

## Boracene-Based Alkylborate Enabling Ni/Ir Hybrid Catalysis

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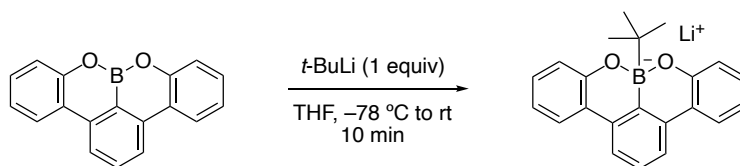
## ■ Instrumentation and Chemicals ■

NMR spectra were recorded on a JEOL 400SS or a Bruker AVANCE NEO 400N, operating at 400 MHz for  $^1\text{H}$  NMR, 100.5 MHz for  $^{13}\text{C}$  NMR. Chemical shift values for  $^1\text{H}$  and  $^{13}\text{C}$  are referenced to  $\text{Me}_4\text{Si}$ , the residual solvent resonances, respectively. Chemical shifts are reported in  $\delta$  ppm. Mass spectra were obtained with a Thermo Scientific Exactive Plus Orbitrap (ESI $^-$ ), JMS-T100TD (DART), or JMS-700 (FAB-MS). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F<sub>254</sub>. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. IR spectra were measured with a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A or MIRacle, or a Thermo Scientific Nicolet iS5 FT-IR attached with iD7 ATR with the absorption band given in  $\text{cm}^{-1}$ . Melting points were measured on a Yanaco MP-500D apparatus. UV-Vis absorption spectra were recorded on a Shimadzu UV-1900. Fluorescence spectra were recorded on a Shimadzu RF-6000. Kessil PR160L 440 nm (highest blue and intensity setting) or Micro Photochemical Reactor (Sigma-Aldrich) was used as a light source.

All reactions were carried out under nitrogen atmosphere unless otherwise noted. Materials were obtained from commercial suppliers stored under nitrogen, and used as received or prepared according to standard procedures unless otherwise noted. 8,9-Dioxa-8a-borabenzof[*fg*]tetracene (boracene) (**1**) was prepared by the reported procedure.<sup>1,2</sup> The alkylborates was prepared by the reported procedure.<sup>3</sup> The borates **2c** and **2e** were used to the reaction without purification after concentration.  $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{dtbpy}]\text{PF}_6^4$  and  $[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6^5$  were prepared by the reported procedure.  $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{bpy}]\text{PF}_6$  and  $\text{Ir}(\text{ppy})_3$  was purchased by Sigma-Aldrich. Dimethylacetamide was purchased from Nacalai Tesque Inc. Dehydrated tetrahydrofuran, acetonitrile, and methanol were purchased from FUJIFILM Wako Pure Chemical Co. *tert*-Butyllithium (in *n*-pentane, 1.6 mol/L), *sec*-butyllithium (in cyclohexane, 1.2 mol/L), and, *n*-butyllithium (in *n*-hexane, 1.6 mol/L) were purchased from Kanto Chemical Co. Inc.  $\text{Ni}(\text{acac})_2$ ,  $\text{Ni}(\text{TMHD})_2$ ,  $\text{NiBr}_2 \cdot \text{diglyme}$ , 4,4'-*di-tert*-butylbiphenyl, and, 1,10-phenanthroline, were purchased from Sigma-Aldrich. 1% transmittance neutral-density filter was purchased from SIGMAKOKI. Longpass filter (cut-off, 430 nm) was purchased from ASAHI SPECTRA.

## ■ Characterization Data for 2a ■

### *tert*-butylborate 2a<sup>3</sup>



To a suspension of boracene (270 mg, 1.00 mmol) in THF (10 mL) was added *t*-butyllithium (1.6 M in *n*-pentane, 0.6 mL, 1.0 mmol) at  $-78\text{ }^{\circ}\text{C}$ . After warming to room temperature, the mixture was stirred for 10 min at the same temperature. The mixture was concentrated under reduced pressure to give **2a** (475 mg, 993  $\mu\text{mol}$ , 99.3%) as a colorless solid.

The molecular weight of **2a** was calculated as [*t*-Bu(boracene)]Li·2THF (MW: 478.36) determined from  $^1\text{H}$  NMR and the X-ray structure, for the use of the experiments.

**M.p.** 163  $^{\circ}\text{C}$  (decomp.).

**IR** (ZnSe,  $\text{cm}^{-1}$ ): 731, 754, 899, 918, 947, 1042, 1130, 1234, 1290, 1406, 1447, 1578, 2843, 2884, 2920.

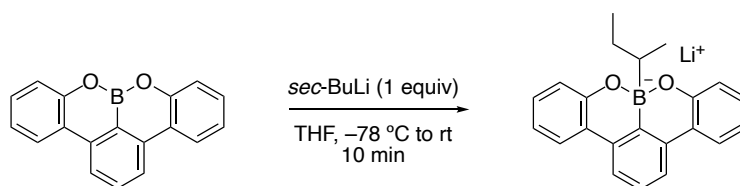
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  0.46 (s, 9H), 1.61–1.72 (m, THF), 3.54–3.65 (m, THF), 6.80–6.89 (m, 4H), 7.10 (ddd,  $J = 1.6, 8.0, 8.0$  Hz, 2H), 7.31 (t,  $J = 8.0$  Hz, 1H), 7.56 (d,  $J = 8.0$  Hz, 2H), 7.76 (dd,  $J = 1.6, 8.0$  Hz, 2H).

$^{13}\text{C}$  NMR (100.5 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  25.6 (THF), 27.3 (3C), 68.6 (THF), 119.0 (2C), 119.5 (2C), 120.4 (2C), 124.0 (2C), 127.1, 128.4 (2C), 128.6 (2C), 135.7 (2C), 156.7 (2C). The signals for the carbons attached to the boron atom were not observed.

$^{11}\text{B}$  NMR (127 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.49 (br).

**HRMS** (ESI<sup>-</sup>  $m/z$ ): [ $\text{M}-(\text{Li}+2\text{THF})$ ]<sup>-</sup> calcd for  $\text{C}_{22}\text{H}_{20}\text{BO}_2^-$ , 327.1562; found, 327.1564.

### *sec*-butylborate 2b



To a suspension of boracene (67.5 mg, 250  $\mu\text{mol}$ ) in THF (2.5 mL) was added *s*-butyllithium (1.0 M in cyclohexane/*n*-hexane, 0.25 mL, 0.25 mmol) at  $-78\text{ }^{\circ}\text{C}$ . After warming to room temperature, the mixture was stirred for 10 min at the same temperature. The mixture was concentrated under reduced pressure to give **2b** (102 mg, quantitative) as a colorless solid.

The molecular weight of **2b** was calculated as [*sec*-Bu(boracene)]Li·2THF (MW: 478.36), which was determined from the integral value of  $^1\text{H}$  NMR, for the use of the experiments.

**M.p.** 116  $^{\circ}\text{C}$  (decomp.).

**IR** (ZnSe,  $\text{cm}^{-1}$ ): 733, 756, 835, 891, 937, 976, 1042, 1128, 1229, 1290, 1406, 1447, 1489, 1580, 1599, 2947, 3057, 3333, 3578.

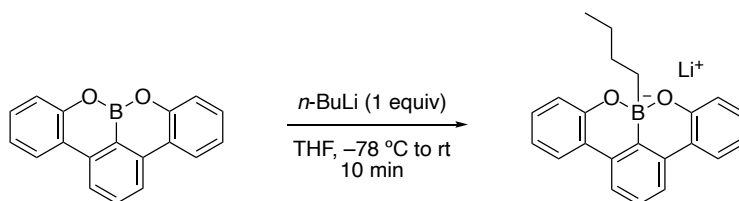
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 0.17–0.28 (m, 1H), 0.59–0.66 (m, 6H), 0.71–0.84 (m, 1H), 1.23–1.34 (m, 1H), 1.63–1.73 (m, THF), 3.56–3.66 (m, THF), 6.81–6.92 (m, 4H), 7.07–7.14 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 1.6, 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 100.5 MHz): δ 13.7, 14.1, 24.9, 25.6 (THF), 68.6 (THF), 119.37, 119.38, 119.65, 119.70, 120.4, 120.6, 124.2, 124.3, 127.1, 128.2, 128.38 (2C), 128.45, 135.0 (2C), 156.0, 156.1. The signals for the carbons attached to the boron atom were not observed.

**<sup>11</sup>B NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 127 MHz): δ 7.35 (br).

**HRMS** (ESI<sup>-</sup>): *m/z* 327.1562 (327.1562 calcd for C<sub>22</sub>H<sub>20</sub>BO<sub>2</sub><sup>-</sup>, [M-(Li+THF)]<sup>-</sup>).

### *n*-butylborate **2d**



To a suspension of boracene (540 mg, 2.00 mmol) in THF (20 mL) was added *n*-butyllithium (1.55 M in *n*-hexane, 1.30 mL, 2.02 mmol) at  $-78$  °C. After warming to room temperature, the mixture was stirred for 10 min at the same temperature. The mixture was purified by recrystallization (THF/hexane). The crystals were washed with *n*-hexane and a small amount of THF to give **2d** (794 mg, 1.66 mmol, 83.0%) as a colorless solid.

The molecular weight of **2d** was calculated as [*sec*-Bu(boracene)]Li·2THF (MW: 478.36), which was determined from the integral value of <sup>1</sup>H NMR, for the use of the experiments.

**M.p.** 117 °C (decomp.);

**IR** (ZnSe, cm<sup>-1</sup>): 737, 752, 920, 930, 1040, 1234, 1292, 1393, 1449, 1493, 1584, 2870, 2953, 3057, 3377.

**<sup>1</sup>H NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 0.19–0.26 (m, 2H), 0.66–0.72 (m, 3H), 1.02–1.12 (m, 4H), 1.65–1.75 (m, THF), 3.58–3.69 (m, THF), 6.85 (dd, *J* = 1.6, 8.0 Hz, 2H), 6.90 (ddd, *J* = 1.6, 8.0, 8.0 Hz, 2H), 7.12 (ddd, *J* = 1.6, 8.0, 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.78 (dd, *J* = 1.6, 8.0 Hz, 2H).

**<sup>13</sup>C NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 100.5 MHz): δ 14.4, 25.6 (THF), 26.9, 27.5, 68.6 (THF), 119.5 (2C), 119.8 (2C), 120.5 (2C), 124.3 (2C), 127.1, 128.0 (2C), 128.4 (2C), 134.5 (2C), 155.6 (2C). The signals for the carbons attached to the boron atom were not observed.

**<sup>11</sup>B NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 127 MHz): δ 7.43 (br).

**<sup>1</sup>H NMR** (THF-*d*<sub>8</sub>, 400 MHz): δ 0.19 (t, *J* = 7.6 Hz, 2H), 0.61 (t, *J* = 7.2 Hz, 3H), 0.94–1.11 (m, 4H), 1.67–1.78 (m, THF), 3.52–3.63 (m, THF), 6.71 (ddd, *J* = 1.6, 8.0, 8.0 Hz, 2H), 6.76 (dd, *J* = 1.6, 8.0 Hz, 2H), 6.95 (ddd, *J* = 1.6, 8.0, 8.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 1.6, 8.0 Hz, 2H).

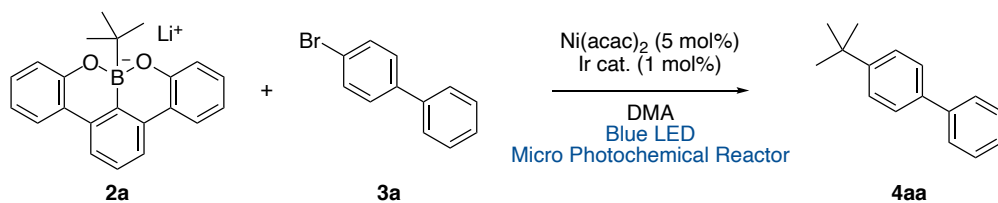
**<sup>13</sup>C NMR** (THF-*d*<sub>8</sub>, 100.5 MHz): δ 14.5, 24.6–26.2 (THF), 27.3, 28.1, 66.7–68.1 (THF), 119.1 (2C), 119.9 (2C), 120.1 (2C), 124.2 (2C), 126.7, 127.9 (2C), 128.7 (2C), 135.2 (2C), 157.1 (2C). The signals for the carbons attached to the boron atom were not observed.

**$^{11}\text{B}$  NMR** (THF- $d_8$ , 127 MHz):  $\delta$  7.09 (br).

**HRMS** (ESI $^-$ ):  $m/z$  327.1564 (327.1562 calcd for  $\text{C}_{22}\text{H}_{20}\text{BO}_2^-$ ,  $[\text{M}-(\text{Li}+2\text{THF})]^-$ ).

## ■ Optimization of Ni-Catalyzed Alkylation ■

Table S1. Optimization of reaction conditions.



Entry	Ir catalyst	Time (h)	Yield (%) <sup>a,b</sup>
1	none	14	76 <sup>c,d</sup>
2	$[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{bpy}]\text{PF}_6$	0.5	1
3	$[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{dtbpy}]\text{PF}_6$	0.5	5
4	$\text{Ir}(\text{ppy})_3$	0.5	3
5	$[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6$	0.5	43
6	$[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6$	1	<b>89<sup>d</sup></b>
7	none	120	22

<sup>a</sup> Reaction was carried out with **2a** (0.15 mmol), **3a** (0.10 mmol), Ir catalyst (1.0  $\mu\text{mol}$ ),  $\text{Ni}(\text{acac})_2$  (5.0  $\mu\text{mol}$ ) in DMA (1 mL) under blue LED irradiation. <sup>b</sup> <sup>1</sup>H NMR yield based on **3a**. <sup>c</sup> Kessil lamp was used as a light source. <sup>d</sup> Isolated yield.

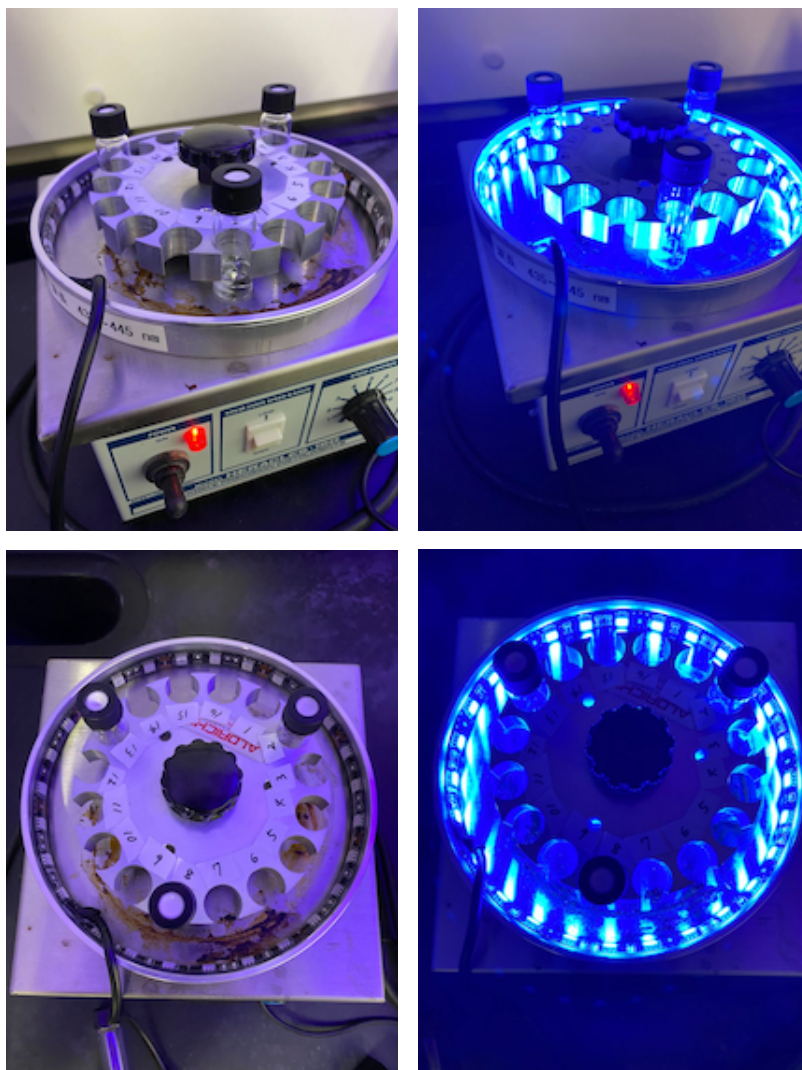
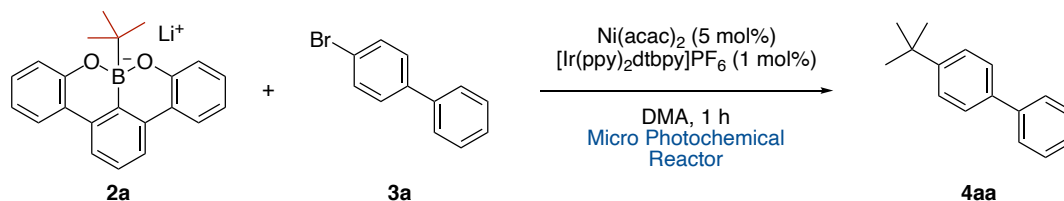
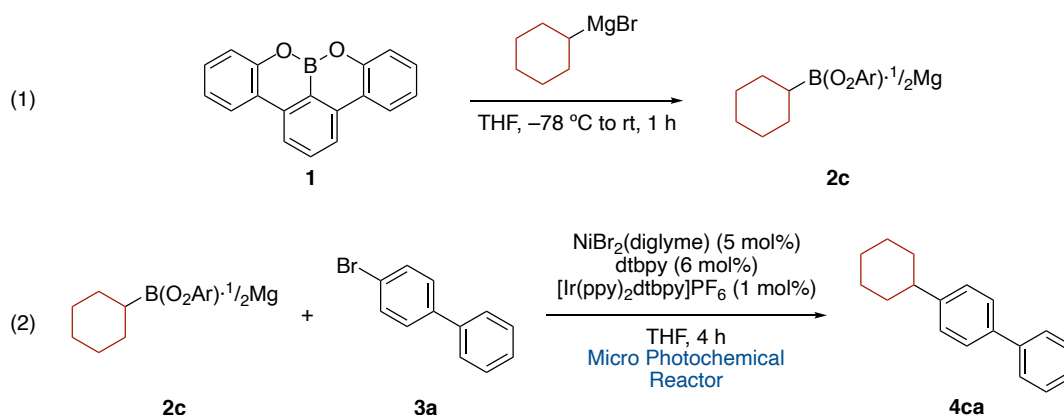


Figure S1. Light set up (Micro Photochemical Reactor)

## ■ Protocols for Ni-Catalyzed Alkylation ■



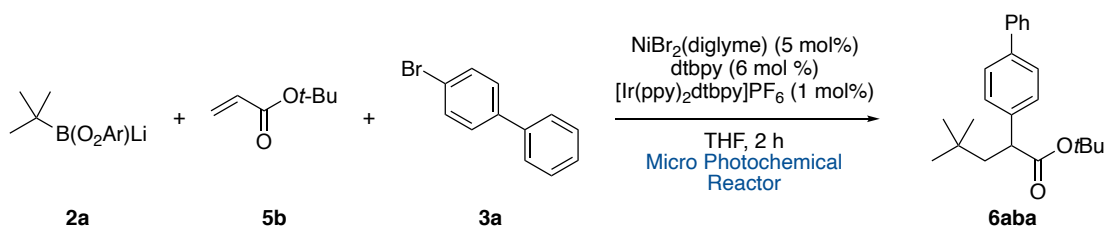
**Method A (synthesis of 4aa as a representative):** In a glovebox, to an oven-dried vial with a stirring bar was added  $[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6$  (0.91 mg, 1.0  $\mu\text{mol}$ ),  $\text{Ni}(\text{acac})_2$  (1.3 mg, 5.0  $\mu\text{mol}$ ), pre-prepared *tert*-butylborate **2a** (71.8 mg, 0.15 mmol), 4-bromo-1,1'-biphenyl (**3a**) (23.3 mg, 0.1 mmol) and DMA (1.0 mL). After sealing the vial with parafilm, the reaction was placed in Micro Photochemical Reactor (Figure S1). After stirred for 1 h, the reaction was quenched with water and extracted with dichloromethane (ca. 2 mL  $\times$  3). The combined organic extract was dried over  $\text{Na}_2\text{SO}_4$  and after filtration, the filtrate was concentrated under reduced pressure. The residue was washed with MeOH to remove most of boracene and after MeOH were removed under reduced pressure, purified by flash column chromatography on silica gel gave **4aa** (18.7 mg, 89%) as a white solid.



**Method B (synthesis of 4ca as a representative):** To a suspension of boracene **1** in THF (1.0 ml) was added cyclohexylmagnesium bromide solution in THF (1.0 M) prepared by conventional method at  $-78\text{ }^\circ\text{C}$  and then allowed to warm up to room temperature. After stirred for 1 h, the mixture was used without further purification.

In a glovebox, to an oven-dried vial with a stirring bar was added  $[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6$  (0.91 mg, 1 mmol),  $\text{NiBr}_2 \cdot \text{diglyme}$  (1.8 mg, 5.0  $\mu\text{mol}$ ), dtbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (1.6 mg, 6.0  $\mu\text{mol}$ ) and 4-bromo-1,1'-biphenyl (**3a**) (23.3 mg, 0.1 mmol). To the mixture was added cyclohexylborate **2c** in THF solution (1.0 mL). After sealing the vial with parafilm, the reaction was placed in Micro Photochemical Reactor (Figure S1). After stirred for 4 h, the reaction mixture was passed through a short plug of silica gel and concentrated under reduced pressure. The residue was washed with MeOH to remove most of boracene and after MeOH was removed under reduced pressure, purified by flash column chromatography on silica gel gave **4ca** (9.9 mg, 42%) as a colorless oil.

