

## Palladium/Copper-Catalyzed Arylation of Alkenes with *N'*-Acyl Arylhydrazines

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## Supporting Information

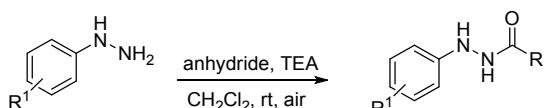
1. General Information
2. General procedure of synthesis of *N'*-acyl arylhydrazines 1a-t
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4. References
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## 1. General Information

Unless otherwise stated, all the commercial reagents and solvents were used as such without further purification. The flash column chromatography was carried out over silica gel (200-300 mesh).  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a INOVA 400 MHz spectrometer. Chemical shifts in  $^1\text{H}$  NMR spectra were reported in parts per million (ppm) downfield from the internal standard Me<sub>4</sub>Si (TMS). Chemical shifts in  $^{13}\text{C}$  NMR spectra were reported relative to the central line of the chloroform signal ( $\delta = 77.0$  ppm). Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were performed on Waters G2-XS QToF mass spectrometer. Gas chromatography mass spectrometer were obtained with GCMS-QP2010 SE mass spectrometer. Melting points were determined on a Tektronix X-4 melting point apparatus. Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

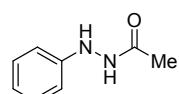
**1u-ac** were prepared according to literatures procedures,<sup>1,2</sup> and **2a-i** were commercial accessible.

## 2. General procedure for the preparation of *N'*-acyl arylhydrazines **1a-t**



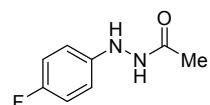
To a solution of arylhydrazine hydrochloride (0.5 g, 4.6 mmol) in DCM (10 ml) was added TEA (0.9 mL, 6.9 mmol) and anhydride (2 mL, 18.4 mmol), and the reaction mixture was stirred at ambient temperature for 24 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and then poured into H<sub>2</sub>O (20 mL). The organic phase was washed with saturated NaHCO<sub>3</sub> (2×30 mL) and saturated NaCl (30 mL) respectively, dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated *in vacuo* and the crude residue was purified by column chromatography on silica gel (eluting with 4:1 to 1:1 petroleum ether/ethyl acetate) to give the title compounds **1a-t**.

### *N'*-Phenylacetohydrazide (**1a**)<sup>1</sup>



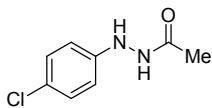
White solid; yield : 87%; mp: 123-125 °C;  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.58 (s, 1H), 7.25-7.20 (m, 2H), 6.92-6.88 (m, 1H), 6.81-6.79 (d,  $J = 8.0$  Hz, 2H), 6.17 (s, 1H), 2.02 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O[M+H]<sup>+</sup>: 151.0866, found: 151.0871.

### *N'*-(4-Fluorophenyl)acetohydrazide (**1b**)<sup>3</sup>



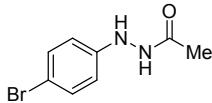
White solid; yield: 84%; mp: 147-149 °C;  $^1\text{H}$  NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.78 (s, 1H), 7.36 (d,  $J = 2.0$  Hz, 1H), 7.27 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.18-7.11 (m, 1H), 6.77-6.71 (m, 2H), 1.92 (s, 3H). HRMS(ESI) calcd. for C<sub>8</sub>H<sub>8</sub>FN<sub>2</sub>O [M-H]<sup>-</sup>: 167.0626, found: 167.0632.

### *N'*-(4-Chlorophenyl)acetohydrazide (**1c**)<sup>3</sup>



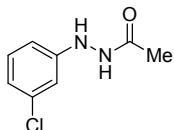
White solid; yield: 73%; mp: 146-148 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.63 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 2.4 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 1.87 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>10</sub>ClN<sub>2</sub>O[M+H]<sup>+</sup>: 185.0476, found: 185.0470.

**N'-(4-Bromophenyl)acetohydrazide (1d)<sup>3</sup>**



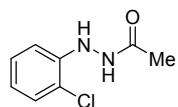
White solid; yield: 83%; mp: 166-168 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.86 (d, *J* = 2.4 Hz, 1H), 7.29-7.23 (m, 2H), 6.64-6.61 (m, 2H), 1.87 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>8</sub>BrN<sub>2</sub>O [M-H]<sup>-</sup>: 226.9826, found: 226.9818.

**N'-(3-Chlorophenyl)acetohydrazide (1e)<sup>4</sup>**



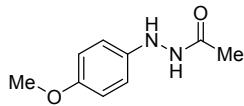
White solid; yield: 86%; mp: 128-131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.50 (s, 1H), 7.19-7.09 (m, 1H), 6.87 (dd, *J* = 14.7, 8.5 Hz, 1H), 6.78 (dt, *J* = 13.1, 2.0 Hz, 1H), 6.70-6.59 (m, 1H), 2.07 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup>: 184.0476, found: 185.0481.

**N'-(2-chlorophenyl)acetohydrazide (1f)<sup>5</sup>**



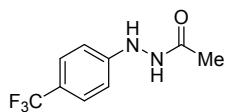
White solid; yield: 98%; mp: 115-117 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.78 (s, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.27 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.18-7.11 (m, 1H), 6.77-6.71 (m, 2H), 1.92 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup>: 184.0476, found: 185.0480.

**N'-(4-Methoxyphenyl)acetohydrazide (1g)<sup>3</sup>**



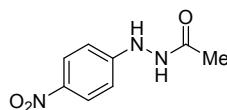
White solid; yield: 69%; mp: 127-128 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.56 (s, 1H), 6.81-6.70 (m, 2H), 6.67-6.61 (m, 2H), 3.64 (d, *J* = 4.5 Hz, 3H), 1.85 (d, *J* = 4.8 Hz, 3H); HRMS(ESI) calcd. for C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 181.0972, found: 181.0971.

***N*'-(4-(Trifluoromethyl)phenyl)acetohydrazide (1h)<sup>6</sup>**



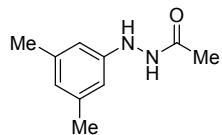
White solid; yield: 80%; mp: 176-178 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.89 (s, 1H), 8.34 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 1.92 (s, 3H); HRMS(ESI) calcd. for C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O[M-H]<sup>-</sup>: 217.0594, found: 217.0598.

***N*'-(4-Nitro-phenyl)-N-acetyl-hydrazin (1i)<sup>7</sup>**



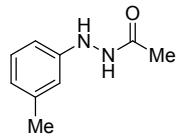
Yellow solid; yield: 81%; mp: 203-206 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.94 (s, 1H), 9.00 (s, 1H), 8.05 (d, *J* = 9.2 Hz, 2H), 6.74 (d, *J* = 9.3 Hz, 2H), 1.94 (s, 3H); HRMS(ESI) calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>3</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 194.0571, found: 194.0568.

***N*'-(3,5-diMethylphenyl)ethanehydrazide (1j)<sup>8</sup>**



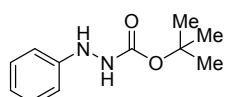
White solid; yield: 71%; mp: 135-137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.53 (d, *J* = 2.8 Hz, 1H), 7.45 (d, *J* = 2.9 Hz, 1H), 6.30 (d, *J* = 12.2 Hz, 3H), 2.15 (d, *J* = 7.8 Hz, 6H), 1.84 (d, *J* = 16.2 Hz, 3H); HRMS(ESI) calcd. for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>O[M-H]<sup>-</sup>: 177.1033, found: 177.1034.

***N*'-(*m*-Tolyl)acetohydrazide (1k)<sup>9</sup>**



White solid; yield: 85%; mp: 99-103 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 7.12 (dt, *J* = 14.5, 8.2 Hz, 1H), 6.73 (dd, *J* = 14.6, 7.5 Hz, 1H), 6.59 (m, 2H), 2.29 (d, *J* = 9.1 Hz, 3H), 2.07 (d, *J* = 21.2 Hz, 3H); HRMS(ESI) calcd. for C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 165.1022, found: 165.1027.

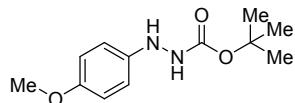
***tert*-Butyl 2-phenylhydrazinecarboxylate (1l)<sup>1</sup>**



White solid; yield: 94%; mp: 94-96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.25-7.20 (m, 2H), 6.87 (tt,

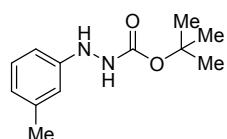
*J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 2H), 6.42 (s, 1H), 5.76 (s, 1H), 1.46 (s, 9H); HRMS(ESI) calcd. for C<sub>11</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 209.1285, found: 209.1290.

***tert*-Butyl 2-(4-methoxyphenyl)hydrazinecarboxylate (1m)<sup>10</sup>**



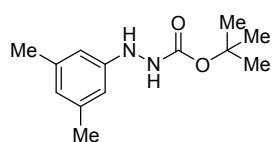
White solid; yield: 87%; mp: 79-81 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.79 (s, 4H) 6.41 (s, 1H) 5.60 (s, 1H) 3.75 (s, 3H) 1.46 (s, 9H); HRMS(ESI) calcd. for C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 239.1390, found: 239.1386.

***tert*-Butyl 2-(*m*-tolyl)hydrazinecarboxylate (1n)<sup>11</sup>**



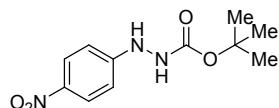
White solid; yield: 85%; mp: 73-77 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.12 (dd, *J* = 11.1, 5.0 Hz, 1H), 6.70 (d, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 6.7 Hz, 2H), 6.41 (s, 1H), 5.72 (s, 1H), 2.29 (s, 3H), 1.47 (s, 9H); HRMS(ESI) calcd. for C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 223.1441, found: 223.1446.

***tert*-Butyl 2-(3,5-dimethylphenyl)hydrazinecarboxylate (1o)**



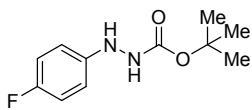
White solid; yield: 94%; mp: 88-92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.53 (s, 1H), 6.44 (s, 1H), 6.36 (s, 1H), 5.64 (s, 1H), 2.25 (s, 6H), 1.47 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 156.2, 148.4, 138.8, 122.8, 110.8, 81.1, 28.2, 21.4. HRMS(ESI) calcd. for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 259.1417, found: 259.1421; HRMS(ESI) calcd. for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na[M+Na]<sup>+</sup>: 259.1417, found: 259.1421.

***tert*-Butyl 2-(4-nitrophenyl)hydrazine (1p)<sup>12</sup>**



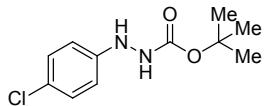
Yellow solid; yield: 82%; mp: 126-129 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 6.48 (s, 1H) 6.29 (s, 1H), 1.48 (s, 9H); HRMS(ESI) calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>3</sub>O<sub>4</sub>[M-H]<sup>+</sup>: 253.0990, found: 252.0995

***tert*-Butyl 2-(4-fluorophenyl)hydrazine (1q)<sup>11</sup>**



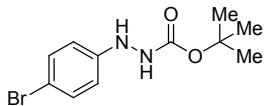
Yellow solid; yield: 87%; mp: 86-98 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.93 (t,  $J$  = 8.7 Hz, 2H), 6.78 (dd,  $J$  = 8.8, 4.4 Hz, 2H), 6.41 (s, 1H), 5.71 (s, 1H), 1.47 (d,  $J$  = 11.5 Hz, 9H); HRMS(ESI) calcd. for  $\text{C}_{11}\text{H}_{15}\text{FN}_2\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$ : 249.1010, found: 249.1015.

**tert-Butyl 2-(4-chlorophenyl)hydrazine (1r)<sup>11</sup>**



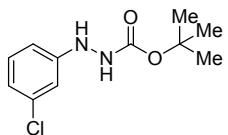
White solid; yield: 87%; mp: 123-124 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.22-7.12 (m, 2H), 6.76 (d,  $J$  = 8.7 Hz, 2H), 6.39 (s, 1H), 5.76 (s, 1H), 1.46 (s, 9H); HRMS(ESI) calcd. for  $\text{C}_{11}\text{H}_{14}\text{ClN}_2\text{O}_2[\text{M}-\text{H}]^-$ : 241.0749, found: 241.0746.

**tert-Butyl 2-(4-bromophenyl)hydrazine (1s)<sup>11</sup>**



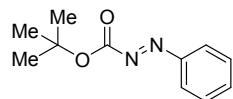
White solid; yield: 95%; mp: 123-125 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.36-7.28 (m, 2H), 6.71 (d,  $J$  = 8.7 Hz, 2H), 6.39 (s, 1H), 5.58 (s, 1H), 1.46 (s, 9H); HRMS(ESI) calcd. for  $\text{C}_{11}\text{H}_{16}\text{BrN}_2\text{O}_2[\text{M}+\text{H}]^+$ : 287.0390, found: 287.0391.

**tert-Butyl 2-(3-chlorophenyl)hydrazine (1t)<sup>11</sup>**



White solid; yield: 91%; mp: 90-97 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.13 (t,  $J$  = 8.0 Hz, 1H), 6.84 (t,  $J$  = 5.3 Hz, 2H), 6.69 (d,  $J$  = 8.4 Hz, 1H), 6.38 (s, 1H), 5.80 (s, 1H), 1.47 (s, 9H); HRMS(ESI) calcd. for  $\text{C}_{11}\text{H}_{14}\text{ClN}_2\text{O}_2[\text{M}-\text{H}]^-$ : 241.0749, found: 241.0746.

**(E)-tert-Butyl 2-phenyldiazenecarboxylate (4)<sup>1</sup>**



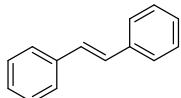
Brown oil; HRMS (ESI) calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$ : 229.0947, found: 229.0944.

