

# Supplementary Materials

## Copper-Catalyzed Synthesis of Axially Chiral Biaryls with Diaryliodonium Salts as Arylation Reagents

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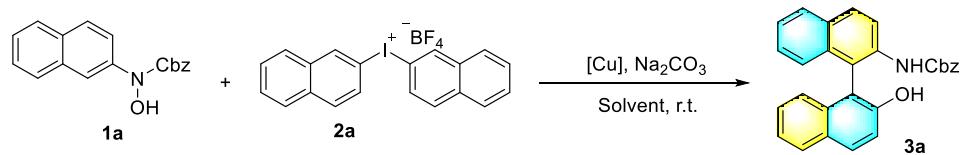
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## I. General information

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR and 376 MHz for <sup>19</sup>F NMR in CDCl<sub>3</sub> or Acetone-*d*<sub>6</sub> or DMSO-*d*<sub>6</sub> with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for <sup>1</sup>H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for <sup>13</sup>C NMR are reported in terms of chemical shift ( $\delta$ , ppm). High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass).

## II. Supplementary Tables for the Reaction Condition Optimizations

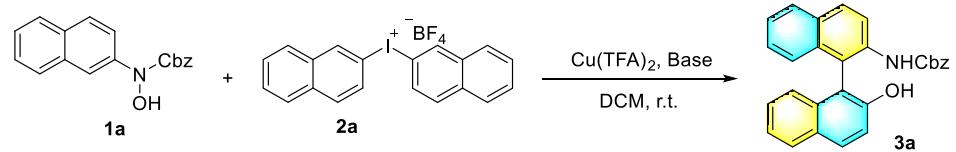
Table S1. Solvent and catalysts screenings for the reaction with *N*-naphthylhydroxylamine<sup>a</sup>



Entry	[Cu]	Solvent	Yield (%) <sup>b</sup>
1 <sup>c</sup>	Cu(TFA) <sub>2</sub>	DCM	96
2	Cu(TFA) <sub>2</sub>	DCM	98
3	Cu(TFA) <sub>2</sub>	DCE	92
4	Cu(TFA) <sub>2</sub>	toluene	80
5	Cu(TFA) <sub>2</sub>	EA	86
6	Cu(TFA) <sub>2</sub>	THF	90
7	Cu(TFA) <sub>2</sub>	MeCN	88
8	Cu(OTf) <sub>2</sub>	DCM	82
9	Cu(OAc) <sub>2</sub>	DCM	89
10	Cu(OTf)	DCM	89
11	CuI	DCM	86

<sup>a</sup>All reactions were performed with [Cu] (10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.13 mmol) in solvent (2.0 mL) at room temperature; <sup>b</sup>Yield was determined by <sup>1</sup>H-NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. <sup>c</sup>**2a** (1.0 equiv) and base (0.12 mmol) were used.

Table S2. Base and loading screenings for the reaction with *N*-naphthylhydroxylamine<sup>a</sup>

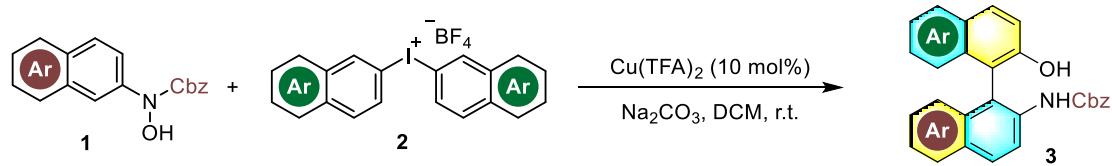


Entry	[M]	Base	Solvent	Yield (%) <sup>b</sup>
1	Cu(TFA) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DCM	93
2	Cu(TFA) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DCM	90
3	Cu(TFA) <sub>2</sub>	NaOH	DCM	75
4	Cu(TFA) <sub>2</sub>	NaO'Bu	DCM	66
5	Cu(TFA) <sub>2</sub>	Et <sub>3</sub> N	DCM	73
6	Cu(TFA) <sub>2</sub>	pyridine	DCM	trace
7	Cu(TFA) <sub>2</sub>	—	DCM	30
8 <sup>c</sup>	Cu(TFA) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	90
9 <sup>d</sup>	Cu(TFA) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	83

<sup>a</sup>Unless otherwise specified, reactions were performed with Cu(TFA)<sub>2</sub> (10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) and base (0.13 mmol) in DCM (2.0 mL) at room temperature; <sup>b</sup>Yield was determined by <sup>1</sup>H-NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard; <sup>c</sup>Cu(TFA)<sub>2</sub> (5 mol%) was used; <sup>d</sup>Cu(TFA)<sub>2</sub> (3 mol%) was used.

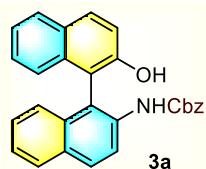
### III. Supplementary Experimental Procedures

#### General procedures for synthesis of NOBIN derivatives **3**



**1** (0.20 mmol), **2** (0.24 mmol), Na<sub>2</sub>CO<sub>3</sub> (27.6 mg, 0.26 mmol) and Cu(TFA)<sub>2</sub> (5.8 mg, 10 mol%) were added to a bottle with a magnetic stirring bar. DCM (4.0 mL) was added and the reaction mixture was stirred at room temperature till **1** was completely consumed (monitored by TLC). After evaporated the solvent, the residue was purified by flash chromatography eluted with DCM to afford the corresponding product **3**.

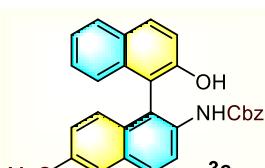
#### Benzyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (**3a**)



#### methyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (**3b**)

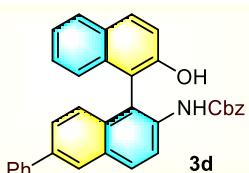


#### benzyl (2'-hydroxy-6-methoxy-[1,1'-binaphthalen]-2-yl)carbamate (**3c**)



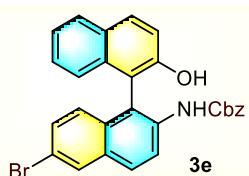
129.0, 128.6, 128.4, 128.3, 128.3, 128.3, 127.4, 126.8, 124.2, 123.9, 120.8, 119.9, 118.0, 117.9, 113.0, 106.5, 67.1, 55.4. **HRMS (ESI)** calcd for [M+H] C<sub>29</sub>H<sub>24</sub>NO<sub>4</sub>, m/z: 450.1700, found: 450.1697.

#### **benzyl (2'-hydroxy-6-phenyl-[1,1'-binaphthalen]-2-yl)carbamate (3d)**



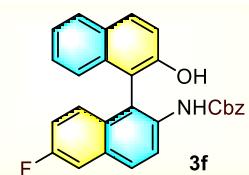
Yield: 93%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.48 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.61 (dd, *J* = 7.6, 2.4 Hz, 2H), 7.49 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35-7.30 (m, 3H), 7.27-7.21 (m, 4H), 7.19-7.14 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 5.46 (s, 1H), 4.98 (d, *J* = 12.4 Hz, 1H), 4.93 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.7, 152.2, 140.7, 138.0, 135.9, 135.7, 133.3, 132.2, 131.3, 131.1, 130.6, 129.5, 129.0, 128.6, 128.5, 128.4, 128.3, 127.5, 127.5, 127.3, 127.0, 126.1, 125.8, 124.2, 124.1, 120.2, 118.1, 117.1, 112.7, 67.2. **HRMS (ESI)** calcd for [M+H] C<sub>34</sub>H<sub>26</sub>NO<sub>3</sub>, m/z: 496.1907, found: 496.1909.

#### **benzyl (6-bromo-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3e)**



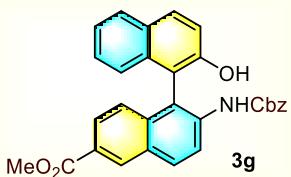
Yield: 96%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.54 (d, *J* = 9.2 Hz, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.43-7.25 (m, 9H), 7.02 (d, *J* = 9.2 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.57 (s, 1H), 5.60 (s, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.6, 152.1, 136.1, 135.6, 133.2, 131.9, 131.6, 131.5, 130.6, 130.2, 129.4, 129.2, 128.6, 128.5, 128.4, 128.3, 127.6, 127.1, 124.1, 124.0, 120.9, 119.3, 118.1, 117.6, 112.2, 67.3. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>21</sub>BrNO<sub>3</sub>, m/z: 498.0700, found: 498.0700.

#### **benzyl (6-fluoro-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3f)**



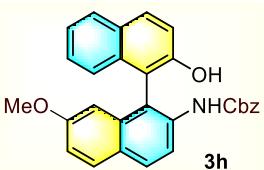
Yield: 92%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.44 (d, *J* = 9.2 Hz, 1H), 7.91 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.35-7.18 (m, 8H), 7.07 (dd, *J* = 9.3, 5.6 Hz, 1H), 7.00 (td, *J* = 8.8, 2.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.45 (s, 1H), 5.46 (s, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.94 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 160.3 (d, *J* = 245.0 Hz), 153.8, 152.1, 135.7, 135.1 (d, *J* = 2.0 Hz), 133.2, 131.6 (d, *J* = 9.0 Hz), 131.4, 130.0, 129.4, 129.4, 129.4, 128.6, 128.5, 128.4, 128.3, 127.8 (d, *J* = 9.0 Hz), 127.6, 124.0 (d, *J* = 6.0 Hz), 121.2, 118.1, 117.9, 117.5 (d, *J* = 25.0 Hz) 112.5, 111.4 (d, *J* = 21.0 Hz), 67.2. **<sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>)** δ -115.88. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>21</sub>FNO<sub>3</sub>, m/z: 438.1500, found: 438.1500

**methyl 2-(((benzyloxy)carbonyl)amino)-2'-hydroxy-[1,1'-binaphthalene]-6-carboxylate (3g)**



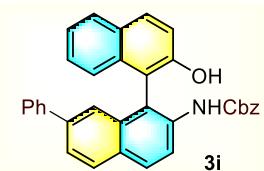
Yield: 93%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.62 (d, *J* = 9.2 Hz, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.75 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.44 (d, *J* = 9.2 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.35-7.26 (m, 6H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.27 (s, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 5.03 (d, *J* = 12.4 Hz, 1H), 3.86 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 167.1, 153.4, 152.6, 138.0, 135.6, 135.5, 133.2, 131.5, 131.5, 131.2, 129.5, 129.4, 128.6, 128.5, 128.4, 128.4, 127.5, 126.5, 126.1, 125.4, 124.0, 123.9, 119.9, 118.5, 117.1, 112.0, 67.3, 52.3. **HRMS (ESI)** calcd for [M+H] C<sub>30</sub>H<sub>24</sub>NO<sub>5</sub>, m/z: 478.1649, found: 478.1649.

**benzyl (2'-hydroxy-7-methoxy-[1,1'-binaphthalen]-2-yl)carbamate (3h)**



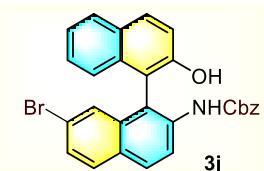
Yield: 97%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.39 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.42-7.39 (m, 2H), 7.37-7.26 (m, 6H), 7.14-7.10 (m, 2H), 6.54 (s, 1H), 6.45 (d, *J* = 2.8 Hz, 1H), 5.48 (s, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 3.51 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 158.9, 153.6, 152.1, 136.4, 135.8, 134.4, 133.0, 131.3, 130.0, 129.9, 129.4, 128.6, 128.5, 128.3, 128.3, 127.4, 126.3, 124.2, 124.0, 118.0, 117.5, 117.3, 115.9, 112.8, 103.9, 67.1, 55.1. **HRMS (ESI)** calcd for [M+H] C<sub>29</sub>H<sub>24</sub>NO<sub>4</sub>, m/z: 450.1700, found: 450.1699.

**benzyl (2'-hydroxy-7-phenyl-[1,1'-binaphthalen]-2-yl)carbamate (3i)**



Yield: 98%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.60 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 9.2 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.48-7.30 (m, 14H), 7.19 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.65 (s, 1H), 5.67 (s, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.7, 152.3, 141.0, 140.2, 136.3, 135.8, 133.4, 133.3, 131.4, 130.1, 130.0, 129.5, 128.9, 128.8, 128.6, 128.6, 128.4, 128.3, 127.5, 127.5, 127.5, 125.2, 124.2, 124.1, 123.1, 119.9, 118.1, 117.6, 112.7, 67.2. **HRMS (ESI)** calcd for [M+H] C<sub>34</sub>H<sub>26</sub>NO<sub>3</sub>, m/z: 496.1907, found: 496.1907.

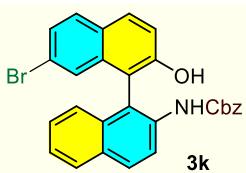
**benzyl (7-bromo-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3j)**



Yield: 95%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.54 (d, *J* = 9.2 Hz, 1H), 8.00 (dd, *J* = 8.8, 3.2 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44-7.25 (m, 9H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.54 (s, 1H), 5.47 (s, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 5.02 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.5, 152.1, 136.7, 135.6, 134.3, 133.0, 131.6, 130.2, 130.0, 129.5, 129.2, 128.7, 128.6, 128.6, 128.4, 128.3, 127.7, 127.1, 124.1, 123.9,

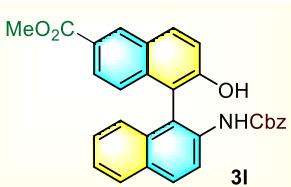
122.0, 120.0, 118.1, 116.4, 111.9, 67.3. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>21</sub>BrNO<sub>3</sub>, m/z: 498.0700, found: 498.0699.

**benzyl (7'-bromo-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3k)**



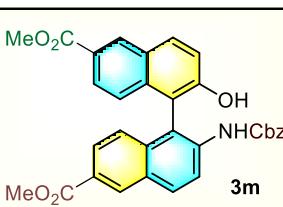
Yield: 94%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.52 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.49-7.45 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.36-7.28 (m, 6H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.48 (s, 1H), 5.49 (s, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.6, 153.0, 135.9, 135.6, 134.6, 132.8, 131.2, 130.9, 130.7, 130.1, 128.6, 128.4, 128.4, 128.4, 127.8, 127.6, 127.5, 126.1, 125.4, 124.9, 122.1, 119.9, 118.5, 116.2, 112.2, 67.3. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>21</sub>BrNO<sub>3</sub>, m/z: 498.0700, found: 498.0701.

**methyl 2'-((benzyloxy)carbonyl)amino-2-hydroxy-[1,1'-binaphthalene]-6-carboxylate (3l)**



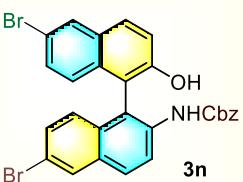
Yield: 90%. **<sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>)** δ 8.96 (s, 1H), 8.62 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 9.2 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.29-7.20 (m, 6H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 5.04 (s, 2H), 3.89 (s, 3H). **<sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>)** δ 171.7, 161.1, 158.9, 141.9, 141.7, 140.8, 138.4, 137.3, 136.4, 136.1, 134.1, 134.1, 133.5, 133.3, 133.3, 133.1, 133.1, 131.7, 131.2, 130.4, 130.1, 129.9, 129.5, 125.8, 124.9, 119.2, 71.3, 56.6. **HRMS (ESI)** calcd for [M+H] C<sub>30</sub>H<sub>24</sub>NO<sub>5</sub>, m/z: 478.1649, found: 478.1651.

**dimethyl 2'-((benzyloxy)carbonyl)amino-2'-hydroxy-[1,1'-binaphthalene]-6,6'-dicarboxylate (3m)**



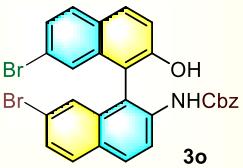
Yield: 81%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.58 (d, *J* = 1.6 Hz, 1H), 8.56 (d, *J* = 8.8 Hz, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.78 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.72 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.31-7.26 (m, 3H), 7.24-7.21 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 6.34 (s, 1H), 5.02 (s, 2H), 3.91 (s, 3H), 3.84 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 167.1, 167.0, 154.6, 153.3, 138.1, 135.7, 135.4, 135.3, 133.0, 131.8, 131.6, 131.2, 129.6, 128.6, 128.5, 128.4, 128.4, 127.0, 126.6, 126.3, 125.6, 125.1, 124.0, 120.0, 119.3, 116.3, 112.3, 67.4, 52.3, 52.2. **HRMS (ESI)** calcd for [M+H] C<sub>32</sub>H<sub>26</sub>NO<sub>7</sub>, m/z: 536.1704, found: 536.1706.

**benzyl (6,6'-dibromo-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3n)**



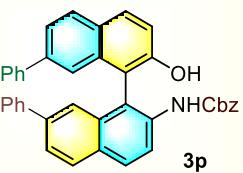
Yield: 90%. **<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)** δ 8.74 (s, 1H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.43 (s, 1H), 7.38 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.34 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.32-7.26 (m, 3H), 7.23-7.21 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 5.03 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, Acetone-*d*<sub>6</sub>)** δ 154.1, 153.6, 136.6, 136.2, 132.5, 132.0, 131.8, 130.3, 130.2, 130.0, 130.0, 129.9, 129.6, 128.3, 128.1, 127.9, 127.5, 126.1, 121.7, 120.5, 120.0, 118.0, 116.5, 113.4, 66.2. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>20</sub>Br<sub>2</sub>NO<sub>3</sub>, m/z: 575.9805, found: 575.9808.

**benzyl (7,7'-dibromo-2'-hydroxy-[1,1'-binaphthalen]-2-yl)carbamate (3o)**



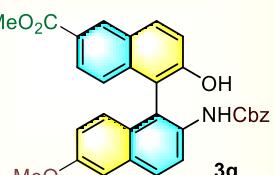
Yield: 85%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.53 (dd, *J* = 9.2, 2.0 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38-7.32 (m, 4H), 7.29-7.26 (m, 2H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 6.44 (s, 1H), 5.49 (s, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.4, 153.0, 136.8, 135.5, 134.4, 134.1, 131.6, 130.5, 130.3, 130.1, 129.2, 128.9, 128.6, 128.5, 128.4, 127.9, 127.7, 126.8, 125.8, 122.4, 122.2, 120.1, 118.6, 115.4, 111.3, 67.4. **HRMS (ESI)** calcd for [M+H] C<sub>28</sub>H<sub>20</sub>Br<sub>2</sub>NO<sub>3</sub>, m/z: 575.9805, found: 575.9804.

**benzyl (2'-hydroxy-7,7'-diphenyl-[1,1'-binaphthalen]-2-yl)carbamate (3p)**



Yield: 83%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.58 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.05-8.01 (m, 3H), 7.74 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.69 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.47-7.41 (m, 7H), 7.39-7.27 (m, 11H), 6.63 (s, 1H), 5.38 (s, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.7, 152.5, 141.0, 141.0, 140.4, 140.3, 136.3, 135.7, 133.5, 133.2, 131.2, 130.2, 130.1, 129.1, 129.0, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 127.5, 127.5, 127.4, 127.4, 125.2, 123.9, 122.9, 121.9, 120.0, 118.0, 117.2, 112.9, 67.2. **HRMS (ESI)** calcd for [M+H] C<sub>40</sub>H<sub>30</sub>NO<sub>3</sub>, m/z: 572.2220, found: 572.2223.

**methyl 2'-((benzyl carbonyl)amino)-2-hydroxy-6'-methoxy-[1,1'-binaphthalene]-6-carboxylate (3q)**



Yield: 88%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.81 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.34-7.20 (m, 6H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 9.2 Hz, 1H),

6.95 (dd,  $J = 9.2, 2.8$  Hz, 1H), 6.45 (s, 1H), 5.99 (s, 1H), 5.05 (d,  $J = 12.0$  Hz, 1H), 5.00 (d,  $J = 12.0$  Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.2, 157.3, 154.3, 153.9, 135.8, 135.7, 133.7, 132.5, 132.2, 131.5, 129.1, 128.5, 128.3, 128.3, 128.2, 128.1, 126.8, 126.6, 125.4, 124.3, 121.0, 120.0, 119.1, 117.7, 113.4, 106.5, 67.1, 55.3, 52.2. **HRMS (ESI)** calcd for [M+H]  $\text{C}_{31}\text{H}_{26}\text{NO}_6$ , m/z: 508.1755, found: 508.1759.

#### benzyl (6'-fluoro-2'-hydroxy-6-methoxy-[1,1'-binaphthalen]-2-yl)carbamate (3r)

Yield: 85%.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.40 (d,  $J = 8.8$  Hz, 1H), 7.94 (d,  $J = 8.8$  Hz, 1H), 7.89 (d,  $J = 8.8$  Hz, 1H), 7.54 (dd,  $J = 9.5, 2.4$  Hz, 1H), 7.40 (d,  $J = 8.8$  Hz, 1H), 7.37-7.31 (m, 3H), 7.28-7.23 (m, 3H), 7.10-6.98 (m, 4H), 6.46 (s, 1H), 5.60 (s, 1H), 5.07 (d,  $J = 12.4$  Hz, 1H), 5.01 (d,  $J = 12.4$  Hz, 1H), 3.91 (s, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  159.5 (d,  $J = 243.0$  Hz), 157.3, 153.9, 151.5 (d,  $J = 2.0$  Hz), 135.8, 133.6, 132.2, 130.2 (d,  $J = 5.0$  Hz), 130.2, 129.9 (d,  $J = 9.0$  Hz), 129.1, 128.6, 128.4, 128.3, 128.1, 120.9, 126.7, 126.5 (d,  $J = 8.0$  Hz), 120.0, 119.3, 118.0, 117.4 (d,  $J = 25.0$  Hz), 113.5, 111.6 (d,  $J = 21.0$  Hz), 106.5, 67.2, 55.4.  **$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**  $\delta$  -118.10. **HRMS (ESI)** calcd for [M+H]  $\text{C}_{29}\text{H}_{23}\text{FNO}_4$ , m/z: 468.1606, found: 468.1607.

#### benzyl (6'-fluoro-2'-hydroxy-7-phenyl-[1,1'-binaphthalen]-2-yl)carbamate (3s)

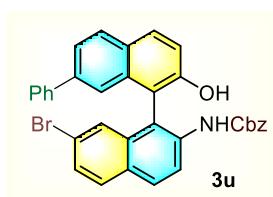
Yield: 84%.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.55 (d,  $J = 9.2$  Hz, 1H), 8.10 (d,  $J = 9.2$  Hz, 1H), 8.02 (d,  $J = 8.8$  Hz, 1H), 7.93 (d,  $J = 8.8$  Hz, 1H), 7.75 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.57 (dd,  $J = 9.6, 2.4$  Hz, 1H), 7.47-7.44 (m, 3H), 7.41-7.28 (m, 9H), 7.16-7.08 (m, 2H), 6.57 (s, 1H), 5.55 (s, 1H), 5.12 (d,  $J = 12.0$  Hz, 1H), 5.06 (d,  $J = 12.4$  Hz, 1H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  159.6 (d,  $J = 242.0$  Hz), 153.7, 151.7 (d,  $J = 2.0$  Hz), 140.9, 140.3, 136.2, 135.7, 133.2, 130.5 (d,  $J = 5.0$  Hz), 130.2, 130.1, 130.1, 130.0 (d,  $J = 10.0$  Hz), 129.0, 128.8, 128.6, 128.5, 128.4, 127.5, 127.5, 126.5 (d,  $J = 8.0$  Hz), 125.3, 122.9, 120.0, 119.4, 117.5 (d,  $J = 25.0$  Hz), 117.3, 113.0, 111.8 (d,  $J = 21.0$  Hz), 67.3.  **$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**  $\delta$  -117.88. **HRMS (ESI)** calcd for [M+H]  $\text{C}_{34}\text{H}_{25}\text{FNO}_3$ , m/z: 514.1813, found: 514.1814.

