Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

9-amino-(9-deoxy)cinchona alkaloids-derived novel chiral phase-transfer catalysts

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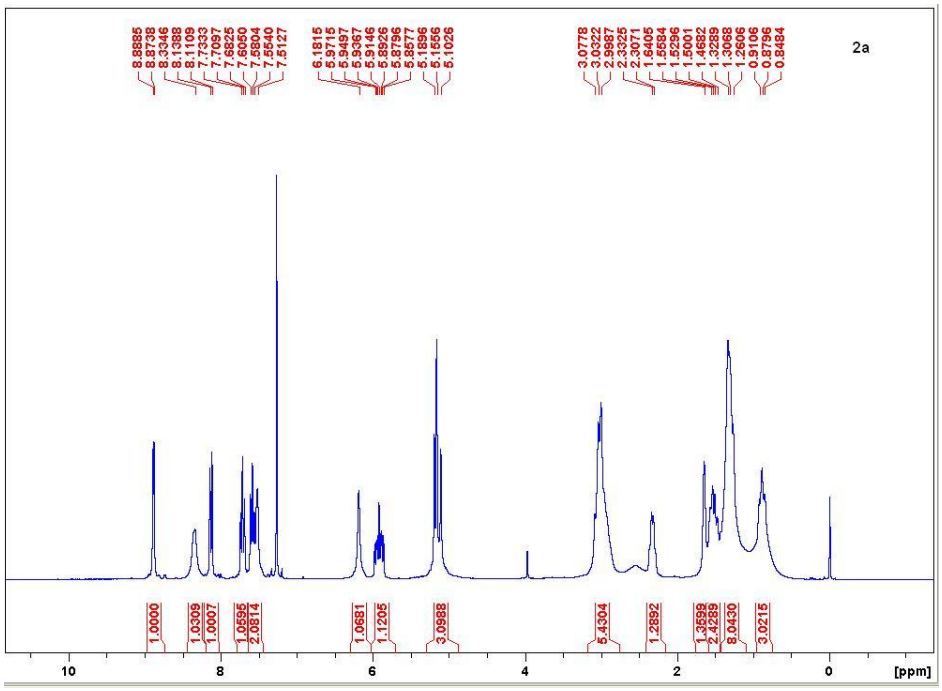
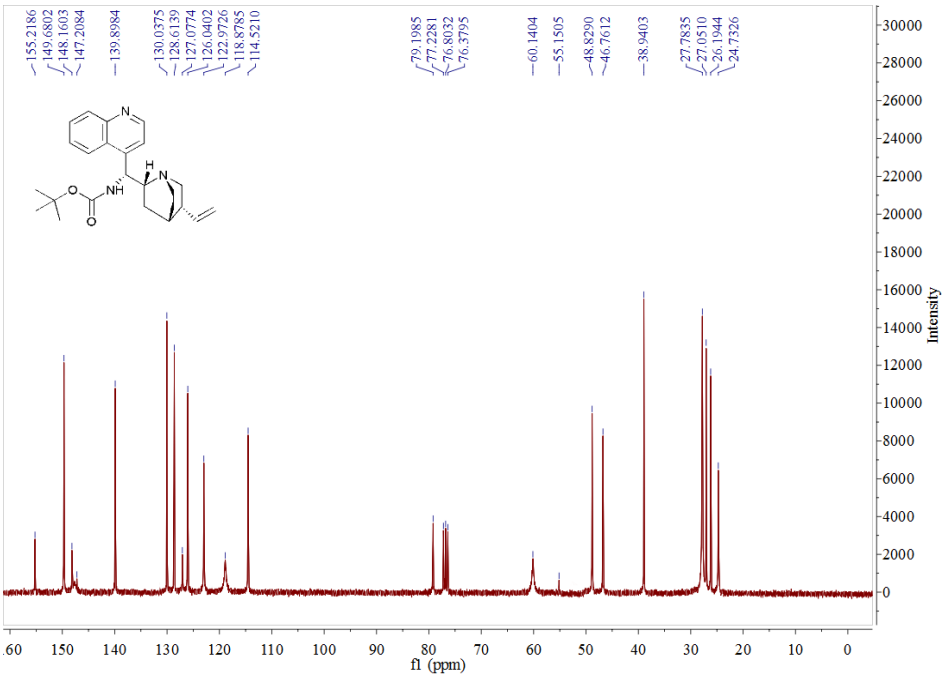
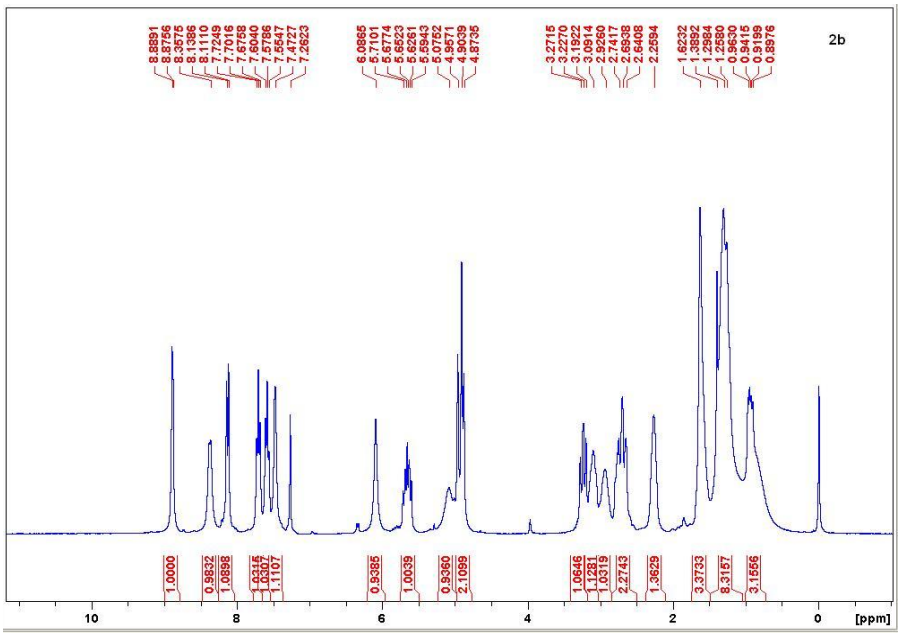
Chongqing, 400715, P. R. China

1. NMR spectra

1.1 ^{1}H and ^{13}C NMR spectra of **2a-d**



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7.4727
7.2623
6.0865
5.7101
5.6774
5.6523
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5.0762
4.9671
4.9631
4.8735
3.2715
3.2270
3.1922
3.0914
2.9260
2.7417
2.6938
2.6408
2.2594
1.6232
1.3892
1.2984
1.2680
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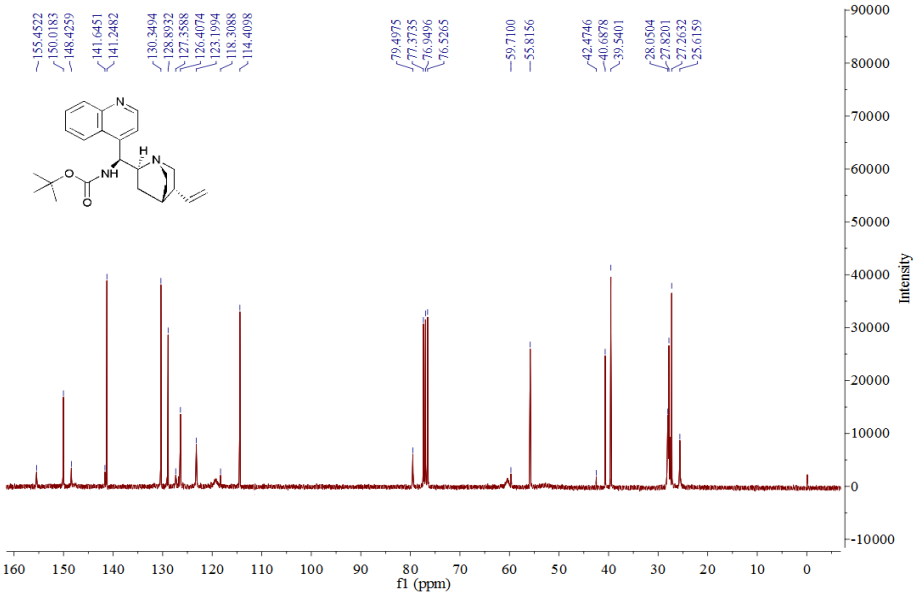
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79.4975
77.3735
76.9496
76.5265
59.7100
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40.6878
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28.0504
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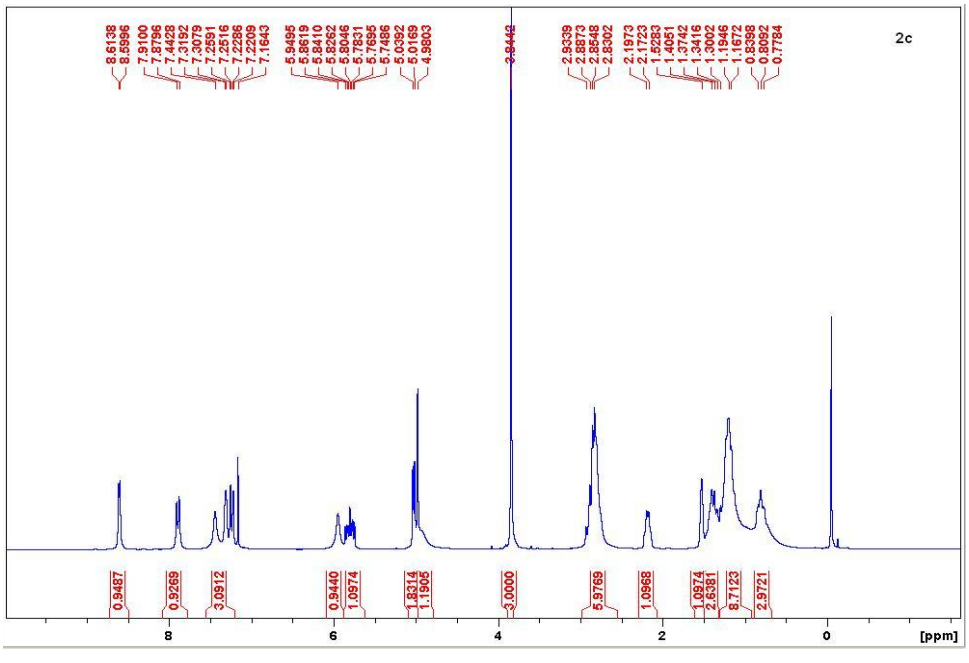
27.2632
25.6159
Intensity
f1 (ppm)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7.2209
7.1643
5.9495
5.8619
5.8410
5.8262
5.8046
5.7831
5.7685
5.7486
5.0392
5.0169
4.9803
3.8442
2.9339
2.8873
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2.1723
1.8283
1.4051
1.3742
1.3416
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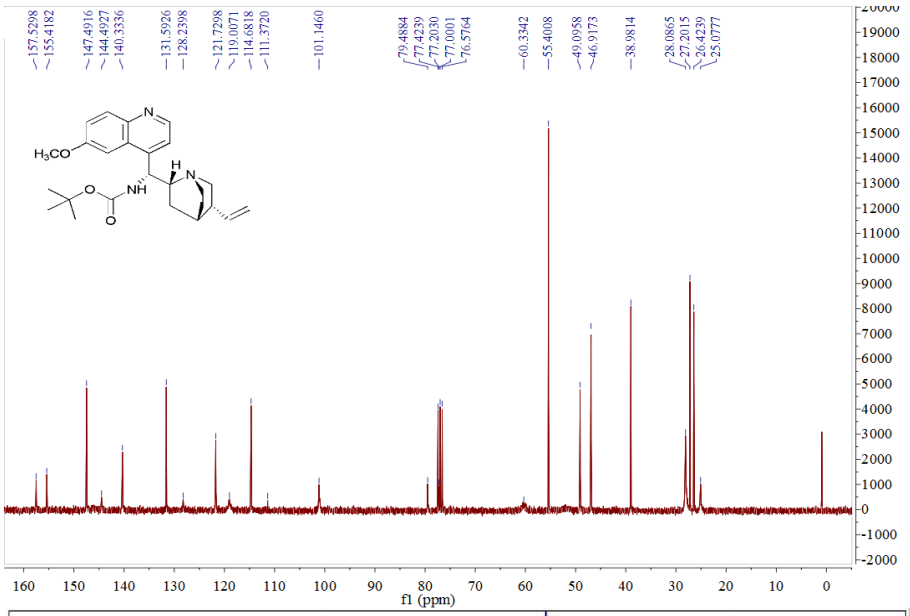
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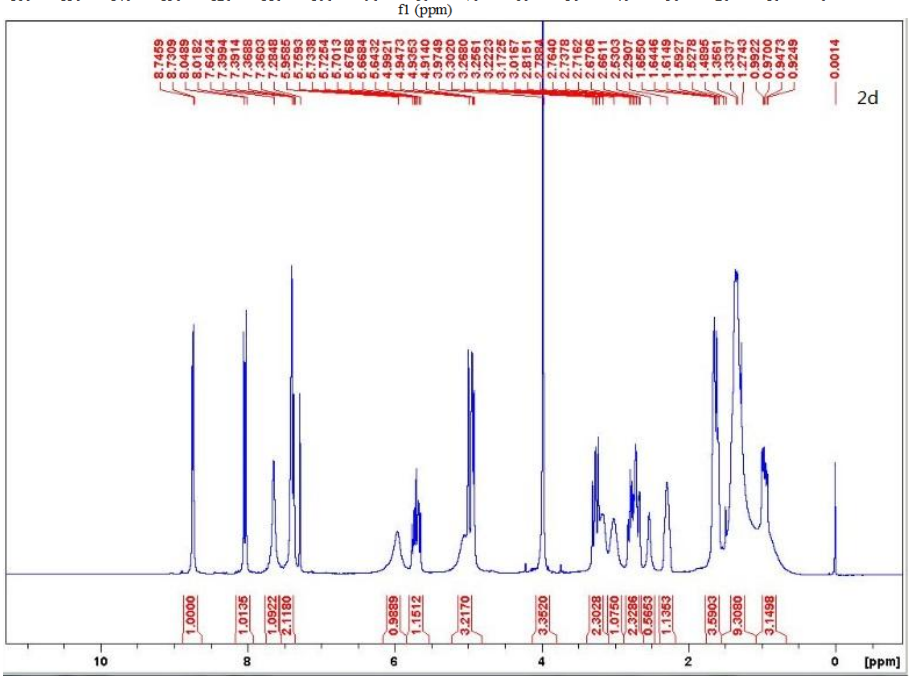
f1 (ppm)


2d
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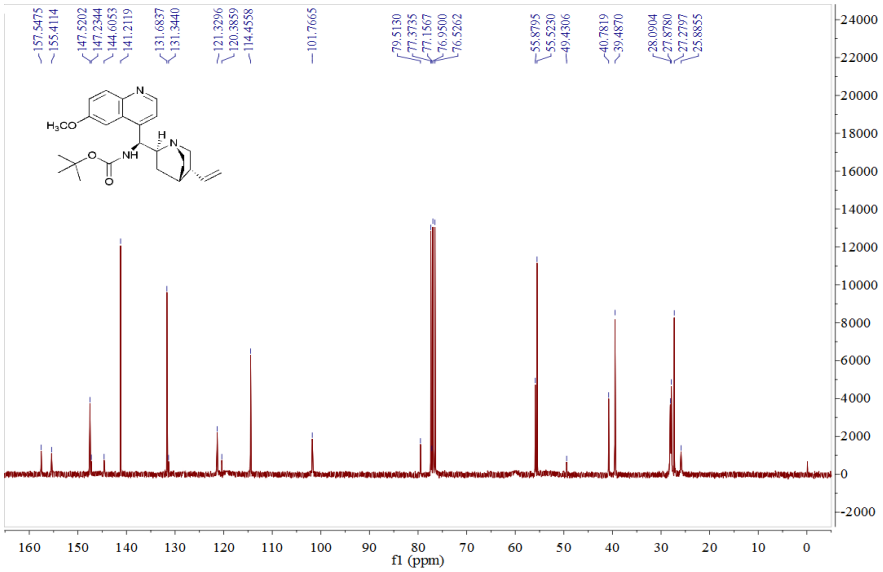
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101.7665
79.5130
77.3735
77.1567
76.9500
76.5262
55.8795
55.5230
49.4306
40.7819
39.4870
28.0904
27.8780
27.2797
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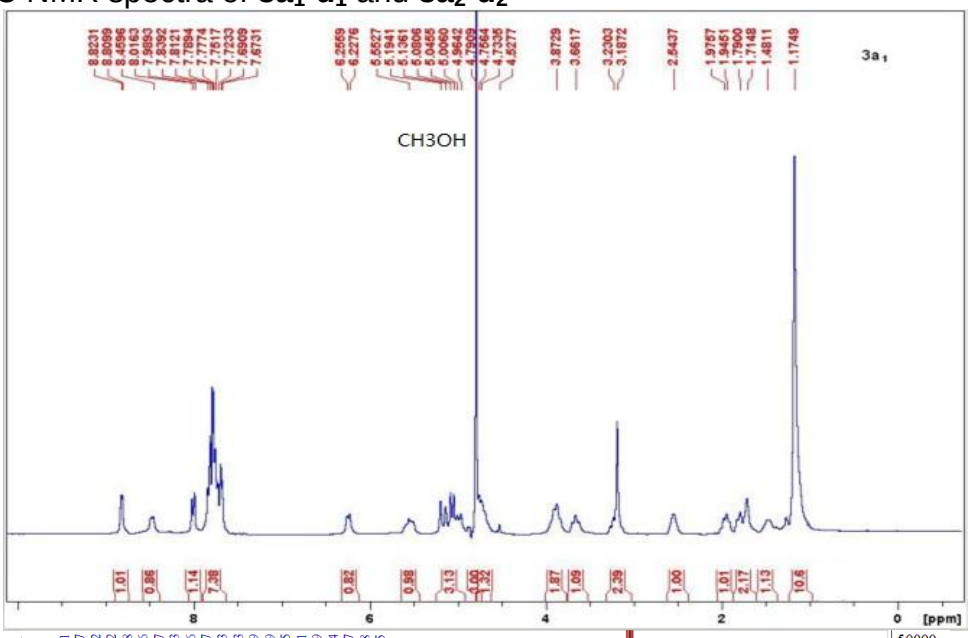
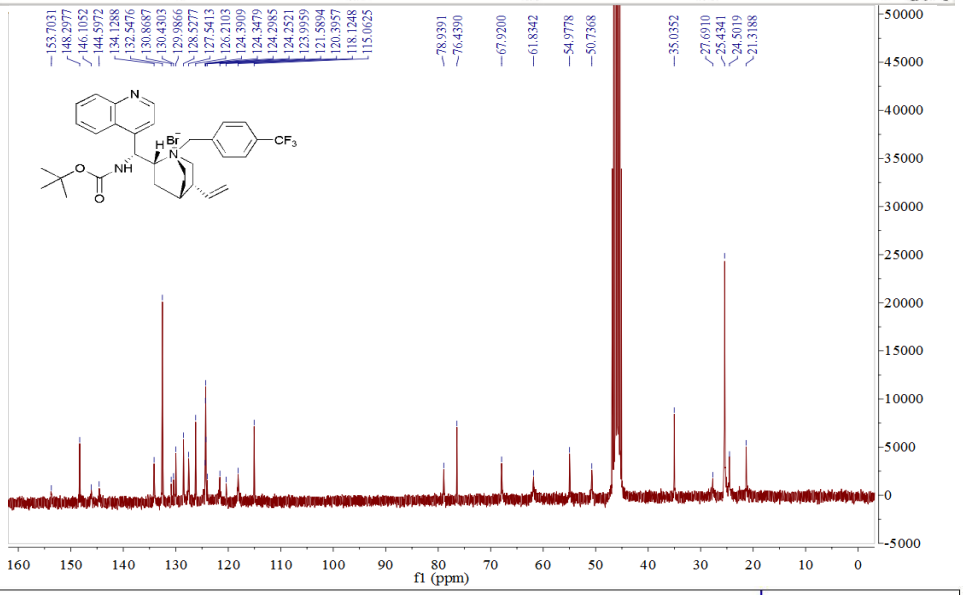
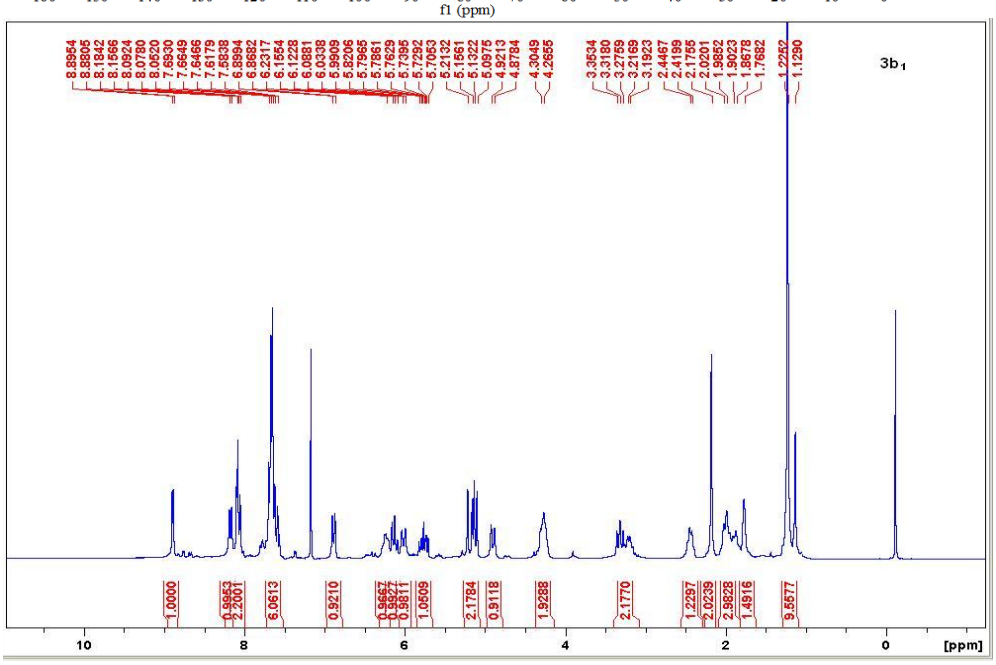
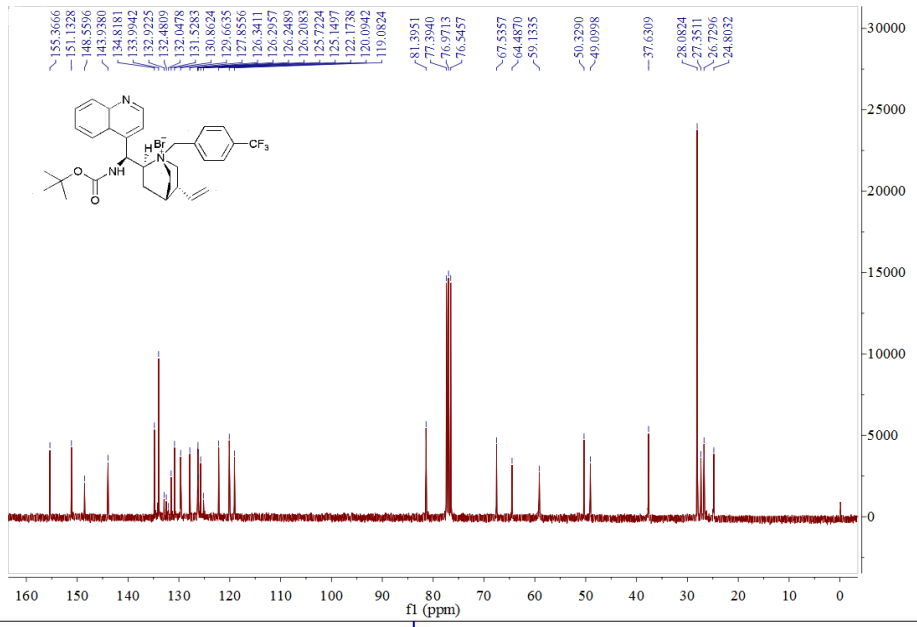
f1 (ppm)