### 3. Typical procedure for the Pd/Cu-catalyzed Heck-type coupling reaction

A mixture of *N*'-acyl arylhydrazine **1** (0.3 mmol), alkene **2** (0.45 mmol),  $\text{PdCl}_2$  (0.015 mmol),

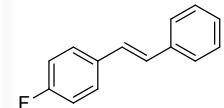
CuI (0.03 mmol) and TFA (0.6 mmol) in DMSO (2.0 mL) was stirred at 80 °C for 12-24 h. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution and extracted with EtOAc, followed by washing with H<sub>2</sub>O and saturated NaCl solution, and finally dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

**1,2-diPhenylethene (**3a**)<sup>13</sup>**



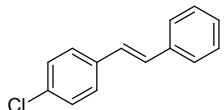
White solid; yield: 86%; mp: 112-114 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 7.57 (dd, *J* = 5.1, 3.4 Hz, 4H), 7.35 (dd, *J* = 10.5, 4.8 Hz, 4H), 7.27-7.19 (m, 4H); GC-MS calcd. for C<sub>14</sub>H<sub>12</sub>: 181.09, found: 181.07.

**(E)-1-Fluoro-4-styrylbenzene (**3b**)<sup>13</sup>**



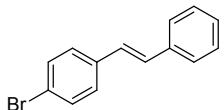
White solid; yield: 83%; mp: 118-120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.52-7.44 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (dd, *J* = 9.4, 2.9 Hz, 2H), 7.10-6.98 (m, 4H); GC-MS calcd. for C<sub>14</sub>H<sub>11</sub>F: 198.08, found: 198.15.

**(E)-1-Chloro-4-styrylbenzene (**3c**)<sup>14</sup>**



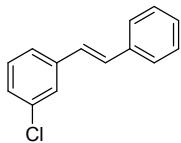
White solid; yield: 86%; mp: 127-129 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.50 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.38-7.32 (m, 3H), 7.28 (dd, *J* = 15.3, 8.0 Hz, 2H), 7.11-7.01 (m, 2H); GC-MS calcd. for C<sub>14</sub>H<sub>11</sub>Cl: 214.05, found: 214.10.

**(E)-1-Bromo-4-styrylbenzene (**3d**)<sup>15</sup>**



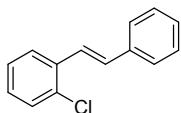
White solid; yield: 82%; mp: 118-120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.53-7.45 (m, 4H), 7.37 (dd, *J* = 11.9, 5.0 Hz, 4H), 7.30-7.25 (m, 1H), 7.06 (q, *J* = 16.3 Hz, 2H); GC-MS calcd. for C<sub>14</sub>H<sub>11</sub>Br: 258.00, found: 258.05

**(E)-1-Chloro-3-styrylbenzene (**3e**)<sup>13</sup>**



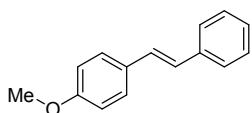
White solid; yield: 83%; mp: 64-68 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.51 (d,  $J = 7.2$  Hz, 3H), 7.40-7.34 (m, 3H), 7.26 (dt,  $J = 19.5, 7.9$  Hz, 3H), 7.07 (q,  $J = 16.3$  Hz, 2H); GC-MS calcd. for  $\text{C}_{14}\text{H}_{11}\text{Cl}$ : 214.05, found: 213.90.

**(E)-1-Chloro-2-styrylbenzene (3f)<sup>16</sup>**



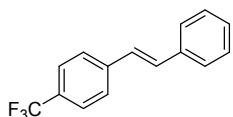
White solid; yield: 72%; mp: 50-57 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.68 (d,  $J = 7.8$  Hz, 1H), 7.53 (t,  $J = 13.0$  Hz, 3H), 7.37 (t,  $J = 7.6$  Hz, 3H), 7.31-7.25 (m, 2H), 7.18 (t,  $J = 7.6$  Hz, 1H), 7.07 (d,  $J = 16.3$  Hz, 1H); GC-MS calcd. for  $\text{C}_{14}\text{H}_{11}\text{Cl}$ : 214.05, found: 214.10

**(E)-1-Methoxy-4-styrylbenzene (3g)<sup>17</sup>**



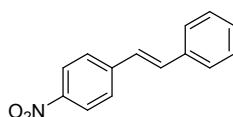
White solid; yield: 92%; mp: 133-134 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.47 (dd,  $J = 13.4, 8.0$  Hz, 4H), 7.34 (t,  $J = 7.6$  Hz, 2H), 7.24 (d,  $J = 7.3$  Hz, 1H), 7.02 (m, 2H), 6.92-6.88 (m, 2H), 3.83 (s, 3H); GC-MS calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}$ : 210.10, found: 210.15

**(E)-1-Styryl-4-(trifluoromethyl)benzene (3h)<sup>13</sup>**



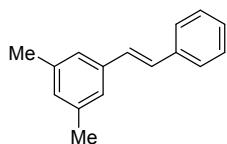
White solid; yield: 74%; mp: 133-134 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60 (s, 4H), 7.54 (d,  $J = 7.6$  Hz, 2H), 7.38 (t,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.16 (m, 2H); GC-MS calcd. for  $\text{C}_{15}\text{H}_{11}\text{F}_3$ : 248.08, found: 248.15.

**(E)-1-Nitro-4-styrylbenzene (3i)<sup>17</sup>**



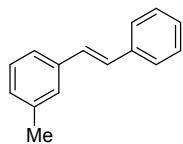
Yellow solid; yield: 67%; mp: 151-153 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.22 (d,  $J = 8.8$  Hz, 2H), 7.64 (d,  $J = 8.8$  Hz, 2H), 7.56 (d,  $J = 7.3$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 2H), 7.31 (m, 2H), 7.15 (m, 1H); GC-MS calcd. for  $\text{C}_{14}\text{H}_{11}\text{NO}_2$ : 225.08, found: 225.10.

**(E)-1,3-diMethyl-5-styrylbenzene (3j)<sup>18</sup>**



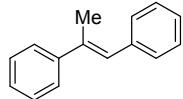
White solid; yield: 89%; mp: 130-131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.50 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26-7.21 (m, 1H), 7.14 (s, 2H), 7.12-7.01 (m, 2H), 6.91 (s, 1H), 2.33 (s, 6H); GC-MS calcd. for C<sub>16</sub>H<sub>16</sub>: 208.13, found: 208.15.

**(E)-1-Methyl-3-styrylbenzene (3k)<sup>15</sup>**



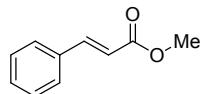
White solid; yield: 89%; mp: 40-45 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.51 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 16.2, 8.5 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 3H), 2.38 (s, 3H); GC-MS calcd. for C<sub>15</sub>H<sub>14</sub>: 194.11, found: 194.15.

**(E)-prop-1-Ene-1,2-diyldibenzene (3l)<sup>19</sup>**



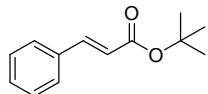
White solid; yield: 71%; mp: 74-76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.53 (d, *J* = 7.4 Hz, 2H), 7.38-7.36 (m, 5H), 7.26 (d, *J* = 7.6 Hz, 3H), 6.84 (d, *J* = 0.9 Hz, 1H), 2.29 (d, *J* = 1.2 Hz, 3H); GC-MS calcd. for C<sub>15</sub>H<sub>14</sub>: 194.11, found: 194.15

**Methyl cinnamate (3m)<sup>20</sup>**



Colorless oil; yield: 65%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.70 (d, *J* = 16.0 Hz, 1H), 7.56-7.48 (m, 2H), 7.43-7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.88-3.73 (m, 3H); GC-MS calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>: 162.07, found: 162.10.

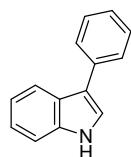
**tert-Butyl cinnamate (3n)<sup>21</sup>**



Colorless oil; yield : 55 %; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.51 (dd, *J* =

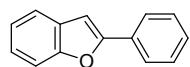
6.5, 3.1 Hz, 2H), 7.37 (dd,  $J$  = 5.0, 1.9 Hz, 3H), 6.37 (d,  $J$  = 16.0 Hz, 1H), 1.54 (s, 9H); GC-MS calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: 204.12, found: 204.15.

**3-Phenyl-1*H*-indole (3o)<sup>22</sup>**



White solid; yield: 49%; mp: 185-187 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.33 (s, 1H), 7.69-7.61 (m, 3H), 7.47-7.38 (m, 3H), 7.32 (t,  $J$  = 7.4 Hz, 1H), 7.22-7.16 (m, 1H), 7.13 (dd,  $J$  = 11.0, 4.0 Hz, 1H), 6.83 (d,  $J$  = 1.5 Hz, 1H); HRMS(ESI) calcd. for C<sub>14</sub>H<sub>12</sub>N[M+H]<sup>+</sup>: 194.0964, found: 194.0968

**2-Phenylbenzofuran (3p)<sup>23</sup>**



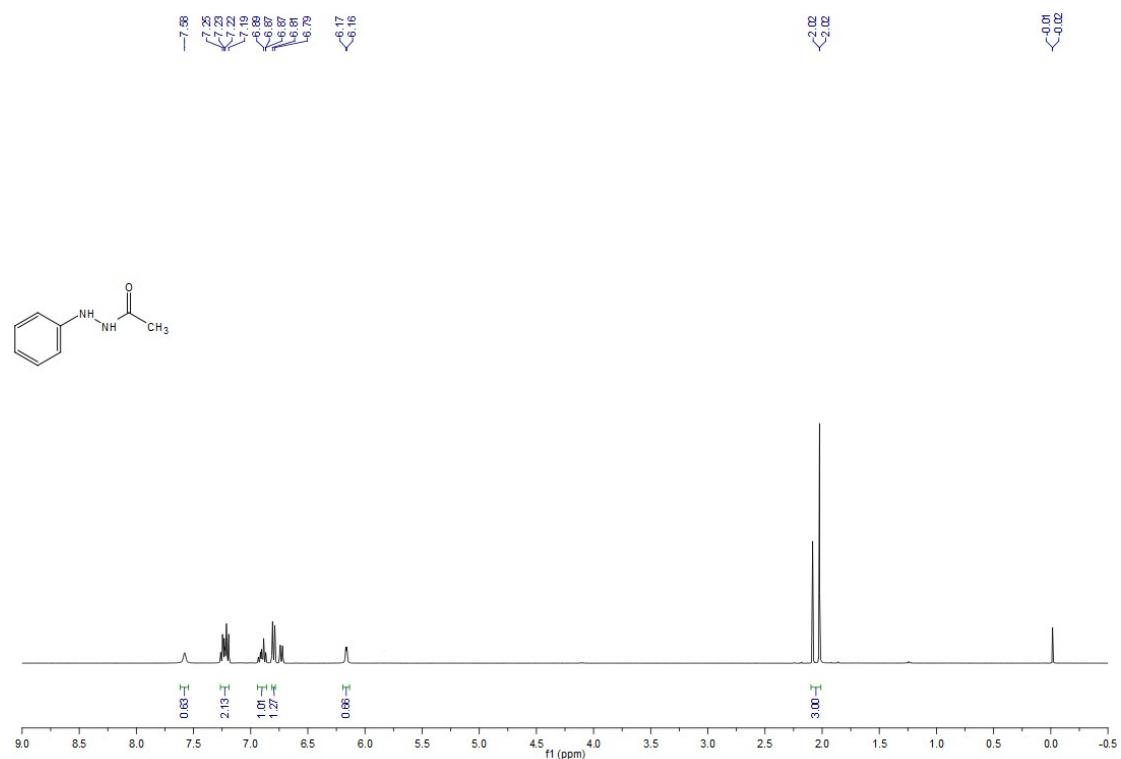
White solid; yield: 57%; mp: 119-122 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.87 (d,  $J$  = 7.4 Hz, 2H), 7.59 (d,  $J$  = 7.5 Hz, 1H), 7.53 (d,  $J$  = 8.2 Hz, 1H), 7.45 (t,  $J$  = 7.7 Hz, 2H), 7.35 (t,  $J$  = 7.4 Hz, 1H), 7.26 (dd,  $J$  = 14.3, 8.3 Hz, 2H), 7.03 (s, 1H); HRMS(ESI) calcd. for C<sub>14</sub>H<sub>11</sub>O[M+H]<sup>+</sup>: 195.0804, found: 195.0809

#### 4. References

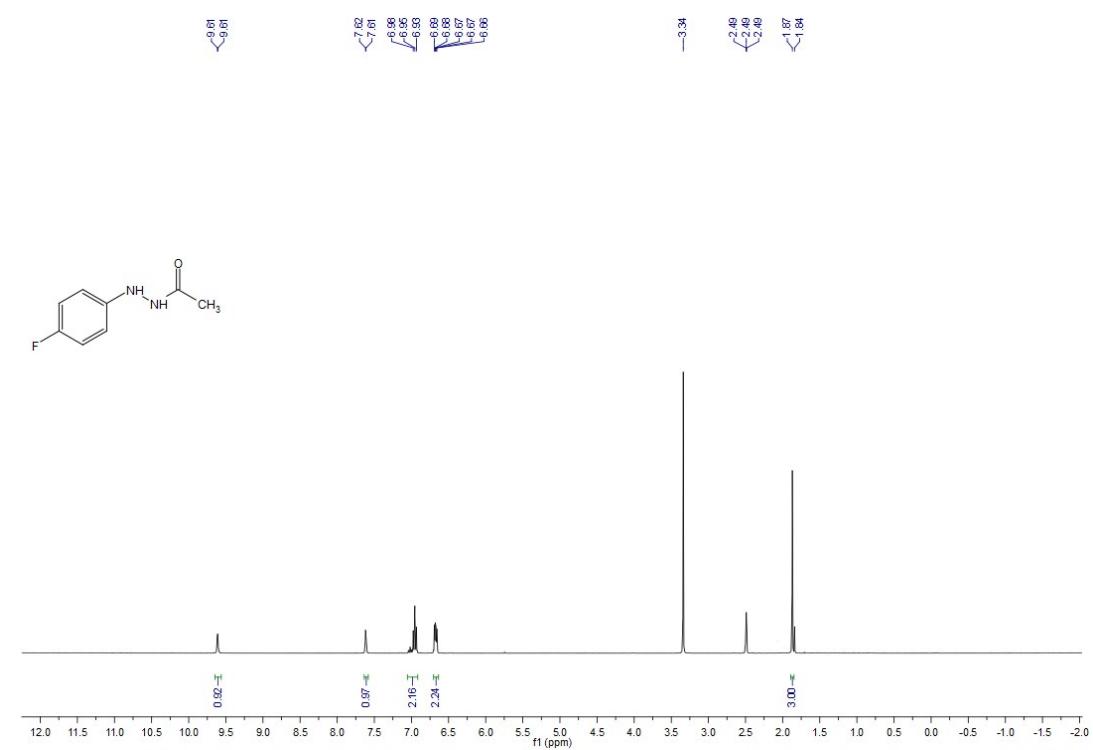
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## 5. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

