Supporting Information for

Enantioselective Ring-Opening of meso-Epoxide by Aromatic Amines Catalysed by a Homochiral Metal-Organic Framework

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General Information

All reagents and solvents were used as received from commercial suppliers without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV400 or AV600 spectrometer. Tetramethylsilane (TMS) and deuterated solvents ($CDCl_3$, δ = 77.0 ppm; DMSO-d_6, δ = 39.5 ppm) were used as internal standards in ^{1}H NMR and ^{13}C NMR experiments, respectively. The coupling constants were reported in Hertz. Thermogravimetric analyses (TGA) were measured using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 3 ^{o}C min^{-1}. Powder X-ray diffraction (PXRD) patterns were recorded by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 degmin^{-1}.

The *cis*-stilbene epoxides used in this study were synthesized according to the reported literature procedures. They were purified either by column chromatography or distillation. Aniline and aniline derivatives were purified by distillation and recrystallization before use.

Crystal structure determination

Intensity data for **UTSA-32** were collected at 185(2) K on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 watts power (50 kV, 40 mA). The structure was solved by direct methods and subsequent difference Fourier syntheses, and refined using the SHELXTL software package. The H atoms on the ligands and coordinated H_2O were placed in idealized positions and refined using

a riding model. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby, to produce a set of solvent-free diffraction intensities. Crystal data for **UTSA-32**: $C_{40}H_{23}Cl_2O_{12}Zn_2$, M = 897.22, monoclinic, space group $P2_1$, a = 10.1889(13) Å, b = 16.651(2) Å, c = 19.730(3) Å, β = 101.825(2)^o, V = 3276.4(7) Å^3, Z = 2, D_c = 0.909 g cm^{-3}, μ(Mo-K$_\alpha$, λ = 0.71073 Å) = 0.851 mm^{-1}, F(000) = 906, $2\theta_{max}$ = 50.1, 17147 reflections collected, 9823 independent reflections (R_{int} = 0.0702), which were used in all the calcualtions, Final R_1 = 0.0893 for $I > 2\sigma(I)$, wR_2 = 0.2404 for all data, GOF = 0.943, Flack parameter = 0.10(3). CCDC 713157. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF or other electronic format.

Synthesis of UTSA-32

A mixture of $Zn(NO_3)_2$ $6H_2O$ (15.0 mg, 0.050 mmol) and organic linker H_4L (15.0 mg, 0.020 mmol) was dissolved into *N*,*N*'-dimethylacetamide (DMA) (2.0 mL)-ethanol (1.0 mL) mixed solvents in a crew-capped vial. The vial was then capped and heated to 110 ^{o}C in 2 hours, maintained at 110 ^{o}C for 48 hours and cooled to room temperature in 12 hours. Colorless rodlike crystals were obtained in 62% yield. **UTSA-32** can be formulated as $[Zn_2(L)(H_2O)_2]$ $(DMA)_4$ on the basis of single crystal X-ray structure determination, TGA and microanalysis. TGA data: Calcd. weight loss for 4DMA and $2H_2O$: 30.7%, Found: 30.1%; Anal. Calcd for $C_{56}H_{64}N_4O_{16}Zn_2Cl_2$: C, 53.77; H, 5.16%; N, 4.48, Found: C, 53.89%; H, 5.22; N, 4.57%

General Experimental Procedure for the *meso*-epoxide opening reaction with aniline derivatives

To a mixture of the epoxide (0.10 mmol) and aniline derivative (0.25 mmol) in a vial, 10 mol % of **UTSA-32a** catalyst was added followed by 1 mL of toluene (**UTSA-32a** was obtained by heating as-synthesized **UTSA-32** under high vacuum at 150 ^{o}C for 24 hrs). The vial was heated at 50 °C for the indicated time. The reaction mixture was cooled and filtered to remove the catalyst, washed with ethanol. The filtrate was evaporated under reduced pressure (rotary evaporator), and the residue was purified by column chromatography to give the product amino alcohol.

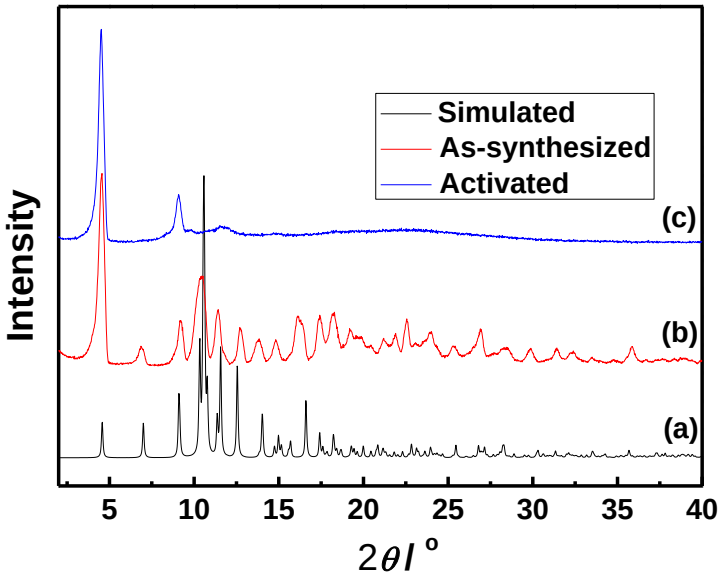

Figure S1. PXRD patterns of (a) as-synthesized **UTSA-32** and (c) activated **UTSA-32a**, along with the simulated PXRD pattern from single X-ray crystal structure.

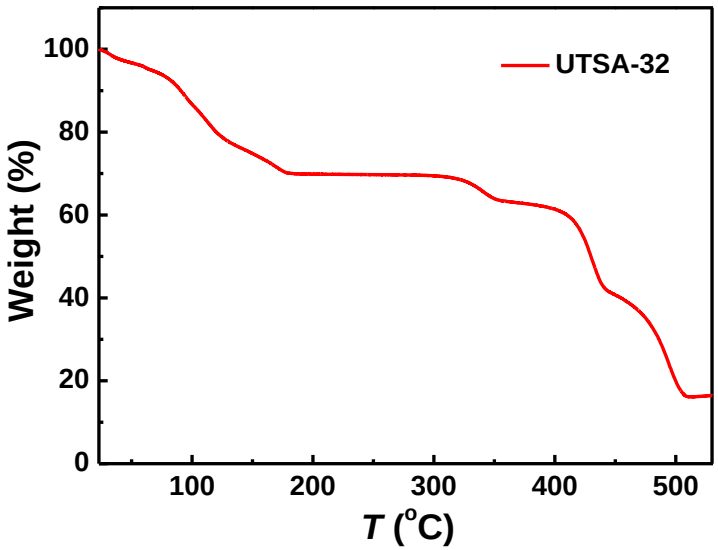

Figure S2. TGA curve of as-synthesized **UTSA-32**.

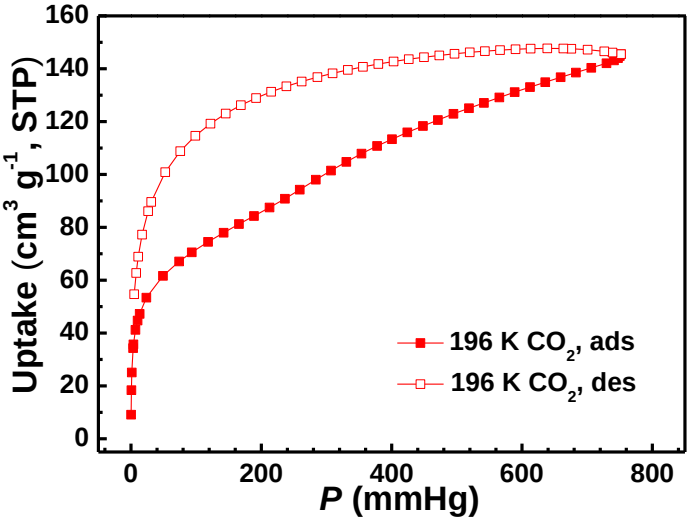

Figure S3. CO_2 sorption isotherm of **UTSA-32a** at 196 K.

Additional References

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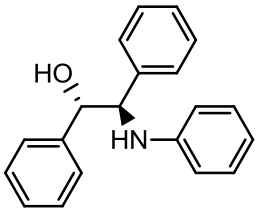
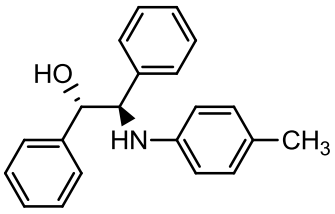
Compound Characterization Data

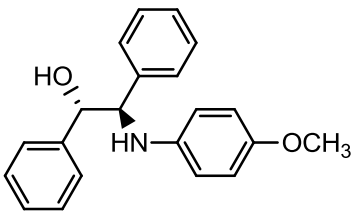
(1*s*,2*s*)-1,2-Diphenyl-2-(phenylamino)ethanol:[1,2] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.10 (m, 10H), 6.83-6.57 (m, 5H), 4.89 (d, J = 6.0 Hz, 1H), 4.56 (d, J = 6.0 Hz, 1H), 3.69 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.5, 140.9, 140.5, 129.3, 128.8, 128.5, 128.1, 127.7, 127.5, 126.8, 118.1, 114.3, 78.3, 64.9. $[\alpha]_D^{24}$ = -31.9^o (c = 0.46, CH_2Cl_2, 85% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): t_R = 24.8 min (minor), t_R = 29.3 min (major).



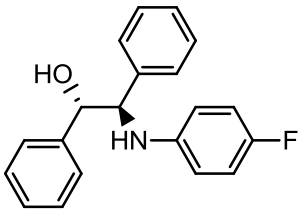
(1*s*,2*s*)-1,2-Diphenyl-2-(*p*-tolylamino)ethanol:[6] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27-7.18 (m, 10H), 6.90-6.87 (m, 4H), 4.83 (d, J = 6 Hz, 1H), 4.48 (d, J = 6.3 Hz, 1H), 2.73 (brs, 1H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 137.7, 137.5, 137.2, 137.0, 129.3, 129.1, 129.0, 127.2, 126.5, 117.8, 114.1, 78.0, 64.4, 21.4. $[\alpha]_D^{24}$ = -37.9^o (c = 0.43, CH_2Cl_2, 75% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): t_R = 24.6 min (major), 26.4 min (minor).



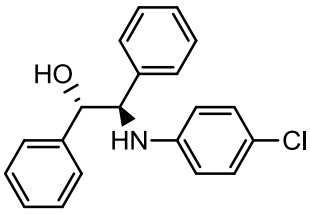
(1*s*,2*s*)-1,2-Diphenyl-2-(*p*-methoxyphenylamino)ethanol:[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25-7.14 (m, 10H), 6.67-6.49 (m, 4H), 4.80 (d, J = 6.6 Hz, 1H), 4.40 (d, J = 6.6 Hz, 1H), 3.67 (s, 3H), 2.81 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 141.4, 140.7, 140.3, 128.6, 128.3, 128.0, 127.6, 127.5, 126.8, 115.9, 114.8, 78.3, 66.4, 55.9. $[\alpha]_D^{24}$ = -28.9^o (c = 0.39, CH_2Cl_2, 62% *ee*). HPLC (Daicel Chiralcel® AD-H column, hexane/*i*-PrOH = 82/20, flow rate = 0.5 mL/min, 247 nm): t_R = 37.1 min (major), t_R = 45.2 min (minor).



(1*s*,2*s*)-1,2-Diphenyl-2-(*p*-fluorophenylamino)ethanol:[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26-7.17 (m, 10H), 6.79-6.43 (m, 4H), 4.82 (d, J = 6.3 Hz, 1H), 4.60 (brs, 1H), 4.43 (d, J = 6.3 Hz, 1H), 3.67 (s, 3H), 2.61 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.5, 140.8, 140.5, 129.2, 128.7, 128.4, 128.0, 127.7, 127.5, 126.8, 125.3, 115.3, 78.2, 64.9. $[\alpha]_D^{24}$ = -43.5^o (c = 0.42, CH_2Cl_2, 89% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 mL/min, 254 nm): t_R = 23.3 min (major), t_R = 26.5 min (minor).

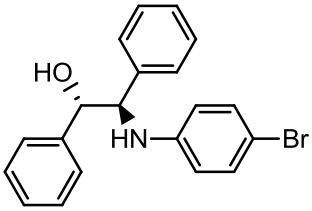


(1*s*,2*s*)-1,2-Diphenyl-2-(*p*-chlorophenylamino)ethanol:[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ =



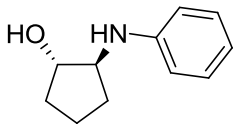
7.32-7.23 (m, 10H), 6.85-6.49 (m, 4H), 4.89 (d, *J* = 6.0 Hz, 1H), 4.66 (brs, 1H), 4.49 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 140.8, 140.4, 129.2, 128.7, 128.4, 128.0, 127.6, 127.4, 126.7, 125.2, 115.3, 78.2, 64.8. $[\alpha]_D^{24}$ = -22.1^o (*c* = 0.375, CH_2Cl_2, 58% *ee*). HPLC (Daicel Chiralcel® AD-H column, hexane/*i*-PrOH = 95/5, flow rate = 1 mL/min, 247 nm): t_R = 35.2 min (major), t_R = 43.1 min (minor).

(1*s*,2*s*)-1,2-Diphenyl-2-(*p*-bromophenylamino)ethanol:[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ =



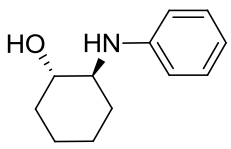
7.24-7.14(m, 10H), 6.77-6.41 (m, 4H), 4.80(d, *J* = 7.5 Hz, 1H), 4.57 (brs, 1H), 4.41 (d, *J* = 6.0 Hz, 1H), 2.59 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 141.0, 140.7, 129.7, 128.9, 128.6, 128.2, 127.7, 126.9, 115.5, 114.5, 78.4, 65.1. $[\alpha]_D^{24}$ = -41.4^o (*c* = 0.49, CH_2Cl_2, 31% *ee*). HPLC (Daicel Chiralcel® AD-H column, hexane/*i*-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): t_R = 21.8 min (major), t_R = 28.4 min (minor).

(1*s*,2*s*)-2-Phenylaminocyclopentanol:[7] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19-7.16 (m, 2H),



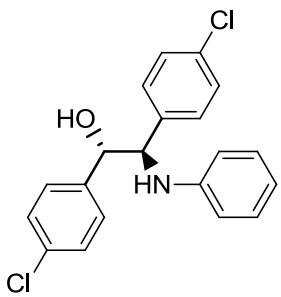
6.72-6.66 (m, 2H), 4.08-4.06 (m, 1H), 3.61-3.56 (m, 1H), 2.30-2.17 (m, 1H), 2.01-1.95 (m, 1H), 1.84-1.64 (m, 3H), 1.43-1.38 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.9, 129.4, 117.7, 113.4, 78.4, 62.2, 33.1, 31.4, 21.2. $[\alpha]_D^{24}$ = 14.6^o (*c* = 0.63, CH_2Cl_2, 12% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): t_R = 26.3 min (major), t_R = 29.4 min (minor).

(1*s*,2*s*)-2-Phenylaminocyclohexanol:[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.14 (m, 2H),



6.76-6.71 (m, 2H), 3.35-3.33 (m, 1H), 3.16-3.14 (m, 1H), 2.75 (brs, 1H), 2.17-2.11 (m, 2H), 1.78-1.72 (m, 2H), 1.43-1.26 (m, 3H), 1.08-1.04 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.9, 129.4, 117.7, 113.4, 78.4, 62.2, 33.1, 31.4, 21.2. $[\alpha]_D^{24}$ = 29.3^o (*c* = 0.48, CH_2Cl_2, 15% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): t_R = 19.4 min (major), t_R = 22.8 min (minor).

