

SUPPORTING INFORMATION

***E,Z*-Stereodivergent Synthesis of *N*-Tosyl  $\alpha,\beta$ -Dehydroamino Esters via a Mukaiyama-Michael Addition†**

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**Table of Contents:**

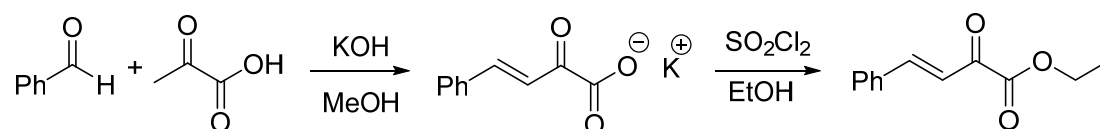
|  |      |
|--|------|
| General Experimental Methods   | S1   |
| Typical procedure for the preparation of imines <b>1</b><br>and characterisation data for compounds <b>1</b>           | S1   |
| General procedure for the non-catalysed Mukaiyama-Michael reaction<br>and characterisation data for compounds <b>3</b> | S6   |
| General procedure for the non-catalysed Mukaiyama-Michael reaction<br>and characterisation data for compounds <b>4</b> | S10  |
| <sup>1</sup> H NMR spectroscopic criteria by Mazurkiewicz<br>et al. to determine the geometry of the double bond       | S15  |
| Literature   | S15  |
| NMR spectra for compounds <b>1</b> , <b>3</b> and <b>4</b>   | S16  |
| Figure S1. Ortep plot for the X-ray structure of compound <b>4m</b>  | S102 |
| Figure S2. Ortep plot for the X-ray structure of compound <b>1b</b>  | S102 |

## General Experimental Methods

Reactions were carried out in glassware dried at 120 °C overnight. Commercial reagents were used as purchased. Dichloromethane was distilled from CaH<sub>2</sub>. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Melting points were determined in capillary tubes. NMR spectra were run at 300 MHz for <sup>1</sup>H and at 75 MHz for <sup>13</sup>C NMR using the residual nondeuterated solvent (CHCl<sub>3</sub>) as internal standard (7.26 for <sup>1</sup>H and 77.0 for <sup>13</sup>C). Chemical shifts are given in ppm. The carbon type was determined by DEPT experiments. Mass spectra (ESI) were recorded on mass spectrometer equipped with an electrospray source with a capillary voltage of 3.3 kV. β,γ-Unsaturated-α-keto esters and their imines were prepared according to modified literature procedures.

### Typical procedure for the preparation of imines 1.

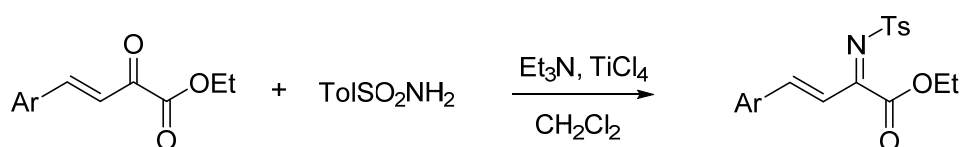
#### a. Synthesis of β,γ-unsaturated-α-keto esters.<sup>1</sup>



A solution of KOH (1.59 g, 28.3 mmol) in methanol (3.8 mL) was added dropwise to a solution of the required aldehyde (18.9 mmol) and pyruvic acid (1.31 mL, 18.9 mmol) in methanol (5 mL) at 0 °C. After several hours the mixture was filtered and the resulting solid was washed with cold methanol and diethyl ether, and dried under reduced pressure to provide the keto acid potassium salt.

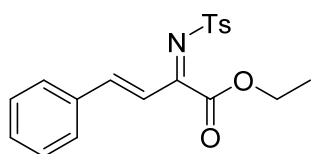
To ethanol (20 mL; MeOH or *i*PrOH were used for the methyl and isopropyl esters) precooled at 0 °C under nitrogen was added thionyl chloride (1.6 mL, 22.0 mmol) followed by the potassium salt (11.0 mmol) in several portions over 5-10 min. After stirring at room temperature for 1 hour, the mixture was heated at reflux temperature for 3 hours. The solvent was removed under reduced pressure, and the residue was partitioned in EtOAc (40 mL) and 5% aqueous NaHCO<sub>3</sub> (30 mL). The organic layer was washed with brine (40 mL) dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. Keto ester was obtained after column chromatography eluting with hexane:EtOAc mixtures.

#### b. Synthesis of *N*-Tosyl imines.<sup>2</sup>



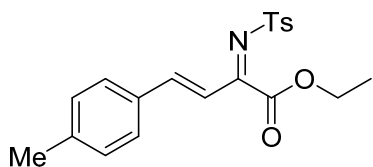
TiCl<sub>4</sub> (0.45 mL, 5.6 mmol) was added dropwise to a solution of keto ester (5.6 mmol), *p*-toluensulfonamide (0.95g, 5.6 mmol) and triethylamine (1.55 mL, 11.2 mmol) in dry dichloromethane (17 ml) at 0 °C under nitrogen. The mixture was heated at reflux temperature for 24 h and, after cooling to room temperature, treated with water (150 ml), extracted with dichloromethane (4 × 80 mL), dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Column chromatography on silica gel eluting with hexane:EtOAc mixtures afforded imines **1**.

**Ethyl (2Z,3E)-4-phenyl-2-(tosylimino)but-3-enoate (1a).**



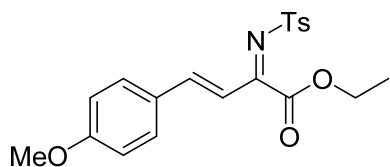
Yield 54%; yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.60–7.28 (m, 6H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 16.5 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.6 (C), 164.4 (C), 149.4 (C), 144.7 (C), 135.8 (C), 133.9 (CH), 131.7 (CH), 129.7 (2CH), 129.6 (3CH), 129.1 (CH), 128.7 (CH), 128.0 (CH), 123.5 (CH), 63.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 357.1037 (M<sup>+</sup>), C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>S requires 357.1035.

**Ethyl (2Z,3E)-4-(*p*-tolyl)-2-(tosylimino)but-3-enoate (1b).**



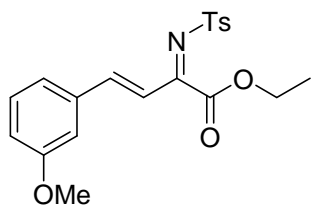
Yield 76%; yellow solid, m.p. 112-116 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 16.4 Hz, 1H overlapped), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 16.4 Hz, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 168.0 (C), 164.8 (C), 149.7 (C), 144.7 (C), 142.9 (C), 131.5 (2CH), 130.1 (4CH), 129.8 (2CH), 128.9 (CH), 128.1 (CH), 122.9 (C), 63.3 (CH<sub>2</sub>), 21.8 (2CH<sub>3</sub>), 14.1 (CH<sub>3</sub>); HRMS (ESI) 371.1195 (M<sup>+</sup>), C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub>S requires 371.1191.

**Ethyl (2Z,3E)-4-(4-methoxyphenyl)-2-(tosylimino)but-3-enoate (1c)**



Yield 67%; yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 16.5 Hz, 1H overlapped), 7.32 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 16.5 Hz, 1H), 4.53 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.9 (C), 164.7 (C), 162.7 (C), 149.4 (C), 144.4 (C), 130.7 (CH), 129.6 (2CH), 127.8 (CH), 126.7 (2CH), 120.9 (C), 114.7 (4CH), 63.0 (CH<sub>2</sub>), 55.4 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 388.1215 (M<sup>+</sup>+H), C<sub>20</sub>H<sub>21</sub>NO<sub>5</sub>S<sup>+</sup> requires 388.1213.

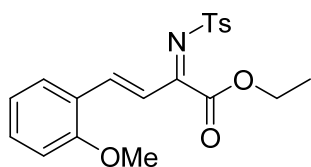
**Ethyl (2Z,3E)-4-(3-methoxyphenyl)-2-(tosylimino)but-3-enoate (1d).**



Yield 47%; yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.40-7.27 (m, 2H overlapped), 7.09 (d, *J* = 7.2 Hz, 1H), 6.99 (s, 1H overlapped), 6.98 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 16.5 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.43 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.6 (C), 164.4 (C), 160.0 (2C), 149.3 (C),

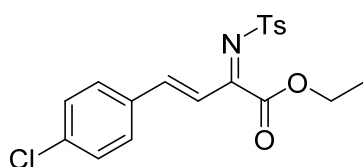
144.7 (C), 135.4 (CH), 130.1 (2CH), 129.7 (2CH), 128.0 (CH), 123.7 (CH), 121.5 (CH), 117.9 (CH), 113.0 (CH), 63.1 (CH<sub>2</sub>), 55.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 388.1215 (M<sup>+</sup>+H), C<sub>20</sub>H<sub>21</sub>NO<sub>5</sub>S<sup>+</sup> requires 388.1213.

**Ethyl (2Z,3E)-4-(2-methoxyphenyl)-2-(tosylimino)but-3-enoate (1e).**



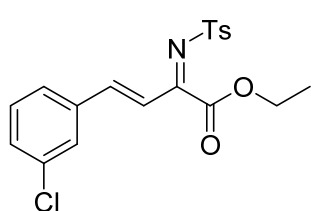
Yield 53%; yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 16.5 Hz, 1H), 7.45–7.30 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.03–6.84 (m, 3H), 4.55 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 168.6 (C), 164.7 (C), 158.7 (C), 145.2 (C), 144.5 (C), 133.3 (CH), 129.6 (2CH), 129.5 (C), 129.1 (CH), 128.0 (CH), 123.8 (CH), 122.9 (CH), 120.9 (CH), 111.3 (2CH), 62.9 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 388.1215 (M<sup>+</sup>+H), C<sub>20</sub>H<sub>21</sub>NO<sub>5</sub>S<sup>+</sup> requires 388.1213.

**Ethyl (2Z,3E)-4-(4-chlorophenyl)-2-(tosylimino)but-3-enoate (1f).**



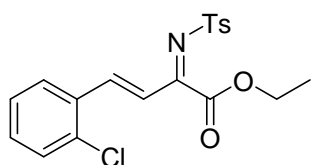
Yield 41%; yellow solid, m.p. 70-73 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.50–7.27 (m, 7H), 6.78 (d, *J* = 16.5 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.2 (C), 164.4 (C), 147.5 (C), 144.8 (C), 137.8 (C), 135.7 (C), 132.4 (CH), 129.7 (3CH), 129.5 (4CH), 128.0 (CH), 124.0 (CH), 63.3 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 391.0645 (M<sup>+</sup>), C<sub>19</sub>H<sub>18</sub>ClNO<sub>4</sub>S requires 391.0645.

**Ethyl (2Z,3E)-4-(3-chlorophenyl)-2-(tosylimino)but-3-enoate (1g).**

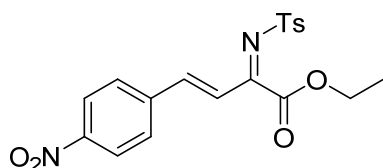


Yield 57%; pale yellow solid, m.p. 84-86 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.41–7.26 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 16.4 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.0 (C), 164.2 (C), 147.1 (C), 144.8 (C), 135.6 (C), 135.2 (C), 131.4 (CH), 130.3 (3CH), 129.7 (2CH), 128.3 (CH), 128.0 (CH), 126.6 (CH), 124.8 (CH), 63.3 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 391.0646 (M<sup>+</sup>), C<sub>19</sub>H<sub>18</sub>ClNO<sub>4</sub>S requires 391.0645.

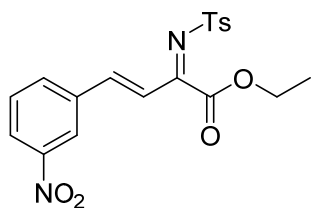
**Ethyl (2Z,3E)-4-(2-chlorophenyl)-2-(tosylimino)but-3-enoate (1h).**



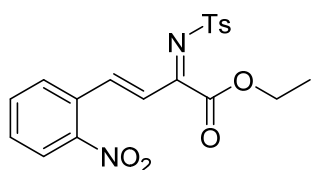
Yield 58%; white solid, m.p. 117-120 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 16.6 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.38–7.28 (m, 2H overlapped), 7.35 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 16.6 Hz, 1H), 4.57 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.6 (C), 164.2 (C), 144.9 (C), 144.8 (C), 135.6 (C), 135.5 (C), 132.3 (CH), 132.0 (CH), 130.4 (2CH), 129.7 (2CH), 128.1 (CH), 127.5 (CH), 127.4 (CH), 125.8 (CH), 63.2 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>), 14.1 (CH<sub>3</sub>); HRMS (ESI) 391.0647 (M<sup>+</sup>), C<sub>19</sub>H<sub>18</sub>ClNO<sub>4</sub>S requires 391.0645.

**Ethyl (2Z,3E)-4-(4-nitrophenyl)-2-(tosylimino)but-3-enoate (1i).**

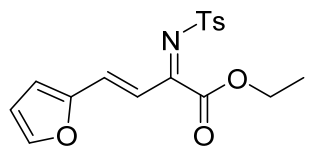
Yield 42%; white solid, m.p. 119-121 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.1, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 16.5 Hz, 1H overlapped), 7.36 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 16.5 Hz, 1H), 4.56 (q, *J* = 7.0, 2H), 2.45 (s, 3H), 1.50 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 166.4 (C), 164.0 (C), 149.0 (C), 145.1 (C), 139.7 (C), 129.8 (4CH), 129.1 (CH), 128.2 (CH), 127.4 (C), 124.3 (4CH), 63.5 (CH<sub>2</sub>), 21.69 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 425.0083, C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>6</sub>S<sup>+</sup> requires 425.0078.

**Ethyl (2Z,3E)-4-(3-nitrophenyl)-2-(tosylimino)but-3-enoate (1j).**

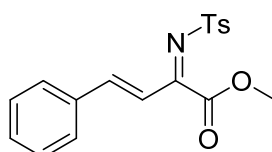
Yield 45%; white solid, m.p. 124-125 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 16.5 Hz, 1H overlapped), 7.36 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 16.5 Hz, 1H), 4.56 (q, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 166.5 (C), 164.0 (C), 148.7 (C), 145.3 (C), 145.1 (C), 135.6 (C), 133.7 (2CH), 130.2 (2CH), 129.8 (2CH), 128.1 (CH), 126.3 (CH), 125.6 (CH), 123.0 (CH), 63.5 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 425.0080, C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>6</sub>S<sup>+</sup> requires 425.0078.

**Ethyl (2Z,3E)-4-(2-nitrophenyl)-2-(tosylimino)but-3-enoate (1k).**

Yield 38%; pale yellow solid, m.p. 161-162 °C (hexane-EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.76-7.50 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 16.4 Hz, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.1 (C), 163.9 (C), 147.9 (C), 145.1 (C), 144.3 (CH), 135.2 (C), 133.9 (CH), 131.3 (CH), 130.0 (C), 129.8 (2CH), 128.9 (CH), 128.2 (2CH), 128.1 (CH), 125.3 (CH), 63.4 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 425.0076, C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>6</sub>S<sup>+</sup> requires 425.0078.

**Ethyl (2Z,3E)-4-(furan-2-yl)-2-(tosylimino)but-3-enoate (1l).**

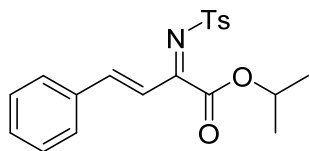
Yield 52%; brown oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 16.1 Hz, 1H), 6.75 (s, 1H overlapped), 6.69 (d, *J* = 16.1 Hz, 1H), 6.53 (s, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.2 (C), 164.5 (C), 150.8 (2CH), 146.7 (CH), 144.8 (C), 136.0 (CH), 134.3 (CH), 129.6 (2CH), 127.9 (CH), 120.8 (C), 118.1 (CH), 113.3 (CH), 63.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); HRMS (ESI) 348.0898 (M<sup>+</sup>+H), C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>O<sub>6</sub>S<sup>+</sup> requires 348.0900.

**Methyl (2Z,3E)-4-phenyl-2-(tosylimino)but-3-enoate (1m).**

Yield 50%; brown oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.66-7.29 (m, 6H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 16.4 Hz, 1H), 4.07 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ

167.4 (C), 164.9 (C), 149.6 (C), 144.8 (C), 135.7 (C), 133.9 (CH), 131.8 (CH), 129.7 (2CH), 129.1 (4CH), 128.7 (CH), 128.0 (CH), 123.4 (CH), 53.0 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>); HRMS (ESI) 343.0880 (M<sup>+</sup>), C<sub>18</sub>H<sub>17</sub>NO<sub>4</sub>S requires 343.0878.

### Isopropyl (2Z,3E)-4-phenyl-2-(tosylimino)but-3-enoate (1n).

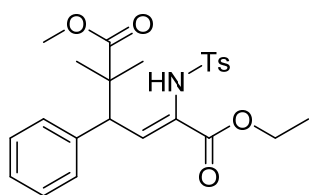


Yield 50%, orange oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.64–7.29 (m, 6H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 16.4 Hz, 1H), 5.45 (hept, *J* = 6.3 Hz, 1H), 2.43 (s, 3H), 1.48 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 167.8 (C), 164.0 (C), 149.1 (C), 144.6 (C), 135.9 (C), 133.9 (2CH), 131.7 (CH), 129.7 (2CH), 129.1 (3CH), 128.6 (CH), 128.0 (CH), 123.7 (CH), 71.58 (CH), 21.65 (CH<sub>3</sub>), 21.62 (CH<sub>3</sub>); HRMS (ESI) 371.1196 (M<sup>+</sup>), C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub>S requires 371.1191.

### General procedure for the non-catalysed Mukaiyama-Michael reaction.

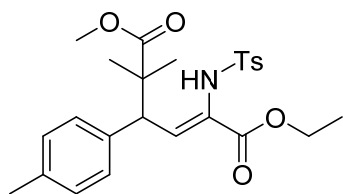
2-Methyl-1-methoxy-1-trimethylsilyloxyprop-1-ene (**2**, 122 μL, 0.6 mmol) was added to a solution of imine **1** (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) at rt under nitrogen atmosphere and the mixture was stirred overnight until the reaction was complete (20-24h). The reaction products were isolated by column chromatography on silica gel eluting with hexane/EtOAc mixtures.

### (Z)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-phenylhex-2-enedioate (3a)



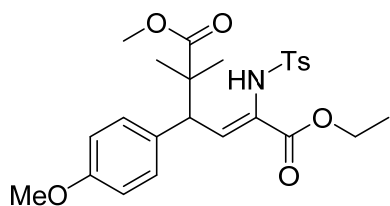
Yield 84%; colourless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.4 Hz, 2H) 7.31 (d, *J* = 11.4, 1H overlapped), 7.30-7.27 (m, 3H), 7.17-7.15 (m, 2H overlapped), 7.16 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.96 (2 overlapped q, *J* = 7.2 Hz, 2H), 3.65 (s, 3H), 2.36 (s, 3H), 1.18 (s, 3H), 1.17 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.9 (C), 164.2 (C), 143.7 (C), 140.5 (C), 138.1 (C), 136.0 (C), 129.5 (CH), 129.3 (CH), 128.1 (CH), 127.6 (CH), 127.2 (CH), 125.9 (C), 61.8 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 50.5 (C), 47.1 (CH), 23.9 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 458.1641 (M-H)<sup>-</sup>, C<sub>24</sub>H<sub>28</sub>NO<sub>6</sub>S<sup>-</sup> requires 458.1643.

### (Z)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(p-tolyl)hex-2-enedioate (3b)



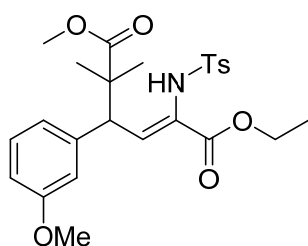
Yield 77%; pale yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 11.1 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.14 (s, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 3.96 (2 overlapped q, *J* = 7.2 Hz, 2H), 3.64 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 1.16 (s, 6H), 1.08 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 177.0 (C), 164.2 (C), 143.7 (C), 140.9 (C), 136.8 (C), 136.1 (C), 135.0 (C), 129.3 (CH), 128.8 (CH), 127.6 (CH), 125.8 (CH), 61.7 (CH<sub>2</sub>), 51.8 (CH<sub>3</sub>), 50.1 (C), 47.1 (CH), 23.8 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 472.1782 (M-H)<sup>-</sup>, C<sub>25</sub>H<sub>30</sub>NO<sub>6</sub>S<sup>-</sup> requires 472.1799.

**(Z)-1-Ethyl 6-methyl 4-(4-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3c)**



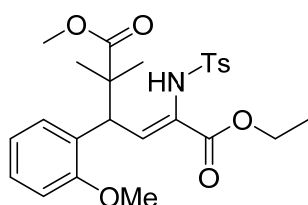
Yield 56%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.1$  Hz, 2H), 7.27 (d,  $J = 11.4$  Hz, 1H), 7.17 (d,  $J = 8.1$  Hz, 2H), 7.09 (d,  $J = 8.7$  Hz, 2H), 6.83 (d,  $J = 8.7$  Hz, 2H), 6.18 (s, 1H), 4.35 (d,  $J = 11.4$  Hz, 1H), 3.96 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.80 (s, 3H), 3.64 (s, 3H), 2.37 (s, 3H), 1.16 (s, 6H), 1.08 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.1 (C), 164.2 (C), 158.6 (C), 143.7 (C), 140.8 (C), 136.0 (C), 130.4 (CH), 130.1 (C), 129.3 (CH), 127.6 (CH), 125.6 (CH), 113.5 (CH), 61.7 ( $\text{CH}_2$ ), 55.1 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_3$ ), 49.7 (C), 47.2 (CH), 23.7 ( $\text{CH}_3$ ), 22.4 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 488.1747 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}^-$  requires 488.1748.

**(Z)-1-Ethyl 6-methyl 4-(3-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3d)**



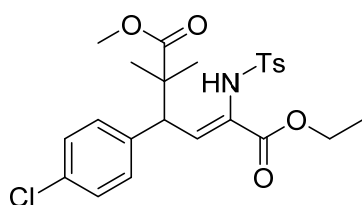
Yield 82%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 11.1$  Hz, 1H), 7.24-7.16 (m, 3H), 6.85-6.70 (m, 3H), 6.18 (s, 1H), 4.37 (d,  $J = 11.1$  Hz, 1H), 3.97 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.36 (s, 3H), 1.18 (s, 3H), 1.17 (s, 3H), 1.08 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9 (C), 164.2 (C), 159.2 (C), 143.8 (C), 140.5 (CH), 139.6 (C), 136.0 (C), 129.3 (CH), 128.9 (CH), 127.6 (CH), 126.0 (C), 121.8 (CH), 115.8 (CH), 112.2 (CH), 61.8 ( $\text{CH}_2$ ), 55.1 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_3$ ), 50.5 ( $\text{CH}_3$ ), 47.1 (C), 23.9 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 488.1746 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}^-$  requires 488.1748.

**(Z)-1-Ethyl 6-methyl 4-(2-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3e)**



Yellow oil; yield 72%;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 10.8$  Hz, 1H), 7.22-7.17 (m, 3H), 7.04 (dd,  $J = 7.8, 1.8$  Hz, 1H), 6.86 (2 overlapped t,  $J = 8.1$  Hz, 2H), 6.19 (s, 1H), 4.69 (d,  $J = 10.8$  Hz, 1H), 4.00 (q,  $J = 6.9$  Hz, 2H), 3.82 (s, 3H), 3.64 (s, 3H), 2.37 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.09 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2 (C), 164.4 (C), 157.4 (C), 143.4 (C), 140.2 (CH), 136.8 (CH), 130.0 (C), 129.2 (CH), 128.2 (C), 127.5 (CH), 127.0 (CH), 126.1 (C), 120.3 (CH), 111.1 (CH), 61.5 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 51.8 ( $\text{CH}_3$ ), 46.7 (C), 43.5 (CH), 24.6 ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 488.1752 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}^-$  requires 488.1748.

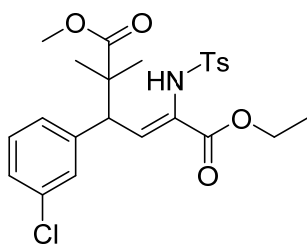
**(Z)-1-Ethyl 6-methyl 4-(4-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3f)**



Yield 80%; pale yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H), 7.26 (d,  $J = 11.4$  Hz, 1H), 7.15 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 6.28 (s, 1H), 4.46 (d,  $J = 11.4$  Hz, 1), 3.84 (m, 2H), 3.63

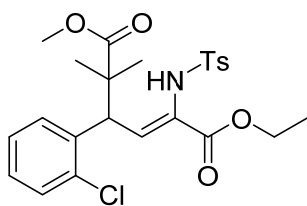
(s, 3H), 2.35 (s, 3H), 1.17 (s, 6H), 1.06 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5 (C), 163.9 (C), 143.8 (C), 139.9 (C), 136.7 (C), 135.7 (CH), 132.9 (C), 130.7 (CH), 129.3 (CH), 128.1 (CH), 127.5 (CH), 126.1 (C), 61.8 ( $\text{CH}_2$ ), 51.8 ( $\text{CH}_3$ ), 49.8 (CH), 47.0 (C), 23.5 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 492.1255 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{ClNO}_6\text{S}^-$  requires 492.1253.

**(Z)-1-Ethyl 6-methyl 4-(3-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3g)**



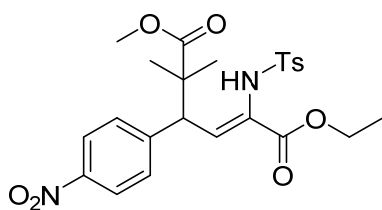
White oil; yield 87%;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.1$  Hz, 2H), 7.23 (d,  $J = 11.4$  Hz, 1H), 7.22-7.03 (m, 4H), 7.16 (d,  $J = 8.4$  Hz, 2H), 6.30 (s, 1H), 4.41 (d,  $J = 11.4$  Hz, 1H), 3.95 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.62 (s, 3H), 2.35 (s, 3H), 1.16 (s, 6H), 1.07 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5 (C), 163.9 (C), 143.8 (C), 140.2 (C), 139.4 (C), 135.8 (CH), 133.7 (C), 129.3 (CH), 129.18 (CH), 129.15 (CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 126.4 (CH), 125.2 (C), 61.9 ( $\text{CH}_2$ ), 51.9 ( $\text{CH}_3$ ), 50.1 (CH), 47.1 (C), 23.5 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 492.1255 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{ClNO}_6\text{S}^-$  requires 492.1253.

**(Z)-1-Ethyl 6-methyl 4-(2-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3h)**



Yield 95%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.4$  Hz, 2H), 7.38-7.35 (m, 1H), 7.35 (d,  $J = 10.5$  Hz, 1H), 7.19 (d,  $J = 8.4$  Hz, 2H), 7.17-7.09 (m, 3H), 6.11 (s, 1H), 5.03 (d,  $J = 10.5$  Hz, 1H), 3.95 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.66 (s, 3H), 2.36 (s, 3H), 1.26 (s, 3H), 1.22 (s, 3H), 1.01 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7 (C), 164.1 (C), 143.6 (C), 140.0 (CH), 136.7 (C), 136.6 (C), 135.2 (C), 130.1 (CH), 129.9 (CH), 129.3 (CH), 128.2 (CH), 127.4 (CH), 126.7 (C), 126.4 (CH), 61.7 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 47.4 (CH), 45.4 (C), 24.5 ( $\text{CH}_3$ ), 22.0 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 492.1255 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{ClNO}_6\text{S}^-$  requires 492.1253.

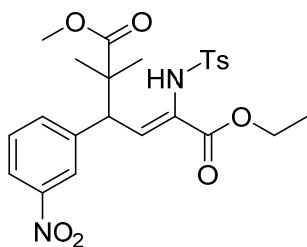
**(Z)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(4-nitrophenyl)hex-2-enedioate (3i)**



Yield 98%; pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 9.0$  Hz, 2H), 7.45-7.40 (m, 4H), 7.31 (d,  $J = 11.4$  Hz, 1H), 7.17 (d,  $J = 8.4$  Hz, 2H), 6.16 (s, 1H), 4.69 (d,  $J = 11.4$  Hz, 1H), 3.93 (m, 2H), 3.65 (s, 3H), 2.36 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 1.05 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0 (C), 163.4 (C), 147.0 (C), 146.1 (C), 144.1 (C), 139.1 (CH), 135.5 (C), 130.4 (CH), 129.4 (CH), 127.5 (CH), 126.8 (C), 123.2 (CH), 62.1 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 50.6 (CH), 47.3 (C), 23.5 ( $\text{CH}_3$ ), 23.0 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 503.1489 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

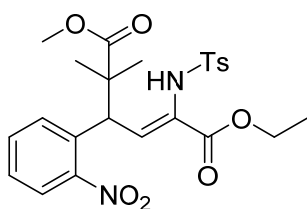


**(Z)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(3-nitrophenyl)hex-2-enedioate (3j)**



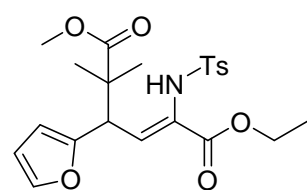
Yield 99%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (ddd,  $J = 8.1, 2.4, 1.2$  Hz, 1H), 8.03 (t,  $J = 2.1$  Hz, 1H), 7.61 (dt,  $J = 7.8, 1.2$  Hz, 1H), 7.49 (t,  $J = 8.1$  Hz, 1H), 7.43 (d,  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 11.4$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 2H), 6.21 (s, 1H), 4.65 (d,  $J = 11.4$  Hz, 1H), 4.10-3.93 (m, 2H), 3.65 (s, 3H), 2.35 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 1.07 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0 (C), 163.6 (C), 147.9 (C), 144.1 (C), 140.5 (C), 138.8 (CH), 136.3 (CH), 135.6 (C), 129.4 (CH), 128.9 (CH), 127.4 (CH), 126.9 (C), 123.6 (CH), 122.2 (CH), 62.1 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 50.3 (CH), 47.2 (C), 23.2 ( $\text{CH}_3$ ), 23.0 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 503.1497 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

**(Z)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(2-nitrophenyl)hex-2-enedioate (3k)**



Yield 58%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (dd,  $J = 8.1, 1.5$  Hz, 1H), 7.67 (d,  $J = 8.4$  Hz, 2H), 7.51 (td,  $J = 7.8, 1.5$  Hz, 1H), 7.38 (td,  $J = 7.8, 1.5$  Hz, 1H), 7.31 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.21 (d,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 10.2$  Hz, 1H), 6.65 (s, 1H), 4.93 (d,  $J = 10.2$  Hz, 1H), 4.06 (q,  $J = 7.2$  Hz, 2H), 3.59 (s, 3H), 2.36 (s, 3H), 1.18 (s, 3H), 1.15 (t,  $J = 7.2$  Hz, 3H), 1.08 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.9 (C), 164.01 (C), 150.6 (C), 143.7 (C), 136.9 (C), 134.0 (CH), 133.0 (C), 132.1 (CH), 130.6 (CH), 129.3 (CH), 129.1 (C), 128.1 (CH), 127.4 (CH), 124.9 (C), 61.8 ( $\text{CH}_2$ ), 52.1 ( $\text{CH}_3$ ), 47.0 (CH), 42.8 (C), 23.3 ( $\text{CH}_3$ ), 23.2 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 503.1496 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

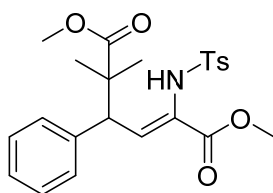
**(Z)-1-Ethyl 6-methyl 4-(furan-2-yl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (3l)**



Yellow oil; yield 69%;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.4$  Hz, 2H), 7.33 (dd,  $J = 1.8, 0.9$  Hz, 1H), 7.18 (d,  $J = 8.7$  Hz, 2H), 7.04 (d,  $J = 11.4$  Hz, 1H), 6.40 (s, 1H), 6.30 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.12 (dt,  $J = 3.3, 0.6$  Hz, 1H), 4.56 (d,  $J = 11.4$  Hz, 1H), 4.02-3.90 (m, 2H), 3.66 (s, 3H), 2.36 (s, 3H), 1.19 (s, 3H), 1.15 (s, 3H), 1.08 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8 (C), 164.0 (C), 151.6 (C), 143.8 (C), 141.7 (CH), 137.1 (CH), 136.0 (C), 129.3 (CH), 127.5 (HC), 126.4 (C), 110.1 (CH), 108.3 (CH), 61.8 ( $\text{CH}_2$ ), 52.1 ( $\text{CH}_3$ ), 46.9 (CH), 44.5 (C), 23.5 ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 448.1437 (M-H) $^-$ ,  $\text{C}_{22}\text{H}_{26}\text{NO}_7\text{S}^-$  requires 448.1435.

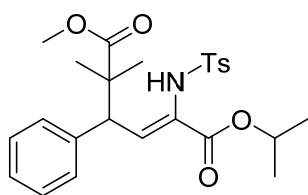
**(Z)-Dimethyl enedioate (3m)**

**5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-phenylhex-2-**



Yield 82%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 11.1$  Hz, 1H overlapped), 7.30-7.25 (m, 3H), 7.17-7.11 (m, 4H), 6.23 (s, 1H), 4.35 (d,  $J = 11.1$  Hz, 1H), 3.64 (s, 3H), 3.52 (s, 3H), 2.37 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0 (C), 164.7 (C), 143.7 (C), 140.6 (CH), 137.9 (C), 136.0 (C), 129.5 (CH), 129.3 (CH), 128.1 (CH), 127.5 (CH), 127.2 (CH), 125.8 (C), 52.5 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_3$ ), 50.4 (C), 47.1 (CH), 24.0 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ); HRMS (ESI) 444.1492 (M-H) $^-$ ,  $\text{C}_{23}\text{H}_{26}\text{NO}_6\text{S}^-$  requires 444.1486.

**(Z)-1-Isopropyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-phenylhex-2-enedioate (3n)**

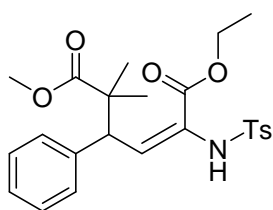


Yield 75%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.4$  Hz, 2H), 7.31-7.26 (m, 3H), 7.29 (d,  $J = 11.4$  Hz, 1H overlapped), 7.19-7.14 (m, 4H), 6.24 (s, 1H), 4.79 (hept,  $J = 6.3$  Hz, 1H), 4.45 (d,  $J = 11.4$  Hz, 1H), 3.65 (s, 3H), 2.36 (s, 3H), 1.19 (s, 6H), 1.11 (d,  $J = 6.3$  Hz, 3H), 1.04 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8 (C), 163.7 (C), 143.7 (C), 140.1 (C), 138.2 (C), 135.9 (C), 129.4 (CH), 129.3 (CH), 128.0 (CH), 127.6 (CH), 127.1 (CH), 126.1 (C), 69.7 (CH), 51.8 ( $\text{CH}_3$ ), 50.4 (C), 47.1 (CH), 23.7 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 21.3 ( $\text{CH}_3$ ); HRMS (ESI) 472.1784 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_6\text{S}^-$  requires 472.1799.

**Experimental procedure for the copper-catalysed Mukaiyama-Michael reaction.**

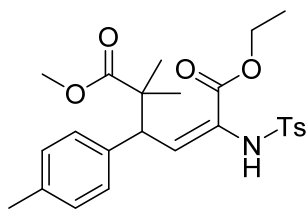
A solution of imine **1** (0.25 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (1 mL) was added to a suspension of anhydrous  $\text{Cu}(\text{OTf})_2$  (9 mg, 0.025 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (0.9 mL) contained in a Schlenk tube under nitrogen at rt, followed by 2-methyl-1-methoxy-1-trimethylsilyoxyprop-1-ene (**2**, 122  $\mu\text{L}$ , 0.6 mmol). The mixture was stirred until the reaction was complete (30-90 min). The reaction products were isolated by column chromatography on silica gel eluting with hexane/EtOAc mixtures.

**(E)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-phenylhex-2-enedioate (4a)**



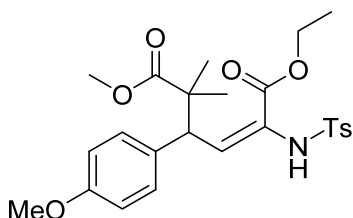
Yield 95%; colourless oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.1$  Hz, 2H), 7.29-7.22 (m, 3H), 7.14-7.09 (m, 4H), 7.01 (d,  $J = 11.4$  Hz, 1H), 6.61 (s, 1H), 4.81 (d,  $J = 11.4$  Hz, 1H), 4.00 (q,  $J = 6.9$  Hz, 2H), 3.59 (s, 3H), 2.36 (s, 3H), 1.173 (s, 3H), 1.168 (s, 3H), 1.12 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2 (C), 162.9 (C), 143.8 (C), 139.7 (C), 136.3 (C), 135.9 (C), 129.4 (CH), 129.3 (CH), 128.0 (CH), 127.5 (CH), 127.0 (CH), 124.8 (C), 61.8 ( $\text{CH}_2$ ), 51.7 ( $\text{CH}_3$ ), 50.4 (C), 46.8 (CH), 23.1 ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 458.1644 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{28}\text{NO}_6\text{S}^-$  requires 458.1643.

**(E)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(p-tolyl)hex-2-enedioate (4b)**



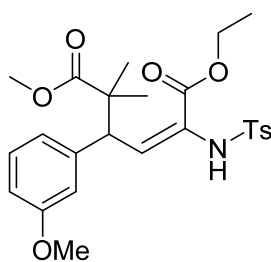
Yield 99%; pale yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 7.06 (d,  $J = 8.1$  Hz, 2H), 6.974 (d,  $J = 11.4$  Hz, 1H), 6.972 (d,  $J = 8.1$  Hz, 2H), 6.58 (br s, 1H), 4.77 (d,  $J = 11.4$  Hz, 1H), 4.00 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.59 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 1.15 (s, 6H), 1.12 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8 (C), 163.0 (C), 143.7 (C), 136.54 (C), 136.51 (C), 129.4 (CH), 129.1 (CH), 128.7 (CH), 127.5 (CH), 124.6 (CH), 124.5 (CH), 61.8 ( $\text{CH}_2$ ), 51.6 ( $\text{CH}_3$ ), 50.0 (C), 46.8 (CH), 23.2 ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 21.0 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 472.1782 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_6\text{S}^-$  requires 472.1799.

**(E)-1-Ethyl 6-methyl 4-(4-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4c)**



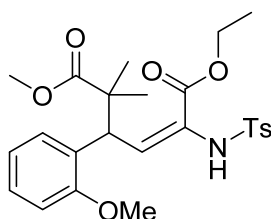
Yield 95%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 7.02 (d,  $J = 8.7$  Hz, 2H), 6.96 (d,  $J = 11.4$  Hz, 1H), 6.80 (d,  $J = 8.7$  Hz, 2H), 6.58 (s, 1H), 4.76 (d,  $J = 11.4$  Hz, 1H), 3.99 (q,  $J = 7.2$  Hz, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.14 (s, 6H), 1.11 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8 (C), 162.9 (C), 158.5 (C), 143.8 (C), 136.8 (C), 136.0 (C), 131.7 (C), 130.2 (CH), 129.4 (CH), 127.5 (CH), 124.5 (CH), 113.4 (CH), 61.8 ( $\text{CH}_2$ ), 55.2 ( $\text{CH}_3$ ), 51.7 ( $\text{CH}_3$ ), 49.6 (C), 46.8 (CH), 23.1 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 488.1741 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}^-$  requires 488.1748.

**(E)-1-Ethyl 6-methyl 4-(3-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4d)**



Yield 99%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.4$  Hz, 2H), 7.17 (t,  $J = 8.1$  Hz, 1H), 7.12 (d,  $J = 8.7$  Hz, 2H), 6.97 (d,  $J = 11.4$  Hz, 1H), 6.77 (ddd,  $J = 8.1, 2.7, 0.9$  Hz, 1H), 6.67 (d,  $J = 8.1$  Hz, 1H), 6.66 (s, 1H overlapped), 6.59 (s, 1H), 4.79 (d,  $J = 11.4$  Hz, 1H), 4.00 (q,  $J = 7.2$  Hz, 2H), 3.78 (s, 3H), 3.60 (s, 3H), 2.35 (s, 3H), 1.167 (s, 3H), 1.165 (s, 3H), 1.12 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9 (C), 164.1 (C), 159.2 (C), 143.8 (C), 140.5 (C), 139.6 (CH), 136.0 (C), 129.3 (CH), 128.9 (CH), 127.6 (CH), 126.0 (C), 121.8 (CH), 115.8 (CH), 112.2 (CH), 61.8 ( $\text{CH}_2$ ), 55.1 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_3$ ), 50.5 ( $\text{CH}_3$ ), 47.1 (C), 23.9 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 488.1749 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}^-$  requires 488.1748.

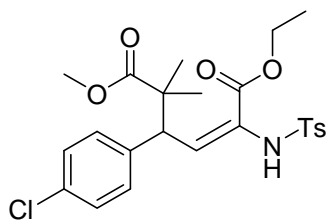
**(E)-1-Ethyl 6-methyl 4-(2-methoxyphenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4e)**



Yield 91%; yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.4$  Hz, 2H), 7.19 (td,  $J = 7.8, 1.8$  Hz, 1H), 7.12 (d,  $J = 8.7$  Hz, 2H), 7.06 (d,  $J = 11.1$  Hz, 1H), 7.04 (dd,  $J = 7.8, 1.8$  Hz, 1H), 6.87 (t,  $J = 7.8$  Hz, 1H), 6.83 (d,  $J = 7.8$  Hz, 1H), 6.57 (s, 1H), 5.18 (d,  $J = 11.1$  Hz, 1H), 4.00 (q,  $J = 7.2$  Hz, 2H), 3.76 (s, 3H), 3.60 (s, 3H), 2.34 (s, 3H), 1.14 (s, 6H), 1.08 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8

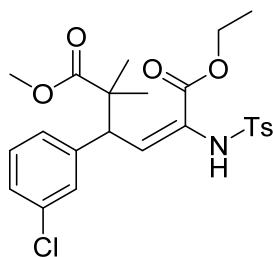
(C), 163.4 (C), 157.2 (C), 143.6 (C), 137.0 (CH), 136.0 (C), 130.4 (CH), 129.3 (CH), 128.2 (C), 127.9 (CH), 127.5 (CH), 124.3 (C), 120.1 (CH), 110.5 (CH), 61.7 (CH<sub>2</sub>), 55.1 (CH<sub>3</sub>), 51.6 (CH<sub>3</sub>), 46.8 (C), 43.7 (CH), 23.9 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>); HRMS (ESI) 488.1752 (M-H)<sup>-</sup>, C<sub>25</sub>H<sub>30</sub>NO<sub>7</sub>S<sup>-</sup> requires 488.1748.

