Supporting Information

Computationally Aided Absolute Stereochemical Determination of Enantio-enriched Amines

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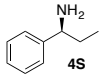
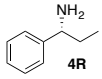
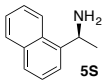
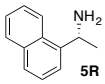
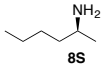
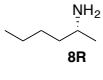
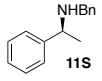
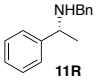
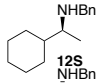
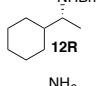
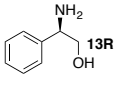
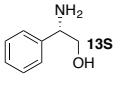
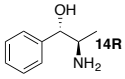
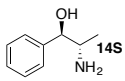
I. Materials and General Instrumentations

Spectra grade solvents used for Circular Dichroism measurements were purchased from Sigma Aldrich. Column chromatography was performed using SiliCycle silica gel (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian 500 MHz instrument and are reported in parts per million (ppm) relative to the solvent resonances (δ), with coupling constants (J) in Hertz (Hz). CD spectra were recorded on a JASCO J-810 spectropolarimeter, equipped with a temperature controller (Neslab 111) and are reported as λ [nm] ($\Delta\varepsilon_{max}$ [mol^{-1} cm^{-1}]). All chiral primary amines were purchased from commercial sources and were used without further purification. HRMS analysis was performed on a Q-TOF Ultima system using electrospray ionization in positive mode. HPLC analysis was performed on DAICEL CHIRALCEL® OD-H column.

II. ECCD Data for BDN-derivatized Enantiomeric Pairs of Chiral Amines.

Table S1. ECCD data for enantiomeric pairs

Entry	Chiral amine	Predicted ECCD (*P*:*M*)	λ (nm), Δε	A
1	 **3S**	Pos (80.9/19.1)	228 (+356) 215 (-176)	+532
2	 **3R**	Neg (17.2/82.8)	228 (-345) 215 (+173)	-518
3	 **4S**	Pos (70.3/29.7)	227 (+393) 216 (-182)	+575
4	 **4R**	Neg (17.4/82.6)	227 (-403) 216 (+190)	-593
5	 **5S**	Pos (65.7/34.3)	228 (+305) 217 (-139)	+444
6	 **5R**	Neg (19.3/80.7)	228 (-342) 217 (+153)	-495
7	 **7S**	Neg (37.2/62.8)	227 (-56) 217 (+30)	-86
8	 **7R**	Pos (55.1/44.9)	227 (+61) 217 (-31)	+92
9	 **8S**	Neg (42.0/58.0)	227 (-79) 216 (+38)	-117
10	 **8R**	Pos (61.8/38.2)	227 (+77) 216 (-39)	+116
11	 **11S**	Pos (95.8/4.2)	228 (+162) 216 (-78)	+240
12	 **11R**	Neg (13.0/87.0)	228 (-156) 216 (+75)	-231
13	 **12S**	Neg (42.3/57.6)	228 (-79) 217 (+70)	-149
14	 **12R**	Pos (77.4/22.6)	227 (+80) 217 (-71)	+151
15	 **13R**	Pos (83.6/16.4)	227 (+264) 215 (-133)	+397
16	 **13S**	Neg (19.1/80.9)	227 (-288) 215 (+147)	-435
17	 **14R**	Neg (12.2/87.8)	226 (-61) 215 (+27)	-88
18	 **14S**	Pos (89.7/10.3)	226 (+77) 215 (-30)	+107

III. Reaction of 1-BDN with Chiral Amines

Recrystallized 1,1'-(bromomethylene)dinaphthalene (**1-BDN**) was dissolved in anhydrous DCM to obtain a 0.01 M stock solution. (*S*)-(–)-α-Methylbenzylamine **3***S* was dissolved in anhydrous DCM to obtain 0.01 M stock solution. To the spectra grade acetonitrile (1 mL) in a CD cuvette was added 1 µL **1-BDN** solution, followed by the addition of 10 µL (*S*)-(–)-α-methylbenzylamine solution (10 equiv). The reaction rate was analyzed by CD at 2 min intervals (100 nm/min scan rate). Addition of $AgNO_3$ solution (2 equiv) in acetonitrile (0.01 M, 2 µL) to a duplicate reaction mixture prepared as described above was used for comparison.

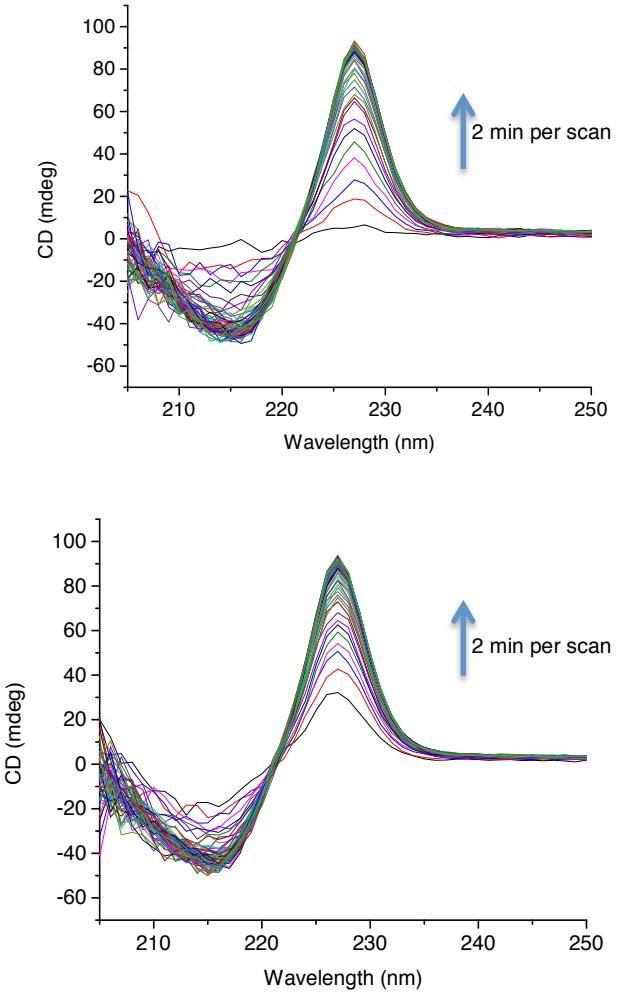


Figure S1. Interval scans study of *S*-α-methyl benzyl amine and **1-BDN**. Top: without additive, Bottom: in presence of 2 equiv of $AgNO_3$.

Comparison of rates was performed by plotting the CD signal (mdeg) at 227 nm for each interval scan as a function of time (min). As shown in Figure S2, $AgNO_3$ accelerated the initial reaction rate, but the overall time to completion remained the same (around 1 h). The reaction was complete in 1 h (10^{-5} M) with no need for additives.

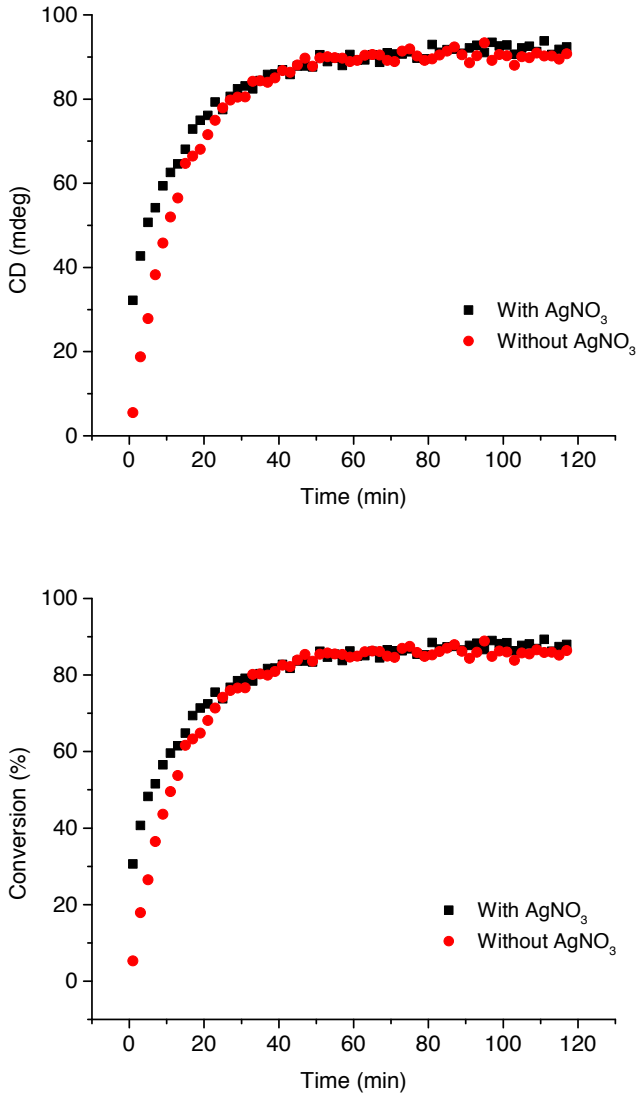


Figure S2. Rate study of the reaction of **3***S* and **1-BDN** at 10 μM. Top: rate profile based on CD read out, Bottom: comparison based on conversion.

IV. Analysis of Enantiomeric Excess

Two enantiomers of α-ethylbenzylamine were purchased from Alfa Aesar. Stock solutions of various *ee*s (-100, -80, -60, -40, -20, 0, +20, +40, +60, +80, +100% *ee* for *R* enantiomer) were prepared (0.01 M solution in DCM). Actual *ee* value for each standard was measured by HPLC analysis of carbamate derivatized analog for each prepared sample. To acetonitrile (1 mL) was added **1-BDN** (1 µL, 0.01 M stock solution), followed by 10 µL of each standard amine stock solution (0.01 M). After incubating for 1.5 h at room temperature, the mixture was directly analyzed by CD (Figure 3S).

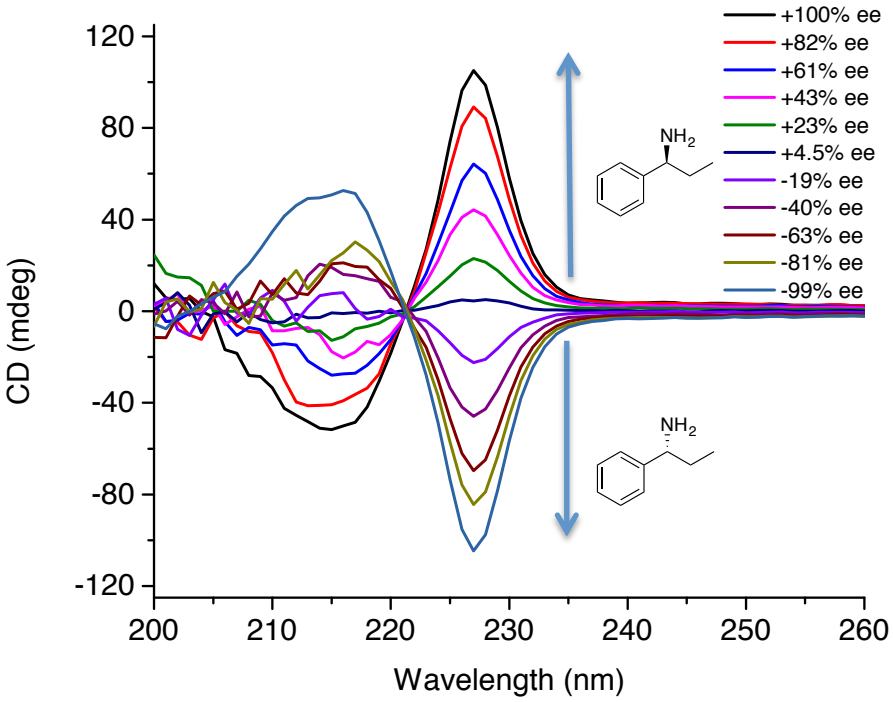
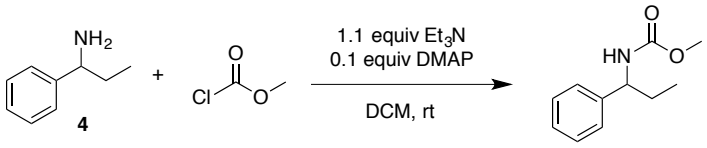


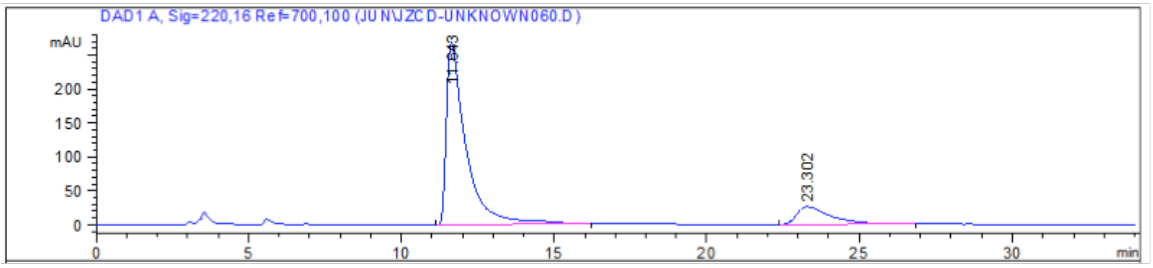
Figure S3. CD spectra of chiral amines at various *ee*s of α-ethylbenzylamine.

HPLC Data:

All chiral amines were derivatized as their corresponding methyl carbamate for HPLC analysis as shown below for ethyl benzyl amine **4**. HPLC analysis was performed with an analytical DAICEL CHIRALCEL® OD-H column, operating with a flow rate of 0.7 mL/min, with 99:1 hexane: isopropyl alcohol as eluent. The **4***S*-enantiomer elutes at 11 min, while the **4***R*-enantiomer appears at 23 min.



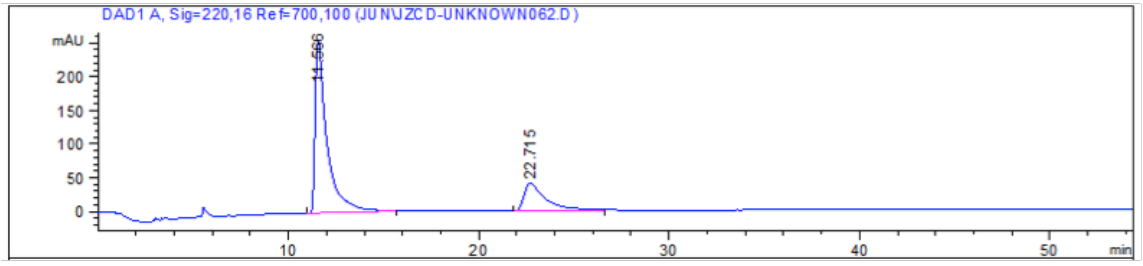
Unknown sample 1



Signal 1: DAD1 A, Sig=220,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.643	BB	0.6261	1.18589e4	268.07932	85.5590
2	23.302	BB	1.0944	2001.59460	25.99415	14.4410
Totals :				1.38605e4	294.07346	

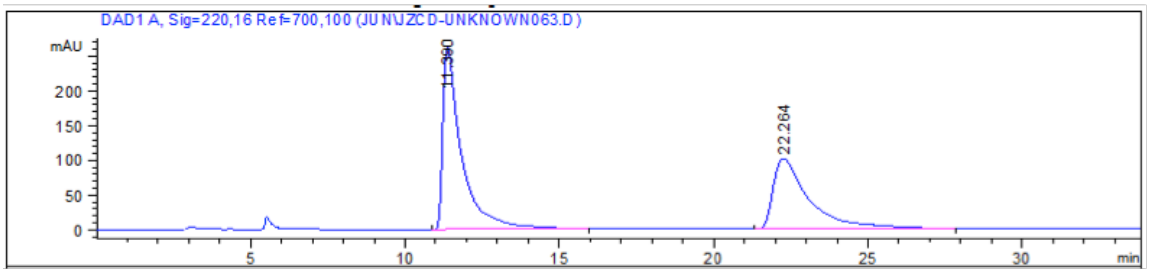
Unknown sample 2



Signal 1: DAD1 A, Sig=220,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.566	BB	0.6054	1.09350e4	254.43579	77.7263
2	22.715	BB	1.0926	3133.58008	40.77359	22.2737
Totals :				1.40685e4	295.20938	

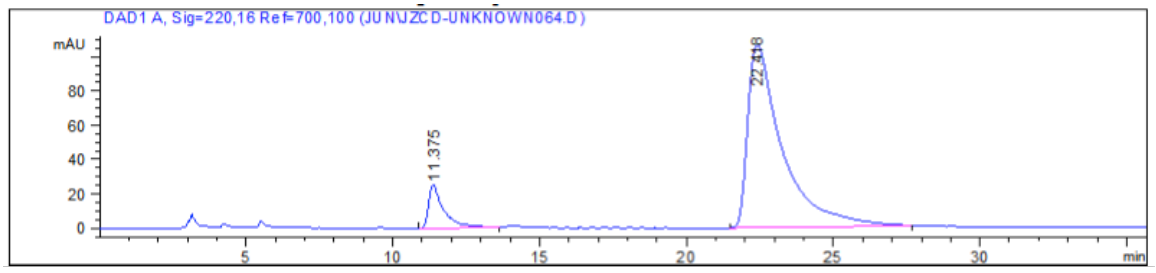
Unknown sample 3



Signal 1: DAD1 A, Sig=220,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.390	BB	0.5895	1.10237e4	262.71075	57.2081
2	22.264	BB	1.1458	8245.74707	101.71544	42.7919
Totals :				1.92694e4	364.42619	

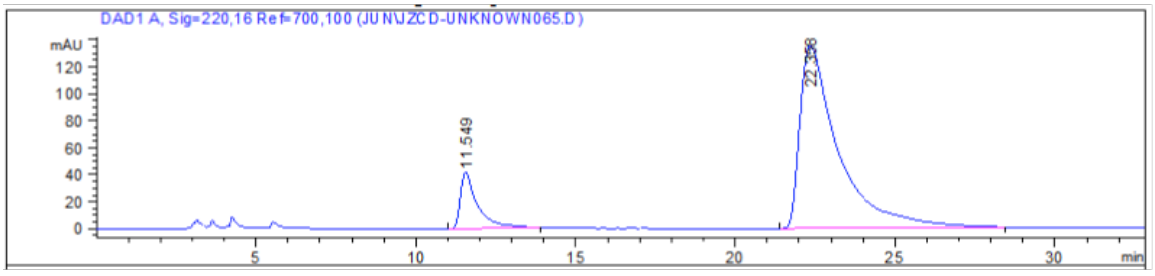
Unknown sample 4



Signal 1: DAD1 A, Sig=220,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.375	BB	0.5007	905.53143	25.35308	9.3949
2	22.418	BB	1.1742	8732.98828	106.55245	90.6051
Totals :				9638.51971	131.90554	

Unknown sample 5



Signal 1: DAD1 A, Sig=220,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.549	MM	0.6176	1560.76135	42.11751	12.1399
2	22.358	BB	1.1893	1.12956e4	135.40125	87.8601
Totals :				1.28564e4	177.51875	

A linear relationship between the CD amplitude at 227 nm and the enantiomeric excess of the analytes was obtained as shown in Figure S4 ($R^2 = 0.999$).

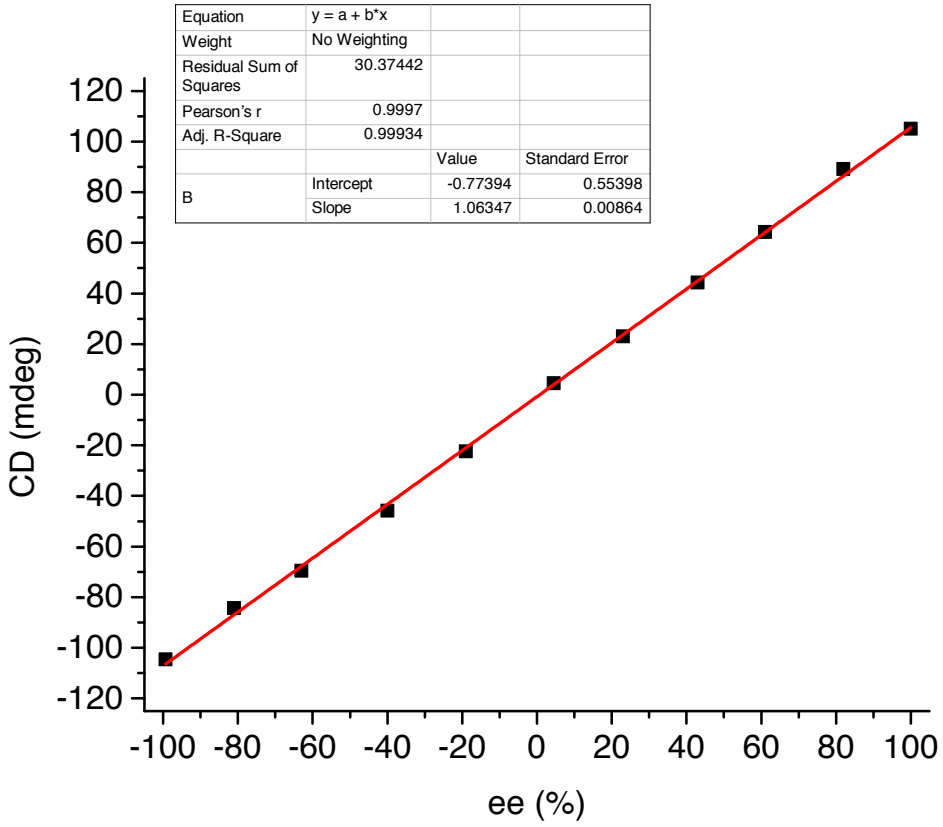


Figure S4. Linear correlation of the CD signal with *ee* values of chiral amines.

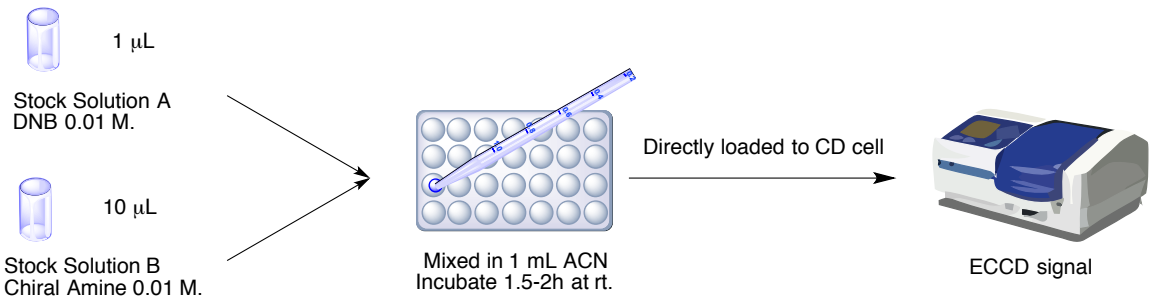
Five unknown samples were prepared by a third party (double blind study) and were subject to the general procedure as described above. The CD amplitude at 227 nm was used to estimate the ee of the unknown solution based on the standard curve shown in Figure S4. Actual *ee*s for each unknown sample were determined through derivatization to their corresponding carbamates and HPLC analysis, as described above for the standard samples. The data for 1 scan measurement is provided in Table S2.

Table S2: Measured *ee*s of unknown samples.

	1 Scan (< 1 min)		
Entry	*ee* (%) known	*ee* (%) measured	Error (%)
A	+71.2	+71.5	0.3
B	+55.4	+55.7	0.3
C	+14.4	+14.9	0.5
D	-81.2	-81.2	0.0
E	-75.7	-74.4	1.3

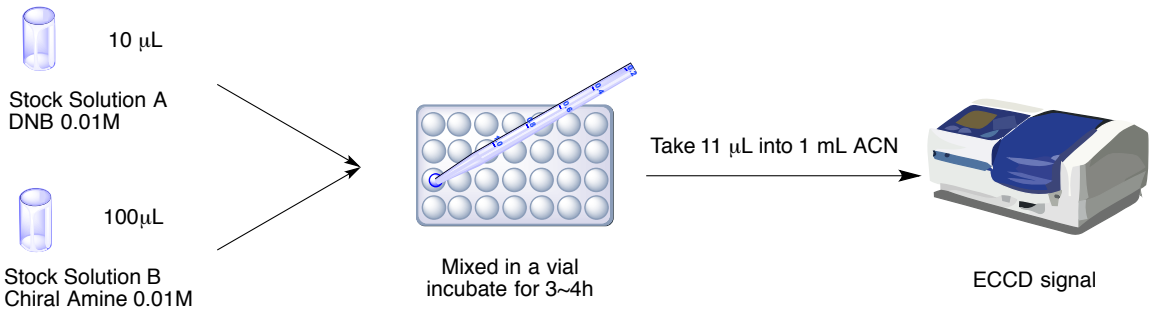
V. General Procedure for Analysis of Absolute Stereochemistry of Amines

Primary Amines: Amines were dissolved in anhydrous DCM to make obtain a 0.01 M stock solution. Similarly, a 0.01 M stock solution of 1,1'-(bromomethylene)dinaphthalene (**1-BDN**) in anhydrous DCM was prepared. To initiate the derivatization, **1-BDN** (1 μL) and 10 μL of the amine stock solution were mixed in acetonitrile (1 mL) and the mixture was incubated at room temperature for 1.5 h (Scheme S1). The solutions were then loaded directly in a CD cuvette and measurements ensued (better signal and faster reaction time can be achieved by increasing the concentration).



Scheme S1: General procedure for preparation of samples for CD analysis.

Secondary Amines: The same procedure as above was followed with the following changes; These reactions required a higher final concentration (10^{-2} M) and a longer reaction time. To initiate the reaction, **1-BDN** (10 μL) and chiral amines (100 μL), each from their respective 0.01 M stock solutions, were incubated for 4 h at room temperature. For CD analysis, 11 μL of the reaction mixture was added to acetonitrile (1 mL).



Scheme S2: General procedure to sense chiral secondary benzyl protected amines.

VI. Impurity study

To test if impure chiral amines would react with **1-BDN**, a control experiment was designed in which (S)-(–)-α-methylbenzylamine and its HCl salt were reacted with **1-BDN** (Figure S5). To acetonitrile (1 mL) was added **1-BDN** solution (1 µL, 0.005 M), followed by the addition of (S)-(–)-α-methylbenzylmine solution (10 µL, 10 equiv) and (S)-(–)-α-methylbenzylamine HCl salt solution (10 µL, 10 equiv) in two vials. After incubating for 1.5 hours at rt, the mixtures were directly analyzed by CD (100 nm/min scan rate). The pure amine yielded a strong ECCD signal, while the amine salt had no signal. This clearly suggests the need for using free base for derivatization with **1-BDN**.

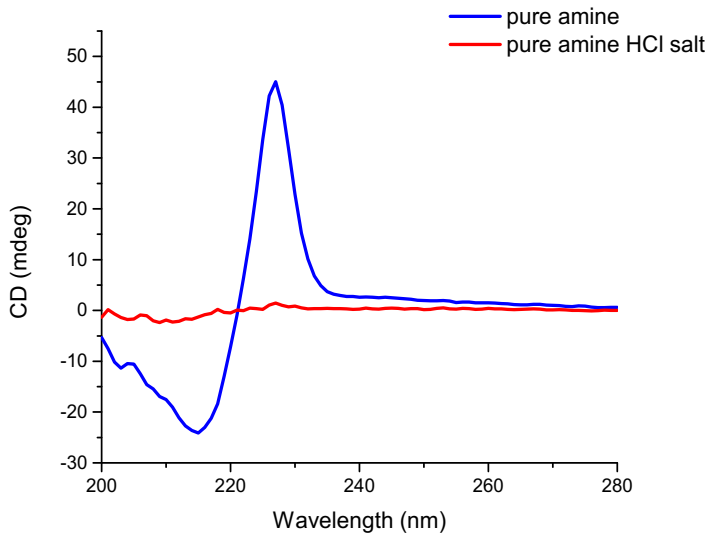
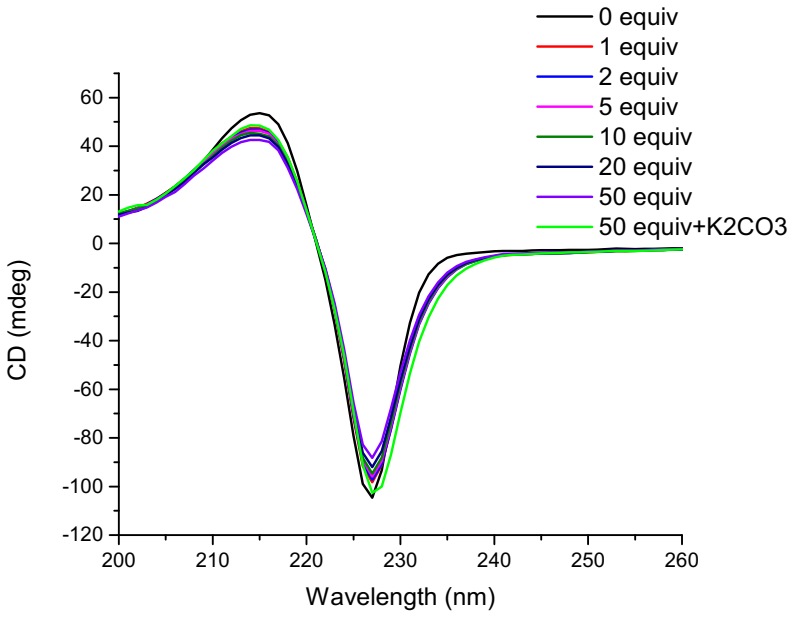


Figure S5. Impure amine study. Blue: pure amine added to **1-BDN**. Red: amine HCl salt added to **1-BDN**.

*Tolerance of the **BDN** derivatized chiral amines under acidic or oxidative conditions*: To (*R*)-*N*-(di(naphthalen-1-yl)methyl)-1-phenylethan-1-amine **(3*R*-BDN)** was added HCl acid and H_2O_2 seperately. Treating pure **3*R*-BDN** with different equivalents of HCl led to a slight decrease in ECCD (6 % loss with 1 equiv HCl and up to 15 % loss with 50 equiv HCl, Figure S6). The original ECCD signal was fully recovered after addition of solid K_2CO_3 (see table for details). For peroxide study, treating **3*R*-BDN** with up to 50 equiv of H_2O_2 stock solution resulted in no change in the signal. Alongating the exposore of **3*R*-BDN** to 50 equiv H_2O_2 for 1.5 h also did not result in deterioration of the ECCD signal (Figure S7).



HCl equivalent	CD (mdeg) at 227 nm
0	-104.57
1	-98.261
2	-97.274
5	-95.917
10	-94.689
20	-92.079
50	-88.196
Treating with K_2CO_3	-102.63

Figure S6. Treatment of **3*R*-BDN** with different equivalents of HCl. Signal decreased upon addition of HCl from 1 equivalent up to 50 equivalents, however, after addition of solid K_2CO_3, the CD signal was recovered.