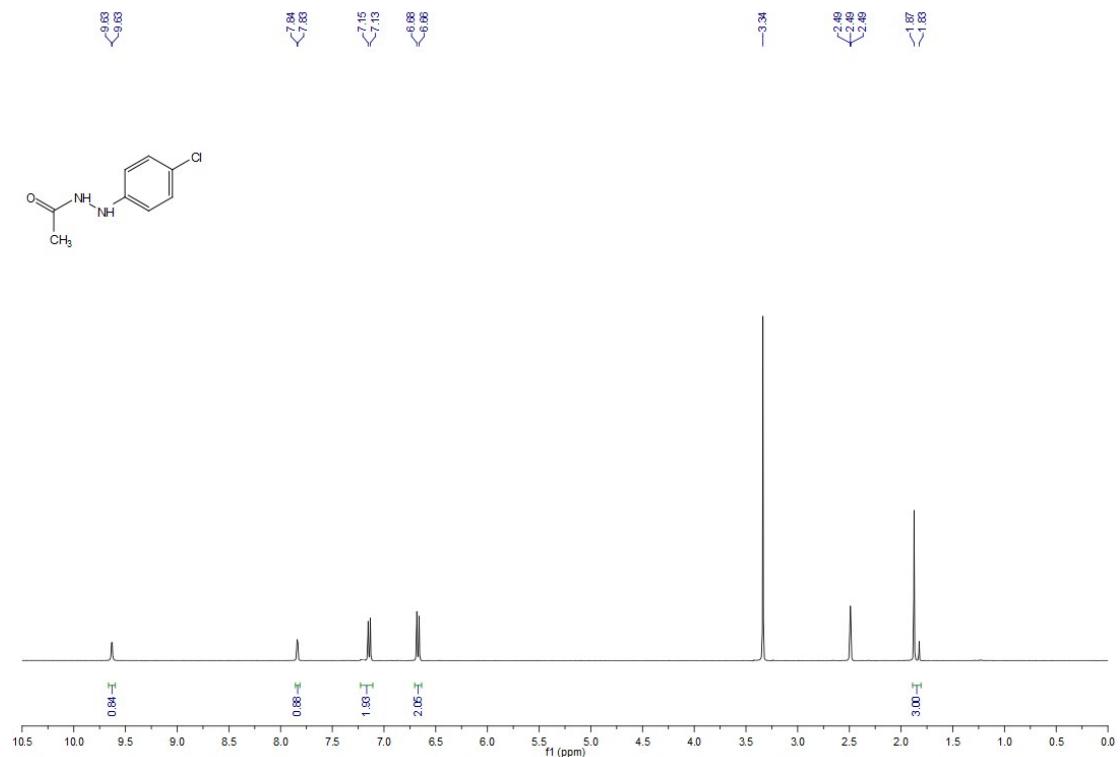
### *N'*-Phenylacetohydrazide (1a)



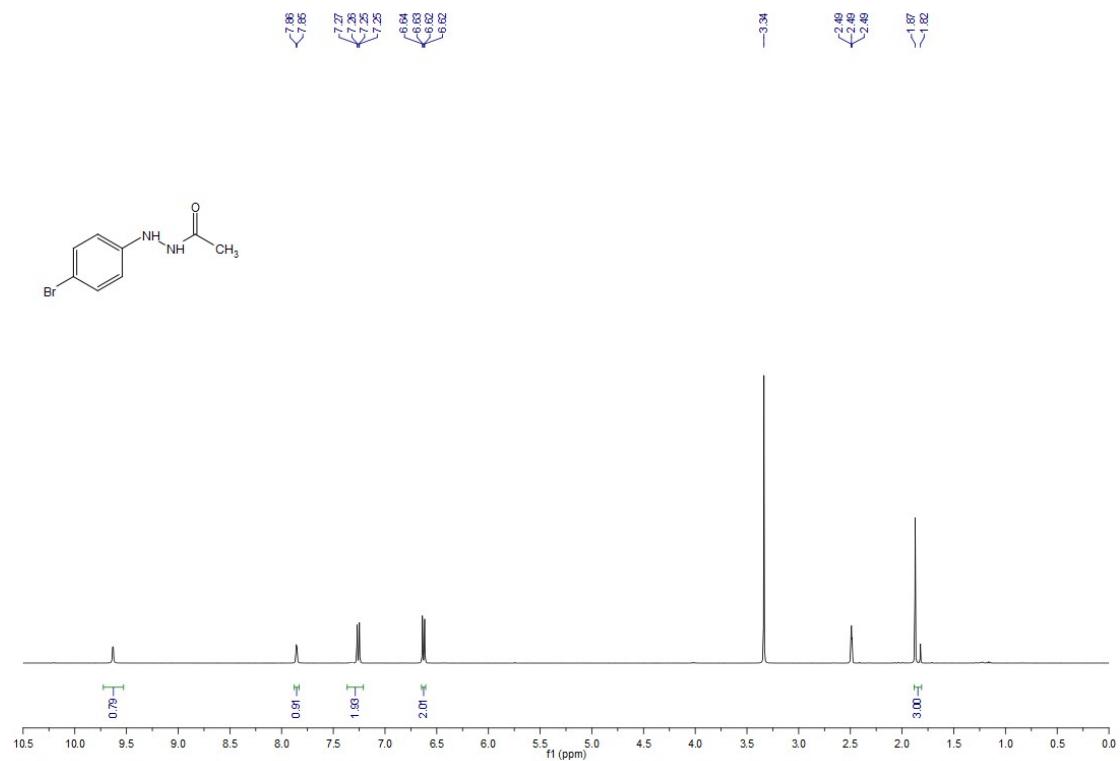
### *N'*-(4-Fluorophenyl)acetohydrazide (1b)



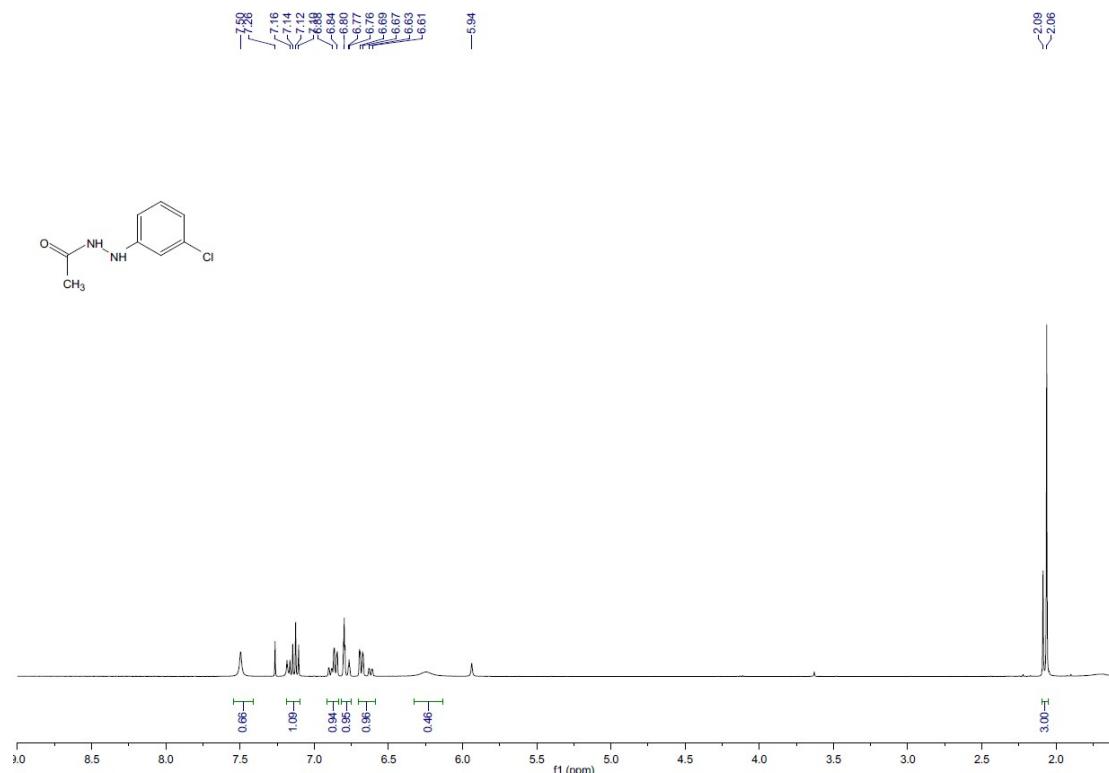
***N'*-(4-Chlorophenyl)acetohydrazide (1c)**



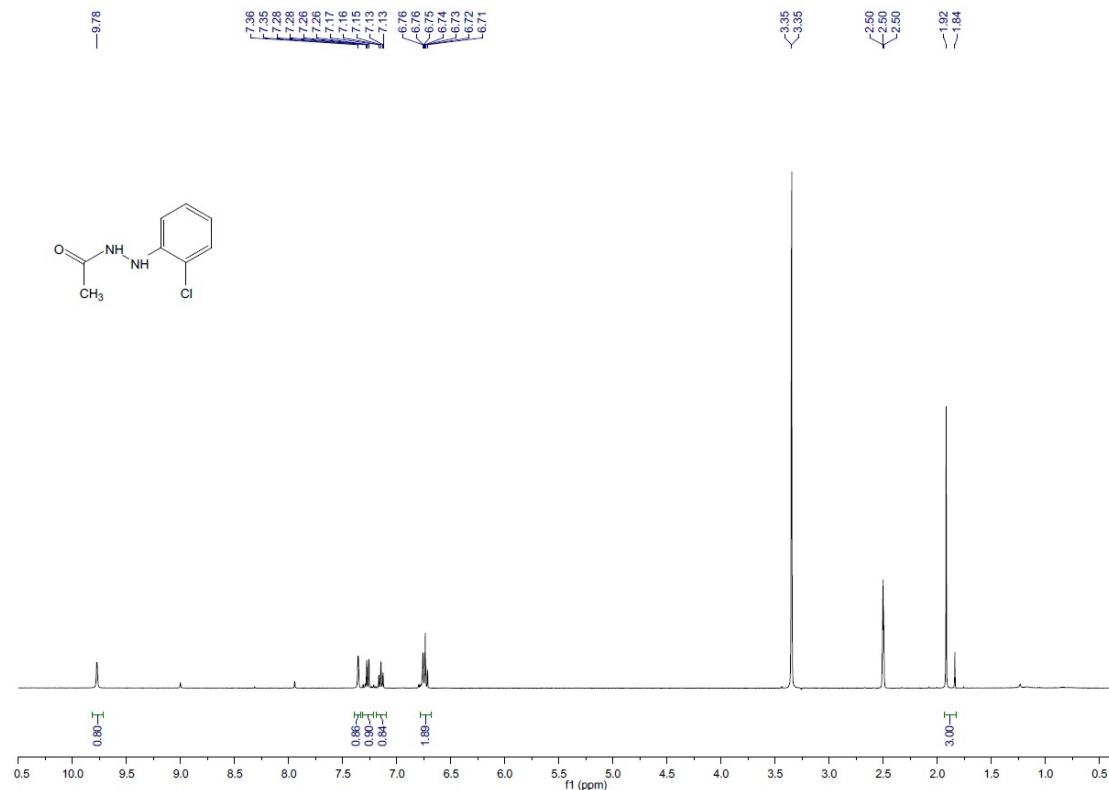
***N'*-(4-Bromophenyl)acetohydrazide (1d)**



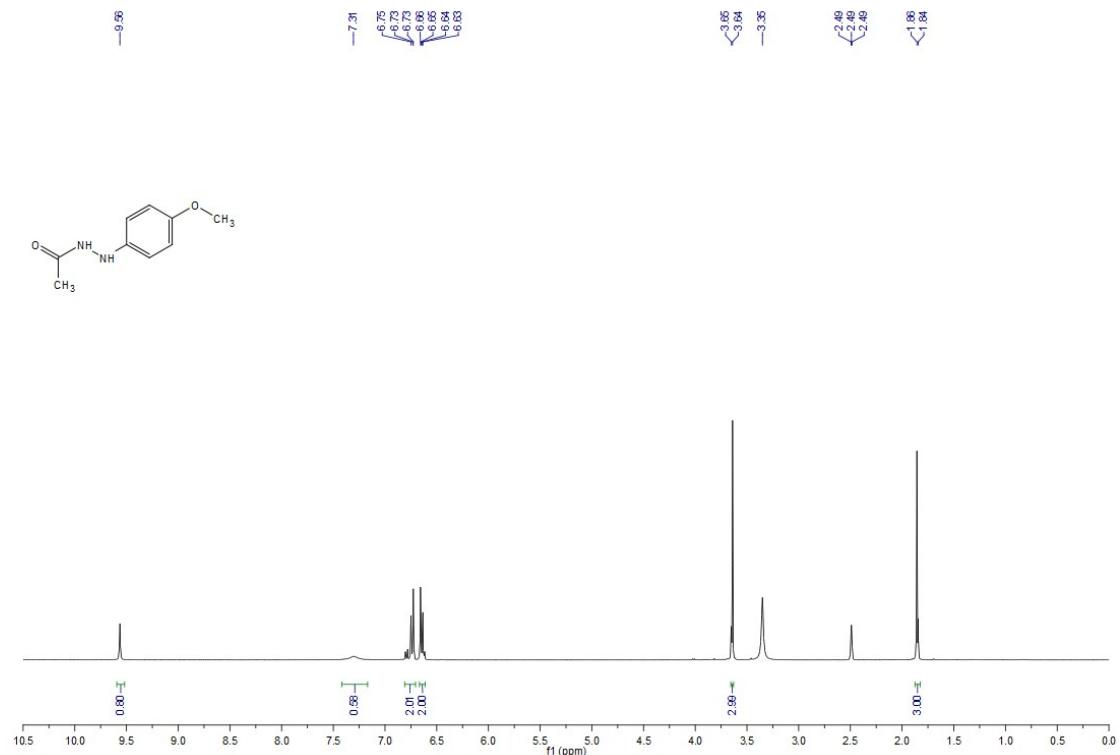
*N*<sup>o</sup>-**(3-Chlorophenyl)acetohydrazide (1e)**



