Supplementary Information

Asymmetric ring-opening reaction of *meso*-epoxides with aromatic amines using homochiral metal-organic frameworks as recyclable heterogeneous catalysts

Koichi Tanaka,*[a] Maya Kinoshita,[a] Jun Kayahara,[a] Yutaro Uebayashi,[a] Kazusada Nakaji,[a] Maja Morawiak [b] and Zofia Urbanczyk-Lipkowska [b]

[a] *Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan. Fax: +81-06-6368-0861; Tel: +81-06-6368-0861; E-mail: ktanaka@kansai-u.ac.jp*
[b] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland. Fax: +48 22 6326681; Tel: +48 22 3432207; E-mail: ocryst@icho.edu.pl*

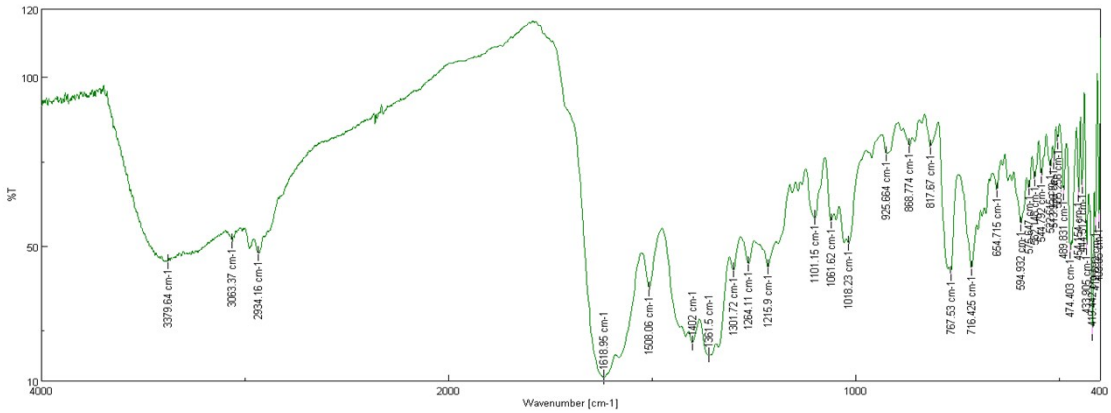


Figure S1. IR spectrum of (*R*)-ZnMOF-**3**

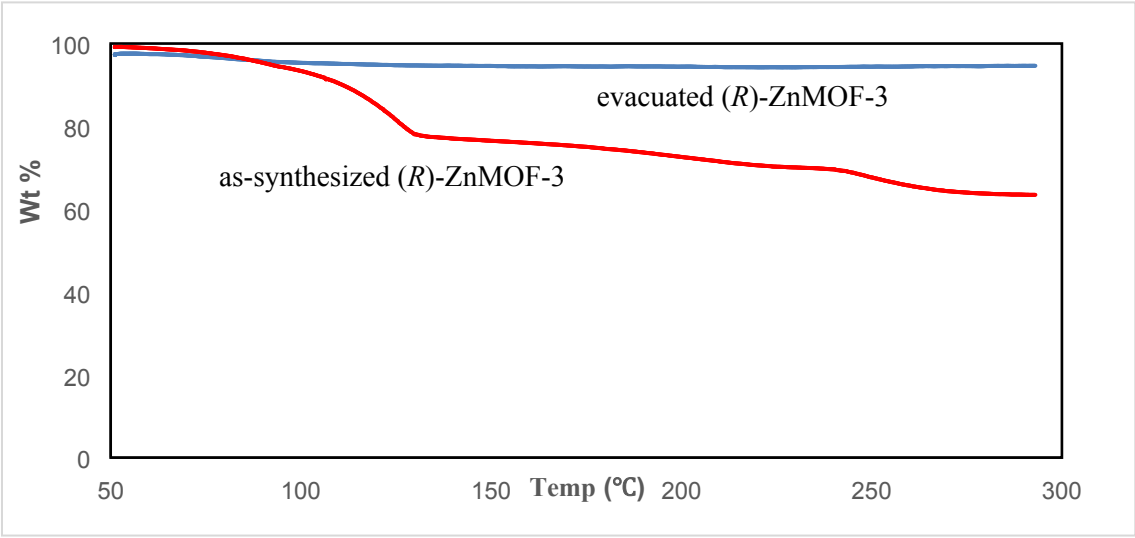


Figure S2. TG trace of (*R*)-ZnMOF-**3**

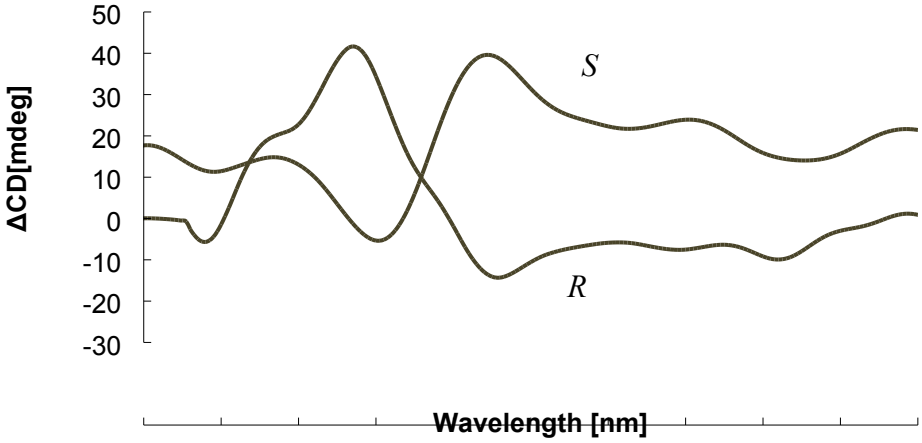


Figure S3. Solid CD spectra of (*R*)- and (*S*)-ZnMOF-**3** in KBr pellet.

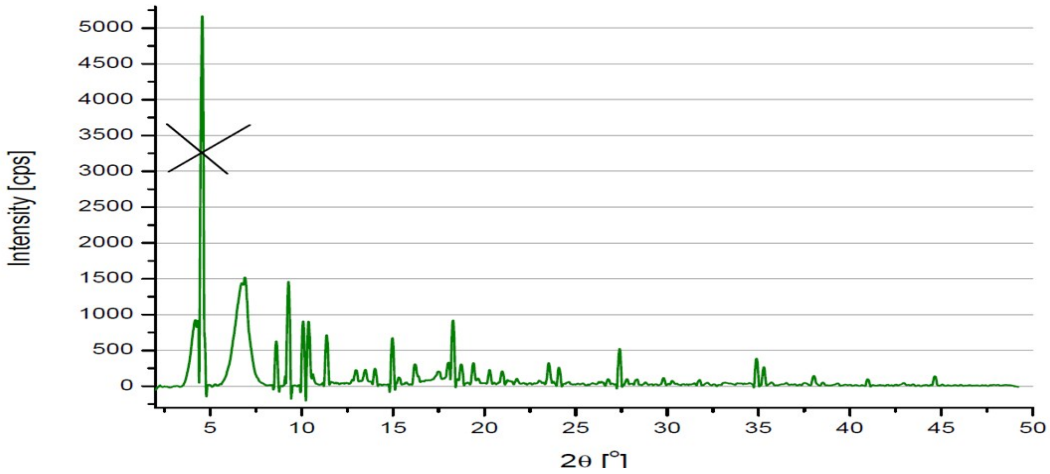


Figure S4. Powder X-Ray diffraction of (*R*)-ZnMOF-**4**.

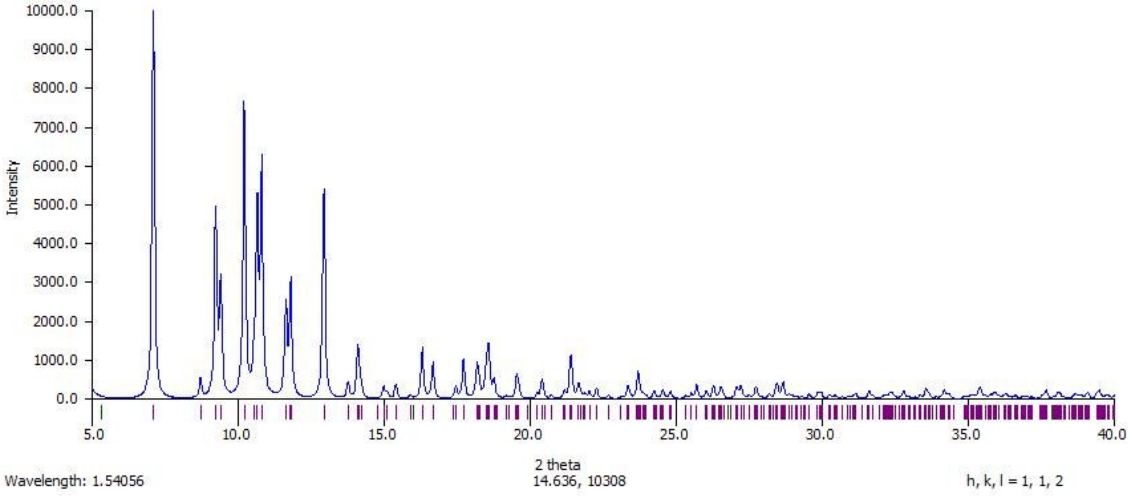


Figure S5. Powder X-ray diffraction of (*R*)-ZnMOF-**4** calculated from monocrystalline data.

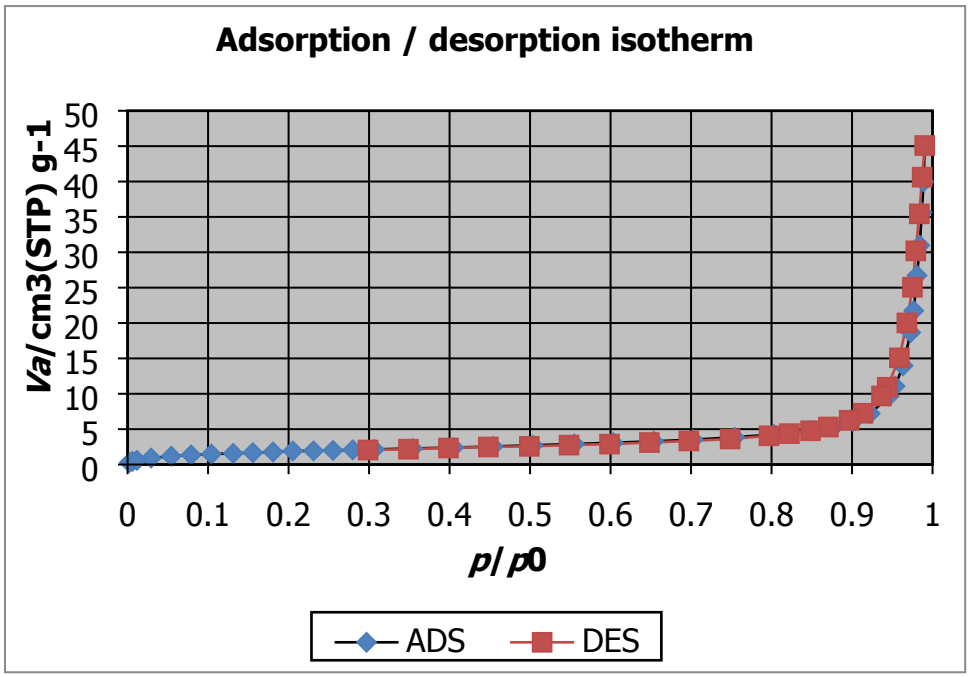


Figure S6. N_2 adsorption isotherm of (*R*)-ZnMOF-**4**.

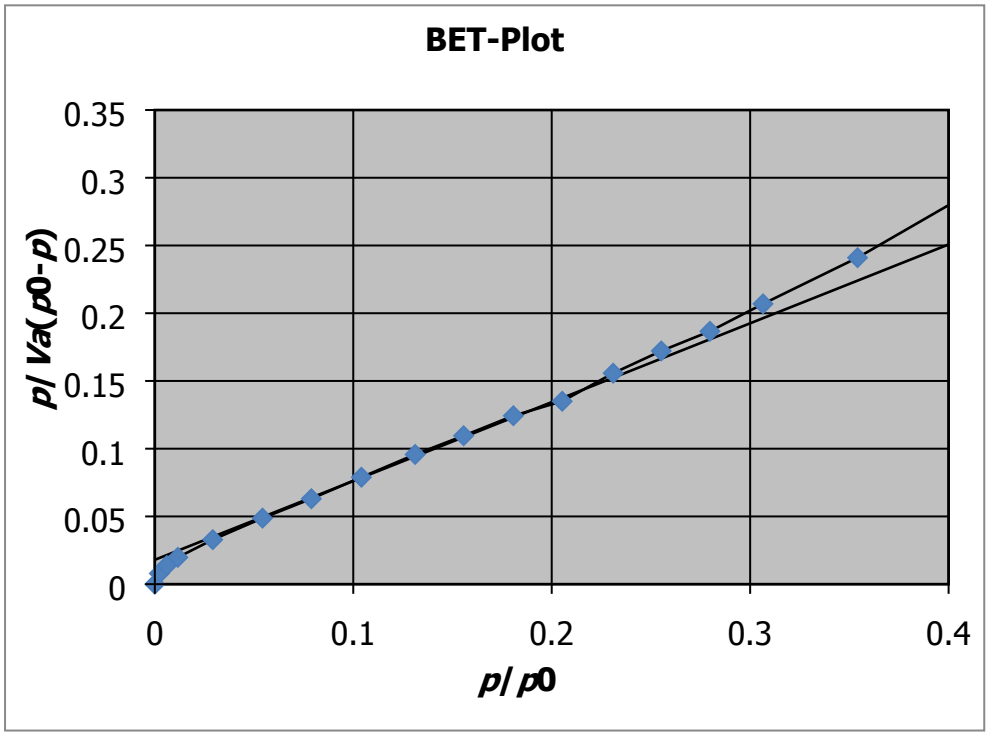


Figure S7. BET plot of (*R*)-ZnMOF-4.

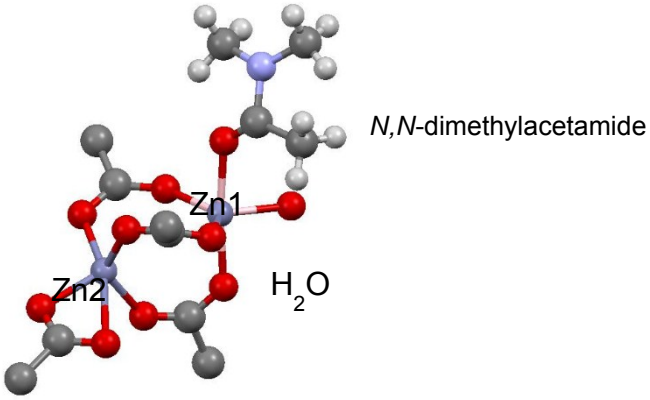


Figure S8. X-ray structure of (*R*)-ZnMOF-4 showing a coordination sphere of Zn cation.

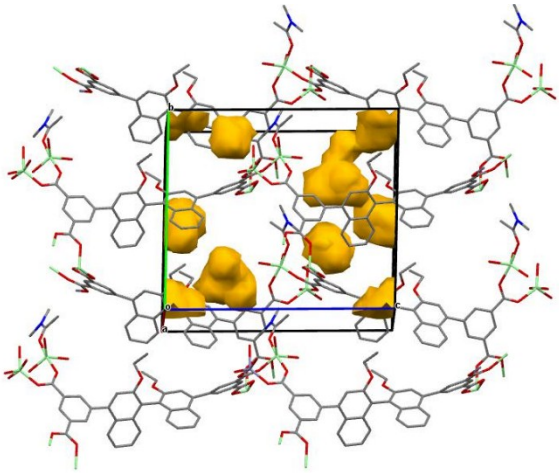


Figure S9. Unit cell of complete structure of (*R*)-ZnMOF-**4** projected down a-axis with Conolly's surfaces depicted in magenta (H-atoms and solvent molecules omitted for clarity).