1.2 ^{1}H and ^{13}C NMR spectra of **$3a_1$-d_1** and **$3a_2$-d_2**





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129.6635
127.8556
126.3411
126.2957
126.2489
126.2083
125.7224
125.1497
122.1738
120.0942
119.0824
81.3951
77.3940
76.9713
76.5457
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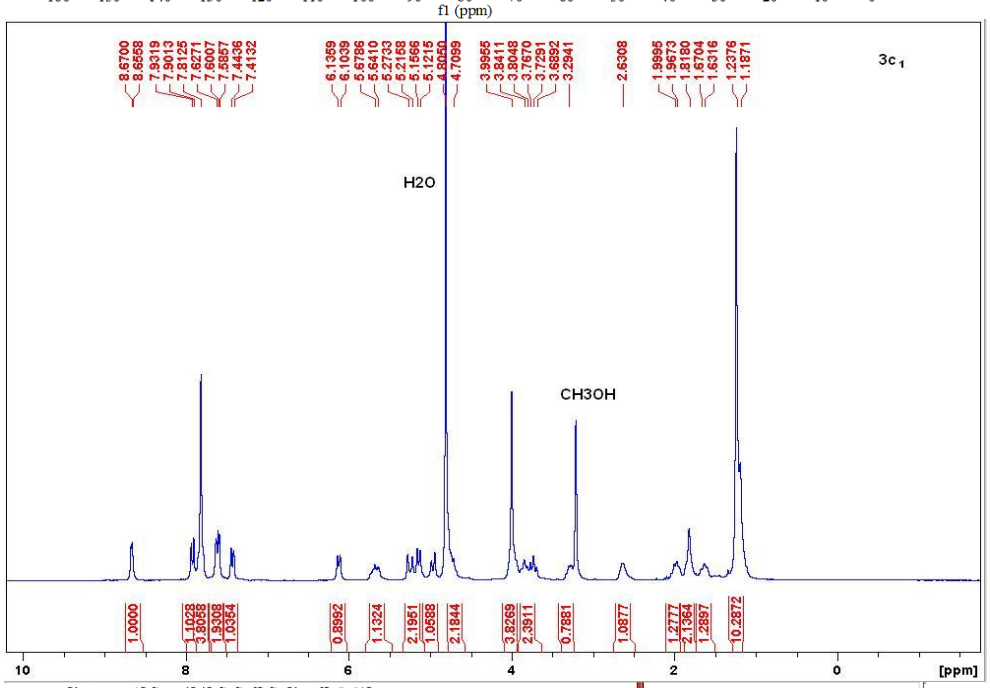
f1 (ppm)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6.1359
6.1039
5.6786
5.6410
5.2733
5.2158
5.1566
5.1215
4.8050
4.7099
3.9965
3.8411
3.8048
3.7670
3.7291
3.6892
3.2941
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1.9995
1.9673
1.8180
1.6704
1.6316
1.2376
1.1871
3c 1
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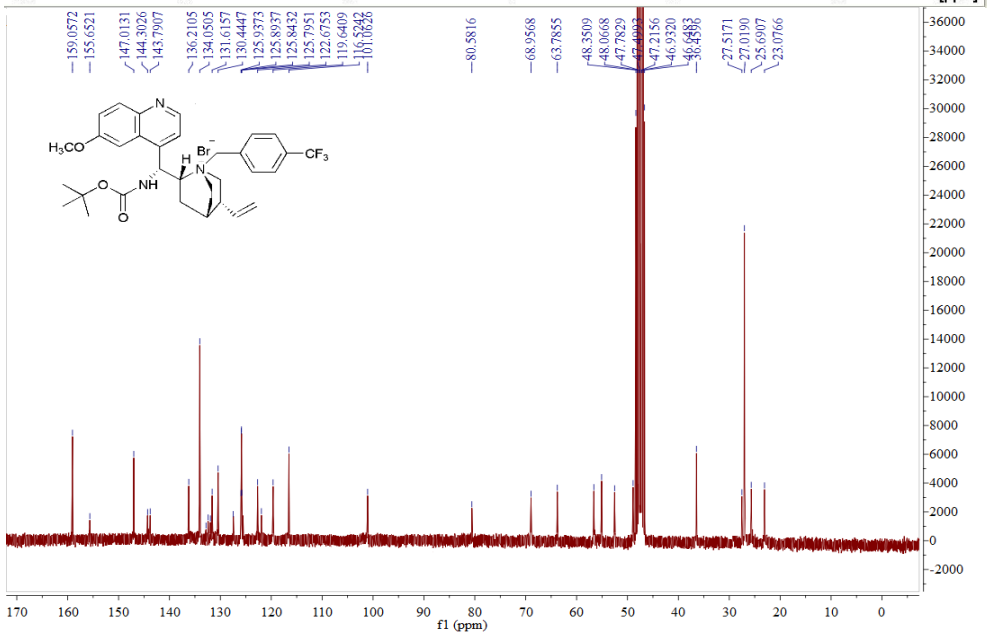
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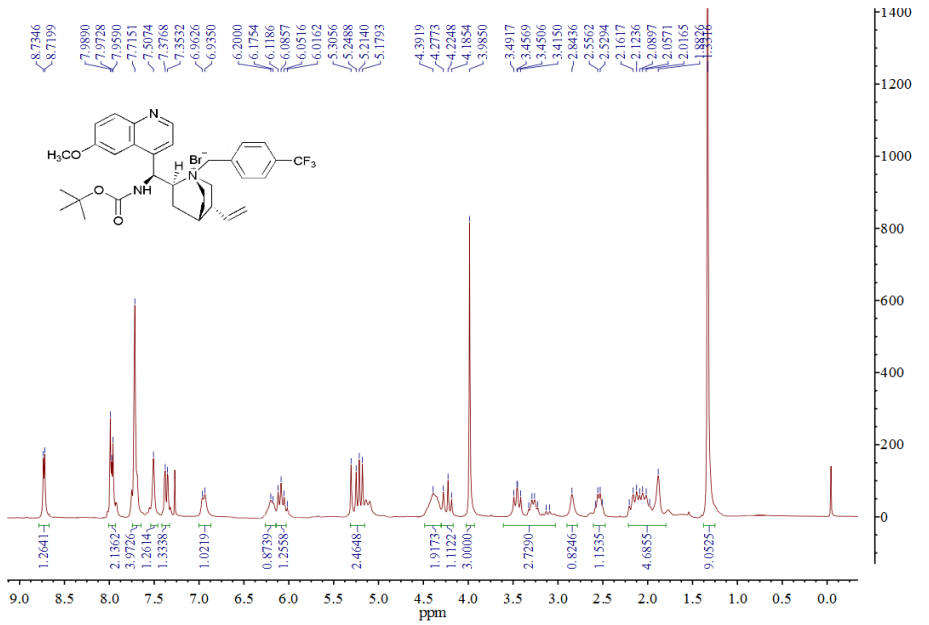
f1 (ppm)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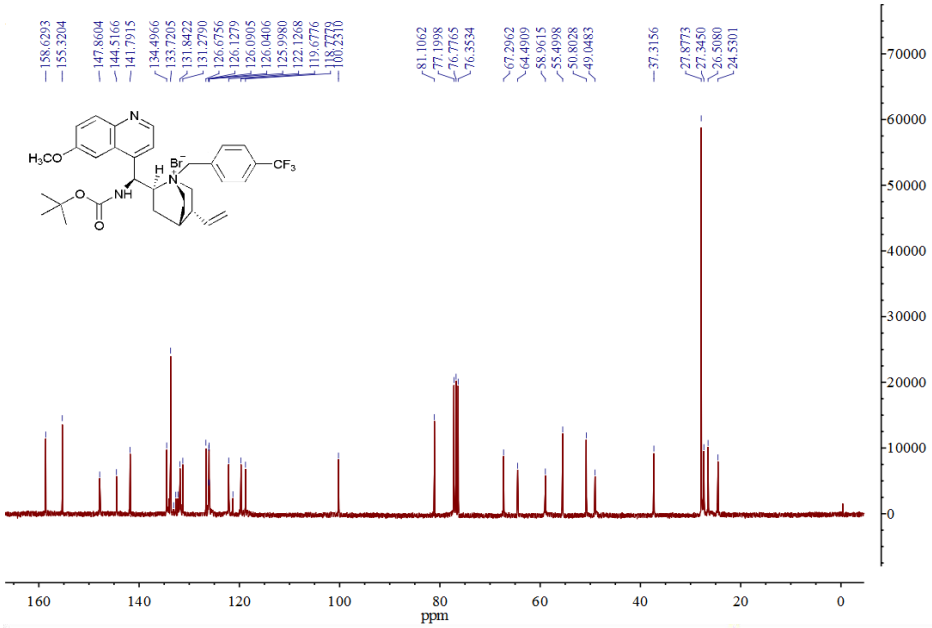
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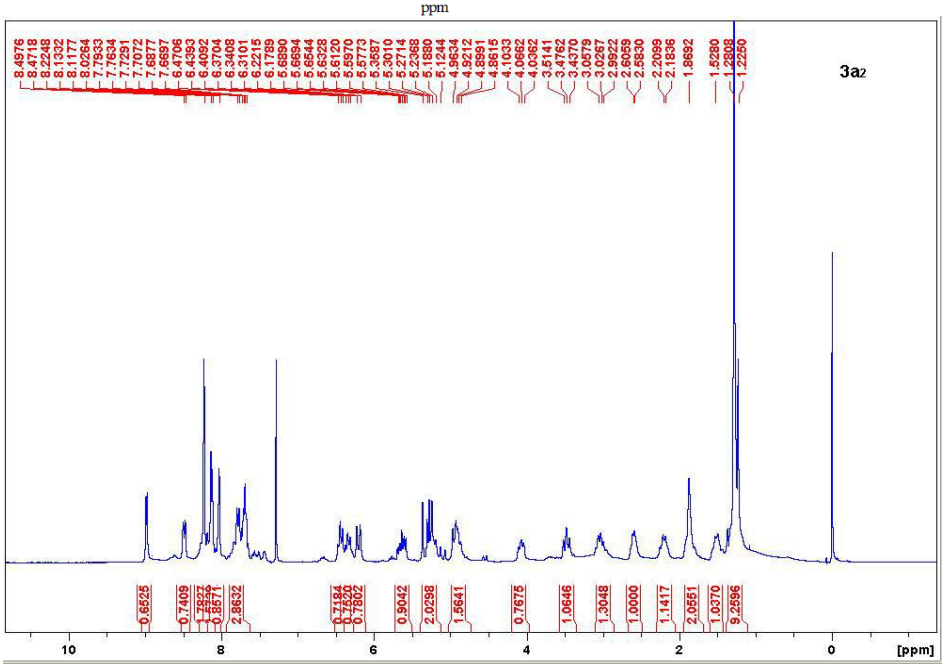
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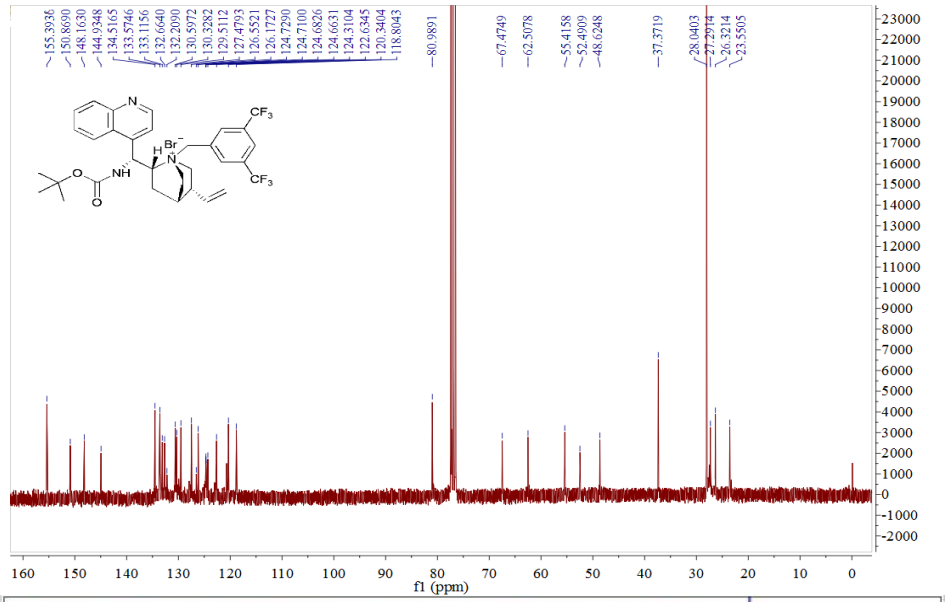
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NH
O
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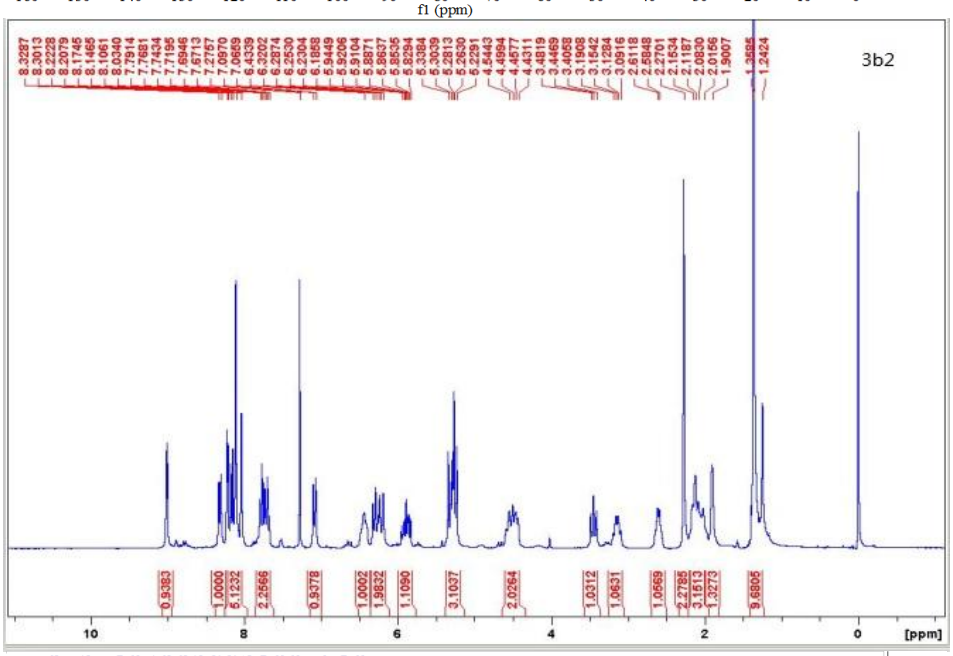
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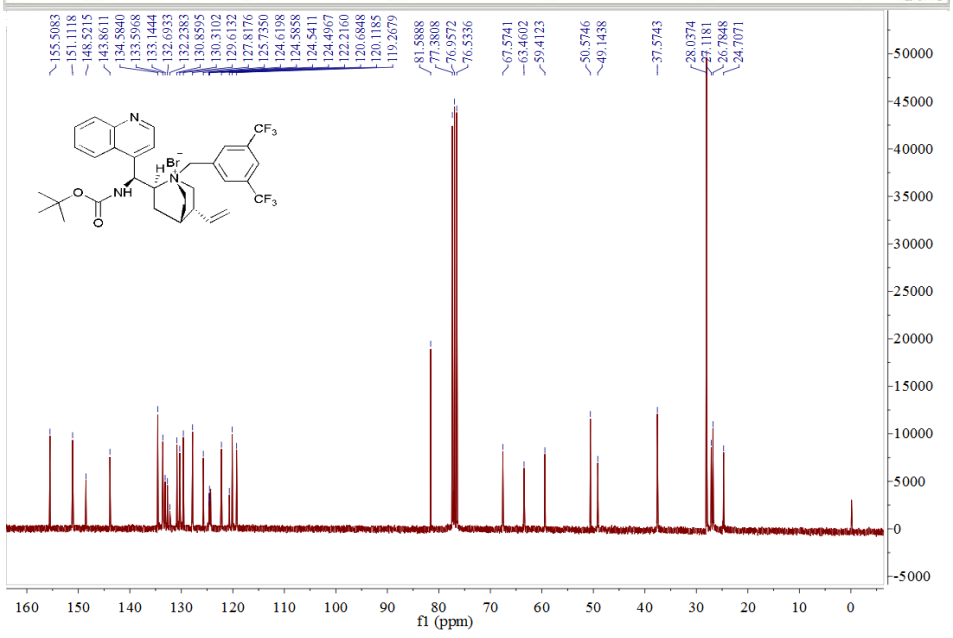
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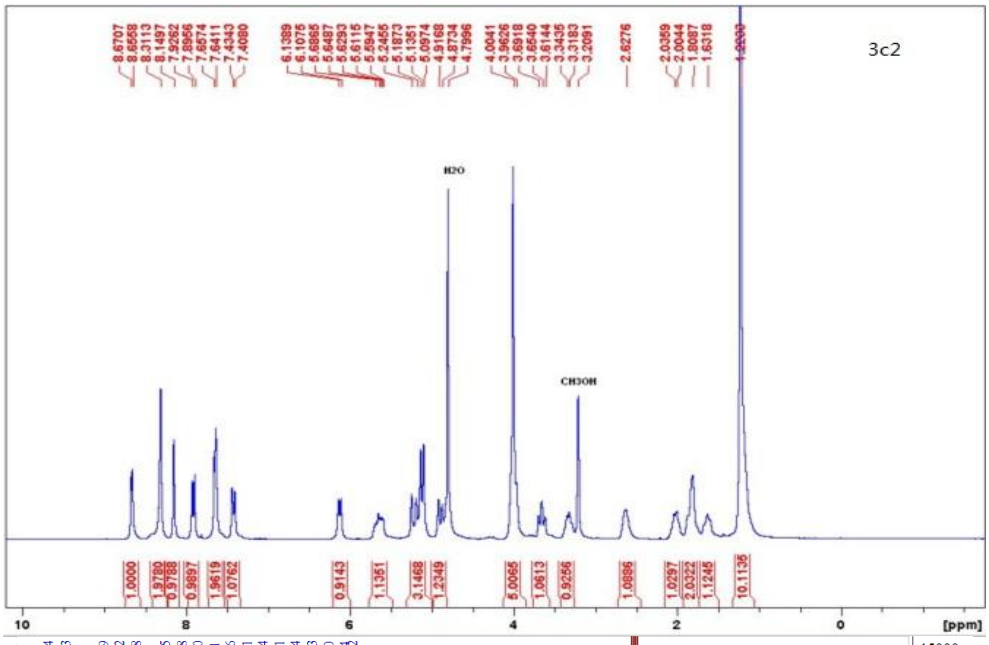
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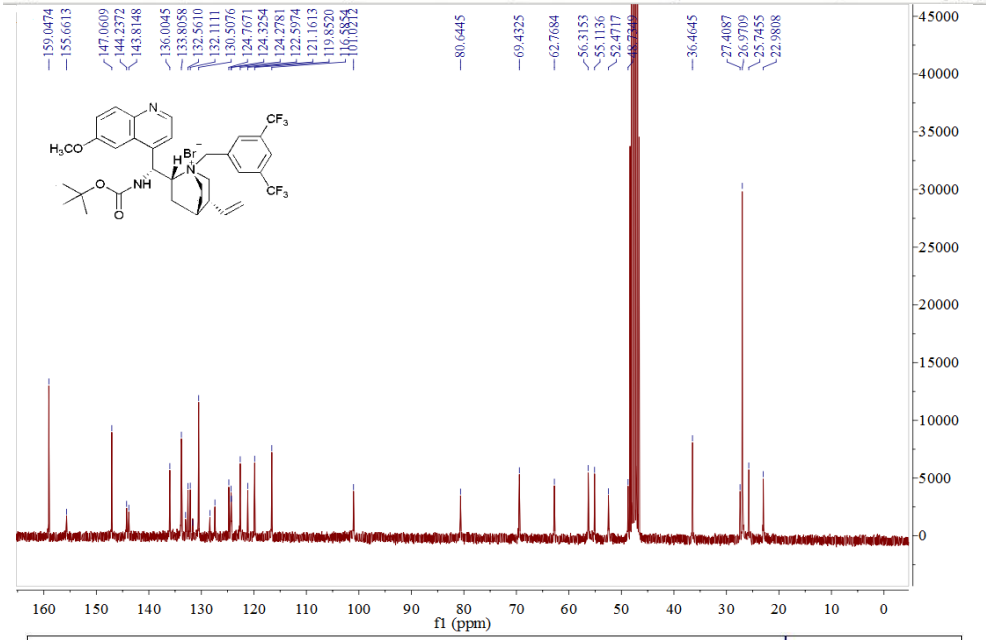
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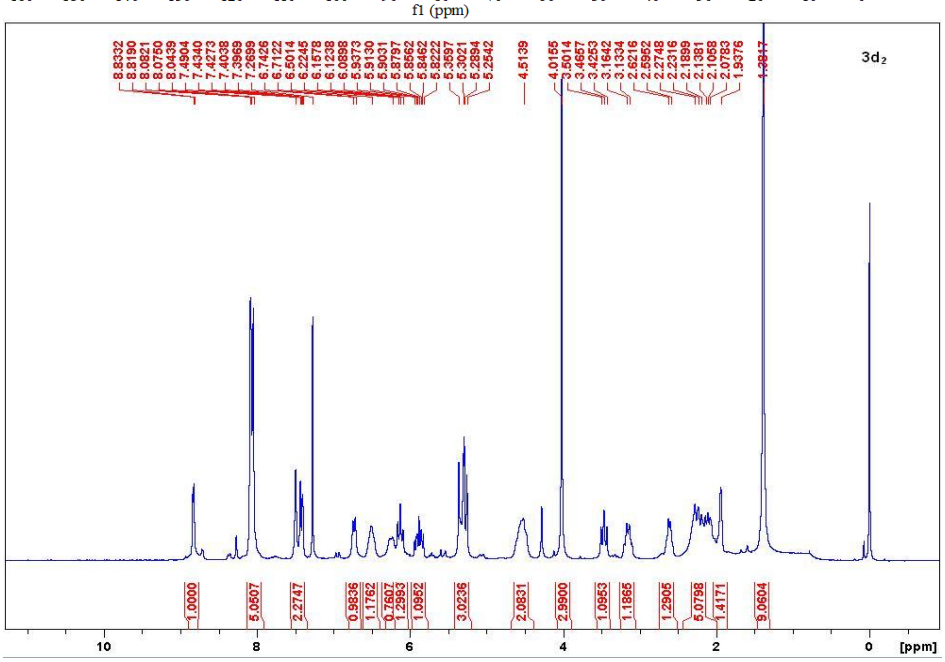
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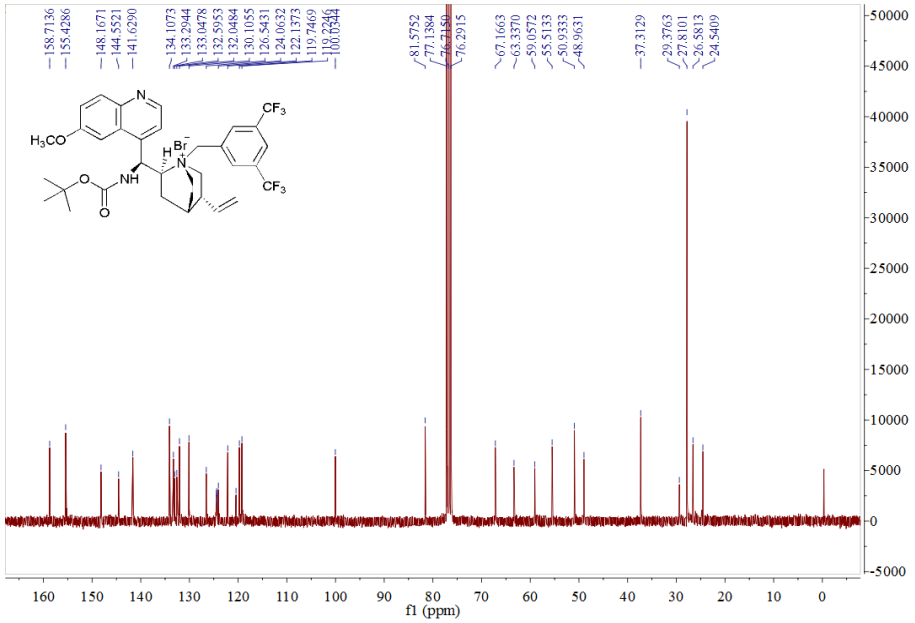
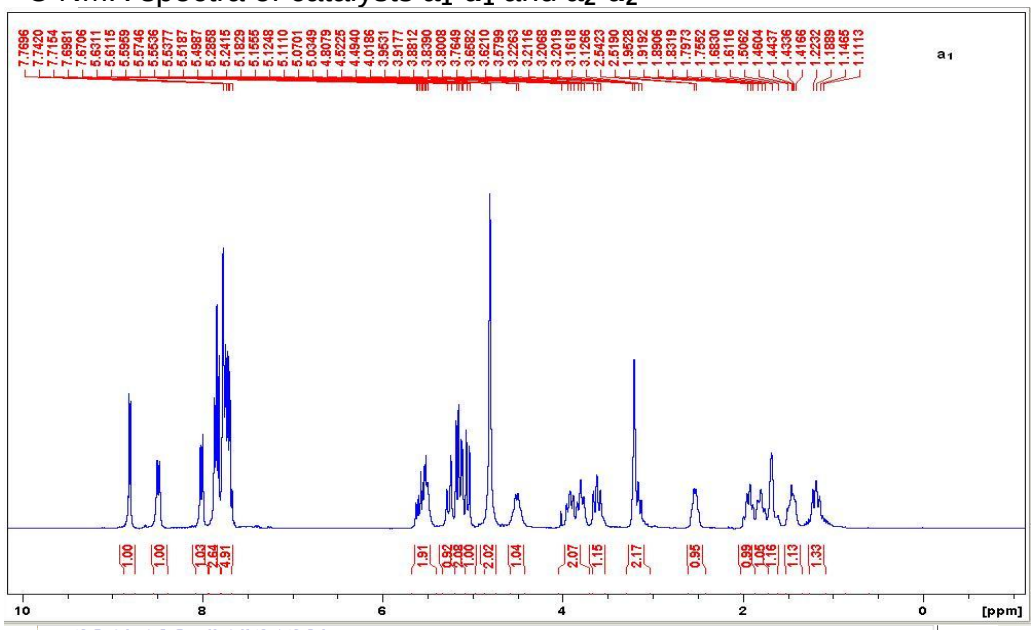
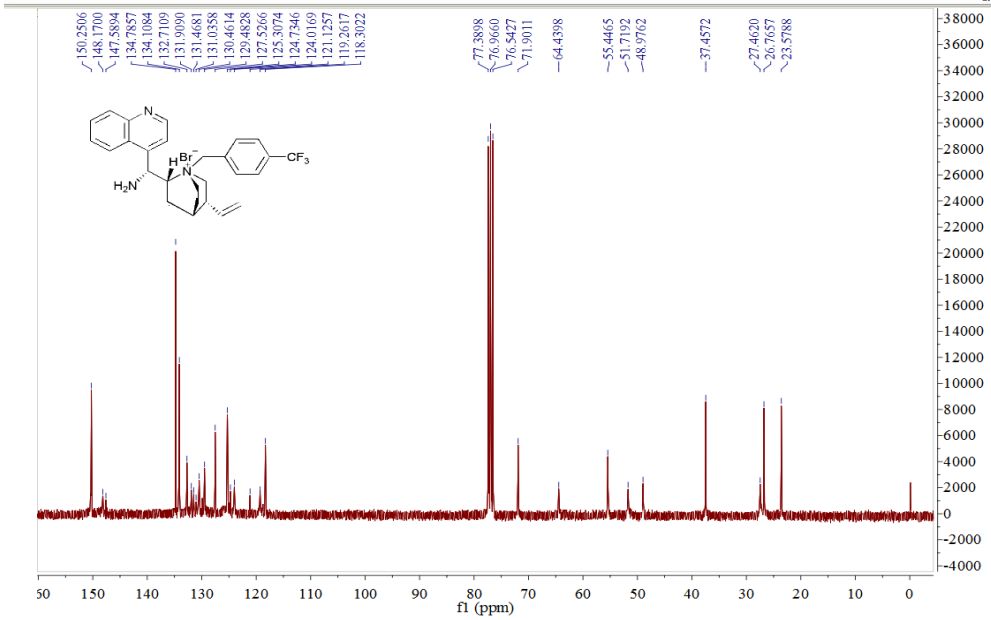
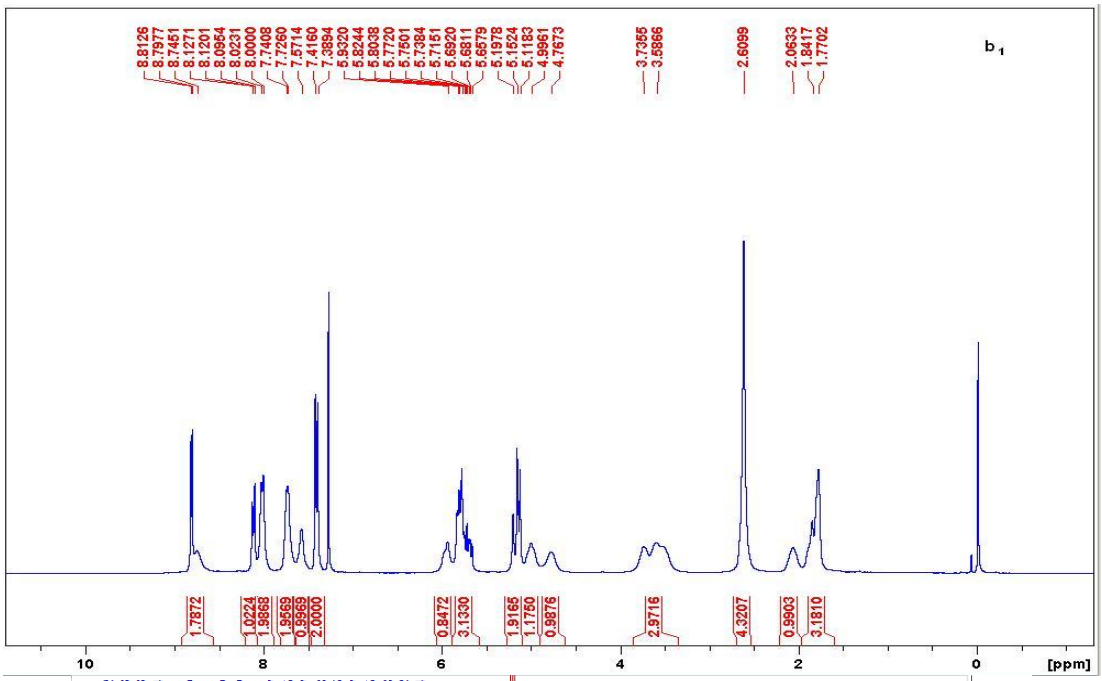


