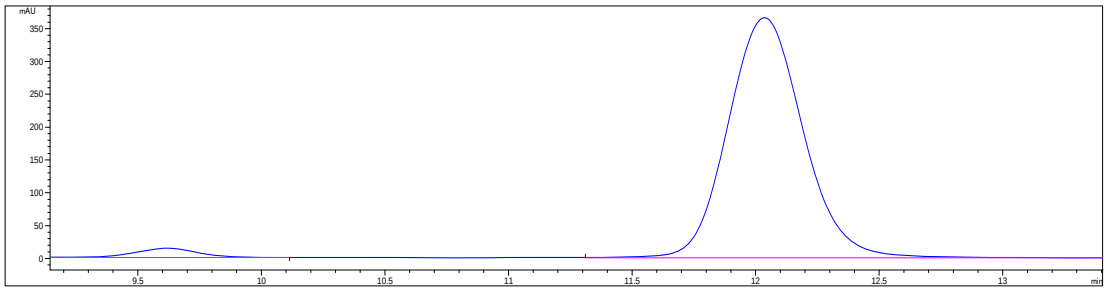


2zb: white solid, Mp 106.3 – 107.4 °C, 26.0 mg, 83% yield, 94% ee, $[\alpha]_D^{22}$ −66.4 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.64 (m, 2H), 7.34 (tt, J = 10.5, 5.7 Hz, 5H), 7.21 (d, J = 8.5 Hz, 1H), 6.12–5.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 146.5, 142.4, 137.0, 131.1, 130.2, 128.8, 128.7, 128.1, 127.4, 126.1, 124.1, 119.6, 75.2; HRMS (ESI) m/z 314.0183 ($M+H^+$), calc. for $C_{16}H_{13}BrNO$ 314.0181.

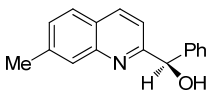
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.6 min (minor) and 12.0 min (major).



Entry	Retention Time	Area	Height	%Area
1	9.706	1944	100.3	50.162
2	12.213	1931.4	90.6	49.838

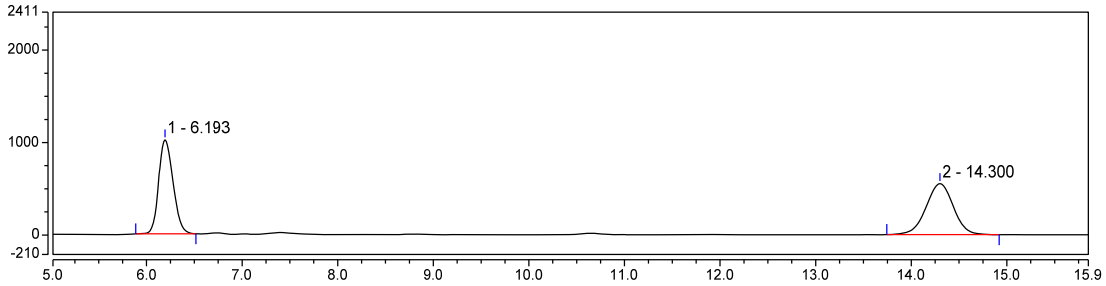


Entry	Retention Time	Area	Height	%Area
1	9.621	248.7	14.1	3.116
2	12.035	7734.7	365.9	96.884

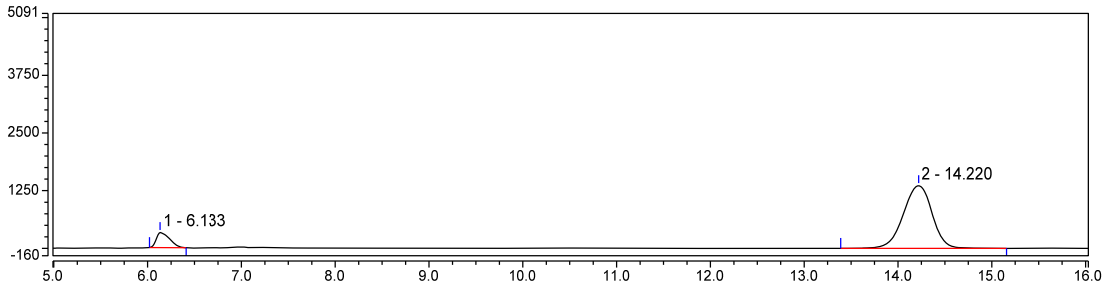


2zc: white solid, Mp 119.8 – 121.3 °C, 22.2 mg, 89% yield, 83% ee, $[\alpha]_D^{22}$ −173.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.34 (m, 6H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.15 (s, 1H), 5.86 (s, 1H), 2.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 146.1, 142.9, 140.4, 136.8, 128.8, 128.6, 127.9, 127.8, 127.4, 127.2, 125.5, 118.4, 75.0, 21.9; HRMS (ESI) m/z 272.1055 ($M+Na^+$), calc. for $C_{17}H_{15}NONa$ 272.1051.

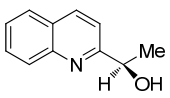
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 6.1 min (minor) and 14.2 min (major).



Entry	Retention Time	Area	Height	%Area
1	6.193	176.8414	1015.93	49.29
2	14.300	181.9184	550.93	50.71

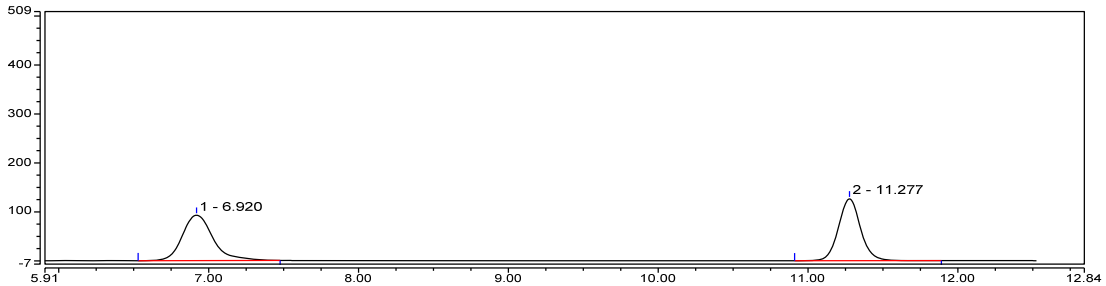


Entry	Retention Time	Area	Height	%Area
1	6.133	299.26	44.5724	8.45
2	14.220	1356.13	483.0176	91.55

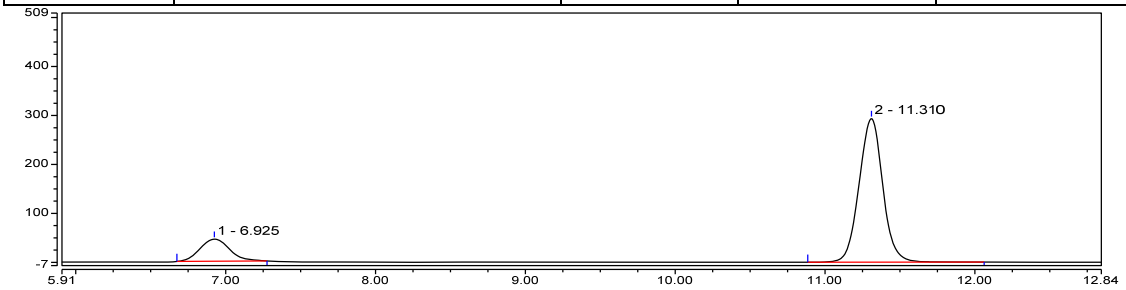


2zd: yellow solid, Mp 84.0 – 85.2 °C, 10.2 mg, 59% yield, 68% ee, $[\alpha]_D^{22}$ +18.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.73 (dd, *J* = 11.2, 4.2 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 5.16 – 4.96 (m, 2H), 1.58 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 146.3, 137.0, 129.8, 128.7, 127.6, 127.4, 126.4, 118.0, 68.7, 24.1; HRMS (ESI) m/z 196.0740 ($M+Na^+$), calc. for $C_{11}H_{11}NONa$ 196.0738.

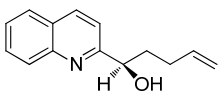
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 6.9 min (minor) and 11.3 min (major).



Entry	Retention Time	Area	Height	%Area
1	6.920	21.9630	92.68	50.48
2	11.277	21.5452	126.36	49.52

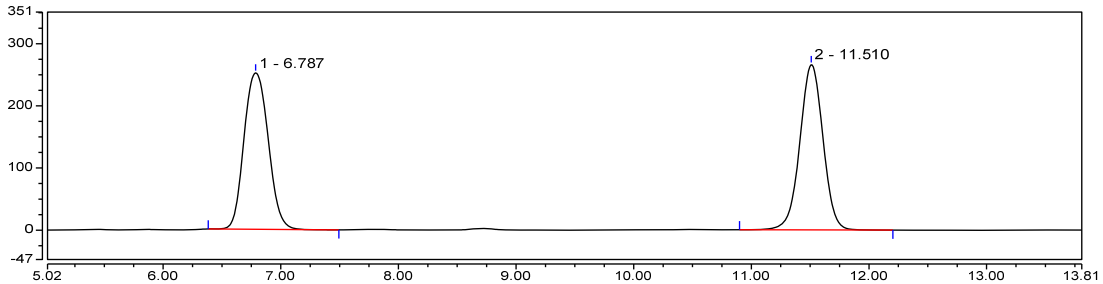


Entry	Retention Time	Area	Height	%Area
1	6.925	10.4176	45.19	16.21
2	11.310	53.8548	293.37	83.79

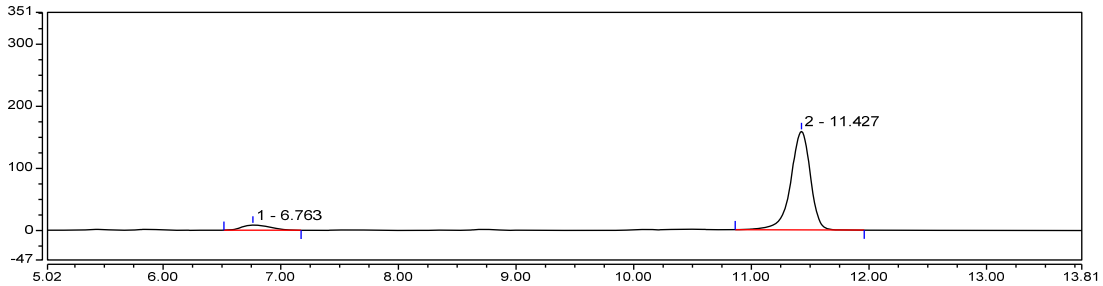


2ze: yellow solid, Mp 64.3 – 66.4 °C, 13.2 mg, 62% yield, 88% ee, $[\alpha]_D^{22}$ −26.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.21 – 4.82 (m, 4H), 2.40 – 2.12 (m, 2H), 2.11 – 1.97 (m, 1H), 1.90 – 1.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 146.3, 138.2, 137.0, 129.8, 128.6, 127.6, 127.4, 126.4, 118.3, 114.8, 72.0, 37.4, 29.4; HRMS (ESI) m/z 214.1241 ($M+H^+$), calc. for $C_{14}H_{16}NO$ 214.1232.

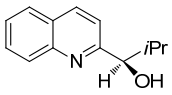
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.8 min (minor) and 11.4 min (major).



Entry	Retention Time	Area	Height	%Area
1	6.787	60.1046	251.73	49.76
2	11.510	60.6760	266.08	50.24

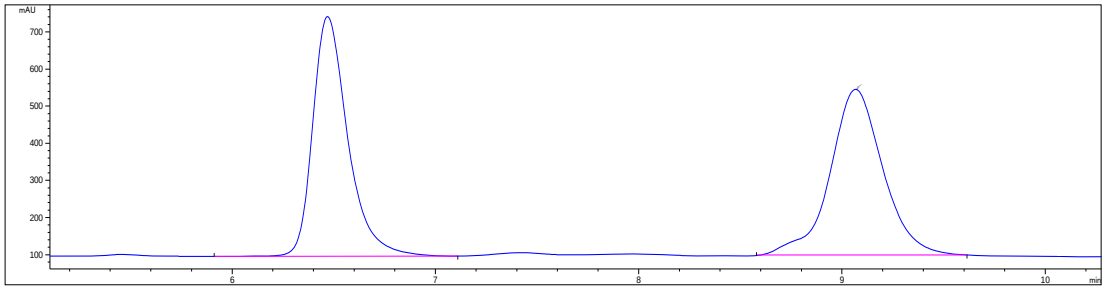


Entry	Retention Time	Area	Height	%Area
1	6.763	1.9223	7.70	5.96
2	11.427	30.3479	158.09	94.04

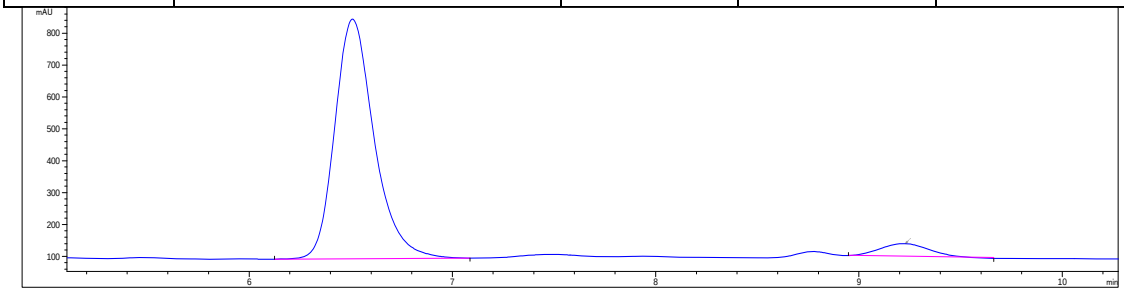


2zf: yellow oil, 13.9 mg, 69% yield, 88% ee, $[\alpha]_D^{22}$ +13.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 14.6, 8.5 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 4.91 (s, 1H), 4.77 (s, 1H), 2.18 (dtd, *J* = 13.6, 6.8, 3.8 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 146.2, 136.7, 129.8, 128.7, 127.6, 127.4, 126.4, 118.8, 34.8, 19.9, 15.5; HRMS (ESI) m/z 202.1237 ($M+H^+$), calc. for $C_{13}H_{16}NO$ 202.1232.

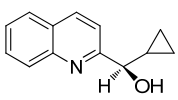
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 6.5 min (major) and 9.2 min (minor).



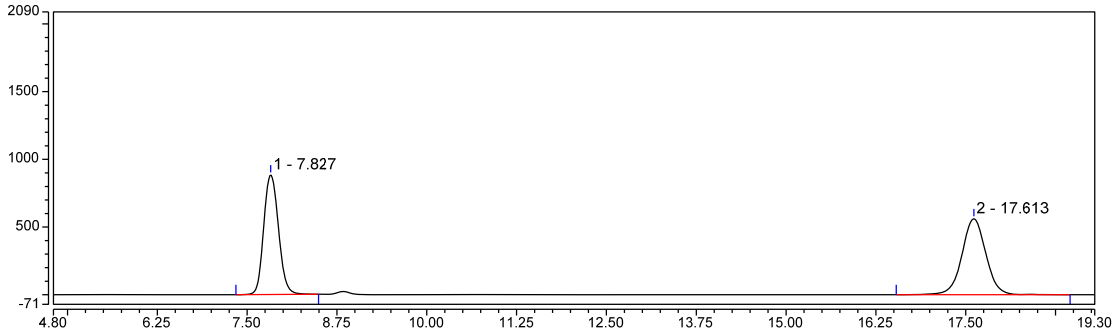
Entry	Retention Time	Area	Height	%Area
1	6.471	7751.1	645.7	49.059
2	9.069	8048.4	446.1	50.941



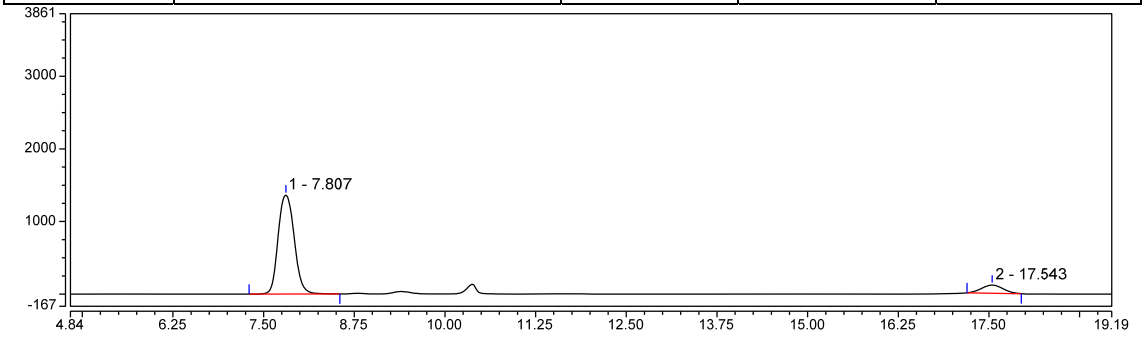
Entry	Retention Time	Area	Height	%Area
1	6.51	10107.4	751.4	94.070
2	9.226	637.2	39.2	5.930



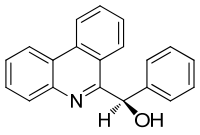
2zg: yellow solid, Mp 65.4 – 66.5 °C, 12.9 mg, 65% yield, 80% ee, $[\alpha]_D^{22}$ +23.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 20.1, 8.5 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 9.1 Hz, 2H), 5.21 (s, 1H), 4.30 (d, *J* = 7.9 Hz, 1H), 1.14 (dd, *J* = 13.1, 5.7 Hz, 1H), 0.73 – 0.52 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 146.2, 136.9, 129.7, 128.7, 127.6, 127.5, 126.3, 118.6, 75.7, 17.8, 2.7, 2.4; HRMS (ESI) m/z 200.1073 ($M+H^+$), calc. for $C_{13}H_{15}NO$ 200.1070. The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 7.8 min (minor) and 17.5 min (major).



Entry	Retention Time	Area	Height	%Area
1	7.827	210.8892	882.95	49.35
2	17.613	216.4143	560.49	50.65

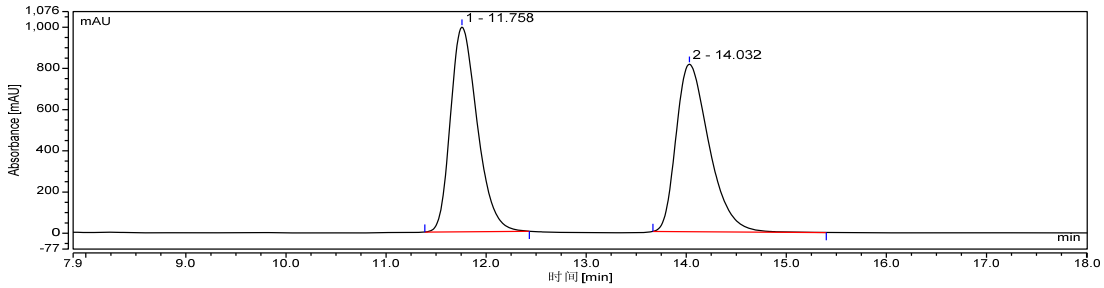


Entry	Retention Time	Area	Height	%Area
1	7.807	351.3053	1363.15	90.07
2	17.543	38.7258	112.43	9.93

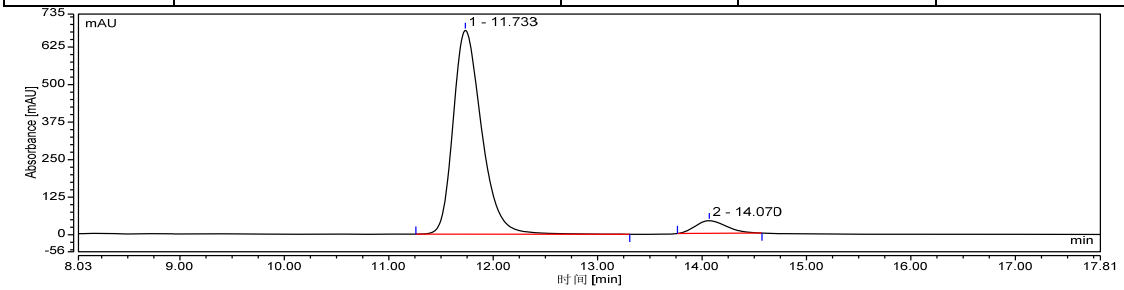


2zh: white solid, Mp 120.6 – 122.1 °C, 28.2 mg, 99% yield, 90% ee, $[\alpha]_D^{22}$ −46.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 13.2, 8.3 Hz, 2H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.80 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 6.7 Hz, 2H), 7.33 (td, *J* = 8.7, 4.2 Hz, 3H), 6.64 (s, 1H), 6.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 142.9, 141.6, 133.4, 130.9, 129.5, 129.0, 128.8, 128.0, 127.8, 127.4, 127.3, 126.0, 124.4, 123.4, 122.5, 122.1, 72.7; HRMS (ESI) m/z 308.1061 ($M+Na^+$), calc. for $C_{20}H_{15}NONa$ 308.1051.

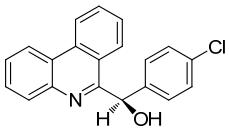
The ee was determined by HPLC analysis: CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 11.7 min (major) and 14.1 min (minor).



Entry	Retention Time	Area	Height	%Area
1	11.758	308.2400	993.30	49.82
2	14.032	310.4418	813.19	50.18



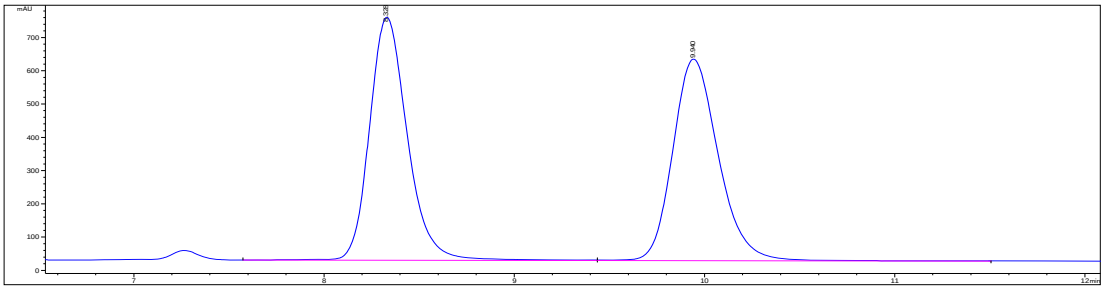
Entry	Retention Time	Area	Height	%Area
1	11.733	214.0873	678.52	95.22
2	14.070	10.7580	36.58	4.78



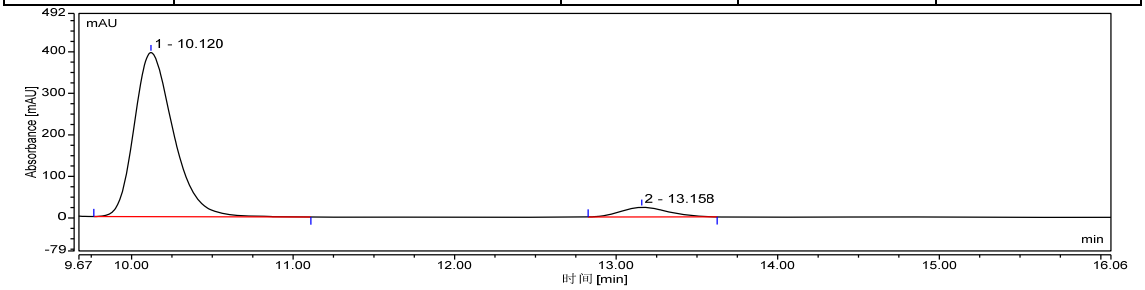
2zi: white solid, Mp 139.3 – 140.8 °C, 27.3 mg, 86% yield, 88% ee, $[\alpha]_D^{22}$ −100.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 15.5, 8.2 Hz, 2H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.66 (dt, *J* = 23.9, 7.2 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 21.8, 8.4 Hz, 4H), 6.47 (s, 1H), 6.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 141.6, 141.4, 133.8, 133.4, 130.9,

129.6, 129.2, 129.0, 129.0, 127.4, 127.4, 125.7, 124.4, 123.2, 122.6, 122.1, 72.0. HRMS (ESI) m/z 342.0653 ($M+Na^+$), calc. for $C_{20}H_{14}NOClNa$ 342.0656.

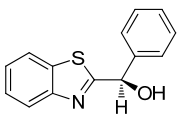
The ee was determined by HPLC analysis: CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 60/40; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 8.3 min (major) and 9.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	8.328	10127.9	730.1	50.070
2	9.94	10099.7	605.6	49.930

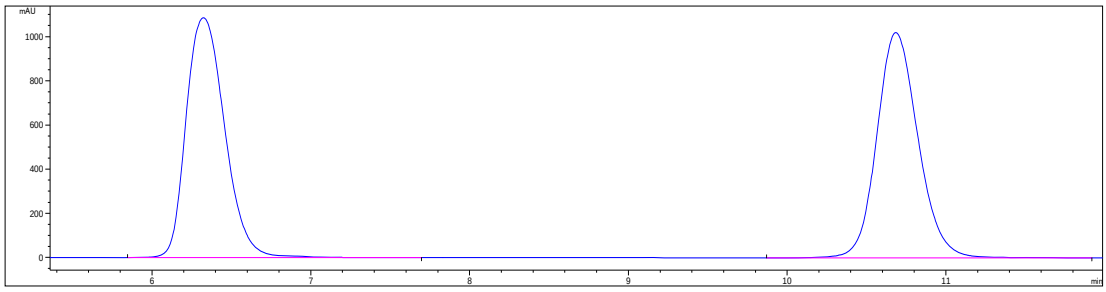


Entry	Retention Time	Area	Height	%Area
1	8.302	28960.4	1699.2	94.171
2	9.938	1792.5	105.9	5.829

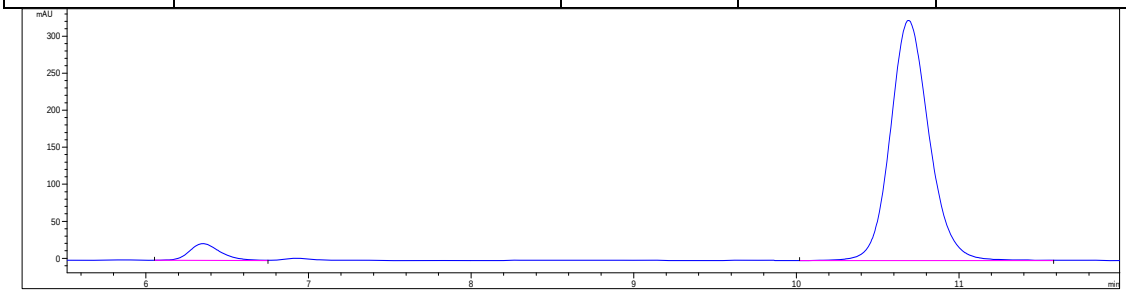


2zj: yellow solid, Mp 132.3 – 134.8 °C, 21.9 mg, 91% yield, 90% ee, $[\alpha]_D^{22}$ −13.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.50 – 7.31 (m, 5H), 6.15 (s, 1H), 3.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 152.4, 140.9, 135.2, 128.8, 128.7, 126.7, 126.2, 125.2, 123.0, 121.8, 74.4; HRMS (ESI) m/z 242.0629 ($M+H^+$), calc. for $C_{14}H_{12}NOS$ 242.0634.

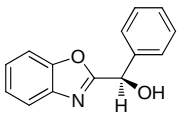
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.4 min (minor) and 10.7 min (major).



Entry	Retention Time	Area	Height	%Area
1	6.325	18336.5	1086.3	49.929
2	10.686	18389	1019.8	50.071

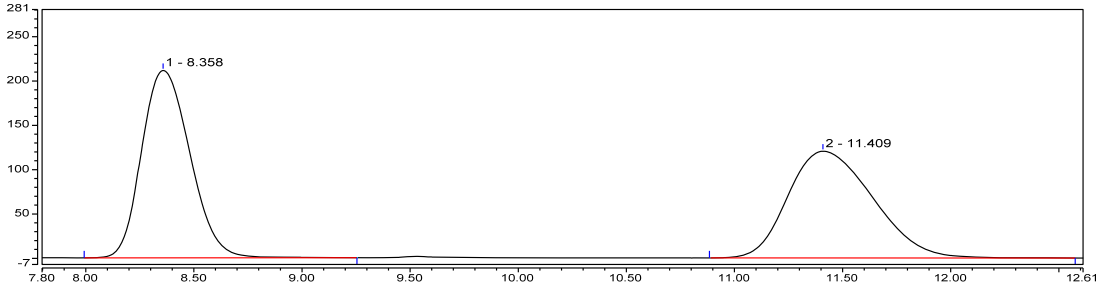


Entry	Retention Time	Area	Height	%Area
1	6.351	294	22.5	5.175
2	10.69	5387.5	324.2	94.825

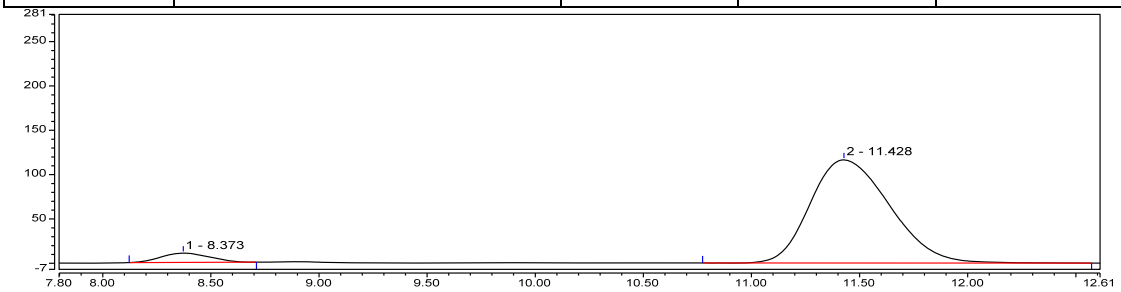


2zk: white solid, Mp 140.0 – 141.5 °C, 17.6 mg, 78% yield, 90% ee, $[\alpha]_D^{22}$ −33.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.54 (d, *J* = 6.7 Hz, 2H), 7.49 (dd, *J* = 6.3, 3.0 Hz, 1H), 7.42 – 7.32 (m, 5H), 6.06 (s, 1H), 2.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 151.0, 139.7, 138.6, 128.9, 128.9, 126.8, 125.5, 124.8, 120.0, 111.0, 70.5; HRMS (ESI) m/z 226.0863 ($M+H^+$), calc. for $C_{14}H_{12}NO_2$ 226.0857.

