

## *Supporting Information*

# Ru-catalyzed 1,4-Addition of Arylboronic Acids to Acrylic Acid Derivatives in the Presence of Phenols

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## General and Materials

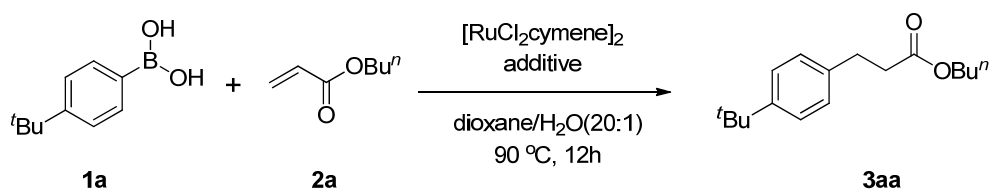
**General:** All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts for  $^1\text{H}$  NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for  $^{13}\text{C}$  NMR were recorded in ppm downfield using the central peak of  $\text{CDCl}_3$  (77.00 ppm) as the internal standard. Coupling constants ( $J$ ) are reported in Hz and refer to apparent peak multiplications.

**Materials:** Commercially available reagents were used throughout without further purification other than those detailed below. The solvents were pretreated by the following procedures: THF, toluene and dioxane was distilled over sodium benzophenone ketyl under nitrogen. DCE was distilled over calcium hydride. Acetone was distilled over calcium sulfate anhydrous under nitrogen.

### Typical Procedure for Conjugate Addition of Arylboronic Acids to Butyl Acrylate.

To a Schlenk tube were added arylboronic acid (1.05 mmol),  $[\text{RuCl}_2(p\text{-cymene})]_2$  (12.3 mg, 0.02 mmol) and 2,6-di-*tert*-butylphenol (20.6 mg, 0.1 mmol) was evacuated and purged with  $\text{N}_2$  for three times, butyl acrylate (128.0 mg, 1.0 mmol), in 1.0 mL dioxane/ $\text{H}_2\text{O}$  = 20 : 1(v/v) and other 2.0 mL dioxane/ $\text{H}_2\text{O}$  = 20 : 1 (v/v) were added sequentially to the system under  $\text{N}_2$ . After solvent was injected the solution turned orange immediately and then the mixture was stirred at 90 °C for 12 h. The reaction mixture was concentrated and the residue was purified by silica gel chromatography (PE/EA = 100) to give the product.

**Table 1** Screening of additives and solvents

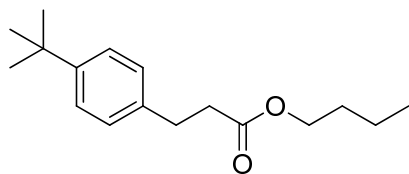


entry	additive <sup>b</sup>	solvent	yield (%) <sup>c</sup>
1	2-chlorophenol	dioxane/ $\text{H}_2\text{O}$	89
2	4-chlorophenol	dioxane/ $\text{H}_2\text{O}$	86
3	naphthalen-2-ol	dioxane/ $\text{H}_2\text{O}$	87
4	2-hydroxybenzoic acid	dioxane/ $\text{H}_2\text{O}$	86 <sup>d</sup>
5	sodium phenolate	dioxane/ $\text{H}_2\text{O}$	30 <sup>e</sup>
6	2,6-di( <i>t</i> -butyl)phenol	dioxane/ $\text{H}_2\text{O}$	92 <sup>f</sup>
7	2,6-di( <i>t</i> -butyl)phenol	dioxane/ $\text{H}_2\text{O}$	94 <sup>g</sup>
8	2,6-di( <i>t</i> -butyl)phenol	dioxane/ $\text{H}_2\text{O}$	93 <sup>h</sup>
9	2,6-di( <i>t</i> -butyl)phenol	dioxane	<5% <sup>i</sup>
10	2,6-di( <i>t</i> -butyl)phenol	THF/ $\text{H}_2\text{O}$	82
11	2,6-di( <i>t</i> -butyl)phenol	toluene/ $\text{H}_2\text{O}$	63
12	2,6-di( <i>t</i> -butyl)phenol	methanol/ $\text{H}_2\text{O}$	43
13	2,6-di( <i>t</i> -butyl)phenol	acetone/ $\text{H}_2\text{O}$	78
14	2,6-di( <i>t</i> -butyl)phenol	DMF/ $\text{H}_2\text{O}$	15

<sup>a</sup>All the reactions were carried out with **1** (1.05 mmol), **2** (1.00 mmol), ruthenium complex (2.0 mol %) in solvent [dioxane/ $\text{H}_2\text{O}$  = 20/1 (v/v)] 3 mL at 90 °C under  $\text{N}_2$  for 12 h. <sup>b</sup>20 mol %. <sup>c</sup>yield determined by GC signal-integration method with durene as an internal standard. <sup>d</sup>with 1.5 equiv of arylboronic acid. <sup>e</sup>With 40% Heck-type product. <sup>f</sup>2,6-di-*tert*-butyl phenol (5 mol %) was added. <sup>g</sup>2,6-di-*tert*-butyl phenol (50 mol %) was added. <sup>h</sup>2,6-di-*tert*-butyl phenol (100 mol %) was added. <sup>i</sup>dry dioxane as the solvent.

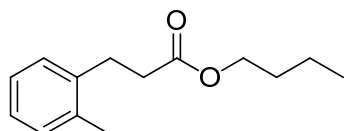
## Spectrum data of 3aa-3oa and 3eb.

### Butyl 3-(4-(tert-butyl)phenyl)propanoate (3aa)



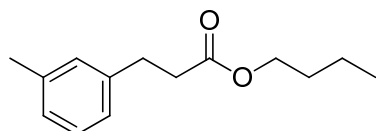
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.4$  Hz, 2H), 7.14 (d,  $J = 8.4$  Hz, 2H), 4.07 (t,  $J = 6.6$  Hz, 2H), 2.92 (t,  $J = 8.0$  Hz, 2H), 2.62 (t,  $J = 8.0$  Hz, 2H), 1.62-1.55 (m, 2H), 1.37-1.31 (m, 2H), 1.30 (s, 9H), 0.92 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 149.2, 137.8, 128.2, 125.6, 64.5, 36.2, 34.6, 31.7, 31.0, 30.8, 19.4, 14.0. HRMS (QTOF-ESI) Calculated for  $\text{C}_{17}\text{H}_{26}\text{NaO}_2$  ( $\text{M}+\text{Na}$ ) 285.1830, found 285.1855.

### *n*-Butyl 3-(*o*-tolyl)propanoate (3ba)<sup>1</sup>



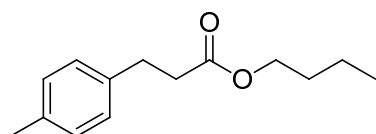
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.09 (m, 4H), 4.08 (t,  $J = 6.6$  Hz, 2H), 2.93 (t,  $J = 8$  Hz, 2H), 2.57 (t,  $J = 8$  Hz, 2H), 2.31 (s, 3H), 1.62-1.55 (m, 2H), 1.38-1.30 (m, 3H), 0.92 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 138.9, 136.2, 130.5, 130.2, 128.7, 126.6, 126.4, 64.6, 34.9, 30.9, 28.6, 19.5, 19.4, 14.0.

### *n*-Butyl 3-(*m*-tolyl)propanoate (3ca)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (t,  $J = 7.8$  Hz, 1H), 7.02-6.99 (m, 3H), 4.07 (t,  $J = 6.6$  Hz, 2H), 2.92 (t,  $J = 7.8$  Hz, 2H), 2.61 (t,  $J = 7.8$  Hz, 2H), 2.33 (s, 3H), 1.62-1.55 (m, 2H), 1.37-1.32 (m, 2H), 0.92 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 140.8, 138.2, 129.4, 128.6, 127.2, 125.5, 64.5, 36.2, 31.2, 30.9, 21.6, 19.4, 14.0. HRMS (QTOF-ESI) Calculated for  $\text{C}_{14}\text{H}_{20}\text{NaO}_2$  ( $\text{M}+\text{Na}$ ) 243.1361, found 243.1361.

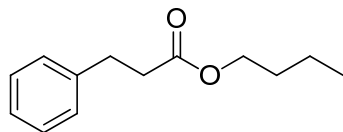
### *n*-Butyl 3-(*p*-tolyl)propanoate (3da)<sup>2</sup>



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (s, 4H), 4.07 (t,  $J = 6.6$  Hz, 2H), 2.91 (t,  $J = 7.8$  Hz, 2H), 2.60 (t,  $J = 7.8$  Hz, 2H), 2.32 (s, 3H), 1.62-1.55 (m, 2H), 1.39-1.29 (m, 2H), 0.92 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 137.8, 135.9, 129.4,

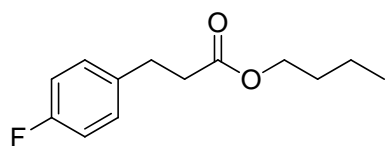
128.4, 64.5, 36.3, 30.9, 30.9, 21.3, 19.4, 14.0.

***n*-Butyl 3-phenylpropanoate (3ea)<sup>2</sup>**



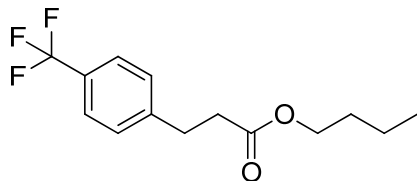
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.27 (m, 2H), 7.21-7.18 (m, 3H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.62-1.55 (m, 2H), 1.37-1.30 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 173.2, 140.8, 128.7, 128.5, 126.5, 64.6, 36.2, 31.3, 30.9, 19.4, 14.0.

**Butyl 3-(4-fluorophenyl)propanoate (3fa)<sup>2</sup>**



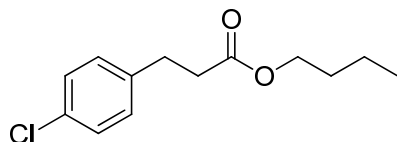
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18-7.14 (m, 2H), 7.99-6.95 (m, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.60-1.55 (m, 2H), 1.34-1.32 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.0, 162.9, 160.4, 136.4, 130.0, 129.9, 115.5, 115.3, 64.5, 36.2, 30.8, 30.4, 19.3, 13.9.

**Butyl 3-(4-(trifluoromethyl)phenyl)propanoate (3ga)**



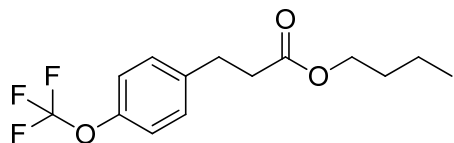
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 3.01 (t, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.61-1.53 (m, 2H), 1.37-1.27 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.7, 144.9, 128.9, 128.6, 128.3, 125.8, 125.6, 125.5, 123.1, 64.7, 35.6, 30.9, 30.8, 19.2, 13.8. HRMS (QTOF-ESI) Calculated for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>NaO<sub>2</sub> (M+Na) 297.1078, found 297.1090.

**Butyl 3-(4-chlorophenyl)propanoate (3ha)<sup>3</sup>**



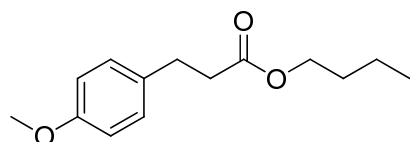
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.61-1.54 (m, 2H), 1.38-1.28 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.8, 139.2, 132.2, 129.9, 128.7, 64.6, 35.9, 30.8, 30.5, 19.3, 13.9.