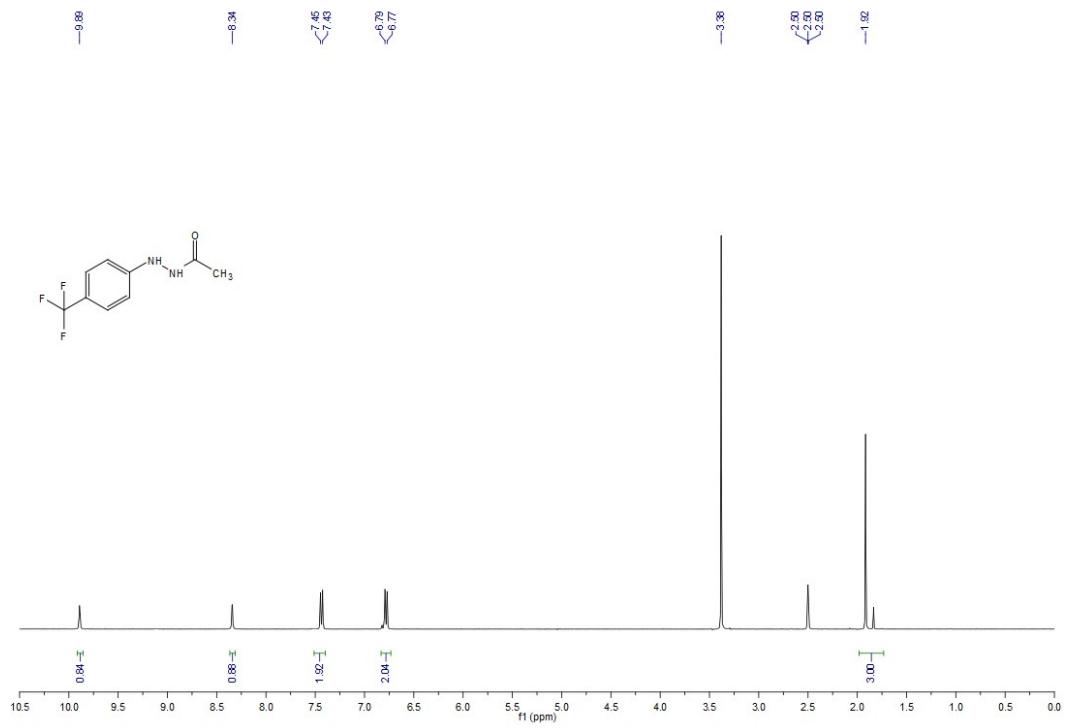
*N*<sup>o</sup>-**(2-Chlorophenyl)acetohydrazide (1f)**



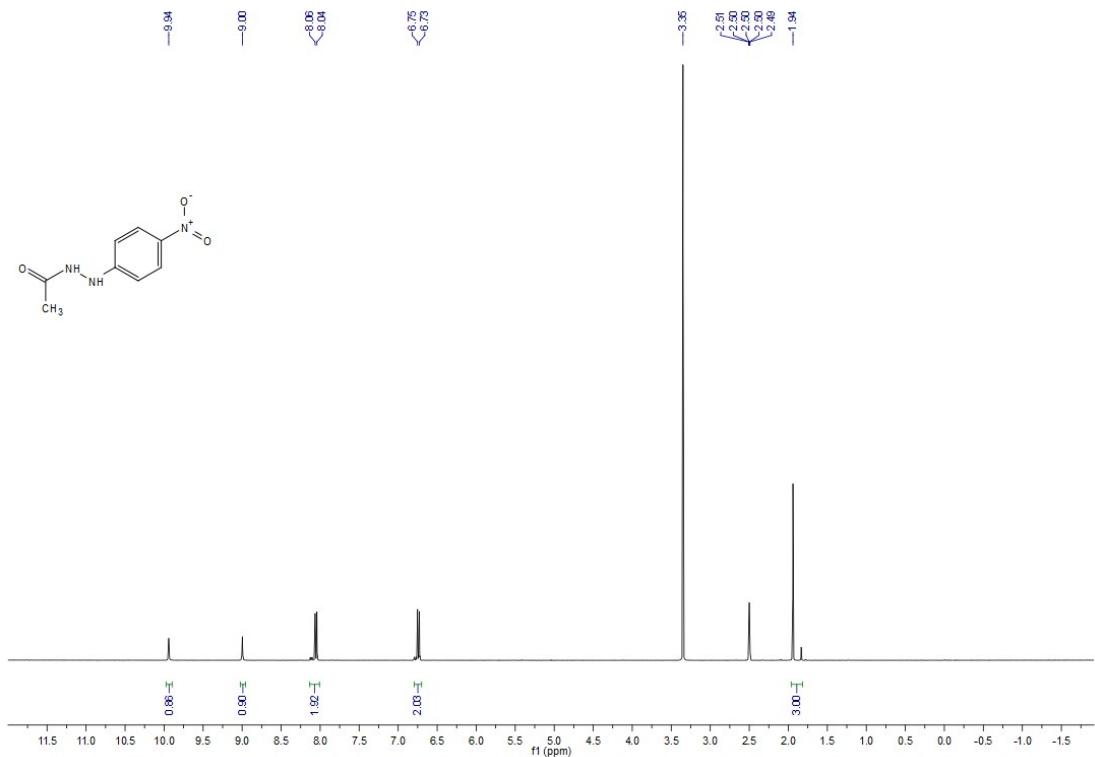
***N'*-(4-Methoxyphenyl)acetohydrazide (1g)**



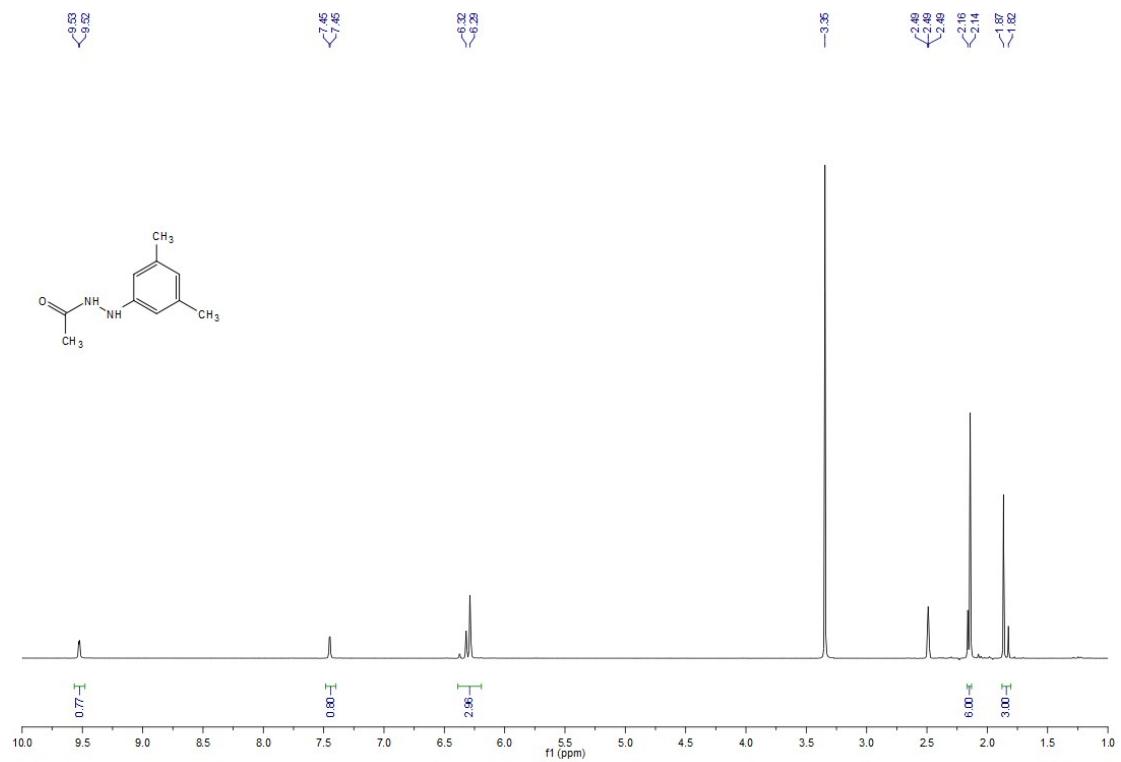
***N'*-(4-(Trifluoromethyl)phenyl)acetohydrazide (1h)**



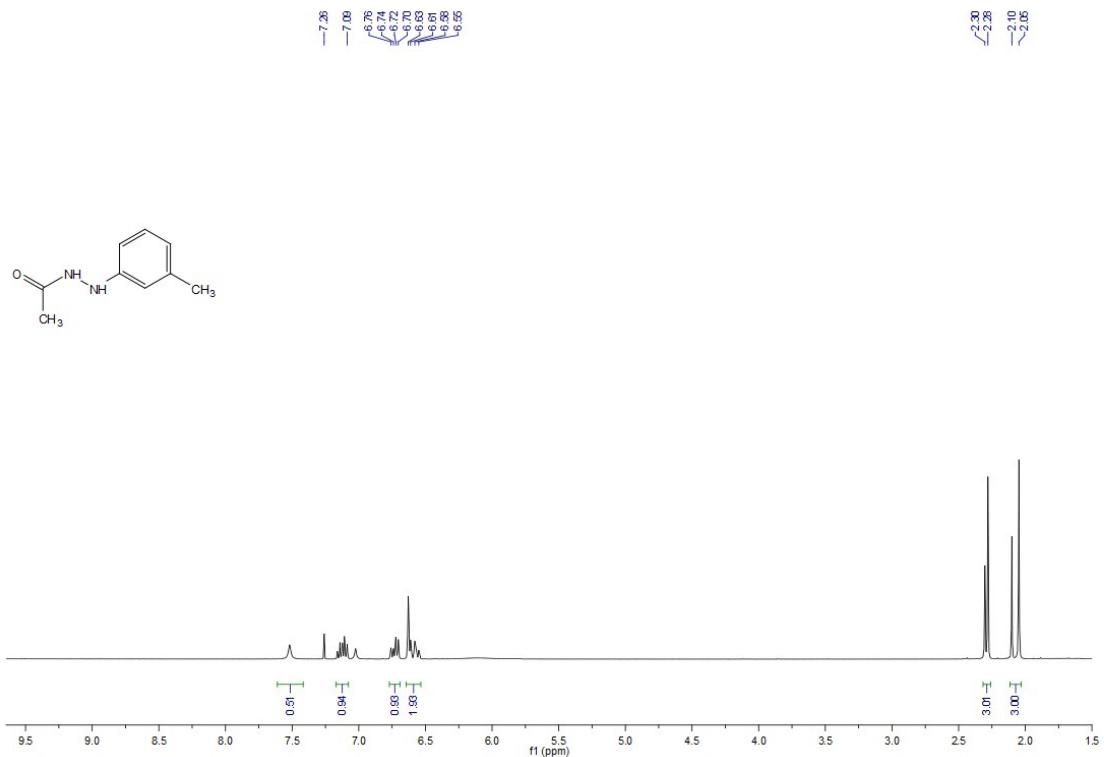
***N*<sup>+</sup>-(4-Nitro-phenyl)-*N*-acetyl-hydrazin (1i)**



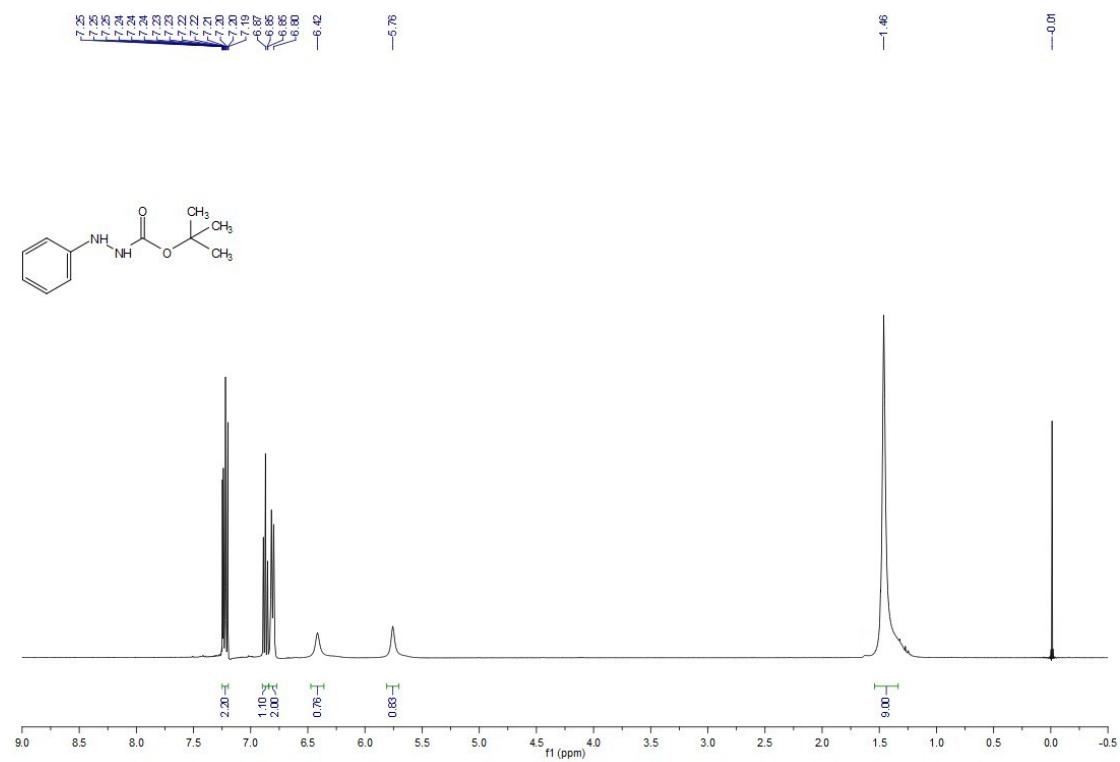
***N*<sup>+</sup>-(3,5-Dimethylphenyl)ethanehydrazide (1j)**