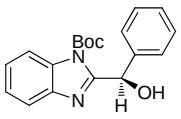
The ee was determined by HPLC analysis: CHIRAL INB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.4 min (minor) and 11.4 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.358	54.7637	211.30	49.99
2	11.409	54.7953	120.43	50.01

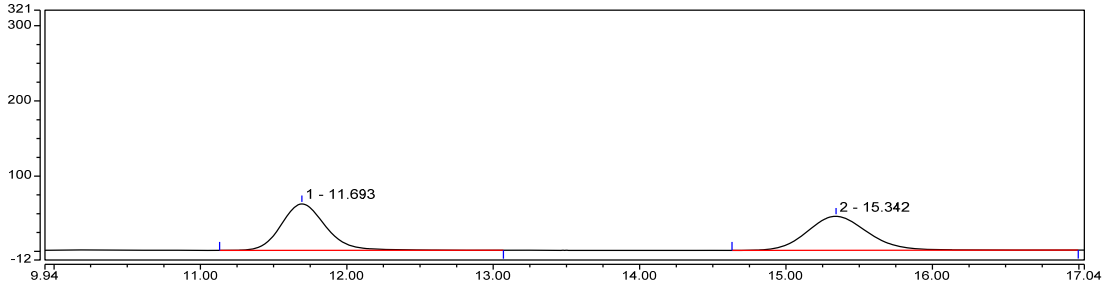


Entry	Retention Time	Area	Height	%Area
1	8.373	2.7186	10.43	5.20
2	11.428	49.5751	116.36	94.80

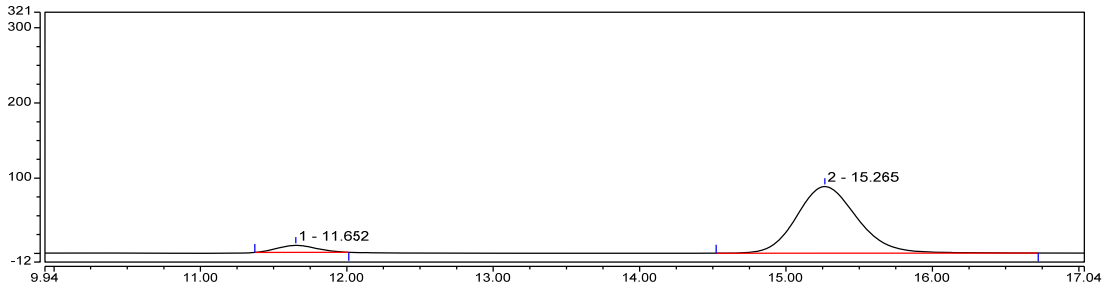


2zl: white solid, Mp 167.7 – 167.9 °C, 22.0 mg, 68% yield, 87% ee, $[\alpha]_D^{22}$ +23.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.0 Hz, 2H), 7.47 (d, *J* = 5.4 Hz, 2H), 7.31 (d, *J* = 5.4 Hz, 3H), 7.26 – 7.19 (m, 2H), 6.93 (s, 1H), 1.44 (d, *J* = 1.6 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 151.5, 136.7, 128.9, 128.8, 127.0, 122.9, 83.6, 74.6, 27.6; HRMS (ESI) m/z 325.1549 ($M+H^+$), calc. for $C_{19}H_{21}N_2O_3$ 325.1547.

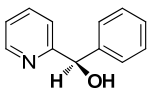
The ee was determined by HPLC analysis: Cellulose-4 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.6 min (minor) and 15.3 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.358	54.7637	211.30	49.99
2	11.409	54.7953	120.43	50.01

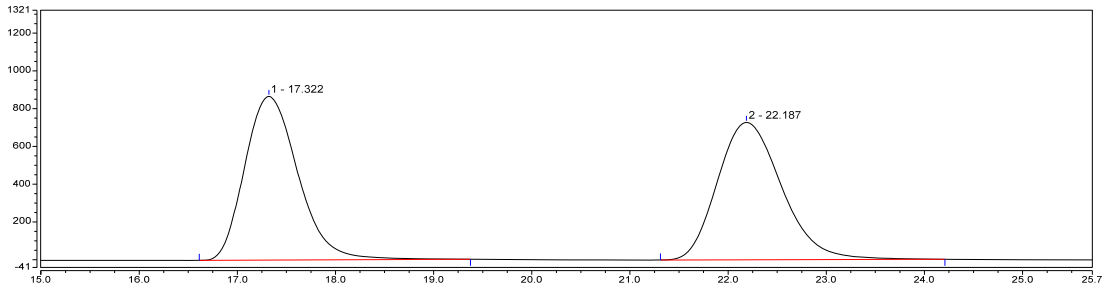


Entry	Retention Time	Area	Height	%Area
1	11.652	2.8860	9.28	6.38
2	15.265	42.3220	88.51	93.62

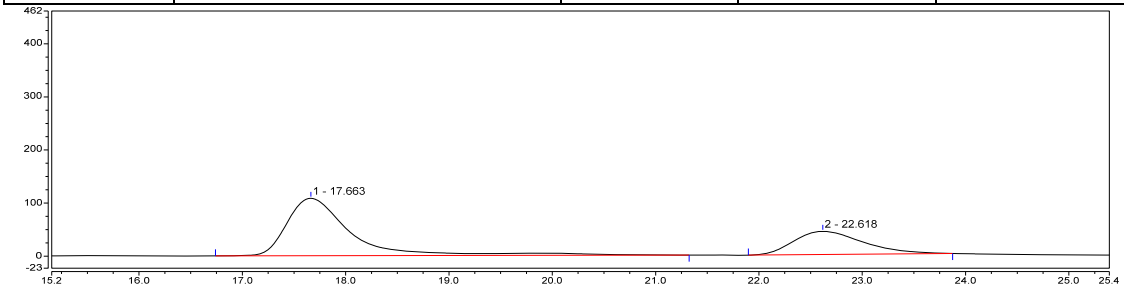


2zm: white solid, Mp 137.2 – 138.1 °C, 11.6 mg, 63% yield, 40% ee, $[\alpha]_D^{22}$ +13.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.5 Hz, 1H), 7.71 (m, 1H), 7.41 (m, 5H), 7.27 (dd, *J* = 14.8, 7.0 Hz, 2H), 5.85 (s, 1H), 5.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 147.7, 143.2, 136.9, 128.5, 127.8, 127.0, 122.4, 121.4, 74.9; HRMS (ESI) m/z 186.0904 ($M+H^+$), calc. for $C_{12}H_{12}NO$ 186.0913.

The ee was determined by HPLC analysis: CHIRAL AD-H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 93/07; flow rate 0.8 mL/min; 25 °C; 220 nm; retention time: 17.7 min (major) and 22.6 min (minor).



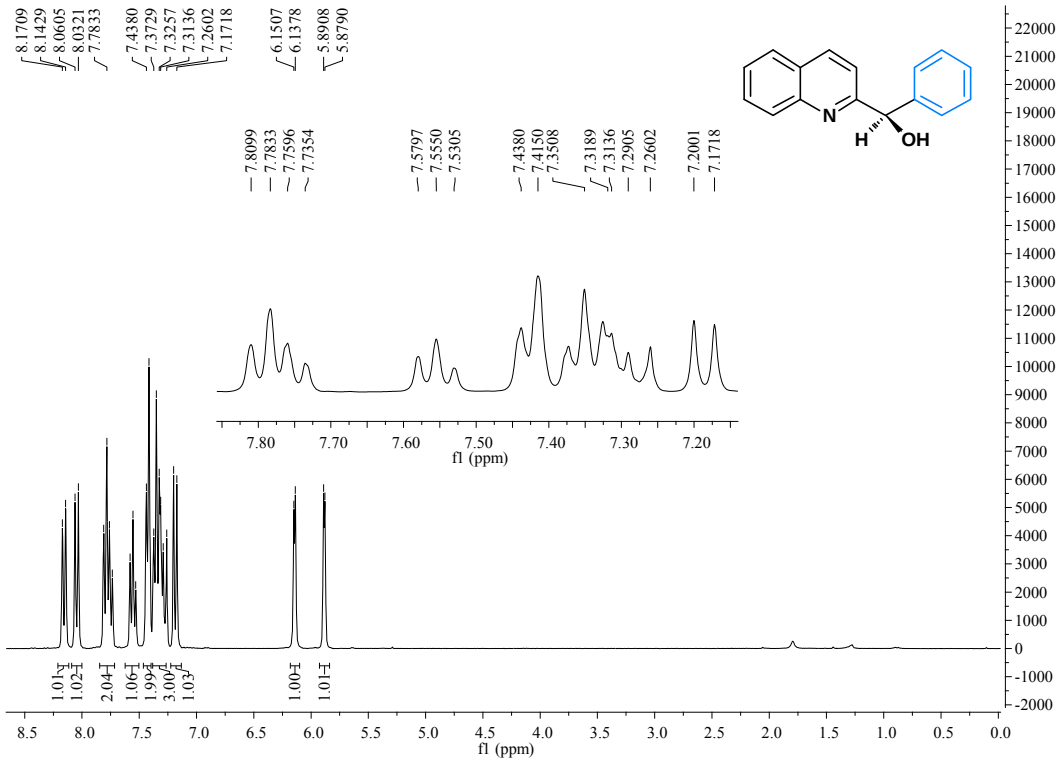
Entry	Retention Time	Area	Height	%Area
1	17.322	545.1152	866.86	49.75
2	22.187	550.5359	727.30	50.25

