

# Supporting Information

## Palladium- and Nickel-Catalyzed Kumada Cross-Coupling Reaction of *gem*-Difluoroalkenes and Monofluoroalkenes with Grignard Reagents

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<sup>‡</sup> Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

<sup>§</sup> School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

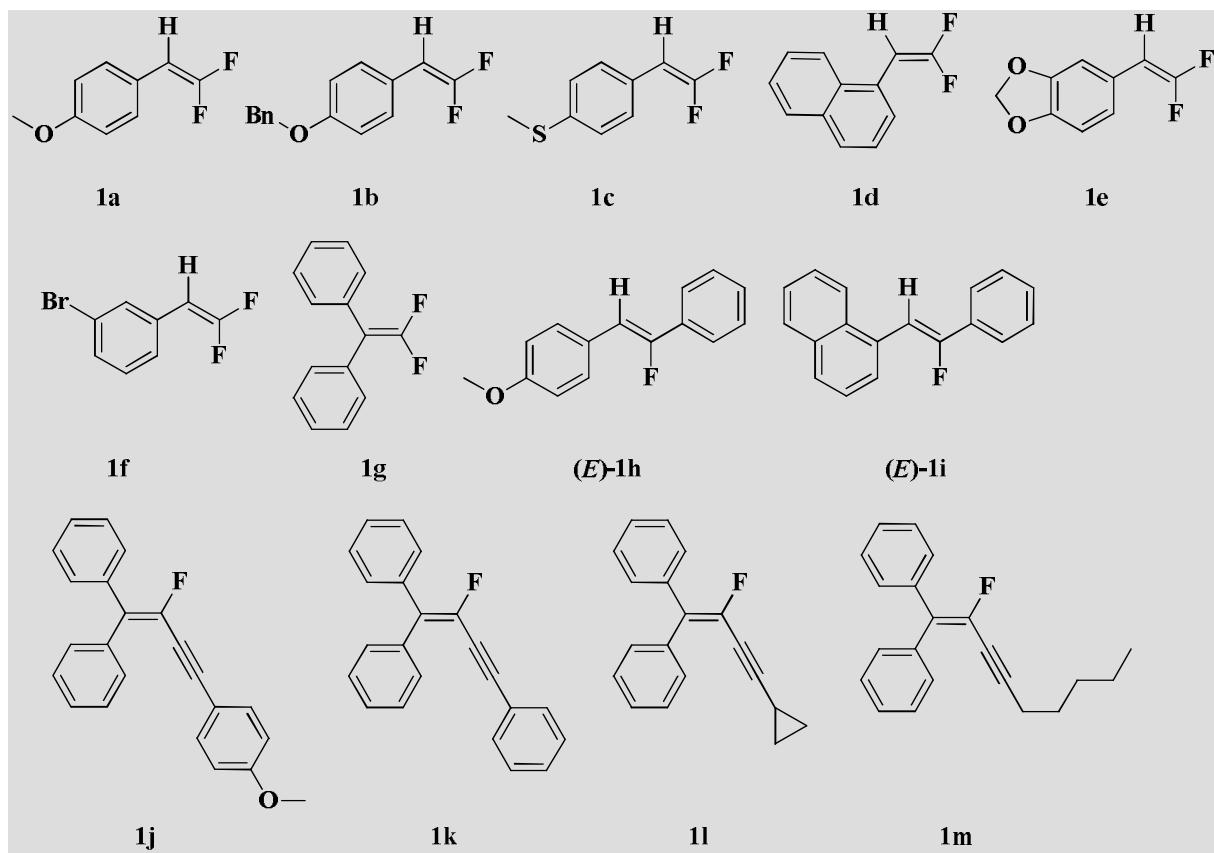
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## Table of Contents

1. Substrates and Grignard Reagents:	2
2. <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR spectra and HRMS (EI) spectra of compounds <b>3</b>	3

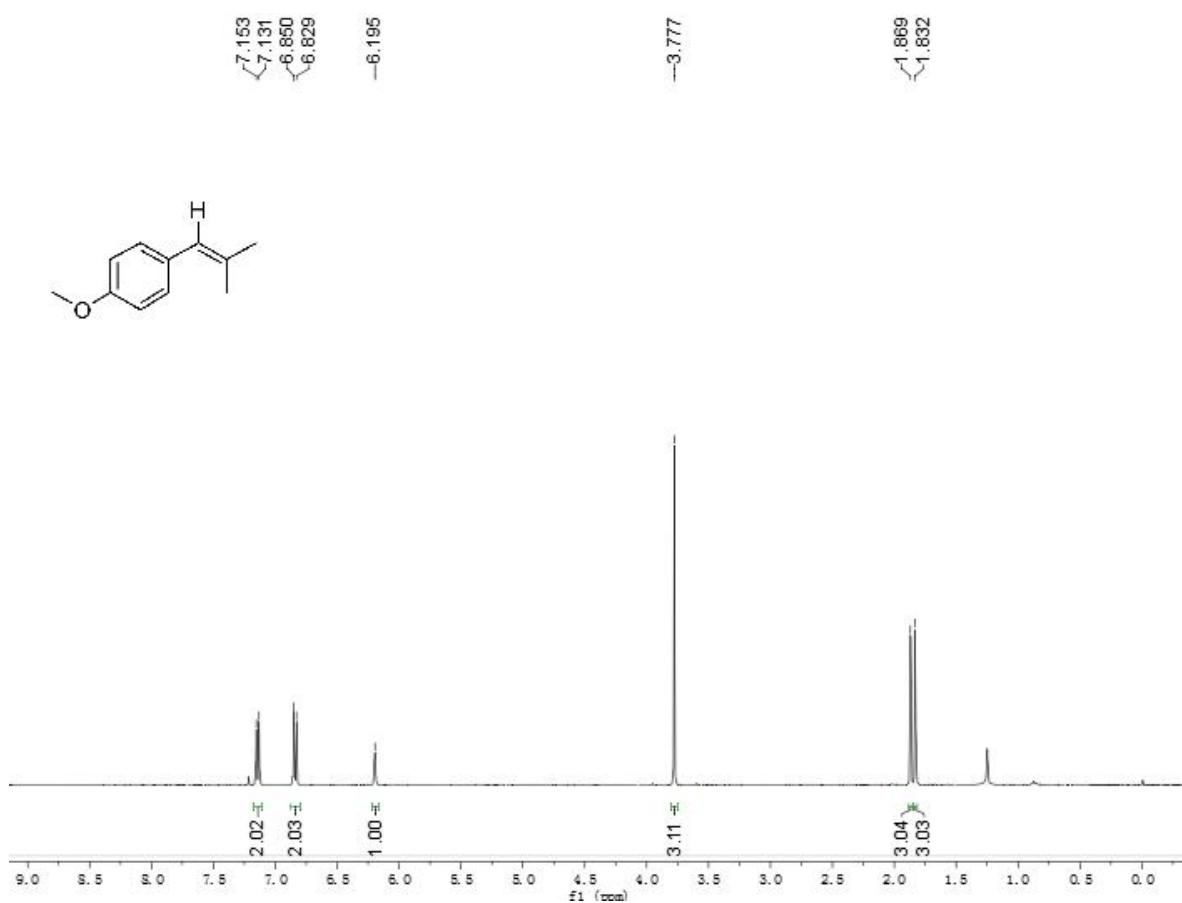
## Substrates and Grignard Reagents:



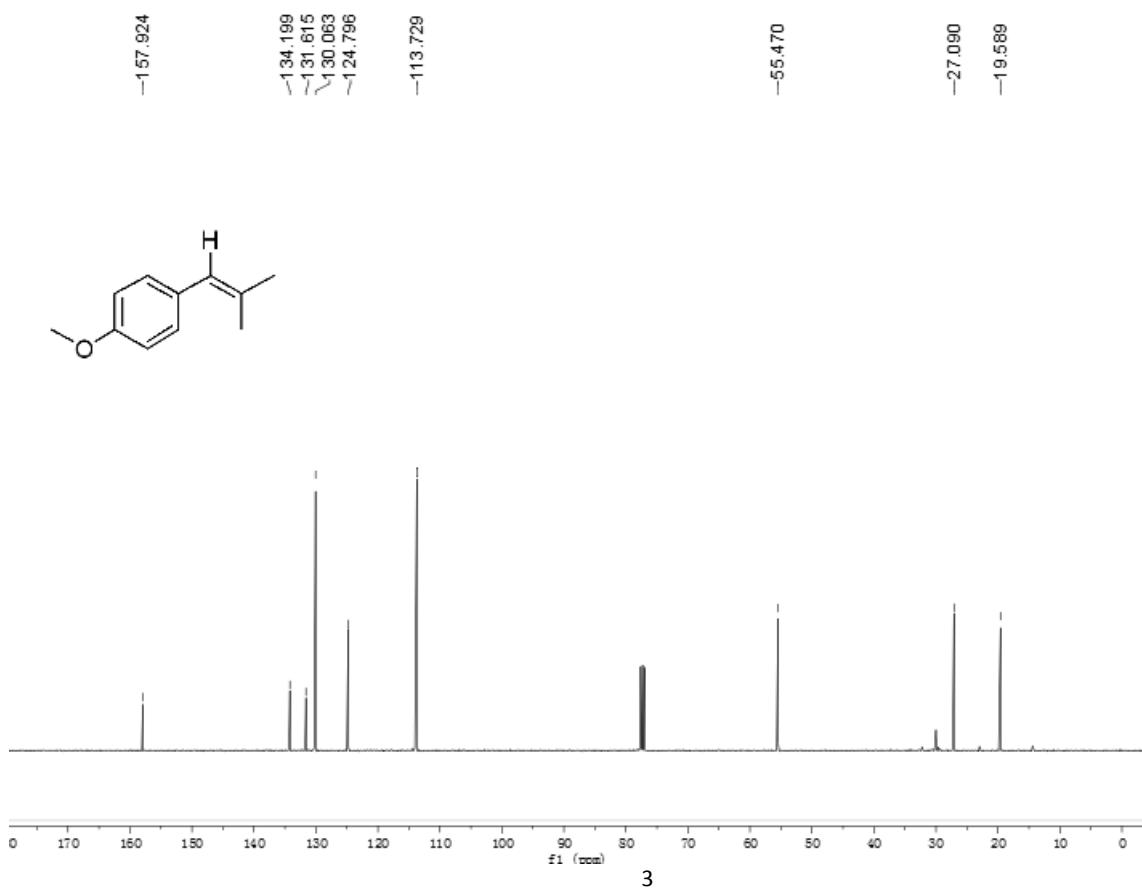
$\text{CH}_3\text{MgCl}$  (2a);  $\text{PhMgBr}$  (2b);  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  (2c);  $p$ -tolylMgBr (2d); 4-FC<sub>6</sub>H<sub>4</sub>MgBr (2e)

*n*-BuMgCl (2f); EtMgCl (2g); *n*-PrMgBr (2h); *n*-C<sub>5</sub>H<sub>11</sub>MgBr (2i); C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>MgCl (2j)

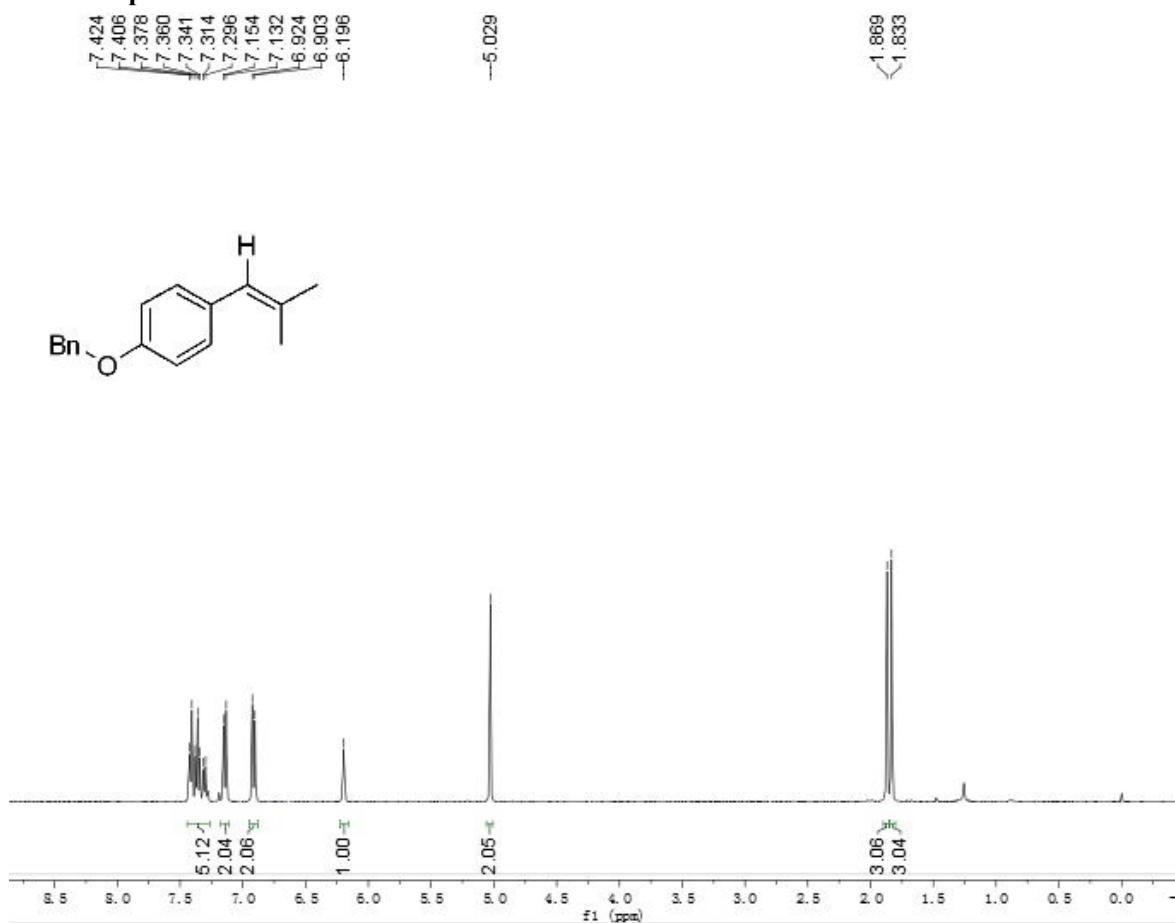
<sup>1</sup>H NMR spectra of 3aa



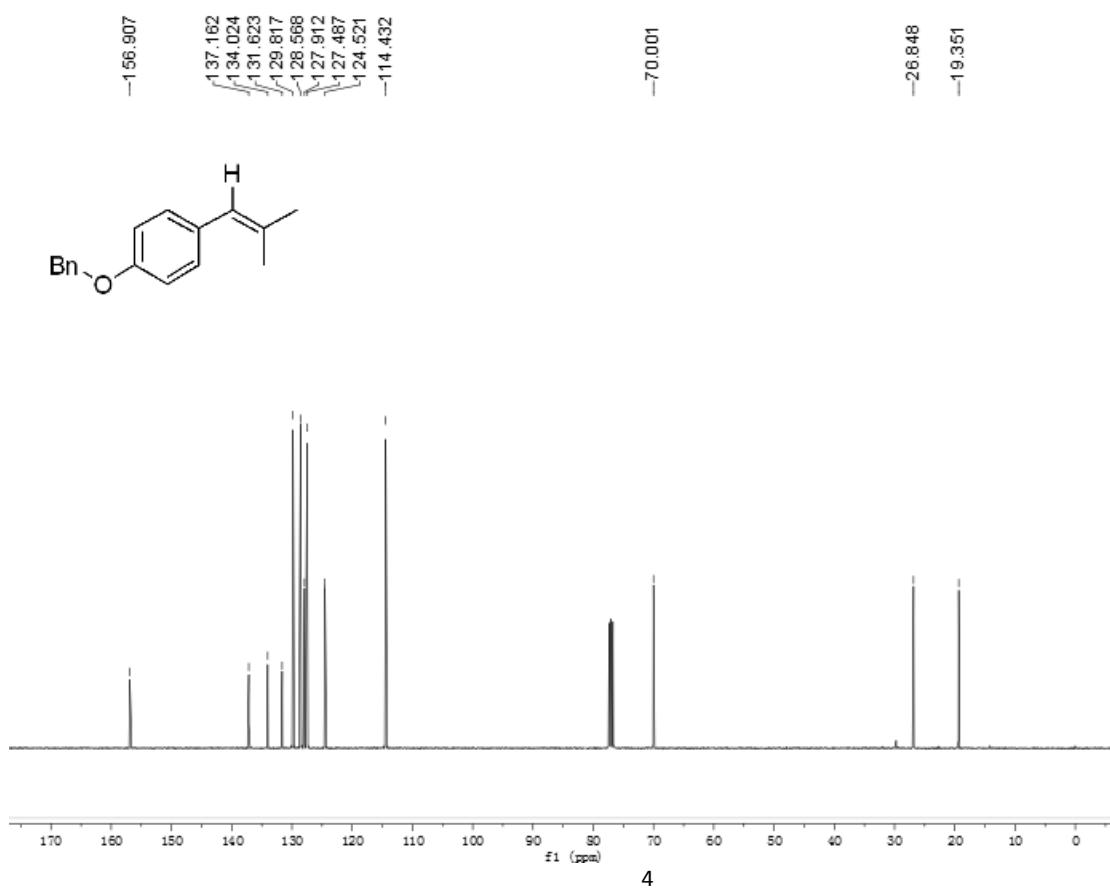
<sup>13</sup>C NMR spectra of 3aa



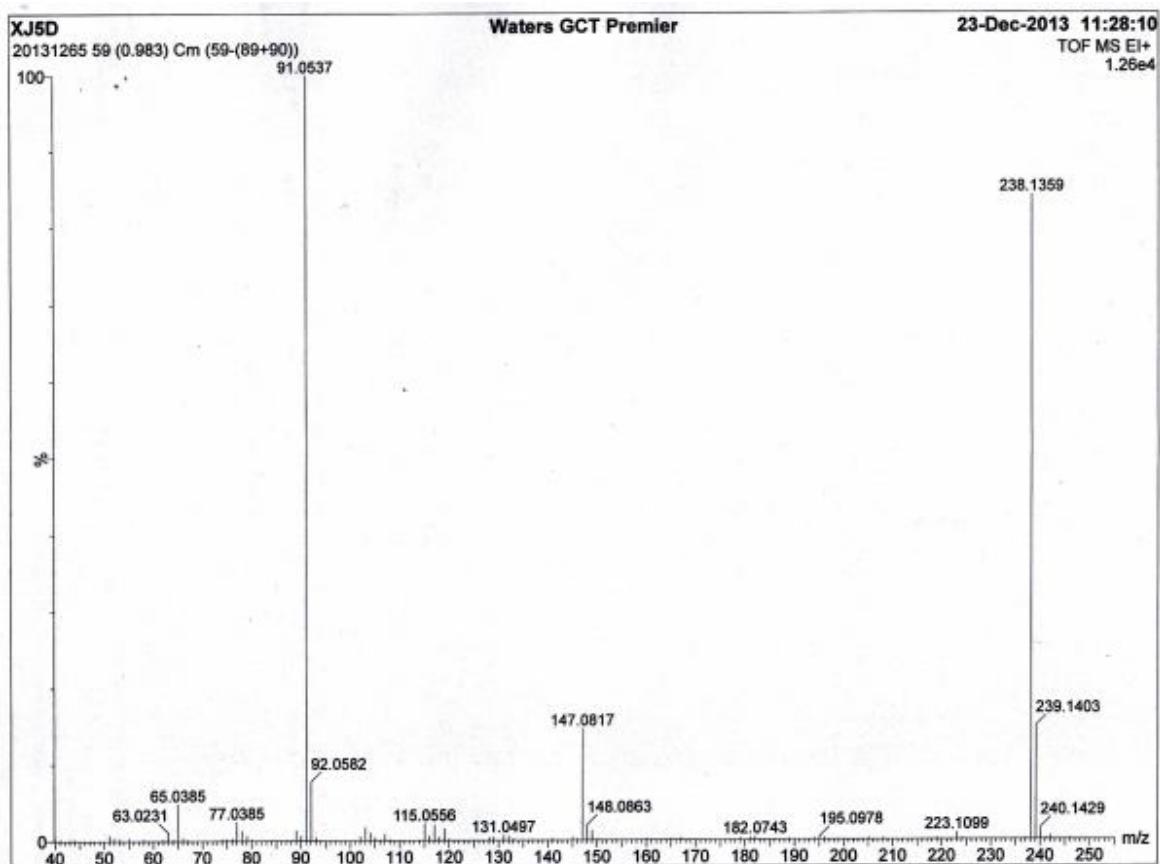
<sup>1</sup>H NMR spectra of 3ba



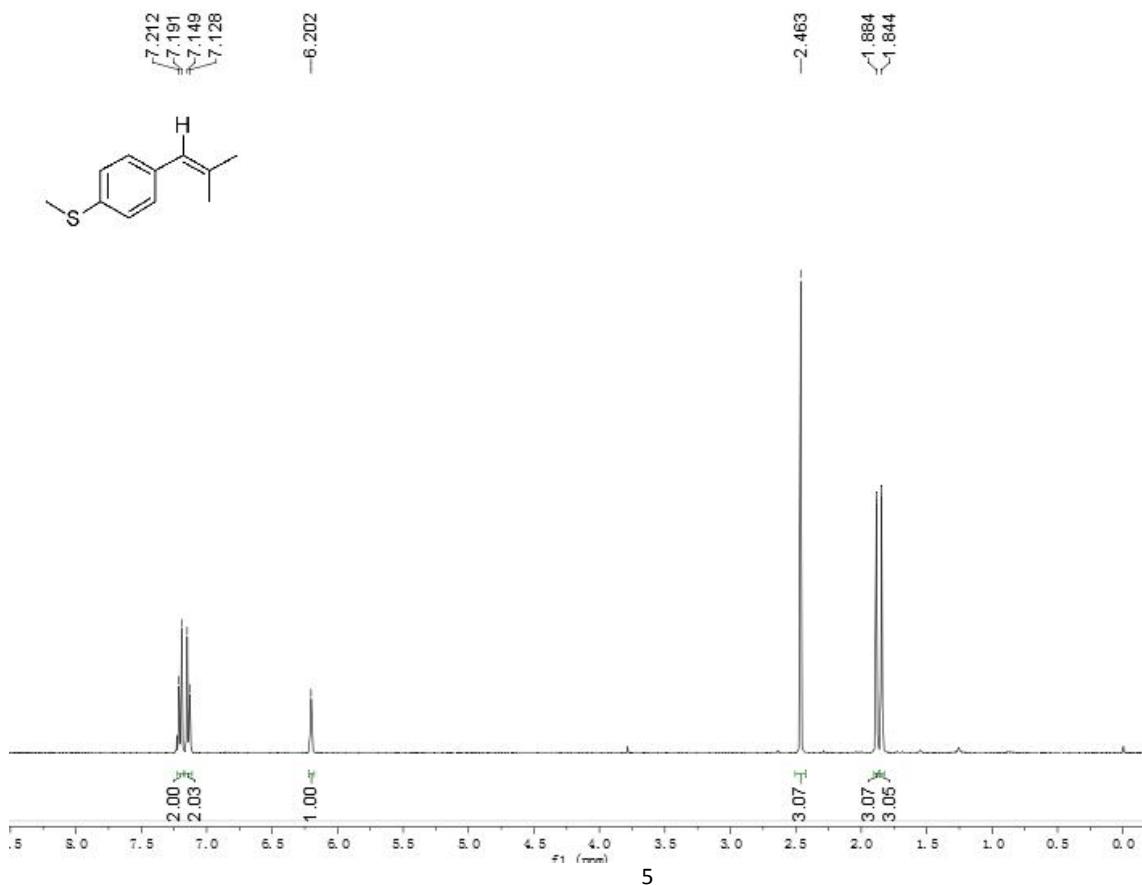
<sup>13</sup>C NMR spectra of 3ba



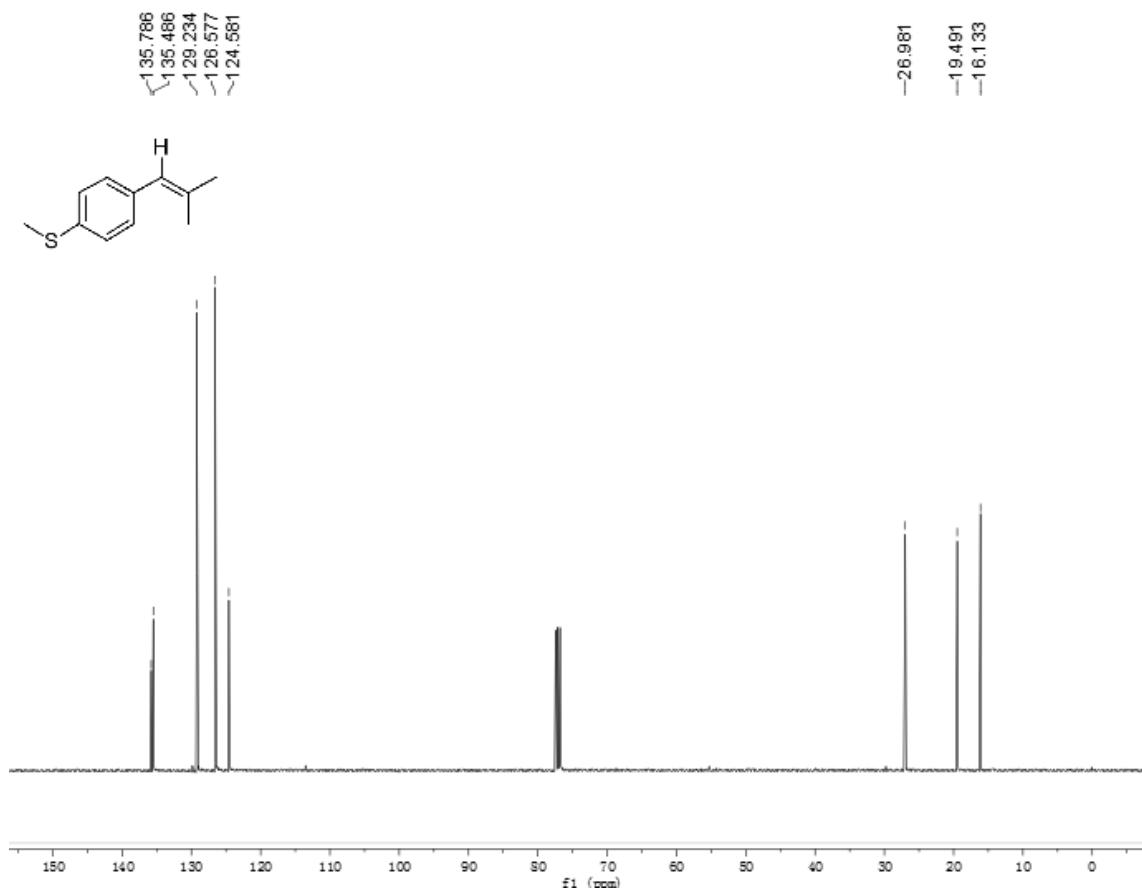
### HRMS (EI) spectra of 3ba



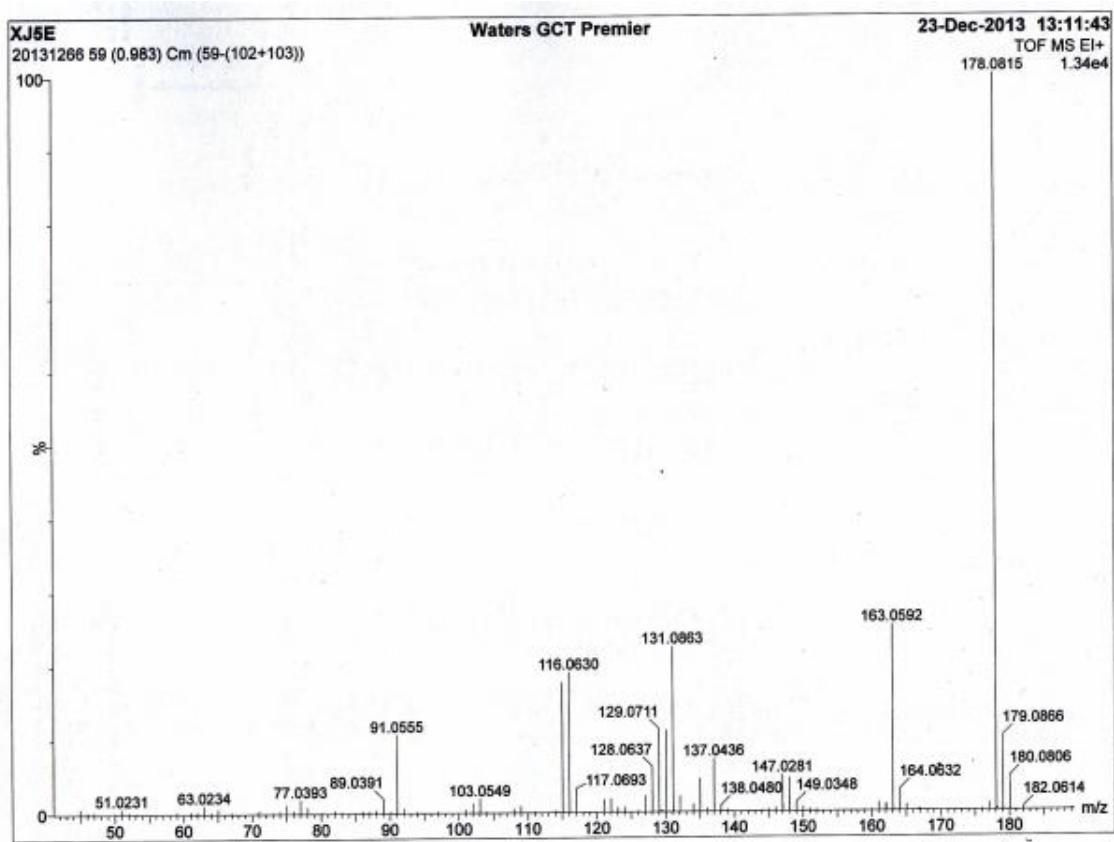
### <sup>1</sup>H NMR spectra of 3ca



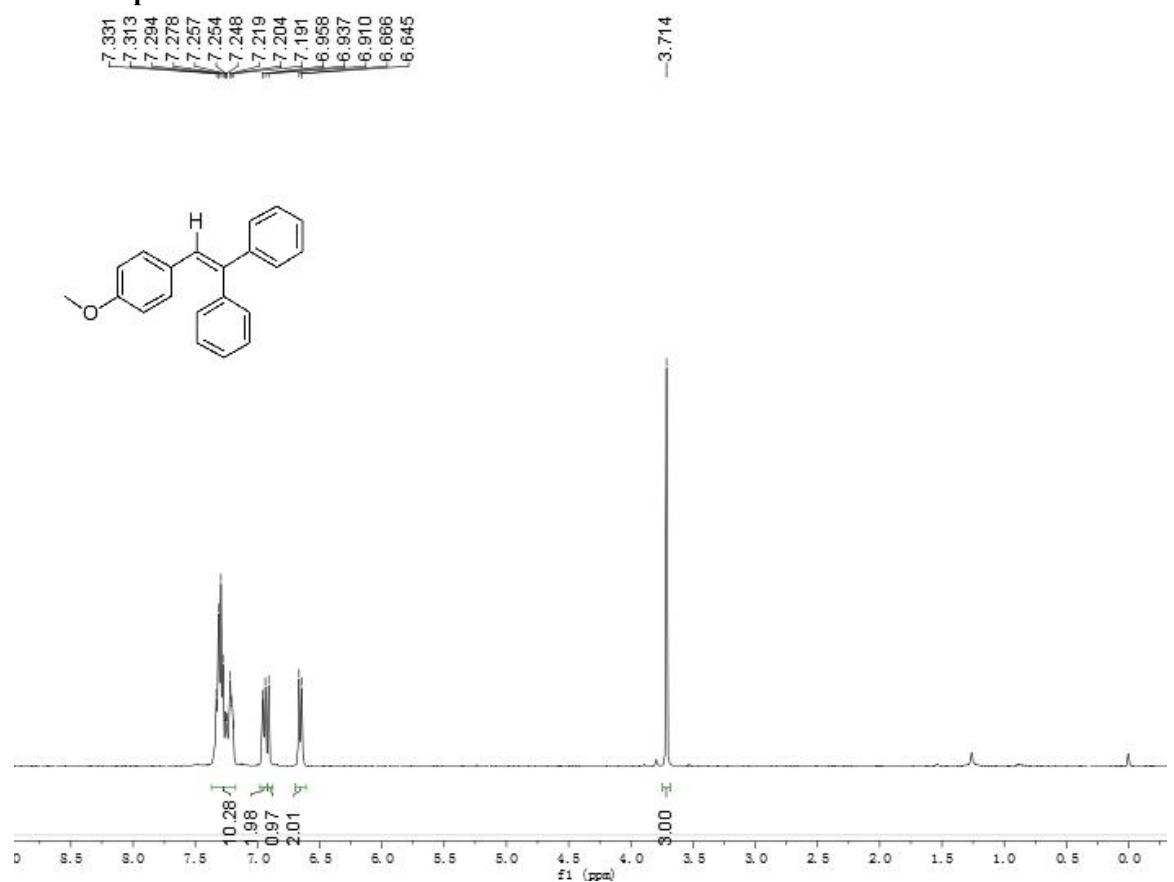
<sup>13</sup>C NMR spectra of 3ca



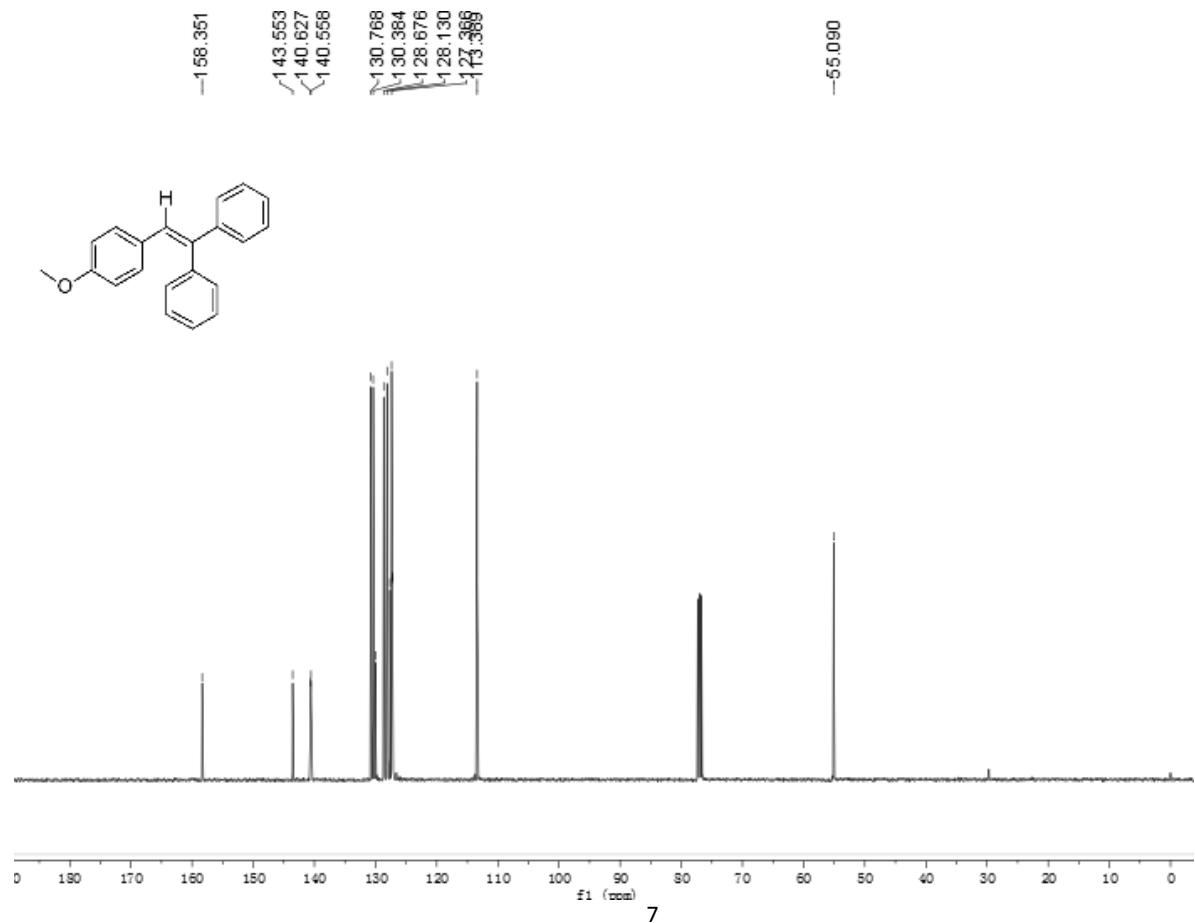
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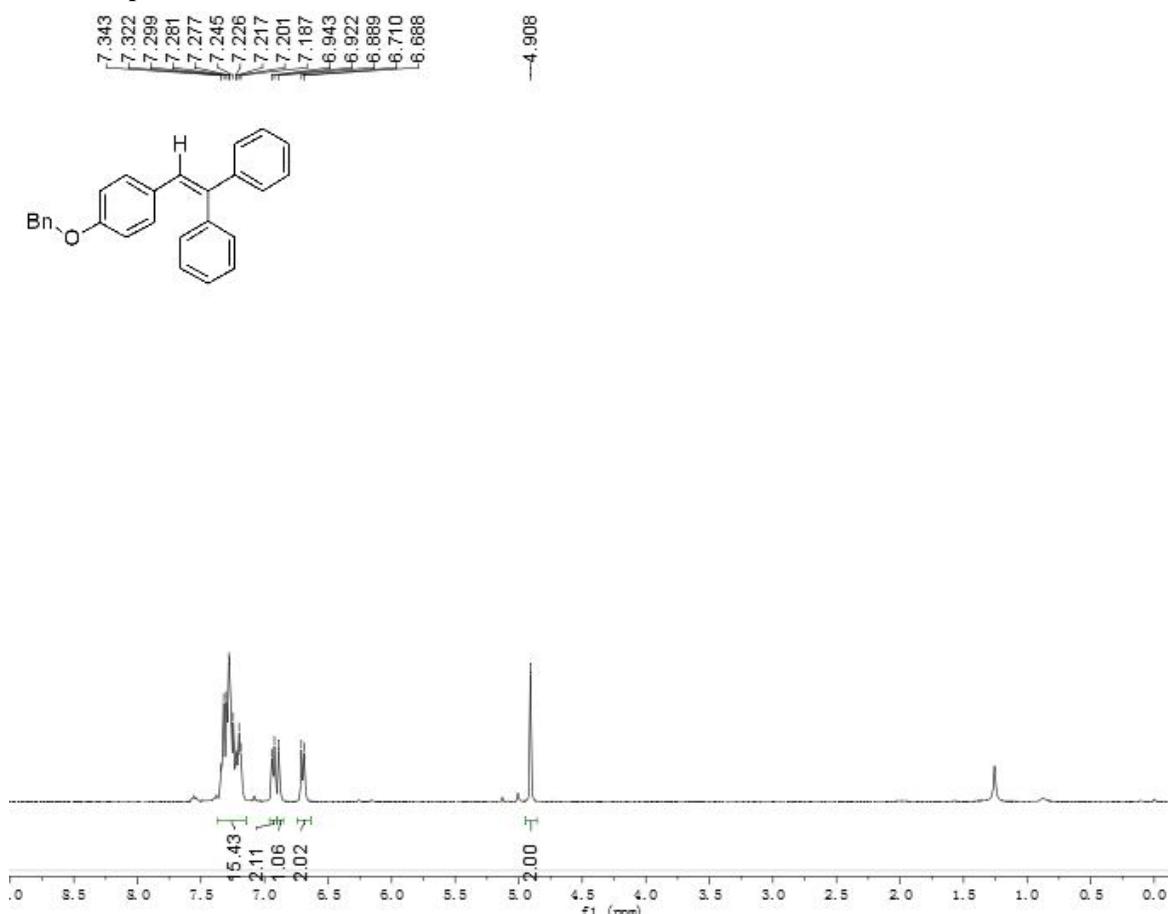
<sup>1</sup>H NMR spectra of 3ab



