

**Phosphanamine-functionalized magnetic nanoparticles (PAFMN): an efficient magnetic reusable ligand in Pd-catalyzed Heck reaction of chloroarenes**

Farhad Panahi,<sup>\*a</sup> Narges Zarnaghash<sup>a</sup> and Ali Khalafi-Nezhad,<sup>\*a</sup>

<sup>a</sup> *Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. E-mail: [khalafi@chem.susc.ac.ir](mailto:khalafi@chem.susc.ac.ir) (A.K.-N.), [panahi@shirazu.ac.ir](mailto:panahi@shirazu.ac.ir) (F.P.). Fax: +98(711)2280926.*

**Outline:**

- 1. Spectral data for synthesized compounds**
- 2. Copy of <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR of DPPPA**
- 3. A comparison between the FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, DPPPA, and PAFMNP**
- 4. Copy of <sup>1</sup>H and <sup>13</sup>C NMR of Heck products**

## 1. Spectral data for synthesized compounds

### 1.1. (*E*)-1,2-Diphenylethene (3a)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 7.16 (s, 2H), 7.28-7.44 (m, 6H), 7.55-7.59 (m, 4H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS): δ (ppm) = 126.3, 127.5, 128.7, 136.2.

### 1.2. (*E*)-1-Methoxy-4-styrylbenzene (3b)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 3.71 (s, 3H), 6.78-6.83 (m, 2H), 6.92 (d, *J* = 10.7, 1H), 7.01 (s, 1H), 7.11-7.27 (m, 3H), 7.33-7.41 (m, 4H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS): δ (ppm) = 55.3, 114.2, 126.3, 126.6, 127.2, 127.8, 128.2, 128.7, 130.2, 137.7, 159.3.

### 1.3. (*E*)-1,2-bis(4-methoxyphenyl)ethene (3c)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 3.75 (s, 6H), 6.80-6.86 (m, 6H), 7.35 (d, *J* = 8.2 Hz, 4H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS): δ (ppm) = 55.3, 114.1, 126.1, 127.4, 129.4, 130.4.

### 1.4. (*E*)-1-Nitro-4-styrylbenzene (3d)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 7.02-7.35 (m, 5H), 7.44-7.57 (m, 4H), 8.14 (d, *J* = 9.0 Hz, 2H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS): δ (ppm) = 124.1, 126.3, 126.8, 127.0, 128.8, 128.9, 133.3, 136.1, 143.8, 146.7.

### 1.5. (*E*)-1-Chloro-4-(4-nitrostyryl)benzene (3e)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 7.07-7.58 (m, 8H), 8.16 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS): δ (ppm) = 119.2, 123.7, 124.2, 126.8, 126.9, 128.1, 129.1, 131.9, 143.4.

### 1.6. (*E*)-1-(4-(4-Methoxystyryl)phenyl)ethan-1-one (3f)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 2.61 (s, 3H), 3.84 (s, 3H), 6.90-6.96 (m, 2H), 7.00 (s, 1H), 7.20 (s, 1H), 7.47-7.57 (m, 4H), 7.94 (d, *J* = 8.2 Hz, 2H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 26.4, 55.3, 114.2, 126.2, 126.8, 127.4, 128.1, 128.9, 137.3, 139.2, 164.0, 197.3.

### 1.7. (*E*)-1-Methyl-4-styrylbenzene (3g)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 2.27 (s, 3H), 6.98 (s, 2H), 7.02-7.18 (m, 3H), 7.23-7.34 (m, 4H), 7.40-7.43 (m, 2H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 21.3, 126.4, 126.5, 127.4, 127.7, 128.6, 128.7, 129.4, 134.6, 137.5.

### 1.8. (*E*)-4-Styrylbenzotrile (3h)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 7.09 (d, *J* = 16.5 Hz, 1H), 7.23 (d, *J* = 16.7 Hz, 1H), 7.32-7.43 (m, 3H), 7.52-7.66 (m, 6H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 110.5, 119.0, 126.7, 126.8, 128.6, 128.8, 130.5, 132.4, 132.5, 134.2, 136.2.

### 1.9. Methyl (*E*)-3-(4-acetylphenyl)acrylate (3i)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 2.61 (s, 3H), 3.82 (s, 3H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 2H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 26.7, 51.9, 120.3, 128.1, 128.8, 138.0, 138.6, 143.3, 166.9, 197.3.

### 1.10. Methyl (*E*)-3-(4-formylphenyl)acrylate (3j)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS) δ (ppm) = 3.83 (s, 3H), 6.55 (dd, *J* = 16.0, 2.7 Hz, 1H), 7.64-7.75 (m, 3H), 7.87-7.92 (m, 2H), 10.03 (s, 1H). <sup>13</sup>C-NMR

(62.5 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 51.9, 120.9, 128.5, 130.1, 137.1, 140.0, 166.8, 191.4.

### 1.11. Cinnamamide (3k)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 5.65 (brs, 2H), 6.46 (d,  $J$  = 15.7 Hz, 1H), 7.36-7.39 (m, 3H), 7.50-7.52 (m, 2H), 7.66 (d,  $J$  = 15.7 Hz, 1H).

<sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 124.1, 127.9, 128.8, 130.0, 135.0, 142.6, 168.0.

### 1.12. (*E*)-3-(4-Formylphenyl)acrylamide (3l)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 5.57 (brs, 2H), 6.57 (d,  $J$  = 15.5 Hz, 1H), 7.66-7.73 (m, 3H), 7.90 (d,  $J$  = 8.0 Hz, 2H), 10.03 (s, 1H).

<sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 120.1, 128.0, 130.2, 134.2, 143.3, 144.8, 172.4, 190.2.

### 1.13. Butyl (*E*)-3-(4-methoxyphenyl)acrylate (3m)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 0.89 (t,  $J$  = 7.5 Hz, 3H), 1.29-1.44 (m, 2H), 1.56-1.67 (m, 2H), 3.77 (s, 3H), 4.12 (t,  $J$  = 6.5 Hz, 2H), 6.24 (d,  $J$  = 16.0 Hz, 1H), 6.83 (d,  $J$  = 8.7 Hz, 2H), 7.41 (d,  $J$  = 9.5 Hz, 2H), 7.57 (d,  $J$  = 16.0 Hz, 1H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 13.7, 19.2, 30.8, 55.3, 64.2, 114.3, 115.7, 129.7, 144.2, 161.3, 167.4.

### 1.14. Butyl (*E*)-3-(4-cyanophenyl)acrylate (3n)

<sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) = 0.97 (t,  $J$  = 7.5 Hz, 3H), 1.37-1.51 (m, 2H), 1.64-1.75 (m, 2H), 4.23 (t,  $J$  = 7.5 Hz, 2H), 6.53(d,  $J$  = 15.0 Hz, 1H), 7.60-7.69 (m, 5H). <sup>13</sup>C-NMR (62.5 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  (ppm) =

13.7, 19.1, 30.6, 64.7, 113.26, 118.3, 121.8, 128.3, 132.6, 138.7, 142.0, 166.1.

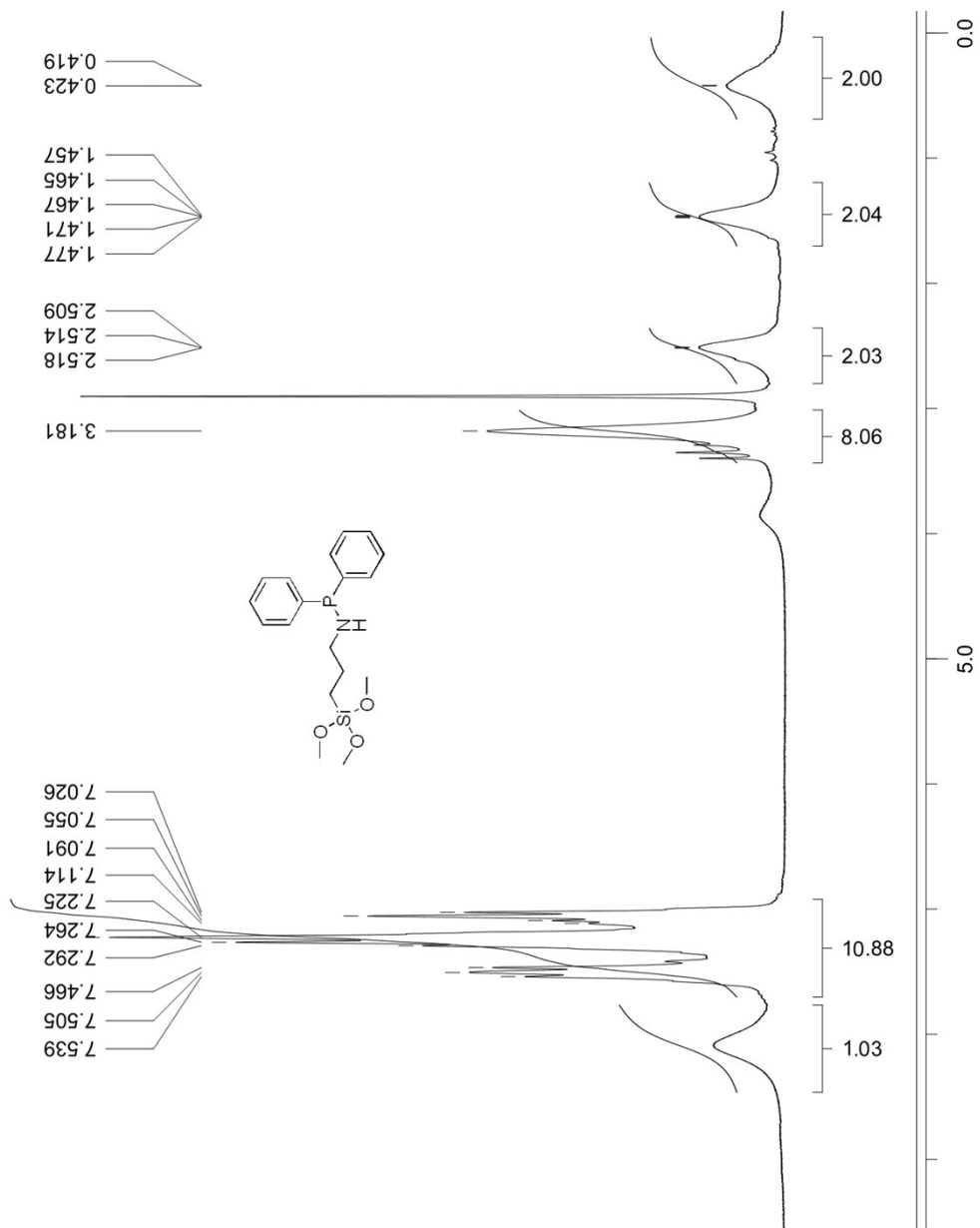
**1.15. (*E*)-3-(4-formylphenyl)acrylonitrile (3o)**

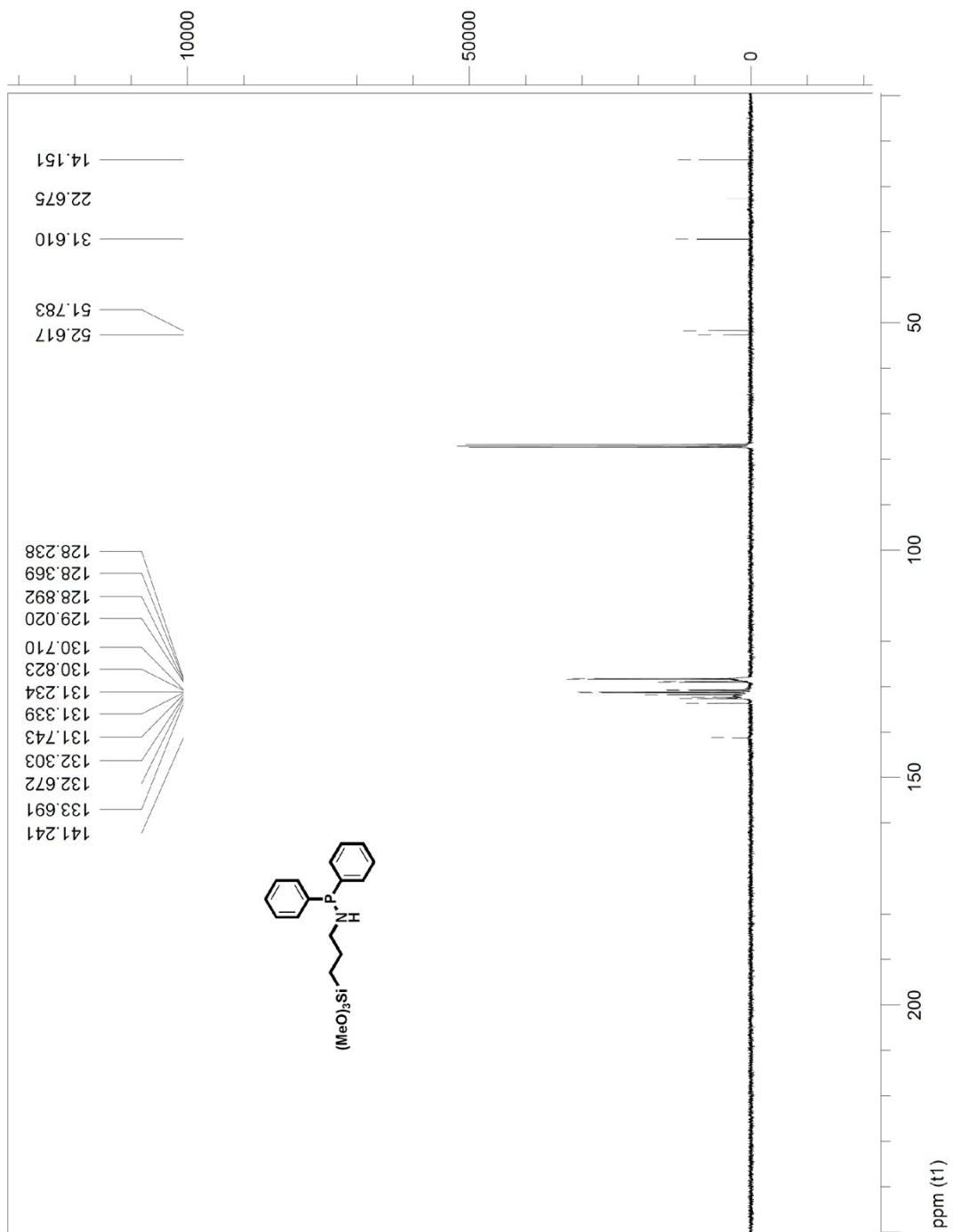
$^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  (ppm) = 6.03 (d,  $J$  = 16.7 Hz, 1H), 7.46 (d,  $J$  = 16.5 Hz, 1H), 7.62 (d,  $J$  = 8.2 Hz, 2H), 7.94 (d,  $J$  = 11.7 Hz, 2H), 10.05 (s, 1H).  $^{13}\text{C}$ -NMR (62.5 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  (ppm) = 99.7, 116.9, 127.9, 130.3, 133.4, 147.2, 148.9, 191.2.