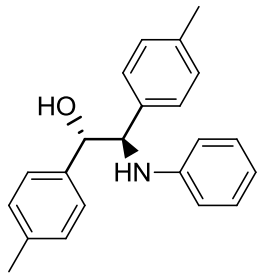
(1*s*,2*s*)-1,2-bis(4-chlorophenyl)-2-(phenylamino)ethanol:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ =



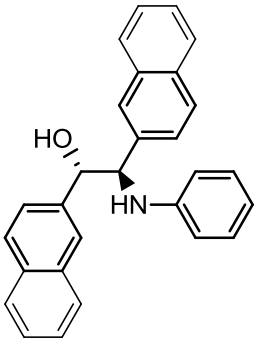
7.28-7.05(m, 10H), 6.70-6.41 (m, 3H), 4.79-4.77(d, *J* = 6.0 Hz, 1H), 4.45-4.29 (d, *J* = 6.3 Hz, 1H), 2.63 (brs, 1H). ^{13}C NMR (75 MHz,

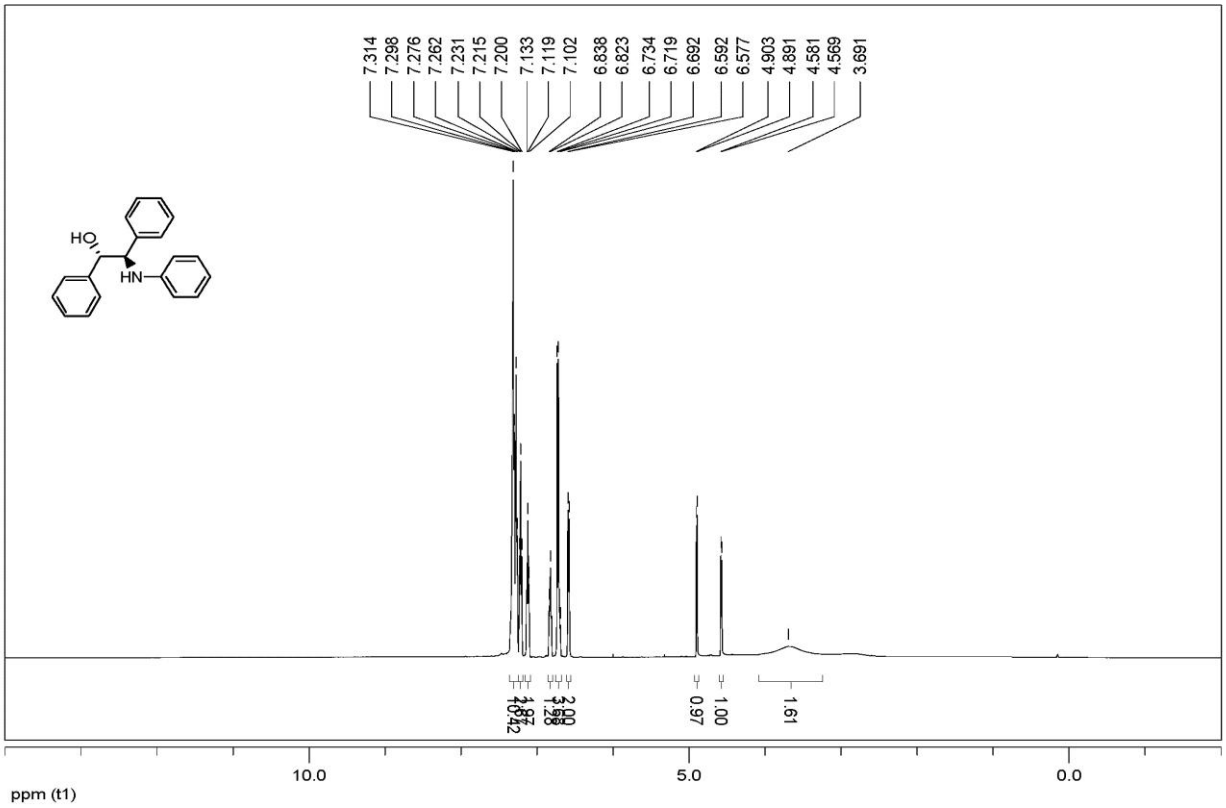
$CDCl_3$): δ = 147.5, 137.8, 137.6, 137.4, 137.2, 129.4, 129.2, 129.1, 127.3, 126.6, 117.9, 114.2, 78.1, 64.5. $[\alpha]_D^{24}$ = -19.2^o (*c* = 0.68, CH_2Cl_2, 34% *ee*). HPLC (Daicel Chiralcel® IB column, hexane/*i*-PrOH = 95/5, flow rate = 1 ml/min, 254 nm): t_R = 50.5 min (major), t_R = 65.2 min (minor).

(1*s*,2*s*)-1,2-bis(*p*-tolyl)-2-(phenylamino)ethanol:[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26-7.04(m, 10H), 6.67-6.62 (m, 1H), 6.55-6.51(m, 2H), 4.84 (d, J = 5.4 Hz, 1H), 4.64 (brs, 1H), 4.50 (d, *J* = 5.4 Hz, 1H), 2.49 (brs, 1H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 137.4, 137.2, 137.0, 136.8, 129.1, 128.8, 128.7, 126.9, 126.2, 117.5, 113.8, 77.7, 64.1, 21.2, 21.1. $[\alpha]_D^{24}$ = -31.9^o (*c* = 0.41, CH_2Cl_2, 17% *ee*). HPLC (Daicel Chiralcel® AD-H column, hexane/*i*-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): t_R = 23.3 min (major), t_R = 27.1 min (minor).



1*s*,2*s*)-1,2-di(naphthalen-2-yl)-2-(phenylamino)ethanol:[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28-7.04(m, 14H), 6.77-6.63 (m, 3H), 6.52-6.54(m, 2H), 4.88 (d, J = 6.0 Hz, 1H), 4.53 (d, *J* = 5.5 Hz, 1H), 3.74 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.2, 140.5, 140.1, 131.3, 129.7, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 127.4, 127.2, 126.5, 125.9, 117.8, 114.1, 78.0, 64.7. $[\alpha]_D^{24}$ = -116.4^o (*c* = 0.31, CH_2Cl_2, 32% *ee*). HPLC (Daicel Chiralcel® AD-H column, hexane/*i*-PrOH = 90/10, flow rate = 1 mL/min, 254 nm): t_R = 23.5 min (major), t_R = 30.5 min (minor).