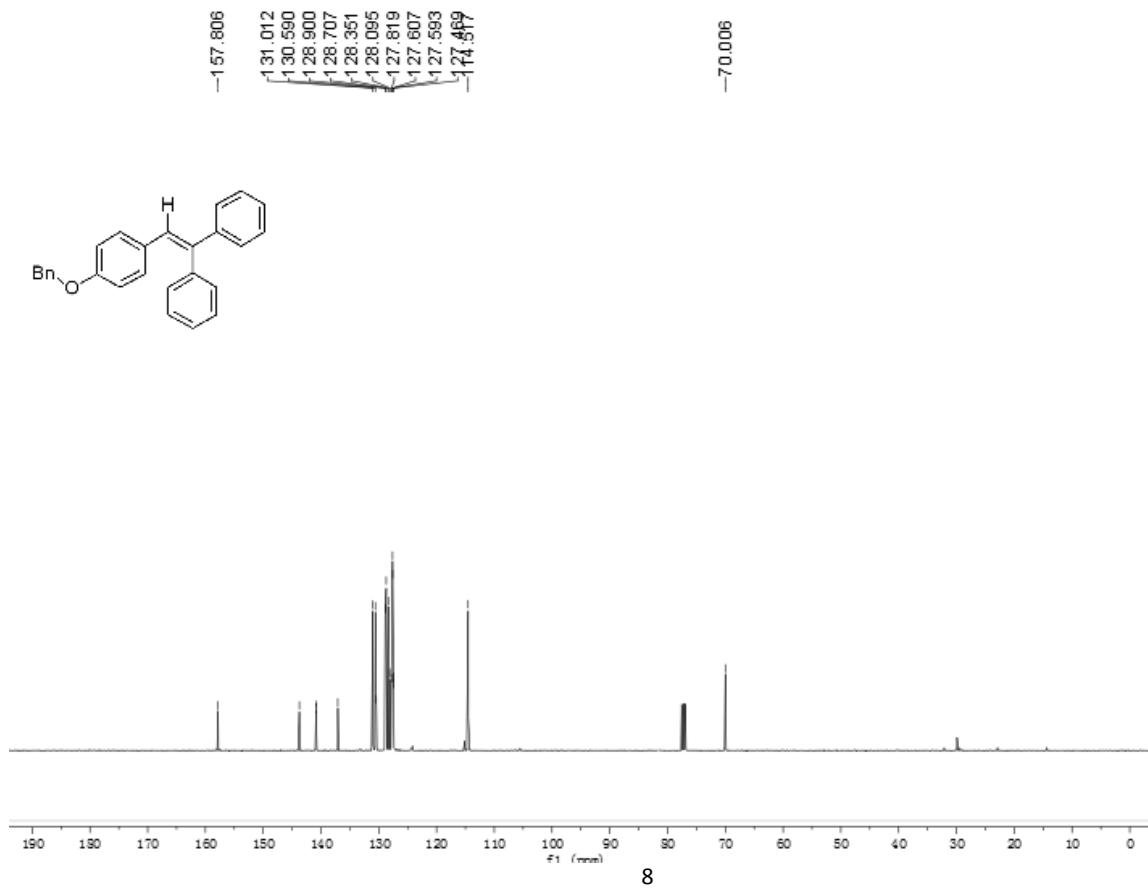
<sup>13</sup>C NMR spectra of 3ab



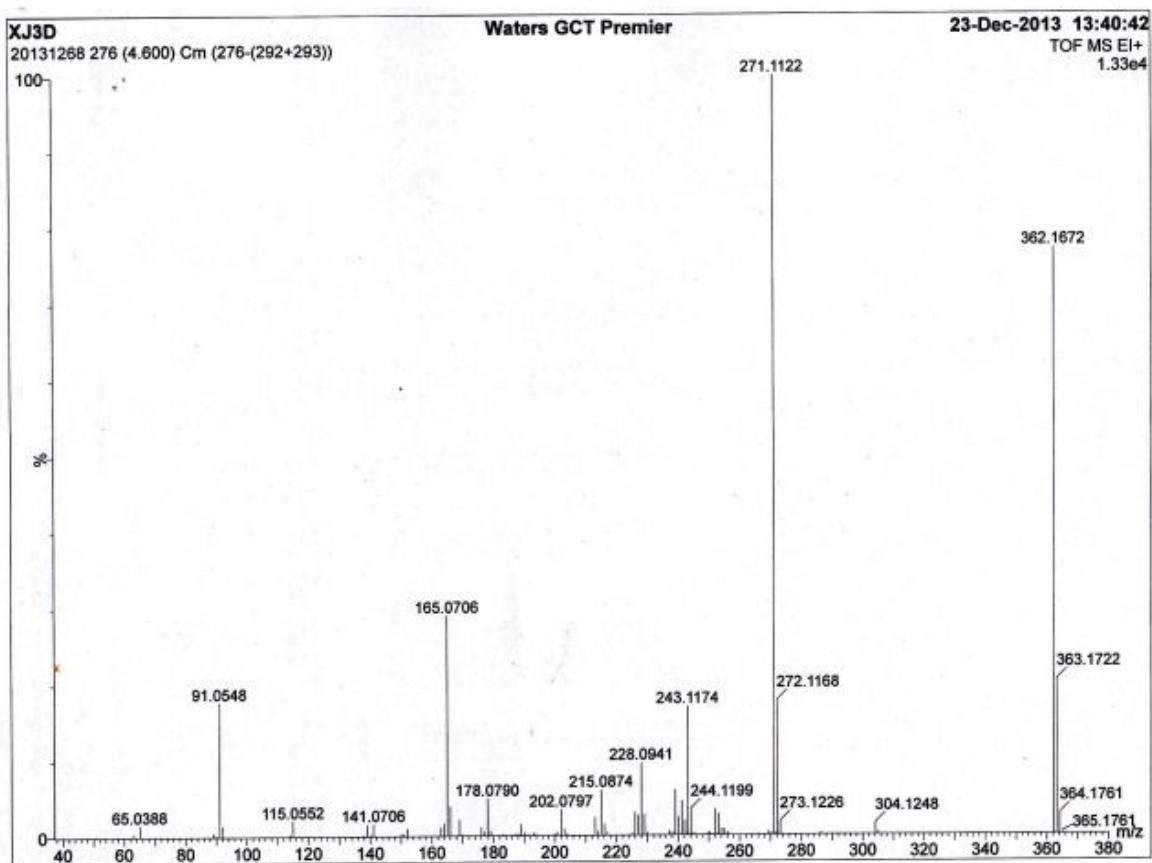
<sup>1</sup>H NMR spectra of 3bb



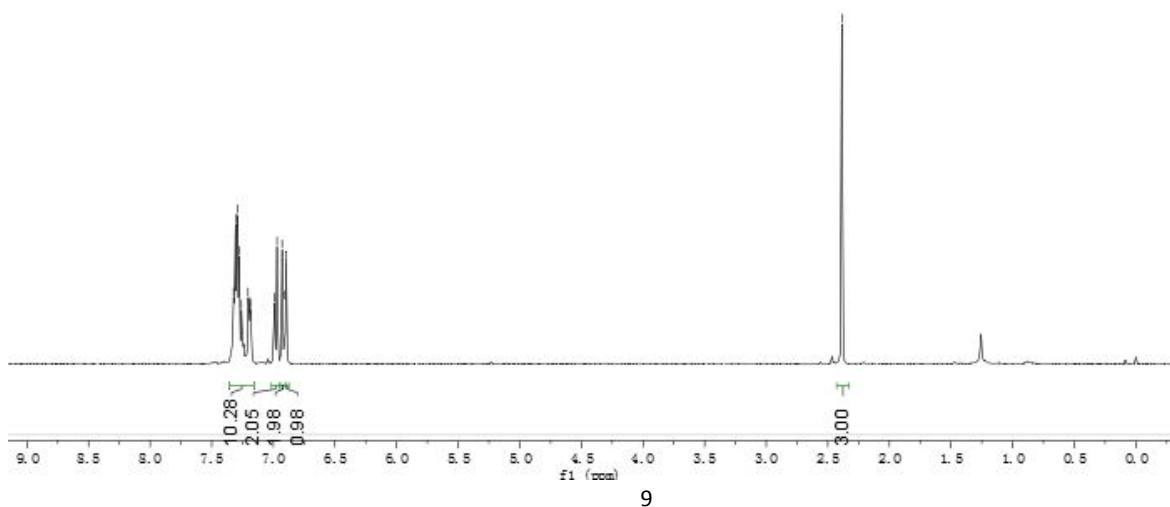
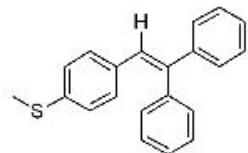
<sup>13</sup>C NMR spectra of 3bb



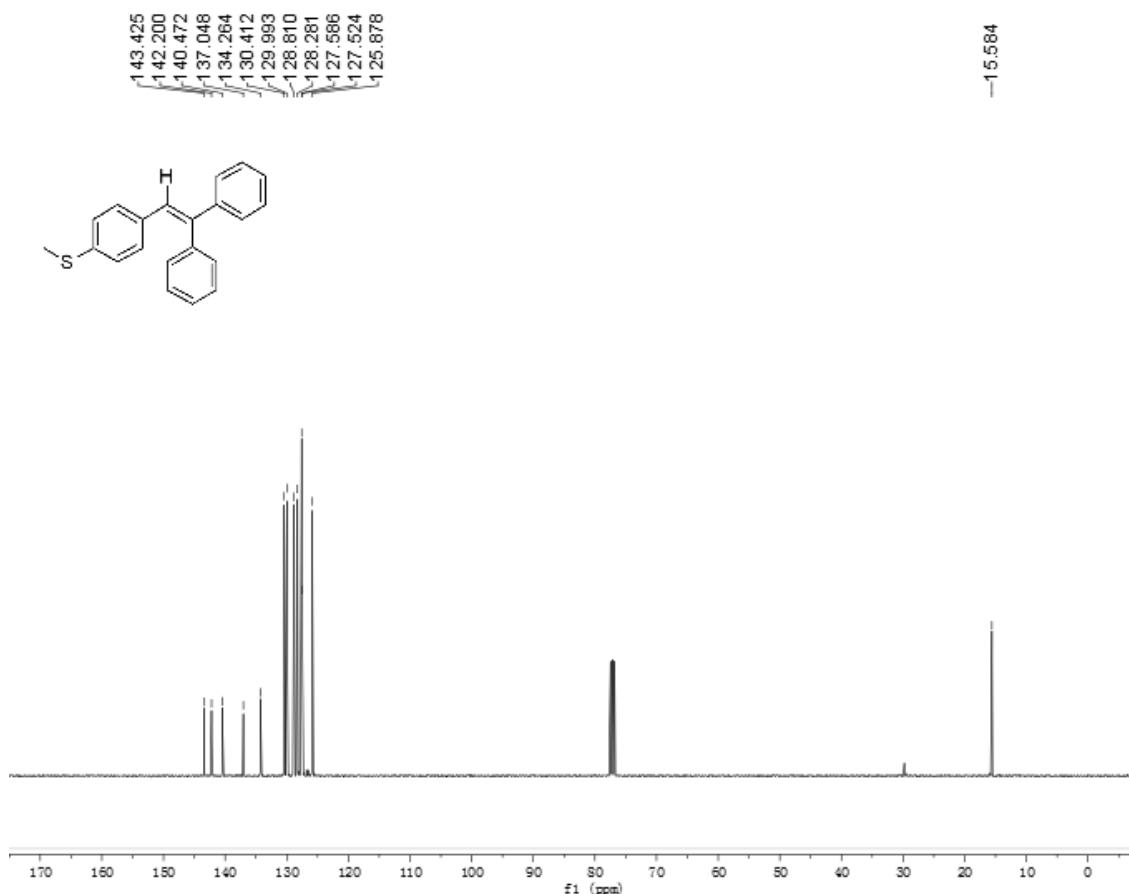
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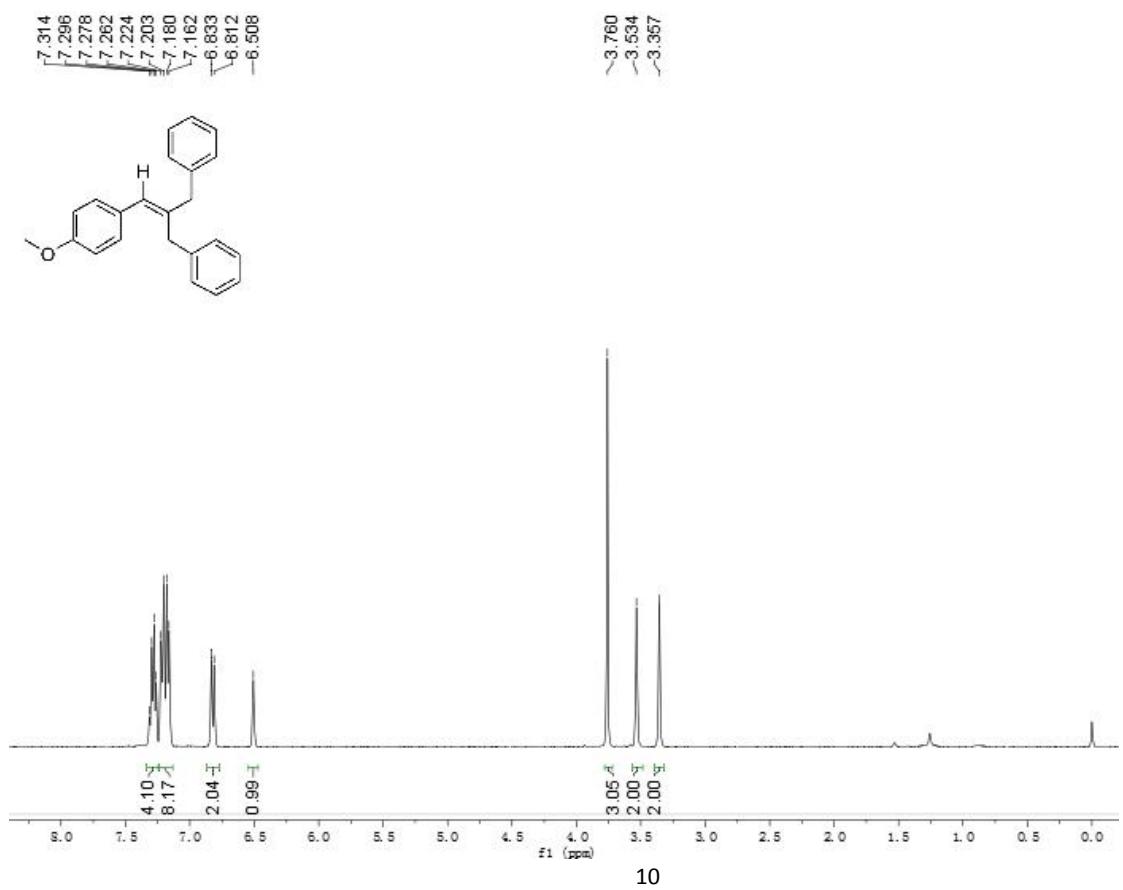
**<sup>1</sup>H NMR spectra of 3cb**



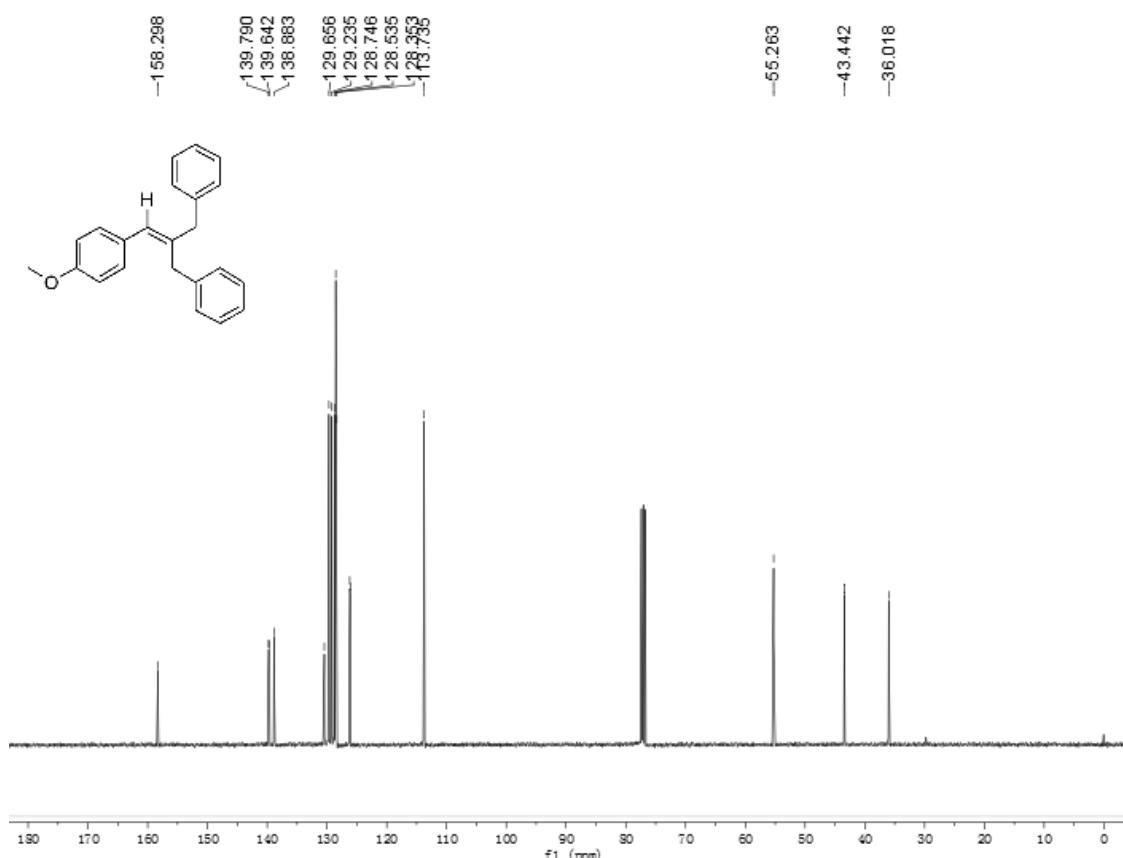
<sup>13</sup>C NMR spectra of 3cb



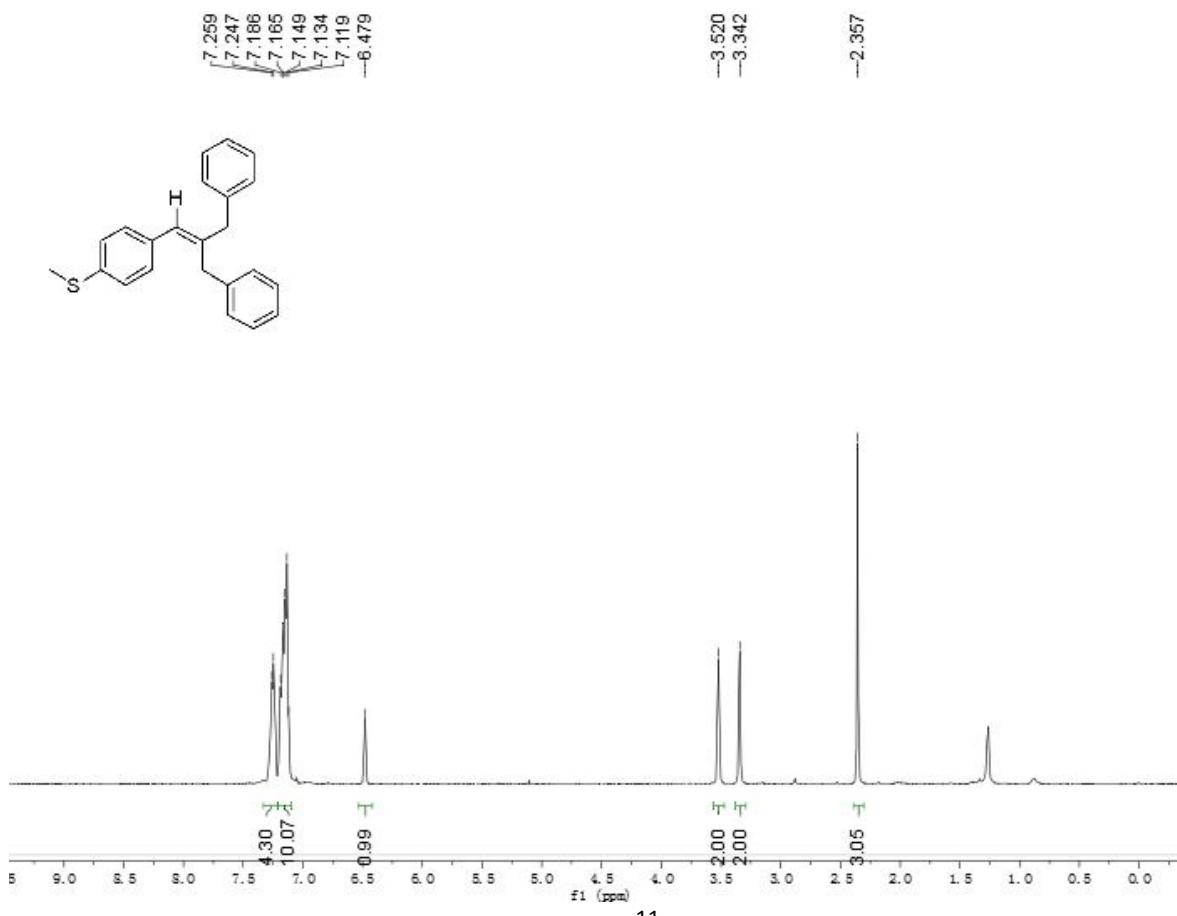
<sup>1</sup>H NMR spectra of 3ac



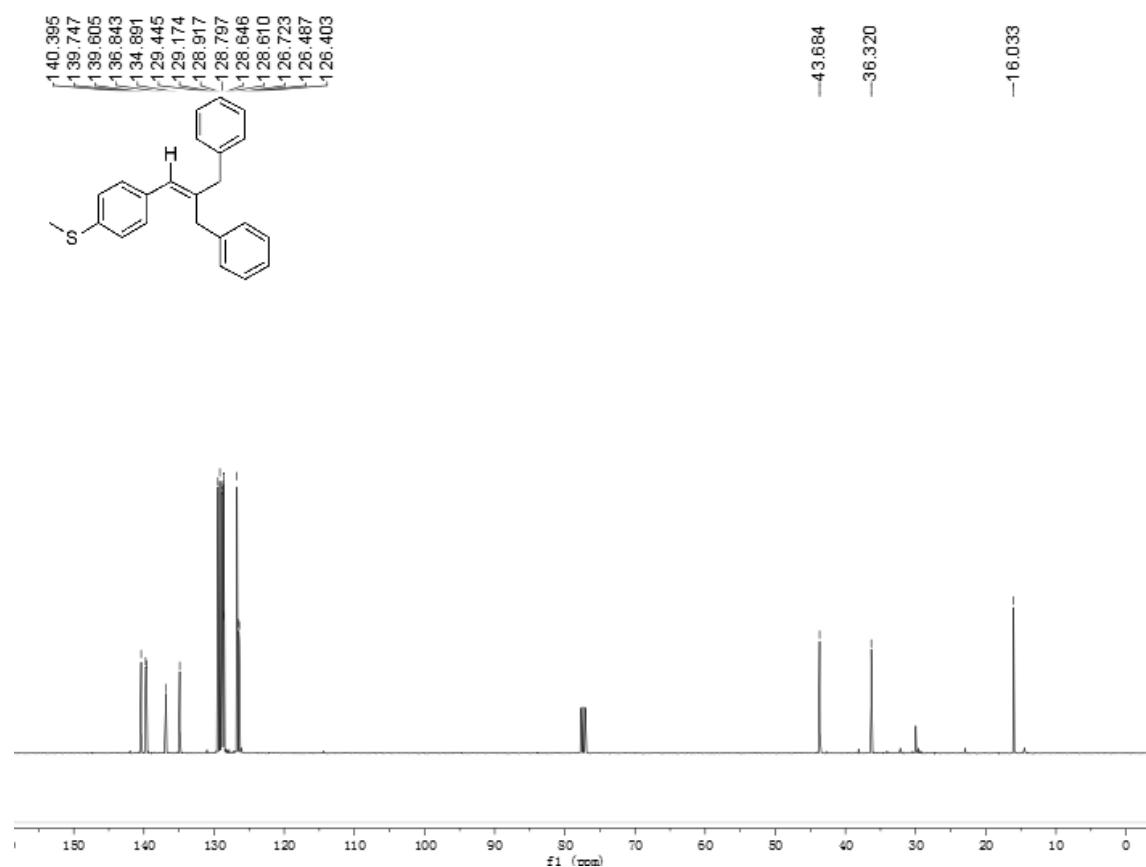
<sup>13</sup>C NMR spectra of 3ac



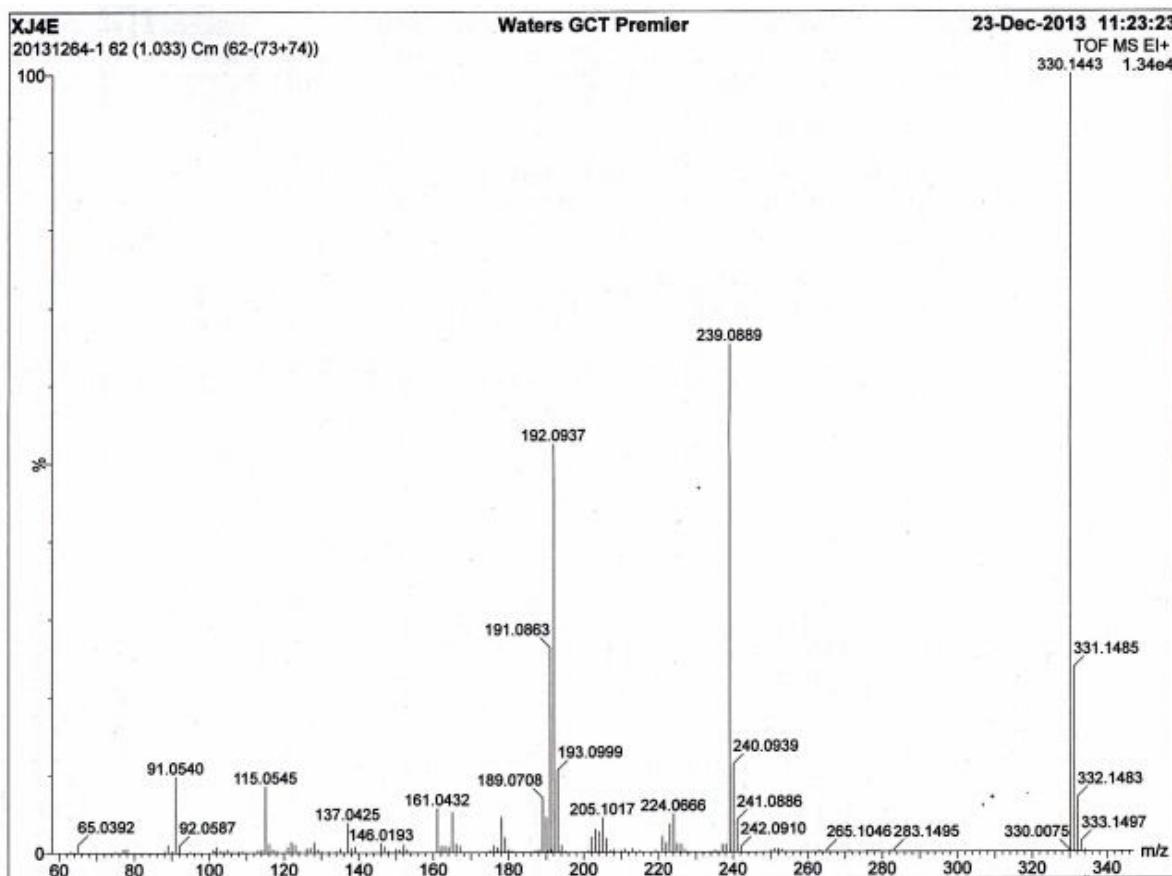
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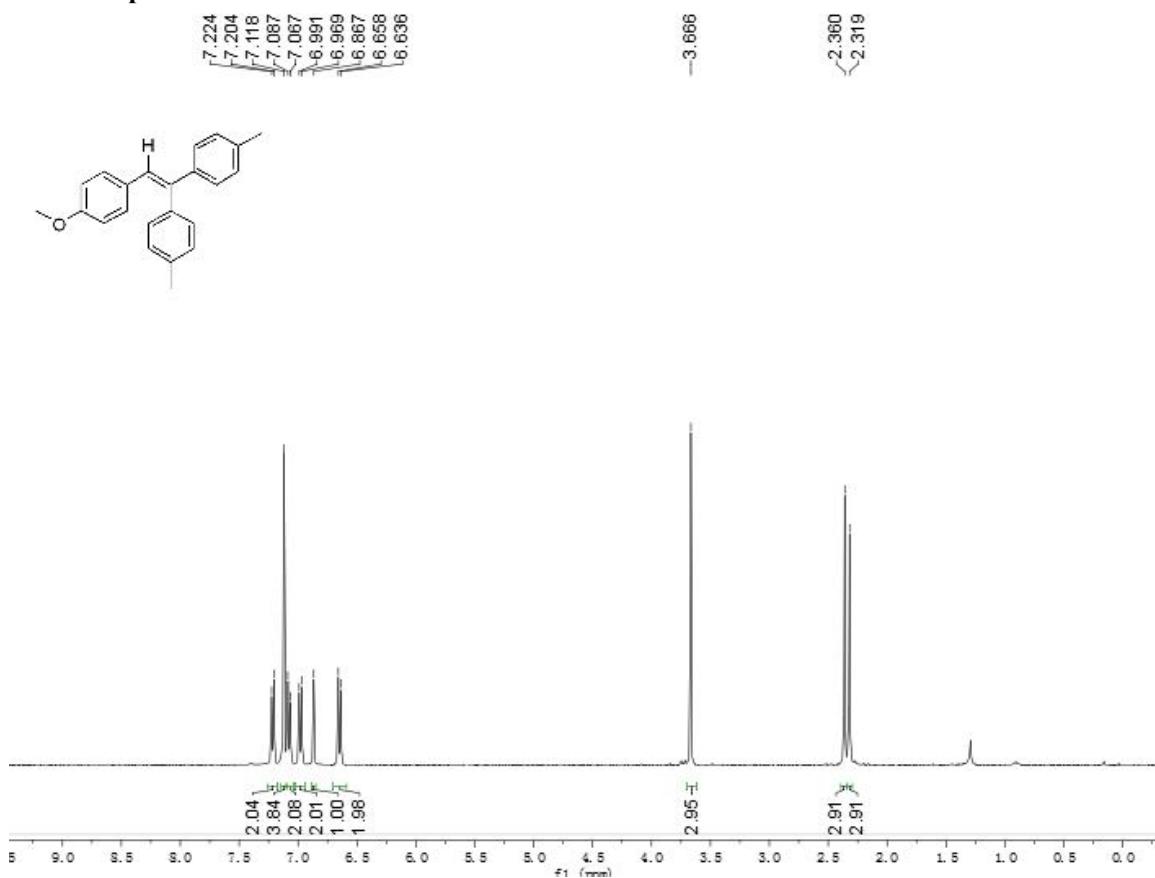
<sup>13</sup>C NMR spectra of 3cc



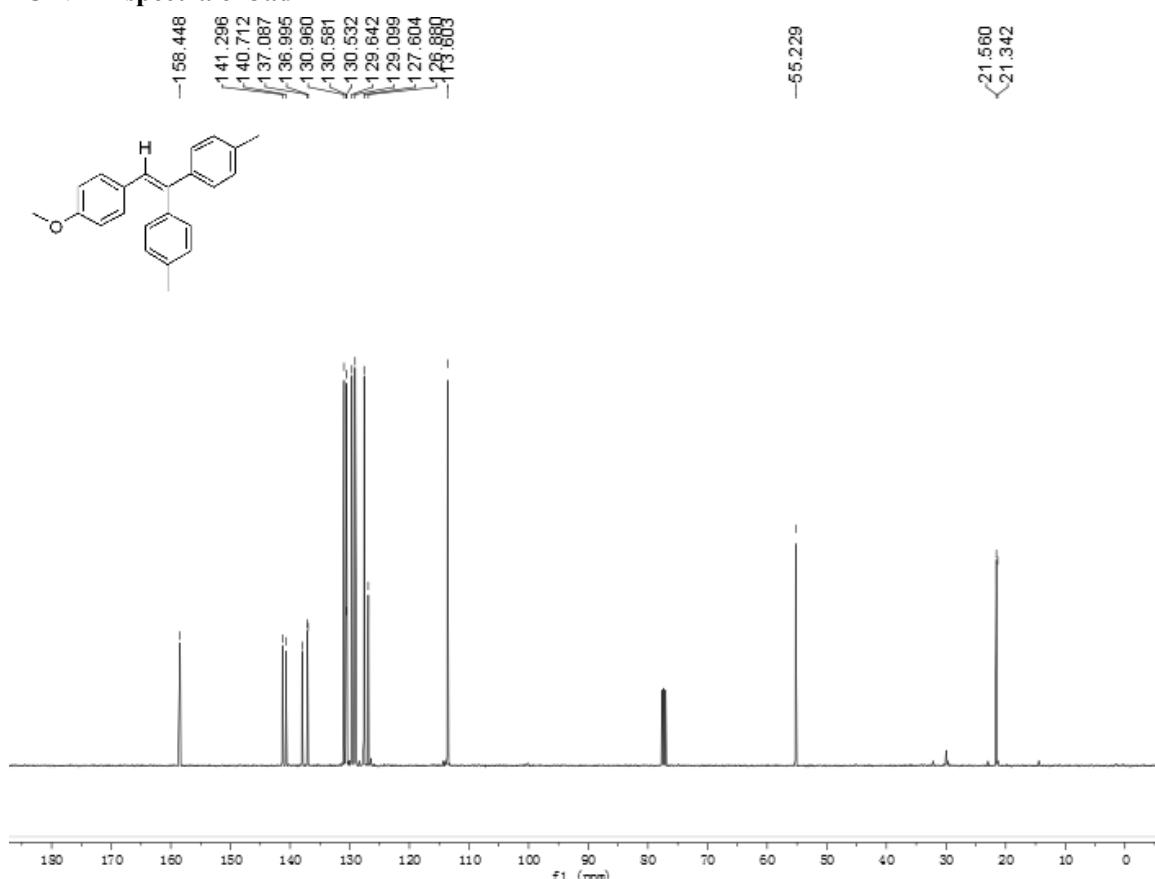
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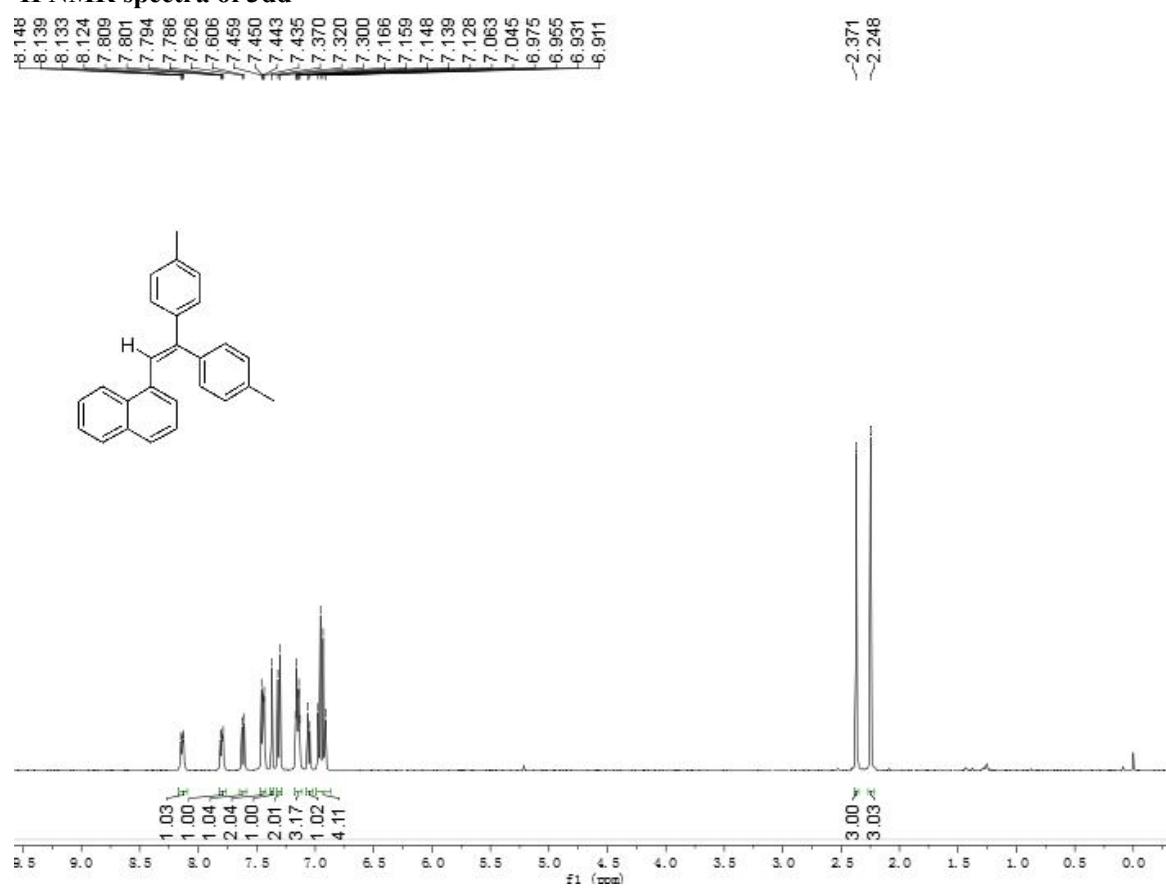
<sup>1</sup>H NMR spectra of 3ad



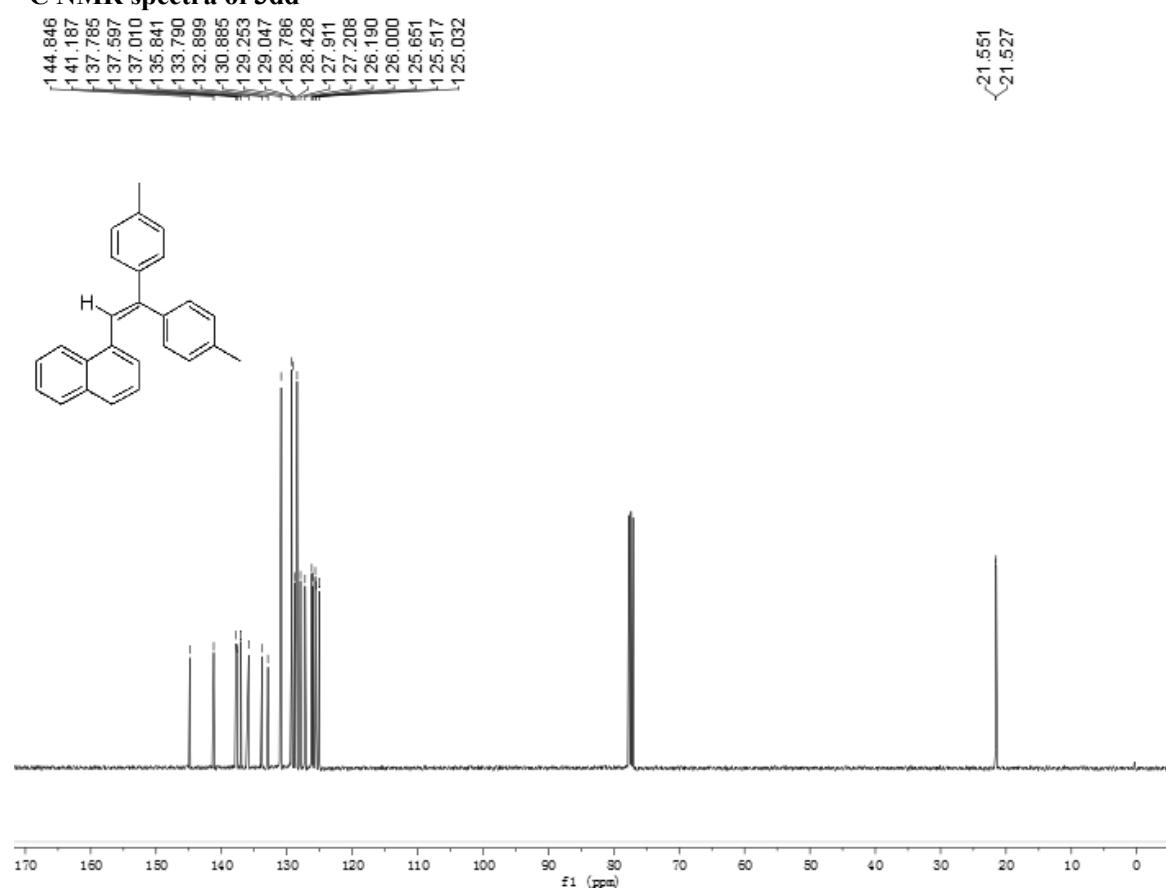
<sup>13</sup>C NMR spectra of 3ad



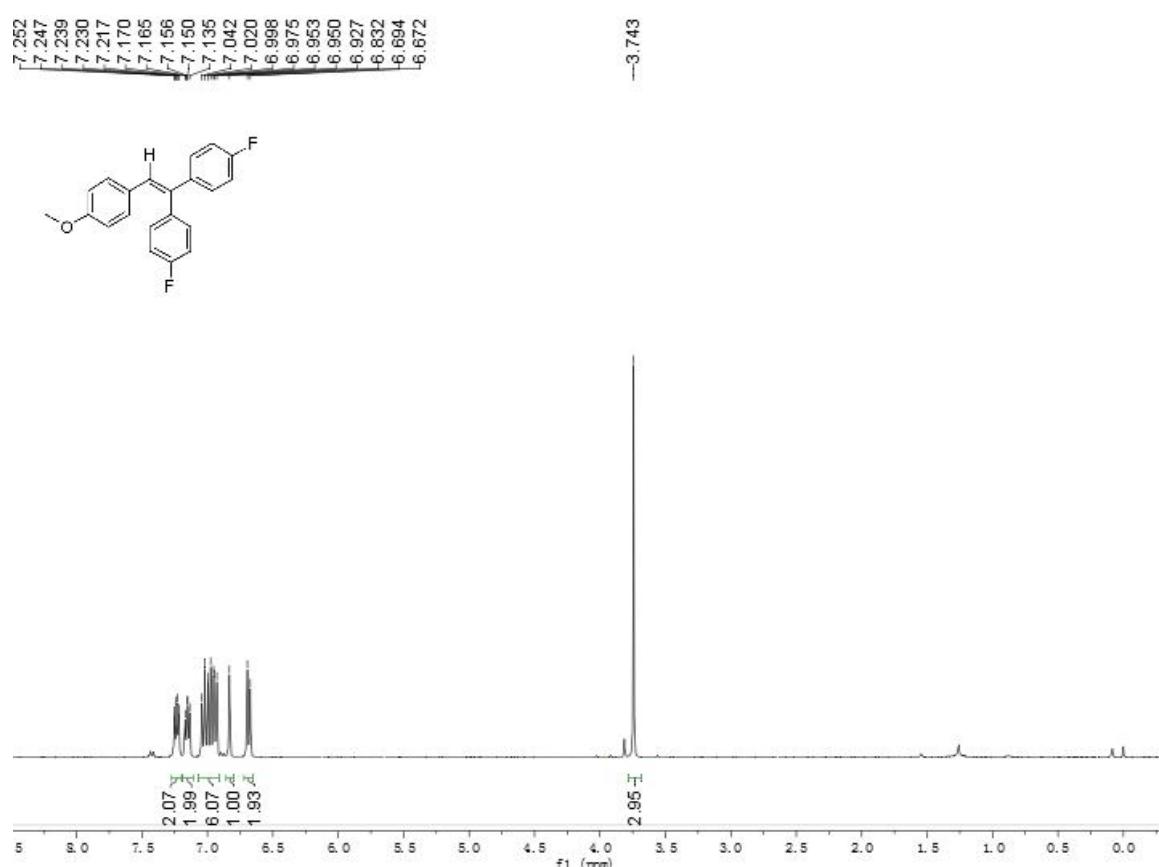
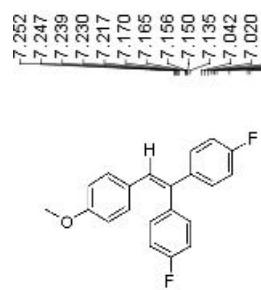
**<sup>1</sup>H NMR spectra of 3dd**



