



***Advanced***  
**Synthesis &  
Catalysis**

Supporting Information

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## Supporting Information

### **Palladium-iminodiacetic acid immobilized on pH-responsive polymeric microspheres: efficient quasi-homogeneous catalyst for Suzuki and Heck reactions in aqueous solution**

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#### **1. $^1\text{H}$ NMR (400 MHz) for the synthesized products**

Biphenyl (1)<sup>1</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ): d (ppm) 7.35 (t,  $J=7.6$  Hz, 2H), 7.45 (t,  $J=7.6$  Hz, 4H), 7.60 (d,  $J=7.6$  Hz, 4H).

4-Hydroxybiphenyl (2)<sup>2</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ): d (ppm) 6.91 (d,  $J=8.4$  Hz, 2H), 7.30 (t,  $J=7.4$  Hz, 1H), 7.41 (t,  $J=7.6$  Hz, 2H), 7.48 (d,  $J=8.8$  Hz, 2H), 7.54 (d,  $J=7.2$  Hz, 2H).

4-Methoxybiphenyl (3)<sup>2</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ): d (ppm) 3.86 (s, 3H), 6.98 (d,  $J=8.4$  Hz, 2H), 7.30 (t,  $J=7.2$  Hz, 1H), 7.41 (t,  $J=7.2$  Hz, 2H), 7.54 (t,  $J=8.4$  Hz, 4H).

Biphenyl-4-carbaldehyde (4)<sup>3</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ): d (ppm) 7.40-7.51 (m, 3H), 7.65 (d,  $J=7.2$  Hz, 2H), 7.76 (d,  $J=8.0$  Hz, 2H), 7.96 (d,  $J=8.4$  Hz, 2H), 10.06 (s, 1H).

Biphenyl-4-carboxylic acid (5)<sup>4</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ): d (ppm) 7.42 (t,  $J=7.4$  Hz, 1H), 7.50 (t,  $J=7.4$  Hz, 2H), 7.73 (d,  $J=7.6$  Hz, 2H), 7.79 (d,  $J=8.4$  Hz, 2H), 8.02 (d,  $J=8.4$  Hz, 2H).

4-Acetylbiphenyl (6)<sup>5</sup>.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ): d (ppm) 2.64 (s, 3H), 7.40 (t,  $J=7.4$  Hz, 1H), 7.48 (t,  $J=7.6$  Hz, 2H), 7.63 (d,  $J=7.2$  Hz, 2H), 7.69 (d,  $J=8.0$  Hz, 2H), 8.04 (d,  $J=8.4$  Hz, 2H).

4-Nitrobiphenyl (7)<sup>6</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 7.43-7.52 (m, 3H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H).

3-Nitrobiphenyl (8)<sup>7</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 7.44 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.59-7.64 (m, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.19-8.22 (dd, *J*<sub>1</sub> = 2.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 8.46 (t, *J* = 2.0 Hz, 1H).

2-Nitrobiphenyl (9)<sup>7</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 7.31-7.34 (m, 2H), 7.40-7.50 (m, 5H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H).

*trans*-Stilbene (10)<sup>8</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 7.12 (s, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.52 (d, *J* = 7.2 Hz, 4H).

4-Methoxy-*trans*-stilbene (11)<sup>9</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 3.84 (s, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 16.4 Hz, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.45-7.50 (m, 4H).

*trans*-Stilben-4-ol (12)<sup>10</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 6.83 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 7.05 (d, *J* = 16.4 Hz, 1H), 7.22-7.26 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H).

4-Methyl-*trans*-stilbene (13)<sup>8</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 2.37 (s, 3H), 7.08 (d, *J* = 2.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 6.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H).

3-Methyl-*trans*-stilbene (14)<sup>11</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 2.39 (s, 3H), 7.09 (d, *J* = 8.0 Hz, 3H), 7.24-7.28 (m, 2H), 7.32-7.38 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 2H).

*trans*-Stilbene-4-carboxylic acid (15)<sup>12</sup>. <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): d (ppm) 7.29-7.43 (m, 5H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H).

4-Acetyl-*trans*-stilbene (16)<sup>13</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 2.61 (s, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 18.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J*

=7.6 Hz, 2H), 7.54 (d,  $J$ =7.6 Hz, 2H), 7.59 (d,  $J$ =8.0 Hz, 2H), 7.96 (d,  $J$ =8.4 Hz, 2H).

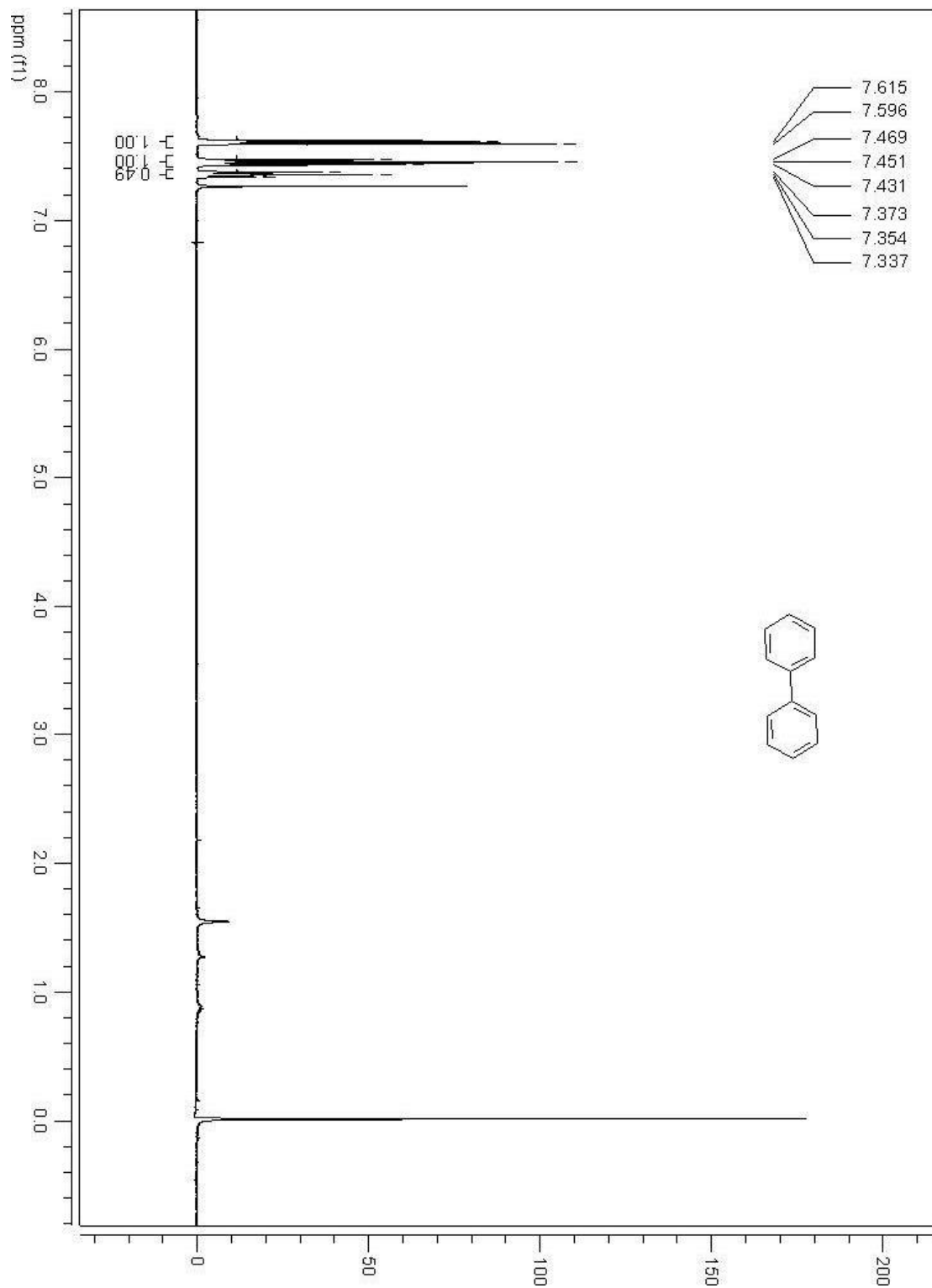
4-Nitro-*trans*-stilbene (17)<sup>8</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): d (ppm) 7.14 (d,  $J$ =16.4 Hz, 1H), 7.28 (d,  $J$ =14.4 Hz, 1H), 7.32-7.73 (m, 3H), 7.56 (d,  $J$ =7.2 Hz, 2H), 7.64 (d,  $J$ =8.8 Hz, 2H), 8.23 (d,  $J$ =8.8 Hz, 2H).