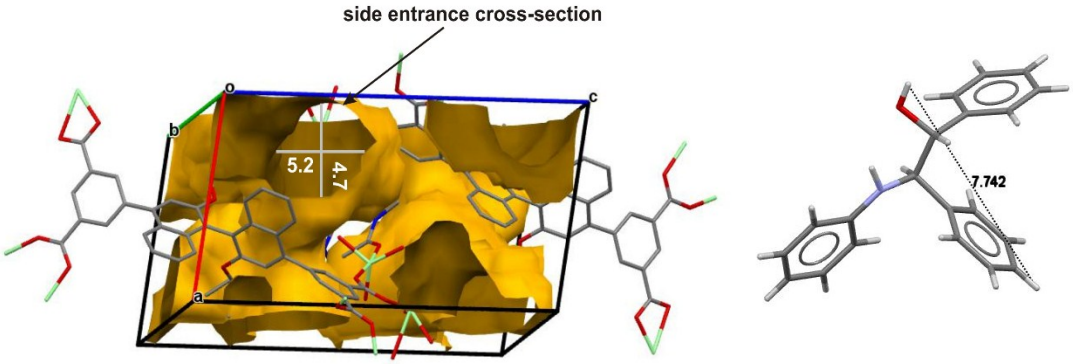
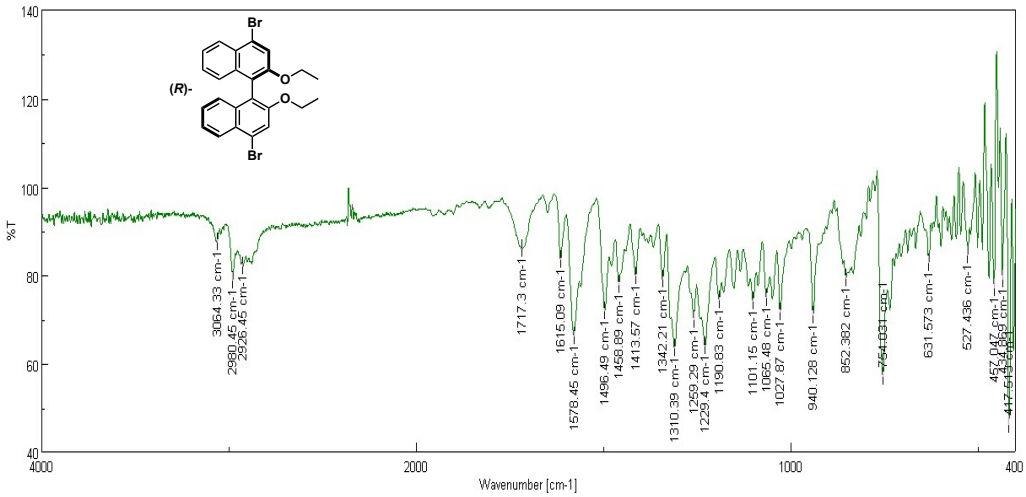
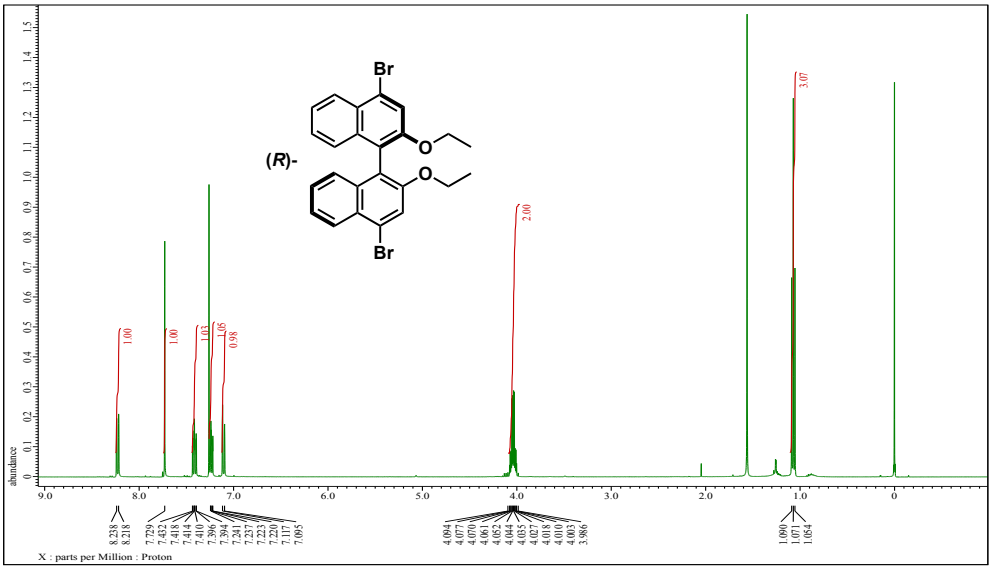
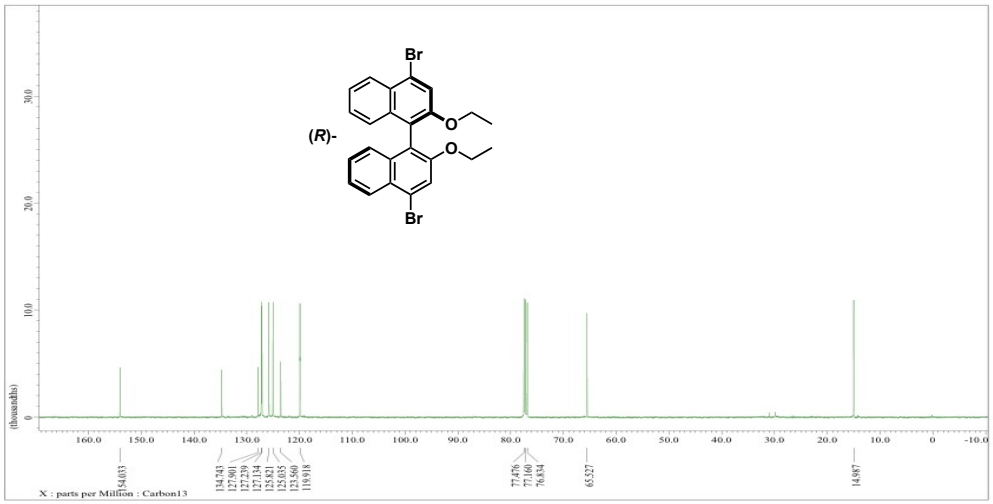
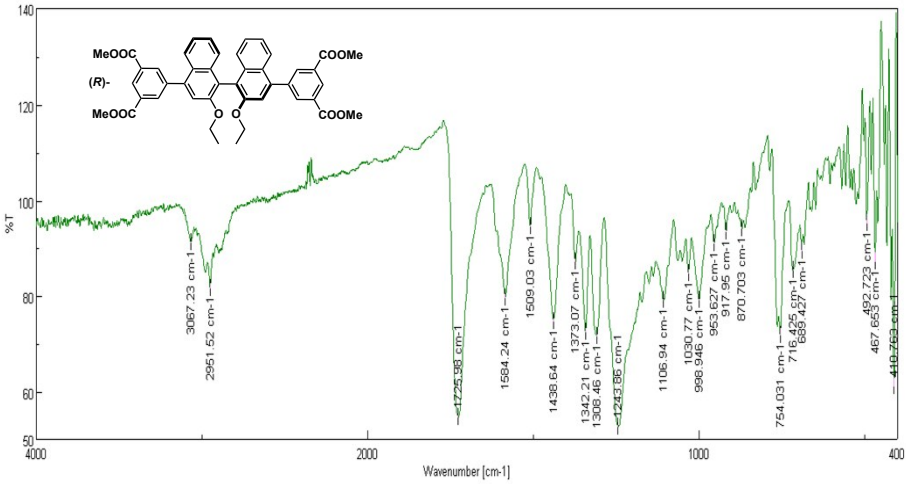


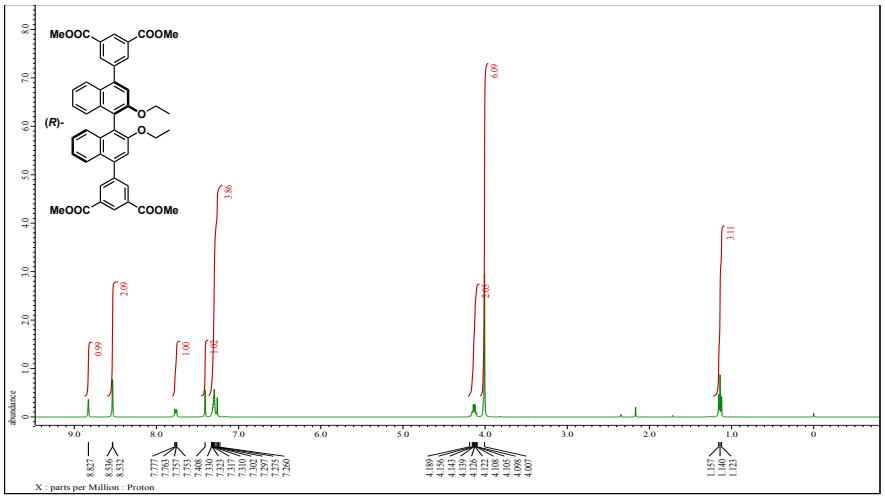
Figure S10. Left - side view of channel 1 with cross-section of the 4.7 x 5.2 Å diameter; right – molecular dimensions of compound **8a** calculated from crystal structure.

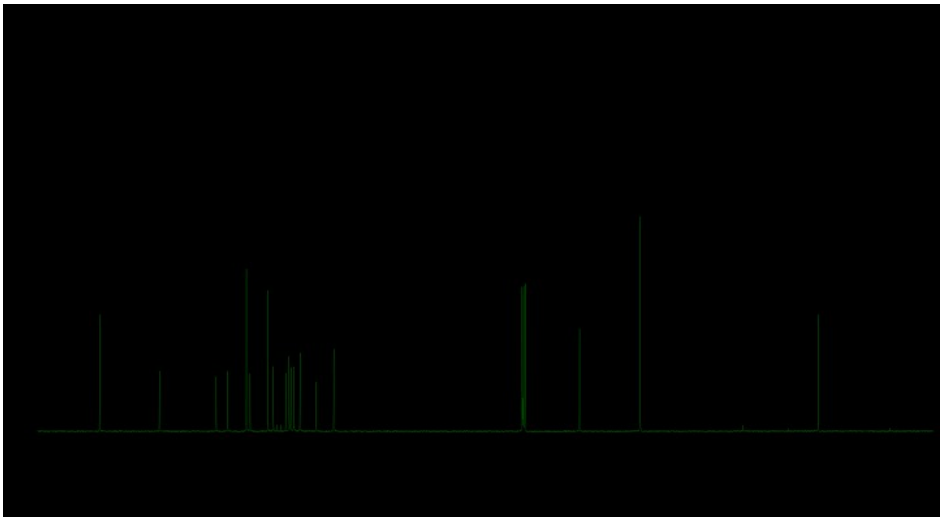

(R)-
Br
O
O
Br
%T
Wavenumber [cm-1]
3064.33 cm-1
2960.45 cm-1
2926.45 cm-1
1717.3 cm-1
1615.09 cm-1
1578.45 cm-1
1496.49 cm-1
1456.89 cm-1
1413.57 cm-1
1342.21 cm-1
1310.39 cm-1
1259.29 cm-1
1229.4 cm-1
1190.83 cm-1
1101.15 cm-1
1065.48 cm-1
1027.87 cm-1
940.128 cm-1
852.382 cm-1
764.031 cm-1
631.573 cm-1
527.436 cm-1
457.047 cm-1

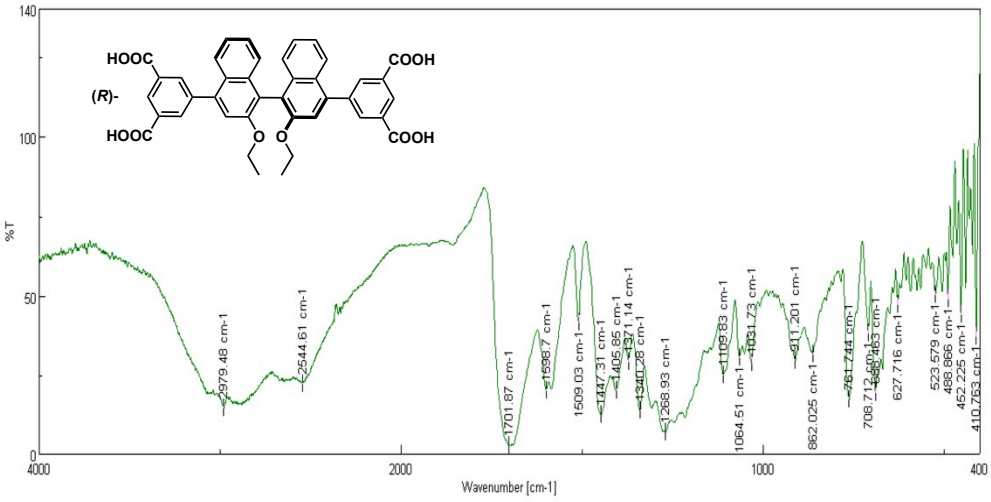

(R)-
Br
O
O
Br
abundance
X : parts per Million : Proton
1.00
1.00
1.03
1.06
0.98
2.00
3.07

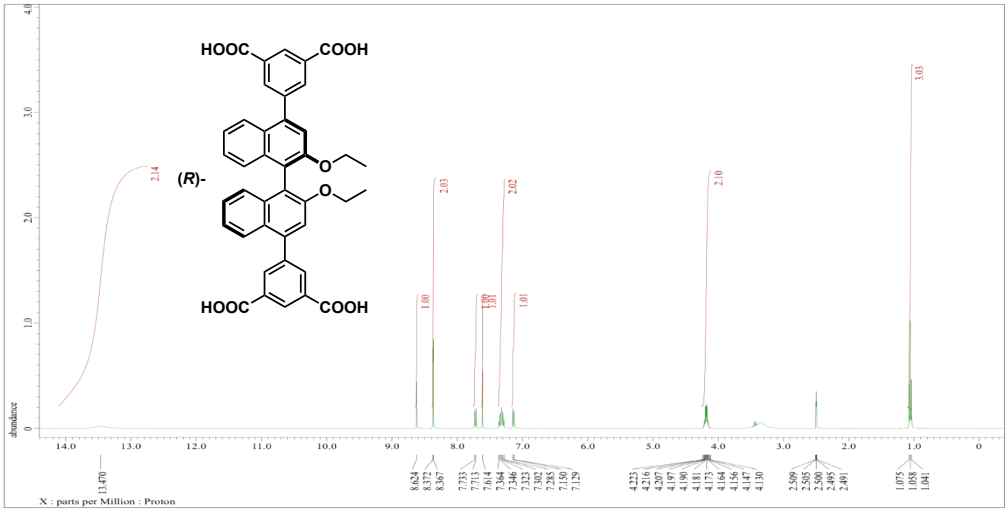

(R)-
Br
O
O
Br
(thousands)
X : parts per Million : Carbon13

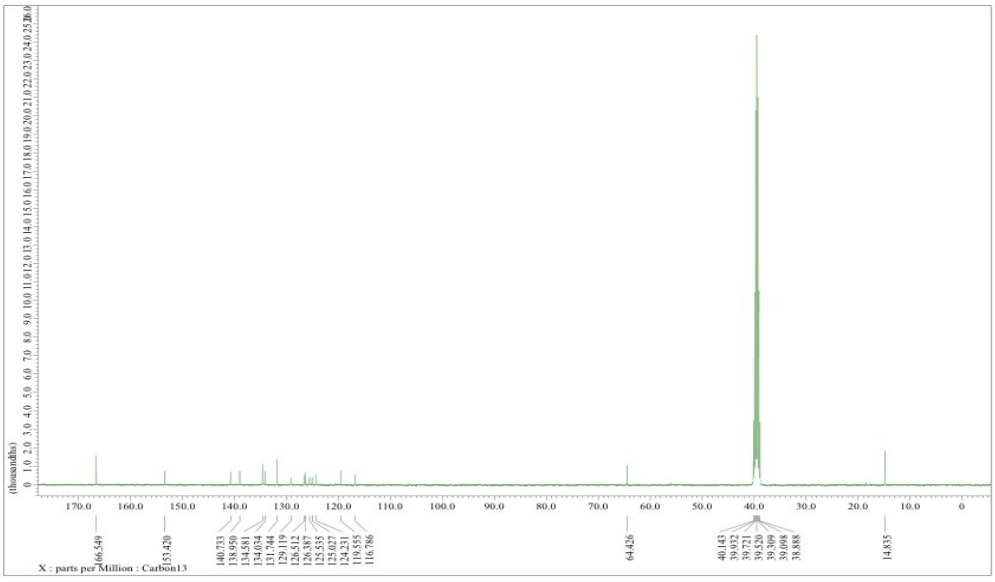

MeOOC
COOMe
(R)-
MeOOC
COOMe
%T
Wavenumber [cm-1]
3067.23 cm-1
2951.52 cm-1
1725.98 cm-1
1584.24 cm-1
1509.03 cm-1
1438.64 cm-1
1373.07 cm-1
1342.21 cm-1
1308.46 cm-1
1243.86 cm-1
1106.94 cm-1
1039.77 cm-1
998.946 cm-1
963.627 cm-1
917.95 cm-1
870.703 cm-1
754.031 cm-1
716.425 cm-1
689.427 cm-1
492.723 cm-1
467.653 cm-1
410.763 cm-1


MeOOC
COOMe
(R)-
MeOOC
COOMe
X : parts per Million : Proton

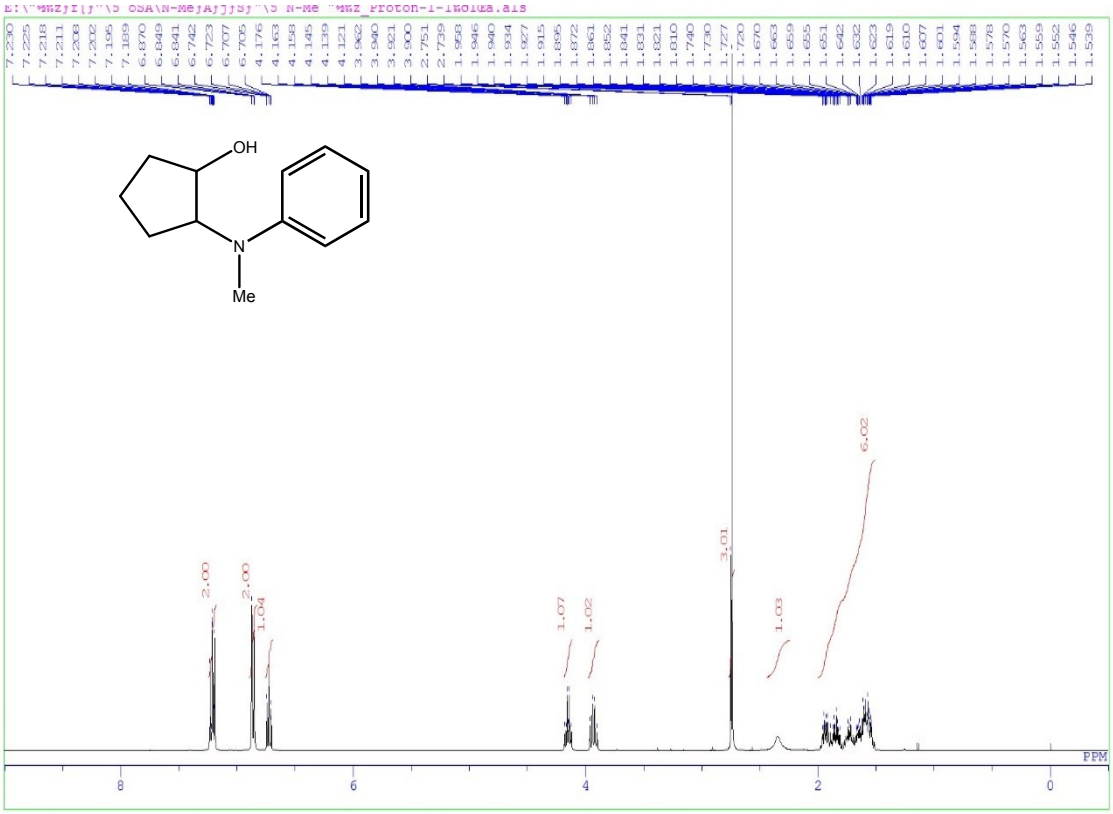


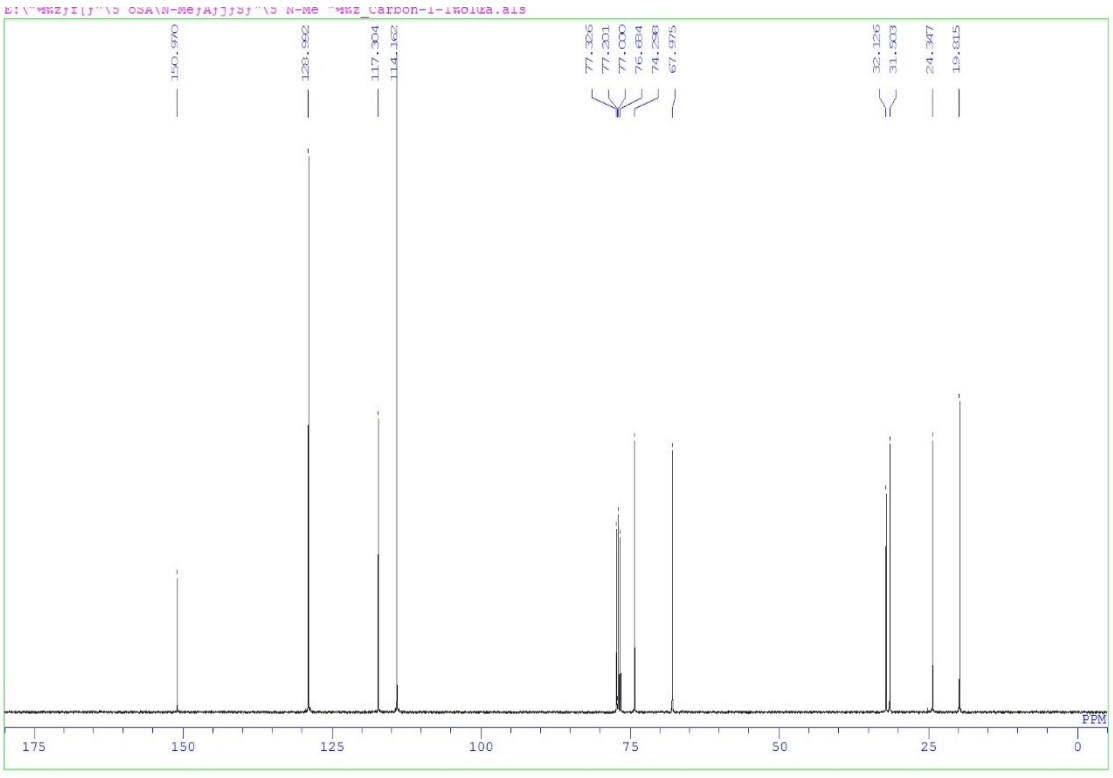

HOOC
COOH
(R)-
HOOC
COOH
O
O
%T
Wavenumber [cm-1]
2979.48 cm-1
2544.61 cm-1
1701.87 cm-1
1598.7 cm-1
1509.03 cm-1
1447.31 cm-1
1405.85 cm-1
1371.14 cm-1
1340.26 cm-1
1268.93 cm-1
1109.83 cm-1
1064.51 cm-1
1031.73 cm-1
911.201 cm-1
862.025 cm-1
761.744 cm-1
708.712 cm-1
668.463 cm-1
627.716 cm-1
523.579 cm-1
488.866 cm-1
452.225 cm-1
410.763 cm-1