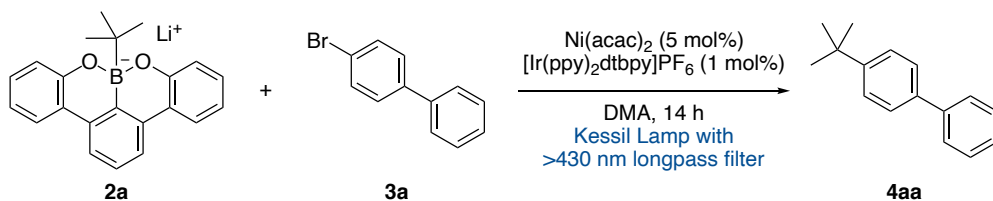
## ■ Procedure for Ni-Catalyzed Three-Component Coupling ■



In a glovebox, to an oven-dried vial with a stirring bar was added [Ir(ppy)<sub>2</sub>dtbpy]PF<sub>6</sub> (0.91 mg, 1 mmol), NiBr<sub>2</sub>·diglyme (1.8 mg, 5.0 μmol) and dtbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (1.6 mg, 6.0 μmol). To the mixture was added *tert*-butylborate **2a** (71.8 mg, 0.15 mmol), *tert*-butyl acrylate (**5b**) (25.6 mg, 29.2 μl, 0.2 mmol), 4-bromo-1,1'-biphenyl (**3a**) (23.3 mg, 0.1 mmol) and THF (1.0 ml). After sealing the vial with parafilm, the reaction was placed in Micro Photochemical Reactor (Figure S1). After stirred for 2 h, the reaction mixture was passed through a short plug of silica gel and concentrated under reduced pressure. The residue was washed with MeOH to remove most of boracene and after MeOH was removed under reduced pressure, purified by flash column chromatography on silica gel gave **6aba** (9.9 mg, 29%) as a colorless oil.

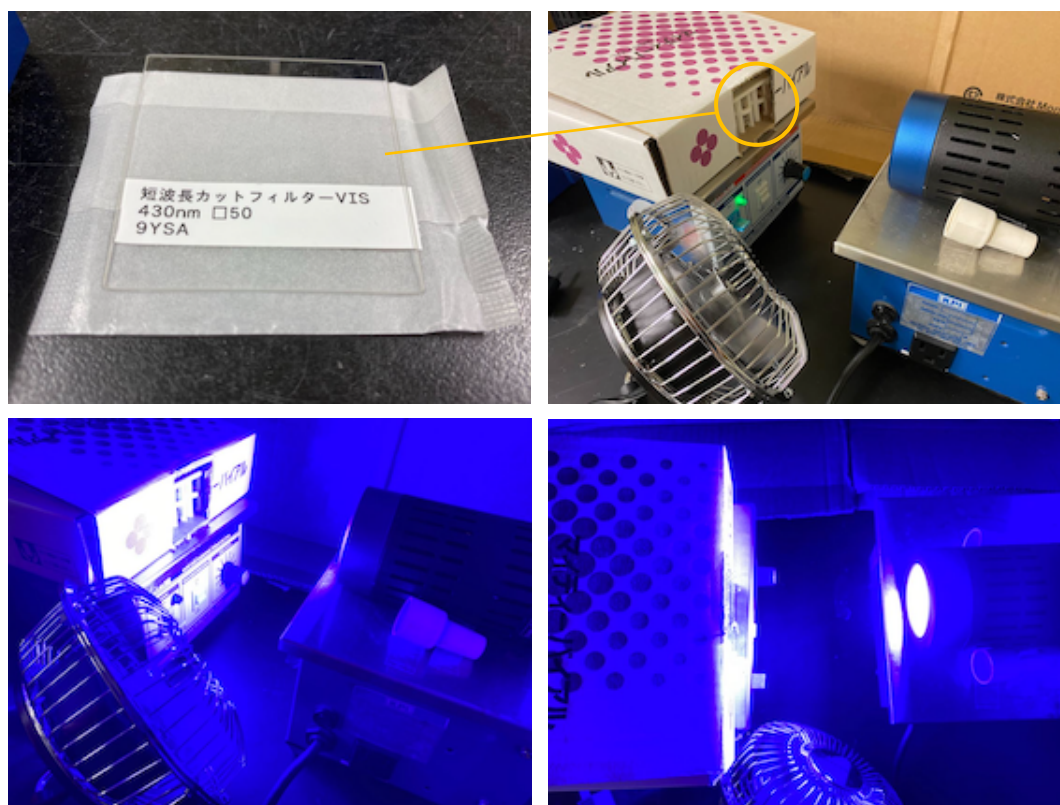


## ■ Longpass Filter Experiment ■



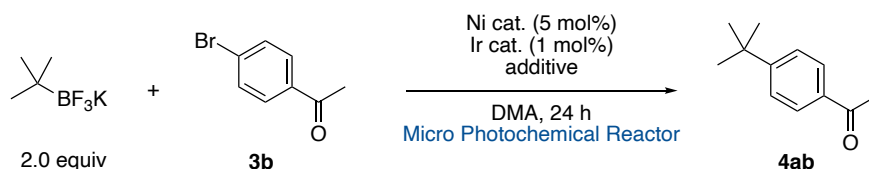
Entry	Ir catalyst	<sup>1</sup> H NMR yield (%)
1	none	79
2	[Ir(ppy) <sub>2</sub> dtbpy]PF <sub>6</sub> ( <b>PC1</b> )	96

In a glovebox, to an oven-dried vial with a stirring bar was added [Ir(ppy)<sub>2</sub>dtbpy]PF<sub>6</sub> (**PC1**) (0.91 mg, 1 μmol), Ni(acac)<sub>2</sub> (1.3 mg, 5 μmol), pre-prepared *tert*-butylborate **2a** (71.8 mg, 0.15 mmol), 4-bromo-1,1'-biphenyl (**3a**) (23.3 mg, 0.1 mmol) and DMA (1.0 mL). After sealing the vial with parafilm, the reaction mixture was irradiated using 45W blue LED shielded with >430 nm longpass filter (Figure S2). After stirred for 14 h, the reaction was quenched with water and extracted with dichloromethane (ca. 2 mL × 3). The combined organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and after filtration, the filtrate was concentrated under reduced pressure. Then the residue was dissolved in CDCl<sub>3</sub> (500 μl) and added 1,1,2,2-tetrachloroethane (11 μl, 105 μmol) as an internal standard. The <sup>1</sup>H NMR yields of **4aa** were obtained from the relative integration values of **4aa** (1.37 ppm, 9H) and 1,1,2,2-tetrachloroethane (5.91 ppm, 2H).



**Figure S2.** Filter Experiment.

## ■ The cross-coupling using *t*BuBF<sub>3</sub>K ■

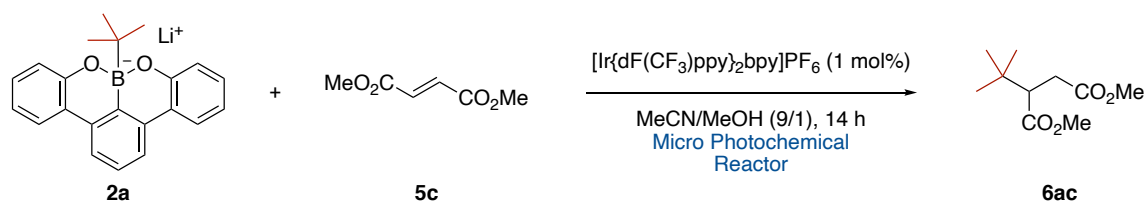


Entry	Ir catalyst	Ni catalyst	additive (mol %)	<sup>1</sup> H NMR yield (%)
1 <sup>a</sup>	[Ir(ppy) <sub>2</sub> dtbpy]PF <sub>6</sub> ( <b>PC1</b> )	Ni(acac) <sub>2</sub>	none	0
2 <sup>b</sup>	[Ir{dF(CF <sub>3</sub> )ppy} <sub>2</sub> bpy]PF <sub>6</sub> ( <b>PC2</b> )	Ni(TMHD) <sub>2</sub> <sup>c</sup>	ZnBr <sub>2</sub> (20)/K <sub>2</sub> HPO <sub>4</sub> (100)	18 (15) <sup>d</sup>

<sup>a</sup> Our optimized conditions. <sup>b</sup> Similar conditions of reference 8b. <sup>c</sup> 10 mol% of catalyst was used. <sup>d</sup> Number in parenthesis is NMR yield of acetophenone via protodebromination. The recovery of **3b** was observed in 29% yield.

In a glovebox, to an oven-dried vial with a stirring bar was added Ir catalyst (1 μmol), Ni cat (10 μmol), pre-prepared *t*BuBF<sub>3</sub>K (32.8 mg, 0.200 mmol), 4'-bromoacetophenone (**3b**) (19.9 mg, 0.1 mmol), ZnBr<sub>2</sub> (4.5 mg, 20 μmol), K<sub>2</sub>HPO<sub>4</sub> (17.4 mg, 0.10 mmol), and DMA (1.0 mL). After sealing the vial with parafilm, the reaction was placed in Micro Photochemical Reactor (Figure S1). After stirred for 24 h, the reaction was quenched with water and extracted with Et<sub>2</sub>O (ca. 2 mL × 3). The combined organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and after filtration, the filtrate was concentrated under reduced pressure. Then the residue was dissolved in CDCl<sub>3</sub> (500 μl) and added 1,1,2,2-tetrachloroethane (10 μl, 0.095 mmol) as an internal standard. The <sup>1</sup>H NMR yields of **4ab** were obtained from the relative integration values of **4ab** (7.48 ppm, 2H) and 1,1,2,2-tetrachloroethane (5.91 ppm, 2H).

## ■ Procedure for Giese Addition ■



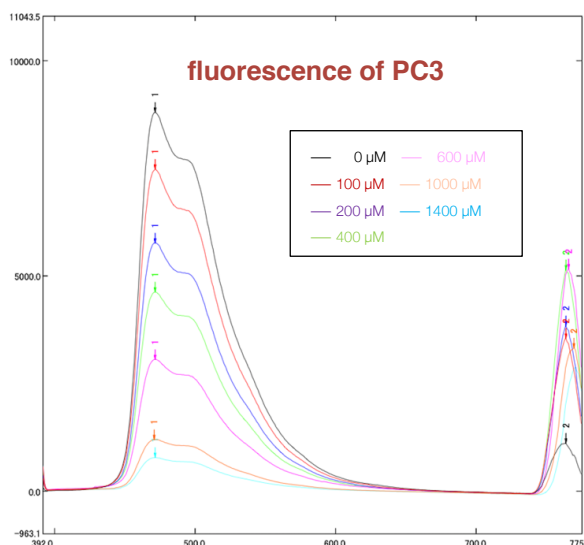
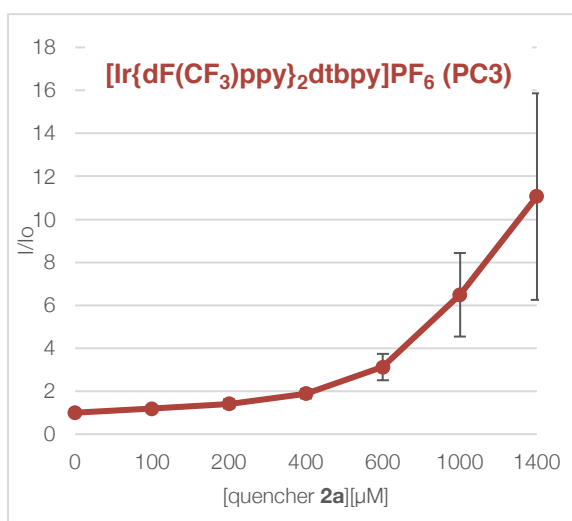
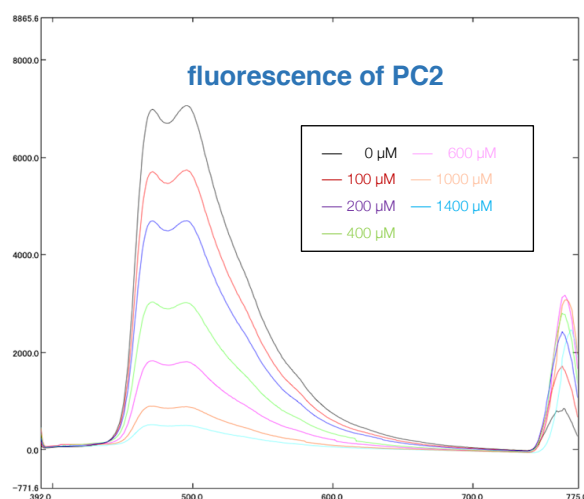
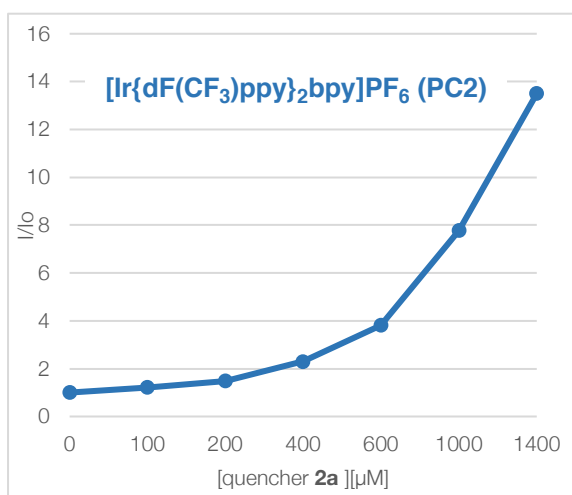
**[Ir{dF(CF<sub>3</sub>)ppy}<sub>2</sub>bpy]PF<sub>6</sub> as a representative:** In a glovebox, to an oven-dried vial with a stirring bar was added [Ir{dF(CF<sub>3</sub>)ppy}<sub>2</sub>bpy]PF<sub>6</sub> (0.10 mg, 1.0 μmol), *tert*-butylborate **2a** (71.8 mg, 0.150 mmol), dimethylfumarate **6a** (14.4 mg, 0.100 mmol) and MeCN/MeOH (9/1, 100 μl). After sealing the vial with parafilm, the reaction was placed in Micro Photochemical Reactor (Figure S1). After stirred for 14 h, the reaction was quenched with a short plug of silica gel using ethyl acetate. After volatiles were removed under reduced pressure, the residue was dissolved in CDCl<sub>3</sub> (500 μl) and added 1,1,2,2-tetrachloroethane (11 μl, 105 μmol) as an internal standard. The <sup>1</sup>H NMR yields of **6ac** were obtained from the relative integration values of **6ac** (2.48 ppm, 2H)<sup>3</sup> and 1,1,2,2-tetrachloroethane (5.91 ppm, 2H).

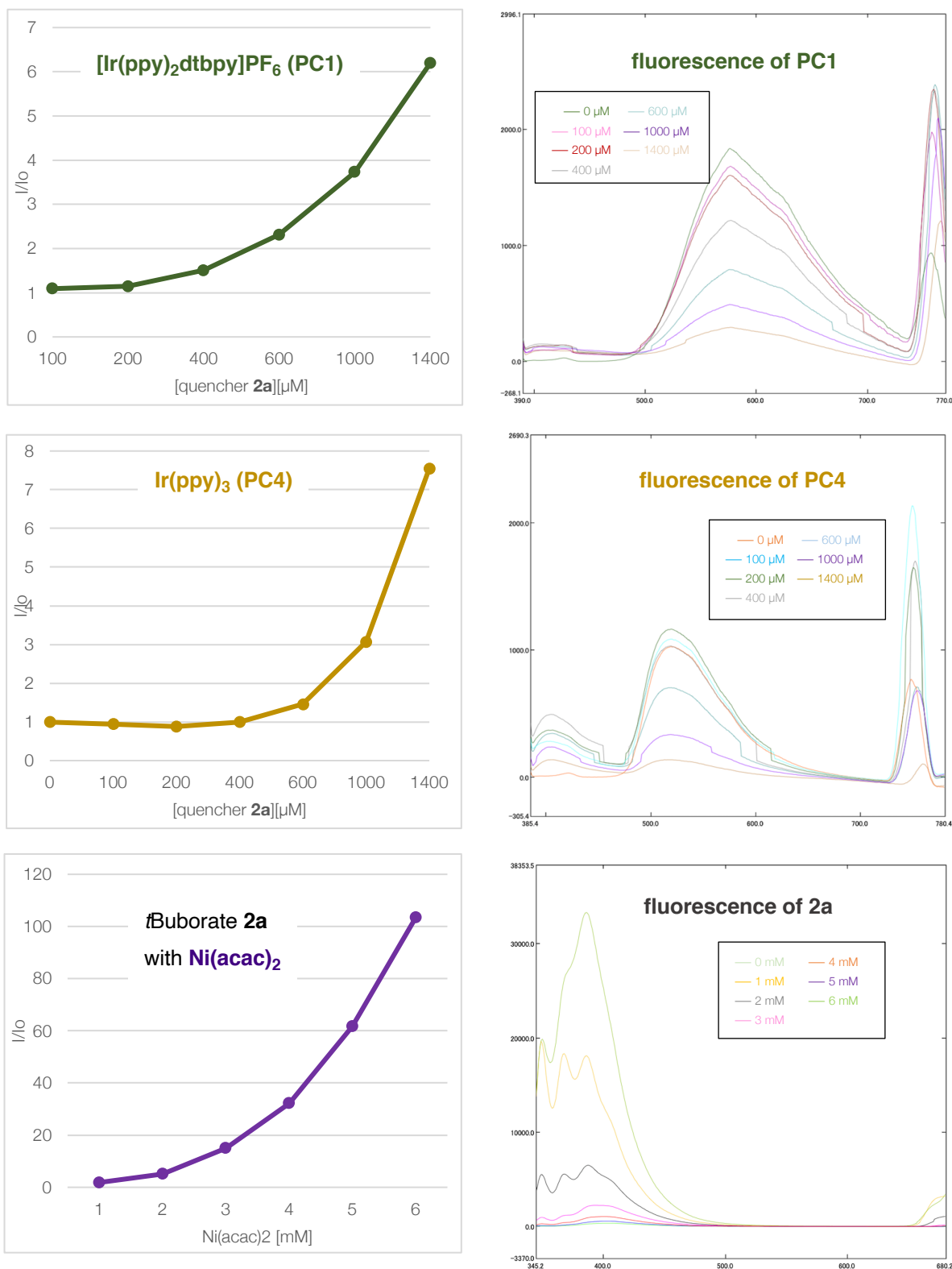
## ■ Stern–Volmer Quenching Studies ■

In a typical experiment, the fluorescence intensity was measured using a screw-top quartz cuvette (10 mm light path). The sample was prepared by mixed 500  $\mu\text{L}$  of 150  $\mu\text{M}$  solution of  $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{bpy}]\text{PF}_6$  in degassed MeCN with degassed MeCN solution of *tert*-butylborate **2a** (quencher) in each concentrations (100, 200, 400, 600, 1000, or 1400  $\mu\text{M}$ , respectively) and degassed MeCN was added until the final volume (5.0 mL). The fluorescence intensity was measured excited by each absorption maximum ( $\lambda_{\text{max}}$ ) and the intensity value was determined by the corresponding value of each emission maximum ( $E_{\text{max}}$ ) as shown below (Table S2).

**Table S2.**  $\lambda_{\text{max}}$  and  $E_{\text{max}}$  of Ir photocatalysts

Ir catalyst	$\lambda_{\text{max}}$	$E_{\text{max}}$
$[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{bpy}]\text{PF}_6$ ( <b>PC2</b> )	382	472
$[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2\text{dtbpy}]\text{PF}_6$ ( <b>PC3</b> )	382	472
$[\text{Ir}(\text{ppy})_2\text{dtbpy}]\text{PF}_6$ ( <b>PC1</b> )	380	576
$\text{Ir}(\text{ppy})_3$ ( <b>PC4</b> )	375	520
<i>t</i> -butylborate <b>2a</b>	335	386



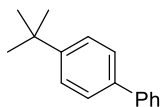


**Figure S3.** Stern-Volmer Quenching Studies.

The result of Stern–Volmer experiments indicated that the excited Ir photocatalyst was quenched by *tert*-butylborate **2a**. Especially, the reductive quenching of photocatalysts was progressed efficiently in the order of their oxidative potential. Similarly, the excited *tert*-butylborate **2a** was quenched by Ni(acac)<sub>2</sub>.

## ■ Characterization Data for Alkylation Products ■

### 4-(*tert*-butyl)-1,1'-biphenyl (**4aa**)



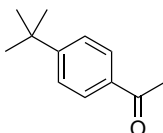
The product **4aa** was synthesized according to **Method A**, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Table 1; 18.7 mg, 0.089 mmol, 89% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.37 (s, 9H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.41–7.48 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 31.4 (3C), 34.6, 125.7 (2C), 126.8 (2C), 126.99, 127.04 (2C), 128.7 (2C), 138.3, 141.1, 150.3.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of **4aa** were consistent with the literature.<sup>3</sup>

### 1-(4-(*tert*-butyl)phenyl)ethan-1-one (**4ab**)



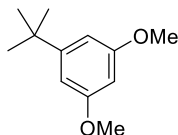
The product **4ab** was synthesized according to **Method A**, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 16.8 mg, 0.095 mmol, 95% isolated yield, including trace amount of isomerization product).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.35 (s, 9H), 2.59 (s, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 26.5, 31.1 (3C), 35.1, 125.5 (2C), 128.3 (2C), 134.7, 156.8, 197.9.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ab** were consistent with the literature.<sup>3</sup>

### 1-(*tert*-butyl)-3,5-dimethoxybenzene (**4ac**)



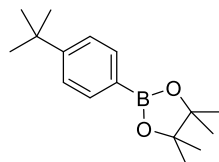
The product **4ac** was synthesized according to **Method A**, and purified by flash chromatography on NH–silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 18.8 mg, 0.097 mmol, 97% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.30 (s, 9H), 3.80 (s, 6H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 31.3 (3C), 35.0, 55.2 (2C), 96.8, 104.1 (2C), 153.9, 160.5 (2C).