## 2. References

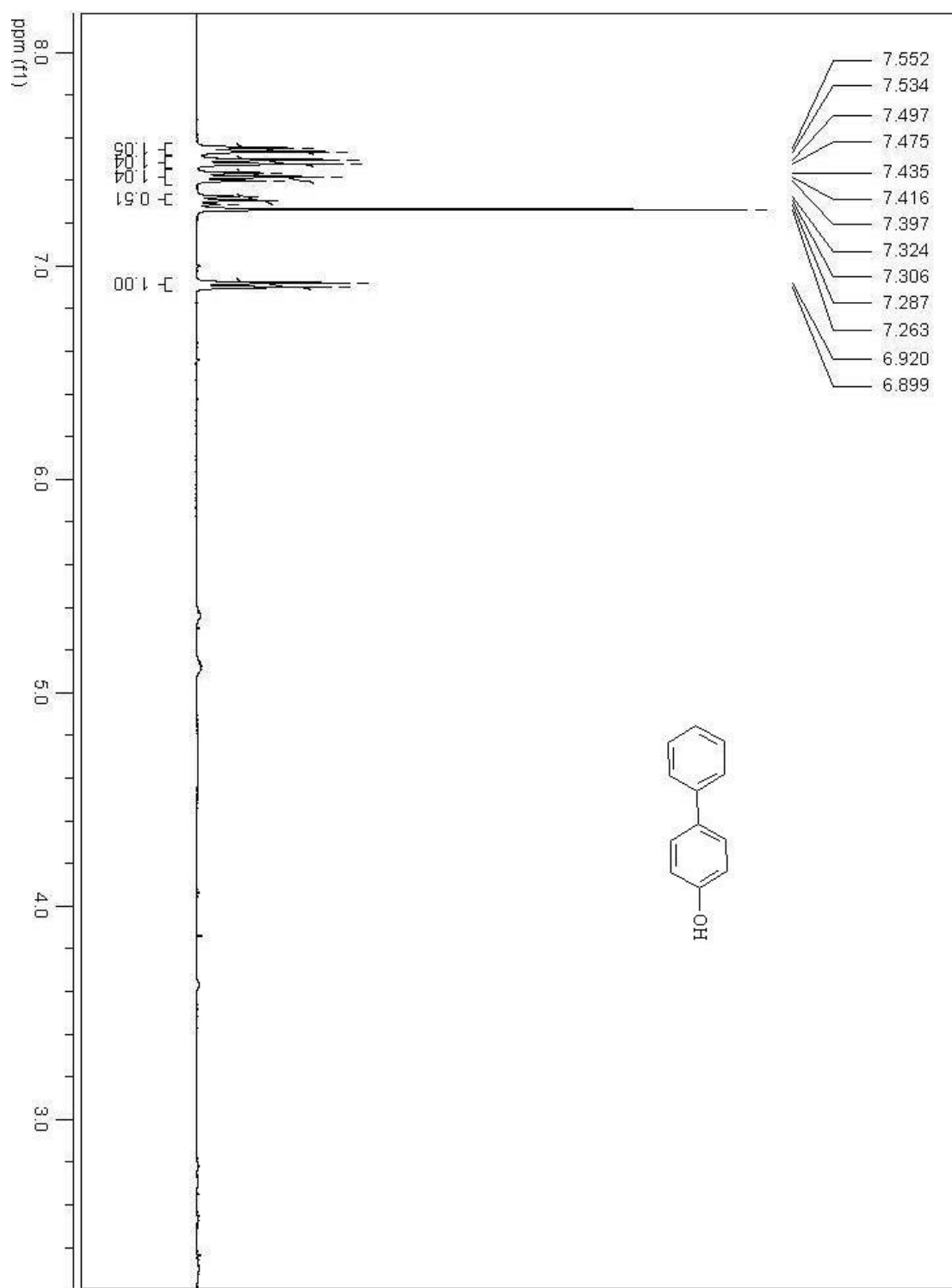
- (1) Hatanaka, Y.; Goda, K.; Hiyama, Y.O.T. *Tetrahedron* **1994**, 50, 8301.
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- (4) Leadbeater, N. E.; Resouly, S. M. *Tetrahedron* **1999**, 55, 11889.
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- (13) Lucas, R. M.; Kevin, H. S. *Org. Lett.* **2004**, 6, 225.

## 3. Spectra

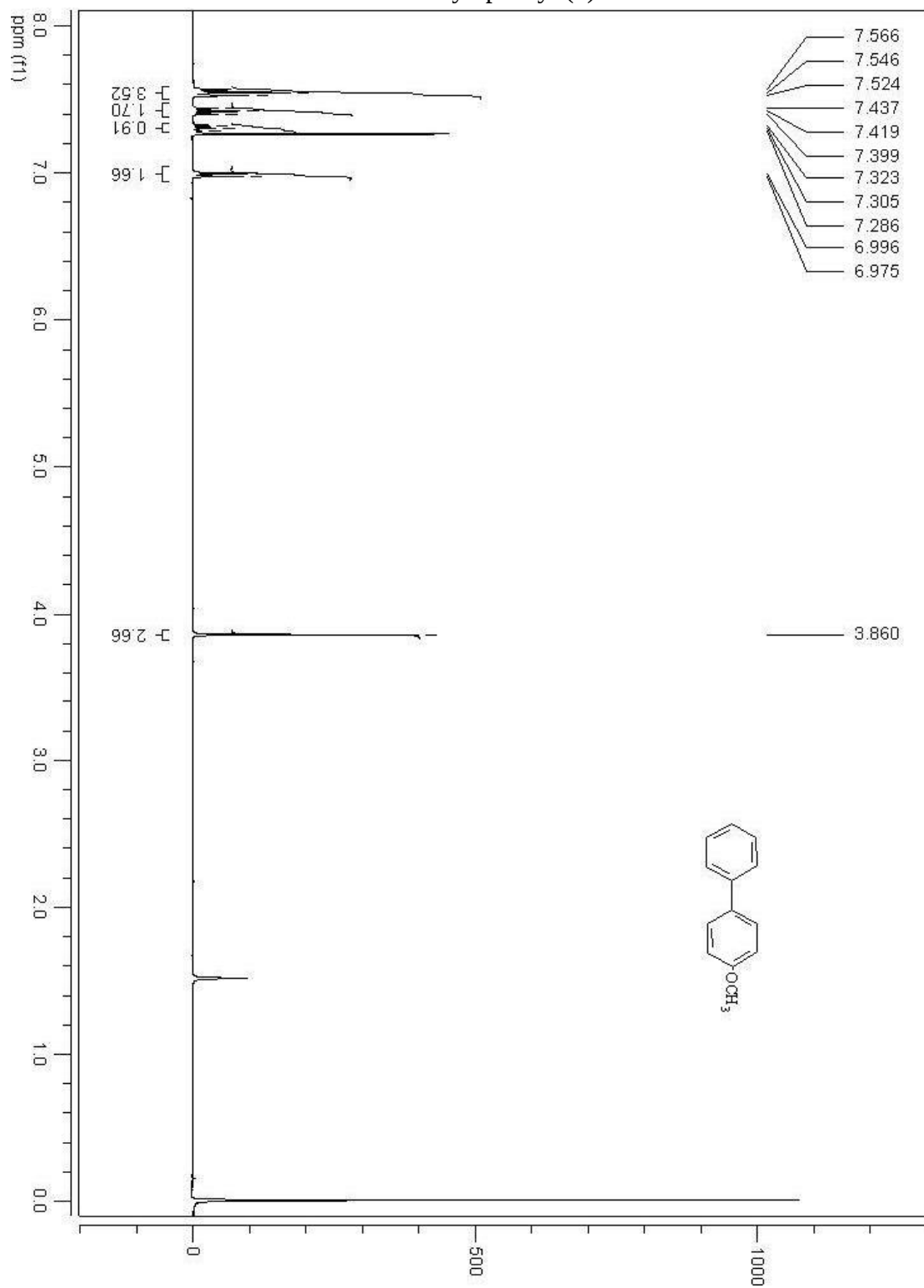
biphenyl (1)