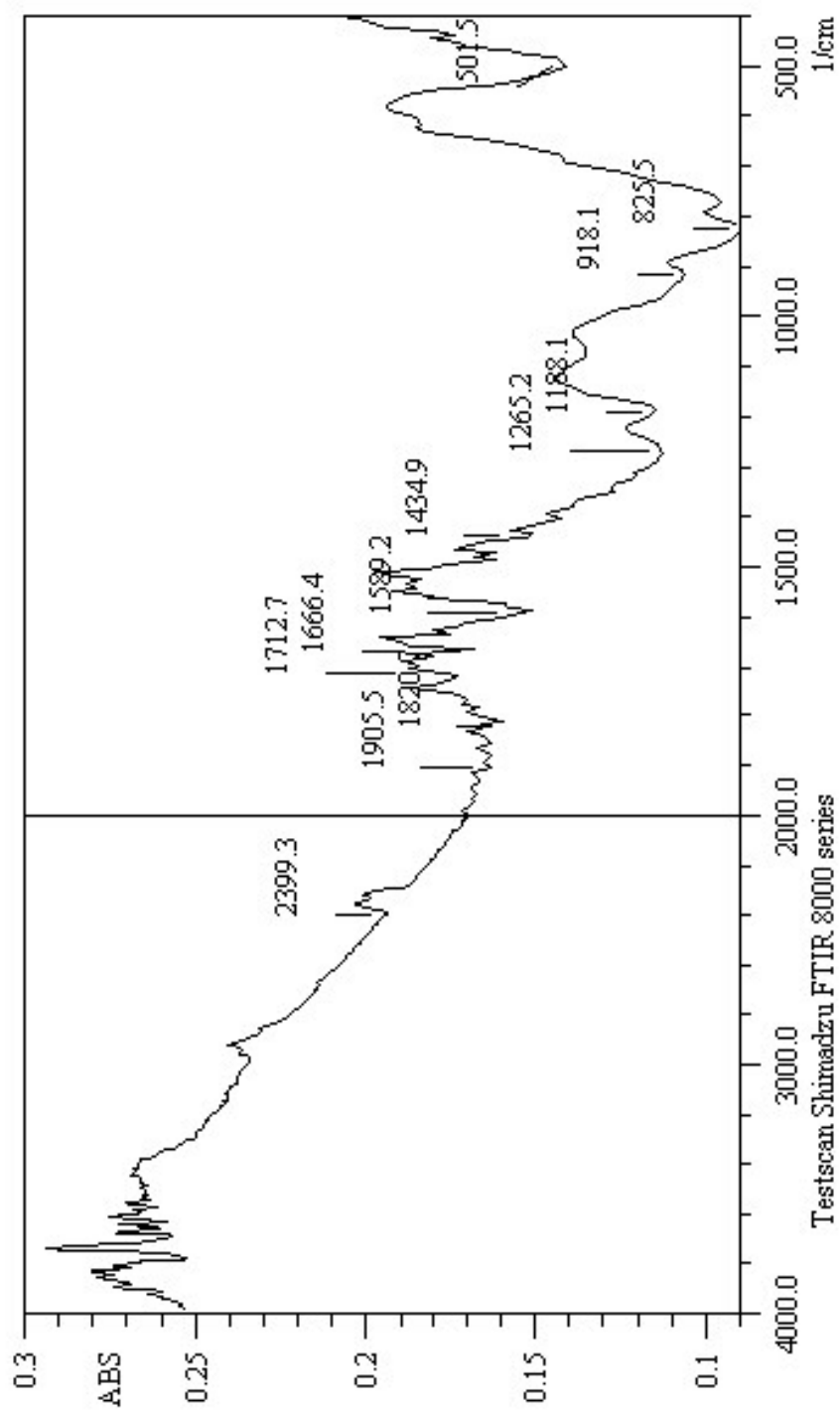
**1.16. (*E*)-3-(4-acetylphenyl)acrylonitrile (3p)**

$^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  (ppm) = 2.62 (s, 3H), 5.99 (d,  $J$  = 16.7 Hz, 1H), 7.44 (d,  $J$  = 16.7 Hz, 1H), 7.55 (d,  $J$  = 8.7 Hz, 2H), 7.99 (d,  $J$  = 8.5 Hz, 2H).  $^{13}\text{C}$ -NMR (62.5 MHz,  $\text{CDCl}_3/\text{TMS}$ )  $\delta$  (ppm) = 26.7, 99.0, 117.5, 127.5, 129.0, 137.5, 147.4, 149.1, 197.0.

## 2. Copy of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and IR of DPPPA

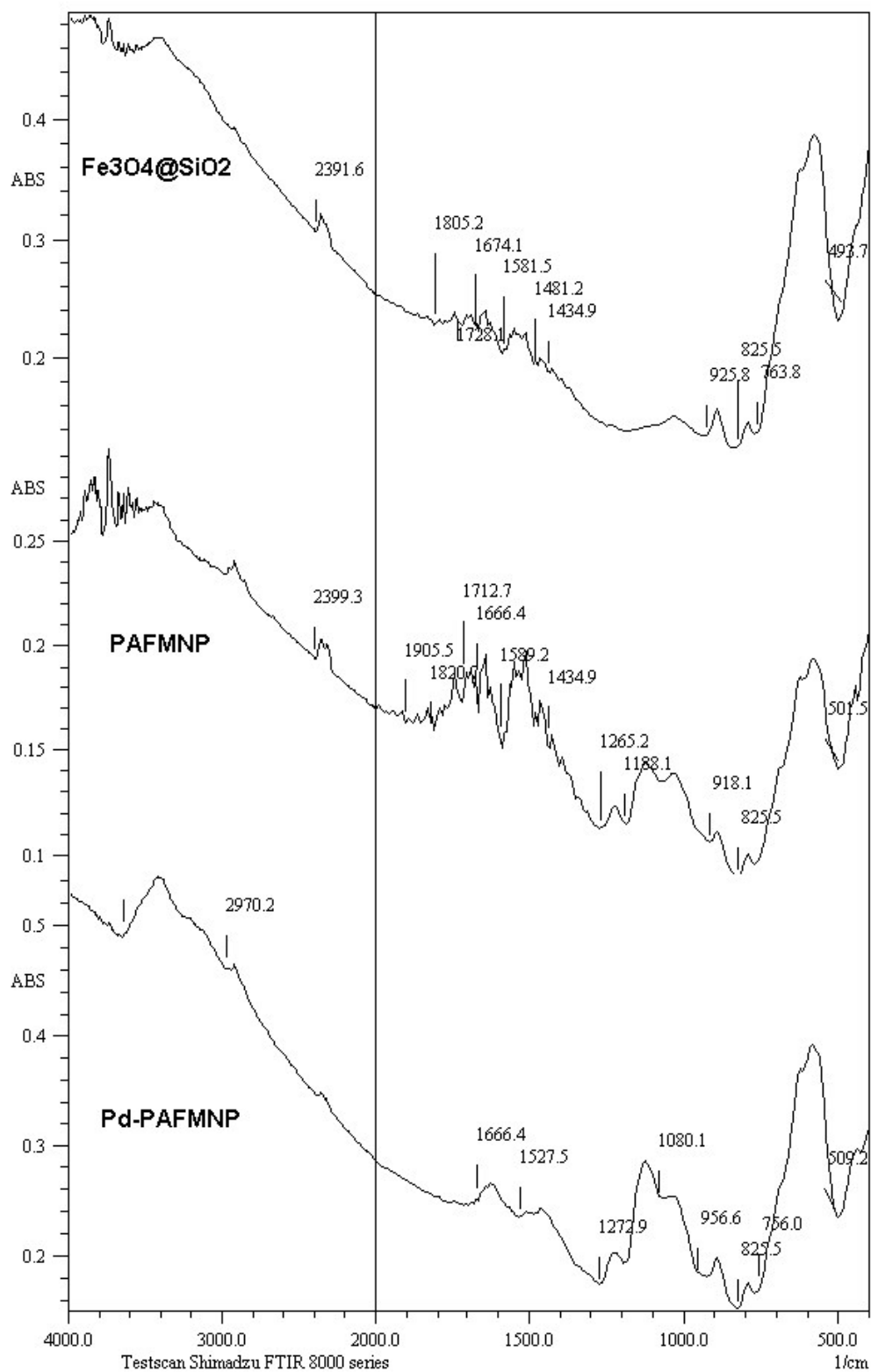






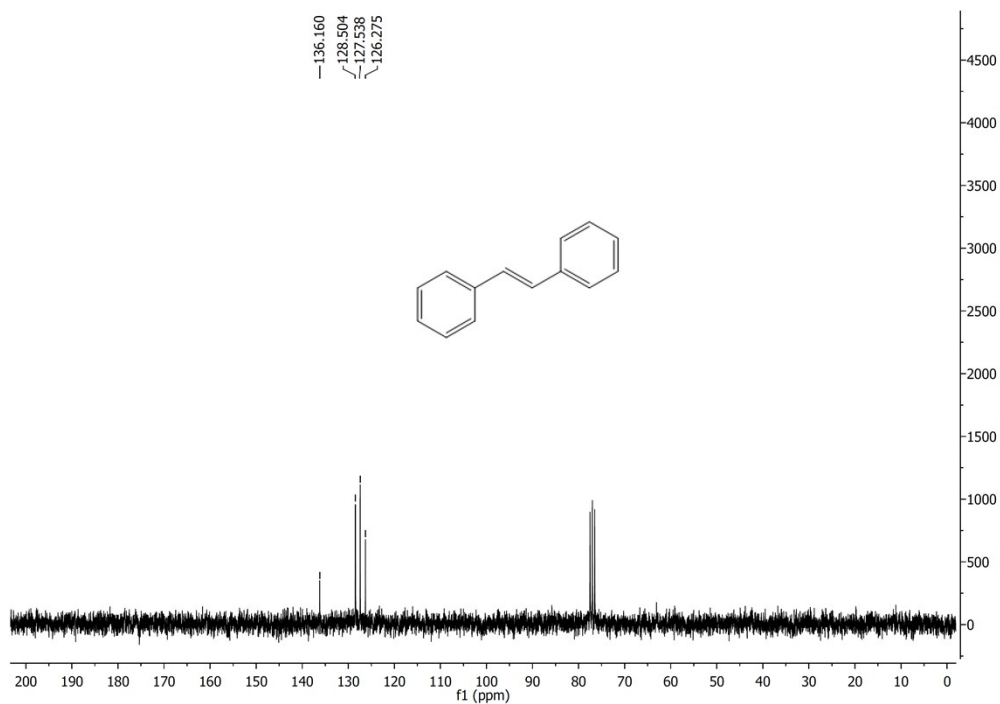
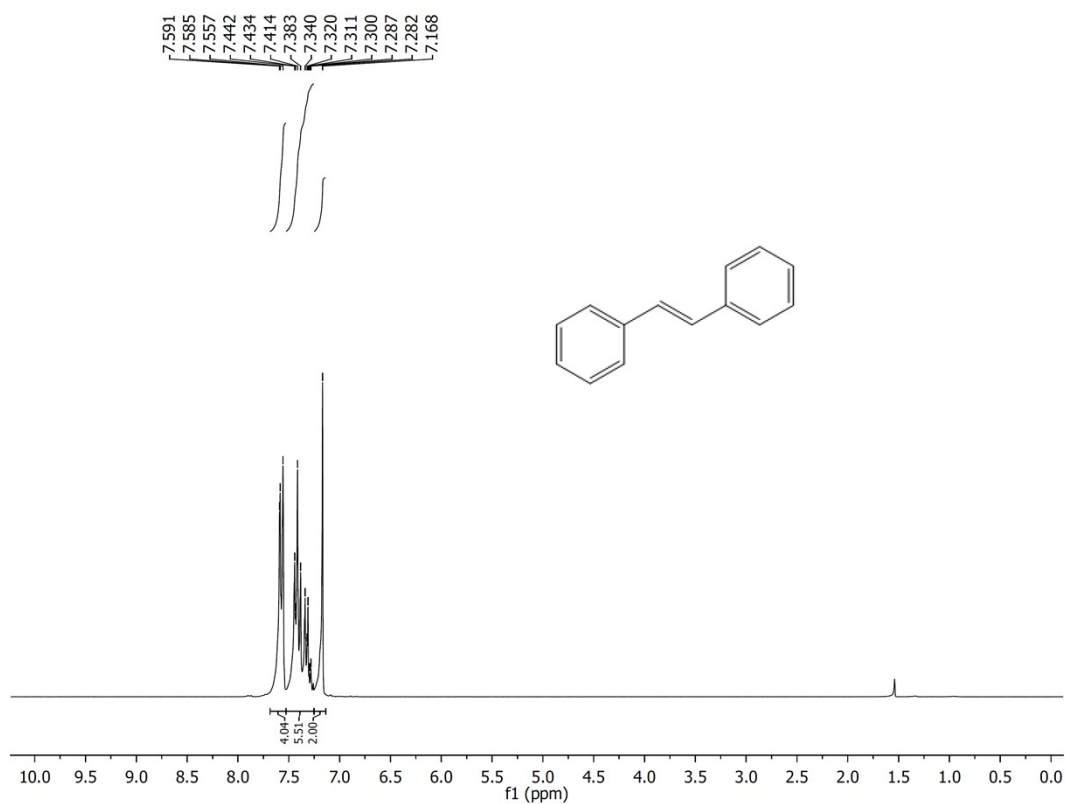