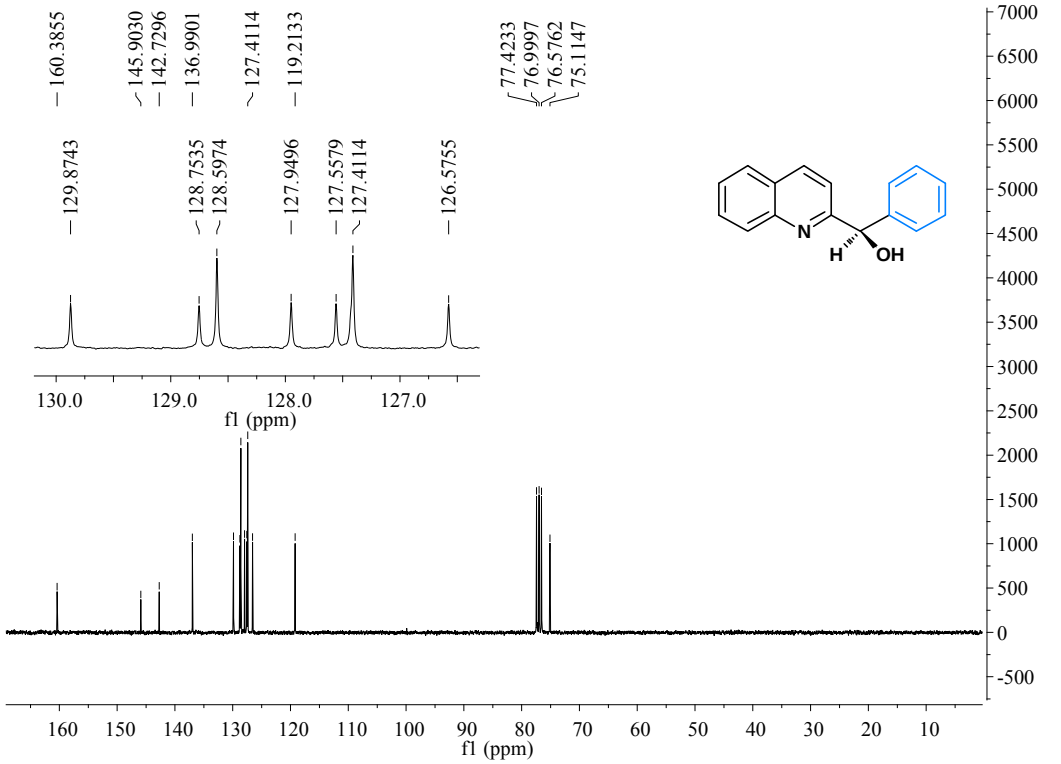


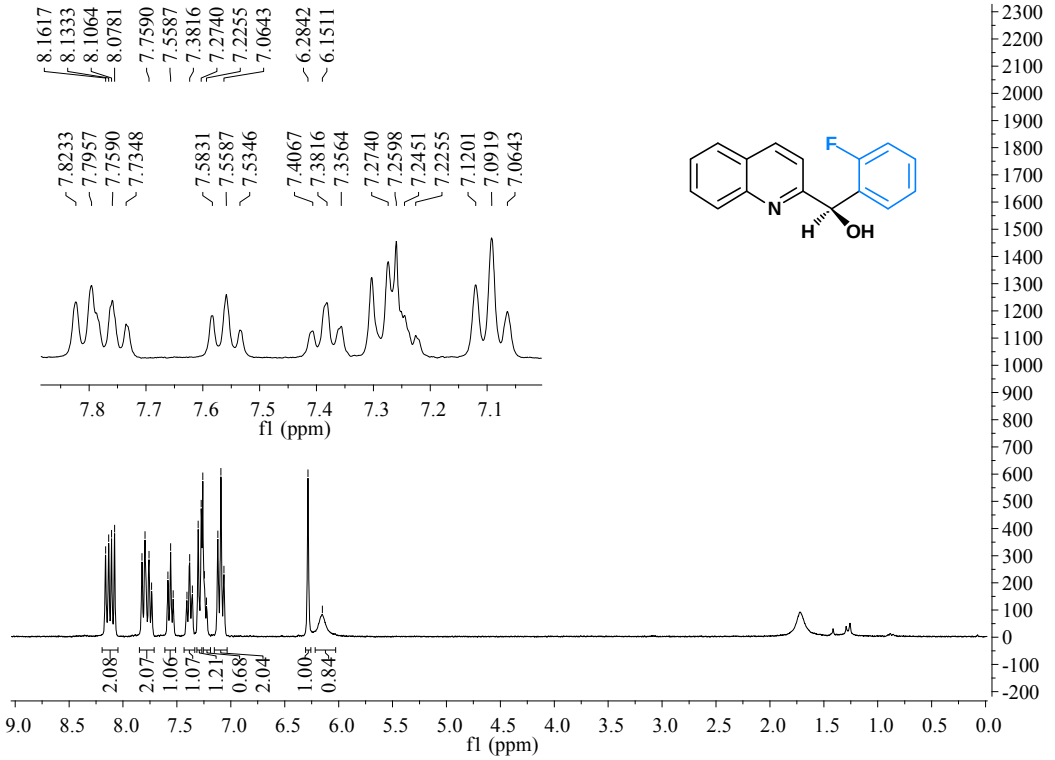
Entry	Retention Time	Area	Height	%Area

1	17.663	77.8796	108.09	69.82
2	22.618	33.6587	43.57	30.18

7. Copies of NMR spectra



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6.1511
7.8233
7.7957
7.7590
7.7348
7.5831
7.5587
7.5346
7.4067
7.3816
7.3564
7.2740
7.2598
7.2451
7.2255
7.1201
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7.0643
F
N
H
OH
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f1 (ppm)
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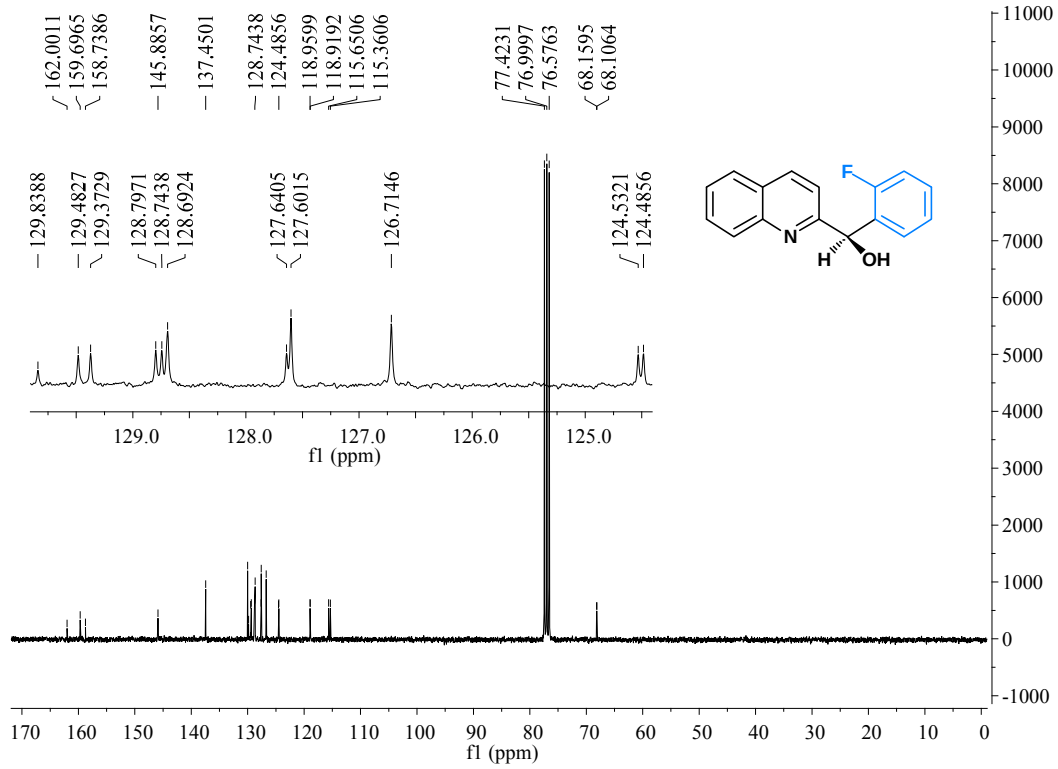
2.07
1.06
1.07
1.21
0.68
2.04
1.00
0.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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H
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f1 (ppm)
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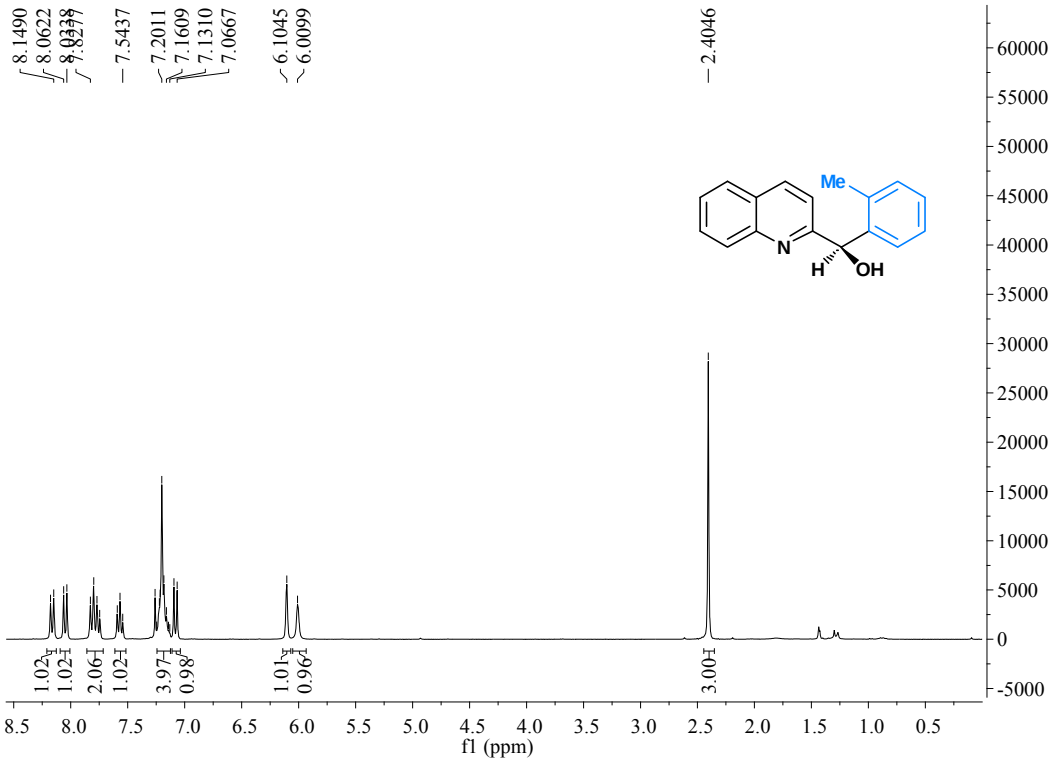
f1 (ppm)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H
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1.02
3.97
0.98
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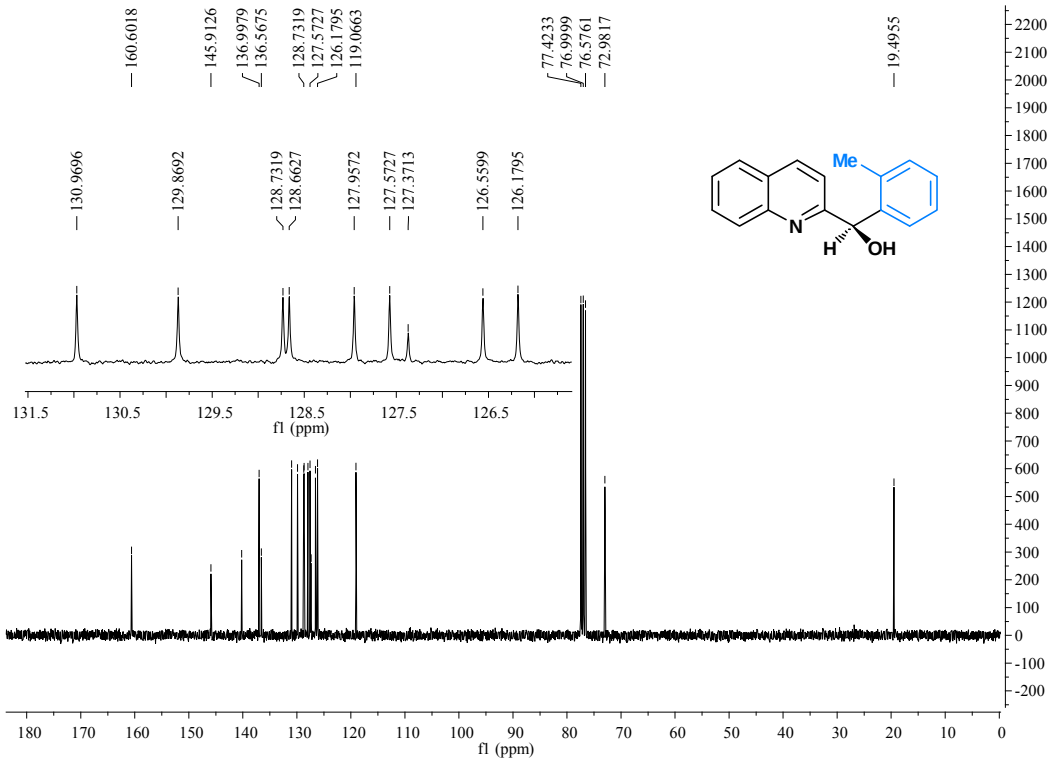
3.00
fl (ppm)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Me
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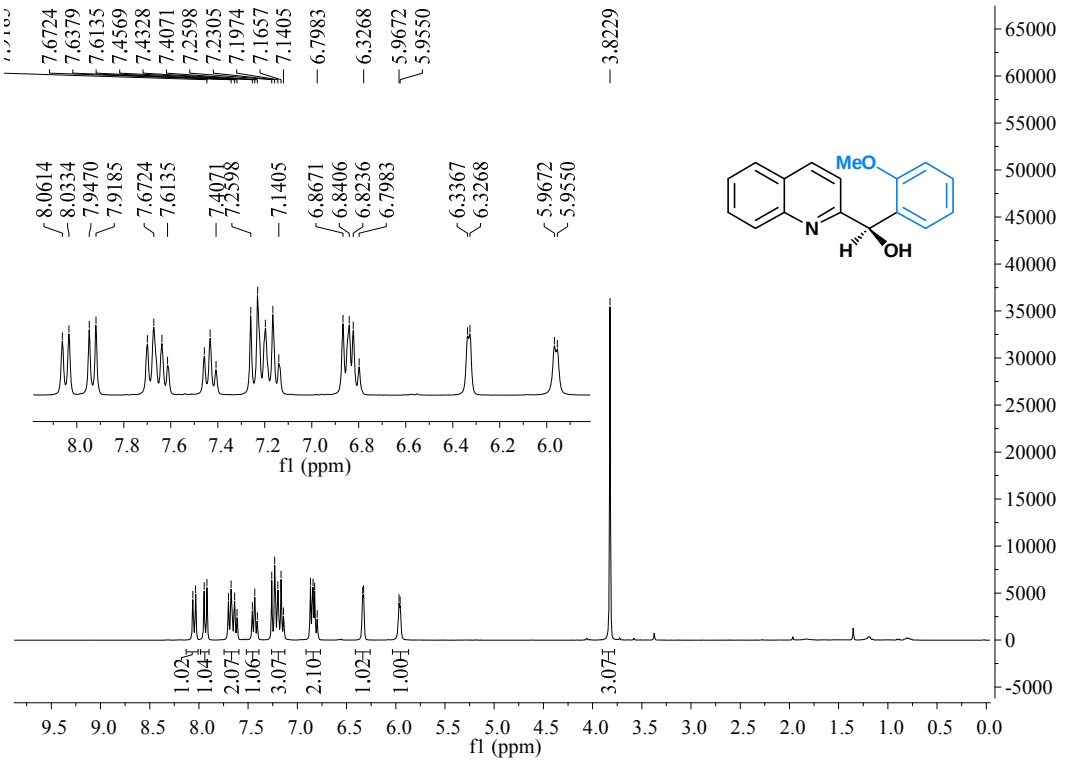
fl (ppm)
fl (ppm)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MeO
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H
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2.10
1.02
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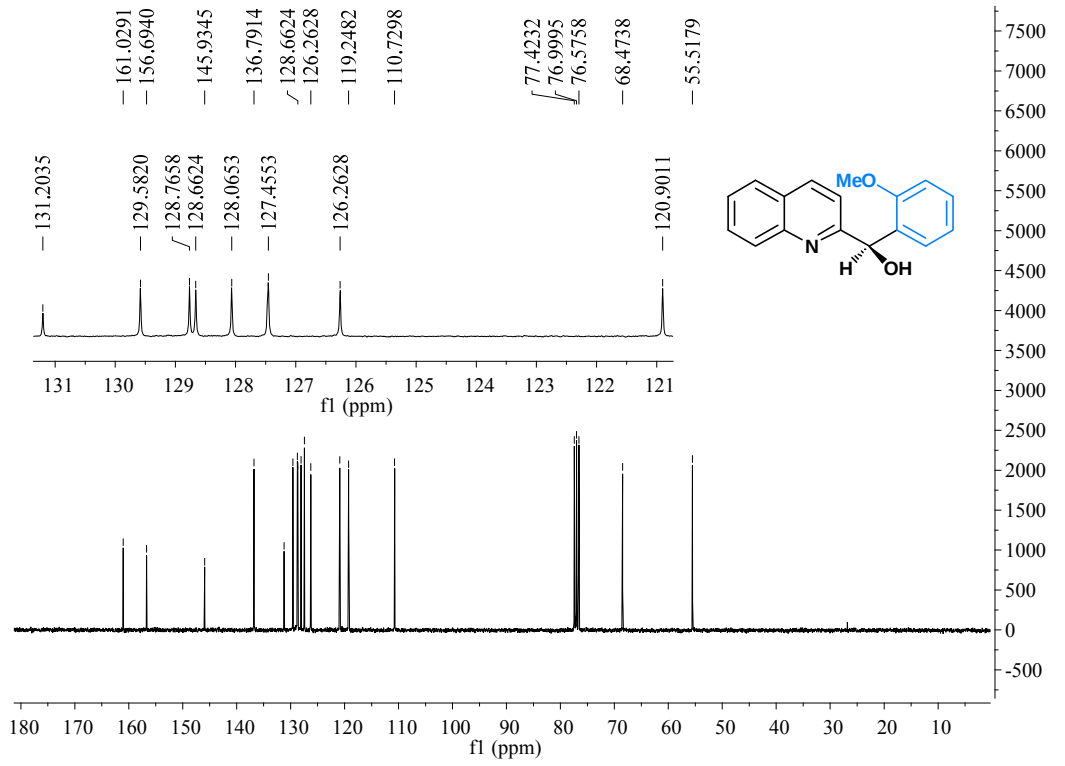
3.07
f1 (ppm)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55.5179
131.2035
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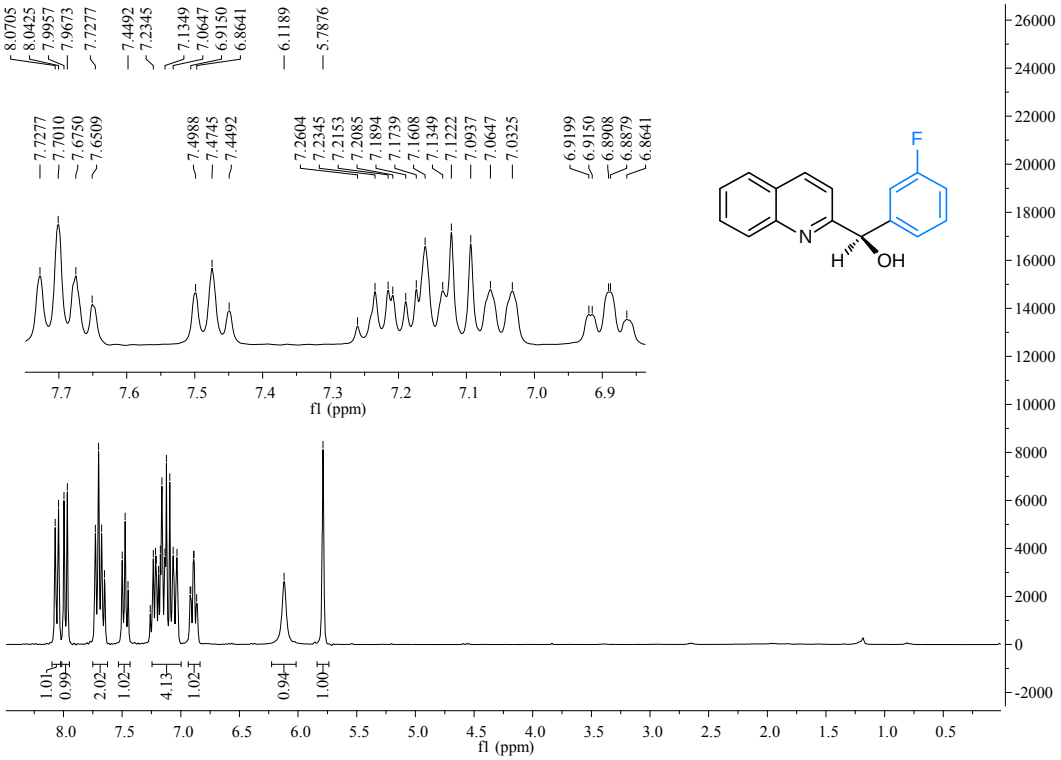
MeO
N
H
OH
f1 (ppm)
f1 (ppm)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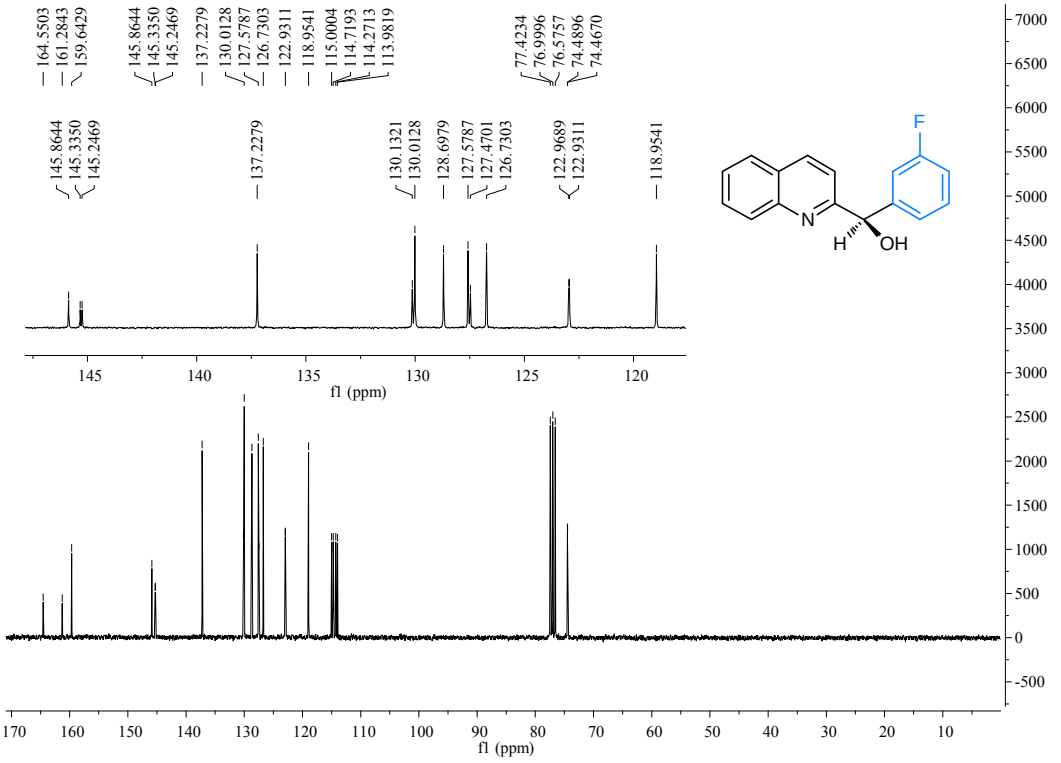
5.7876
F
N
H
OH
f1 (ppm)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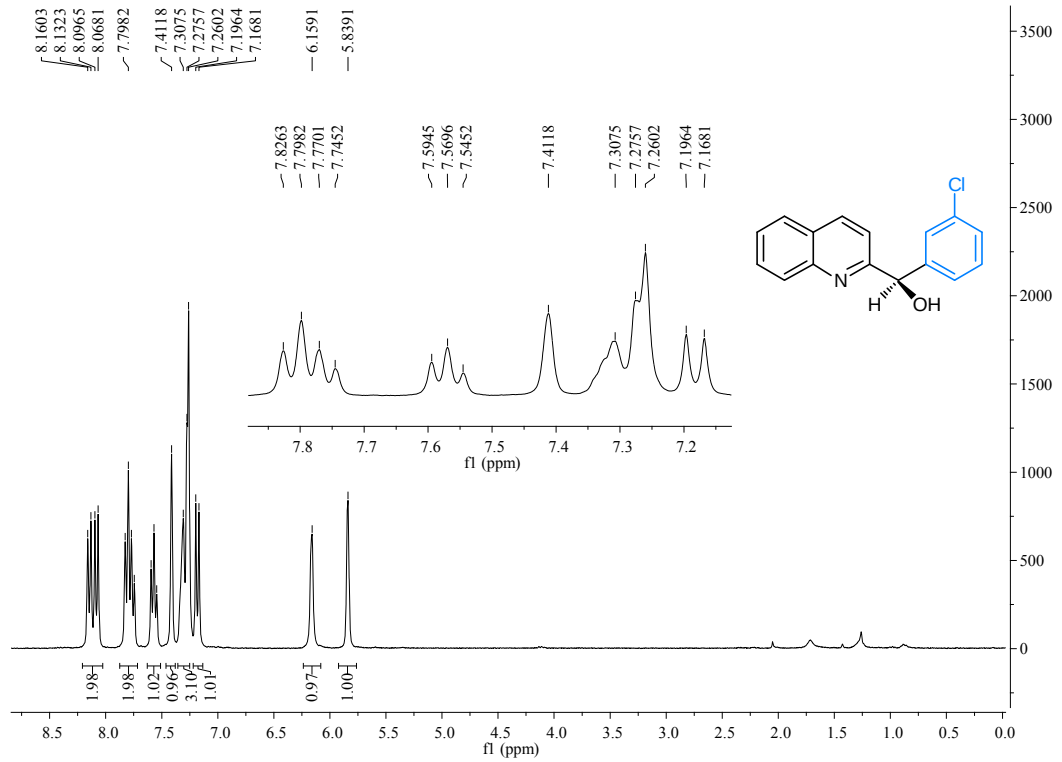
74.4670
130.1321
128.6979
127.4701
F
N
H
OH
f1 (ppm)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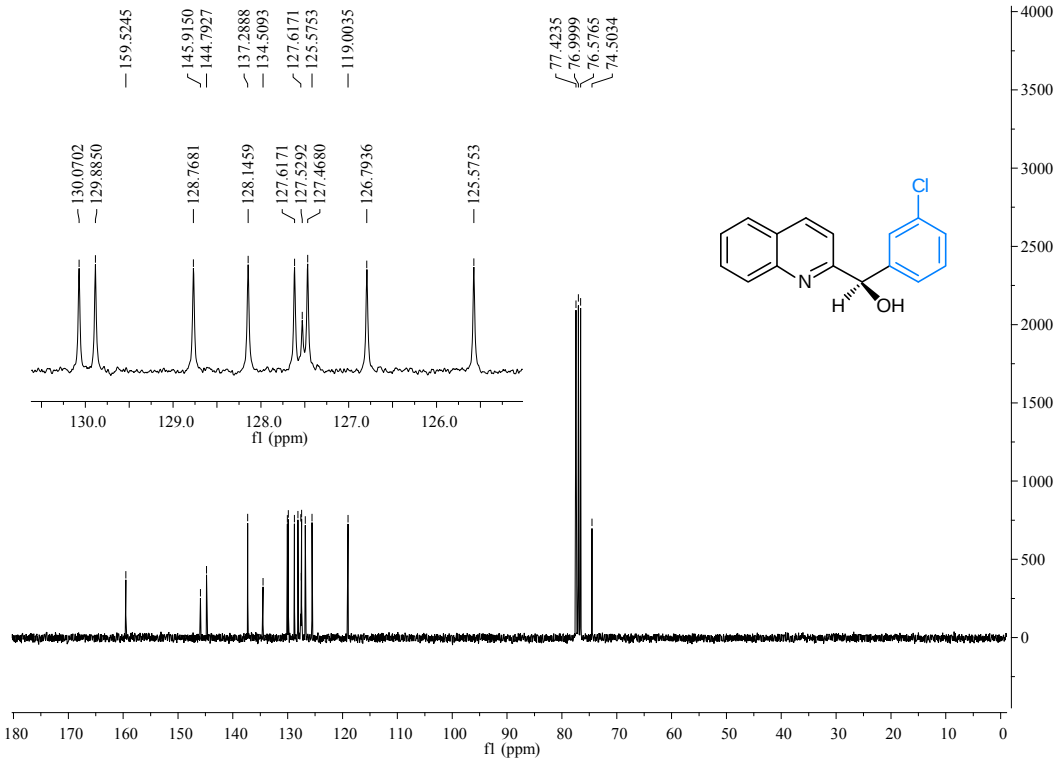
8.1323
8.0965
8.0681
7.7982
7.4118
7.3075
7.2757
7.2602
7.1964
7.1681
6.1591
5.8391
7.8263
7.7982
7.7701
7.7452
7.5945
7.5696
7.5452
7.4118
7.3075
7.2757
7.2602
7.1964
7.1681
Cl
N
H
OH
1.98
1.98
1.02
0.96
3.10
1.01
0.97
1.00
fl (ppm)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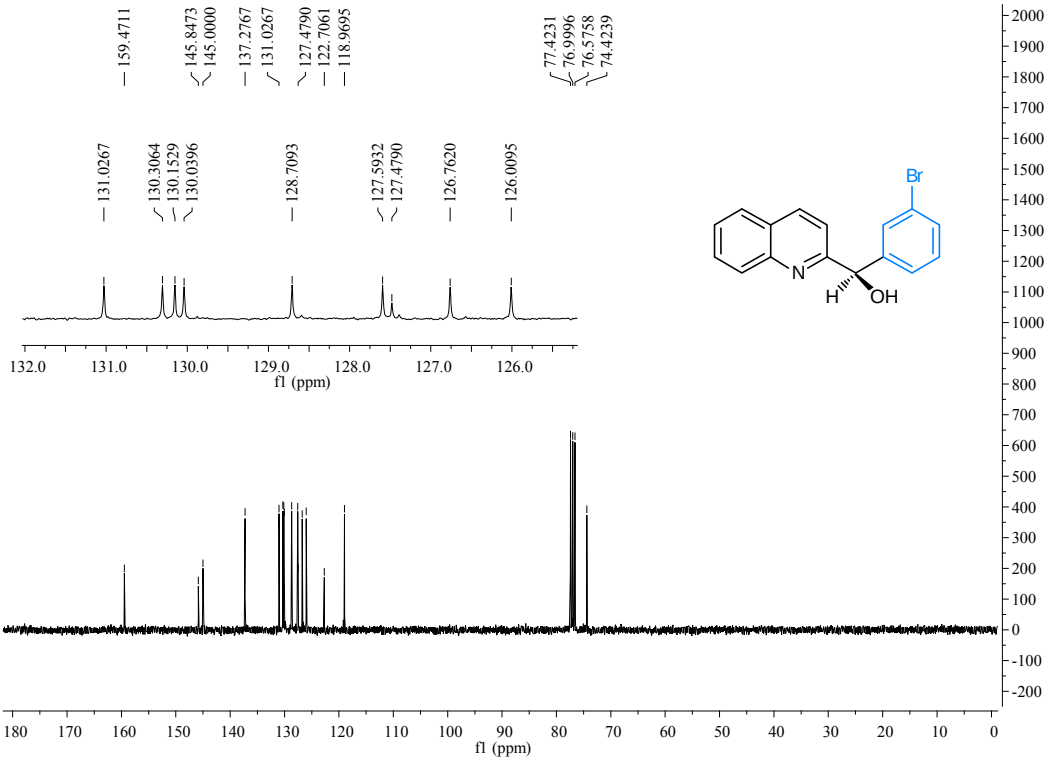
144.7927
137.2888
134.5093
127.6171
125.5753
119.0035
77.4235
76.9999
76.5765
74.5034
130.0702
129.8850
128.7681
128.1459
127.6171
127.5292
127.4680
126.7936
125.5753
Cl
N
H
OH
fl (ppm)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145.0000
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131.0267
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122.7061
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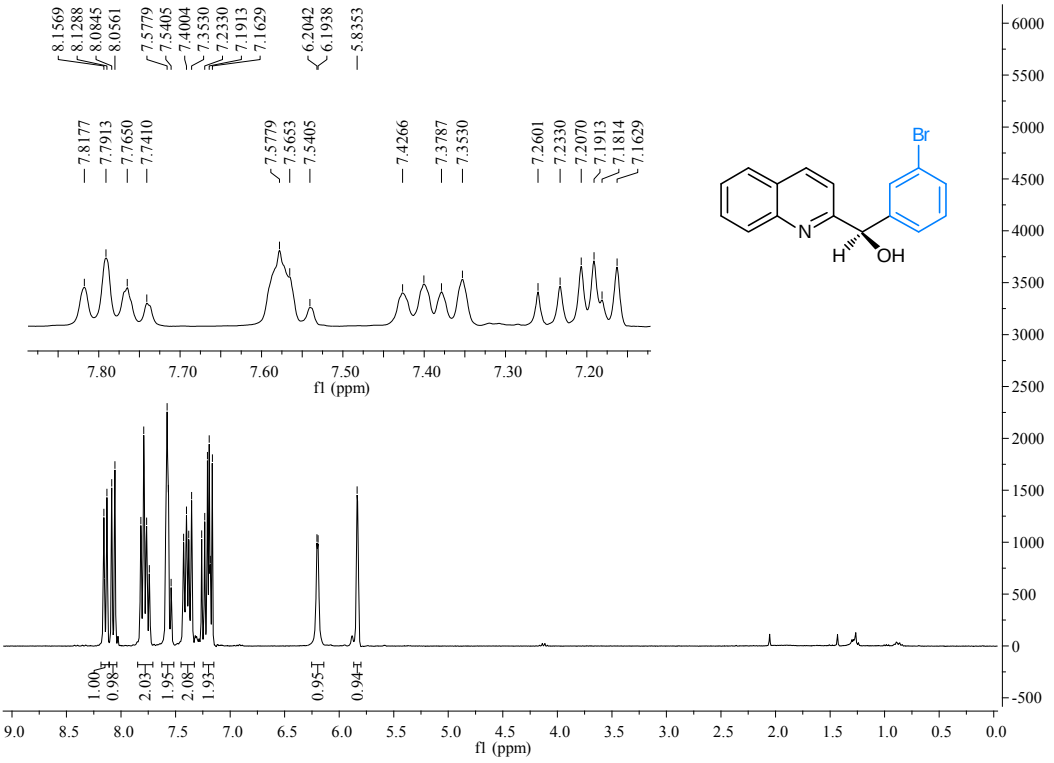
77.4231
76.9996
76.5758
74.4239
131.0267
130.3064
130.1529
130.0396
128.7093
127.5932
127.4790
126.7620
126.0095
Br
N
H
OH
fl (ppm)
fl (ppm)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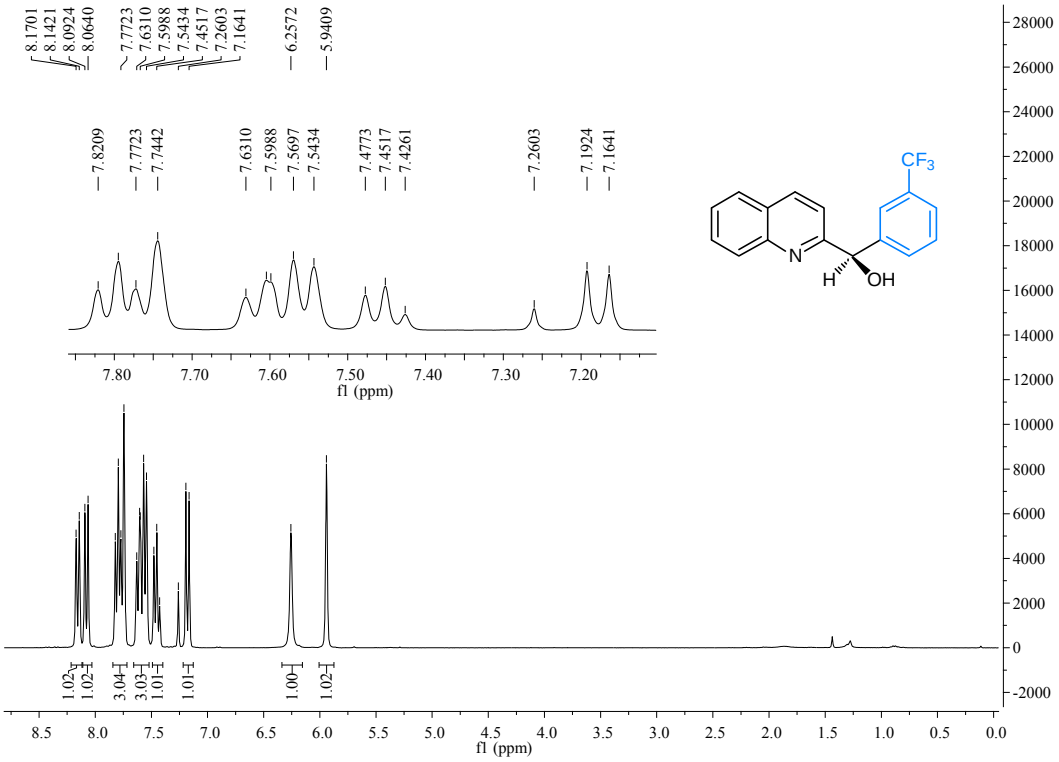
8.1288
8.0845
8.0561
7.5779
7.5405
7.4004
7.3530
7.2330
7.1913
7.1629
6.2042
6.1938
5.8353
7.8177
7.7913
7.7650
7.7410
7.5779
7.5653
7.5405
7.4266
7.3787
7.3530
7.2601
7.2330
7.2070
7.1913
7.1814
7.1629
Br
N
H
OH
1.00
0.98
2.03
1.95
2.08
1.93
0.95
0.94
fl (ppm)
fl (ppm)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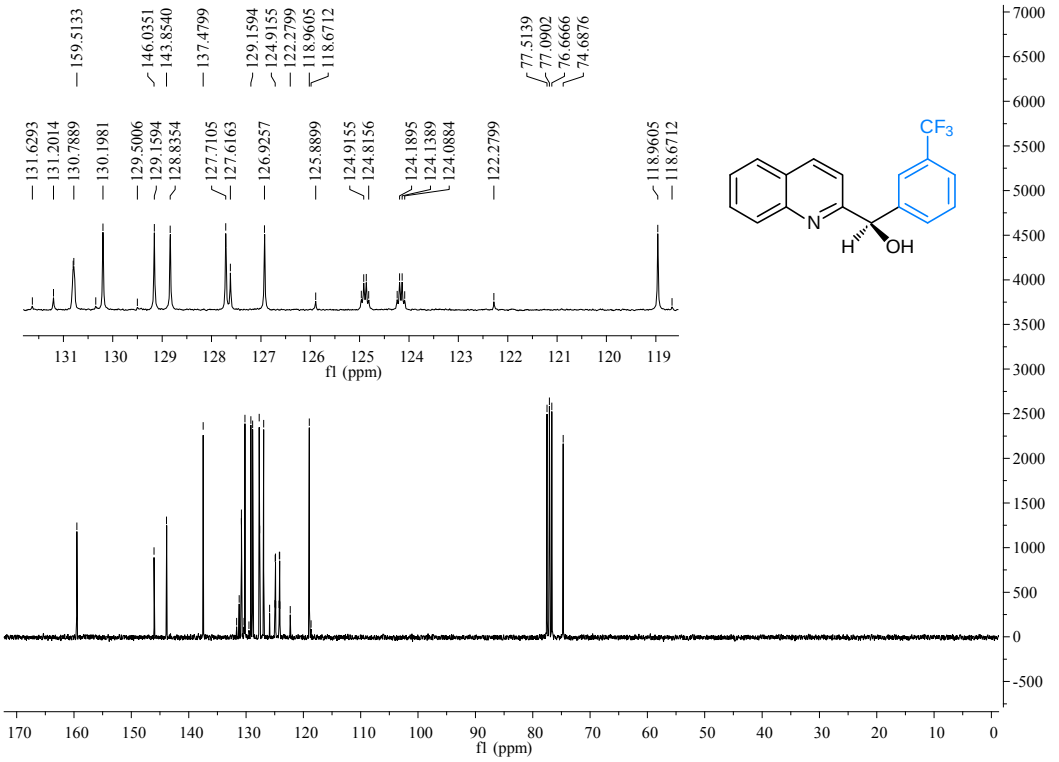
8.1421
8.0924
8.0640
7.7723
7.6310
7.5988
7.5434
7.4517
7.2603
7.1641
6.2572
5.9409
7.8209
7.7723
7.7442
7.6310
7.5988
7.5697
7.5434
7.4773
7.4517
7.4261
7.2603
7.1924
7.1641
CF3
N
H
OH
1.02
1.02
3.04
3.03
1.01
1.01
1.00
1.02
f1 (ppm)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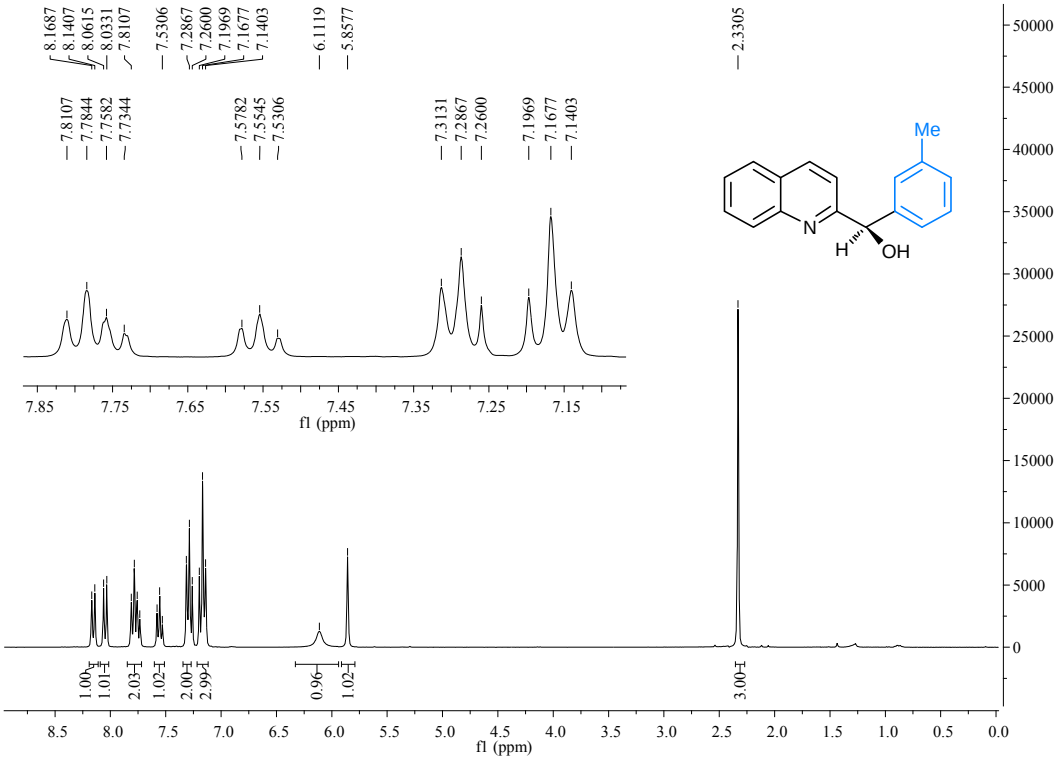
143.8540
137.4799
129.1594
124.9155
122.2799
118.9605
118.6712
77.5139
77.0902
76.6666
74.6876
131.6293
131.2014
130.7889
130.1981
129.5006
129.1594
128.8354
127.7105
127.6163
126.9257
125.8899
124.9155
124.8156
124.1895
124.1389
124.0884
122.2799
118.9605
118.6712
CF3
N
H
OH
f1 (ppm)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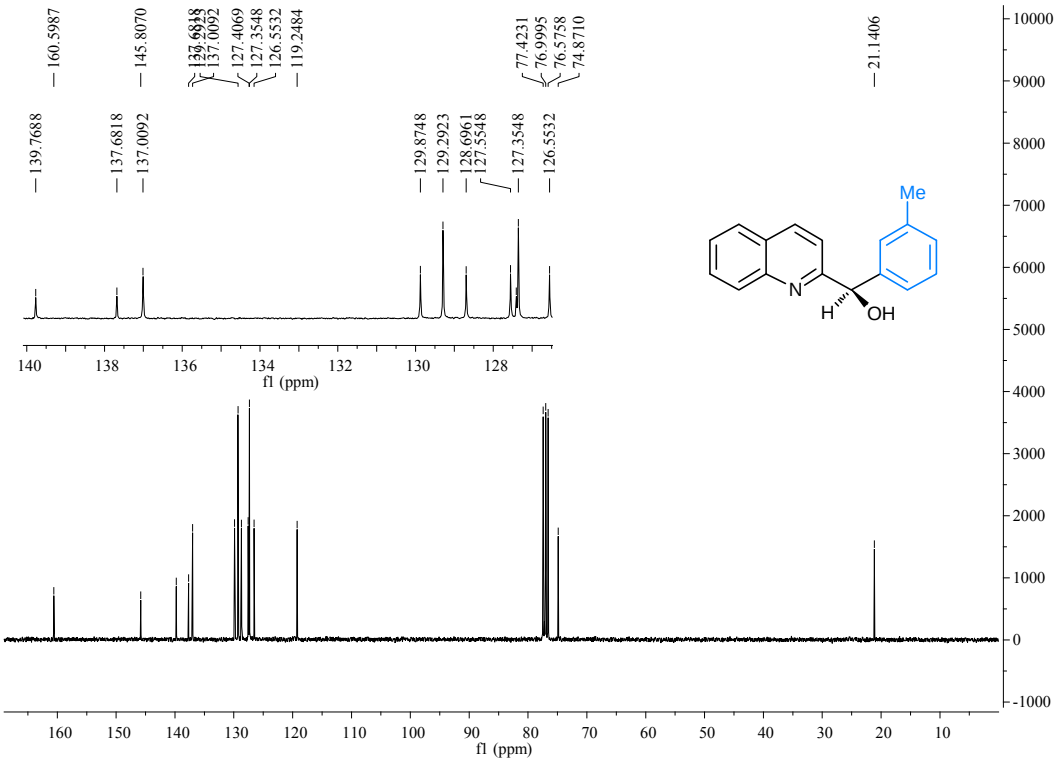
8.1407
8.0615
8.0331
7.8107
7.5306
7.2867
7.2600
7.1969
7.1677
7.1403
6.1119
5.8577
2.3305
Me
N
H
OH
fl (ppm)
1.00
1.01
2.03
1.02
2.00
2.99
0.96
1.02
3.00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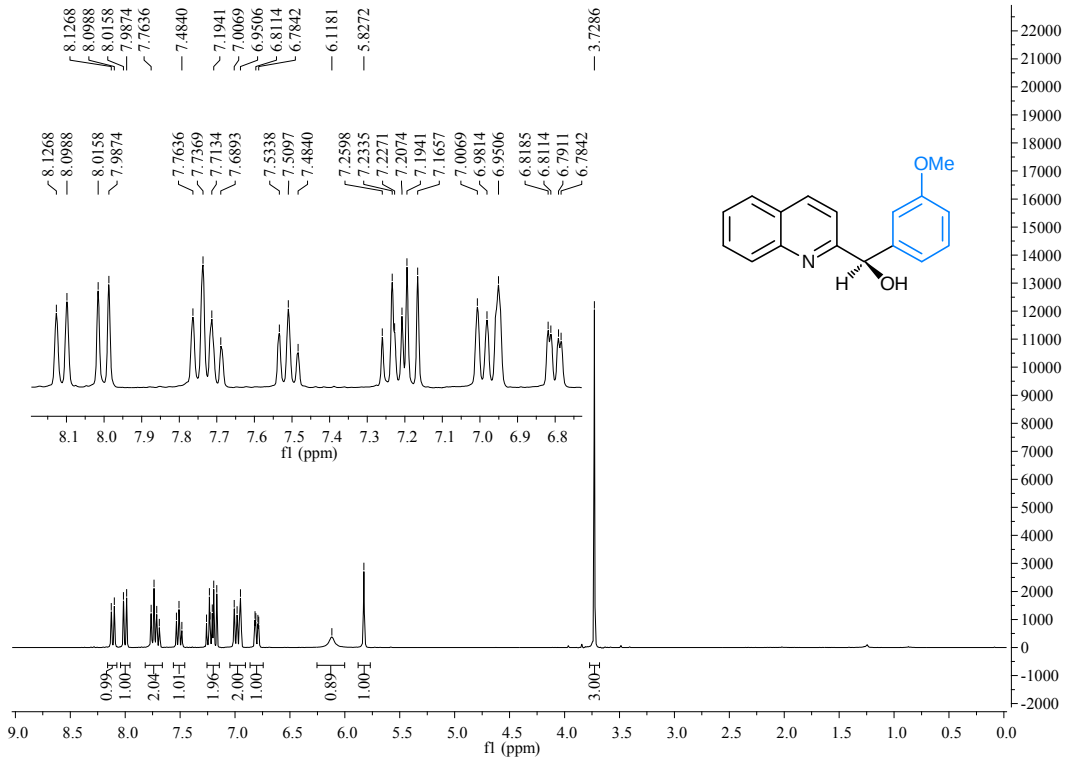
139.7688
137.6818
137.0092
127.4069
127.3548
126.5532
119.2484
129.8748
129.2923
128.6961
127.5548
77.4231
76.9995
76.5758
74.8710
21.1406
Me
N
H
OH
fl (ppm)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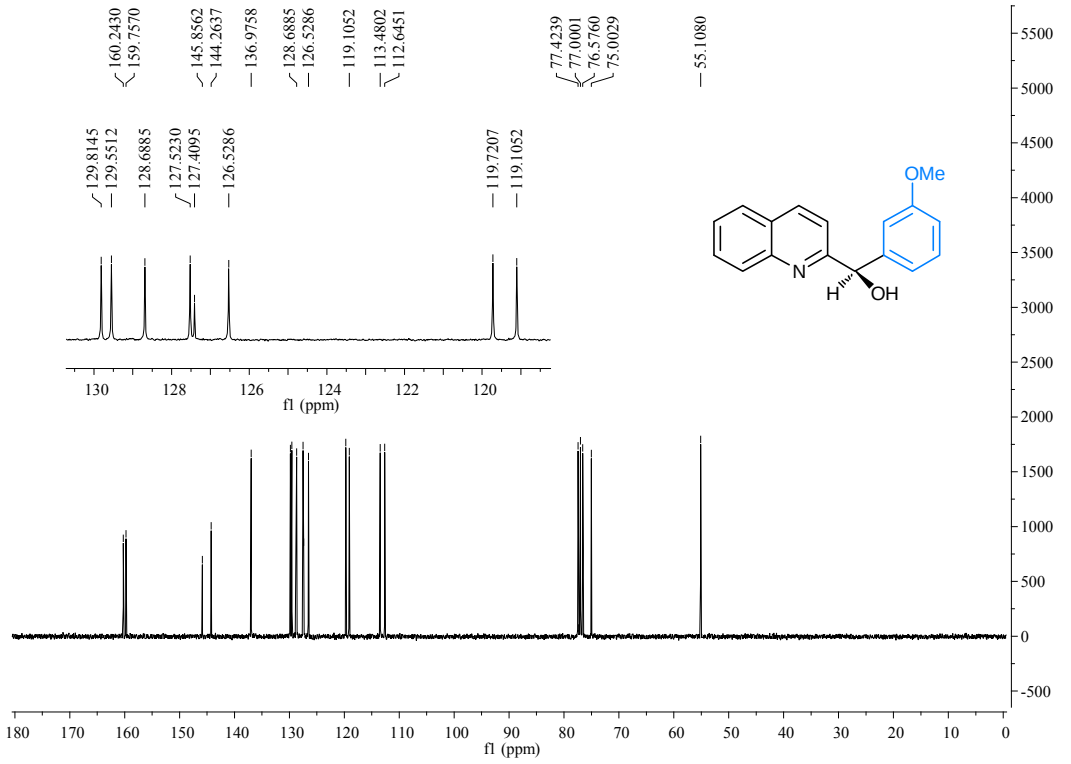
8.0988
8.0158
7.9874
7.7636
7.4840
7.1941
7.0069
6.9506
6.8114
6.7842
6.1181
5.8272
3.7286
OMe
N
H
OH
fl (ppm)
0.99
1.00
2.04
1.01
1.96
2.00
1.00
0.89
1.00
3.00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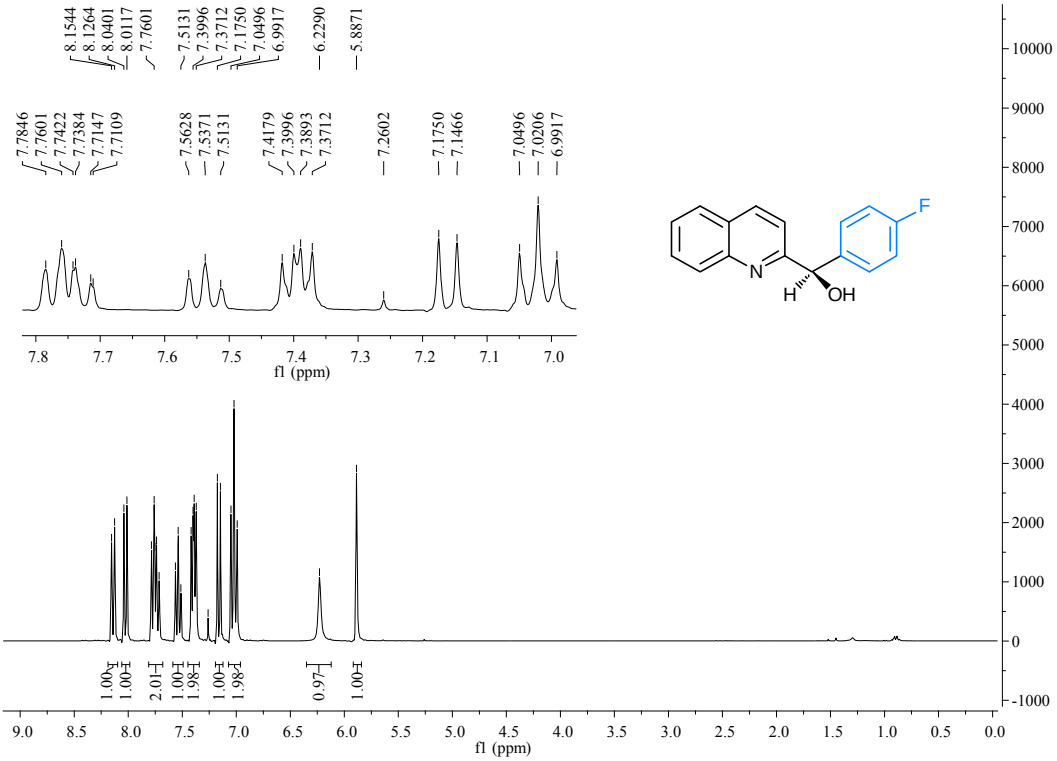
159.7570
145.8562
144.2637
136.9758
128.6885
126.5286
119.1052
113.4802
112.6451
77.4239
77.0001
76.5760
75.0029
55.1080
129.8145
129.5512
128.6885
127.5230
127.4095
126.5286
119.7207
119.1052
OMe
N
H
OH
fl (ppm)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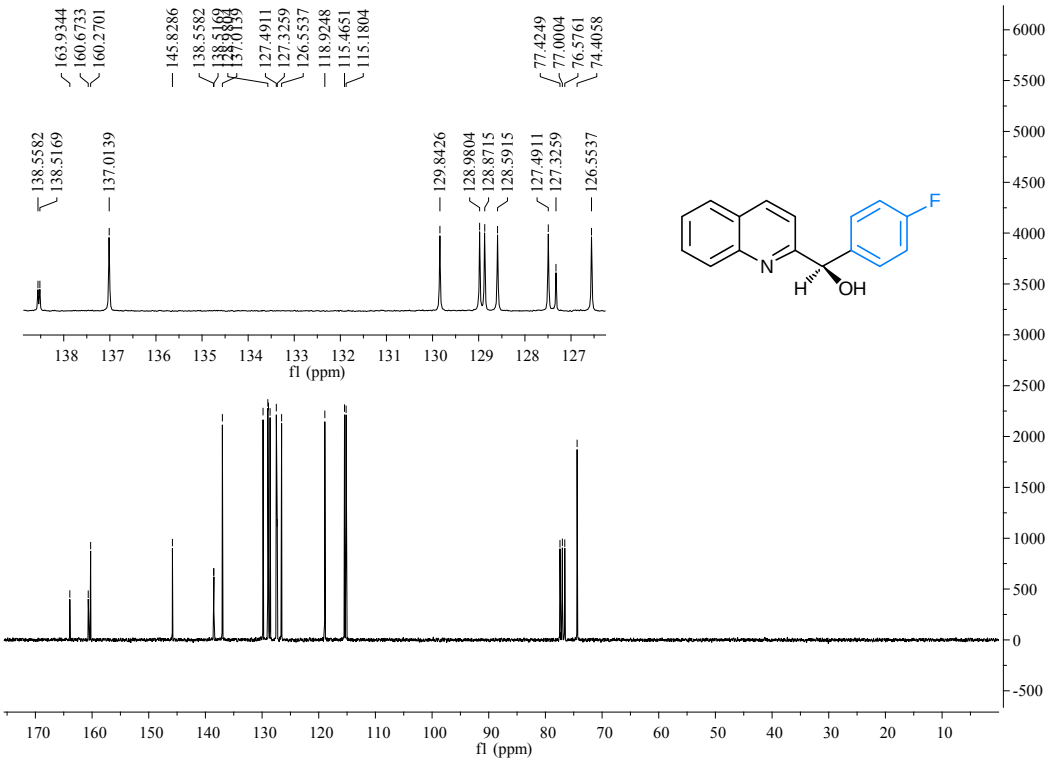
8.1264
8.0401
8.0117
7.7601
7.5131
7.3996
7.3712
7.1750
7.0496
6.9917
6.2290
