

## ELECTRONIC SUPPORTING INFORMATION

### Biomass-derived safer medium to replace toxic dipolar solvents and access cleaner Heck coupling

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## Experimental Section

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources without further purification. GLC analyses were performed by using Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and hydrogen as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz ( $^1\text{H}$  at 400 MHz and  $^{13}\text{C}$  at 100.6 MHz) in  $\text{CDCl}_3$  using TMS as the internal standard. Elemental Analyses were conducted on a Fisons EA1108CHN. Melting points were measured on a Büchi 510. . ICP-OES 710 Agilent Technology.

### Preparation of the samples for ICP

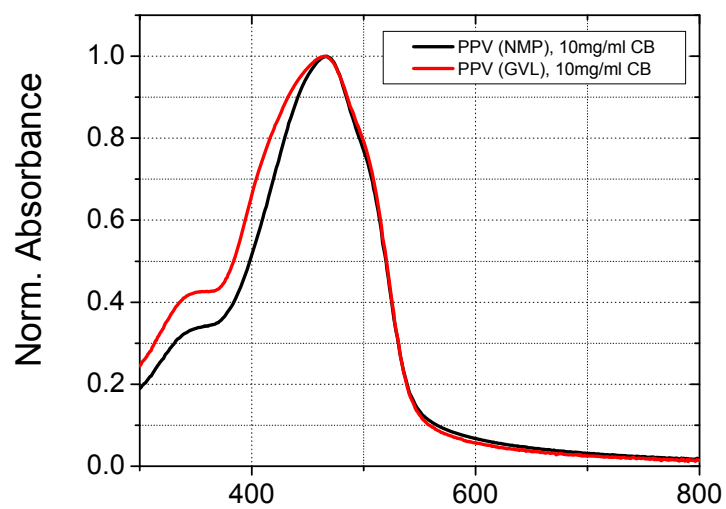
The compounds (ca. 100 mg) were dissolved in ca. 3 mL of aqua regia and stirred for 10 minutes at room temperature. Water was added to reach a final volume of 10 mL. If present, residual solid was filtered off and the sample was taken to the ICP analyzer.

Compounds **3a**<sup>1</sup>, **3b**<sup>1</sup>, **3c**<sup>2</sup>, **3d**<sup>3</sup>, **3e**<sup>4</sup>, **3f**<sup>3</sup>, **3g**<sup>1</sup>, **3h**<sup>5</sup>, **3i**<sup>6</sup>, **3j**<sup>6</sup>, **3k**<sup>6</sup>, **3l**<sup>6</sup>, **5a**<sup>1</sup>, **5b**<sup>3</sup>, **5c**<sup>7</sup>, **5d**<sup>7</sup>, **5e**<sup>8</sup>, **5f**<sup>9</sup>, **5g**<sup>10</sup>, **5h**<sup>11</sup> are known compounds.

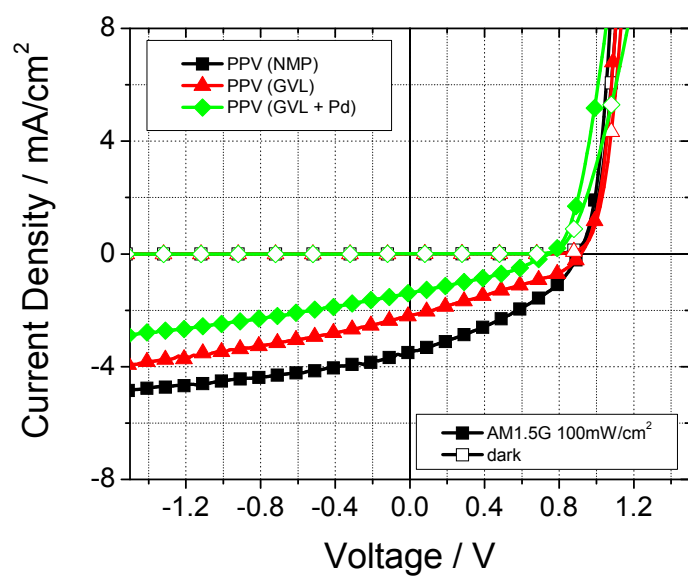
Characterization data and copies of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR are reported below.

## References

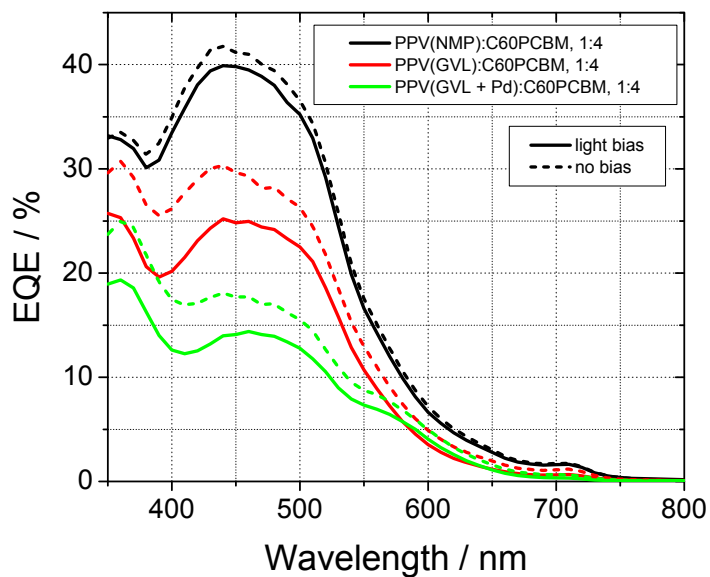
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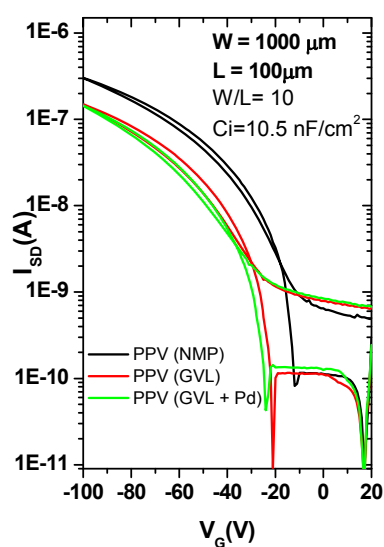
**Figure S1.** Normalized absorption spectra of PPV derivative **1** through NMP-based protocol (black line) and GVL-based protocol (red line) in thin film.



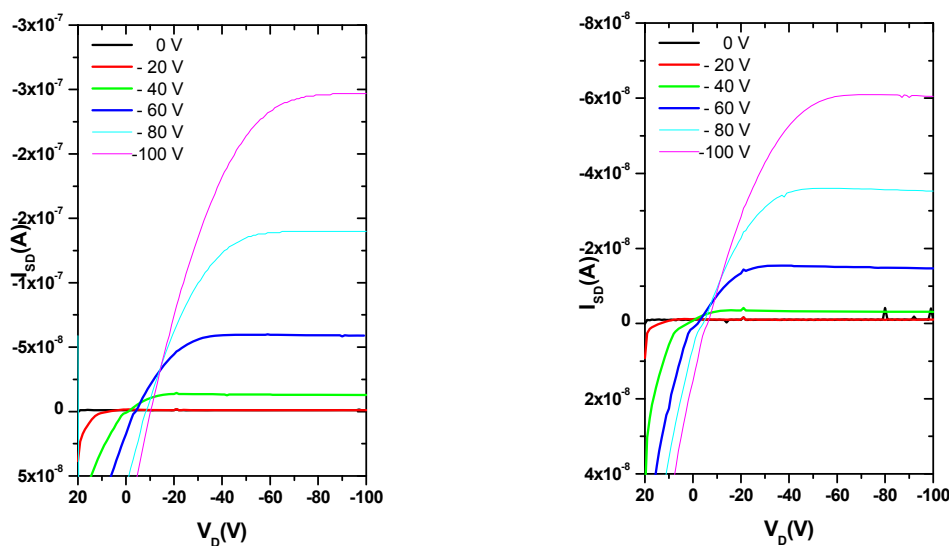
**Figure S2.** J-V characteristics of 1/PCBM based OPVs.



**Figure S3.** EQE spectra of BHJ **1** / PCBM. Black curves represent data using polymer **1** through NMP-based protocol. Red curves represent data using pure **1** through GVL-based protocol, while green curves represent data obtained using contaminated **1** through GVL-based protocol.

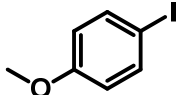
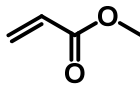
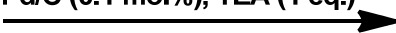
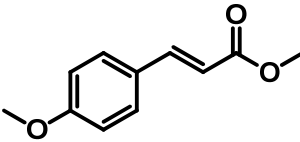


**Figure S4.** Typical transfer plot for spin-coated **1** OFETs. Black curves represent data using polymer **1** through NMP-based protocol. Red curves represent data using pure **1** through GVL-based protocol, while green curves represent data obtained using contaminated **1** through GLV-based protocol.

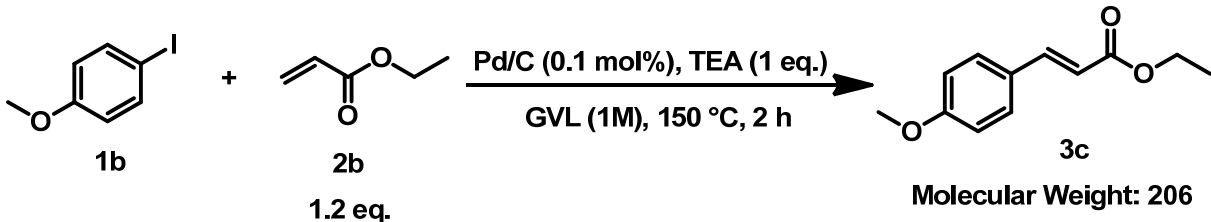


**Figure S5.** Typical output plot for spin-coated **1** OFETs through a) NMP-based and b) GVL based protocol.



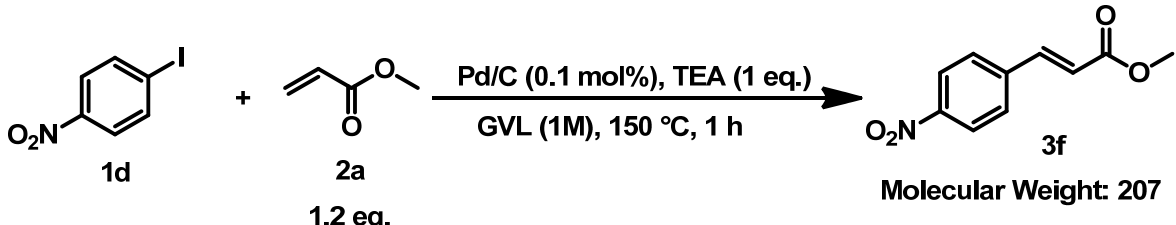
Chem. Name	(E)-methyl 3-(4methoxyphenyl)acrylate ( <b>3b</b> )			
Lit. Ref.	J. Org. Chem., <b>2006</b> , 71, 4339-4342			
<div><div><div><div><div></div><div>1b</div></div><div><div></div><div>2a</div></div></div><div><div>+</div><div>1.2 eq.</div></div><div><div><div><div><div></div><div>Pd/C (0.1 mol%), TEA (1 eq.)</div><div>GVL (1M), 150 °C, 2 h</div></div><div></div><div>3b</div></div><div>Molecular Weight: 192</div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole ( <b>1b</b> ) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and methyl acrylate ( <b>2a</b> ) (207 mg, 0.216 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0 °C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3b</b> was obtained as a slightly yellow solid (315 mg, 82% yield).				
Mol Formula	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	m.p.	90-91 °C	
Elemental Analysis: Calc.: 68.74; H: 6.29; found: C: 68.82; H: 6.34				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	3.78	3	s	
	3.82	3	s	
	6.30	1	d	16
	6.89	2	d	8.8
	7.46	2	d	8.8
	7.64	1	d	16
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 51.5, 55.3, 114.2, 115.1, 127.0, 130.0, 144.4, 161.2, 167.7				
GC-EIMS (m/z, %): 63 (15), 89 (25), 90 (16), 118 (17), 133 (34), 134 (16), 161 (100), 192 (M <sup>+</sup> , 70)				

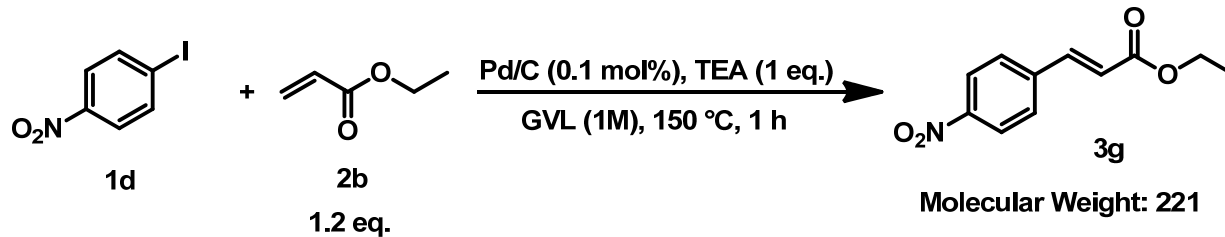


Chem. Name	(E)-ethyl 3-(4methoxyphenyl)acrylate ( <b>3c</b> )			
Lit. Ref.	J. Org. Chem., <b>2005</b> , 70, 6111-6113			
<div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole ( <b>1b</b> ) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and ethyl acrylate ( <b>2b</b> ) (240 mg, 0.264 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3c</b> was obtained as a white solid (371 mg, 90% yield).				
Mol Formula	C <sub>12</sub> H <sub>14</sub> O <sub>3</sub>	m.p.	49 °C	
Elemental Analysis: Calc.: C: 69.88; H: 6.84; found: C: 69.92; H: 6.78				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	1.30	3	<i>t</i>	7.0
	3.79	3	<i>s</i>	
	4.22	2	<i>q</i>	7.2
	6.86	2	<i>d</i>	8.8
	7.44	2	<i>d</i>	8.4
	7.61	1	<i>d</i>	16
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 14.3, 55.2, 60.2, 114.2, 115.6, 127.0, 129.6, 144.1, 161.1, 167.3				
GC-EIMS (m/z, %): 63 (15), 89 (24), 90 (18), 118 (17), 133 (36), 134 (16), 161 (100), 192 (M <sup>+</sup> , 71)				

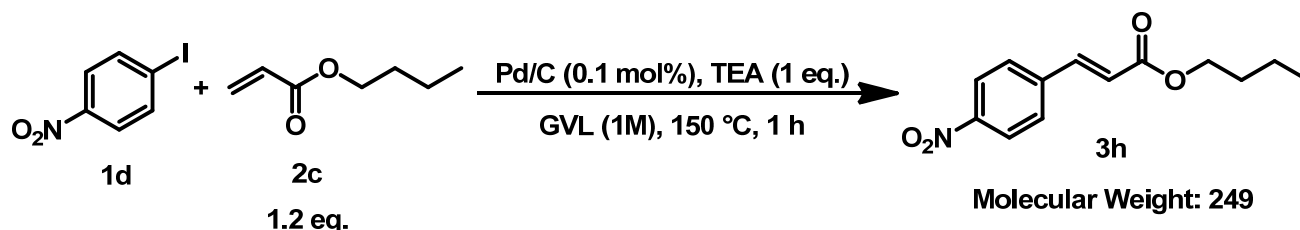




Chem. Name	(E)-methyl 3-(4-nitrophenyl) acrylate (3f)			
Lit. Ref.	Adv. Synth. & Cat., 2008, 350, 2559-2565			
<div></div> <p>Reaction scheme showing the synthesis of (E)-methyl 3-(4-nitrophenyl) acrylate (<b>3f</b>) from 4-iodonitrobenzene (<b>1d</b>) and methyl acrylate (<b>2a</b>). The reaction conditions are Pd/C (0.1 mol%), TEA (1 eq.) in GVL (1M) at 150 °C for 1 h. The product <b>3f</b> has a molecular weight of 207.</p>				
METHOD:				
In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene ( <b>1d</b> ) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and methyl acrylate ( <b>2a</b> ) (207 mg, 0.216 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3f</b> was obtained as a slightly yellow solid (348 mg, 84% yield).				
Mol Formula	C <sub>10</sub> H <sub>9</sub> NO <sub>4</sub>	m.p.	161 °C	
Elemental Analysis: Calc.: C: 57.97; H: 4.38; N: 6.76; found: C: 57.91; H: 4.43; N: 6.83				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	3.84	3	s	
	6.57	1	d	14.8
	7.67-7.74	3	m	
	8.27	2	d	8.8
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 52.2, 122.0, 124.1, 128.6, 140.4, 141.8, 148.4, 166.4				
GC-EIMS (m/z, %): 50 (26), 51 (22), 63 (21), 74 (19), 75 (22), 76 (38), 89 (22), 90 (31), 102 (61), 118 (26), 130 (38), 176 (100), 207 (M <sup>+</sup> , 57)				

Chem. Name	(E)-ethyl 3-(4-nitrophenyl) acrylate (3g)			
Lit. Ref.	J. Org. Chem., <b>2006</b> , 71, 4339-4342			
<div><p>1d + 2b (1.2 eq.) <math>\xrightarrow[\text{GVL (1M), 150 }^{\circ}\text{C, 1 h}]{\text{Pd/C (0.1 mol\%), TEA (1 eq.)}}</math> 3g</p><p>Molecular Weight: 221</p></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene ( <b>1d</b> ) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and ethyl acrylate ( <b>2b</b> ) (240 mg, 0.264 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3g</b> was obtained as a slightly yellow solid (380 mg, 86% yield).				
Mol Formula	C <sub>11</sub> H <sub>11</sub> NO <sub>4</sub>	m.p.	135 °C	
Elemental Analysis: Calc.: C: 59.73; H: 5.01; N: 6.33; found: C: 59.81; H: 5.10; N: 6.24				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	1.35	3	<i>t</i>	7.0
	4.29	2	<i>q</i>	7.0
	6.56	1	<i>d</i>	16
	7.66-7.72	3	<i>m</i>	
	8.25	2	<i>d</i>	8.8
<sup>13</sup> C NMR (100.6 MHz, DMSO) δ : 14.5, 60.8, 122.8, 124.3, 129.8, 140.8, 142.2, 148.4, 166.0				
GC-EIMS (m/z, %): 50 (17), 51 (16), 75 (19), 76 (35), 102 (60), 130 (47), 176 (100), 193 (46), 221 (M <sup>+</sup> , 22)				

Chem. Name	(E)-butyl 3-(4-nitrophenyl) acrylate (3h)
Lit. Ref.	Adv. Synth.& Cat., 2002, 344, 495-498



#### METHOD:

In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (**1d**) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and butyl acrylate (**2c**) (311 mg, 0.348 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0 °C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way **3h** was obtained as a slightly yellow solid (408 mg, 82% yield).

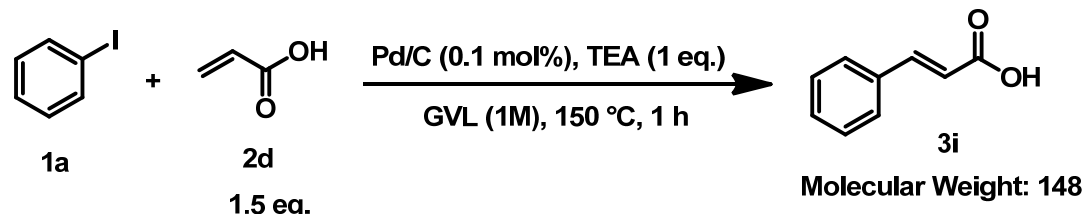
Mol Formula	C <sub>13</sub> H <sub>15</sub> NO <sub>4</sub>	m.p.	64-65 °C
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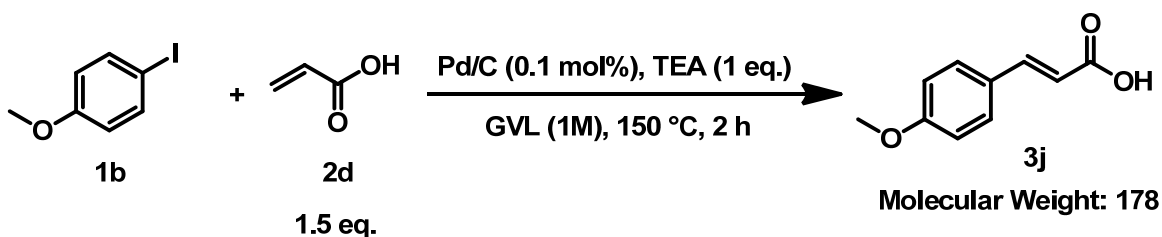
**Elemental Analysis:** Calc.: C: 62.64; H: 6.07; N: 5.62; found: C: 62.72; H: 6.12; N: 5.68

<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	0.939	3	<i>t</i>	7.4
	1.37-1.46	2	<i>m</i>	
	1.64-1.71	2	<i>m</i>	
	4.21	2	<i>t</i>	6.6
	6.54	1	<i>d</i>	16
	7.64-7.69	3	<i>m</i>	
	8.21	2	<i>d</i>	8.0

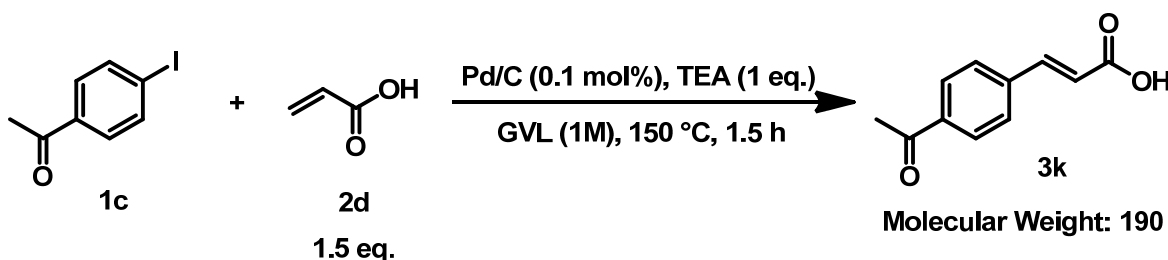
<sup>13</sup>C NMR (100.6 MHz, DMSO) δ : 14.5, 60.8, 122.8, 124.3, 129.8, 140.8, 142.2, 148.4, 166.0

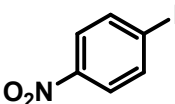
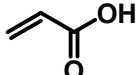
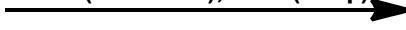
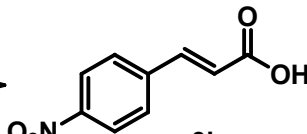
GC-EIMS (m/z, %): 56 (47), 76 (29), 90 (21), 102 (66), 130 (38), 176 (100), 177 (21), 193 (39), 194 (48)