4-hydroxybiphenyl (2)



# 4-methoxybiphenyl (3)



Chemical structure: C1=CC=C(C=C1)/C=C/C2=CC=CC=C2

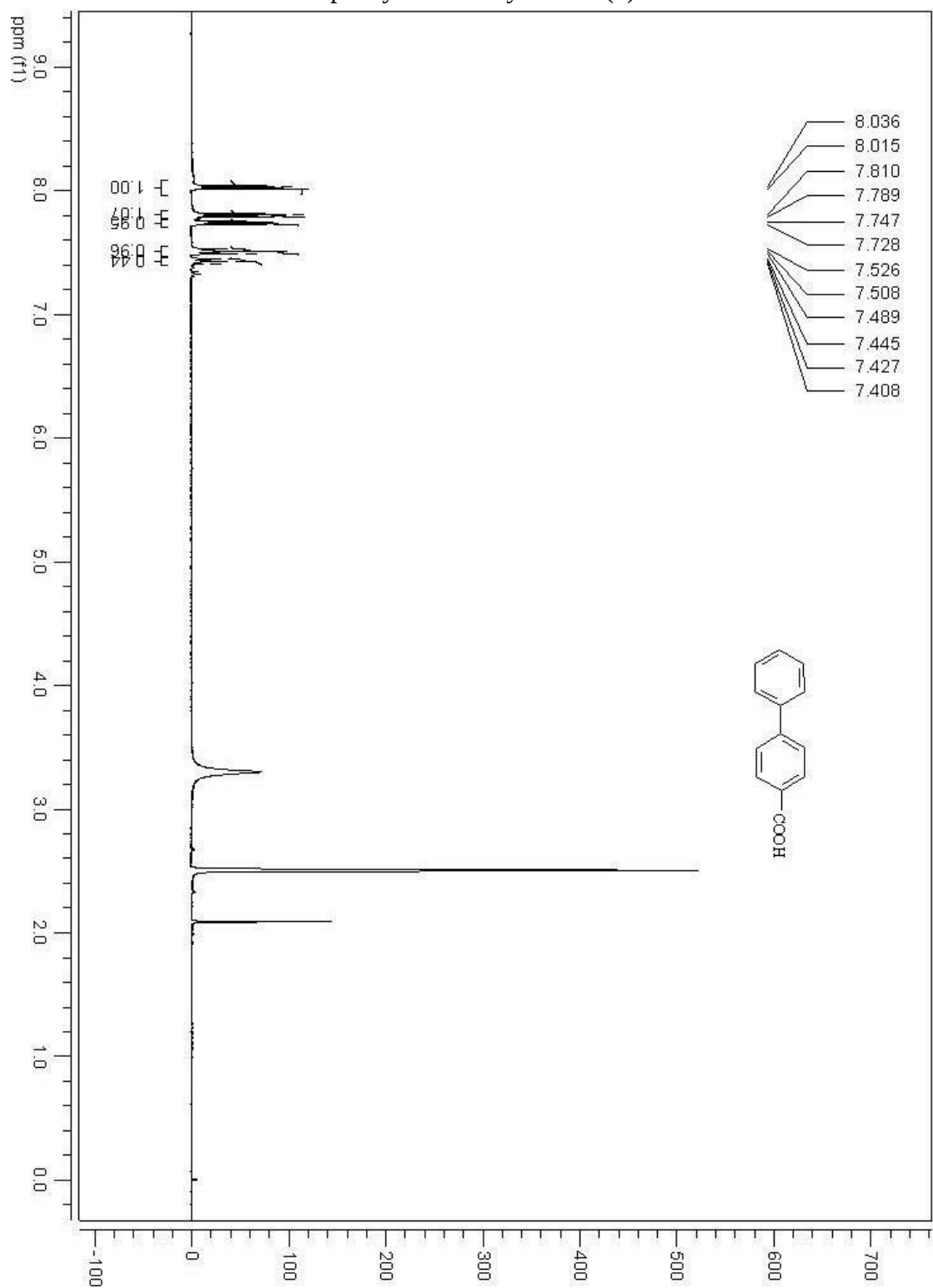
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks at the following chemical shifts (ppm):

- 10.069
- 7.974
- 7.953
- 7.775
- 7.755
- 7.656
- 7.638
- 7.510
- 7.492
- 7.473
- 7.443
- 7.430
- 7.425
- 7.419
- 7.406
- 7.264

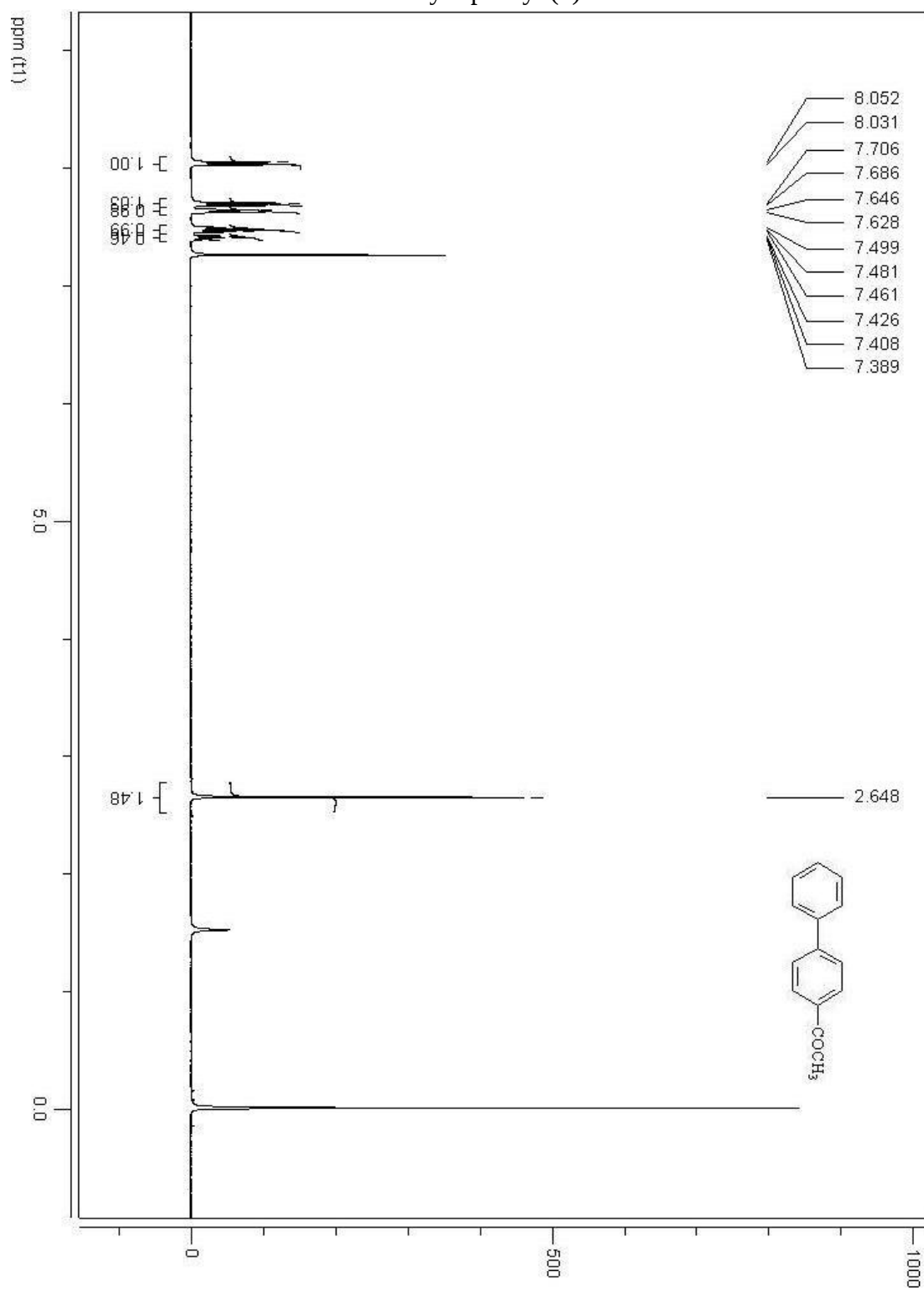
Integration values (from left to right):