### 3. A comparison between the FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, DPPPA, and PAFMNP

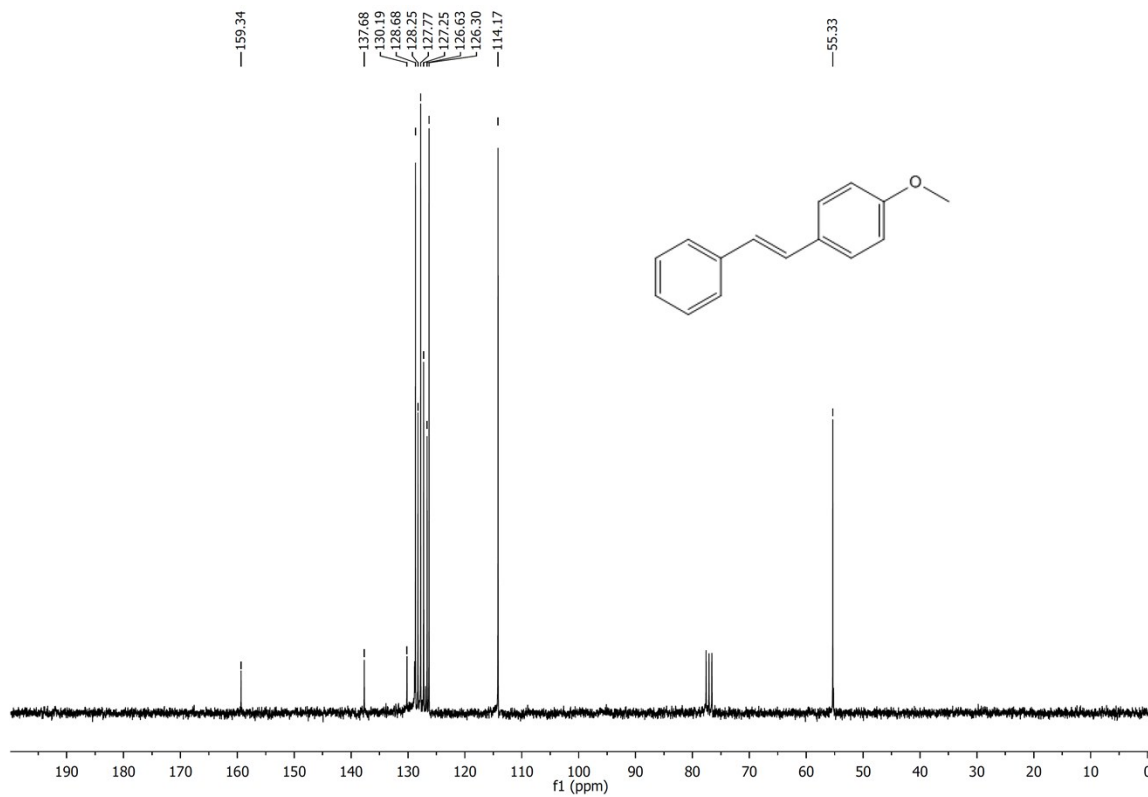
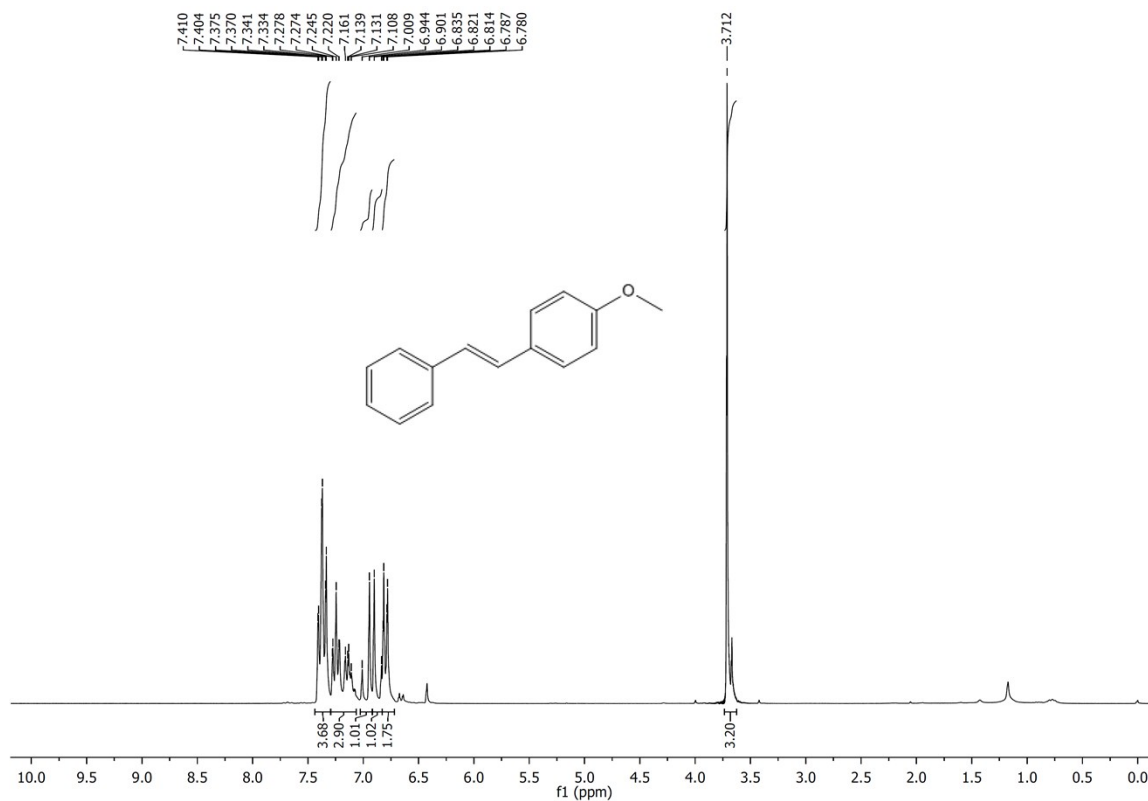


## 4. Copy of $^1\text{H}$ and $^{13}\text{C}$ NMR of Heck products

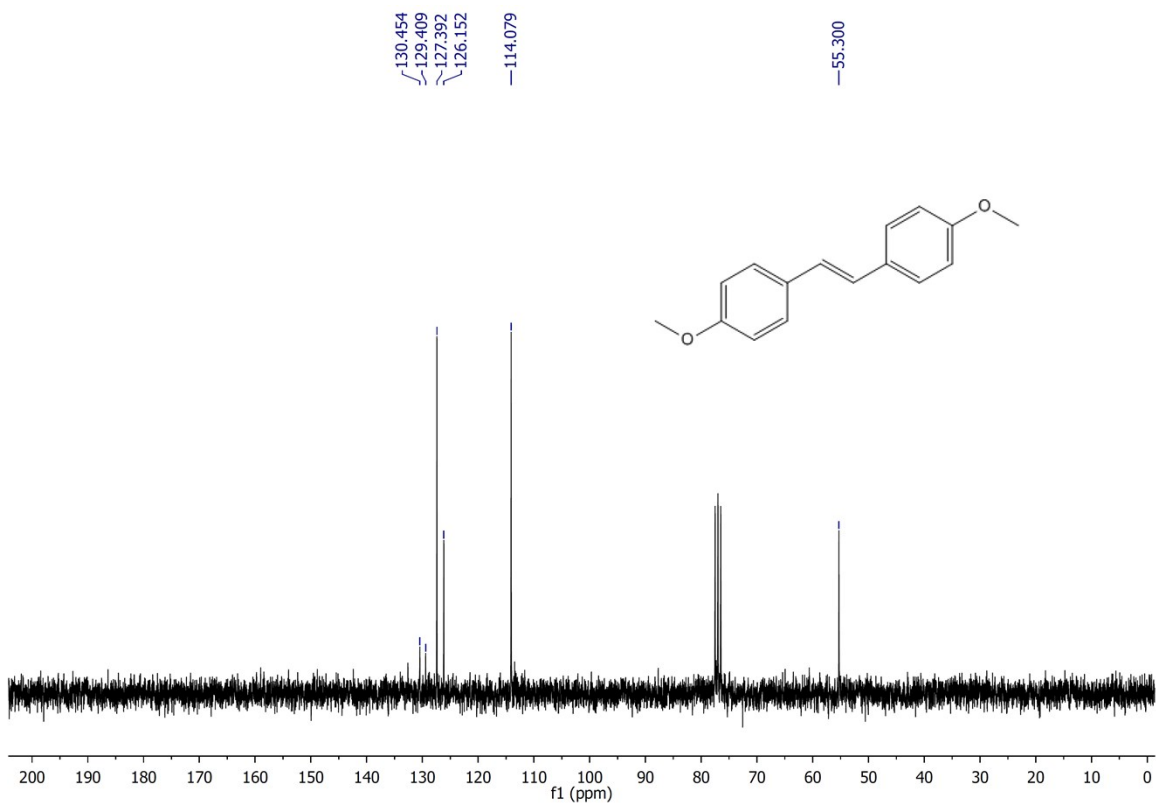
### 4.1. (*E*)-1,2-Diphenylethene (3a)



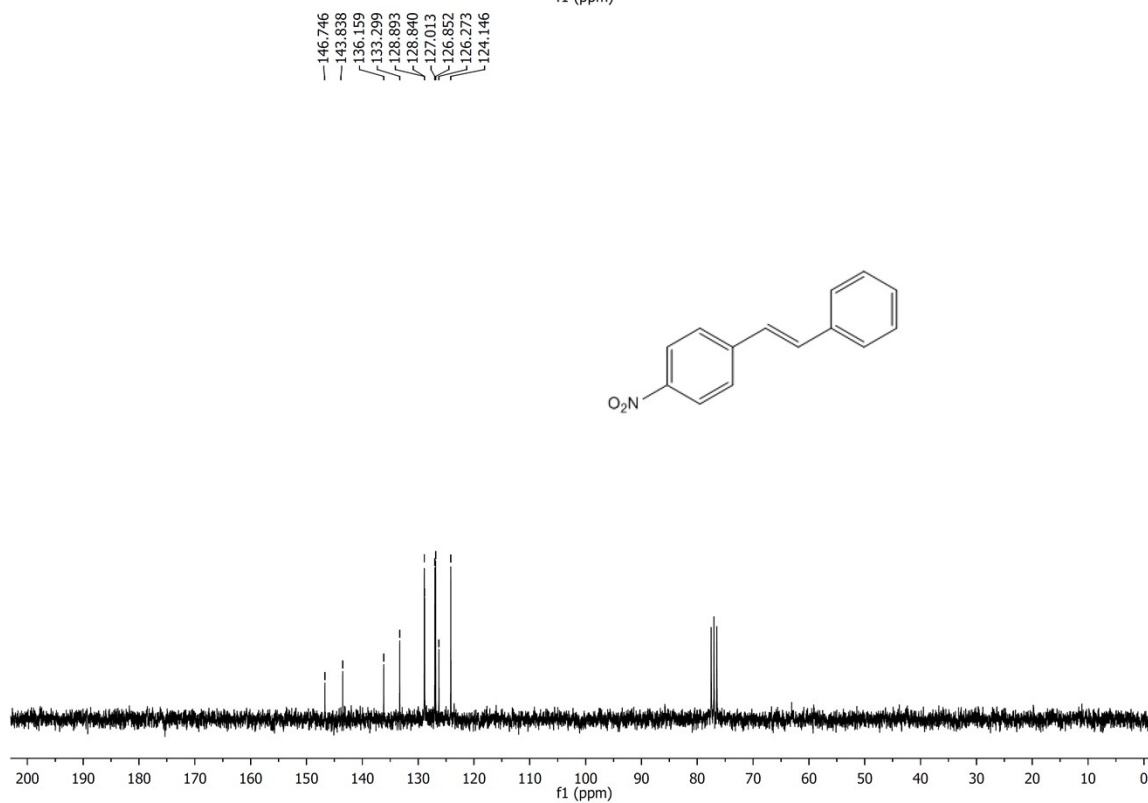
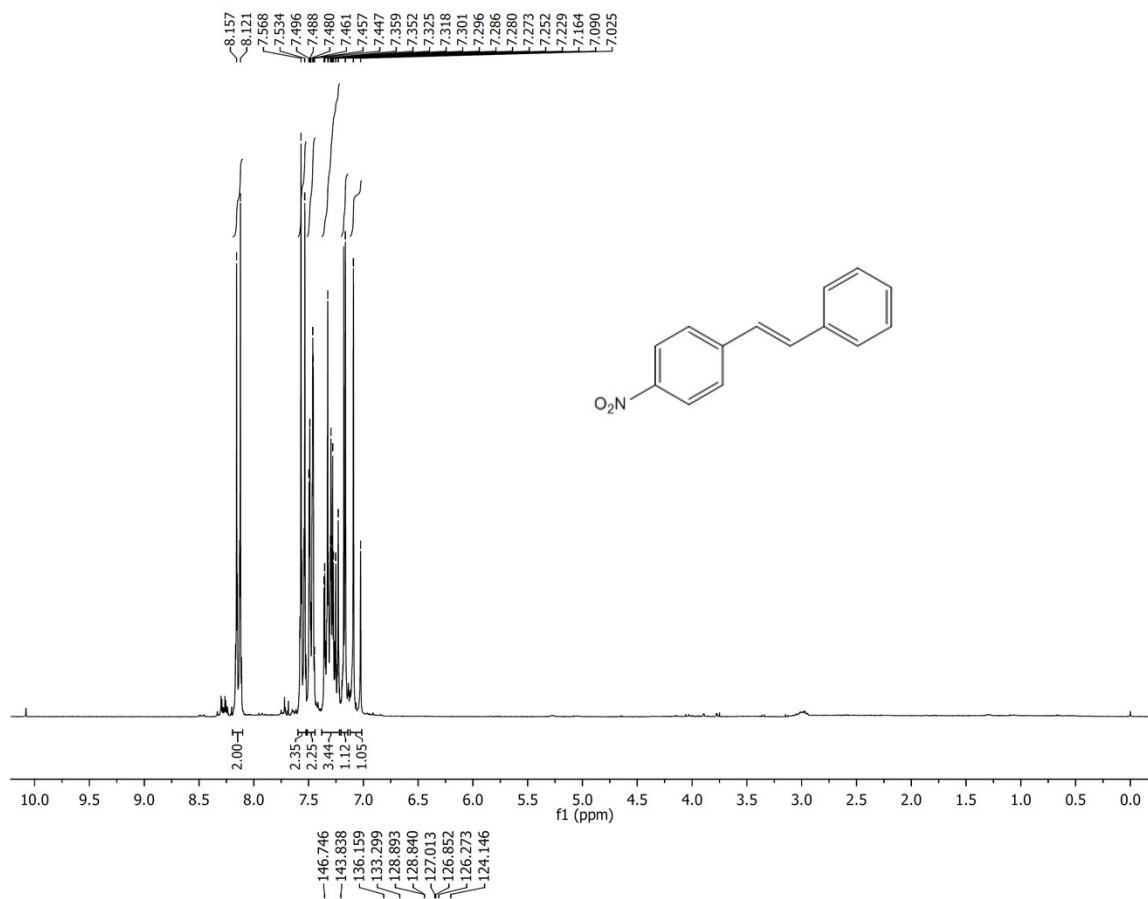
## 4.2. (*E*)-1-Methoxy-4-styrylbenzene (3b)