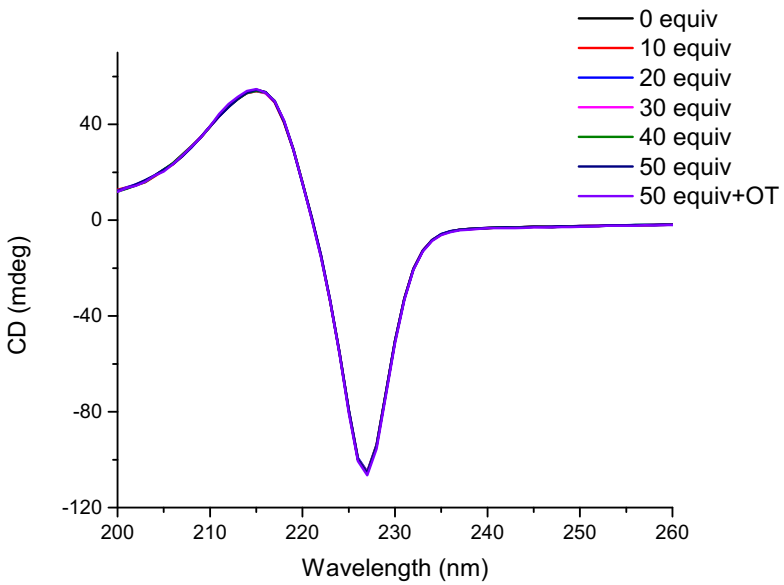
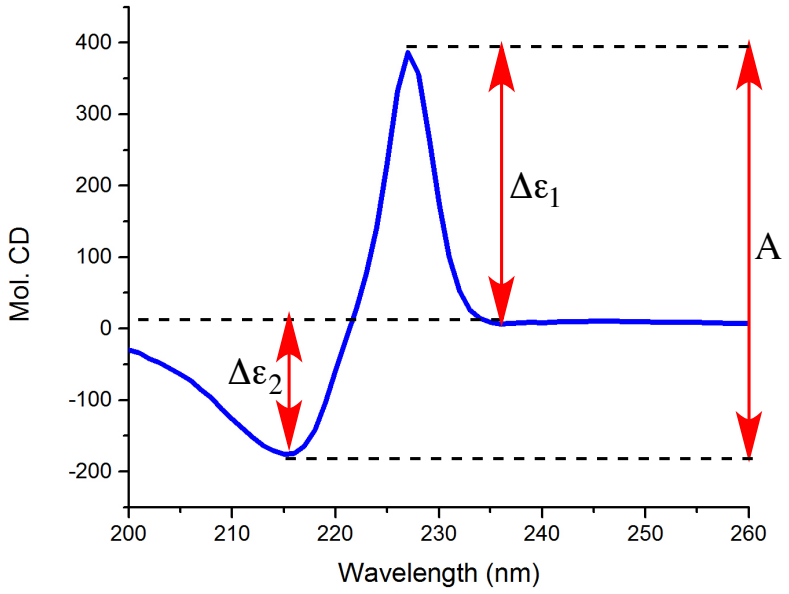


Figure S7. Treatment of **3*R*-BDN** with H_2O_2 stock solution at different equivalents. The ECCD signal remained unchanged.

VII. General Procedure for CD Measurement

Chiral amines were derivatized as their **BDN** derivatives and analyzed by CD in pure form. The ECCD spectra were recorded in millidegrees and normalized based on the concentration of the derivatized **BDN** samples to obtain the molecular CD (Mol CD).

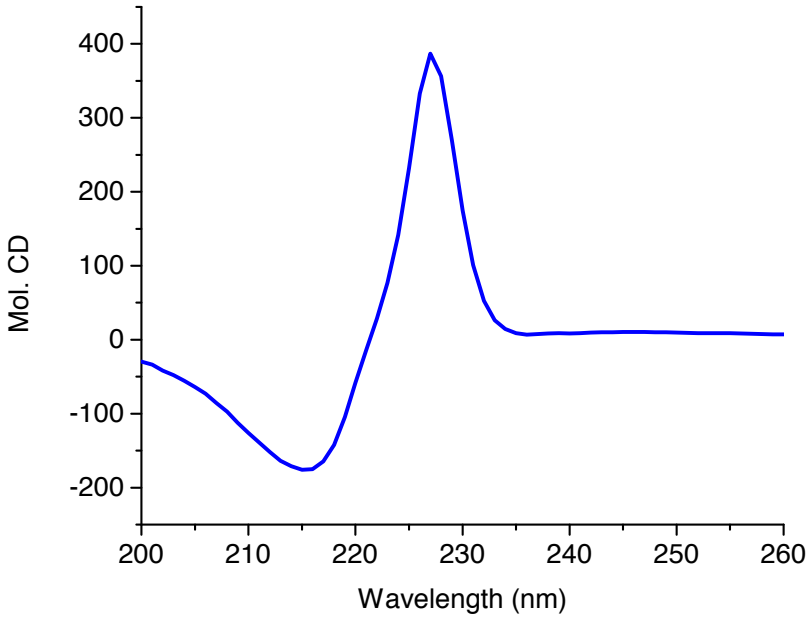


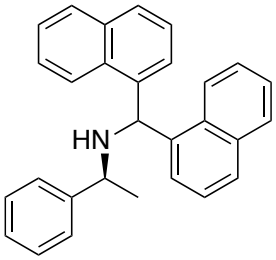
Common symbol:

Amplitude: $A = \Delta\varepsilon_1 - \Delta\varepsilon_2$

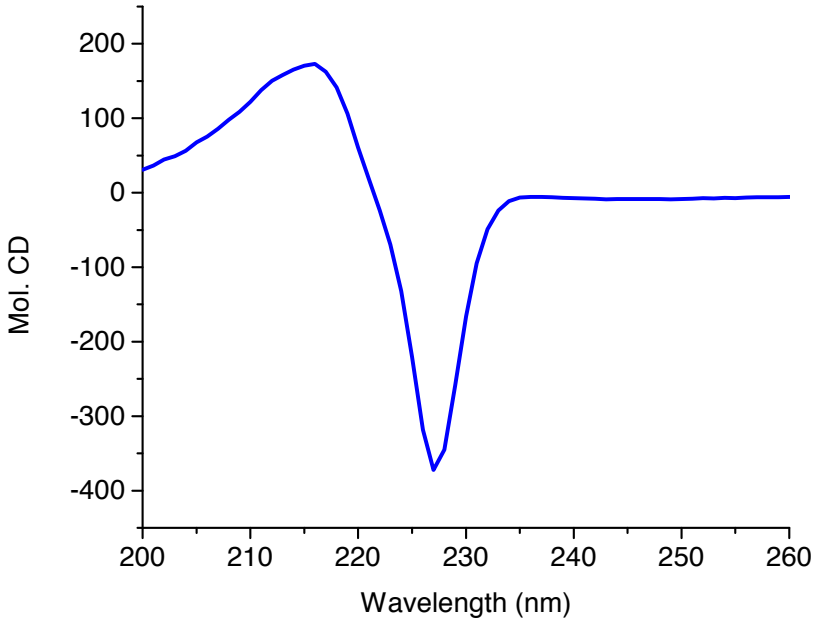
$\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the maximum intensities of the lower and higher energy bands respectively (higher and lower wavelengths accordingly).

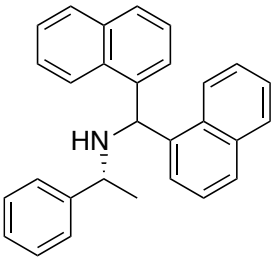
VIII. ECCD Spectra of 1-BDN Derivatized Chiral Amines





3*S*-BDN





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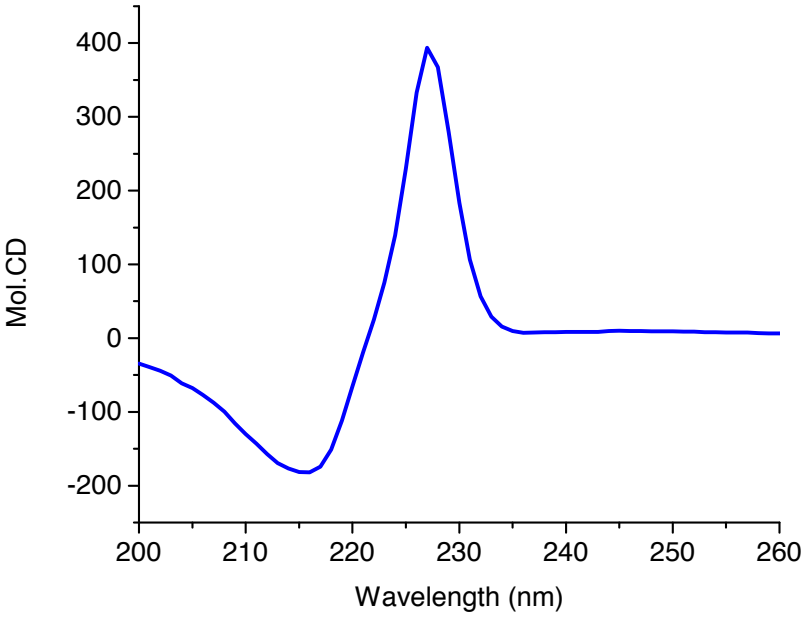
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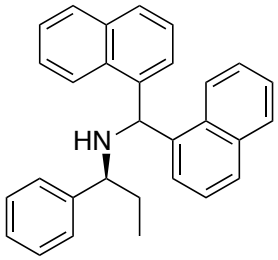
Wavelength (nm)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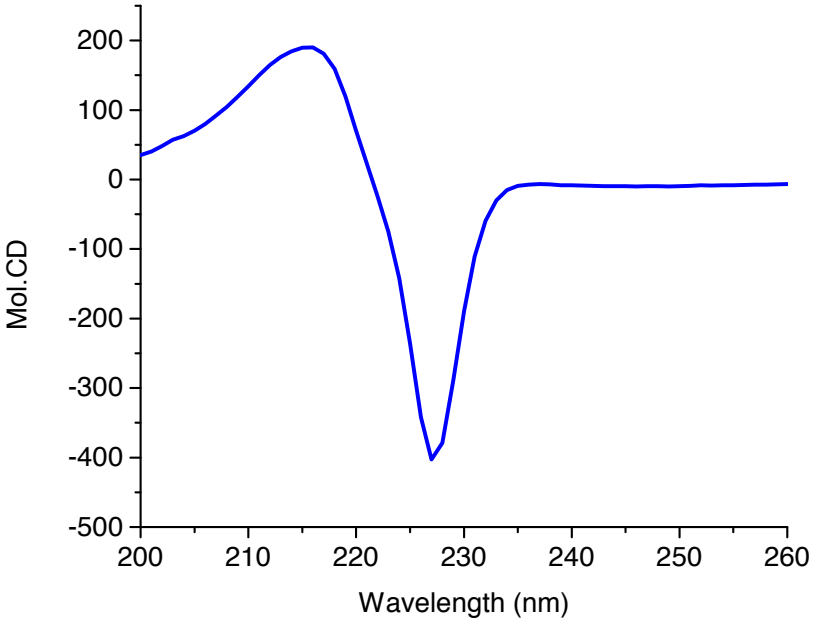
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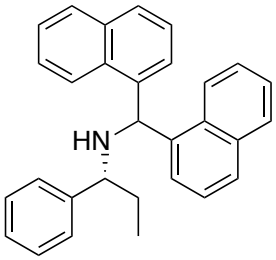
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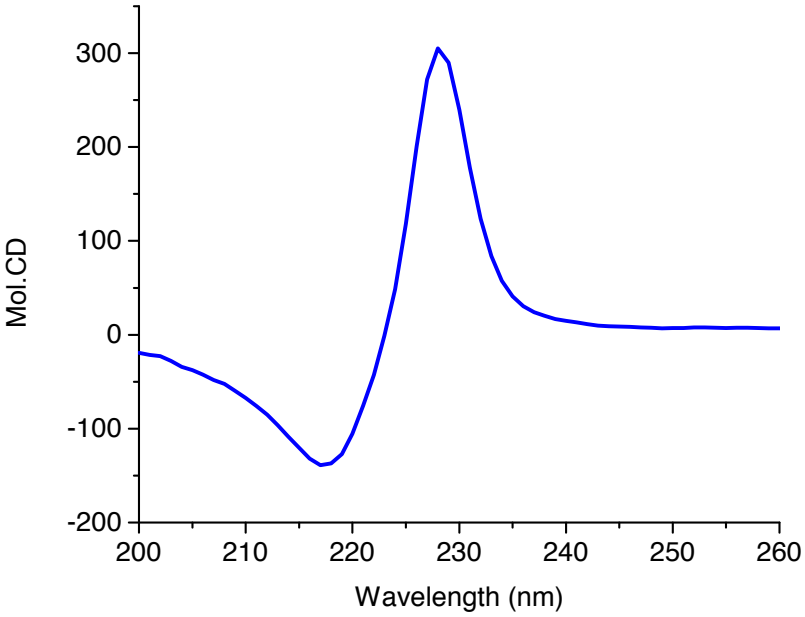
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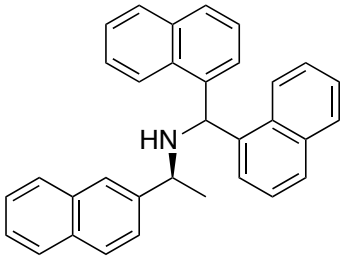
Wavelength (nm)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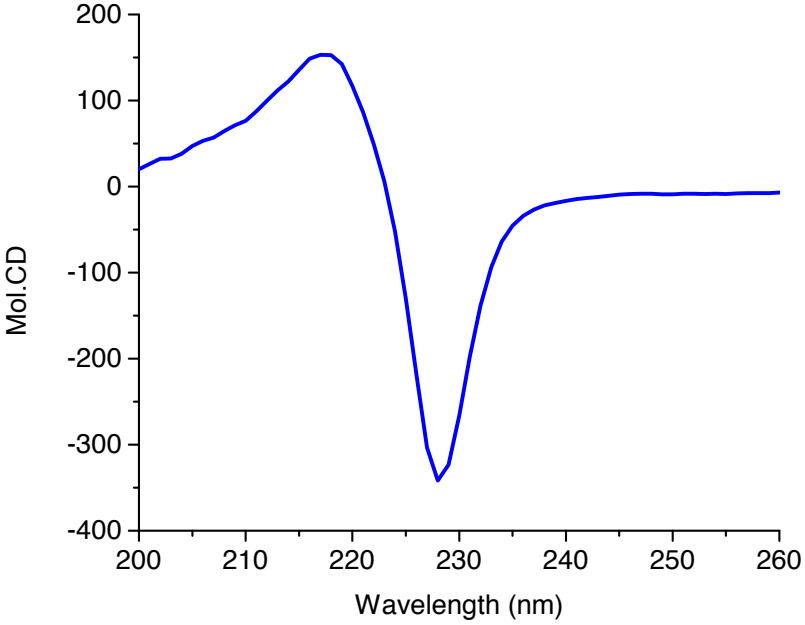
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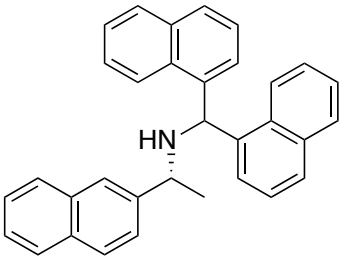
Wavelength (nm)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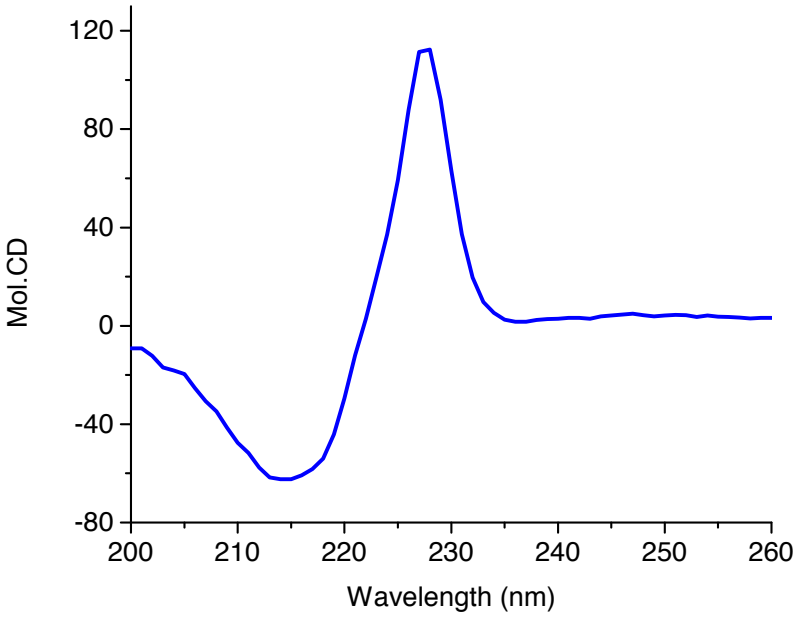
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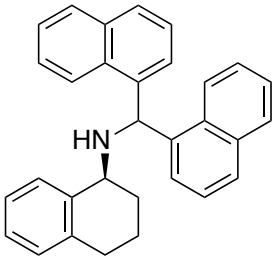
Wavelength (nm)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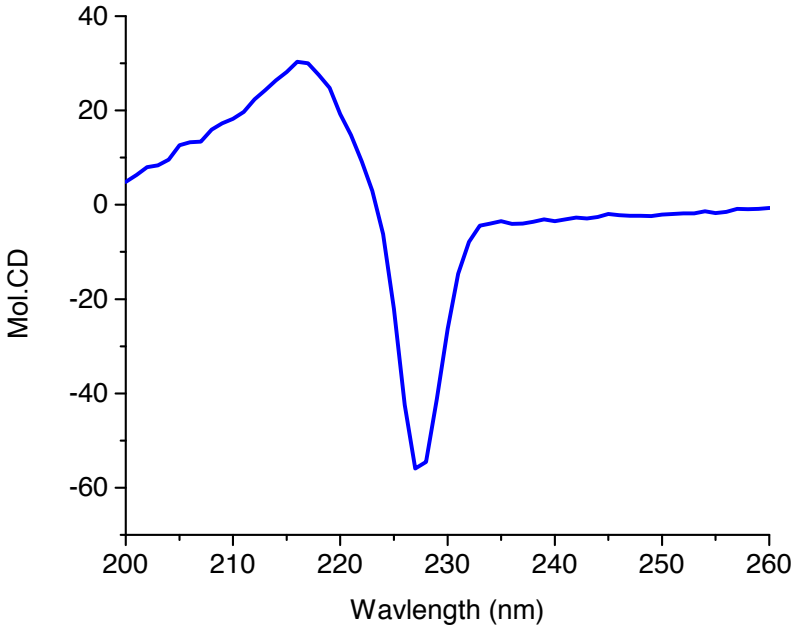
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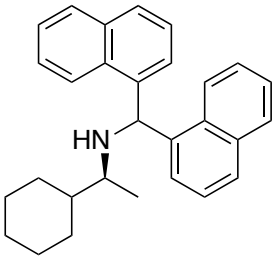
Wavlength (nm)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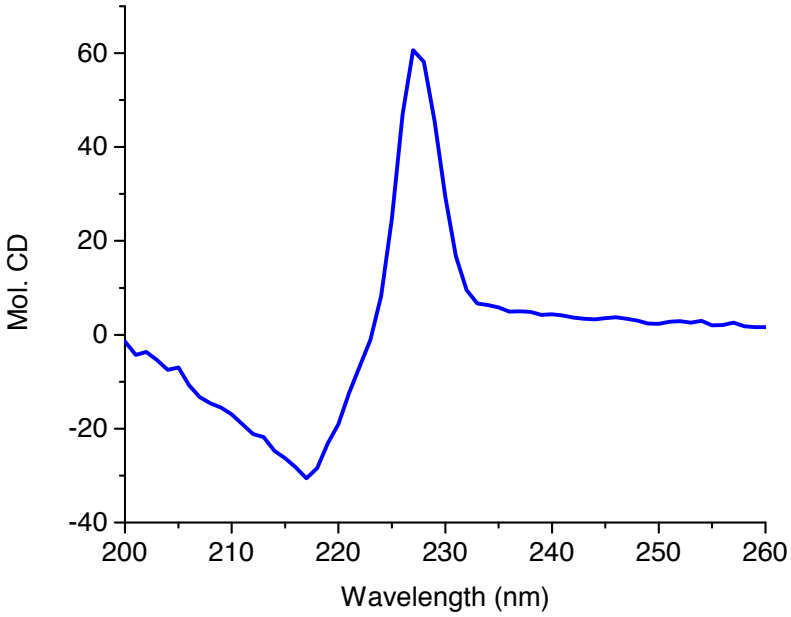
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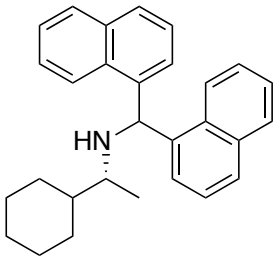
Wavelength (nm)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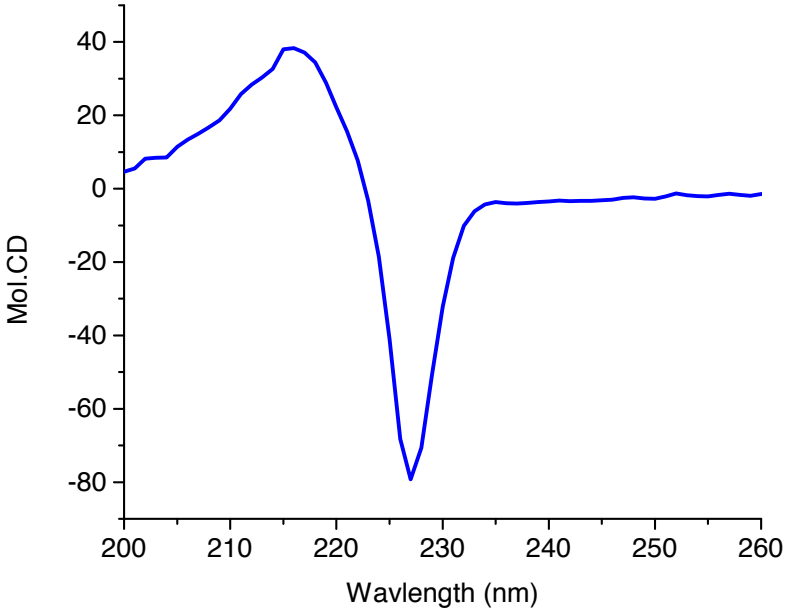
7*R*-BDN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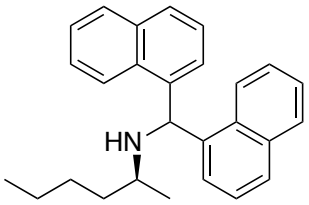
Wavlength (nm)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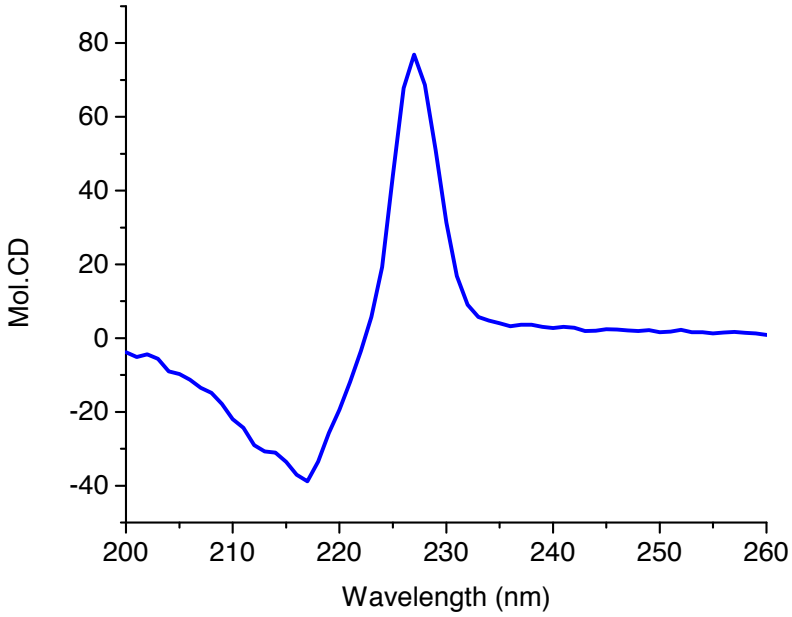
8*S*-BDN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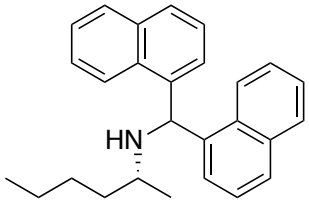
Wavelength (nm)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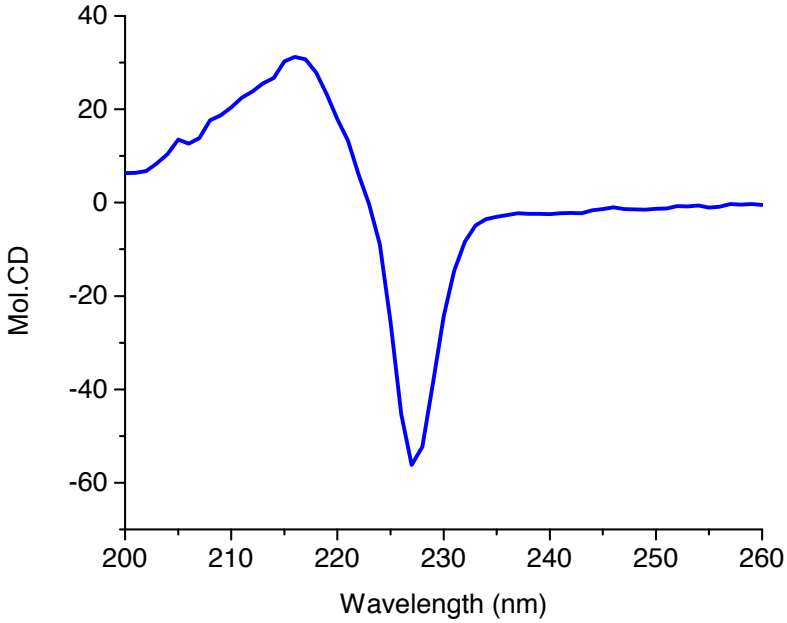
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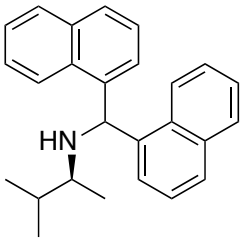
Wavelength (nm)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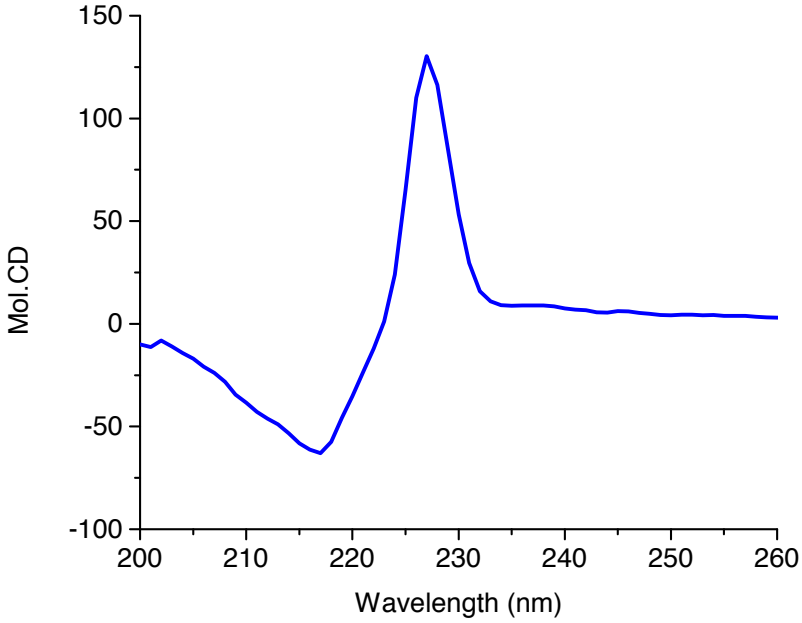
9*S*-BDN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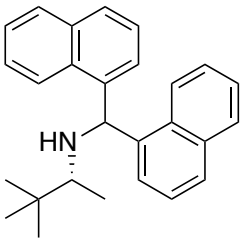
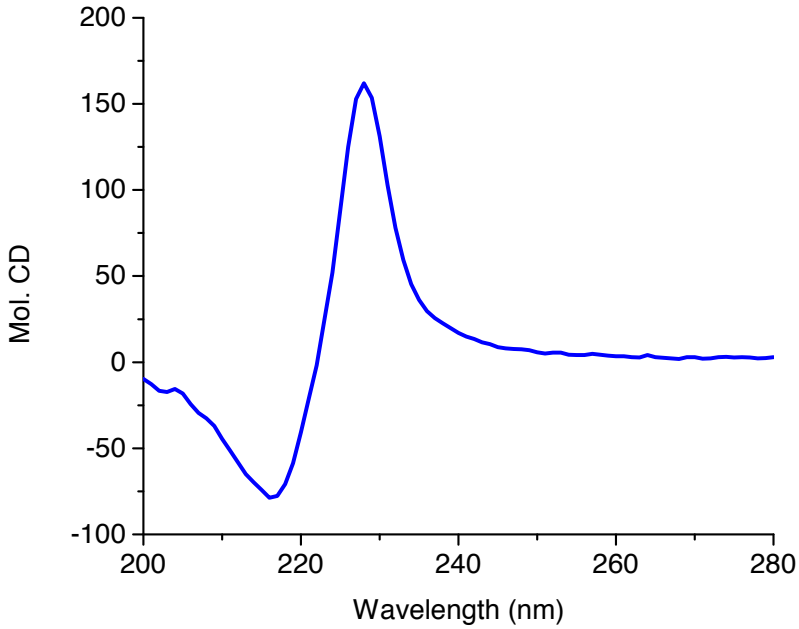
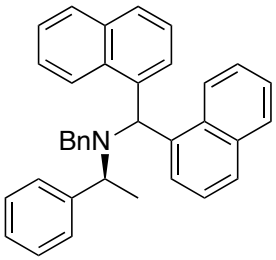
Wavelength (nm)


HN

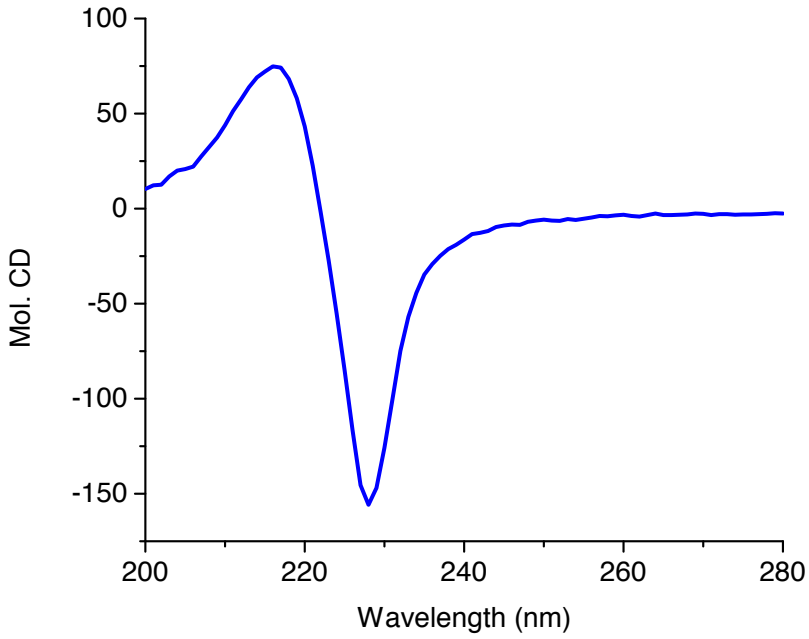
10*R*-BDN

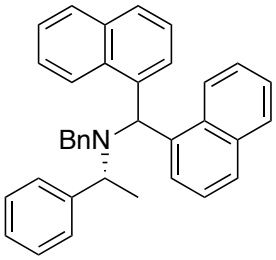
IX. ECCD Spectra of 1-BDN Derivatized Bn-protected Chiral Amines