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ac** were consistent with the literature.<sup>3</sup>

### 2-(4-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ad**)



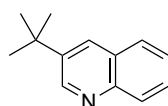
The product **4ad** was synthesized according to **Method A**, and purified by flash chromatography on silica gel (100:0–70:30, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 18.2 mg, 0.070 mmol, 70 % isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32 (s, 9H), 1.33 (s, 12H), 7.40 (d, *J* = 6.8 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 24.8 (4C), 31.2 (3C), 34.9, 83.6 (2C), 124.7 (2C), 134.7 (2C), 154.5.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ad** were consistent with the literature.<sup>3</sup>

### 3-(*tert*-butyl)quinoline (**4ae**)



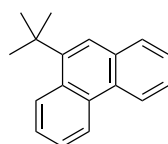
The product **4ae** was synthesized according to **Method A**, and purified by flash chromatography on silica gel (100:0–80:20, hexane/AcOEt) (Figure 3; 7.8 mg, 0.042 mmol, 42% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.46 (s, 9H), 7.52 (m, 1H), 7.66 (m, 1H), 7.79 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.04 (d, *J* = 2.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 9.04 (d, *J* = 2.4 Hz, 1H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 30.2 (3C), 33.0, 125.7, 126.9, 127.1, 127.8, 128.1, 130.0, 142.5, 145.6, 149.3.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ae** were consistent with the literature.<sup>6</sup>

### 9-(*tert*-butyl)phenanthrene (**4ag**)



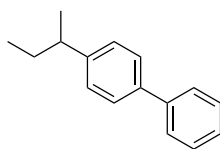
The product **4ag** was synthesized according to **Method A**, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 11.6 mg, 0.050 mmol, 50% isolated yield, including isomerization product).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.69 (s, 9H), 7.54–7.64 (m, 4H), 7.75 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 31.9 (3C), 34.0, 35.9, 122.2, 123.7, 124.1, 125.3, 125.4, 126.2, 126.6, 127.7, 128.7, 129.7, 130.9, 131.7, 131.8, 144.0.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ag** were consistent with the literature.<sup>7</sup>

#### 4-(*sec*-butyl)-1,1'-biphenyl (**4ba**)



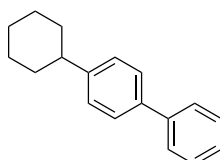
The product **4ba** was synthesized according to **Method A** using *sec*-butyllithium, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 16.7 mg, 0.080 mmol, 80% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.86 (t,  $J$  = 7.2 Hz, 3H), 1.27 (d,  $J$  = 7.3 Hz, 3H), 1.64 (dq,  $J$  = 1.8, 7.2 Hz, 2H), 2.64 (tq,  $J$  = 6.9, 7.2 Hz, 1H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 7.31 (m, 1H), 7.42 (dd,  $J$  = 7.3, 7.8 Hz, 2H), 7.55 (d,  $J$  = 17.2 Hz, 2H), 7.59 (d,  $J$  = 6.8 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$  12.3, 21.8, 31.2, 41.4, 127.00, 127.01 (4C), 127.5 (2C), 128.7 (2C), 138.7, 141.2, 146.9.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **8ba** were consistent with the literature.<sup>3</sup>

#### 4-cyclohexyl-1,1'-biphenyl (**4ca**)



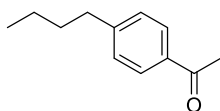
The product **4ca** was synthesized according to **Method B** using cyclohexylmagnesium bromide, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 9.9 mg, 0.042 mmol, 42% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.29–1.48 (m, 5H), 1.77 (m, 1H), 1.85–1.93 (m, 4H), 2.54 (m, 1H), 7.28 (d,  $J$  = 9.6 Hz, 2H), 7.32 (d,  $J$  = 7.2 Hz, 1H), 7.42 (dd,  $J$  = 7.3, 7.8 Hz, 2H), 7.52 (d,  $J$  = 8.0 Hz, 2H), 7.58 (d,  $J$  = 7.2 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$  26.2, 26.9 (2C), 34.5 (2C), 44.3, 126.9, 127.02 (2C), 127.03 (2C), 127.2 (2C), 128.7 (2C), 138.7, 141.2, 147.2.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **4ca** were consistent with the literature.<sup>3</sup>

#### 1-(4-butylphenyl)ethan-1-one (**4db**)



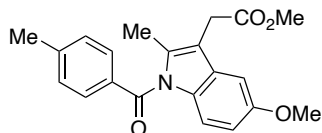
The product **4db** was synthesized according to **Method A** using *n*-butyllithium, and purified by flash chromatography on silica gel (100:0–90:10, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 10.7 mg, 0.061 mmol, 61% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.93 (t,  $J$  = 7.6 Hz, 3H), 1.31–1.41 (m, 2H), 1.58–1.66 (m, 2H), 2.58 (s, 3H), 2.67 (t,  $J$  = 8.0 Hz, 2H), 7.26 (d,  $J$  = 8.0 Hz, 2H), 7.88 (d,  $J$  = 8.4 Hz, 2H).

$^{13}\text{C}$  NMR (100.5 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 22.3, 26.5, 33.2, 35.7, 128.5 (2C), 128.6 (2C), 134.9, 148.8, 197.9.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra data of product **4db** were consistent with the literature.<sup>3</sup>

#### methyl 2-(5-methoxy-2-methyl-1-(4-methylbenzoyl)-1H-indol-3-yl)acetate (**4eh**)



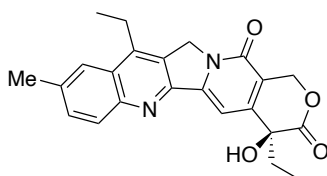
The product **4eh** was synthesized according to **Method A** using indomethacin methylester (37.2 mg, 0.1 mmol)<sup>8</sup>,  $\text{NiBr}_2 \cdot \text{diglyme}$  (3.5 mg, 10  $\mu\text{mol}$ ), dtbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12  $\mu\text{mol}$ ), pre-prepared methylborate $\cdot$ 2.5THF (141.7 mg, 0.300 mmol) and THF (0.25 ml). Then, the residue was purified by flash chromatography on silica gel (100:0–60:40, hexane/EtOAc) (Figure 3; 28.7 mg, 0.082 mmol, 82% isolated yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.39 (s, 3H), 2.46 (s, 3H), 3.67 (s, 2H), 3.70 (s, 3H), 3.84 (s, 3H), 6.65 (d,  $J = 9.0$  Hz, 1H), 6.88 (d,  $J = 9.0$  Hz, 1H), 6.96 (s, 1H), 7.28 (d,  $J = 7.6$  Hz, 2H), 7.62 (d,  $J = 7.6$  Hz, 2H).

$^{13}\text{C}$  NMR (100.5 MHz,  $\text{CDCl}_3$ )  $\delta$  13.2, 21.8, 30.2, 52.1, 55.7, 101.1, 111.4, 111.9, 115.0, 129.4 (2C), 130.0 (2C), 130.5, 131.1, 132.7, 136.1, 143.7, 155.8, 169.5, 171.5.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra data of product **4eh** were consistent with the literature.<sup>3</sup>

#### 10-methyl-7-ethyl camptothecin (**4ei**)



The product **4ei** was synthesized according to **Method A** using SN-38 triflylated derivative,<sup>9</sup> (52.4 mg, 0.100 mmol),  $\text{NiBr}_2 \cdot \text{diglyme}$  (3.5 mg, 10  $\mu\text{mol}$ ), dtbpy (3.2 mg, 12  $\mu\text{mol}$ ), pre-prepared methylborate $\cdot$ 2.5THF (141.7 mg, 0.300 mmol) and THF (0.5 mL). Then, the residue was purified by flash chromatography on silica gel (100:0–50:50, hexane/EtOAc) and recycling preparative HPLC using a high resolution GPC column (eluent: EtOAc) (Figure 3; 3.5 mg, 0.090 mmol, 9% isolated yield). White solid.

**M.p.** 237  $^\circ\text{C}$  (decomp.).

**IR** (neat) 1319, 1596, 1653, 1747, 1958, 2155, 2363, 3398  $\text{cm}^{-1}$ .

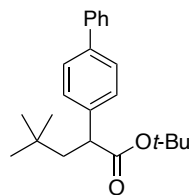
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04 (t,  $J = 7.4$  Hz, 3H), 1.41 (t,  $J = 7.6$  Hz, 3H), 1.82–1.97 (m, 2H), 2.62 (s, 3H), 3.19 (q,  $J = 7.6$  Hz, 2H), 3.71 (s, 1H), 5.25 (s, 2H), 5.31 (d,  $J = 16.2$  Hz, 1H), 5.76 (d,  $J = 16.2$  Hz, 1H) 7.63–7.65 (m, 2H), 7.87 (s, 1H), 8.13 (d,  $J = 8.7$  Hz, 1H).

$^{13}\text{C}$  NMR (100.5 MHz,  $\text{CDCl}_3$ )  $\delta$  7.8, 14.1 (2C), 22.1, 23.0, 31.6, 49.5, 66.4, 72.8, 97.7, 118.1, 122.4, 126.9, 130.4, 132.4, 138.0, 144.7, 147.4, 148.1, 150.2, 151.1, 157.8, 174.1.

**HRMS–FAB** ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_4^+$ , 391.1652; found, 391.1664.



***tert*-butyl 2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoate (**6aba**)**



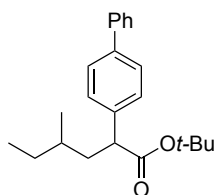
The product **6aba** was purified by flash chromatography on silica gel (100:0–10:1, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 9.9 mg, 0.029 mmol, 29% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.93 (s, 9H), 1.39 (s, 9H), 1.53 (dd, *J* = 7.2, 12.0 Hz, 1H), 2.30 (dd, *J* = 9.6, 13.8 Hz, 1H), 3.57 (dd, *J* = 3.2, 9.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 7.2, 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H).

<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 27.9 (3C), 29.5 (3C), 31.1, 47.3, 49.0, 80.4, 127.0 (2C), 127.2 (2C), 128.1 (4C), 128.7 (2C), 139.5, 140.8, 173.9.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **6aba** were consistent with the literature.<sup>3</sup>

***tert*-butyl 2-([1,1'-biphenyl]-4-yl)-4-methylhexanoate (**6bba**)**



The product **6bba** was purified by flash chromatography on silica gel (100:0–10:1, hexane/CH<sub>2</sub>Cl<sub>2</sub>) (Figure 3; 18.6 mg, 0.055 mmol, 55% isolated yield).

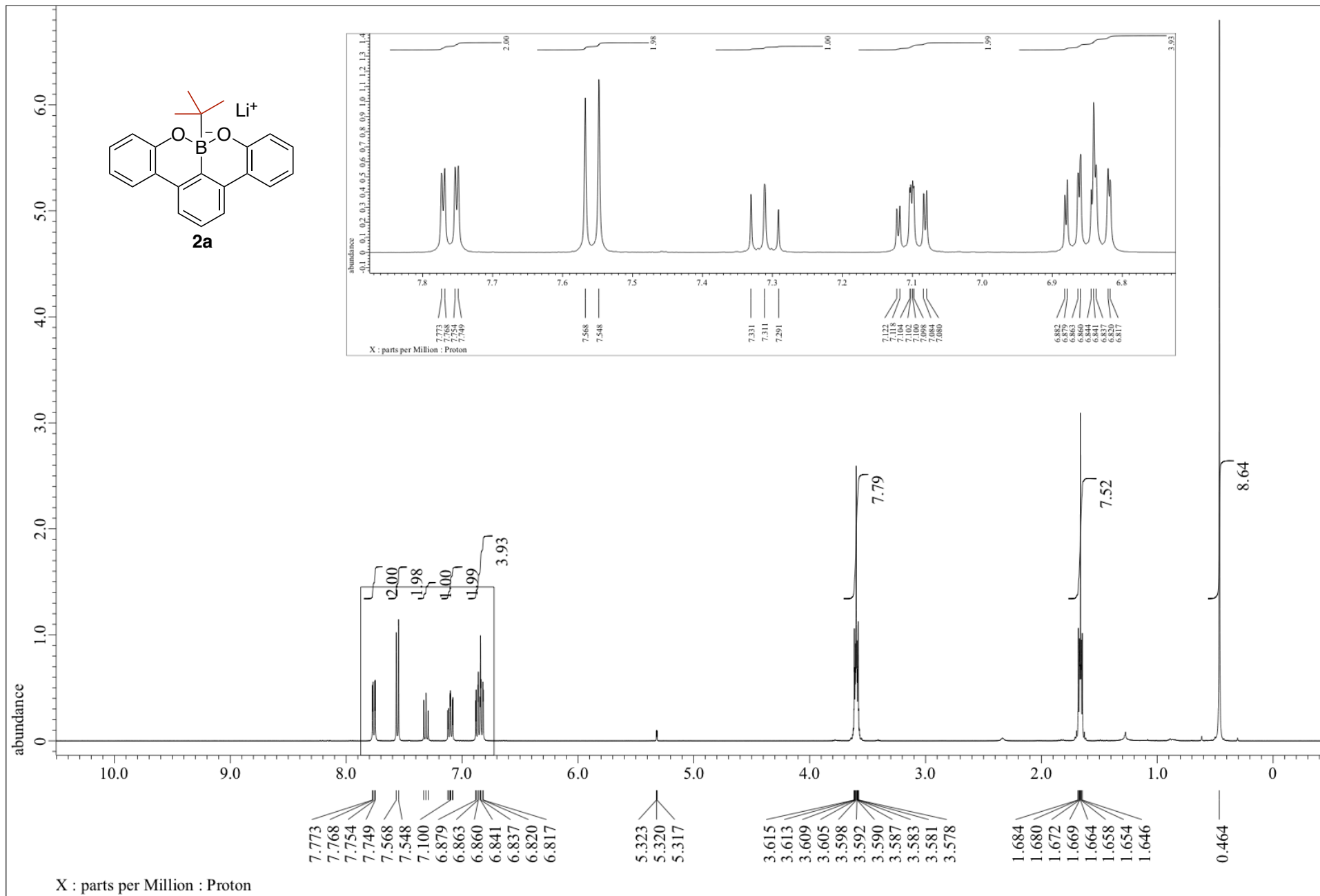
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.83–0.93 (m, 7H), 1.16–1.35 (m, 1.5H), 1.37–1.53 (m, 1H), 1.41 (s, 4.5H), 1.42 (s, 4.5H), 1.83 (t, *J* = 7.6 Hz, 1H), 2.10–2.17 (m, 0.5H), 3.57–3.63 (m, 1H), 7.31–7.44 (m, 5H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H).

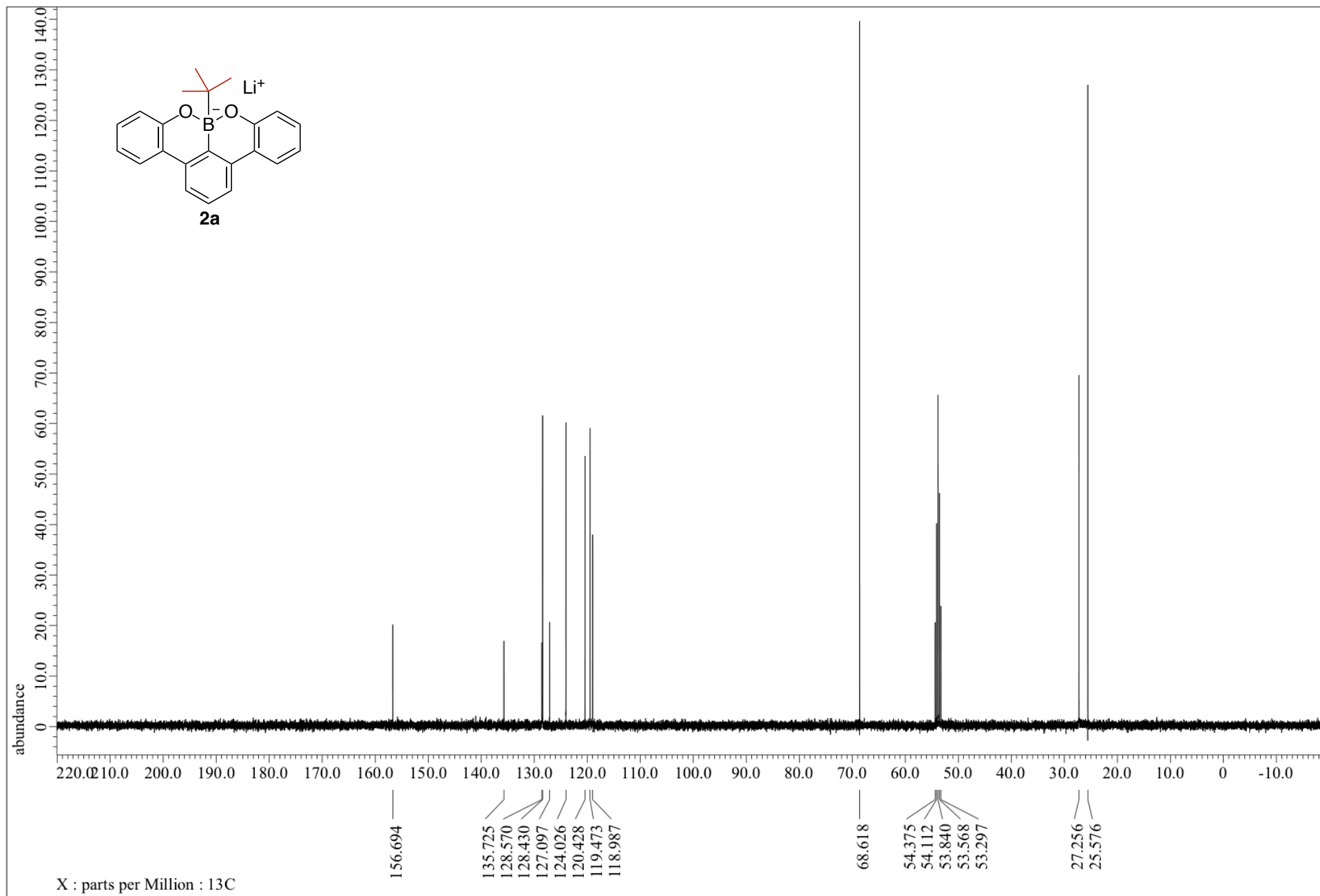
<sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 11.13 (0.5C), 11.14 (0.5C), 18.9 (0.5C), 19.1 (0.5C), 28.00 (0.5C), 28.01 (0.5C), 29.4 (0.5C), 29.5 (0.5C), 32.1 (0.5C), 32.5 (0.5C), 40.2 (0.5C), 40.9 (0.5C), 50.15 (0.5C), 50.20 (0.5C), 80.6 (1C), 127.0 (2C), 127.11 (1C), 127.15 (2C), 128.2 (1C), 128.4 (1C), 128.7 (1C), 138.9 (1C), 139.4 (1C), 139.67 (0.5C), 139.69 (0.5C), 140.9 (1C), 173.4 (0.5C), 173.7 (0.5C).