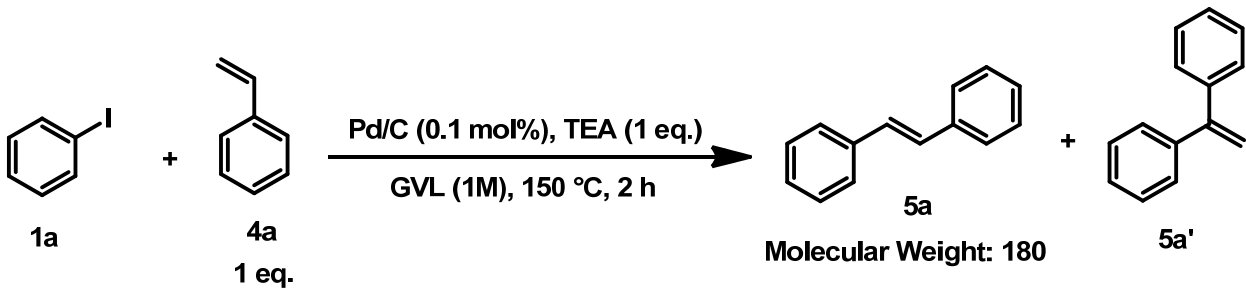
Chem. Name	Cinnamic Acid (3i)			
Lit. Ref.	J. Org. Chem. 2004, 69, 8805-8807			
<div><div><div><div><div></div></div><div><div>1a</div><div>2d</div><div>1.5 eq.</div></div><div><div>3i</div><div>Molecular Weight: 148</div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene ( <b>1a</b> ) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid ( <b>2d</b> ) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3i</b> was obtained as a white solid (249 mg, 84% yield).				
Mol Formula	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	m.p.	132-135 °C	
Elemental Analysis: Calc.: C: 72.96; H: 5.44; found: C: 73.04; H: 5.38				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	6.57	1	<i>d</i>	16
	7.45-7.46	3	<i>m</i>	
	7.63	1	<i>d</i>	16
	7.72-7.74	2	<i>m</i>	
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 117.2, 128.3, 128.9, 130.7, 133.9, 147.0, 128.8, 172.4				
GC-EIMS (m/z, %): 43 (22), 45 (21), 50 (29), 51 (45), 77 (65), 91 (37), 102 (40), 103 (66), 131 (32), 147 (100), 148 (67), 207 (M <sup>+</sup> , 15)				

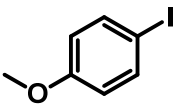
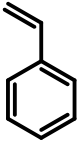
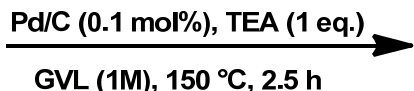
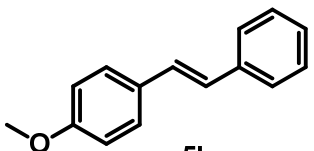
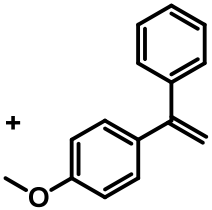
Chem. Name	(E)-3-(4-methoxyphenyl)acrylic acid ( <b>3j</b> )			
Lit. Ref.	J. Org. Chem., <b>2004</b> , 69, 8805-8807			
<div></div> <p>Reaction scheme showing the synthesis of <b>3j</b> from <b>1b</b> and <b>2d</b> using Pd/C (0.1 mol%), TEA (1 eq.) in GVL (1M) at 150 °C for 2 h. The molecular weight of <b>3j</b> is 178.</p>				
<b>METHOD:</b> In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole ( <b>1b</b> ) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid ( <b>2d</b> ) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3j</b> was obtained as a white solid (285 mg, 80 % yield).				
Mol Formula	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	m.p.	172-173 °C	
<b>Elemental Analysis:</b> Calc.: C: 67.41; H: 5.66; found: C: 67.34; H: 5.45				
<sup>1</sup> H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz
	3.83	3	s	
	6.41	1	d	16
	7.01	2	d	8.4
	7.58	1	d	16
	7.68	2	d	8.4
<sup>13</sup> C NMR (100.6 MHz, DMSO) δ : 55.7, 114.7, 116.8, 127.1, 130.3, 144.1, 161.3, 168.2				
<b>GC-EIMS (m/z, %):</b> 63 (20), 77 (31), 79 (16), 89 (30), 90 (15), 132 (22), 133 (26), 161 (44), 177 (26), 178 (M <sup>+</sup> , 100)				

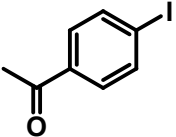
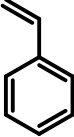
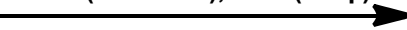
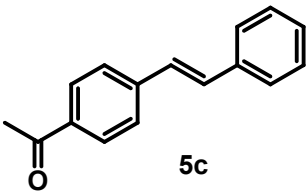
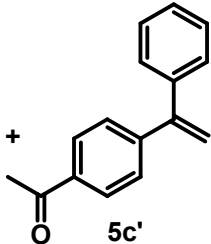


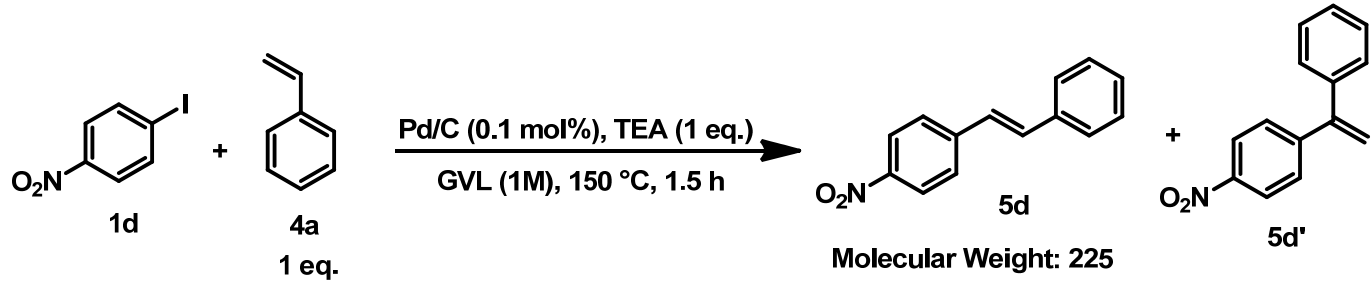
Chem. Name	(E)-methyl 3-(4-acetylphenyl) acrylic acid (3k)			
Lit. Ref.	J. Org. Chem., <b>2004</b> , 69, 8805-8807			
<div></div> <p>1c + 2d (1.5 eq.) <math>\xrightarrow[\text{GVL (1M), 150 }^{\circ}\text{C, 1.5 h}]{\text{Pd/C (0.1 mol\%), TEA (1 eq.)}}</math> 3k</p> <p>Molecular Weight: 190</p>				
<p><b>METHOD:</b></p> <p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone (<b>1c</b>) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (<b>2d</b>) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3k</b> was obtained as a yellowish solid (323 mg, 85 % yield).</p>				
Mol Formula	C <sub>11</sub> H <sub>10</sub> O <sub>3</sub>	m.p.	224-225 °C	
<p><b>Elemental Analysis:</b> Calc.: C: 69.46; H: 5.30; found: C: 69.51; H: 5.22</p>				
<sup>1</sup> H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz
	2.59	3	s	
	6.67	1	d	16
	7.64	1	s	16
	77.83	2	d	8
	7.96	2	d	8.4
<p><b><sup>13</sup>C NMR (100.6 MHz, DMSO) δ :</b> 27.2, 122.1, 128.8, 129.0, 137.9, 138.9, 142.9, 167.7, 197.8</p>				
<p><b>GC-EIMS (m/z, %):</b> Not performed</p>				

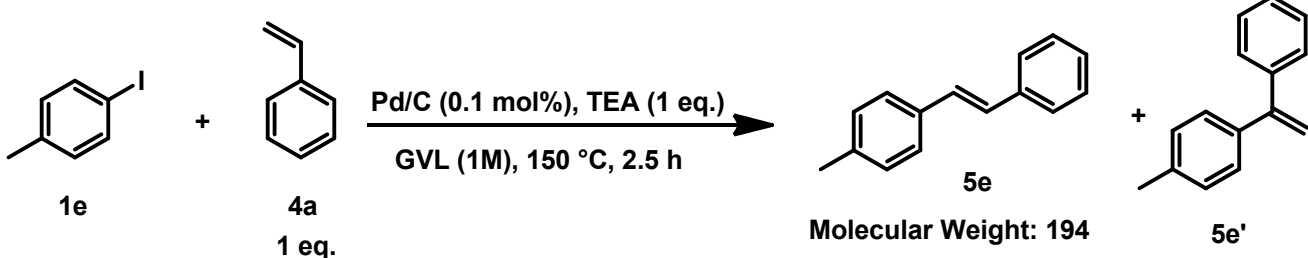
Chem. Name	(E)-3-(4-nitrophenyl) acrylic acid ( <b>3I</b> )																																															
Lit. Ref.	J. Org. Chem., <b>2004</b> , 69, 8805-8807																																															
<div><div><div><div><div></div><div>1d</div></div><div><div></div><div>2d</div></div></div><div><div>+</div><div>1.5 eq.</div></div><div><div><div><div><div></div><div><div>Pd/C (0.1 mol%), TEA (1 eq.)</div><div>GVL (1M), 150 °C, 1 h</div></div></div><div><div></div><div>3I</div></div><div>Molecular Weight: 193</div></div></div></div><tr><td colspan="4">METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene (<b>1d</b>) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid (<b>2d</b>) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3I</b> was obtained as a yellowish solid (320 mg, 83% yield).</td></tr><tr><td>Mol Formula</td><td>C<sub>9</sub>H<sub>7</sub>NO<sub>4</sub></td><td>m.p.</td><td>286-287 °C</td></tr><tr><td colspan="4">Elemental Analysis: Calc.: C: 55.96; H: 3.65; N: 7.25; found: C: 55.89; H: 3.61; N: 7.29</td></tr><tr><td rowspan="6"><sup>1</sup>H NMR 400 MHz DMSO</td><td>δ value</td><td>No. H</td><td>Mult.</td><td>j value/Hz</td></tr><tr><td>6.76-6.84</td><td>1</td><td><i>m</i></td><td></td></tr><tr><td>7.71-7.77</td><td>1</td><td><i>m</i></td><td></td></tr><tr><td>7.67-7.74</td><td>3</td><td><i>m</i></td><td></td></tr><tr><td>7.97</td><td>2</td><td><i>d</i></td><td>8.4</td></tr><tr><td>8.23</td><td>2</td><td><i>d</i></td><td>8.4</td></tr><tr><td colspan="4"><sup>13</sup>C NMR (100.6 MHz, DMSO) δ : 124.0, 124.3, 129.7, 141.1, 141.7, 148.4, 167.4</td></tr><tr><td colspan="4">GC-EIMS (m/z, %): Not performed</td></tr></div></div>				METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene ( <b>1d</b> ) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid ( <b>2d</b> ) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3I</b> was obtained as a yellowish solid (320 mg, 83% yield).				Mol Formula	C <sub>9</sub> H <sub>7</sub> NO <sub>4</sub>	m.p.	286-287 °C	Elemental Analysis: Calc.: C: 55.96; H: 3.65; N: 7.25; found: C: 55.89; H: 3.61; N: 7.29				<sup>1</sup> H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz	6.76-6.84	1	<i>m</i>		7.71-7.77	1	<i>m</i>		7.67-7.74	3	<i>m</i>		7.97	2	<i>d</i>	8.4	8.23	2	<i>d</i>	8.4	<sup>13</sup> C NMR (100.6 MHz, DMSO) δ : 124.0, 124.3, 129.7, 141.1, 141.7, 148.4, 167.4				GC-EIMS (m/z, %): Not performed			
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene ( <b>1d</b> ) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and acrylic acid ( <b>2d</b> ) (216 mg, 0.206 mL, 3 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1 hour the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way <b>3I</b> was obtained as a yellowish solid (320 mg, 83% yield).																																																
Mol Formula	C <sub>9</sub> H <sub>7</sub> NO <sub>4</sub>	m.p.	286-287 °C																																													
Elemental Analysis: Calc.: C: 55.96; H: 3.65; N: 7.25; found: C: 55.89; H: 3.61; N: 7.29																																																
<sup>1</sup> H NMR 400 MHz DMSO	δ value	No. H	Mult.	j value/Hz																																												
	6.76-6.84	1	<i>m</i>																																													
	7.71-7.77	1	<i>m</i>																																													
	7.67-7.74	3	<i>m</i>																																													
	7.97	2	<i>d</i>	8.4																																												
	8.23	2	<i>d</i>	8.4																																												
<sup>13</sup> C NMR (100.6 MHz, DMSO) δ : 124.0, 124.3, 129.7, 141.1, 141.7, 148.4, 167.4																																																
GC-EIMS (m/z, %): Not performed																																																

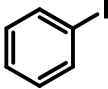
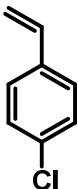
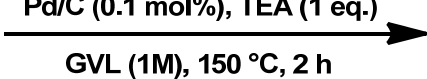
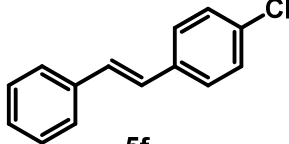
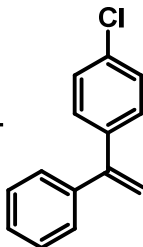
Chem. Name	(E)-1,2-diphenylethene (5a)			
Lit. Ref.	J. Org. Chem., 2006, 71, 4339-4342			
<div><p>1a + 4a (1 eq.) <math>\xrightarrow[\text{GVL (1M), 150 }^{\circ}\text{C, 2 h}]{\text{Pd/C (0.1 mol\%), TEA (1 eq.)}}</math> 5a + 5a'</p><p>Molecular Weight: 180</p></div>				
<p><b>METHOD:</b></p> <p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene (<b>1a</b>) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene (<b>4a</b>) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 94:6 mixture of <b>5a</b> and <b>5a'</b> (295 mg, 83% yield).</p>				
Mol Formula	C <sub>14</sub> H <sub>12</sub>	m.p.	126-127 °C	
<p><b>Elemental Analysis:</b> Calc.: C: 93.29; H: 6.71; found: 93.38; H: 6.61</p>				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	J value/Hz
	7.13	2	s	
	7.28-7.30	2	m	
	7.36-7.40	4	m	
	7.53-7.55	4	m	
<p><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 126.6, 127.7, 128.8, 137.4</p>				
<p><b>GC-EIMS (m/z, %):</b> 89 (15), 152 (17), 165 (52), 178 (64), 179 (99), 180 (M<sup>+</sup>, 100), 181 (14)</p>				

Chem. Name	(E)-1-methoxy-4-styrylbenzene ( <b>5b</b> )			
Lit. Ref.	Adv. Synth. & Cat., <b>2008</b> , 350, 2551-2558			
<div><div><div><div><div></div><div>1b</div></div><div>+</div><div><div><div><div></div><div>4a</div></div><div>1 eq.</div></div></div><div><div><div><div></div></div></div><div><div><div><div></div><div>5b</div></div><div>+</div><div><div><div><div></div><div>5b'</div></div></div></div><div>Molecular Weight: 210</div></div></div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole ( <b>1b</b> ) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene ( <b>4a</b> ) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 95:5 mixture of <b>5b</b> and <b>5b'</b> (344 mg, 82% yield).				
Mol Formula	C <sub>15</sub> H <sub>14</sub>	m.p.	138 °C	
Elemental Analysis: Calc.: C: 85.68; H: 6.71; found: C: 85.71; H: 6.65				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	3.84	3	s	
	6.90-7.09	4	m	
	7.22-7.24	2	m	
	7.33-7.37	2	m	
	7.45-7.50	4	m	
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 55.2, 114.6, 126.2, 126.5, 127.1, 127.6, 128.1, 128.5, 130.1, 137.6, 159.2				
GC-EIMS (m/z, %): 152 (33), 165 (51), 166 (19), 167 (38), 179 (16), 195 (29), 209 (27), 210 (M <sup>+</sup> , 100), 211 (25)				

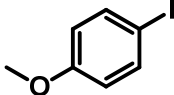
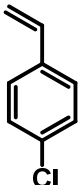
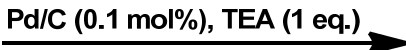
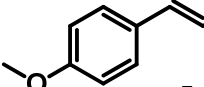
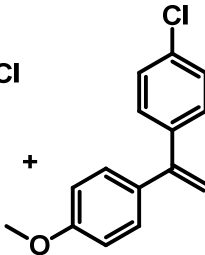
Chem. Name	(E)-1-(4-styrylphenyl) ethanone ( <b>5c</b> )			
Lit. Ref.	Eur. J. Org. Chem., <b>2007</b> , 13, 2197-2201			
<div><div><div><div><div></div><div>1c</div></div><div><div></div><div>4a 1 eq.</div></div></div><div><div><div><div></div><div>Molecular Weight: 222</div></div><div><div></div><div>5c</div></div><div><div></div><div>5c'</div></div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone ( <b>1c</b> ) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene ( <b>4a</b> ) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 99:1 mixture of <b>5c</b> and <b>5c'</b> (382 mg, 86% yield).				
Mol Formula	C <sub>15</sub> H <sub>14</sub>	m.p.	140-144 °C	
Elemental Analysis: Calc.: C: 86.45; H: 6.35; found: C: 86.39; H: 6.31				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	2.61	3	s	
	7.12-7.22	2	m	
	7.33-7.29	1	m	
	7.37-7.41	2	m	
	7.54-7.60	4	m	
	7.96	2	d	8
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 26.6, 126.4, 126.7, 127.3, 128.3, 128.7, 128.8, 131.4, 135.8, 136.6, 141.9, 197.5				
GC-EIMS (m/z, %): 152 (18), 176 (15), 178 (70), 179 (24), 207 (100), 208 (17), 222 (M <sup>+</sup> , 64)				

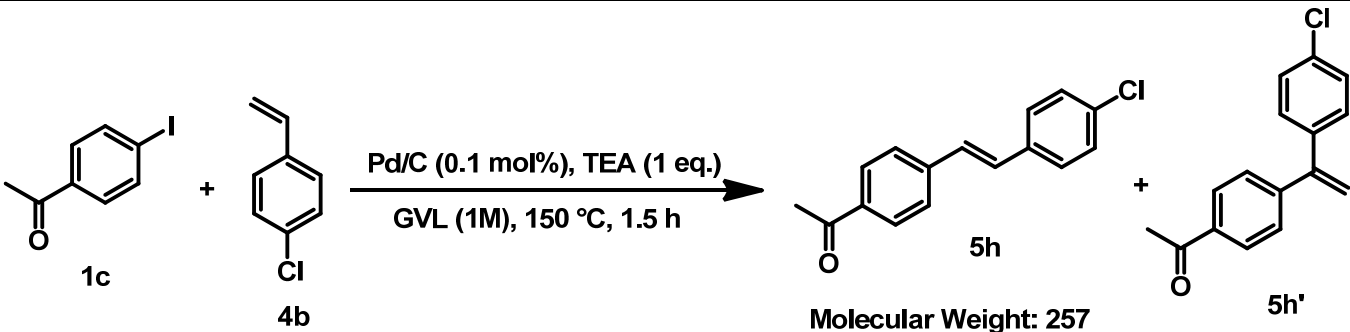
Chem. Name	(E)-1-nitro-4-styrylbenzene (5d)			
Lit. Ref.	Eur. J. Org. Chem., 2007, 13, 2197-2201			
				
<b>METHOD:</b> In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodonitrobenzene ( <b>1d</b> ) (508 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene ( <b>4a</b> ) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a yellowish solid consisting in a 99:1 mixture of <b>5d</b> and <b>5d'</b> (378 mg, 84% yield).				
Mol Formula	C <sub>15</sub> H <sub>14</sub>	m.p.	158-159 °C	
<b>Elemental Analysis:</b> Calc.: C: 74.65; H: 4.92; N: 6.22; found: C: 74.72; H: 4.87; N: 6.28				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	7.15	1	<i>d</i>	16.4
	7.30-7.44	4	<i>m</i>	
	7.56-7.65	4	<i>m</i>	
	8.23	2	<i>d</i>	8.4
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 124.1, 126.2, 126.8, 127.0, 128.8, 133.2, 136.1, 143.8, 146.6				
GC-EIMS (m/z, %): 151 (14), 152 (36), 165 (18), 176 (20), 177 (19), 178 (100), 179 (36), 225 (M <sup>+</sup> , 70)				

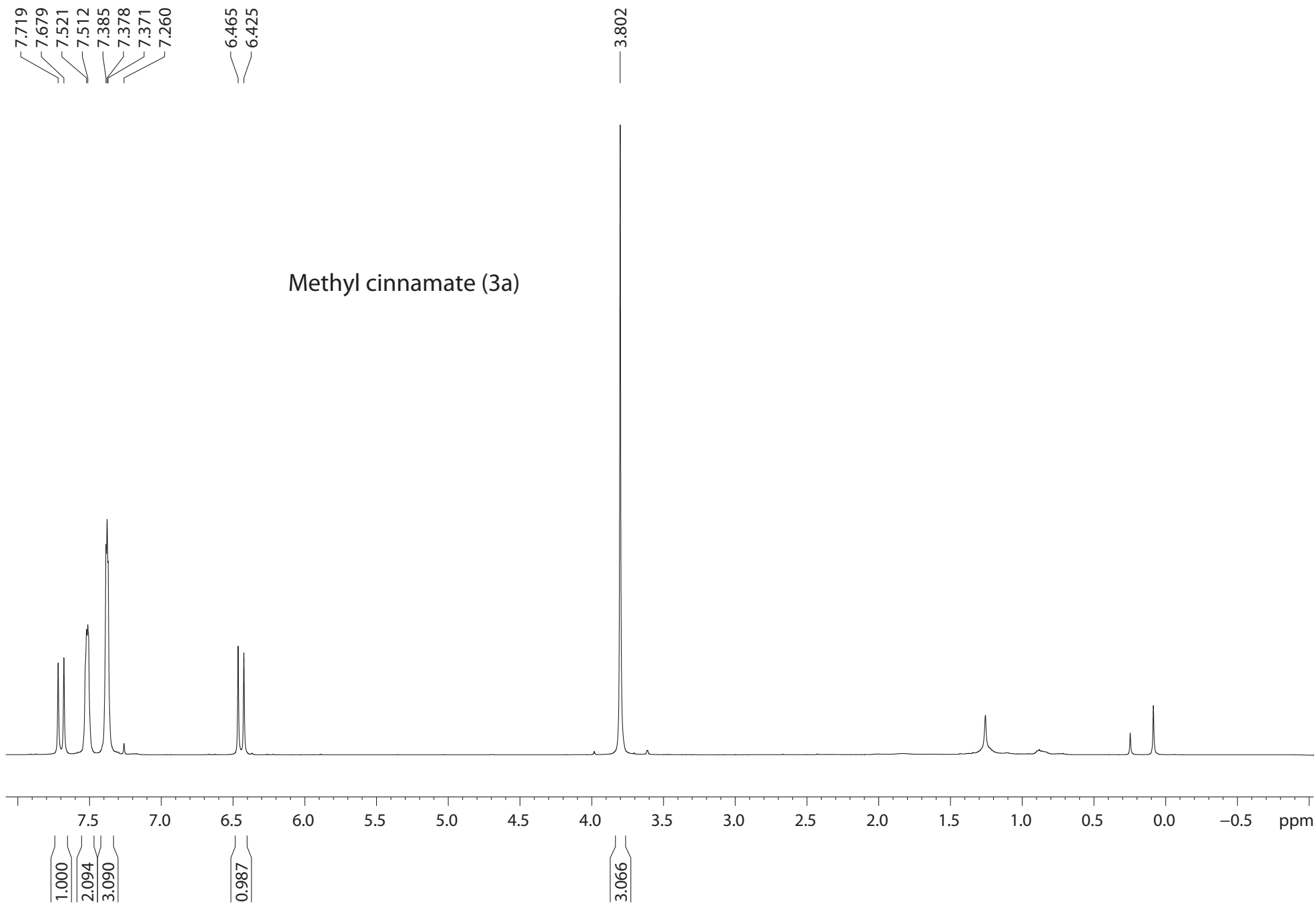
Chem. Name	(E)-1-methyl-4-styrylbenzene ( <b>5e</b> )			
Lit. Ref.	Tetrahedron, <b>2013</b> , 69, 7925-7930			
<div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodotoluene ( <b>1e</b> ) (440 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and styrene ( <b>4a</b> ) (206 mg, 0.228 mL, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this way a white solid consisting in a 94:6 mixture of <b>5e</b> and <b>5e'</b> (322 mg, 83% yield).				
Mol Formula	C <sub>15</sub> H <sub>14</sub>	m.p.	124 °C	
Elemental Analysis: Calc.: C: 85.68; H: 6.71; found: C: 85.71; H: 6.65				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	2.36	3	s	
	7.07-7.08	2	m	
	7.16-7.18	2	m	
	7.23-7.25	1	m	
	7.33-7.37	2	m	
	7.41-7.43	2	m	
	7.50-7.52	2	m	
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 21.4, 126.5, 126.6, 127.5, 127.8, 128.7, 128.8, 129.5, 134.6, 137.6, 137.7				
GC-EIMS (m/z, %): 89 (12), 115 (23), 152 (15), 165 (18), 178 (82), 179 (100), 180 (16), 193 (19), 194 (M <sup>+</sup> , 94), 195 (19)				