11*S*-BDN





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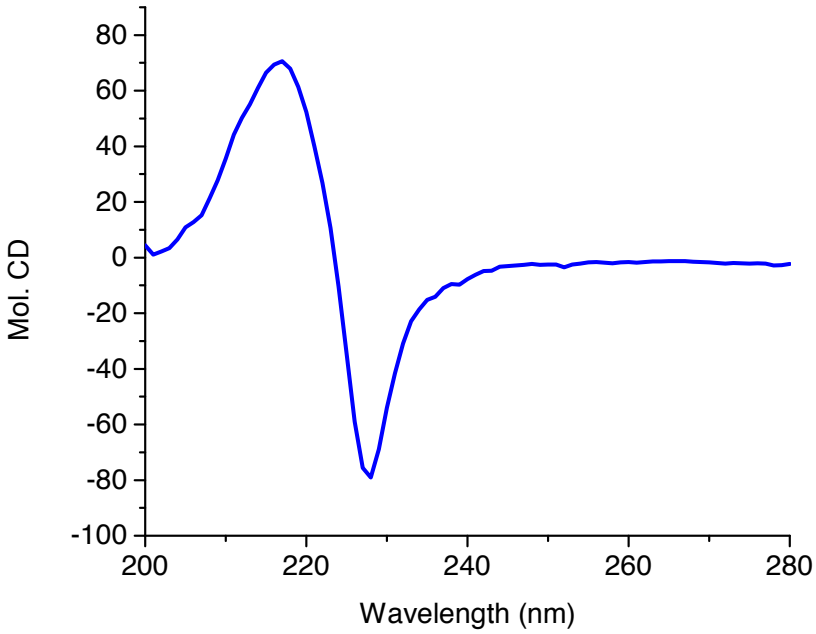
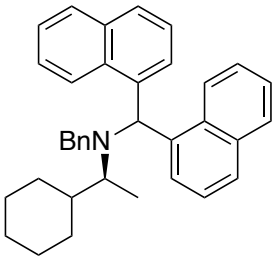
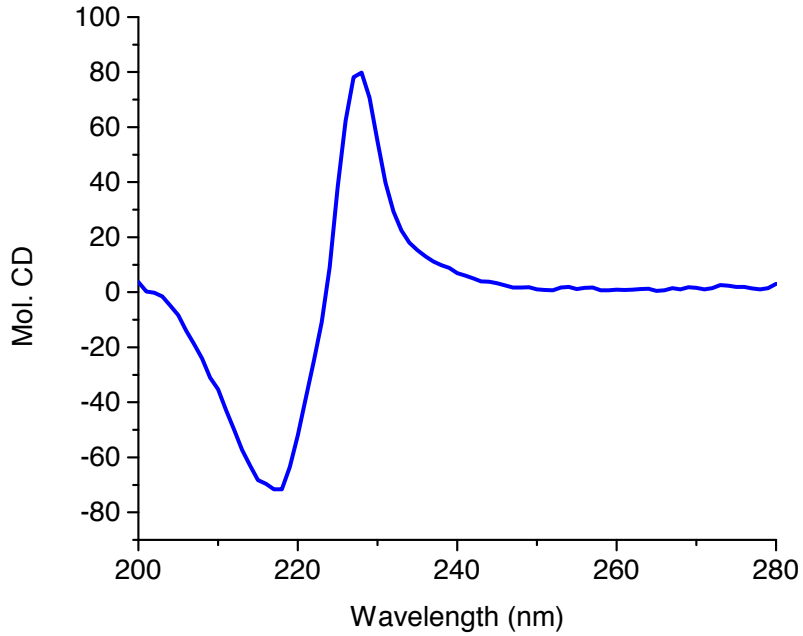
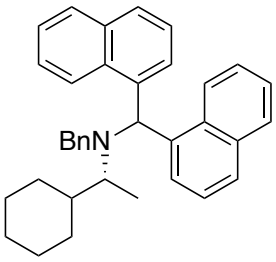




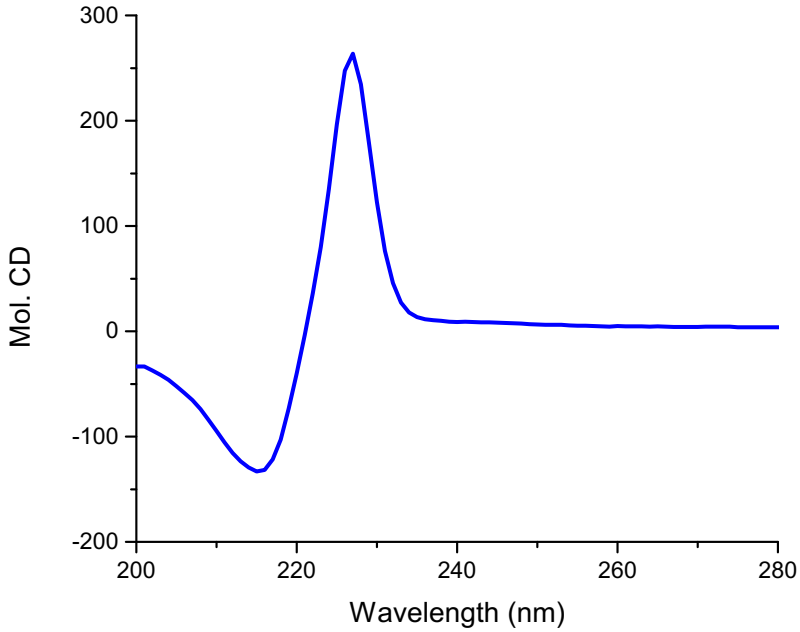
12*S*-BDN

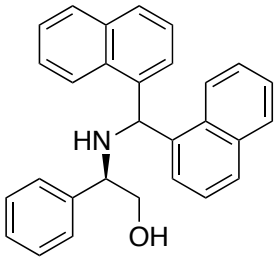




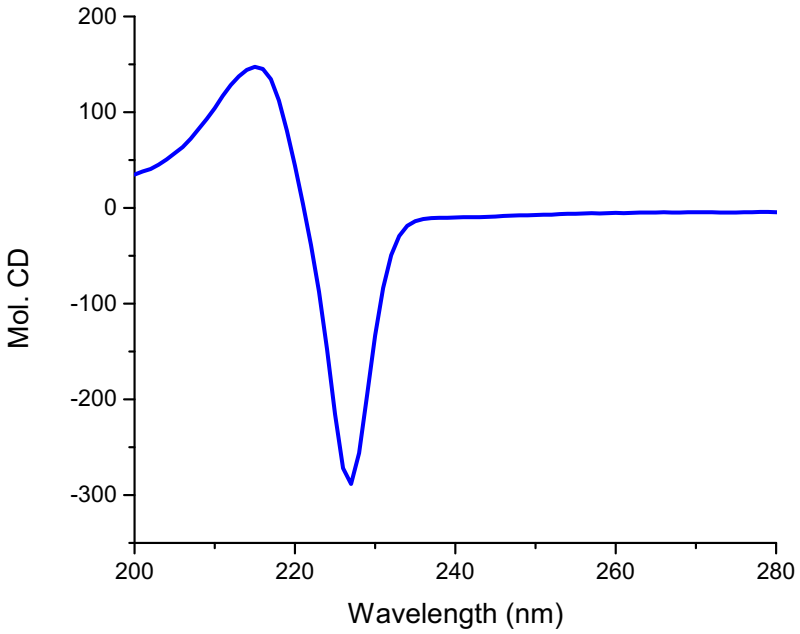
12*R*-BDN

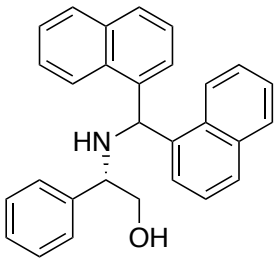
X. ECCD Spectra of 1-BDN Derivatized Chiral Amino Alcohols





13*R*-BDN





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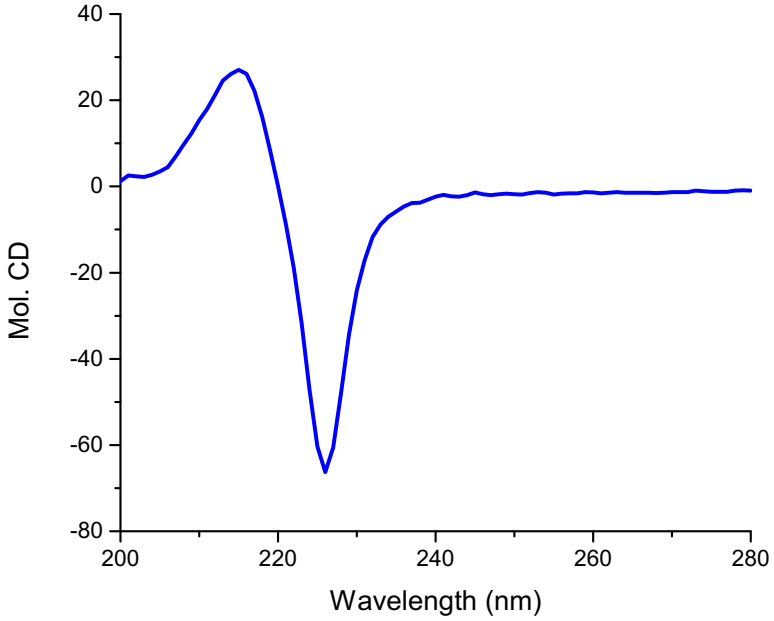

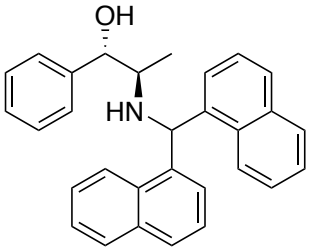

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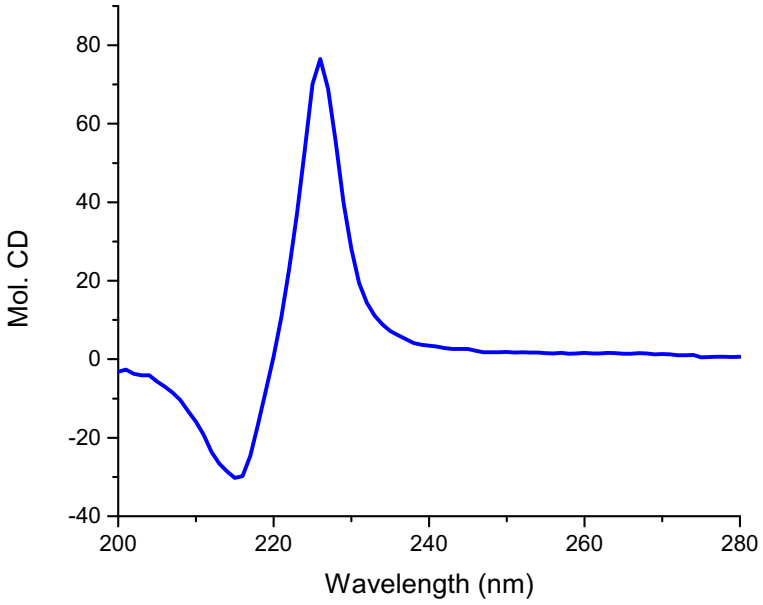
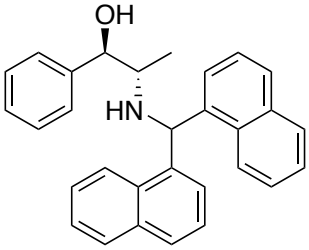
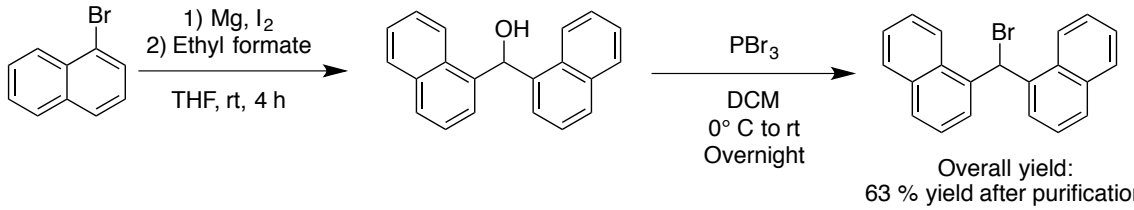




14*S*-BDN

XI. Synthesis of New Compounds



1,1'-(bromomethylene)dinaphthalene (1-BDN)[1]

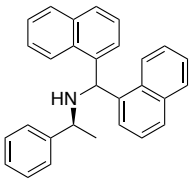
To a dried 250 mL round bottom flask was added magnesium turnings (504 mg, 21 mmol, 1.05 equiv) and Iodine (12 mg, 0.05 mmol) in dry THF (100 mL). 1-Bromonapthalene (4.14 g, 20 mmol) was dissolved in dry THF (10 mL) and was added to the mixture slowly over 15 min. After stirring for 2 h at room temperature, ethyl formate (740 mg, 10 mmol) in dry THF (10 mL) was added to the mixture and stirred for 2 h. The reaction was quenched by addition of cold 1N HCl solution (10 mL) and extracted with ethyl acetate (200 mL), washed with brine, dried over sodium sulfate and concentrated in vacuo to afford the crude product. The product was purified by recrystallization from ethyl acetate and hexane to afford an off white solid product [di(naphthalen-1-yl)methanol] (2.57 g, 90%). ^{1}HNMR ($CDCl_3$, 500 MHz): 8.06 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.50–7.38 (m, 9H), 7.33 (d, J = 4.5 Hz, 1H), 2.40 (d, J = 4.5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 138.3, 133.9, 131.0, 128.8, 128.6, 126.5, 125.7, 125.4, 125.0, 123.6, 69.7.

To a dried 200 mL round bottom flask was added di(naphthalen-1-yl)methanol (2.57 g, 9.05 mmol) in DCM (70 mL), cooled to 0 ºC, and PBr_3 (6 mL, 6 mmol) was added. The reaction was slowly warm up to room temperature and was stirred overnight. The reaction was quenched with the addition of water (40 mL), extracted by DCM (2 x 100 mL), and the combined organics were washed with brine, dried over sodium sulfate and concentrated on vacuo. The product was purified by recrystallized from DCM to afford an off white solid (2.2 g, 71%). It should be noted that in our hands, exposure to silica gel leads to decomposition.

^{1}HNMR ($CDCl_3$, 500 MHz): 8.06–8.04 (m, 2H), 7.90–7.88 (m, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.79 (s, 1H), 7.72-7.70 (d, J = 7.5 Hz, 2H), 7.51-7.48 (m, 4H), 7.42 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): 135.9, 133.8, 130.14, 129.2, 129.0, 128.2, 126.8, 126.0, 125.0, 123.2, 50.0; HRMS (ESI^+) for $C_{21}H_{15}$ $[M - Br]^+$ calculated: 267.1174 found: 267.1177.

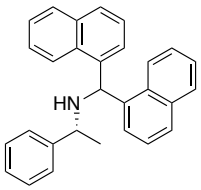
General Procedures for the Synthesis of 1-BDN Amine Derivatives

General Procedure A: To a 5 mL round bottom flask was added chiral amine (0.15 mmol, 1.5 equiv) and 1,1'-(bromomethylene)dinaphthalene (0.1 mmol, 35 mg) in a 1:1 mixture of acetonitrile and DCM (2 mL overall). K_2CO_3 (0.2 mmol, 2 equiv, 28 mg) was added to the flask and the mixture was stirred under N_2 for 1.5 h. The reaction mixture was concentrated under vacuo and the mixture was directly loaded onto silica gel for purification.



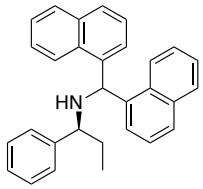
(*S*)-*N*-(di(naphthalen-1-yl)methyl)-1-phenylethan-1-amine (3*S*-BDN)

Following the general procedure A, a white solid product was obtained (18.1 mg, 46.8%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.03 (d, J = 6.5 Hz, 1H), 7.87-7.81 (m, 3H), 7.67-7.60 (m, 3H), 7.45-7.42 (m, 2H), 7.39-7.36 (m, 4H), 7.30-7.25 (m, 3H), 7.21-7.18 (m, 2H), 7.10 (d, J = 5 Hz, 1 H), 6.21 (s, 1H), 3.92 (q, J = 6.5 Hz, 1H), 1.50 (d, J = 6.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 144.9, 139.3, 137.9, 134.1, 133.9, 131.8, 130.9, 128.8, 128.7, 128.4, 127.8, 127.6, 127.4, 127.3, 126.2, 126.0, 125.9, 125.5, 125.4, 125.3, 124.9, 123.4, 122.9, 56.0, 55.0, 23.2. **HRMS** (ESI^+) for $C_{29}H_{26}N$ $[M + H]^+$ calculated: 388.2065 found: 388.2064.



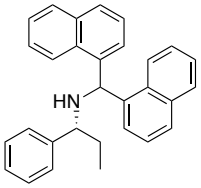
(*R*)-*N*-(di(naphthalen-1-yl)methyl)-1-phenylethan-1-amine (3*R*-BDN)

Following the general procedure A, a white solid product was obtained (12 mg, 31%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.02 (d, J = 7.0 Hz, 1H), 7.86-7.80 (m, 3H), 7.66-7.59 (m, 3H), 7.44-7.42 (m, 2H), 7.38-7.35 (m, 4H), 7.30-7.25 (m, 3H), 7.21-7.19 (m, 2H), 7.09-7.07 (m, 1 H), 6.19 (s, 1H), 3.91 (q, J = 6.5 Hz, 1H), 1.49 (d, J = 6.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 144.9, 139.3, 137.9, 134.1, 133.9, 131.8, 130.9, 128.8, 128.7, 128.4, 127.8, 127.6, 127.4, 127.3, 126.2, 126.0, 125.9, 125.5, 125.4, 125.3, 124.9, 123.4, 122.9, 56.0, 55.0, 23.2. **HRMS** (ESI^+) for $C_{29}H_{26}N$ $[M + H]^+$ calculated: 388.2065 found: 388.2067.



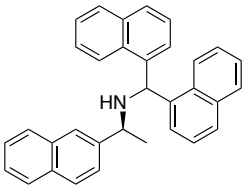
(*S*)-*N*-(di(naphthalen-1-yl)methyl)-1-phenylpropan-1-amine (4*S*-BDN)

Following the general procedure A, a white solid product was obtained (35 mg, 88%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.13 (d, J = 7.0 Hz, 1H), 7.86-7.81 (m, 3H), 7.66-7.63 (m, 2H), 7.58 (d, J = 9 Hz, 1H), 7.44-7.35 (m, 6H), 7.30-7.27 (m, 1H), 7.22-7.16 (m, 4H), 7.08-7.07 (d, J = 7.0 Hz, 1 H), 6.20 (s, 1H), 3.62 (t, J = 7.0 Hz, 1H), 1.98-1.96 (m, 1 H), 1.78-1.75 (m, 1H), 0.87 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.6, 139.5, 138.0, 134.1, 133.9, 131.9, 130.9, 128.8, 128.7, 128.4, 128.1, 127.7, 127.5, 127.3, 126.2, 126.1, 125.9, 125.5, 125.4, 125.3, 125.0, 123.4, 123.0, 62.7, 54.7, 30.0, 11.4. **HRMS** (ESI^+) for $C_{30}H_{28}N$ $[M + H]^+$ calculated: 402.2222 found: 402.2223.



(*S*)-*N*-(di(naphthalen-1-yl)methyl)-1-phenylpropan-1-amine (4*R*-BDN)

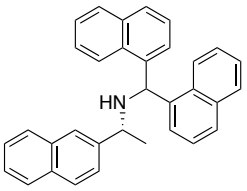
Following the general procedure A, a white solid product was obtained (34 mg, 86%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.12 (d, J = 7.0 Hz, 1H), 7.86-7.80 (m, 3H), 7.67-7.63 (m, 2H), 7.58 (d, J = 8.5 Hz, 1H), 7.45-7.35 (m, 6H), 7.30-7.27 (m, 1H), 7.22-7.16 (m, 4H), 7.08-7.07 (d, J = 6.5 Hz, 1 H), 6.20 (s, 1H), 3.63 (t, J = 8.0 Hz, 1H), 1.98-1.96 (m, 1 H), 1.78-1.75 (m, 1H), 0.87 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.5, 139.5, 137.9, 134.1, 133.9, 131.9, 130.9, 128.8, 128.7, 128.4, 128.1, 127.7, 127.5, 127.3, 126.2, 126.1, 125.9, 125.5, 125.4, 125.3, 125.0, 123.3, 123.0, 62.7, 54.7, 30.0, 11.4. **HRMS** (ESI^+) for $C_{30}H_{28}N$ $[M + H]^+$ calculated: 402.2222 found: 402.2231.



(*S*)-*N*-(di(naphthalen-1-yl)methyl)-1-(naphthalen-2-yl)ethan-1-amine (5*S*-BDN)

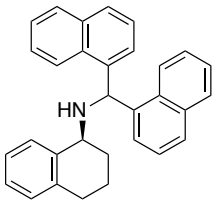
Following the general procedure A, a white solid product was obtained (41 mg, 93%). **^{1}H NMR**

($CDCl_3$, 500 MHz): 7.97 (d, J = 7.5 Hz, 1H), 7.88-7.81 (m, 5H), 7.77 (d, J = 8.0 Hz, 1H), 7.72-7.68 (m, 2H), 7.62-7.58 (m, 2H), 7.53-7.50 (m, 2H), 7.42-7.26 (m, 5H), 7.22-7.19 (m, 1H), 7.14-7.09 (m, 2H), 6.29 (s, 1H), 4.86 (q, J = 7.0 Hz, 1H), 1.62 (d, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 141.6, 139.3, 138.7, 134.0, 133.9, 133.8, 131.8, 131.7, 131.0, 128.8, 128.7, 128.6, 127.8, 127.7, 127.5, 126.1, 125.9, 125.8, 125.7, 125.5, 125.5, 125.4, 125.4, 125.3, 124.9, 123.8, 123.4, 123.2, 123.1, 55.6, 51.2, 23.7. HRMS (ESI^+) for $C_{33}H_{28}N$ $[M + H]^+$ calculated: 438.2222 found: 438.2230.



(*R*)-*N*-(di(naphthalen-1-yl)methyl)-1-(naphthalen-2-yl)ethan-1-amine (5*R*-BDN)

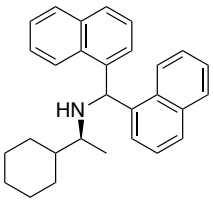
Following the general procedure A, a white solid product was obtained (42 mg, 97%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 7.99 (m, 1H), 7.89-7.82 (m, 5H), 7.78 (m, 1H), 7.73-7.69 (m, 2H), 7.63-7.60 (m, 2H), 7.55-7.51 (m, 2H), 7.43-7.27 (m, 5H), 7.23-7.20 (m, 1H), 7.15-7.10 (m, 2H), 6.30 (s, 1H), 4.88 (q, J = 7.0 Hz, 1H), 1.64 (d, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 141.6, 139.3, 138.7, 134.0, 133.9, 133.8, 131.8, 131.7, 131.0, 128.8, 128.7, 128.6, 127.8, 127.7, 127.5, 126.1, 125.9, 125.8, 125.7, 125.5, 125.5, 125.4, 125.4, 125.3, 124.9, 123.8, 123.4, 123.2, 123.1, 55.6, 51.2, 23.7. **HRMS** (ESI^+) for $C_{33}H_{28}N$ $[M + H]^+$ calculated: 438.2222 found: 438.2224.



***(S)*-*N*-(di(naphthalen-1-yl)methyl)-1,2,3,4-tetrahydronaphthalen-1-amine (6*S*-BDN)**

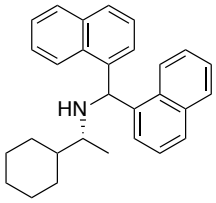
Following the general procedure A, a white solid product was obtained (36 mg, 87%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.13 (d, J = 8.5 Hz, 1 H), 7.92-7.87 (m, 2H), 7.82-7.76 (m, 3H), 7.69 (d, J = 8.5 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.50-7.37 (m, 6H), 7.33-7.30 (m, 1H), 7.24-7.21 (m, 1H), 7.17-7.15 (m, 2H), 6.67 (s, 1H), 4.02 (m, 1H), 2.88-2.77 (m, 2H), 2.13-2.03 (m, 2H), 1.79-1.76 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz): 138.7, 138.5, 137.3, 134.1, 134.1, 131.5, 131.4, 129.3, 129.0, 129.0, 128.9, 127.8, 127.7, 126.9, 126.2, 126.1, 126.0, 125.6, 125.5, 125.4, 125.4, 123.0, 122.9,

54.7, 53.3, 28.9, 28.5, 18.6. **HRMS** (ESI^+) for $C_{31}H_{28}N$ $[M + H]^+$ calculated: 414.2222 found: 414.2227.



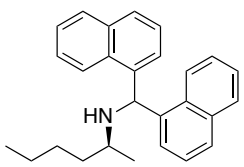
(*S*)-1-cyclohexyl-*N*-(di(naphthalen-1-yl)methyl)ethan-1-amine (7*S*-BDN)

Following the general procedure A, a white solid product was obtained (18 mg, 47%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.20-8.18 (m, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.87-7.85 (m, 2H), 7.76-7.73 (m, 2H), 7.59 (d, J = .07 Hz, 1H), 7.50-7.35 (m, 7H), 6.51 (s, 1H), 2.80 (m, 1H), 1.76-1.54 (m, 6H), 1.26-1.21 (m, 2H), 1.11 (d, J = 7.0 Hz, 3H), 1.07-1.03 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 139.6, 138.9, 134.0, 134.0, 131.5, 131.4, 128.9, 128.9, 127.6, 127.5, 126.2, 126.0, 125.9, 125.8, 125.5, 125.5, 125.3, 123.2, 123.1, 56.0, 55.2, 43.2, 30.1, 27.7, 26.8, 26.7, 26.5, 16.5. **HRMS** (ESI^+) for $C_{29}H_{32}N$ $[M + H]^+$ calculated: 394.2535 found: 394.2538.



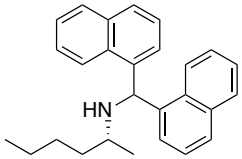
(*R*)-1-cyclohexyl-*N*-(di(naphthalen-1-yl)methyl)ethan-1-amine (7*R*-BDN)

Following the general procedure A, a white solid product was obtained (29 mg, 73%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.21-8.19 (m, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.88-7.86 (m, 2H), 7.77-7.73 (m, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.51-7.36 (m, 7H), 6.57 (s, 1H), 2.81-2.79 (m, 1H), 1.77-1.55 (m, 6H), 1.26-1.21 (m, 2H), 1.12 (d, J = 7.0 Hz, 3H), 1.08-1.03 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 139.6, 138.9, 134.1, 134.0, 131.6, 131.4, 128.9, 128.9, 127.6, 127.5, 126.2, 126.1, 125.9, 125.8, 125.5, 125.5, 125.3, 123.2, 123.1, 56.0, 55.2, 43.2, 30.1, 27.7, 26.8, 26.7, 26.6, 16.5. **HRMS** (ESI^+) for $C_{29}H_{32}N$ $[M + H]^+$ calculated: 394.2535 found: 394.2541.



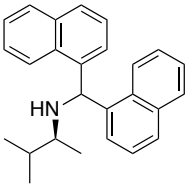
(*S*)-*N*-(di(naphthalen-1-yl)methyl)hexan-2-amine (8*S*-BDN)

Following the general procedure A, a white solid product was obtained (30 mg, 80%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.25 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.88-7.86 (m, 2H), 7.77-7.73 (m, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.49-7.34 (m, 7H), 6.58 (s, 1H), 2.95-2.91 (m, 1H), 1.64-1.58 (m, 1H), 1.44-1.25 (m, 5H), 1.19 (d, J = 6.5 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 139.4, 138.8, 134.1, 134.1, 131.6, 131.4, 129.0, 128.9, 127.6, 127.6, 126.3, 126.1, 125.8, 125.6, 125.5, 125.4, 125.4, 125.4, 123.1, 123.1, 55.3, 51.6, 37.3, 28.1, 23.0, 20.6, 14.1. **HRMS** (ESI^+) for $C_{27}H_{30}N$ $[M + H]^+$ calculated: 368.2378 found: 368.2374.



(*R*)-*N*-(di(naphthalen-1-yl)methyl)hexan-2-amine (8*R*-BDN)

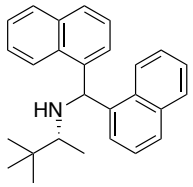
Following the general procedure A, a white solid product was obtained (28 mg, 76%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.25 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.88-7.86 (m, 2H), 7.77-7.73 (m, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.48-7.34 (m, 7H), 6.58 (s, 1H), 2.95-2.91 (m, 1H), 1.64-1.60 (m, 1H), 1.41-1.26 (m, 5H), 1.19 (d, J = 6.5 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 139.4, 138.8, 134.1, 134.1, 131.6, 131.4, 129.0, 128.9, 127.6, 127.6, 126.3, 126.1, 125.8, 125.6, 125.5, 125.4, 125.4, 125.4, 123.1, 123.1, 55.3, 51.6, 37.3, 28.1, 23.0, 20.6, 14.1. **HRMS** (ESI +) for $C_{27}H_{30}N$ $[M + H]^+$ calculated: 368.2378 found: 368.2369.



(*S*)-*N*-(di(naphthalen-1-yl)methyl)-3-methylbutan-2-amine (9*S*-BDN)

Following the general procedure A, a white solid product was obtained (30 mg, 86%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.22-8.20 (m, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.87-7.85 (m, 2H), 7.76-7.73 (m, 2H), 7.61 (d, J = 7.0 Hz, 1H), 7.49-7.35 (m, 7H), 6.55 (s, 1H), 2.83-2.81 (m, 1H), 1.92-1.88 (m, 1H), 1.08 (d, J = 6.5 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125

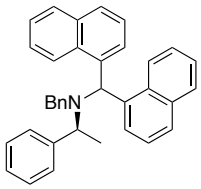
MHz): 139.6, 139.0, 134.0, 134.0, 131.5, 131.4, 128.9, 128.9, 127.6, 127.5, 126.2, 126.1, 125.9, 125.8, 125.5, 125.4, 125.3, 123.1, 56.6, 55.4, 32.5, 19.6, 16.9, 15.5. **HRMS** (ESI^+) for $C_{26}H_{28}N$ [M + H]$^+$ calculated: 354.2222 found: 354.2234.