**(E)-1-Ethyl 6-methyl 4-(4-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4f)**



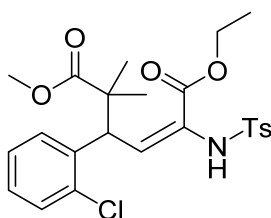
Yield 99%; colourless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 11.4 Hz, 1H), 6.62 (s, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 2.37 (s, 3H), 1.14 (s, 6H), 1.11 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.5 (C), 162.6 (C), 144.0 (C), 138.4 (C), 135.9 (C), 135.3 (CH), 132.8 (C), 130.6 (CH), 129.5 (CH), 128.2 (CH), 127.4 (CH), 125.2 (C), 61.9 (CH<sub>2</sub>), 51.8 (CH<sub>3</sub>), 49.7 (CH), 46.7 (C), 23.2 (CH<sub>3</sub>), 22.1 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 492.1257 (M-H)<sup>-</sup>, C<sub>24</sub>H<sub>27</sub>ClNO<sub>6</sub>S<sup>-</sup> requires 492.1253.

**(E)-1-Ethyl 6-methyl 4-(3-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4g)**



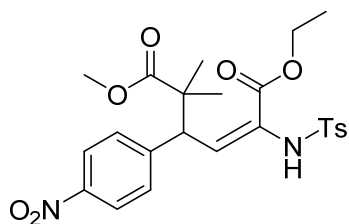
Yield 99%; white oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.20-7.19 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.04 (t, *J* = 0.9 Hz, 1H), 6.98 (m, 1H), 6.89 (d, *J* = 11.1 Hz, 1H), 6.67 (s, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.60 (s, 3H), 2.36 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.4 (C), 162.7 (C), 144.0 (C), 141.9 (C), 135.9 (C), 134.4 (CH), 133.8 (C), 129.5 (CH), 129.4 (CH), 129.2 (CH), 127.44 (CH), 127.38 (CH), 127.1 (CH), 125.4 (C), 62.0 (CH<sub>2</sub>), 51.8 (CH<sub>3</sub>), 50.0 (CH), 46.8 (C), 23.3 (CH<sub>3</sub>), 22.1 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 492.1255 (M-H)<sup>-</sup>, C<sub>24</sub>H<sub>27</sub>ClNO<sub>6</sub>S<sup>-</sup> requires 492.1253.

**(E)-1-Ethyl 6-methyl 4-(2-chlorophenyl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4h)**



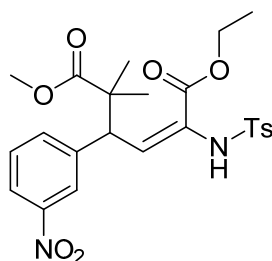
Yield 99%; pale yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.23-7.14 (m, 3H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 11.4 Hz, 1H), 6.65 (s, 1H), 5.35 (d, *J* = 11.4 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.62 (s, 3H), 2.35 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.3 (C), 163.2 (C), 143.8 (C), 137.7 (C), 135.8 (C), 134.8 (CH), 134.7 (C), 130.4 (CH), 129.8 (CH), 129.4 (CH), 128.1 (CH), 127.5 (CH), 126.5 (CH), 125.2 (C), 62.2 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 47.4 (CH), 45.4 (C), 24.0 (CH<sub>3</sub>), 22.3 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>); HRMS (ESI) 492.1258 (M-H)<sup>-</sup>, C<sub>24</sub>H<sub>27</sub>ClNO<sub>6</sub>S<sup>-</sup> requires 492.1253.

**(E)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(4-nitrophenyl)hex-2-enedioate (4i)**



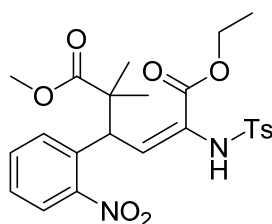
Yield 99%; pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.4$  Hz, 2H), 7.57 (d,  $J = 8.4$  Hz, 2H), 7.24 (d,  $J = 8.4$  Hz, 2H), 7.18 (d,  $J = 8.4$  Hz, 2H), 6.90 (d,  $J = 10.8$  Hz, 1H), 6.71 (s, 1H), 4.88 (d,  $J = 10.8$  Hz, 1H), 4.00 (q,  $J = 7.2$  Hz, 2H), 3.60 (s, 3H), 2.37 (s, 3H), 1.16 (s, 3H), 11.5 (s, 3H), 1.10 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1 (C), 162.2 (C), 147.7 (C), 146.7 (C), 144.2 (C), 135.9 (C), 133.3 (CH), 130.1 (CH), 129.6 (CH), 127.4 (CH), 126.0 (C), 123.0 (CH), 62.1 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 50.1 (CH), 46.8 (C), 23.4 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ); HRMS (ESI) 503.1491 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

**(E)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(3-nitrophenyl)hex-2-enedioate (4j)**



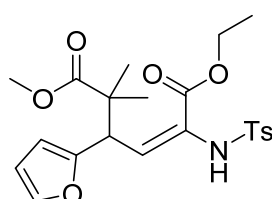
Yield 93%; pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09-8.05 (m, 1H), 7.91 (t,  $J = 1.4$  Hz, 1H), 7.59 (d,  $J = 8.4$  Hz, 2H) 7.44-7.42 (m, 2H), 7.18 (d,  $J = 8.4$  Hz, 2H), 6.89 (d,  $J = 10.8$  Hz, 1H), 6.74 (s, 1H), 4.88 (d,  $J = 10.8$  Hz, 1H), 4.03 (q,  $J = 6.9$  Hz, 2H), 3.62 (s, 3H), 2.36 (s, 3H), 1.16 (s, 6H), 1.12 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1 (C), 162.3 (C), 147.8 (C), 144.2 (C), 142.2 (C), 135.9 (C), 135.3 (CH), 132.8 (CH), 129.6 (CH), 128.8 (CH), 127.3 (CH), 126.1 (C), 124.0 (C), 122.0 (CH), 62.2 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 50.0 (CH), 46.8 (C), 23.5 ( $\text{CH}_3$ ), 21.9 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ). HRMS (ESI) 503.1495 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

**(E)-1-Ethyl 6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-(2-nitrophenyl)hex-2-enedioate (4k)**



Yield 99%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dd,  $J = 7.8$  Hz, 1H), 7.56-7.53 (m, 1H), 7.46-7.31 (m, 3H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.10 (d,  $J = 8.4$  Hz, 2H), 6.88 (d,  $J = 11.4$  Hz, 1H), 6.69 (s, 1H), 5.42 (d,  $J = 11.4$  Hz, 1H), 4.11 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.60 (s, 3H), 2.34 (s, 3H), 1.24 (s, 3H), 1.18 (s, 3H), 1.13 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.9 (C), 163.0 (C), 150.5 (C), 144.0 (C), 135.6 (C), 134.0 (C), 132.6 (CH), 132.0 (CH), 130.4 (CH), 129.5 (CH), 127.8 (CH), 127.4 (CH), 126.0 (C), 124.5 (CH), 62.5 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3$ ), 47.3 (CH), 42.9 (C), 23.6 ( $\text{CH}_3$ ), 23.3 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 503.1496 (M-H) $^-$ ,  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_8\text{S}^-$  requires 503.1494.

**(E)-1-Ethyl 6-methyl 4-(furan-2-yl)-5,5-dimethyl-2-(4-methylphenylsulfonamido)hex-2-enedioate (4l)**

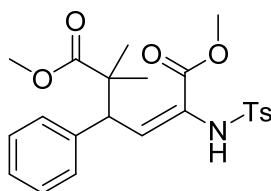


Yield 80%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 1.8$  Hz, 1H), 7.21 (d,  $J = 8.4$  Hz, 2H), 6.71 (s, 1H overlapped), 6.69 (d,  $J = 11.4$  Hz, 1H), 6.26 (dd,  $J = 3.3, 1.8$  Hz, 1H), 5.98 (d,  $J = 3.3$  Hz, 1H), 5.04 (d,  $J = 11.4$  Hz, 1H), 4.07 (2 overlapped q,  $J = 7.2$  Hz, 2H), 3.62 (s, 3H), 2.37 (s, 3H), 1.17 (t,  $J = 7.2$  Hz, 3H),

1.13 (s, 3H), 1.12 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6 (C), 163.0 (C), 153.1 (C), 143.9 (C), 141.5 (CH), 135.9 (C), 131.5 (CH), 129.5 (CH), 127.5 (CH), 125.7 (C), 111.0 (CH), 107.2 (CH), 62.1 ( $\text{CH}_2$ ), 51.9 ( $\text{CH}_3$ ), 46.7 (CH), 44.4 (C), 23.3 ( $\text{CH}_3$ ), 21.7 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ); HRMS (ESI) 448.1437 (M-H) $^-$ ,  $\text{C}_{22}\text{H}_{26}\text{NO}_7\text{S}^-$  requires 448.1435.

**(E)-Dimethyl  
enedioate (4m)**

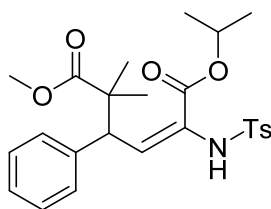
**5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-phenylhex-2-**



Yield 99%; pale yellow solid, m.p. 126-129 °C (hexane- $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.4$  Hz, 2H), 7.26-7.21 (m, 3H), 7.13 (d,  $J = 8.4$  Hz, 2H), 7.07 (dd,  $J = 7.6, 2.4$  Hz, 2H), 7.00 (d,  $J = 11.1$  Hz, 1H), 6.57 (s, 1H), 4.72 (d,  $J = 11.1$  Hz, 1H), 3.59 (s, 3H), 3.52 (s, 3H), 2.37 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7 (C), 163.4 (C), 144.0 (C), 140.0 (CH), 136.8 (C), 136.0 (C), 129.6 (CH), 129.4 (CH), 128.1 (CH), 127.7 (CH), 127.1 (CH), 124.8 (C), 52.4 ( $\text{CH}_3$ ), 51.9 ( $\text{CH}_3$ ), 50.7 (C), 46.9 (CH), 23.1 ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ); HRMS (ESI) 444.1491 (M-H) $^-$ ,  $\text{C}_{23}\text{H}_{26}\text{NO}_6\text{S}^-$  requires 444.1486.

**(E)-1-Isopropyl  
phenylhex-2-enedioate (4n)**

**6-methyl 5,5-dimethyl-2-(4-methylphenylsulfonamido)-4-**



Yield 87%; yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.4$  Hz, 2H), 7.31-7.23 (m, 3H), 7.14-7.08 (m, 4H), 6.98 (d,  $J = 11.7$  Hz, 1H), 6.60 (s, 1H), 4.89-4.83 (m, 2H), 3.59 (s, 3H), 2.34 (s, 3H), 1.17 (s, 6H), 1.15 (d,  $J = 6.3$  Hz, 3H), 1.04 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7 (C), 162.6 (C), 143.7 (C), 139.6 (C), 136.0 (C), 135.9 (C), 129.4 (CH), 129.3 (CH), 128.0 (CH), 127.5 (CH), 127.0 (CH), 125.0 (C), 70.1 (CH), 51.7 ( $\text{CH}_3$ ), 50.2 (C), 46.8 (CH), 23.3 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 21.43 ( $\text{CH}_3$ ), 21.41 ( $\text{CH}_3$ ); HRMS (ESI) 472.1780 (M-H) $^-$ ,  $\text{C}_{25}\text{H}_{30}\text{NO}_6\text{S}^-$  requires 472.1799.

### Application of $^1\text{H}$ NMR spectroscopic criteria by Mazurkiewicz et al. to determine the geometry of the double bond in compounds **3** and **4**.<sup>3</sup>

These criteria were established by Mazurkiewicz et al. to determine the configuration of the double bond in *N*-acyl- $\alpha,\beta$ -dehydro- $\alpha$ -amino acid esters. When we tried to apply them to *N*-tosyl- $\alpha,\beta$ -dehydro- $\alpha$ -amino acid esters we obtained contradictory results.

| Criterion <sup>3</sup>   | $\delta$ for <b>Z-3a</b>                                      | $\delta$ for <b>E-4a</b>                                   | criterion concordance |
|--|---|--|-----------------------|
| $\delta_{\text{CH}=\text{Z}} < \delta_{\text{CH}=\text{E}}$                              | 7.31  | 6.91   | –                     |
| $\delta_{\text{NH}=\text{Z}} < \delta_{\text{NH}=\text{E}}$                              | 6.16  | 6.65   | +                     |
|  | $\delta_{\text{CH}=\text{Z}} (\text{CDCl}_3)$ for <b>Z-3a</b> | $\delta_{\text{CH}=\text{Z}} (\text{TFA})$ for <b>Z-3a</b> |                       |
| $\delta_{\text{CH}=\text{Z}} (\text{CDCl}_3) < \delta_{\text{CH}=\text{Z}} (\text{TFA})$ | 7.31  | 7.64   | +                     |
|  | $\delta_{\text{CH}=\text{E}} (\text{CDCl}_3)$ for <b>E-4a</b> | $\delta_{\text{CH}=\text{E}} (\text{TFA})$ for <b>E-4a</b> |                       |
| $\delta_{\text{CH}=\text{E}} (\text{CDCl}_3) > \delta_{\text{CH}=\text{E}} (\text{TFA})$ | 6.91  | 7.04   | –                     |

### Literature

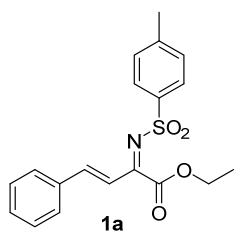
1. L.-Y Mei, Y. Wei, Q. Xu and M. Shi, *Organometallics*, 2012, **31**, 7591-7599.
2. J. Esquivias, R. Gomez Arrayas and J. C. Carretero, *J. Org. Chem.*, 2005, **70**, 7451-7454.
3. Mazurkiewicz, A. Kuznik, M. Grymel and N. Kuznik, *Magn. Reson. Chem.*, 2005, **43**, 36-40

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7.915  
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7.349  
7.337  
7.333  
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6.801

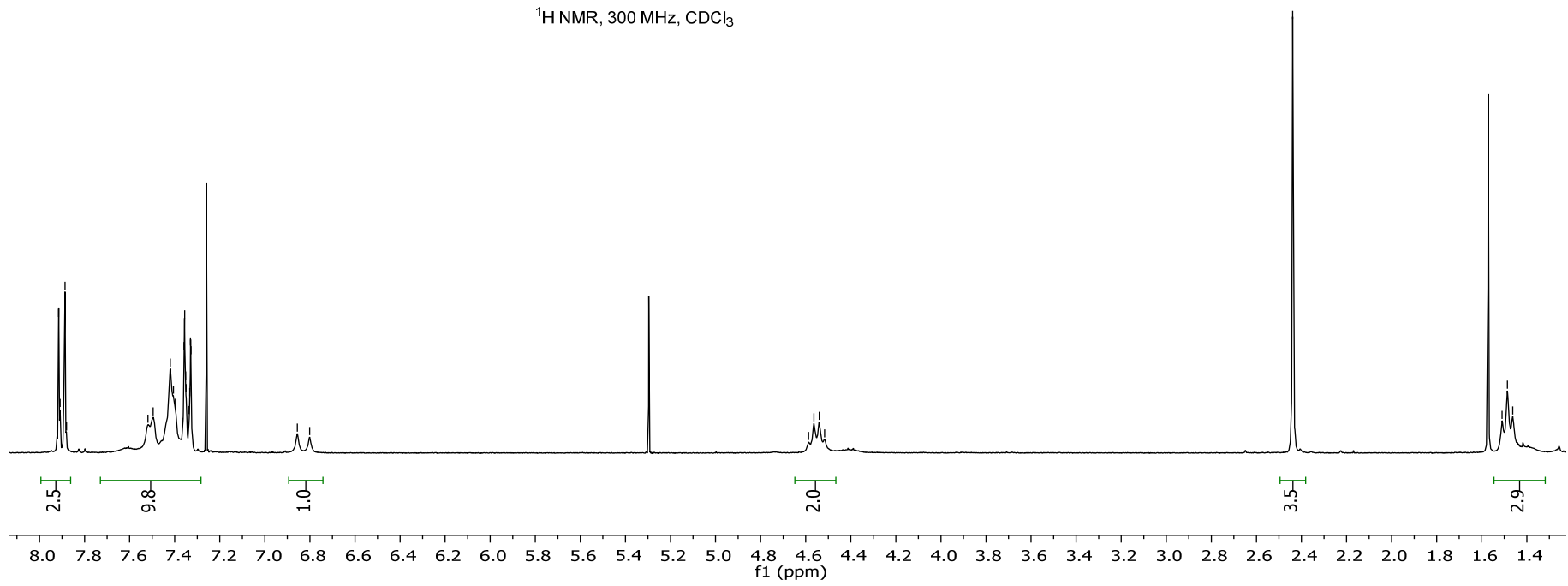
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4.516

— 2.439

1.510  
1.486  
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<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





— 167.62  
— 164.43

— 149.35  
— 144.68

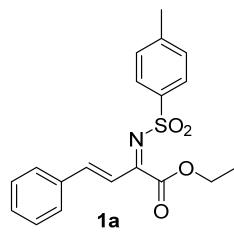
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128.66  
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123.51

77.42  
77.00  
76.58

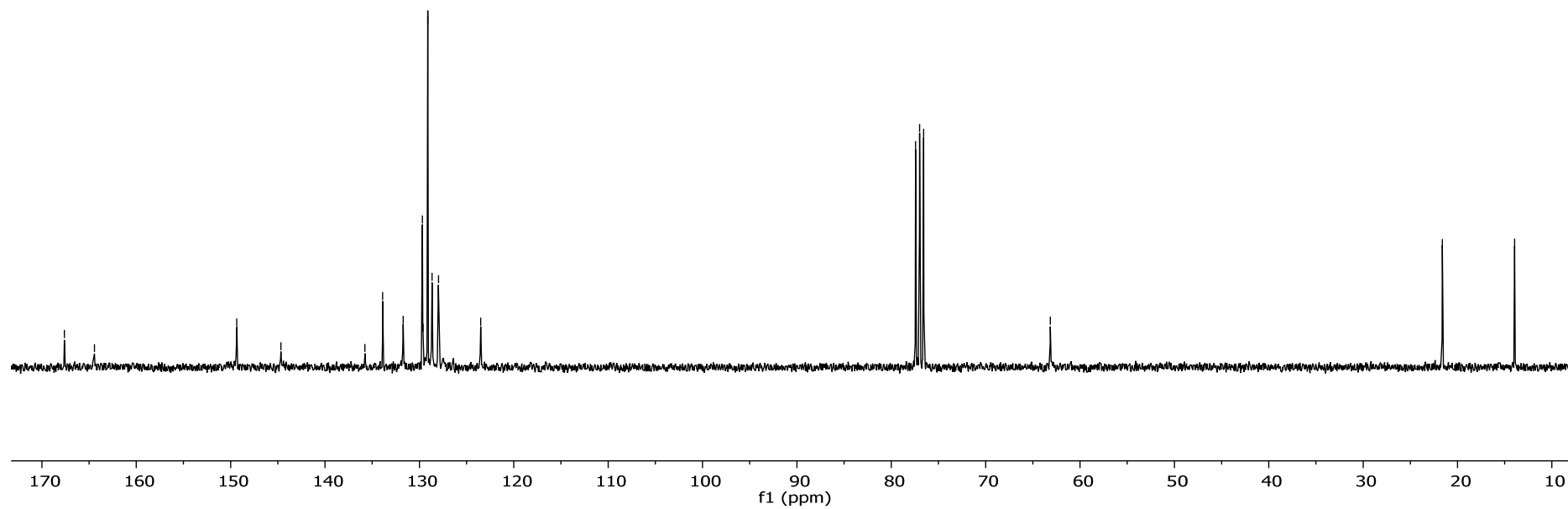
— 63.14

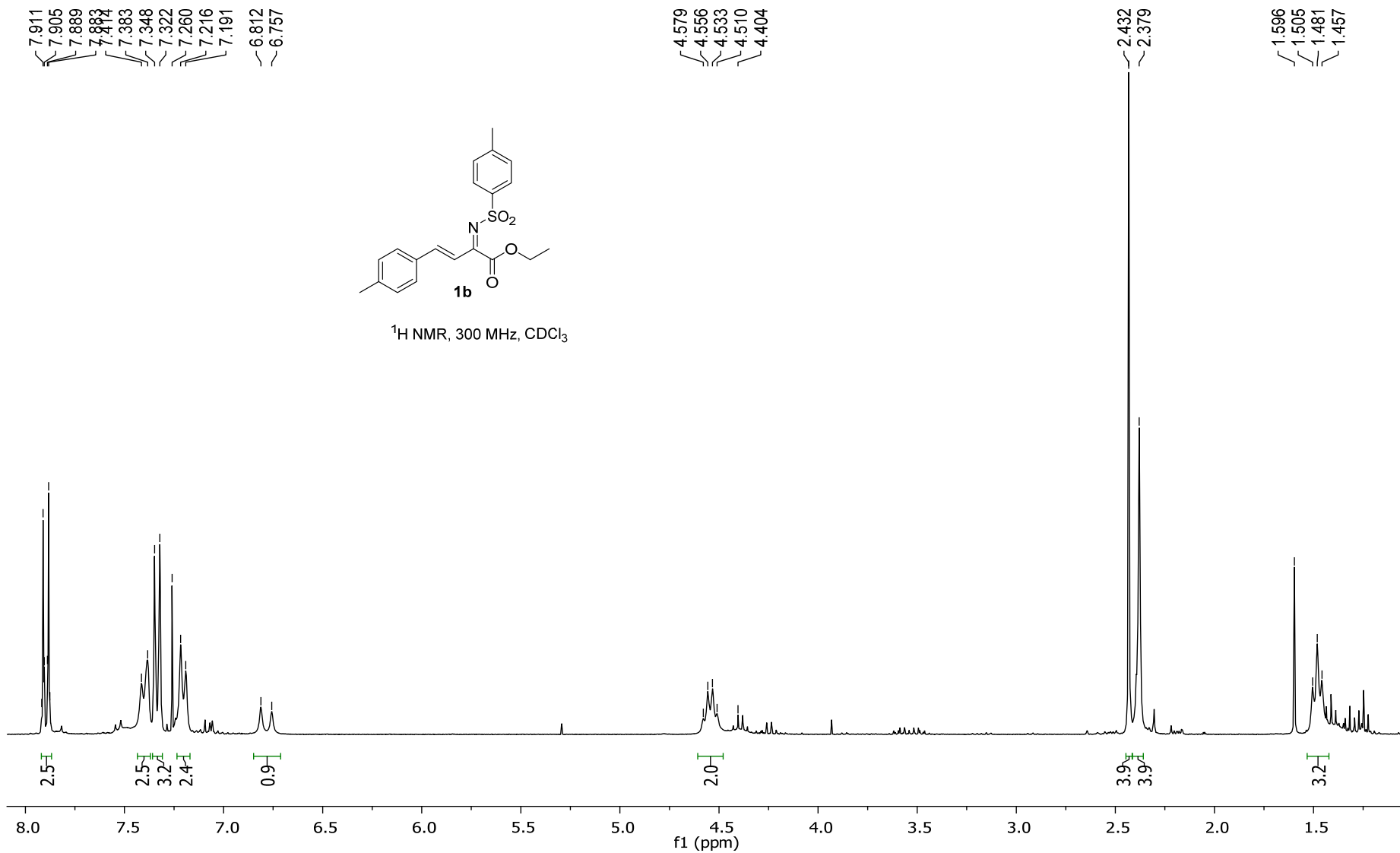
— 21.62

— 13.95



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>





— 167.83  
— 164.58

— 149.58  
— 144.57  
— 142.70

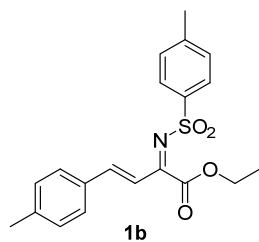
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128.76  
127.97  
— 122.50

77.42  
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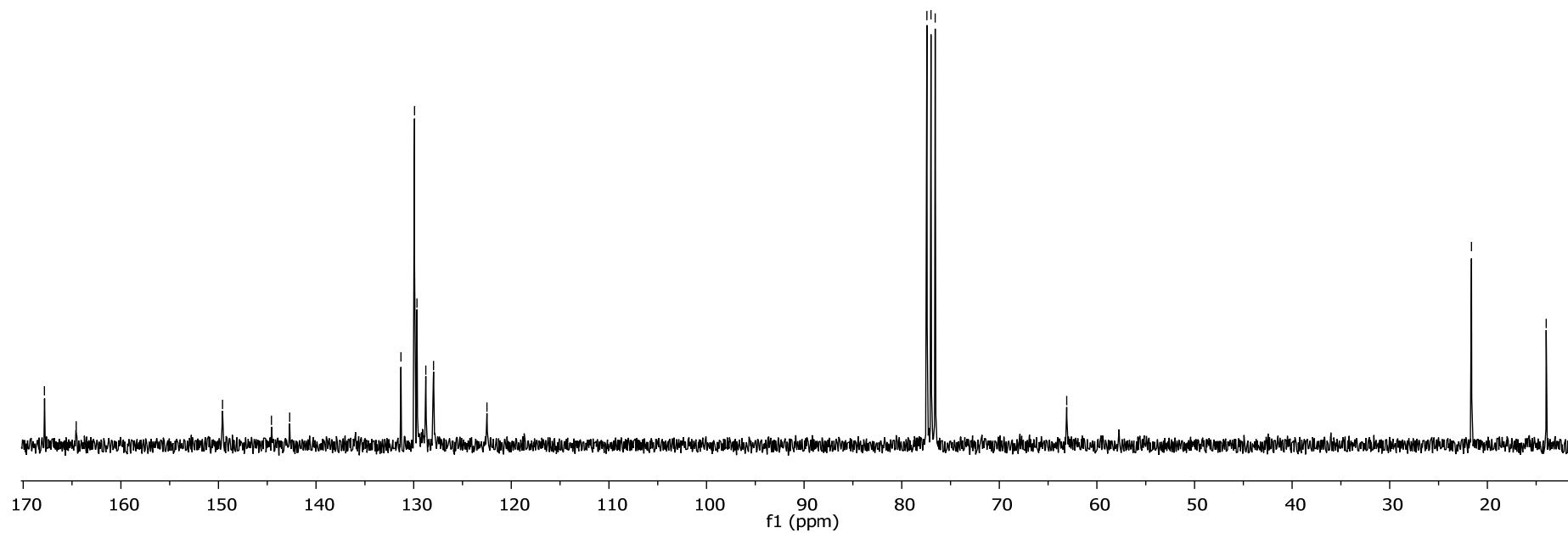
— 63.09

— 21.63

— 13.97



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



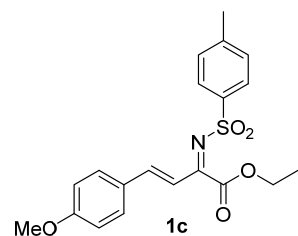
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7.260  
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6.885  
6.717  
6.662

4.544  
4.521  
4.501

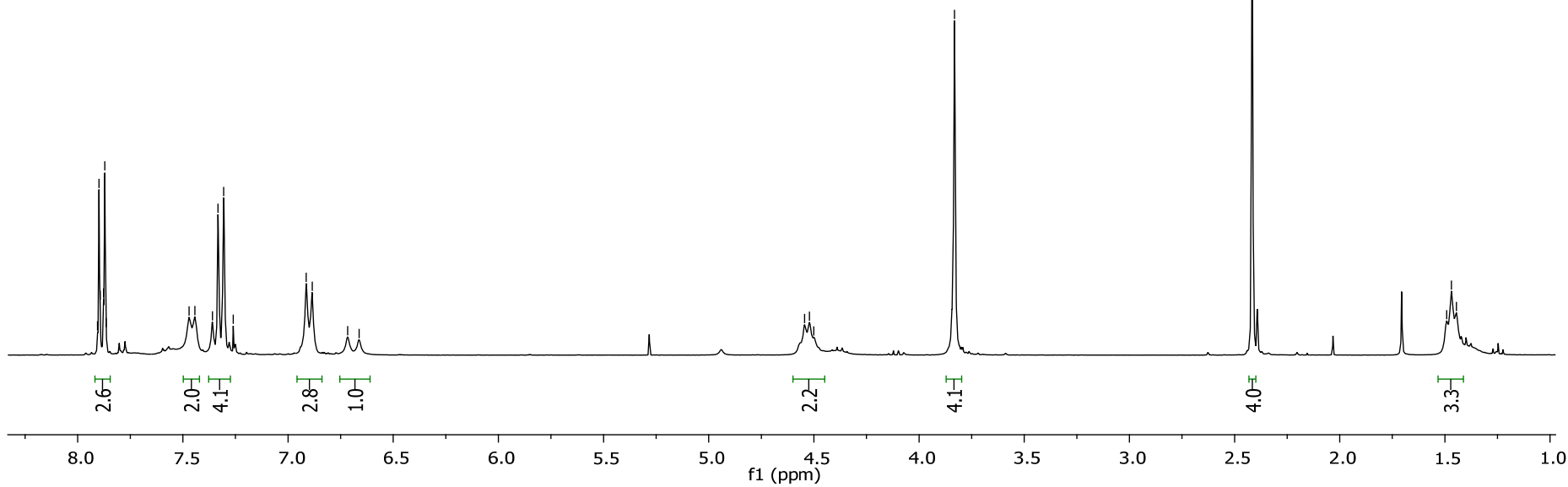
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2.416

1.492  
1.469  
1.445



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



167.87  
164.70  
162.73

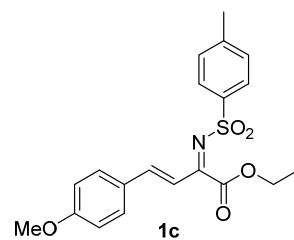
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130.73  
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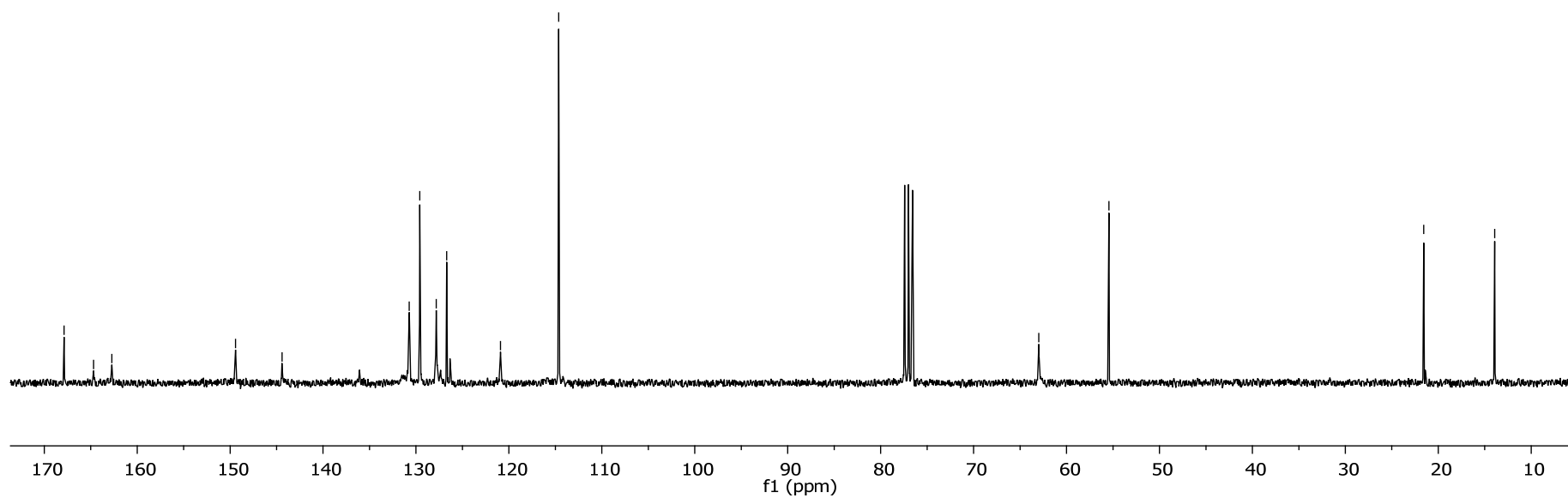
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62.98  
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21.56  
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<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



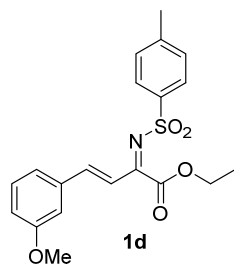
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7.305  
7.276  
7.260  
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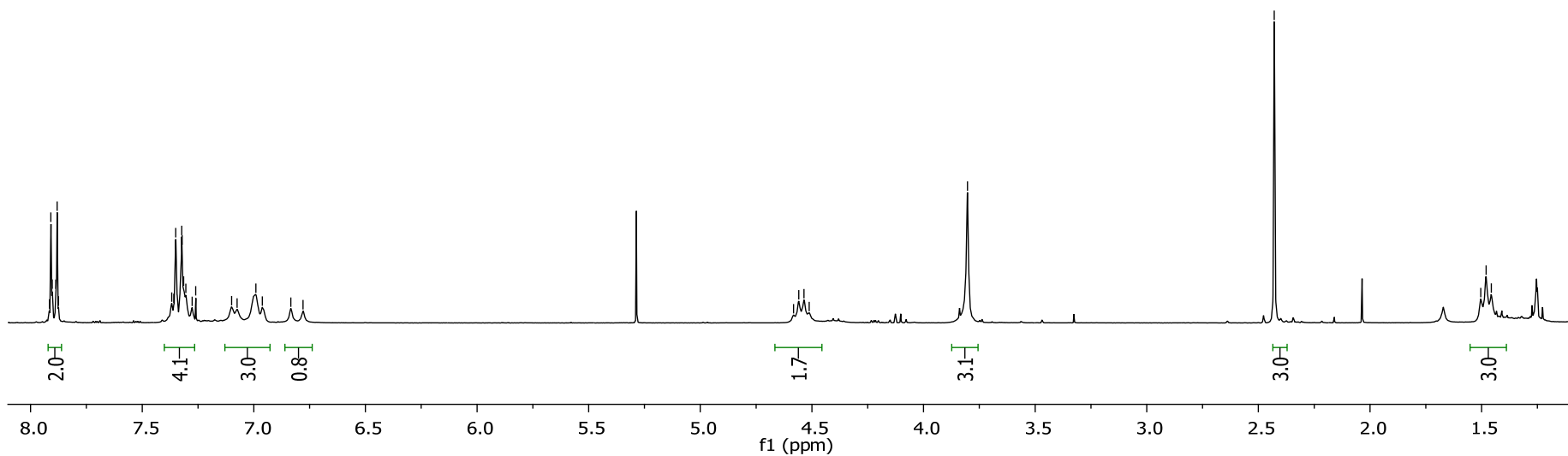
— 3.803

— 2.429

1.504  
1.480  
1.457



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 167.55  
— 164.40  
— 159.96

— 149.26  
— 144.68

— 135.19  
— 130.09  
— 129.68  
— 127.96

— 123.74  
— 121.50  
— 117.84

— 113.03

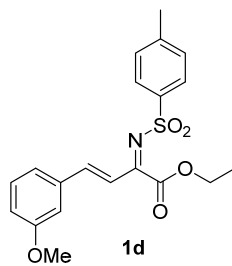
— 77.42  
— 77.00  
— 76.58

— 63.14

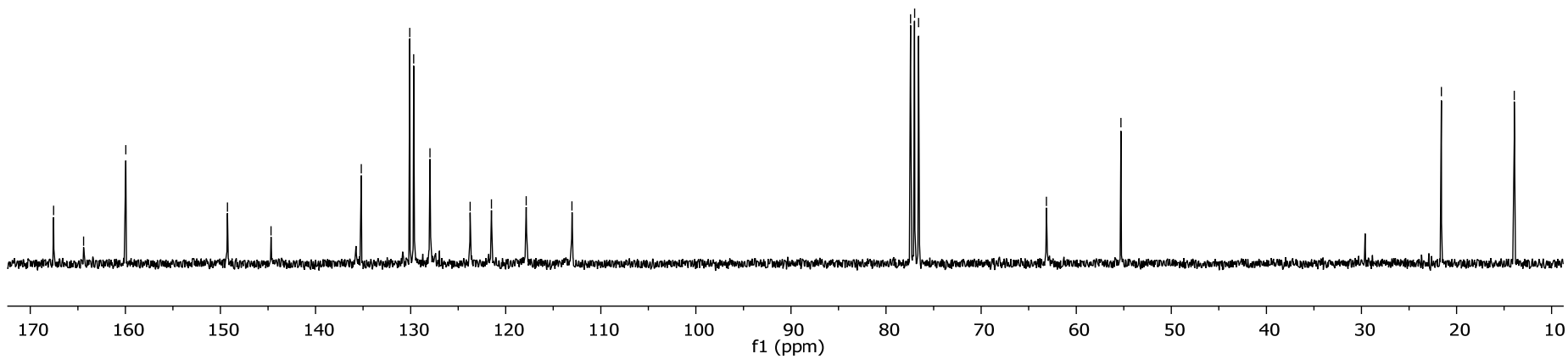
— 55.30

— 21.60

— 13.93



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



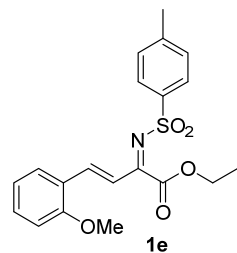
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7.757  
7.702  
7.454  
7.388  
7.339  
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6.974  
6.954  
6.917  
6.900  
6.889

4.587  
4.564  
4.540  
4.517

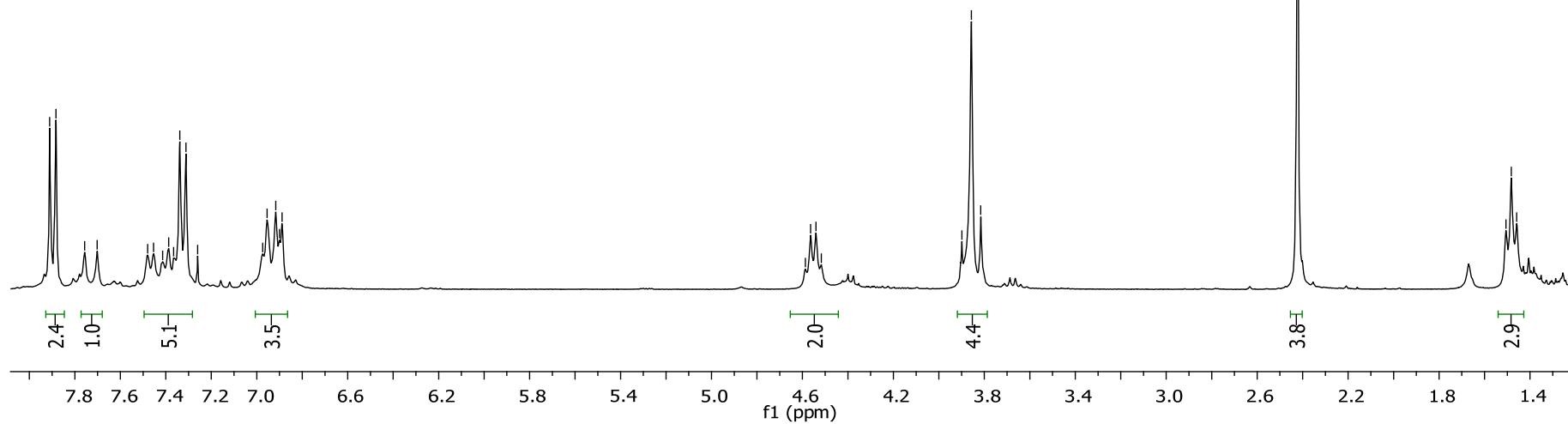
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2.422

1.506  
1.482  
1.459



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





— 168.61  
— 164.68  
— 158.72

— 145.24  
— 144.47

— 133.27  
— 129.61  
— 129.53  
— 129.06  
— 127.92  
— 123.79  
— 122.89  
— 120.90

— 111.30

— 77.42  
— 77.00  
— 76.58

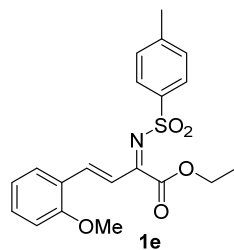
— 62.90

— 55.57

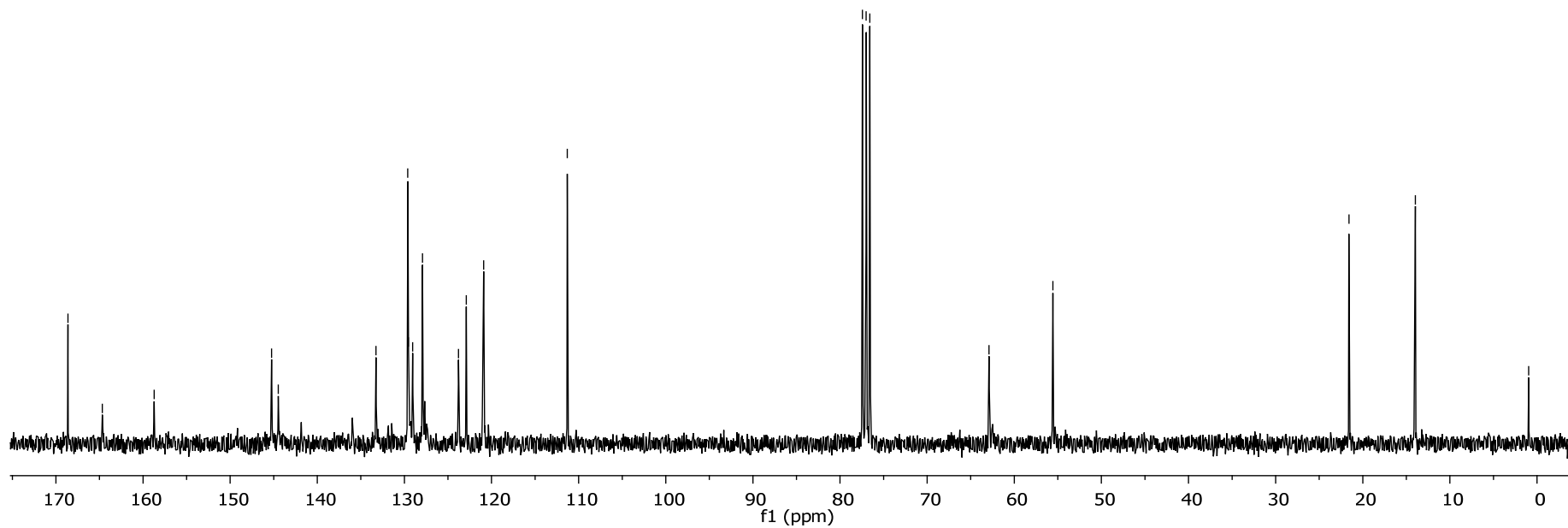
— 21.59

— 13.97

— 0.96



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>

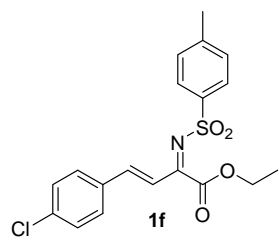


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7.900  
7.884  
7.878  
7.874  
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7.425  
7.389  
7.357  
7.331  
7.293  
6.811  
6.756