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6.734
6.719
6.692
6.592
6.577
4.903
4.891
4.581
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3.691
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HN
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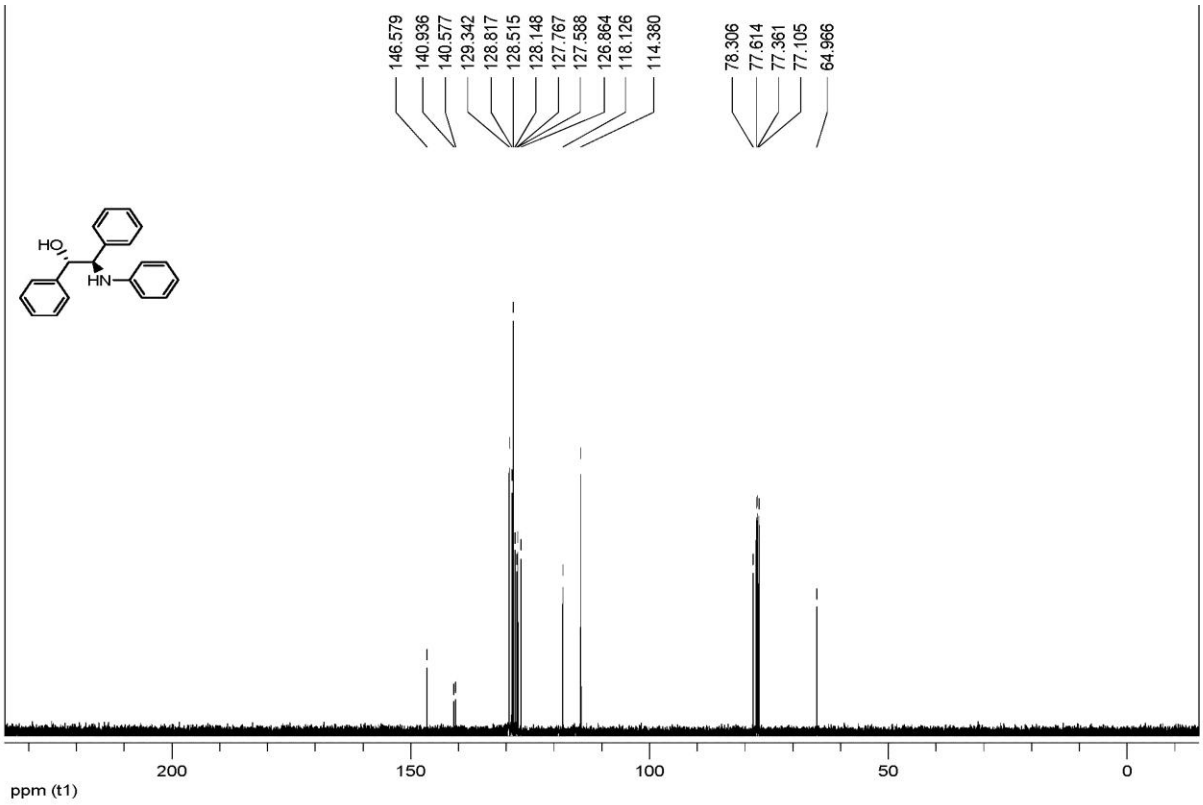
1.61
10.0
5.0
0.0
ppm (t1)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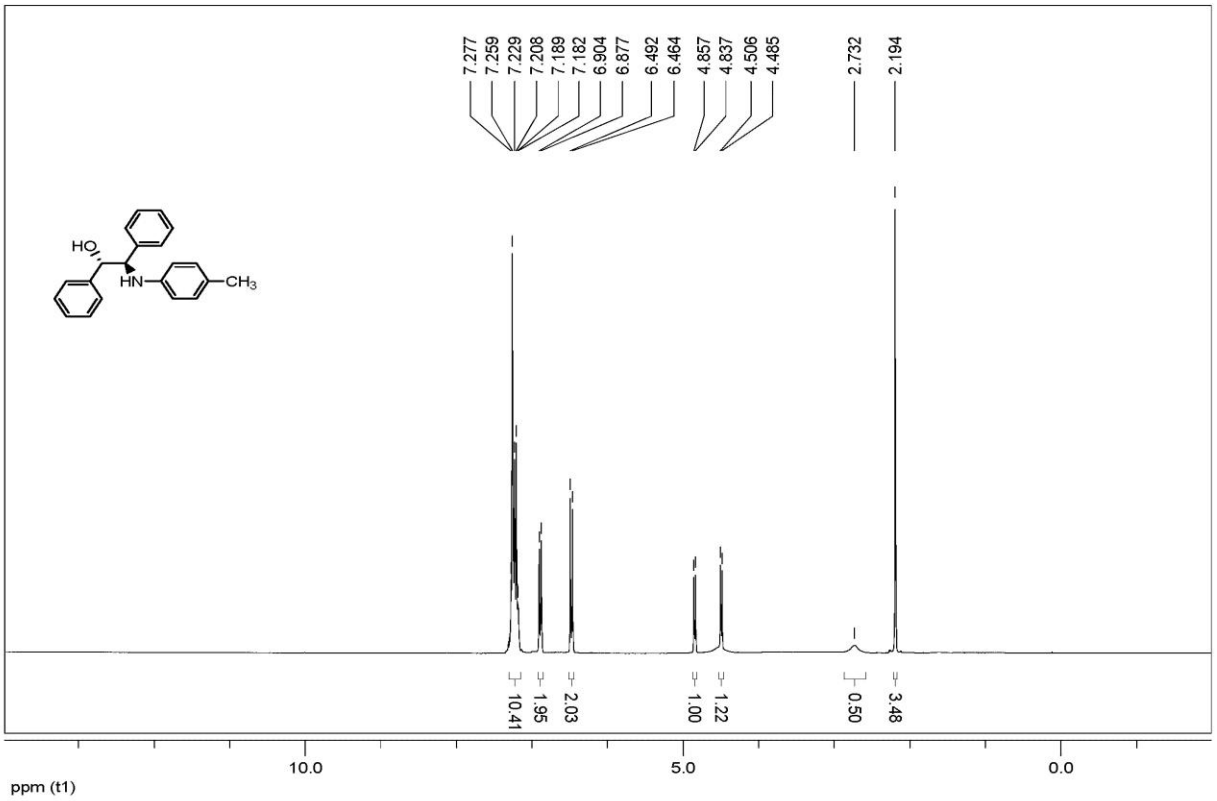
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2.194
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HN
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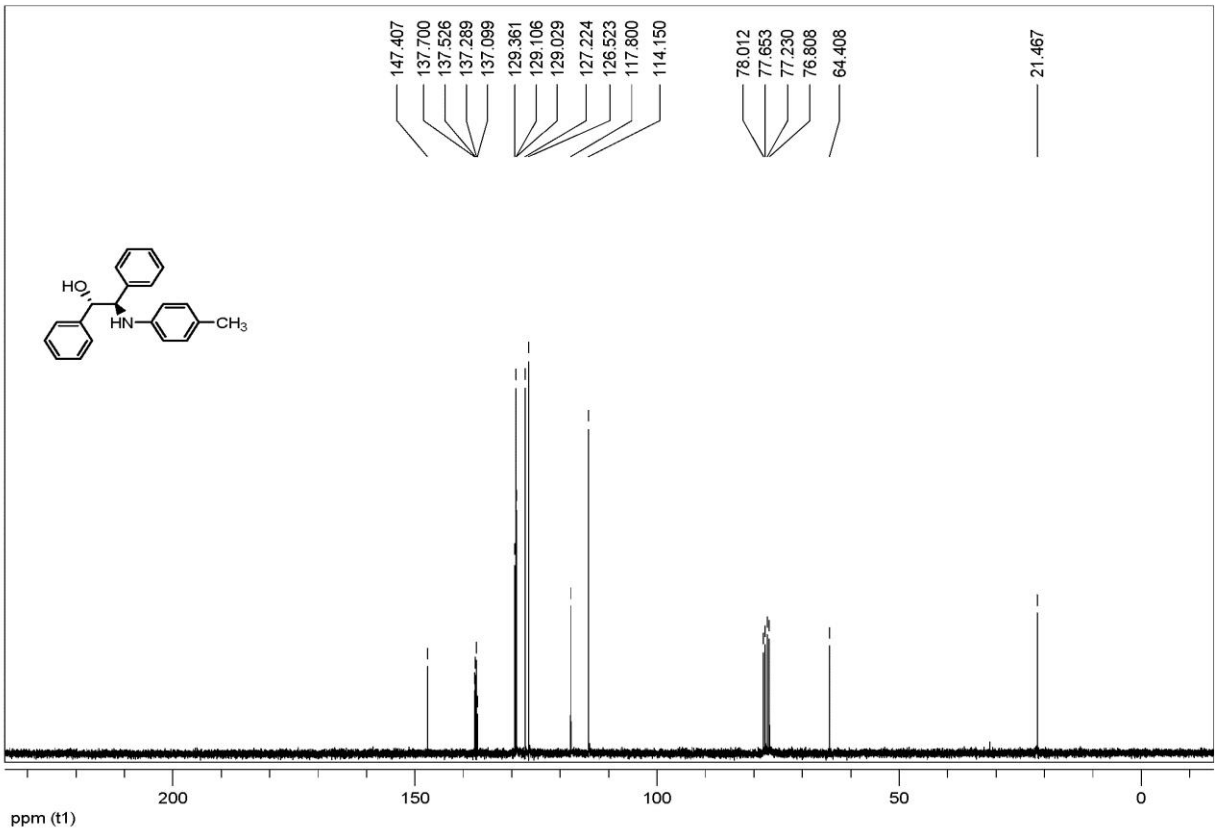
ppm (t1)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126.523
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77.653
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76.808
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HO
HN
CH3
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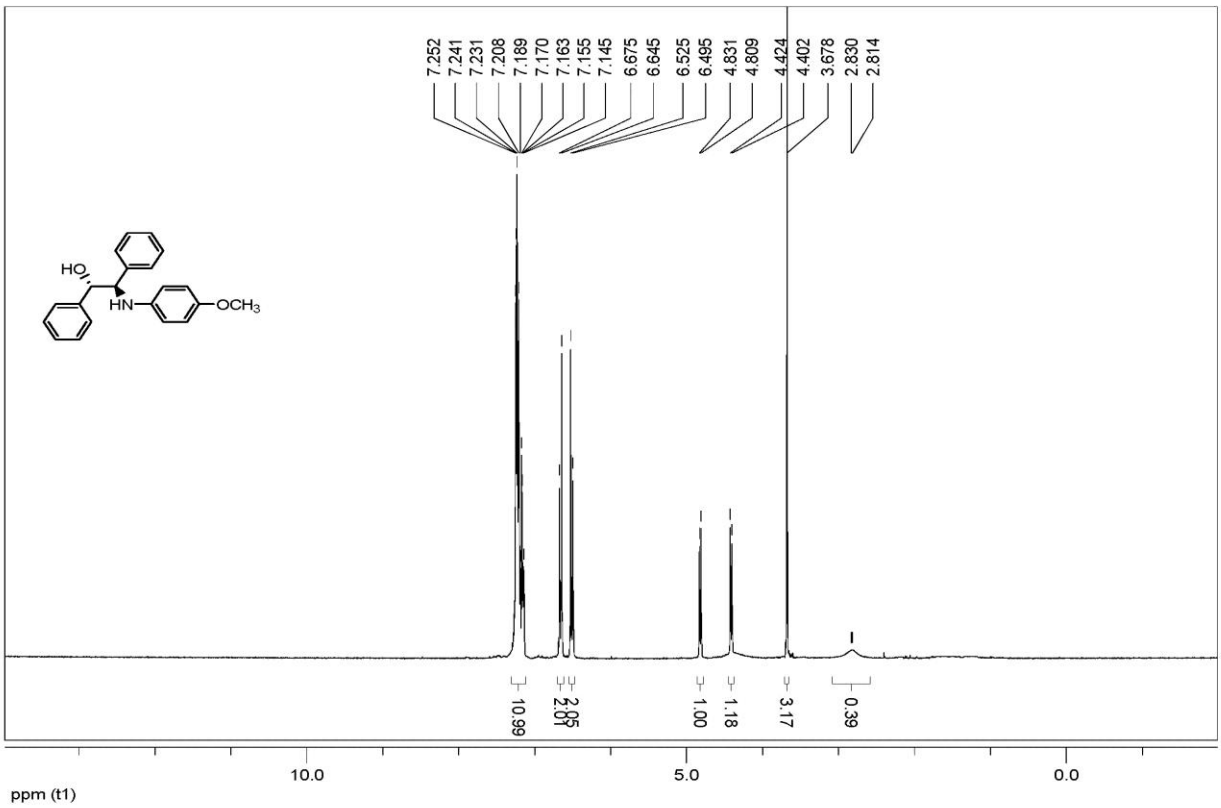
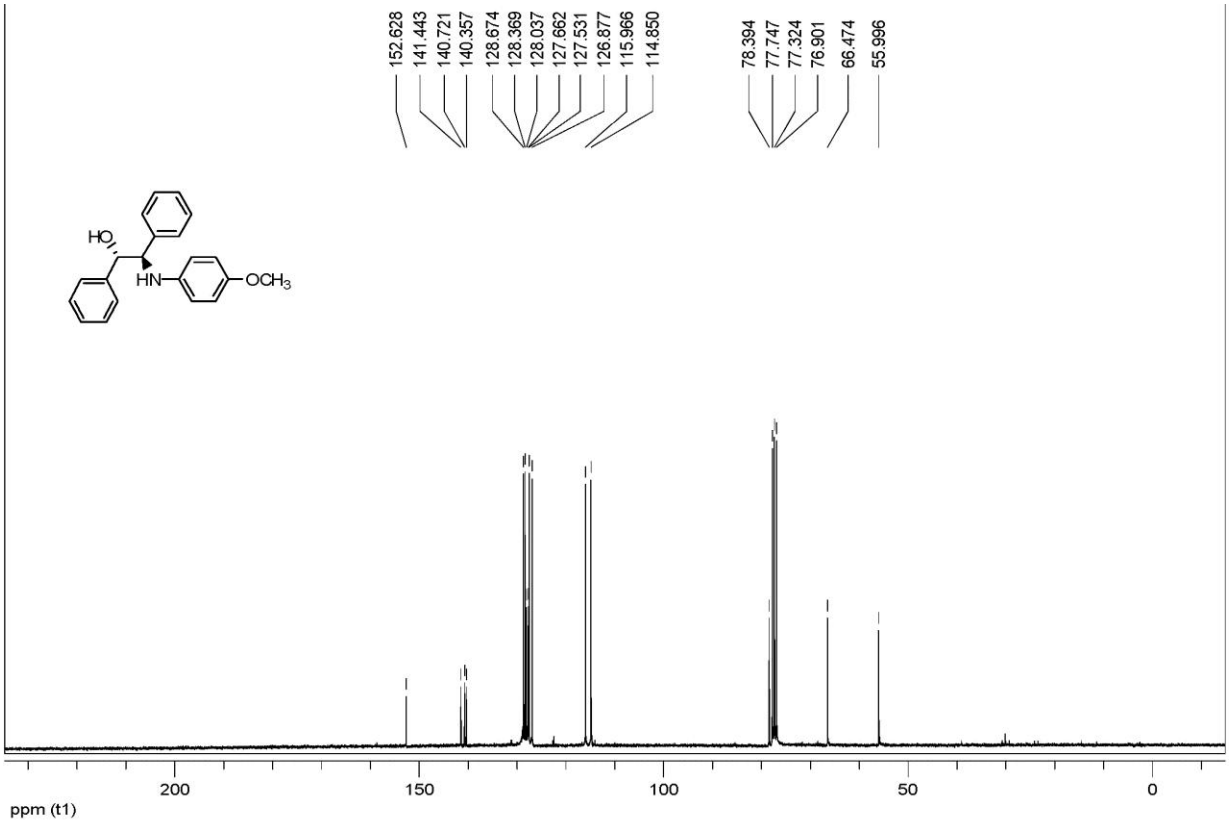
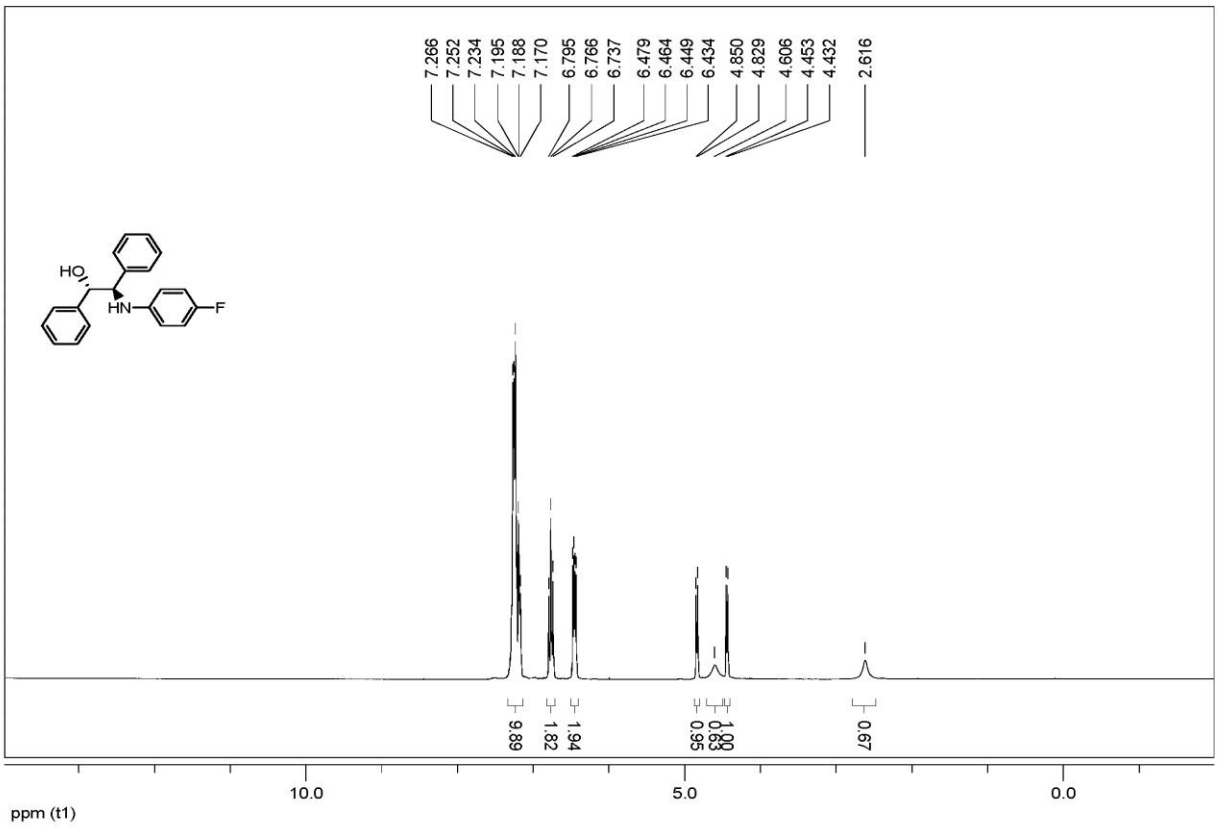
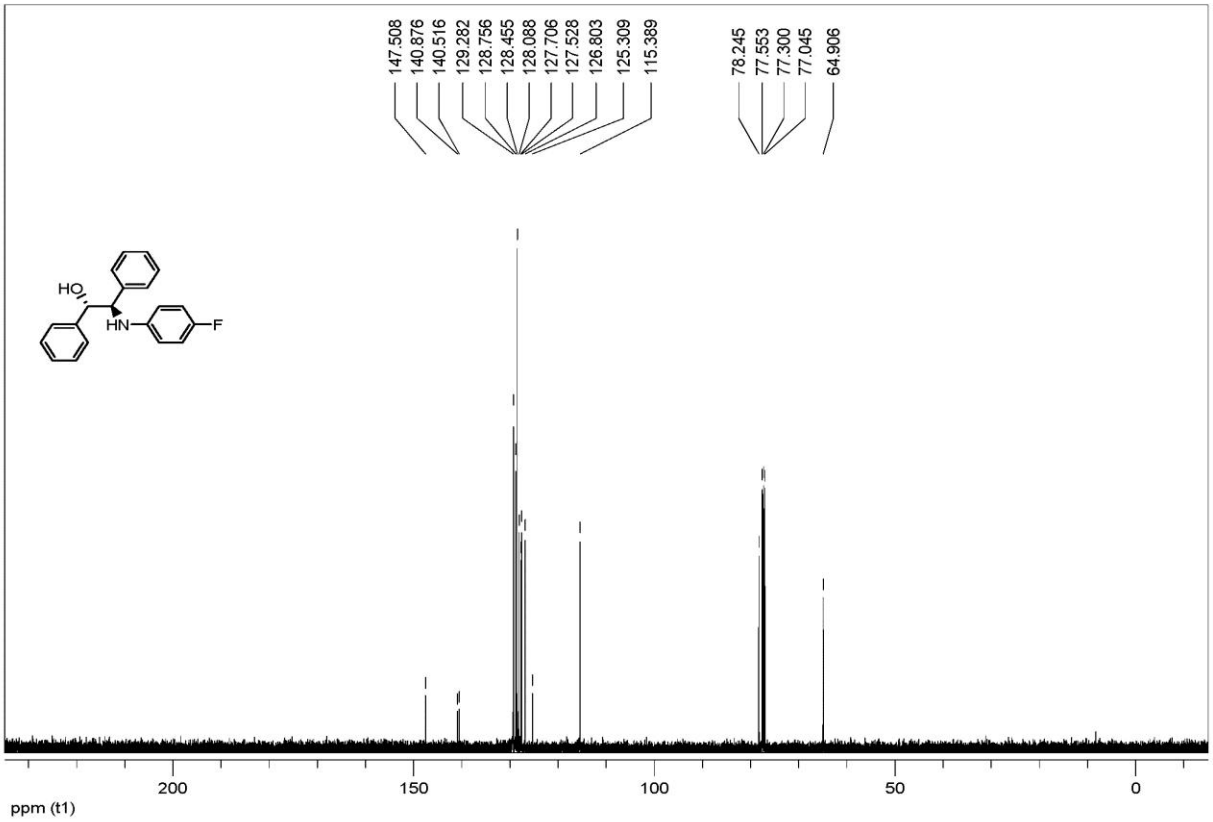
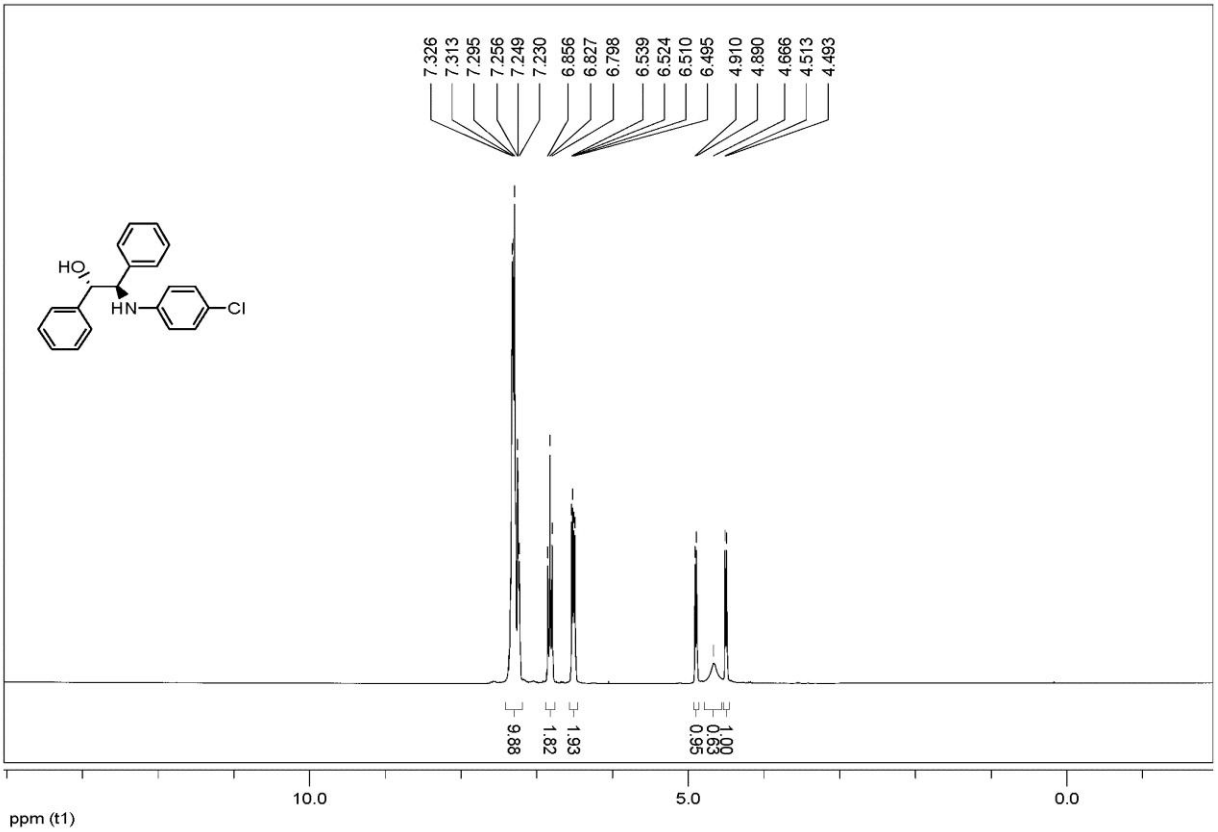
150
100
50
0
ppm (t1)