### Butyl 3-(4-(trifluoromethoxy)phenyl)propanoate (3ia)



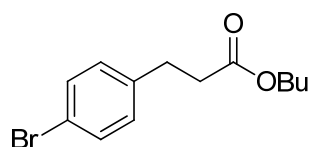
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 8.4$  Hz, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 4.05 (t,  $J = 6.6$  Hz, 2H), 2.94 (t,  $J = 8.0$  Hz, 2H), 2.60 (t,  $J = 8.0$  Hz, 2H), 1.59-1.52 (m, 2H), 1.36-1.26 (m, 2H), 0.89 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 147.8, 139.5, 129.8, 122.0, 121.2, 120.5, 119.4, 64.6, 35.9, 30.8, 30.4, 19.3, 13.8. HRMS (QTOF-ESI) Calculated for  $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NaO}_3$  ( $\text{M}+\text{Na}$ ) 313.1027, found 313.1003.

### Butyl 3-(4-methoxyphenyl)propanoate (3ja)<sup>3</sup>



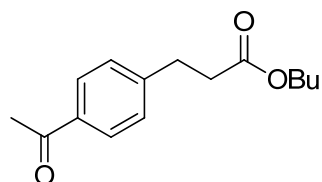
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12-7.09 (m, 2H), 6.83-6.80 (m, 2H), 4.05 (t,  $J = 6.4$  Hz, 2H), 3.76 (s, 3H), 2.88 (t,  $J = 7.8$  Hz, 2H), 2.58 (t,  $J = 7.8$  Hz, 2H), 1.60-1.53 (m, 2H), 1.38-1.28 (m, 2H), 0.91 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 158.2, 132.8, 129.5, 114.0, 64.5, 55.4, 36.5, 30.9, 30.4, 19.4, 14.0.

### Butyl 3-(4-bromophenyl)propanoate (3ka)<sup>2</sup>



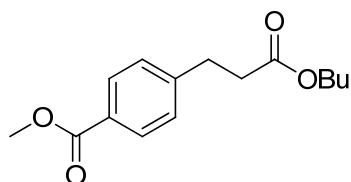
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.4$  Hz, 2H), 7.07 (d,  $J = 8.4$  Hz, 2H), 4.05 (t,  $J = 6.8$  Hz, 2H), 2.89 (t,  $J = 7.6$  Hz, 2H), 2.59 (t,  $J = 7.6$  Hz, 2H), 1.60 – 1.53 (m, 2H), 1.37 – 1.27 (m, 2H), 0.90 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 139.7, 131.7, 130.3, 120.2, 64.6, 35.8, 30.9, 30.6, 19.3, 13.9.

### Butyl 3-(4-acetylphenyl)propanoate (3la)<sup>4</sup>



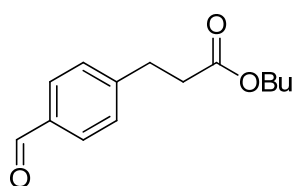
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H), 4.04 (t,  $J = 6.4$  Hz, 2H), 2.98 (t,  $J = 7.6$  Hz, 2H), 2.63 (t,  $J = 7.6$  Hz, 2H), 2.56 (s, 3H), 1.59-1.51 (m, 2H), 1.35-1.264 (m, 2H), 0.88 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 172.5, 146.4, 135.5, 128.7, 128.6, 64.5, 35.4, 31.0, 30.7, 26.6, 19.2, 13.8.

### Methyl 4-(3-butoxy-3-oxopropyl)benzoate (3ma)<sup>3</sup>



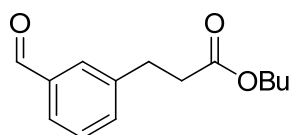
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.04 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.58–1.51 (m, 2H), 1.35–1.25 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.6, 167.0, 146.1, 129.9, 128.5, 128.4, 64.5, 52.0, 35.4, 31.0, 30.8, 19.2, 13.8.

### Butyl 3-(4-formylphenyl)propanoate (3na)<sup>2</sup>



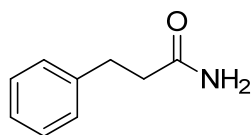
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.95 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.58–1.51 (m, 2H), 1.33–1.27 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.9, 172.5, 148.0, 135.0, 130.1, 129.2, 64.6, 35.3, 31.2, 30.7, 19.2, 13.8.

### Butyl 3-(3-formylphenyl)propanoate (3oa)<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.94 (s, 1H), 7.69–7.66 (m, 2H), 7.46–7.39 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.56–1.49 (m, 2H), 1.32–1.23 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 192.4, 172.7, 141.8, 136.8, 134.7, 129.4, 129.3, 128.1, 64.5, 35.6, 30.8, 30.7, 19.2, 13.8.

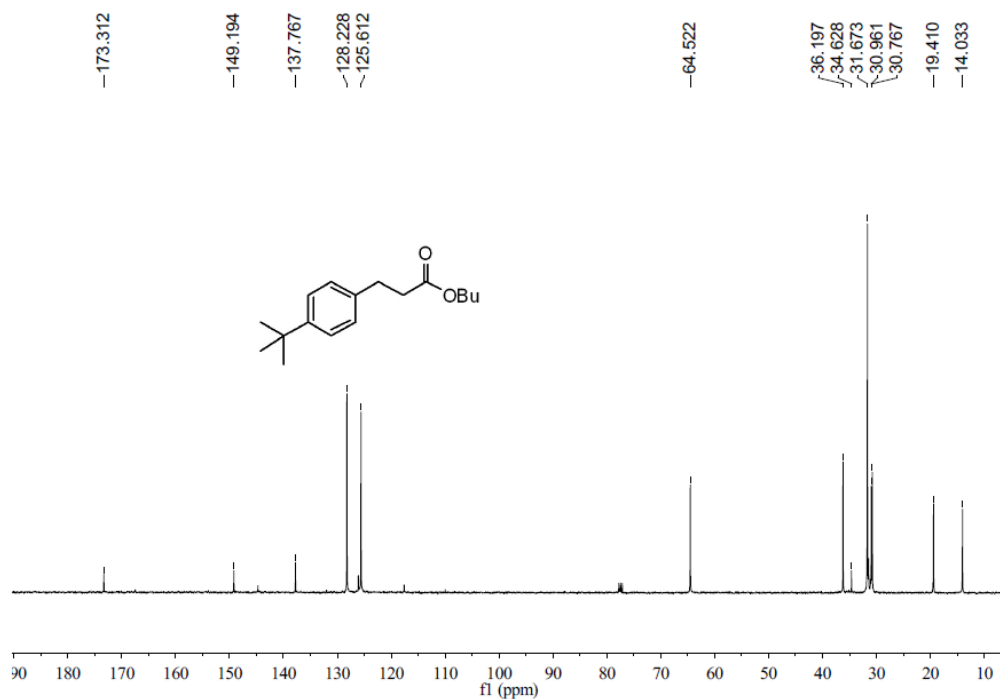
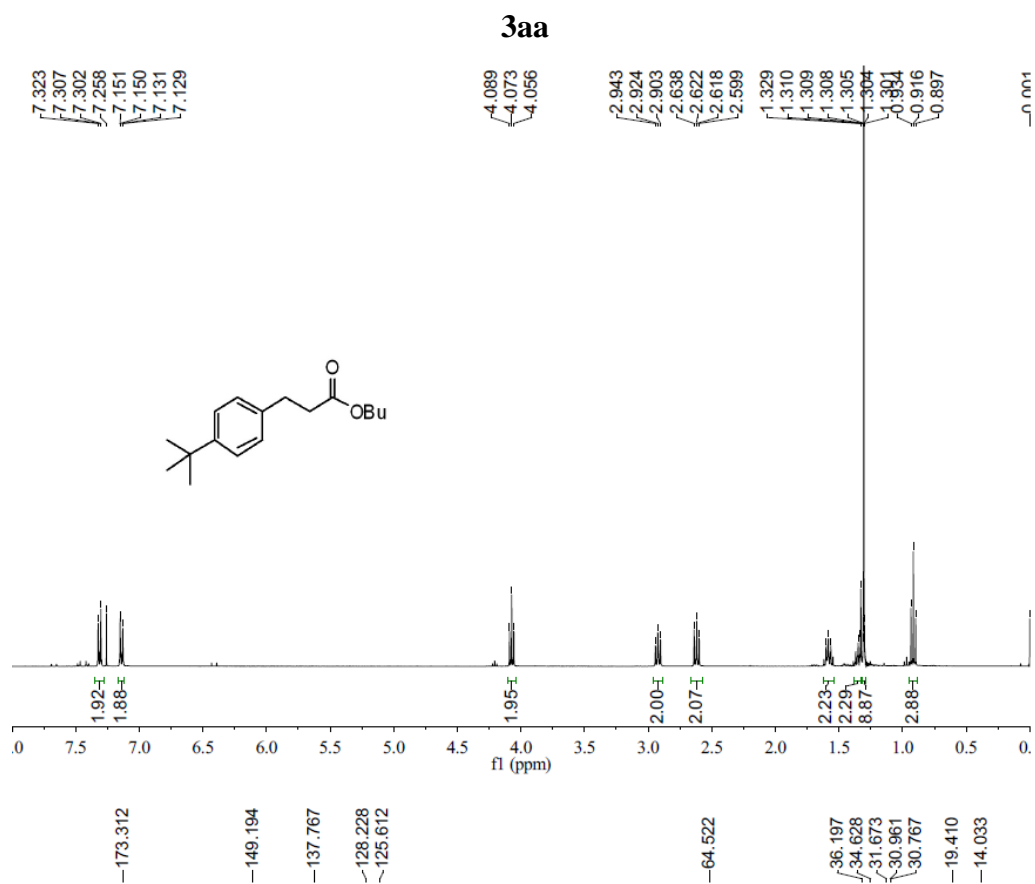
### 3-Phenylpropanamide (3eb)<sup>5</sup>



