Nickel-Catalyzed s*yn*-Stereocontrolled Ring-Opening of Oxa- and Azabicyclic Alkenes with Dialkylzinc Reagents

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Supporting Information

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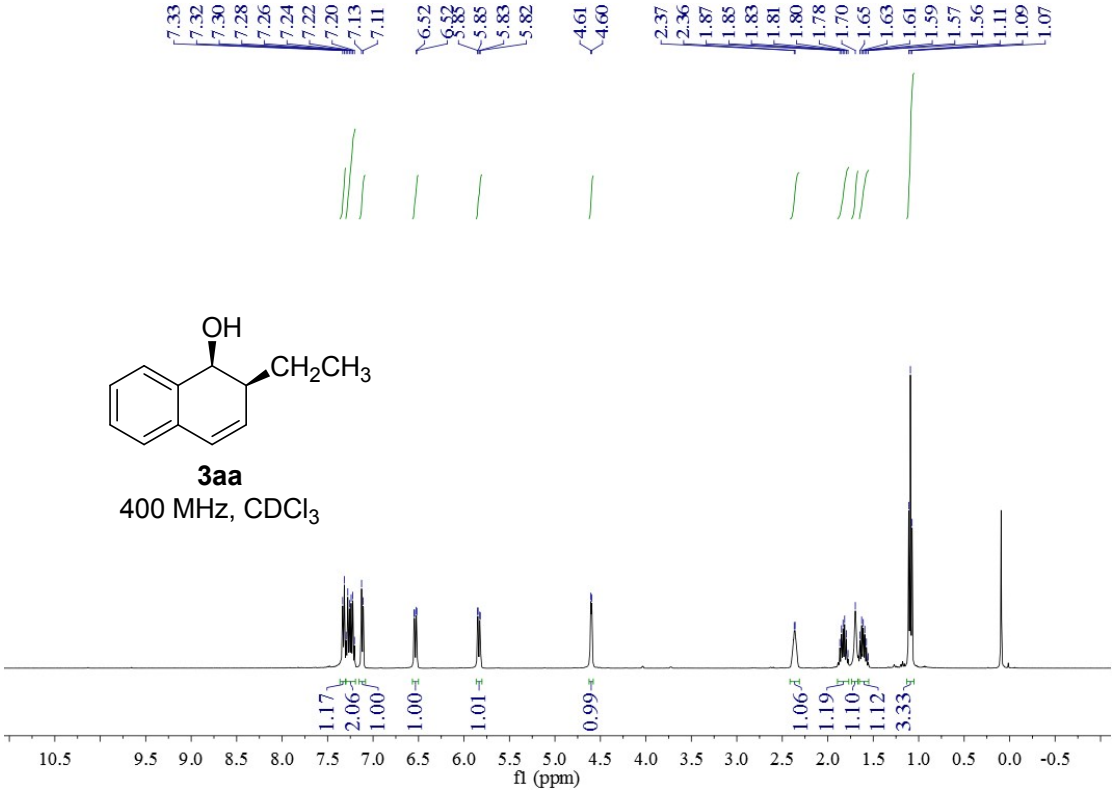
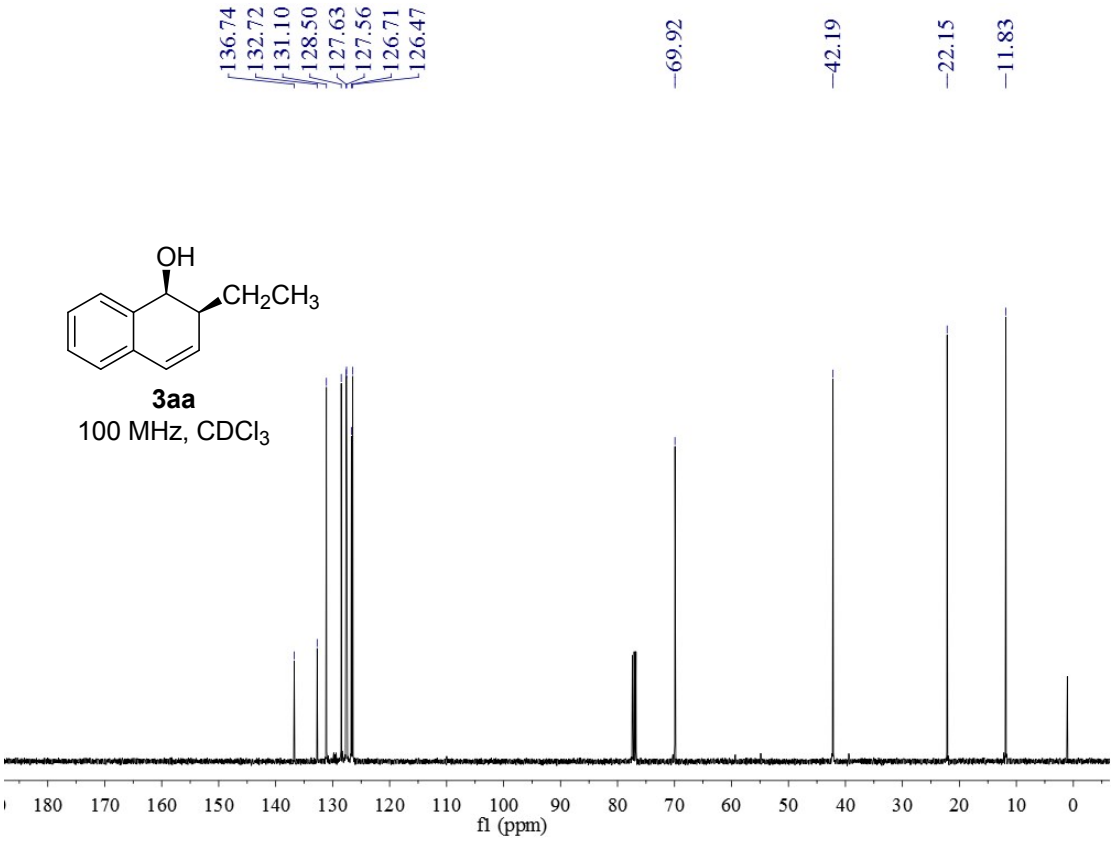
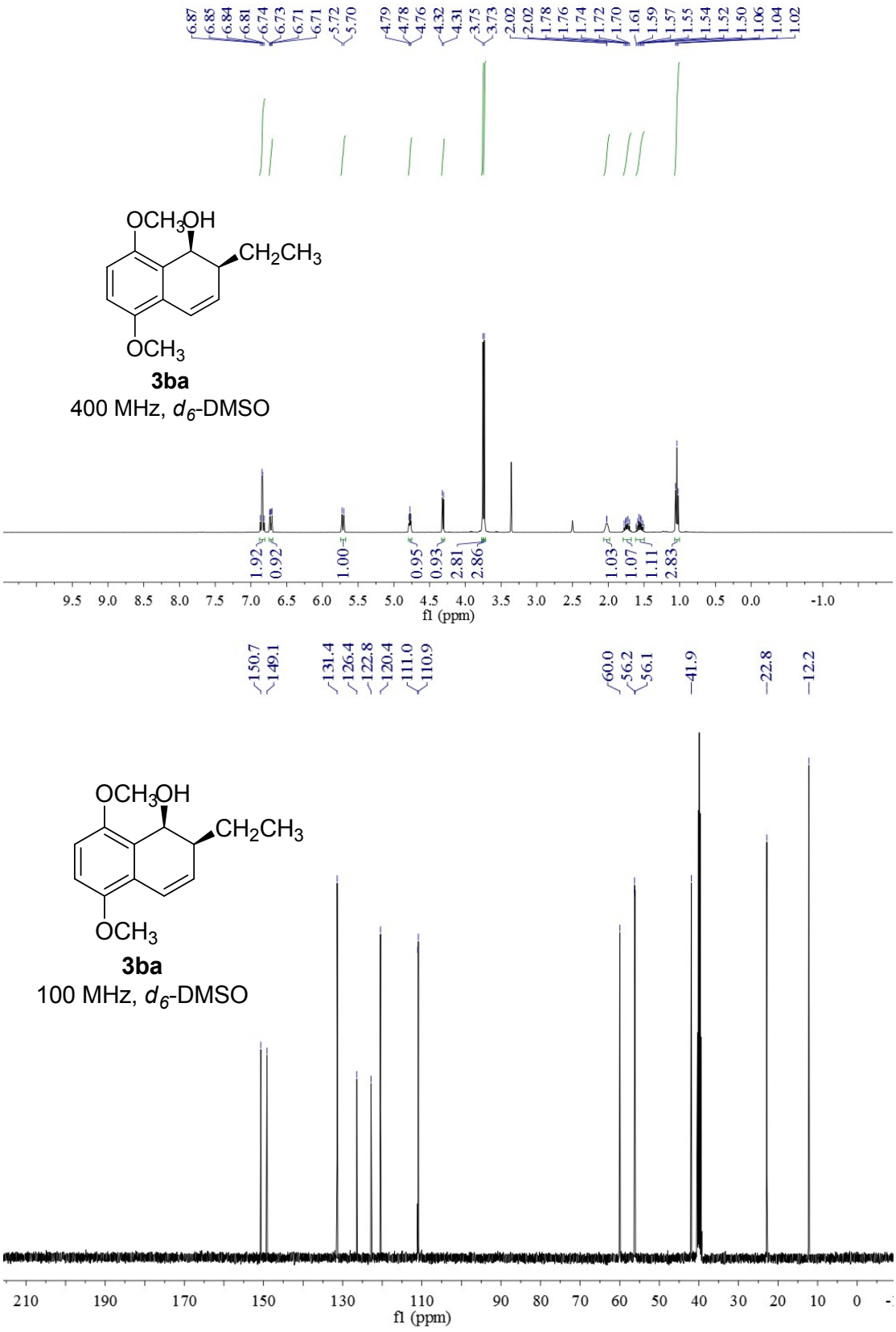
1. General information

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without further purification. Toluene and pentane was distilled from sodium benzophenone ketyl and CH_2Cl_2 was distilled from calcium hydride. Super dry solvent THF, DMF, 1,4-dioxane, *i*-PrOH and CH_3CN were used without any pretreatment. All flasks were flame-dried under a stream of nitrogen and cooled to room temperature before use. Flash column chromatography was performed using the indicated solvent system on Qingdao-Haiyang silica gel (200−300 mesh). Peaks recorded are relative to the internal standards: TMS (δ = 0.00) for ^{1}H NMR and $CDCl_3$ (δ = 77.00) for ^{13}C NMR spectra. ^{1}H and ^{13}C NMR spectra were recorded at 400/500/600 MHz and 101/126/151 MHz at 25 ^{o}C in $CDCl_3$/d_6-DMSO/CD_3OD, respectively. ^{19}F NMR spectra was recorded at 376/470/565 MHz at 25 ^{o}C in $CDCl_3$. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet); coupling constants (*J*, Hz) and number of protons. HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Melting points were uncorrected.

2. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



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4.78
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4.32
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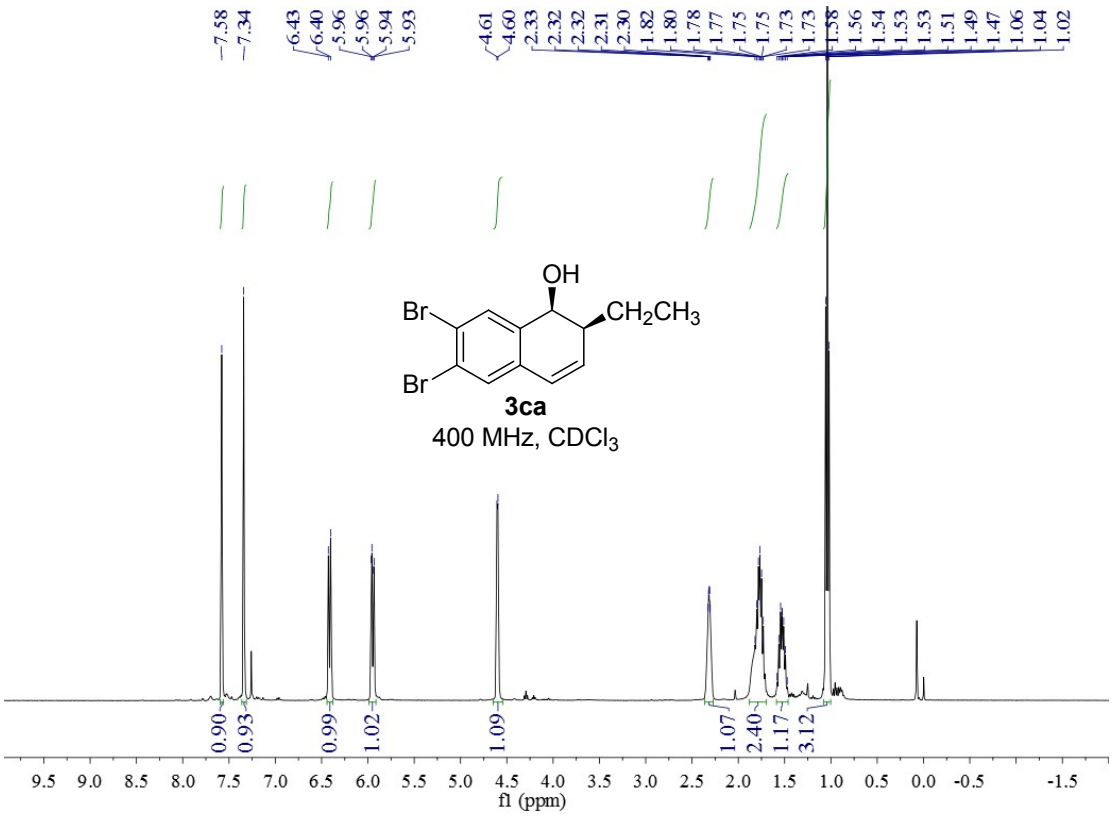
3.75
3.73
2.02
2.02
1.78
1.76
1.74
1.72
1.70
1.61
1.59
1.57
1.55
1.54
1.52
1.50
1.06
1.04
1.02
OCH3
OH
CH2CH3
OCH3
3ba
400 MHz, d6-DMSO
1.92
0.92
1.00
0.95
0.93
2.81
2.86
1.03
1.07
1.11
2.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)
150.7
149.1
131.4
126.4
122.8
120.4
111.0
110.9
60.0
56.2
56.1
41.9
22.8
12.2
OCH3
OH
CH2CH3
OCH3
3ba
100 MHz, d6-DMSO
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.96
5.94
5.93
4.61
4.60
2.33
2.32
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2.31
2.30
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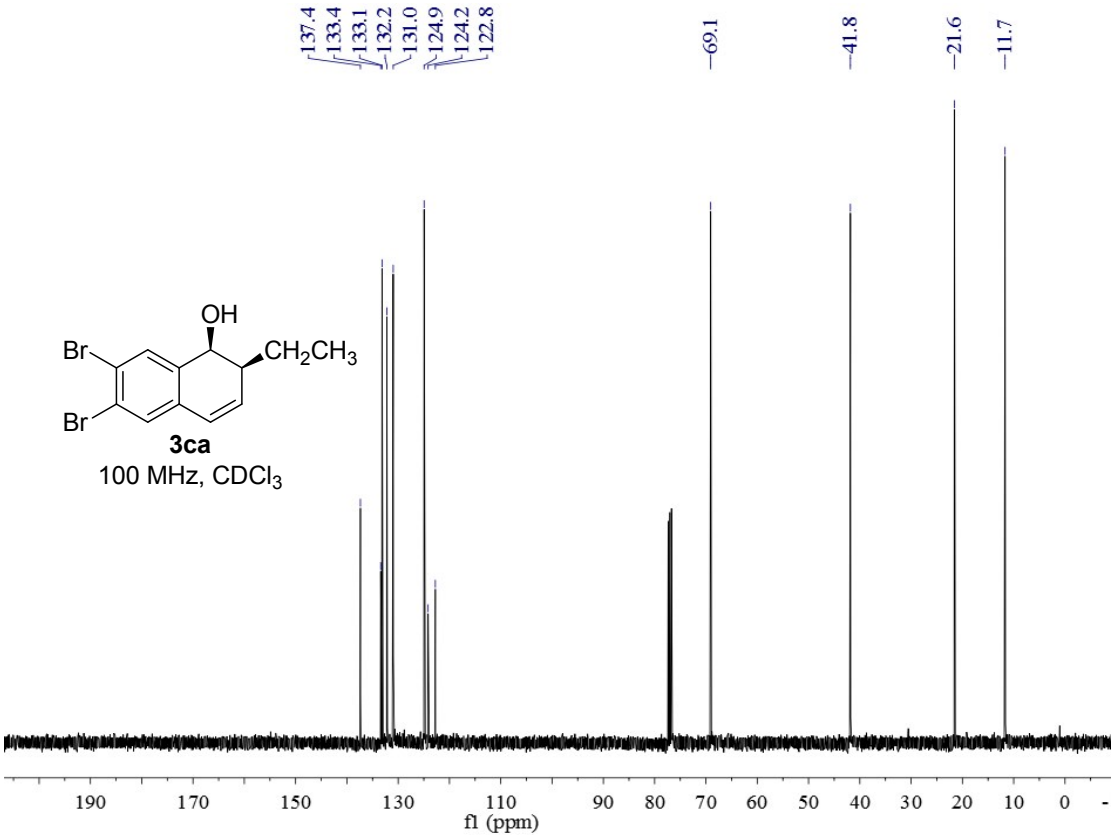
1.80
1.78
1.77
1.75
1.75
1.73
1.73
1.58
1.56
1.54
1.53
1.53
1.51
1.49
1.47
1.06
1.04
1.02
OH
Br
Br
CH2CH3
3ca
400 MHz, CDCl3
0.90
0.93
0.99
1.02
1.09
1.07
2.40
1.17
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)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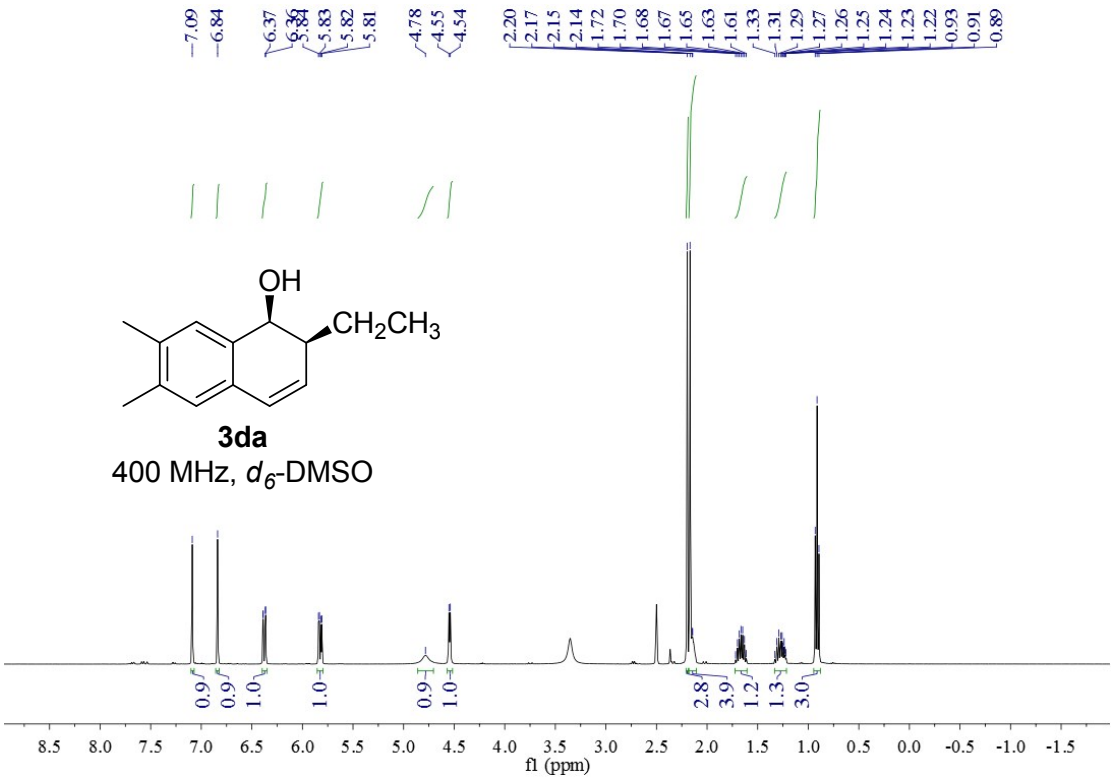
132.2
131.0
124.9
124.2
122.8
69.1
41.8
21.6
11.7
OH
Br
Br
CH2CH3
3ca
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)