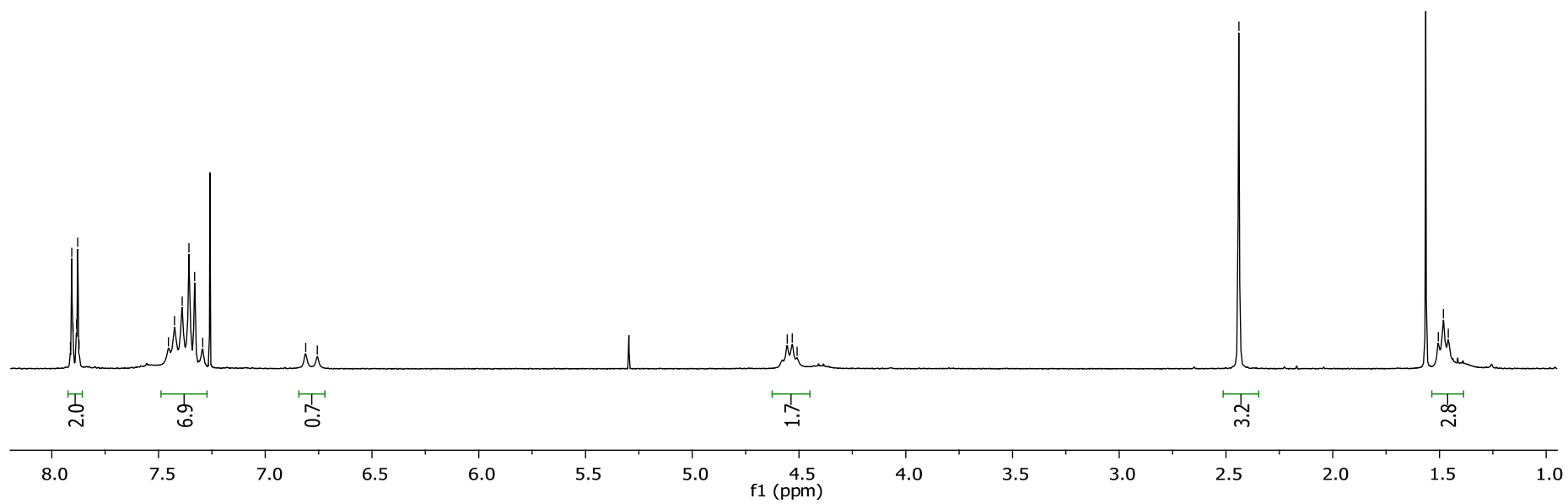
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4.532  
4.509

2.440

1.506  
1.482  
1.458



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 167.23  
— 164.35

— 147.51  
— 144.79

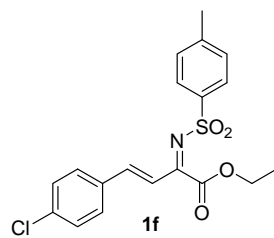
— 137.76  
— 135.66  
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— 77.42  
— 77.00  
— 76.58

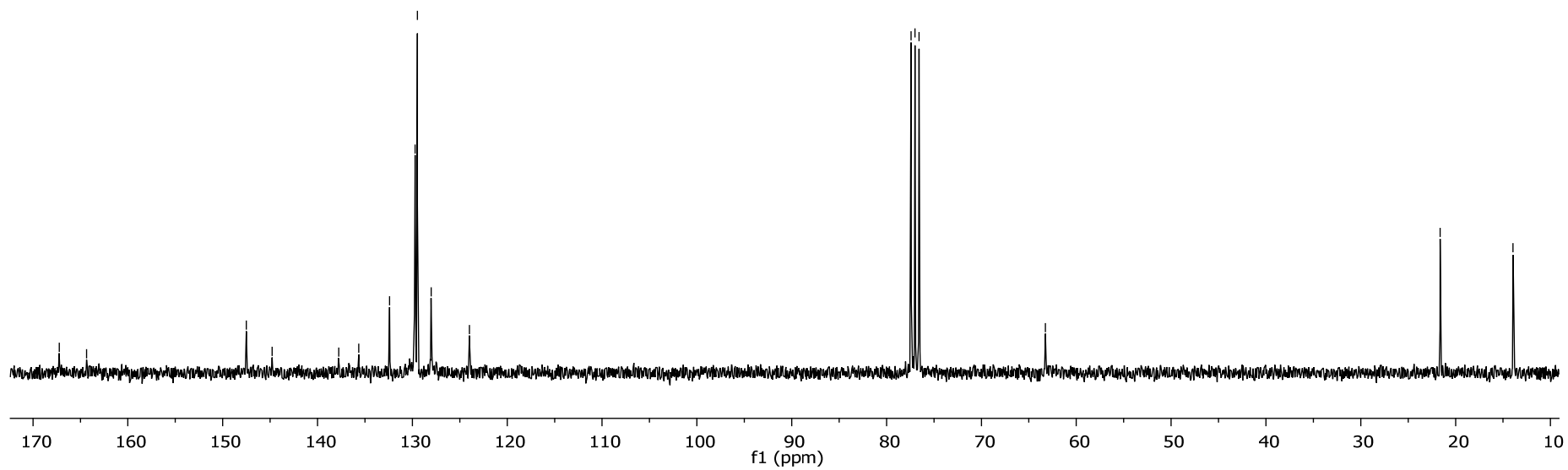
— 63.25

— 21.64

— 13.95



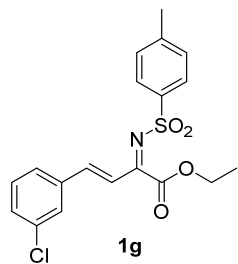
<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



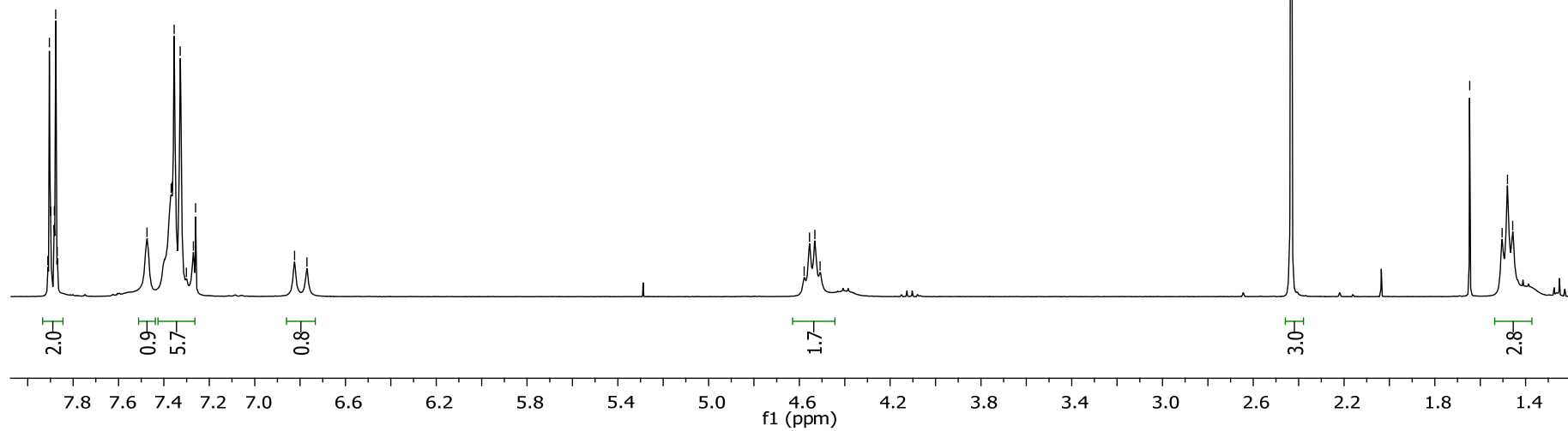
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6.825  
6.770

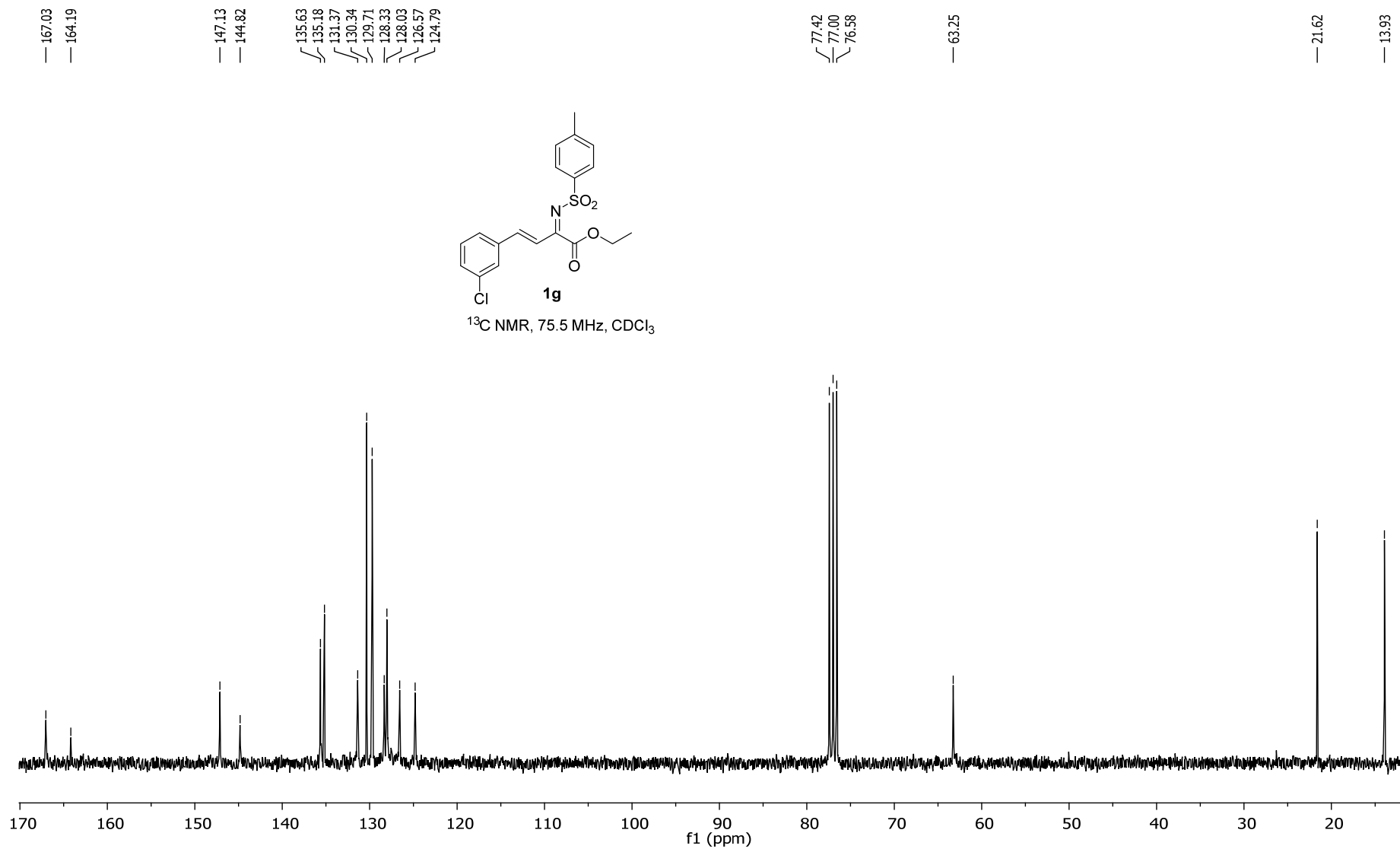
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1.457



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



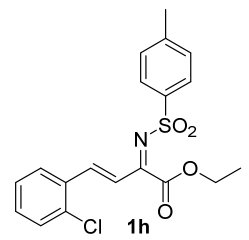


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7.883  
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7.362  
7.336  
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6.787

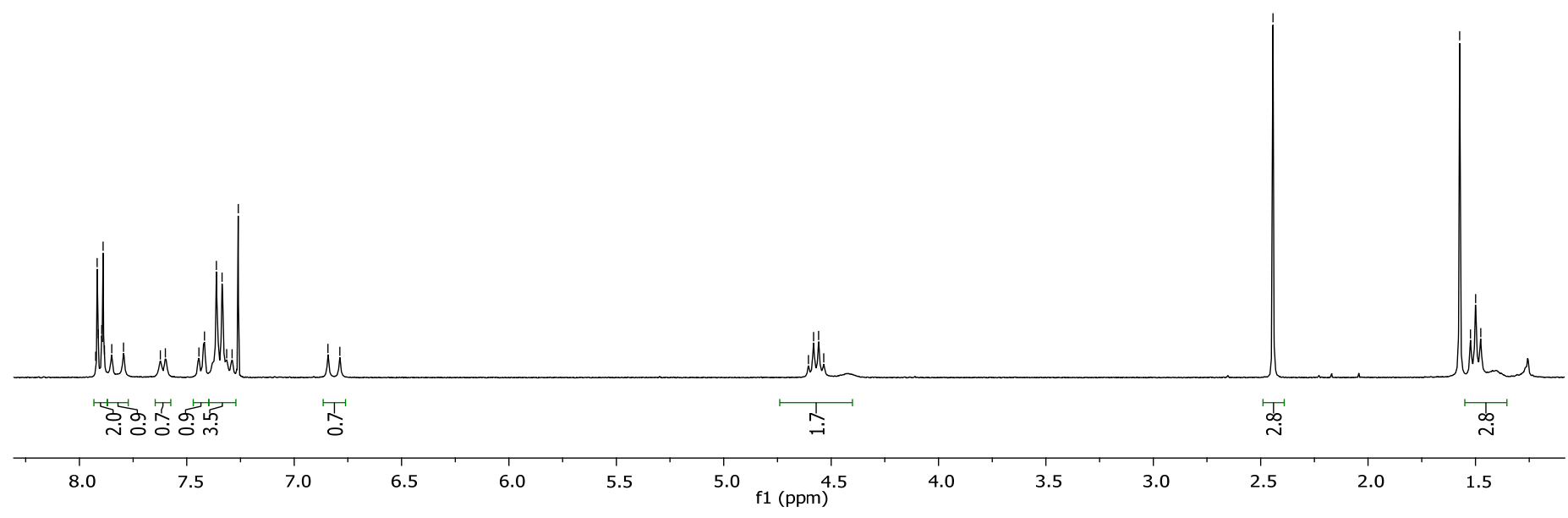
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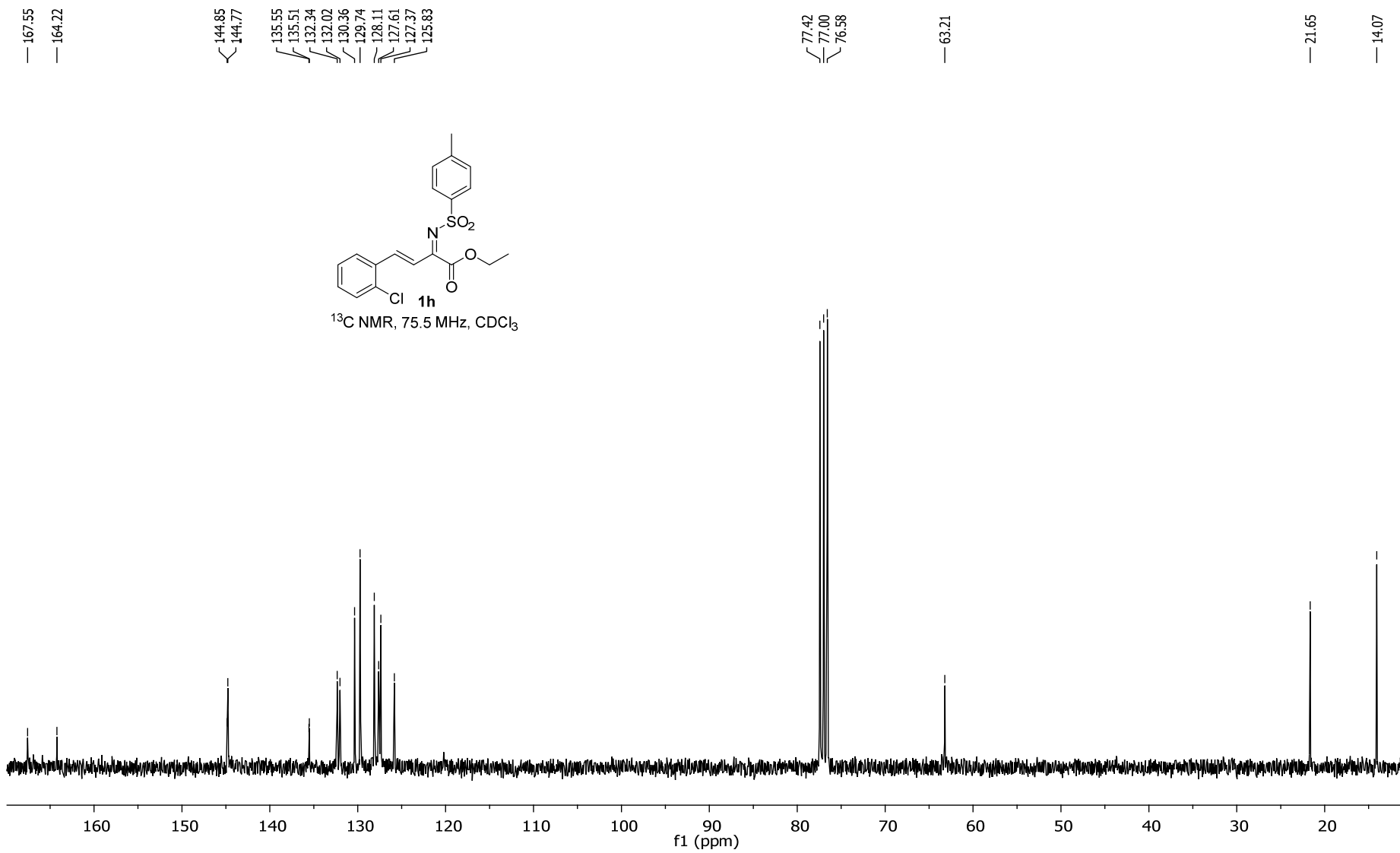
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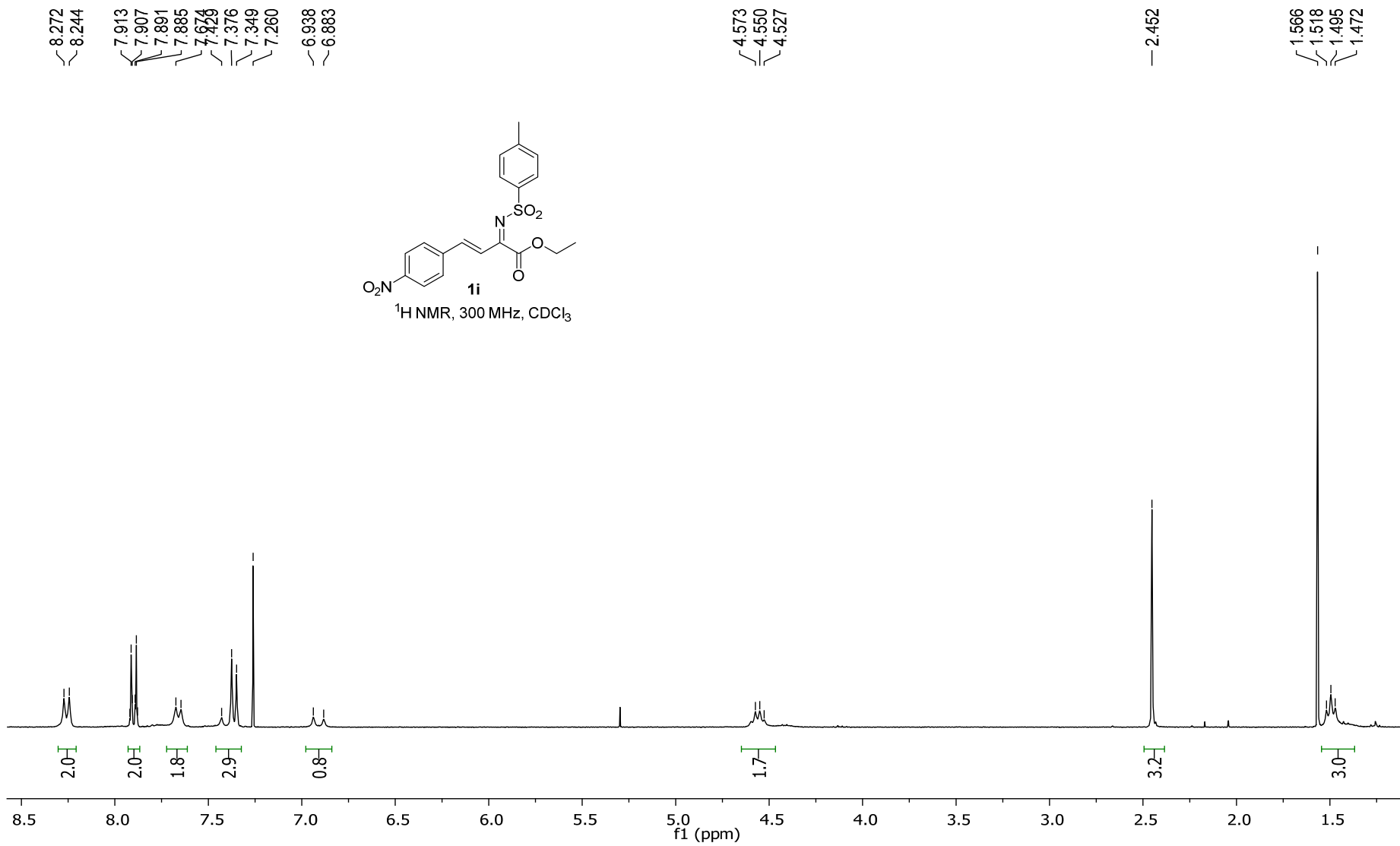
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1.499  
1.476



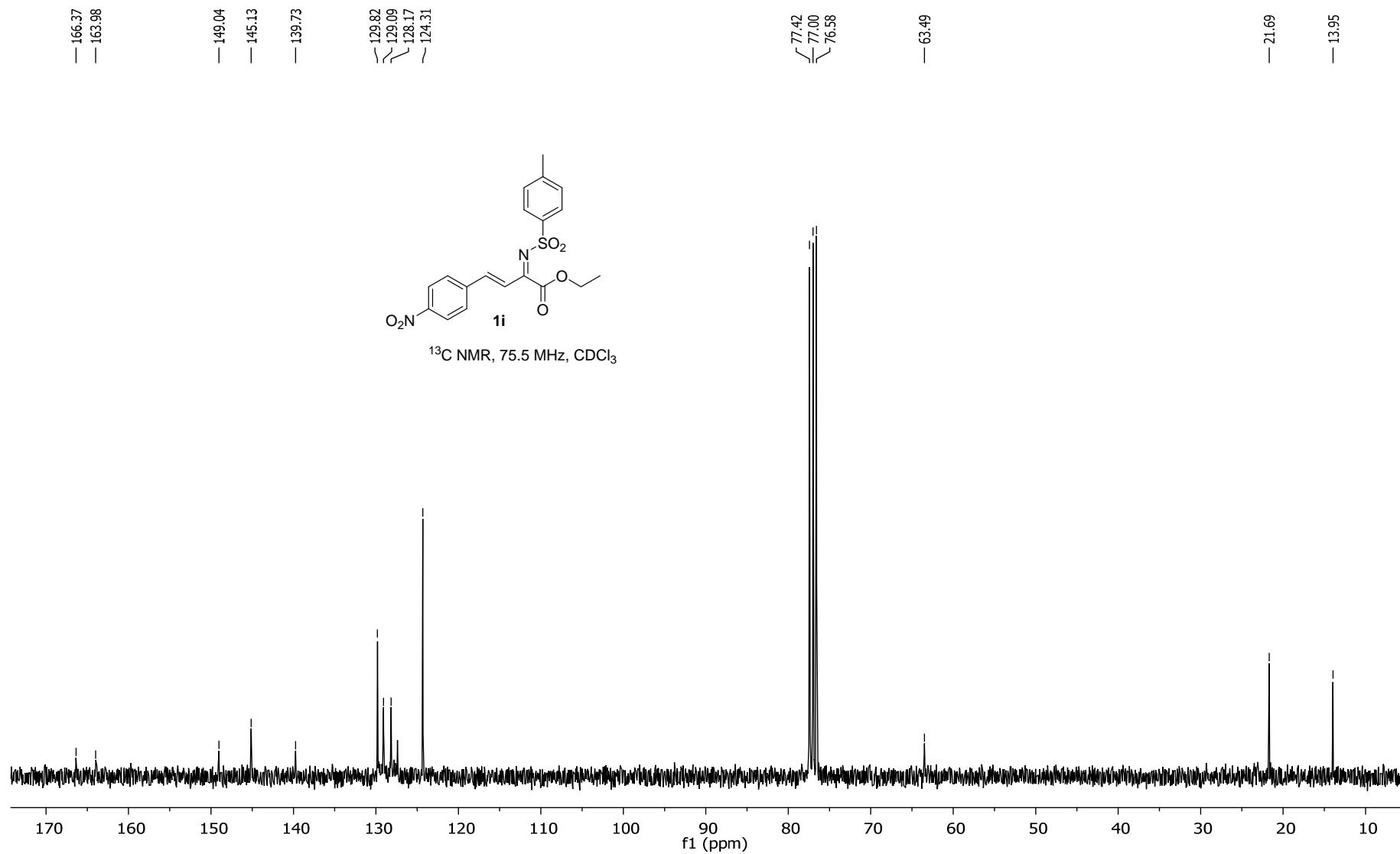
<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>

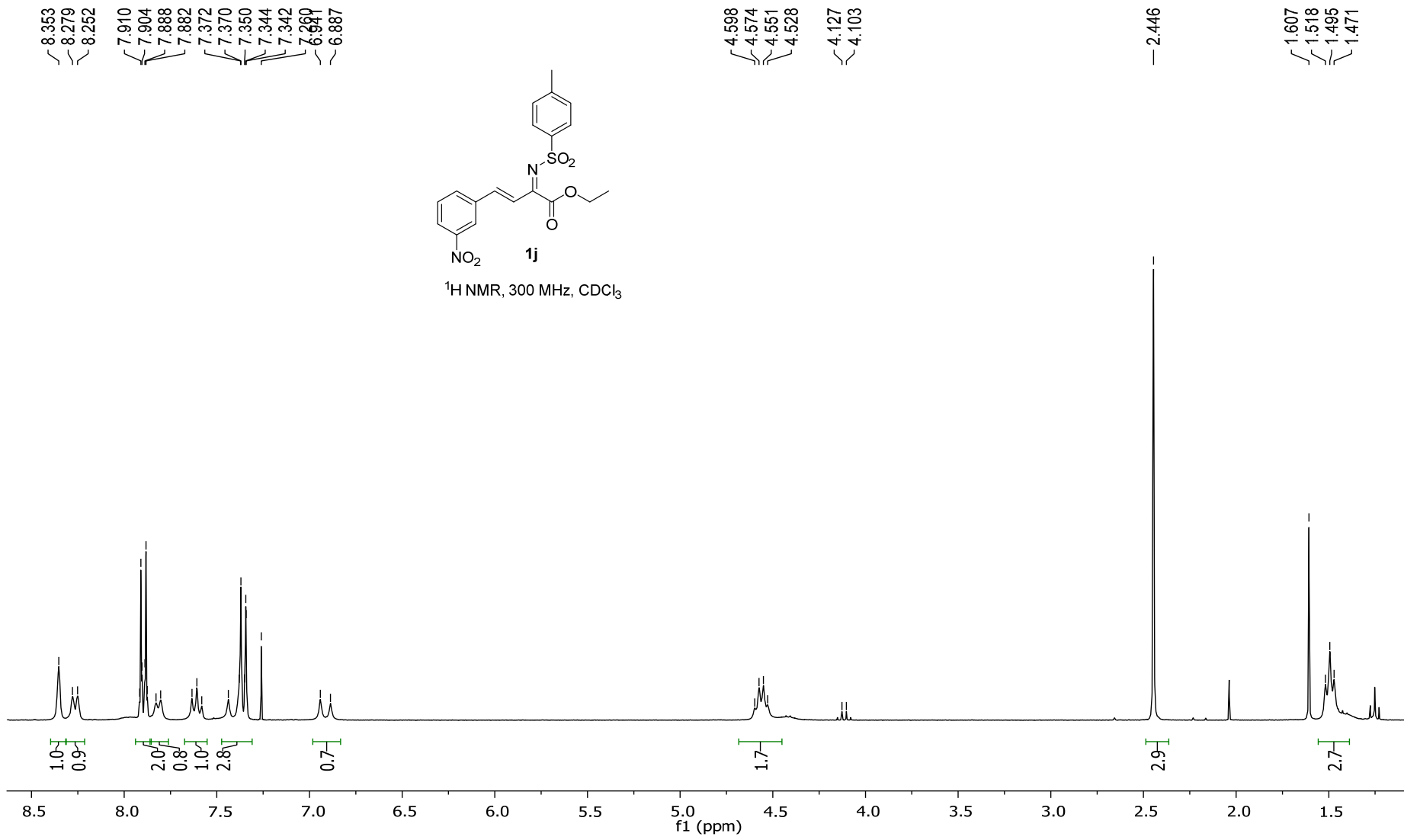












— 166.47  
— 164.00

— 148.71  
— 145.33  
— 145.05

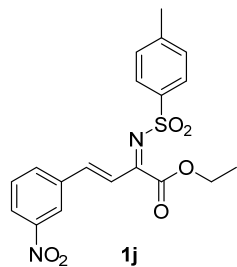
— 135.57  
— 133.66  
— 130.24  
— 129.80  
— 128.13  
— 126.32  
— 125.56  
— 122.98

— 77.42  
— 77.00  
— 76.58

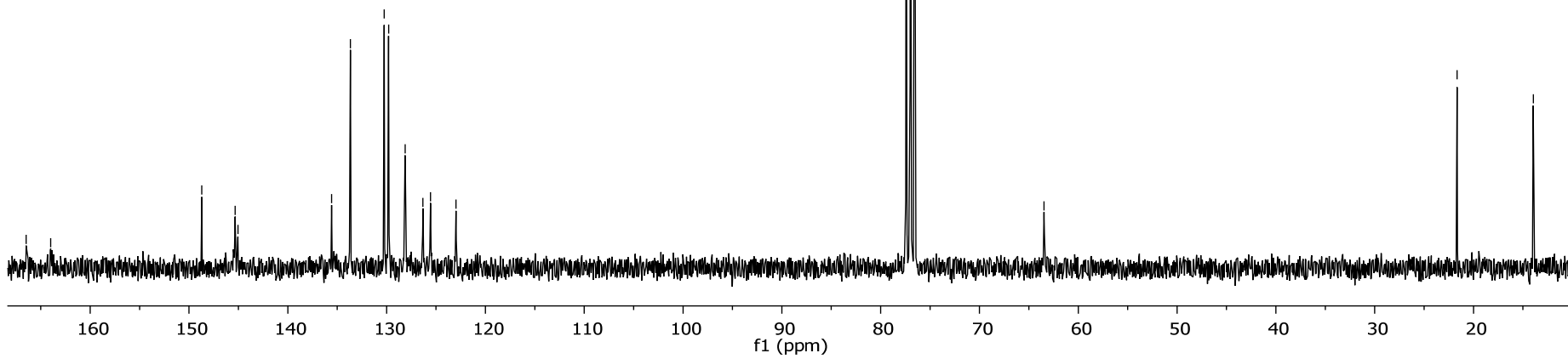
— 63.47

— 21.67

— 13.95



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



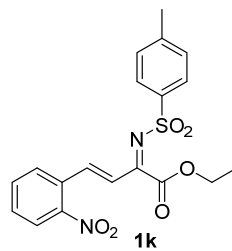
8.107  
8.081  
7.934  
7.906  
7.879  
7.653  
7.627  
7.613  
7.603  
7.336  
7.260

6.751  
6.697

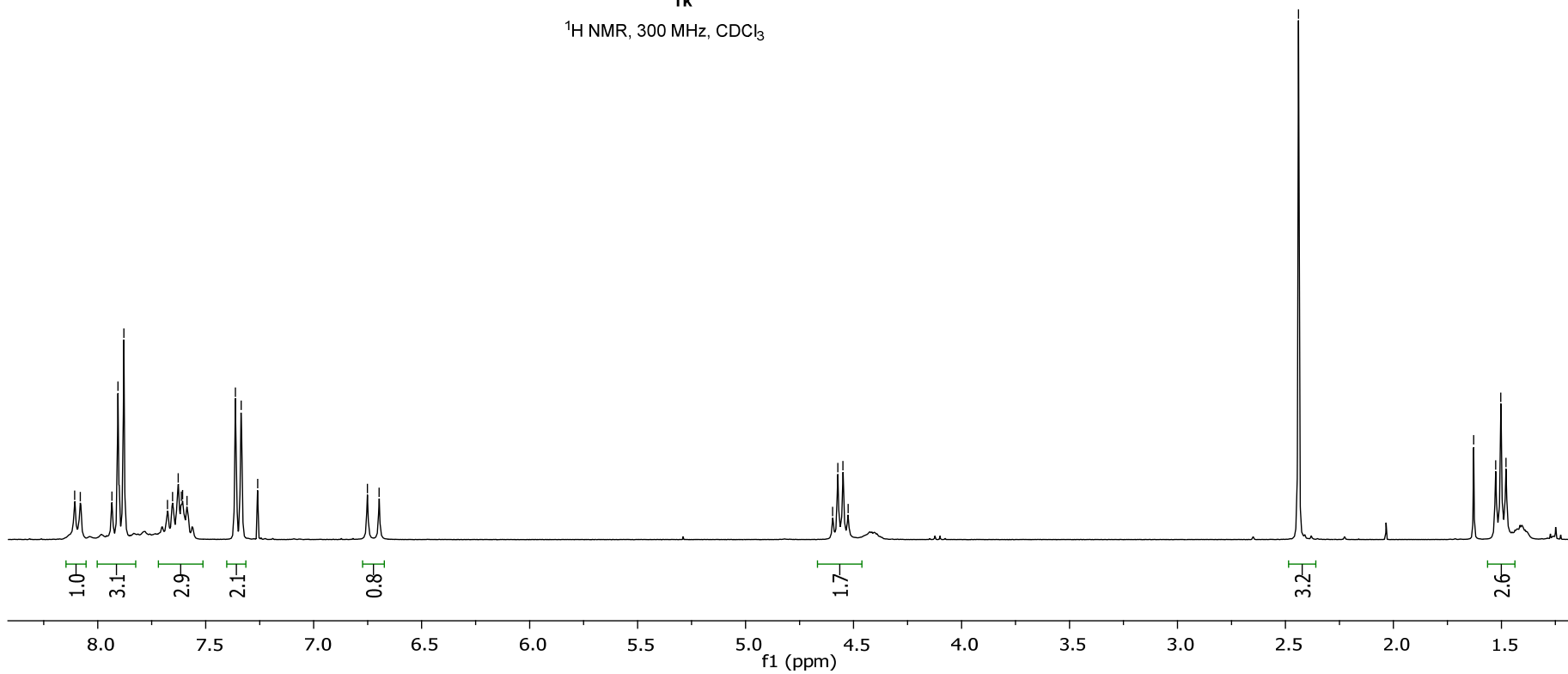
4.597  
4.573  
4.549  
4.525

2.440

1.628  
1.527  
1.503  
1.479



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 167.09  
— 163.88

— 147.91  
— 145.06  
— 144.28

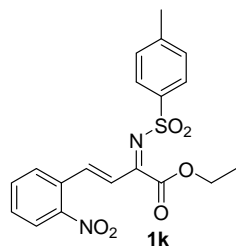
135.19  
133.91  
131.33  
129.96  
129.78  
128.94  
128.20  
128.08  
125.30

77.42  
77.00  
76.58

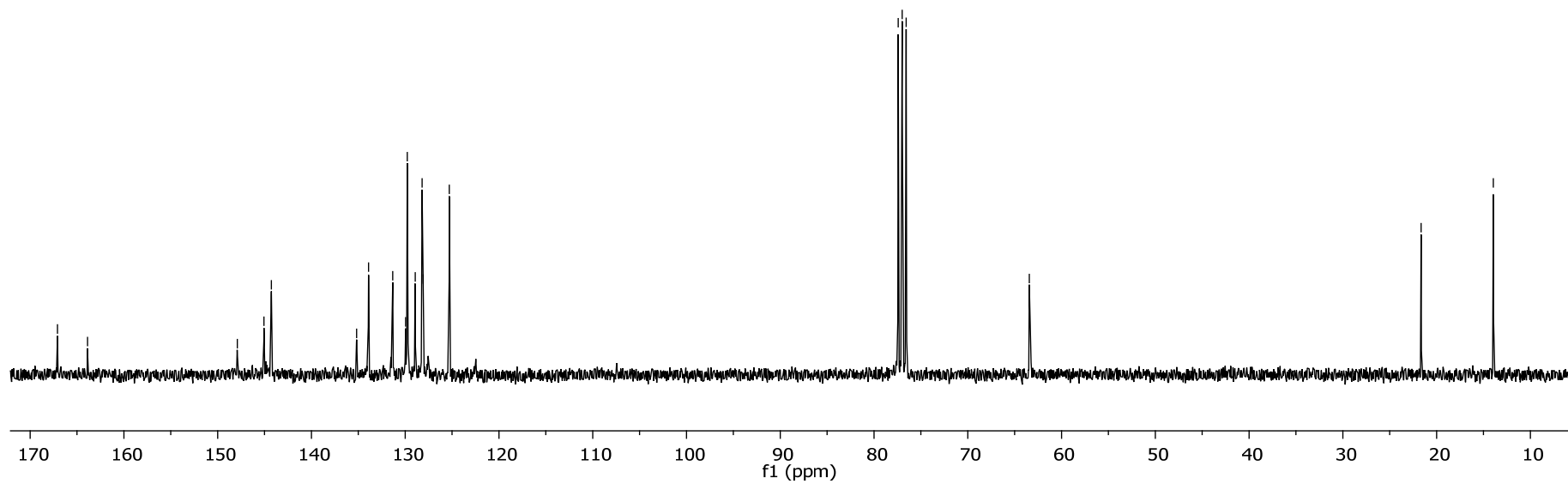
— 63.44

— 21.65

— 13.95



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>

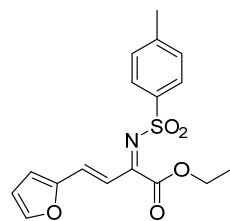


7.897  
7.875  
7.869  
— 7.553  
7.341  
7.314  
7.260  
7.179  
7.125  
— 6.842  
6.750  
6.668  
6.527

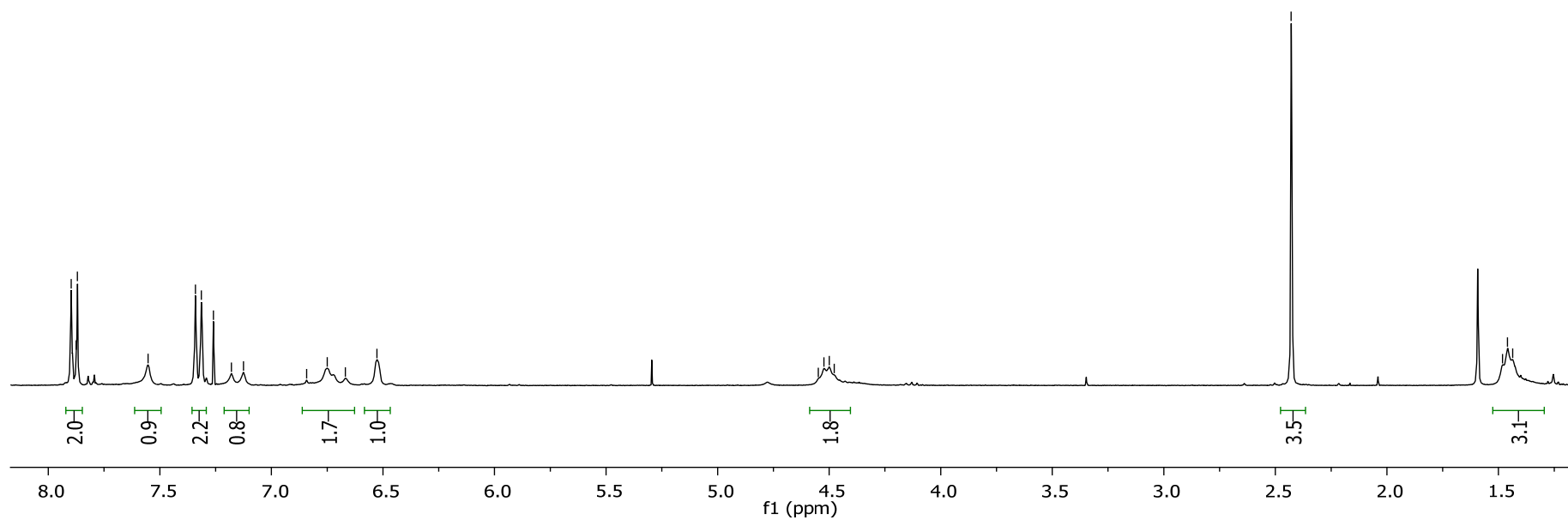
4.549  
4.523  
4.500  
4.477

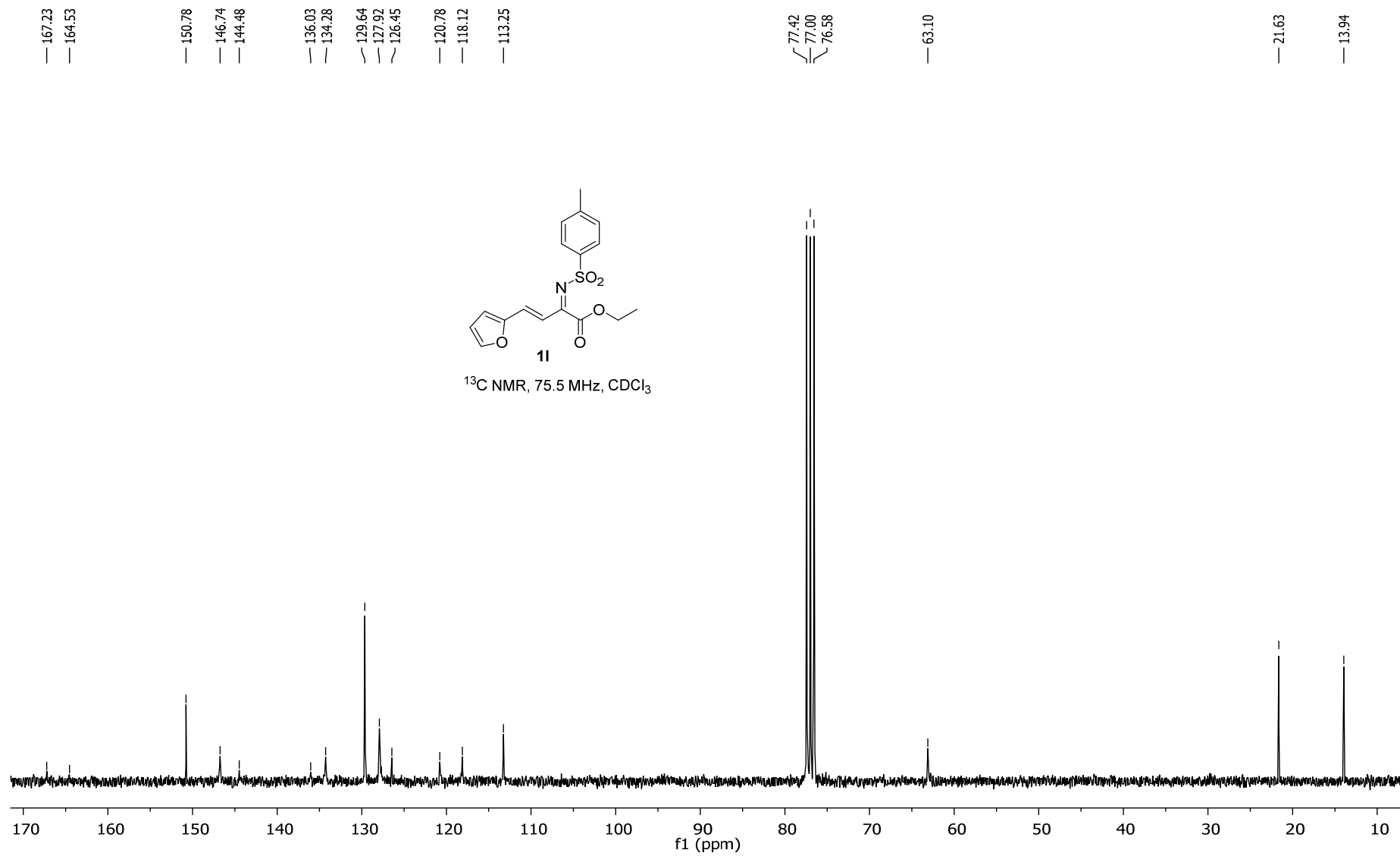
— 2.429

1.482  
1.459  
1.436



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





7.908  
7.903  
7.886  
7.881

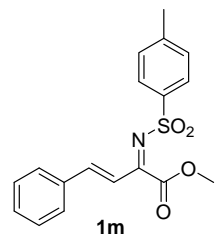
7.519  
7.495  
7.417  
7.394  
7.358  
7.331  
7.260