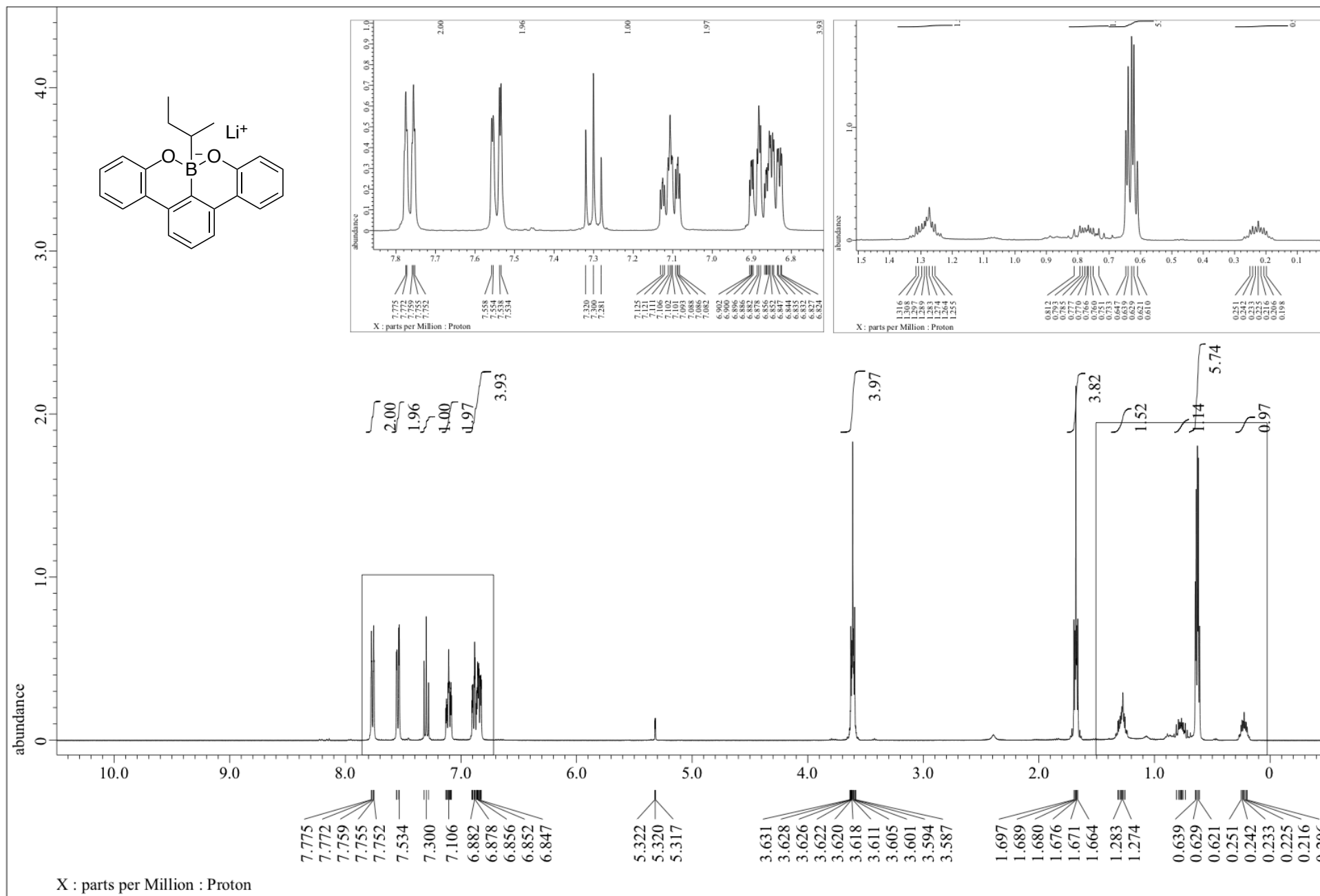
The <sup>1</sup>H and <sup>13</sup>C NMR spectra data of product **6bba** were consistent with the literature.<sup>3</sup>

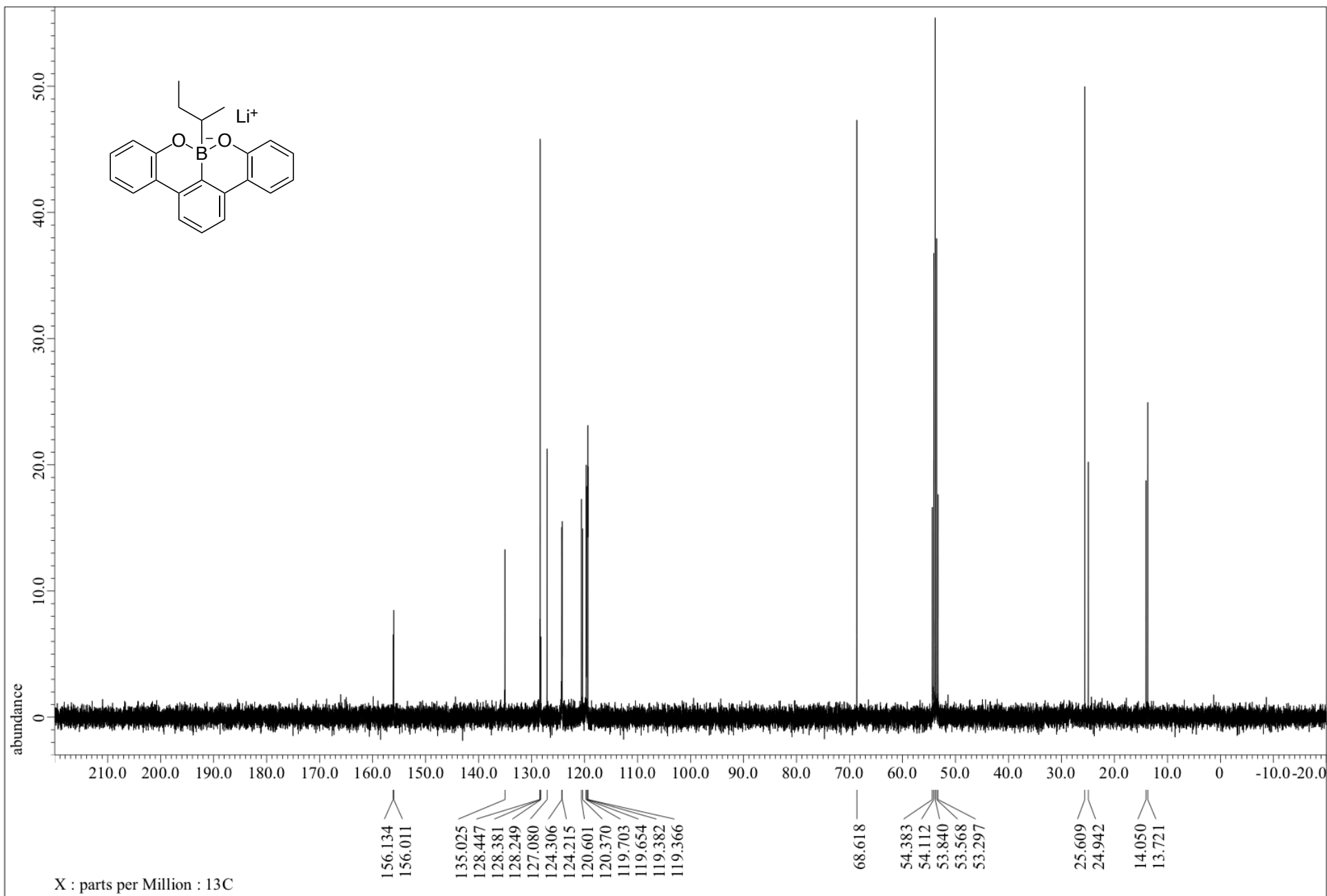
## ■ References ■

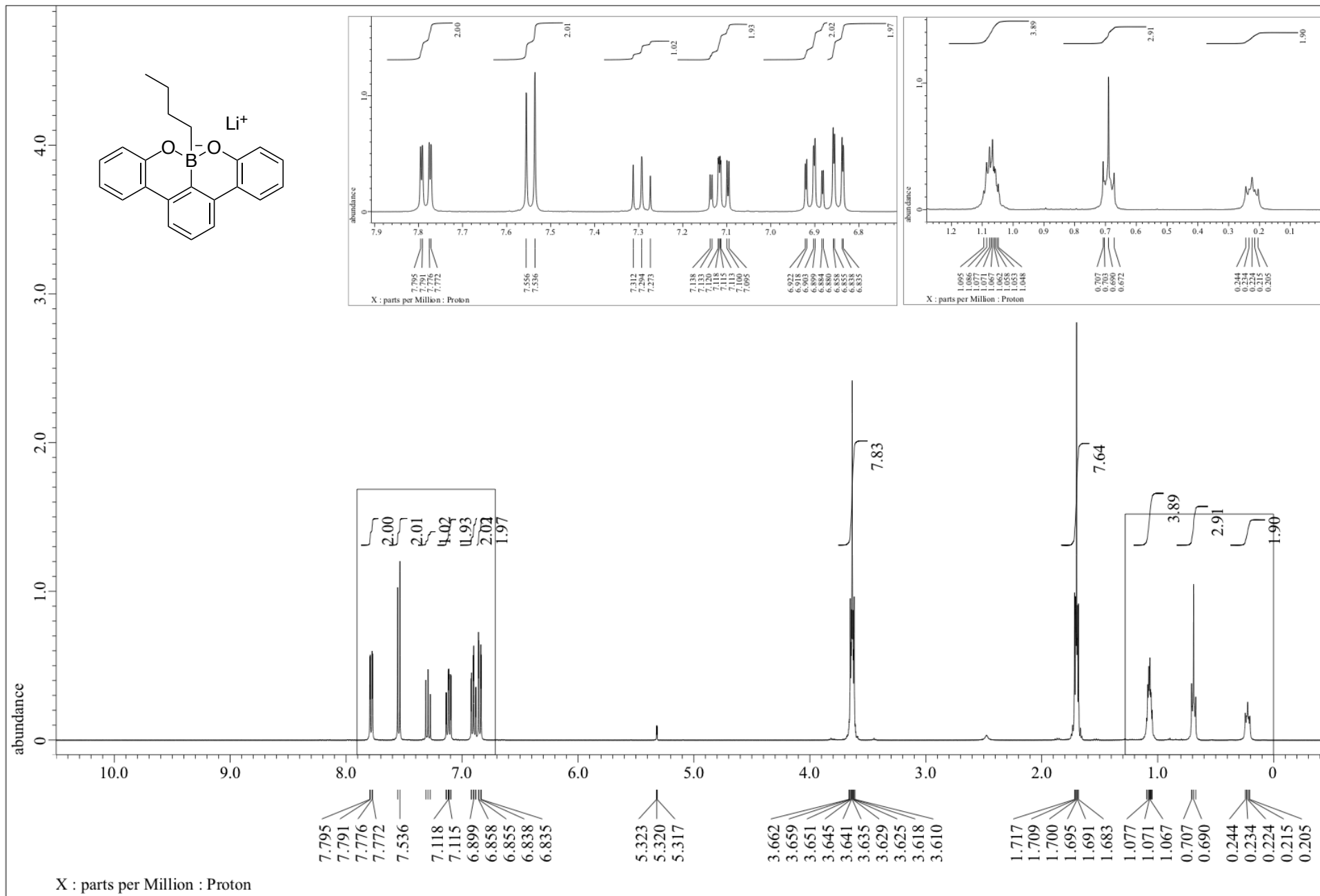
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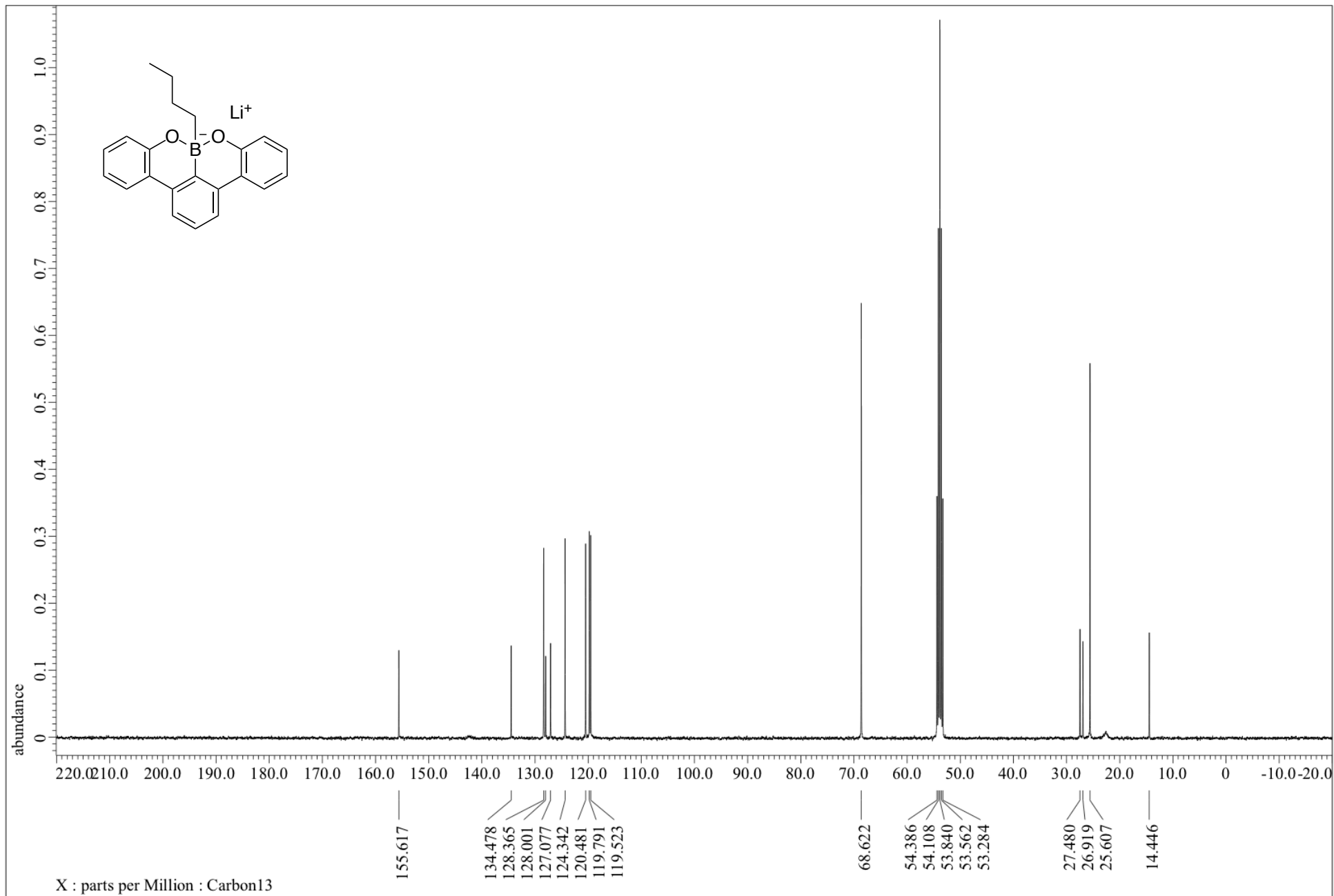




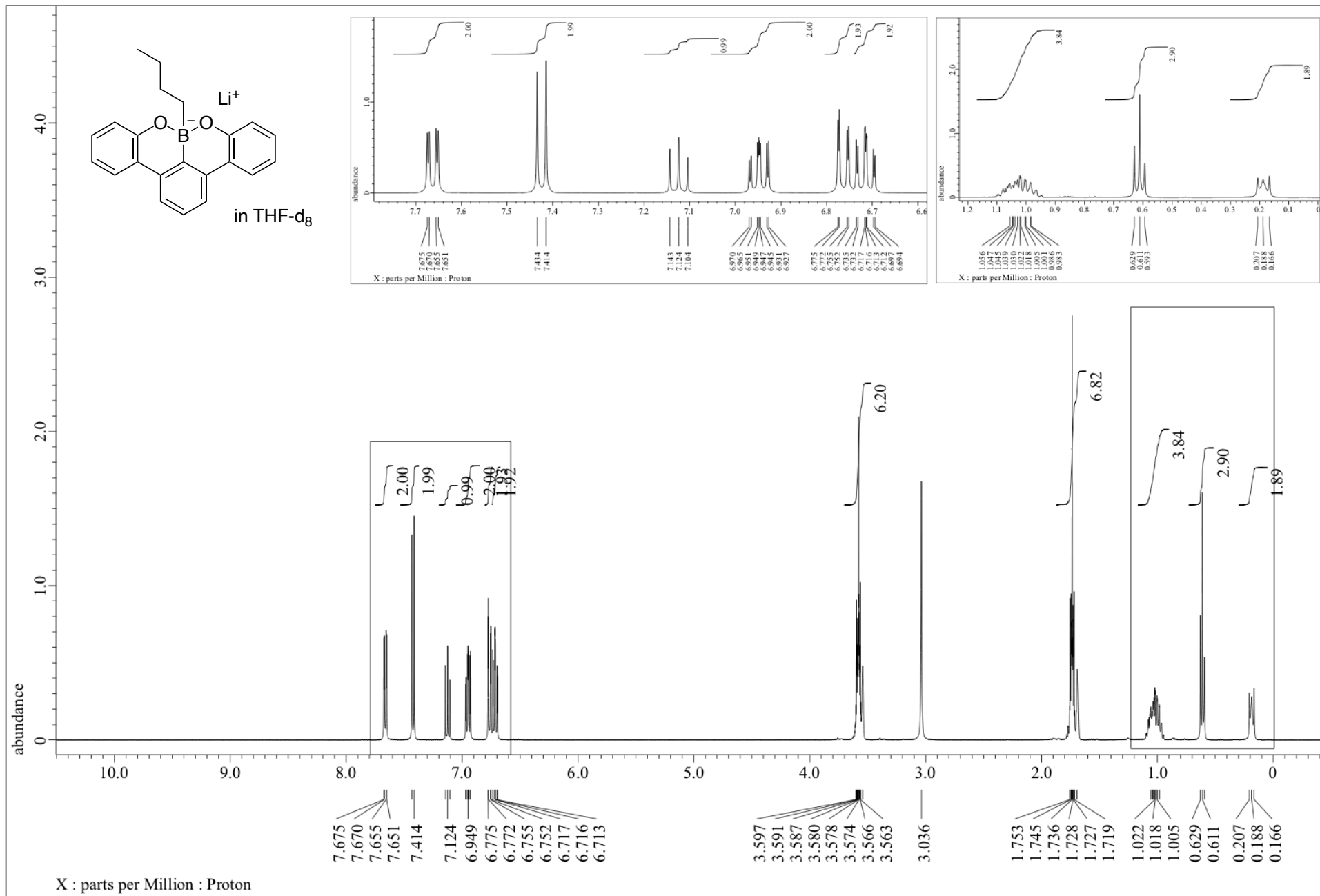


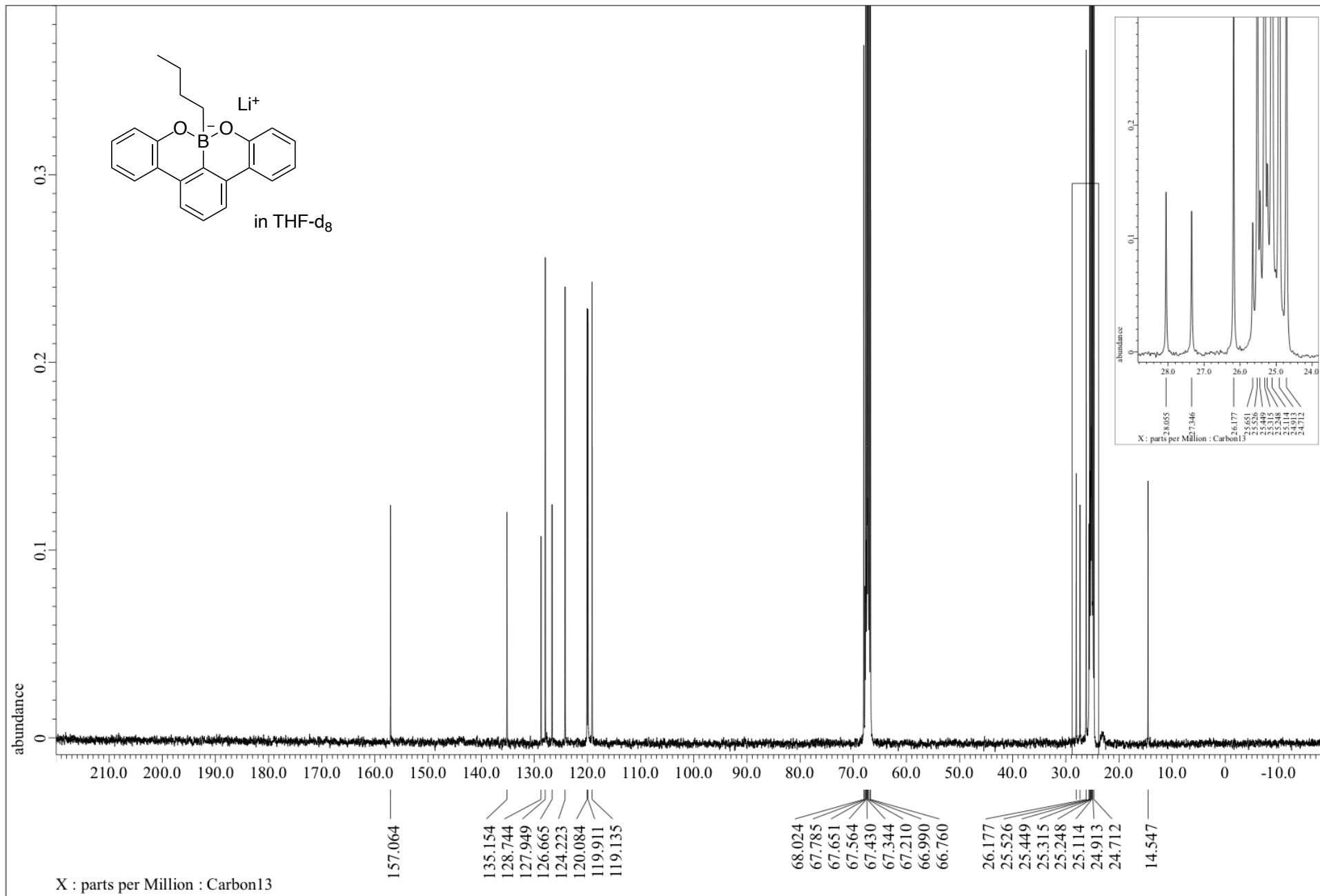


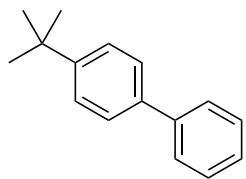








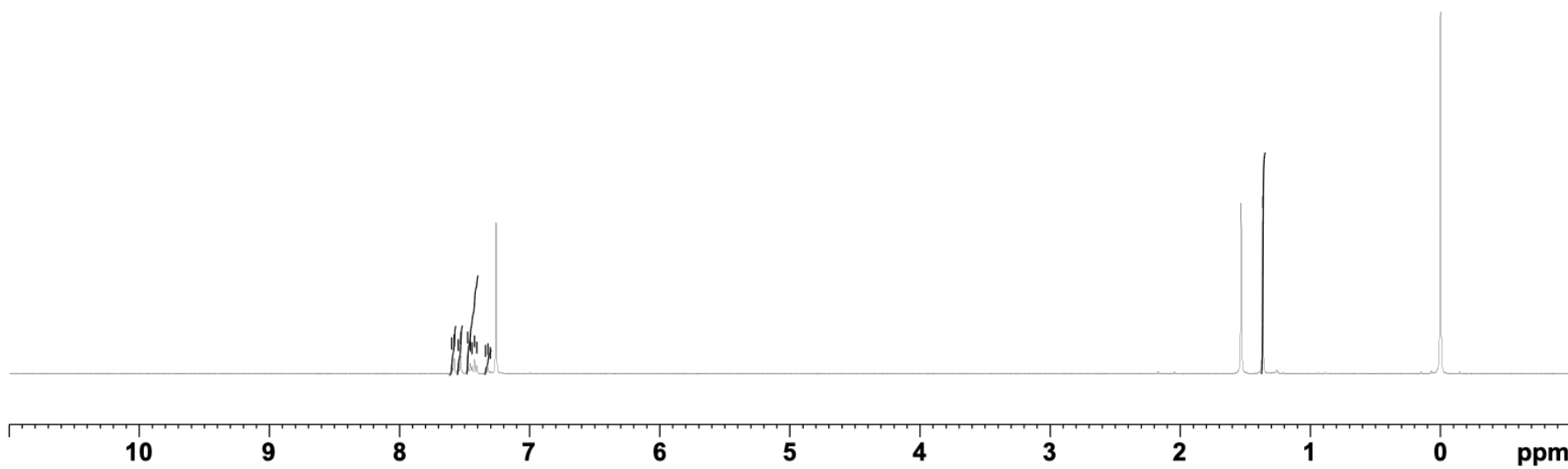




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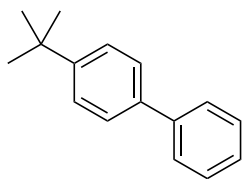
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— 1.366

