

## Supplementary Information for

### **Chemo- and Regioselective Cyclization of Diene-tethered Enynes via Palladium-Catalyzed Aminomethylation**

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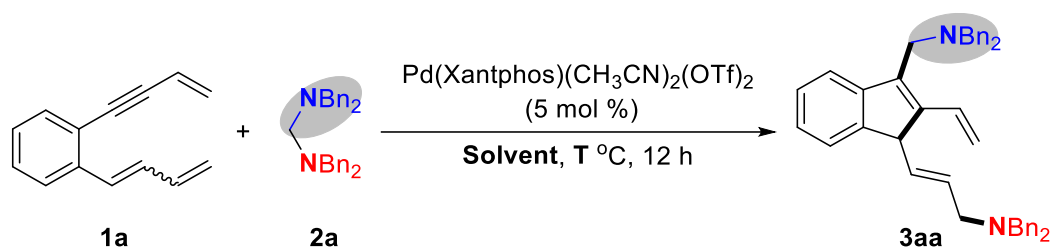
## 1. General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before using were dried by standard methods and stored under N<sub>2</sub> atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avance III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass instrument (ESI). All commercially available compounds were purchased from Adamas or Energy Chemical. Aminals used here were known compounds and synthesized according to the reported methods.<sup>1</sup> Diene-tethered enynes used here were synthesized from enynals<sup>2</sup> according to the reported methods.<sup>3</sup> Flash column chromatography was performed using 200-300 mesh silica gels.

## 2. Optimization of the Reaction Conditions

**Table S1.** Screening of temperature and solvents<sup>a</sup>

*N,N,N',N'*-tetrabenzylmethanediamine **2a** (146.2 mg, 0.36 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (16.0 mg, 5 mol %), 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene **1a** (54.0 mg, 0.30 mmol) and solvent (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at designed temperature in an oil bath for 12 hours, and then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as yellow oil.



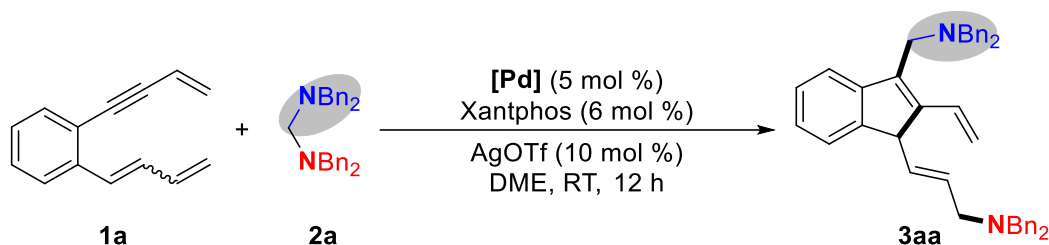
entry	catalyst	solvent	T/°C	yield (%) <sup>b</sup>
1	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	DME	80	30
2	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	DME	40	68
3	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	DME	RT	77
4	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	RT	87
5	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	THF	RT	44
6	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	CH <sub>3</sub> CN	RT	76
7	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	anisole	RT	85
8	Pd(Xantphos)(CH <sub>3</sub> CN) <sub>2</sub> (OTf) <sub>2</sub>	toluene	RT	52

<sup>a</sup>Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (5 mol %), solvent (1.0 mL), 12 h. <sup>b</sup>Isolated yield.

**Table S2.** Screening of catalyst precursors<sup>a</sup>

*N,N,N',N'*-tetrabenzylmethanediamine **2a** (146.2 mg, 0.36 mmol), catalyst precursor (0.015 mmol, 5 mol %), Xantphos (10.4 mg, 6 mol %), AgOTf (7.7 mg, 10 mol %), 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene **1a** (54.0 mg, 0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere.

The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as yellow oil.

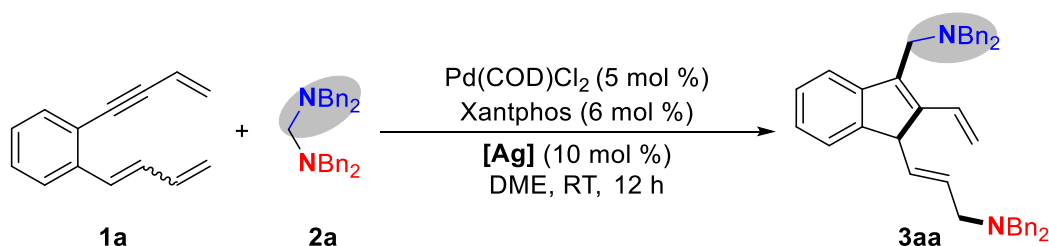


entry	[Pd]	ligand/[Ag]	solvent	yield(%) <sup>b</sup>
1	[Pd(allyl)Cl] <sub>2</sub>	Xantphos/AgOTf	DME	69
2	Pd(COD)Cl <sub>2</sub>	Xantphos/AgOTf	DME	72
3	Pd(OAc) <sub>2</sub>	Xantphos/AgOTf	DME	23
4	PdBr <sub>2</sub>	Xantphos/AgOTf	DME	65
5	Pd <sub>2</sub> (dba) <sub>3</sub>	Xantphos/AgOTf	DME	28

<sup>a</sup>Reaction conditions: **1a** (0.30 mmol), **2a** (0.36 mmol), [Pd] (5 mol %), Xantphos (6 mol %), AgOTf (10 mol %), DME (1.0 mL), RT, 12 h. <sup>b</sup>Isolated yield.

### Table S3. Screening of silver salts<sup>a</sup>

*N,N,N',N'*-tetrabenzylmethanediamine **2a** (146.2 mg, 0.36 mmol), Pd(COD)Cl<sub>2</sub> (4.3 mg, 5 mol %), Xantphos (10.4 mg, 6 mol %), silver salt (0.03 mmol, 10 mol %), 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene **1a** (54.0 mg, 0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as yellow oil.

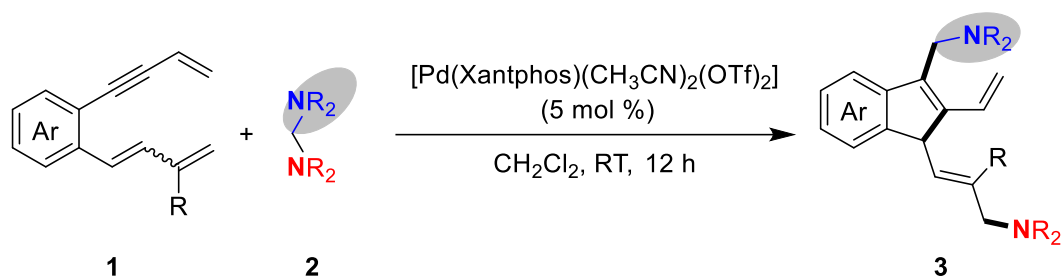


entry	catalyst	[Ag]	solvent	yield(%) <sup>b</sup>
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1	Pd(COD)Cl <sub>2</sub> /Xantphos	AgOTf	DME	72
2	Pd(COD)Cl <sub>2</sub> /Xantphos	AgOMs	DME	42
3	Pd(COD)Cl <sub>2</sub> /Xantphos	AgBF <sub>4</sub>	DME	37
4	Pd(COD)Cl <sub>2</sub> /Xantphos	AgOAc	DME	24
5	Pd(COD)Cl <sub>2</sub> /Xantphos	AgSbF <sub>6</sub>	DME	58

<sup>a</sup>Reaction conditions: **1a** (0.30 mmol), **2a** (0.36 mmol), Pd(COD)Cl<sub>2</sub> (5 mol %), Xantphos (6 mol %), [Ag] (10 mol %), DME (1.0 mL), RT, 12 h. <sup>b</sup>Isolated yield.

### 3. General Procedure for the Catalytic Reaction

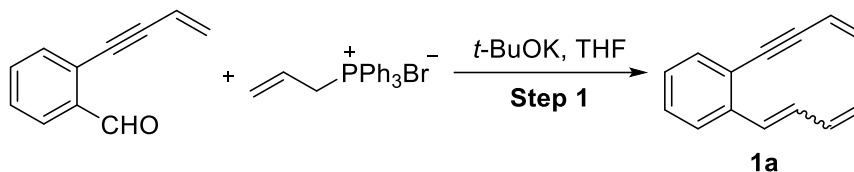


Aminal **2** (0.36 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (16.0 mg, 5 mol %), diene-tethered enyne **1** (0.30 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3** as yellow oil.

## 4. Preparation and Spectral Data of Substrates

### 4.1. Preparation of Diene-tethered enyne Derivatives

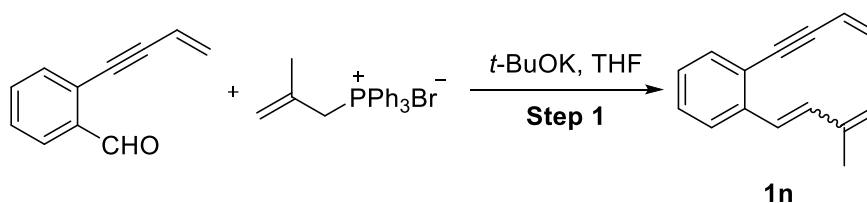
#### General Procedure A. Synthesis of diene-tethered enyne substrate **1a**



Diene-tethered enynes **1a-1m** were synthesized by using enynal as starting materials according to the **General Procedure A**.

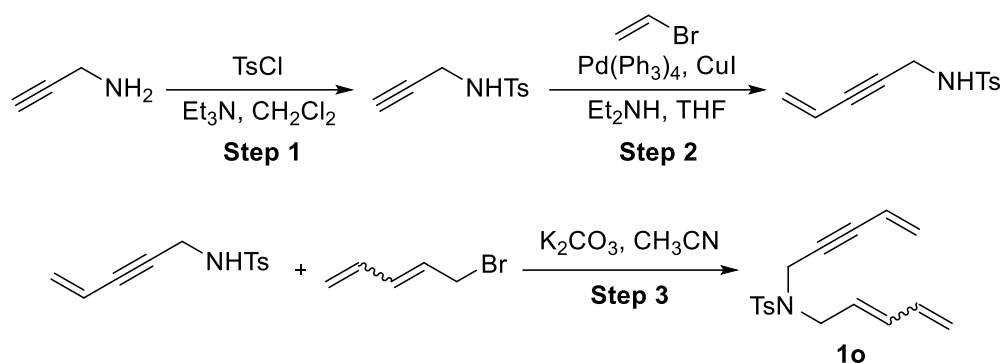
**Step 1.** Allyltriphenylphosphonium bromide (4.6 g, 12 mmol) was dissolved in anhydrous THF (20 mL) under  $\text{N}_2$  atmosphere at 0 °C. Potassium *tert*-butoxide (1.6 g, 14 mmol) was added slowly and stirred at 0 °C for 30 minutes. 2-(but-3-en-1-yn-1-yl)benzaldehyde (1.6 g, 10 mmol) was added and the resulting mixture was stirred at room temperature until complete conversion of the starting material. The reaction mixture was diluted with petroleum ether (20 mL) and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether) to afford 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene **1a** (1.48 g, 82% yield).

#### General Procedure B. Synthesis of diene-tethered enyne substrate **1n**



**Step 1.** (2-Methylallyl)triphenylphosphonium bromide (4.8 g, 12 mmol) was dissolved in anhydrous THF (20 mL) under  $\text{N}_2$  atmosphere at 0 °C. Potassium *tert*-butoxide (1.6 g, 14 mmol) was added slowly and stirred at 0 °C for 30 minutes. 2-(but-3-en-1-yn-1-yl)benzaldehyde (1.6 g, 10 mmol) was added and the resulting mixture was stirred at room temperature until complete conversion of the starting material. The reaction mixture was diluted with petroleum ether (20 mL) and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether) to afford 1-(but-3-en-1-yn-1-yl)-2-(3-methylbuta-1,3-dien-1-yl)benzene **1n** (1.51 g, 78% yield).

### General Procedure C. Synthesis of aliphatic diene-tethered enyne substrate **1o**



**Step 1.** Prop-2-yn-1-amine (1.3 mL, 21 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the solution was cooled to 0 °C. To this solution were added triethylamine (7.0 mL, 50 mmol) and then *p*-toluenesulfonyl chloride (3.8 g, 20 mmol). The mixture was stirred at room temperature for overnight. Then the reaction mixture was dissolved in Et<sub>2</sub>O (200 mL), washed with a solution of HCl (1M) and a saturated solution of NH<sub>4</sub>Cl. The organic layer was dried over NaSO<sub>4</sub> and filtered. After evaporation of the solvent under reduced pressure, the desired 4-methyl-*N*-(prop-2-yn-1-yl)benzene-1-sulfonamide was obtained as a white powder (3.76 g, 90%).

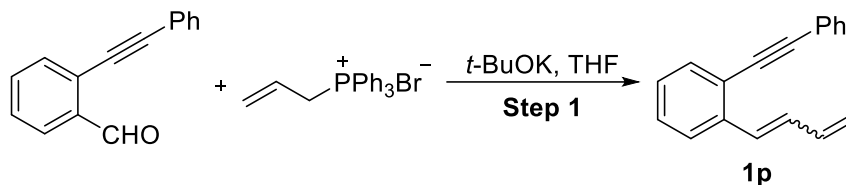
**Step 2.** The mixture of copper (I) iodide (68.6 mg, 0.36 mmol) and tetrakis(triphenylphosphine)palladium (208.0 mg, 0.18 mmol) was dissolved in diethylamine (10 mL) under N<sub>2</sub> atmosphere at 0 °C. 4-methyl-*N*-(prop-2-yn-1-yl)benzene-1-sulfonamide (3.8 g, 18 mmol) and vinyl bromide (1.0 M in THF, 21.6 mL, 21.6 mmol) were added and the resulting mixture was stirred at 45 °C in an oil bath until complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1 to 3/1) to afford 4-methyl-*N*-(pent-4-en-2-yn-1-yl)benzenesulfonamide (3.43 g, 81% yield).

**Step 3.** The mixture of 4-methyl-*N*-(pent-4-en-2-yn-1-yl)benzenesulfonamide (2.4 g, 10 mmol), 5-bromopenta-1,3-diene (2.9 g, 20 mmol), potassium carbonate (5.5 mg, 40 mmol) and tetrabutylammonium iodide (369.4 mg, 1 mmol) were dissolved in CH<sub>3</sub>CN (40 mL). After being stirred at 70 °C for 14 hours, the reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate =



30/1 to 10/1) to afford 4-methyl-*N*-(pent-4-en-2-yn-1-yl)-*N*-(penta-2,4-dien-1-yl)benzenesulfonamide **1o** (2.29 g, 76% yield).

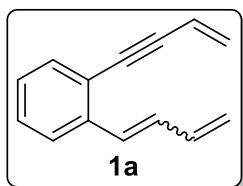
**General Procedure D.** Synthesis of diene-tethered phenylacetylene substrate **1p**



**Step 1.** Allyltriphenylphosphonium bromide (4.6 g, 12 mmol) was dissolved in anhydrous THF (20 mL) under N<sub>2</sub> atmosphere at 0 °C. Potassium *tert*-butoxide (1.6 g, 14 mmol) was added slowly and stirred at 0 °C for 30 minutes. 2-(phenylethynyl)benzaldehyde (2.1 g, 10 mmol) was added and the resulting mixture was stirred at room temperature until complete conversion of the starting material. The reaction mixture was diluted with petroleum ether (20 mL) and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether) to afford 1-(buta-1,3-dien-1-yl)-2-(phenylethynyl)benzene **1p** (1.77 g, 77% yield).

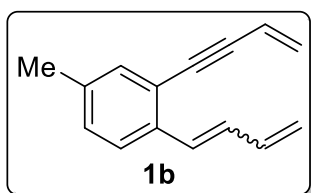
## 4.2. Substrates Characterization

### 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene (1a)



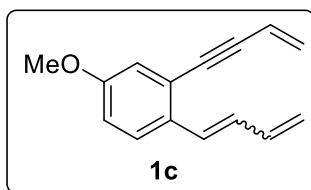
The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.48 g, 82% yield (*E/Z* = 1:2.3). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.9 Hz, 0.3H), 7.37-7.46 (m, 1.7H), 7.14-7.29 (m, 2H), 7.03 (d, *J* = 15.8 Hz, 0.3H), 6.74-6.88 (m, 1H), 6.70 (d, *J* = 11.5 Hz, 0.7H), 6.54-6.61 (m, 0.3H), 6.35 (t, *J* = 11.4 Hz, 0.7H), 6.00-6.10 (m, 1H), 5.70-5.77 (m, 1H), 5.51-5.57 (m, 1H), 5.34-5.40 (m, 1H), 5.20-5.23 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.2, 138.6, 137.5, 133.4, 132.9, 132.5, 131.7, 131.4, 130.8, 129.6, 129.2, 128.6, 128.1, 127.3, 127.1, 127.0, 124.8, 122.8, 122.1, 120.0, 118.5, 117.4, 93.1, 93.0, 88.7, 88.5; HRMS (ESI) calcd for C<sub>14</sub>H<sub>13</sub> [M+H]<sup>+</sup>: 181.1017, found: 181.1011.

### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (1b)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.55 g, 80% yield (*E/Z* = 1:1.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 8.1 Hz, 0.38H), 7.44-7.48 (m, 1.62H), 7.26-7.29 (m, 1H), 7.18 (d, *J* = 15.7 Hz, 0.38H), 6.92-7.04 (m, 1H), 6.86 (d, *J* = 11.5 Hz, 0.62H), 6.47-6.80 (m, 1H), 6.19-6.30 (m, 1H), 5.88-5.96 (m, 1H), 5.70-5.76 (m, 1H), 5.51-5.58 (m, 1H), 5.36-5.41 (m, 1H), 2.49-2.51 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.6, 137.3, 137.0, 136.4, 135.8, 133.5, 133.2, 132.9, 131.2, 130.8, 130.4, 129.7, 129.4, 129.1, 129.0, 126.9, 124.7, 122.6, 121.9, 119.6, 117.9, 117.4, 92.7, 92.6, 88.9, 88.7, 21.1; HRMS (ESI) calcd for C<sub>15</sub>H<sub>15</sub> [M+H]<sup>+</sup>: 195.1174, found: 195.1160.

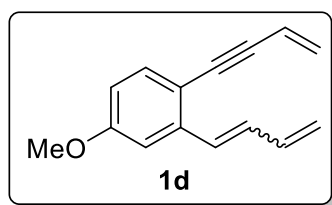
### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1c)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.64 g, 78% yield (*E/Z* = 1:3.8). <sup>1</sup>H NMR

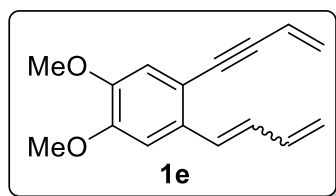
(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.51 (m, 1H), 6.93-7.00 (m, 1.21H), 6.71-6.87 (m, 2.21H), 6.64 (d,  $J$  = 11.4 Hz, 0.79H), 6.25-6.60 (m, 1H), 6.00-6.11 (m, 0.79H), 5.71-5.79 (m, 1H), 5.53-5.59 (m, 1H), 5.29-5.38 (m, 1H), 5.14-5.21 (m, 1H), 3.79-3.80 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 158.4, 137.7, 133.5, 132.0, 131.6, 130.7, 130.5, 130.4, 129.4, 128.7, 127.2, 126.0, 123.7, 123.0, 119.4, 117.4, 117.3, 116.6, 116.3, 116.2, 115.0, 92.9, 92.8, 88.6, 88.4, 55.5; HRMS (ESI) calcd for C<sub>15</sub>H<sub>15</sub>O [M+H]<sup>+</sup>: 211.1123, found: 211.1116.

#### 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)-4-methoxybenzene (1d)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.70 g, 81% yield ( $E/Z$  = 1:4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34-7.40 (m, 1H), 6.99-7.07 (m, 0.4H), 6.90 (s, 0.8H), 6.74-6.85 (m, 2H), 6.66 (d,  $J$  = 11.5 Hz, 0.8H), 6.52-6.62 (m, 0.2H), 6.31-6.37 (m, 0.8H), 5.98-6.10 (m, 1H), 5.65-5.73 (m, 1H), 5.47-5.53 (m, 1H), 5.37-5.41 (m, 1H), 5.21-5.24 (m, 1H), 3.79-3.80 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 159.3, 140.6, 140.0, 137.4, 134.2, 133.8, 133.3, 131.9, 131.4, 130.8, 129.1, 126.2, 126.2, 120.3, 118.7, 117.5, 115.1, 115.1, 114.7, 114.0, 113.0, 109.4, 91.8, 91.6, 88.7, 88.5, 55.5, 55.4; HRMS (ESI) calcd for C<sub>15</sub>H<sub>15</sub>O [M+H]<sup>+</sup>: 211.1123, found: 211.1118.

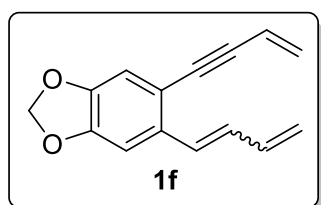
#### 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)-4,5-dimethoxybenzene (1e)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.63 g, 68% yield ( $E/Z$  = 1:1.9). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02-7.03 (m, 1H), 6.95 (d,  $J$  = 11.6 Hz, 0.66H), 6.89-6.90 (m, 1H), 6.65-6.85 (m, 1.34H), 6.52 (dt,  $J$  = 16.8 Hz, 10.3 Hz, 0.66H), 6.29 (t,  $J$  = 11.2 Hz, 0.34H), 5.99-6.11 (m, 1H), 5.68-5.76 (m, 1H), 5.49-5.55 (m, 1H), 5.32-5.41 (m, 1H), 5.17-5.24 (m, 1H), 3.87-3.93 (m, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  149.8, 149.0, 148.6, 148.1, 137.6, 133.4, 132.9, 132.4,

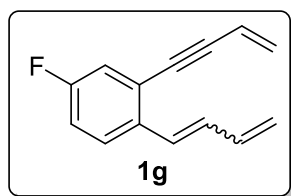
130.7, 130.7, 129.5, 129.0, 126.4, 126.4, 119.7, 117.6, 117.4, 115.1, 114.7, 114.6, 114.6, 112.4, 106.9, 92.0, 91.7, 88.8, 88.6, 56.1, 56.1, 56.0; HRMS (ESI) calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 241.1229, found: 241.1215.

#### 5-(but-3-en-1-yn-1-yl)-6-(buta-1,3-dien-1-yl)benzo[d][1,3]dioxole (1f)



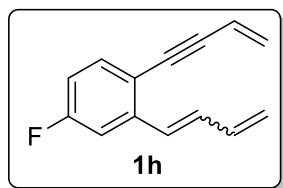
The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.61 g, 72% yield (*E/Z* = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.98-7.03 (m, 1H), 6.50-6.89 (m, 3.5H), 6.27 (t, *J* = 11.4 Hz, 0.5H), 5.92-6.09 (m, 3H), 5.66-5.74 (m, 1H), 5.49-5.55 (m, 1H), 5.30-5.39 (m, 1H), 5.16-5.24 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.6, 147.8, 147.1, 146.6, 137.5, 134.4, 134.1, 133.2, 130.9, 130.6, 129.8, 128.8, 126.6, 126.6, 120.0, 117.9, 117.4, 116.2, 115.9, 111.8, 111.7, 109.6, 104.2, 101.6, 101.6, 92.0, 91.9, 88.7, 88.5; HRMS (ESI) calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 225.0916, found: 225.0908.

#### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (1g)



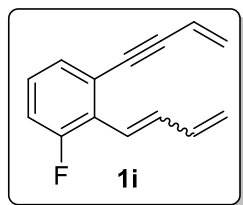
The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.56 g, 79% yield (*E/Z* = 1:1.2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 (dd, *J* = 8.7 Hz, 5.8 Hz, 0.45H), 7.31 (dd, *J* = 8.4 Hz, 6.0 Hz, 0.55H), 7.10-7.16 (m, 1H), 6.95-7.01 (m, 1.45H), 6.66-6.80 (m, 1H), 6.61 (d, *J* = 11.5 Hz, 0.55H), 6.50-6.60 (m, 0.45H), 6.33 (t, *J* = 11.4 Hz, 0.55H), 5.99-6.10 (m, 1H), 5.72-5.80 (m, 1H), 5.55-5.62 (m, 1H), 5.33-5.41 (m, 1H), 5.20-5.25 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.6 (d, *J*<sub>C-F</sub> = 246 Hz), 160.4 (d, *J*<sub>C-F</sub> = 246 Hz), 137.3, 135.4 (d, *J*<sub>C-F</sub> = 3 Hz), 135.0 (d, *J*<sub>C-F</sub> = 3 Hz), 133.0, 131.7, 131.1, 131.1, 131.1, 129.7, 128.1, 127.8, 126.4 (d, *J*<sub>C-F</sub> = 8 Hz), 124.4 (d, *J*<sub>C-F</sub> = 10 Hz), 123.5 (d, *J*<sub>C-F</sub> = 10 Hz), 120.3, 118.9 (d, *J*<sub>C-F</sub> = 23 Hz), 118.8 (d, *J*<sub>C-F</sub> = 23 Hz), 118.5, 117.0, 116.2 (d, *J*<sub>C-F</sub> = 22 Hz), 115.4 (d, *J*<sub>C-F</sub> = 21 Hz), 93.8, 93.7, 87.5 (d, *J*<sub>C-F</sub> = 3 Hz), 87.3 (d, *J*<sub>C-F</sub> = 3 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -114.6, -114.9; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>F [M+H]<sup>+</sup>: 199.0923, found: 199.0912.

### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-5-fluorobenzene (1h)



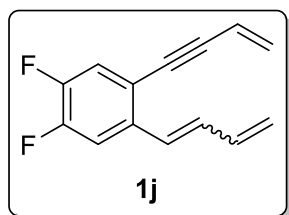
The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.49 g, 75% yield (*E/Z* = 1:1.1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56-7.63 (m, 1H), 7.26-7.45 (m, 1H), 7.16 (d, *J* = 15.7 Hz, 0.48H), 7.04-7.13 (m, 1H), 6.90-7.03 (m, 1H), 6.81 (d, *J* = 11.6 Hz, 0.52H) 6.53-6.80 (m, 1H), 6.17-6.28 (m, 1H), 5.88-5.96 (m, 1H), 5.70-5.77 (m, 1H), 5.57-5.63 (m, 1H), 5.44-5.48 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5 (d, *J*<sub>C-F</sub> = 247 Hz), 160.9 (d, *J*<sub>C-F</sub> = 248 Hz), 141.3 (d, *J*<sub>C-F</sub> = 8 Hz), 140.9 (d, *J*<sub>C-F</sub> = 8 Hz), 137.1, 134.6 (d, *J*<sub>C-F</sub> = 9 Hz), 134.1 (d, *J*<sub>C-F</sub> = 9 Hz), 132.8, 132.6, 132.4, 129.8 (d, *J*<sub>C-F</sub> = 3 Hz), 128.0, 127.9, 127.1, 121.1, 119.6, 118.9, 118.2, 117.2, 116.5, 116.3, 114.7 (d, *J*<sub>C-F</sub> = 23Hz), 114.3 (d, *J*<sub>C-F</sub> = 22 Hz), 111.2 (d, *J*<sub>C-F</sub> = 23 Hz), 92.7, 92.6, 87.7, 87.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -111.0, -111.3; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>F [M+H]<sup>+</sup>: 199.0923, found: 199.0913.

### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-6-fluorobenzene (1i)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.45 g, 73% yield (*E/Z* = 1.5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15-7.27 (m, 2H), 6.98-7.11 (m, 1.6H), 6.83 (d, *J* = 16.0 Hz, 0.6H), 6.34-6.59 (m, 2H), 5.95-6.10 (m, 0.8H), 5.69-5.79 (m, 1H), 5.52-5.60 (m, 1H), 5.33-5.41 (m, 1H), 5.19-5.25 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8 (d, *J*<sub>C-F</sub> = 249 Hz), 158.3 (d, *J*<sub>C-F</sub> = 246 Hz), 138.3, 136.5, 136.3, 134.3, 134.2, 128.9 (d, *J*<sub>C-F</sub> = 3 Hz), 128.4 (d, *J*<sub>C-F</sub> = 9 Hz), 128.1 (d, *J*<sub>C-F</sub> = 3 Hz), 127.7 (d, *J*<sub>C-F</sub> = 10 Hz), 127.6, 127.5, 127.0 (d, *J*<sub>C-F</sub> = 17 Hz), 126.4 (d, *J*<sub>C-F</sub> = 13 Hz), 125.4, 124.9 (d, *J*<sub>C-F</sub> = 5 Hz), 124.0 (d, *J*<sub>C-F</sub> = 6 Hz), 122.0, 119.7, 119.2, 117.2, 116.2 (d, *J*<sub>C-F</sub> = 23 Hz), 115.8 (d, *J*<sub>C-F</sub> = 23 Hz), 93.8, 93.2, 88.1, 88.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.0, -112.9; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>F [M+H]<sup>+</sup>: 199.0923, found: 199.0912.

### 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)-4,5-difluorobenzene (1j)

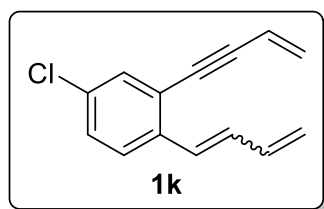


The title compound was prepared according to the **general procedure A** and purified by column chromatography to give

yellow oil, 1.40 g, 65% yield (*E/Z* = 1:1.5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 (dd, *J* = 11.6 Hz, 8.0 Hz, 0.4H), 7.16-

7.27 (m, 1.6H), 6.90 (d, *J* = 15.6 Hz, 0.4H), 6.66-6.75 (m, 1H), 6.50-6.58 (m, 1H), 6.35 (t, *J* = 11.4 Hz, 0.6H), 5.97-6.08 (m, 1H), 5.72-5.80 (m, 1H), 5.56-5.62 (m, 1H), 5.37-5.46 (m, 1H), 5.25-5.31 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.7 (dd, *J*<sub>C-F</sub> = 250 Hz, 13 Hz), 148.9 (dd, *J*<sub>C-F</sub> = 250 Hz, 13 Hz), 148.2 (dd, *J*<sub>C-F</sub> = 249 Hz, 14 Hz), 147.9 (dd, *J*<sub>C-F</sub> = 248 Hz, 13 Hz), 136.9, 136.4 (dd, *J*<sub>C-F</sub> = 6 Hz, 4 Hz), 136.2 (dd, *J*<sub>C-F</sub> = 6 Hz, 4 Hz), 132.5, 132.5, 132.2, 132.1, 128.9, 127.8, 127.0, 121.4, 121.1, 120.9, 120.8, 119.6, 119.4 (dd, *J*<sub>C-F</sub> = 8 Hz, 4 Hz), 118.5 (d, *J*<sub>C-F</sub> = 7 Hz), 118.2 (d, *J*<sub>C-F</sub> = 18 Hz), 116.9, 113.2 (d, *J*<sub>C-F</sub> = 18 Hz), 93.4, 93.4, 86.6, 86.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -135.3, -135.3, -135.8, -135.8, -138.3, -138.4, -138.8, -138.8; HRMS (ESI) calcd for C<sub>14</sub>H<sub>11</sub>F<sub>2</sub> [M+H]<sup>+</sup>: 217.0823, found: 217.0821.

#### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (1k)

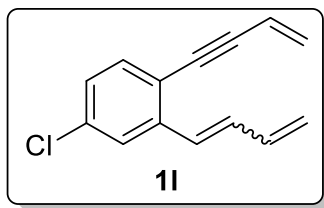


The title compound was prepared according to the **general procedure A** and purified by column chromatography to

give yellow oil, 1.65 g, 77% yield (*E/Z* = 1:6.1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56-7.65 (m, 1H), 7.36-7.47 (m, 2H),

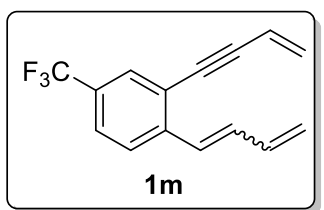
7.11 (d, *J* = 15.7 Hz, 0.14H), 6.83-7.00 (m, 1H), 6.77 (d, *J* = 11.5 Hz, 0.86H), 6.67-6.74 (m, 0.14H), 6.51 (t, *J* = 11.4 Hz, 0.86H), 6.15-6.26 (m, 1H), 5.88-5.96 (m, 1H), 5.71-5.78 (m, 1H), 5.52-5.59 (m, 1H), 5.39-5.43 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.6, 137.3, 137.1, 133.2, 132.9, 132.8, 132.7, 132.5, 132.3, 132.2, 132.0, 131.8, 130.6, 129.6, 128.8, 128.2, 127.9, 127.8, 125.9, 124.3, 123.4, 120.7, 119.0, 117.0, 94.0, 94.0, 87.4, 87.2; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>Cl [M+H]<sup>+</sup>: 215.0628, found: 215.0620.

#### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-5-chlorobenzene (1l)



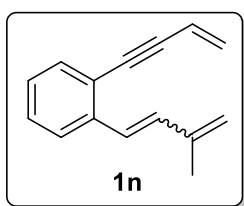
The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.69 g, 79% yield (*E/Z* = 1:1.9). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 2.0 Hz, 0.35H), 7.33-7.38 (m, 1.65H), 7.12-7.20 (m, 1H), 6.94 (d, *J* = 15.7 Hz, 0.35H), 6.69-6.86 (m, 1H), 6.60 (d, *J* = 11.5 Hz, 0.65H), 6.34-6.58 (m, 1H), 5.98-6.09 (m, 1H), 5.70-5.79 (m, 1H), 5.53-5.60 (m, 1H), 5.38-5.45 (m, 1H), 5.25-5.30 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.7, 140.2, 137.1, 134.6, 134.0, 133.9, 133.5, 132.8, 132.7, 132.5, 129.5, 129.4, 127.7, 127.4, 127.3, 124.8, 121.3, 121.2, 120.5, 119.6, 117.2, 93.8, 93.7, 87.7, 87.5; HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>Cl [M+H]<sup>+</sup>: 215.0628, found: 215.0629.

#### 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1m)



The title compound was prepared according to the **general procedure A** and purified by column chromatography to give yellow oil, 1.84 g, 74% yield (*E/Z* = 1:1.1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65-7.72 (m, 1.48H), 7.47-7.52 (m, 1.52H), 7.01 (d, *J* = 15.7 Hz, 0.48H), 6.88-6.95 (m, 0.52H), 6.67-6.77 (m, 1H), 6.40-6.63 (m, 1H), 6.00-6.11 (m, 1H), 5.75-5.83 (m, 1H), 5.58-5.64 (m, 1H), 5.42-5.47 (m, 1H), 5.29-5.31 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 142.4, 141.7, 137.1, 133.5, 133.3, 132.7, 129.9, 129.8 (d, *J*<sub>C-F</sub> = 4 Hz), 129.5, 129.3 (d, *J*<sub>C-F</sub> = 4 Hz), 129.2 (d, *J*<sub>C-F</sub> = 7 Hz), 128.1, 127.8, 125.1, 125.0, 124.5 (d, *J*<sub>C-F</sub> = 4 Hz), 123.5, 122.8, 122.5, 121.5, 120.6 (q, *J*<sub>C-F</sub> = 271 Hz), 120.2, 116.9, 116.9, 94.3, 94.2, 87.2, 87.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.8, -62.8; HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>F<sub>3</sub> [M+H]<sup>+</sup>: 249.0891, found: 249.0873.

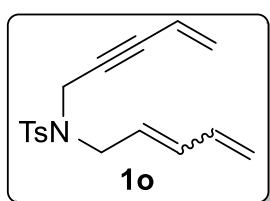
#### 1-(but-3-en-1-yn-1-yl)-2-(3-methylbuta-1,3-dien-1-yl)benzene (1n)



The title compound was prepared according to the **general procedure B** and purified by column chromatography to give yellow oil, 1.51 g, 78% yield (*E/Z* = 1:1.8). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56-7.77 (m, 2H), 7.34-7.49 (m, 2H), 7.22 (d, *J* = 15.7

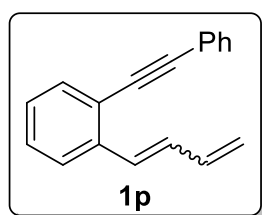
Hz, 0.36H), 6.93-7.09 (m, 1H), 6.89 (d,  $J = 11.4$  Hz, 0.64H), 6.71-6.80 (m, 0.36H), 6.54 (t,  $J = 11.4$  Hz, 0.64H), 5.54-5.61 (m, 2H), 5.48-5.51 (m, 1H), 5.40-5.43 (m, 1H), 2.18-2.22 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 138.4, 137.6, 133.4, 132.8, 132.4, 131.6, 131.2, 130.9, 129.5, 129.2, 128.5, 127.9, 127.3, 127.1, 127.0, 124.8, 122.8, 122.1, 122.0, 122.0, 118.4, 95.6, 95.5, 87.1, 87.0, 23.6; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{15}$   $[\text{M}+\text{H}]^+$ : 195.1174, found: 195.1172.

#### 4-methyl-*N*-(pent-4-en-2-yn-1-yl)-*N*-(penta-2,4-dien-1-yl)benzenesulfonamide (**1o**)



The title compound was prepared according to the **general procedure C** and purified by column chromatography to give yellow oil, 2.29 g, 76% yield ( $E/Z = 9:1$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.75 (m, 2H), 7.28-7.30 (m, 2H), 6.59-6.68 (m, 0.1H), 6.19-6.36 (m, 1.9H), 5.47-5.63 (m, 2H), 5.30-5.39 (m, 2H), 5.10-5.23 (m, 2H), 4.18 (d,  $J = 1.7$  Hz, 2H), 3.96 (d,  $J = 7.5$  Hz, 0.2H), 3.84 (d,  $J = 6.8$  Hz, 1.8H), 2.41-2.41 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 136.0, 135.9, 135.5, 134.5, 131.0, 129.5, 129.3, 127.9, 129.7, 127.4, 127.1, 124.6, 120.1, 118.4, 116.3, 84.4, 82.6, 82.6, 48.3, 43.4, 36.8, 36.7, 21.6; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 302.1215, found:302.1212.

#### 1-(buta-1,3-dien-1-yl)-2-(phenylethynyl)benzene (**1p**)

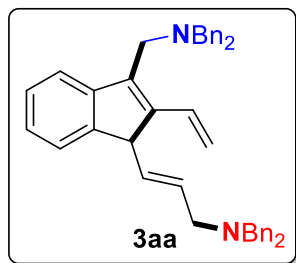


The title compound was prepared according to the **general procedure D** and purified by column chromatography to give yellow oil, 1.77 g, 77% yield ( $E/Z = 1:1.4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.57 (m, 3.42H), 7.38 (d,  $J = 7.6$  Hz, 0.58H), 7.26-7.35 (m, 3.42H), 7.14-7.24 (m, 2H), 6.76-6.91 (m, 1.58H), 6.53-6.62 (m, 0.42H), 6.37 (t,  $J = 11.4$  Hz, 0.58H), 5.34-5.41 (m, 1H), 5.19-5.23 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 138.6, 137.6, 133.4, 132.8, 132.4, 131.7, 131.7, 131.7, 131.4, 130.9, 129.6, 129.2, 128.6, 128.5, 128.5, 128.5, 128.4, 128.0, 127.4, 127.2, 124.8, 123.4, 122.8, 122.1, 120.1, 118.5, 94.4, 94.3, 88.2, 88.0; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}$   $[\text{M}+\text{H}]^+$ :231.1174, found: 231.1176.



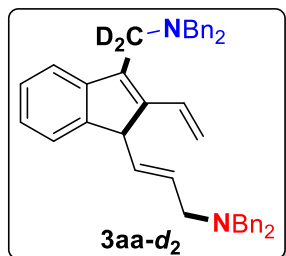
## 5. Products Characterization

### *(E)*-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl)-2-vinyl-1*H*-inden-1-yl)prop-2-en-1-amine (3aa)



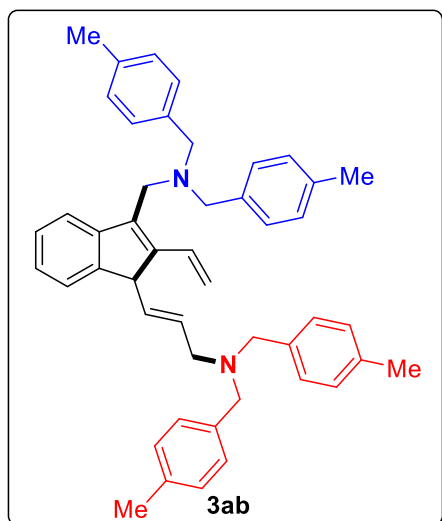
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 153.0 mg, 87% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 7.5$  Hz, 1H), 7.25-7.34 (m, 16H), 7.18-7.23 (m, 6H), 7.11-7.14 (m, 1H), 6.85 (dd,  $J = 17.6$  Hz, 11.2 Hz, 1H), 5.88-5.96 (m, 1H), 5.47 (dd,  $J = 17.2$  Hz, 1.2 Hz, 1H), 5.15-5.22 (m, 2H), 4.19 (d,  $J = 9.2$  Hz, 1H), 3.51-3.59 (m, 10H), 2.96-3.06 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.0, 144.9, 144.7, 139.8, 139.6, 138.6, 134.0, 130.3, 129.7, 129.4, 129.0, 128.3, 127.1, 126.9, 125.8, 123.6, 121.2, 116.8, 59.0, 57.7, 55.3, 52.7, 49.2; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{43}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 587.3426, found: 587.3431.

### *(E)*-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl- $d_2$ )-2-vinyl-1*H*-inden-1-yl)prop-2-en-1-amine (3aa- $d_2$ )



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 137.7 mg, 78% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.6$  Hz, 1H), 7.18-7.34 (m, 22H), 7.11-7.14 (m, 1H), 6.84 (dd,  $J = 17.6$  Hz, 11.2 Hz, 1H), 5.89-5.96 (m, 1H), 5.47 (dd,  $J = 17.2$  Hz, 1.2 Hz, 1H), 5.15-5.21 (m, 2H), 4.19 (d,  $J = 9.2$  Hz, 1H), 3.51-3.58 (m, 8H), 2.96-3.06 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.0, 144.9, 144.7, 139.8, 139.6, 138.5, 134.0, 130.3, 129.7, 129.4, 129.0, 128.3, 127.1, 126.9, 125.7, 123.6, 121.2, 116.8, 58.9, 57.7, 55.3, 52.7; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{41}\text{D}_2\text{N}_2$   $[\text{M}+\text{H}]^+$ : 589.3552, found: 589.3547.

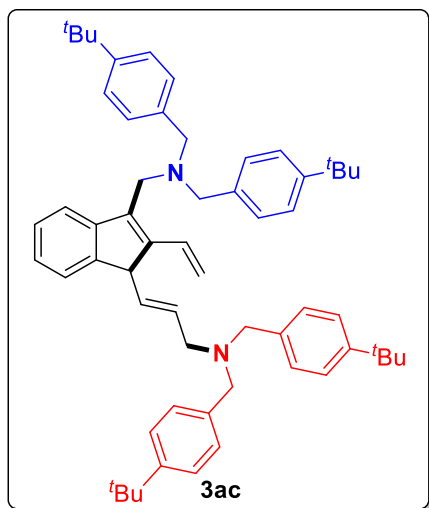
### *(E)*-3-(3-((bis(4-methylbenzyl)amino)methyl)-2-vinyl-1*H*-inden-1-yl)-*N,N*-bis(4-methylbenzyl)prop-2-en-1-amine (3ab)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 152.3 mg, 79% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 7.6 Hz, 1H), 7.20 (d,  $J$  = 7.6 Hz, 10H), 7.06-7.14 (m, 9H), 6.85 (dd,  $J$  = 17.6 Hz, 11.2 Hz, 1H), 5.88-5.95 (m, 1H), 5.46 (dd,  $J$  = 17.2 Hz, 1.6 Hz, 1H), 5.13-5.19 (m, 2H), 4.18 (d,  $J$  = 9.2 Hz, 1H), 3.43-3.54 (m, 10H), 2.94-3.04 (m, 2H), 2.31 (s,

6H), 2.31 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 144.8, 144.7, 138.8, 136.7, 136.5, 136.5, 136.4, 134.0, 130.4, 129.8, 129.3, 129.0, 126.8, 125.7, 123.6, 121.3, 116.6, 58.5, 57.3, 55.1, 52.8, 49.1, 21.3, 21.2; HRMS (ESI) calcd for  $\text{C}_{47}\text{H}_{51}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 643.4052, found: 643.4048.

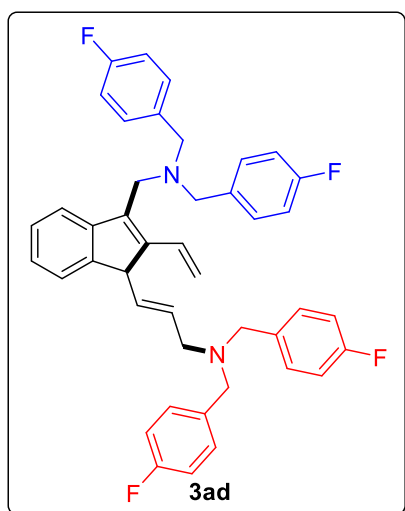
**(*E*)-3-(3-((bis(4-(*tert*-butyl)benzyl)amino)methyl)-2-vinyl-1*H*-inden-1-yl)-*N,N*-bis(4-(*tert*-butyl)benzyl)prop-2-en-1-amine (3ac)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 194.5 mg, 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J$  = 7.5 Hz, 1H), 7.27-7.32 (m, 16H), 7.20-7.23 (m, 2H), 7.11-7.14 (m, 1H), 6.87 (dd,  $J$  = 17.5 Hz, 11.1 Hz, 1H), 5.91-5.98 (m, 1H), 5.48 (dd,  $J$  = 17.6 Hz, 1.2 Hz, 1H), 5.17-5.23 (m, 2H), 4.18 (d,  $J$  = 9.1 Hz, 1H), 3.46-3.56 (m, 10H), 2.98-3.08 (m, 2H), 1.29-

1.30 (m, 36H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 149.6, 146.1, 144.8, 144.7, 138.8, 136.8, 136.6, 133.9, 130.6, 129.8, 129.0, 128.6, 126.8, 125.7, 125.1, 125.1, 123.6, 121.4, 116.7, 58.5, 57.3, 55.4, 52.8, 49.4, 34.6, 34.6, 31.6; HRMS (ESI) calcd for  $\text{C}_{59}\text{H}_{75}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 811.5930, found: 811.5936.

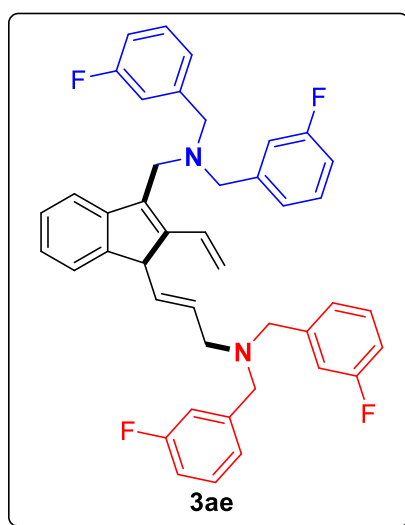
**(E)-3-(3-((bis(4-fluorobenzyl)amino)methyl)-2-vinyl-1H-inden-1-yl)-N,N-bis(4-fluorobenzyl)prop-2-en-1-amine (3ad)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 160.0 mg, 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.46 (m, 5H), 7.11-7.23 (m, 7H), 7.04-7.08 (m, 4H), 6.95-7.01 (m, 4H), 6.84 (dd, *J* = 17.6 Hz, 11.0 Hz, 1H), 5.90-5.97 (m, 1H), 5.46 (dd, *J* = 17.6 Hz, 1.4 Hz, 1H), 5.17-5.25 (m, 2H), 4.19 (d, *J* = 9.1 Hz, 1H), 3.62-3.65 (m, 10H), 3.01-3.11 (m, 2H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>) δ 160.3 (d, *J*<sub>C-F</sub> = 245 Hz), 160.3 (d, *J*<sub>C-F</sub> = 245 Hz), 145.9, 144.6 (d, *J*<sub>C-F</sub> = 29 Hz), 138.3, 134.2, 131.8 (d, *J*<sub>C-F</sub> = 4 Hz), 131.1 (d, *J*<sub>C-F</sub> = 5 Hz), 130.1, 129.5, 128.7 (d, *J*<sub>C-F</sub> = 8 Hz), 128.4 (d, *J*<sub>C-F</sub> = 8 Hz), 126.9, 126.3 (d, *J*<sub>C-F</sub> = 14 Hz), 126.0 (d, *J*<sub>C-F</sub> = 14 Hz), 125.8, 124.0 (d, *J*<sub>C-F</sub> = 3 Hz), 121.1, 116.9, 115.1 (d, *J*<sub>C-F</sub> = 22 Hz), 55.7, 52.7, 51.3, 50.4, 49.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.2, -118.3; HRMS (ESI) calcd for C<sub>43</sub>H<sub>39</sub>F<sub>4</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 659.3049, found: 659.3047.

**(E)-3-(3-((bis(3-fluorobenzyl)amino)methyl)-2-vinyl-1H-inden-1-yl)-N,N-bis(3-fluorobenzyl)prop-2-en-1-amine (3ae)**

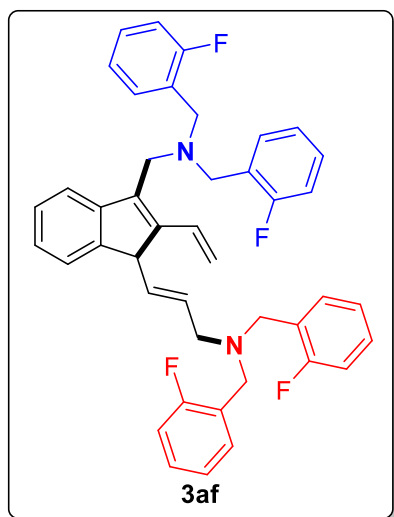


The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 159.6 mg, 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 7.5 Hz, 1H), 7.20-7.29 (m, 6H), 7.13-7.17 (m, 1H), 7.03-7.10 (m, 8H), 6.82-6.94 (m, 5H), 5.85-5.93 (m, 1H), 5.46 (dd, *J* = 17.6 Hz, 1.4 Hz, 1H), 5.16-5.23 (m, 2H), 4.19 (d, *J* = 9.0 Hz, 1H), 3.49-3.57 (m, 10H), 2.95-3.06 (m, 2H); <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>) δ 161.9 (d, *J*<sub>C-F</sub> = 244 Hz), 161.8 (d, *J*<sub>C-F</sub> = 244 Hz), 145.8, 145.1, 144.5, 142.4

(d,  $J_{C-F} = 7$  Hz), 142.0 (d,  $J_{C-F} = 7$  Hz), 138.1, 134.4, 129.8 (d,  $J_{C-F} = 6$  Hz), 129.7 (d,  $J_{C-F} = 5$  Hz), 129.7, 129.5, 127.1, 126.0, 124.8 (d,  $J_{C-F} = 2$  Hz), 124.3 (d,  $J_{C-F} = 3$  Hz), 123.7, 120.9, 117.1, 115.9 (d,  $J_{C-F} = 21$  Hz), 115.4 (d,  $J_{C-F} = 21$  Hz), 114.0 (d,  $J_{C-F} = 21$  Hz), 113.8, 58.6 (d,  $J_{C-F} = 2$  Hz), 57.3 (d,  $J_{C-F} = 2$  Hz), 55.4, 52.6, 49.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.5, -113.6; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{39}\text{F}_4\text{N}_2$   $[\text{M}+\text{H}]^+$ : 659.3049, found: 659.3043.

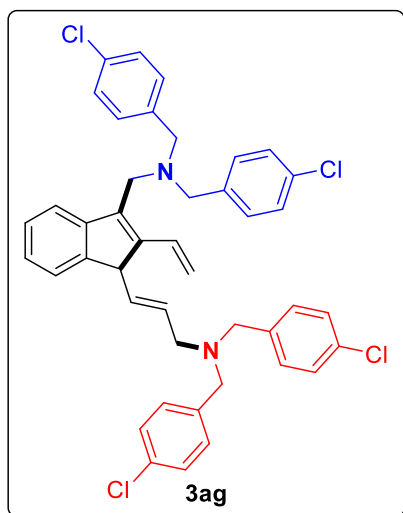
**(*E*)-3-(3-((bis(2-fluorobenzyl)amino)methyl)-2-vinyl-1*H*-inden-1-yl)-*N,N*-bis(2-fluorobenzyl)prop-2-en-1-amine (3af)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 150.2 mg, 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 7.5$  Hz, 1H), 7.21-7.27 (m, 10H), 7.13-7.17 (m, 1H), 6.93-7.00 (m, 8H), 6.81 (dd,  $J = 17.1$  Hz, 11.2 Hz, 1H), 5.84-5.91 (m, 1H), 5.45 (dd,  $J = 17.6$  Hz, 1.5 Hz, 1H), 5.15-5.21 (m, 2H), 4.19 (d,  $J = 9.0$  Hz, 1H), 3.53 (s, 2H), 3.44-3.49 (m, 8H), 2.93-3.03 (m, 2H);  $^{13}\text{C}$

NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9 (d,  $J_{C-F} = 244$  Hz), 160.8 (d,  $J_{C-F} = 243$  Hz), 145.9, 144.9, 144.6, 138.4, 135.3, 135.1, 135.1, 130.8, 130.7, 130.3, 130.3, 130.0, 129.6, 127.0, 125.9, 123.7, 121.0, 116.9, 115.0 (d,  $J_{C-F} = 21$  Hz), 115.0 (d,  $J_{C-F} = 21$  Hz), 58.1, 56.9, 55.1, 52.6, 49.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.8, -116.1; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{39}\text{F}_4\text{N}_2$   $[\text{M}+\text{H}]^+$ : 659.3049, found: 659.3054.

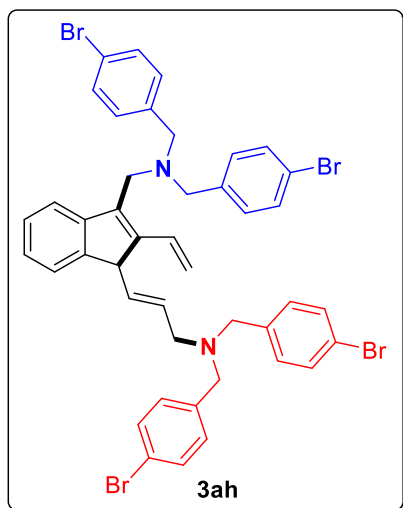
**(*E*)-3-(3-((bis(4-chlorobenzyl)amino)methyl)-2-vinyl-1*H*-inden-1-yl)-*N,N*-bis(4-chlorobenzyl)prop-2-en-1-amine (3ag)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 141.2 mg, 65% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 7.6$  Hz, 1H), 7.19-7.27 (m, 18H), 7.15-7.17 (m, 1H), 6.80 (dd,  $J = 17.2$  Hz, 10.8 Hz, 1H), 5.82-5.92 (m, 1H), 5.44 (dd,  $J = 17.6$  Hz, 1.6 Hz, 1H), 5.13-5.21 (m, 2H), 4.18 (d,  $J = 8.8$  Hz, 1H), 3.44-3.53 (m, 10H), 2.92-3.02 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$

145.9, 145.0, 144.5, 138.2, 138.1, 137.8, 134.3, 132.9, 132.7, 130.6, 130.1, 129.8, 129.5, 128.5, 127.1, 126.0, 123.7, 120.9, 117.0, 58.3, 57.0, 55.2, 52.6, 49.2; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{39}\text{Cl}_4\text{N}_2$   $[\text{M}+\text{H}]^+$ : 723.1867, found: 723.1865.

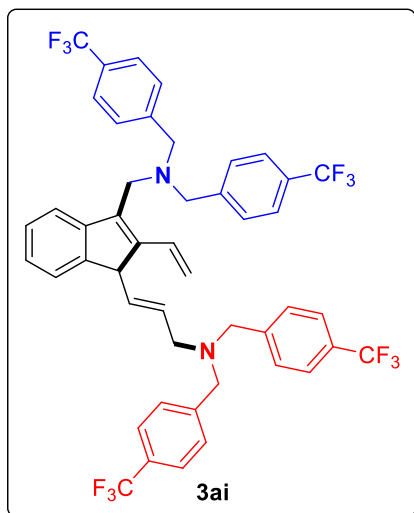
**(E)-3-(3-((bis(4-bromobenzyl)amino)methyl)-2-vinyl-1H-inden-1-yl)-N,N-bis(4-bromobenzyl)prop-2-en-1-amine (3ah)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 205.8 mg, 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.41 (m, 9H), 7.13-7.26 (m, 11H), 6.80 (dd,  $J = 17.6$  Hz, 11.1 Hz, 1H), 5.81-5.88 (m, 1H), 5.44 (dd,  $J = 17.5$  Hz, 1.2 Hz, 1H), 5.12-5.21 (m, 2H), 4.17 (d,  $J = 9.1$  Hz, 1H), 3.42-3.53 (m, 10H), 2.92-3.02 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 145.0, 144.4,

138.6, 138.3, 138.1, 134.3, 131.4, 130.9, 130.6, 130.5, 129.7, 129.5, 127.0, 126.0, 123.7, 121.0, 120.9, 120.8, 117.0, 58.3, 57.0, 55.1, 52.6, 49.2; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{38}\text{Br}_4\text{N}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 920.9661, found: 920.9645.

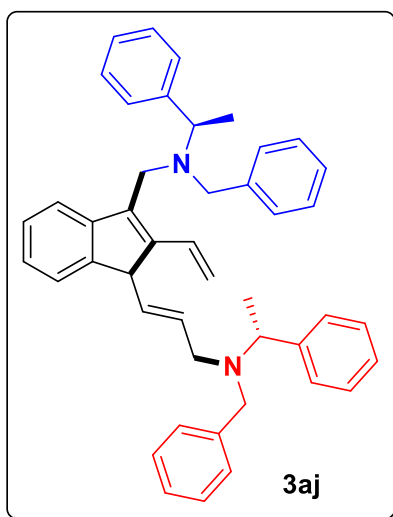
**(E)-3-(3-((bis(4-(trifluoromethyl)benzyl)amino)methyl)-2-vinyl-1H-inden-1-yl)-N,N-bis(4-(trifluoromethyl)benzyl)prop-2-en-1-amine (3ai)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 233.8 mg, 91% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.54 (m, 8H), 7.41-7.44 (m, 9H), 7.24-7.29 (m, 1H), 7.14-7.21 (m, 2H), 6.82 (dd,  $J = 17.6$  Hz, 11.2 Hz, 1H), 5.86-5.93 (m, 1H), 5.46 (dd,  $J = 17.6$  Hz, 1.2 Hz, 1H), 5.16-5.23 (m, 2H), 4.18 (d,  $J = 8.8$  Hz, 1H), 3.55-3.63 (m, 10H), 2.96-3.07 (m, 2H);  $^{13}\text{C}$  NMR

(100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 145.2, 144.4, 143.7, 143.4, 138.0, 134.5, 129.5, 129.4, 129.2 (q,  $J_{\text{C-F}} = 32$  Hz), 128.9, 127.1, 126.1, 125.3 (q,  $J_{\text{C-F}} = 4$  Hz), 125.3 (q,  $J_{\text{C-F}} = 4$  Hz), 123.8, 123.0 (q,  $J_{\text{C-F}} = 271$  Hz), 123.0 (q,  $J_{\text{C-F}} = 271$  Hz), 120.9, 117.2, 58.8, 57.4, 55.5, 52.6, 49.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4; HRMS (ESI) calcd for  $\text{C}_{47}\text{H}_{39}\text{F}_{12}\text{N}_2$   $[\text{M}+\text{H}]^+$ :859.2922, found: 859.2924.