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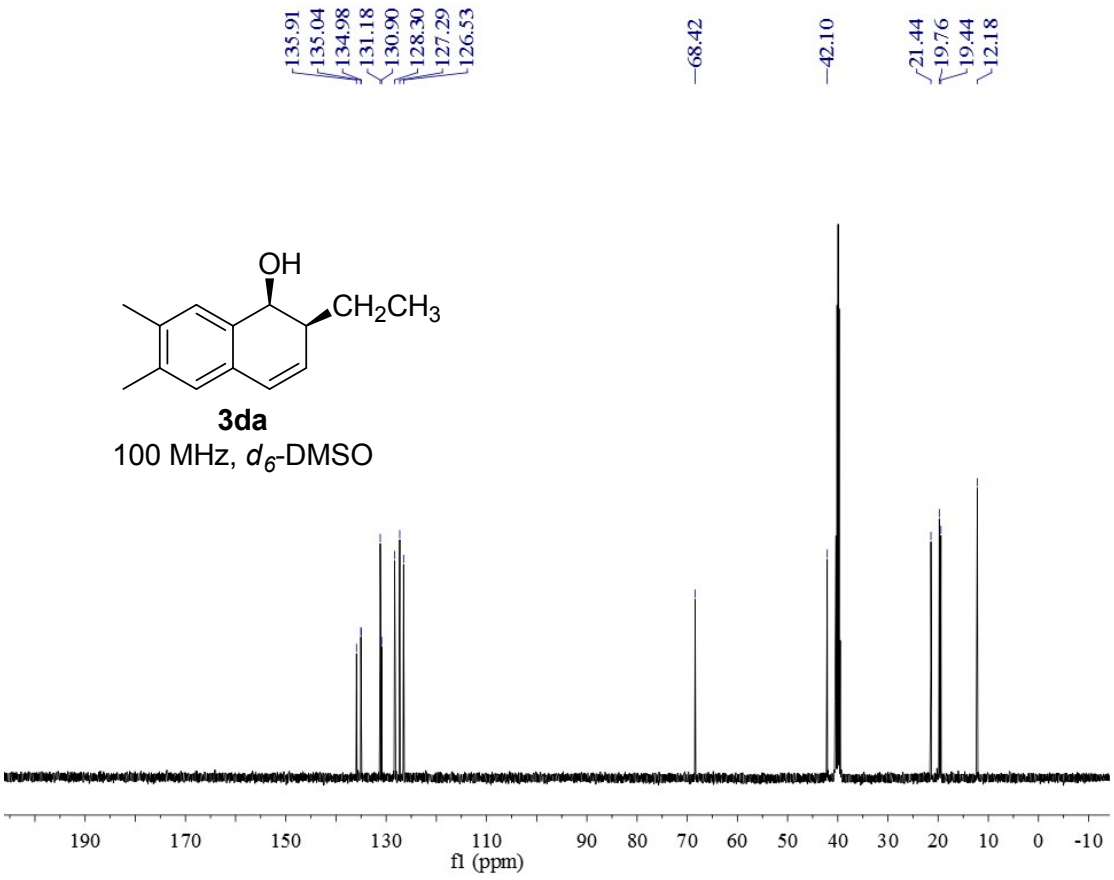

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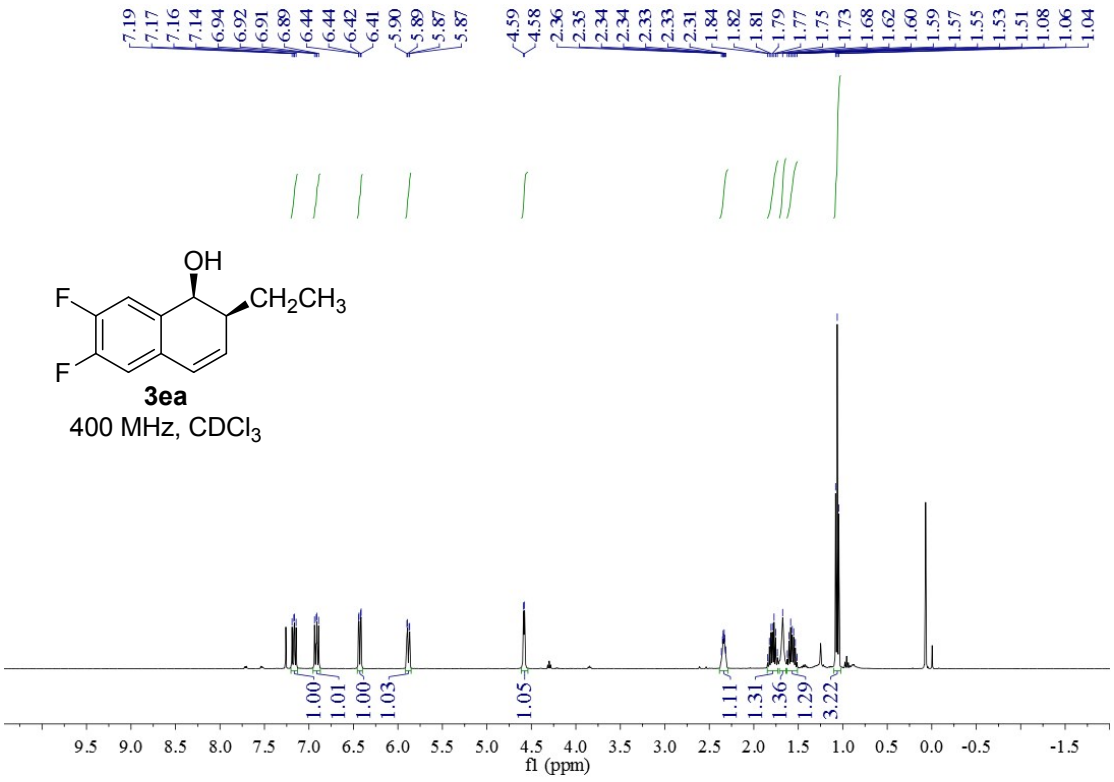
100 MHz, d_6-DMSO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6.89
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6.44
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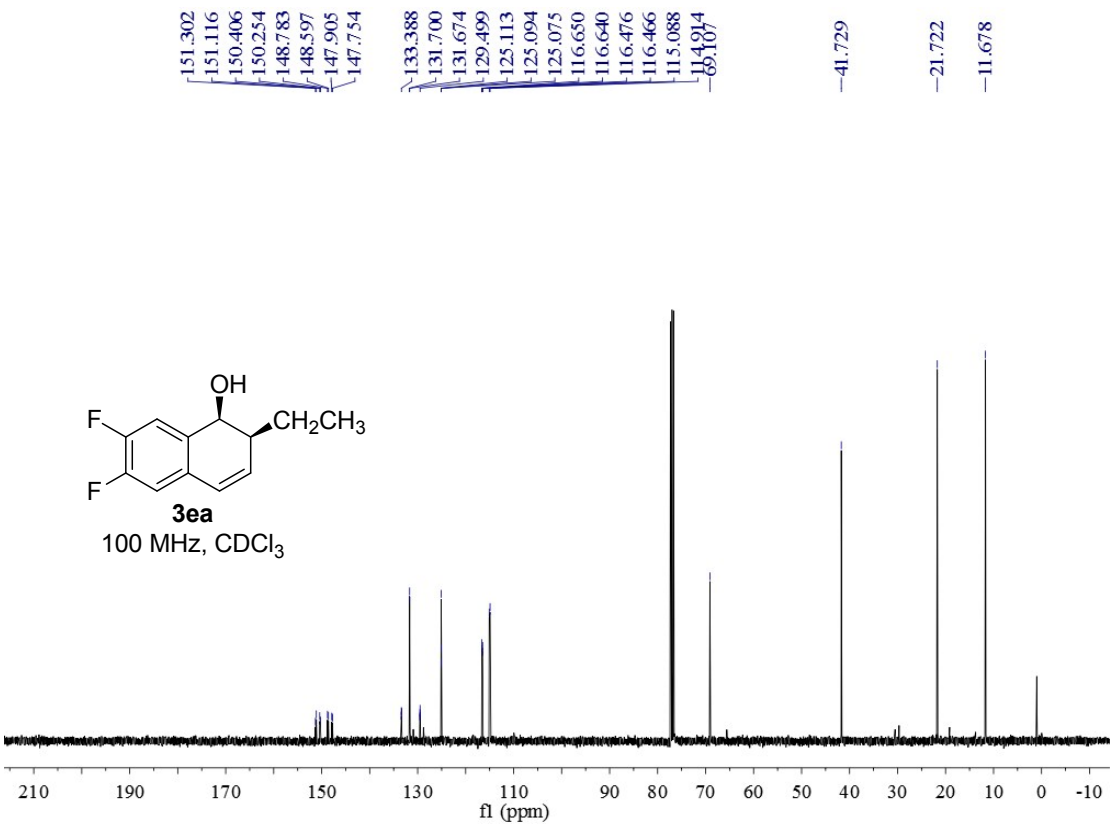
6.41
5.90
5.89
5.87
5.87
4.59
4.58
2.36
2.35
2.34
2.34
2.33
2.33
2.31
1.84
1.82
1.81
1.79
1.77
1.75
1.73
1.68
1.62
1.60
1.59
1.57
1.55
1.53
1.51
1.08
1.06
1.04
OH
F
CH2CH3
F
3ea
400 MHz, CDCl3
1.00
1.01
1.00
1.03
1.05
1.11
1.31
1.36
1.29
3.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)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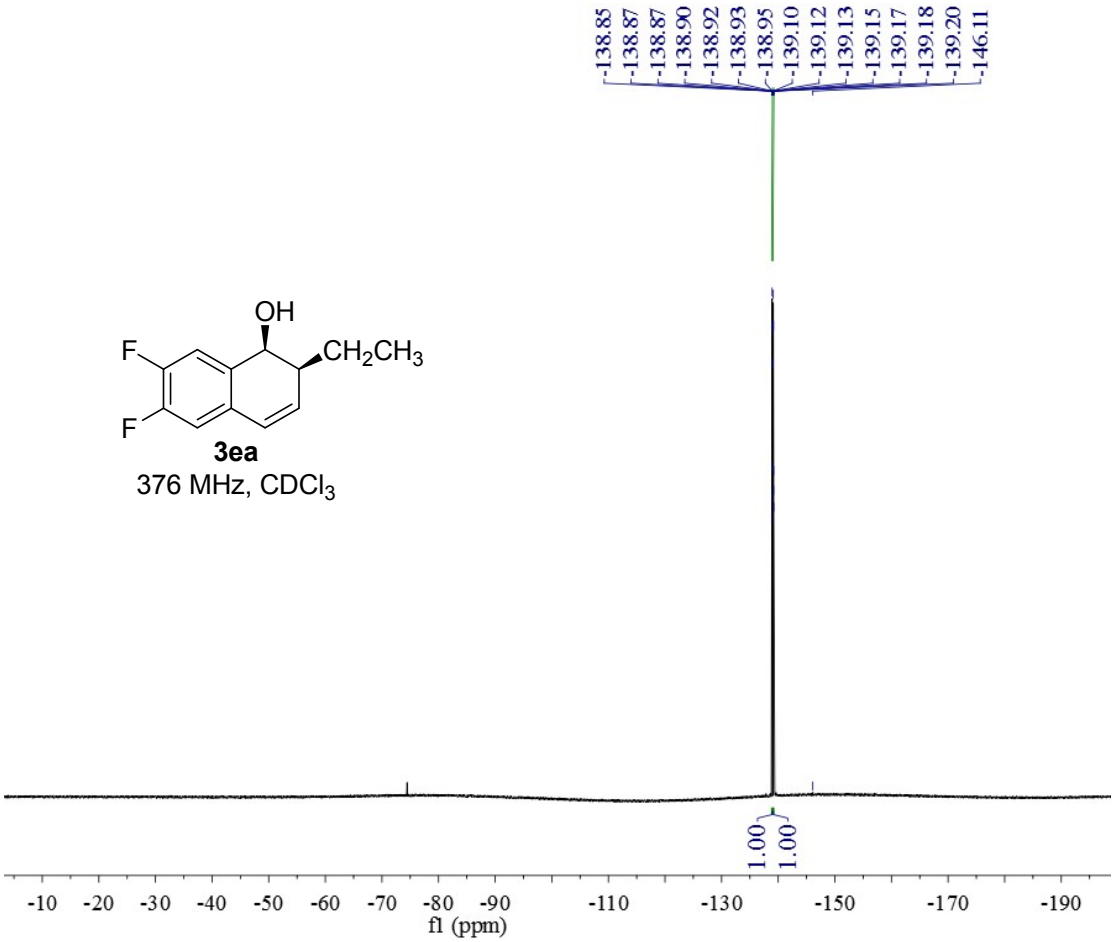
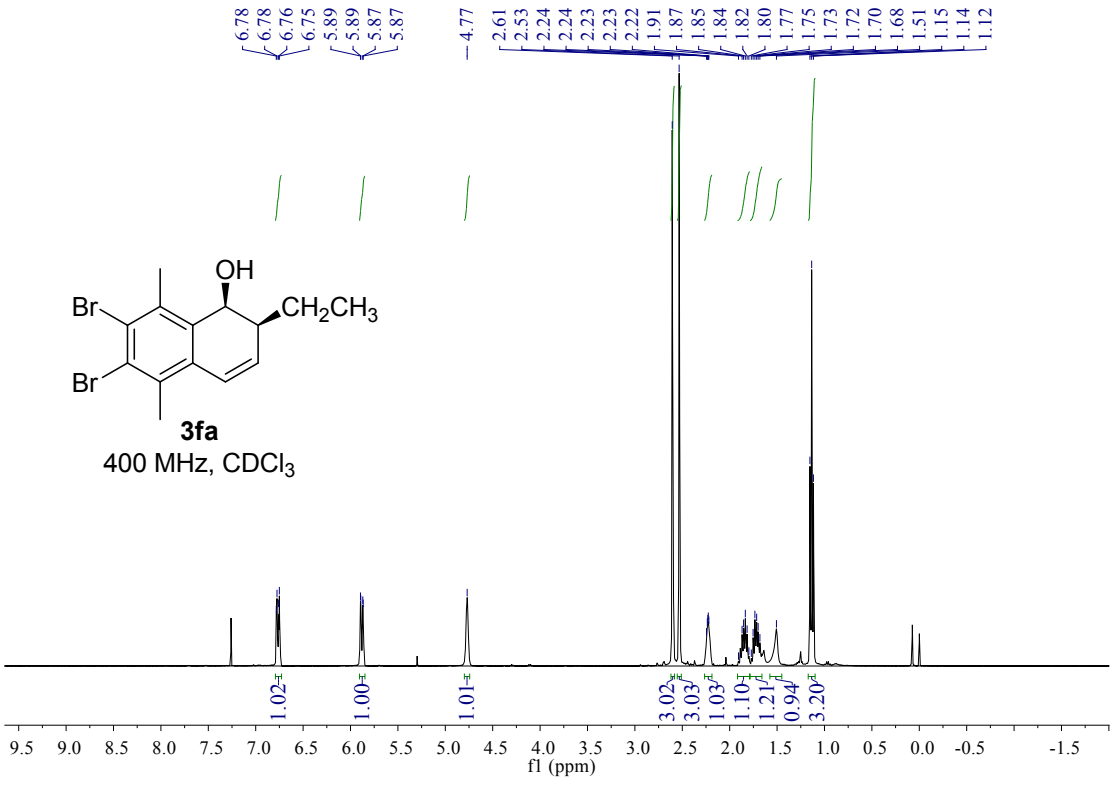
125.113
125.094
125.075
116.650
116.640
116.476
116.466
115.088
114.914
69.107
41.729
21.722
11.678
OH
F
CH2CH3
F
3ea
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