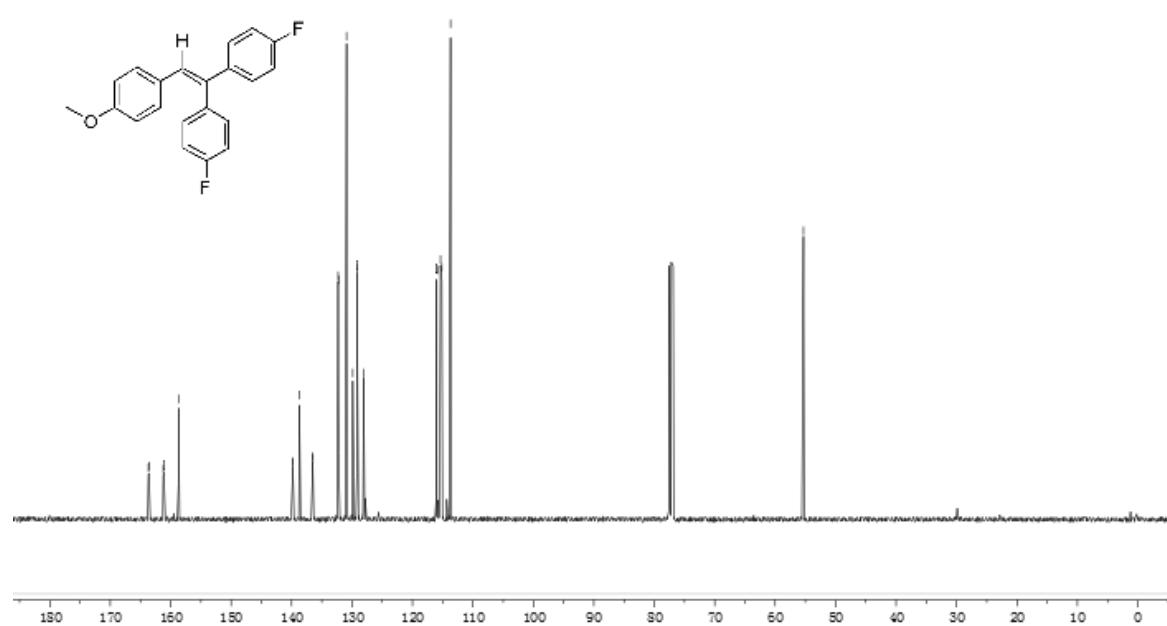
**<sup>13</sup>C NMR spectra of 3dd**



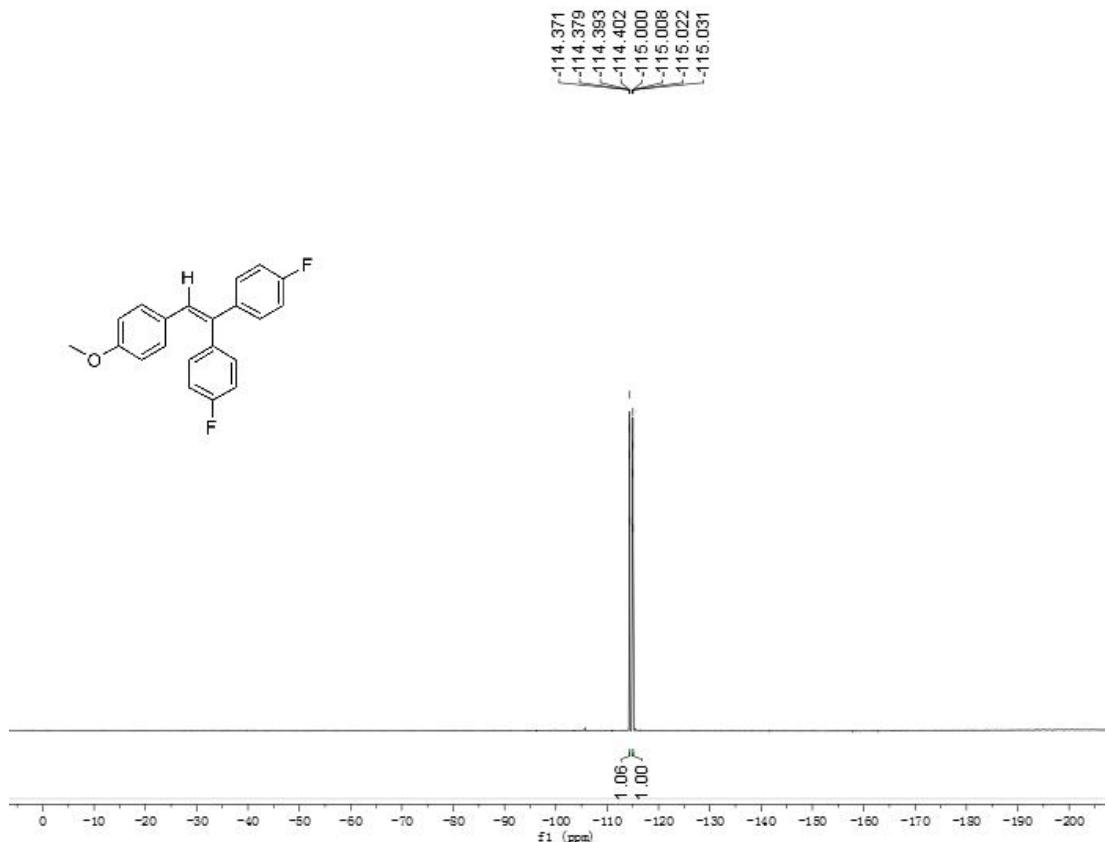
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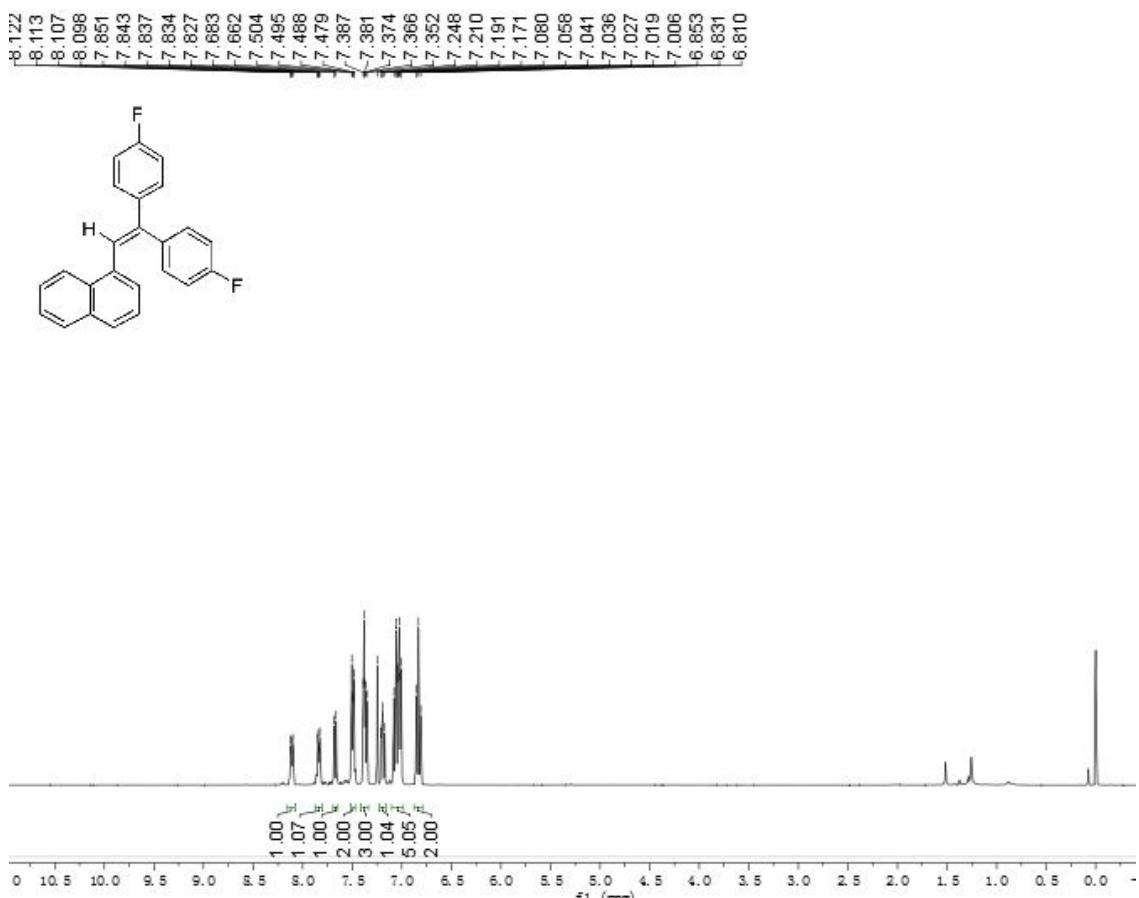
### **<sup>13</sup>C NMR spectra of 3ae**



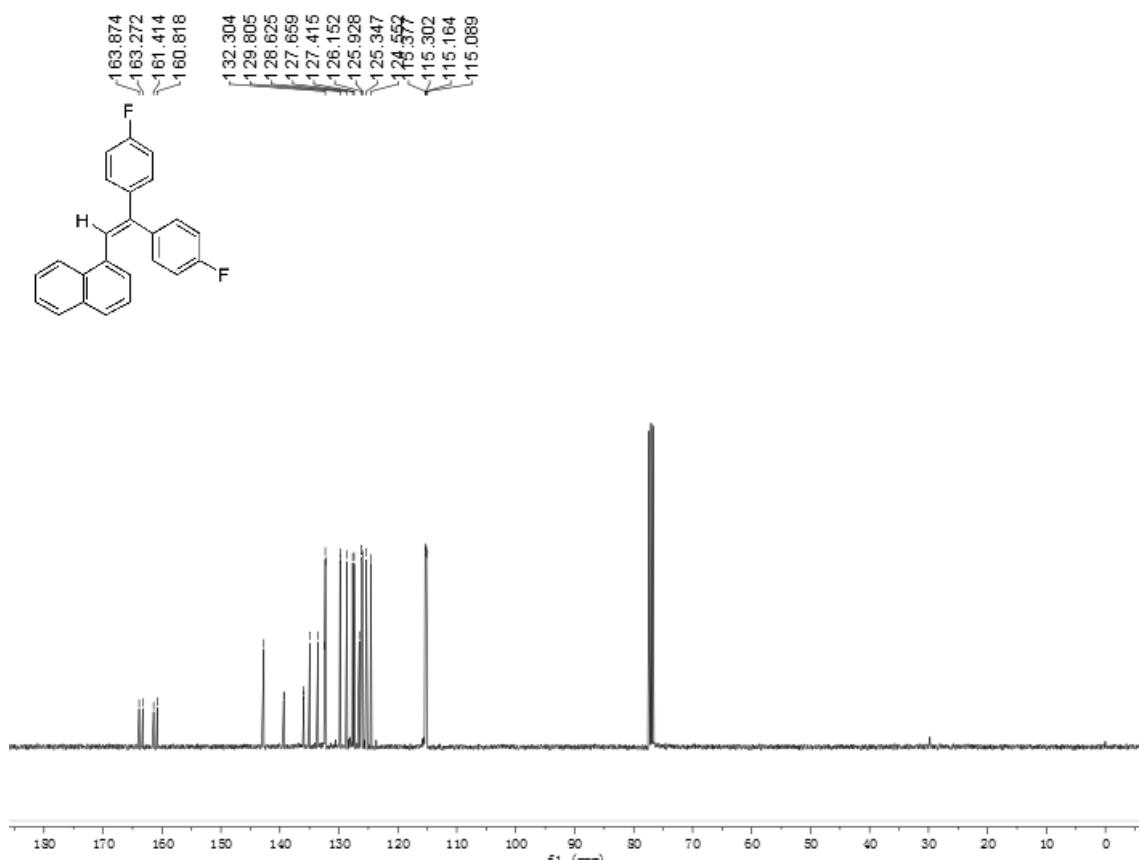
<sup>19</sup>F NMR spectra of 3ae



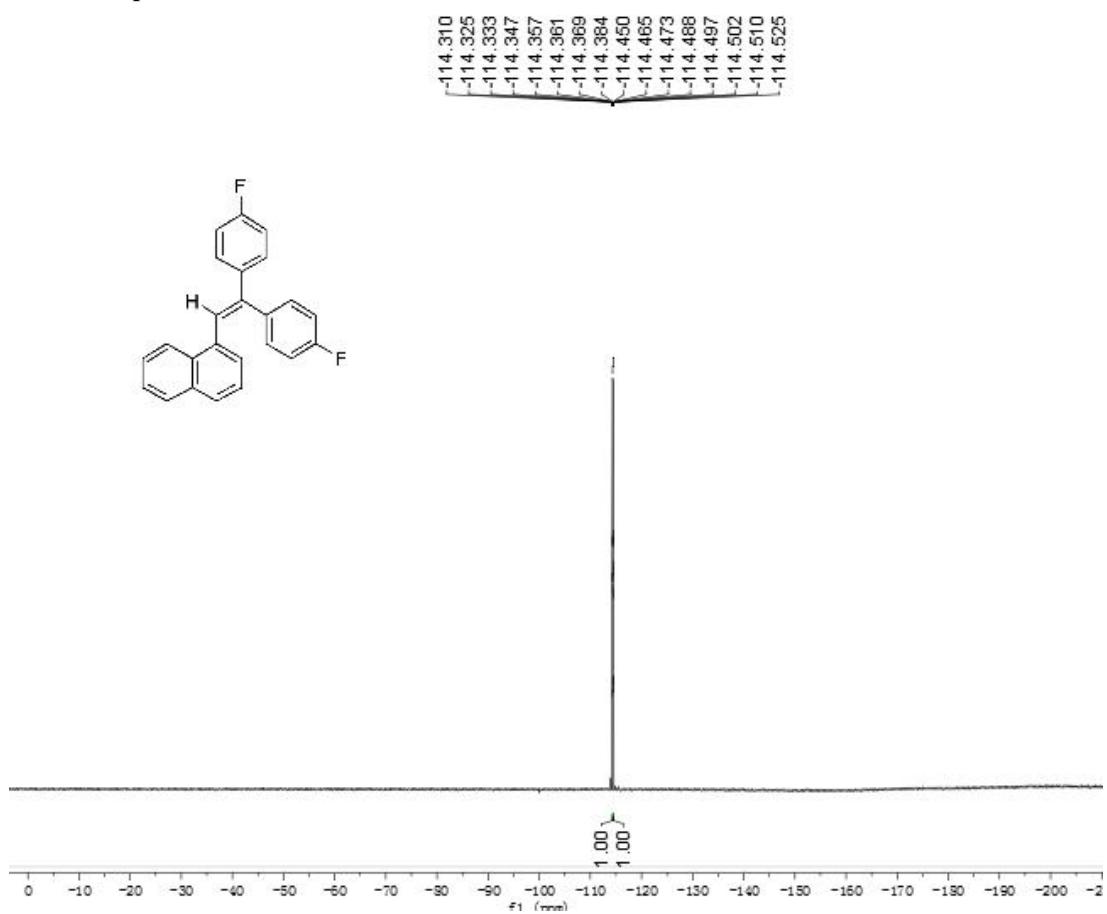
<sup>1</sup>H NMR spectra of 3de



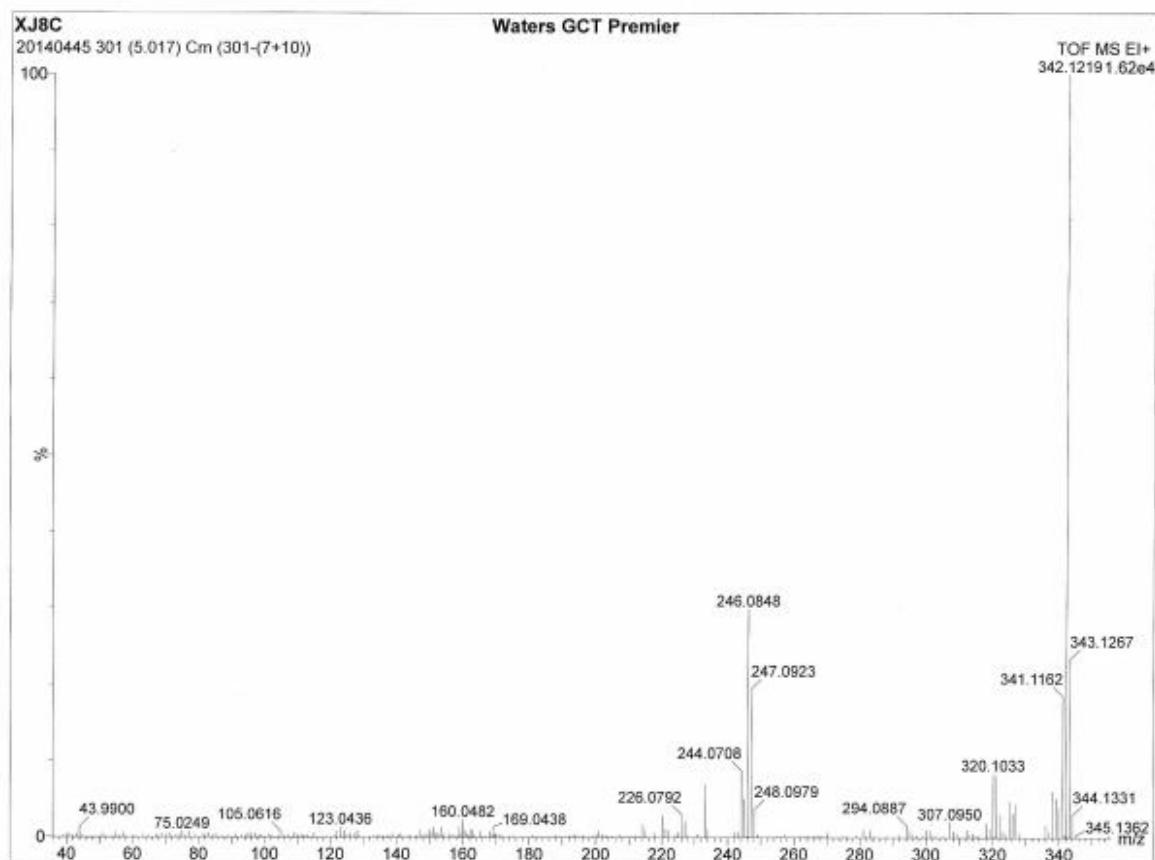
<sup>13</sup>C NMR spectra of 3de



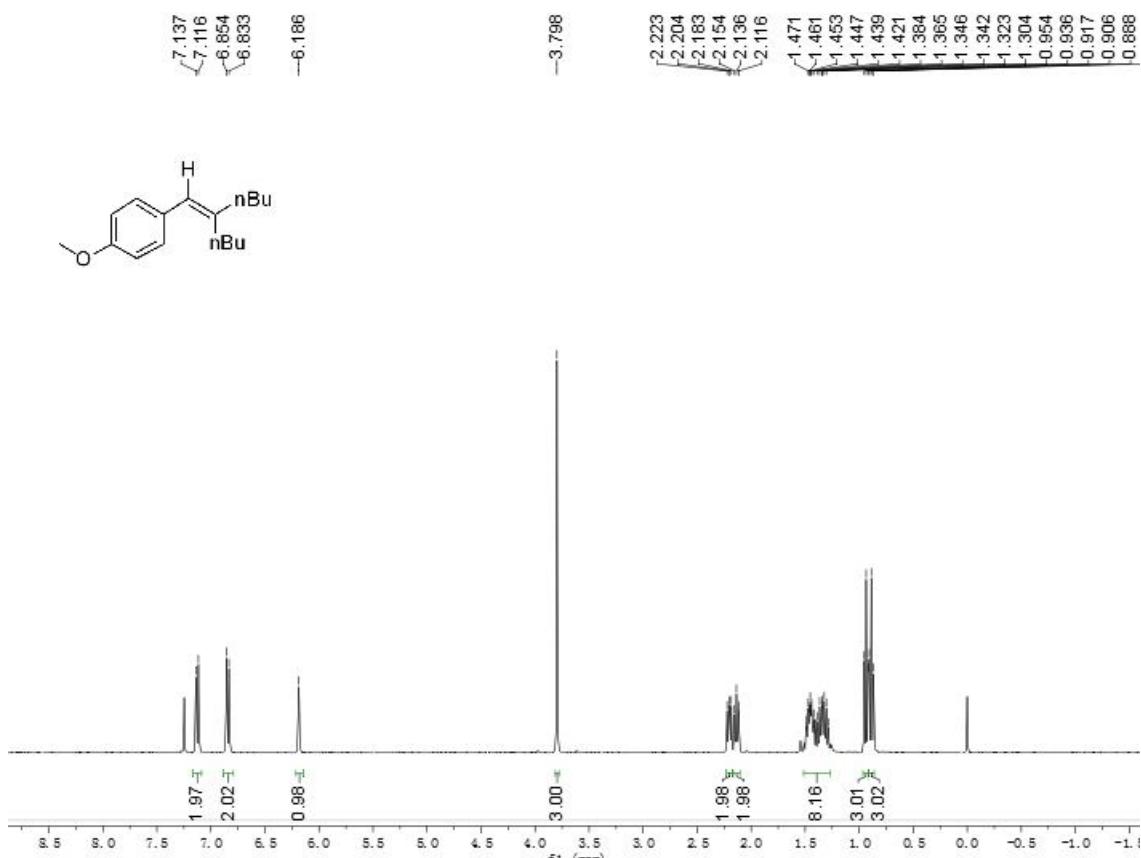
<sup>19</sup>F NMR spectra of 3de



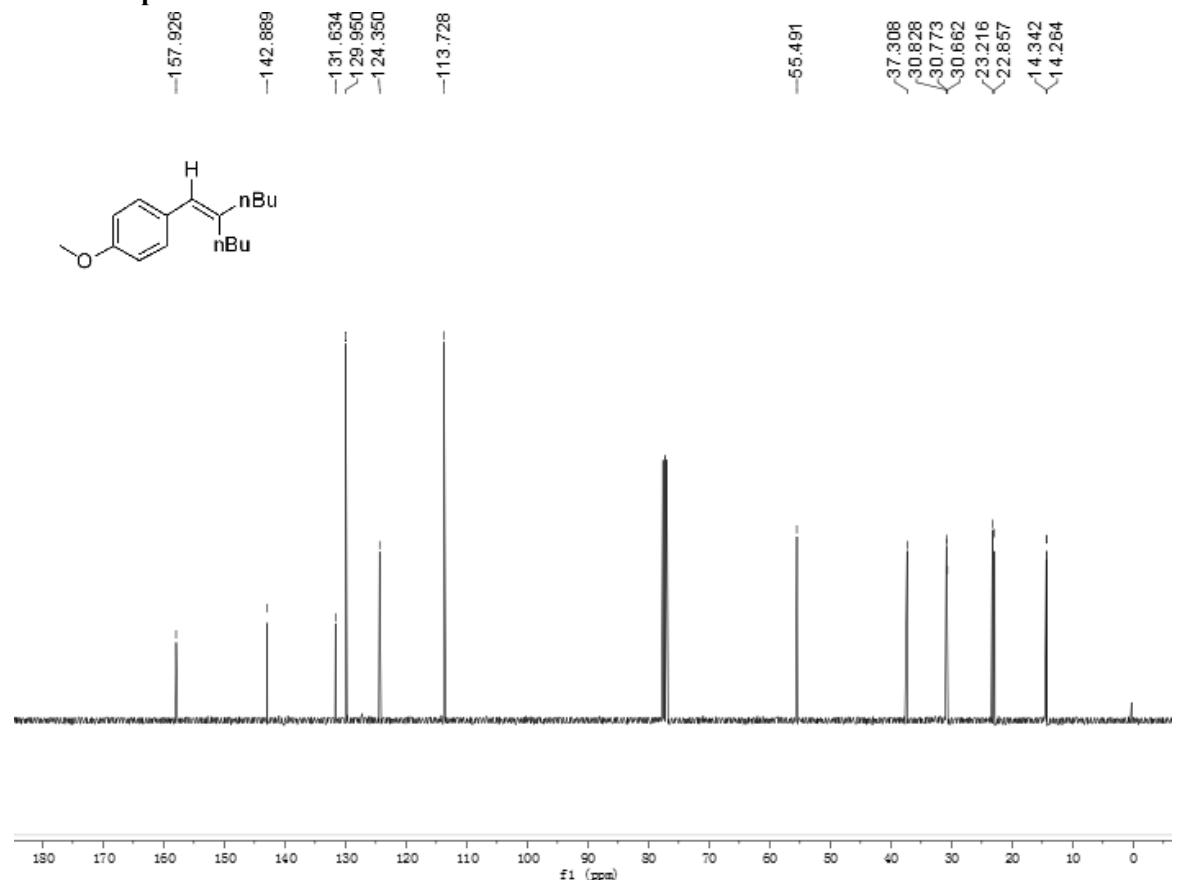
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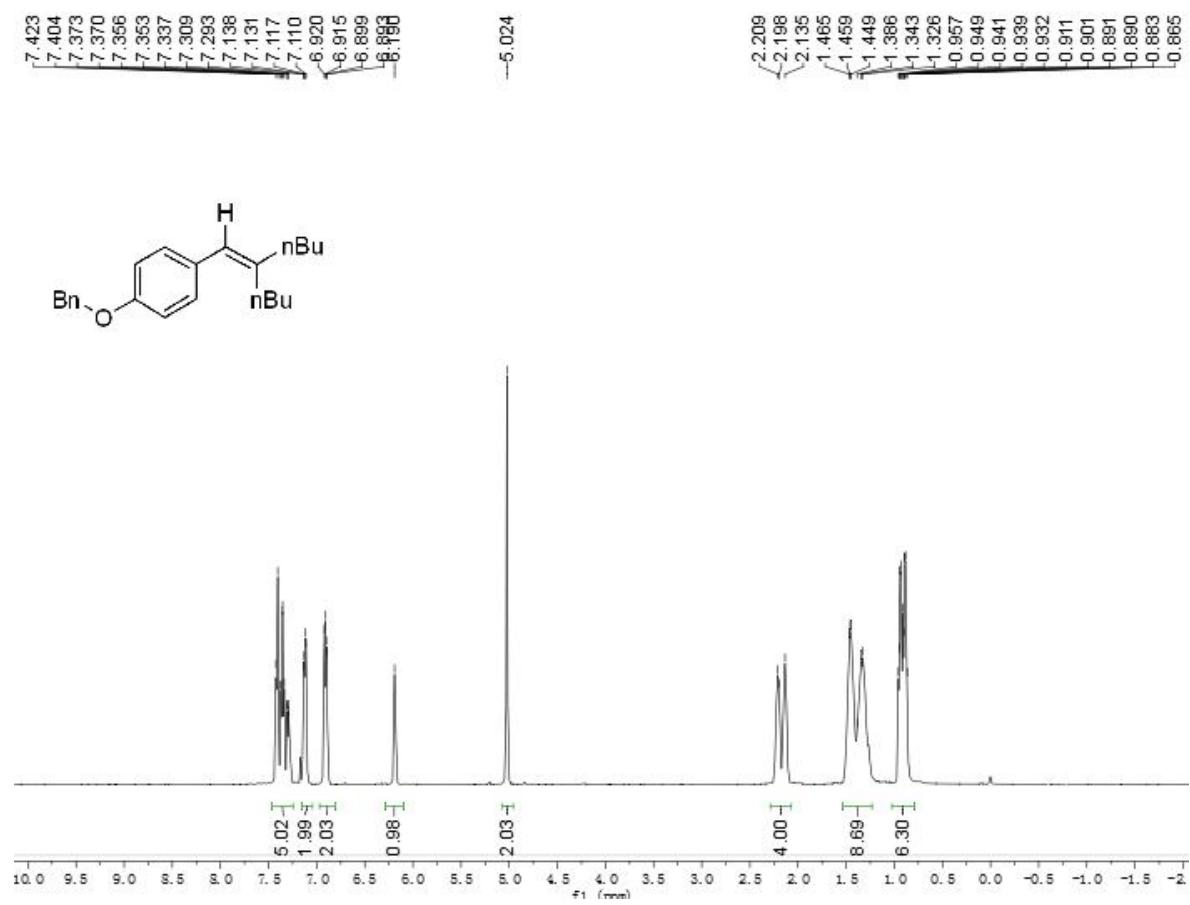
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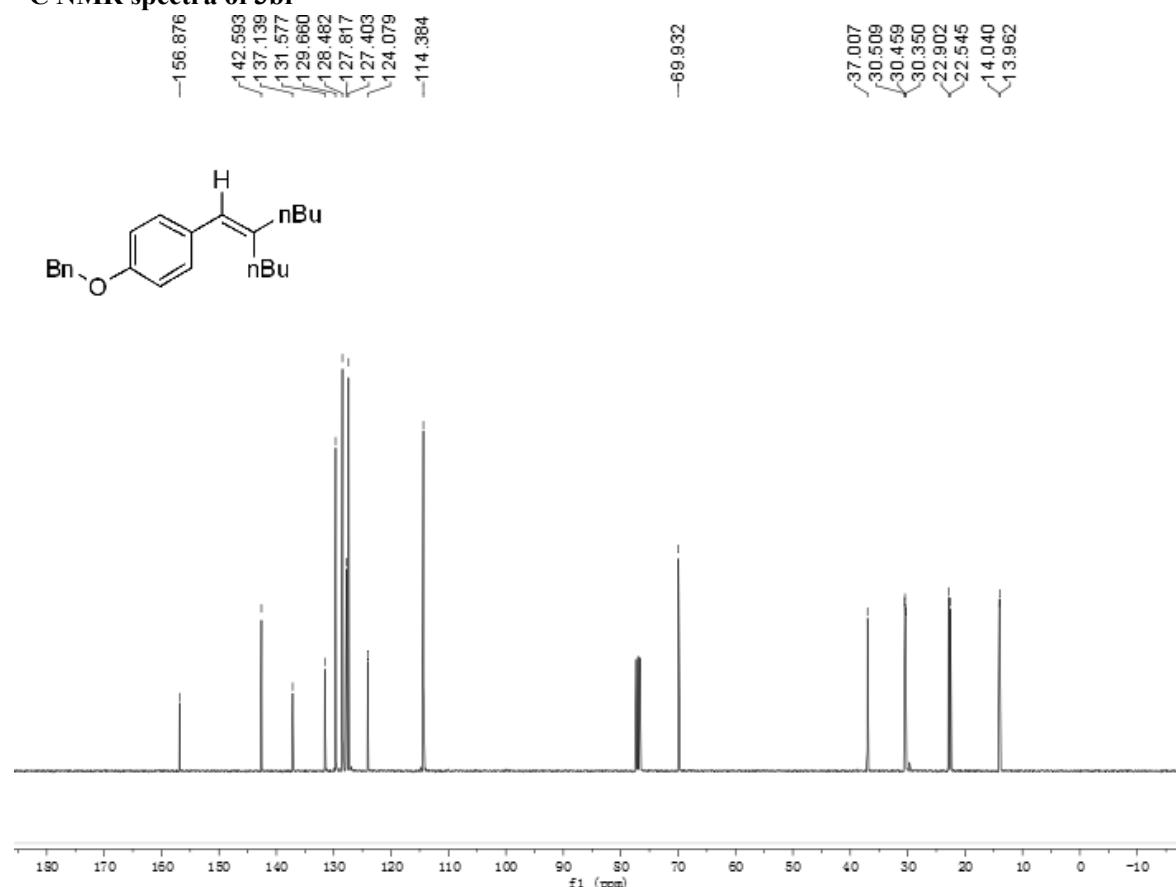
<sup>13</sup>C NMR spectra of 3af



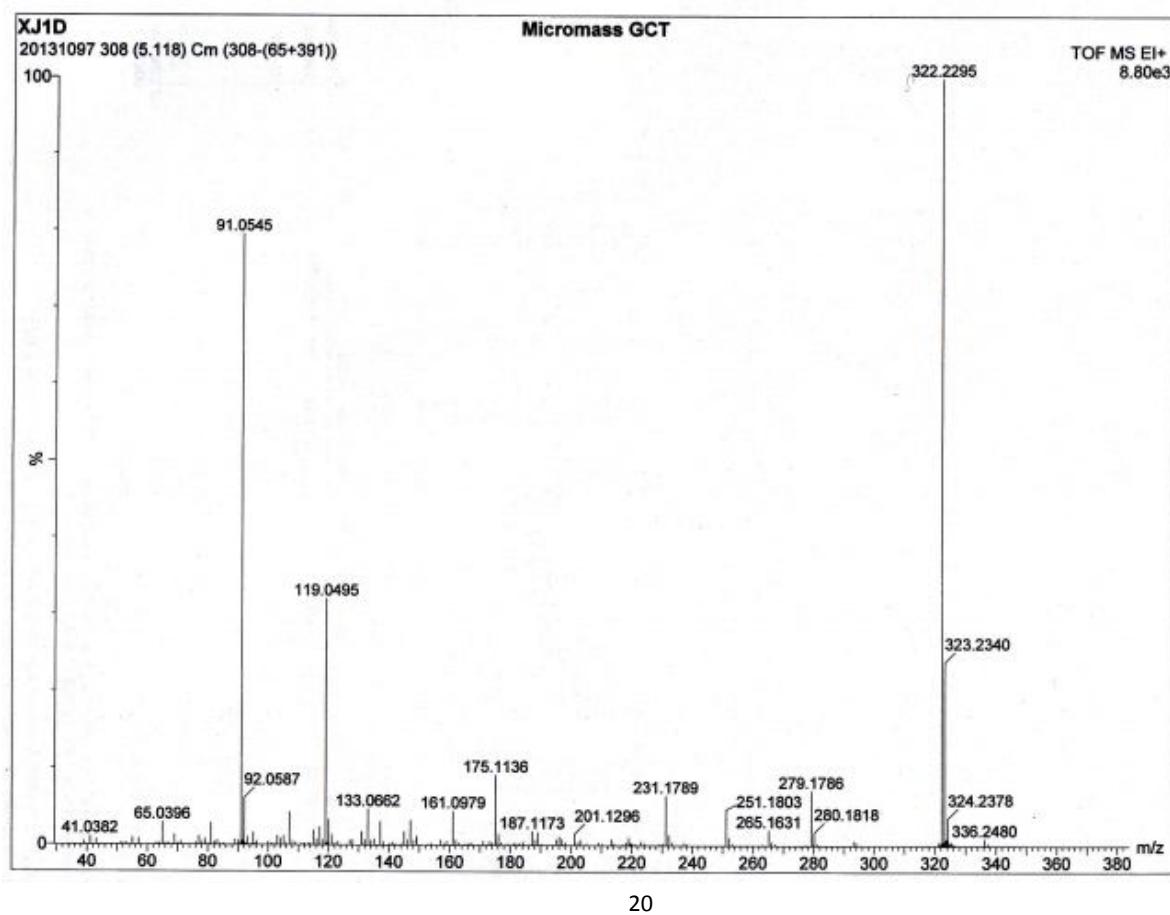
<sup>1</sup>H NMR spectra of 3bf



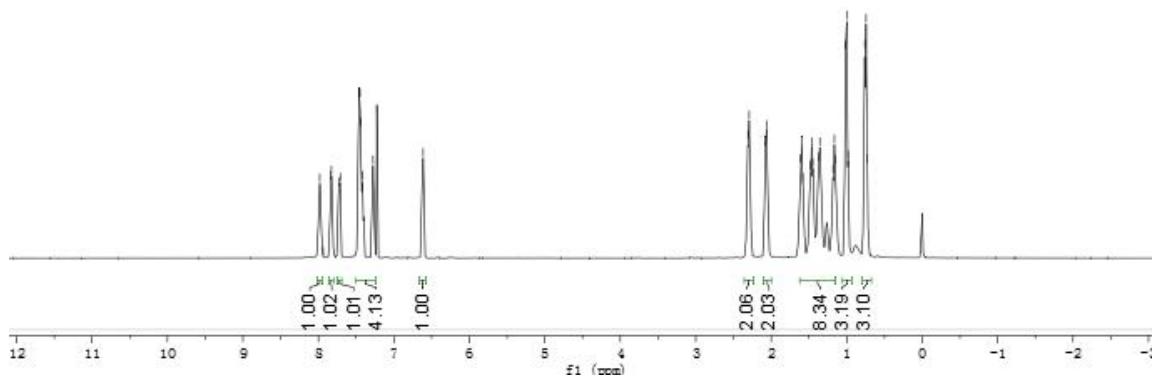
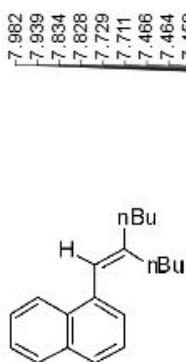
<sup>13</sup>C NMR spectra of 3bf



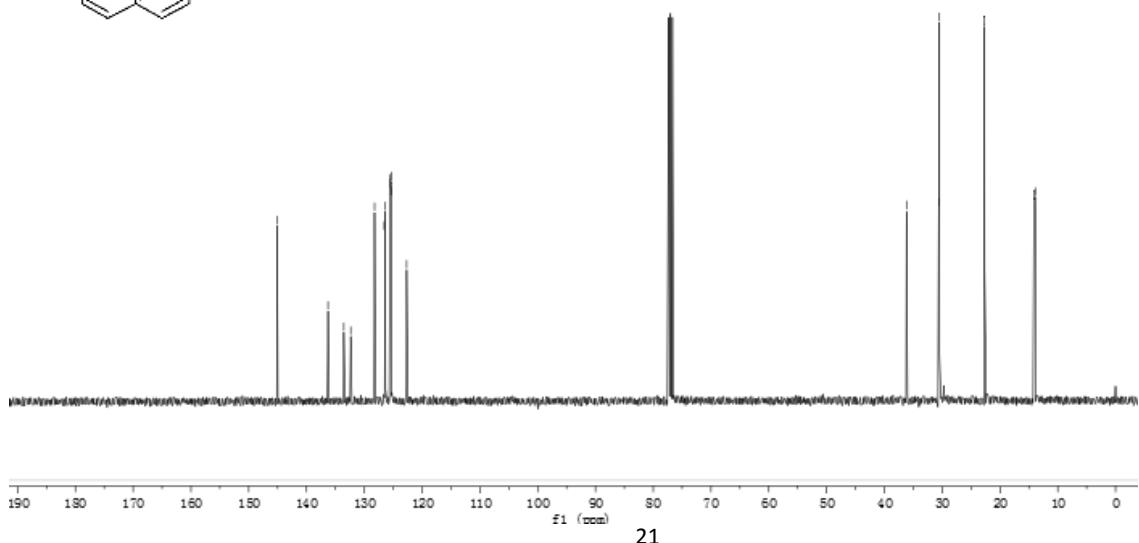
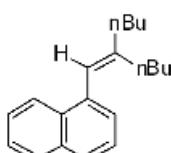
HRMS (EI) spectra of 3bf



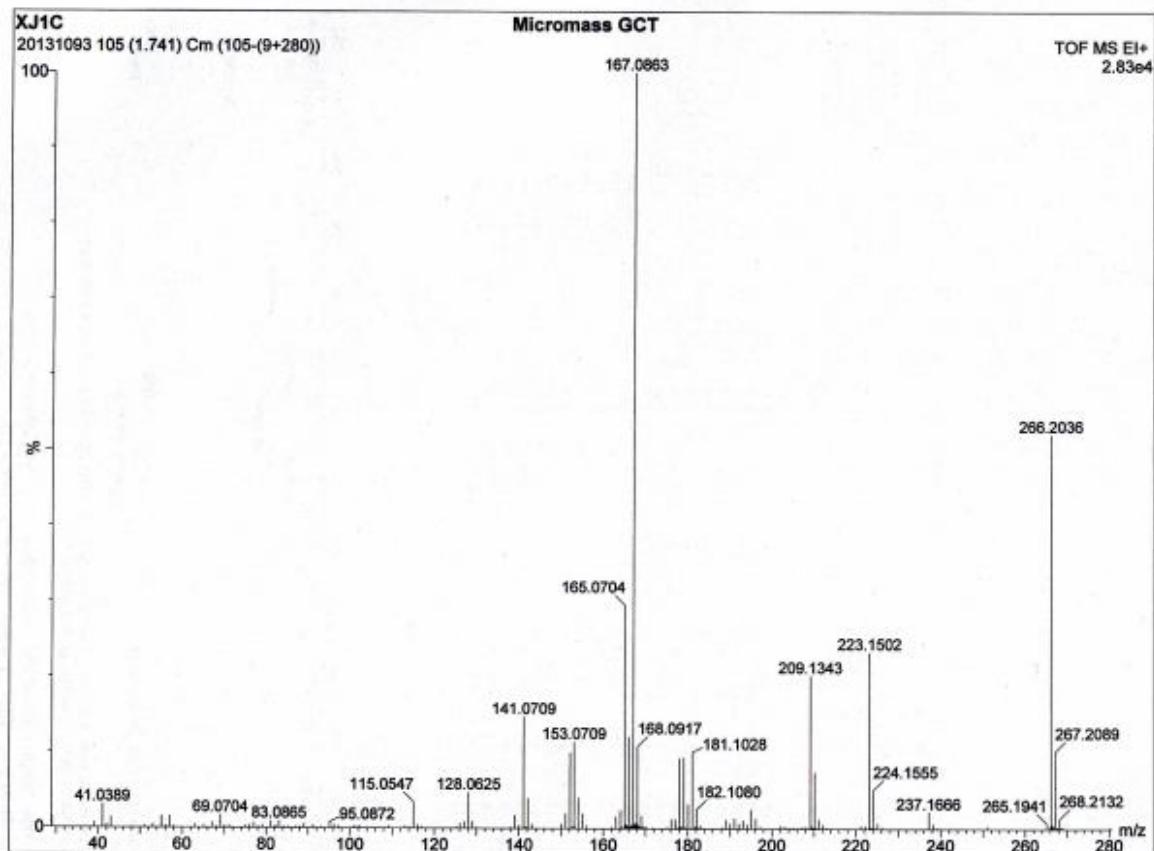
### **<sup>1</sup>H NMR spectra of 3df**