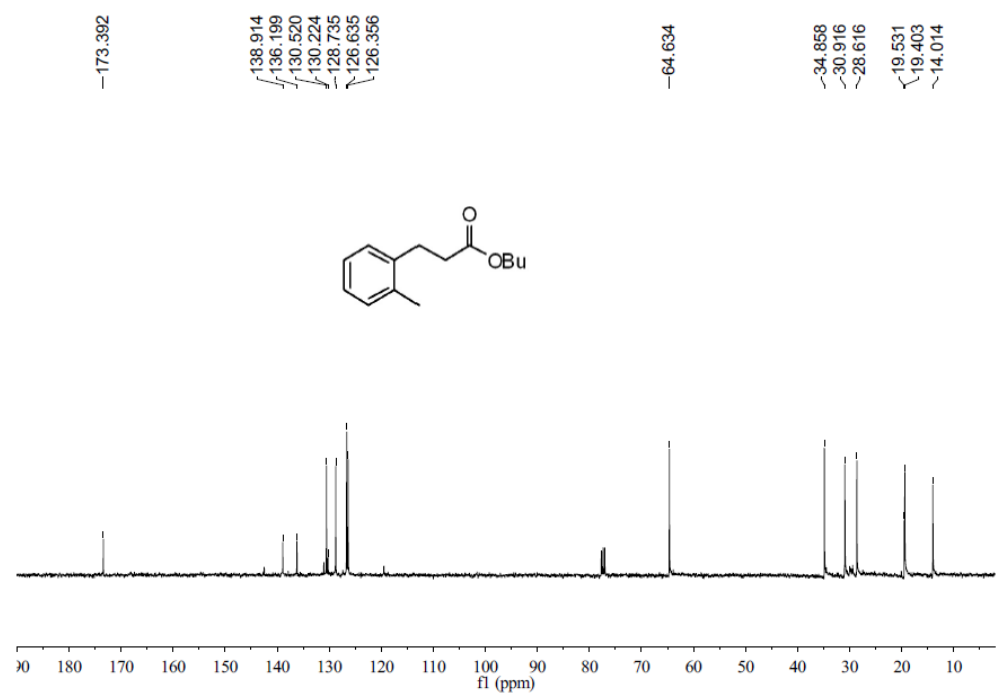
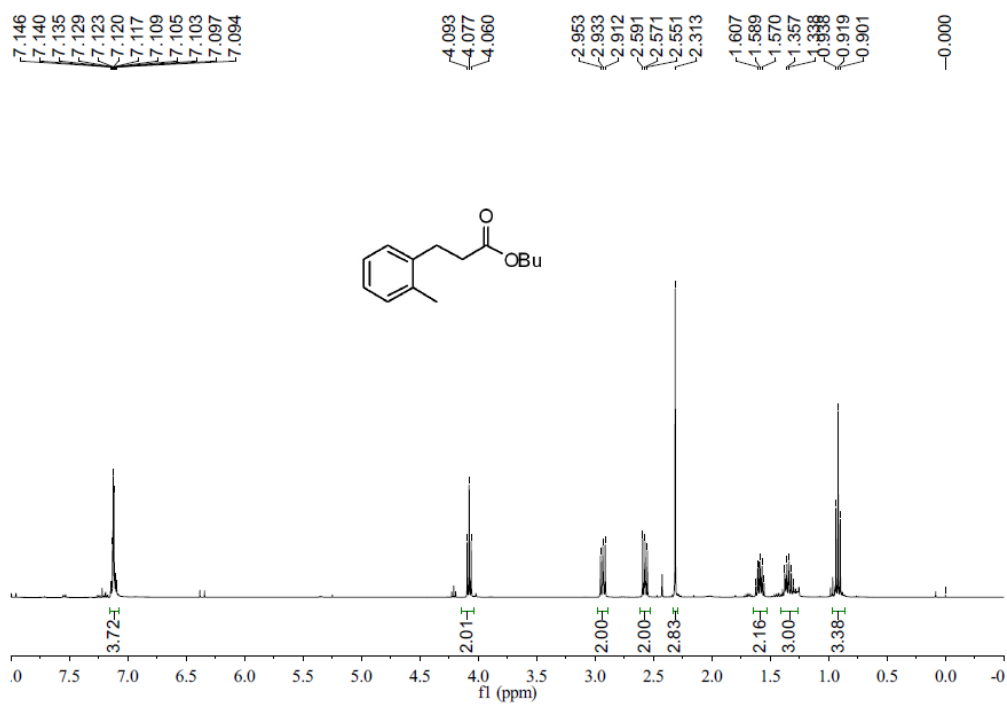
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32–7.27 (m, 2H), 7.23–7.21 (m, 3H), 5.45 (br, 2H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.5, 140.9, 128.8, 128.6, 126.5, 37.8, 31.6.

1. Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 7666.
2. Lin, P.; Jeganmohan, M.; Cheng, C. *Chem.–Asian J.* **2007**, *2*, 1409.
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4. Zou, G.; Guo, J.; Wang, Z.; Huang, W.; Tang, J. *Dalton Trans.* **2007**, 3055.
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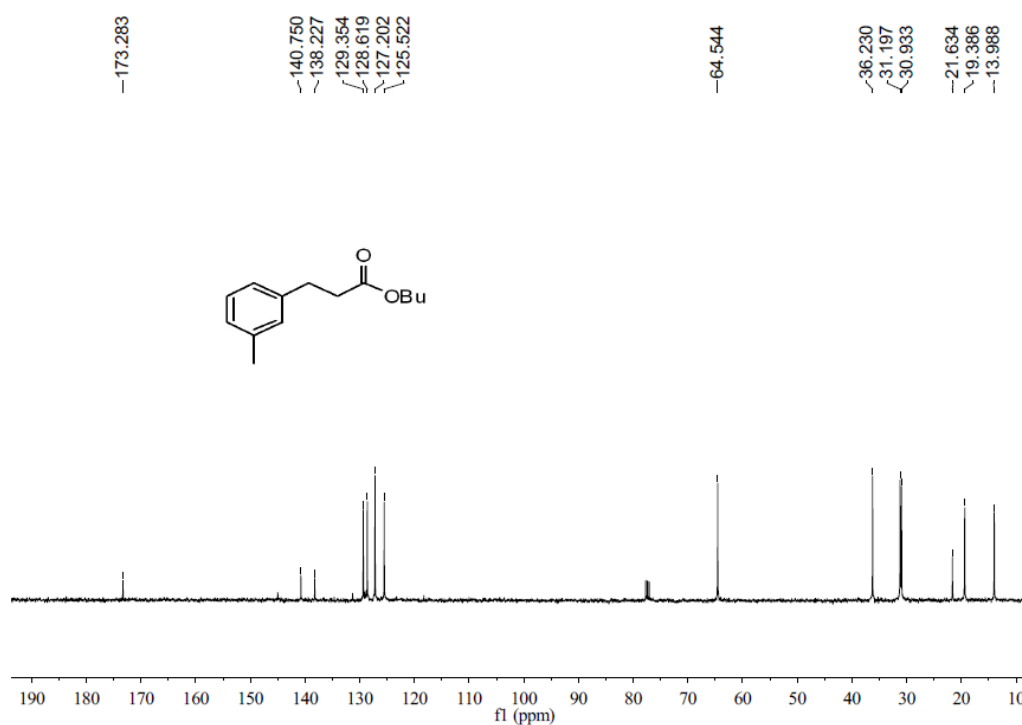
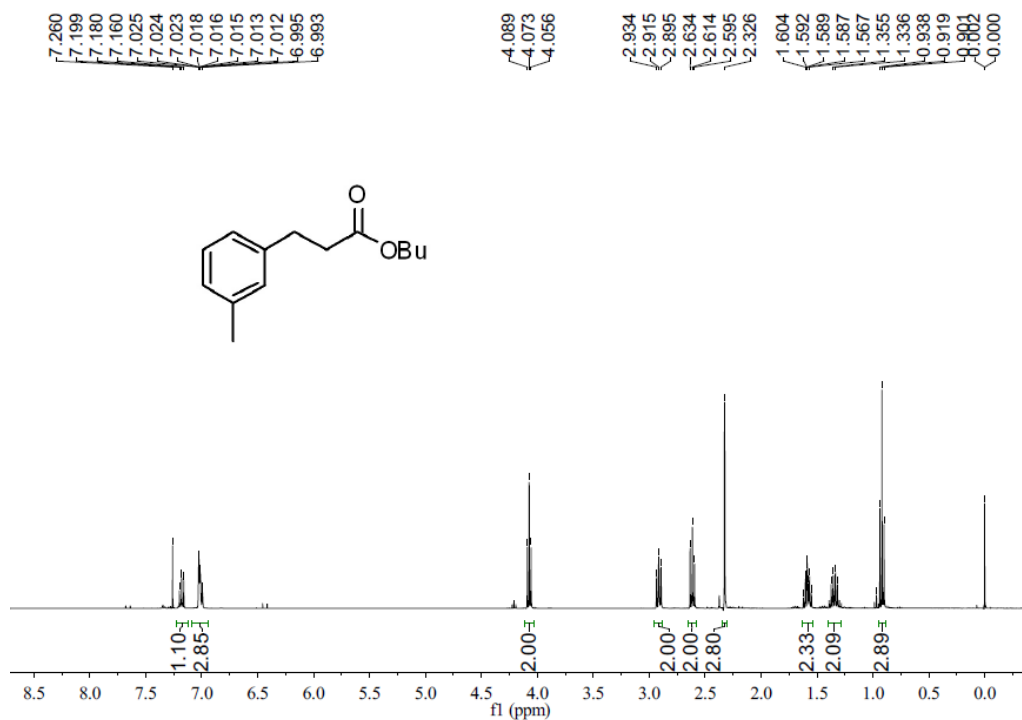