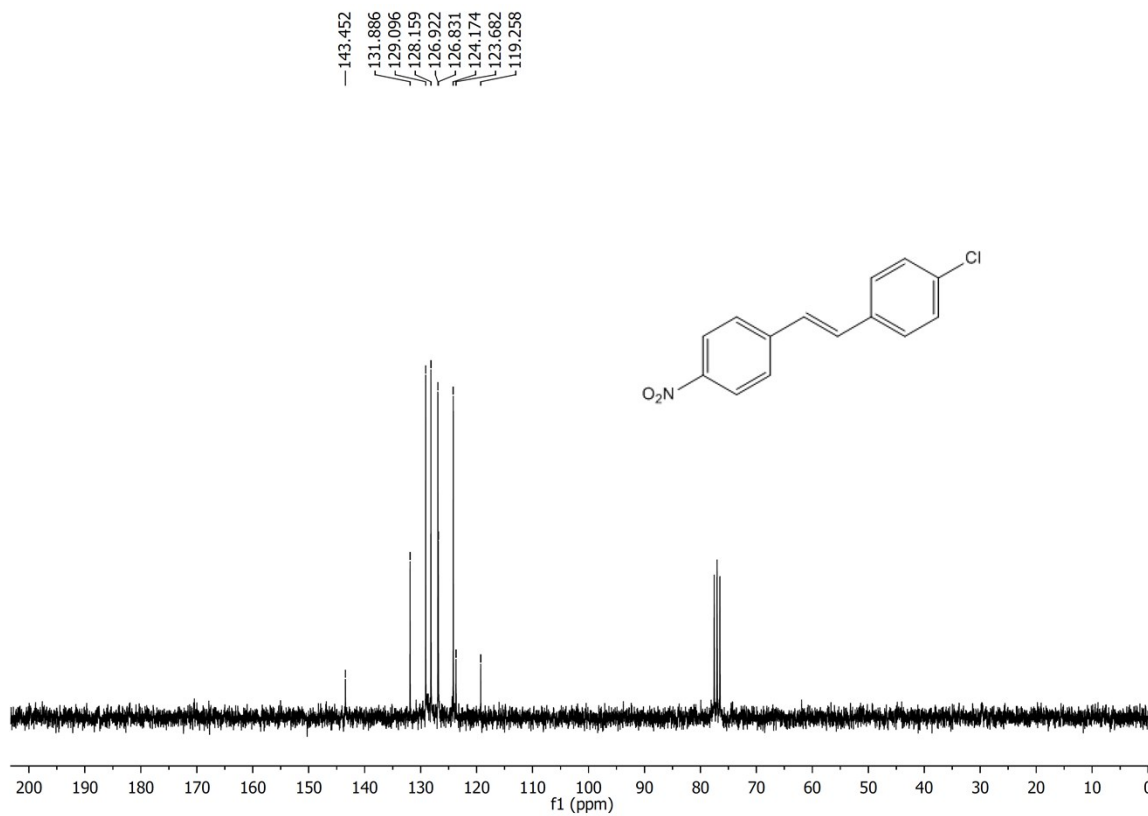
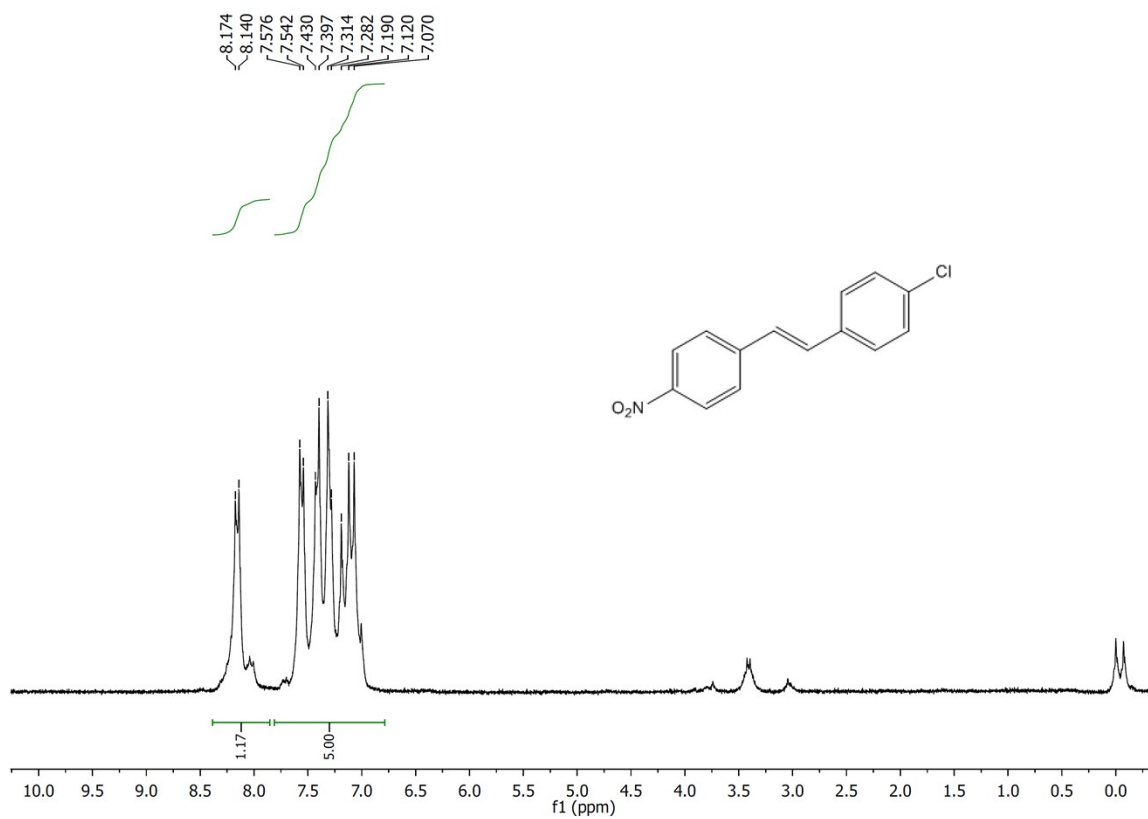
### 4.3. (*E*)-1,2-bis(4-methoxyphenyl)ethene (3c)



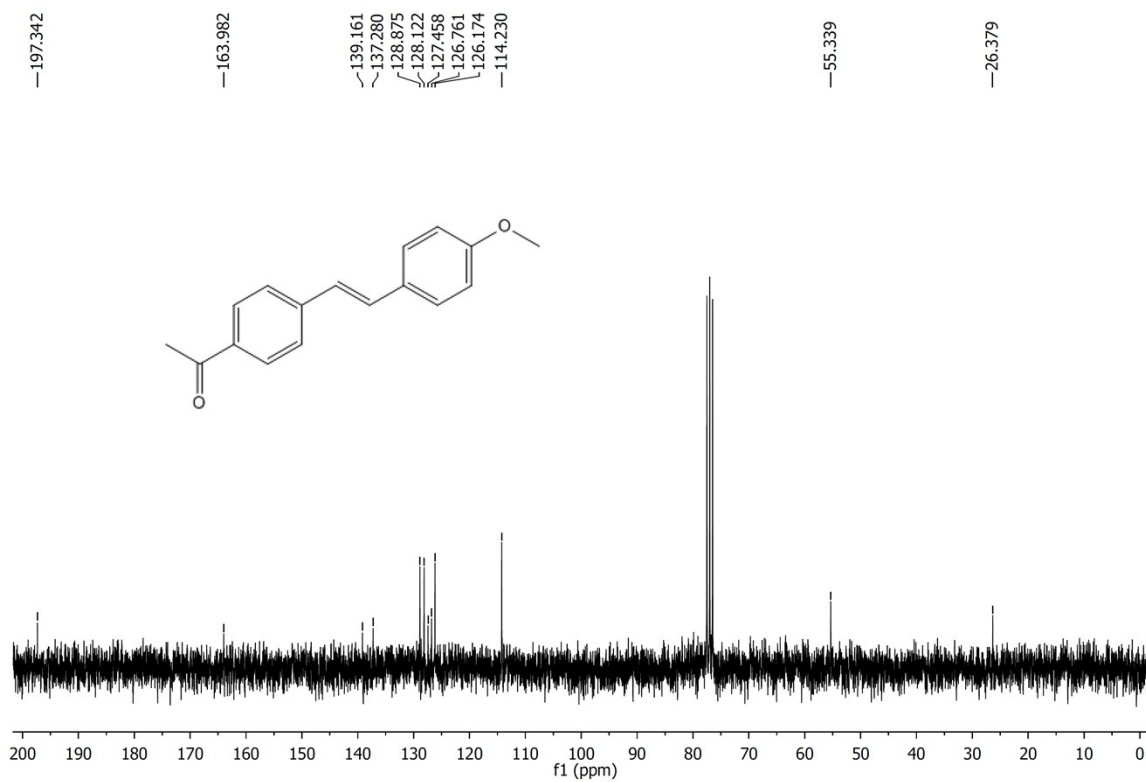
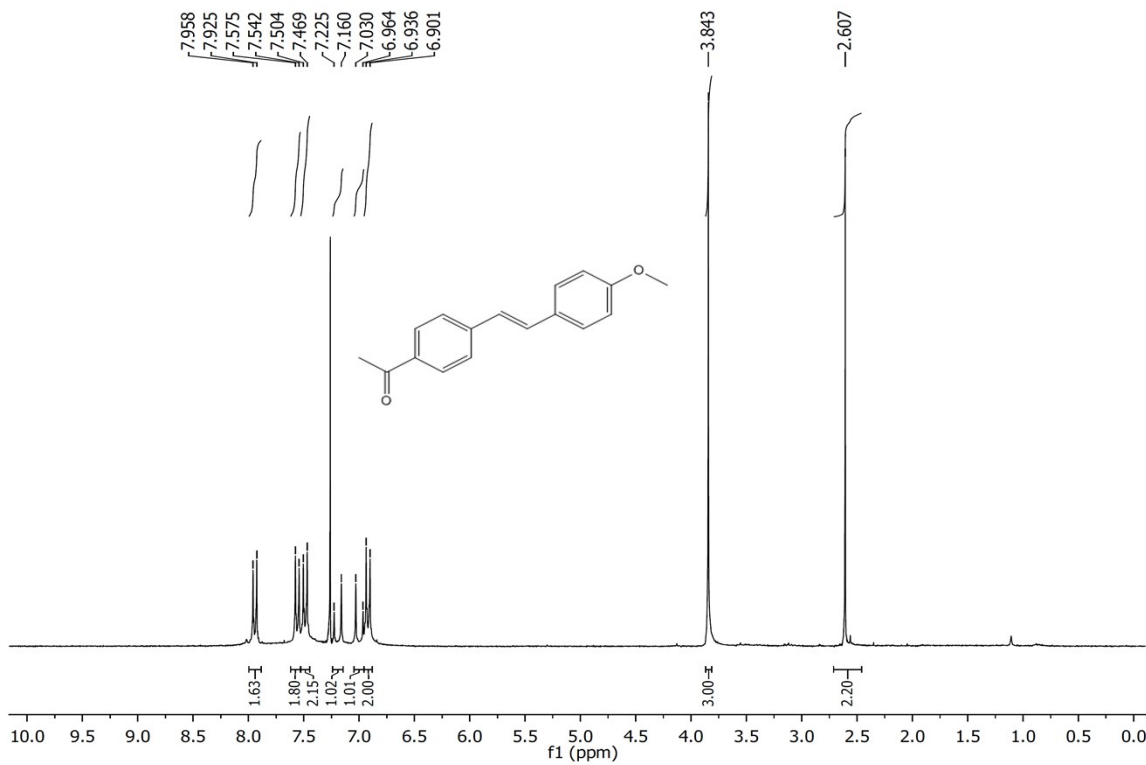
#### 4.4. (*E*)-1-Nitro-4-styrylbenzene (3d)