#### Methyl 2-(((benzyloxy)carbonyl)amino)-7'-bromo-2'-hydroxy-[1,1'-binaphthalene]-6-carboxylate (3t)

Yield: 86%.  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.61 (d,  $J = 9.2$  Hz, 1H), 8.41 (d,  $J = 2.0$  Hz, 1H), 8.04 (d,  $J = 9.2$  Hz, 1H), 7.95 (d,  $J = 8.8$  Hz, 1H), 7.77 (d,  $J = 8.8$  Hz, 1H), 7.76 (dd,  $J = 8.8, 2.0$  Hz, 1H), 7.46 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.42 (d,  $J = 8.8$  Hz, 1H), 7.37-7.27 (m, 5H), 7.09 (d,  $J = 8.8$  Hz, 1H), 7.09 (d,  $J = 2.0$  Hz, 1H), 6.60 (s, 1H), 6.29 (s, 1H), 5.09 (d,  $J = 12.0$  Hz, 1H), 5.05 (d,  $J = 12.0$  Hz, 1H) 3.87 (s, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.1, 153.4, 153.3, 138.0, 135.4, 135.3, 134.5, 131.9, 131.5, 131.3, 130.2,

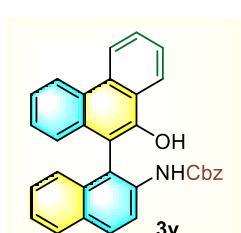
129.6, 128.6, 128.5, 128.4, 127.8, 127.5, 126.7, 126.3, 125.8, 125.1, 122.2, 119.9, 118.9, 116.1, 111.4, 67.4, 52.3. **HRMS (ESI)** calcd for [M+H] C<sub>30</sub>H<sub>23</sub>BrNO<sub>5</sub>, m/z: 556.0754, found: 556.0756.

#### **benzyl (7-bromo-2'-hydroxy-7'-phenyl-[1,1'-binaphthalen]-2-yl)carbamate (3u)**



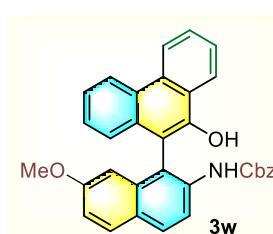
Yield: 88%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.50 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38-7.18 (m, 12H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.52 (s, 1H), 5.35 (s, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.6, 152.5, 140.9, 140.5, 136.8, 135.6, 134.3, 133.3, 131.4, 130.3, 130.0, 129.3, 129.2, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 127.5, 127.5, 127.1, 124.0, 122.1, 121.6, 120.1, 118.1, 116.2, 112.2, 67.3. **HRMS (ESI)** calcd for [M+H] C<sub>34</sub>H<sub>25</sub>BrNO<sub>3</sub>, m/z: 574.1013, found: 574.1016.

#### **benzyl (1-(10-hydroxyphenanthren-9-yl)naphthalen-2-yl)carbamate (3v)**



Yield: 91%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.85 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.8 Hz, 1H), 8.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.87-7.83 (m, 1H), 7.79-7.75 (m, 1H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 1H), 7.41-7.37 (m, 1H), 7.33-7.28 (m, 5H), 7.27-7.22 (m, 2H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.68 (s, 1H), 5.61 (s, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.6, 148.4, 136.3, 135.7, 133.0, 132.0, 131.6, 130.9, 130.5, 128.5, 128.3, 128.3, 128.3, 128.0, 127.7, 127.5, 127.0, 126.9, 125.3, 125.2, 125.1, 124.8, 124.8, 123.6, 123.0, 122.8, 119.7, 116.7, 108.9, 67.1. **HRMS (ESI)** calcd for [M+H] C<sub>32</sub>H<sub>24</sub>NO<sub>3</sub>, m/z: 470.1751, found: 470.1753.

#### **benzyl (1-(10-hydroxyphenanthren-9-yl)-7-methoxynaphthalen-2-yl)carbamate (3w)**



Yield: 90%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.79 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.72 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.44 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.41 (d, *J* = 9.2 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.82-7.78 (m, 1H), 7.73-7.69 (m, 1H), 7.54-7.50 (m, 1H), 7.36-7.32 (m, 1H), 7.27-7.23 (m, 3H), 7.20-7.17 (m, 2H), 7.10-7.06 (m, 2H), 6.54 (s, 1H), 6.48 (d, *J* = 2.4 Hz, 1H), 5.47 (s, 1H), 5.03 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.4 Hz, 1H), 3.43 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 159.0, 153.6, 148.2, 136.8, 135.7, 134.4, 131.9, 131.3, 130.3, 129.9, 128.5, 128.3, 128.3, 128.0, 127.7, 127.0, 126.8, 126.3, 125.0, 124.8, 124.7, 123.6, 123.0, 122.7, 117.5, 117.2, 115.3, 109.0, 103.8, 67.1, 55.1. **HRMS (ESI)** calcd for [M+H] C<sub>33</sub>H<sub>26</sub>NO<sub>4</sub>, m/z: 500.1857, found: 500.1859.

**methyl 6-(((benzyloxy)carbonyl)amino)-5-(10-hydroxyphenanthren-9-yl)-2-naphthoate (3x)**



Yield: 92%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.79 (d, *J* = 7.2 Hz, 1H), 8.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.68 (d, *J* = 8.8 Hz, 1H), 8.57 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.13 (d, *J* = 9.6 Hz, 1H), 7.84-7.79 (m, 1H), 7.77 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.74-7.70 (m, 1H), 7.55-7.50 (m, 1H), 7.35-7.30 (m, 1H), 7.28-7.24 (m, 3H), 7.23-7.19 (m, 3H), 6.96 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.70 (s, 1H), 5.65 (s, 1H), 5.04 (d, *J* = 12.4 Hz, 1H), 5.01 (d, *J* = 12.4 Hz, 1H), 3.90 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 167.0, 153.3, 148.5, 138.5, 135.4, 135.4, 132.0, 131.9, 131.3, 131.3, 129.7, 128.5, 128.4, 128.4, 128.2, 127.8, 127.1, 126.9, 126.8, 126.6, 125.4, 125.0, 124.9, 124.6, 123.6, 123.1, 122.7, 119.9, 116.3, 108.1, 67.3, 52.3. **HRMS (ESI)** calcd for [M+H] C<sub>34</sub>H<sub>26</sub>NO<sub>5</sub>, m/z: 528.1806, found: 528.1807.

**benzyl (1-(2-hydroxyphenyl)naphthalen-2-yl)carbamate (3y)**



Yield: 75%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.90-7.86 (m, 2H), 7.59-7.53 (m, 1H), 7.42-7.38 (m, 2H), 7.33-7.24 (m, 9H), 6.42 (s, 1H), 5.36 (s, 1H), 5.08 (s, 2H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.5, 151.3, 137.4, 135.8, 133.0, 132.0, 130.8, 130.1, 129.2, 128.5, 128.3, 128.3, 128.3, 127.3, 124.4, 124.1, 123.8, 122.7, 120.5, 117.8, 115.3, 67.0.

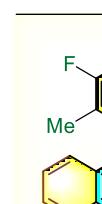
**HRMS (ESI)** calcd for [M+H] C<sub>24</sub>H<sub>20</sub>NO<sub>3</sub>, m/z: 370.1438, found: 370.1435.

**benzyl (1-(5-bromo-2-hydroxyphenyl)naphthalen-2-yl)carbamate (3z)**



Yield: 72%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.45-7.29 (m, 8H), 7.28-7.22 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 5.47 (s, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.8, 153.2, 135.7, 134.4, 134.0, 133.5, 132.5, 130.8, 130.2, 128.7, 128.5, 128.4, 128.2, 127.4, 125.4, 124.9, 123.2, 120.3, 119.7, 118.5, 113.2, 67.4. **HRMS (ESI)** calcd for [M+H] C<sub>24</sub>H<sub>19</sub>BrNO<sub>3</sub>, m/z: 448.0543, found: 448.0540.

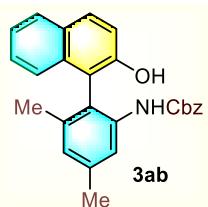
**benzyl (1-(3-fluoro-6-hydroxy-2,4-dimethylphenyl)naphthalen-2-yl)carbamate (3aa)**



Yield: 72%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.91-7.87 (m, 2H), 7.42-7.14 (m, 9H), 6.16 (s, 1H), 5.45 (s, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 2.41 (d, *J* = 2.4 Hz, 3H), 1.86 (d, *J* = 2.8 Hz, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 156.8 (d, *J* = 240.3 Hz), 153.8, 151.4, 135.8, 132.6, 131.0, 129.3, 128.5, 128.5, 128.3, 128.2, 127.5, 126.1 (d, *J* = 19.0 Hz), 125.8 (d, *J* = 17.9 Hz), 123.9, 123.5, 122.1, 121.0, 117.9, 113.5, 113.4, 67.0, 15.1 (d, *J* = 3.7 Hz), 11.9 (d, *J* = 4.4 Hz). **<sup>19</sup>F NMR (375 MHz,**

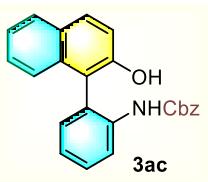
**CDCl<sub>3</sub>**) δ -123.4. **HRMS (ESI)** calcd for [M+H] C<sub>26</sub>H<sub>23</sub>FNO<sub>3</sub>, m/z: 416.1657, found: 416.1658.

**benzyl (2-(2-hydroxynaphthalen-1-yl)-3,5-dimethylphenyl)carbamate (3ab)**



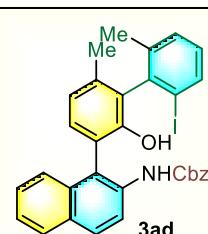
Yield: 62%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.03 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.88-7.85 (m, 1H), 7.41-7.30 (m, 6H), 7.27-7.15 (m, 3H), 7.02 (d, *J* = 1.6 Hz, 1H), 7.02 (s, 1H), 6.25 (s, 1H), 5.04 (s, 2H), 2.47 (s, 3H), 1.90 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.5, 151.4, 139.9, 139.3, 137.3, 135.9, 132.7, 130.8, 129.4, 128.5, 128.5, 128.3, 128.2, 127.3, 126.7, 123.8, 123.7, 118.8, 118.3, 117.7, 114.1, 66.9, 21.7, 19.8. **HRMS (ESI)** calcd for [M+H] C<sub>26</sub>H<sub>24</sub>NO<sub>3</sub>, m/z: 398.1751, found: 398.1750.

**benzyl (2-(2-hydroxynaphthalen-1-yl)phenyl)carbamate (3ac)**



Yield: 68%. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.28 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.35-7.21 (m, 9H), 7.08-6.99 (m, 3H), 6.99 (s, 1H), 5.05 (s, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.9, 153.7, 135.9, 134.6, 132.7, 131.7, 130.7, 130.6, 129.8, 128.6, 128.4, 128.4, 128.2, 127.1, 125.1, 125.1, 121.5, 120.7, 120.0, 119.8, 116.6, 67.2. **HRMS (ESI)** calcd for [M+H] C<sub>24</sub>H<sub>20</sub>NO<sub>3</sub>, m/z: 370.1438, found: 370.1438.

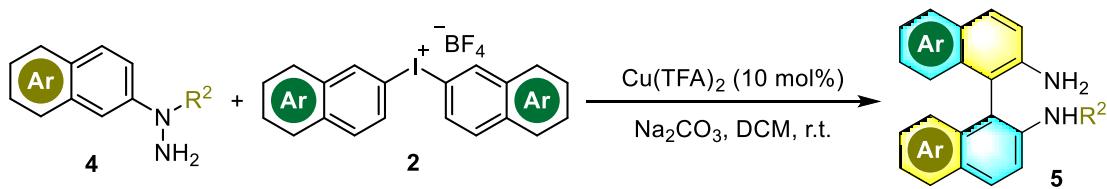
**benzyl (1-(2-hydroxy-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-3-yl)naphthalen-2-yl)carbamate (3ad)**  
72% yield, dr = 1.2/1



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.48 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.90-7.88 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.50-7.30 (m, 9H), 7.19-7.10 (m, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 5.16-5.09 (m, 2H), 4.62 (s, 1H), 2.20 (s, 3H), 2.06 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.5, 149.9, 140.2, 138.8, 138.2, 136.9, 135.8, 134.6, 133.1, 131.6, 131.6, 130.5, 130.1, 129.8, 129.4, 128.6, 128.5, 128.3, 128.1, 126.7, 125.1, 124.7, 123.2, 120.2, 119.3, 118.6, 102.2, 67.1, 21.4, 19.6. **HRMS (ESI)** calcd for [M+H] C<sub>32</sub>H<sub>27</sub>INO<sub>3</sub>, m/z: 600.1030, found: 600.1031.

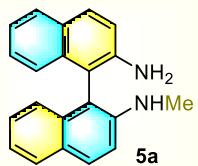
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.89-7.87 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.48-7.31 (m, 8H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 5.21-5.14 (m, 2H), 4.65 (s, 1H), 2.08 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 153.5, 149.9, 140.3, 138.8, 138.3, 137.0, 136.0, 134.1, 132.8, 131.6, 131.4, 130.7, 130.2, 129.8, 129.5, 128.6, 128.3, 128.2, 126.9, 125.7, 124.9, 123.2, 121.0, 119.6, 118.7, 115.6, 101.9, 67.1, 21.3, 19.6. **HRMS (ESI)** calcd for [M+H] C<sub>32</sub>H<sub>27</sub>INO<sub>3</sub>, m/z: 600.1030, found: 600.1030.

### General procedures for synthesis of BINAM derivatives 5



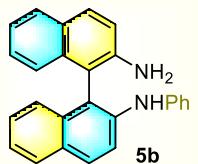
**4** (0.20 mmol), **2** (0.24 mmol), Na<sub>2</sub>CO<sub>3</sub> (27.6 mg, 0.26 mmol) and Cu(TFA)<sub>2</sub> (5.8 mg, 10 mol%) were added to a bottle with a magnetic stirring bar. DCM (4.0 mL) was added and the reaction mixture was stirred at room temperature till **4** was completely consumed (monitored by TLC). After evaporated the solvent, the residue was purified by flash chromatography eluted with DCM to afford the corresponding product **5**.

#### N<sup>2</sup>-methyl-[1,1'-binaphthalene]-2,2'-diamine (**5a**)



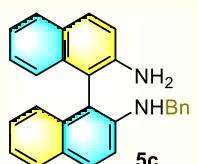
Yield: 52%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.83-7.79 (m, 3H), 7.27-7.24 (m, 2H), 7.22-7.17 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.85 (brs, 1H), 2.85 (s, 3H), 2.55 (brs, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.9, 142.5, 133.5, 133.0, 129.3, 129.1, 128.1, 127.8, 127.7, 127.2, 126.4, 126.3, 123.6, 123.2, 122.0, 121.4, 117.9, 113.0, 112.1, 111.5, 30.7. HRMS (ESI) calcd for [M+H] C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>, m/z: 299.1543, found: 299.1544.

#### N<sup>2</sup>-phenyl-[1,1'-binaphthalene]-2,2'-diamine (**5b**)



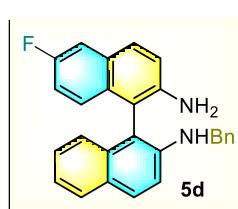
Yield: 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93-7.84 (m, 4H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.48-7.06 (m, 11H), 6.98 (t, *J* = 7.6 Hz, 1H), 5.67 (brs, 1H), 3.22 (brs, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.9, 142.8, 140.2, 134.0, 133.8, 129.8, 129.5, 129.3, 129.2, 128.5, 128.3, 128.2, 127.1, 126.9, 124.6, 123.9, 123.4, 122.6, 122.0, 119.8, 118.4, 118.0, 116.9, 112.1. HRMS (ESI) calcd for [M+H] C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>, m/z: 361.1699, found: 361.1699.

#### N<sup>2</sup>-benzyl-[1,1'-binaphthalene]-2,2'-diamine (**5c**)



Yield: 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86-7.78 (m, 4H), 7.31-7.18 (m, 11H), 7.15-7.13 (m, 1H), 7.08-7.05 (m, 1H), 4.44 (s, 2H), 3.92 (brs, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.9, 143.0, 139.8, 134.0, 133.6, 129.7, 129.6, 128.6, 128.5, 128.2, 128.2, 127.8, 126.9, 126.9, 126.9, 126.8, 124.2, 123.8, 122.5, 122.0, 118.4, 114.4, 112.5, 112.3, 47.7. HRMS (ESI) calcd for [M+H] C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>, m/z: 375.1856, found: 375.1855.

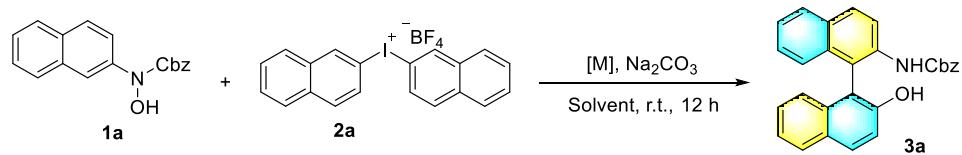
**N<sup>2</sup>-benzyl-6'-fluoro-[1,1'-binaphthalene]-2,2'-diamine (5d)**



Yield: 56%. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.82-7.79 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.46 (dd, *J* = 10.0, 2.8 Hz, 1H), 7.28-7.20 (m, 9H), 7.12-7.09 (m, 1H), 7.05-7.00 (m, 2H), 4.44 (s, 2H), 4.19 (brs, 1H), 3.72 (brs, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.9 (d, *J* = 241.0 Hz), 143.9, 142.4 (d, *J* = 2.0 Hz), 139.8, 133.5, 130.9, 129.7, 128.9 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 5.0 Hz), 128.5, 128.2, 127.7, 127.0, 126.9, 126.8, 126.5 (d, *J* = 8.0 Hz), 123.6, 122.1, 119.6, 116.7 (d, *J* = 24.0 Hz), 114.3, 112.7, 112.1, 111.3 (d, *J* = 20.0 Hz), 47.7. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -120.50. **HRMS (ESI)** calcd for [M+H] C<sub>27</sub>H<sub>22</sub>FN<sub>2</sub>, m/z: 393.1762, found: 393.1762.

#### IV. Control experiments

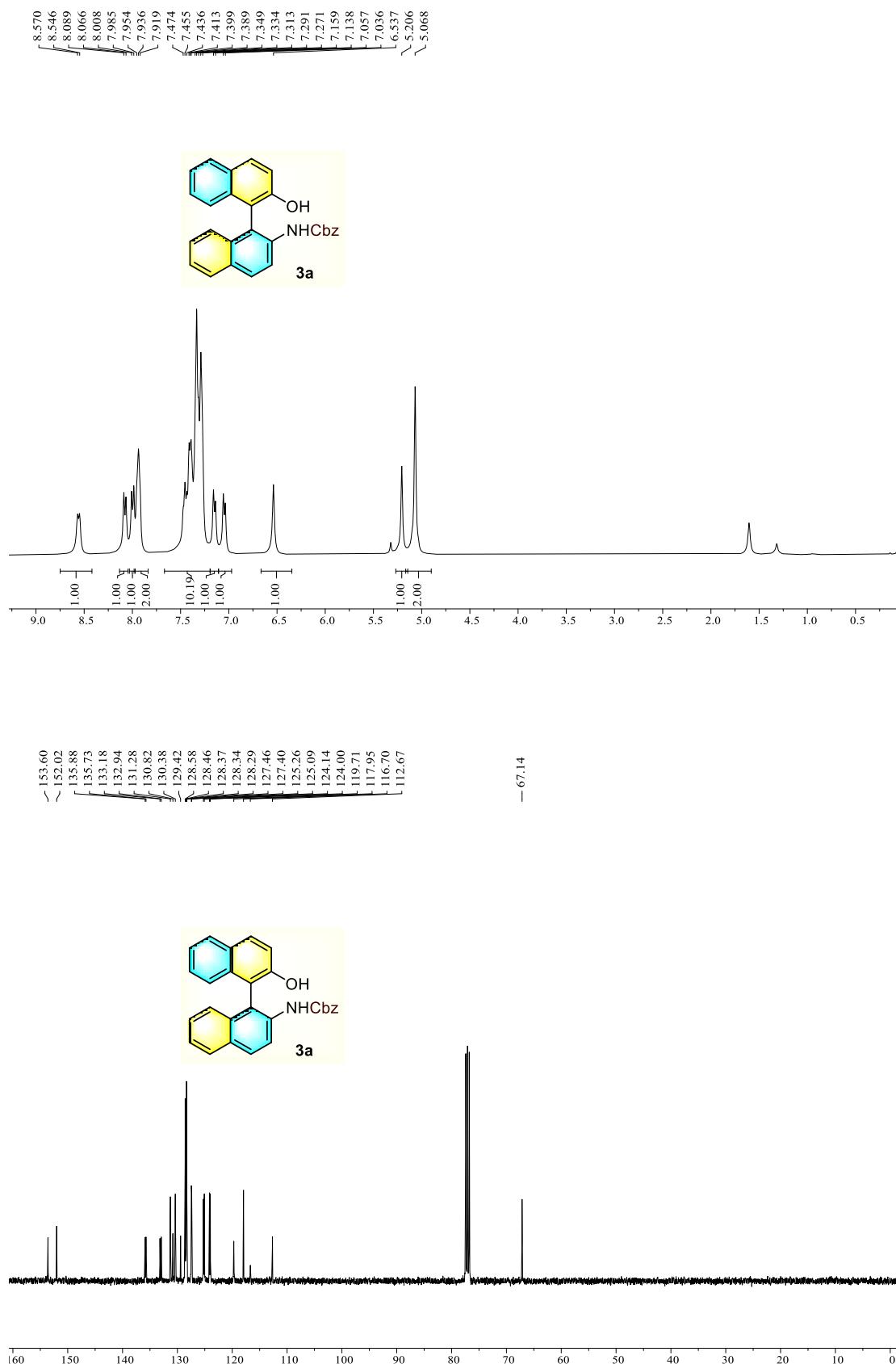
Table S3. The role of copper catalyst and base in the conditions<sup>a</sup>