(*R*)-*N*-(di(naphthalen-1-yl)methyl)-3,3-dimethylbutan-2-amine (10*R*-BDN)

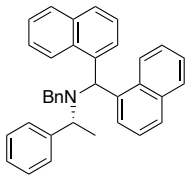
Following the general procedure A, a white solid product was obtained (33 mg, 90%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.37 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.88-7.85 (m, 2H), 7.78-7.76 (m, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.53-7.30 (m, 7H), 6.54 (s, 1H), 2.68 (q, J = 6.5 Hz, 1H), 1.12 (d, J = 6.5 Hz, 1H), 0.91 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 140.4, 138.5, 134.0, 134.0, 131.8, 131.3, 128.9, 128.9, 127.6, 127.4, 126.4, 126.2, 126.0, 125.5, 125.3, 125.3, 125.3, 123.3, 123.2, 60.1, 55.3, 34.6, 26.7, 14.4. **HRMS** (ESI^+) for $C_{27}H_{30}N$ [M + H]$^+$ calculated: 368.2378 found: 368.2378.

General Procedure B: To a 5 mL round bottom flask was added chiral Bn protected amine (0.12 mmol, 1.2 equiv) and 1,1'-(bromomethylene)dinaphthalene (0.1 mmol, 35 mg) in a 1:1 mixture of acetonitrile and DCM (2 mL). K_2CO_3 (0.2 mmol, 2 equiv, 28 mg) was added to the flask and the mixture was stirred under N_2 for 4 h. The reaction mixture was concentrated under vacuo and the mixture was directly loaded onto silica gel for purification.



(*S*)-*N*-benzyl-*N*-(di(naphthalen-1-yl)methyl)-1-phenylethan-1-amine (11*S*-BDN)

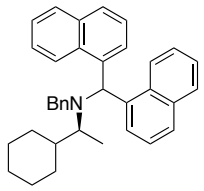
Following the general procedure B, a white solid product was obtained (27 mg, 57%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.00 (d, J = 7.0 Hz, 1H), 7.82-7.74 (m, 3H), 7.62 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.48-7.40 (m, 2H), 7.38-7.25 (m, 6H), 7.21-7.17 (m, 2H), 7.03-6.96 (m, 4H), 6.73-6.70 (m, 3H), 4.31 (q, J = 7.0 Hz, 1H), 4.21 (d, J = 16.0 Hz, 1H), 3.77 (d, J = 16.0 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.5, 142.3, 138.6, 137.7, 134.1, 133.8, 132.3, 132.0, 128.8, 128.8, 128.7, 128.6, 128.1, 127.6, 127.5, 127.2, 127.2, 126.5, 126.0, 125.9, 125.5, 125.2, 125.1, 124.9, 123.5, 123.5, 60.3, 59.5, 50.4, 19.5. **HRMS** (ESI^+) for $C_{36}H_{32}N$ $[M + H]^+$ calculated: 478.2529 found: 478.2534.



(*R*)-*N*-benzyl-*N*-(di(naphthalen-1-yl)methyl)-1-phenylethan-1-amine (11*R*-BDN)

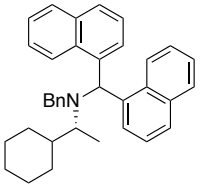
Following the general procedure B, a white solid product was obtained (25 mg, 52%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 7.97 (d, J = 7.5 Hz, 1H), 7.81-7.76 (m, 3H), 7.60 (d, J = 8.5 Hz, 1H), 7.56-7.53 (m, 2H), 7.46-7.39 (m, 2H), 7.36-7.22 (m, 6H), 7.19-7.14 (m, 2H), 7.01-6.94 (m, 4H), 6.70-6.67 (m, 3H), 4.29 (q, J = 7.5 Hz, 1H), 4.18 (d, J = 15.0 Hz, 1H), 3.74 (d, J = 15.0 Hz, 1H), 1.46 (d, J = 7.5 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.5, 142.3, 138.6, 137.7, 134.0, 133.7, 132.3, 132.0, 128.8, 128.8, 128.7, 128.6, 128.1, 127.6, 127.5, 127.2, 127.2, 126.5, 126.0, 125.9, 125.5, 125.2, 125.1, 124.9, 123.5, 123.5, 60.3, 59.5, 50.4, 19.5. **HRMS** (ESI^+) for $C_{36}H_{32}N$ $[M + H]^+$ calculated:

478.2529 found: 478.2530.



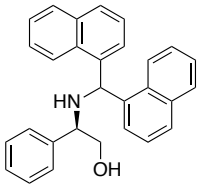
(*S*)-*N*-benzyl-1-cyclohexyl-*N*-(di(naphthalen-1-yl)methyl)ethan-1-amine (12*S*-BDN)

Following the general procedure B, a white solid product was obtained (30 mg, 61%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 8.47 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 9 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8 Hz, 1H), 7.58-7.46 (m, 4H), 7.37-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.01-6.95 (m, 4H), 6.80-6.77 (m, 3H), 4.03 (d, J = 16.0 Hz, 1H), 3.78 (d, J = 16.0 Hz, 1H), 2.90-2.88 (m, 1H), 2.06-2.04 (m, 1H), 1.70-1.52 (m, 4H), 1.36-1.34 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H), 1.03-0.88 (m, 4H), 0.79-0.76 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.1, 139.1, 137.8, 134.0, 133.8, 132.4, 131.9, 129.0, 129.0, 128.8, 127.5, 127.5, 127.4, 127.3, 126.8, 126.0, 125.9, 125.4, 125.1, 125.1, 125.0, 124.9, 123.4, 123.4, 61.4, 59.8, 51.8, 42.6, 32.0, 29.4, 26.7, 26.6, 26.5, 12.7. **HRMS** (ESI^+) for $C_{36}H_{38}N$ $[M + H]^+$ calculated: 484.2999 found: 484.3006.



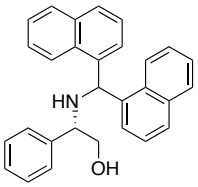
(*R*)-*N*-benzyl-1-cyclohexyl-*N*-(di(naphthalen-1-yl)methyl)ethan-1-amine (12*R*-BDN)

Following the general procedure B, a white solid product was obtained (28 mg, 58%).**^{1}H NMR** ($CDCl_3$, 500 MHz): 8.47 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 6.5 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 1H), 7.58-7.46 (m, 4H), 7.38-7.33 (m, 2H), 7.30-7.27 (m, 1H), 7.01-6.95 (m, 4H), 6.80-6.77 (m, 3H), 4.04 (d, J = 16.0 Hz, 1H), 3.78 (d, J = 16.0 Hz, 1H), 2.90-2.88 (m, 1H), 2.07-2.04 (m, 1H), 1.71-1.50 (m, 4H), 1.36-1.35 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H), 1.04-0.86 (m, 4H), 0.79-0.76 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 143.1, 139.1, 137.9, 134.0, 133.8, 132.5, 131.9, 129.0, 129.0, 128.8, 127.5, 127.5, 127.4, 127.3, 126.8, 126.0, 125.9, 125.5, 125.1, 125.1, 125.0, 124.9, 123.4, 123.4, 61.4, 59.8, 51.8, 42.6, 32.0, 29.4, 26.7, 26.6, 26.5, 12.8. **HRMS** (ESI^+) for $C_{36}H_{38}N$ $[M + H]^+$ calculated: 484.2999 found: 484.3003.



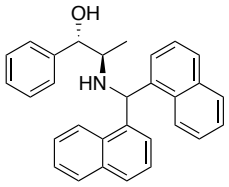
(*R*)-2-((di(naphthalen-1-yl)methyl)amino)-2-phenylethan-1-ol (13*R*-BDN)

Following the general procedure A, a white solid product was obtained (26.9 mg, 66%).**^{1}H NMR** ($CDCl_3$, 500 MHz): 8.12 (d, J = 7.0 Hz, 1H), 7.88-7.84 (m, 3H), 7.71 (d, J = 7.5 Hz, 1H), 7.66-7.61(m, 2H), 7.54 (d, J = 8.5 Hz, 1H), 7.48-7.45 (m, 1H), 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 7.26-7.20 (m, 5H), 6.34 (s, 1H), 4.00 (t, J = 7 Hz, 1H), 3.78(d, J = 7 Hz, 2H), 2.45 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 140.1, 138.7, 136.9, 134.1, 133.9, 131.7, 130.7, 129.0, 128.8, 128.7, 128.2, 128.2, 128.1, 127.9, 126.4, 126.2, 126.1, 125.6, 125.5, 125.4, 125.2, 123.1, 122.6. 66.2, 62.3, 54.4. **HRMS** (ESI^+) for $C_{29}H_{26}NO$ $[M + H]^+$ calculated: 404.2014. found: 404.2003.



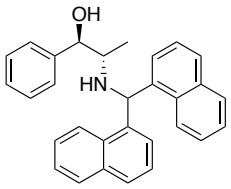
(*S*)-2-((di(naphthalen-1-yl)methyl)amino)-2-phenylethan-1-ol (13*S*-BDN)

Following the general procedure A, a white solid product was obtained (22.7 mg, 56%).**^{1}H NMR** ($CDCl_3$, 500 MHz): 8.11 (d, J = 7.0 Hz, 1H), 7.89-7.85 (m, 3H), 7.71 (d, J = 8.0 Hz, 1H), 7.67-7.63(m, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.49-7.46 (m, 1H), 7.43-7.38 (m, 4H), 7.35-7.31 (m, 1H), 7.27-7.21 (m, 5H), 6.34 (s, 1H), 4.01 (t, J = 7 Hz, 1H), 3.79 (d, J = 7 Hz, 2H), 2.45 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 140.2, 138.8, 137.0, 134.1, 133.9, 131.8, 130.8, 129.0, 128.8, 128.7, 128.1, 128.0, 127.8, 126.4, 126.1, 126.1, 125.5, 125.5, 125.4, 125.2, 123.1, 122.7, 66.3, 62.2, 54.4. **HRMS** (ESI^+) for $C_{29}H_{26}NO$ $[M + H]^+$ calculated: 404.2014 found: 404.2021.



(1*S*,2*R*)-2-((di(naphthalen-1-yl)methyl)amino)-1-phenylpropan-1-ol (14*R*-BDN)

Following the general procedure A, a white solid product was obtained (24.5 mg, 58%).**^{1}H NMR** ($CDCl_3$, 500 MHz): 8.33 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 9.0 Hz, 2H), 7.84-7.79 (m, 2H), 7.59-7.44 (m, 6H), 7.39-7.38 (m, 2H), 7.30-7.21(m, 5H), 6.76 (s, 1H), 5.04 (d, J = 3.5 Hz, 1H), 3.28 (dt, J = 6.5, 3.5 Hz, 1H), 0.97(d, J = 6.5 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 141.0, 134.2, 134.1, 131.5, 131.4, 129.1, 129.0, 128.1, 128.1, 128.0, 127.0, 126.7, 126.6, 125.9, 125.7, 125.7, 125.4, 125.4, 125.3, 124.8, 123.0, 122.7, 73.4, 57.4, 55.4, 13.9. **HRMS** (ESI^+) for $C_{30}H_{28}NO$ $[M + H]^+$ calculated: 418.2171. found:418.2177.



(1*R*,2*S*)-2-((di(naphthalen-1-yl)methyl)amino)-1-phenylpropan-1-ol (14*S*-BDN)

Following the general procedure A, a white solid product was obtained (21.9 mg, 52%).**^{1}H NMR** ($CDCl_3$, 500 MHz): 8.32 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.83-7.78 (m, 2H), 7.58-7.43 (m, 6H), 7.38-7.37 (m, 2H), 7.29-7.21(m, 5H), 6.75 (s, 1H), 5.03 (d, J = 3.0 Hz, 1H), 3.26 (dt, J = 7.0, 3.0 Hz, 1H), 0.96(d, J = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz): 141.0, 134.1, 134.1, 131.5, 131.3, 129.1, 129.0, 128.8, 128.1, 128.1, 128.0, 127.0, 126.7, 126.5, 125.9, 125.7, 125.7, 125.4, 125.3, 124.8, 123.0, 122.7, 73.4, 57.3, 55.4, 13.9. **HRMS** (ESI^+) for $C_{30}H_{28}NO$ $[M + H]^+$ calculated: 418.2171. found: 418.2175.

XII. Quantum Chemical Modeling Studies

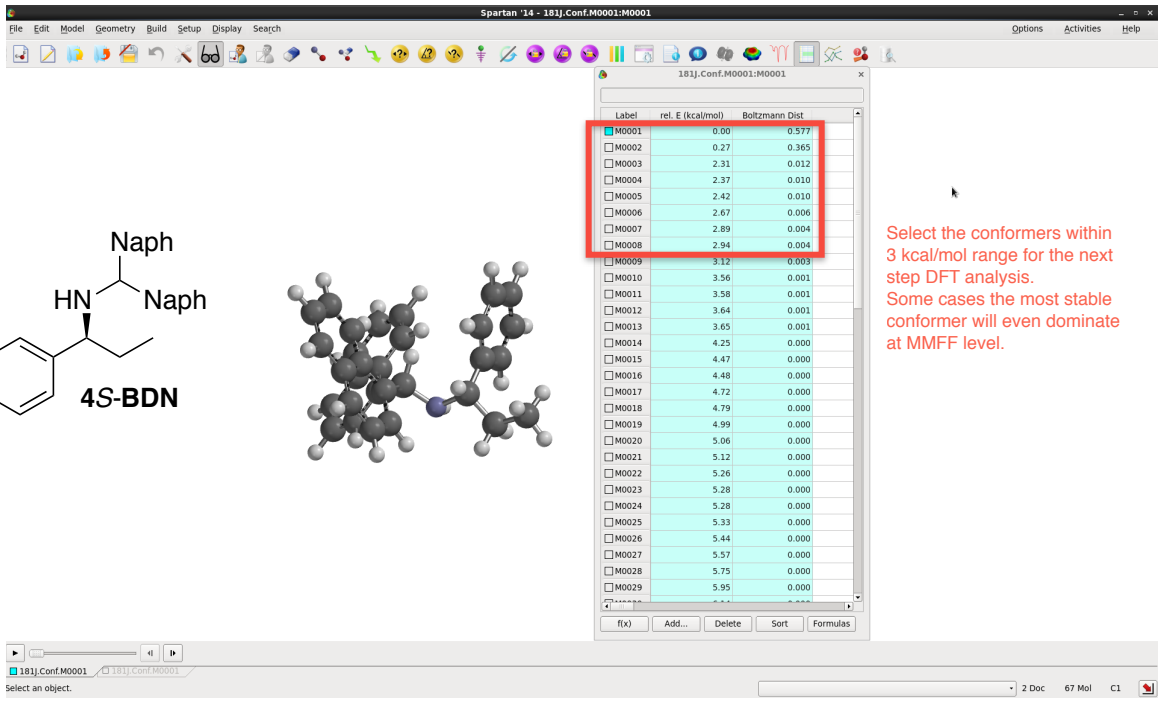
All calculations were performed with SPARTAN 14 software using a commercial PC with 15 core Intel Xeon X5647 @2.93 GHz with 48 G memory on a Kernel Linux platform.

Conformer analysis:

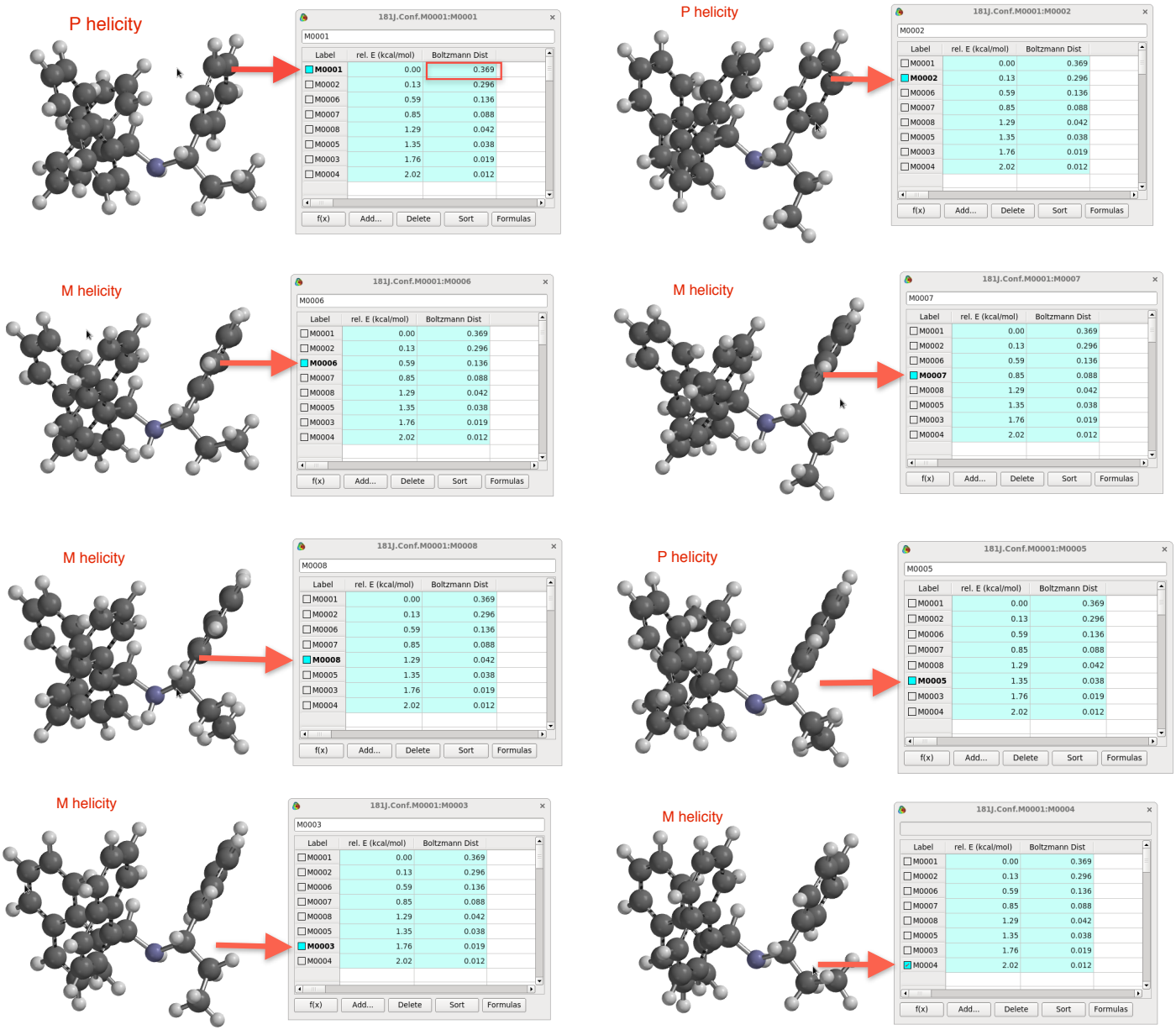
Conformer distribution calculations were performed at the MMFF level of theory utilizing Monte Carlo search parameters, starting from 10,000 K. All stable conformers (within 3 kcal for aromatic compounds and within 2 kcal for aliphatic compounds) were subject to further optimization by density functional theory at B3LYP/6-31G* level in vacuum. The resulting geometries for each conformer were analyzed and scored to yield either the *P* or *M* helicity by considering the calculated Boltzmann distribution values.

The following is the step by step procedure for computational studies performed to obtain the anticipated ECCD signs for the derivatized chiral amines:

Step 1: Perform a conformer distribution calculation with the MMFF force field. From the list of generated conformer structures, select all within 3 kcal/mol for DFT geometry optimization.



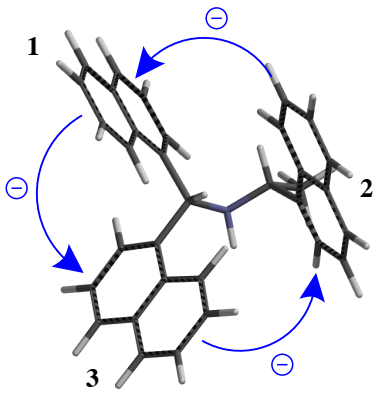
Step 2: Upon geometry optimization (DFT, B3LYP/6-31G*), the helicity of the two naphthyl rings is assigned.



Step 3: Sum up the Boltzmann values for all structures that lead to *P* and *M* helicities. In this example, the *P*:*M* ratio is 70.3:29.7, thus predicting that the *P* helicity will dominate in the CD spectra and leads to a positive ECCD signal. This prediction is in agreement with experimental result.

Naphthyl containing substrates:

Substrates with a naphthyl group can contribute to the overall ECCD in addition to the naphthyl groups from **BDN**. The following is a step by step demonstration of how to calculate the predicted ECCD for **5***R*-**BDN**. As before, the energy minimized conformations are considered. The prediction is based on assigning the helicities of each interacting naphthyl group. For example, in the first conformer the ECCD for all three interactions; i.e, 1→2, 2→3, and 1→3, predict a negative ECCD. Thus, all 45% population of that conformer is assigned as *M*-helicity. In contrast, for the second structure, the 1→2 and 1→3 interactions are negative, while the 2→3 interaction yield a positive helicity. As such, the 10.8% population assigned to this conformer is 66.6% *M*-helicity and 33.3% *P*-helicity. The aggregate of all these calculations leads to the overall predicted helicity for the system.



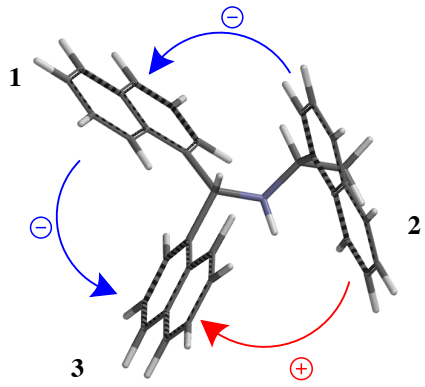
M1

F-Spart

M0001

Label	rel. E (kcal/mol)	Boltzmann Dist
M0001	0.00	0.451
M0002	0.85	0.108
M0003	0.08	0.393
M0004	1.98	0.016
M0005	1.57	0.032

M = 45.1 x 100% = 45.1 *P* = 0 x 100% = 0



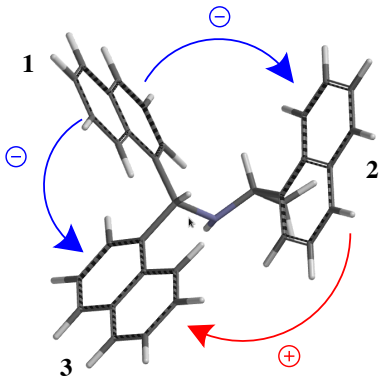
M2

F-Spart

M0002

Label	rel. E (kcal/mol)	Boltzmann Dist
M0001	0.00	0.451
M0002	0.85	0.108
M0003	0.08	0.393
M0004	1.98	0.016
M0005	1.57	0.032

M = 10.8 x 66.6% = 7.2 *P* = 10.8 x 33.3% = 3.6



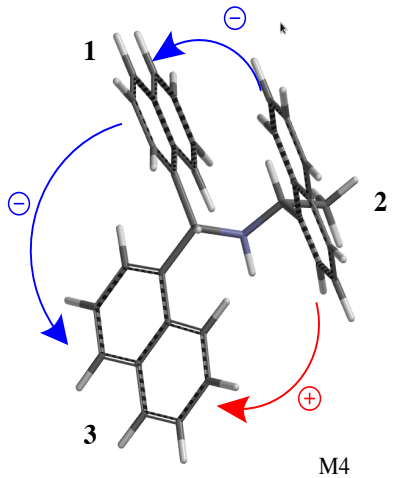
M3

F-Spar

M0003

Label	rel. E (kcal/mol)	Boltzmann Dist
M0001	0.00	0.451
M0002	0.85	0.108
M0003	0.08	0.393
M0004	1.98	0.016
M0005	1.57	0.032

M = 39.3 x 66.6% = 26.2 *P* = 39.3 x 33.3% = 13.1



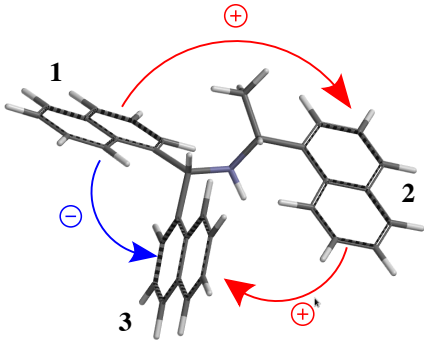
M4

F-Spar

M0004

Label	rel. E (kcal/mol)	Boltzmann Dist
M0001	0.00	0.451
M0002	0.85	0.108
M0003	0.08	0.393
M0004	1.98	0.016
M0005	1.57	0.032

M = 1.98 x 66.6% = 1.1 *P* = 1.98 x 33.3% = 0.5



M5

F-Spar

M0005

Label	rel. E (kcal/mol)	Boltzmann Dist
M0001	0.00	0.451
M0002	0.85	0.108
M0003	0.08	0.393
M0004	1.98	0.016
M0005	1.57	0.032

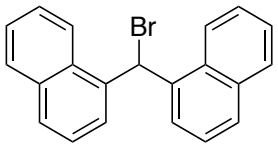
M = 3.2 x 33.3% = 1.1 *P* = 3.2 x 66.6 % = 2.1

Conformer Entry	M helicity	P helicity
M1	45.1	0
M2	7.2	3.6
M3	26.2	13.1
M4	1.1	0.5
M5	1.1	2.1
Overall	80.7	19.3

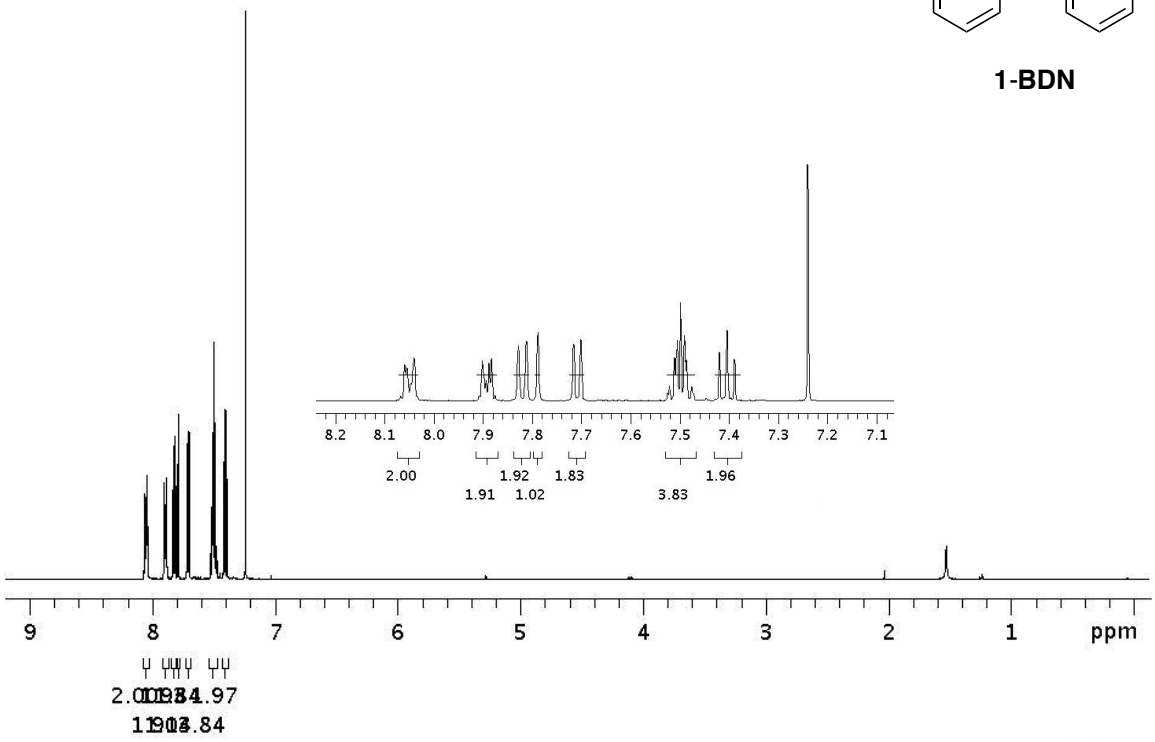
XIII. References:

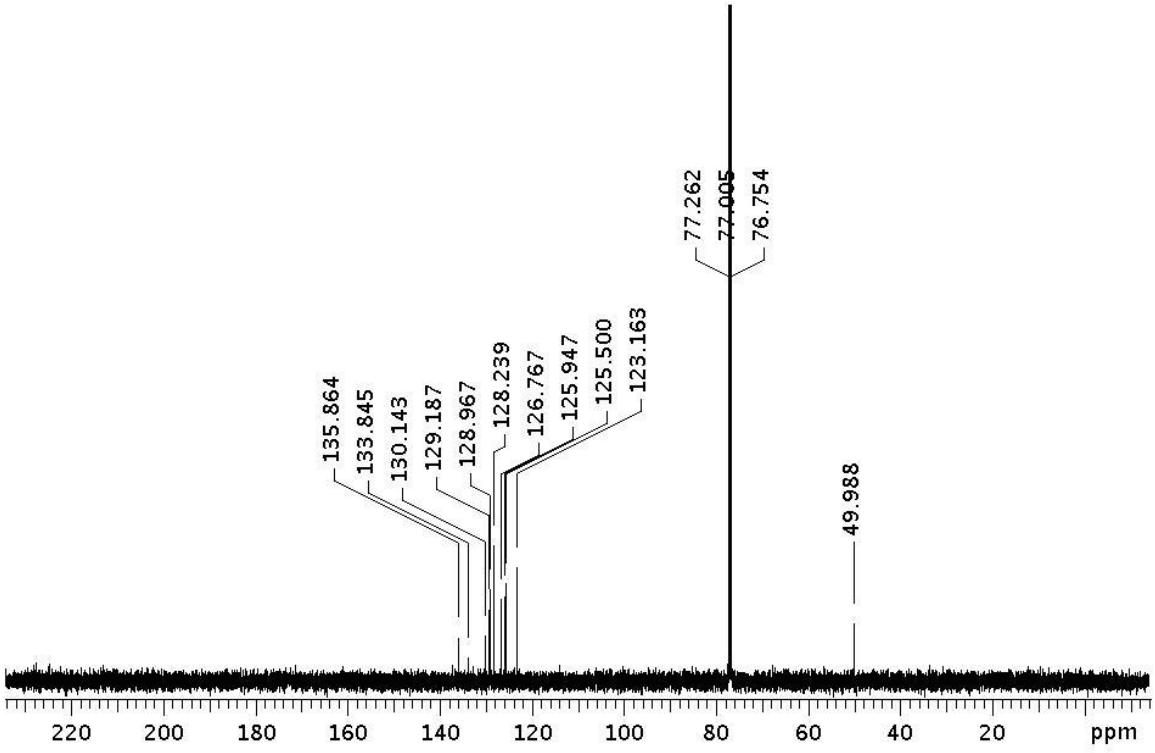
[1] a) O. Bassas, J. Huuskonen, K. Rissanen, A. M. P. Koskinen, *Eur J Org Chem* **2009**, 1340-1351; b) M. Holtz-Mulholland, S. K. Collins, *Synthesis-Stuttgart* **2014**, *46*, 375-380.