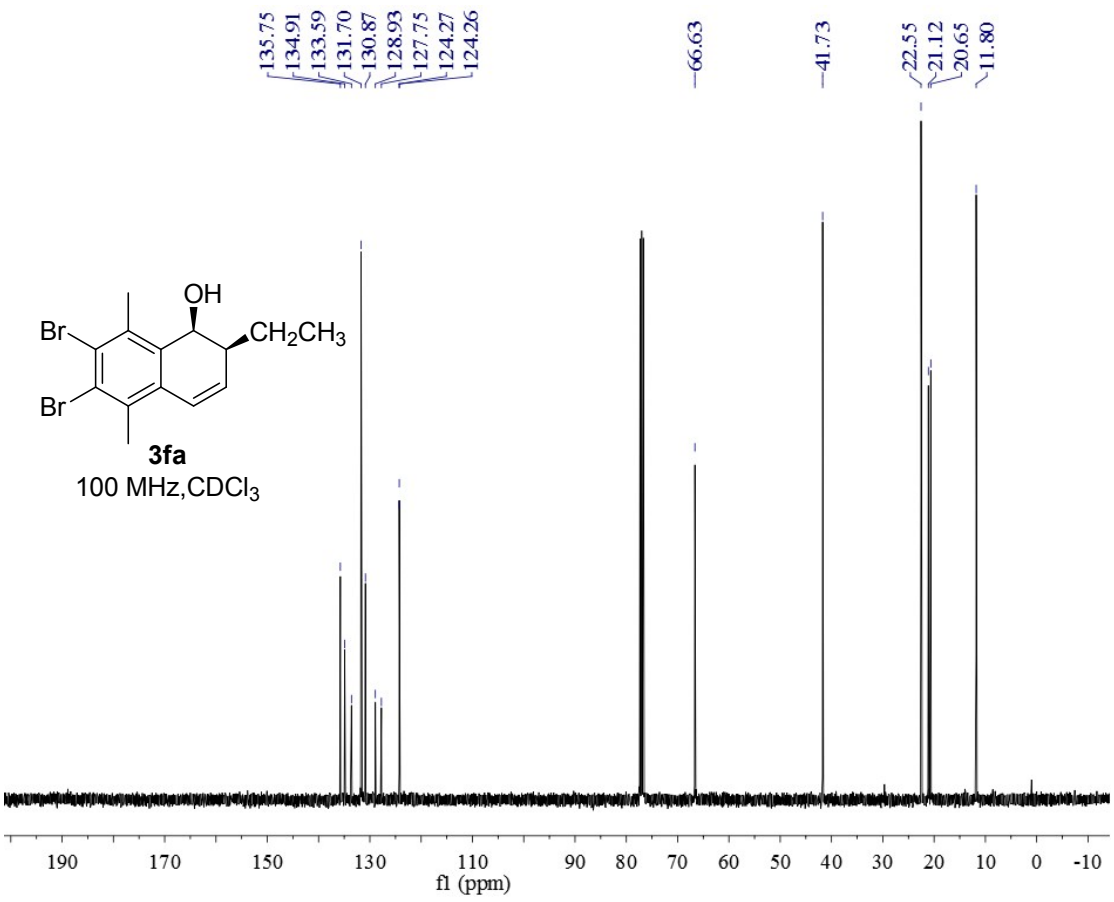
3ea

376 MHz, $CDCl_3$



3fa

400 MHz, $CDCl_3$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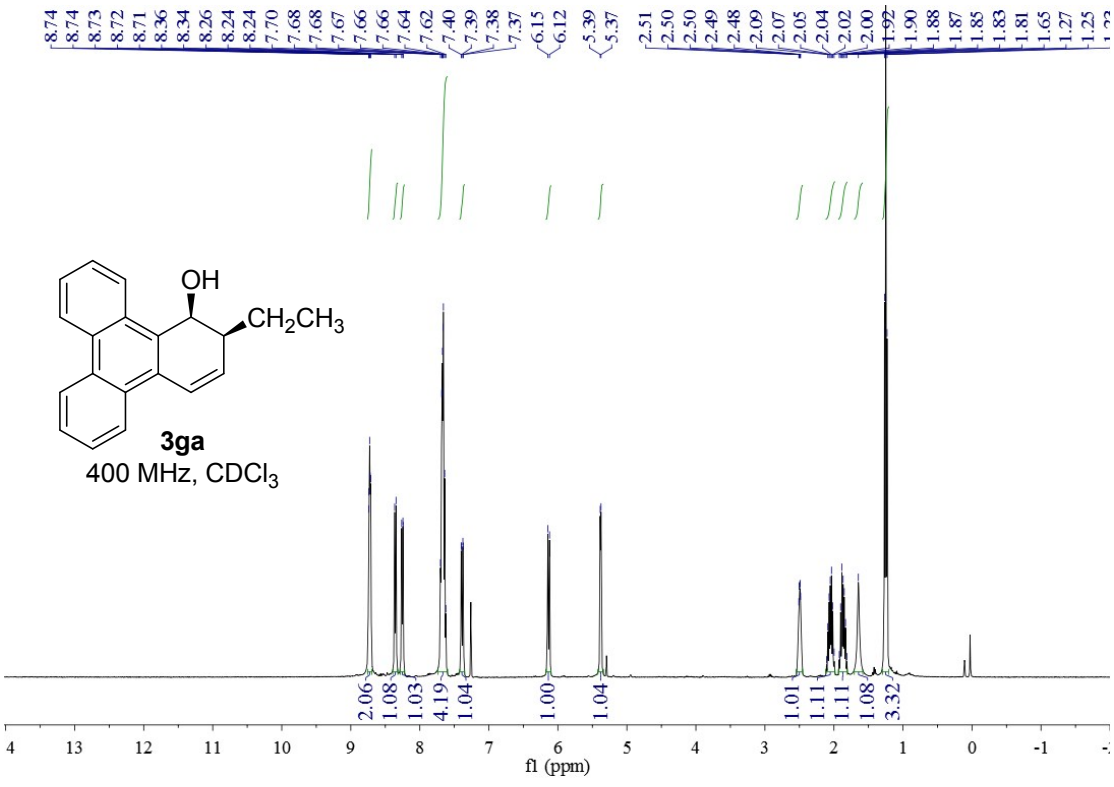
128.93
127.75
124.27
124.26
66.63
41.73
22.55
21.12
20.65
11.80
OH
Br
Br
CH2CH3
3fa
100 MHz,CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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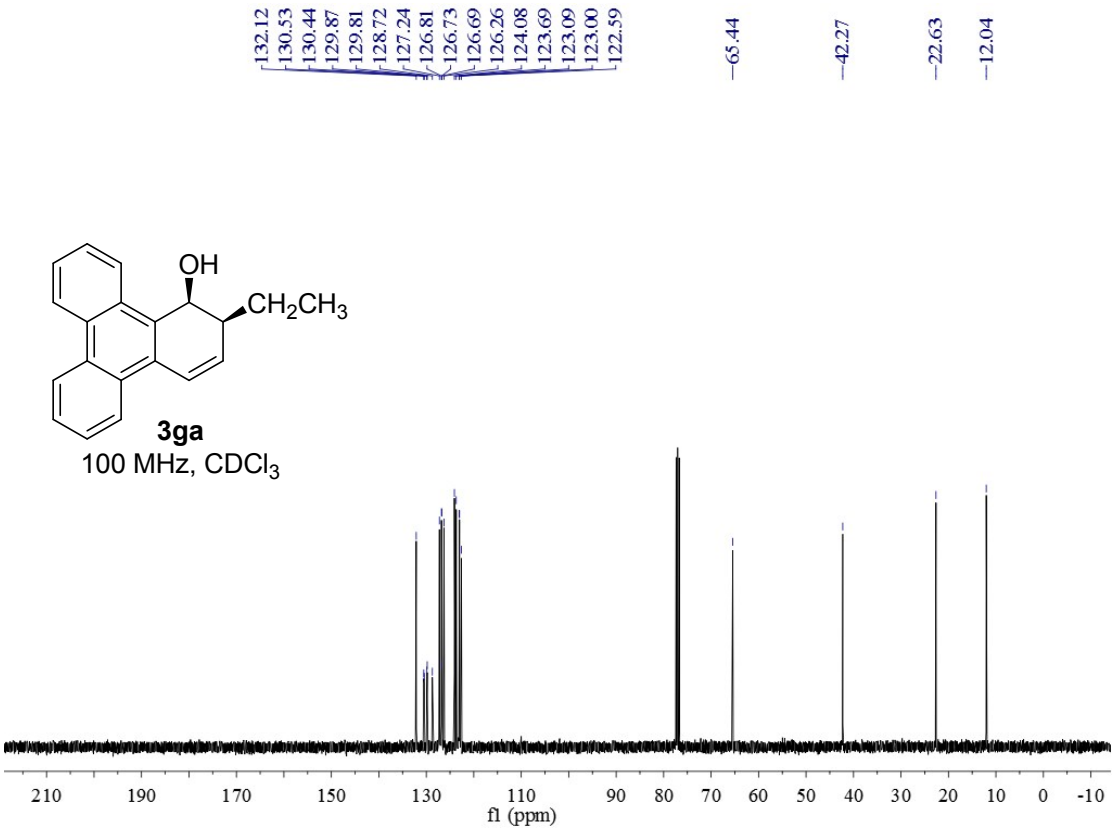
7.68
7.67
7.66
7.66
7.64
7.62
7.40
7.39
7.38
7.37
6.15
6.12
5.39
5.37
2.51
2.50
2.50
2.49
2.48
2.09
2.07
2.05
2.04
2.02
2.00
1.92
1.90
1.88
1.87
1.85
1.83
1.81
1.65
1.27
1.25
OH
CH2CH3
3ga
400 MHz, CDCl3
2.06
1.08
1.03
4.19
1.04
1.00
1.04
1.01
1.11
1.11
1.08
3.32
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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126.73
126.69
126.26
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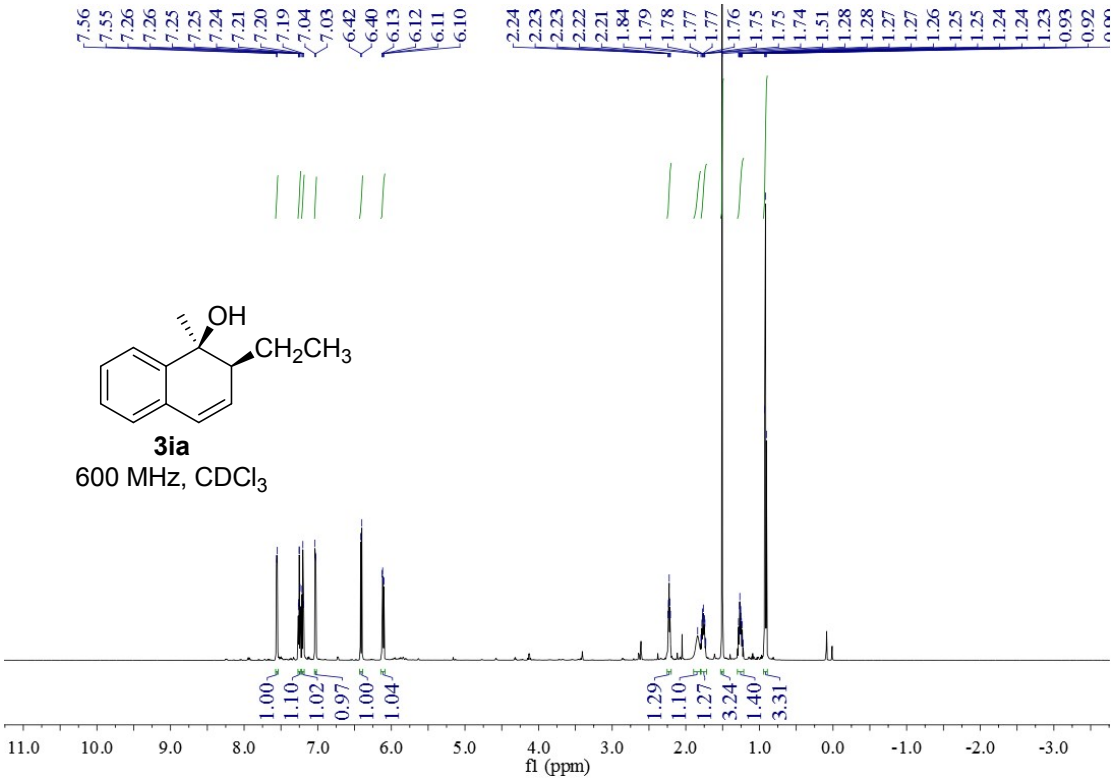
123.69
123.09
123.00
122.59
65.44
42.27
22.63
12.04
OH
CH2CH3
3ga
100 MHz, CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.20
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7.04
7.03
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6.40
6.13
6.12
6.11
6.10
2.24
2.23
2.23
2.22
2.21
1.84
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.74
1.51
1.28
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.24
1.23
0.93
0.92
OH
CH2CH3
3ia
600 MHz, CDCl3
1.00
1.10
1.02
0.97
1.00
1.04
1.29
1.10
1.27
3.24
1.40
3.31
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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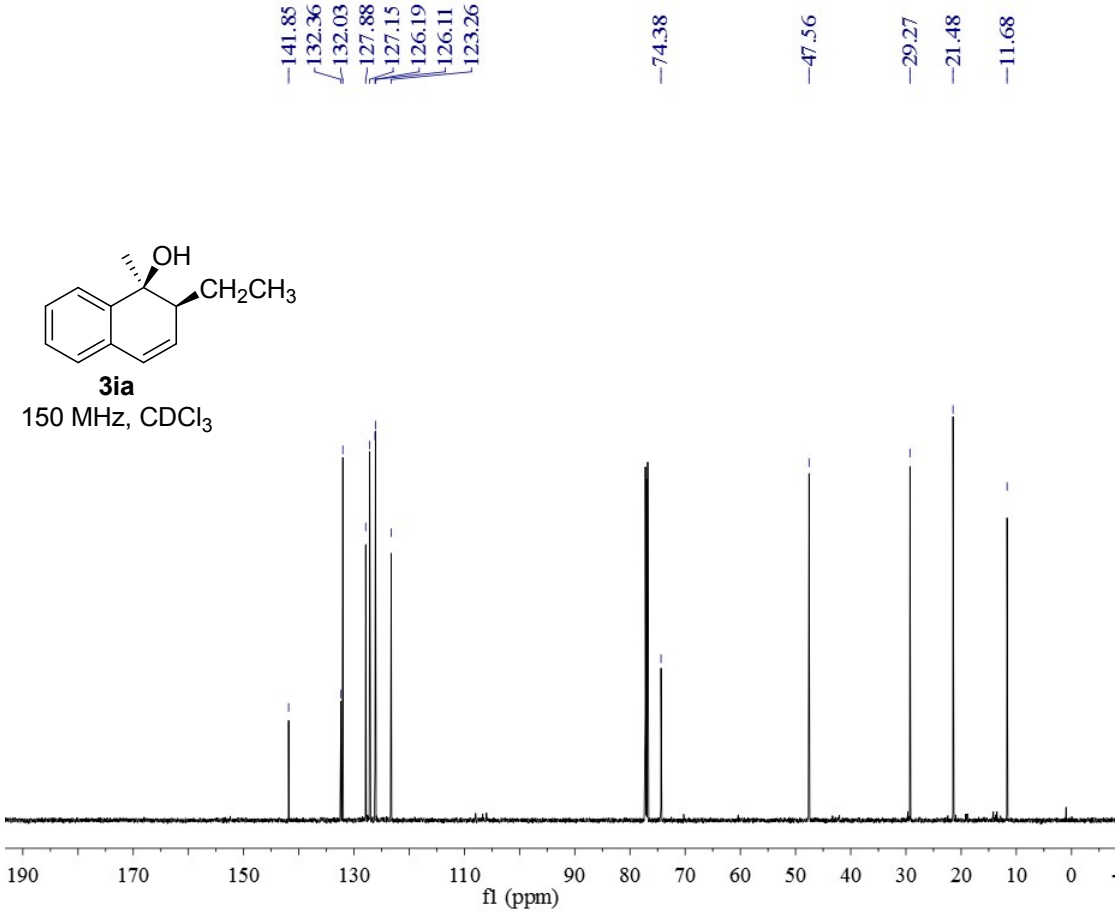
1.0
0.0
-1.0
-2.0
-3.0
f1 (ppm)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123.26
74.38
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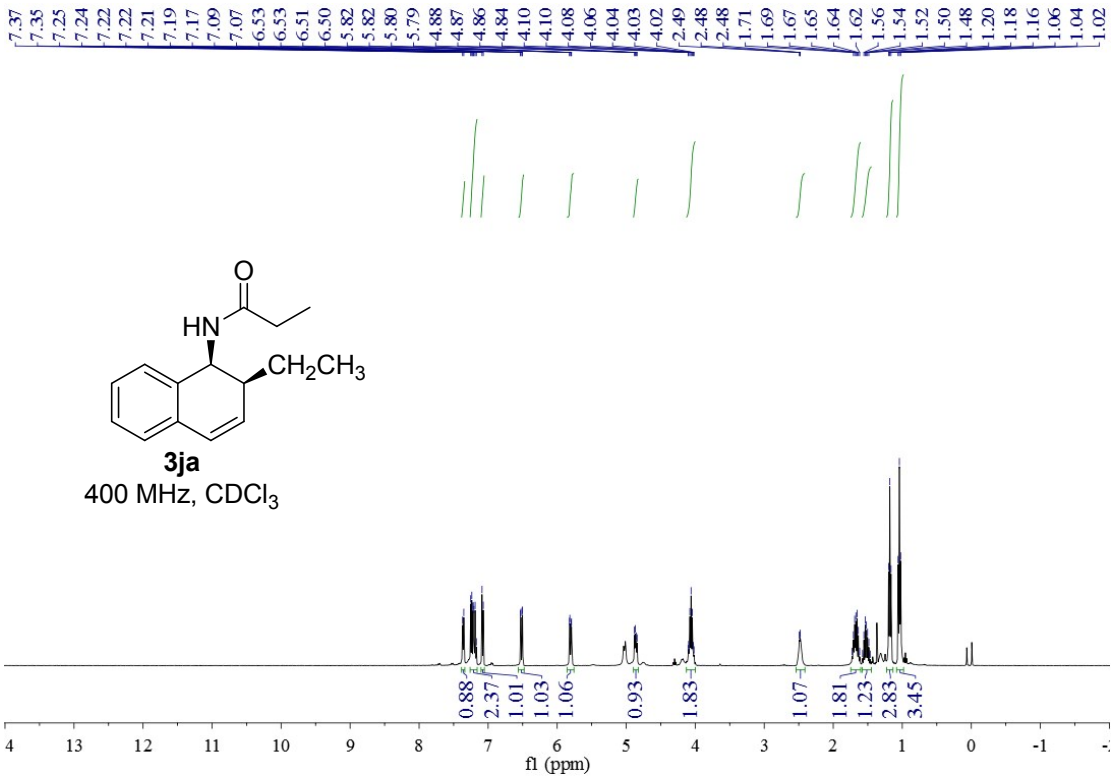
29.27
21.48
11.68
OH
CH2CH3
3ia
150 MHz, CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.07
6.53
6.53
6.51
6.50
5.82
5.82
5.80
5.79
4.88
4.87
4.86
4.84
4.10
4.10
4.08
4.06
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2.48
1.71
1.69
1.67
1.65
1.64
1.62
1.56
1.54
1.52
1.50
1.48
1.20
1.18
1.16
1.06
1.04
1.02
O
HN
CH2CH3
3ja
400 MHz, CDCl3
0.88
2.37
1.01
1.03
1.06
0.93
1.83
1.07
1.81
1.23
2.83
3.45
4
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12
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10
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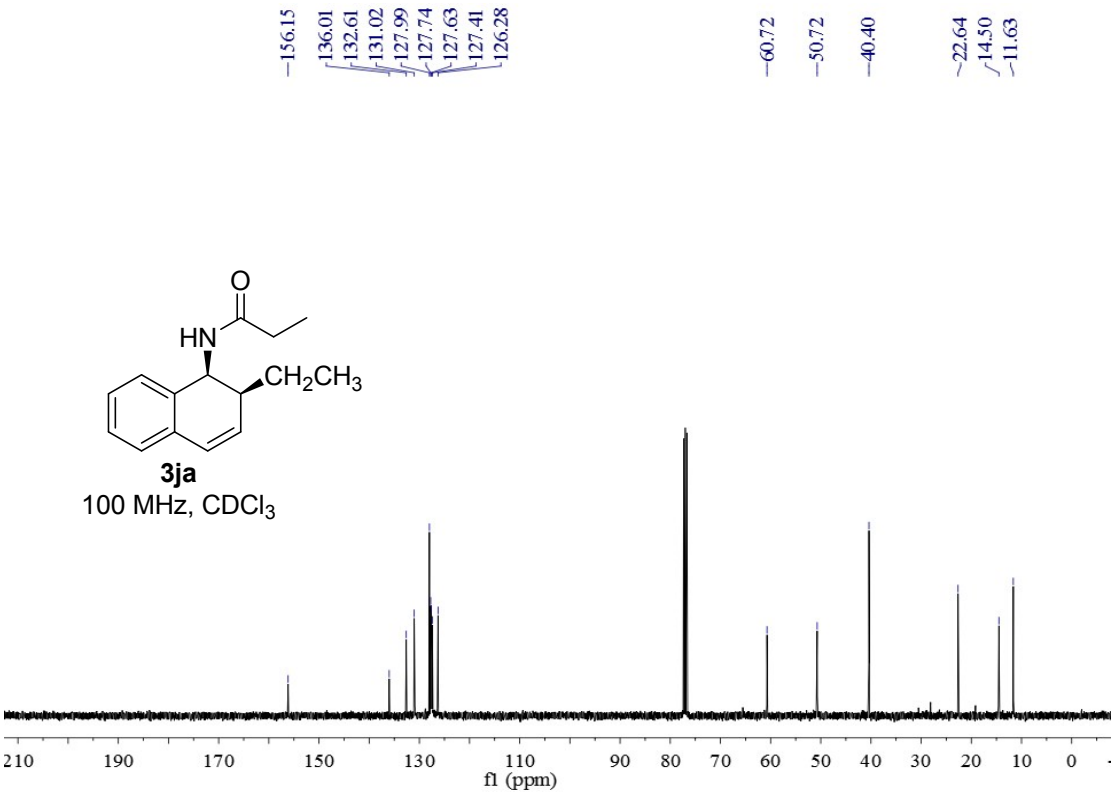
6
5
4
3
2
1
0
-1
f1 (ppm)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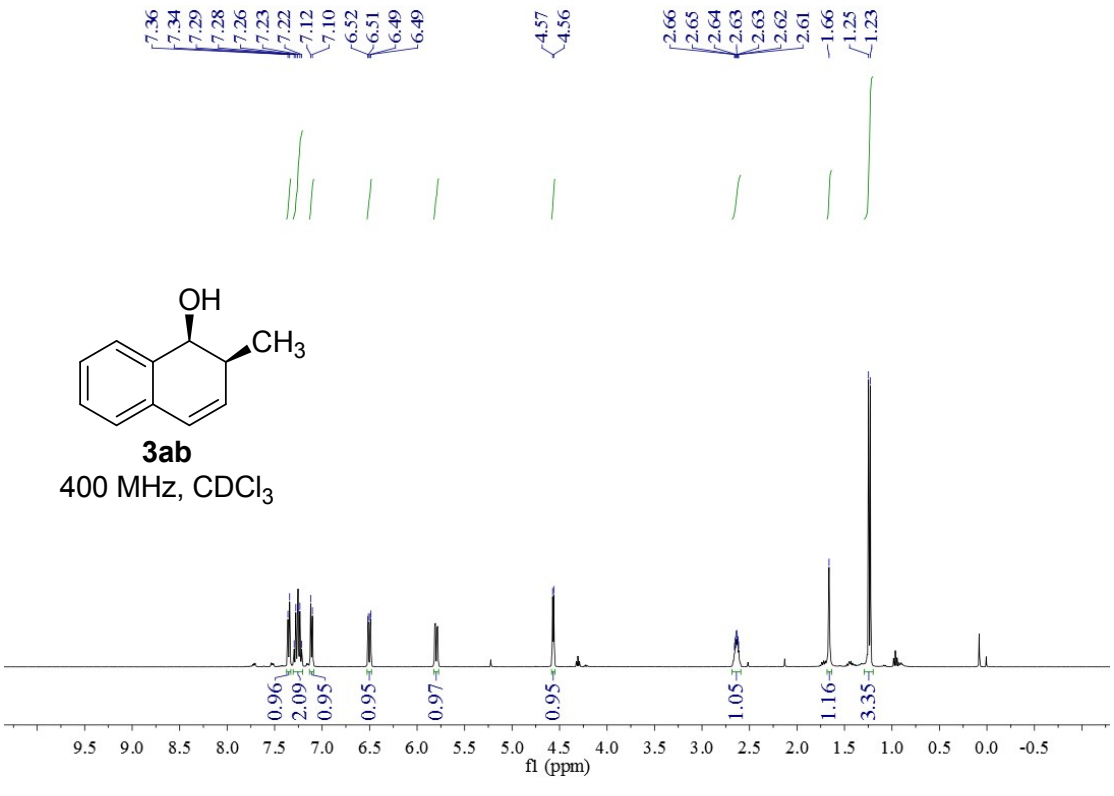
127.63
127.41
126.28
60.72
50.72
40.40
22.64
14.50
11.63
O
HN
CH2CH3
3ja
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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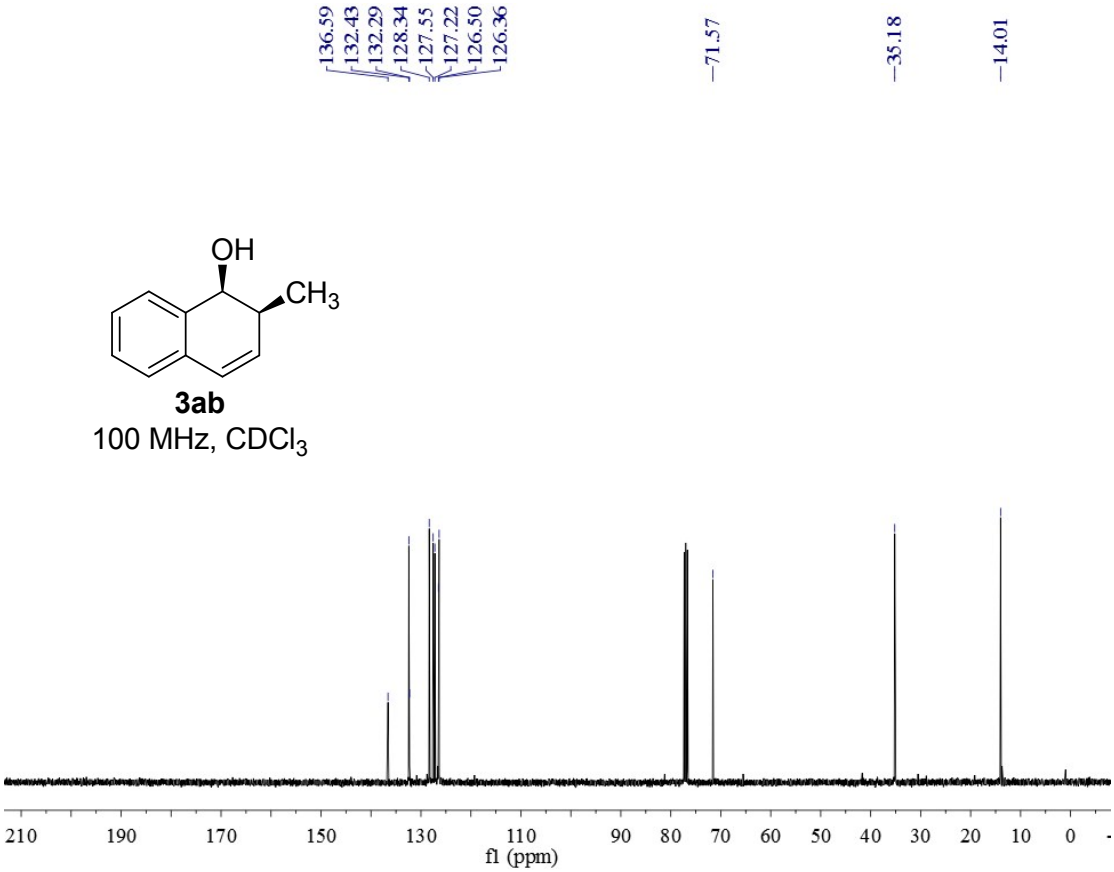
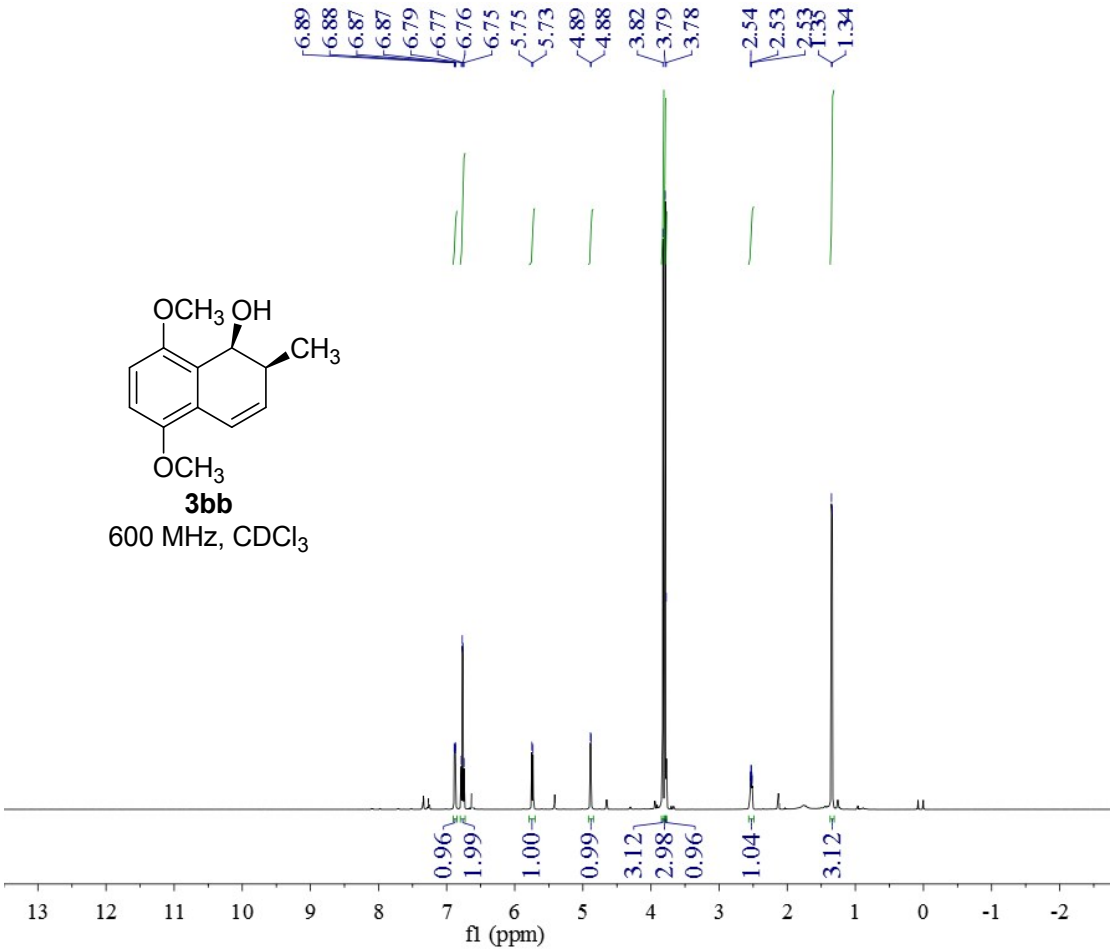
7.34
7.29
7.28
7.26
7.23
7.22
7.12
7.10
6.52
6.51
6.49
6.49
4.57
4.56
2.66
2.65
2.64
2.63
2.63
2.62
2.61
1.66
1.25
1.23
OH
CH3
3ab
400 MHz, CDCl3
0.96
2.09
0.95
0.95
0.97
0.95
1.05
1.16
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