HOOC
COOH
(R)-
HOOC
COOH
O
O
abundance
X : parts per Million : Proton

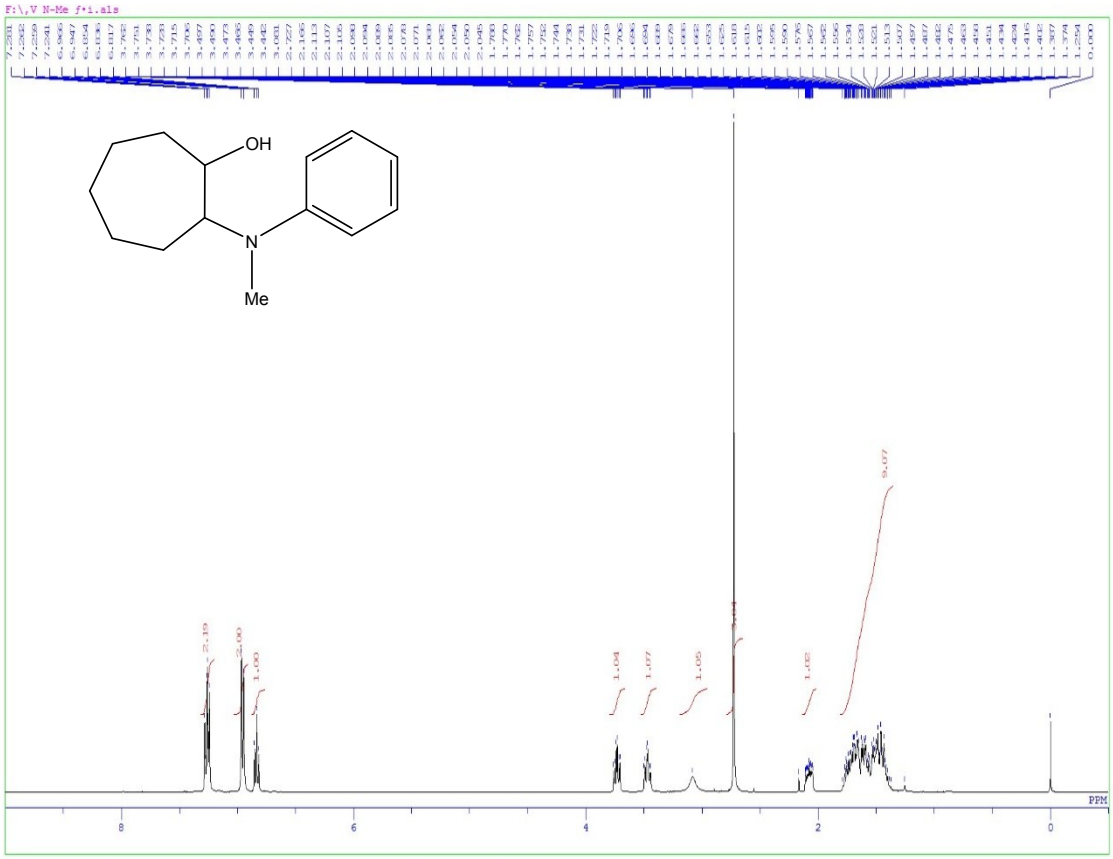

(thousands)
X : parts per Million : Carbon13

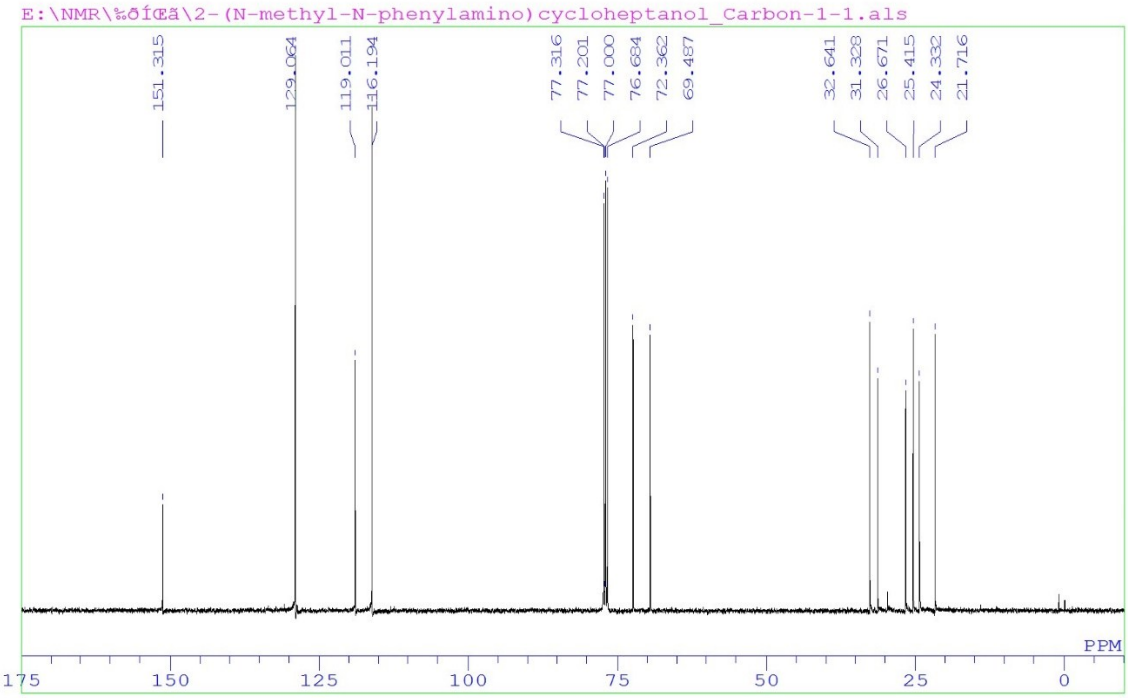
2-(*N*-methyl-*N*-phenylamino)cyclopentanol



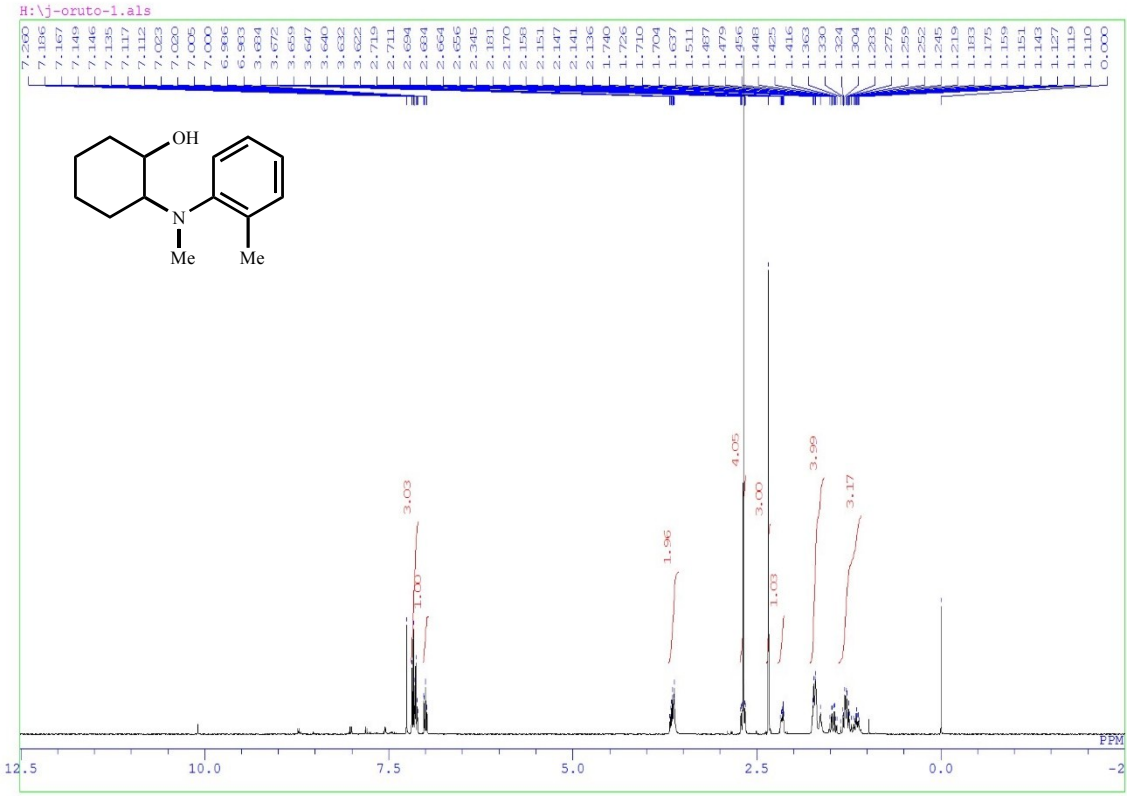


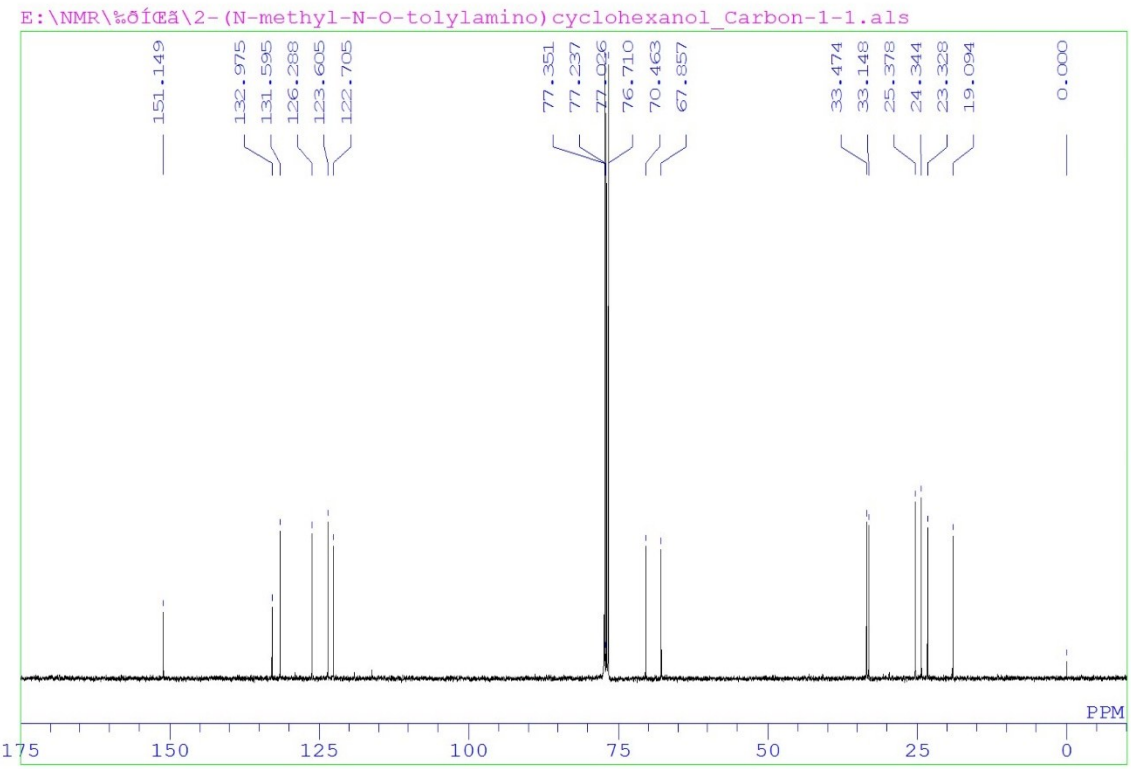
2-(*N*-methyl-*N*-phenylamino)cycloheptanol



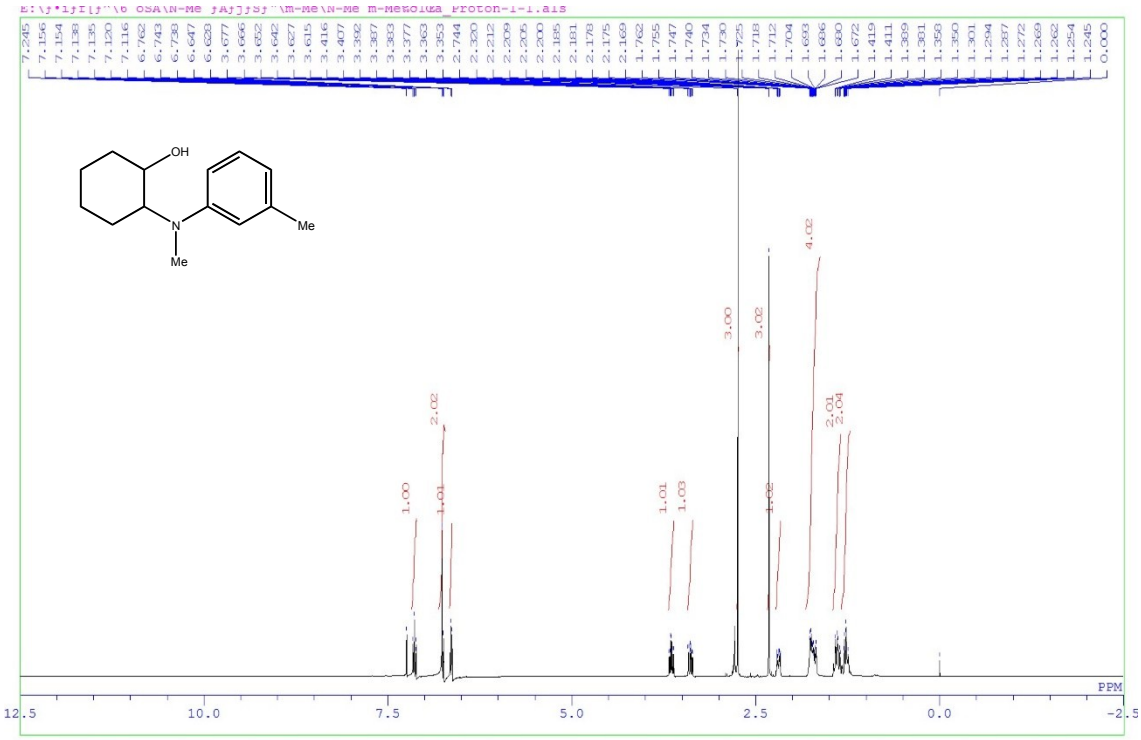


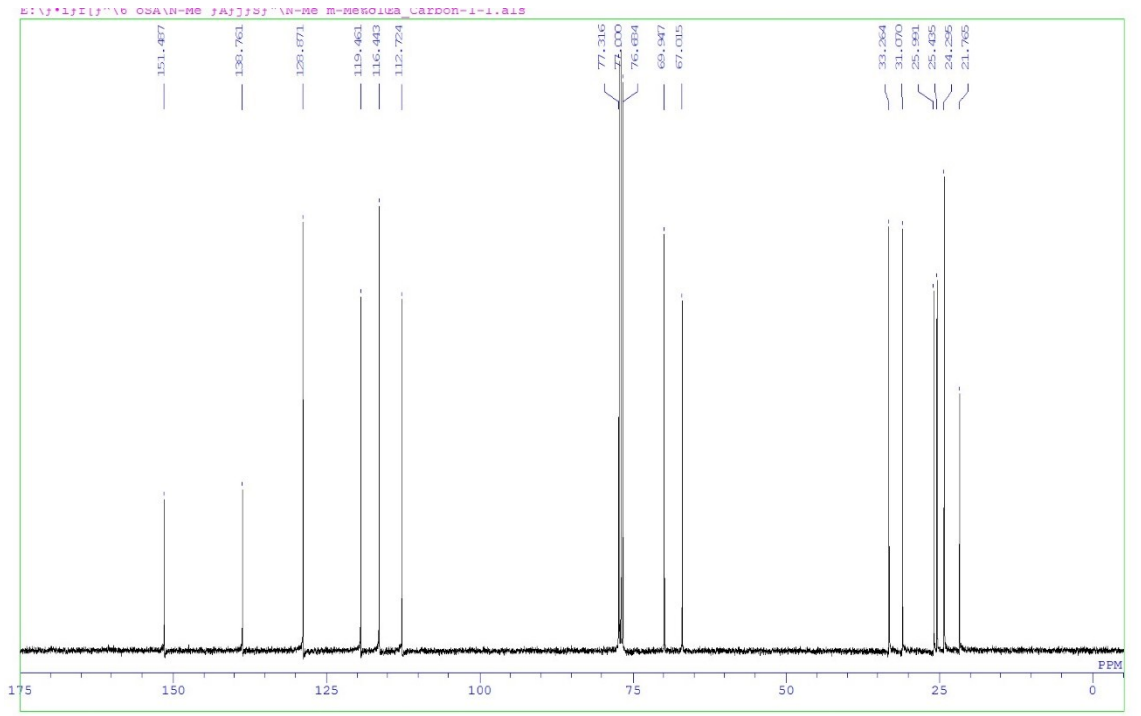
2-(*N*-methyl-*N*-*o*-tolylamino)cyclohexanol