**(E)-N-benzyl-3-(3-((benzyl((R)-1-phenylethyl)amino)methyl)-2-vinyl-1H-inden-1-yl)-N-((R)-1-phenylethyl)prop-2-en-1-amine (3aj)**

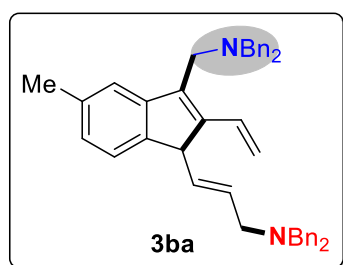


The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 143.7 mg, 78% yield, 3:2 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.33 (m, 3H), 7.10-7.25 (m, 20H), 7.01-7.05 (m, 1H), 6.69-6.78 (m, 1H), 5.77-5.81 (m, 1H), 5.36 (d,  $J = 17.5$  Hz, 1H), 5.04-5.10 (m, 2H), 4.07-4.10 (m, 1H), 3.84-3.91 (m, 2H), 3.60-3.63 (m, 1H), 3.35-3.51 (m, 5H), 2.96-3.06 (m, 1H), 2.82-2.91 (m, 1H), 1.39 (d,  $J$

$= 6.9$  Hz, 3H), 1.27 (d,  $J = 6.8$  Hz, 1.8H), 1.24 (d,  $J = 6.8$  Hz, 1.2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  146.1, 146.1, 144.8, 144.8, 144.7, 144.1, 143.9, 142.3, 142.3, 140.8, 140.8, 140.4, 140.4, 138.8, 138.7, 133.5, 130.7, 129.7, 129.6, 129.3, 129.2, 128.7, 128.6, 128.6, 128.2, 128.2, 128.2, 128.0, 127.9, 127.9, 126.9, 126.9, 126.8, 126.8, 126.7, 126.7,

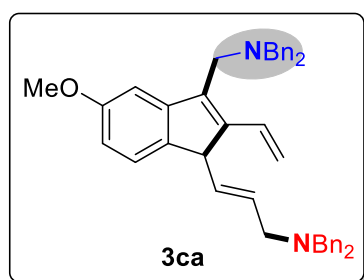
125.7, 125.6, 123.6, 123.5, 121.3, 121.2, 116.6, 116.6, 57.7, 57.6, 56.9, 56.8, 54.2, 54.1, 53.5, 53.5, 52.7, 52.7, 51.3, 51.3, 44.6, 44.5, 16.2, 15.6, 12.9, 12.8; HRMS (ESI) calcd for C<sub>45</sub>H<sub>47</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 615.3739, found: 615.3747.

**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methyl-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ba)**



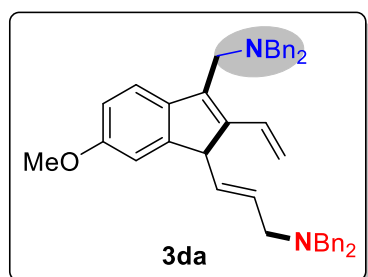
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 140.1 mg, 78% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17-7.34 (m, 21H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 17.4 Hz, 11.0 Hz, 1H), 5.86-5.93 (m, 1H), 5.45 (dd, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.15-5.21 (m, 2H), 4.16 (d, *J* = 9.1 Hz, 1H), 3.52-3.54 (m, 10H), 2.95-3.05 (m, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.1, 144.9, 143.1, 139.8, 139.7, 138.5, 136.4, 134.3, 130.0, 129.7, 129.5, 129.0, 128.3, 127.1, 126.9, 126.5, 123.2, 121.9, 116.5, 58.9, 57.7, 55.3, 52.4, 48.9, 21.6; HRMS (ESI) calcd for C<sub>44</sub>H<sub>45</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 601.3583, found: 601.3582.

**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methoxy-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ca)**



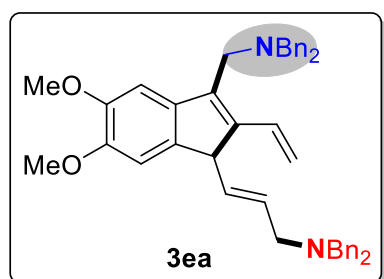
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 149.9 mg, 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.34 (m, 8H), 7.25-7.30 (m, 8H), 7.20-7.23 (m, 4H), 7.04-7.09 (m, 2H), 6.84 (dd, *J* = 17.5 Hz, 11.2 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 5.86-5.93 (m, 1H), 5.47 (d, *J* = 17.5 Hz, 1H), 5.13-5.19 (m, 2H), 4.14 (d, *J* = 9.1 Hz, 1H), 3.80 (s, 3H), 3.50-3.58 (m, 10H), 2.95-3.06 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 146.1, 146.0, 139.8, 139.7, 138.4, 138.2, 134.4, 129.9, 129.5, 129.4, 129.0, 128.3, 128.3, 127.1, 126.9, 124.0, 116.9, 112.7, 106.0, 59.0, 57.7, 55.7, 55.3, 52.1, 49.2; HRMS (ESI) calcd for C<sub>44</sub>H<sub>45</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 617.3532, found: 617.3536.

**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-6-methoxy-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3da)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 136.9 mg, 74% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.38 (m, 9H), 7.24-7.30 (m, 8H), 7.16-7.22 (m, 4H), 6.78-6.89 (m, 3H), 5.88-5.95 (m, 1H), 5.40 (d,  $J = 17.4$  Hz, 1H), 5.18 (dd,  $J = 15.2$  Hz, 9.2 Hz, 1H), 5.10 (d,  $J = 11.2$  Hz, 1H), 4.16 (d,  $J = 9.1$  Hz, 1H), 3.65 (s, 3H), 3.50-3.55 (m, 10H), 2.96-3.05 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 148.0, 142.9, 139.8, 139.6, 138.4, 137.7, 134.4, 130.3, 129.7, 129.4, 128.9, 128.3, 127.1, 126.9, 121.8, 115.4, 112.9, 109.5, 58.9, 57.7, 55.5, 55.2, 52.7, 49.3; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{45}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 617.3532, found: 617.3533.

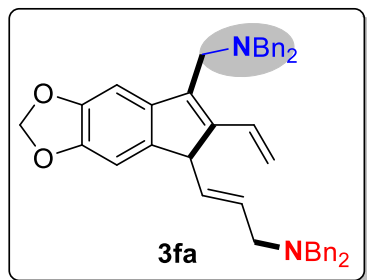
**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5,6-dimethoxy-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ea)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 141.9 mg, 73% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.36 (m, 8H), 7.18-7.29 (m, 12H), 7.05 (s, 1H), 6.82 (dd,  $J = 17.5$  Hz, 11.1 Hz, 1H), 6.76 (s, 1H), 5.88-5.95 (m, 1H), 5.41 (d,  $J = 17.4$  Hz, 1H), 5.10-5.20 (m, 2H), 4.14 (d,  $J = 9.2$  Hz, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 3.49-3.60 (m, 10H), 2.96-3.06 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 148.0, 143.8, 139.8, 139.8, 138.5, 138.4, 137.1, 134.8, 130.2, 129.4, 129.4, 128.8, 128.4, 128.3, 127.1, 126.9, 115.3, 107.0, 104.9, 58.9, 57.6, 56.3, 55.9, 55.2, 52.7, 49.3; HRMS (ESI) calcd for  $\text{C}_{45}\text{H}_{47}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 647.3638, found: 647.3636.

**(E)-N,N-dibenzyl-3-(7-((dibenzylamino)methyl)-6-vinyl-5H-indeno[5,6-d][1,3]dioxol-5-yl)prop-2-en-1-amine (3fa)**

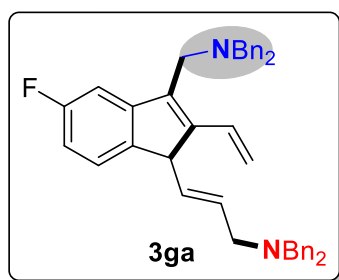




The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 145.6 mg, 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18-7.34 (m, 20H), 6.93 (s, 1H), 6.78 (dd,  $J = 17.5$  Hz, 11.1 Hz, 1H),

6.70 (s, 1H), 5.84-5.96 (m, 3H), 5.39 (d,  $J = 17.5$  Hz, 1H), 5.09-5.18 (m, 2H), 4.07 (d,  $J = 9.1$  Hz, 1H), 3.47-3.66 (m, 10H), 2.94-3.08 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 146.5, 144.1, 140.2, 139.8, 139.5, 138.6, 138.3, 134.1, 130.2, 129.4, 128.9, 128.3, 128.3, 127.1, 126.9, 115.5, 105.0, 102.2, 101.0, 58.9, 57.7, 55.2, 52.4, 49.2; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{43}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 631.3325, found: 631.3330.

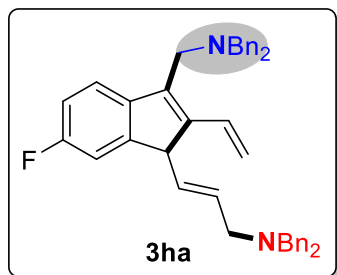
**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5-fluoro-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ga)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 155.7 mg, 86% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.33 (m, 15H), 7.18-7.25 (m, 5H), 7.07-7.13 (m, 2H), 6.77-6.88 (m, 2H), 5.86-5.93 (m, 1H), 5.48

(d,  $J = 17.4$  Hz, 1H), 5.12-5.22 (m, 2H), 4.13 (d,  $J = 9.2$  Hz, 1H), 3.50-3.58 (m, 10H), 2.95-3.06 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8 (d,  $J_{\text{C-F}} = 240$  Hz), 146.7, 146.5 (d,  $J_{\text{C-F}} = 9$  Hz), 141.2, 141.2, 139.8, 139.4, 137.9 (d,  $J_{\text{C-F}} = 3$  Hz), 133.6, 130.5, 129.4, 128.9, 128.4, 128.3, 127.2, 126.9, 124.2 (d,  $J_{\text{C-F}} = 9$  Hz), 117.6, 112.3 (d,  $J_{\text{C-F}} = 23$  Hz), 108.3 (d,  $J_{\text{C-F}} = 23$  Hz), 59.0, 57.8, 55.2, 52.1, 49.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.4; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{42}\text{FN}_2$   $[\text{M}+\text{H}]^+$ : 605.3332, found: 605.3329.

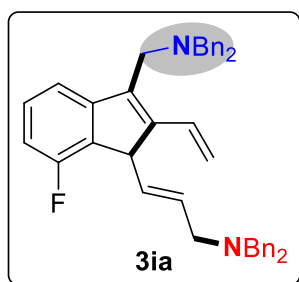
**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-6-fluoro-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ha)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 119.6 mg, 66% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.37 (m, 17H), 7.18-7.23 (m, 4H), 6.81-6.94 (m, 3H), 5.86-5.93 (m, 1H), 5.43 (d,  $J = 17.5$  Hz, 1H),

5.15-5.21 (m, 2H), 4.15 (d,  $J = 9.0$  Hz, 1H), 3.49-3.61 (m, 10H), 2.95-3.09 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1 (d,  $J_{\text{C-F}} = 243$  Hz), 148.2 (d,  $J_{\text{C-F}} = 8$  Hz), 144.5 (d,  $J_{\text{C-F}} = 4$  Hz), 140.5, 140.5, 139.7, 139.5, 137.8, 133.3, 130.8, 129.4, 128.9, 128.3, 128.3, 127.2, 126.9, 122.0 (d,  $J_{\text{C-F}} = 8$  Hz), 116.7, 113.7 (d,  $J_{\text{C-F}} = 23$  Hz), 111.1 (d,  $J_{\text{C-F}} = 23$  Hz), 59.0, 57.8, 55.2, 52.7, 52.7, 49.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.8; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{42}\text{FN}_2$   $[\text{M}+\text{H}]^+$ : 605.3332, found: 605.3332.

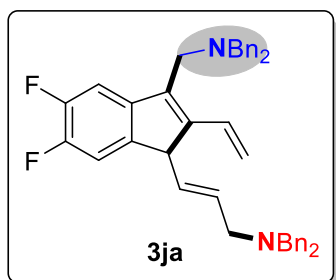
**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-7-fluoro-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ia)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 159.3 mg, 88% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17-7.33 (m, 22H), 6.78-6.88 (m, 2H), 5.84-5.91 (m, 1H), 5.46 (d,  $J = 17.1$  Hz, 1H), 5.23-5.31 (m, 2H), 4.39 (d,  $J = 8.6$

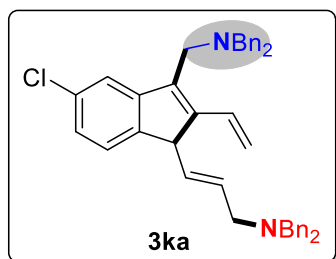
Hz, 1H), 3.46-3.55 (m, 10H), 2.98 (d,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8 (d,  $J_{\text{C-F}} = 246$  Hz), 147.8 (d,  $J_{\text{C-F}} = 6$  Hz), 145.8, 139.8, 139.5, 138.1 (d,  $J_{\text{C-F}} = 3$  Hz), 131.3, 130.8 (d,  $J_{\text{C-F}} = 16$  Hz), 130.7, 129.4, 129.0, 129.0, 128.9, 128.3, 128.2, 127.2, 126.8, 117.8, 117.4 (d,  $J_{\text{C-F}} = 3$  Hz), 112.9 (d,  $J_{\text{C-F}} = 20$  Hz), 58.9, 57.6, 55.2, 50.0, 49.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.8; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{42}\text{FN}_2$   $[\text{M}+\text{H}]^+$ : 605.3332, found: 605.3337.

**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5,6-difluoro-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ja)**



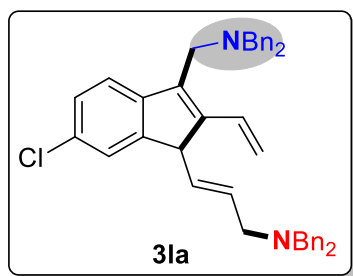
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 100.8 mg, 54% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.33 (m, 15H), 7.16-7.25 (m, 6H), 6.94 (dd,  $J = 9.7$  Hz, 7.4 Hz, 1H), 6.79 (dd,  $J = 17.6$  Hz, 11.1 Hz, 1H), 5.85-5.92 (m, 1H), 5.45 (dd,  $J = 17.5$  Hz, 1.1 Hz, 1H), 5.11-5.22 (m, 2H), 4.11 (d,  $J = 9.1$  Hz, 1H), 3.57 (d,  $J = 13.6$  Hz, 2H), 3.48-3.51 (m, 8H), 2.95-3.08 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1 (dd,  $J_{\text{C-F}} = 243$  Hz, 13 Hz), 148.4 (dd,  $J_{\text{C-F}} = 245$  Hz, 14 Hz), 145.9 (d,  $J_{\text{C-F}} = 4$  Hz), 141.8, 140.7 (d,  $J_{\text{C-F}} = 5$  Hz), 139.7, 139.3, 137.3, 132.9, 131.1, 129.4, 129.1, 128.9, 128.4, 128.3, 127.3, 127.0, 117.5, 112.5 (d,  $J_{\text{C-F}} = 19$  Hz), 109.8 (d,  $J_{\text{C-F}} = 19$  Hz), 59.0, 57.8, 55.2, 52.5, 49.1;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -140.4, -140.4, -141.2, -141.2; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{41}\text{F}_2\text{N}_2$   $[\text{M}+\text{H}]^+$ : 623.3238, found:623.3229.

**(E)-N,N-dibenzyl-3-(5-chloro-3-((dibenzylamino)methyl)-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3ka)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 107.9 mg, 58% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (s, 1H), 7.18-7.32 (m, 20H), 7.07 (s, 2H), 6.81 (dd,  $J = 17.3$  Hz, 11.1 Hz, 1H), 5.85-5.92 (m, 1H), 5.47 (d,  $J = 17.6$  Hz, 1H), 5.11-5.23 (m, 2H), 4.14 (d,  $J = 9.0$  Hz, 1H), 3.51-3.58 (m, 10H), 2.95-3.05 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 146.3, 144.1, 139.7, 139.4, 137.7, 133.3, 132.9, 130.8, 129.4, 129.3, 128.9, 128.4, 128.3, 127.2, 126.9, 125.6, 124.4, 121.5, 117.7, 59.0, 57.8, 55.2, 52.3, 48.9; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{42}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 621.3037, found:621.3034.

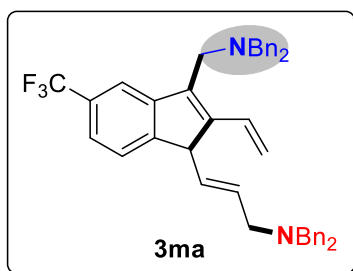
**(E)-N,N-dibenzyl-3-(6-chloro-3-((dibenzylamino)methyl)-2-vinyl-1H-inden-1-yl)prop-2-en-1-amine (3la)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 111.2 mg, 60% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.33 (m, 17H), 7.17-7.24 (m, 6H), 6.82 (dd,  $J = 17.6$  Hz, 11.2 Hz, 1H), 5.87-5.93 (m, 1H), 5.47 (d,  $J = 17.5$  Hz, 1H), 5.13-5.21 (m, 2H), 4.15 (d,  $J = 9.1$  Hz, 1H), 3.48-3.62 (m, 10H), 2.94-3.10 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.7, 145.1, 143.1, 139.7, 139.4, 137.9, 133.0, 131.7, 130.9, 129.4, 129.3, 128.9, 128.3, 128.3, 127.2, 127.1, 126.9, 124.0, 122.1, 117.3, 59.0, 57.8, 55.2, 52.6, 49.1; HRMS (ESI) calcd for  $\text{C}_{43}\text{H}_{42}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 621.3037, found: 621.3031.

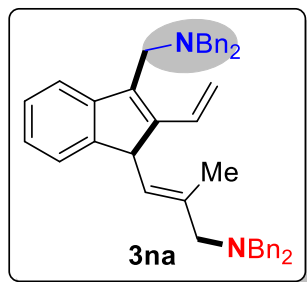
**(*E*)-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl)-5-(trifluoromethyl)-2-vinyl-1*H*-inden-1-yl)prop-2-en-1-amine (3ma)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 60.6 mg, 31% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.27-7.38 (m, 18H), 7.19-7.23 (m, 4H), 6.83 (dd,  $J = 17.5$  Hz, 11.1 Hz, 1H), 5.89-5.96 (m, 1H), 5.50 (dd,  $J = 17.6$  Hz, 1.2 Hz, 1H), 5.24 (dd,  $J = 11.2$  Hz, 1.0 Hz, 1H), 5.13 (dd,  $J = 15.3$  Hz, 9.1 Hz, 1H), 4.21 (d,  $J = 9.1$  Hz, 1H), 3.51-3.58 (m, 10H), 2.96-3.07 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 146.2, 145.1, 139.7, 139.4, 137.8, 132.7, 131.4, 129.3, 129.1, 129.1 (q,  $J_{\text{C-F}} = 32$  Hz), 128.9, 128.4, 128.3, 127.3, 127.0, 123.8 (q,  $J_{\text{C-F}} = 271$  Hz), 123.6, 122.5 (d,  $J_{\text{C-F}} = 4$  Hz), 118.7 (d,  $J_{\text{C-F}} = 4$  Hz), 118.1, 59.1, 57.8, 55.3, 52.8, 49.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.7; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{42}\text{F}_3\text{N}_2$   $[\text{M}+\text{H}]^+$ : 655.3300, found: 655.3297.

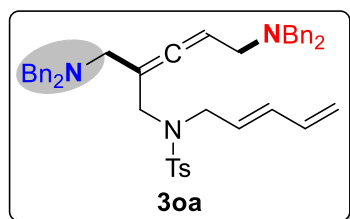
**(*E*)-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl)-2-vinyl-1*H*-inden-1-yl)prop-2-en-1-amine (3na)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 129.9 mg, 72% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.5$  Hz, 1H), 7.27-7.36 (m, 16H), 7.19-7.23 (m, 5H), 7.06-7.13 (m, 2H), 6.81 (dd,  $J = 17.5$  Hz, 11.0 Hz, 1H),

5.24 (d,  $J = 17.5$  Hz, 1H), 5.07 (d,  $J = 11.9$  Hz, 1H), 4.90 (d,  $J = 10.0$  Hz, 1H), 4.45 (d,  $J = 10.0$  Hz, 1H), 3.41-3.54 (m, 10H), 2.86-2.92 (m, 2H), 2.04 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 145.9, 144.9, 140.1, 139.6, 138.5, 135.4, 129.7, 129.4, 128.9, 128.6, 128.3, 127.1, 126.9, 126.7, 125.7, 123.3, 121.1, 116.1, 62.5, 58.9, 57.9, 49.3, 48.5, 15.8; HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{45}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 601.3583, found: 601.3589.

**(*E*)-*N*-(5-(dibenzylamino)-2-((dibenzylamino)methyl)penta-2,3-dien-1-yl)-4-methyl-*N*-(penta-2,4-dien-1-yl)benzenesulfonamide (3oa)**

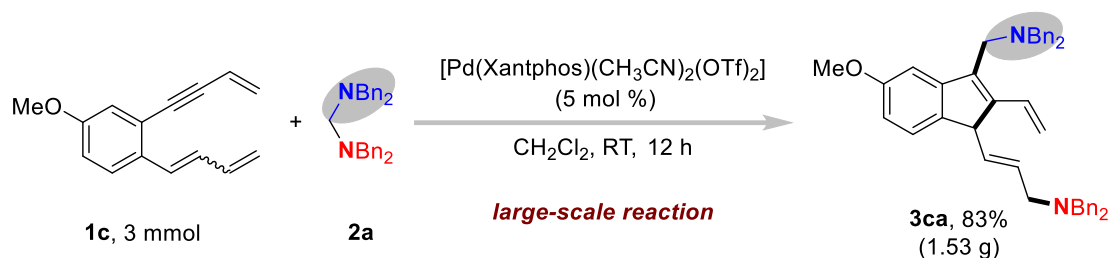


The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 123.1 mg, 58% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59-7.61 (m, 2H), 7.26-7.33 (m, 16H), 7.16-7.23 (m, 6H), 6.06-6.16 (m, 1H), 5.89 (dd,  $J = 15.2$  Hz, 10.4 Hz, 1H), 5.31-5.38 (m, 1H), 5.13-5.14 (m, 1H), 4.99-5.04 (m, 2H), 3.65-3.87 (m, 4H), 3.44-3.62 (m, 8H), 2.89-3.09 (m, 4H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.4, 143.1, 139.5, 139.2, 137.5, 135.9, 134.6, 129.6, 128.9, 128.8, 128.4, 128.0, 127.4, 127.0, 127.0, 117.9, 98.4, 90.4, 57.8, 57.7, 54.7, 52.5, 49.1, 47.6, 21.6; HRMS (ESI) calcd for  $\text{C}_{46}\text{H}_{50}\text{N}_3\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 708.3624, found: 708.3624.

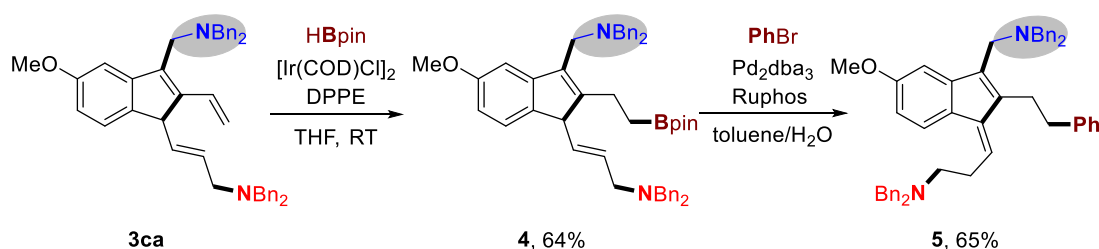
## 6. Synthetic Transformation of Products

### Gram-scale synthesis of 3ca



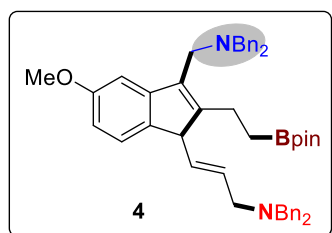
*N,N,N',N'*-tetrabenzylmethanediamine **2a** (1.46 g, 3.6 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (160.0 mg, 0.15 mmol), 2-(but-3-en-1-yn-1-yl)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene **1c** (0.63 g, 3 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added to a 100 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3ca** (1.53 g, 83% yield).

### Synthetic utility of the product



[IrCl(COD)]<sub>2</sub> (10.1 mg, 5 mol%), 1,2-bis(diphenylphosphino)ethane (DPPE) (12.0 mg, 10 mol%) and THF (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The mixture was stirred for 10 minutes at room temperature. HBpin (87.1 μL, 0.6 mmol) and (*E*)-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methoxy-2-vinyl-1*H*-inden-1-yl)prop-2-en-1-amine **3ca** (184.9 mg, 0.3 mmol) were added dropwise in the order. The reaction was stirred at room temperature for 36 hours. The reaction was quenched by addition of MeOH (0.5 mL) at 0 °C, followed by water (0.5 mL). The reaction mixture was extracted with Et<sub>2</sub>O (5 mL × 3 mL), the combined organics were dried over sodium sulfate. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 30/1 to 10/1) to give the desired product **4** (142.1 mg, 64% yield).

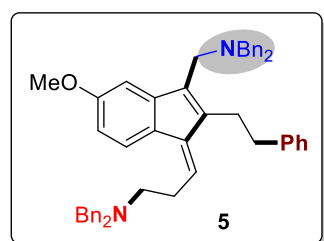
**(E)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methoxy-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1H-inden-1-yl)prop-2-en-1-amine (4)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.36 (m, 8H), 7.26-7.29 (m, 9H), 7.20-7.22 (m, 3H), 7.04-7.06 (m, 2H), 6.62 (d,  $J = 8.0$  Hz, 1H), 5.86-5.93 (m, 1H), 5.02 (dd,  $J = 15.0$  Hz, 9.6 Hz, 1H), 3.91 (d,  $J = 9.3$  Hz, 1H), 3.81 (s, 3H), 3.41-3.56 (m, 10H), 3.02 (d,  $J = 6.2$  Hz, 2H), 2.65-2.73 (m, 1H), 2.30-2.37 (m, 1H), 1.14 (s, 12H), 0.88-1.07 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 152.7, 146.9, 140.0, 139.9, 137.8, 133.7, 132.7, 130.7, 129.4, 129.0, 128.3, 128.3, 127.0, 126.9, 123.7, 111.0, 105.6, 83.2, 58.9, 57.7, 55.7, 55.3, 54.0, 49.8, 24.9, 24.9, 21.3;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5; HRMS (ESI) calcd for  $\text{C}_{50}\text{H}_{58}\text{BN}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : 745.4540, found: 745.4601.

$\text{Pd}_2(\text{dba})_3$  (4.6 mg, 2.5 mol%), Ruphos (5.6 mg, 6 mol%), bromobenzene (37.7 mg, 0.24 mmol), Sodium *tert*-butoxide (57.7 mg, 0.60 mmol), (*E*)-*N,N*-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methoxy-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1*H*-inden-1-yl)prop-2-en-1-amine **4** (148.9 mg, 0.2 mmol), toluene (0.8 mL), and water (0.08 mL) were added to a 25 mL flame-dried Young-type tube under  $\text{N}_2$  atmosphere. The reaction mixture was stirred at 80  $^\circ\text{C}$  for 20 hours, and then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **5** (90.2 mg, 65% yield).

**(Z)-N,N-dibenzyl-3-(3-((dibenzylamino)methyl)-5-methoxy-2-phenethyl-1*H*-inden-1-ylidene)propan-1-amine (5)**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.38 (m, 5H), 7.25-7.31 (m, 13H), 7.18-7.23 (m, 6H), 7.14-7.15 (m, 2H), 7.07 (d,  $J = 2.4$  Hz, 1H), 6.58 (dd,  $J = 8.3$  Hz, 2.5 Hz, 1H), 6.14 (t,  $J = 6.8$  Hz, 1H), 3.83 (s, 3H), 3.63 (s, 4H), 3.42 (s, 4H), 3.24 (s, 2H), 2.88 (dd,  $J = 13.9$  Hz, 6.9 Hz, 2H), 2.75-2.84 (m, 4H), 2.69 (t,  $J = 7.1$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 146.2, 142.0, 141.1, 139.8, 139.8, 139.3, 134.9, 129.5, 129.4, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 127.0, 127.0, 126.1, 123.7, 110.4, 105.8, 58.9, 58.5, 55.6, 52.8, 49.8, 37.7, 27.4, 26.8; HRMS (ESI) calcd for  $\text{C}_{50}\text{H}_{51}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 695.4001, found: 695.4009.

## 7. Mechanistic Experiments

To gain insights into the possible mechanism of this reaction, some mechanism experiments were conducted. The Xantphos-ligated palladium-complex-A was synthesized according to our previous report procedure in gram scale. With the Xantphos-ligated palladium-complex-A in hand, a series of control experiments were conducted.

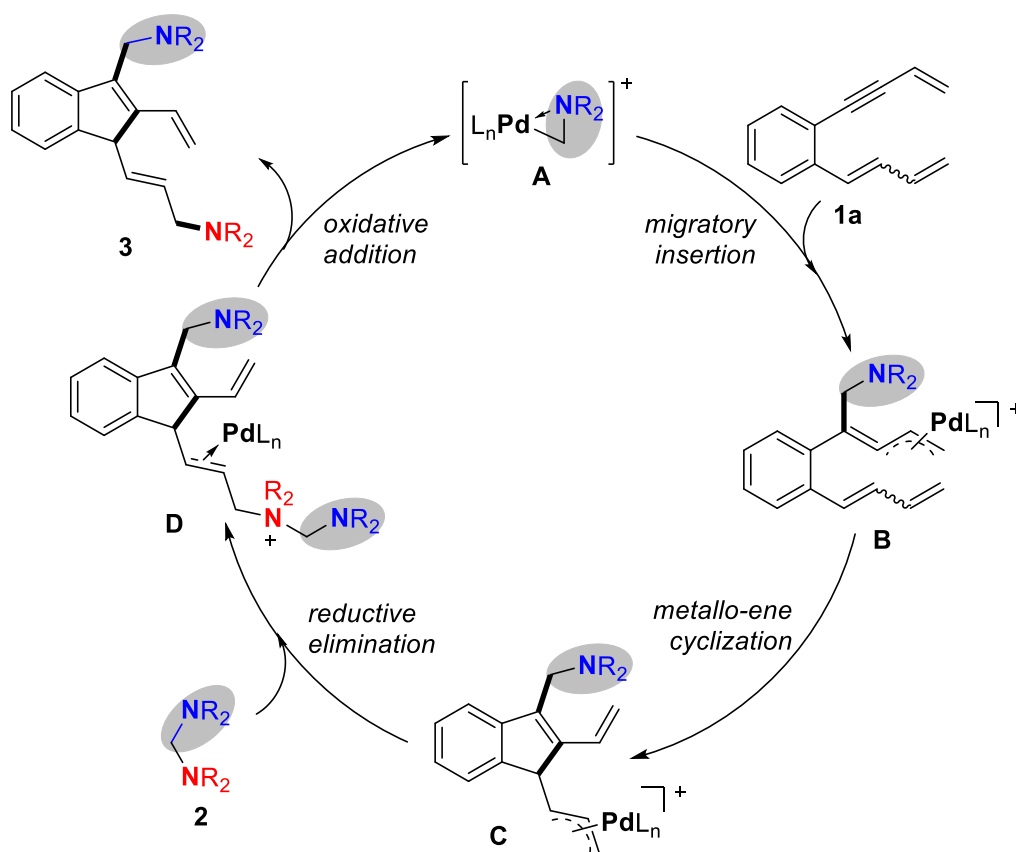
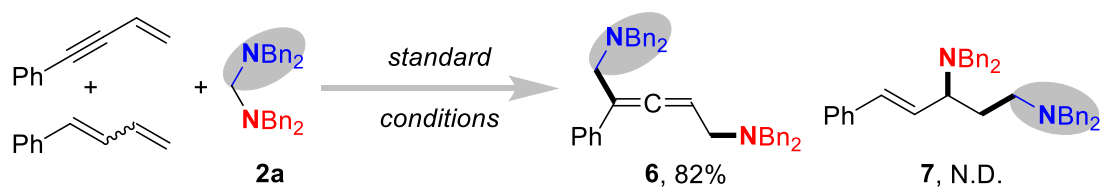


Figure S1. Proposed reaction mechanism.

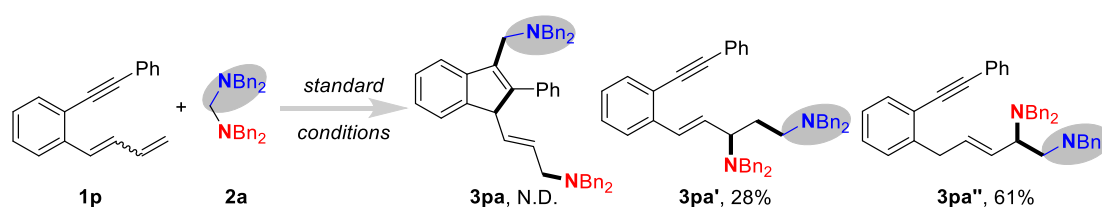
### Competitive reaction between 1,3-enyne and 1,3-diene to amination 2a





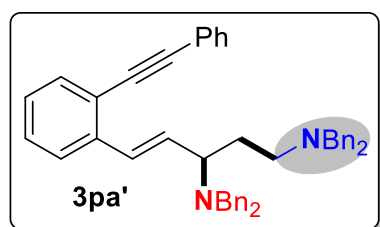
*N,N,N',N'*-tetrabenzylmethanediamine **2a** (122 mg, 0.30 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (16.0 mg, 5 mol %), but-3-en-1-yn-1-ylbenzene (46.1 mg, 0.36 mmol), buta-1,3-dien-1-ylbenzene (46.8 mg, 0.36 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the 1,4-difunctionalization product **6** of 1,3-enyne as yellow oil (131.4 mg, 82% yield).

### Catalytic reaction of diene-tethered phenylacetylene **1p** and amination **2a**



*N,N,N',N'*-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), Pd(Xantphos)(CH<sub>3</sub>CN)<sub>2</sub>(OTf)<sub>2</sub> (16.0 mg, 5 mol %), 1-(buta-1,3-dien-1-yl)-2-(phenylethynyl)benzene **1p** (69.3 mg, 0.30 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the difunctionalization product of 1,3-diene **3pa'** (52.6 mg, 28% yield) and **3pa''** (115.8 mg, 61% yield) as yellow oil.

### (*E*)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>3</sup>,*N*<sup>3</sup>-tetrabenzyl-5-(2-(phenylethynyl)phenyl)pent-4-ene-1,3-diamine (**3pa'**)

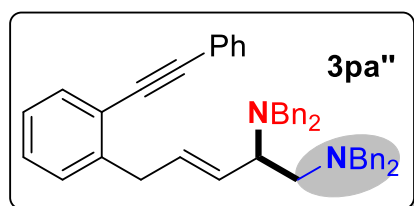


The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 52.6 mg, 28% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52-7.55 (m, 3H),

7.45 (d, *J* = 7.7 Hz, 1H), 7.34-7.35 (m, 3H), 7.22-7.31 (m, 15H), 7.15-7.17 (m, 7H), 6.83 (d, *J* = 15.8 Hz, 1H), 6.17 (dd, *J* = 15.8 Hz, 8.8 Hz, 1H), 3.75 (d, *J* = 13.6 Hz, 2H), 3.61 (d, *J* = 13.5 Hz, 2H), 3.32 (dd, *J* = 18.2 Hz, 13.6 Hz, 4H), 3.25-3.29 (m, 1H), 2.68-

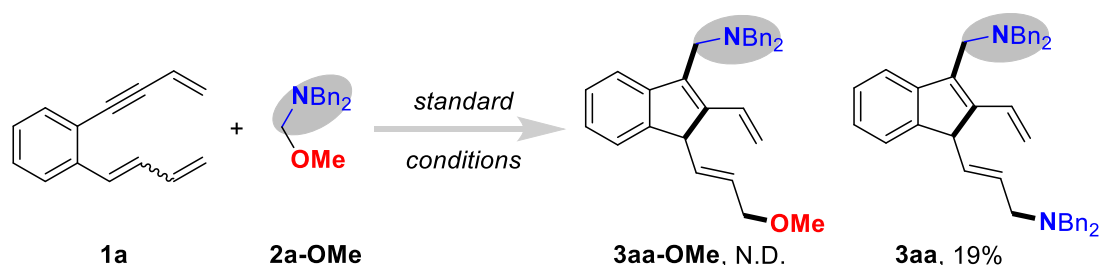
2.75 (m, 1H), 2.29-2.36 (m, 1H), 1.99-2.08 (m, 1H), 1.73-1.81 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 139.8, 138.7, 132.8, 131.8, 131.5, 130.2, 129.0, 128.9, 128.6, 128.5, 128.5, 128.3, 128.2, 127.2, 126.8, 126.8, 125.2, 123.5, 121.8, 93.9, 88.2, 58.7, 58.5, 53.8, 51.2, 30.3; HRMS (ESI) calcd for  $\text{C}_{47}\text{H}_{45}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 637.3583, found: 637.3576.

**(E)- $N^1, N^1, N^2, N^2$ -tetrabenzyl-5-(2-(phenylethynyl)phenyl)pent-3-ene-1,2-diamine (3pa'')**



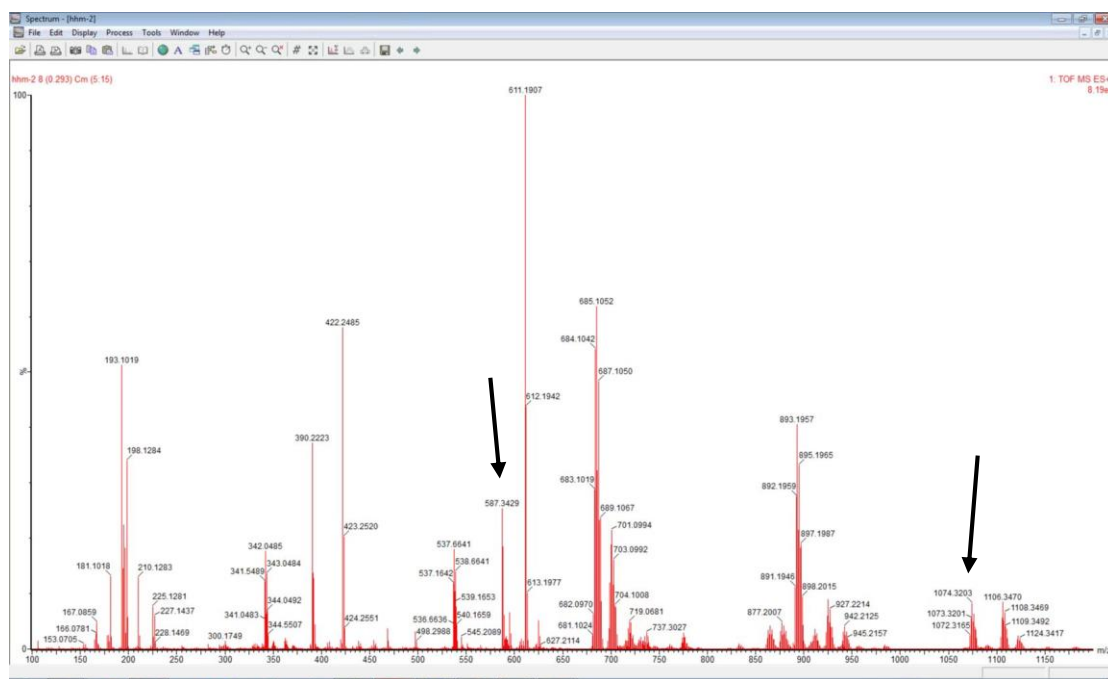
The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 115.8 mg, 61% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.53 (m, 1H), 7.37-7.39 (m, 2H), 7.24-7.32 (m, 12H), 7.16-7.21 (m, 13H), 6.91-6.93 (m, 1H), 5.59-5.73 (m, 2H), 4.40-4.46 (m, 1H), 3.48-3.64 (m, 8H), 3.01 (d,  $J = 5.7$  Hz, 2H), 2.69-2.80 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 139.9, 139.7, 135.4, 132.5, 131.6, 129.0, 128.9, 128.6, 128.5, 128.3, 128.2, 127.6, 126.8, 126.1, 123.5, 122.8, 93.2, 88.5, 58.9, 58.5, 57.9, 55.7, 44.3; HRMS (ESI) calcd for  $\text{C}_{47}\text{H}_{45}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 637.3583, found: 637.3585.

**Catalytic reaction of diene-tethered enyne **1a** and  $N,O$ -acetal **2a-OMe****

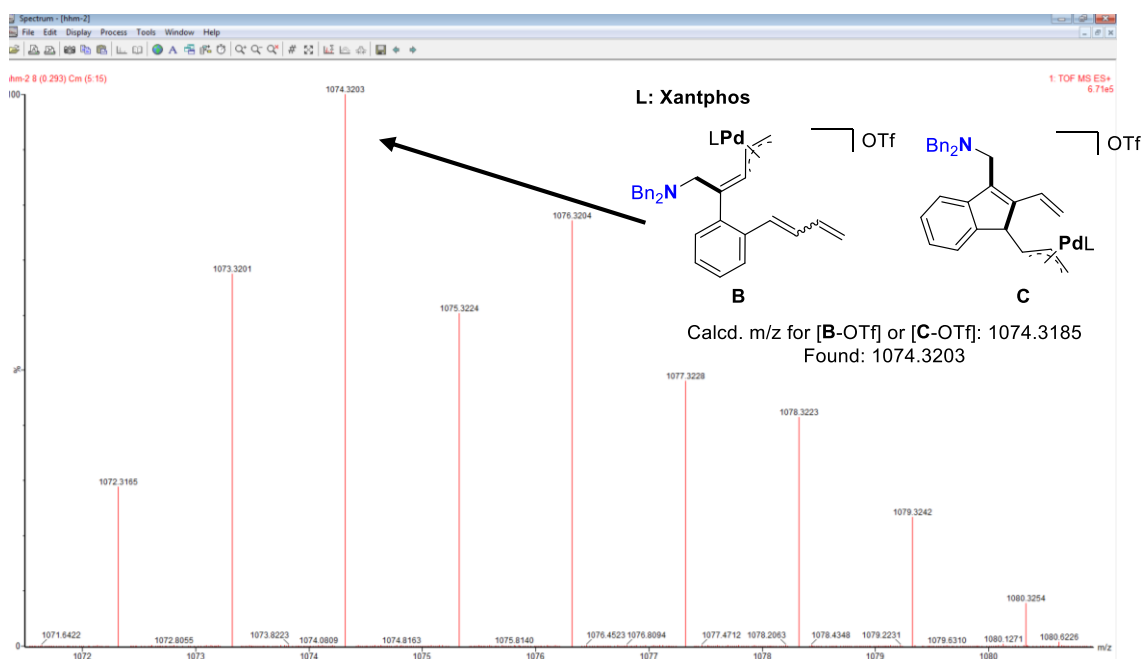


$N,N$ -dibenzyl-1-methoxymethanamine **2a-OMe** (86.8 mg, 0.36 mmol),  $\text{Pd}(\text{Xantphos})(\text{CH}_3\text{CN})_2(\text{OTf})_2$  (16.0 mg, 5 mol %), 1-(but-3-en-1-yn-1-yl)-2-(buta-1,3-dien-1-yl)benzene **1a** (54.0 mg, 0.30 mmol) and  $\text{CH}_2\text{Cl}_2$  (1.0 mL) were added to a 25 mL flame-dried Young-type tube under  $\text{N}_2$  atmosphere. The reaction mixture was

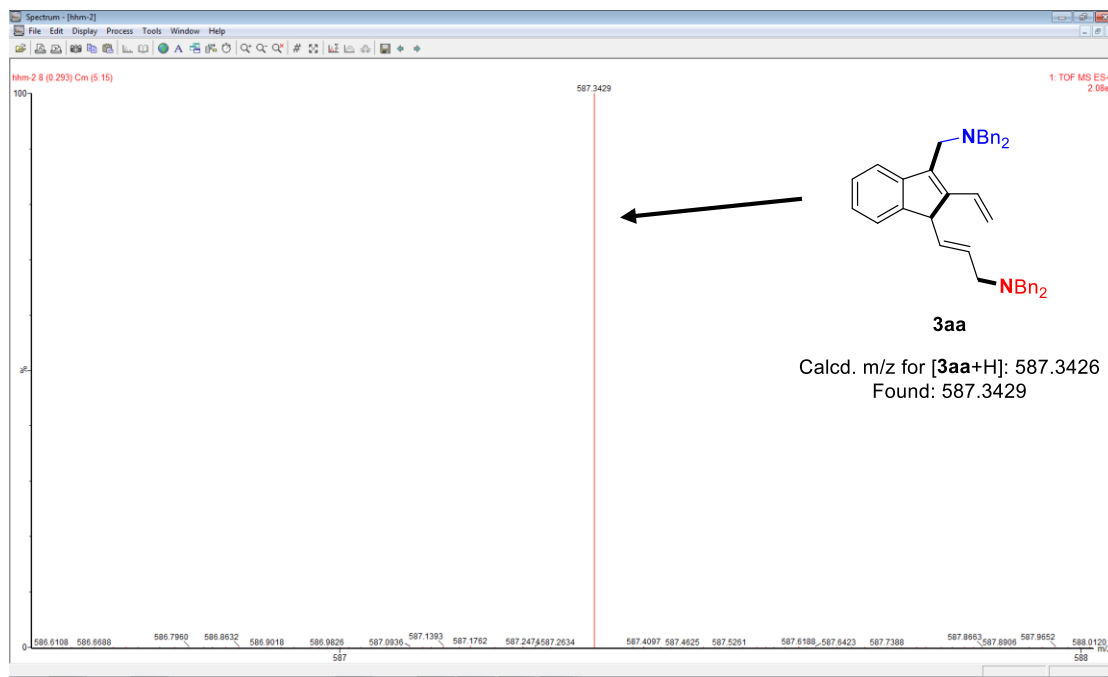




**Figure S2.** Observed HRMS date for the catalytic reaction system.



**Figure S3.** Observed HRMS date for palladium complex **B** or **C**.



**Figure S4.** Observed HRMS data for target product **3aa**.

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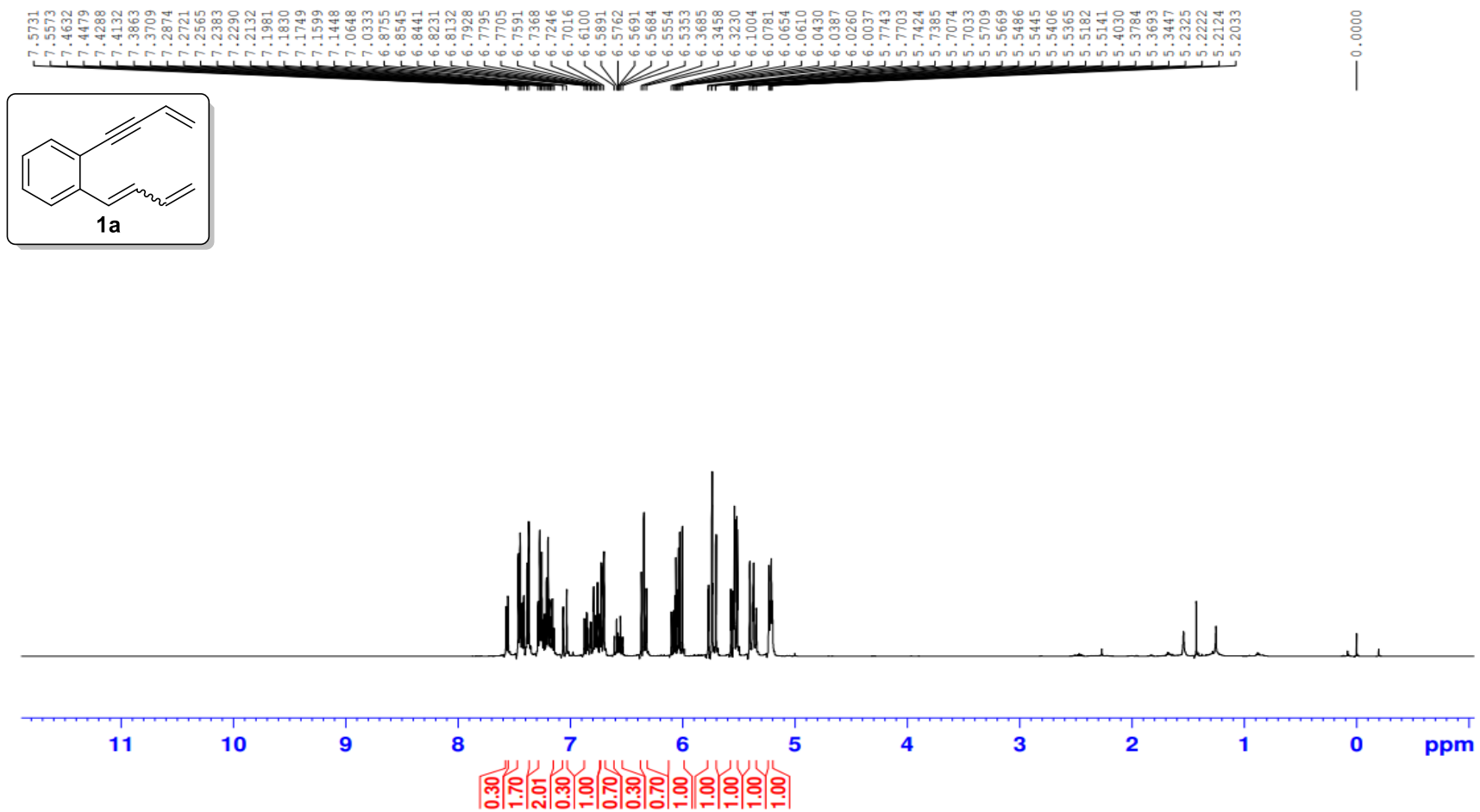
## 8. References

1. (a) Heaney, H.; Papageorgiou, G.; Wilkins, R. F. The Generation of Iminium Ions Using Chlorosilanes and Their Reactions with Electron Rich Aromatic Heterocycles. *Tetrahedron* **1997**, *53*, 2941. (b) Rosenau, T.; Potthast, A.; Kosma, P. Studies on the Carbenium-Iminium Ions Derived from *N*-methylnmorpholine-*N*-oxide (NMMO). *Tetrahedron* **2004**, *60*, 301.
2. Yu, B.; Huang, R.; Li, R.; Zhang, H.; Huang, H. Silver-Catalyzed Chemodivergent Assembly of Aminomethylated Isochromenes and Naphthols. *Chem. Commun.* **2022**, *58*, 3969.
- 3.(a) Röse, P.; Emge, S.; Yoshida, J.-i.; Hilt, G. Electrochemical Selenium- and Iodonium-Initiated Cyclisation of Hydroxy-functionalised 1,4-dienes. *Beilstein J. Org. Chem.* **2015**, *11*, 174. (b) Sardini, S. R.; Brown, M. K. Catalyst Controlled Regiodivergent Arylboration of Dienes. *J. Am. Chem. Soc.* **2017**, *139*, 9823.