6.859  
6.805

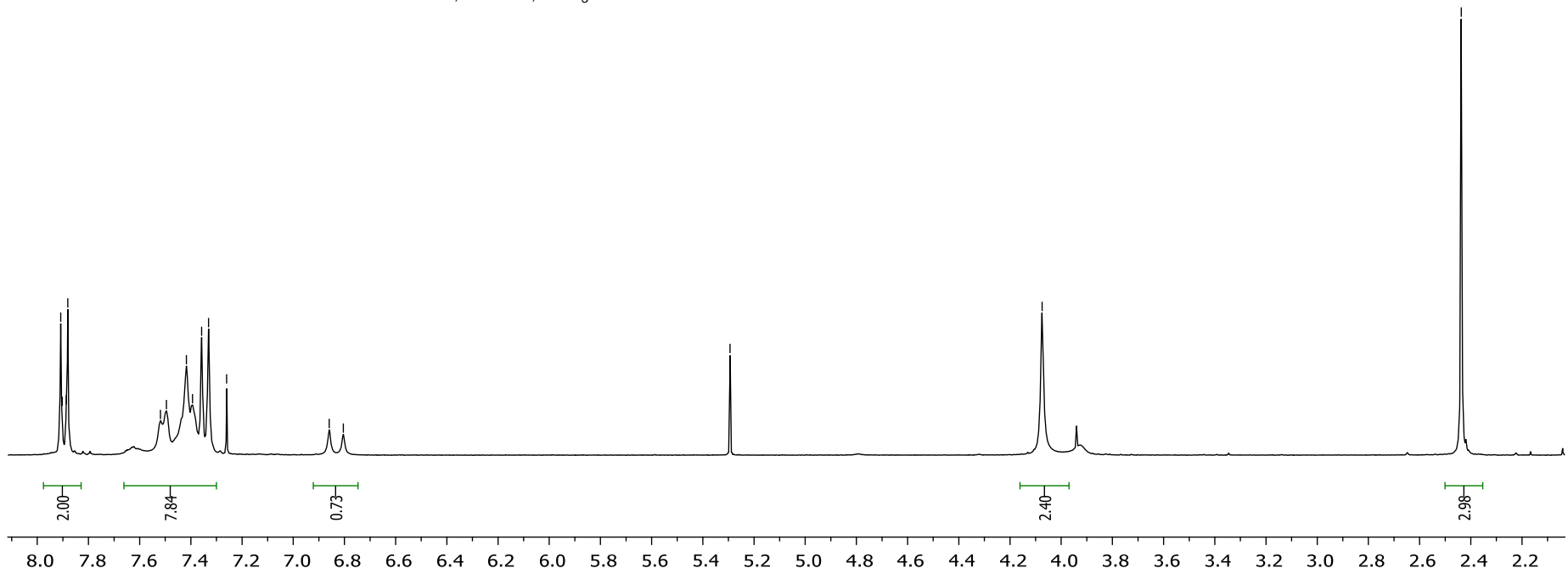
5.294

4.075

2.437



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





— 167.40  
— 164.92

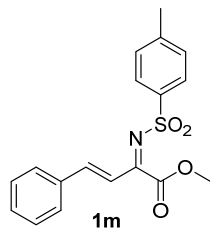
— 149.57  
— 144.76

— 135.68  
— 133.86  
— 131.78  
— 129.73  
— 129.14  
— 128.70  
— 128.02  
— 123.39

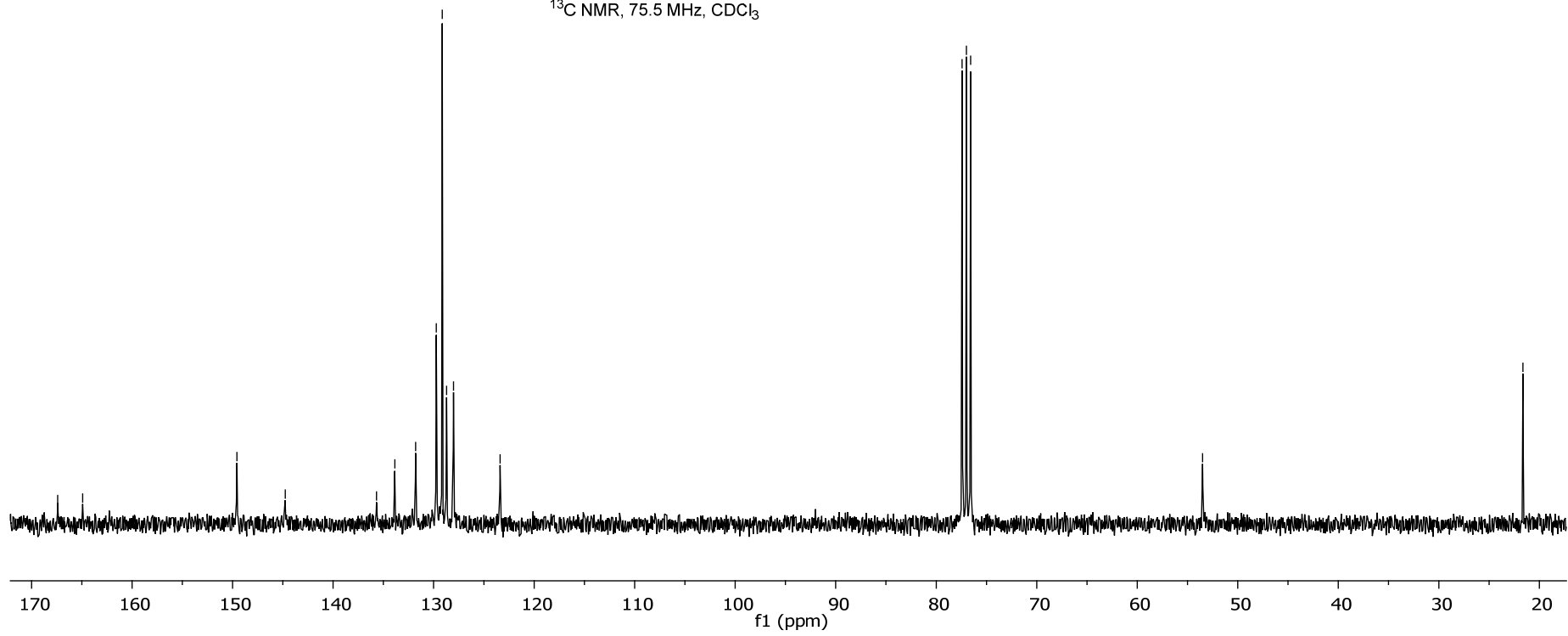
— 77.42  
— 77.00  
— 76.58

— 53.50

— 21.64



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>

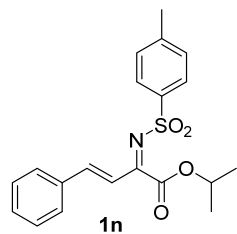


7.920  
7.914  
7.898  
7.892  
7.886  
7.482  
7.416  
7.397  
7.352  
7.343  
7.324  
7.260  
6.842  
6.788

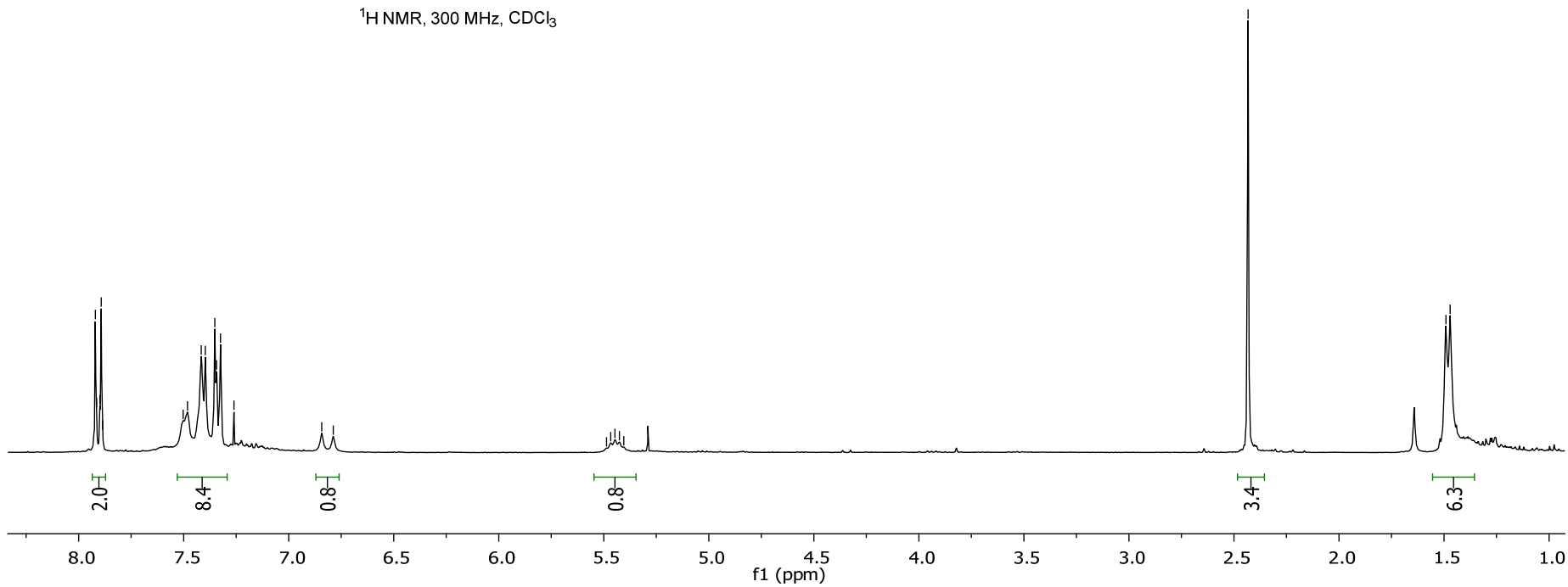
5.487  
5.467  
5.447  
5.426  
5.405

2.433

1.491  
1.470



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



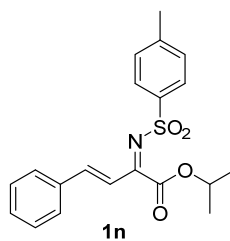
— 167.77  
— 163.96

— 149.13  
— 144.61

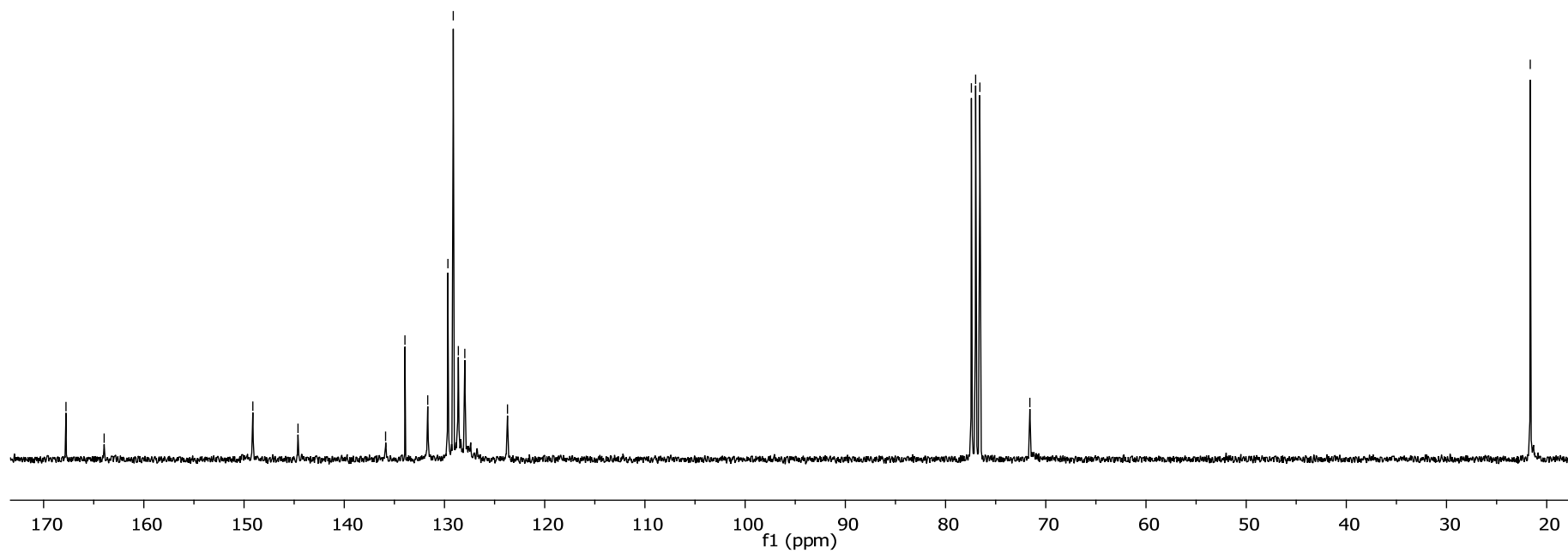
— 135.87  
— 133.94  
— 131.67  
— 129.66  
— 129.13  
— 128.62  
— 127.98  
— 123.71

— 77.42  
— 77.00  
— 76.58  
— 71.58

— 21.65  
— 21.62



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



7.513  
7.507  
7.492  
7.485  
7.330  
7.301  
7.293  
7.289  
7.281  
7.275  
7.268  
7.263  
7.254  
7.251  
7.182  
7.179  
7.176  
7.172  
7.170  
7.165  
7.158  
7.151  
7.146  
6.204

4.825  
4.787

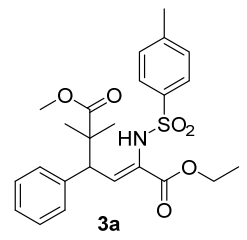
4.429  
4.391

3.986  
3.982  
3.962  
3.958

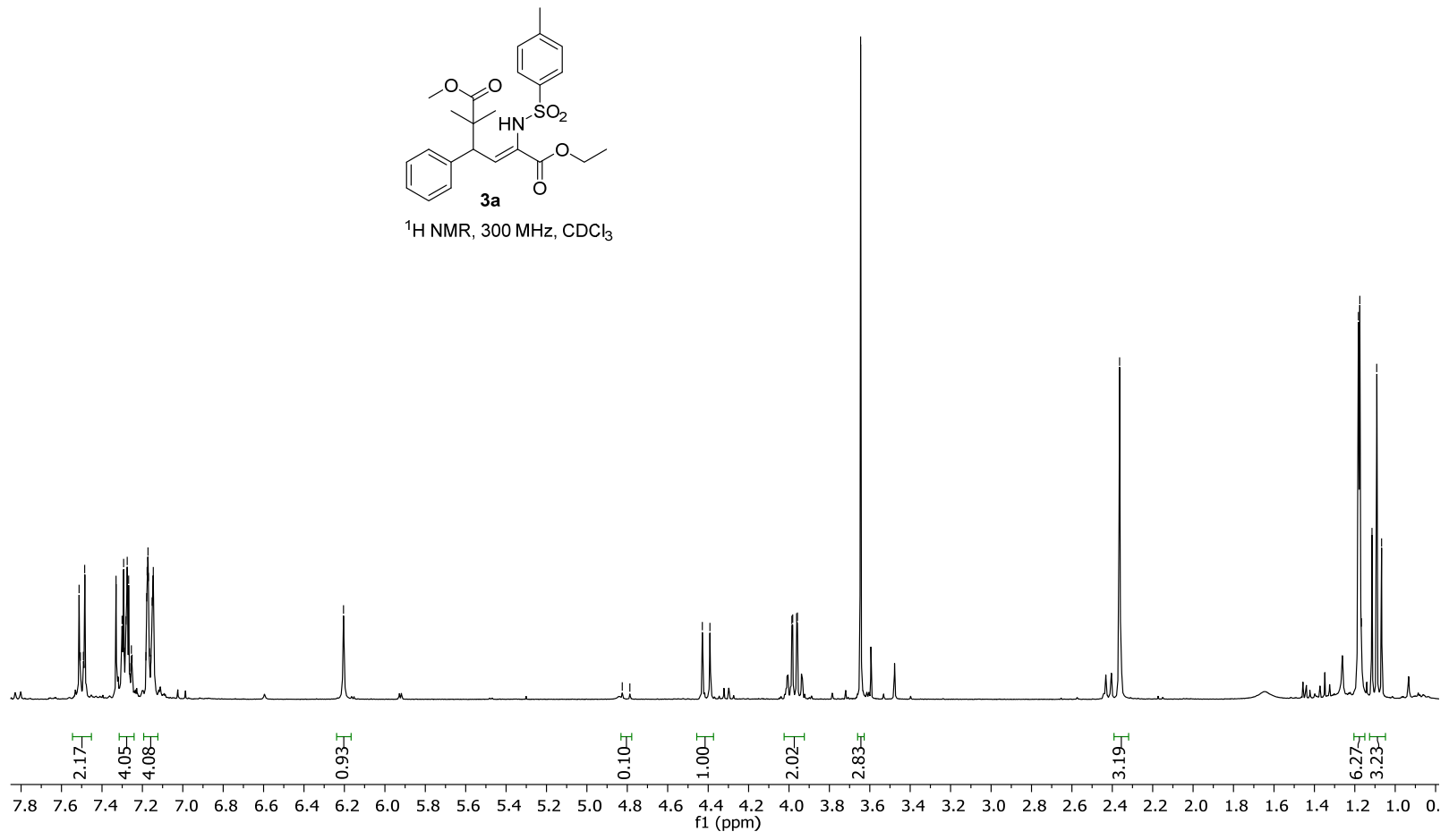
3.645

2.364

1.183  
1.175  
1.167  
1.115  
1.091  
1.068



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 176.93

— 164.16

~ 143.72

~ 140.53

~ 138.09

~ 135.99

~ 129.47

~ 129.30

~ 128.05

~ 127.57

~ 127.17

~ 125.91

~ 77.42

~ 77.00

~ 76.58

— 61.78

~ 51.87

~ 50.47

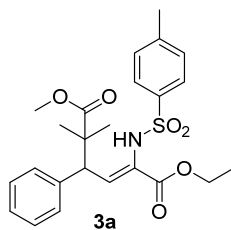
~ 47.12

~ 23.85

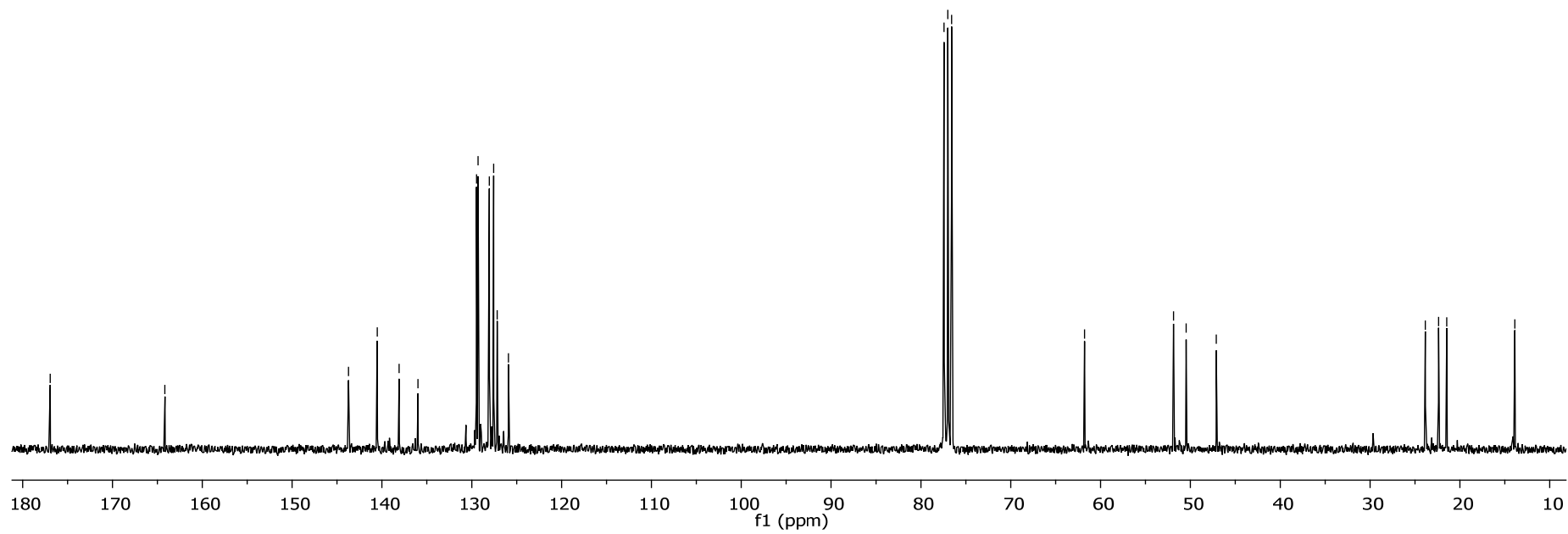
~ 22.38

~ 21.47

— 13.89



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



7.527  
7.521  
7.499  
7.312  
7.275  
7.260  
7.179  
7.177  
7.151  
7.148  
7.109  
7.082  
7.053  
7.046  
6.919

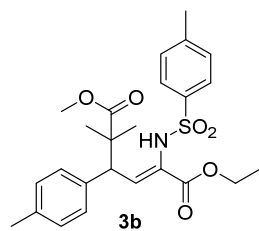
4.789  
4.751

4.367  
4.329

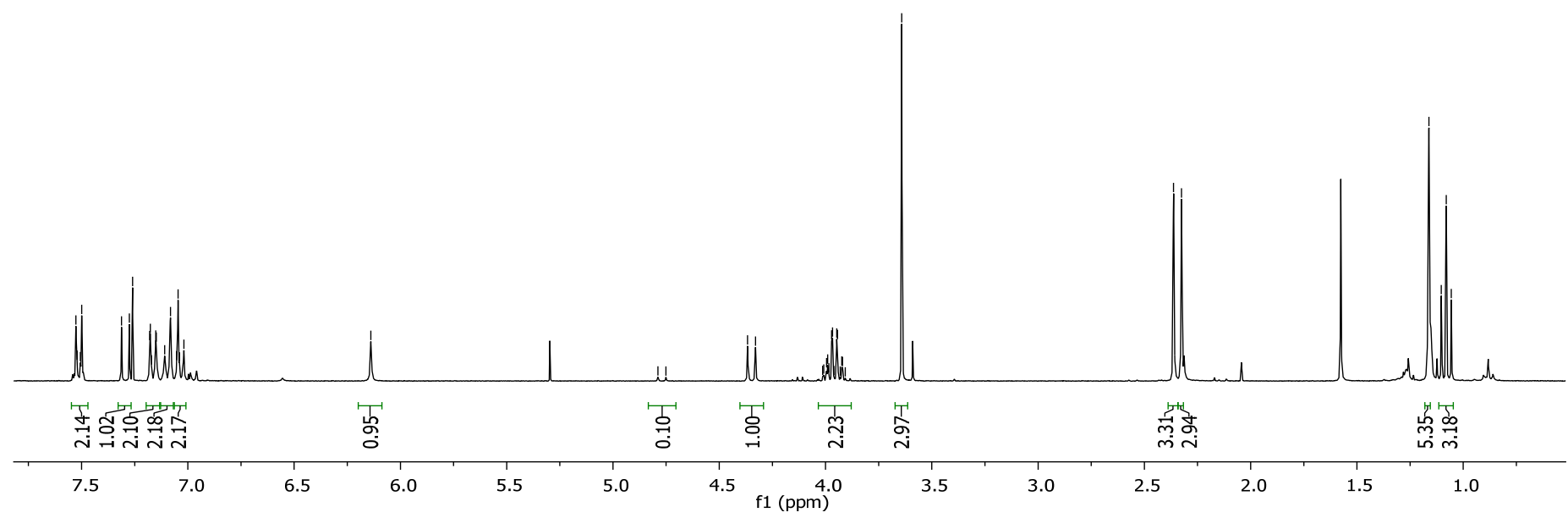
3.990  
3.971  
3.967  
3.947  
3.943  
3.642

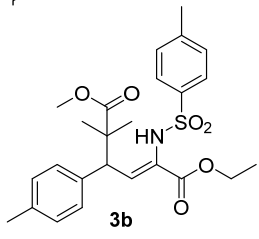
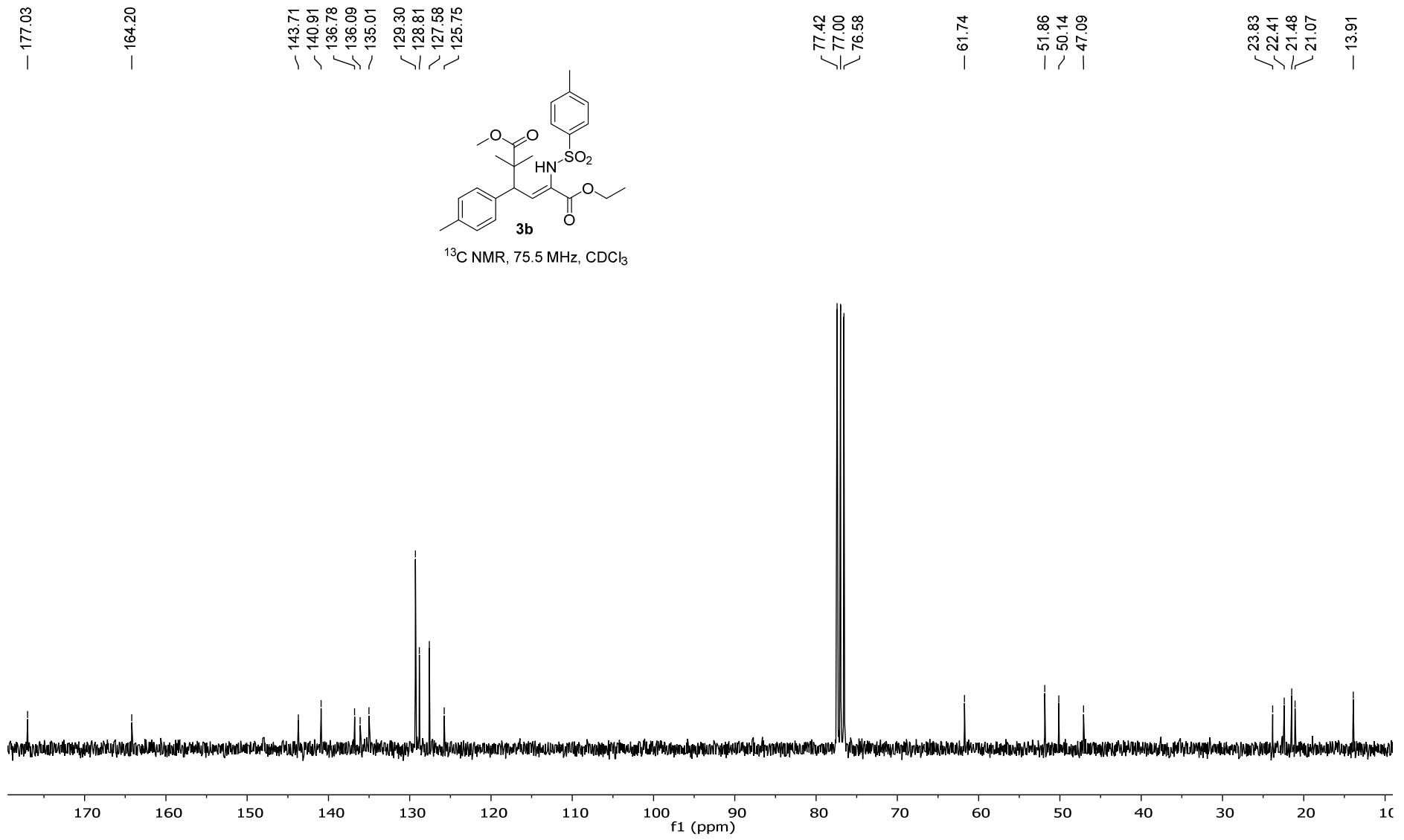
2.363  
2.325

1.161  
1.104  
1.080  
1.056



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





7.520  
7.493  
7.293  
7.255  
7.182  
7.156  
7.100  
6.846  
6.821  
6.817

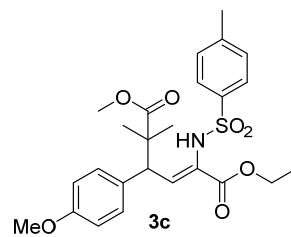
— 6.179

4.786  
4.748

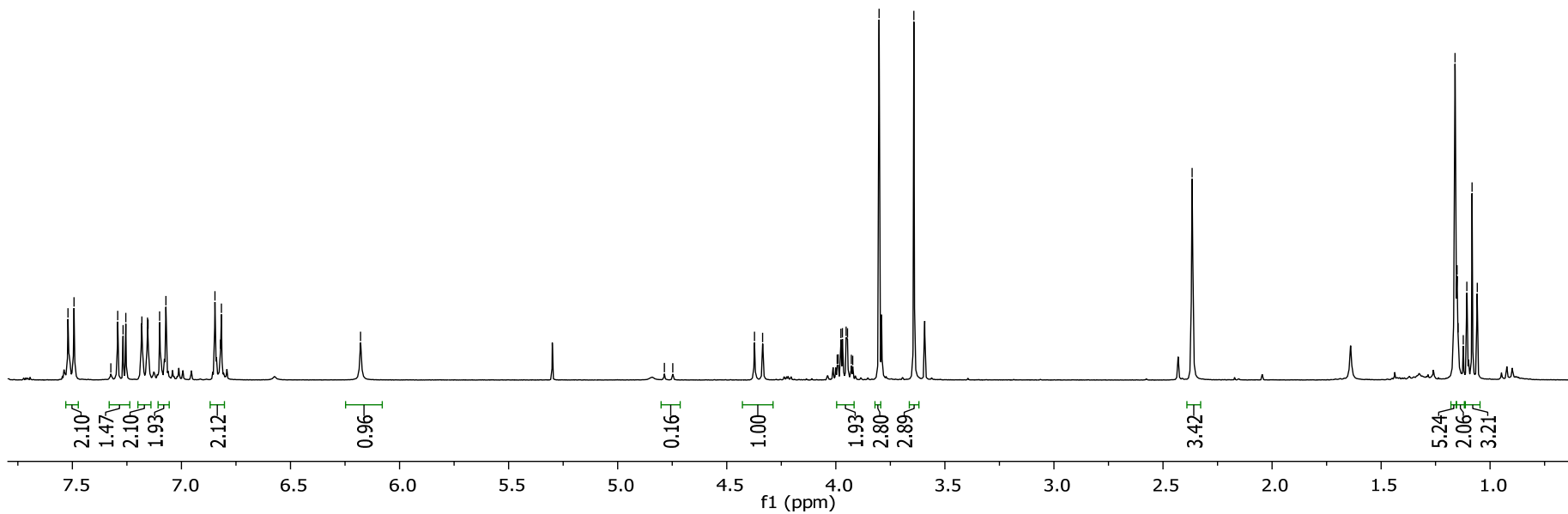
4.373  
4.335  
3.994  
3.989  
3.977  
3.970  
3.953  
3.946  
3.929  
3.923  
3.802  
3.642

— 2.366

1.161  
1.151  
1.147  
1.123  
1.107  
1.083  
1.059



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>





— 177.01

— 164.20

— 158.62

— 143.71

— 140.78

— 136.01

— 130.42

— 130.08

— 129.29

— 127.58

— 125.62

— 113.46

— 113.40

— 77.42

— 77.00

— 76.58

— 61.74

— 55.14

— 51.85

— 49.71

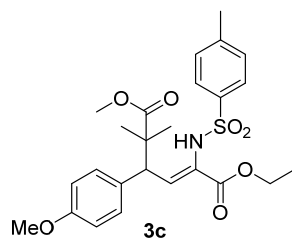
— 47.15

— 23.73

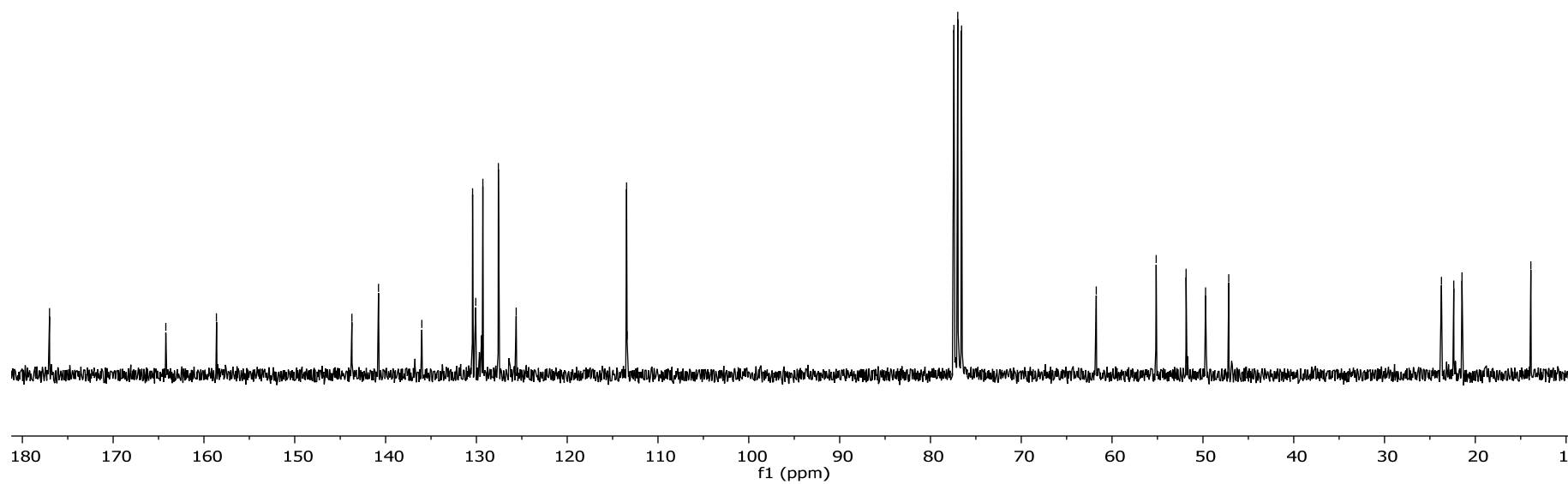
— 22.38

— 21.47

— 13.89



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>

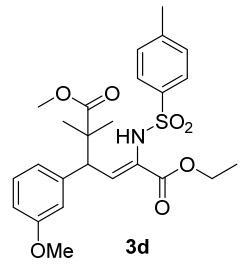


7.530  
7.525  
7.509  
7.503  
7.260  
7.251  
7.179  
6.812  
6.803  
6.762  
6.736  
6.713  
6.706  
6.699  
6.677

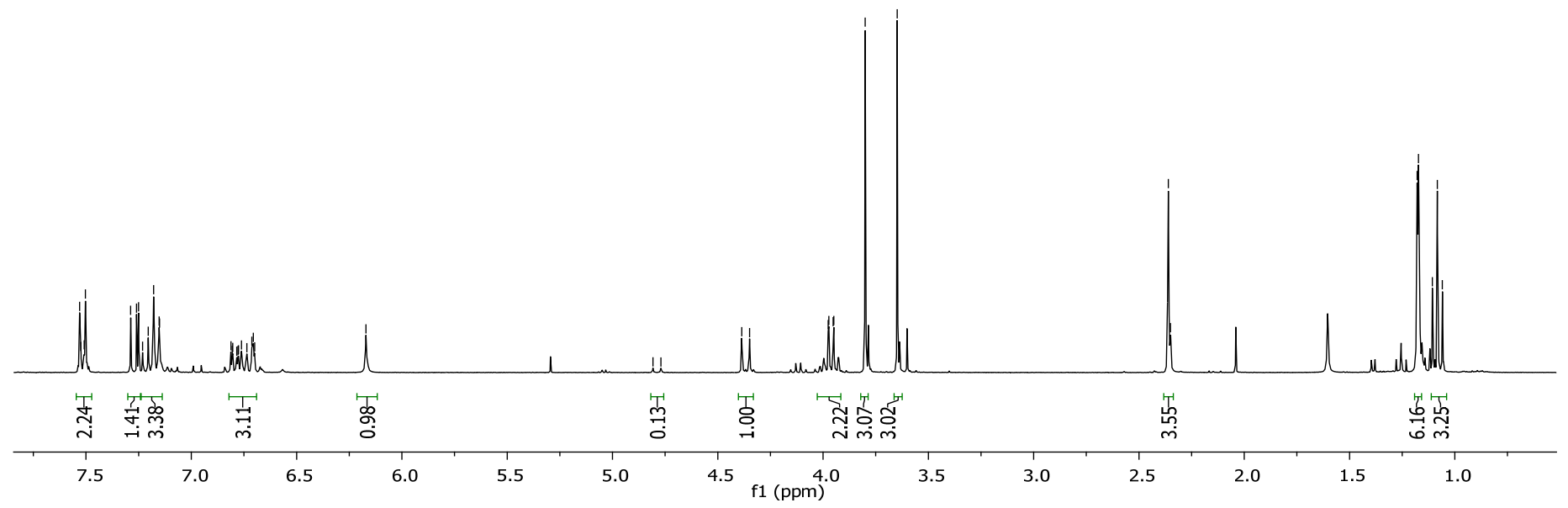
4.808  
4.770  
4.386  
4.349  
3.976  
3.973  
3.952  
3.949  
3.800  
3.648

2.361  
2.350

1.179  
1.173  
1.107  
1.083  
1.059



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 176.93

— 164.16

— 159.20

~ 143.76

~ 140.45

~ 139.62

~ 136.03

~ 129.31

~ 128.94

~ 127.58

~ 125.95

~ 121.83

— 115.76

— 112.16

~ 77.42

~ 77.00

~ 76.58

— 61.79

~ 55.19

~ 51.91

~ 50.46

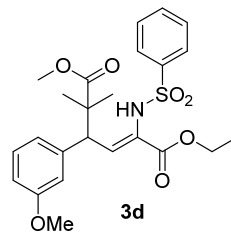
~ 47.11

~ 23.91

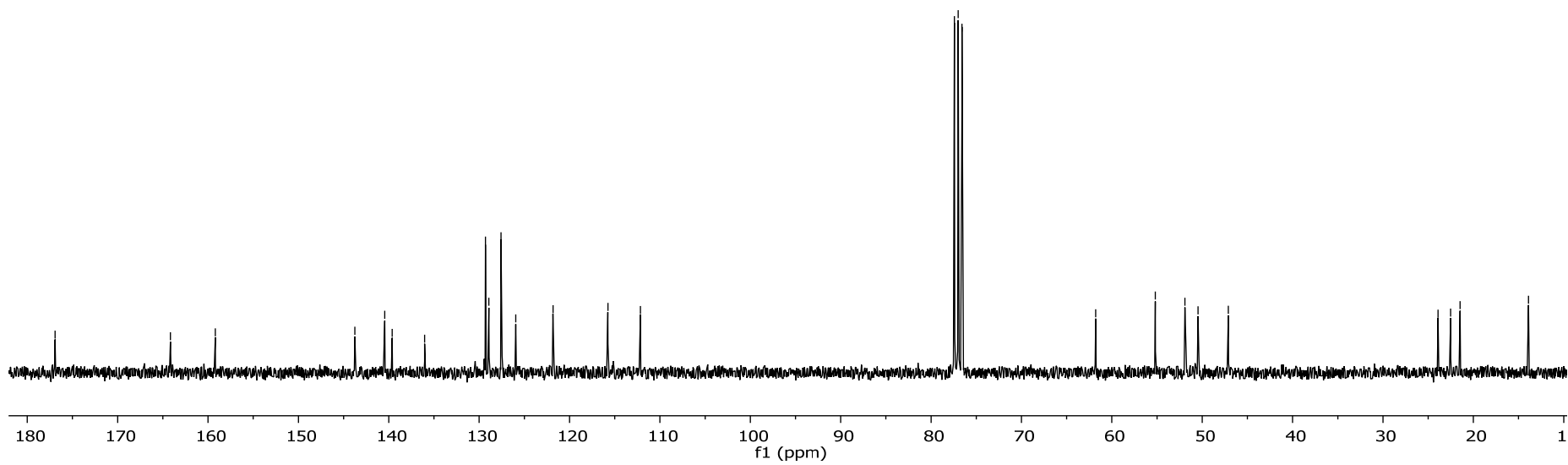
~ 22.52

~ 21.47

— 13.90



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



7.614  
7.607  
7.592  
7.586  
7.358  
7.322  
7.207  
7.198  
7.196  
7.171  
7.168  
7.033  
7.027  
6.873  
6.846  
6.186

