

**Organocatalytic asymmetric vinylogous Michael addition of  
3-alkylidene oxindoles to  $\alpha$ -substituted  $\beta$ -nitroacrylates: Facile  
construction of chiral all-carbon quaternary center**

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**Supporting Information**

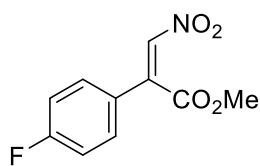
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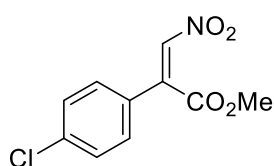
## 1. General methods

Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were purified and dried according to standard methods prior to use.  $\alpha$ -substituted  $\beta$ -Nitroacrylates **1**<sup>1</sup>, 3-alkylidene oxindoles **2**<sup>2</sup> and catalysts **3**<sup>3</sup> were prepared according to literature procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel GF254. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F spectra were recorded on a Varian instrument (300 MHz, 75 MHz and 282 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet) and coupling constant in Hertz (Hz). Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. HRMS was measured with an APEX II 47e mass spectrometer. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel OD-H column, Chiracel IC-H column or Chiracel IB-H column on Waters with a 2998 UV-detector.

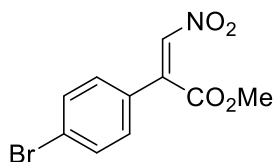
## 2. Characterization of substrates **1b-1d**, **1g**, **1h**, **2b** and **2c**



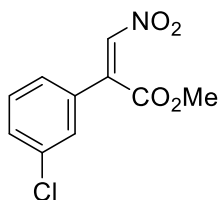
(*Z*)-methyl 2-(4-fluorophenyl)-3-nitroacrylate (**1b**): 64% yield; Yellow solid;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.54-7.49 (m, 2H), 7.33 (s, 1H), 7.17 (t,  $J = 8.5$  Hz, 2H), 4.00 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 165.2, 165 ( $J_{\text{C-F}} = 253.5$  Hz), 163.3, 142.0, 134.5, 129.8 ( $J_{\text{C-F}} = 9.0$  Hz), 125.5 ( $J_{\text{C-F}} = 3.0$  Hz), 117.0 ( $J_{\text{C-F}} = 22.5$  Hz), 53.6;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -105.84; **ESI-HRMS**: calcd. for  $\text{C}_{10}\text{H}_8\text{FNO}_4 + \text{Na}^+$  248.0330, found 248.0332.



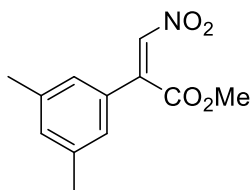
(*Z*)-methyl 2-(4-chlorophenyl)-3-nitroacrylate (**1c**): 68% yield; Yellow solid;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.45 (s, 4H), 7.35 (s, 1H), 4.00 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 165.0, 141.9, 138.7, 134.9, 129.9, 128.8, 127.8, 53.6; **ESI-HRMS**: calcd. for  $\text{C}_{10}\text{H}_8\text{ClNO}_4 + \text{Na}^+$  264.0034, found 264.0039.



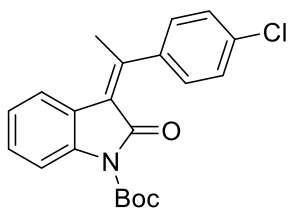
(*Z*)-methyl 2-(4-bromophenyl)-3-nitroacrylate (**1d**): 61% yield; Yellow solid;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.64-7.59 (m, 2H), 7.39-7.37 (m, 1H), 7.35 (s, 2H), 3.99 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.9, 142.0, 134.8, 132.9, 128.9, 128.2, 127.1, 53.6; **ESI-HRMS**: calcd. for  $\text{C}_{10}\text{H}_8\text{BrNO}_4 + \text{Na}^+$  307.9529, found 307.9535.



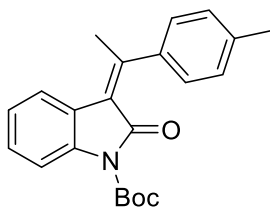
(*Z*)-methyl 2-(3-chlorophenyl)-3-nitroacrylate (**1g**): 52% yield; Yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.52-7.49 (m, 2H), 7.42-7.40 (m, 2H), 7.34 (s, 1H), 4.00 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.8, 141.6, 135.7, 135.6, 132.1, 131.1, 130.8, 127.4, 125.6, 53.7; **ESI-HRMS**: calcd. for  $\text{C}_{10}\text{H}_8\text{ClNO}_4 + \text{Na}^+$  264.0034, found 264.0041.



(*Z*)-methyl 2-(3,5-dimethylphenyl)-3-nitroacrylate (**1b**): 62% yield; Yellow solid; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.34 (s, 1H), 7.16 (s, 1H), 7.09 (s, 2H), 3.99 (s, 3H), 2.35 (s, 6H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) 165.5, 143.5, 139.4, 134.3, 134.1, 129.2, 125.2, 53.4, 21.2; **ESI-HRMS**: calcd. for C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>+Na<sup>+</sup> 258.0737, found 258.0745.

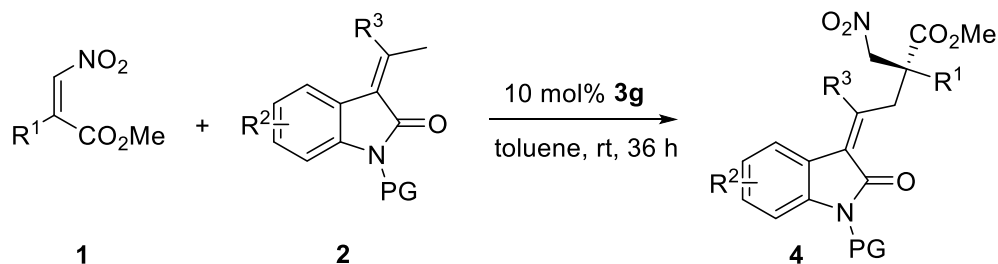


(*Z*)-tert-butyl 3-(1-(4-chlorophenyl)ethylidene)-2-oxoindoline-1-carboxylate (**2b**): 54% yield; Yellow oil; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.82 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.19 (m, 3H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 7.7 Hz, 1H), 2.75 (s, 3H), 1.67 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) 166.0, 154.7, 149.5, 141.2, 138.3, 134.6, 129.7, 128.6, 128.0, 123.4, 122.8, 122.7, 122.6, 114.6, 84.2, 28.2, 23.7; **ESI-HRMS**: calcd. for C<sub>21</sub>H<sub>20</sub>ClNO<sub>3</sub>+Na<sup>+</sup> 392.1024, found 392.1030.



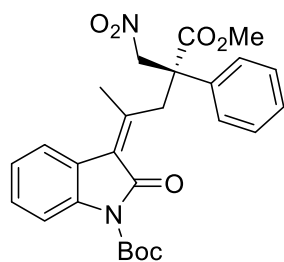
(*Z*)-tert-butyl 2-oxo-3-(1-(*p*-tolyl)ethylidene)indoline-1-carboxylate (**2c**): 68% yield; Yellow oil; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.81 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.17-7.13 (m, 3H), 6.77-6.72 (m, 1H), 6.30 (d, *J* = 7.7 Hz, 1H), 2.77 (s, 3H), 2.45 (s, 3H), 1.68 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ (ppm) 166.3, 157.1, 149.6, 143.5, 139.9, 138.6, 138.1, 130.0, 128.1, 126.4, 123.2, 122.6, 122.2, 114.4, 84.0, 28.2, 23.9, 21.4; **ESI-HRMS**: calcd. for C<sub>22</sub>H<sub>23</sub>NO<sub>3</sub>+H<sup>+</sup> 350.1751, found 350.1757.

### 3. General procedure for Michael addition of $\alpha$ -substituted $\beta$ -nitroacrylates **1** and 3-alkylidene oxindole **2**

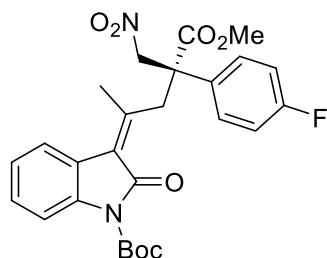


An ordinary vial equipped with a magnetic stirring bar was charged with  $\alpha$ -substituted  $\beta$ -nitroacrylates **1** (0.3 mmol) and 3-alkylidene oxindole **2** (0.45mmol) in toluene (1.2 mL), and then quinine-derived squaramide **3g** (18.9 mg, 10mol %) was added. The stirring was maintained at room temperature for 36 hours. The reaction mixture was directly charged onto silica gel and purified through flash chromatography (PE/EtOAc = 10:1) to furnish the corresponding products **4**.

#### 4. Characterization of products 4 and 5

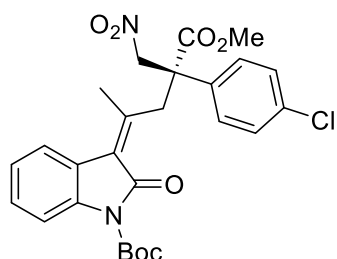


(*S,Z*)-tert-butyl 3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4a**): 99% yield; Yellow solid;  $[\alpha]_{\text{D}}^{27} = +59$  ( $c = 1.00$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis [Daicel chiralpak OD-H, n-hexane/*i*-PrOH = 95/5, 0.5 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 22.44 min,  $t$  (major) = 25.09 min]; *Z:E* > 20:1;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.73 (d,  $J = 8.2$  Hz, 1H), 7.40 (d,  $J = 7.7$  Hz, 1H), 7.32 (m, 4H), 7.26-7.20 (m, 2H), 7.07-7.04 (m, 1H), 5.37 (d,  $J = 15.7$  Hz, 1H), 5.06 (d,  $J = 15.7$  Hz, 1H), 4.15 (d,  $J = 12.7$  Hz, 1H), 3.76 (s, 3H), 3.65 (d,  $J = 12.9$  Hz, 1H), 2.10 (s, 3H), 1.60 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.8, 166.3, 154.7, 149.0, 138.6, 138.1, 128.9, 128.7, 128.0, 126.4, 125.6, 124.5, 123.9, 123.4, 114.5, 84.6, 78.2, 55.2, 52.9, 43.1, 28.2, 25.5; **ESI-HRMS**: calcd. for  $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_7 + \text{Na}^+$  503.1789, found 503.1794.

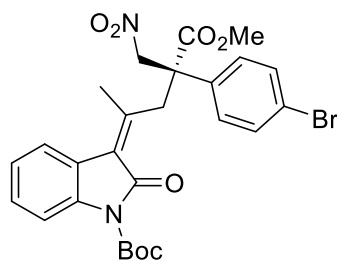


(*S,Z*)-tert-butyl 3-(4-(4-fluorophenyl)-5-methoxy-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4b**): 83% yield; Yellow solid;  $[\alpha]_{\text{D}}^{27} = +91$  ( $c = 1.00$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis [Daicel chiralpak OD-H, n-hexane/*i*-PrOH = 95/5, 0.5 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 24.21 min,  $t$  (major) = 31.63 min]; *Z:E* > 20:1;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.80 (d,  $J = 7.7$  Hz, 1H), 7.50 (d,  $J = 7.6$  Hz, 1H), 7.46-7.39 (m, 2H), 7.40-7.29 (m, 1H), 7.18-7.13 (m, 1H), 7.10-7.01 (m, 2H), 5.40 (d,  $J = 15.6$  Hz, 1H), 5.11 (d,  $J = 15.6$  Hz, 1H), 4.28 (d,  $J = 12.7$  Hz, 1H), 3.84 (s, 3H), 3.59 (d,  $J = 12.7$  Hz, 1H), 2.22 (s, 3H), 1.68 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.7, 166.4, 162.1 ( $J_{\text{C-F}} = 246.8$  Hz), 154.0, 148.9, 138.1, 134.5 ( $J_{\text{C-F}} = 3.8$  Hz), 128.8, 128.5 ( $J_{\text{C-F}} = 8.3$  Hz), 125.8, 124.5, 124.0, 123.2, 115.7 ( $J_{\text{C-F}} = 21.8$  Hz), 114.6, 84.7, 78.2, 54.7, 53.0, 43.4, 28.2, 25.4;  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -113.8; **ESI-HRMS**:

calcd. for  $C_{26}H_{27}FN_2O_7+Na^+$  521.1695, found 521.1717.

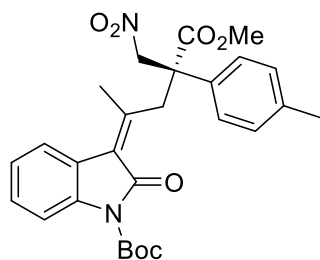


(*S,Z*)-tert-butyl 3-(4-(4-chlorophenyl)-5-methoxy-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4c**): 81% yield; Yellow solid;  $[\alpha]_D^{27} = +114$  ( $c = 1.00$  in  $CHCl_3$ ); 95% ee, determined by HPLC analysis [Daicel chiralpak OD-H, n-hexane/*i*-PrOH = 95/5, 0.5 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 23.74 min,  $t$  (major) = 28.07 min]; *Z:E* = 17:1;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.80 (d,  $J = 7.7$  Hz, 1H), 7.50 (d,  $J = 7.6$  Hz, 1H), 7.43-7.37 (m, 2H), 7.36-7.29 (m, 3H), 7.18-7.13 (m, 1H), 5.39 (d,  $J = 15.7$  Hz, 1H), 5.10 (d,  $J = 15.7$  Hz, 1H), 4.29 (d,  $J = 12.7$  Hz, 1H), 3.84 (s, 3H), 3.57 (d,  $J = 12.7$  Hz, 1H), 2.22 (s, 3H), 1.68 (s, 9H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 172.4, 166.4, 153.7, 148.9, 138.1, 137.2, 134.0, 128.9, 128.9, 128.1, 125.9, 124.5, 124.0, 123.2, 114.6, 84.7, 78.0, 54.8, 53.0, 43.3, 28.2, 25.4; **ESI-HRMS**: calcd. for  $C_{26}H_{27}ClN_2O_7+Na^+$  537.1399, found 537.1421.

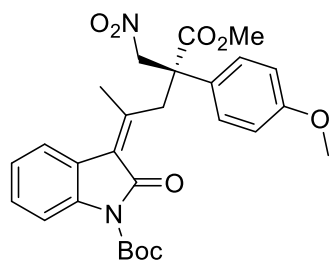


(*S,Z*)-tert-butyl 3-(4-(4-bromophenyl)-5-methoxy-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4d**): 82% yield; Yellow solid;  $[\alpha]_D^{27} = +129$  ( $c = 1.00$  in  $CHCl_3$ ); 96% ee, determined by HPLC analysis [Daicel chiralpak OD-H, n-hexane/*i*-PrOH = 95/5, 0.5 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 23.39 min,  $t$  (major) = 27.41 min]; *Z:E* > 20:1;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.80 (d,  $J = 7.7$  Hz, 1H), 7.56-7.44 (m, 3H), 7.38-7.28 (m, 3H), 7.19-7.14 (m, 1H), 5.38 (d,  $J = 15.7$  Hz, 1H), 5.10 (d,  $J = 15.7$  Hz, 1H), 4.28 (d,  $J = 12.7$  Hz, 1H), 3.84 (s, 3H), 3.56 (d,  $J = 12.7$  Hz, 1H), 2.22 (s, 3H), 1.68 (s, 9H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 172.4, 166.4, 153.6, 148.9, 138.2, 137.8, 131.9, 128.9, 128.4, 125.9, 124.6, 124.0, 123.2, 122.2, 114.6, 84.7, 77.9, 54.8, 53.0, 43.3, 28.2, 25.4; **ESI-HRMS**: calcd. for  $C_{26}H_{27}BrN_2O_7+H^+$  559.1074,

found 559.1098; C<sub>26</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 581.0894, found 581.0919.



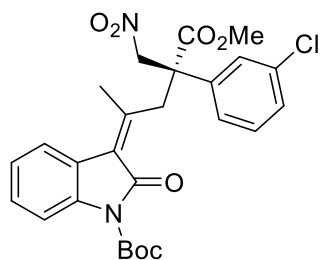
(*S,Z*)-tert-butyl 3-(5-methoxy-4-(nitromethyl)-5-oxo-4-(*p*-tolyl)pentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4e**): 53% yield; Yellow oil;  $[\alpha]_{\text{D}}^{27} = +50$  ( $c = 1.00$  in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 27.67 min,  $t$  (major) = 35.13 min]; *Z:E* = 11:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.71 (d,  $J = 8.1$  Hz, 1H), 7.38 (d,  $J = 7.7$  Hz, 1H), 7.21-7.16 (m, 3H), 7.08-7.02 (m, 3H), 5.31 (d,  $J = 15.6$  Hz, 1H), 5.01 (d,  $J = 15.6$  Hz, 1H), 4.08 (d,  $J = 12.7$  Hz, 1H), 3.72 (s, 3H), 3.64 (d,  $J = 12.7$  Hz, 1H), 2.23 (s, 3H), 2.06 (s, 3H), 1.58 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 172.9, 166.2, 155.0, 149.1, 138.1, 137.9, 135.6, 129.6, 128.6, 126.2, 125.5, 124.5, 123.9, 123.4, 114.5, 84.5, 78.2, 54.9, 52.8, 43.1, 28.2, 25.6, 21.0; **ESI-HRMS**: calcd. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 517.1945, found 517.1961.



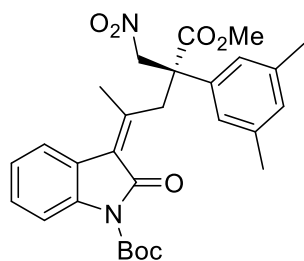
(*S,Z*)-tert-butyl 3-(5-methoxy-4-(4-methoxyphenyl)-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4f**): 36% yield; Yellow oil;  $[\alpha]_{\text{D}}^{27} = +58$  ( $c = 1.00$  in CHCl<sub>3</sub>); 92% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 26.23 min,  $t$  (major) = 35.91 min]; *Z:E* = 9:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.80 (d,  $J = 8.1$  Hz, 1H), 7.50 (d,  $J = 7.7$  Hz, 1H), 7.32-7.30 (m, 3H), 7.17-7.11 (m, 1H), 6.87 (d,  $J = 8.7$  Hz, 2H), 5.40 (d,  $J = 15.6$  Hz, 1H), 5.09 (d,  $J = 15.6$  Hz, 1H), 4.19 (d,  $J = 12.7$  Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.71 (d,  $J = 13.5$  Hz, 1H), 2.17 (s, 3H), 1.67 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.0, 166.2, 159.0, 154.9, 149.0, 138.1, 132.2, 130.5, 128.6, 127.6, 125.6, 124.5, 123.9, 123.4, 114.1, 84.6, 78.3, 55.3, 54.6, 52.8, 43.1, 28.2, 25.6; **ESI-HRMS**: calcd. for



C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>+Na<sup>+</sup> 533.1894, found 533.1920.

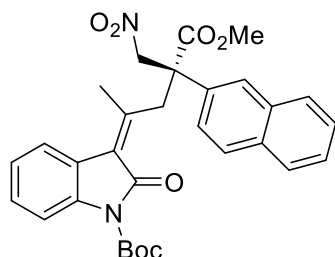


(*S,Z*)-tert-butyl 3-(4-(3-chlorophenyl)-5-methoxy-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4g**): 68% yield; Yellow oil; [ $\alpha$ ]<sub>D</sub><sup>27</sup> = +23 (c = 1.00 in CHCl<sub>3</sub>); 86% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda$  = 254 nm, t (minor) = 16.00 min, t (major) = 19.08 min]; *Z:E* > 20:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.74 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36 (s, 1H), 7.30-7.21 (m, 4H), 7.11-7.06 (m, 1H), 5.33 (d, *J* = 15.7 Hz, 1H), 5.06 (d, *J* = 15.7 Hz, 1H), 4.19 (d, *J* = 12.6 Hz, 1H), 3.77 (s, 3H), 3.52 (d, *J* = 12.7 Hz, 1H), 2.16 (s, 3H), 1.61 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 172.2, 166.3, 153.5, 149.0, 140.7, 138.2, 134.7, 130.1, 128.9, 128.3, 126.9, 126.0, 124.7, 124.5, 124.0, 123.2, 114.6, 84.7, 77.8, 54.9, 53.1, 43.3, 28.2, 25.4; **ESI-HRMS**: calcd. for C<sub>26</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 537.1399, found 537.1398.

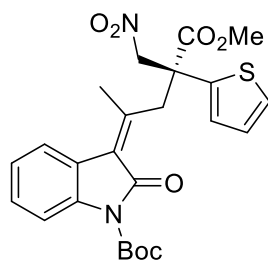


(*S,Z*)-tert-butyl 3-(4-(3,5-dimethylphenyl)-5-methoxy-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4h**): 56% yield; Yellow oil; [ $\alpha$ ]<sub>D</sub><sup>27</sup> = +68 (c = 1.00 in CHCl<sub>3</sub>); 96% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda$  = 254 nm, t (minor) = 19.23 min, t (major) = 26.34 min]; *Z:E* = 11:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.74 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.24-7.18 (m, 1H), 7.08-7.03 (m, 1H), 6.85 (d, *J* = 4.2 Hz, 3H), 5.33 (d, *J* = 15.7 Hz, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.03 (d, *J* = 12.6 Hz, 1H), 3.72 (s, 3H), 3.66 (d, *J* = 1.3 Hz, 1H), 2.21 (s, 6H), 2.08 (s, 3H), 1.59 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 172.9, 166.1, 155.1, 149.2, 138.5, 138.4, 138.1, 129.7, 128.6, 125.5, 124.4, 123.9, 123.7, 123.5, 114.5, 84.4, 78.1, 54.9, 52.8, 42.9, 29.7, 28.1, 25.7, 21.5; **ESI-HRMS**: calcd.

for  $C_{28}H_{32}N_2O_7+H^+$  509.2282, found 509.2302.

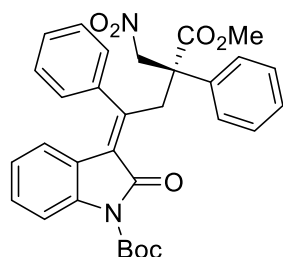


(*S,Z*)-tert-butyl 3-(5-methoxy-4-(naphthalen-2-yl)-4-(nitromethyl)-5-oxopentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4i**): 86% yield; Yellow solid;  $[\alpha]_D^{27} = +92$  ( $c = 1.00$  in  $CHCl_3$ ); 92% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 32.11 min,  $t$  (major) = 41.13 min];  $Z:E = 18:1$ ;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.77-7.68 (m, 5H), 7.50 (d,  $J = 8.6$  Hz, 1H), 7.39 (dd,  $J = 6.1, 3.1$  Hz, 2H), 7.34 (d,  $J = 7.8$  Hz, 1H), 7.20 (t,  $J = 8.0$  Hz, 1H), 7.02 (t,  $J = 7.6$  Hz, 1H), 5.45 (d,  $J = 15.6$  Hz, 1H), 5.17 (d,  $J = 15.7$  Hz, 1H), 4.19 (d,  $J = 12.7$  Hz, 1H), 3.75 (s, 3H), 3.68 (d,  $J = 26.8$  Hz, 1H), 2.04 (s, 3H), 1.58 (s, 9H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 172.8, 166.2, 154.5, 149.1, 138.2, 136.0, 133.0, 132.5, 128.7, 128.3, 127.5, 126.6, 125.8, 125.4, 124.5, 124.2, 123.9, 123.3, 114.6, 84.6, 78.1, 55.3, 53.0, 43.1, 28.2, 25.7; **ESI-HRMS**: calcd. for  $C_{30}H_{30}N_2O_7+Na^+$  553.1945, found 553.1967.

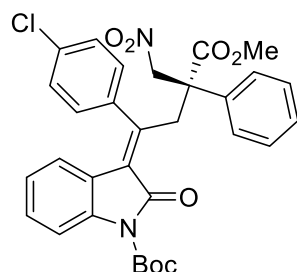


(*S,Z*)-tert-butyl 3-(5-methoxy-4-(nitromethyl)-5-oxo-4-(thiophen-2-yl)pentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4j**): 29% yield; Yellow oil;  $[\alpha]_D^{27} = +16$  ( $c = 1.00$  in  $CHCl_3$ ); 86% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 16.91 min,  $t$  (major) = 27.45 min];  $Z:E = 6:1$ ;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.82 (d,  $J = 8.1$  Hz, 1H), 7.48 (d,  $J = 7.8$  Hz, 1H), 7.30-7.26 (m, 2H), 7.18-7.13 (m, 1H), 7.06 (d,  $J = 3.1$  Hz, 1H), 6.97-6.94 (m, 1H), 5.48 (d,  $J = 15.7$  Hz, 1H), 5.19 (d,  $J = 15.6$  Hz, 1H), 4.04 (d,  $J = 12.4$  Hz, 1H), 3.86 (s, 3H), 3.75 (d,  $J = 12.9$  Hz, 1H), 2.05 (s, 3H), 1.67 (s, 9H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 173.9, 167.9, 154.2, 151.0, 142.7, 140.4, 131.0, 128.4, 128.3, 127.9, 127.3, 126.6, 126.0, 125.2, 116.7, 86.7, 80.7, 55.3, 54.8, 47.1, 30.2, 27.1; **ESI-HRMS**:

calcd. for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>7</sub>S+Na<sup>+</sup> 509.1353, found 509.1366

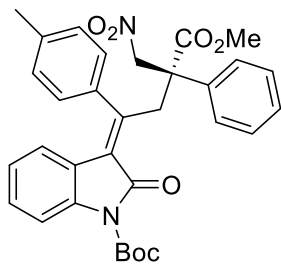


(*S,E*)-tert-butyl 3-(4-methoxy-3-(nitromethyl)-4-oxo-1,3-diphenylbutylidene)-2-oxoindoline-1-carboxylate (**4k**): 87% yield; Yellow solid;  $[\alpha]_{\text{D}}^{27} = -10$  ( $c = 1.00$  in CHCl<sub>3</sub>); 97% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 35.95 min,  $t$  (major) = 40.69 min]; *Z:E* > 20:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.71 (d,  $J = 8.1$  Hz, 1H), 7.43 (m, 2H), 7.42-7.34 (m, 3H), 7.33-7.27 (m, 2H), 7.25-7.20 (d, 1H), 7.20-7.10 (m, 2H), 7.04 (s, 1H), 6.70-6.65 (m, 1H), 5.99 (d,  $J = 7.3$  Hz, 1H), 5.24 (d,  $J = 15.1$  Hz, 1H), 5.07 (d,  $J = 11.7$  Hz, 1H), 5.02 (d,  $J = 10.3$  Hz, 1H), 3.69 (d,  $J = 13.7$  Hz, 1H), 3.35 (s, 3H), 1.70 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.8, 166.4, 153.5, 148.8, 139.3, 138.4, 138.1, 129.3, 129.2, 128.8, 128.4, 128.2, 127.7, 126.9, 126.6, 123.4, 123.1, 122.3, 114.3, 84.6, 78.3, 54.7, 52.3, 40.8, 28.1; **ESI-HRMS**: calcd. for C<sub>31</sub>H<sub>30</sub>N<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 565.1945, found 565.1958.

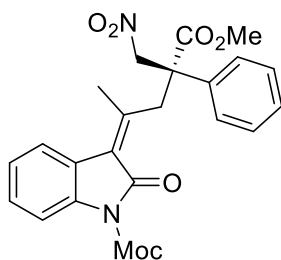


(*S,E*)-tert-butyl 3-(1-(4-chlorophenyl)-4-methoxy-3-(nitromethyl)-4-oxo-3-phenylbutylidene)-2-oxoindoline-1-carboxylate (**4l**): 86% yield; Yellow oil;  $[\alpha]_{\text{D}}^{27} = -4$  ( $c = 1.00$  in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 29.32 min,  $t$  (major) = 35.51 min]; *Z:E* > 20:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.65 (d,  $J = 8.1$  Hz, 1H), 7.27 (d,  $J = 8.7$  Hz, 2H), 7.22-7.08 (m, 5H), 7.10 (dd,  $J = 11.6$ , 4.3 Hz, 1H), 7.01 (d,  $J = 7.2$  Hz, 1H), 6.79 (d,  $J = 7.6$  Hz, 1H), 6.64 (dd,  $J = 11.3$ , 4.2 Hz, 1H), 6.00 (d,  $J = 7.6$  Hz, 1H), 5.16-5.04 (m, 2H), 4.77 (d,  $J = 13.7$  Hz, 1H), 3.70 (d,  $J = 13.7$  Hz, 1H), 3.38 (s, 3H), 1.61 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.8, 166.3, 152.1, 148.9, 138.6, 138.0, 137.8, 137.3, 135.1, 129.6, 129.0, 128.5, 127.8, 126.9, 126.1, 123.6, 123.1, 122.1, 114.6,

84.8, 78.7, 54.8, 52.6, 40.7, 28.2; **ESI-HRMS**: calcd. for C<sub>31</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 599.1556, found 599.1569.

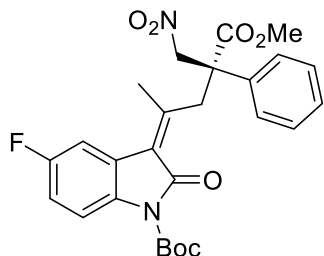


(*S,E*)-tert-butyl 3-(4-methoxy-3-(nitromethyl)-4-oxo-3-phenyl-1-(*p*-tolyl)butylidene)-2-oxoindoline-1-carboxylate (**4m**): 82% yield; Yellow solid;  $[\alpha]_D^{27} = -24$  ( $c = 1.00$  in CHCl<sub>3</sub>); 94% ee, determined by HPLC analysis [Daicel chiralpak OD-H, n-hexane/*i*-PrOH = 90/10, 0.5 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 15.05 min,  $t$  (major) = 16.84 min]; *Z:E* > 20:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.63 (d,  $J = 8.2$  Hz, 1H), 7.33 (d,  $J = 7.0$  Hz, 2H), 7.23-7.14 (m, 4H), 7.11-7.05 (m, 2H), 6.90 (m, 2H), 6.62 (t,  $J = 7.7$  Hz, 1H), 6.04 (d,  $J = 7.8$  Hz, 1H), 5.15 (d,  $J = 15.1$  Hz, 1H), 4.97 (d,  $J = 7.9$  Hz, 1H), 4.92 (d,  $J = 6.4$  Hz, 1H), 3.58 (d,  $J = 13.7$  Hz, 1H), 3.28 (s, 3H), 2.35 (s, 3H), 1.61 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.9, 166.5, 154.0, 149.0, 139.5, 138.4, 136.3, 130.2, 129.6, 129.2, 128.4, 127.7, 127.1, 126.4, 126.2, 123.5, 123.2, 122.6, 114.4, 84.7, 78.3, 54.8, 52.4, 41.0, 28.2, 21.4; **ESI-HRMS**: calcd. for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>O<sub>7</sub>+Na<sup>+</sup> 579.2102, found 579.2119.