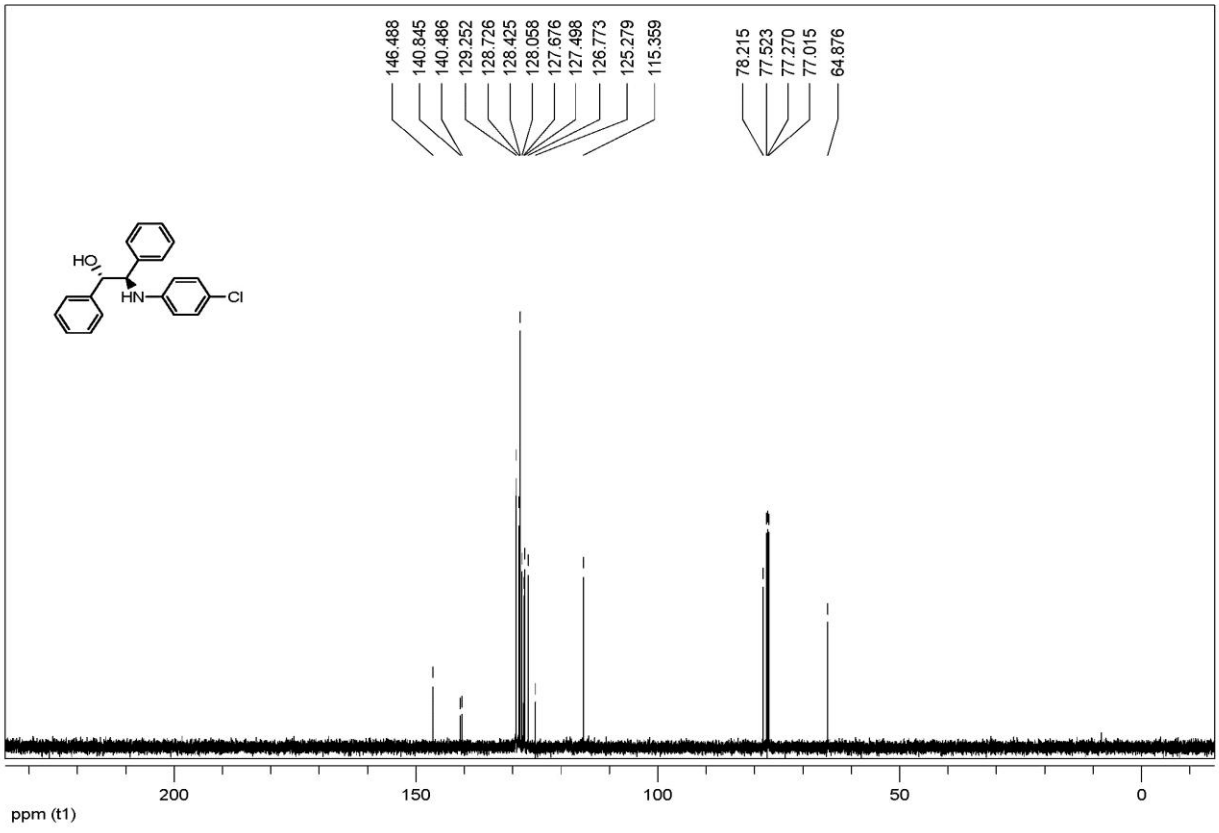


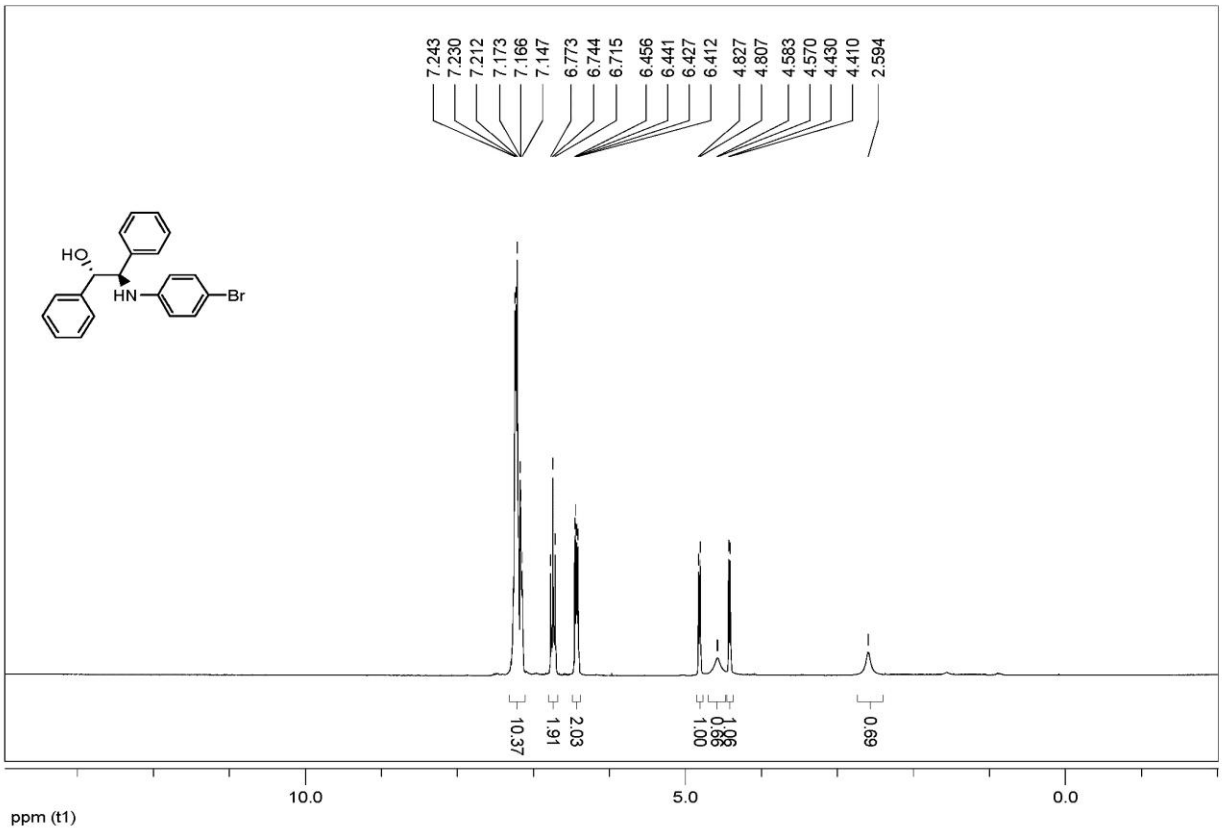


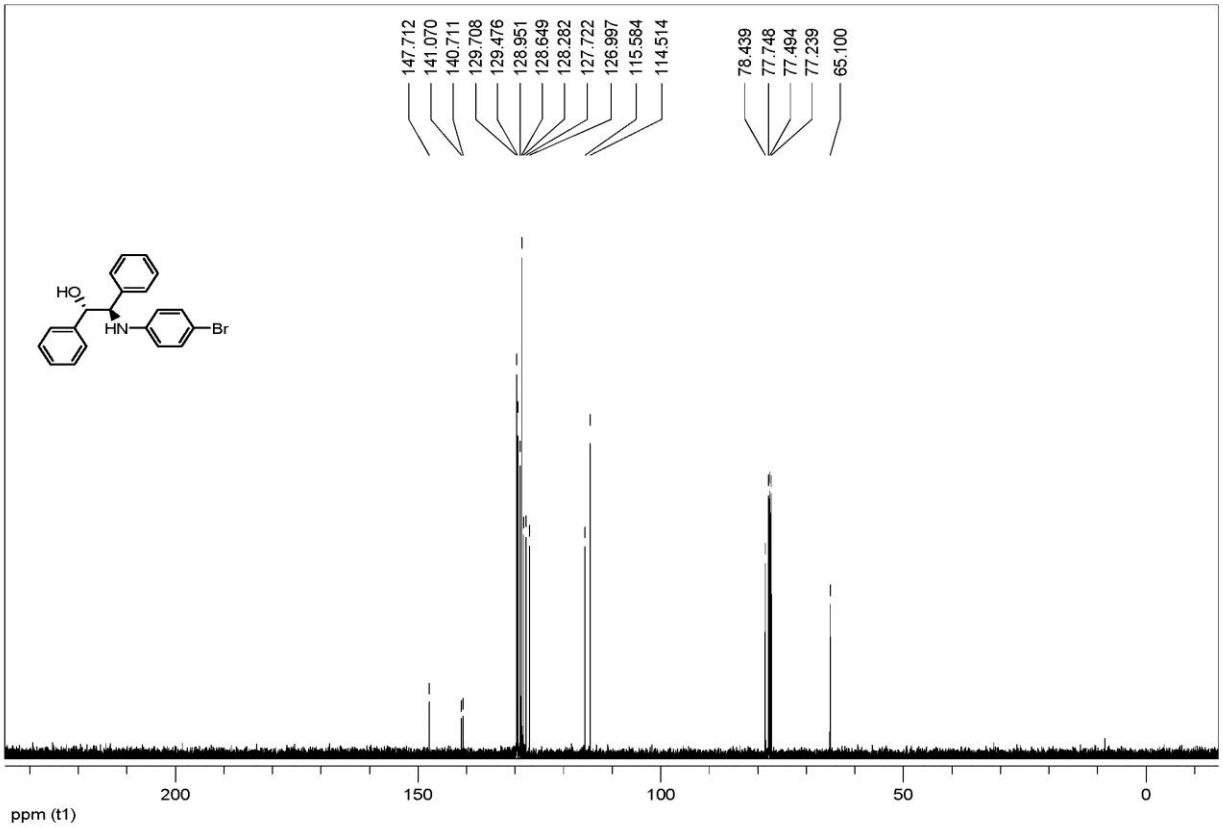


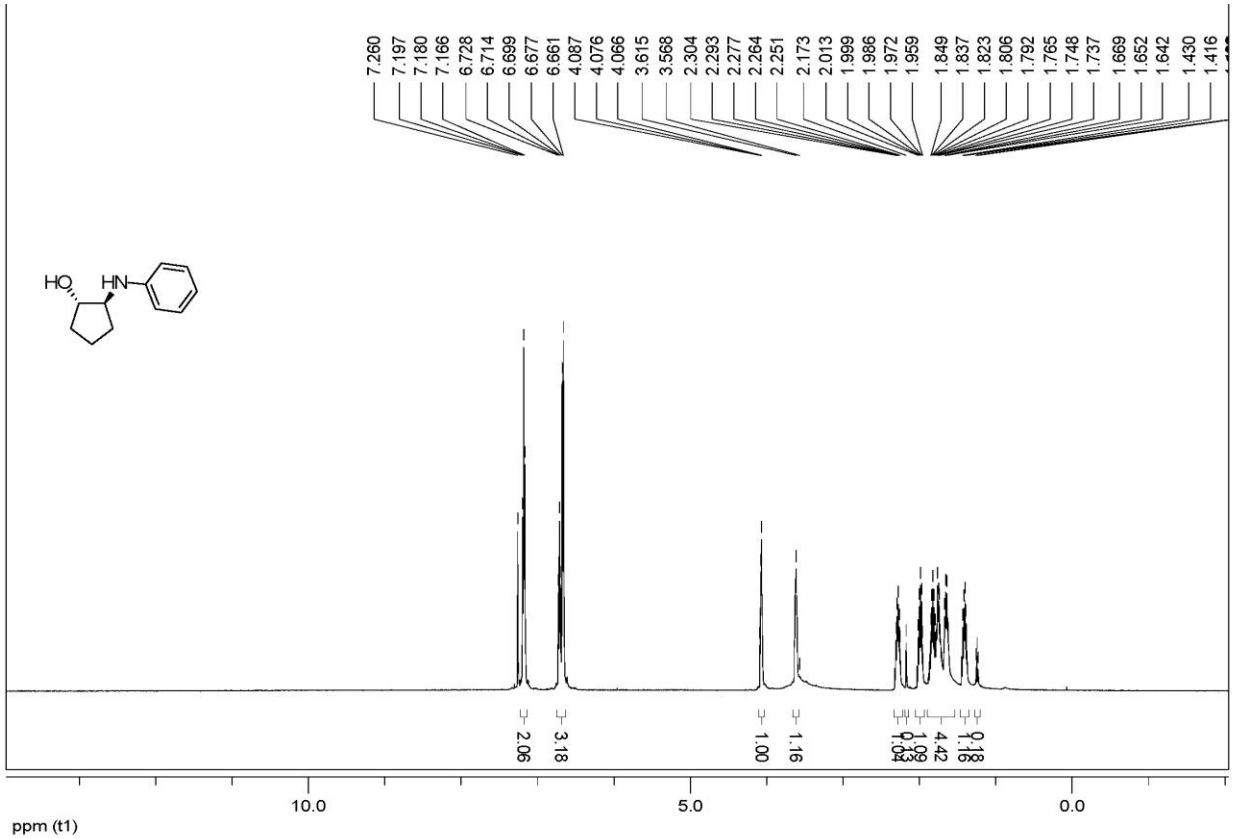


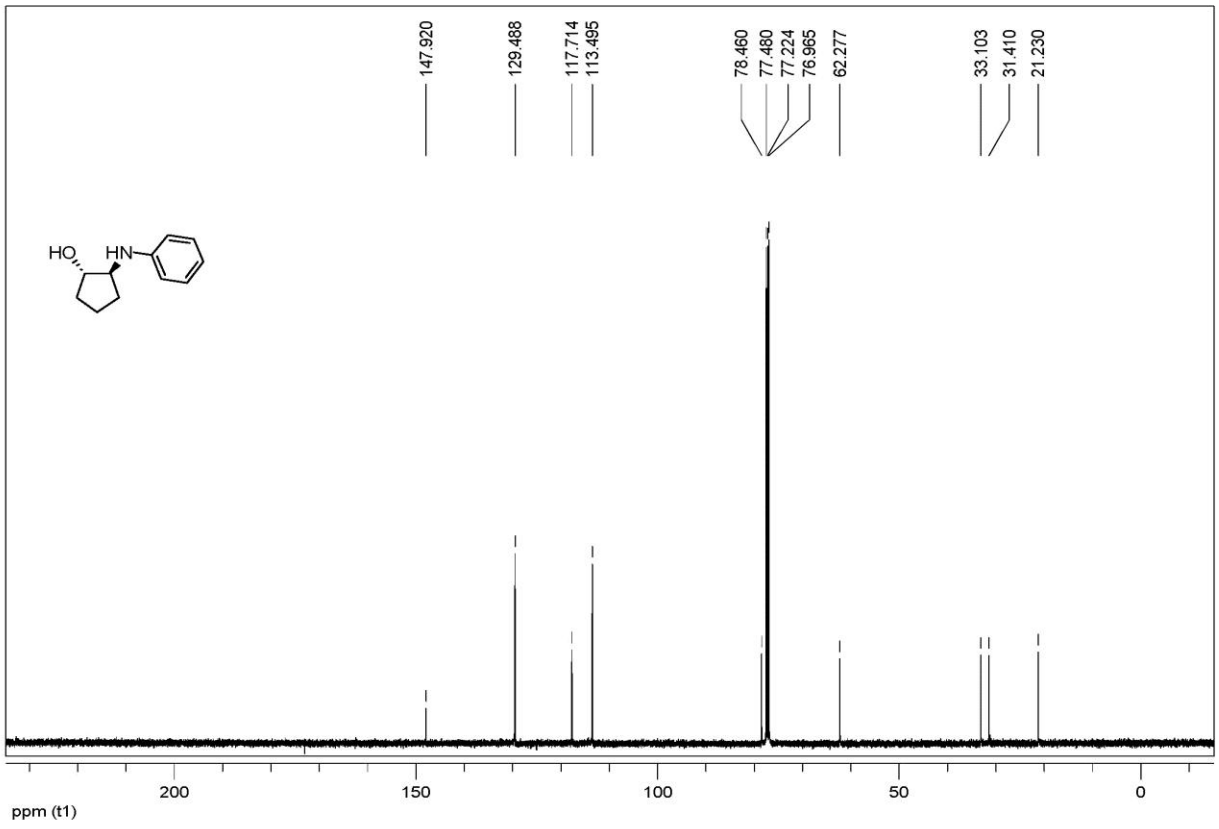


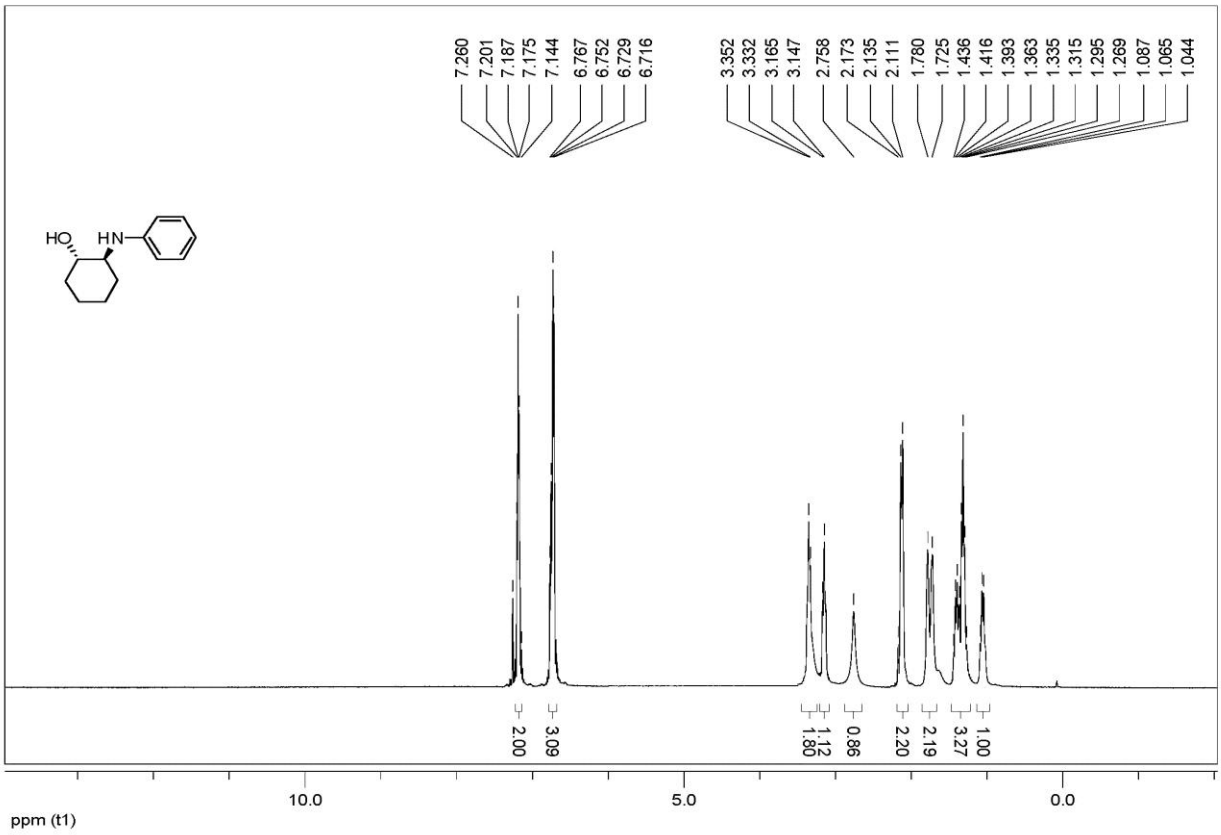


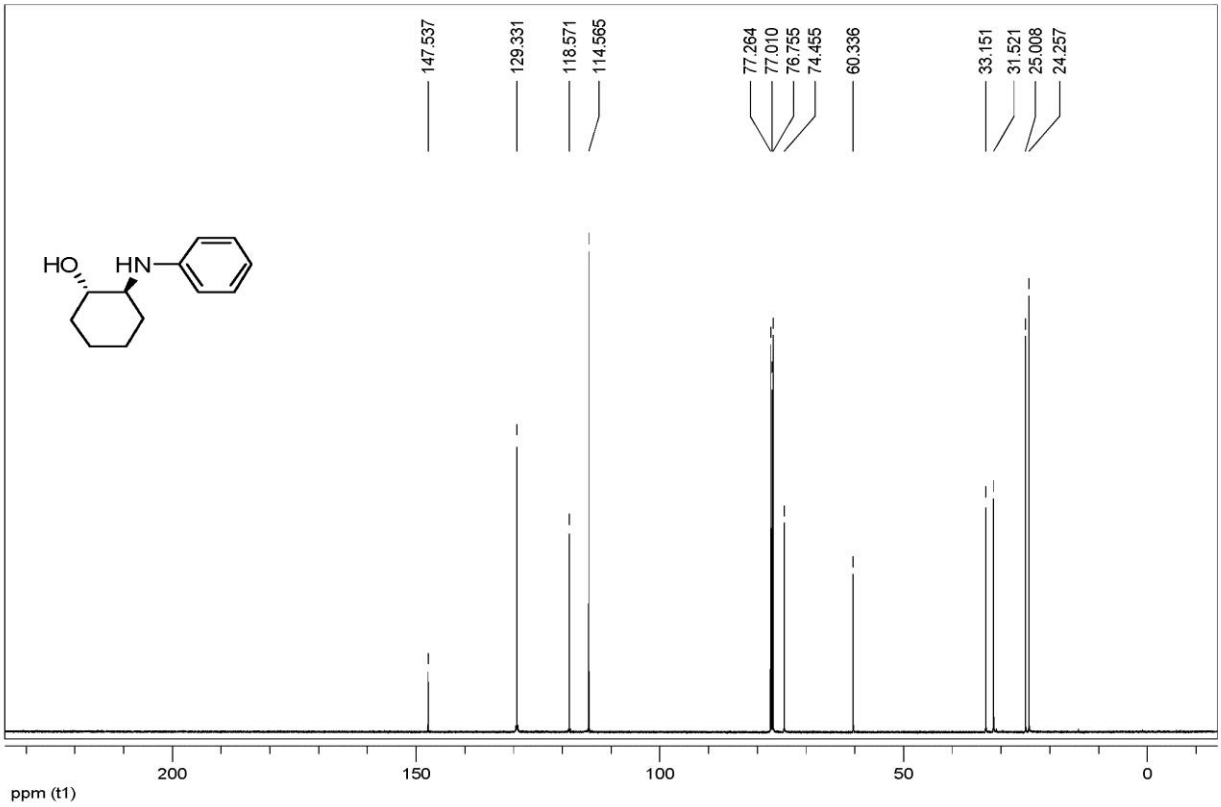


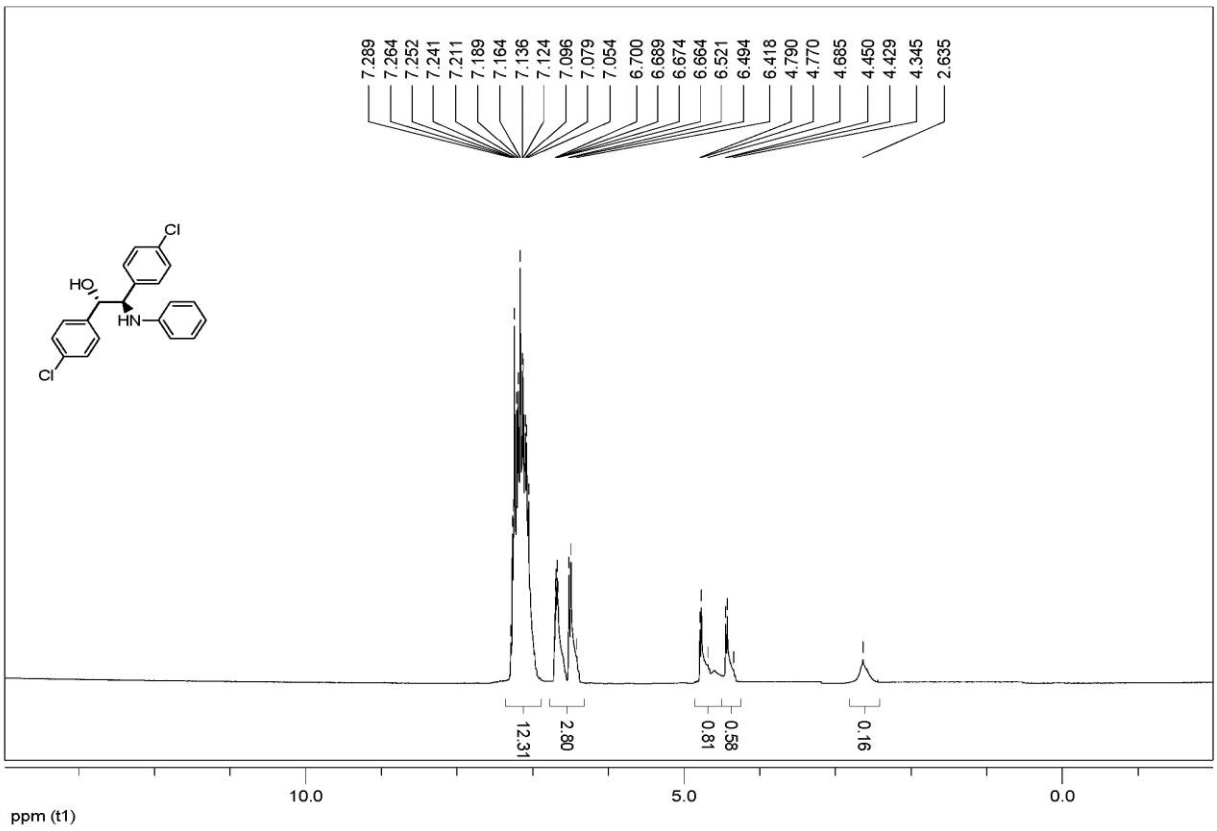


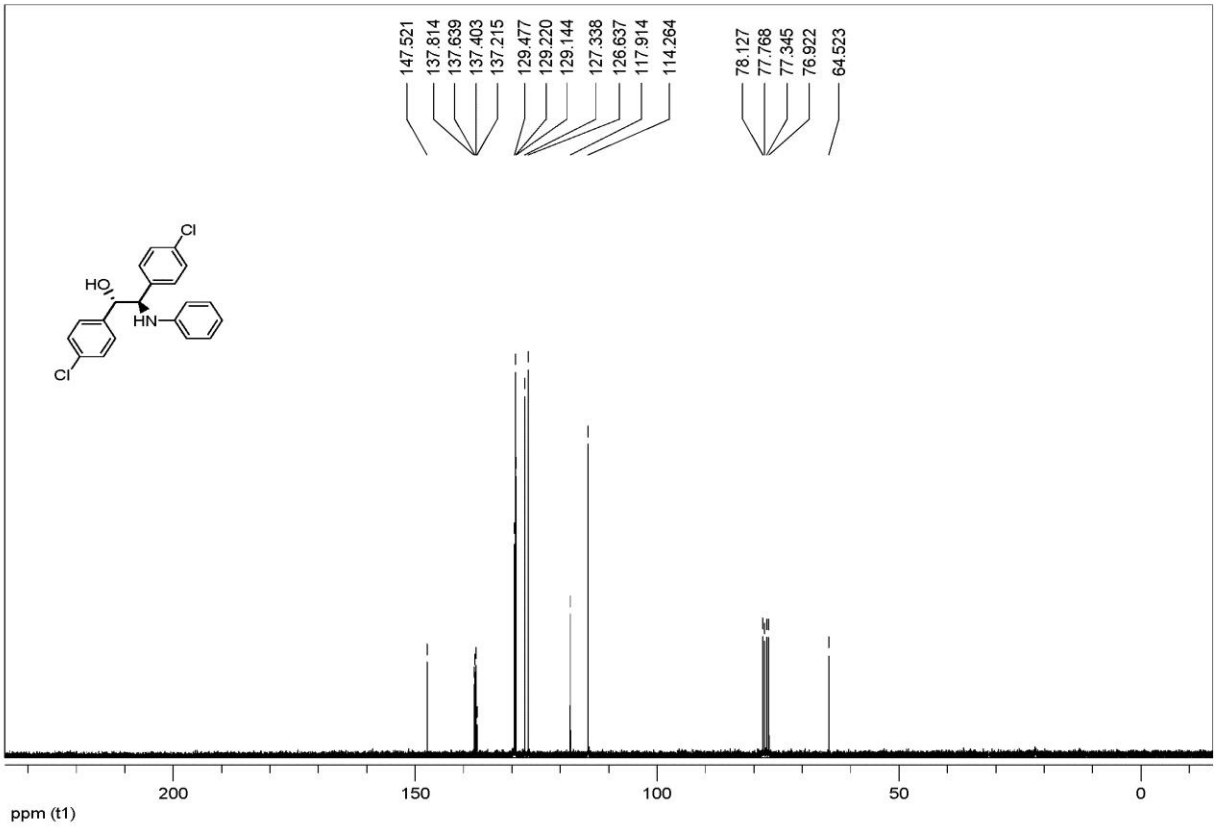

7.260
7.197
7.180
7.166
6.728
6.714
6.699