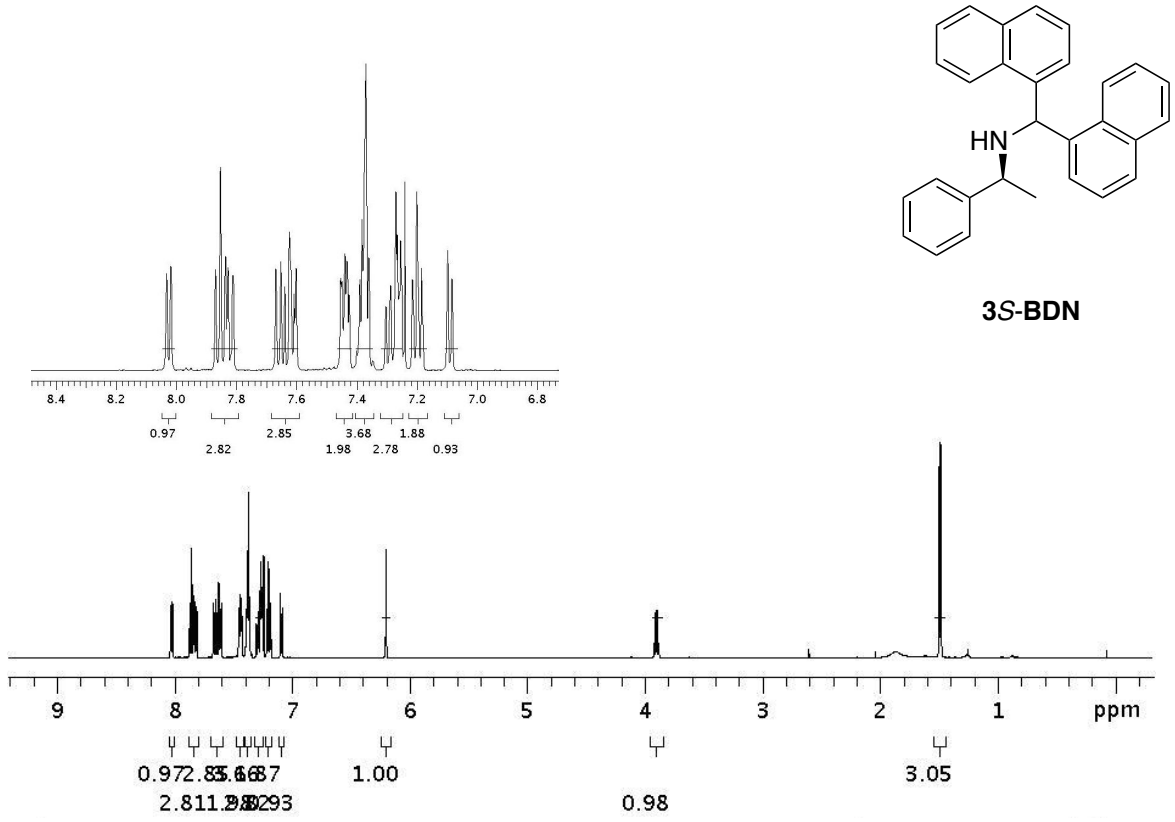
XIV. NMR Spectra

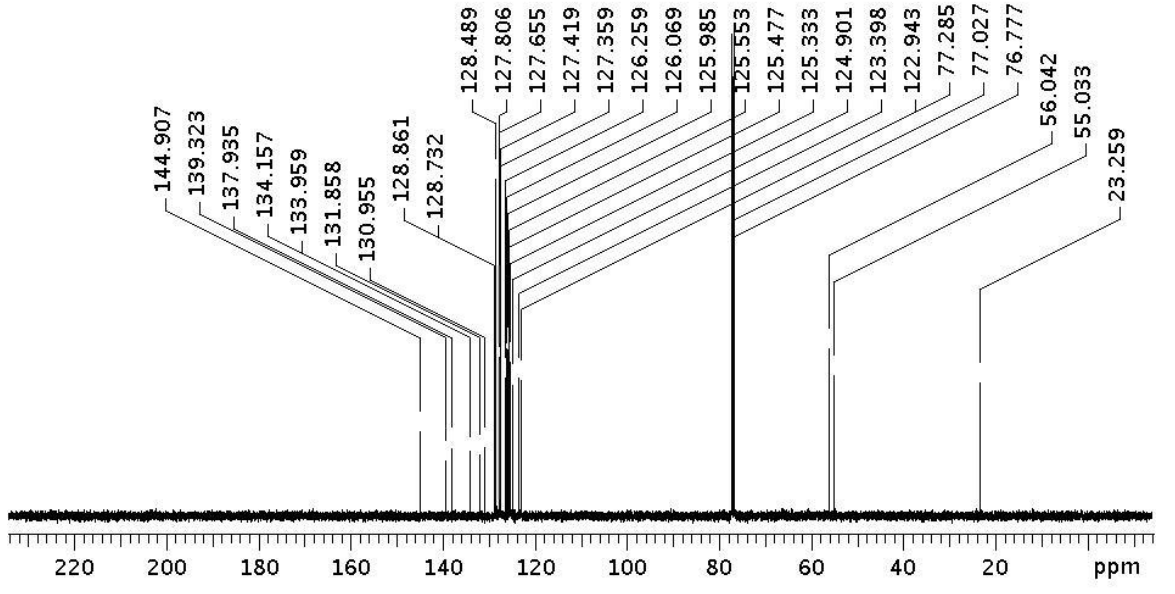


1-BDN






HN
3S-BDN
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
0.97 2.82 2.85 3.68 1.98 1.88 2.78 0.93
9 8 7 6 5 4 3 2 1 ppm
1.00
0.98
3.05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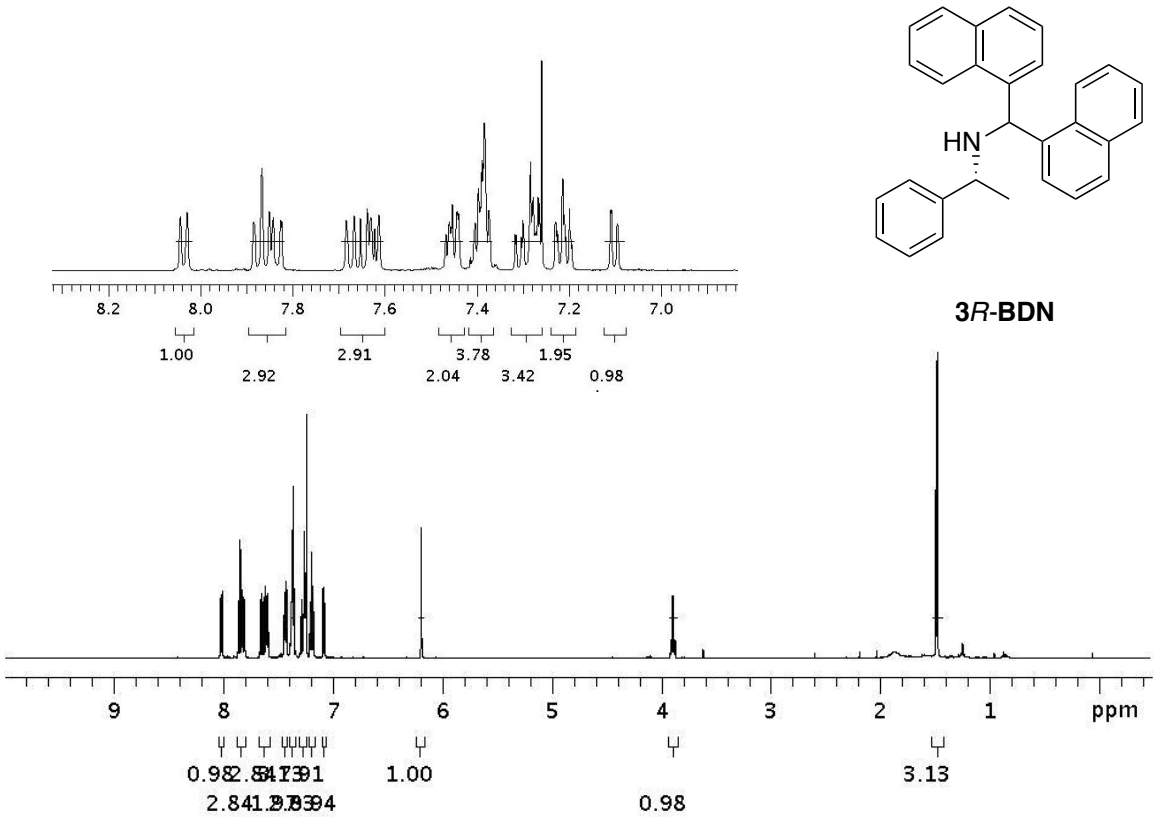
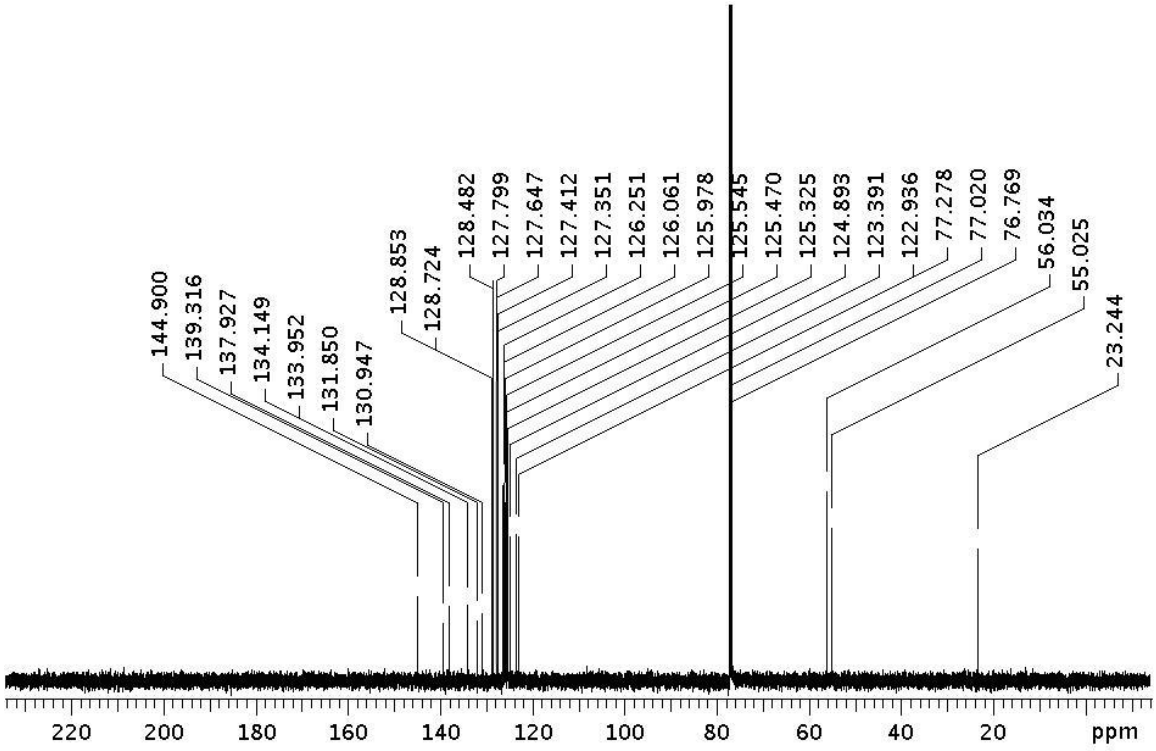
139.323
137.935
134.157
133.959
131.858
130.955
128.861
128.732
128.489
127.806
127.655
127.419
127.359
126.259
126.069
125.985
125.553
125.477
125.333
124.901
123.398
122.943
77.285
77.027
76.777
56.042
55.033
23.259
220 200 180 160 140 120 100 80 60 40 20 ppm


HN
3R-BDN
8.2
8.0
7.8
7.6
7.4
7.2
7.0
1.00
2.92
2.91
2.04
3.78
3.42
1.95
0.98
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
3.13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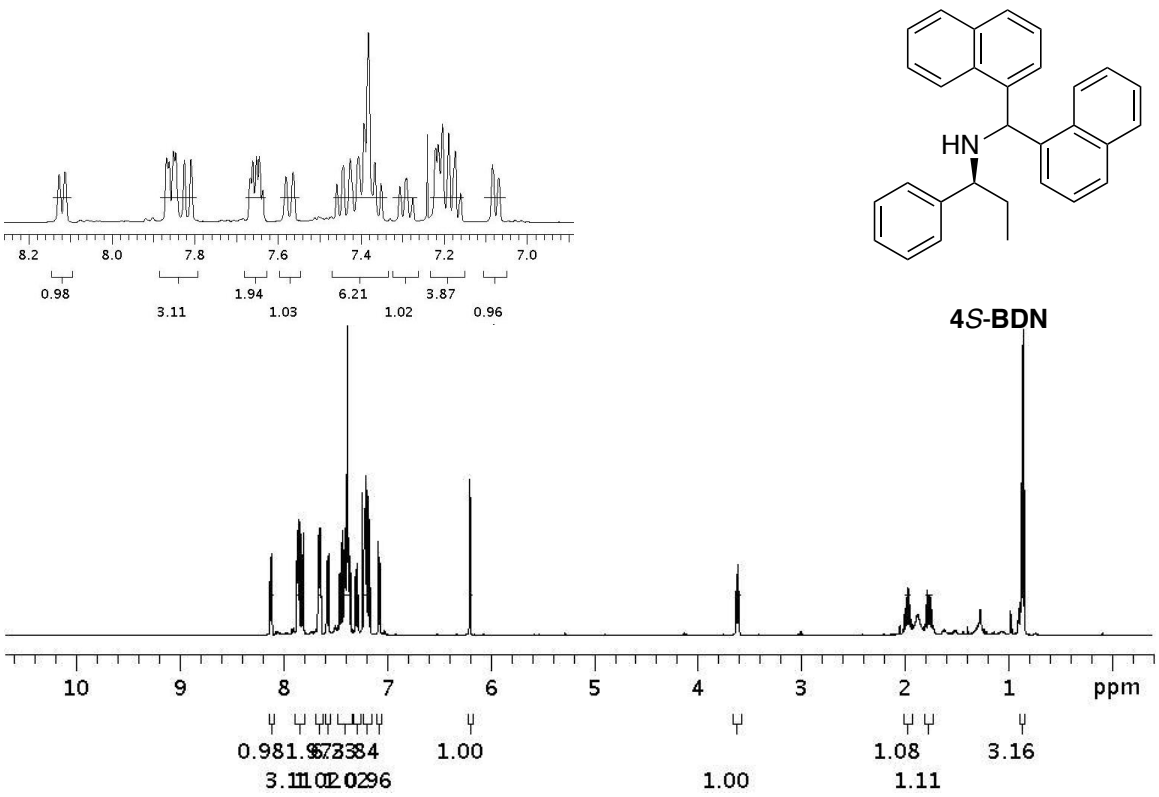
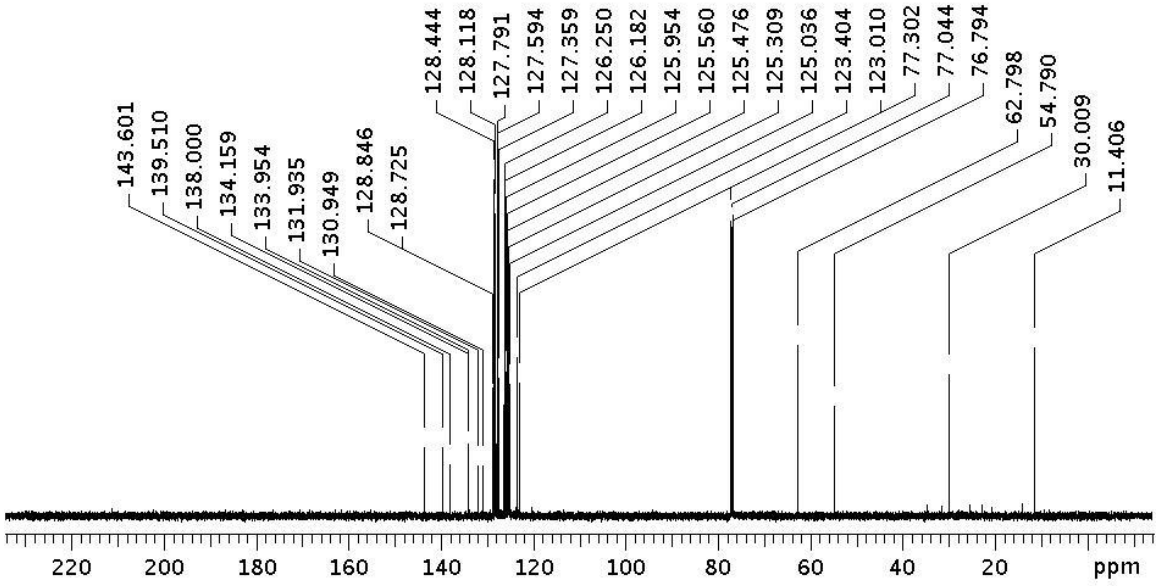
139.316
137.927
134.149
133.952
131.850
130.947
128.853
128.724
128.482
127.799
127.647
127.412
127.351
126.251
126.061
125.978
125.545
125.470
125.325
124.893
123.391
122.936
77.278
77.020
76.769
56.034
55.025
23.244
220
200
180
160
140
120
100
80
60
40
20
ppm


HN
4S-BDN
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0.98
3.11
1.94
1.03
6.21
1.02
3.87
0.96
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.08
3.16
1.00
1.11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139.510
138.000
134.159
133.954
131.935
130.949
128.846
128.725
128.444
128.118
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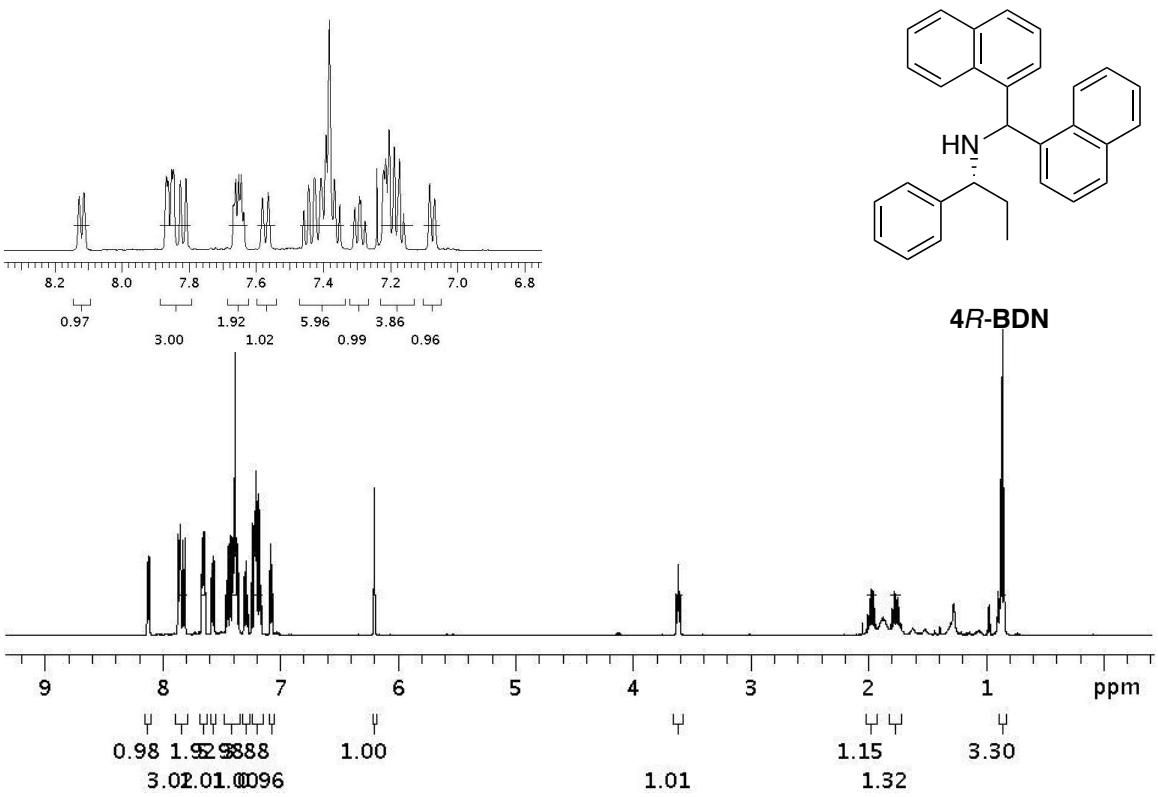
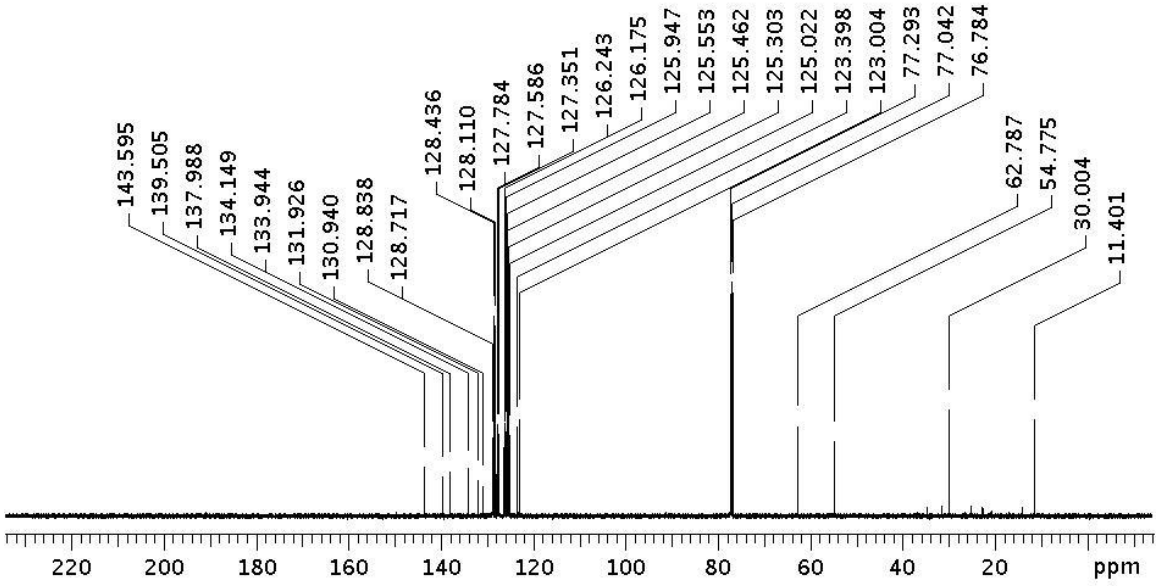
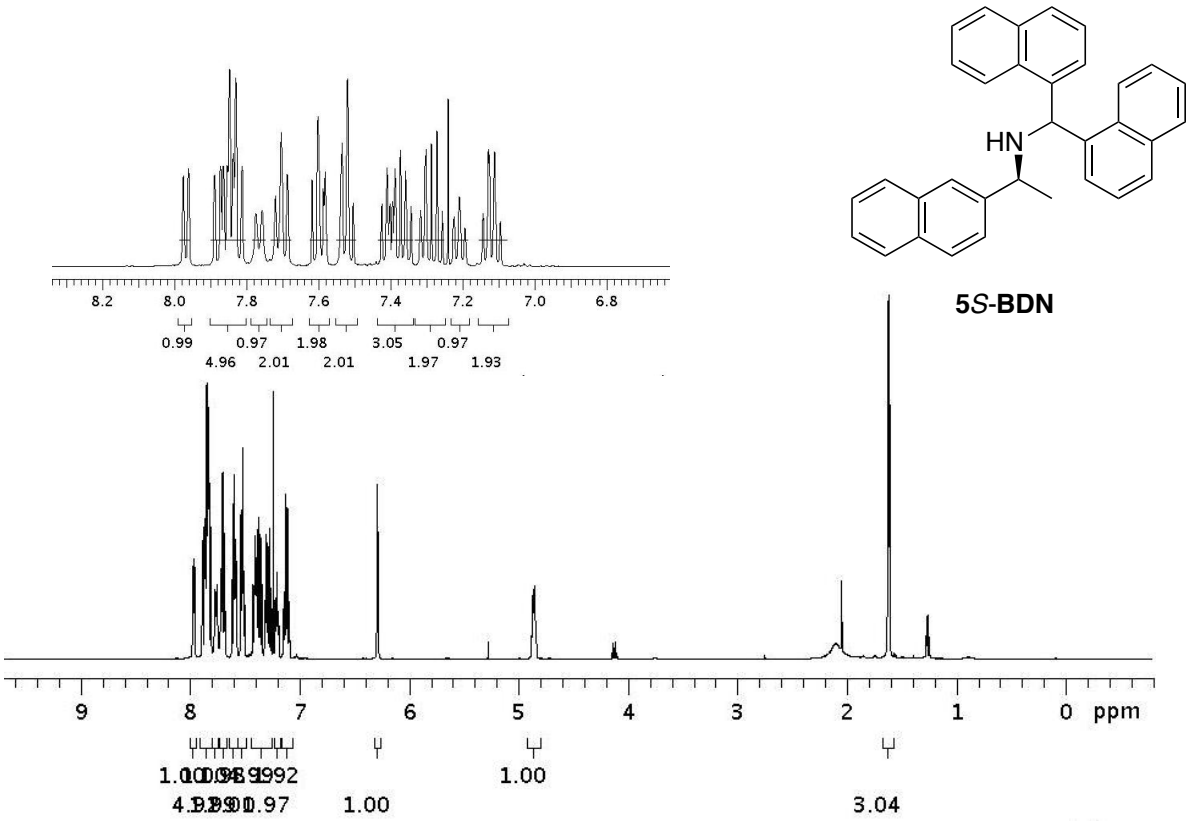
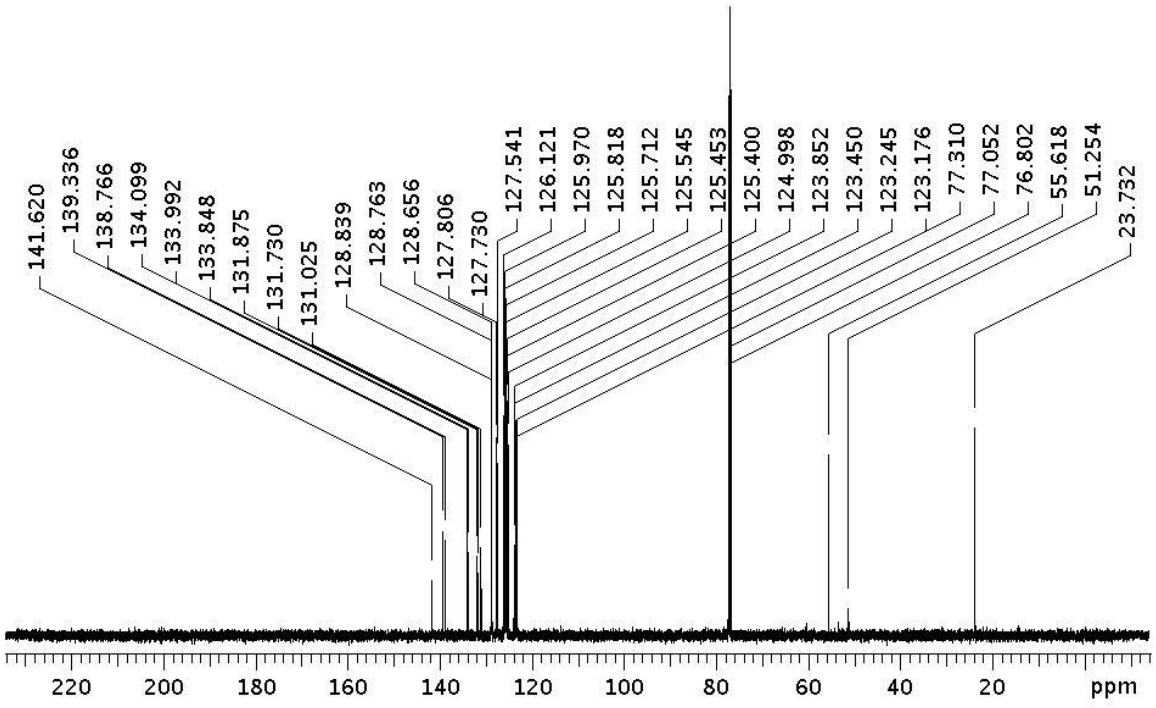
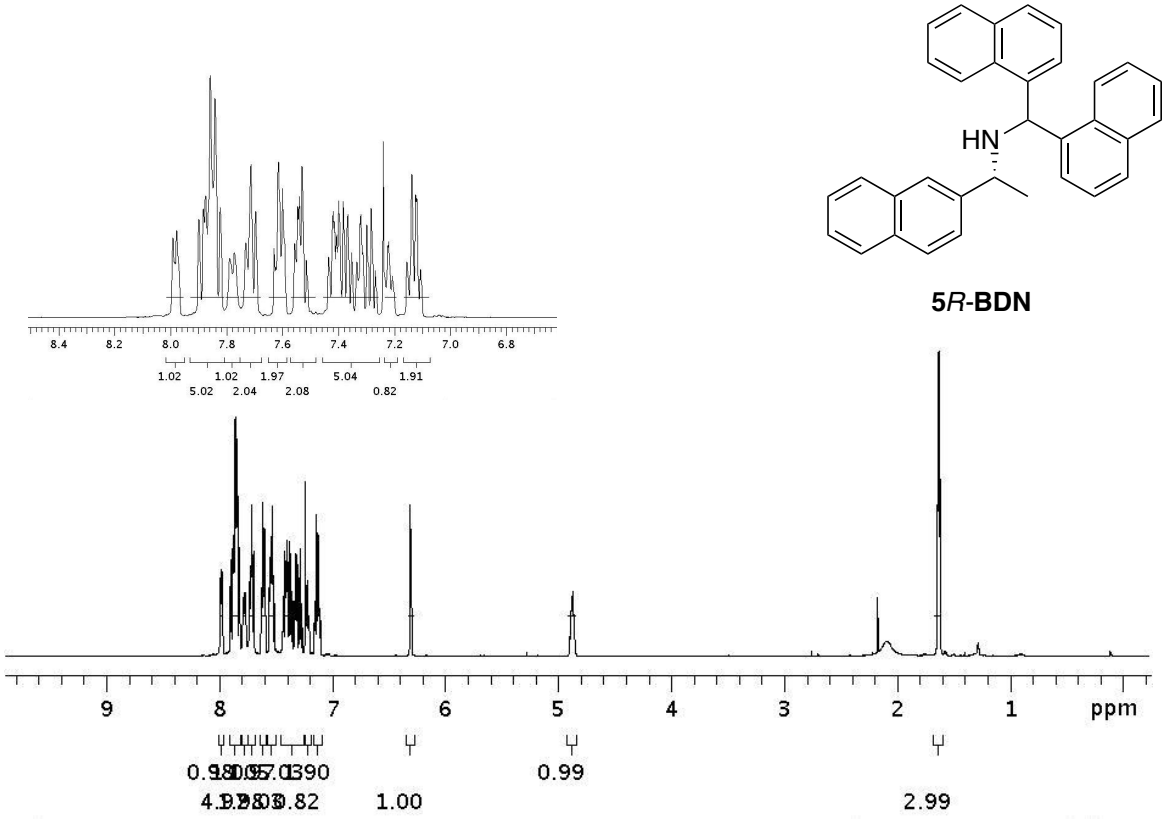
127.594
127.359
126.250
126.182
125.954
125.560
125.476
125.309
125.036
123.404
123.010
77.302
77.044
76.794
62.798
54.790
30.009
11.406
220
200
180
160
140
120
100
80
60
40
20
ppm