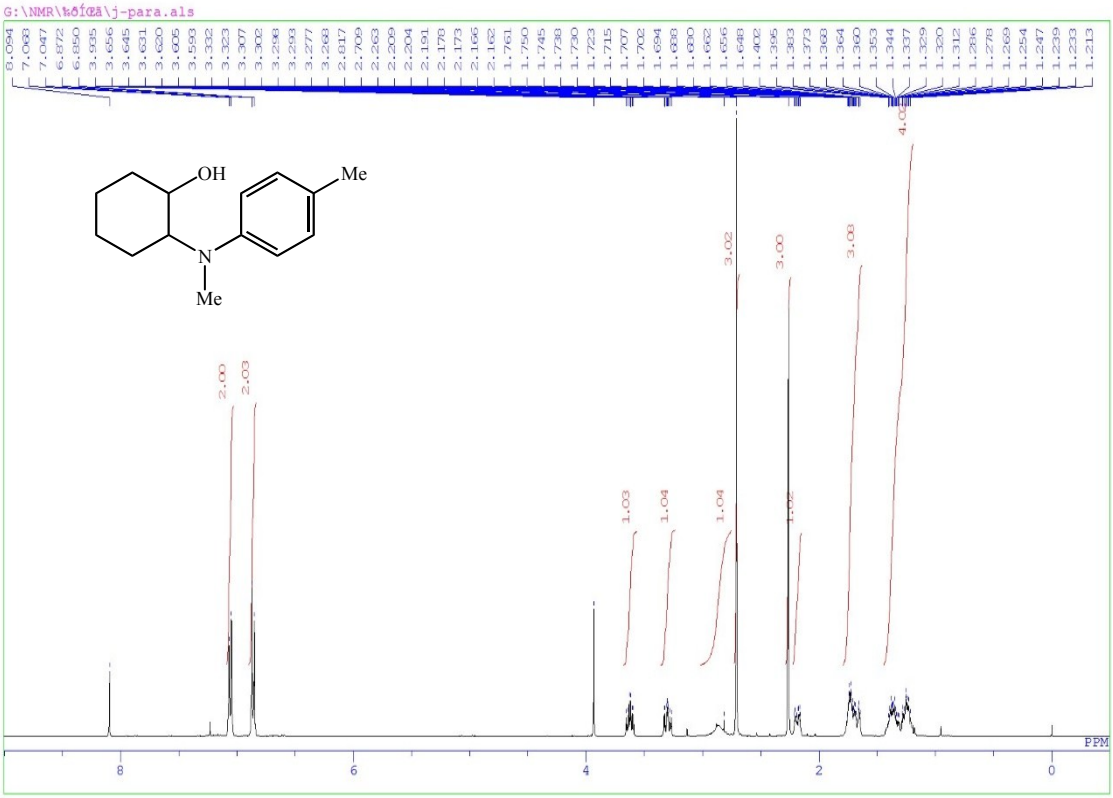


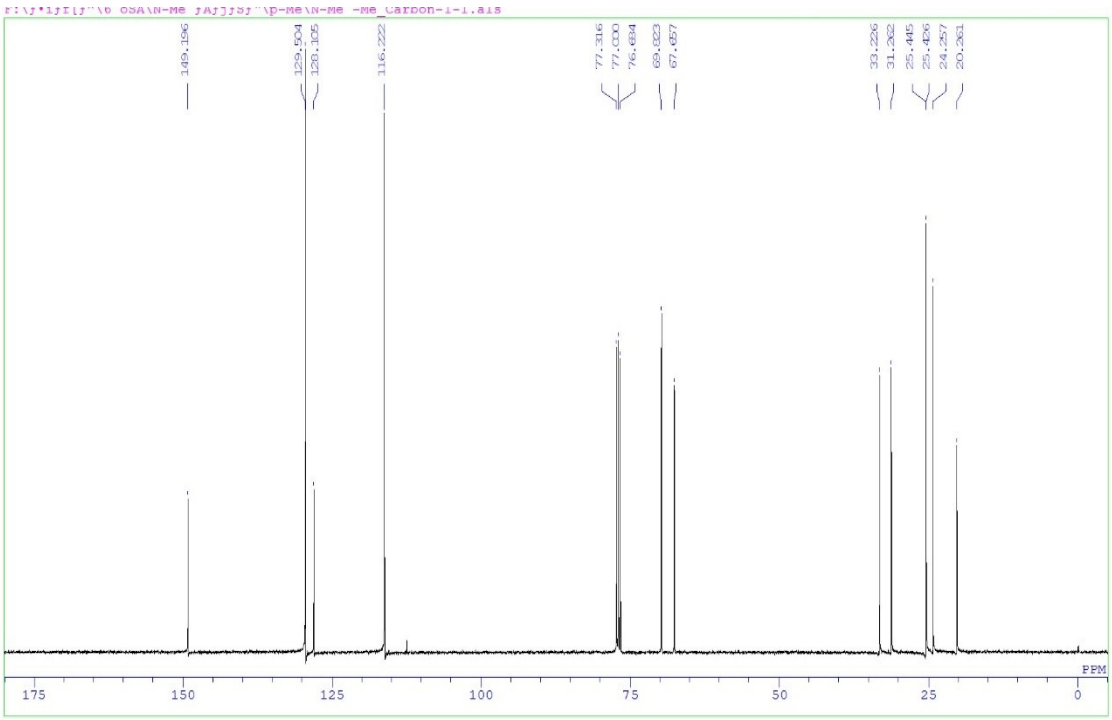
2-(*N*-methyl-*N*-*m*-tolylamino)cyclohexanol



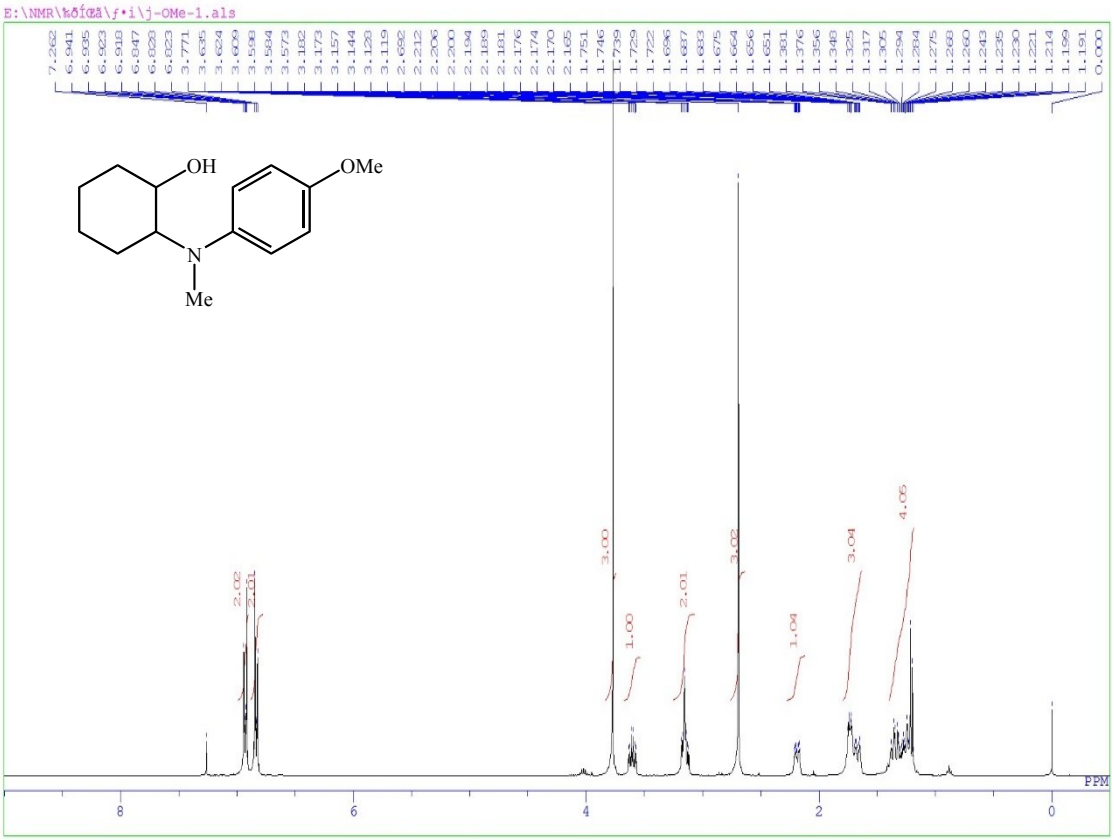


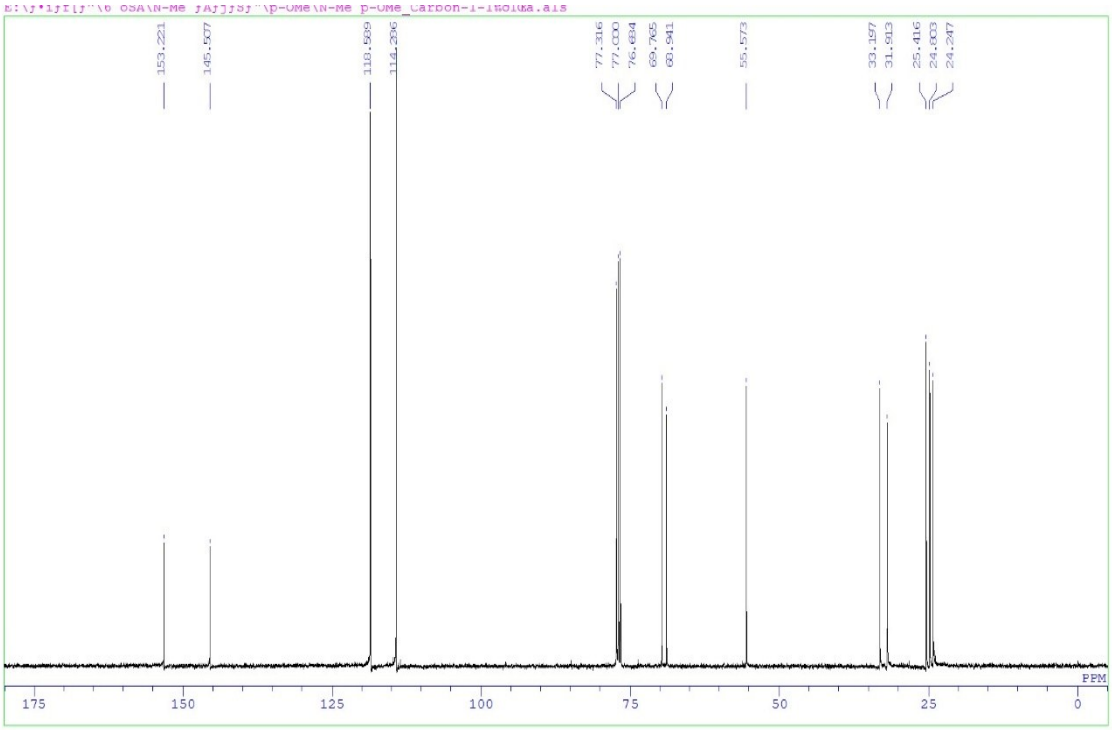
2-(*N*-methyl-*N*-*p*-tolylamino)cyclohexanol



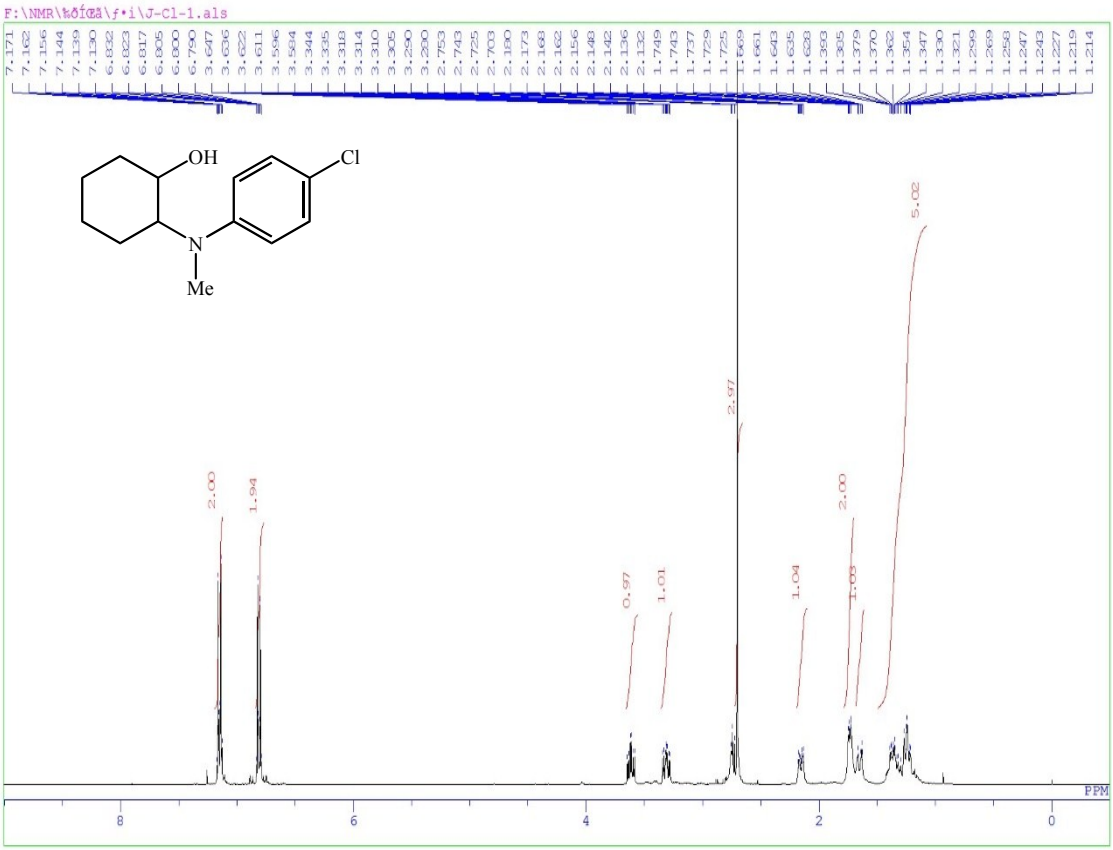


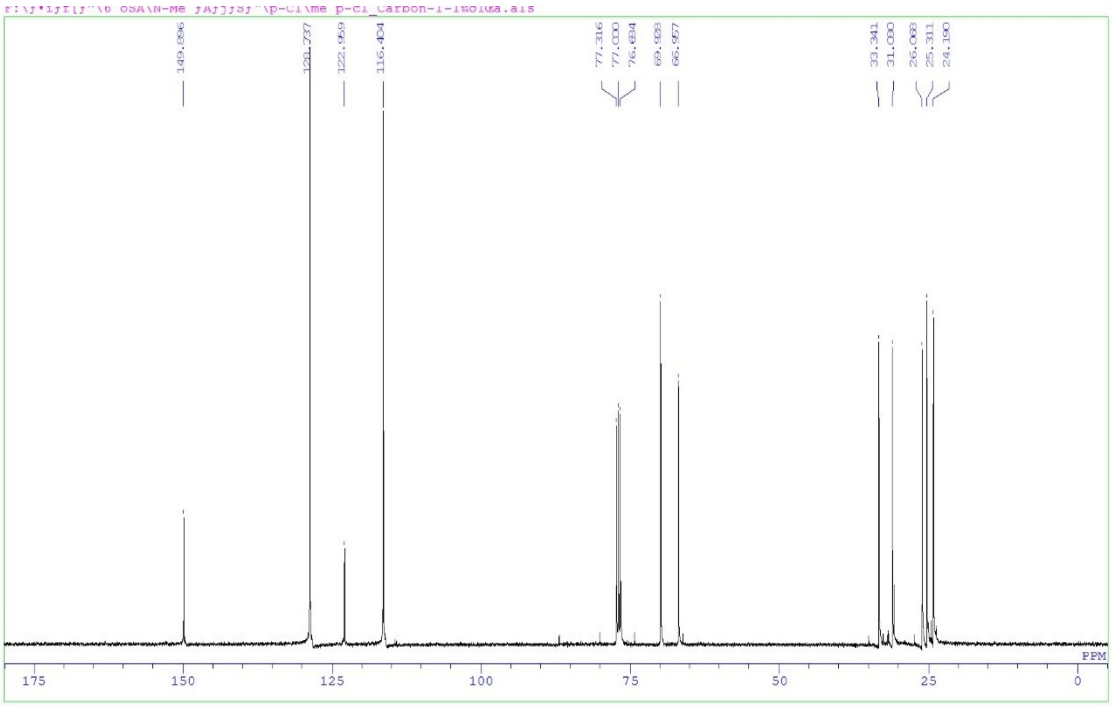
2-(*N*-(4-methoxyphenyl)-*N*-methylamino)cyclohexanol