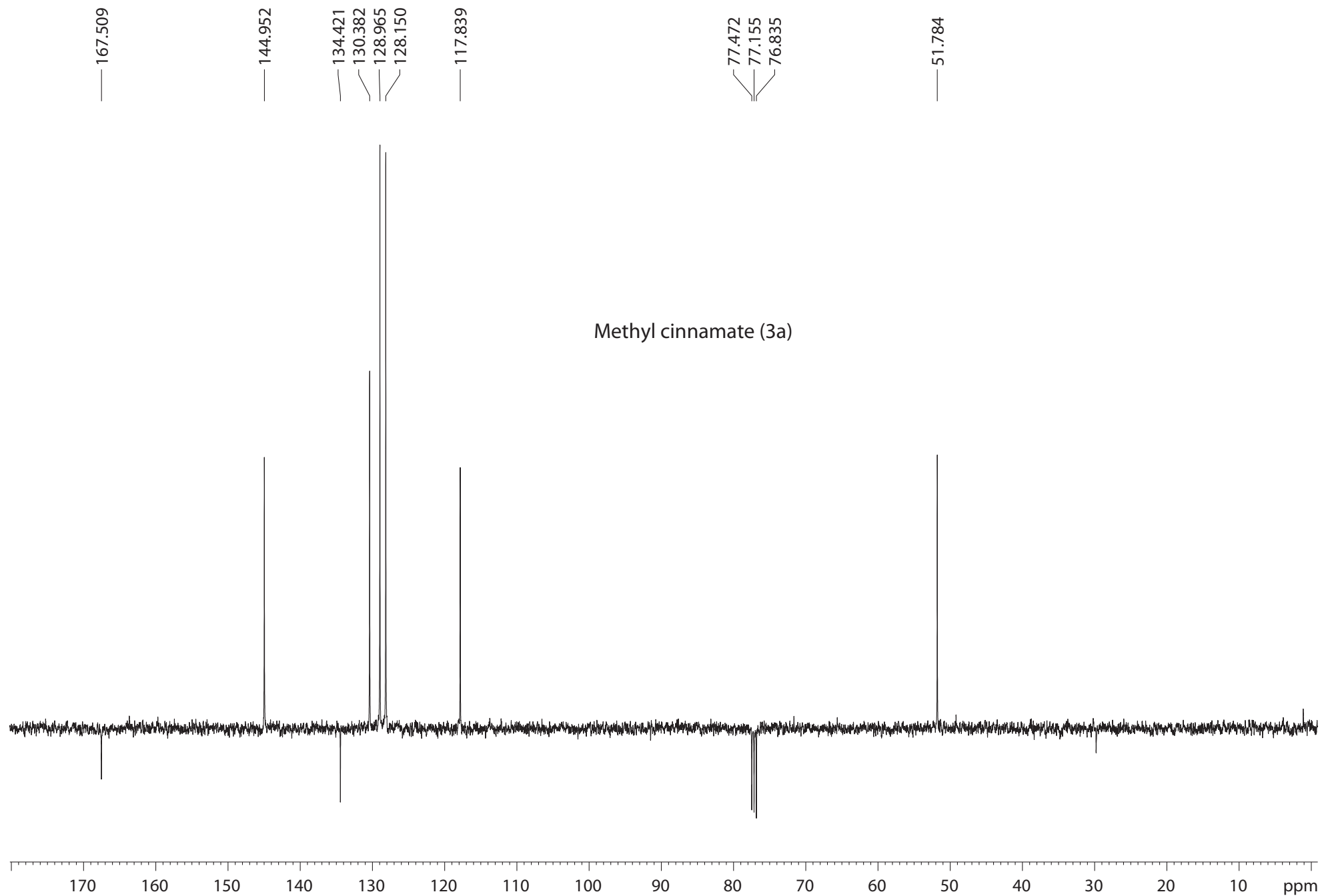
Chem. Name	(E)-1-chloro-4-styrylbenzene (5f)																												
Lit. Ref.	Green Chem., 2012, 14, 2513-2522																												
<div><div><div><div><div></div><div>1a</div></div><div><div></div><div>4b</div></div></div><div>+</div><div><div><div><div></div><div>Molecular Weight: 214</div></div><div><div></div><div>5f</div></div><div>+</div><div><div></div><div>5f'</div></div></div></div><p>METHOD:</p><p>In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), iodobenzene (<b>1a</b>) (416 mg, 0.228 mL, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and 4-chlorostyrene (<b>4b</b>) (286 mg, 0.247 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this a white solid consisting in a 92:8 mixture of <b>5f</b> and <b>5f'</b> (385 mg, 90% yield).</p><table><tr><td>Mol Formula</td><td>C<sub>14</sub>H<sub>11</sub>Cl</td><td>m.p.</td><td>127-129°C</td></tr></table><p>Elemental Analysis: Calc.: C: 78.32; H: 5.16; found: 78.64; H: 5.08.</p><table><tr><td rowspan="5"><sup>1</sup>H NMR 400 MHz CDCl<sub>3</sub></td><td>δ value</td><td>No. H</td><td>Mult.</td><td>J value/Hz</td></tr><tr><td>7.07</td><td>2</td><td><i>m</i></td><td></td></tr><tr><td>7.26-7.39</td><td>5</td><td><i>m</i></td><td></td></tr><tr><td>7.44</td><td>2</td><td><i>d</i></td><td>8.4</td></tr><tr><td>7.51</td><td>2</td><td><i>d</i></td><td>7.6</td></tr></table><p><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 126.7, 127.5, 127.8, 128.0, 128.9, 129.0, 129.4, 133.3, 135.9, 137.1</p><p>GC-EIMS (m/z, %): 50 (17), 51 (21), 63 (18), 75 (20), 76 (27), 89 (24), 152 (17), 176 (24), 178 (100), 179 (94), 214 (70), 216 (23).</p></div></div>					Mol Formula	C <sub>14</sub> H <sub>11</sub> Cl	m.p.	127-129°C	<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	J value/Hz	7.07	2	<i>m</i>		7.26-7.39	5	<i>m</i>		7.44	2	<i>d</i>	8.4	7.51	2	<i>d</i>	7.6
Mol Formula	C <sub>14</sub> H <sub>11</sub> Cl	m.p.	127-129°C																										
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	J value/Hz																									
	7.07	2	<i>m</i>																										
	7.26-7.39	5	<i>m</i>																										
	7.44	2	<i>d</i>	8.4																									
	7.51	2	<i>d</i>	7.6																									

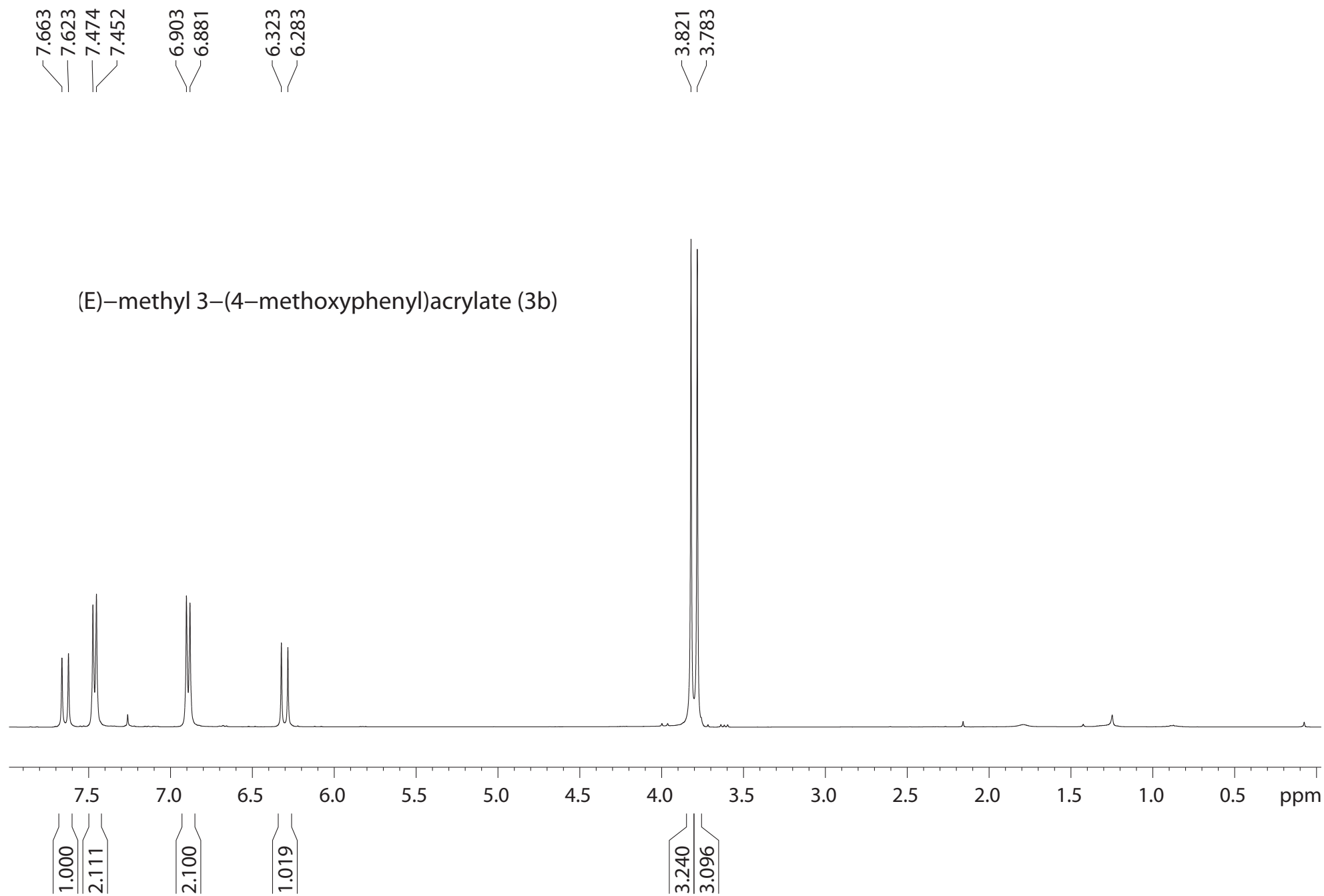


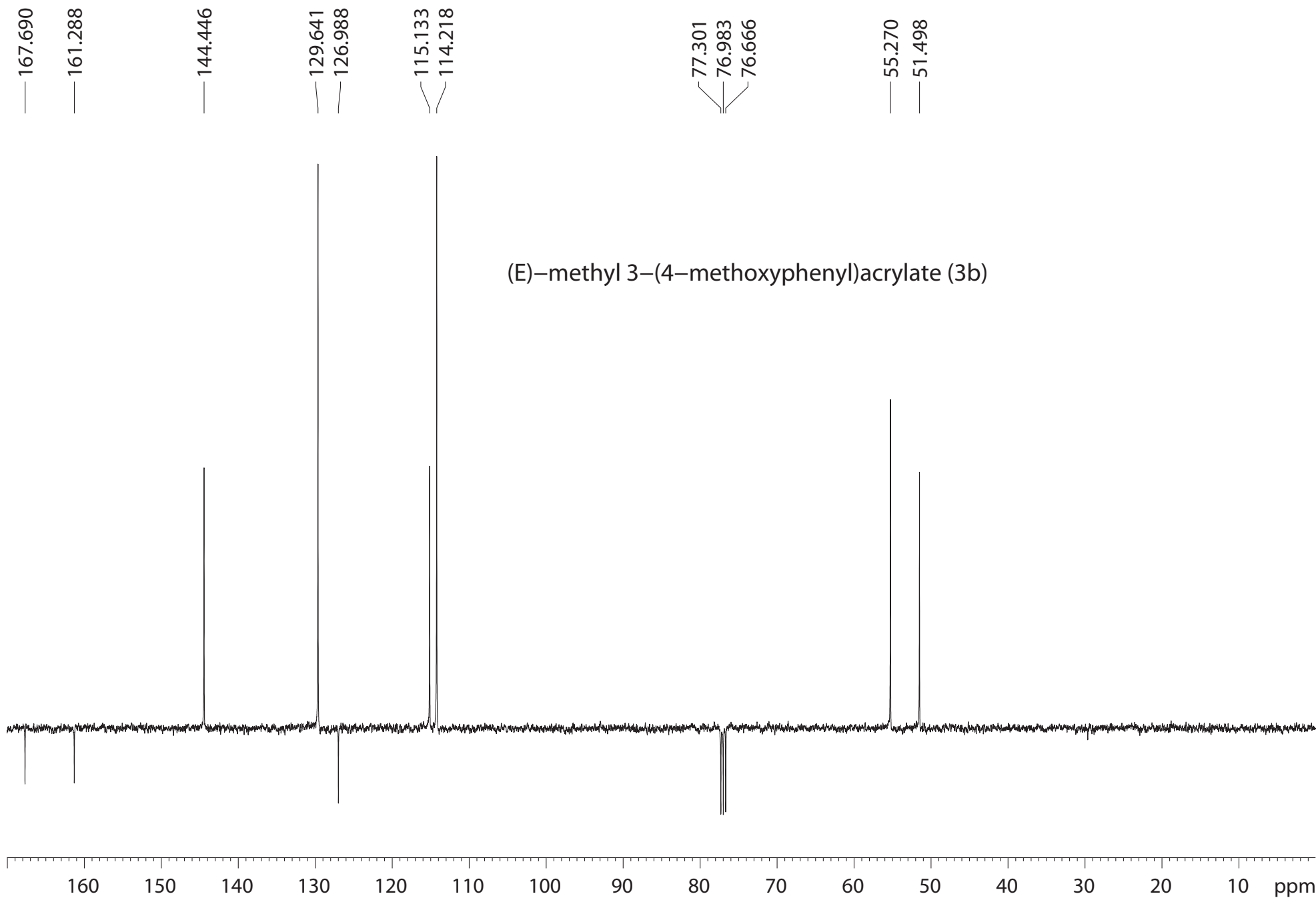
Chem. Name	(E)-1-chloro-4-(4-methoxystyryl)benzene ( <b>5g</b> )			
Lit. Ref.	J. Mol. Cat. A: Chem., <b>2006</b> , 254, 58-63			
<div><div><div><div><div></div><div>1b</div></div><div><div></div><div>4b 1 eq.</div></div><div><div><div><div></div><div><div><div><div></div><div>5g</div></div><div><div></div><div>5g'</div></div></div><div>Molecular Weight: 245</div></div></div></div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoanisole ( <b>1b</b> ) (478 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and 4-chlorostyrene ( <b>4b</b> ) (286 mg, 0.247 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 2.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this a white solid consisting in a 90:10 mixture of <b>5g</b> and <b>5g'</b> ( 441 mg, 90% yield).				
Mol Formula	C <sub>15</sub> H <sub>13</sub> ClO	m.p.	193-194°C	
Elemental Analysis: Calc.: C: 73.62; H: 5.35; found: 74.01; H: 5.37.				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	J value/Hz
	3.84	3	s	
	6.89-6.94	3	m	
	7.03	1	d	16.4
	7.30-7.32	2	m	
	7.40-7.46	4	m	
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 55.4, 114.3, 125.3, 127.5, 127.9, 128.9, 129.8, 132.8, 136.2, 159.5				
GC-EIMS (m/z, %): 165 (91), 166 (54), 229 (20), 244 (100), 245 (17), 246 (34)				

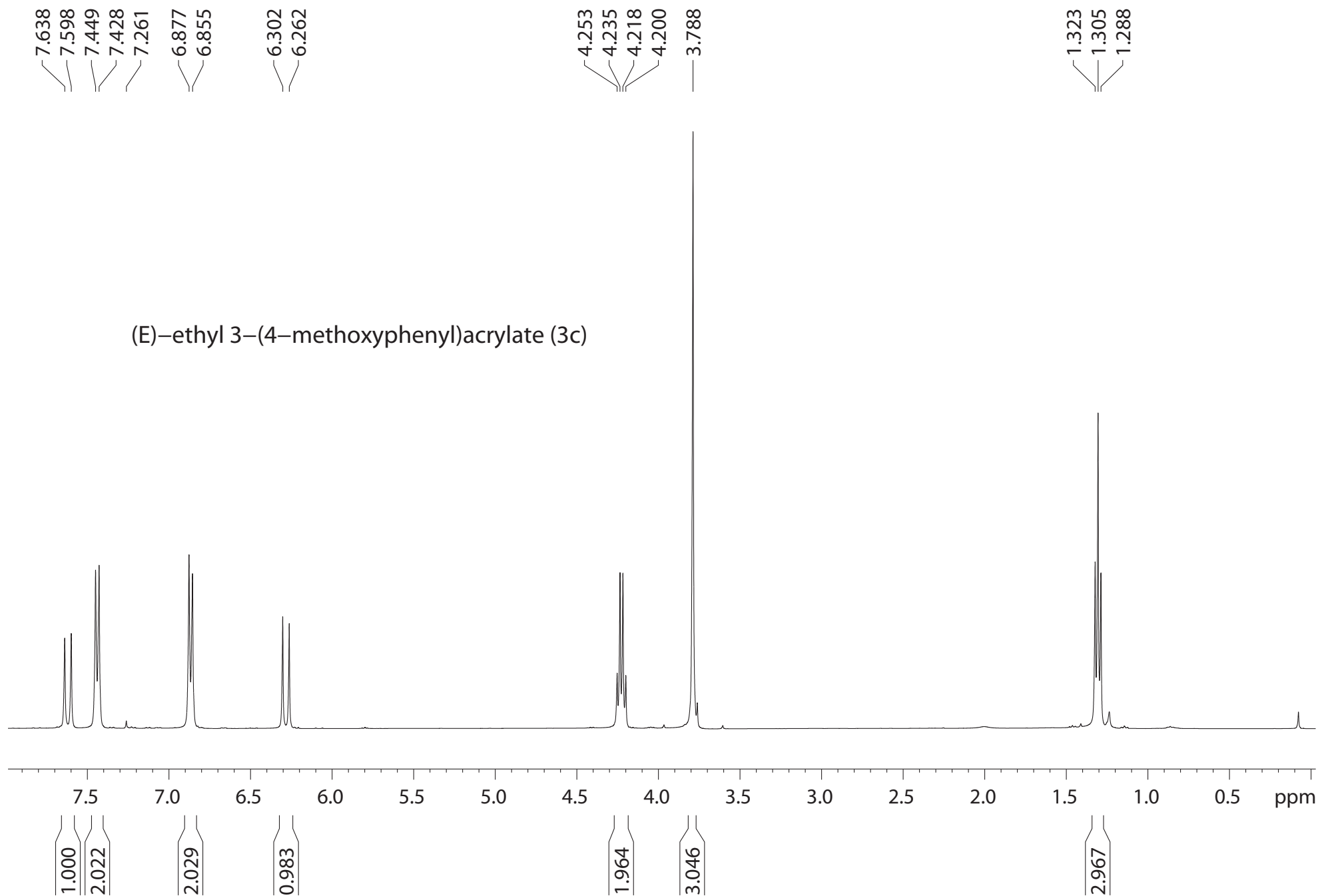
Chem. Name	(E)-1-(4-(4-chlorostyryl)phenyl)ethanone (5h)			
Lit. Ref.	Tetrahedron Lett., 2012, 53, 5961-5965			
<div><div><div><div><div><div></div></div></div><div><div>1c</div><div>4b</div><div>5h</div><div>5h'</div><div>Molecular Weight: 257</div></div></div></div></div>				
METHOD: In a screw capped vial equipped with a magnetic stirrer Pd/C 10 wt% (2.1 mg, 0.002 mmol, 0.1 mol%), GVL (2 mL), 4-iodoacetophenone ( <b>1c</b> ) (502 mg, 2 mmol), triethylamine (202 mg, 0.279 mL, 2 mmol) and 4-chlorostyrene ( <b>4b</b> ) (286 mg, 0.247 mL, 2.4 mmol) were consecutively added and the resulting mixture was left under stirring at 150 °C. After 1.5 hours the catalyst was filtered off, 3 mL of water were added and the mixture was cooled down to 0°C, then the precipitate was filtered off and washed with 1 mL of cold water. Ultimately the obtained solid was dried on high vacuum. In this a white solid consisting in a 97:3 mixture of <b>5h</b> and <b>5h'</b> (437 mg, 85% yield).				
Mol Formula	C <sub>16</sub> H <sub>13</sub> ClO		m.p.	
Elemental Analysis: Calc.: C: 74.85; H: 5.10; found: 75.03; H: 5.12.				
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	J value/Hz
	2.61	3	s	
	7.07-7.19	2	m	
	7.34	2	d	8.4
	7.46	2	d	8.4
	7.57	2	d	8.4
	7.95	2	d	8.4
<sup>13</sup> C NMR (100.6 MHz, CDCl <sub>3</sub> ) δ : 26.7, 126.6, 128.0, 128.1, 129.0, 129.1, 130.2, 134.0, 135.3, 136.2, 141.7				
GC-EIMS (m/z, %): 43 (25), 176 (29), 177 (18), 178 (56), 241 (100), 243 (36), 256 (74), 258 (24).				