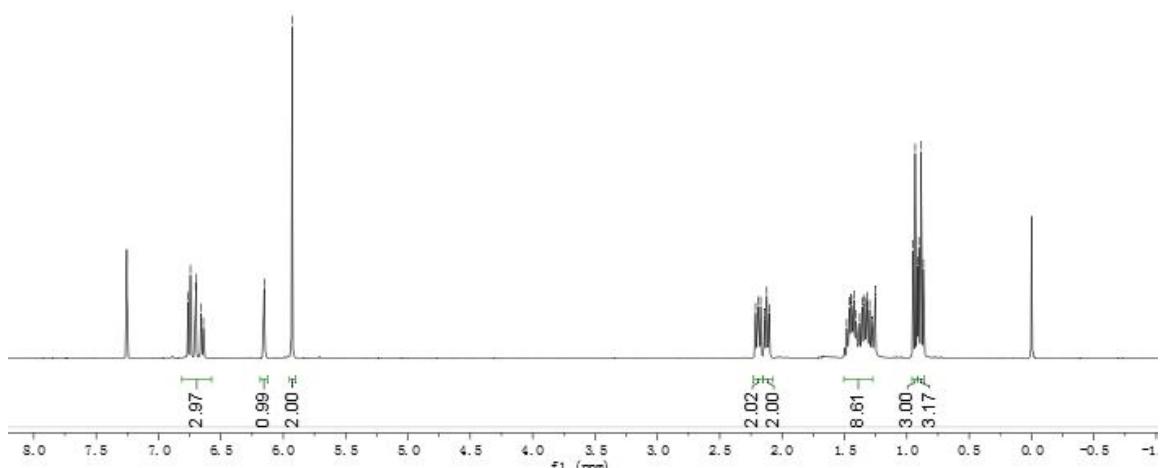
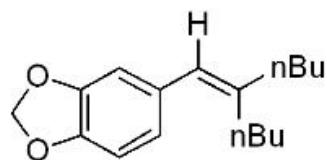
### **<sup>13</sup>C NMR spectra of 3df**



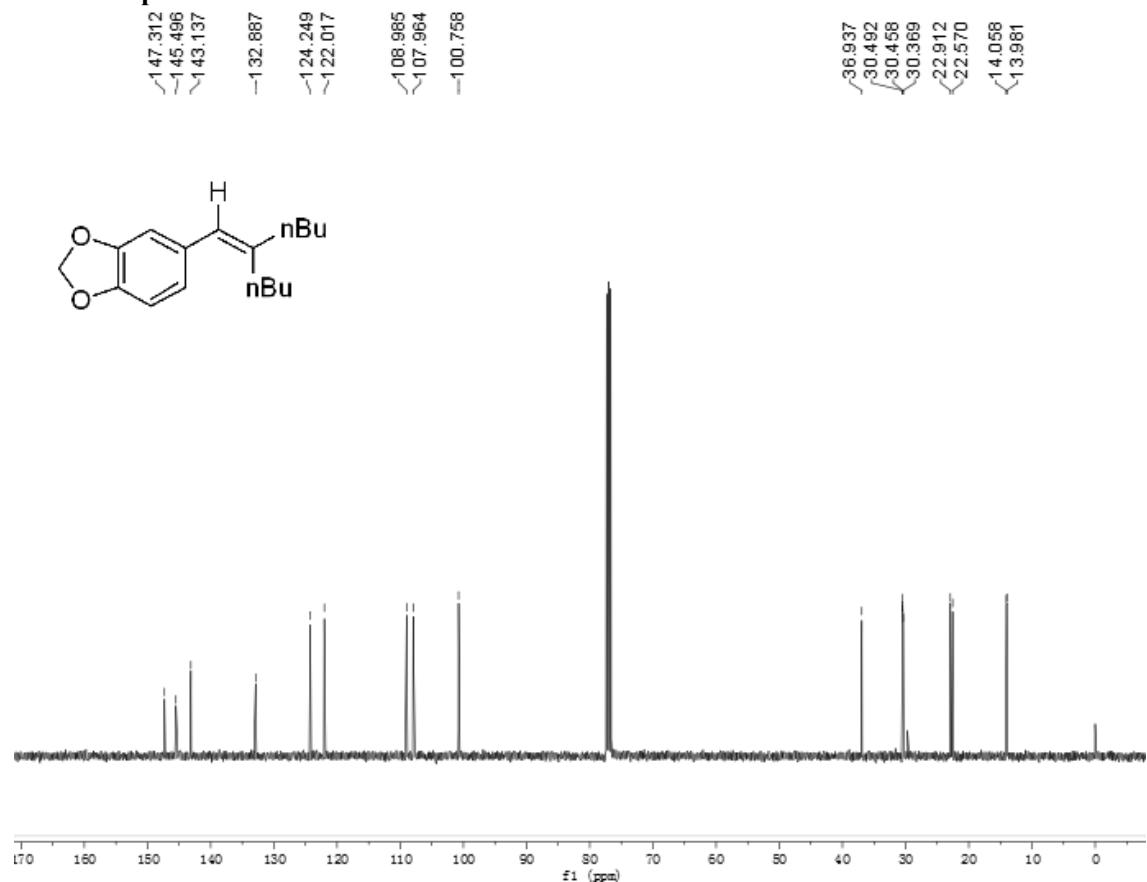
**HRMS (EI) spectra of 3df**



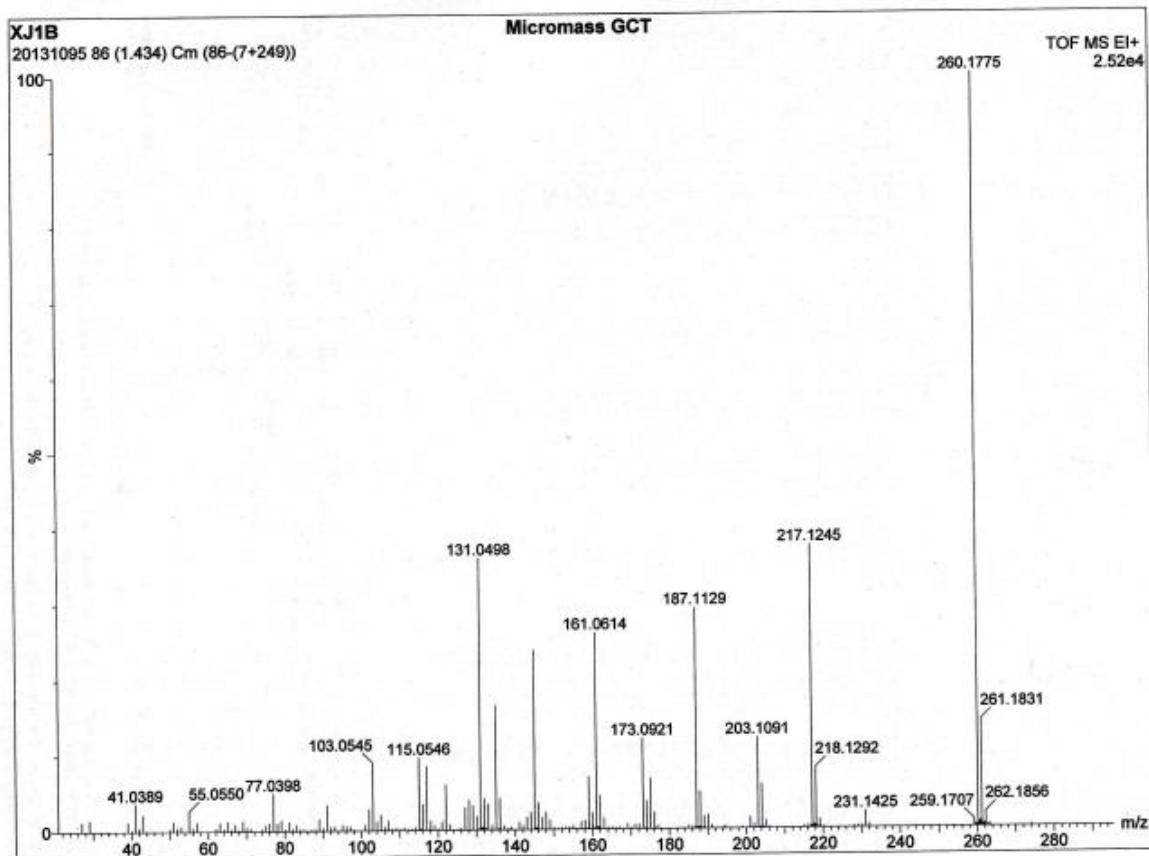
**<sup>1</sup>H NMR spectra of 3ef**



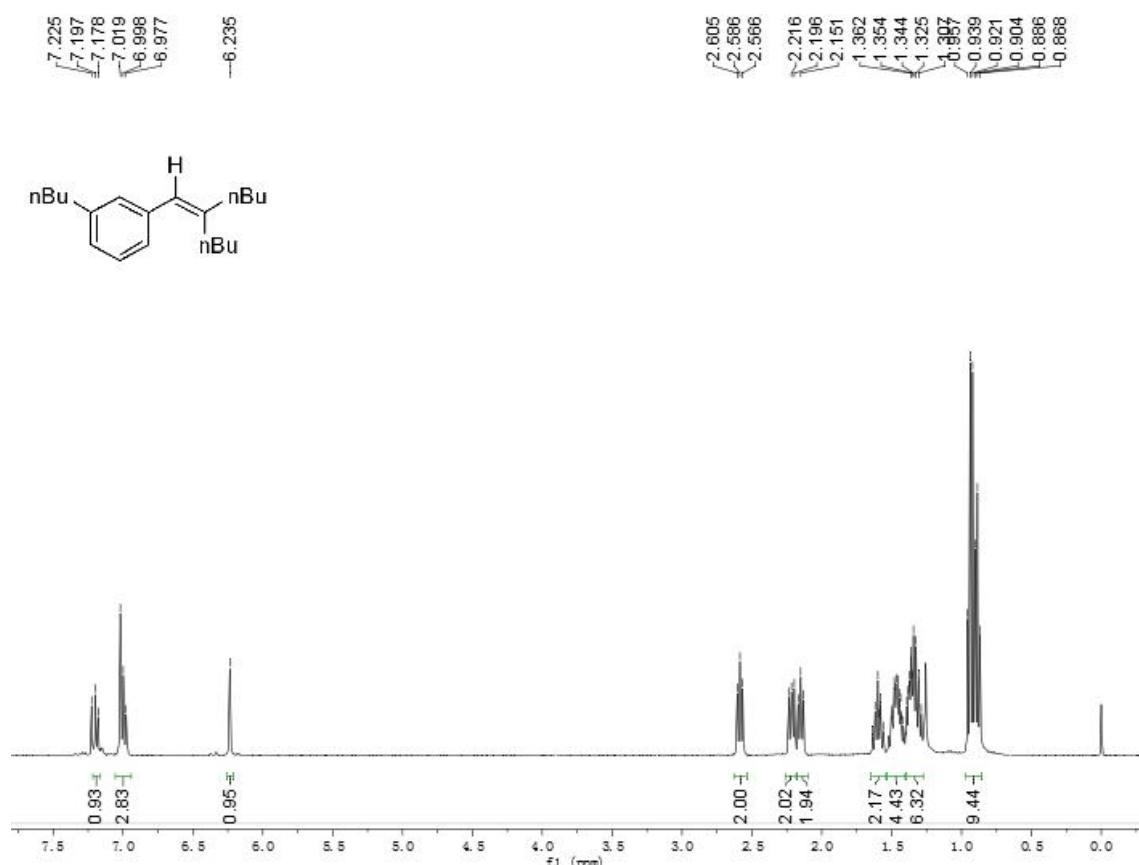
<sup>13</sup>C NMR spectra of 3ef



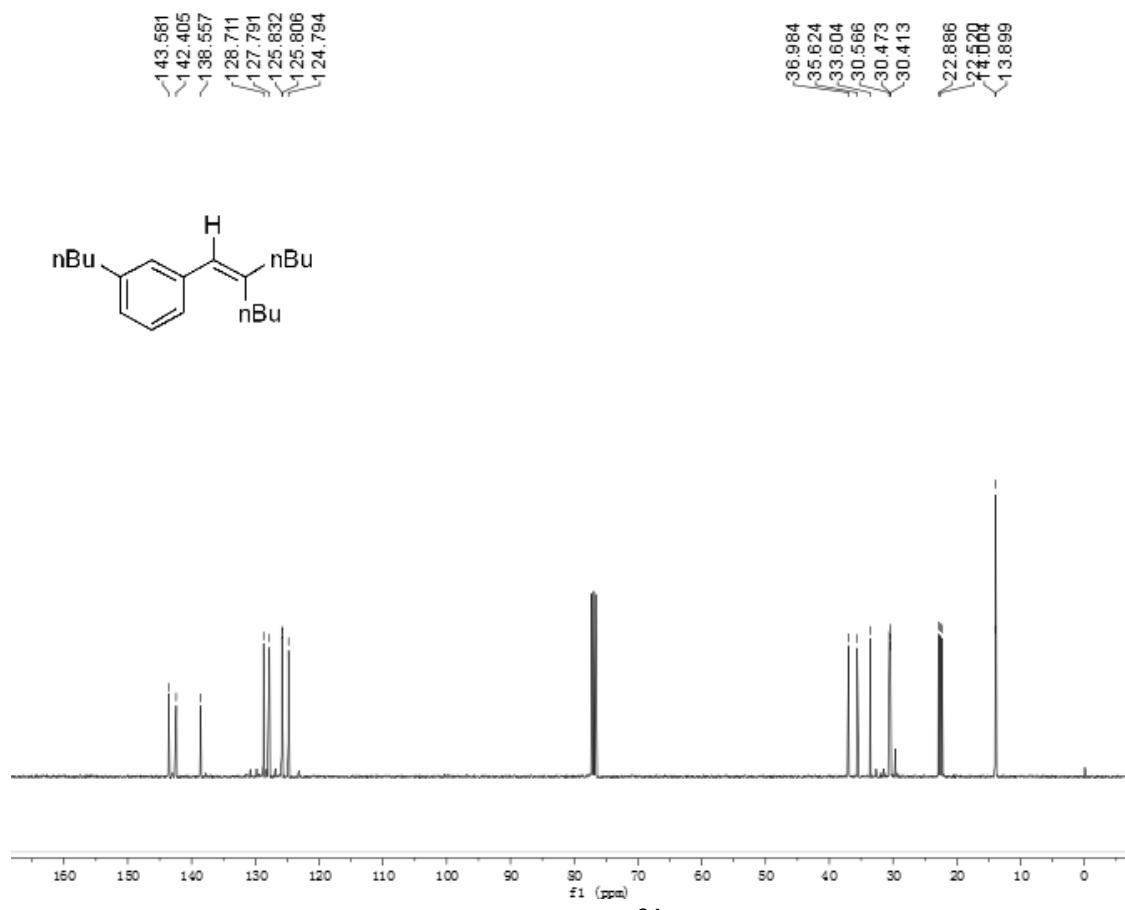
HRMS (EI) spectra of 3ef



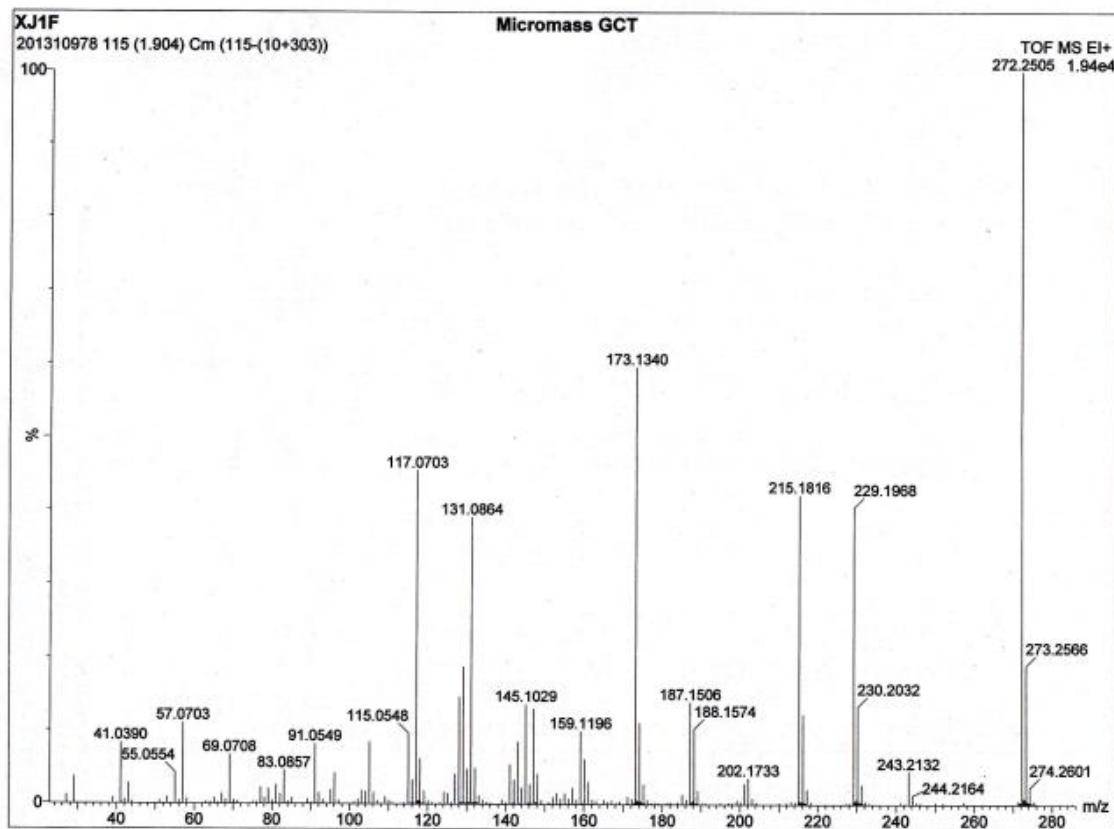
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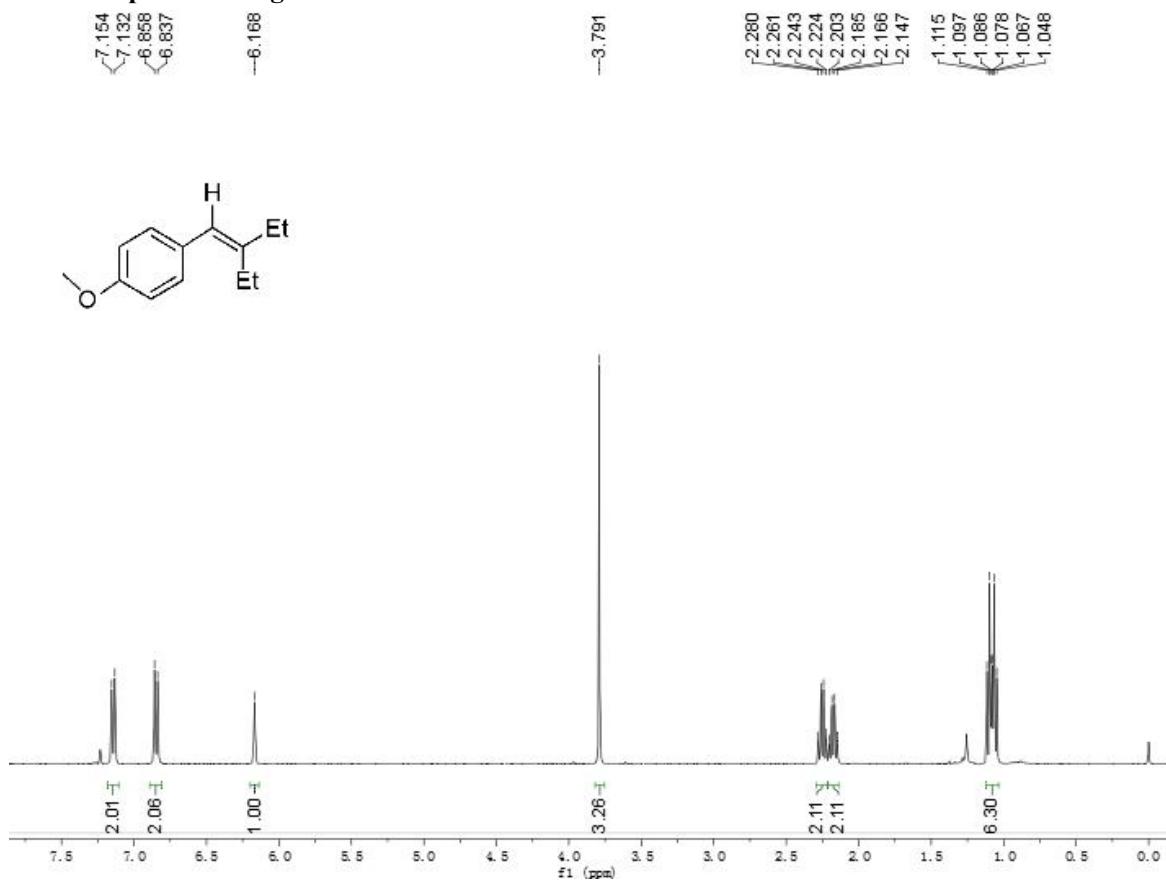
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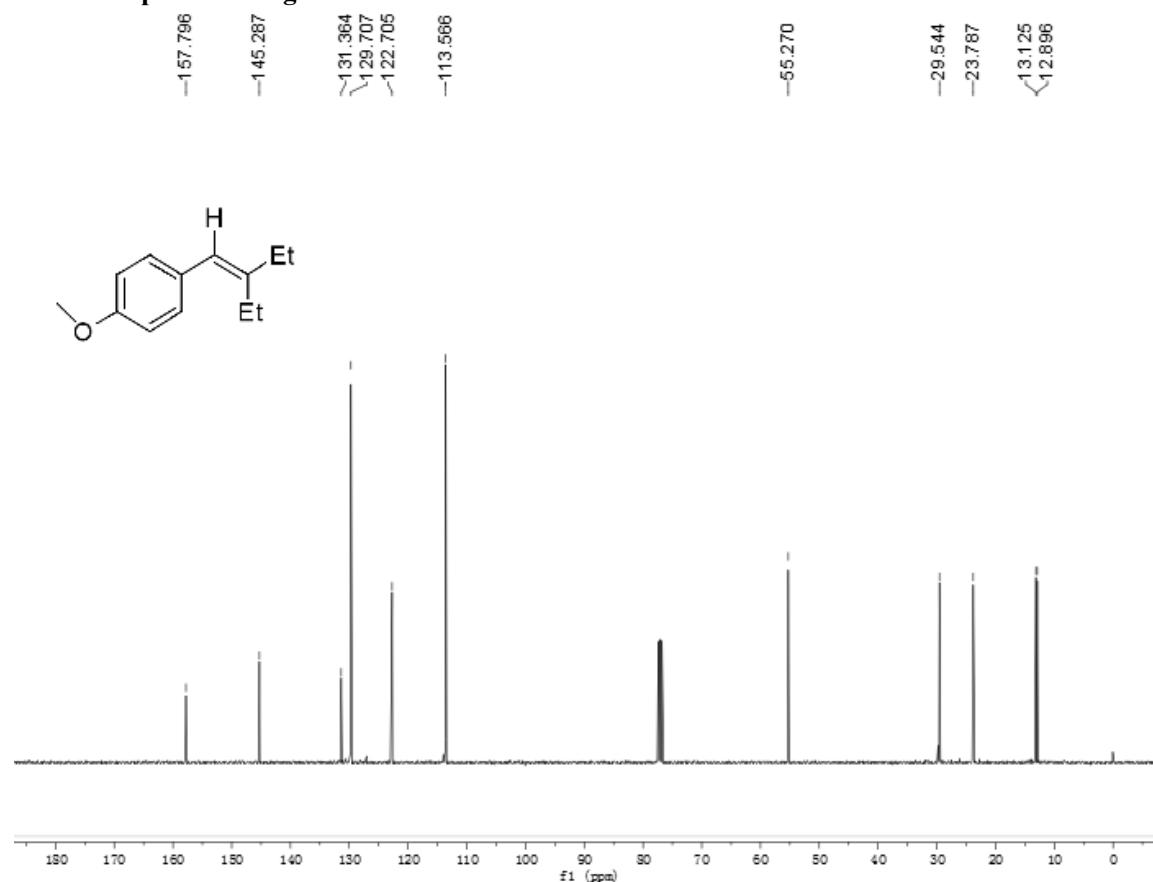
**HRMS (EI) spectra of 3ff**



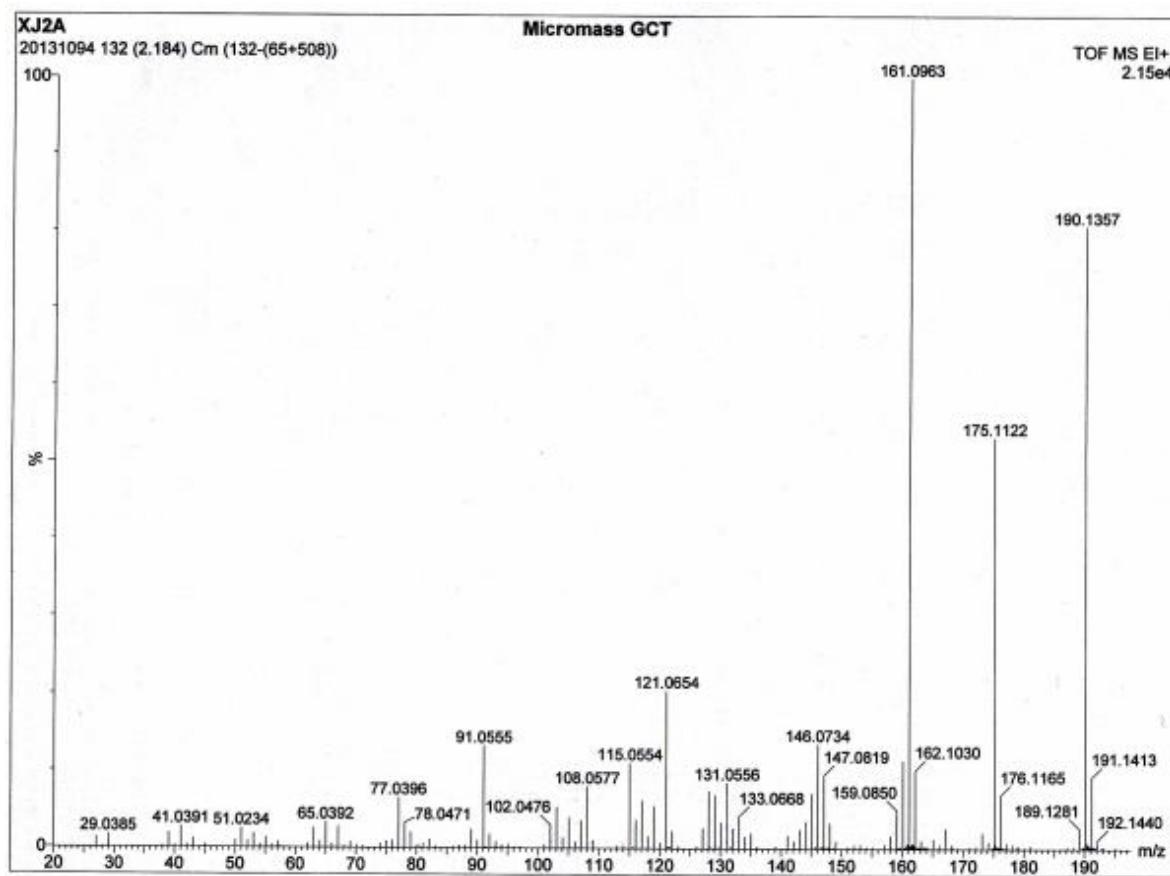
**<sup>1</sup>H NMR spectra of 3ag**



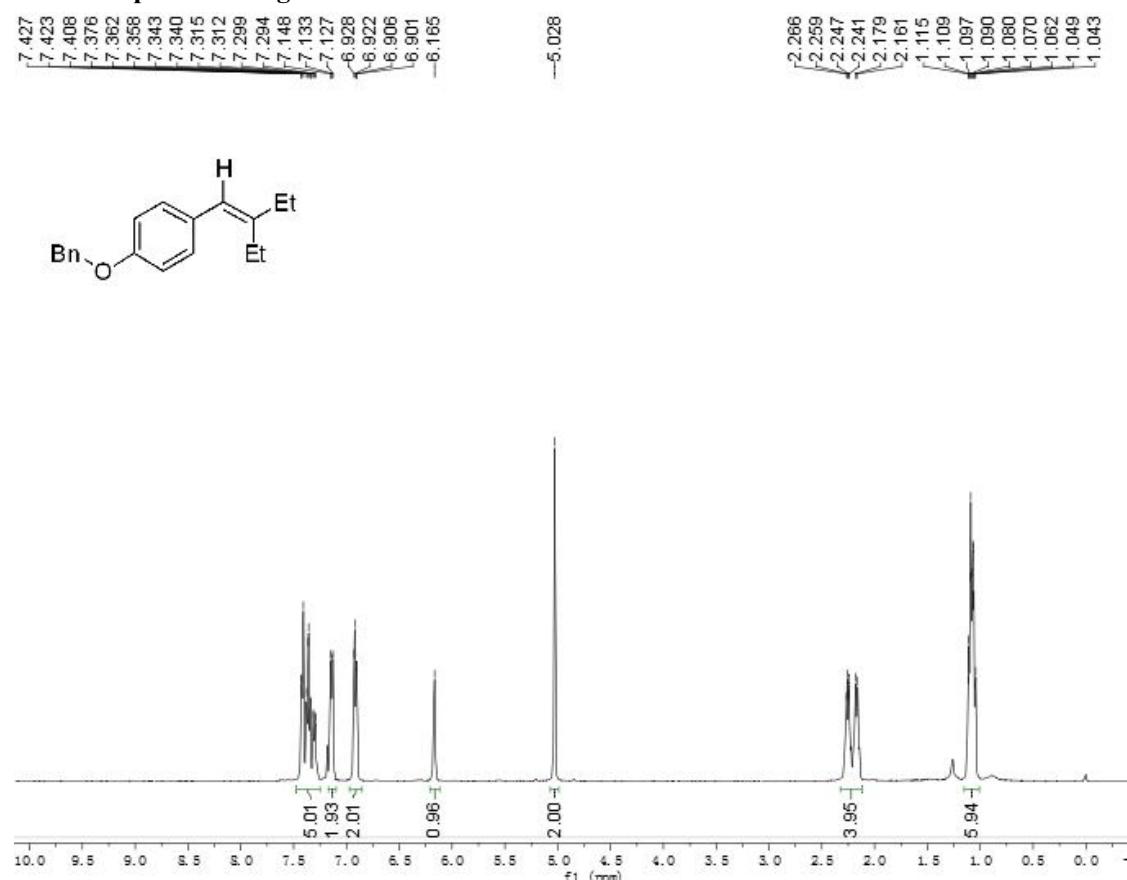
<sup>13</sup>C NMR spectra of 3ag



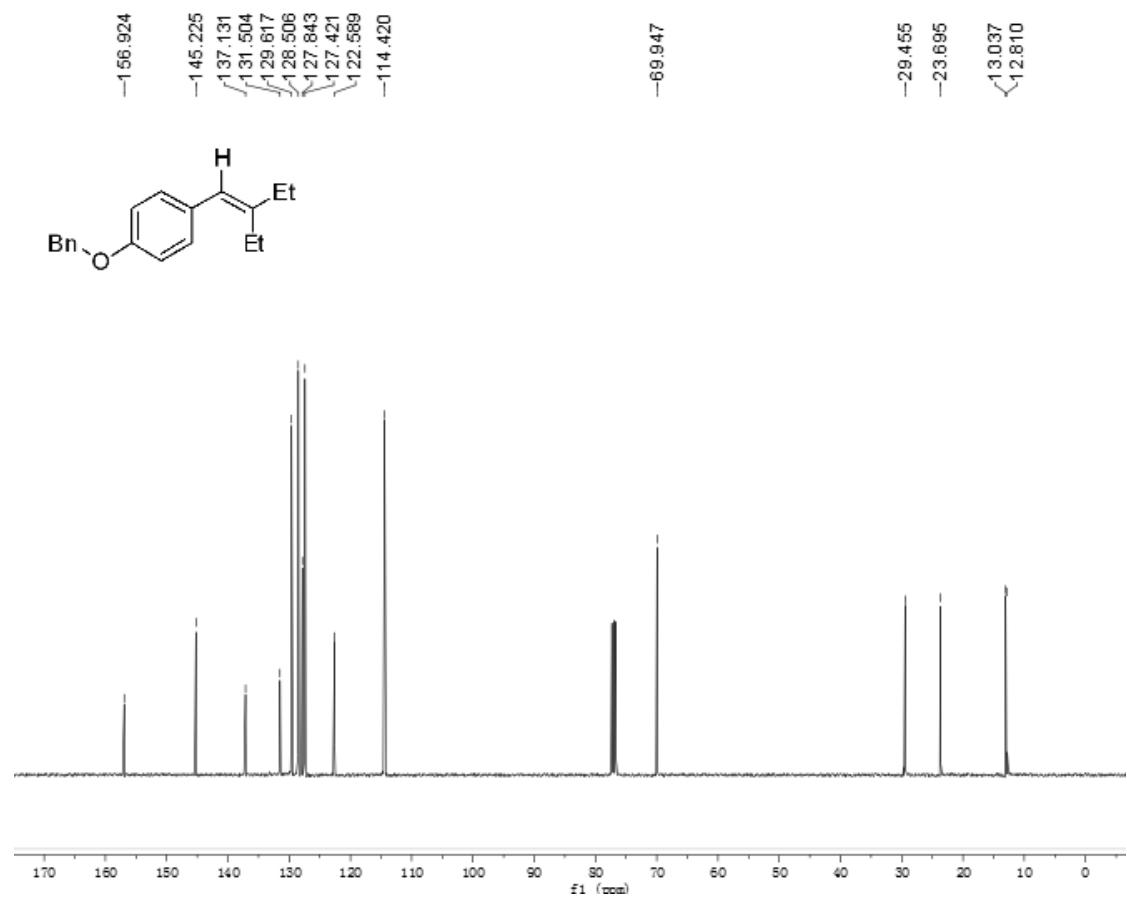
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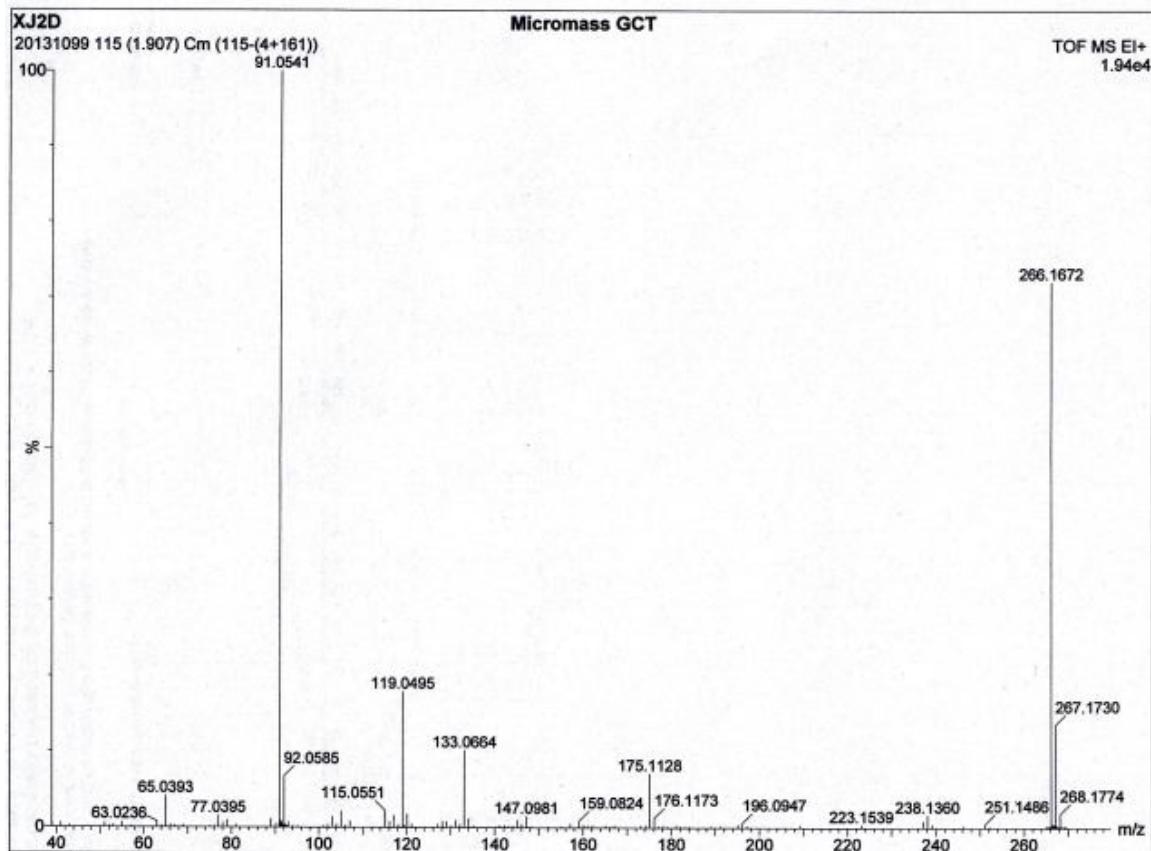
**<sup>1</sup>H NMR spectra of 3bg**



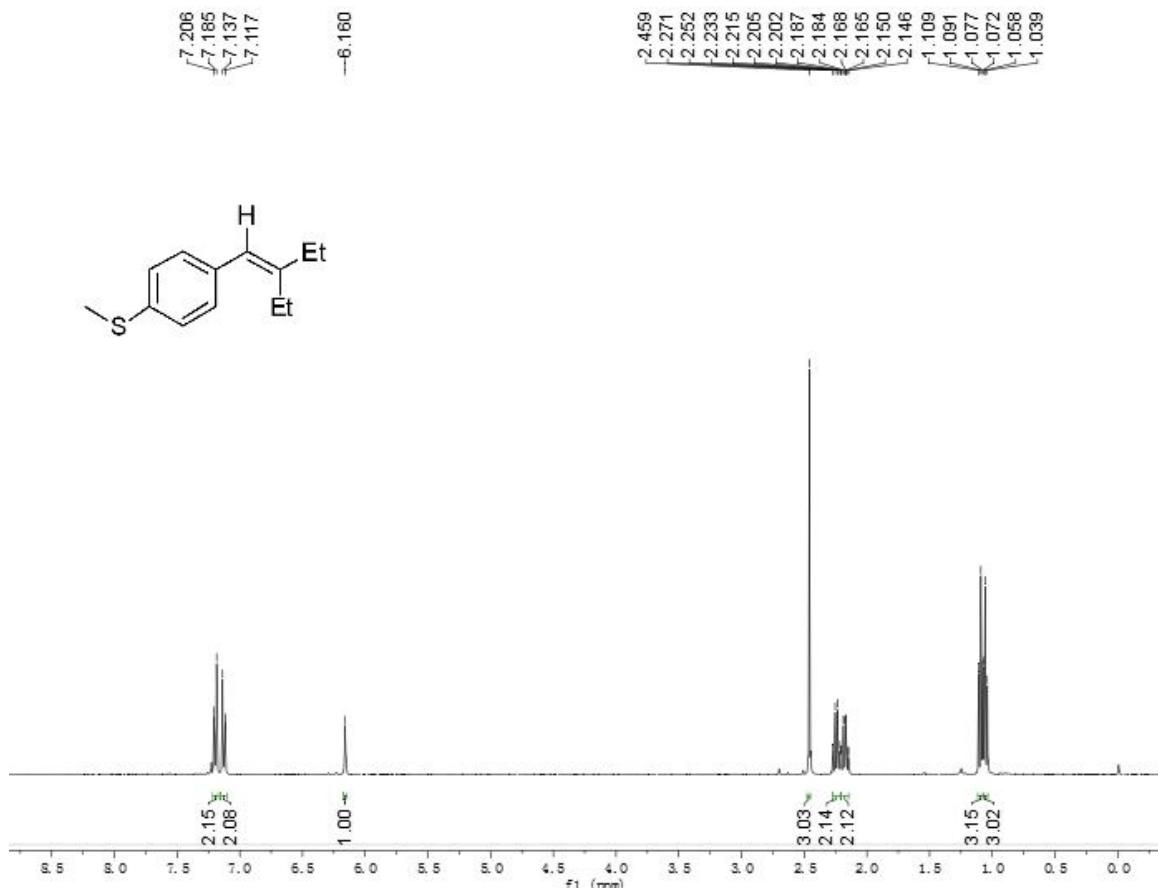
**<sup>13</sup>C NMR spectra of 3bg**



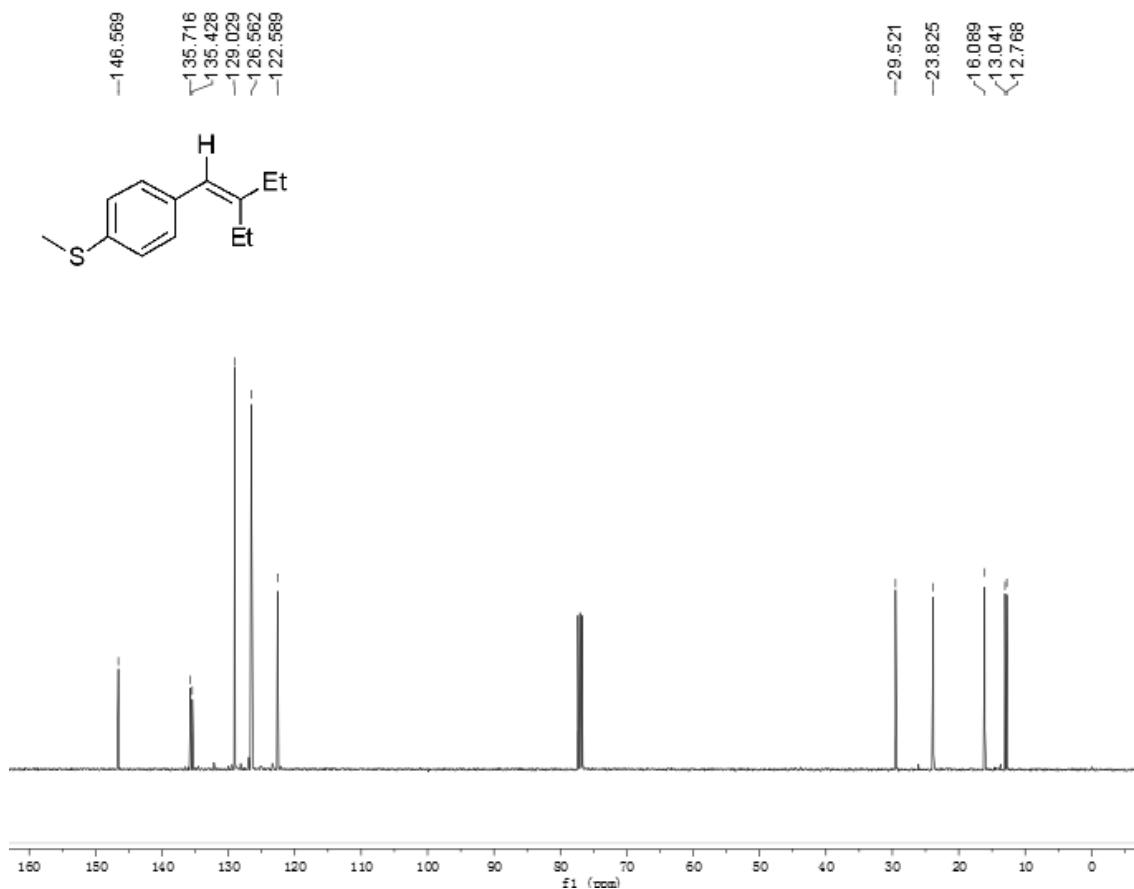
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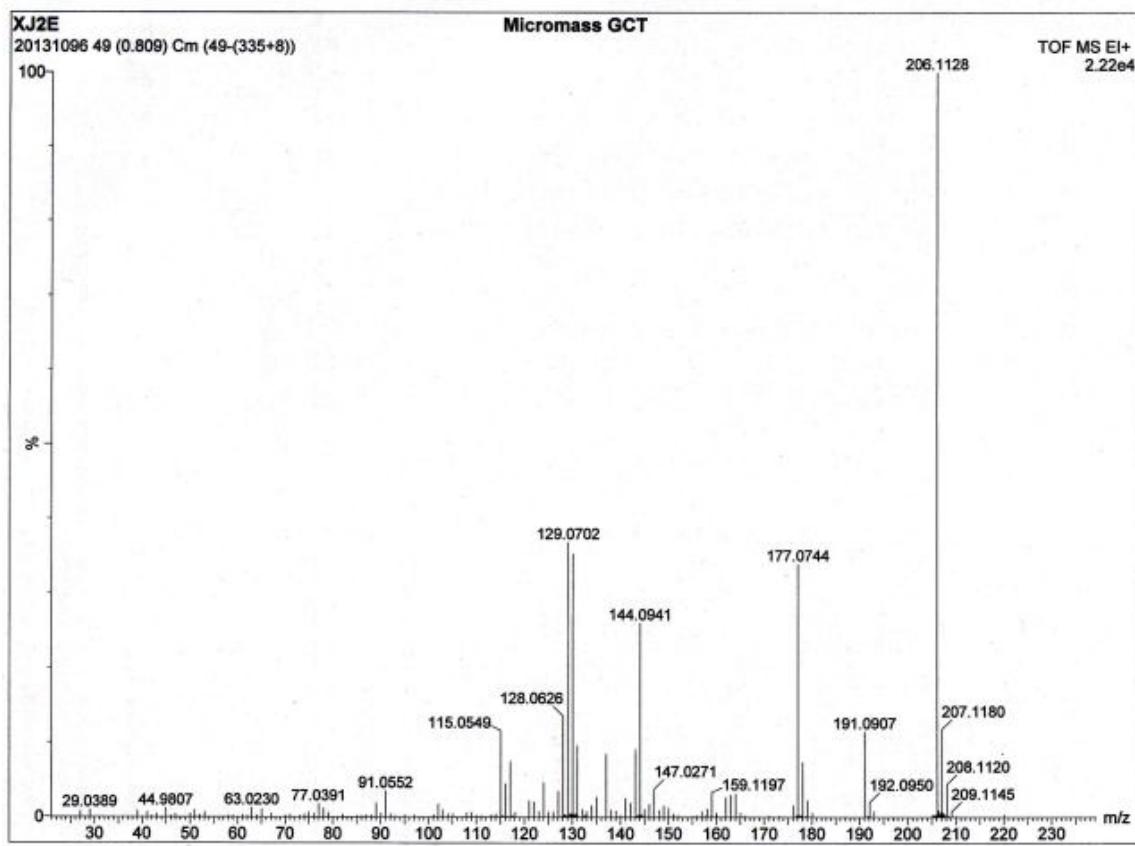
**<sup>1</sup>H NMR spectra of 3cg**