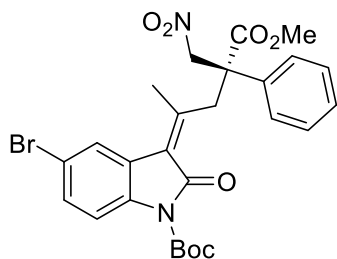


(*S,Z*)-methyl 3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4p**): 45% yield; Yellow oil;  $[\alpha]_D^{27} = +225$  ( $c = 1.00$  in CHCl<sub>3</sub>); 85% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 38.27 min,  $t$  (major) = 53.22 min]; *Z:E* = 9:1; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.85 (d,  $J = 8.1$  Hz, 1H), 7.38 (d,  $J = 7.7$  Hz, 1H), 7.30-7.25 (m, 4H), 7.24-7.18 (m, 2H), 7.07 (t,  $J = 7.5$  Hz, 1H), 5.33 (d,  $J = 15.6$  Hz, 1H), 5.06 (d,  $J = 15.6$  Hz, 1H), 4.10 (d,  $J = 12.7$  Hz, 1H), 3.94 (s, 3H), 3.73 (s, 3H), 3.65 (d,  $J = 12.7$  Hz, 1H), 2.09 (s, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$

(ppm)171.5, 164.7, 154.5, 150.4, 137.3, 136.6, 127.8, 127.7, 127.0, 125.2, 124.3, 123.3, 123.2, 122.4, 113.6, 77.1, 52.8, 51.8, 41.8, 28.6, 24.4; **ESI-HRMS**: calcd. for  $C_{23}H_{22}N_2O_7+Na^+$  461.1319, found 461.1320.

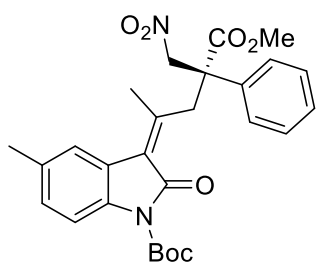


(*S,Z*)-tert-butyl 5-fluoro-3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4q**): 62% yield; Yellow solid;  $[\alpha]_D^{27} = +39$  ( $c = 1.00$  in  $CHCl_3$ ); 97% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 13.31 min,  $t$  (major) = 17.85 min]; *Z:E* = 13:1; **<sup>1</sup>H NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.70 (dd,  $J = 9.0, 4.9$  Hz, 1H), 7.29-7.27 (m, 4H), 7.23-7.19 (m, 1H), 7.10 (dd,  $J = 9.3, 2.5$  Hz, 1H), 6.92 (td,  $J = 8.8, 2.6$  Hz, 1H), 5.35 (d,  $J = 15.6$  Hz, 1H), 5.05 (d,  $J = 15.7$  Hz, 1H), 4.10 (d,  $J = 12.7$  Hz, 1H), 3.74 (s, 3H), 3.68 (d,  $J = 12.6$  Hz, 1H), 2.07 (s, 3H), 1.58 (s, 9H); **<sup>13</sup>C NMR** (75 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 172.7, 165.9, 159.3 ( $J_{C-F} = 240$  Hz), 156.9, 148.2, 138.4, 134.1, 134.1, 129.0, 128.2, 126.2, 125.2 ( $J_{C-F} = 3.0$  Hz), 124.5 ( $J_{C-F} = 9.0$  Hz), 115.6 ( $J_{C-F} = 8.3$  Hz), 114.9 ( $J_{C-F} = 23.3$  Hz), 111.8 ( $J_{C-F} = 25.5$  Hz), 84.7, 78.2, 55.3, 52.9, 42.9, 28.1, 25.4; **<sup>19</sup>F NMR** (282 MHz,  $CDCl_3$ )  $\delta$  (ppm) -118.3; **ESI-HRMS**: calcd. for  $C_{26}H_{27}FN_2O_7+Na^+$  521.1695, found 521.1711.

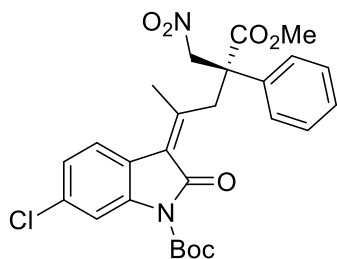


(*S,Z*)-tert-butyl 5-bromo-3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-2-oxoindoline-1-carboxylate (**4r**): 51% yield; Yellow oil liquid;  $[\alpha]_D^{27} = +8$  ( $c = 1.00$  in  $CHCl_3$ ); 97% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 16.22 min,  $t$  (major) = 20.20 min]; *Z:E* = 9:1; **<sup>1</sup>H NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.63 (d,  $J = 8.7$  Hz, 1H), 7.49 (d,  $J = 1.8$  Hz, 1H), 7.34 (dd,  $J = 8.7, 1.9$  Hz,

1H), 7.29-7.24 (m, 4H), 7.22-7.19 (m, 1H), 5.34 (d,  $J = 15.7$  Hz, 1H), 5.05 (d,  $J = 15.6$  Hz, 1H), 4.08 (d,  $J = 12.7$  Hz, 1H), 3.75 (s, 3H), 3.70 (d,  $J = 12.7$  Hz, 1H), 2.09 (s, 3H), 1.59 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.6, 165.5, 157.2, 148.8, 138.4, 137.0, 131.3, 129.0, 128.2, 127.1, 126.2, 126.0, 125.1, 124.7, 116.1, 84.9, 78.2, 55.3, 52.9, 42.9, 28.1, 25.7 ; **ESI-HRMS**: calcd. for  $\text{C}_{26}\text{H}_{27}\text{BrN}_2\text{O}_7+\text{Na}^+$  581.0894, found 581.0910.

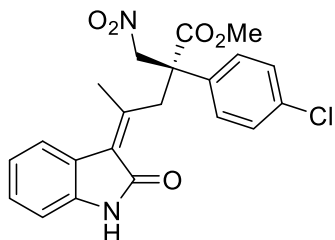


(*S,Z*)-tert-butyl 3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-5-methyl-2-oxindoline-1-carboxylate (**4s**): 81% yield; Yellow oil;  $[\alpha]_{\text{D}}^{27} = +66$  ( $c = 1.00$  in  $\text{CHCl}_3$ ); 94% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 14.97 min,  $t$  (major) = 20.30 min];  $Z:E > 20:1$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.67 (d,  $J = 8.3$  Hz, 1H), 7.42-7.36 (m, 3H), 7.33-7.28 (m, 3H), 7.11 (d,  $J = 8.2$  Hz, 1H), 5.44 (d,  $J = 15.7$  Hz, 1H), 5.13 (d,  $J = 15.7$  Hz, 1H), 4.23 (d,  $J = 12.7$  Hz, 1H), 3.83 (s, 3H), 3.68 (d,  $J = 12.7$  Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H), 1.67 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.8, 166.5, 154.3, 149.1, 138.7, 135.9, 133.3, 129.2, 128.9, 128.0, 126.4, 125.8, 125.2, 123.4, 114.4, 84.4, 78.1, 55.2, 52.8, 43.2, 28.2, 25.6, 21.4; **ESI-HRMS**: calcd. for  $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_7+\text{Na}^+$  517.1945, found 517.1959.



(*S,Z*)-tert-butyl 6-chloro-3-(5-methoxy-4-(nitromethyl)-5-oxo-4-phenylpentan-2-ylidene)-2-oxindoline-1-carboxylate (**4t**): 64% yield; Yellow oil;  $[\alpha]_{\text{D}}^{27} = +20$  ( $c = 1.00$  in  $\text{CHCl}_3$ ); 94% ee, determined by HPLC analysis [Daicel chiralpak IC-H, n-hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (minor) = 15.55 min,  $t$  (major) = 19.58 min];  $Z:E = 14:1$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.87 (d,  $J = 1.9$  Hz, 1H), 7.40-7.36 (m, 1H), 7.35-7.15 (m, 4H), 7.13-7.10 (m, 2H), 5.42 (d,

$J = 15.7$  Hz, 1H), 5.12 (d,  $J = 15.7$  Hz, 1H), 4.16 (d,  $J = 12.7$  Hz, 1H), 3.82 (s, 3H), 3.73 (d,  $J = 12.0$  Hz, 1H), 2.15 (s, 3H), 1.68 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.7, 165.8, 155.7, 148.7, 138.8, 138.5, 134.4, 129.0, 128.1, 126.2, 125.1, 124.8, 123.9, 121.8, 115.3, 85.1, 78.2, 55.2, 52.9, 42.9, 28.1, 25.6; **ESI-HRMS**: calcd. for  $\text{C}_{26}\text{H}_{27}\text{ClN}_2\text{O}_7+\text{Na}^+$  537.1399, found 537.1414.

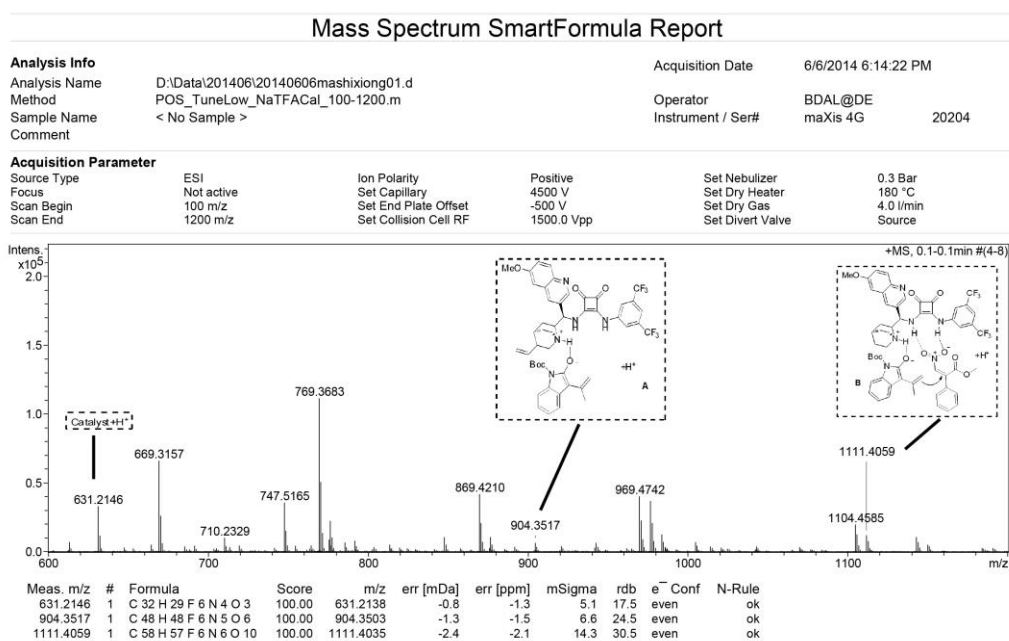


(*S,Z*)-methyl-2-(4-chlorophenyl)-2-(nitromethyl)-4-(2-oxoindolin-3-ylidene)pentanoate (**5**): 92% yield; Yellow solid;  $[\alpha]_{\text{D}}^{27} = +23$  ( $c = 1.00$  in  $\text{CHCl}_3$ ); 100% ee, determined by HPLC analysis [Daicel chiralpak IB-H, n-hexane/*i*-PrOH = 95/5, 1.0 mL/min,  $\lambda = 254$  nm,  $t$  (major) = 23.90 min]; *Z:E* > 20:1;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.55 (s, 1H), 7.39 (d,  $J = 8.0$  Hz, 1H), 7.37-7.29 (m, 4H), 7.24 (d,  $J = 7.8$  Hz, 1H), 7.02 (m, 1H), 6.95 (d,  $J = 7.7$  Hz, 1H), 5.35 (d,  $J = 15.7$  Hz, 1H), 5.10 (d,  $J = 15.7$  Hz, 1H), 4.07 (d,  $J = 12.7$  Hz, 1H), 3.87 (d,  $J = 12.7$  Hz, 1H), 3.83 (s, 3H), 2.02 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 172.5, 169.5, 152.3, 139.8, 137.2, 134.1, 129.1, 128.9, 127.8, 127.4, 124.9, 123.5, 122.1, 109.9, 78.6, 54.2, 53.1, 42.2, 25.1; **ESI-HRMS**: calcd. for  $\text{C}_{21}\text{H}_{19}\text{ClN}_2\text{O}_5+\text{H}^+$  415.1055, found 415.1065.

## 5. In-situ ESI-HRMS analysis experiment

An ordinary vial equipped with a magnetic stirring bar was charged with  $\alpha$ -substituted  $\beta$ -nitroacrylates **1a** (0.1 mmol) and 3-alkylidene oxindole **2a** (0.15mmol) in toluene (0.4 mL), and then quinine-derived squaramide **3g** (6.3 mg, 10mol %) was added. After stirring for 12 hours at room temperature, the reaction mixture was directly injected to electrospray ionization high resolution mass spectrometry (ESI-HRMS).

### Using **3g** as catalyst



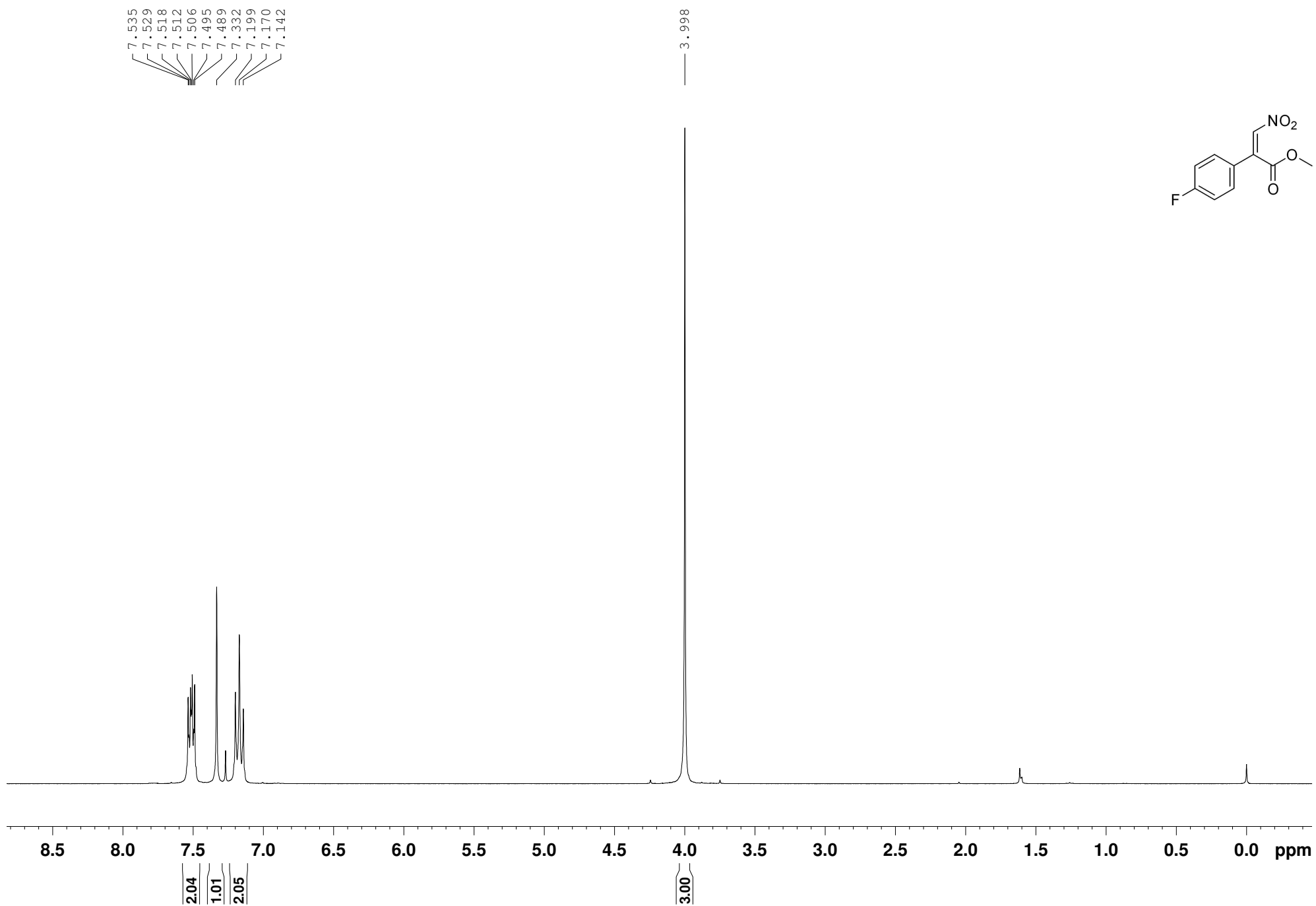


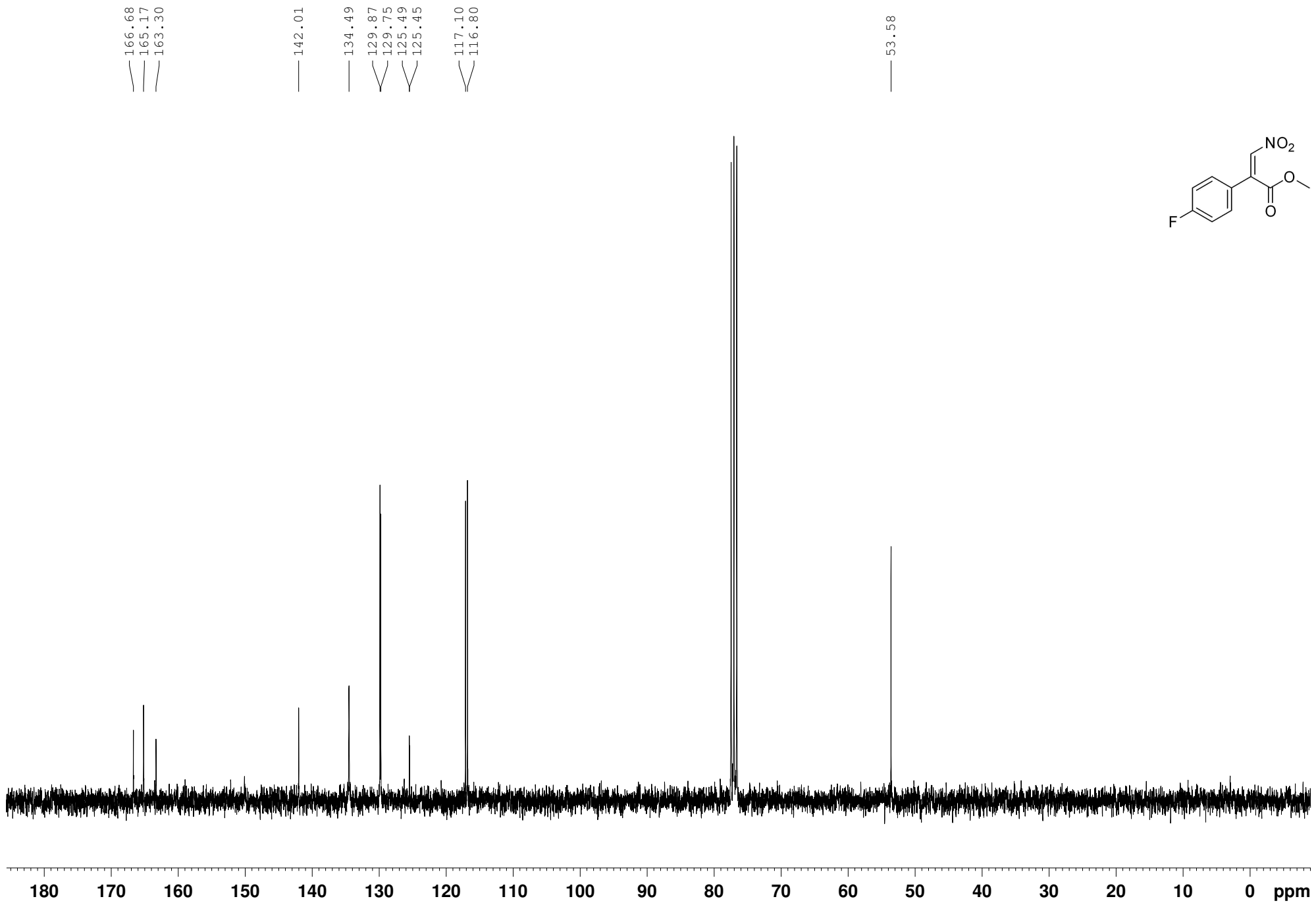
## 6. Reference

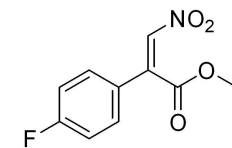
1. K. Mori, M. Wakazawa and T. Akiyama, *Chem. Sci.*, **2014**, 5, 1799.
2. (a) B. M. Trost, N. Cramer and S. M. Silverman, *J. Am. Chem. Soc.*, **2007**, 129, 12396. (b) G. Rassu, V. Zambrano, R. Tanca, A. Sartori, L. Battistini, F. Zanardi, C. Curti and G. Casiraghi, *Eur. J. Org. Chem.*, **2012**, 466.
3. (a) K. Asano and S. Matsubara, *J. Am. Chem. Soc.*, **2011**, 133, 16711. (b) M. X. Zhao, Z. W. Zhang, M. X. Chen, W. H. Tang and M. Shi, *Eur. J. Org. Chem.*, **2011**, 3001. (c) C. J. Wang, Z. H. Zhang, X. Q. Dong, X. J. Wu, *Chem. Comm.*, **2008**, 48, 1431. (d) B. Tan, N. R. Candeias, C. F. Barbas III, *Nat. Chem.*, **2011**, 3, 473. (e) Y. Zhu, J. P. Malerich, V. H. Rawal, *Angew. Chem. Int. Ed.*, **2010**, 49, 153. (f) W. Yang, D. M. Du, *Org. Lett.*, **2010**, 12, 5450.



# 8. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of compounds 1b-1d, 1g, 1h, 2b, 2c, 4 and 5







-105.844



0

-20

-40

-60

-80

-100

-120

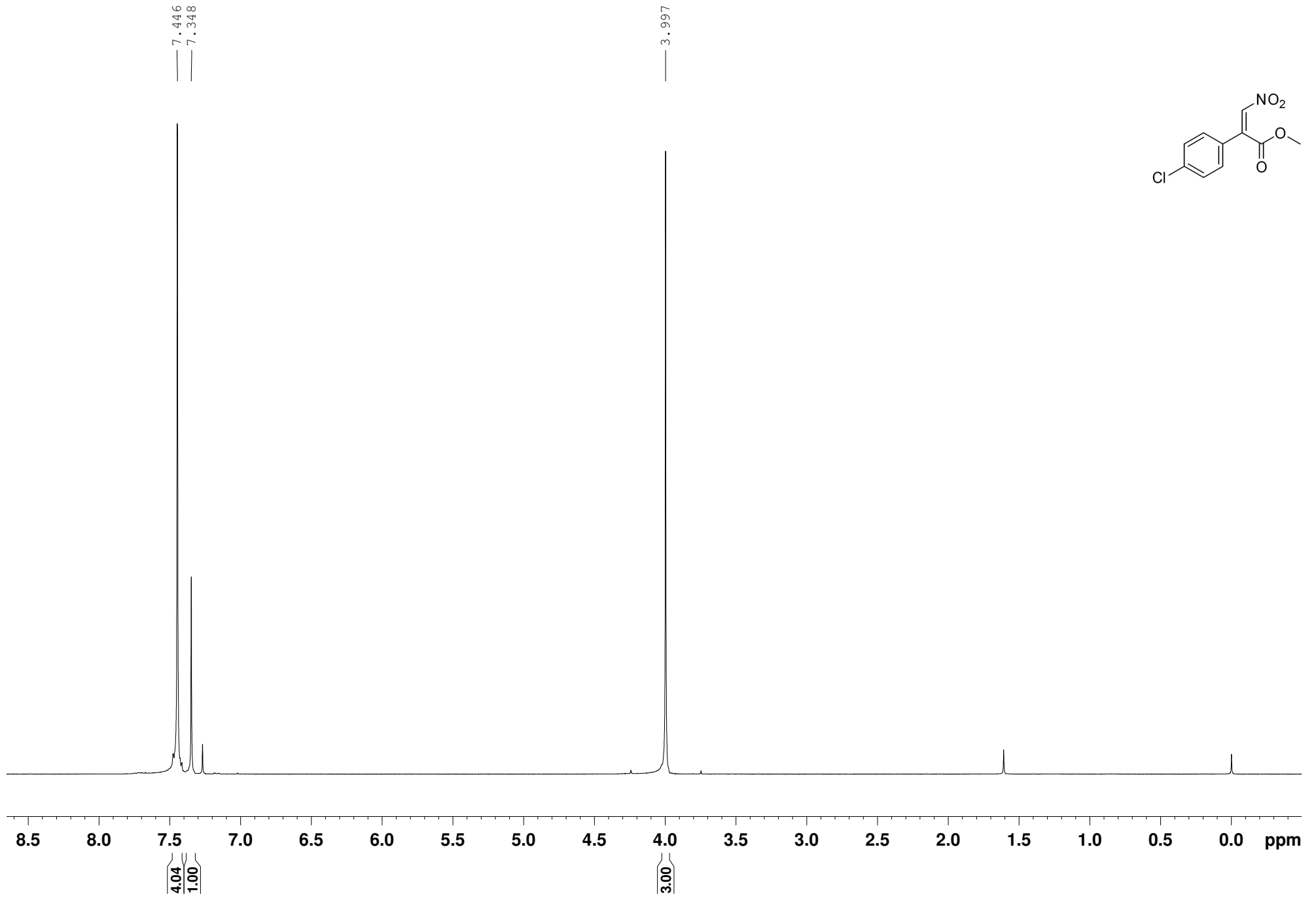
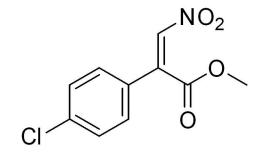
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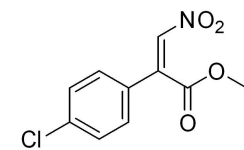
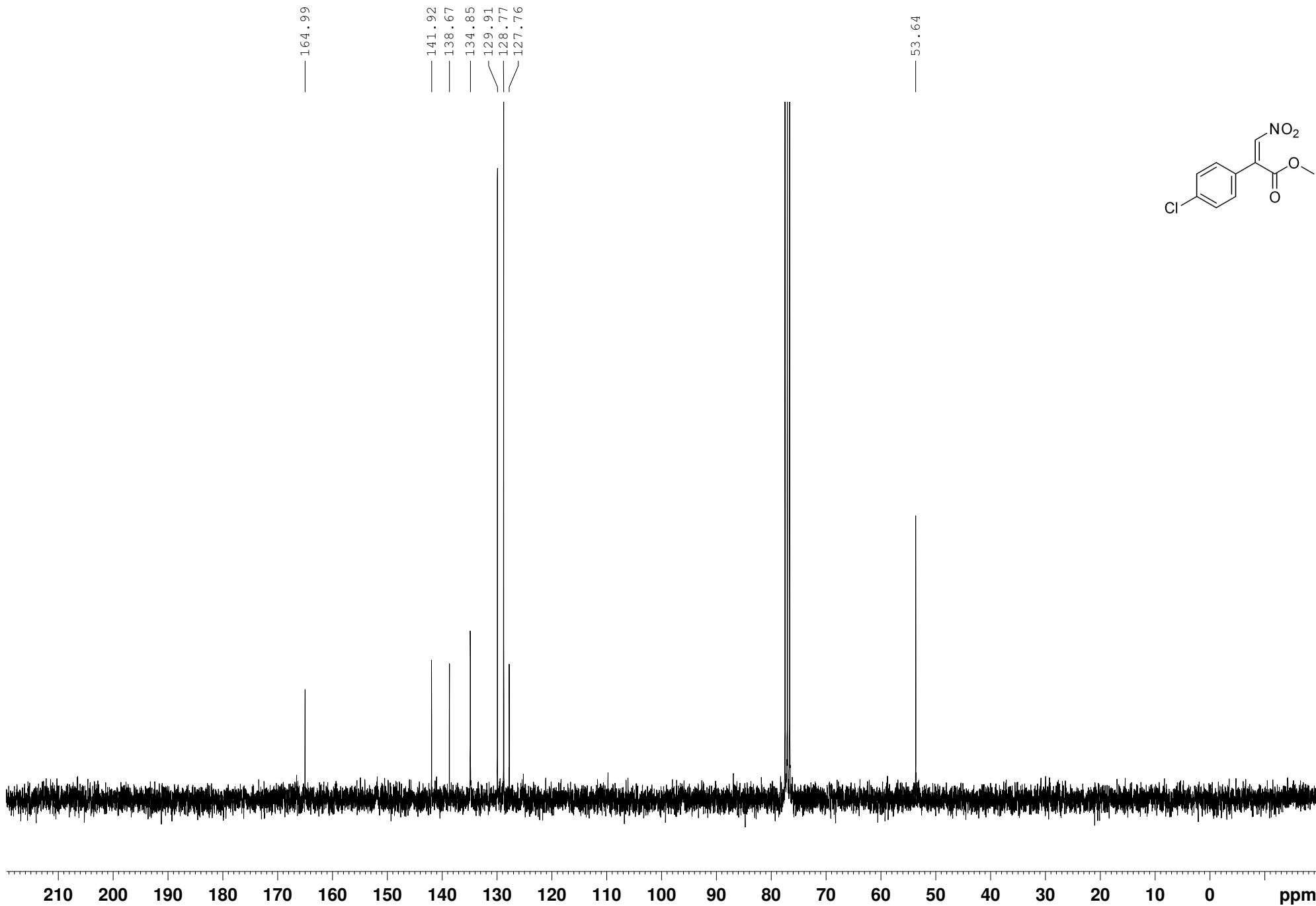
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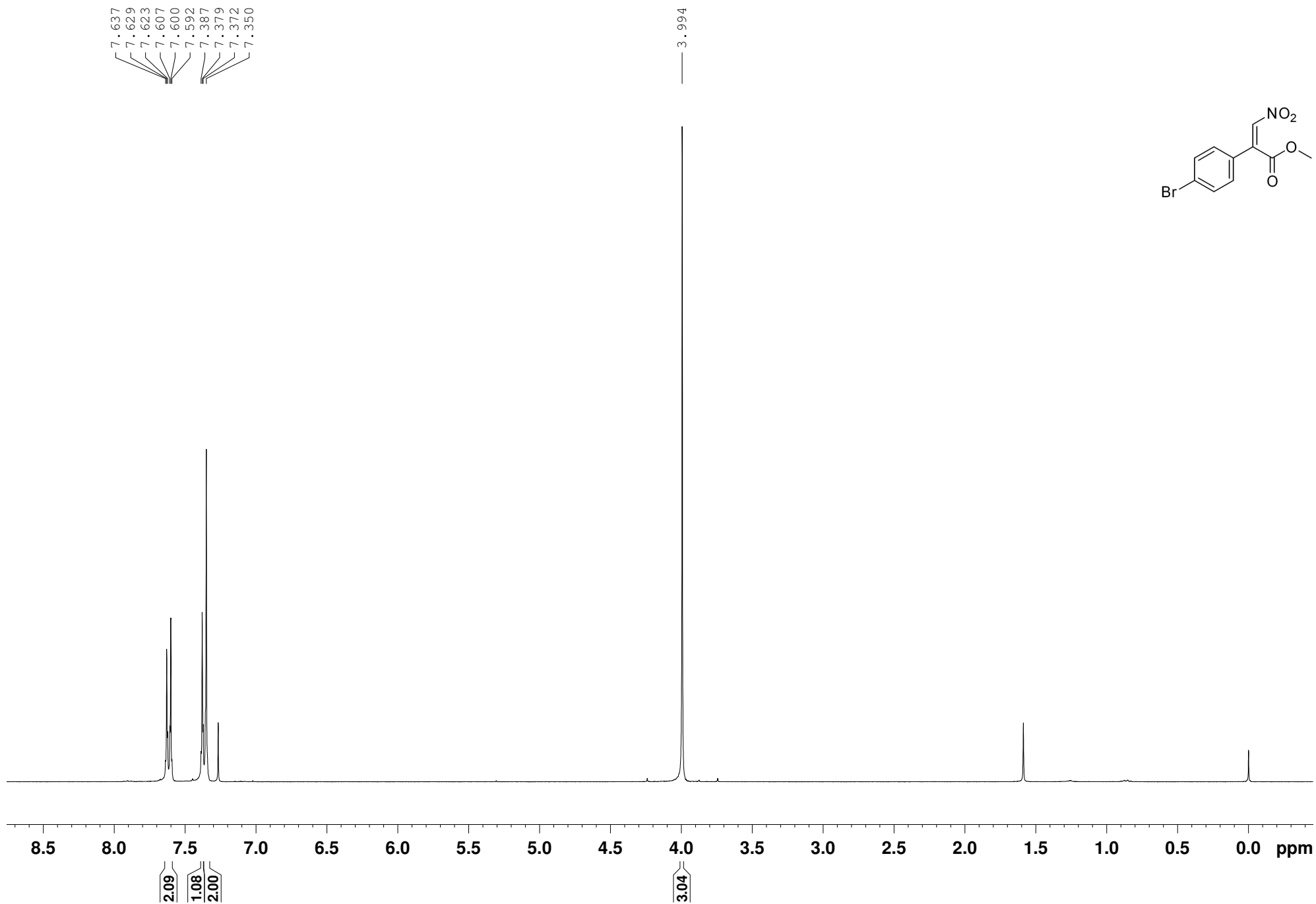
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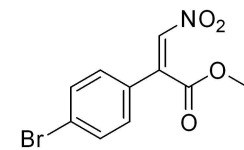
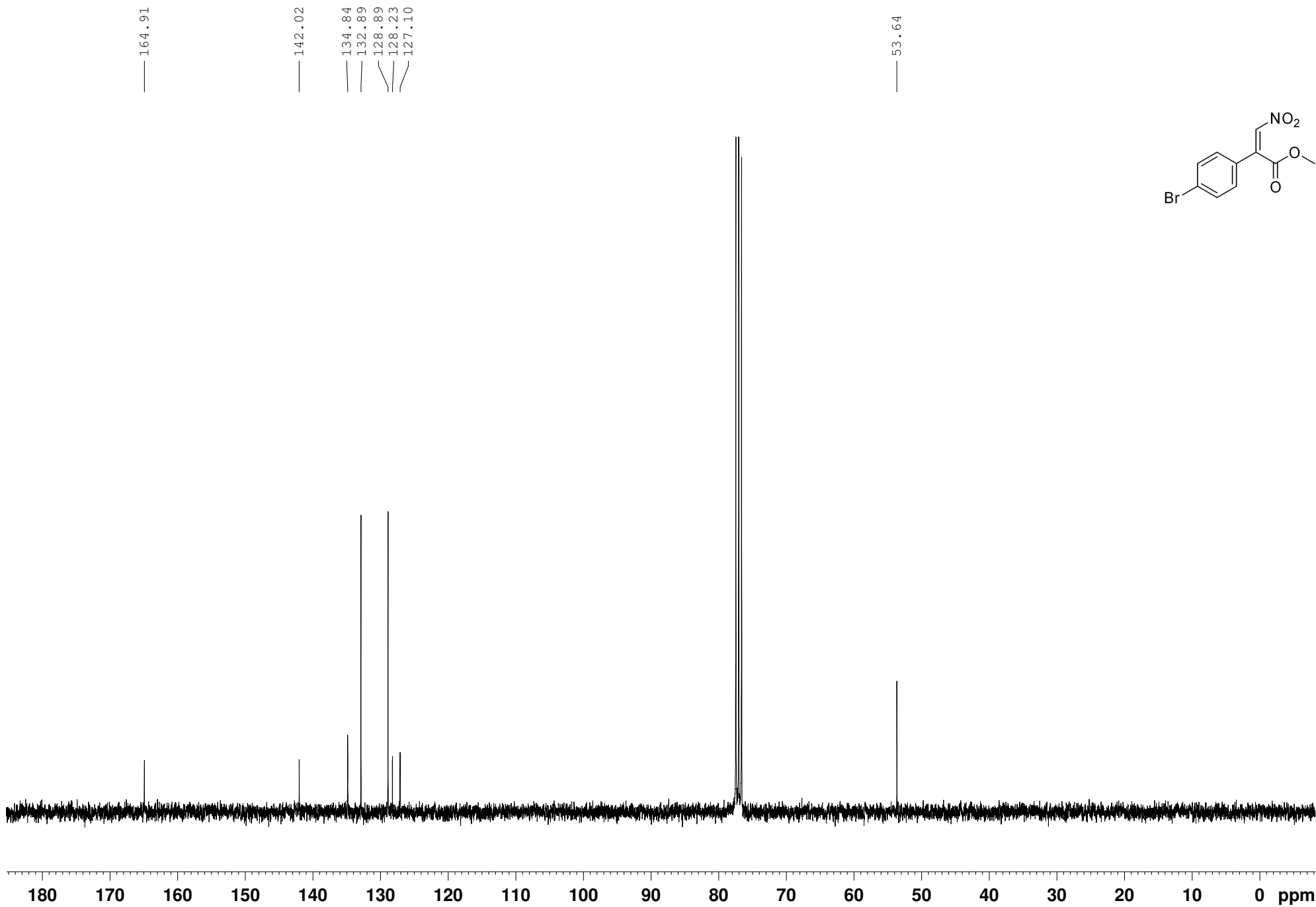
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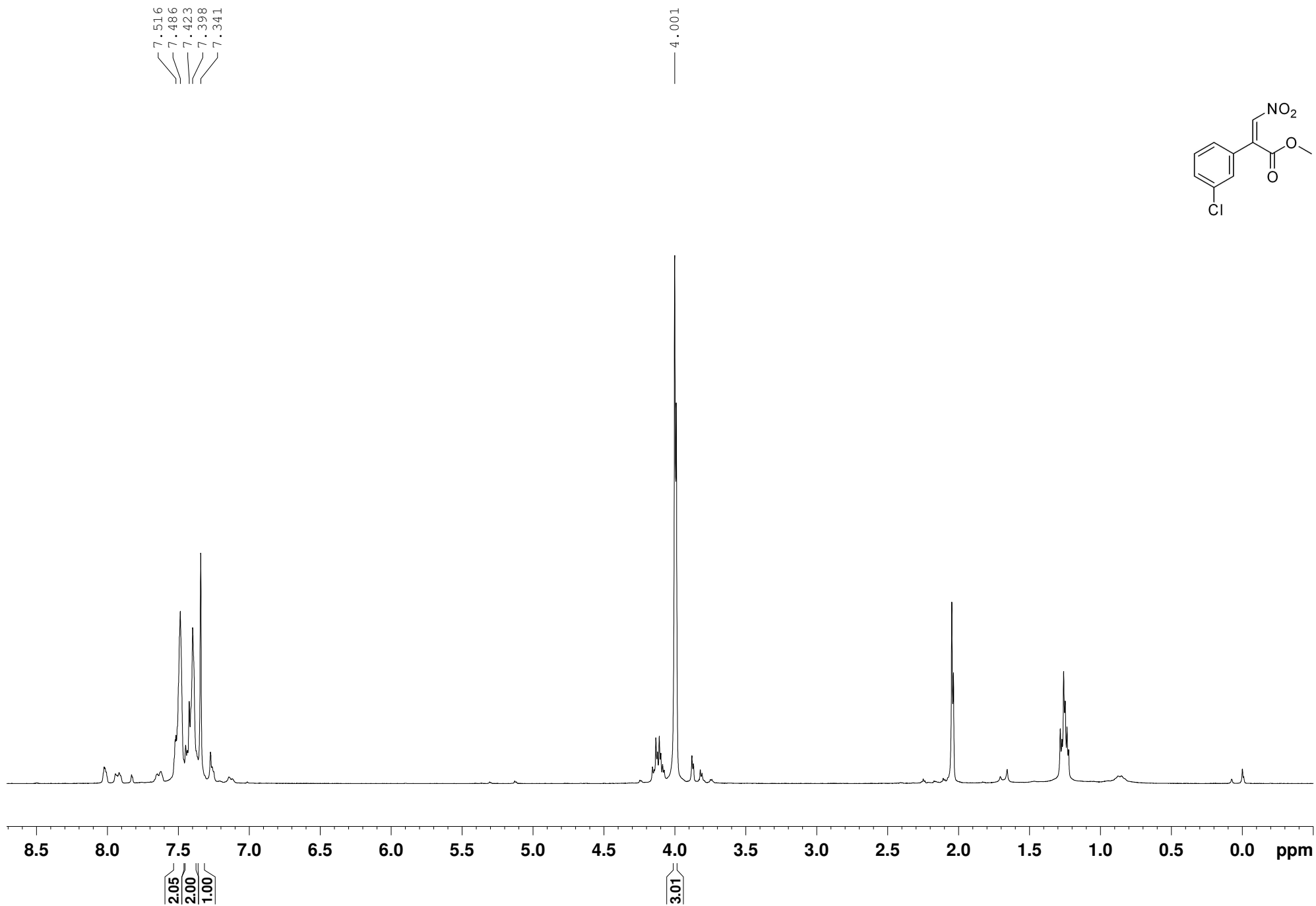
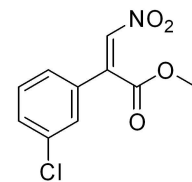