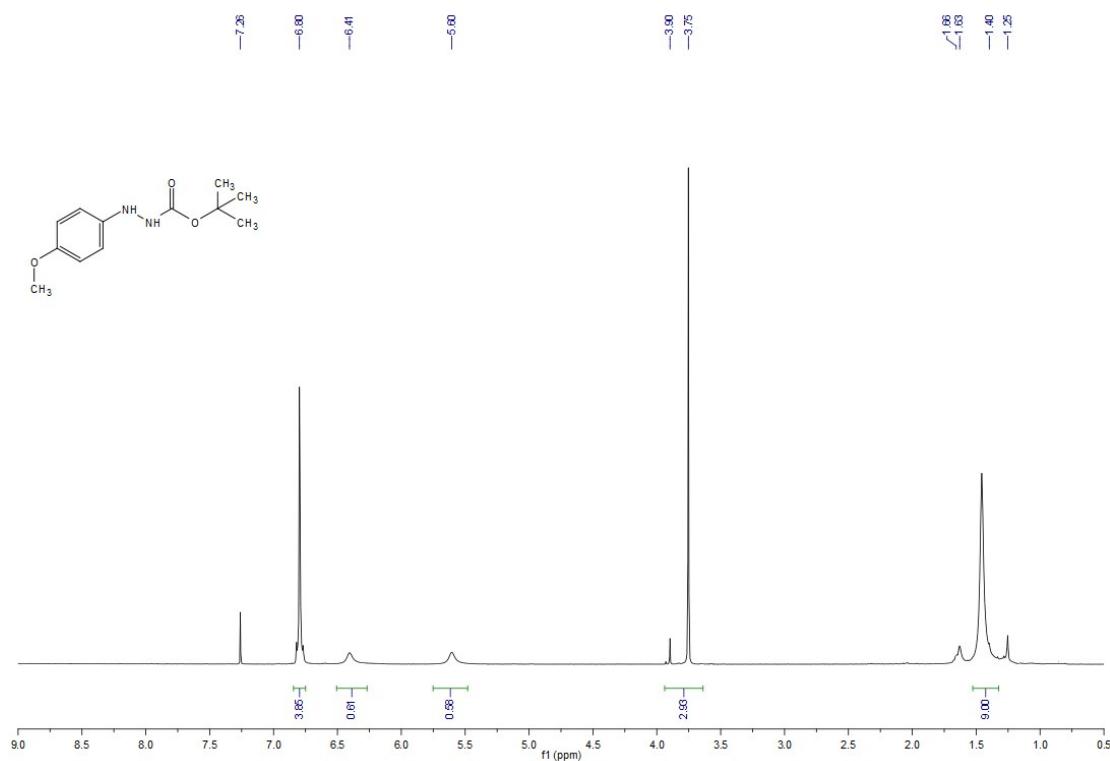
***N'*-(*m*-Tolyl)acetohydrazide (1k)**



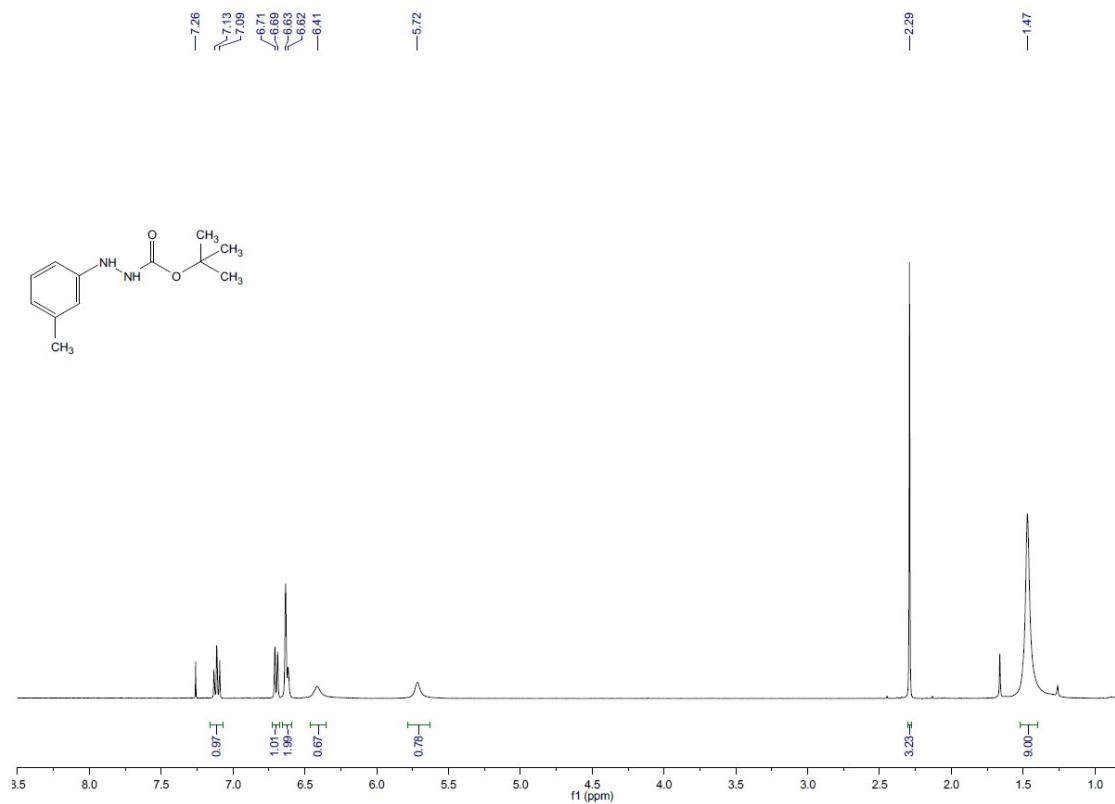
***tert*-Butyl 2-phenylhydrazinecarboxylate (1l)**



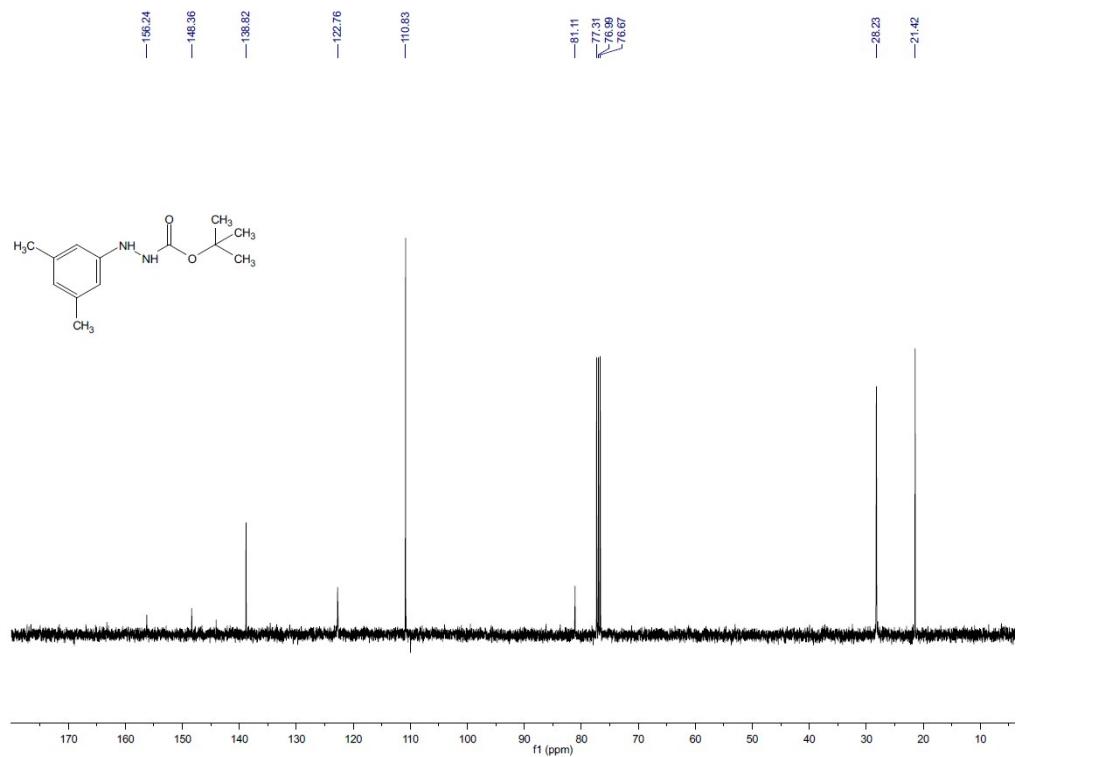
***tert*-Butyl 2-(4-methoxyphenyl)hydrazinecarboxylate (1m)**



***tert*-Butyl 2-(m-tolyl)hydrazinecarboxylate (1n)**



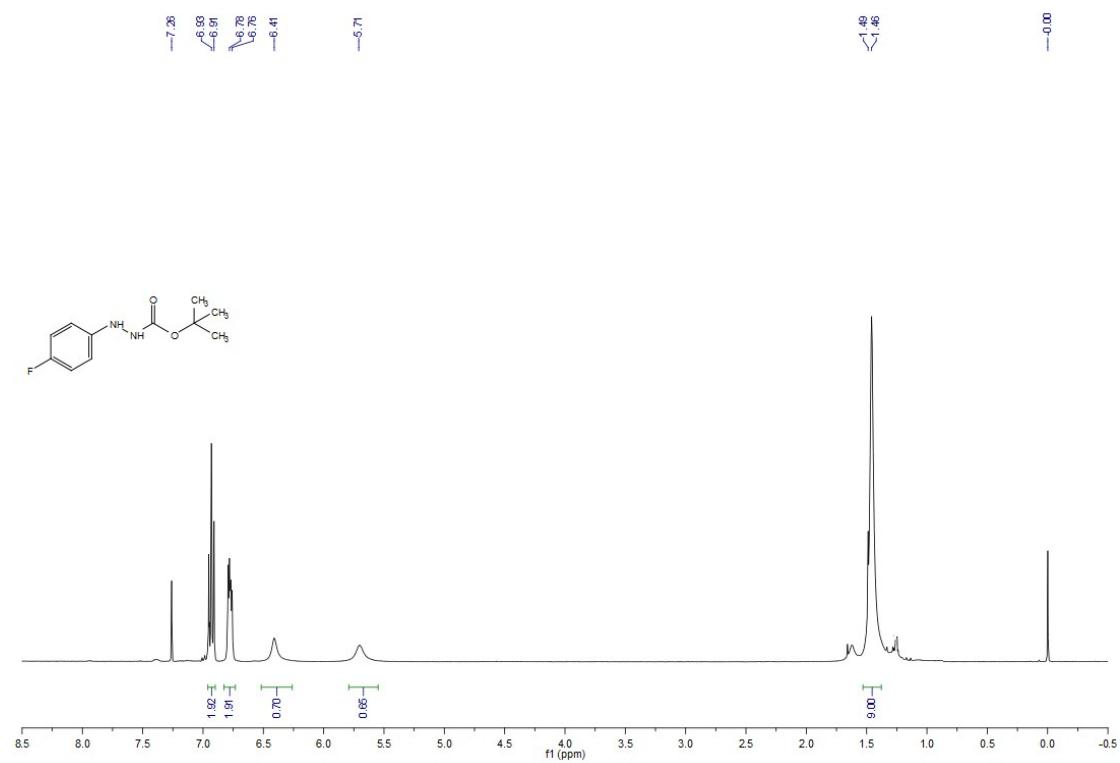
**tert-Butyl 2-(3,5-dimethylphenyl)hydrazinecarboxylate (1o)**



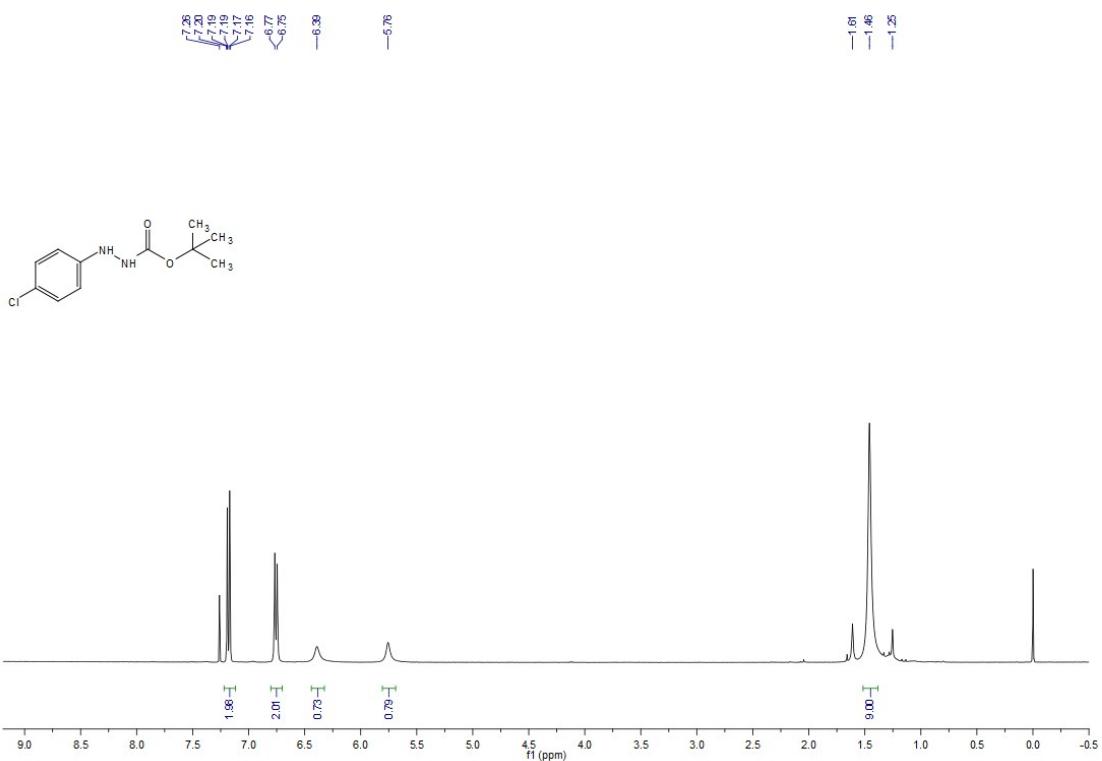
***tert*-Butyl 2-(4-nitrophenyl)hydrazine (1p)**