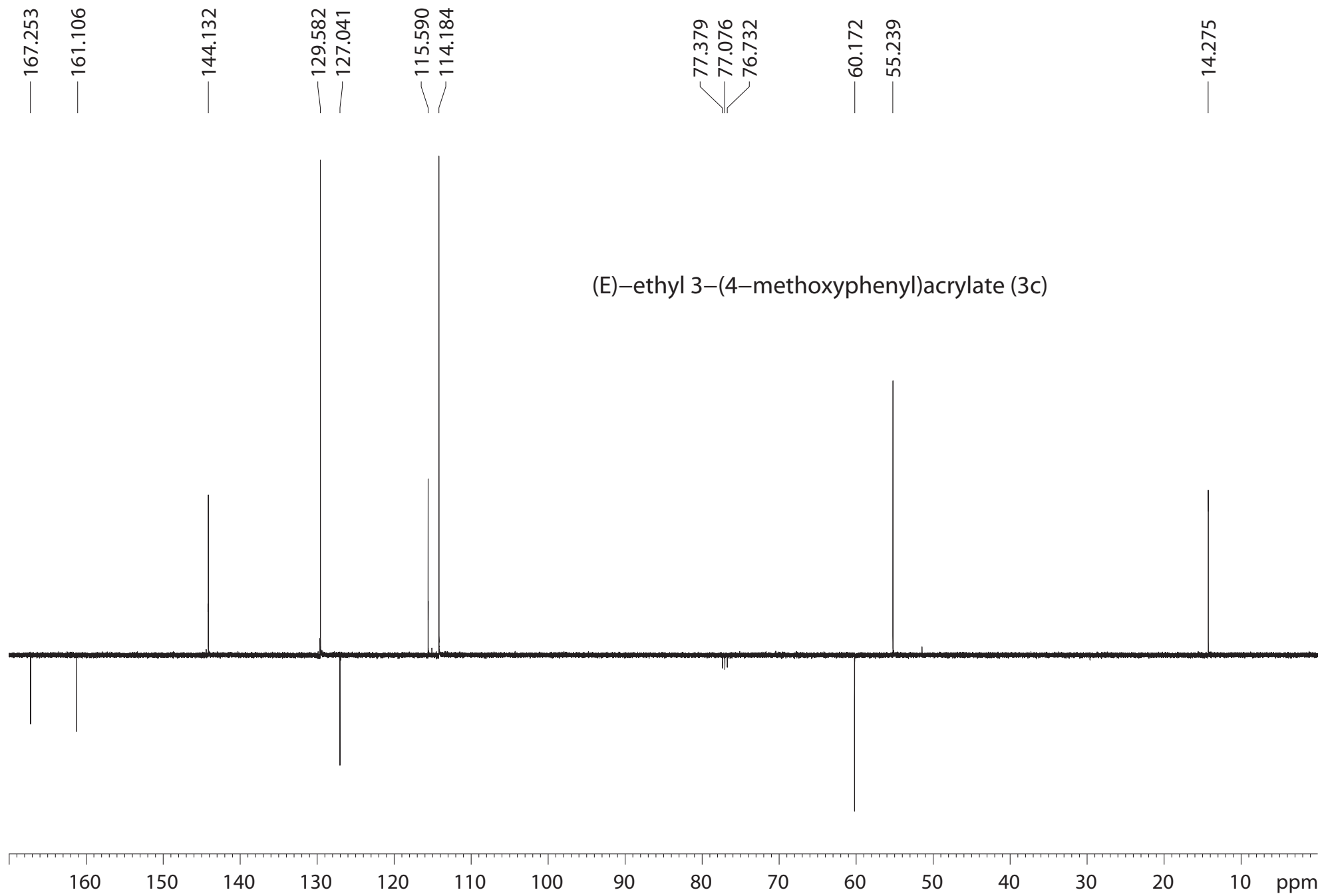




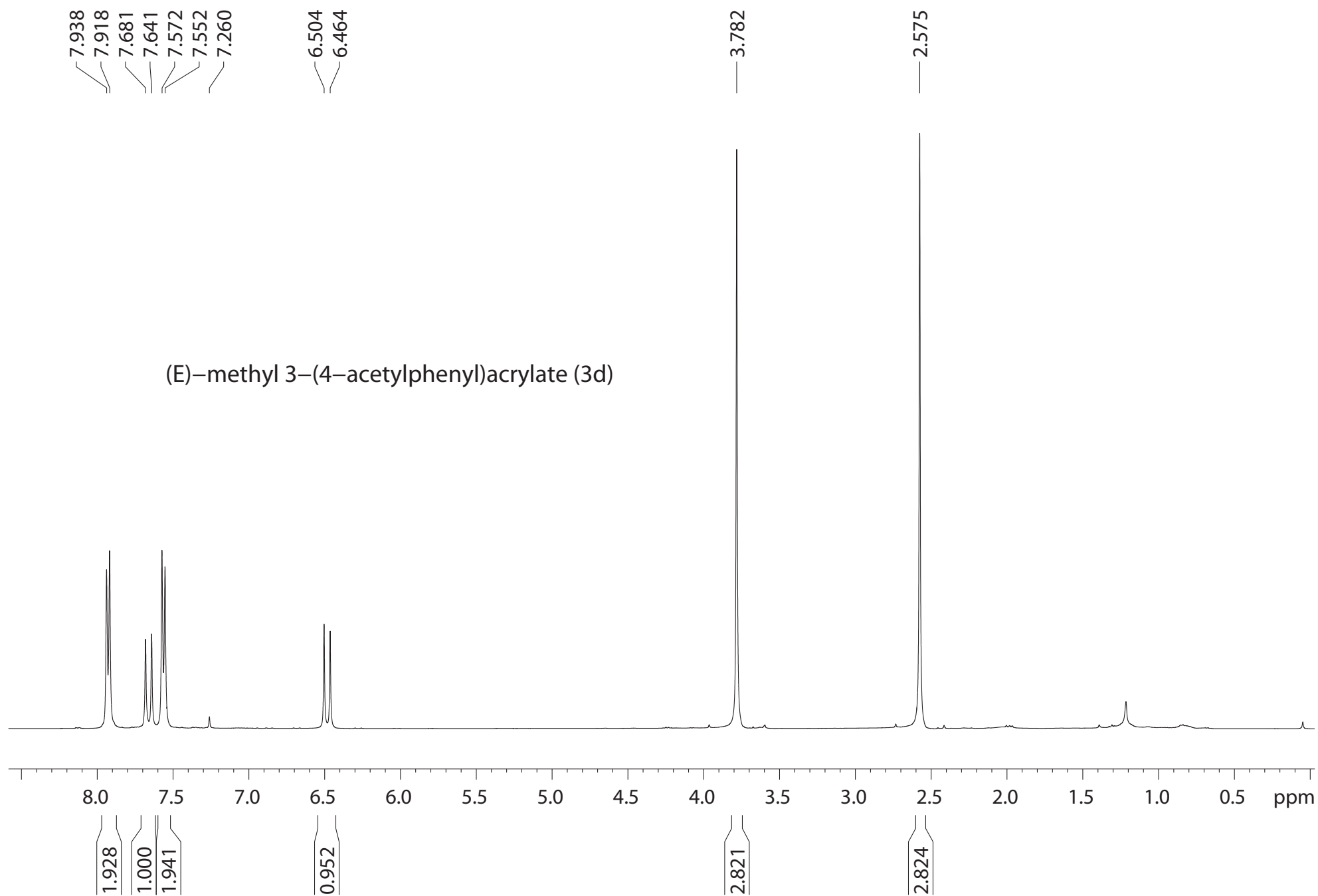


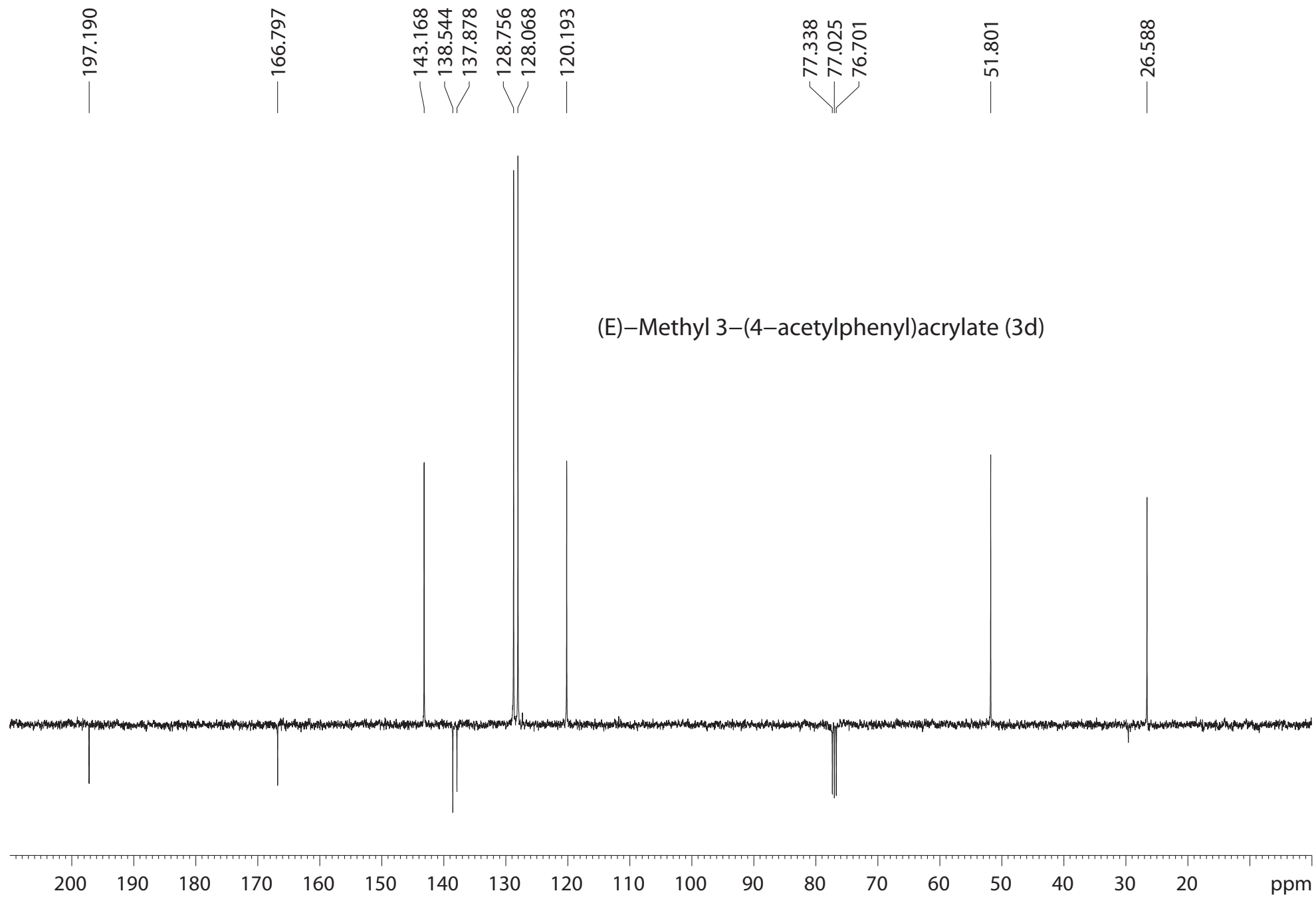


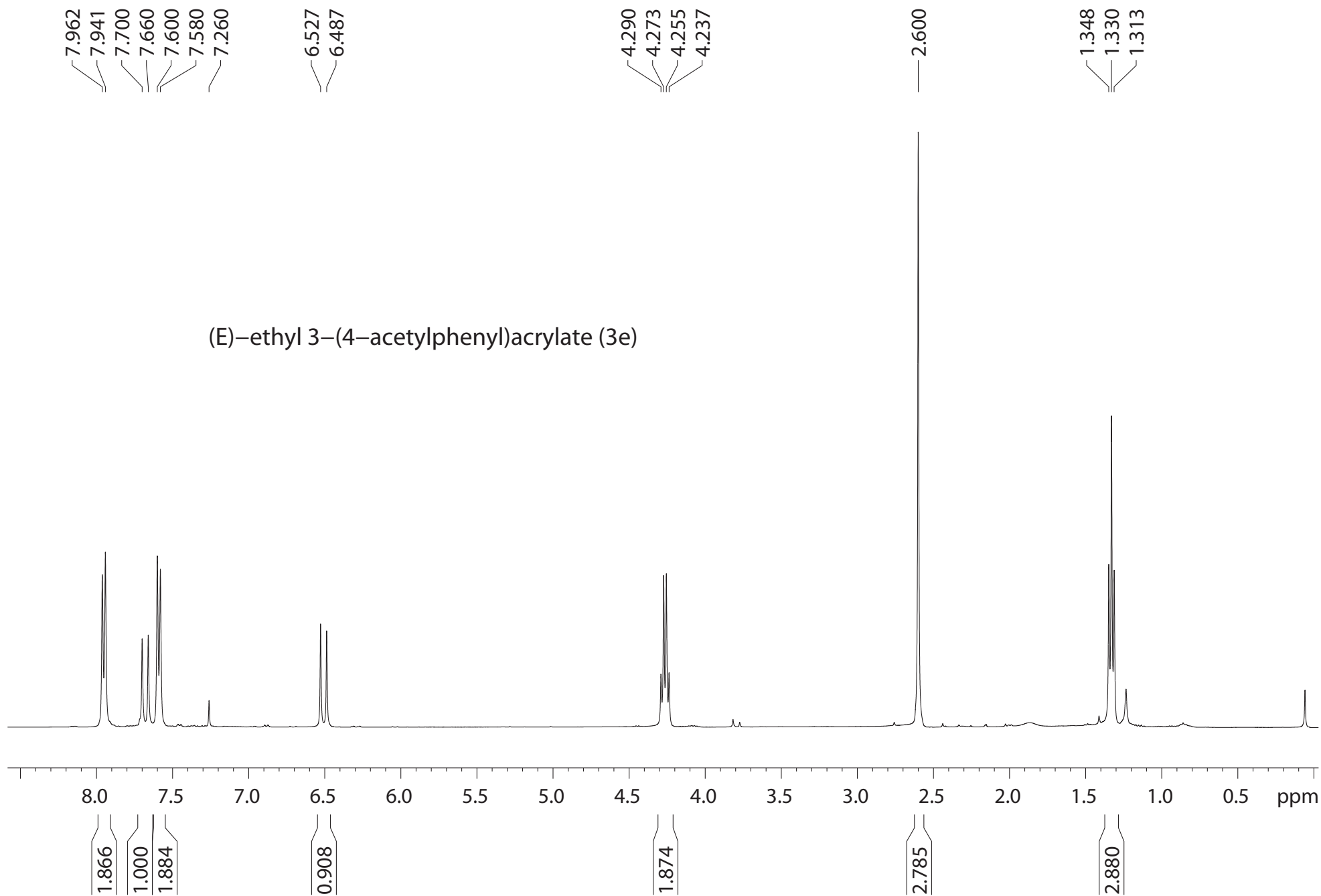


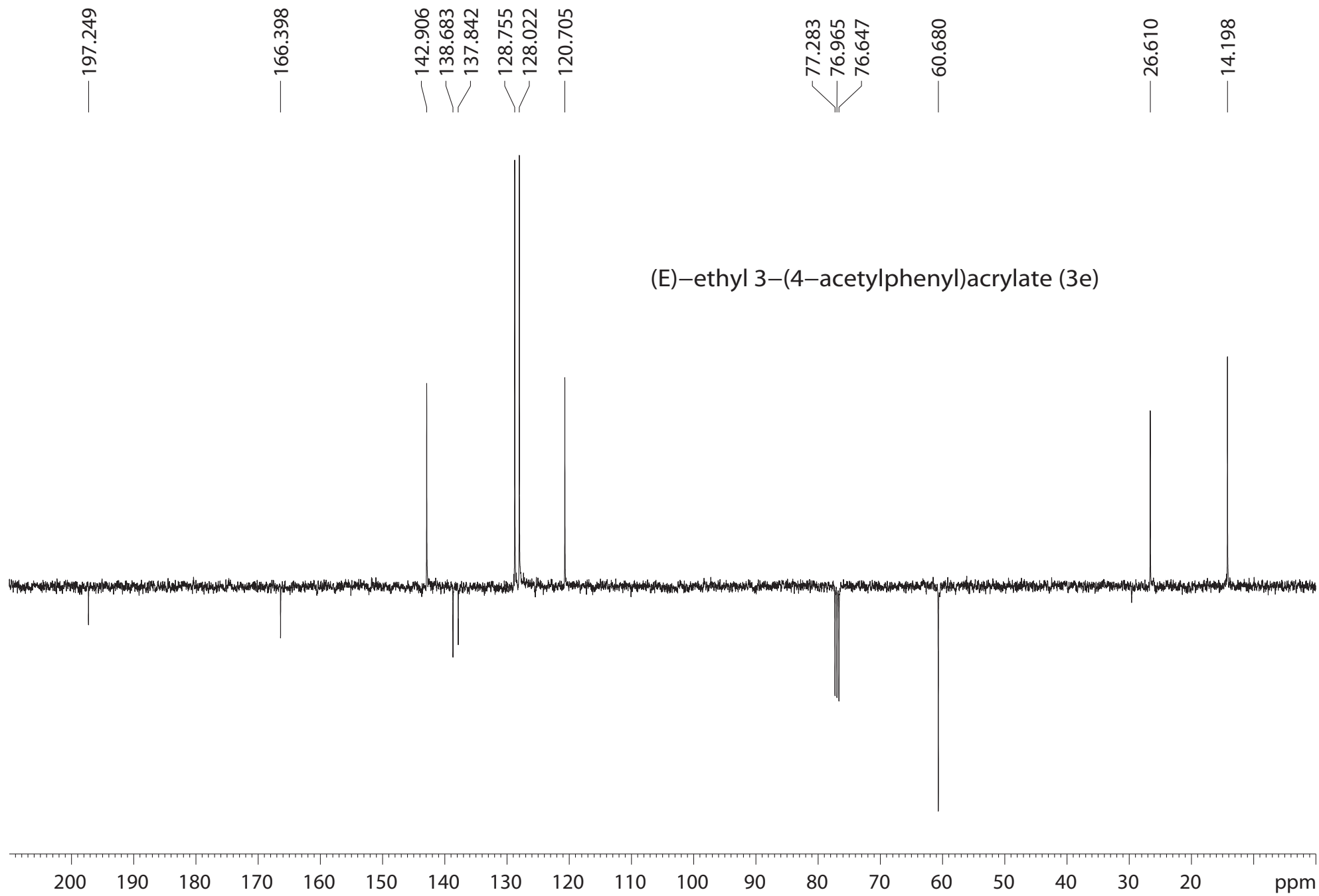


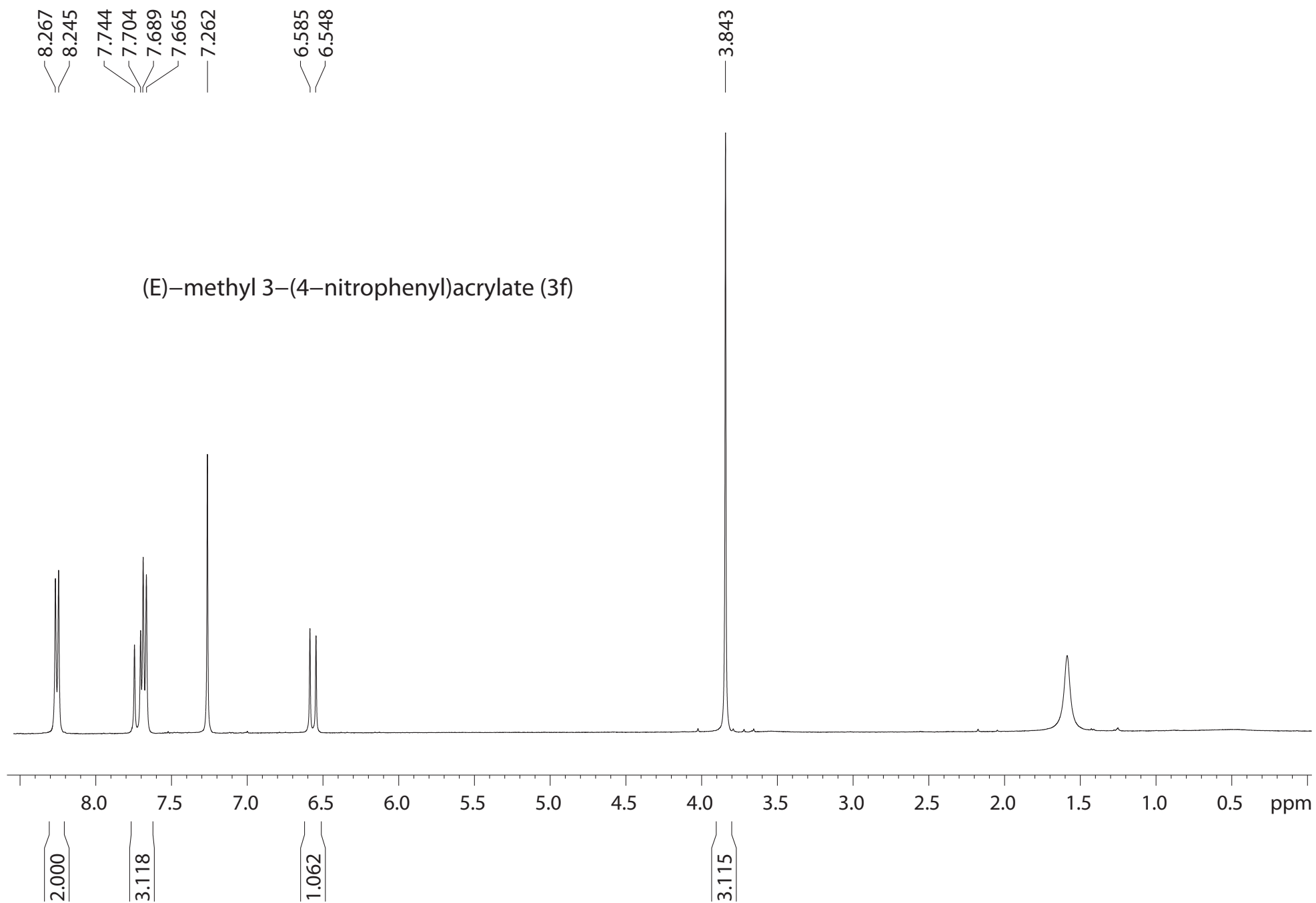


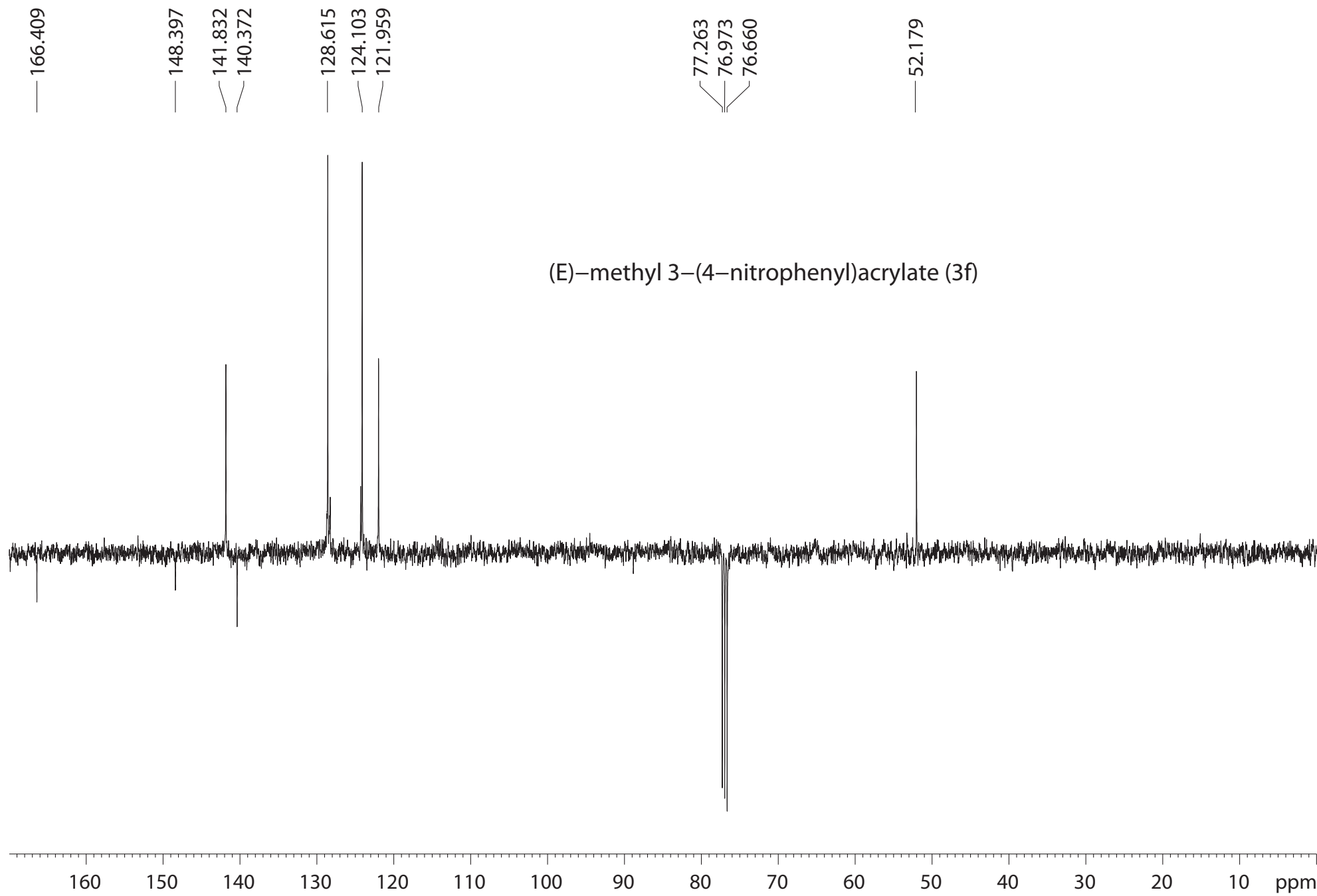