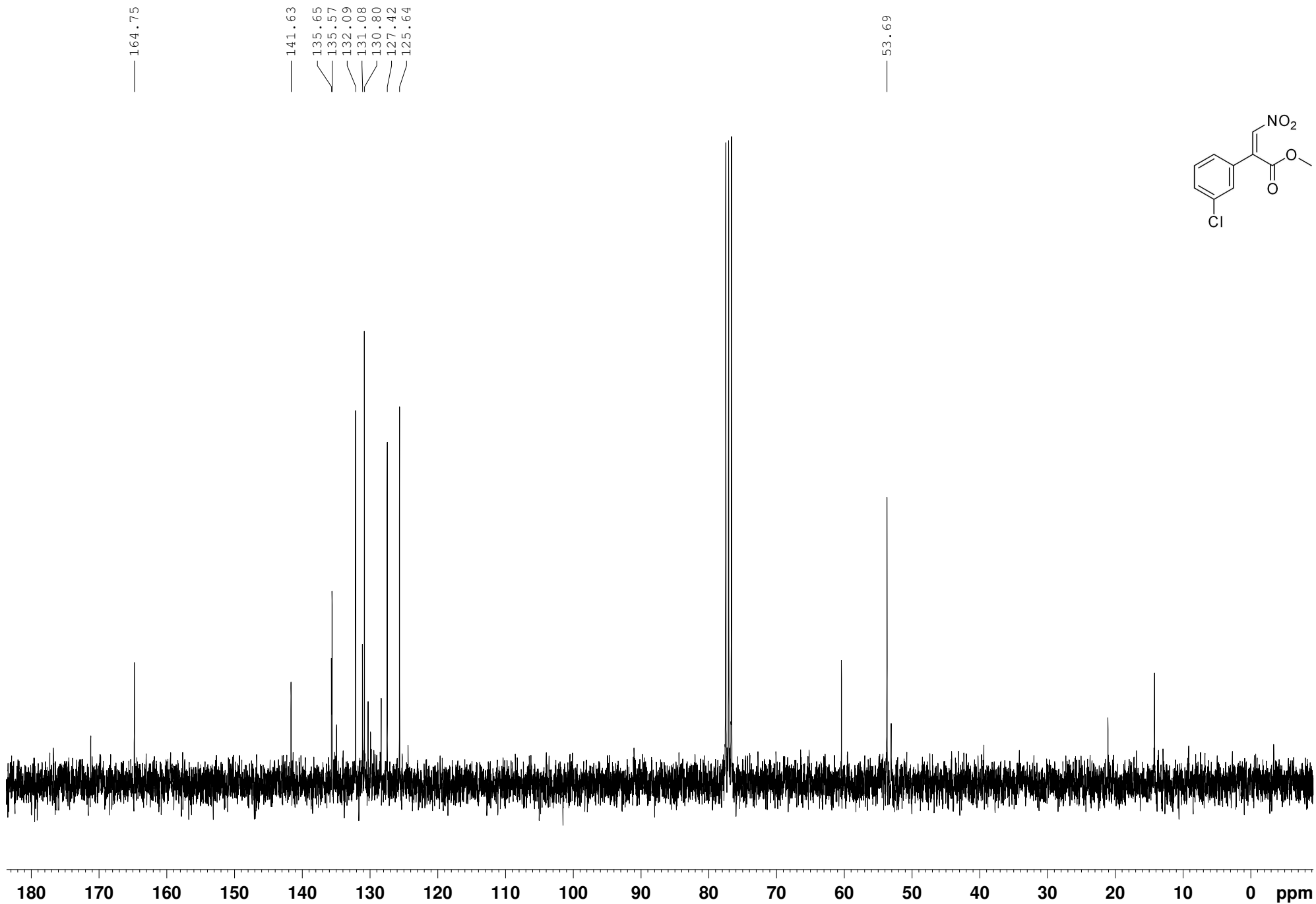


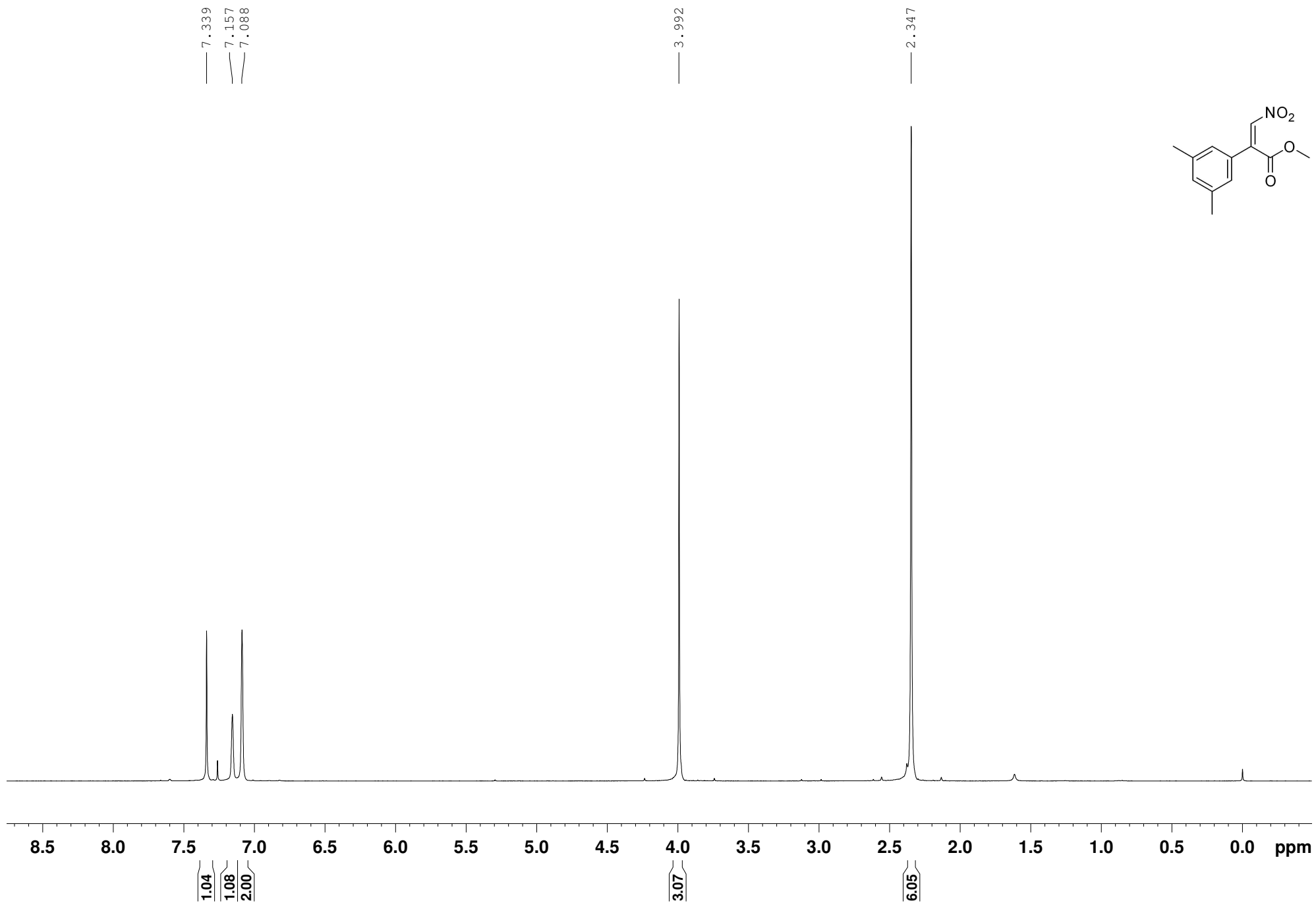


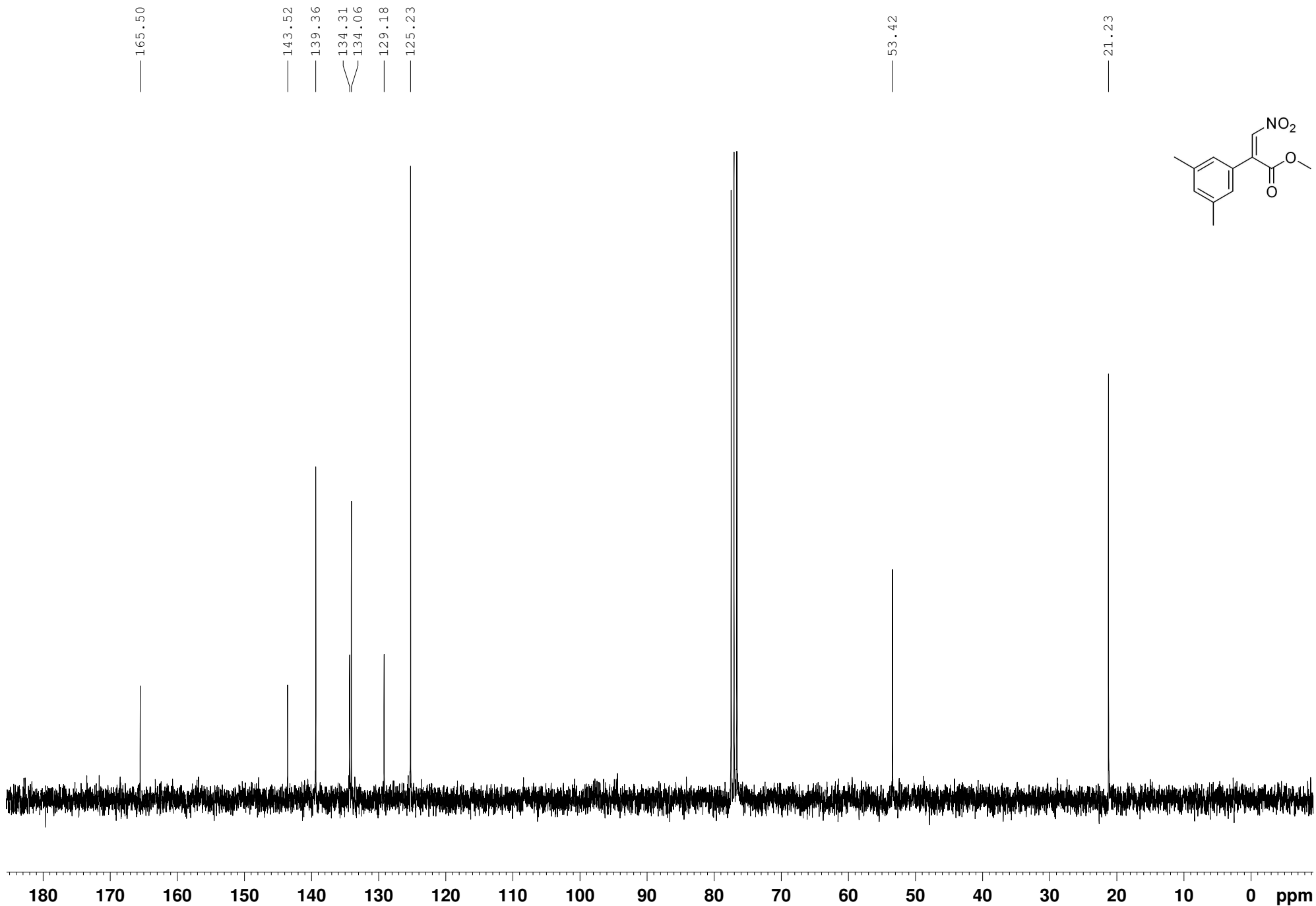


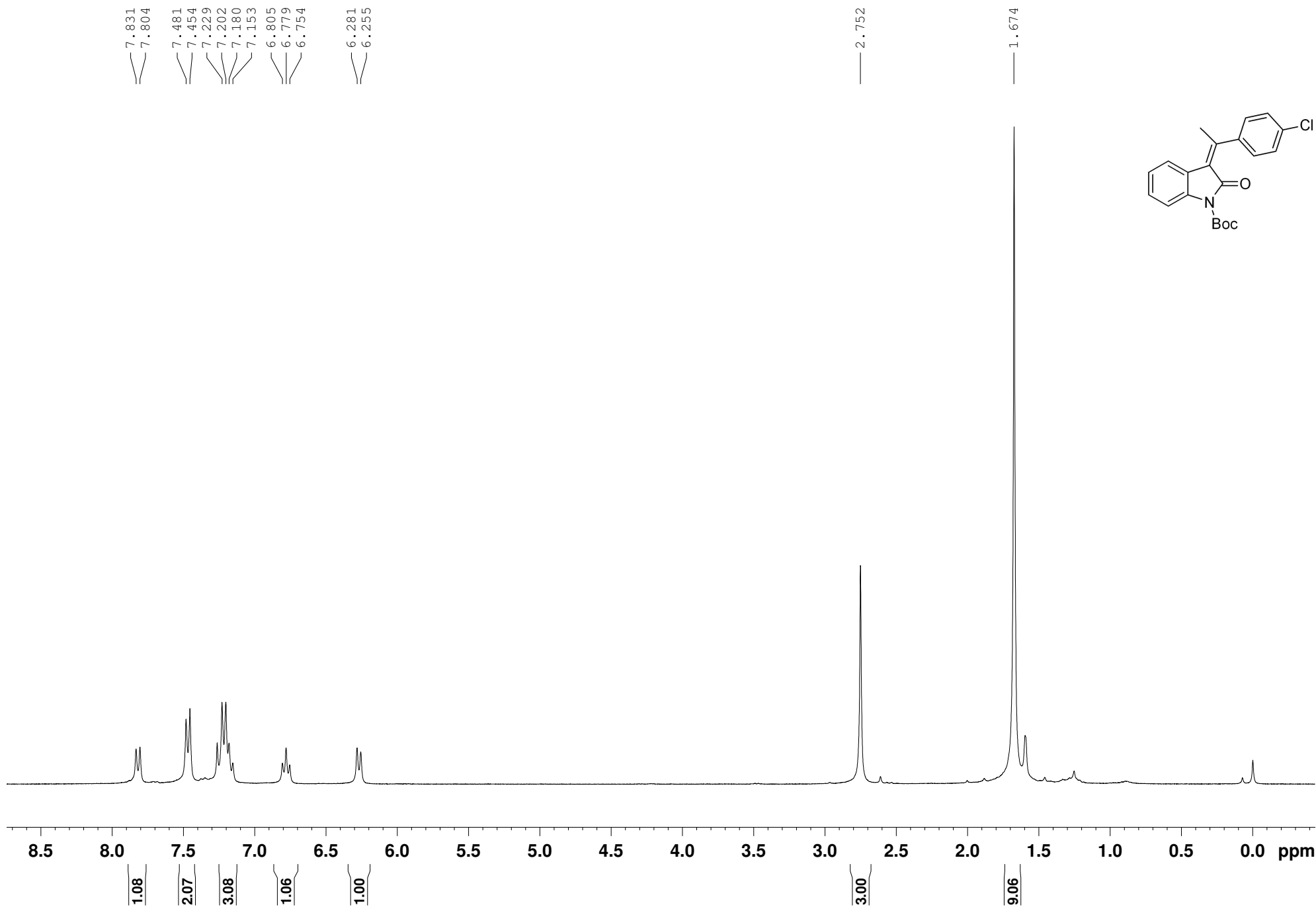


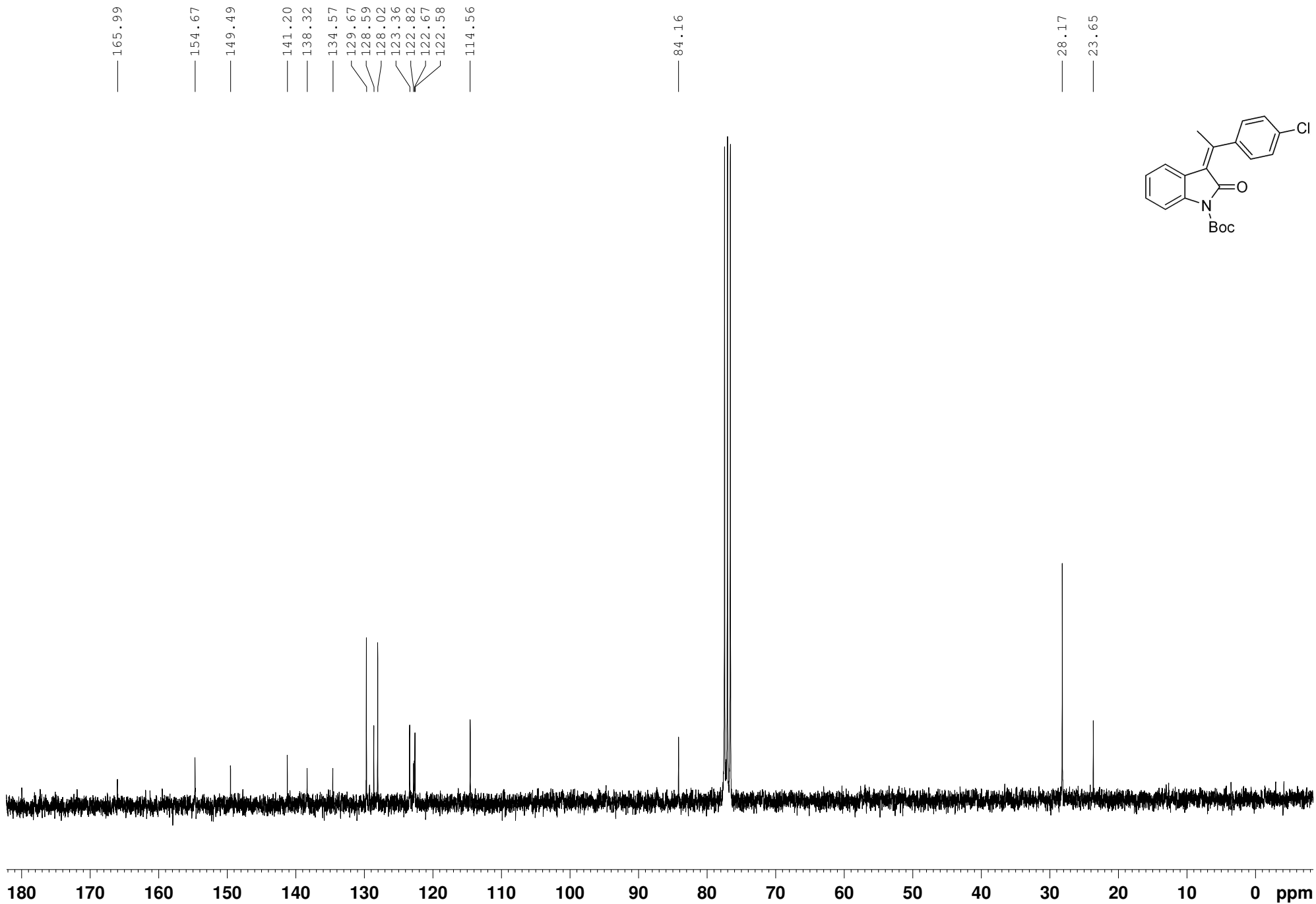


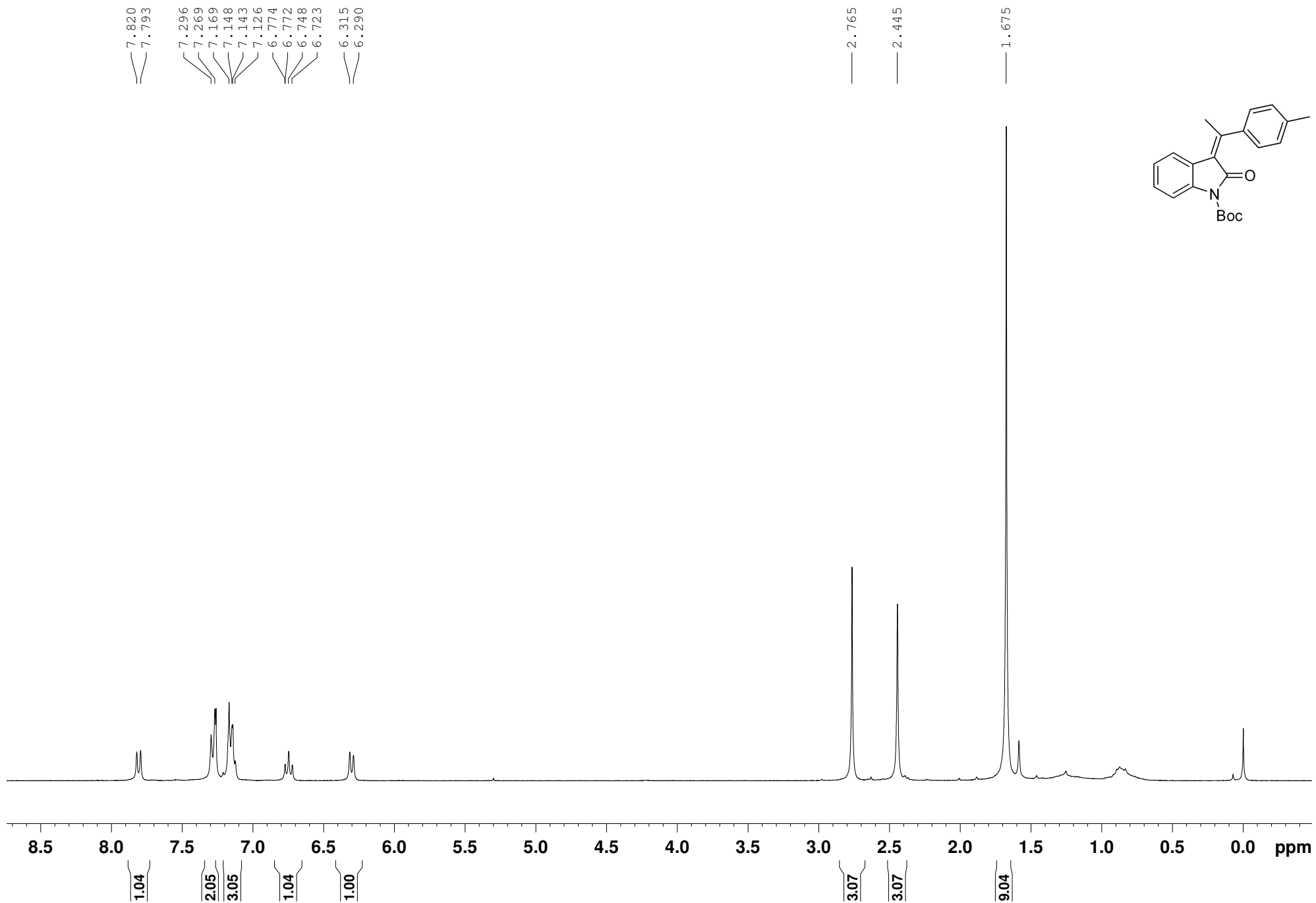




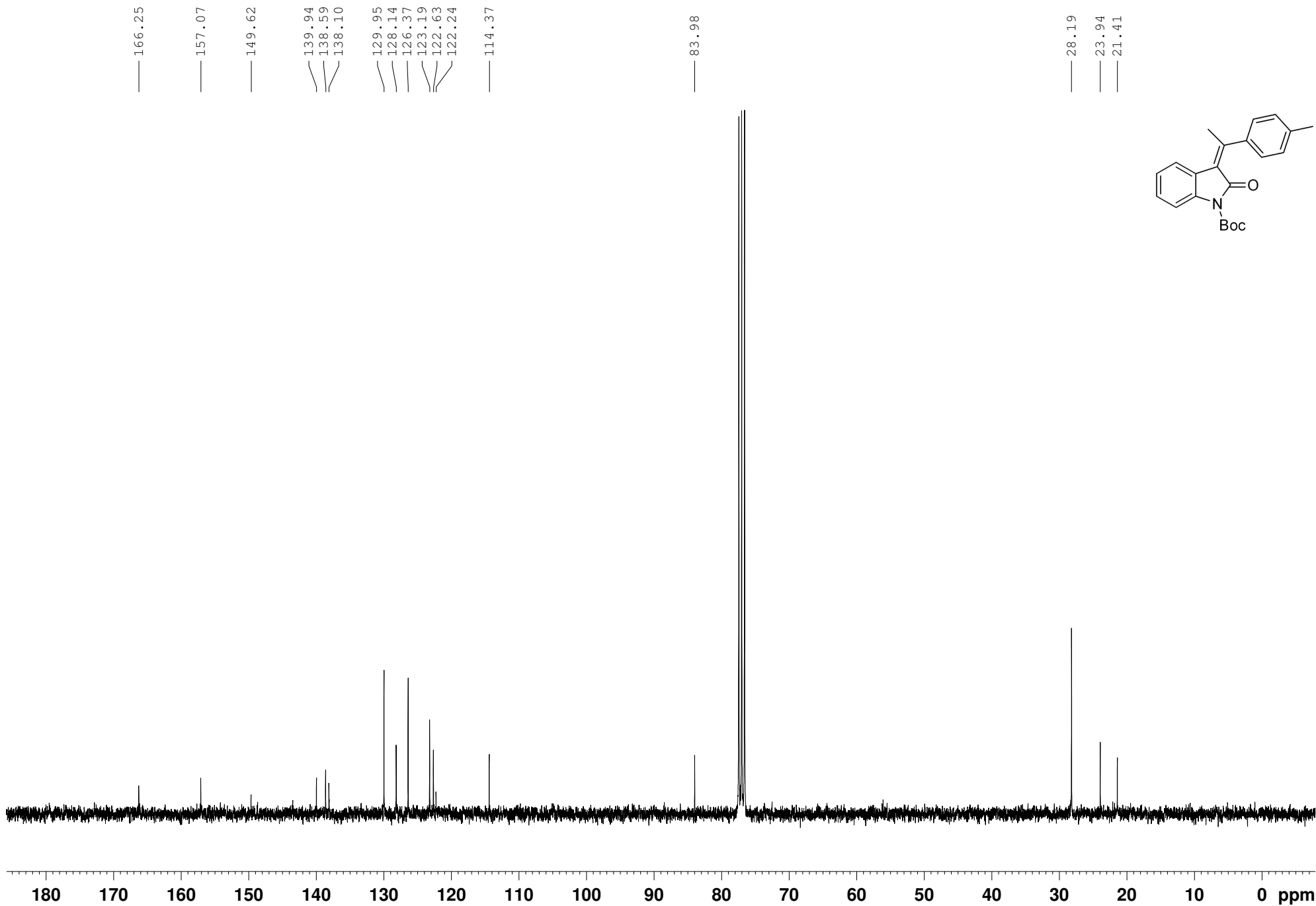


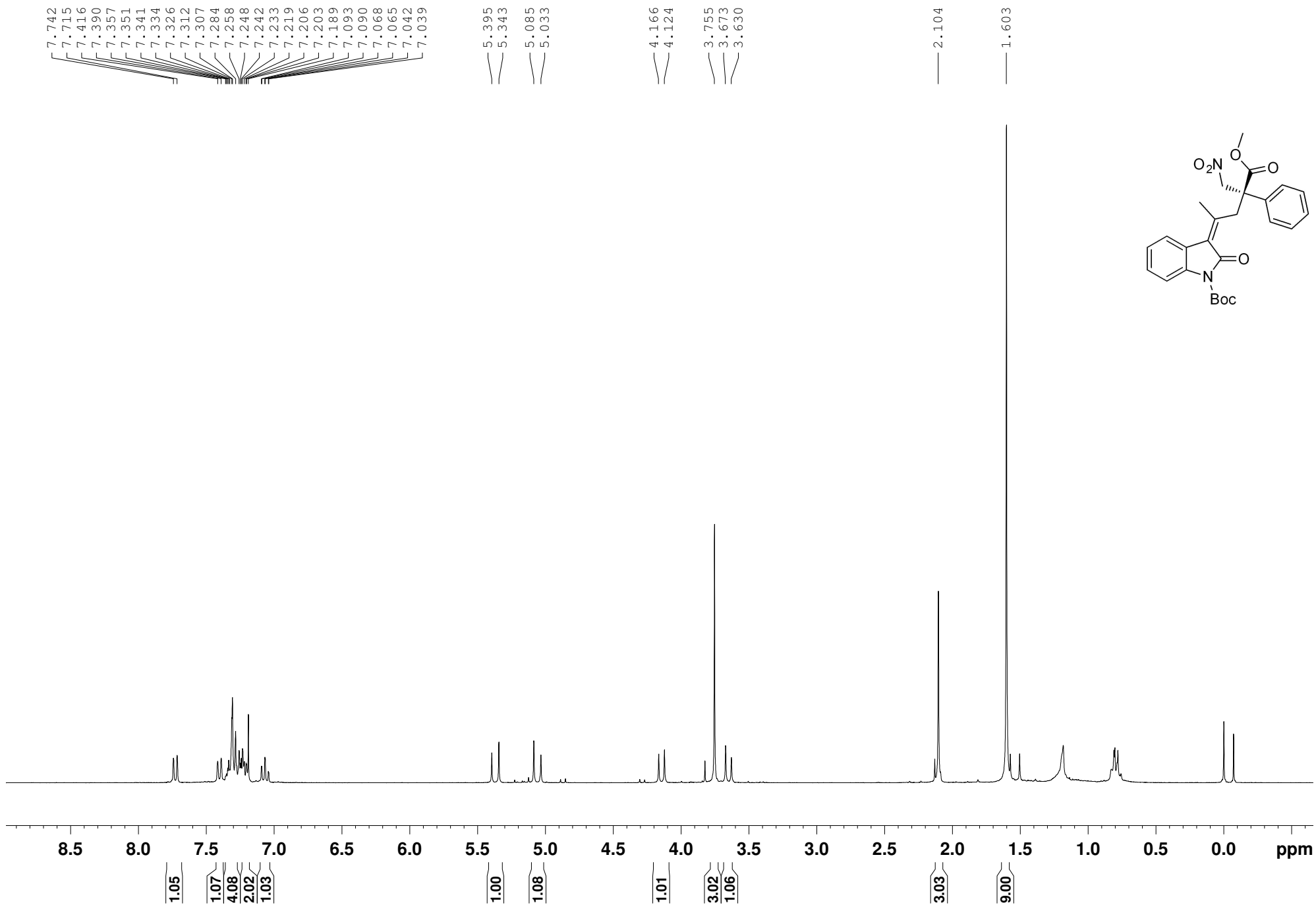


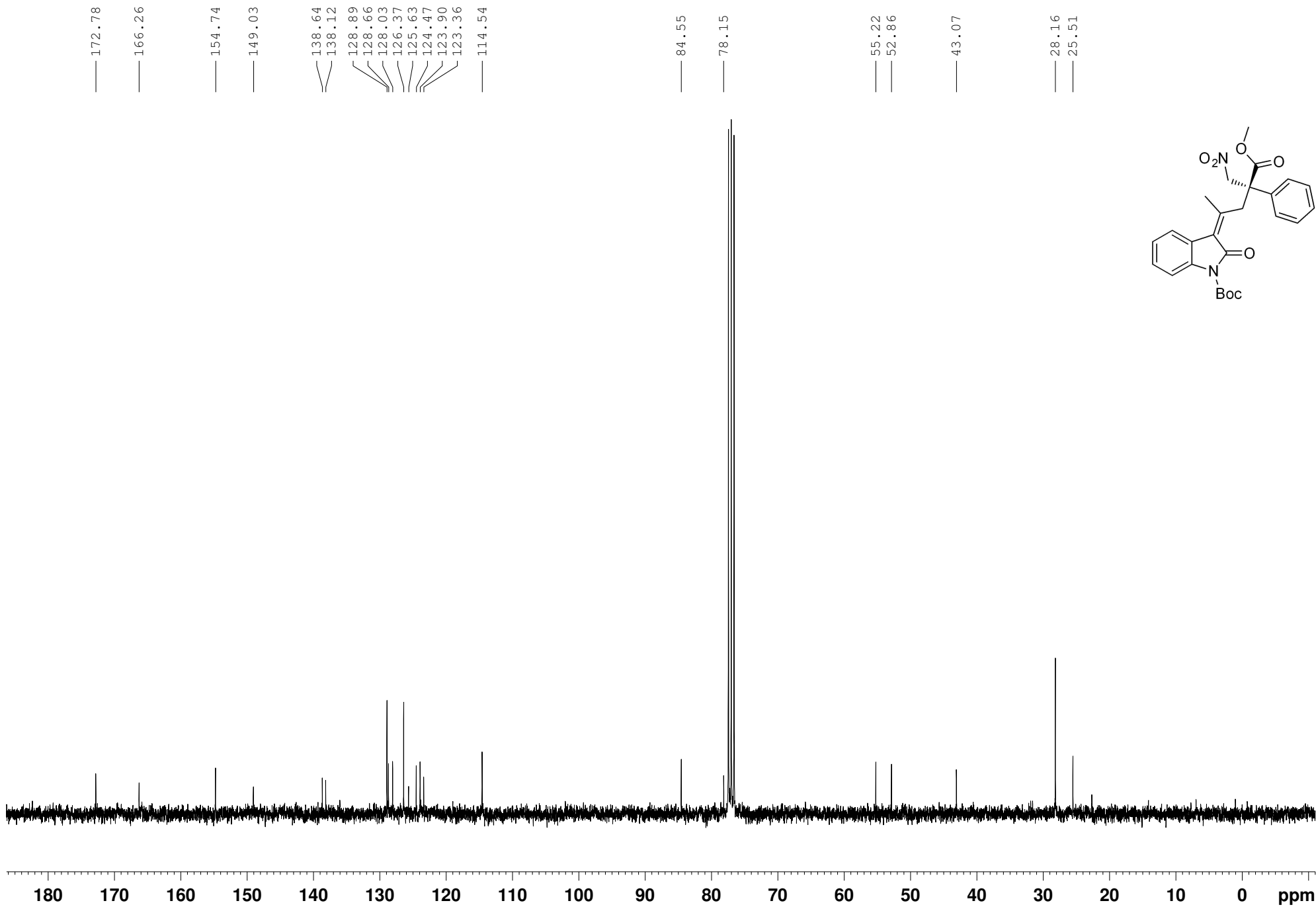


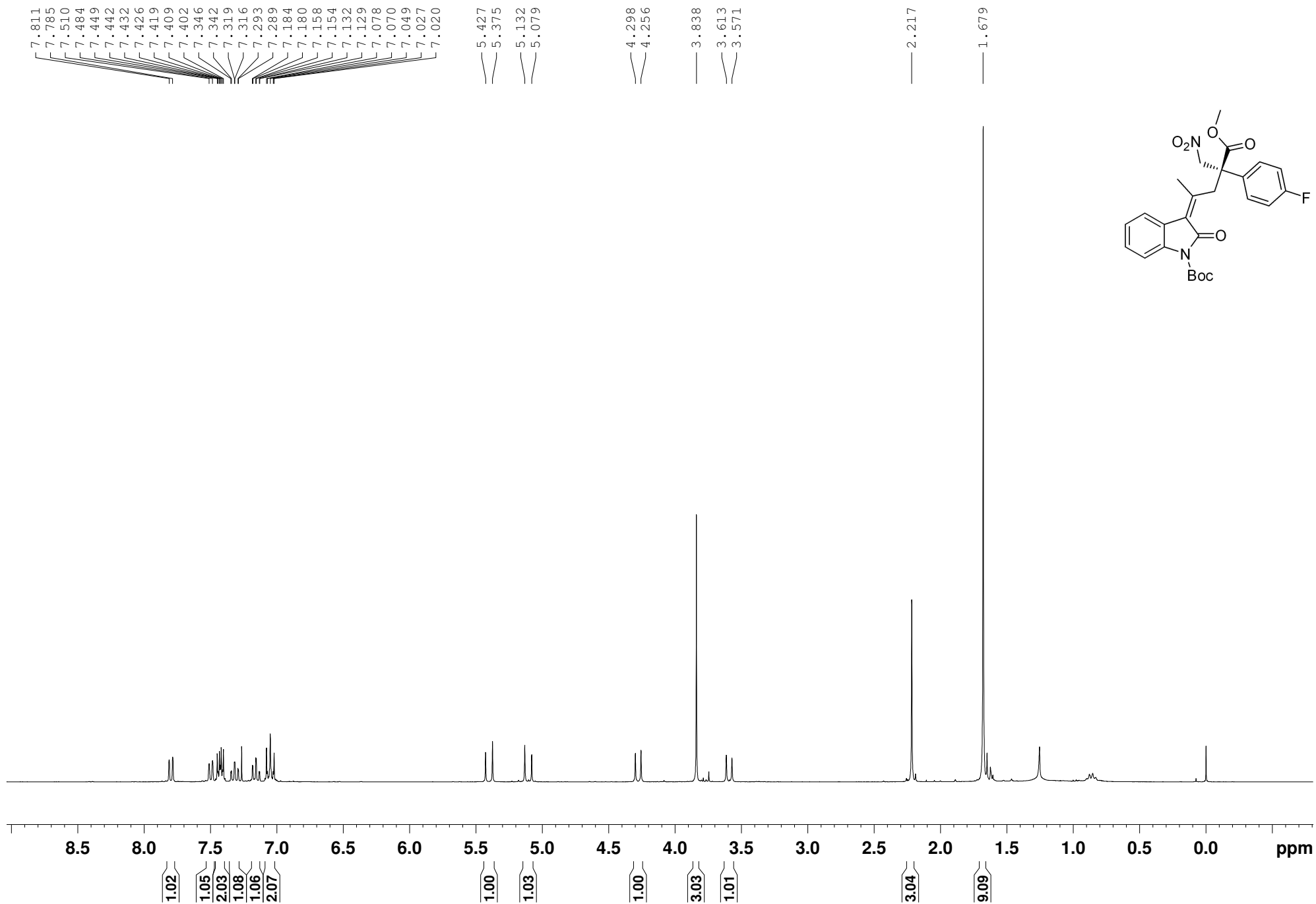


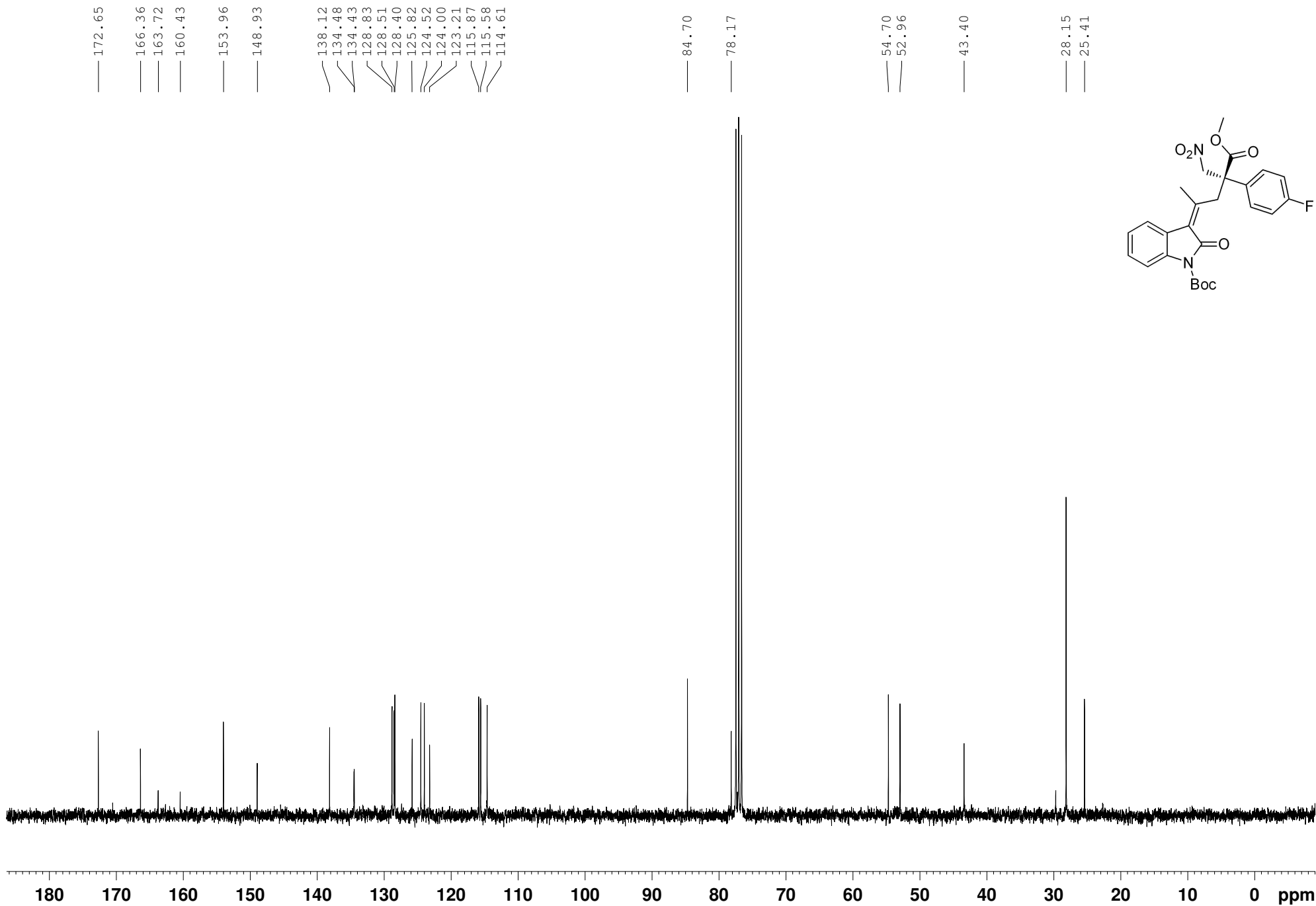