5.8871
7.7846
7.7601
7.7422
7.7384
7.7147
7.7109
7.5628
7.5371
7.5131
7.4179
7.3996
7.3893
7.3712
7.2602
7.1750
7.1466
7.0496
7.0206
6.9917
F
N
H
OH
fl (ppm)
1.00
1.00
2.01
1.00
1.98
1.00
1.98
0.97
1.00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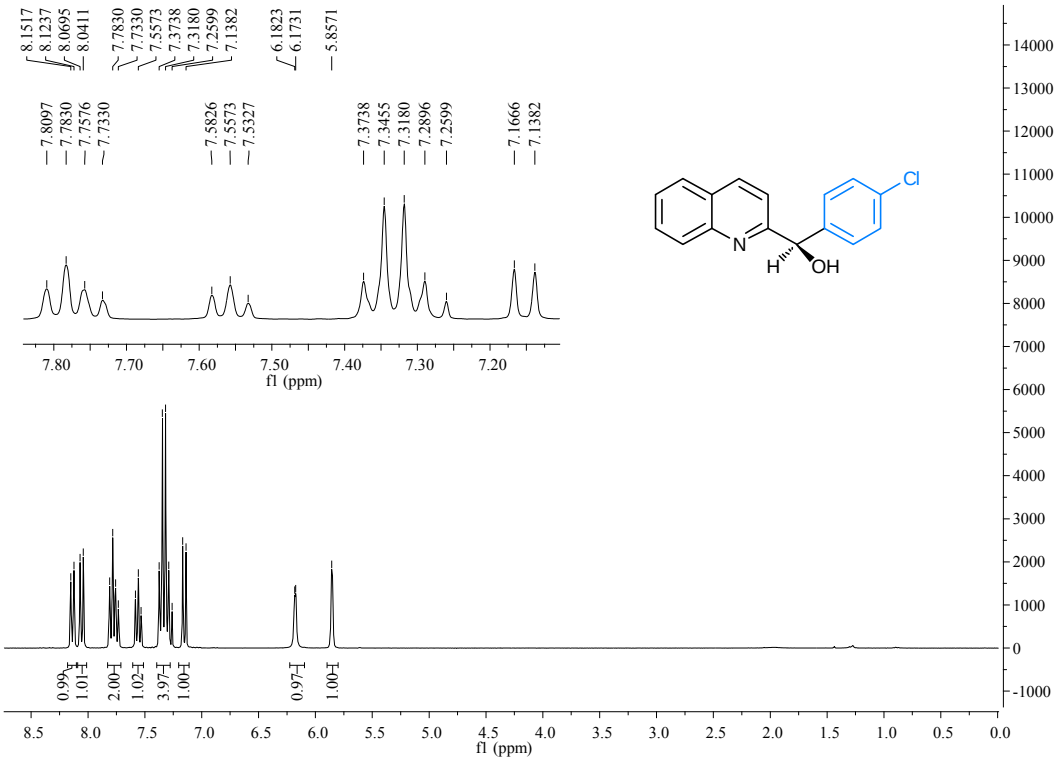
160.2701
145.8286
138.5582
138.5169
137.0139
127.4911
127.3259
126.5537
118.9248
115.4651
115.1804
77.4249
77.0004
76.5761
74.4058
129.8426
128.9804
128.8715
128.5915
F
N
H
OH
fl (ppm)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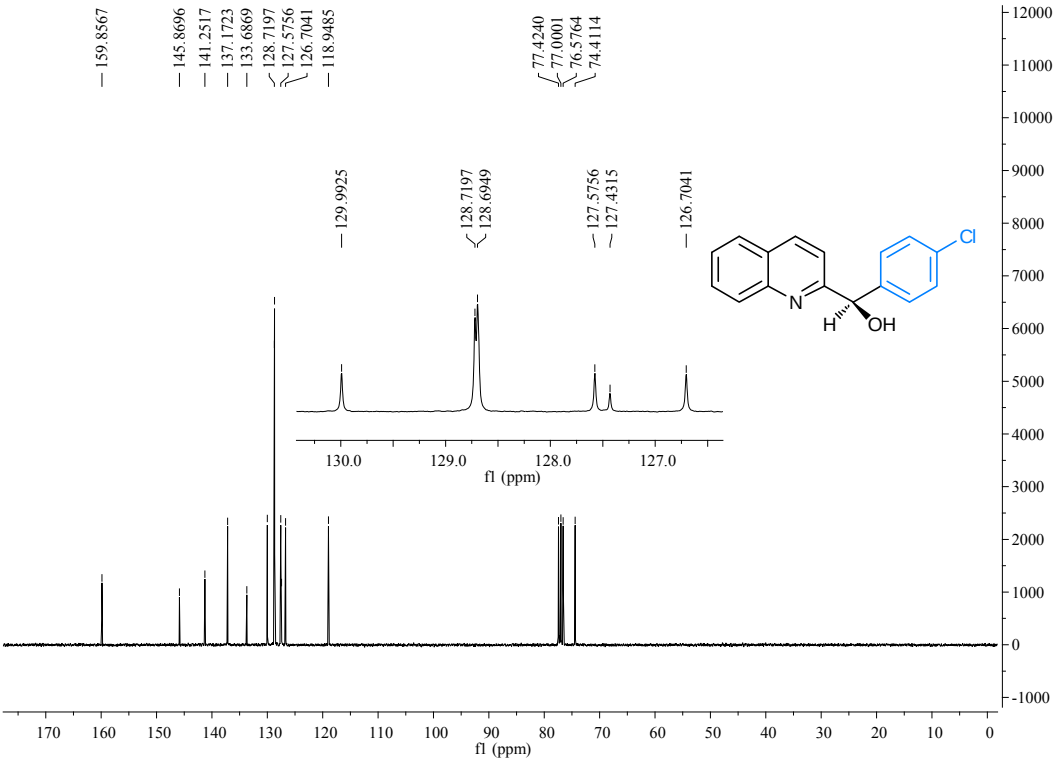
8.0695
8.0411
7.7830
7.7330
7.5573
7.3738
7.3180
7.2599
7.1382
6.1823
6.1731
5.8571
7.8097
7.7830
7.7576
7.7330
7.5826
7.5573
7.5327
7.3738
7.3455
7.3180
7.2896
7.2599
7.1666
7.1382
Cl
N
H
OH
f1 (ppm)
0.99
1.01
2.00
1.02
3.97
1.00
0.97
1.00
f1 (ppm)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133.6869
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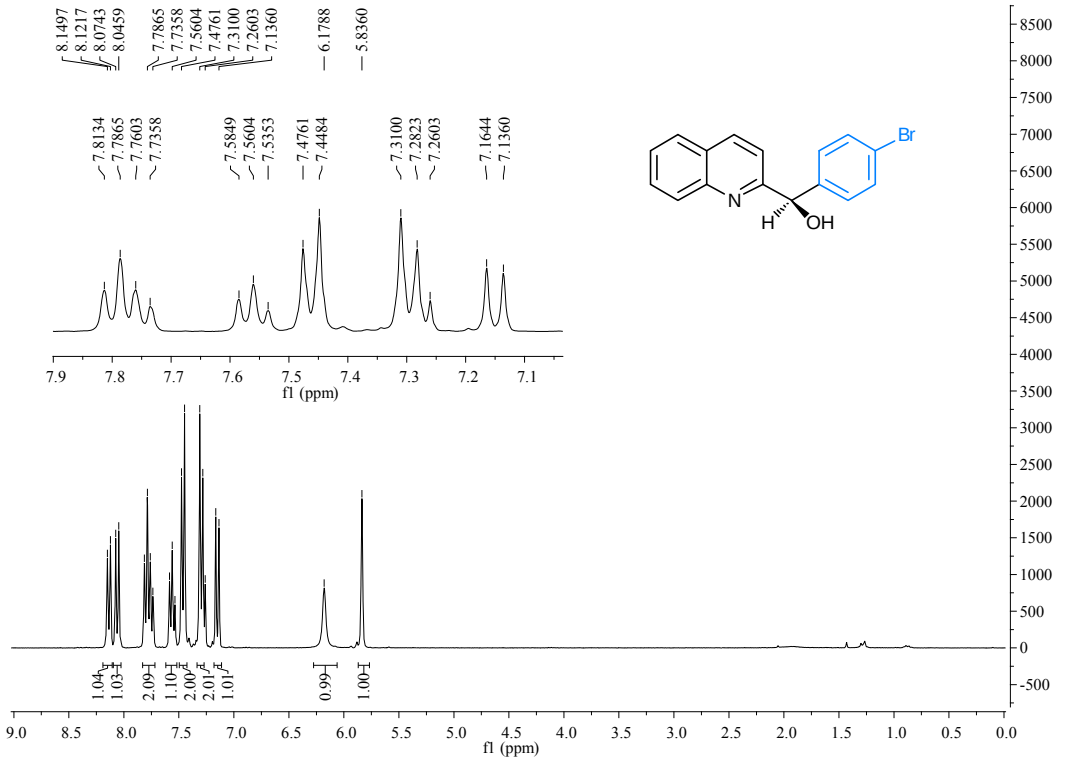
127.5756
126.7041
118.9485
77.4240
77.0001
76.5764
74.4114
129.9925
128.7197
128.6949
127.5756
127.4315
126.7041
Cl
N
H
OH
f1 (ppm)
f1 (ppm)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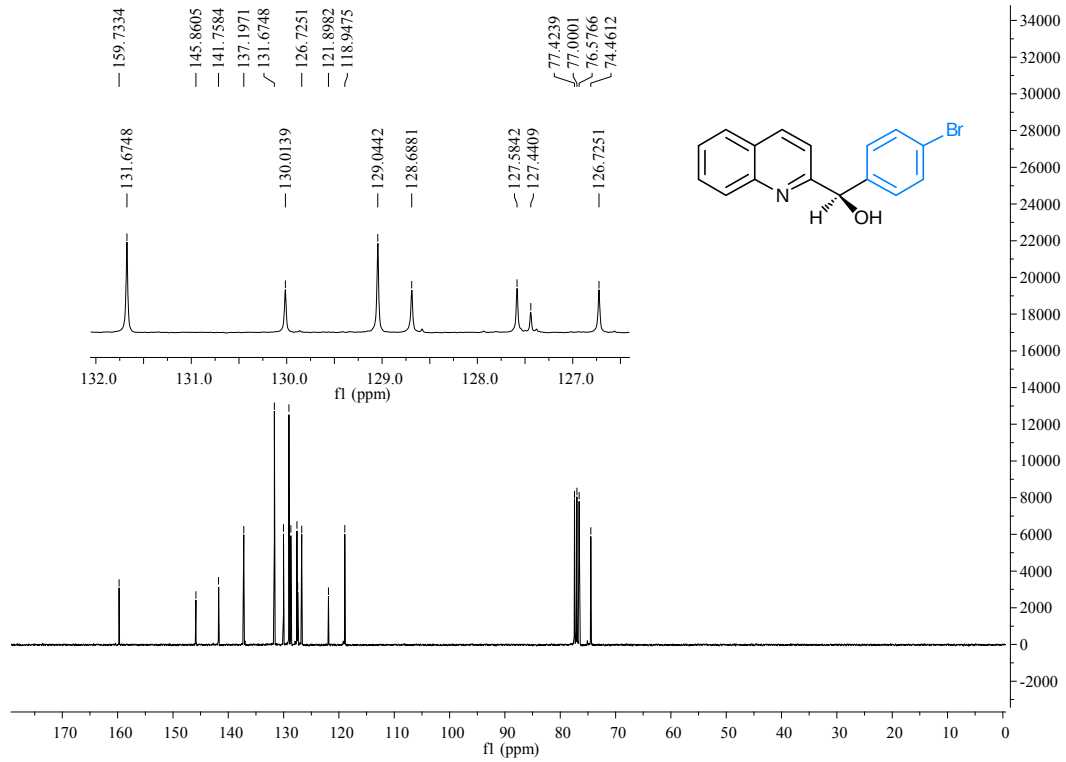
8.0743
8.0459
7.7865
7.7358
7.5604
7.4761
7.3100
7.2603
7.1360
6.1788
5.8360
7.8134
7.7865
7.7603
7.7358
7.5849
7.5604
7.5353
7.4761
7.4484
7.3100
7.2823
7.2603
7.1644
7.1360
Br
N
H
OH
f1 (ppm)
1.04
1.03
2.09
1.10
2.00
2.01
1.01
0.99
1.00
f1 (ppm)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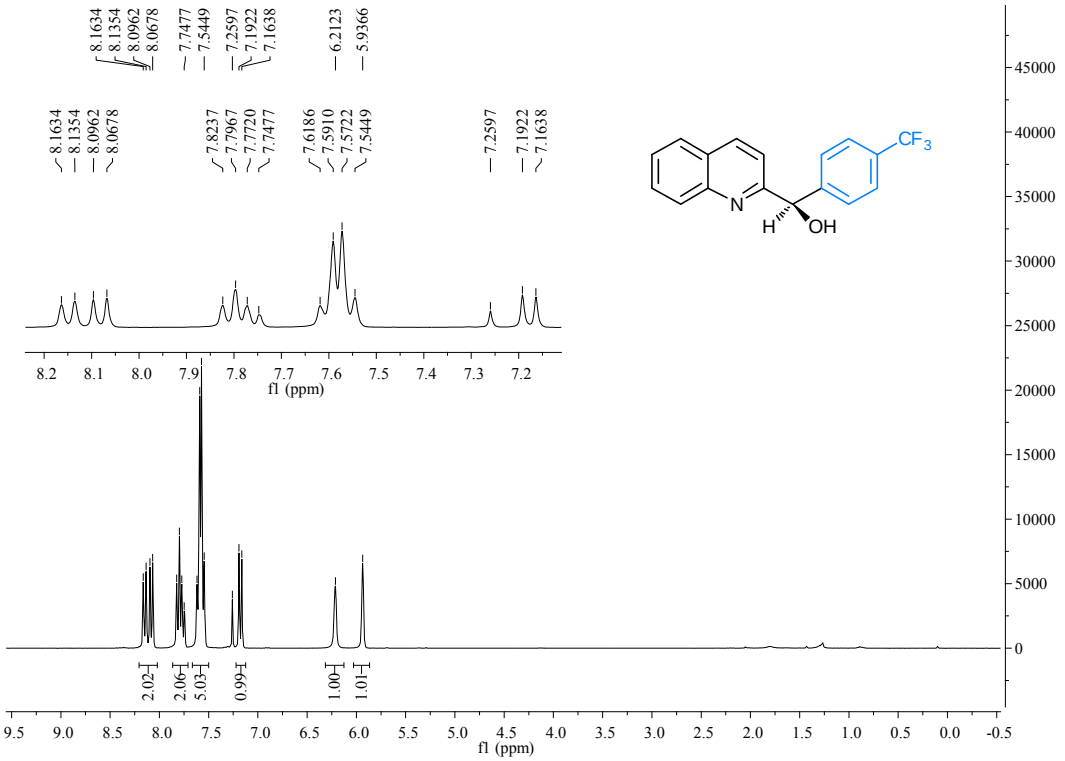
121.8982
118.9475
77.4239
77.0001
76.5766
74.4612
131.6748
130.0139
129.0442
128.6881
127.5842
127.4409
126.7251
Br
N
H
OH
f1 (ppm)
f1 (ppm)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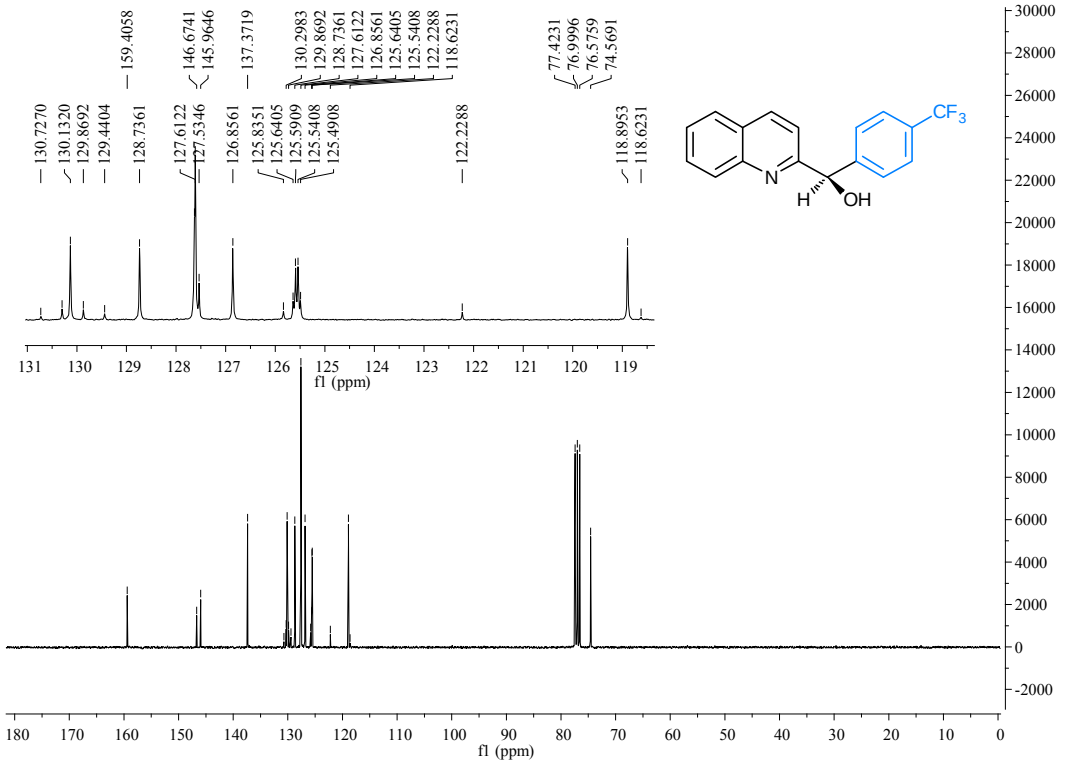
8.0962
8.0678
7.7477
7.5449
7.2597
7.1922
7.1638
6.2123
5.9366
7.8237
7.7967
7.7720
7.7477
7.6186
7.5910
7.5722
7.5449
7.2597
7.1922
7.1638
CF3
N
H
OH
f1 (ppm)
2.02
2.06
5.03
0.99
1.00
1.01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145.9646
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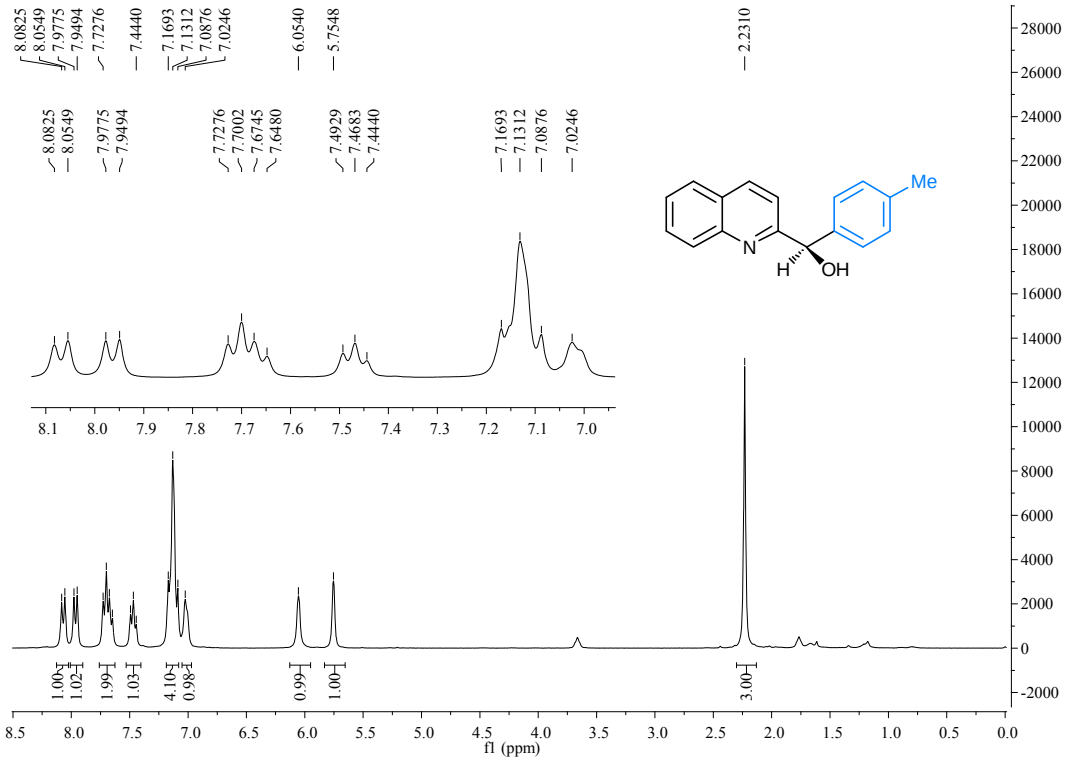
129.8692
128.7361
127.6122
126.8561
125.6405
125.5408
122.2288
118.6231
77.4231
76.9996
76.5759
74.5691
130.7270
130.1320
129.8692
129.4404
128.7361
127.6122
127.5346
126.8561
125.8351
125.6405
125.5909
125.5408
125.4908
122.2288
118.8953
118.6231
CF3
N
H
OH
f1 (ppm)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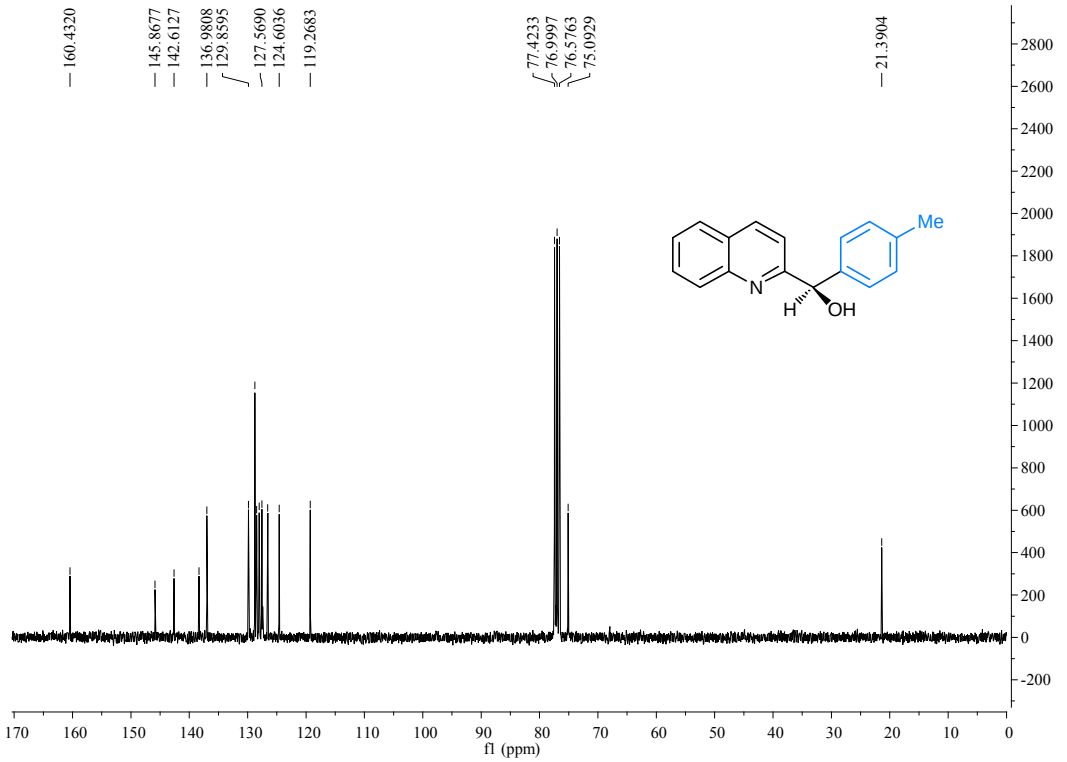
7.7276
7.4440
7.1693
7.1312
7.0876
7.0246
6.0540
5.7548
2.2310
Me
N
H
OH
1.00
1.02
1.99
1.03
4.10
0.98
0.99
1.00
3.00
f1 (ppm)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127.5690
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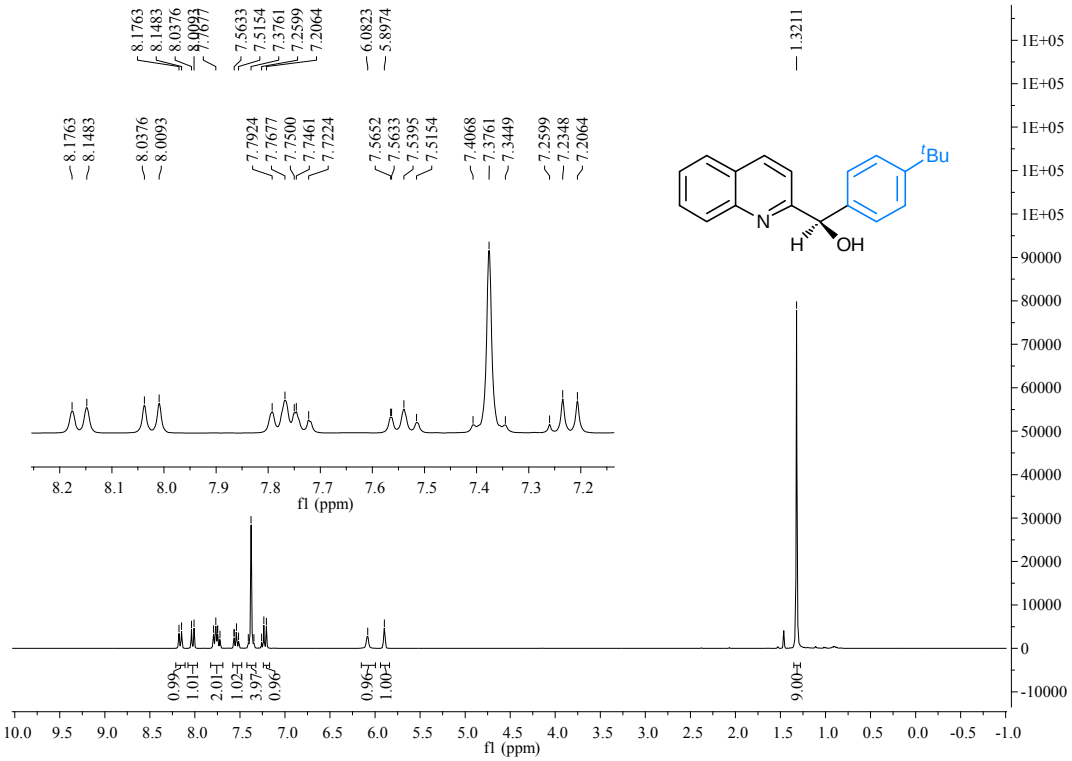
77.4233
76.9997
76.5763
75.0929
21.3904
Me
N
H
OH
f1 (ppm)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8.0376
8.0093
7.7677
7.5633
7.5154
7.3761
7.2599
7.2064
6.0823
5.8974
1.3211
7.7924
7.7677
7.7500
7.7461
7.7224
7.5652
7.5633
7.5395
7.5154
7.4068
7.3761
7.3449
7.2599
7.2348
7.2064
tBu
N
H
OH
f1 (ppm)
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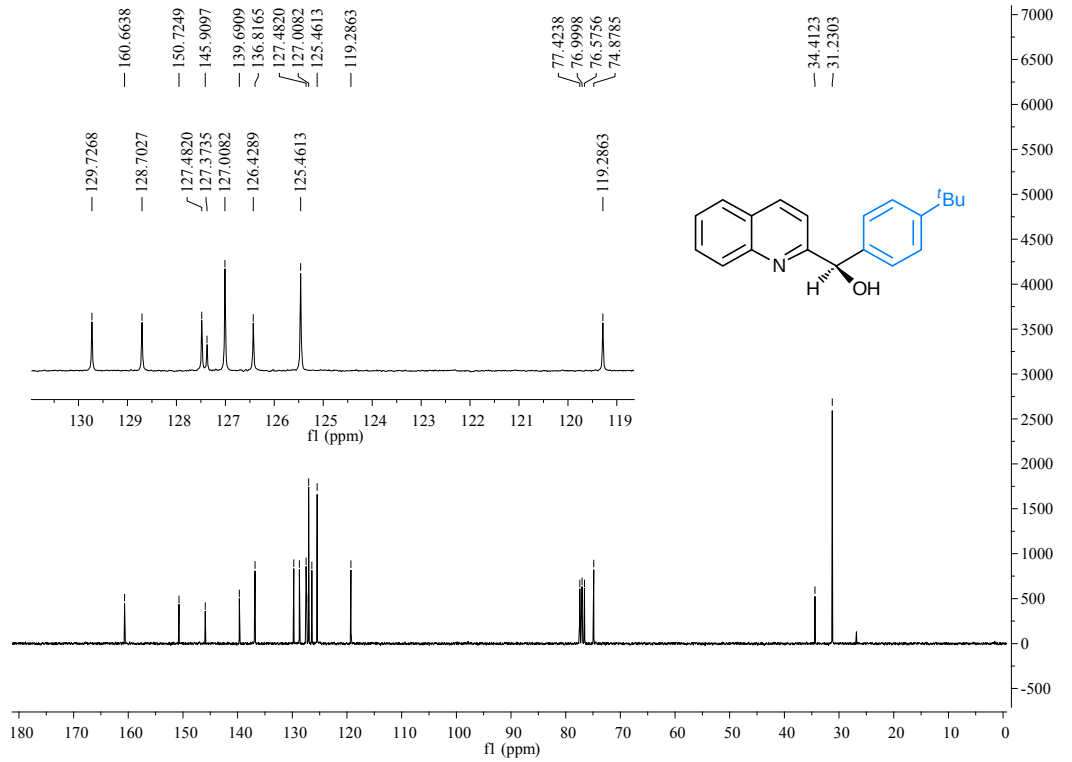
1.01
2.01
1.02
3.97
0.96
0.96
1.00
9.00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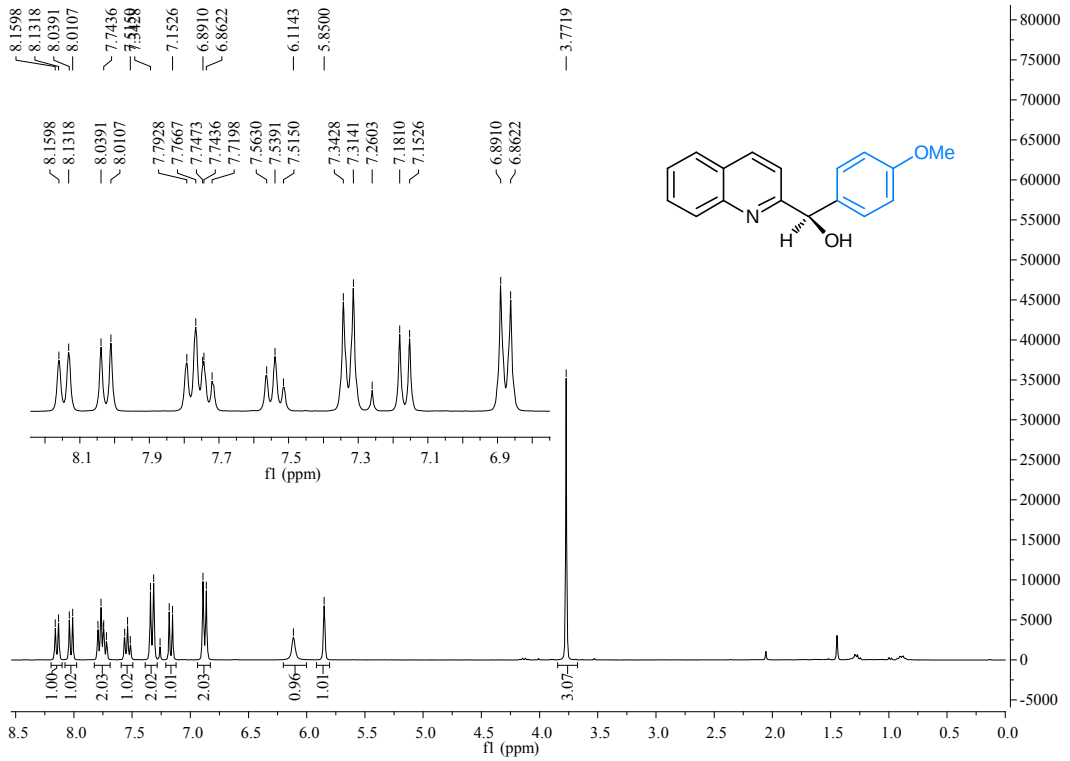
127.0082
125.4613
119.2863
77.4238
76.9998
76.5756
74.8785
34.4123
31.2303
129.7268
128.7027
127.4820
127.3735
127.0082
126.4289
125.4613
119.2863
tBu
N
H
OH
f1 (ppm)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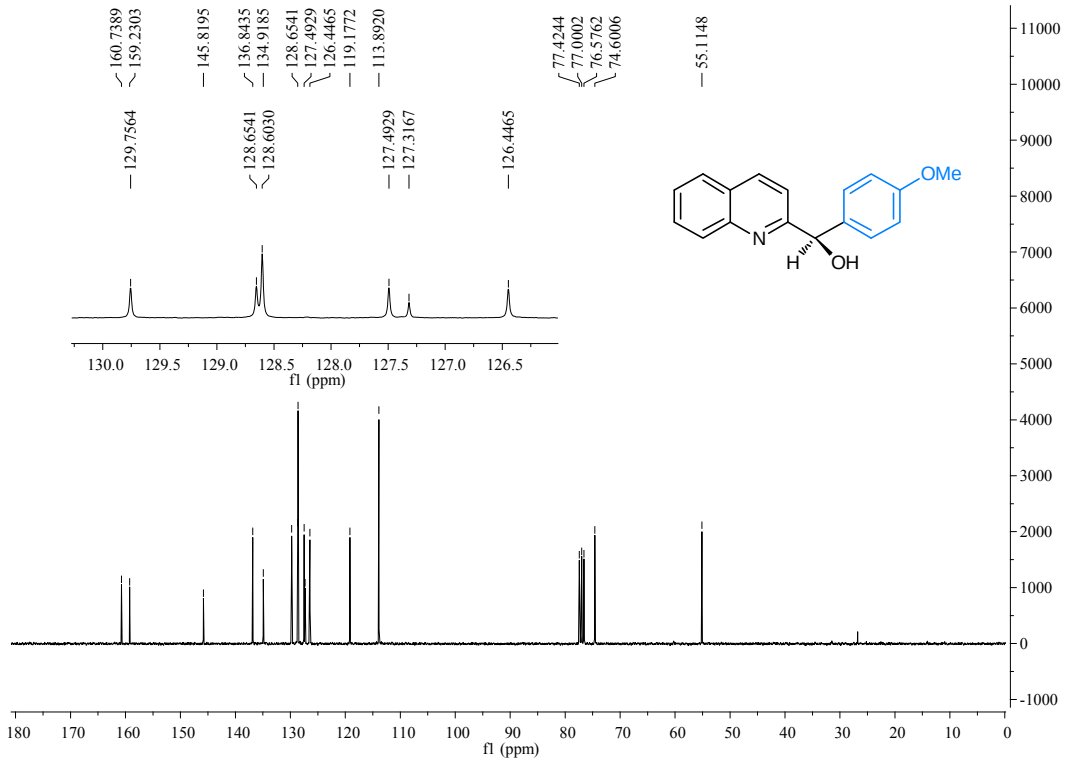
8.0107
7.7436
7.1526
6.8910
6.8622
6.1143
5.8500
3.7719
7.7928
7.7667
7.7473
7.7436
7.7198
7.5630
7.5391
7.5150
7.3428
7.3141
7.2603
7.1810
7.1526
OMe
N
H
OH
fl (ppm)
1.00
1.02
2.03
1.02
2.02
1.01
2.03
0.96
1.01
3.07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134.9185
128.6541
127.4929
126.4465
119.1772
113.8920
77.4244
77.0002
76.5762
74.6006
55.1148
129.7564
128.6541
128.6030
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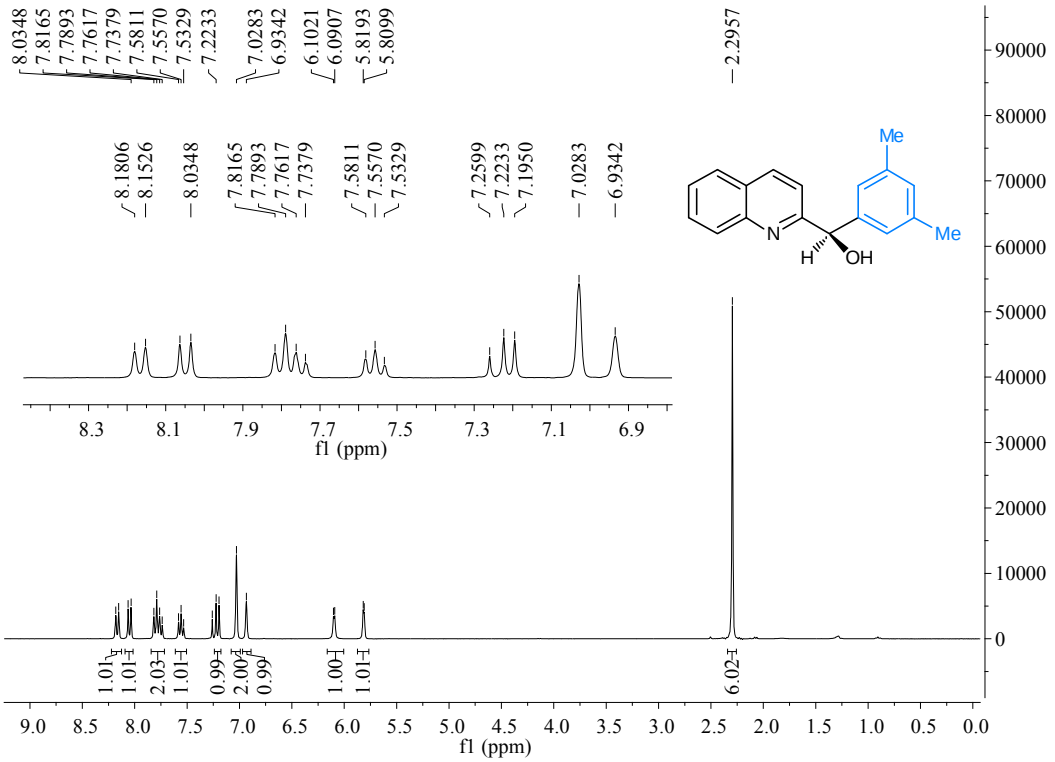
126.4465
OMe
N
H
OH
fl (ppm)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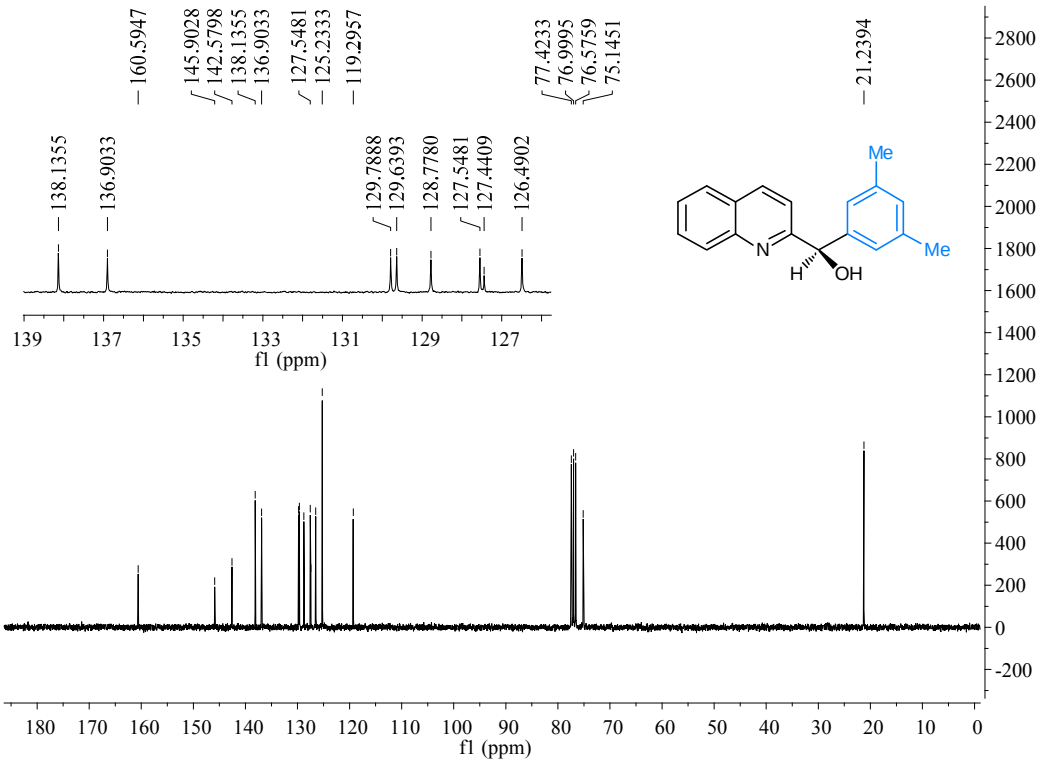
7.7893
7.7617
7.7379
7.5811
7.5570
7.5329
7.2233
7.0283
6.9342
6.1021
6.0907
5.8193
5.8099
2.2957
Me
Me
N
H
OH
fl (ppm)
1.01
1.01
2.03
1.01
0.99
2.00
0.99
1.00
1.01
6.02
fl (ppm)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127.5481
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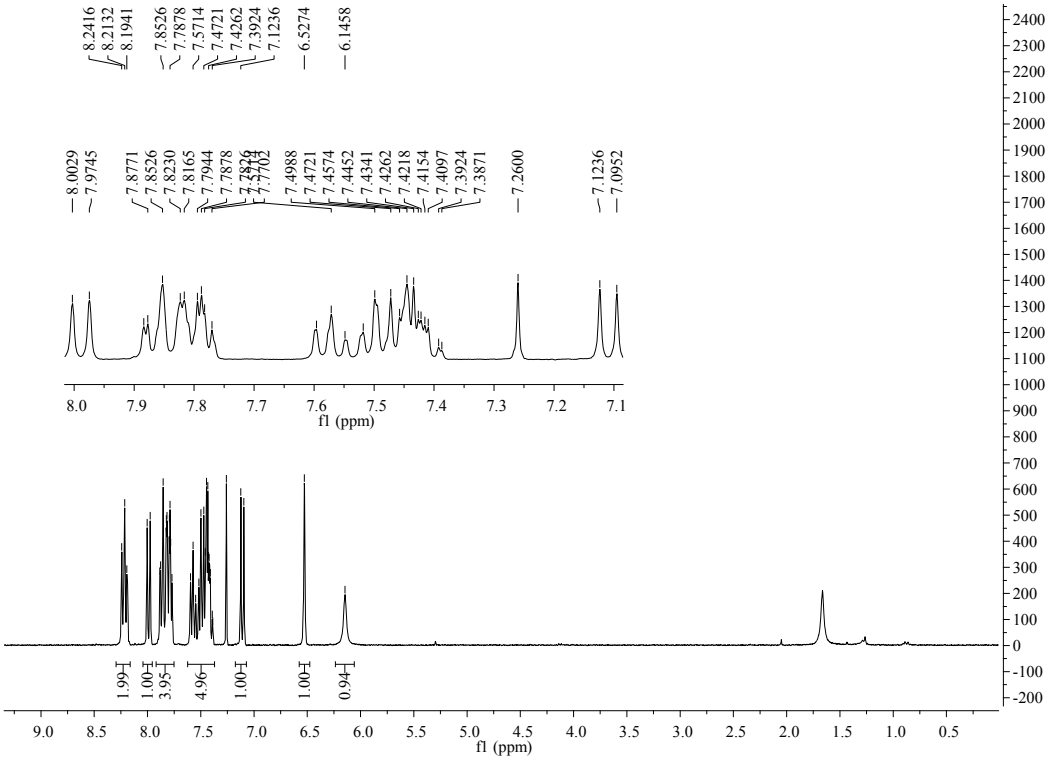
77.4233
76.9995
76.5759
75.1451
21.2394
138.1355
136.9033
129.7888
129.6393
128.7780
127.5481
127.4409
126.4902
Me
Me
N
H
OH
fl (ppm)
fl (ppm)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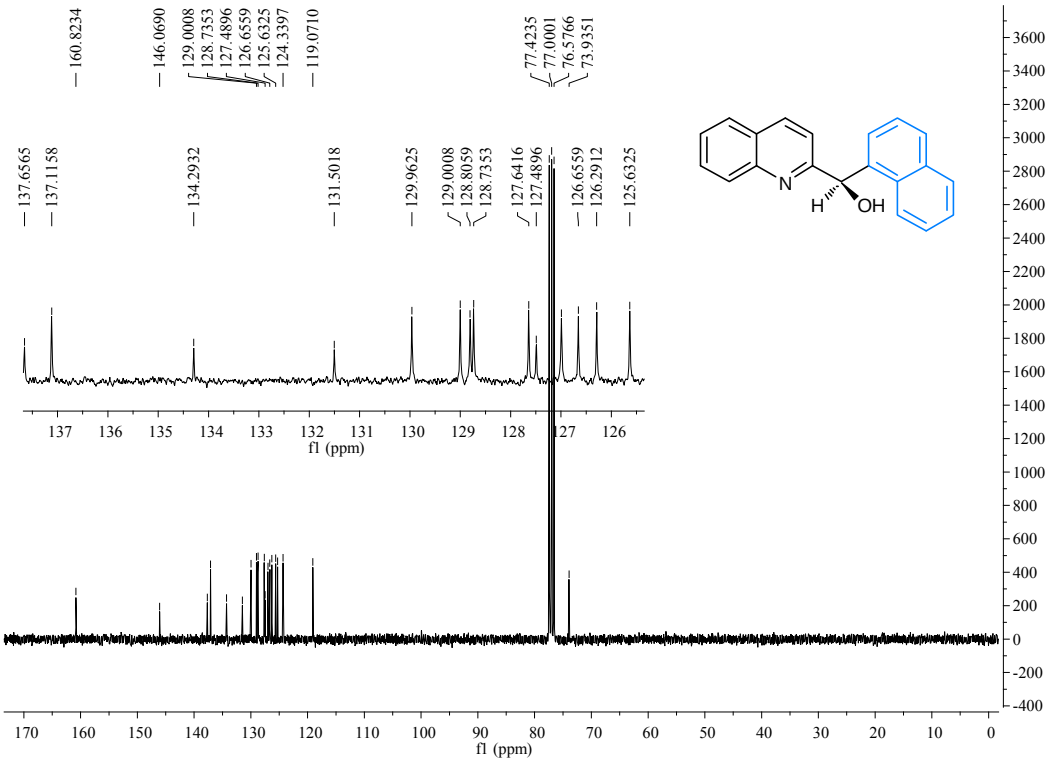
8.1941
7.8526
7.8878
7.5714
7.4721
7.4262
7.3924
7.1236
6.5274
6.1458
8.0029
7.9745
7.8771
7.8526
7.8230
7.8165
7.7944
7.7878
7.7826
7.7702
7.4988
7.4721
7.4574
7.4452
7.4341
7.4262
7.4218
7.4154
7.4097
7.3924
7.3871
7.2600
7.1236
7.0952
fl (ppm)
1.99
1.00
3.95
4.96
1.00
1.00
0.94
fl (ppm)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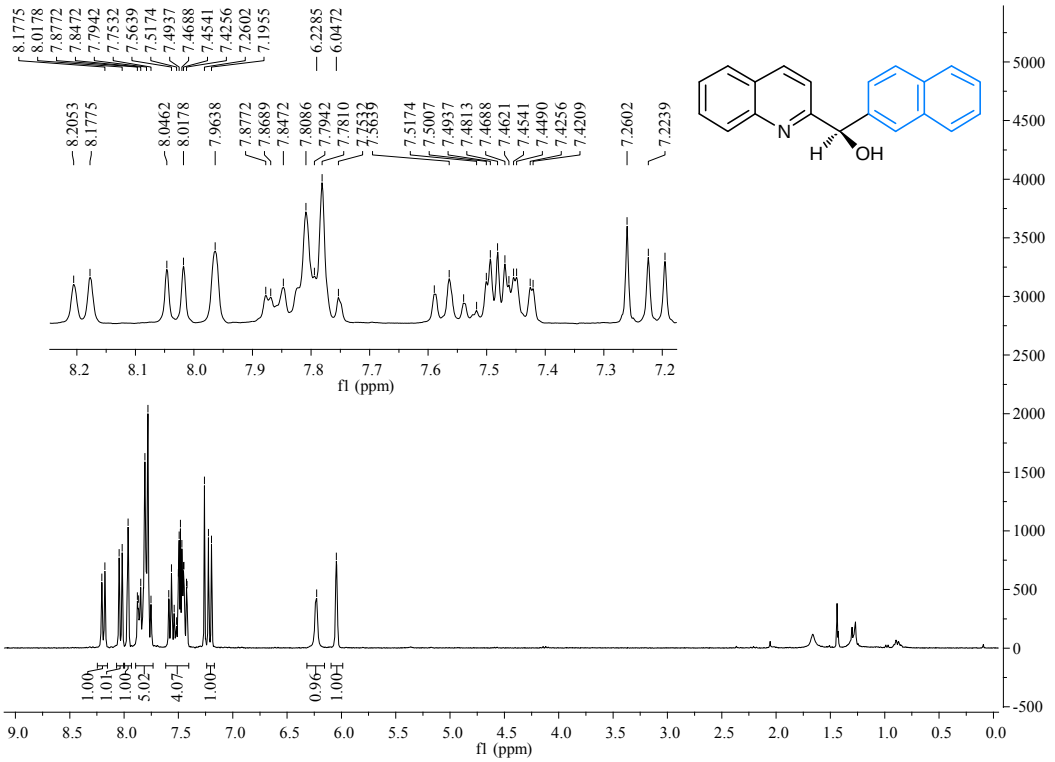
129.0008
128.7353
127.4896
126.6559
125.6325
124.3397
119.0710
77.4235
77.0001
76.5766
73.9351
137.6565
137.1158
134.2932
131.5018
129.9625
129.0008
128.8059
128.7353
127.6416
127.4896
126.6559
126.2912
125.6325
fl (ppm)
fl (ppm)