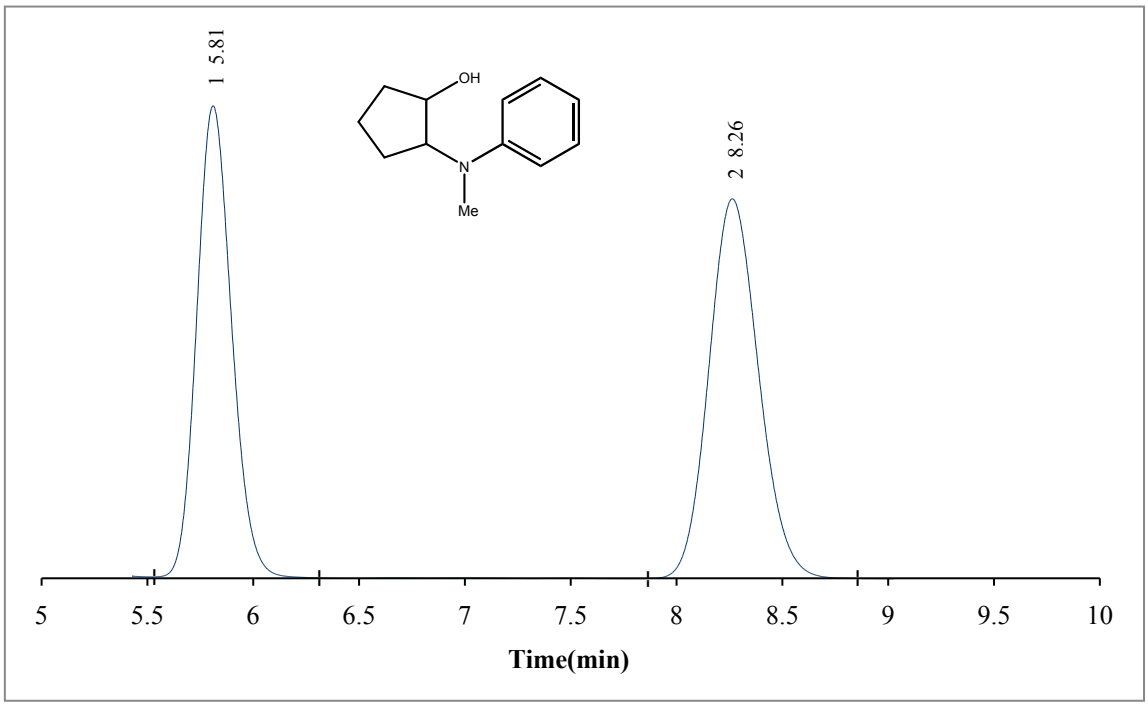


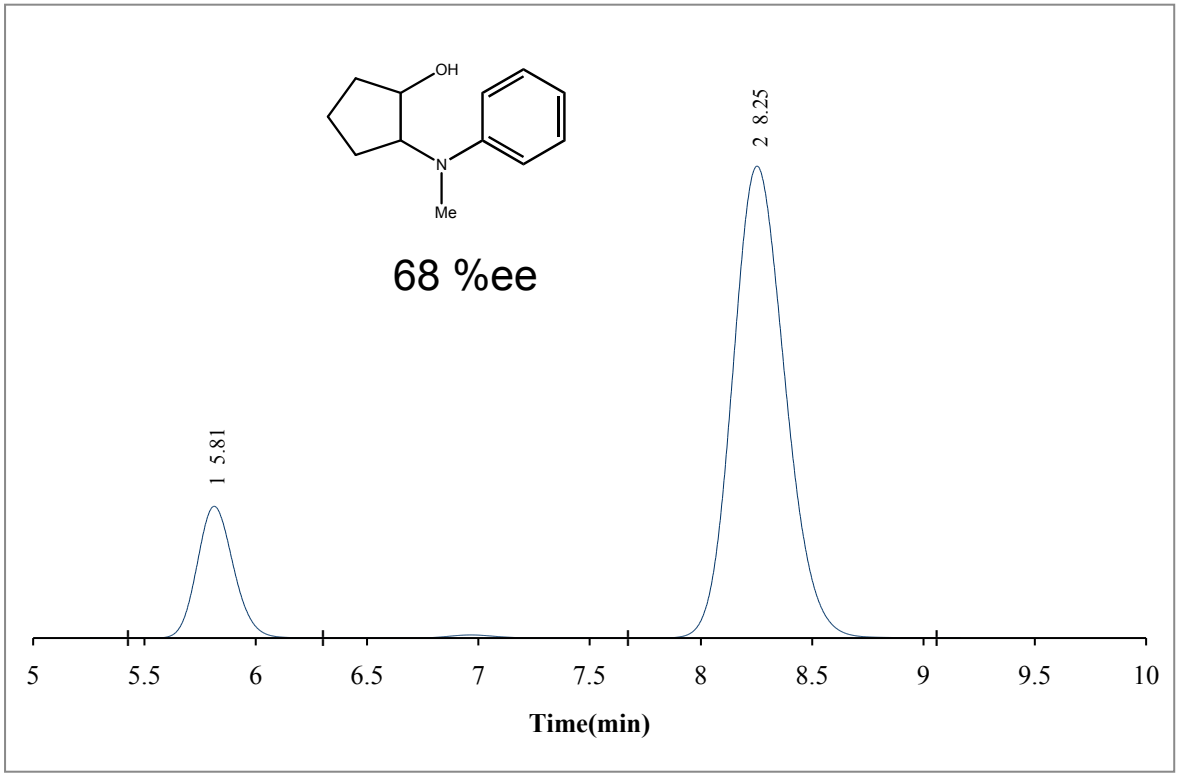


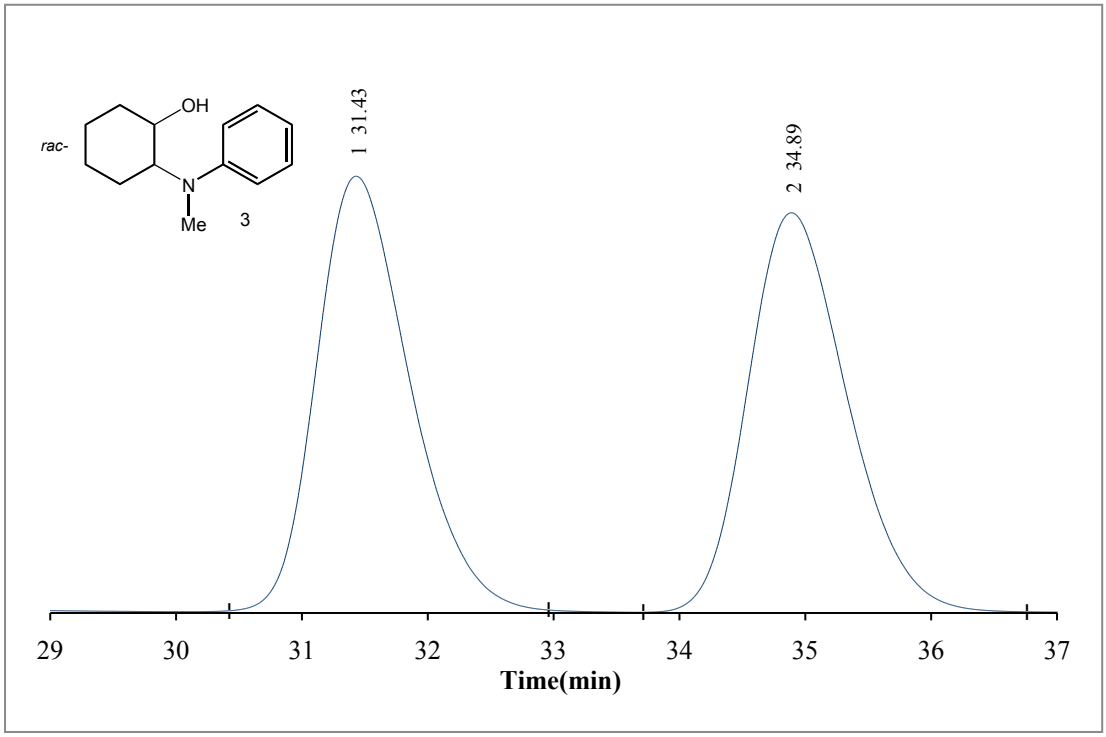
2-(*N*-(4-chlorophenyl)-*N*-methylamino)cyclohexanol

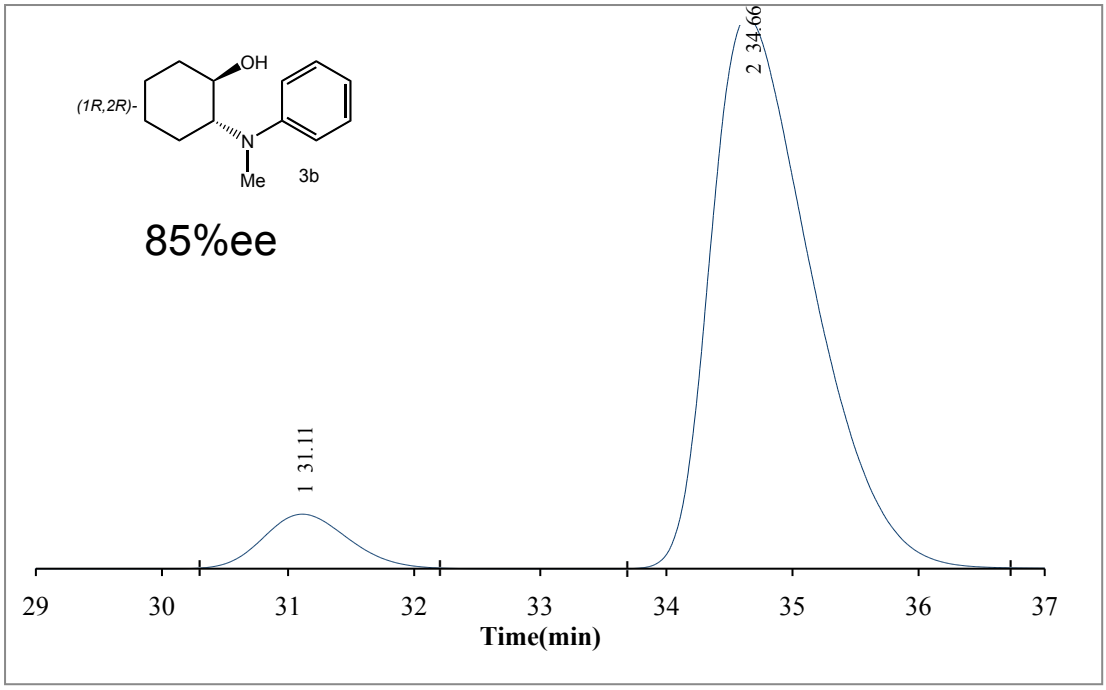


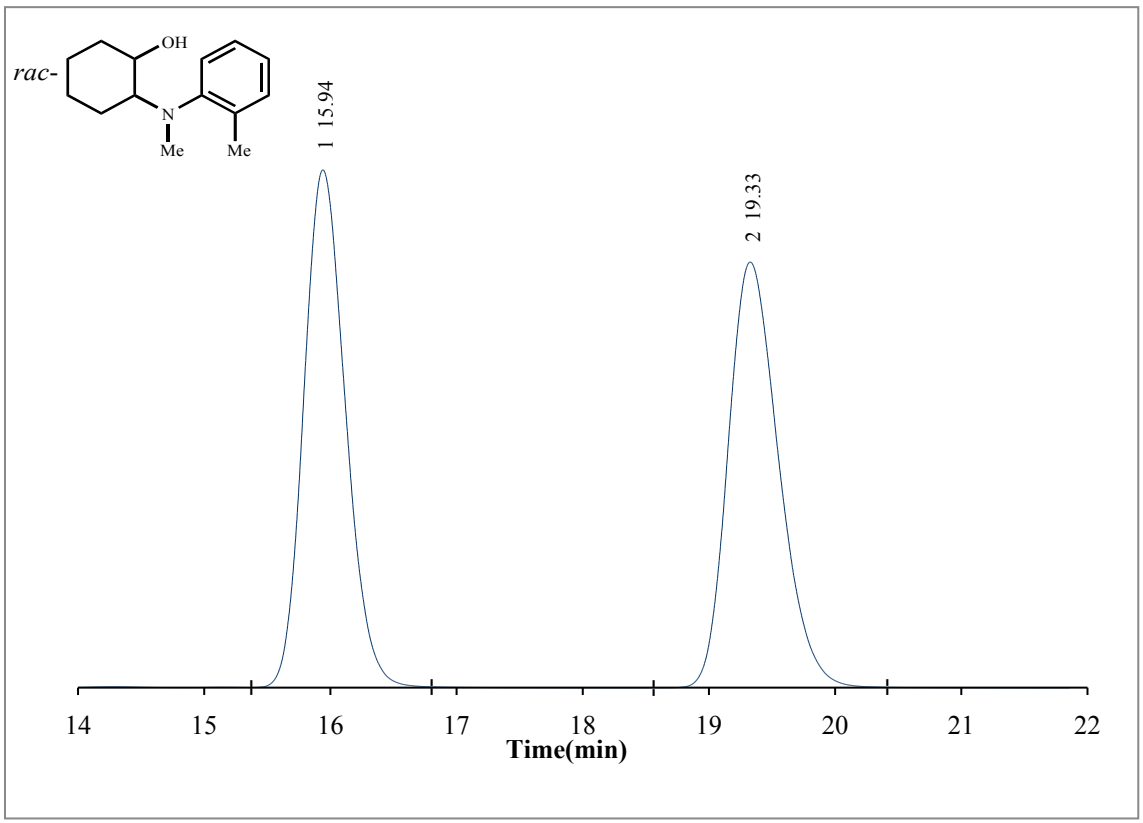


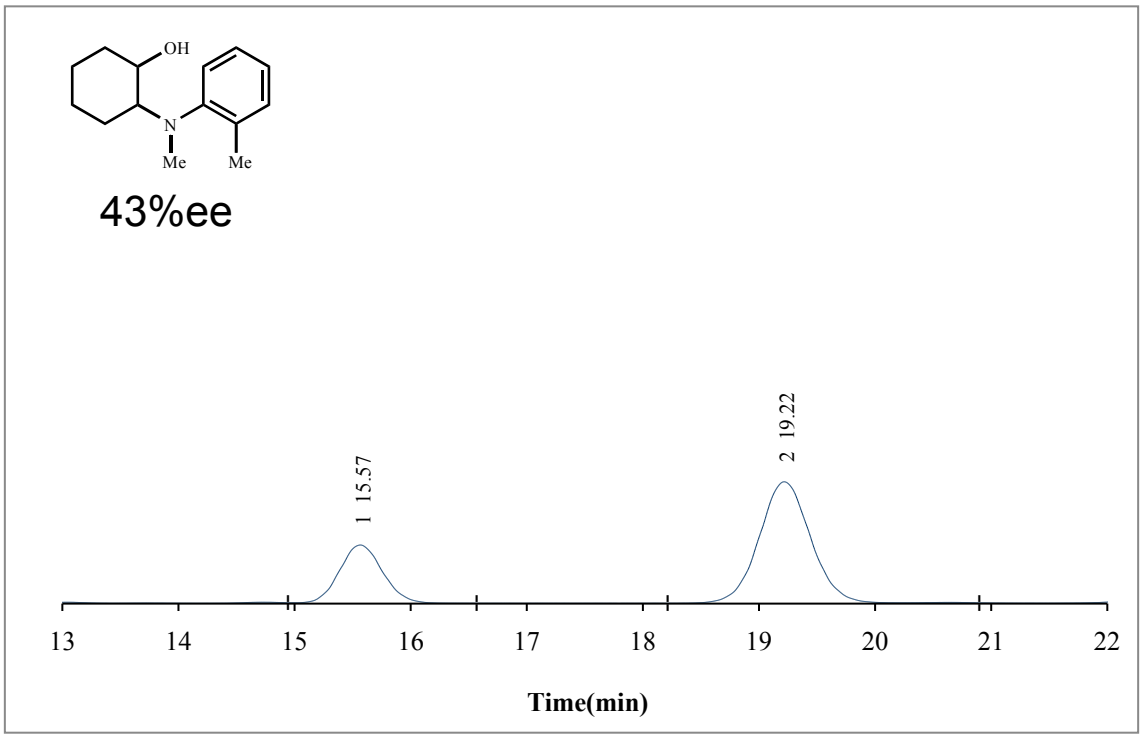

1 5.81
OH
N
Me
2 8.26
5
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Time(min)

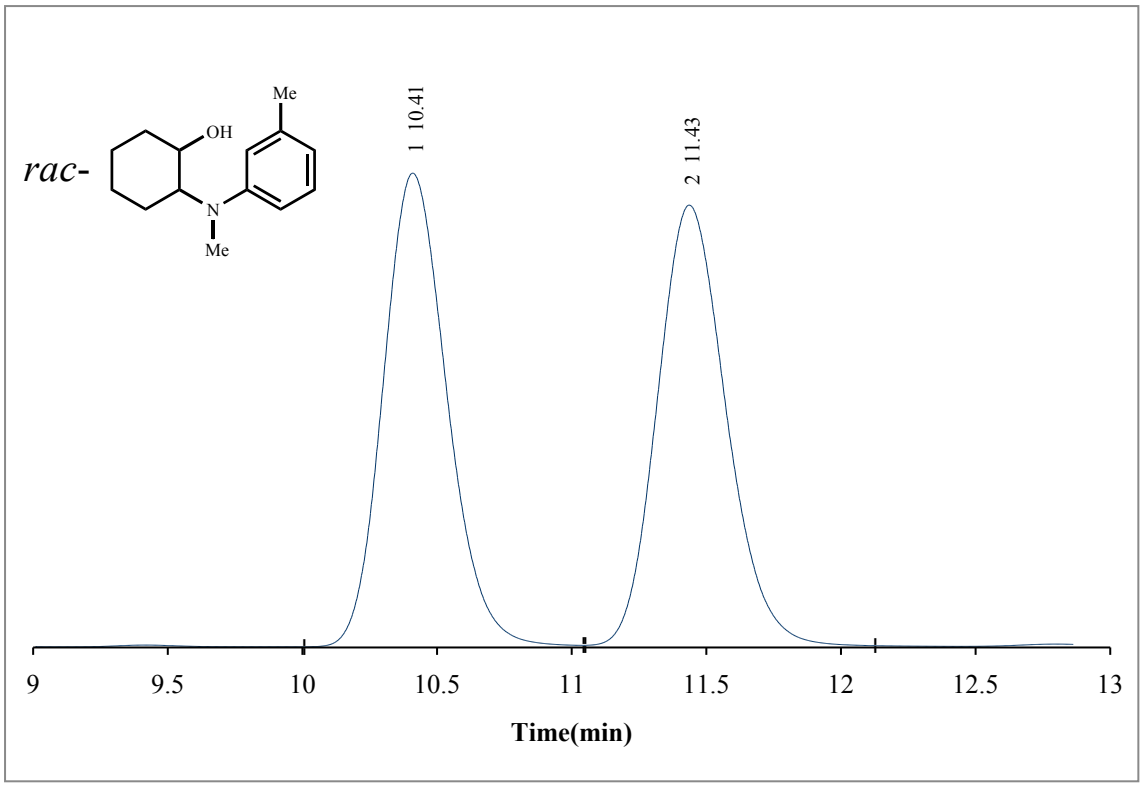

OH
N
Me
68 %ee
2 8.25
1 5.81
5
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
Time(min)

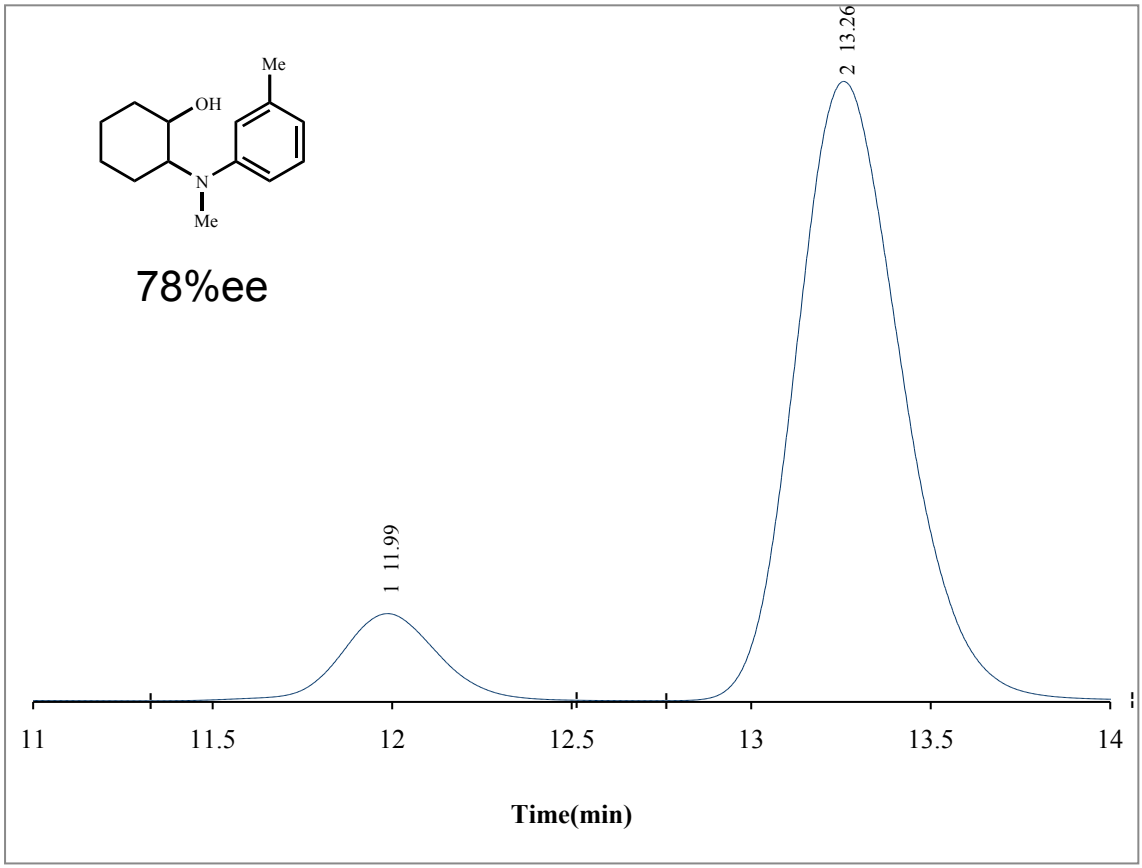

rac-
OH
N
Me
3
1 31.43
2 34.89
29
30
31
32
33
34
35
36
37
Time(min)