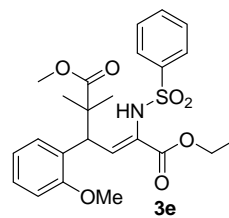
5.195  
5.158

4.707  
4.671

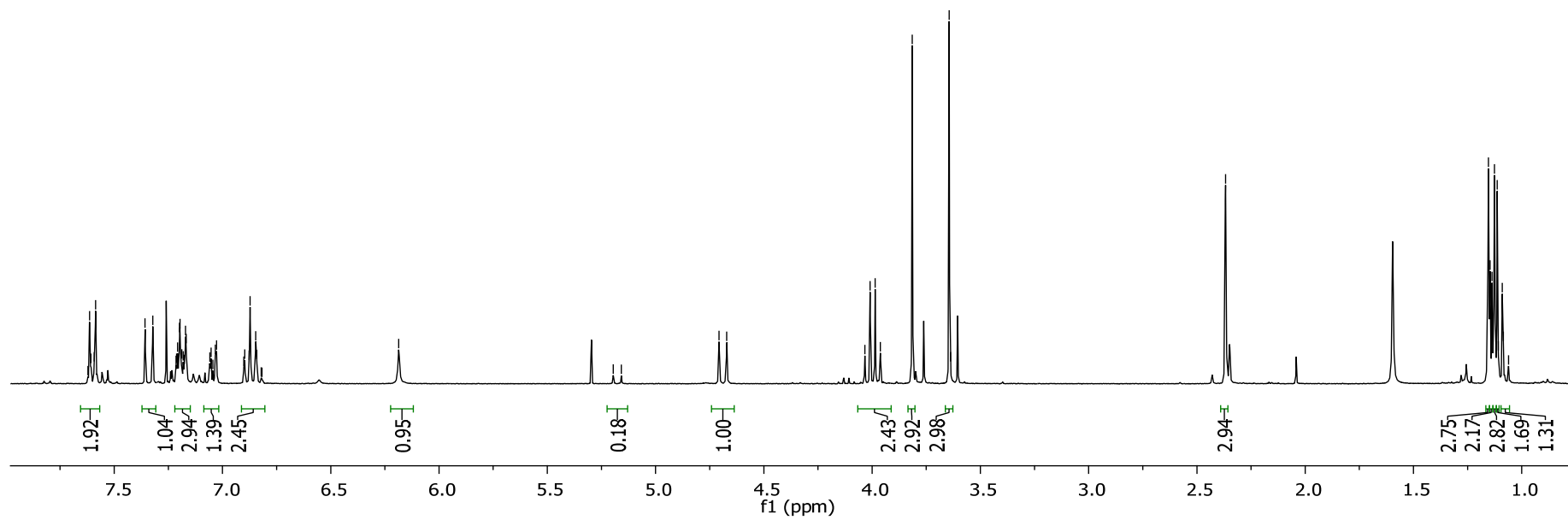
4.033  
4.010  
3.986  
3.962  
3.815  
3.644  
3.638

2.368

1.154  
1.146  
1.137  
1.126  
1.113  
1.108  
1.090  
1.085  
1.061



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 177.36

— 164.59

— 157.54

143.59

140.40

137.00

130.19

129.52

129.37

128.38

127.61

127.13

126.27

— 120.48

— 111.30

— 61.69

— 55.70

— 51.99

— 46.89

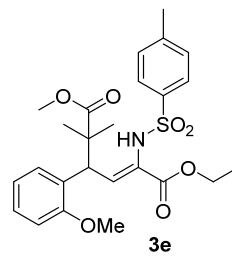
— 43.68

24.80

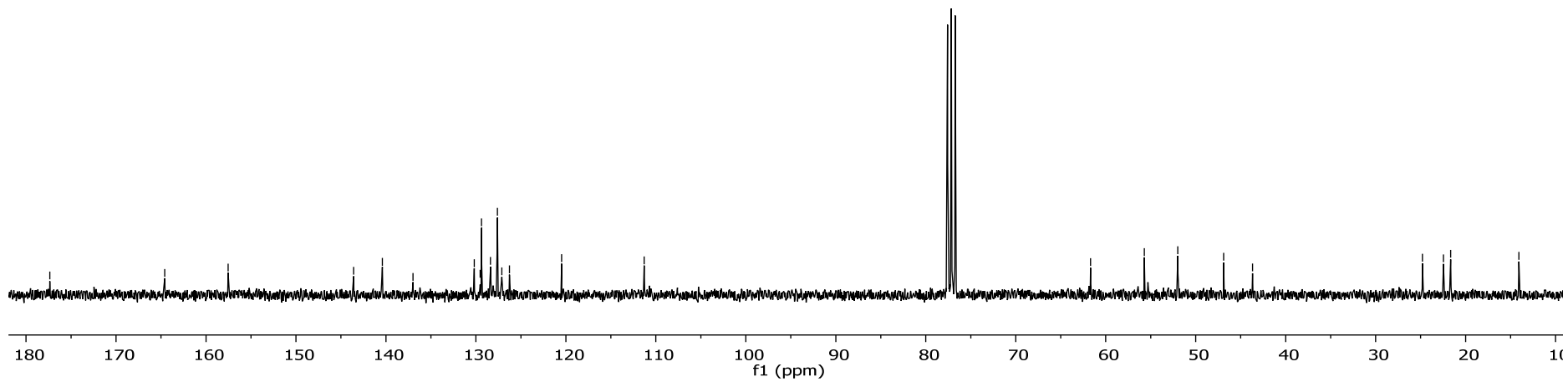
22.46

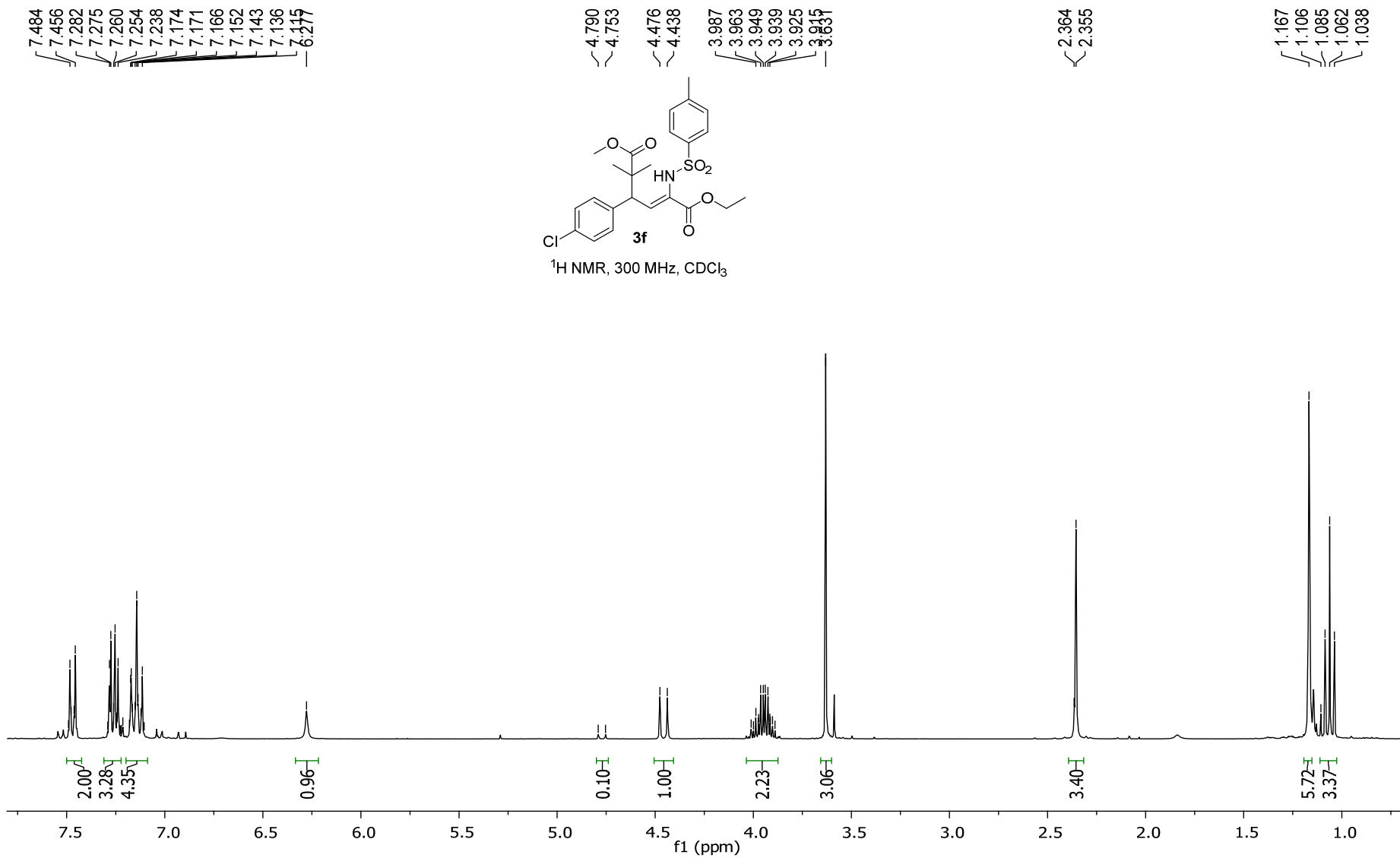
21.66

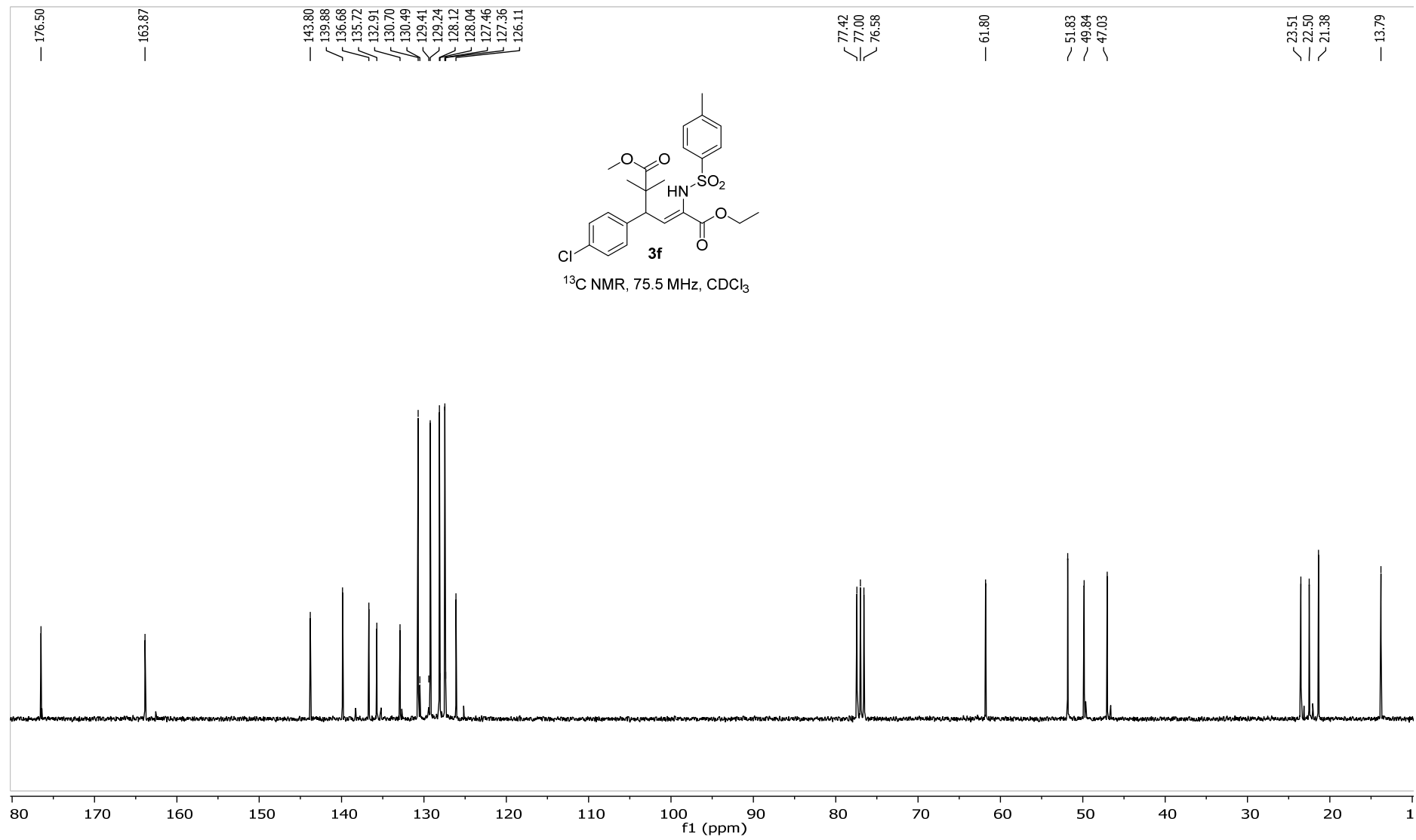
— 14.08



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>





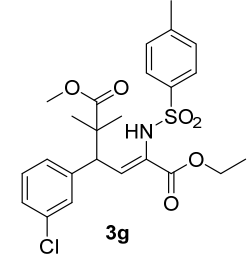


7.486  
7.459  
7.260  
7.245  
7.224  
7.207  
7.204  
7.169  
7.100  
7.092  
7.076  
7.072  
7.063  
7.057  
6.299

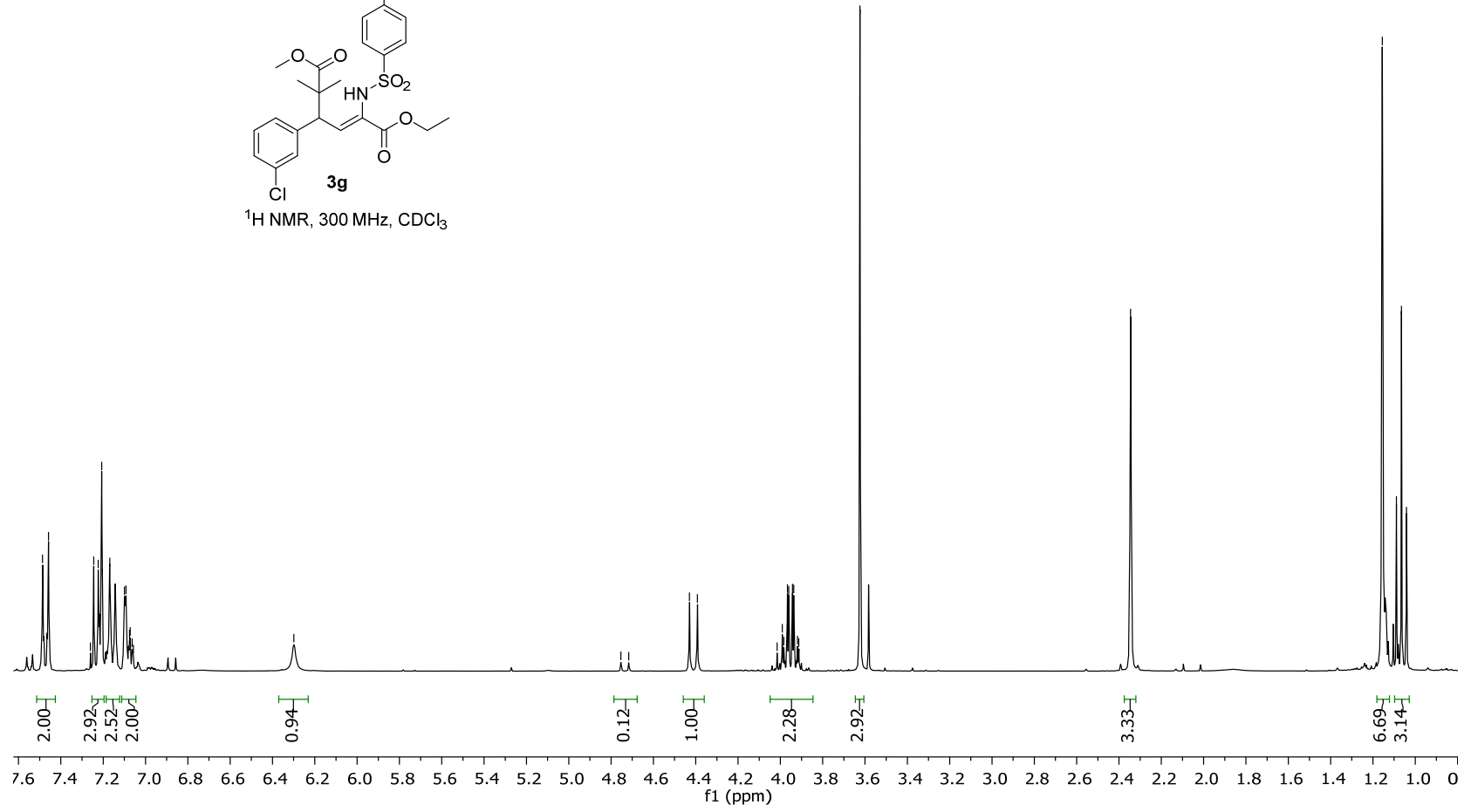
4.754  
4.717  
4.430  
4.392  
4.016  
3.991  
3.984  
3.967  
3.960  
3.943  
3.937  
3.919  
3.913  
3.624

2.345

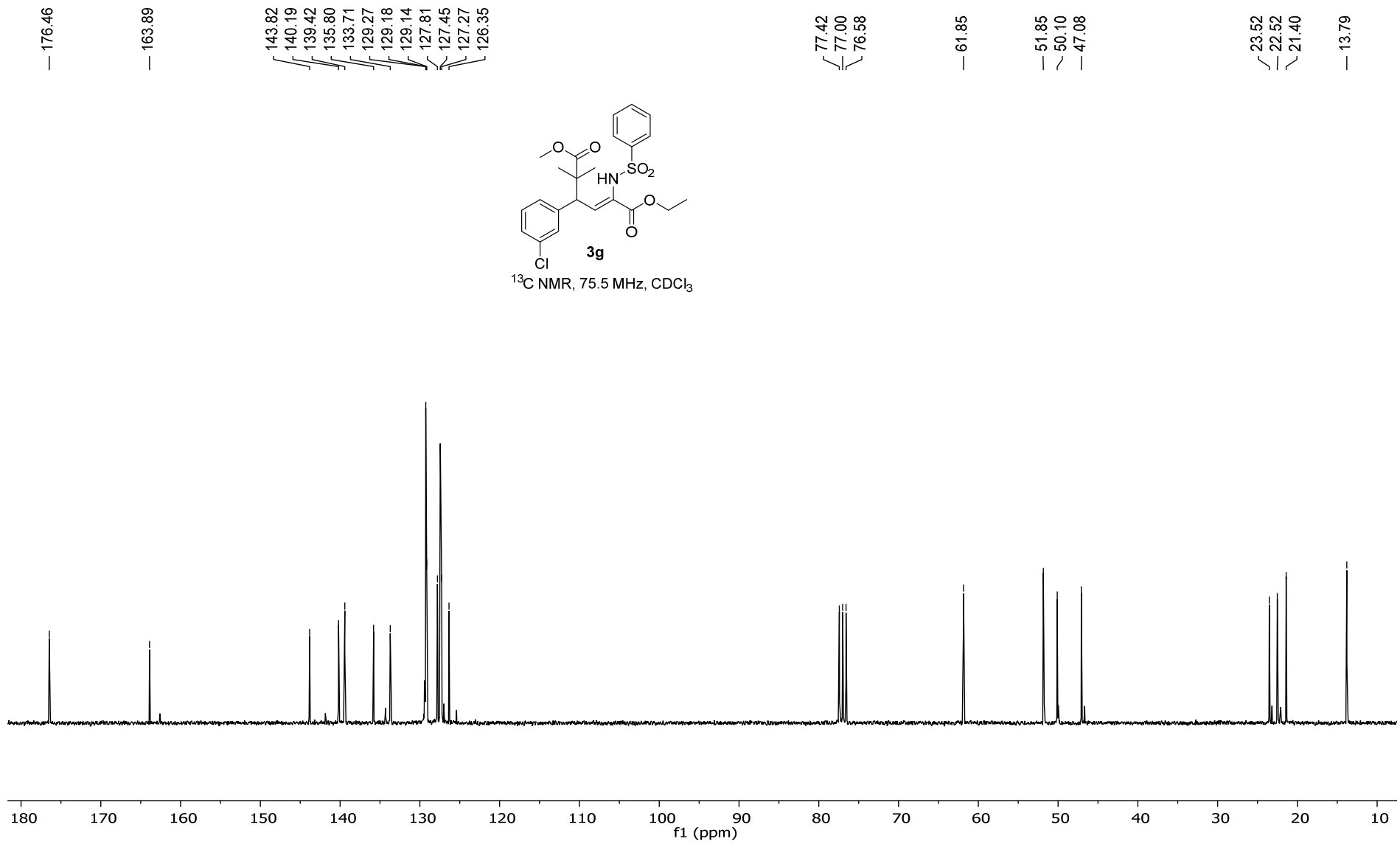
1.156  
1.089  
1.065  
1.041

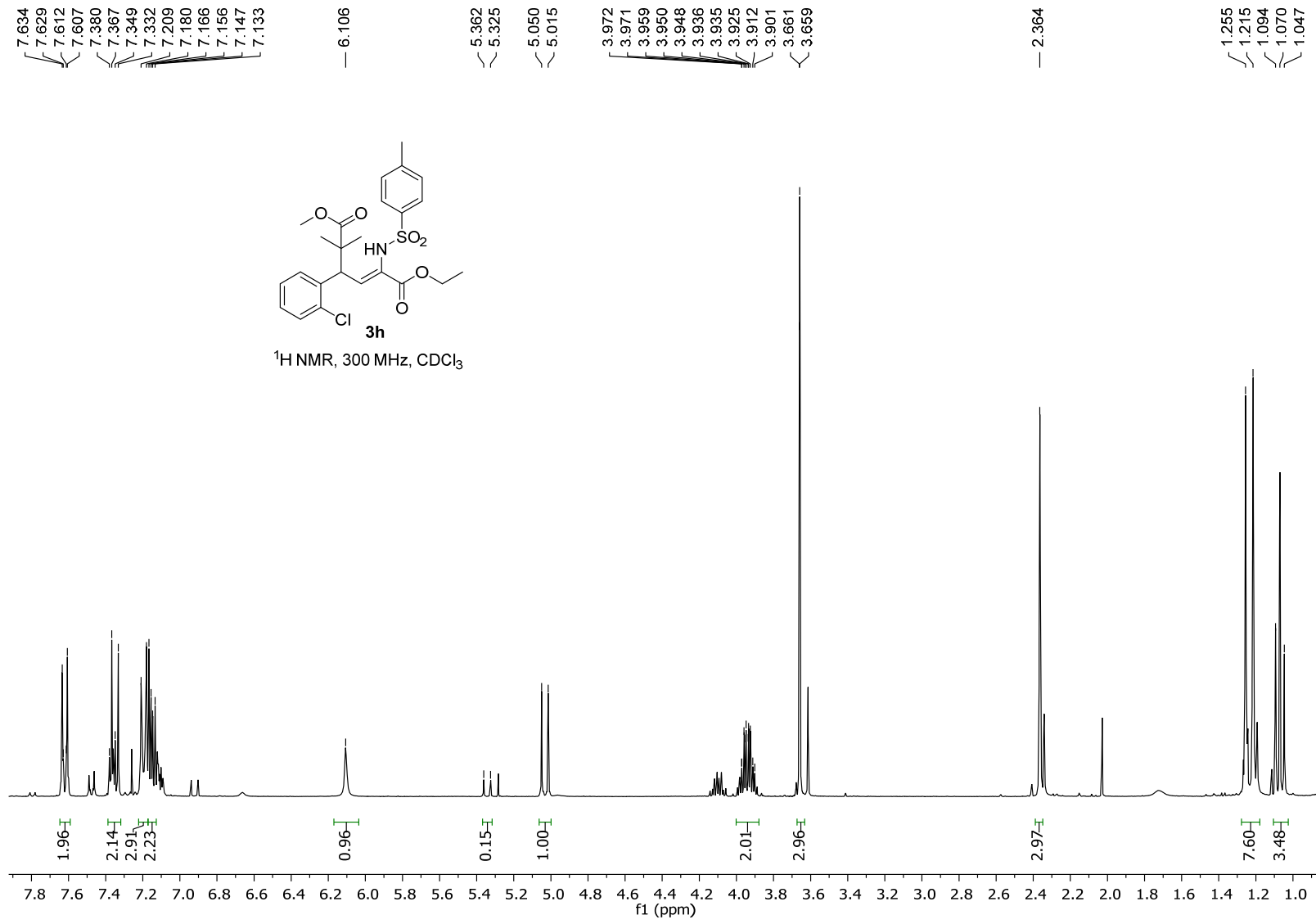


<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>









— 176.74

— 164.11

~ 143.62  
~ 140.03  
~ 136.67  
~ 136.62  
~ 135.18  
~ 130.10  
~ 129.89  
~ 129.29  
~ 128.18  
~ 127.41  
~ 126.69  
~ 126.37

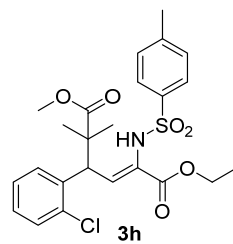
~ 77.42  
~ 77.00  
~ 76.58

— 61.67

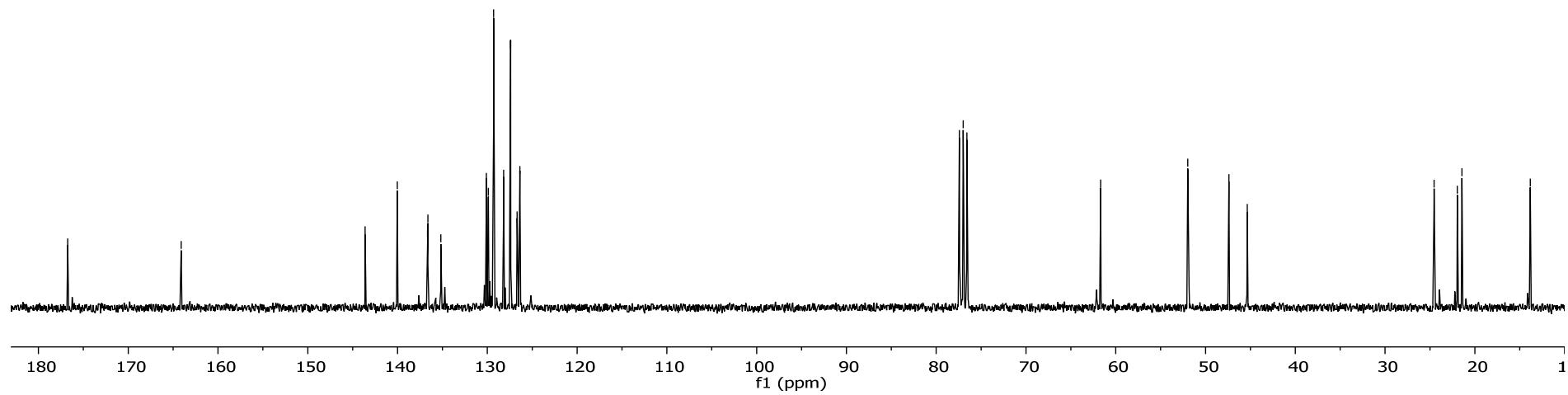
~ 51.98  
~ 47.40  
~ 45.36

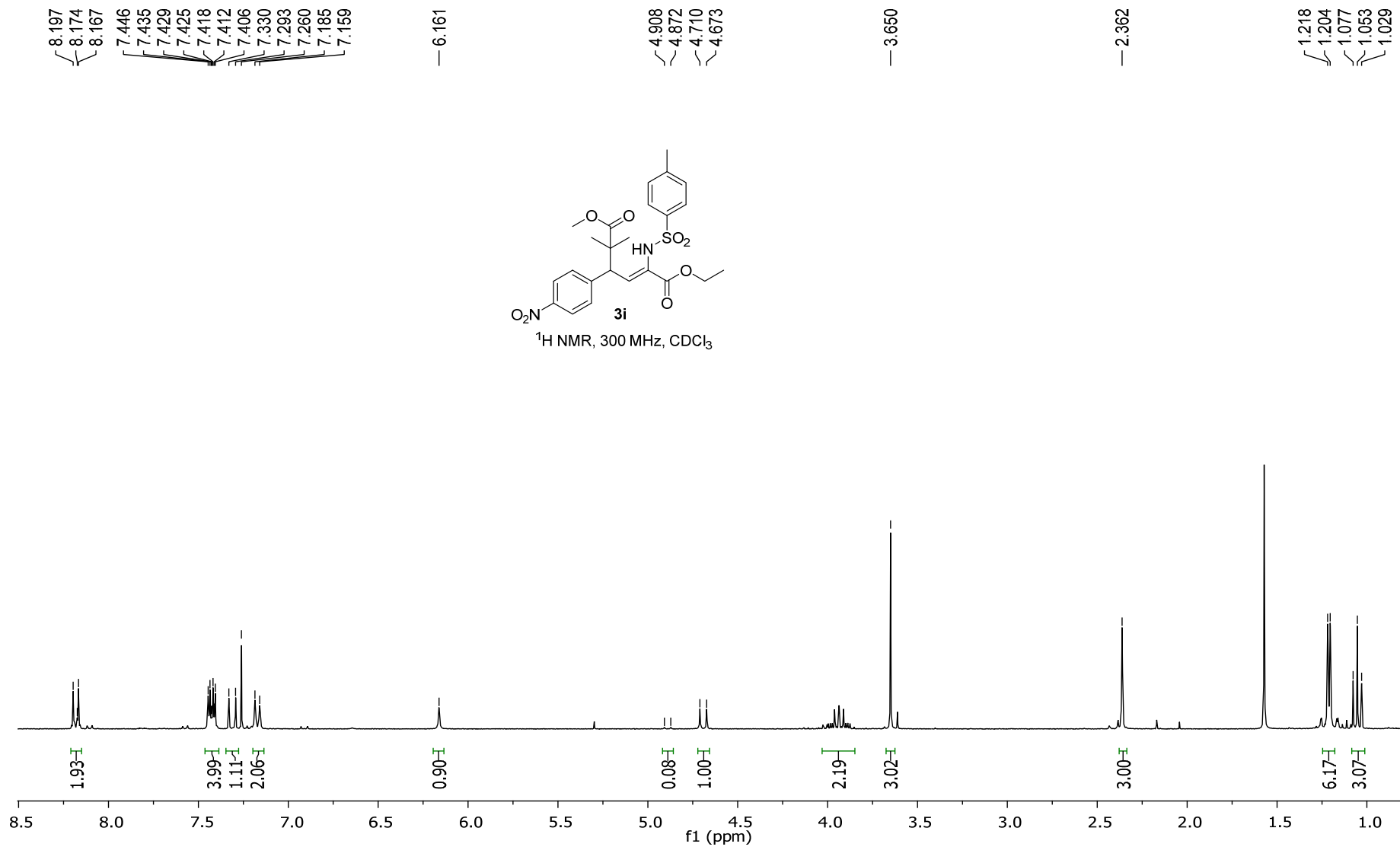
~ 24.54  
~ 21.95  
~ 21.44

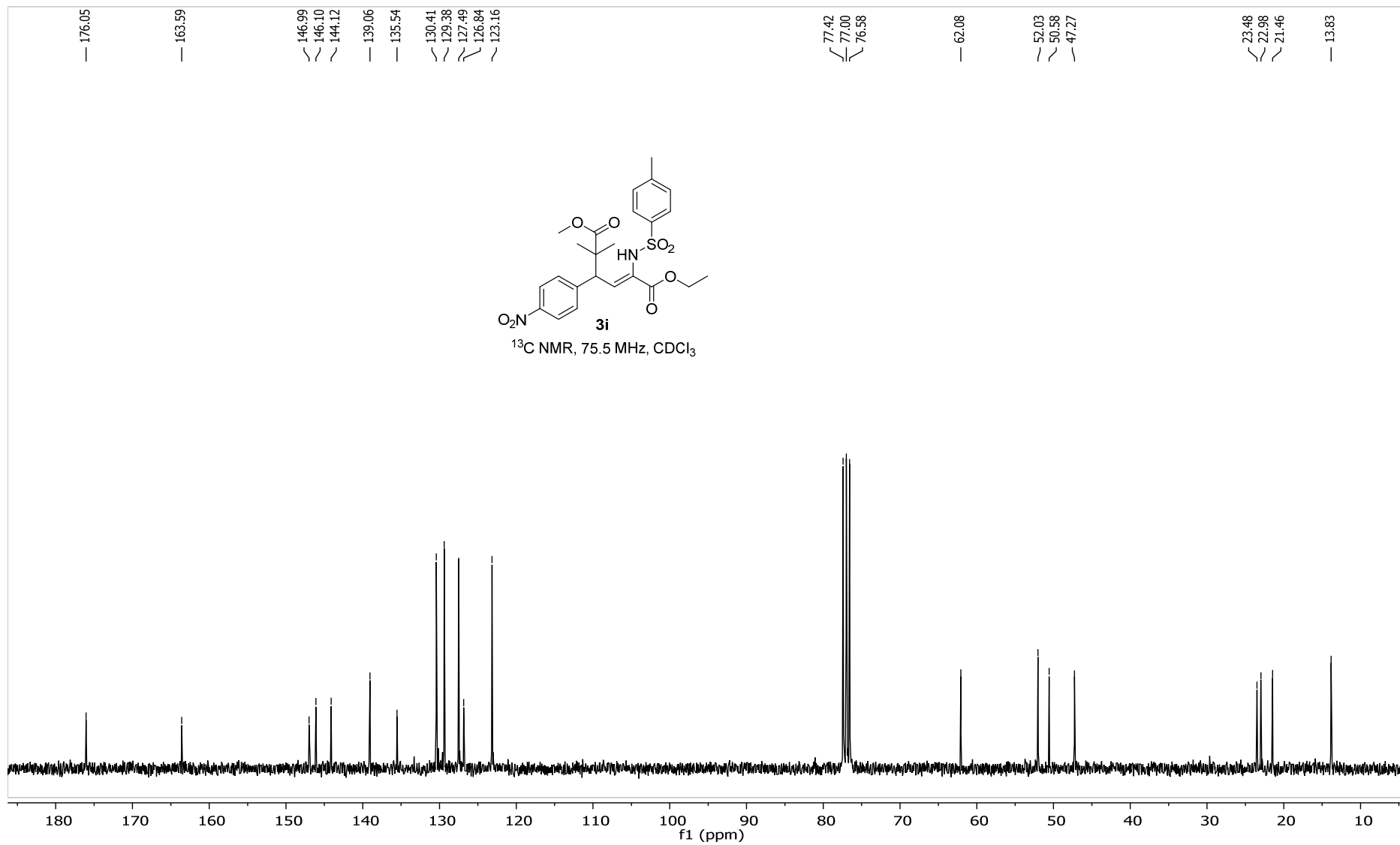
— 13.82

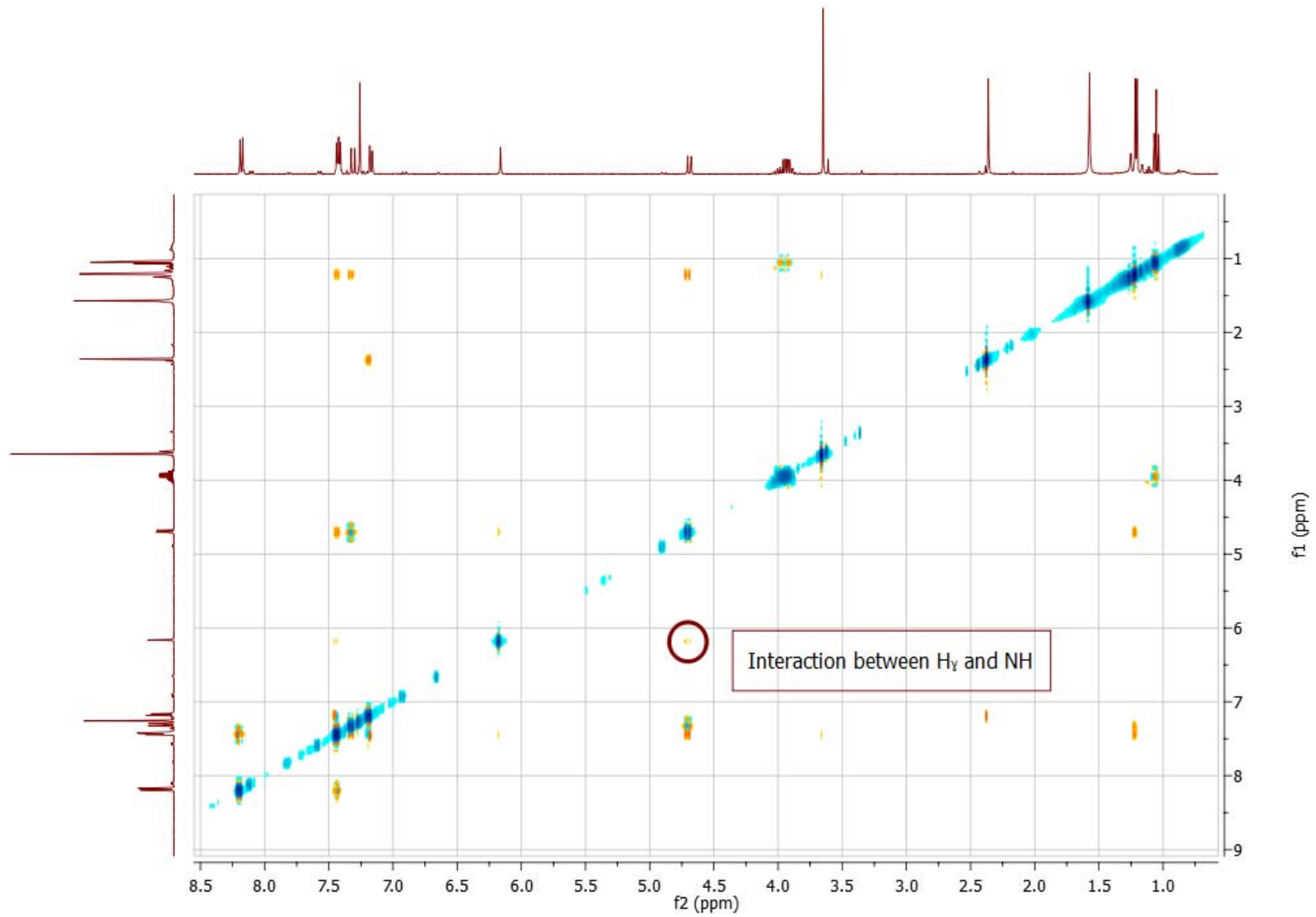


<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>









S62

8.123  
8.119  
8.050  
8.044  
8.037

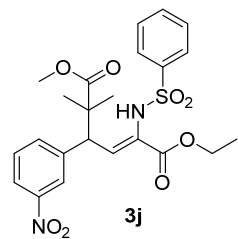
7.605  
7.524  
7.497  
7.451  
7.445  
7.429  
7.423  
7.319  
7.281  
7.260  
7.181  
7.155  
6.209

4.900  
4.864  
4.684  
4.647

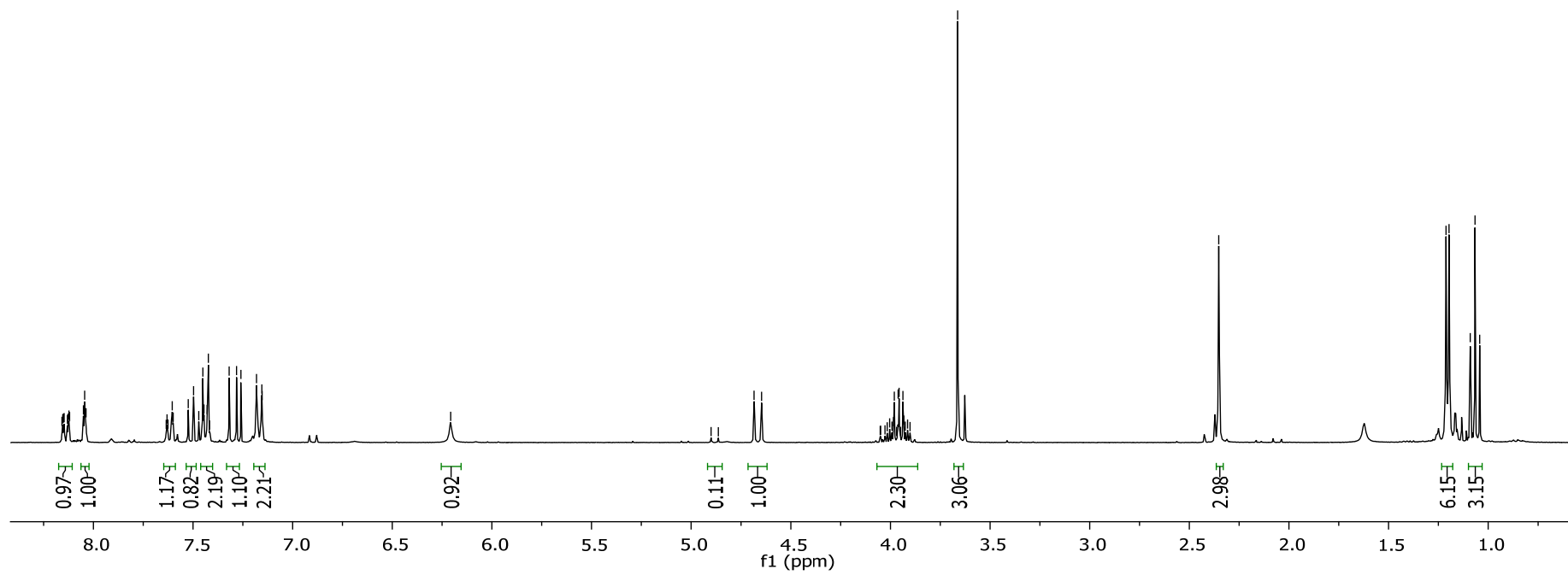
4.004  
3.985  
3.980  
3.961  
3.957  
3.938  
3.823  
3.863

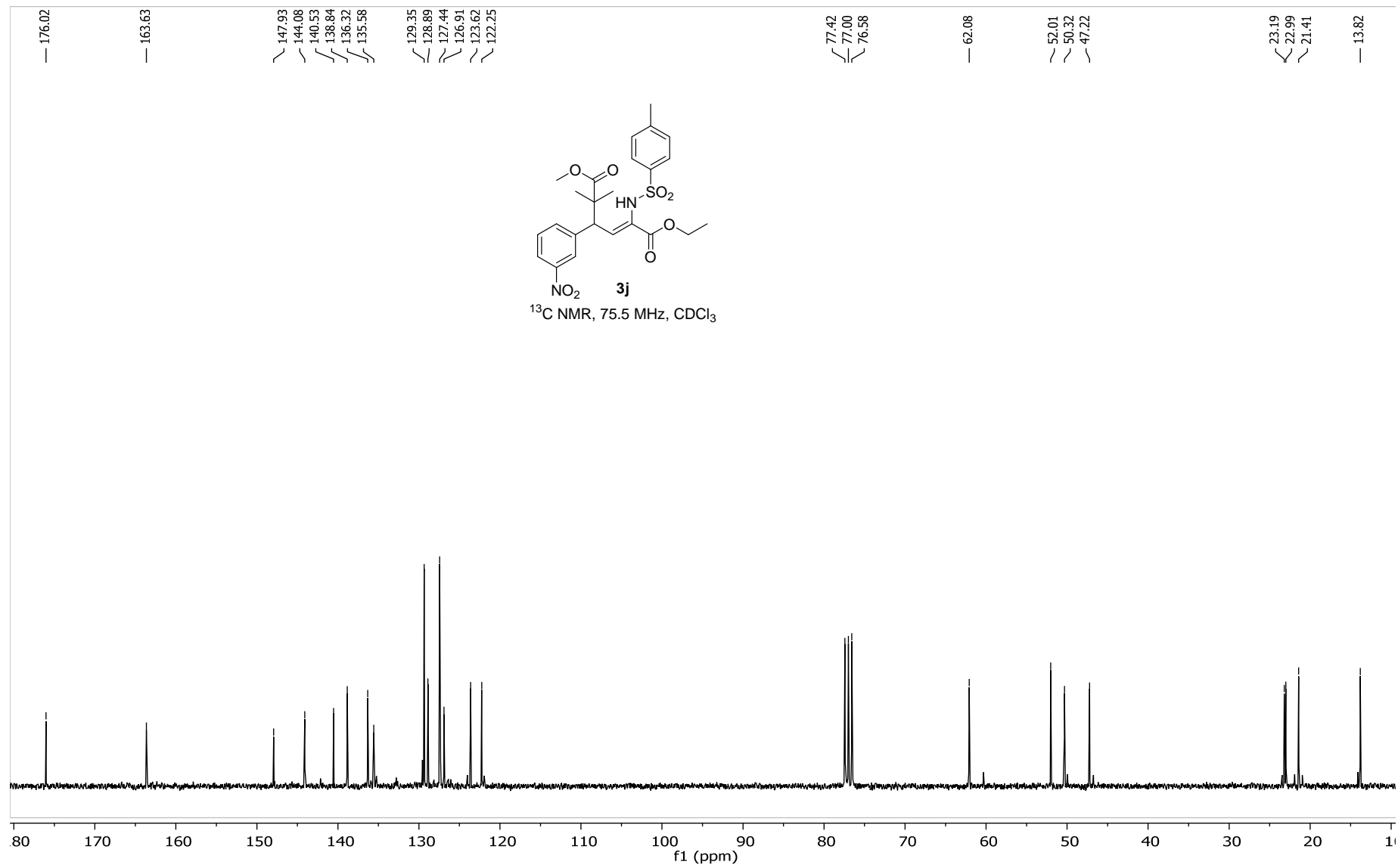
2.352

1.212  
1.197  
1.090  
1.067  
1.043



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>







7.790  
7.785  
7.763  
7.758  
7.682  
7.654  
7.324  
7.319  
7.224  
7.197  
7.043  
6.859