1.3 ^{1}H and ^{13}C NMR spectra of catalysts **a_1-d_1** and **a_2-d_2**



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2.6099
2.0633
1.8417
1.7702
1.7872
1.0224
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2.0000
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10
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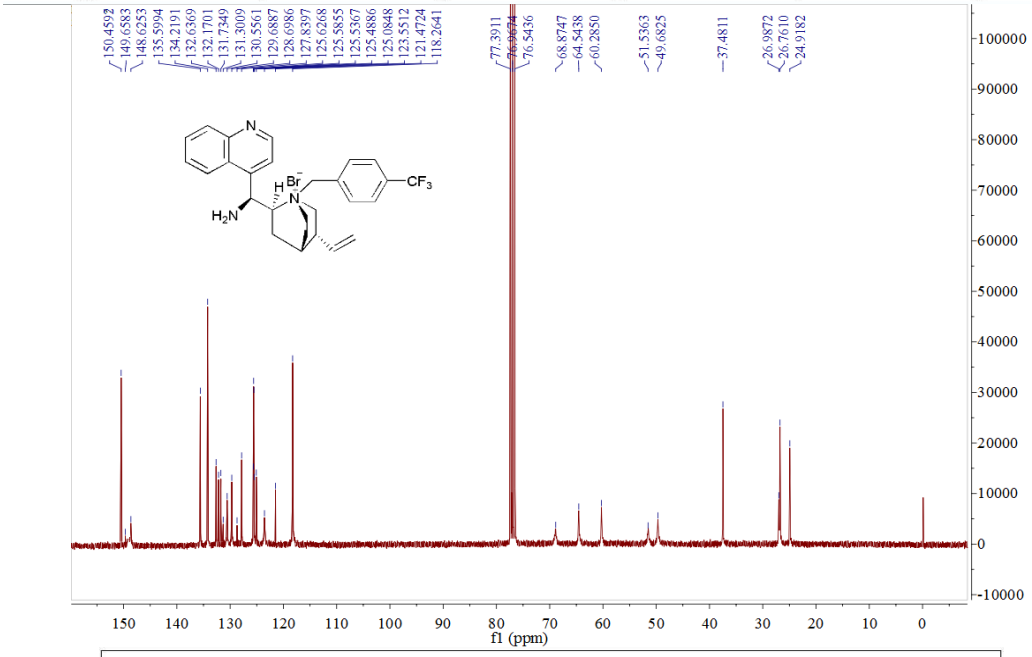
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125.6268
125.5855
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125.0848
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Br
N
H2N
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20000
10000
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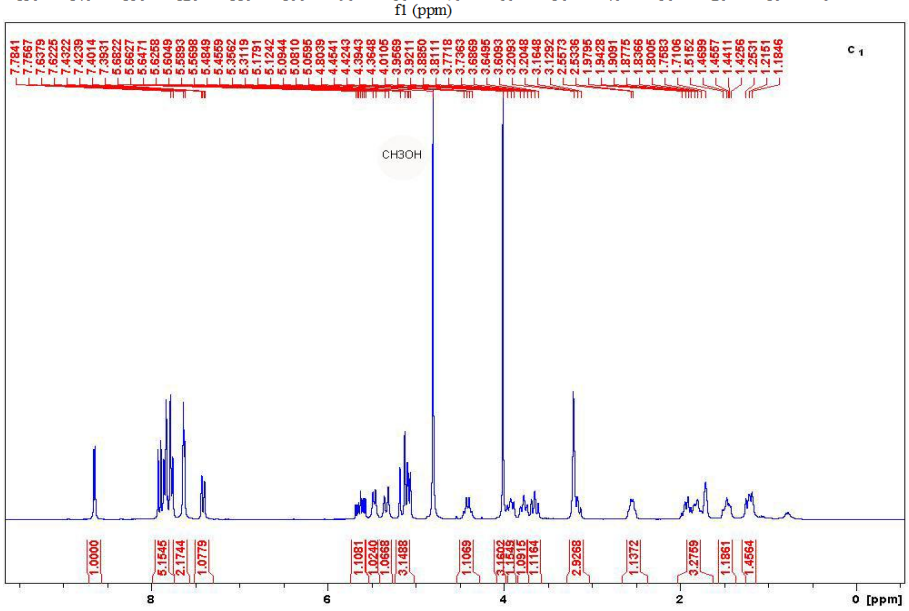
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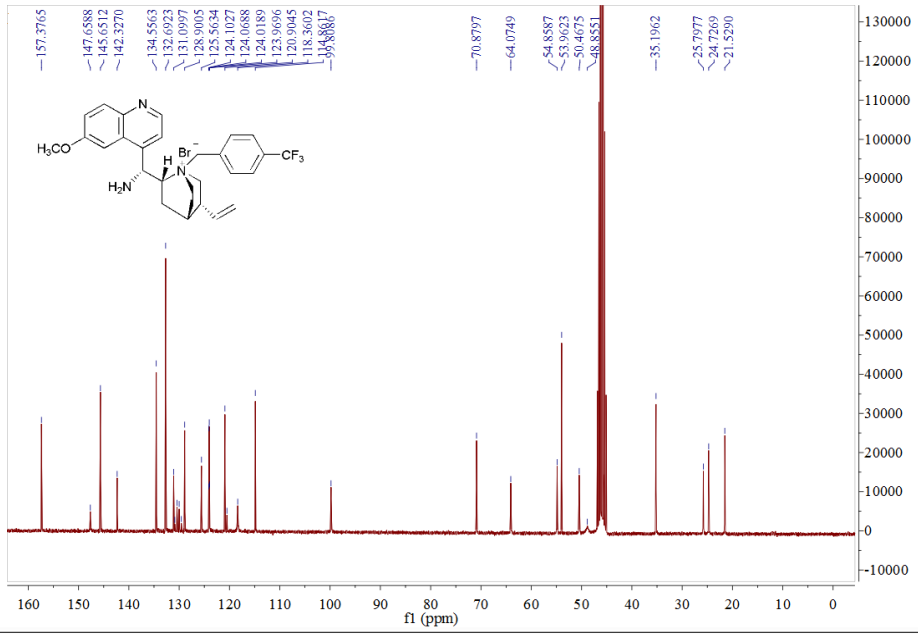
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Br
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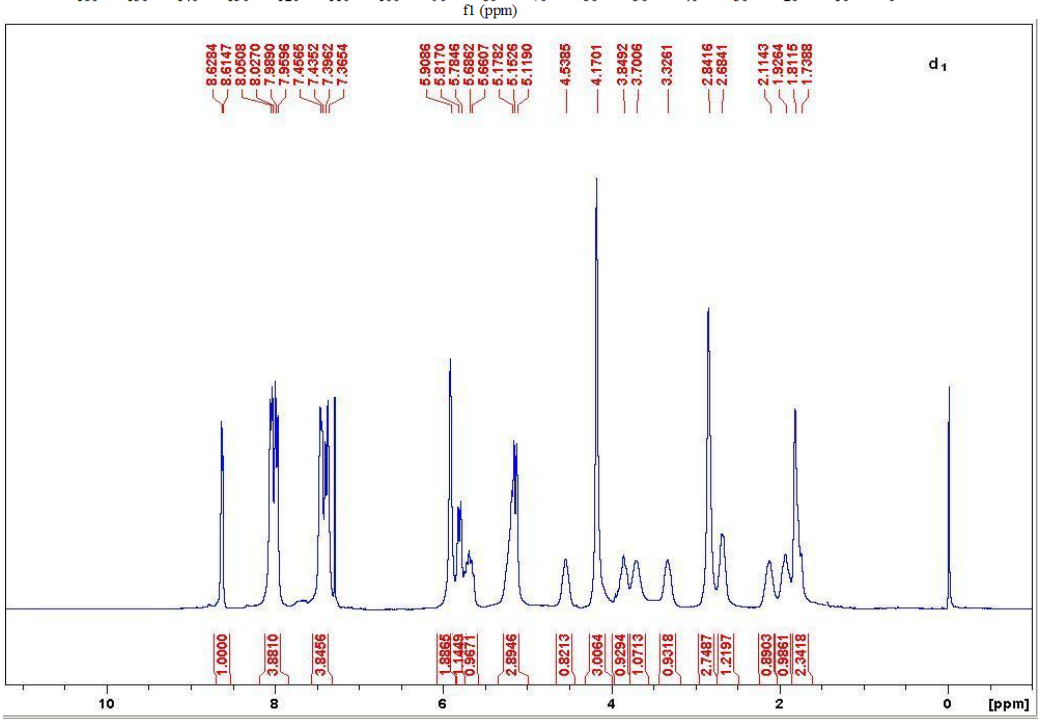
f1 (ppm)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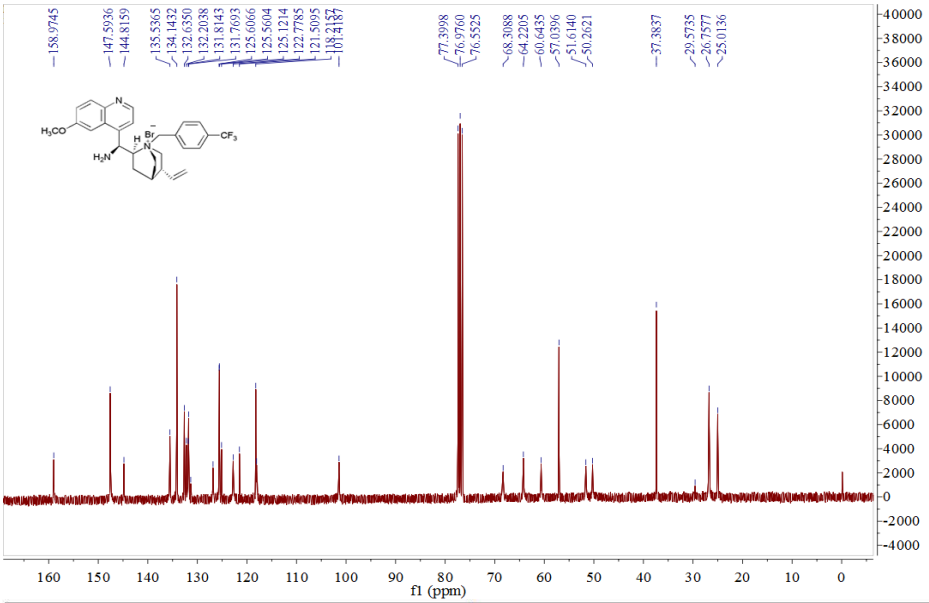
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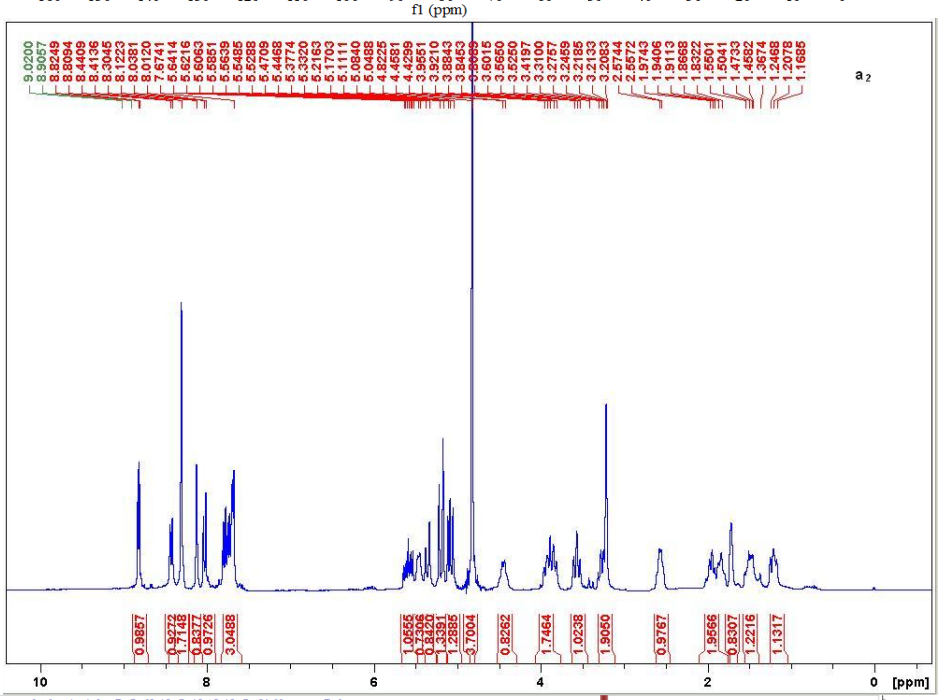
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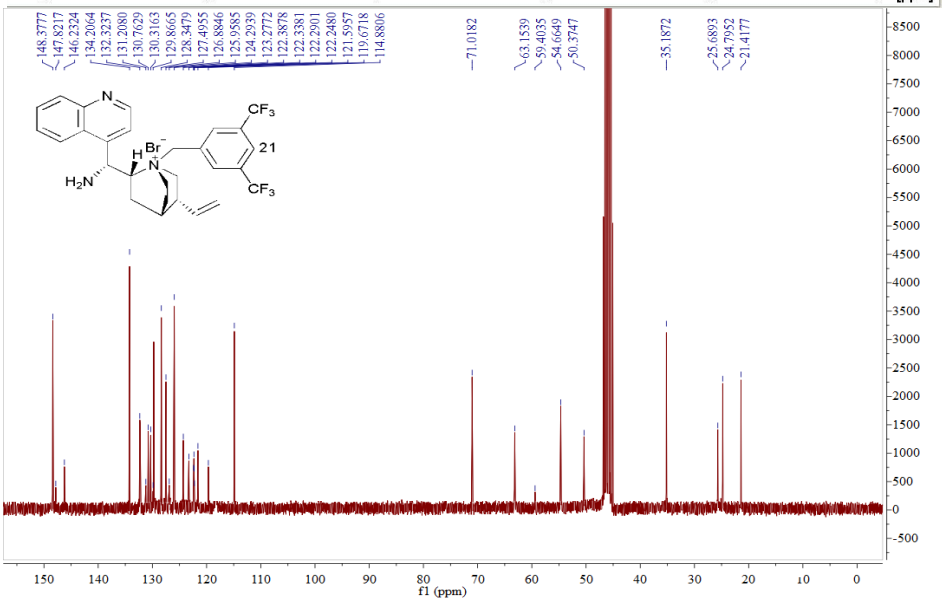
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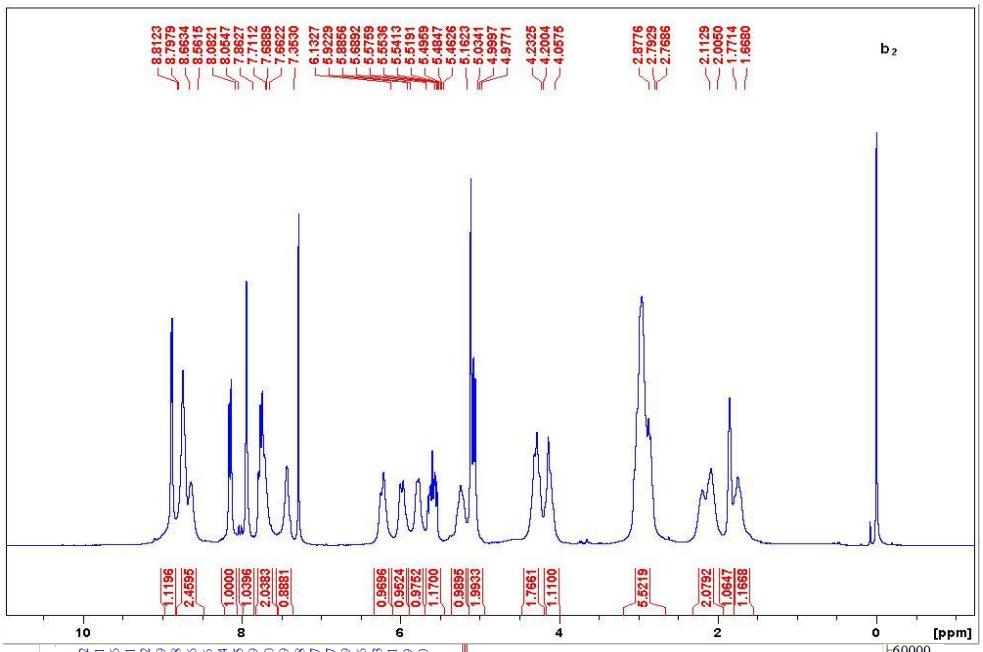
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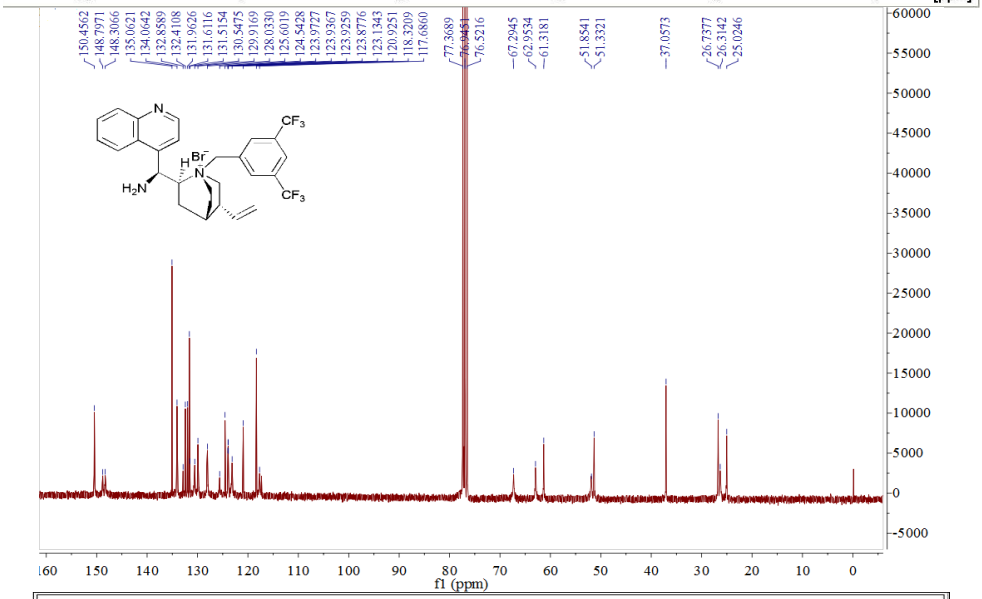
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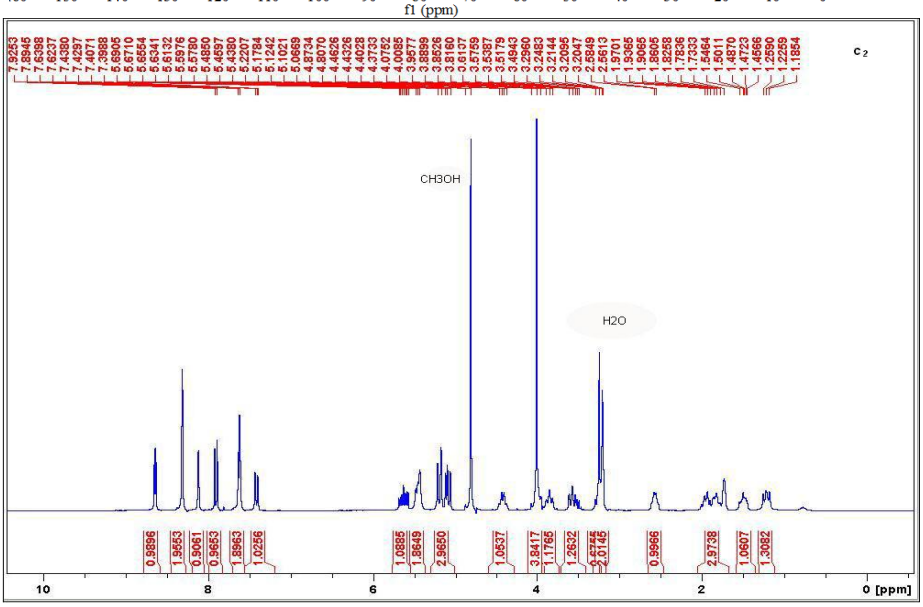
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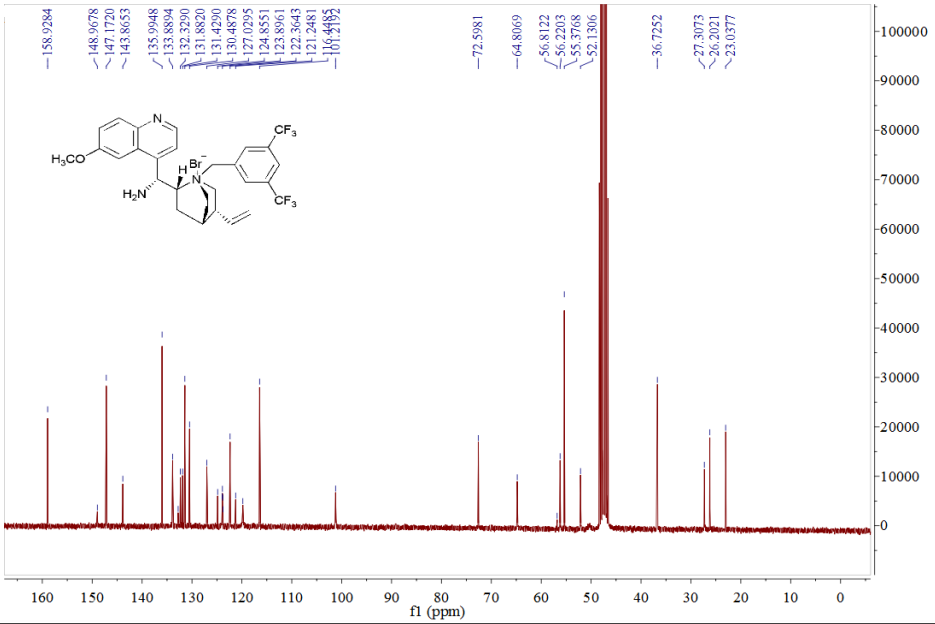