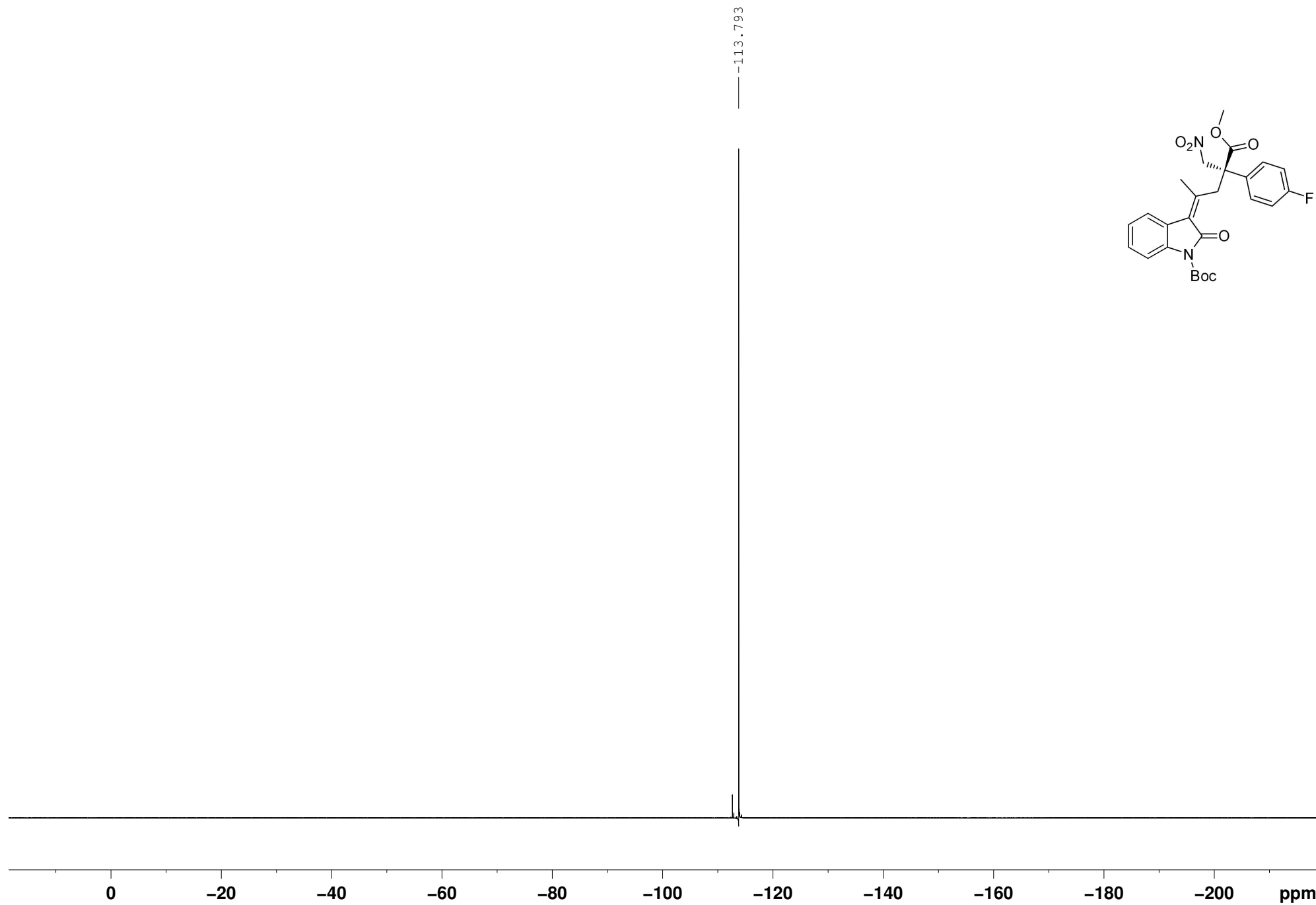


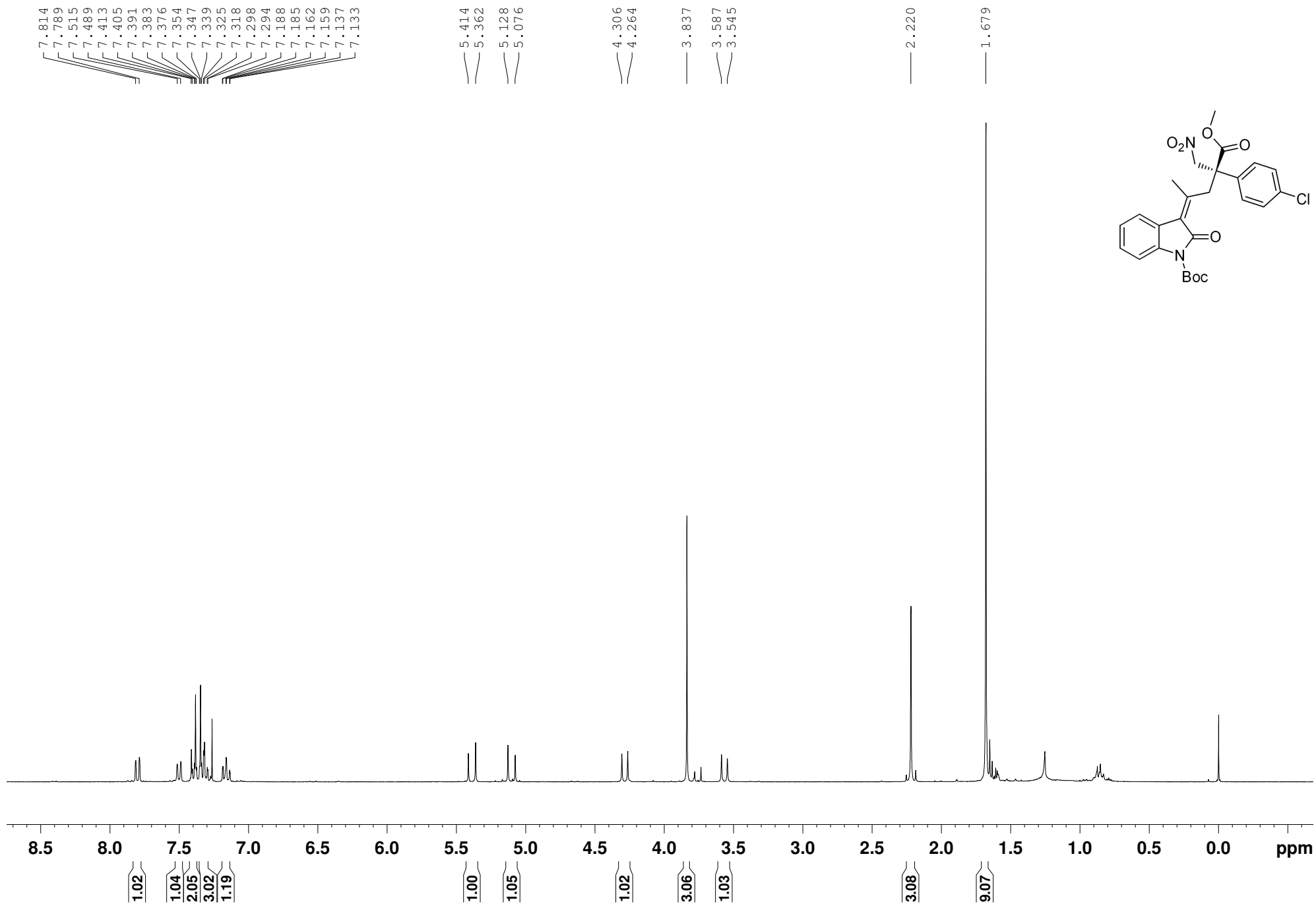


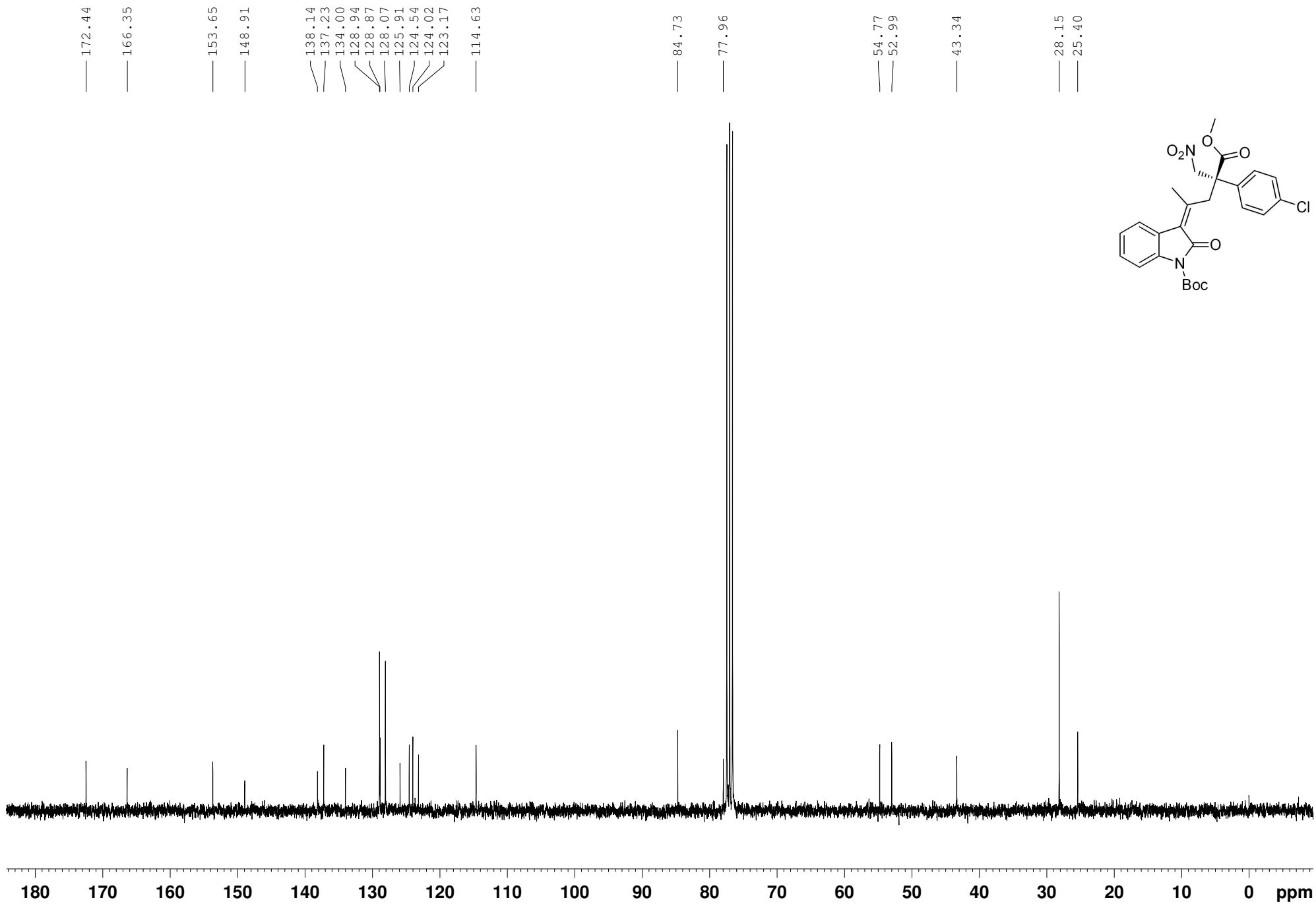




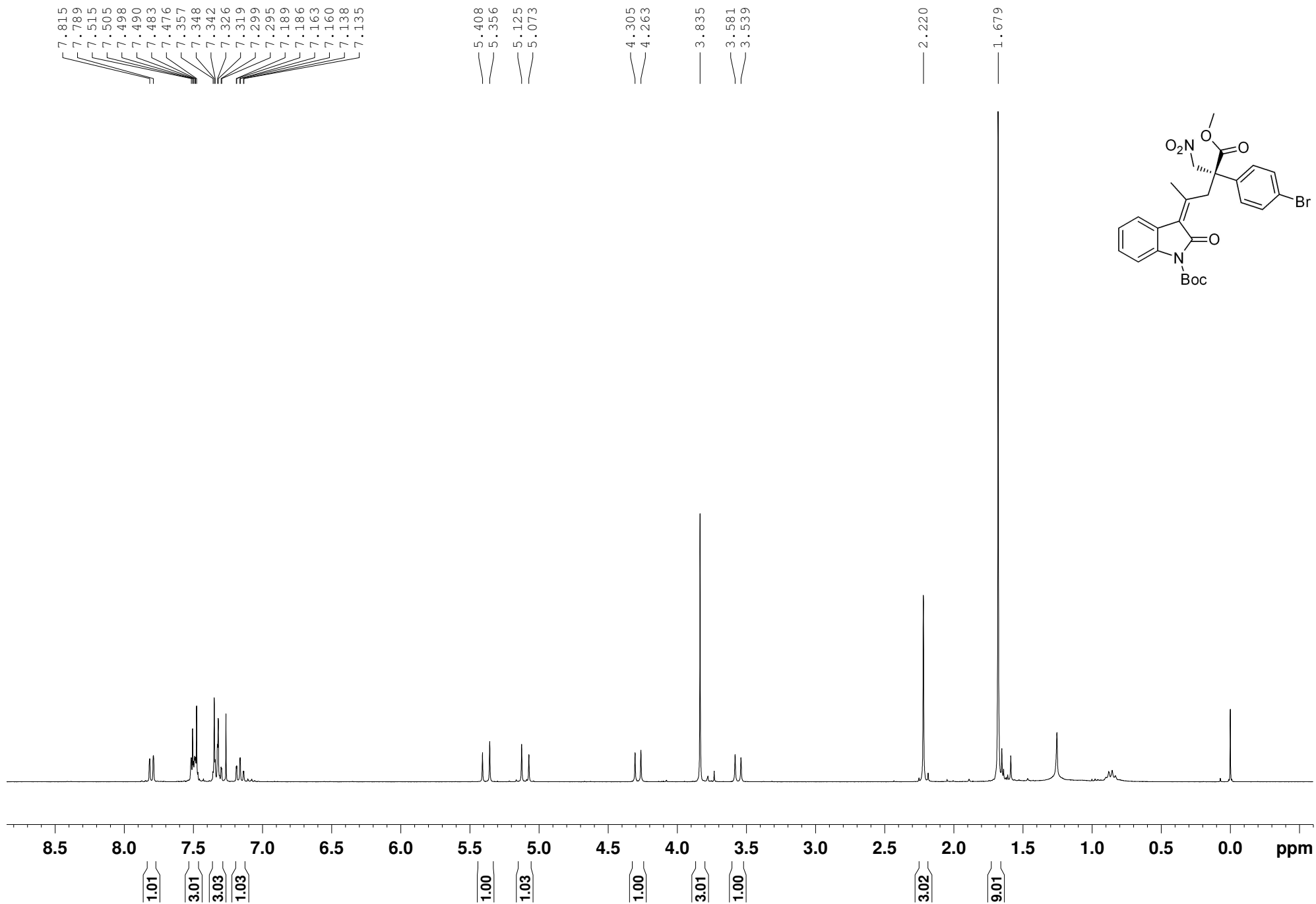


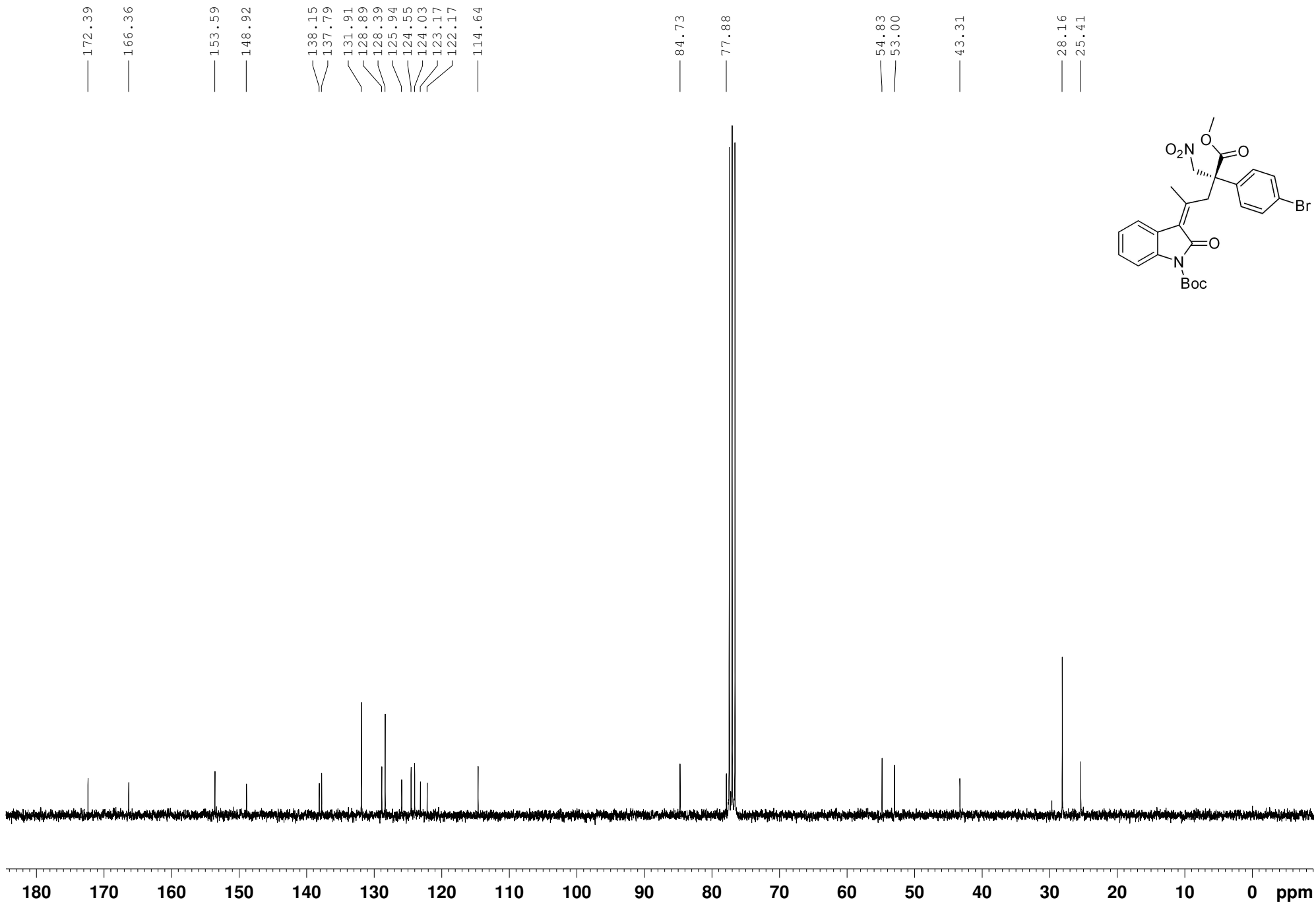


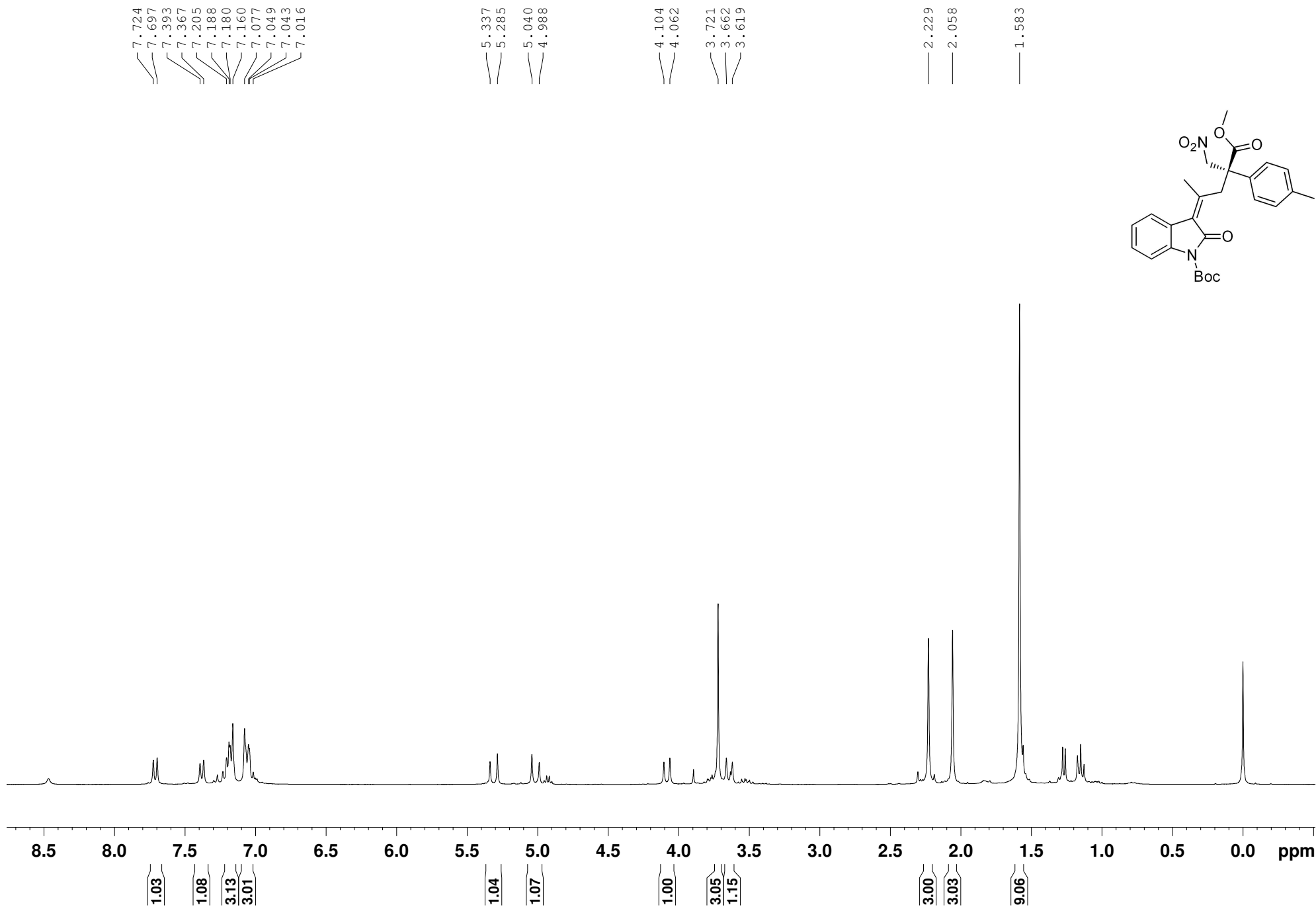


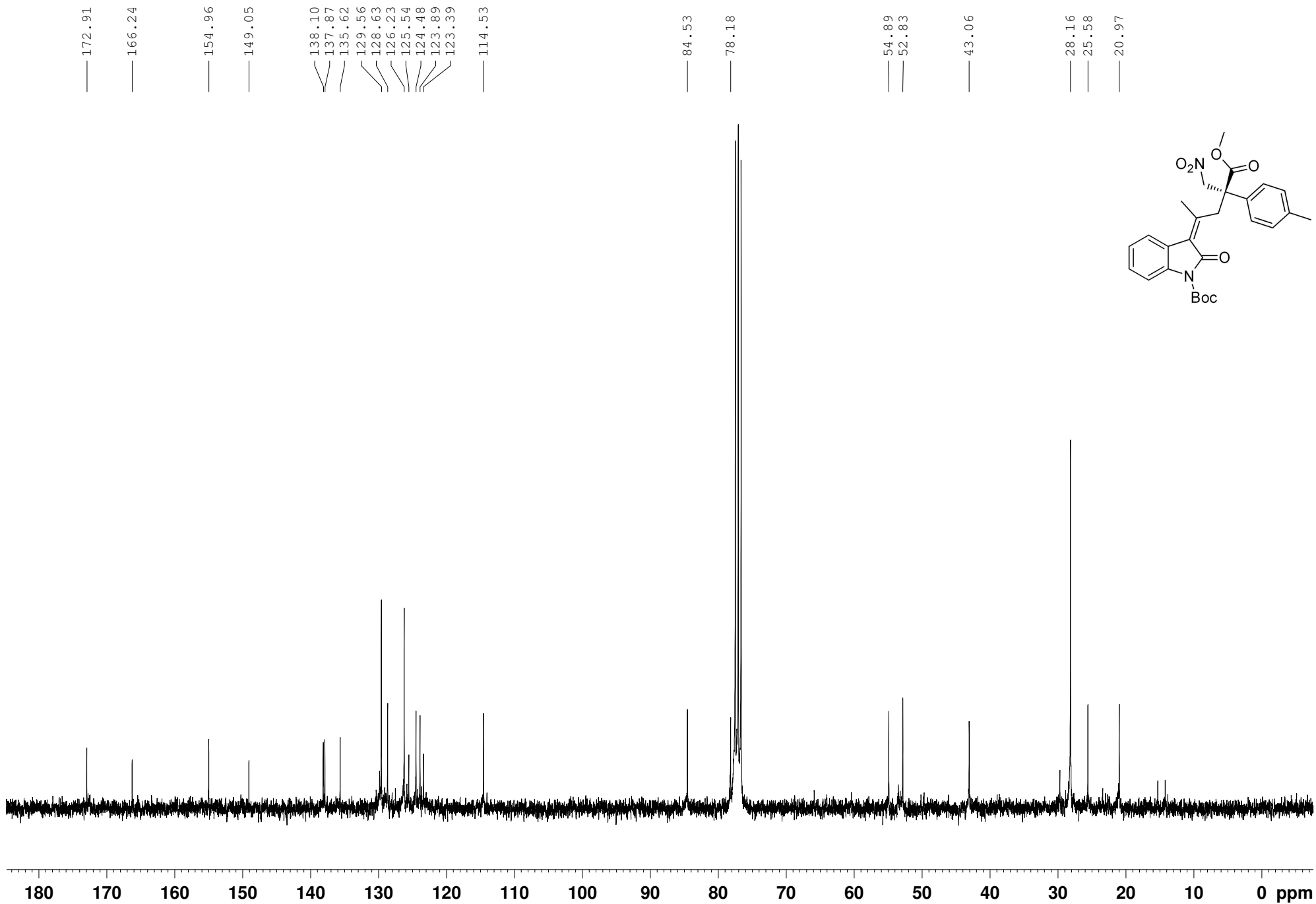


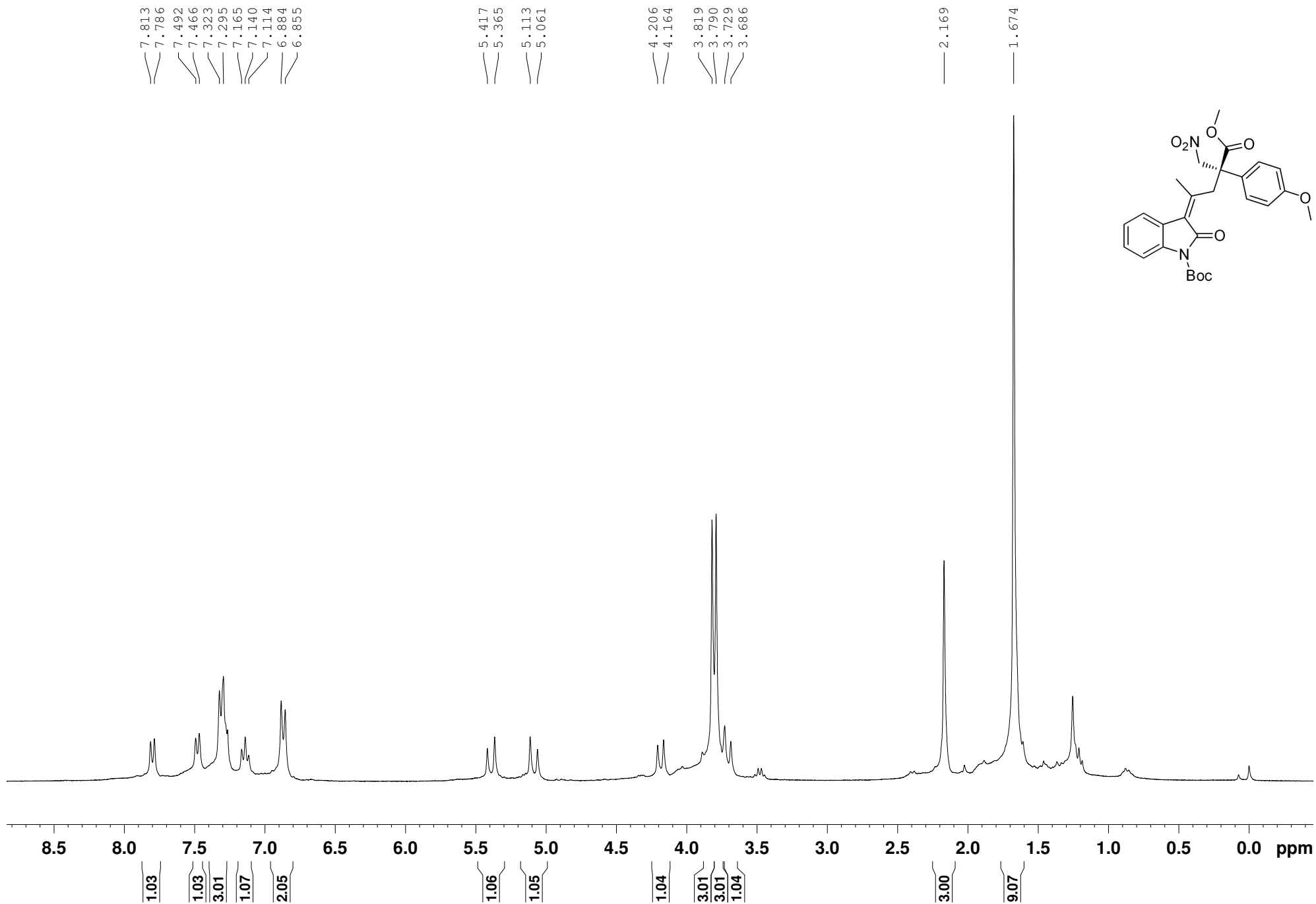


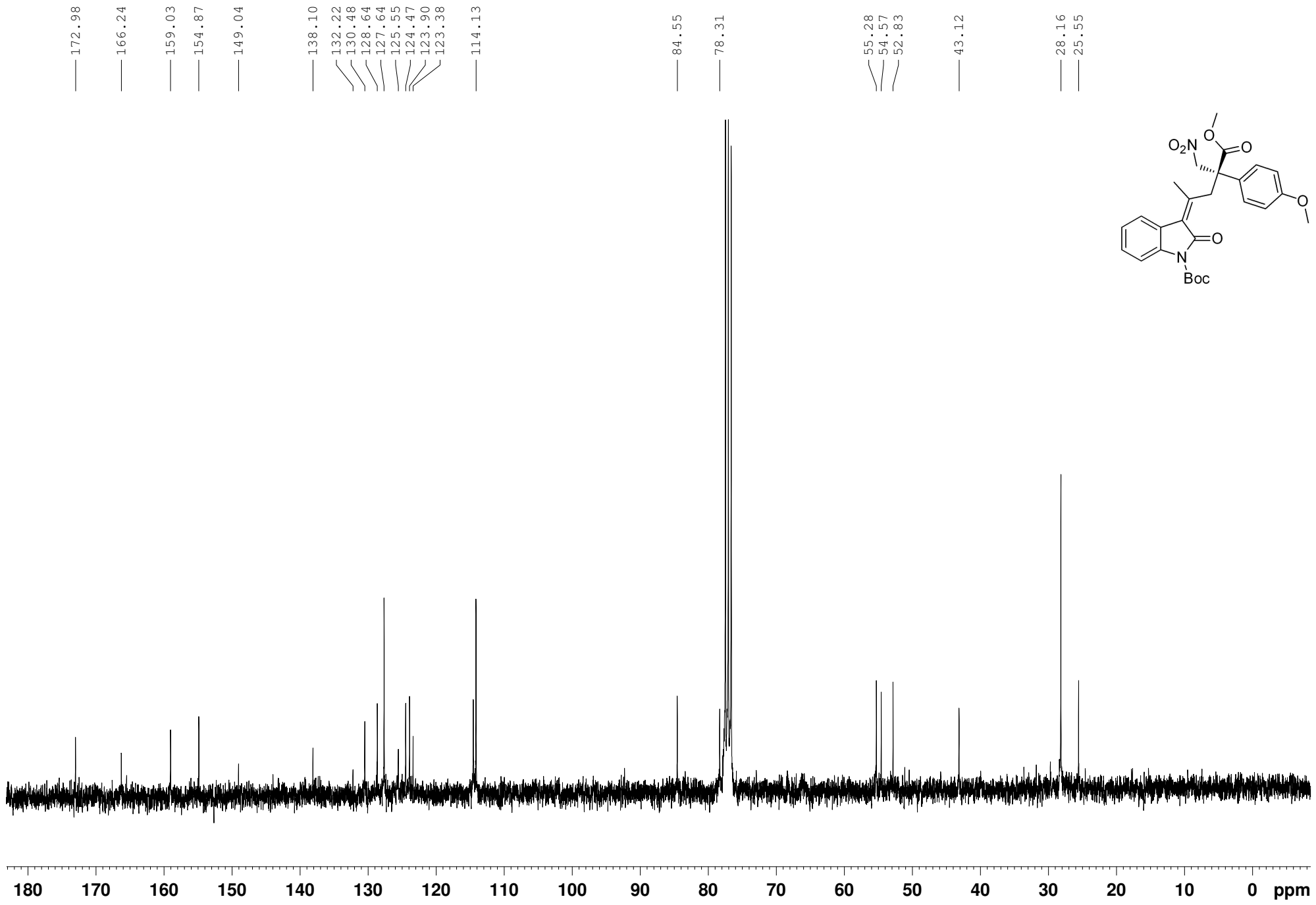












— 172.98

— 166.24

— 159.03

— 154.87

— 149.04