6.677
6.661
4.087
4.076
4.066
3.615
3.568
2.304
2.293
2.277
2.264
2.251
2.173
2.013
1.999
1.986
1.972
1.959
1.849
1.837
1.823
1.806
1.792
1.765
1.748
1.737
1.669
1.652
1.642
1.430
1.416
HO
HN
2.06
3.18
1.00
1.16
1.04
0.93
1.09
4.42
0.18
0.16
10.0
5.0
0.0
ppm (t1)

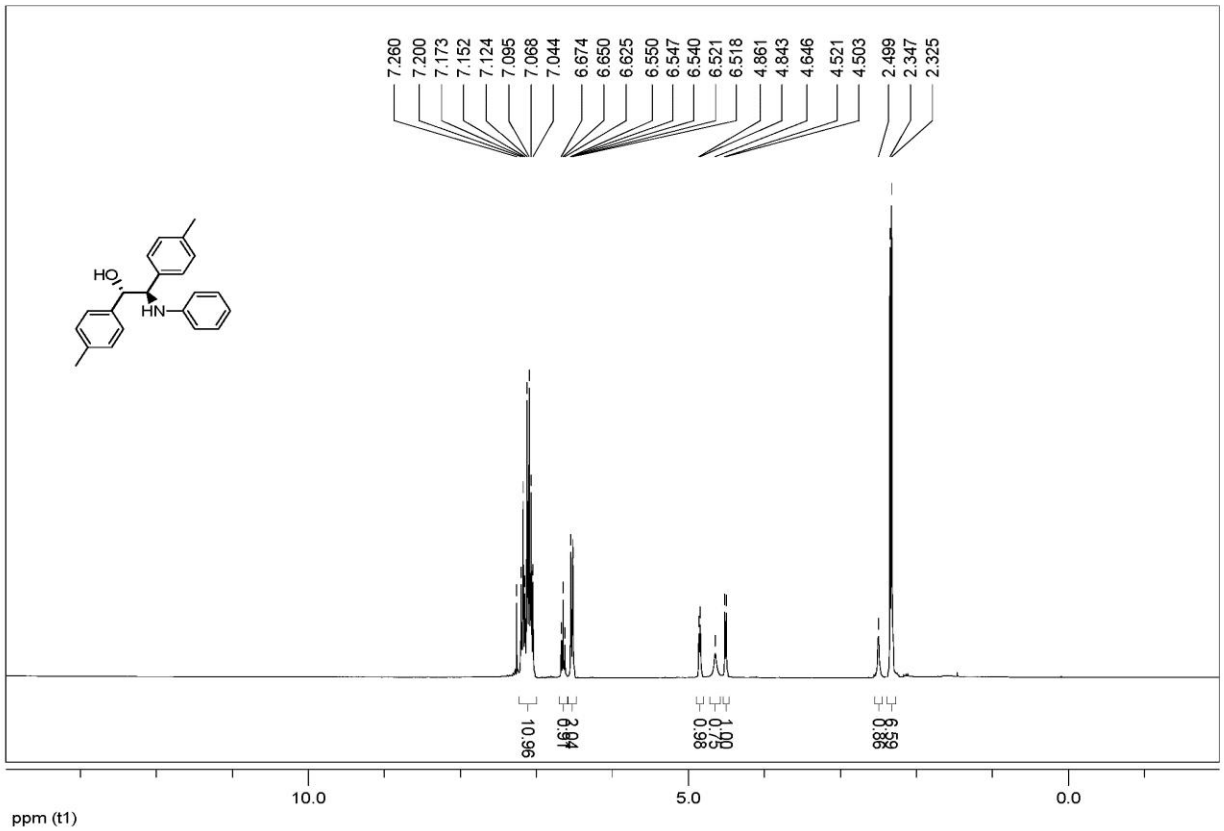

147.920
129.488
117.714
113.495
78.460
77.480
77.224
76.965
62.277
33.103
31.410
21.230
HO
HN
200
150
100
50
0
ppm (t1)