5.427  
5.389

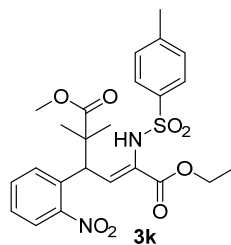
4.942  
4.909

4.074  
4.051

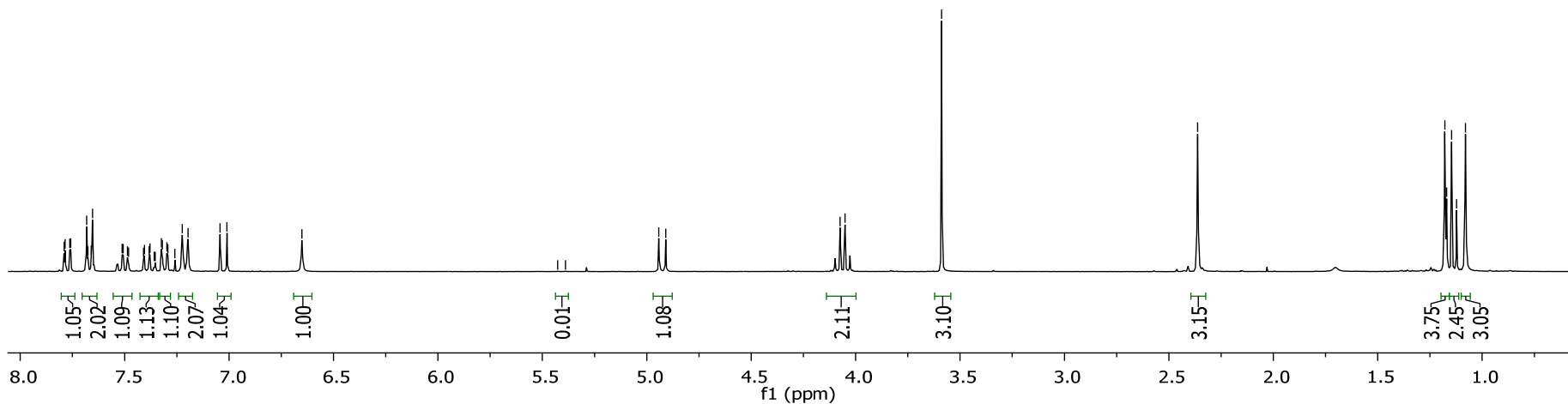
3.588

2.362

1.179  
1.170  
1.146  
1.122  
1.080



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>

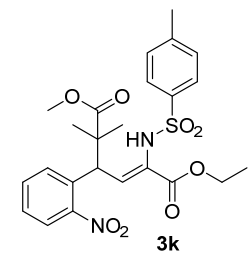


— 175.90  
 — 164.06  
 — 150.57  
 — 143.67  
 136.89  
 134.02  
 133.04  
 132.13  
 130.61  
 129.30  
 129.06  
 128.11  
 127.37  
 124.89

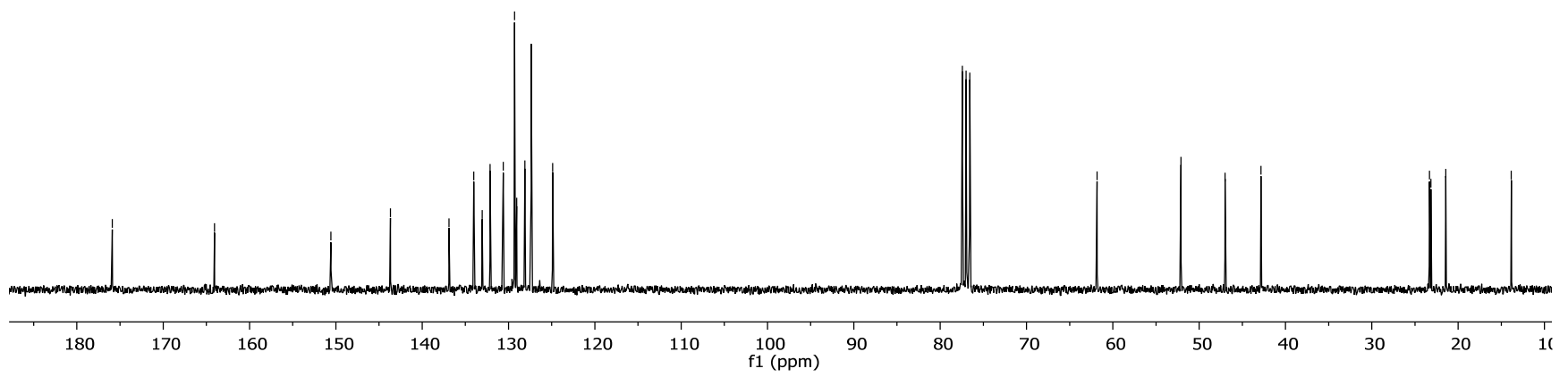
77.42  
 77.00  
 76.58

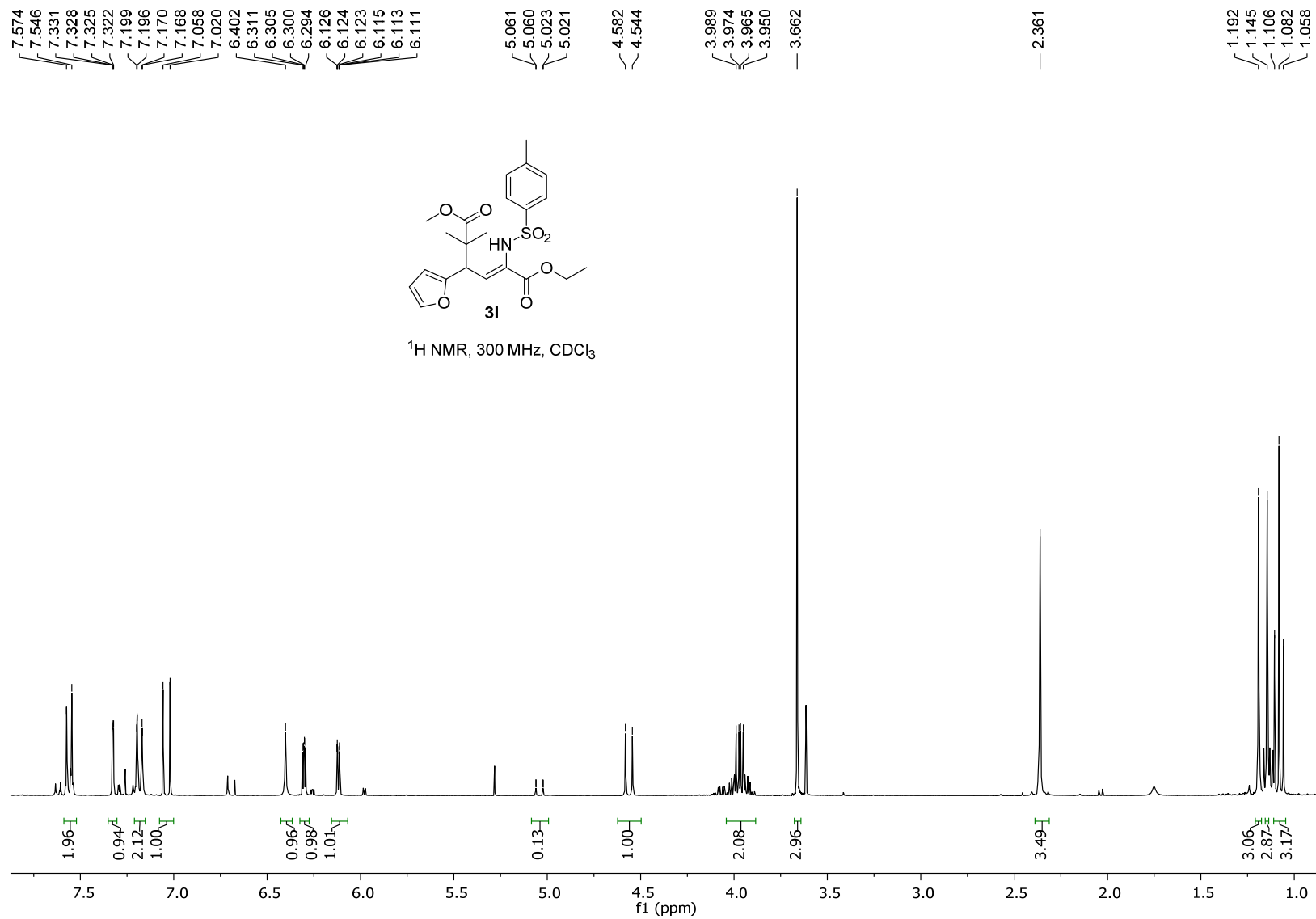
— 61.83  
 — 52.11  
 — 47.00  
 — 42.84

23.33  
 23.15  
 21.44  
 — 13.85



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>





— 176.84

— 164.00

— 151.63

~ 143.76

~ 141.73

~ 137.06

~ 135.95

~ 129.48

~ 129.29

~ 127.53

~ 126.42

~ 110.11

~ 108.32

~ 77.42

~ 77.00

~ 76.58

— 61.83

— 52.07

— 46.90

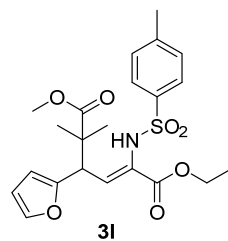
— 44.52

~ 23.50

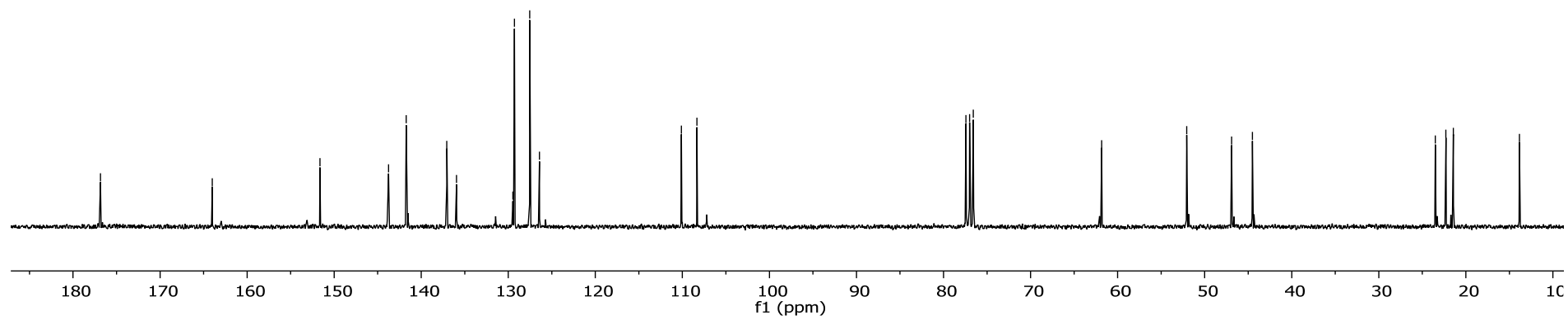
~ 22.29

~ 21.44

— 13.84



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



7.516  
7.510  
7.488  
7.315  
7.285  
7.277  
7.267  
7.260  
7.255  
7.173  
7.171  
7.144  
7.143  
7.136  
6.227

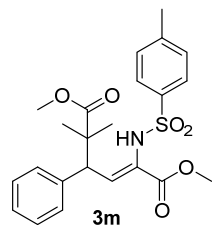
4.738  
4.700

4.360  
4.323

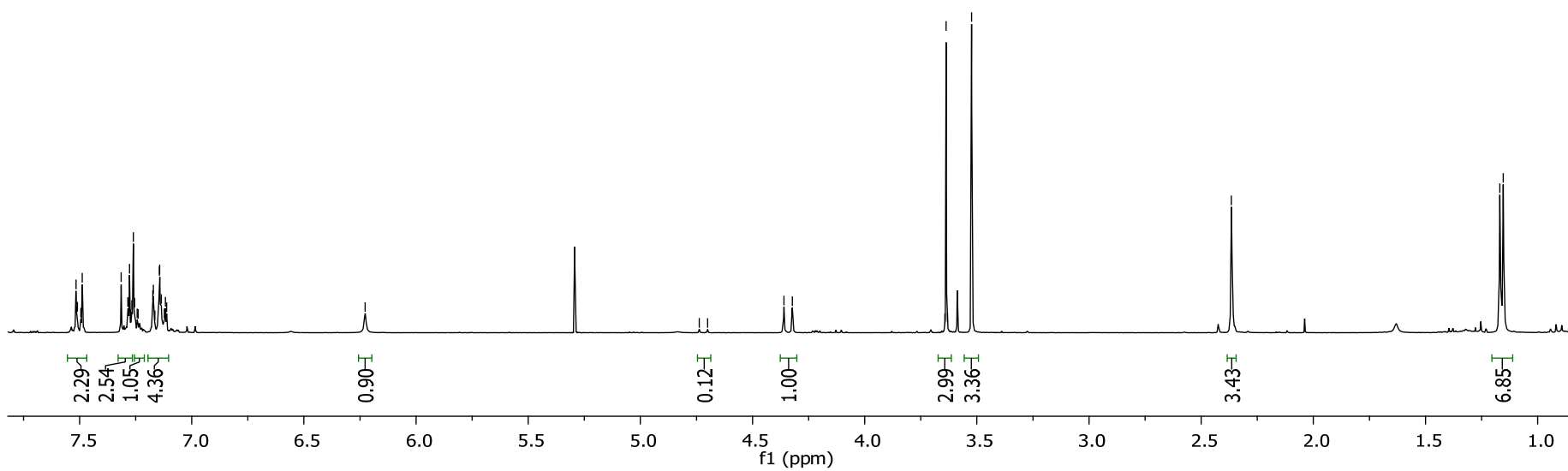
3.642  
3.637  
3.631  
3.523

2.365

1.169  
1.153



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 177.02

— 164.69

— 143.74

— 140.63

— 137.94

— 136.04

— 129.45

— 129.30

— 128.07

— 127.52

— 127.21

— 125.75

— 77.42

— 77.00

— 76.58

— 52.52

— 51.93

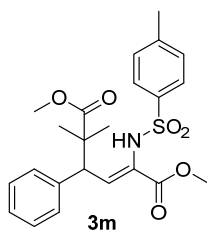
— 50.44

— 47.07

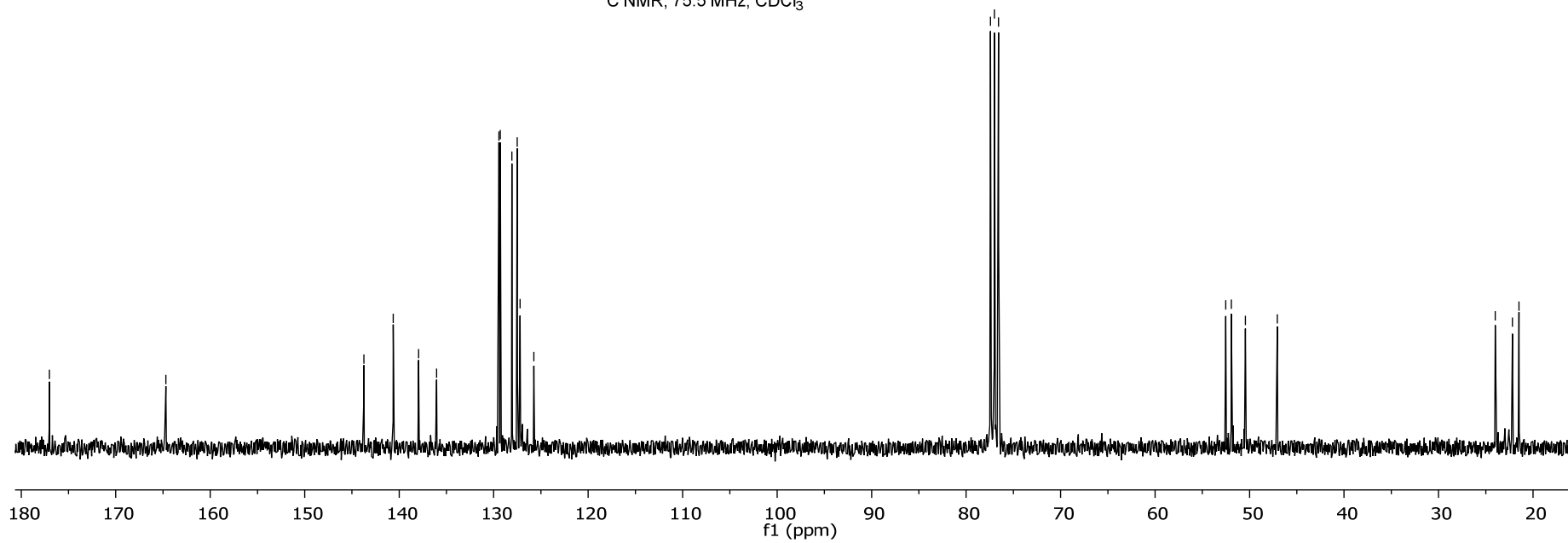
— 24.00

— 22.18

— 21.49



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



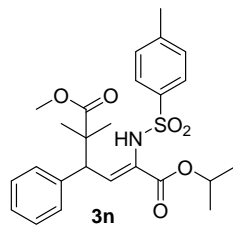
7.504  
7.481  
7.476  
7.310  
7.291  
7.286  
7.281  
7.278  
7.272  
7.260  
7.197  
7.190  
7.170  
7.143  
6.243

4.829  
4.808  
4.787  
4.766  
4.745  
4.471  
4.434

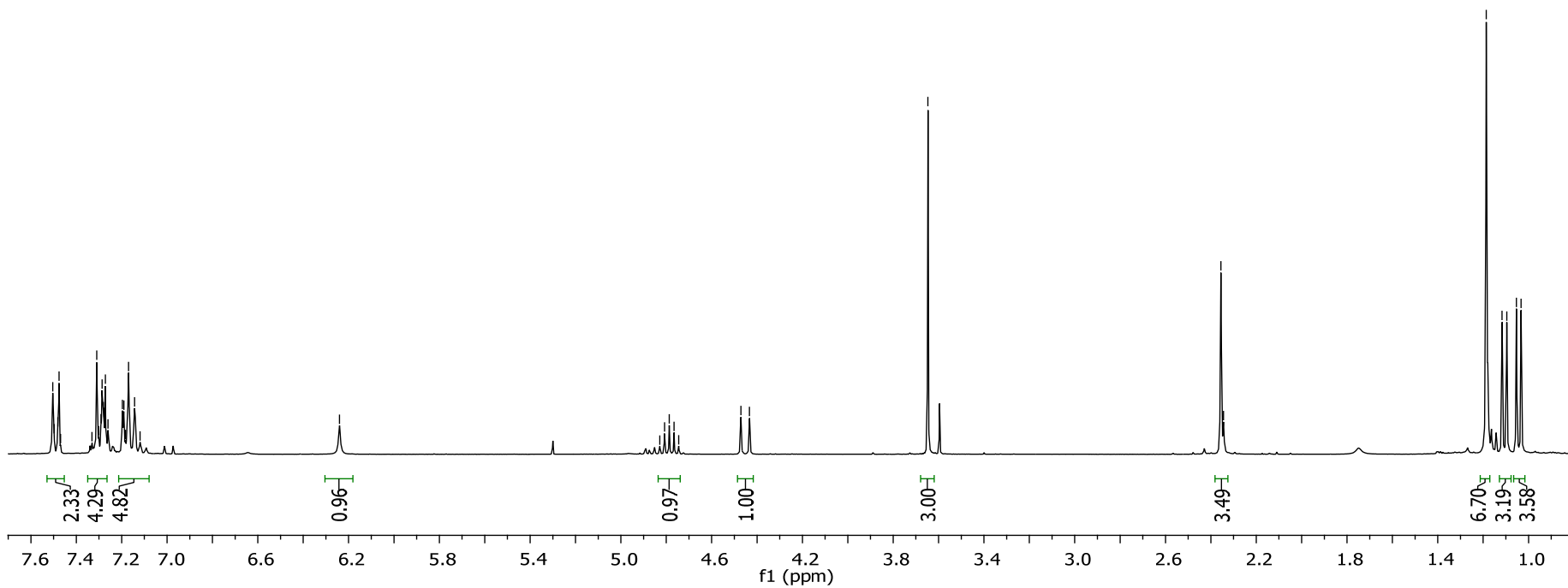
3.647

2.356  
2.344

1.186  
1.117  
1.096  
1.054  
1.033



<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>



— 176.82

— 163.66

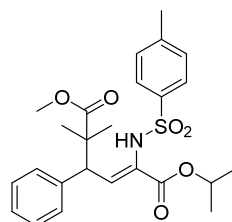
143.68  
140.08  
138.16  
135.90  
129.43  
129.36  
129.28  
129.23  
127.99  
127.58  
127.47  
127.10  
126.07

77.42  
77.00  
76.58

— 69.73

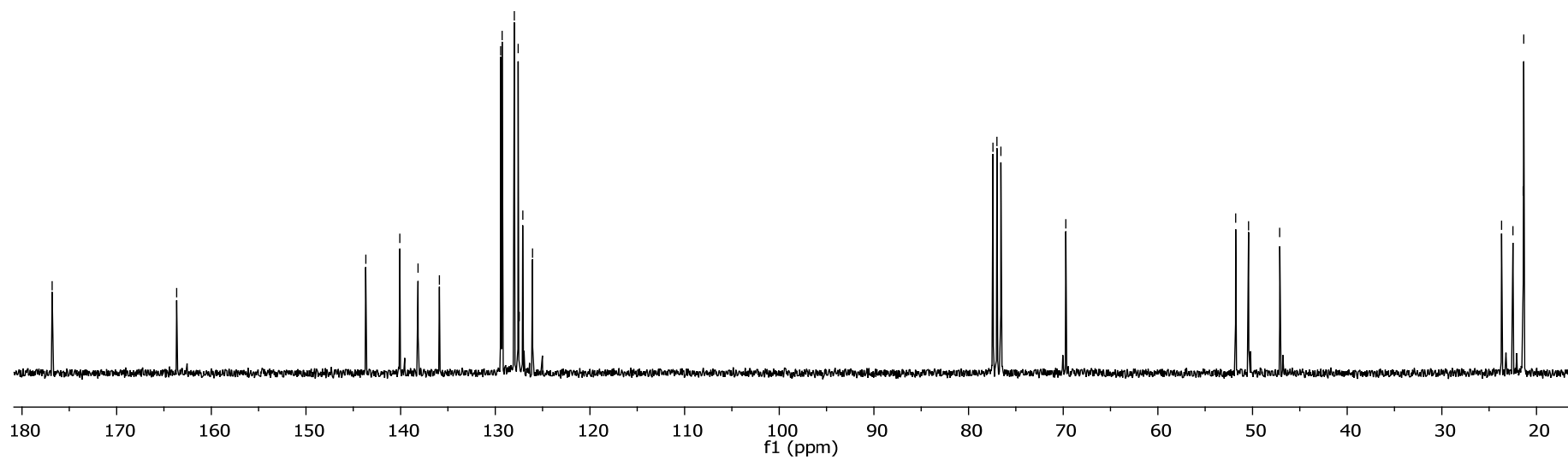
51.78  
50.42  
47.13

23.69  
22.48  
21.39  
21.34

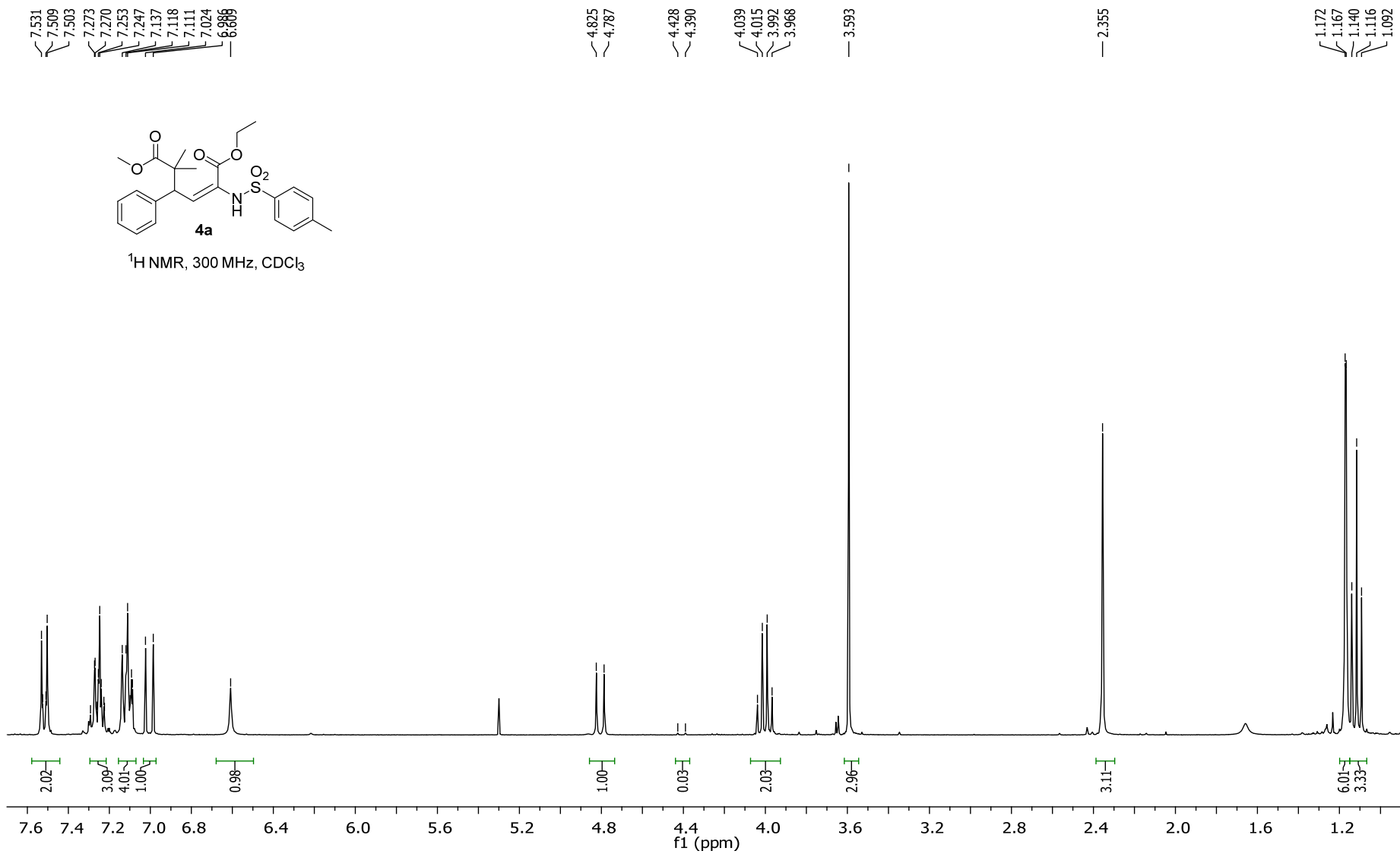


$^{13}\text{C}$  NMR, 75.5 MHz,  $\text{CDCl}_3$

**3n**







— 176.71

— 162.90

143.77  
139.66  
136.27  
135.88

129.42  
129.28  
127.98  
127.49  
126.95  
124.83

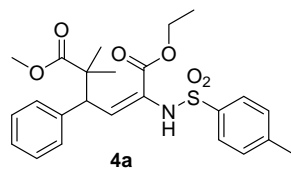
77.42  
77.00  
76.58

— 61.83

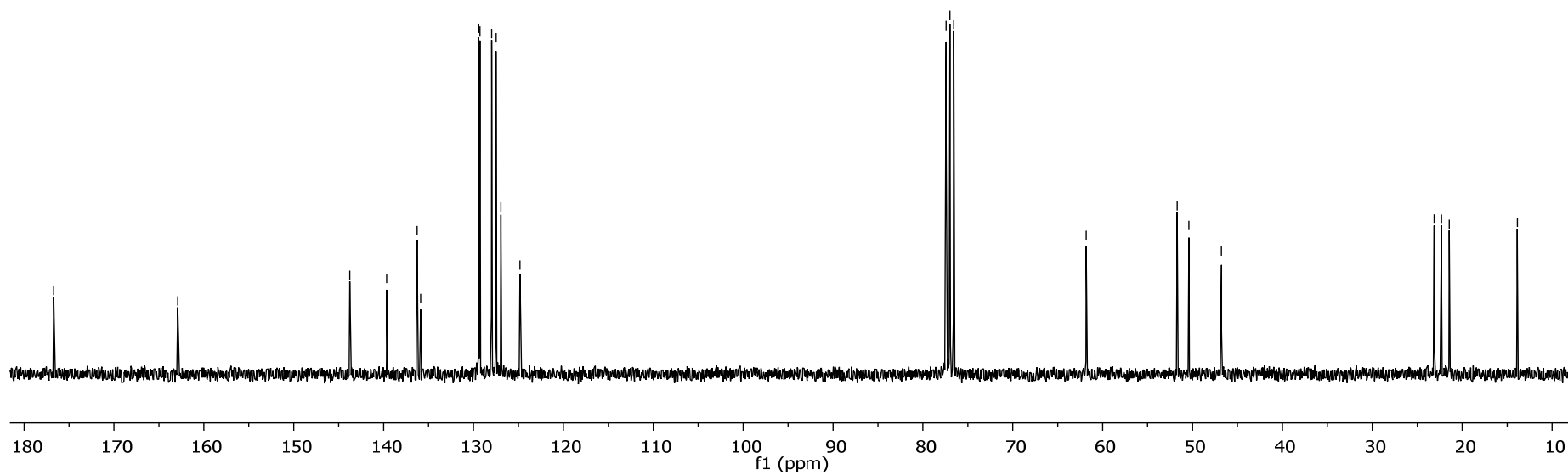
51.71  
50.40  
46.78

23.12  
22.30  
21.44

— 13.87



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



7.540  
7.534  
7.518  
7.512

7.141  
7.114  
7.077  
7.050  
6.993  
6.985  
6.957  
6.579

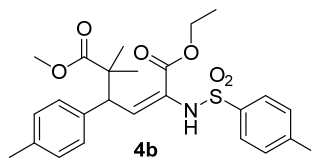
4.786  
4.748

4.363  
4.326

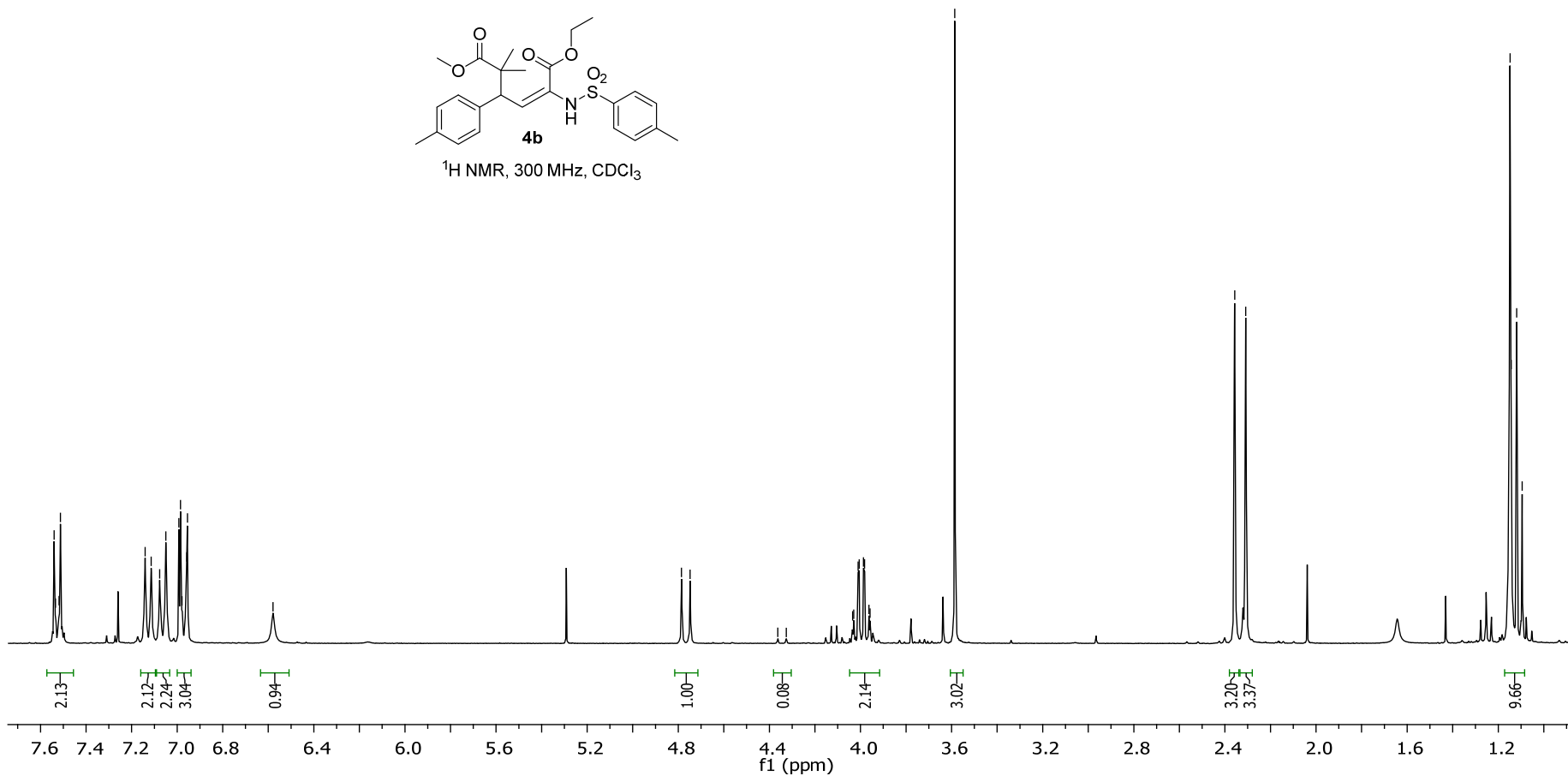
4.029  
4.011  
4.006  
3.987  
3.982  
3.963  
3.888