## 9. NMR Spectra of Materials and Products

### $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ ) spectra for 1a

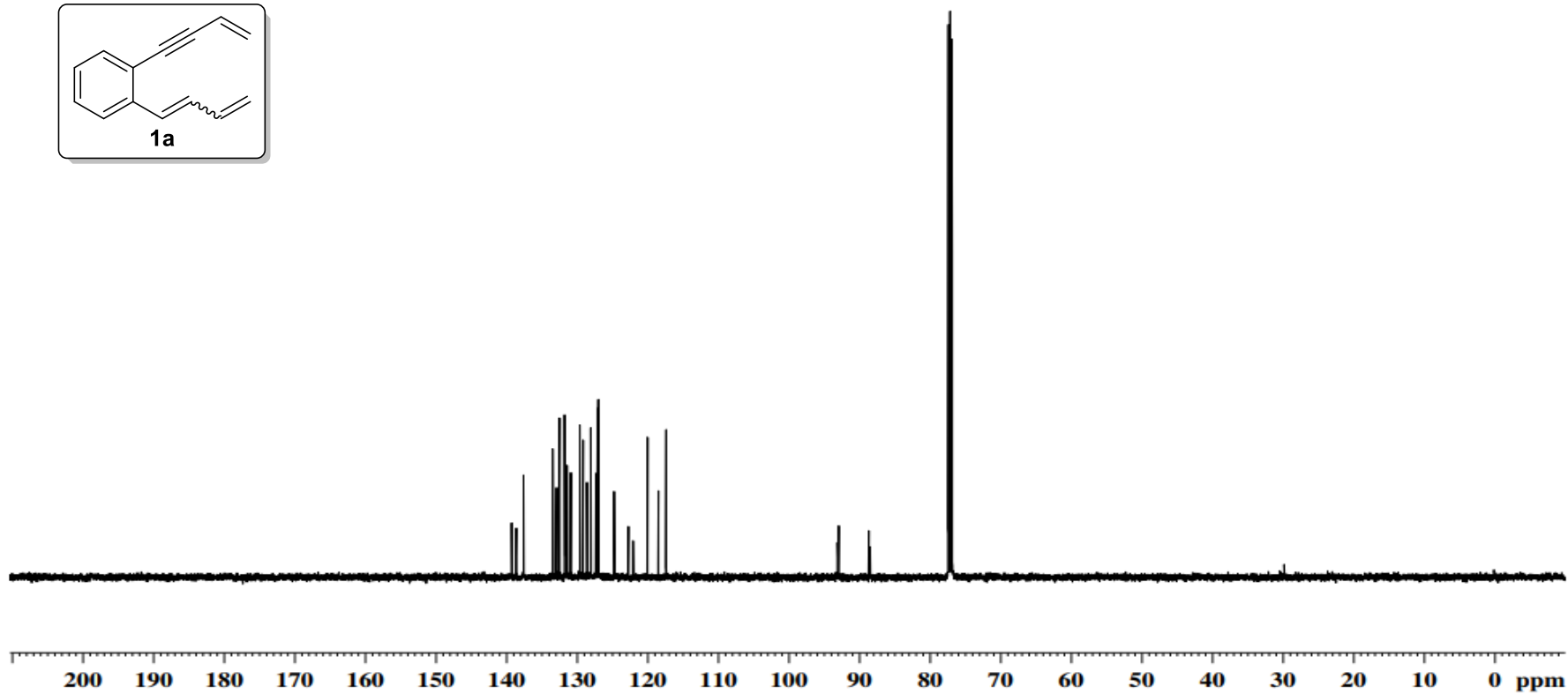
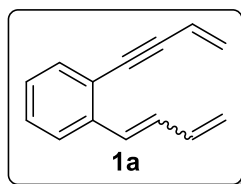
LRR-X220817-BZ-500M (in  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1a

LRR-X220818-BZ-125M(in CDCl<sub>3</sub>)

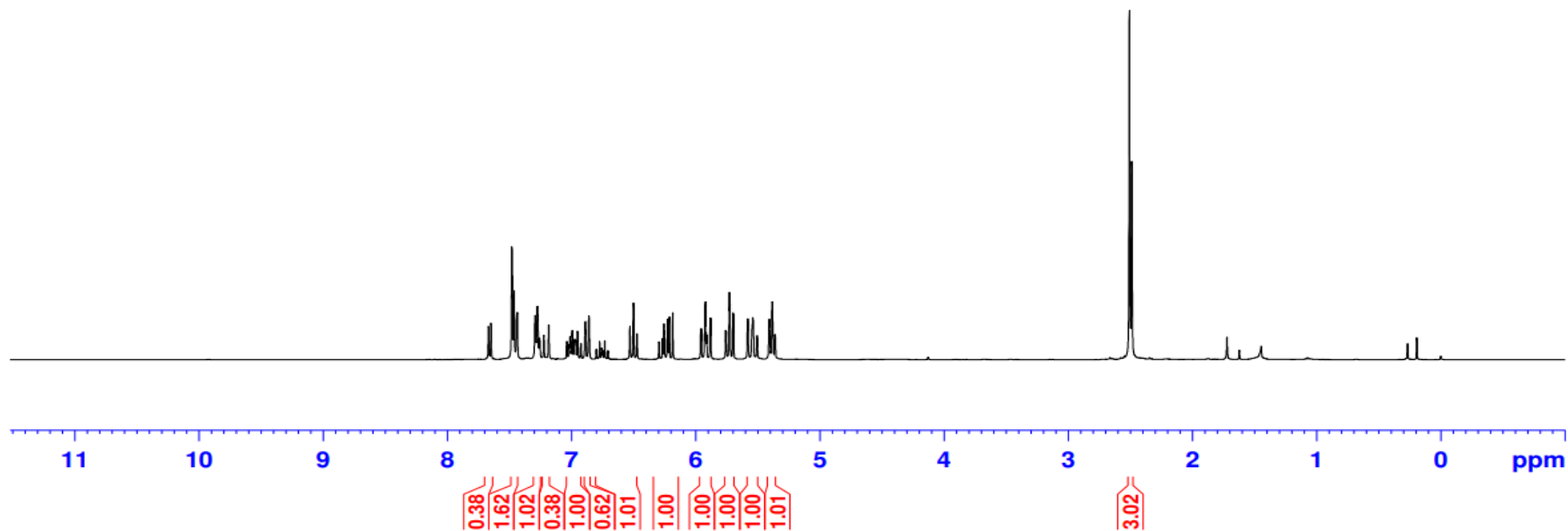
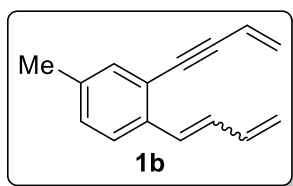
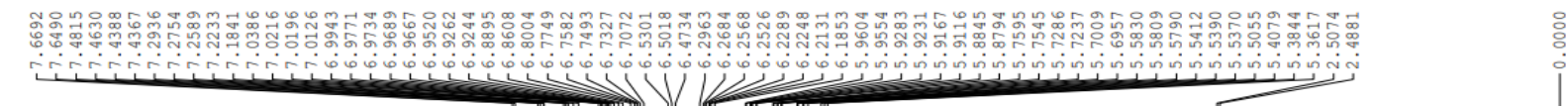
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127.1  
127.0  
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122.1  
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93.0  
88.7  
88.5  
77.4  
77.2  
76.9





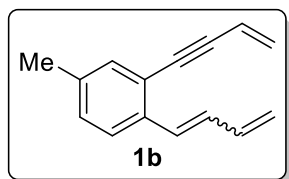
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1b

LRR-X220329-1-4-Me-400M(in CDCl<sub>3</sub>)



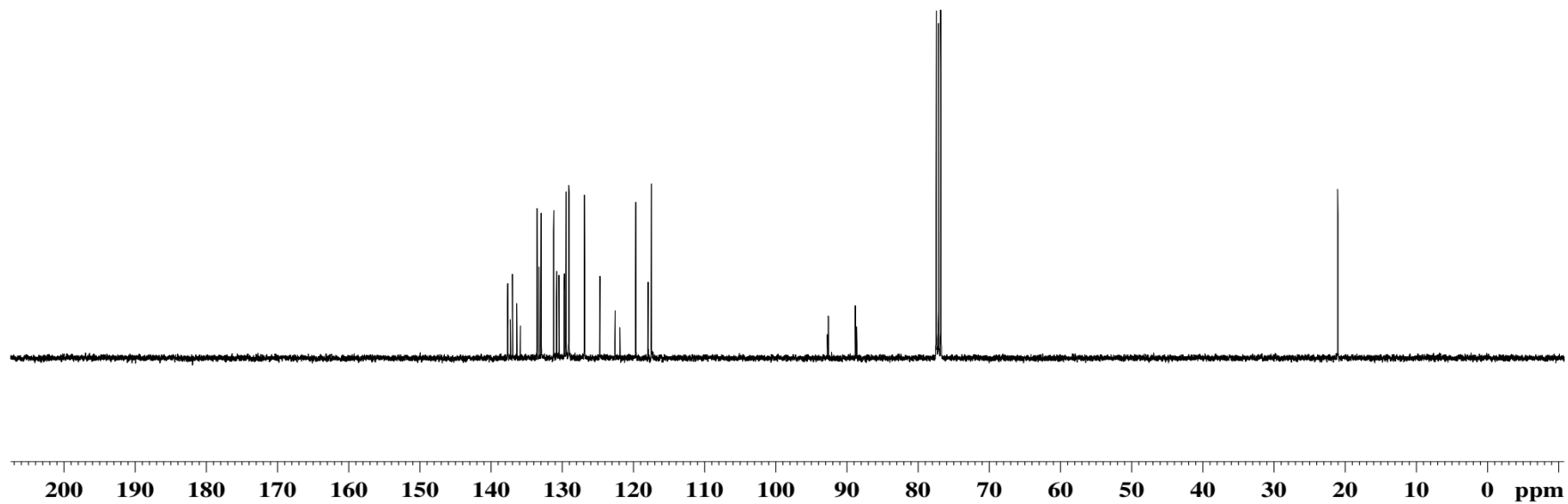
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 1b**

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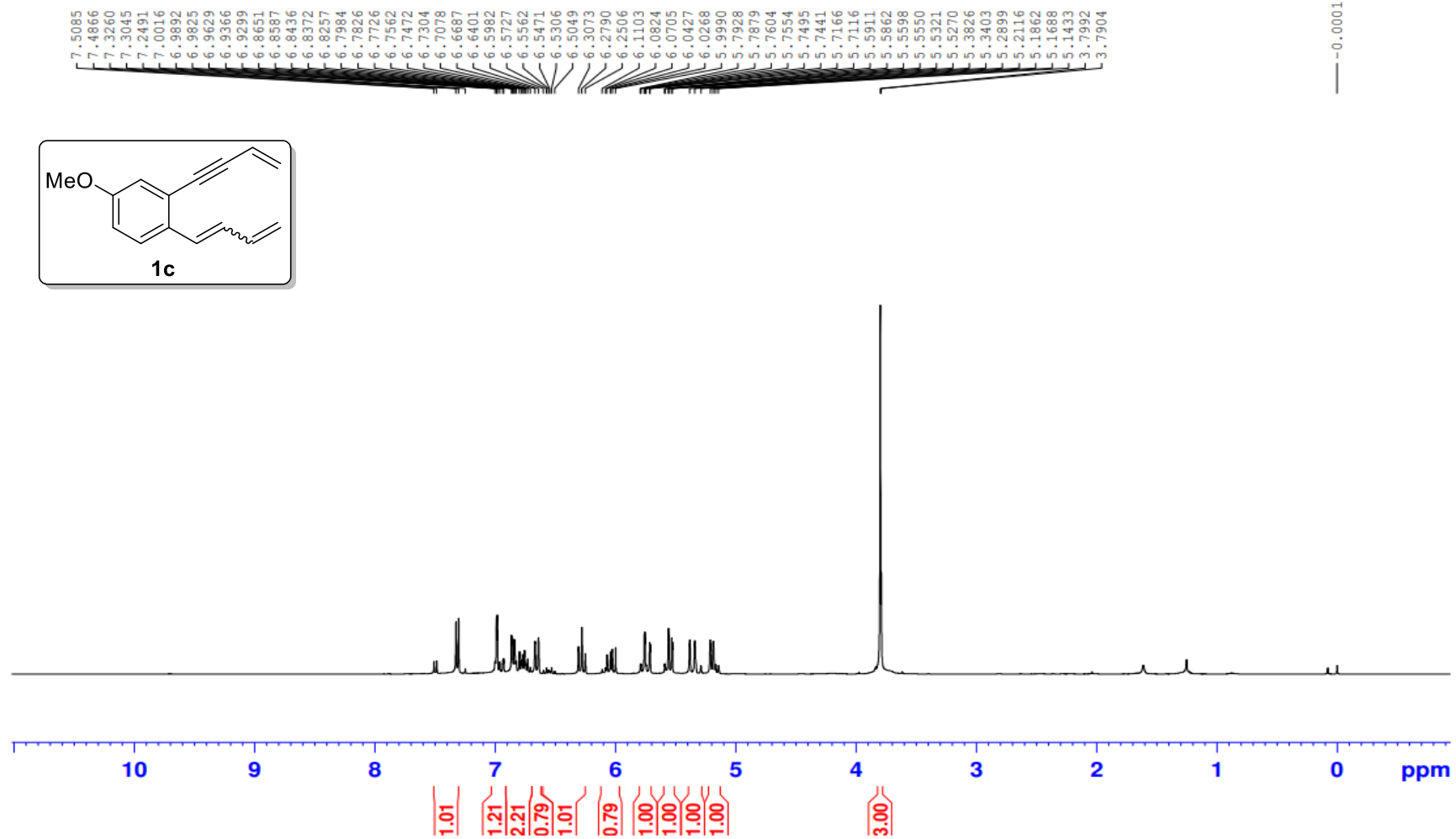
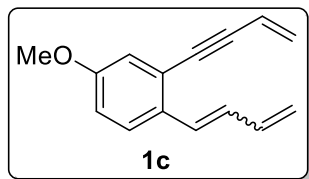
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129.7  
129.4  
129.1  
129.0  
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119.6  
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77.2  
76.8

— 21.1



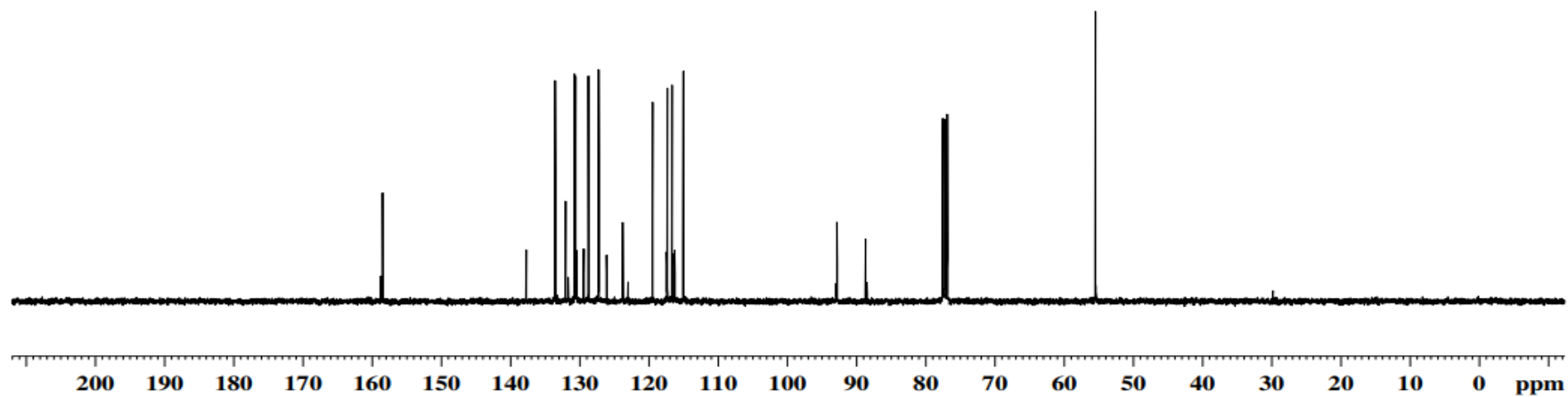
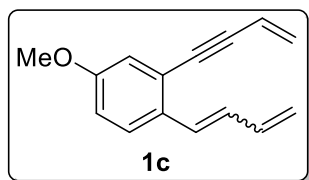
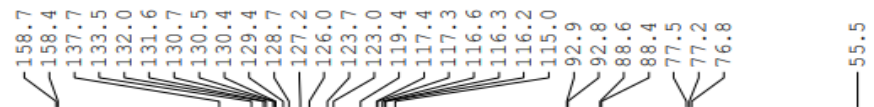
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1c**

LRR-X210917-4-OMe-400M(in CDCl<sub>3</sub>)



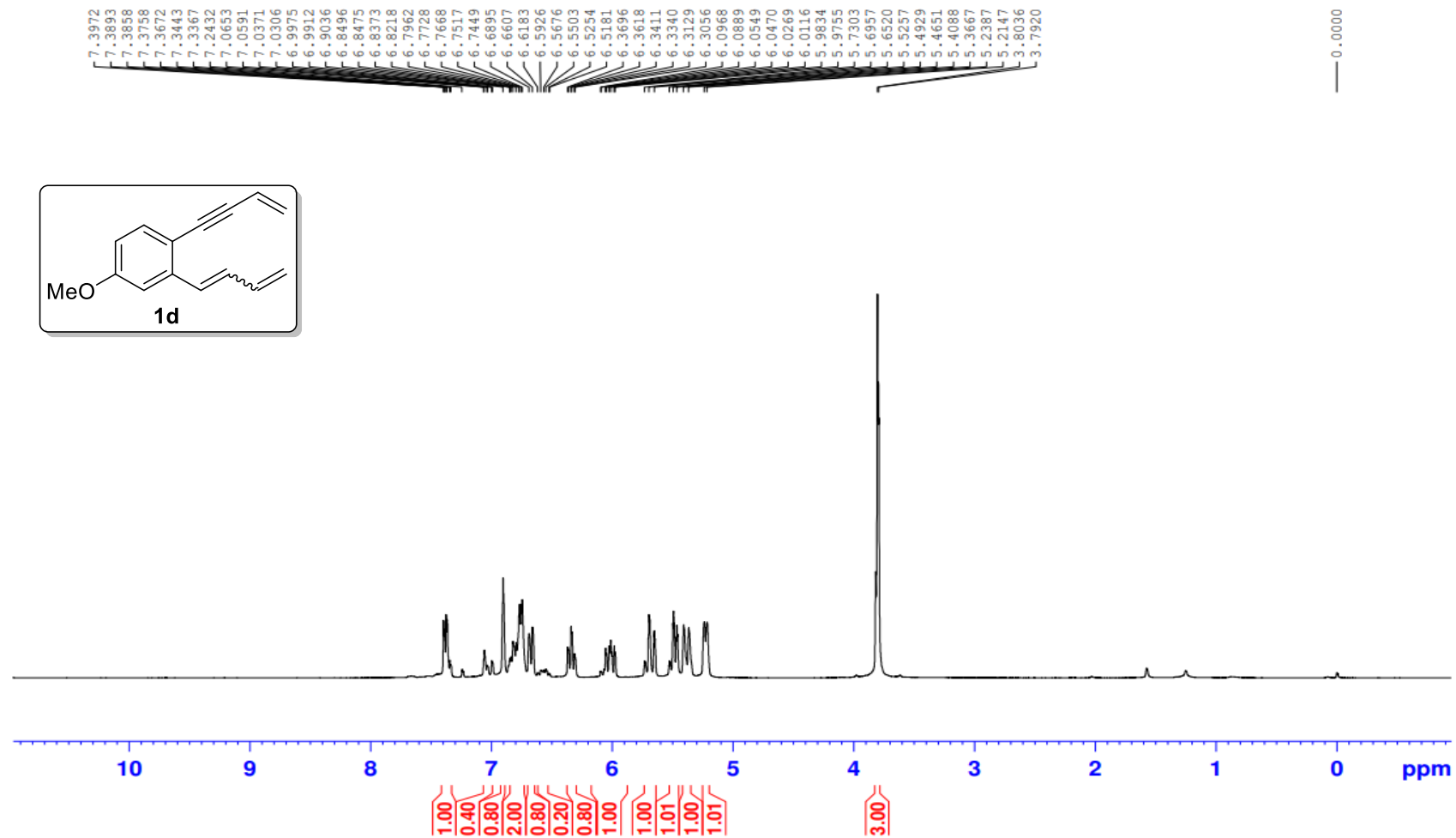
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 1c**

LRR-X210917-4-OMe-100M(in CDCl<sub>3</sub>)



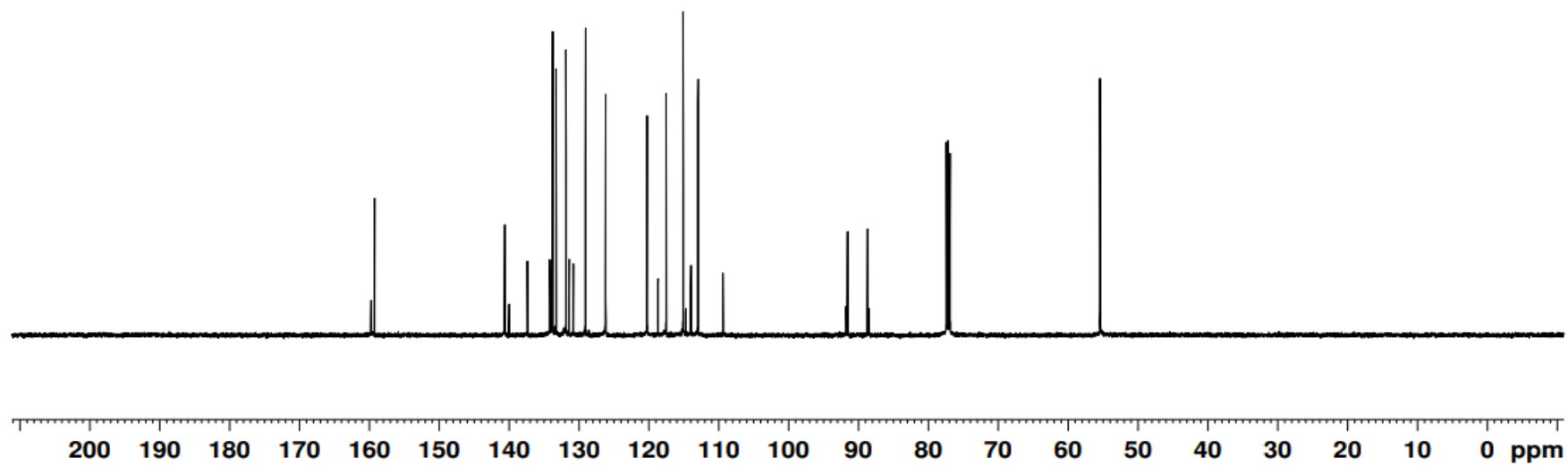
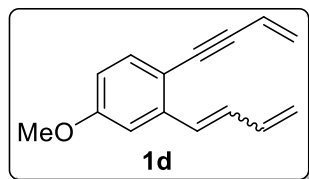
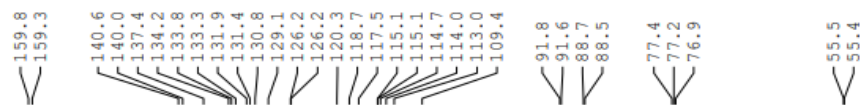
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1d

LRR-X22X15-5-OMe-400M(in CDCl<sub>3</sub>)



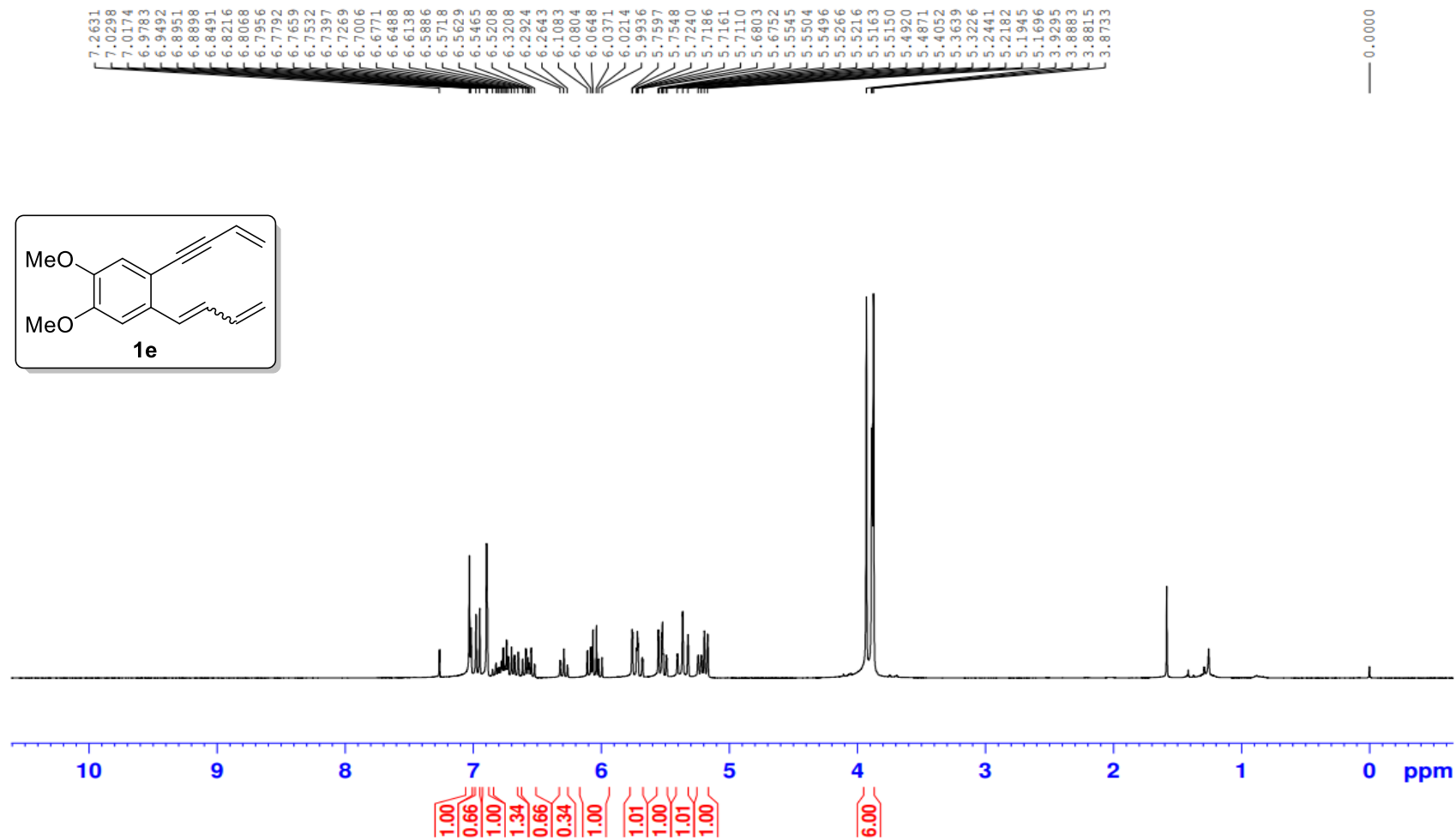
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1d**

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**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1e**

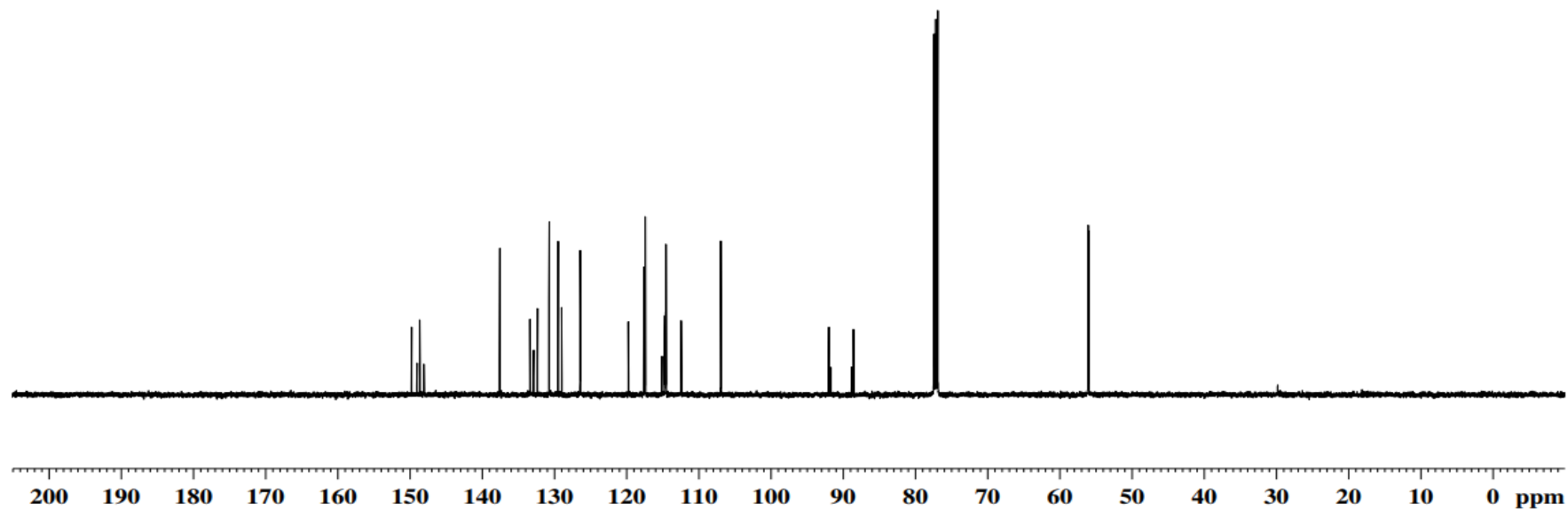
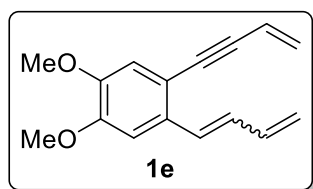
LRR-X220822-2OMe-400 (in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1e**

LRR-X220822-2OME-125M(in CDCl<sub>3</sub>)

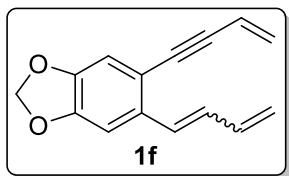
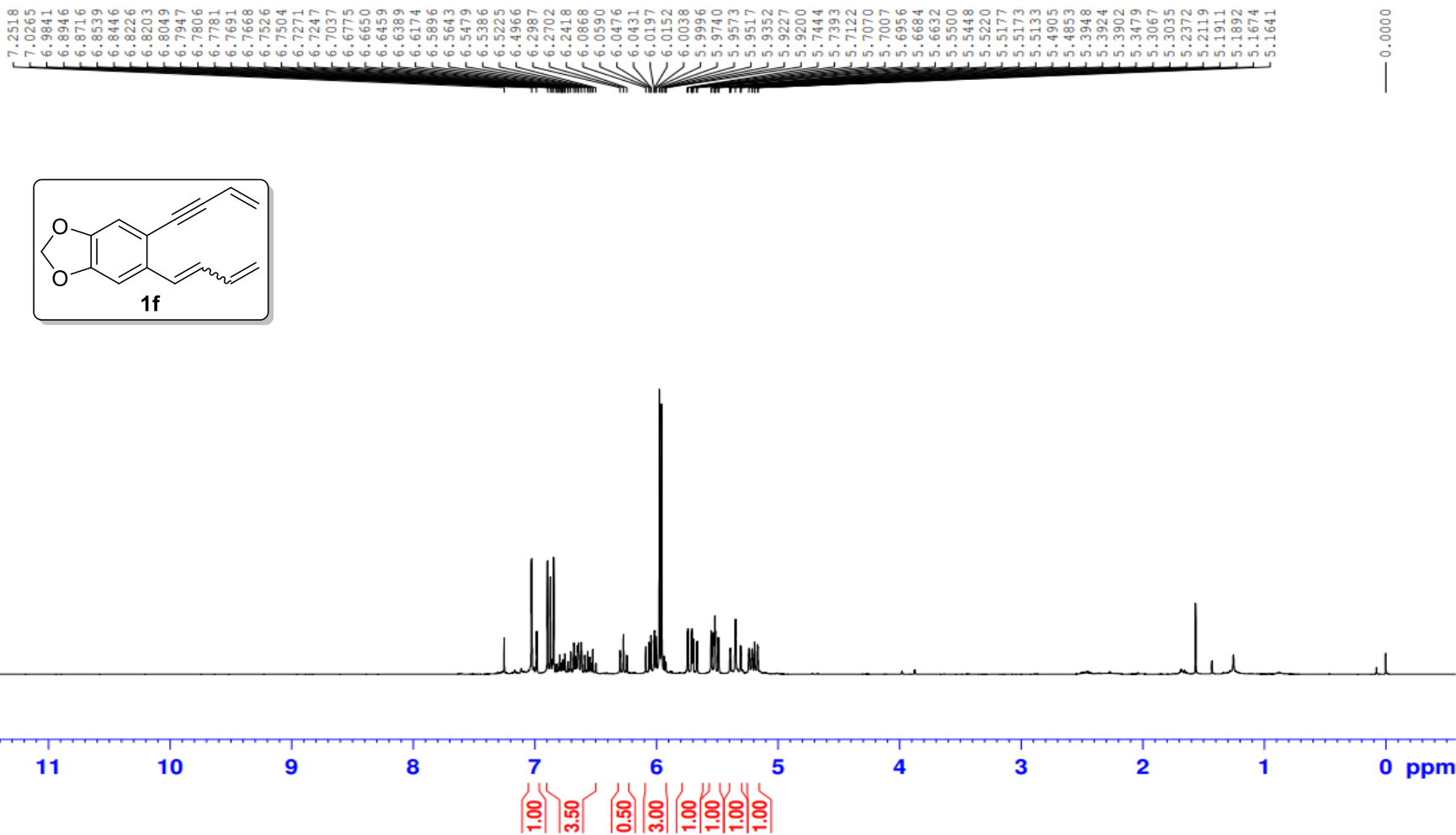
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126.4  
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117.4  
115.1  
114.7  
114.6  
114.6  
112.4  
106.9  
92.0  
91.7  
88.8  
88.6  
77.4  
77.2  
76.9  
56.1  
56.1  
56.0





**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1f**

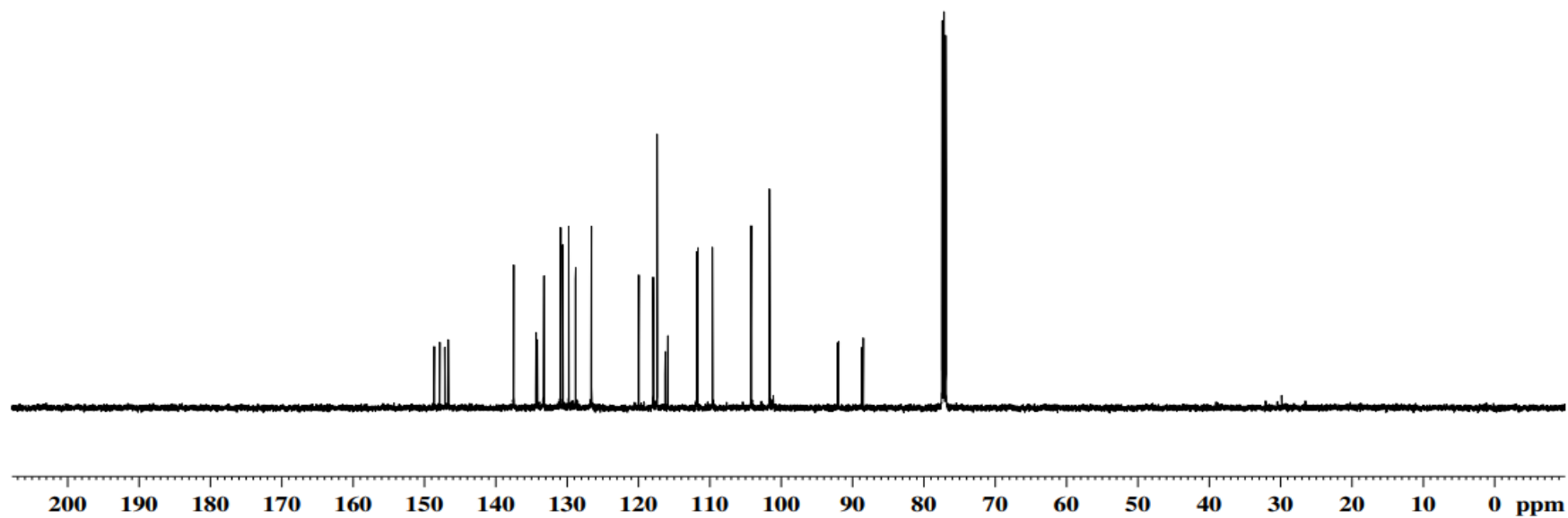
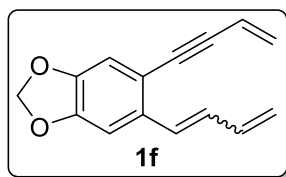
LRR-X22X06-2OMe-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1f**

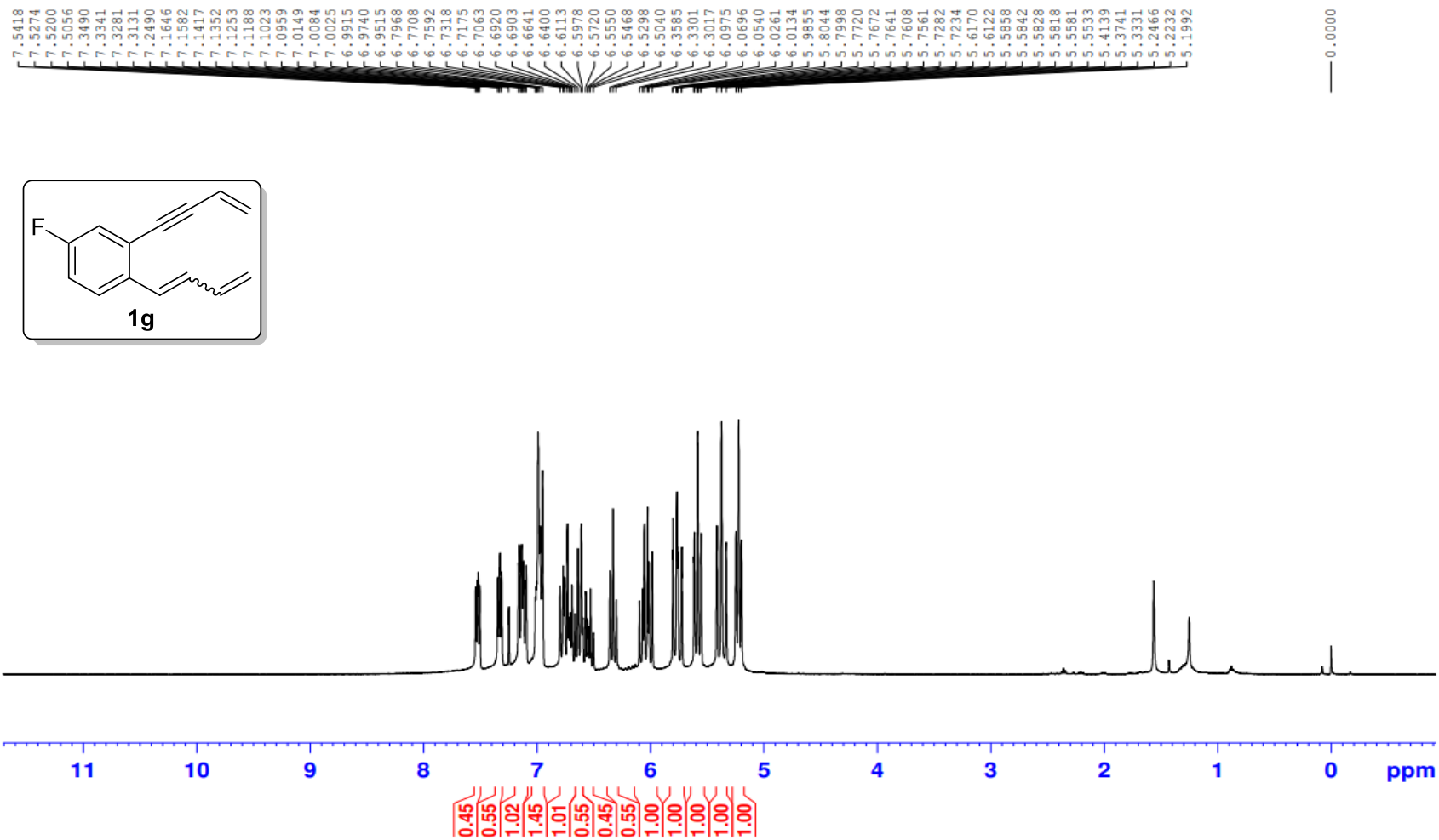
LRR-X22X06-2OMe-125M(in CDCl<sub>3</sub>)

148.6  
147.8  
147.1  
146.6  
137.5  
134.4  
134.1  
133.2  
130.9  
130.6  
129.8  
128.8  
126.6  
126.6  
120.0  
117.9  
117.4  
116.2  
115.9  
111.8  
111.7  
109.6  
104.2  
101.6  
101.6  
92.0  
91.9  
88.7  
88.5  
77.4  
77.2  
76.9



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1g

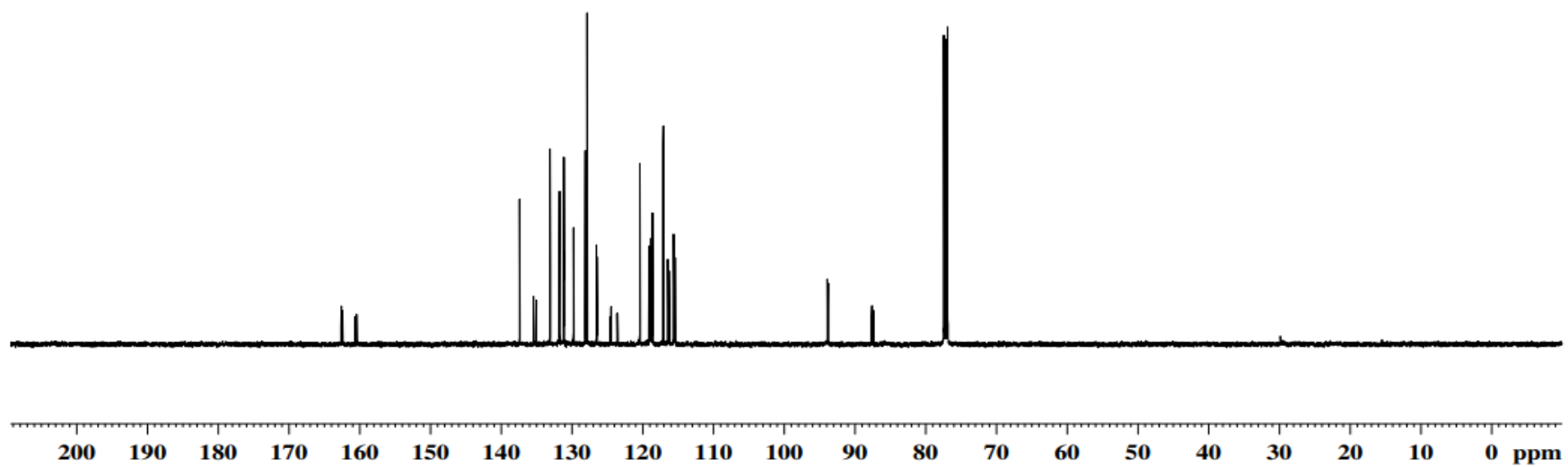
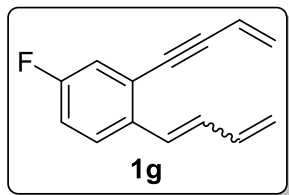
LRR-X220823-4-F-400M(in CDCl<sub>3</sub>)



**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra for 1g**

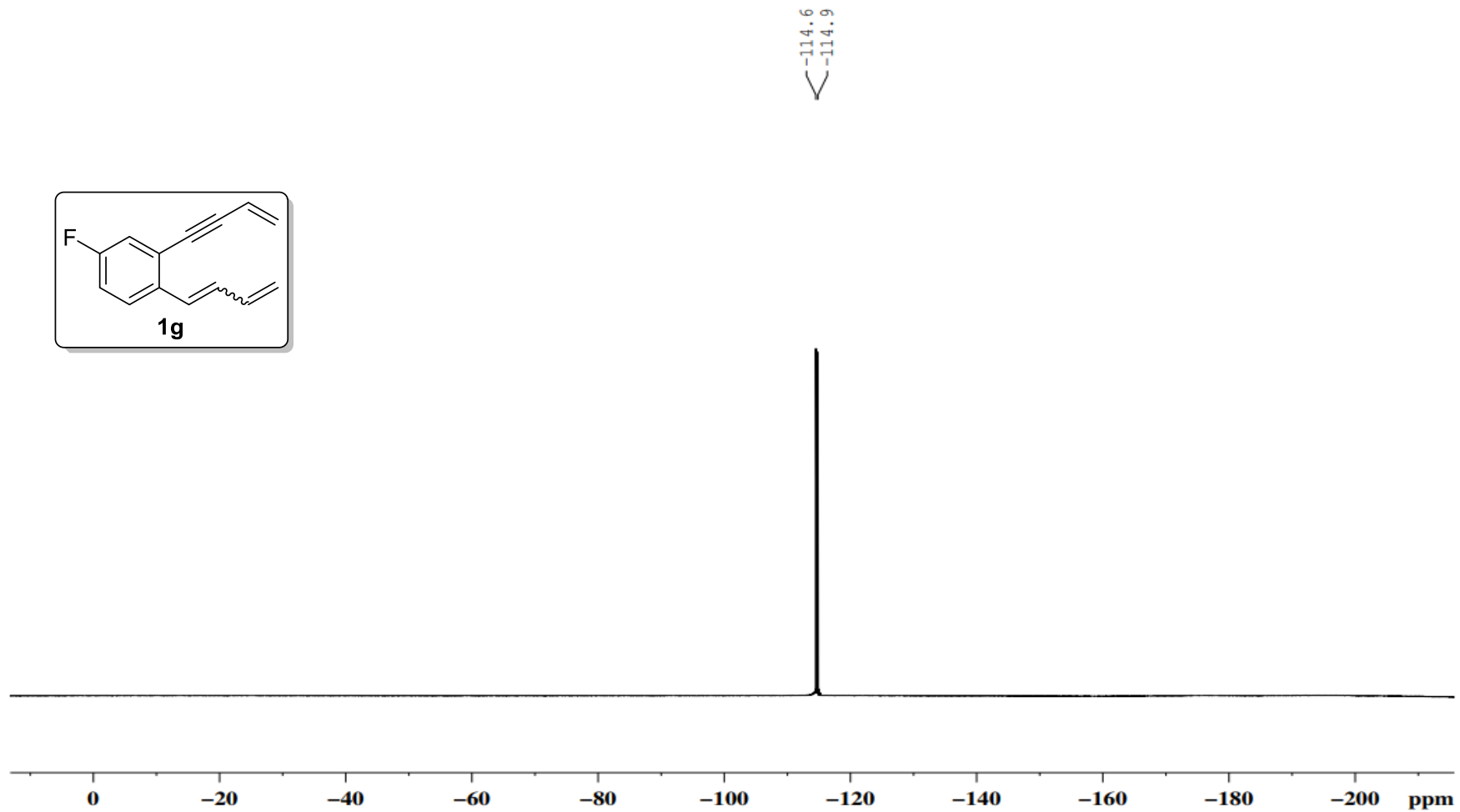
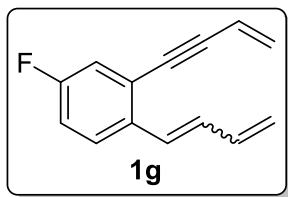
LRR-X220823-4-F-125M(in  $\text{CDCl}_3$ )

162.6  
162.4  
160.6  
160.4  
137.3  
135.4  
135.4  
135.0  
135.0  
133.0  
131.7  
131.1  
131.1  
131.1  
129.7  
128.1  
127.8  
126.5  
126.4  
124.5  
124.4  
123.6  
123.5  
120.3  
119.1  
118.9  
118.9  
118.8  
118.5  
117.0  
116.4  
116.2  
115.5  
115.4  
93.8  
93.7  
87.6  
87.5  
87.3  
87.3  
77.4  
77.2  
76.9



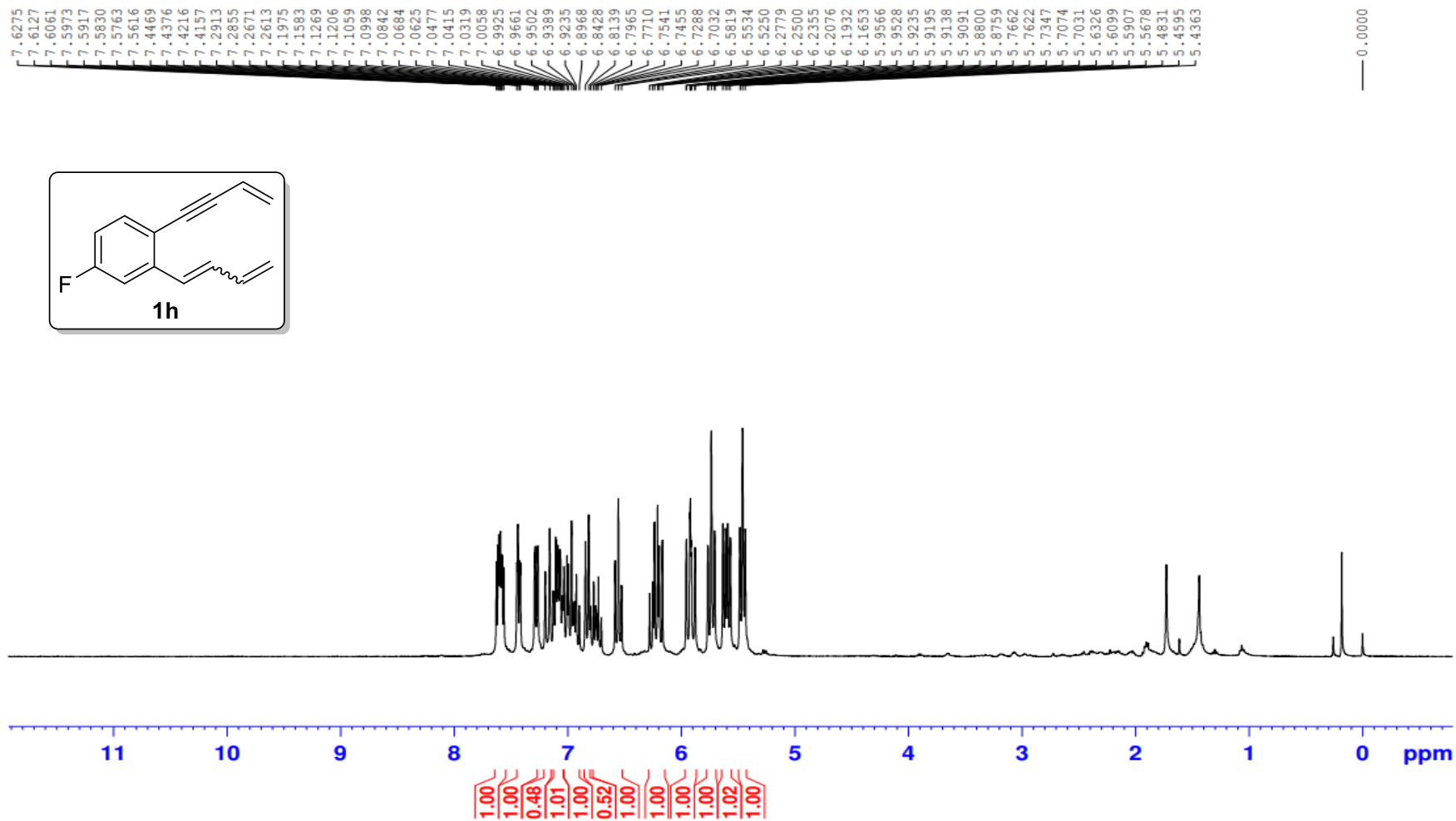
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 1g**

LRR-X220823-4-F-376M(in  $\text{CDCl}_3$ )



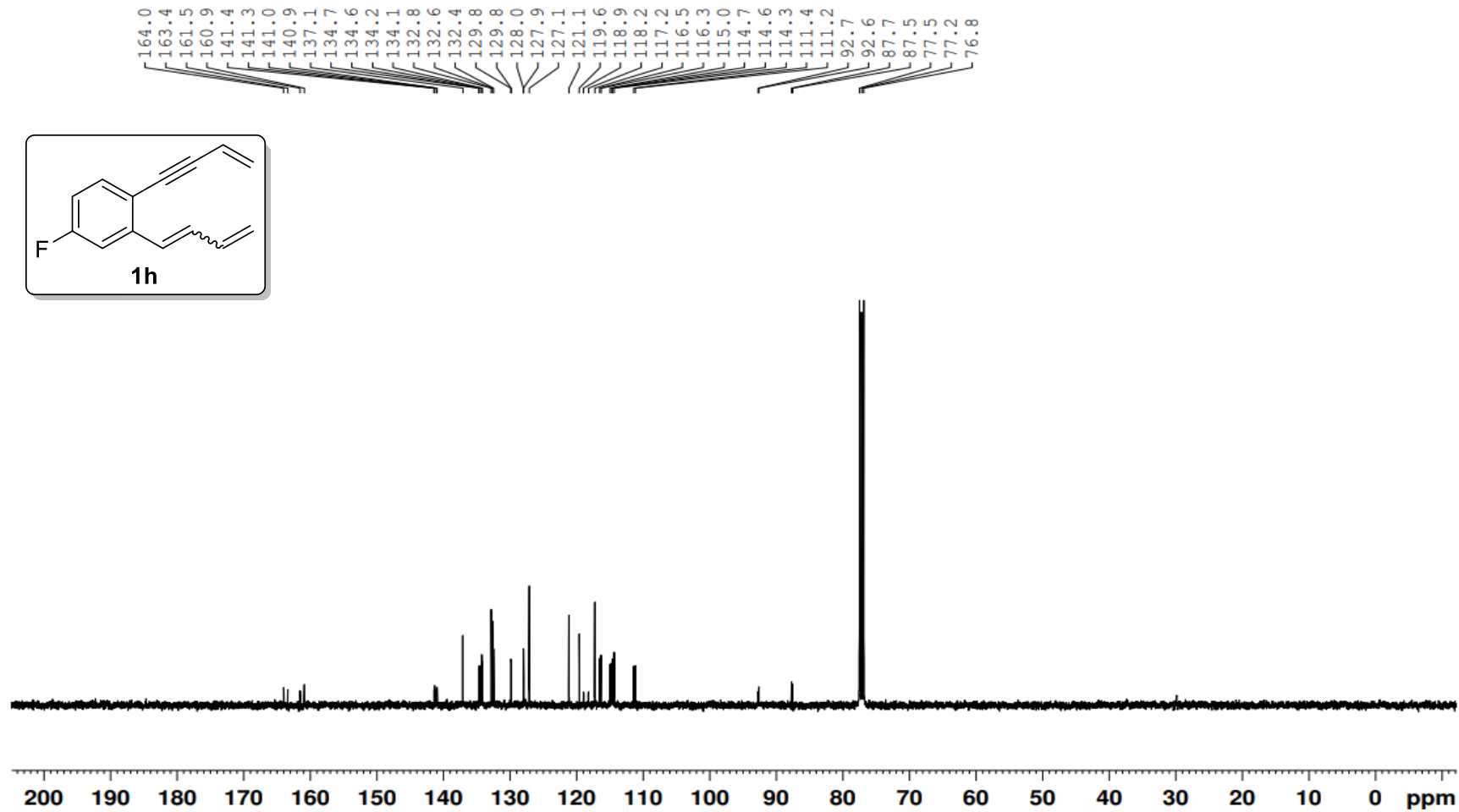
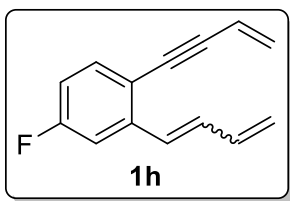
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1h

LRR-X220331-4-5-F-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 1h**

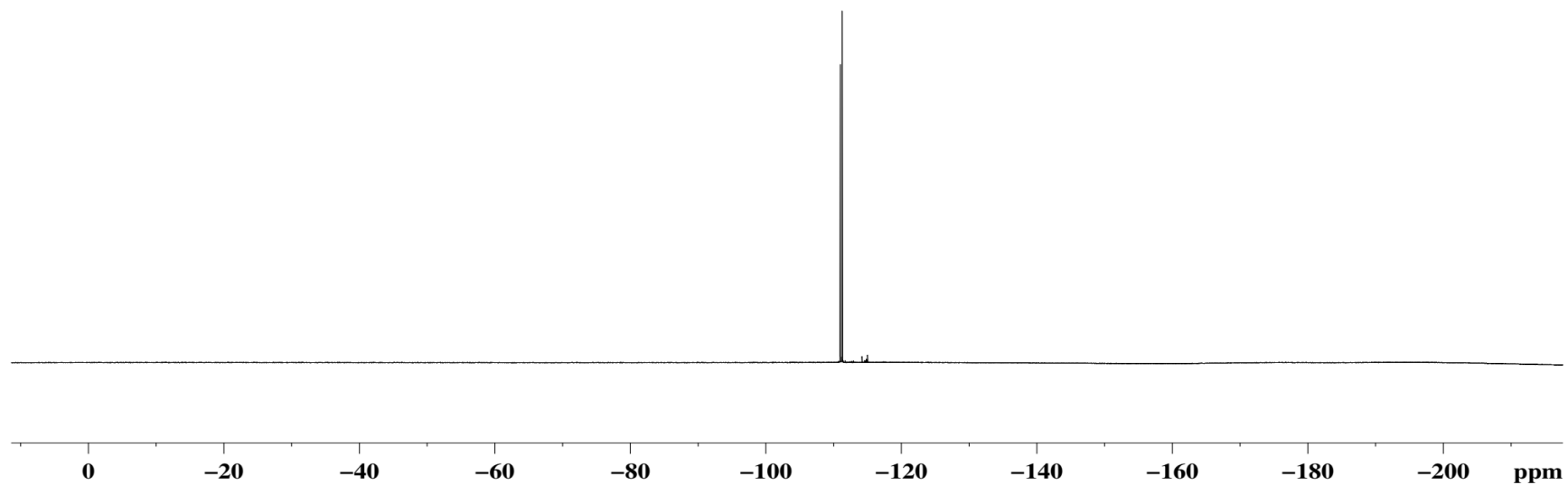
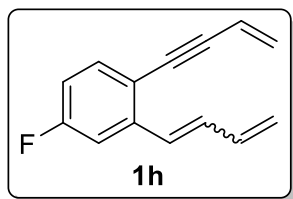
LRR-X210331-4-5-F-100M(in CDCl<sub>3</sub>)



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 1h**

LRR-X210331-4-5-F-376M (in  $\text{CDCl}_3$ )

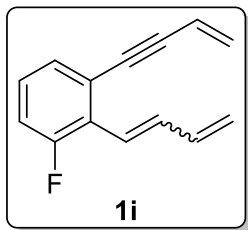
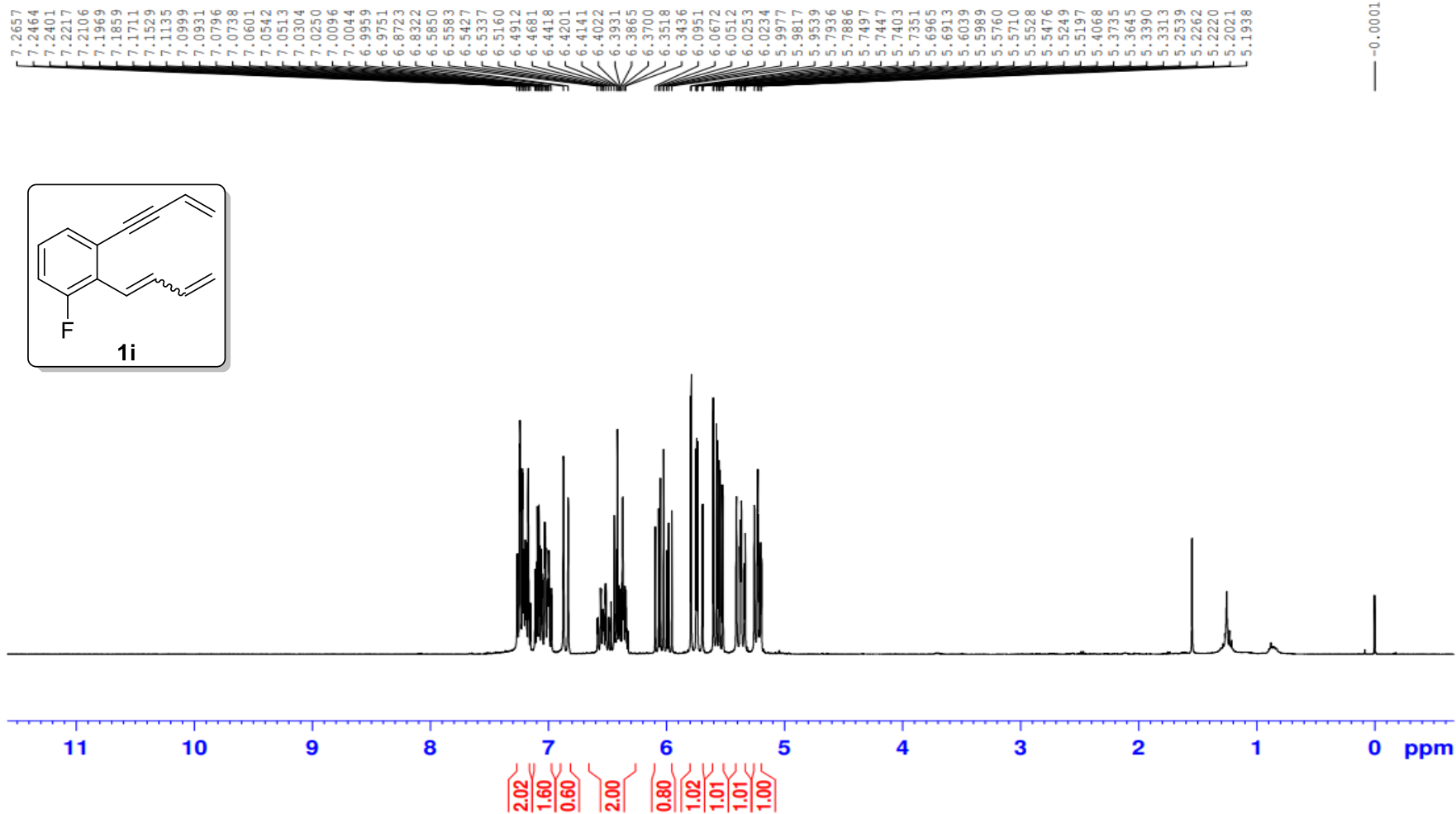
-111.0  
-111.3





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1i

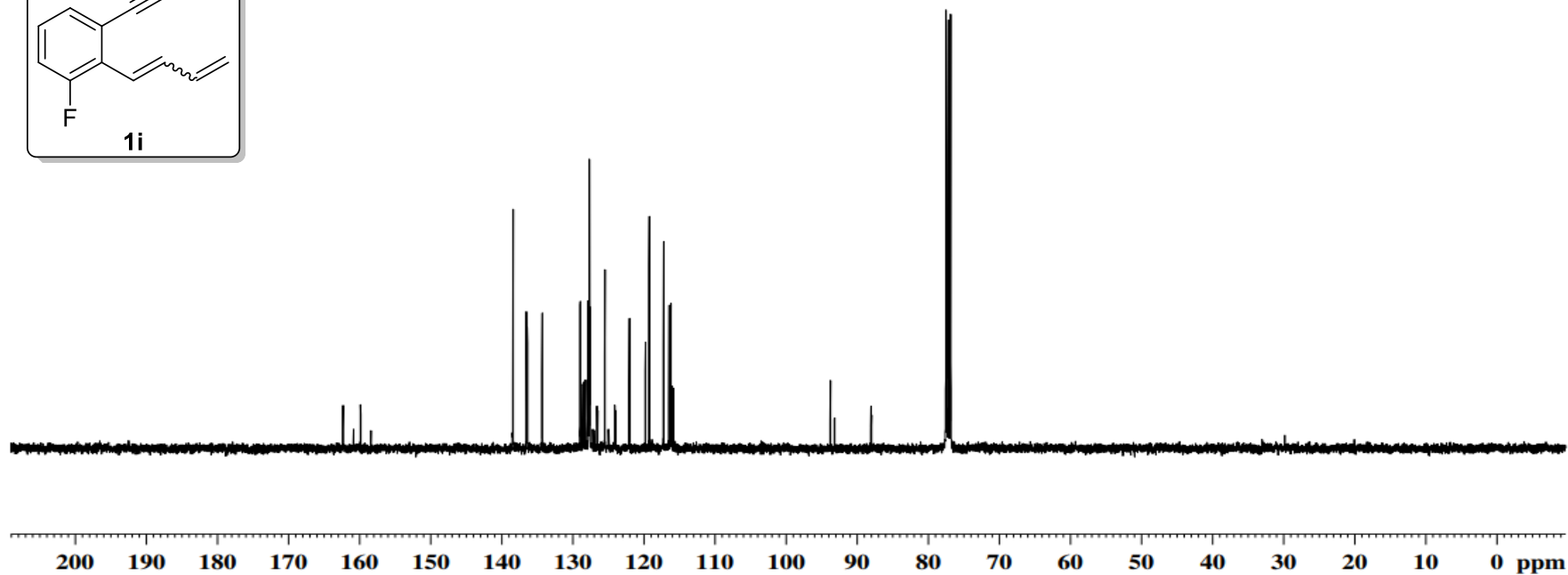
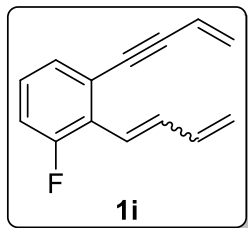
LRR-X210910-6-F-400M(in CDCl<sub>3</sub>)