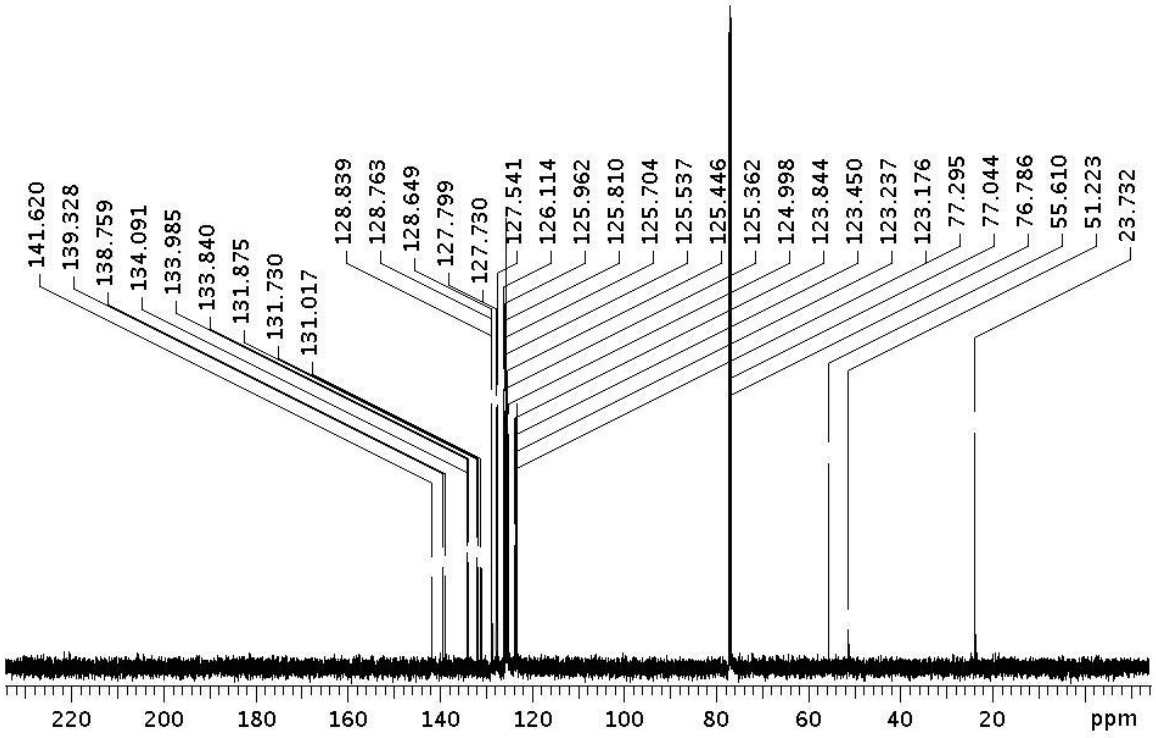

HN
4R-BDN
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
0.97
1.92
5.96
3.86
3.00
1.02
0.99
0.96
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.01
1.15
3.30
3.01
1.32

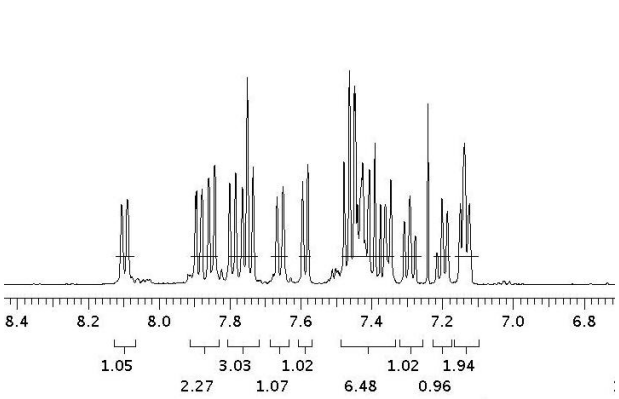

143.595
139.505
137.988
134.149
133.944
131.926
130.940
128.838
128.717
128.436
128.110
127.784
127.586
127.351
126.243
126.175
125.947
125.553
125.462
125.303
125.022
123.398
123.004
77.293
77.042
76.784
62.787
54.775
30.004
11.401
220
200
180
160
140
120
100
80
60
40
20
ppm

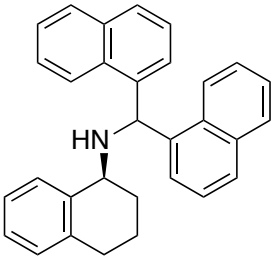

HN
5S-BDN
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
0.99
0.97
1.98
3.05
0.97
4.96
2.01
2.01
1.97
1.93
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
3.04


141.620
139.336
138.766
134.099
133.992
133.848
131.875
131.730
131.025
128.839
128.763
128.656
127.806
127.730
127.541
126.121
125.970
125.818
125.712
125.545
125.453
125.400
124.998
123.852
123.450
123.245
123.176
77.310
77.052
76.802
55.618
51.254
23.732
220
200
180
160
140
120
100
80
60
40
20
ppm

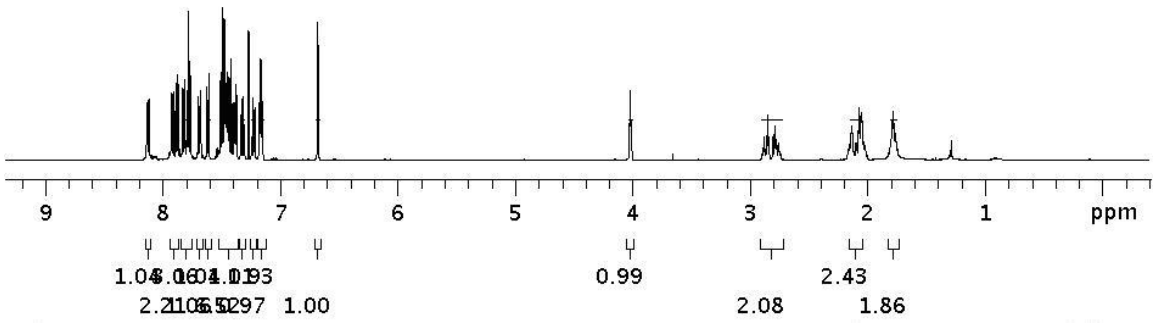

HN
5R-BDN
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
1.02 1.02 1.97 5.04 1.91
5.02 2.04 2.08 0.82
9 8 7 6 5 4 3 2 1 ppm
1.00
0.99
2.99

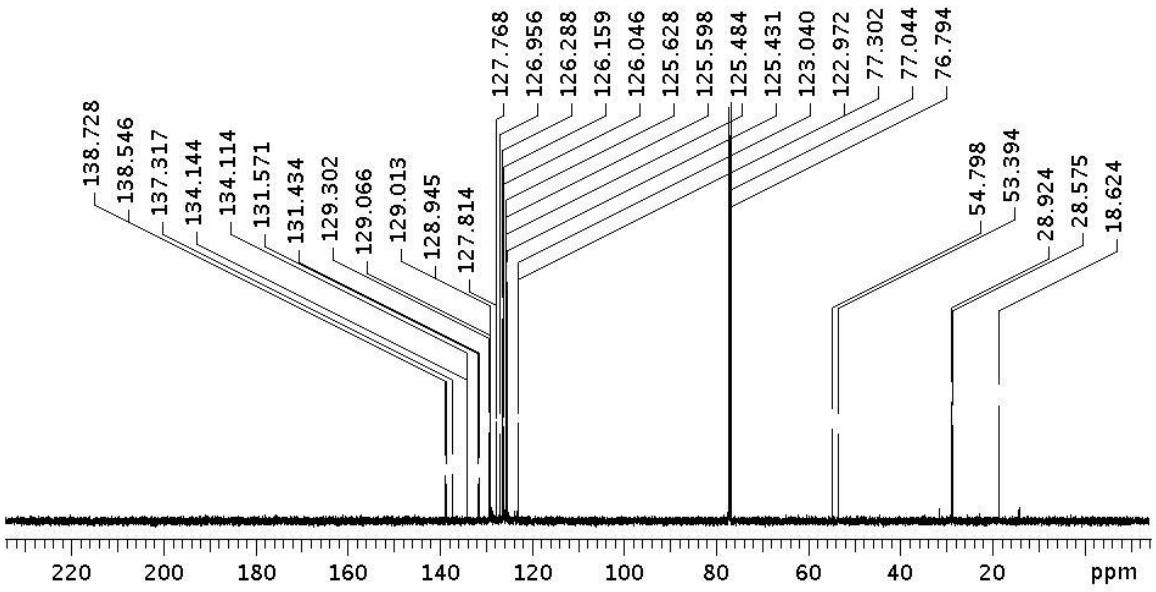

141.620
139.328
138.759
134.091
133.985
133.840
131.875
131.730
131.017
128.839
128.763
128.649
127.799
127.730
127.541
126.114
125.962
125.810
125.704
125.537
125.446
125.362
124.998
123.844
123.450
123.237
123.176
77.295
77.044
76.786
55.610
51.223
23.732
220 200 180 160 140 120 100 80 60 40 20 ppm

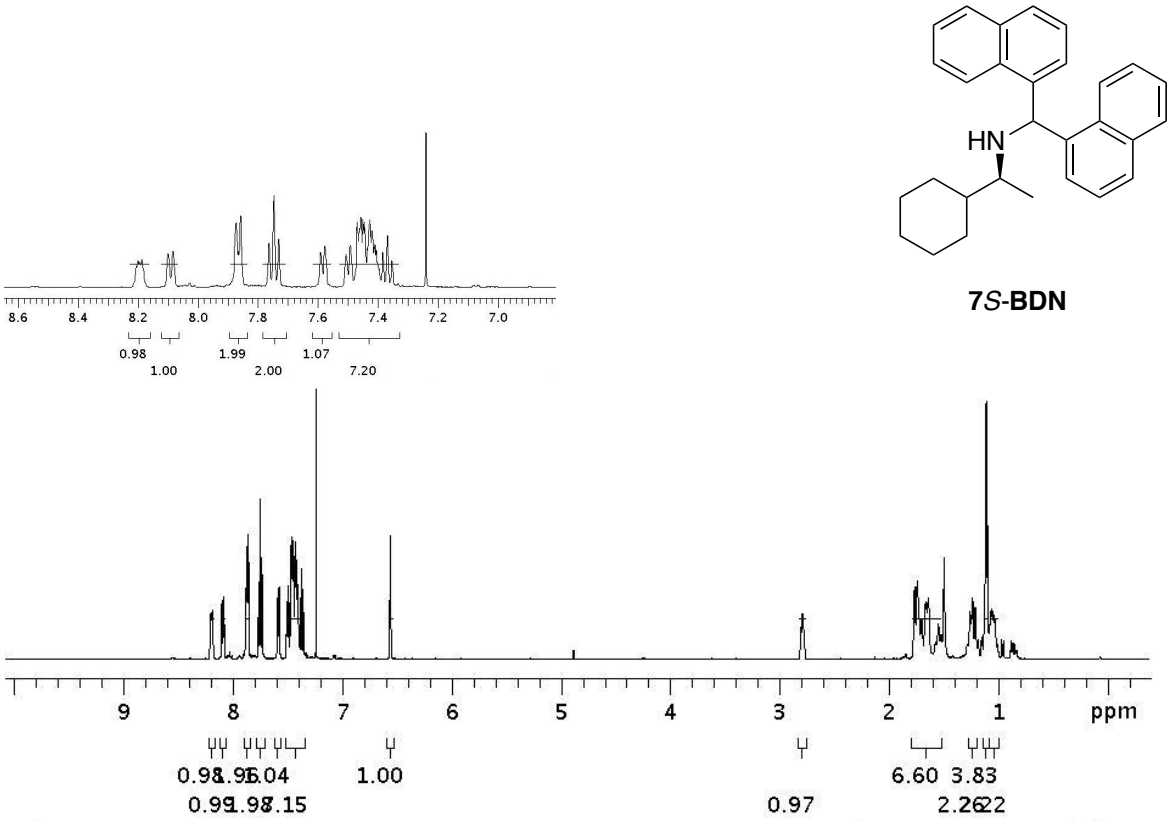

8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
1.05
3.03
1.02
1.02
1.94
2.27
1.07
6.48
0.96

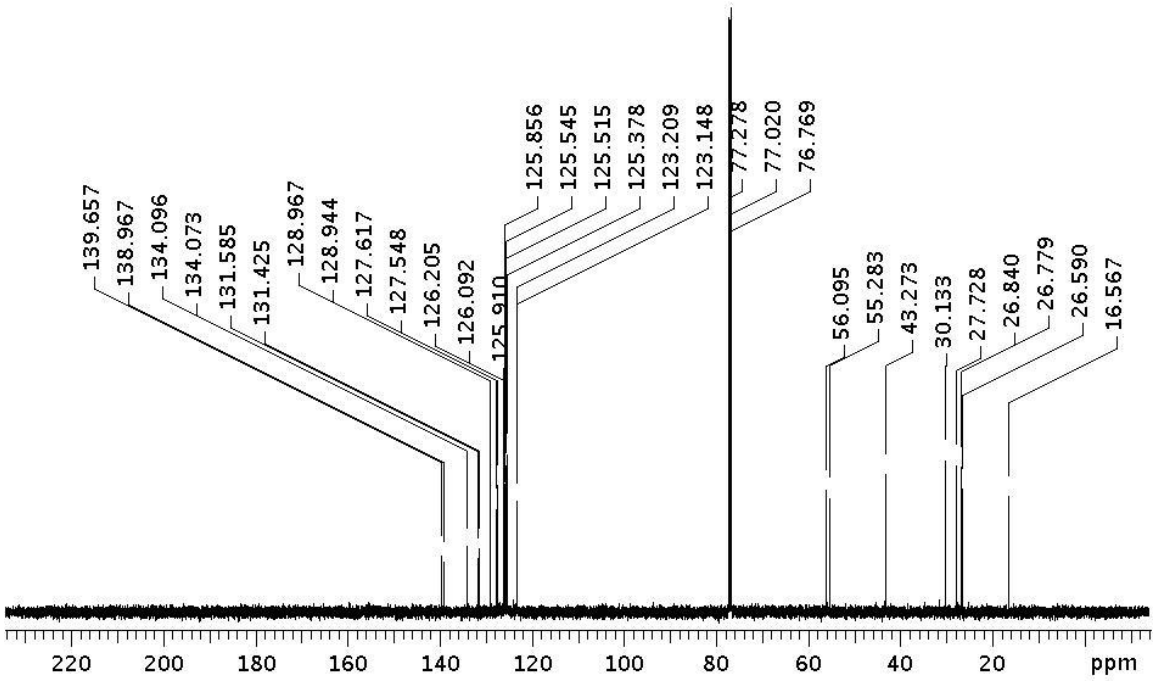

HN

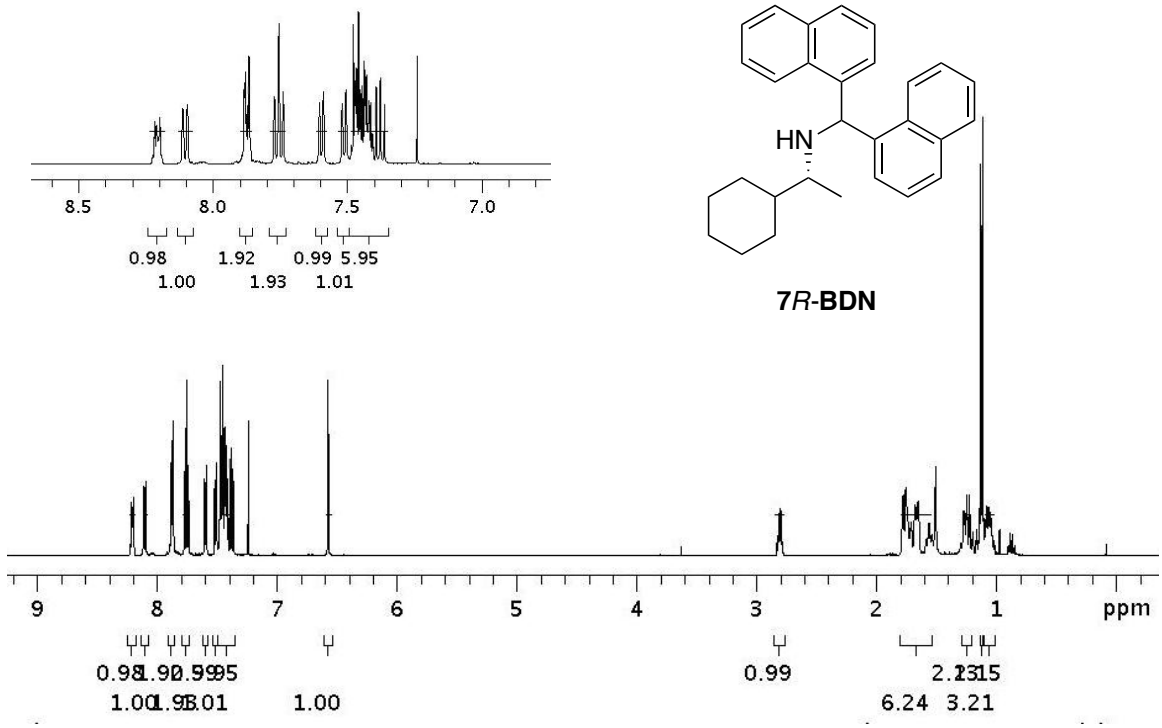
6*S*-BDN

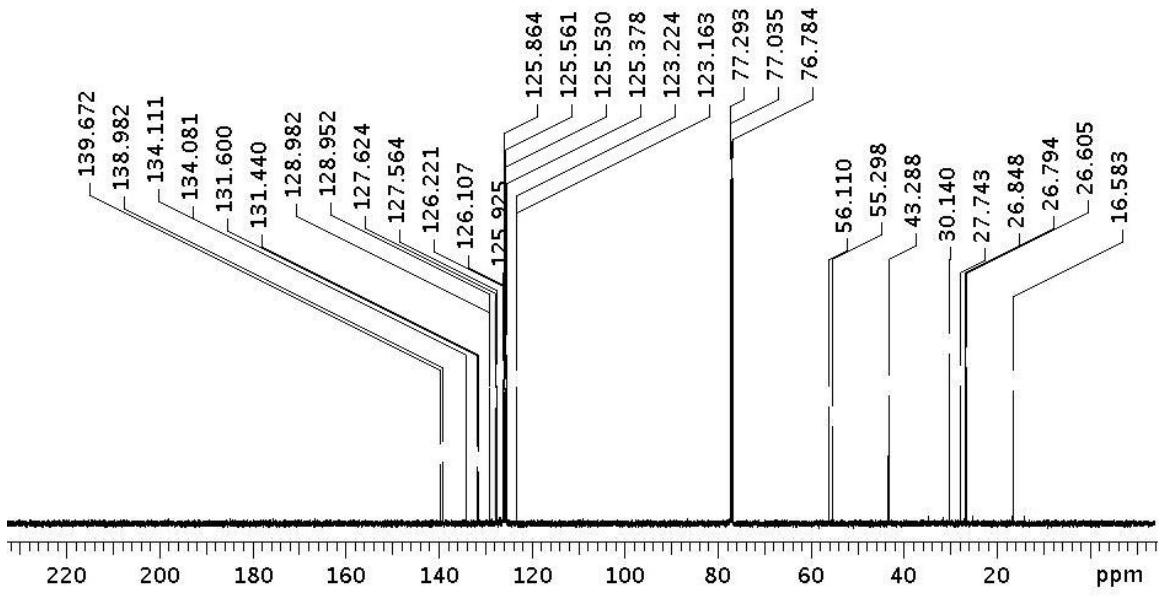

9
8
7
6
5
4
3
2
1
ppm
0.99
2.43
2.08
1.86
1.00

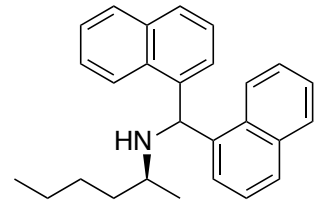

138.728
138.546
137.317
134.144
134.114
131.571
131.434
129.302
129.066
129.013
128.945
127.814
127.768
126.956
126.288
126.159
126.046
125.628
125.598
125.484
125.431
123.040
122.972
77.302
77.044
76.794
54.798
53.394
28.924
28.575
18.624
220
200
180
160
140
120
100
80
60
40
20
ppm


HN
7S-BDN
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
0.98 1.00 1.99 2.00 1.07 7.20
9 8 7 6 5 4 3 2 1 ppm
1.00
0.97
6.60 3.83
2.26

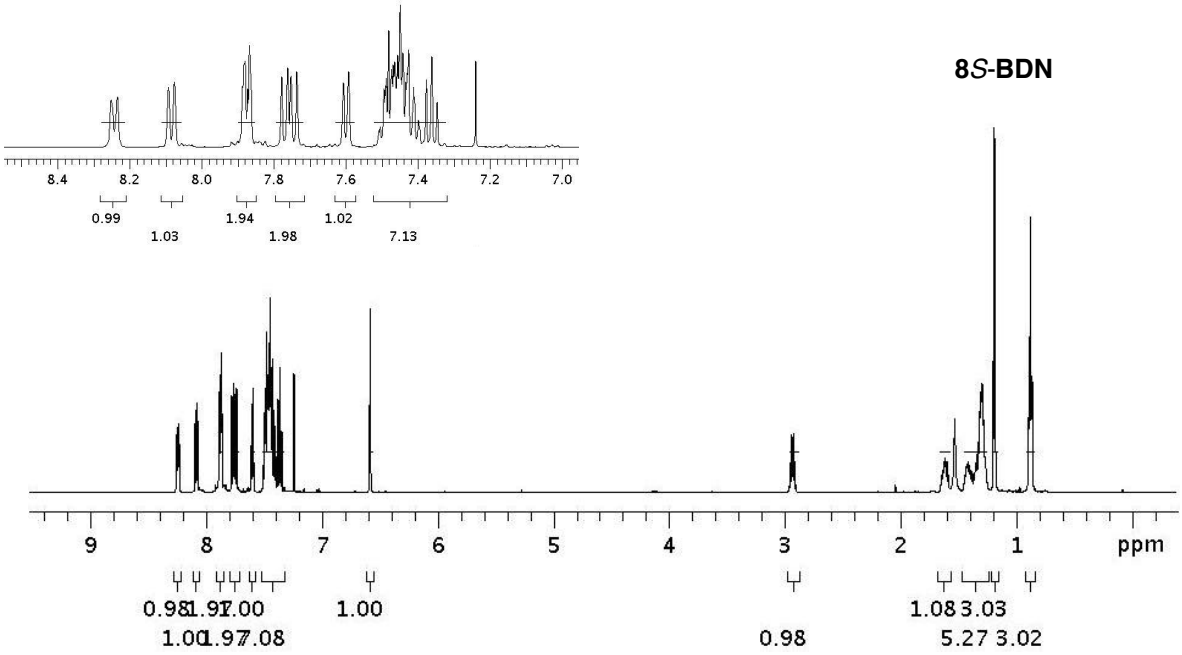

139.657
138.967
134.096
134.073
131.585
131.425
128.967
128.944
127.617
127.548
126.205
126.092
125.910
125.856
125.545
125.515
125.378
123.209
123.148
77.278
77.020
76.769
56.095
55.283
43.273
30.133
27.728
26.840
26.779
26.590
16.567
220 200 180 160 140 120 100 80 60 40 20 ppm

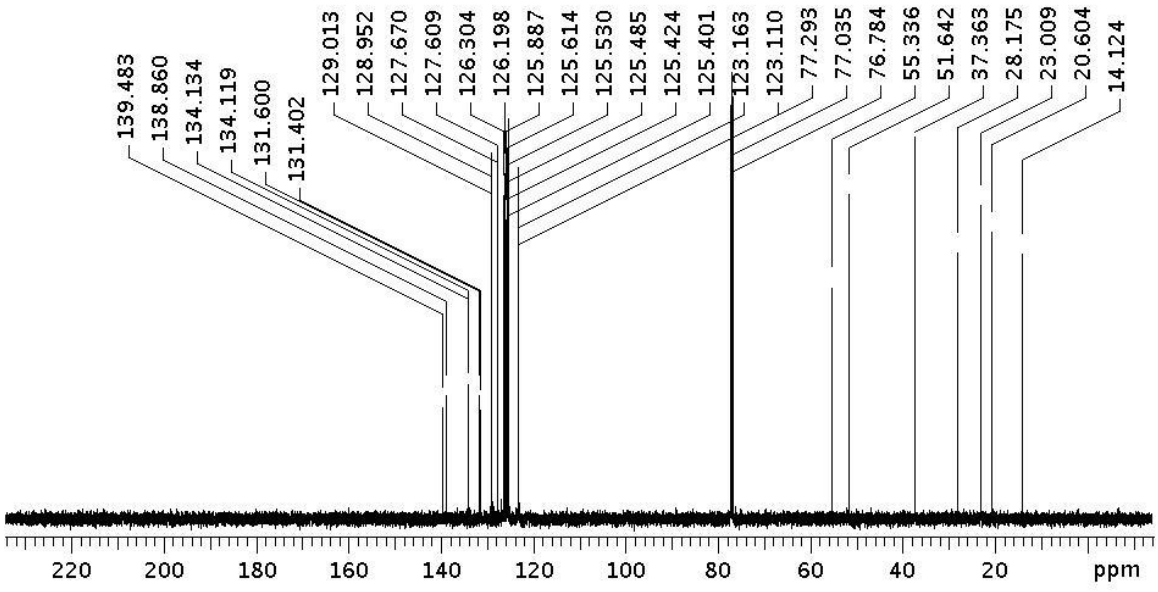

HN
7R-BDN
ppm

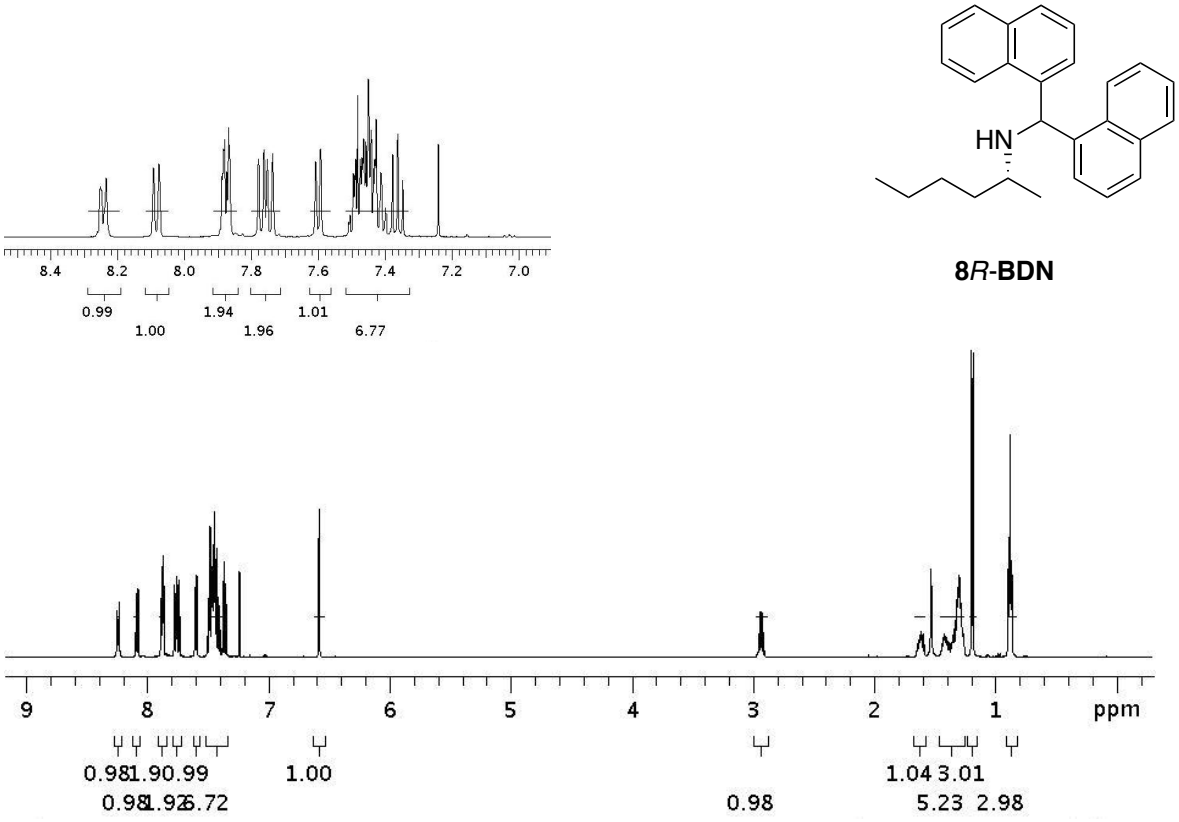

139.672
138.982
134.111
134.081
131.600
131.440
128.982
128.952
127.624
127.564
126.221
126.107
125.925
125.864
125.561
125.530
125.378
123.224
123.163
77.293
77.035
76.784
56.110
55.298
43.288
30.140
27.743
26.848
26.794
26.605
16.583
ppm