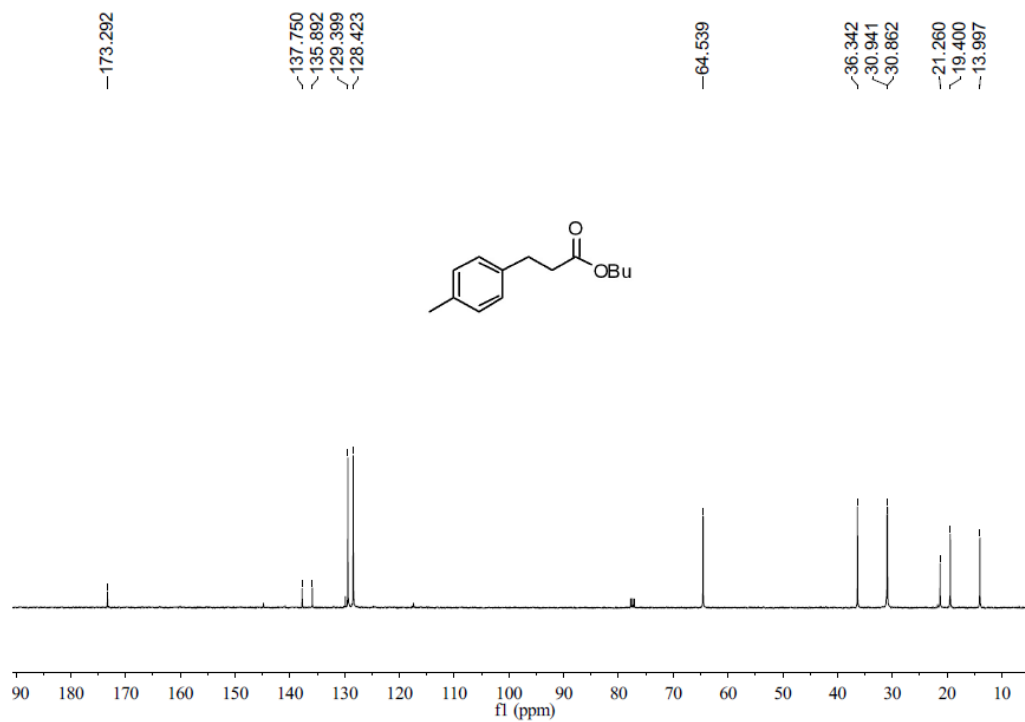
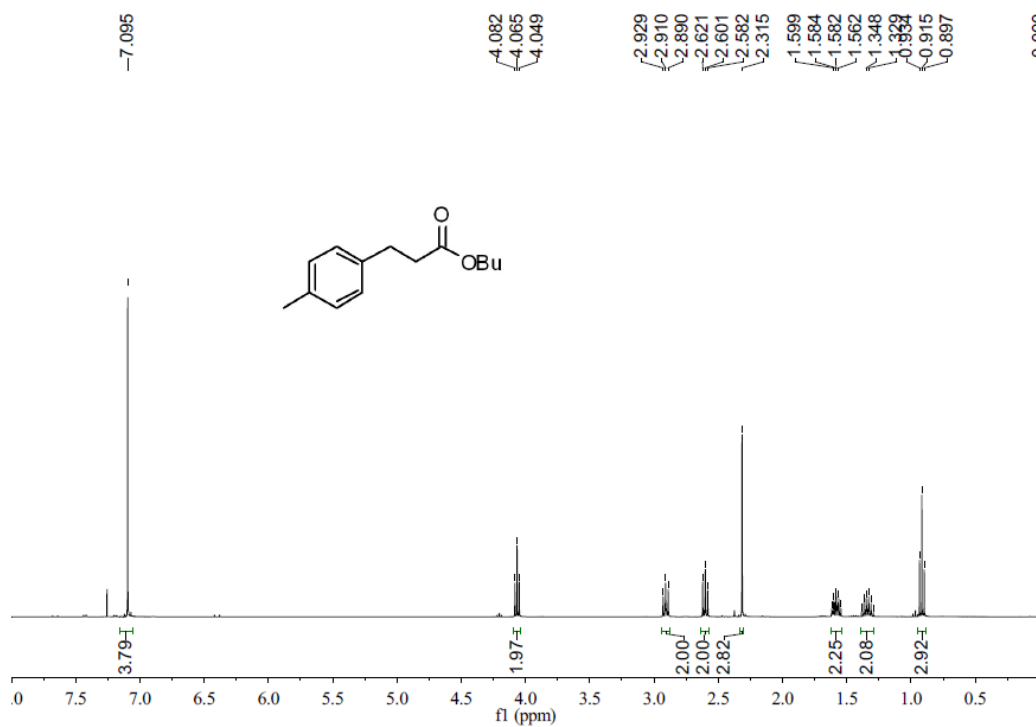
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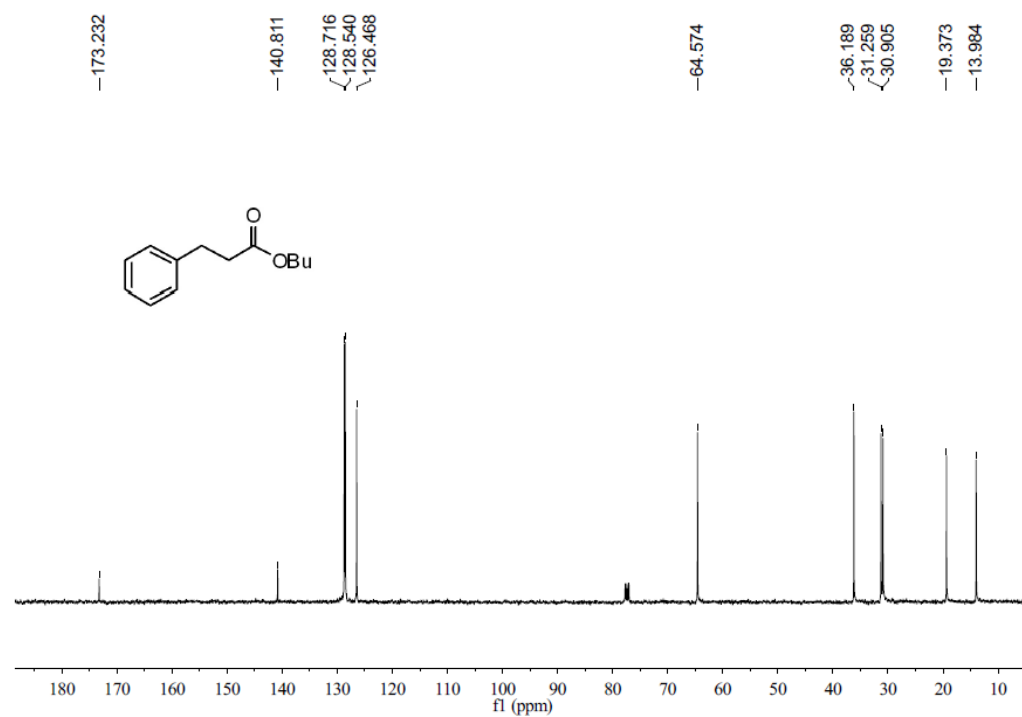
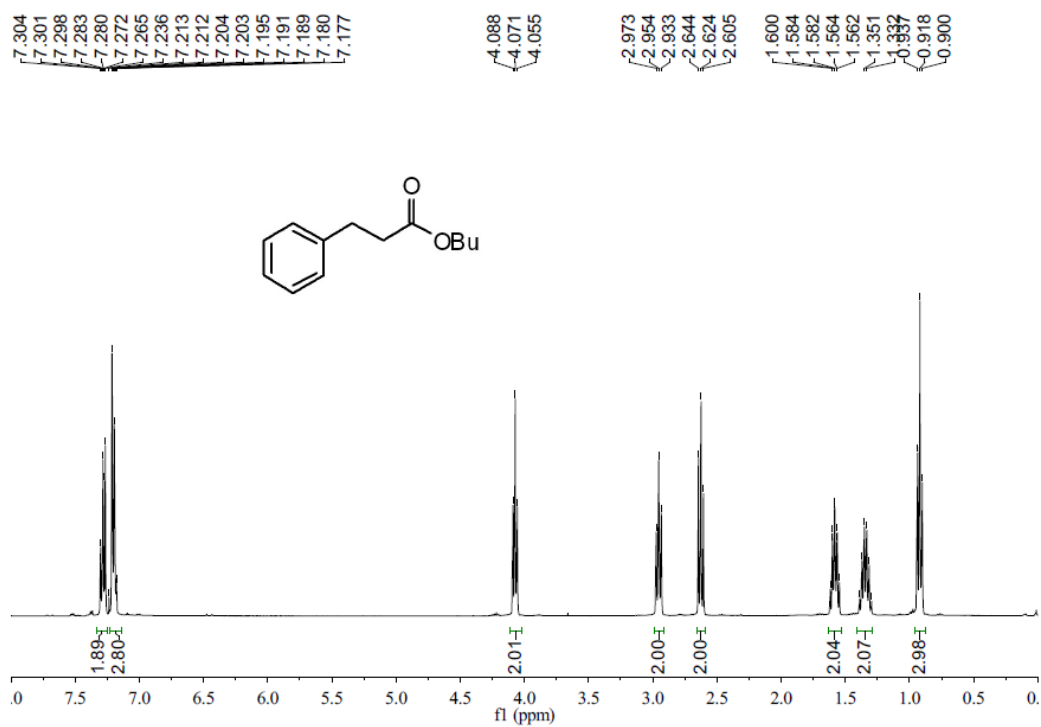
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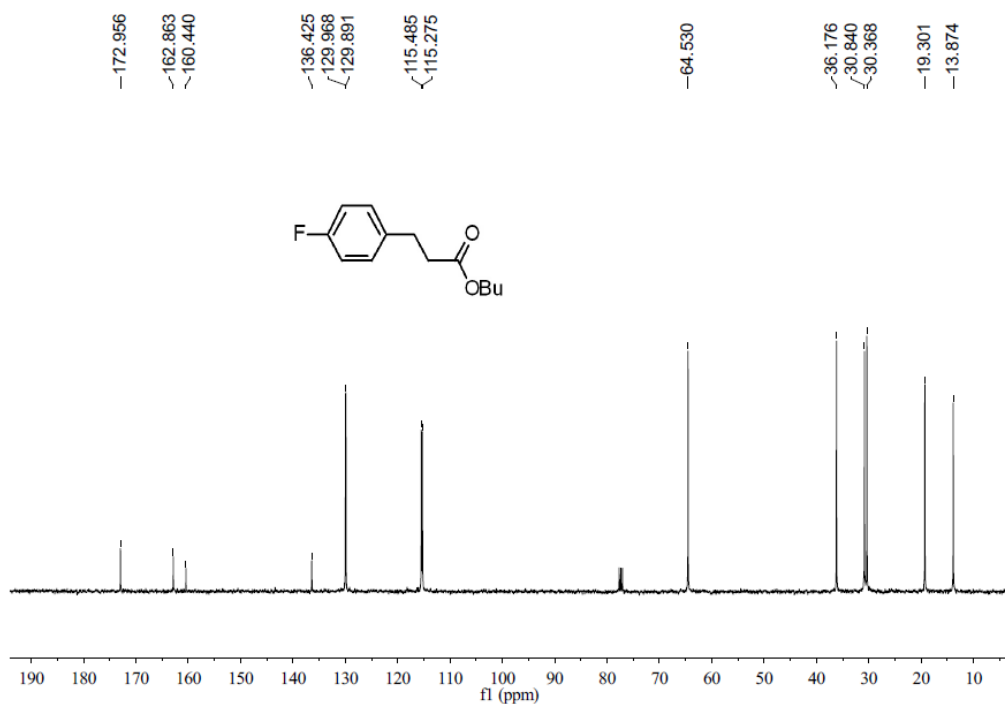
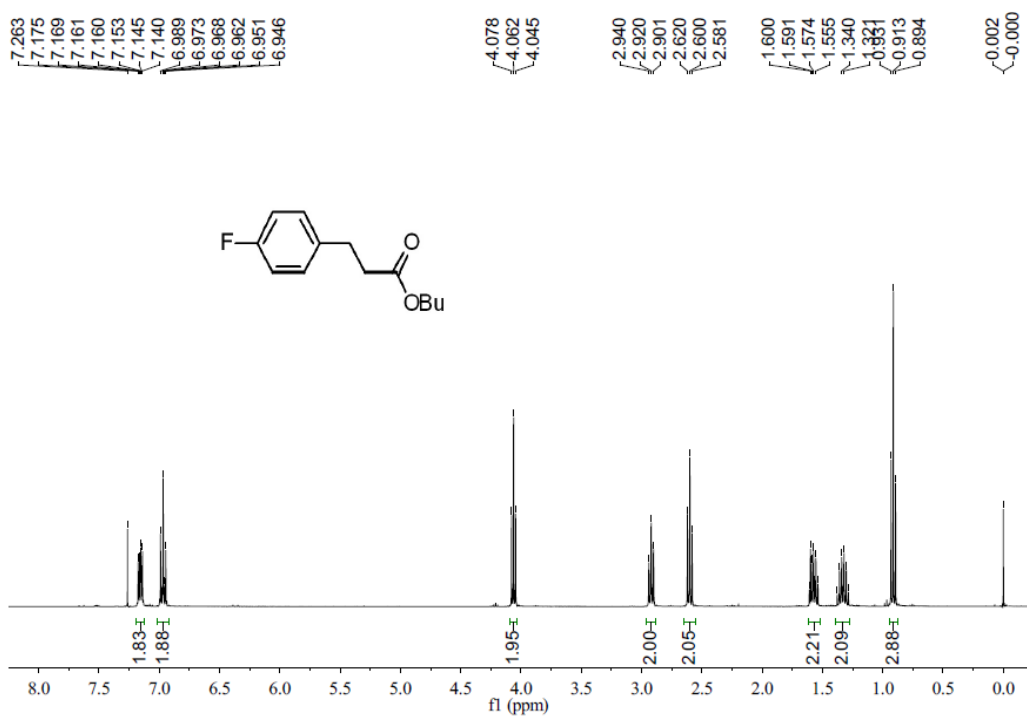