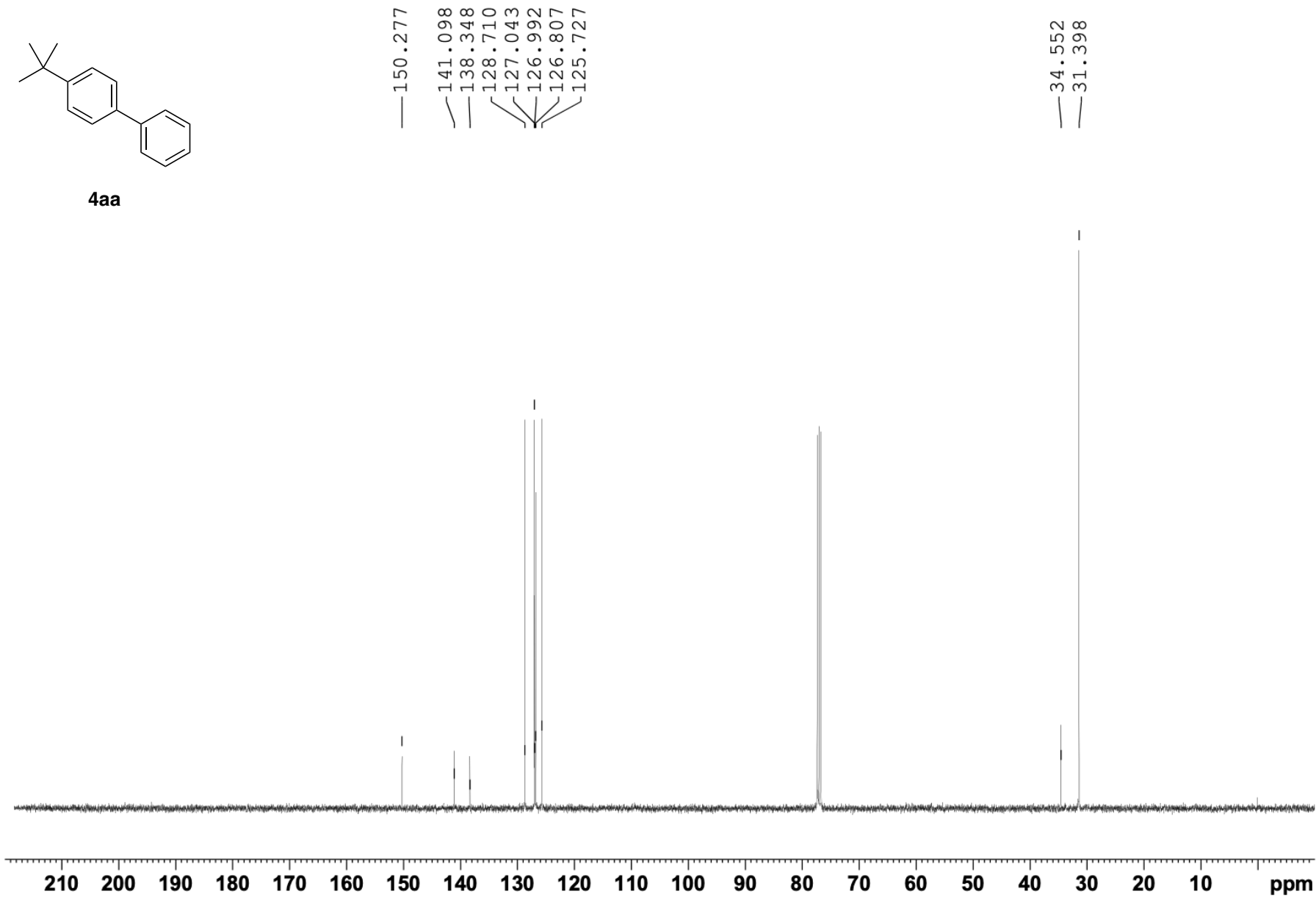


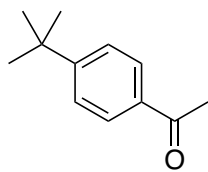
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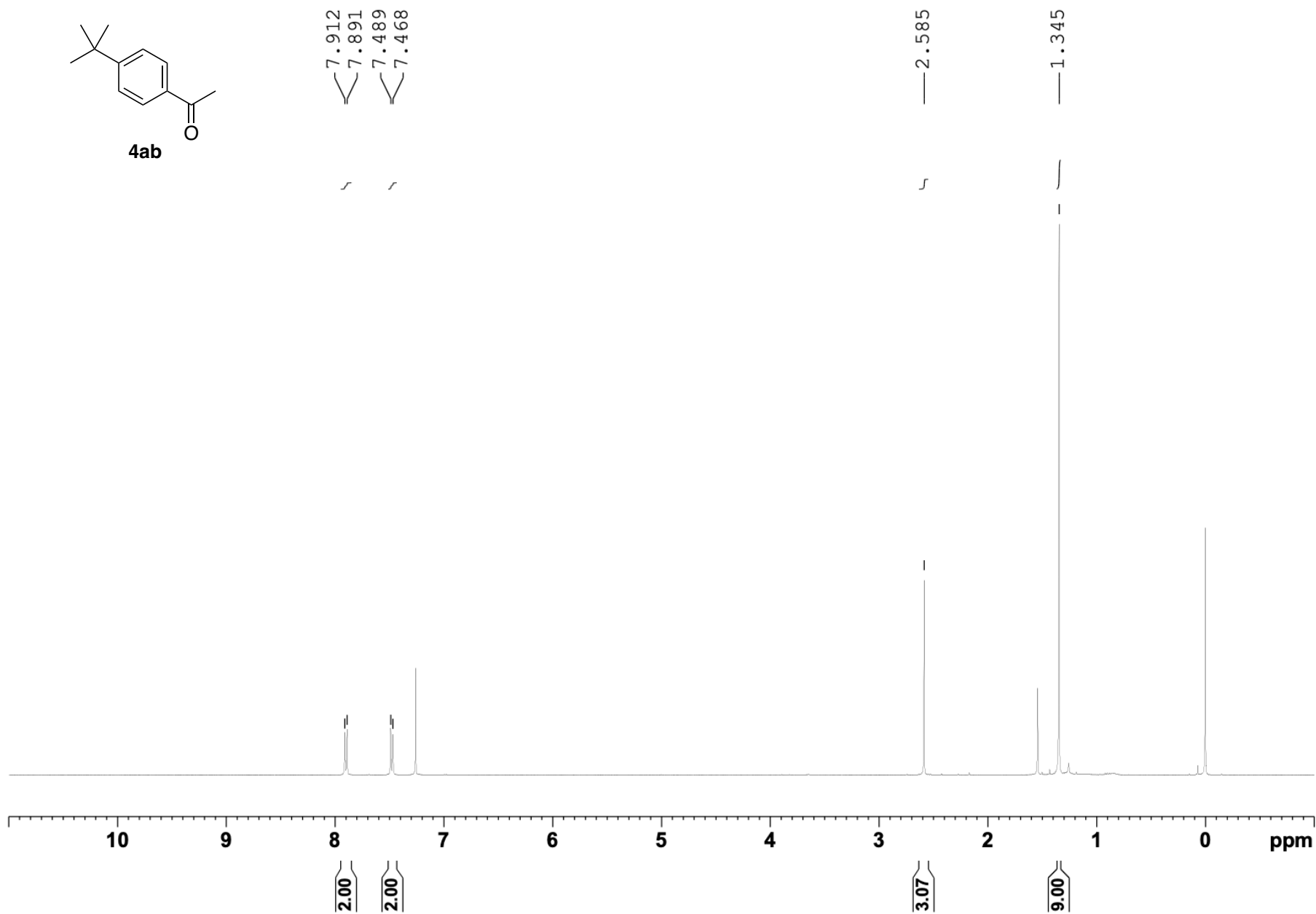


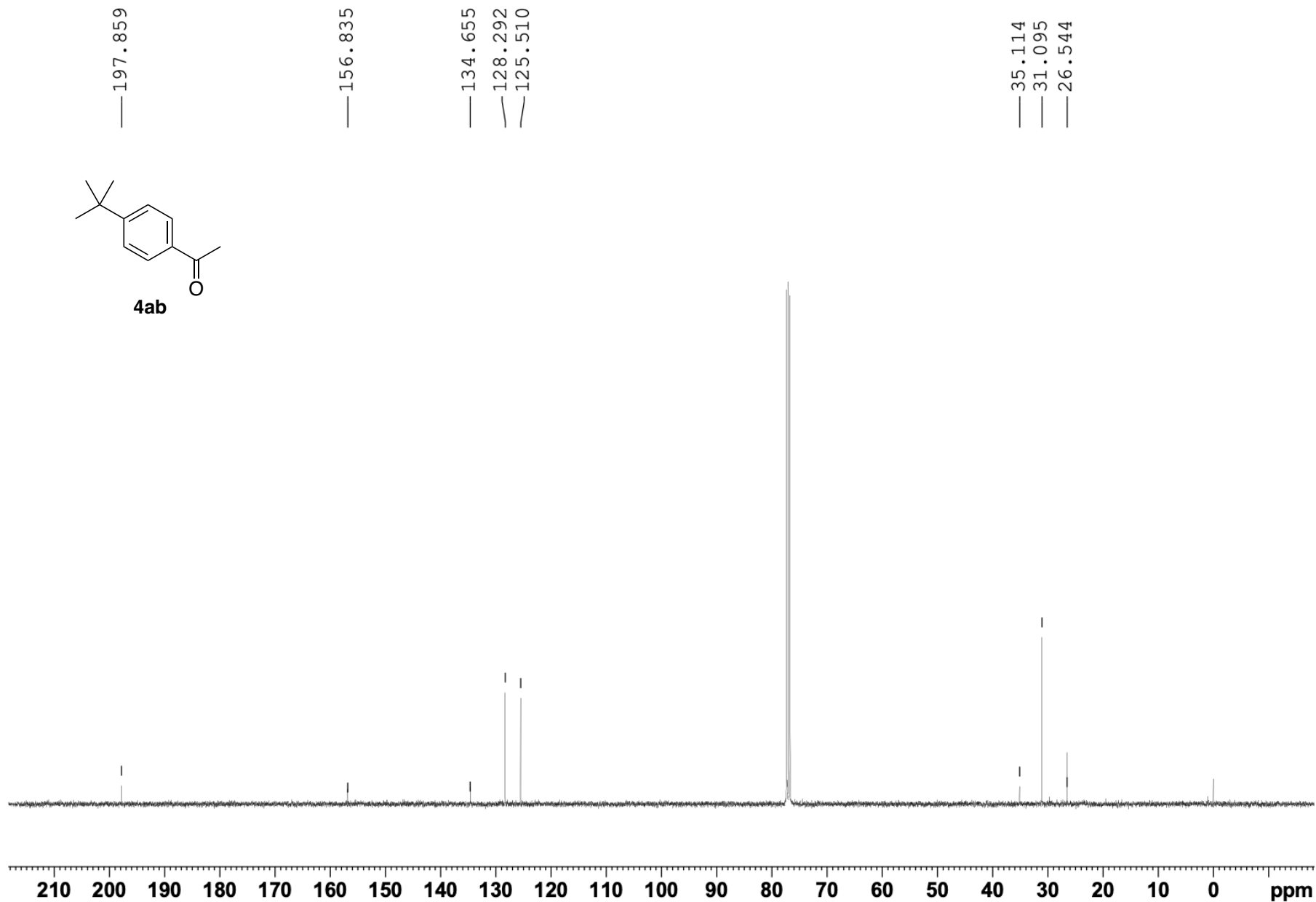
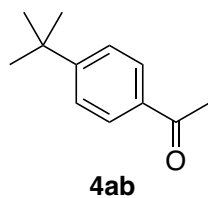
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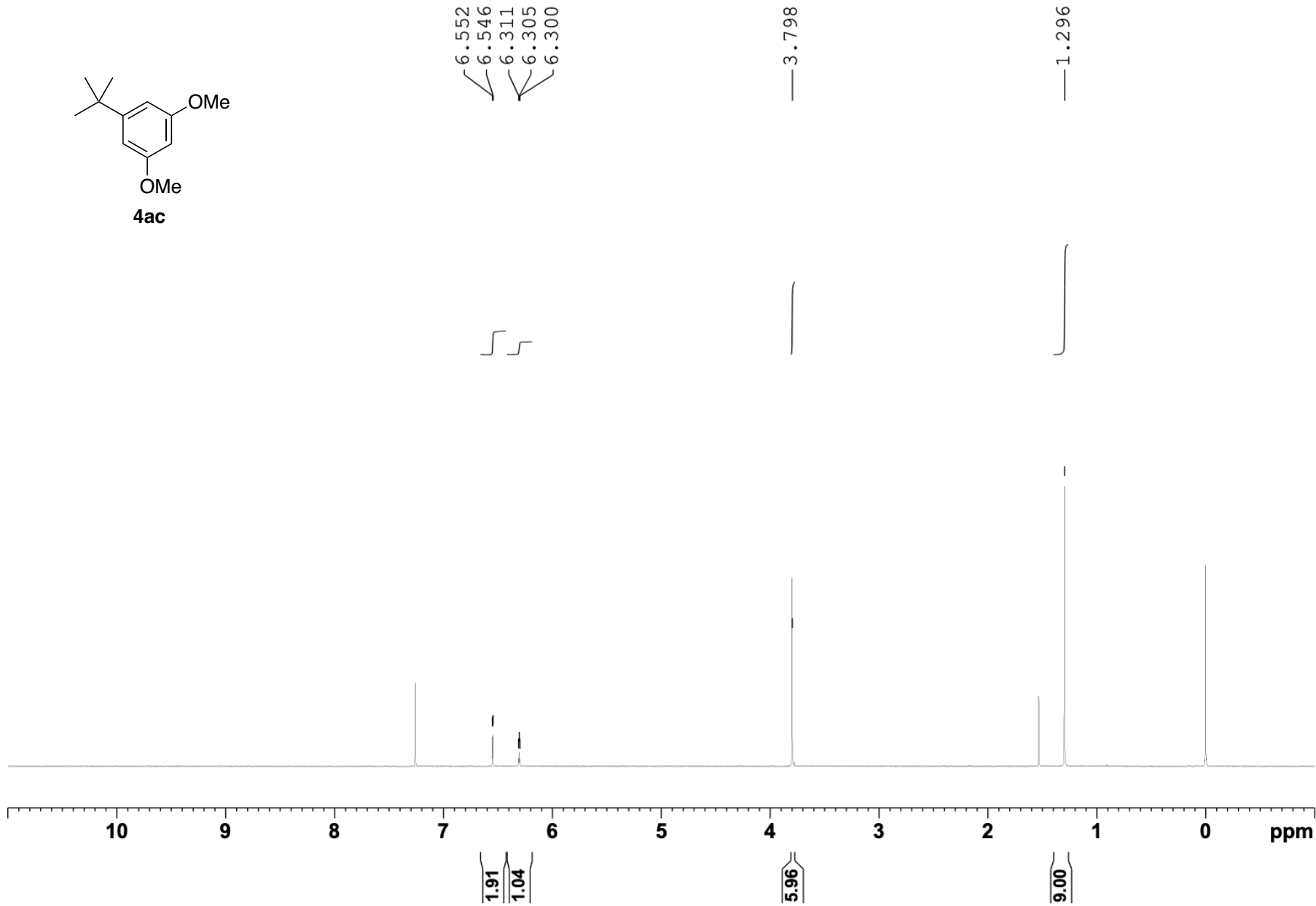
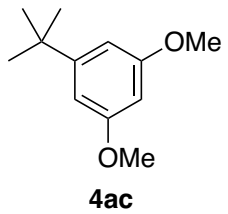


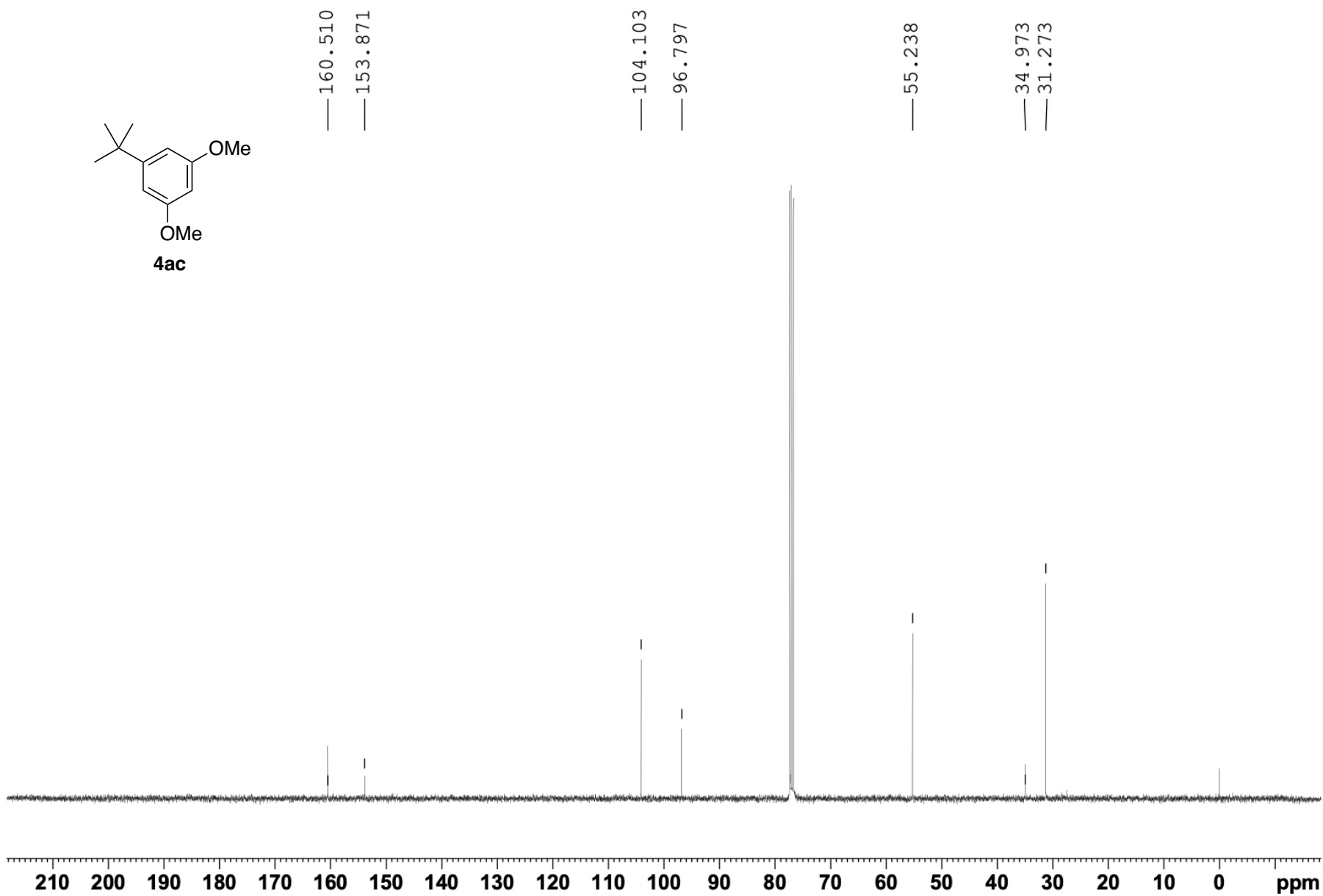
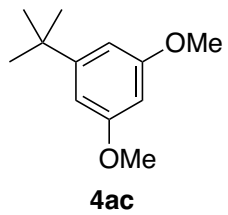


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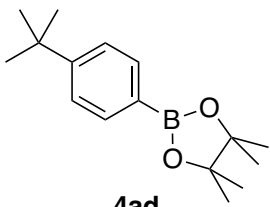