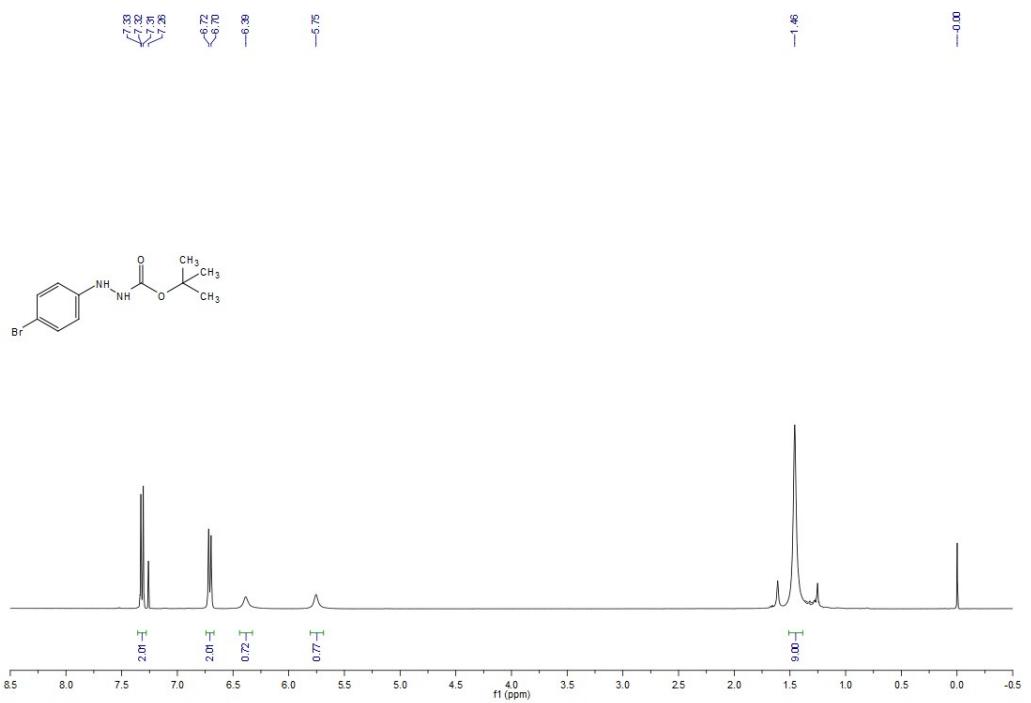
***tert*-Butyl 2-(4-fluorophenyl)hydrazine (1q)**



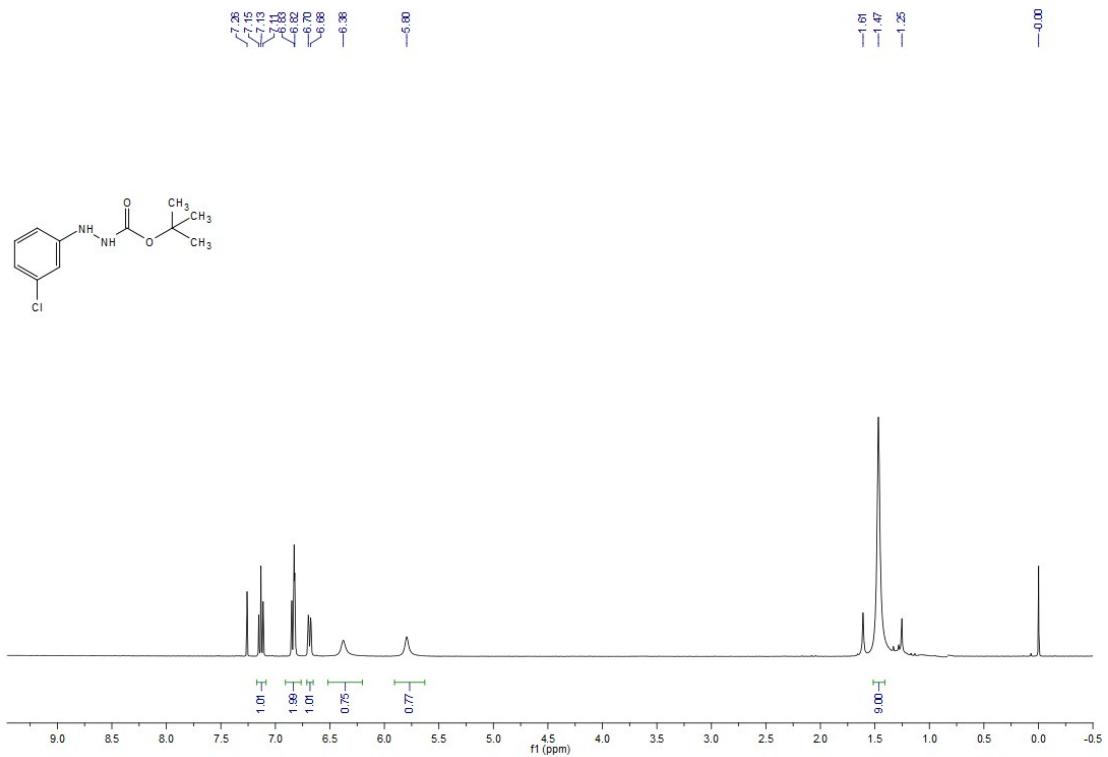
***tert*-Butyl 2-(4-chlorophenyl)hydrazine (1r)**



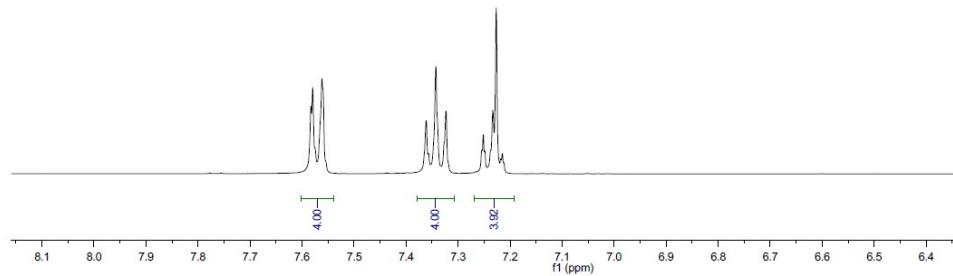
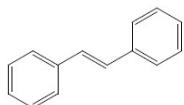
***tert*-Butyl 2-(4-bromophenyl)hydrazine (1s)**



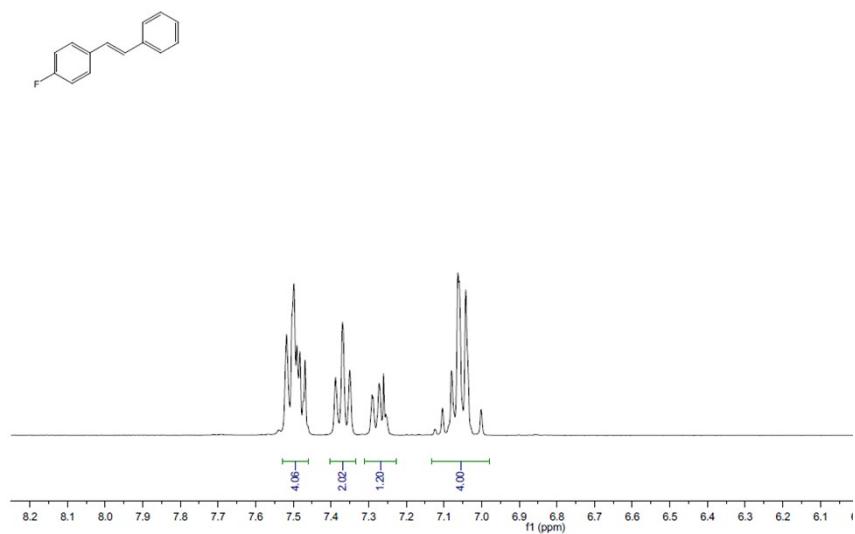
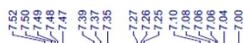
***tert*-Butyl 2-(3-chlorophenyl)hydrazine (1t)**



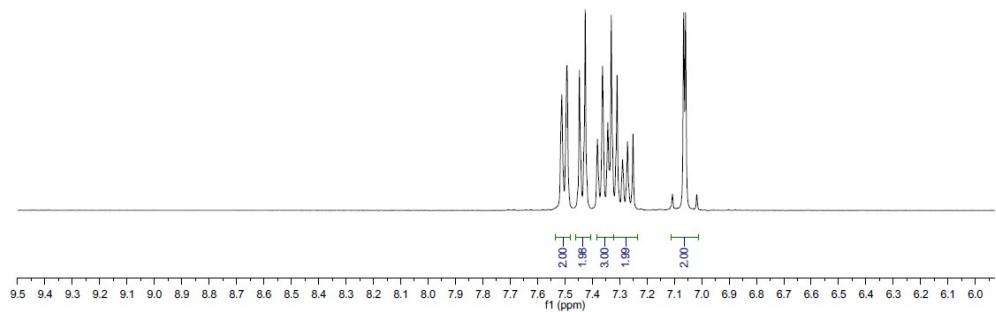
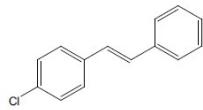
**1,2-diPhenylethene (3a)**



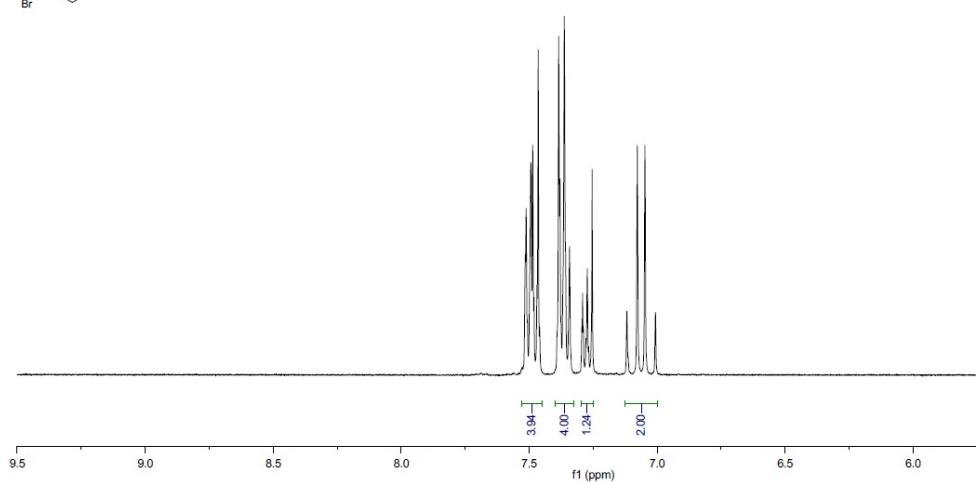
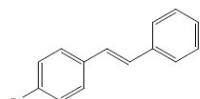
**(E)-1-Fluoro-4-styrylbenzene (3b)**



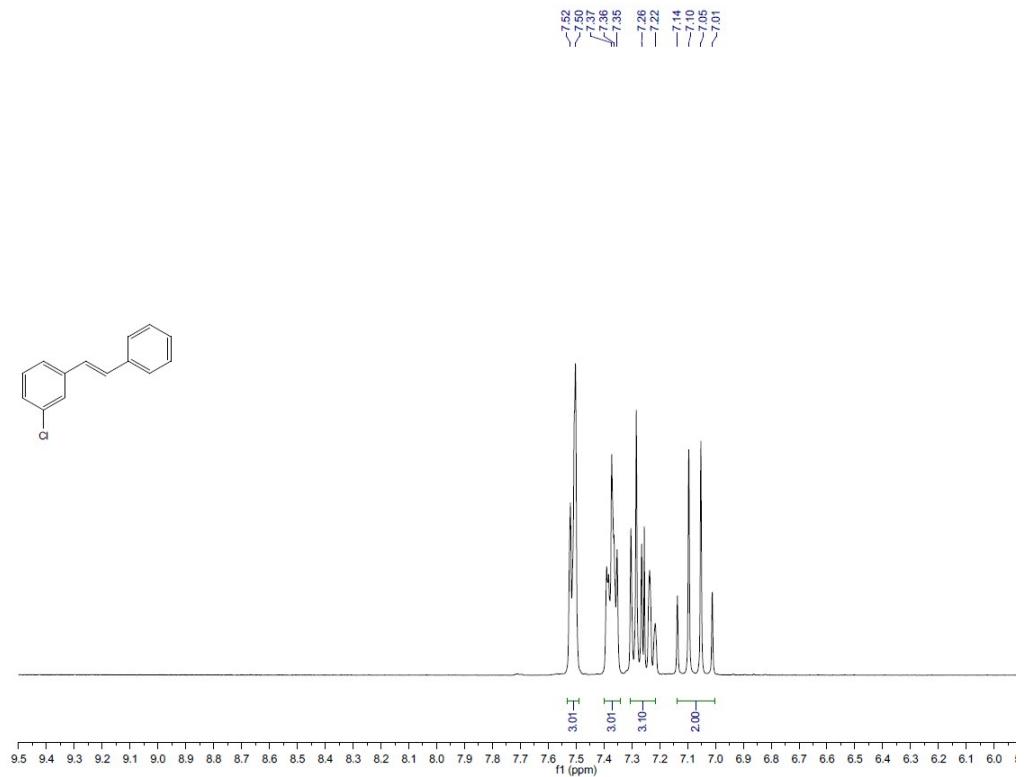
### (E)-1-Chloro-4-styrylbenzene (3c)