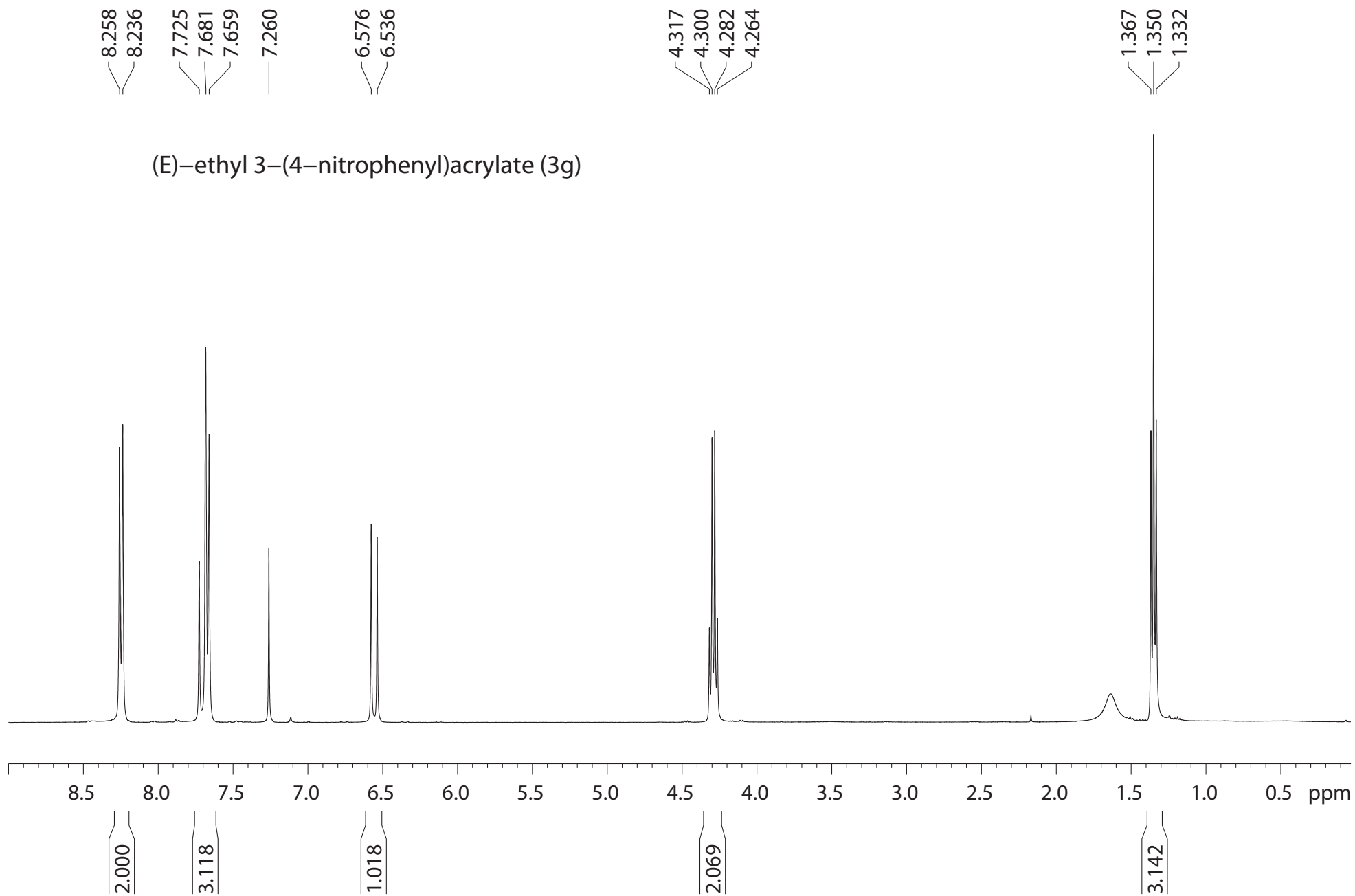


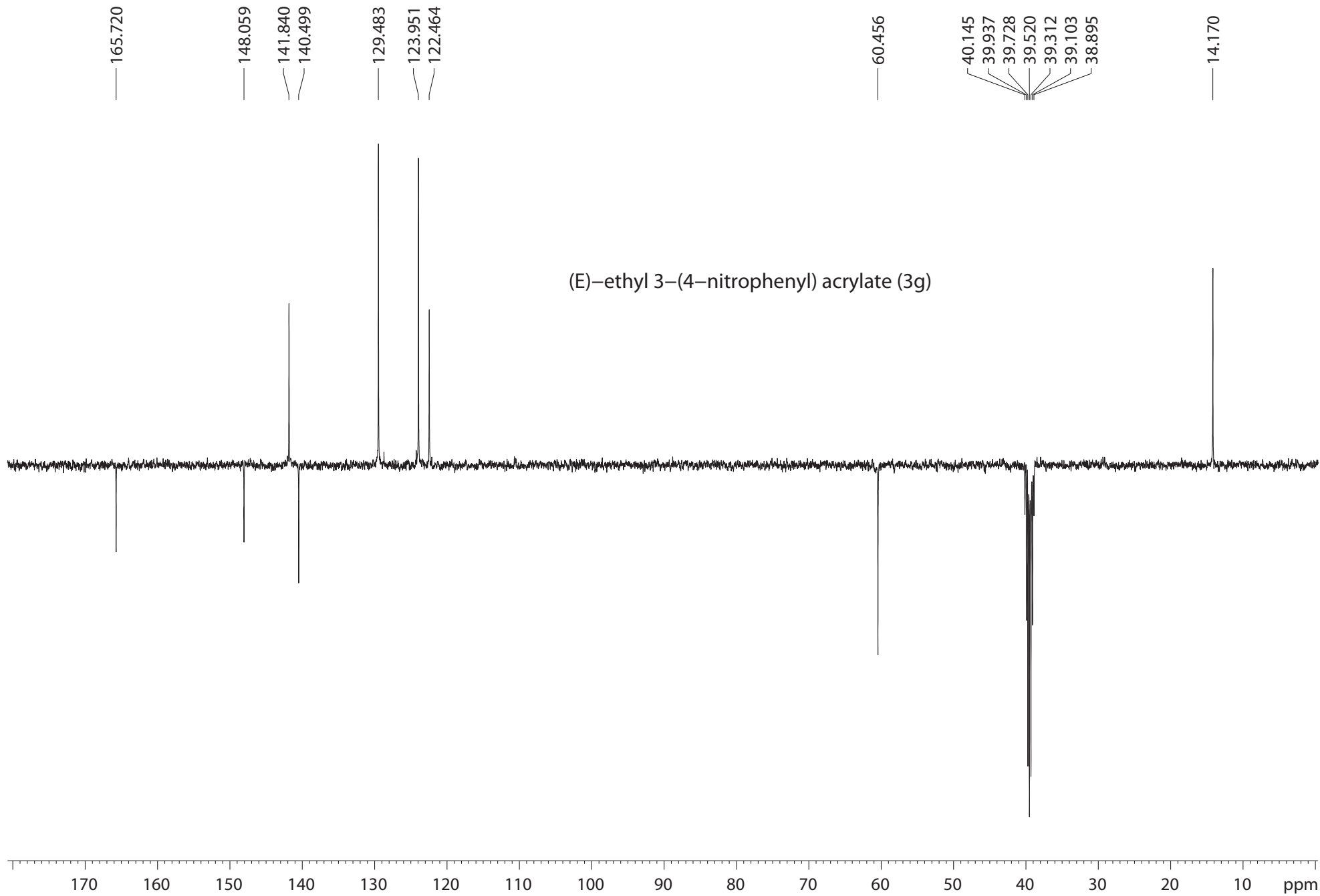




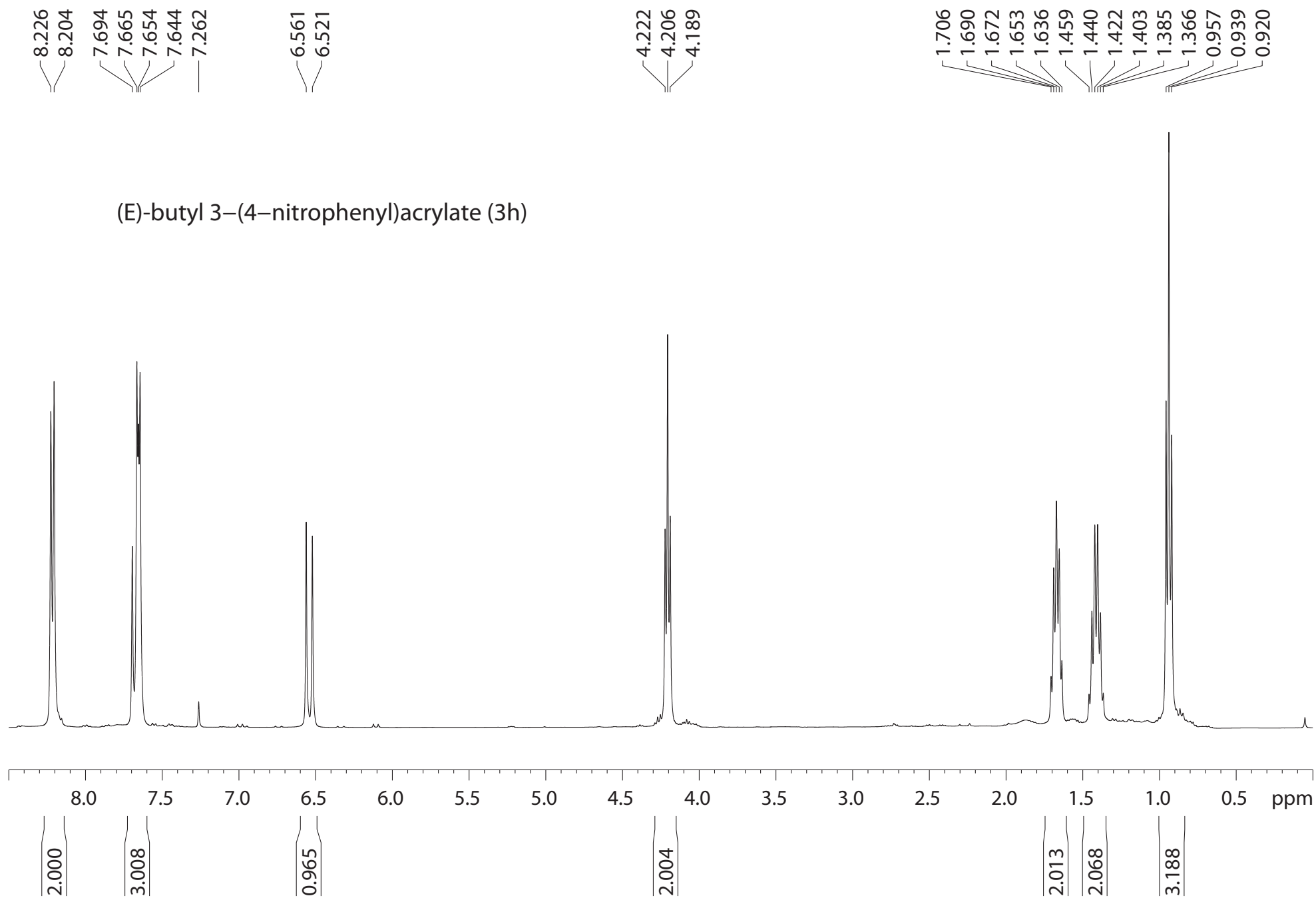


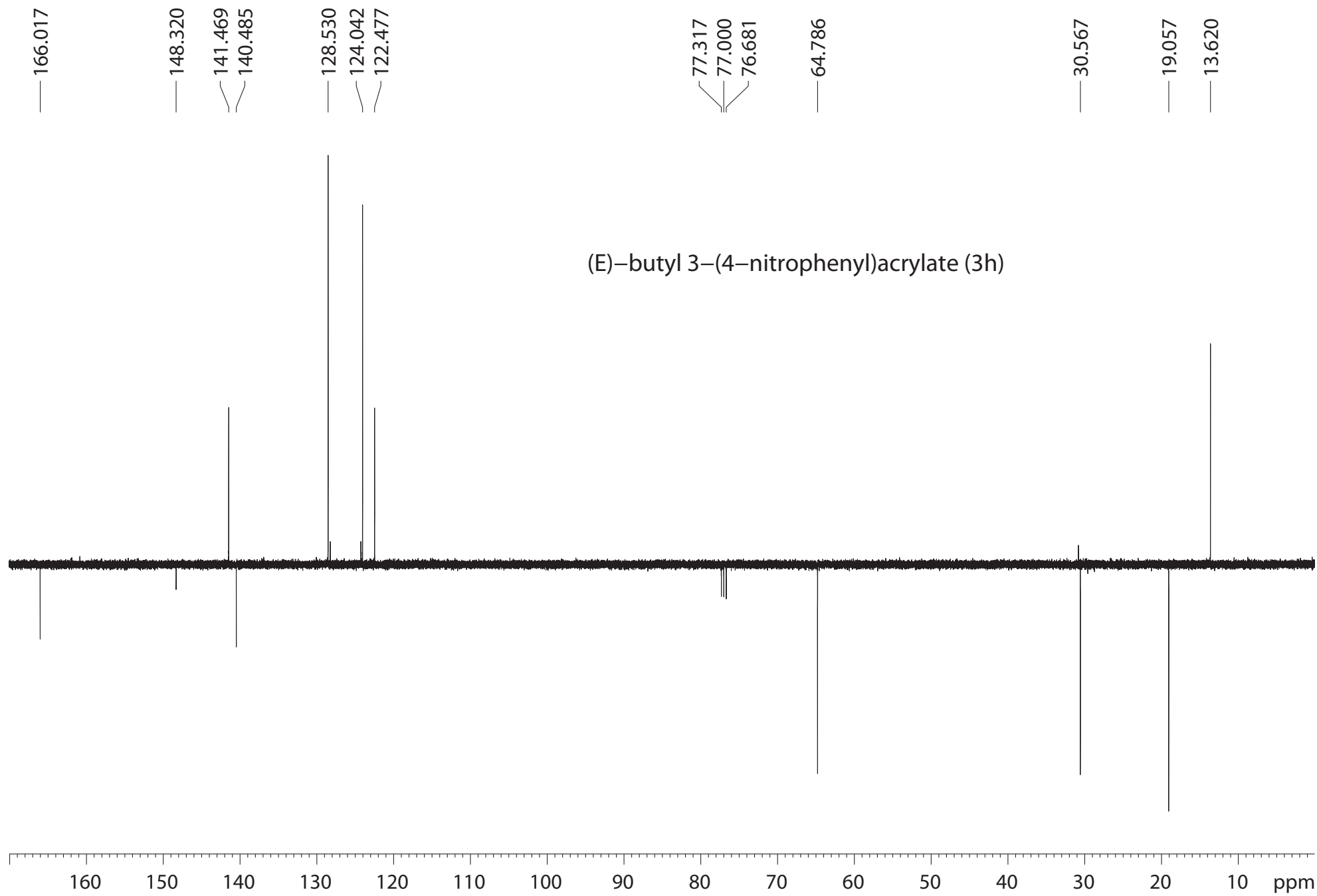


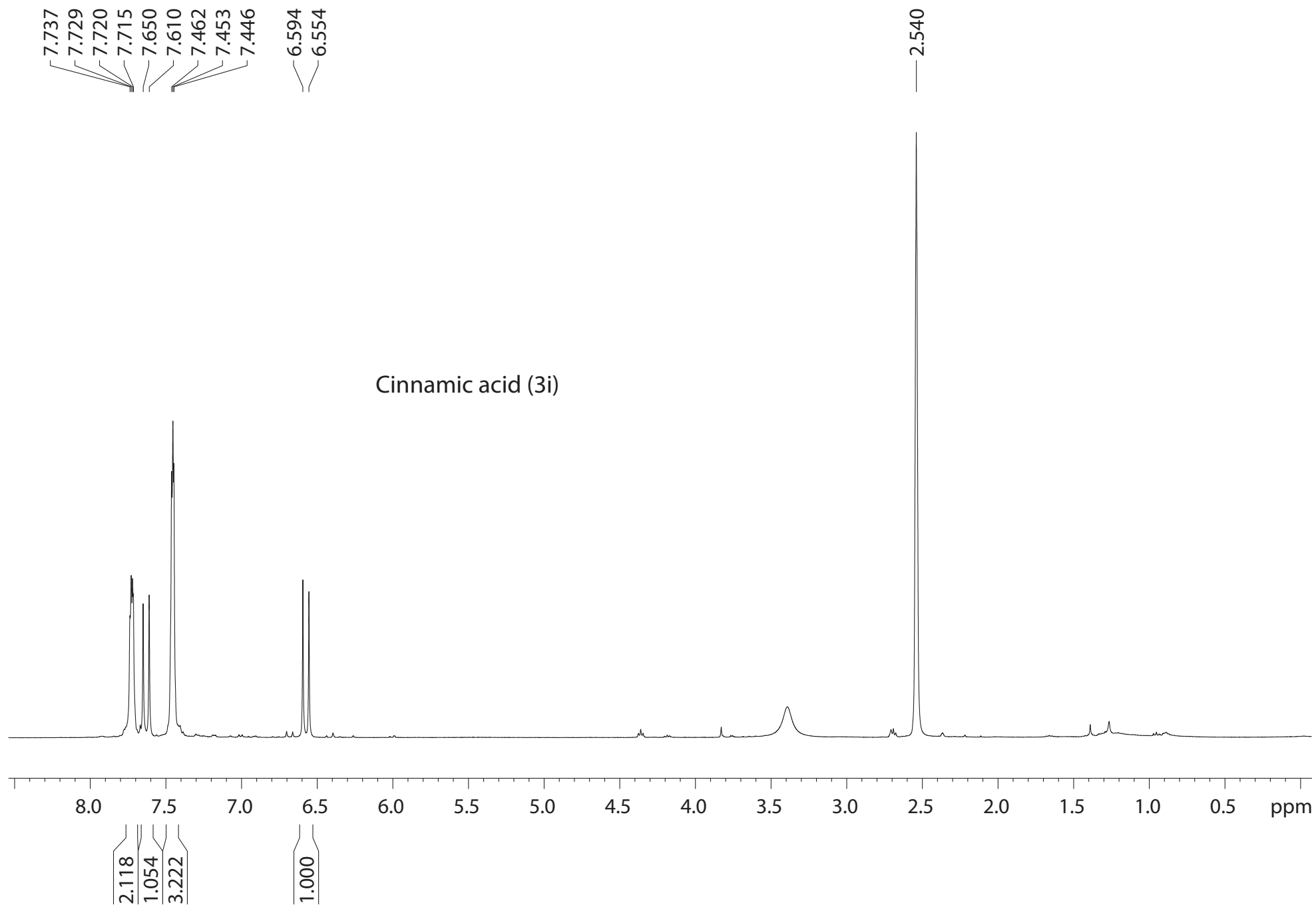


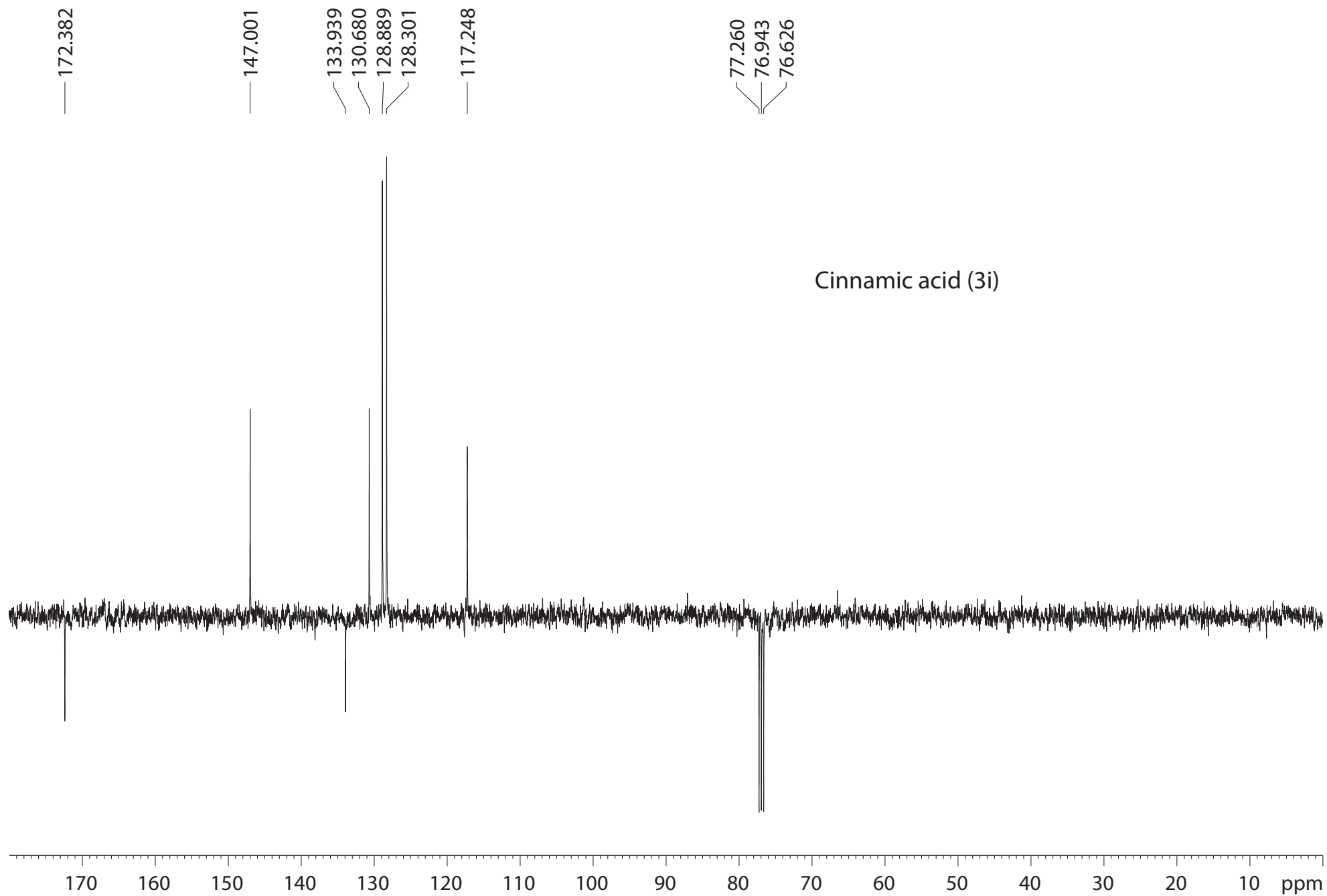


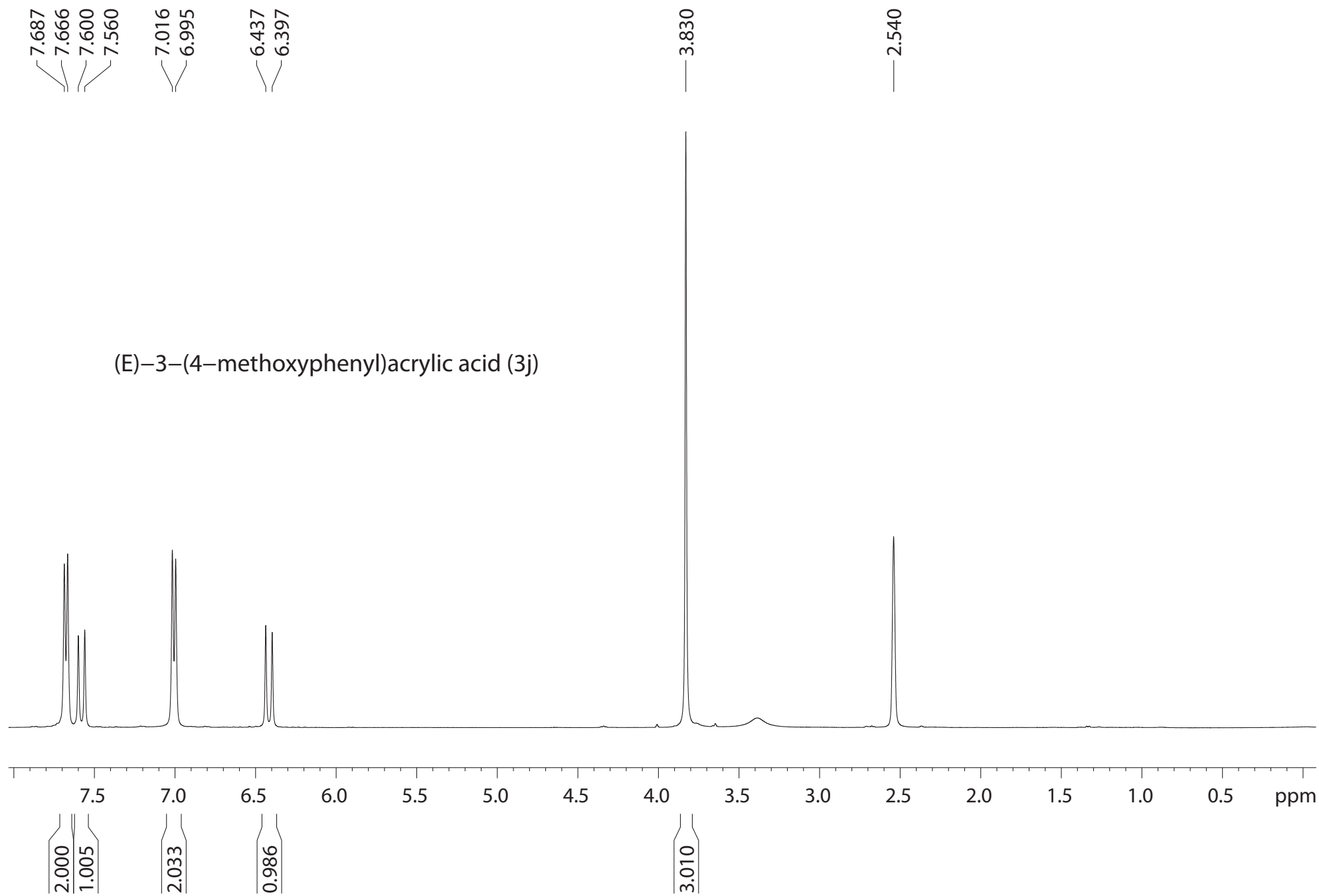