N
H
OH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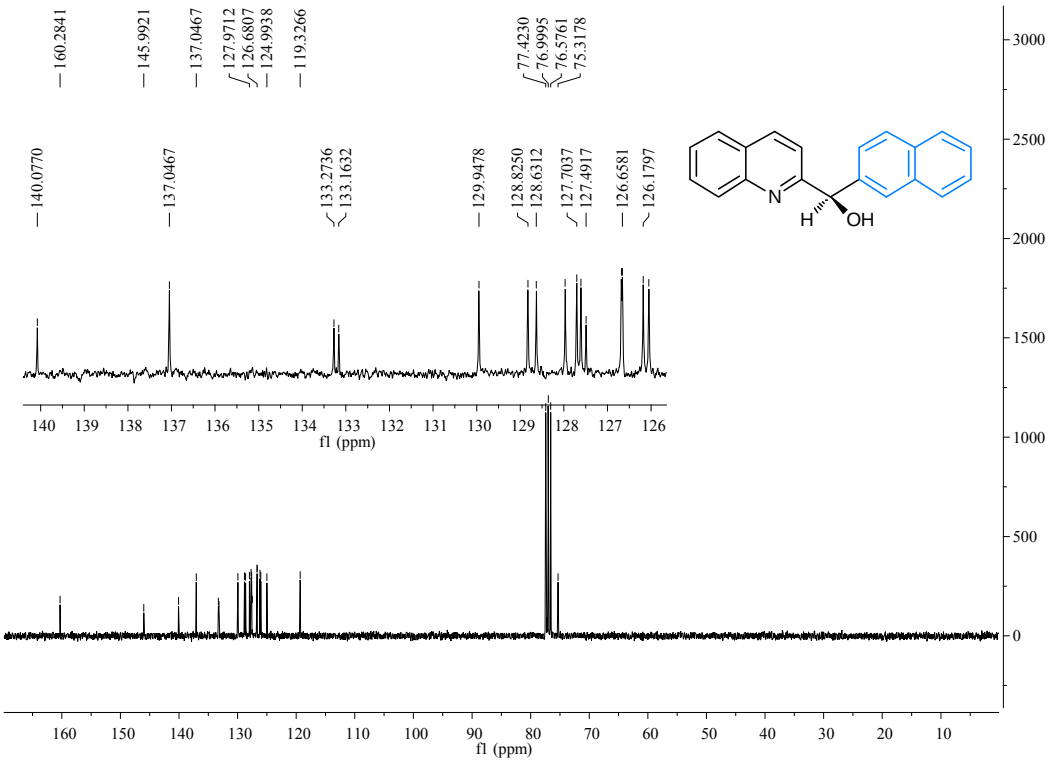
7.8772
7.8472
7.7942
7.7532
7.5639
7.5174
7.4937
7.4688
7.4541
7.4256
7.2602
7.1955
6.2285
6.0472
8.2053
8.1775
8.0462
8.0178
7.9638
7.8772
7.8689
7.8472
7.8086
7.7942
7.7810
7.7532
7.5639
7.5174
7.5007
7.4937
7.4813
7.4688
7.4621
7.4541
7.4490
7.4256
7.4209
7.2602
7.2239
N
H
OH
f1 (ppm)
1.00
1.01
1.00
5.02
4.07
1.00
0.96
1.00
f1 (ppm)


160.2841
145.9921
137.0467
127.9712
126.6807
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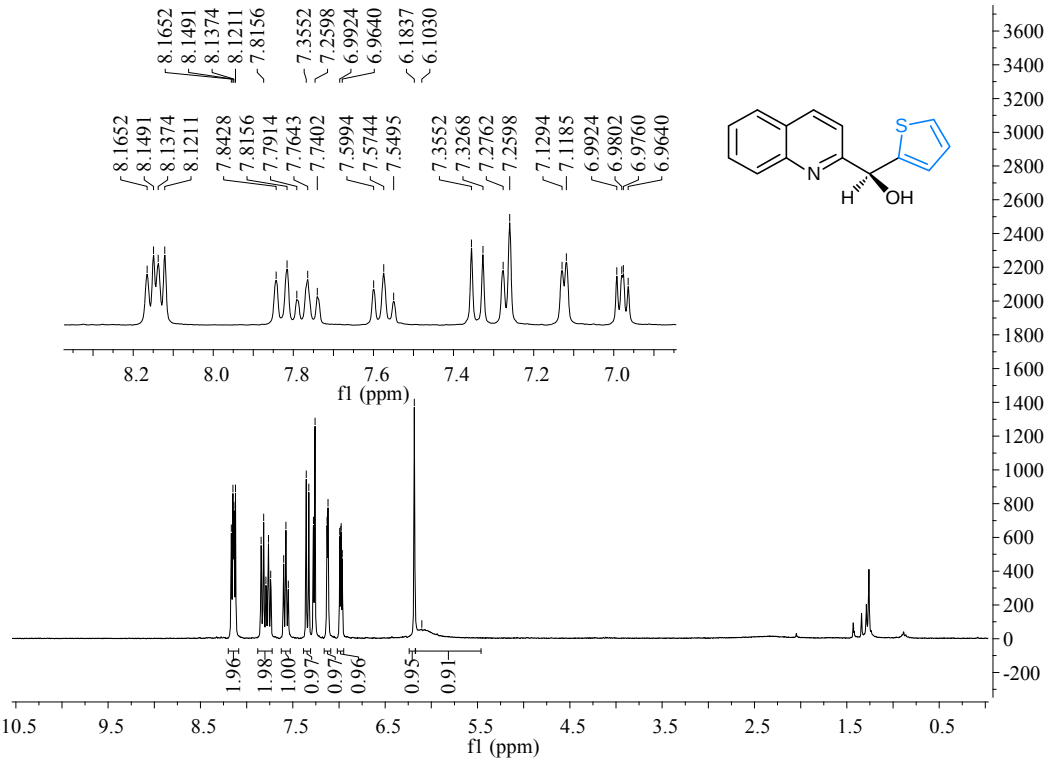
119.3266
77.4230
76.9995
76.5761
75.3178
140.0770
137.0467
133.2736
133.1632
129.9478
128.8250
128.6312
127.7037
127.4917
126.6581
126.1797
N
H
OH
f1 (ppm)
f1 (ppm)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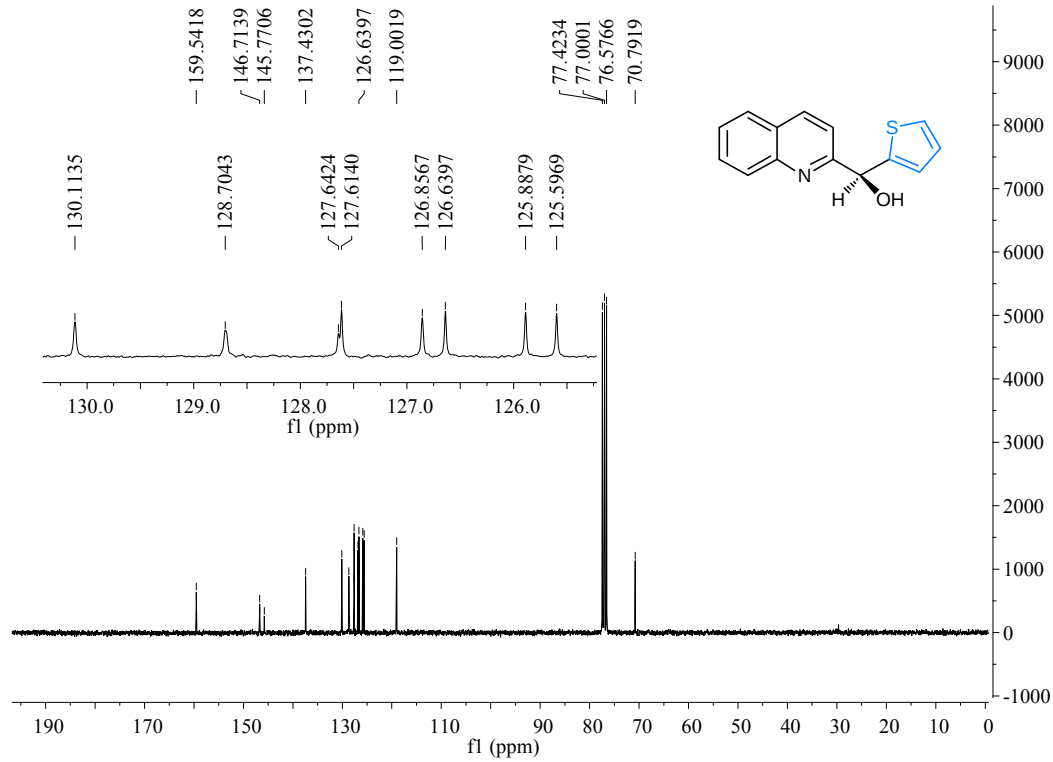
8.1491
8.1374
8.1211
7.8156
7.3552
7.2598
6.9924
6.9640
6.1837
6.1030
7.8428
7.7914
7.7643
7.7402
7.5994
7.5744
7.5495
7.3268
7.2762
7.1294
7.1185
6.9802
6.9760
1.96
1.98
1.00
0.97
0.97
0.96
0.95
0.91
S
N
H
OH
f1 (ppm)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145.7706
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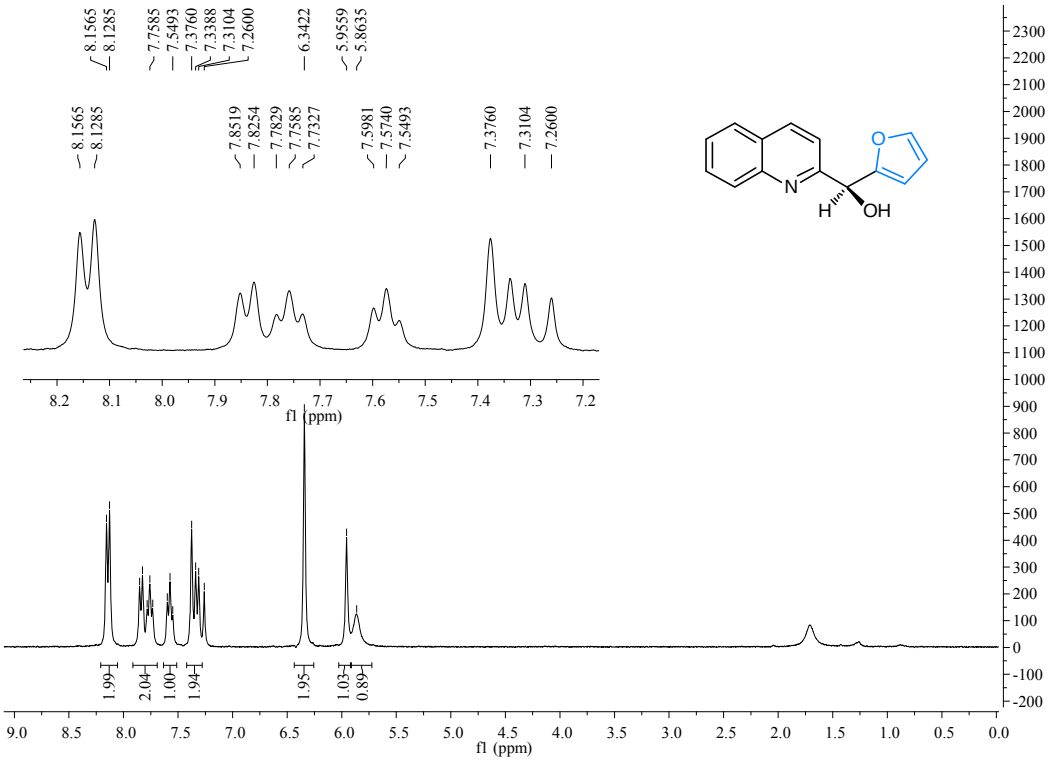
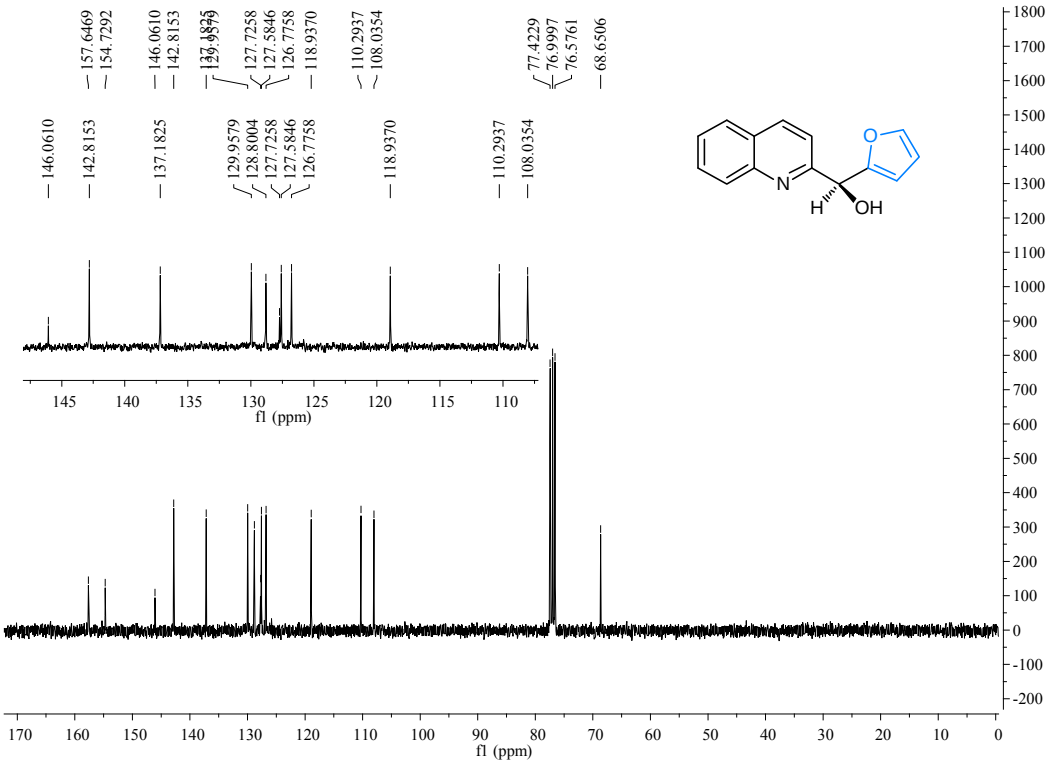
126.6397
119.0019
77.4234
77.0001
76.5766
70.7919
130.1135
128.7043
127.6424
127.6140
126.8567
126.6397
125.8879
125.5969
S
N
H
OH
f1 (ppm)