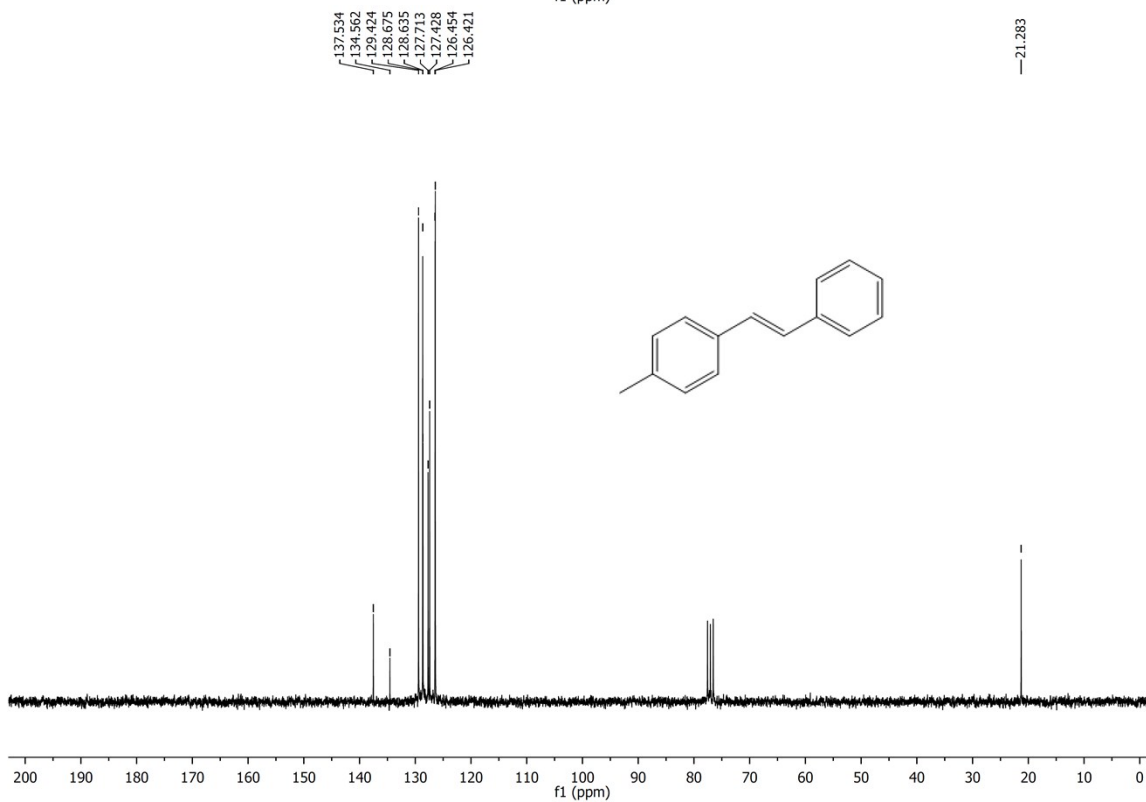
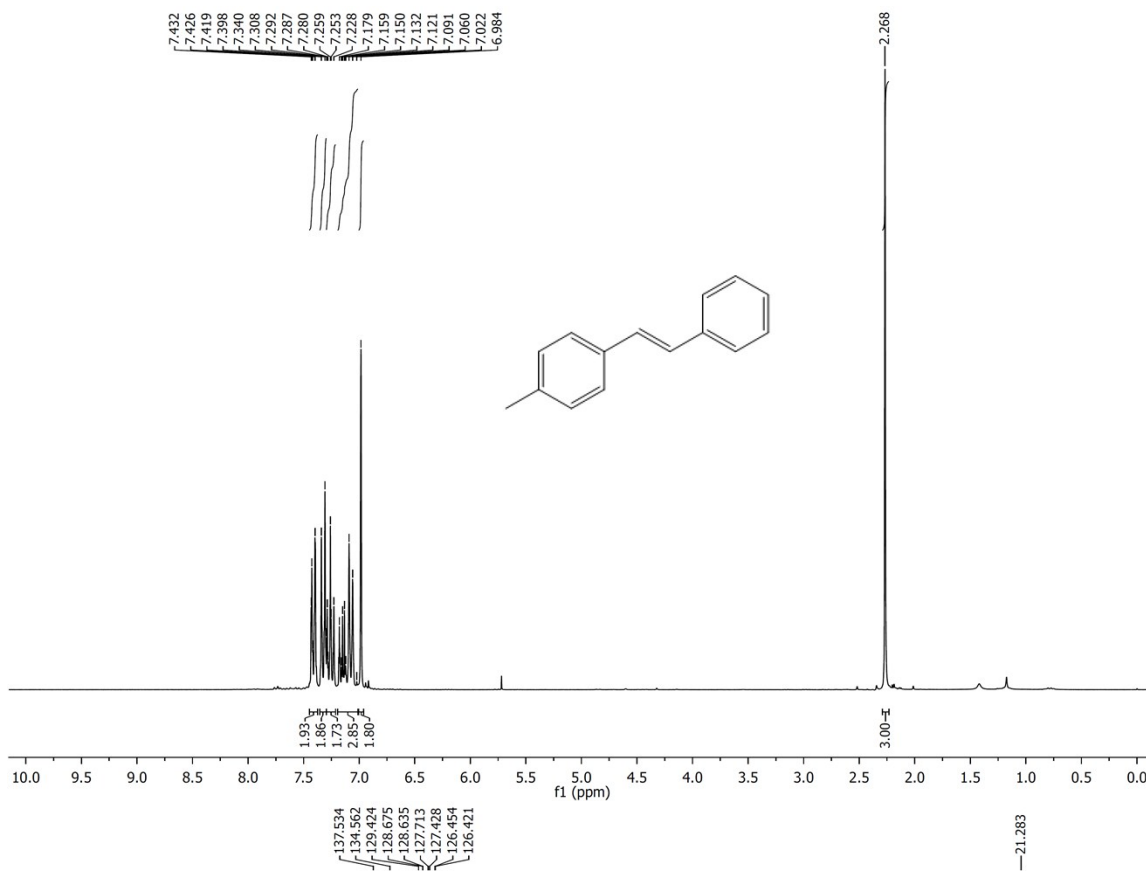
#### 4.5. (*E*)-1-Chloro-4-(4-nitrostyryl)benzene (**3e**)



#### 4.6. (*E*)-1-(4-(4-Methoxystyryl)phenyl)ethan-1-one (**3f**)

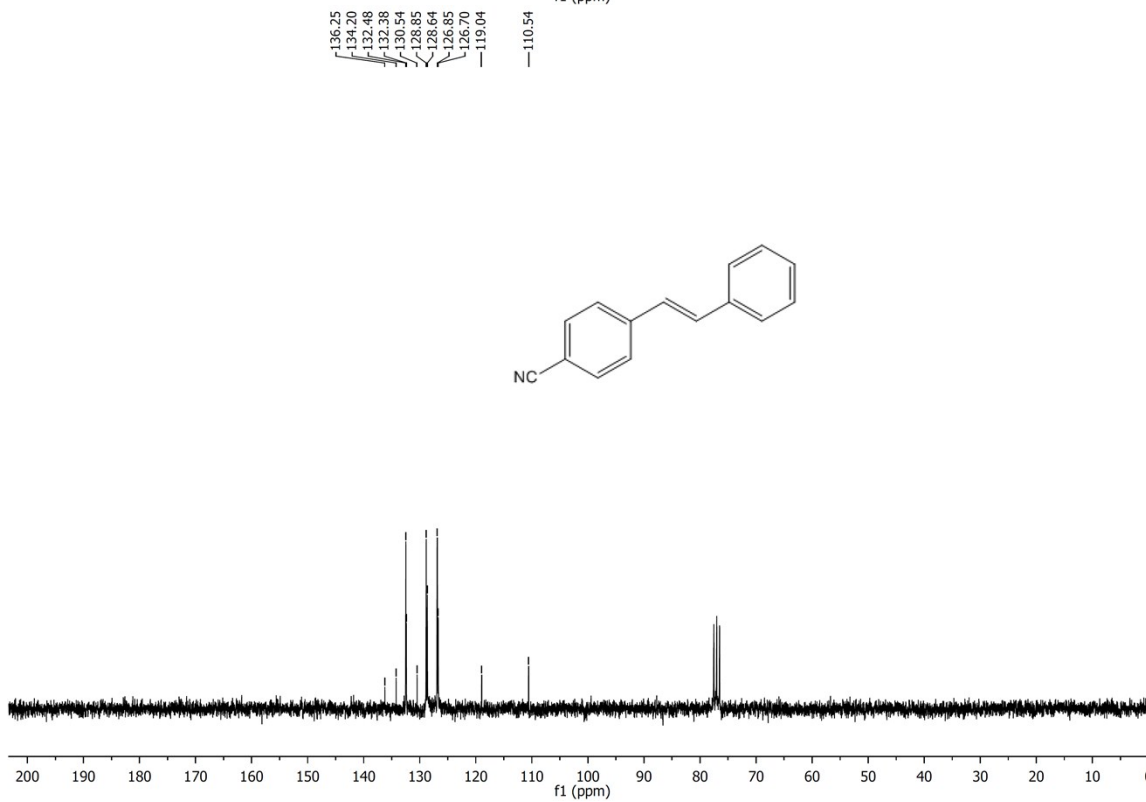
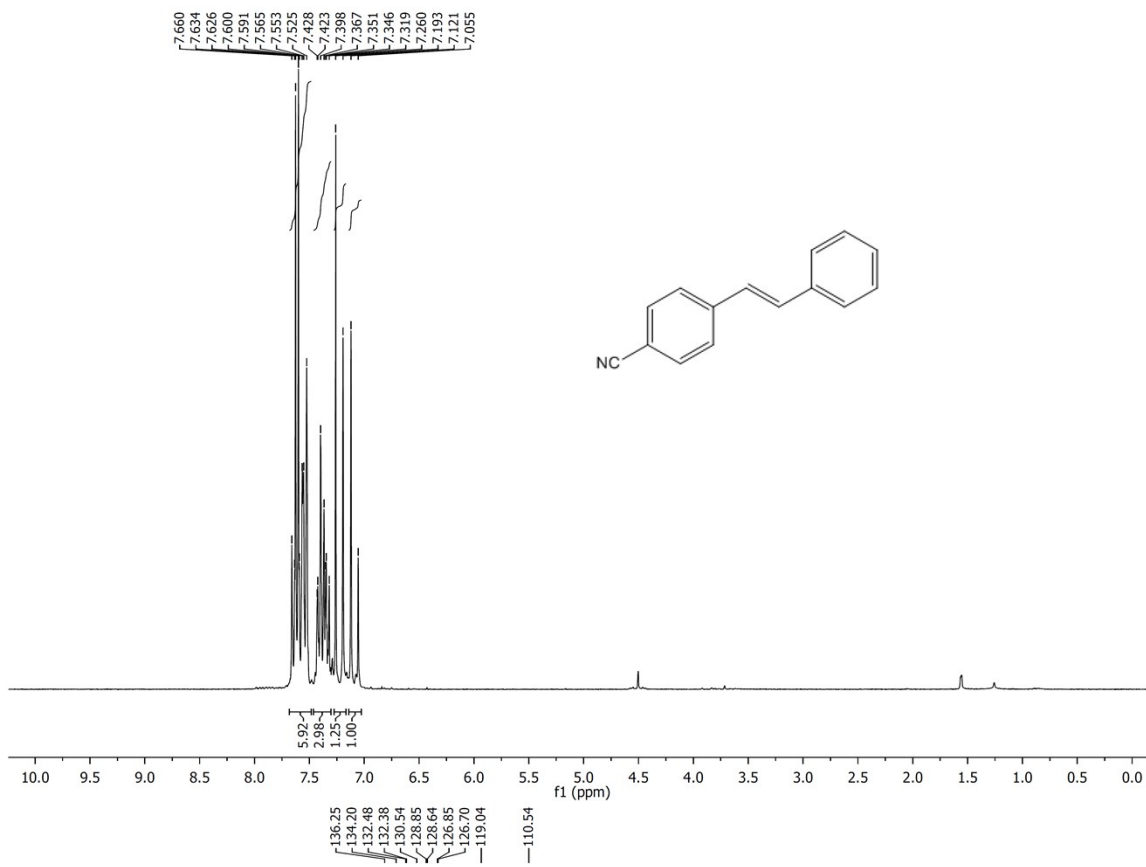