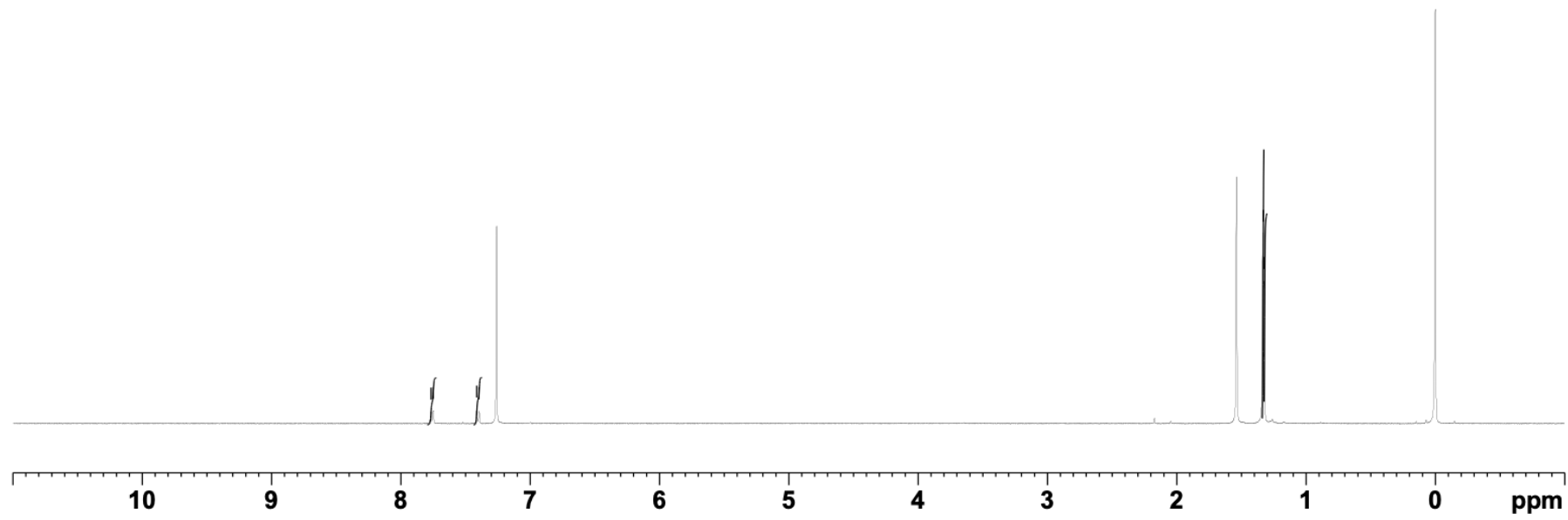






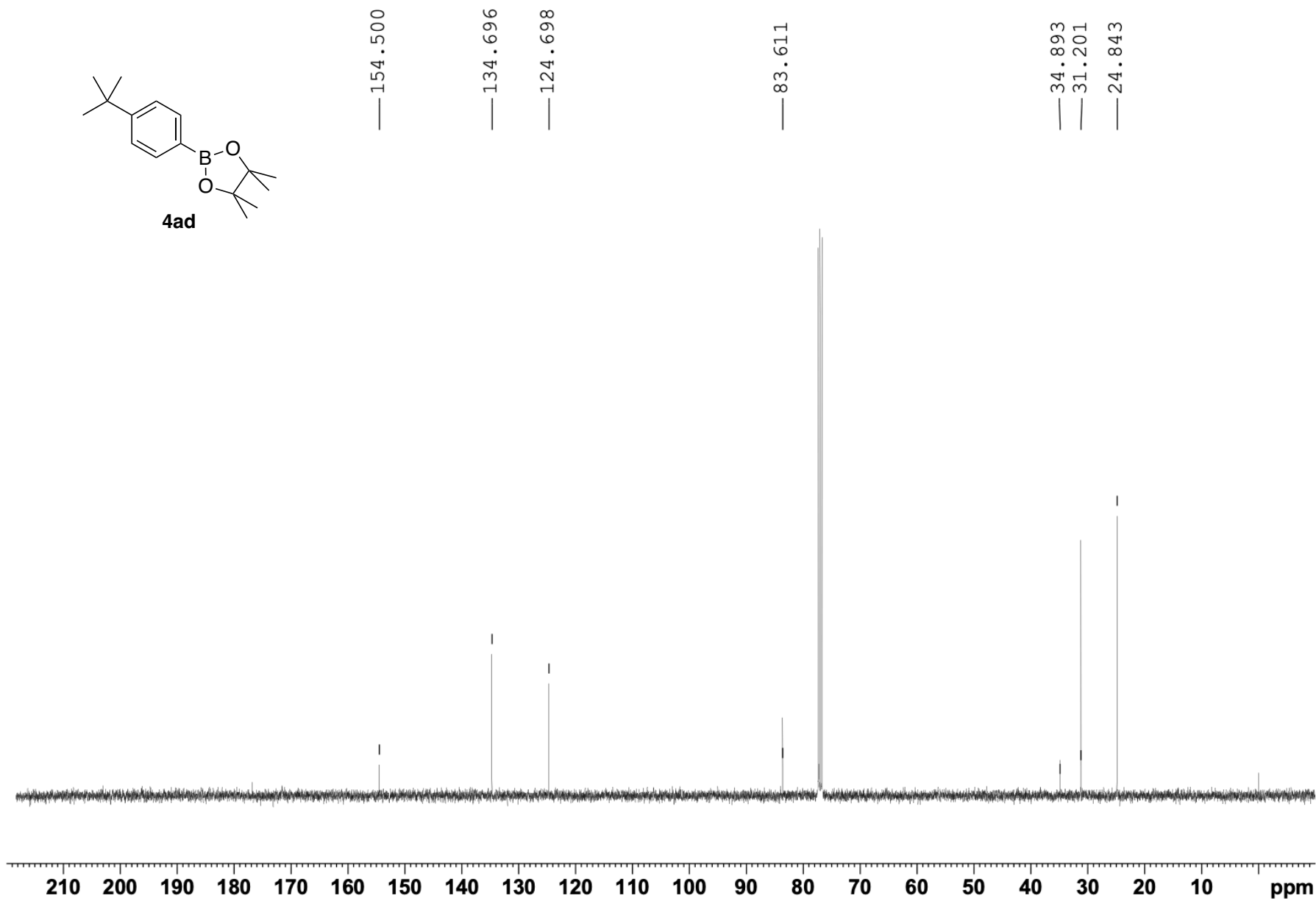
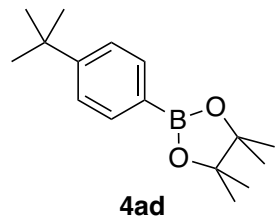
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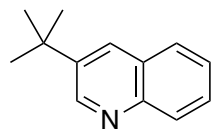
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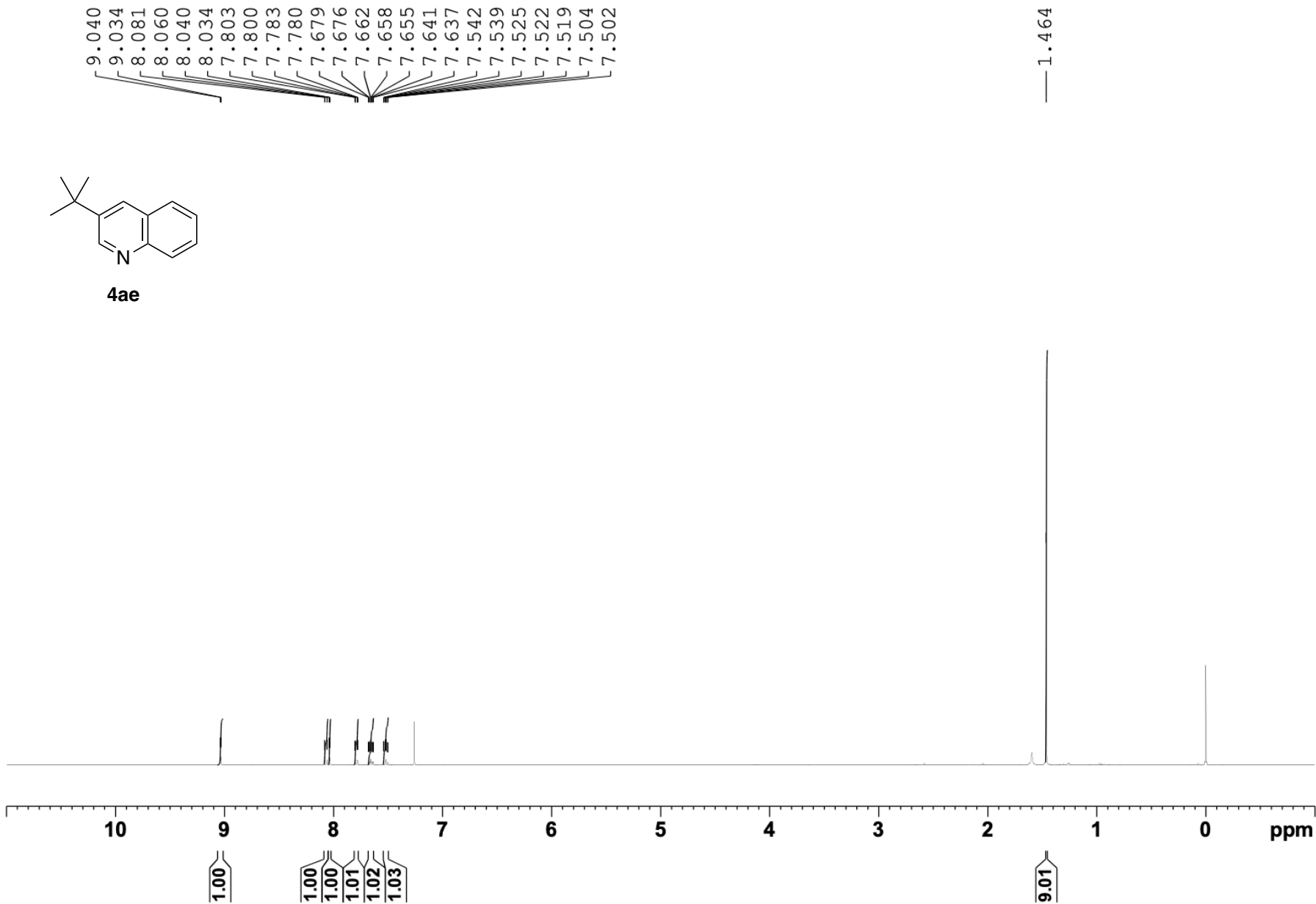
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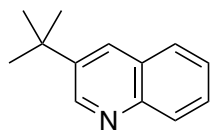
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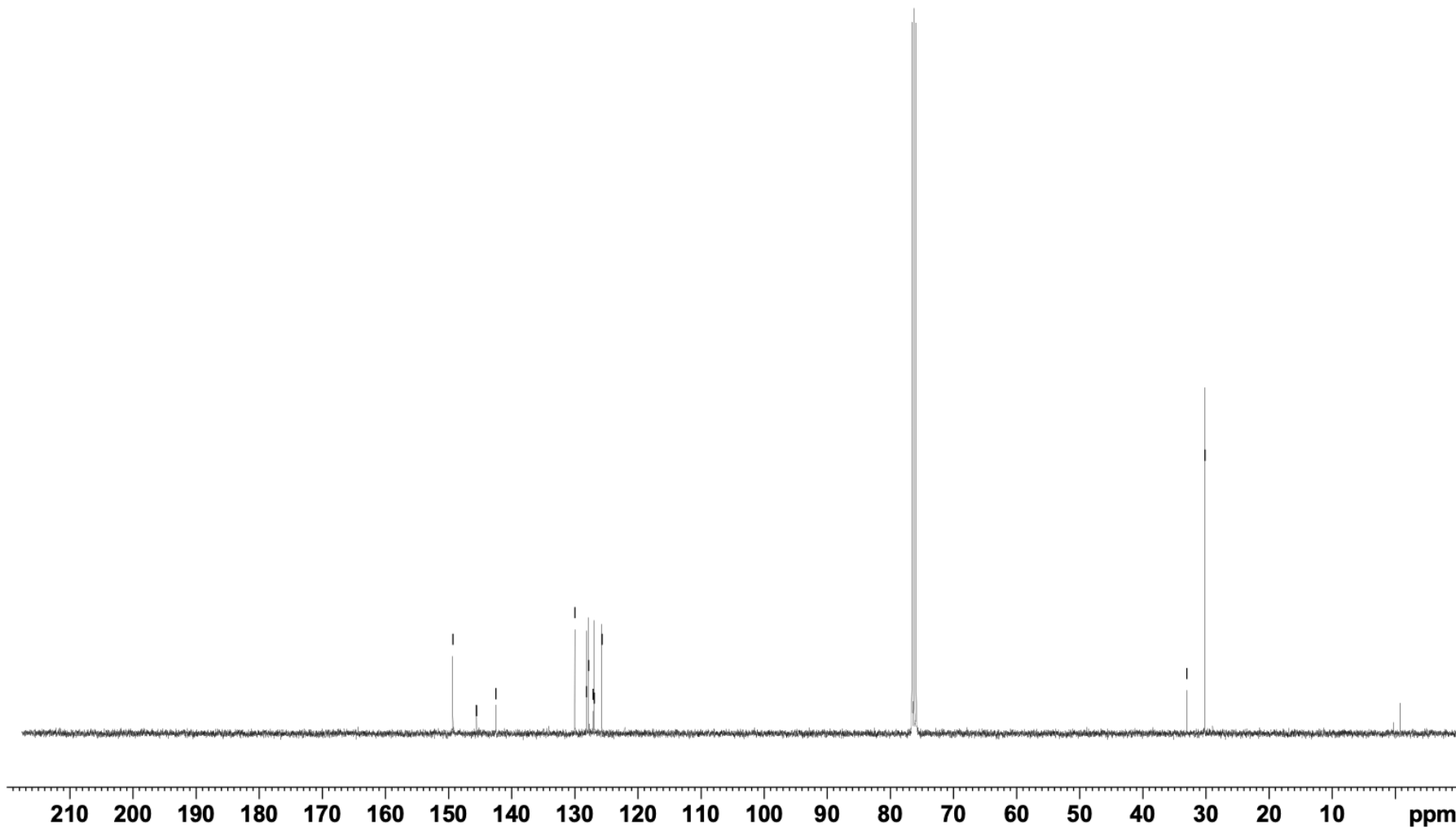


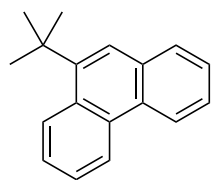


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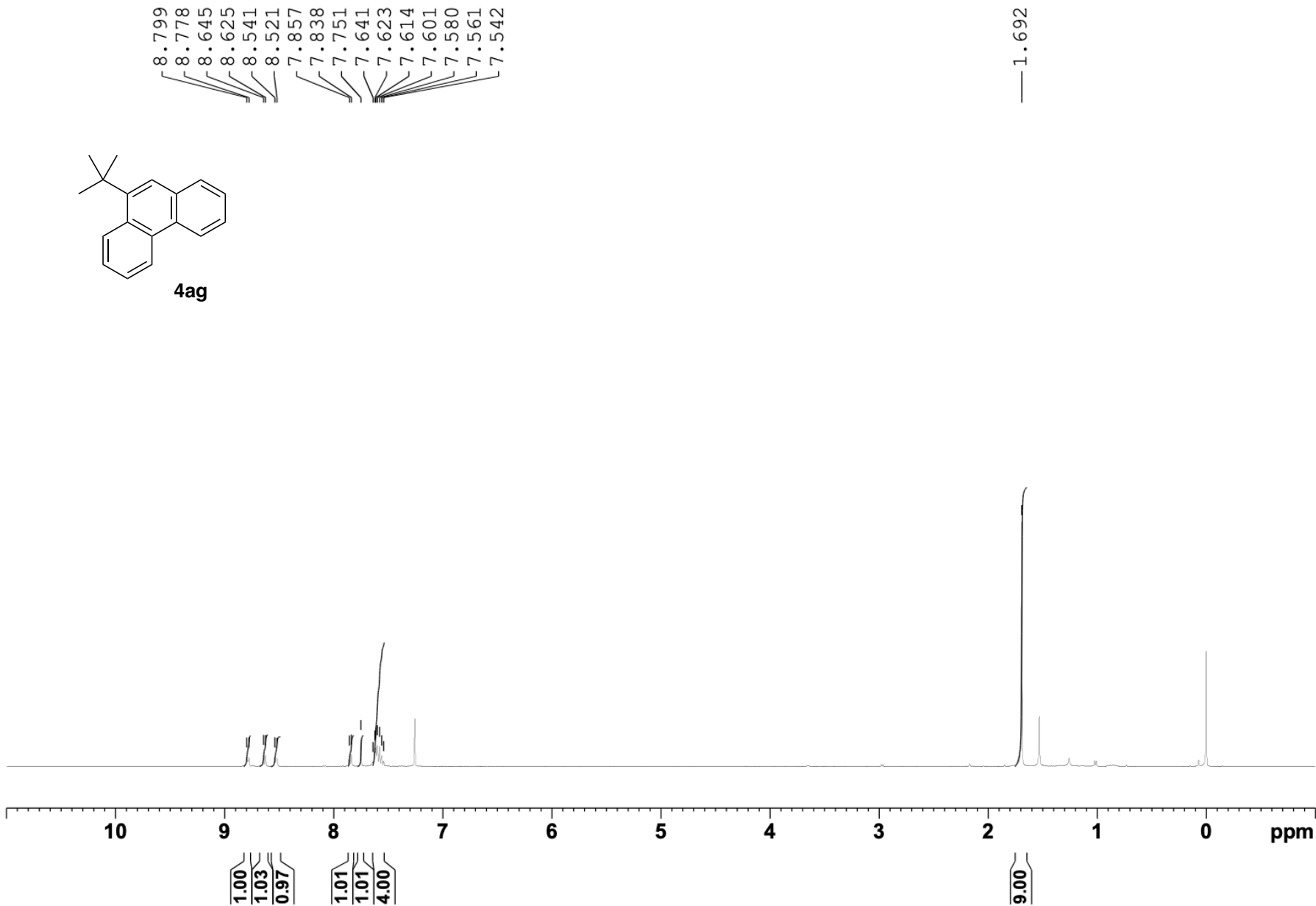
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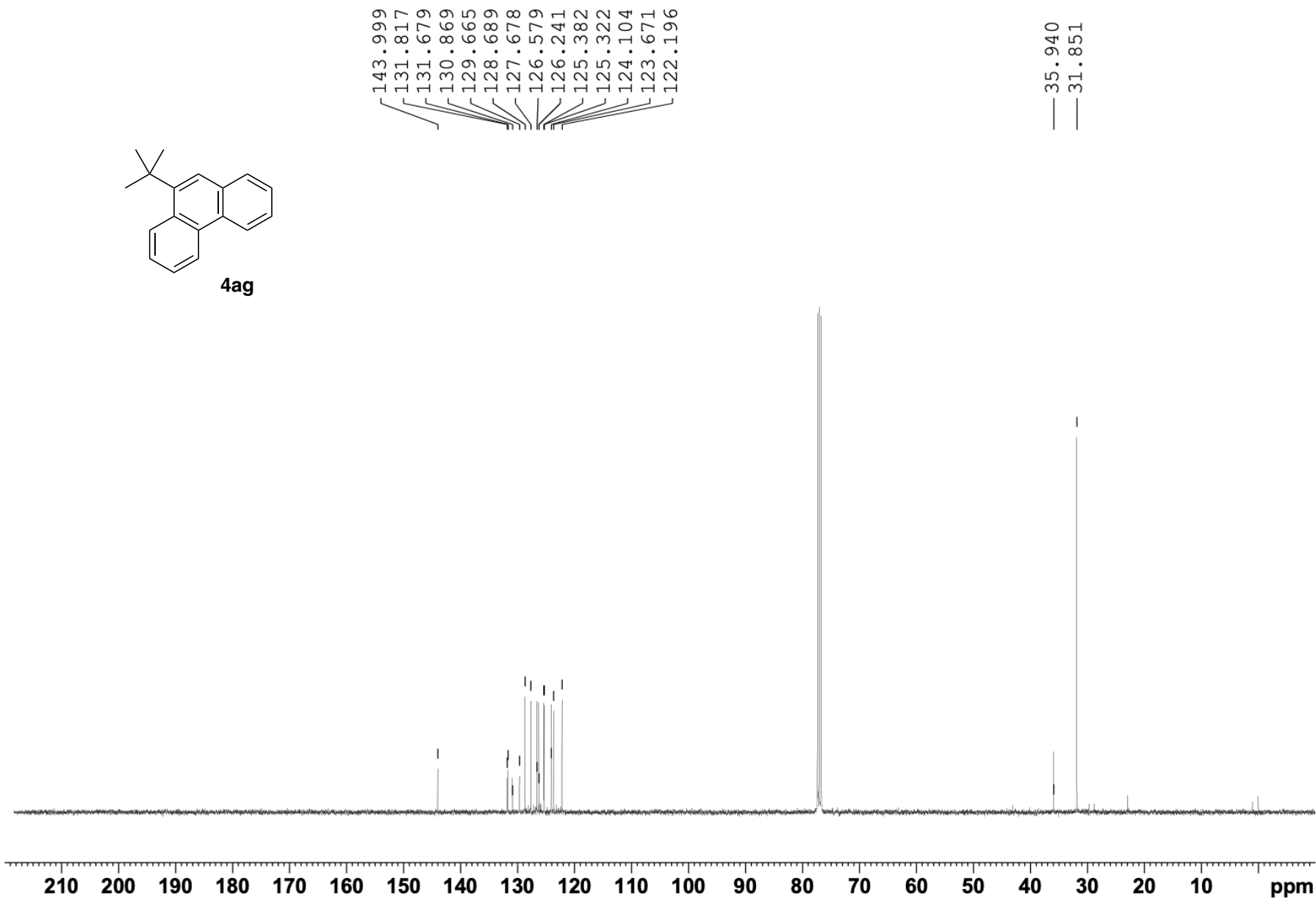
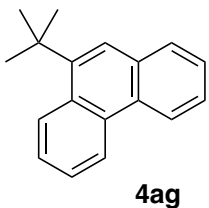
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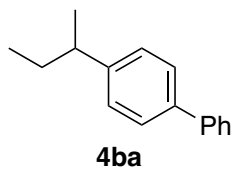