- 1.00
- 2.19
- 2.18
- 2.19
- 3.27

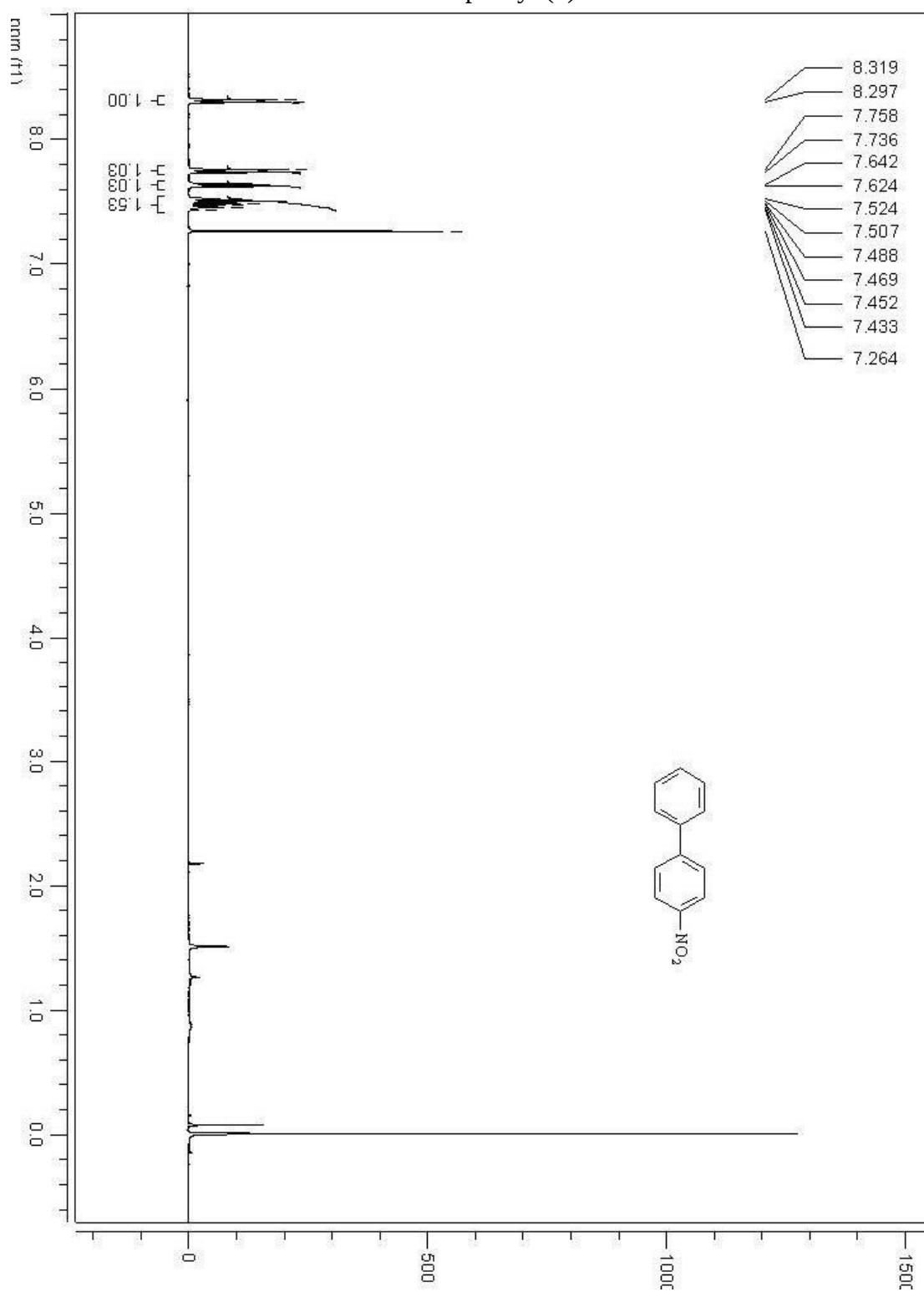
biphenyl-4-carboxylic acid (5)



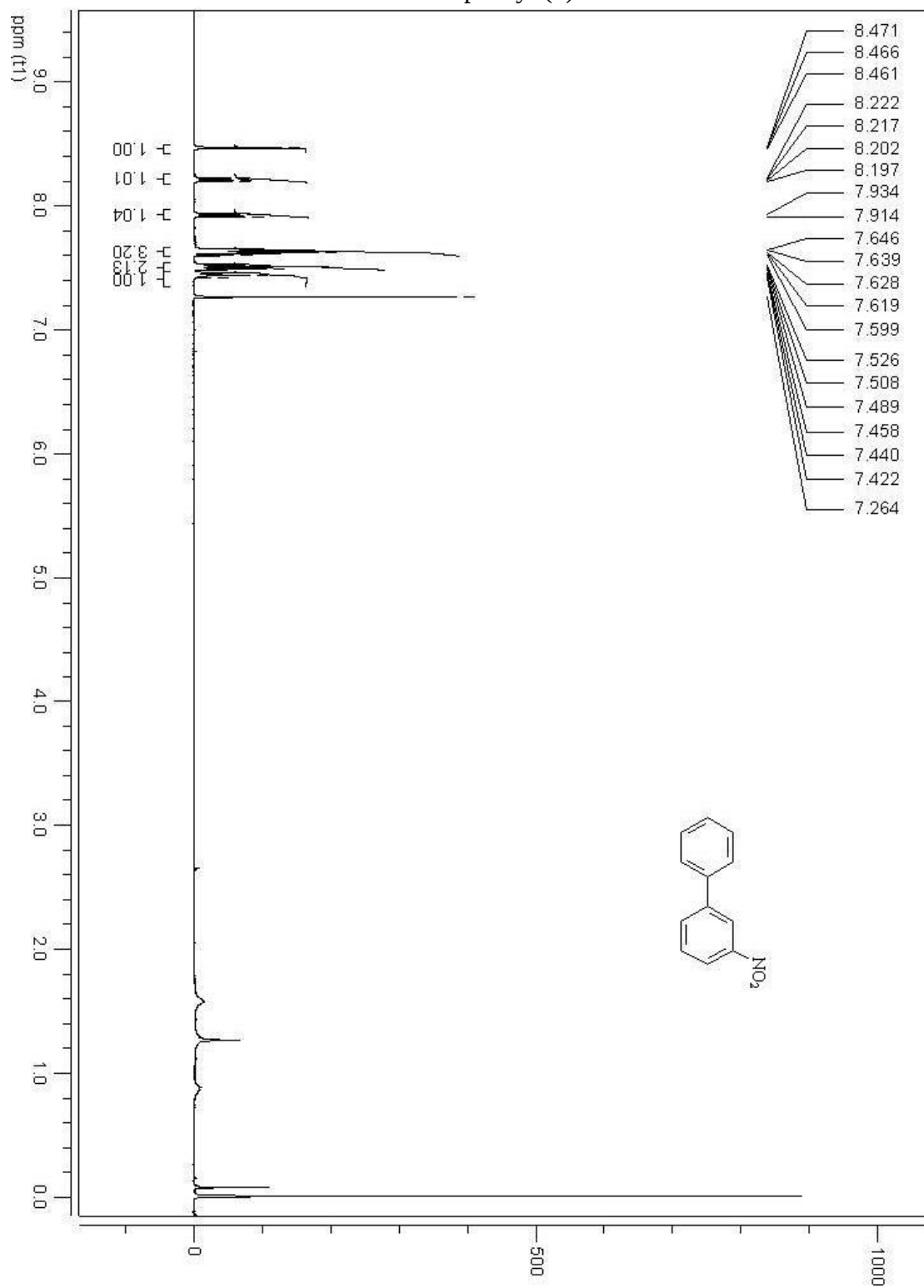
4-acetylbiphenyl (6)