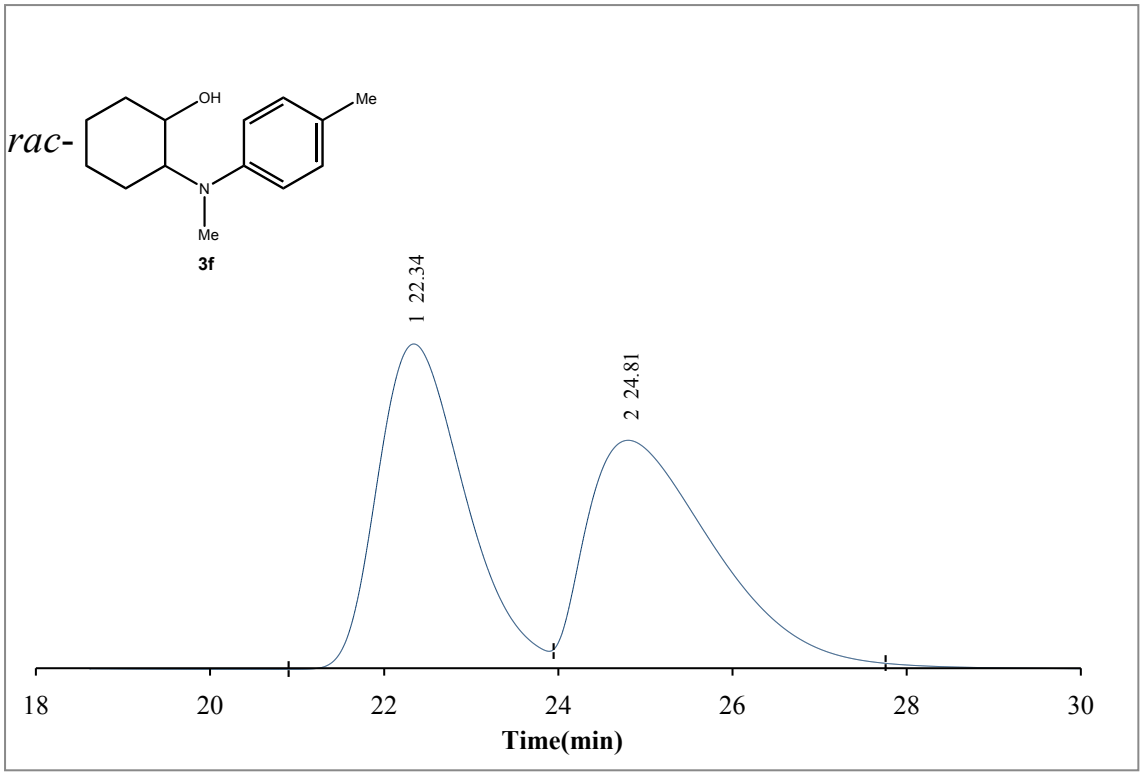

(1R,2R)-
OH
N
Me
3b
85%ee
2 34.66
1 31.11
29
30
31
32
33
34
35
36
37
Time(min)

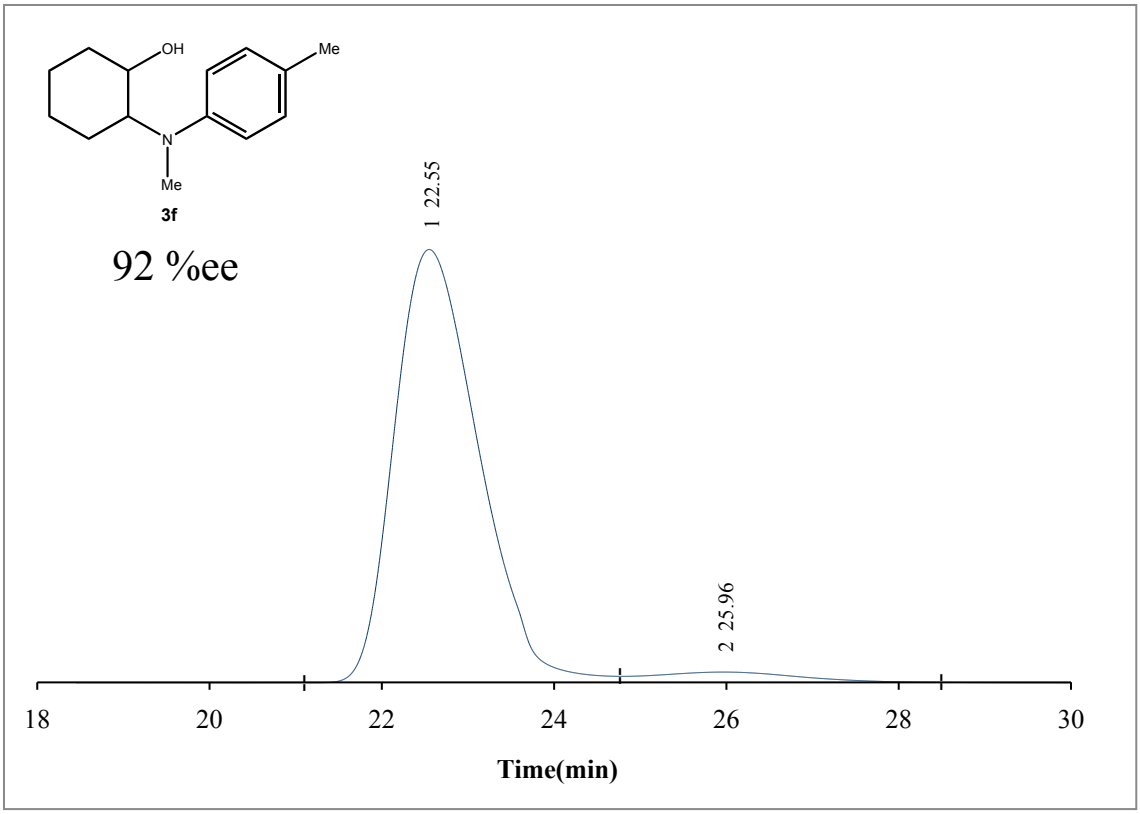

rac-
OH
N
Me
Me
1 15.94
2 19.33
14
15
16
17
18
19
20
21
22
Time(min)

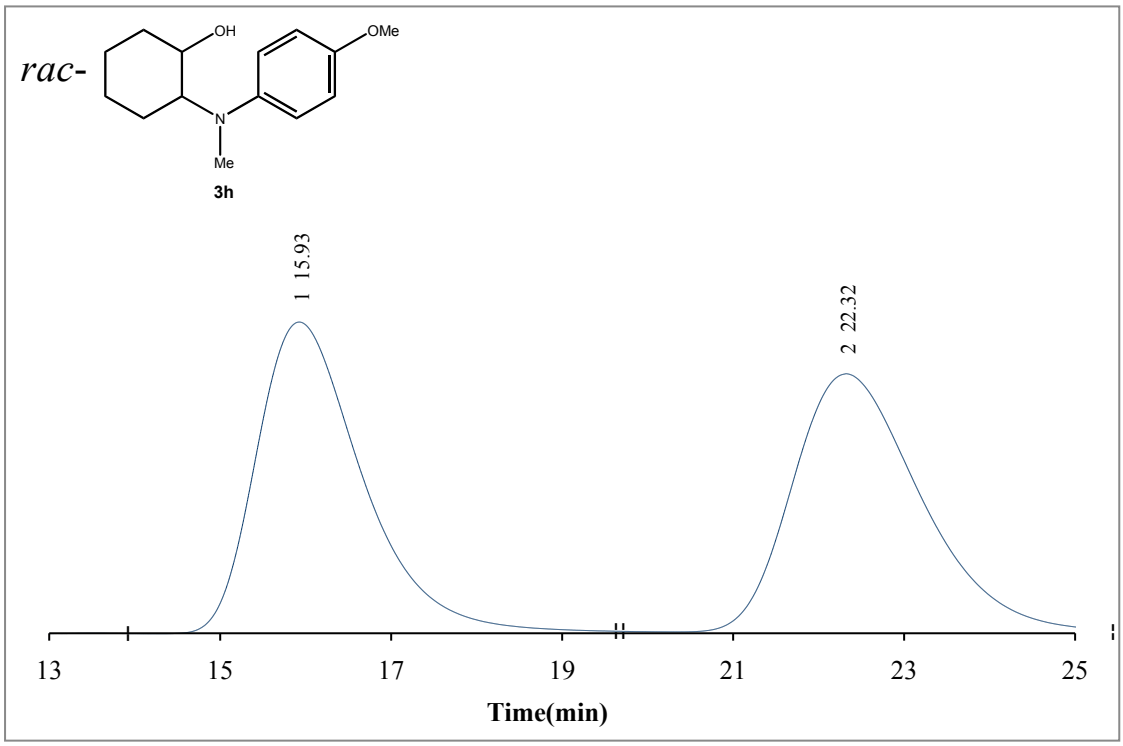

OH
N
Me
Me
43%ee
1 15.57
2 19.22
13
14
15
16
17
18
19
20
21
22
Time(min)

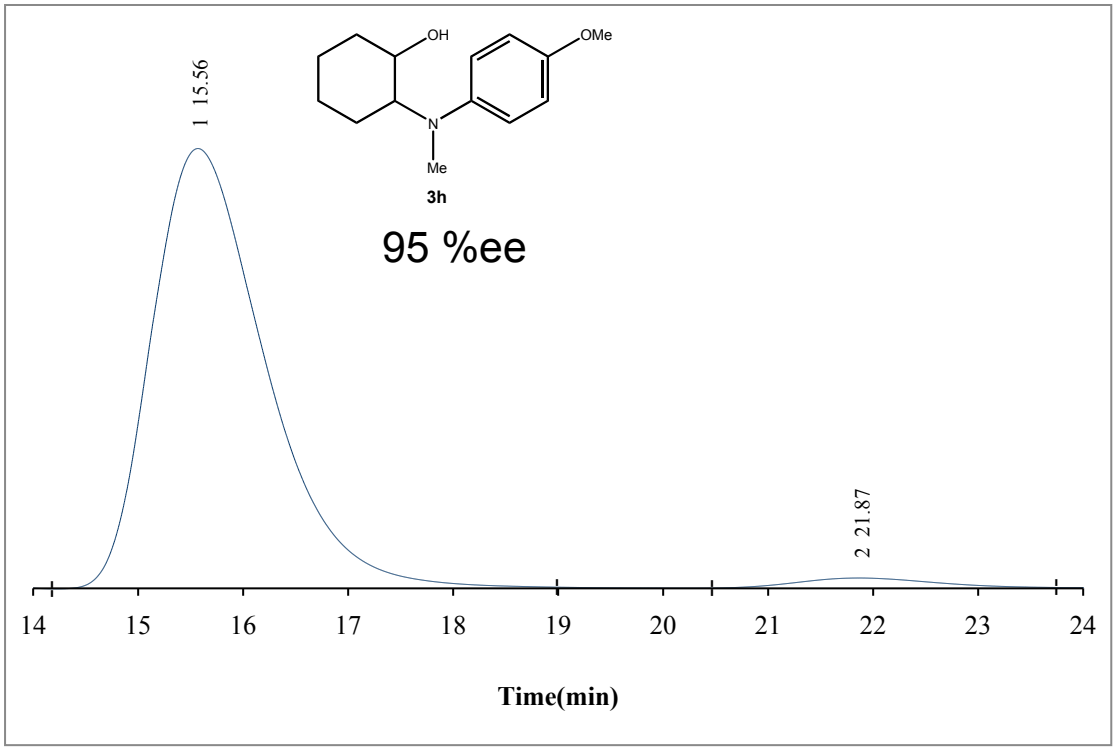

rac-
Me
OH
N
Me
1 10.41
2 11.43
9
9.5
10
10.5
11
11.5
12
12.5
13
Time(min)

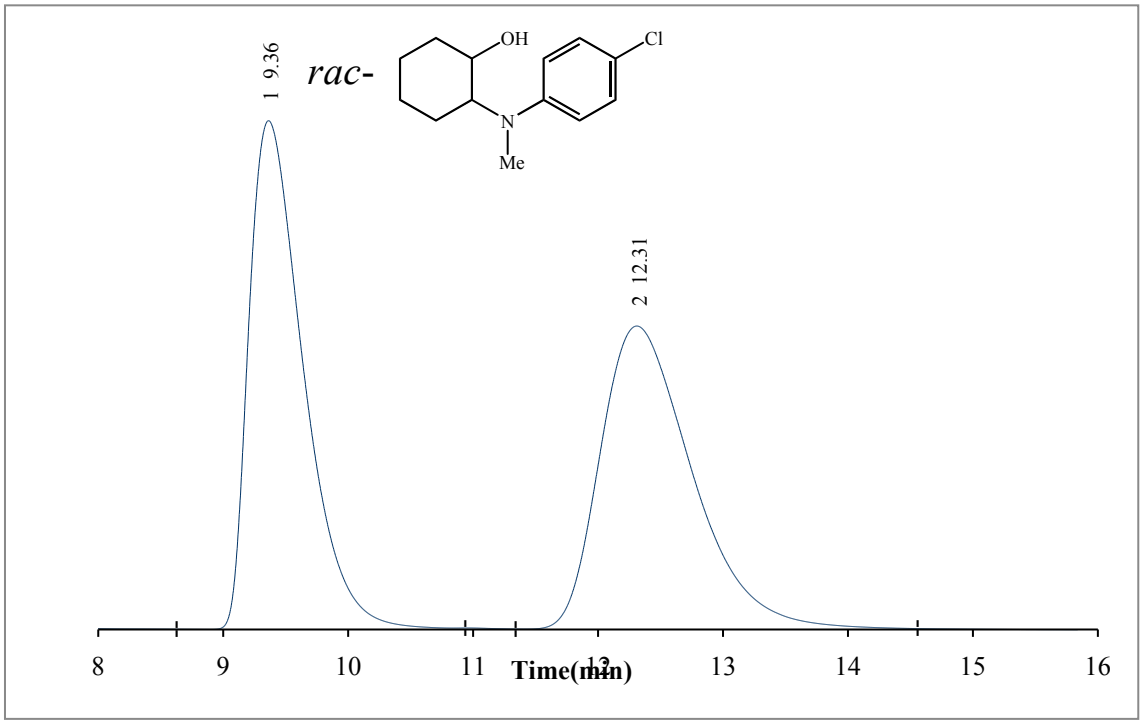

Me
OH
N
Me
78%ee
2 13.26
1 11.99
11
11.5
12
12.5
13
13.5
14
Time(min)

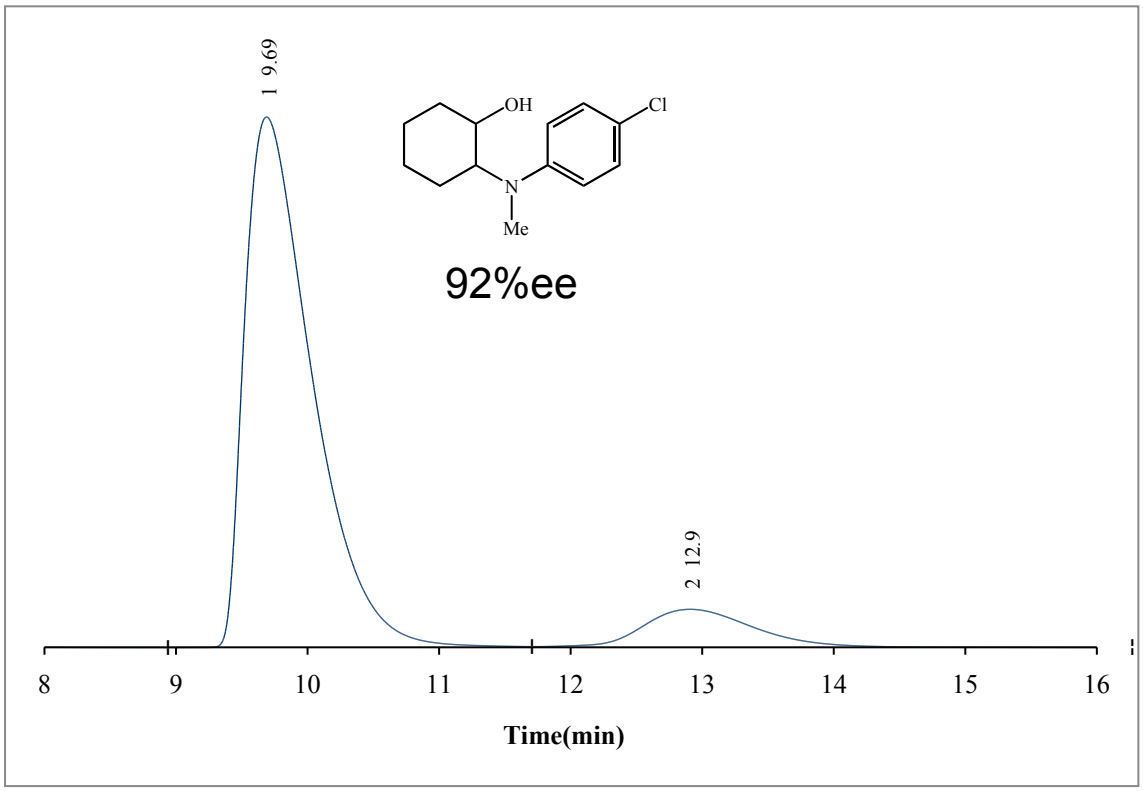

rac-
OH
Me
N
Me
3f
1 22.34
2 24.81
18
20
22
24
26
28
30
Time(min)