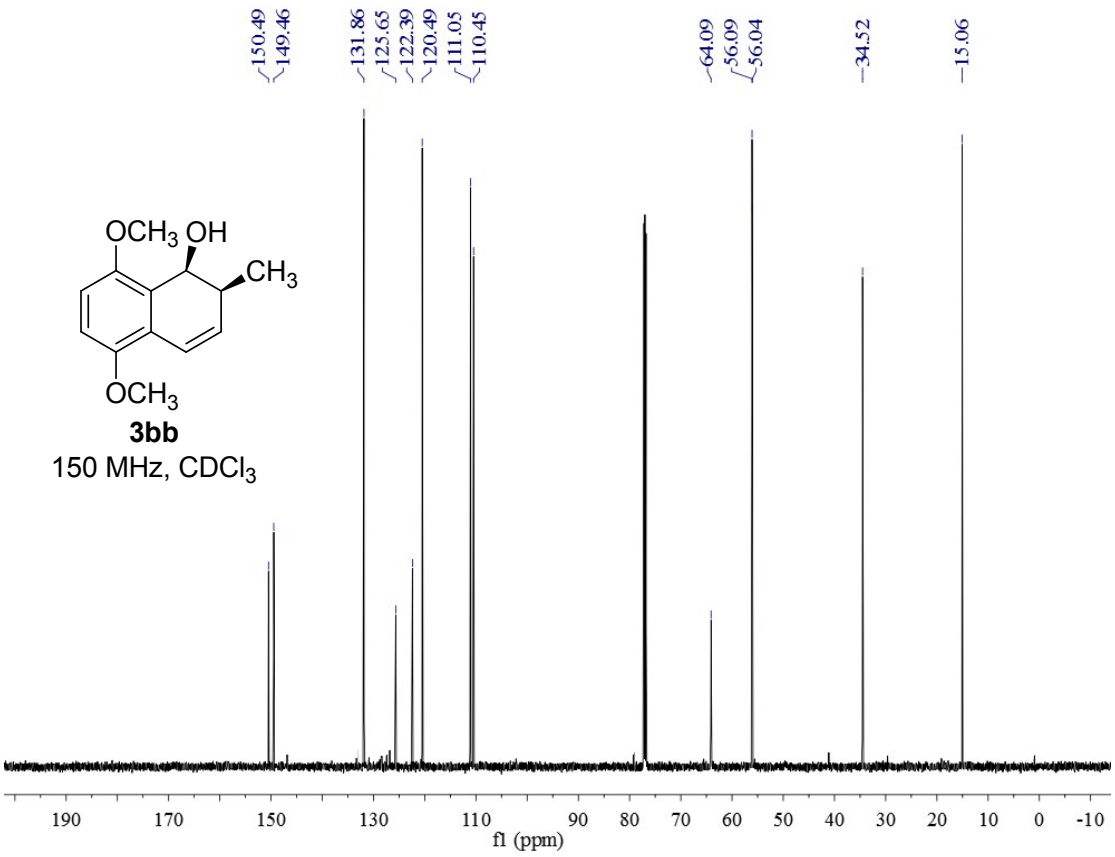
3ab

100 MHz, $CDCl_3$



3bb

600 MHz, $CDCl_3$



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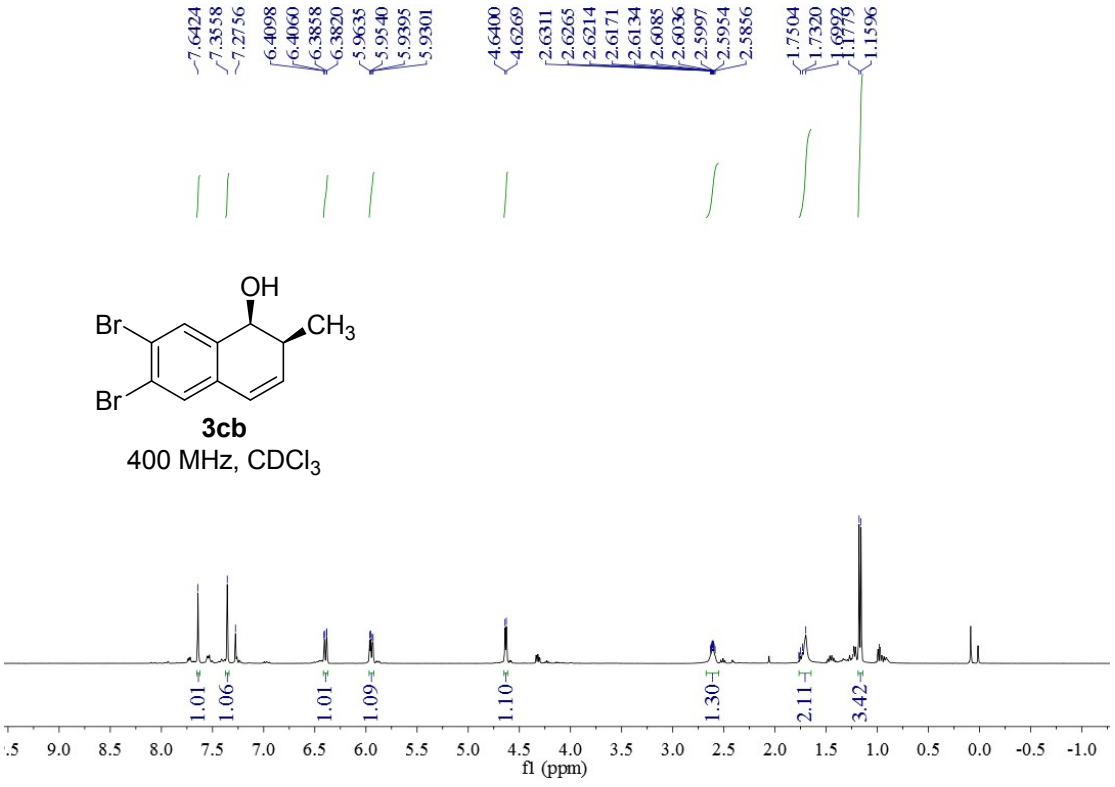
150 MHz, $CDCl_3$