HN

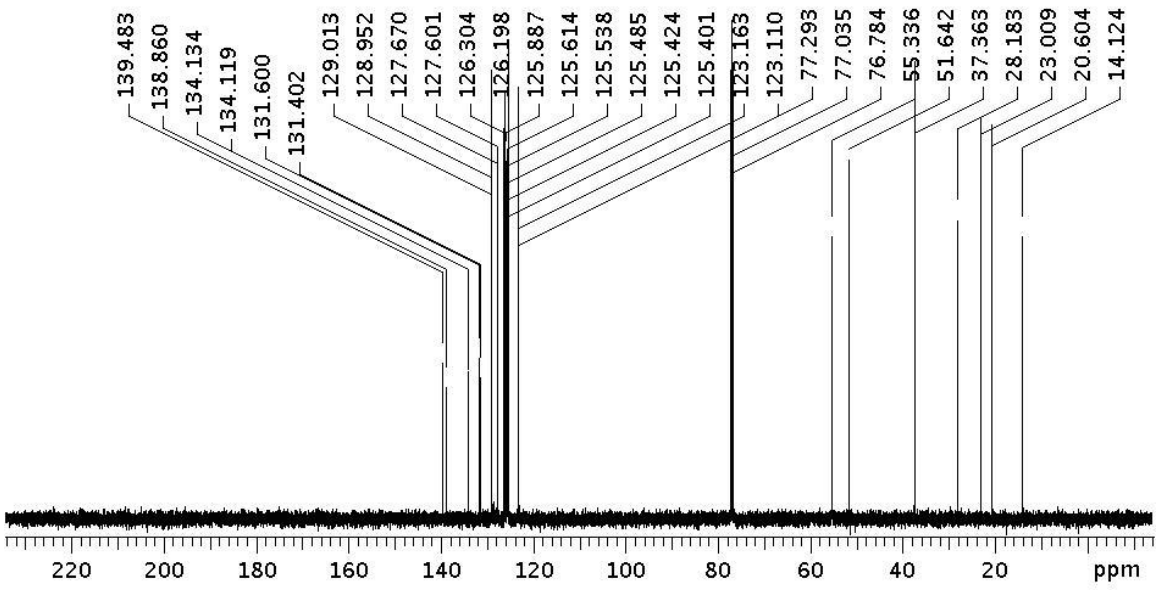
8*S*-BDN

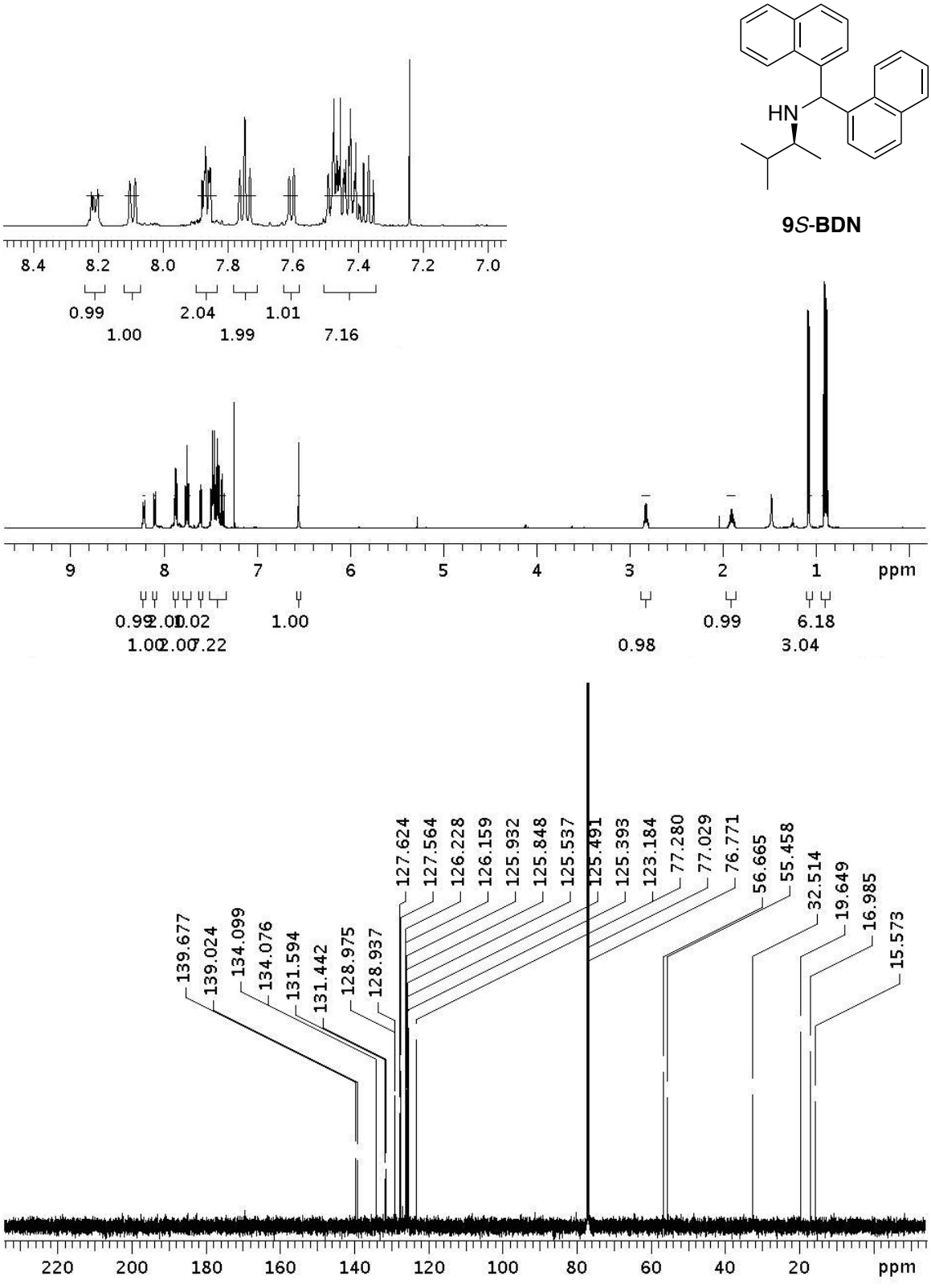

8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0.99
1.03
1.94
1.98
1.02
7.13
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.97
7.00
1.00
1.08
3.03
5.27
3.02

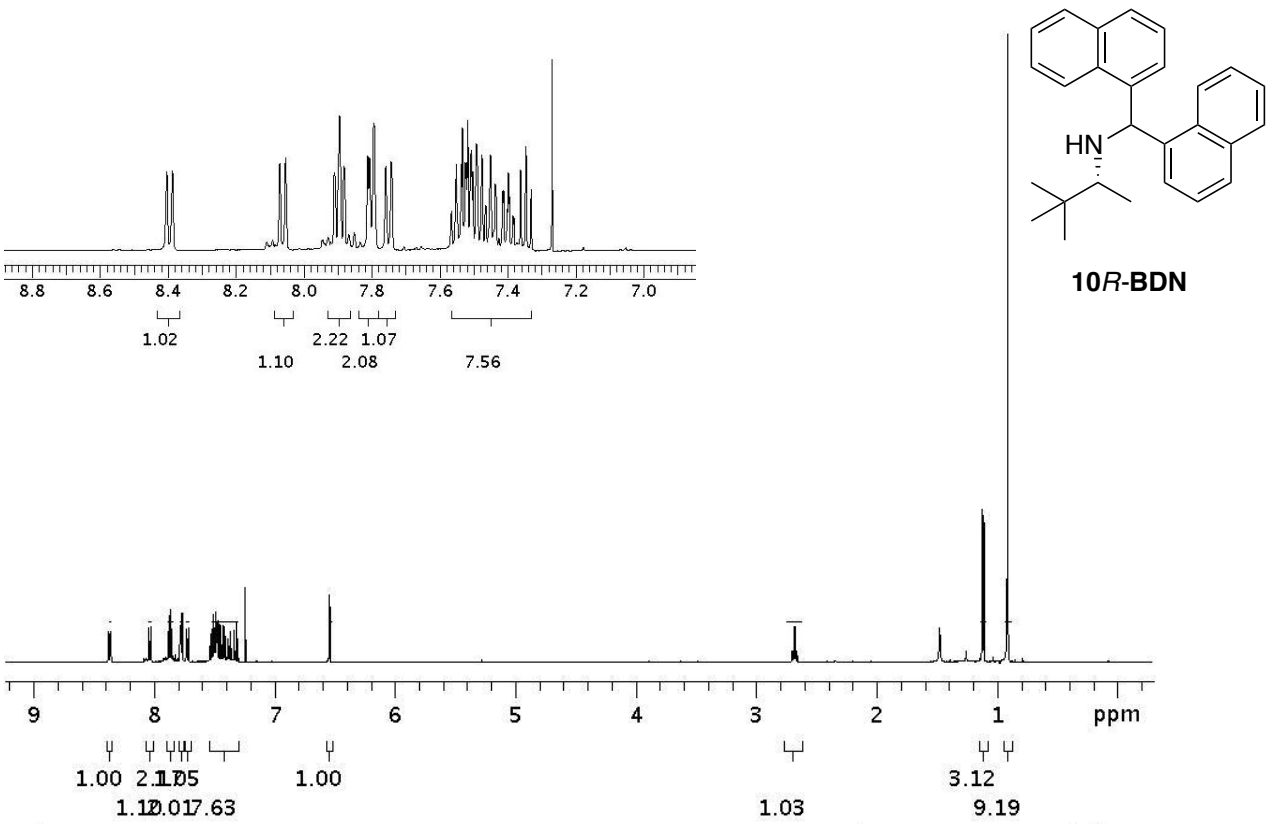

139.483
138.860
134.134
134.119
131.600
131.402
129.013
128.952
127.670
127.609
126.304
126.198
125.887
125.614
125.530
125.485
125.424
125.401
123.163
123.110
77.293
77.035
76.784
55.336
51.642
37.363
28.175
23.009
20.604
14.124
220
200
180
160
140
120
100
80
60
40
20
ppm

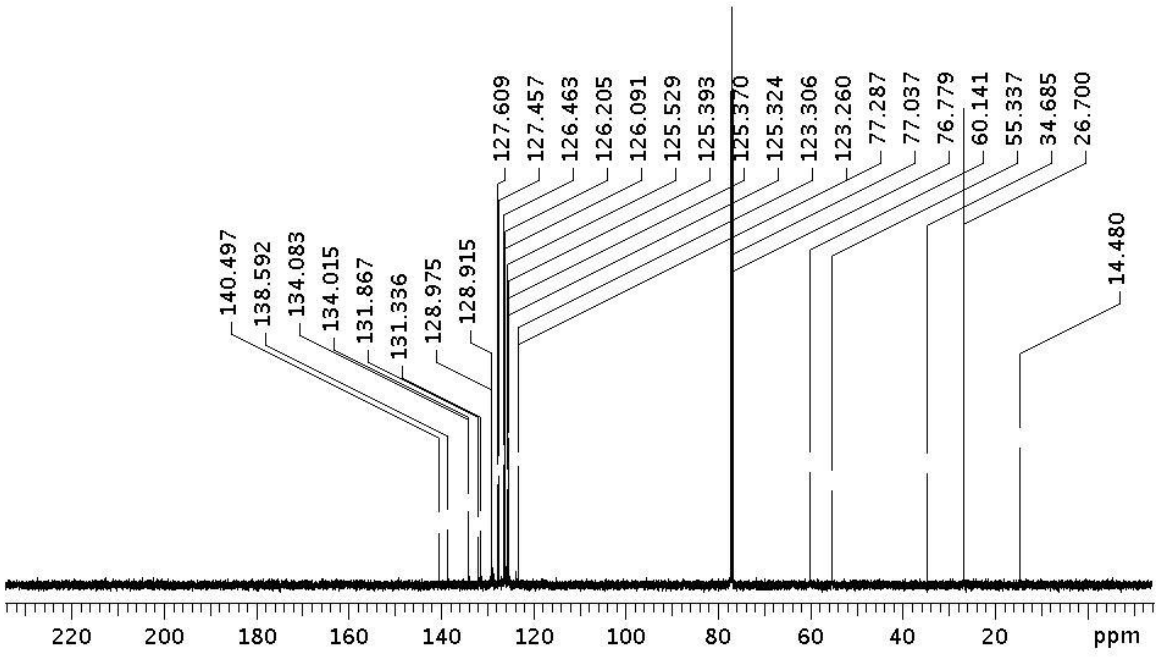

HN
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0.99
1.00
1.94
1.96
1.01
6.77
9
8
7
6
5
4
3
2
1
ppm
0.98
1.90
0.99
1.00
0.98
1.04
3.01
0.98
1.92
6.72
5.23
2.98

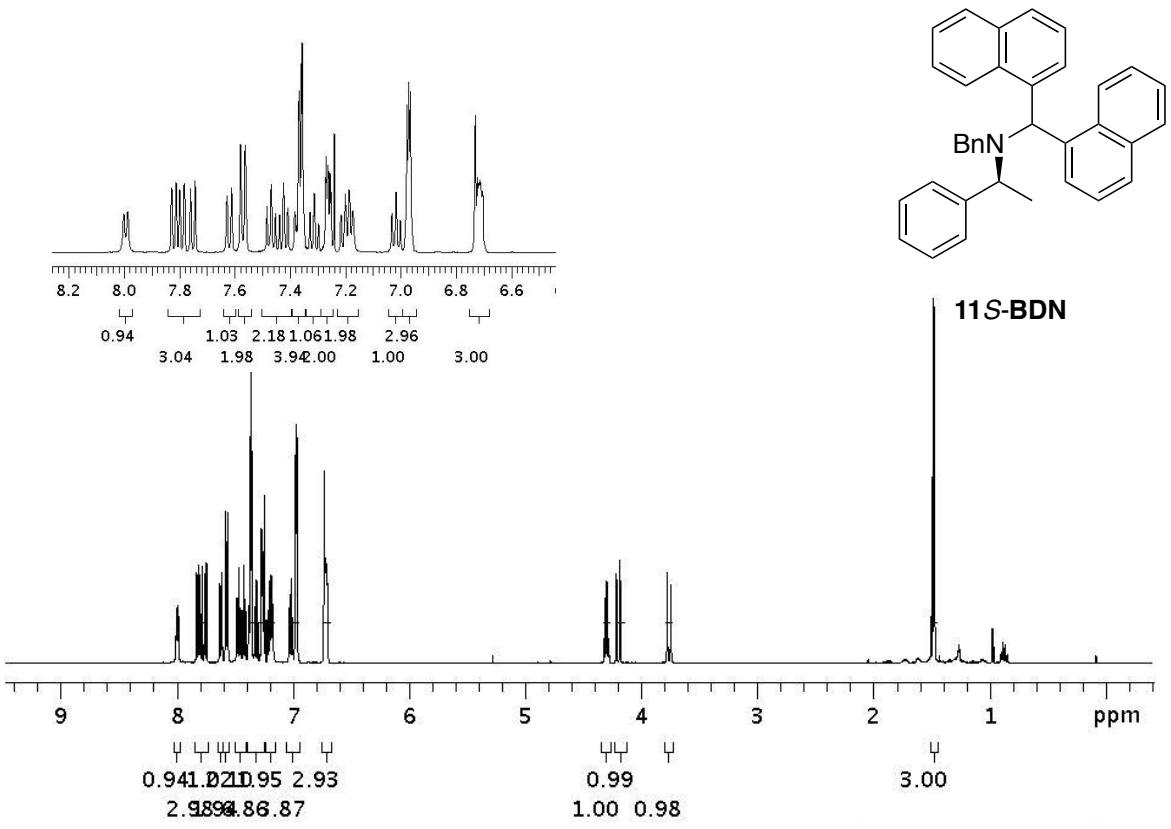
8*R*-BDN

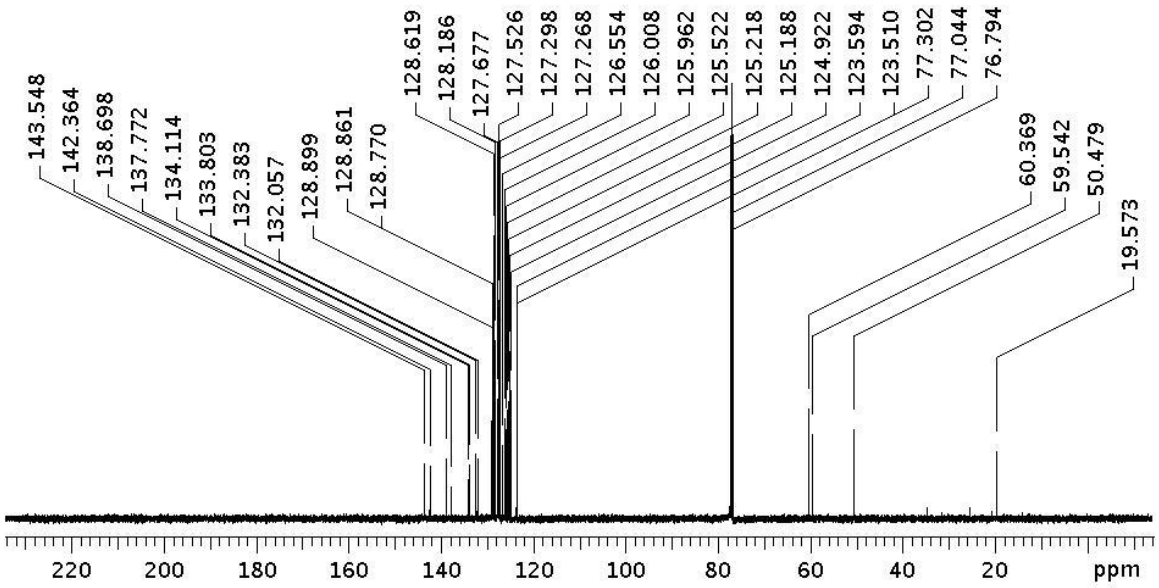

139.483
138.860
134.134
134.119
131.600
131.402
129.013
128.952
127.670
127.601
126.304
126.198
125.887
125.614
125.538
125.485
125.424
125.401
123.163
123.110
77.293
77.035
76.784
55.336
51.642
37.363
28.183
23.009
20.604
14.124
220
200
180
160
140
120
100
80
60
40
20
ppm

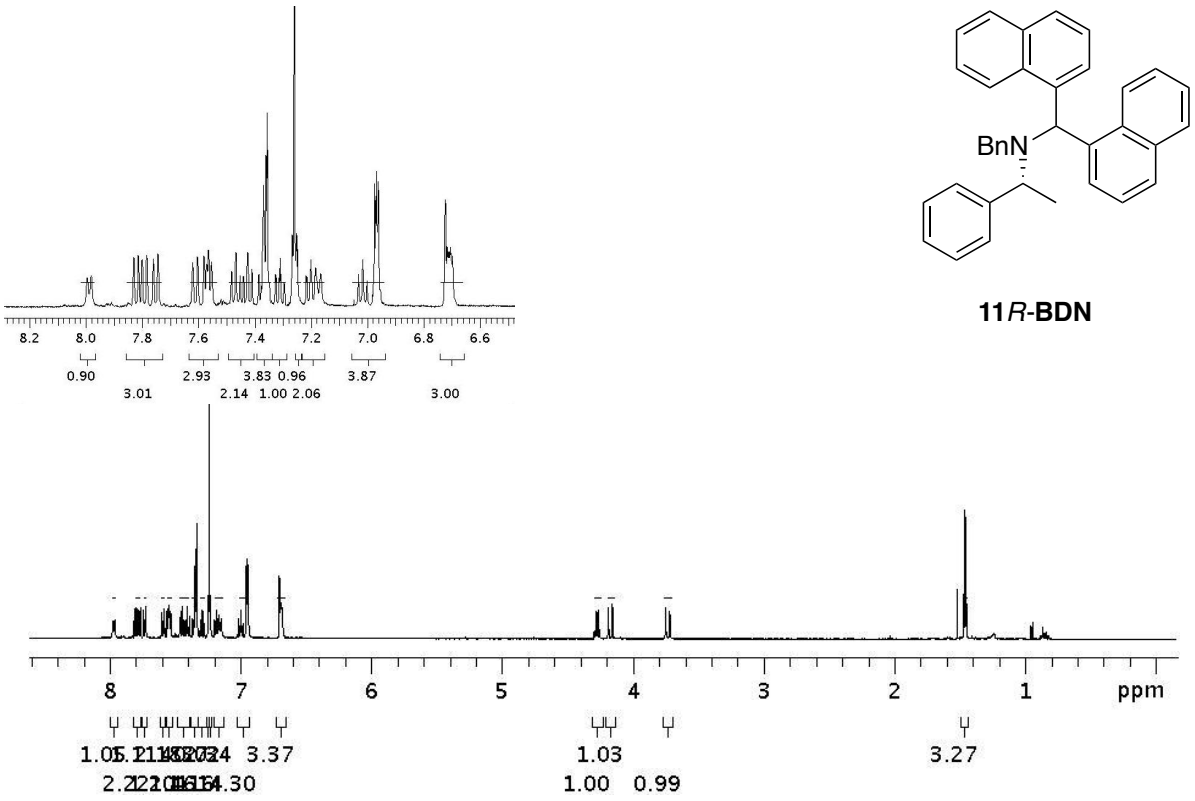

HN
9S-BDN
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0.99
1.00
2.04
1.99
1.01
7.16
9
8
7
6
5
4
3
2
1
ppm
0.98
0.99
6.18
3.04
1.00
139.677
139.024
134.099
134.076
131.594
131.442
128.975
128.937
127.624
127.564
126.228
126.159
125.932
125.848
125.537
125.491
125.393
123.184
77.280
77.029
76.771
56.665
55.458
32.514
19.649
16.985
15.573
220
200
180
160
140
120
100
80
60
40
20
ppm


HN
10R-BDN
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
1.02 1.10 2.22 2.08 1.07 7.56
9 8 7 6 5 4 3 2 1 ppm
1.00 1.00 1.03 3.12 9.19


127.609
127.457
126.463
126.205
126.091
125.529
125.393
125.370
125.324
123.306
123.260
77.287
77.037
76.779
60.141
55.337
34.685
26.700
140.497
138.592
134.083
134.015
131.867
131.336
128.975
128.915
14.480
220 200 180 160 140 120 100 80 60 40 20 ppm

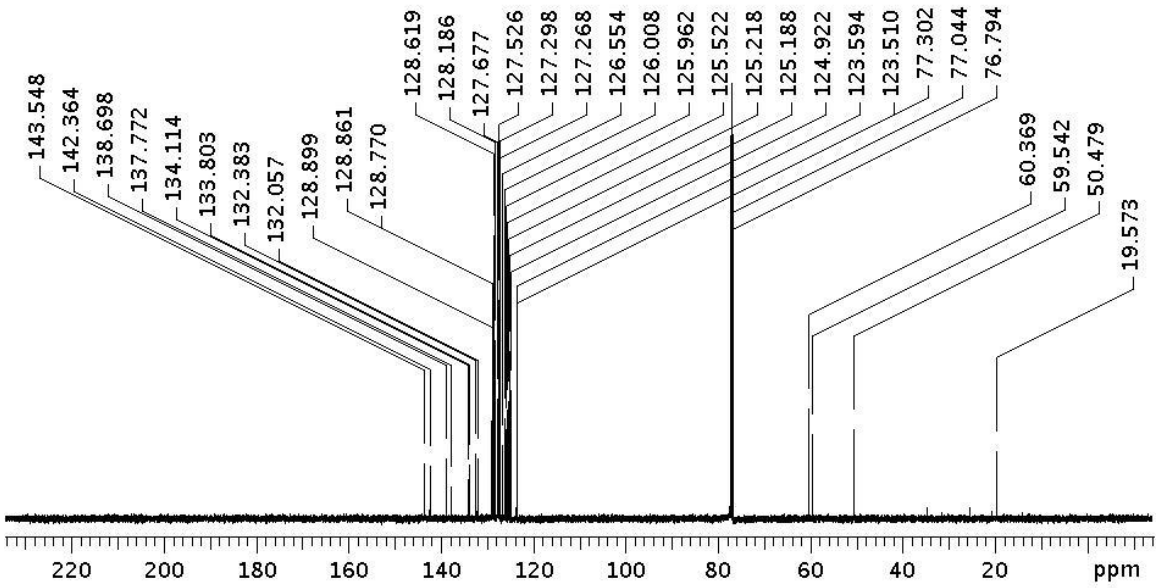

BnN
11S-BDN
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
0.94 1.03 2.18 1.06 1.98 2.96
3.04 1.98 3.94 2.00 1.00 3.00
9 8 7 6 5 4 3 2 1 ppm
0.99 3.00
1.00 0.98

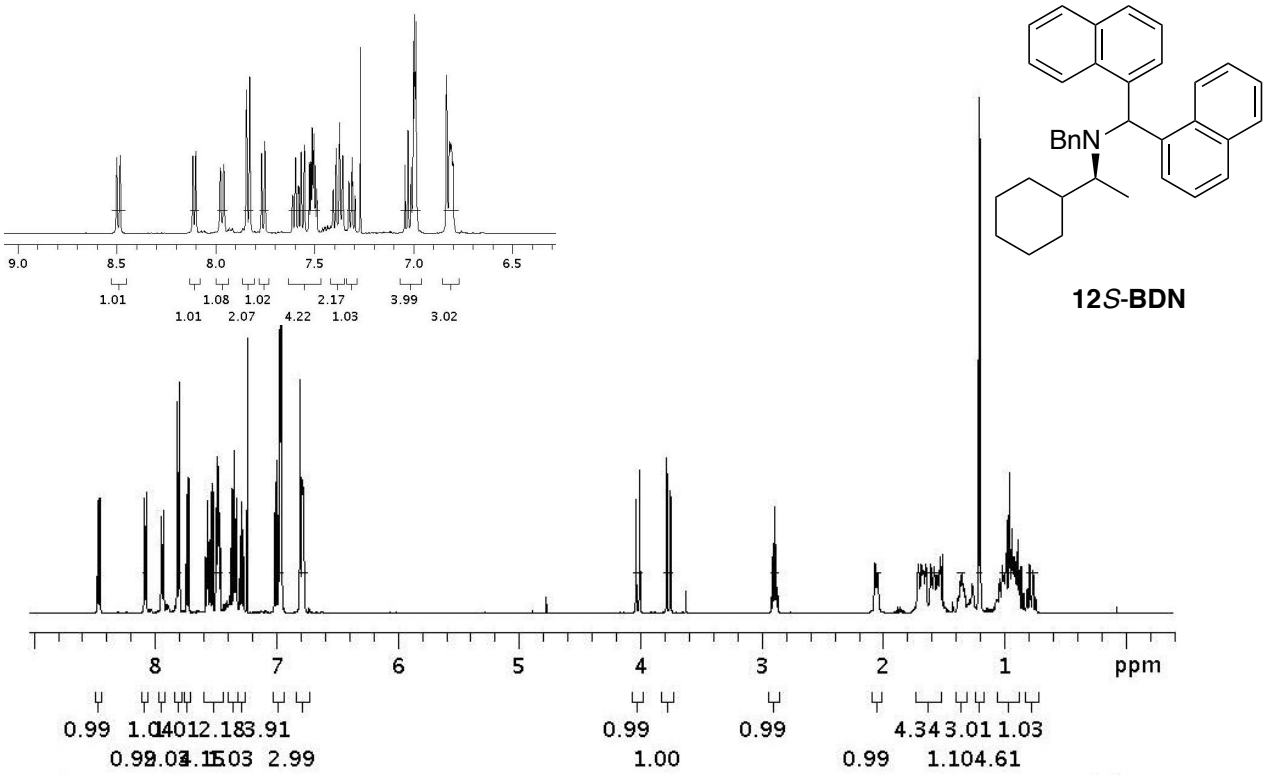

143.548
142.364
138.698
137.772
134.114
133.803
132.383
132.057
128.899
128.861
128.770
128.619
128.186
127.677
127.526
127.298
127.268
126.554
126.008
125.962
125.522
125.218
125.188
124.922
123.594
123.510
77.302
77.044
76.794
60.369
59.542
50.479
19.573
220 200 180 160 140 120 100 80 60 40 20 ppm

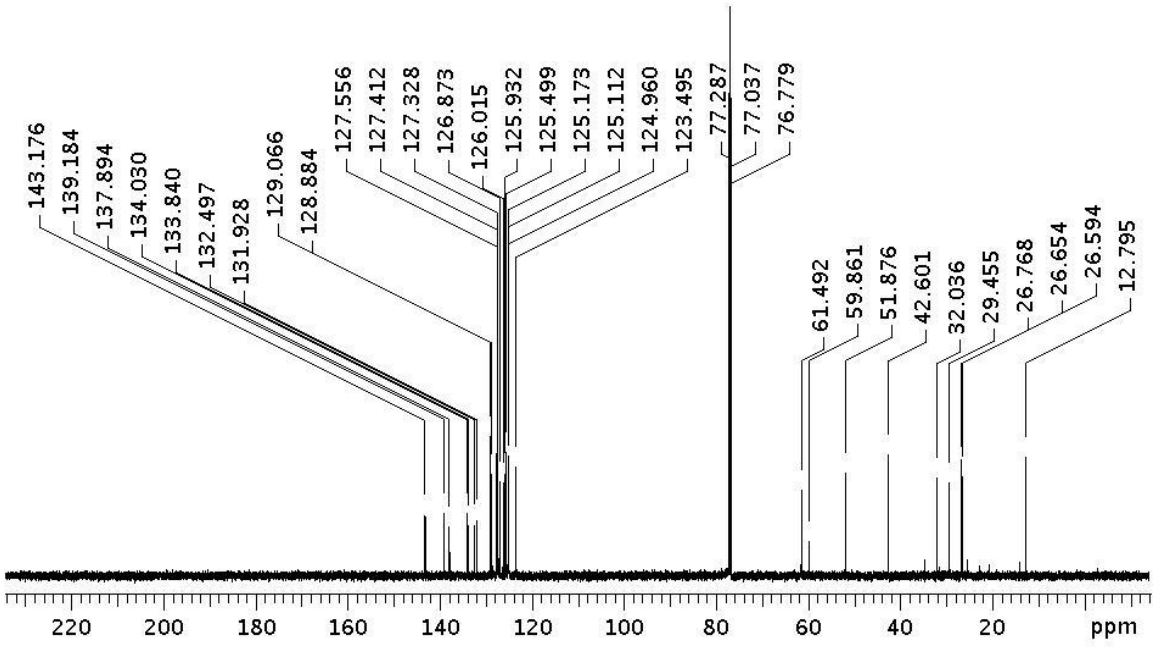

8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
0.90
3.01
2.93
3.83
0.96
2.14
1.00
2.06
3.87
3.00
8
7
6
5
4
3
2
1
ppm
3.37
1.03
1.00
0.99
3.27