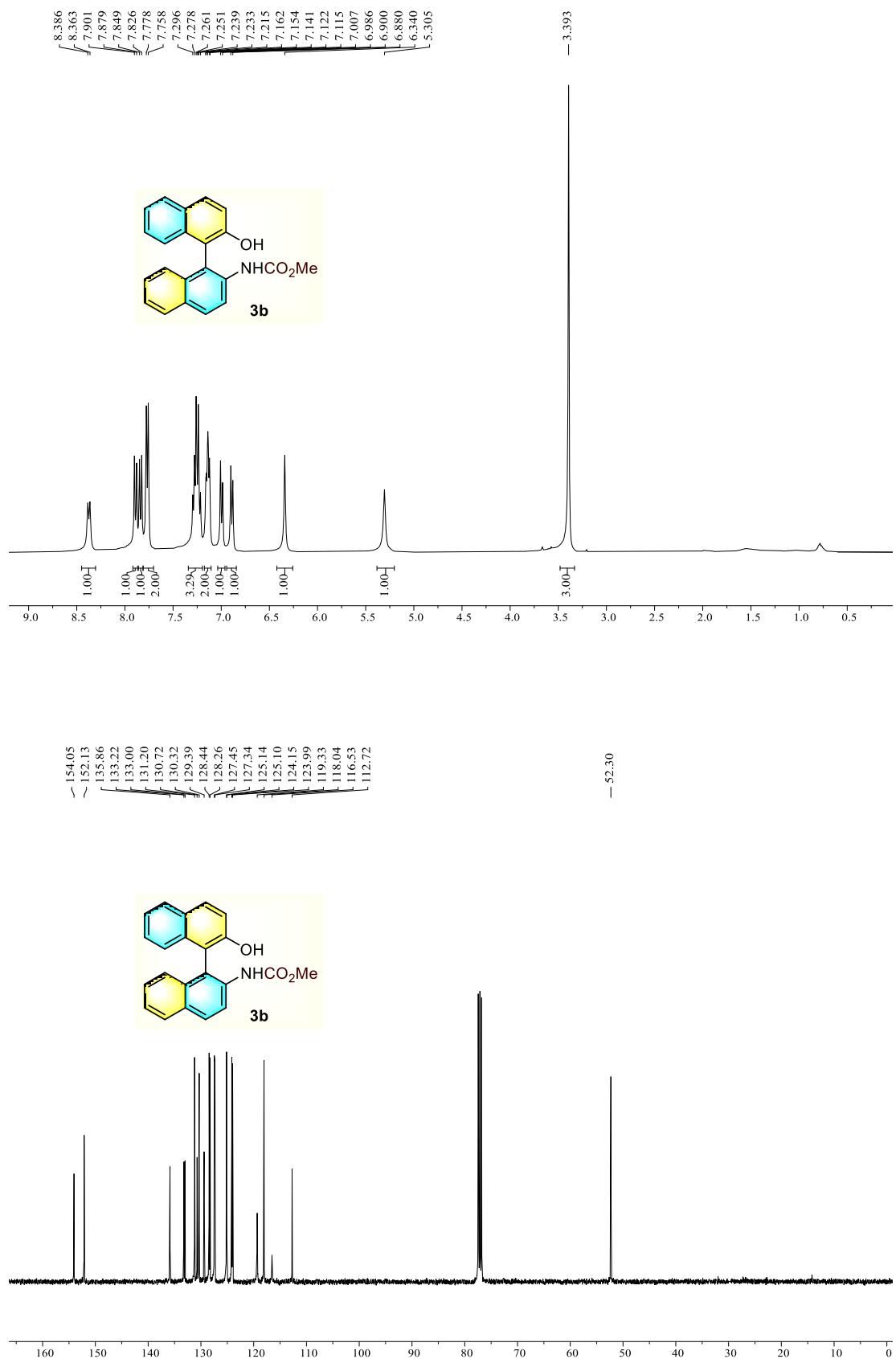


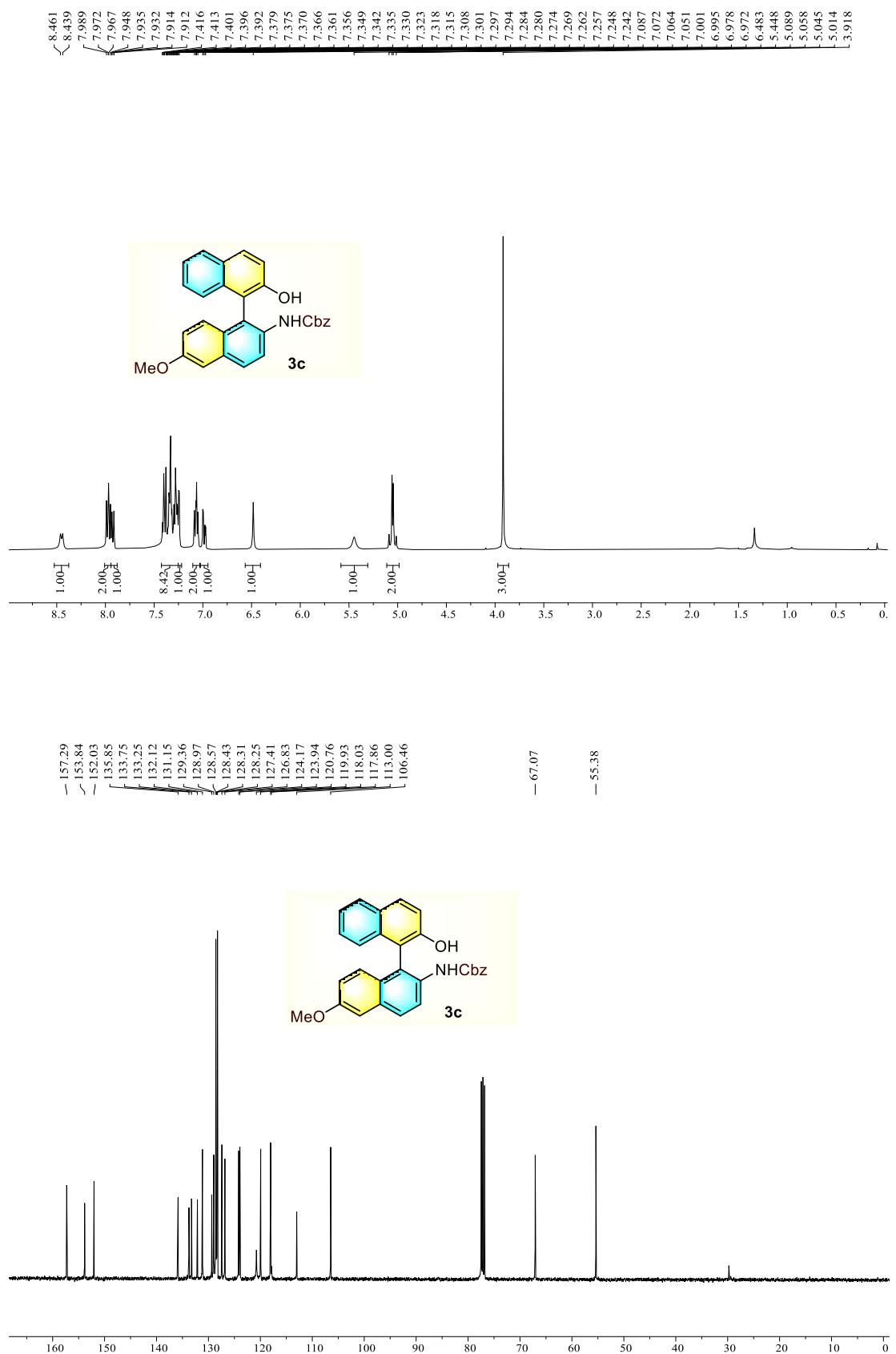
Entry	[M](10 mol%)	Base	Solvent	Yield (%) <sup>b</sup>
1	Al(OTf) <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	71
2	Mg(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	72
3	Zn(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	70
4	Ni(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	68
5	—	Na <sub>2</sub> CO <sub>3</sub>	DCM	70
6	Cu(TFA) <sub>2</sub>	—	DCM	33
7	Cu(TFA) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	98

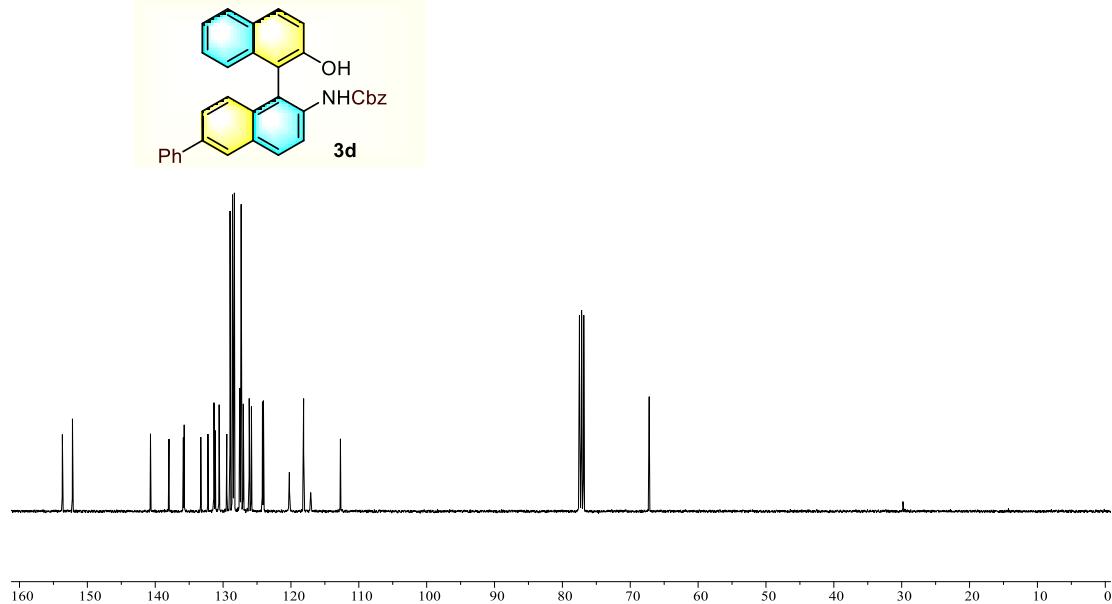
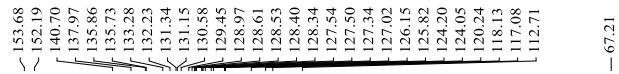
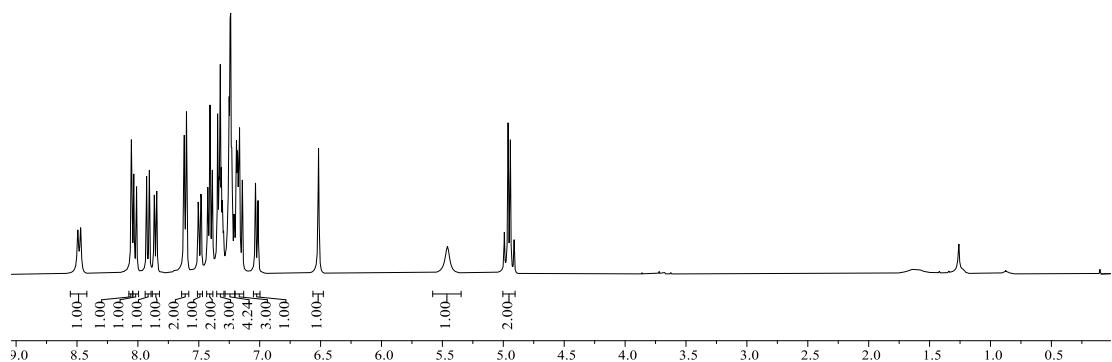
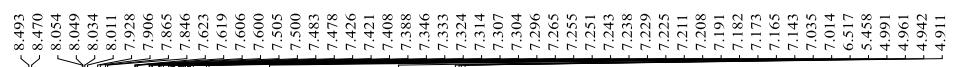
<sup>a</sup>All reactions were performed with [M] (10 mol%), **1a** (0.10 mmol), **2a** (0.12 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.13 mmol) in DCM (2.0 mL) at room temperature for 12 h; <sup>b</sup>Yield was determined by <sup>1</sup>H-NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

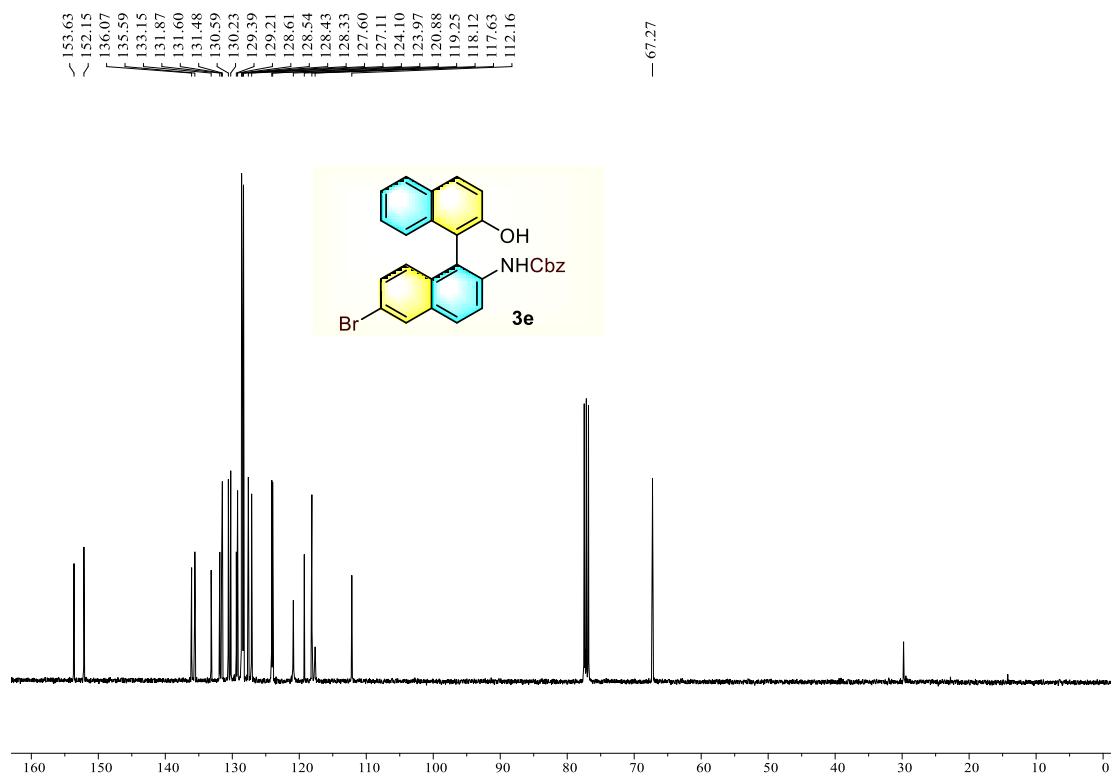
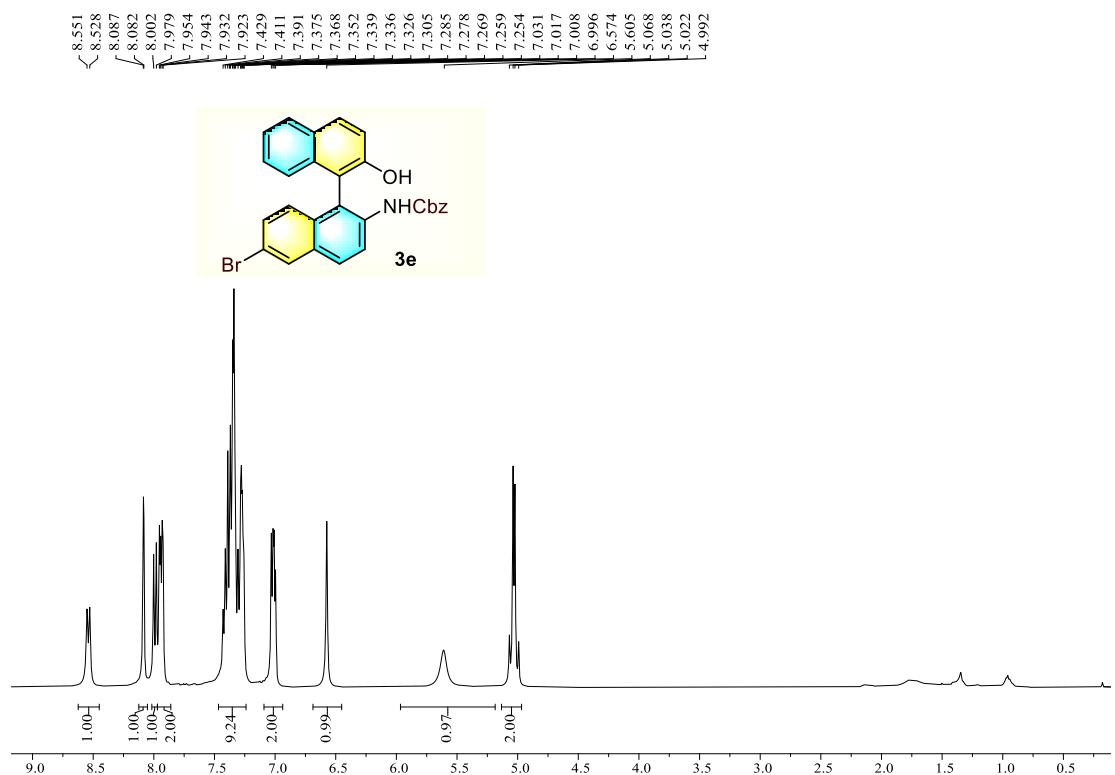
## V. Copies of NMR spectra