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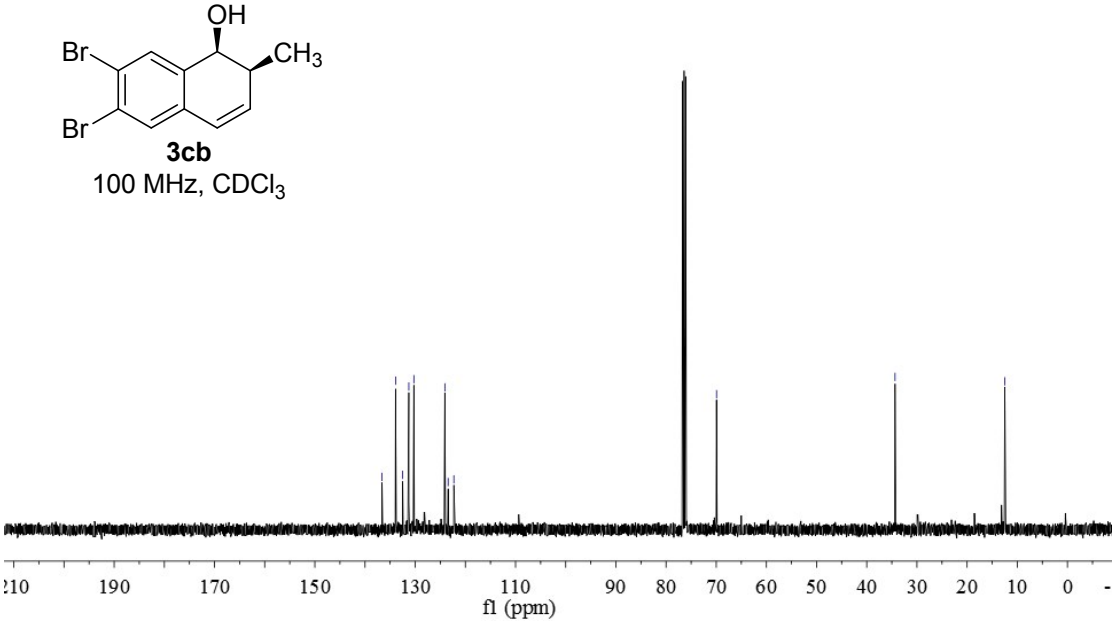
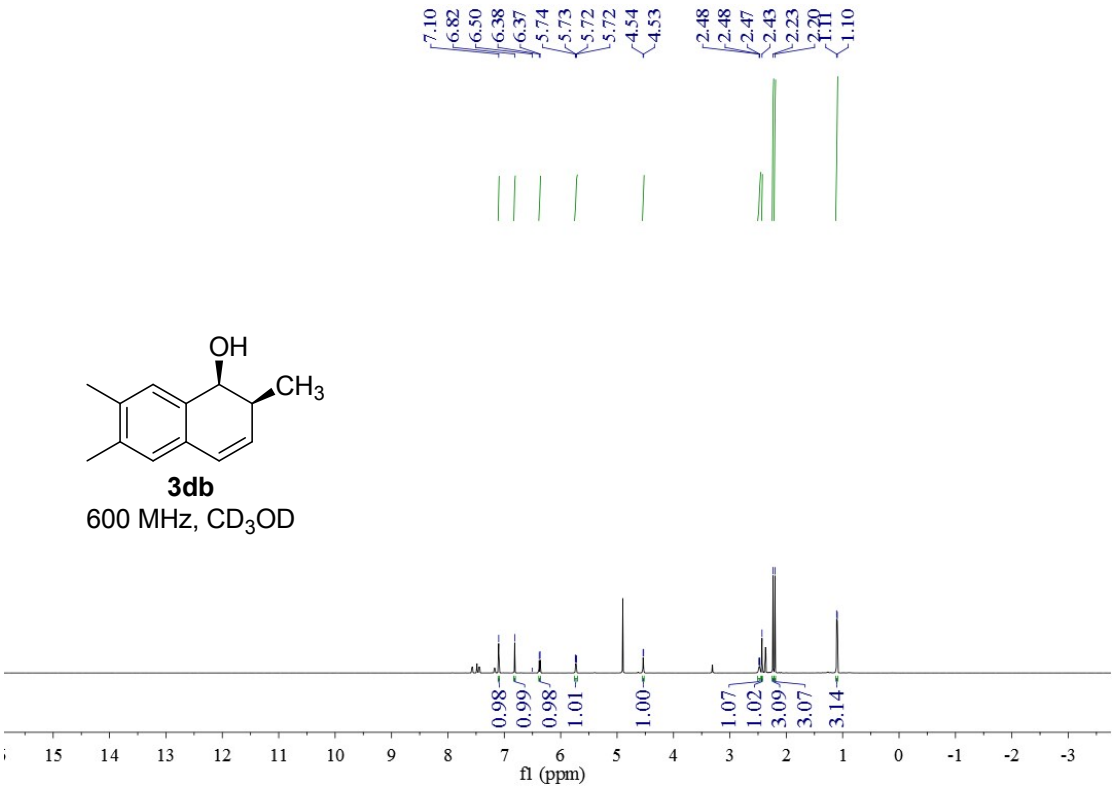
400 MHz, $CDCl_3$


136.61
133.91
132.49
131.27
130.26
124.09
123.44
122.29
69.94
34.36
12.48
OH
Br
CH3
Br
3cb
100 MHz, CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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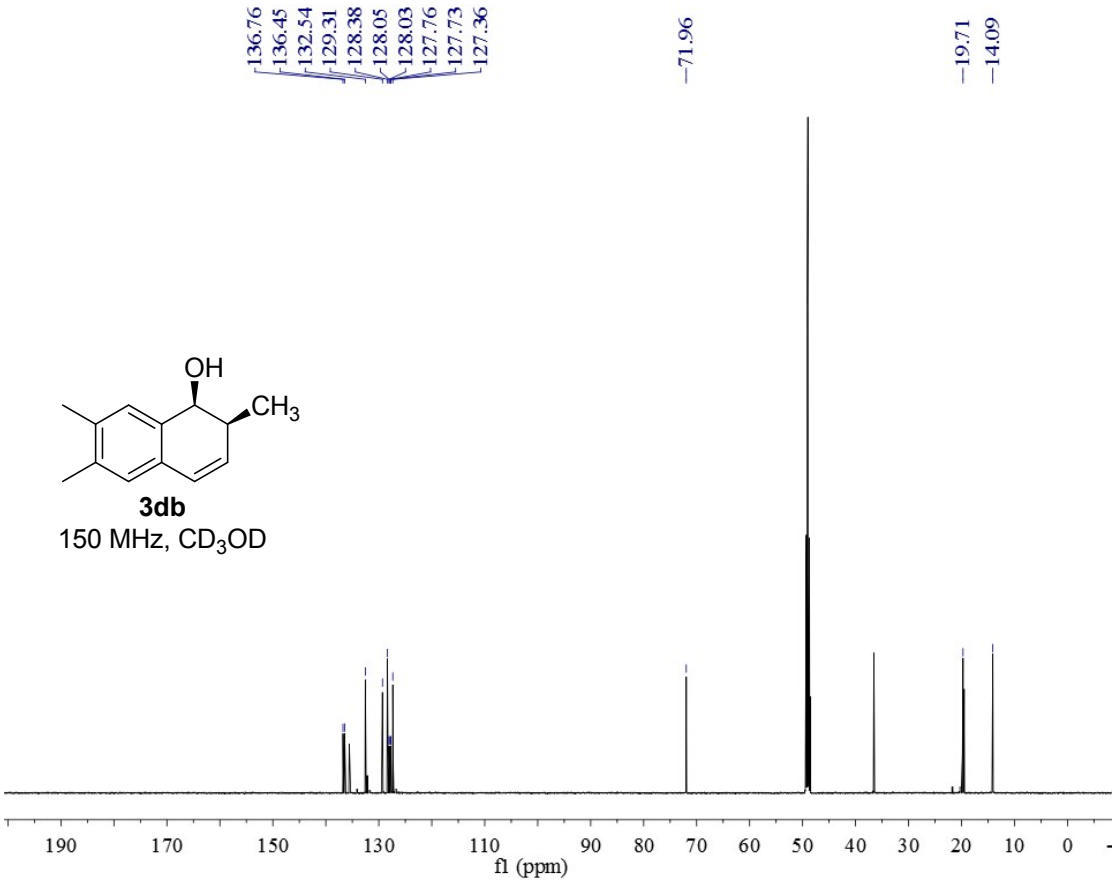
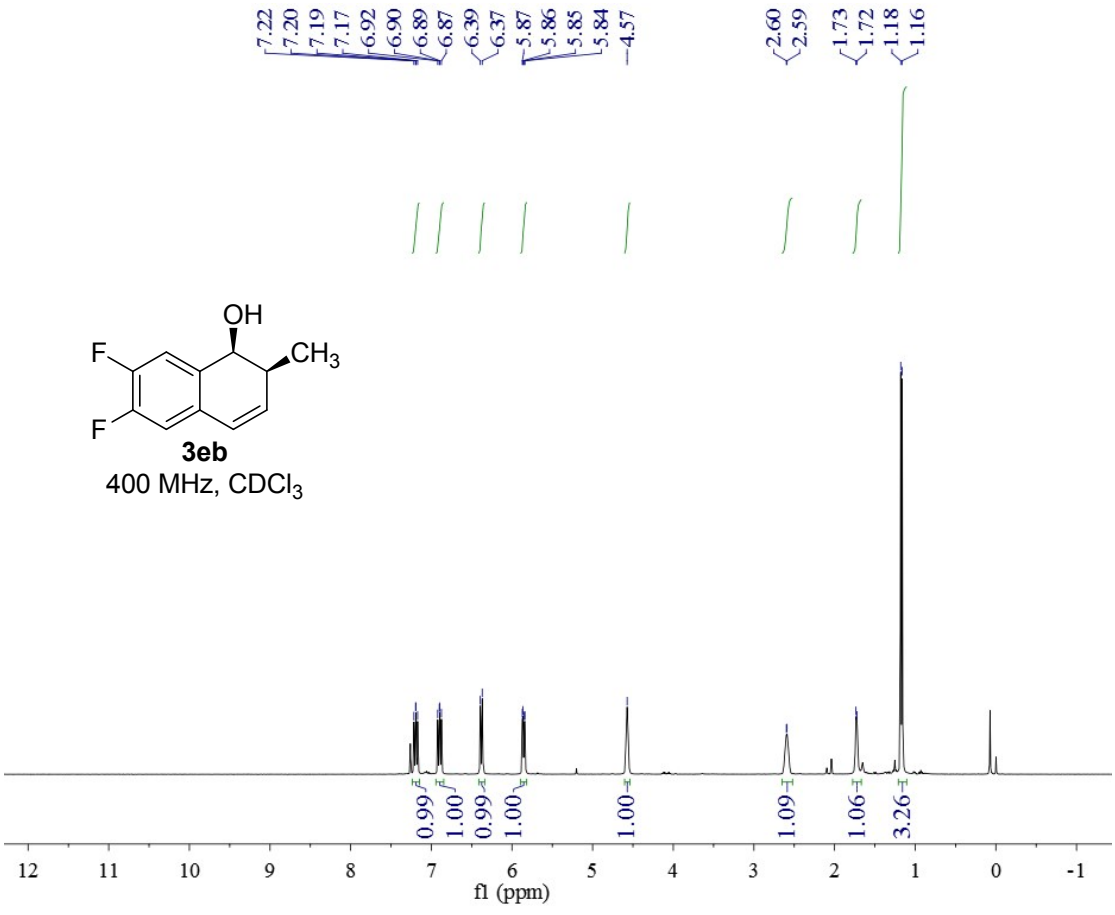
6.82
6.50
6.38
6.37
5.74
5.73
5.72
5.72
4.54
4.53
2.48
2.48
2.47
2.43
2.23
2.20
1.11
1.10
OH
CH3
3db
600 MHz, CD3OD
0.98
0.99
0.98
1.01
1.00
1.07
1.02
3.09
3.07
3.14
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