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra for **1i****

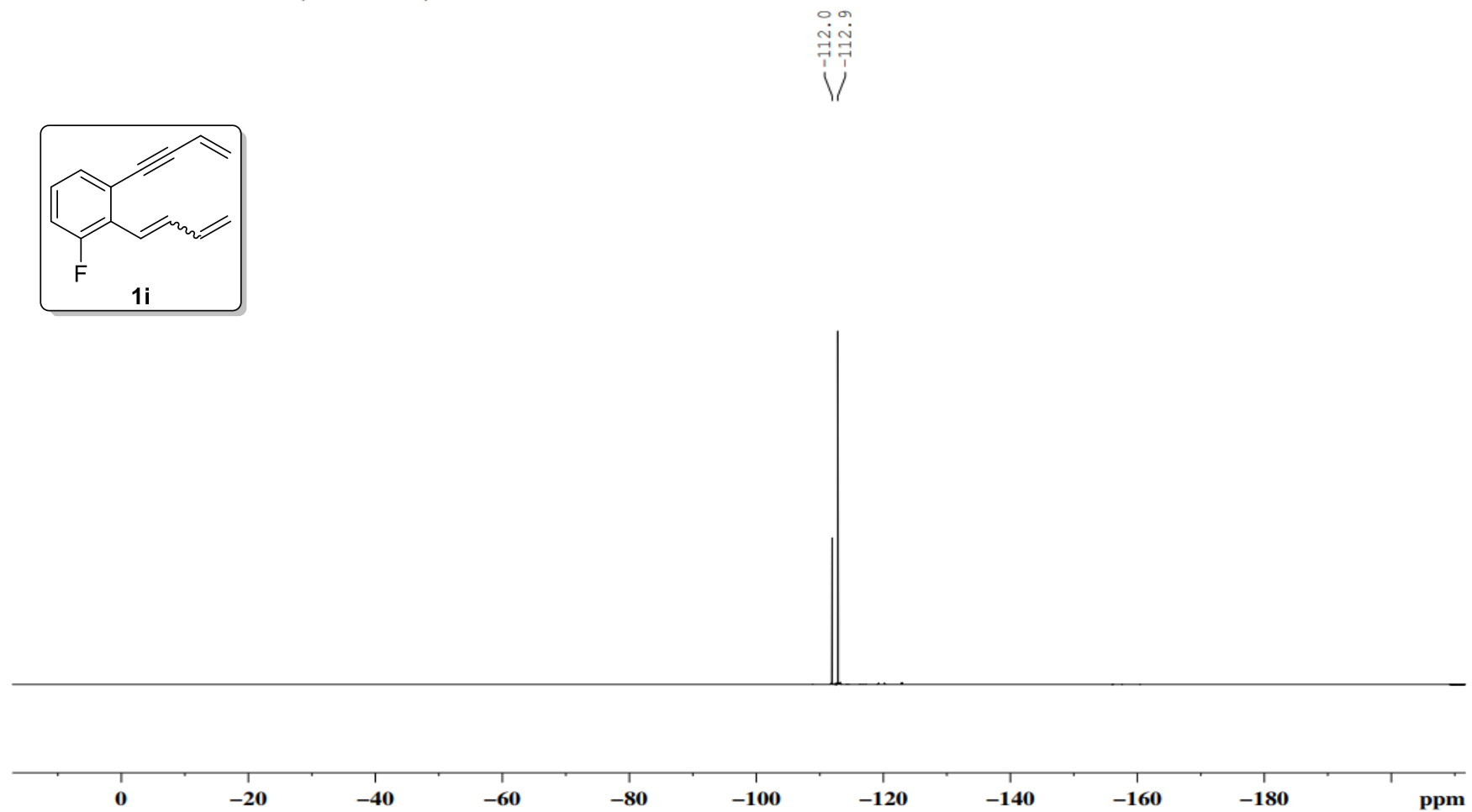
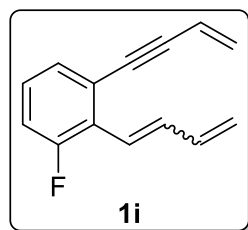
LRR-X220819-6-F-100M(in  $\text{CDCl}_3$ )

162.3  
160.8  
159.8  
158.3  
138.3  
136.5  
136.3  
134.3  
134.2  
128.9  
128.9  
128.5  
128.4  
128.2  
128.1  
127.8  
127.7  
127.6  
127.5  
127.1  
127.0  
126.5  
126.4  
125.4  
124.9  
124.9  
124.0  
124.0  
122.0  
119.7  
119.2  
117.2  
116.4  
116.2  
116.0  
115.8  
93.8  
93.2  
88.1  
88.0  
77.5  
77.2  
76.8



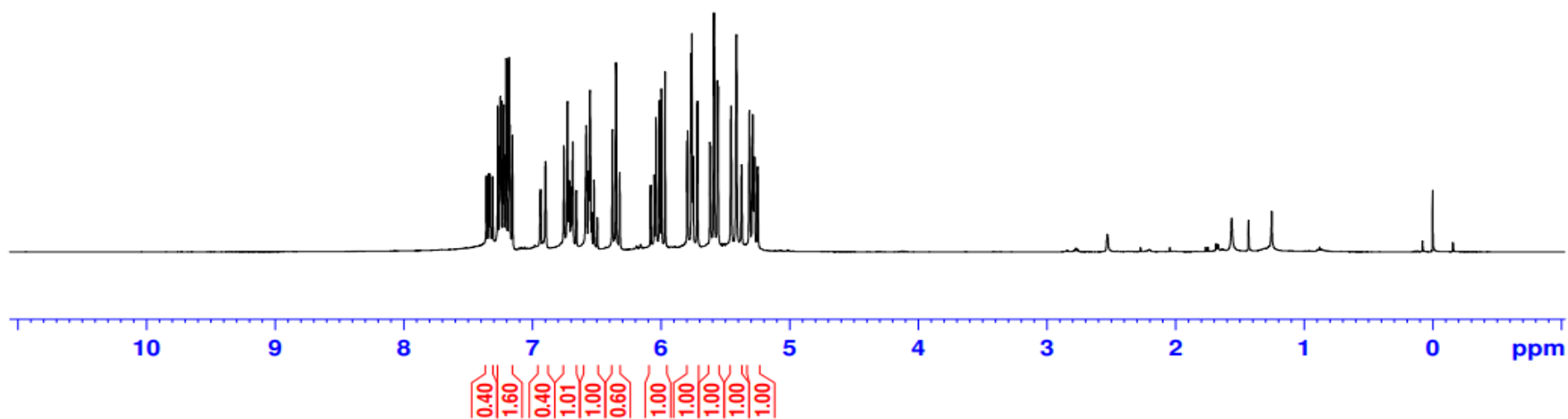
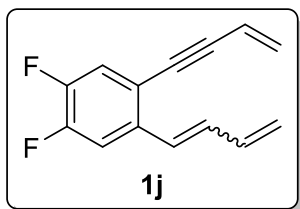
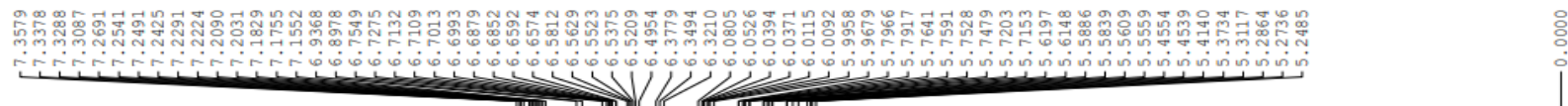
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for **1i****

LRR-X210910-6-F-376M(in  $\text{CDCl}_3$ )



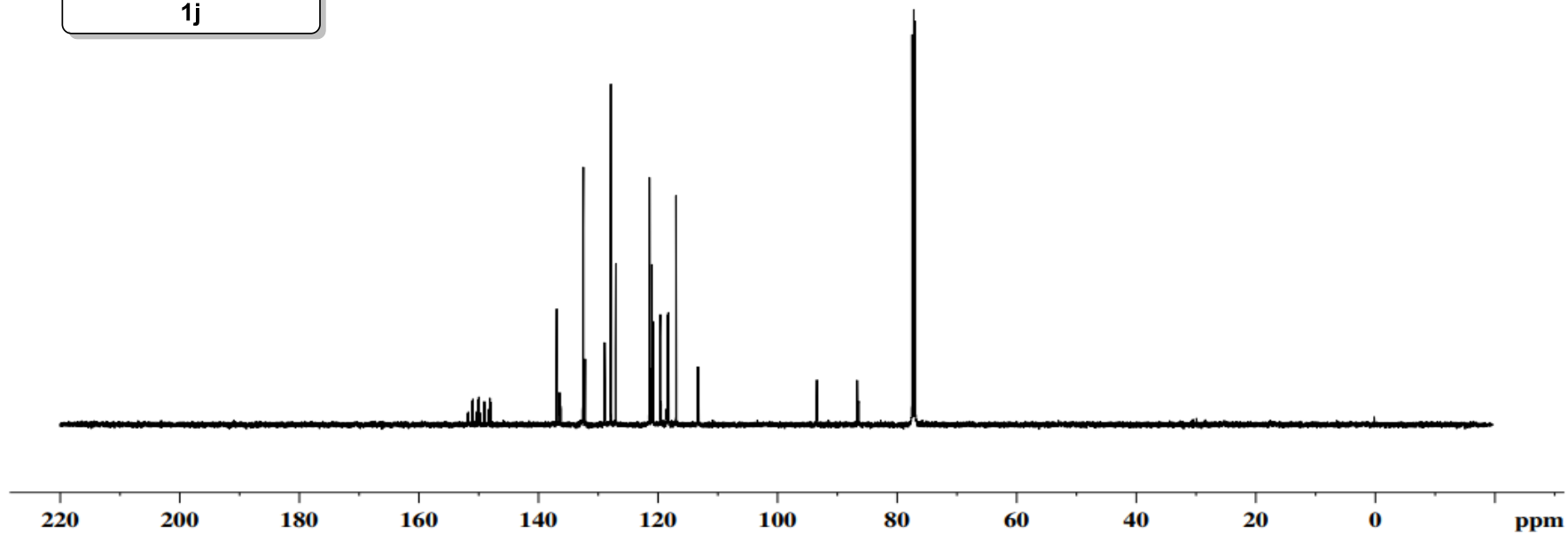
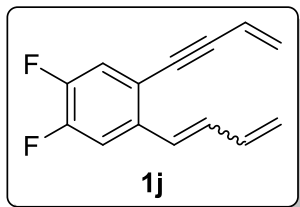
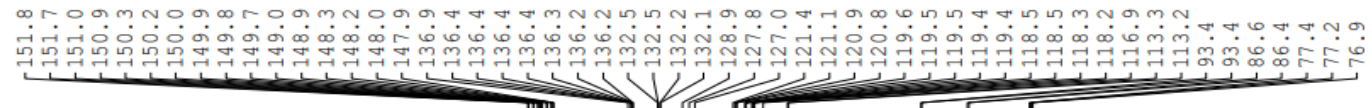
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1j**

LRR-X22X05-2F-400M(in CDCl<sub>3</sub>)



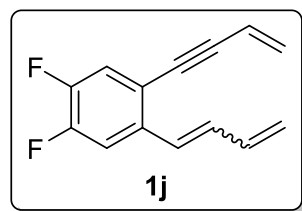
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1j

LRR-X22X05-2F-125M(in CDCl<sub>3</sub>)

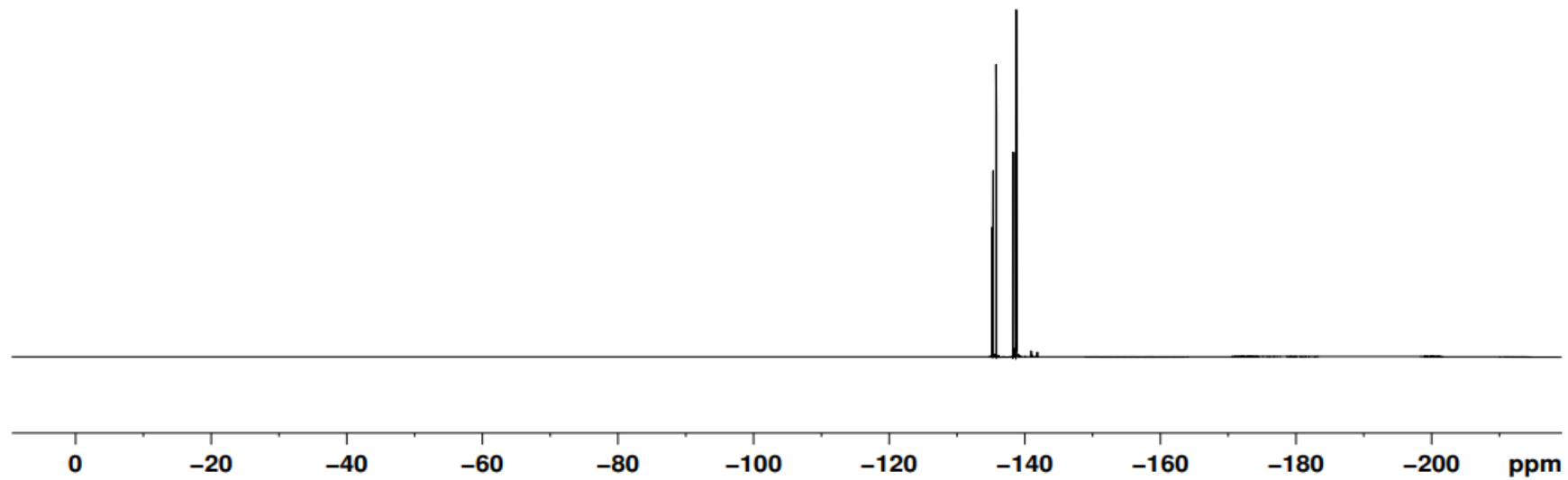


**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectra for 1j**

LRR-X22X05-2F-470M(in  $\text{CDCl}_3$ )

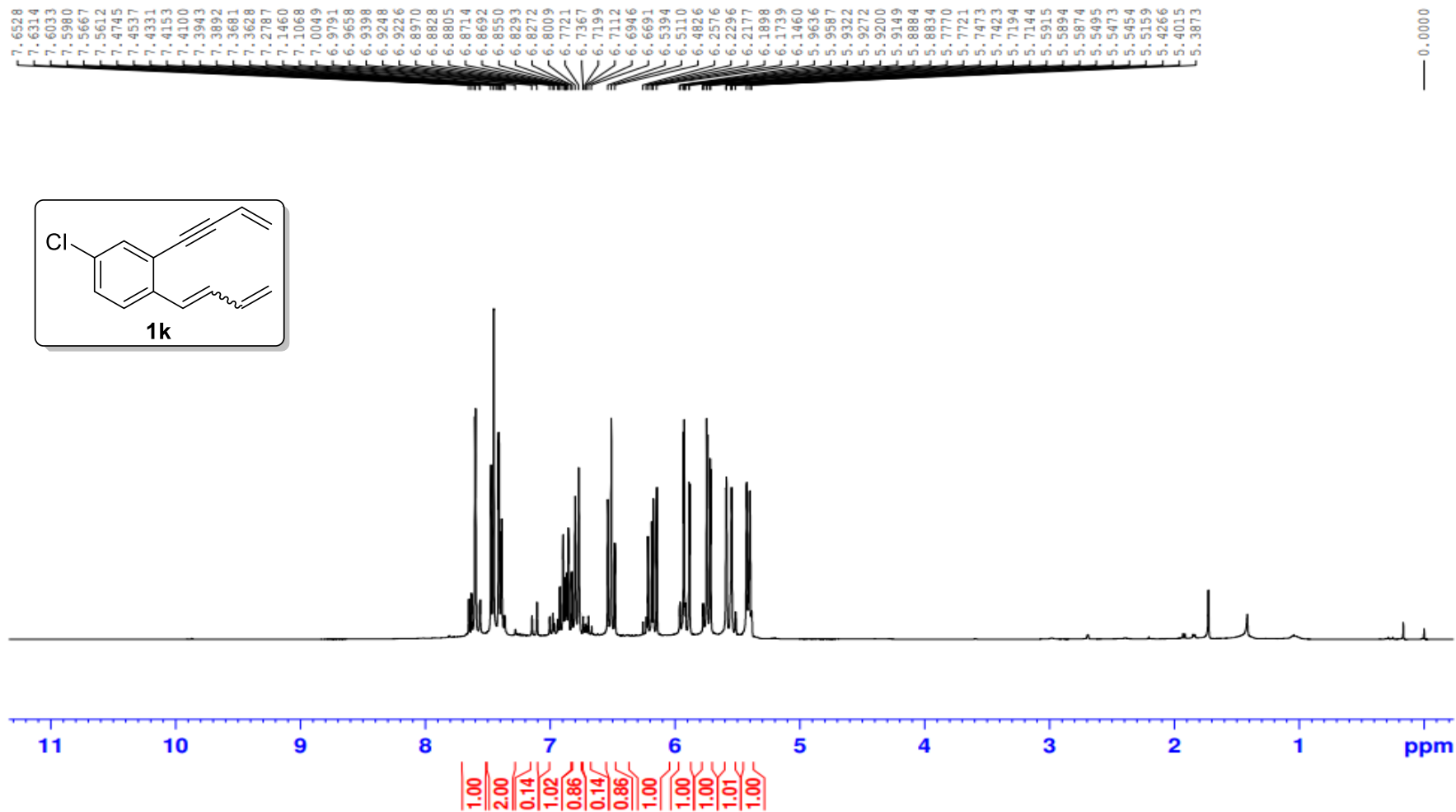


-135.3  
-135.3  
-135.8  
-135.8  
-138.3  
-138.4  
-138.8  
-138.8



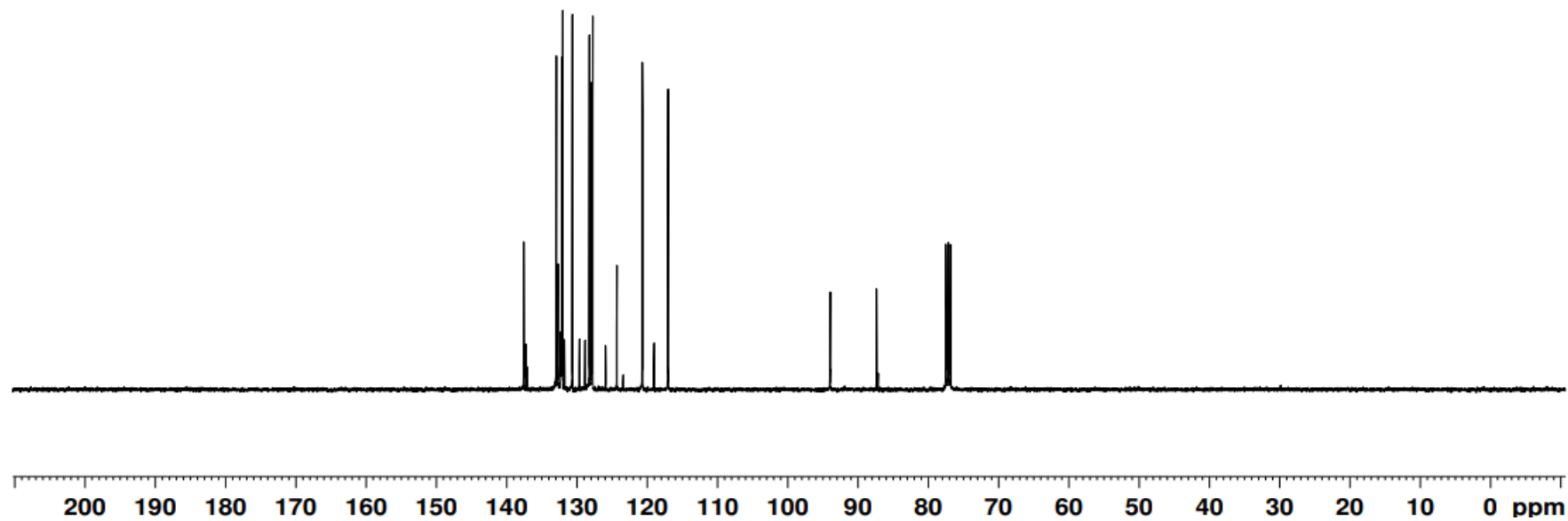
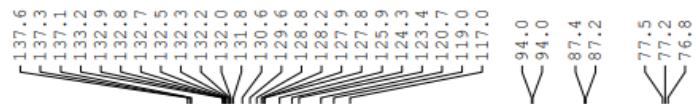
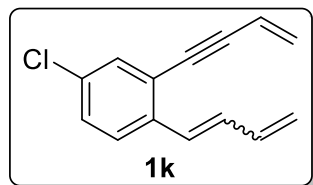
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1k**

LRR-X22X31-4-Cl-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 1k**

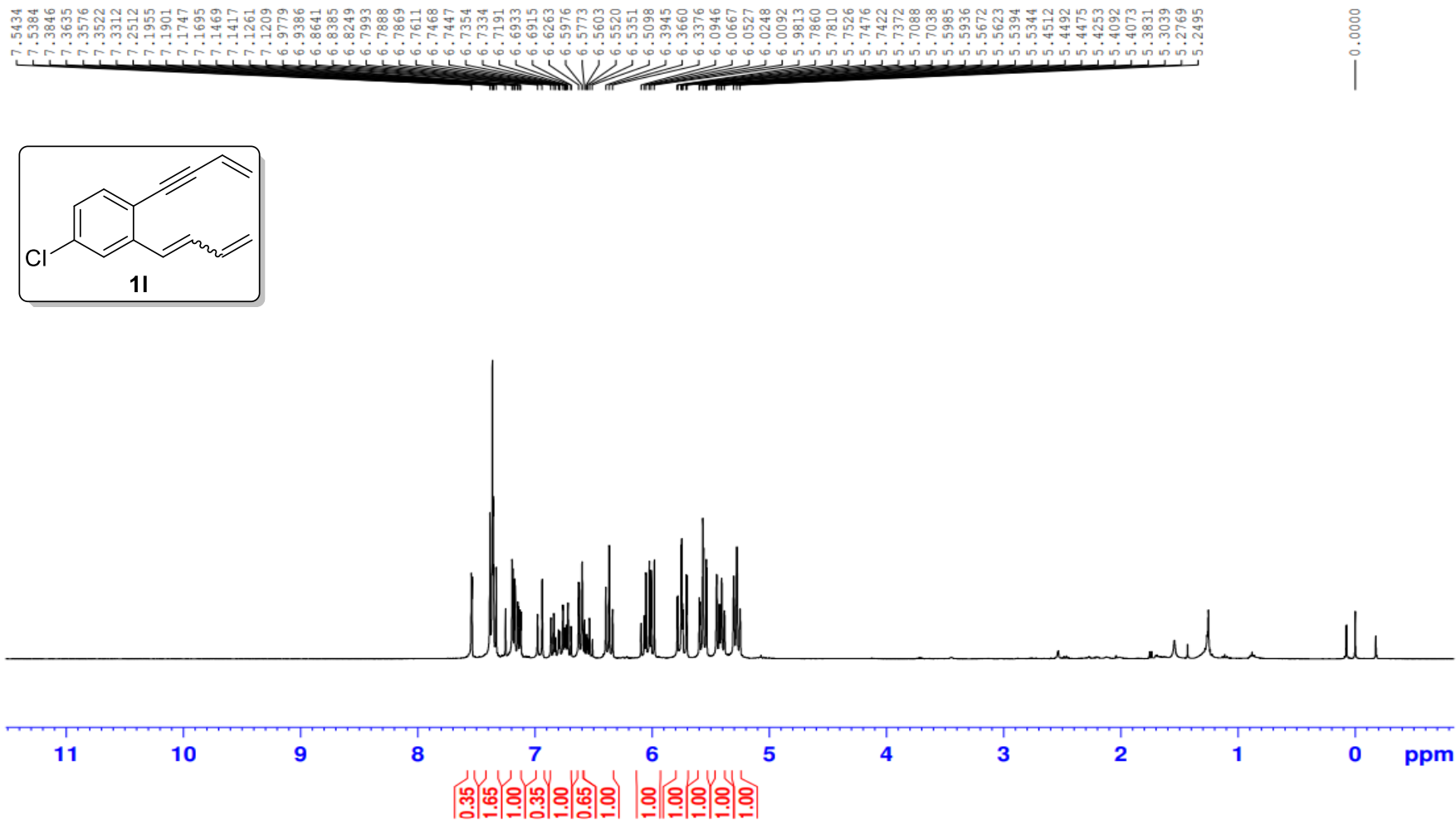
LRR-X22X31-4-Cl-100M(in CDCl<sub>3</sub>)





**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1l**

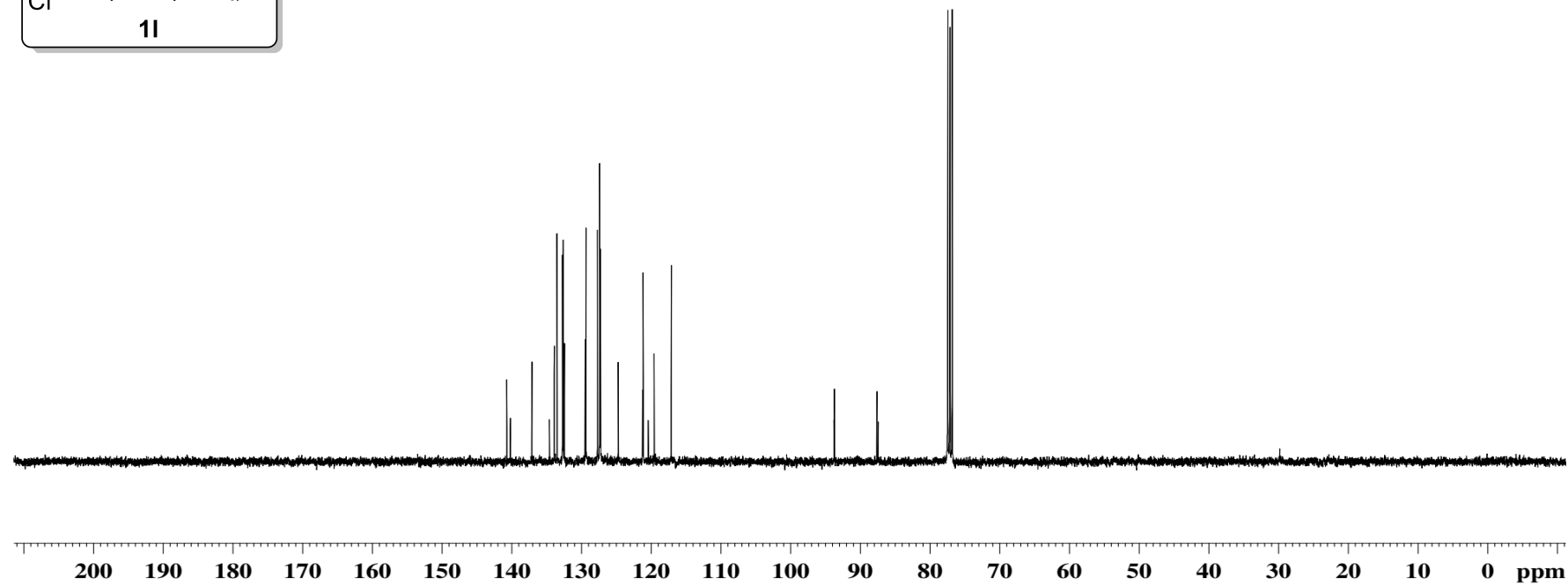
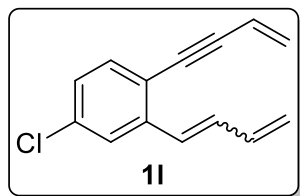
LRR-X210331-5Cl-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 11**

LRR-X210331-1-5-Cl-100M (in CDCl<sub>3</sub>)

140.7  
140.2  
137.1  
134.6  
134.0  
133.9  
133.5  
132.8  
132.7  
132.5  
129.5  
129.4  
127.7  
127.4  
127.3  
124.8  
121.3  
121.2  
120.5  
119.6  
117.2  
93.8  
93.7  
87.7  
87.5  
77.5  
77.2  
76.8

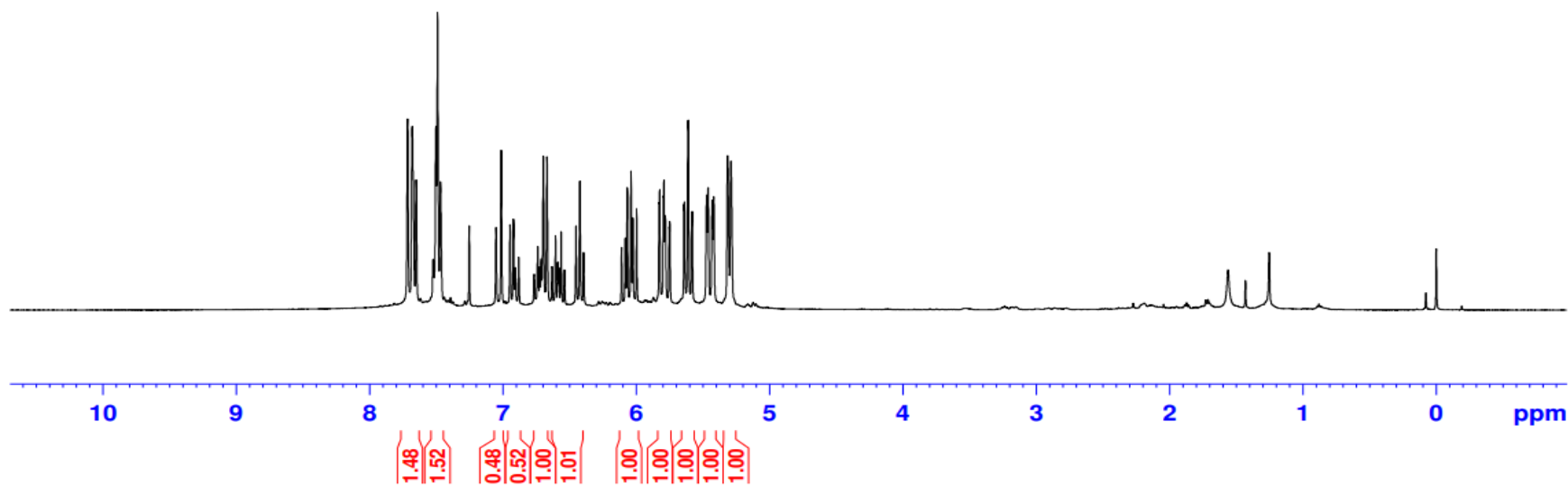
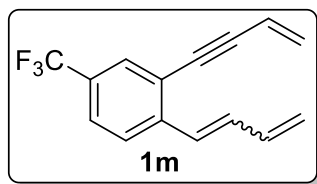


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1m**

LRR-X22X05-1-CF3-400M(in CDCl<sub>3</sub>)

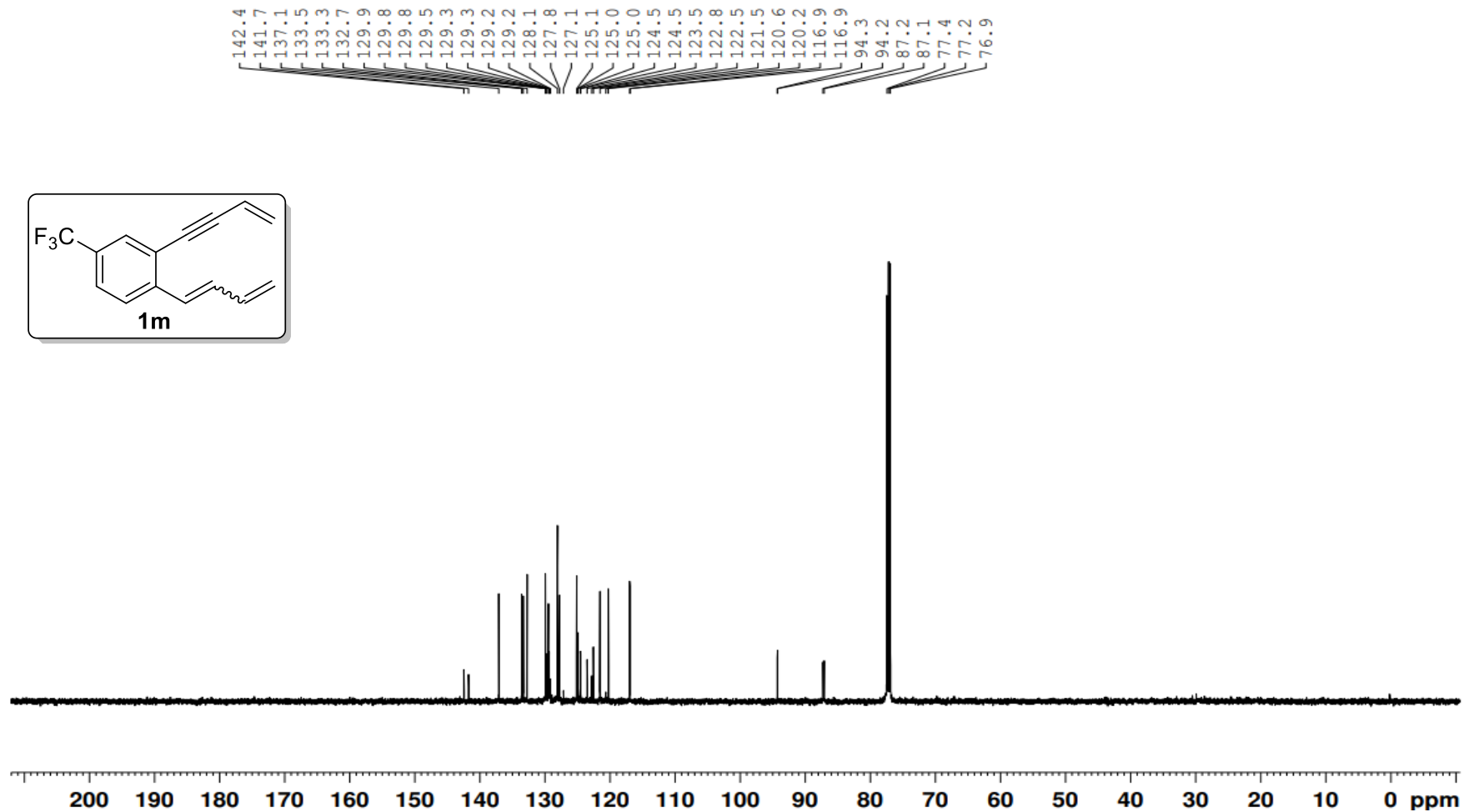
7.7151  
7.6805  
7.6508  
7.5240  
7.5024  
7.4912  
7.4697  
7.2540  
7.0523  
7.0130  
6.9471  
6.9216  
6.9078  
6.8823  
6.7660  
6.7396  
6.7241  
6.7125  
6.6978  
6.6700  
6.6314  
6.6062  
6.5892  
6.5811  
6.5640  
6.5387  
6.4522  
6.4235  
6.3952  
6.1106  
6.0827  
6.0676  
6.0397  
6.0261  
5.9981  
5.8277  
5.8249  
5.7958  
5.7927  
5.7857  
5.7811  
5.7521  
5.7490  
5.6415  
5.6385  
5.6131  
5.6109  
5.6089  
5.5838  
5.5805  
5.4731  
5.4613  
5.4312  
5.4191  
5.3149  
5.2905

0.0000



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 1m**

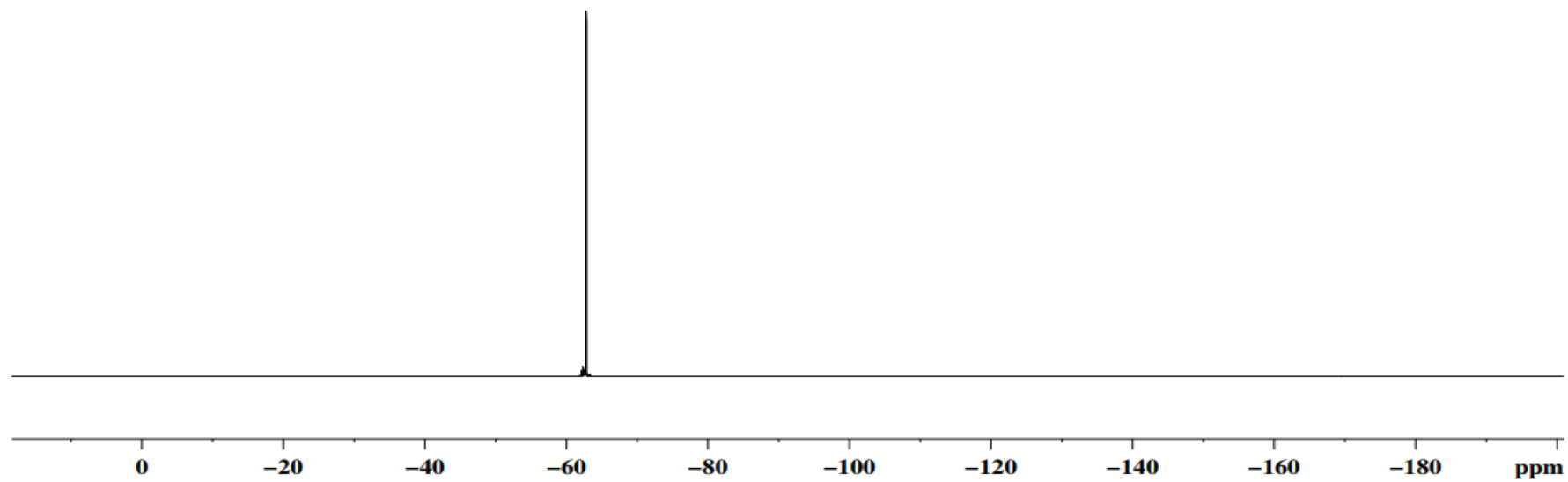
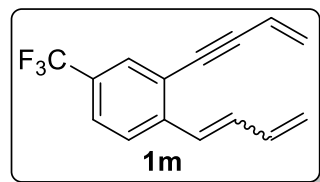
LRR-X22X05-1-CF3-125M(in CDCl<sub>3</sub>)



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 1m**

LRR-X22X05-1-CF3-376M(in  $\text{CDCl}_3$ )

-62.8  
-62.8



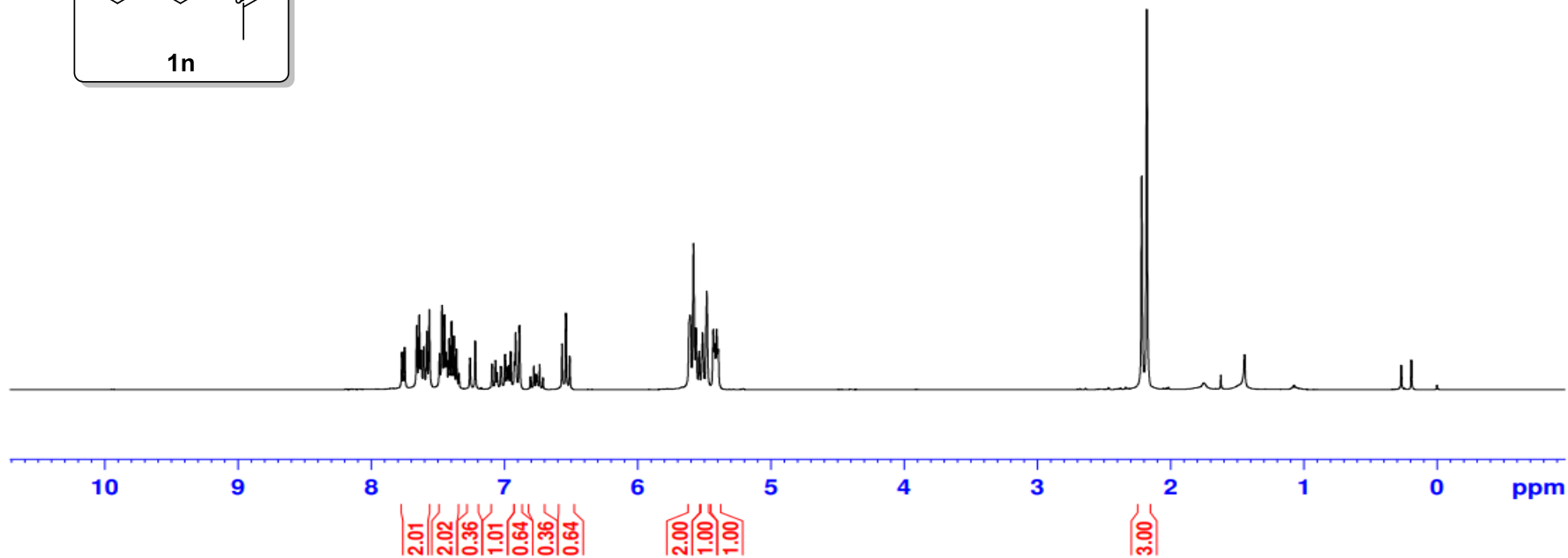
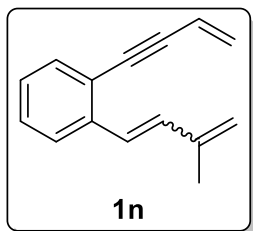
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1n

LRR-X210416-9-400M(in CDCl<sub>3</sub>)

7.7697  
7.7500  
7.6584  
7.6394  
7.6255  
7.6062  
7.5833  
7.5642  
7.4871  
7.4697  
7.4516  
7.4396  
7.4160  
7.3974  
7.3790  
7.3604  
7.3417  
7.2594  
7.2201  
7.0941  
7.0681  
7.0548  
7.0282  
7.0245  
6.9962  
6.9804  
6.9692  
6.9540  
6.9267  
6.9165  
6.8878  
6.8049  
6.7795  
6.7626  
6.7540  
6.7372  
6.7117  
6.6799  
6.5395  
6.5111  
5.6078  
5.5812  
5.5628  
5.5390  
5.5136  
5.4824  
5.4324  
5.4207  
5.4073  
5.3960

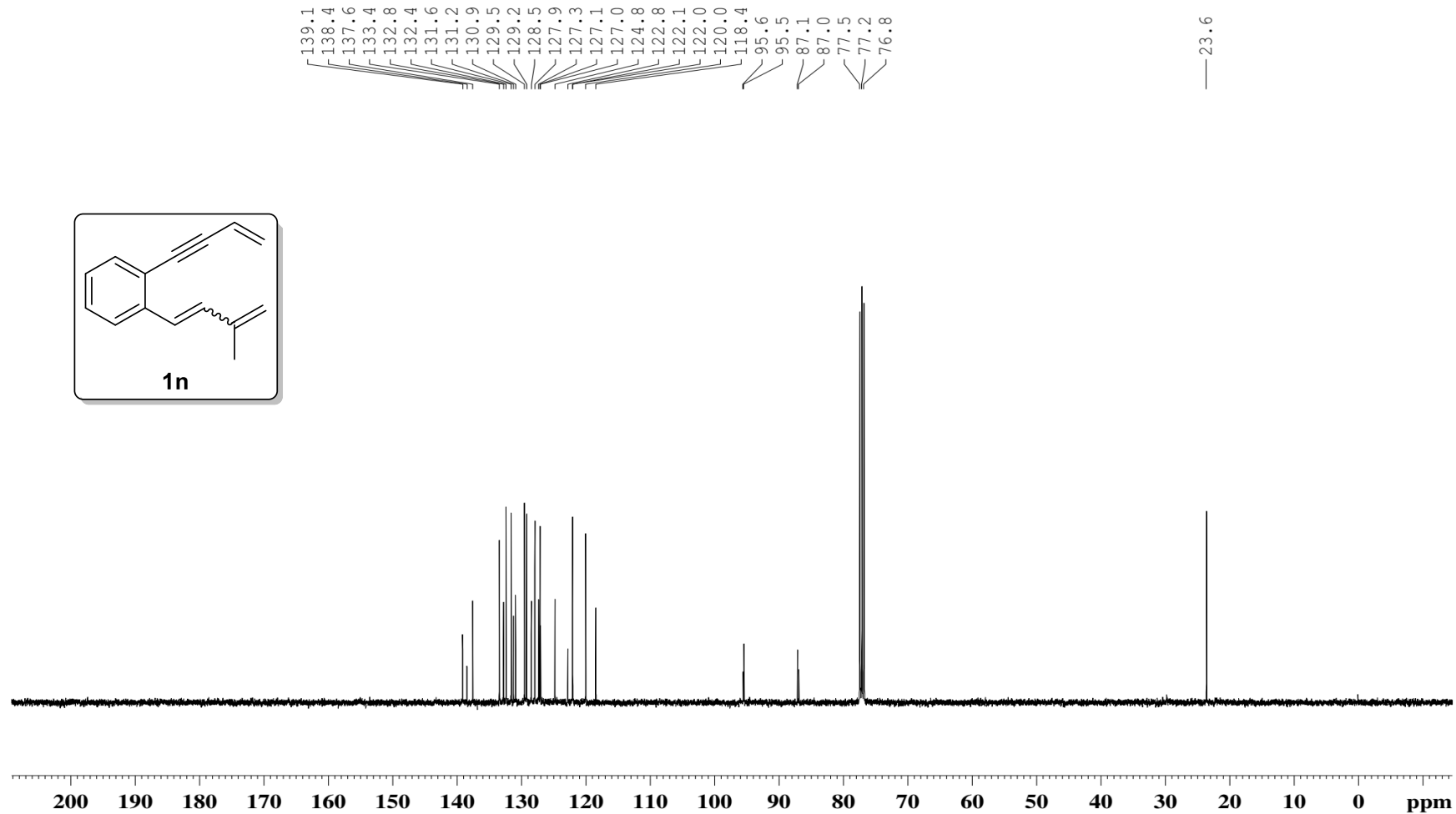
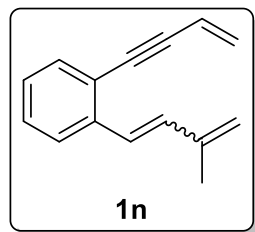
2.2171  
2.1793

0.0000



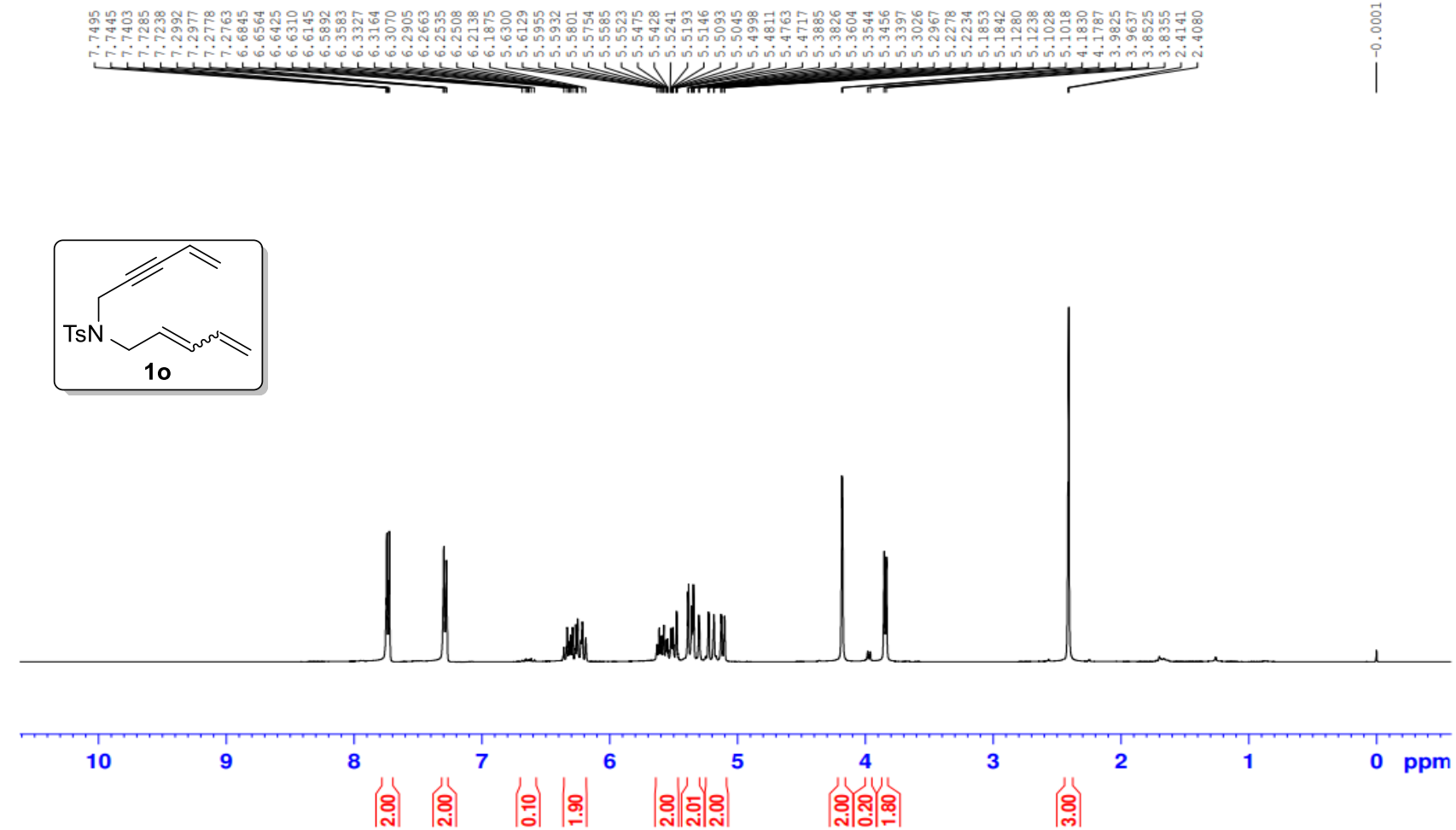
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra for 1n**

LRR-X210416-9-XI-CH3-1000M (in  $\text{CDCl}_3$ )



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1o

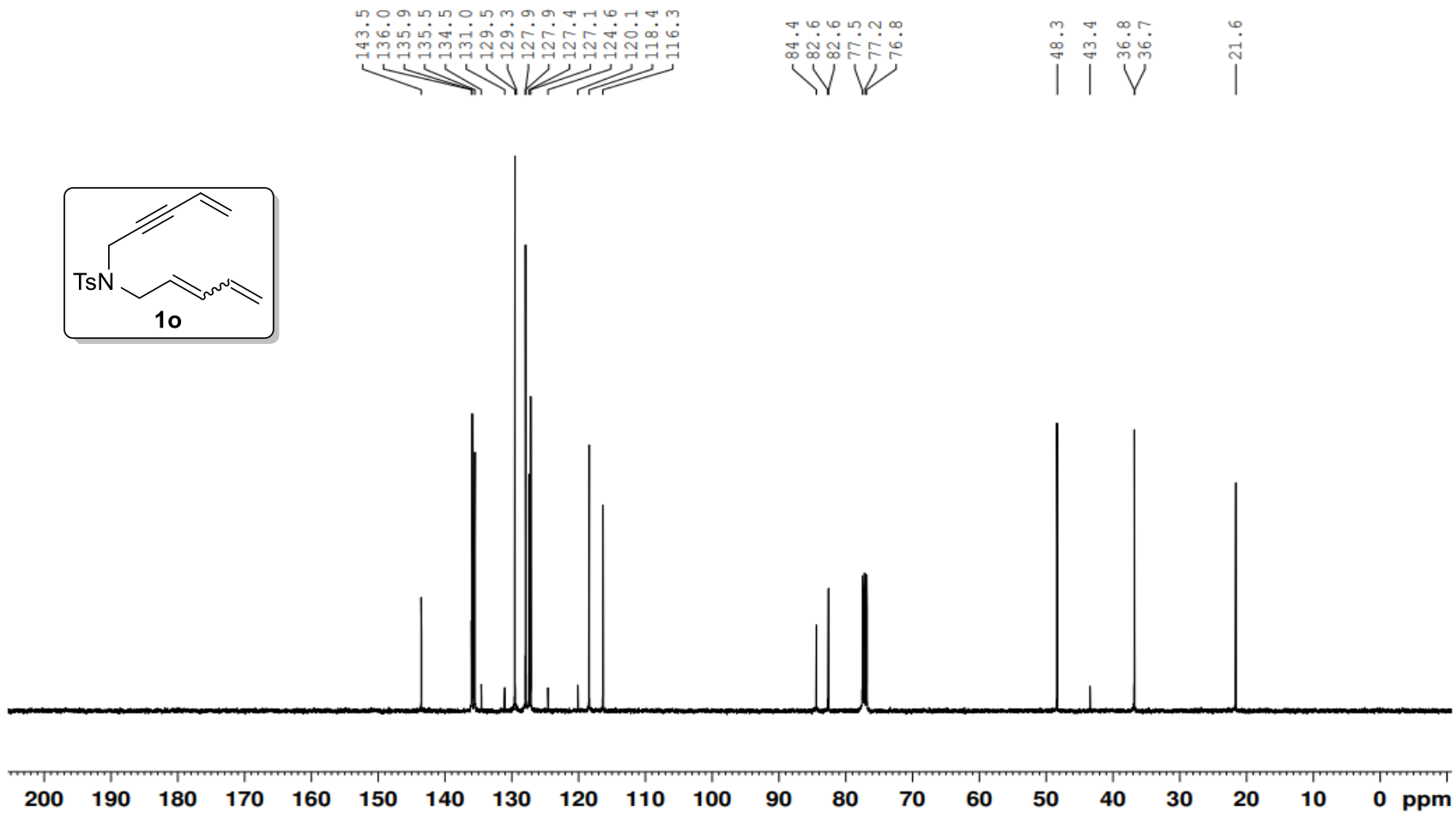
LRR-X220926-NTS-400M(in CDCl<sub>3</sub>)





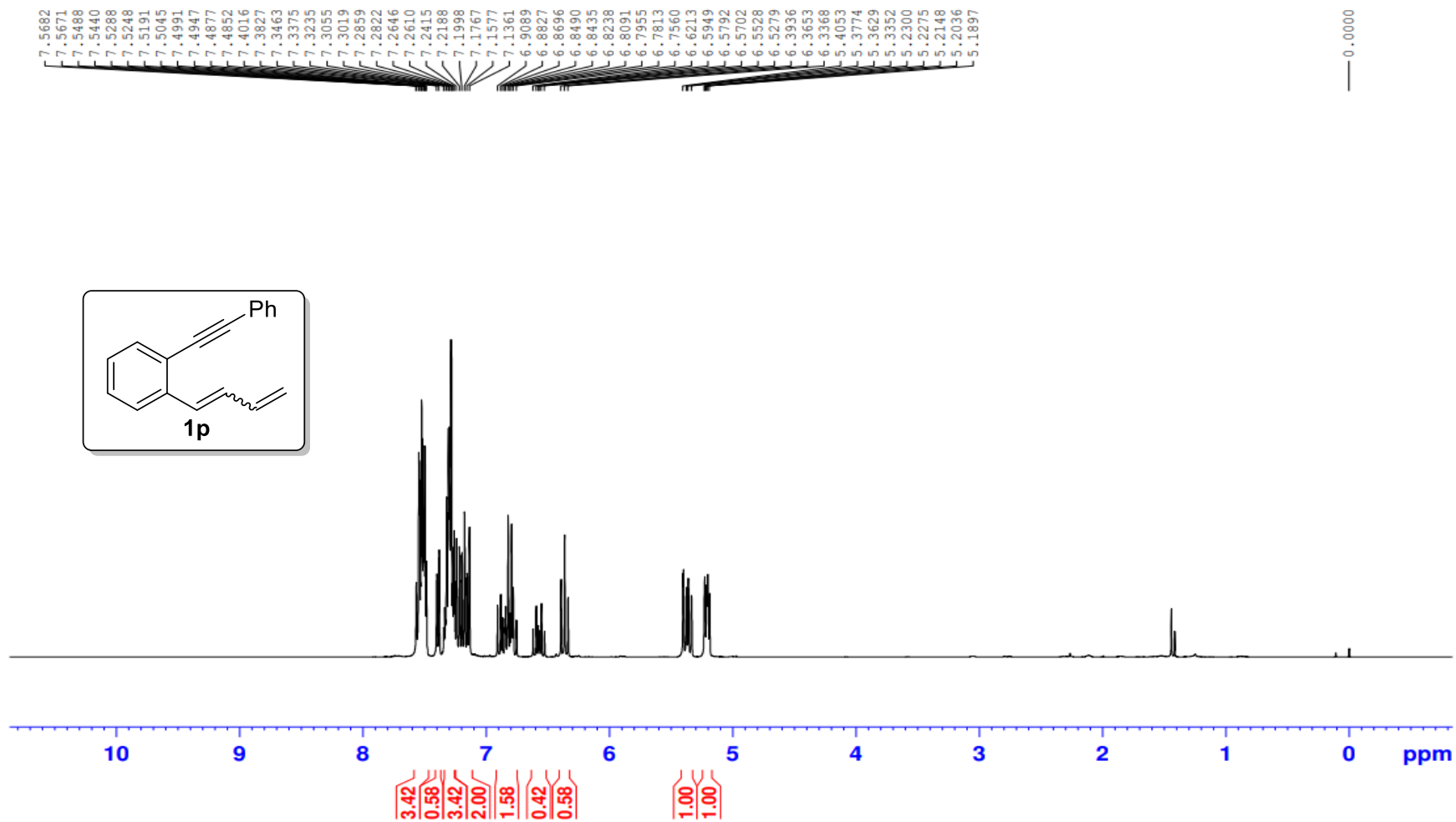
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 1o**

LRR-X220926-NTS-100M(in CDCl<sub>3</sub>)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 1p**

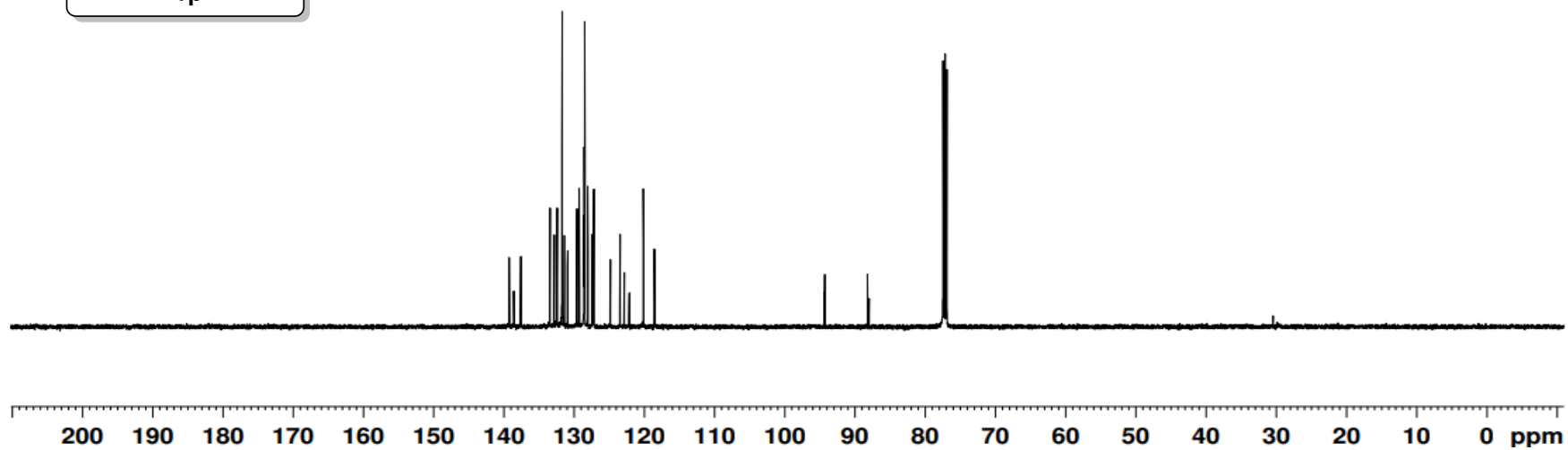
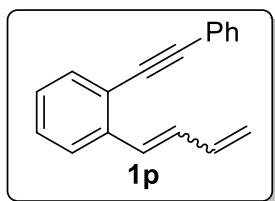
LRR-X210902-1-400M(in CDCl<sub>3</sub>)