8.1565
8.1285
7.7585
7.5493
7.3760
7.3388
7.3104
7.2600
6.3422
5.9559
5.8635
7.8519
7.8254
7.7829
7.7585
7.7327
7.5981
7.5740
7.5493
7.3760
7.3104
7.2600
1.99
2.04
1.00
1.94
1.95
1.03
0.89
f1 (ppm)
N
H
OH
O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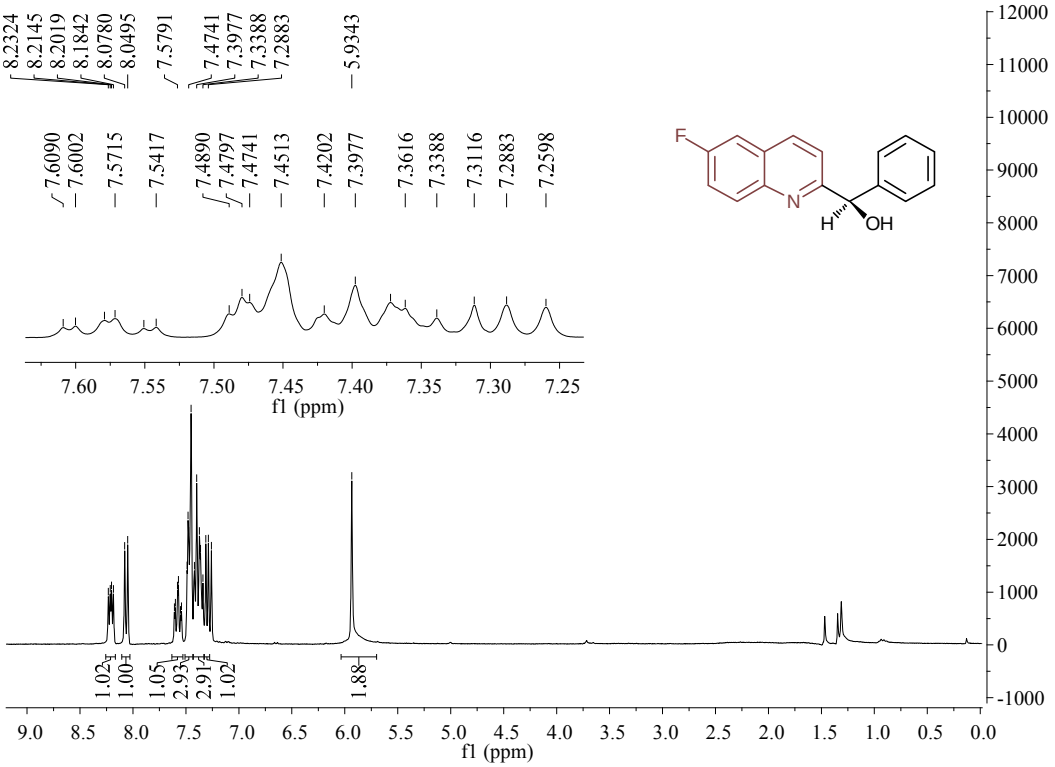
154.7292
146.0610
142.8153
137.1825
129.9579
128.8004
127.7258
127.5846
126.7758
118.9370
110.2937
108.0354
77.4229
76.9997
76.5761
68.6506
f1 (ppm)
N
H
OH
O