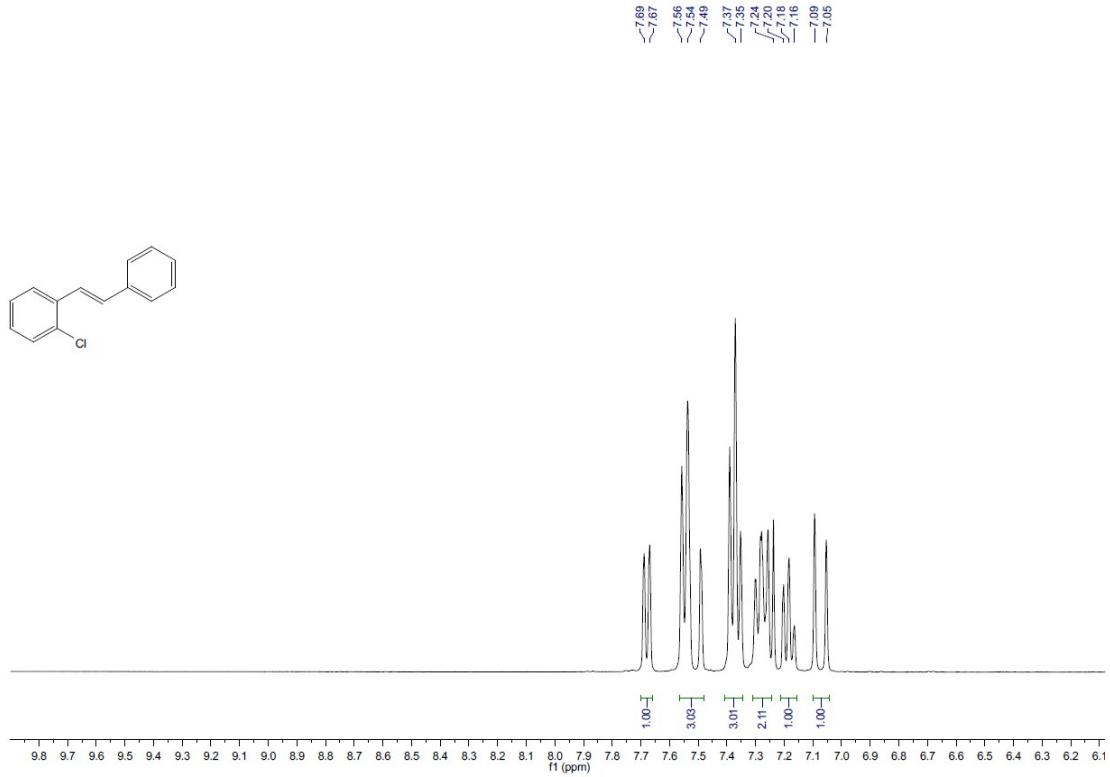
### (E)-1-Bromo-4-styrylbenzene (3d)



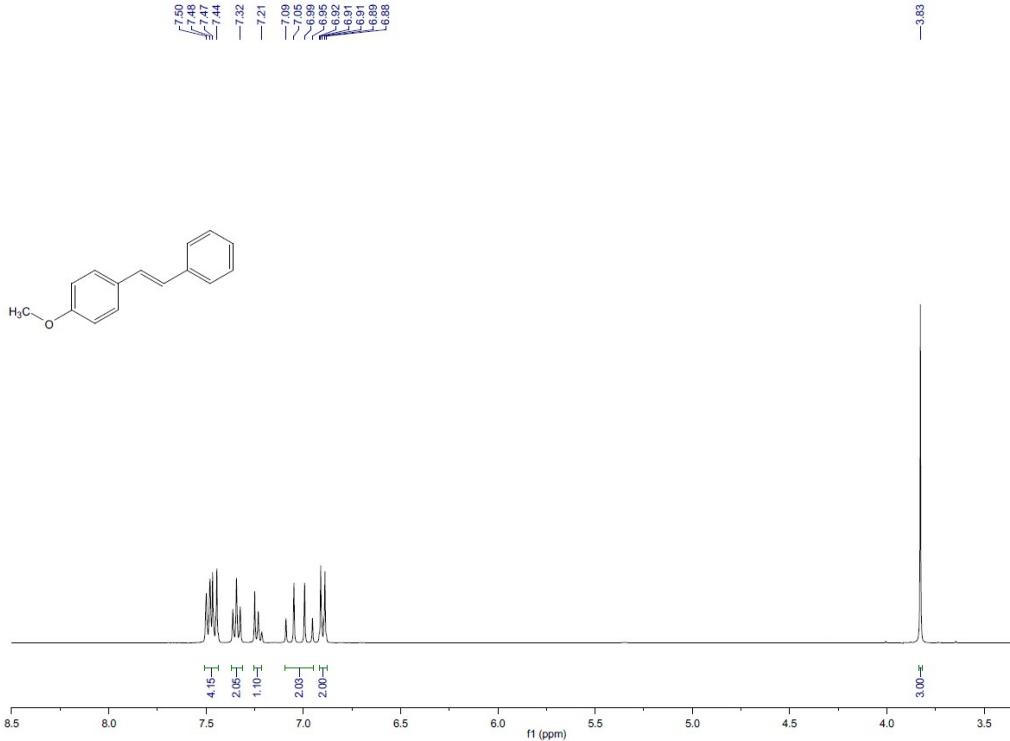
**(E)-1-Chloro-3-styrylbenzene (3e)**



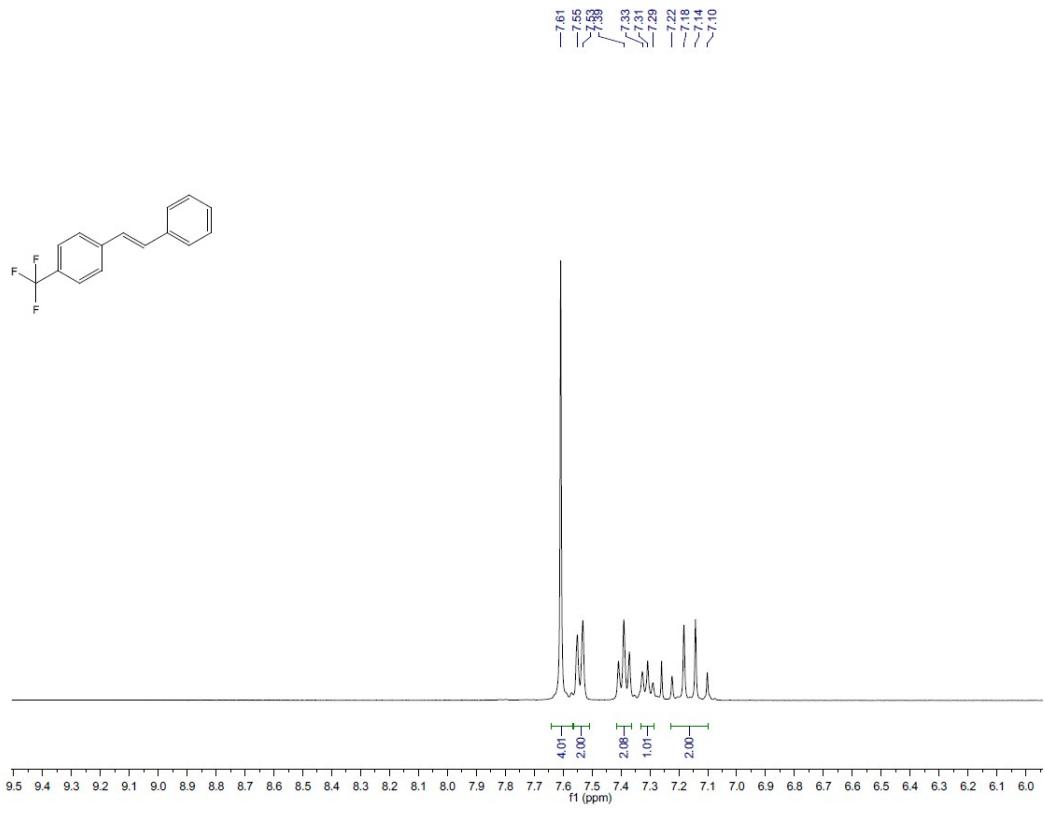
**(E)-1-Chloro-2-styrylbenzene (3f)**



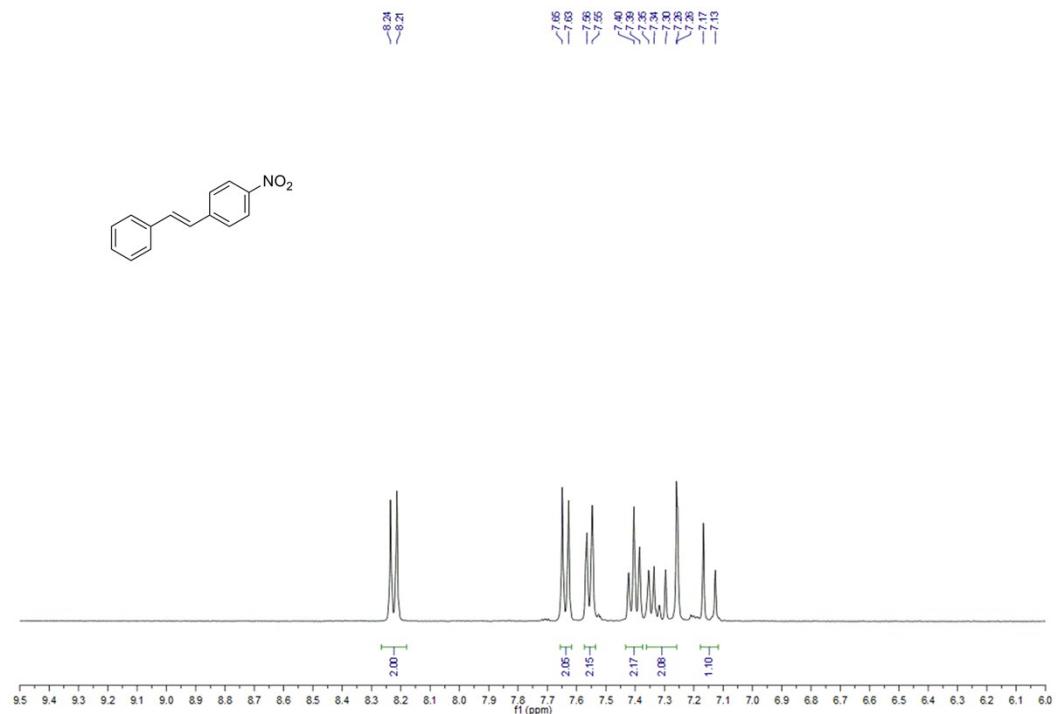
### (E)-1-Methoxy-4-styrylbenzene (3g)



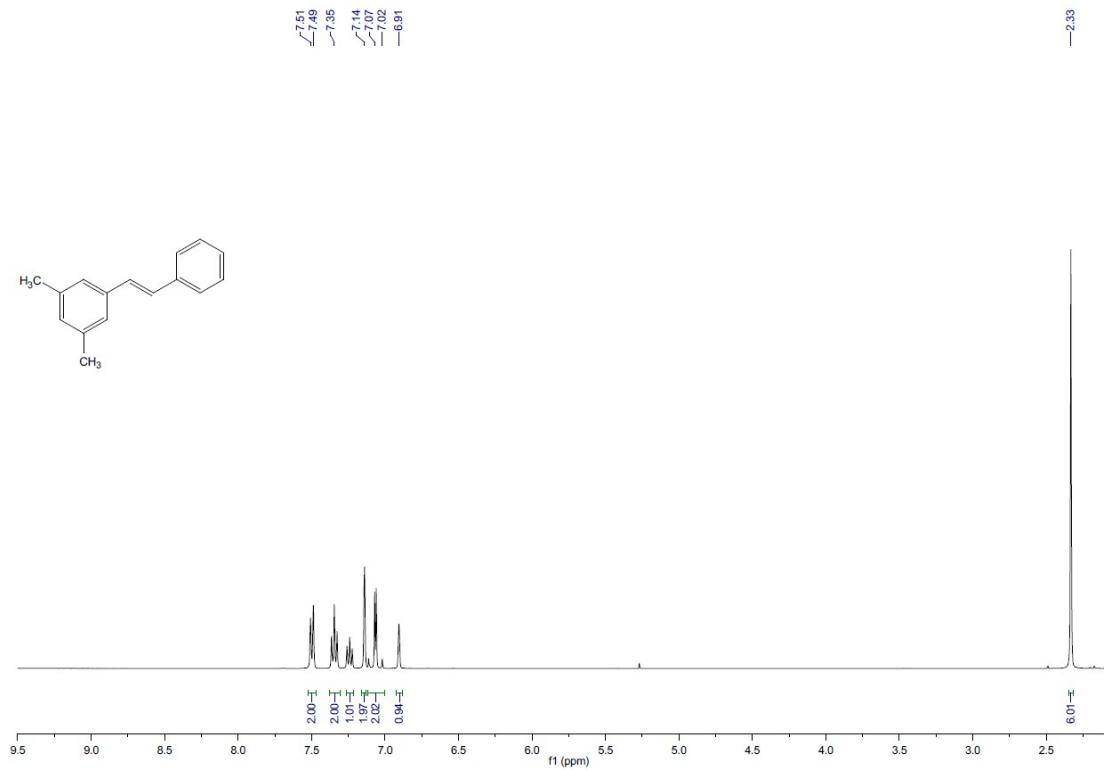
**(E)-1-Styryl-4-(trifluoromethyl)benzene (3h)**