### 4.7. (*E*)-1-Methyl-4-styrylbenzene (3g)

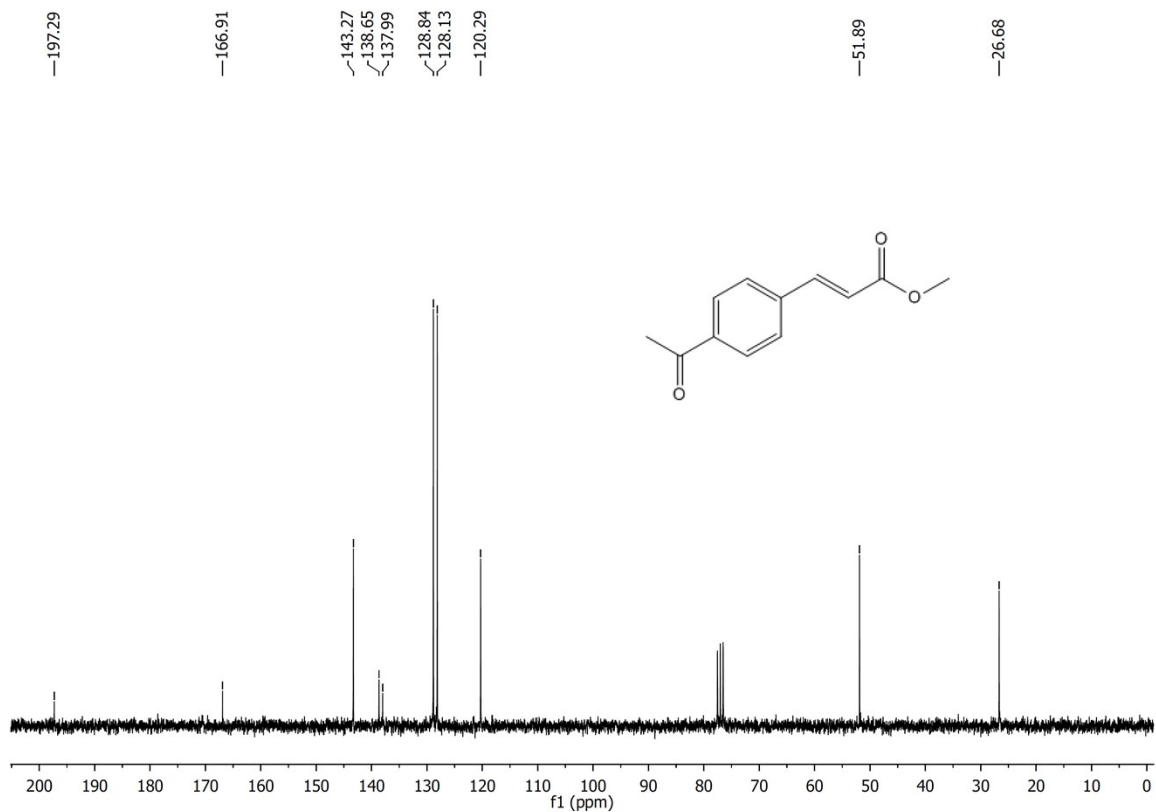
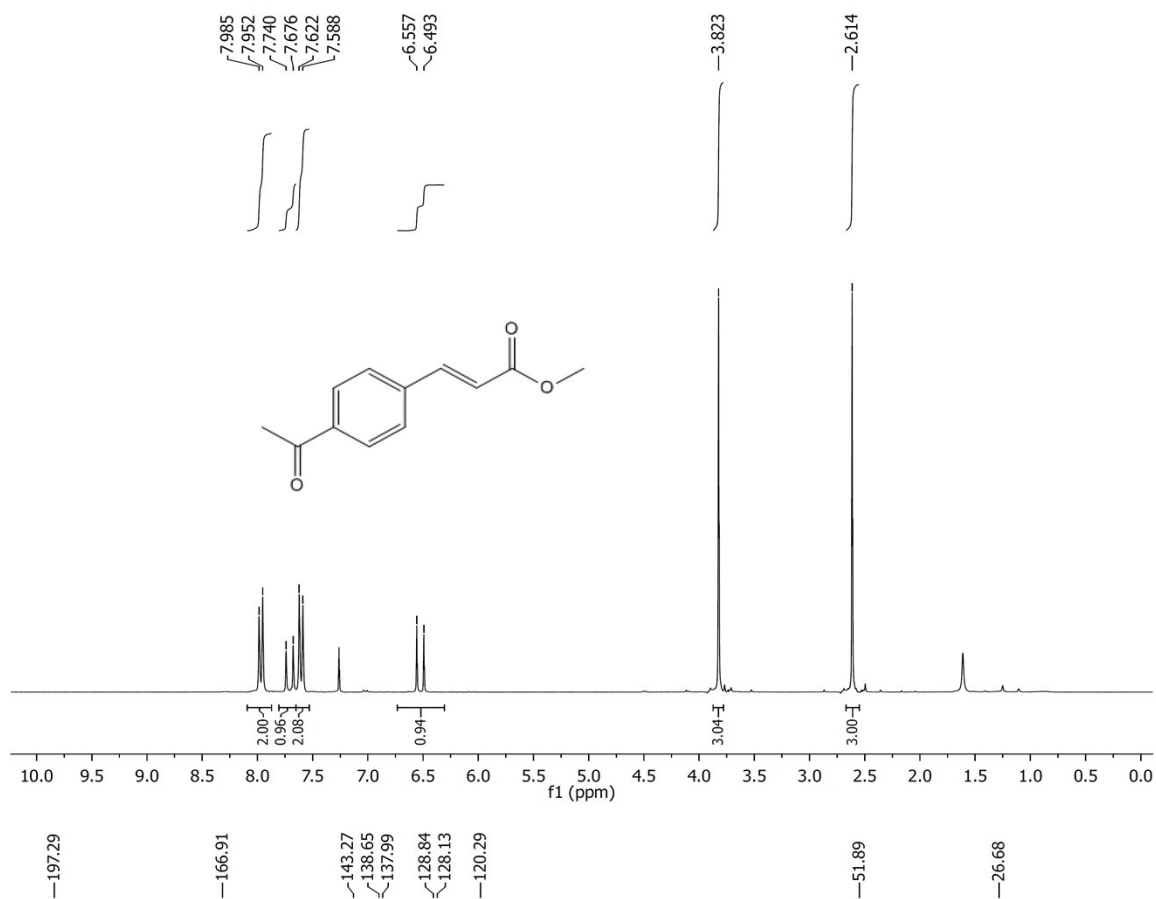




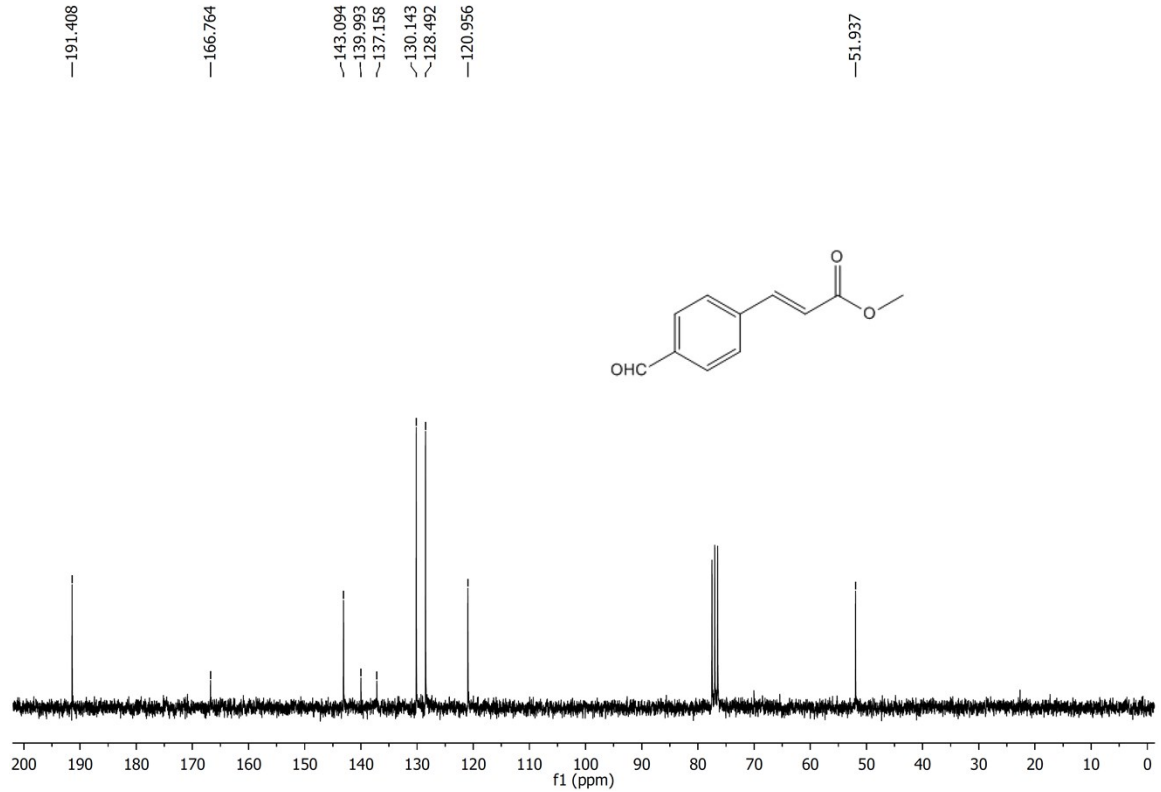
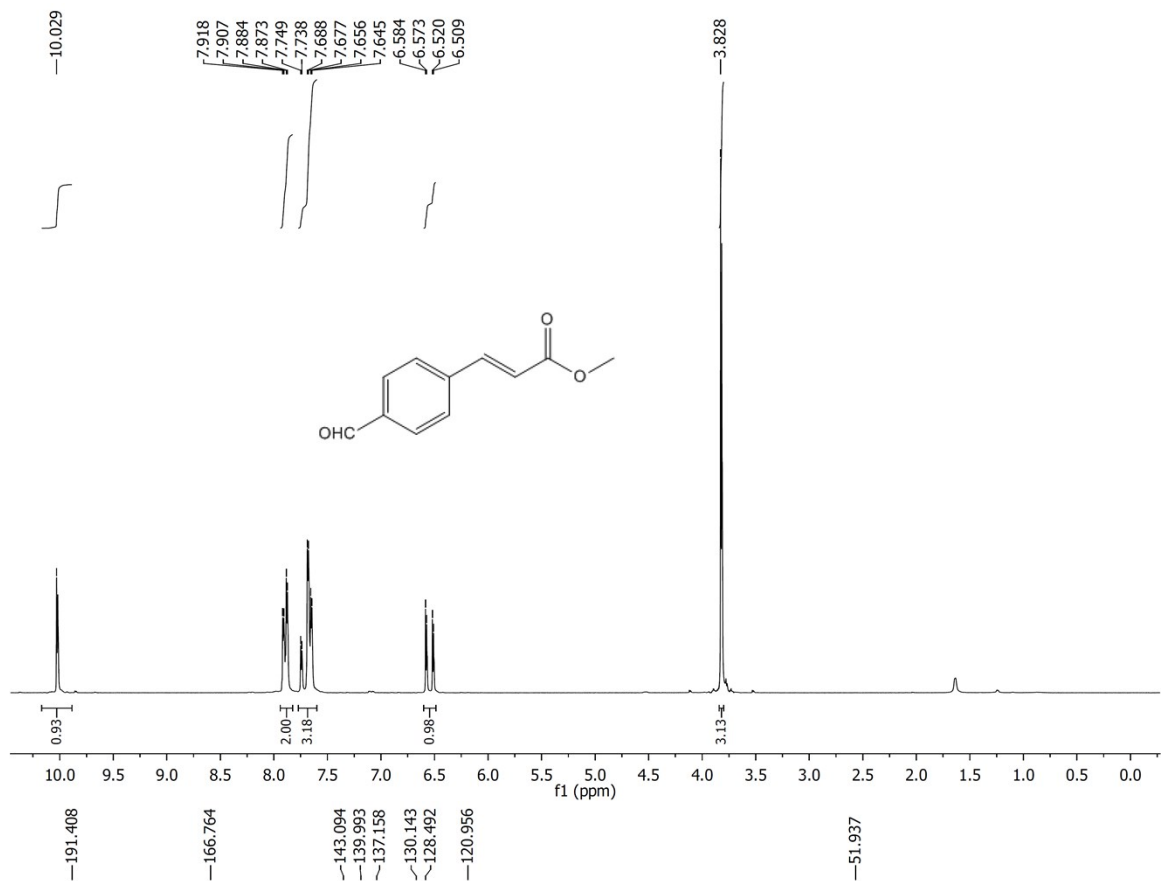
### 4.8. (*E*)-4-Styrylbenzonitrile (3h)