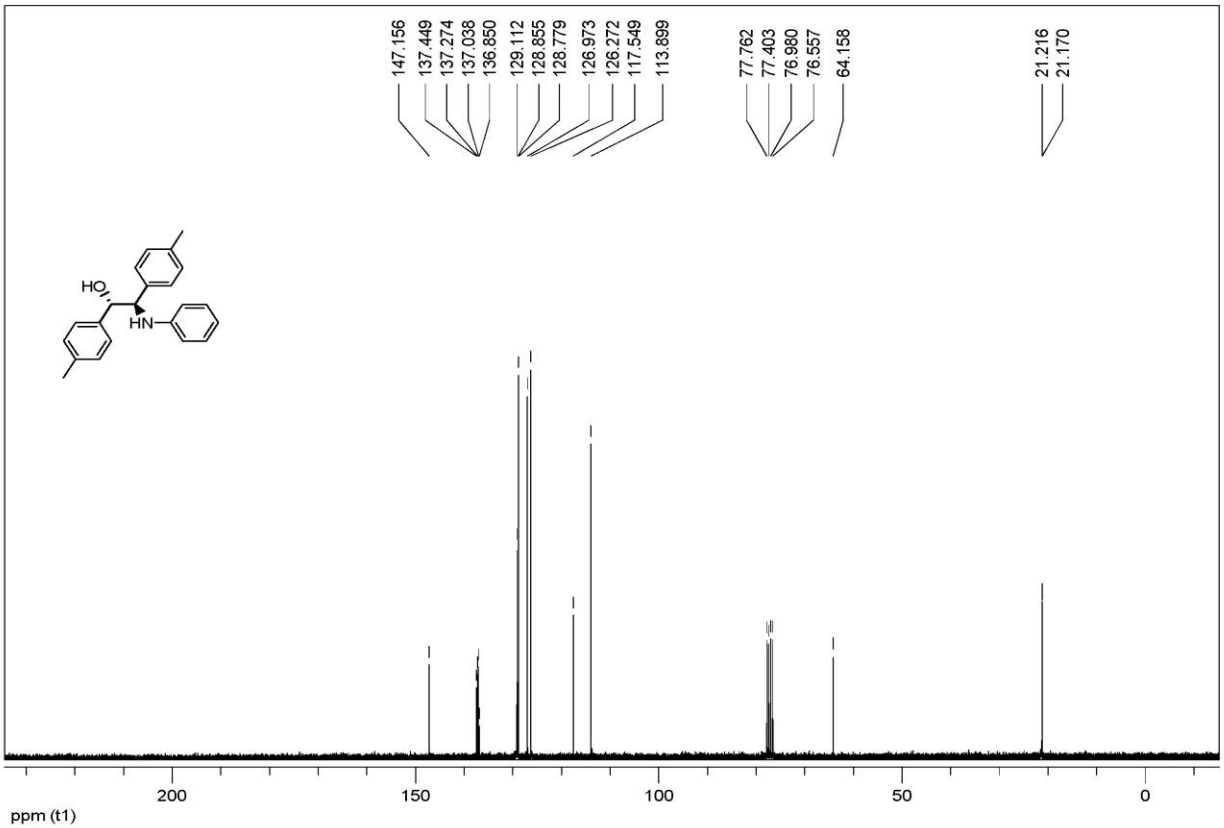

7.260
7.201
7.187
7.175
7.144
6.767
6.752
6.729
6.716
3.352
3.332
3.165
3.147
2.758
2.173
2.135
2.111
1.780
1.725
1.436
1.416
1.393
1.363
1.335
1.315
1.295
1.269
1.087
1.065
1.044
HO
HN
2.00
3.09
1.12
1.80
0.86
2.20
2.19
3.27
1.00
10.0
5.0
0.0
ppm (t1)

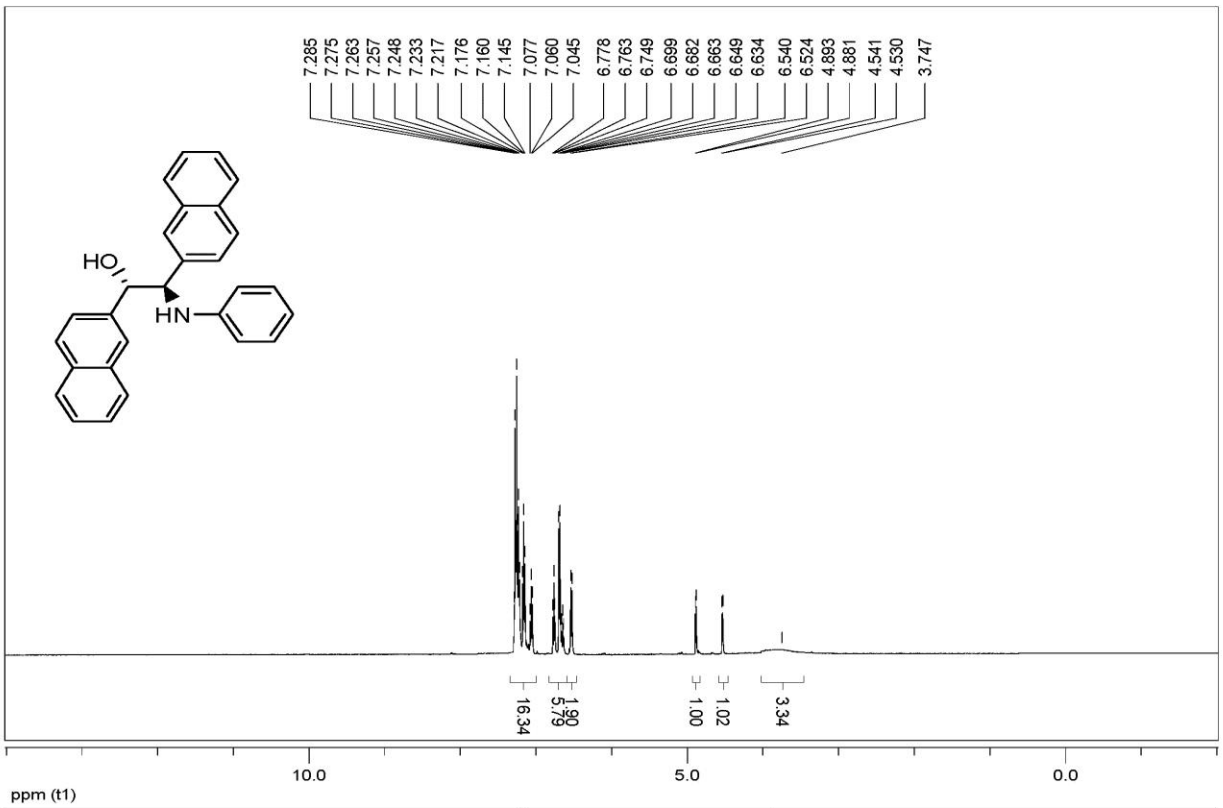

147.537
129.331
118.571
114.565
77.264
77.010
76.755
74.455
60.336
33.151
31.521
25.008
24.257
HO
HN
200
150
100
50
0
ppm (t1)

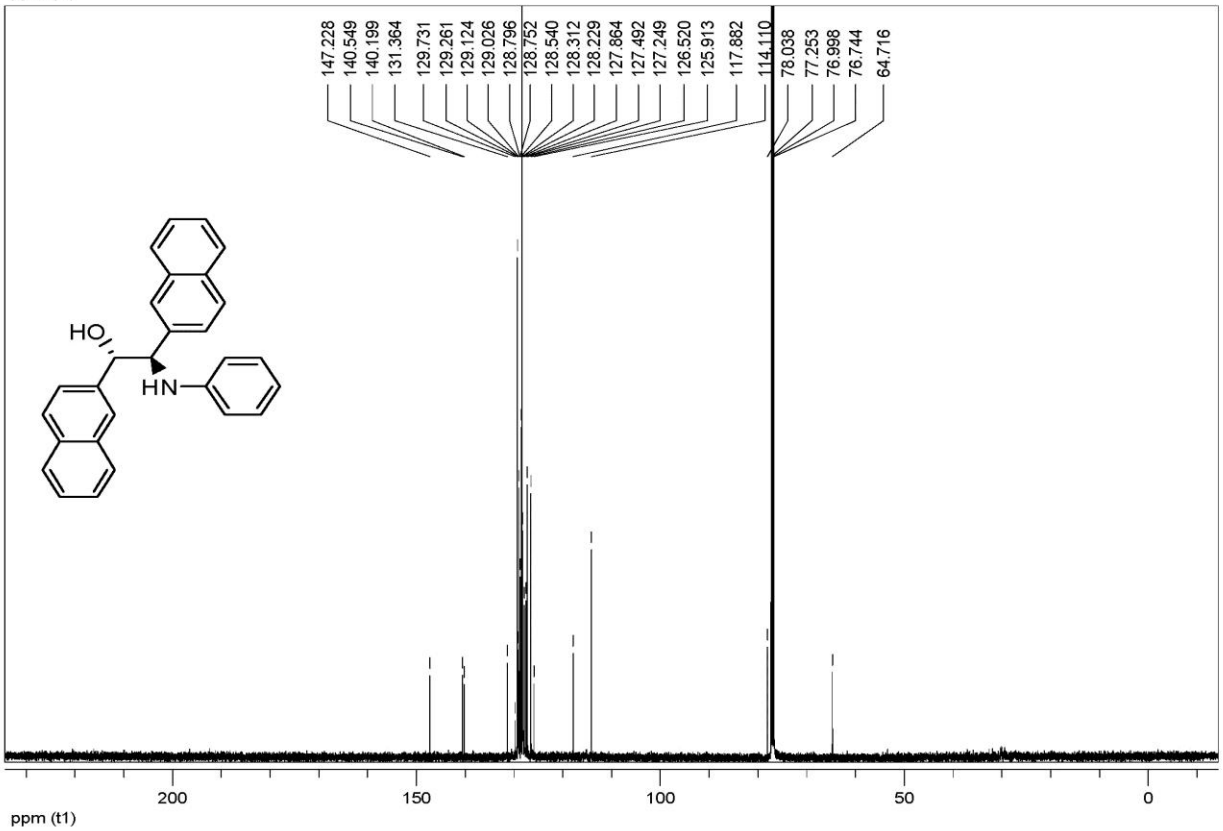

7.289
7.264
7.252
7.241
7.211
7.189
7.164
7.136
7.124
7.096
7.079
7.054
6.700
6.689
6.674
6.664
6.521
6.494
6.418
4.790
4.770
4.685
4.450
4.429
4.345
2.635
Cl
HO
HN
Cl
1.31
2.80
0.81
0.58
0.16
10.0
5.0
0.0
ppm (t1)


147.521
137.814
137.639
137.403
137.215
129.477
129.220
129.144
127.338
126.637
117.914
114.264
78.127
77.768
77.345
76.922
64.523
Cl
HO
HN
Cl
200
150
100
50
0
ppm (t1)

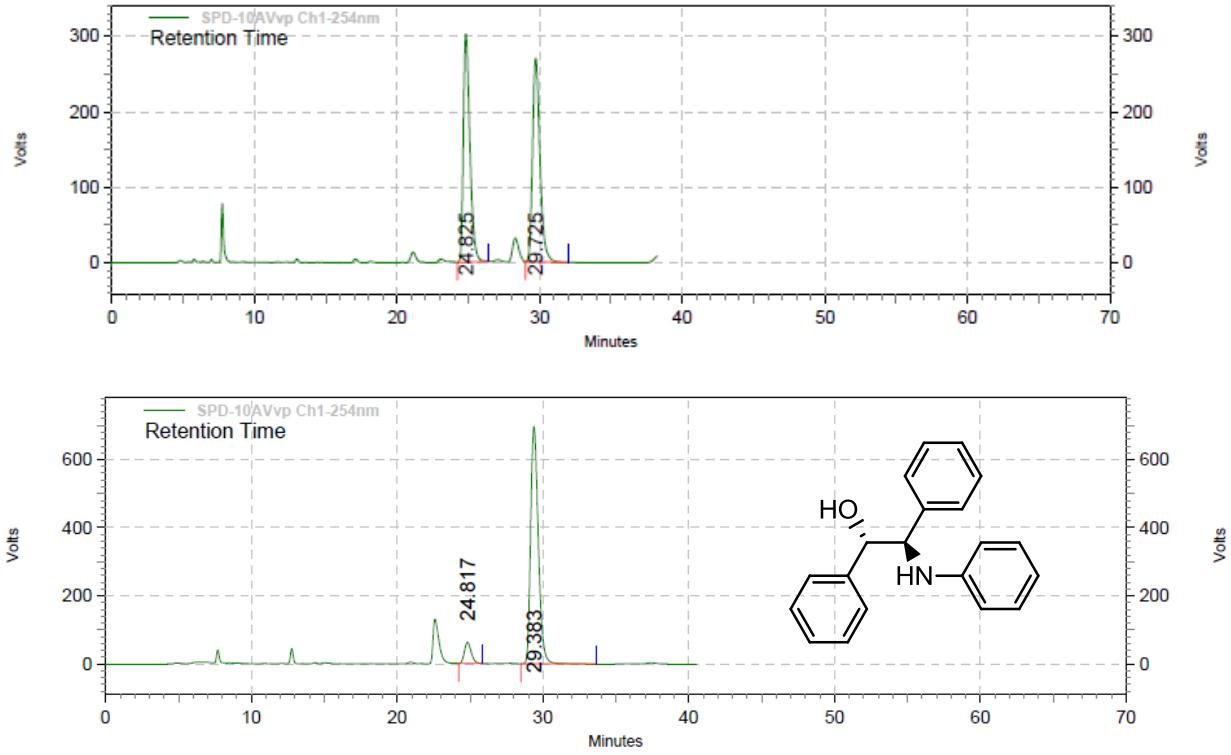

7.260
7.200
7.173
7.152
7.124
7.095
7.068
7.044
6.674
6.650
6.625
6.550
6.547
6.540
6.521
6.518
4.861
4.843
4.646
4.521
4.503
2.499
2.347
2.325
HO
HN
10.96
2.94
2.84
0.98
0.95
1.00
6.58
6.56
6.38
10.0
5.0
0.0
ppm (t1)


147.156
137.449
137.274
137.038
136.850
129.112
128.855
128.779
126.973
126.272
117.549
113.899
77.762
77.403
76.980
76.557
64.158
21.216
21.170
HO
HN
200
150
100
50
0
ppm (t1)



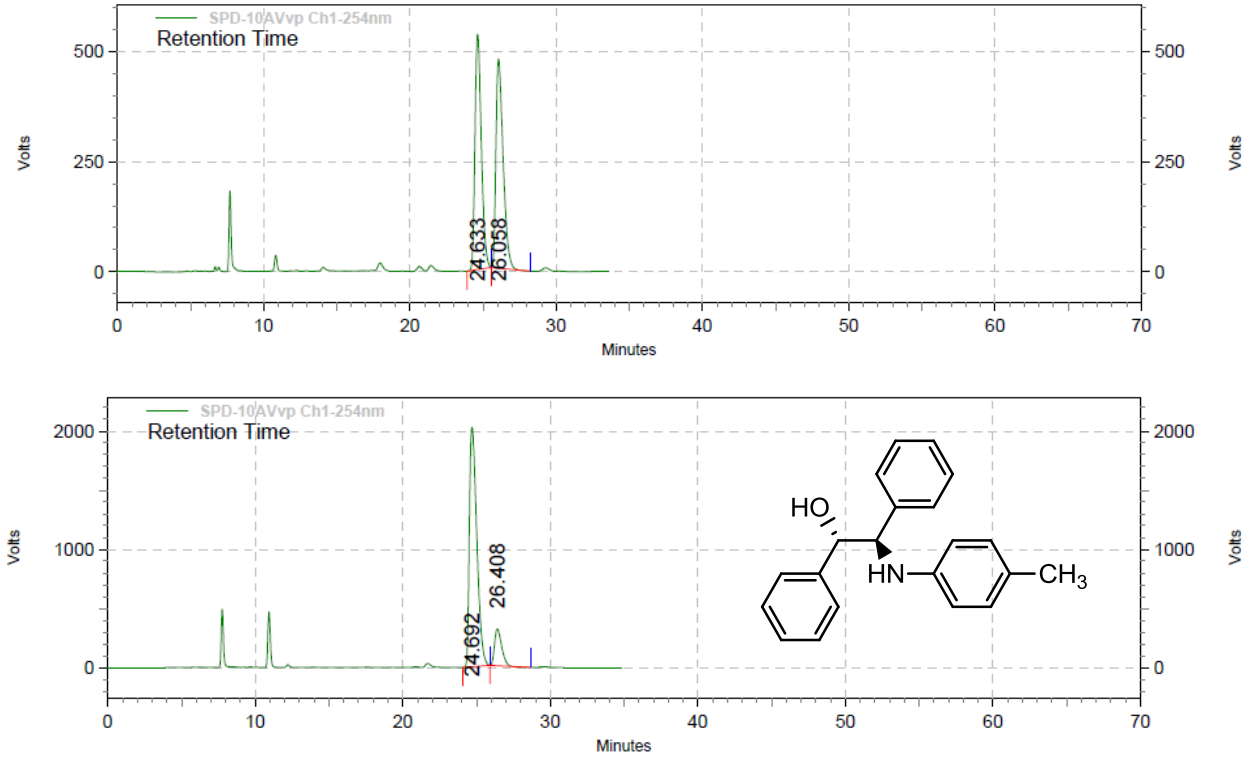


Method Name: C:\EZStart\Projects\Default\Methods\1-mt-17,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-17,IB,1ml,5%IPA,254nm-1