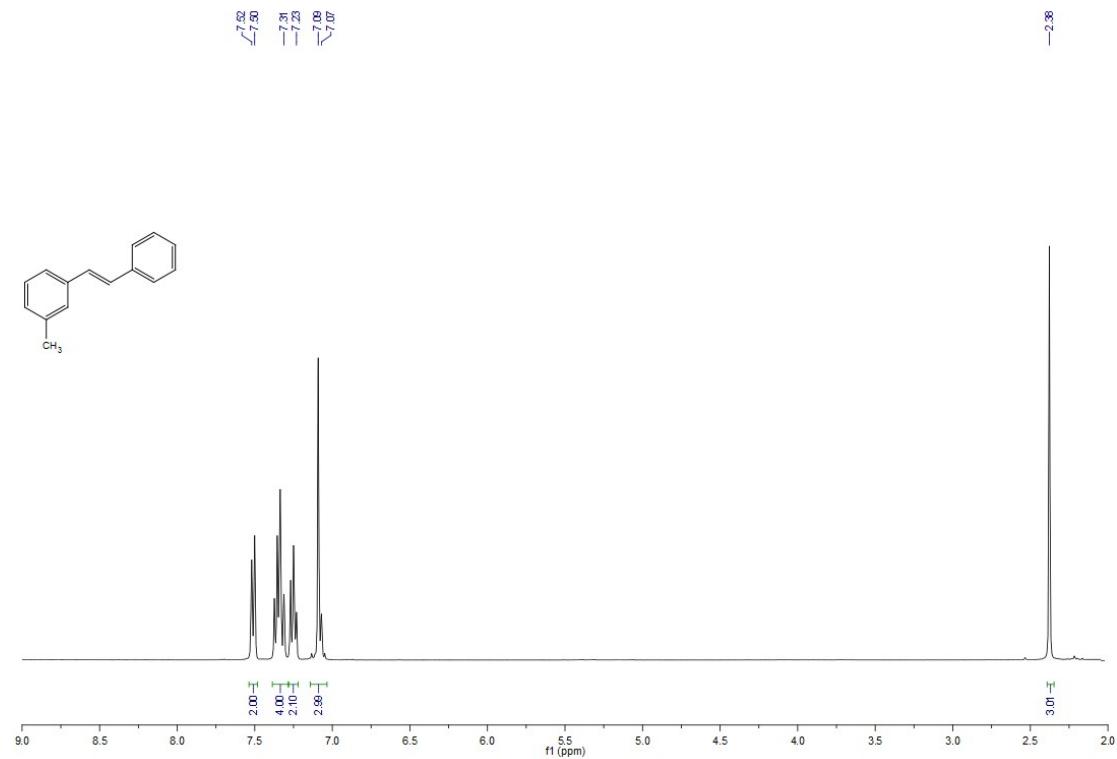
**(E)-1-Nitro-4-styrylbenzene (3i)**



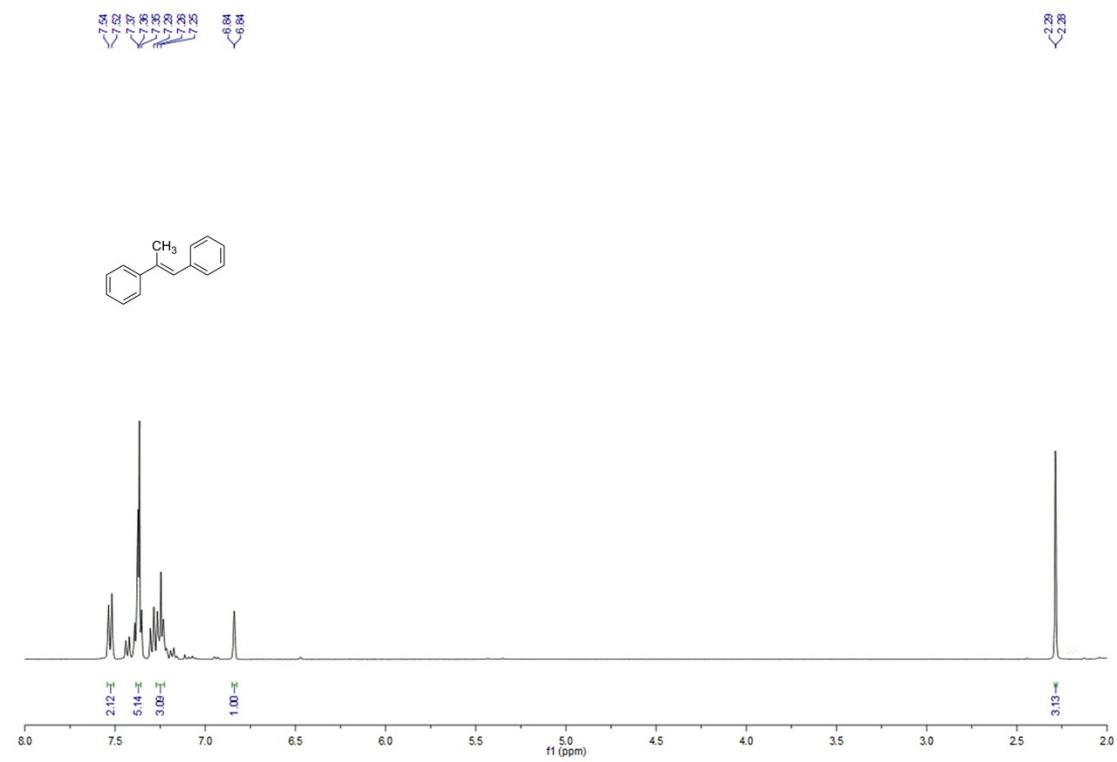
**(E)-1,3-diMethyl-5-styrylbenzene (3j)**



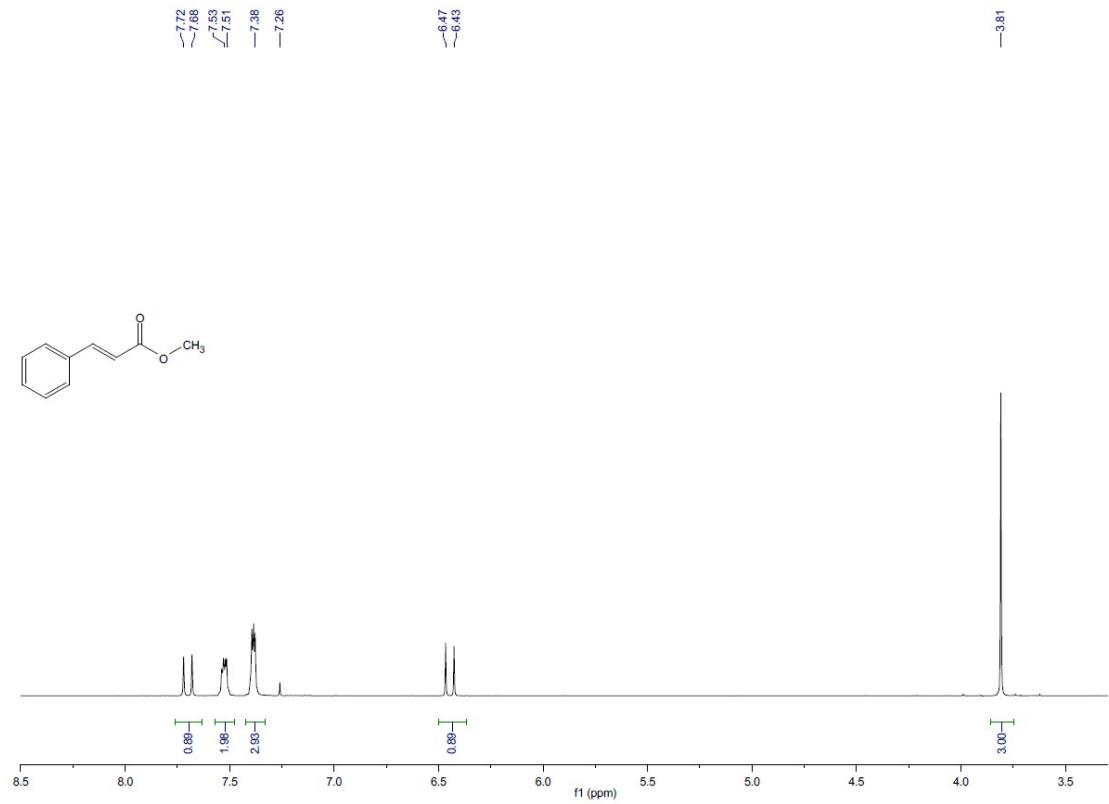
**(E)-1-Methyl-3-styrylbenzene (3k)**



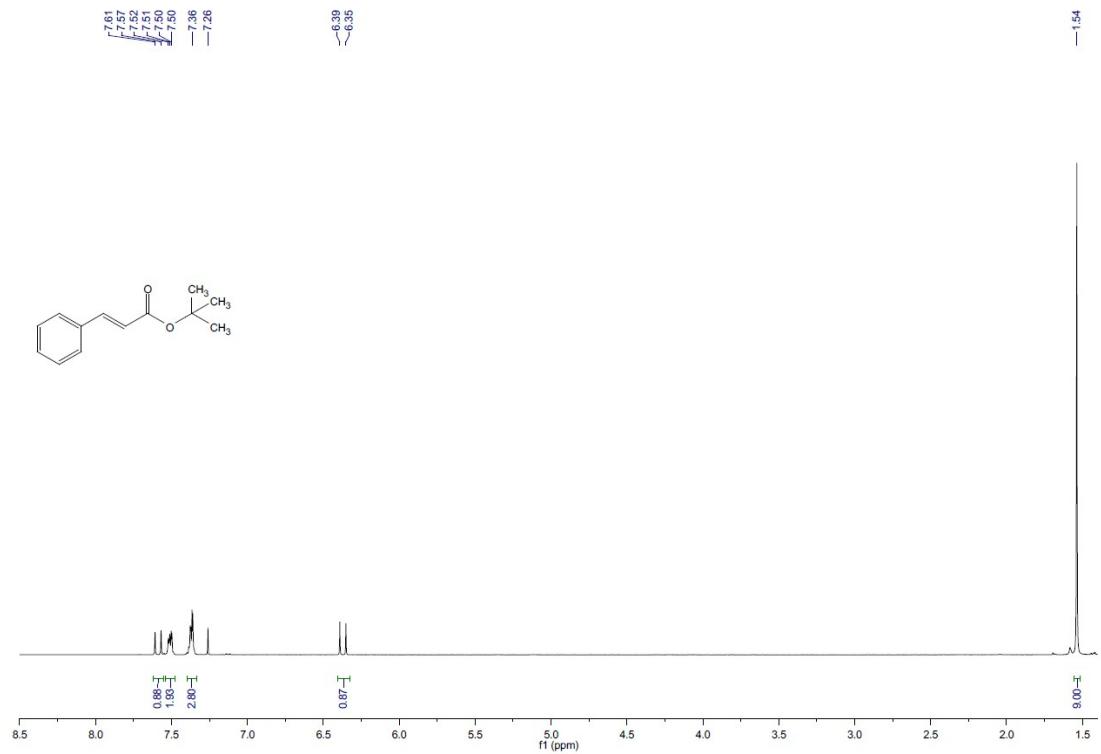
**(E)-prop-1-Ene-1,2-diyldibenzene (3l)**



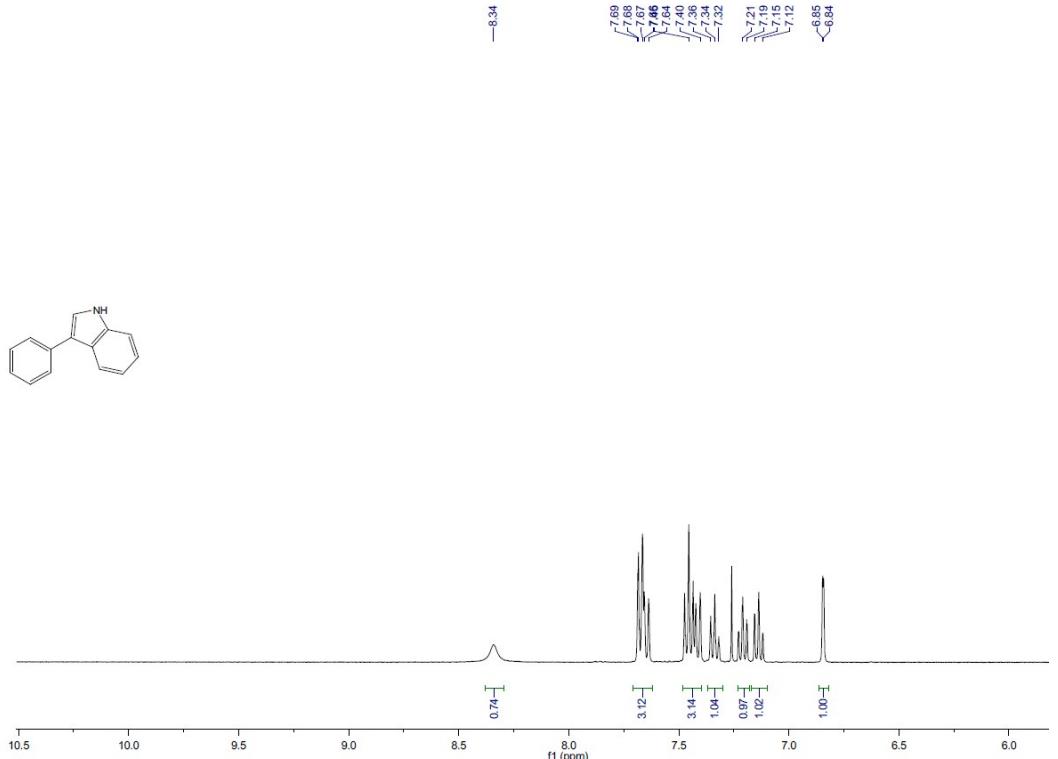
**Methyl cinnamate (3m)**



***tert*-Butyl cinnamate(3n)**



**3-Phenyl-1*H*-indole (3o)**



**2-Phenylbenzofuran (3p)**