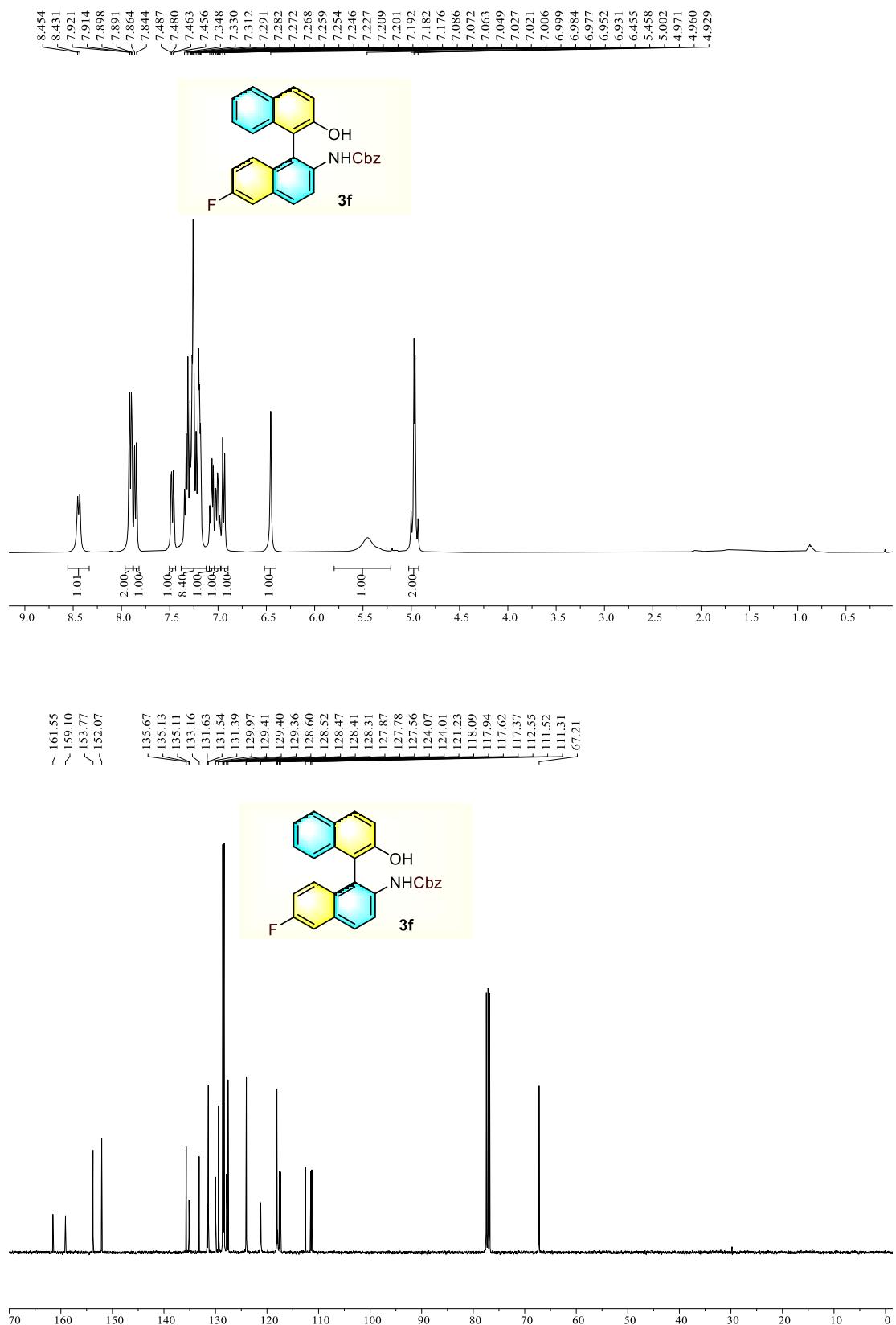


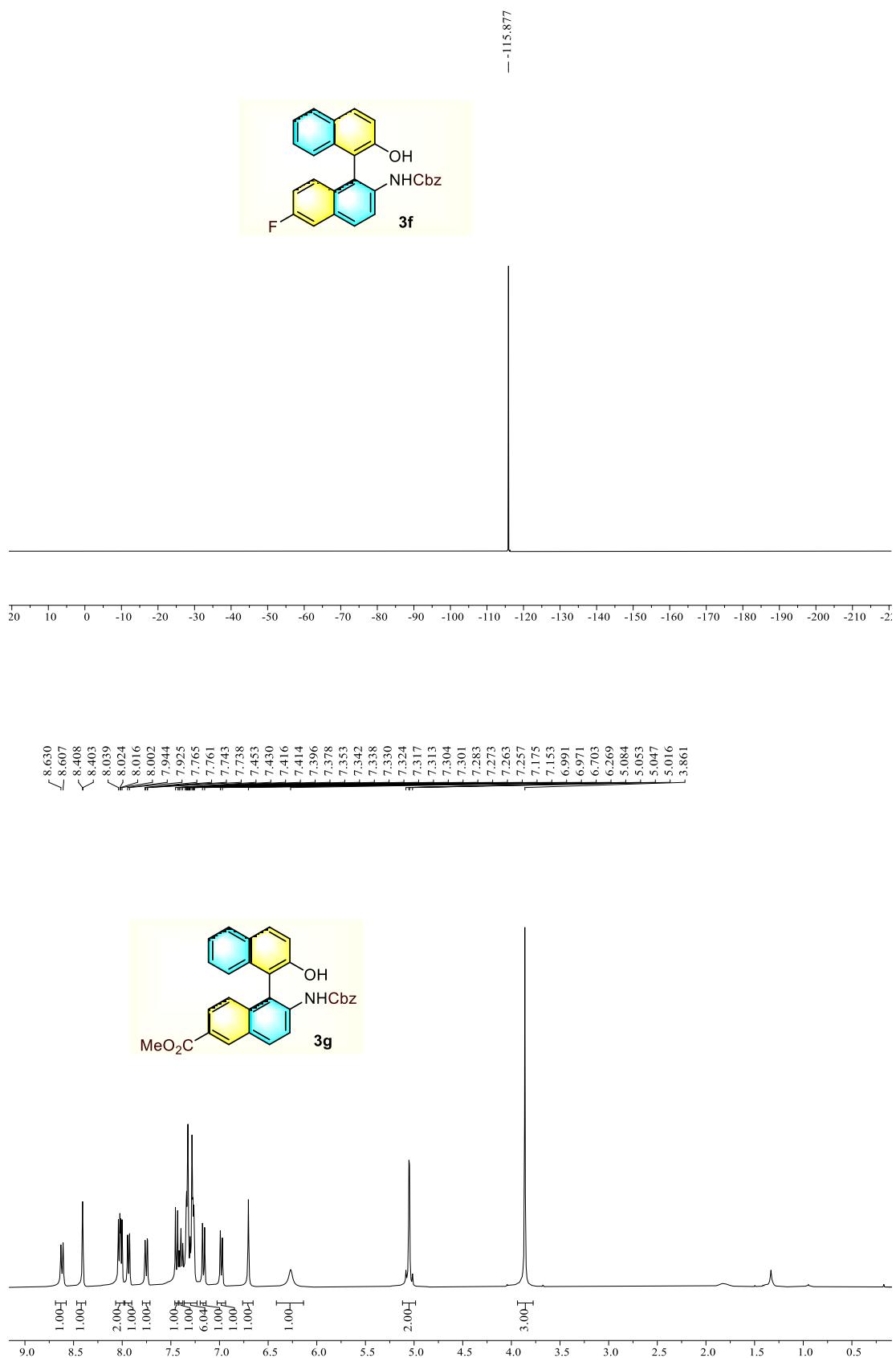


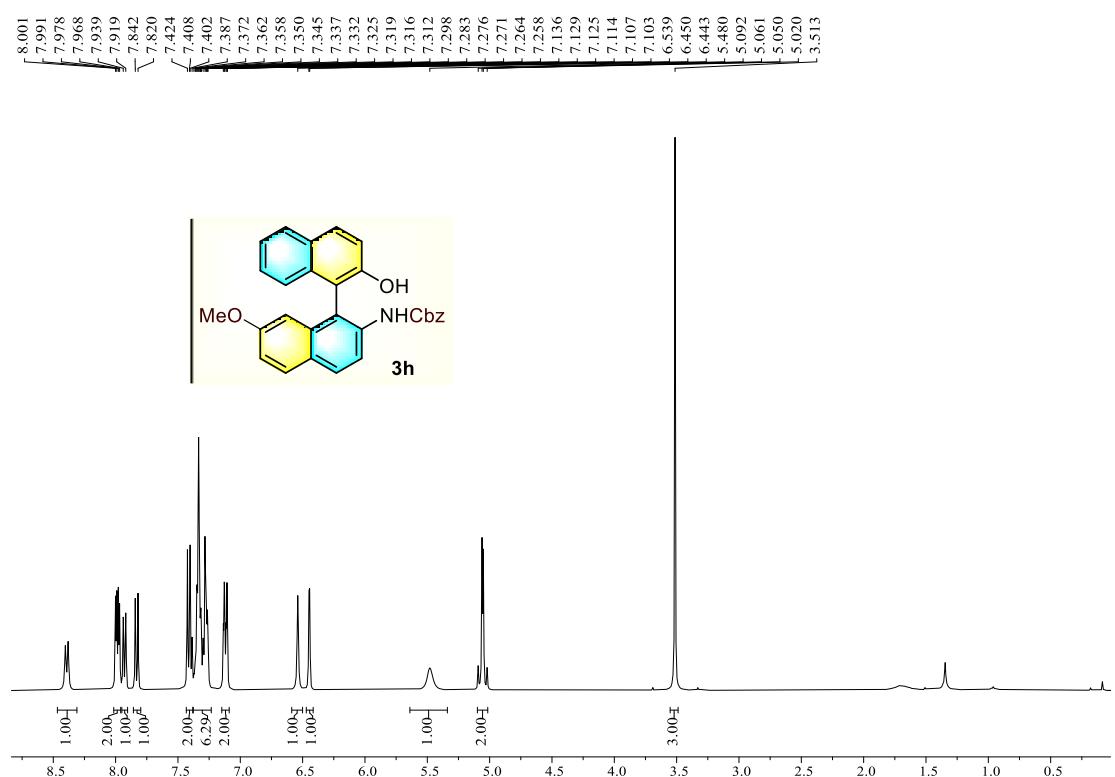
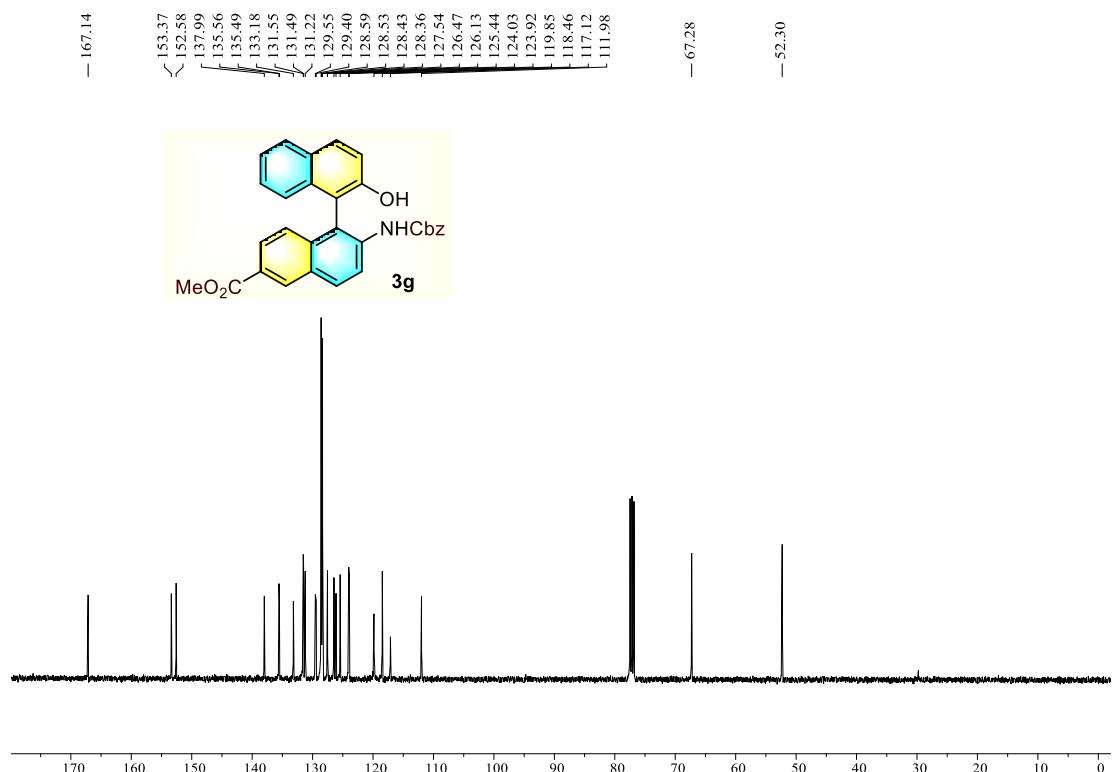


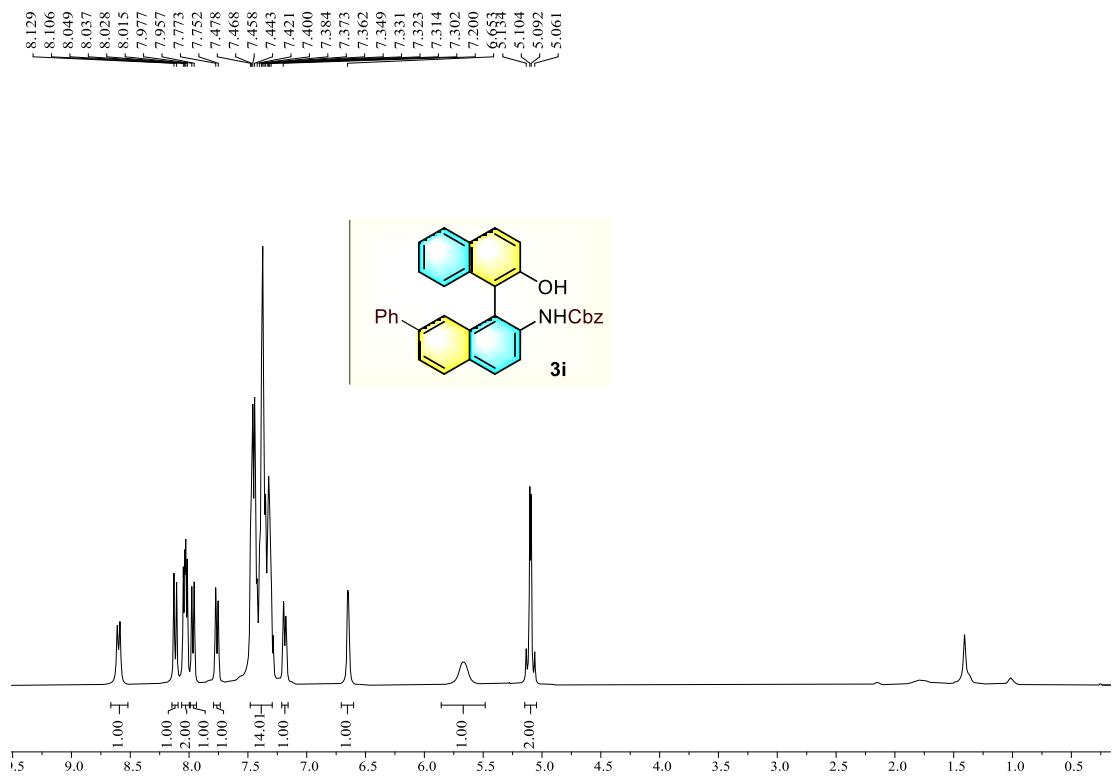
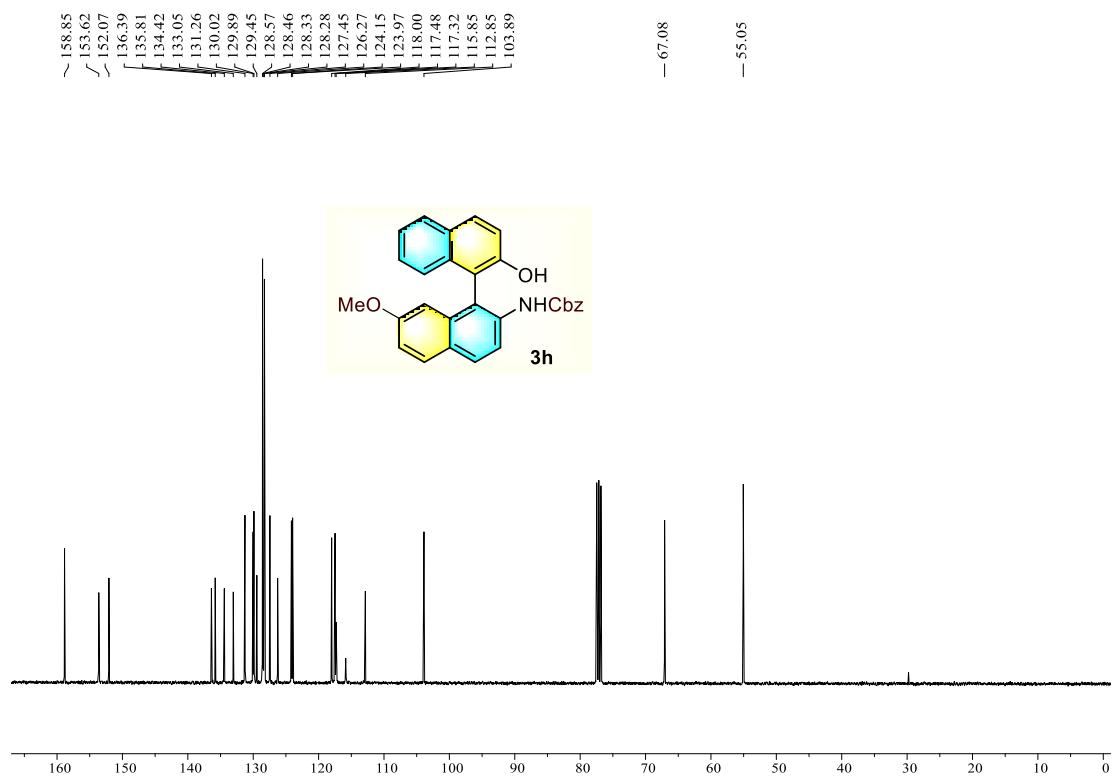


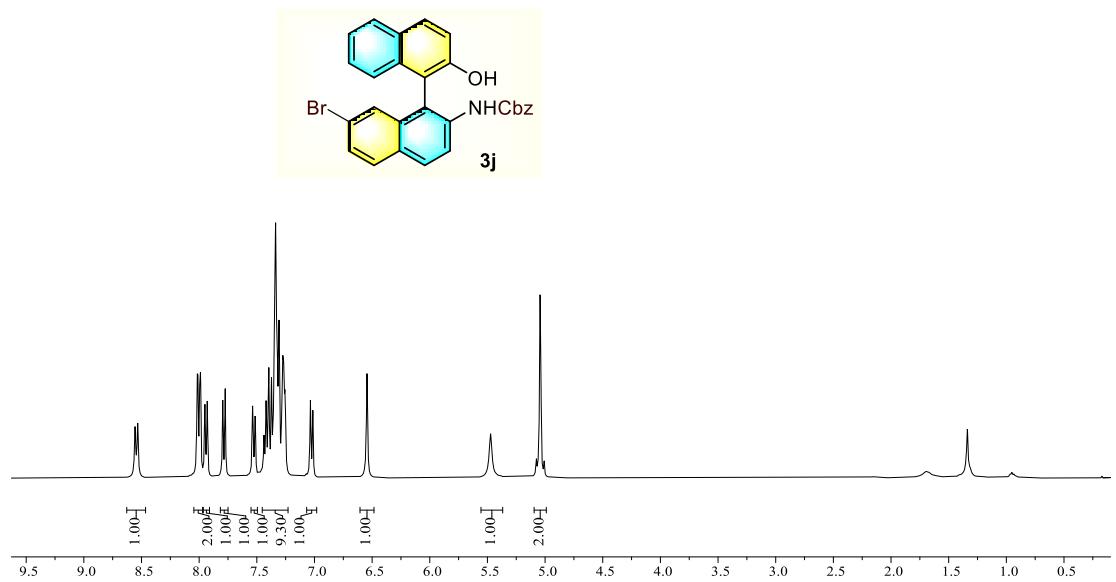
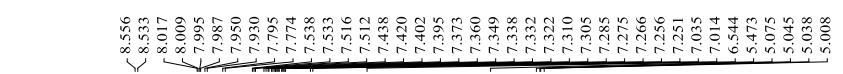
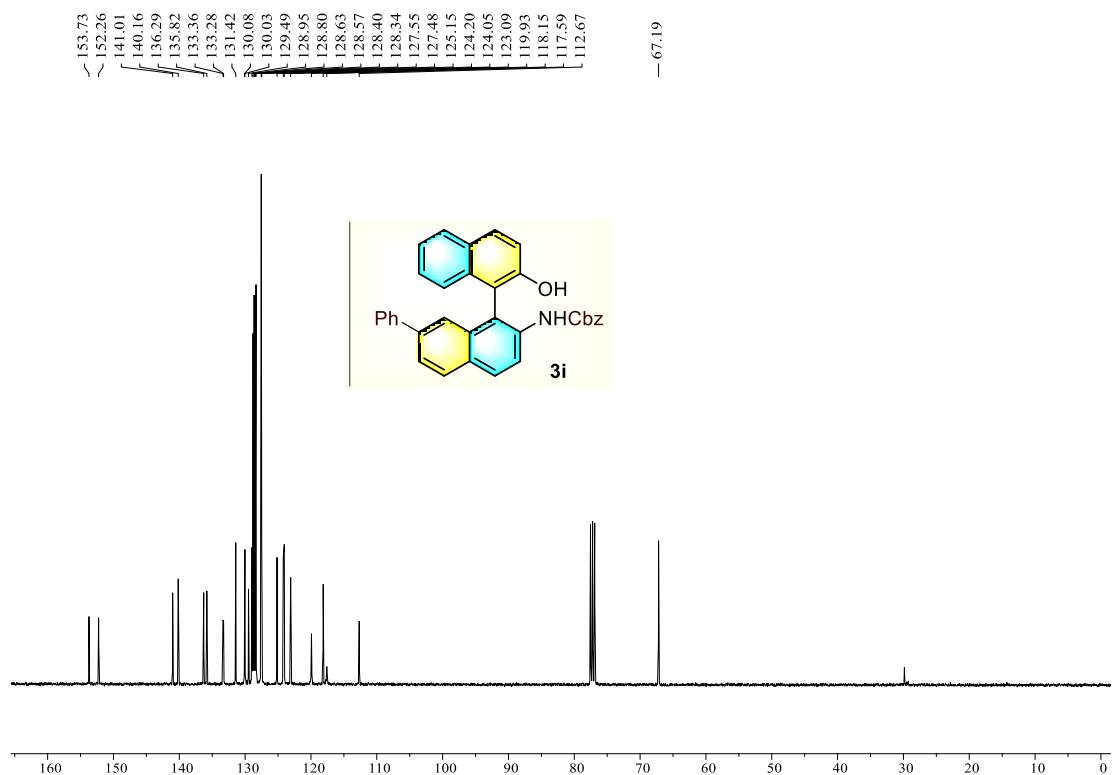


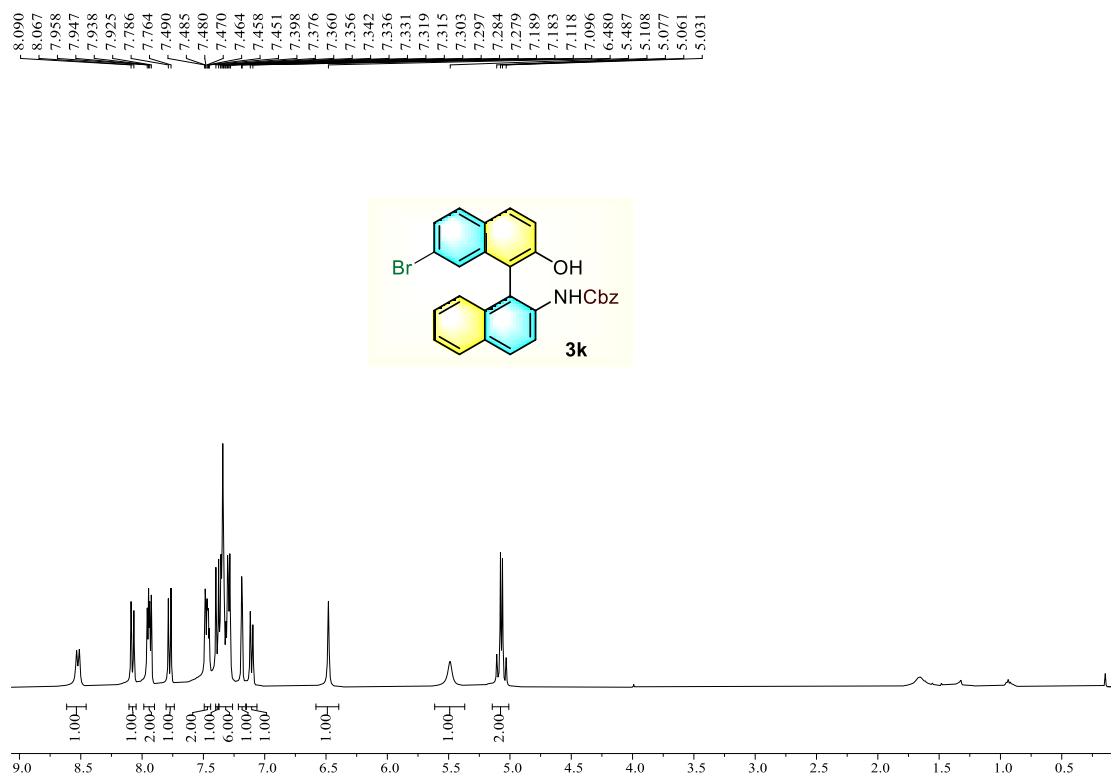
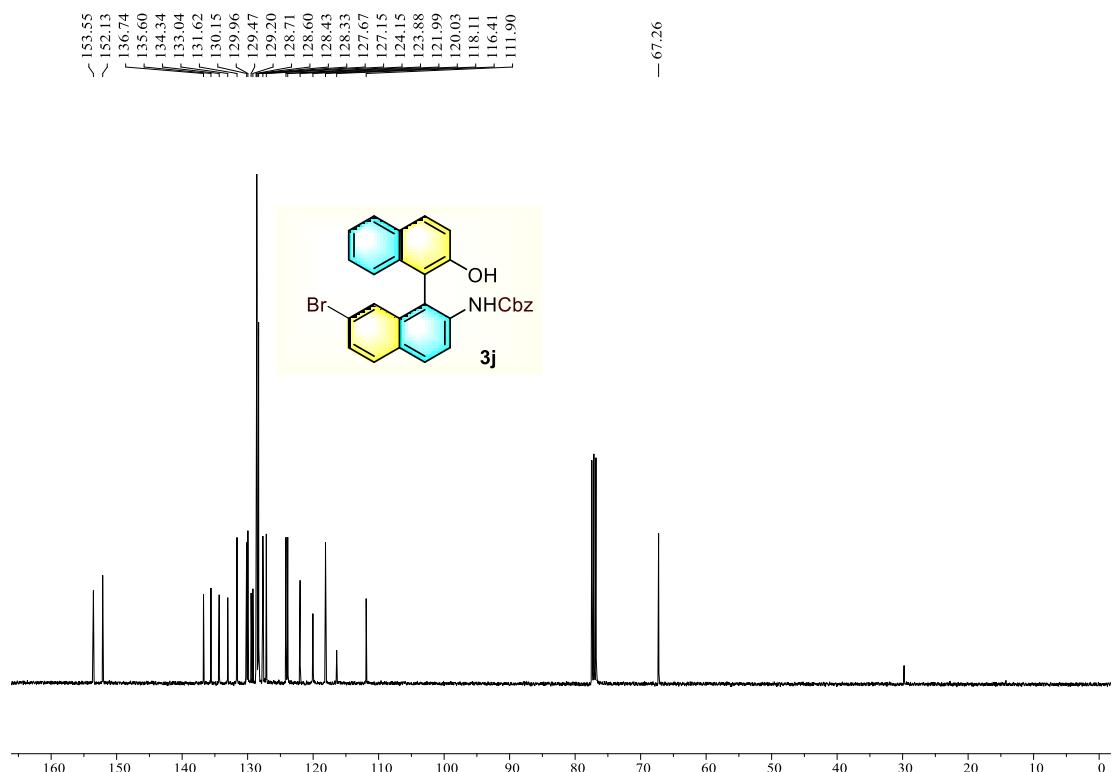