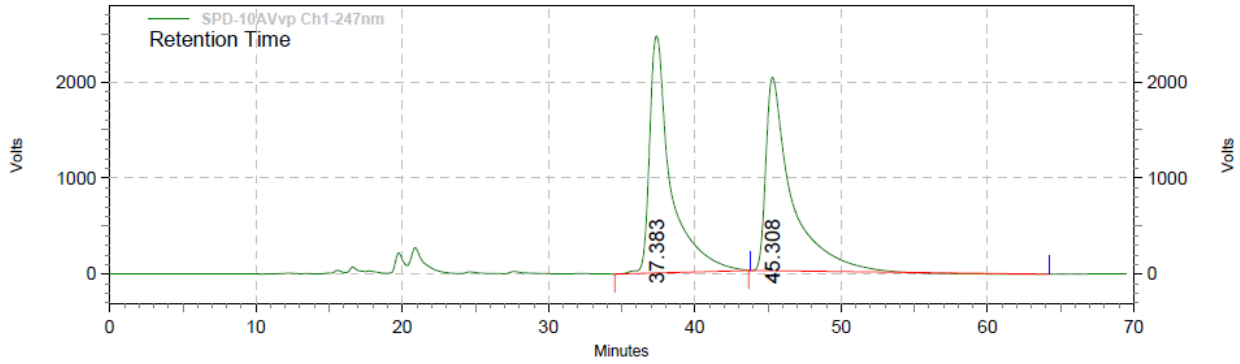
Retention Time	Area	Area %	Height	Height %
24.817	2023375	7.37	61898	8.16
29.383	25422566	92.63	696407	91.84

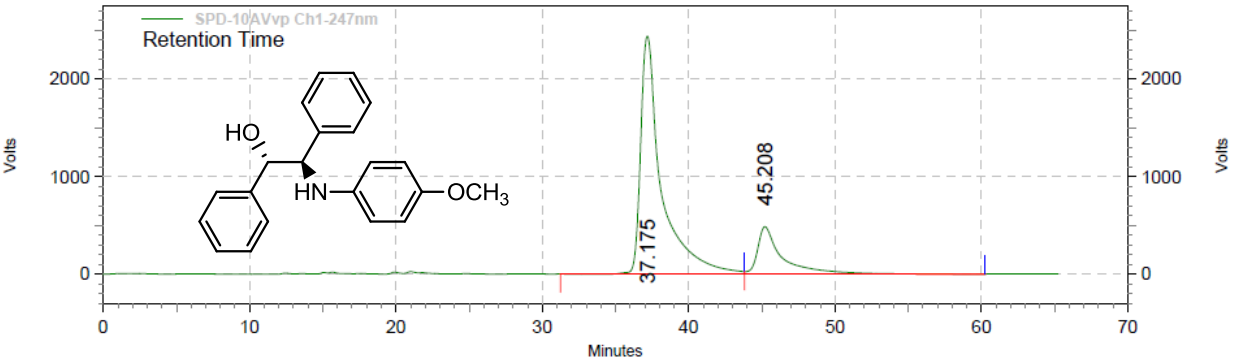
Method Name: C:\EZStart\Projects\Default\Methods\1-mt-22,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-22,IB,1ml,5%IPA,254nm



Retention Time	Area	Area %	Height	Height %
24.692	71062196	87.42	2023909	86.69
26.408	10229023	12.58	310782	13.31

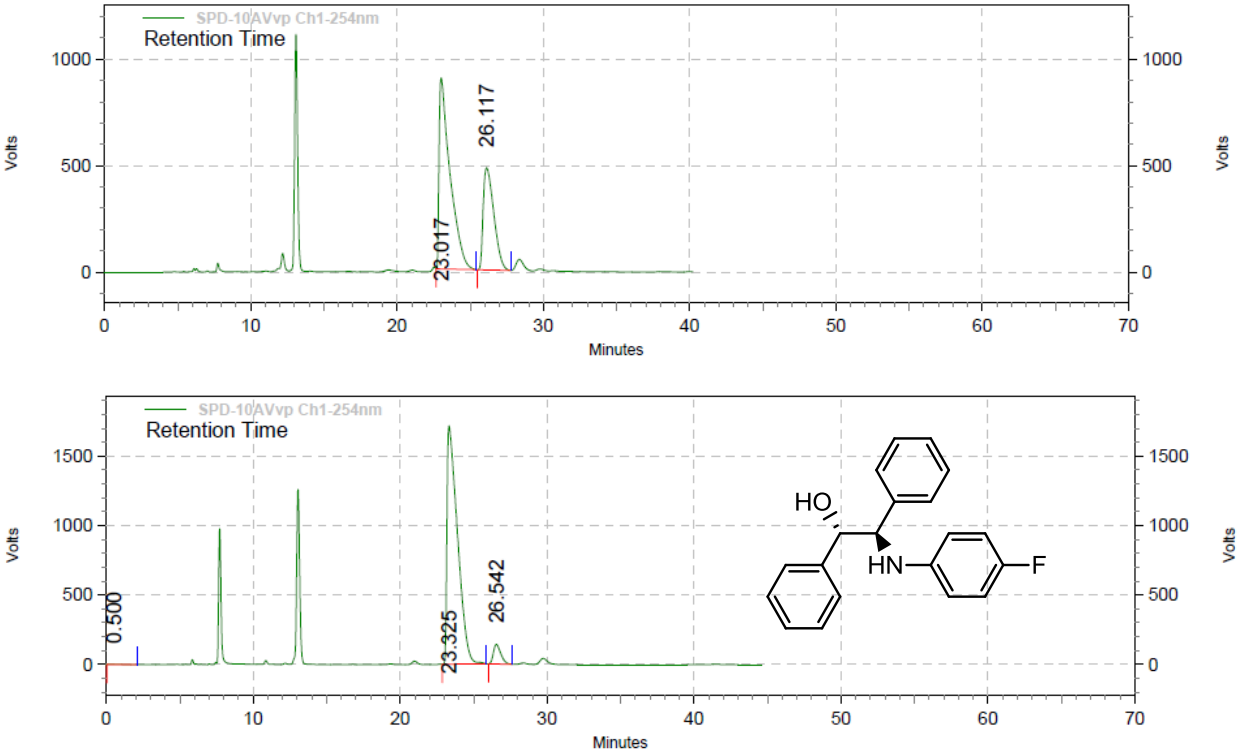
Method Name: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-19,racemic,1ml,5%IPA,247nm.met





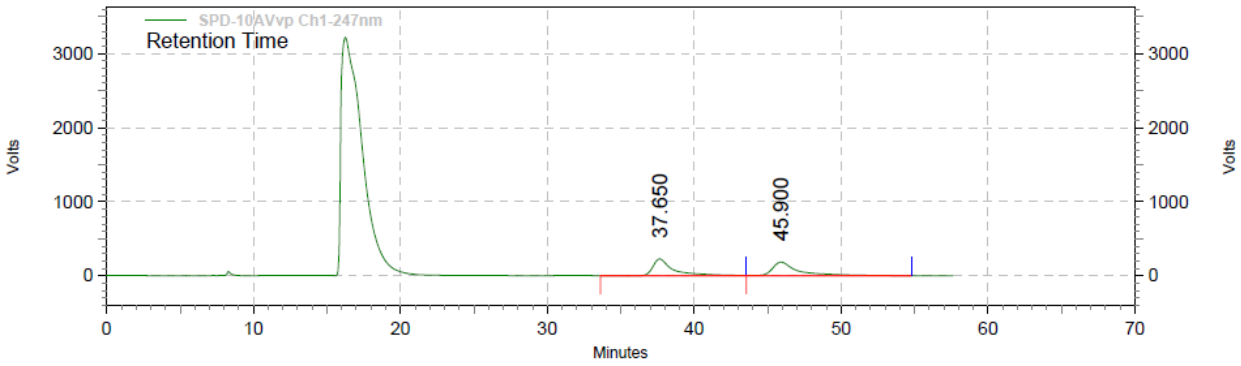
Retention Time	Area	Area %	Height	Height %
37.175	240265769	80.89	2437578	83.40
45.208	56746737	19.11	485274	16.60

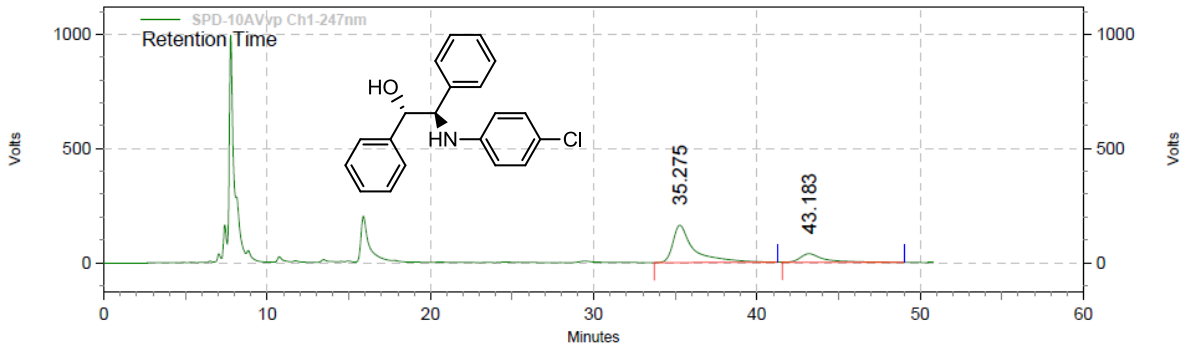
Method Name: C:\EZStart\Projects\Default\Methods\1-mt-21,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-21,IB,1ml,5%IPA,254nm



Retention Time	Area	Area %	Height	Height %
0.500	55640	0.06	981	0.05
23.325	85657368	94.45	1715248	92.36
26.542	4981399	5.49	140971	7.59

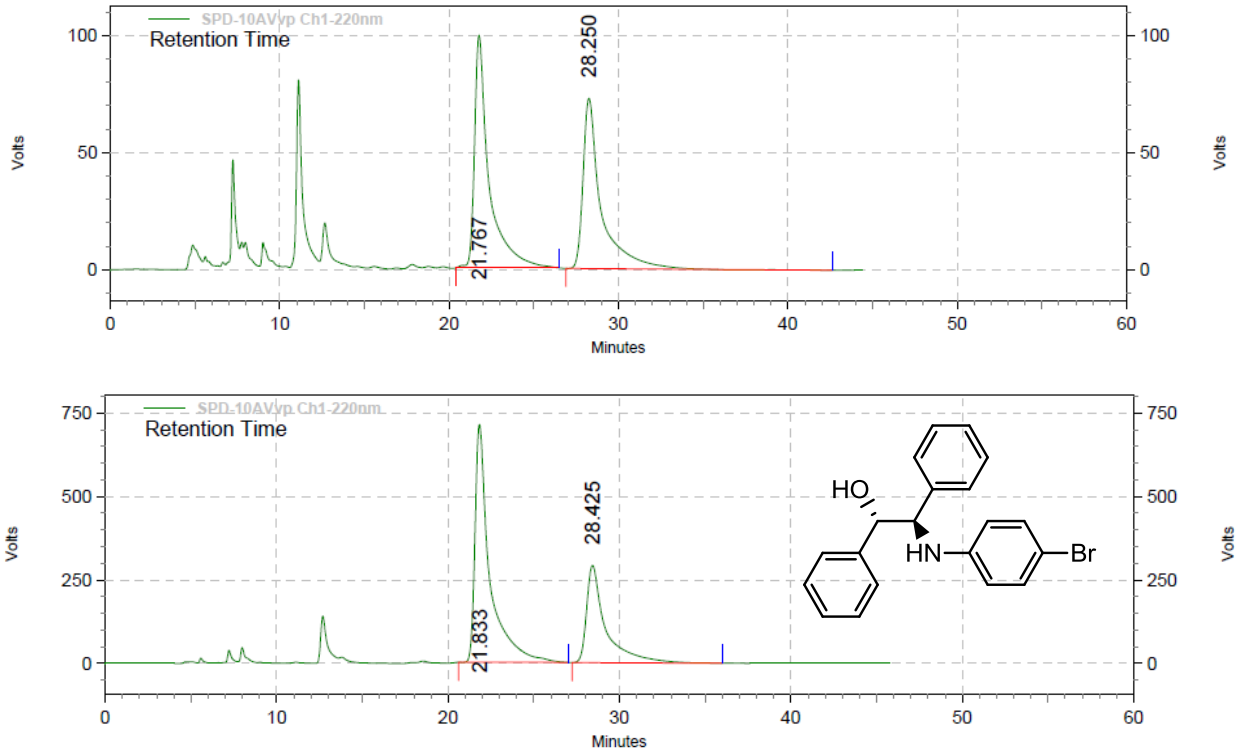
Method Name: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-20,racemic,1ml,5%IPA,247nm.met





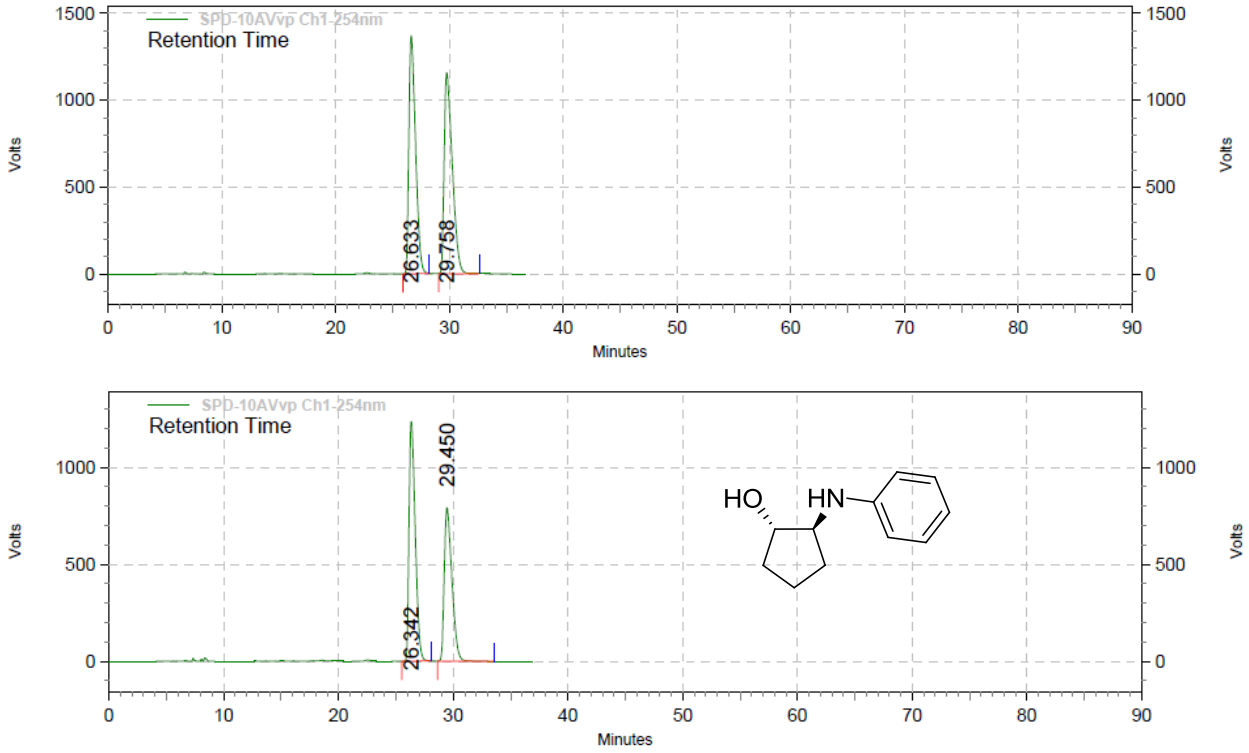
Retention Time	Area	Area %	Height	Height %
35.275	14548898	79.11	163209	81.39
43.183	3841991	20.89	37323	18.61