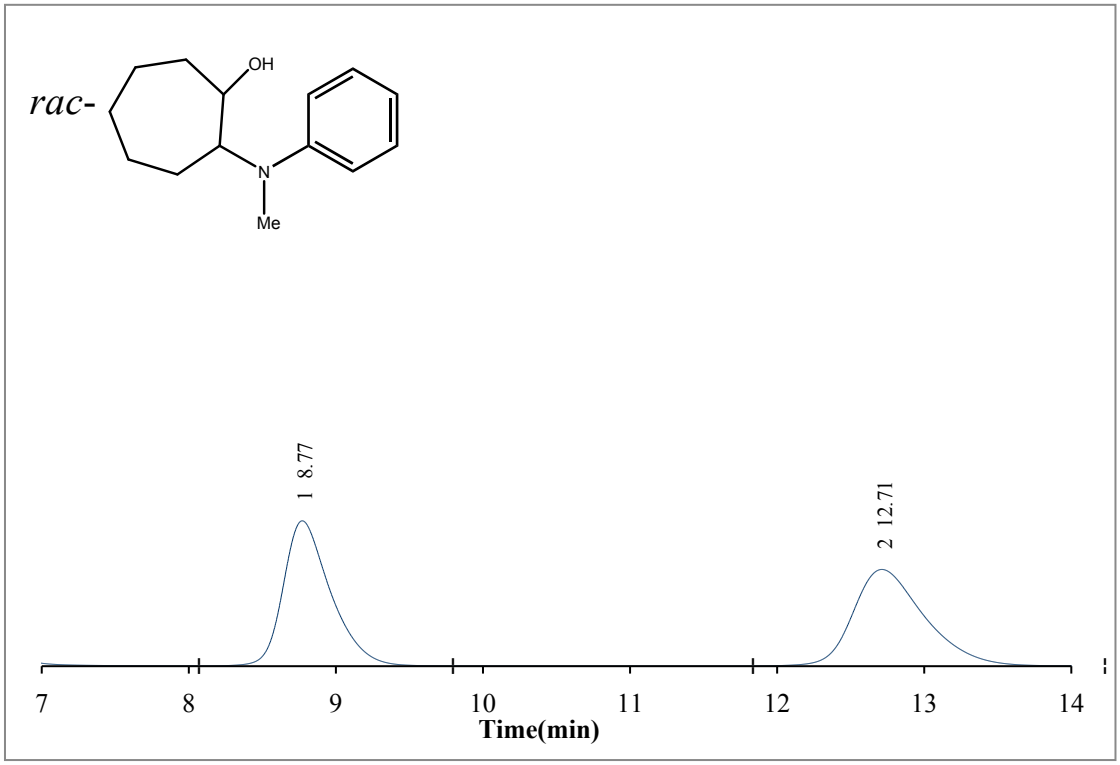

OH
Me
N
Me
3f
92 %ee
1 22.55
2 25.96
18
20
22
24
26
28
30
Time(min)

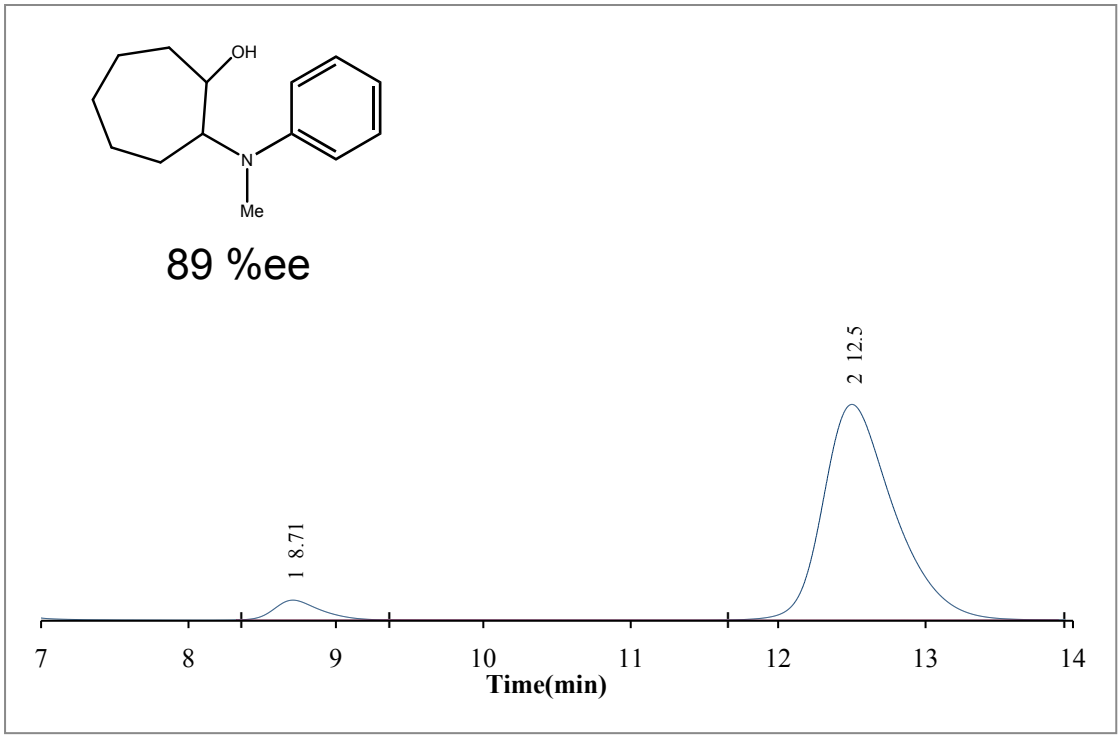

rac-
OH
OMe
N
Me
3h
1 15.93
2 22.32
13
15
17
19
21
23
25
Time(min)


OH
OMe
N
Me
3h
95 %ee
1 15.56
2 21.87
14
15
16
17
18
19
20
21
22
23
24
Time(min)

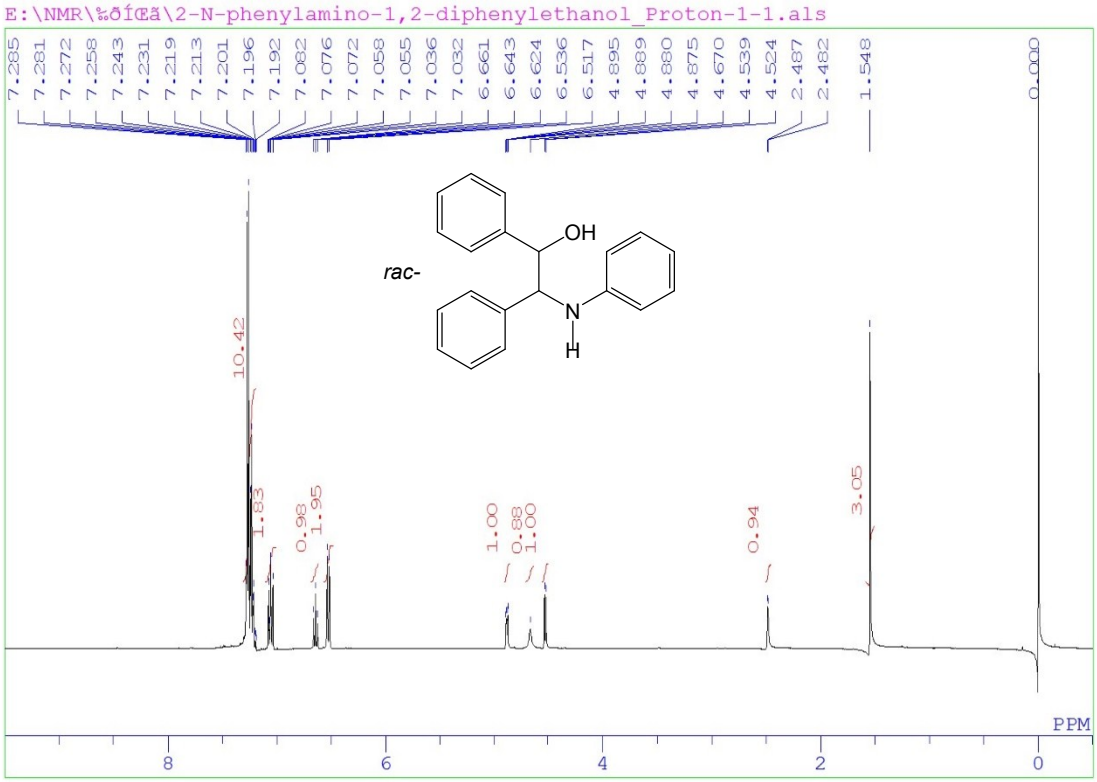

rac-
OH
Cl
N
Me
1 9.36
2 12.31
8
9
10
11
12
13
14
15
16
Time(min)

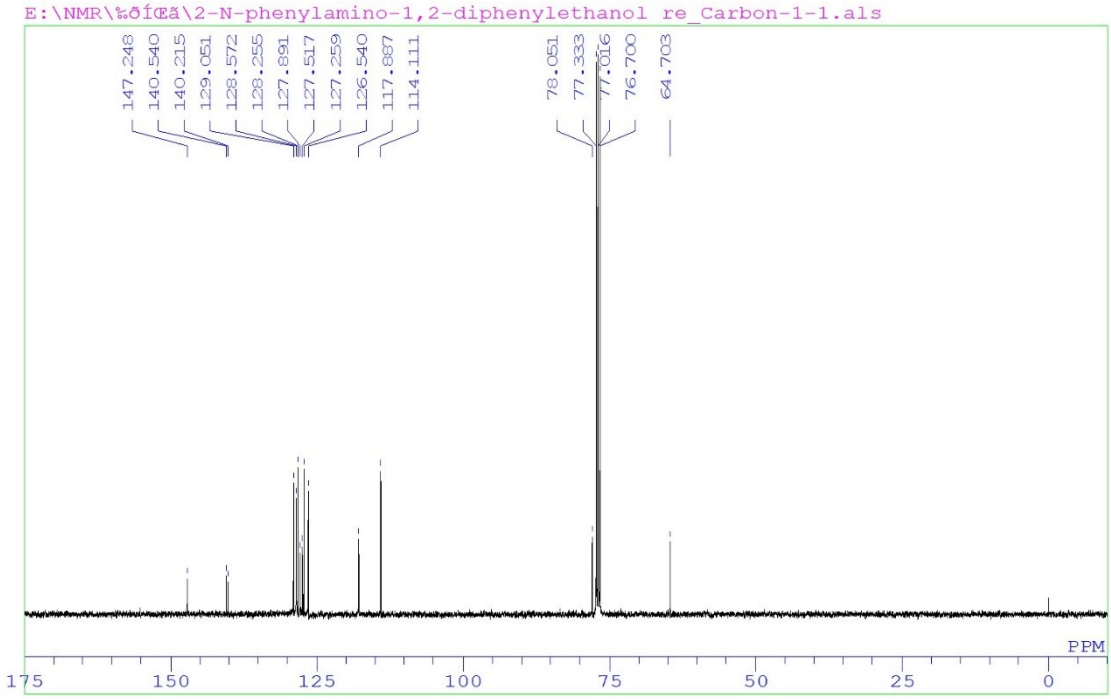

1 9.69
OH
Cl
N
Me
92%ee
2 12.9
8
9
10
11
12
13
14
15
16
Time(min)


rac-
OH
N
Me
1 8.77
2 12.71
7
8
9
10
11
12
13
14
Time(min)

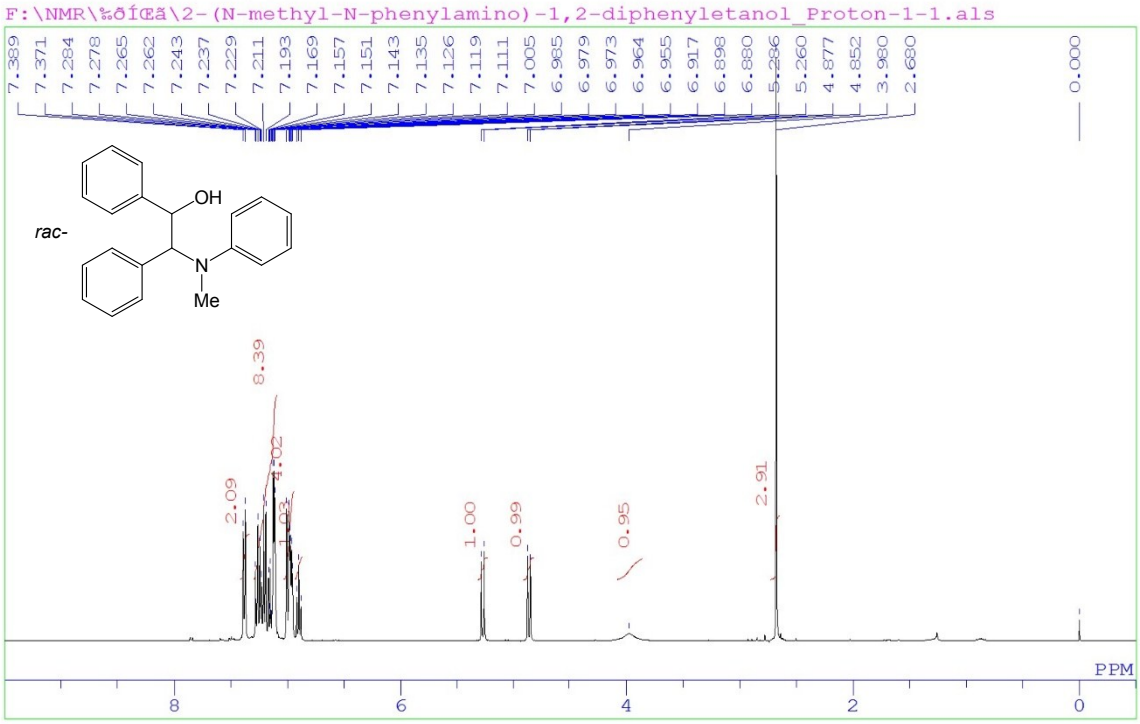

OH
N
Me
89 %ee
2 12.5
1 8.71
7
8
9
10
11
12
13
14
Time(min)

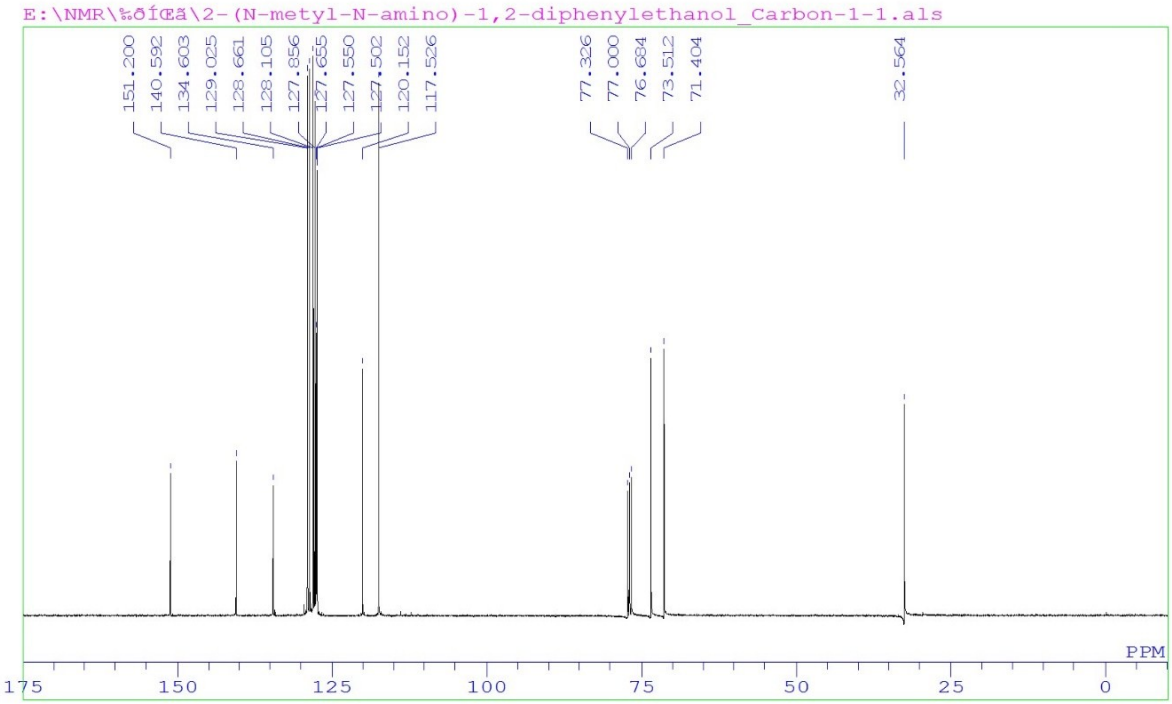
2-*N*-phenylamino-1,2-diphenylethaol



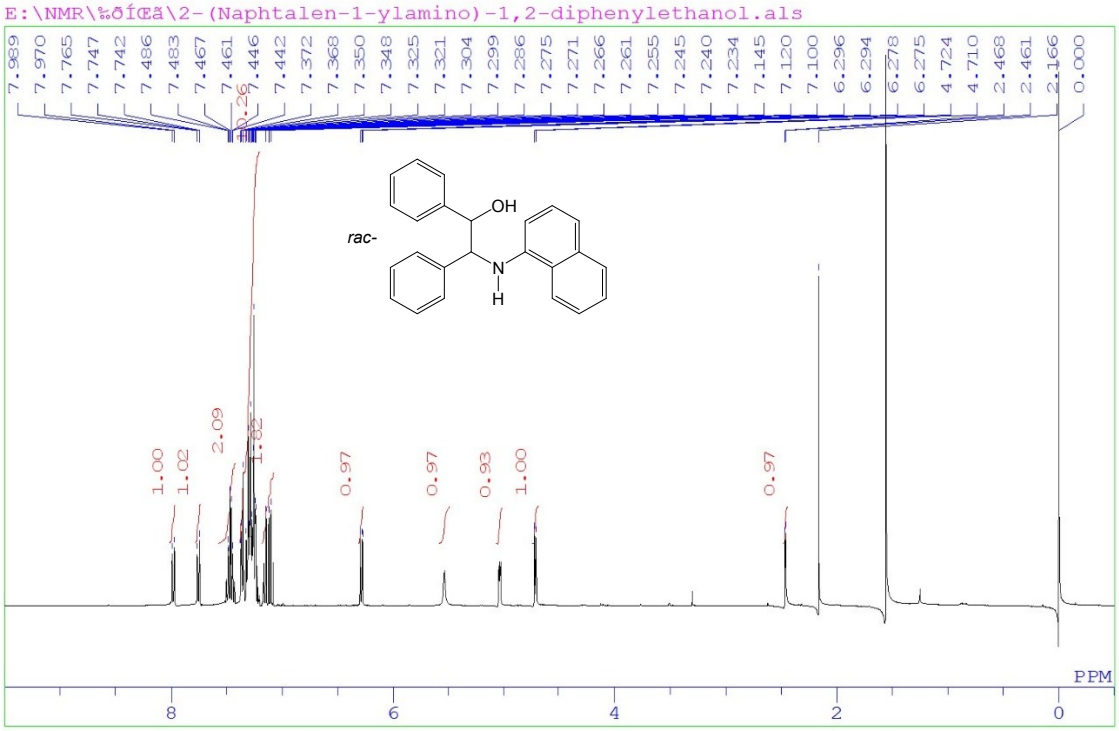


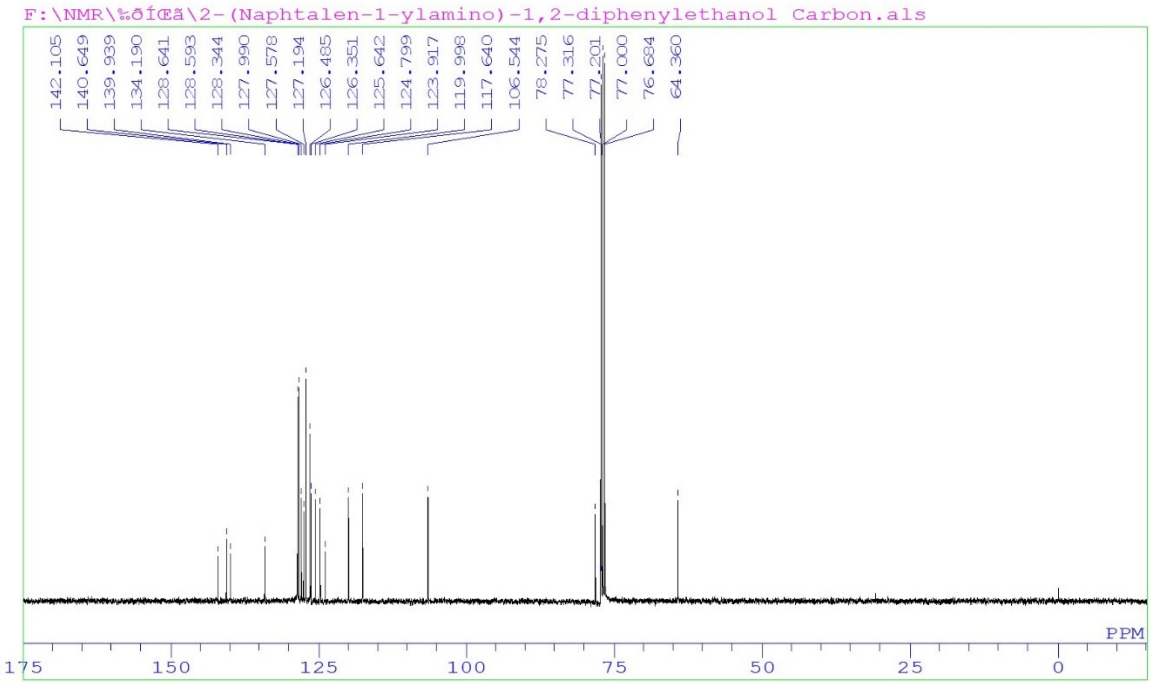
2-(*N*-Methyl-*N*-phenylamino)-1,2-diphenylethaol