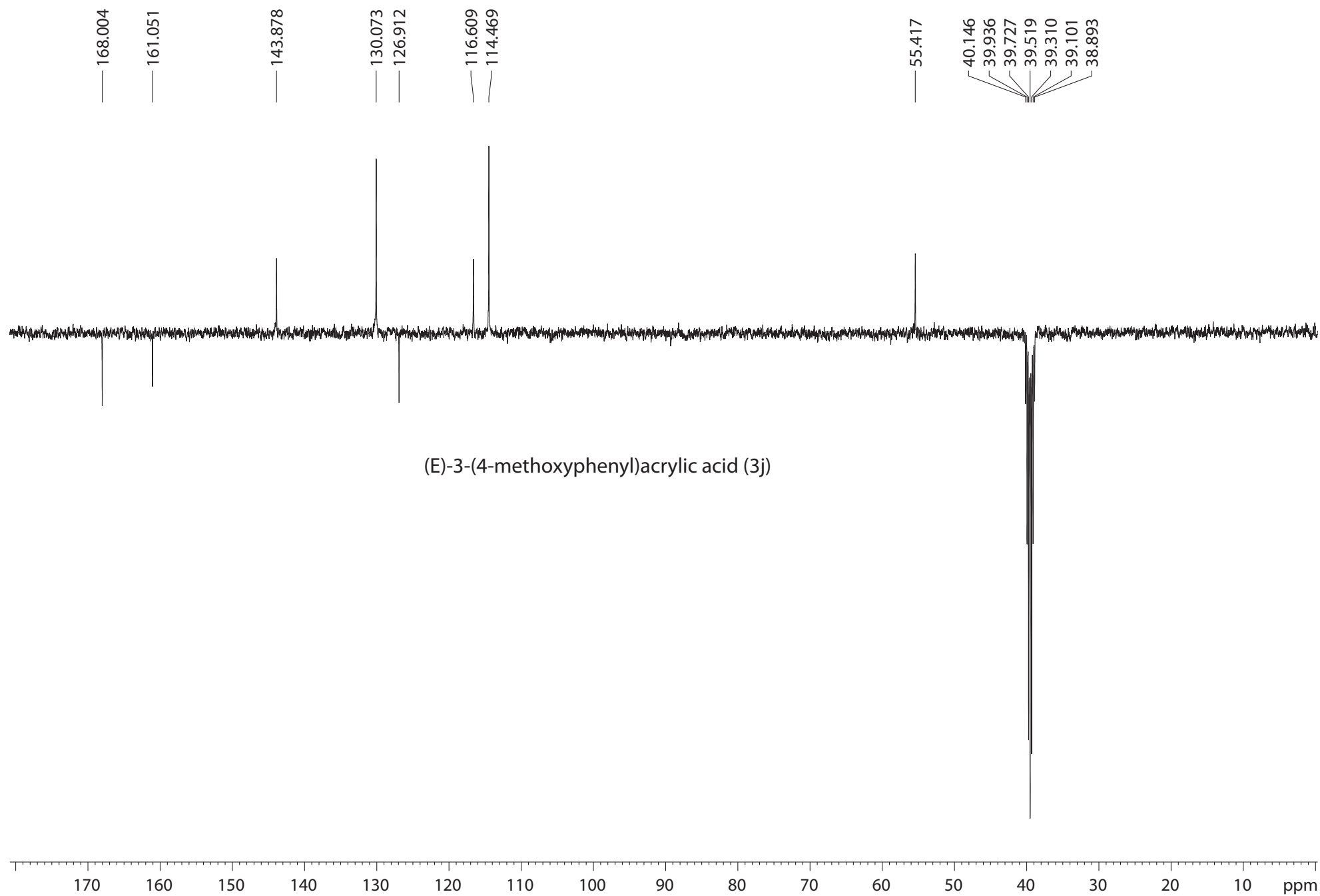


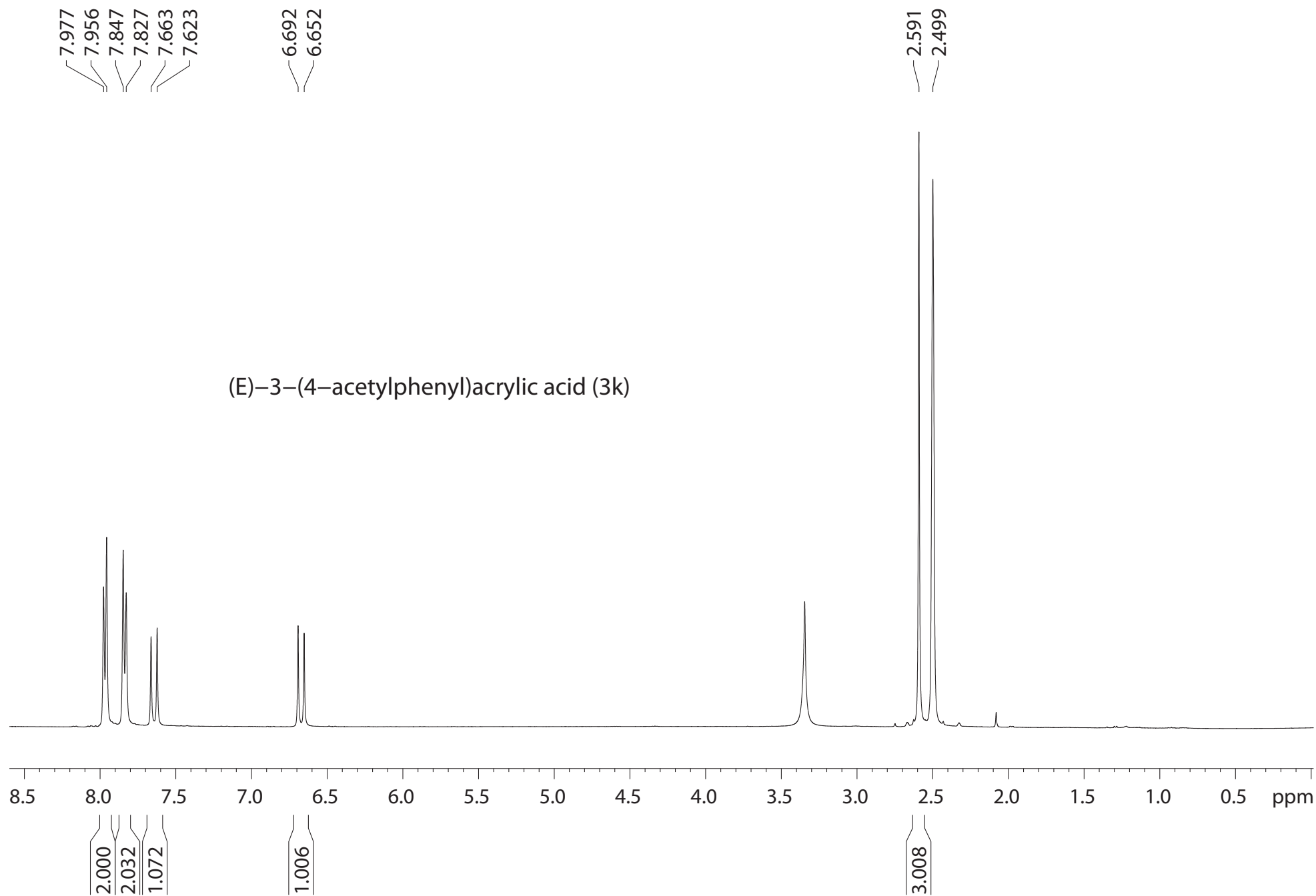


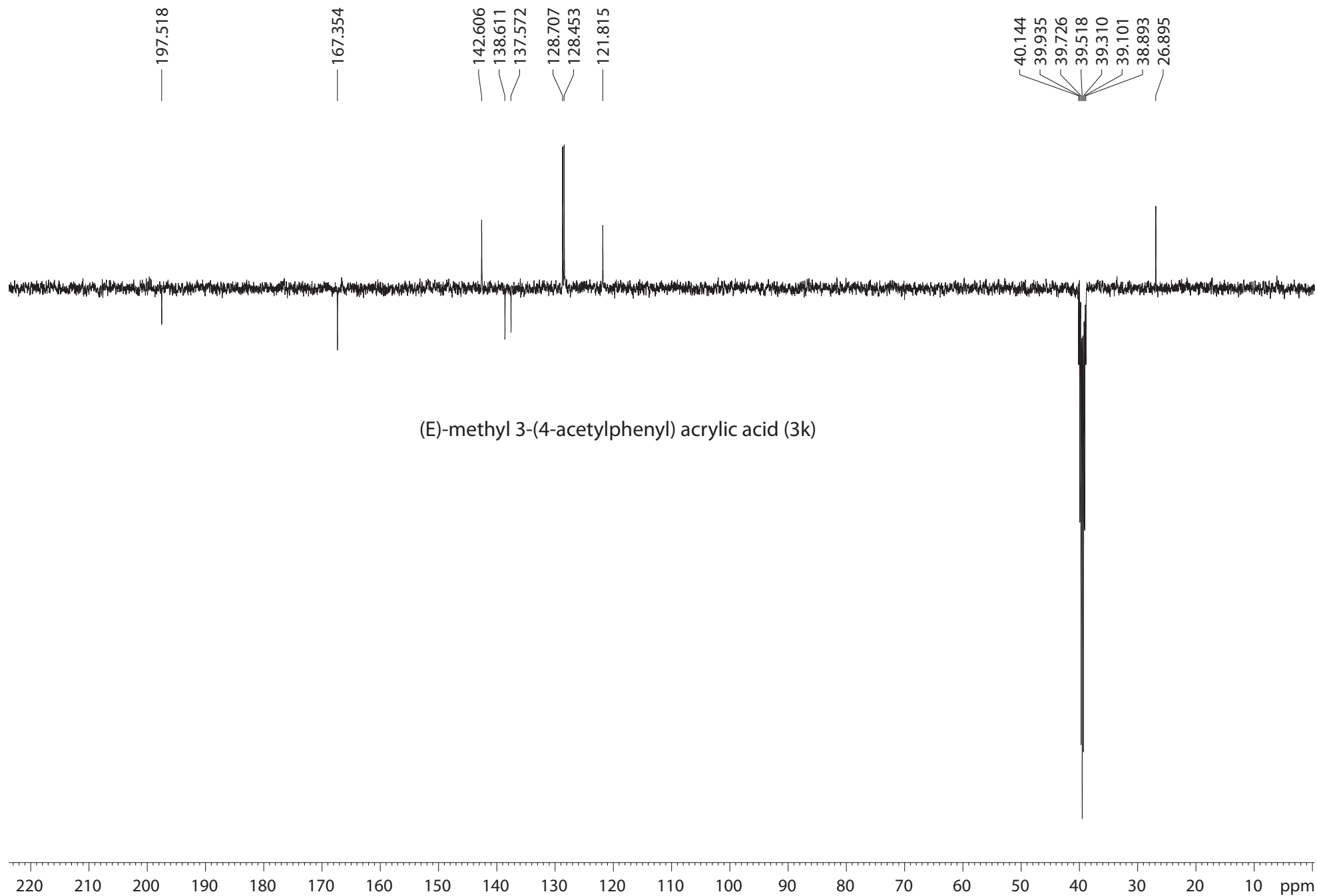




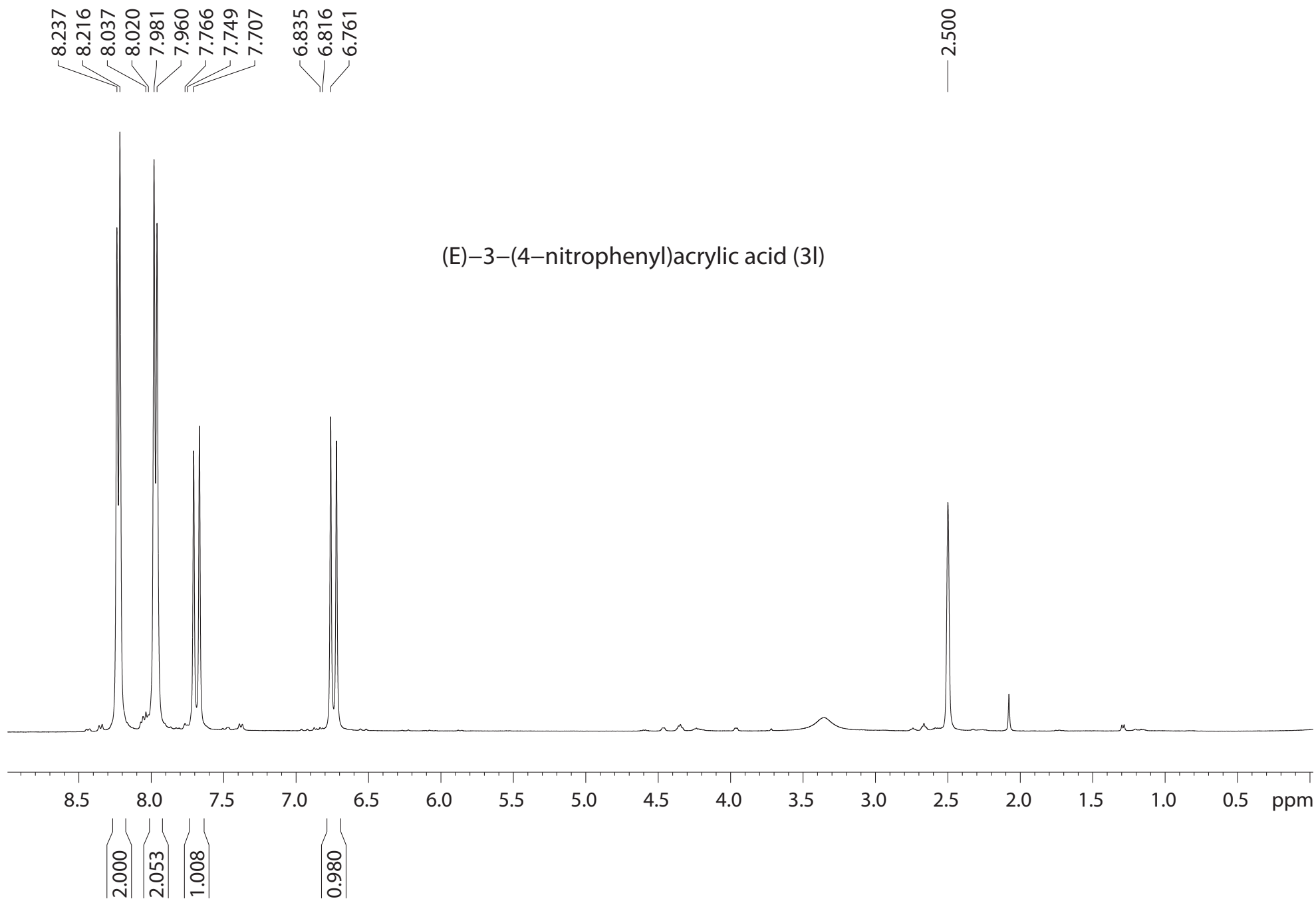


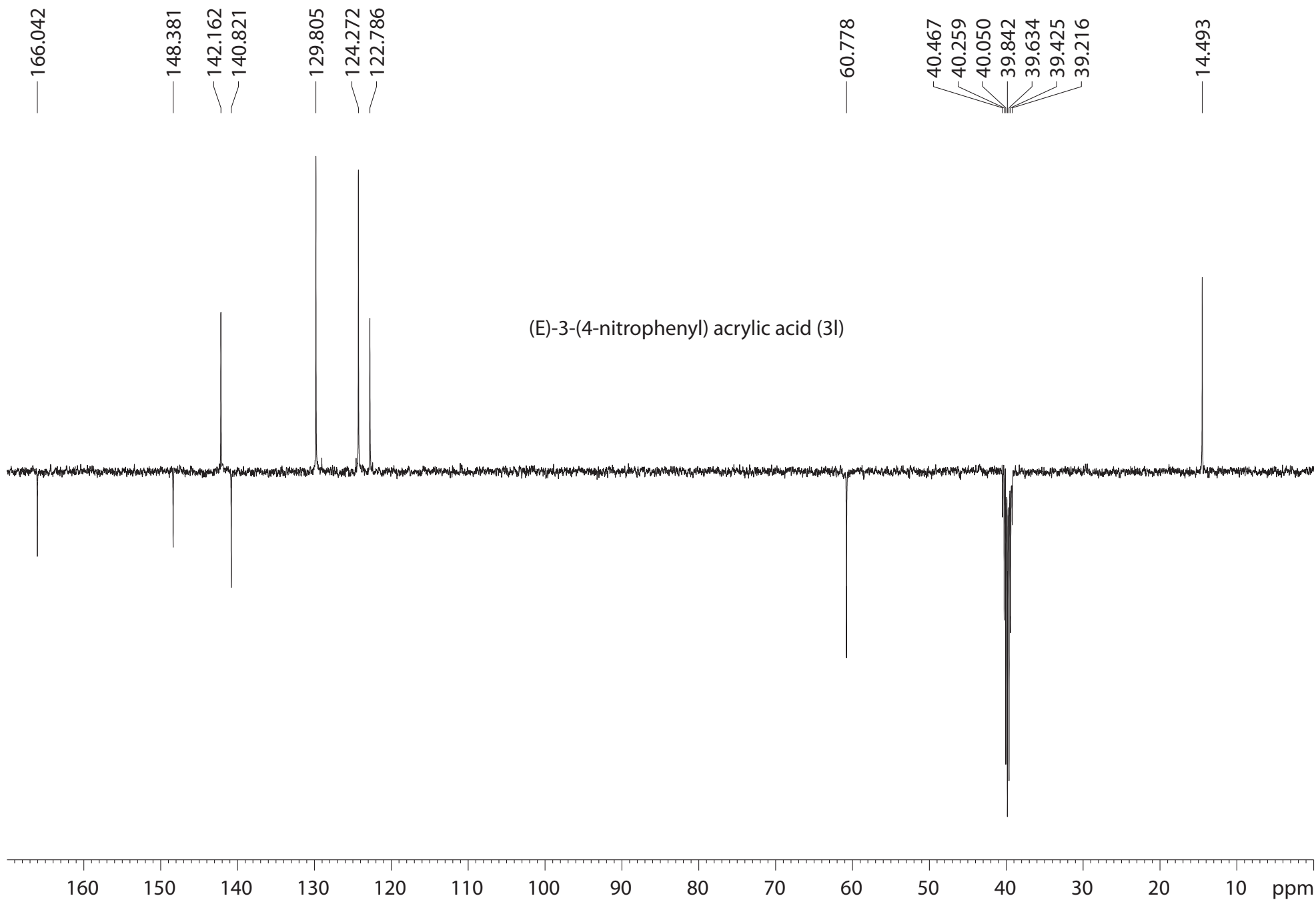


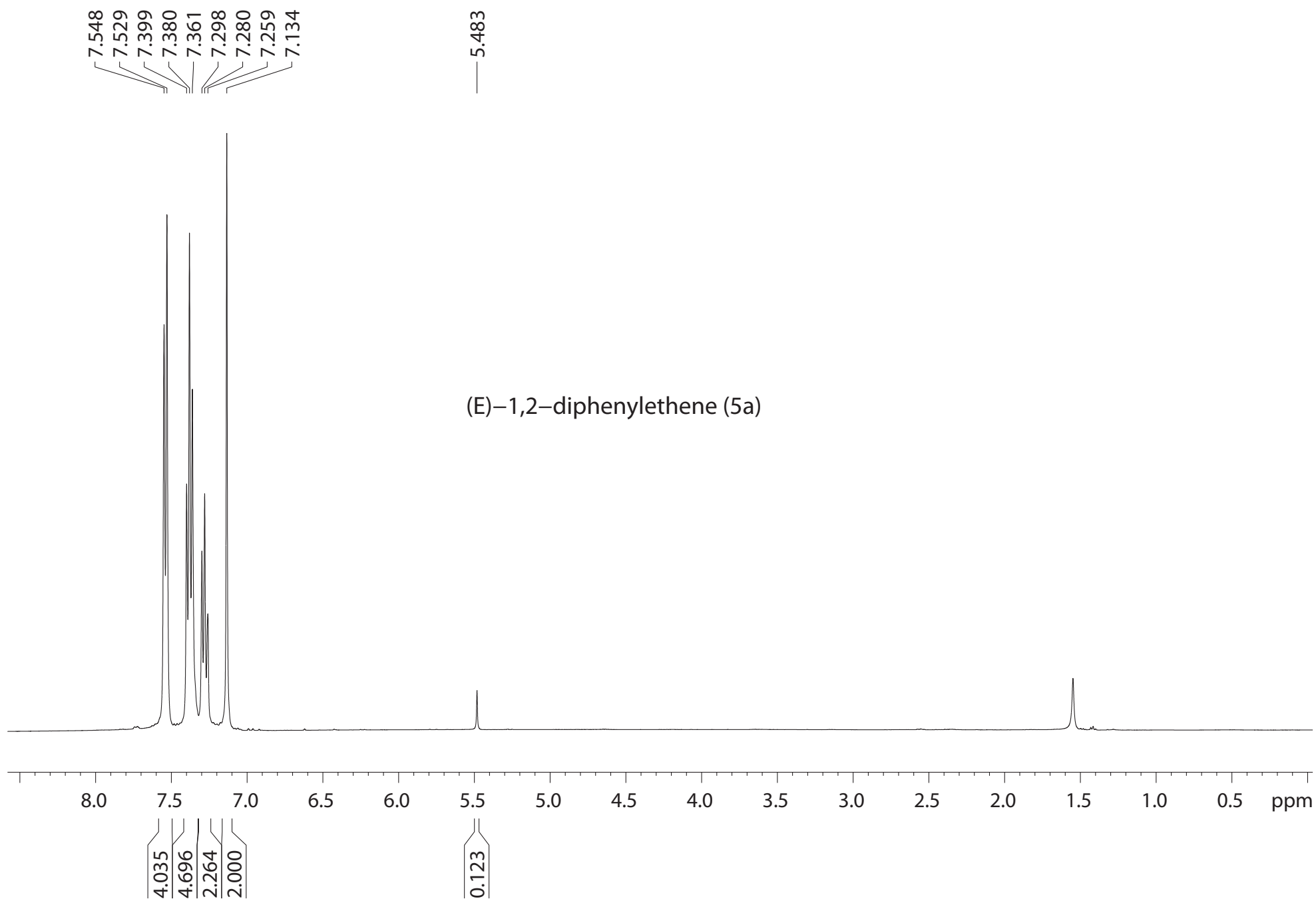