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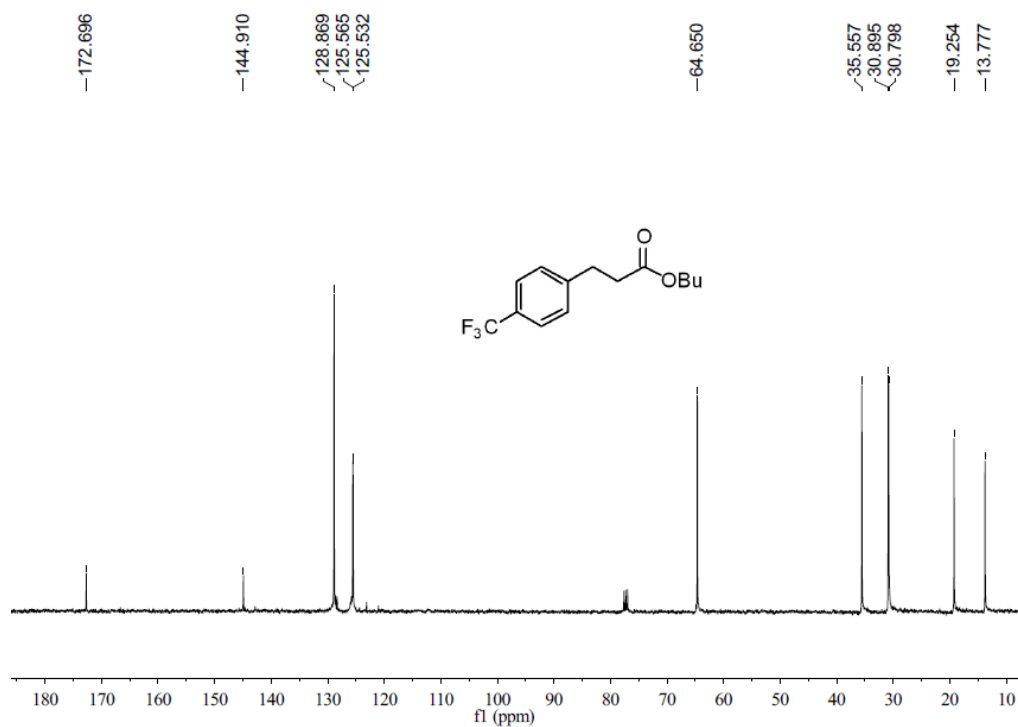
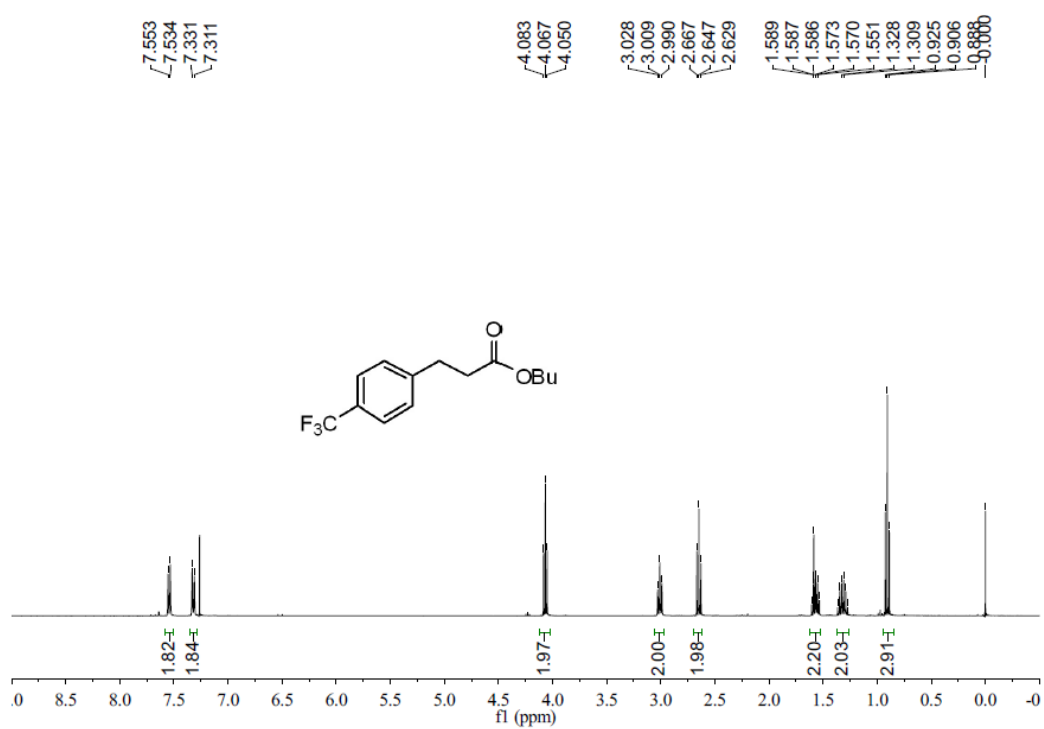
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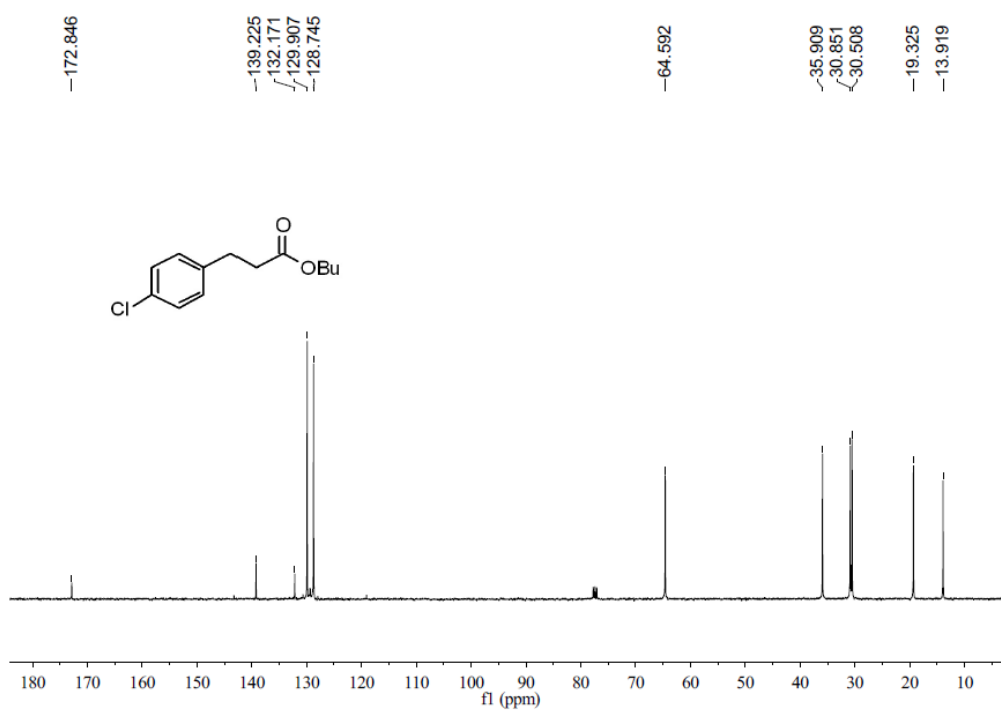
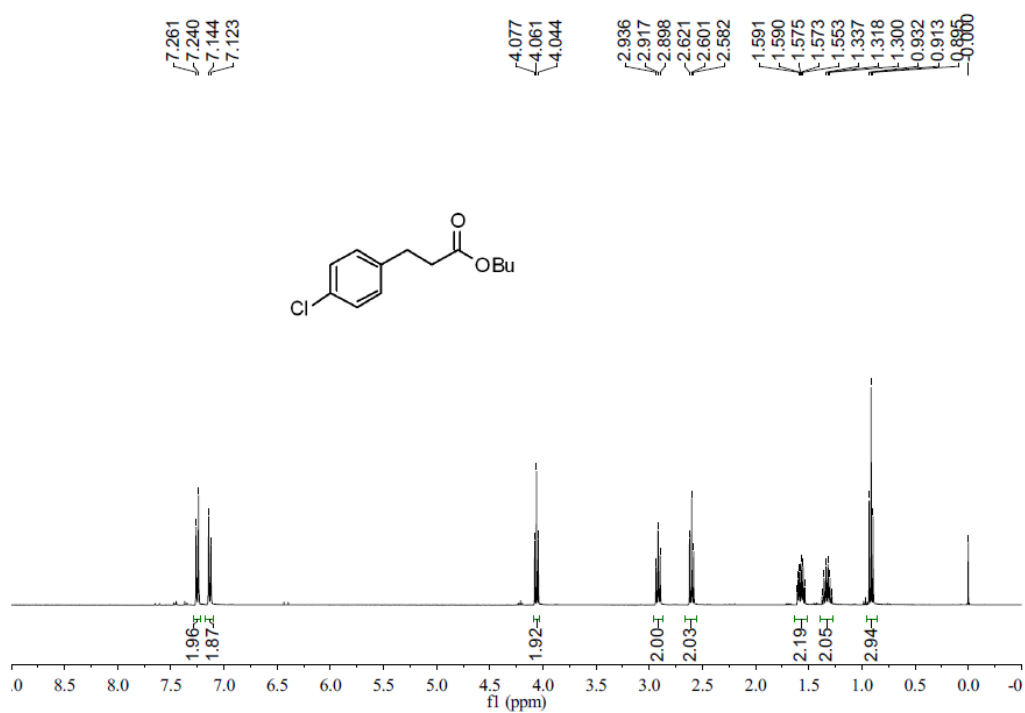
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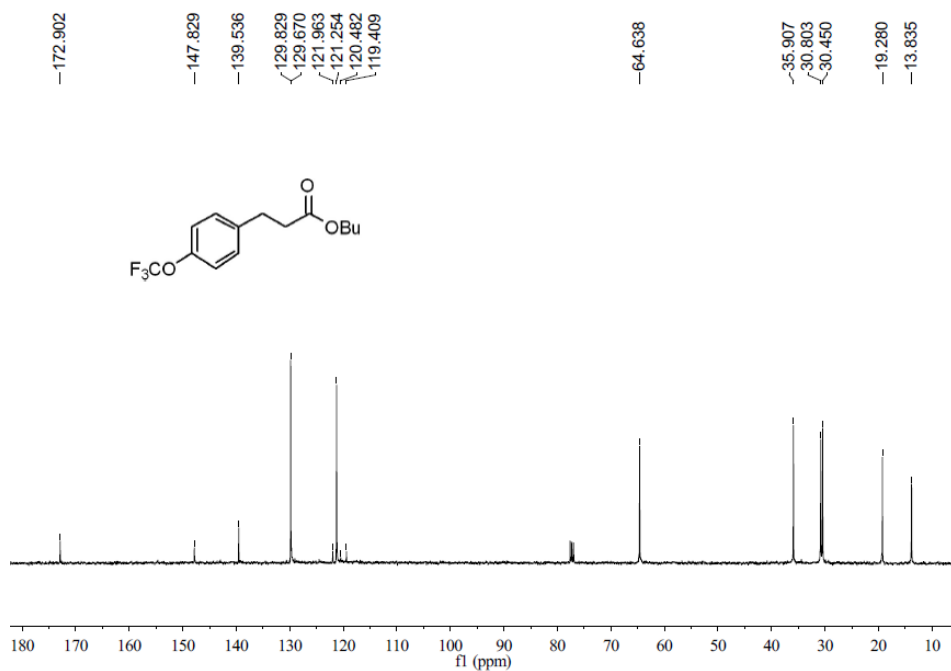
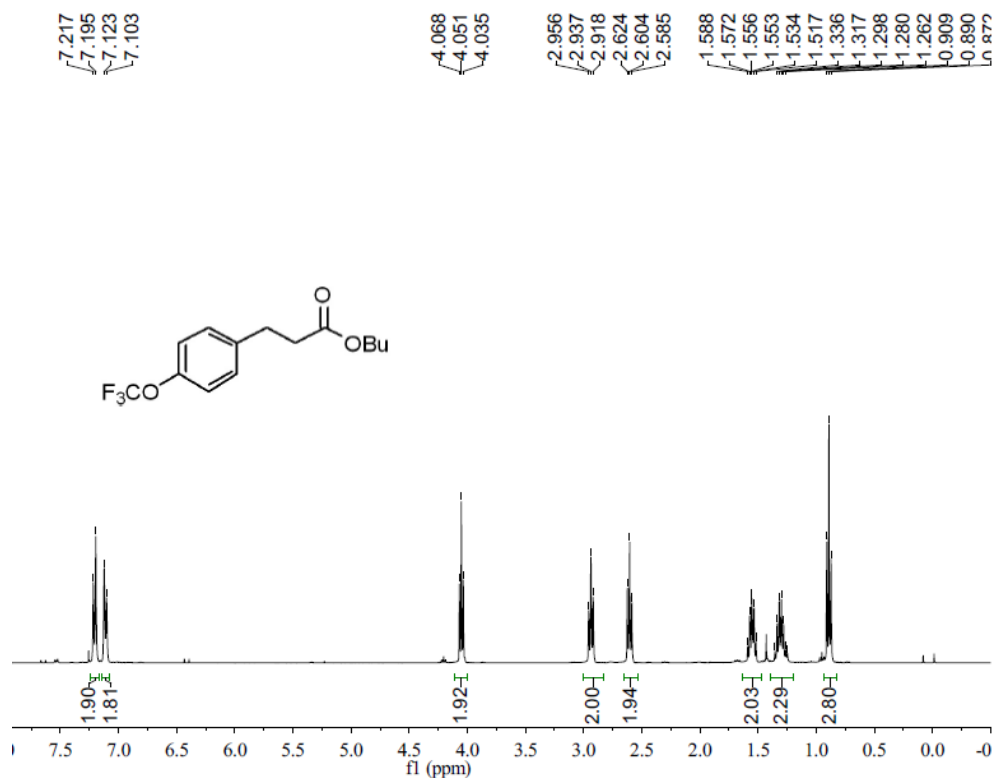