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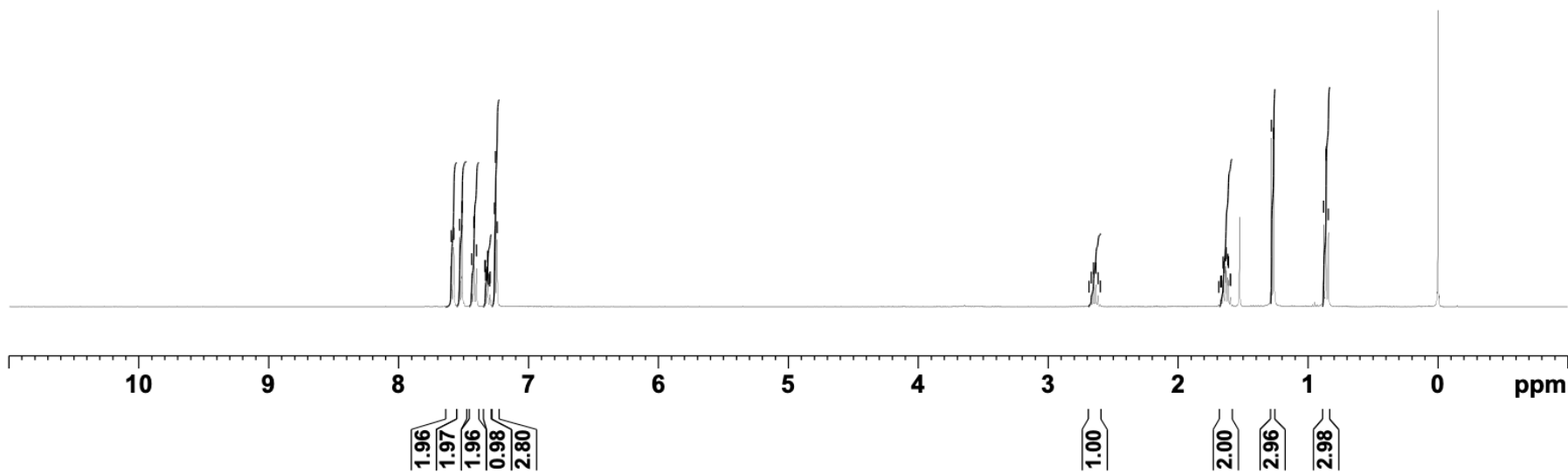


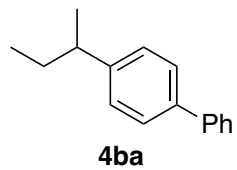




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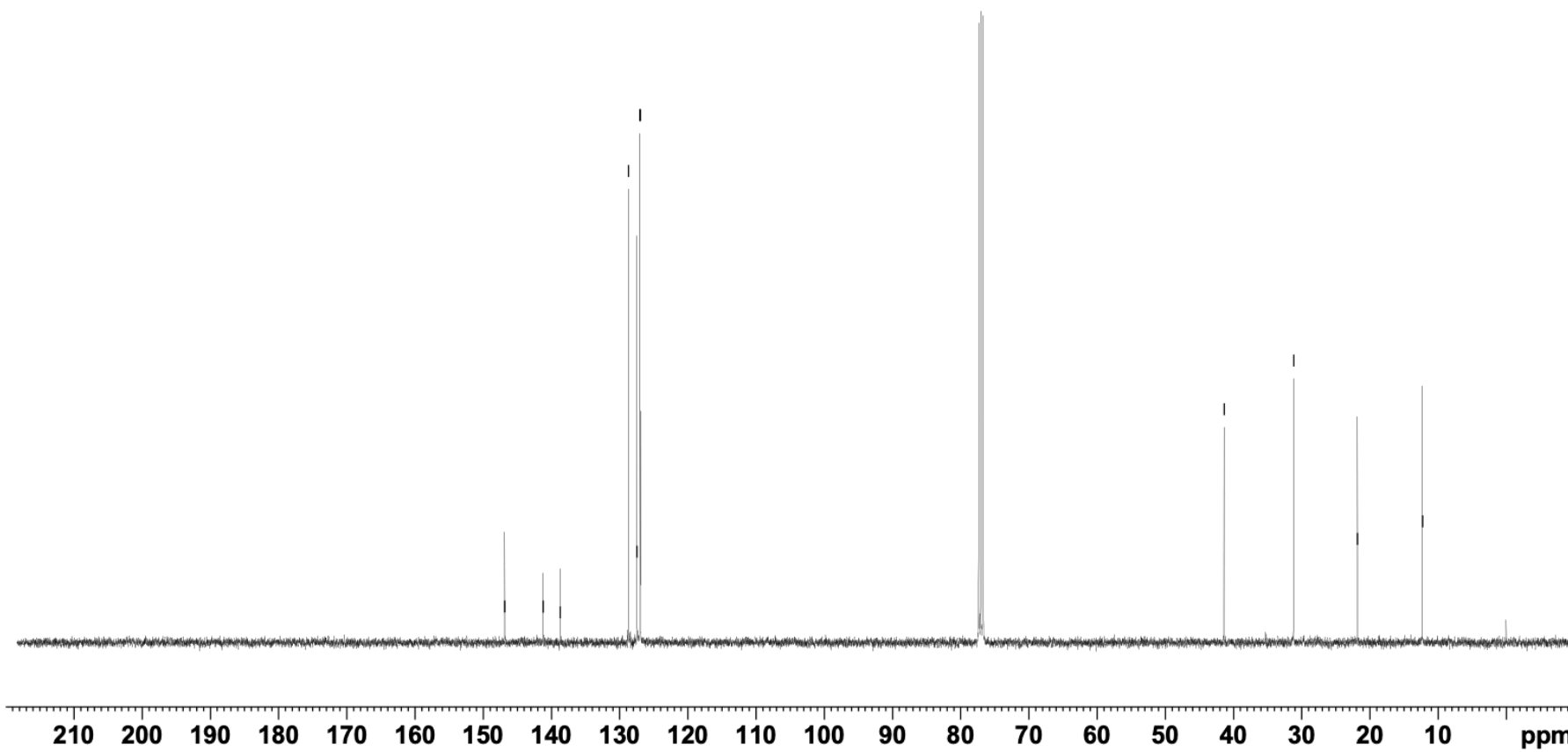
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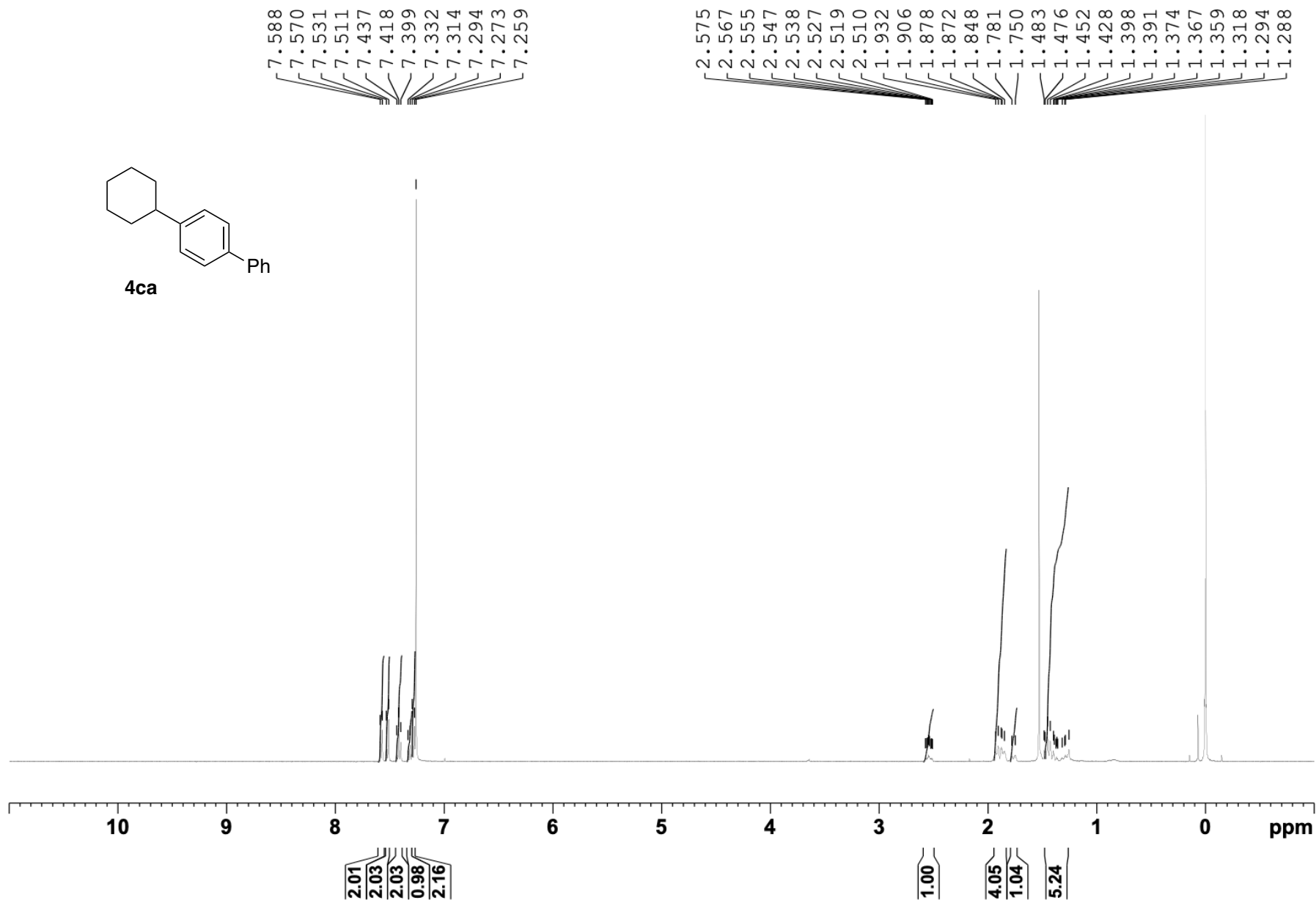


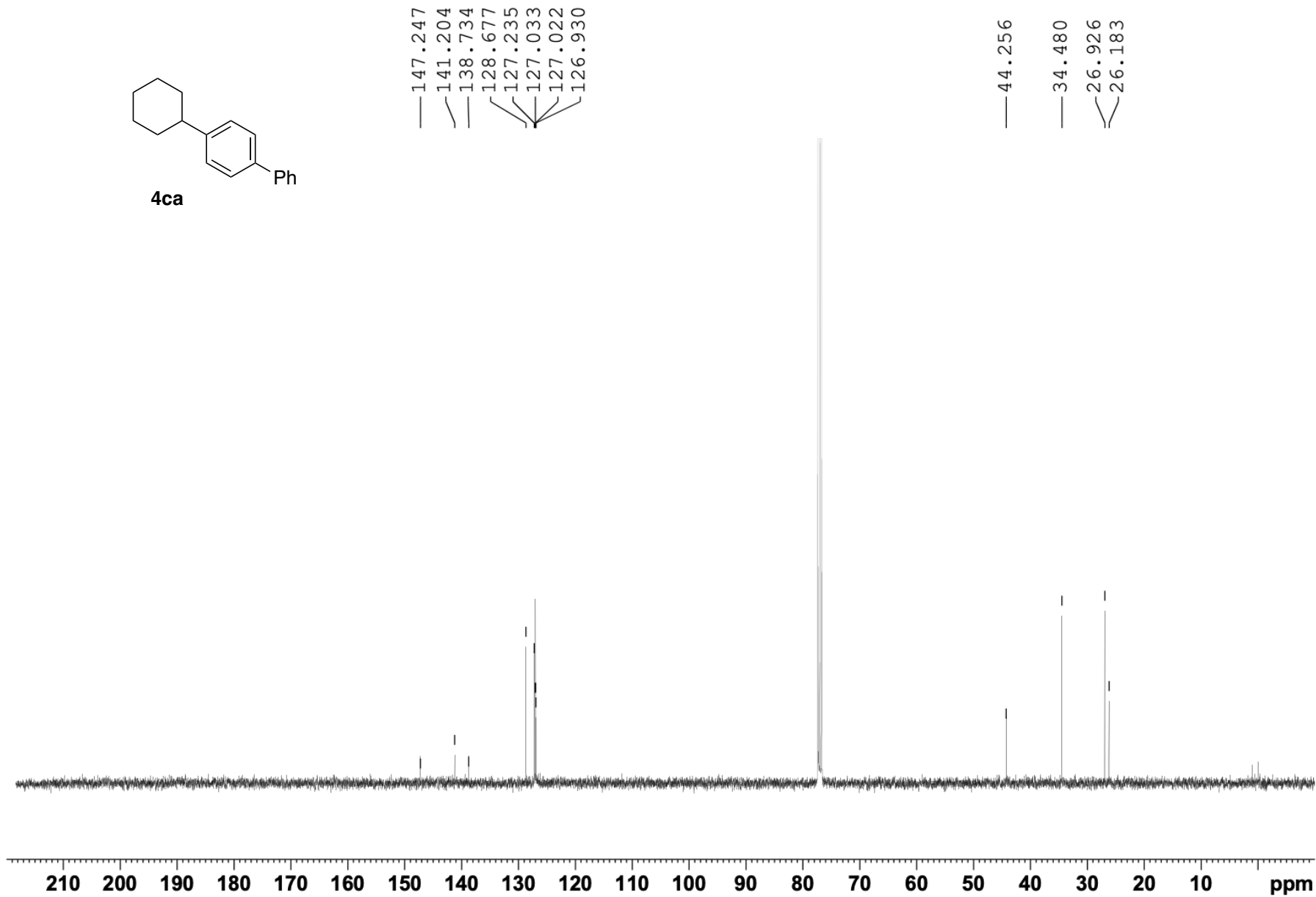
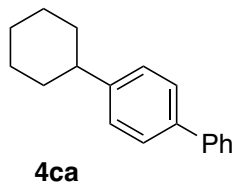
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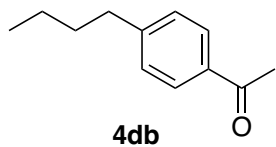
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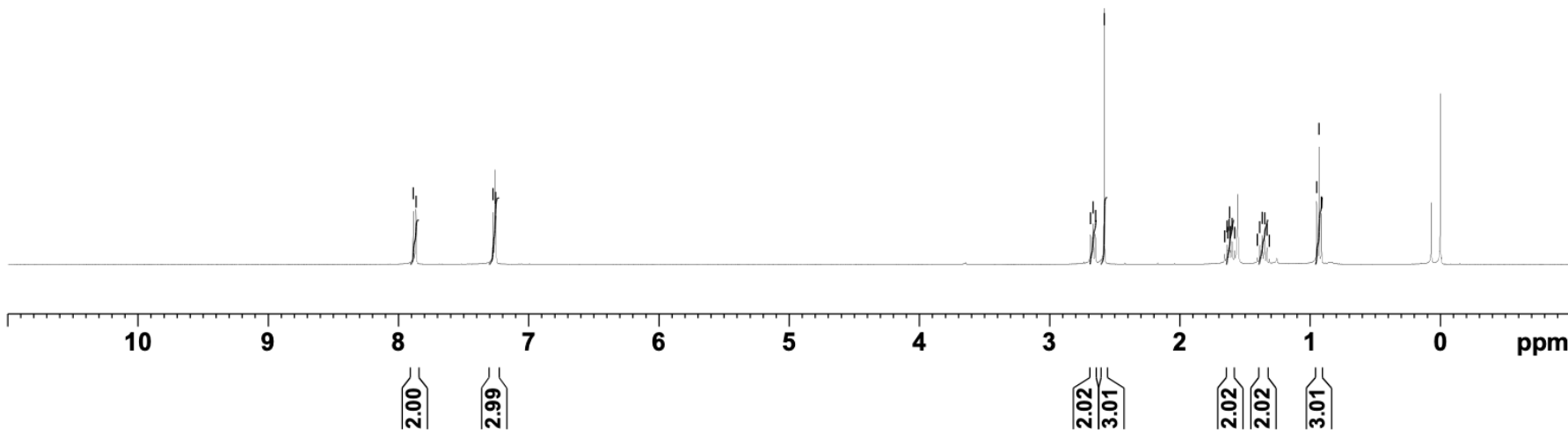


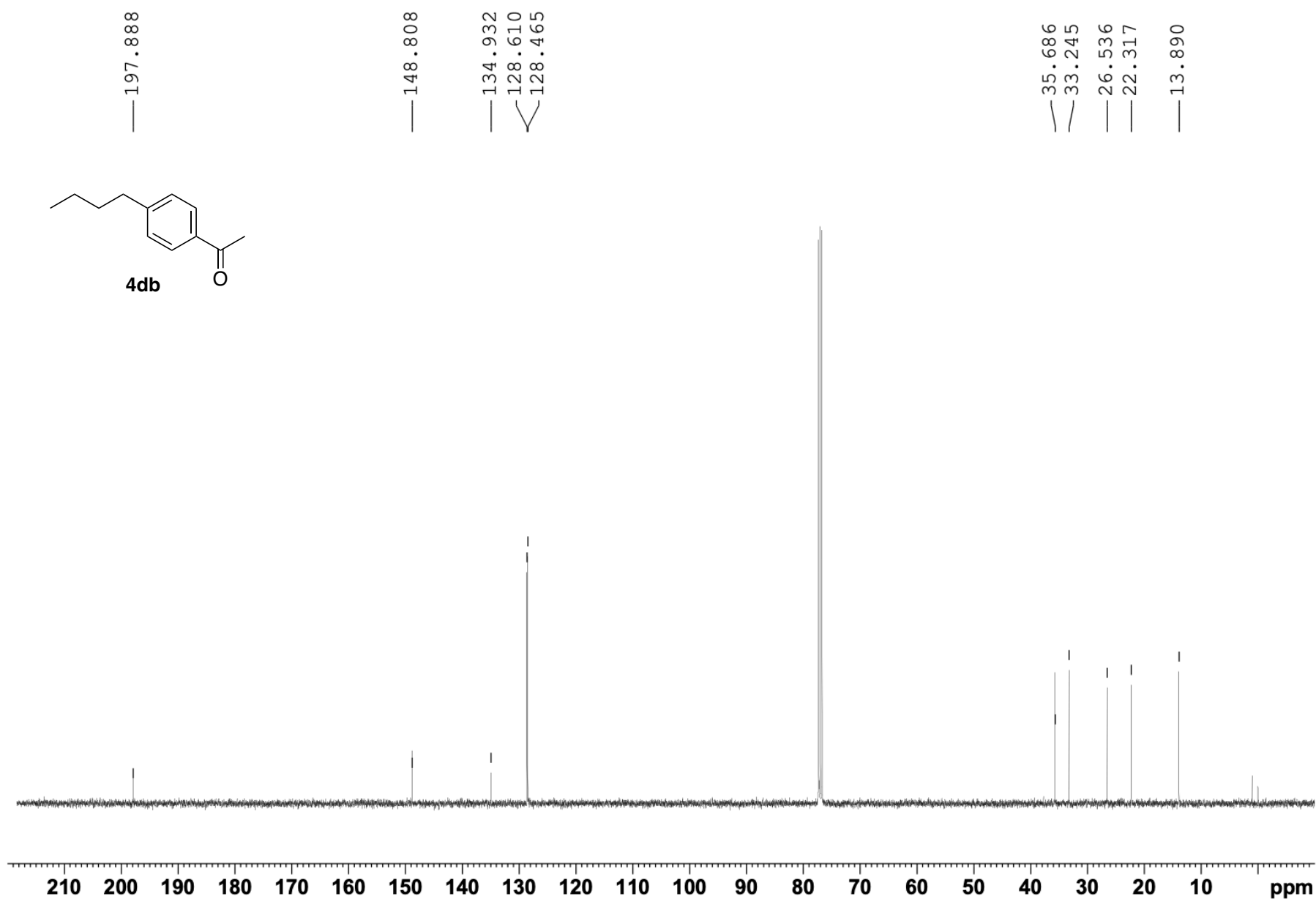
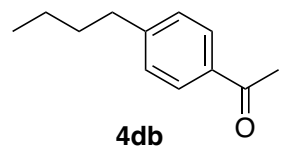


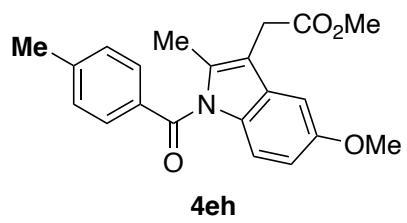
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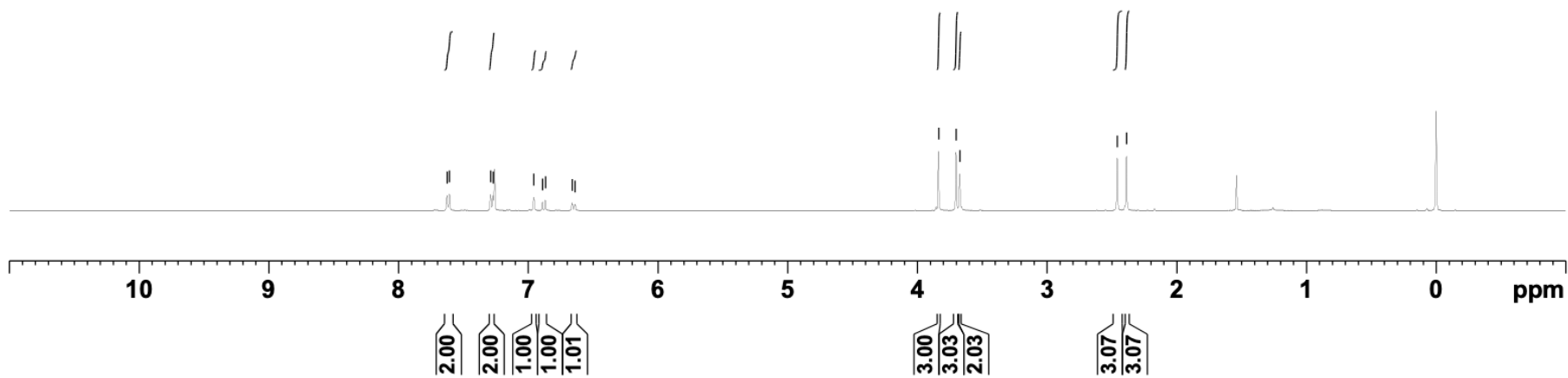