**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra for 1p**

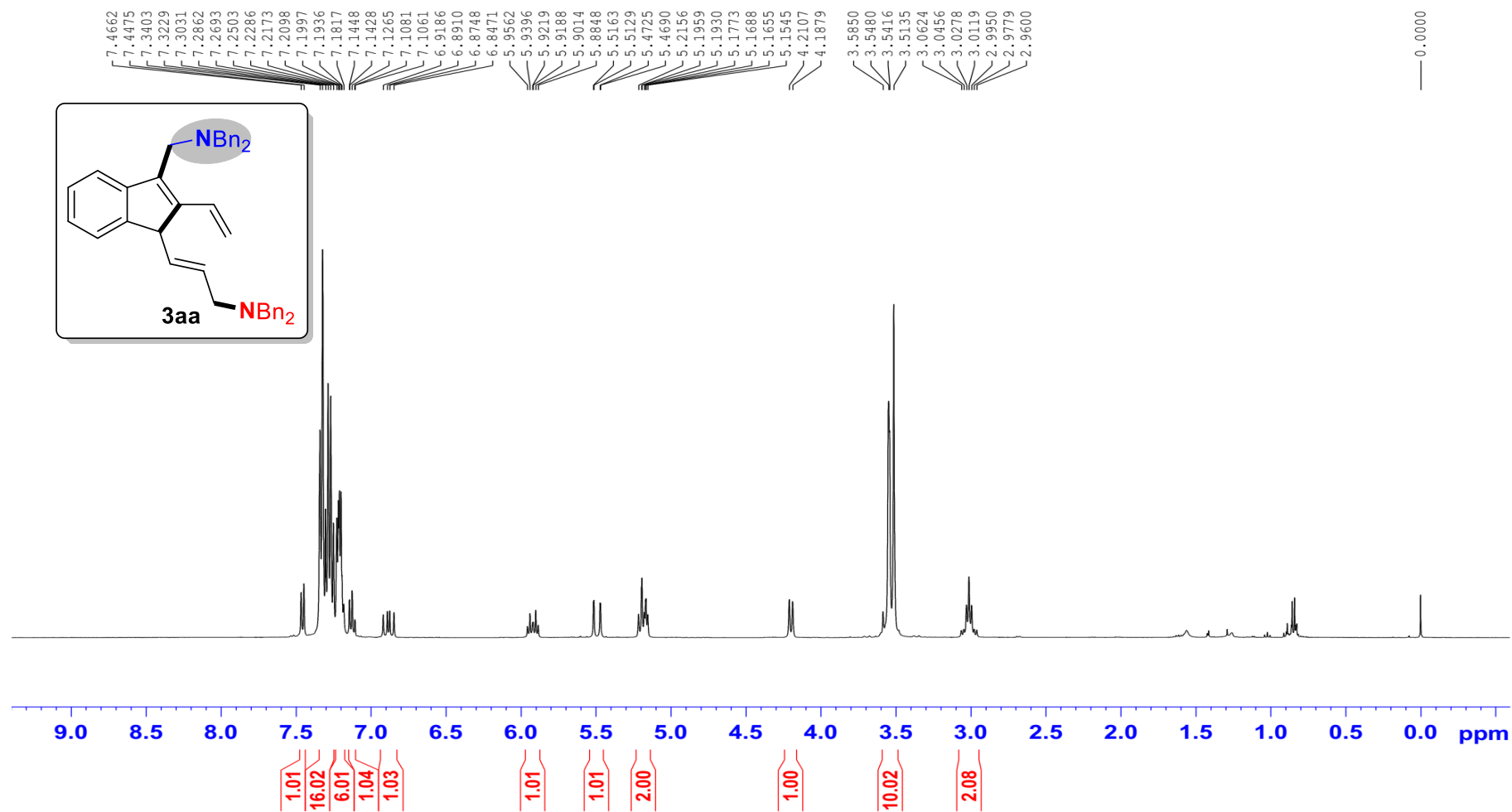
LRR-X22Z14-PH-125M(in  $\text{CDCl}_3$ )

139.2  
138.6  
137.6  
133.4  
132.8  
132.4  
131.7  
131.7  
131.4  
130.9  
129.6  
129.2  
128.6  
128.5  
128.5  
128.5  
128.4  
128.0  
127.4  
127.2  
124.8  
123.4  
122.8  
122.1  
120.1  
118.5  
94.4  
94.3  
88.2  
88.0  
77.4  
77.2  
76.9



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3aa**

YHJ-X210120-2-6 (in CDCl<sub>3</sub>)



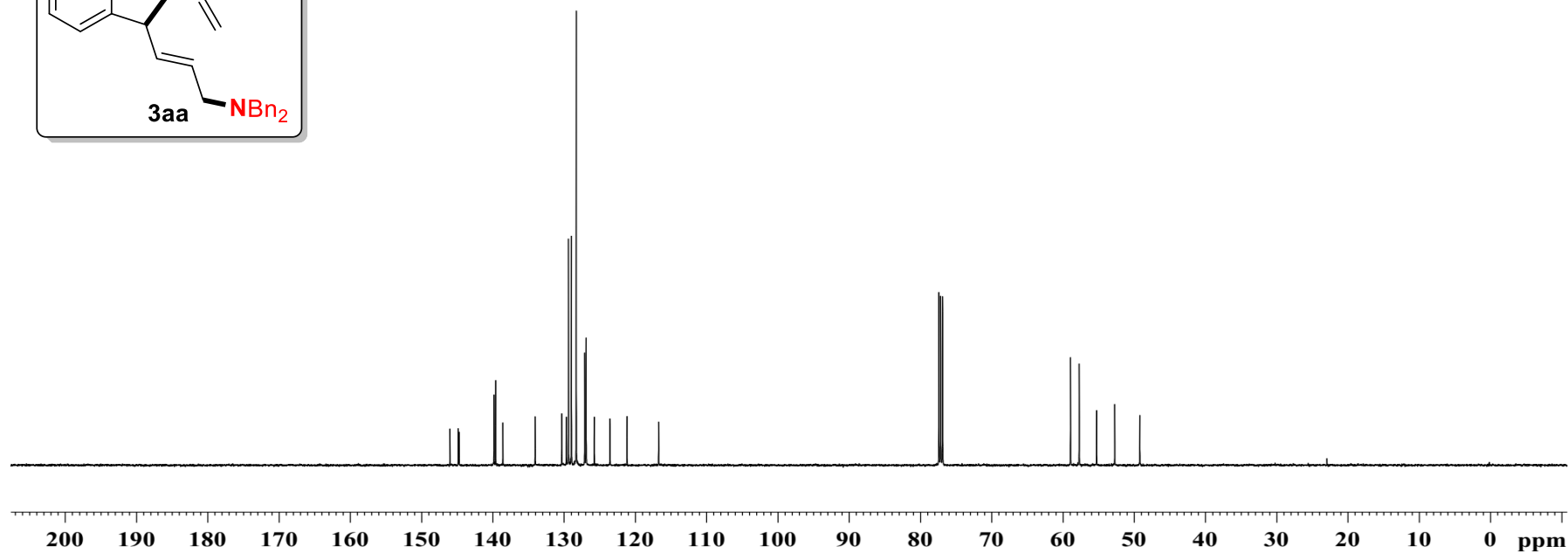
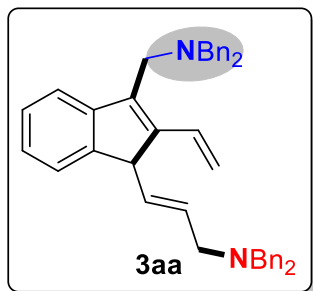
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3aa**

YHJ-X210120-2-6 (in CDCl<sub>3</sub>)

146.0  
144.8  
144.7  
139.8  
139.6  
138.6  
134.0  
130.3  
129.7  
129.4  
129.0  
128.3  
127.1  
126.9  
125.8  
123.6  
121.2  
116.8

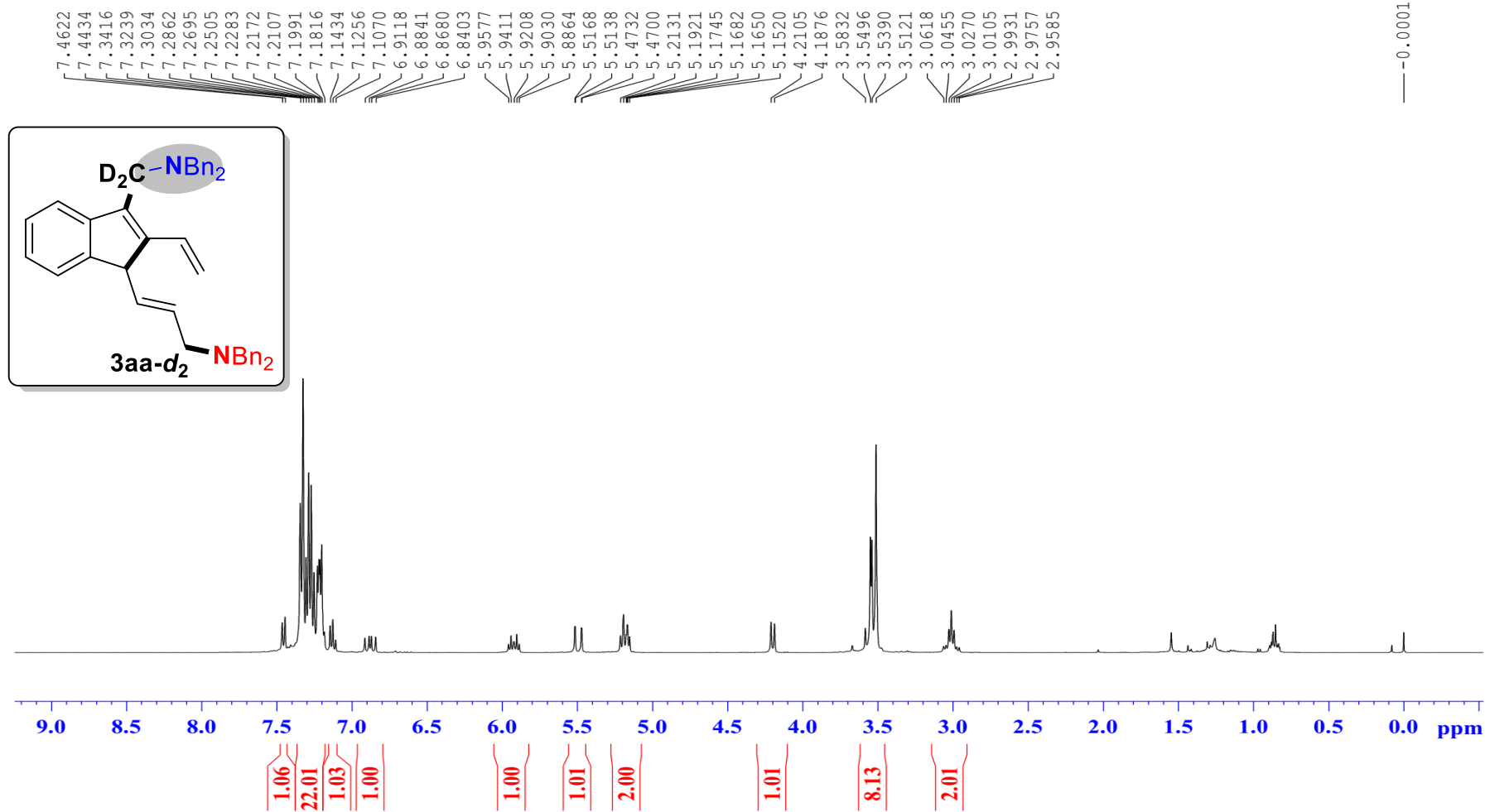
77.4  
77.2  
76.9

59.0  
57.7  
55.3  
52.7  
49.2



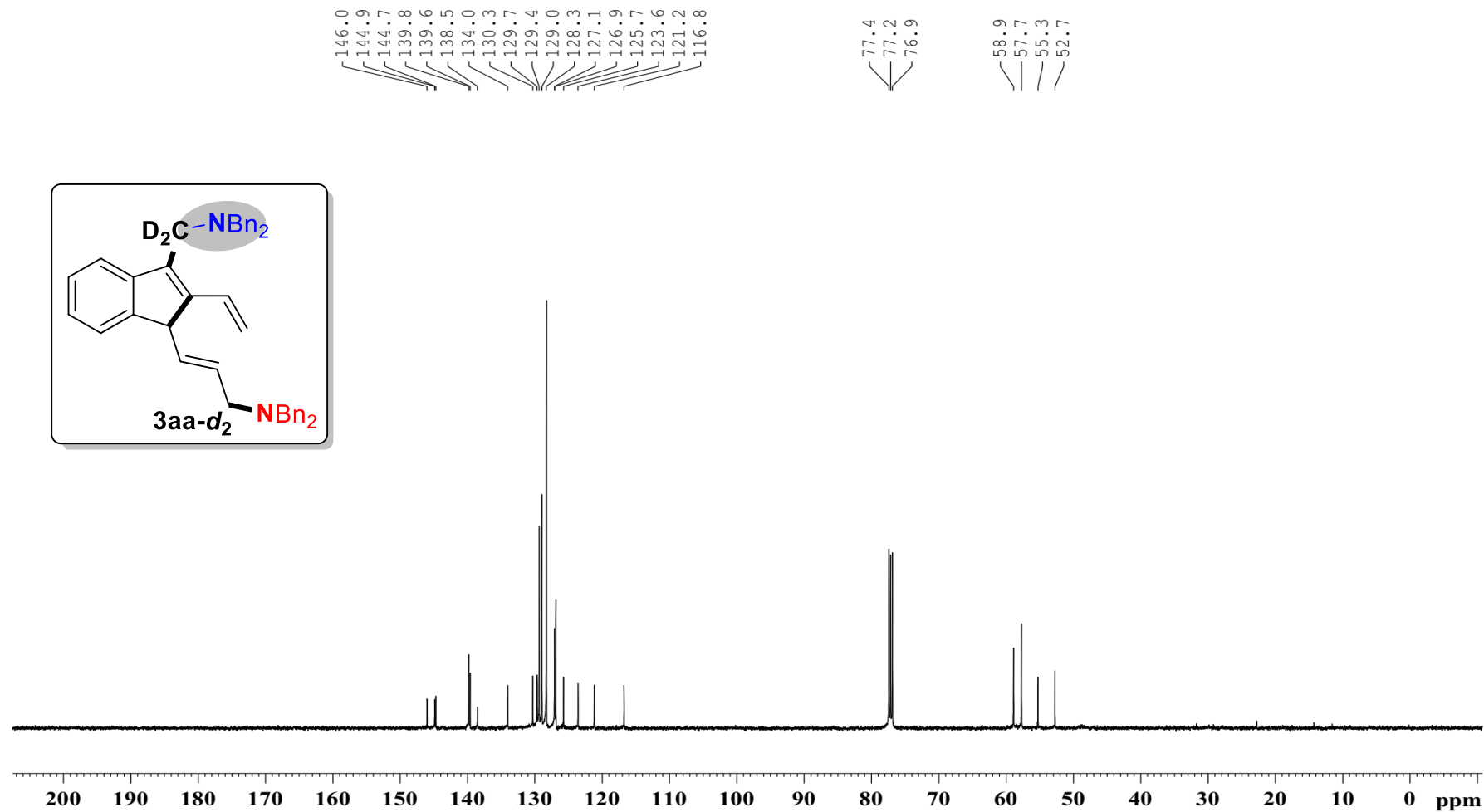
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3aa-d<sub>2</sub>**

YBK-X210414-2-D (in CDCl<sub>3</sub>)



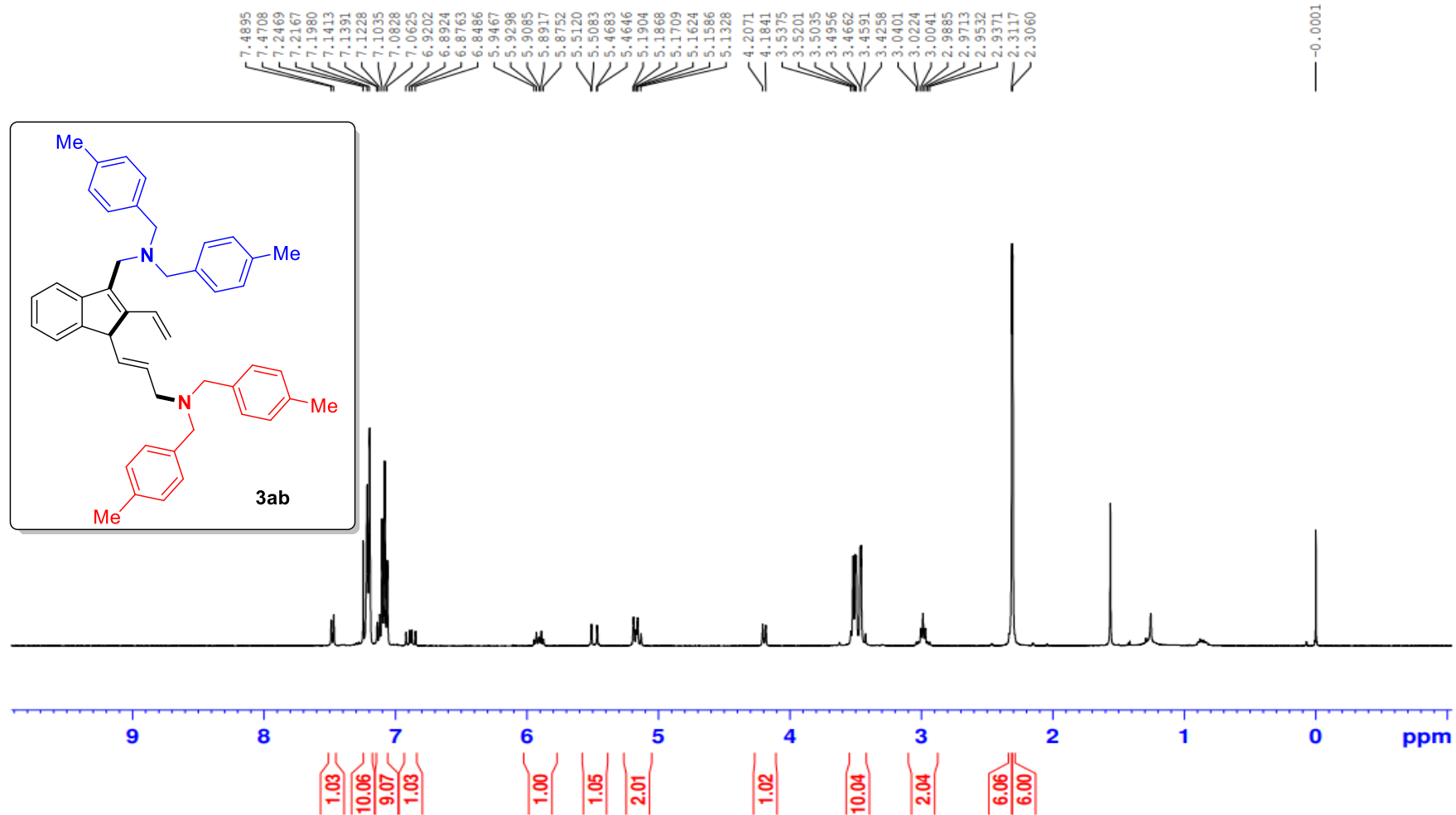
**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra for 3aa- $d_2$**

YBK-X210416-2-D (in  $\text{CDCl}_3$ )



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ab**

YHJ-X210202-1-4CH3-400M(in CDCl<sub>3</sub>)

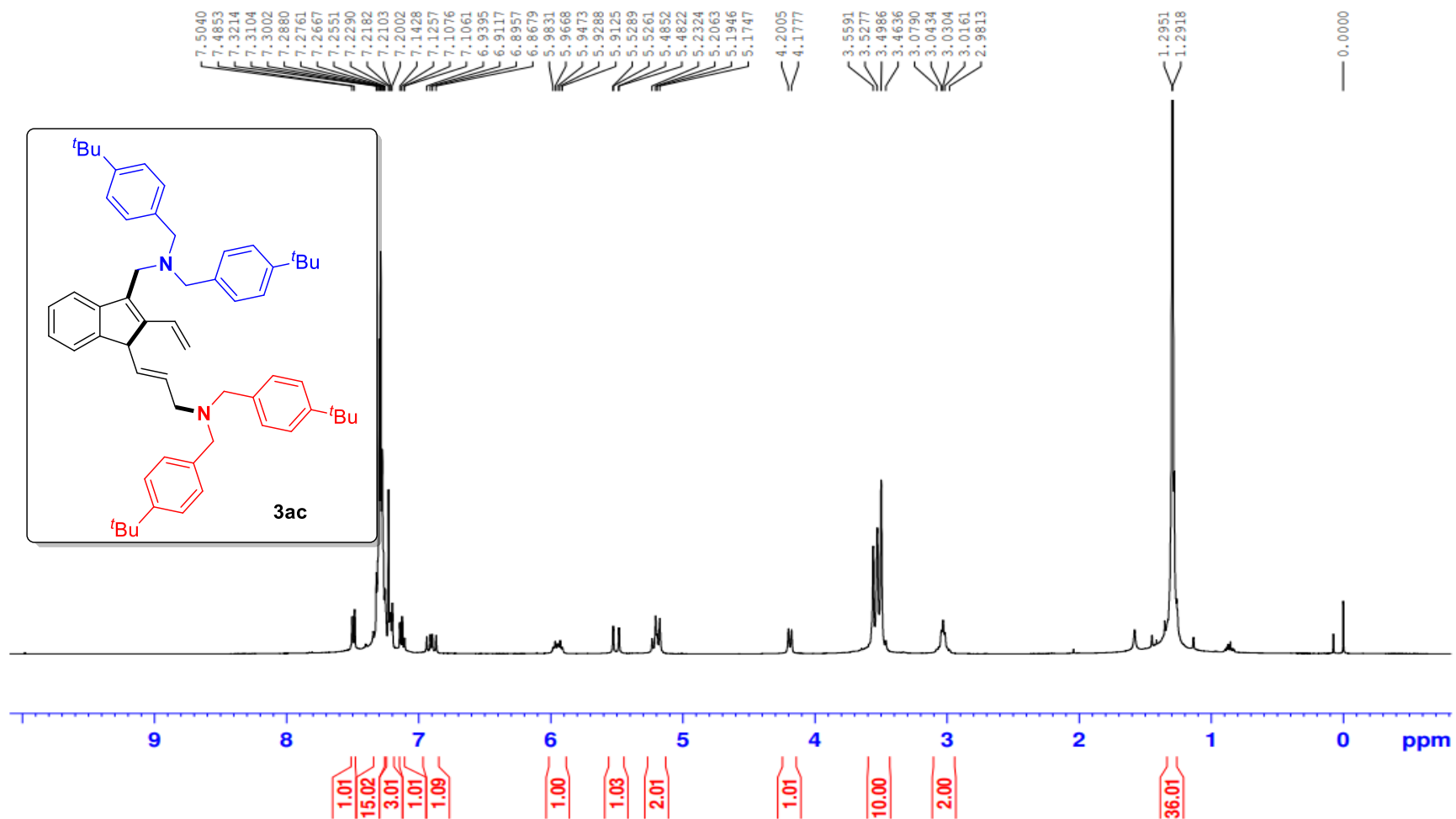






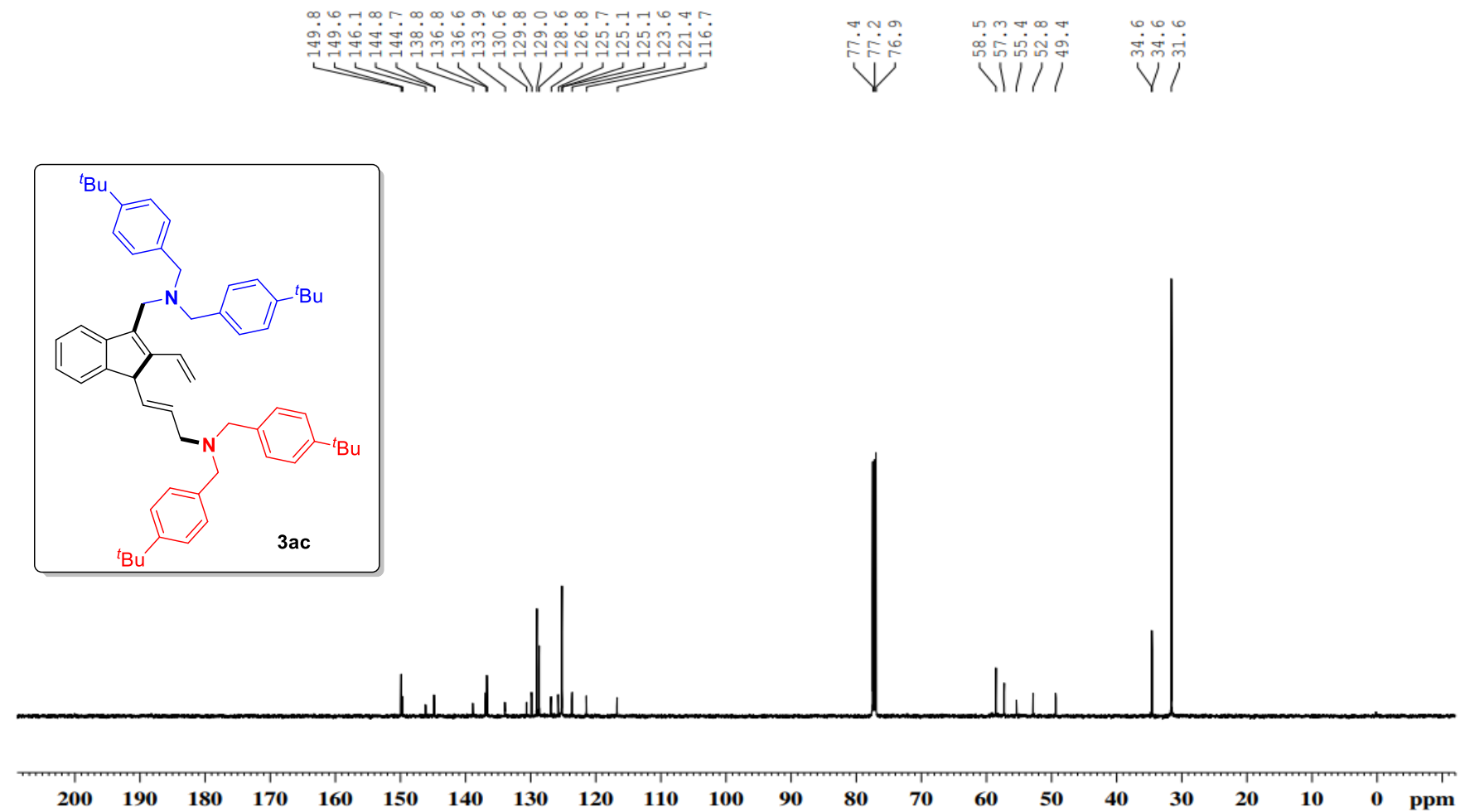
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ac

LRR-X220925-4nBu-500M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ac**

LRR-X220925-4-tBu-125M(in CDCl<sub>3</sub>)

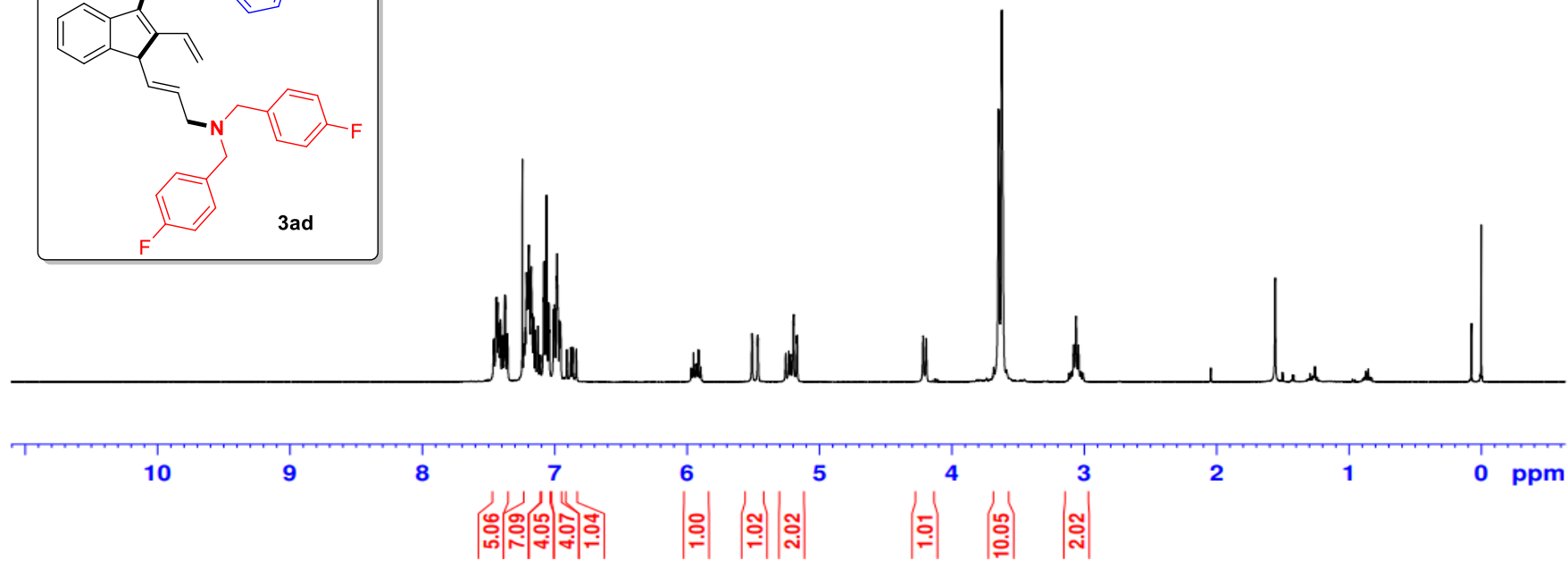
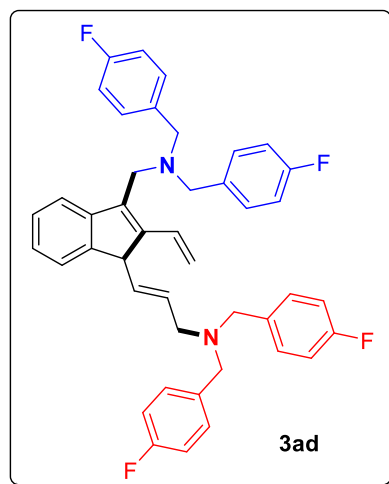


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ad

YBK-X210202-1-1-400M(in CDCl<sub>3</sub>)



—0.0001



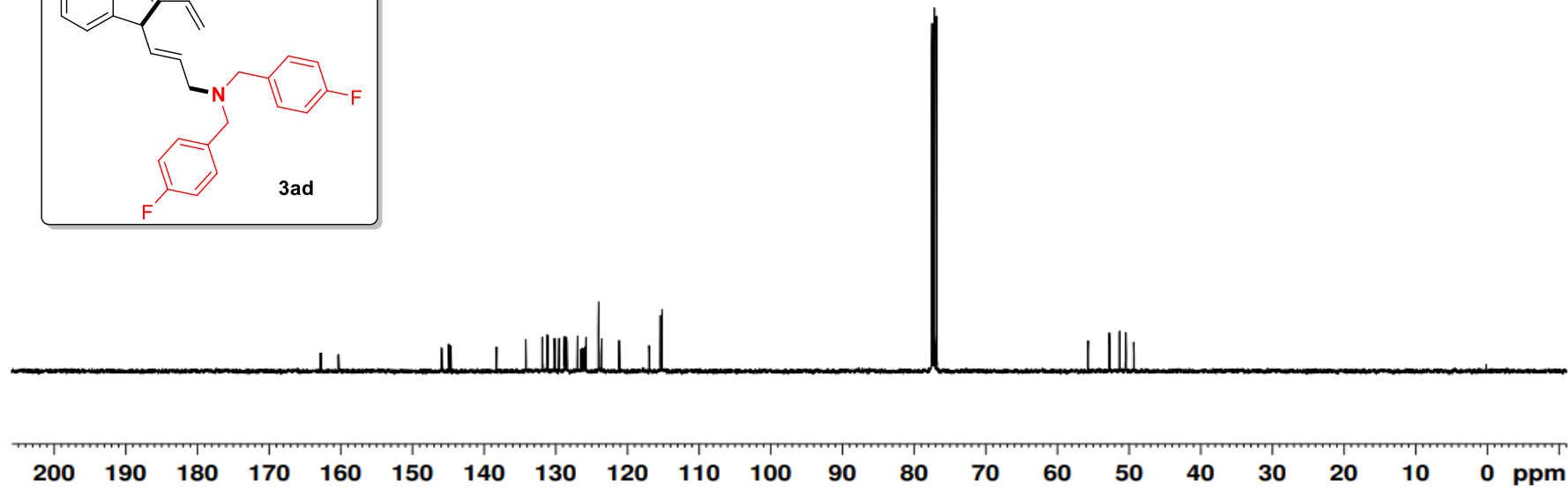
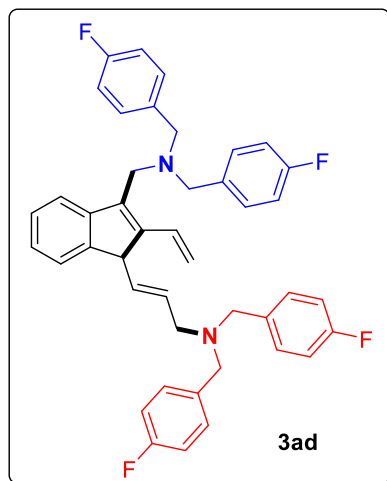
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ad

YHJ-X210202-1-1-100M(in CDCl<sub>3</sub>)

162.8  
162.7  
160.3  
160.3  
145.9  
144.9  
144.6  
138.3  
134.2  
131.9  
131.8  
131.2  
131.1  
130.1  
129.5  
128.8  
128.7  
128.5  
128.4  
126.9  
126.4  
126.3  
126.1  
126.0  
125.8  
124.0  
124.0  
121.1  
116.9  
115.4  
115.1

77.5  
77.2  
76.8

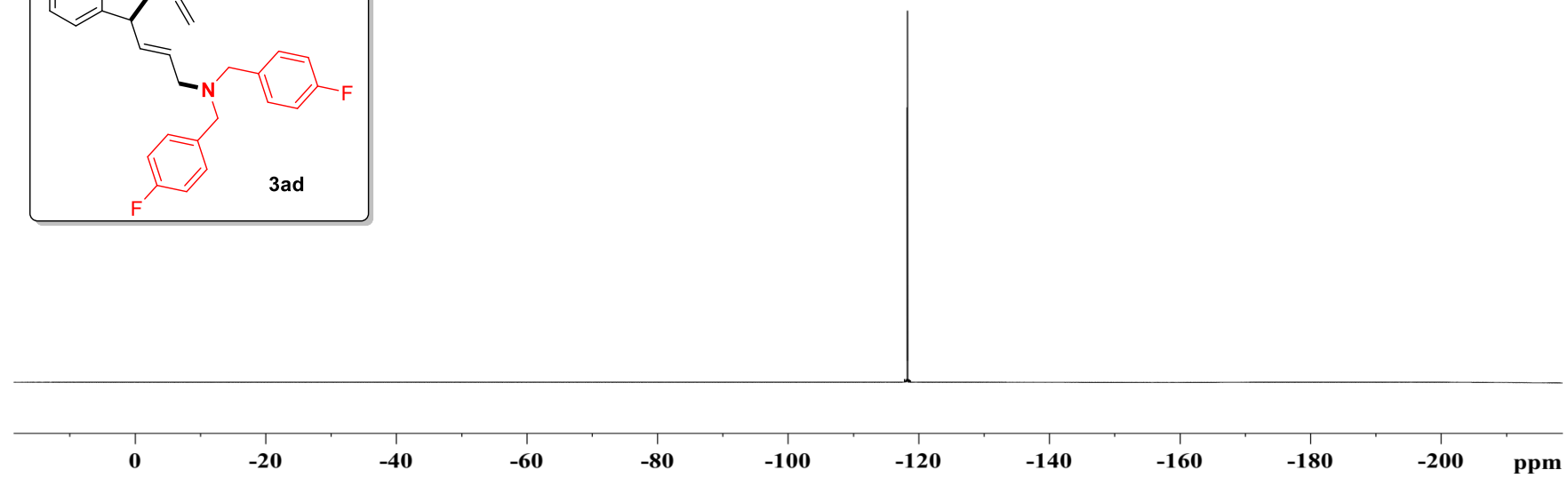
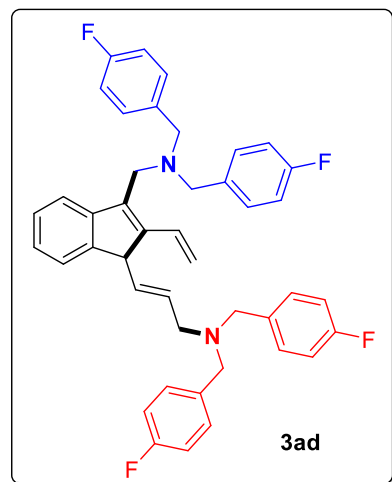
55.7  
52.7  
51.3  
50.4  
49.3



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 3ad**

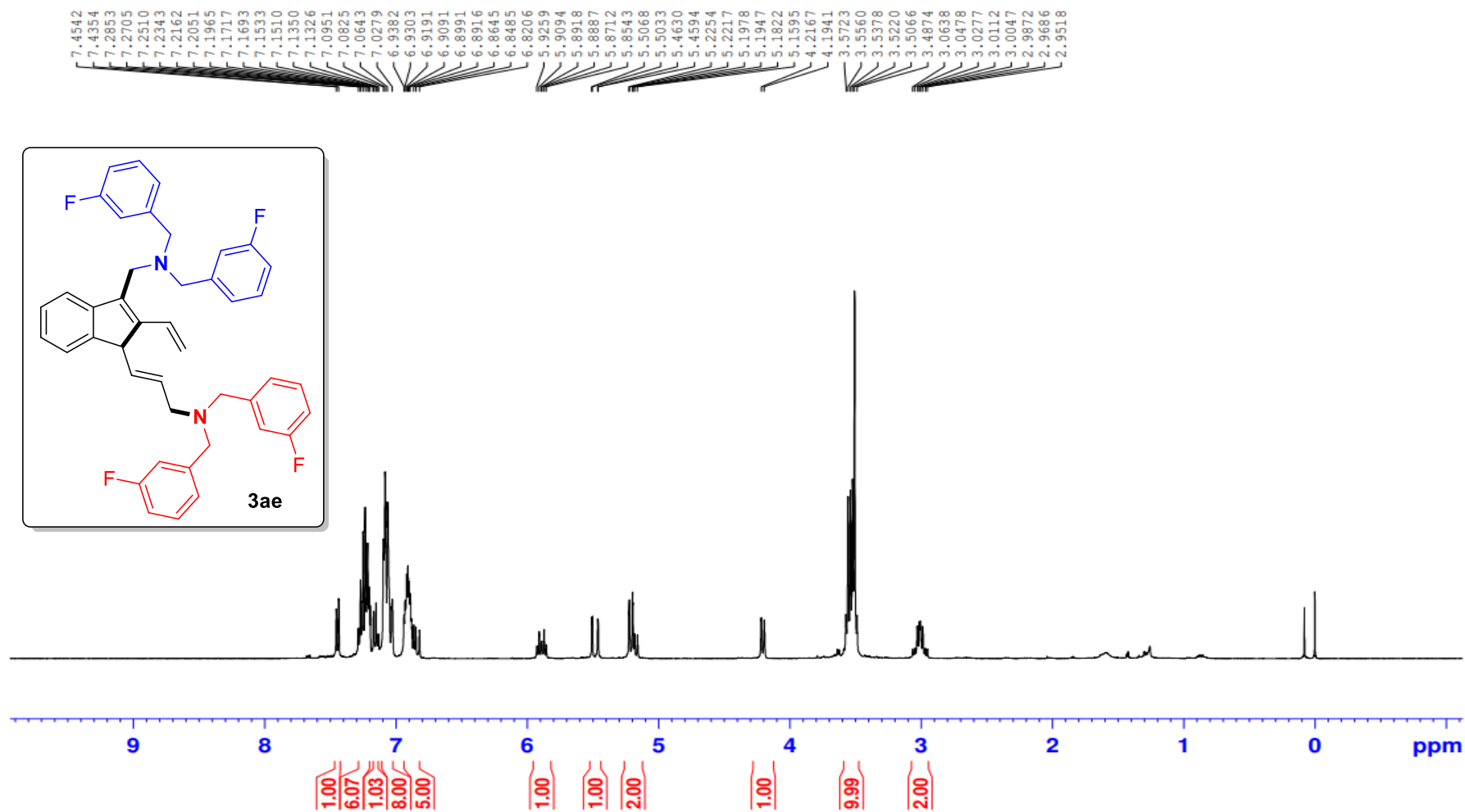
YBK-X210202-1-1 (in  $\text{CDCl}_3$ )

-118.2  
-118.3



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ae

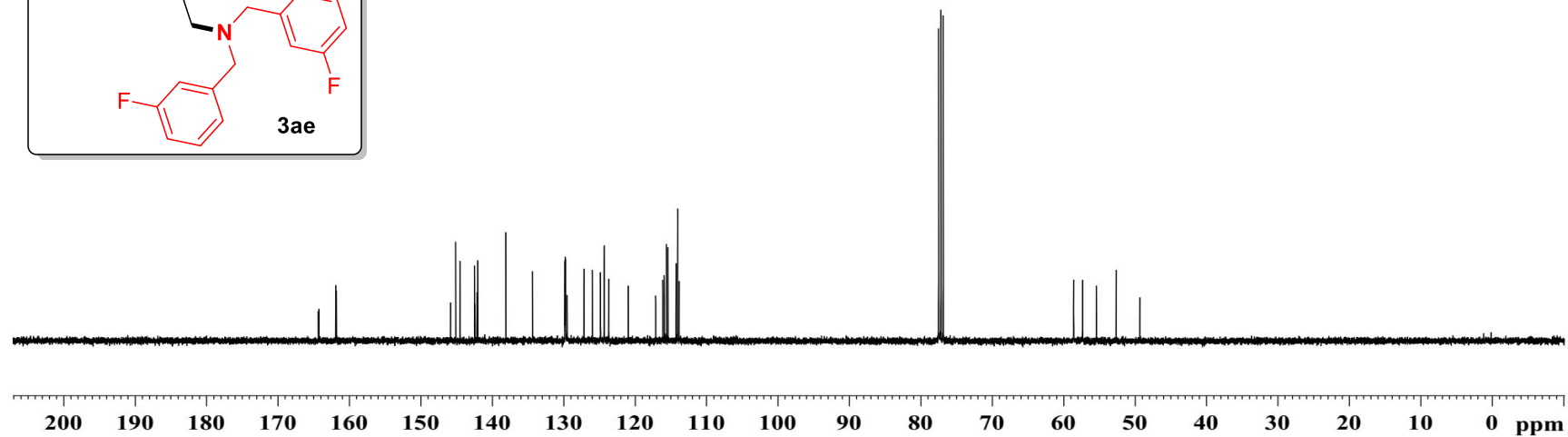
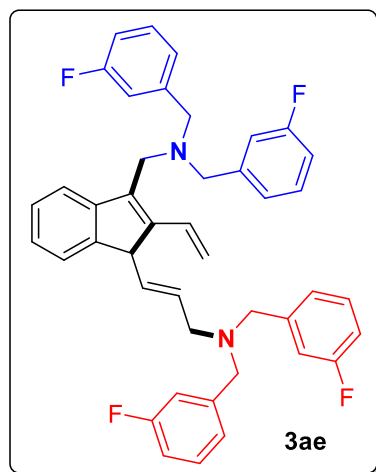
YBK-X210202-1-2-400M (in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ae**

YBK-X210202-1-2 (in CDCl<sub>3</sub>)

164.3  
164.2  
161.9  
161.8  
145.8  
145.1  
144.5  
142.5  
142.4  
142.1  
142.0  
138.1  
134.4  
129.8  
129.8  
129.8  
129.7  
129.7  
129.5  
127.1  
126.0  
124.8  
124.8  
124.3  
124.3  
123.7  
120.9  
117.1  
116.1  
115.9  
115.6  
115.4  
114.3  
114.0  
113.8  
77.5  
77.2  
76.8  
58.6  
58.6  
57.3  
57.3  
55.4  
52.6  
49.3

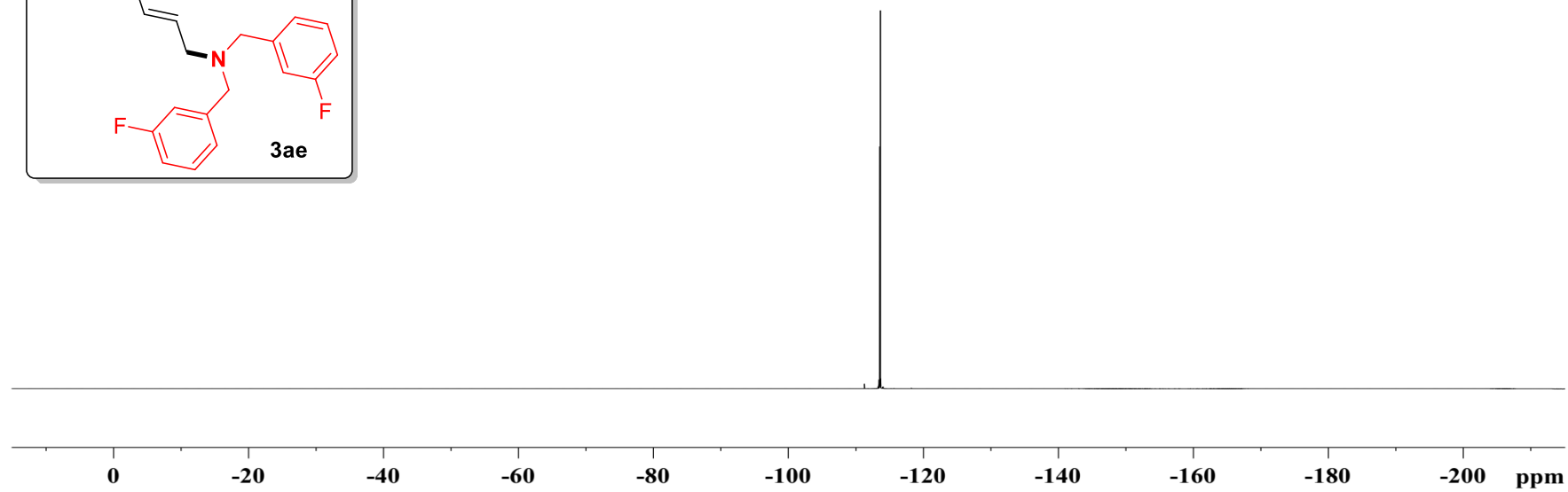
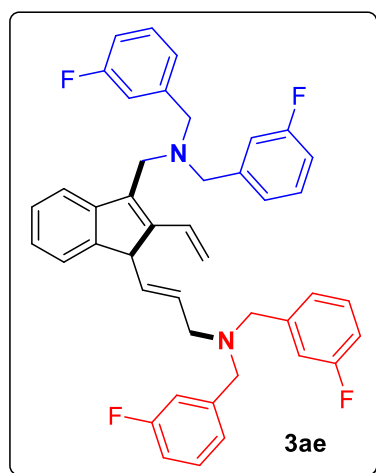




**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra for 3ae**

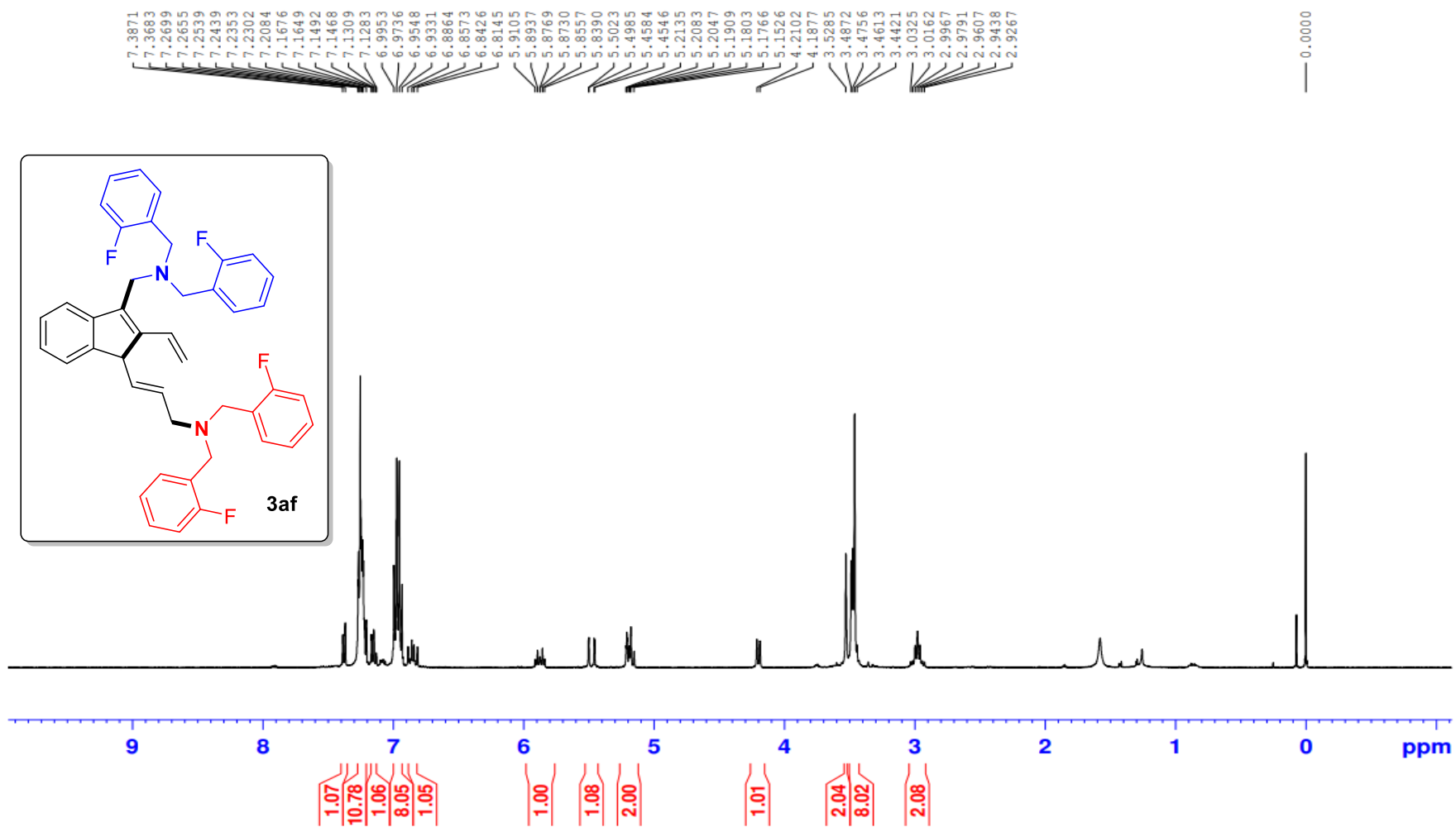
YBK-X210202-1-2 (in CDCl<sub>3</sub>)

-113.5  
-113.6



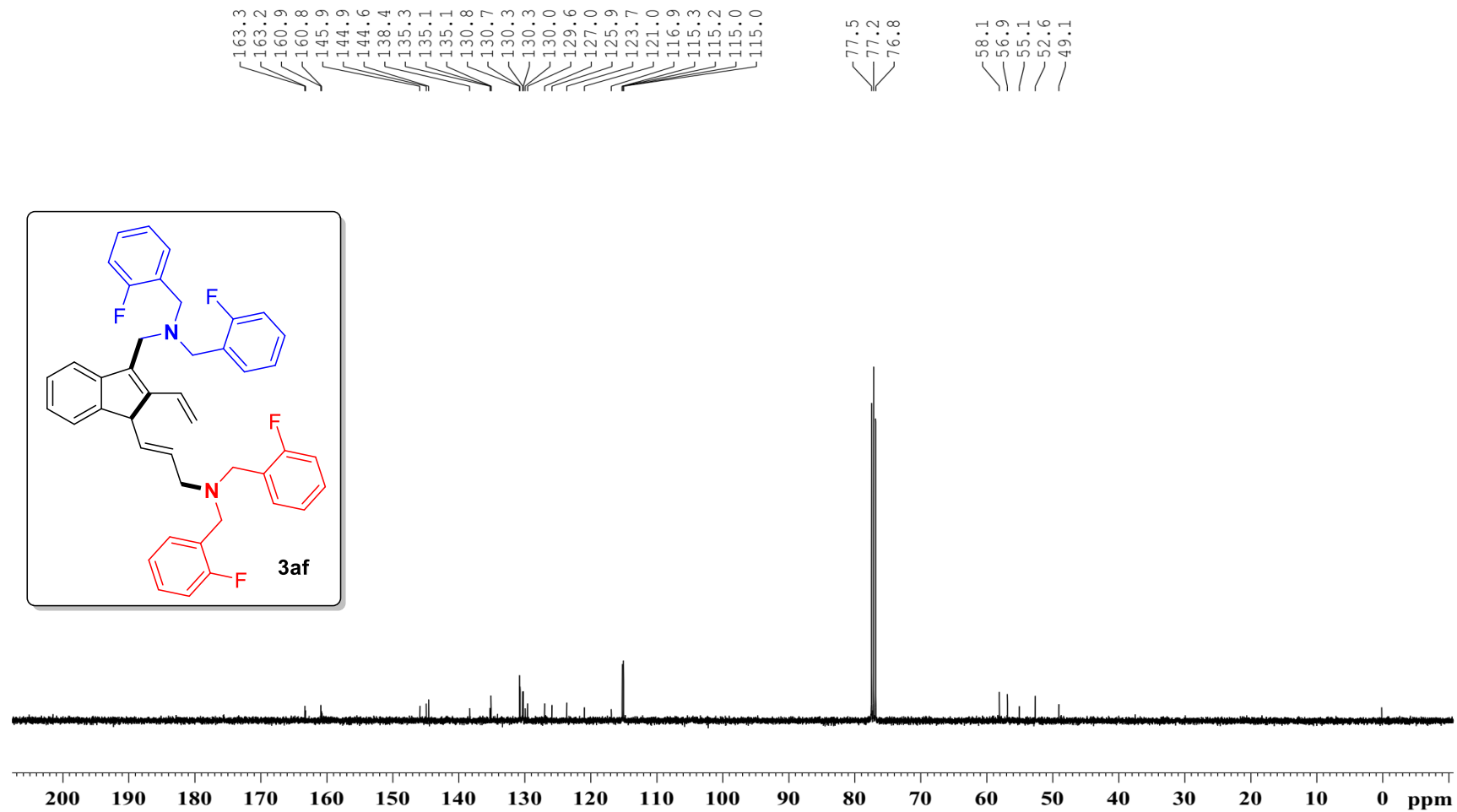
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3af**

YBK-X210202-1-3-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3af**

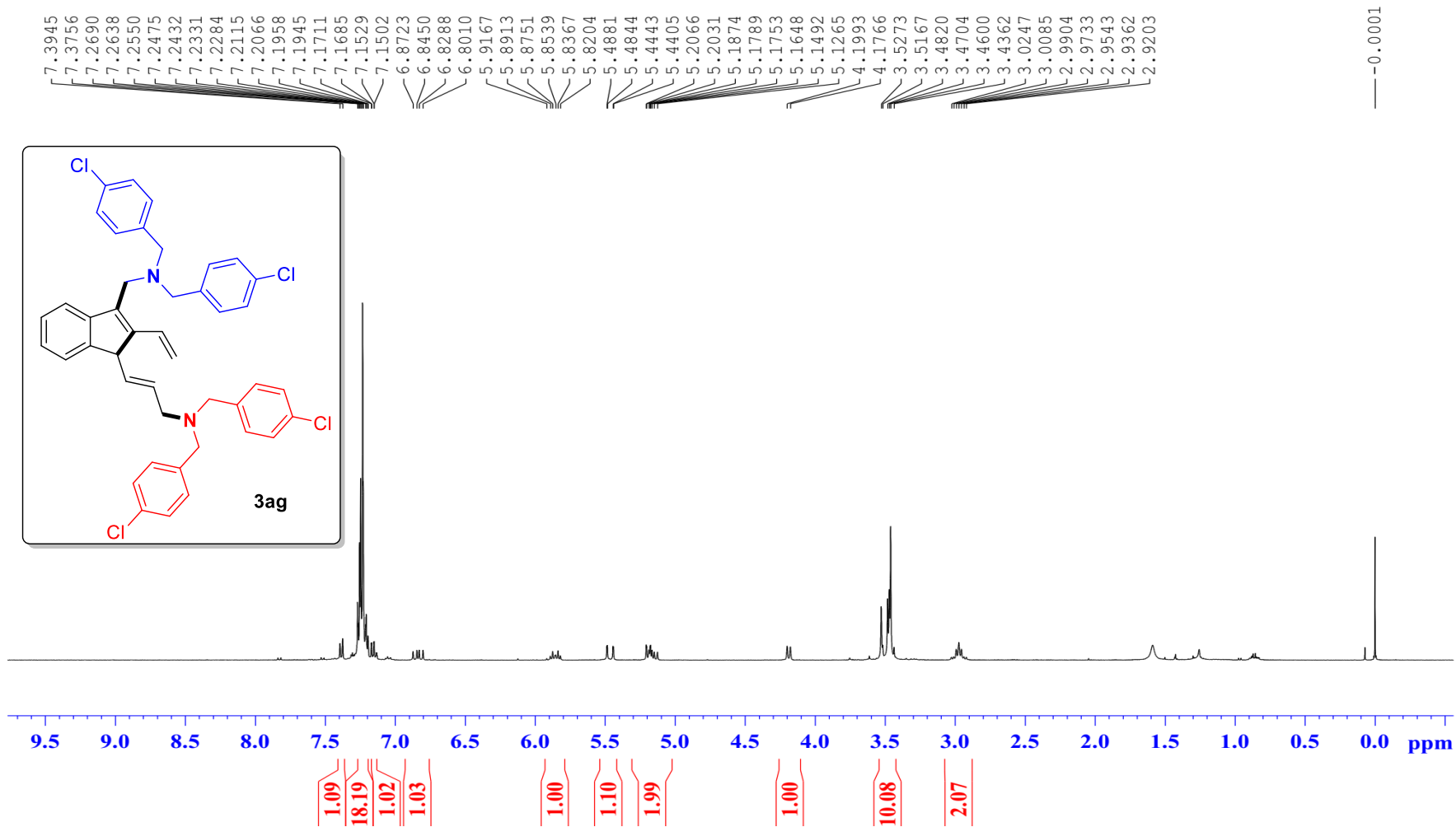
YBK-X210202-1-3 (in CDCl<sub>3</sub>)