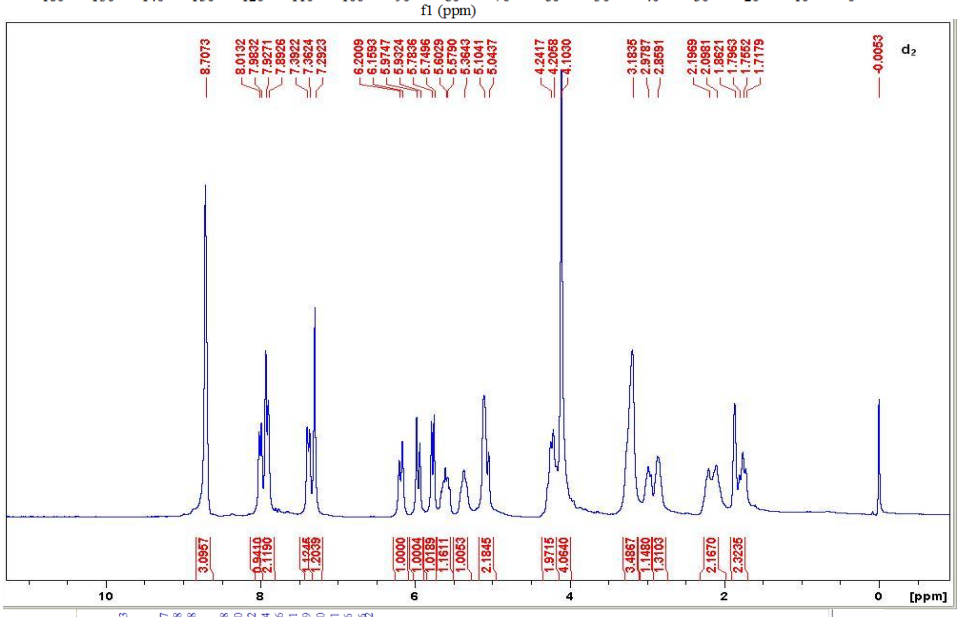

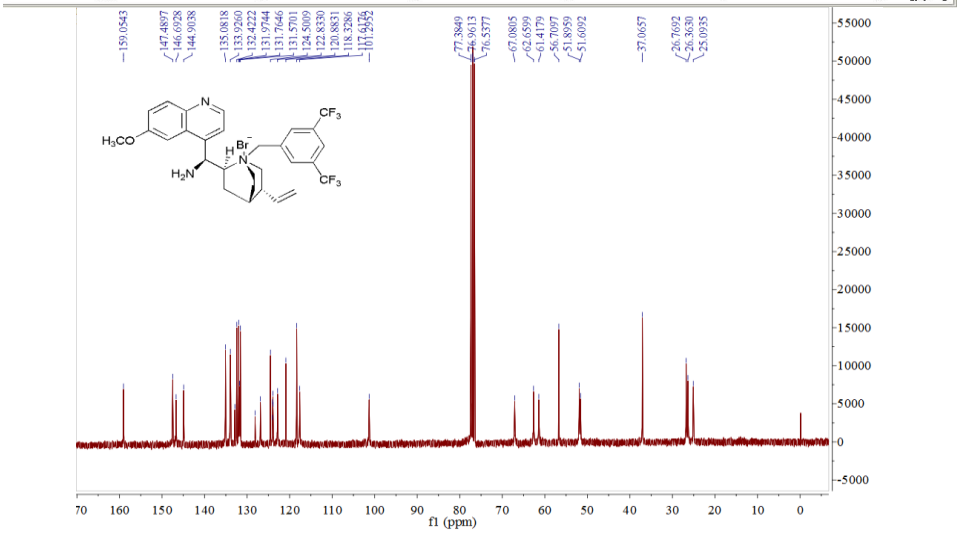

2. High resolution mass spectroscopy (HRMS)

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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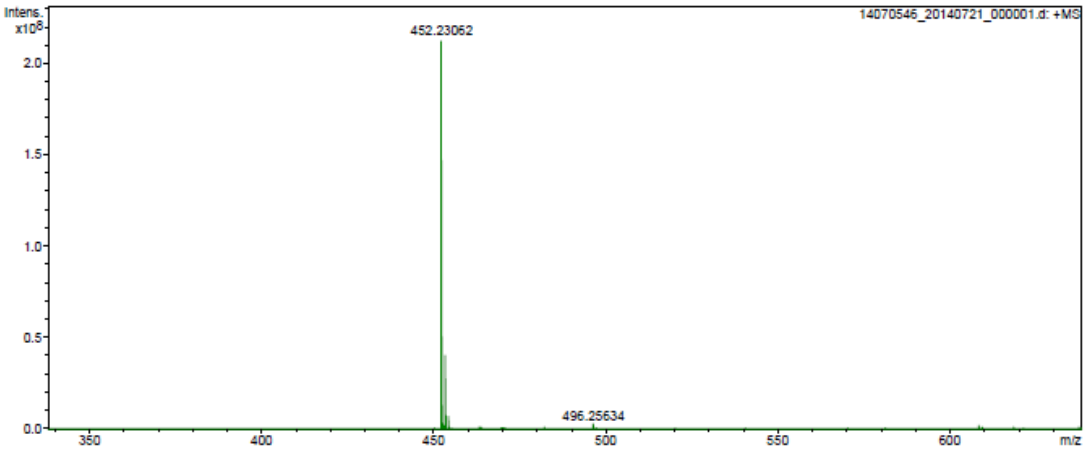
Sample	b1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



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Analysis Info

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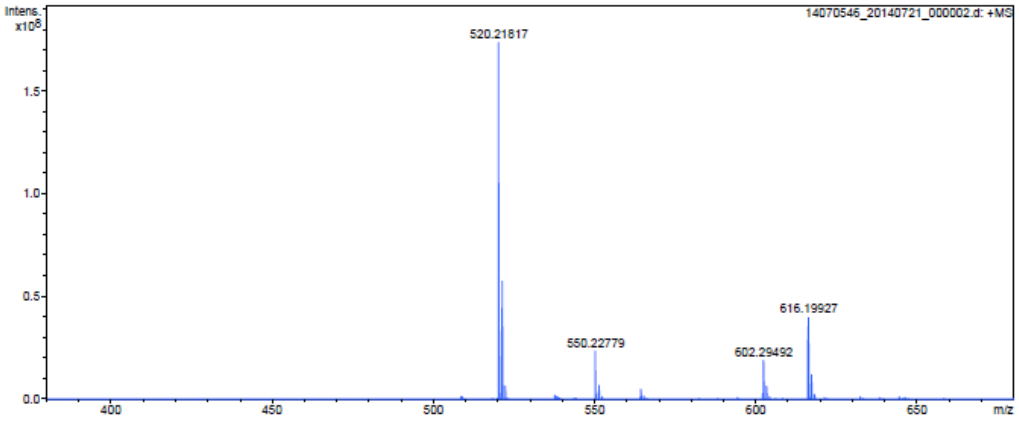

Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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Analysis Info

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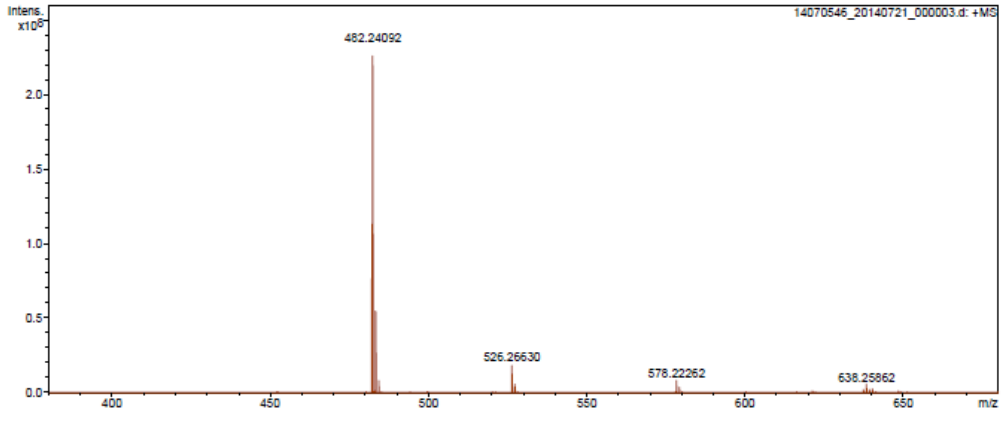

Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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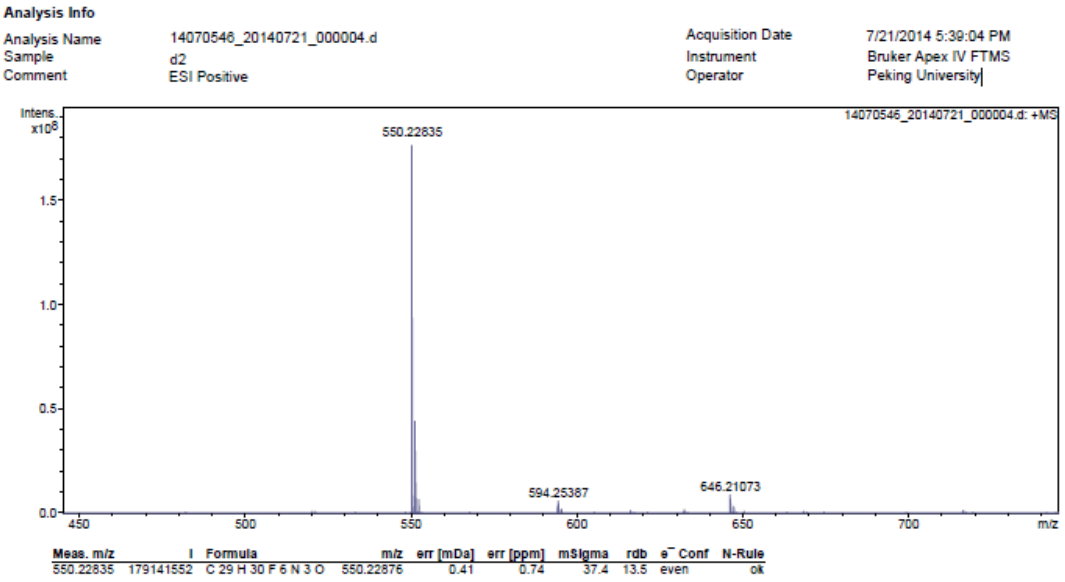
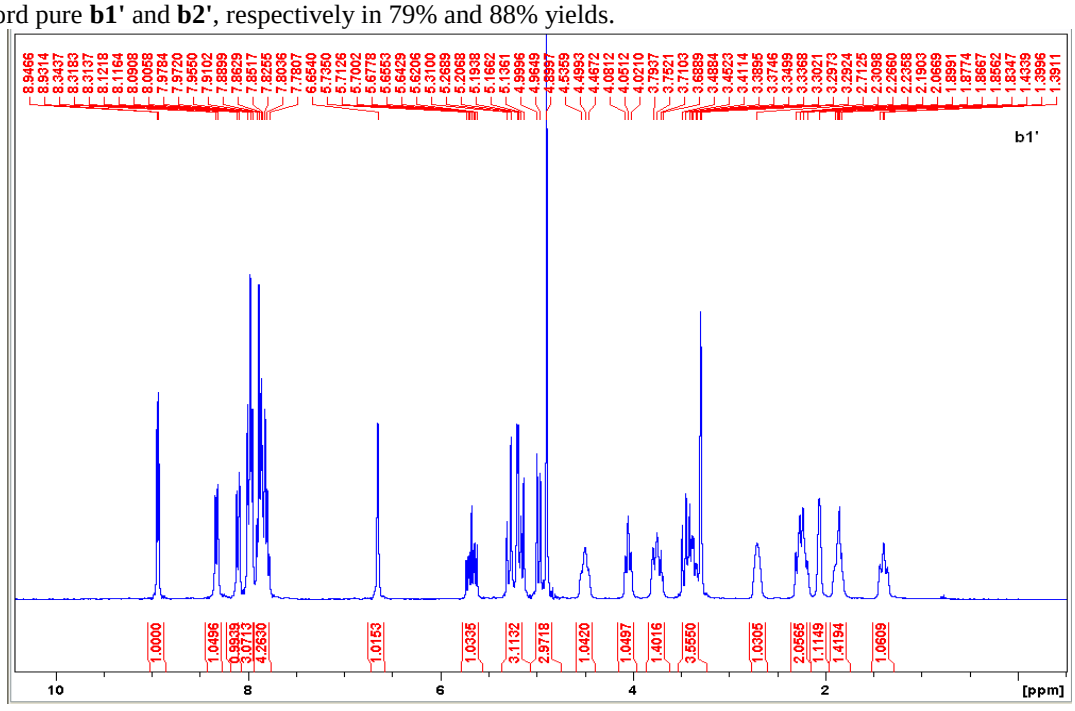
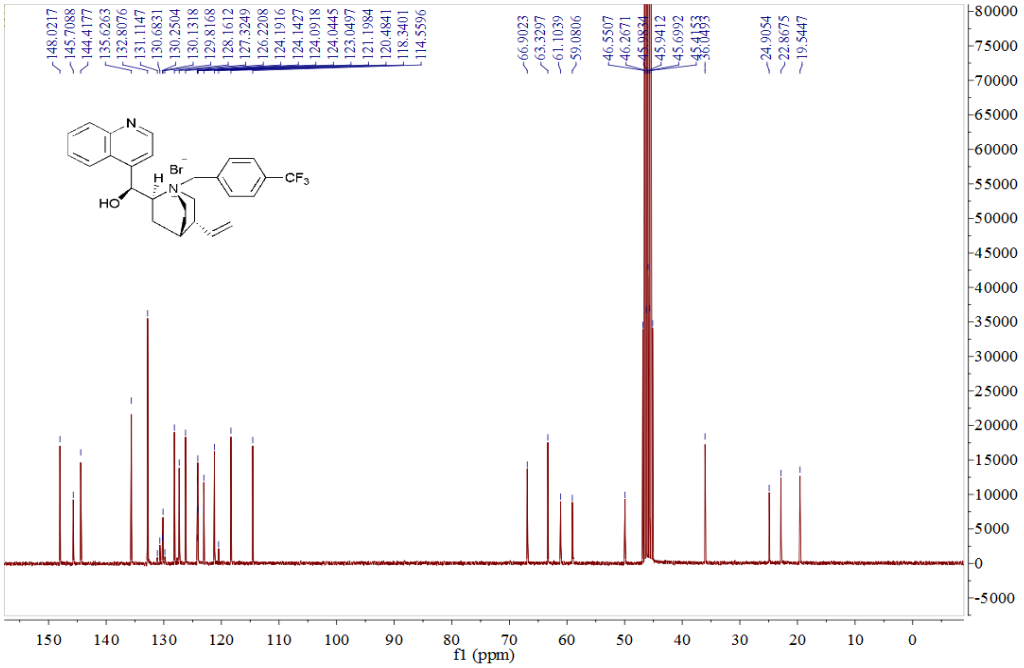


3. Synthesis of N-benzyl ammoniumsalts b_1' and b_2'

The first conversion of cinchonidine (CD) to 9-epimers of *cinchona* alkaloids (*epi*-CD) was achieved by one-pot inversion of Mitsunobu esterification–saponification (Ł. Sidorowicz, J. Skarżewski, Synthesis, 2011, **5**, 708-710).

The anhydrous THF solution (4 mL) containing CD (0.20 g, 0.68 mmol) and 3, 5-bis(trifluoromethyl)benzyl bromide (0.21 g, 0.68 mmol) or 4- trifluoromethyl benzyl bromide (0.16 g, 0.68 mmol) was stirred at 65 ℃ for 5 h. During this process, white solid gradually separate out. The white precipitate was filtered, washed with THF (3 mL ×2) and dried under reduced pressure to afford pure **b1'** and **b2'**, respectively in 79% and 88% yields.