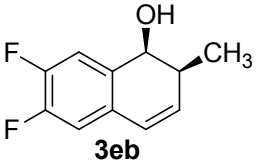
3db

150 MHz, CD_3OD



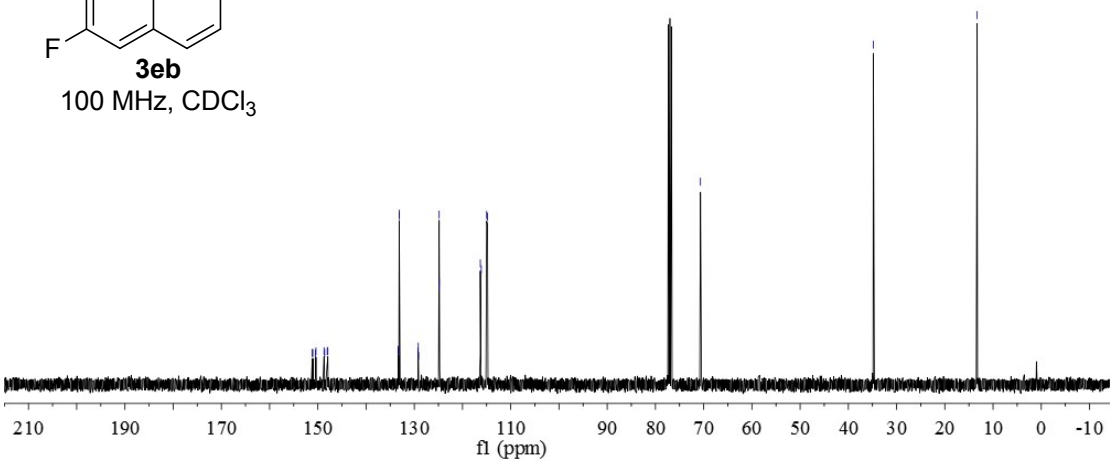
3eb

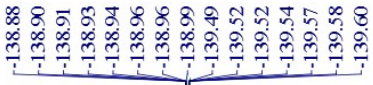
400 MHz, $CDCl_3$

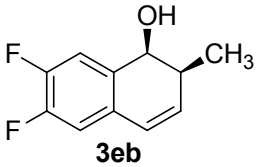


3eb

100 MHz, $CDCl_3$

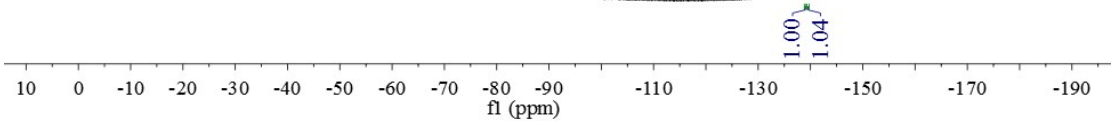


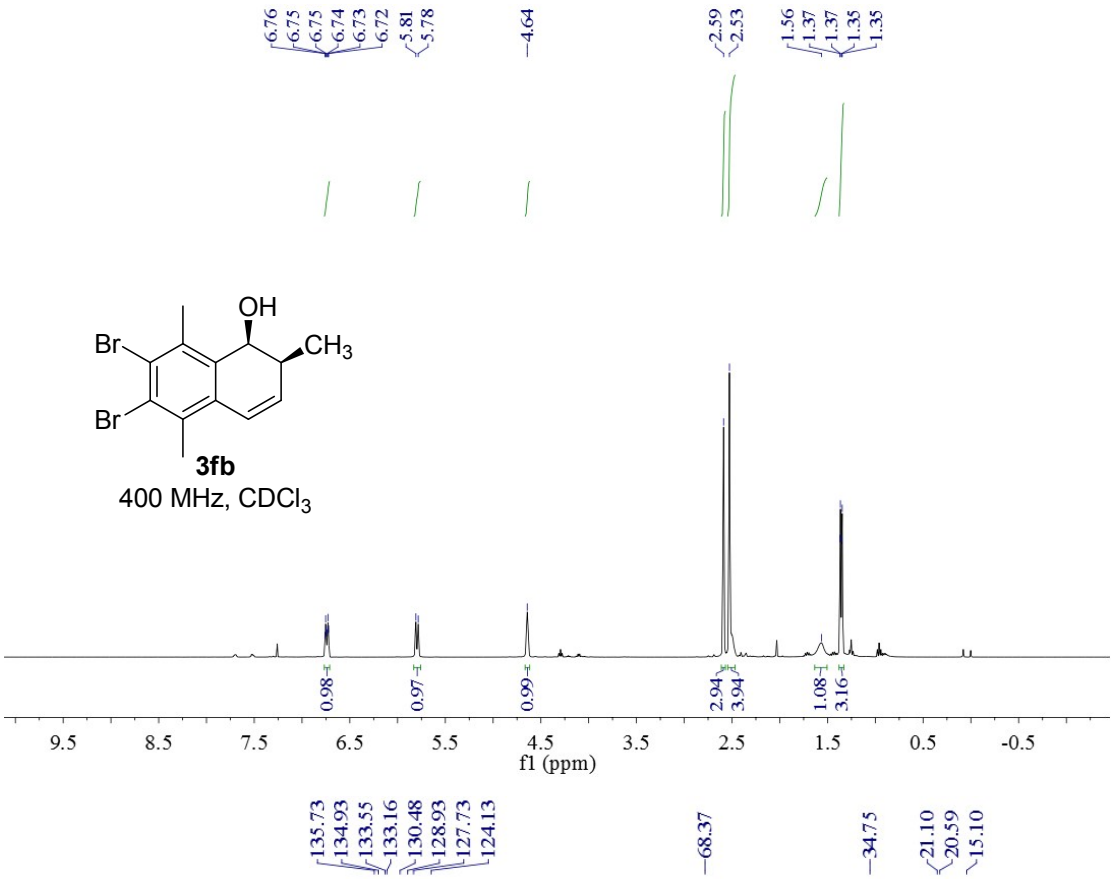




3eb

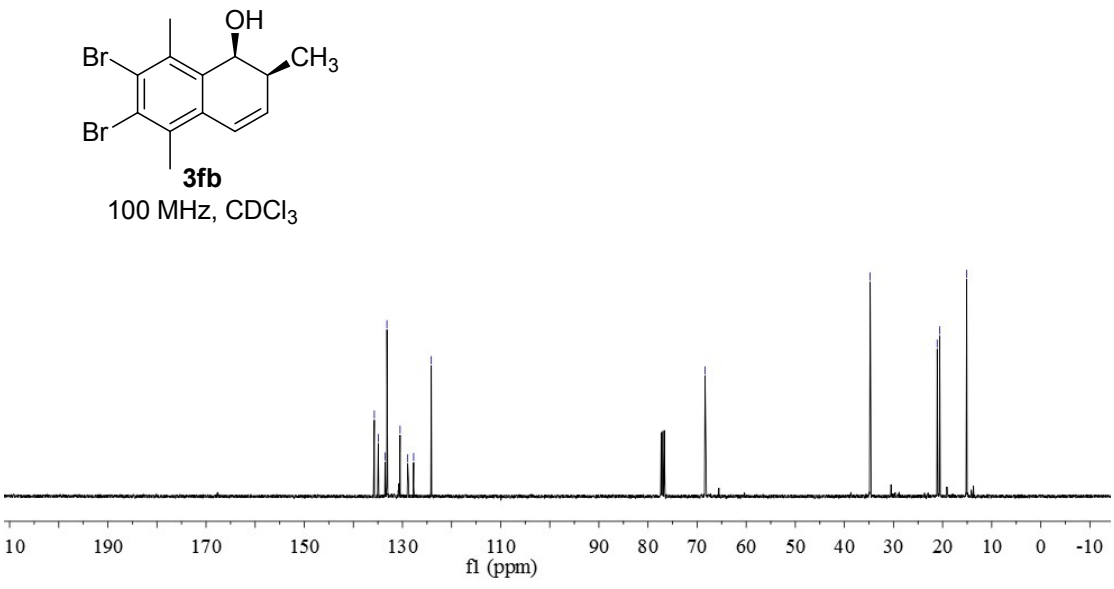
376 MHz, $CDCl_3$





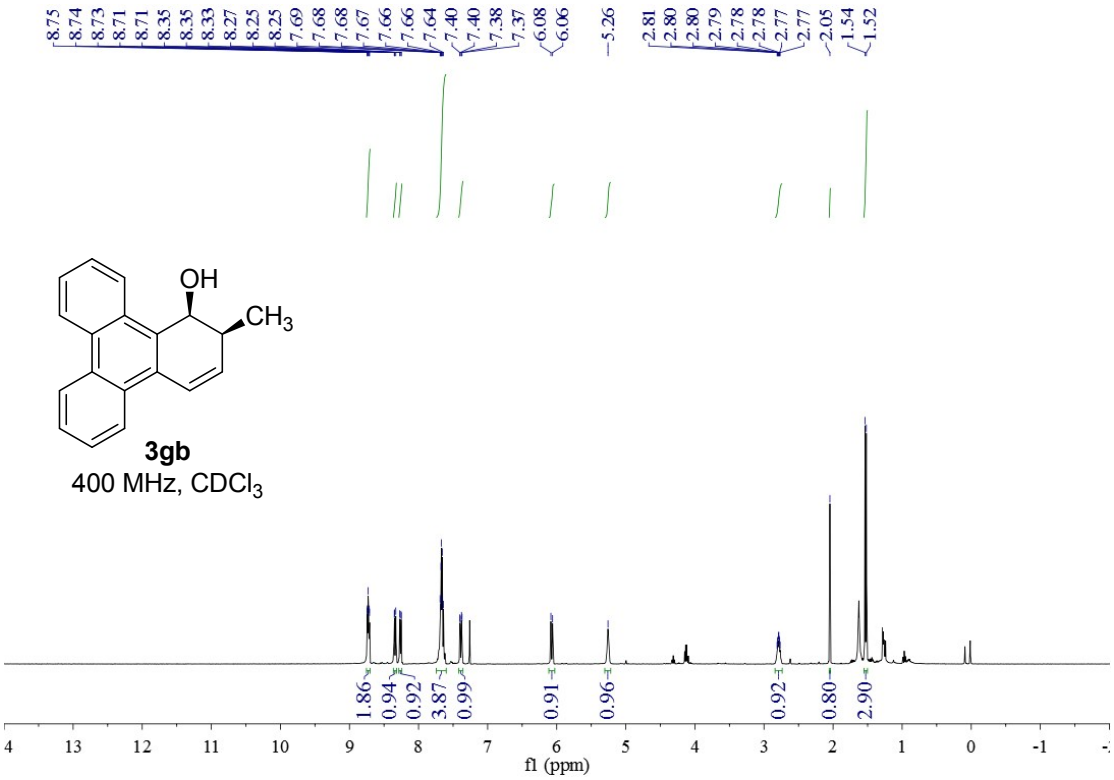
3fb

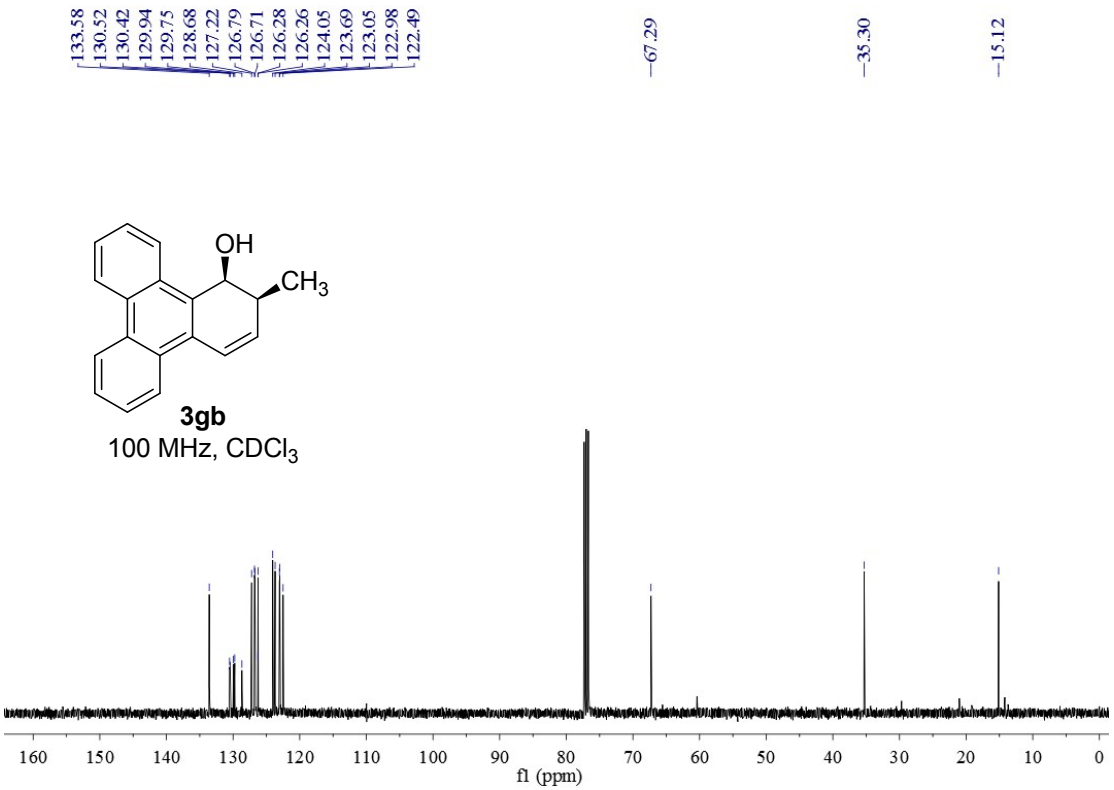
400 MHz, $CDCl_3$

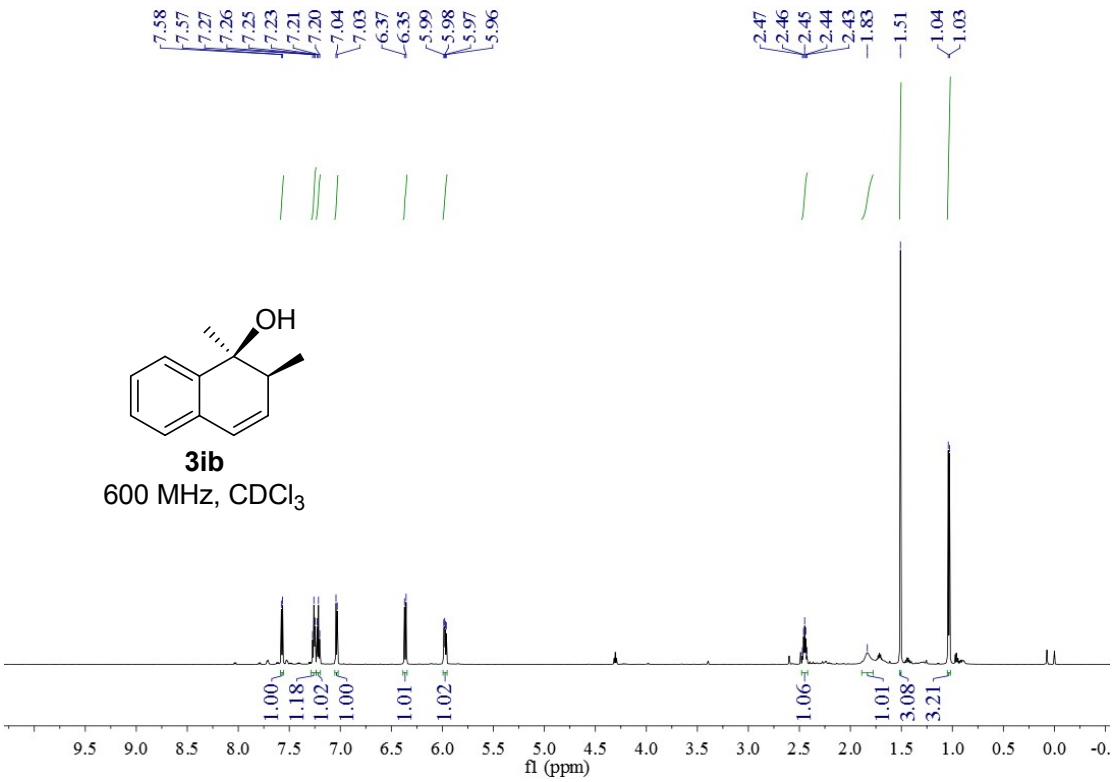


3fb

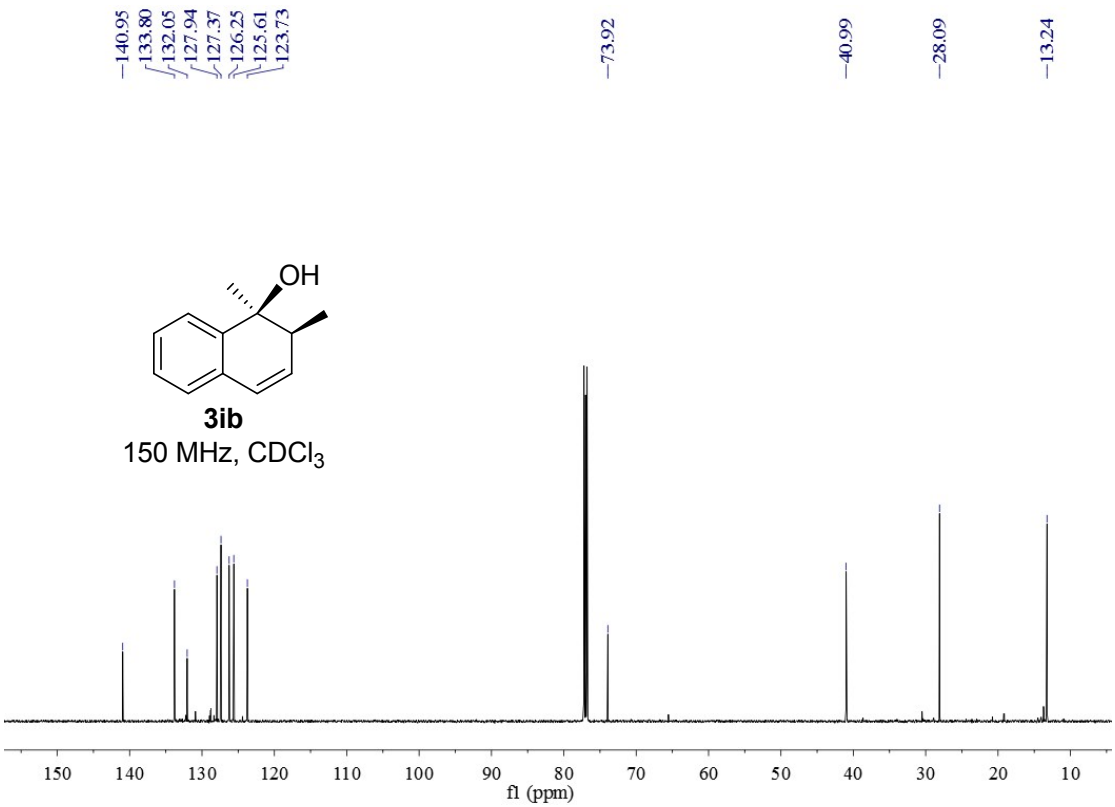
100 MHz, $CDCl_3$


8.75
8.74
8.73
8.71
8.71
8.35
8.35
8.33
8.27
8.25
8.25
7.69
7.68
7.68
7.67
7.66
7.66
7.64
7.40
7.40
7.38
7.37
6.08
6.06
5.26
2.81
2.80
2.80
2.79
2.78
2.78
2.77
2.77
2.05
1.54
1.52
OH
CH3
3gb
400 MHz, CDCl3
1.86
0.94
0.92
3.87
0.99
0.91
0.96
0.92
0.80
2.90
f1 (ppm)

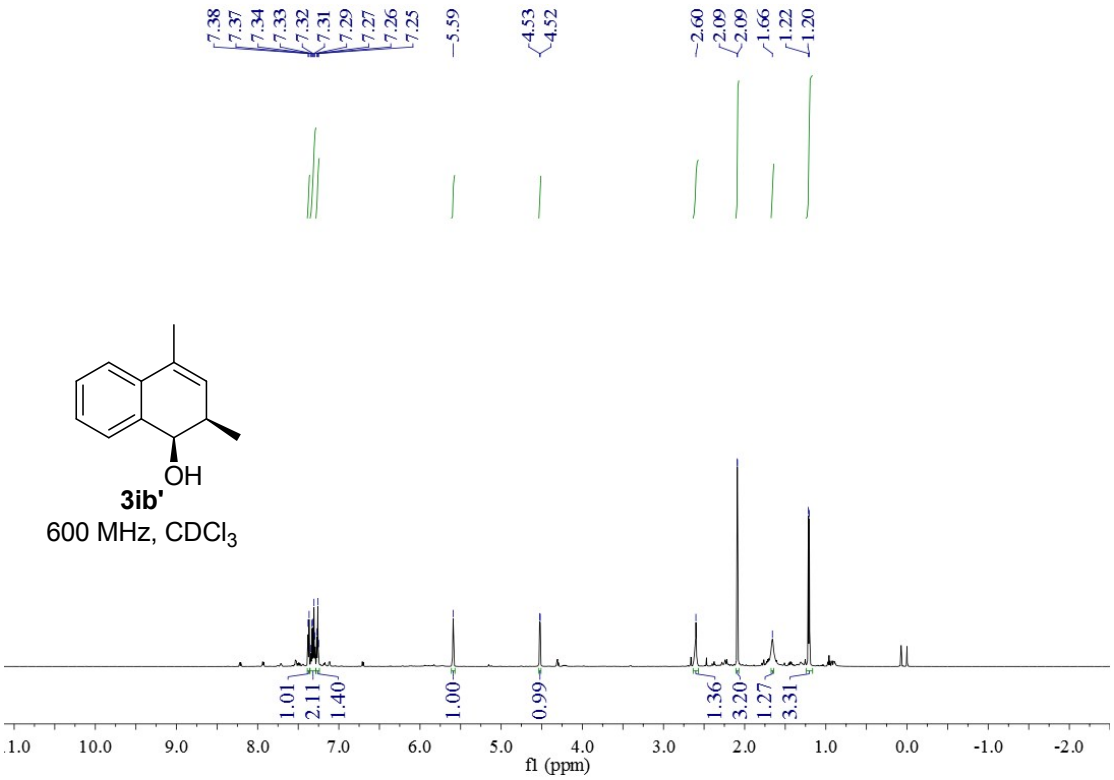

133.58
130.52
130.42
129.94
129.75
128.68
127.22
126.79
126.71
126.28
126.26
124.05
123.69
123.05
122.98
122.49
67.29
35.30
15.12
OH
CH3
3gb
100 MHz, CDCl3
f1 (ppm)