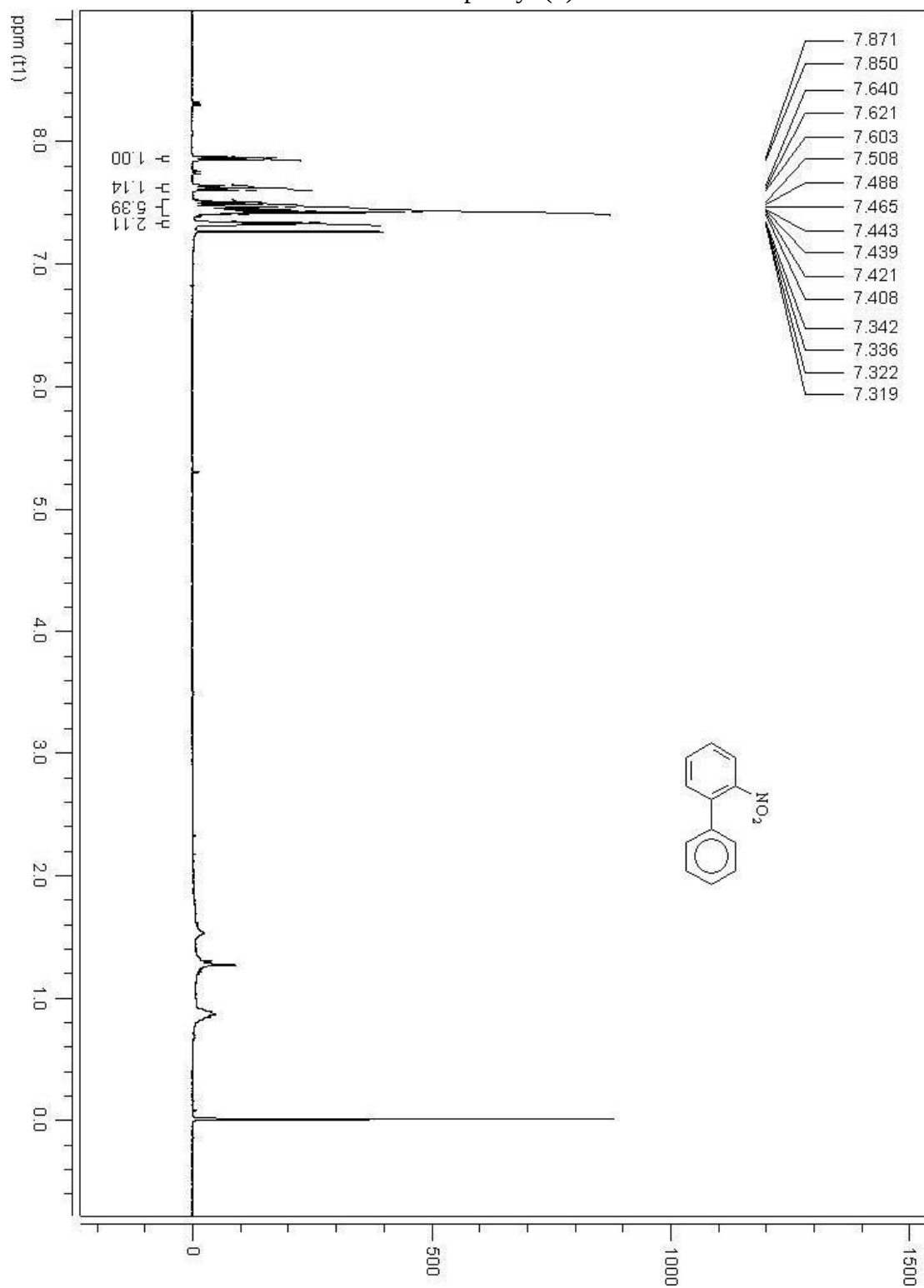
# 4-nitrobiphenyl (7)



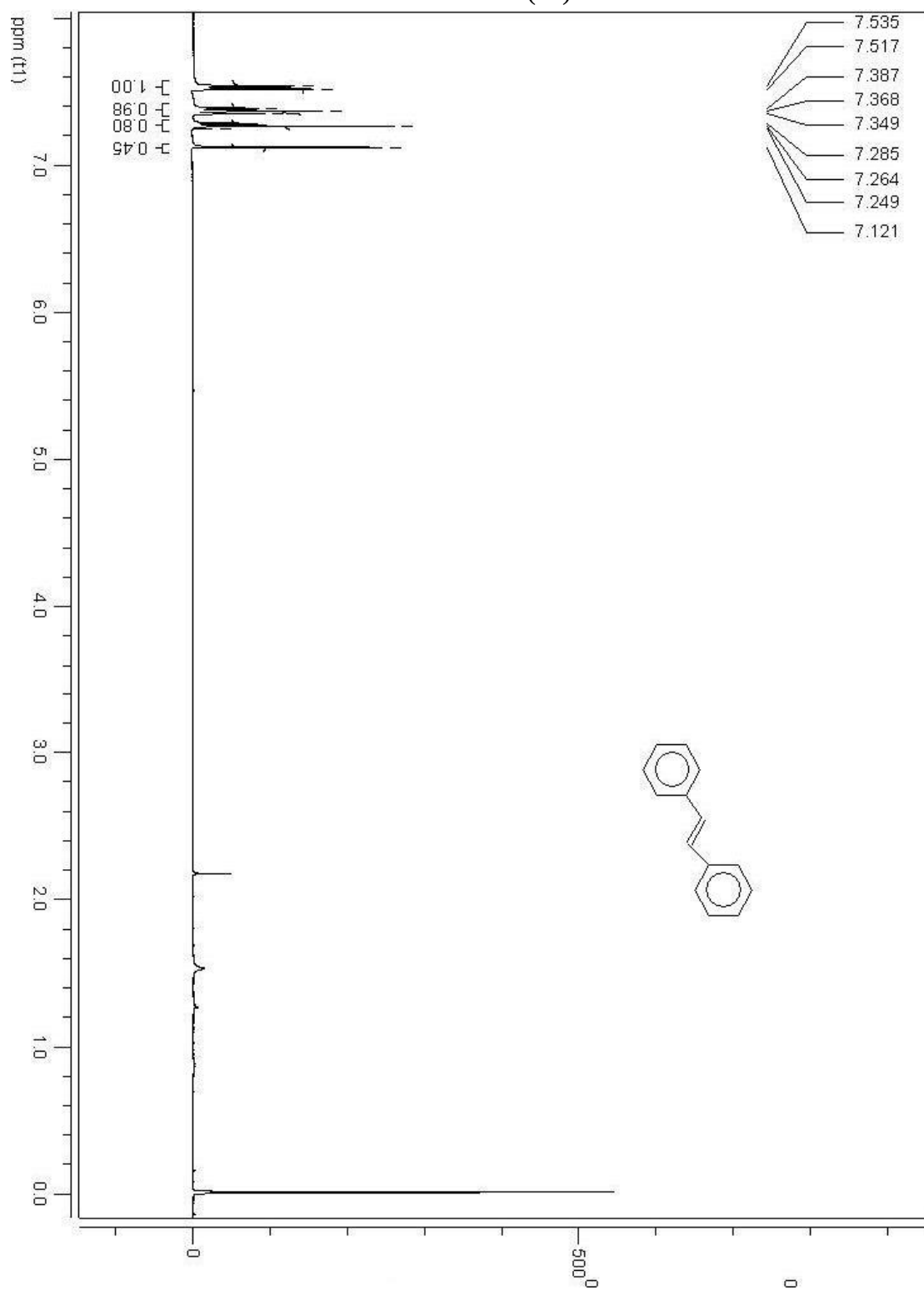
# 3-nitrobiphenyl (8)