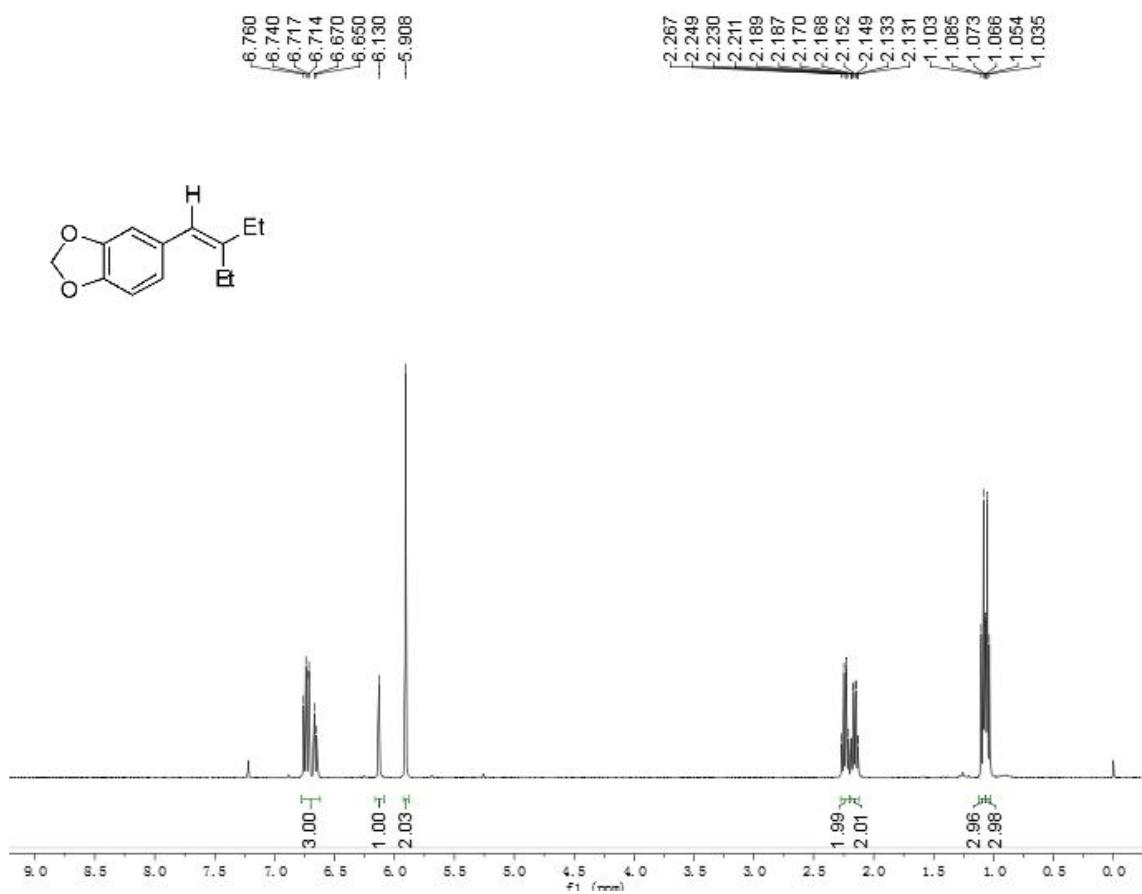
<sup>13</sup>C NMR spectra of 3cg



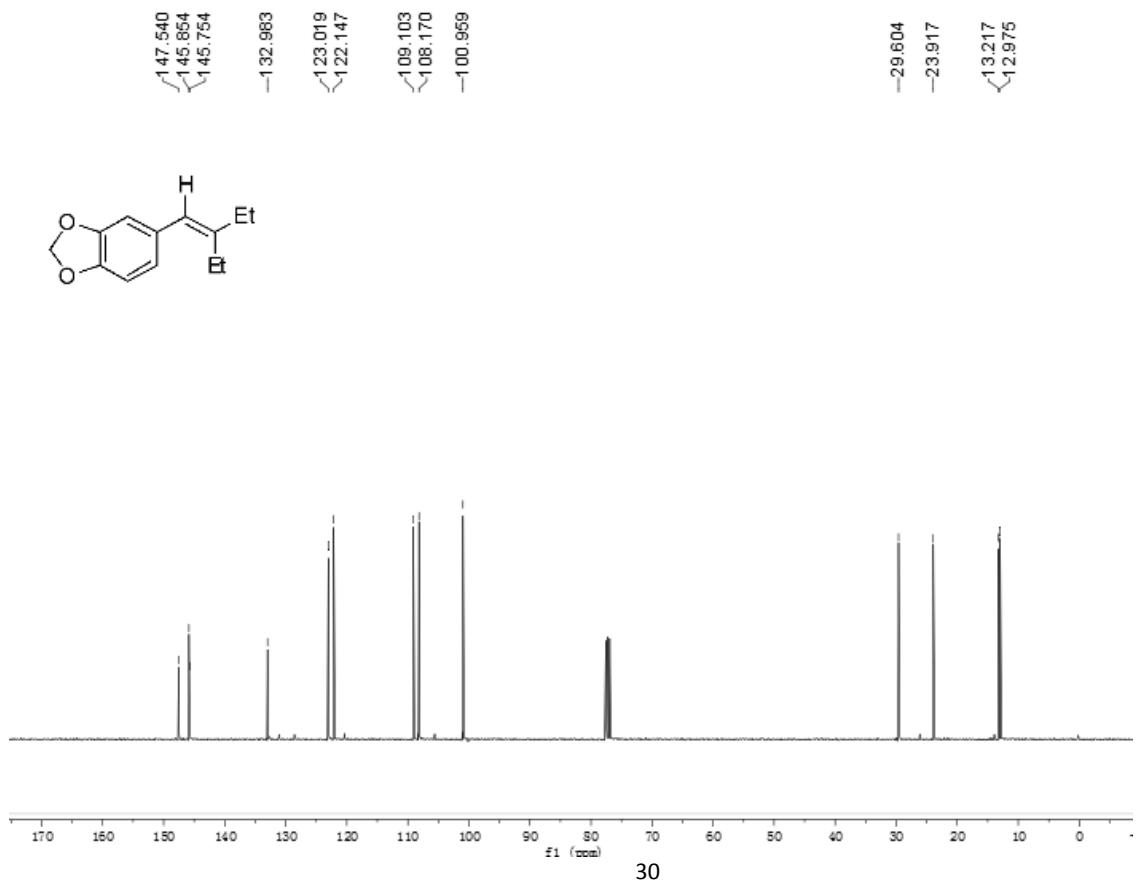
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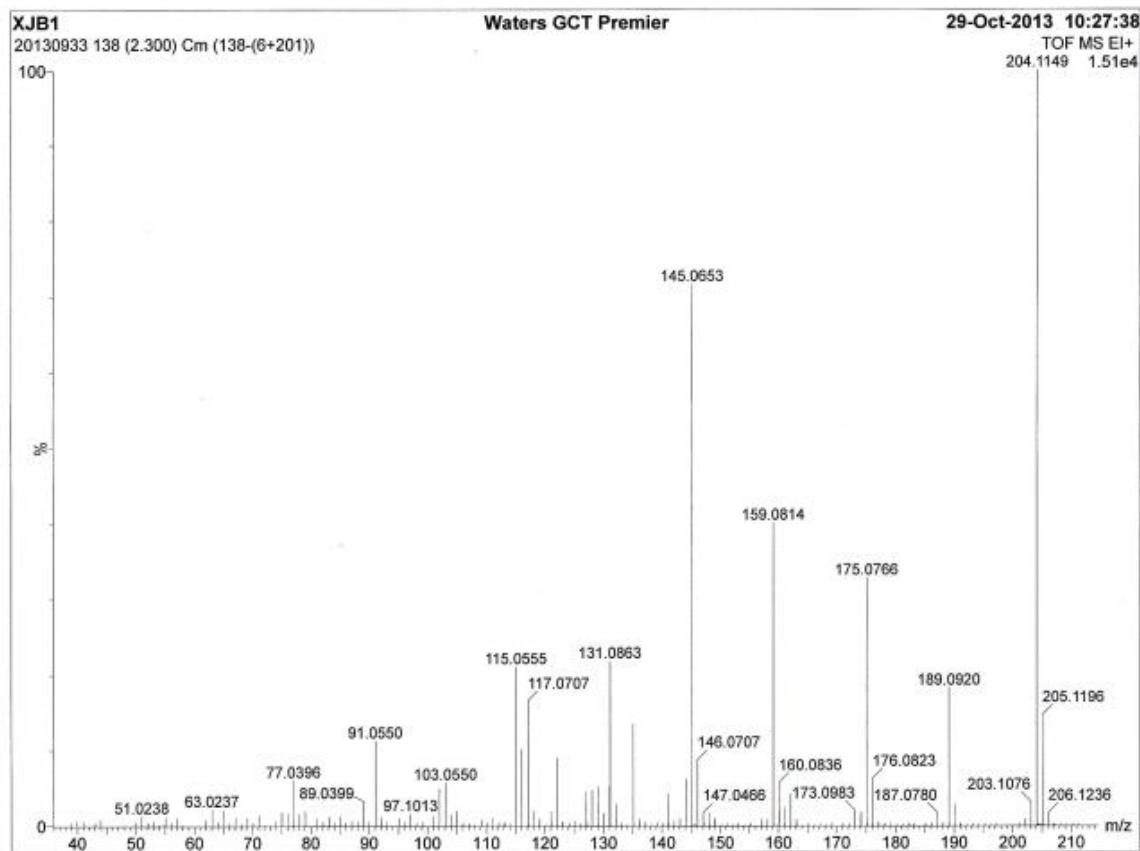
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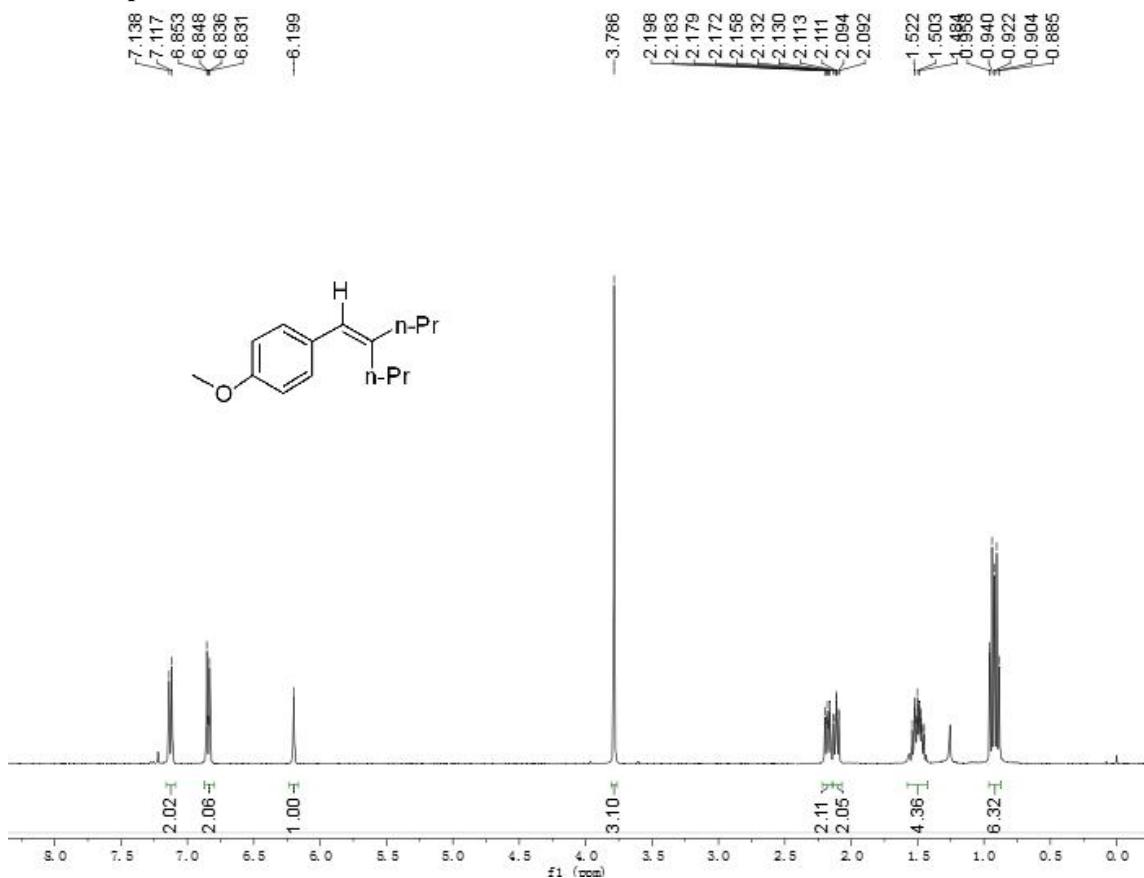
<sup>13</sup>C NMR spectra of 3eg



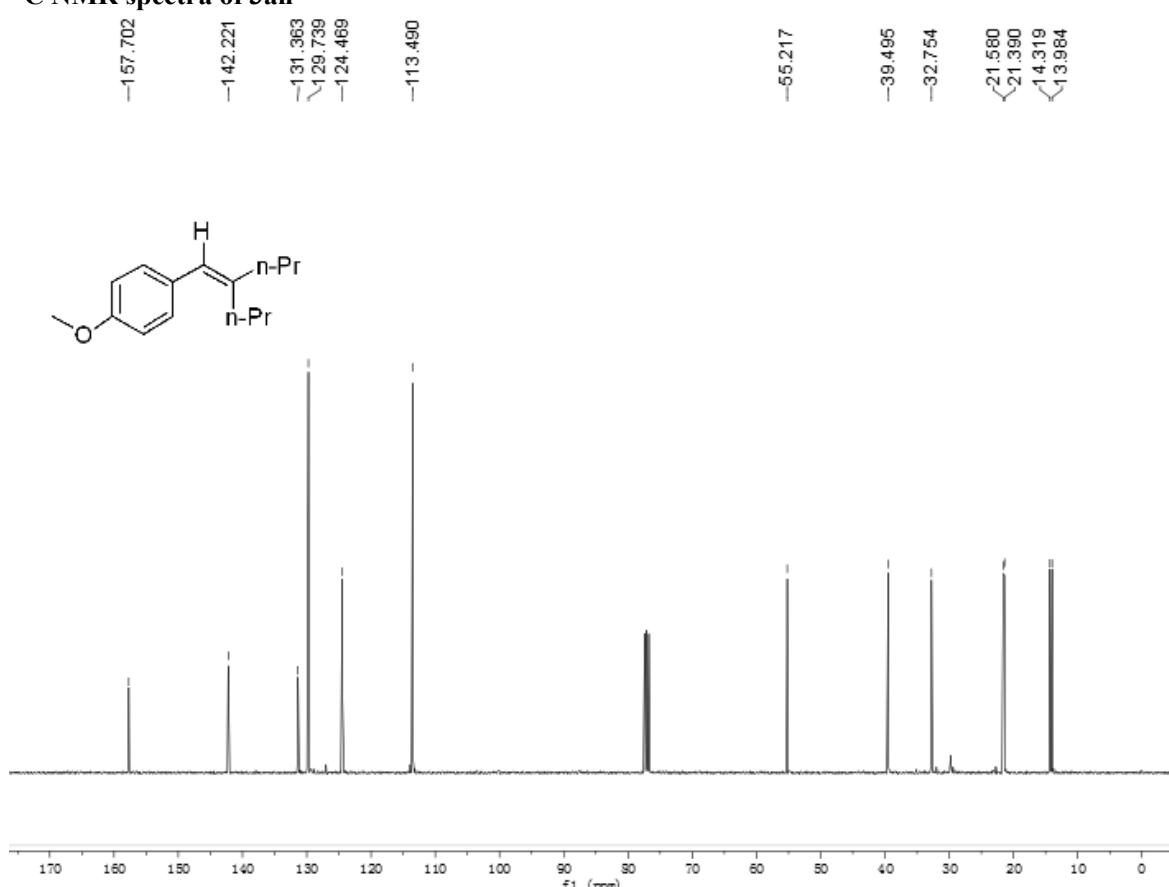
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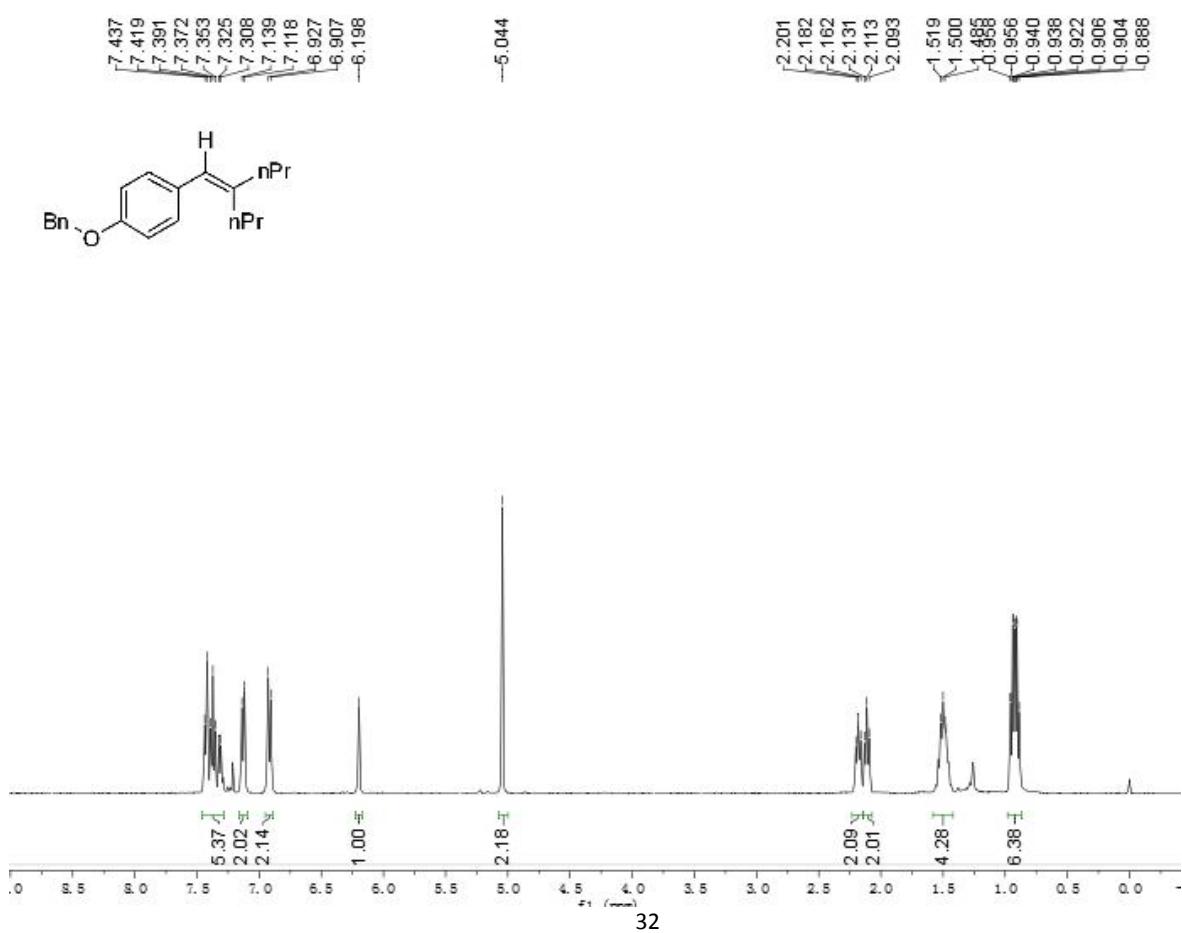
**<sup>1</sup>H NMR spectra of 3ah**



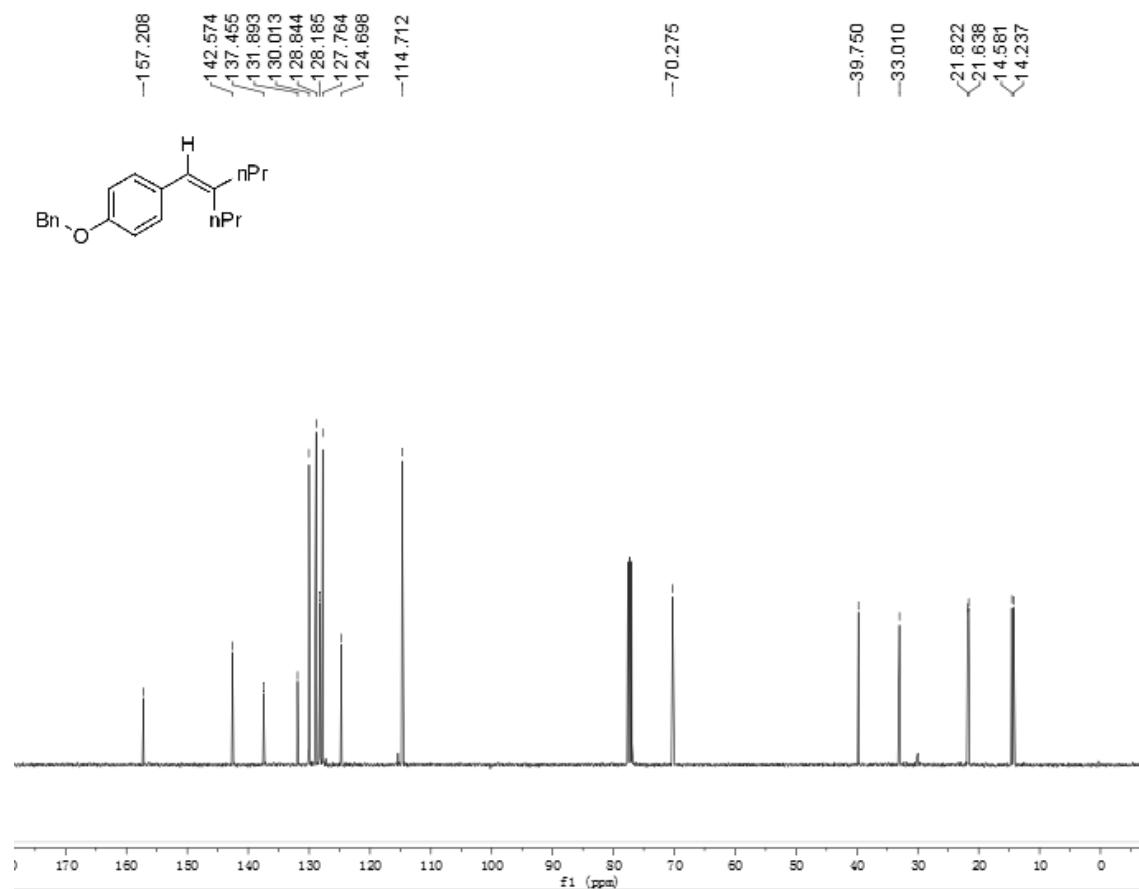
<sup>13</sup>C NMR spectra of 3ah



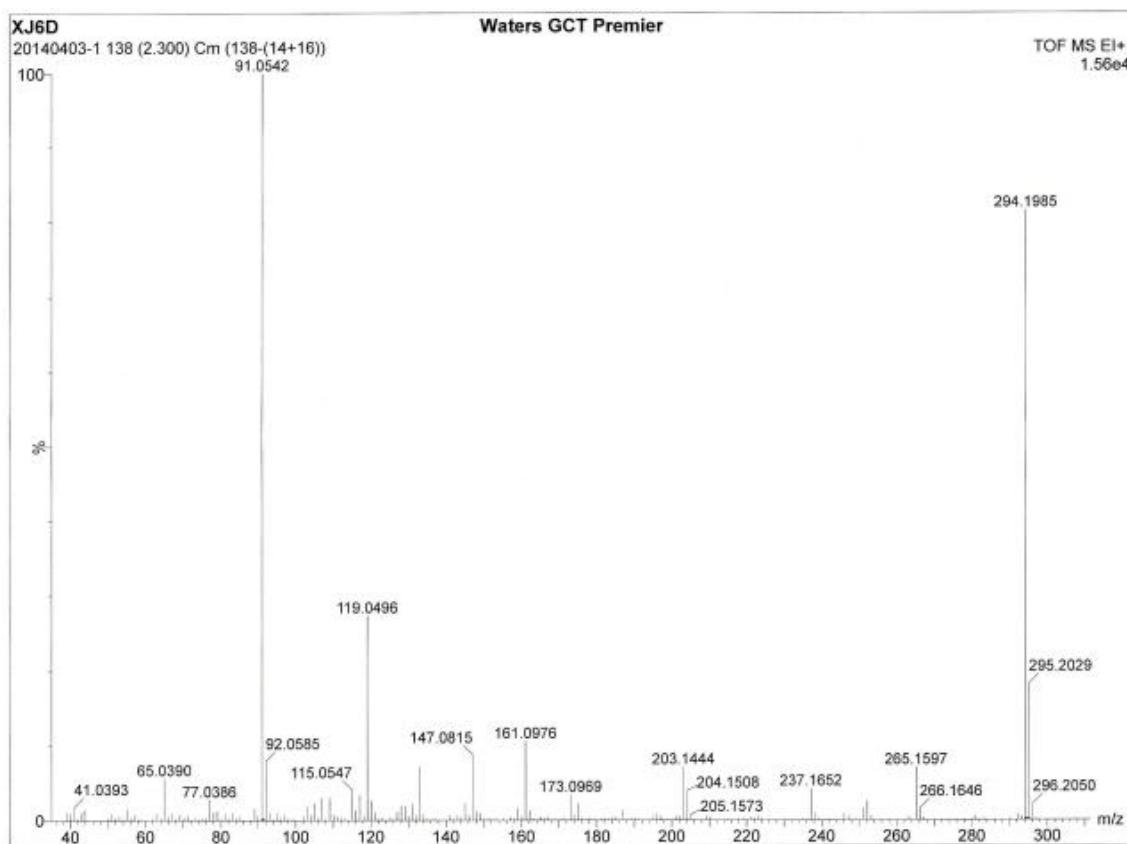
<sup>1</sup>H NMR spectra of 3bh



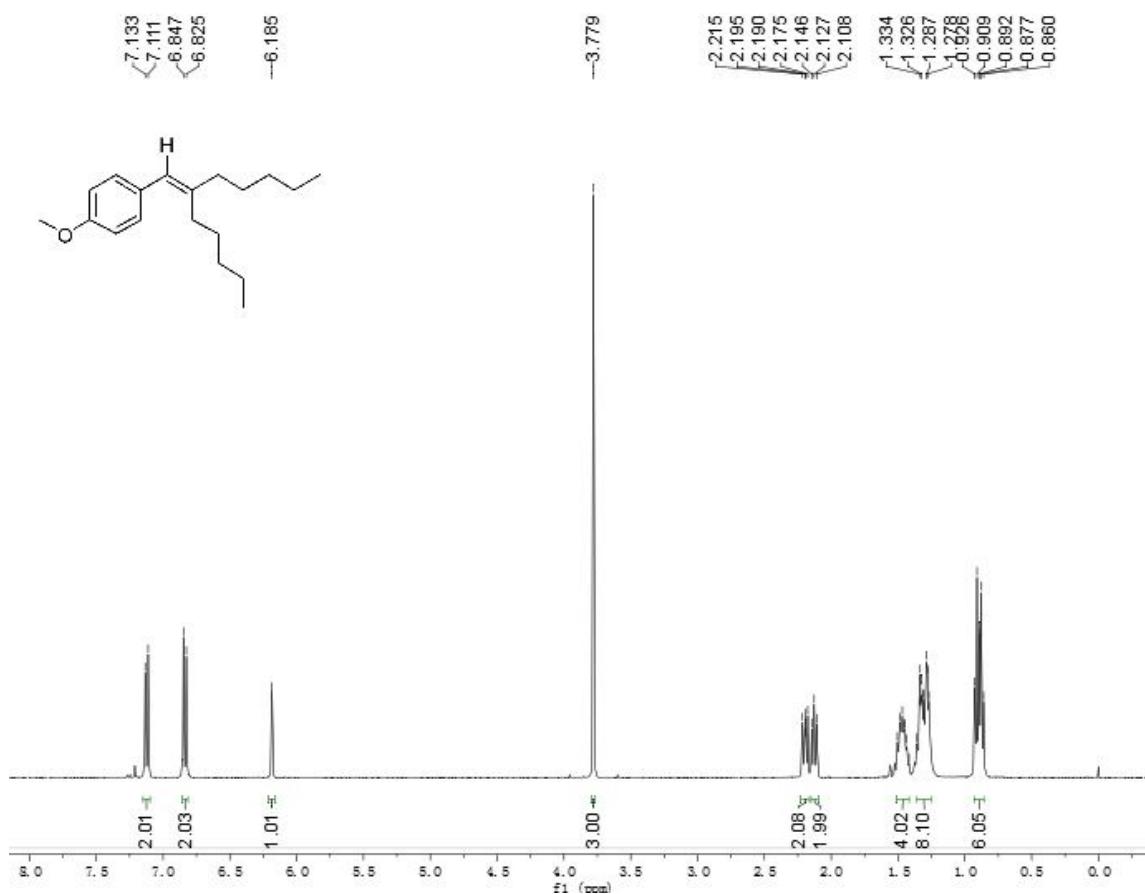
<sup>13</sup>C NMR spectra of 3bh



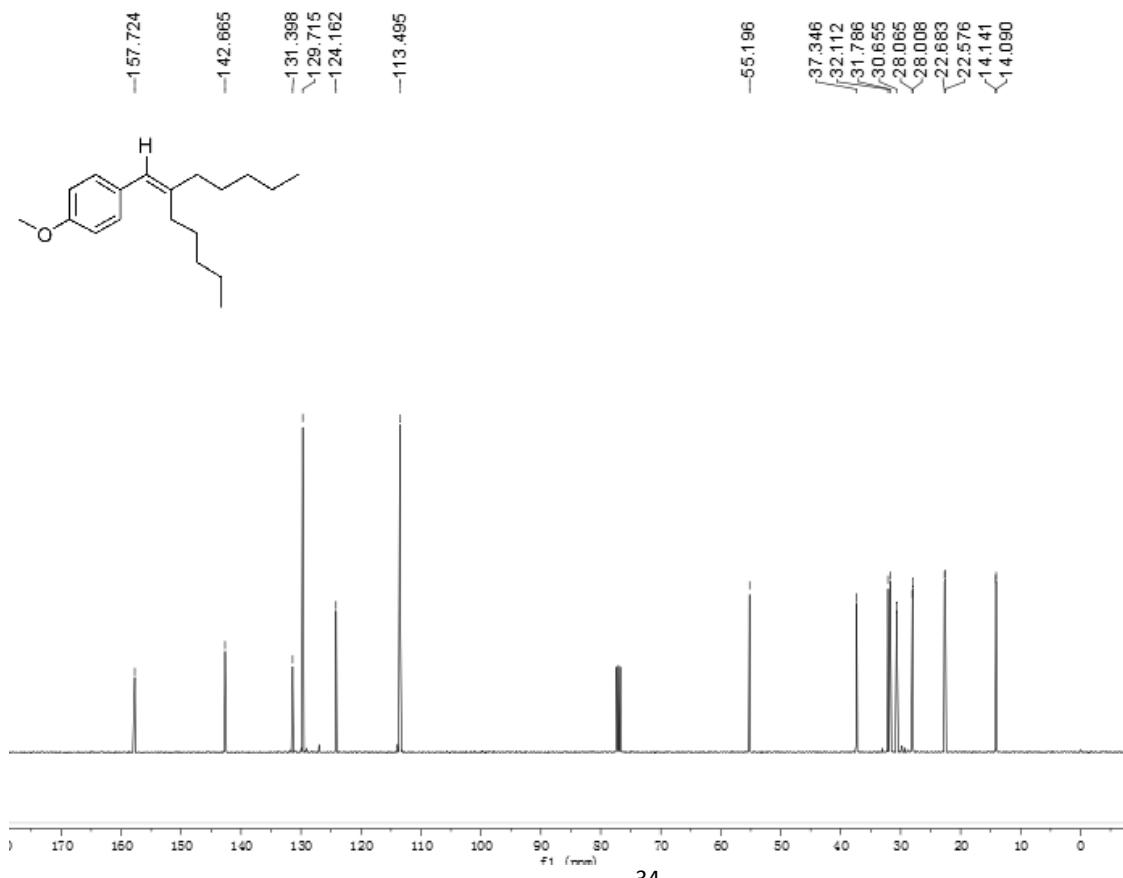
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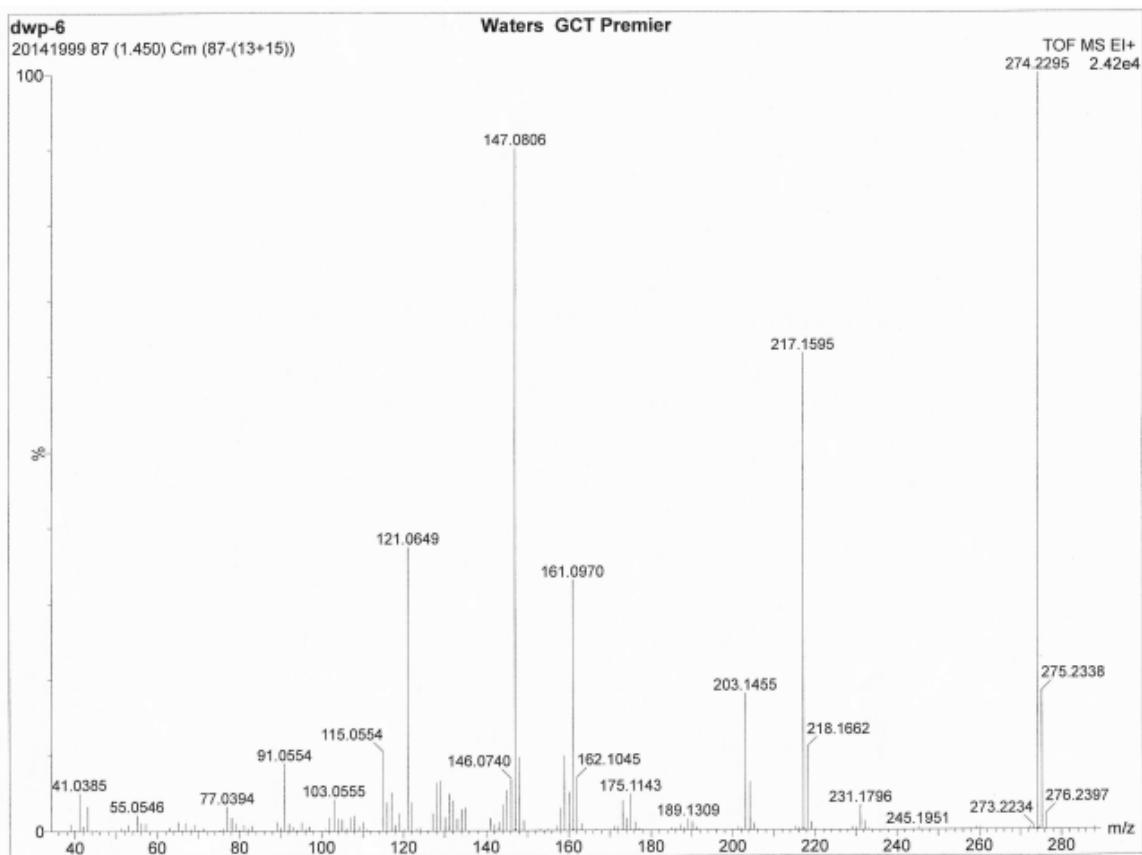
<sup>1</sup>H NMR spectra of 3ai