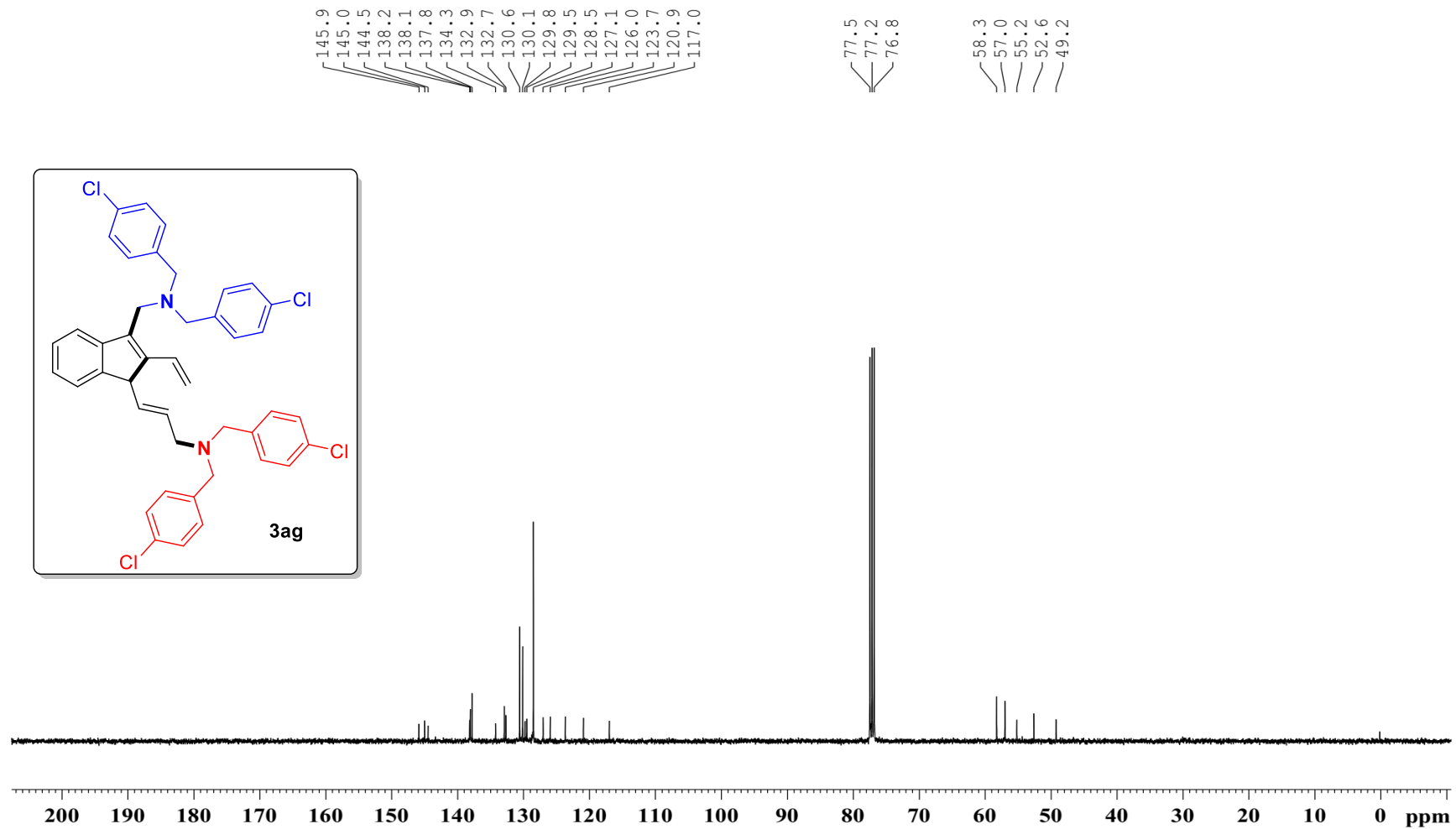
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ag**

YHJ-X210304-1-4-Cl (in CDCl<sub>3</sub>)



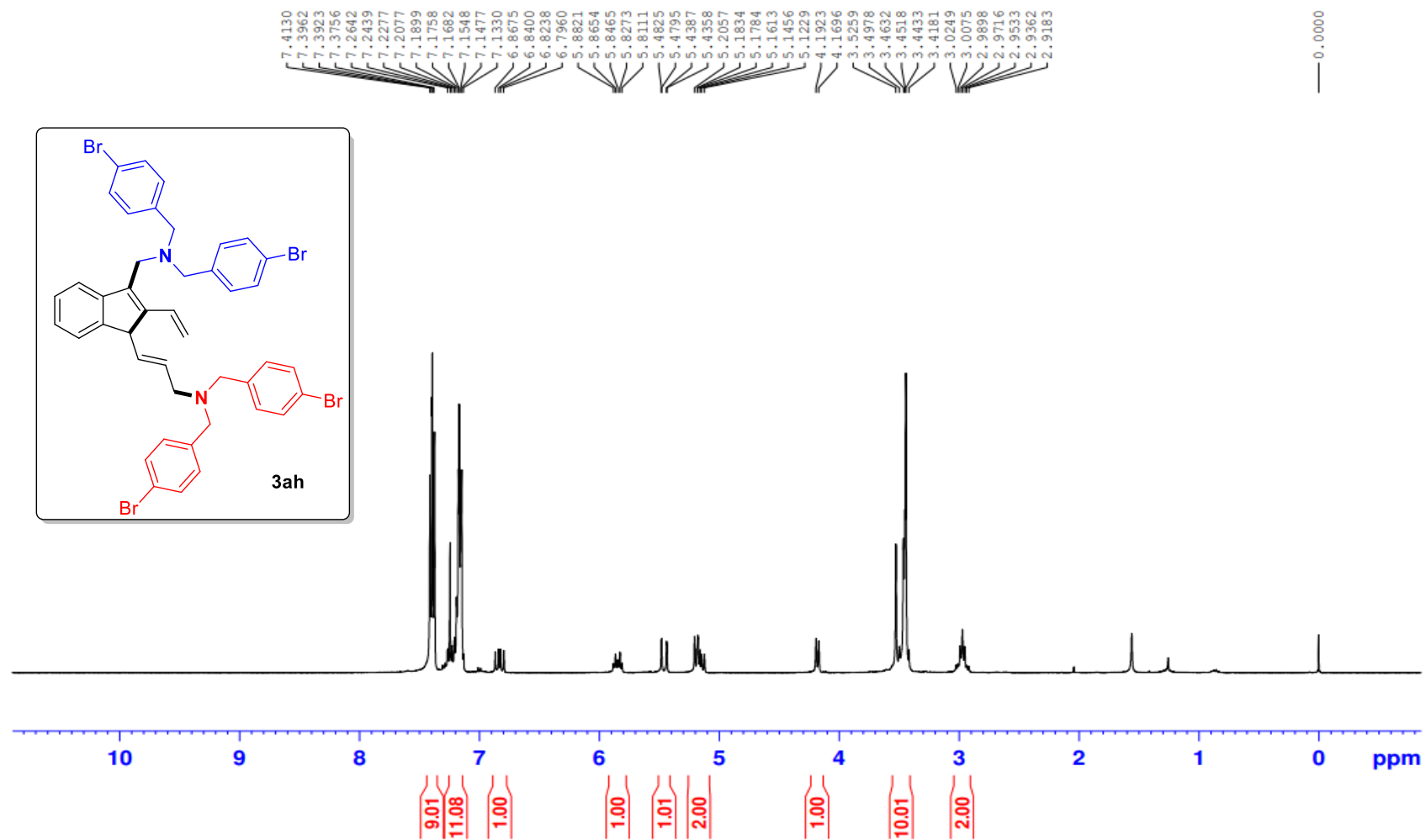
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ag**

YHJ-X210304-1-4-Cl (in CDCl<sub>3</sub>)



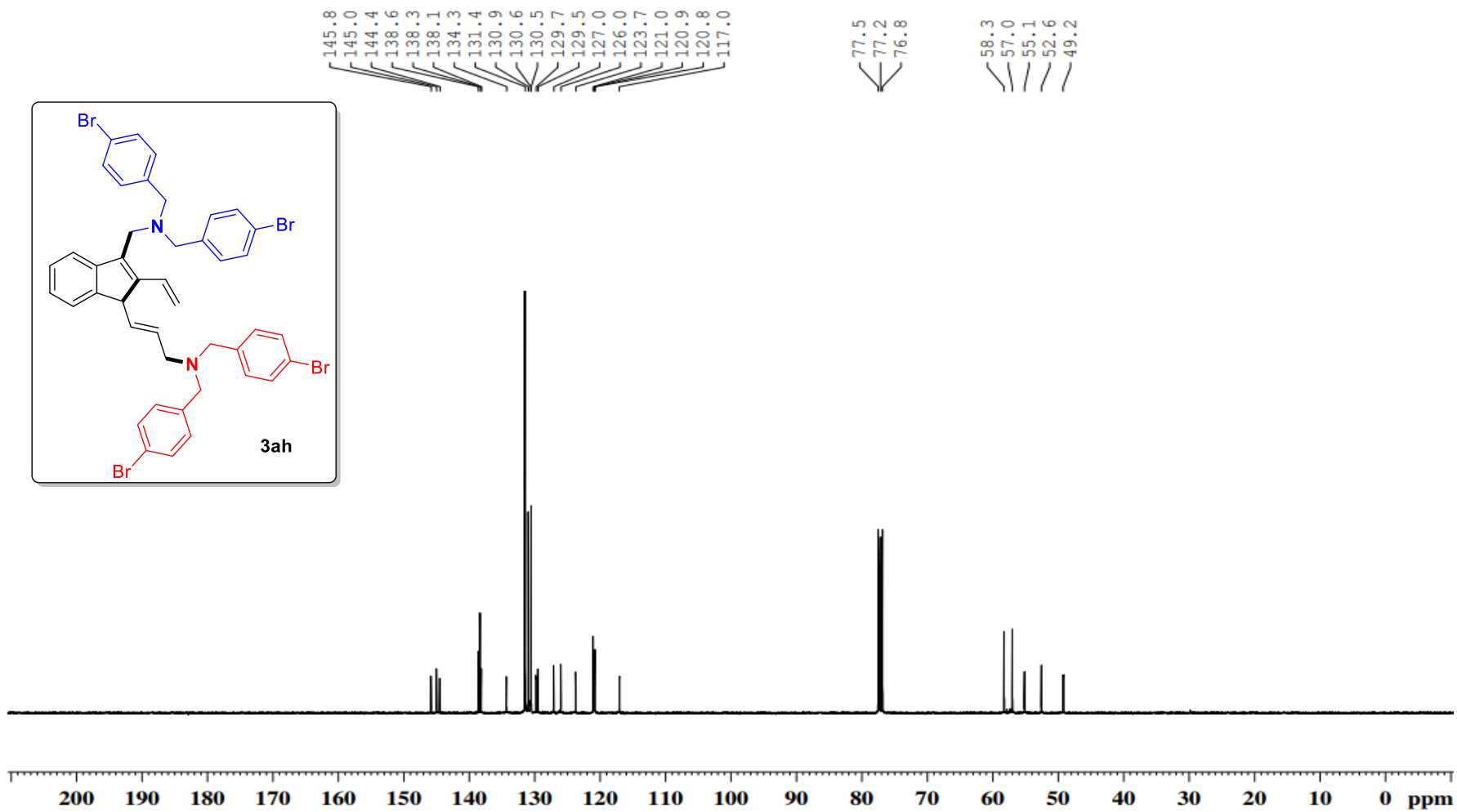
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ah

LRR-X220926-4-Br-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ah**

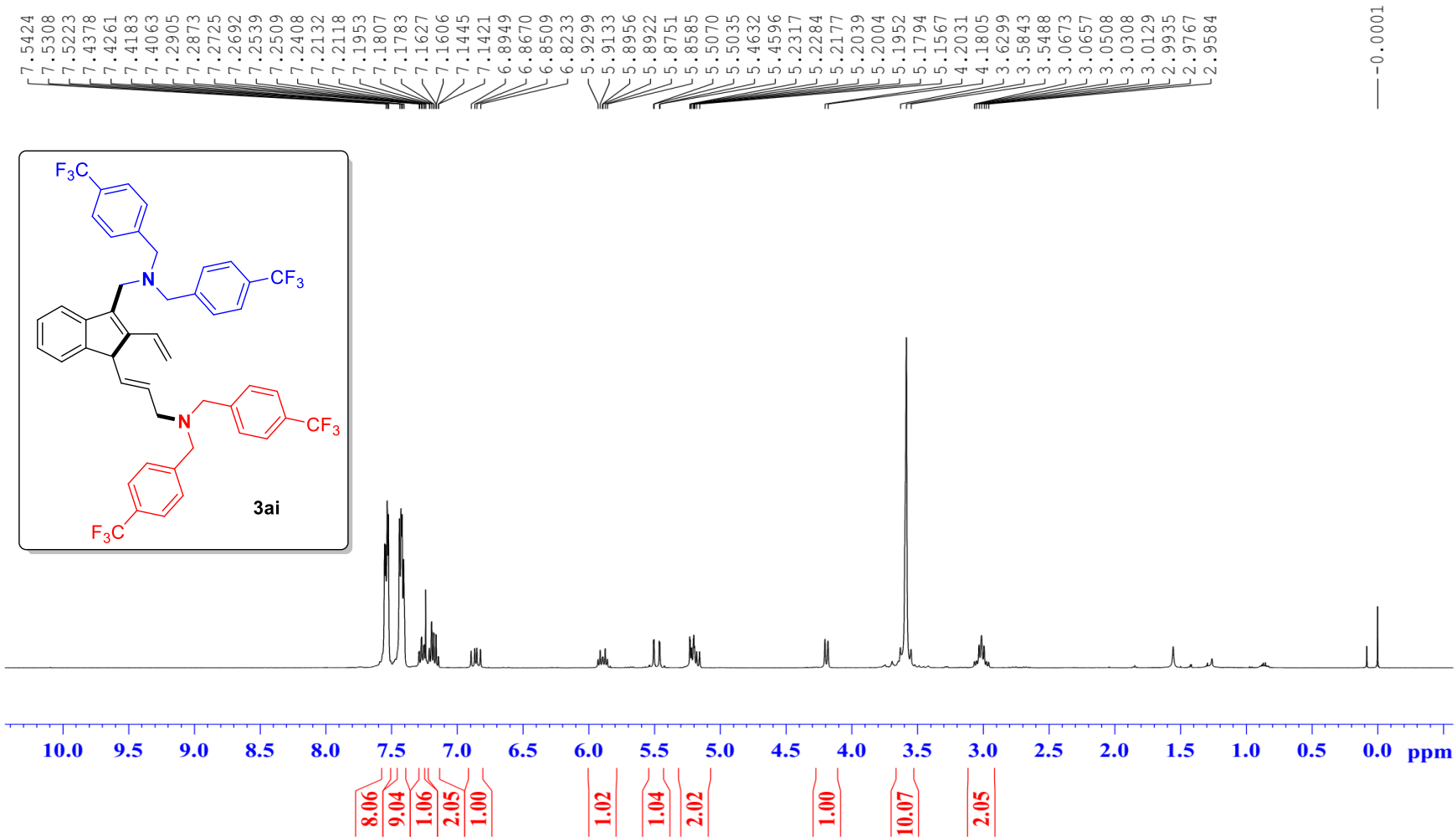
LRR-X220926-4-Br-100M(in CDCl<sub>3</sub>)





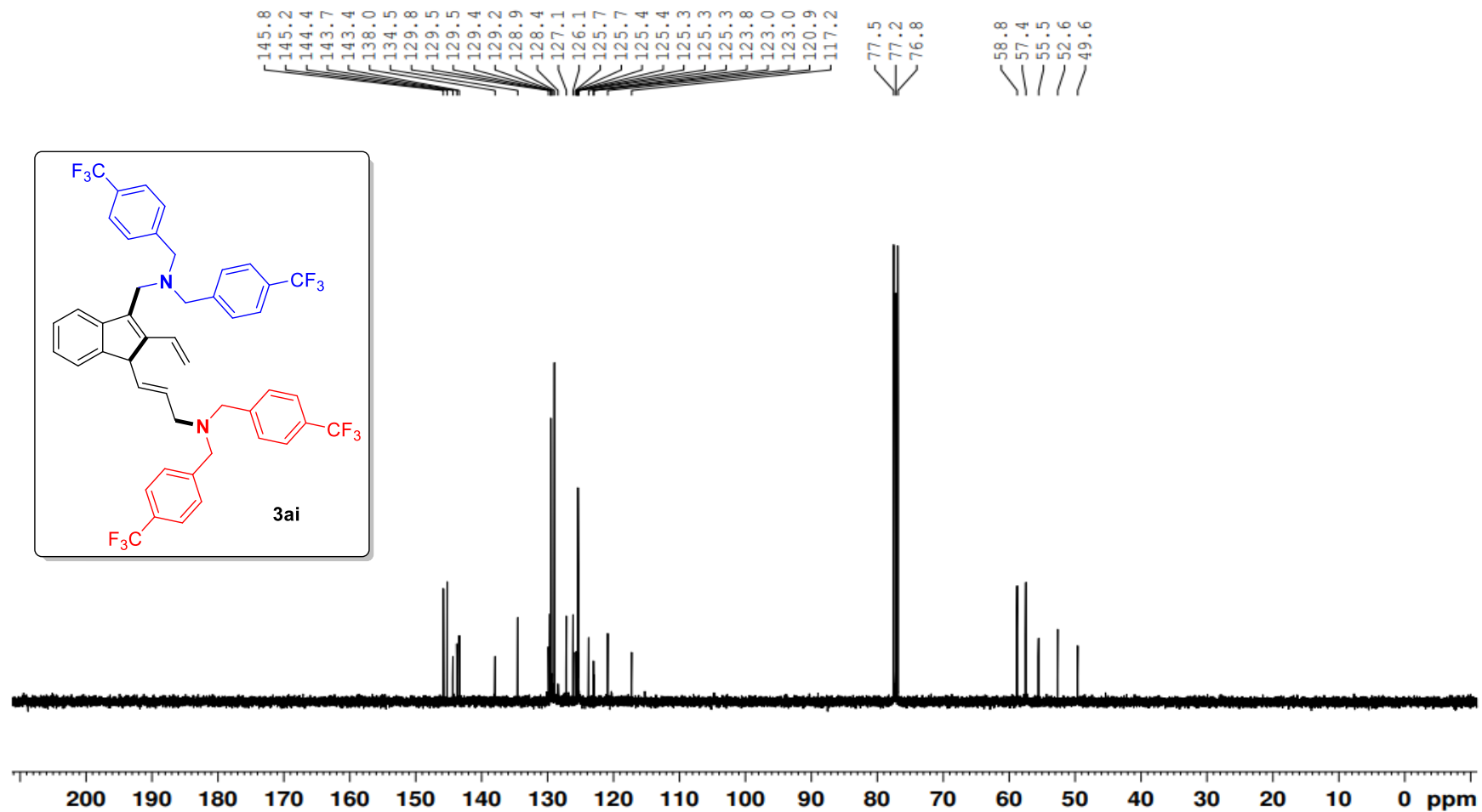
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ai**

YHJ-X210202-1-4-CF<sub>3</sub> (in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ai**

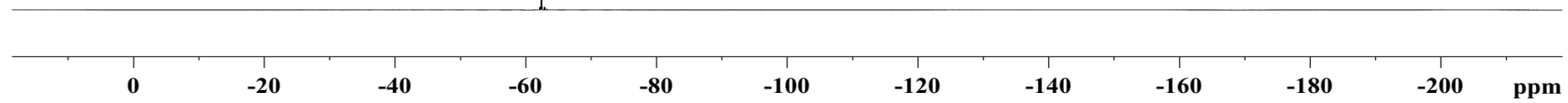
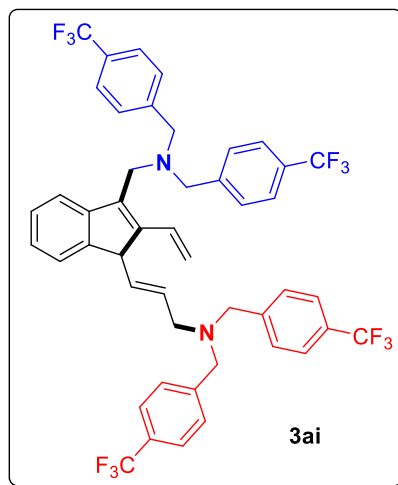
YHJ-X210202-1-6-100M(in CDCl<sub>3</sub>)



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 3ai**

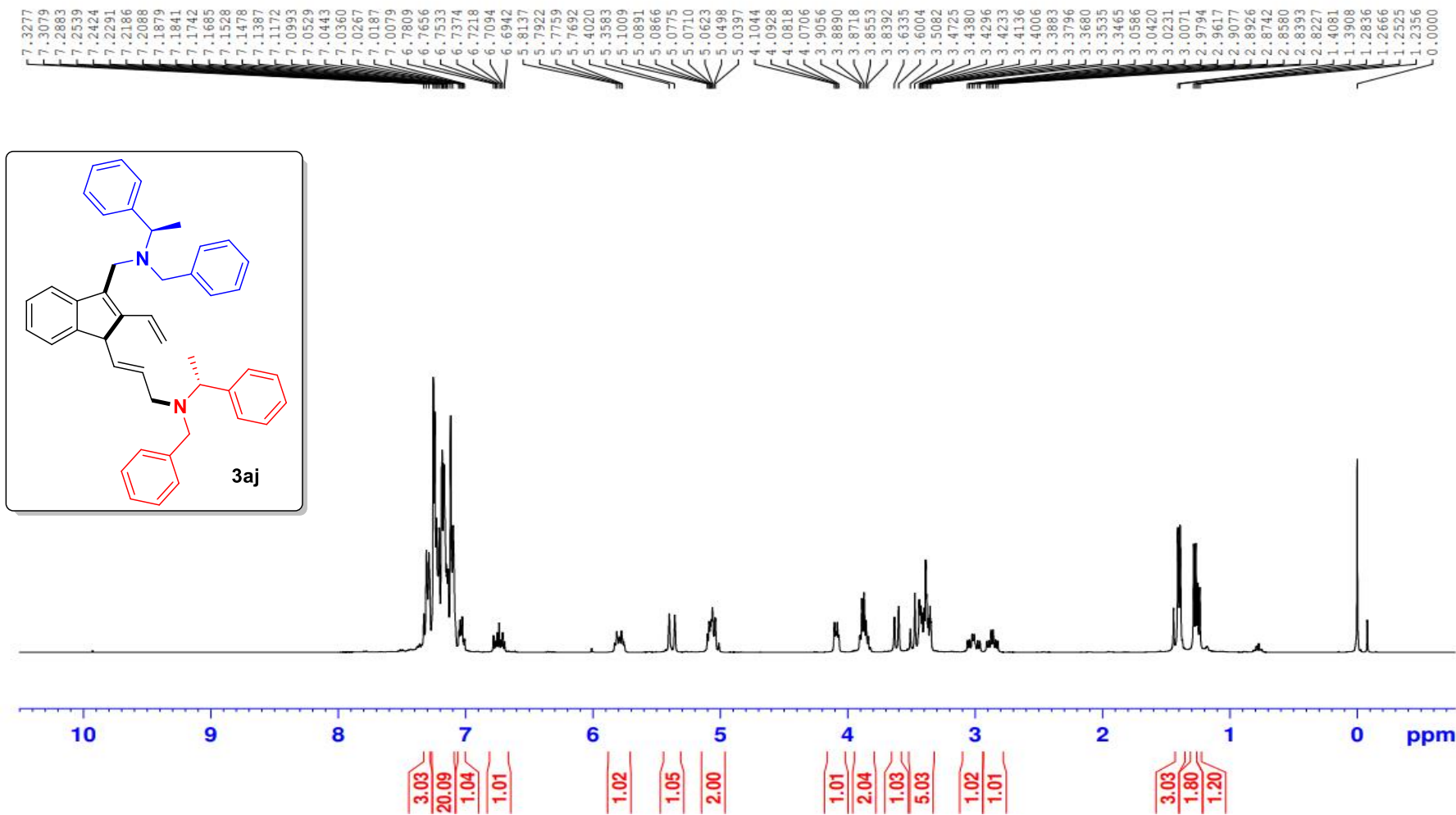
YHJ-X210202-1-4-CF3 (in  $\text{CDCl}_3$ )

— -62.4



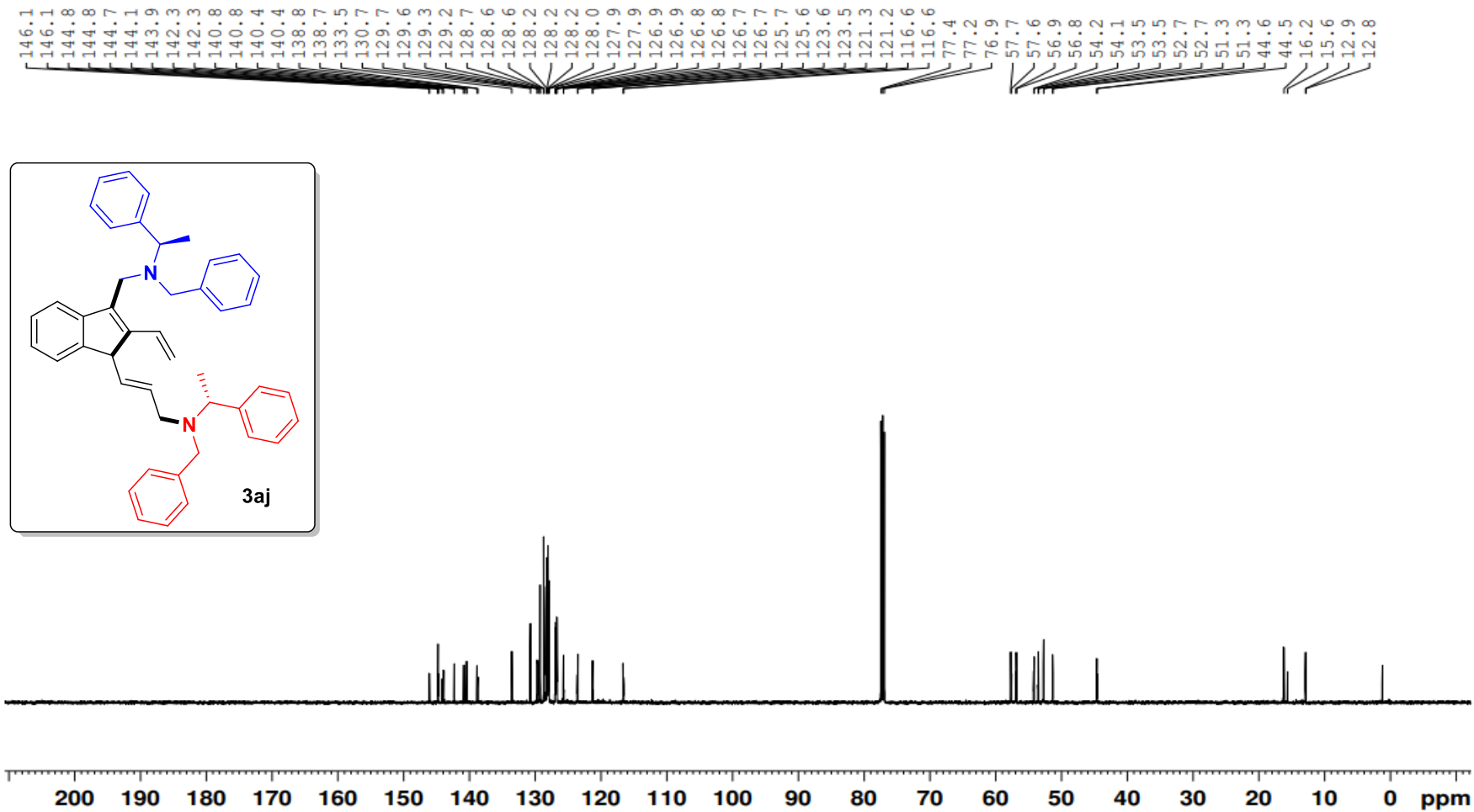
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3aj**

YBK-X210414-4-R-400M(in CDCl<sub>3</sub>)



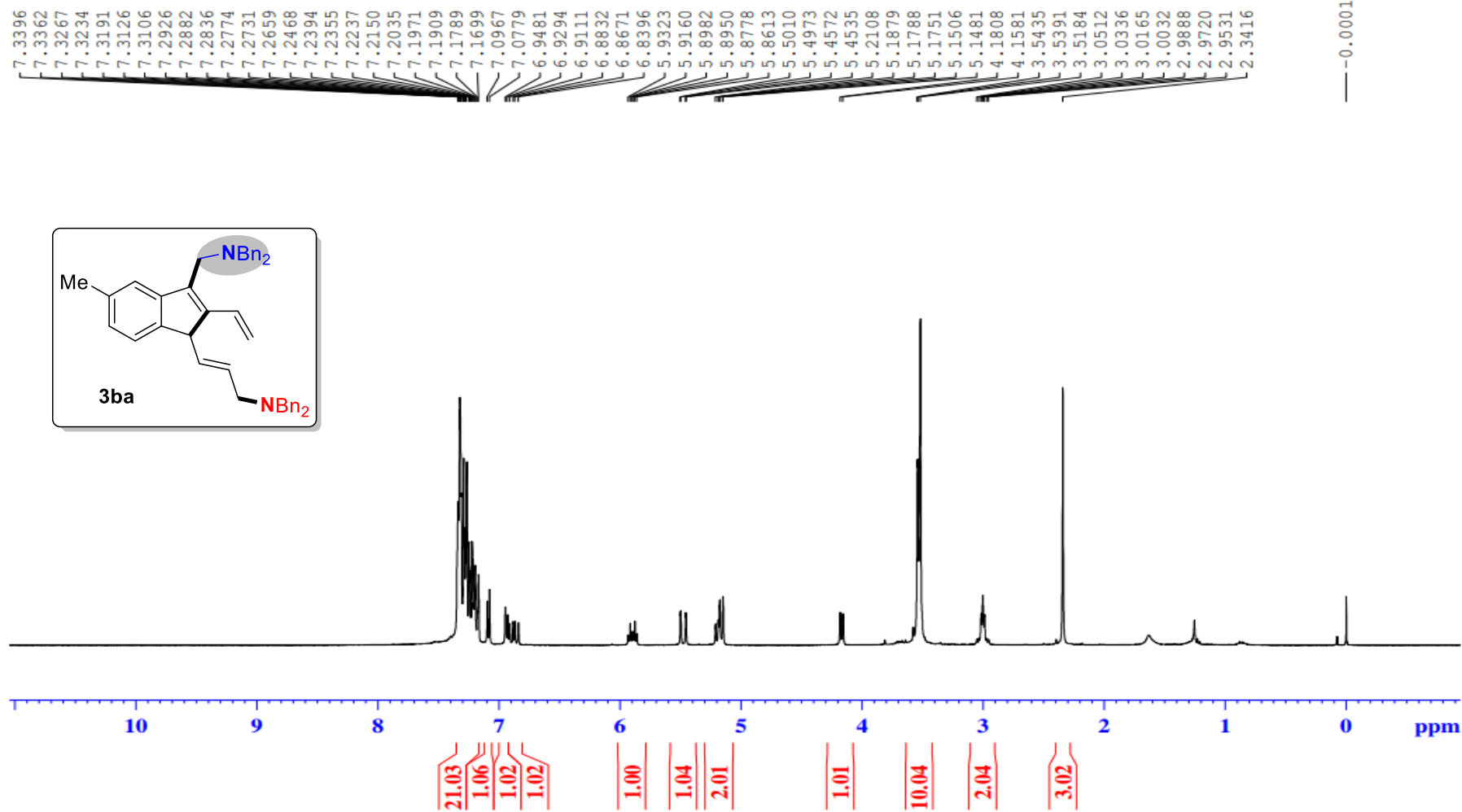
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3aj

YBK-X210414-R-125M(in CDCl<sub>3</sub>)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ba

YBK-X220413-7-4-Me-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ba**

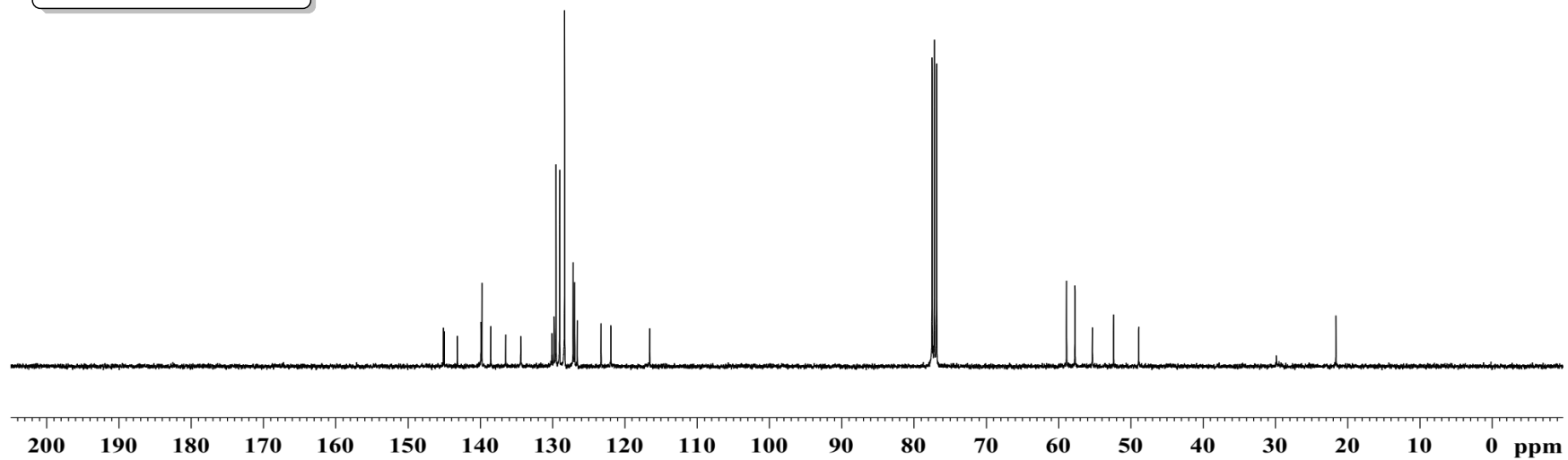
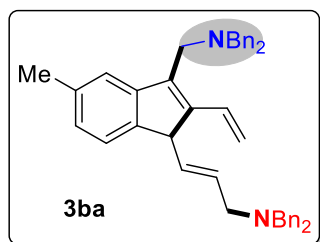
YBK-X210413-7-CH3 (in CDCl<sub>3</sub>)

145.1  
144.9  
143.1  
139.8  
139.7  
138.5  
136.4  
134.3  
130.0  
129.7  
129.5  
129.0  
128.3  
127.1  
126.9  
126.5  
123.2  
121.9  
116.5

77.5  
77.2  
76.8

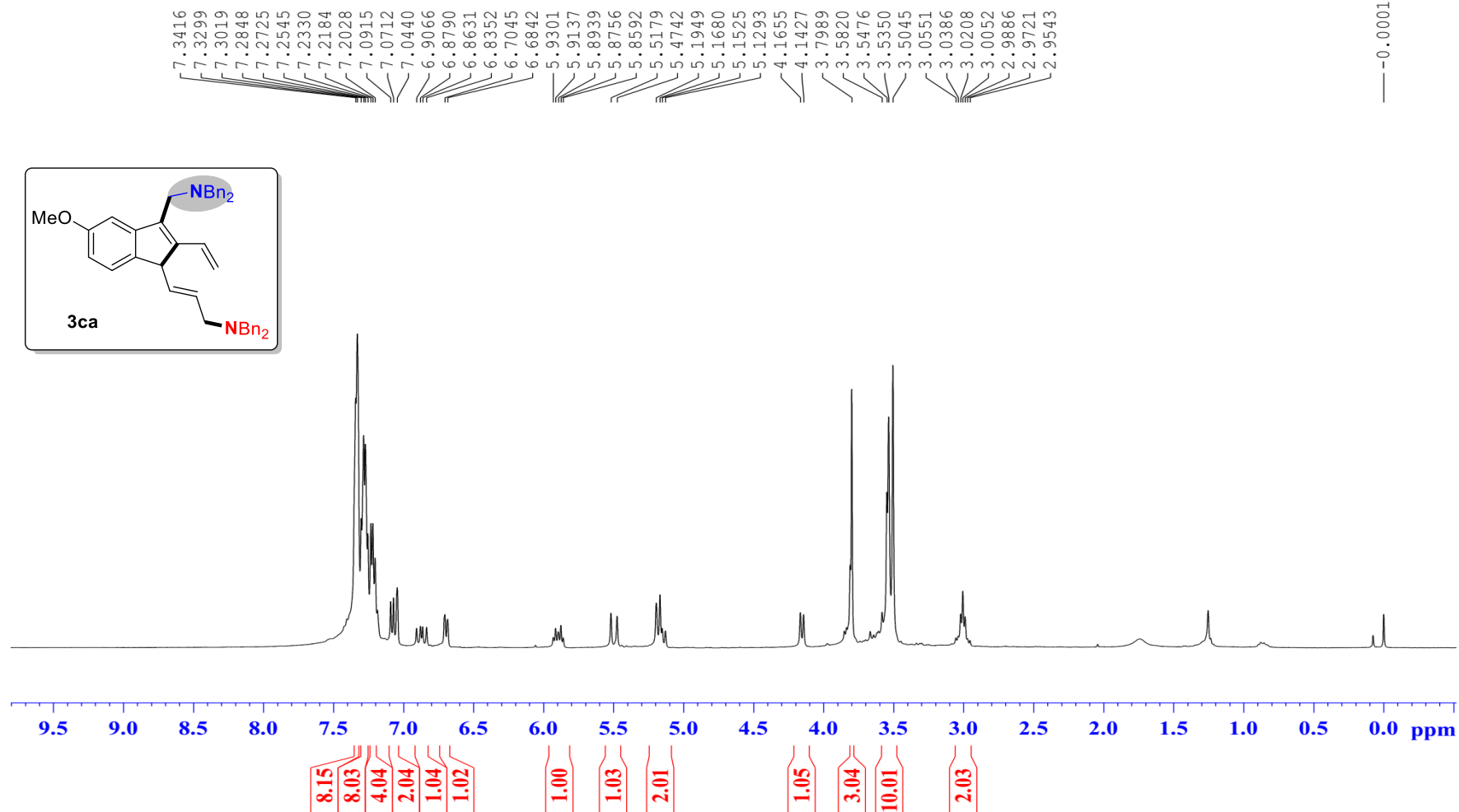
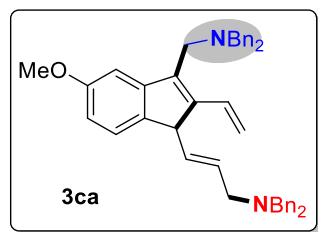
58.9  
57.7  
55.3  
52.4  
48.9

21.6



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ca

YBK-X210414-1-4-OCH3 (in CDCl<sub>3</sub>)

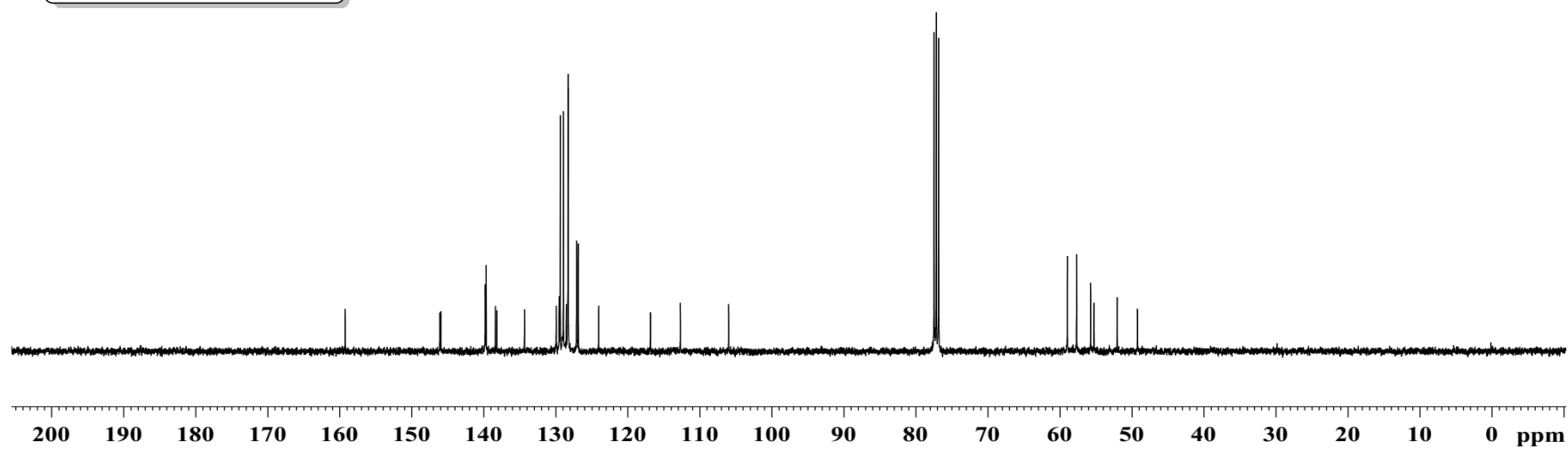
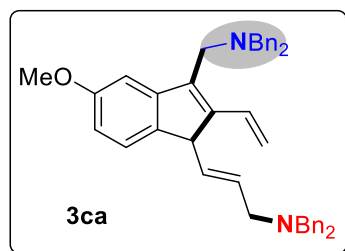
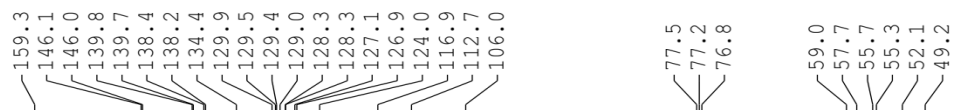


— -0.0001



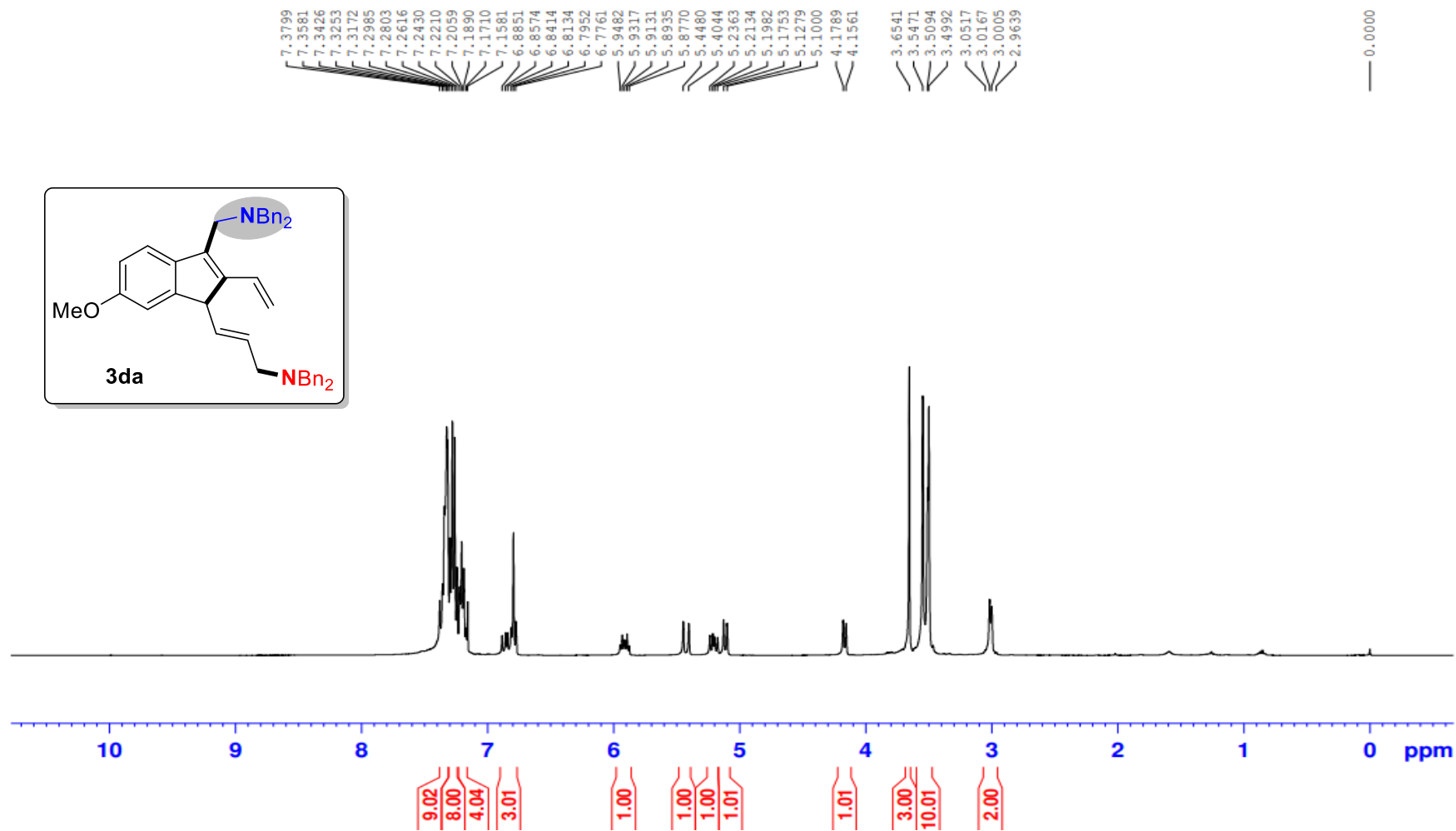
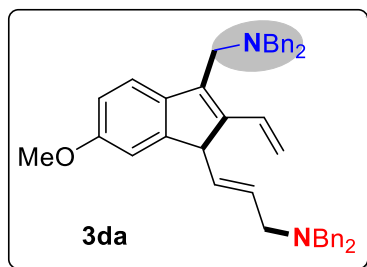
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ca**

YBK-X210414-1-CH3 (in CDCl<sub>3</sub>)



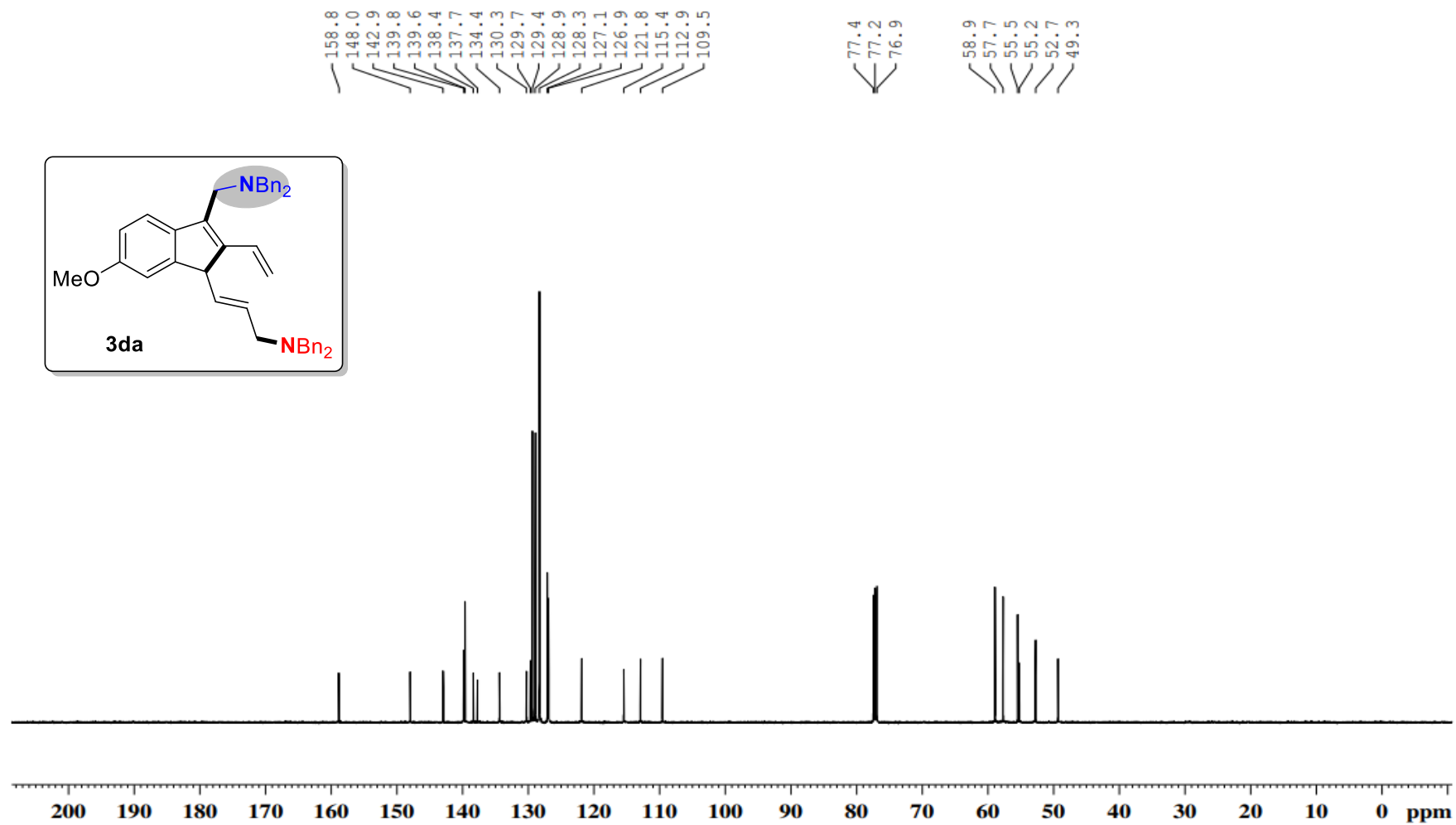
<sup>1</sup>H NMR (400 MHz, CCl<sub>3</sub>) spectra for 3da

LRR-X22X19-5-OMe-400M (in CDCl<sub>3</sub>)



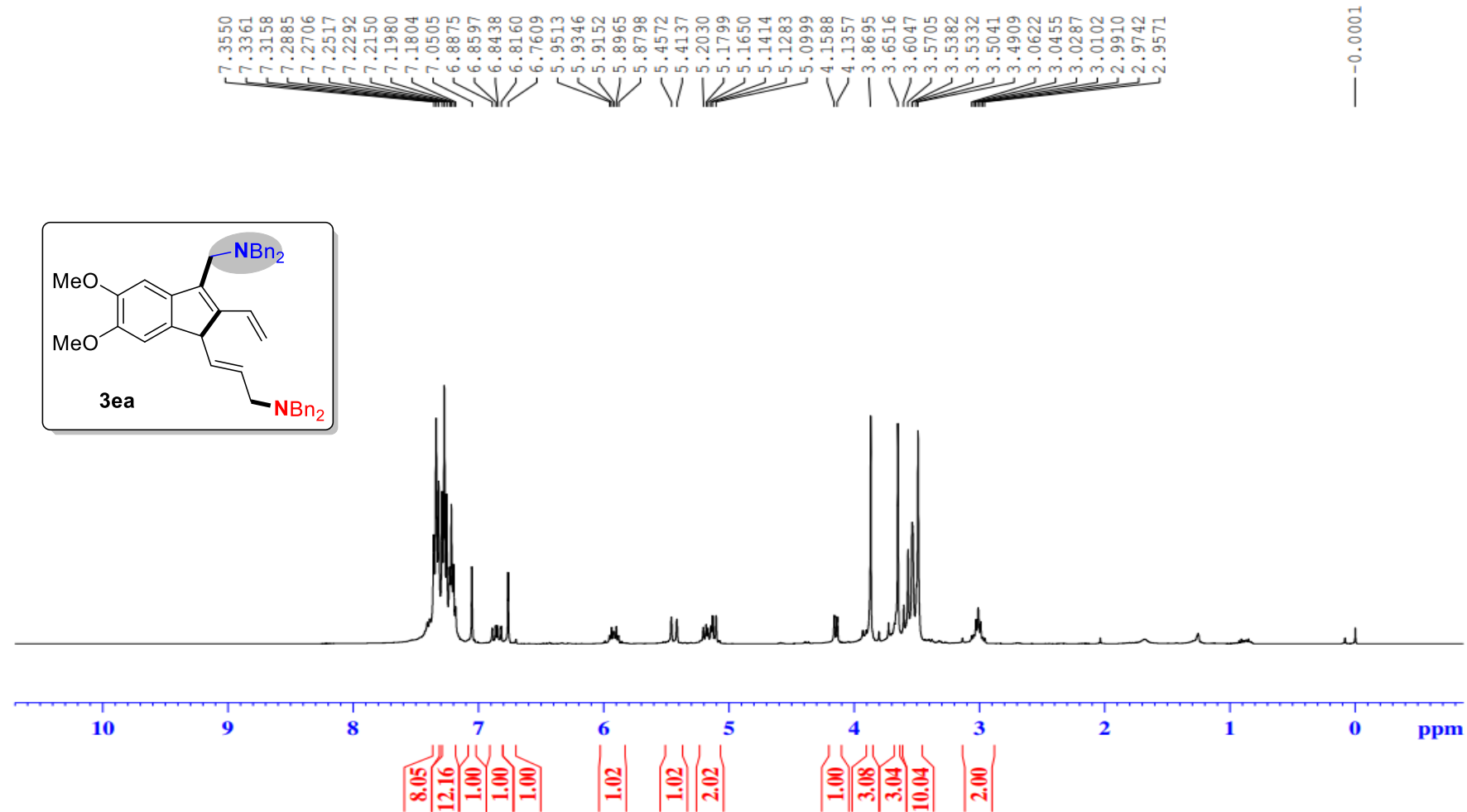
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3da

LRR-X22X19-5-OMe-125M (in CDCl<sub>3</sub>)



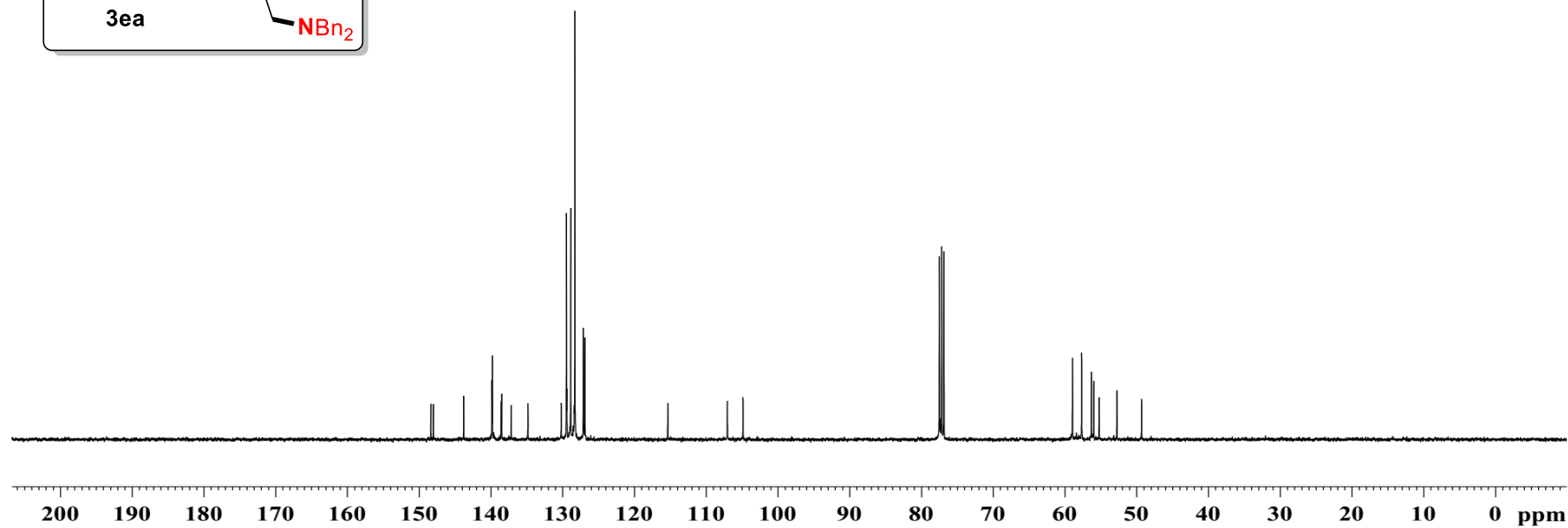
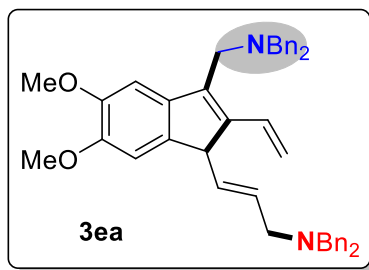
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ea

YBK-X210414-6-2OMe-400M(in CDCl<sub>3</sub>)



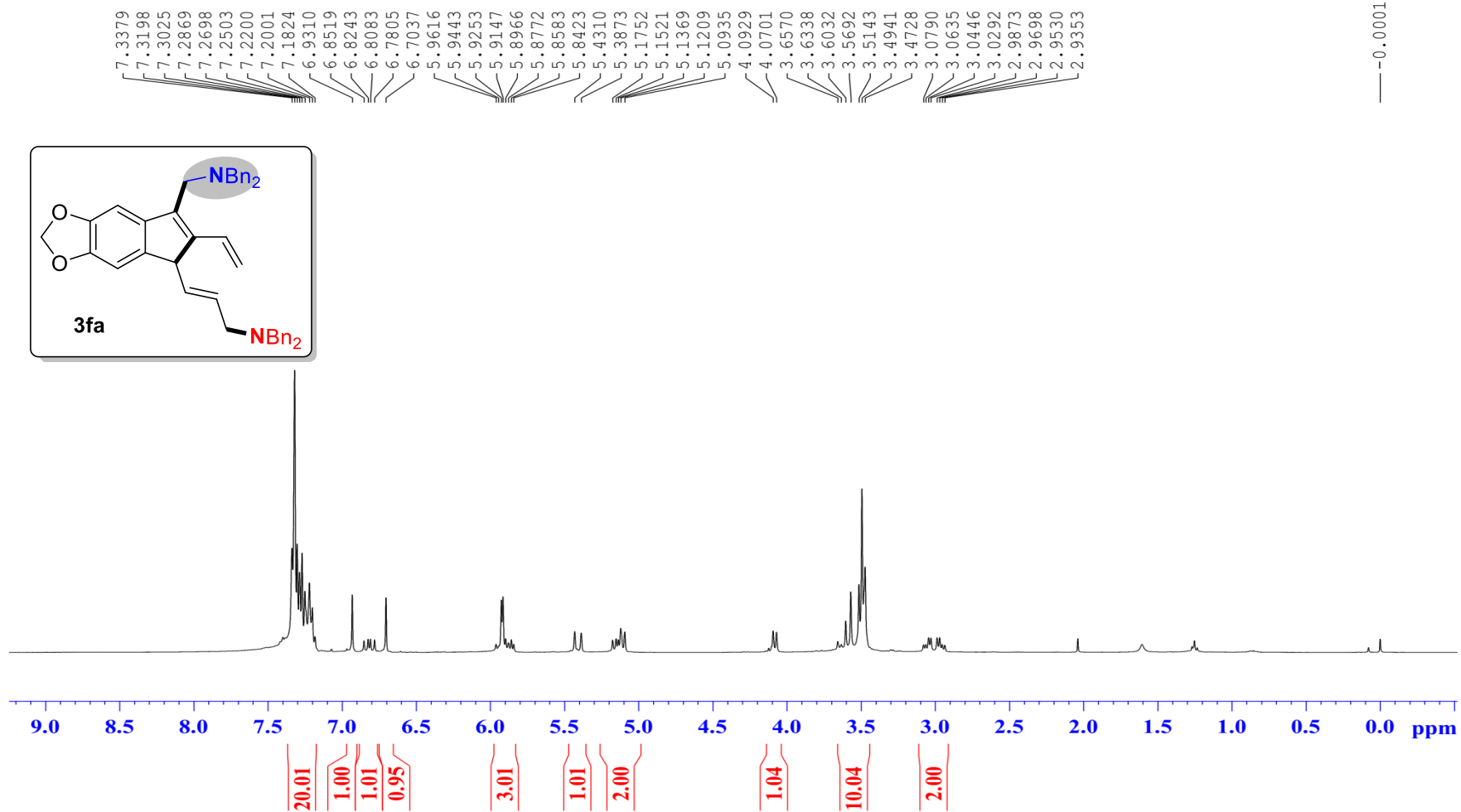
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3ea**