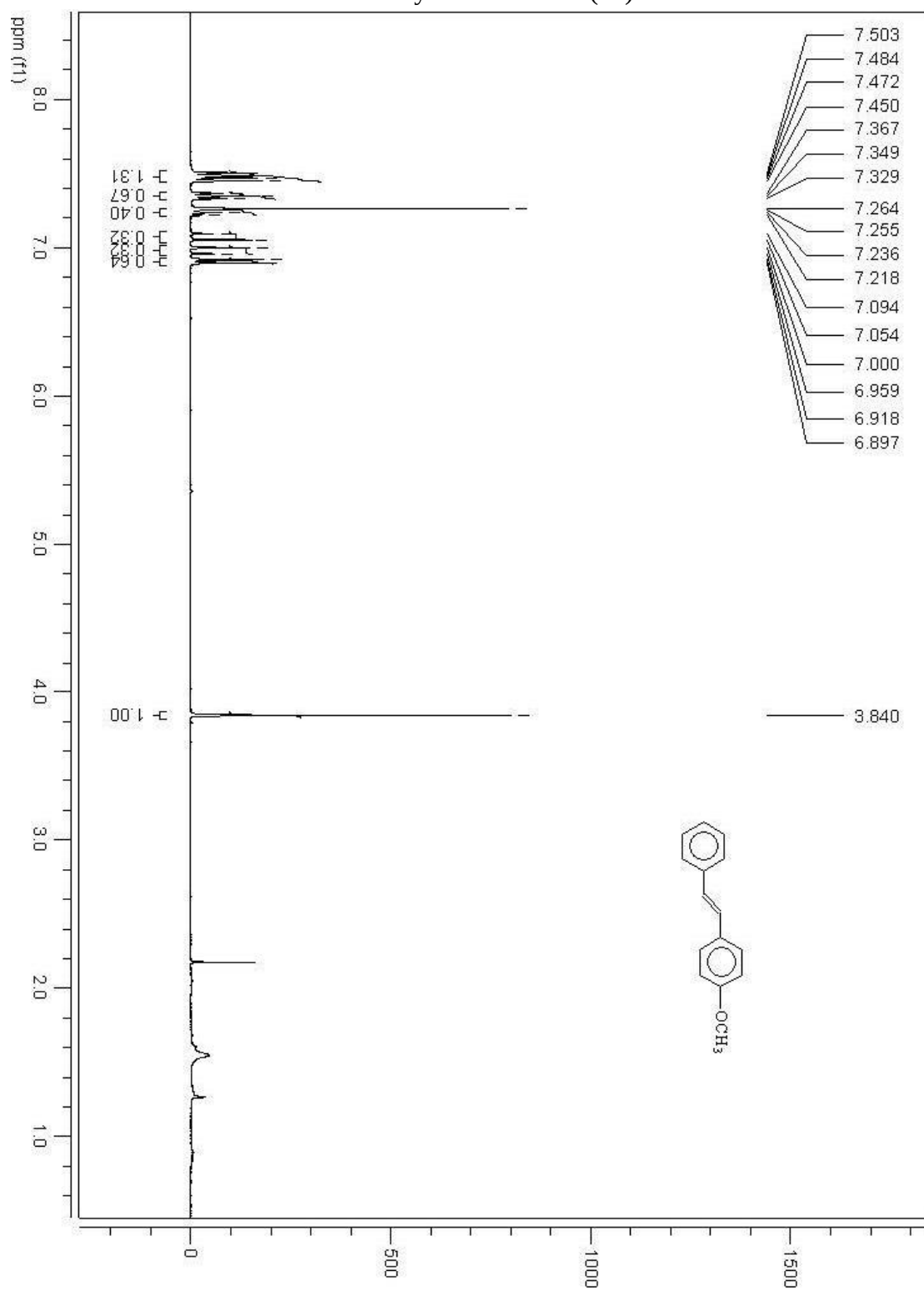
# 2-nitrobiphenyl (9)



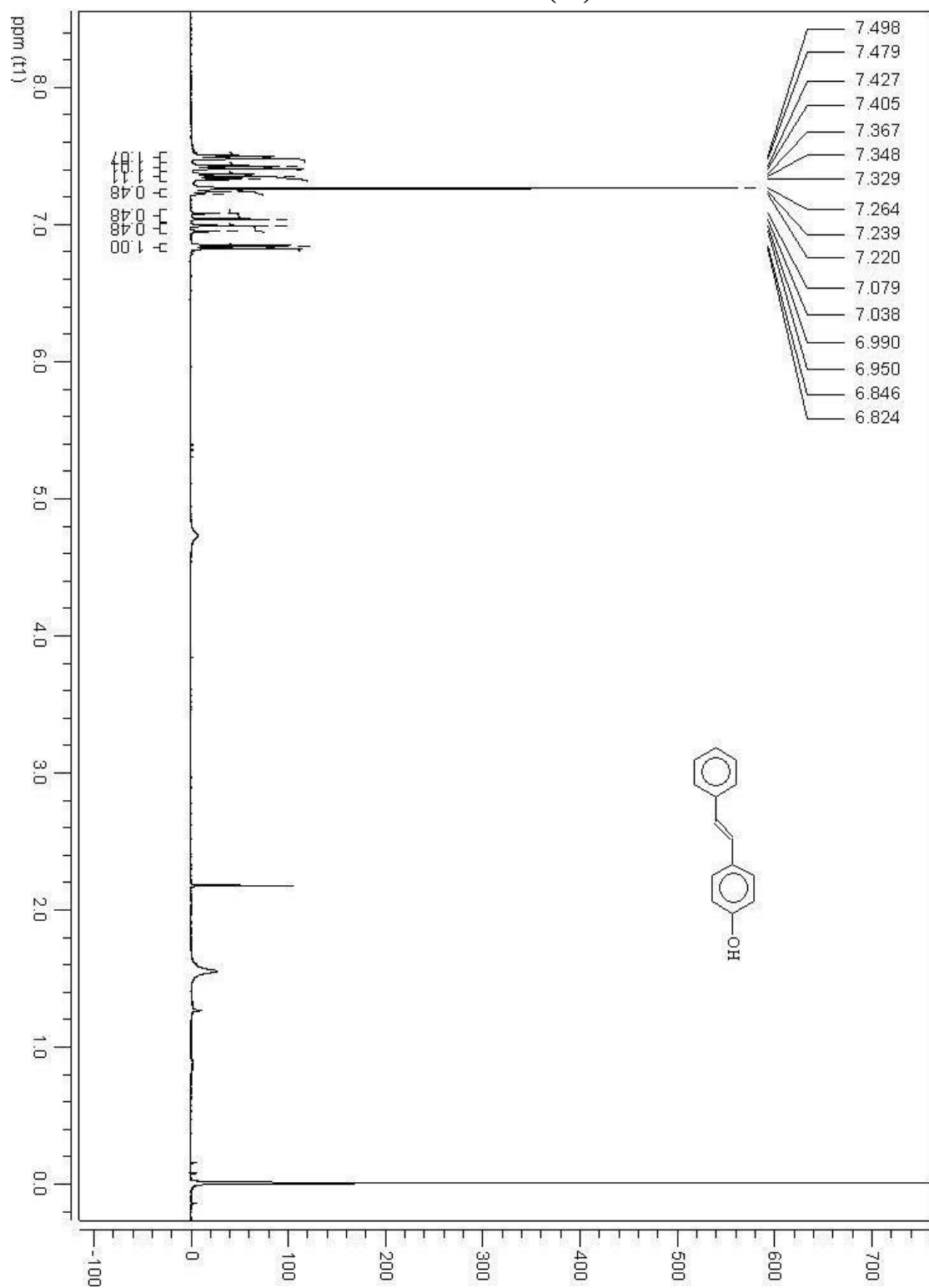
*trans*-stilbene (10)