— 138.10

— 132.22

— 130.48

— 128.64

— 127.64

— 125.55

— 124.47

— 123.90

— 123.38

— 114.13

— 84.55

— 78.31

— 55.28

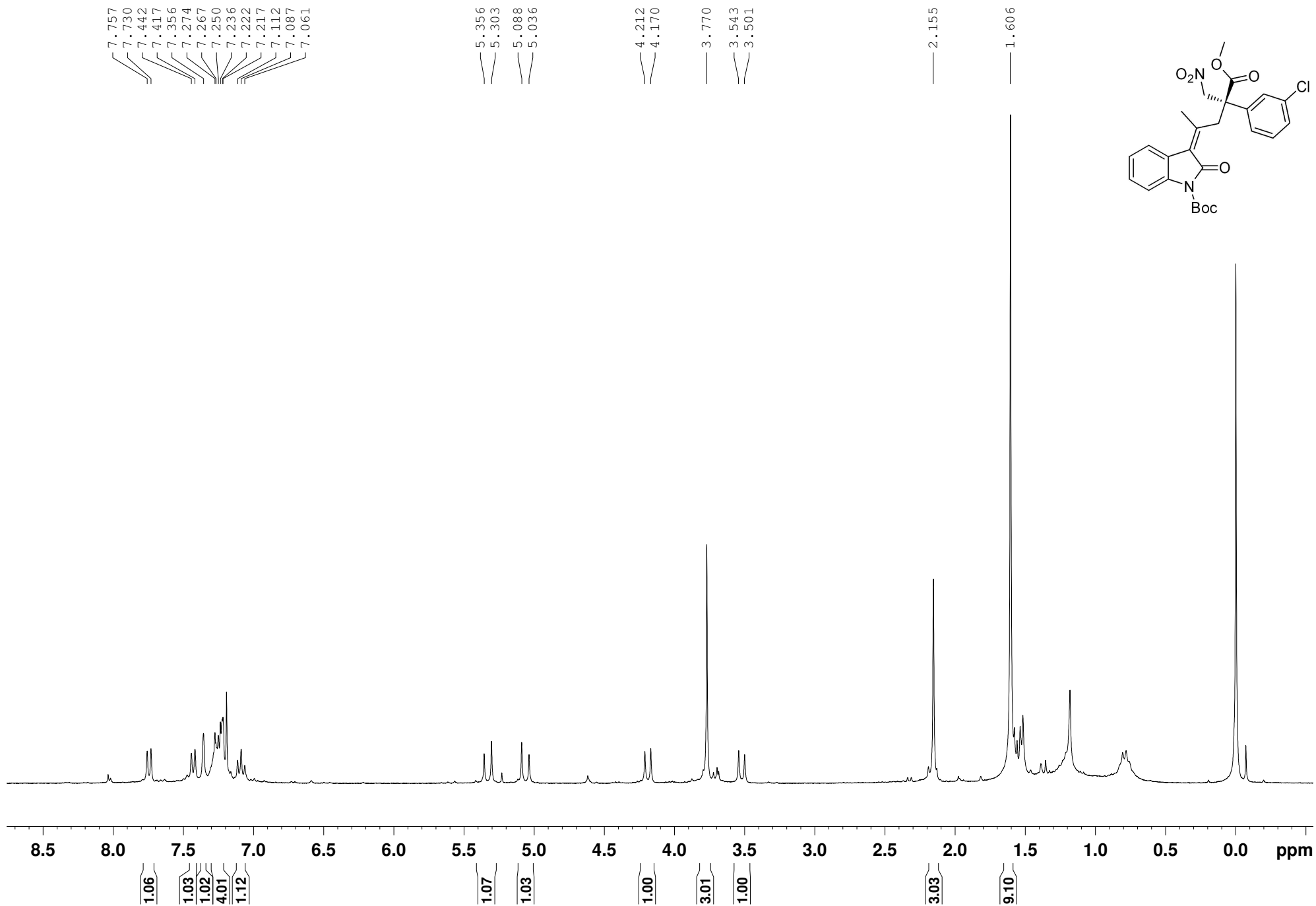
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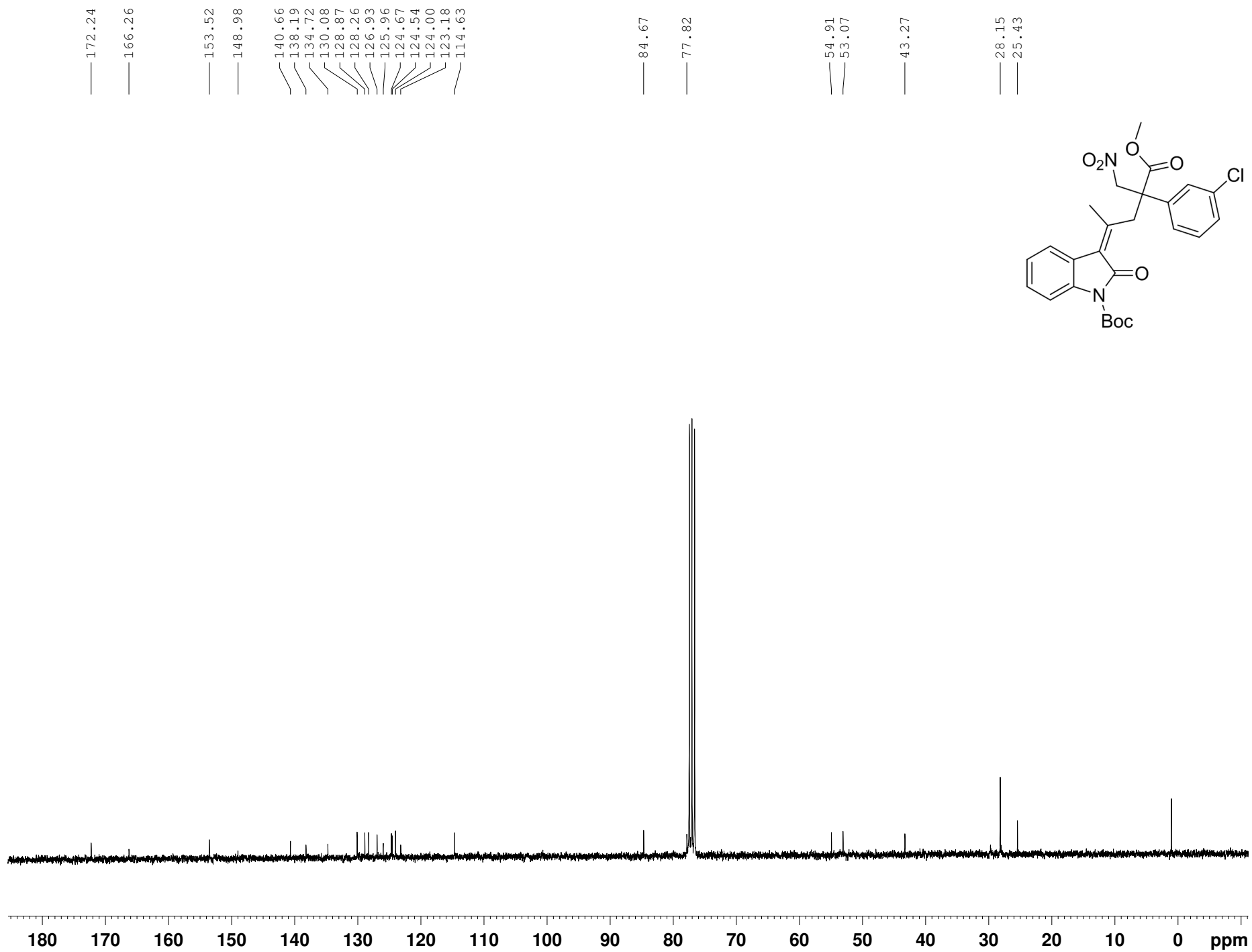
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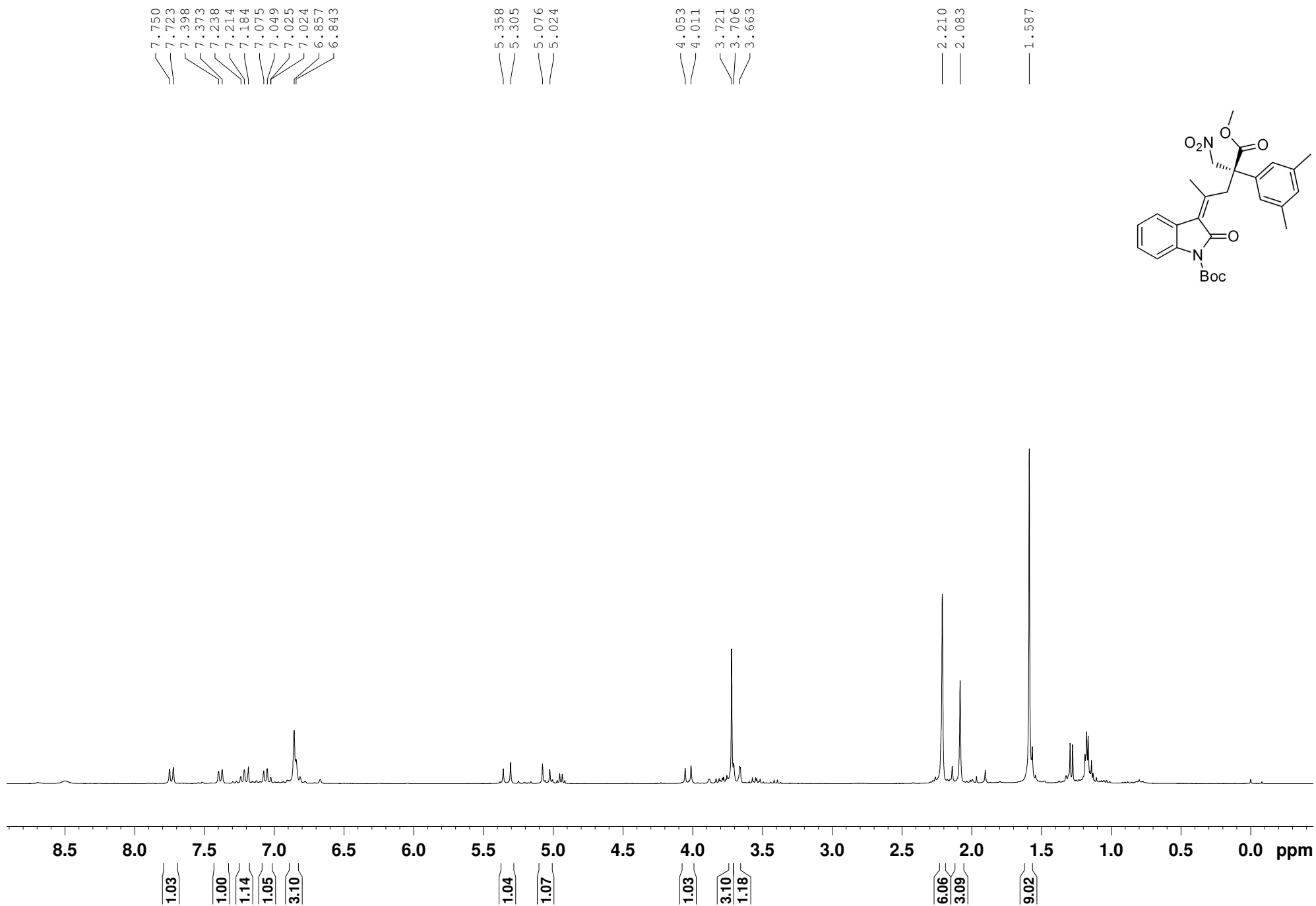
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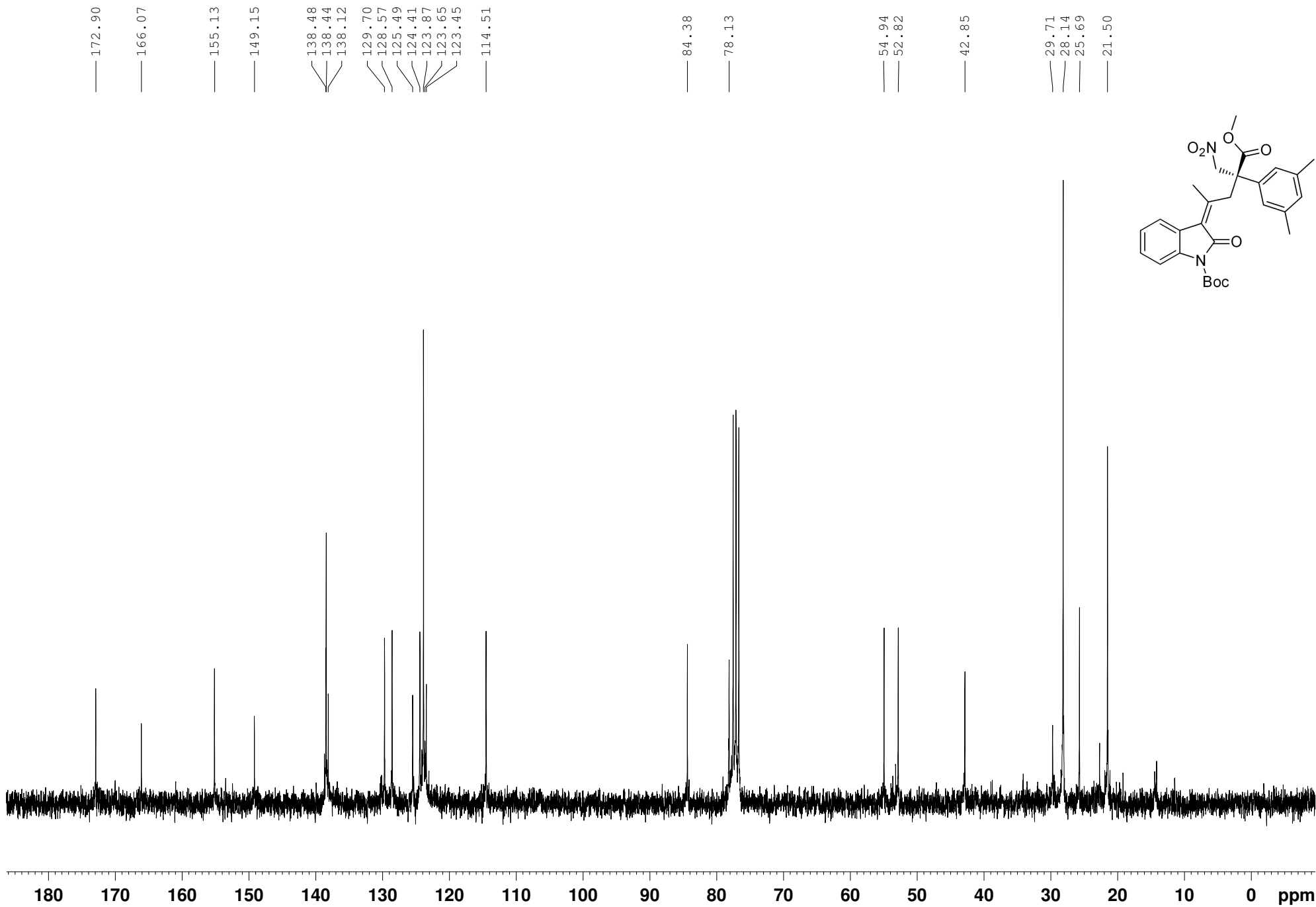
— 25.55