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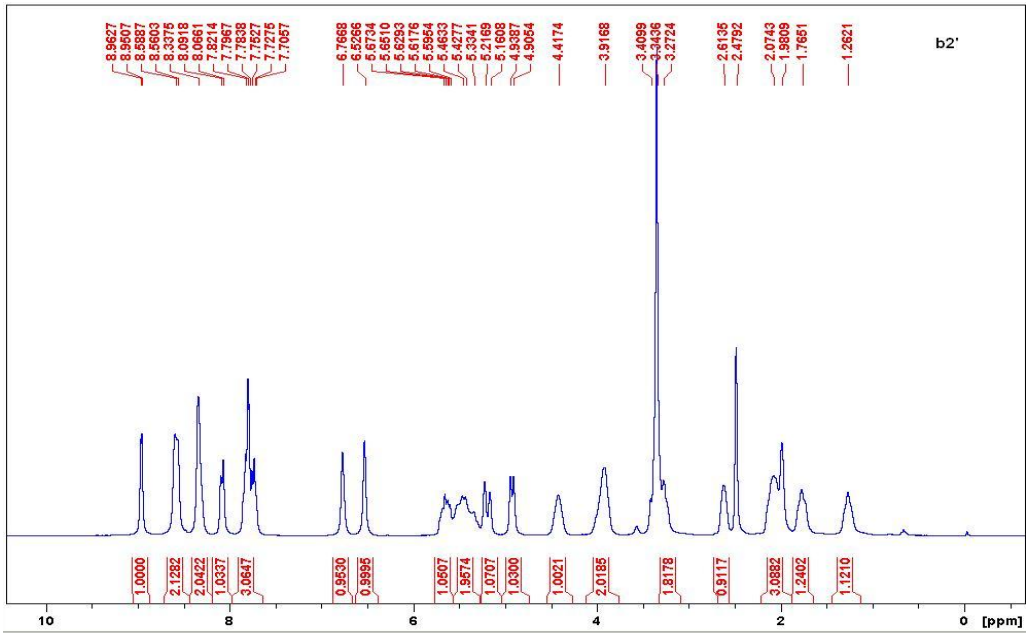
Br
N
HO
CF3
f1 (ppm)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b2'
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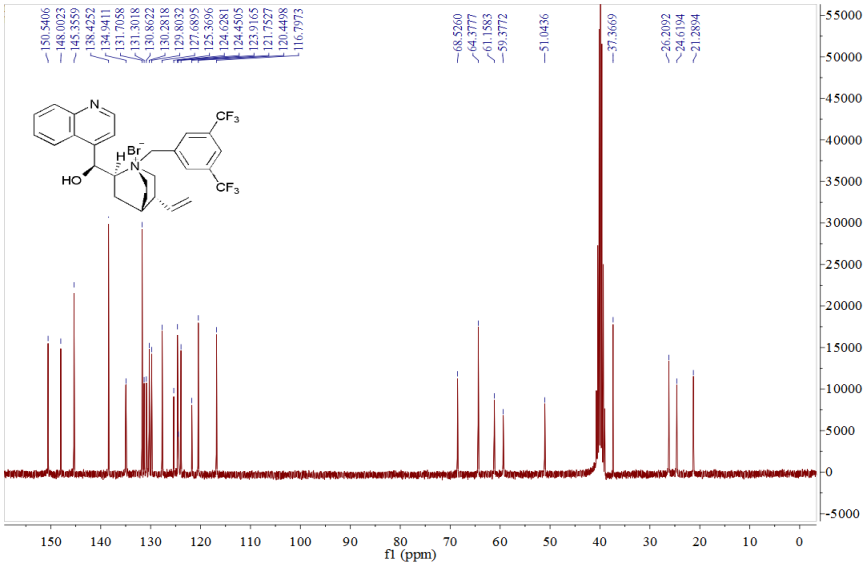
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51.0436
37.3669
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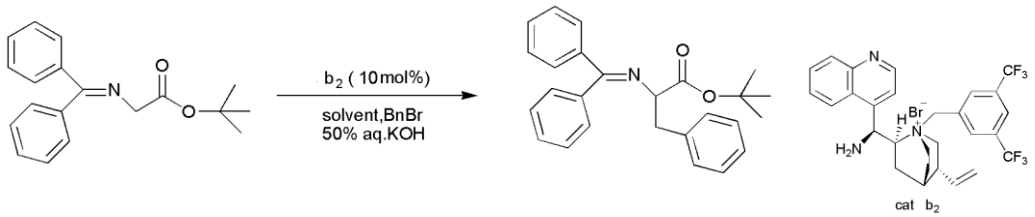
21.2894
N
H
Br
N
HO
CF3
CF3
f1 (ppm)

4. The optimization of catalytic conditions

The catalytic reaction conditions such as solvents, temperature, species and concentrations of base and used amounts of catalyst were carefully optimized and shown in Table 1-

Table 1 The influence of various solvents on the catalytic performances [a]



Entry	Solvent	Yield [%][b]	%ee[c]
1	**CH_2Cl_2**	85	-
2	***t*-BuOCH$_3$**	99	60.7(*R*)
3	**CH_3OH**	-	-
4	**acetone**	90	5(*R*)
5	**toluene**	98	73.9(*R*)
6	**EAc**	98	30.6(*R*)
7	**CH_3CN**	98	5.0(*R*)
8	**DMF**	99	-
9	**$CHCl_3$**	-	-
10	**DMSO**	-	-
11	**ether**	99	82.5(*R*)

[a] Reaction conditions: **b_2**, S=0.1 mmol, S/C=10, -20 ℃, 12 h, Solvent: 2 mL, KOH: 50% aq 0.4mL.
[b] Isolated yield.
[c] Determined by charil HPLC.

Table 2 The influence of reaction temperature on catalytic performances[a]

Entry	Temp.[℃]	Time	Yield [%][b]	%ee[c]
1	**25**	5	99	49.0(*R*)
2	**0**	5	99	67.0(*R*)
3	**-20**	8	99	82.5(*R*)
4	**-40**	12	97	90.5(*R*)
5	**-60**	24	73	71.3(*R*)

[a] Reaction conditions: **b_2**, S=0.1 mmol, S/C=10, ether: 2 mL, KOH: 50% aq 0.4 mL
[b] Isolated yield.
[c] Determined by charil HPLC.

Table 3 The influence of various base on catalytic performances [a]

Entry	Base	Yield [%][b]	%ee[c]
1	**LiOH**	52	52.1(*R*)
2	**NaOH**	63	59.8(*R*)
3	**KOH**	97	90.5(*R*)
4	**CsOH**	60	65.0(*R*)

[a] Reaction conditions: **b_2**, S=0.1 mmol, S/C=10, -40℃, 12 h, ether: 2 mL, MOH: 50% aq 0.4 mL (LiOH:11%).
[b] Isolated yield.
[c] Determined by charil HPLC.

Table 4 The influence of concentration of the base on catalytic performances [a]

Entry	Wt (%)	Base	Yield [%][b]	%ee[c]
1	**10**	KOH	13	85.3(*R*)
2	**20**	KOH	21	83.8(*R*)
3	**30**	KOH	58	88.7(*R*)
4	**40**	KOH	62	88.2(*R*)
5	**50**	KOH	97	90.5(*R*)

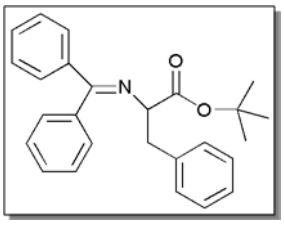
[a] Reaction conditions: **b_2**, S=0.1 mmol, S/C=10, -40 ℃, 12 h, ether: 2 mL. KOH: 0.4 mL
[b] Isolated yield.
[c] Determined by charil HPLC.

Table 5 The influence of loading amount on catalytic performances [a]

Entry	S/C	Cat. (mol%)	Yield [%][b]	%ee[c]
1	20	5	98	87.9(*R*)
2	10	10	97	90.5(*R*)
3	7	15	84	87.9(*R*)
4	5	20	82	87.9(*R*)
5	4	25	78	85.7(*R*)

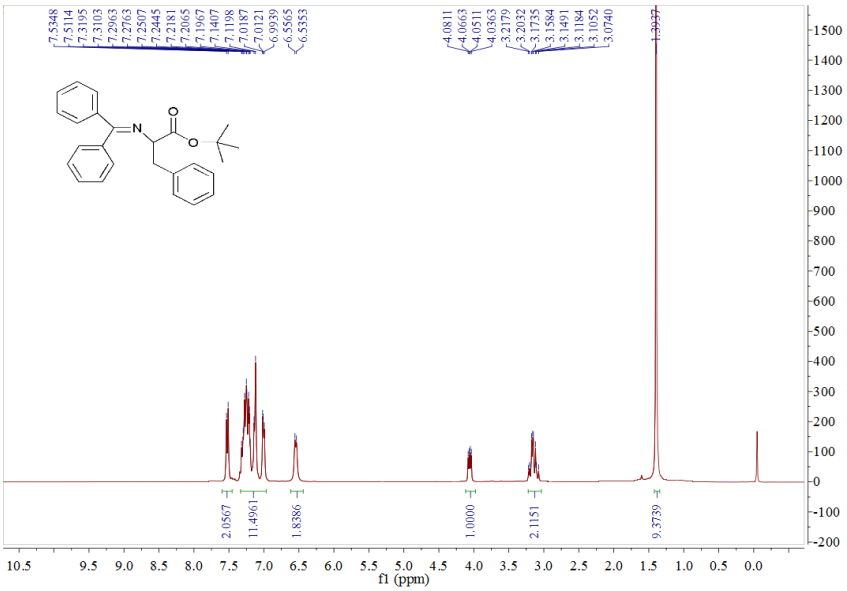
[a] Reaction conditions: **b_2**, S=0.1 mmol, -40 ℃, 12 h, ether: 2 mL, KOH: 50% aq. 0.4 mL.
[b] Isolated yield.
[c] Determined by charil HPLC.

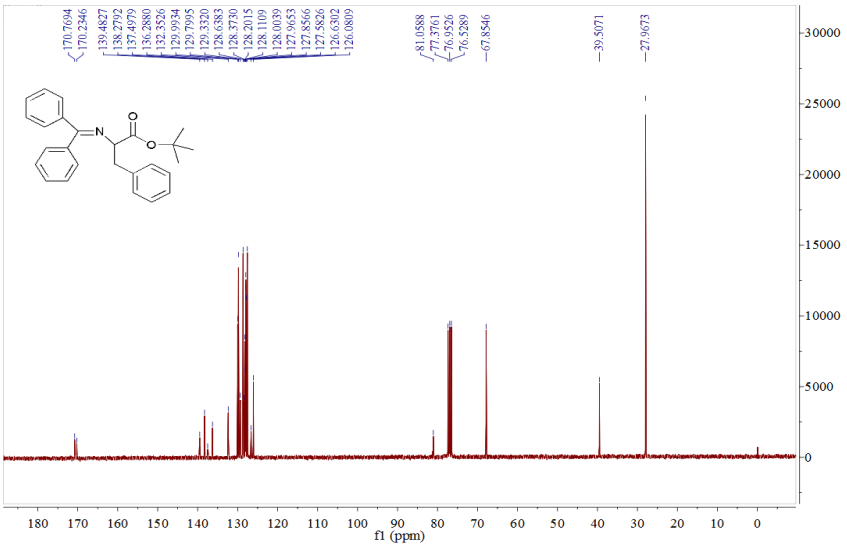
5. The data of catalytic products

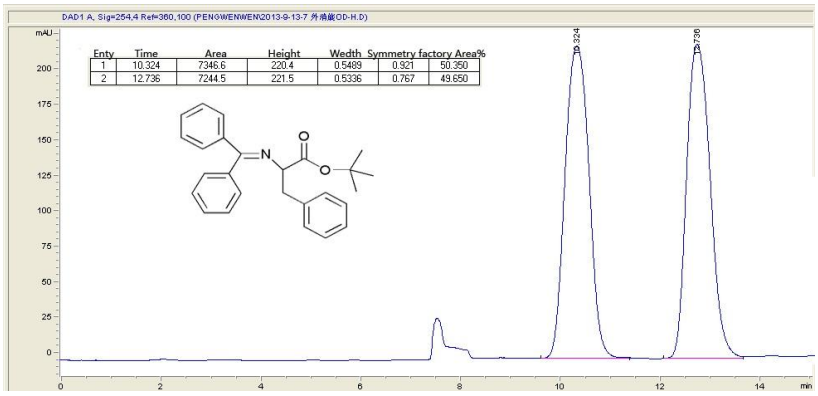


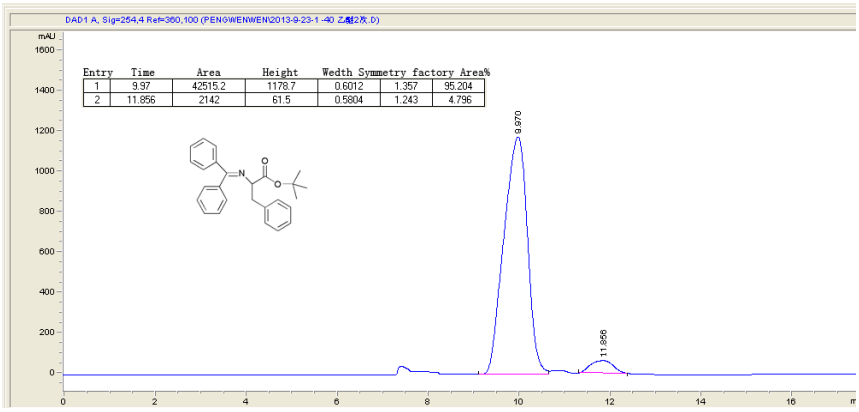
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.52 (d, 2 H, ^3J=7.0 Hz, Ph-H), 7.30−7.00 (m, 11 H, Ph-H), 6.54 (d, 2H, ^3J=6.4 Hz, Ph-H), 4.06 (dd, 1 H, ^3J = 4.4 Hz, 4.4 Hz, CH), 3.22−3.07 (m,

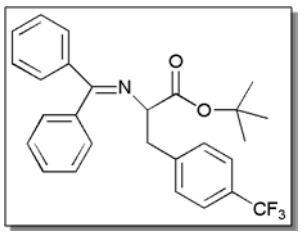
2 H, CH_2), 1.39 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.8, 170.2 (C=N, C=O), 139.5, 138.3, 137.5, 136.3, 132.4, 130.0, 129.8, 129.3, 128.6, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.6, 126.6, 126.1, 81.1 (O-C), 67.9 (CH), 39.5 (CH2), 28.0 (CH_3). Rt HPLC (Daicel Chiralpak OD-H, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.0 min (*R*-isomer), 11.9min (*S*-isomer).



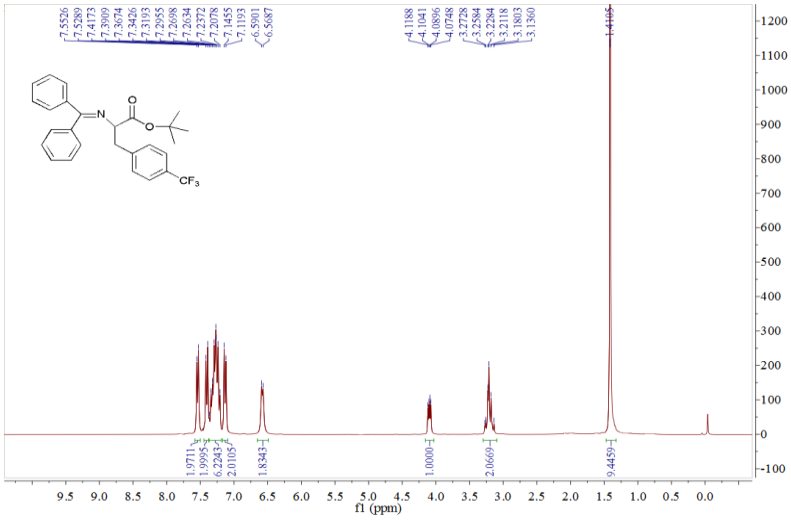


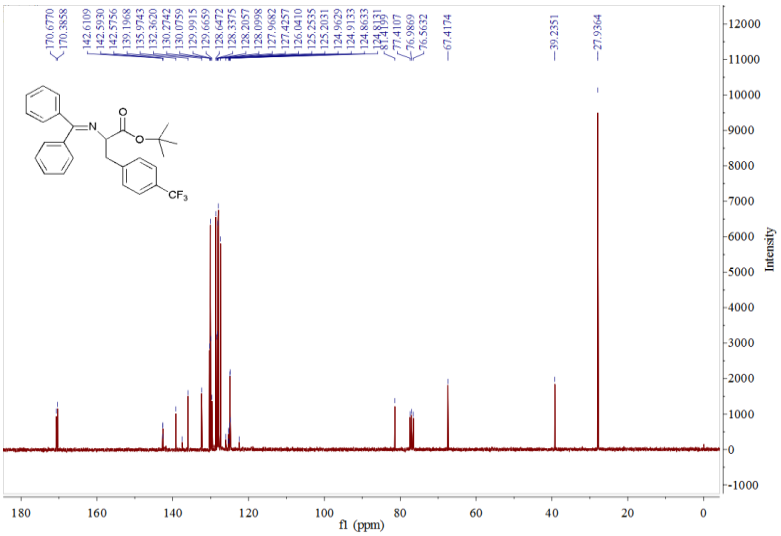


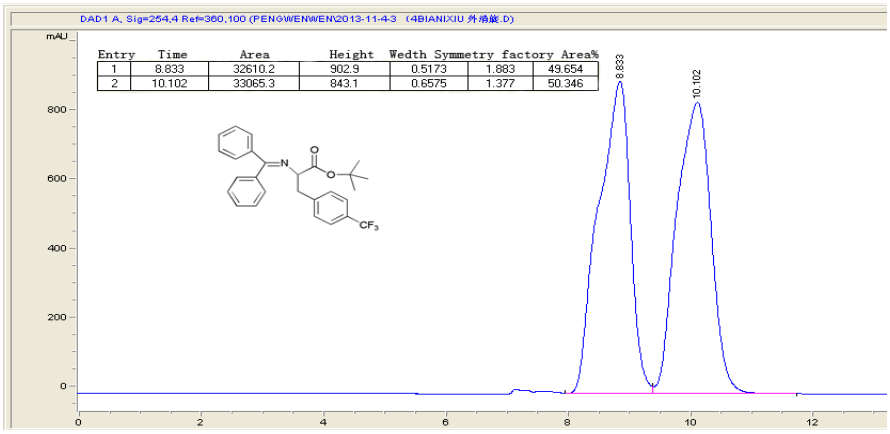


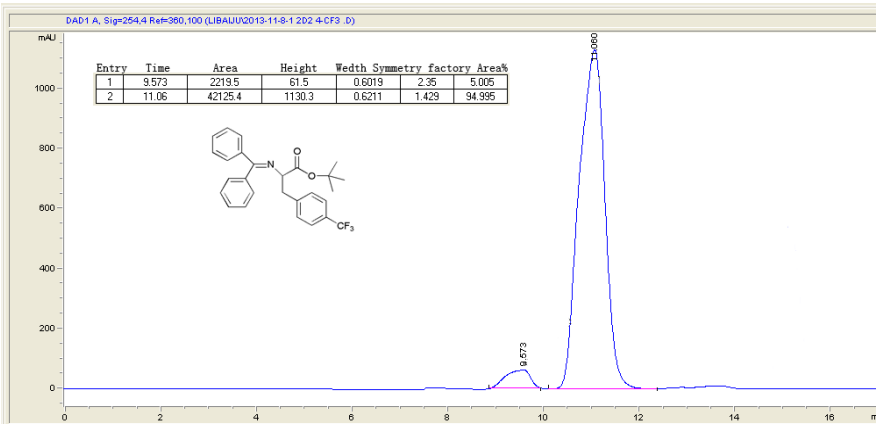


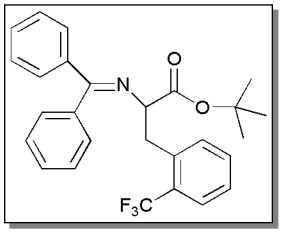
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.54 (d, 2 H, ^{3}J = 7.1 Hz, Ph-H), 7.40 (d, 2 H, ^{3}J = 7.9 Hz, Ph-H), 7.37−7.21 (m, 6 H, Ph-H), 7.13 (d, 2 H, ^{3}J = 7.9 Hz, Ph-H), 6.58 (d, 2 H, ^{3}J = 6.4 Hz, Ph-H), 4.10 (dd, 1 H, ^{3}J = 4.4 Hz, 4.4 Hz, CH), 3.27−3.14 (m, 2 H, CH_2), 1.41 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.7, 170.4 (C=N, C=O), 142.6 (q, $^{3}J_{C\text{-}F}$ = 1.3 Hz), 139.2, 137.5, 136.0, 132.4, 130.3, 130.1, 130.0, 130.0, 129.7, 128.6, 128.3, 128,2, 128.1, 128.0, 127.4, 126.0, 125.2 (q, $^{2}J_{C\text{-}F}$ = 3.8 Hz), 124.9 (q, $^{1}J_{C\text{-}F}$ = 3.8 Hz, CF_3), 81.4 (O-C), 67.4 (CH), 39.2 (CH_2), 27.9 (CH_3). Rt HPLC (Daicel Chiralpak OD-H, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 9.6 min (*S* -isomer), 11.1min (*R* -isomer).