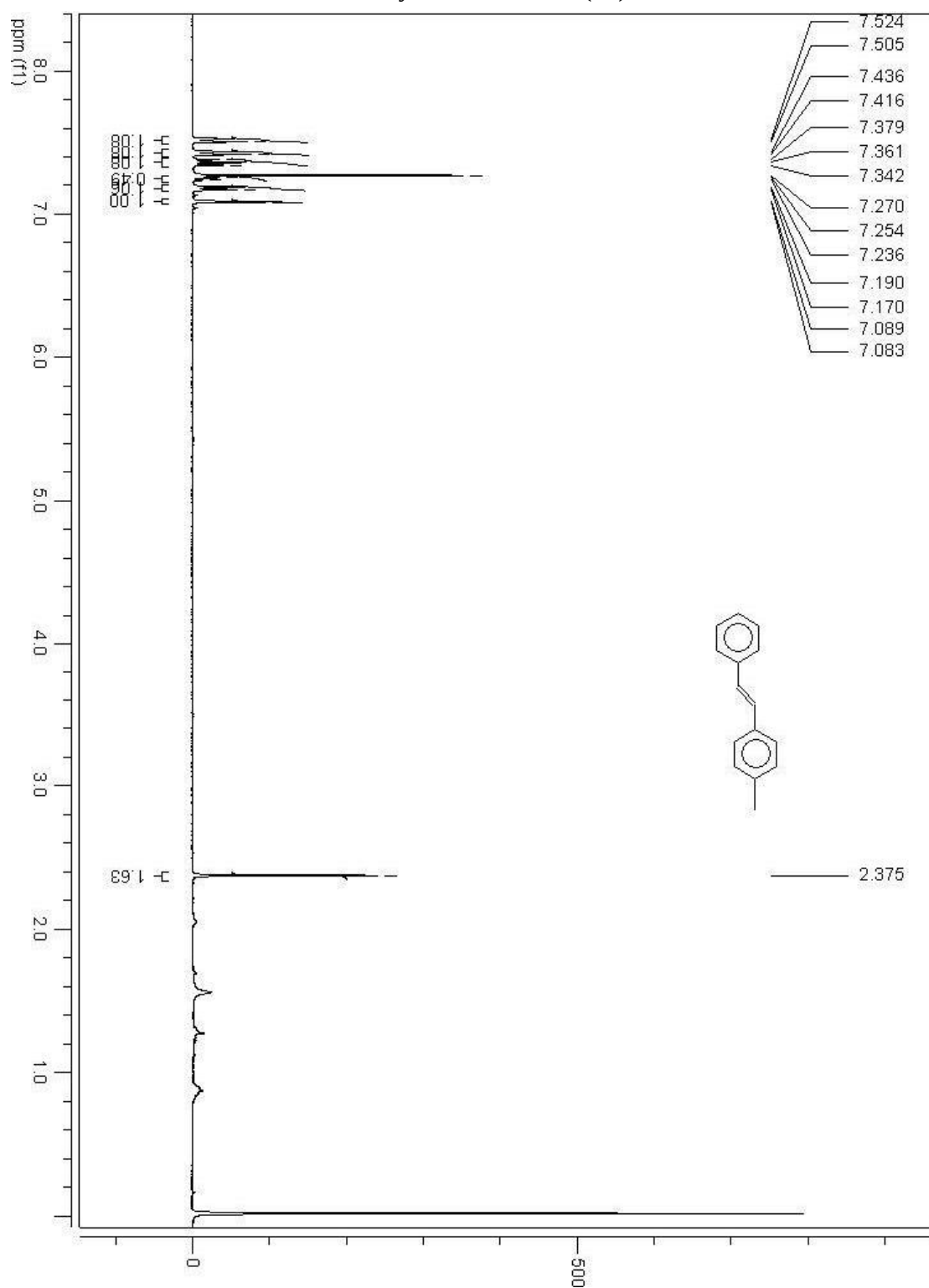
4-methoxy-*trans*-stilbene (11)



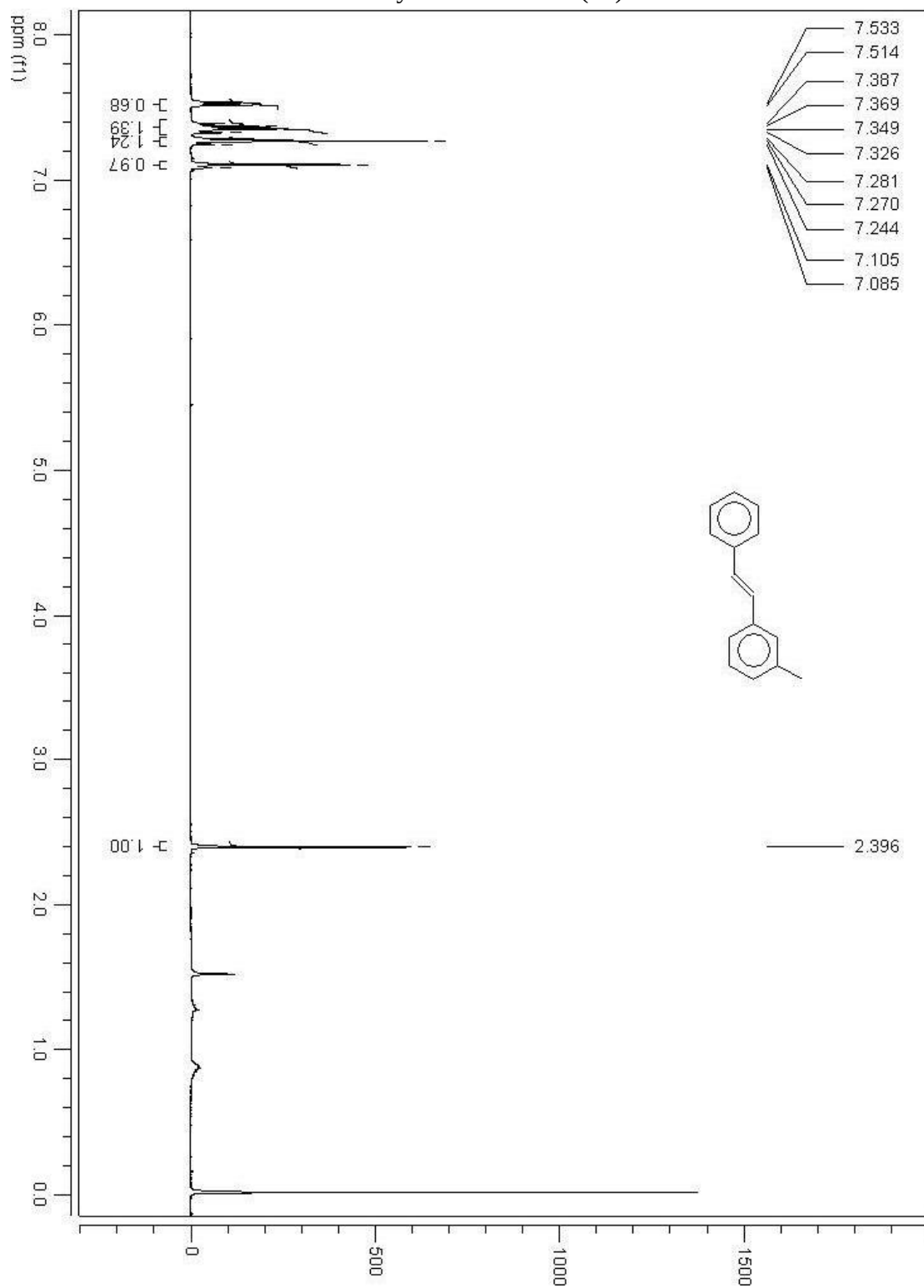
*trans*-stilben-4-ol (12)