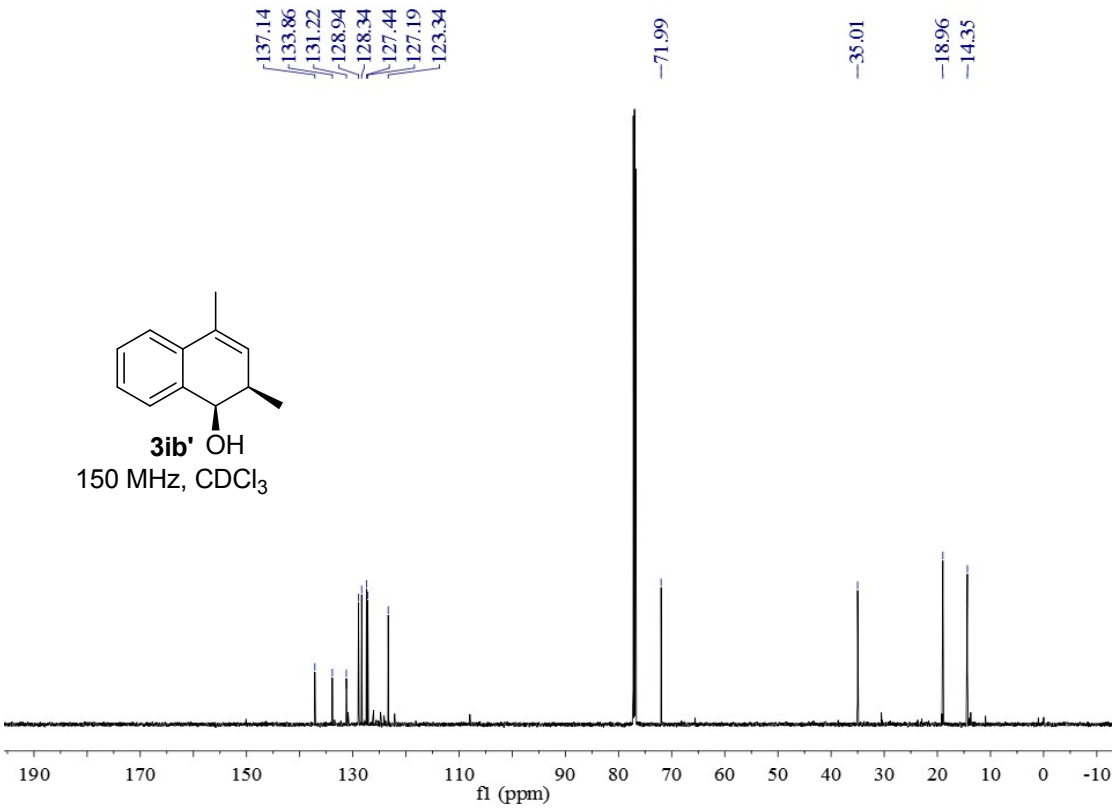


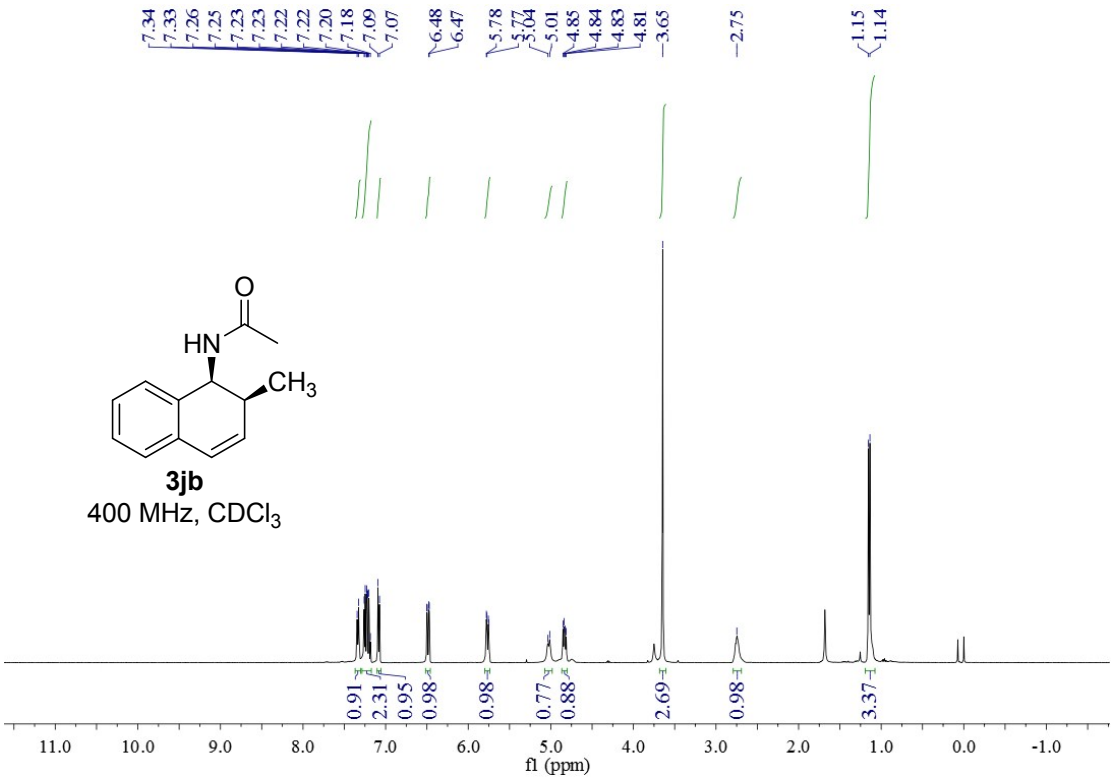
3ib
600 MHz, $CDCl_3$



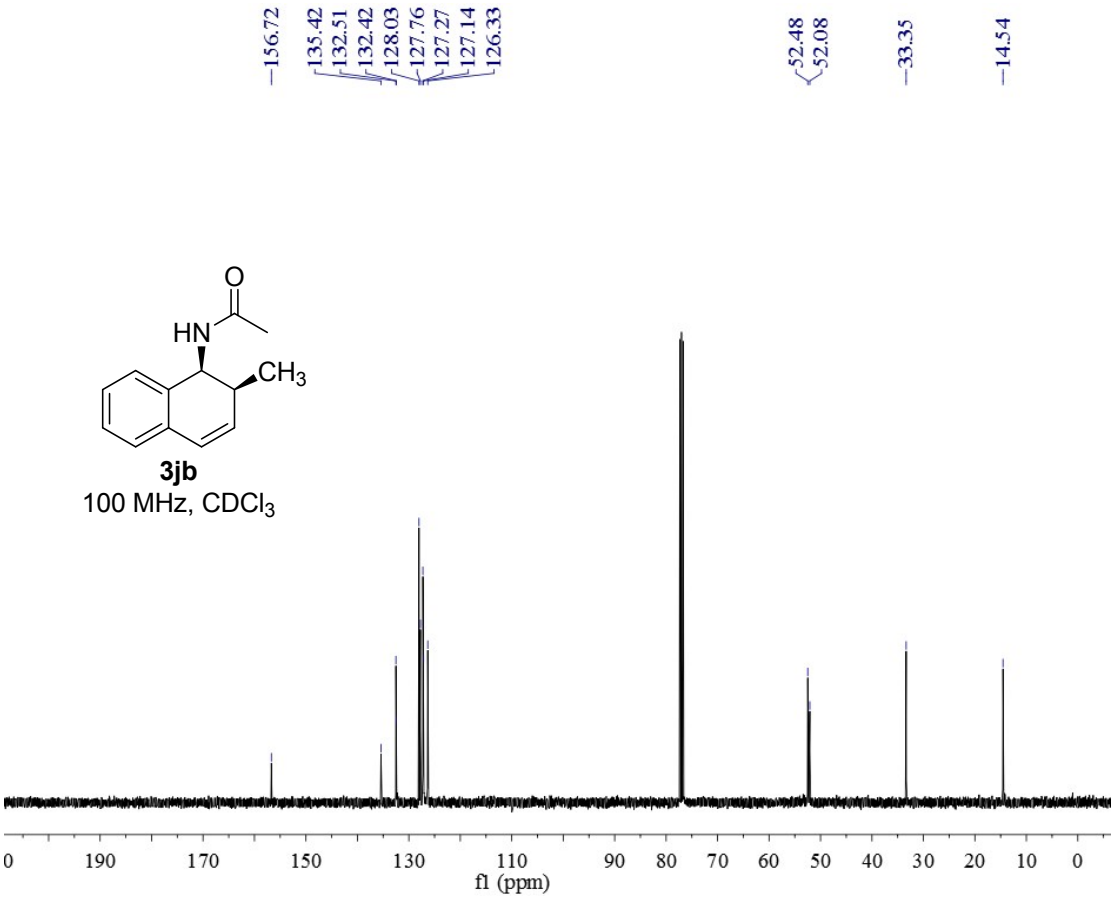
3ib
150 MHz, $CDCl_3$


7.38
7.37
7.34
7.33
7.32
7.31
7.29
7.27
7.26
7.25
5.59
4.53
4.52
2.60
2.09
2.09
1.66
1.22
1.20
OH
3ib'
600 MHz, CDCl3
1.01
2.11
1.40
1.00
0.99
1.36
3.20
1.27
3.31
fl (ppm)

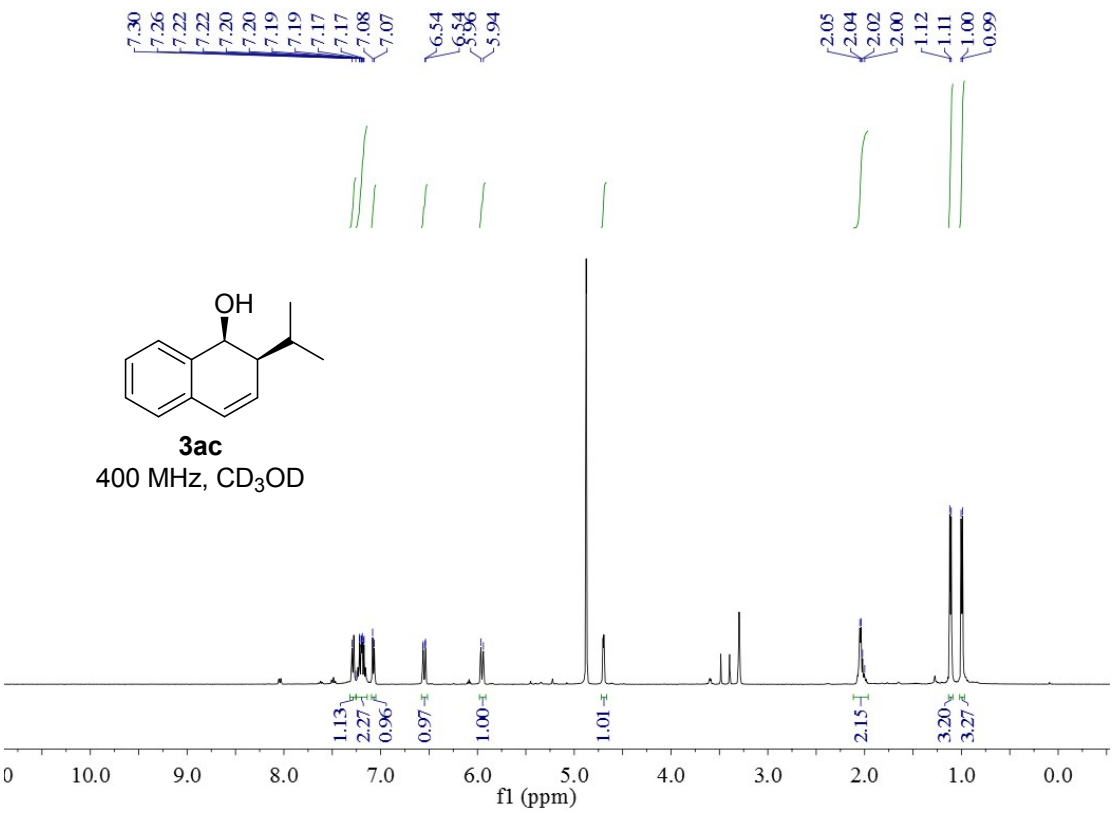

137.14
133.86
131.22
128.94
128.34
127.44
127.19
123.34
71.99
35.01
18.96
14.35
3ib' OH
150 MHz, CDCl3
fl (ppm)



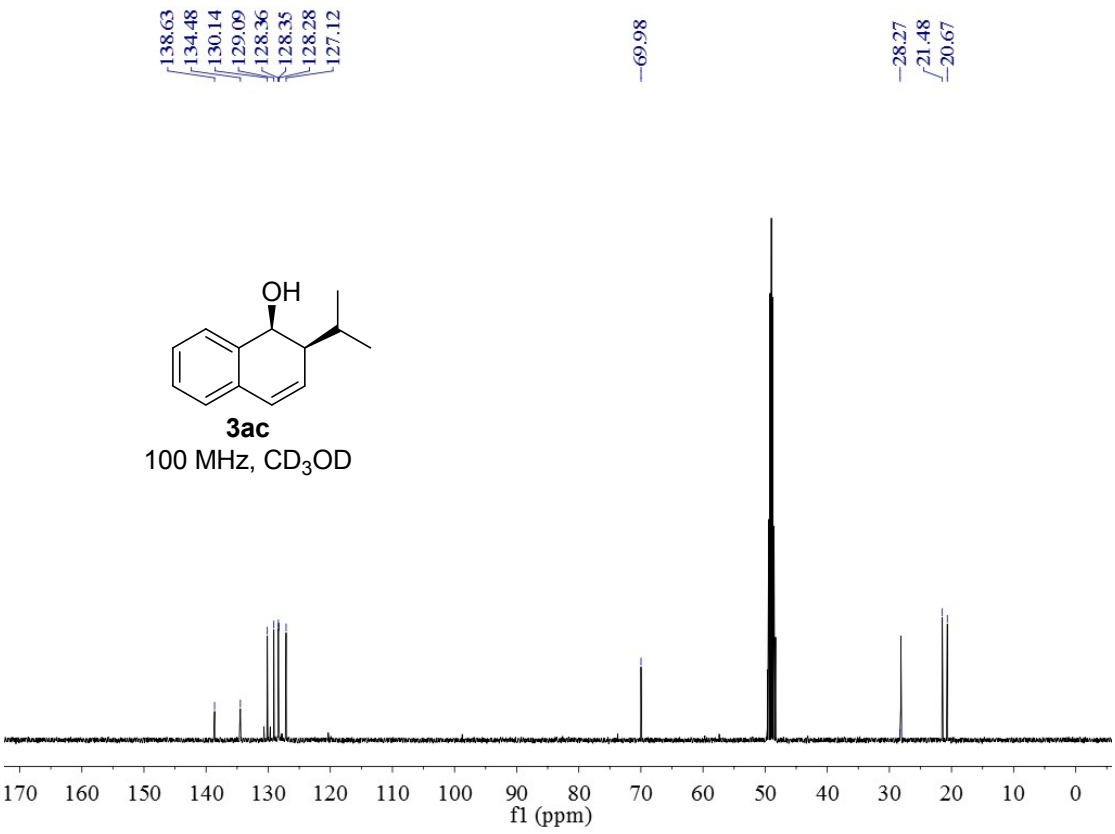
3jb
400 MHz, $CDCl_3$



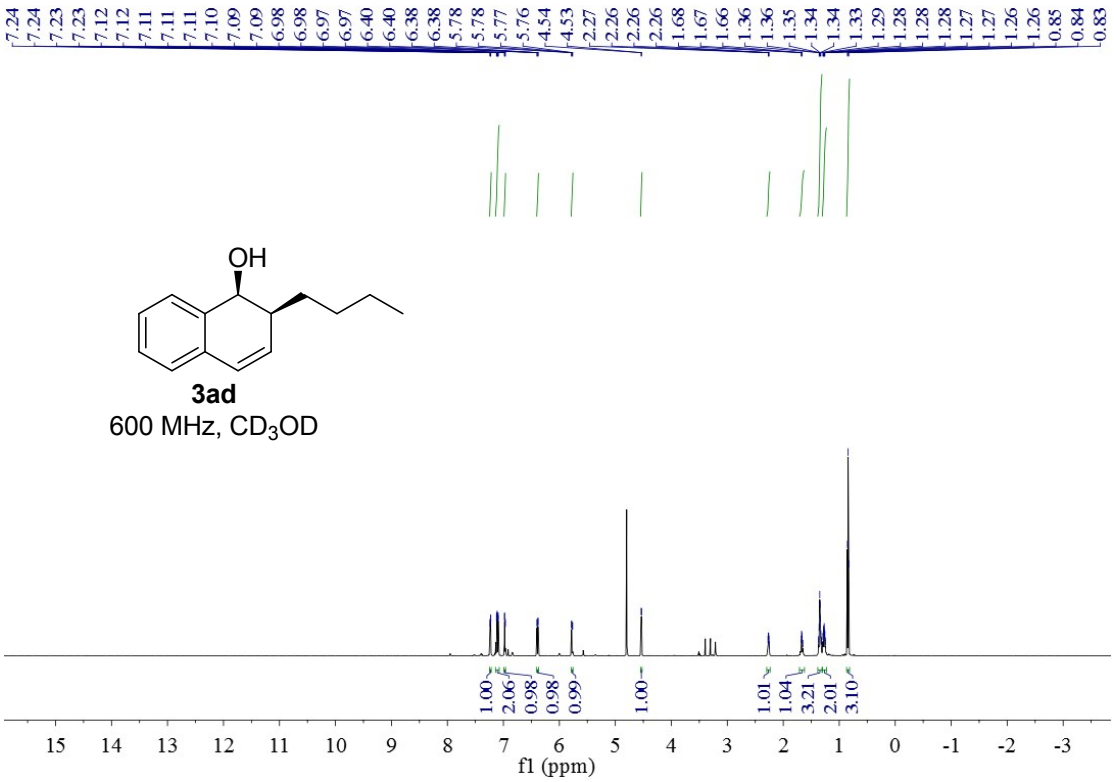
3jb
100 MHz, $CDCl_3$

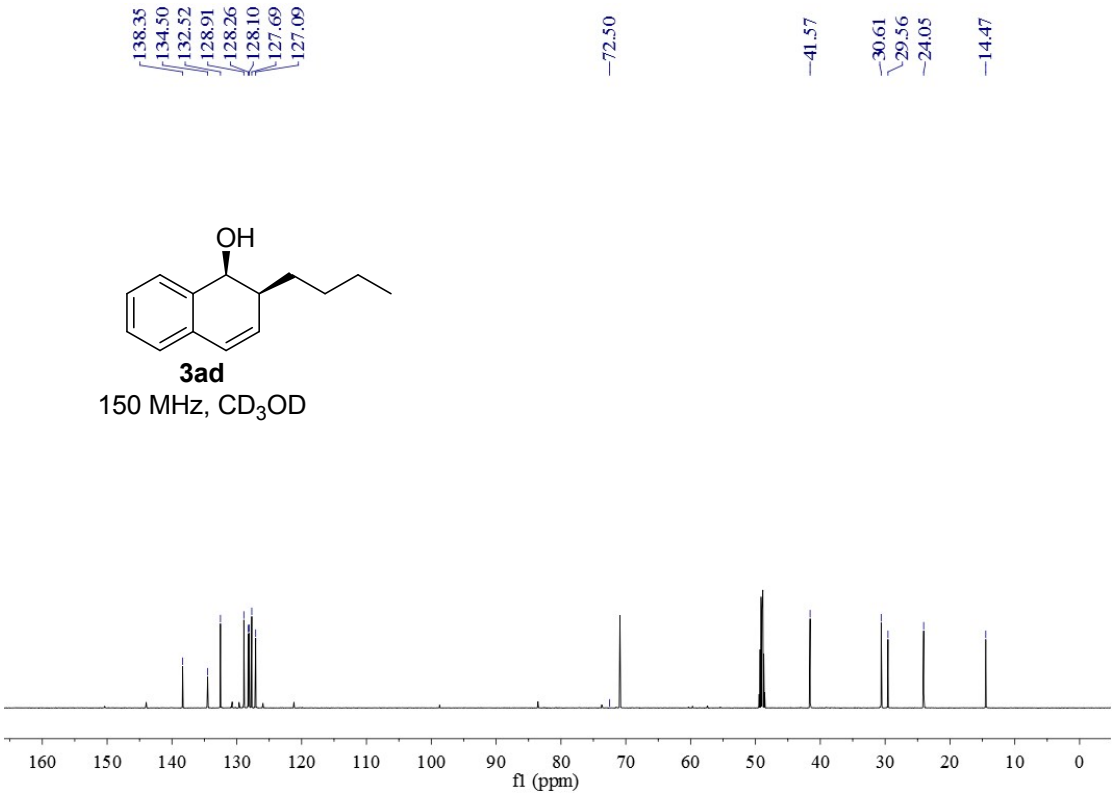


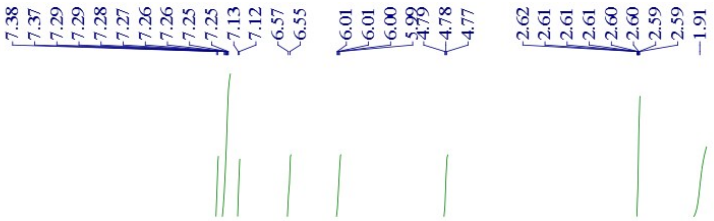
3ac
400 MHz, CD_3OD

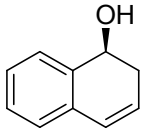


3ac
100 MHz, CD_3OD

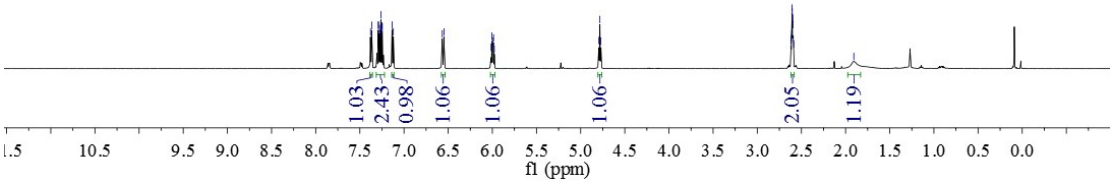

7.24
7.24
7.23
7.23
7.12
7.12
7.11
7.11
7.11
7.10
7.09
7.09
6.98
6.98
6.97
6.97
6.40
6.40
6.38
6.38
5.78
5.78
5.77
5.76
4.54
4.53
2.27
2.26
2.26
2.26
1.68
1.67
1.66
1.36
1.36
1.35
1.34
1.34
1.33
1.29
1.28
1.28
1.28
1.27
1.27
1.26
1.26
0.85
0.84
0.83
OH
3ad
600 MHz, CD3OD
1.00
2.06
0.98
0.98
0.99
1.00
1.01
1.04
3.21
2.01
3.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