8.2324
8.2145
8.2019
8.1842
8.0780
8.0495
7.5791
7.4741
7.3977
7.3388
7.2883
5.9343
7.6090
7.6002
7.5715
7.5417
7.4890
7.4797
7.4741
7.4513
7.4202
7.3977
7.3616
7.3388
7.3116
7.2883
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H
OH
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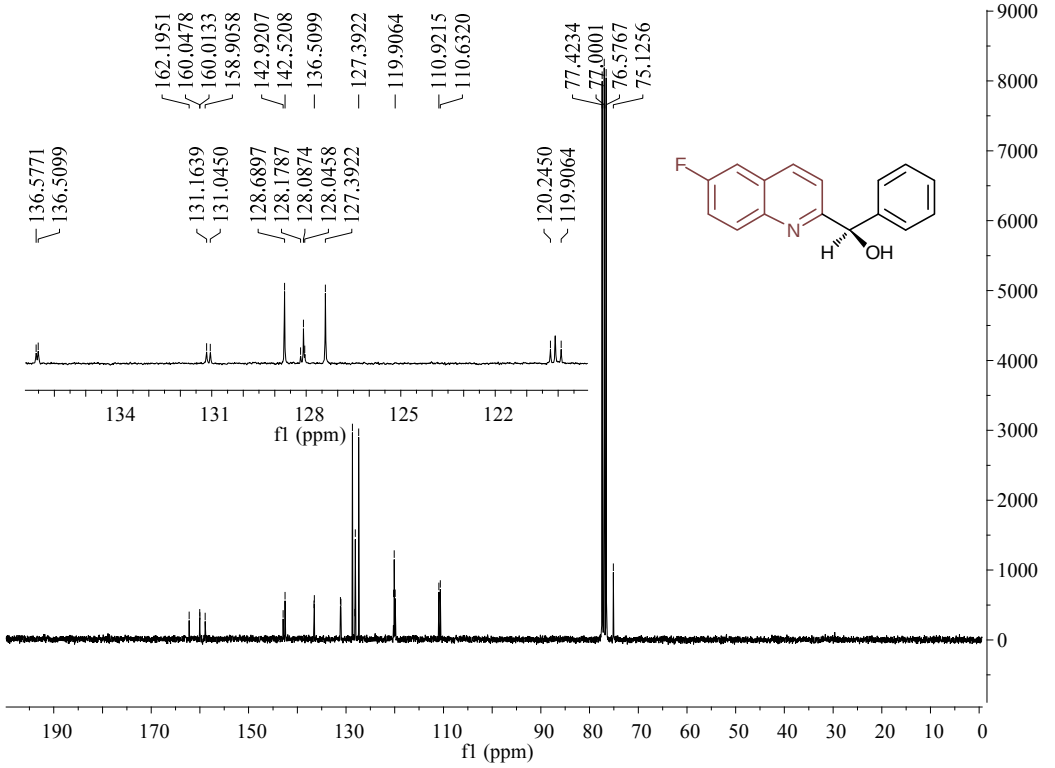
1.05
2.93
2.91
1.02
1.88
f1 (ppm)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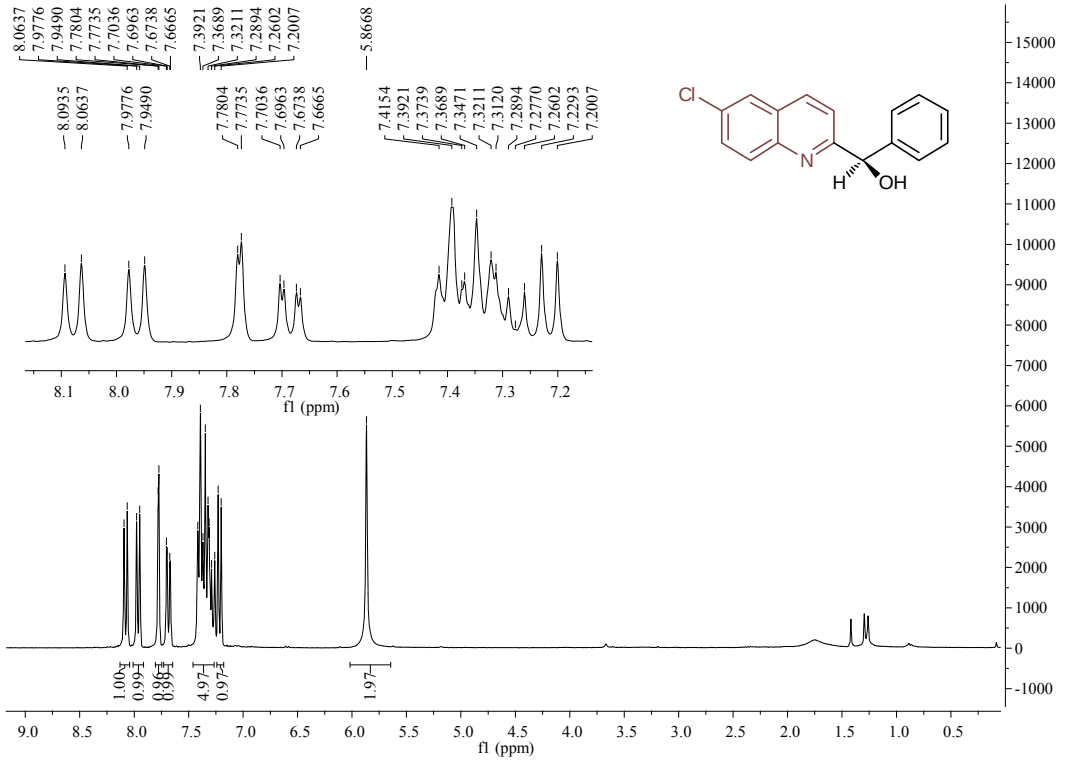
160.0133
158.9058
142.9207
142.5208
136.5099
127.3922
119.9064
110.9215
110.6320
77.4234
77.0001
76.5767
75.1256
136.5771
136.5099
131.1639
131.0450
128.6897
128.1787
128.0874
128.0458
127.3922
120.2450
119.9064
F
N
H
OH
f1 (ppm)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7.9776
7.9490
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7.7735
7.7036
7.6963
7.6738
7.6665
7.3921
7.3689
7.3211
7.2894
7.2602
7.2007
5.8668
7.4154
7.3921
7.3739
7.3689
7.3471
7.3211
7.3120
7.2894
7.2770
7.2602
7.2293
7.2007
Cl
N
H
OH
fl (ppm)
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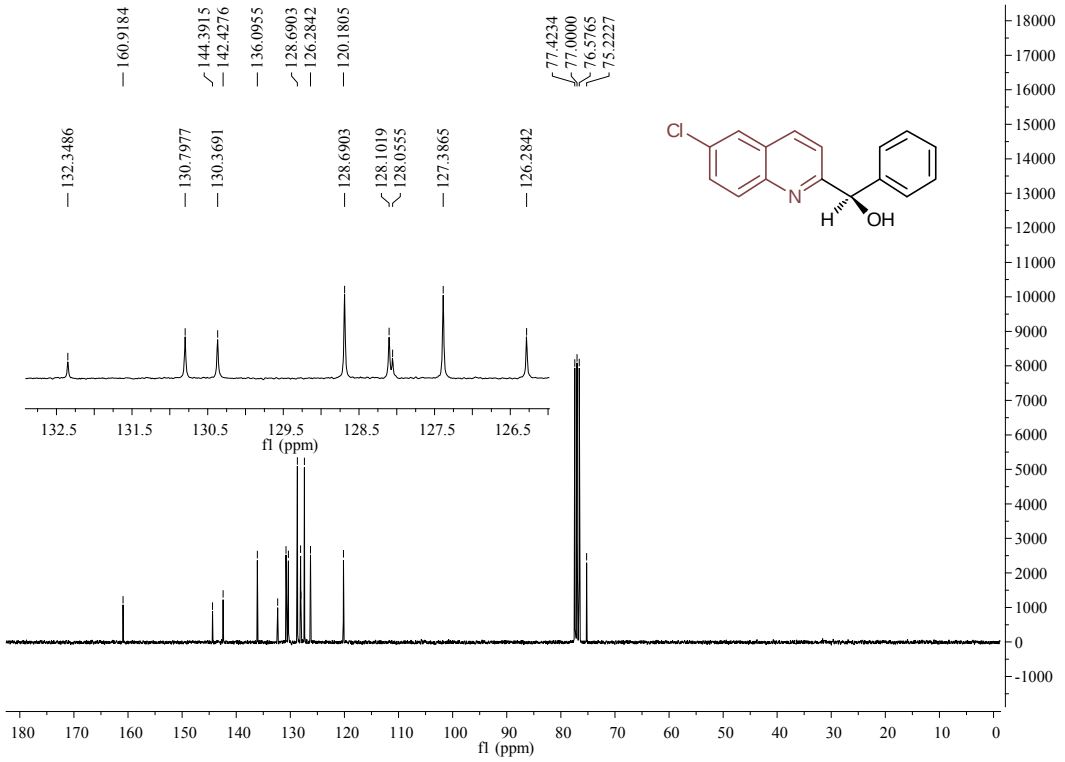
0.99
0.96
0.98
4.97
0.97
1.97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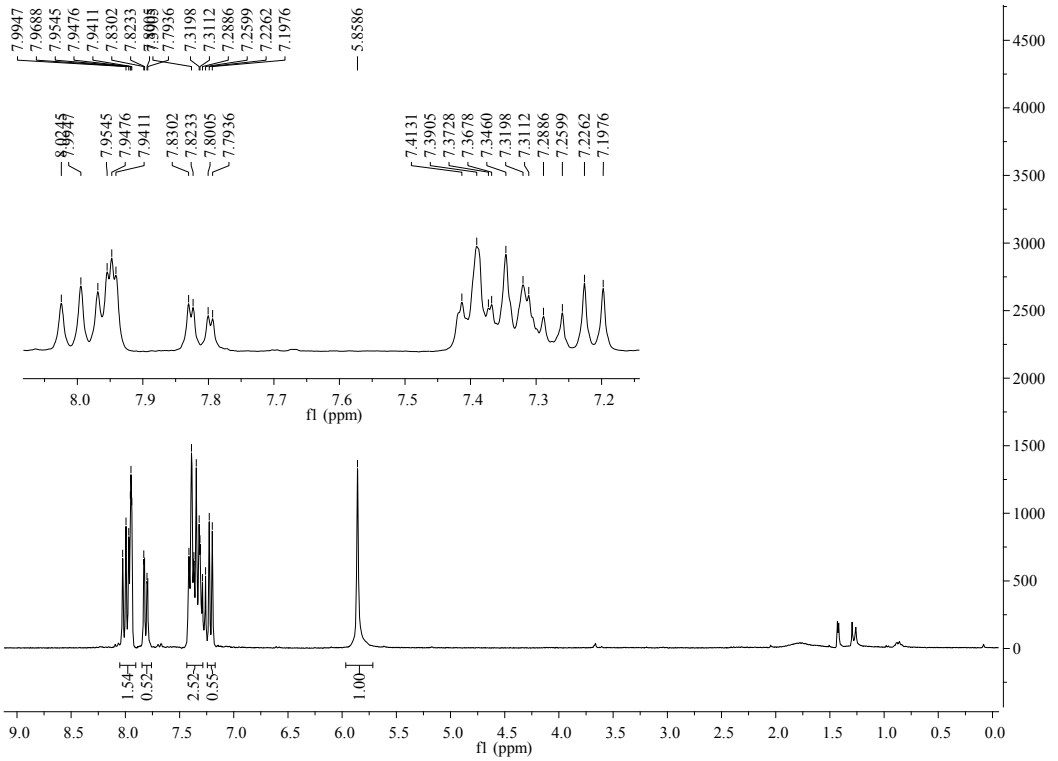
142.4276
136.0955
128.6903
126.2842
120.1805
77.4234
77.0000
76.5765
75.2227
132.3486
130.7977
130.3691
128.6903
128.1019
128.0555
127.3865
126.2842
Cl
N
H
OH
fl (ppm)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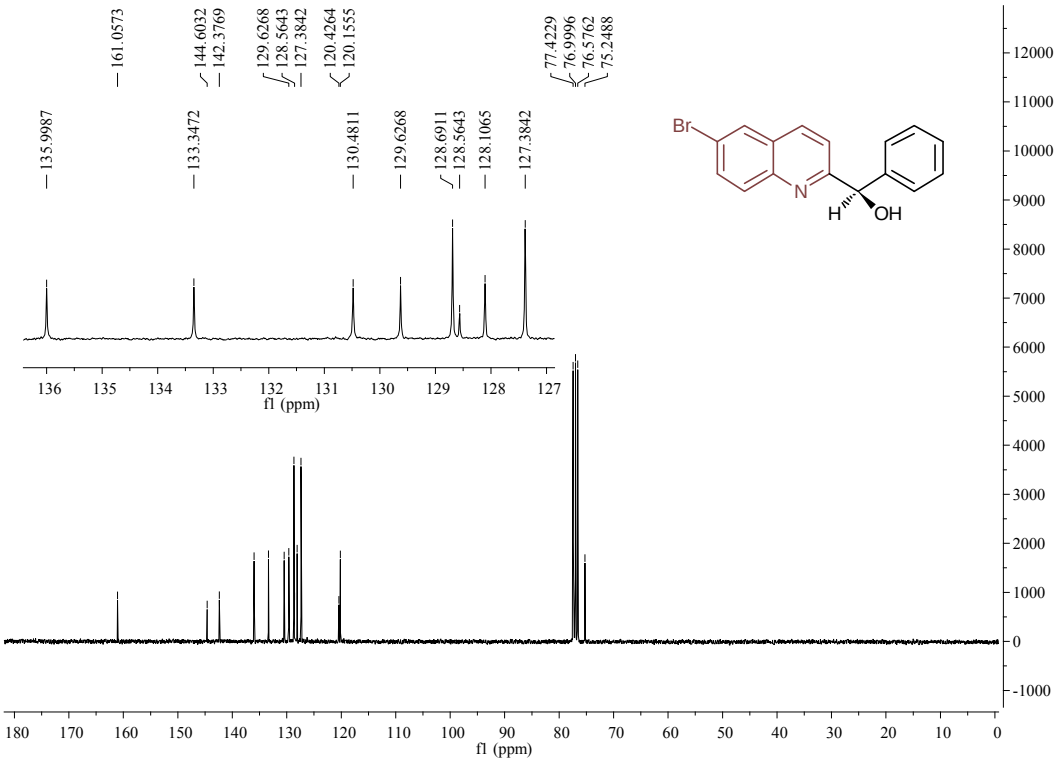
7.9545
7.9476
7.9411
7.8302
7.8233
7.7936
7.3198
7.3112
7.2886
7.2599
7.2262
7.1976
5.8586
7.4131
7.3905
7.3728
7.3678
7.3460
7.3198
7.3112
7.2886
7.2599
7.2262
7.1976
f1 (ppm)
1.54
0.52
2.52
0.55
1.00
f1 (ppm)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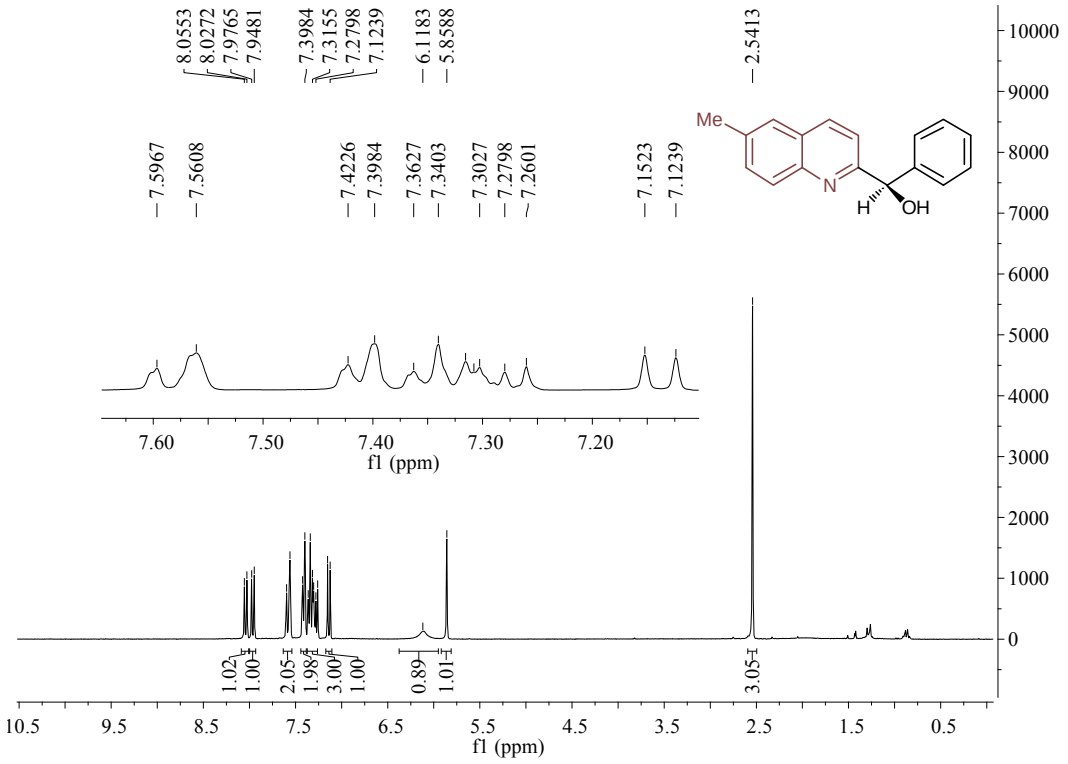
128.5643
127.3842
120.4264
120.1555
77.4229
76.9996
76.5762
75.2488
135.9987
133.3472
130.4811
129.6268
128.6911
128.5643
128.1065
127.3842
f1 (ppm)
Br
N
H
OH
f1 (ppm)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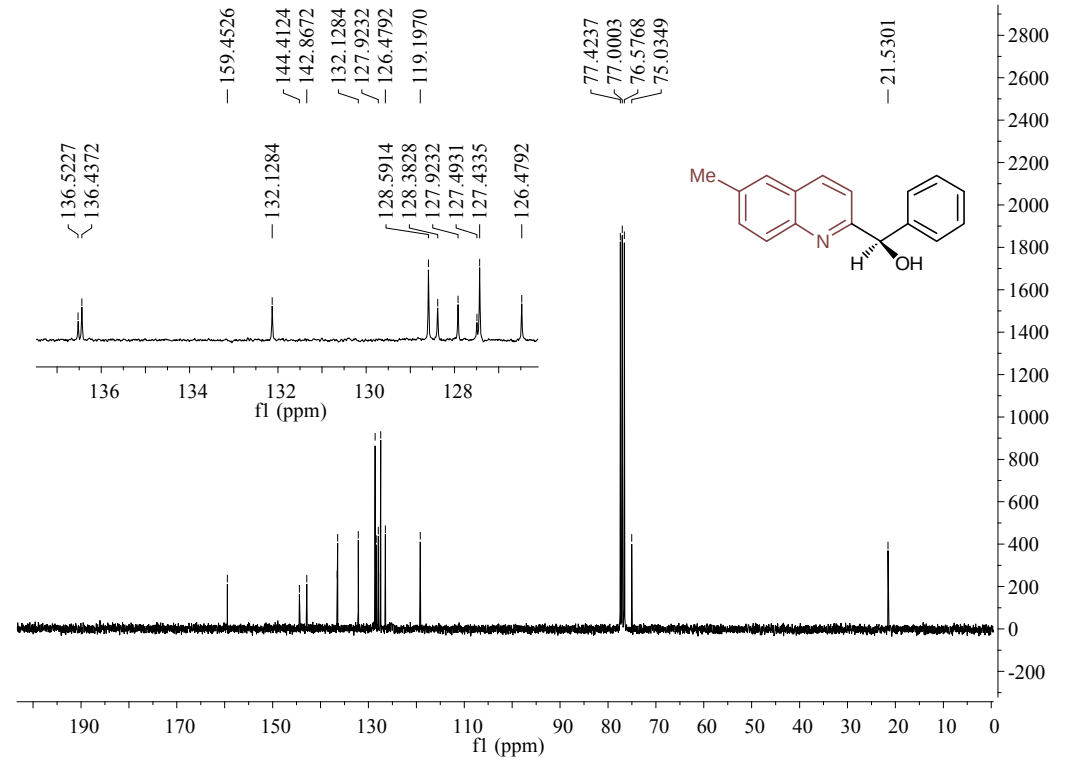
7.9481
7.3984
7.3155
7.2798
7.1239
6.1183
5.8588
2.5413
7.5967
7.5608
7.4226
7.3984
7.3627
7.3403
7.3027
7.2798
7.2601
7.1523
7.1239
Me
N
H
OH
1.02
1.00
2.05
1.98
3.00
1.00
0.89
1.01
3.05
f1 (ppm)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127.9232
126.4792
119.1970
77.4237
77.0003
76.5768
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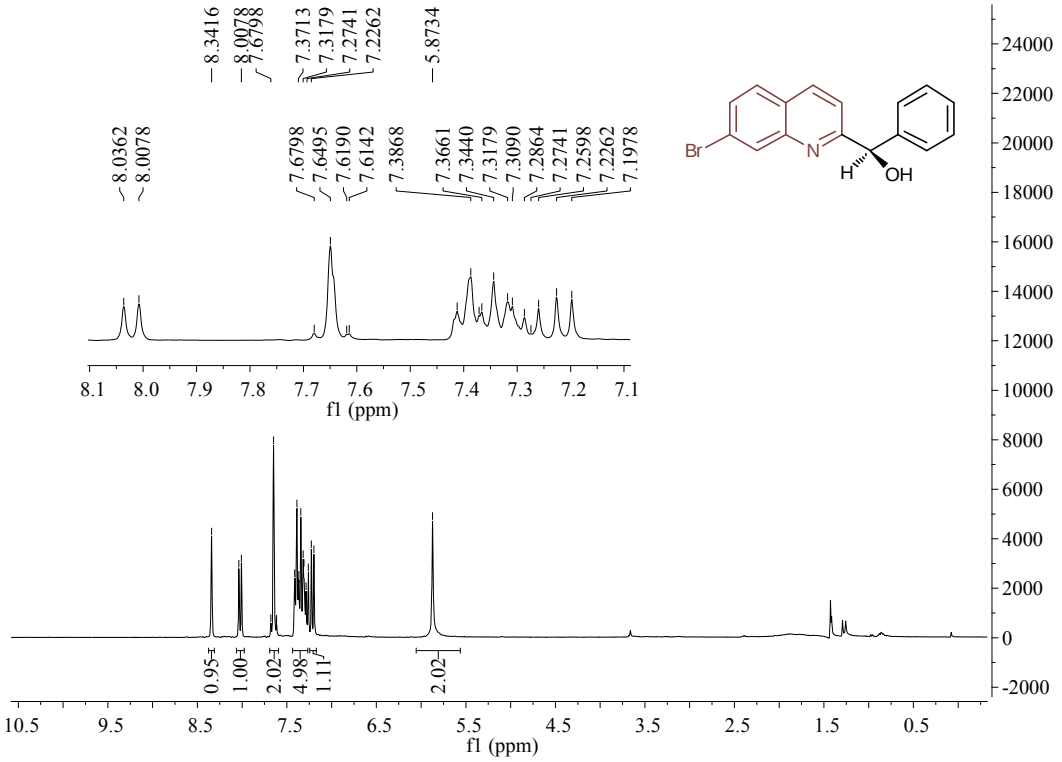
21.5301
136.5227
136.4372
132.1284
128.5914
128.3828
127.9232
127.4931
127.4335
126.4792
Me
N
H
OH
f1 (ppm)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8.0078
7.6798
7.6495
7.6190
7.6142
7.3868
7.3713
7.3661
7.3440
7.3179
7.3090
7.2864
7.2741
7.2598
7.2262
7.1978
5.8734
Br
N
H
OH
f1 (ppm)
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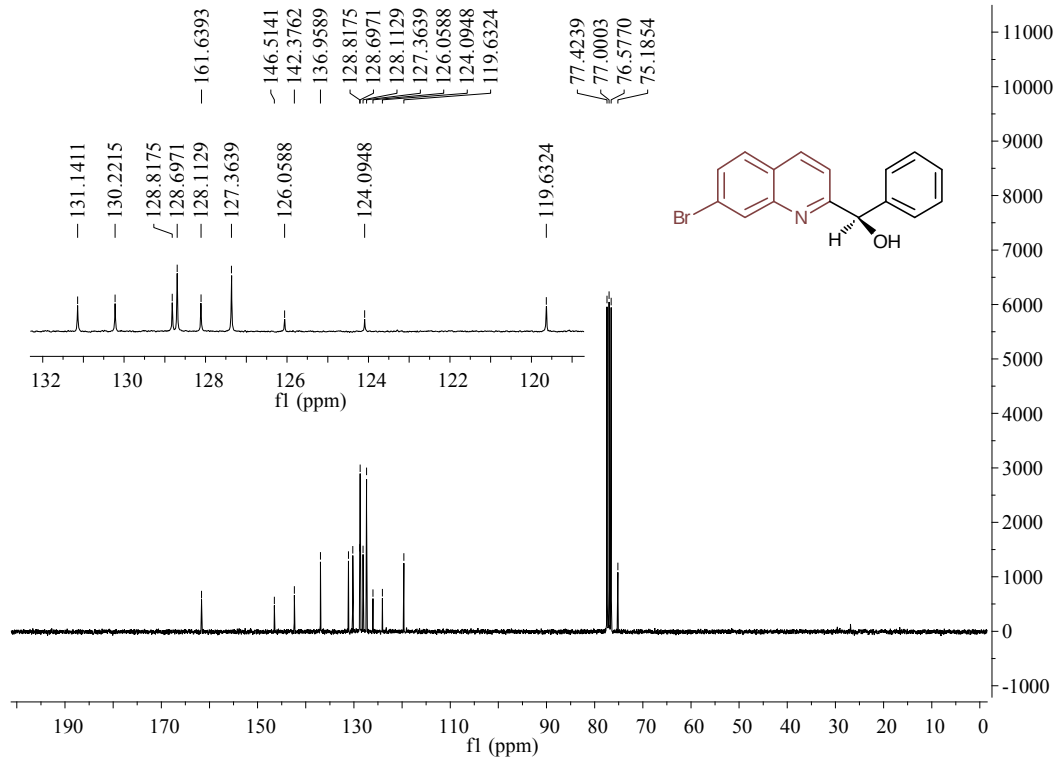
1.00
2.02
4.98
1.11
2.02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128.1129
127.3639
126.0588
124.0948
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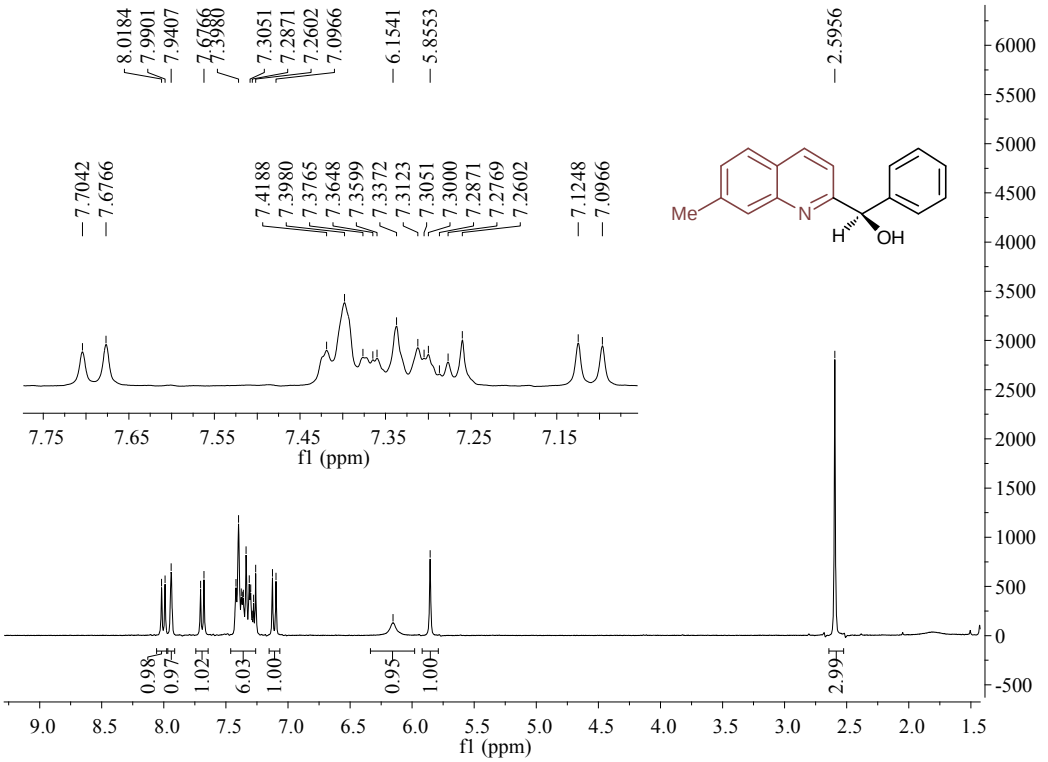
77.4239
77.0003
76.5770
75.1854
131.1411
130.2215
Br
N
H
OH
f1 (ppm)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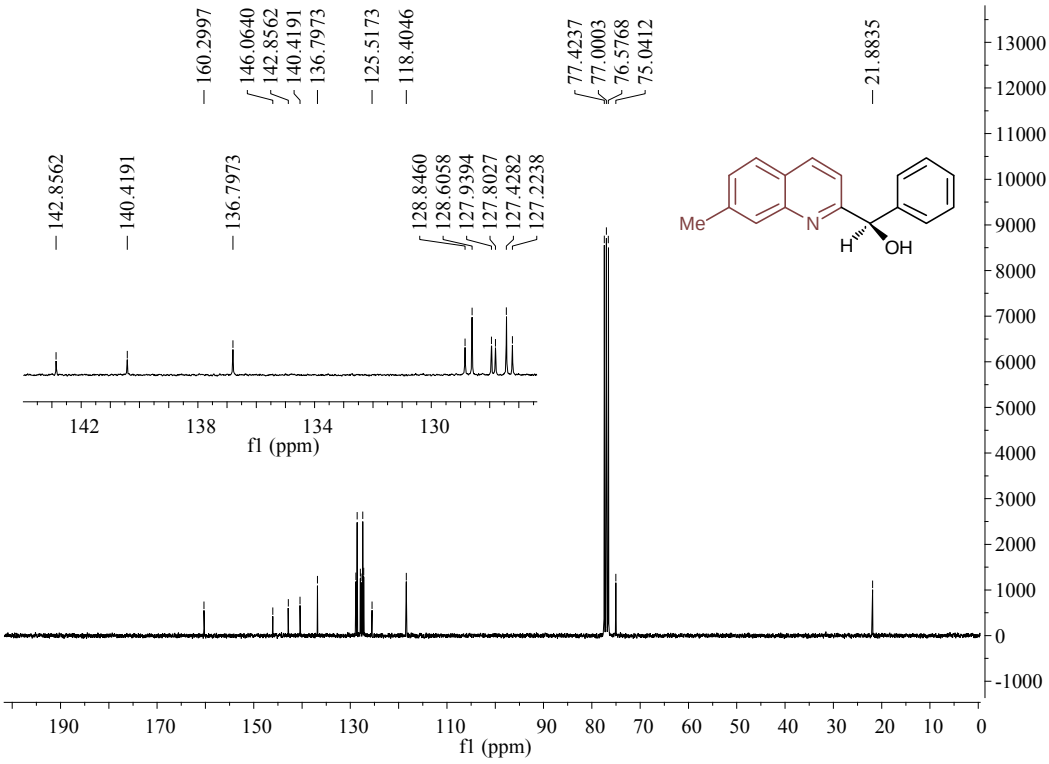
7.9407
7.6766
7.6599
7.3051
7.2871
7.2602
7.0966
6.1541
5.8553
2.5956
7.7042
7.6766
7.4188
7.3980
7.3765
7.3648
7.3599
7.3372
7.3123
7.3051
7.3000
7.2871
7.2769
7.2602
7.1248
7.0966
Me
N
H
OH
0.98
0.97
1.02
6.03
1.00
0.95
1.00
2.99
f1 (ppm)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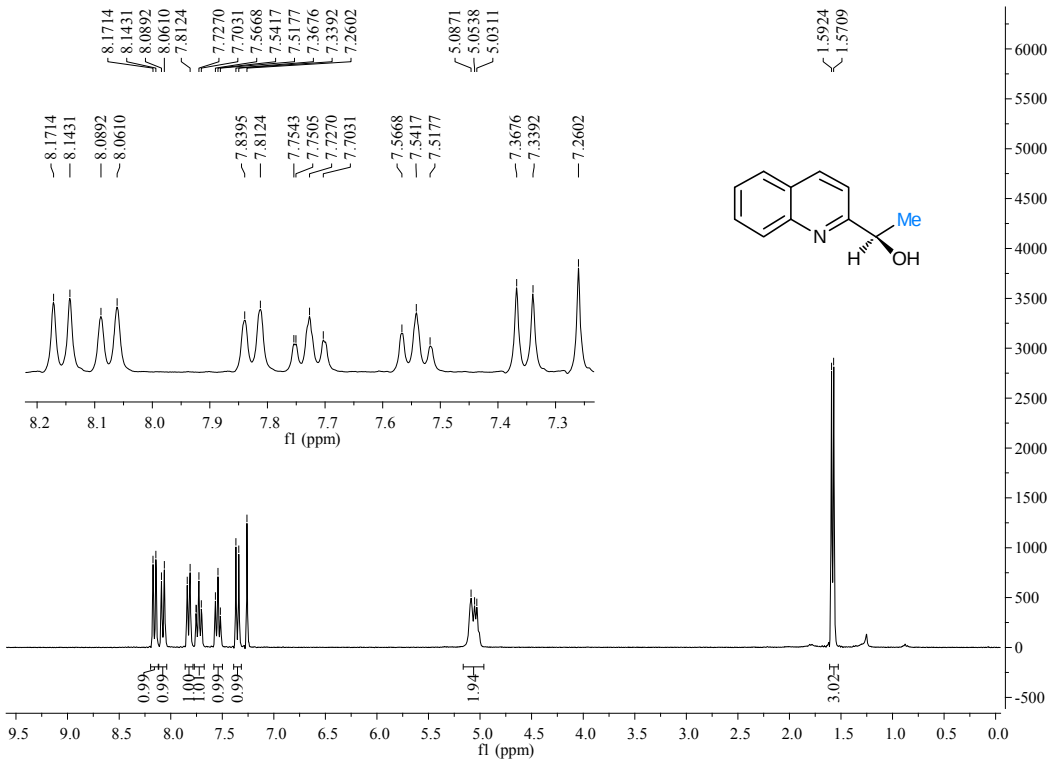
21.8835
142.8562
140.4191
136.7973
128.8460
128.6058
127.9394
127.8027
127.4282
127.2238
Me
N
H
OH
f1 (ppm)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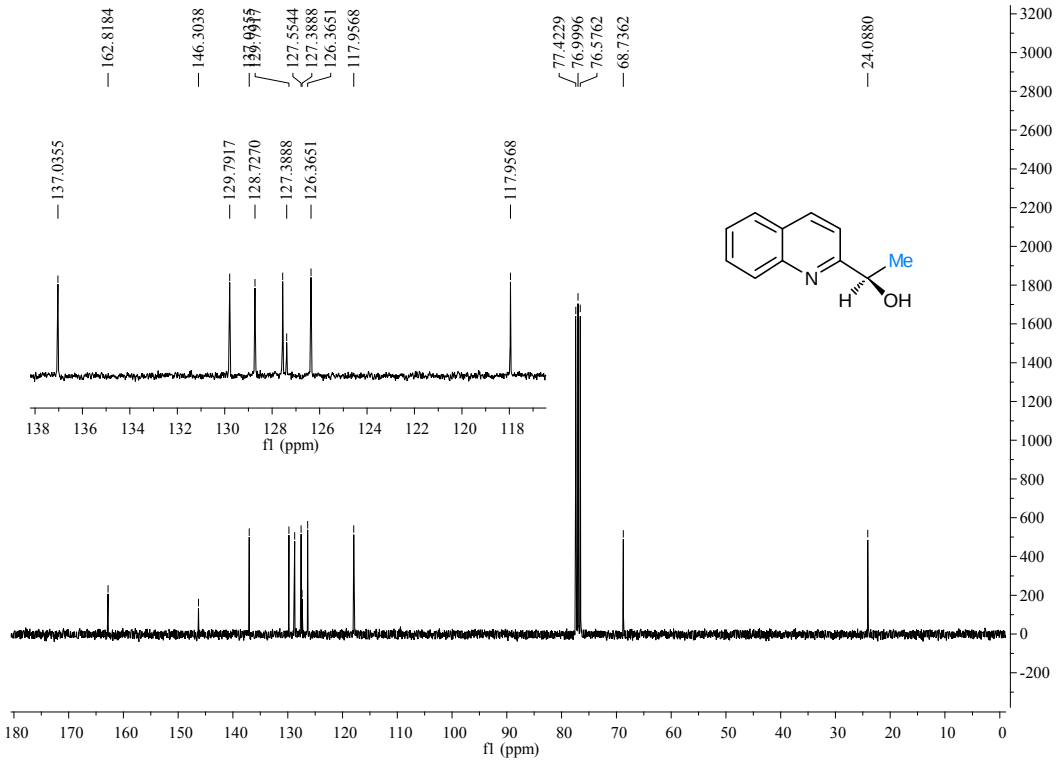
7.7031
7.5668
7.5417
7.5177
7.3676
7.3392
7.2602
5.0871
5.0538
5.0311
1.5924
1.5709
Me
N
H
OH
fl (ppm)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127.3888
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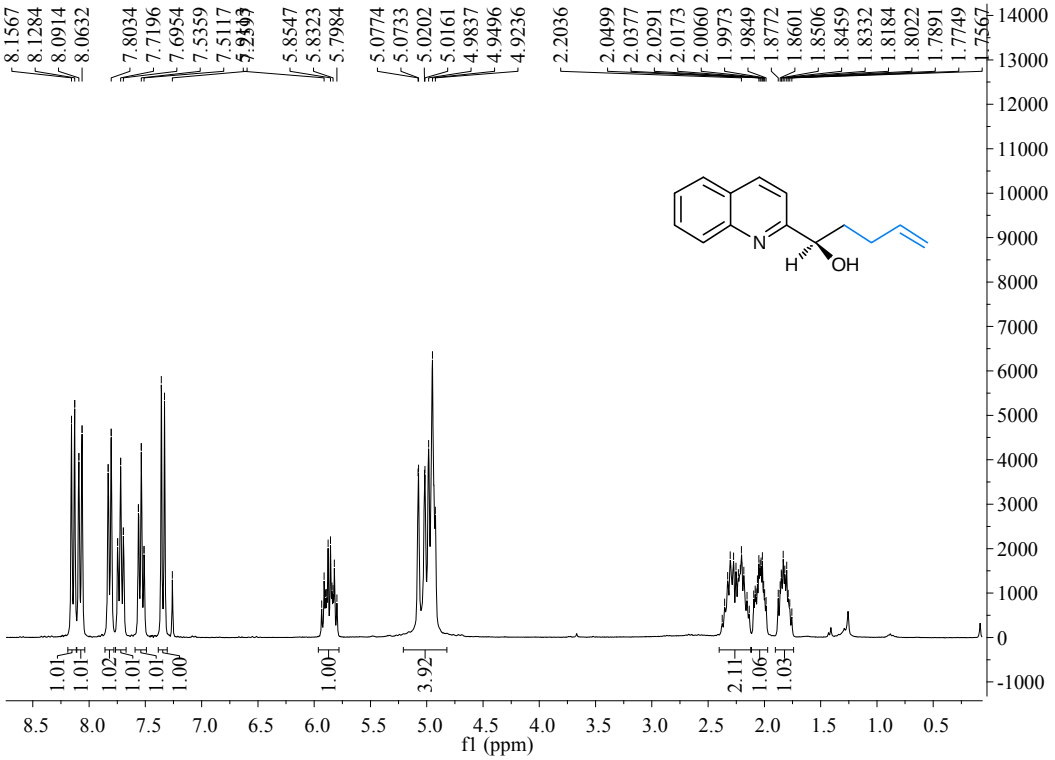
68.7362
24.0880
Me
N
H
OH
fl (ppm)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8.0914
8.0632
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7.5117
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5.8323
5.7984
5.0774
5.0733
5.0202
5.0161
4.9837
4.9496
4.9236
2.2036
2.0499
2.0377
2.0291
2.0173
2.0060
1.9973
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1.8772
1.8601
1.8506
1.8459
1.8332
1.8184
1.8022
1.7891
1.7749
1.7567
N
H
OH
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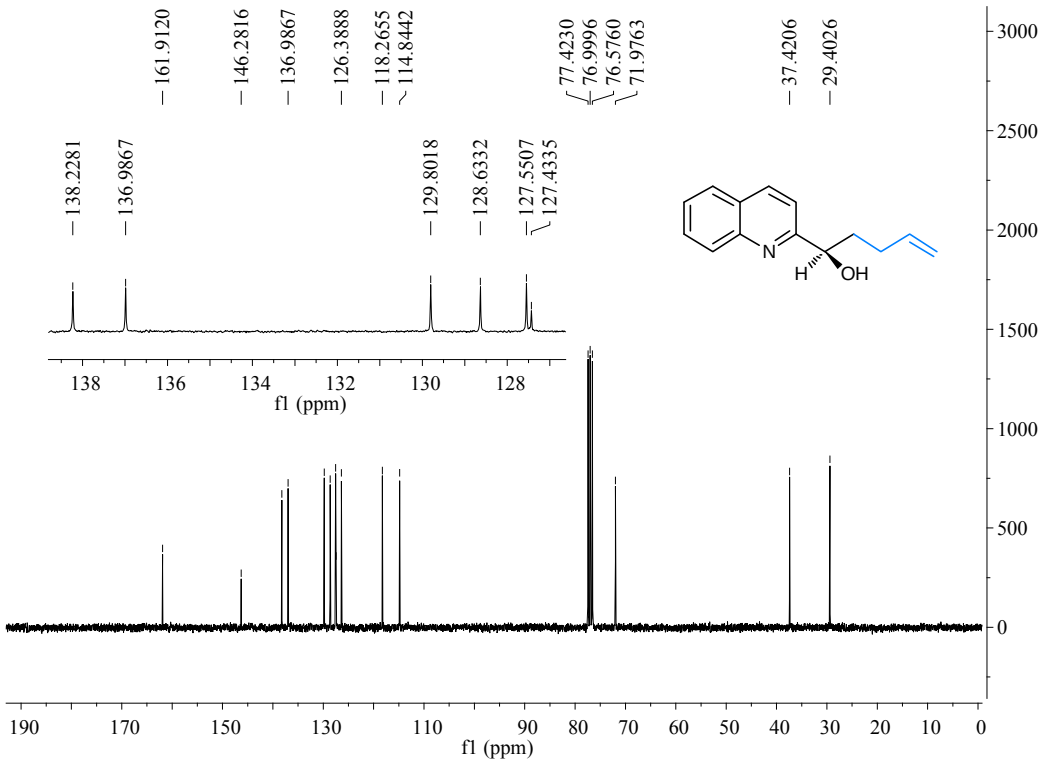
1.01
1.02
1.01
1.01
1.00
1.00
3.92
2.11
1.06
1.03
f1 (ppm)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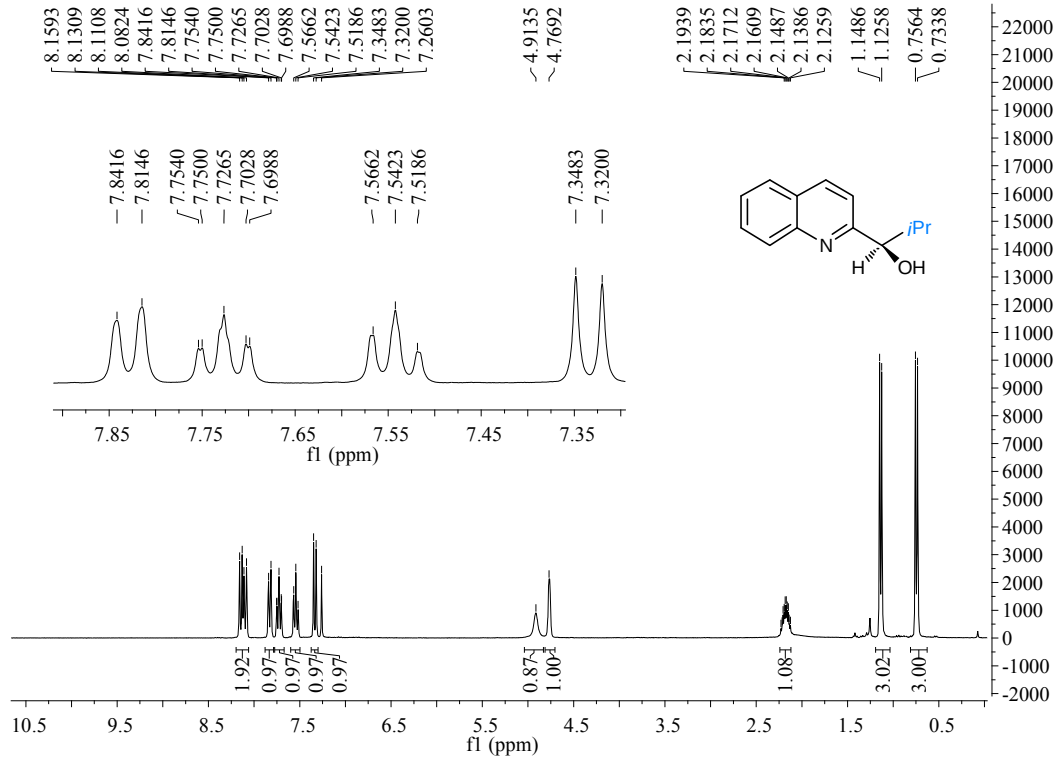
77.4230
76.9996
76.5760
71.9763
37.4206
29.4026
138.2281
136.9867
129.8018
128.6332
127.5507
127.4335
N
H
OH
f1 (ppm)
f1 (ppm)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8.0824
7.8416
7.8146
7.7540
7.7500
7.7265
7.7028
7.6988
7.5662
7.5423
7.5186
7.3483
7.3200
7.2603
4.9135
4.7692
2.1939
2.1835
2.1712
2.1609
2.1487
2.1386
2.1259
1.1486
1.1258
0.7564
0.7338