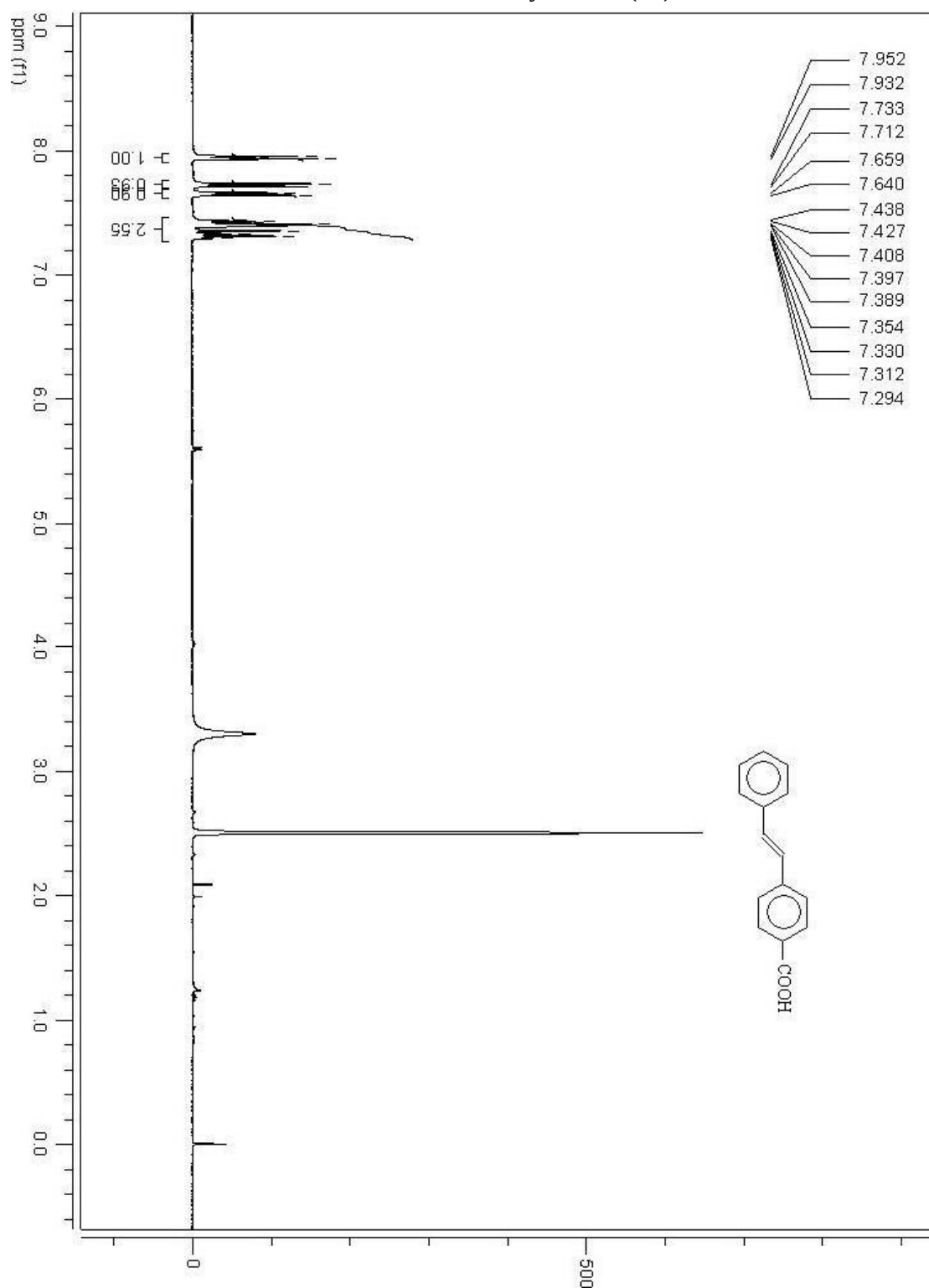
4-methyl-*trans*-stilbene (13)



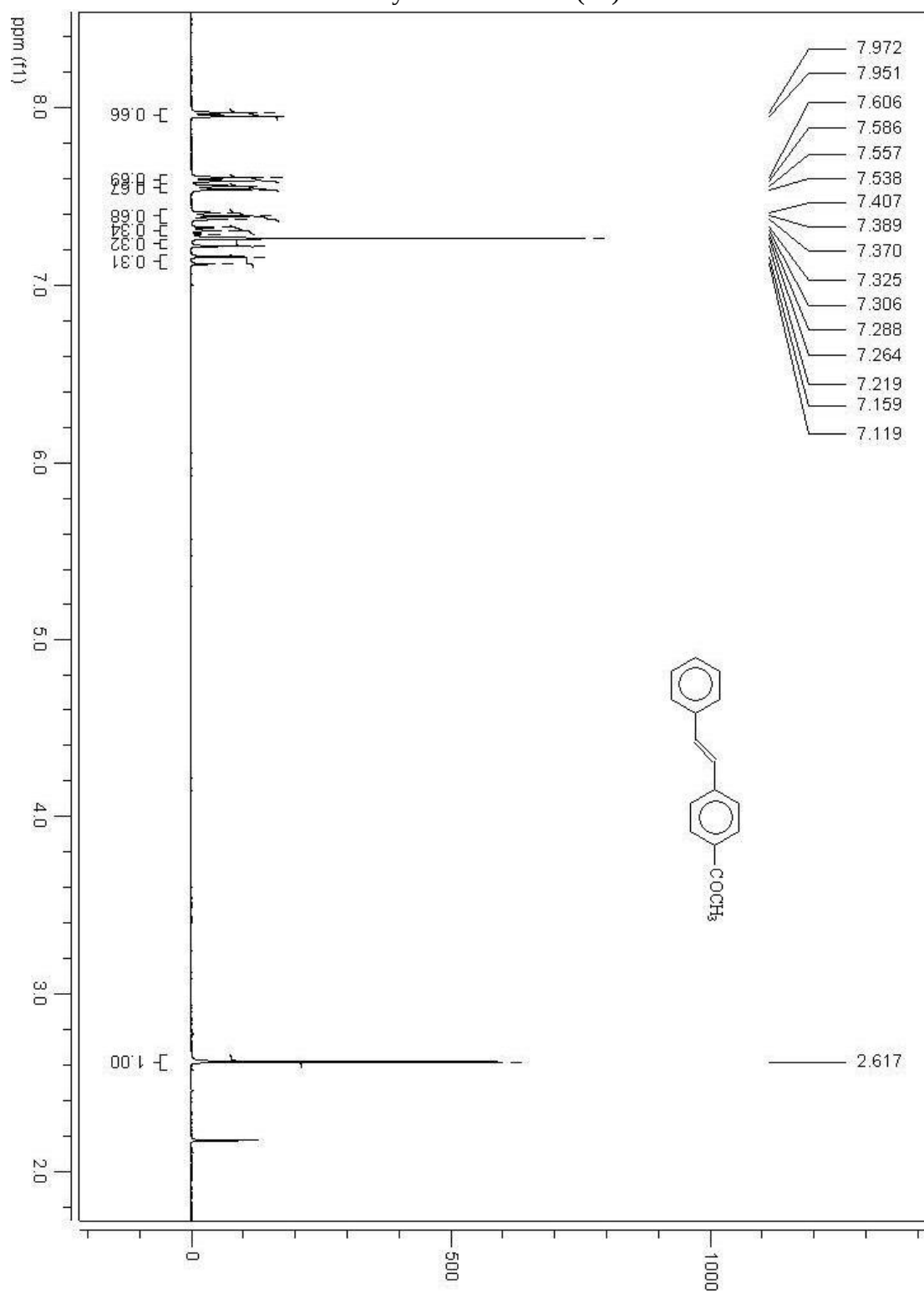
3-methyl-*trans*-stilbene (14)



*trans*-stilbene-4-carboxylic acid (15)



4-acetyl-*trans*-stilbene (16)



4-nitro-*trans*-stilbene (17)