Method Name: C:\EZStart\Projects\Default\Methods\1-mt-18,AD-H,1ml,10%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-18,AD-H,1ml,10%IPA,254nm-1



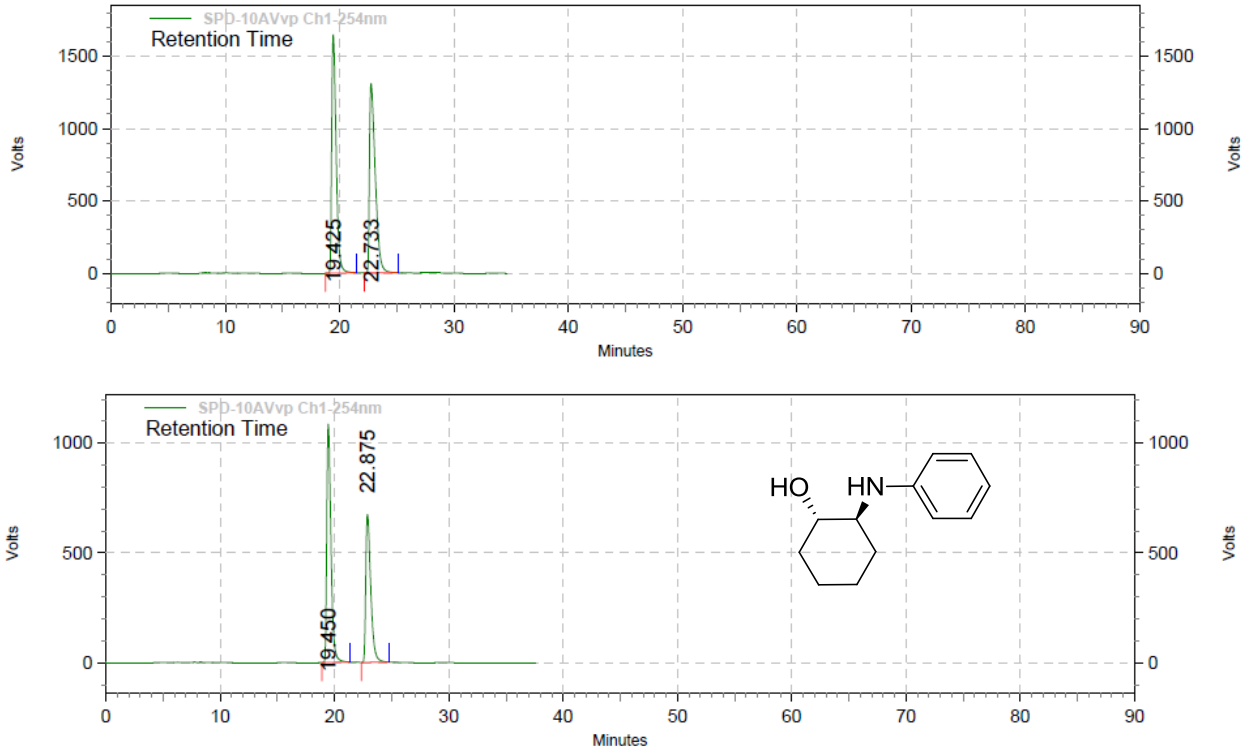
Retention Time	Area	Area %	Height	Height %
21.833	42580921	65.47	711590	70.97
28.425	22455922	34.53	291098	29.03

Method Name: C:\EZStart\Projects\Default\Methods\1-mt-150,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-150,IB,1ml,5%IPA,254nm



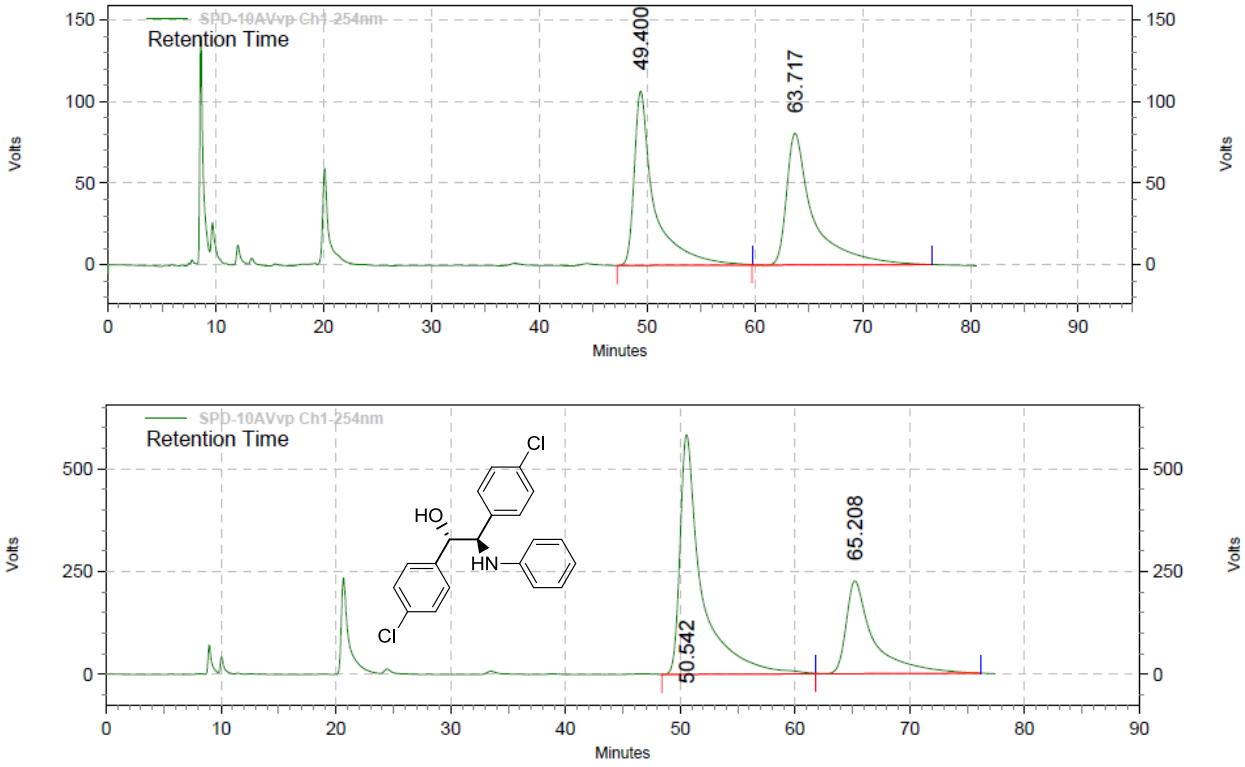
Retention Time	Area	Area %	Height	Height %
26.342	46597517	55.98	1234472	60.98
29.450	36649496	44.02	789888	39.02

Method Name: C:\EZStart\Projects\Default\Methods\1-mt-151,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\1-mt-151,IB,1ml,5%IPA,254nm

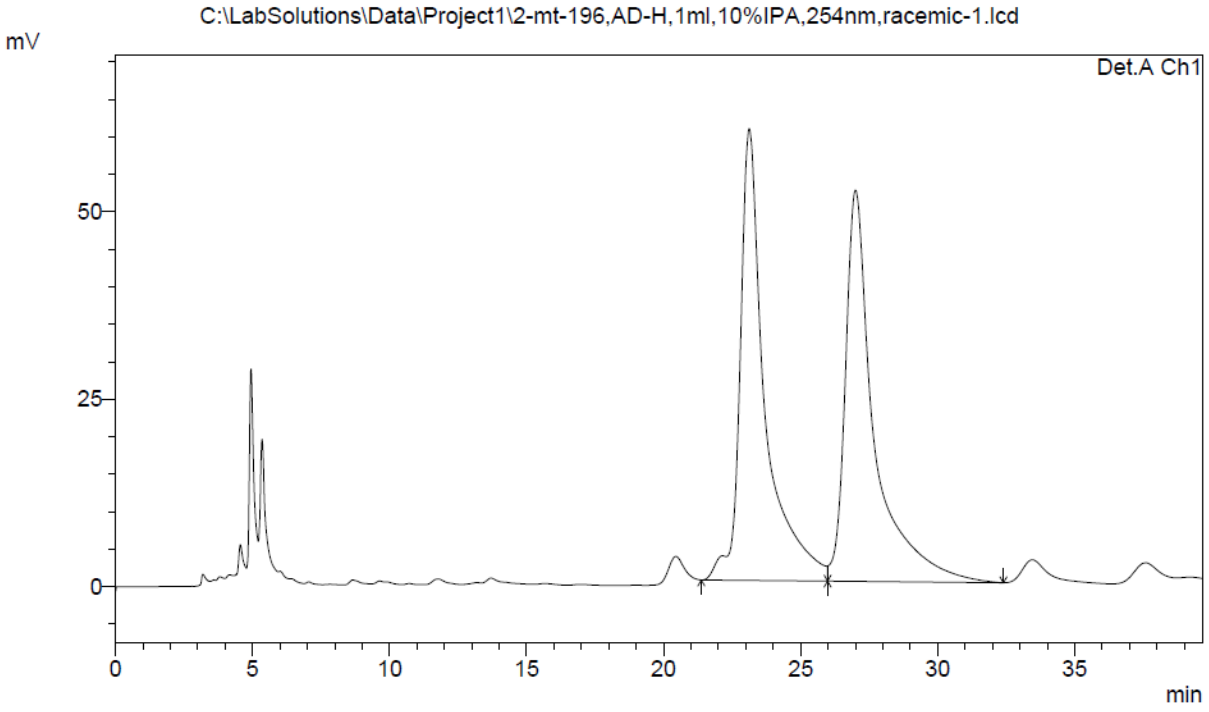


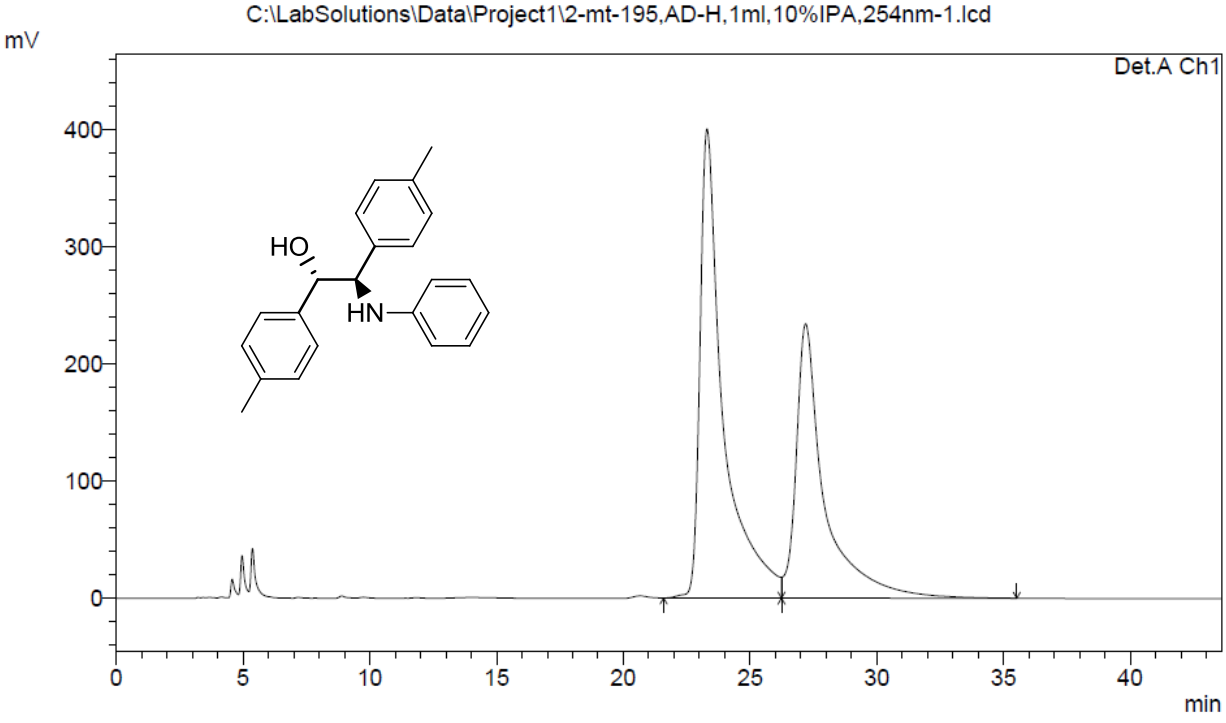
Retention Time	Area	Area %	Height	Height %
19.450	27678150	57.60	1086769	61.73
22.875	20376044	42.40	673656	38.27

Method Name: C:\EZStart\Projects\Default\Methods\2-mt-189,IB,1ml,5%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\2-mt-189,IB,1ml,5%IPA,254nm



Retention Time	Area	Area %	Height	Height %
50.542	76689940	67.13	583233	72.09
65.208	37555833	32.87	225758	27.91

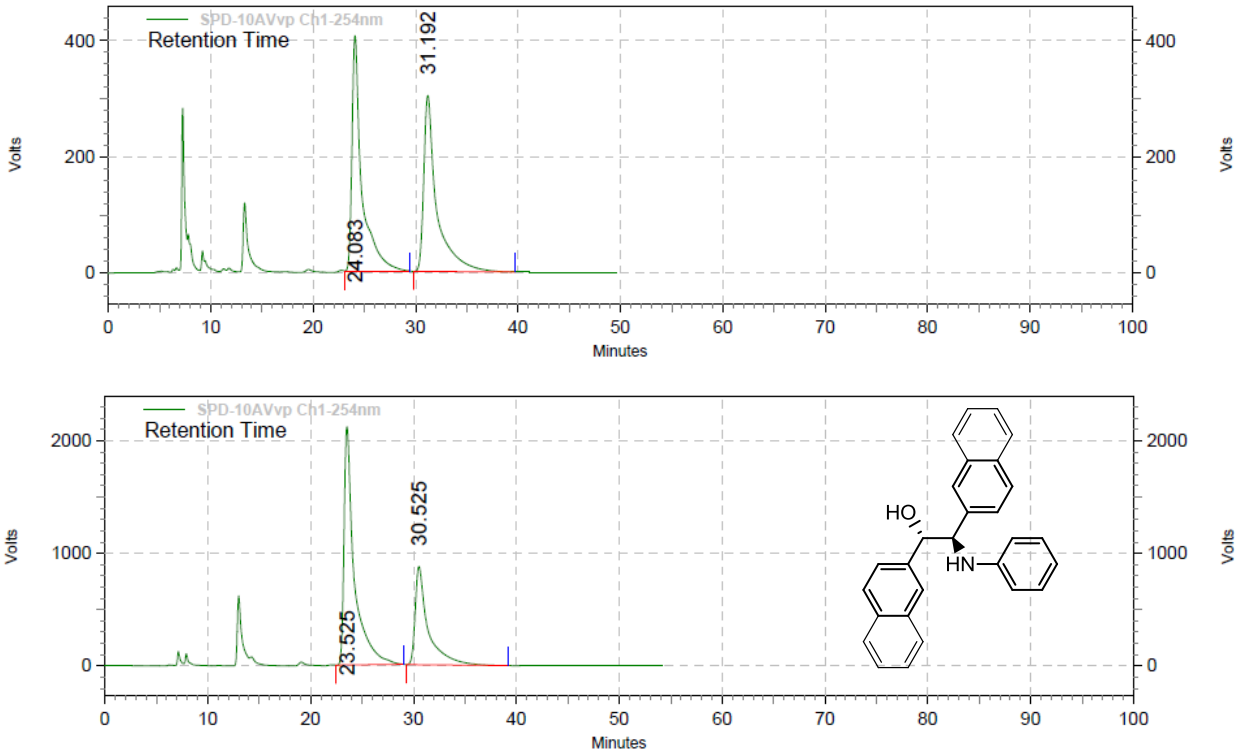




Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.301	25461974	400441	58.473	63.100
2	27.190	18082853	234167	41.527	36.900

Method Name: C:\EZStart\Projects\Default\Methods\2-mt-193,AD-H,1ml,10%IPA,254nm.met
Data: C:\Documents and Settings\Administrator\Desktop\murali\2-mt-193,AD-H,1ml,10%IPA,254nm,racemic



Retention Time	Area	Area %	Height	Height %
23.525	147144569	65.95	2116099	70.81
30.525	75972361	34.05	872152	29.19