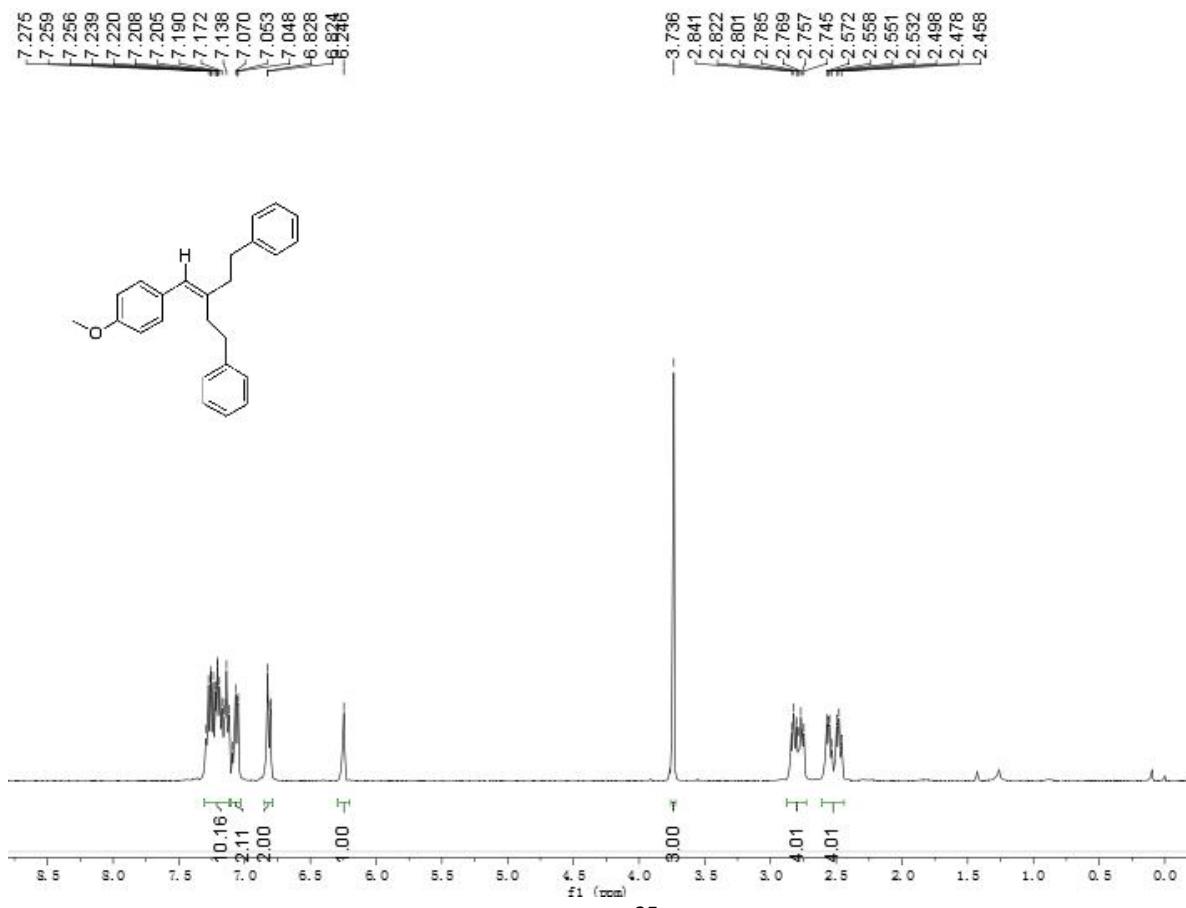
<sup>13</sup>C NMR spectra of 3ai



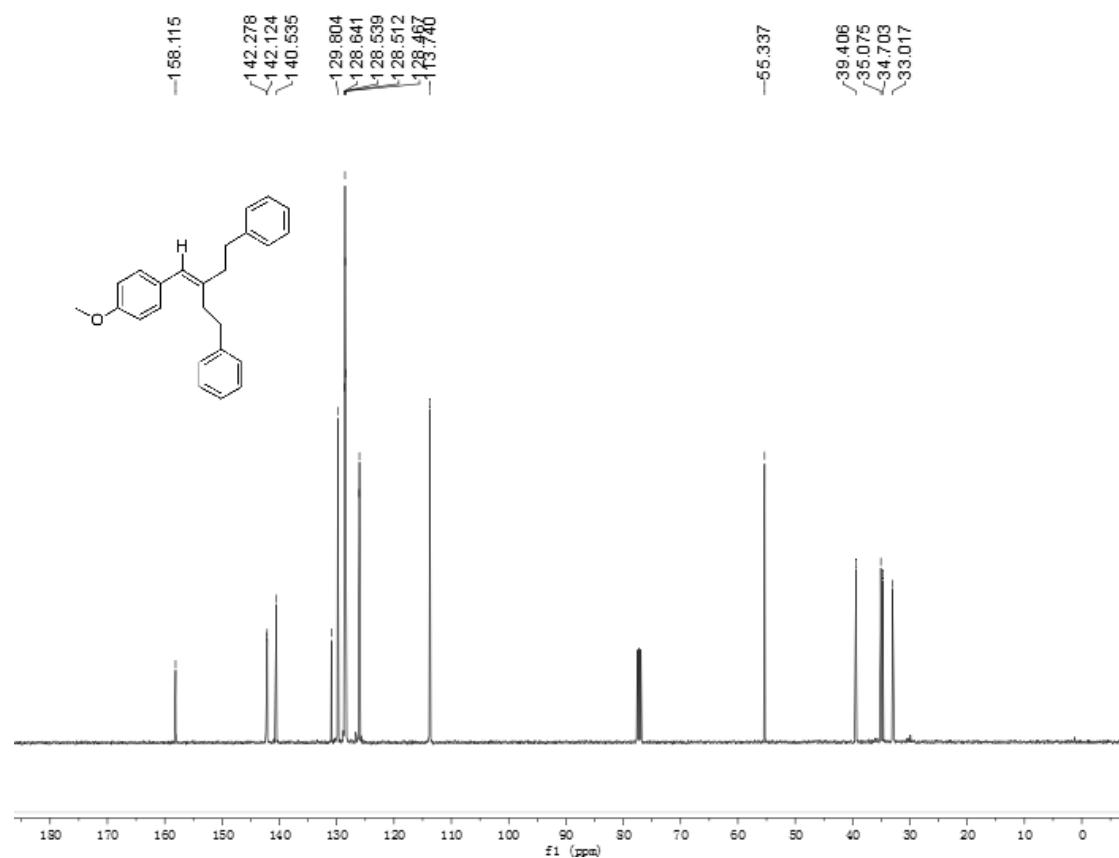
### HRMS (EI) spectra of 3ai



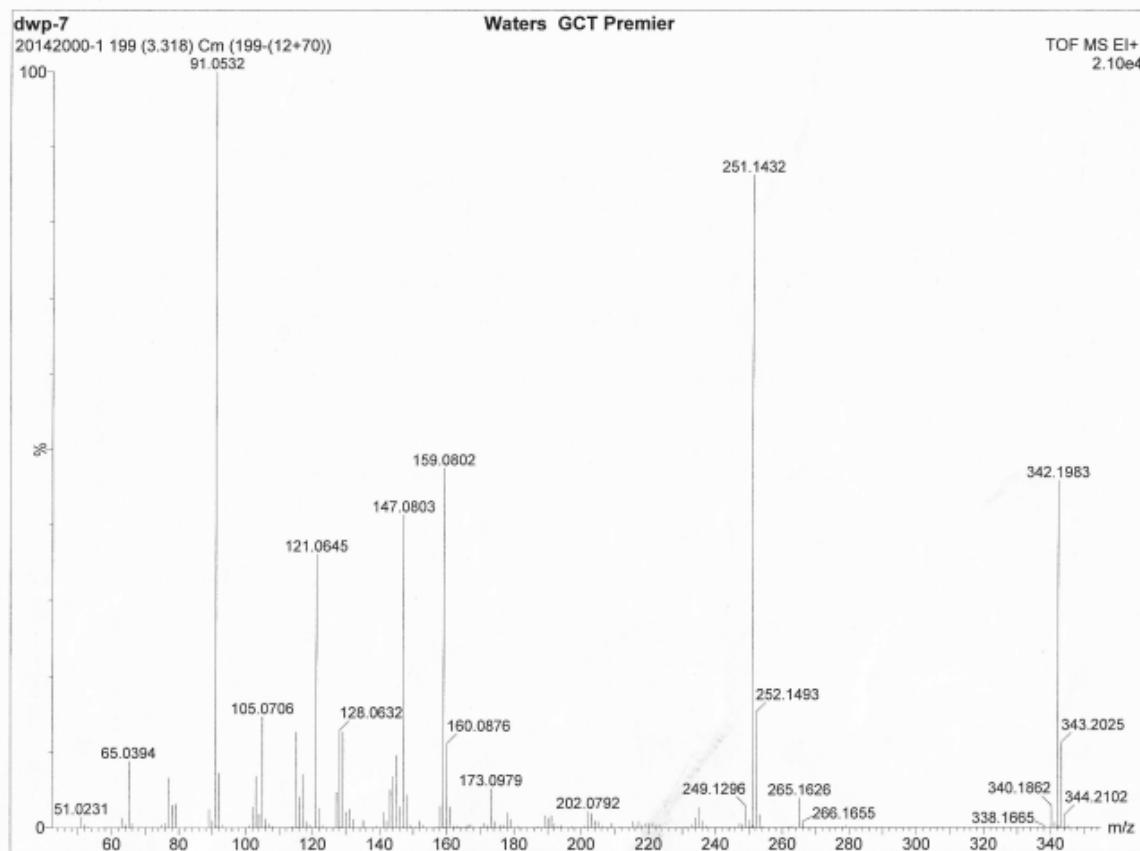
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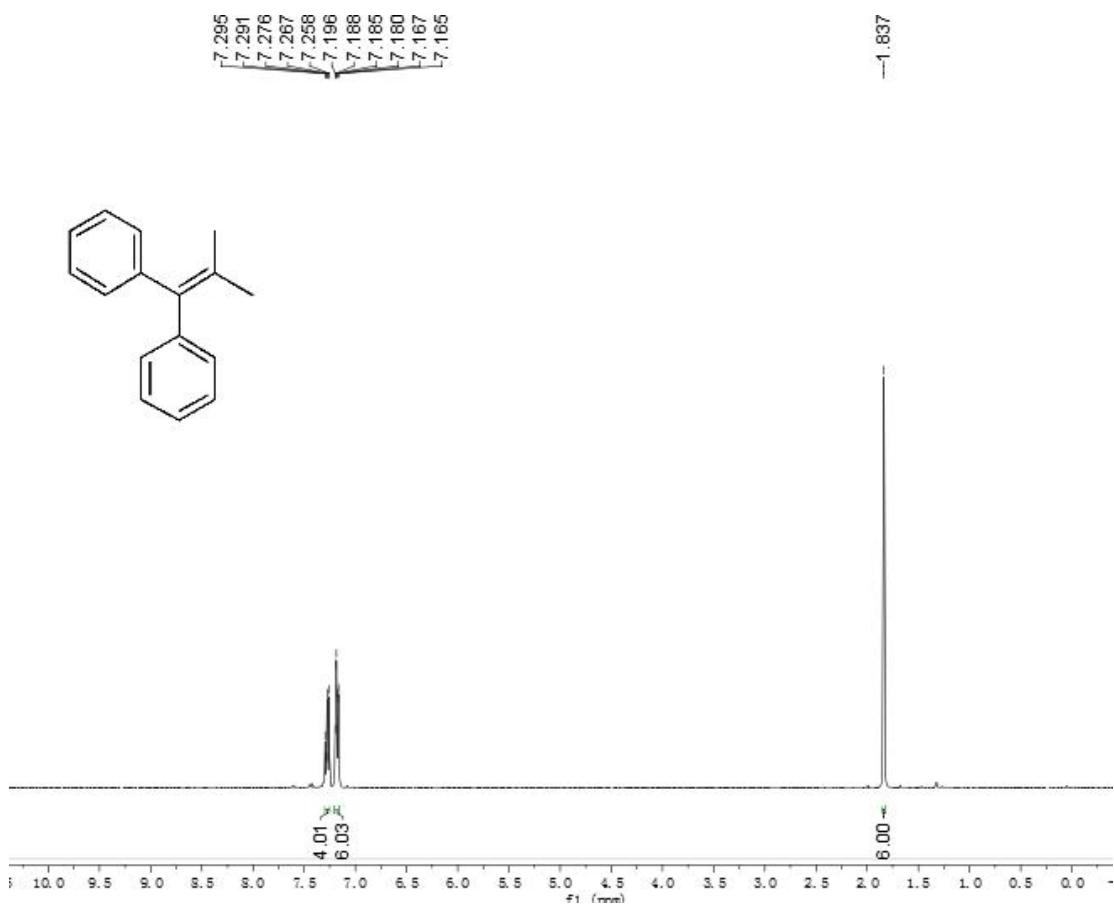
<sup>13</sup>C NMR spectra of 3aj