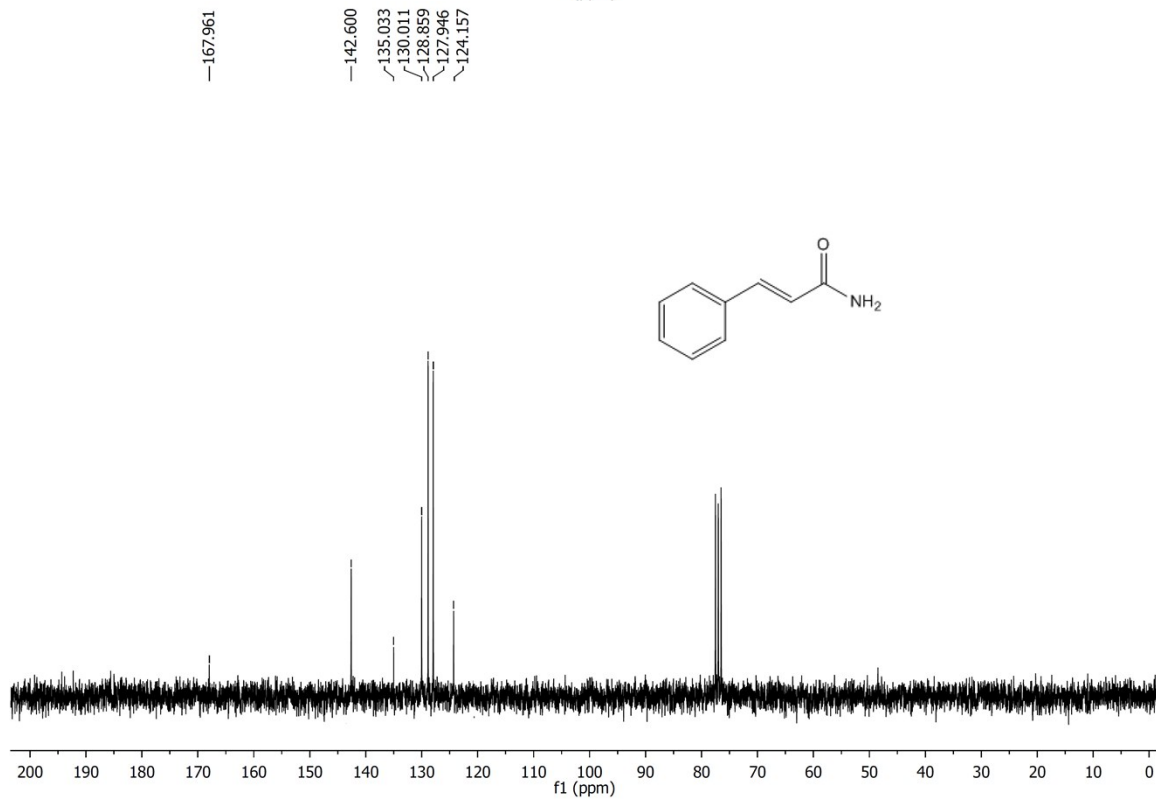
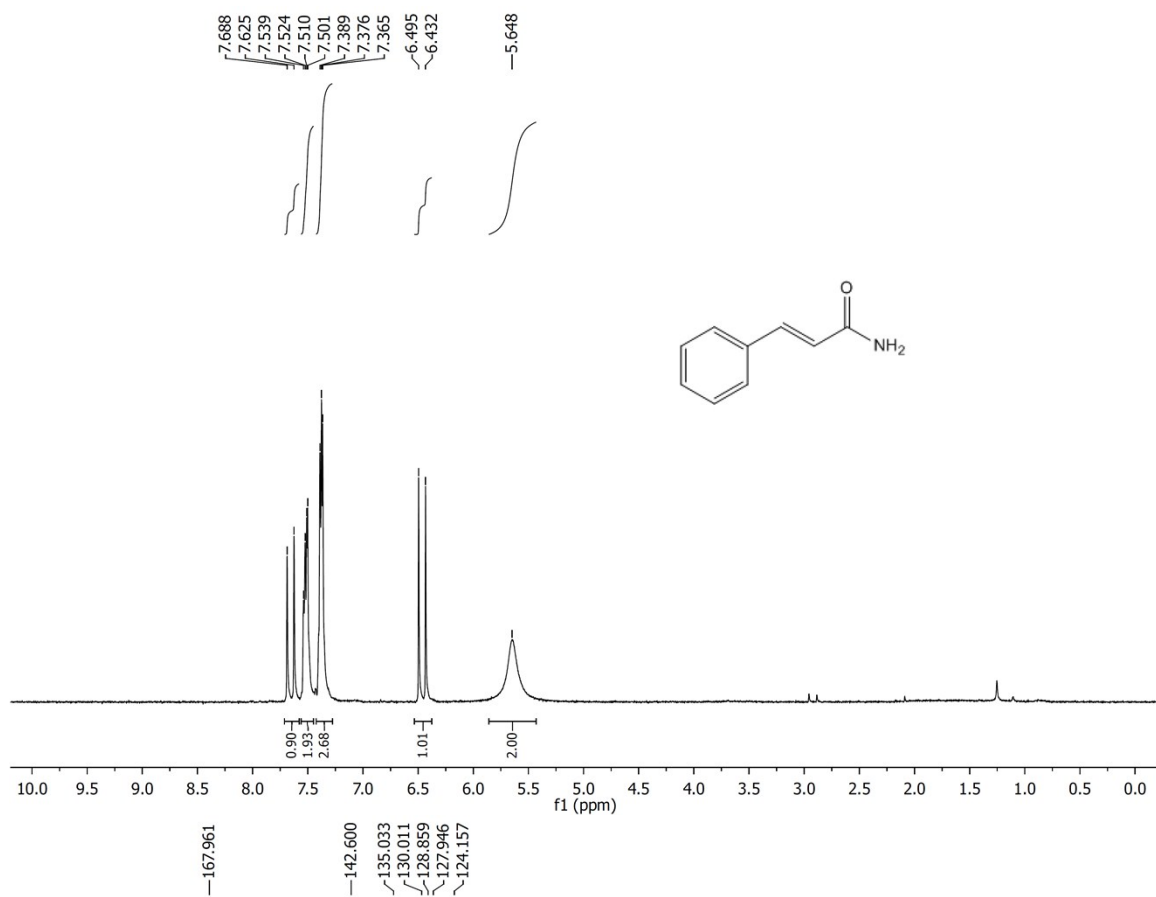
### 4.9. Methyl (*E*)-3-(4-acetylphenyl)acrylate (**3i**)



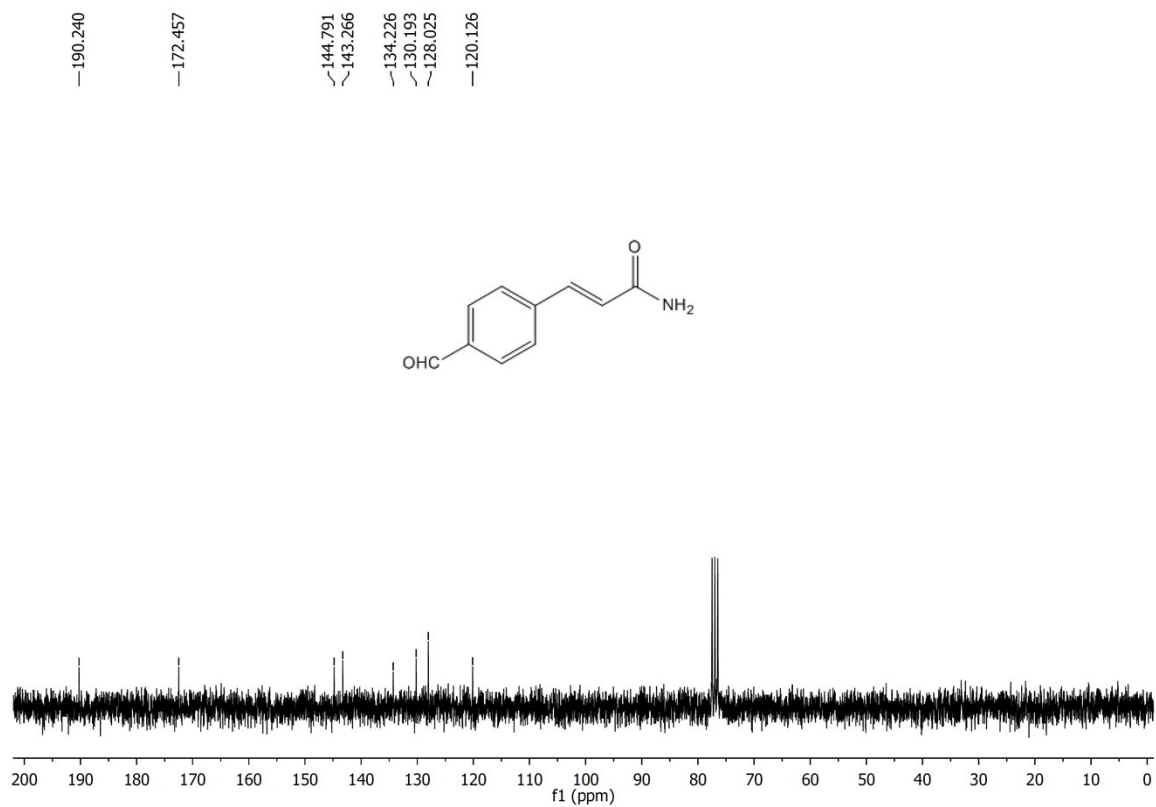
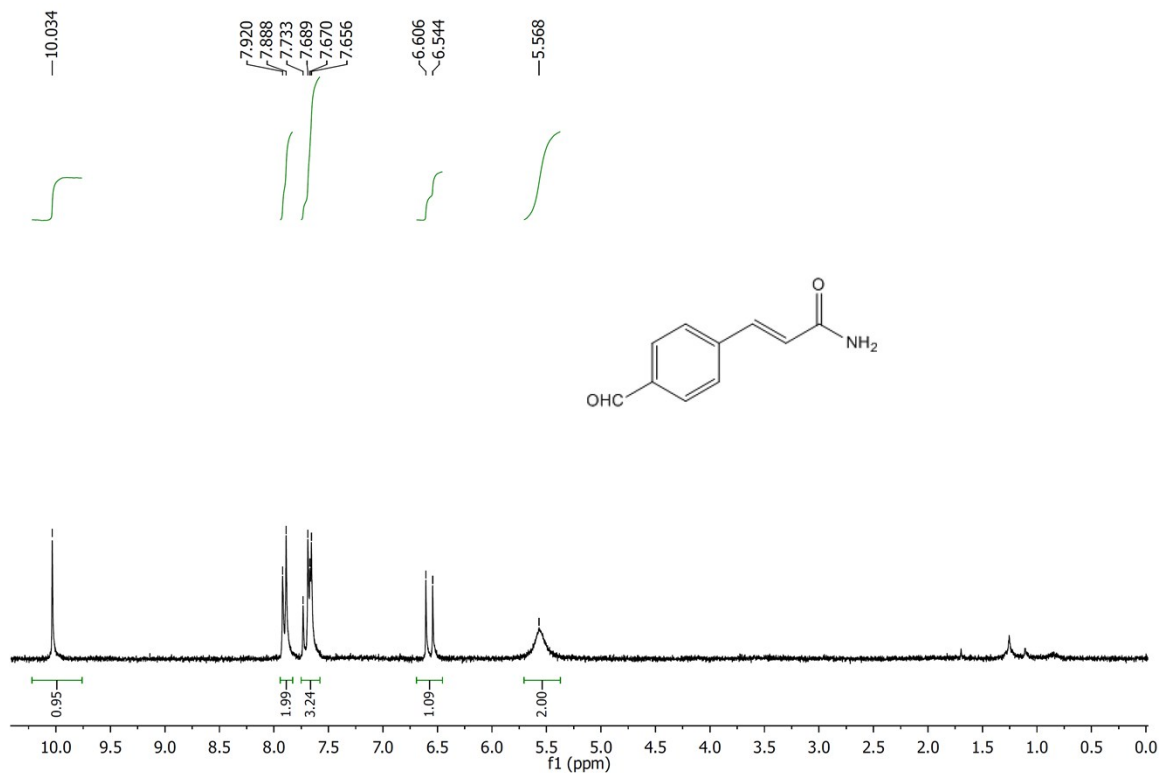
## 4.10. Methyl (*E*)-3-(4-formylphenyl)acrylate (**3j**)



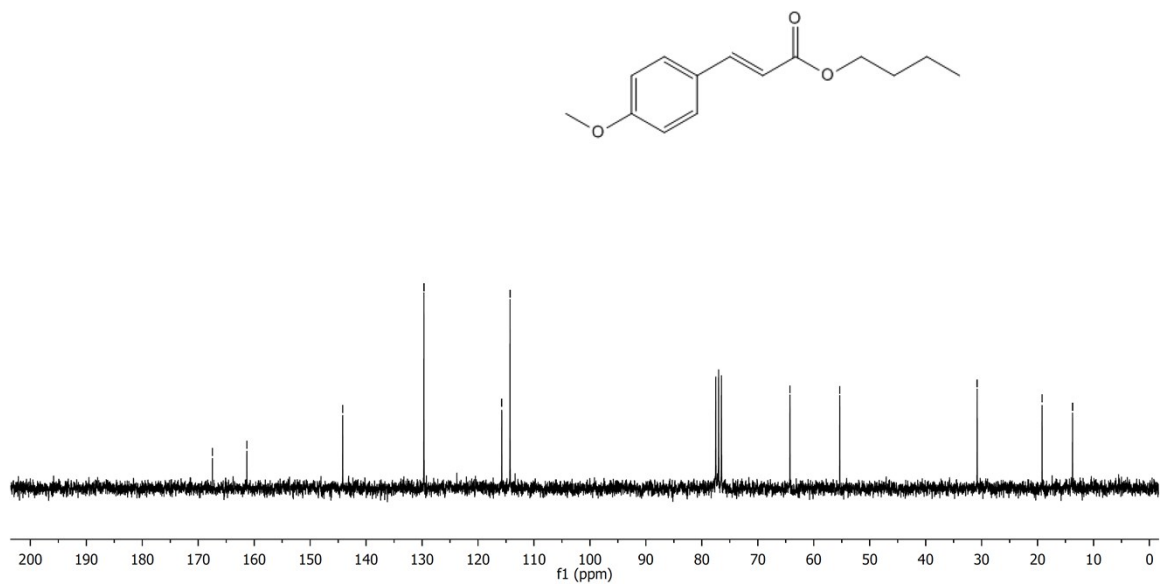
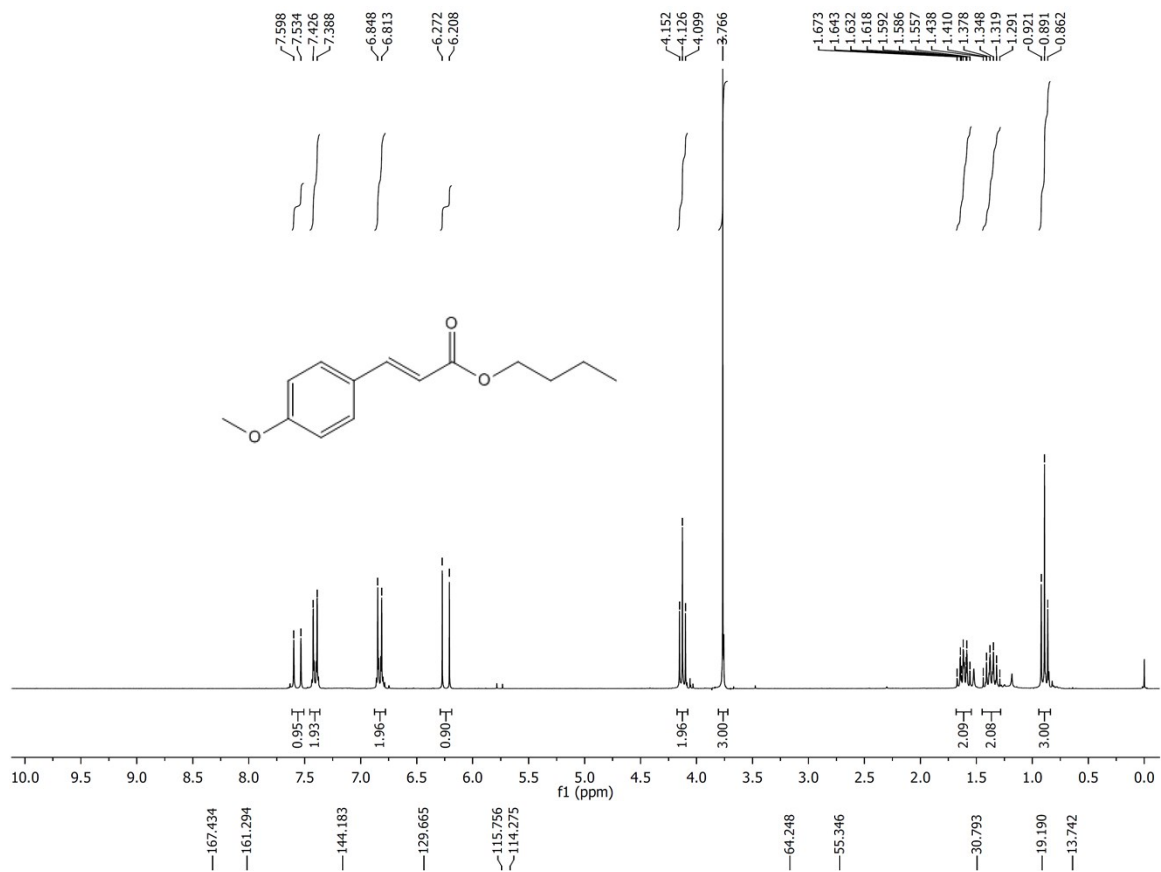
## 4.11. Cinnamamide (3k)