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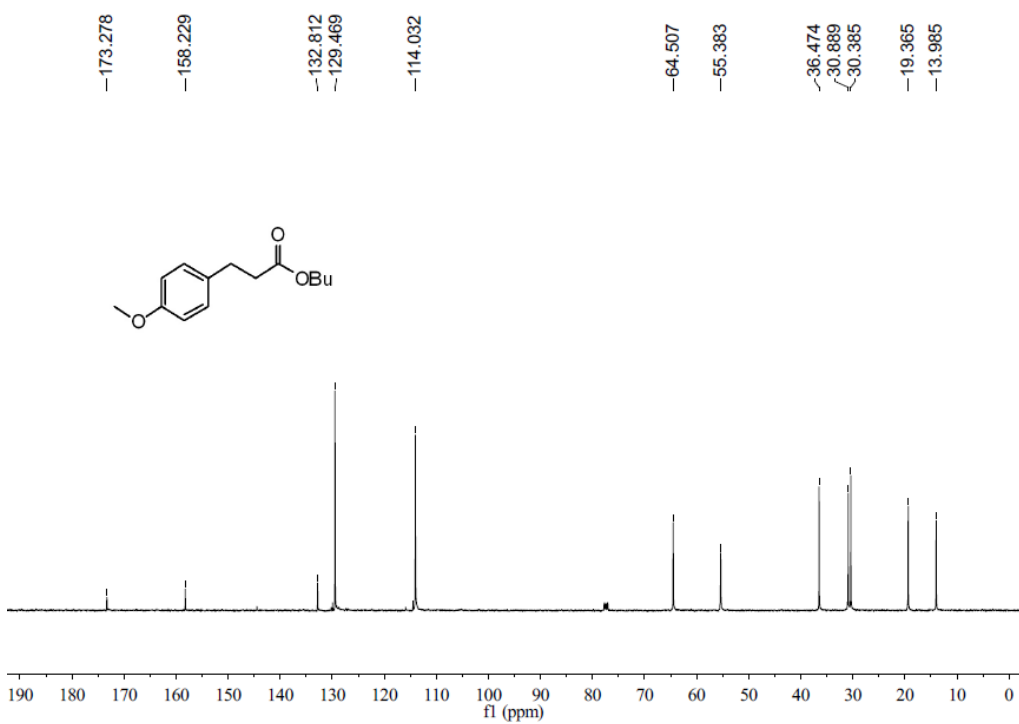
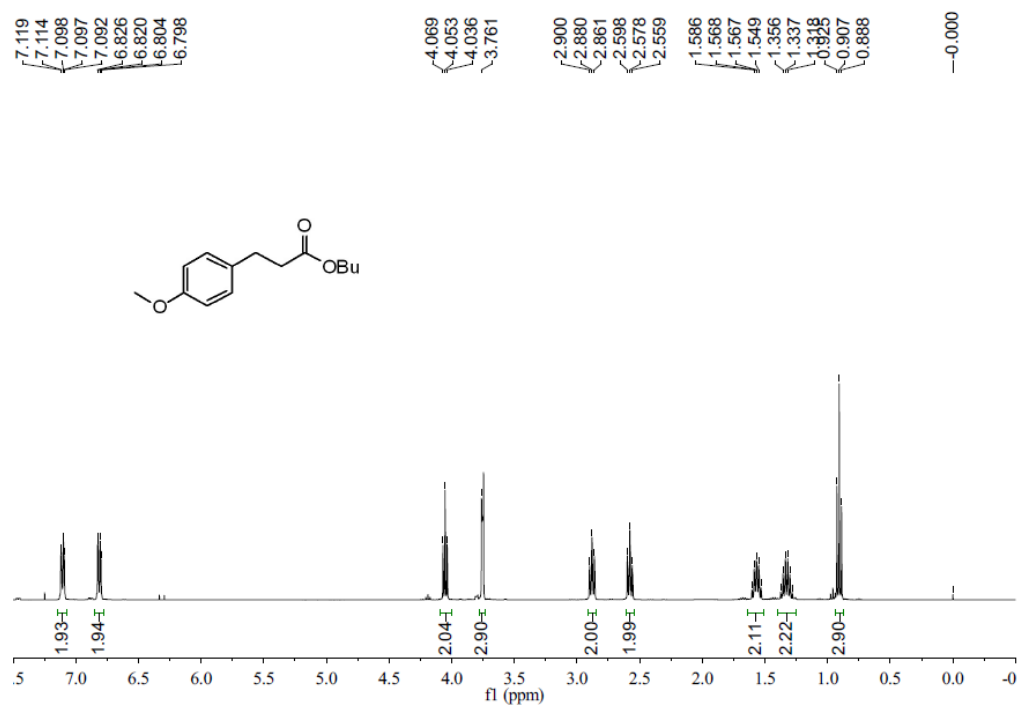