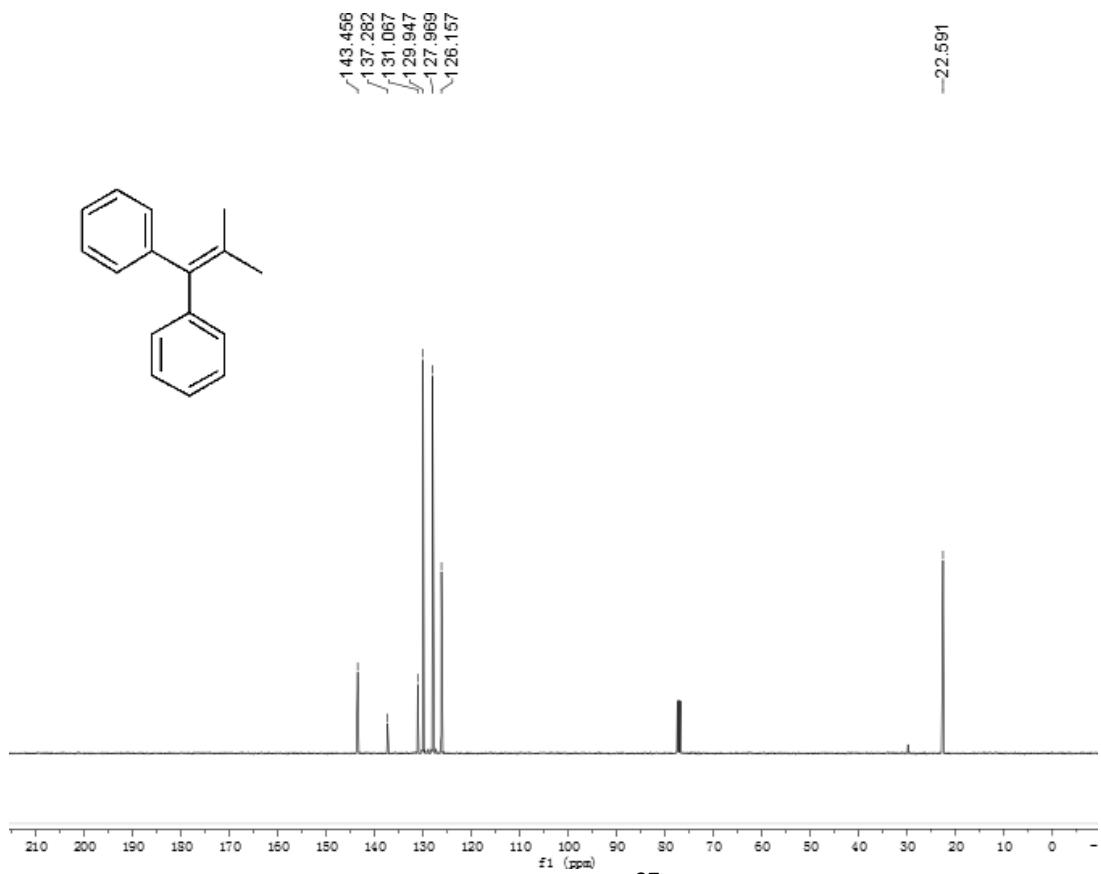
HRMS (EI) spectra of 3aj



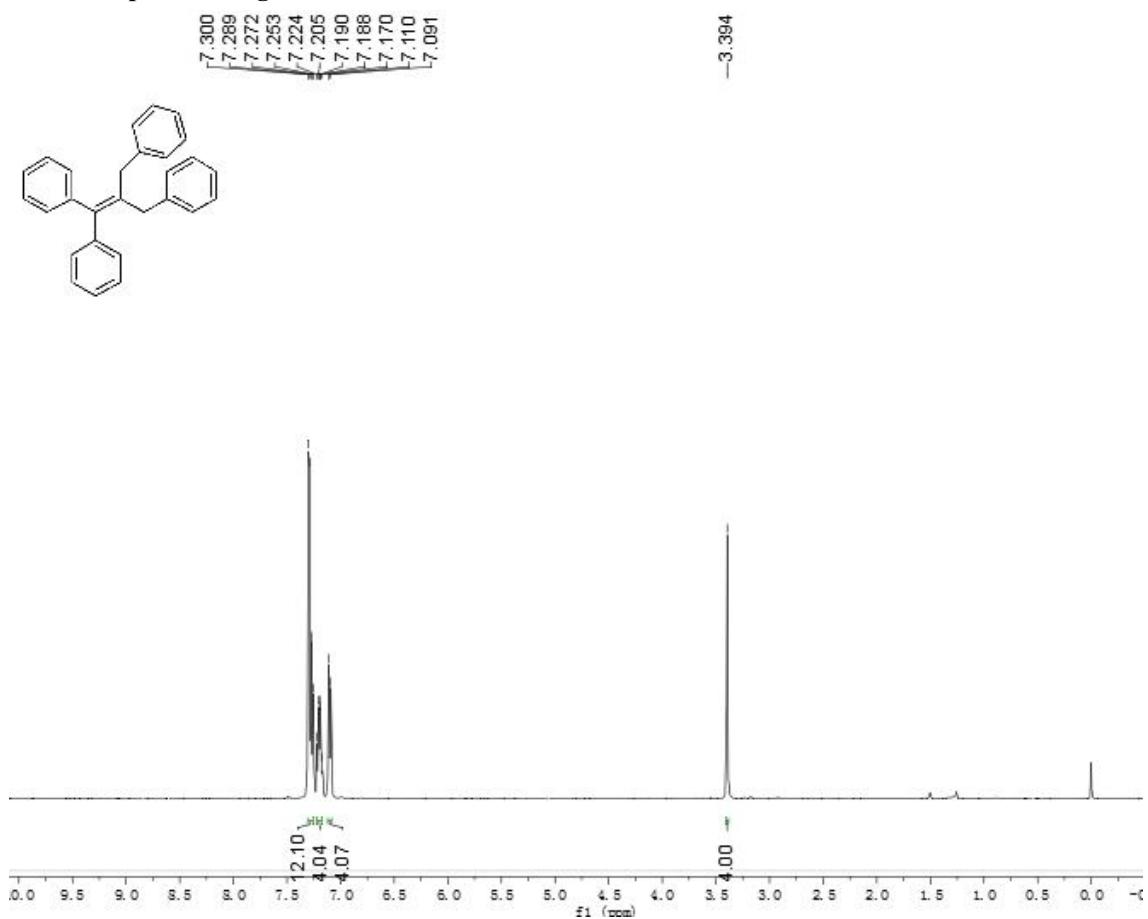
<sup>1</sup>H NMR spectra of 3ga



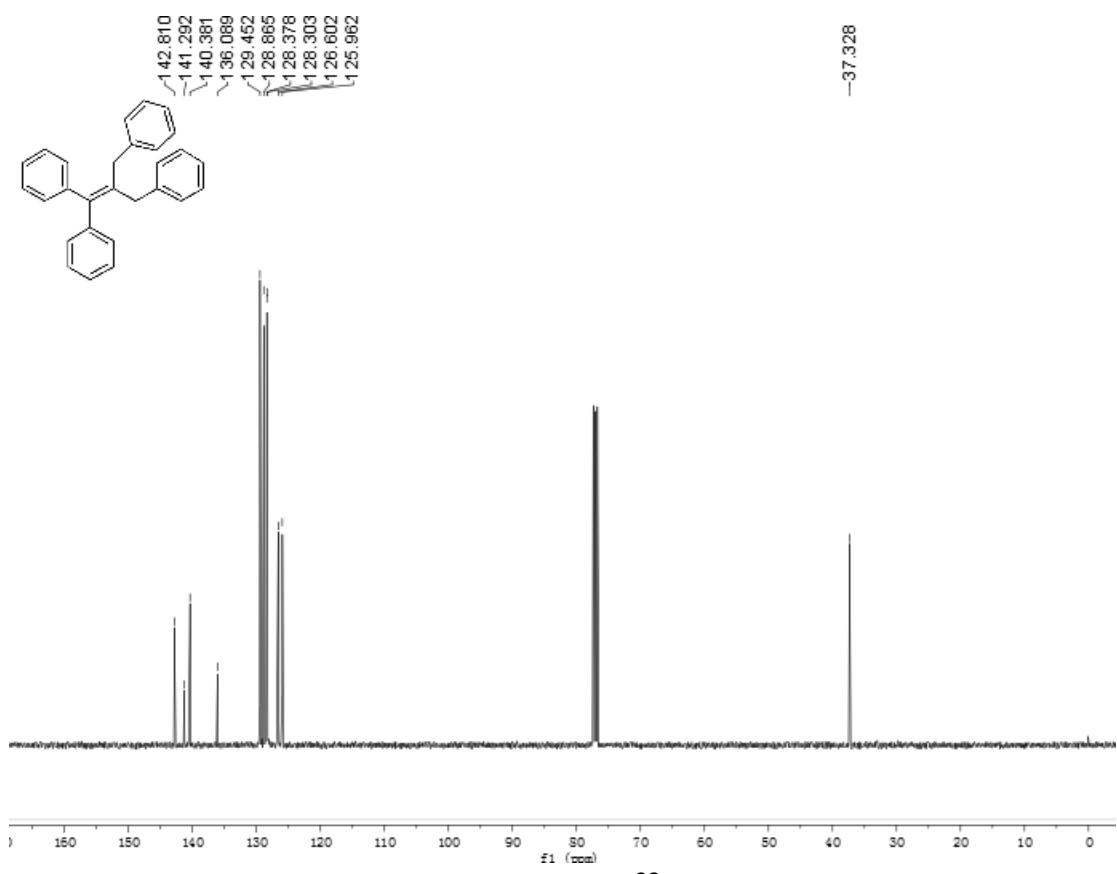
<sup>13</sup>C NMR spectra of 3ga



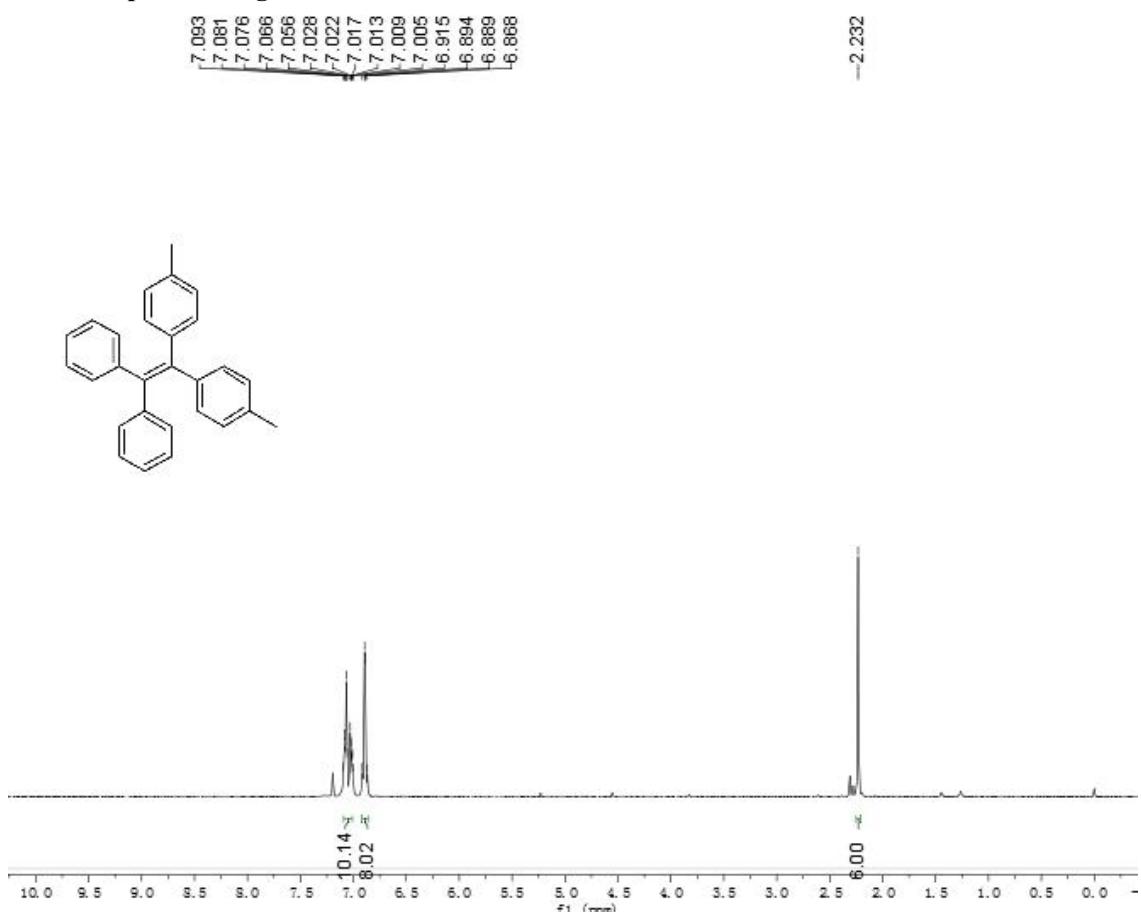
<sup>1</sup>H NMR spectra of 3gc



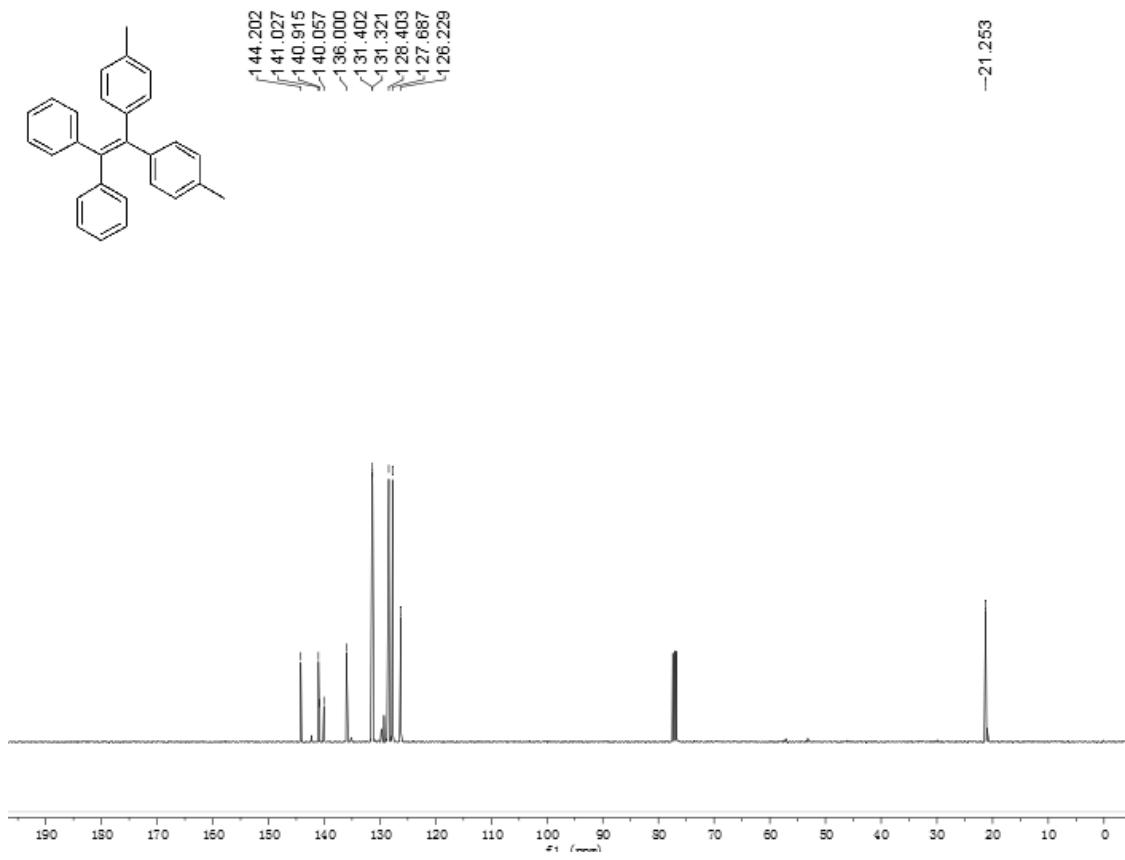
<sup>13</sup>C NMR spectra of 3gc



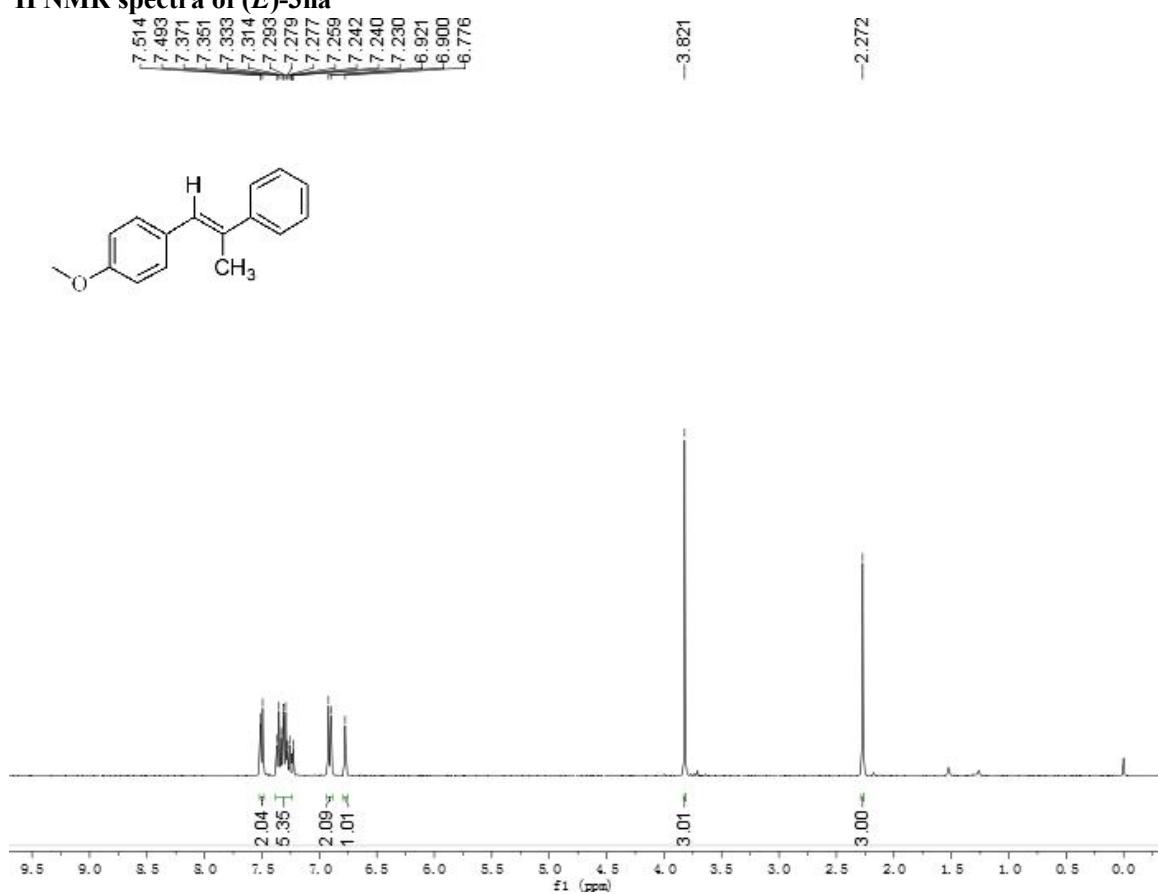
<sup>1</sup>H NMR spectra of 3gd



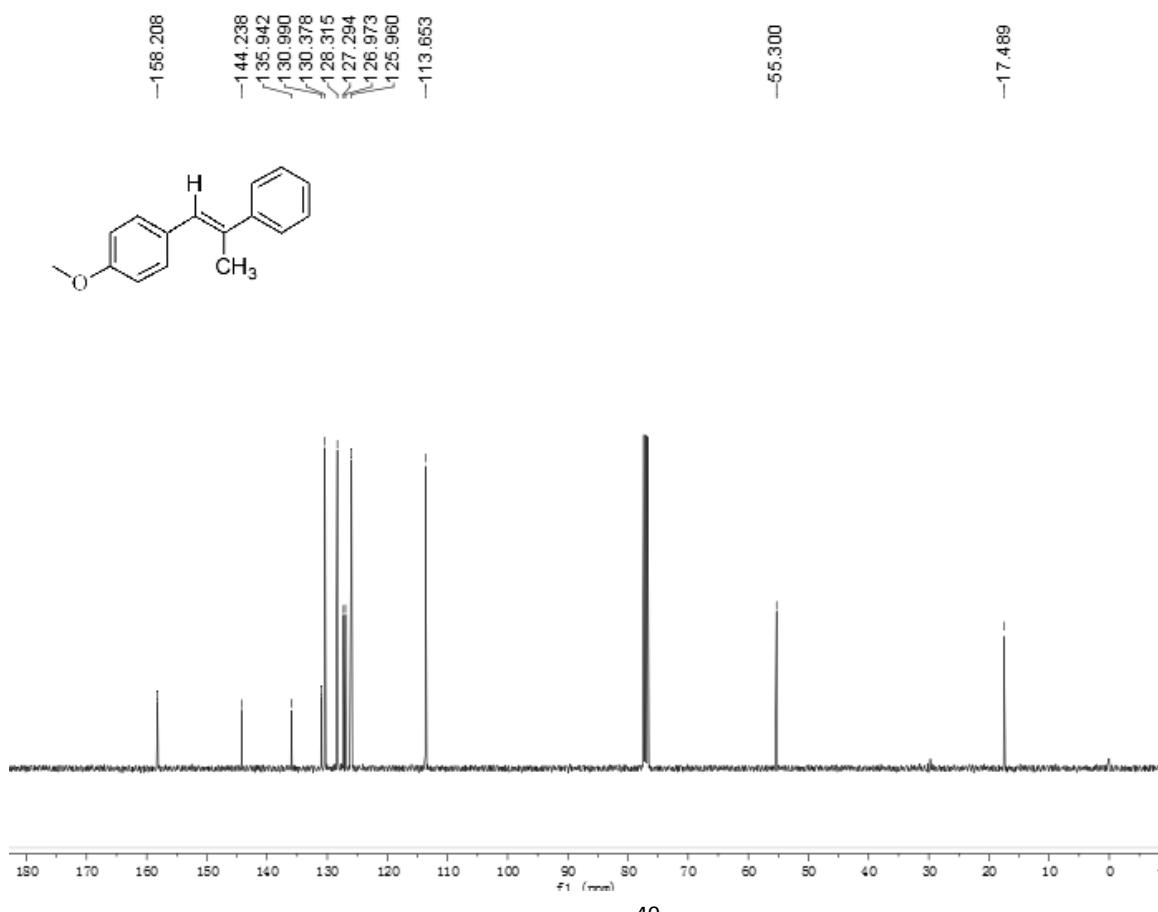
<sup>13</sup>C NMR spectra of 3gd



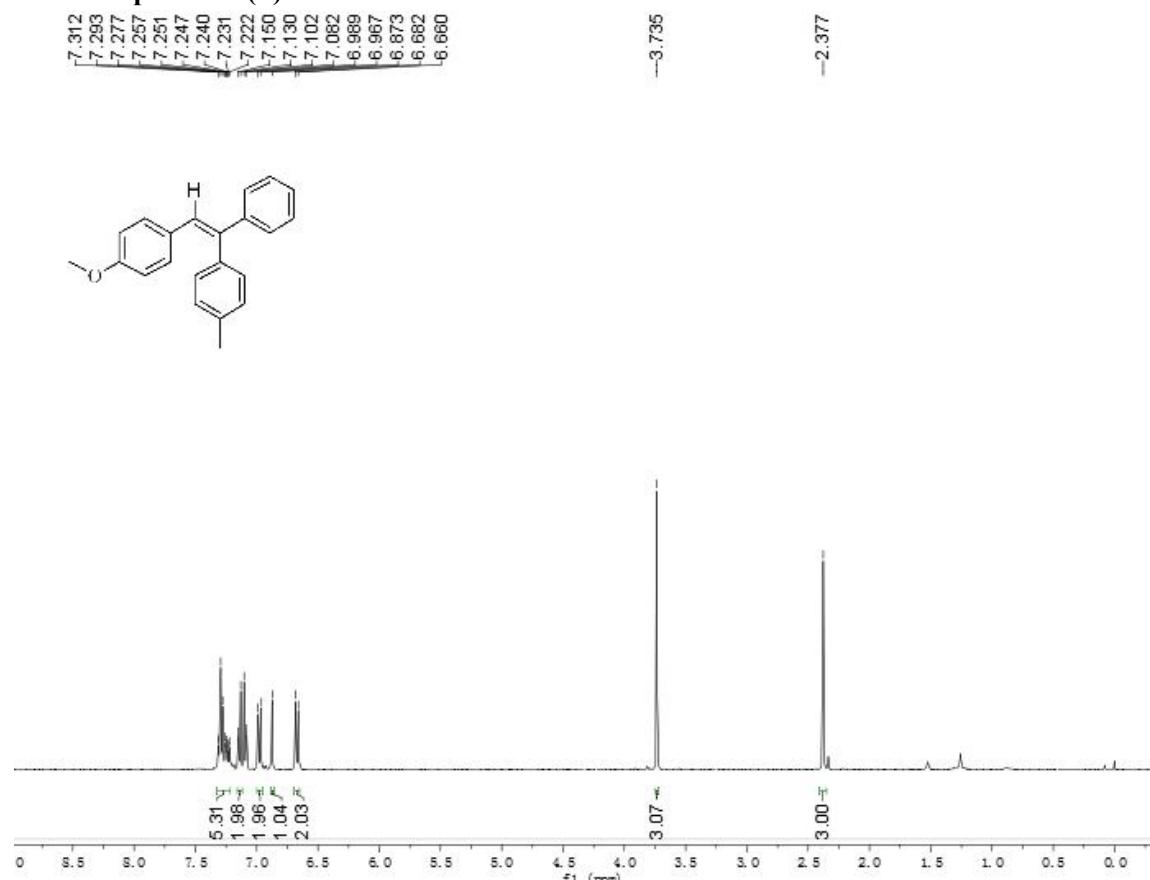
<sup>1</sup>H NMR spectra of (*E*)-3ha



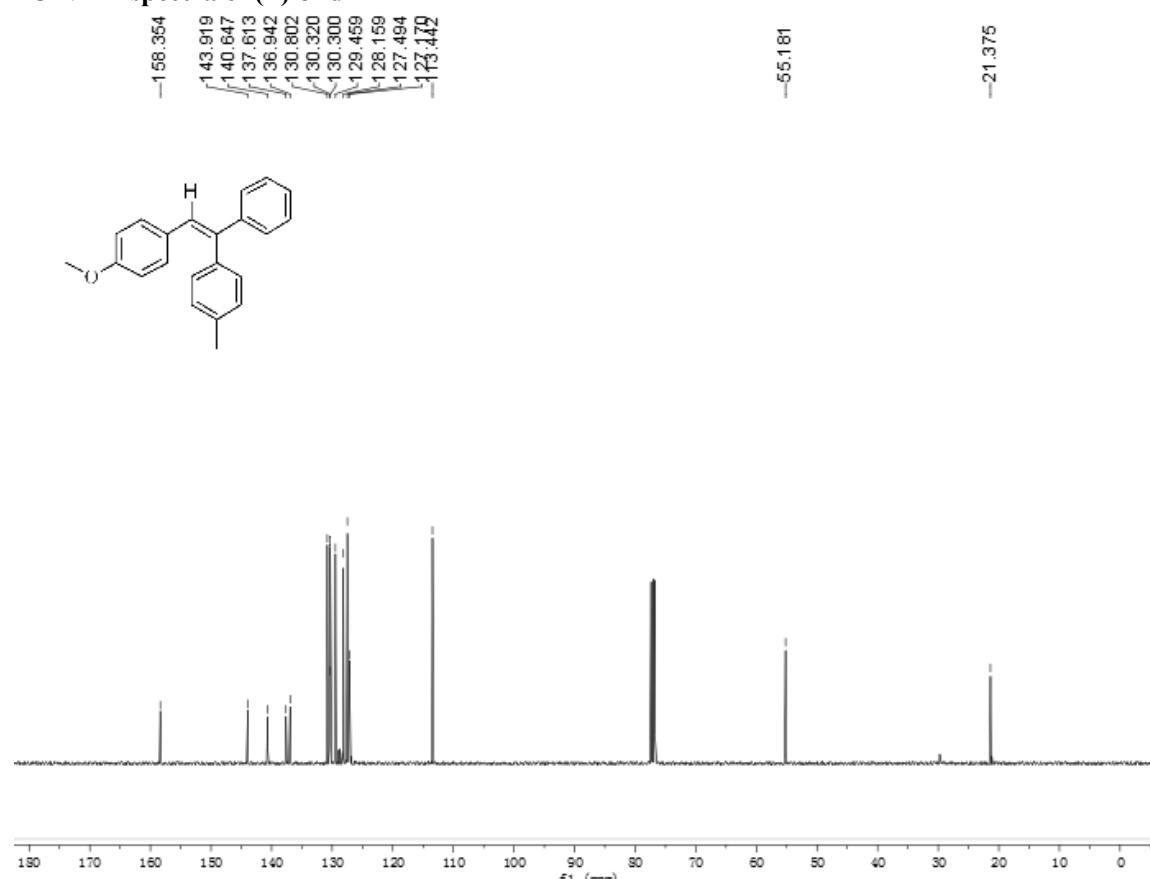
<sup>13</sup>C NMR spectra of (*E*)-3ha



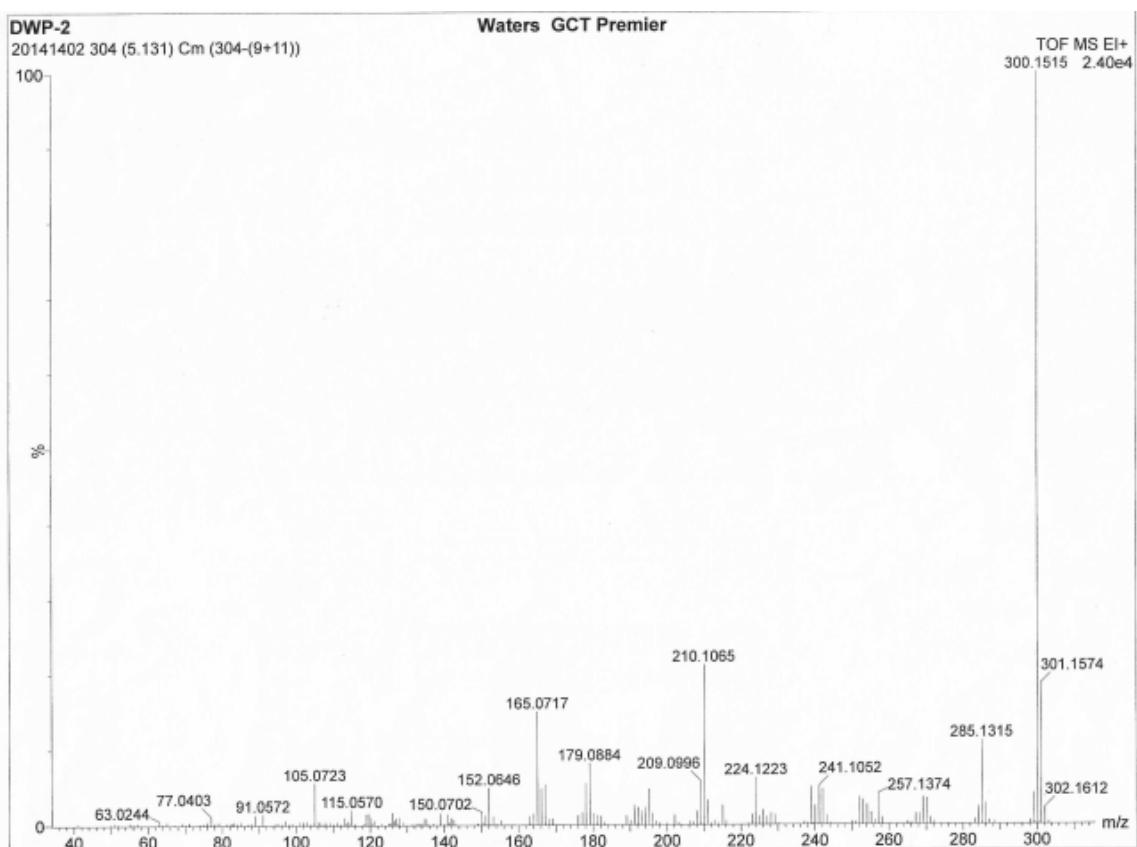
<sup>1</sup>H NMR spectra of (Z)-3hd



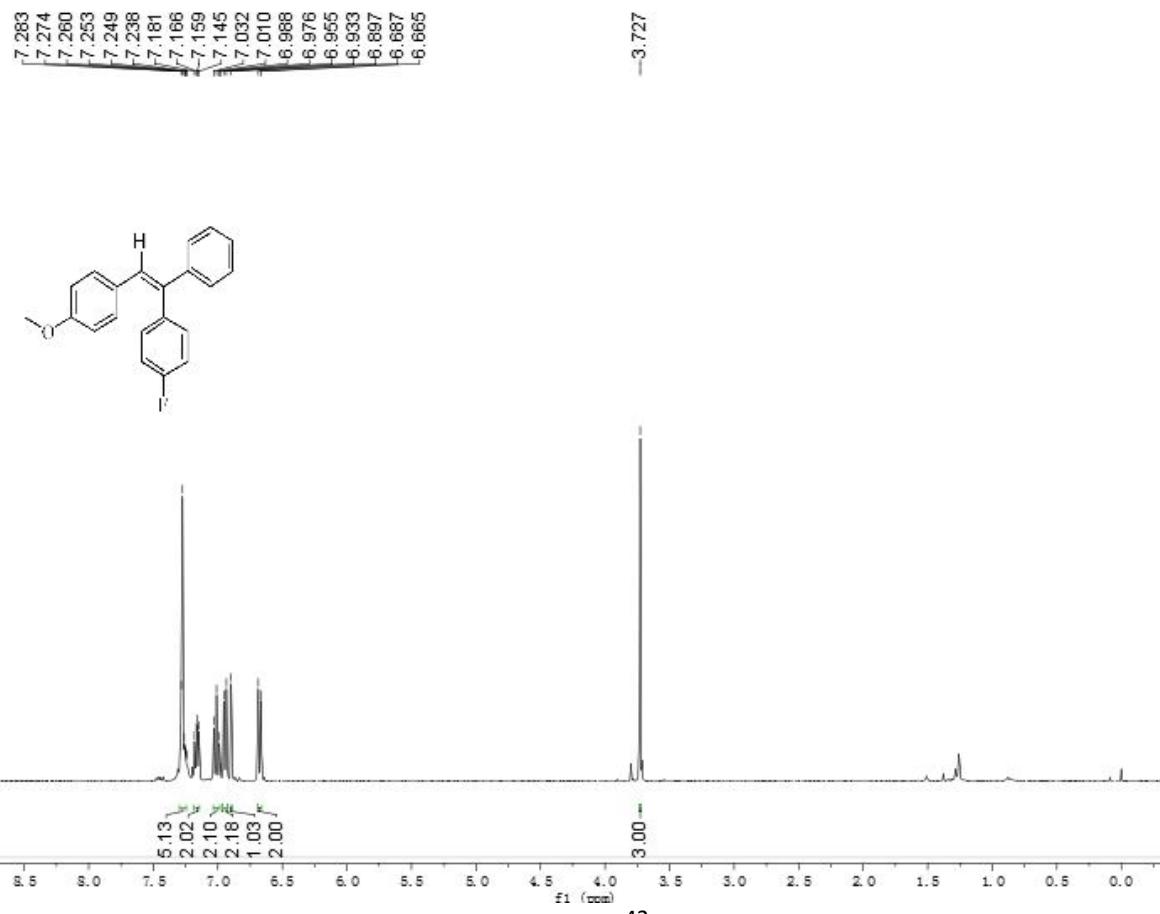
<sup>13</sup>C NMR spectra of (Z)-3hd



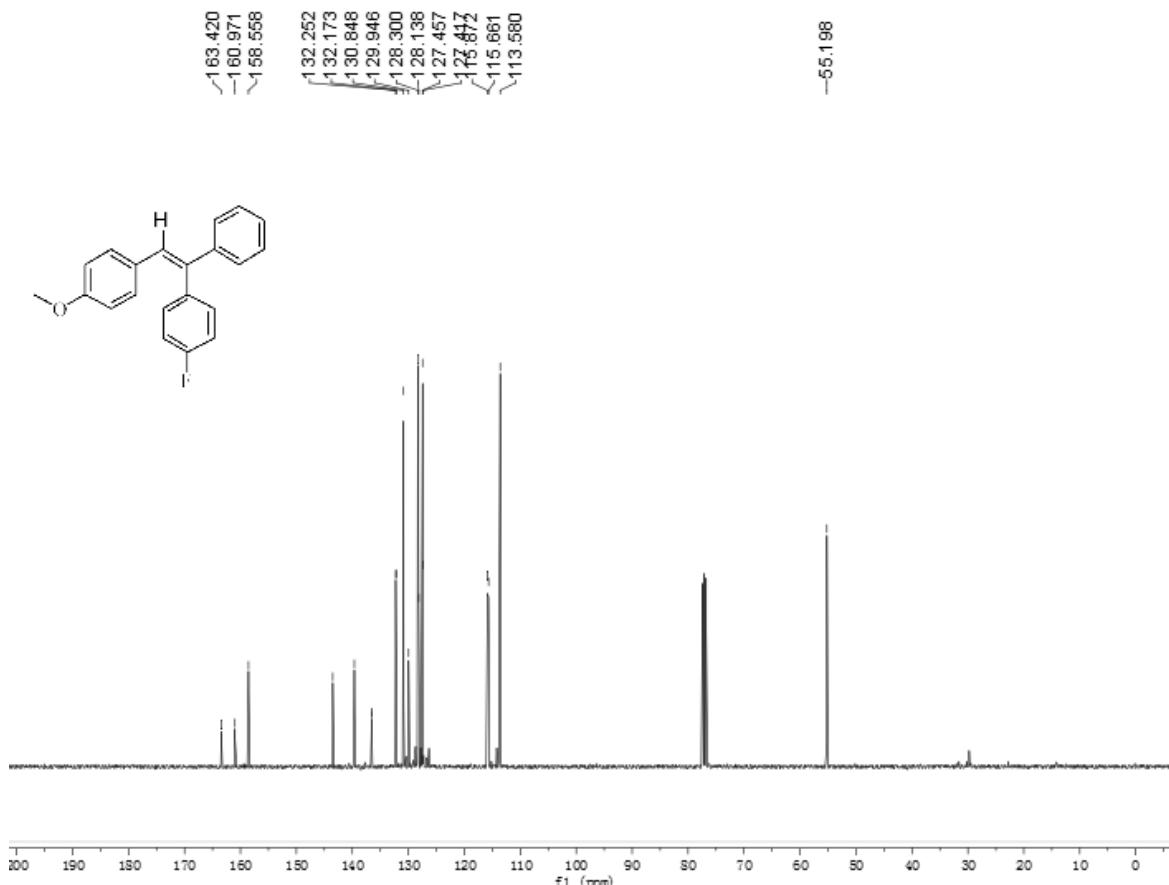
### HRMS (EI) spectra of (*Z*)-3hd



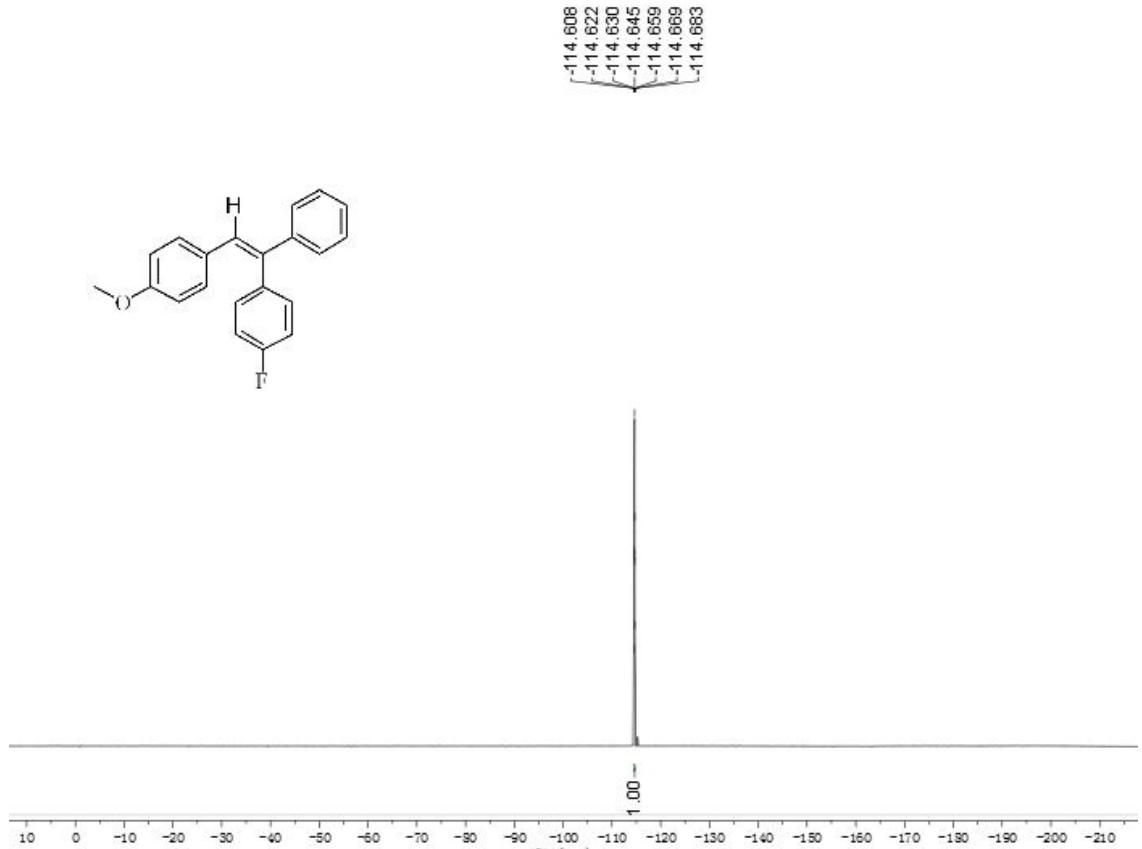
### <sup>1</sup>H NMR spectra of (*Z*)-3he



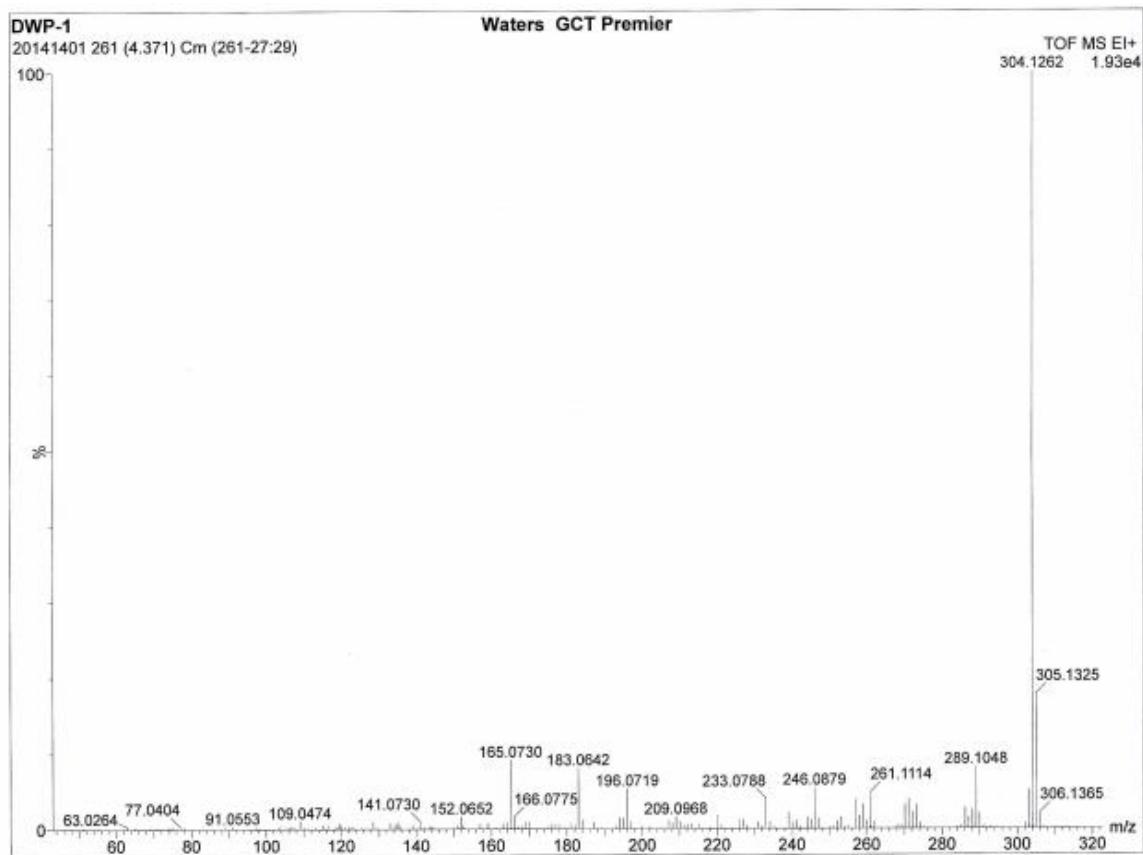
<sup>13</sup>C NMR spectra of (Z)-3he



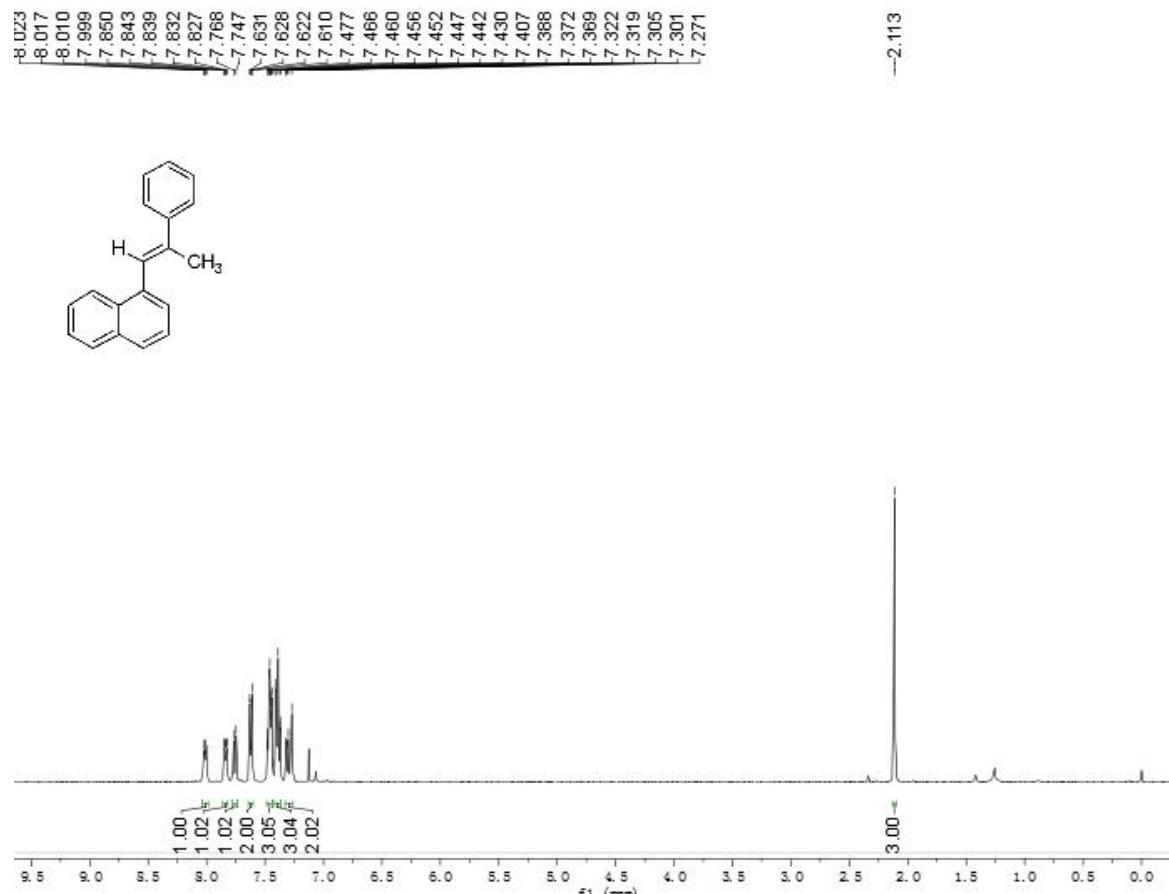
<sup>19</sup>F NMR spectra of (Z)-3he



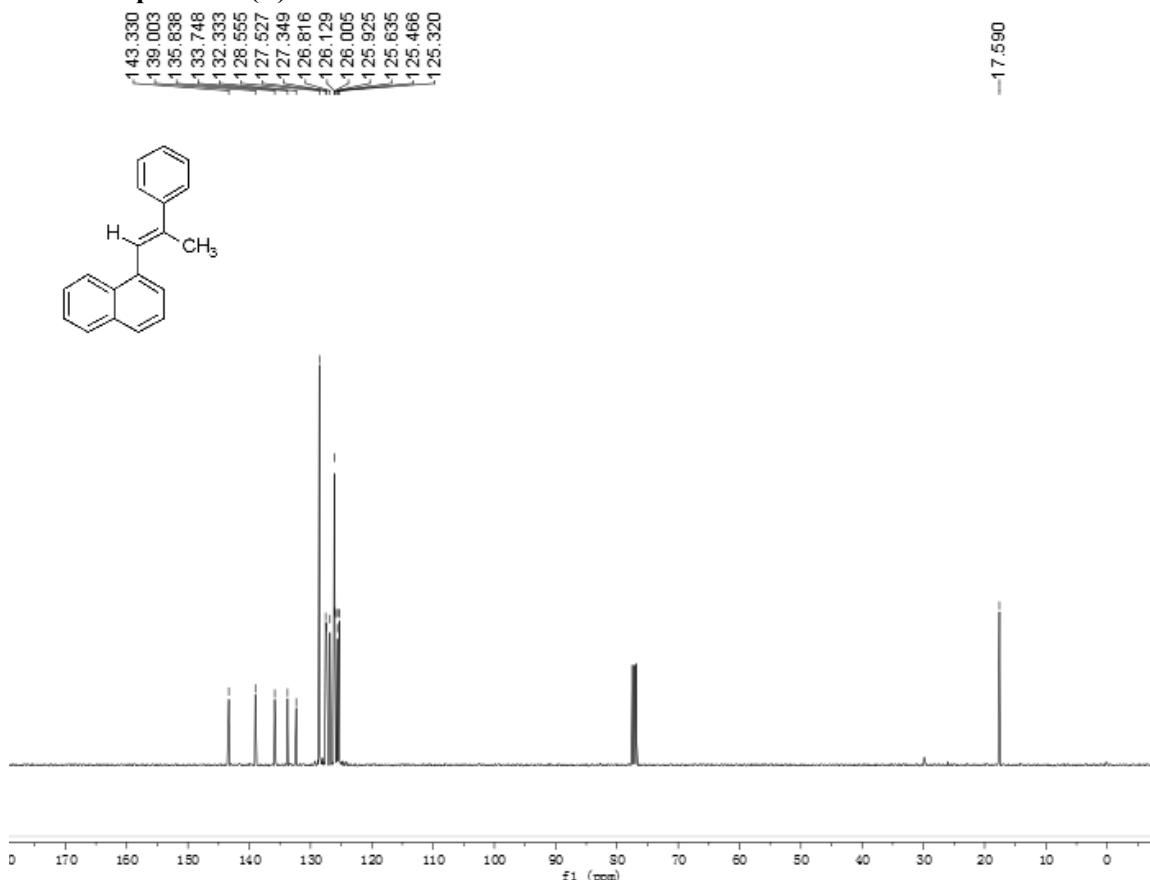
## HRMS (EI) spectra of (Z)-3he



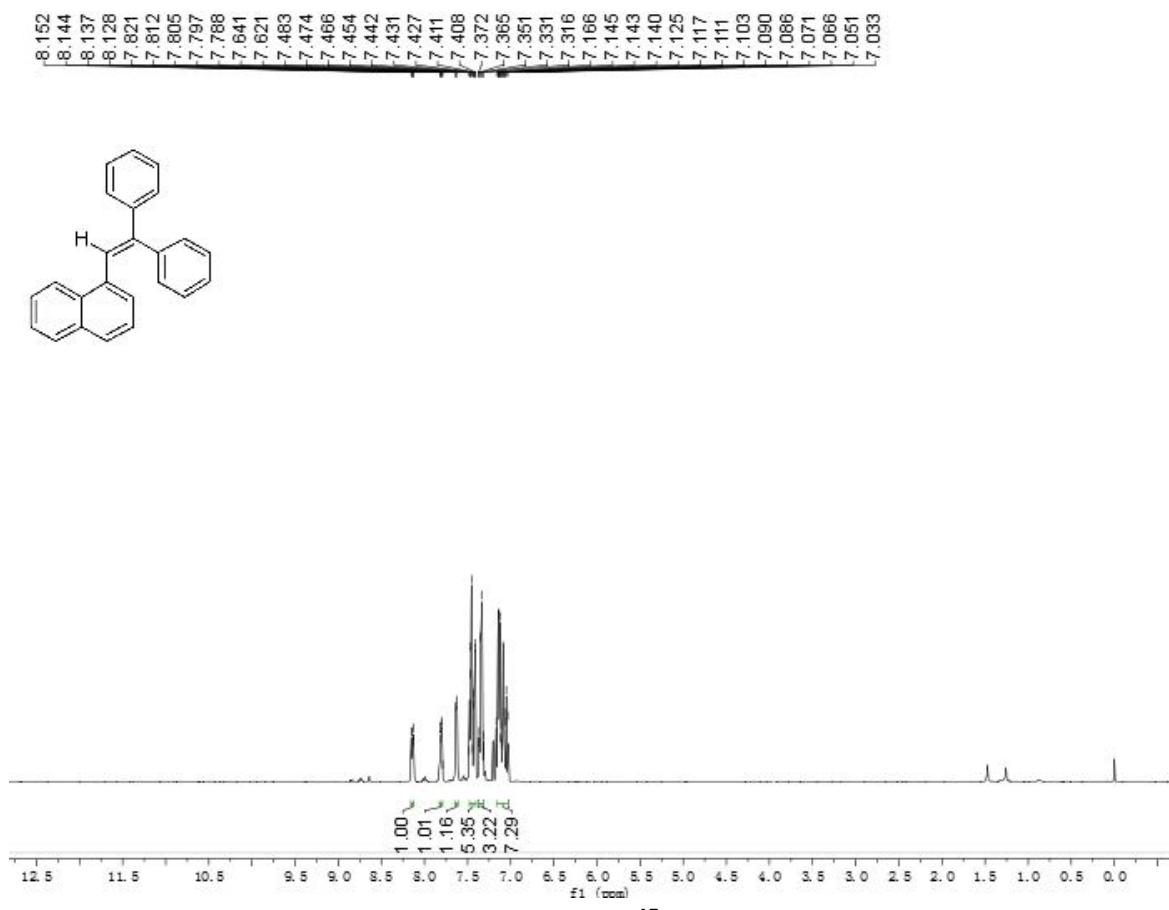
## <sup>1</sup>H NMR spectra of (E)-3ia



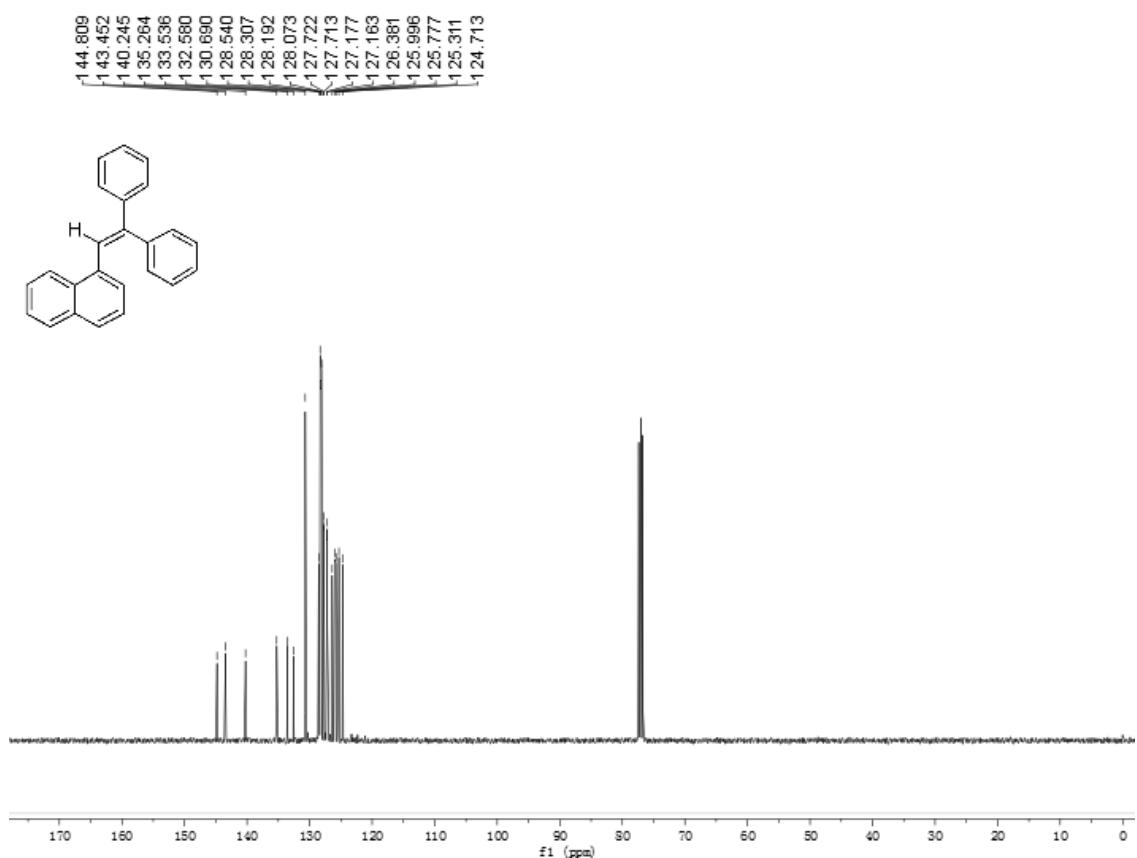
<sup>13</sup>C NMR spectra of (*E*)-3ia



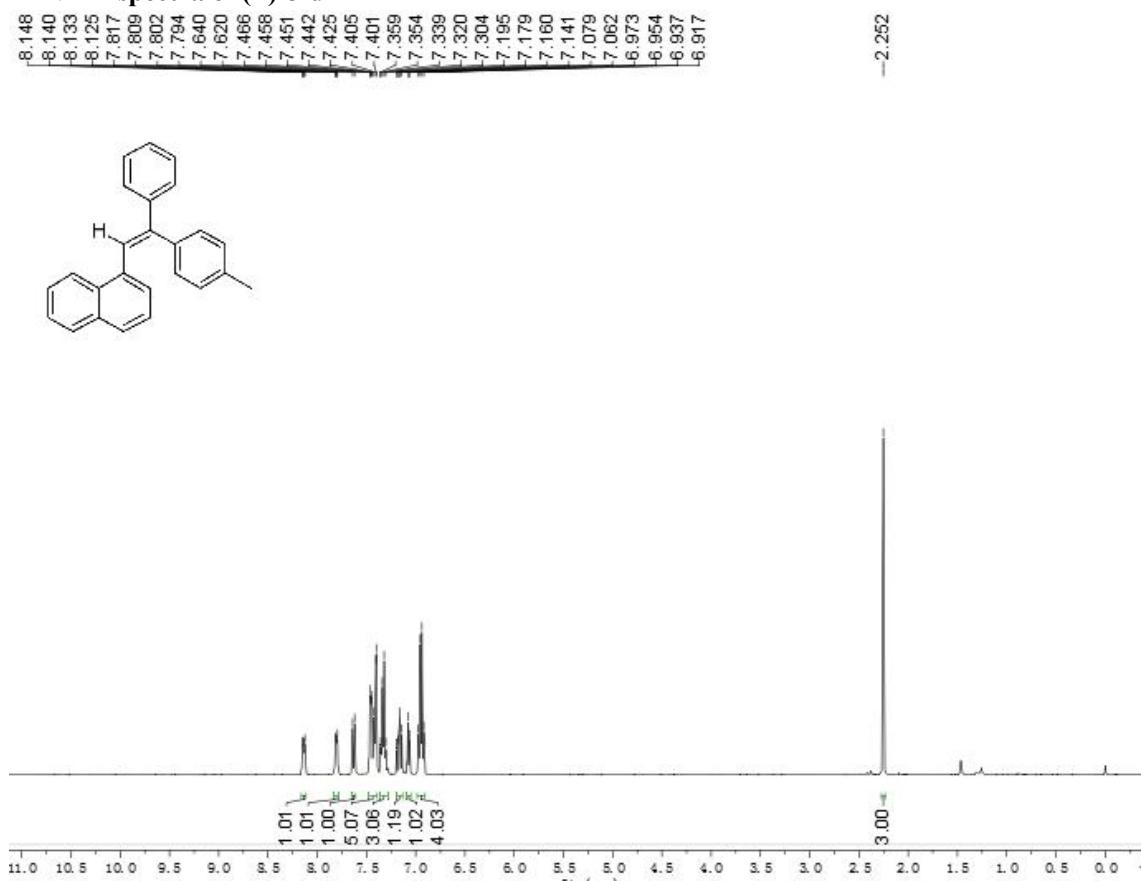
<sup>1</sup>H NMR spectra of 3ib



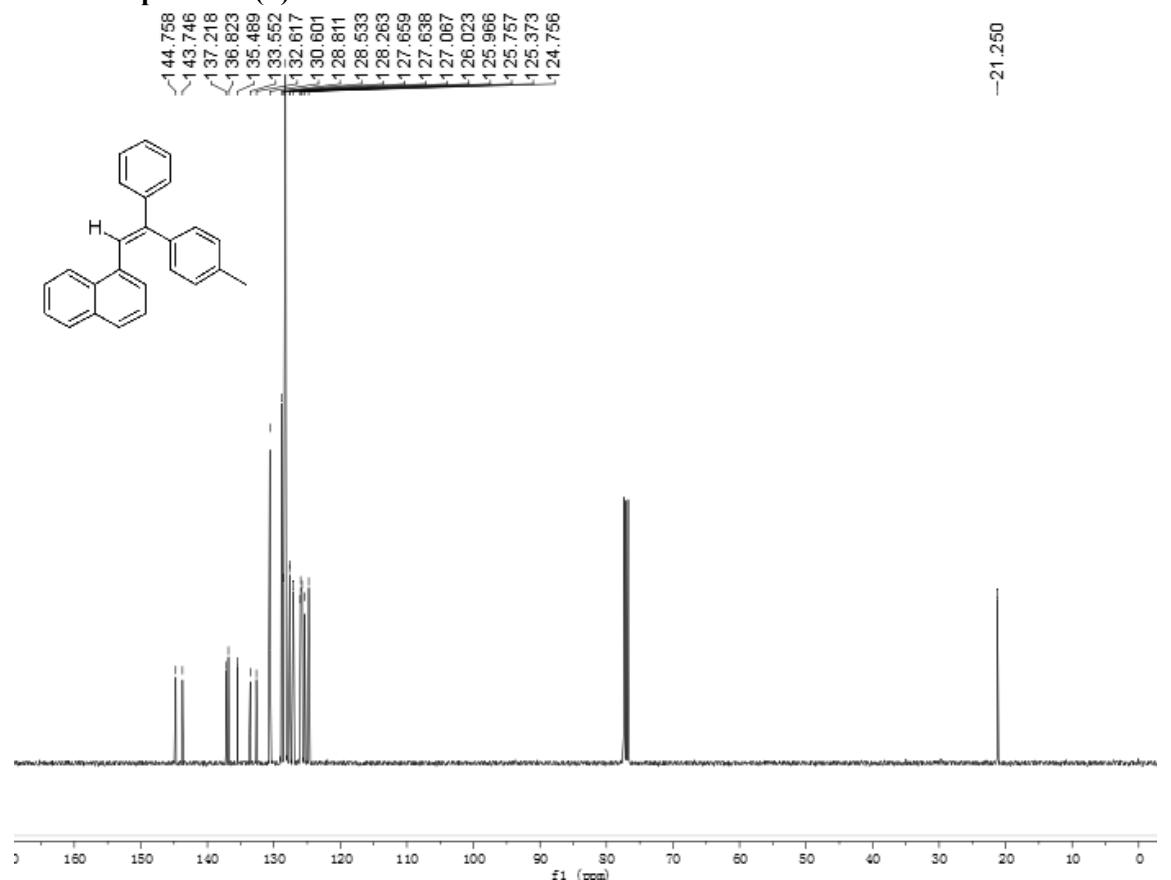
<sup>13</sup>C NMR spectra of 3ib



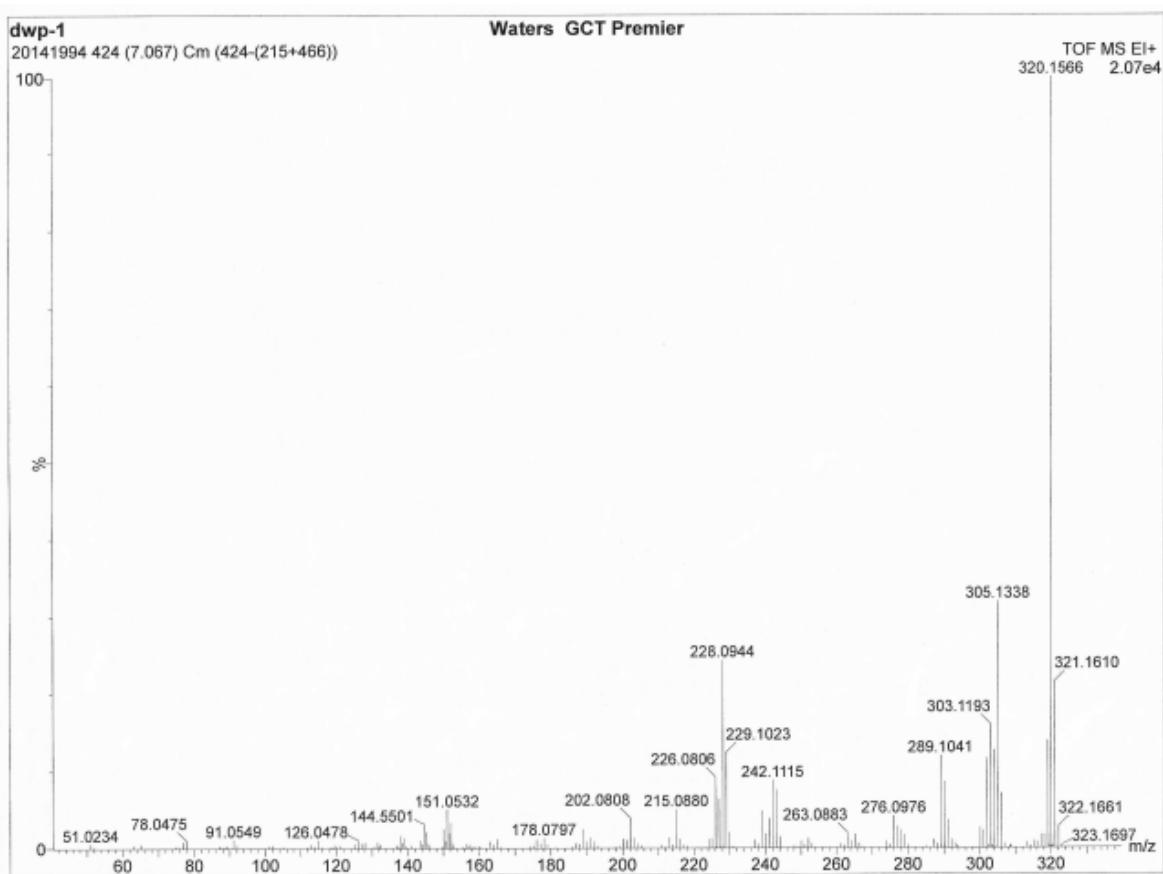
<sup>1</sup>H NMR spectra of (Z)-3id



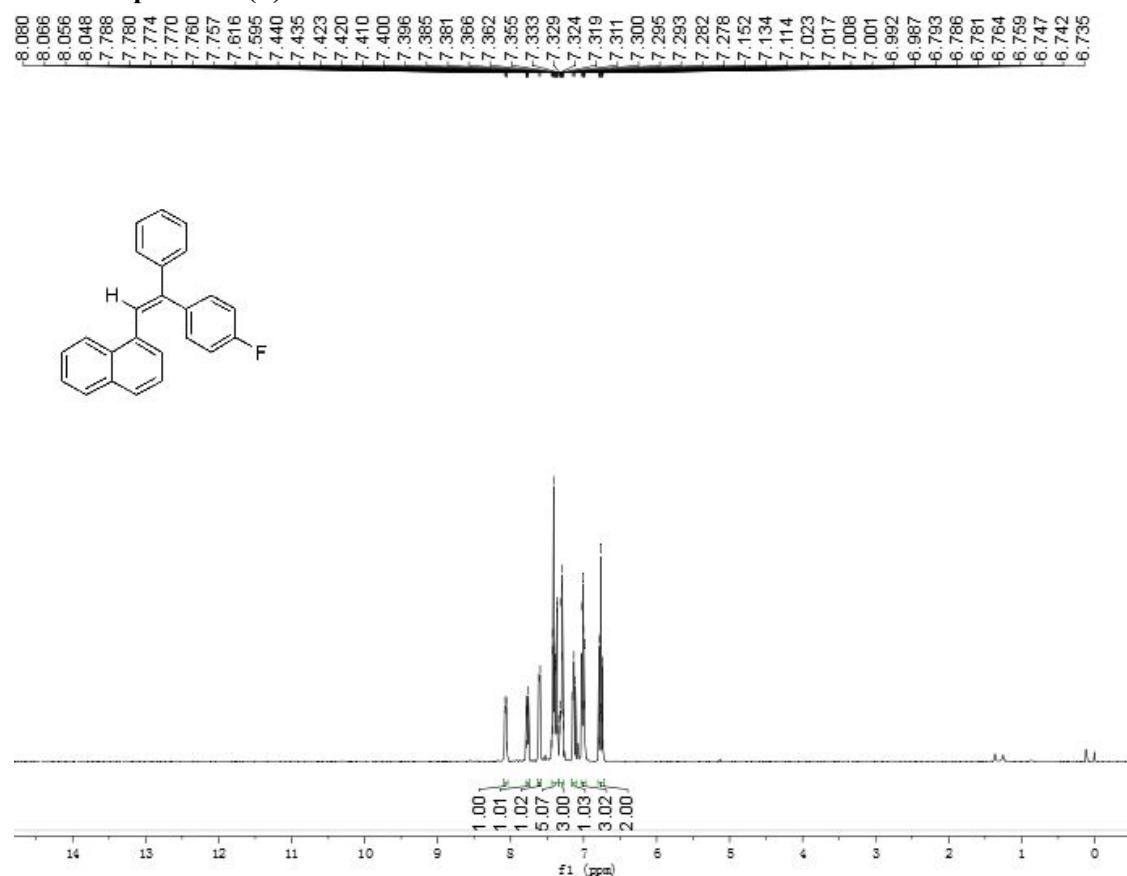
<sup>13</sup>C NMR spectra of (Z)-3id



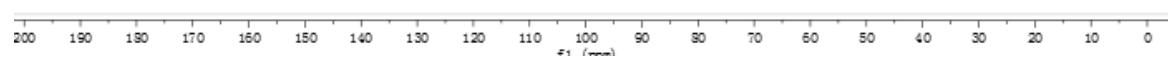
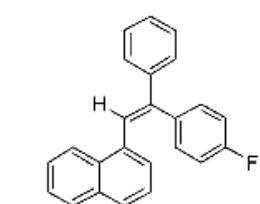
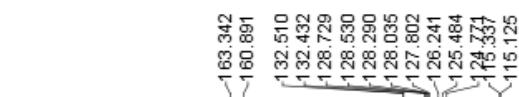
HRMS (EI) spectra of (Z)-3id



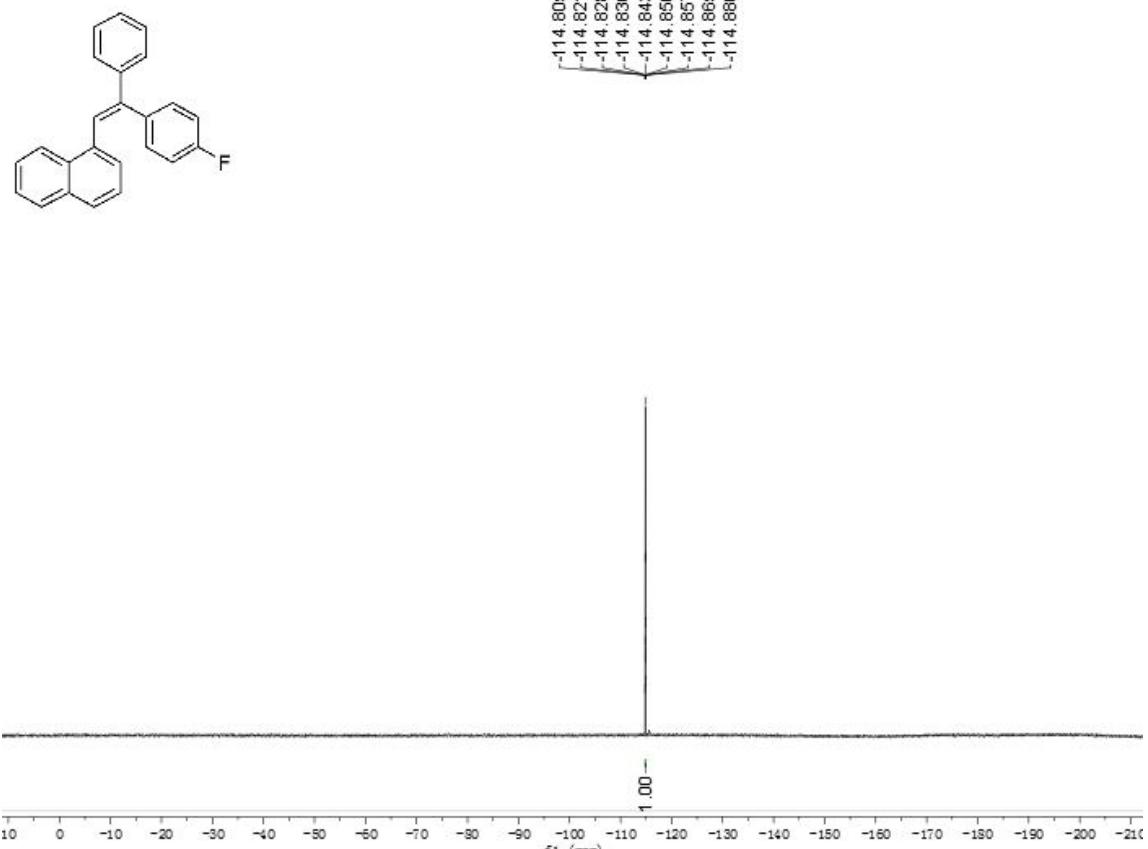
**<sup>1</sup>H NMR spectra of (Z)-3ie**