YBK-X210414-6-2OCH3 (in CDCl<sub>3</sub>)



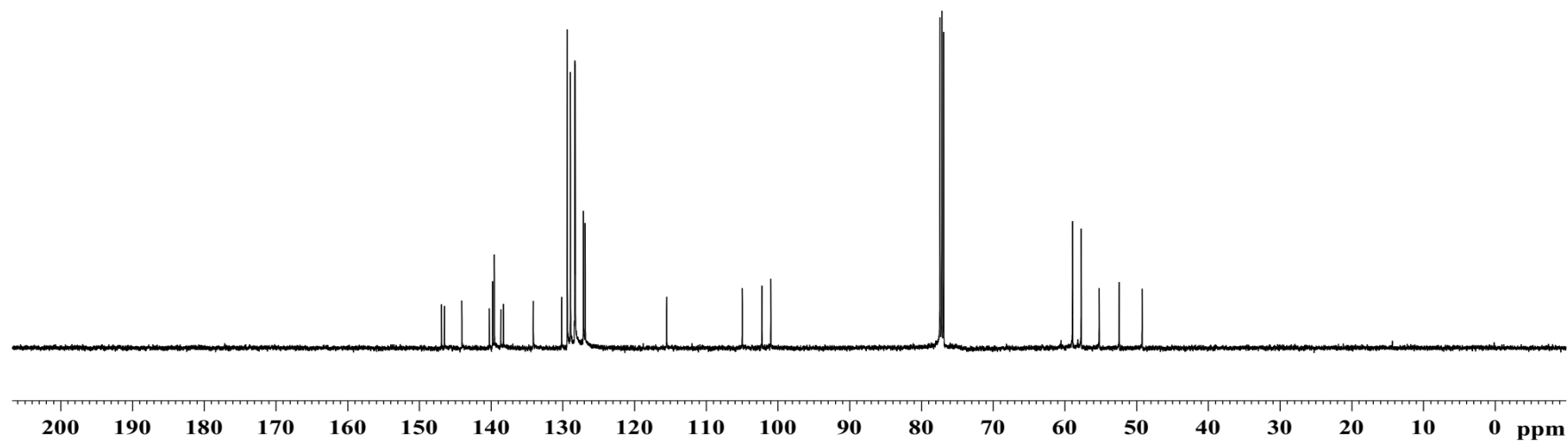
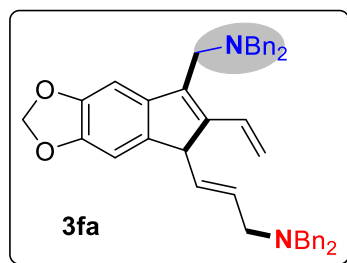
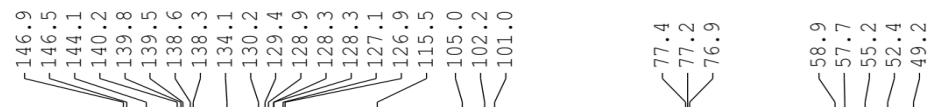
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3fa**

YBK-X210414-3-OCH2O (in CDCl<sub>3</sub>)



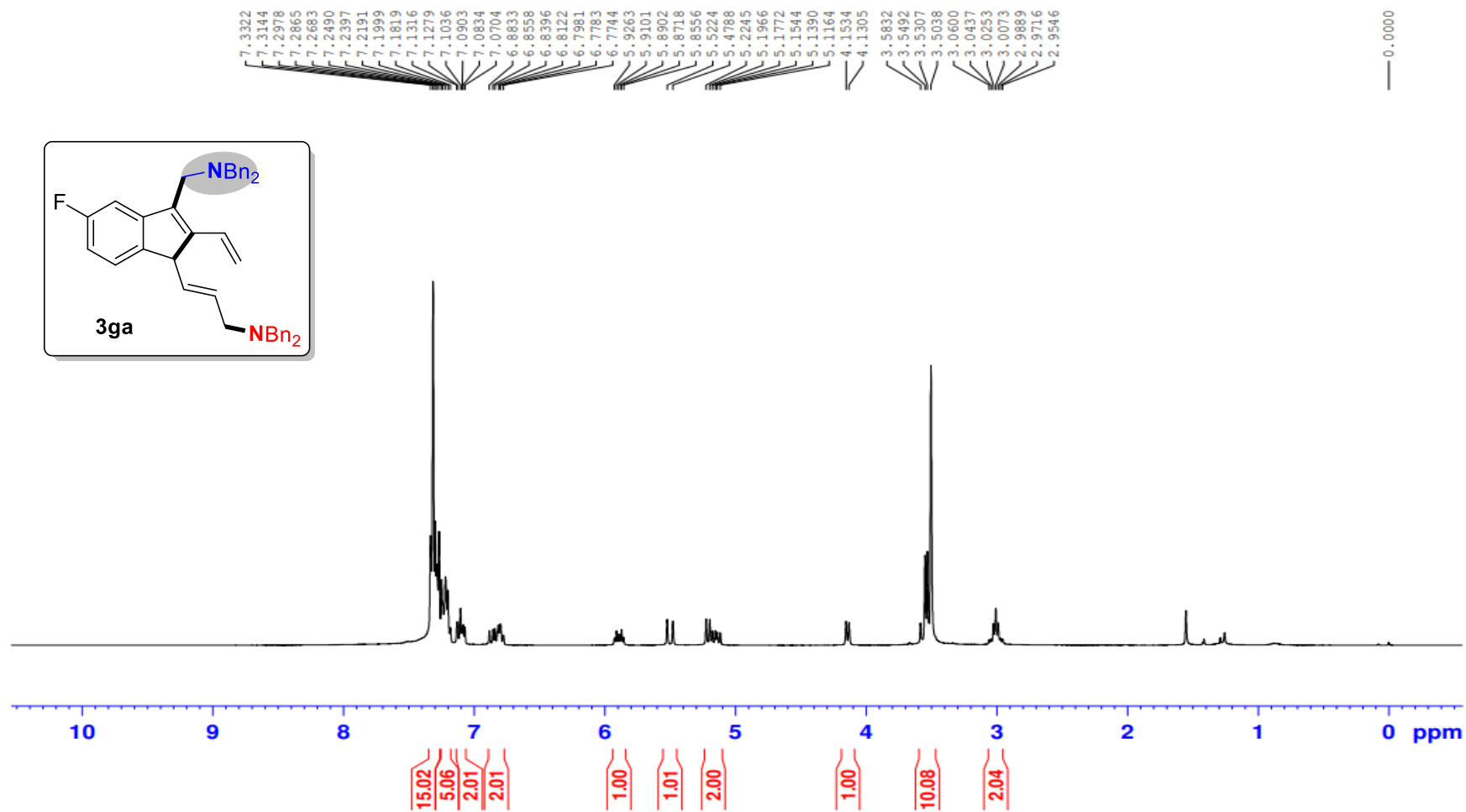
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3fa**

YBK-X210414-3 (in CDCl<sub>3</sub>)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ga

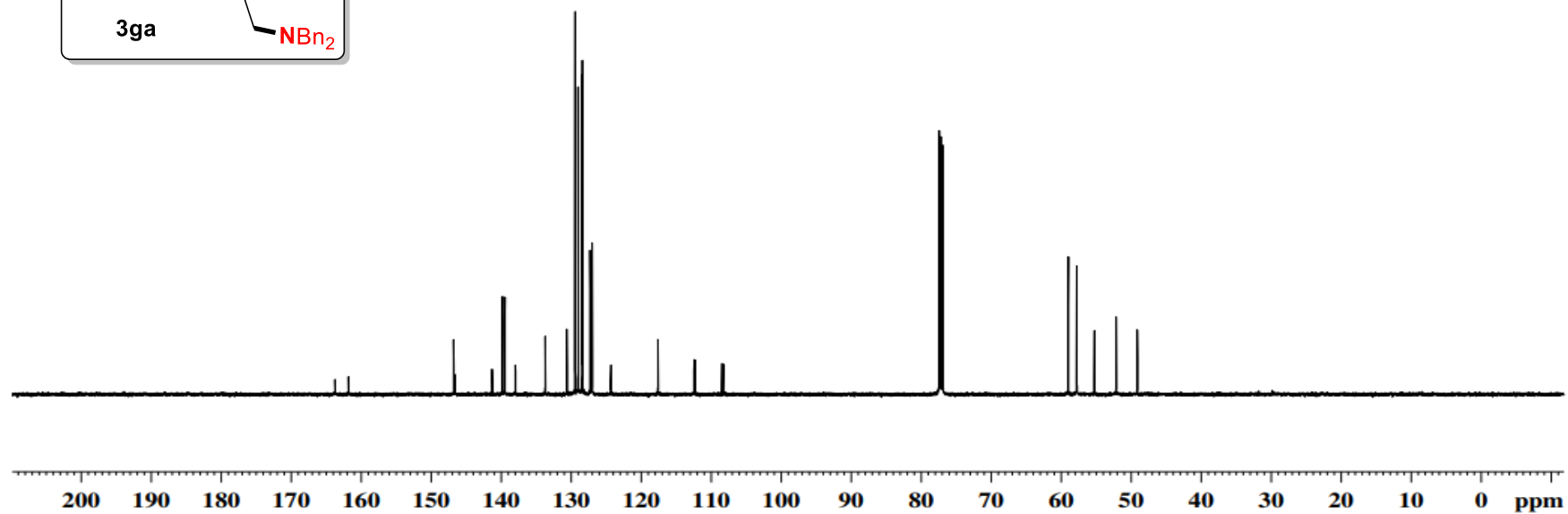
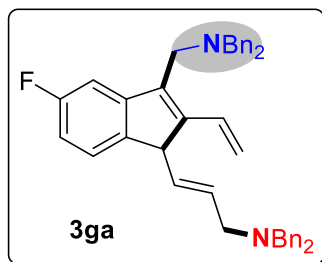
LRR-X220831-4-F-400M (in CDCl<sub>3</sub>)





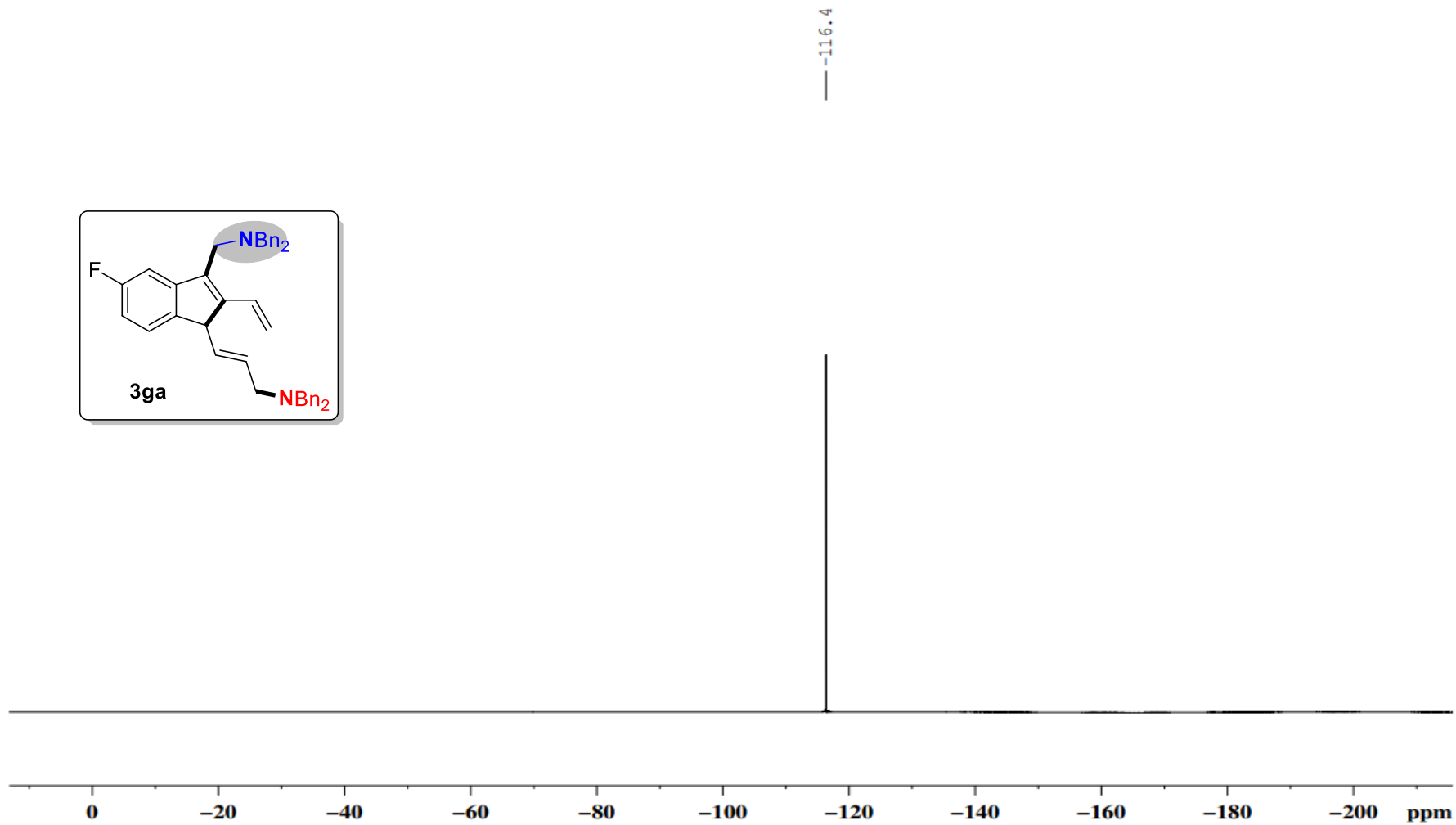
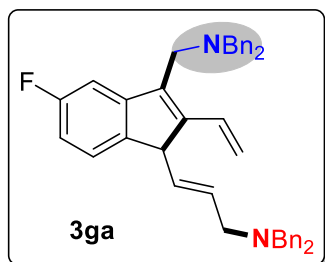
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ga**

LRR-X220831-4-F-125M(in CDCl<sub>3</sub>)



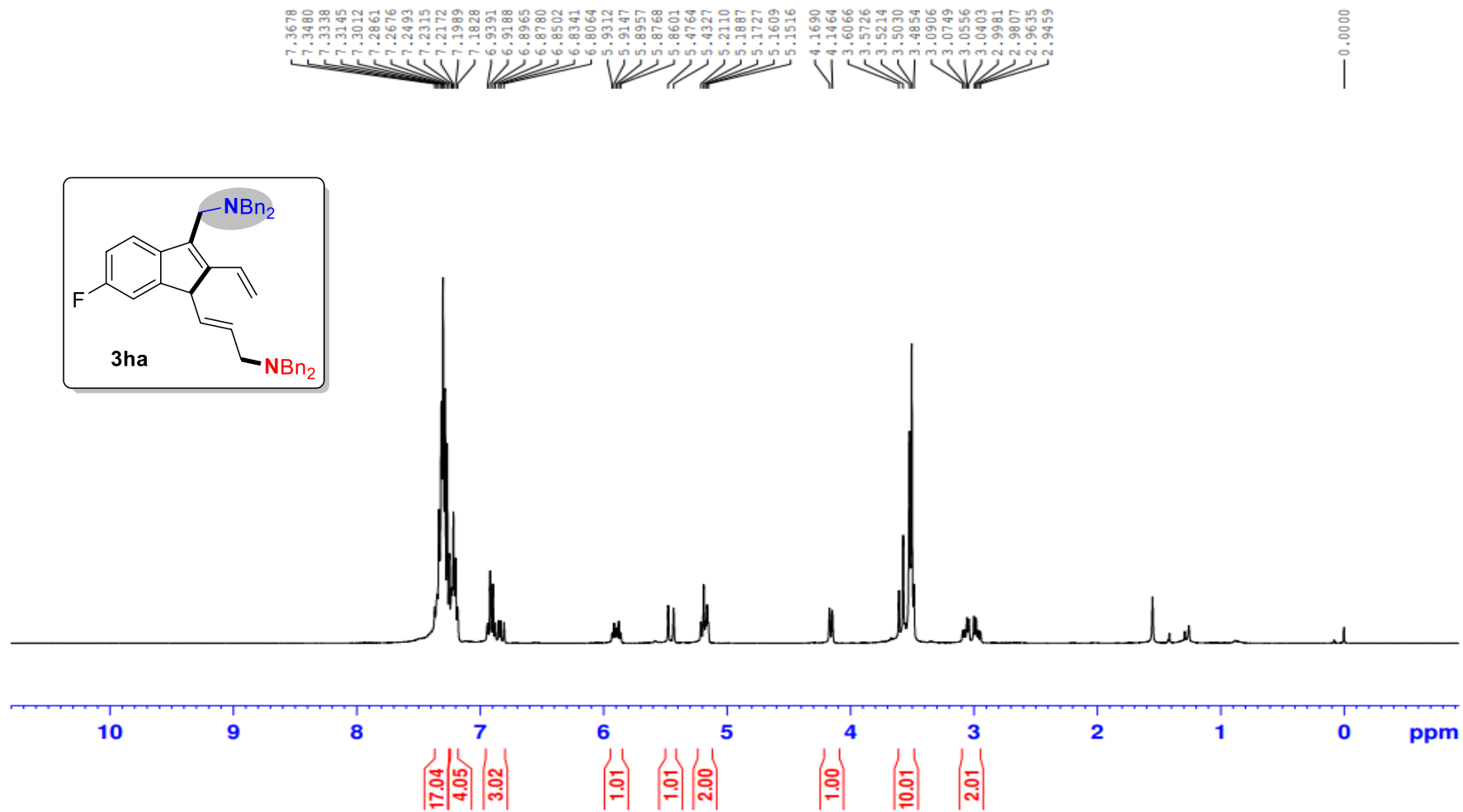
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 3ga**

LRR-X220831-4-F-376M(in  $\text{CDCl}_3$ )



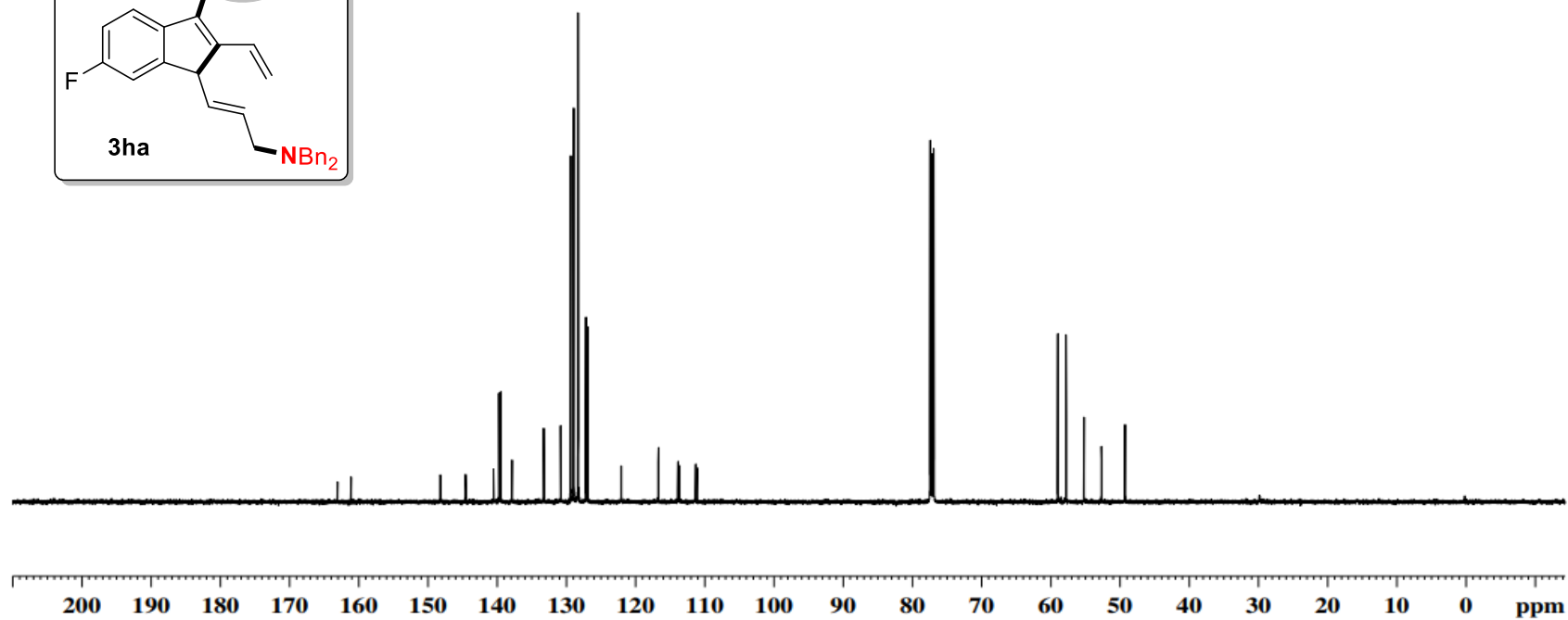
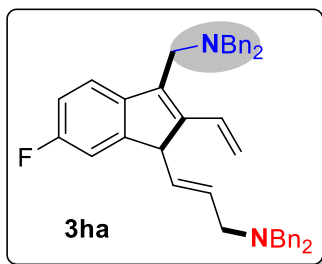
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ha

LRR-X220831-5-F-400M(in CDCl<sub>3</sub>)



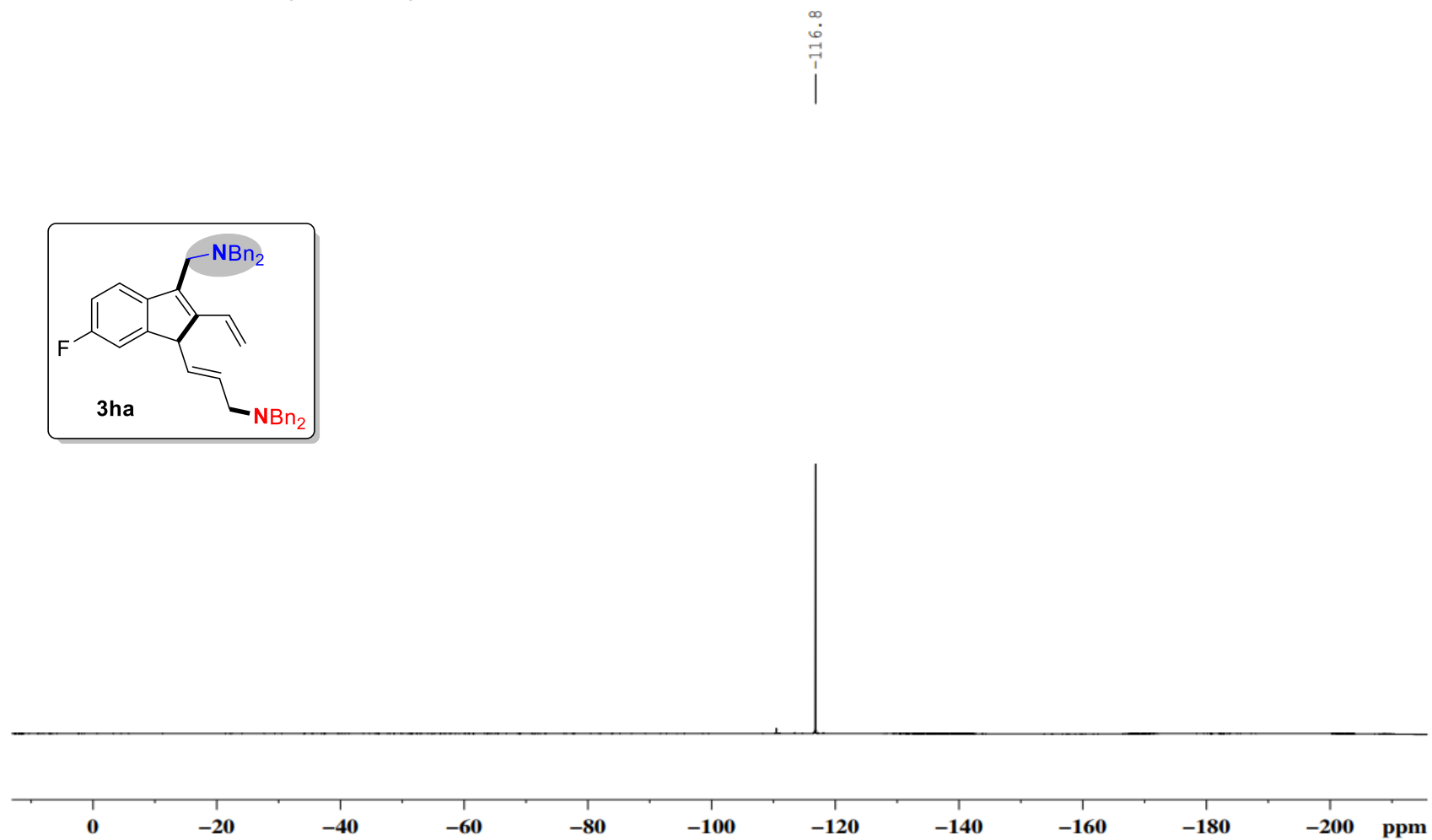
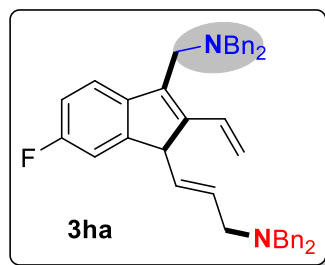
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ha**

LRR-X220831-5-F-125M(in CDCl<sub>3</sub>)



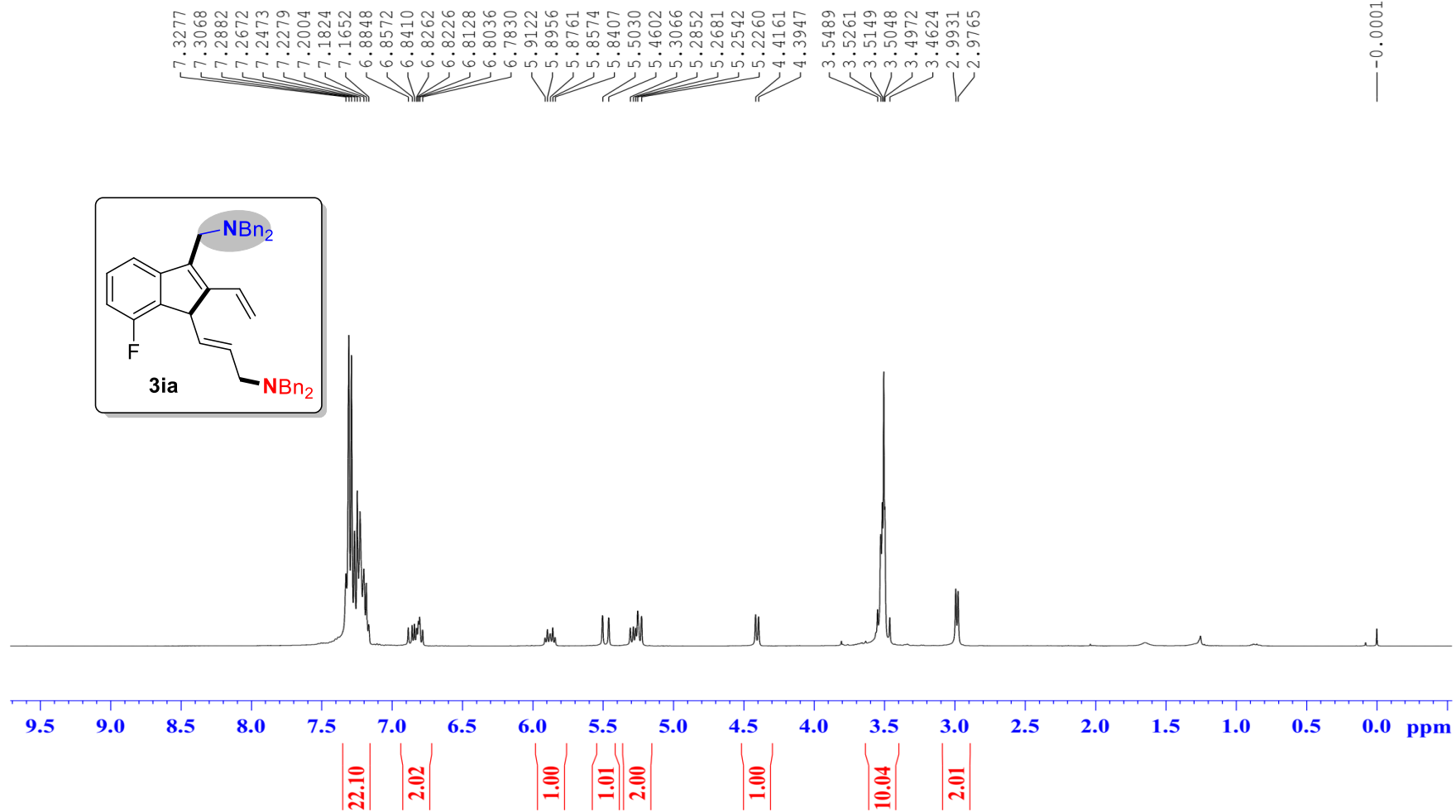
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 3ha**

LRR-X220831-5-F-376M(in  $\text{CDCl}_3$ )



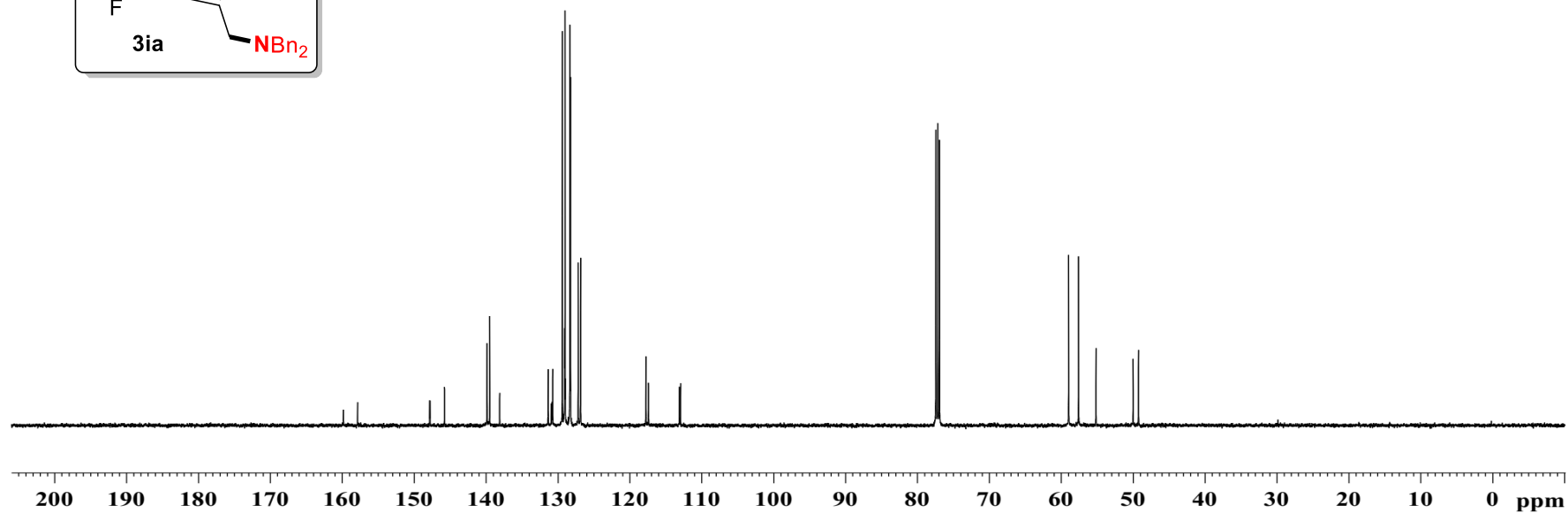
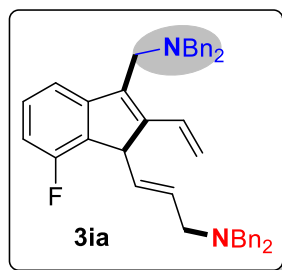
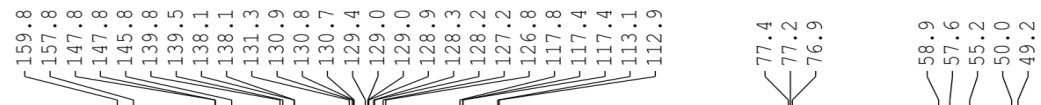
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ia**

YBK-X210414-5-6-F (in CDCl<sub>3</sub>)



**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectra for 3ia**

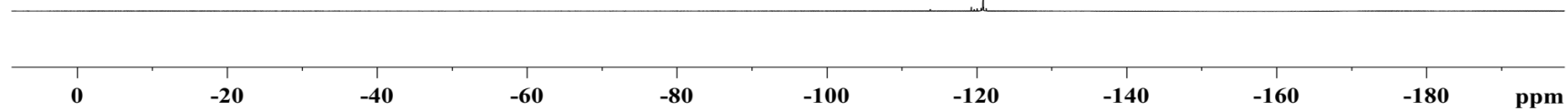
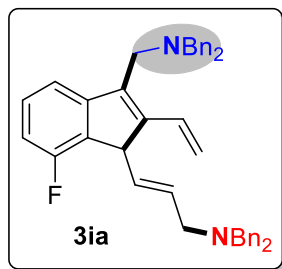
YBK-X210414-5 (in  $\text{CDCl}_3$ )



**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectra for 3ia**

YBK-X210414-5-6-F (in  $\text{CDCl}_3$ )

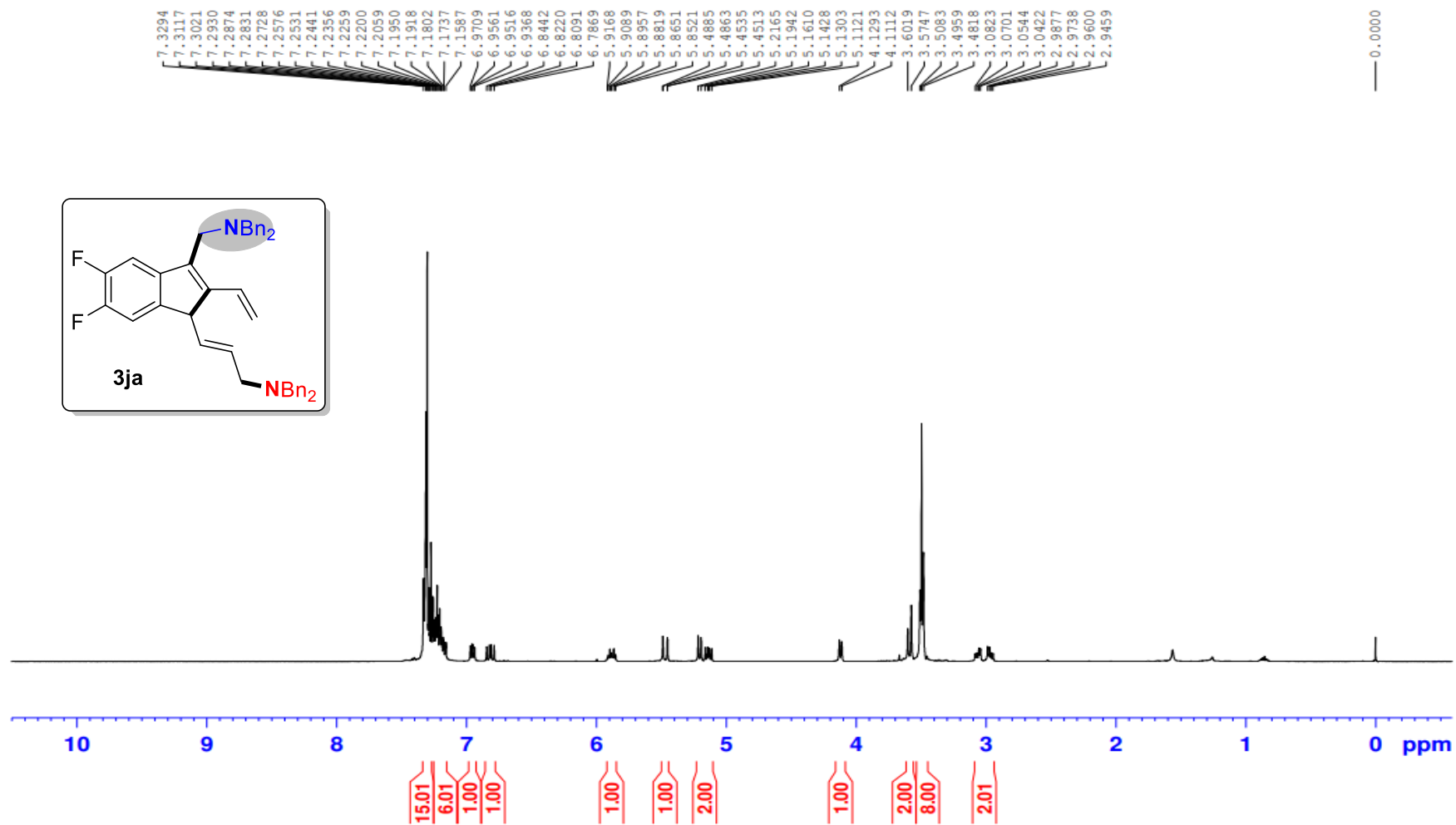
— -120.8





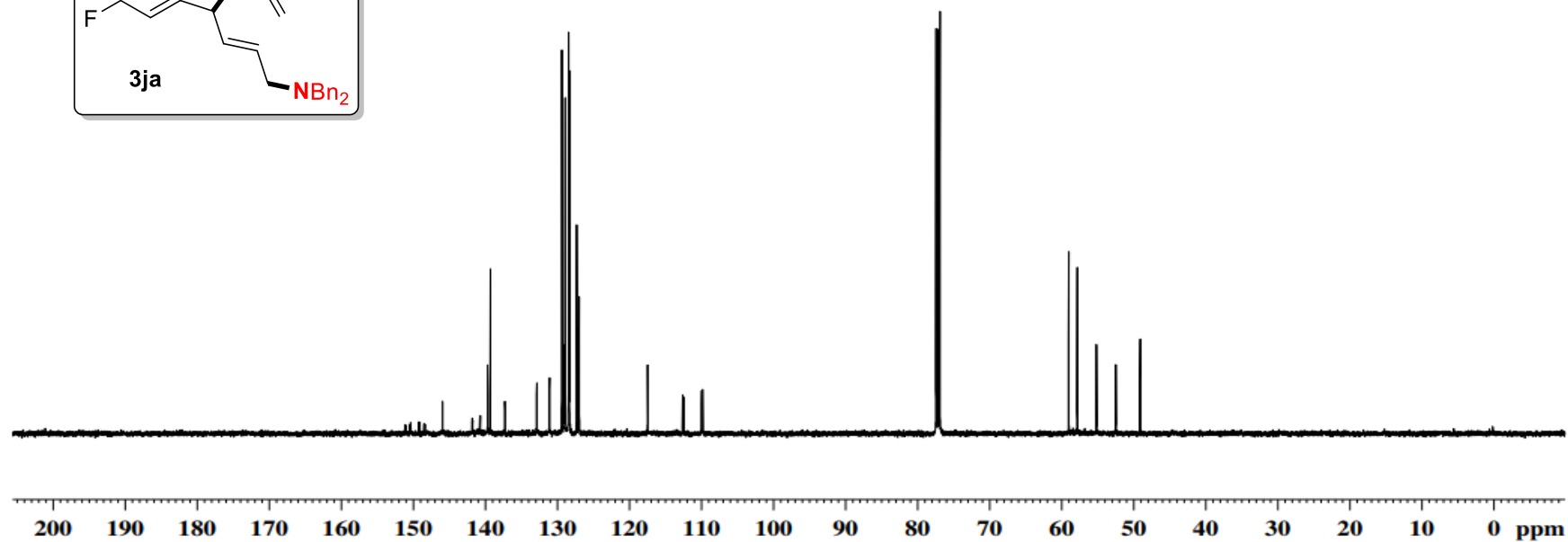
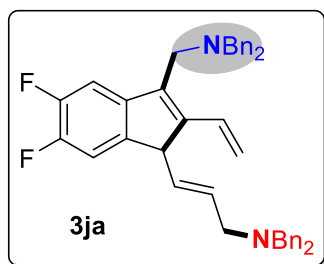
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra for 3ja**

LRR-X220918-2F-500M(in CDCl<sub>3</sub>)



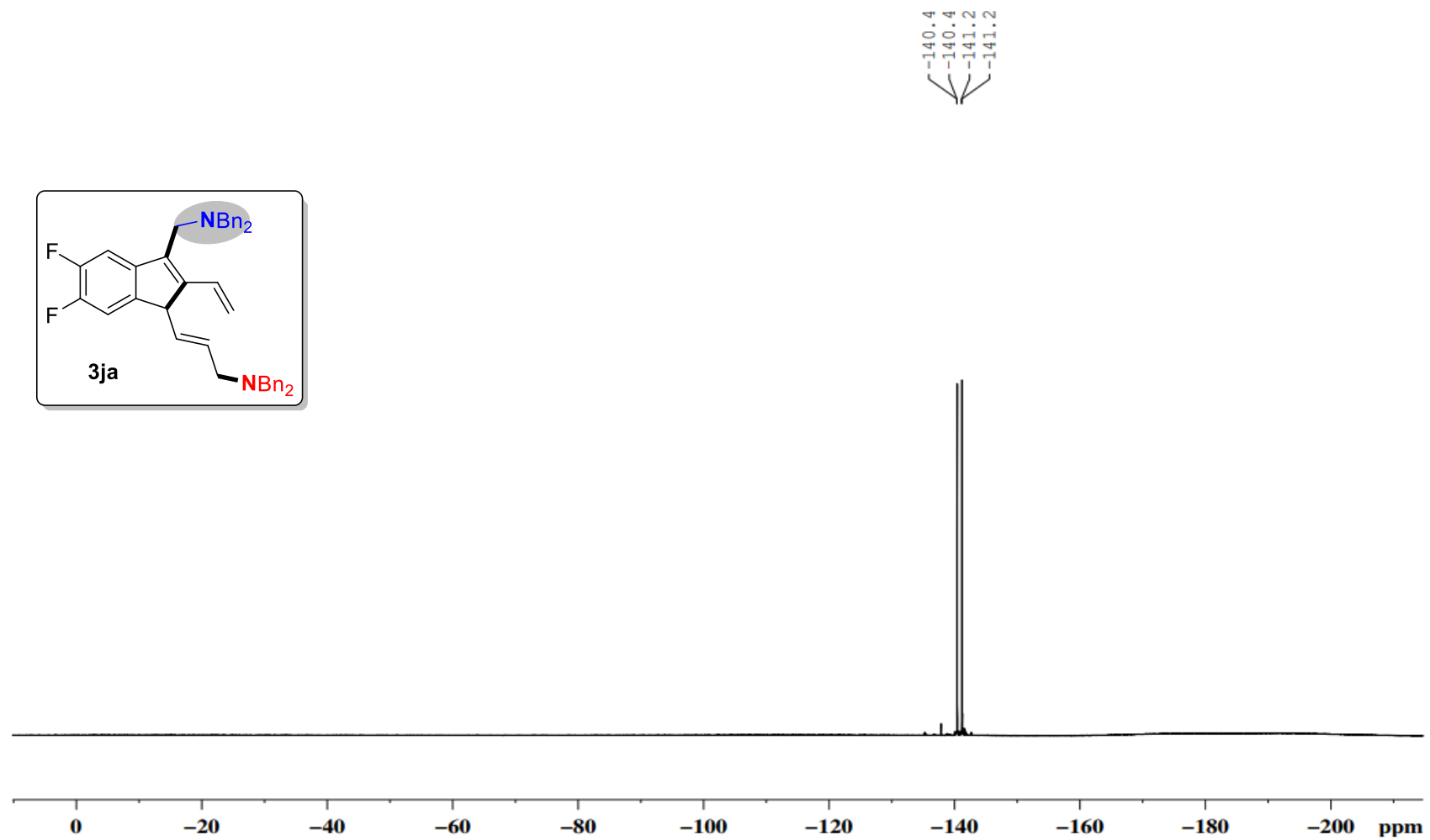
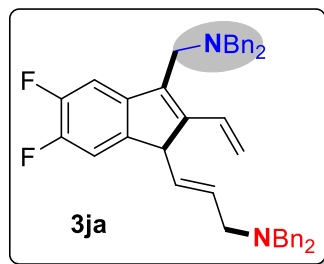
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ja**

LRR-X220917-2F-125M(in CDCl<sub>3</sub>)



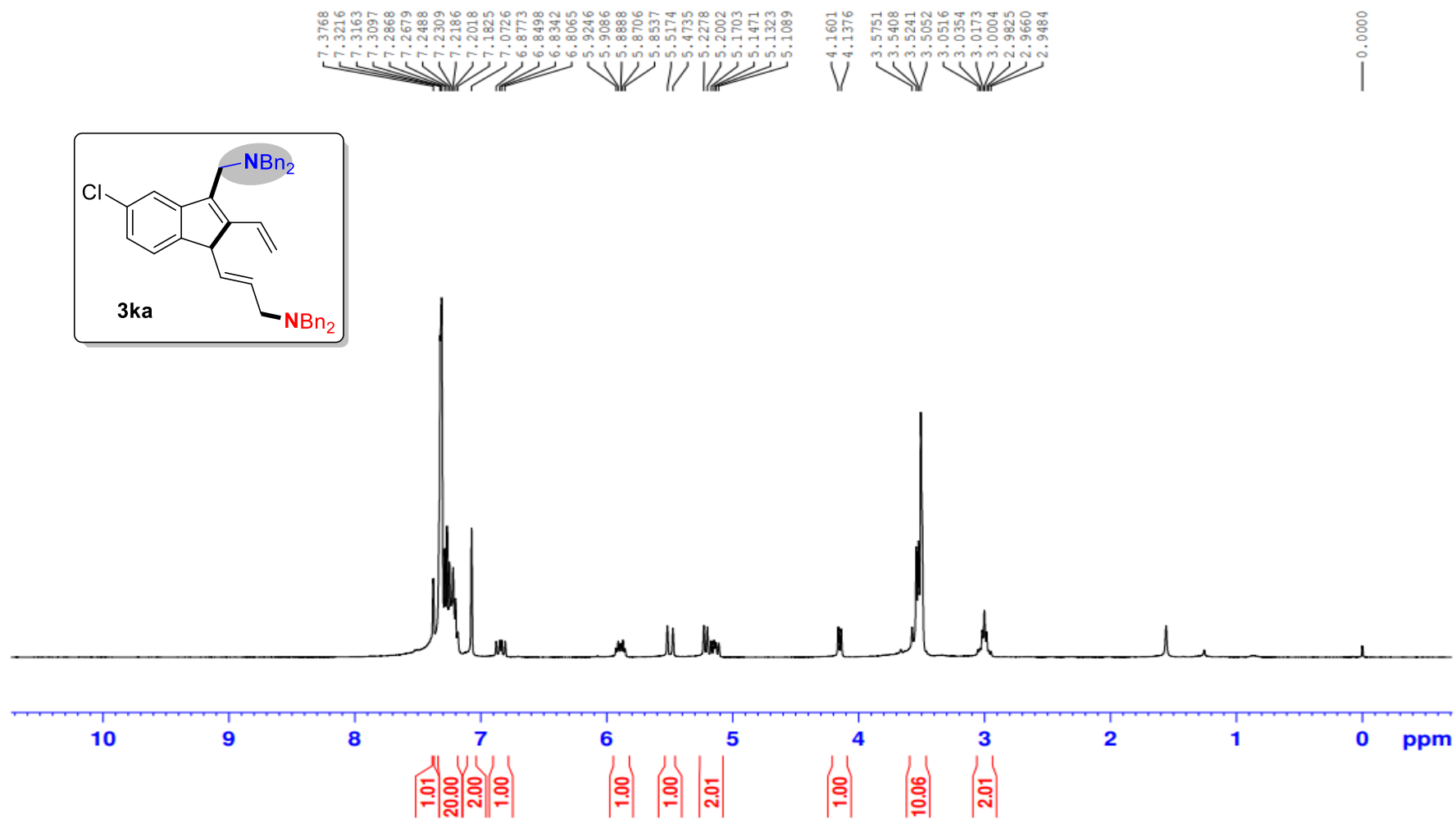
**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectra for 3ja**

LRR-X220917-2F-470M(in  $\text{CDCl}_3$ )



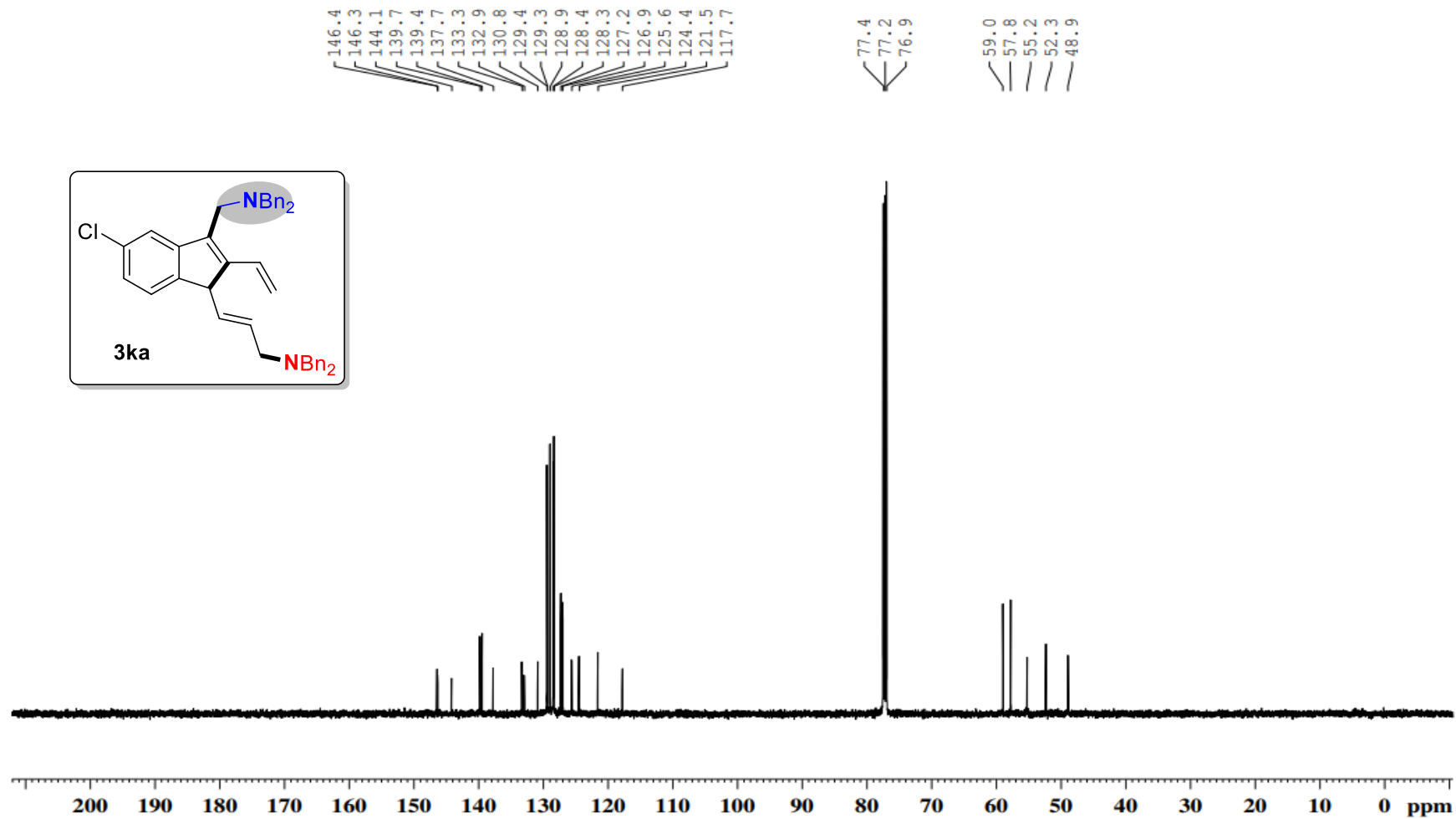
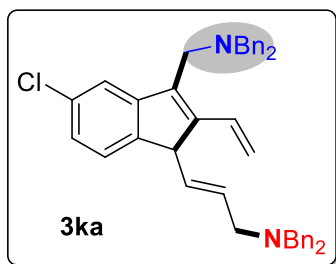
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ka

LRR-X220913-4-C1-400M(in CDCl<sub>3</sub>)



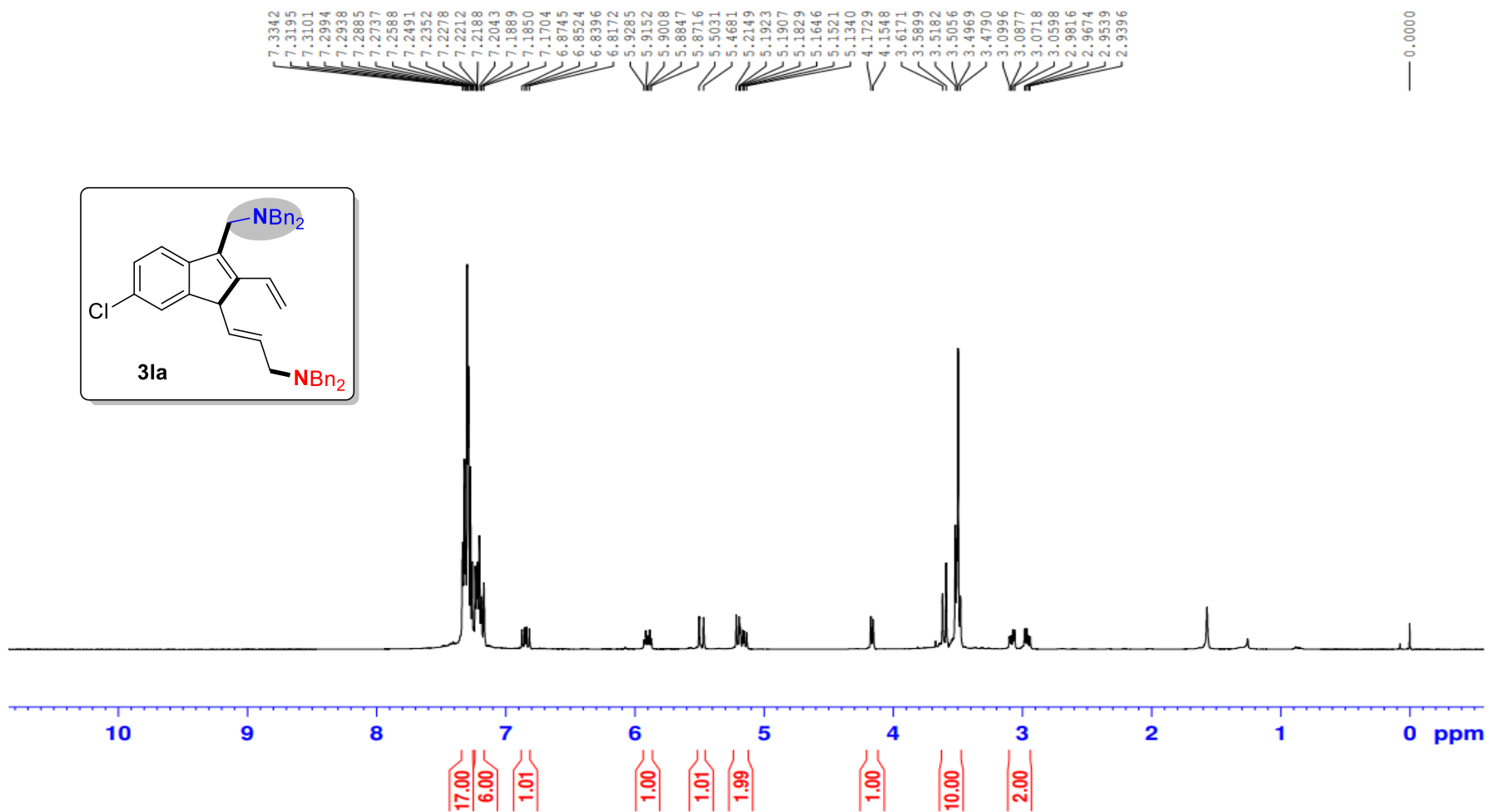
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ka

LRR-X220913-4-C1-125M(in CDCl<sub>3</sub>)



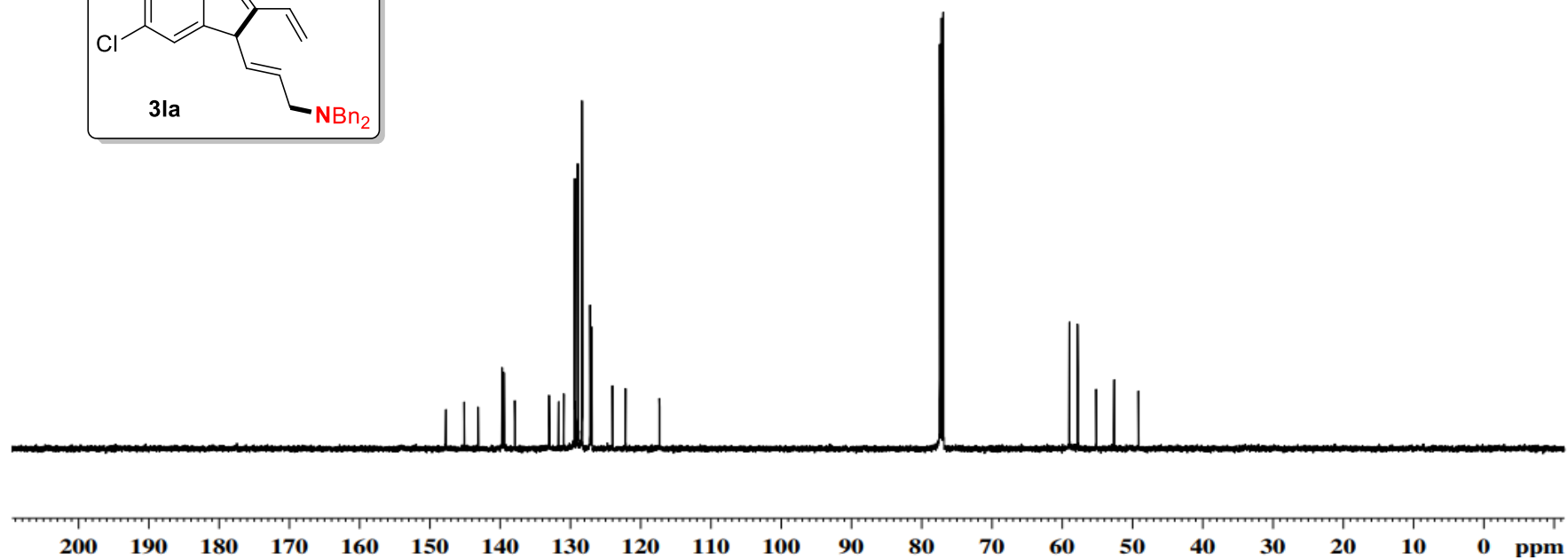
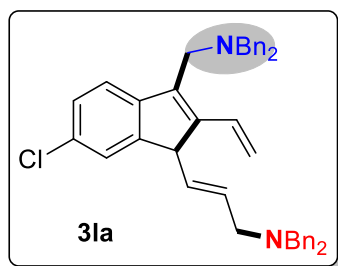
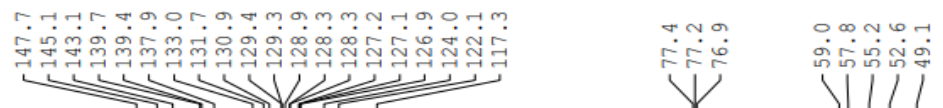
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra for 3a**