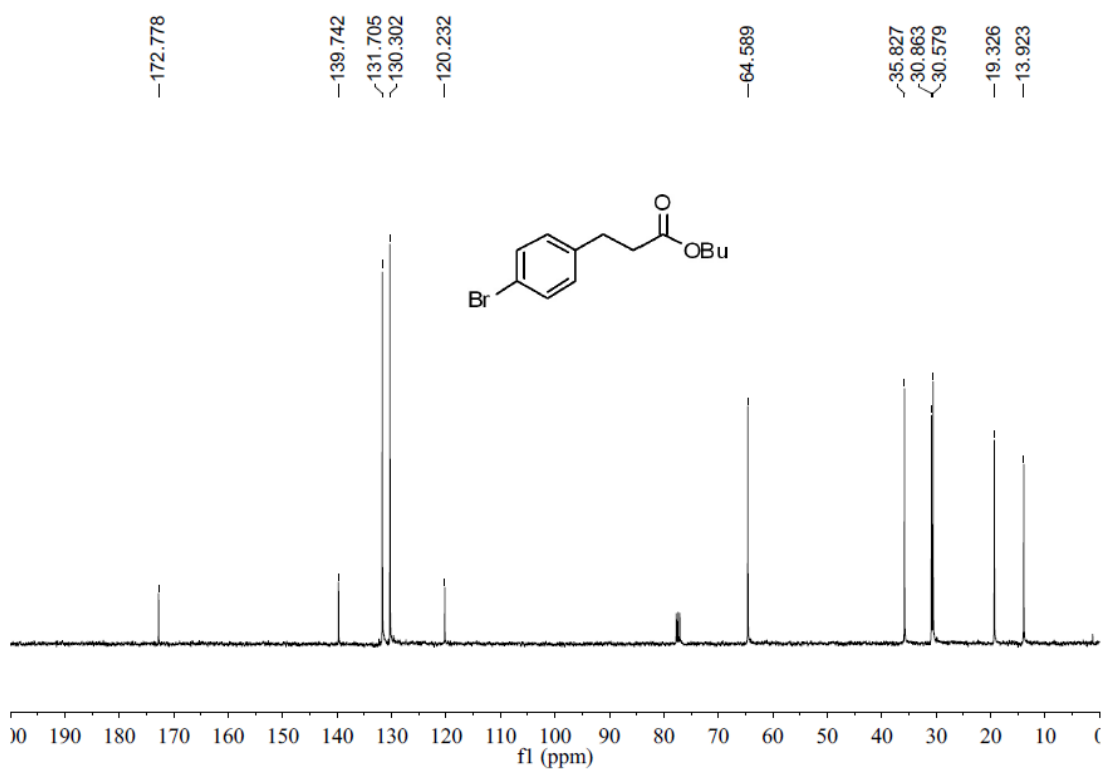
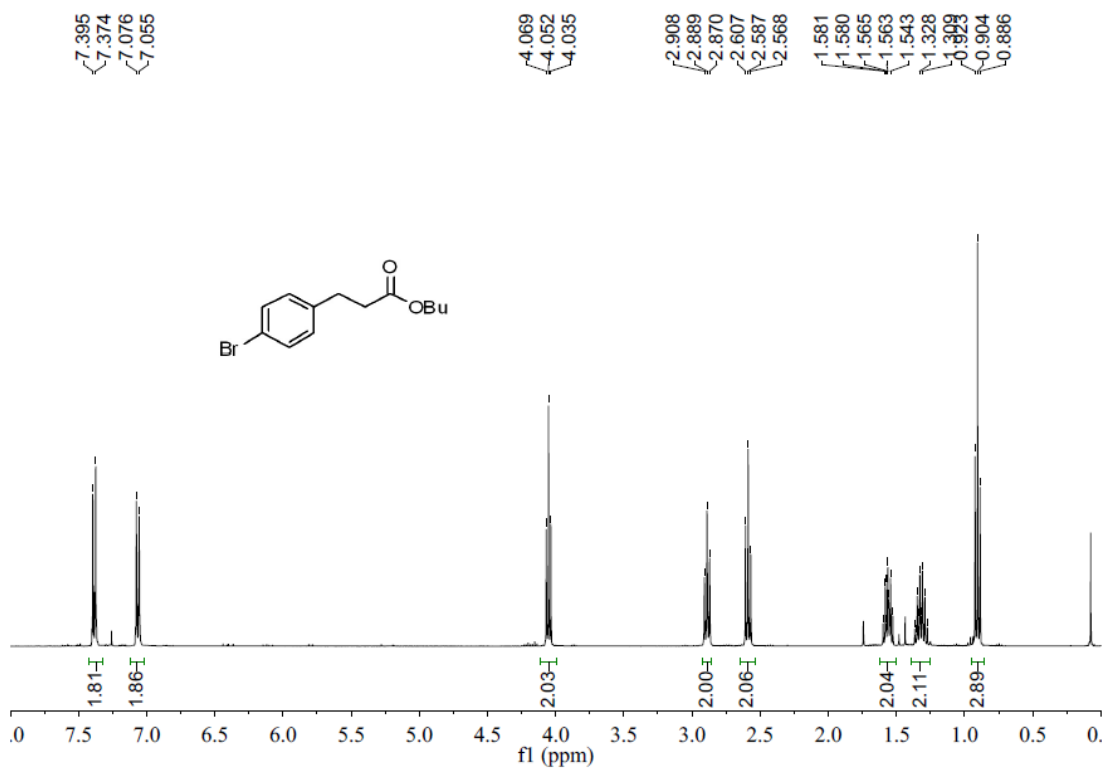
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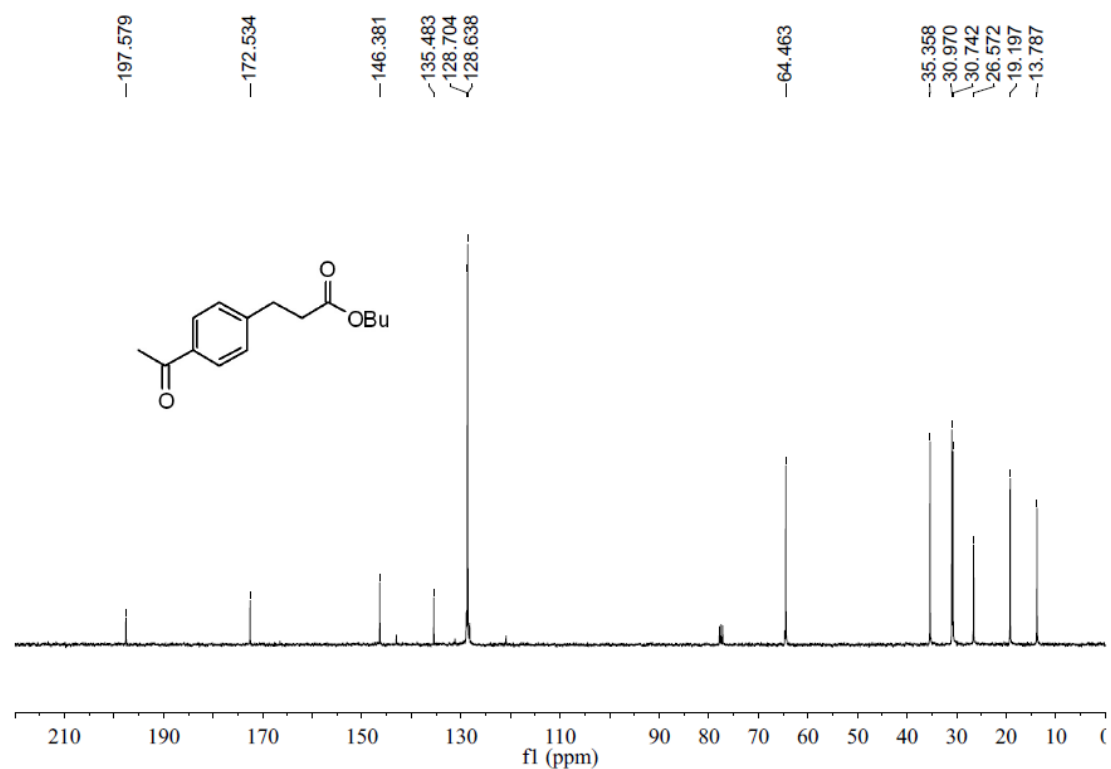
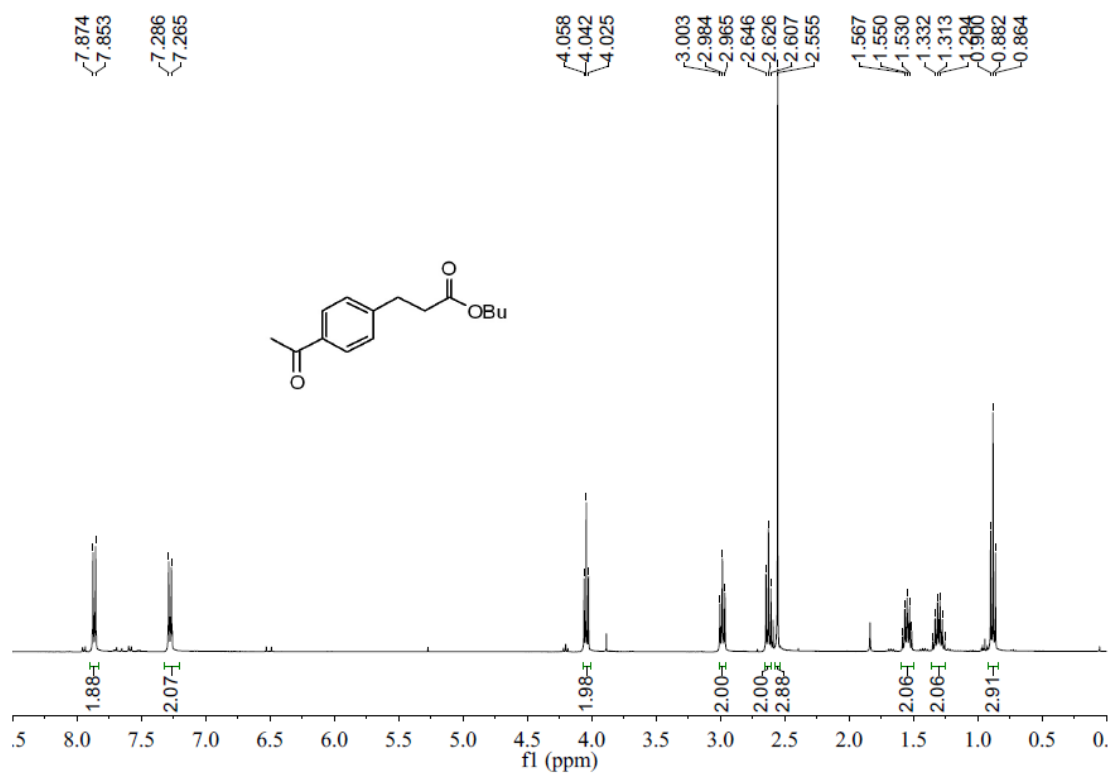
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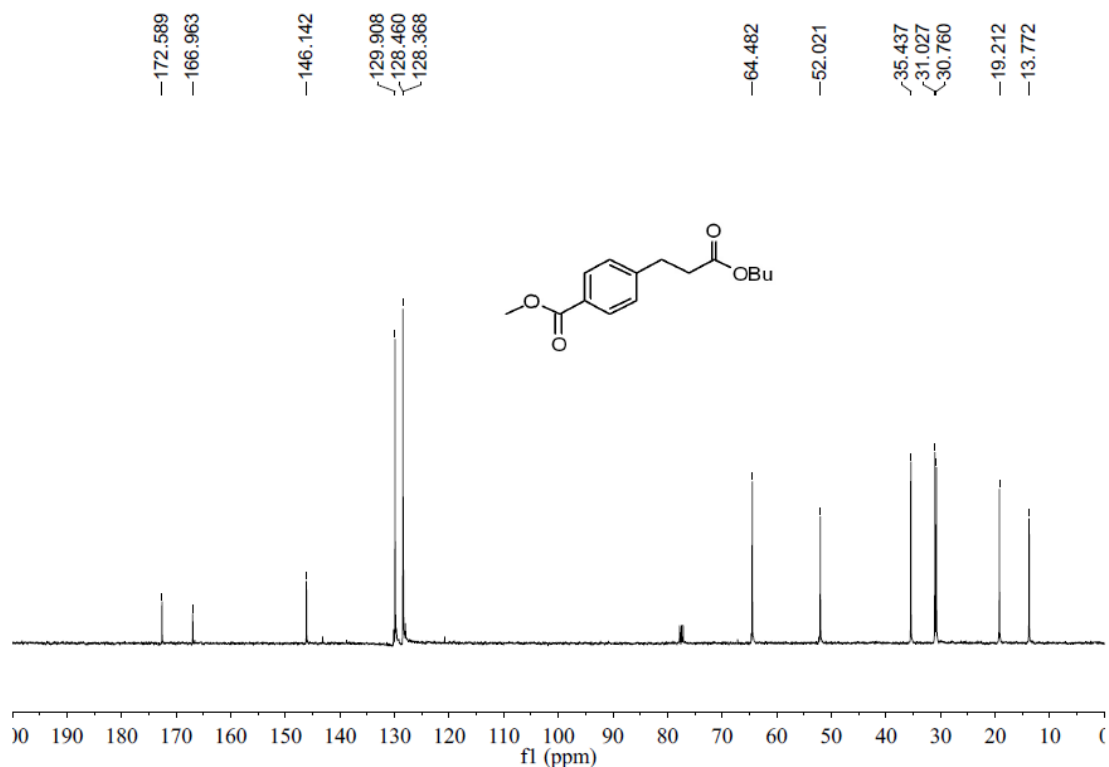