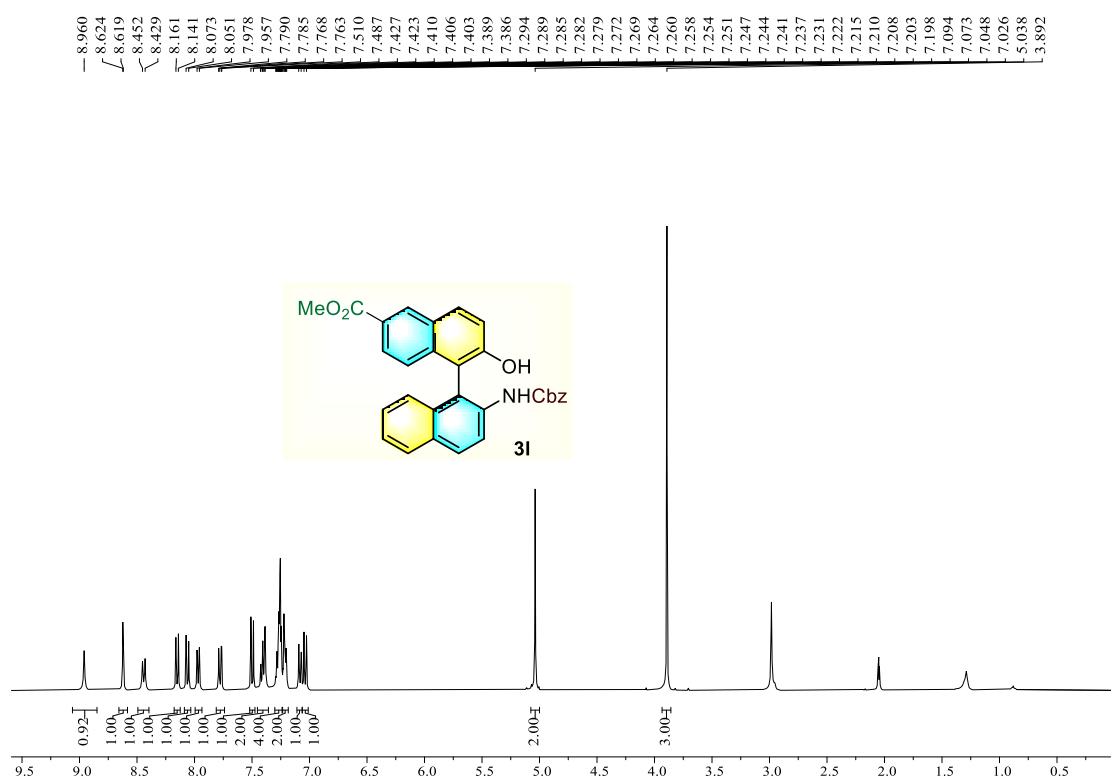
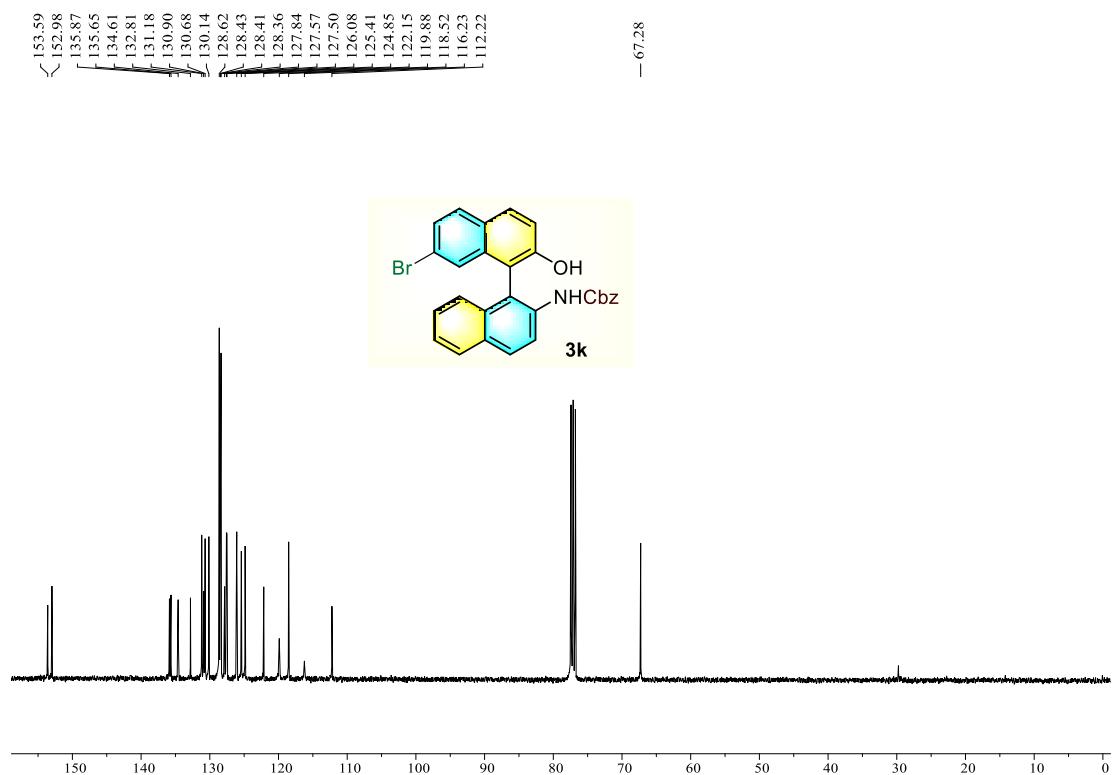


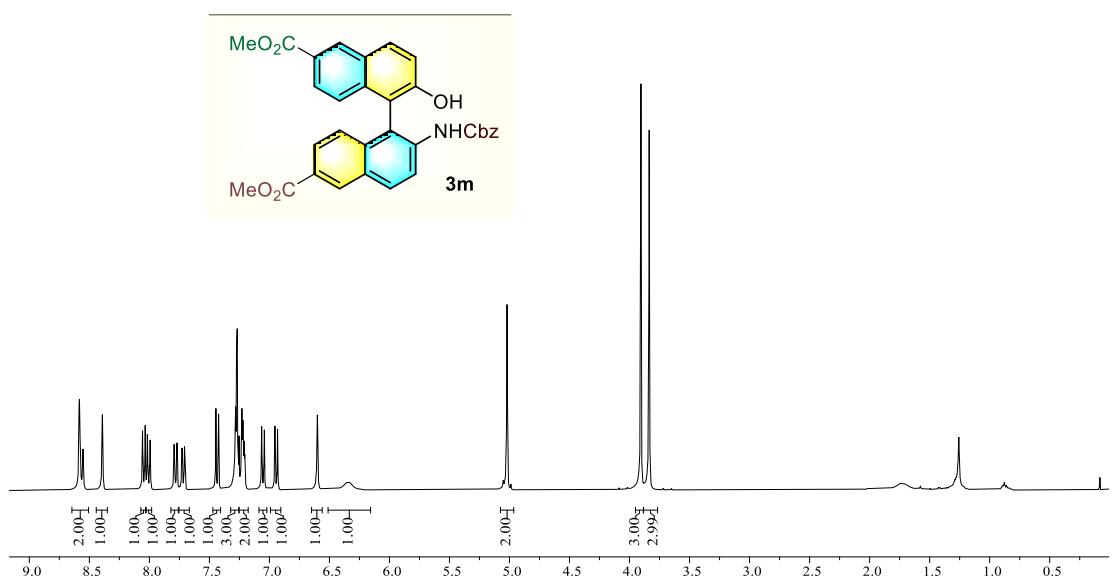
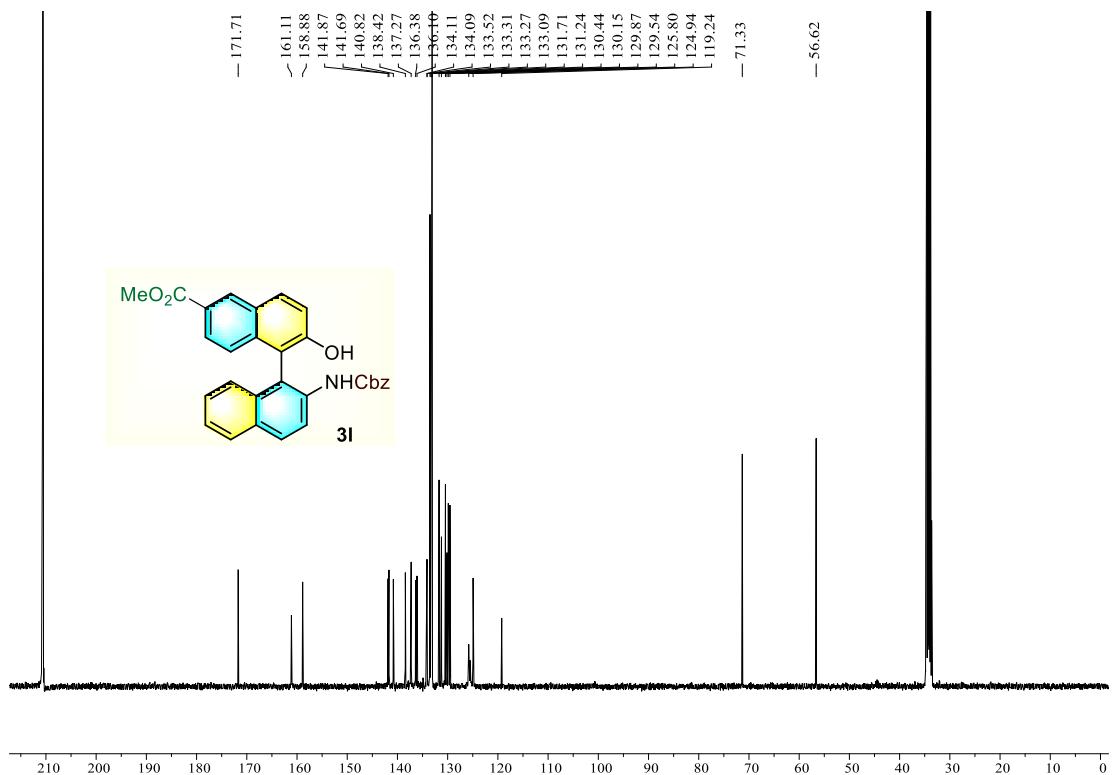


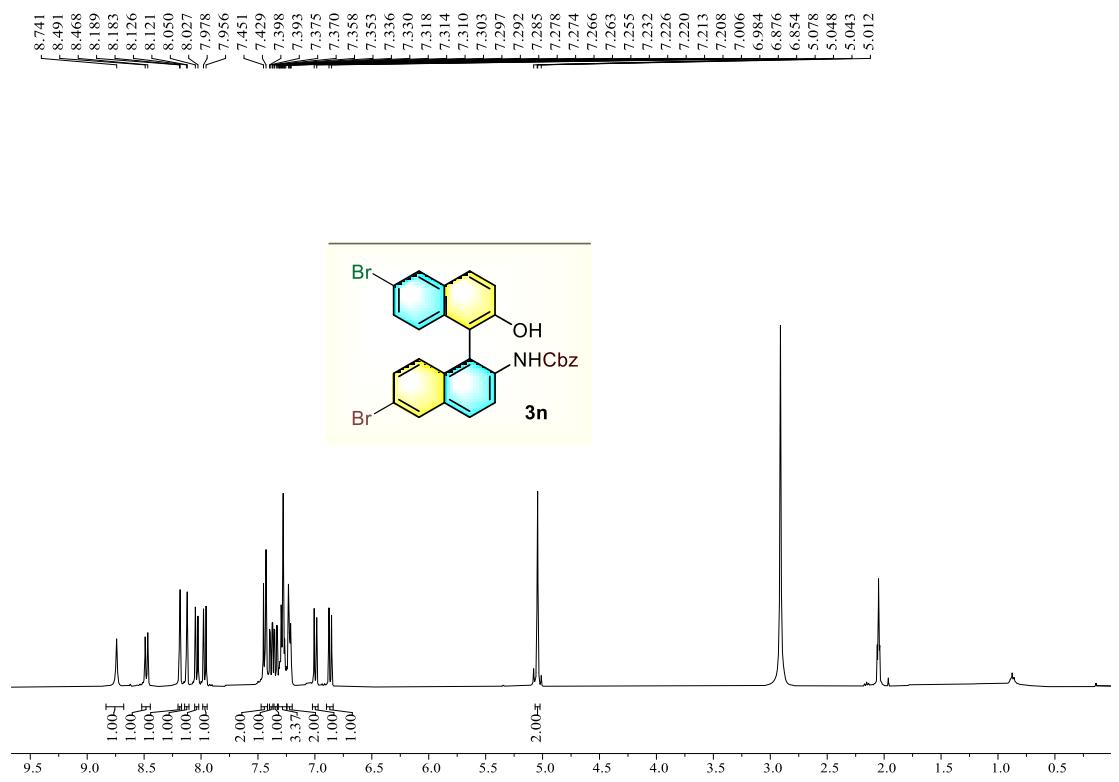
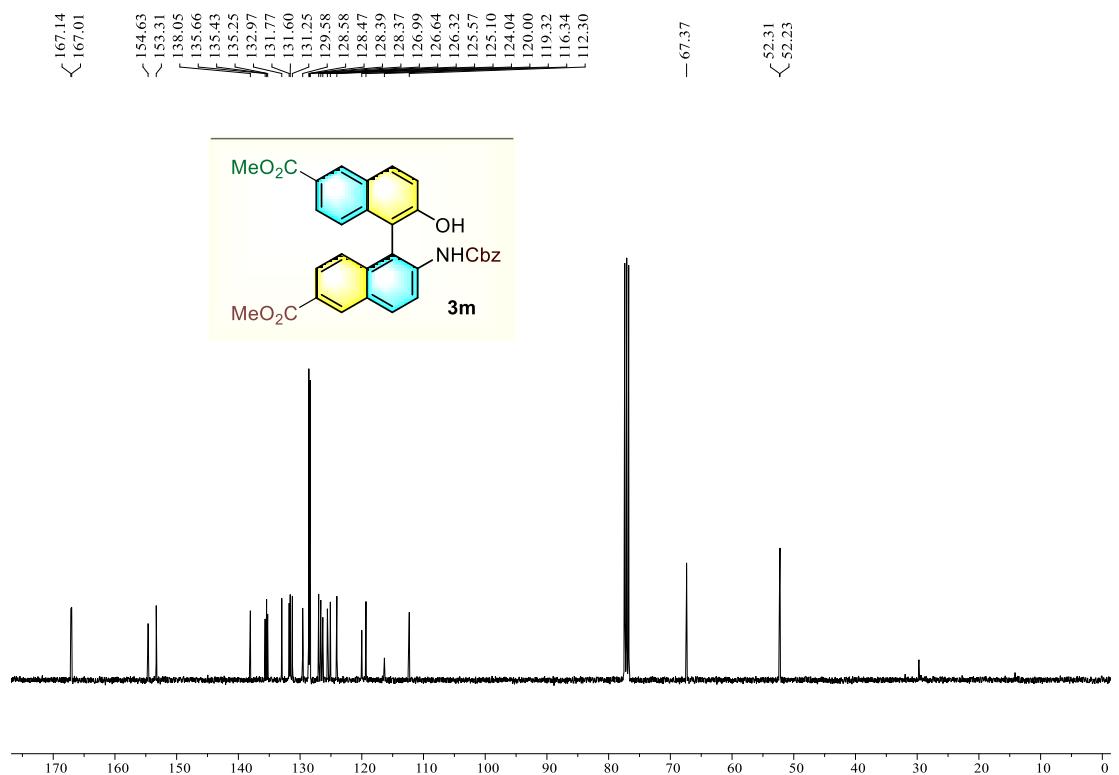


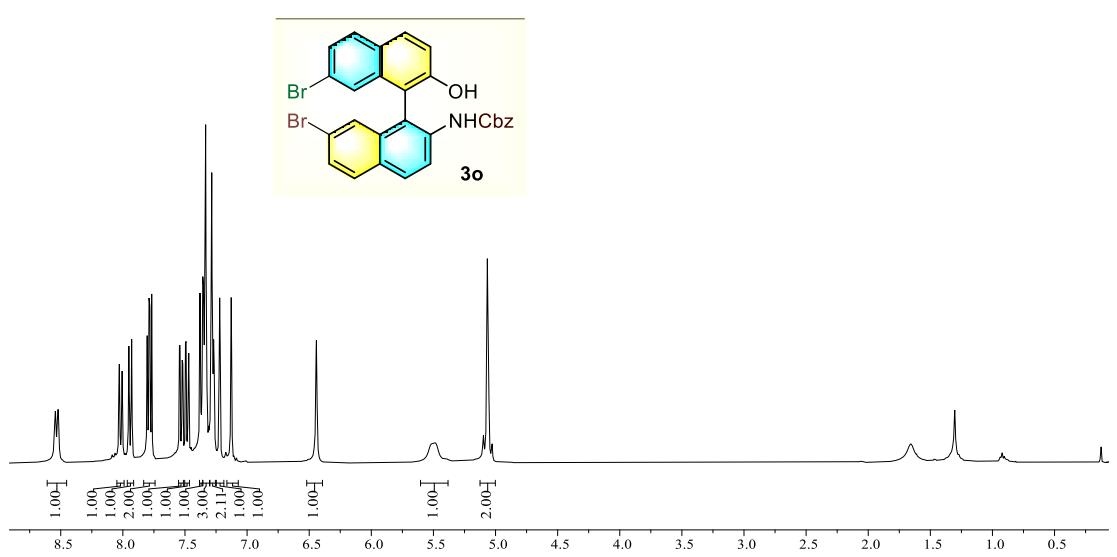
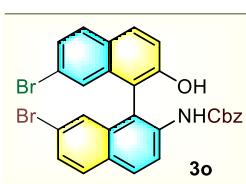
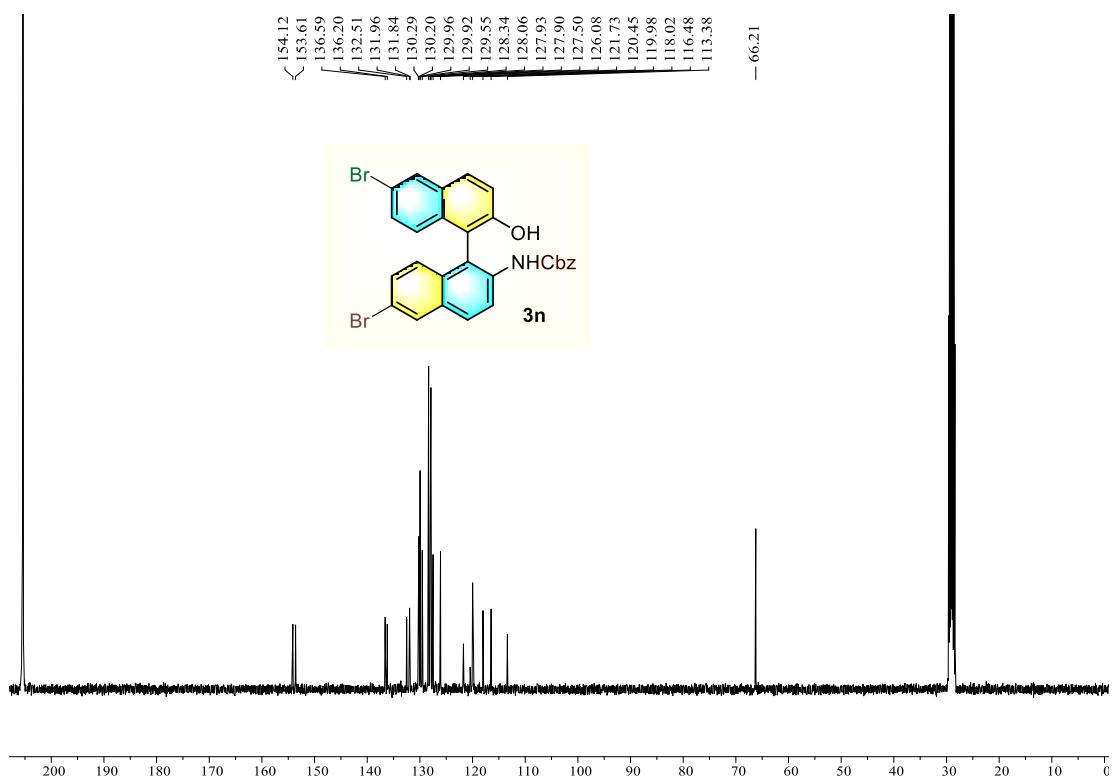