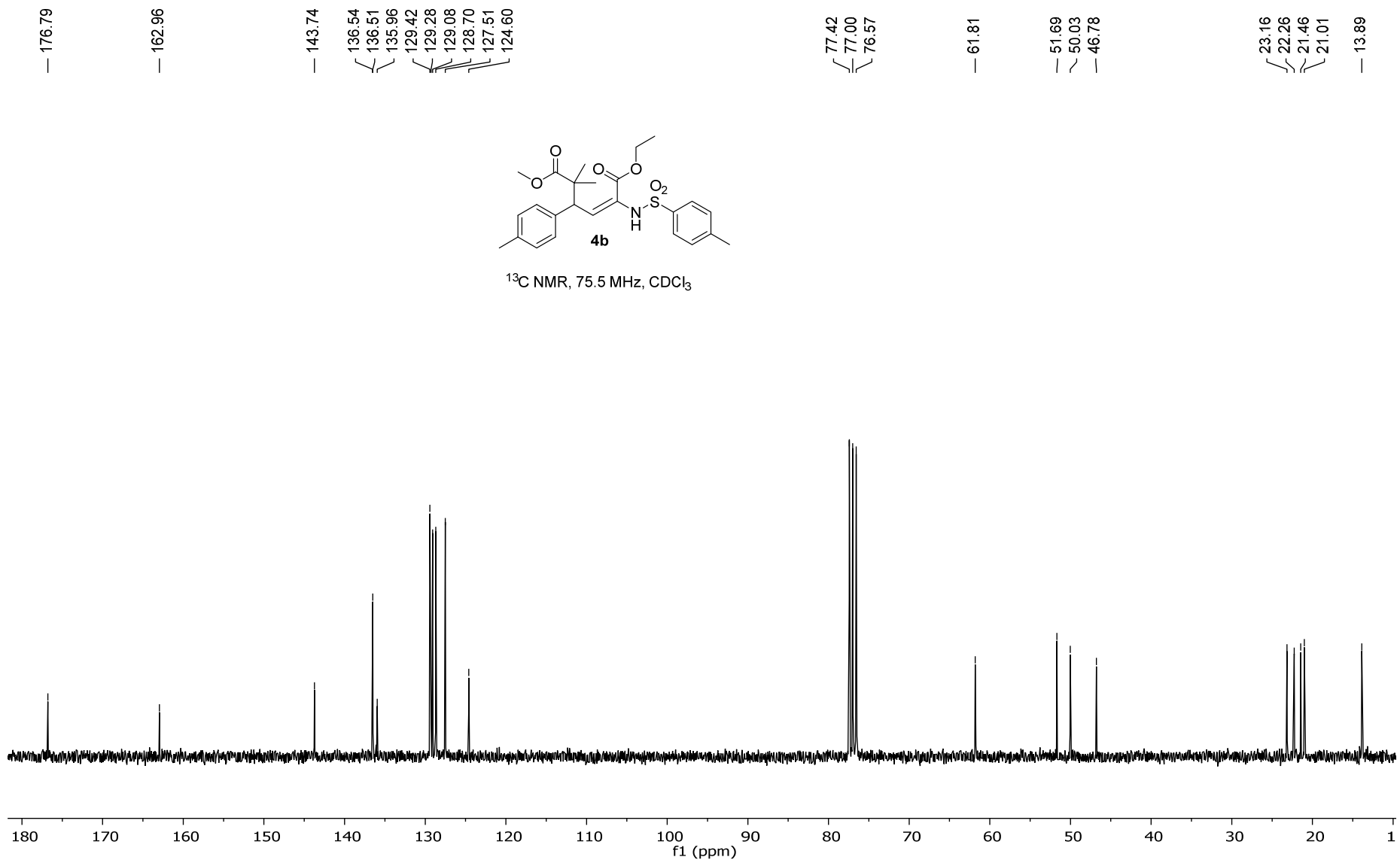
2.357  
2.309

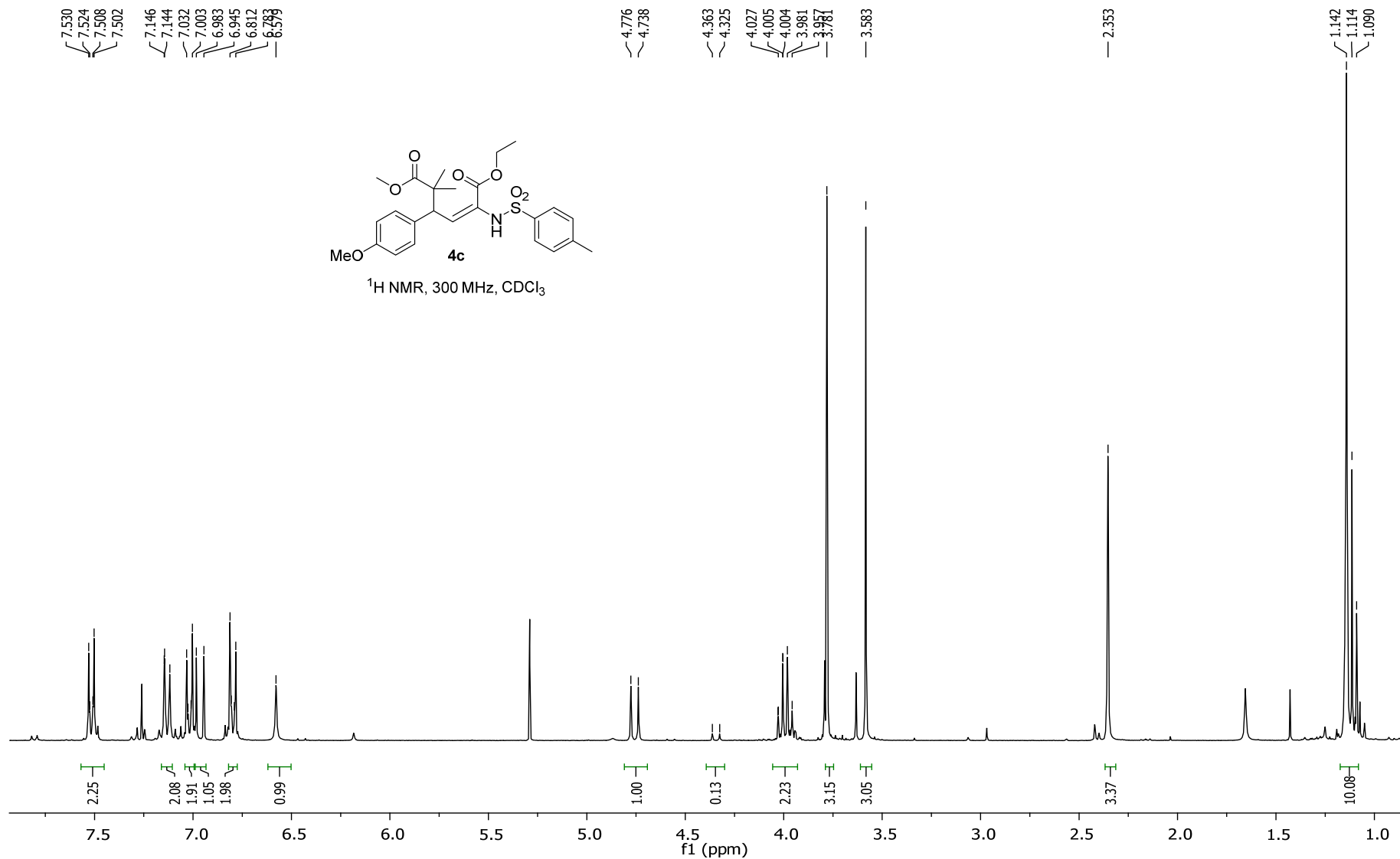
1.148  
1.143  
1.119  
1.095

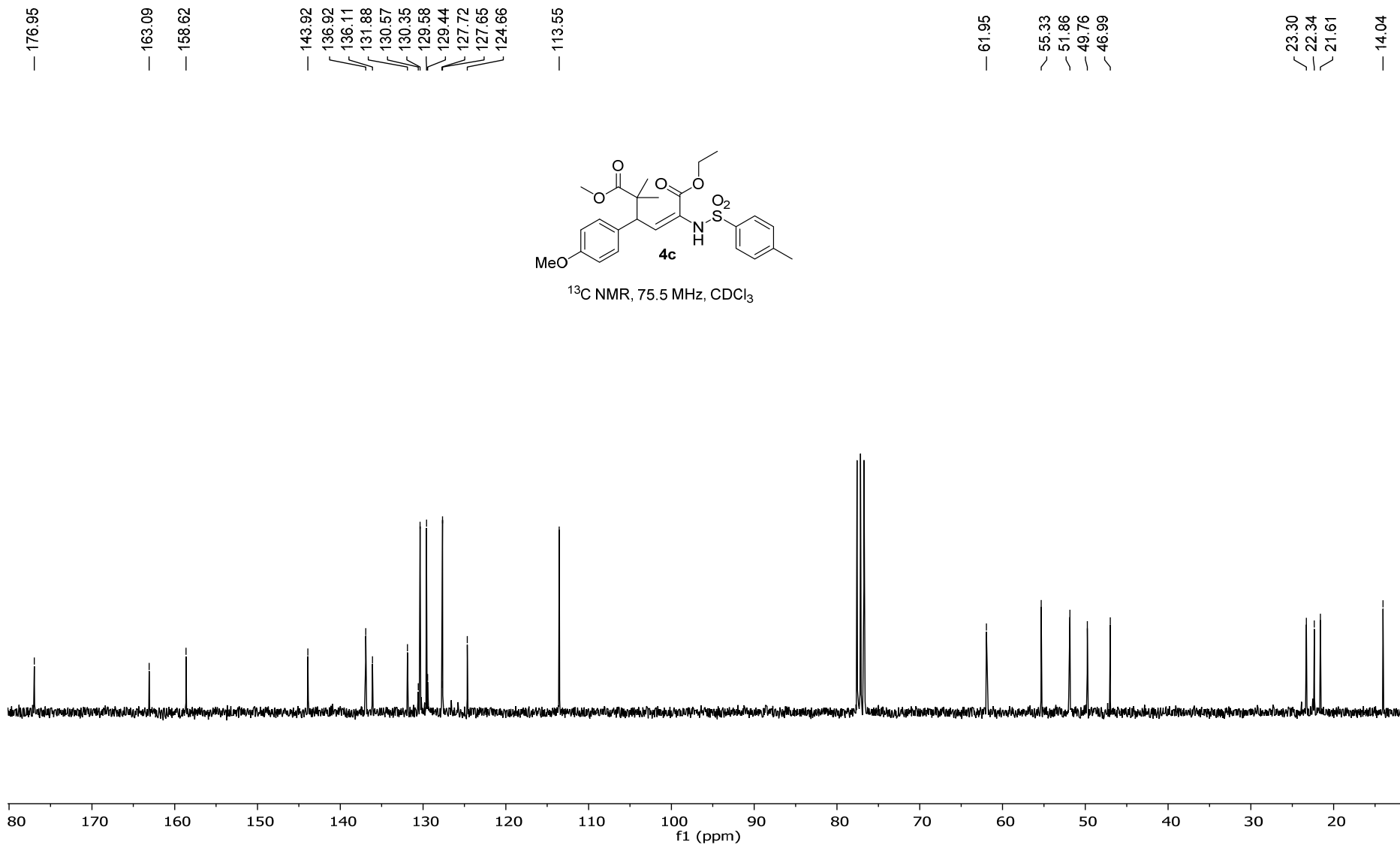


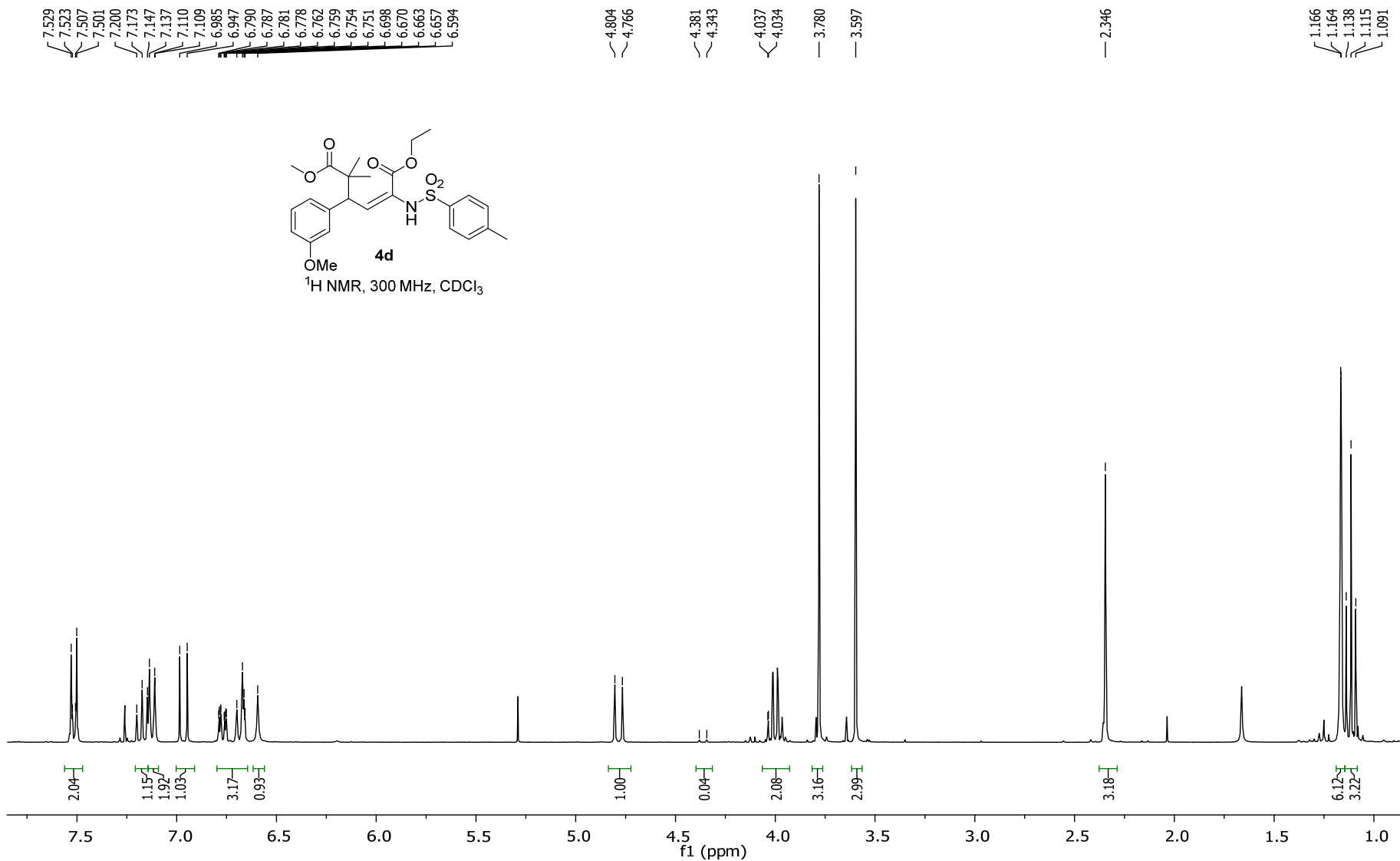
<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>

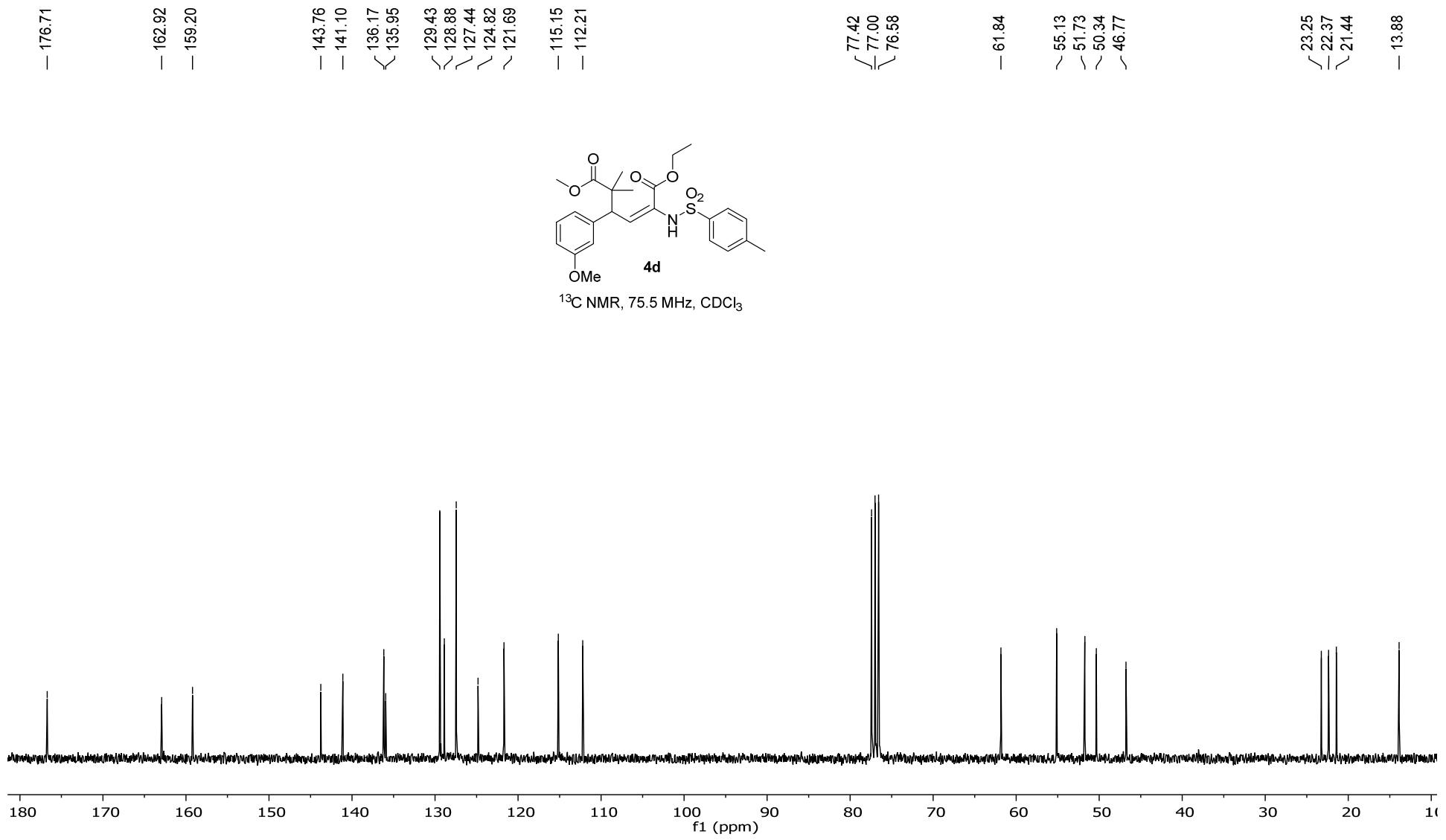




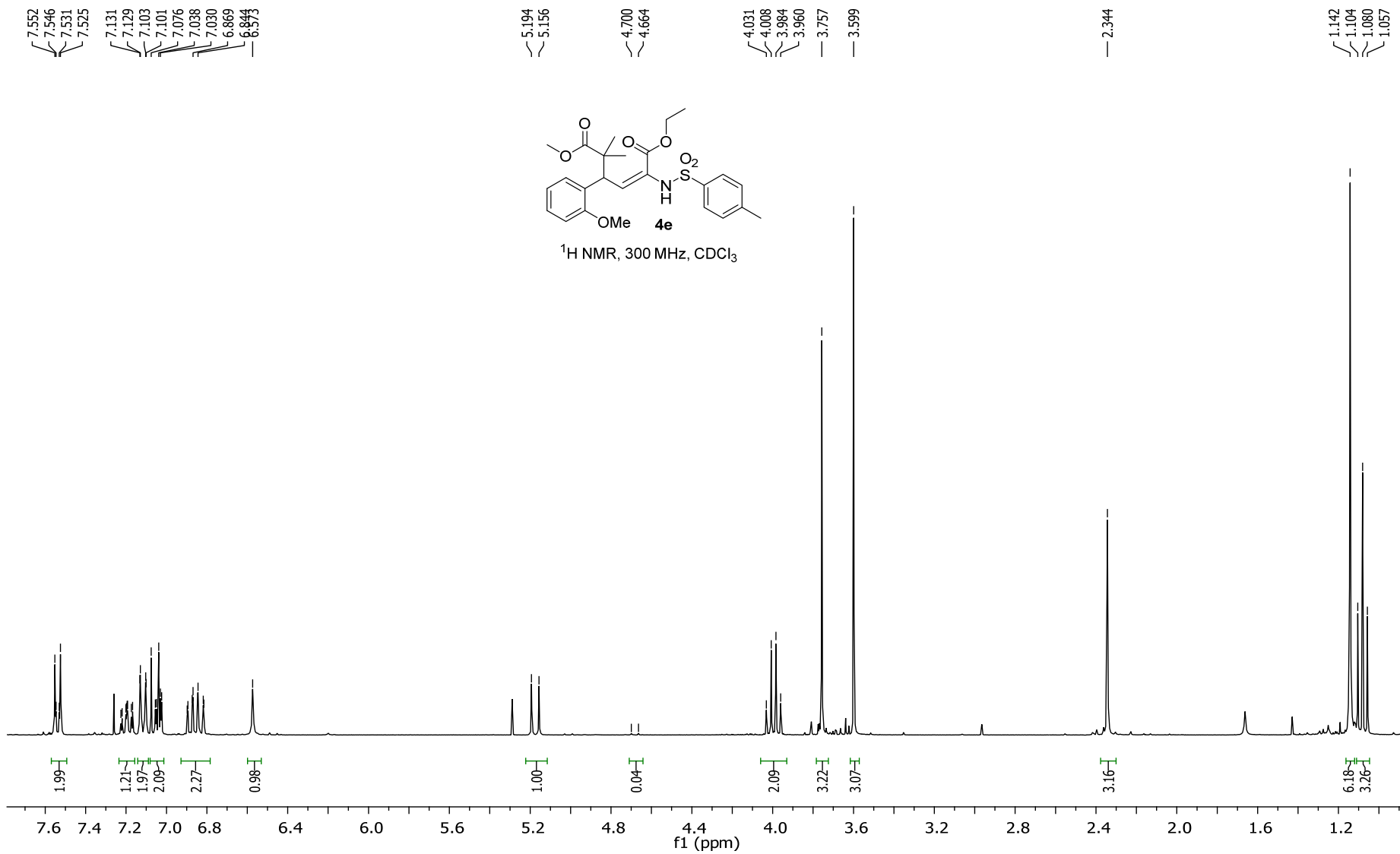












— 176.84

— 163.35

— 157.22

— 143.56

— 137.00

— 136.02

— 130.34

— 129.34

— 128.23

— 127.90

— 127.52

— 124.29

— 120.10

— 110.52

— 77.42

— 77.00

— 76.58

— 61.69

— 55.12

— 51.63

— 46.81

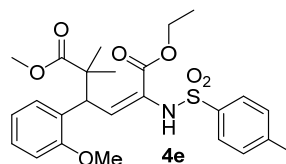
— 43.69

— 23.87

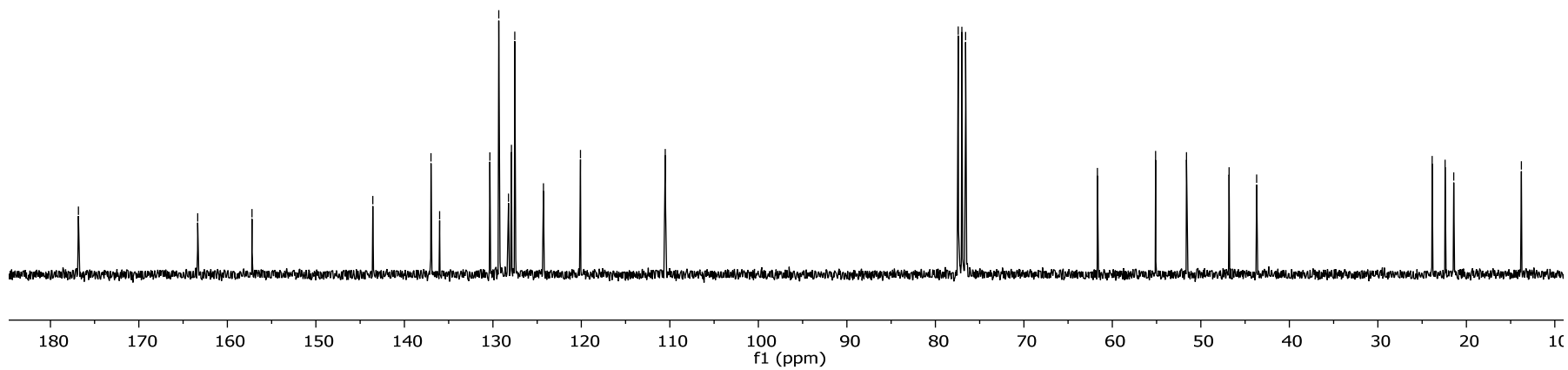
— 22.40

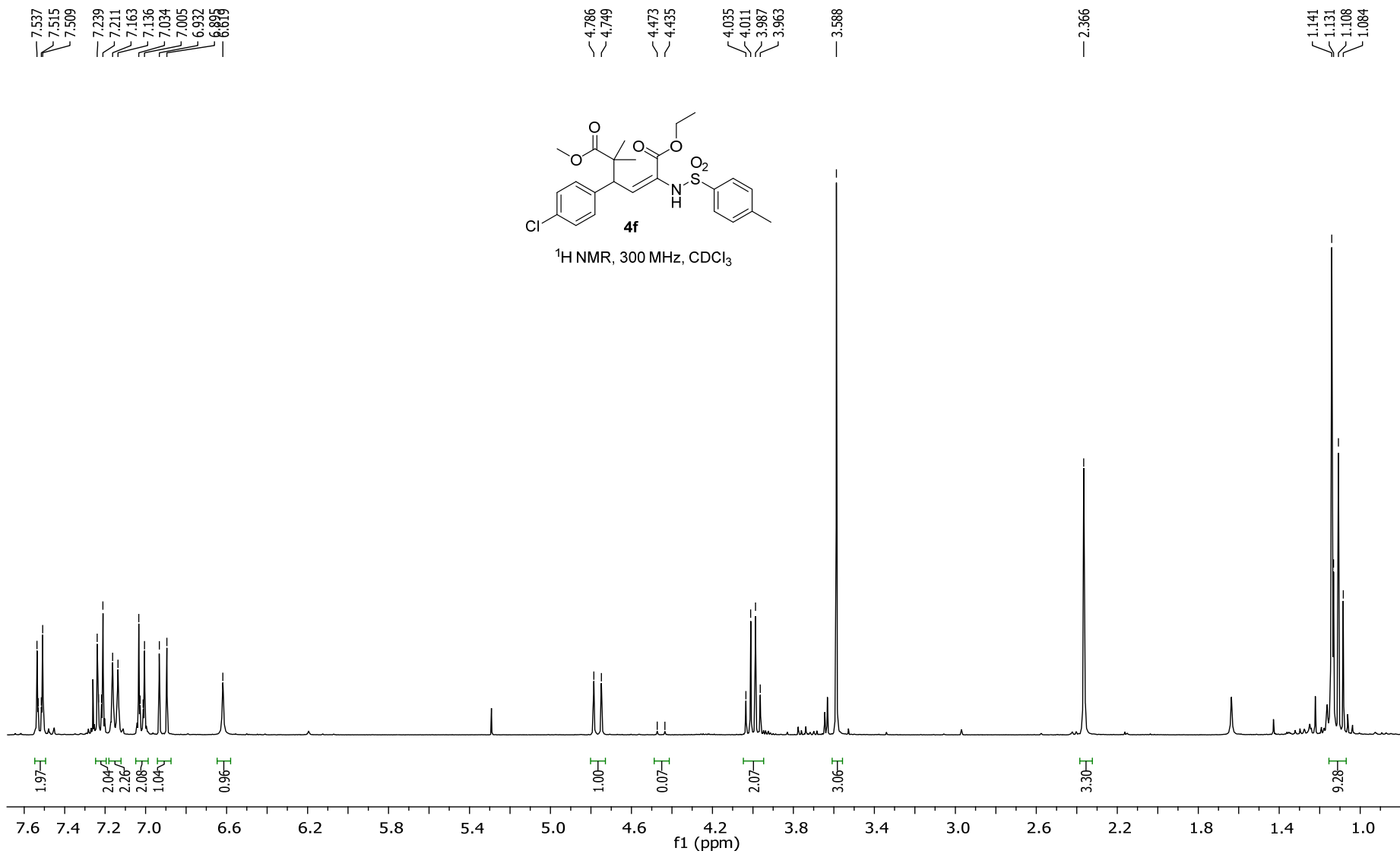
— 21.43

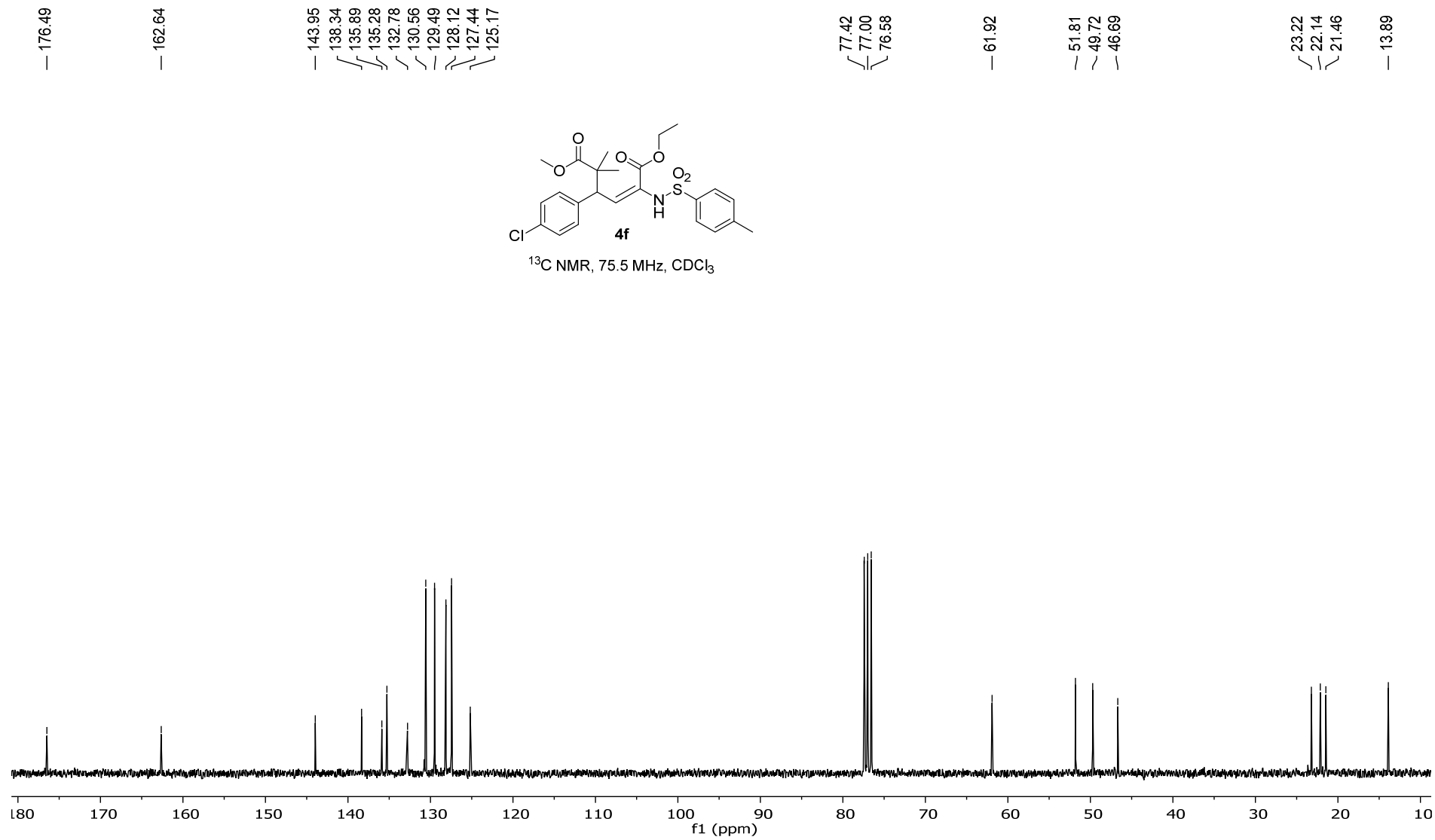
— 13.78

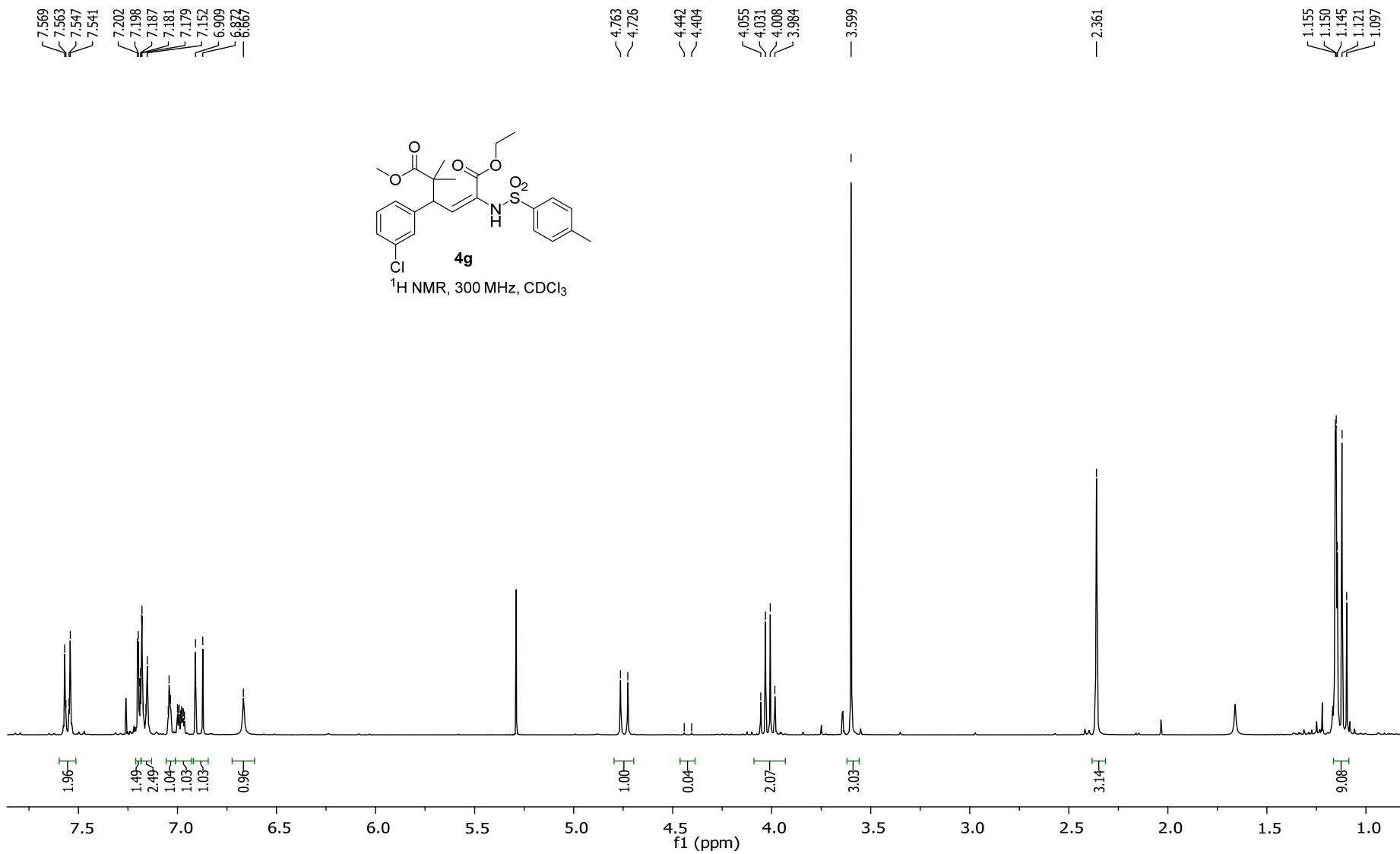


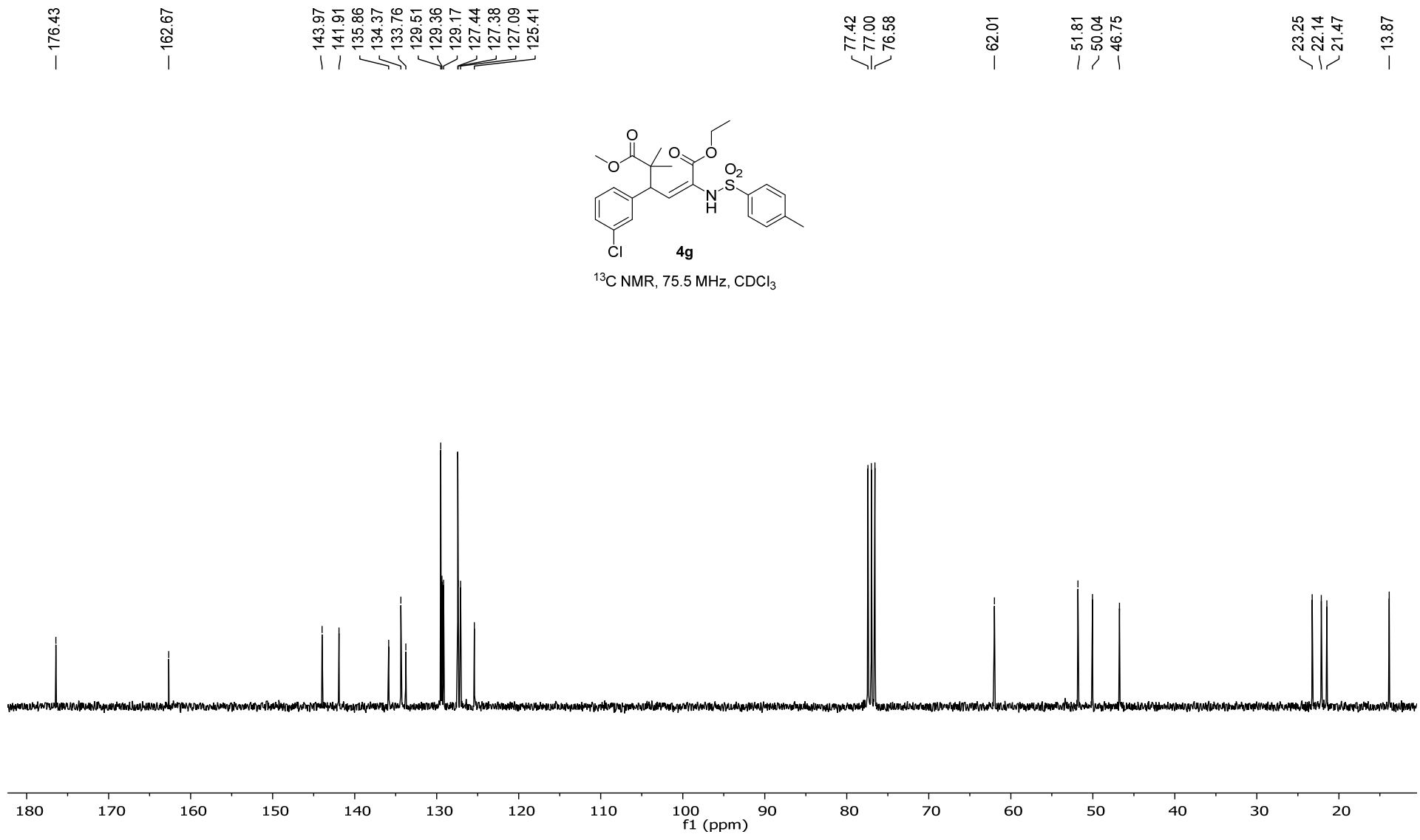
<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>

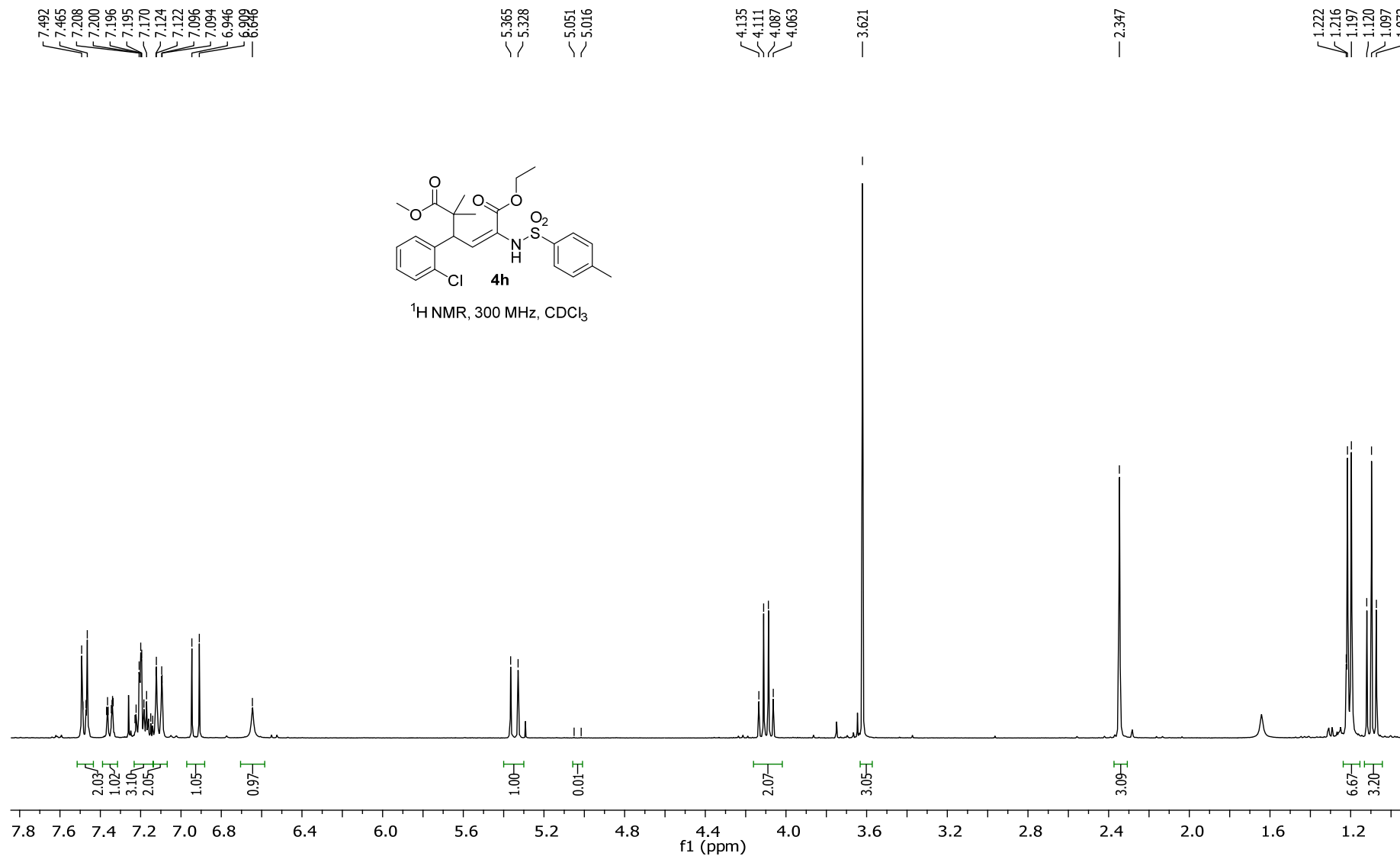












— 176.29

— 163.15

— 143.78

137.65

135.76

134.78

134.72

130.37

129.77

129.39

128.05

127.48

126.50

125.15

77.42

77.00

76.58

— 62.17

51.87

47.42

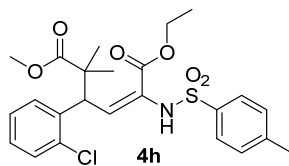
45.41

23.96

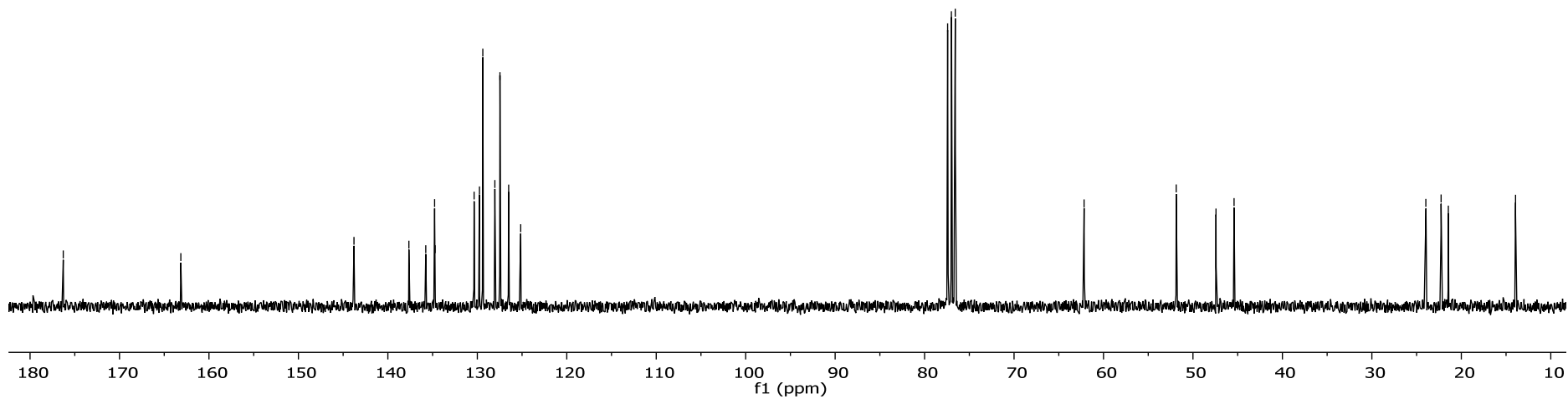
22.26

21.45

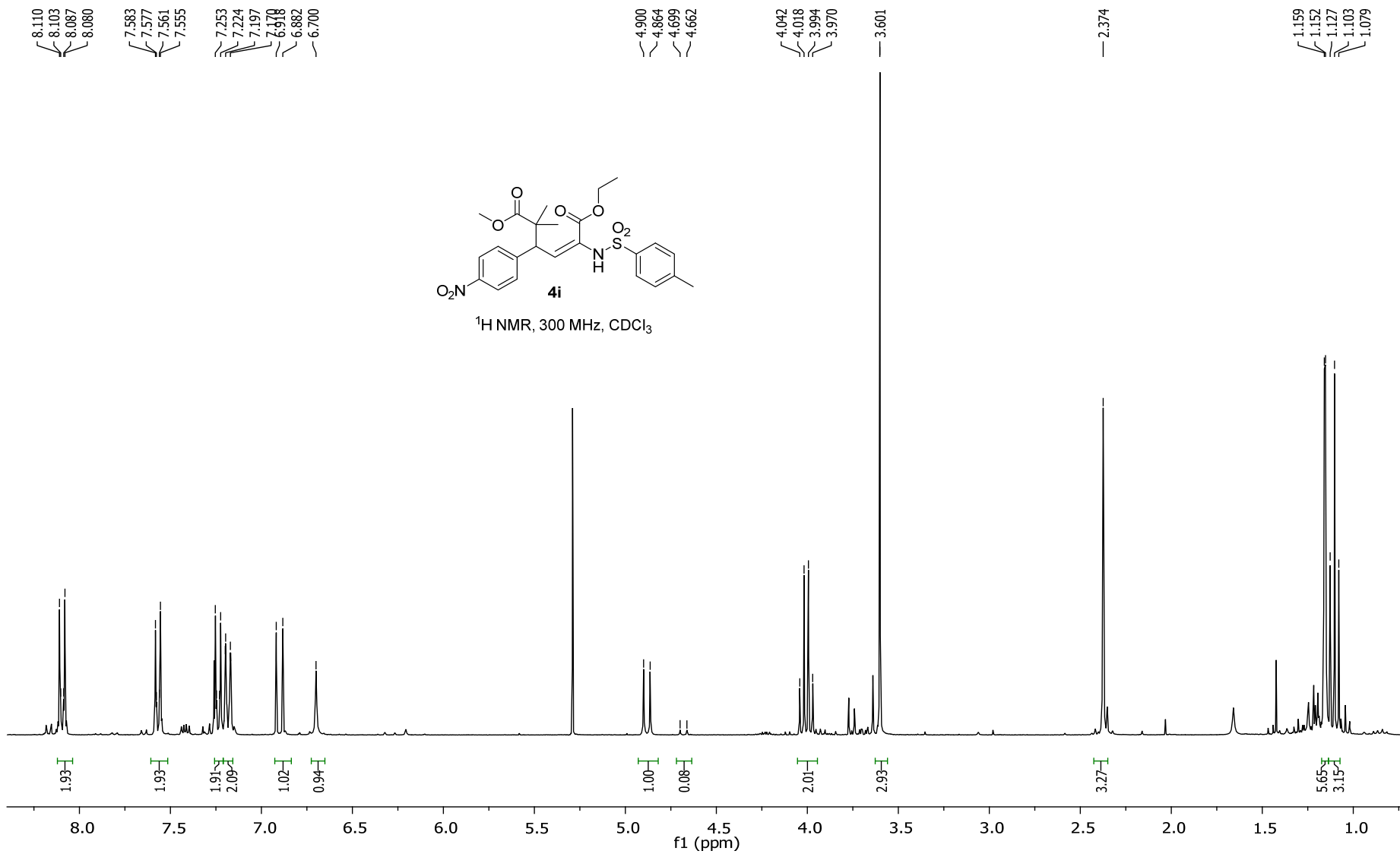
— 13.94



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>







— 176.07

— 162.20

~ 147.69  
~ 146.73  
~ 144.19  
~ 135.93  
~ 133.31  
~ 130.40  
~ 130.13  
~ 129.59  
~ 129.36  
~ 127.47  
~ 127.35  
~ 126.03  
~ 123.14  
~ 123.01