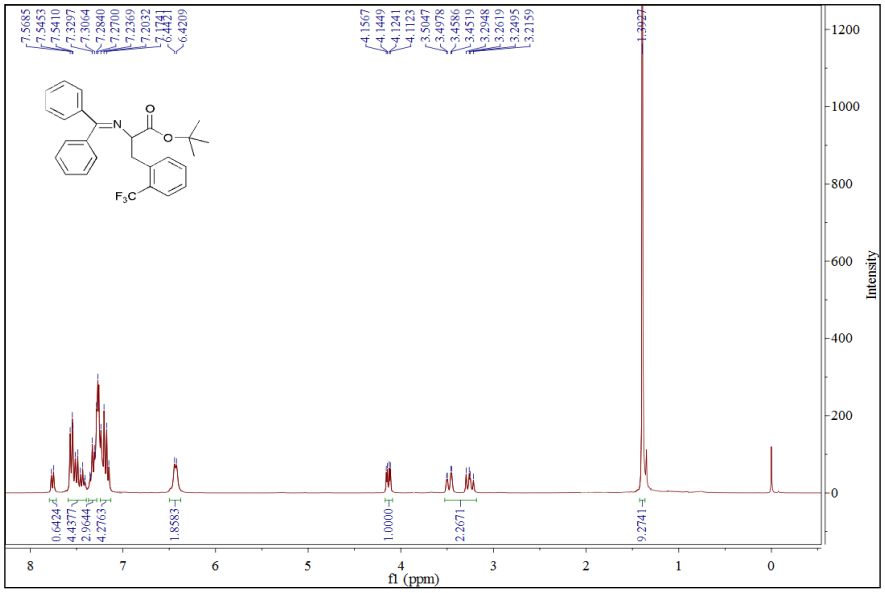


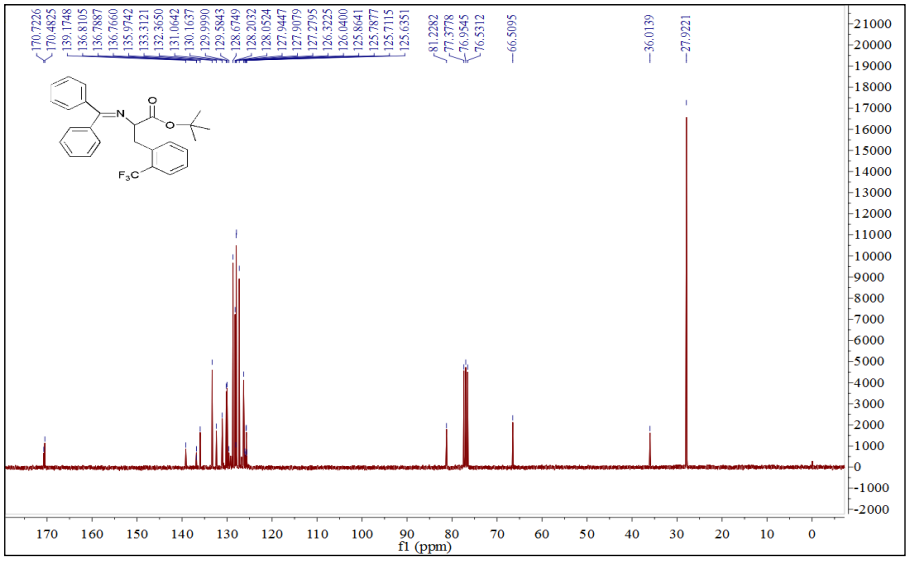


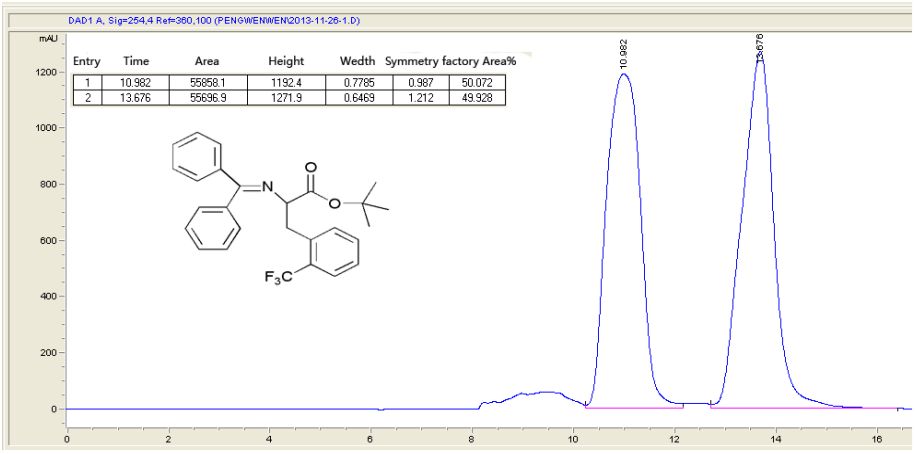


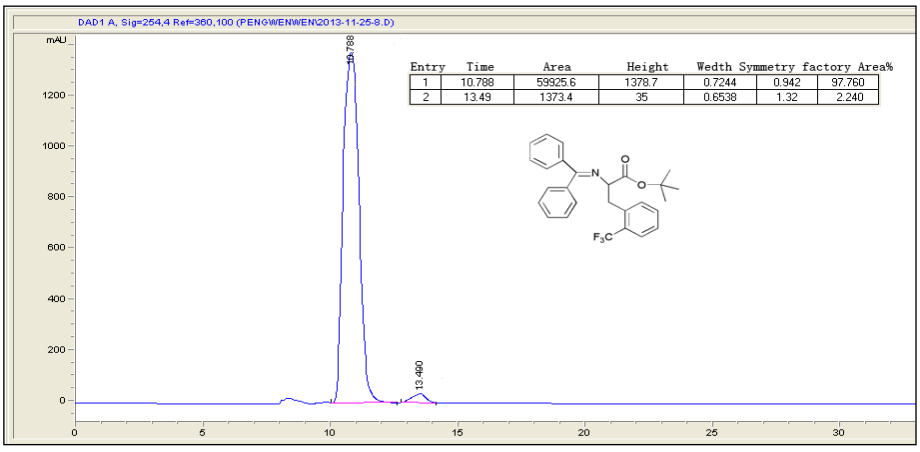


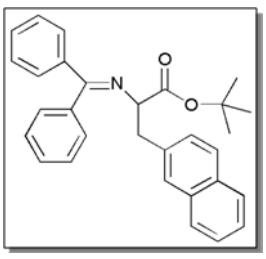
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.76 (d, 1 H, ^{3}J=7.1 Hz, Ph-H), 7.57−7.41 (m, 4 H, Ph-H), 7.35−7.15 (m, 7 H, Ph-H), 6.43 (d, 2 H, ^{3}J = 6.4 Hz, Ph-H), 4.13 (dd, 1 H, ^{3}J=3.5 Hz, 3.5 Hz, CH), 3.50−3.22 (m, 2 H, CH_2), 1.39 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.7, 170.5 (C=N, C=O), 139.2, 136.8 (q, $^{2}J_{C\text{-}F}$ = 1.6 Hz), 136.0, 133.3, 132.4, 131.1, 130.2, 131.0, 129.6, 128.7, 128.2, 128,1, 127.9, 127.9, 127.3, 126.3, 126.0 (Ph), 125.7 (q, $^{1}J_{C\text{-}F}$ = 5.7 Hz, CF_3), 81.2 (O-C), 66.5 (CH), 36.0 (CH_2), 27.9 (CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.8 min (*R*-isomer), 13.5min (*S*-isomer).



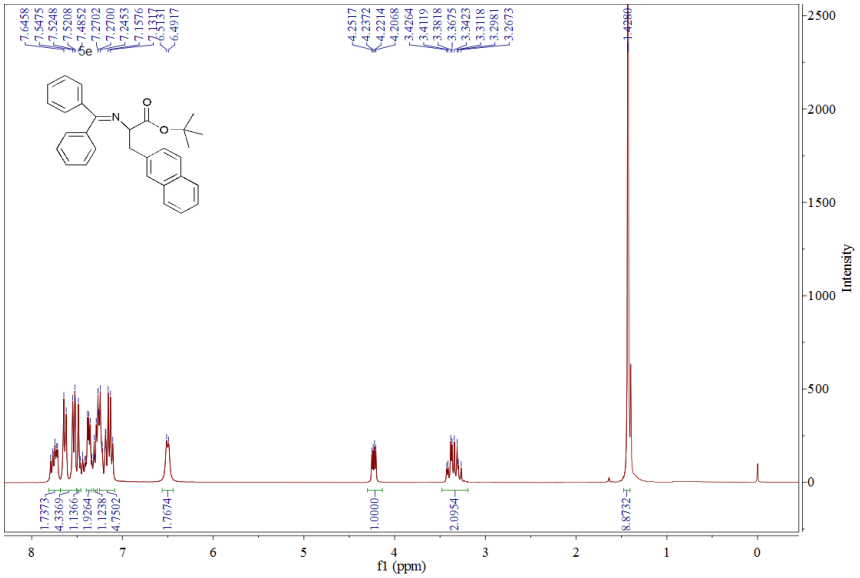


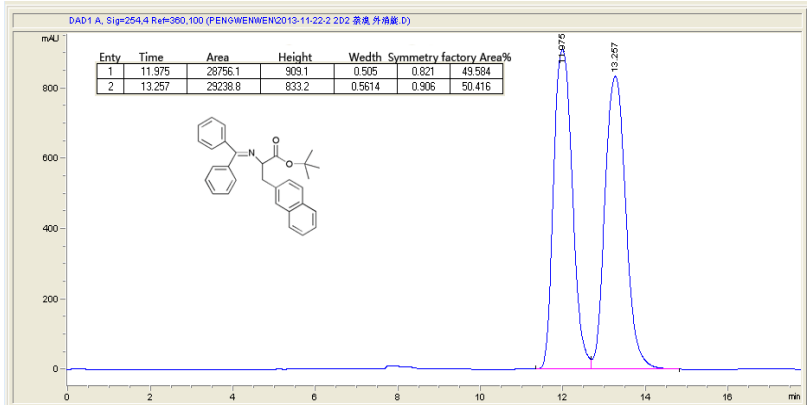


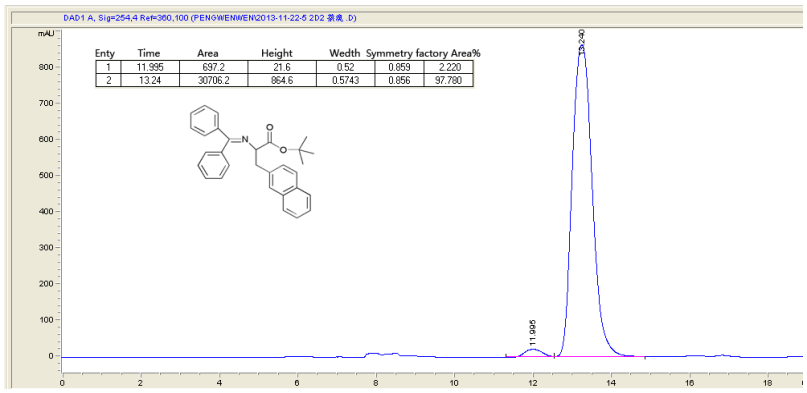


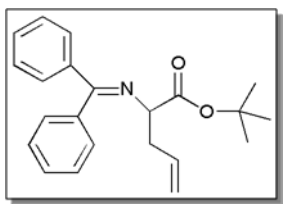


^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.79−7.11 (m, 15 H, Ar-H), 6.50 (d, 2 H, ^{3}J = 6.4 Hz), 4.23 (dd, 1 H, ^{3}J = 4.4 Hz, 4.4 Hz, CH), 3.43−3.27 (m, 2 H, CH_2), 1.43 (s, 9 H, CH_3). Rt HPLC (Daicel Chiralpak OD-H, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 12.0 min (*S* -isomer), 13.2 min (*R* -isomer).

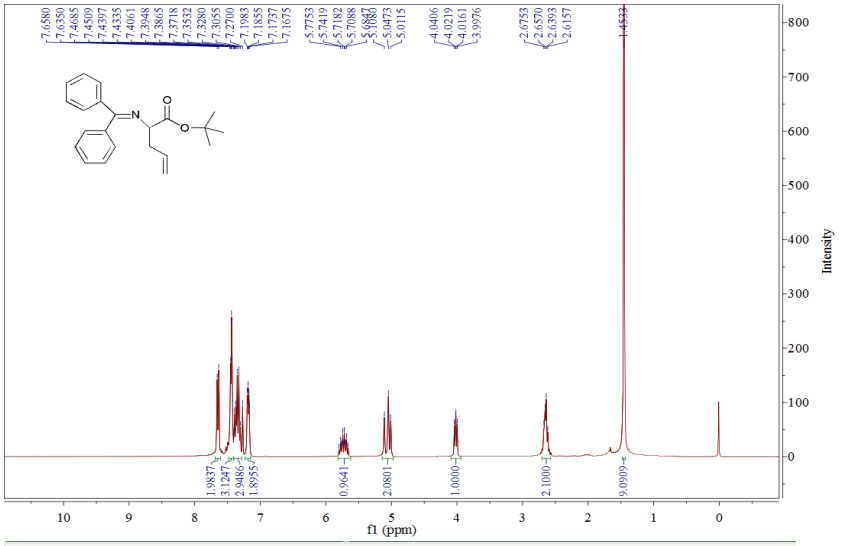


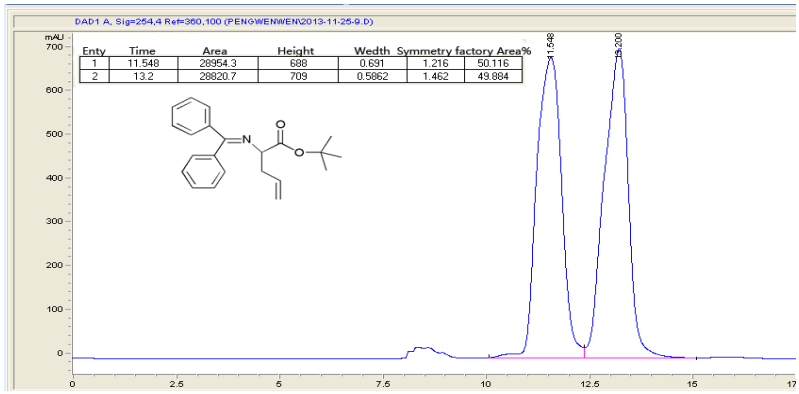


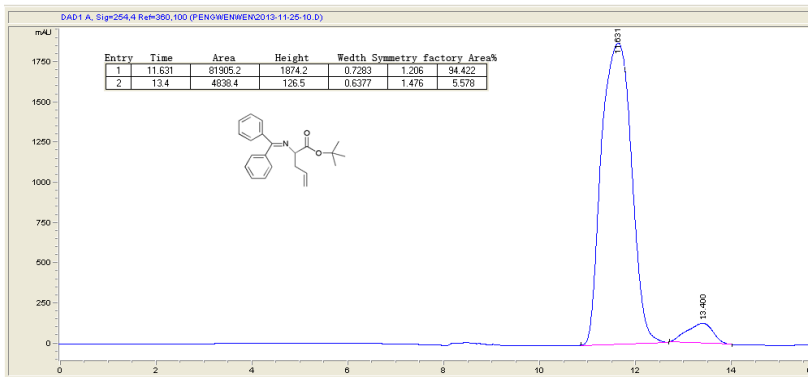


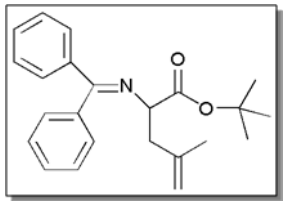


^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.64 (d, 2 H, ^{3}J = 6.9 Hz, Ph-H), 7.47−7.43 (m, 3 H, Ph-H), 7.41−7.35 (m, 3 H, Ph-H), 7.20−7.17 (m, 2 H, Ph-H), 5.80−5.66 (m, 1 H, -CH=), 5.11−5.01 (m, 2 H, $=CH_2$), 4.02 (dd, 1 H, ^{3}J = 5.6 Hz, 5.6 Hz, CH), 2.68−2.62 (m, 2 H, CH_2), 1.45 (s, 9 H, CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 11.6 min (*R*-isomer), 13.4 min (*S*-isomer).

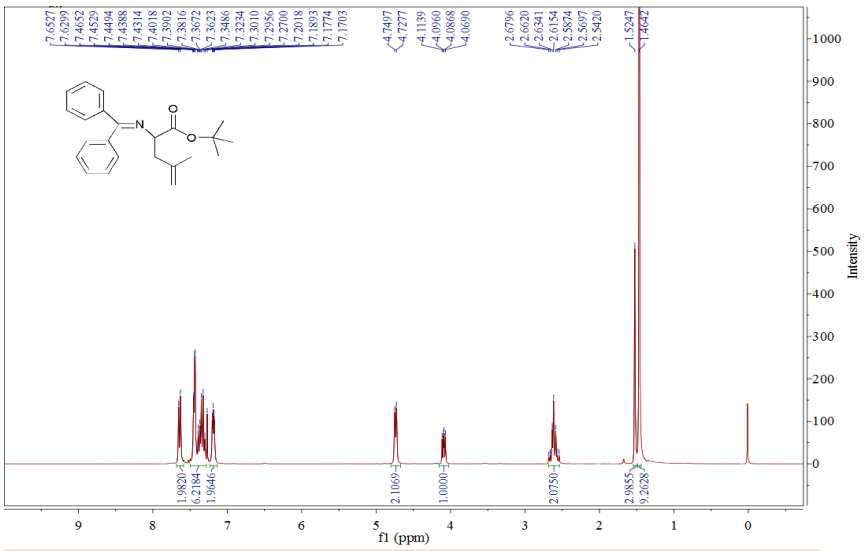


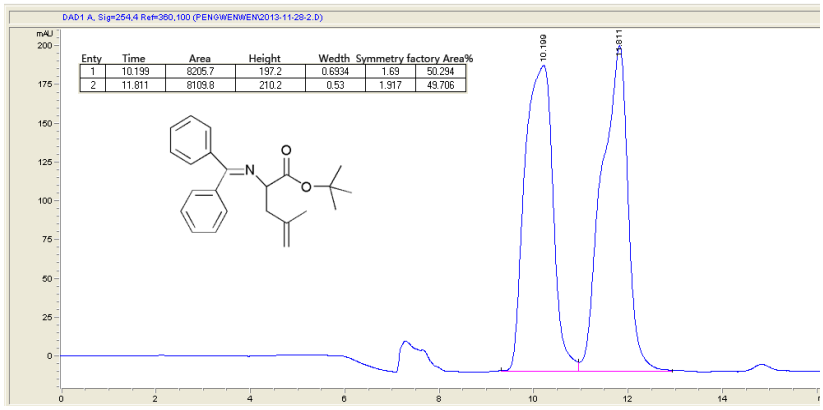


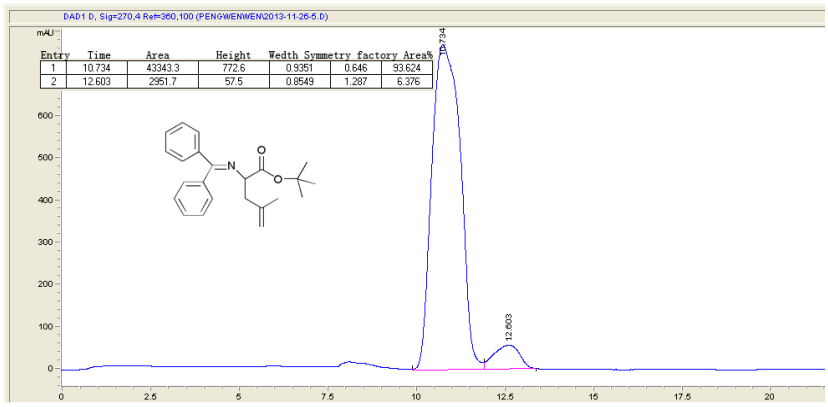


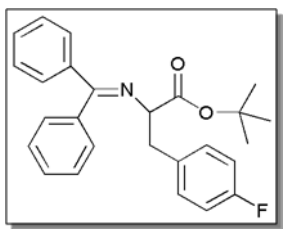


^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.64 (d, 2 H, ^{3}J = 6.8 Hz, Ph-H), 7.47−7.30 (m, 6 H, Ph-H), 7.20−7.17 (m, 2 H, Ph-H), 4.75 (d, 2 H, ^{3}J = 6.6 Hz, $=CH_2$), 4.09 (dd, 1 H, ^{3}J = 5.4 Hz, 5.3 Hz, CH), 2.68−2.54 (m, 2 H, CH_2), 1.52 (s, 3 H, CH_3), 1.46 (s, 9 H, CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.7 min (*R*-isomer), 12.6 min (*S*-isomer).