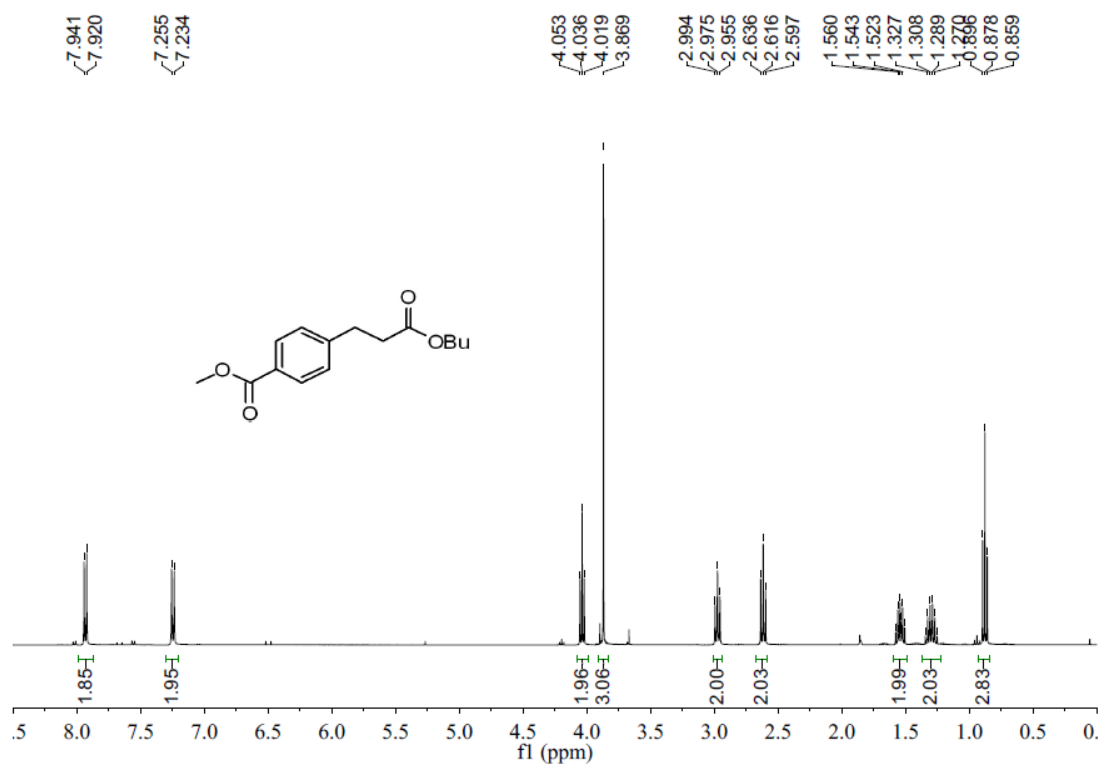
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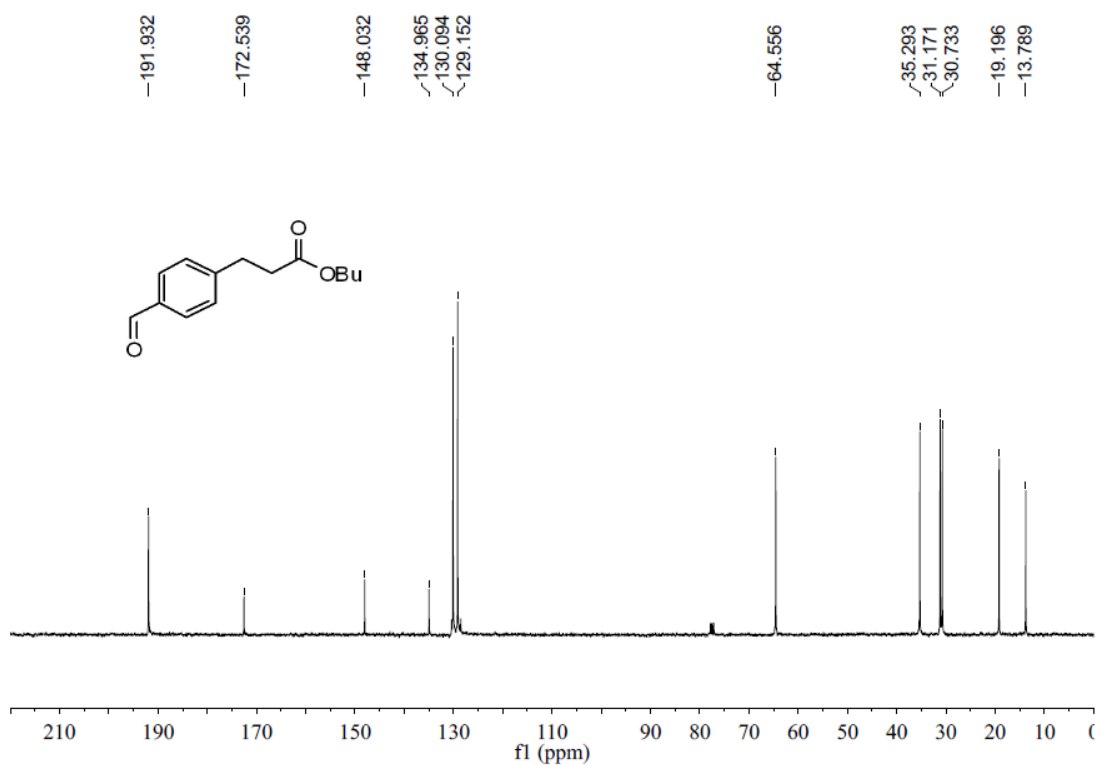
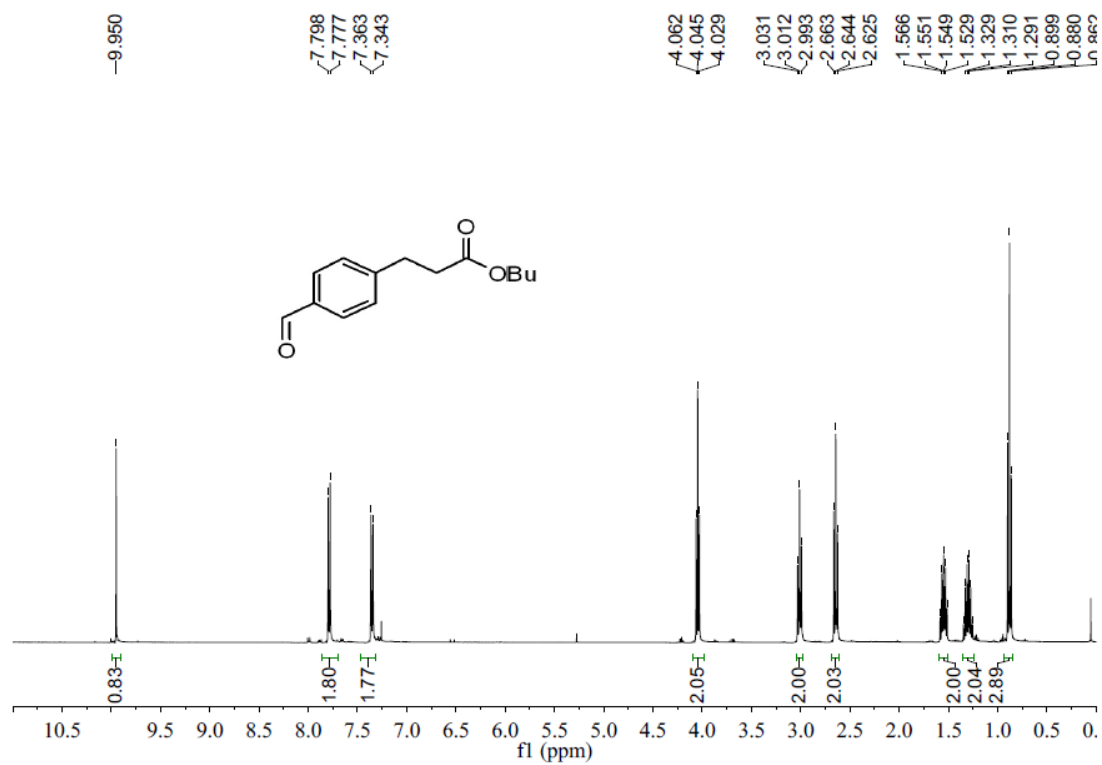
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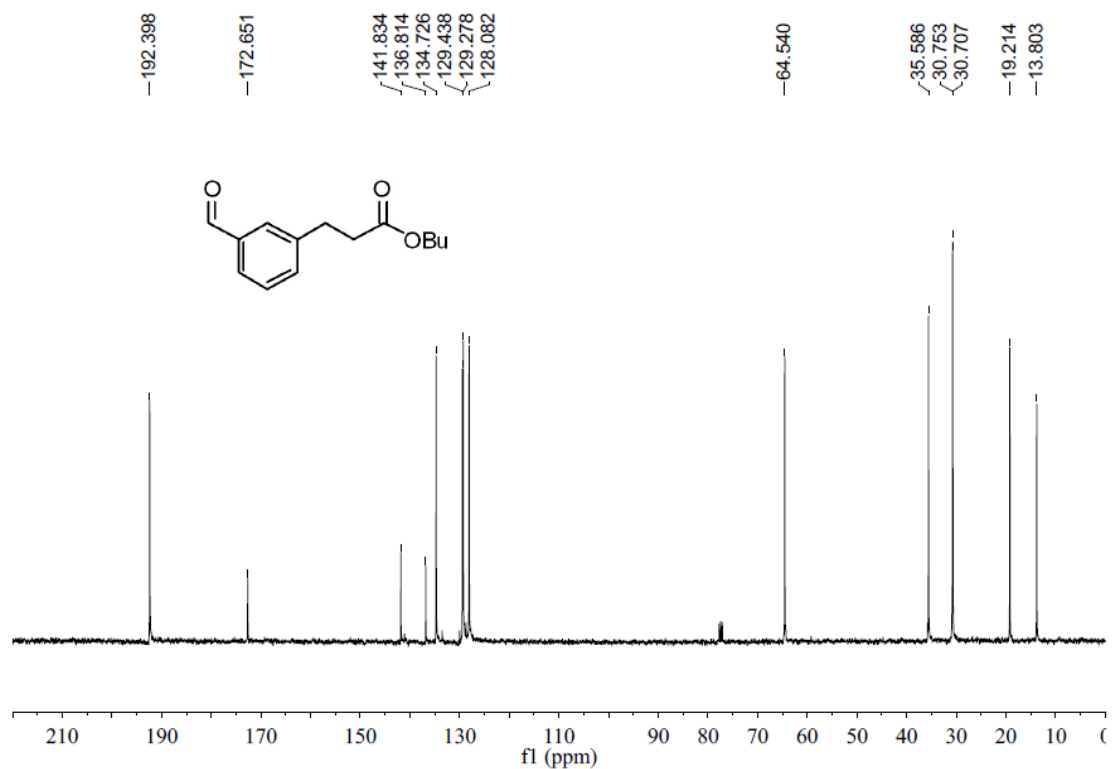
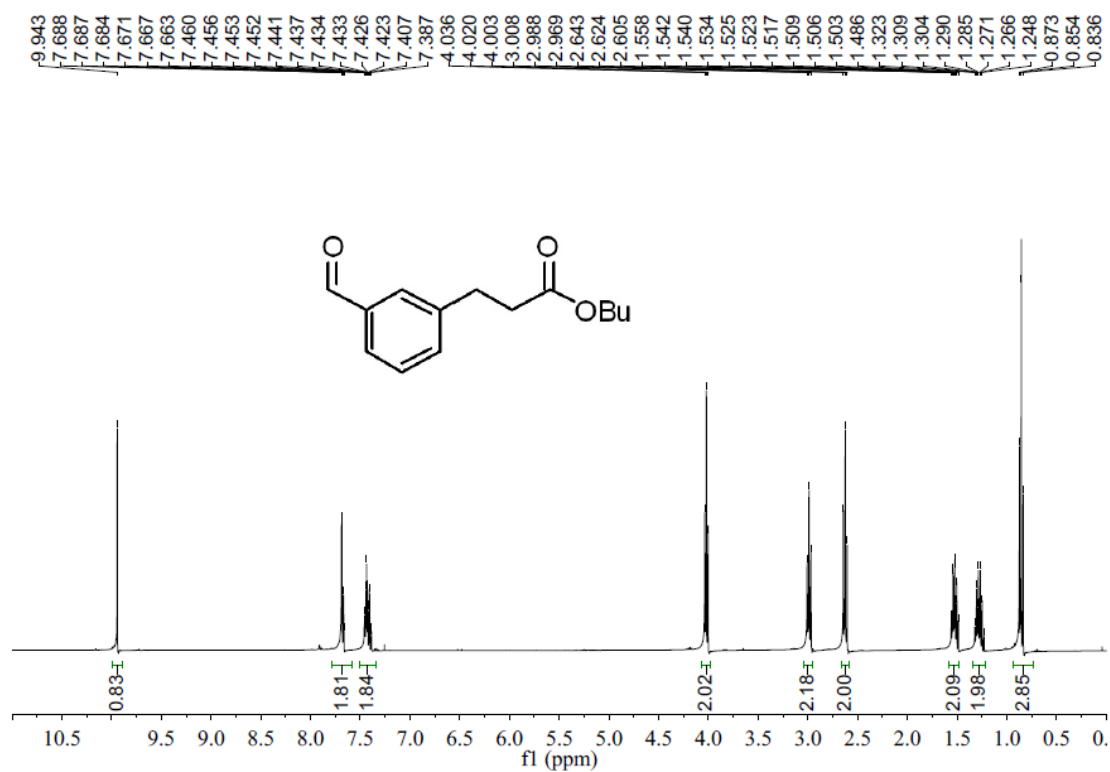
### 3ma



### 3na



### 30a



3eb