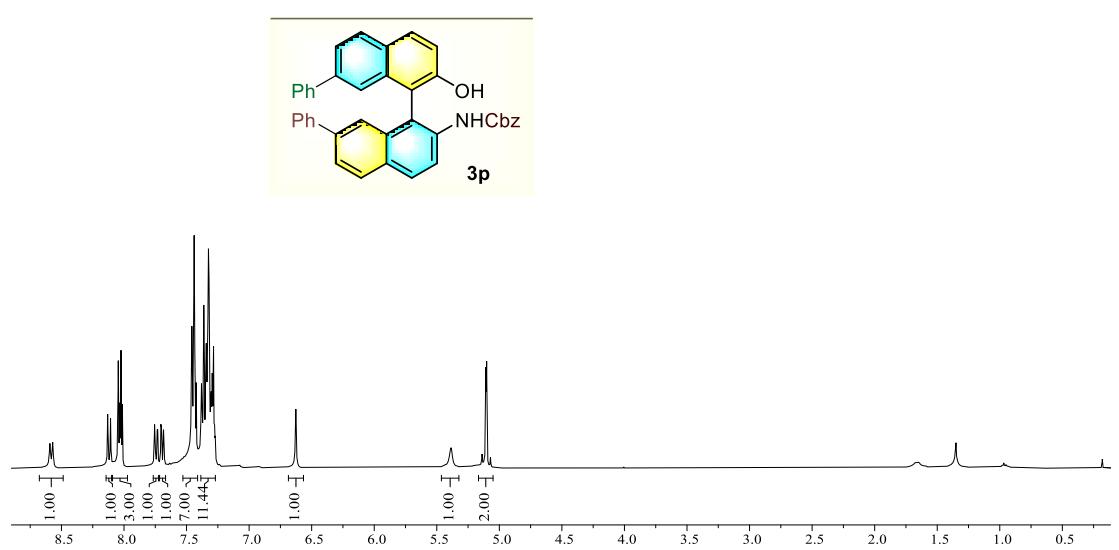
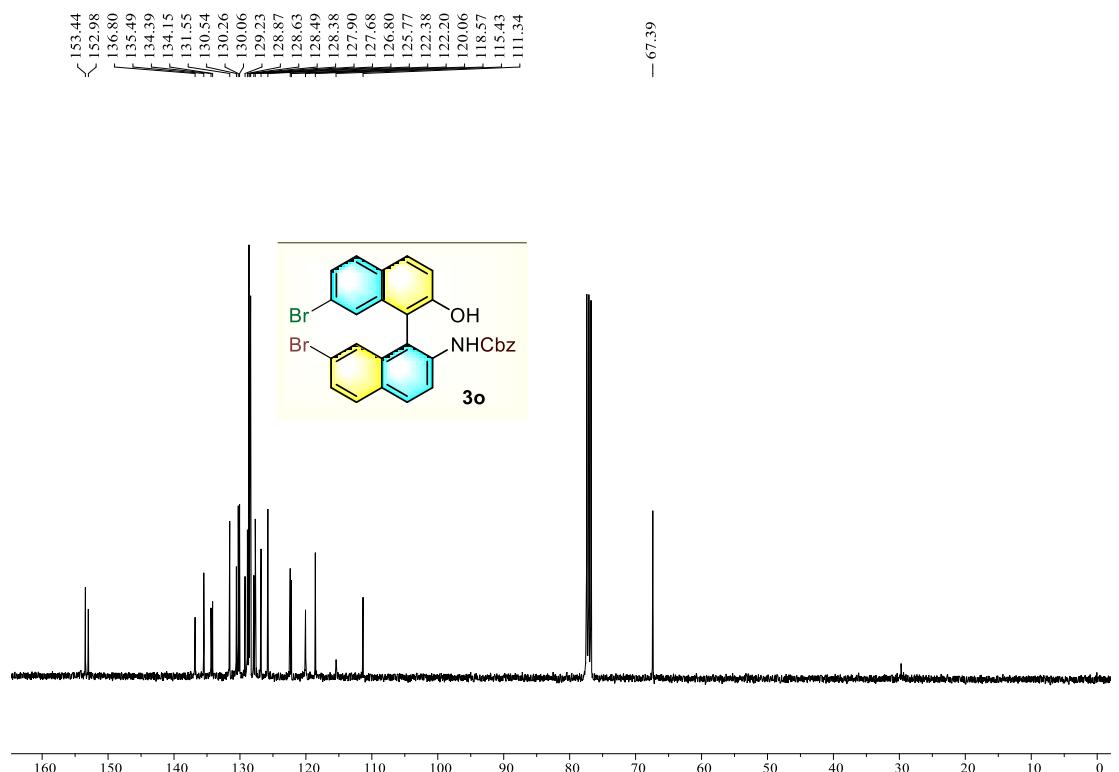


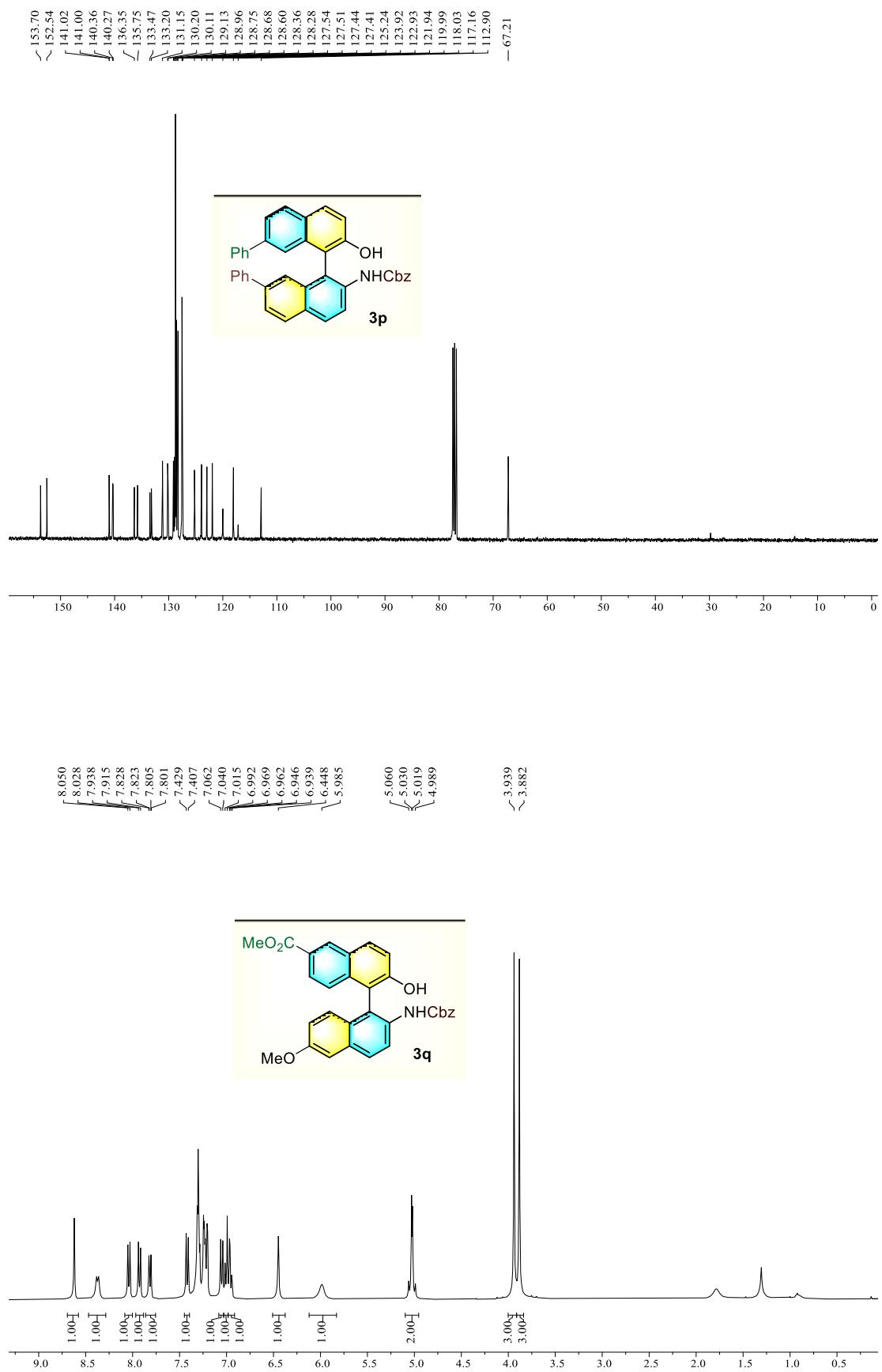


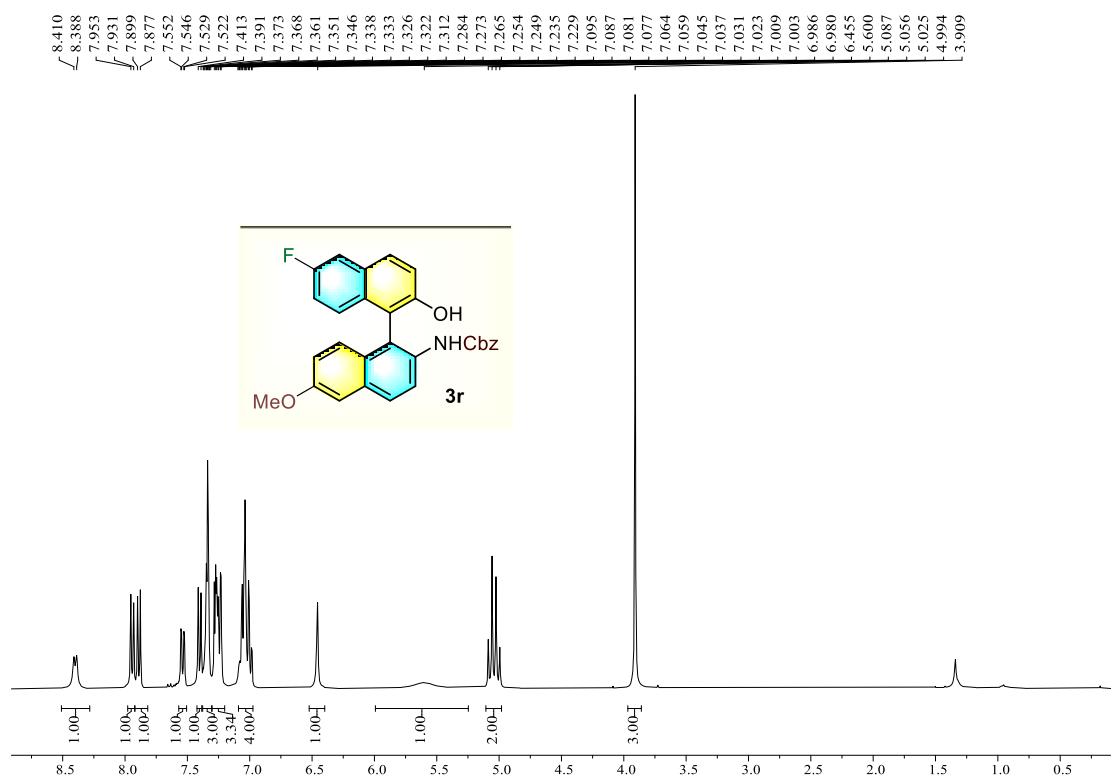
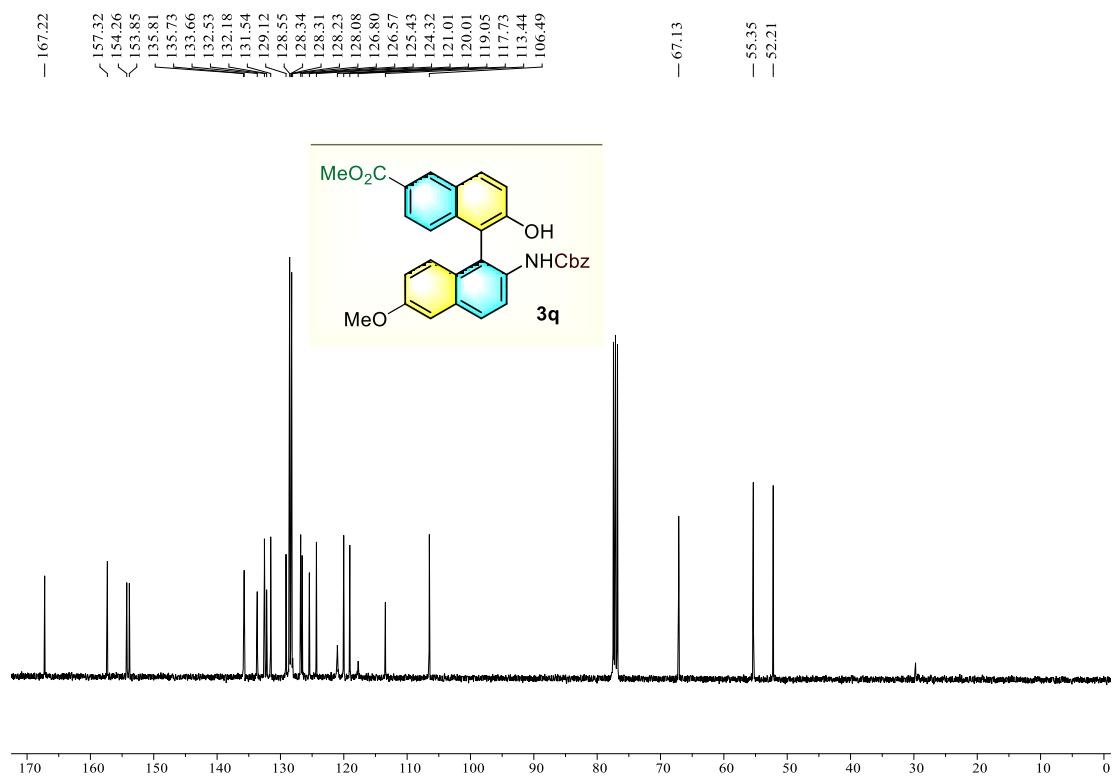