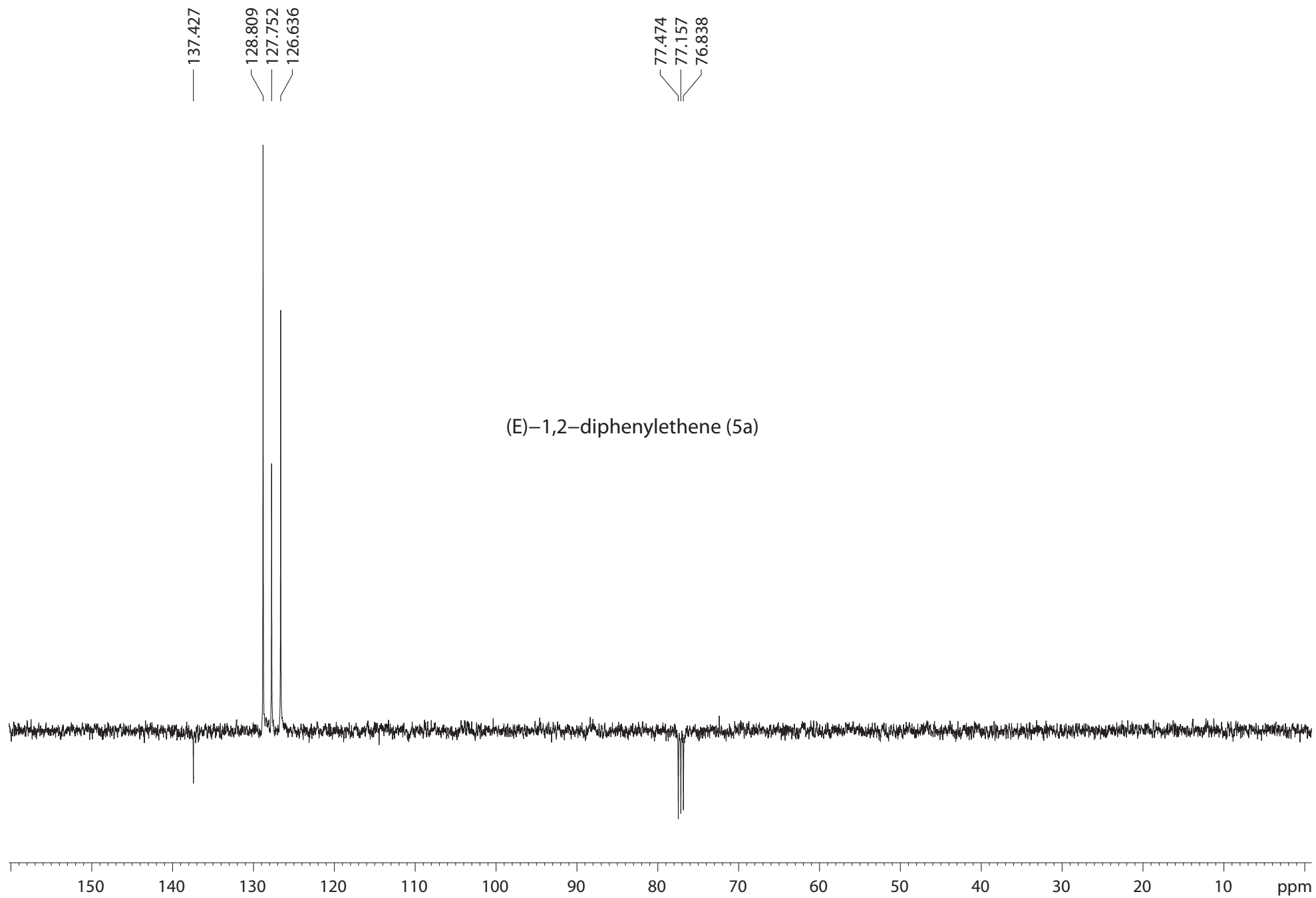


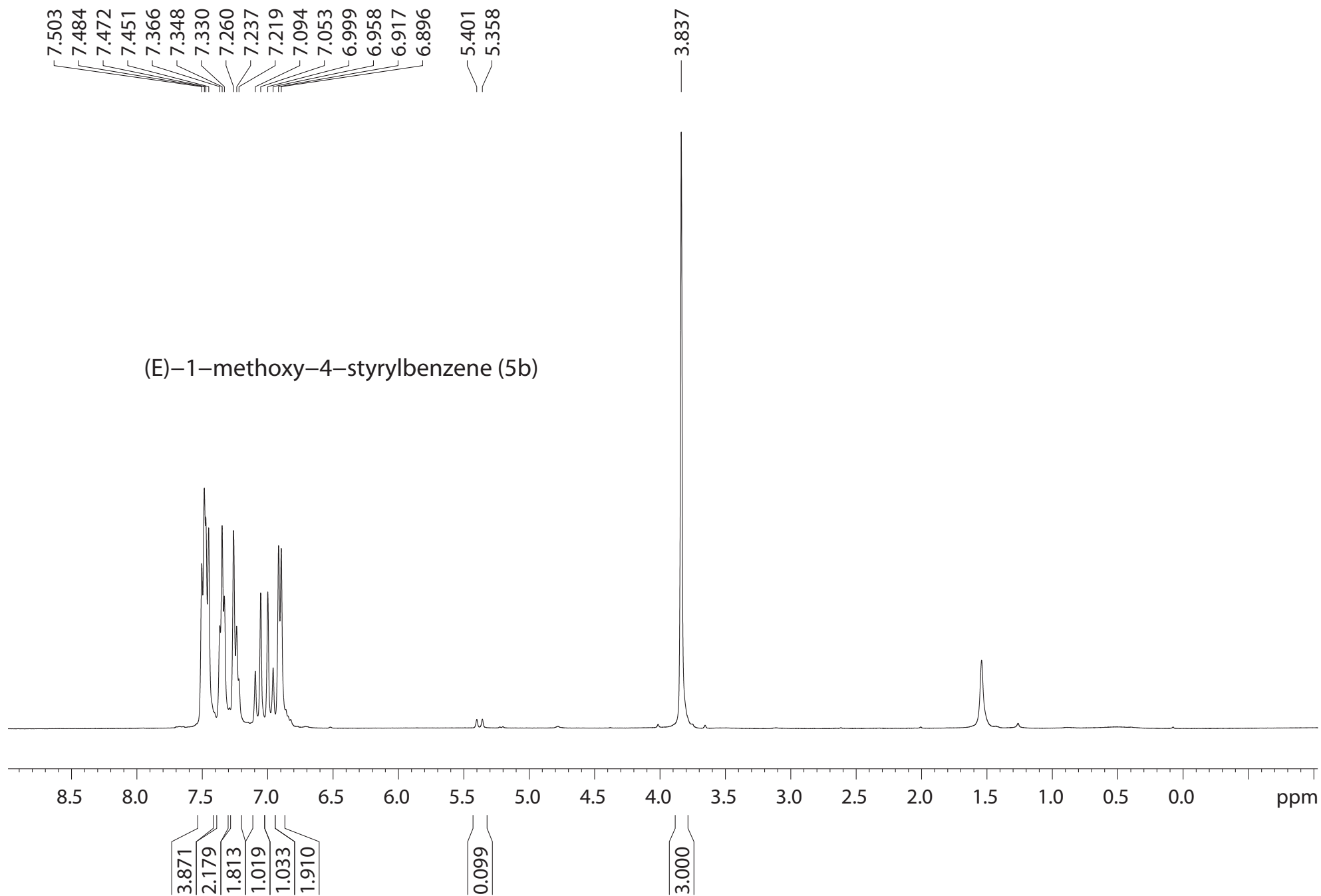


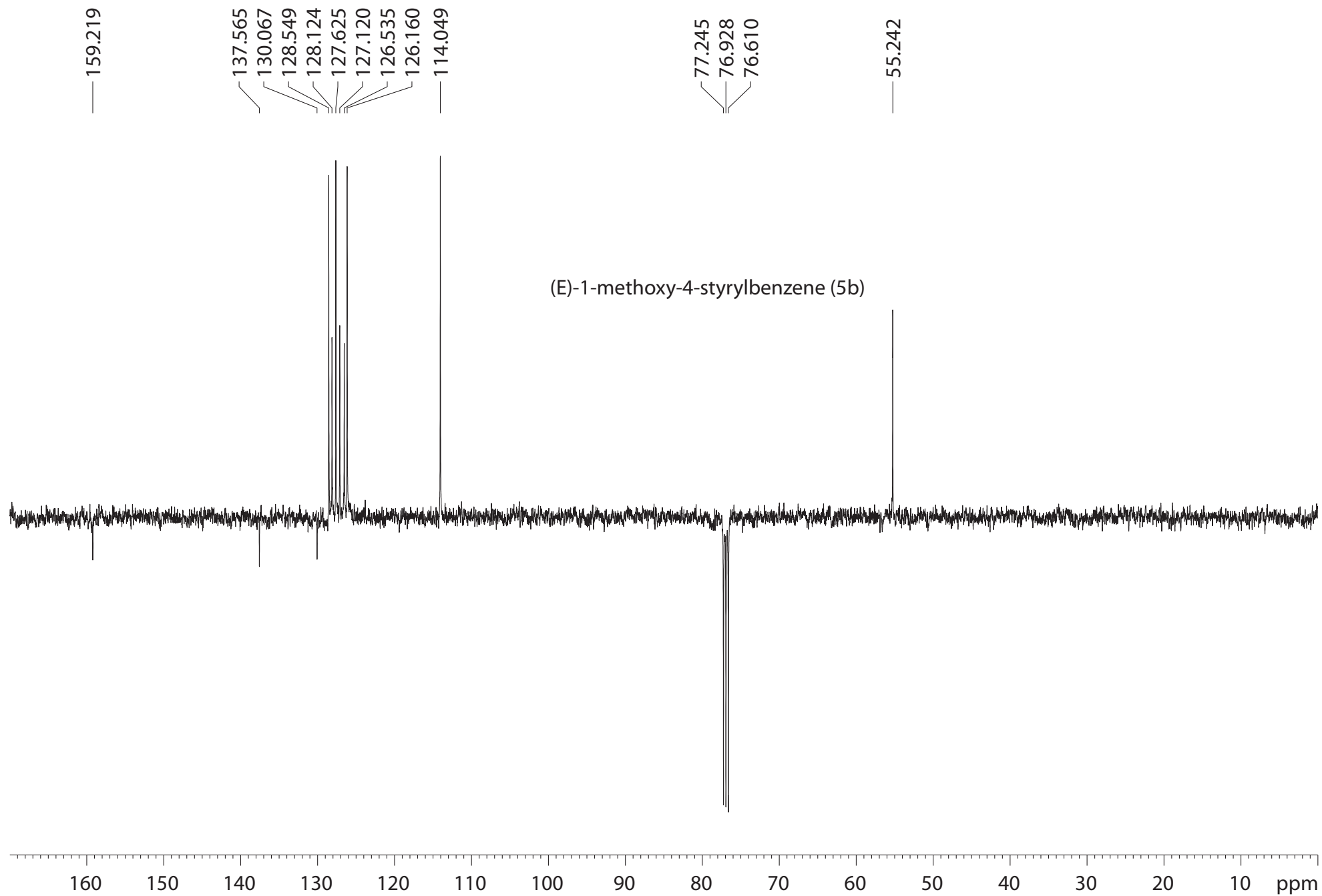


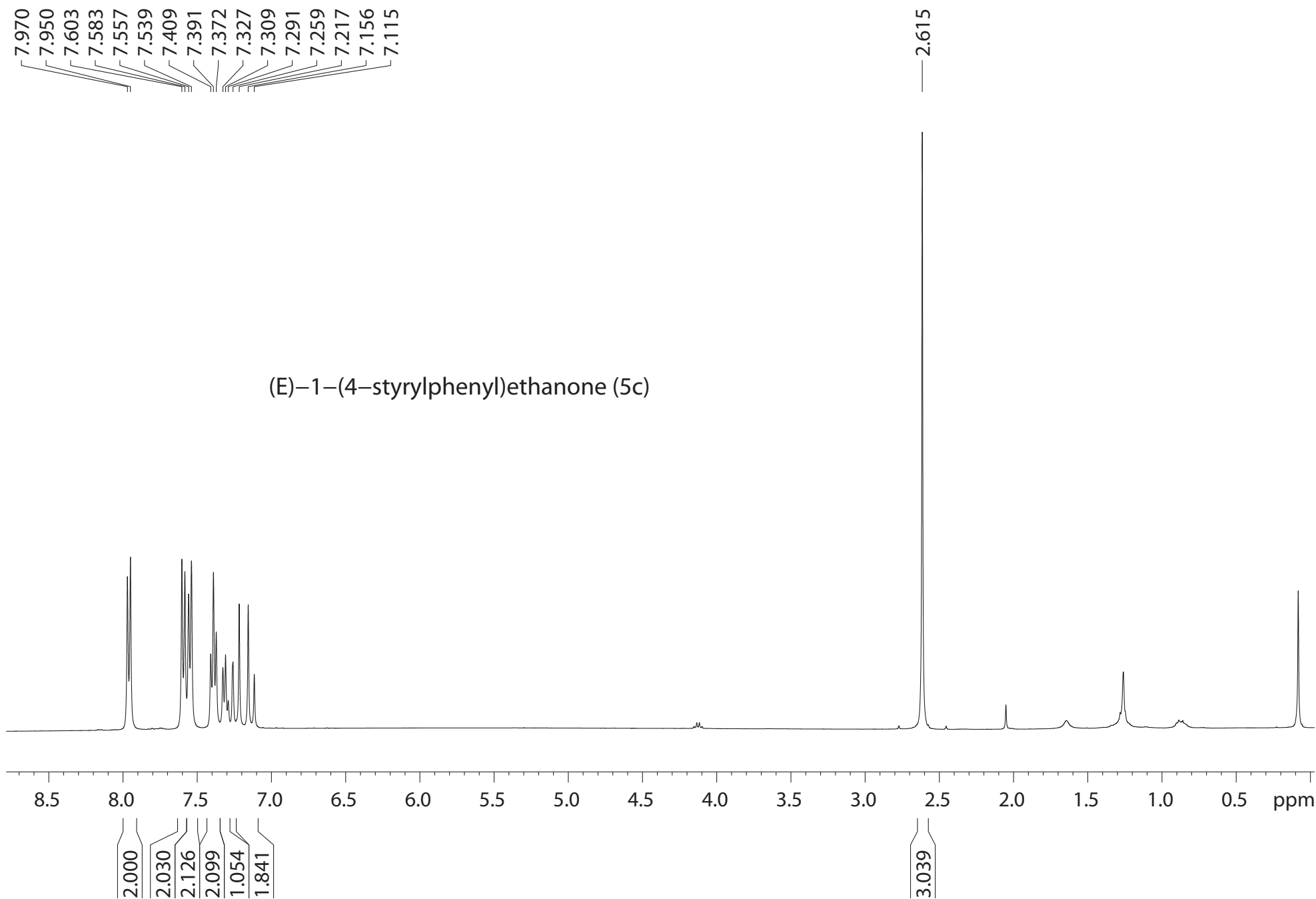


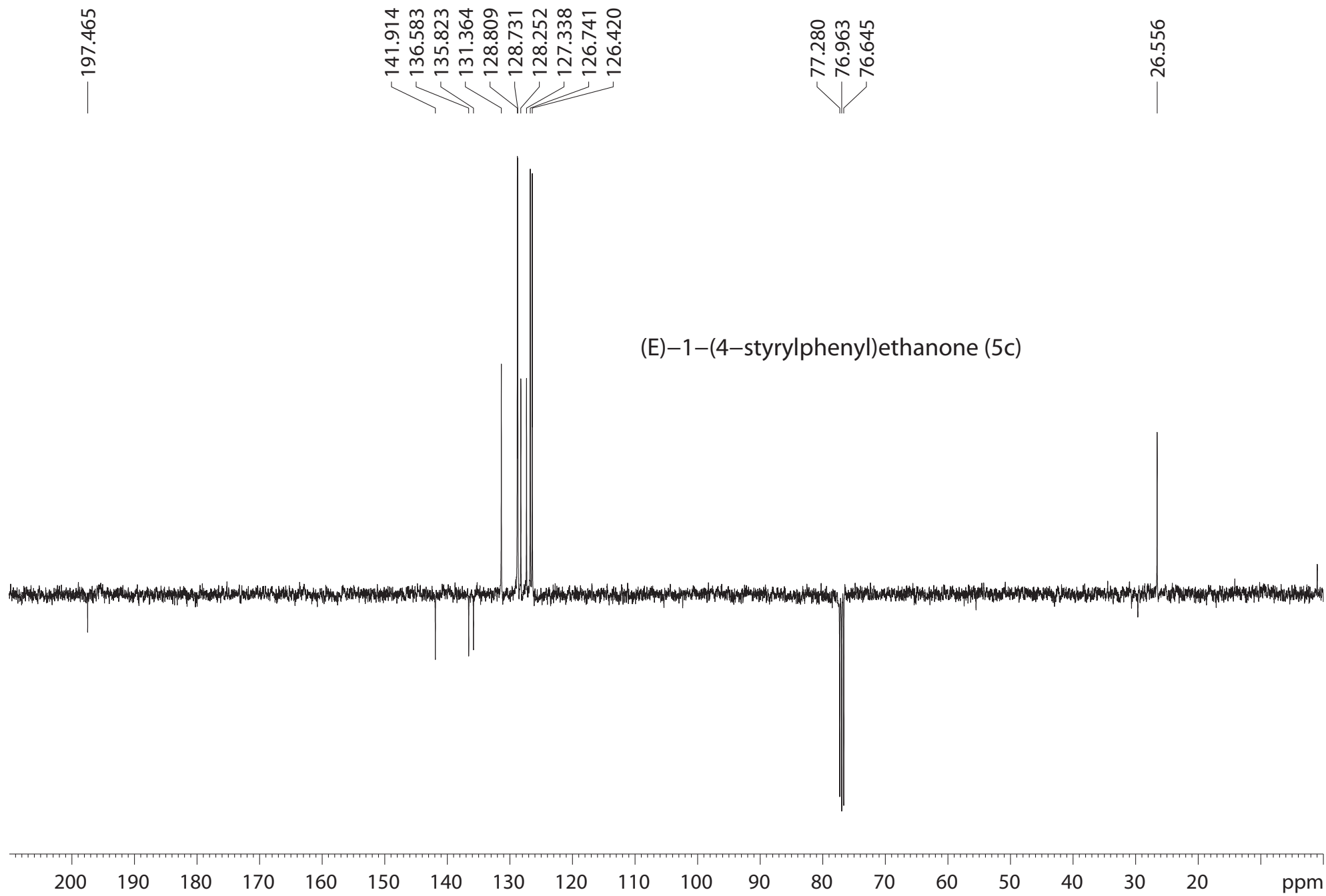




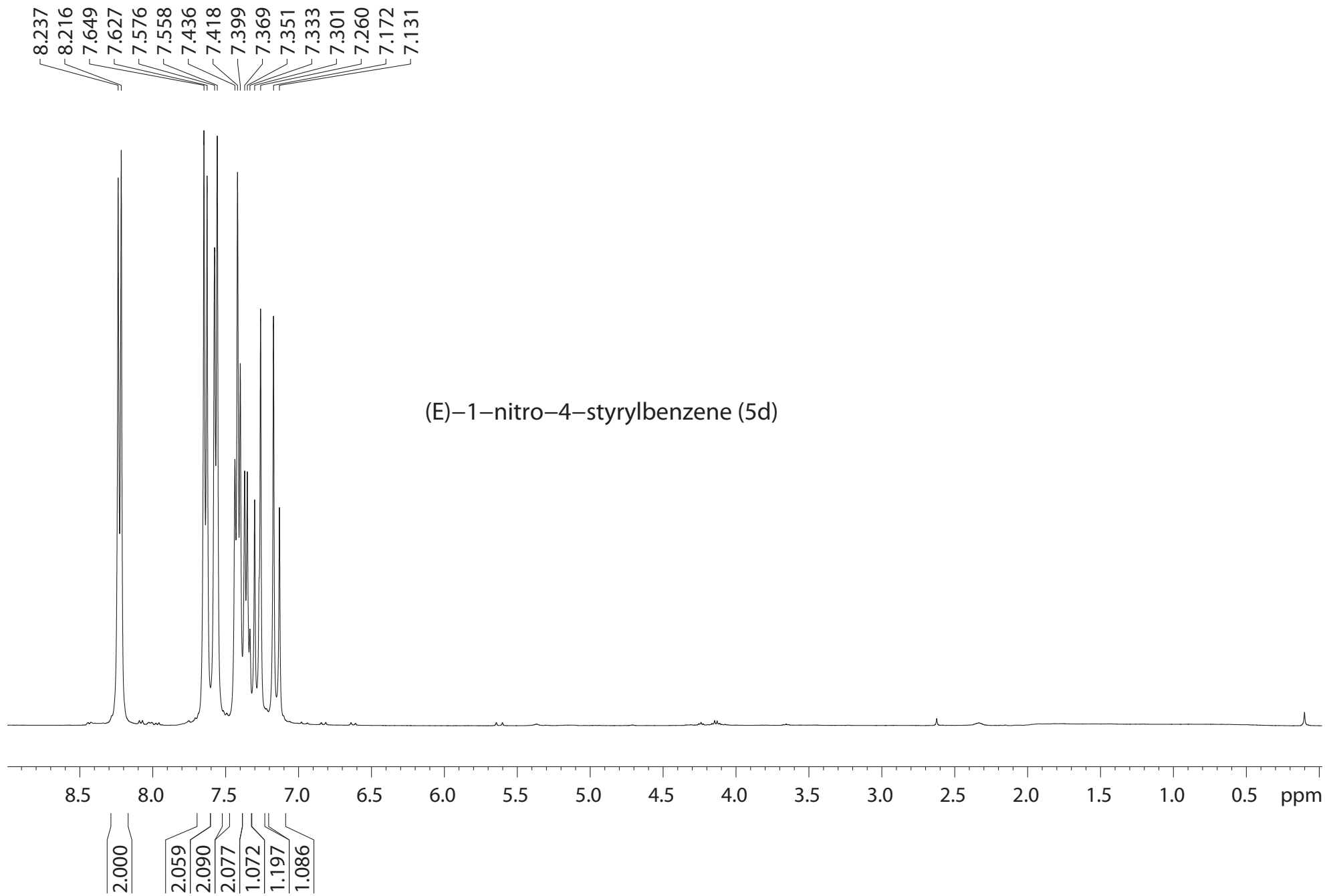


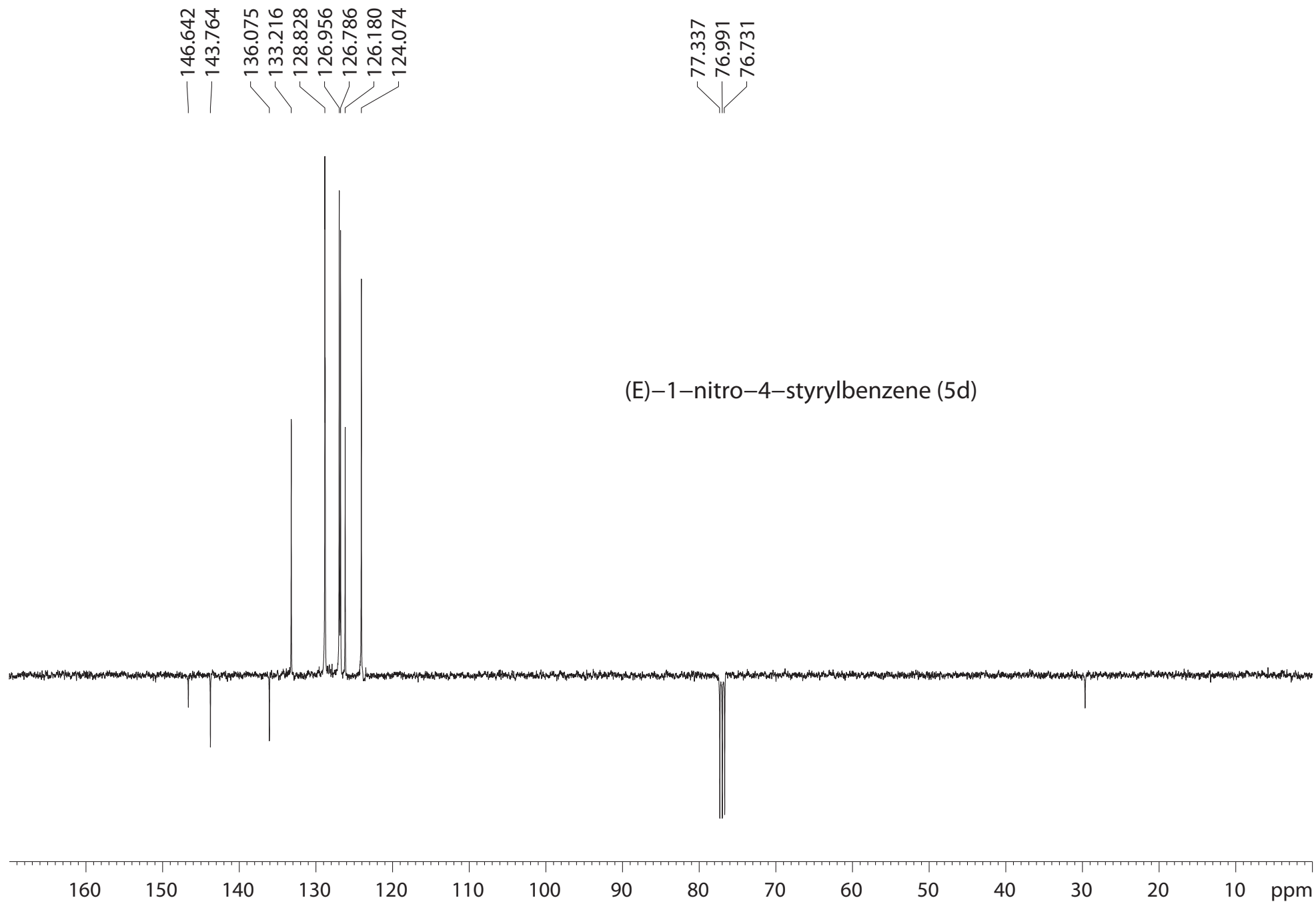