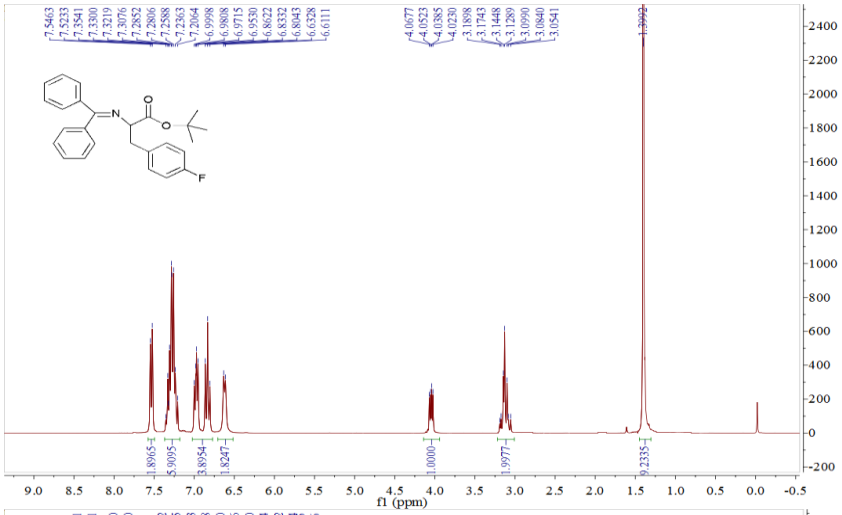








^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.53 (d, 2 H, ^{3}J = 6.9 Hz, Ph-H), 7.35−7.21 (m, 6 H, Ph-H), 7.00−6.80 (m, 4 H, Ph-H), 6.62 (d, 2 H, ^{3}J = 6.5 Hz), 4.04 (dd, 1 H, ^{3}J = 4.6 Hz, 4.7 Hz, CH), 3.19−3.05 (m, 2 H, CH_2), 1.40 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.6, 170.4 (C=N, C=O), 163.1, 160.0, 139.3, 134.0, 132.4, 131.2 (d, $^{2}J_{C\text{-}F}$ = 7.8 Hz, F), 131.1, 130.9, 130.2, 130.0, 128.6, 128.3, 128.2, 128.1, 128,0, 127.5 (Ph), 114.7, (d, $^{1}J_{C\text{-}F}$ = 20.9 Hz, F), 81.2 (O-C), 67.7 (CH), 38.7 (CH_2), 28.0 (CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.3 min (*R*-isomer), 12.5 min (*S*-isomer).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6.9715
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6.8822
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6.6328
6.6111
4.0677
4.0523
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4.0230
3.1808
3.1743
3.1448
3.1289
3.0990
3.0840
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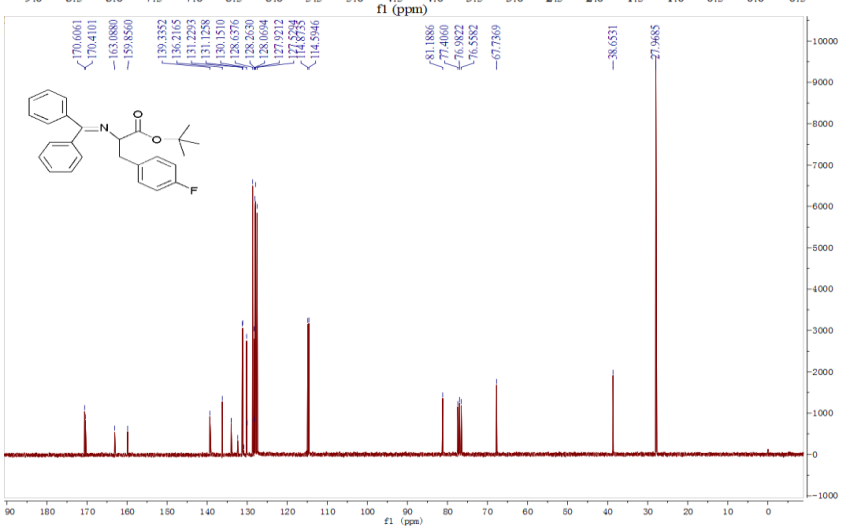
1.0000
1.9977
9.2335
f1 (ppm)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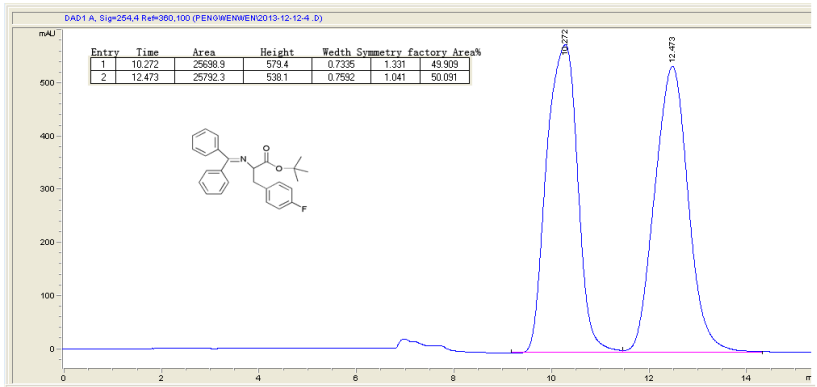
27.9685
f1 (ppm)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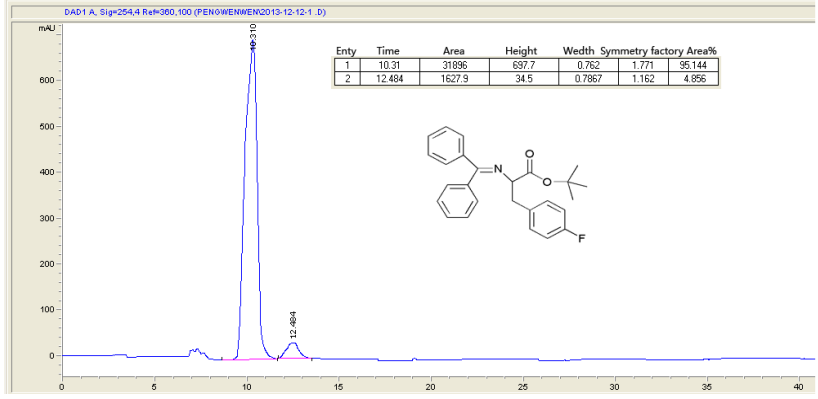
10.272
12.473
min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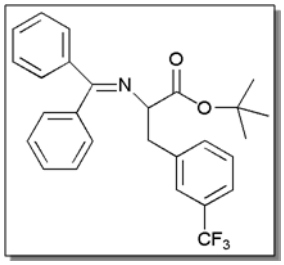
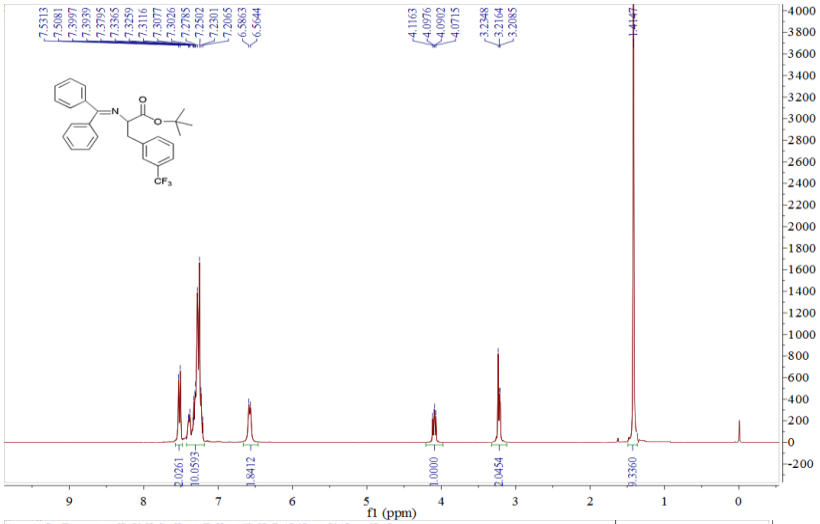
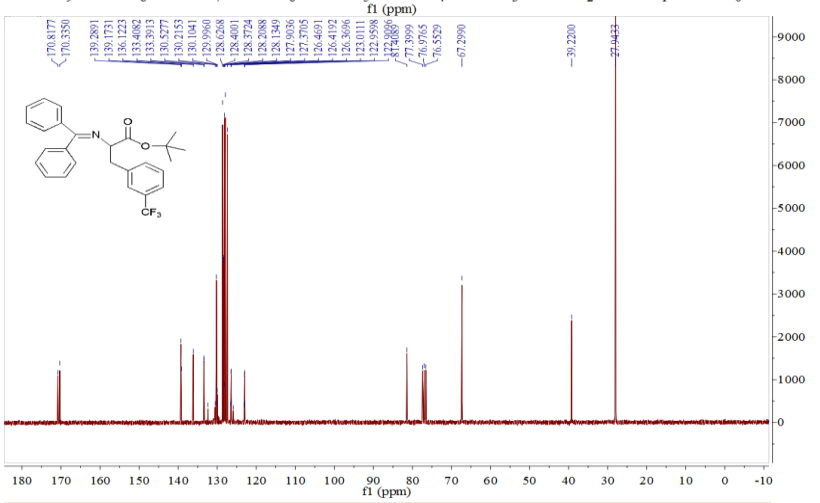
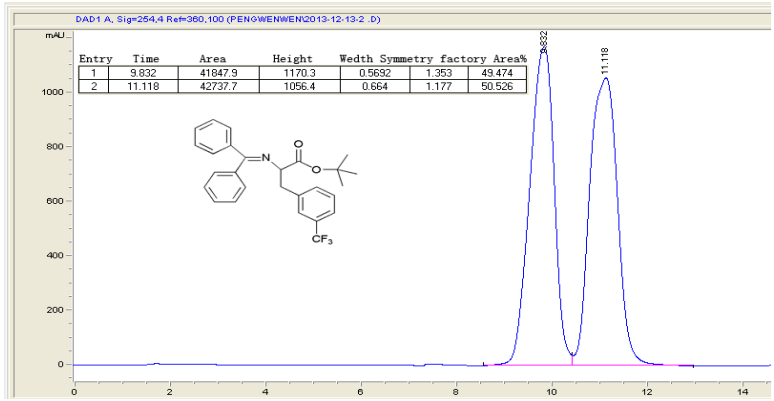
min

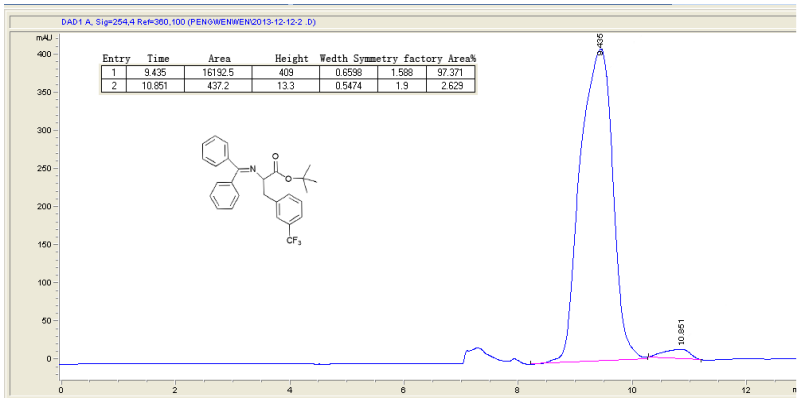


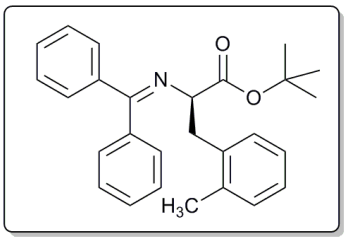
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.52 (d, 2 H, ^{3}J = 7.0 Hz, Ph-H), 7.40−7.21 (m, 10 H, Ph-H), 6.57 (d, 2 H, ^{3}J = 6.6 Hz, Ph-H), 4.09 (dd, 1 H, ^{3}J = 5.6 Hz, 5.6 Hz, CH), 3.23−3.21 (m, 2 H, CH_2), 1.41 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.8, 170.3 (C=N, C=O), 139.3, 139.2, 136.1, 133.4, 133.4, 132.4, 130.5, 130.2, 130.1, 130.0, 128.6, 128.4, 128.3, 128.2, 128,1, 127.9, 127.4, 126.4 (q, $^{2}J_{C\text{-}F}$ = 3.7 Hz, CF_3), 125.9 (Ph), 123.0 (q, $^{1}J_{C\text{-}F}$ = 3.8 Hz, CF_3), 81.4 (O-C), 67.3 (CH), 39.2 (CH_2), 27.9 (CH_3). Rt HPLC (Daicel Chiralpak OD-H, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 9.4 min (*R* -isomer), 10.9 min (*S* -isomer).



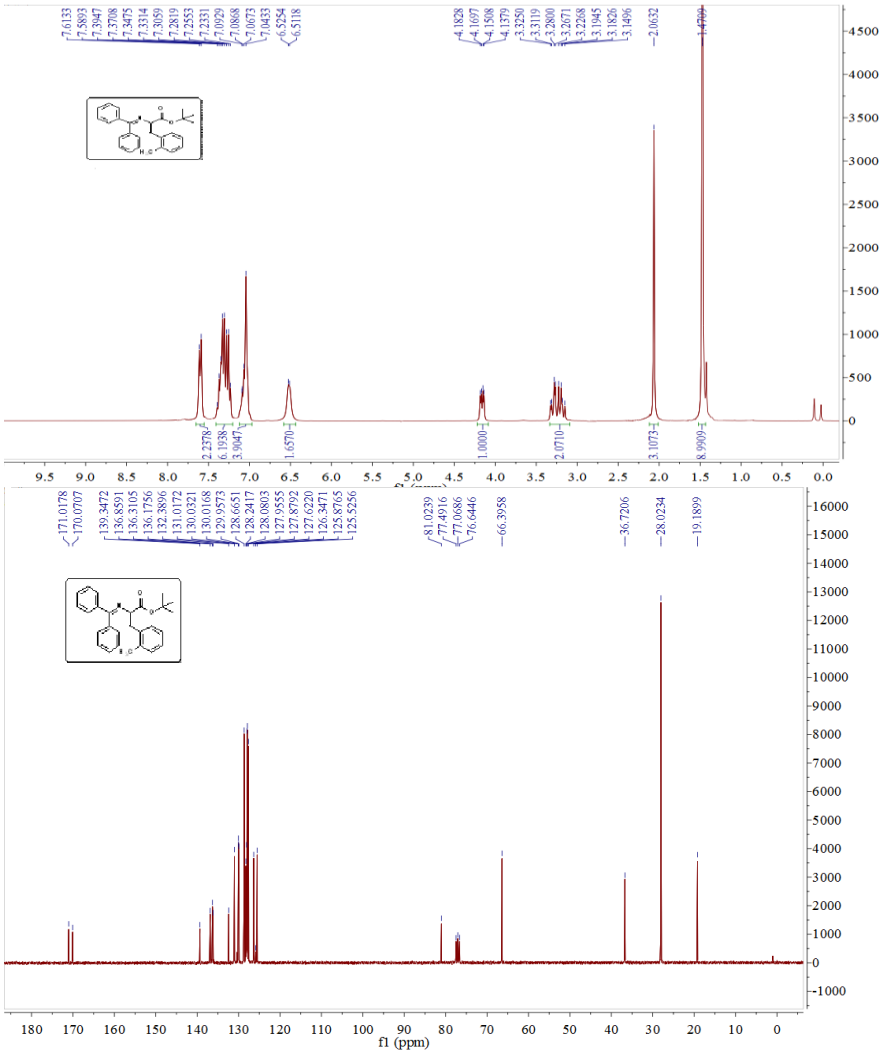


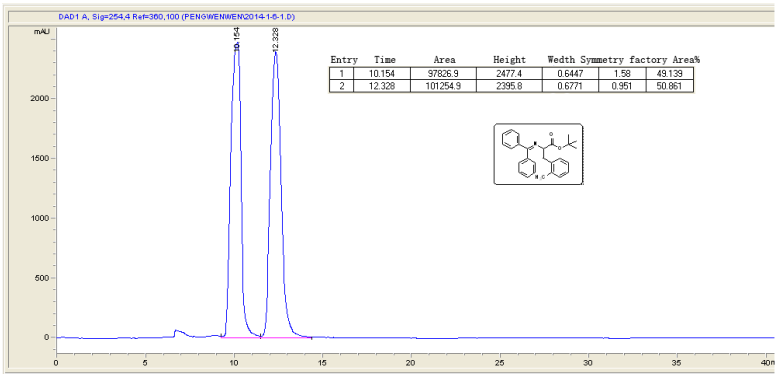


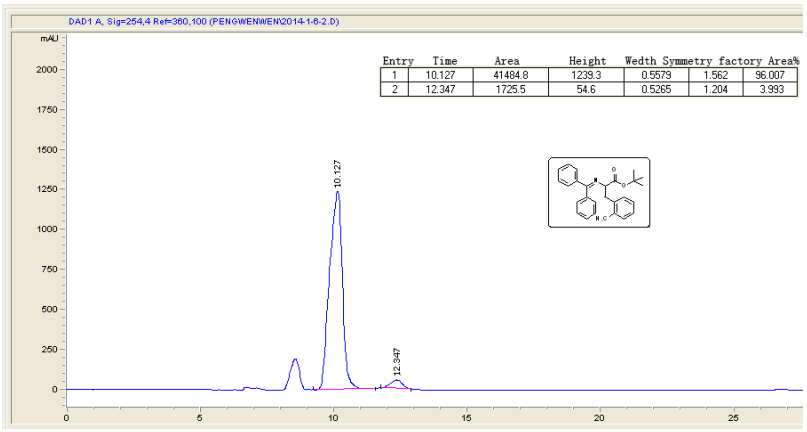


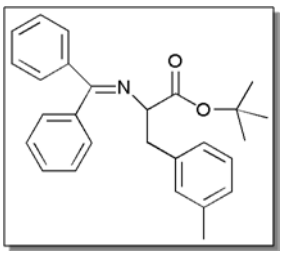


^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.60 (d, 2 H, ^{3}J = 7.2 Hz, Ph-H), 7.35−7.23 (m, 6 H, Ph-H), 7.09−7.04 (m, 4 H, Ph-H), 6.52 (d, 2 H, ^{3}J = 4.1 Hz, Ph-H), 4.15 (dd, 1 H, ^{3}J = 3.9 Hz, 3.9 Hz, CH), 3.33-3.15 (m, 2 H, CH_2), 2.06 (s, 3 H, Ph-CH_3), 1.39 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 171.0, 170.1 (C=N, C=O), 139.3, 136.9, 136.3, 136.2, 132.4, 131.0, 130.0, 130.0, 129.9, 128.7, 128.2, 128.1, 127.9, 127.8, 127.6, 126.3, 125.9, 125.5 (C-Ph), 81.0 (O-C), 66.4 (CH), 36.7 (CH_2), 28.0 (CH_3), 19.2 (Ph-CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.1 min (*R*-isomer), 12.3 min (*S*-isomer).

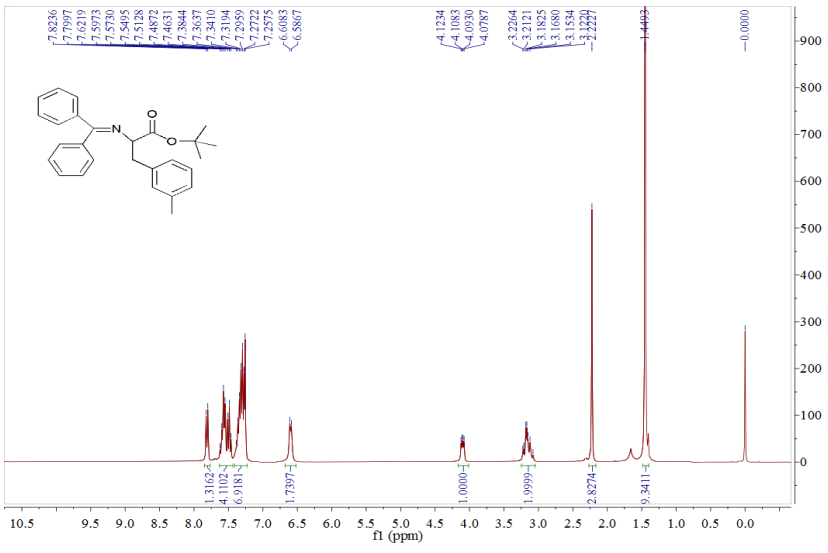


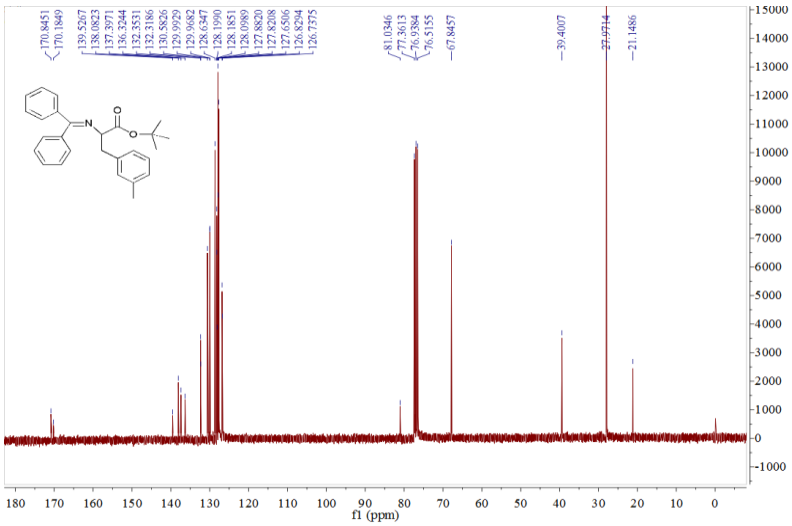


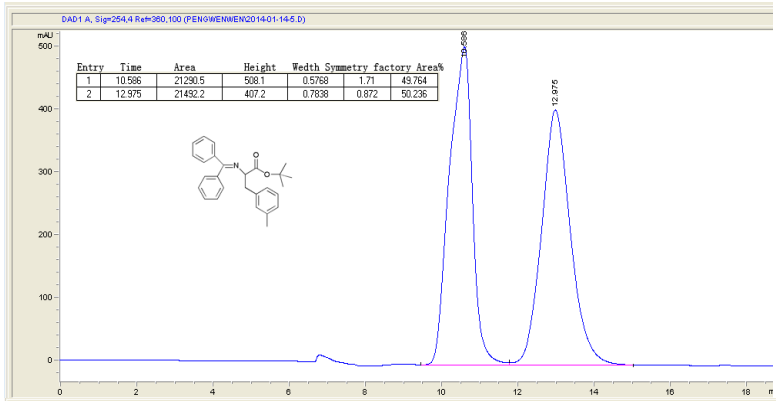


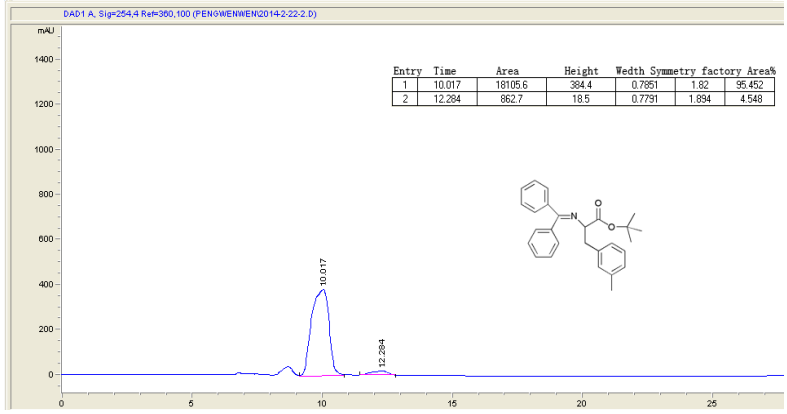


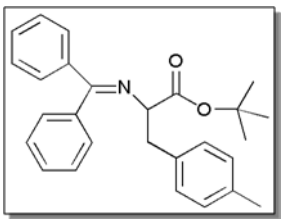
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.81 (d, 1 H, ^{3}J = 7.2 Hz, Ph-H), 7.62−7.46 (m, 4 H, Ph-H), 7.38−7.26 (m, 7 H, Ph-H), 6.59 (d, 2 H, ^{3}J = 6.5 Hz, Ph-H), 4.09 (dd, 1 H, ^{3}J = 4.5 Hz, 4.3 Hz, CH), 3.23−3.08 (m, 2 H, CH_2), 2.22 (s, 3 H, Ph-CH_3), 1.45 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.8, 170.2 (C=N, C=O), 139.5, 138.1, 137.4, 136.3, 132.4, 132.3, 130.6, 130.0, 130.0, 128.6, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 126.8, 126.7 (C-Ph), 81.0 (O-C), 67.8 (CH), 39.4 (CH_2), 28.0 (CH_3), 21.1 (Ph-CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.0 min (*R*-isomer), 12.3 min (*S*-isomer).