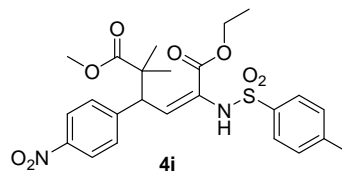
~ 77.42  
~ 77.00  
~ 76.58

— 62.08

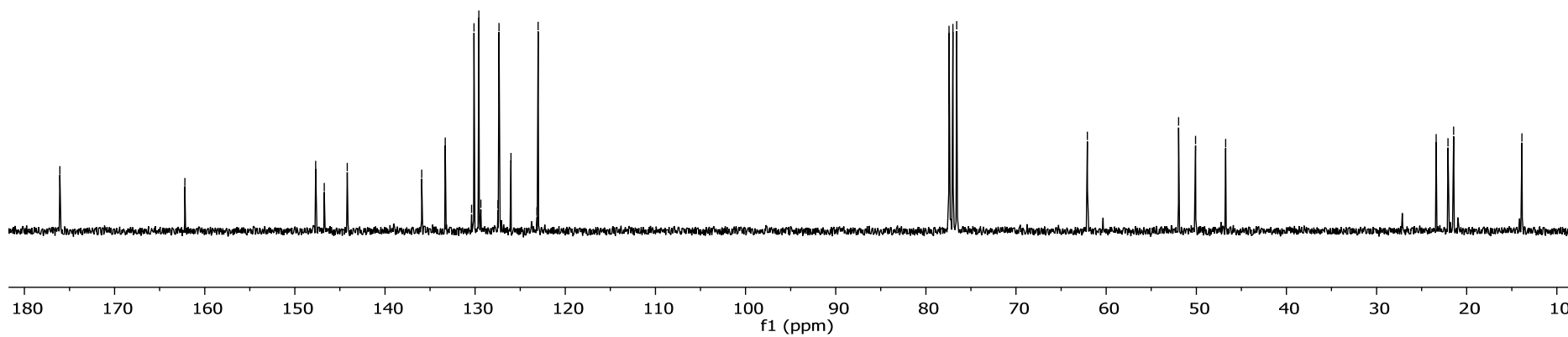
~ 51.96  
~ 50.08  
~ 46.75

~ 23.40  
~ 22.08  
~ 21.45

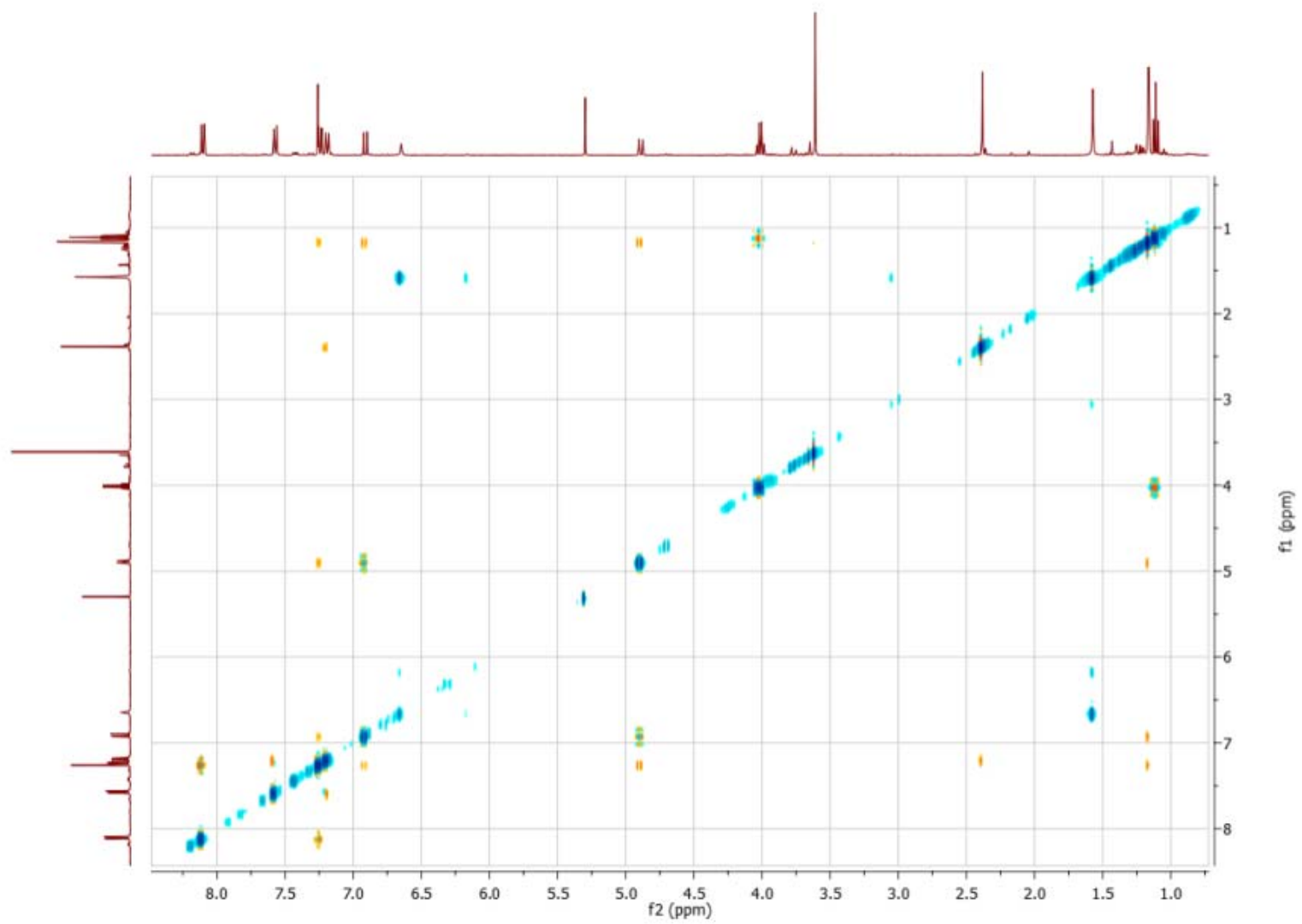
— 13.87



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



S90



S91

8.083  
8.071  
8.061  
8.053  
7.909  
7.905  
7.900  
7.602  
7.575  
7.443  
7.441  
7.435  
7.194  
7.166  
6.907  
6.871  
6.742

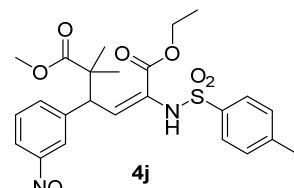
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4.857  
4.673  
4.636

4.066  
4.042  
4.018  
3.995

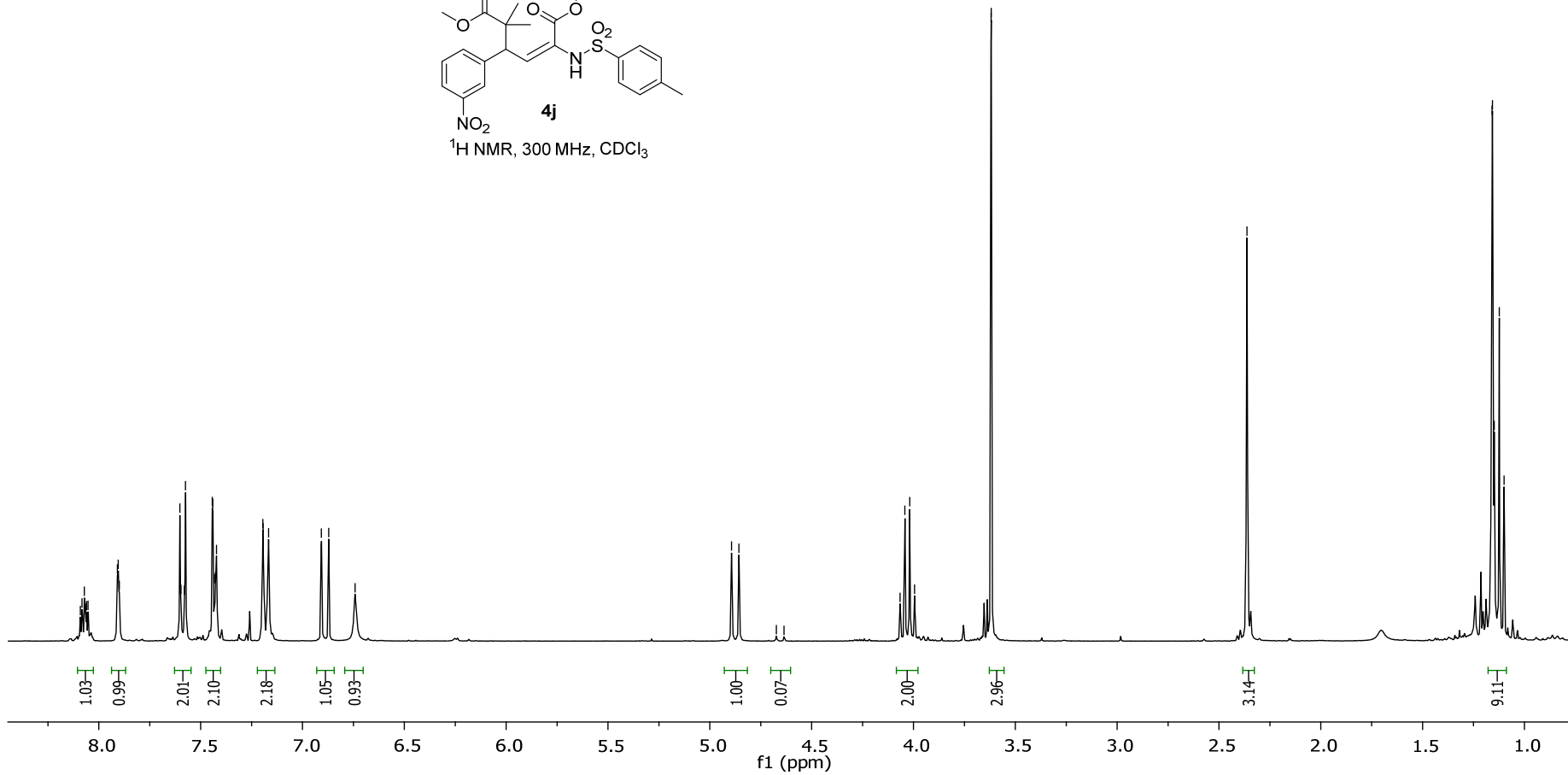
3.619  
3.618

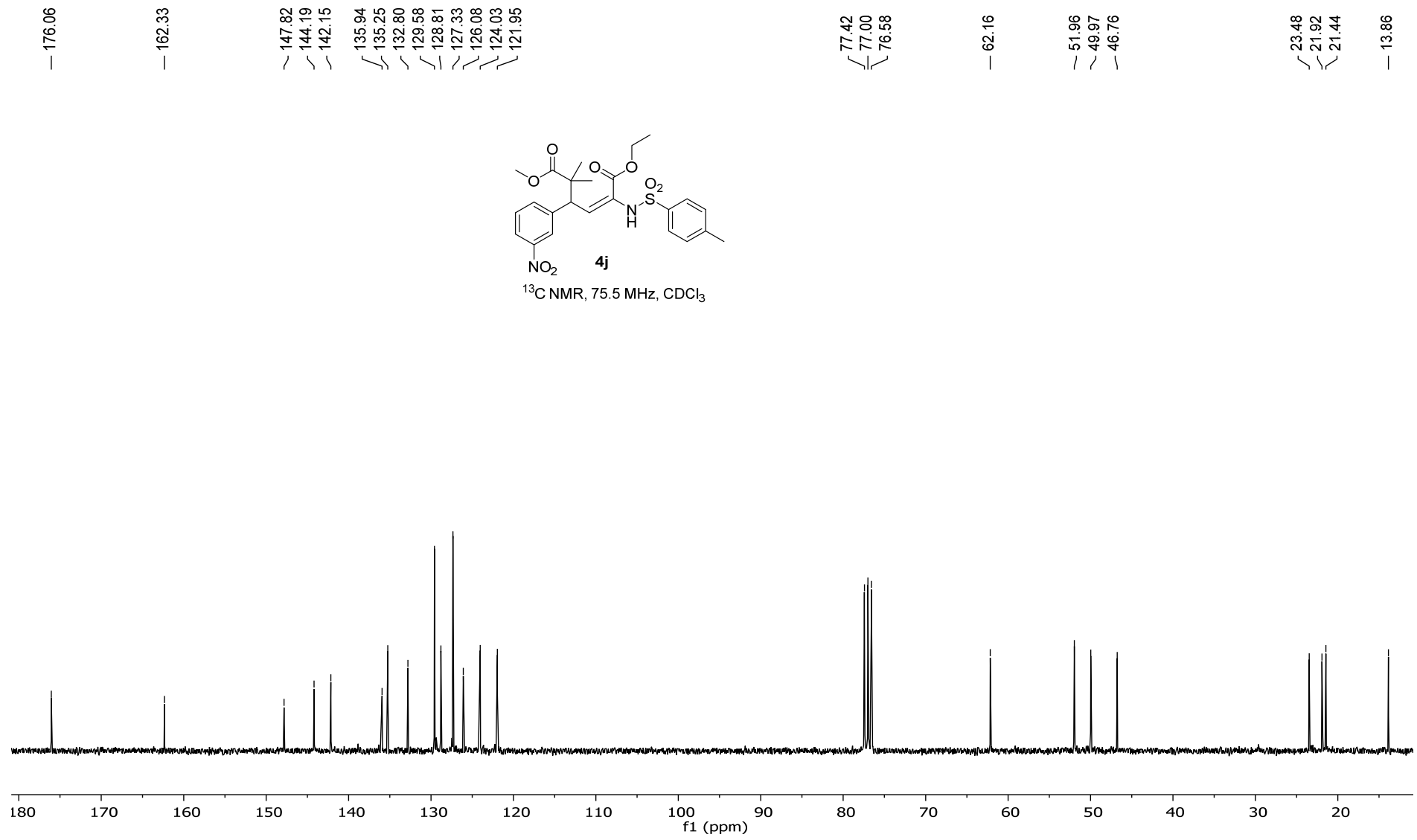
2.363

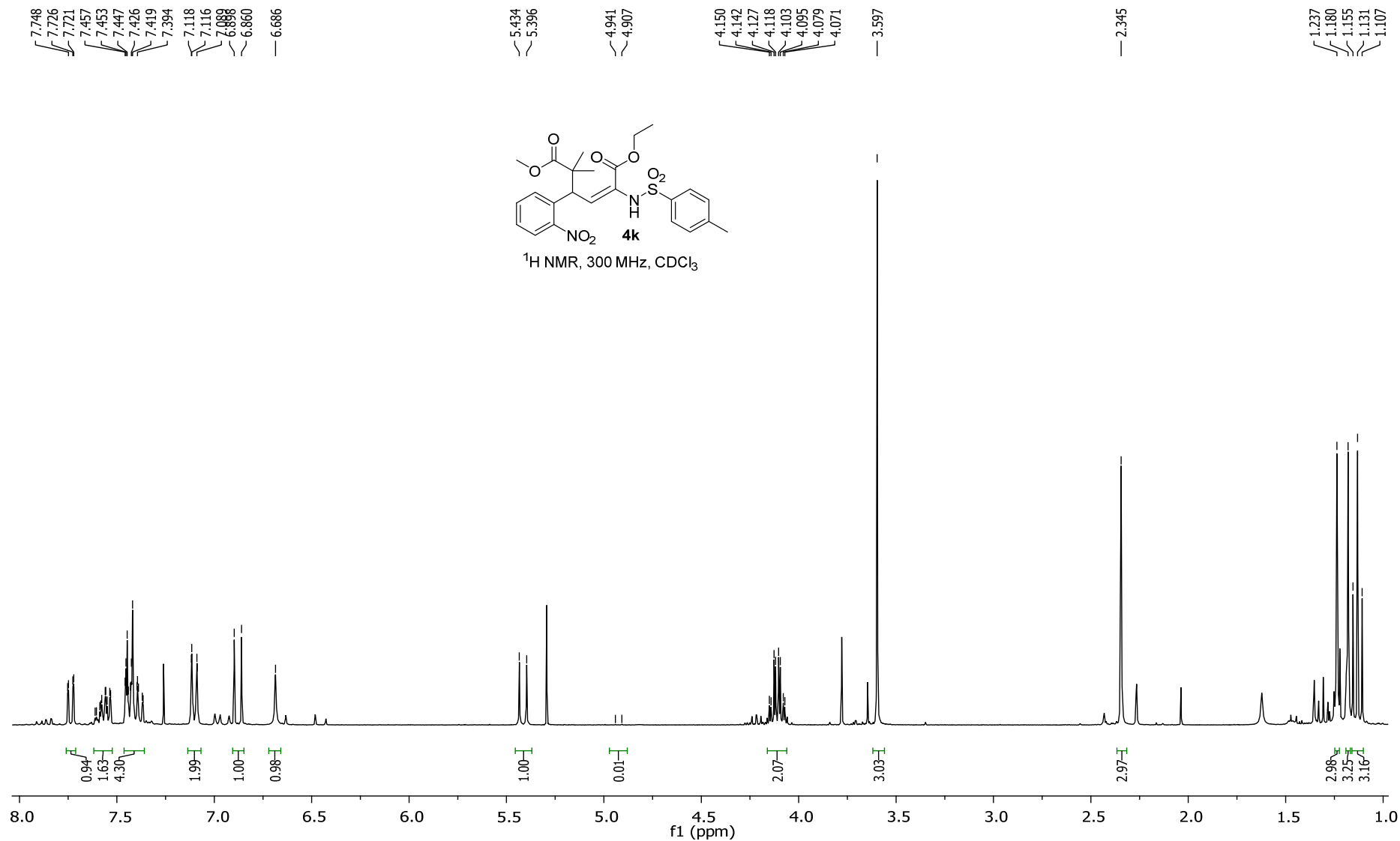
1.159  
1.157  
1.148  
1.124  
1.100

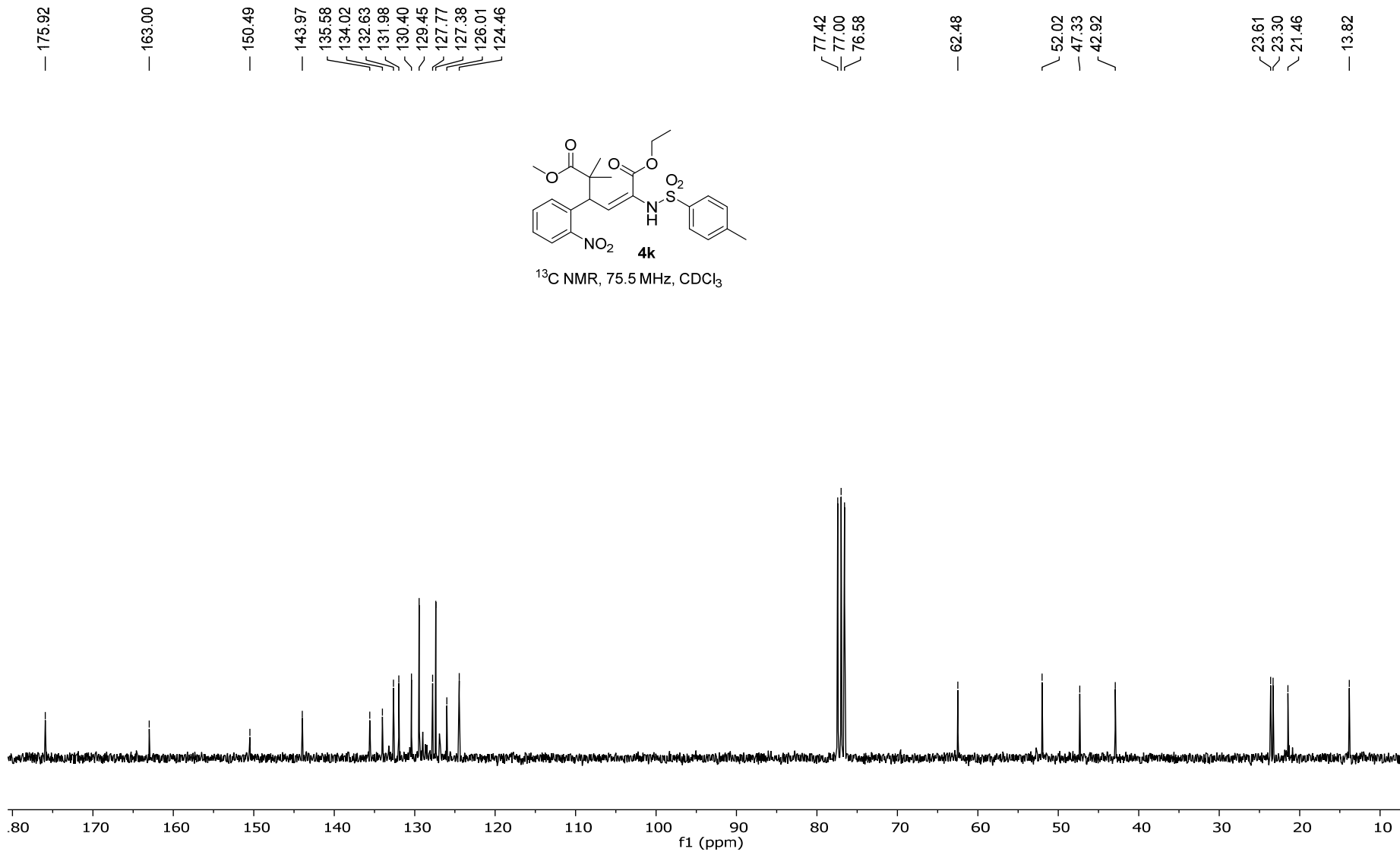


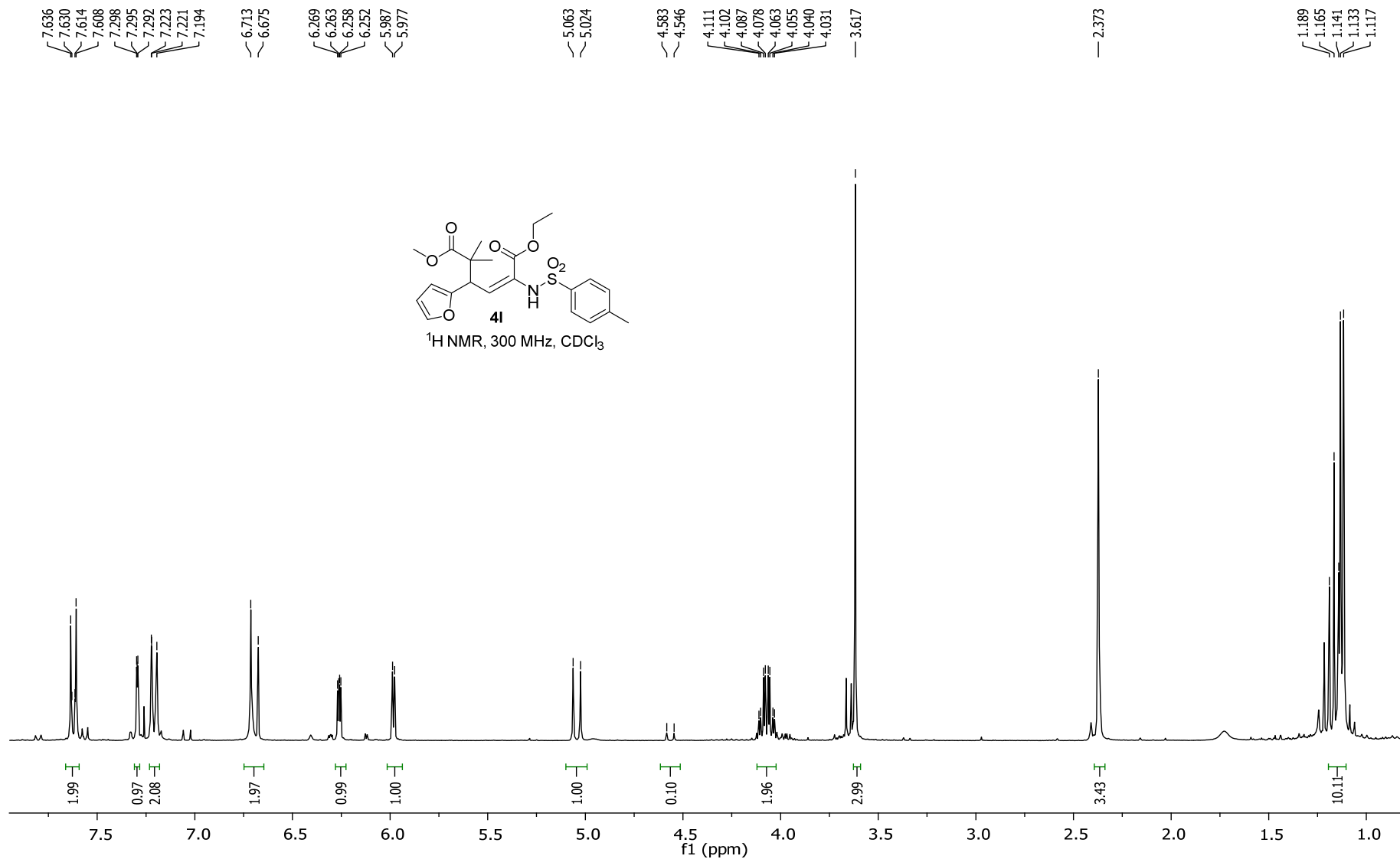
<sup>1</sup>H NMR, 300 MHz, CDCl<sub>3</sub>













— 176.64

— 162.99

— 153.12

— 143.92

— 141.52

✓ 135.93

✓ 131.49

✓ 129.49

✓ 129.31

✓ 127.54

✓ 125.73

— 110.03

— 107.22

✓ 77.42

✓ 77.00

✓ 76.58

— 62.09

— 51.87

— 46.65

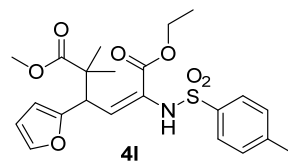
— 44.35

✓ 23.31

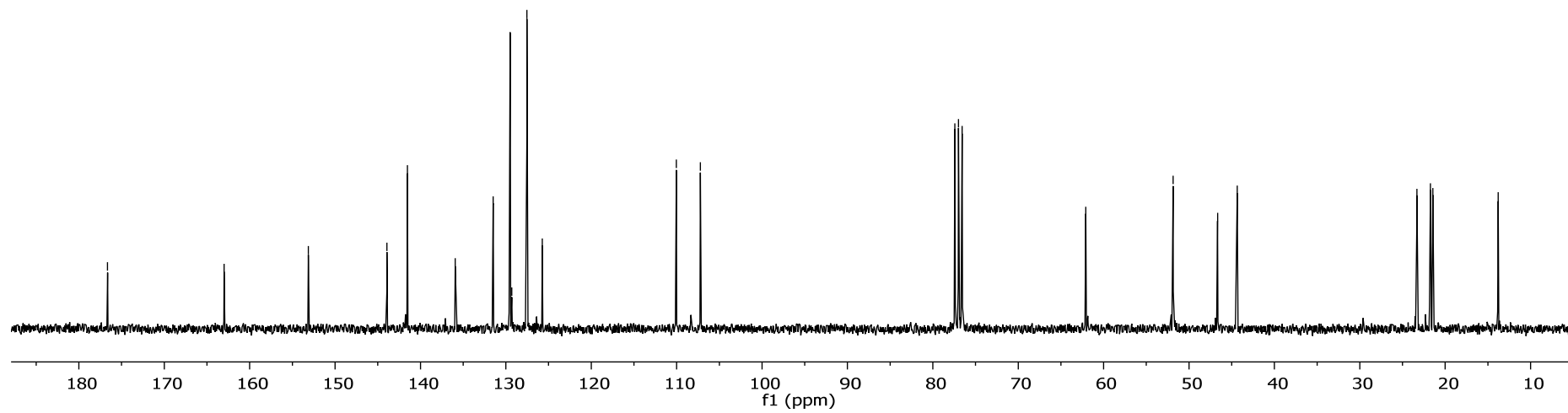
✓ 21.73

✓ 21.45

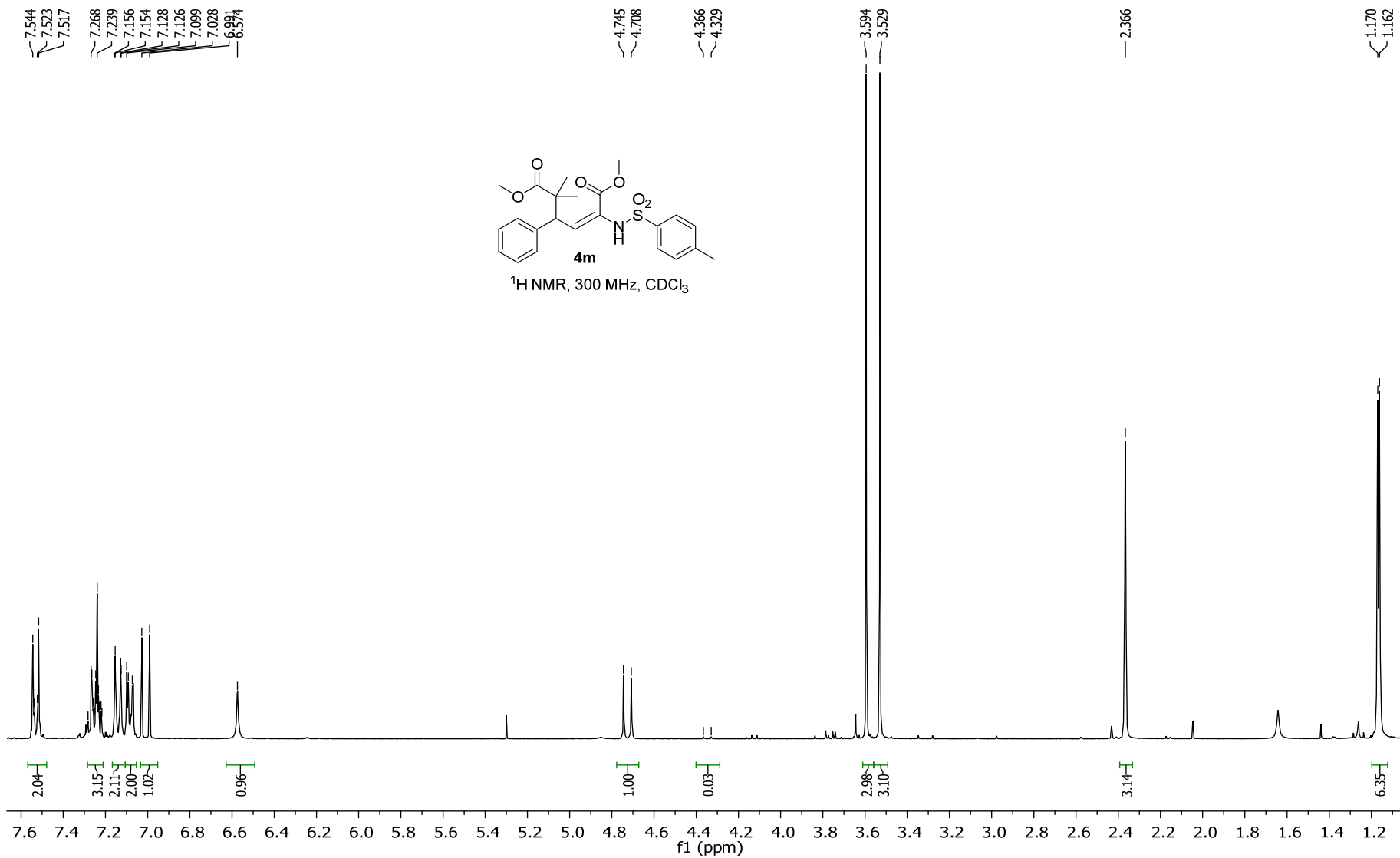
— 13.80



<sup>13</sup>C NMR, 75.5 MHz, CDCl<sub>3</sub>



S97



— 176.71

— 163.23

— 143.83

— 139.70

— 136.69

— 135.83

— 129.44

— 129.28

— 127.97

— 127.49

— 126.95

— 124.69

— 77.42

— 77.00

— 76.58

— 52.25

— 51.74

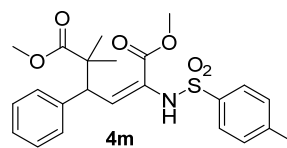
— 50.99

— 46.73

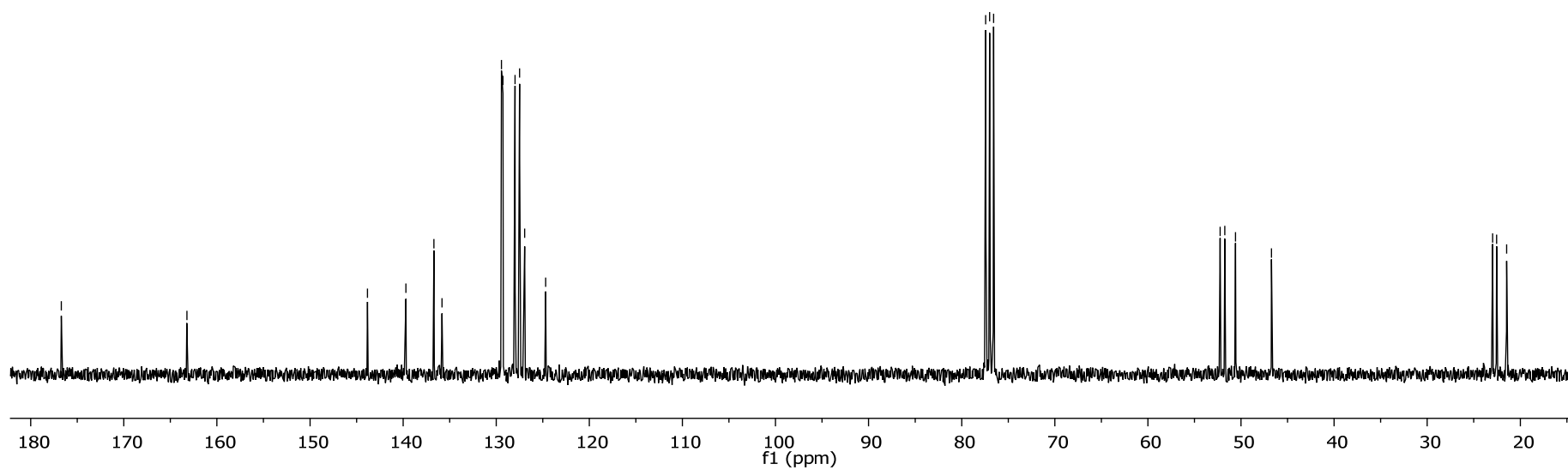
— 22.97

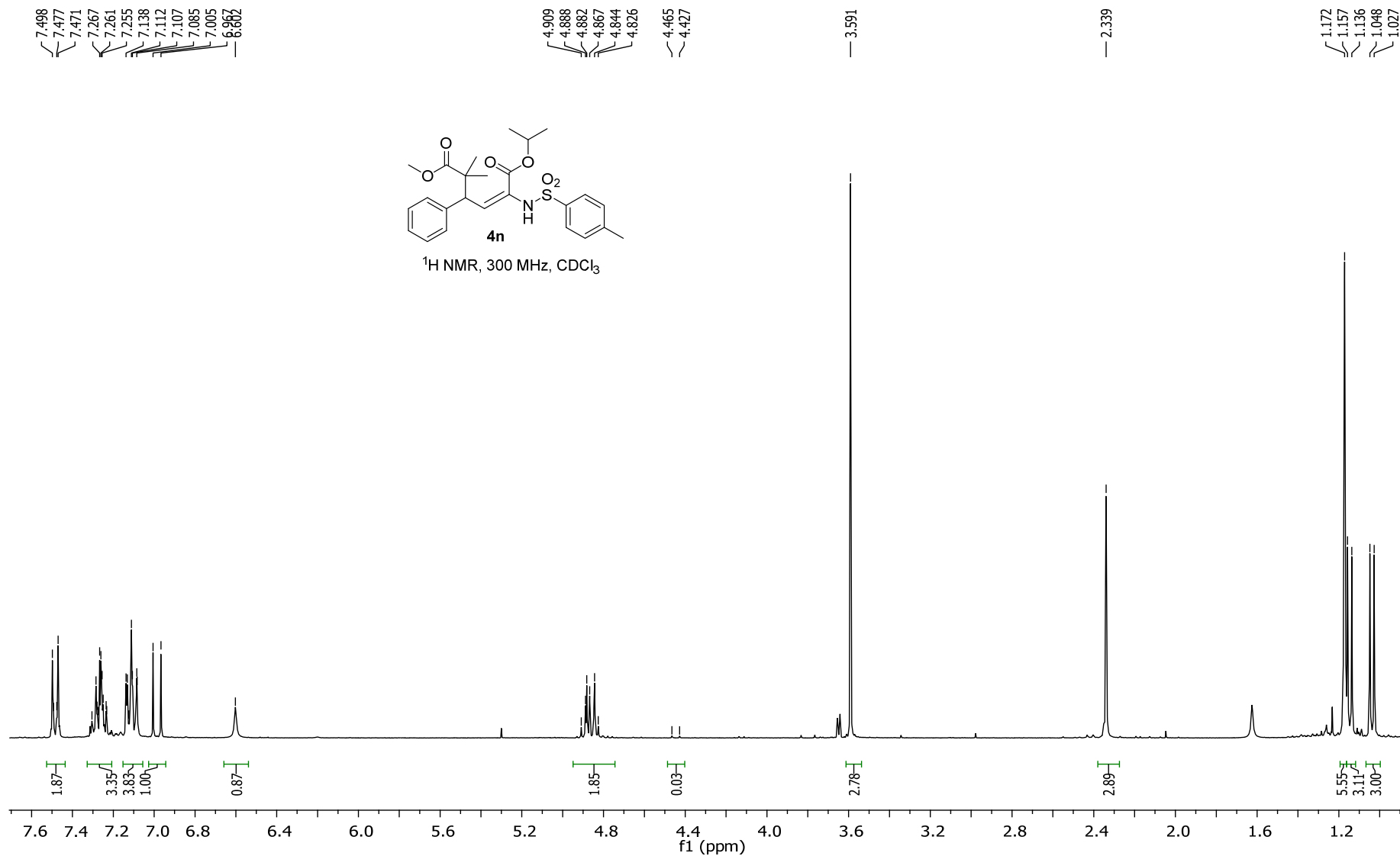
— 22.55

— 21.47



$^{13}\text{C}$  NMR, 75.5 MHz,  $\text{CDCl}_3$





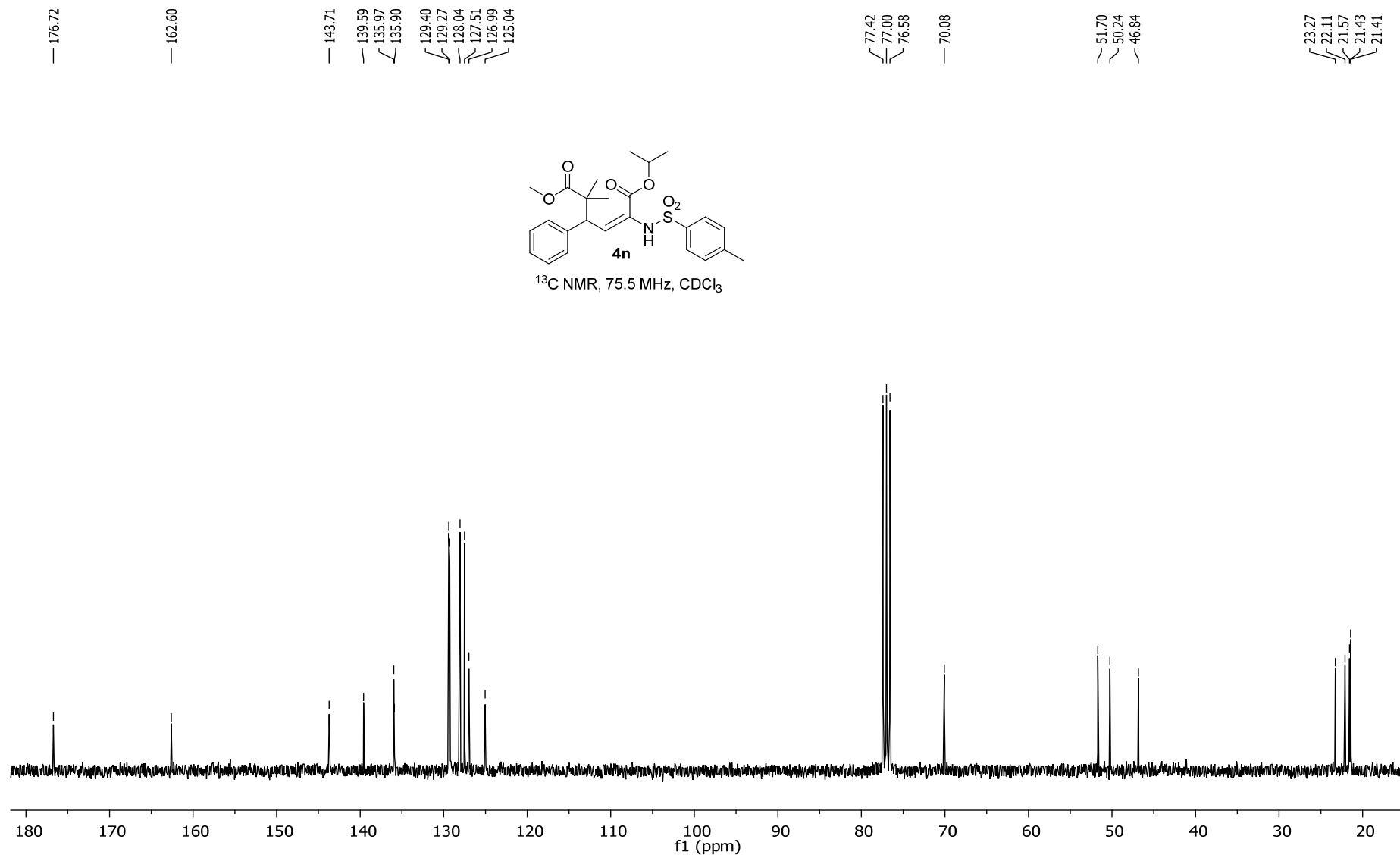


Figure S1. Ortep plot for the X-ray structure of compound *E-4m* (copper catalysed reaction). The thermal ellipsoids are drawn at the 50% probability level.

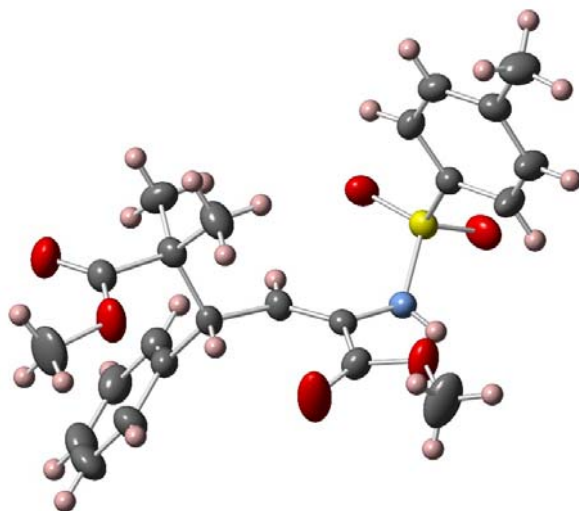


Figure S2. Ortep plot for the X-ray structure of compound **1b**. The thermal ellipsoids are drawn at the 50% probability level.