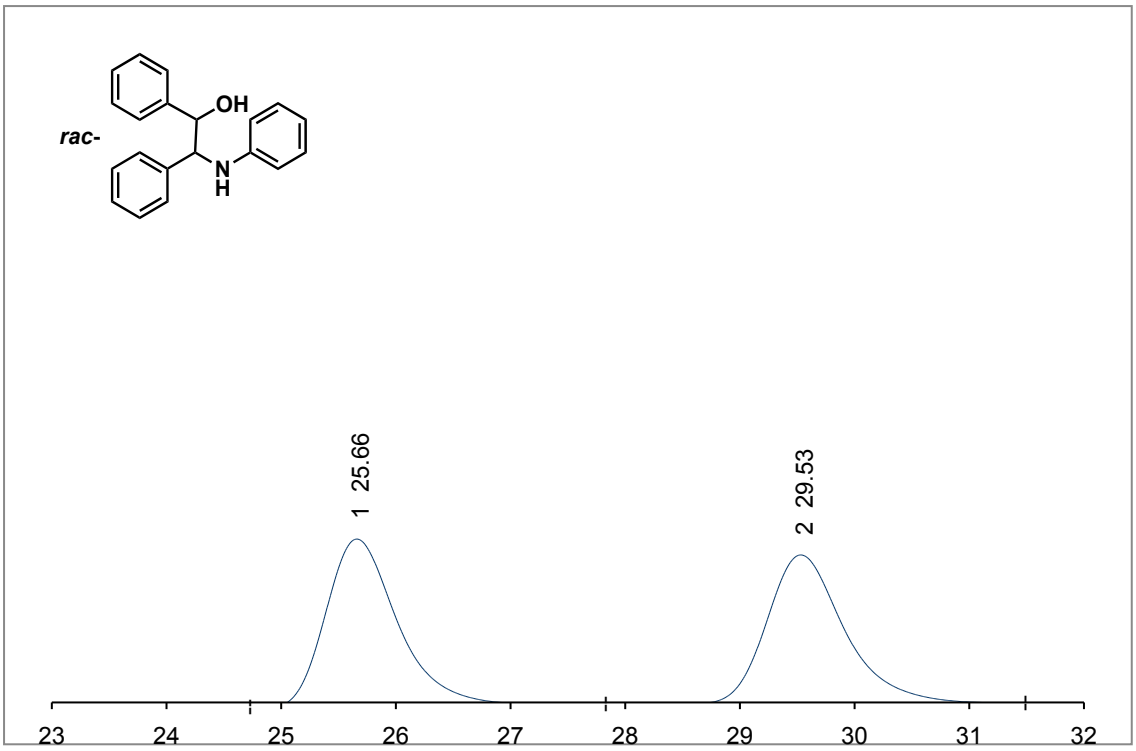


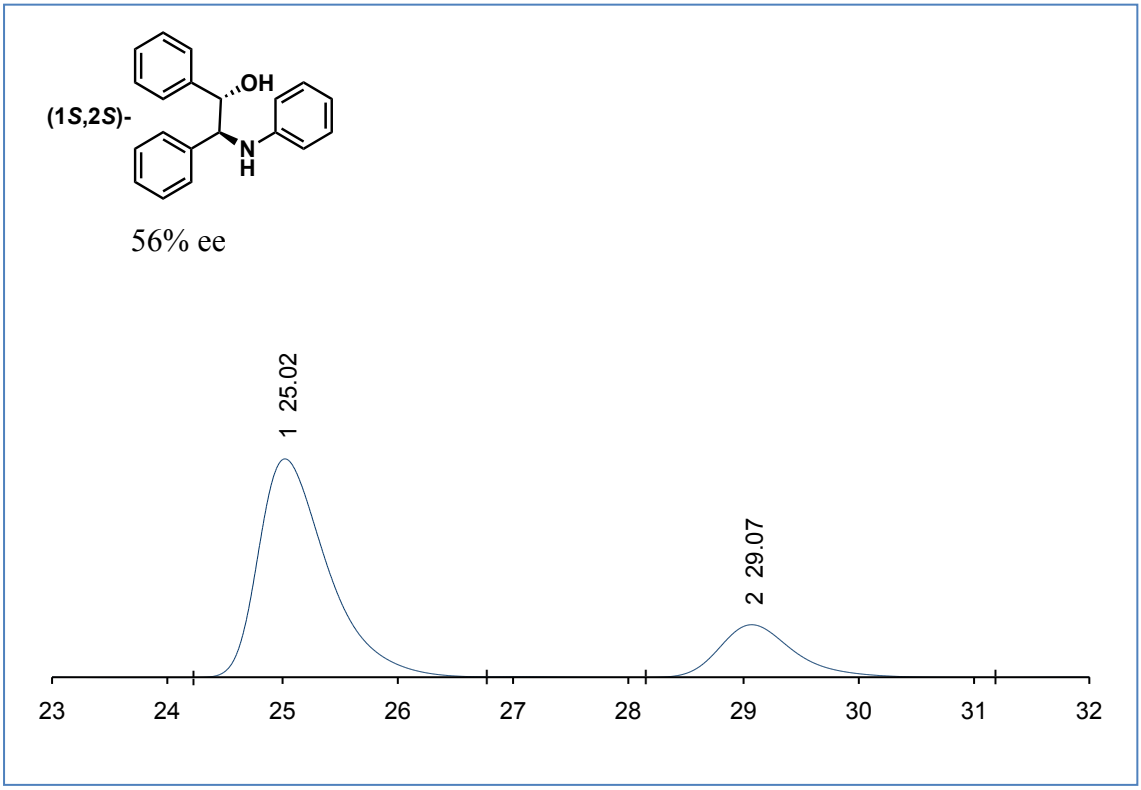


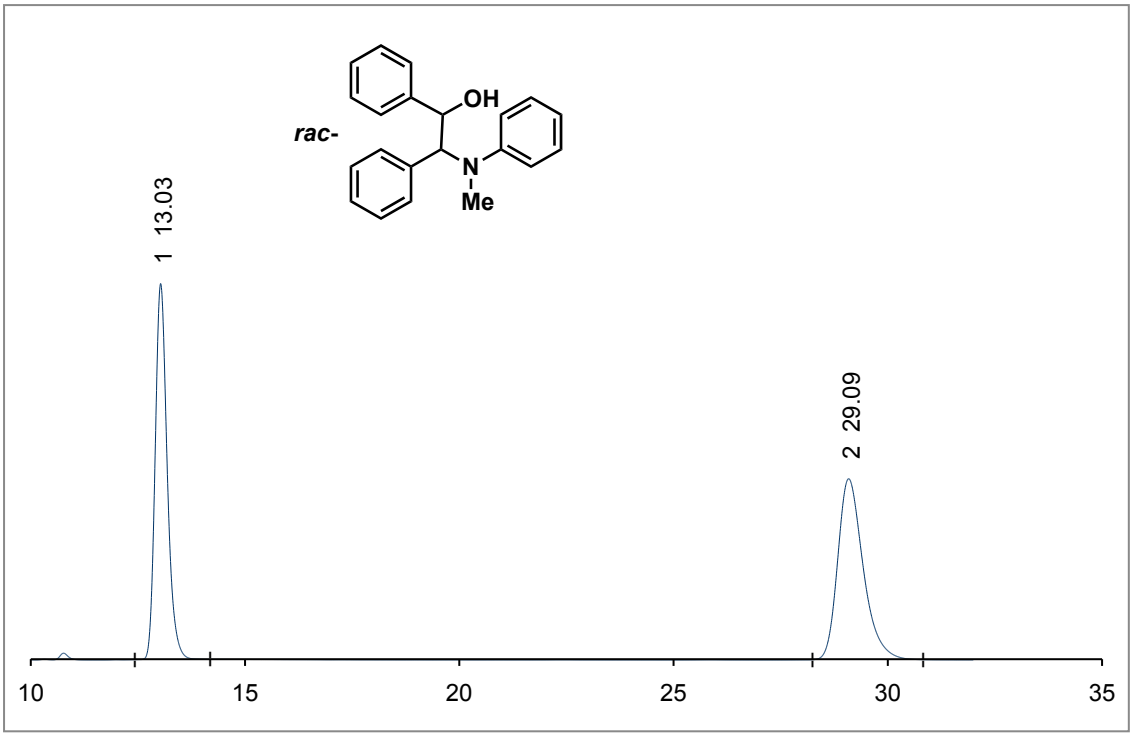
2-(Naphtalene-1-ylamino)-1,2-diphenylethaol

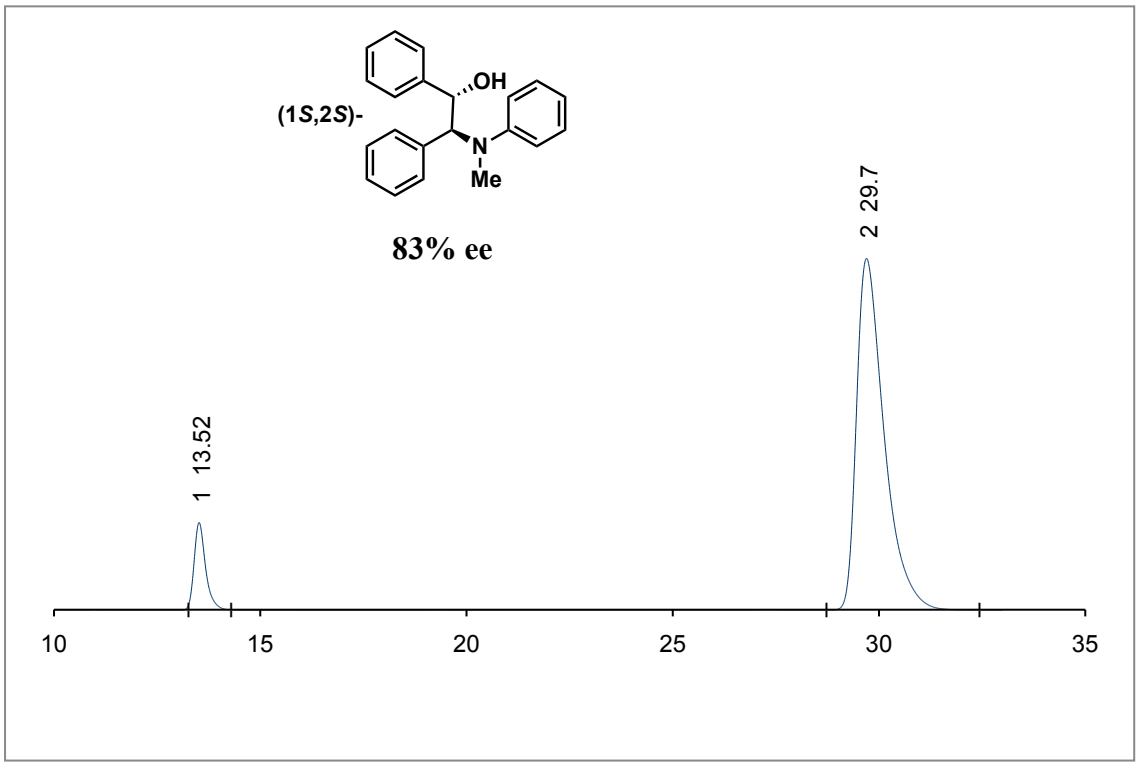


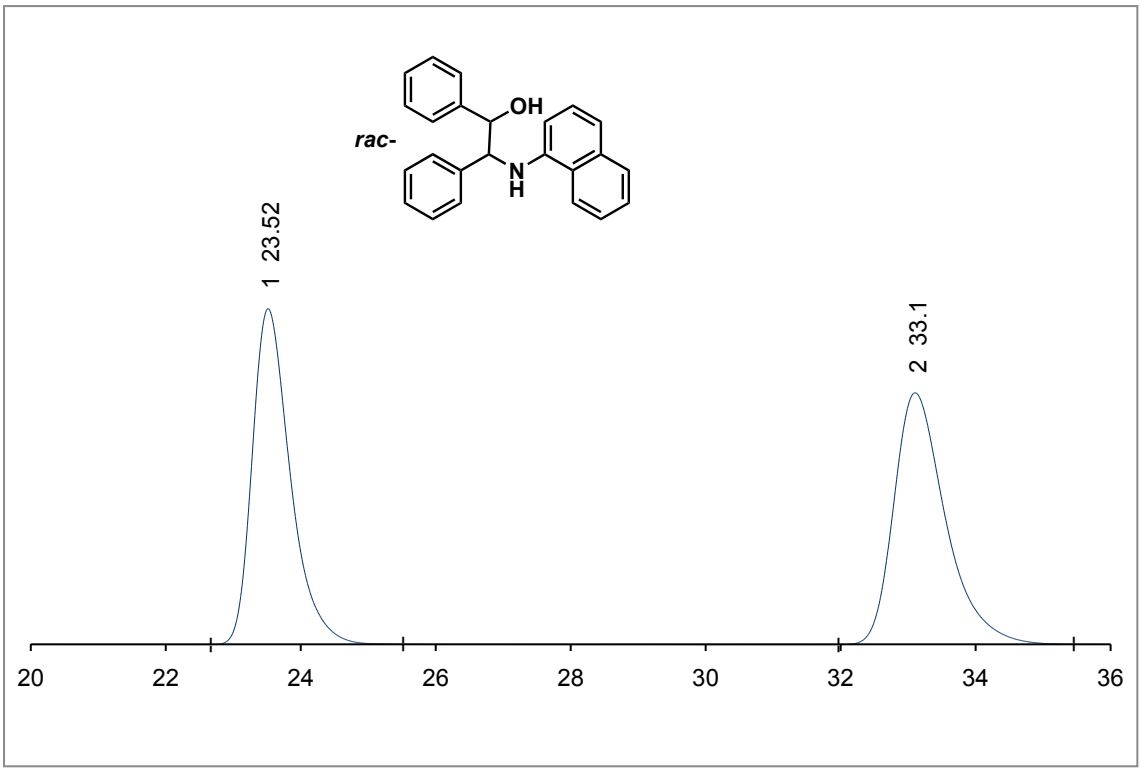


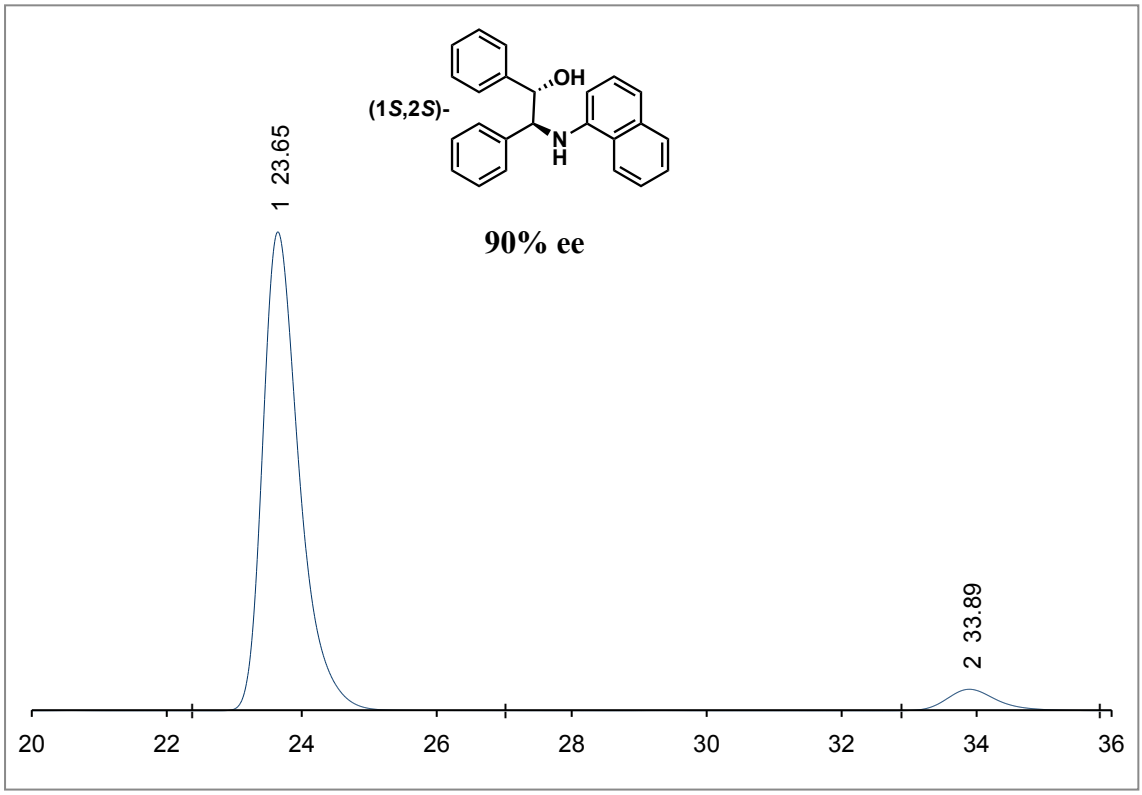

rac-
OH
N
H
1 25.66
2 29.53
23
24
25
26
27
28
29
30
31
32


(1S,2S)-
OH
N
H
56% ee
1 25.02
2 29.07
23
24
25
26
27
28
29
30
31
32


rac-
OH
N
Me
1 13.03
2 29.09
10
15
20
25
30
35


(1S,2S)-
OH
N
Me
83% ee
1 13.52
2 29.7
10
15
20
25
30
35


rac-
OH
N
H
1 23.52
2 33.1
20
22
24
26
28
30
32
34
36


(1S,2S)-
OH
N
H
1 23.65
2 33.89
20
22
24
26
28
30
32
34
36

90% ee