— 172.90

— 166.07

— 155.13

— 149.15

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— 138.44

— 138.12

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— 123.45

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— 54.94

— 52.82

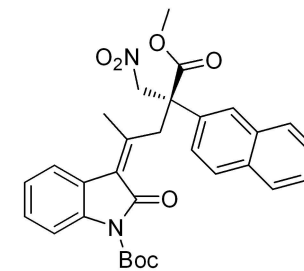
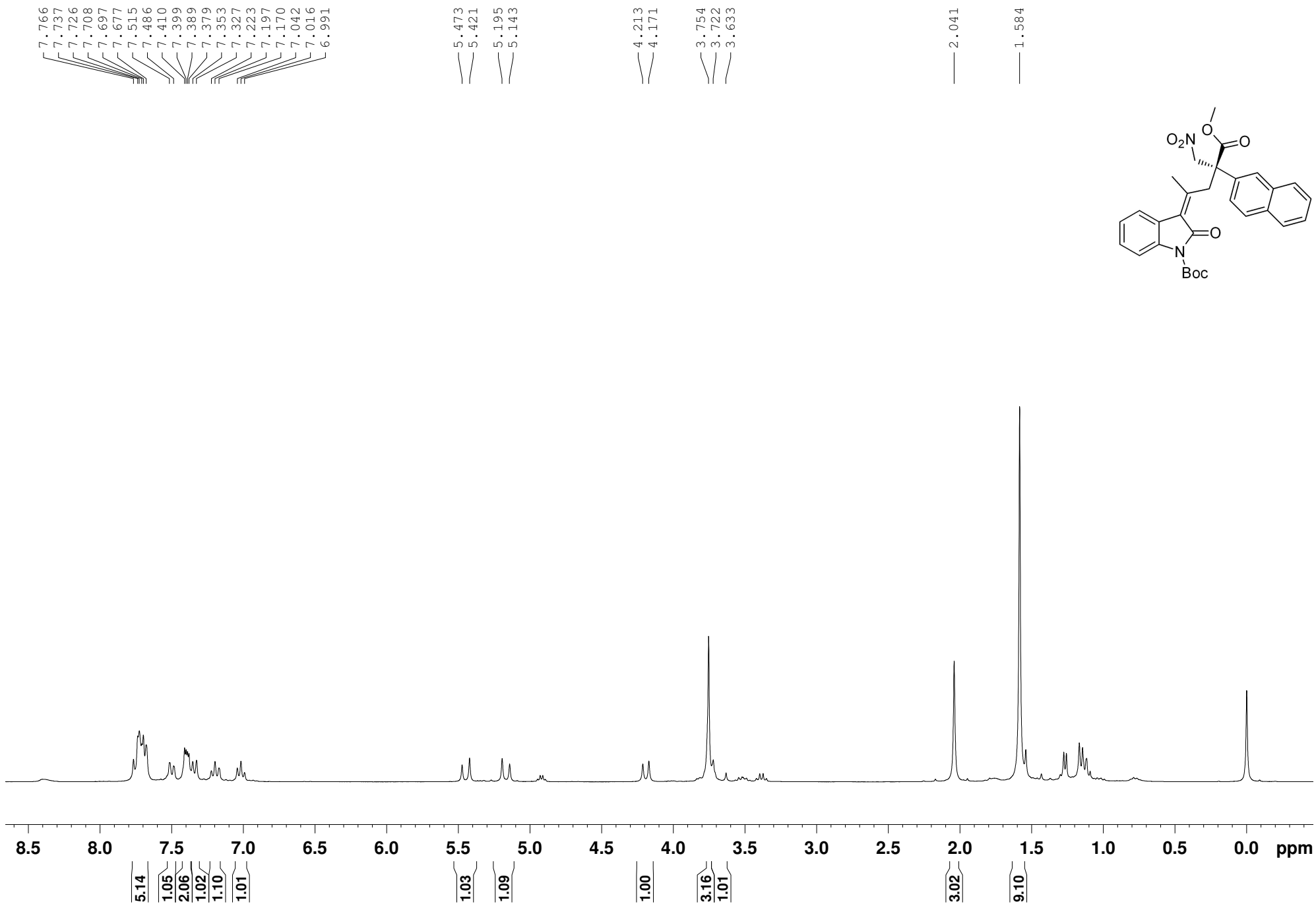
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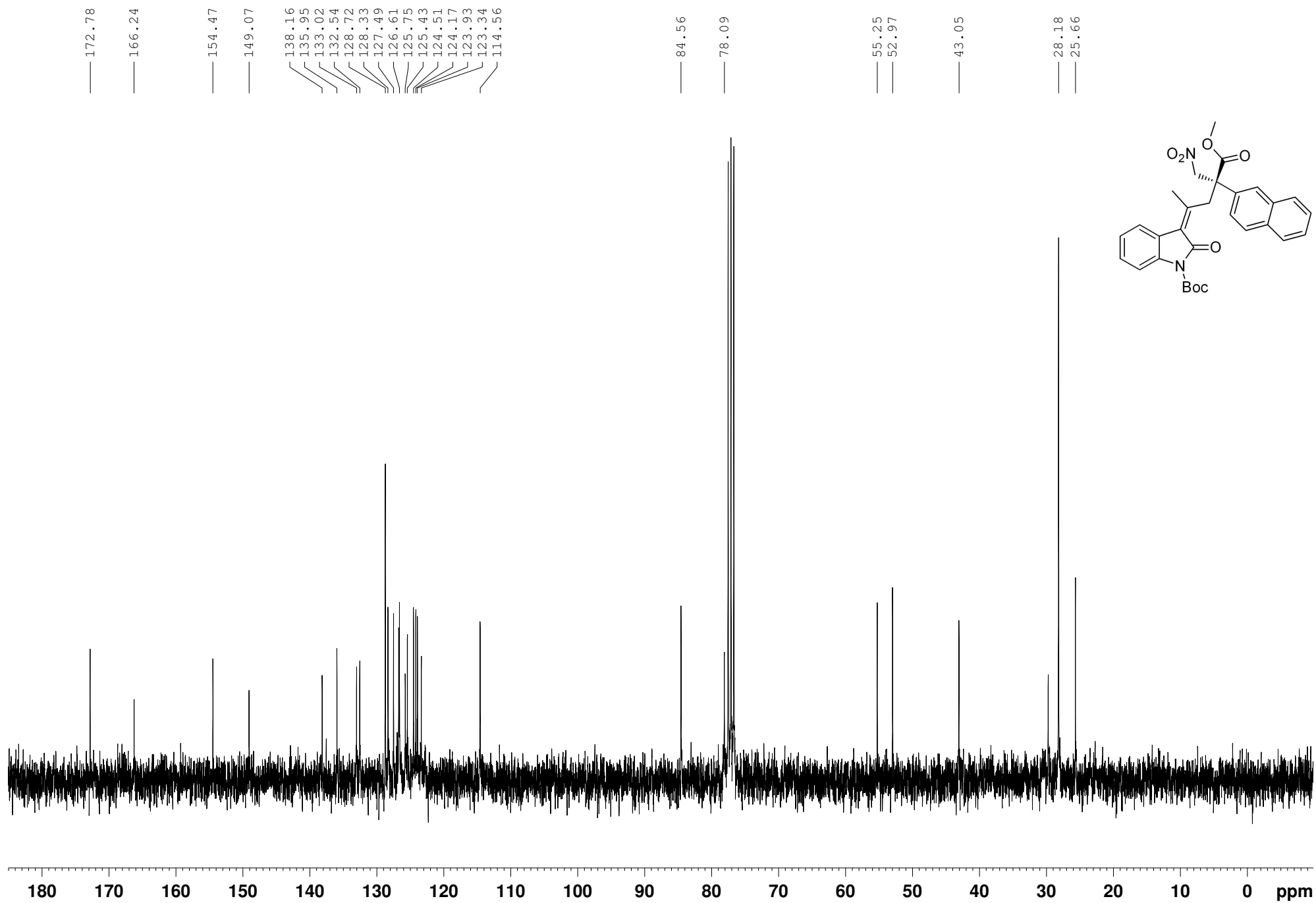
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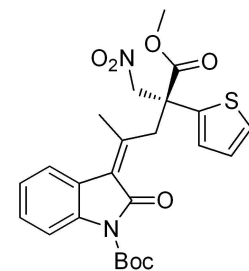
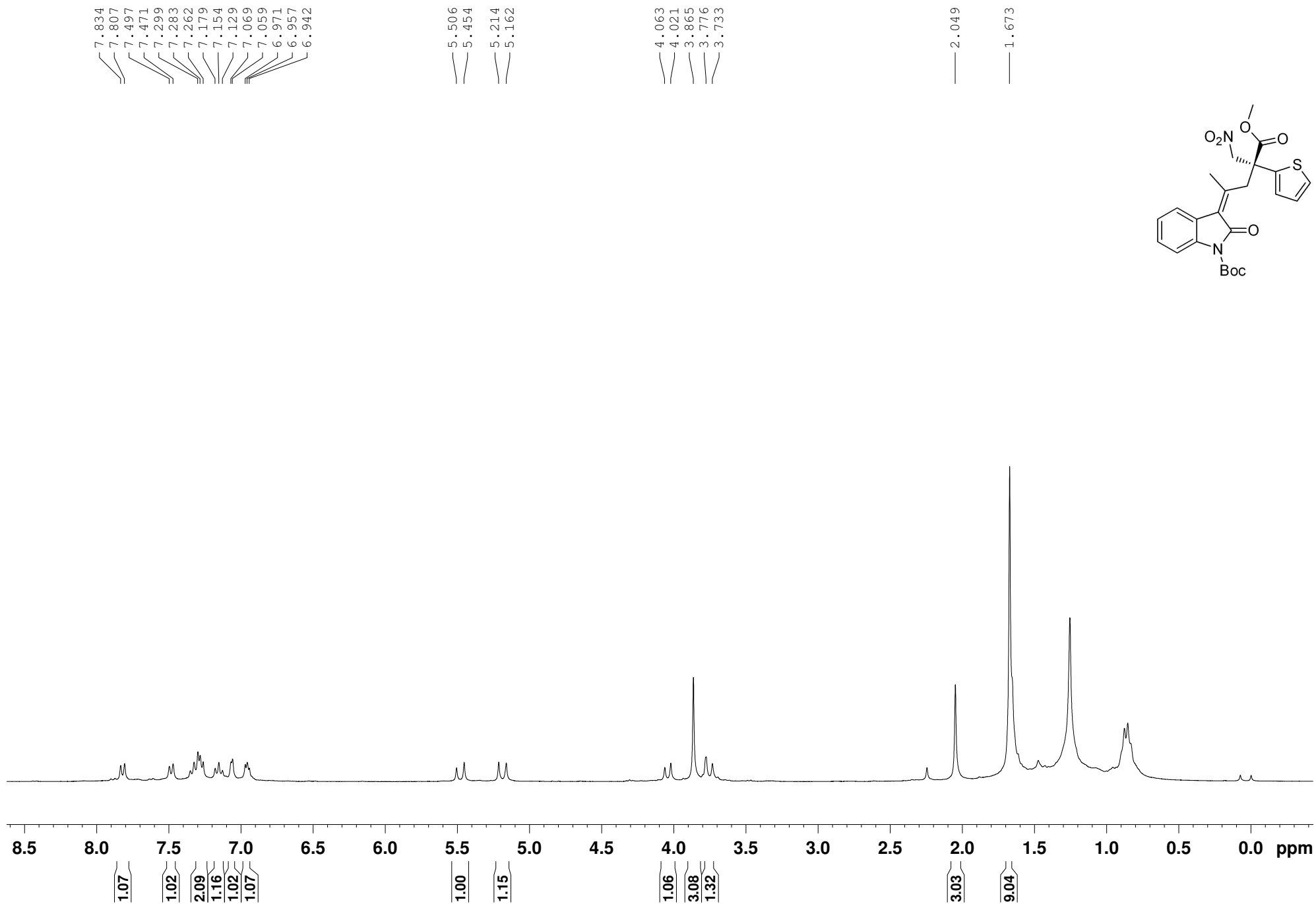
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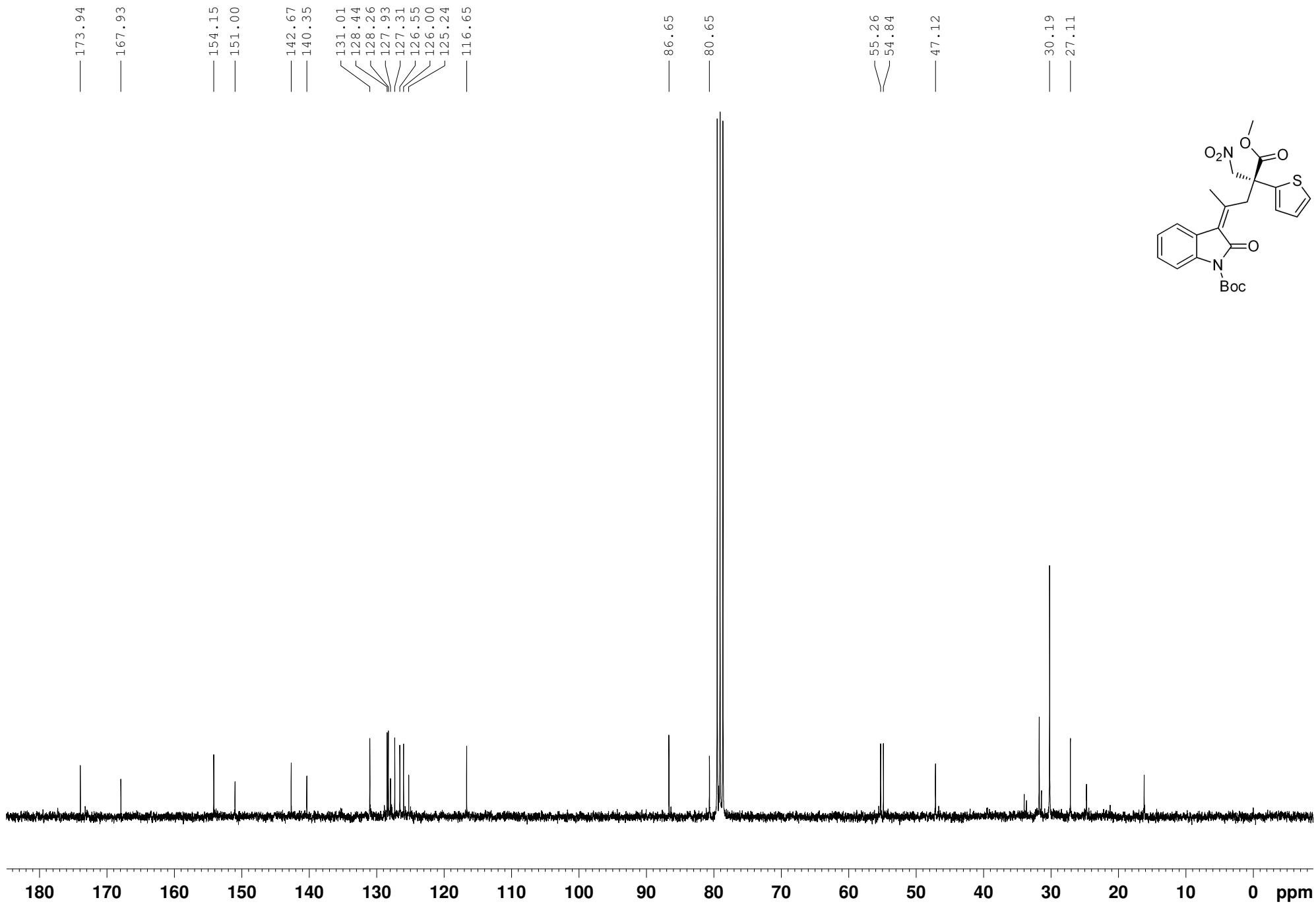
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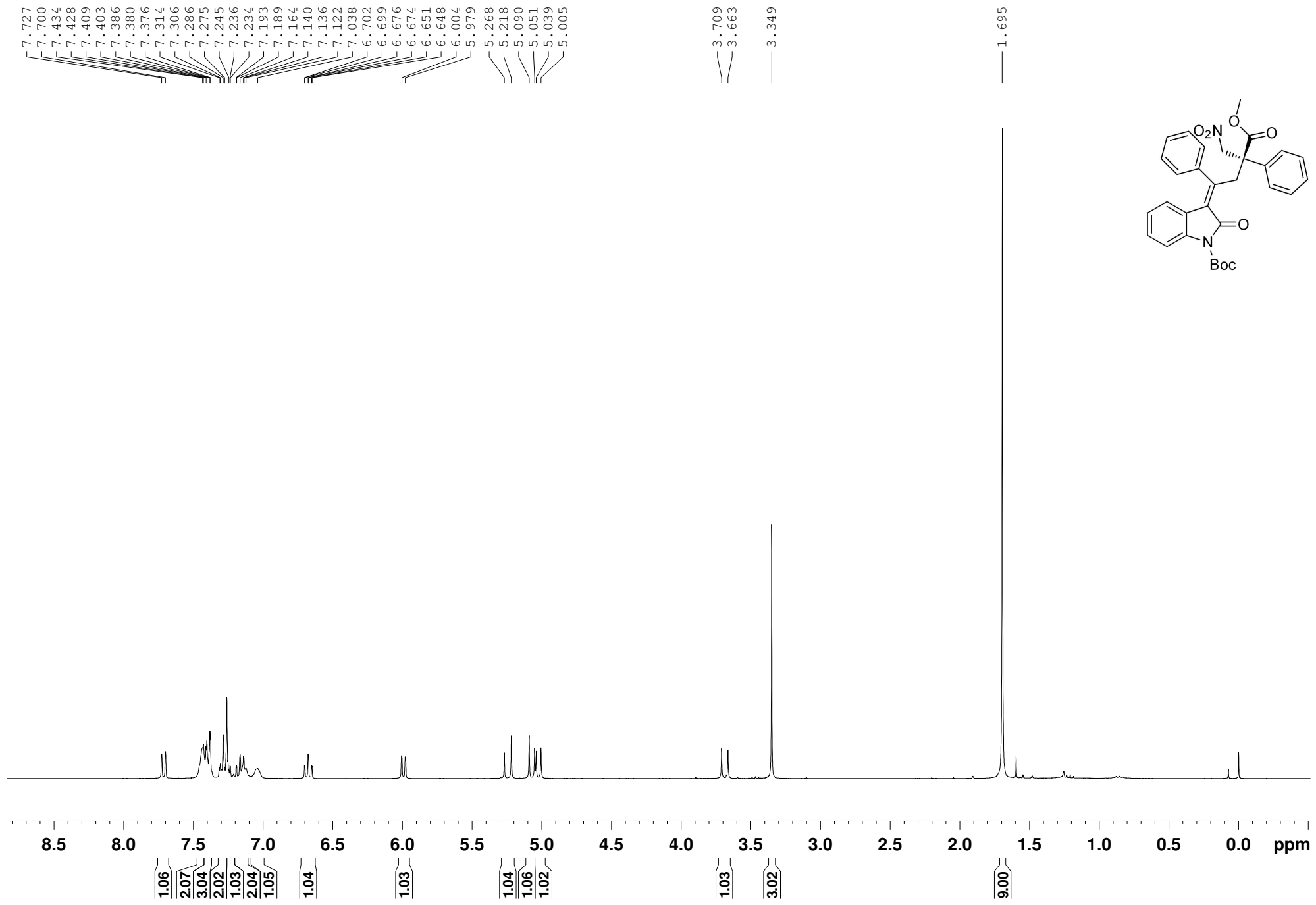
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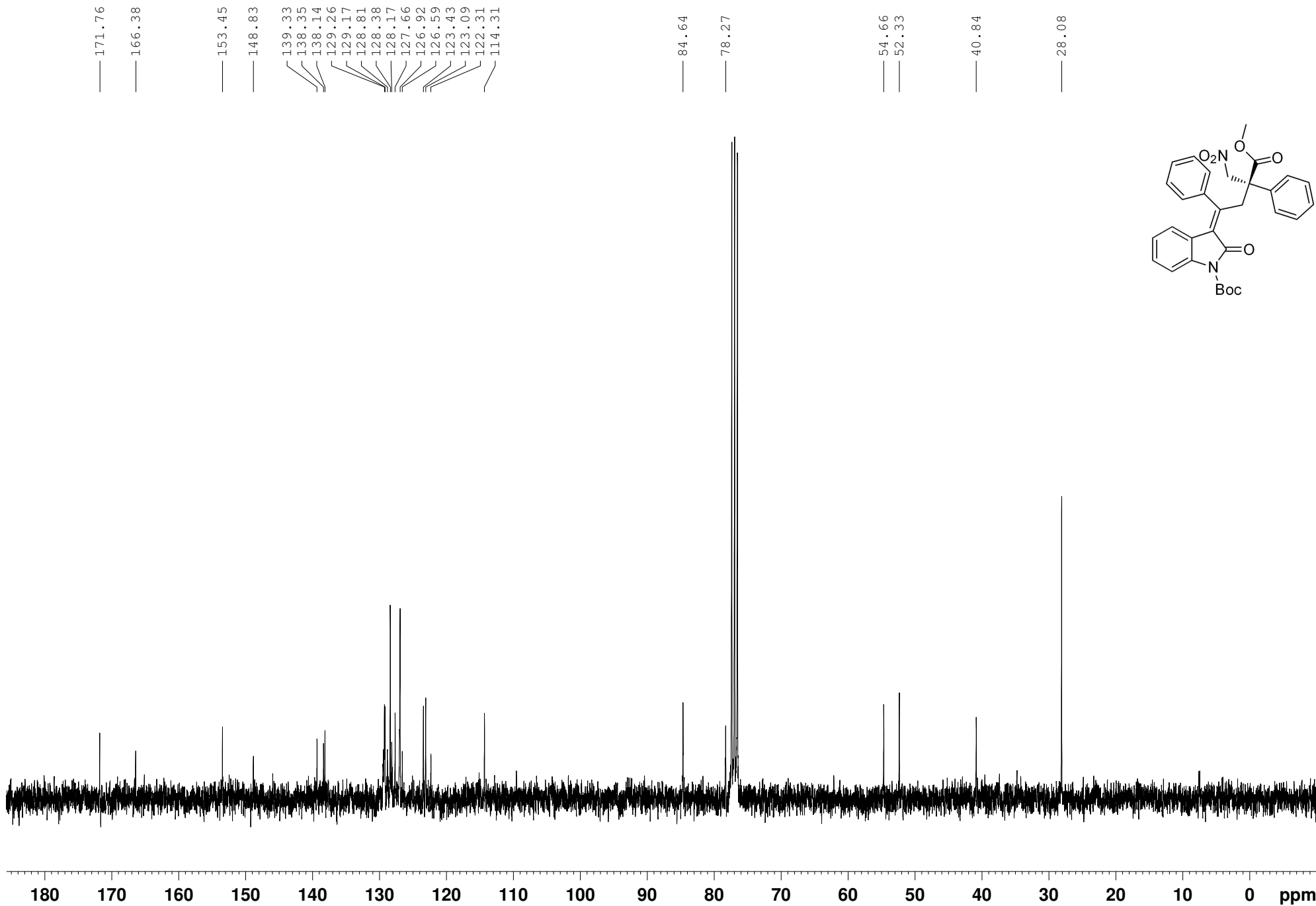




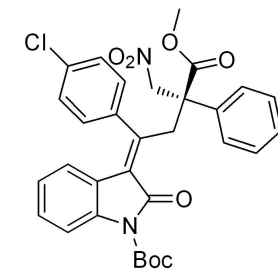
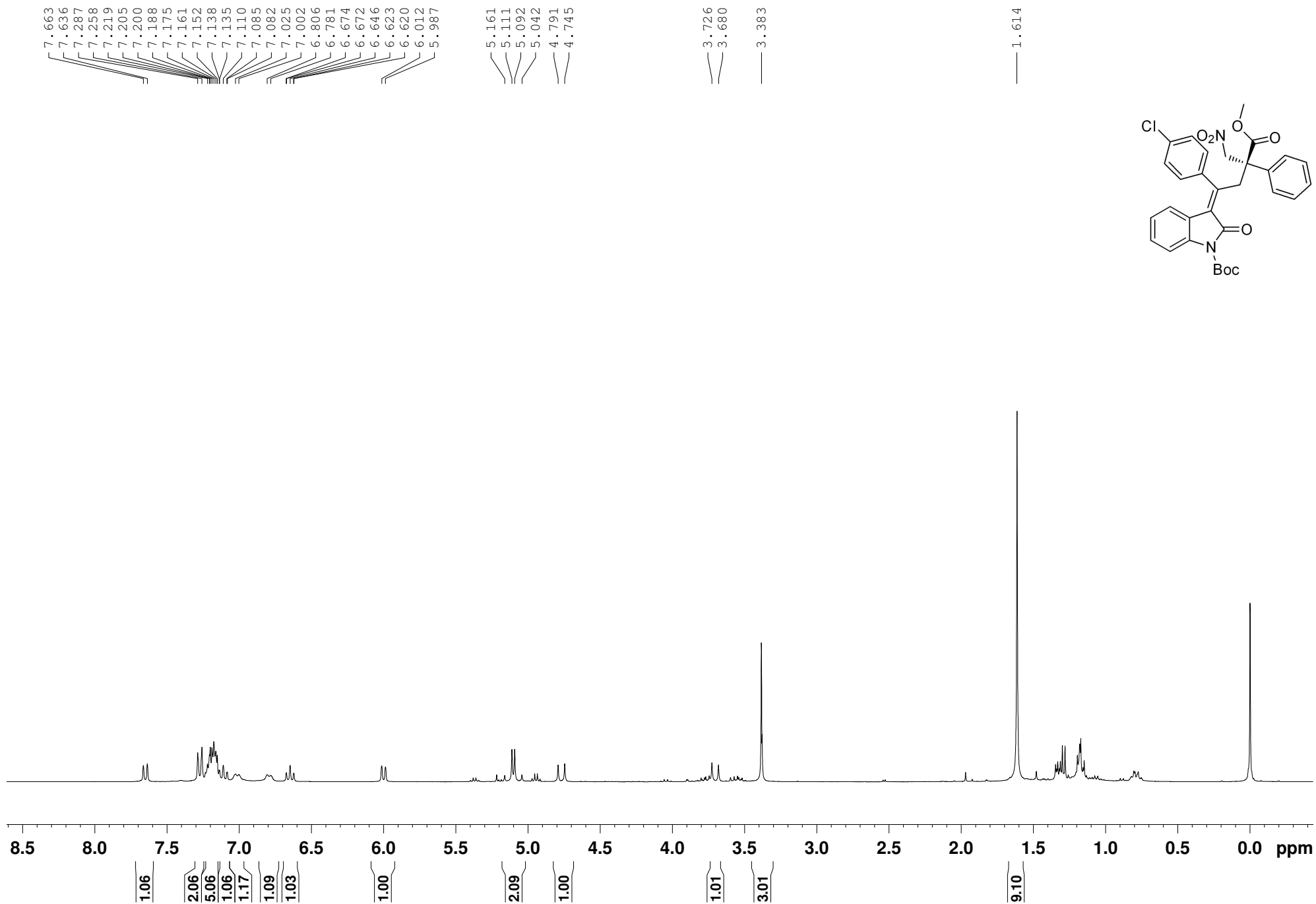