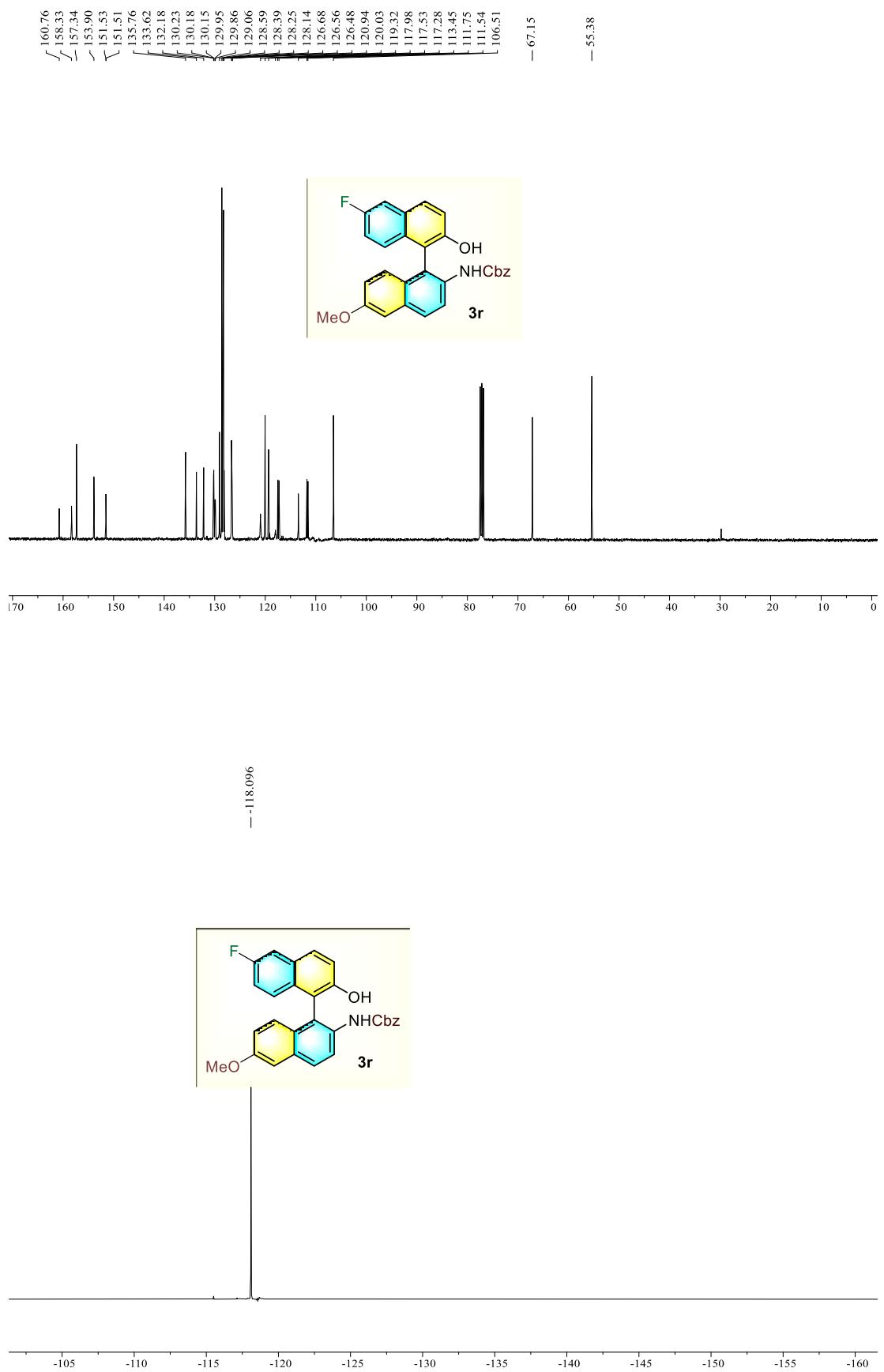


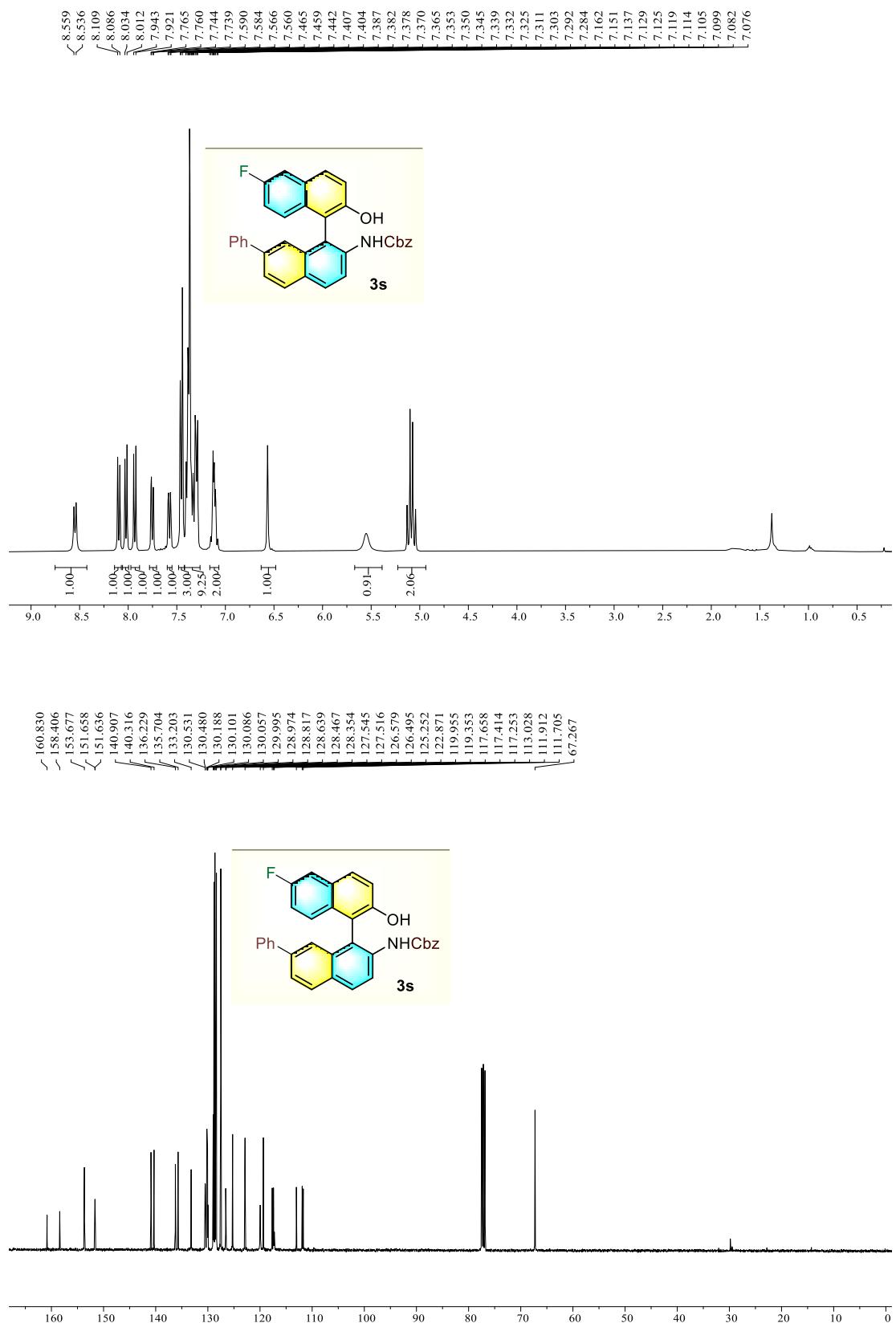


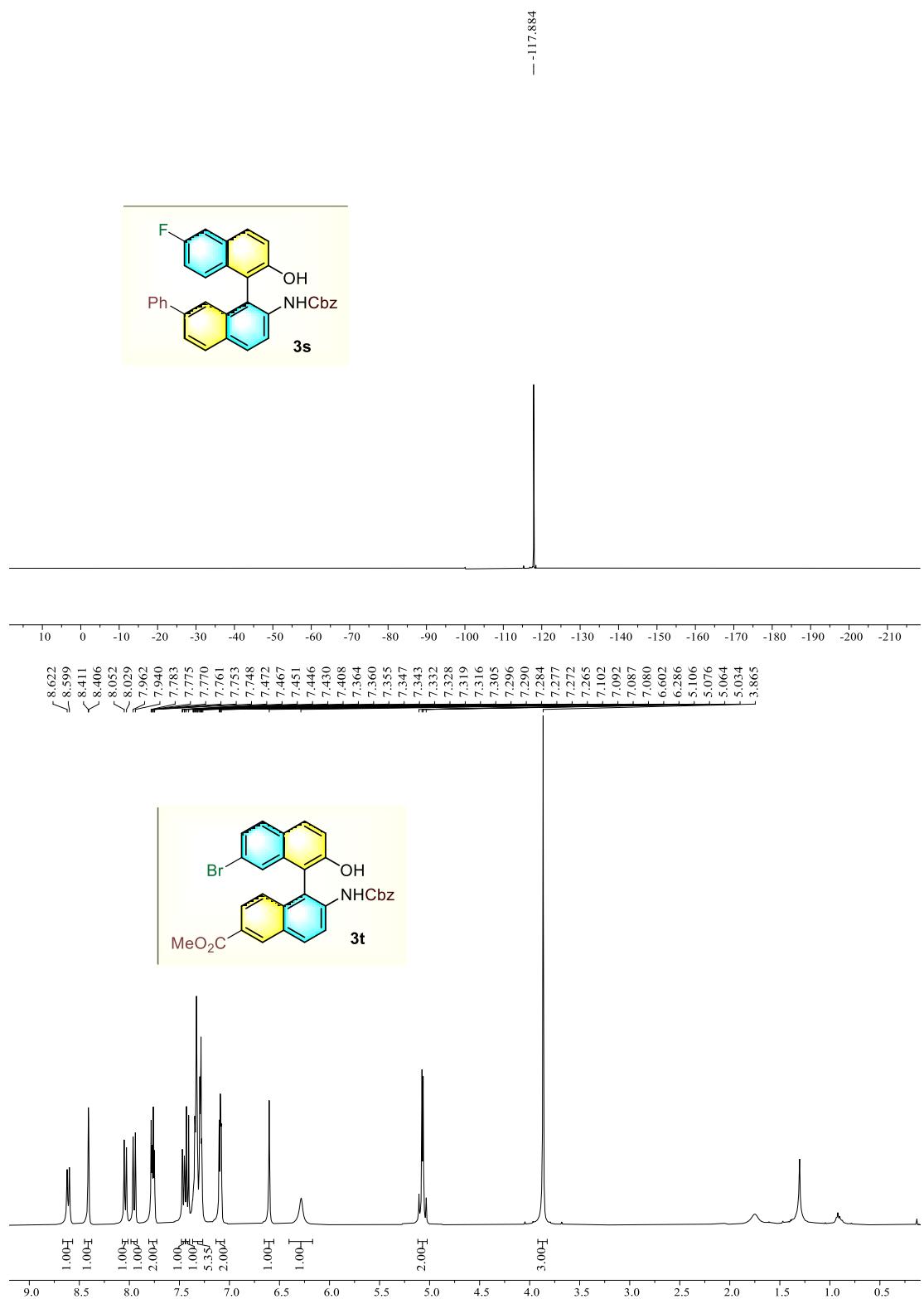


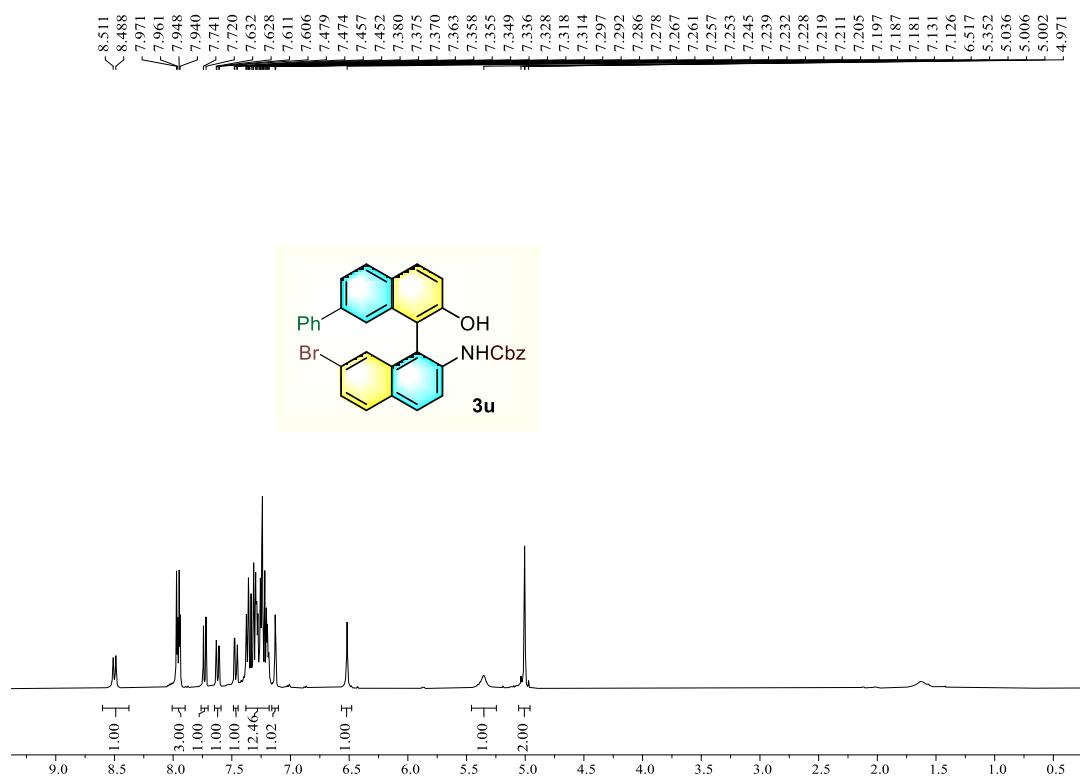
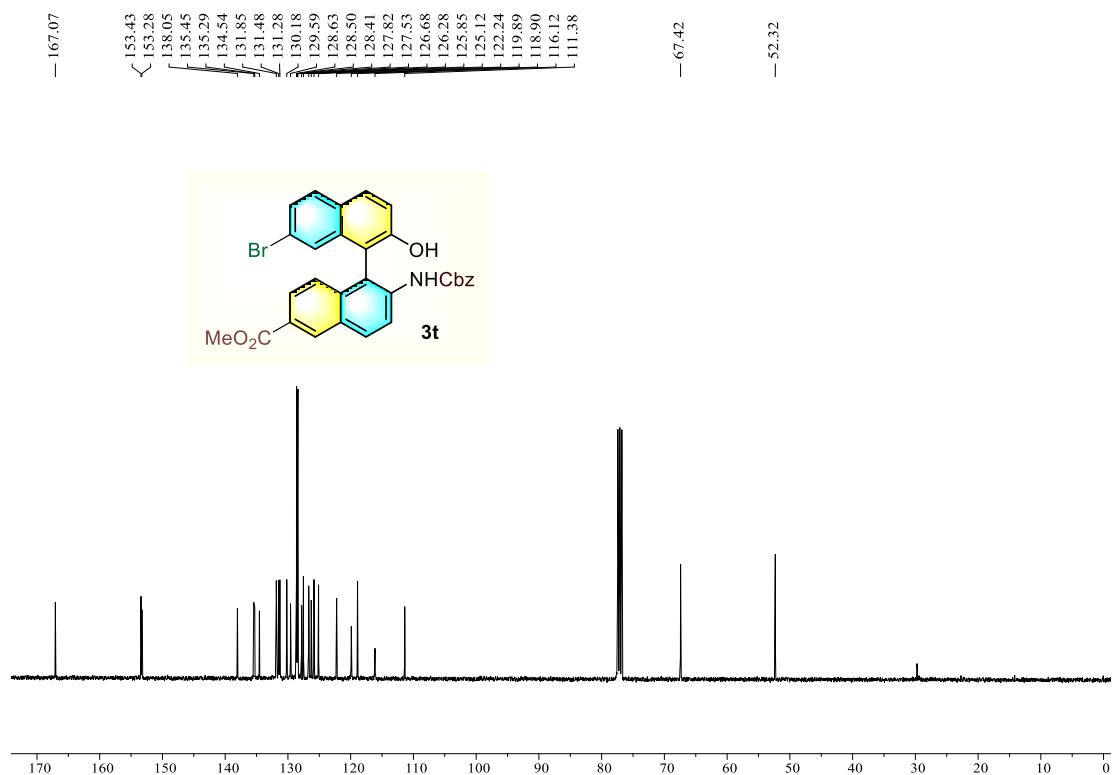


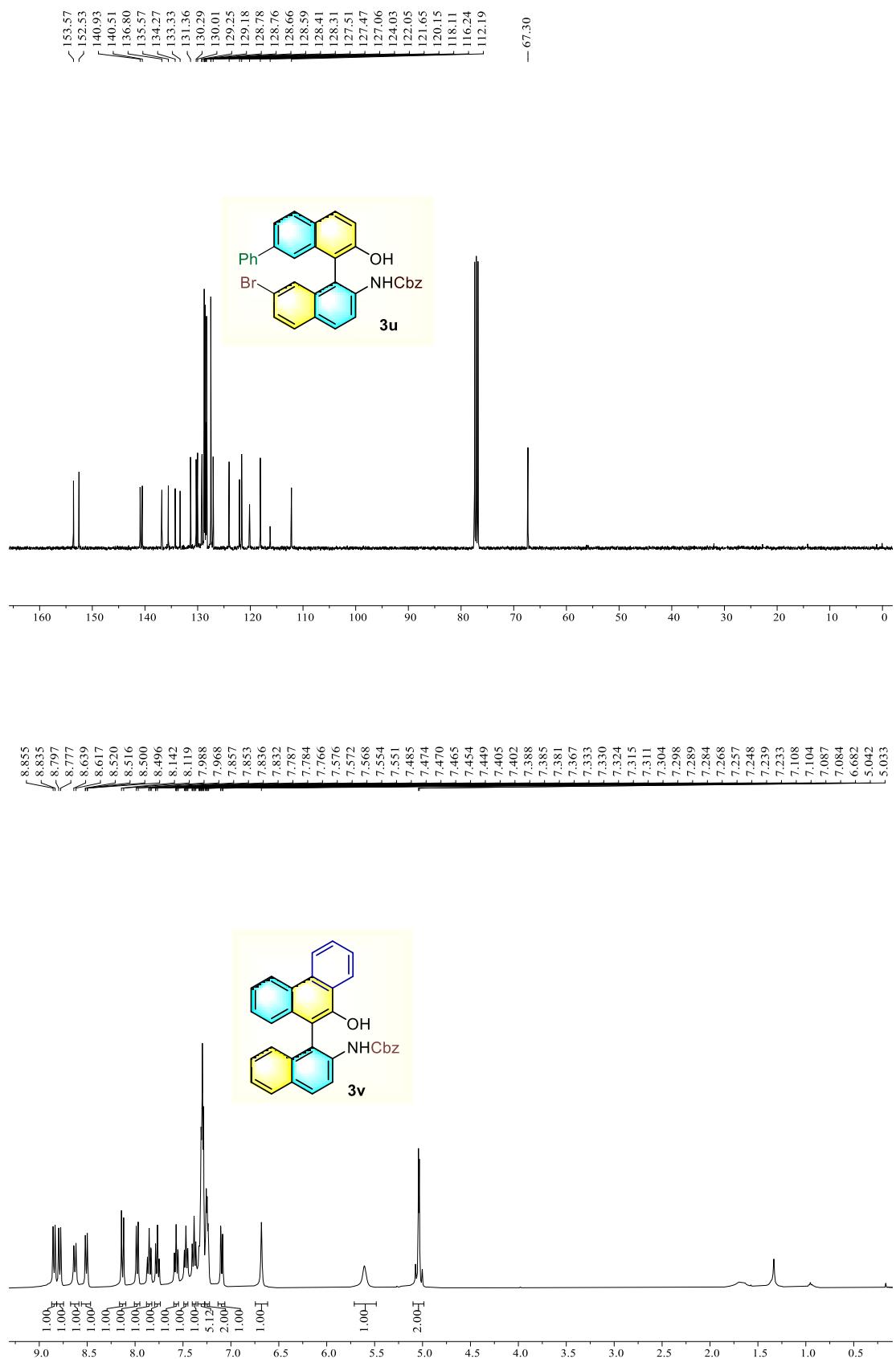


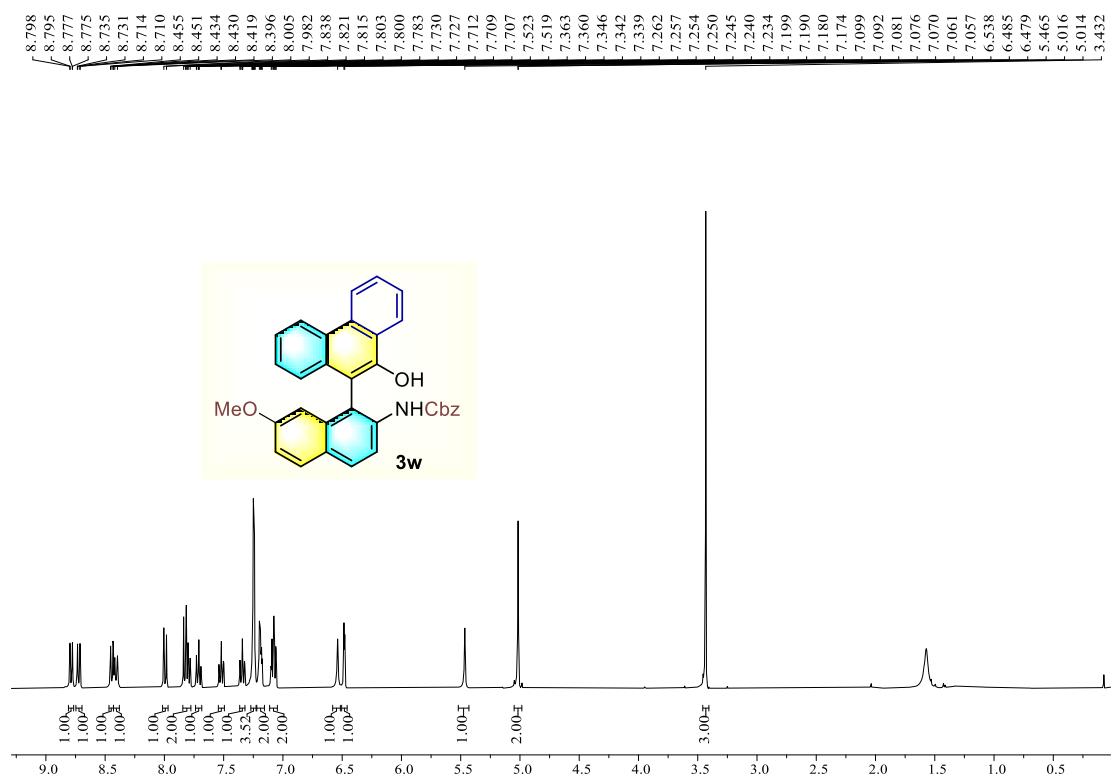
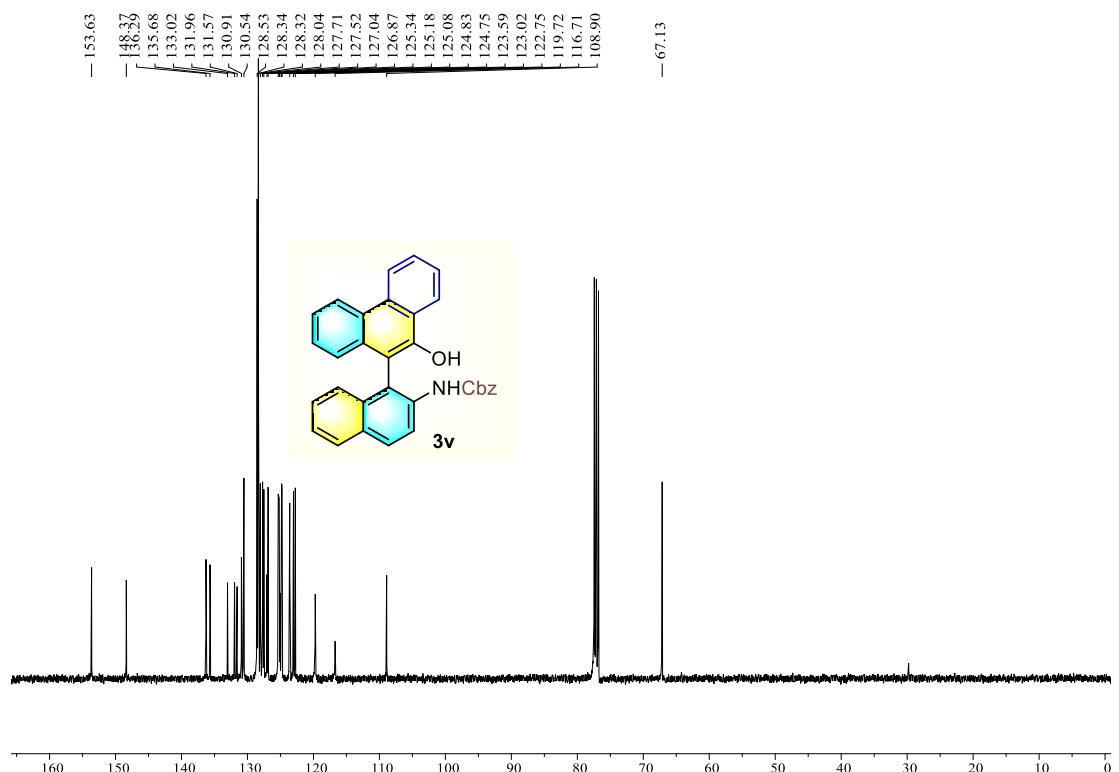


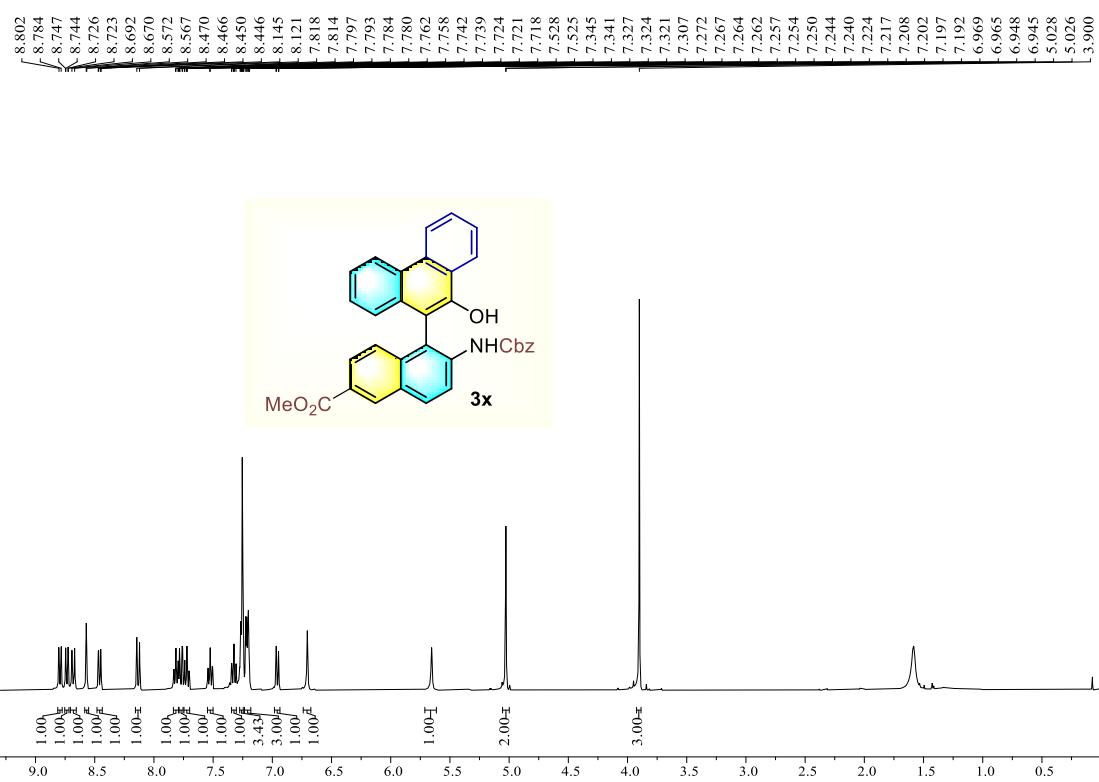
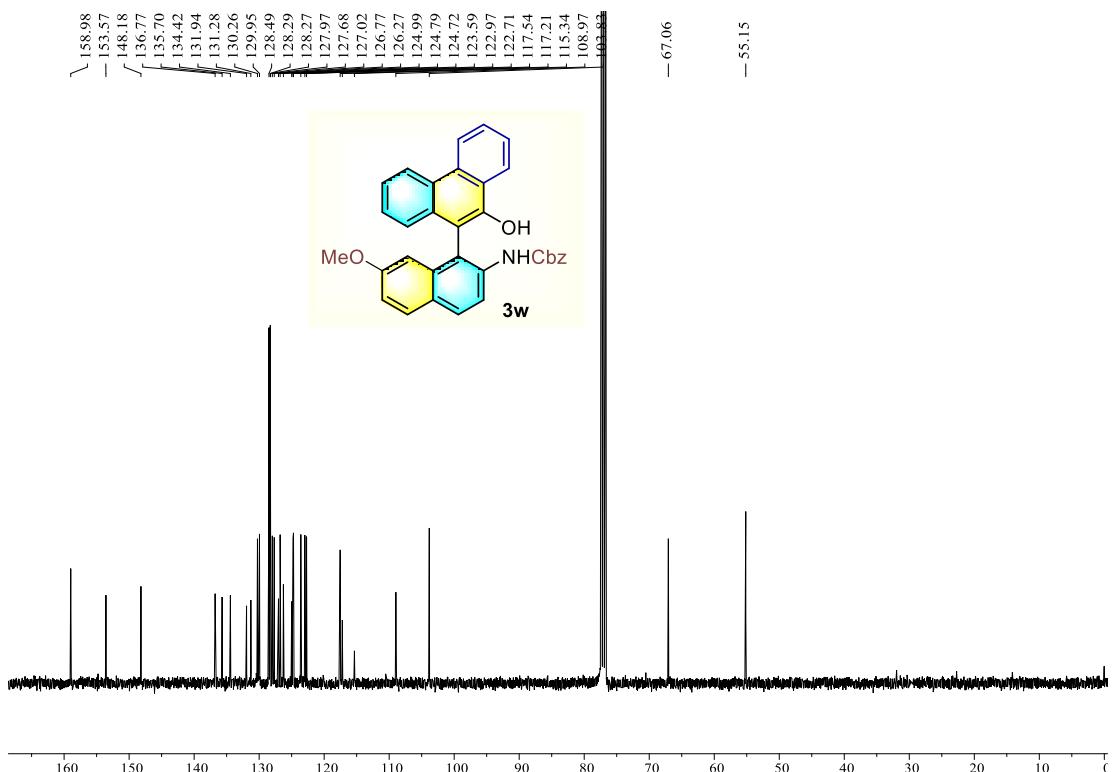