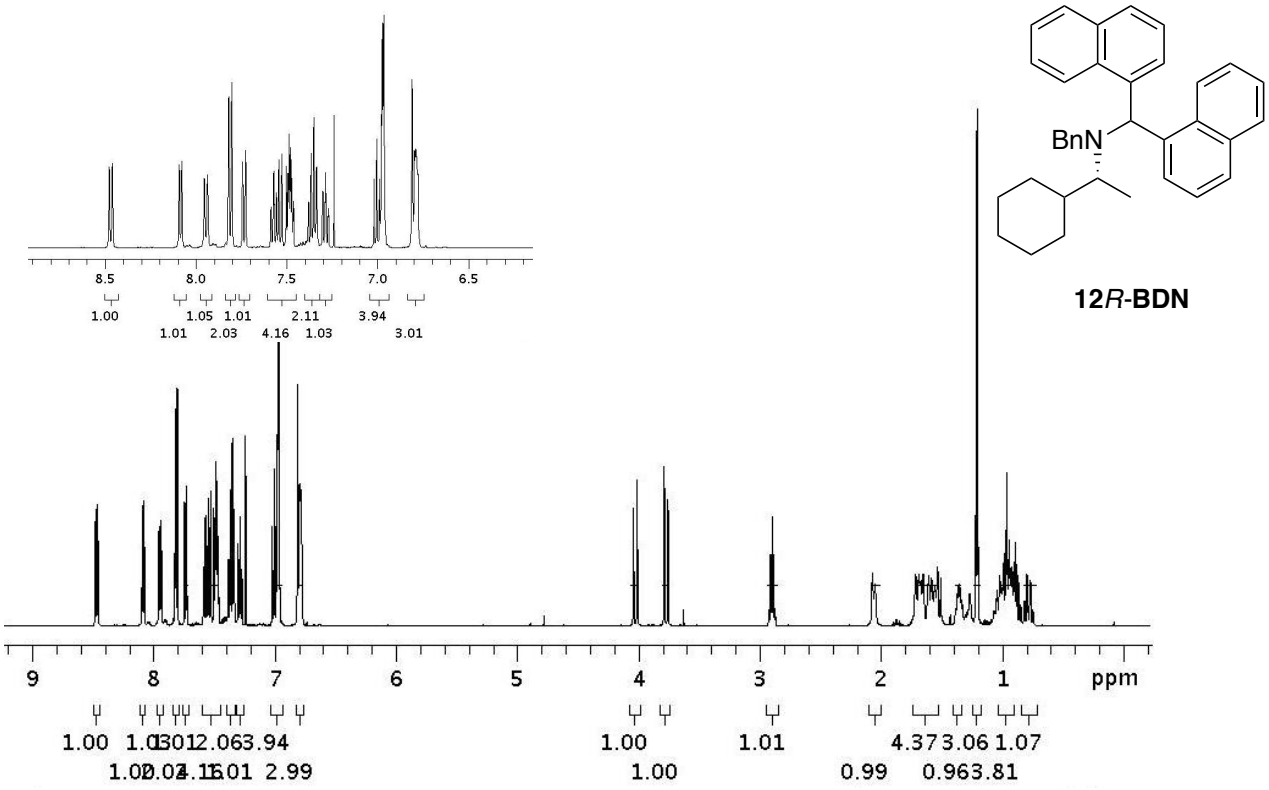
BnN

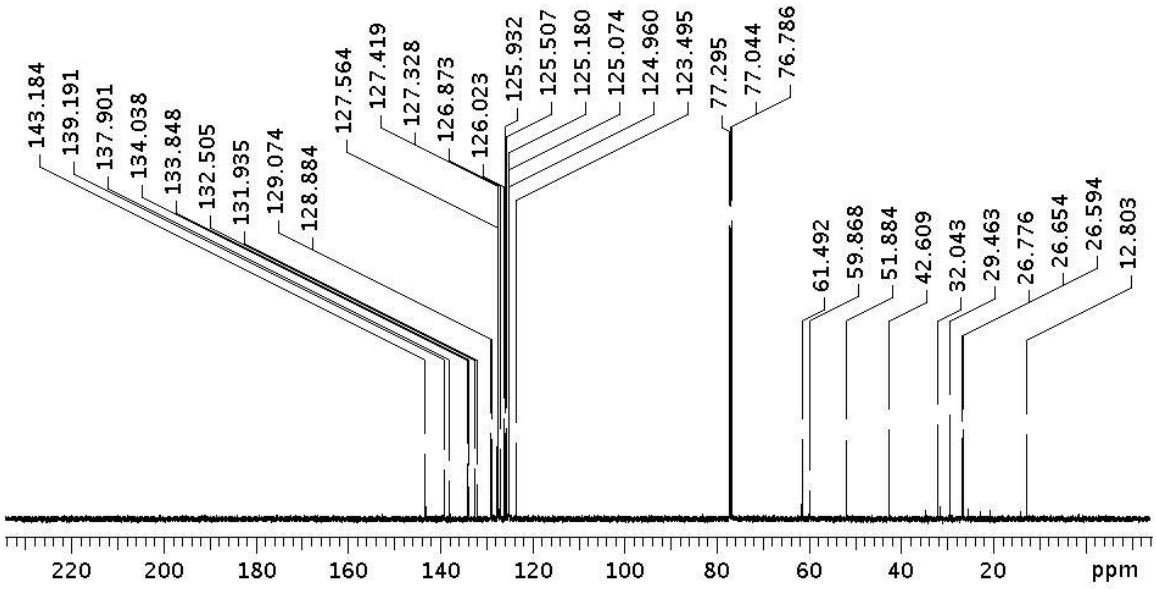
11*R*-BDN

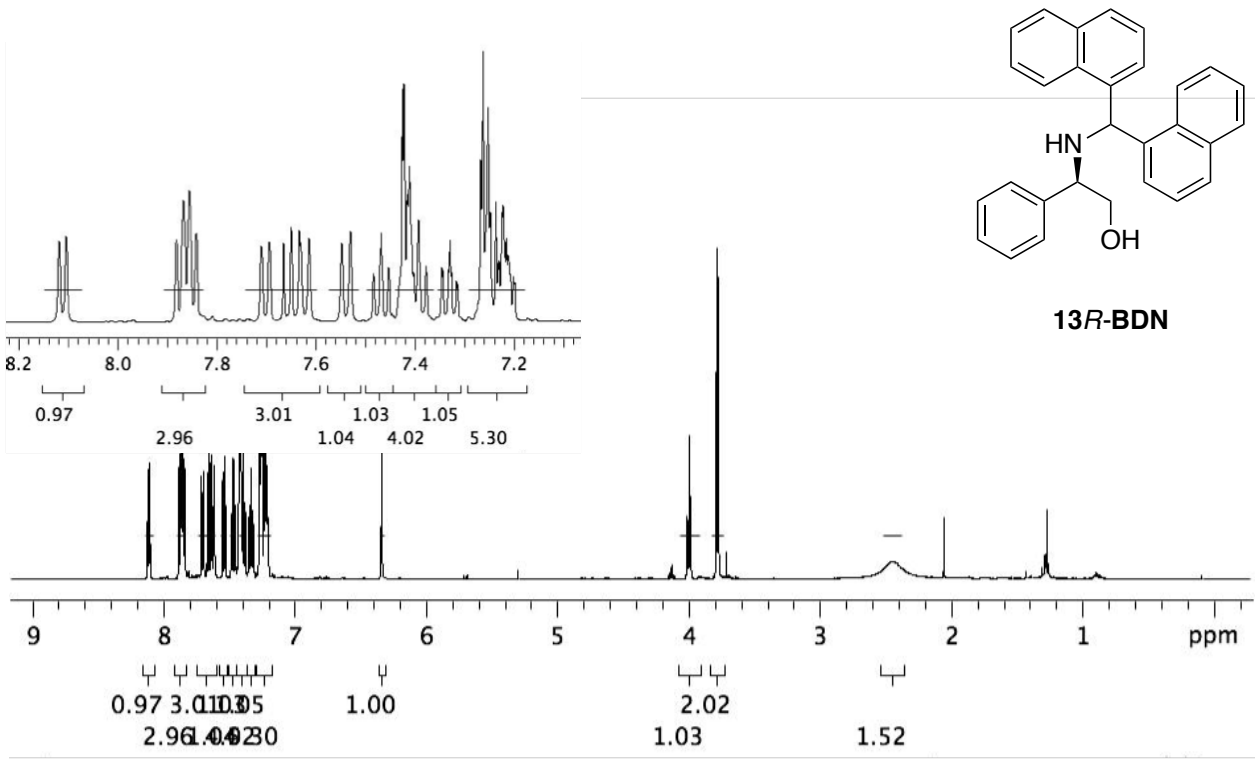

143.548
142.364
138.698
137.772
134.114
133.803
132.383
132.057
128.899
128.861
128.770
128.619
128.186
127.677
127.526
127.298
127.268
126.554
126.008
125.962
125.522
125.218
125.188
124.922
123.594
123.510
77.302
77.044
76.794
60.369
59.542
50.479
19.573
220
200
180
160
140
120
100
80
60
40
20
ppm

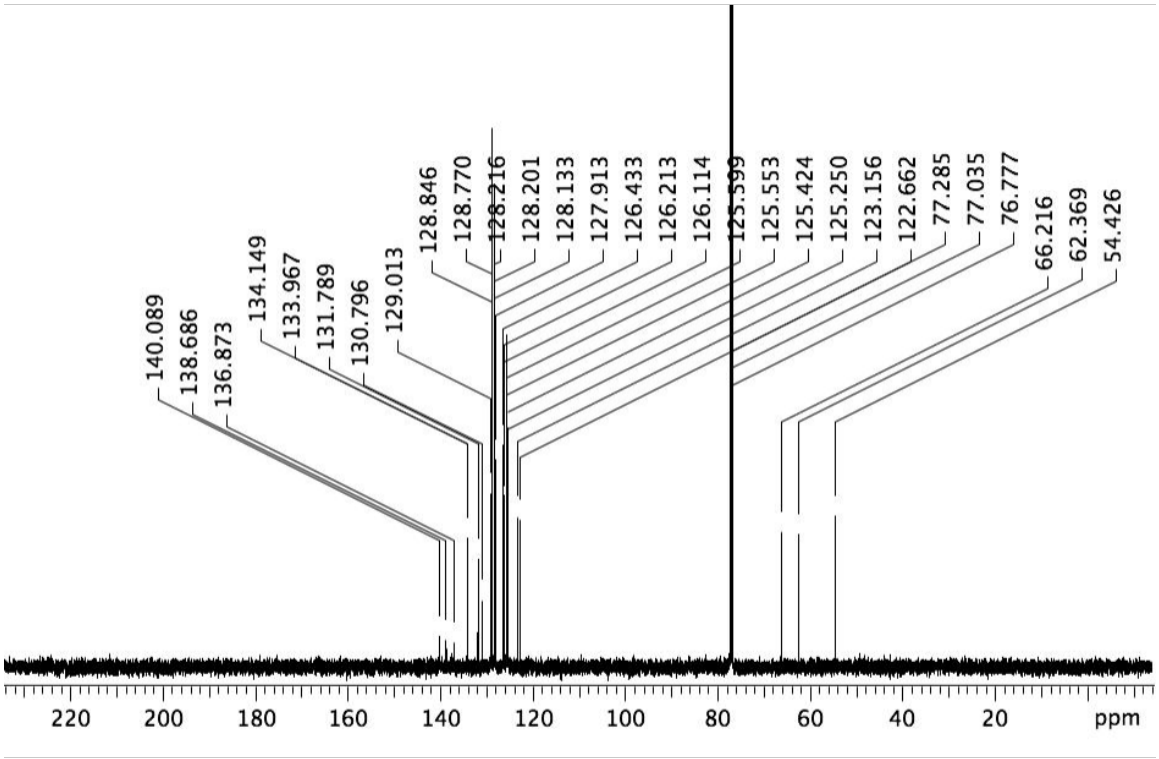

BnN
12S-BDN
ppm

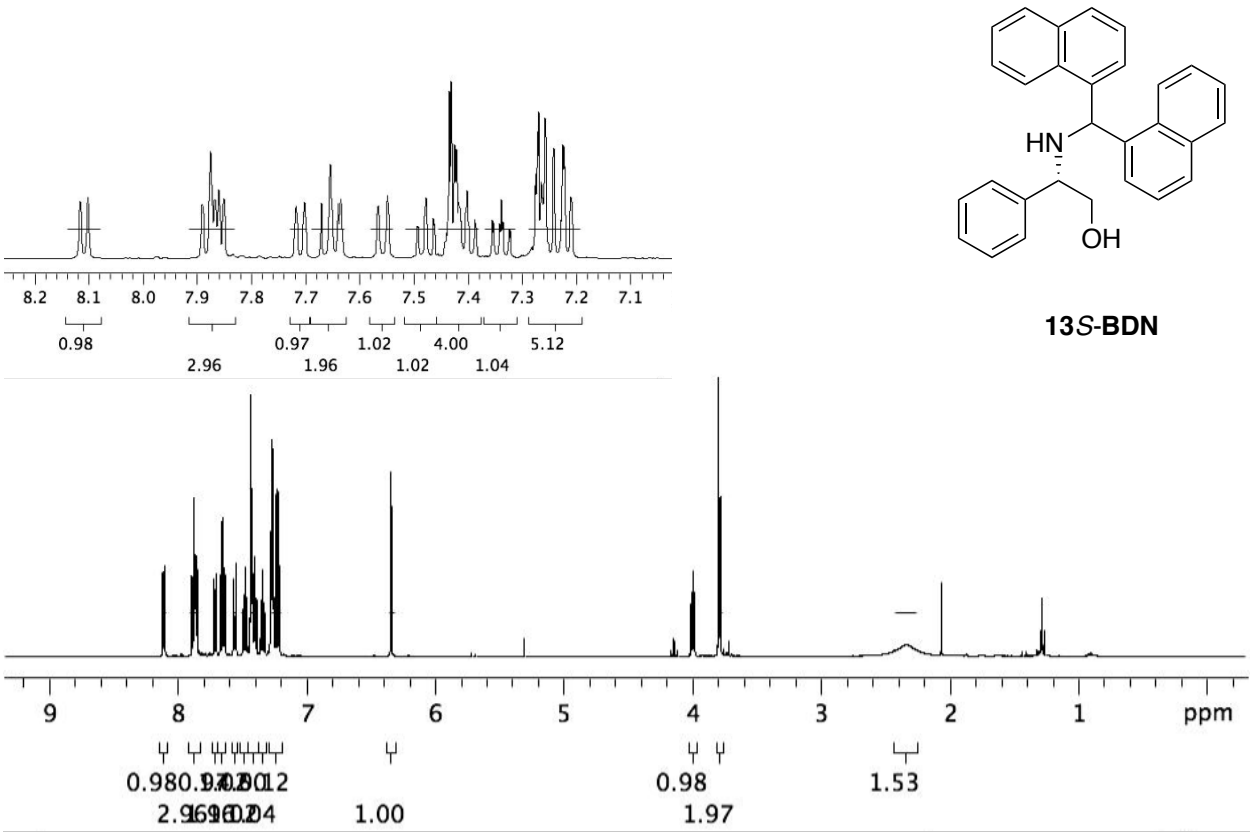

143.176
139.184
137.894
134.030
133.840
132.497
131.928
129.066
128.884
127.556
127.412
127.328
126.873
126.015
125.932
125.499
125.173
125.112
124.960
123.495
77.287
77.037
76.779
61.492
59.861
51.876
42.601
32.036
29.455
26.768
26.654
26.594
12.795
ppm

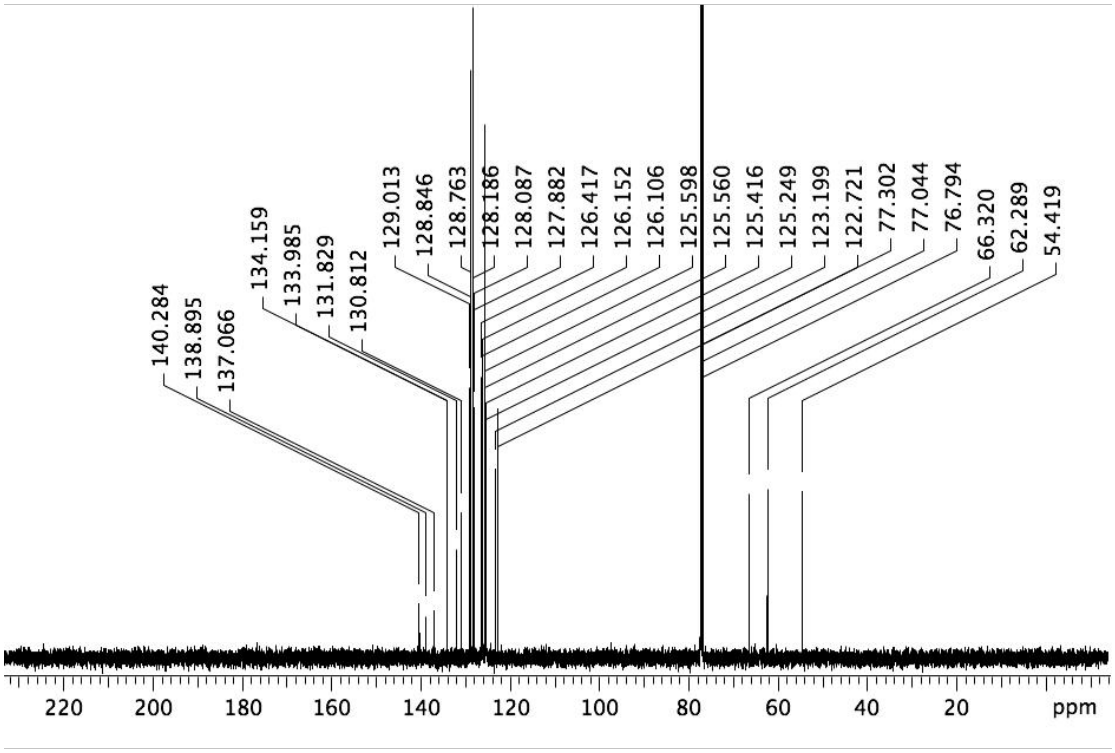

BnN
12R-BDN
ppm

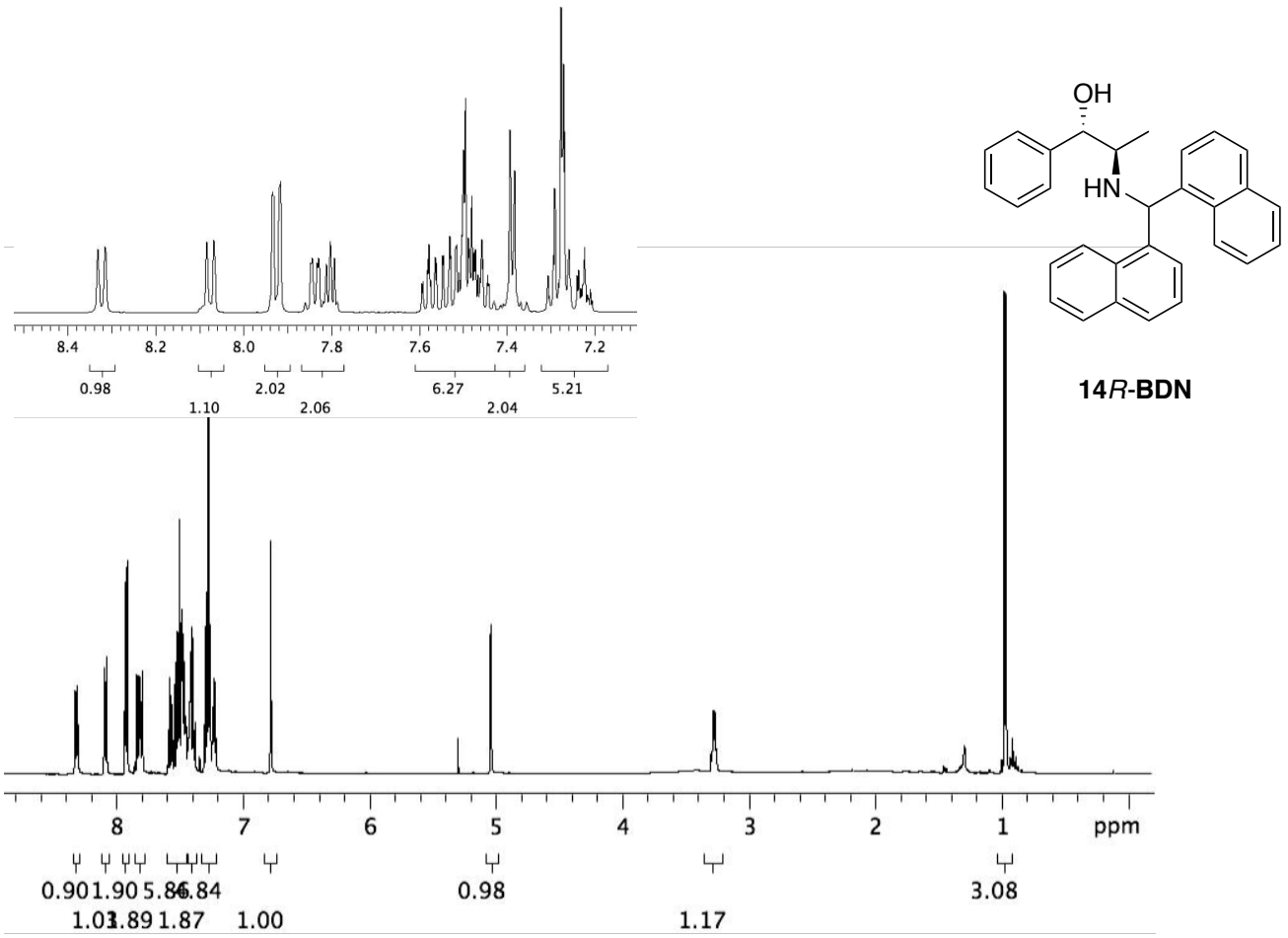

143.184
139.191
137.901
134.038
133.848
132.505
131.935
129.074
128.884
127.564
127.419
127.328
126.873
126.023
125.932
125.507
125.180
125.074
124.960
123.495
77.295
77.044
76.786
61.492
59.868
51.884
42.609
32.043
29.463
26.776
26.654
26.594
12.803
ppm

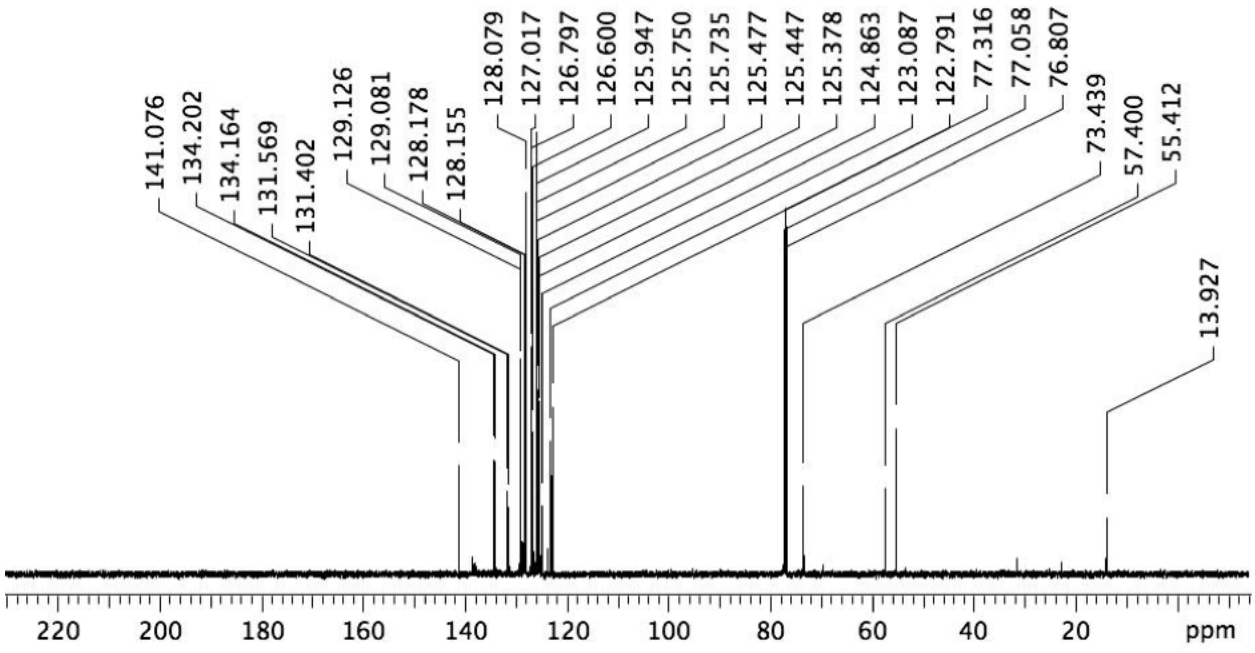

HN
OH
13R-BDN
8.2
8.0
7.8
7.6
7.4
7.2
0.97
3.01
1.03
1.05
2.96
1.04
4.02
5.30
9
8
7
6
5
4
3
2
1
ppm
0.97
1.00
2.02
1.03
1.52

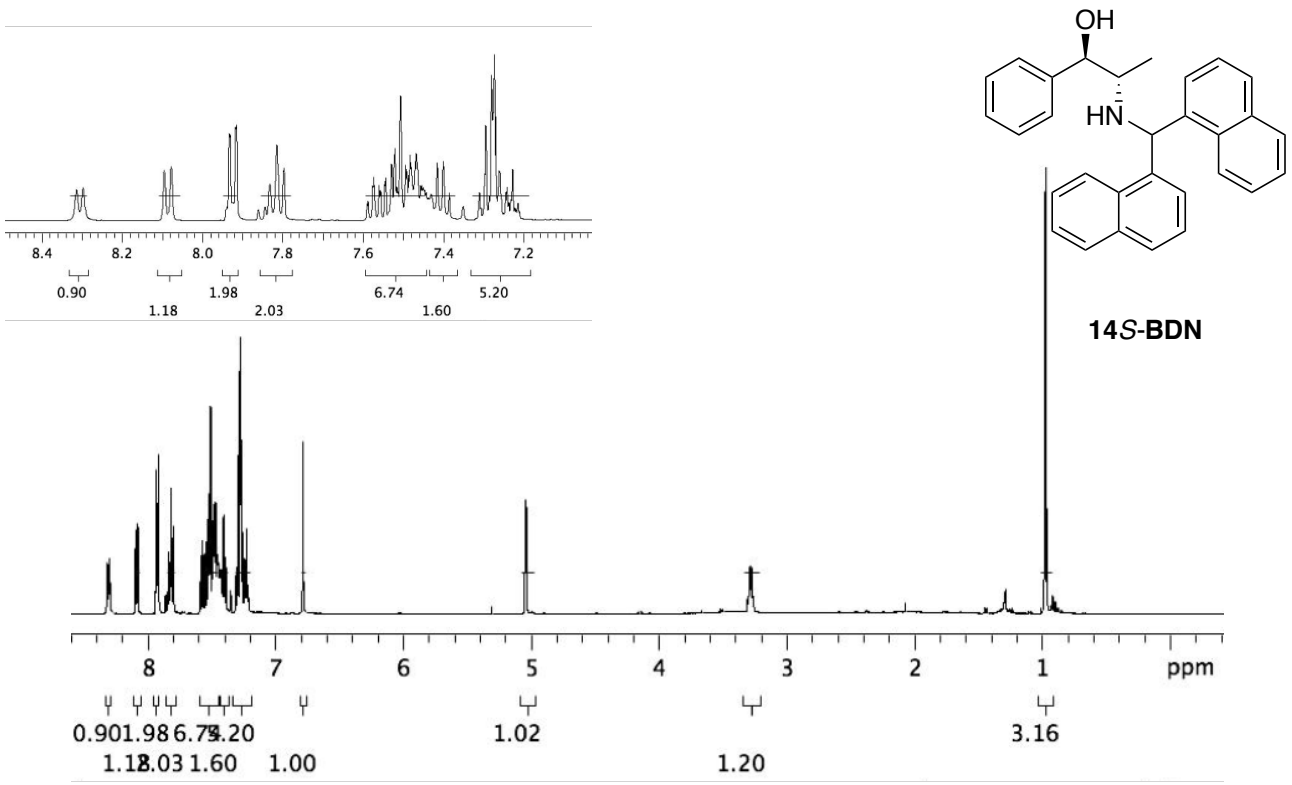

140.089
138.686
136.873
134.149
133.967
131.789
130.796
129.013
128.846
128.770
128.216
128.201
128.133
127.913
126.433
126.213
126.114
125.553
125.424
125.250
123.156
122.662
77.285
77.035
76.777
66.216
62.369
54.426
220
200
180
160
140
120
100
80
60
40
20
ppm

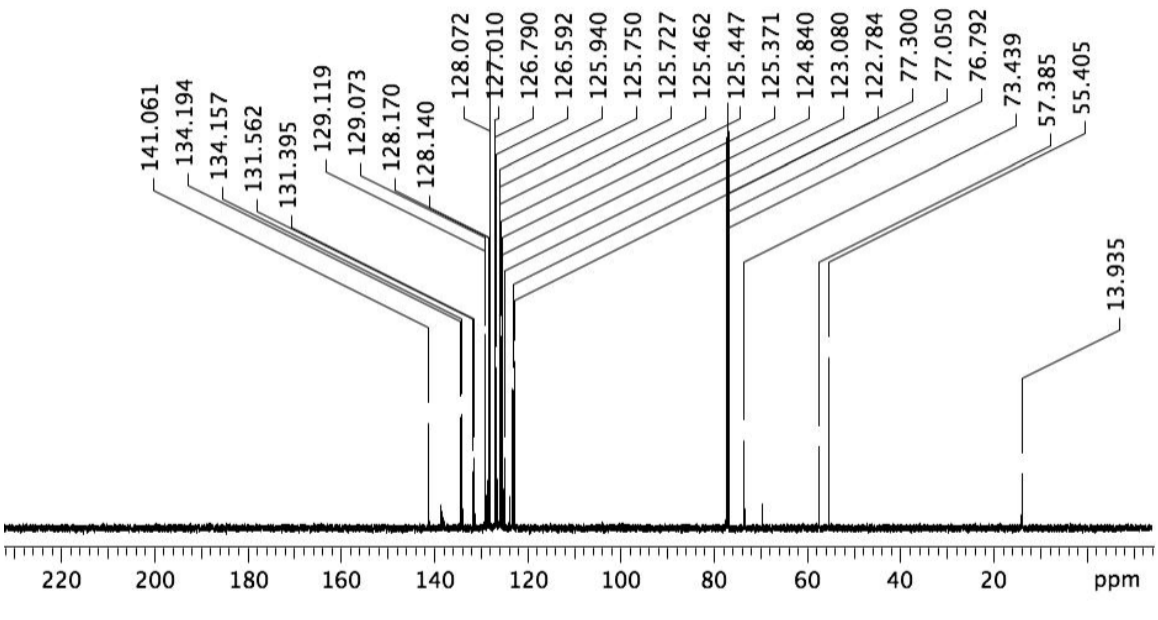

HN
OH
13S-BDN
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
0.98 2.96 0.97 1.96 1.02 1.02 4.00 1.04 5.12
9 8 7 6 5 4 3 2 1 ppm
0.98 1.00 1.97 1.53


140.284
138.895
137.066
134.159
133.985
131.829
130.812
129.013
128.846
128.763
128.186
128.087
127.882
126.417
126.152
126.106
125.598
125.560
125.416
125.249
123.199
122.721
77.302
77.044
76.794
66.320
62.289
54.419
220 200 180 160 140 120 100 80 60 40 20 ppm


OH
HN
14R-BDN
8.4
8.2
8.0
7.8
7.6
7.4
7.2
0.98
2.02
6.27
5.21
1.10
2.06
2.04
8
7
6
5
4
3
2
1
ppm
0.90
1.90
5.86
6.84
1.03
1.89
1.87
1.00
0.98
1.17
3.08


141.076
134.202
134.164
131.569
131.402
129.126
129.081
128.178
128.155
128.079
127.017
126.797
126.600
125.947
125.750
125.735
125.477
125.447
125.378
124.863
123.087
122.791
77.316
77.058
76.807
73.439
57.400
55.412
13.927
220
200
180
160
140
120
100
80
60
40
20
ppm


OH
HN
14S-BDN
8.4
8.2
8.0
7.8
7.6
7.4
7.2
0.90
1.18
1.98
2.03
6.74
1.60
5.20
8
7
6
5
4
3
2
1
ppm
0.90
1.98
6.74
5.20
1.02
3.16
1.18
8.03
1.60
1.00
1.20


141.061
134.194
134.157
131.562
131.395
129.119
129.073
128.170
128.140
128.072
127.010
126.790
126.592
125.940
125.750
125.727
125.462
125.447
125.371
124.840
123.080
122.784
77.300
77.050
76.792
73.439
57.385
55.405
13.935
220
200
180
160
140
120
100
80
60
40
20
ppm