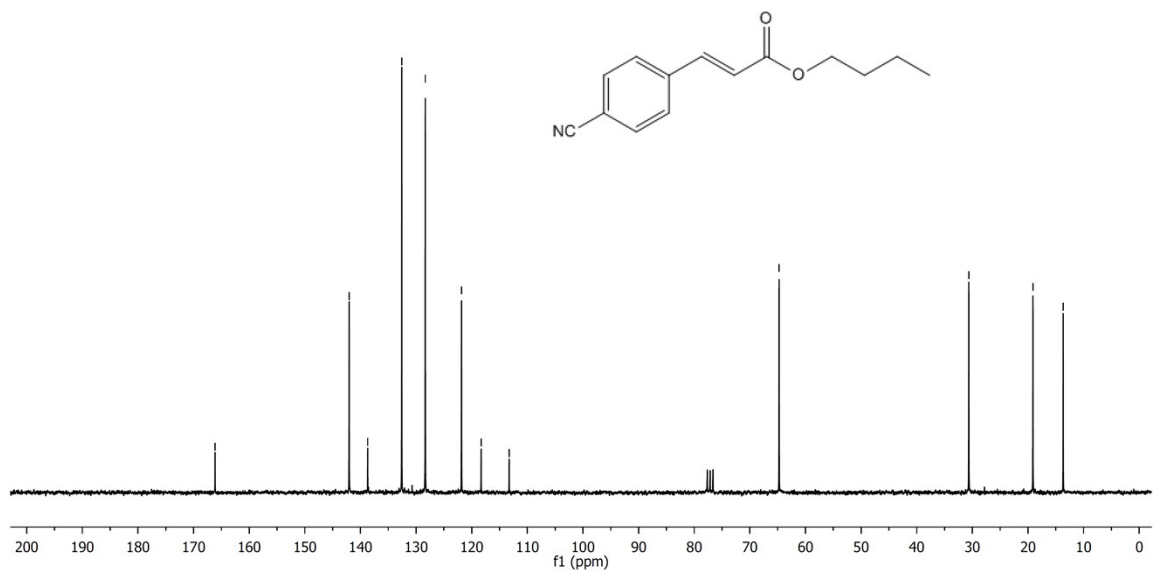
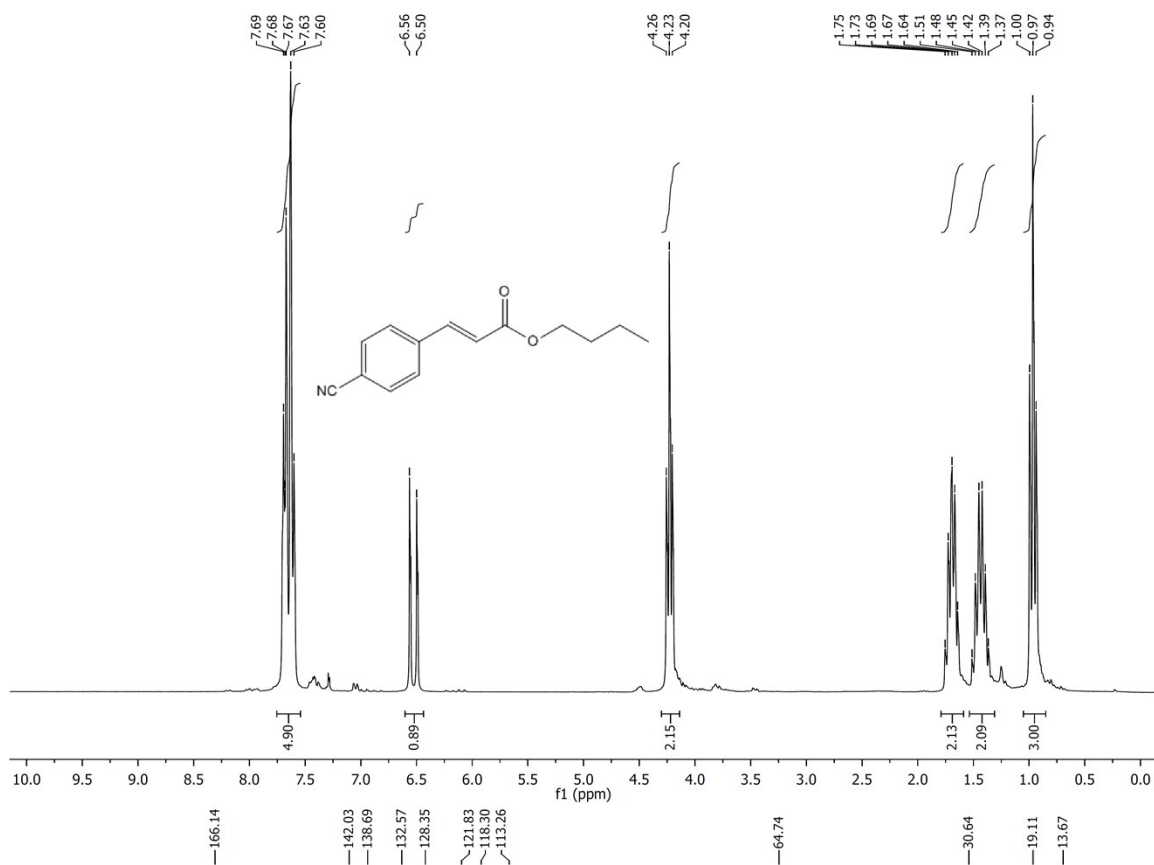
### 4.12. (*E*)-3-(4-Formylphenyl)acrylamide (3l)



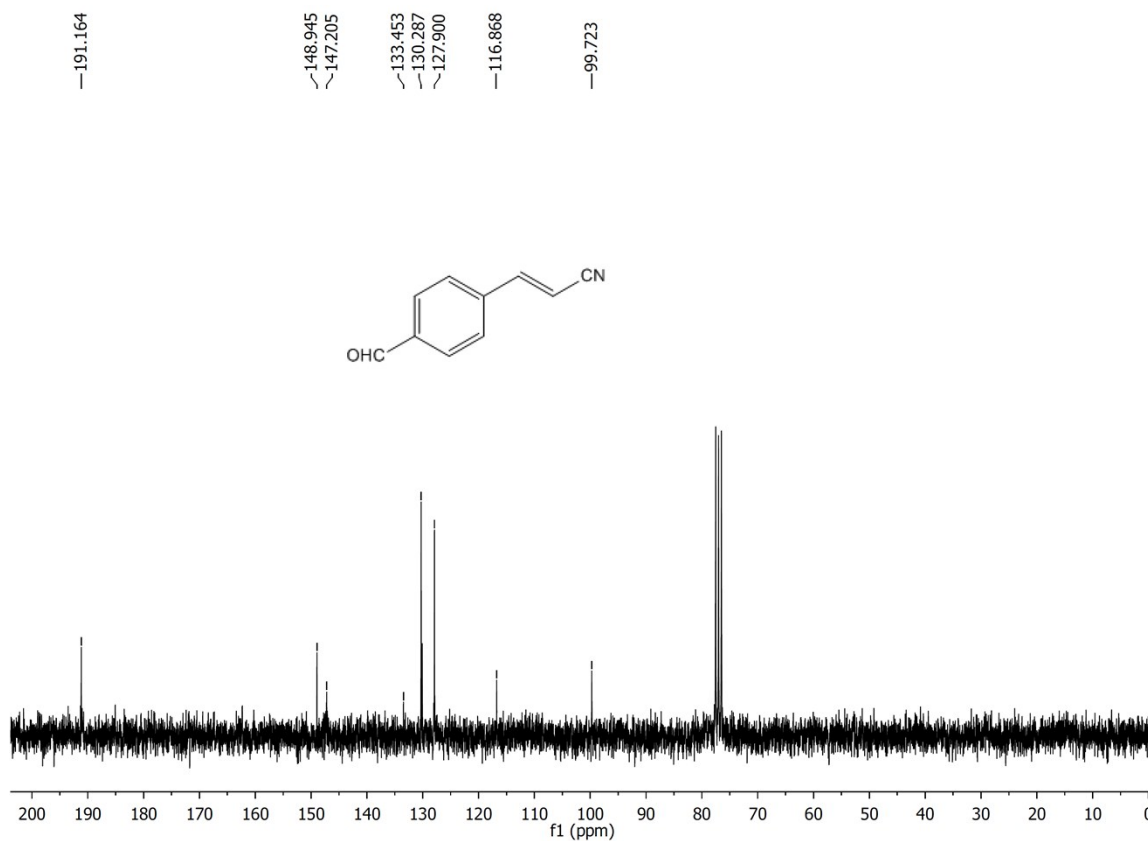
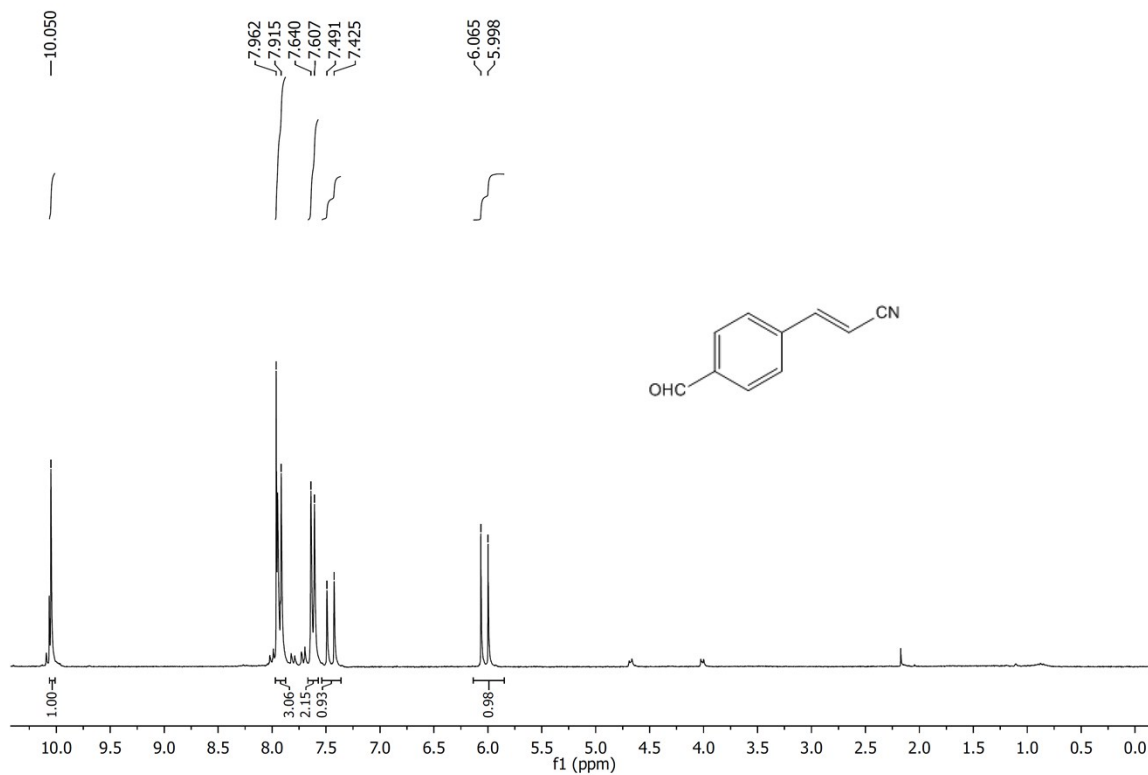
### 4.13. Butyl (*E*)-3-(4-methoxyphenyl)acrylate (3m)



#### 4.14. Butyl (*E*)-3-(4-cyanophenyl)acrylate (**3n**)



### 4.15. (*E*)-3-(4-formylphenyl)acrylonitrile (3o)





### 4.16. (*E*)-3-(4-acetylphenyl)acrylonitrile (3p)