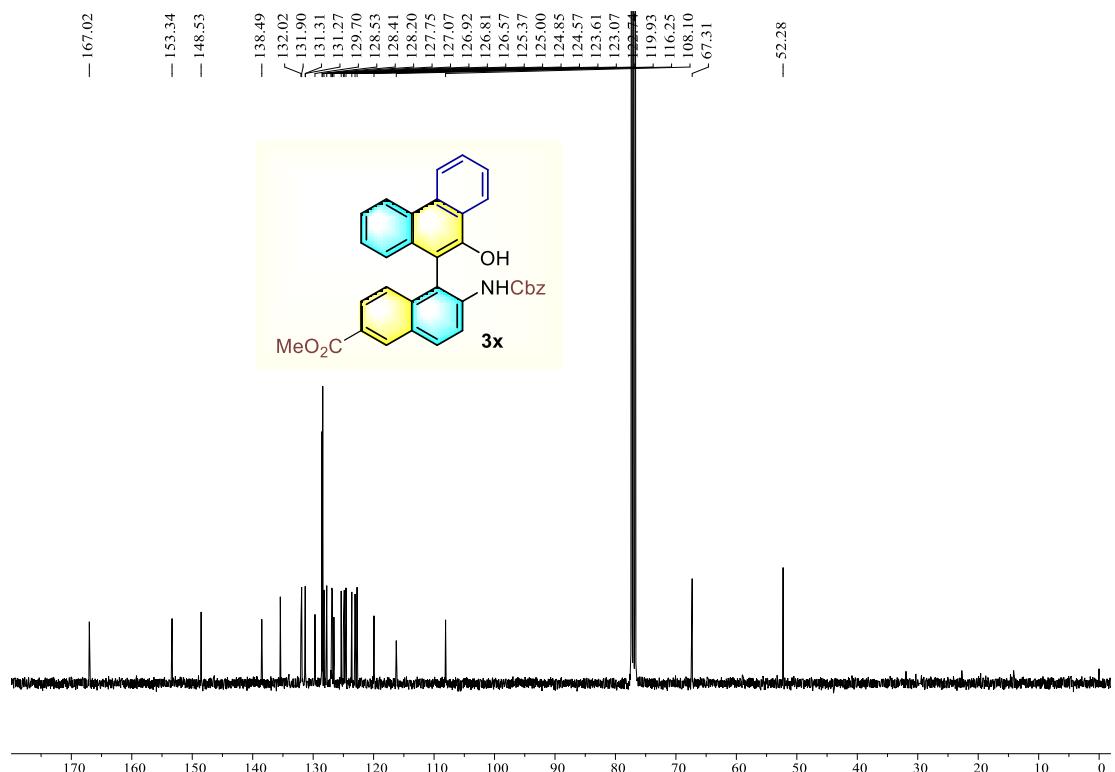






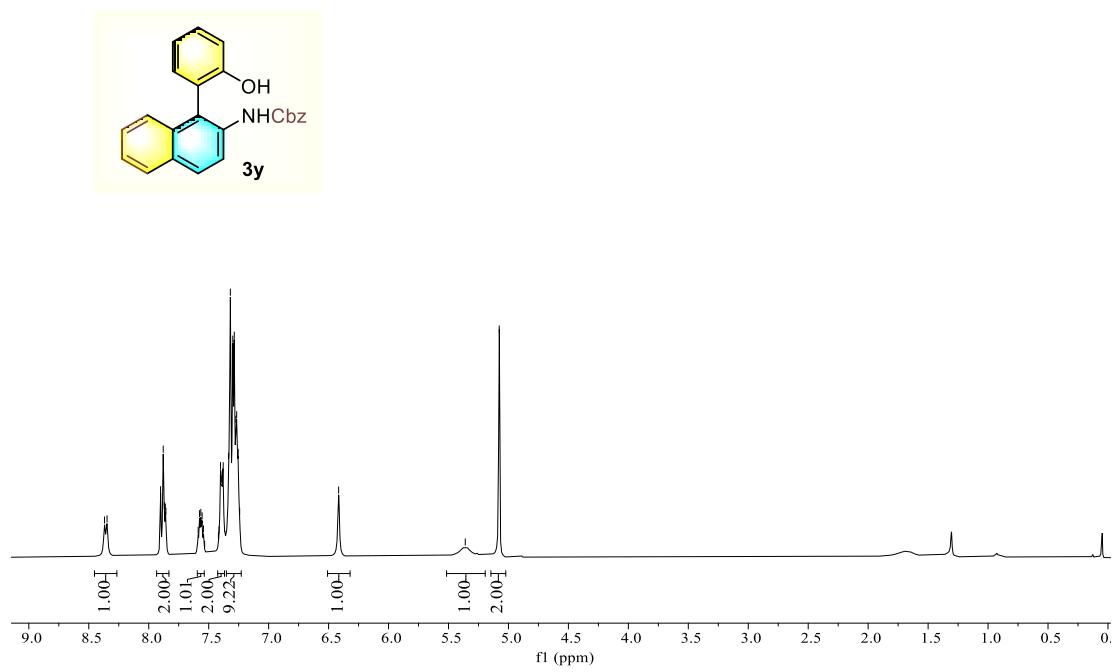


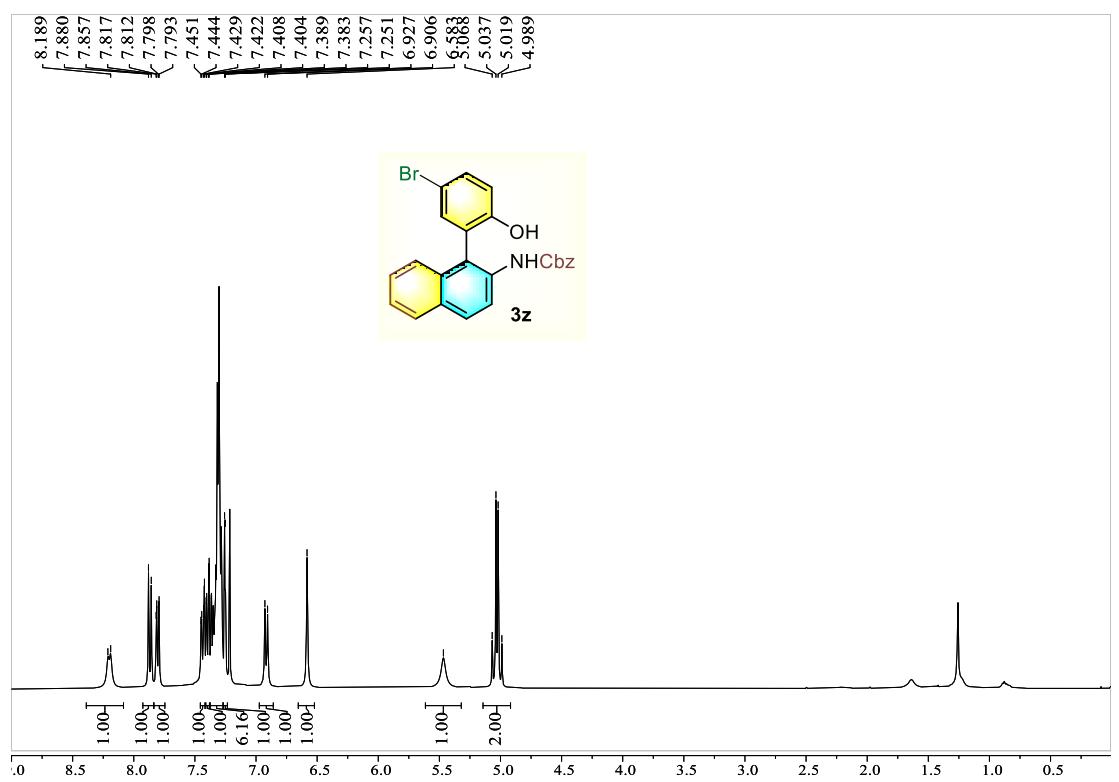
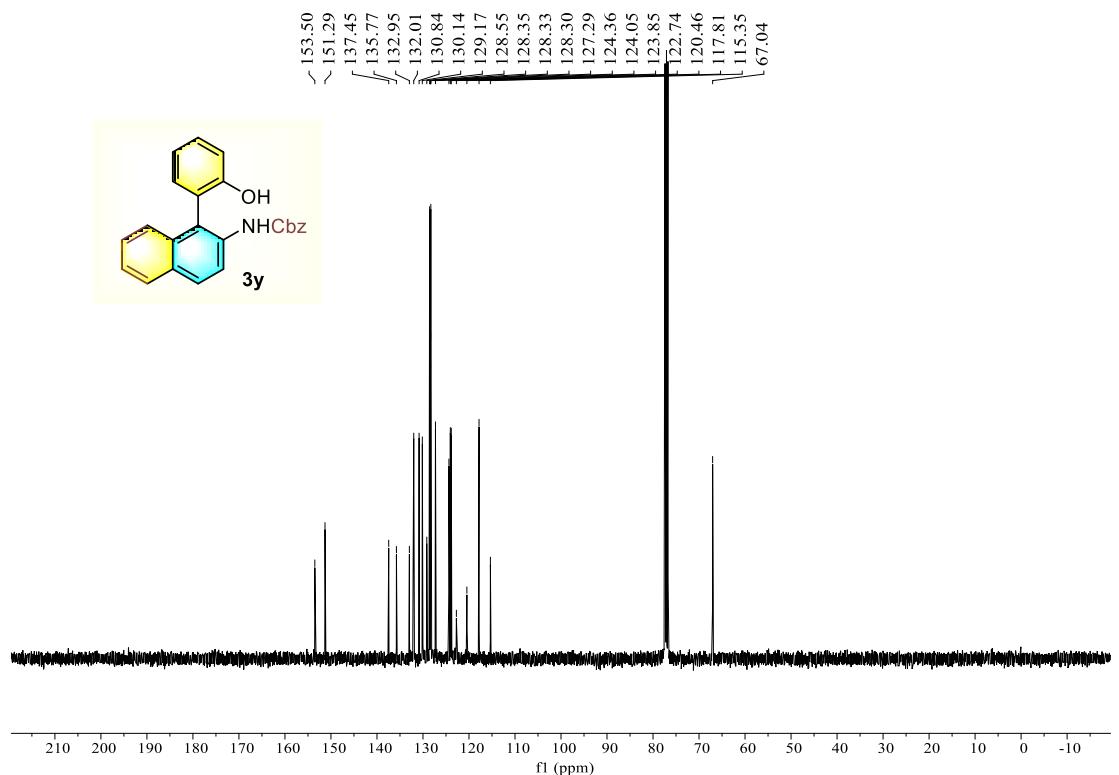


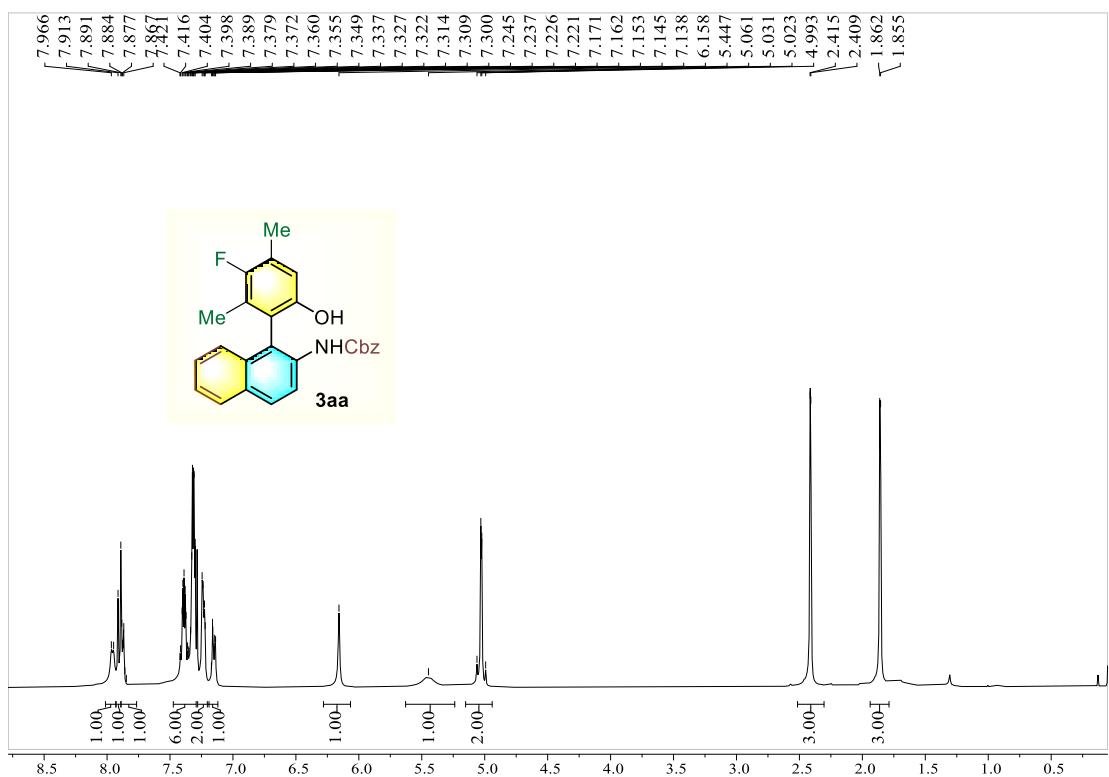
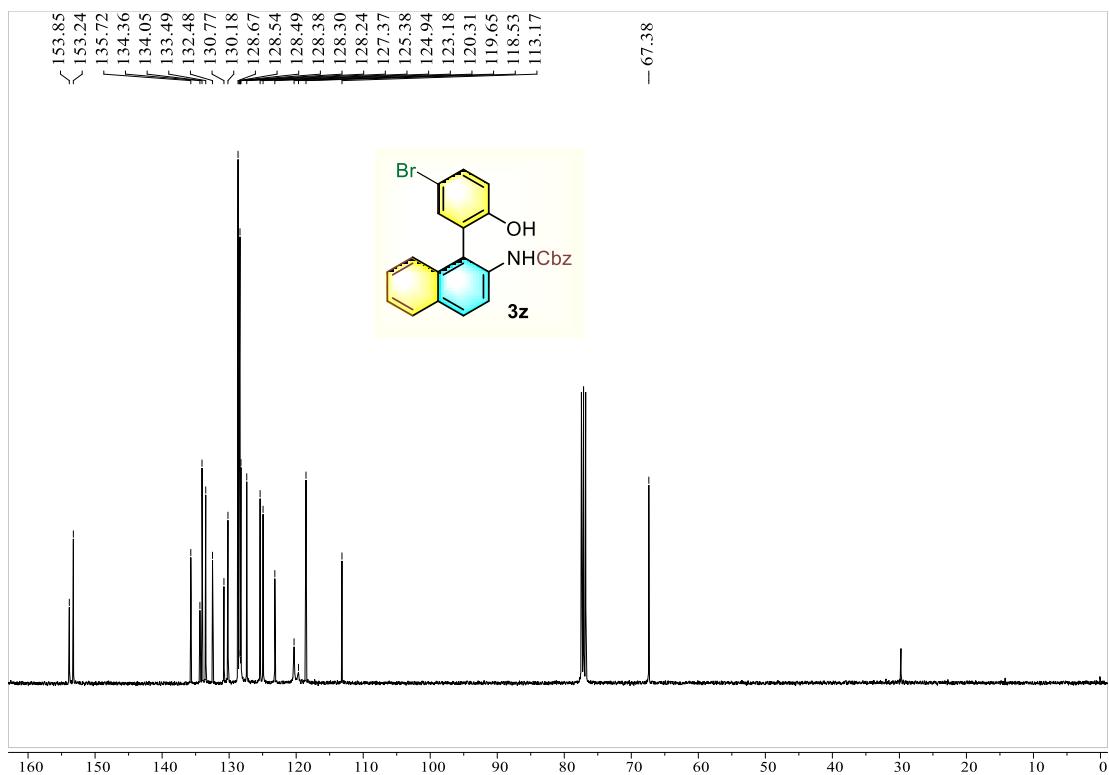


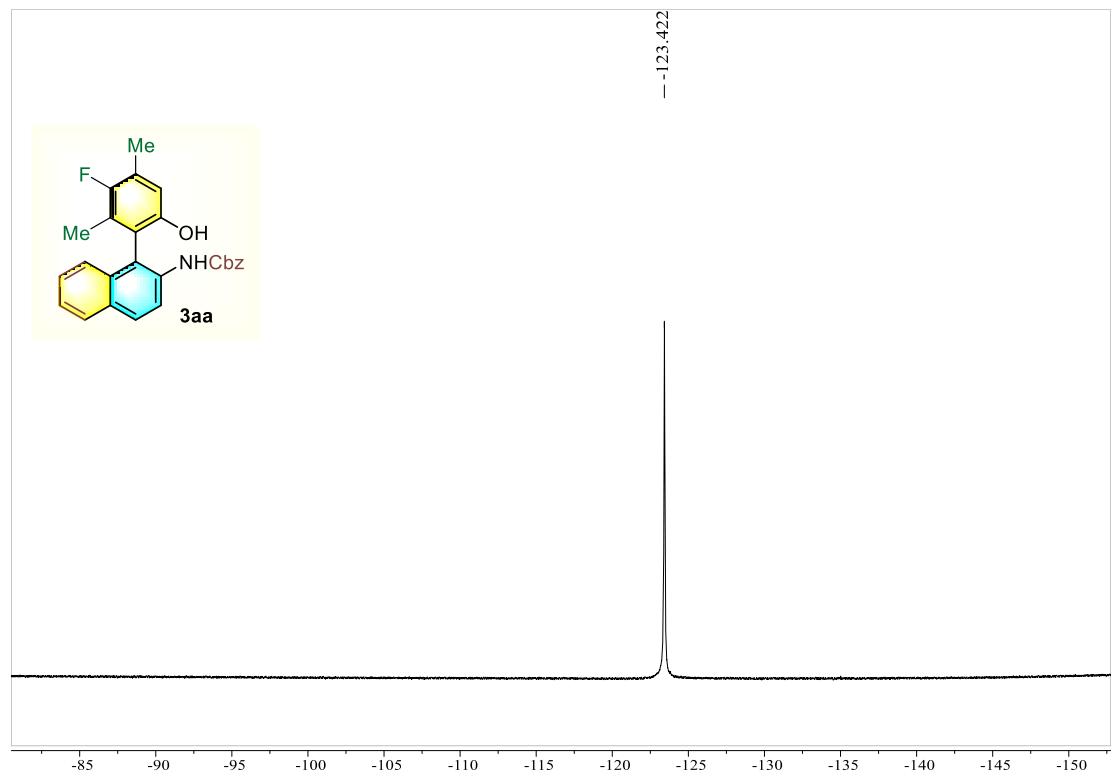
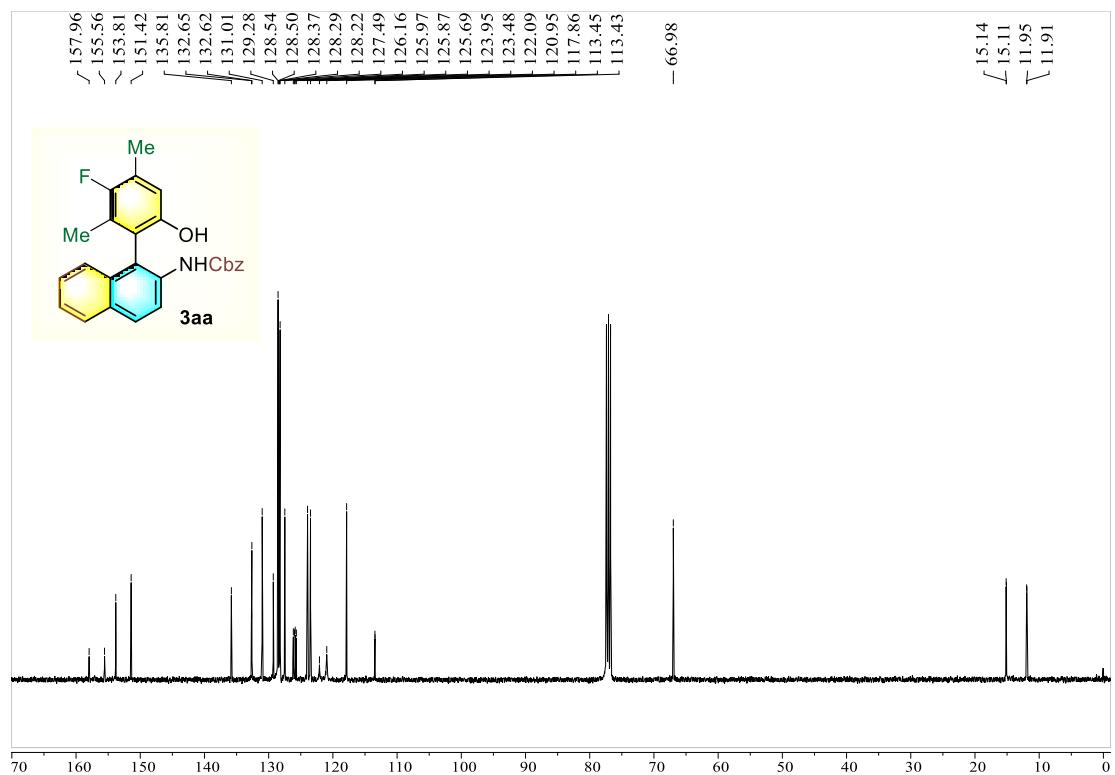
**<sup>13</sup>C NMR Peaks (ppm):**

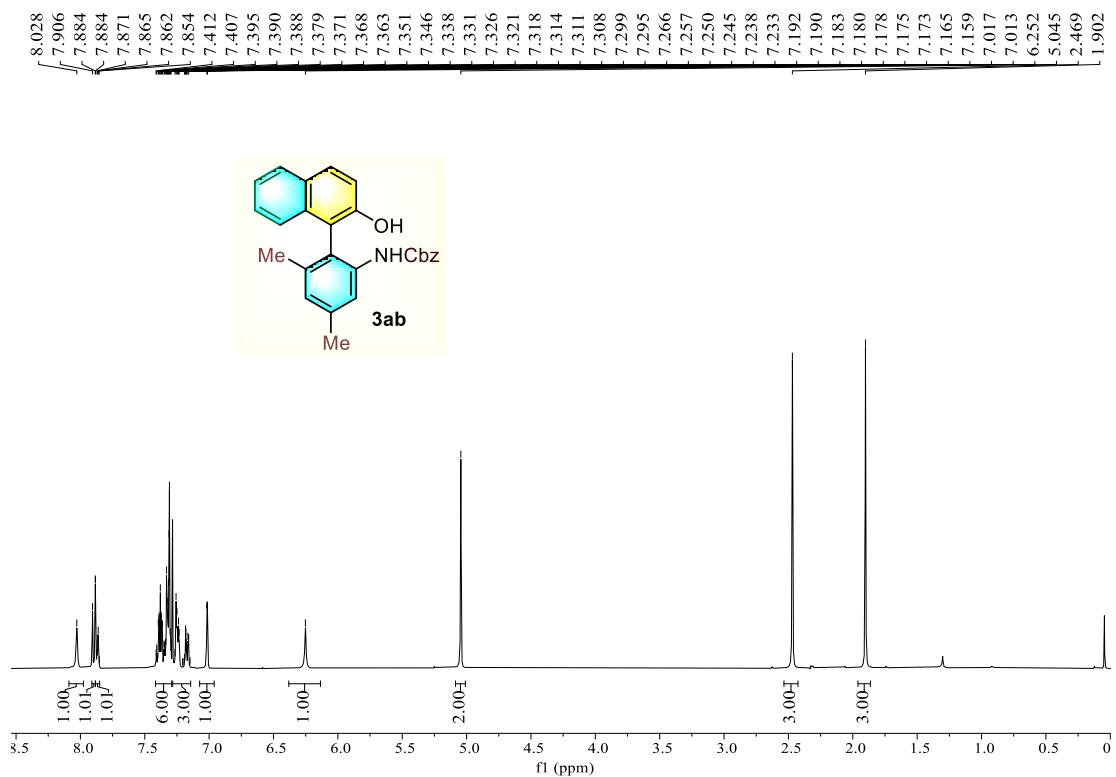
- 8.369
- 8.348
- 7.901
- 7.879
- 7.870
- 7.861
- 7.857
- 7.588
- 7.587
- 7.576
- 7.565
- 7.555
- 7.544
- 7.534
- 7.419
- 7.414
- 7.402
- 7.394
- 7.388
- 7.379
- 7.334
- 7.319
- 7.299
- 7.287
- 7.274
- 7.266
- 7.254
- 7.242
- 6.416
- 5.360
- 5.077











<sup>13</sup>C NMR chemical shifts (δ, ppm): 153.55, 151.37, 139.91, 139.28, 137.32, 135.90, 132.75, 130.75, 129.35, 128.53, 128.46, 128.27, 128.23, 127.34, 126.72, 123.84, 123.65, 118.80, 118.27, 117.72, 114.07, -66.90, ~21.70, and ~19.84.