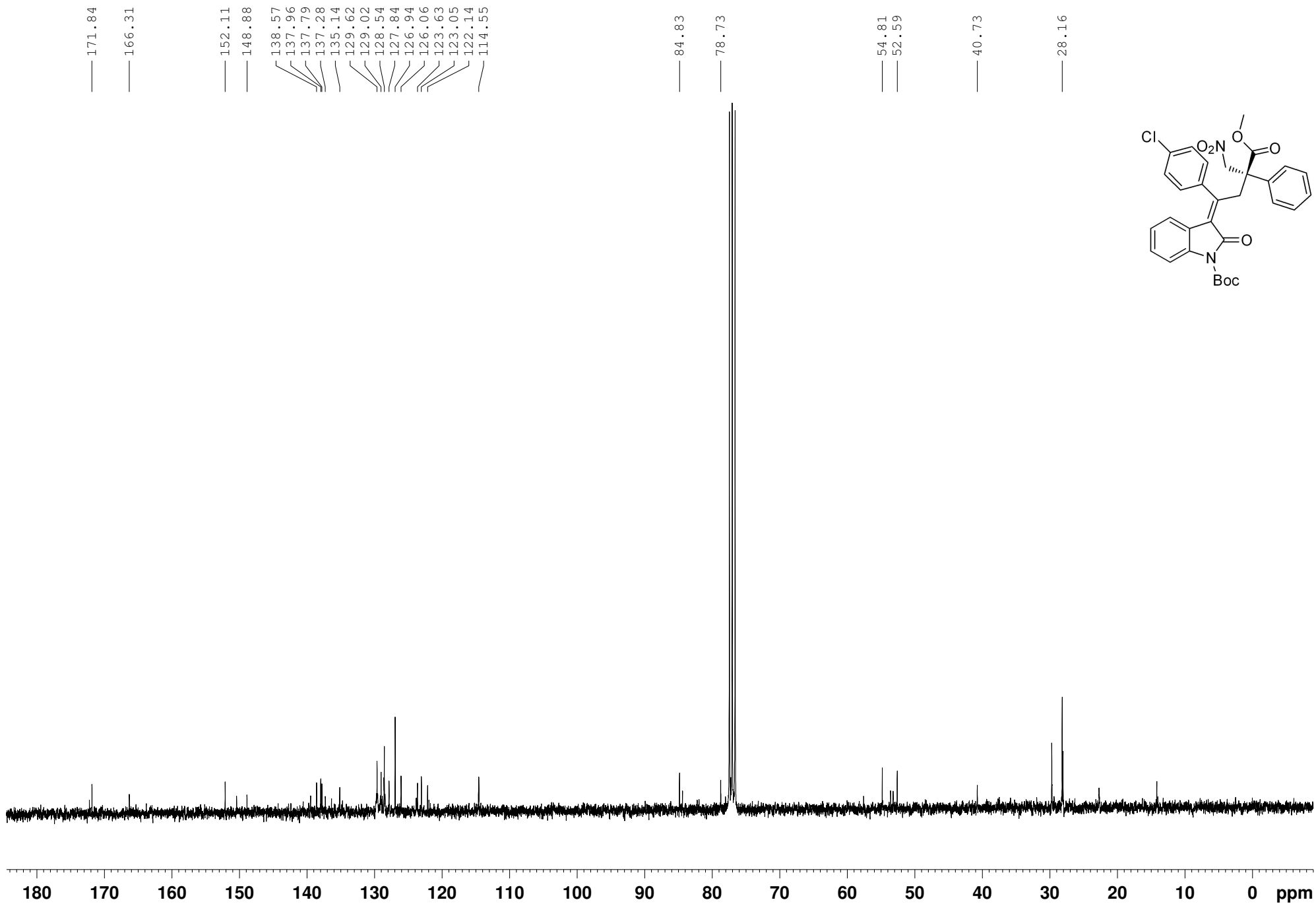


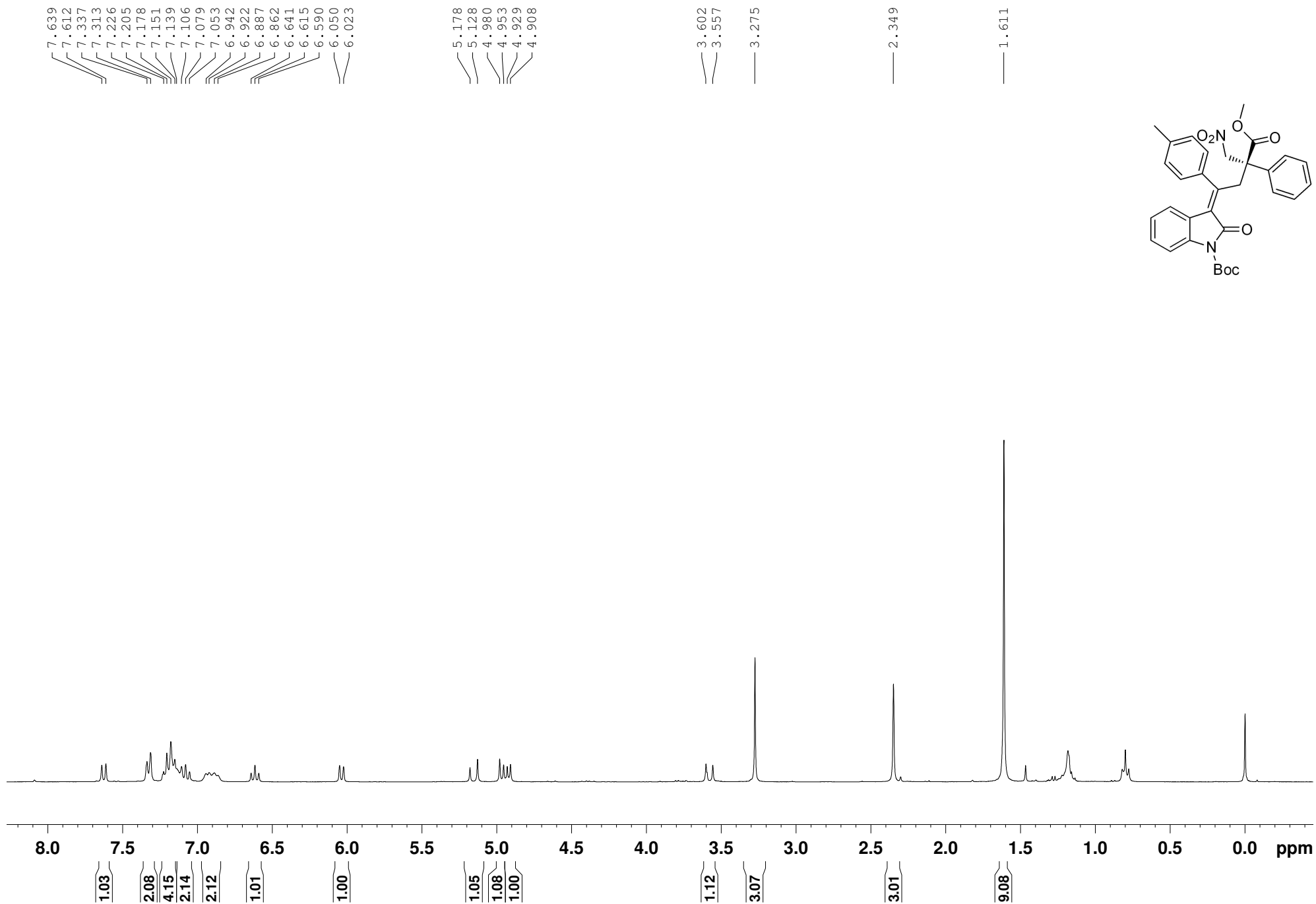


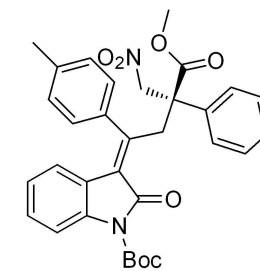
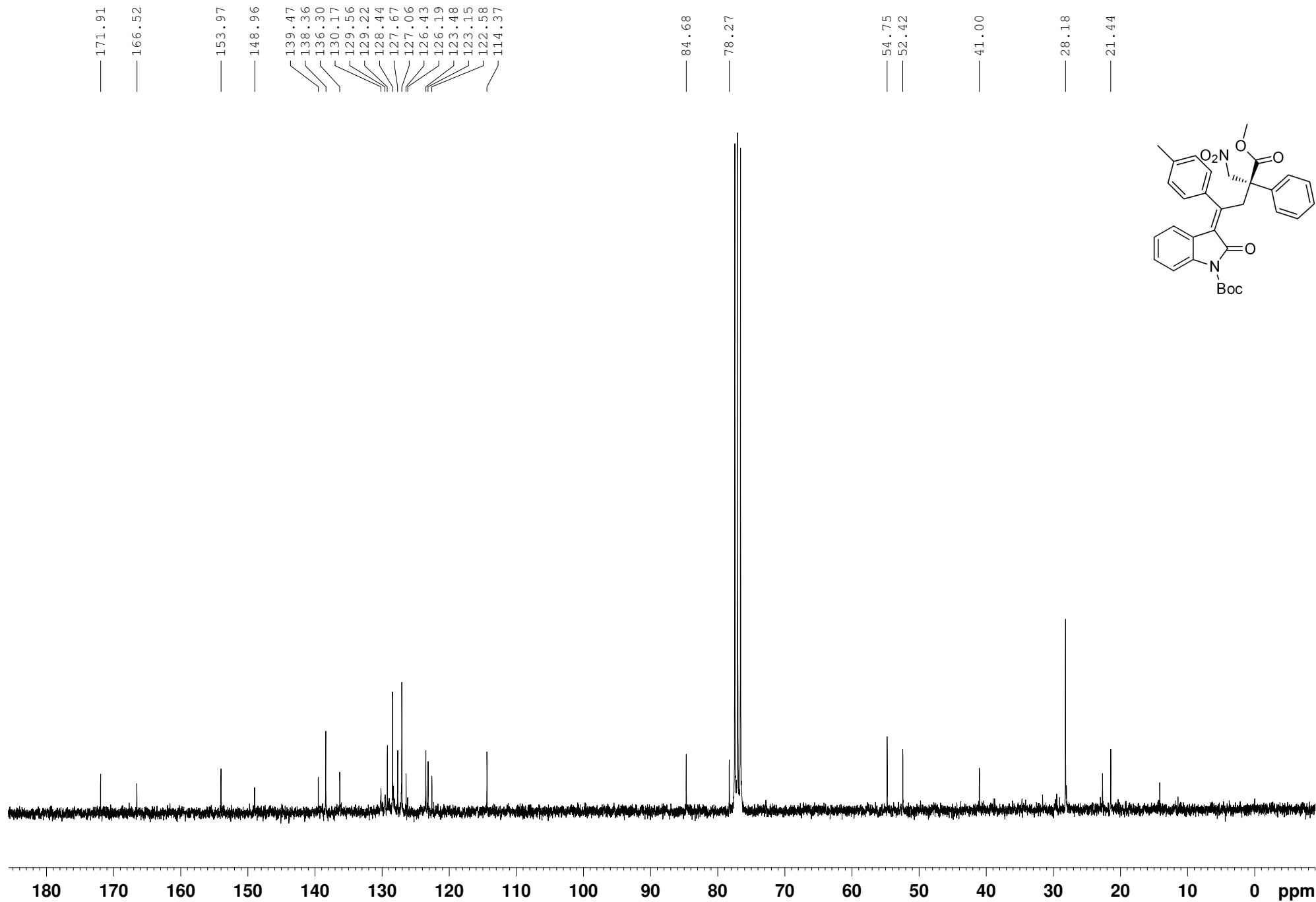


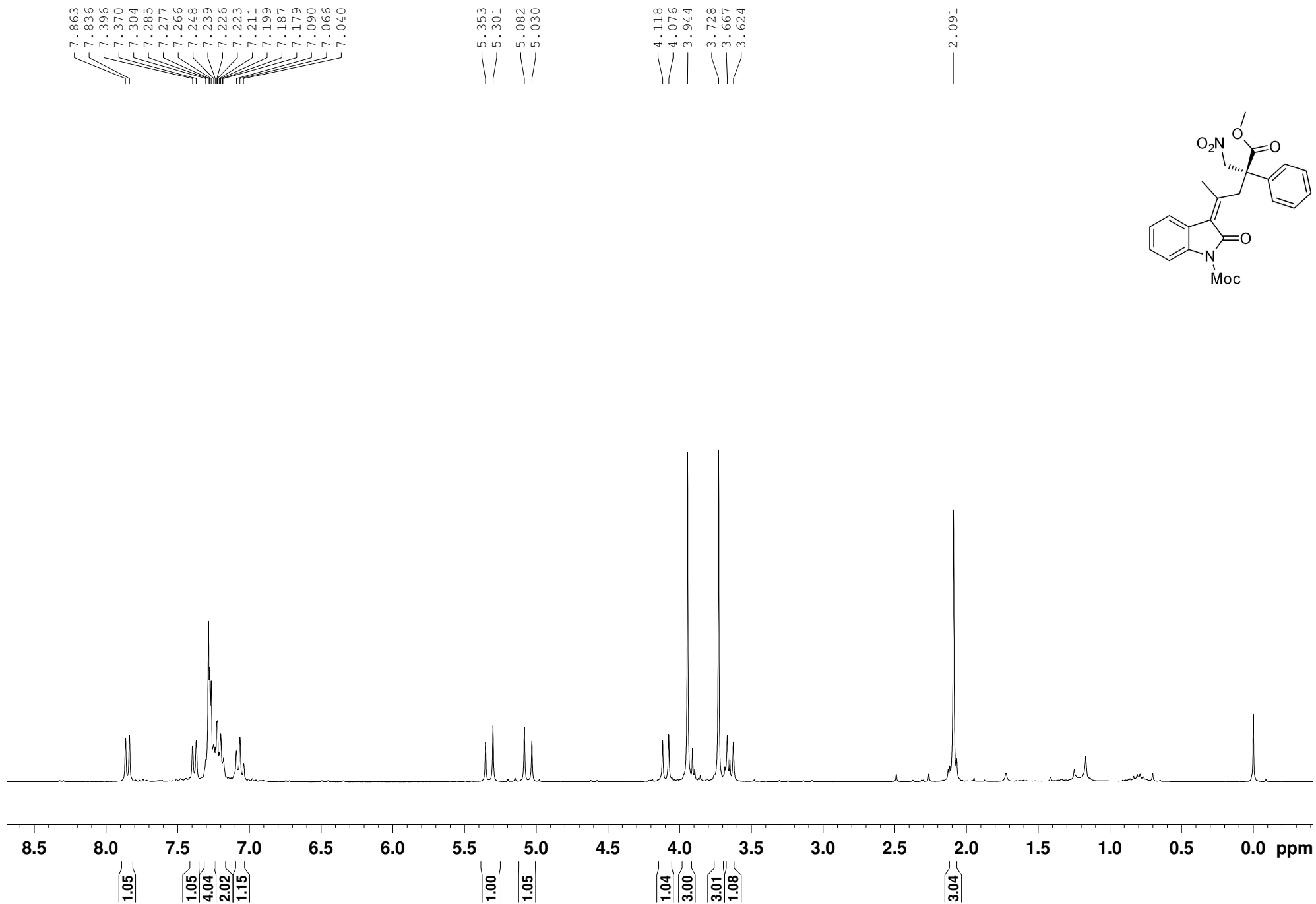


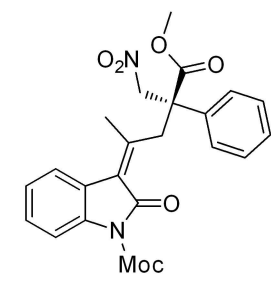
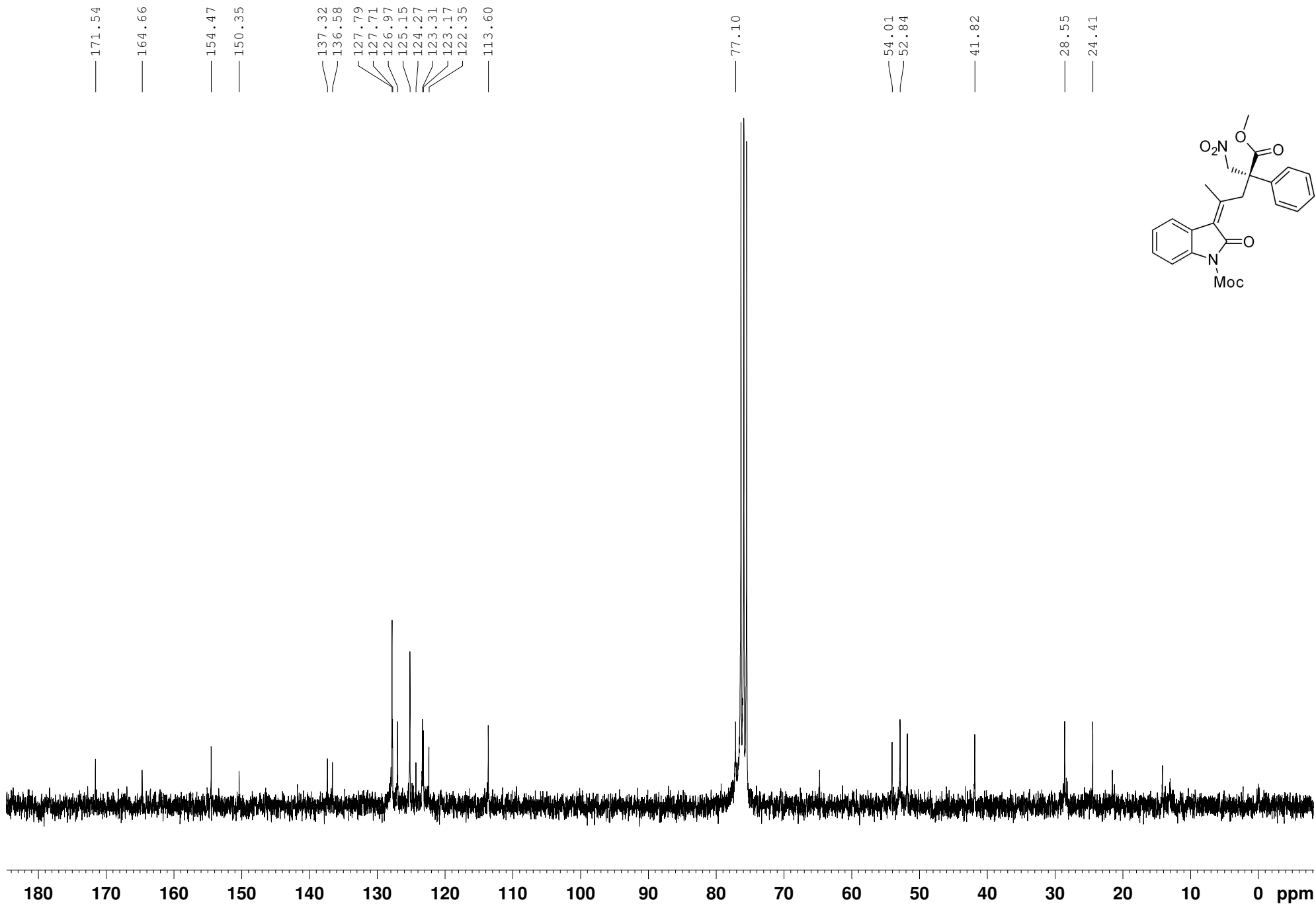