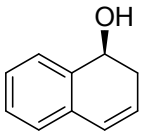

138.35
134.50
132.52
128.91
128.26
128.10
127.69
127.09
72.50
41.57
30.61
29.56
24.05
14.47
OH
3ad
150 MHz, CD3OD
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



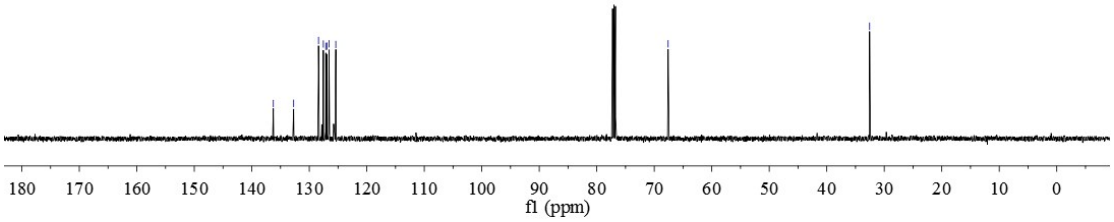


4aa
500 MHz, $CDCl_3$





4aa
125 MHz, $CDCl_3$



3. HPLC chromatograms for compounds

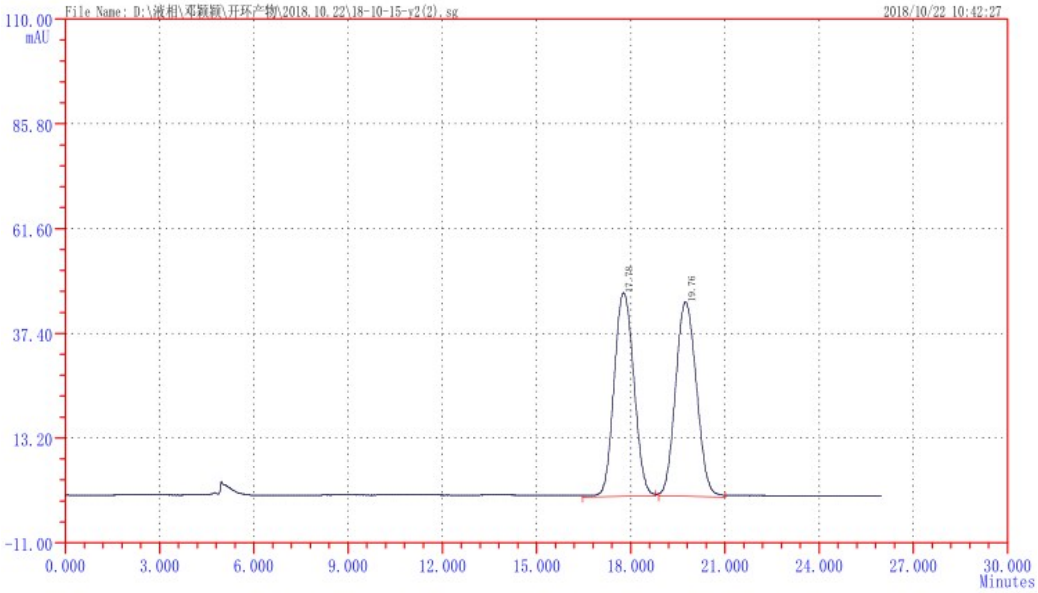


Figure 1: HPLC trace of racemic-**3aa** (2.5 mol% Ni(dppe)Cl_2). HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 17.8 min and 19.8 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	17.779	207536.4	49.91
2	19.755	208319.7	50.09

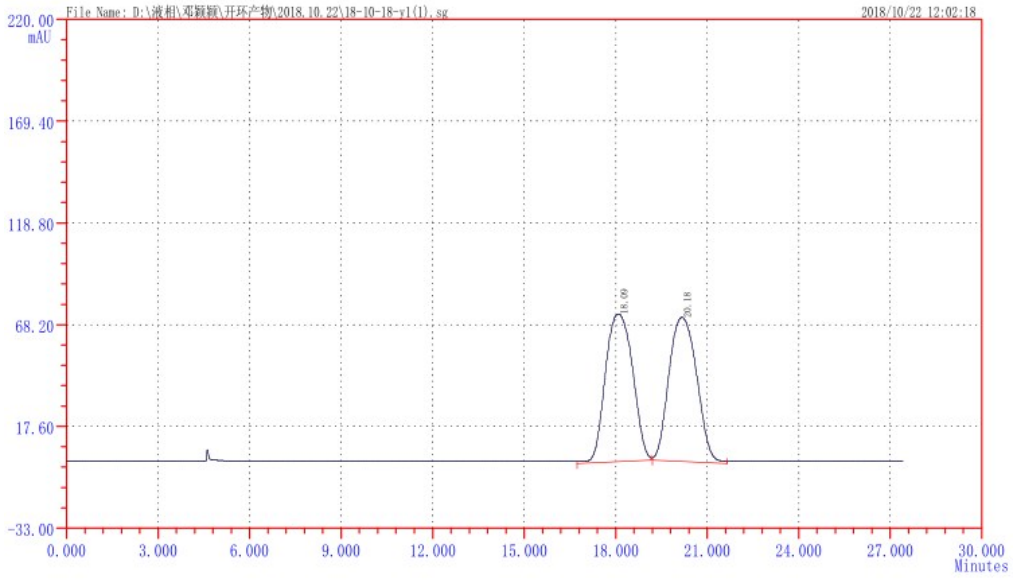


Figure 2: HPLC trace of enantioenriched-**3aa** (2.5 mol% Ni(dppe)Cl_2 and 2.5 mol% (*S*)-BINAP). The *ee* of 0% was determined by HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 18.1 min and 20.2 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	18.092	455758.3	50.06
2	20.178	454502.6	49.93

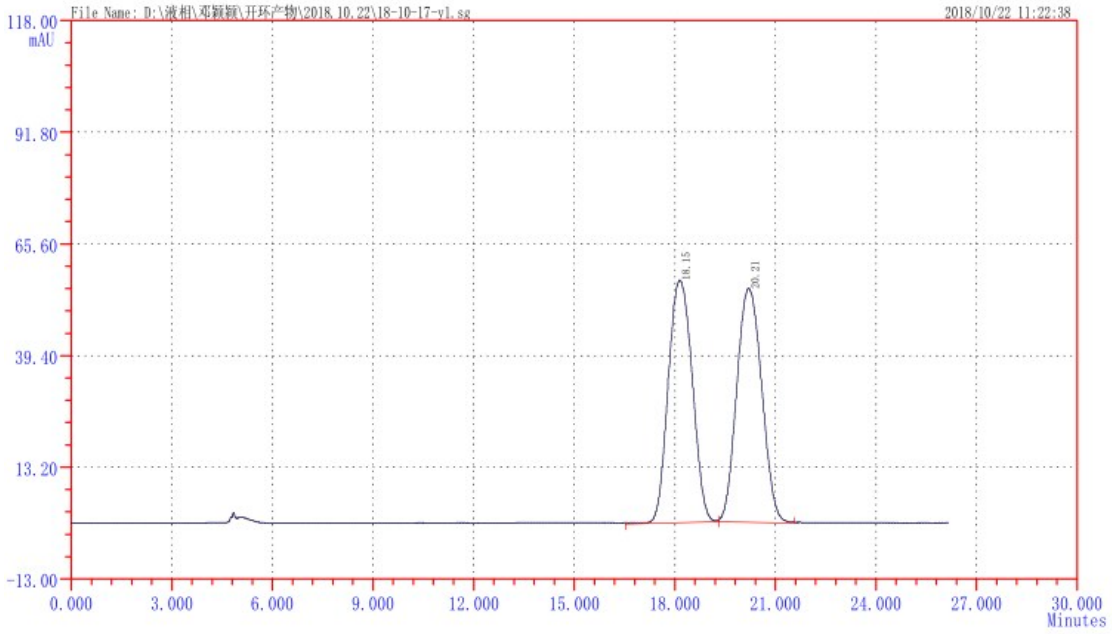


Figure 3: HPLC trace of enantioenriched-**3aa** (2.5 mol% Ni(dppe)Cl_2 and 2.5 mol% **L1**). The *ee* of 0% was determined by HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH 99/1, flow: 1 mL/min, λ = 254), retention times were 18.2 min and 20.2 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	18.152	284021.0	49.93
2	20.210	284821.2	50.07

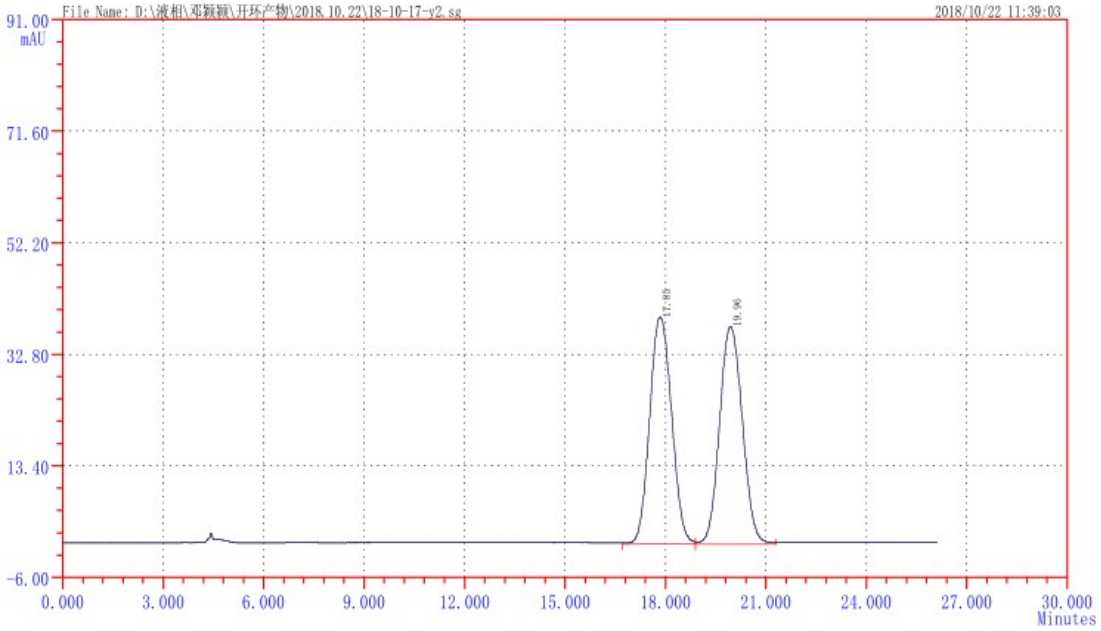


Figure 4: HPLC trace of enantioenriched-**3aa** (2.5 mol% Ni(dppe)Cl_2 and 2.5 mol% **L2**). The *ee* of 0% was determined by HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 17.9 min and 20.0 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	17.854	180615.2	49.89
2	19.956	181379.0	50.10

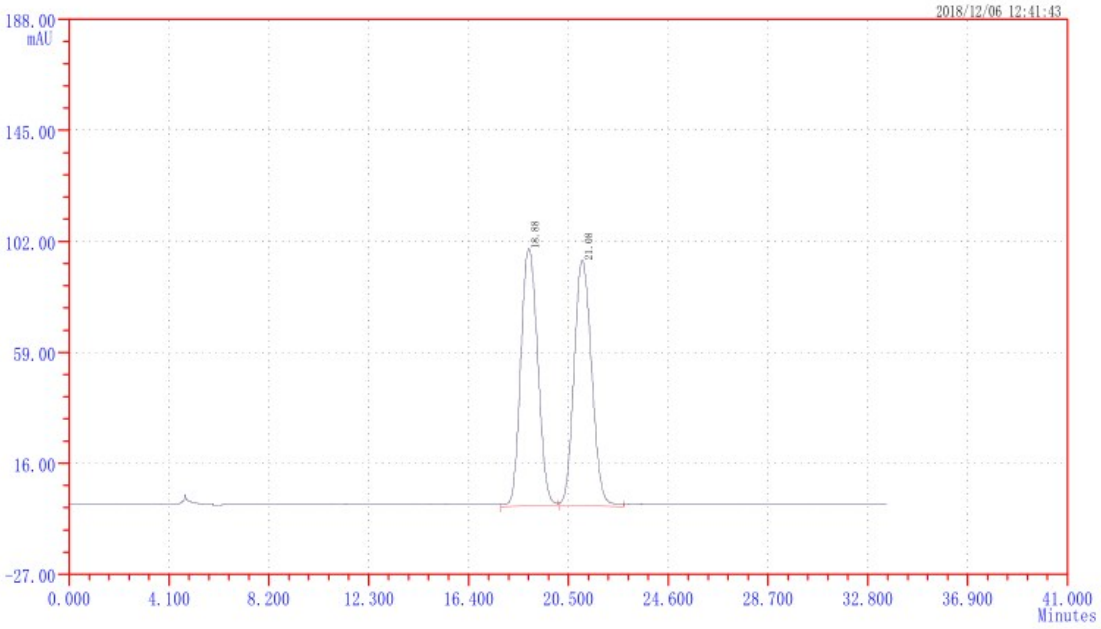


Figure 5: HPLC trace of racemic-**3aa** (2.5 mol% $Ni(COD)_2$ and 2.5 mol% dppe). HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 18.9 min and 21.0 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	18.883	478674.6	49.90
2	21.080	480478.2	50.10

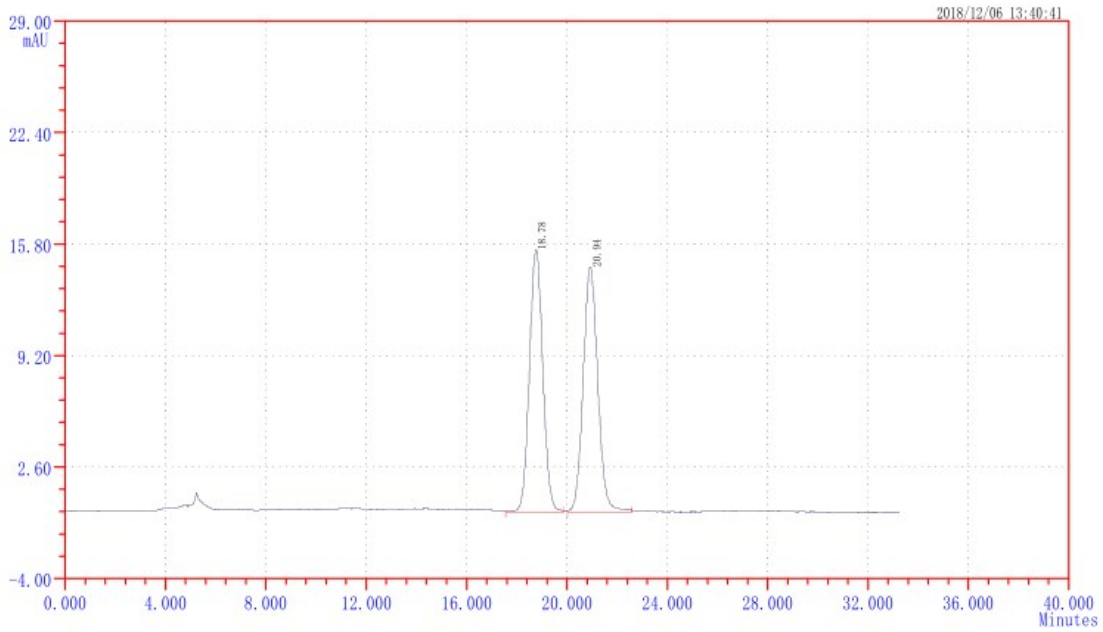


Figure 6: HPLC trace of trace of enantioenriched-**3aa** (2.5 mol% $Ni(COD)_2$ and 2.5 mol% **L1**).. The *ee* of 1% was determined by HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 18.8 min and 20.9 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	18.777	57823.9	49.45
2	20.942	59104.4	48.45

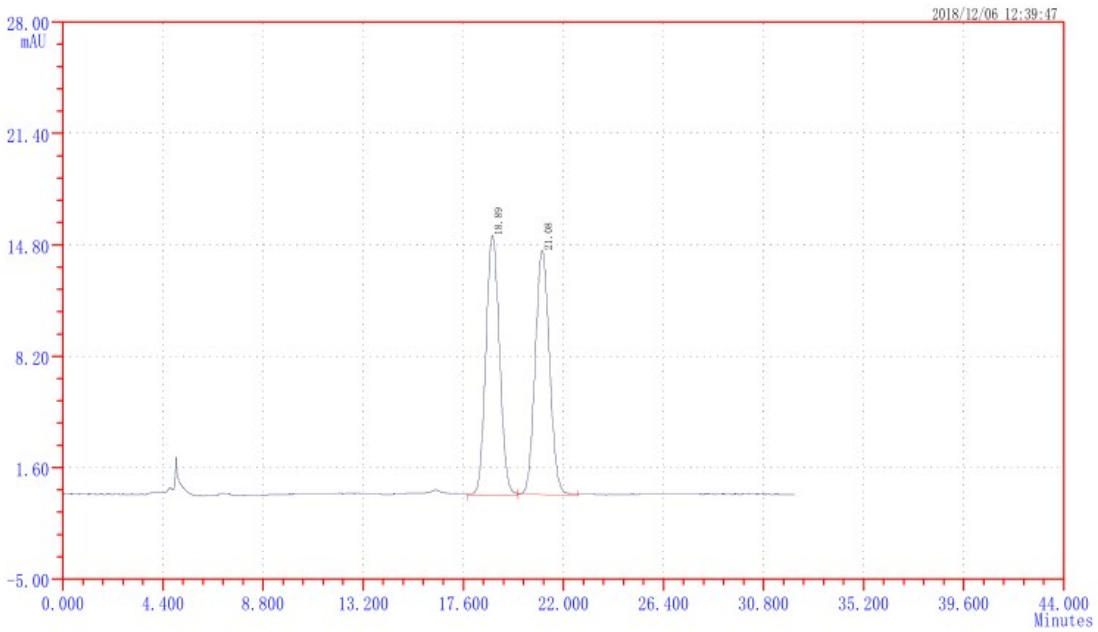


Figure 7: HPLC trace of trace of enantioenriched-**3aa** (2.5 mol% $Ni(COD)_2$ and 2.5 mol% **L2**). The *ee* of 1% was determined by HPLC ananlysis on chiral stationary phase (DAICEL CHIRACEL OD-H, heptane/i-PrOH = 99/1, flow: 1 mL/min, λ = 254), retention times were 18.9 min and 21.1 min.

Peak No.	Time (min)	Area (mV*s)	Area (%)
1	18.892	63730.9	49.95
2	21.077	63856.0	48.95