iPr
OH
fl (ppm)
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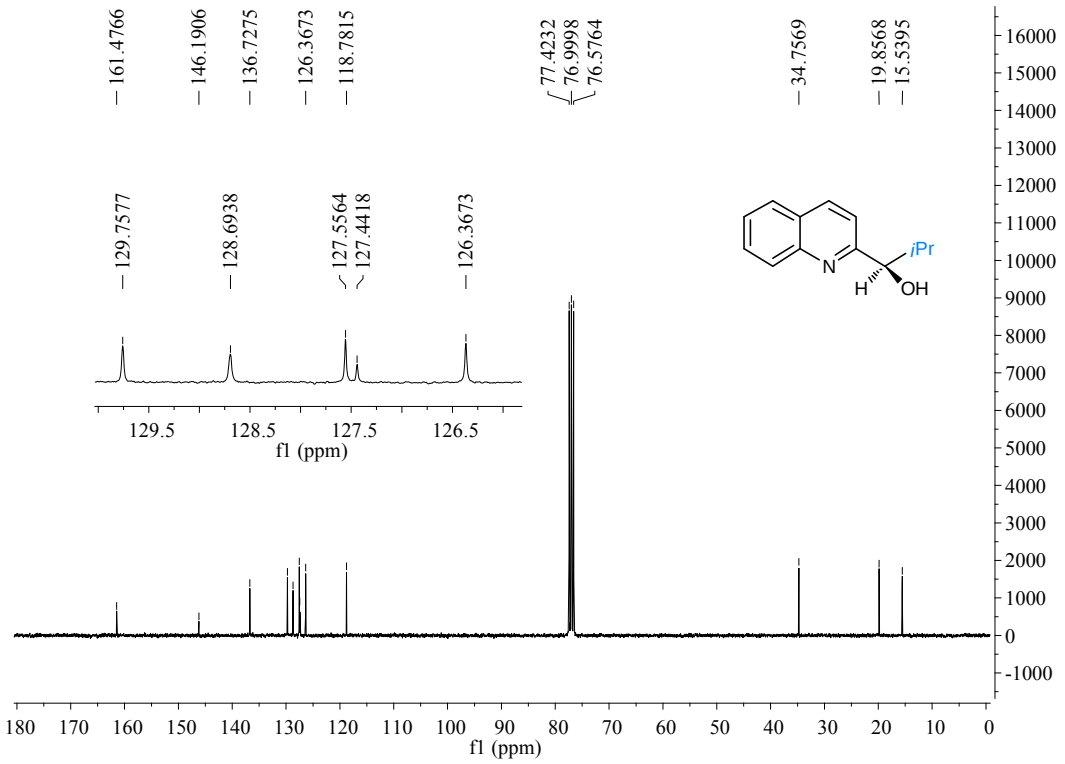
0.97
0.97
0.97
0.97
0.87
1.00
1.08
3.02
3.00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136.7275
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118.7815
77.4232
76.9998
76.5764
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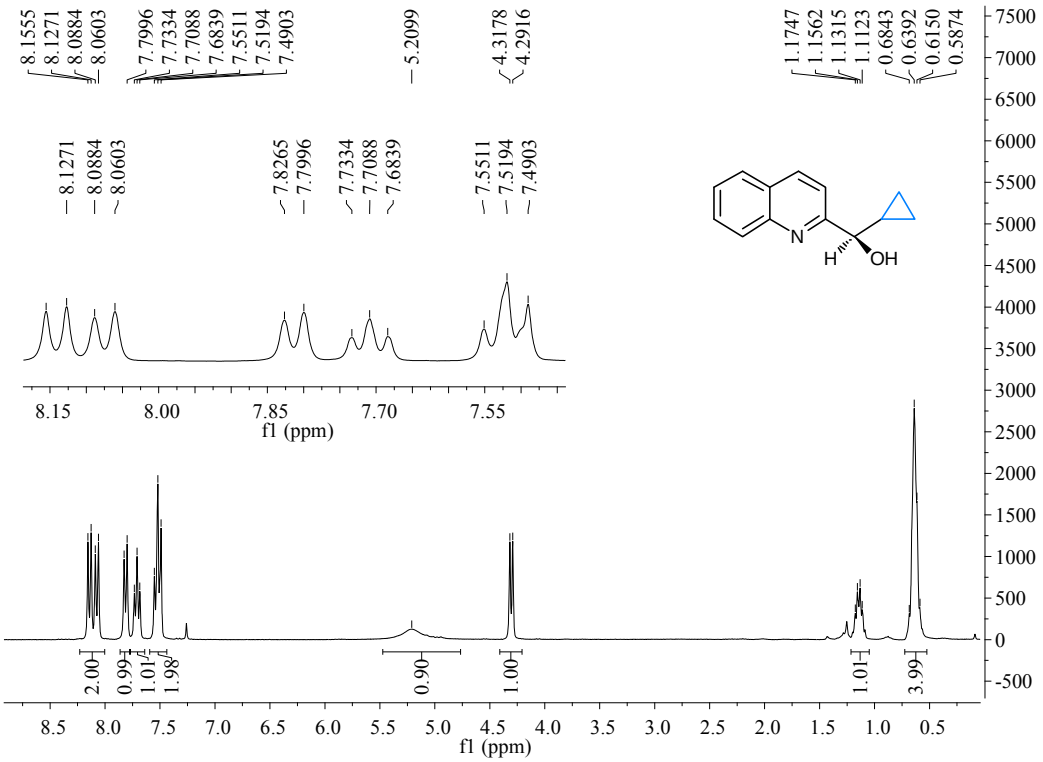
15.5395
129.7577
128.6938
127.5564
127.4418
126.3673
iPr
OH
fl (ppm)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8.1271
8.0884
8.0603
7.7996
7.7334
7.7088
7.6839
7.5511
7.5194
7.4903
5.2099
4.3178
4.2916
1.1747
1.1562
1.1315
1.1123
0.6843
0.6392
0.6150
0.5874
8.8265
7.7996
7.7334
7.7088
7.6839
7.5511
7.5194
7.4903
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H
OH
f1 (ppm)
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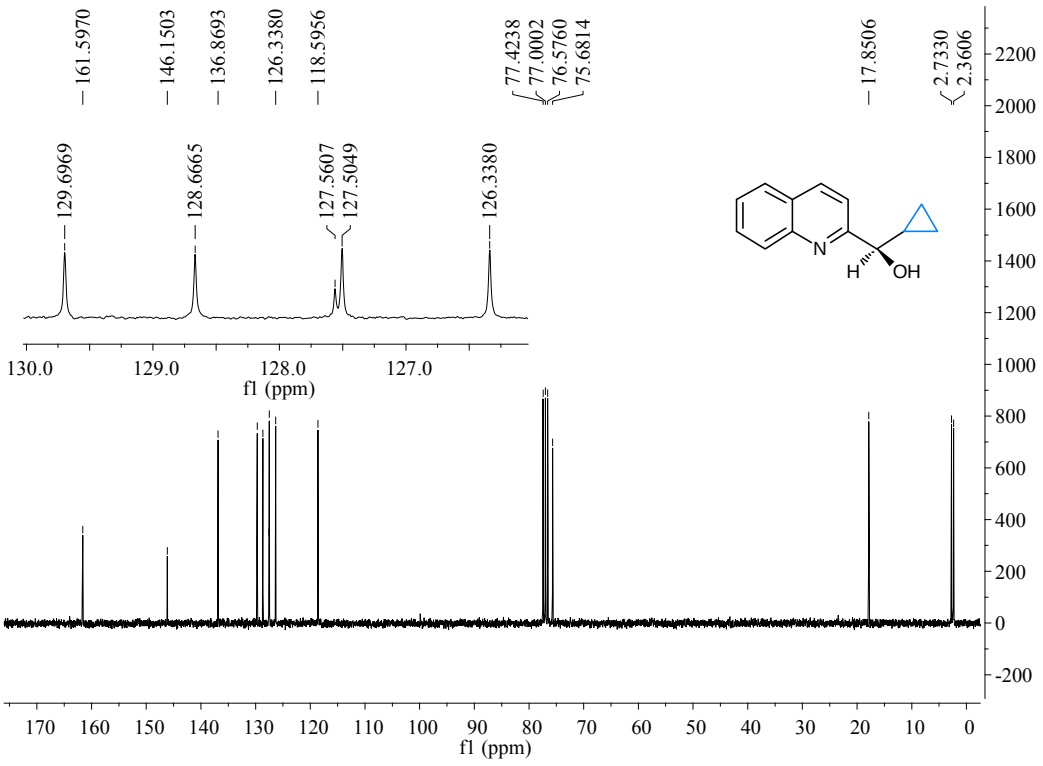
1.01
1.98
0.90
1.00
1.01
3.99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2.3606
129.6969
128.6665
127.5607
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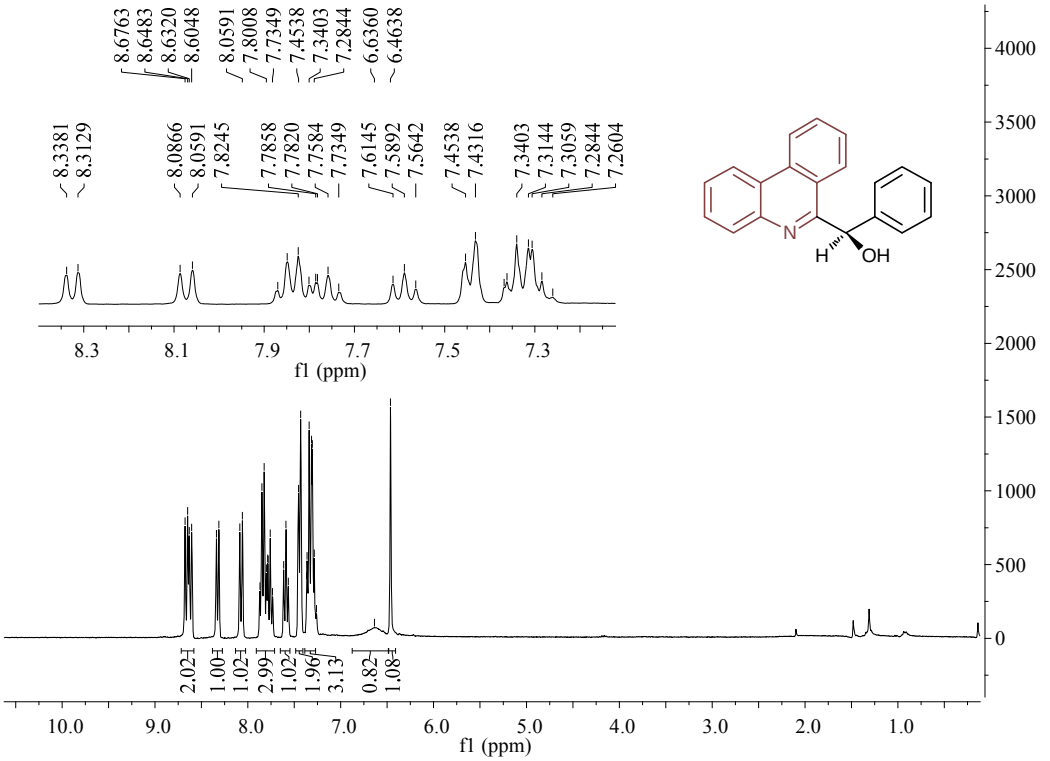
N
H
OH
f1 (ppm)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7.7349
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7.3403
7.2844
6.6360
6.4638
8.3381
8.3129
8.0866
8.0591
7.8245
7.7858
7.7820
7.7584
7.7349
7.6145
7.5892
7.5642
7.4538
7.4316
7.3403
7.3144
7.3059
7.2844
7.2604
N
H
OH
fl (ppm)
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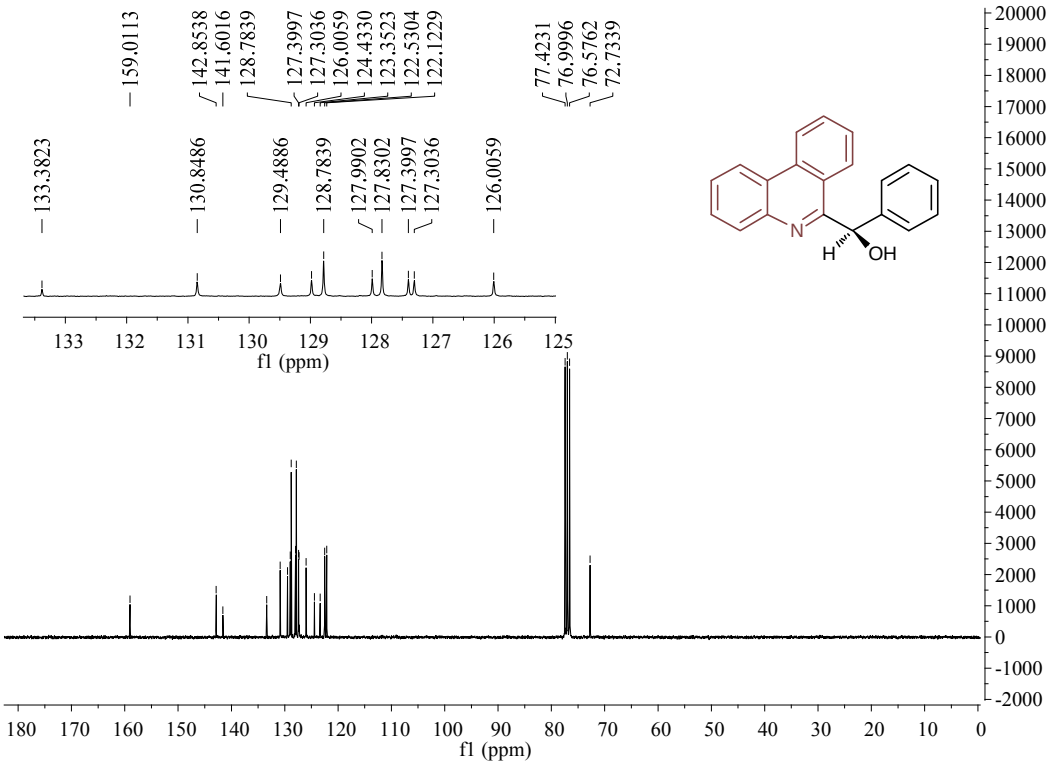
1.00
1.02
2.99
1.02
1.96
3.13
0.82
1.08
fl (ppm)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142.8538
141.6016
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127.3997
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126.0059
124.4330
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122.1229
77.4231
76.9996
76.5762
72.7339
133.3823
130.8486
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127.8302
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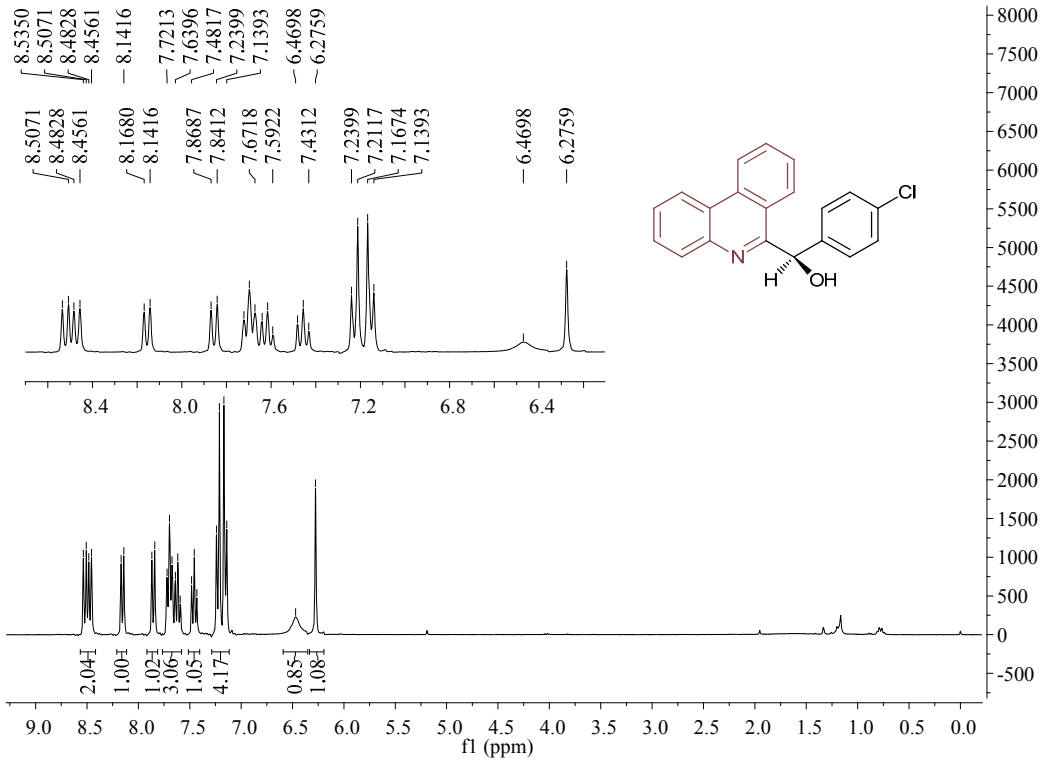
127.3036
126.0059
N
H
OH
fl (ppm)
fl (ppm)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7.6396
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7.2399
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6.4698
6.2759
8.1680
7.8687
7.8412
7.6718
7.5922
7.4312
7.2117
7.1674
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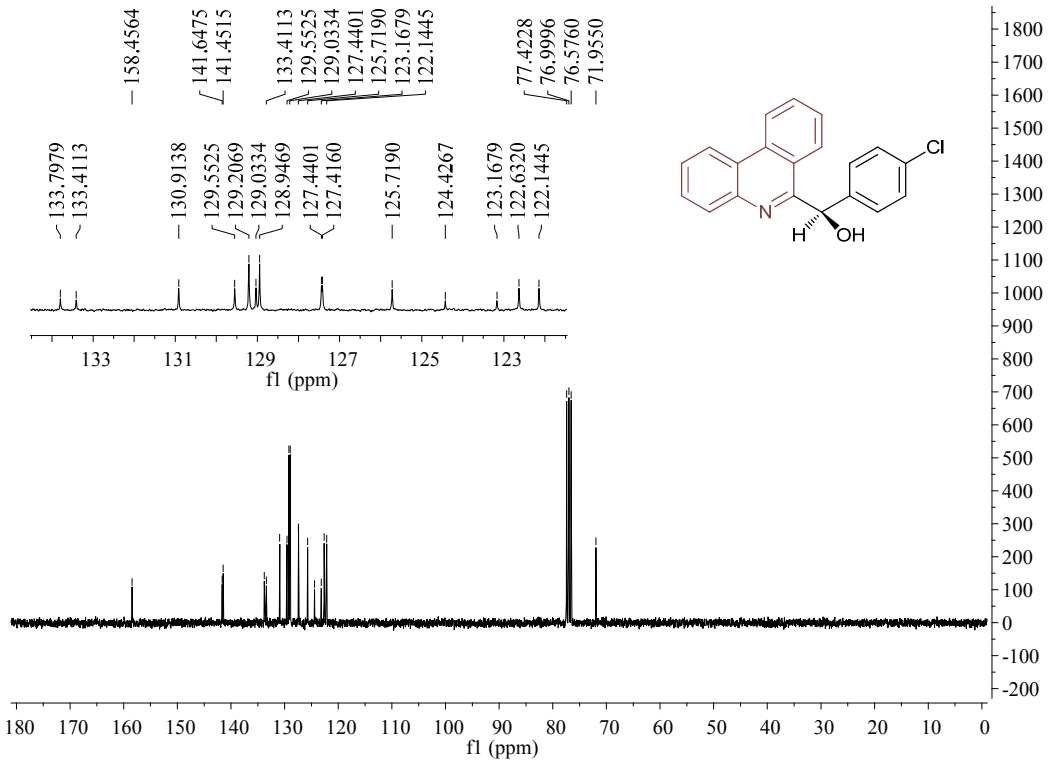
1.00
1.02
3.06
1.05
4.17
0.85
1.08
Cl
N
H
OH
f1 (ppm)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141.4515
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129.5525
129.0334
127.4401
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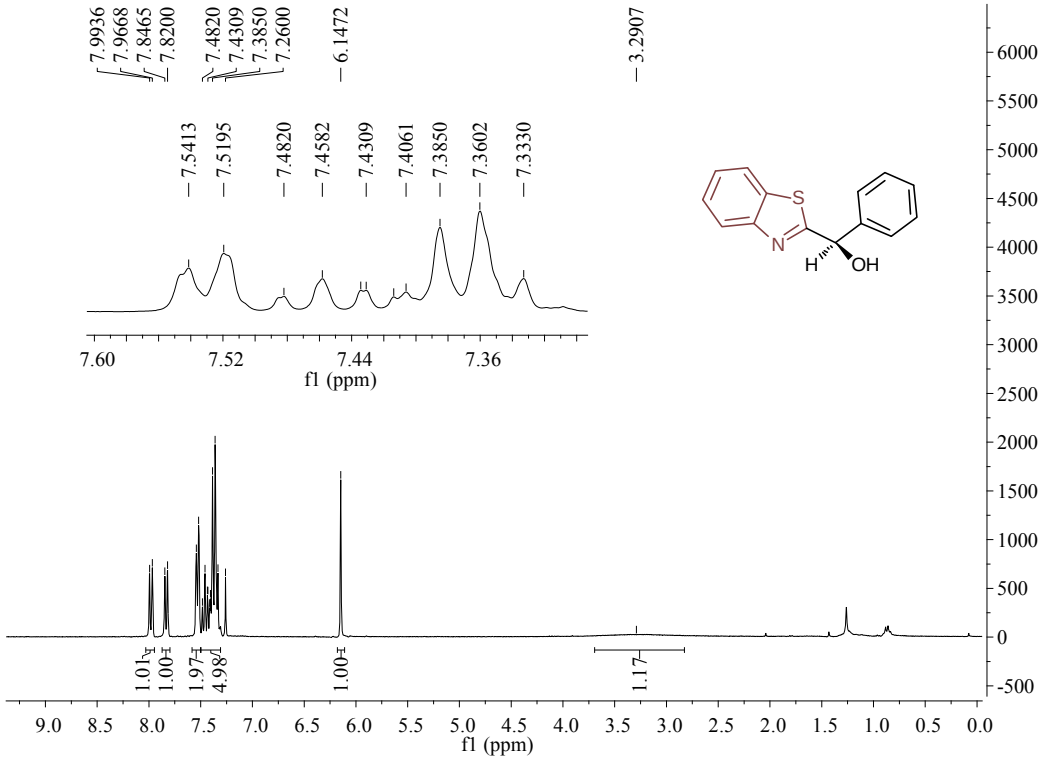
123.1679
122.1445
77.4228
76.9996
76.5760
71.9550
133.7979
130.9138
129.2069
128.9469
127.4160
124.4267
122.6320
Cl
N
H
OH
f1 (ppm)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7.4820
7.4309
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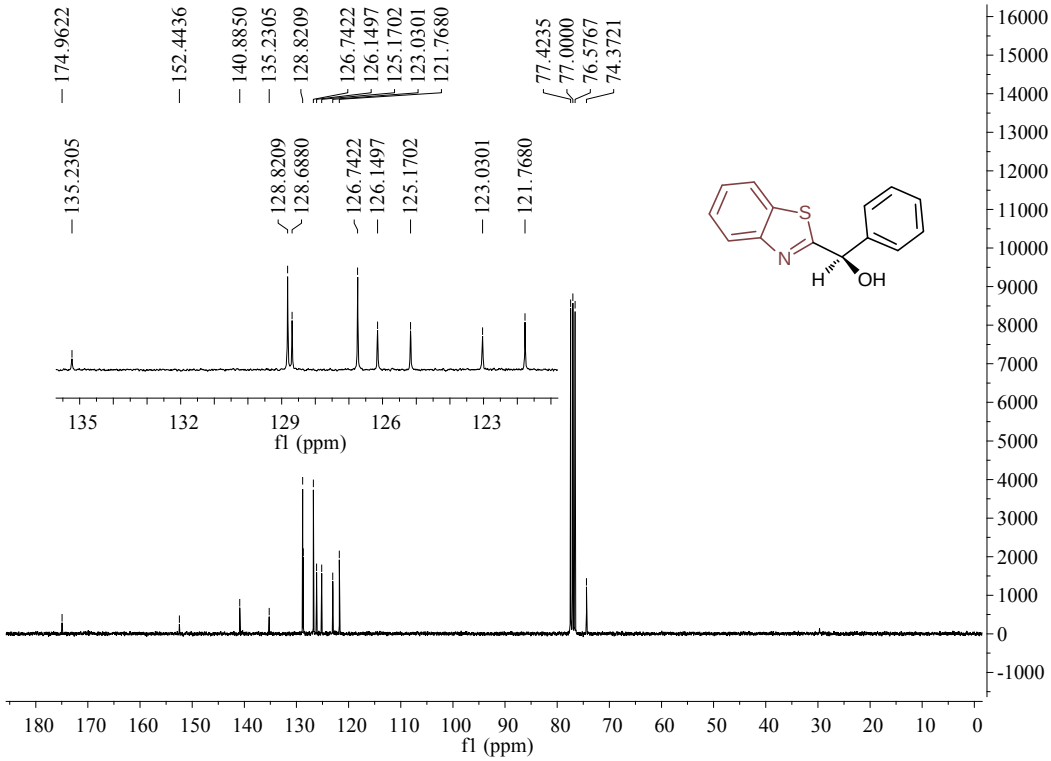
3.2907
7.5413
7.5195
7.4820
7.4582
7.4309
7.4061
7.3850
7.3602
7.3330
7.60
7.52
7.44
7.36
f1 (ppm)
S
N
H
OH
1.01
1.00
1.97
4.98
1.00
1.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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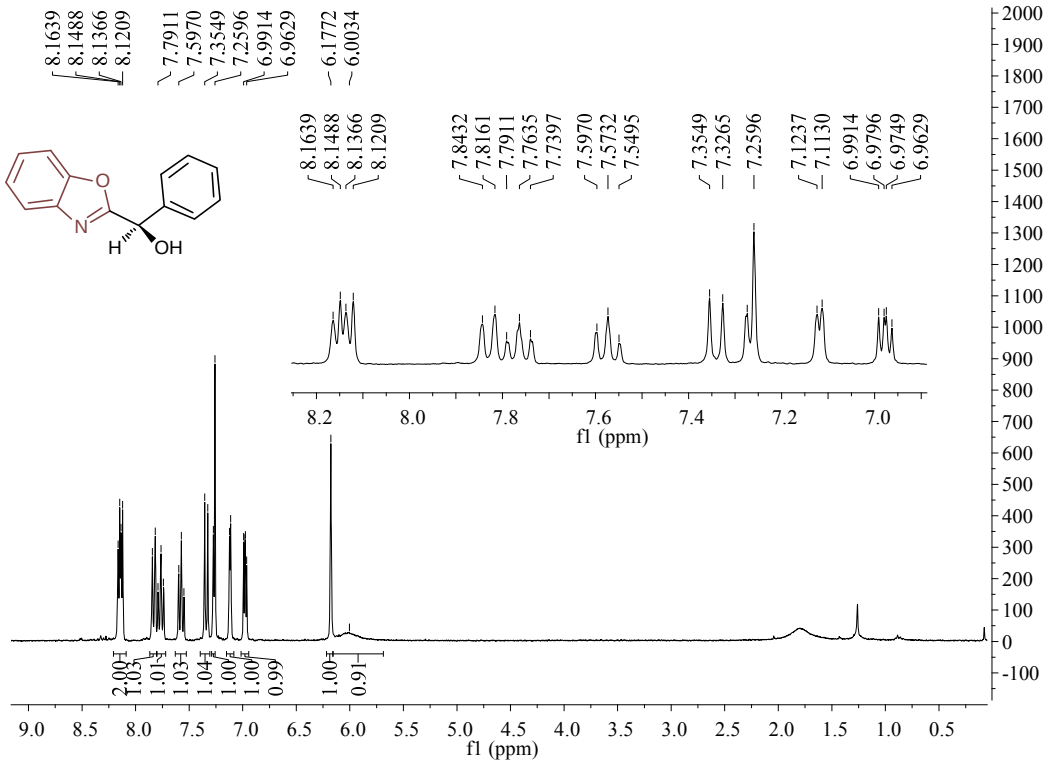
152.4436
140.8850
135.2305
128.8209
126.7422
126.1497
125.1702
123.0301
121.7680
77.4235
77.0000
76.5767
74.3721
135.2305
128.8209
128.6880
126.7422
126.1497
125.1702
123.0301
121.7680
135
132
129
126
123
f1 (ppm)
S
N
H
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.1488
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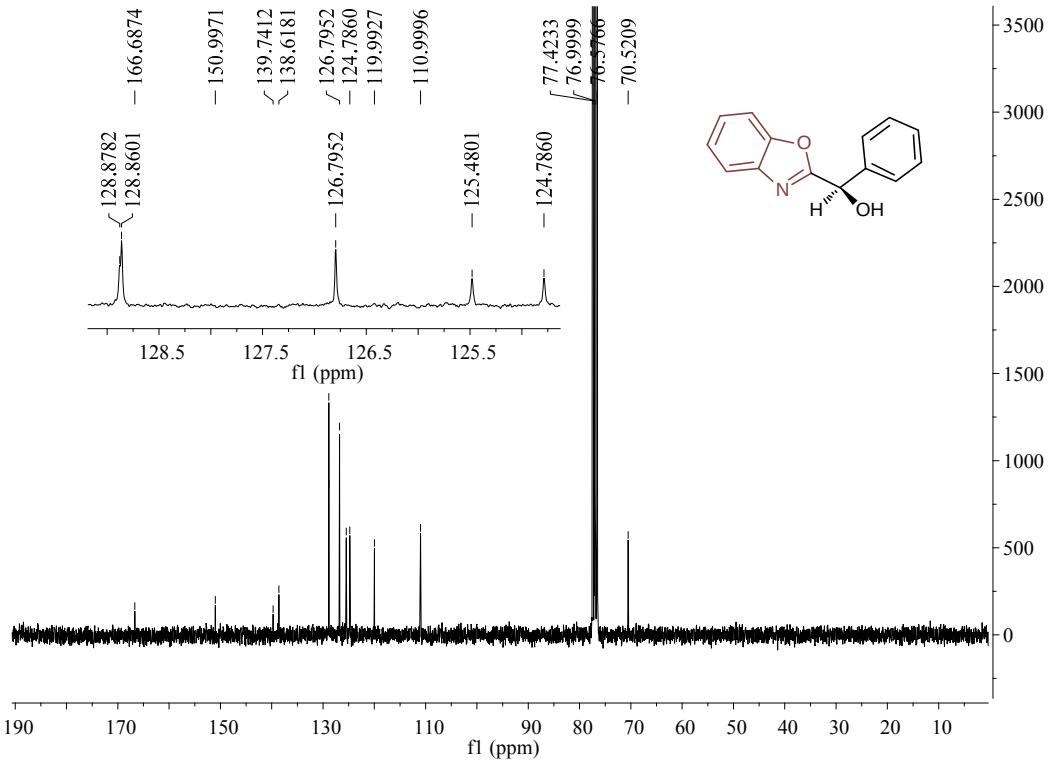
6.9914
6.9629
6.1772
6.0034
7.8432
7.8161
7.7911
7.7635
7.7397
7.5970
7.5732
7.5495
7.3549
7.3265
7.2596
7.1237
7.1130
6.9914
6.9796
6.9749
6.9629
2.00
2.03
1.01
1.03
1.04
1.00
1.00
0.99
1.00
0.91
f1 (ppm)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150.9971
139.7412
138.6181
126.7952
124.7860
119.9927
110.9996
77.4233
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76.5766
70.5209
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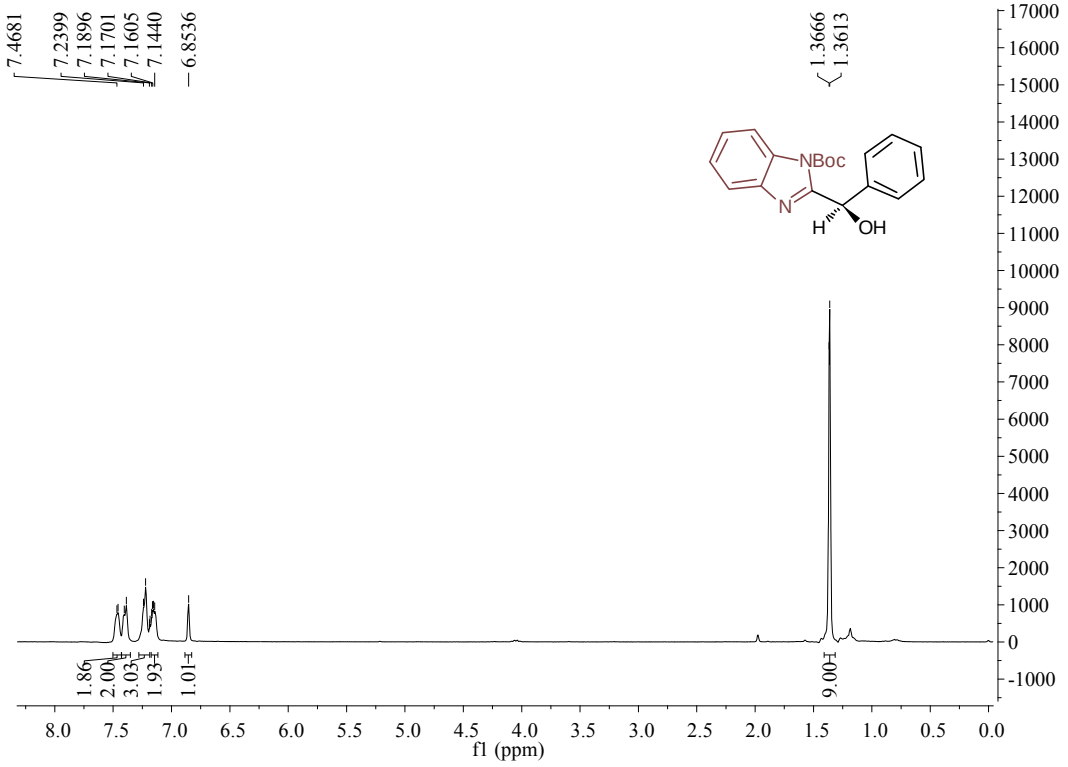
128.8601
126.7952
125.4801
124.7860
f1 (ppm)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7.1896
7.1701
7.1605
7.1440
6.8536
1.3666
1.3613
NBoc
N
H
OH
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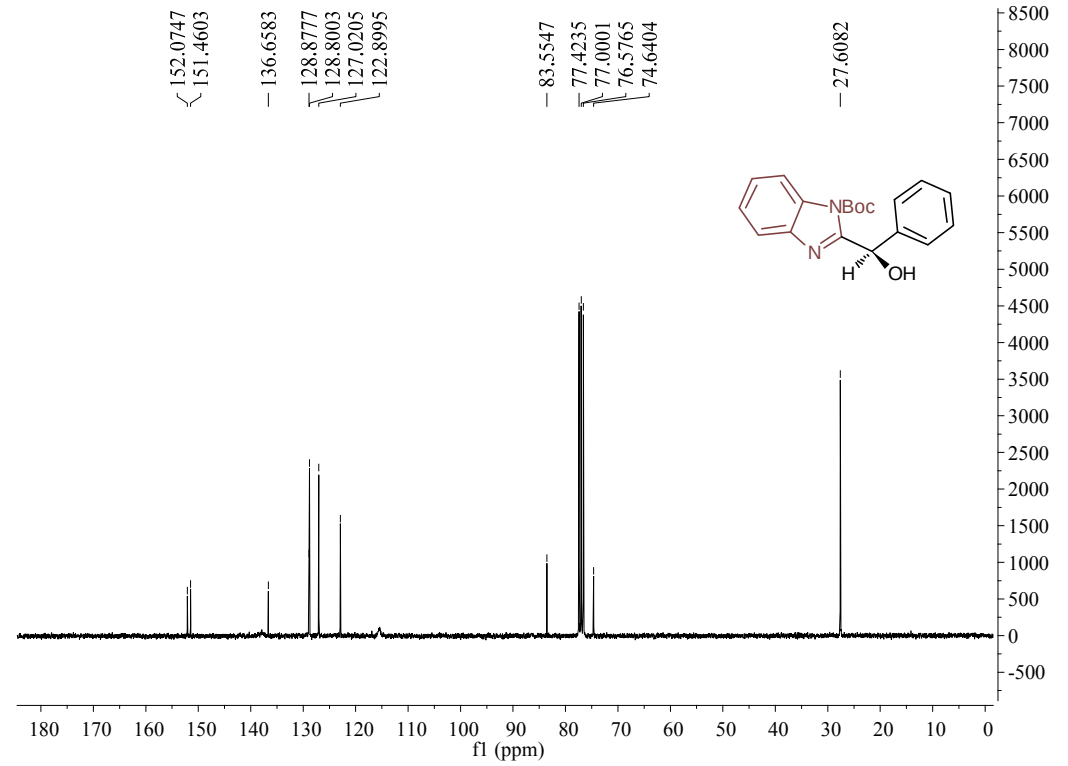
2.00
3.03
1.93
1.01
9.00
f1 (ppm)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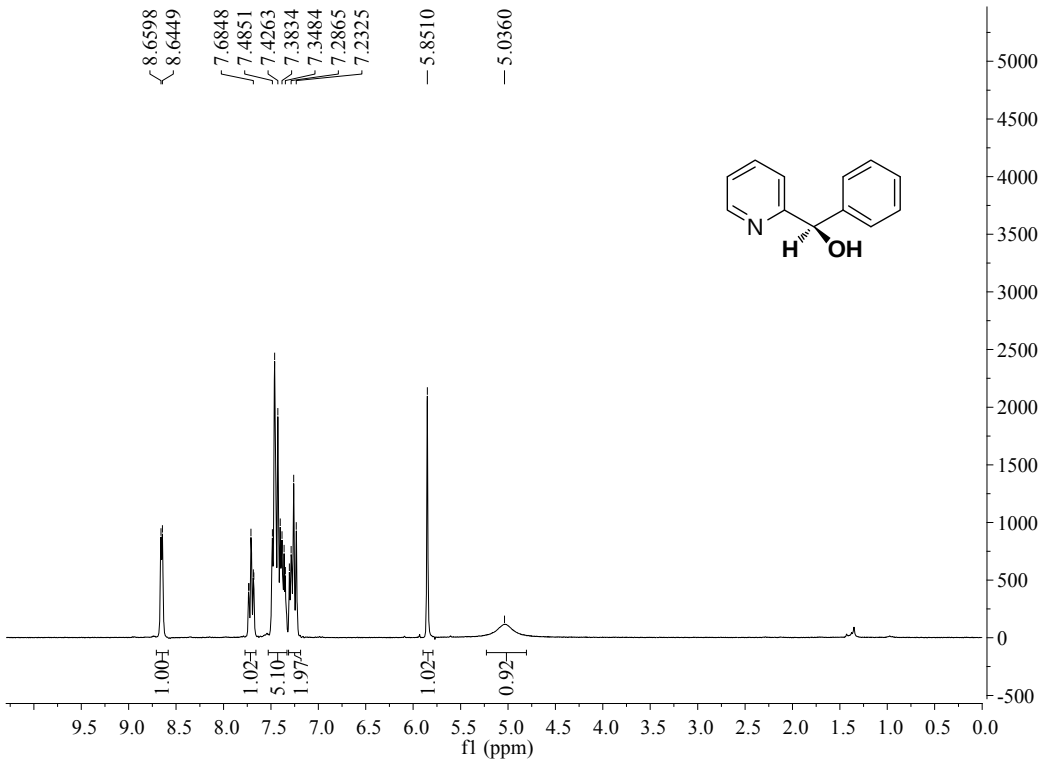
NBoc
N
H
OH
f1 (ppm)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7.3484
7.2865
7.2325
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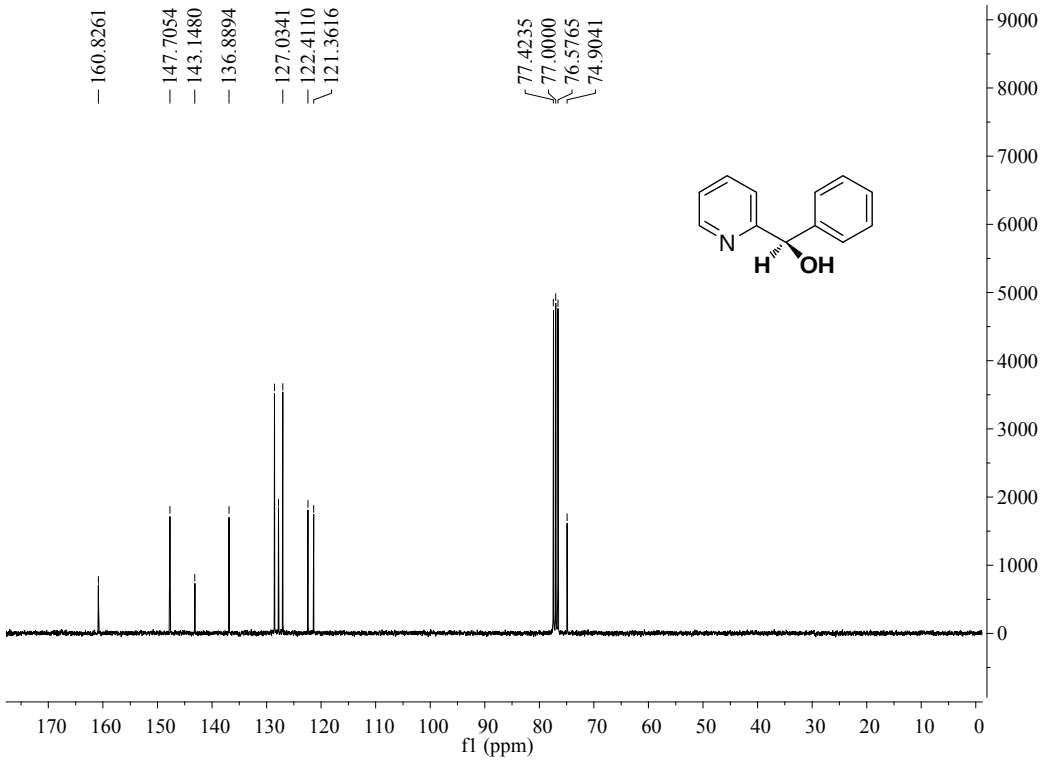
1.00
1.02
5.10
1.97
1.02
0.92
N
H
OH
f1 (ppm)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127.0341
122.4110
121.3616
77.4235
77.0000
76.5765
74.9041
N
H
OH
f1 (ppm)

8. References

1. (a) S. Sultan, M. A. Rizvi, J. Kumar, B. A. Shah *Chem. Eur. J.* 2018, **24**, 10617; (b) X. Wu, X. Geng, P. Zhao, J. Zhang, X. Gong, Y.-D. Wu, A.-X. Wu *Org. Lett.* 2017, **19**, 1550.