LRR-X220917-5-C1-500M(in CDCl<sub>3</sub>)



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3la

LRR-X220917-5-Cl-125M(in CDCl<sub>3</sub>)

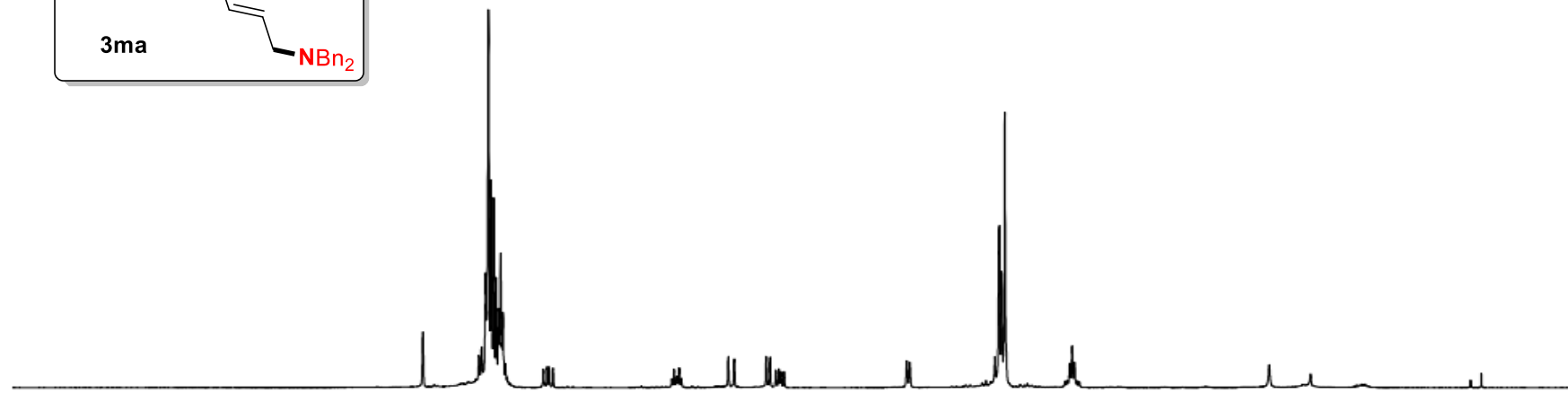
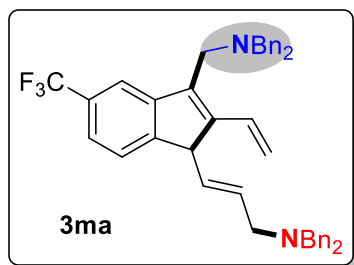


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3ma

LRR-X22X05-4-CF3-400M(in CDCl<sub>3</sub>)

7.7932  
7.3809  
7.3600  
7.3318  
7.3110  
7.2920  
7.2718  
7.2532  
7.2347  
7.2204  
7.2106  
7.2039  
7.1975  
7.1862  
6.9060  
6.8783  
6.8622  
6.8345  
5.9603  
5.9436  
5.9264  
5.9224  
5.9054  
5.8891  
5.8459  
5.5432  
5.5022  
5.4993  
5.2665  
5.2641  
5.2386  
5.2361  
5.1941  
5.1714  
5.1558  
5.1331  
4.2302  
4.2075  
3.5816  
3.5487  
3.5311  
3.5080  
3.0650  
3.0484  
3.0300  
3.0128  
2.9946  
2.9755  
2.9599

0.0000



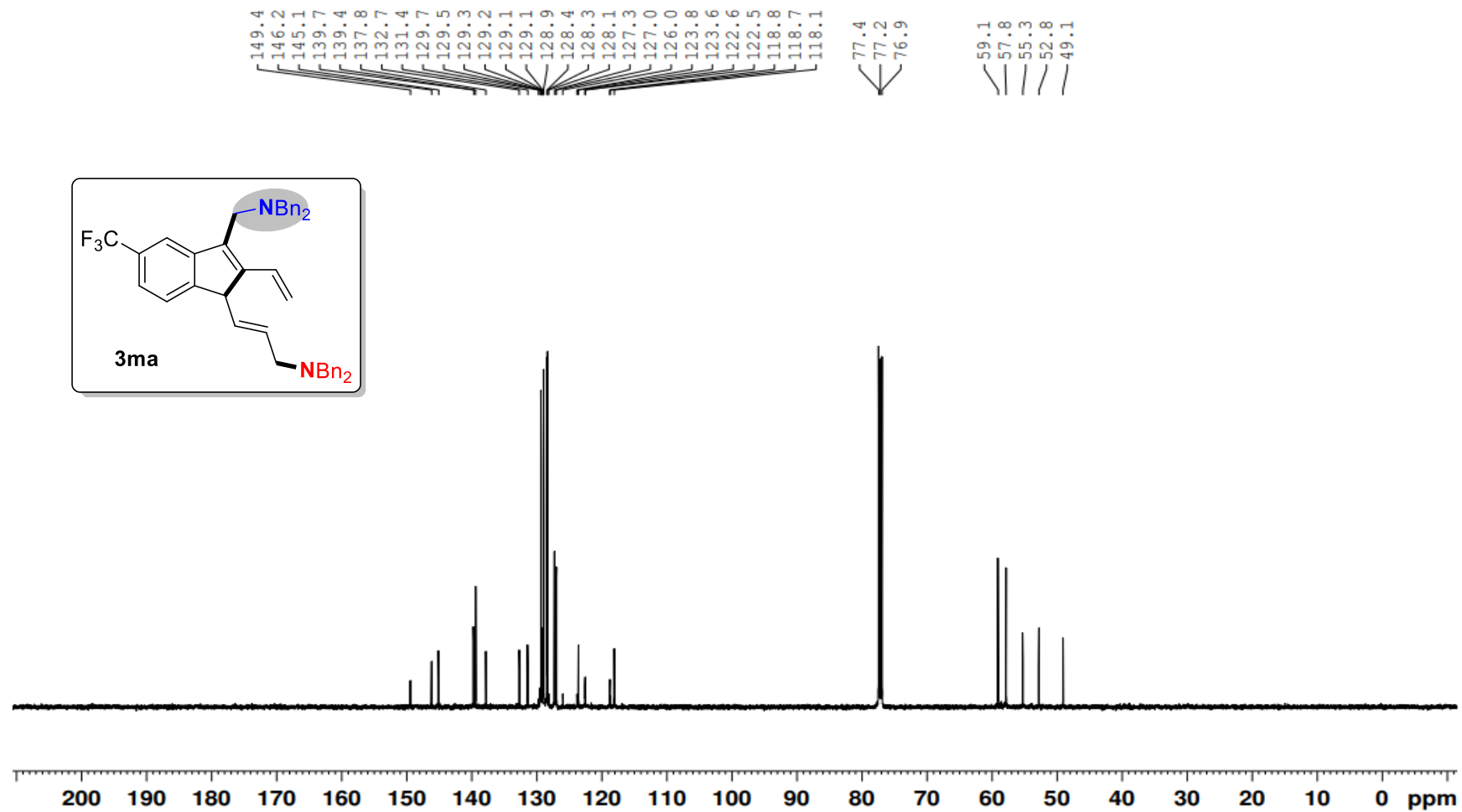
10 9 8 7 6 5 4 3 2 1 0 ppm

1.00  
17.99  
4.02  
1.04  
1.00  
1.00  
1.00  
1.00  
1.00  
10.00  
2.01



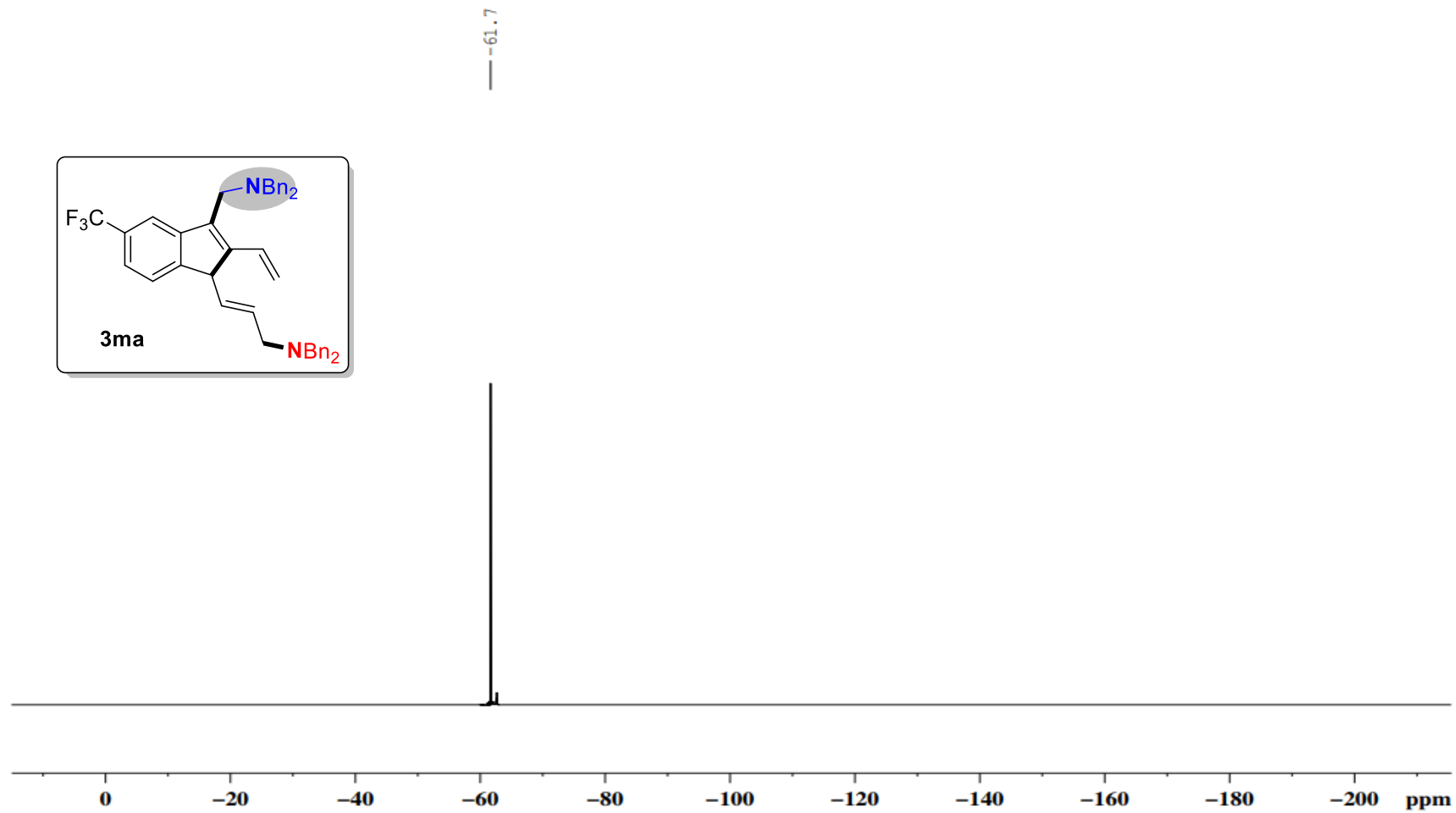
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3ma

LRR-X22X05-4-CF3-125M(in CDCl<sub>3</sub>)



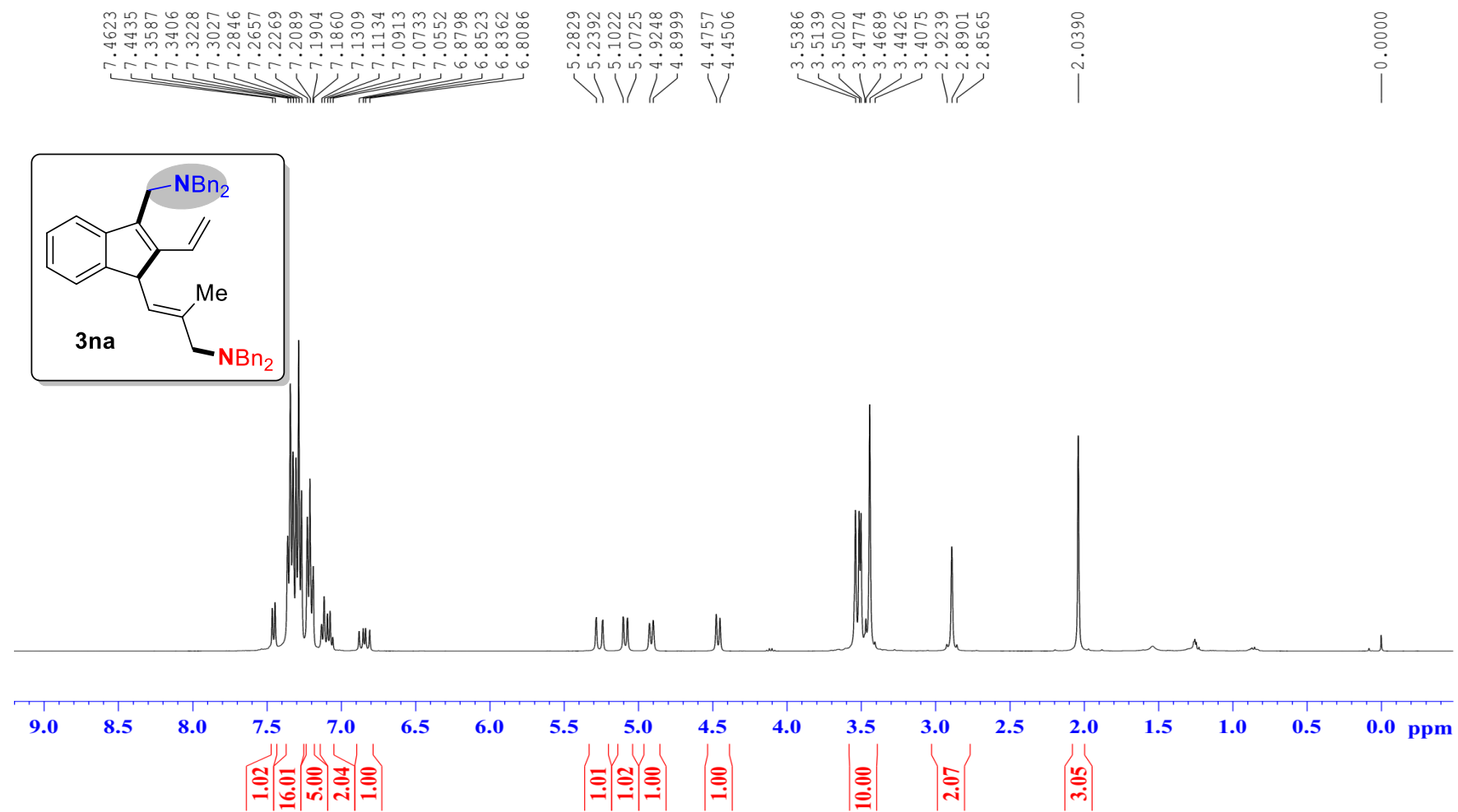
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra for 3ma

LRR-X22X05-4-CF3-376M(in CDCl<sub>3</sub>)



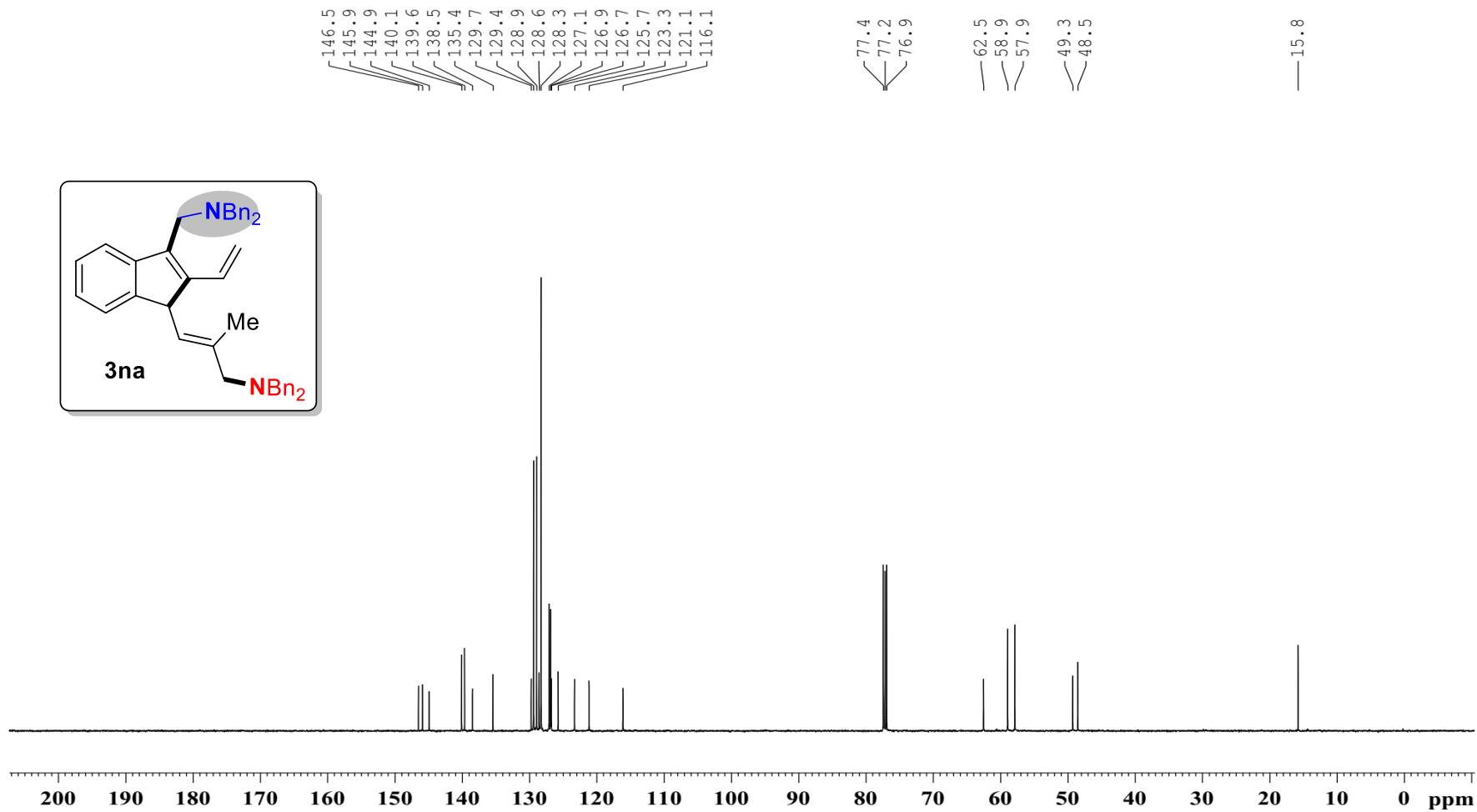
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3na**

YBK-X210414-7-2-CH3 (in CDCl<sub>3</sub>)



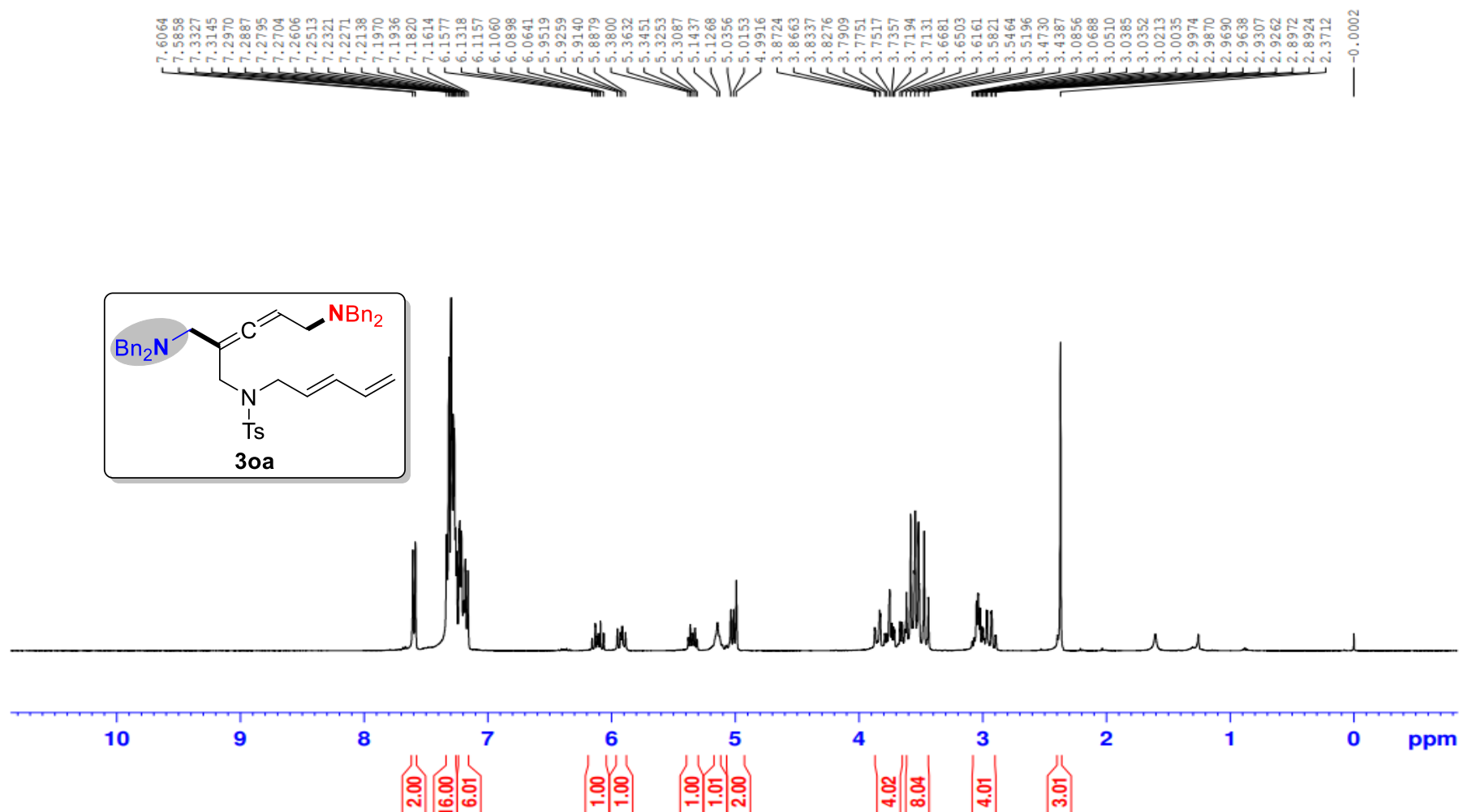
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3na**

YBK-X210414-7-CH3 (in CDCl<sub>3</sub>)



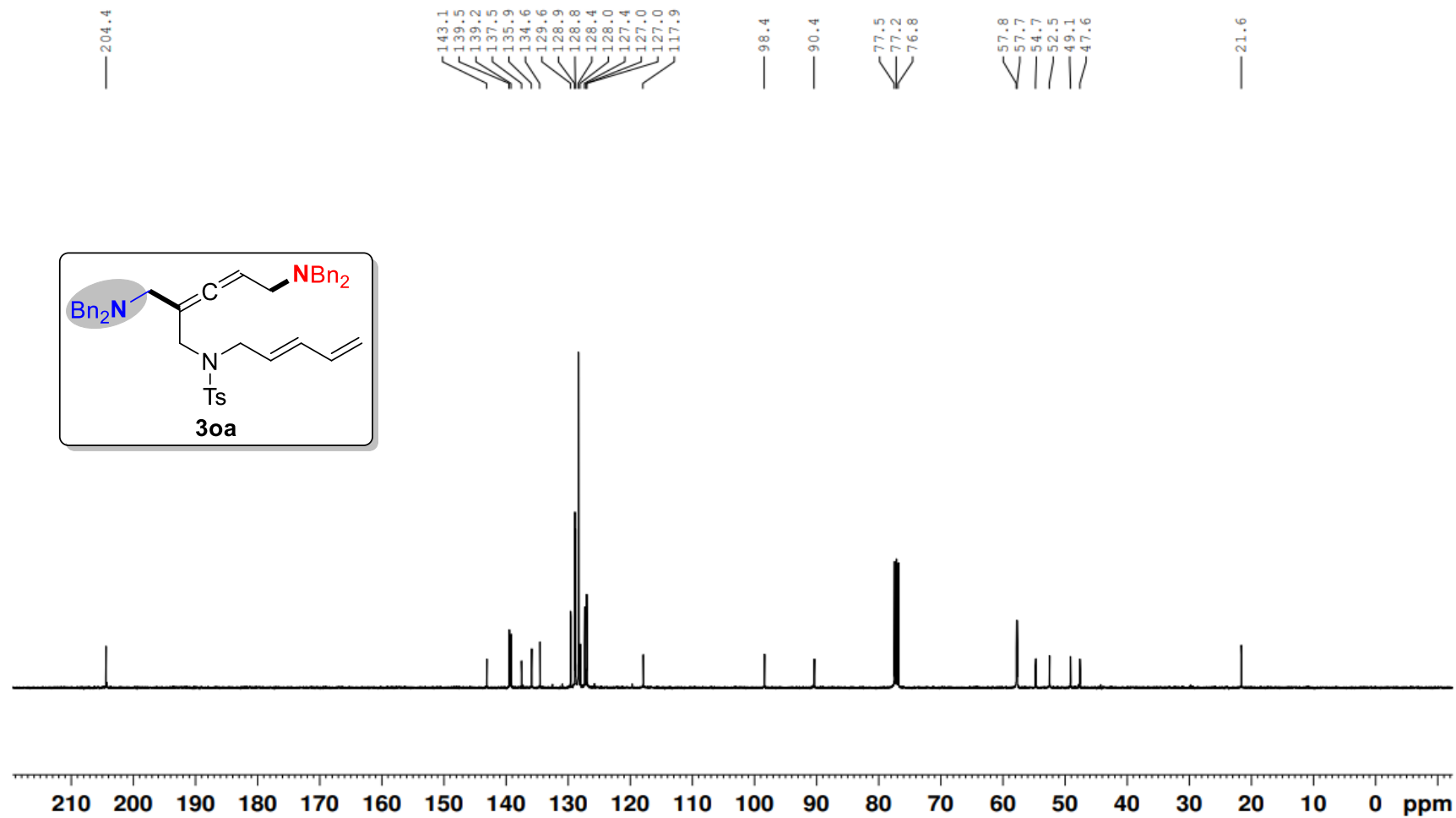
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3oa

LRR-X220929-NTS-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra for 3oa**

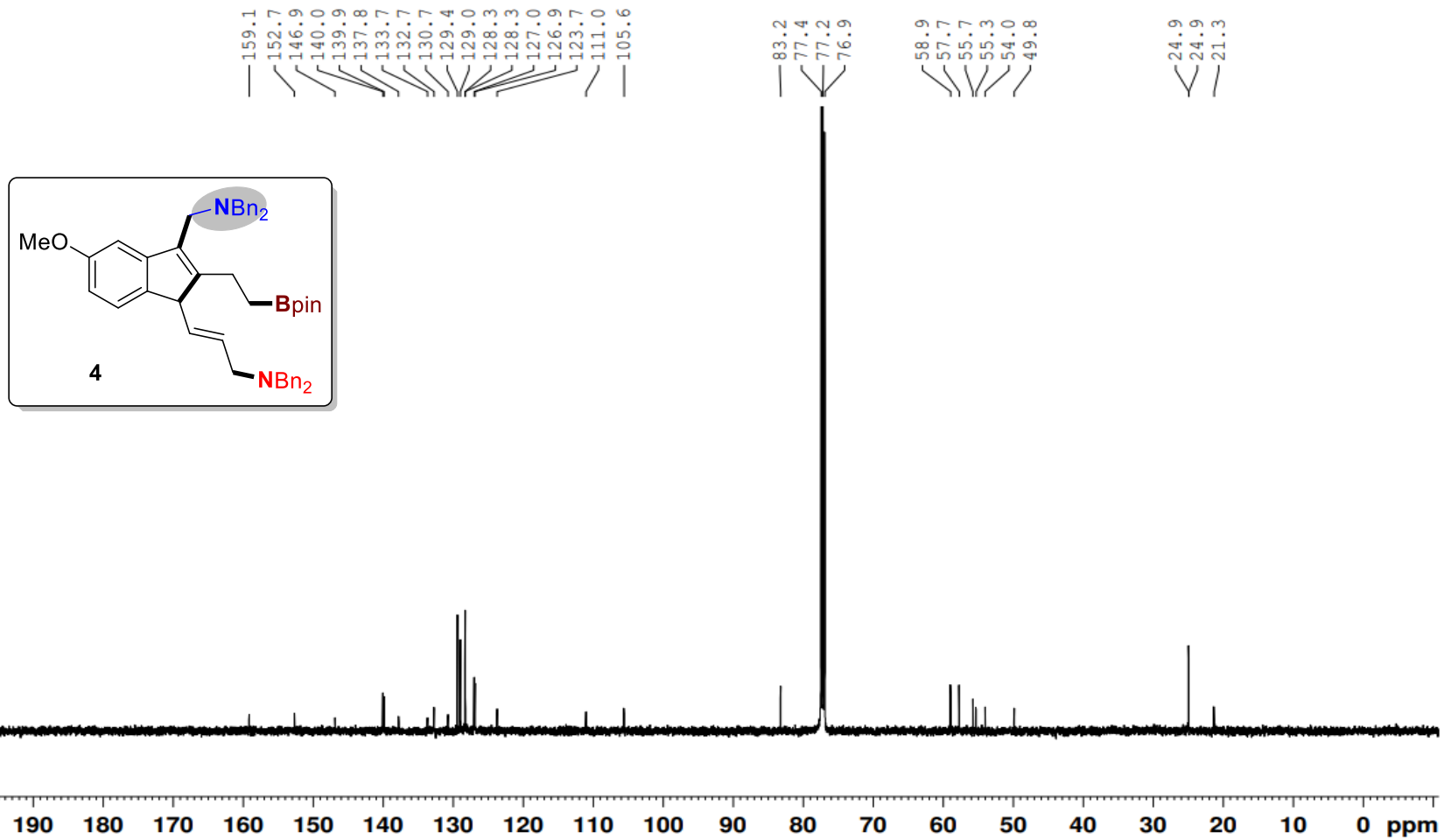
LRR-X220929-NTS-100M(in CDCl<sub>3</sub>)





<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 4

LRR-X230216-BPin-125M(in CDCl<sub>3</sub>)

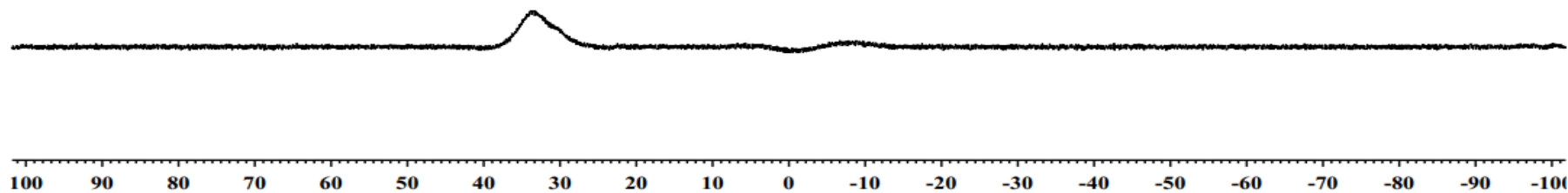
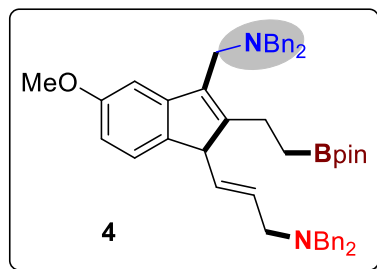




$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ) spectra for 4

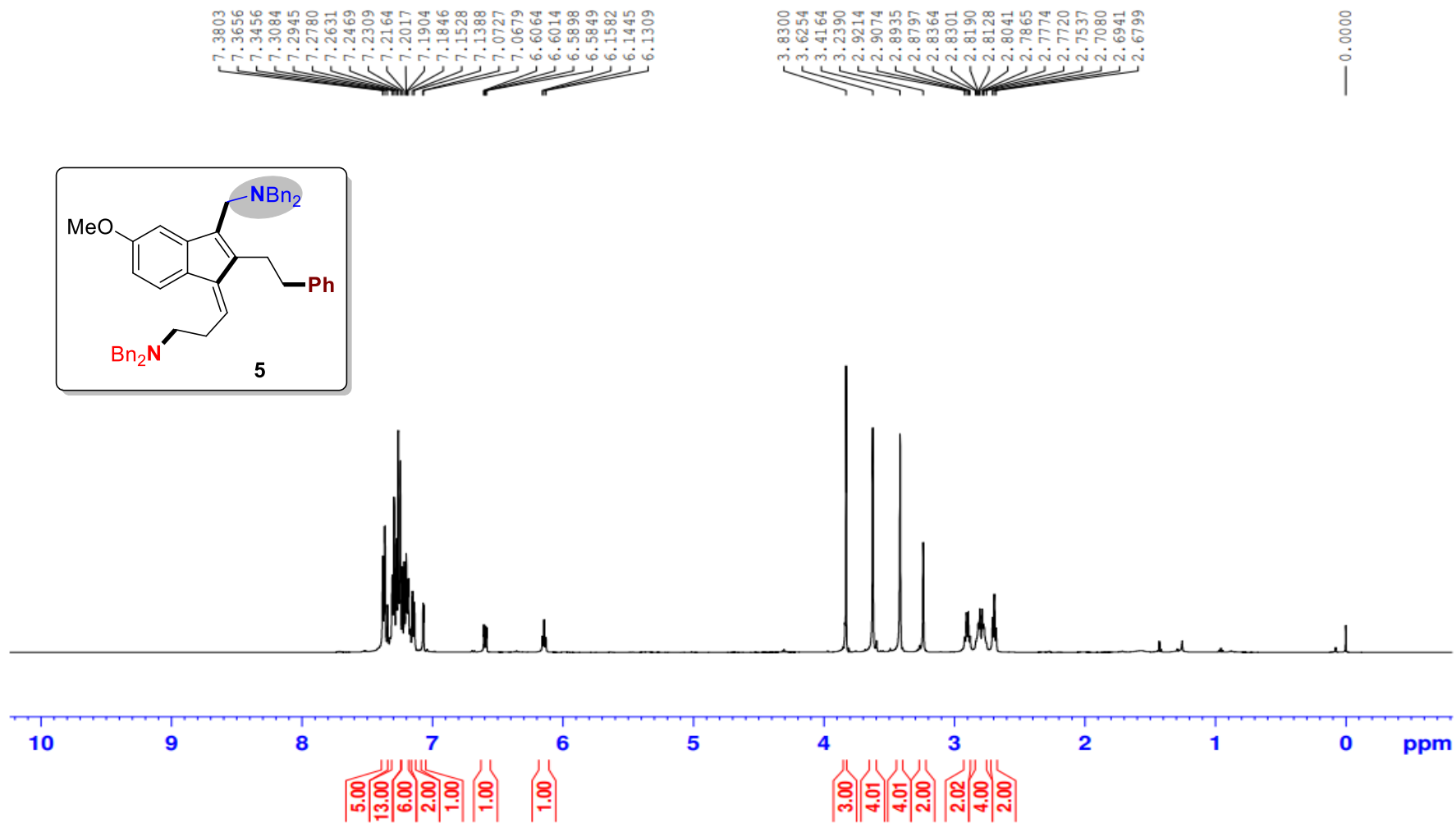
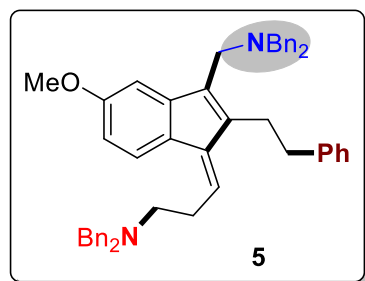
LRR-X230216-BPIN.3.fid -

-33.5



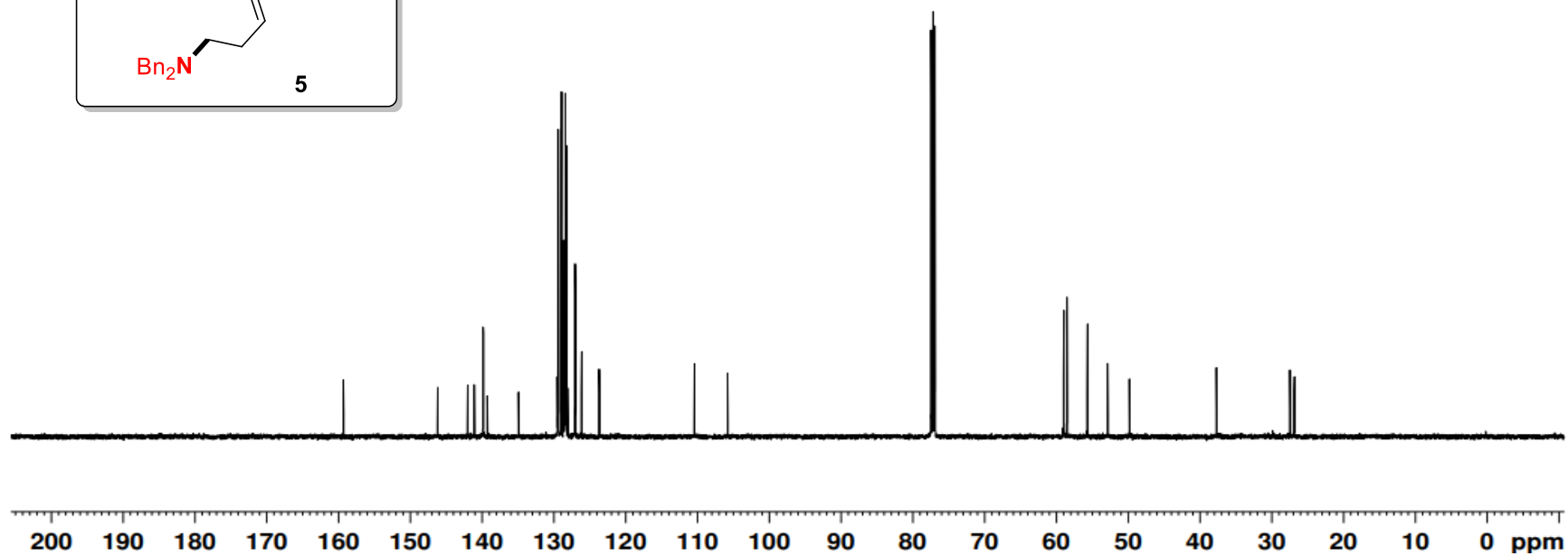
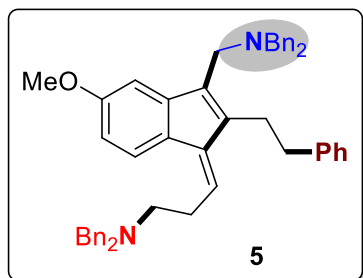
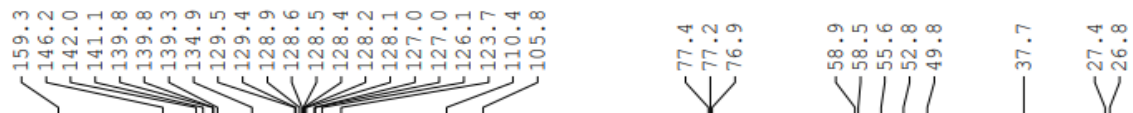
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra for 5

LRR-X230225-Ph-500M (in CDCl<sub>3</sub>)

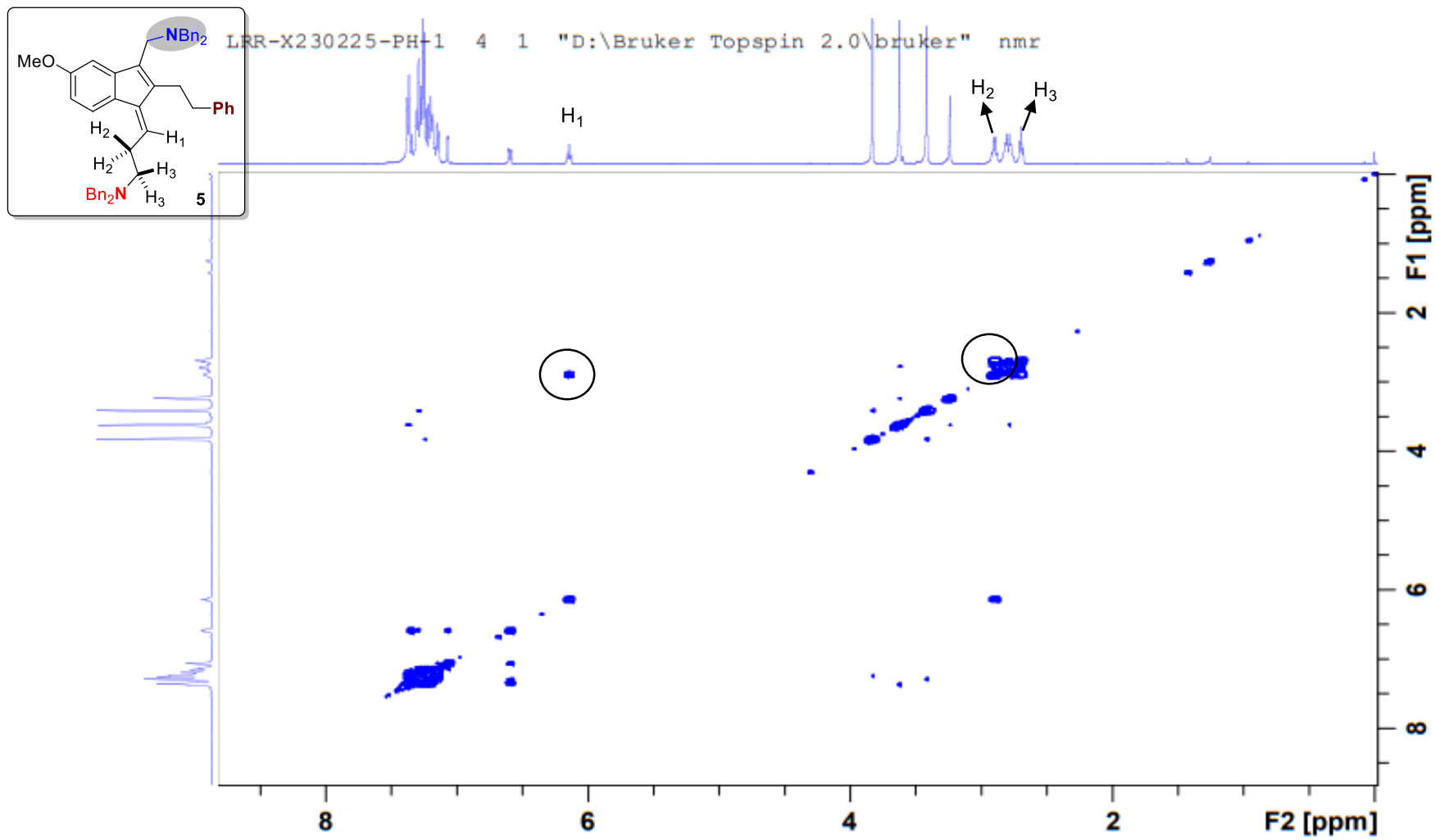


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 5

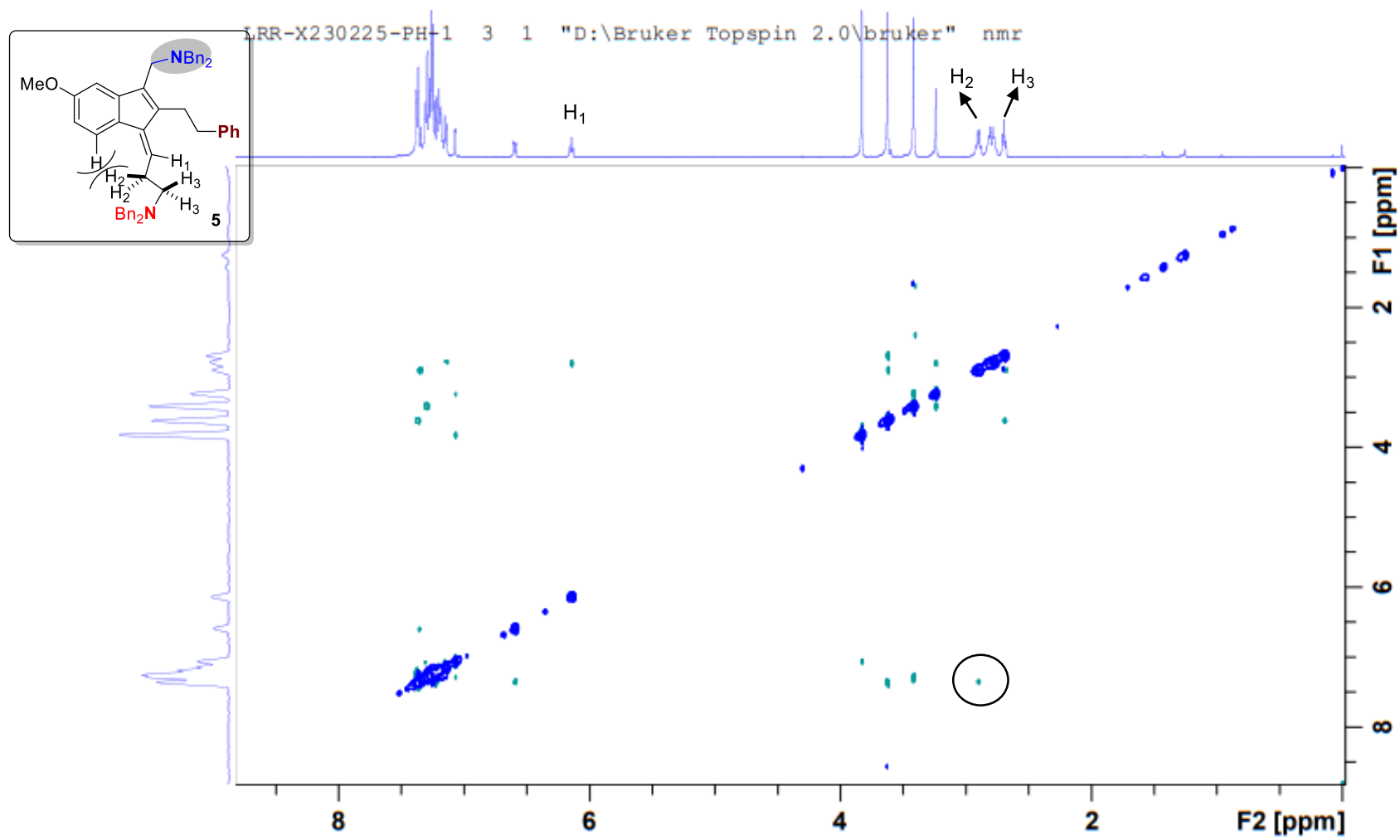
LRR-X230225-Ph-125M(in CDCl<sub>3</sub>)



$^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ ) spectra for 5

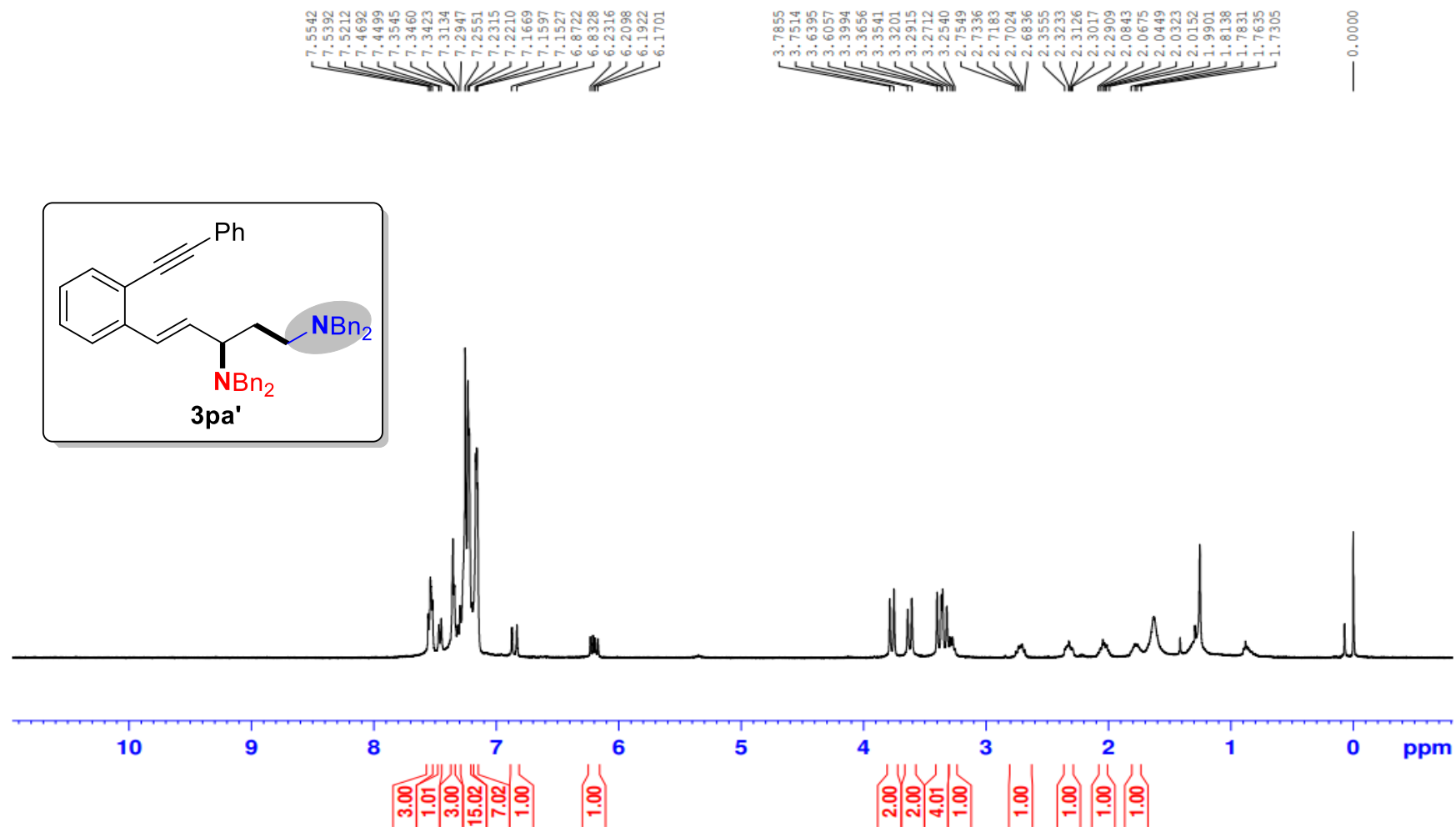


NOESY NMR (500 MHz, CDCl<sub>3</sub>) spectra for 5



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3pa'**

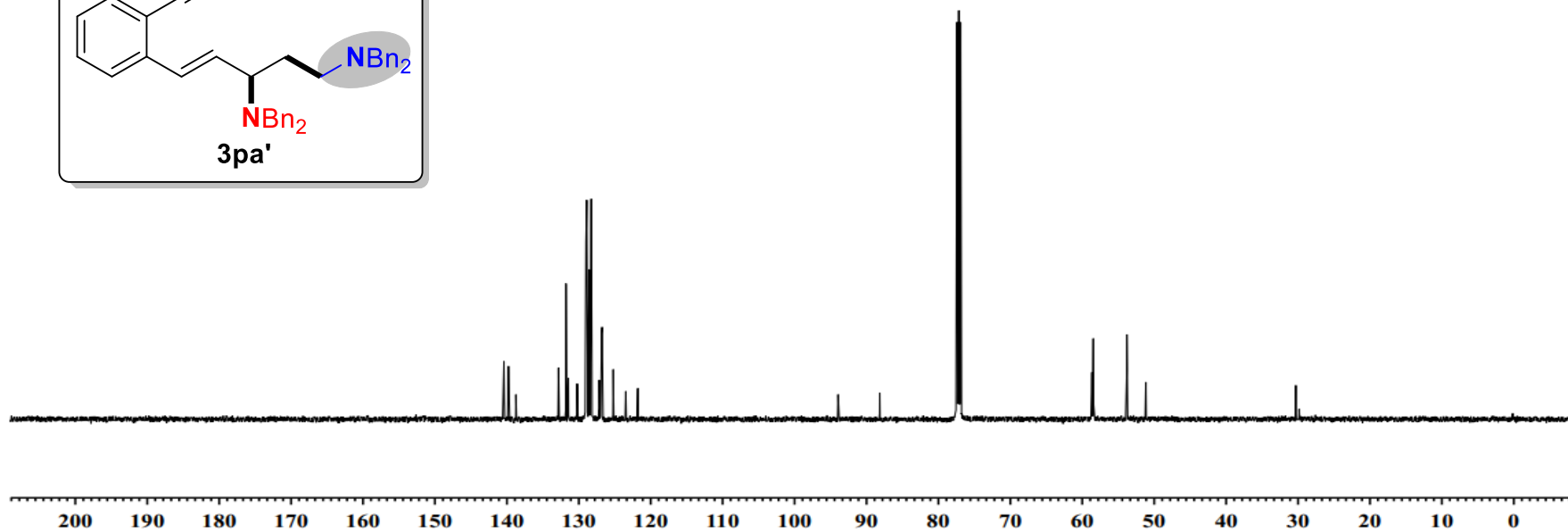
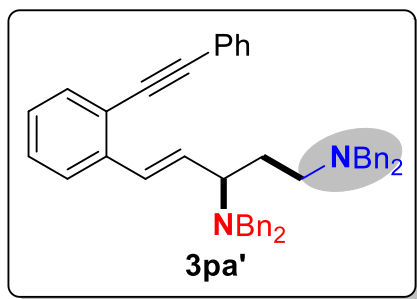
LRR-X22X30-PH-2-400M(in CDCl<sub>3</sub>)



**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3pa'**

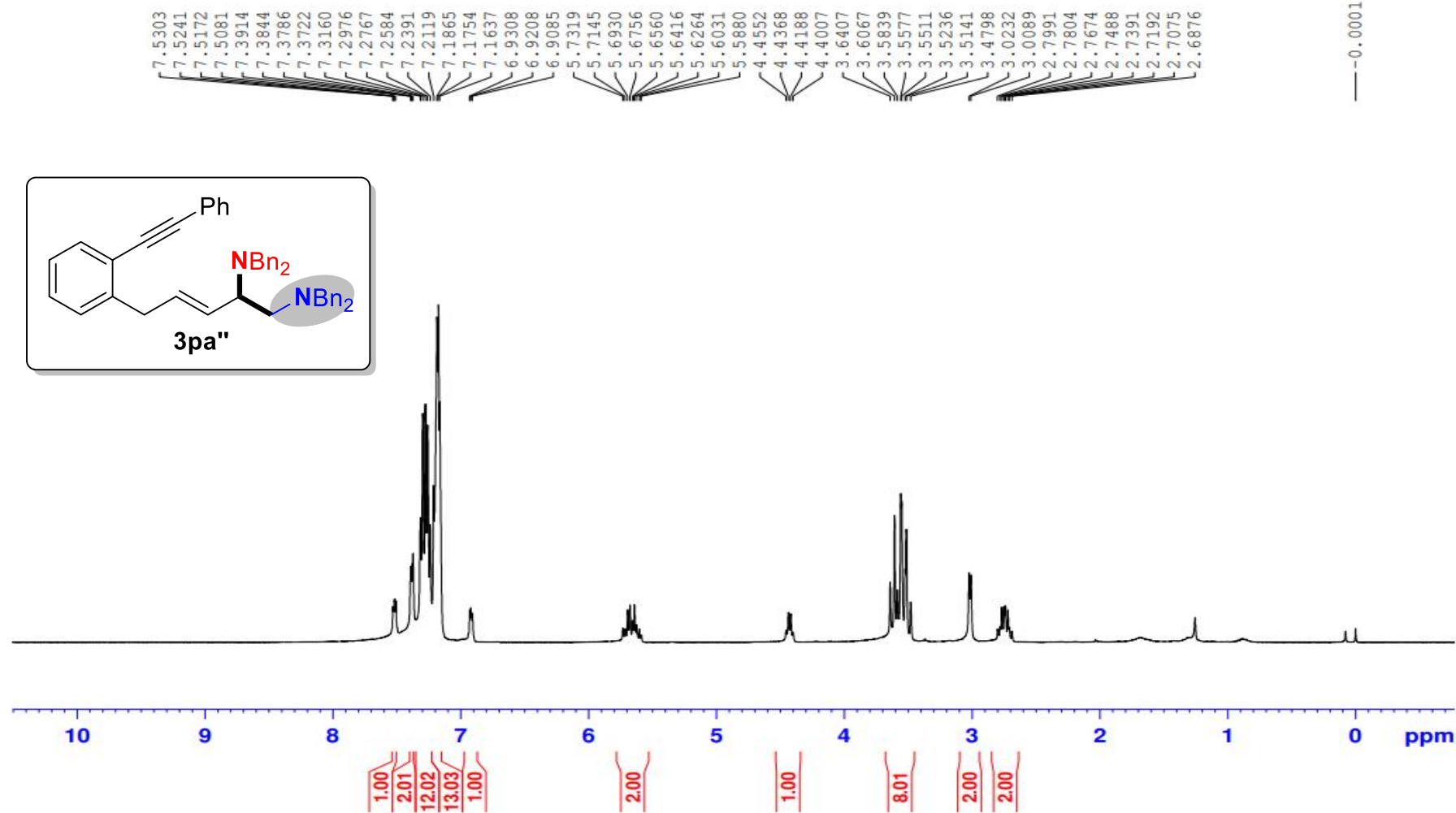
LRR-X22Y02-PH-2.2.fid -

140.4  
139.8  
138.7  
132.8  
131.8  
131.5  
130.2  
129.0  
128.9  
128.6  
128.5  
128.5  
128.3  
128.2  
127.2  
126.8  
126.8  
125.2  
123.5  
121.8  
-93.9  
-88.2  
77.4  
77.2  
76.9  
58.7  
58.5  
53.8  
51.2  
-30.3



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for 3pa''**

LRR-X22X30-Ph-1-400M(in CDCl<sub>3</sub>)





<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectra for 3pa''

LRR-X22X30-PH-1-C.1.fid -

145.3  
139.9  
139.7  
135.4  
132.5  
131.6  
129.0  
128.9  
128.6  
128.5  
128.3  
128.2  
127.6  
126.8  
126.1  
123.5  
122.8  
-93.2  
-88.5  
77.4  
77.2  
76.9  
58.9  
58.5  
57.9  
55.7  
-44.3