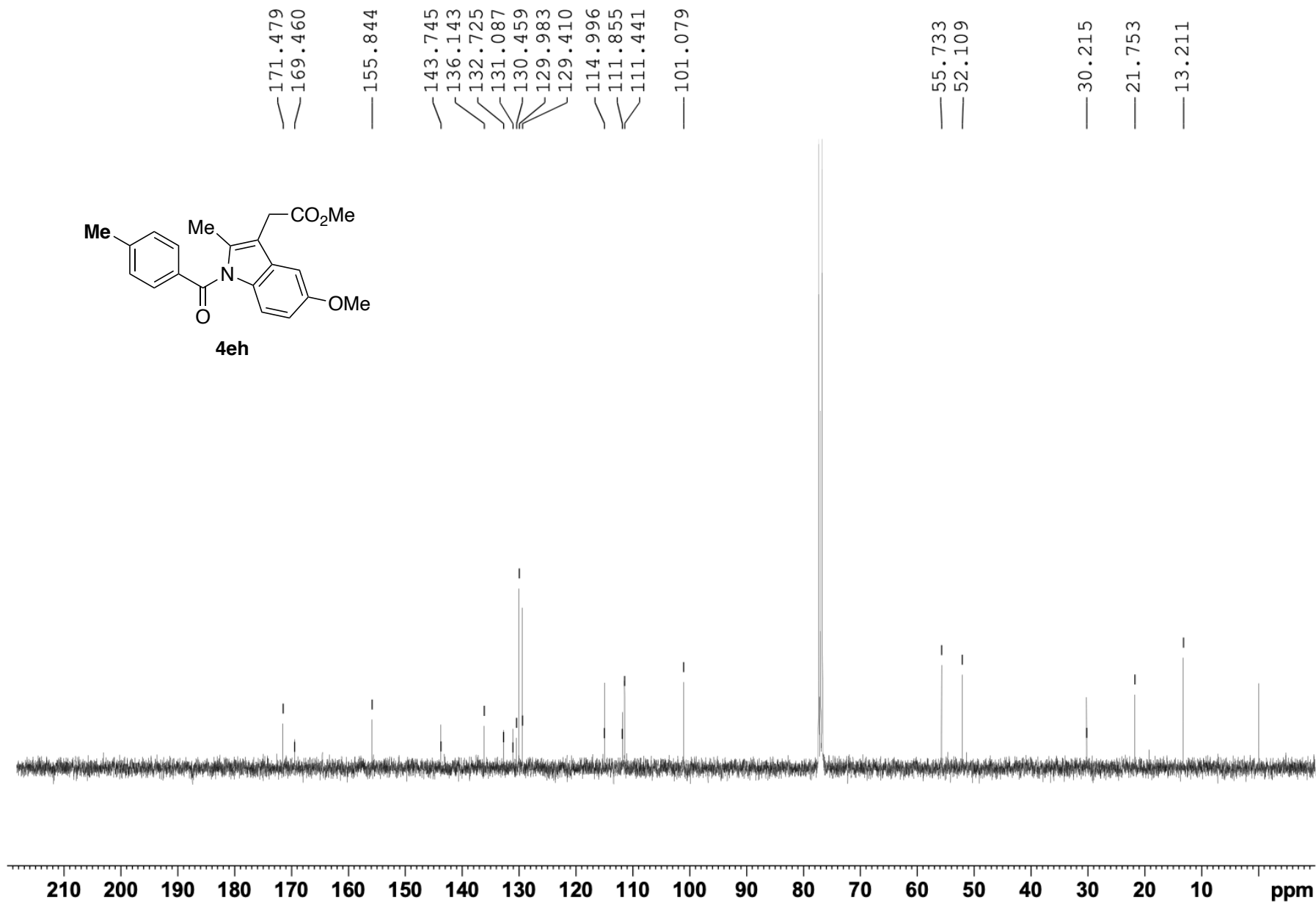


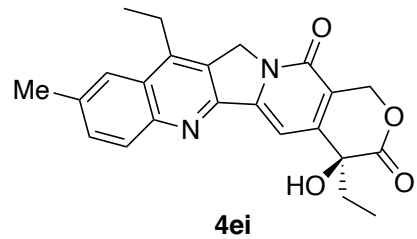
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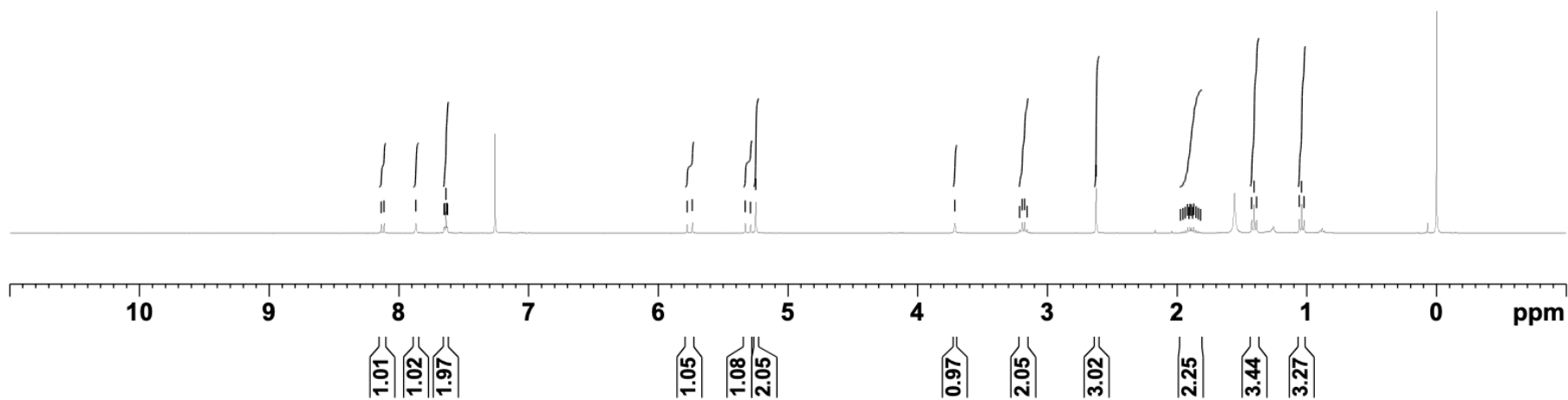


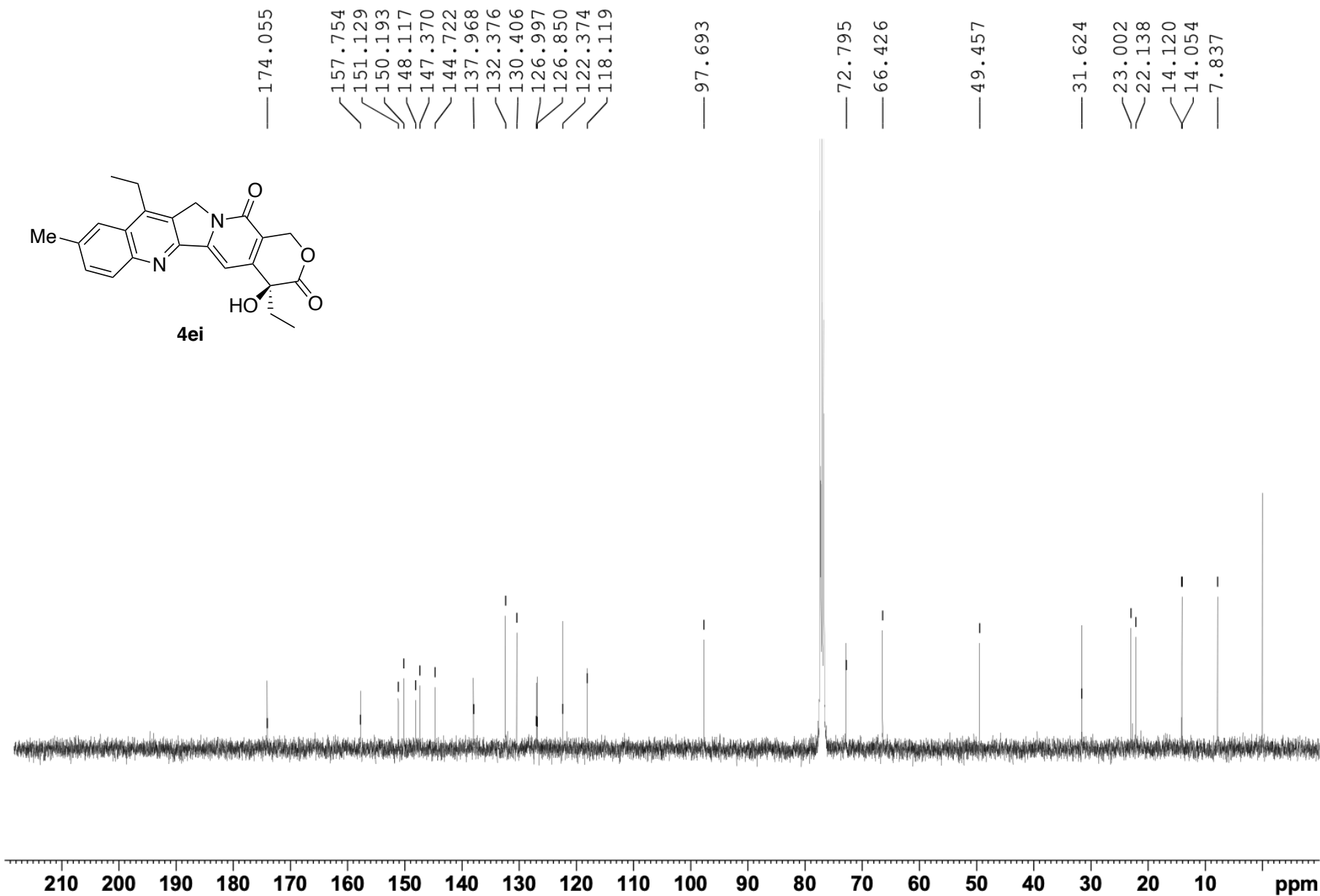
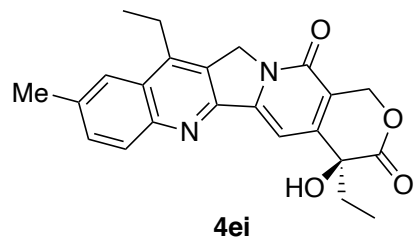


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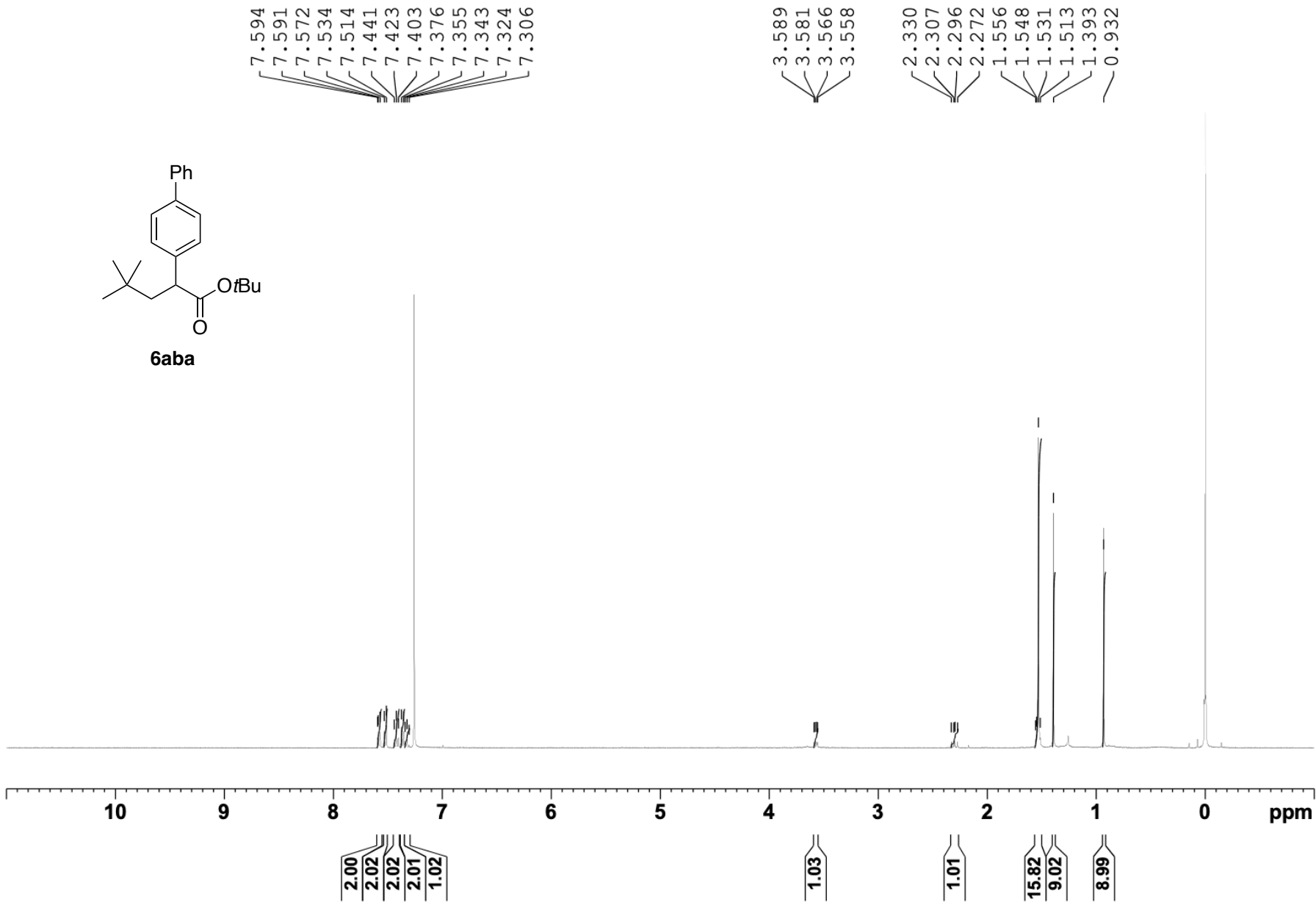
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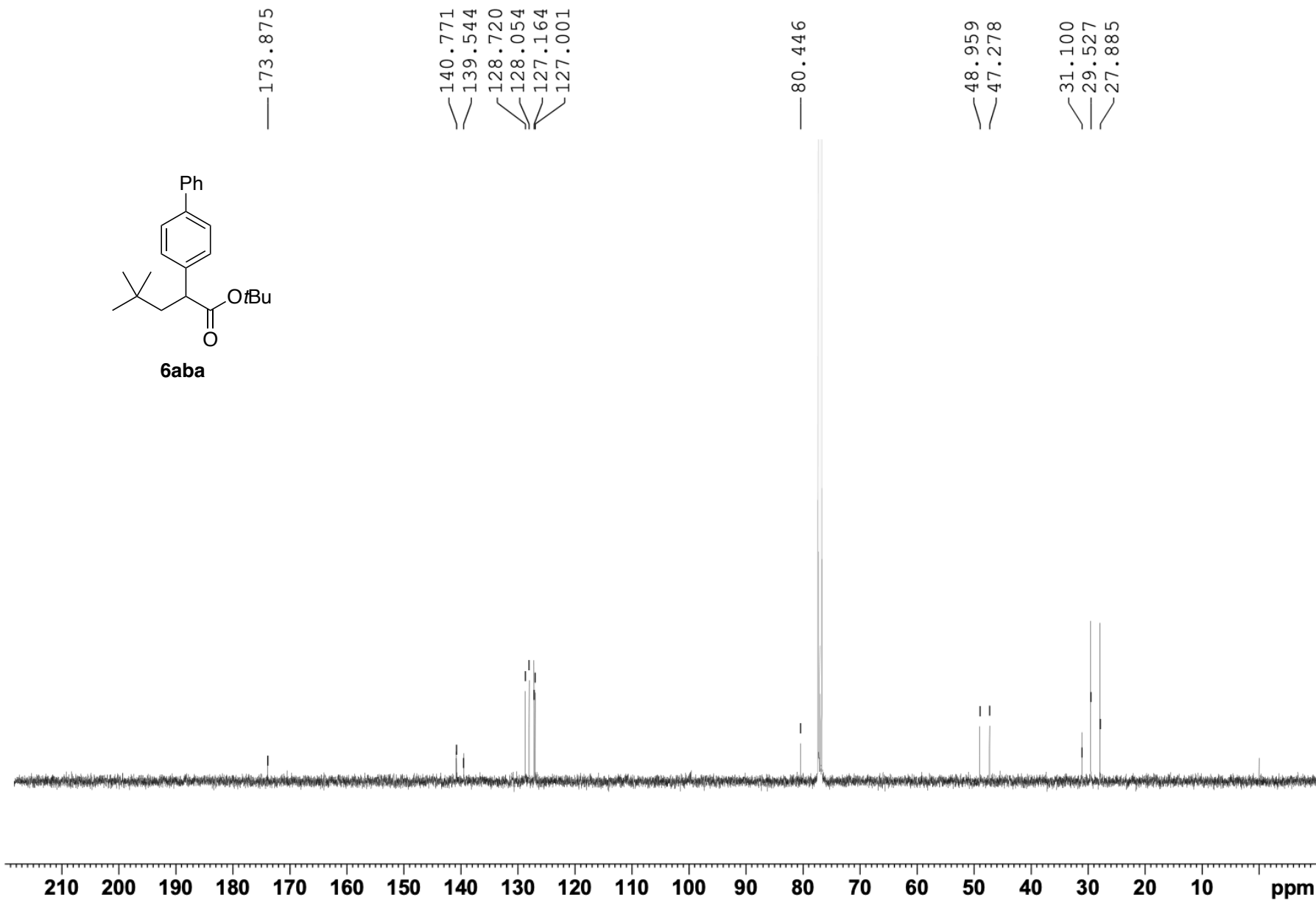
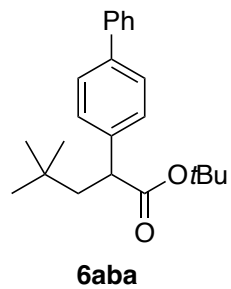
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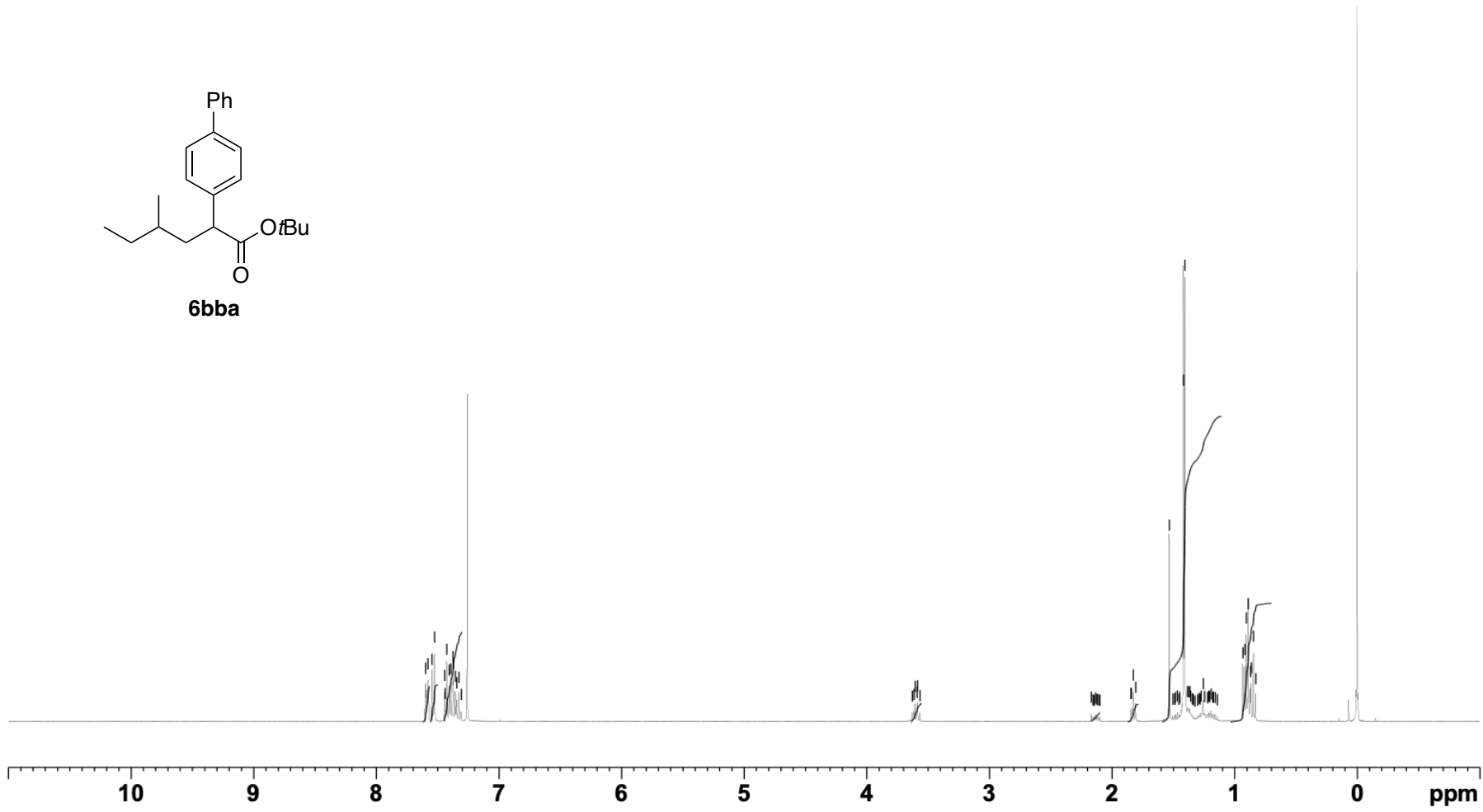
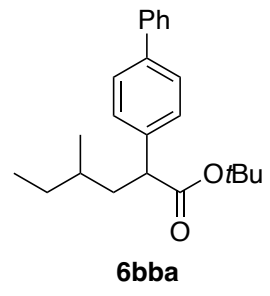




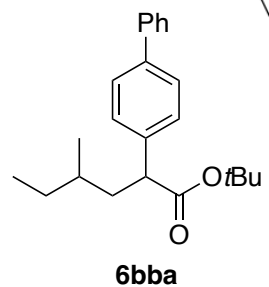




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