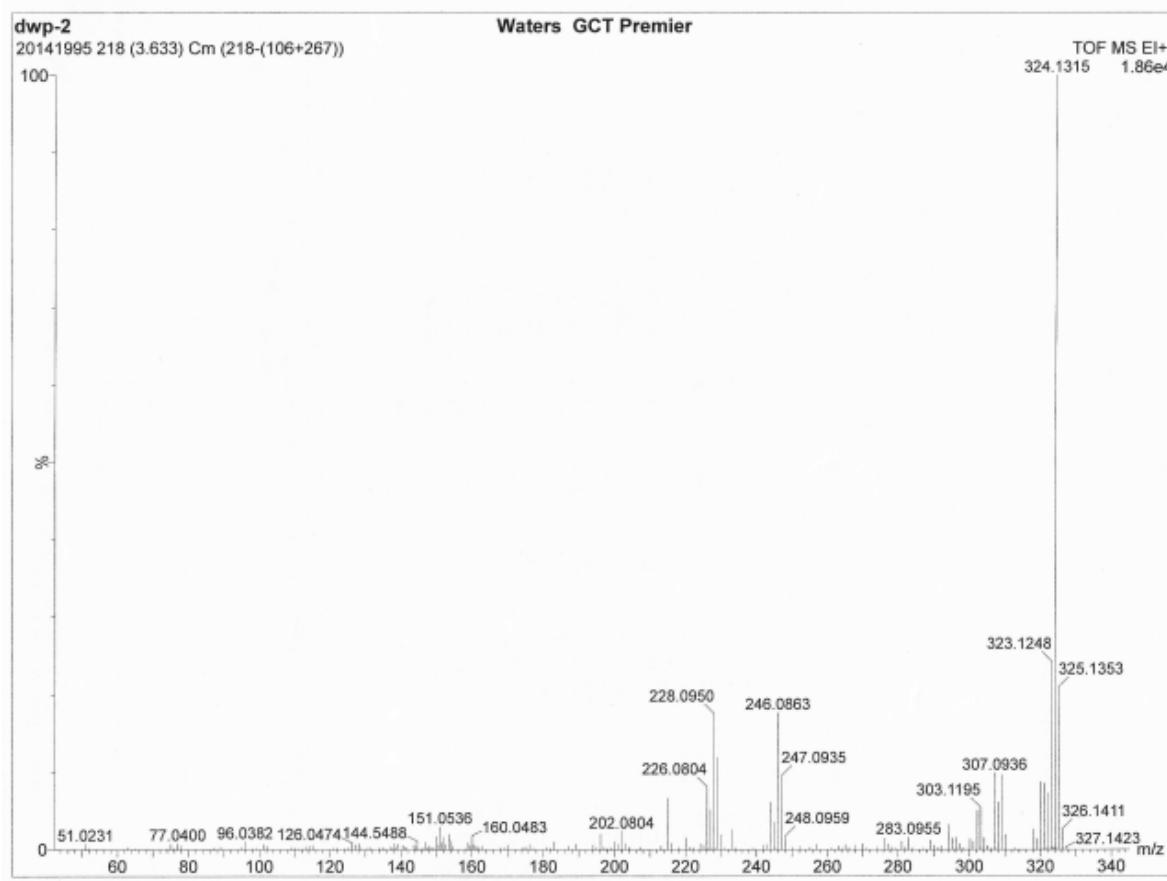
**<sup>13</sup>C NMR spectra of (Z)-3ie**



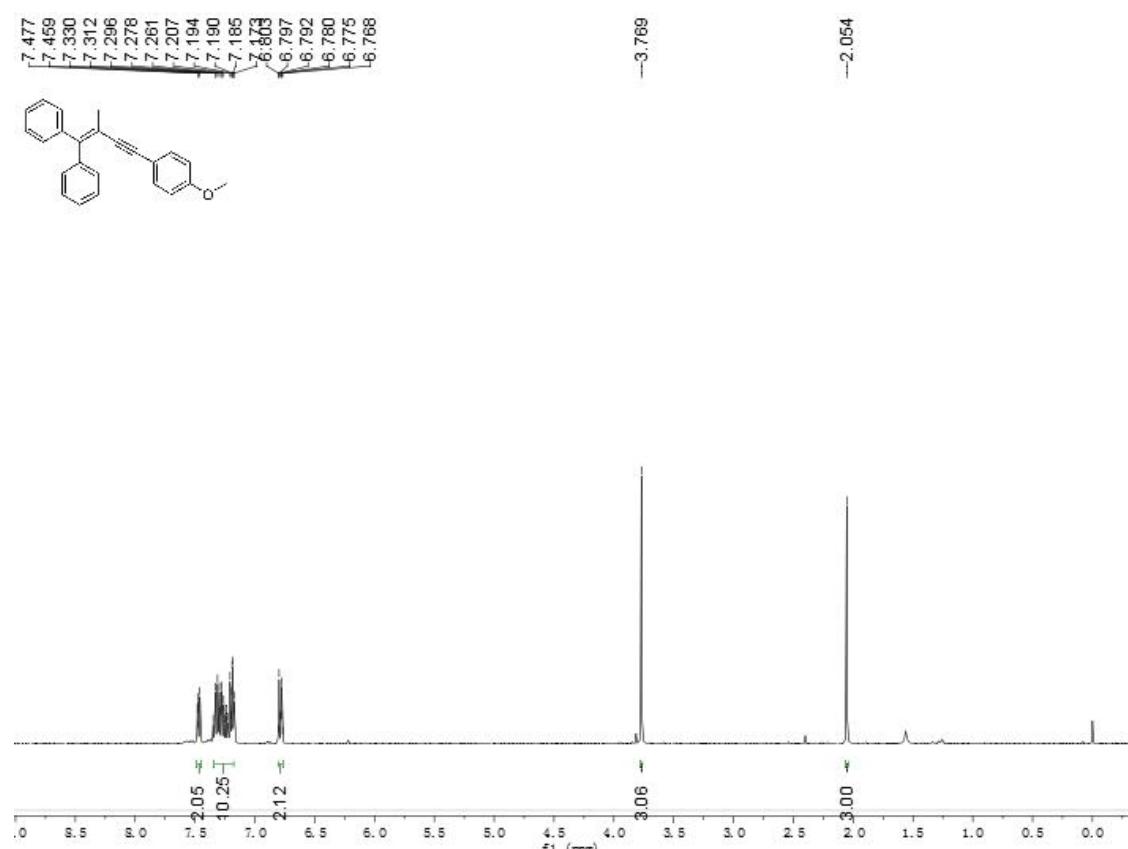
<sup>19</sup>F NMR spectra of (*E*)-3ie



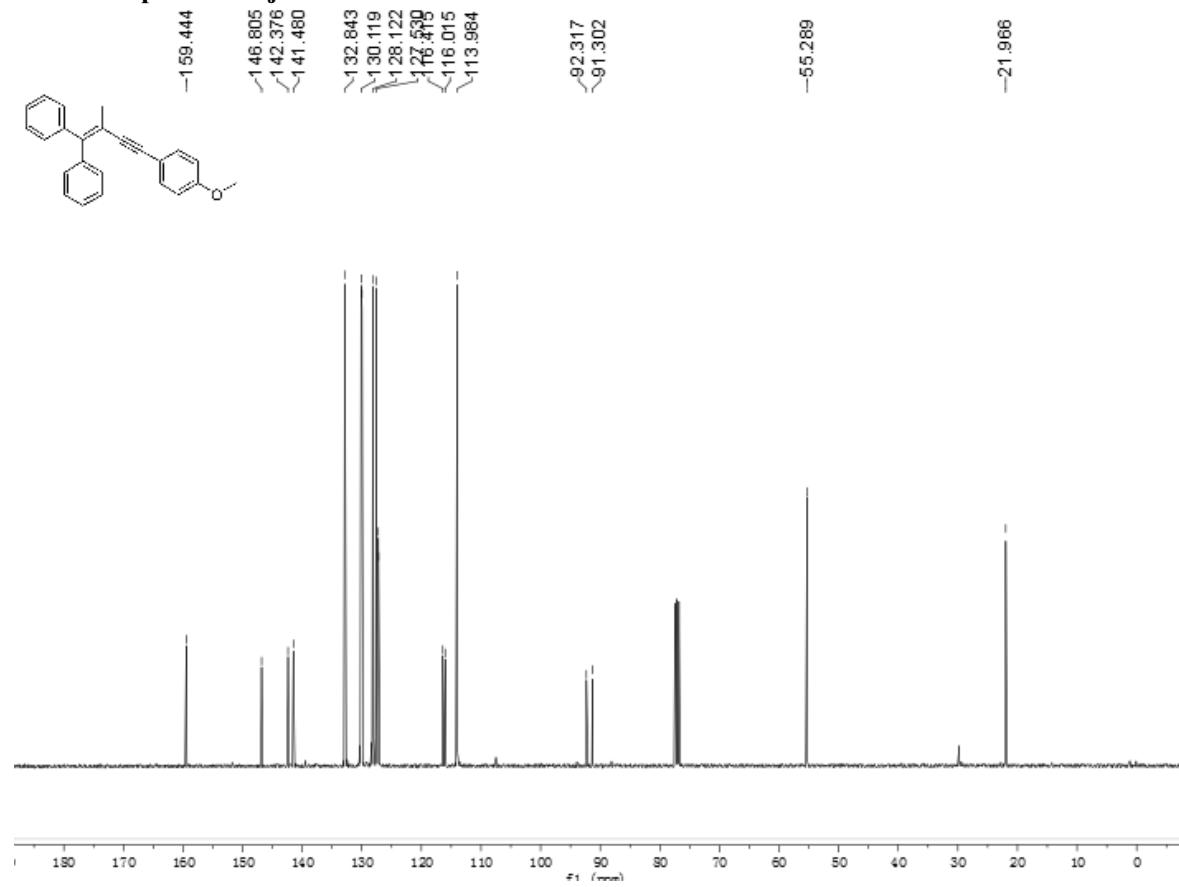
HRMS (EI) spectra of (*Z*)-3ie



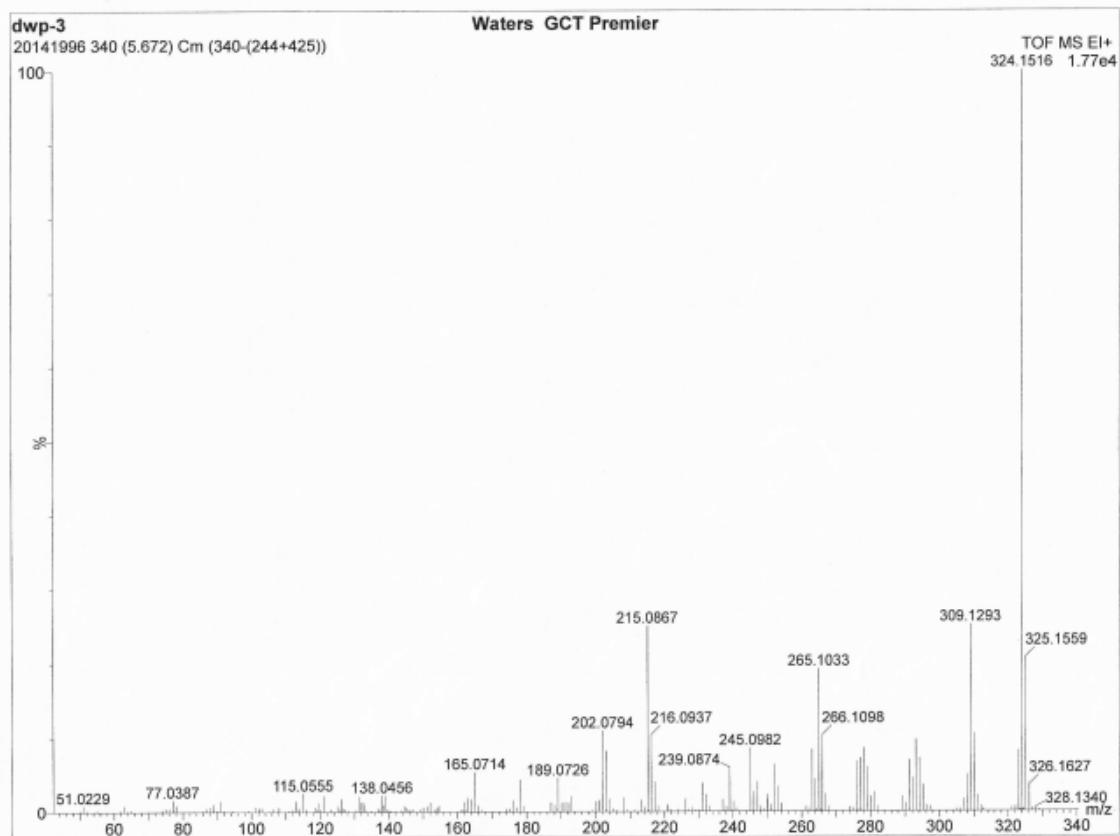
<sup>1</sup>H NMR spectra of 3ja



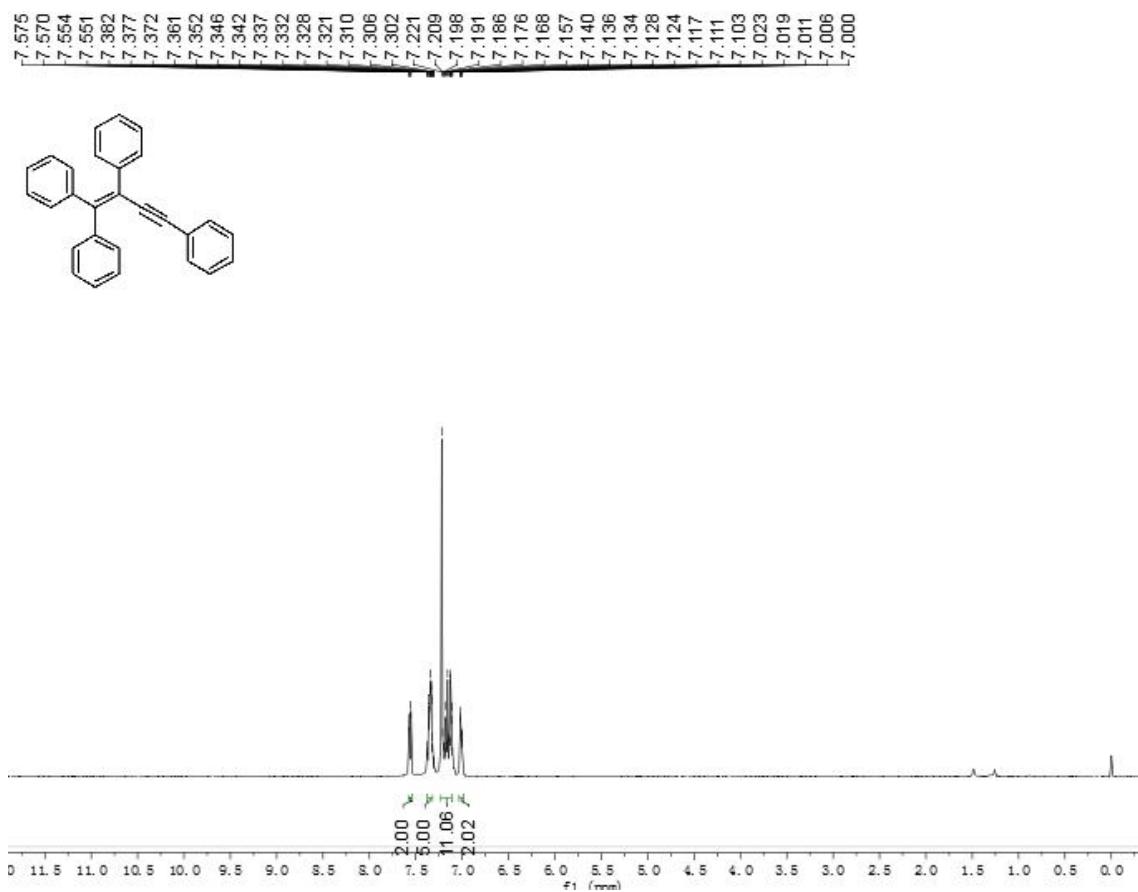
<sup>13</sup>C NMR spectra of 3ja



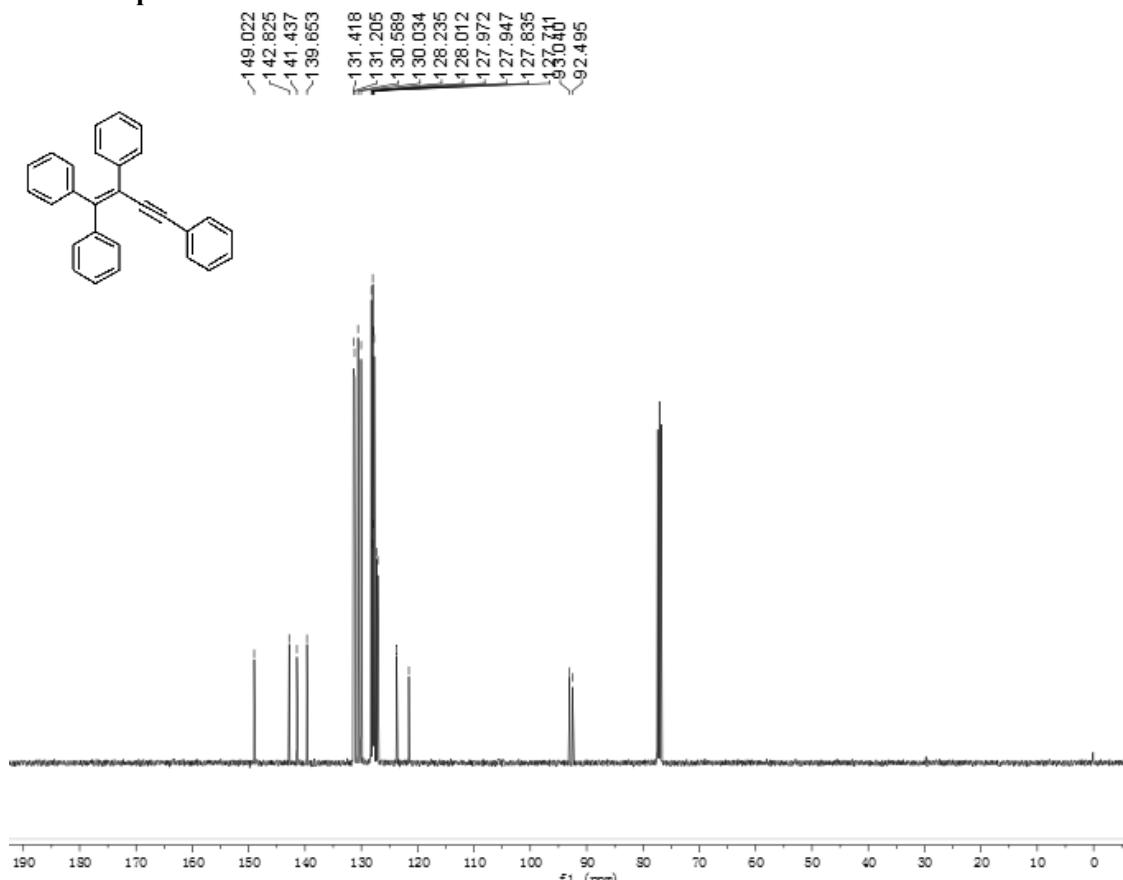
**HRMS (EI) spectra of 3ja**



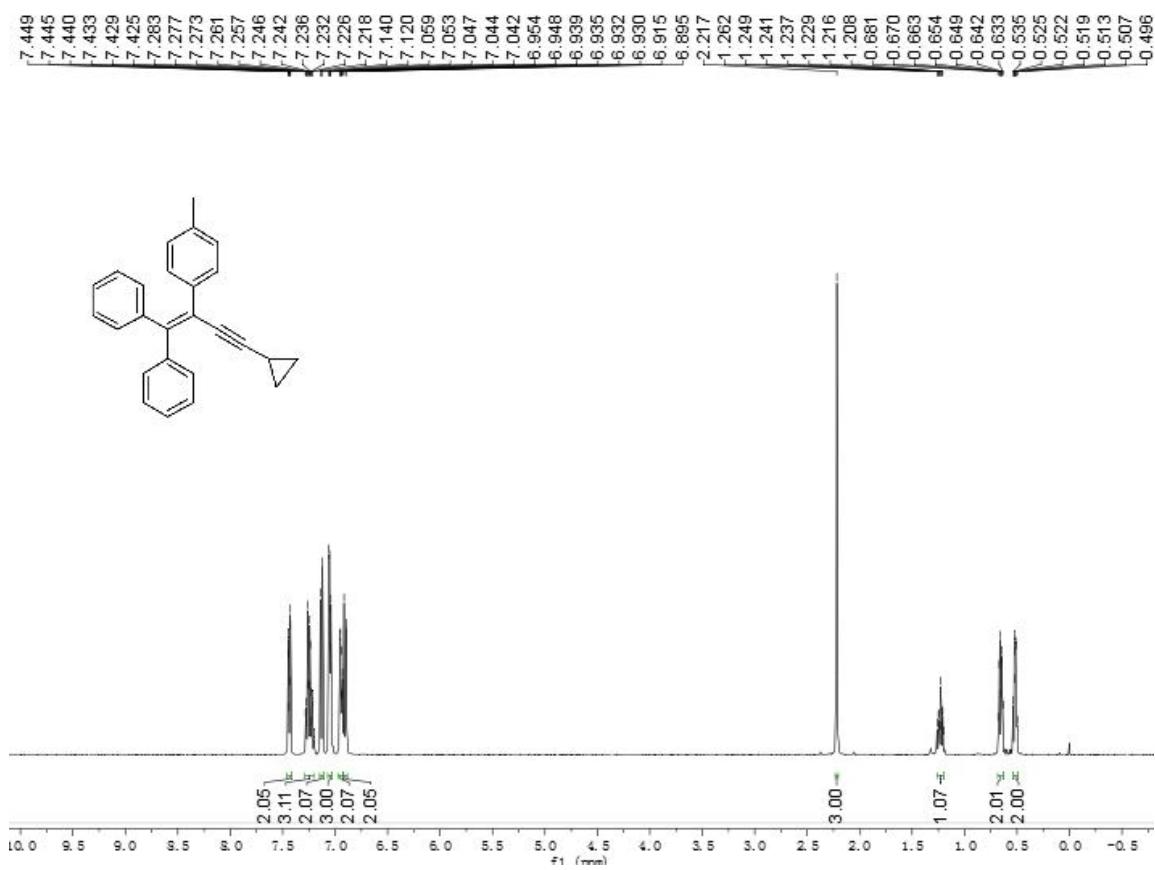
**$^1\text{H}$  NMR spectra of 3kb**



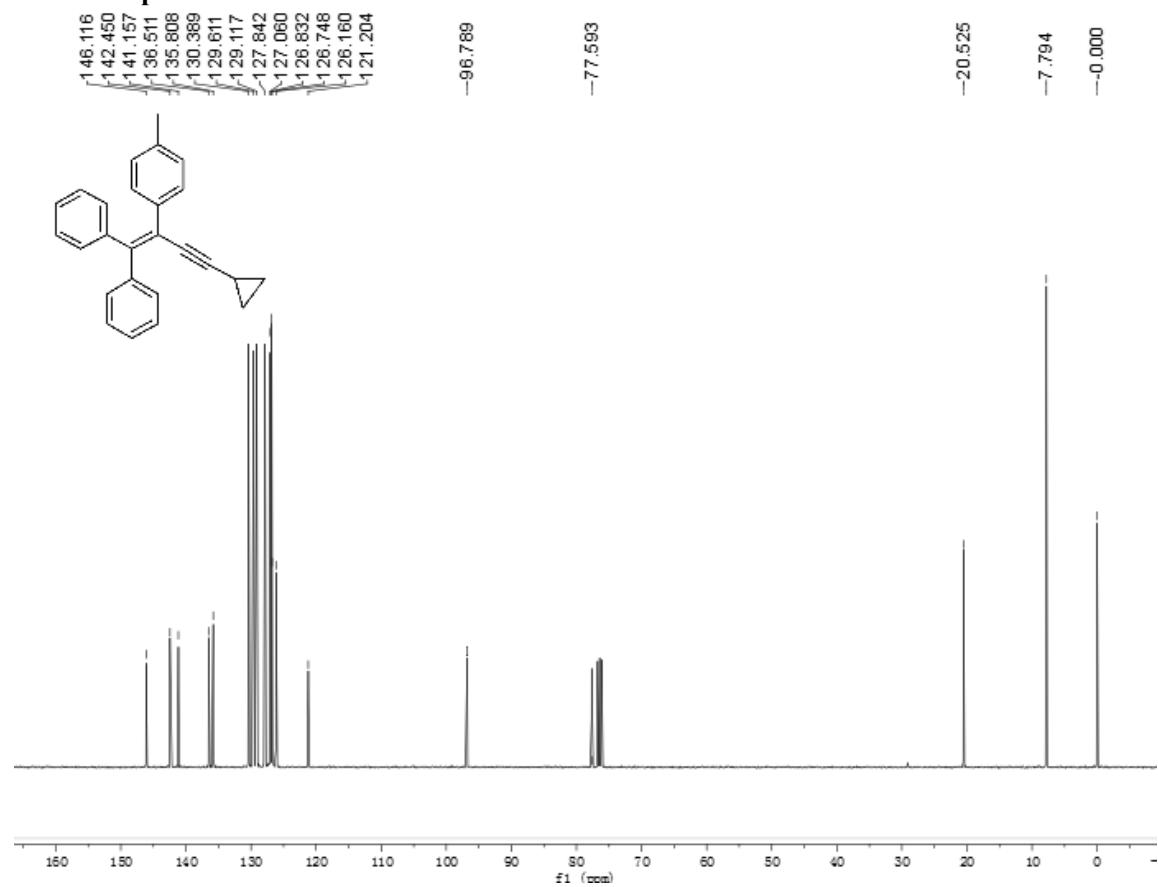
<sup>13</sup>C NMR spectra of 3kb



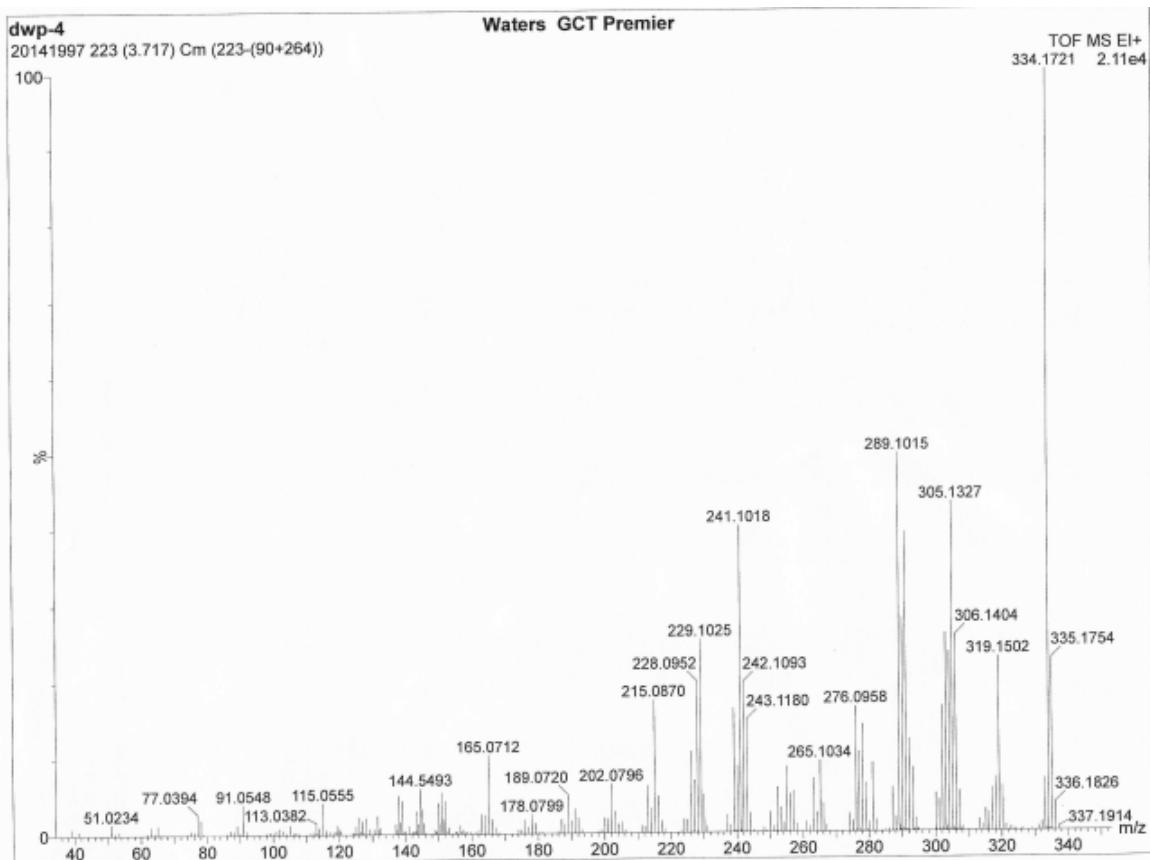
<sup>1</sup>H NMR spectra of 3ld



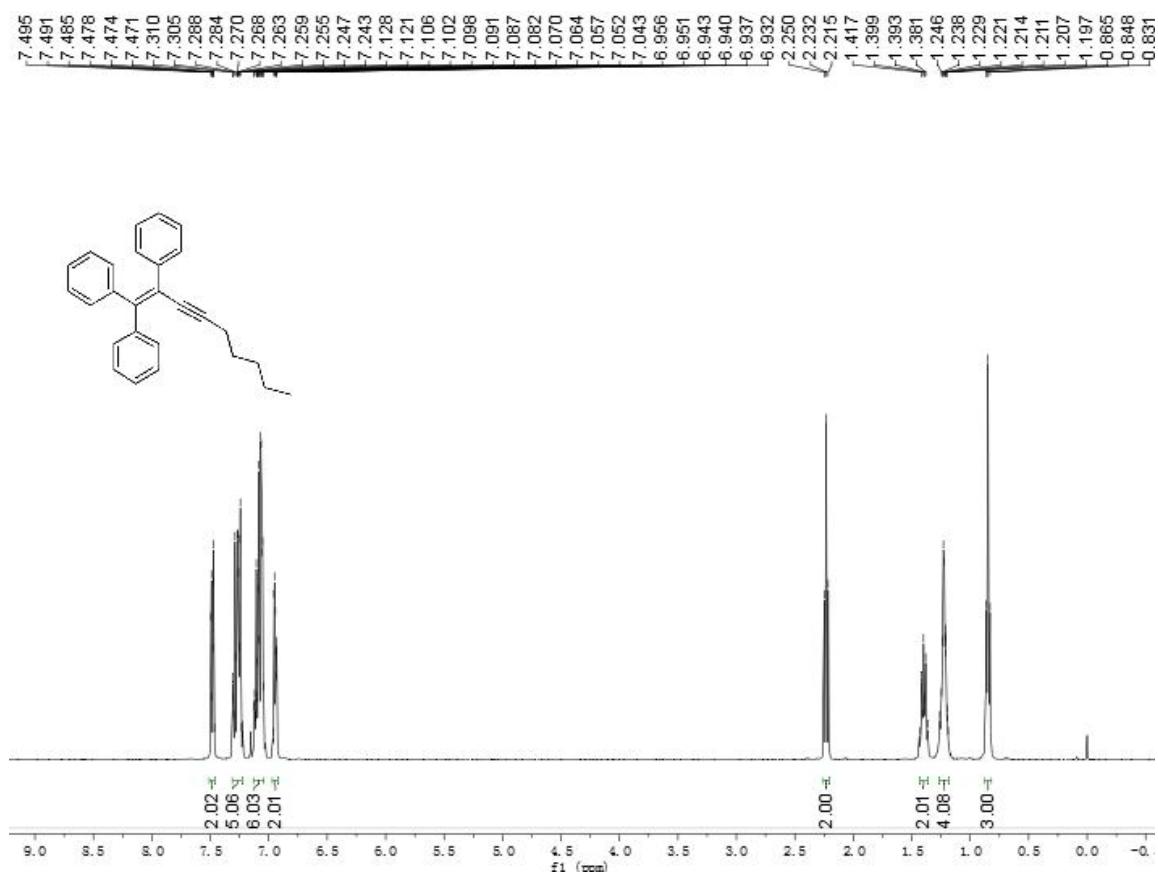
<sup>13</sup>C NMR spectra of 3ld



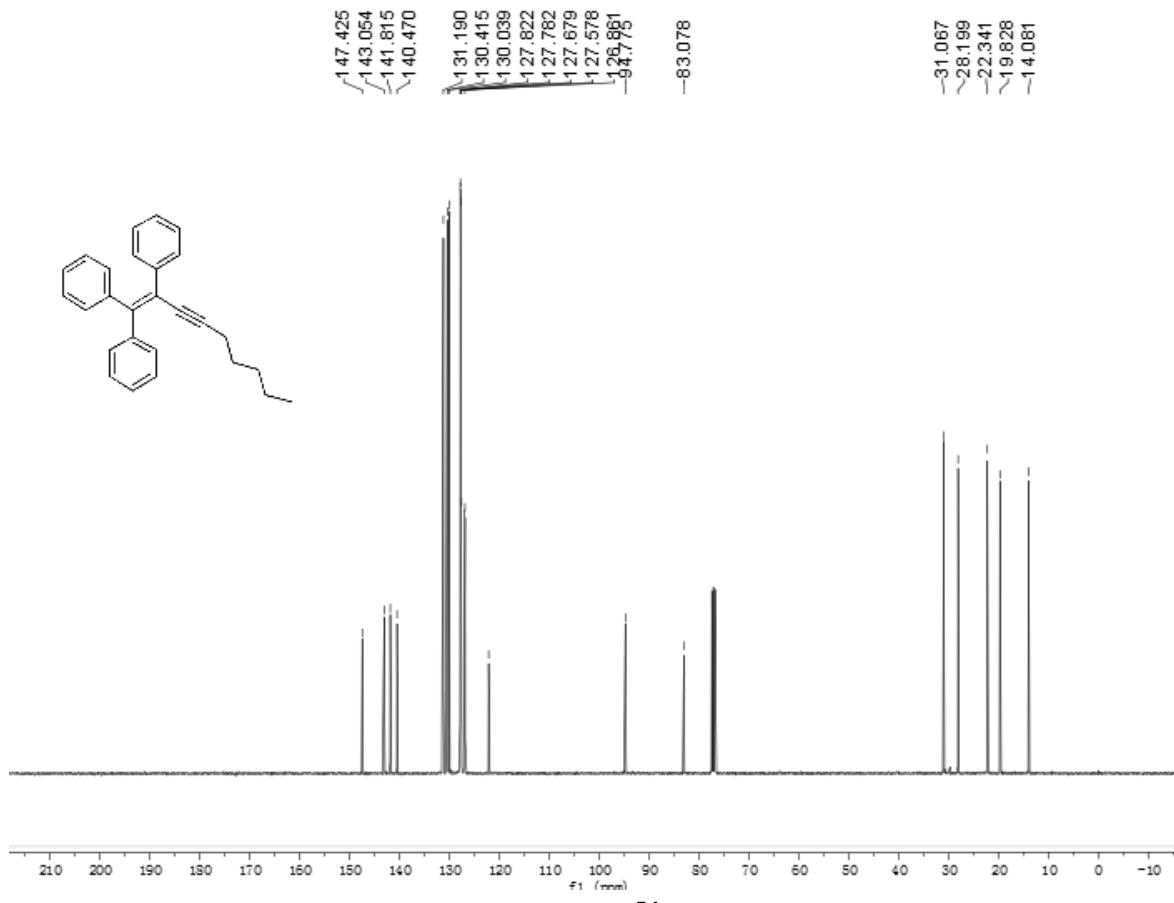
HRMS (EI) spectra of 3ld



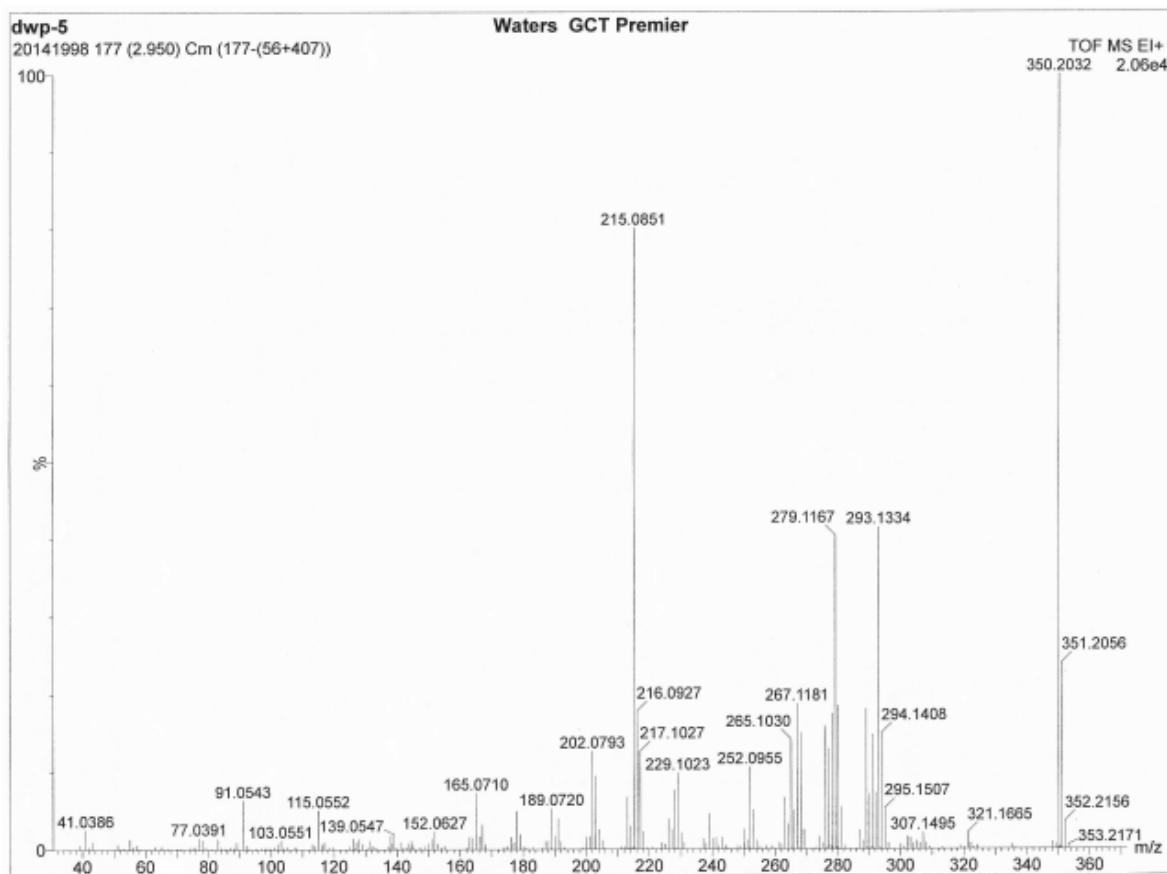
<sup>1</sup>H NMR spectra of 3mb



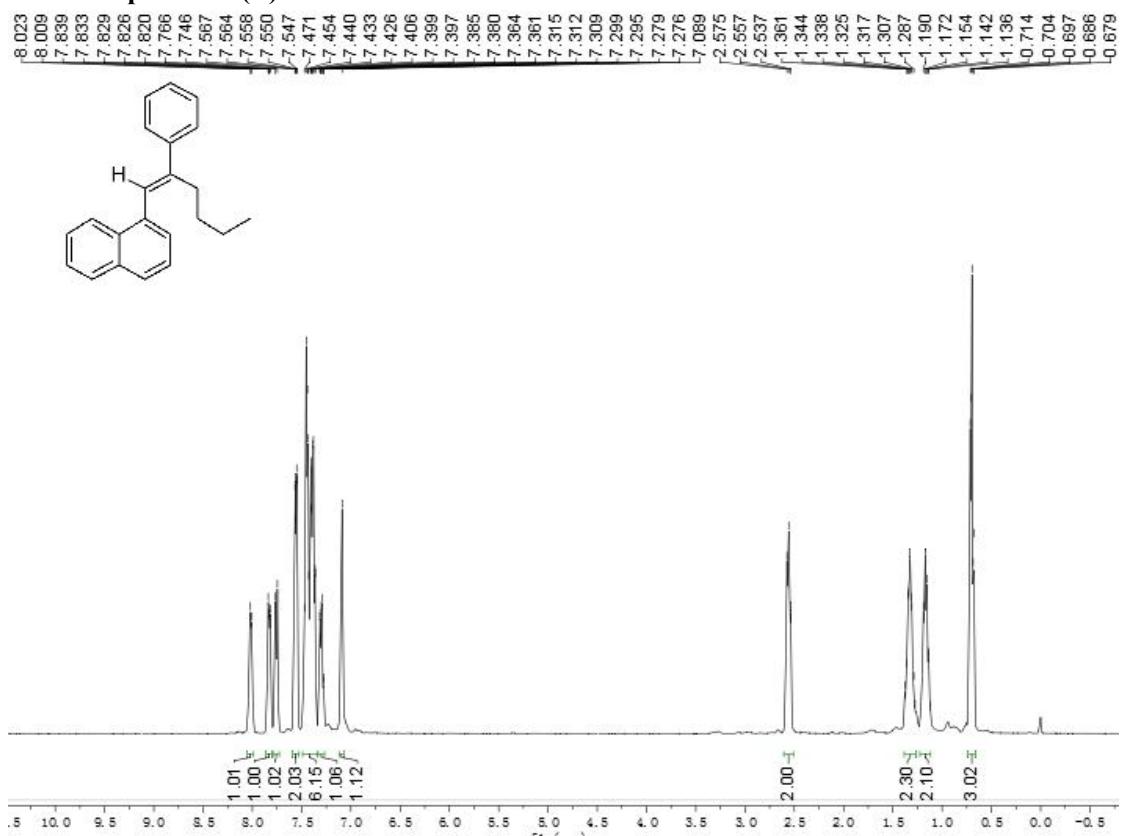
<sup>13</sup>C NMR spectra of 3mb



**HRMS (EI) spectra of 3mb**



**<sup>1</sup>H NMR spectra of (E)-3if**



<sup>13</sup>C NMR spectra of (*E*)-3if