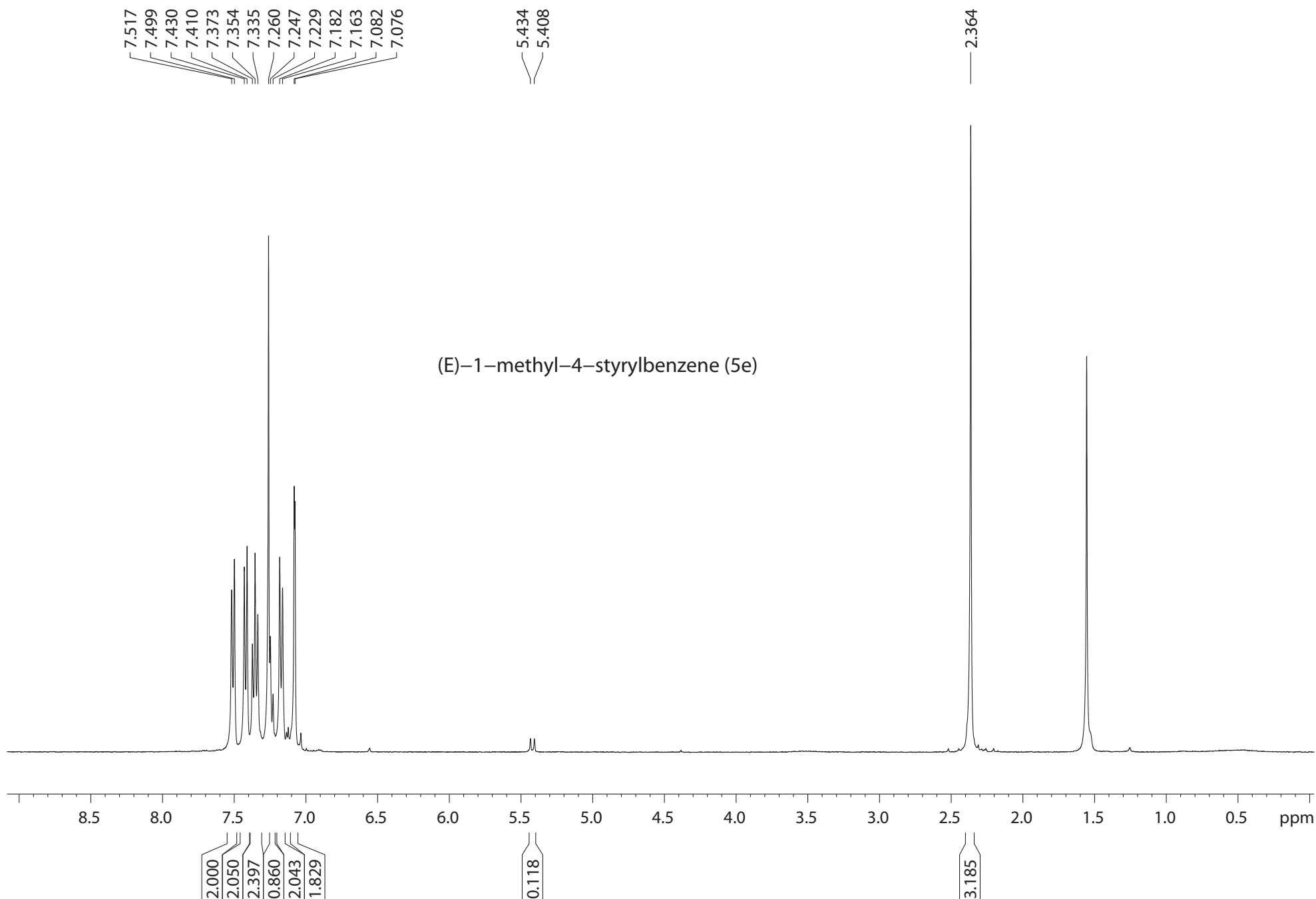


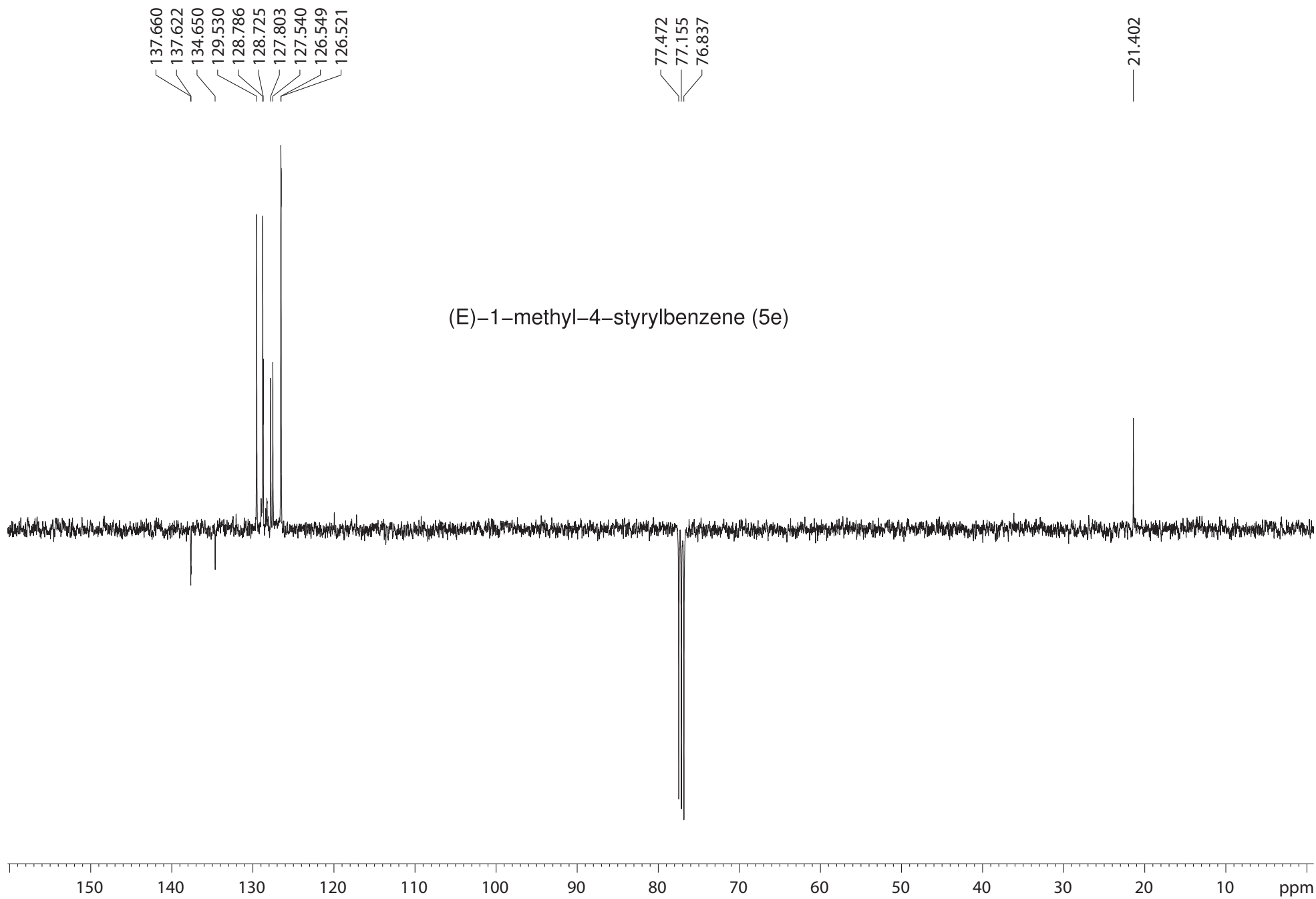




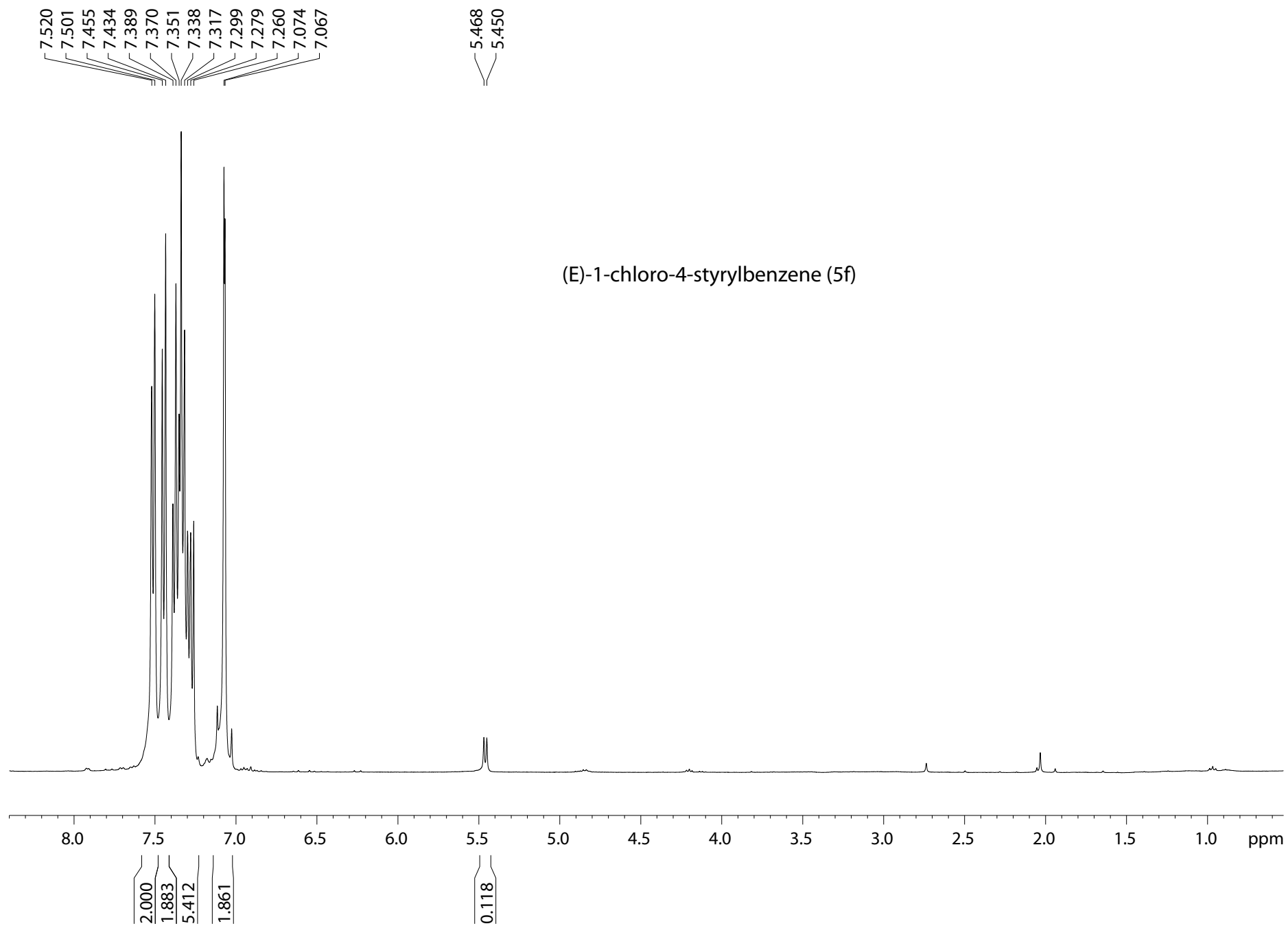


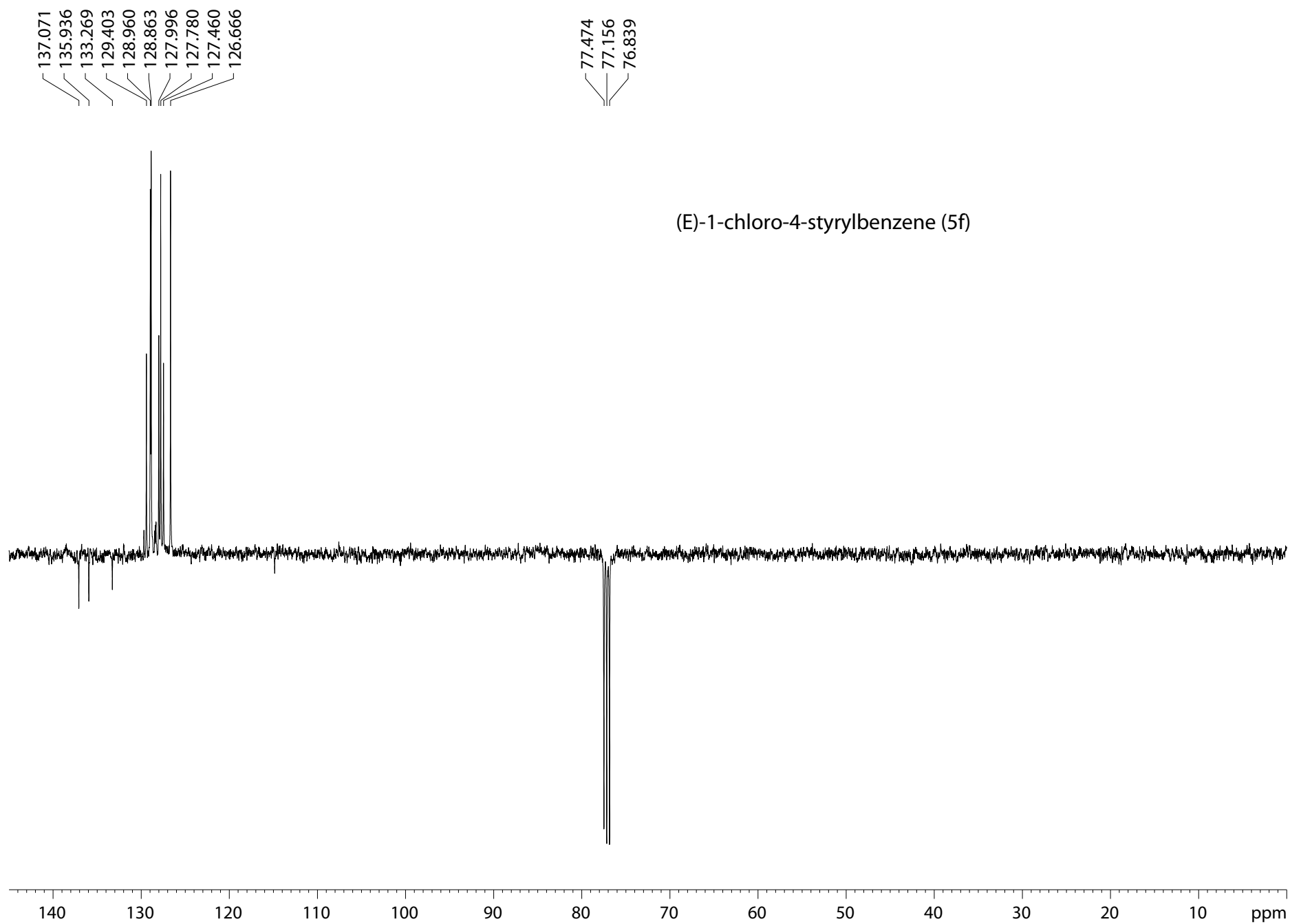


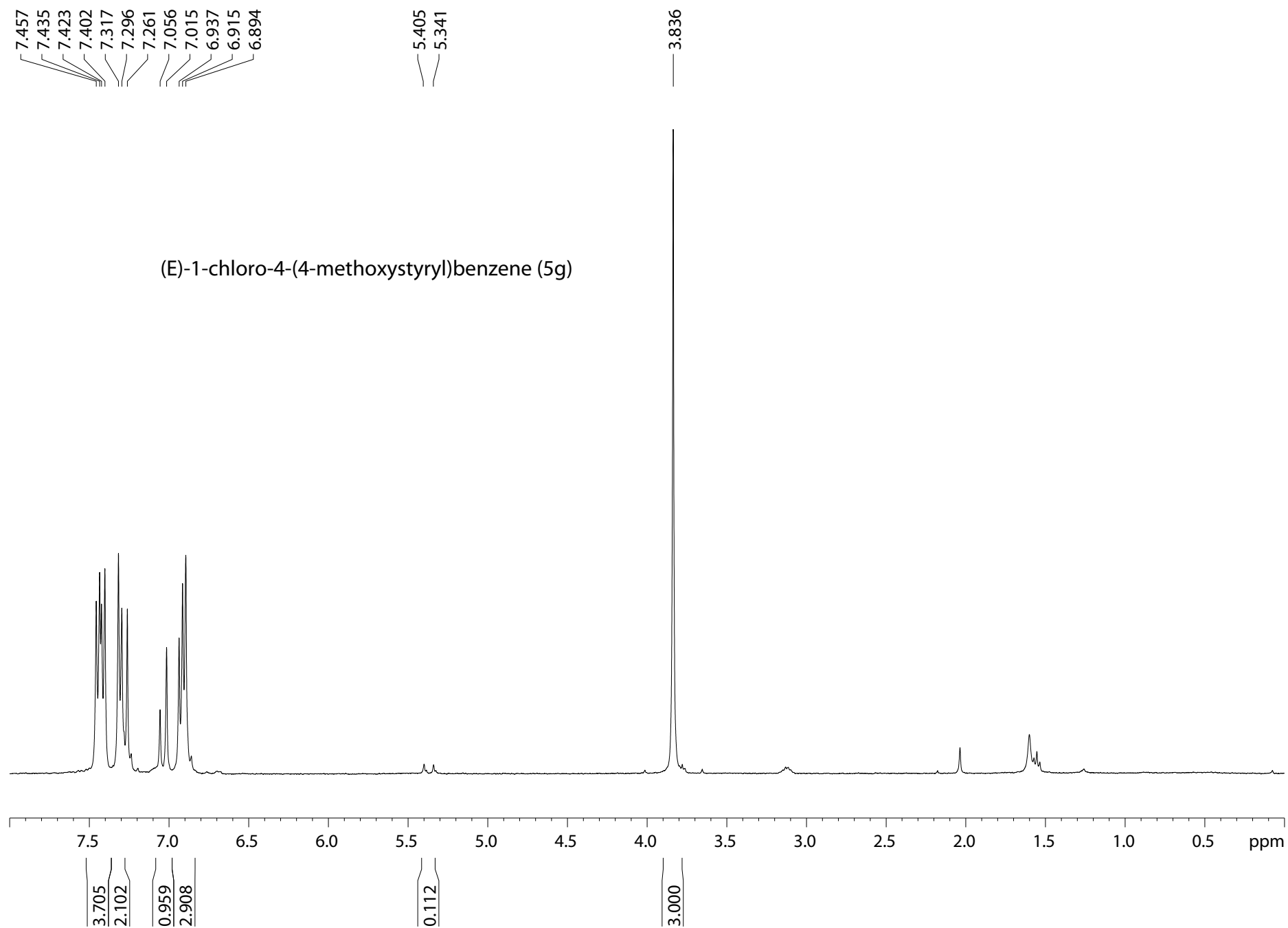




(E)-1-chloro-4-styrylbenzene (5f)







(E)-1-chloro-4-(4-methoxystyryl)benzene (5g)