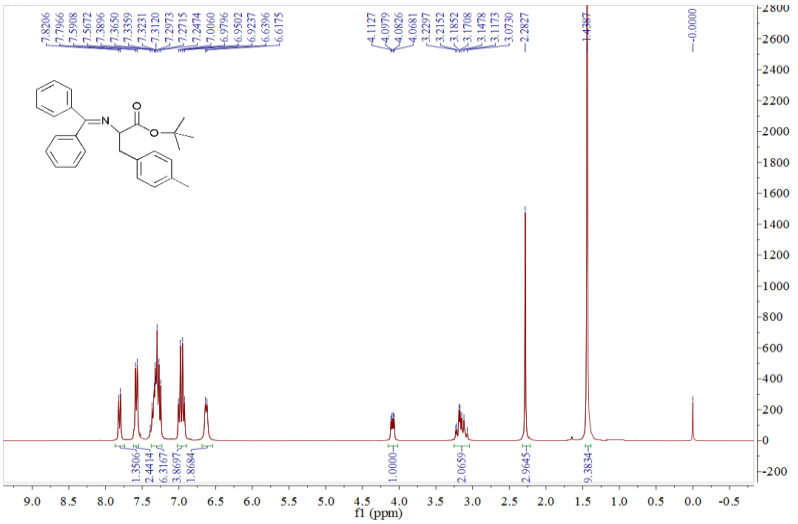








^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.81 (d, 1 H, ^{3}J = 7.2 Hz, Ph-H), 7.58 (d, 2H, ^{3}J = 7.1 Hz, Ph-H), 7.39−7.25 (m, 6 H, Ph-H), 6.96 (q, 4 H, ^{3}J = 7.9 Hz, Ph-H), 6.62 (d, 2 H, ^{3}J = 6.6 Hz, Ph-H), 4.09 (dd, 1 H, ^{3}J=4.4 Hz, 4.4 Hz, CH), 3.23−3.07 (m, 2 H, CH_2), 2.28 (s, 3 H, Ph-CH_3), 1.44 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.9, 170.1 (C=N, C=O), 139.5, 137.5, 136.3, 135.5, 135.1, 132.4, 130.0, 129.6, 128.7, 128.2, 128.1, 128.0, 127.9, 127.6 (C-Ph), 81.0 (O-C), 68.0 (CH), 39.1 (CH_2), 28.0 (CH_3), 21.0 (Ph-CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.7 min (*R*-isomer), 13.1 min (*S*-isomer).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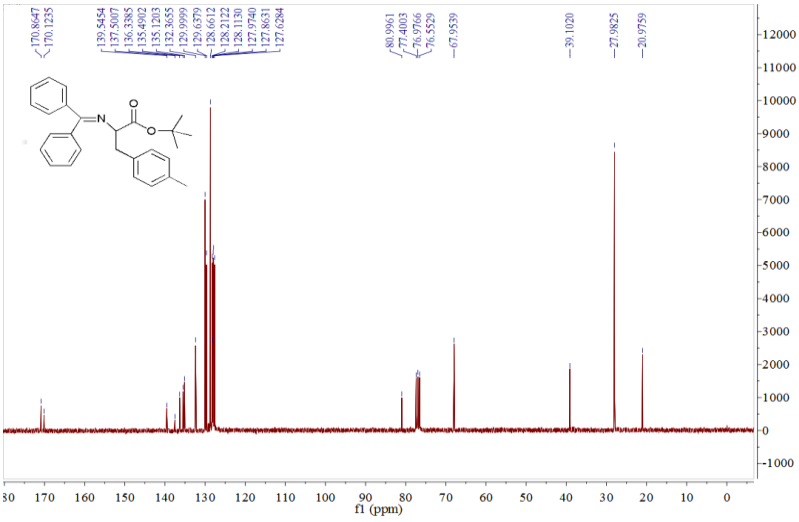
7.5908
7.5672
7.3896
7.3650
7.3359
7.3231
7.3120
7.2973
7.2715
7.2474
7.0060
6.9796
6.9502
6.9237
6.6396
6.6175
4.1127
4.0979
4.0826
4.0681
3.2297
3.2152
3.1852
3.1708
3.1478
3.1173
3.0730
2.2627
1.4387
0.0000
1.3506
2.4414
6.3167
3.8697
1.8684
1.0000
2.0659
2.9645
9.3834
f1 (ppm)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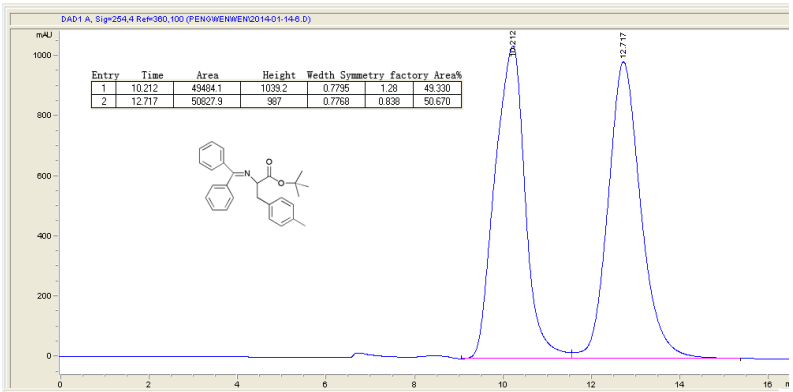
170.1255
139.5454
137.5007
136.3385
135.4902
135.1203
132.3655
129.9999
129.6379
128.6612
128.2122
128.1130
127.9740
127.8631
127.6284
80.9961
77.4003
76.9766
76.5529
67.9539
39.1020
27.9825
20.9759
f1 (ppm)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12.717
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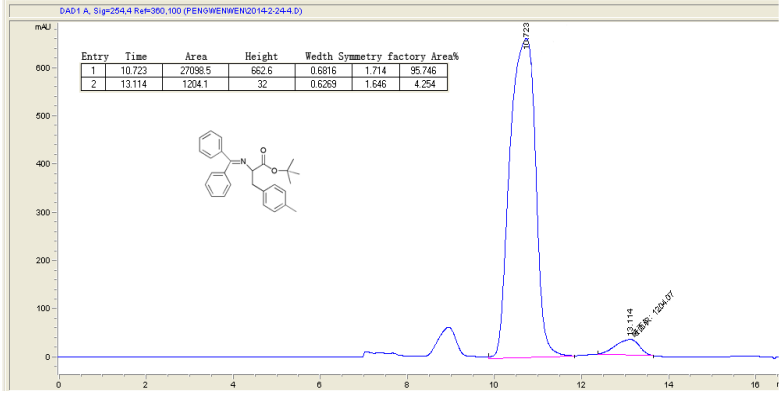
2 12.717 50827.9 987 0.7768 0.838 50.670


DAD1 A, Sig=254,4 Ref=360,100 (PENGWENWEN\2014-2-24-4.D)
mAU
10.723
13.114
Entry Time Area Height Wedth Symmetry factory Area%
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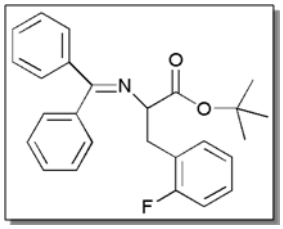
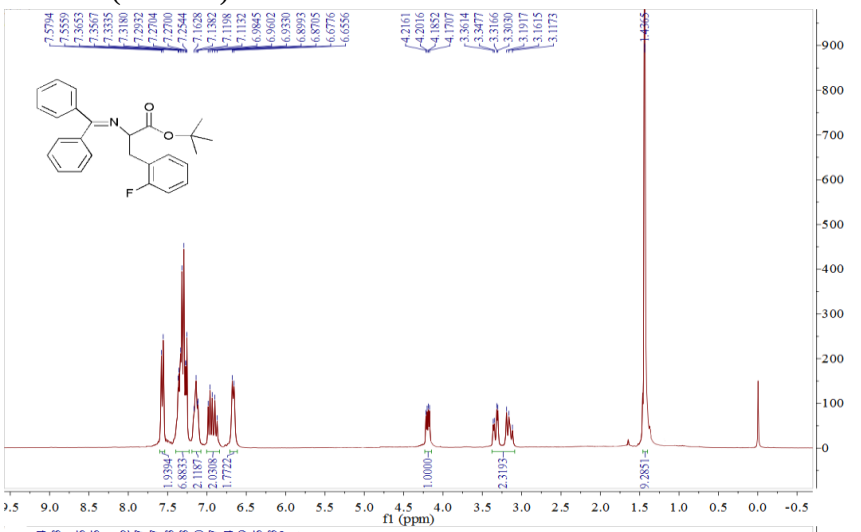
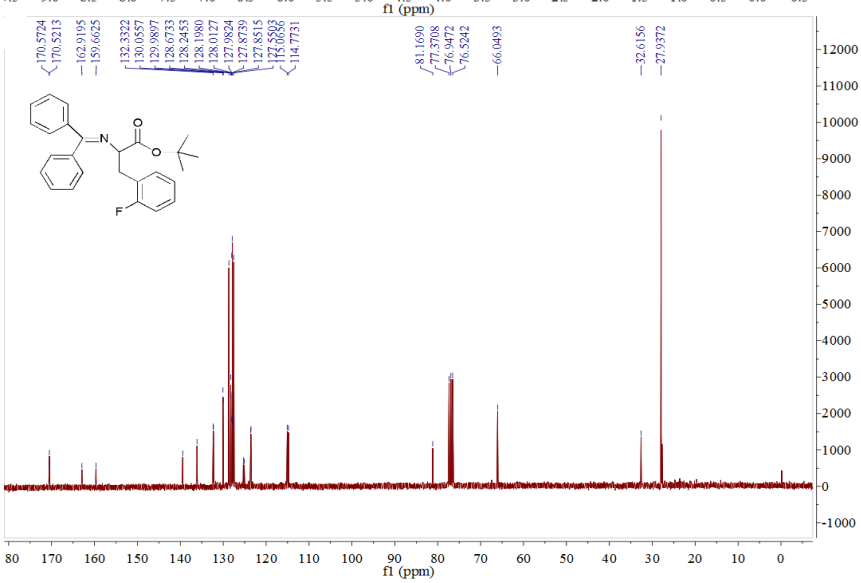
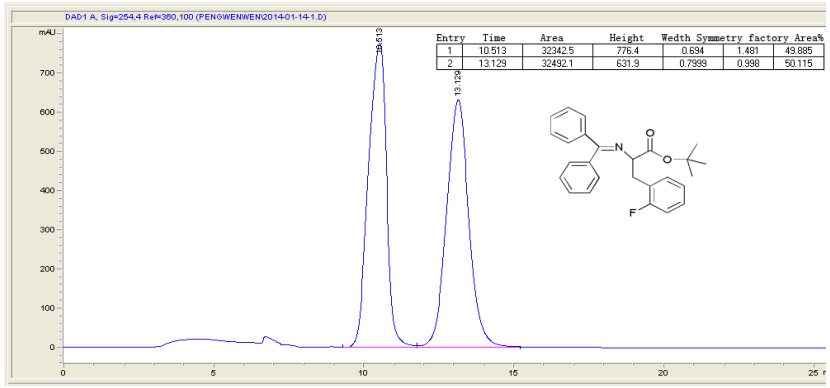
2 13.114 1204.1 32 0.6269 1.646 4.254

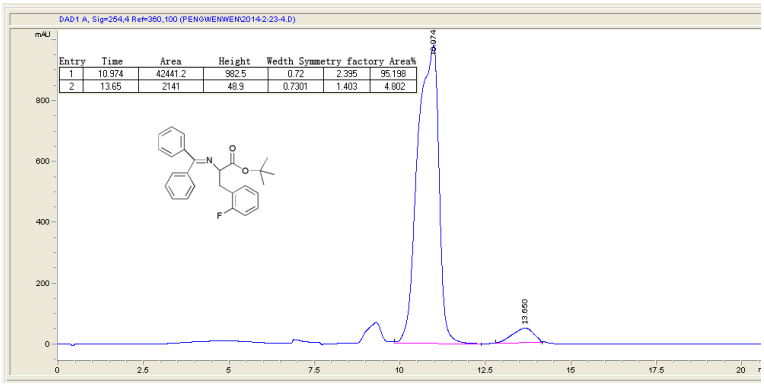


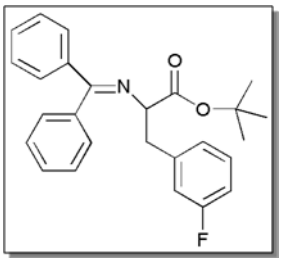
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.56 (d, 2 H, ^{3}J = 7.1 Hz, Ph-H), 7.37−7.25 (m, 6 H, Ph-H), 7.16−7.11 (m, 2 H, Ph-H), 6.98−6.87 (m, 2 H, Ph-H), 6.66 (d, 2 H, ^{3}J = 6.6 Hz, Ph-H), 4.19 (dd, 1 H, ^{3}J=4.4 Hz, 4.4 Hz, CH), 3.36-3.12 (m, 2 H, CH_2), 1.44 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.6, 170.5 (C=N, C=O), 162.9, 159.7, 139.4, 136.1, 132.3, 130.1, 130.0, 128.7, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.6 (C-Ph), 125.2 (d, $^{3}J_{C\text{-}F}$ = 15.5 Hz, F), 123.5 (d, $^{2}J_{C\text{-}F}$ = 3.5 Hz, F), 114.9 (d, $^{1}J_{C\text{-}F}$ = 21.9 Hz, F), 81.2 (O-C), 66.0 (CH), 32.6 (CH_2), 27.9 (CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 11.0 min (*R*-isomer), 13.7 min (*S*-isomer).



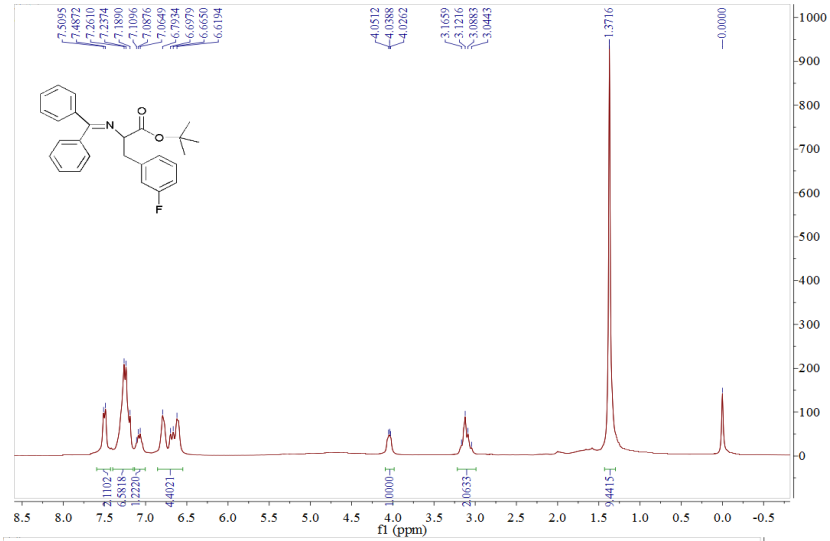


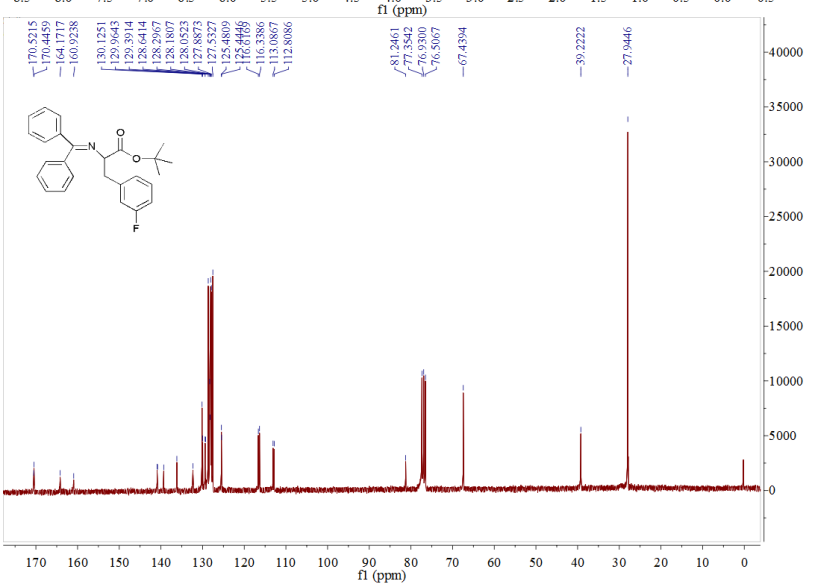


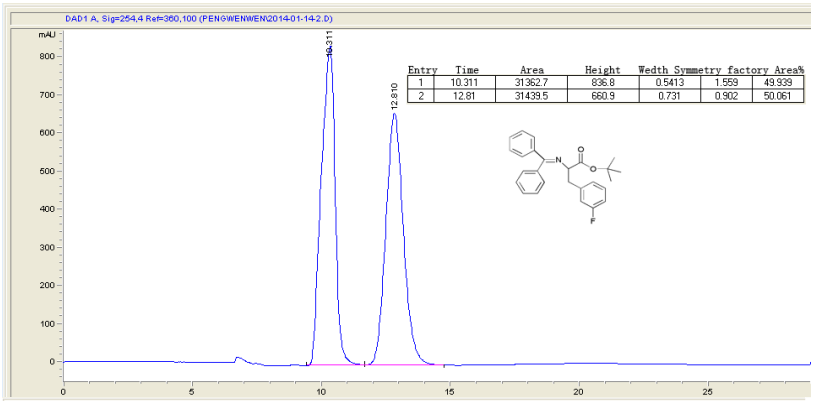


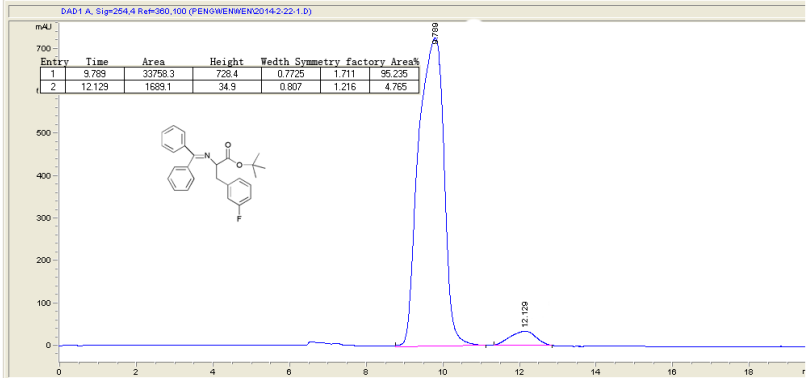


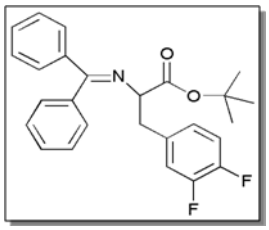
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.49 (d, 2 H, ^{3}J = 6.7 Hz, Ph-H), 7.26−7.19 (m, 7 H, Ph-H), 7.08 (q, 1 H, ^{3}J = 6.6 Hz, Ph-H), 6.79−6.62 (m, 4 H, Ph-H), 6.66 (d, 2 H, ^{3}J = 6.6 Hz, Ph-H), 4.04 (dd, 1 H, ^{3}J = 3.8 Hz, 3.8 Hz, CH), 3.17−3.04 (m, 2 H, CH_2), 1.37 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.5, 170.4 (C=N, C=O), 164.2, 160.9, 140.8 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz, F), 139.3, 136.2, 132.3, 130.1, 130.0, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 125.5, 125.4 (C-Ph), 116.4 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz, F), 112.9 (d, $^{1}J_{C\text{-}F}$ = 20.9 Hz, F), 81.2 (O-C), 67.4 (CH), 39.2 (CH_2), 27.9 (CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 9.8 min (*R*-isomer), 12.1 min (*S*-isomer).



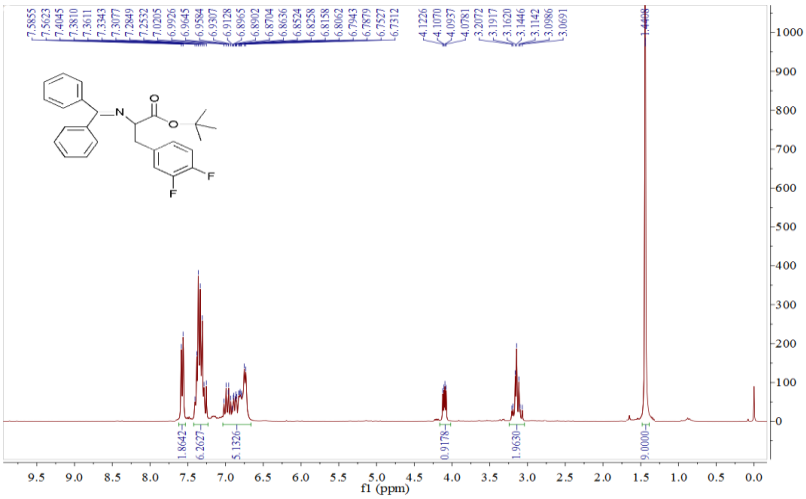


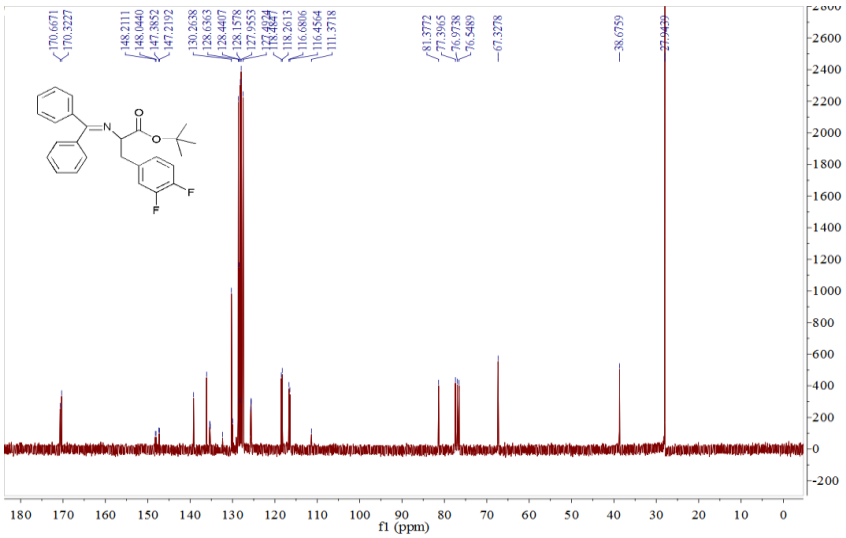






^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.57 (d, 2 H, ^{3}J = 7.0 Hz, Ph-H), 7.40−7.25 (m, 6 H, Ph-H), 7.02−6.73 (m, 5 H, Ph-H), 4.10 (dd, 1 H, ^{3}J = 4.7 Hz, 4.7 Hz, CH), 3.21−3.07 (m, 2 H, CH_2), 1.44 (s, 9 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 170.7, 170.3 (C=N, C=O), 148.1 (d, $^{3}J_{C\text{-}F}$ = 12.5 Hz, F), 147.3 (d, $^{3}J_{C\text{-}F}$ = 12.5 Hz, F), 139.2, 136.1, 135.3 (dd, $^{1}J_{C\text{-}F}$ = 5.7 Hz, F, $^{2}J_{C\text{-}F}$ = 3.9 Hz, F), 132.3, 130.3, 130.0, 128.6, 128.4, 128.2, 128.1, 127.9, 127.5, 125.6 (dd, $^{1}J_{C\text{-}F}$ = 6.0 Hz, F, $^{2}J_{C\text{-}F}$ = 3.6 Hz, F), 118.4 (d, $^{2}J_{C\text{-}F}$ = 16.8 Hz, F), 116.6 (d, $^{2}J_{C\text{-}F}$ = 16.8 Hz, F), 114.4 (C-Ph), 81.4 (O-C), 67.3 (CH), 38.7 (CH_2), 27.9 (CH_3). Rt HPLC (Phenomenex Lux 5u Amylose-2, 95:5, hexane/dioxane, 254 nm, 0.5 ml/min), 10.3 min (*R*-isomer), 12.3 min (*S*-isomer).

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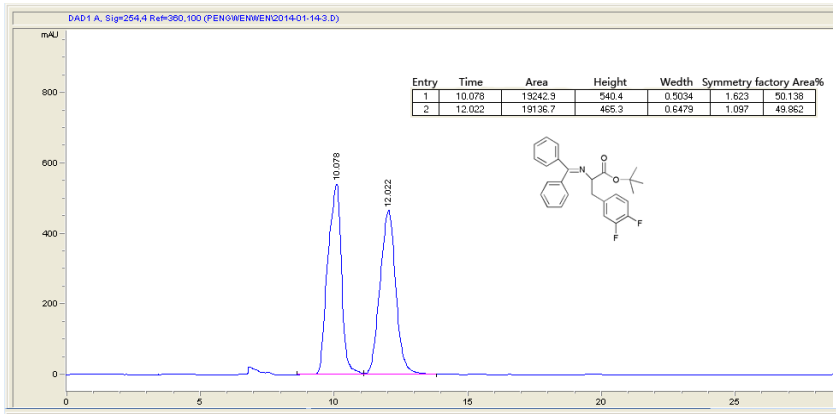
67.3278
38.6759
27.9439
f1 (ppm)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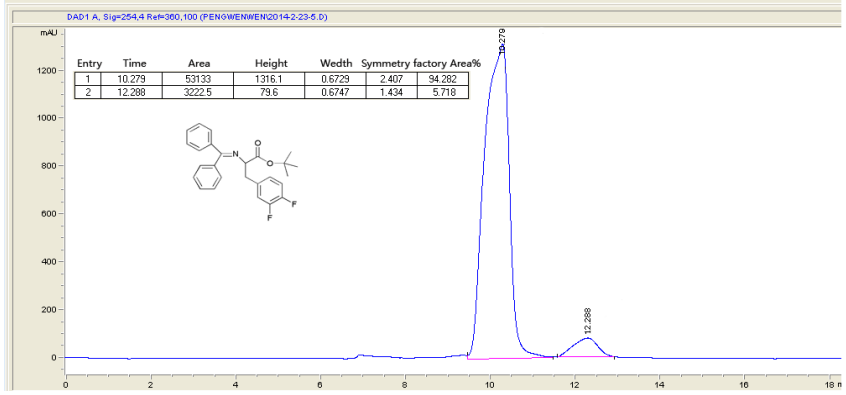
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12.288
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