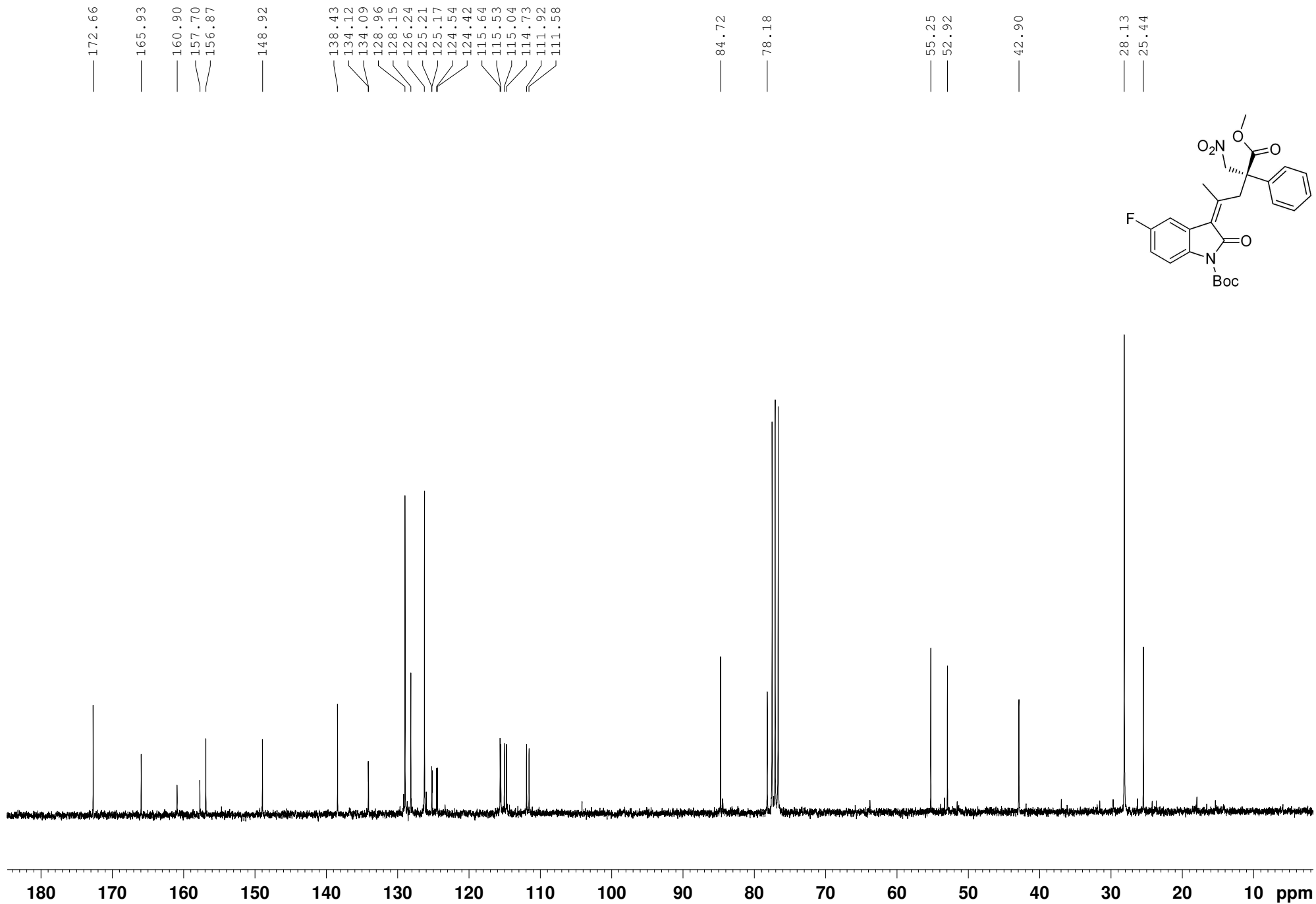




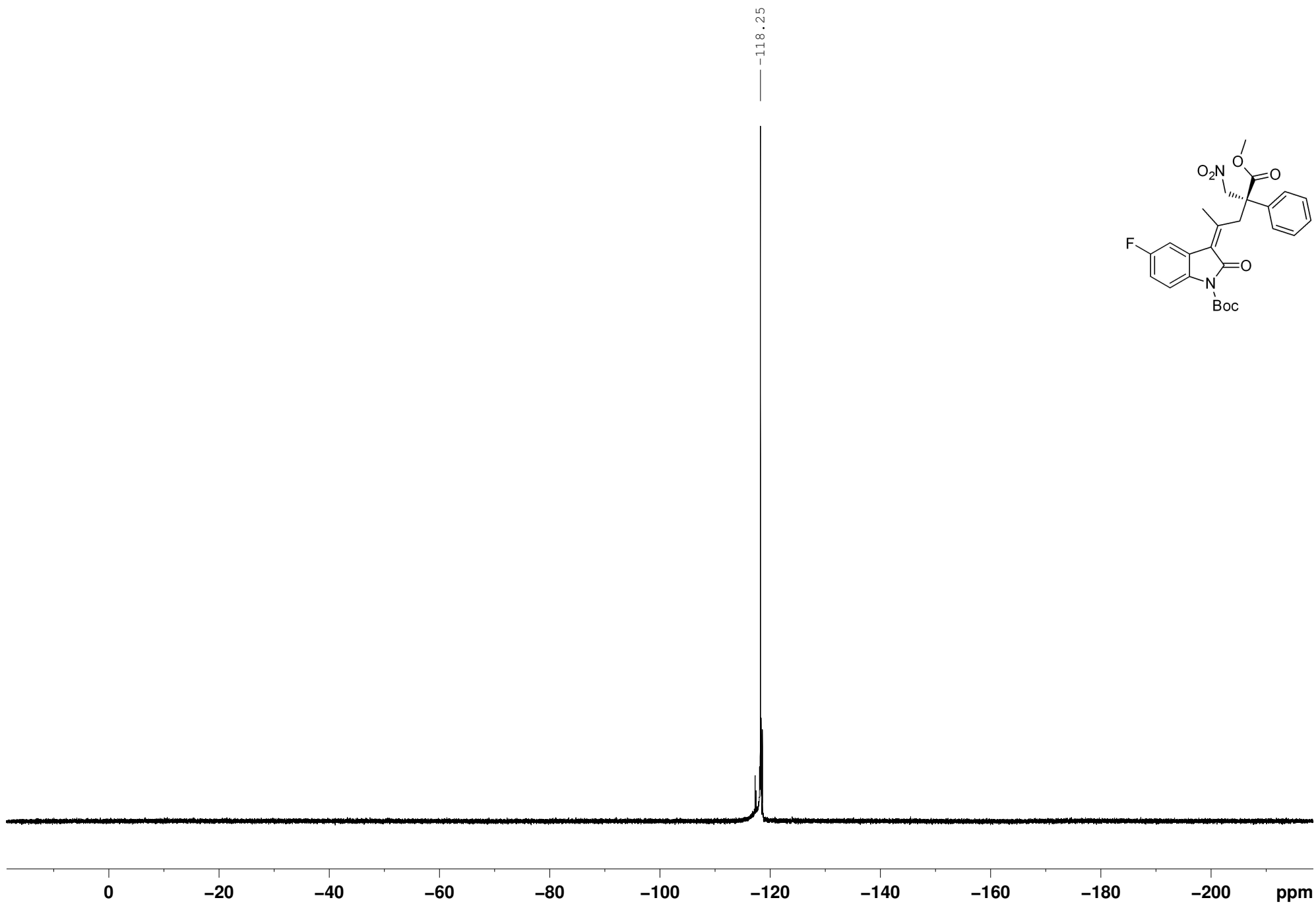












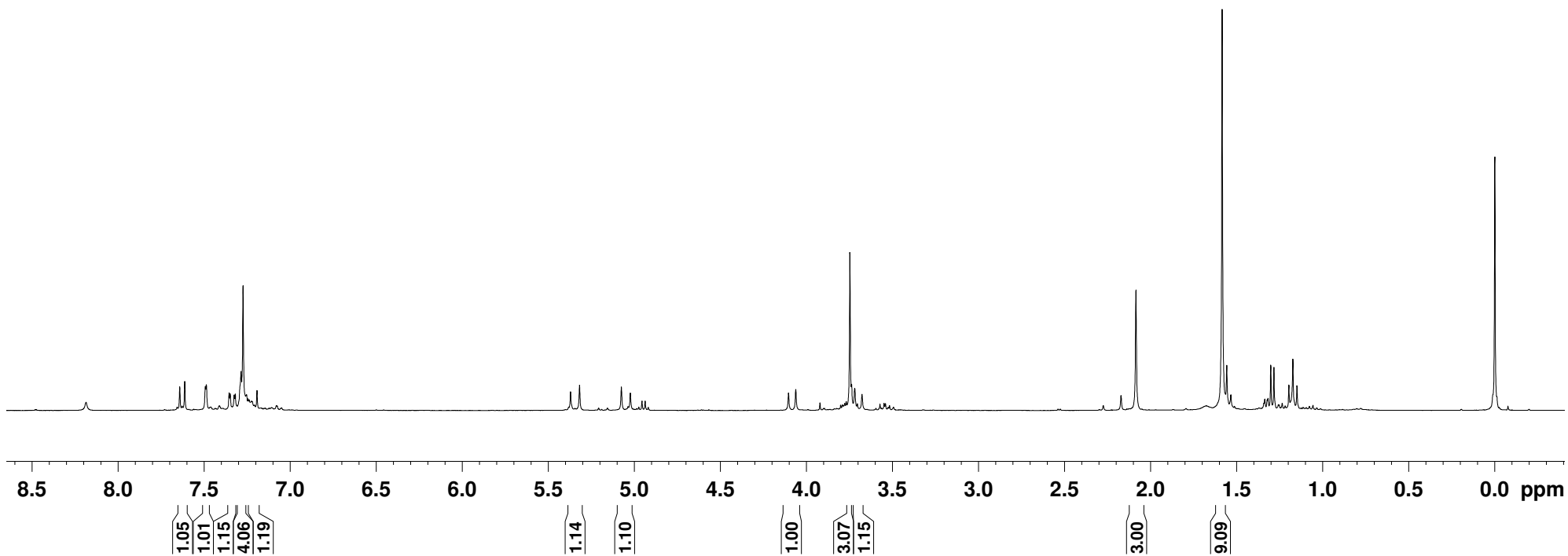
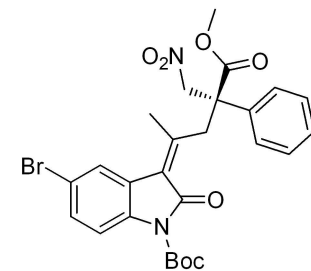
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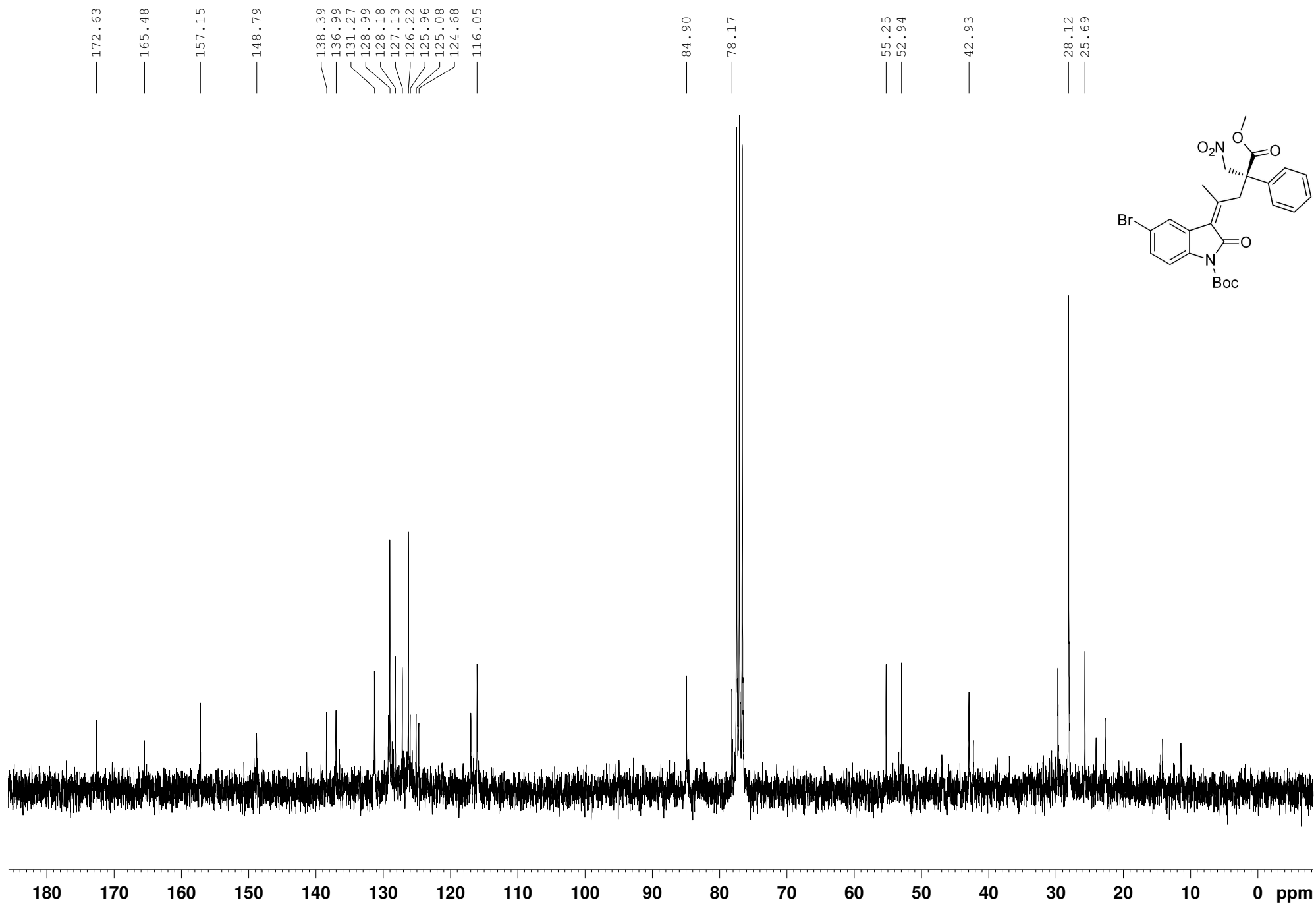
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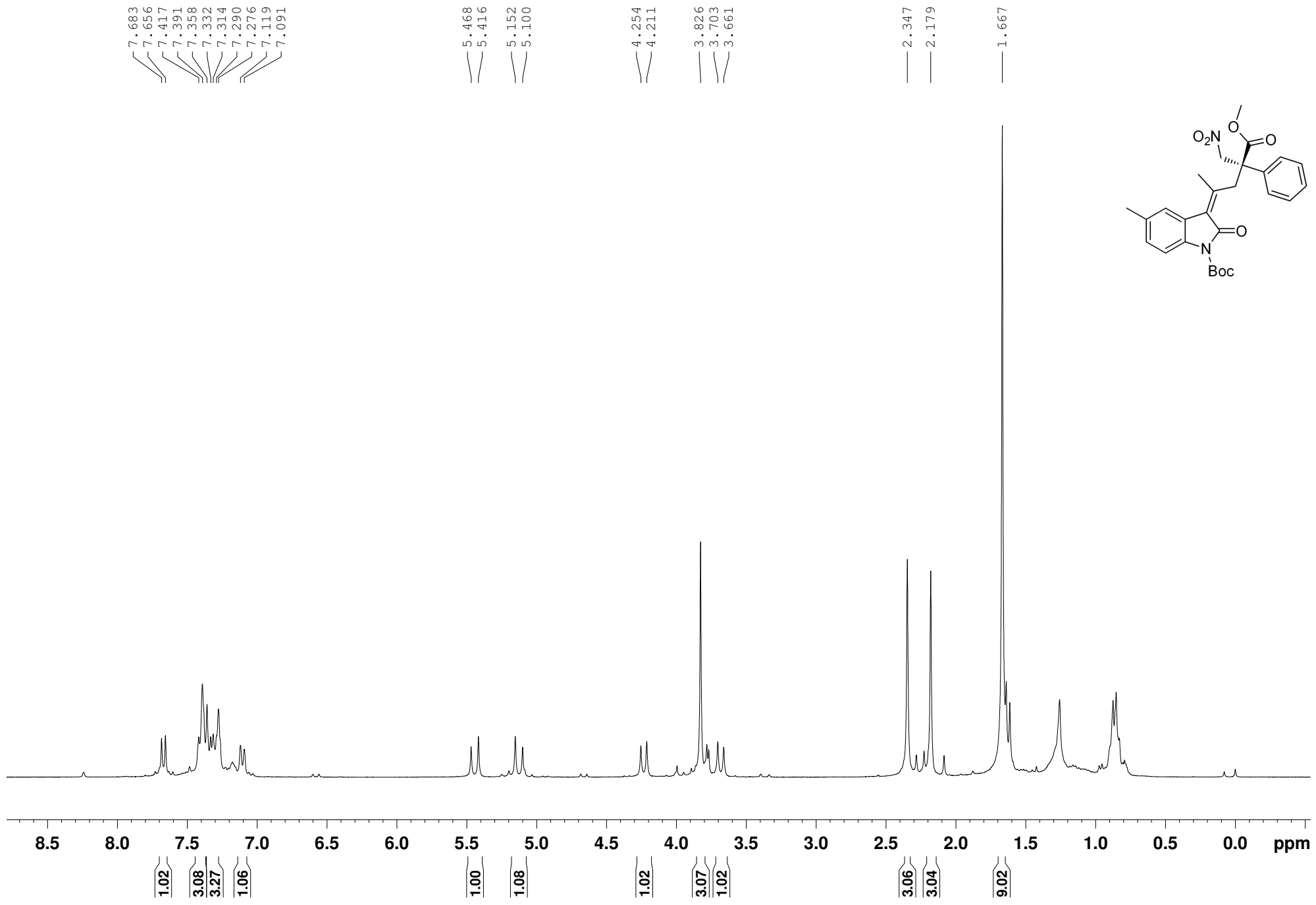
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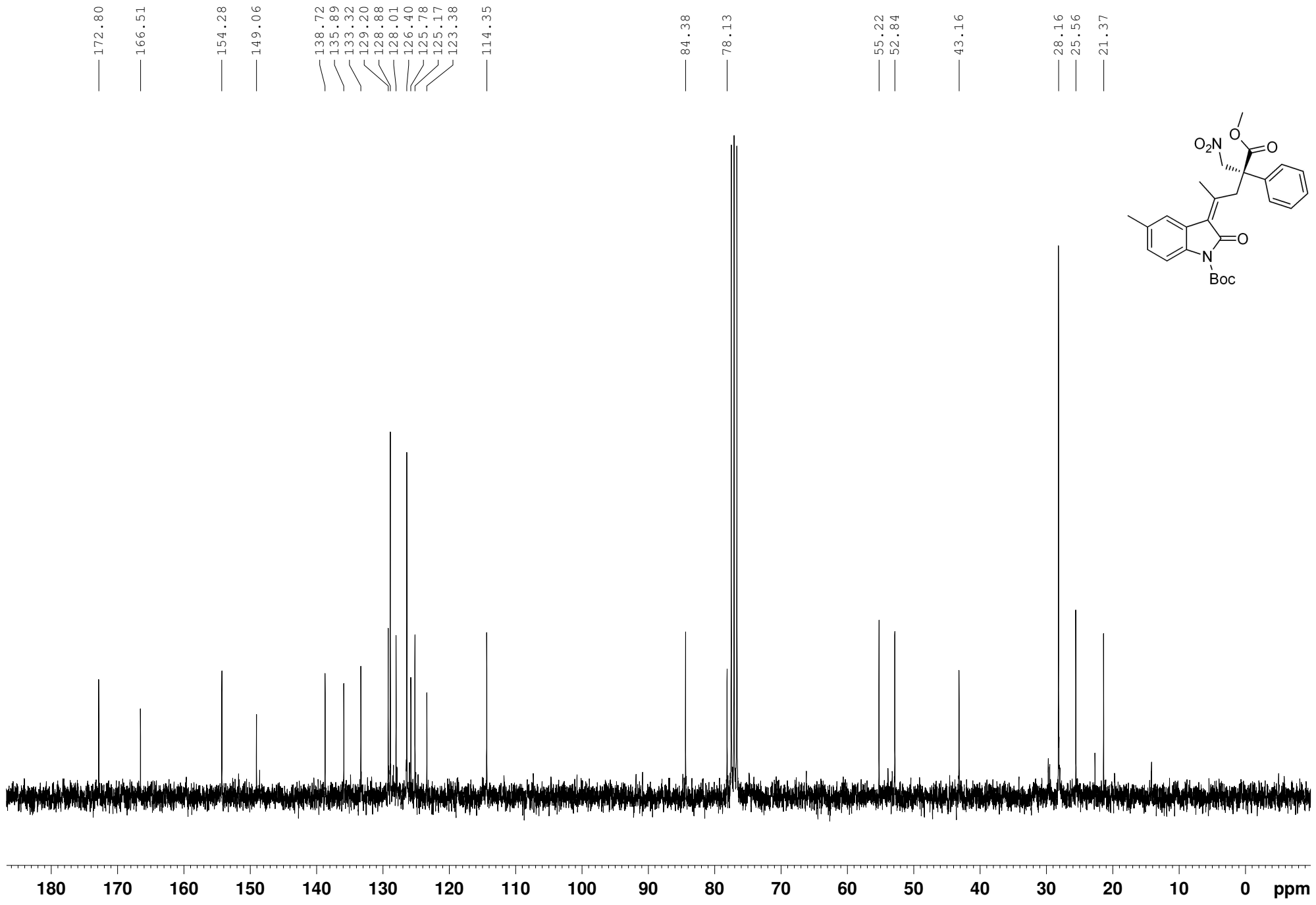
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1.585









— 172.80

— 166.51

— 154.28

— 149.06

— 138.72

— 135.89

— 133.32

— 129.20

— 128.88

— 128.01

— 126.40

— 125.78

— 125.17

— 123.38

— 114.35

— 84.38

— 78.13

— 55.22

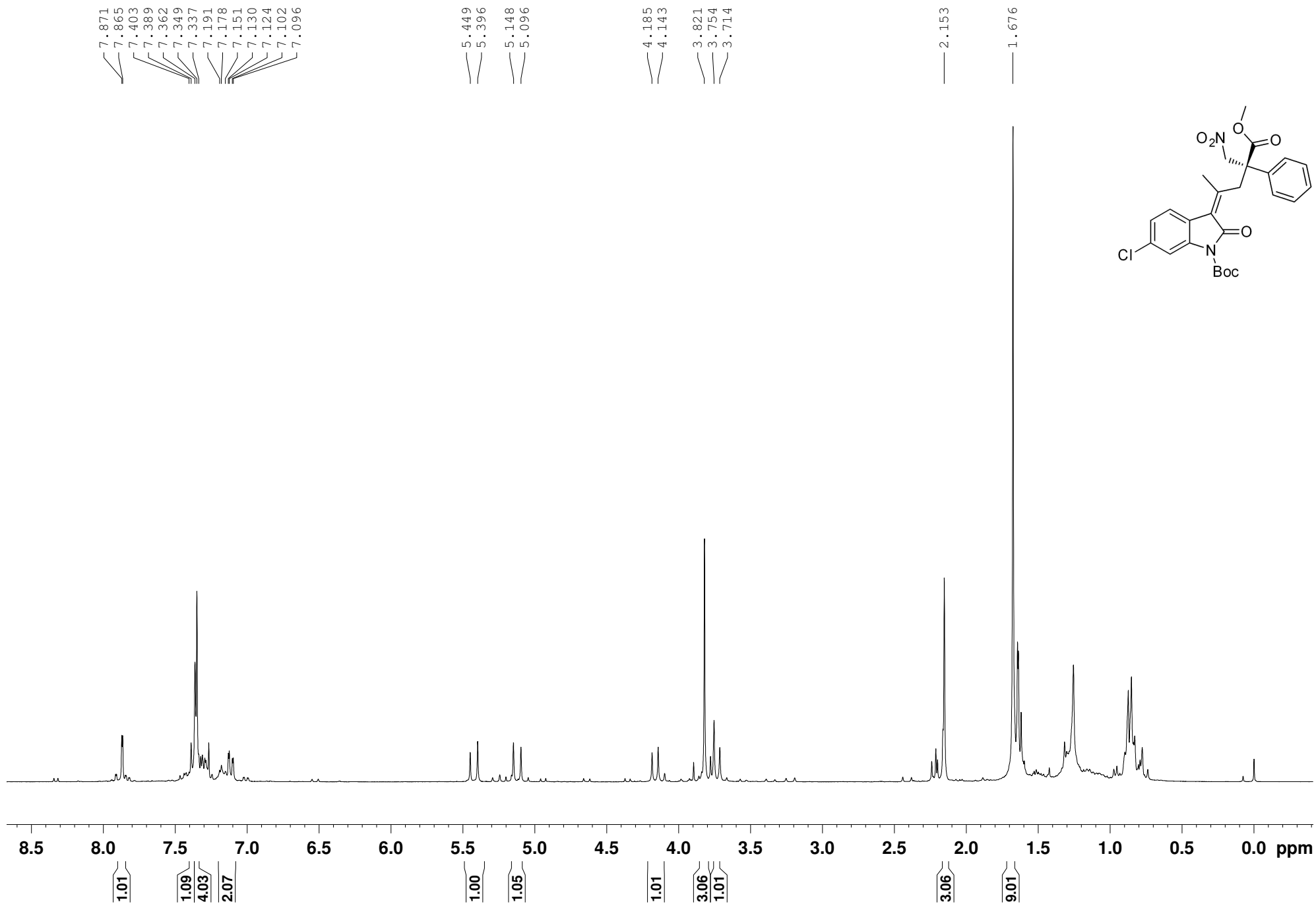
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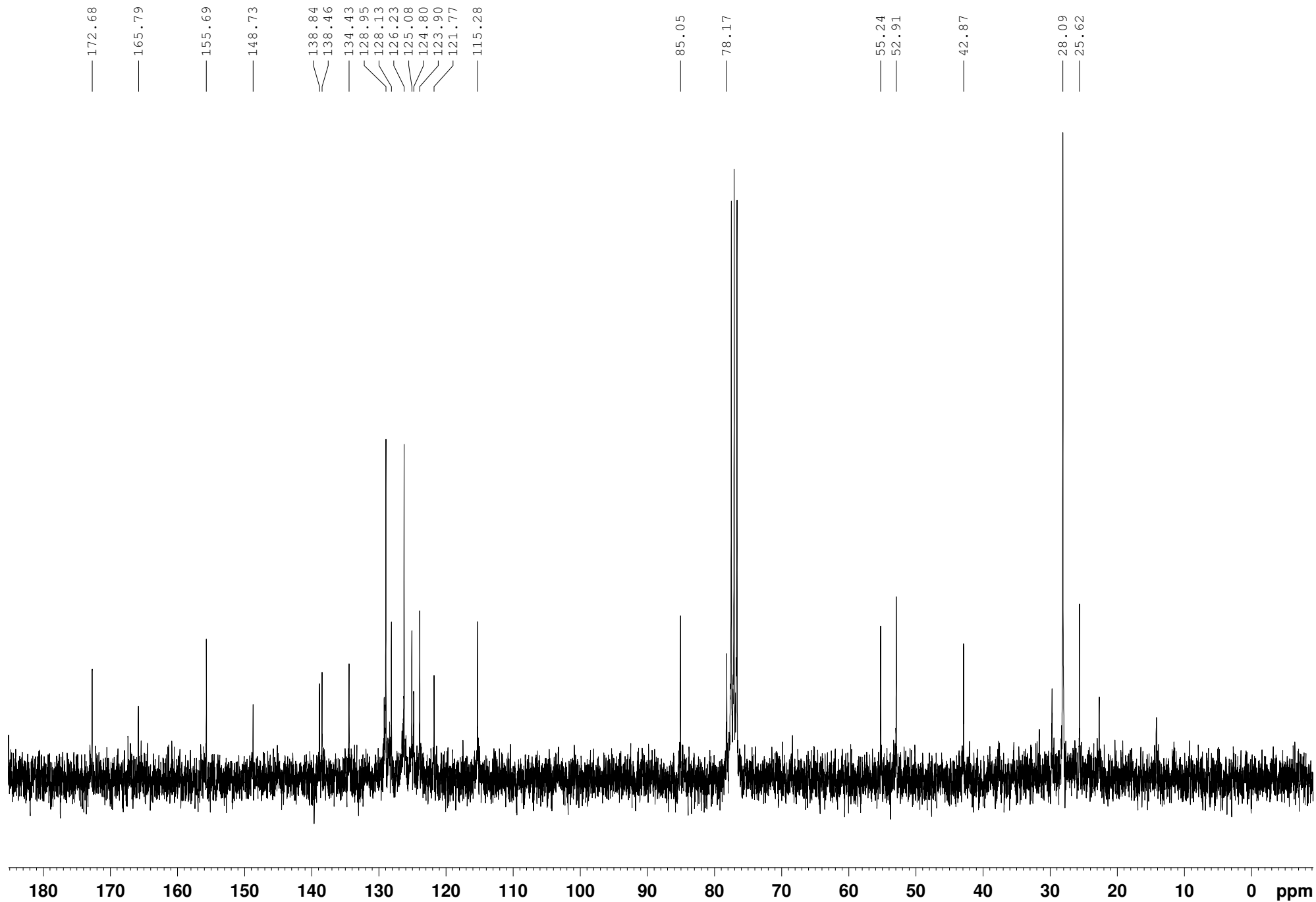
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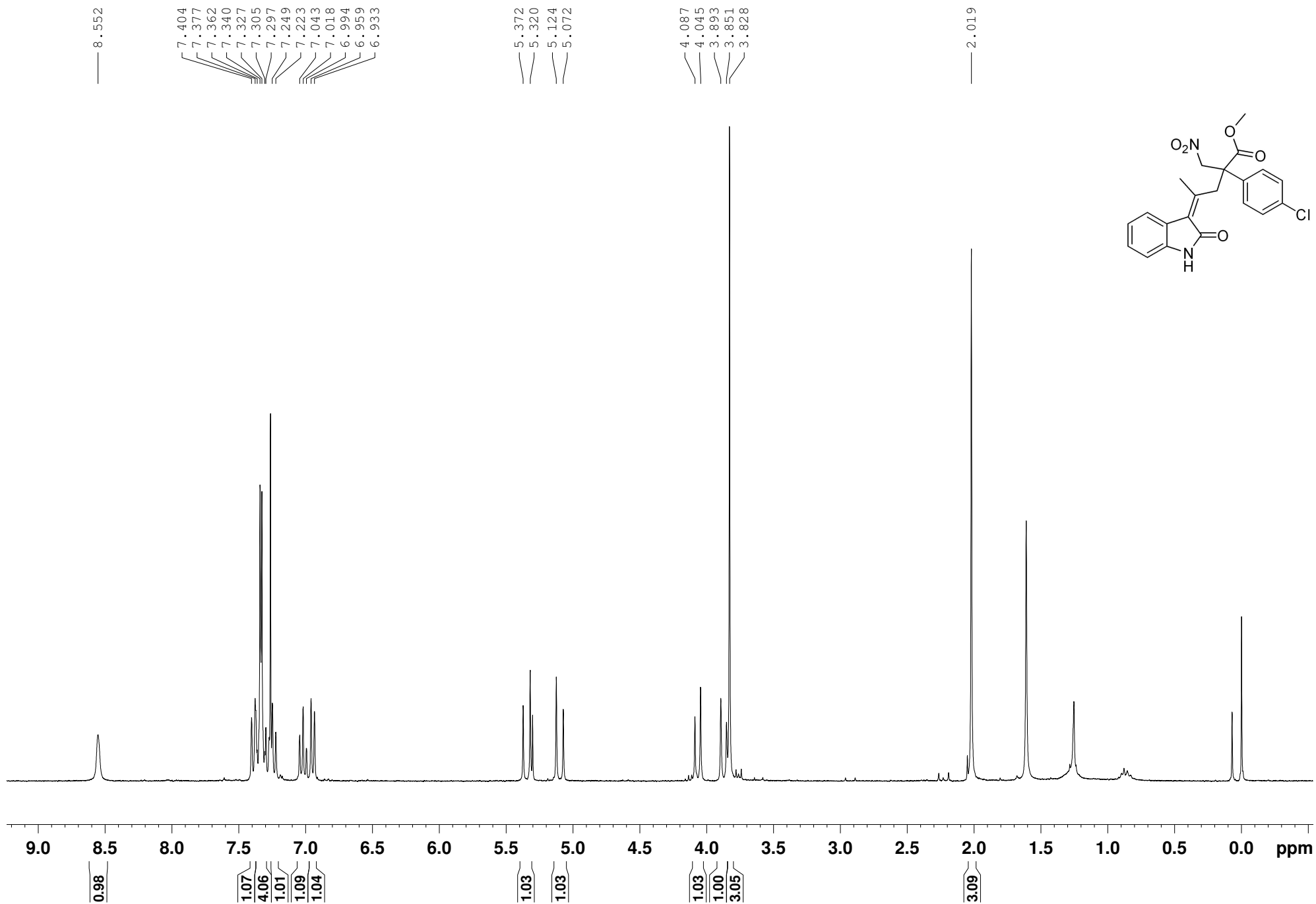
— 28.16

— 25.56

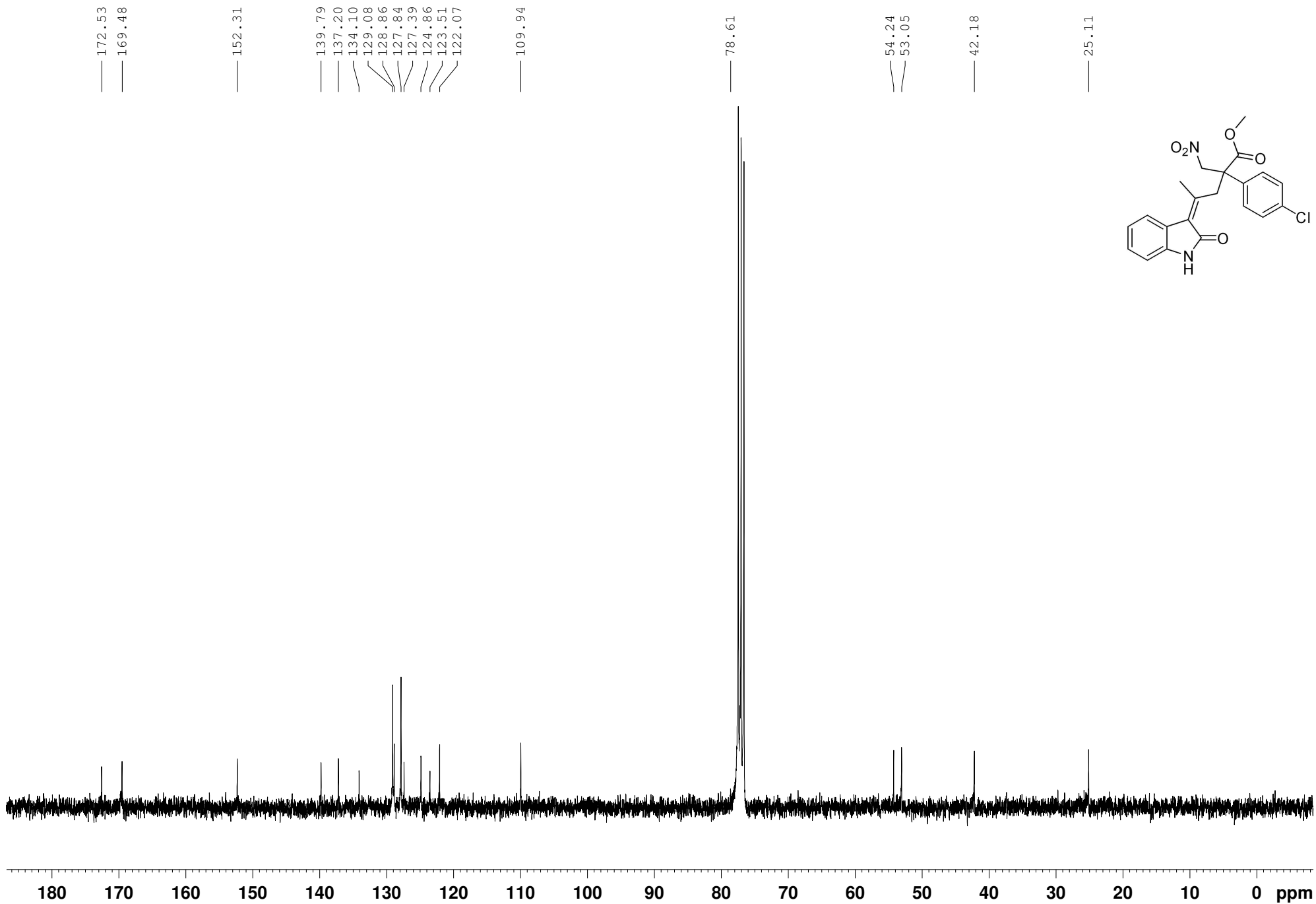
— 21.37



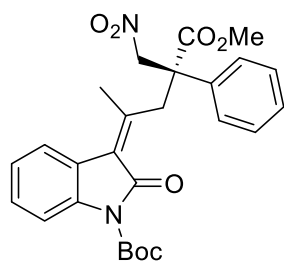




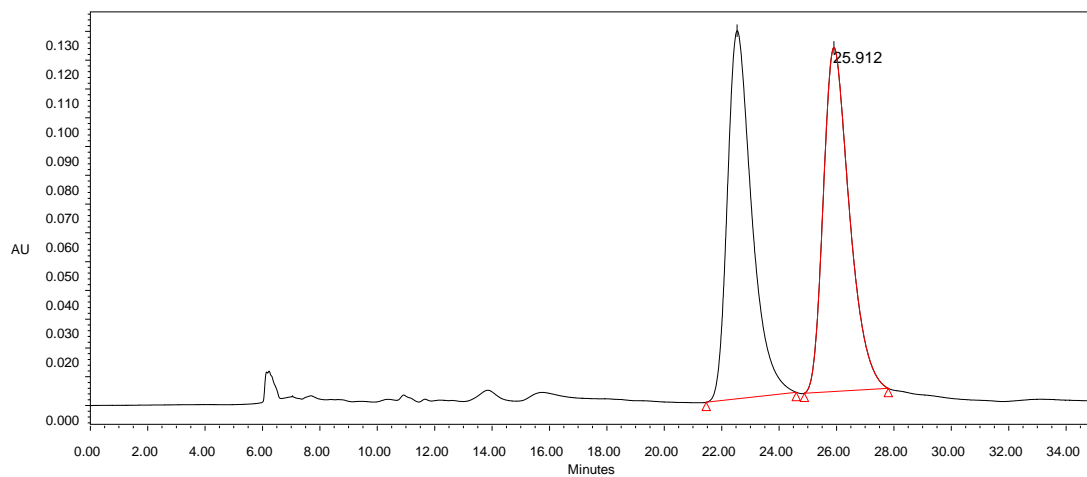




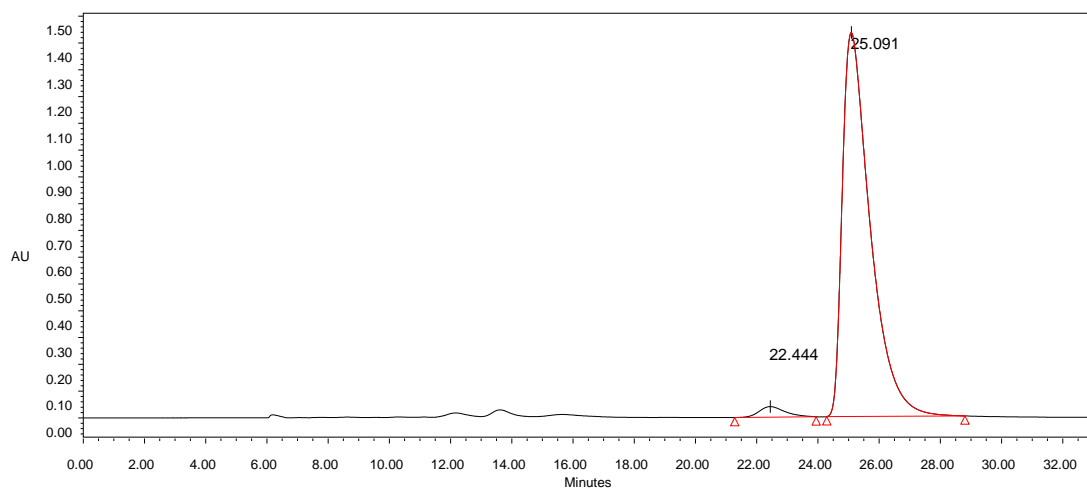
## 9. HPLC Chromatogram of Compounds 4



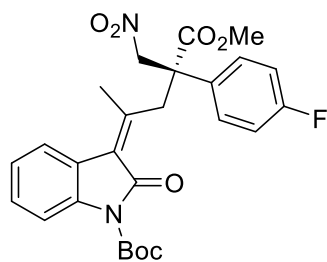
4a



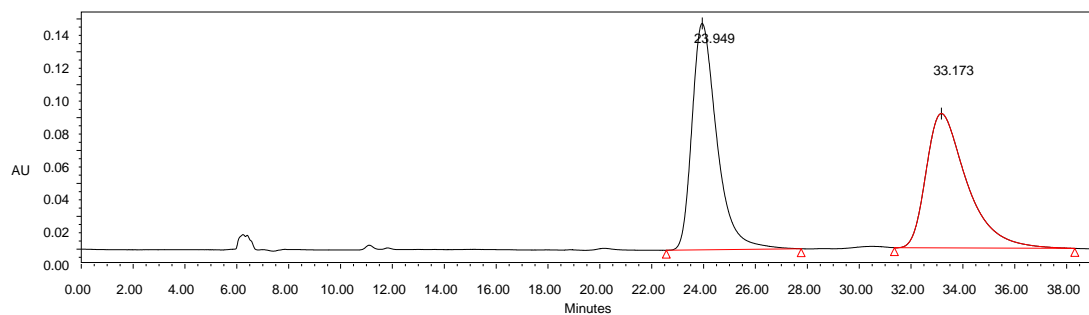
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	22.538	7548024	49.93	127947	bb	Unknown
2	25.912	7569823	50.07	119586	bb	Unknown



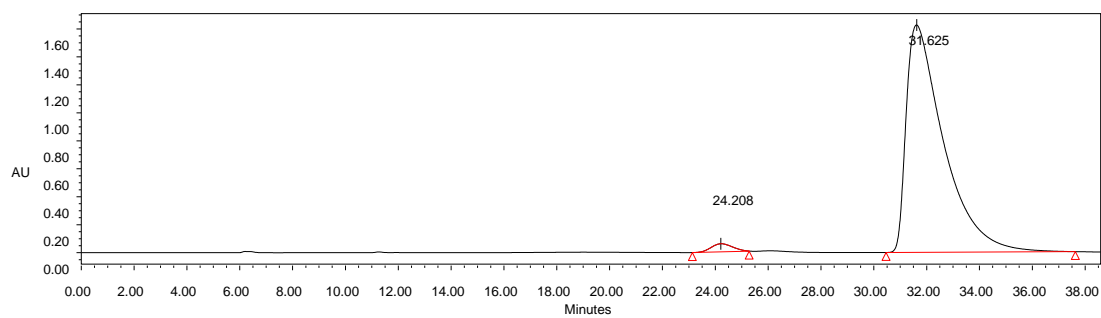
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	22.444	2308798	2.48	39322	bb	Unknown
2	25.091	90694221	97.52	1434018	bb	Unknown



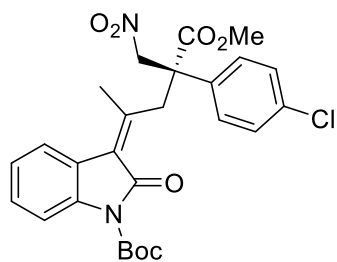
4b



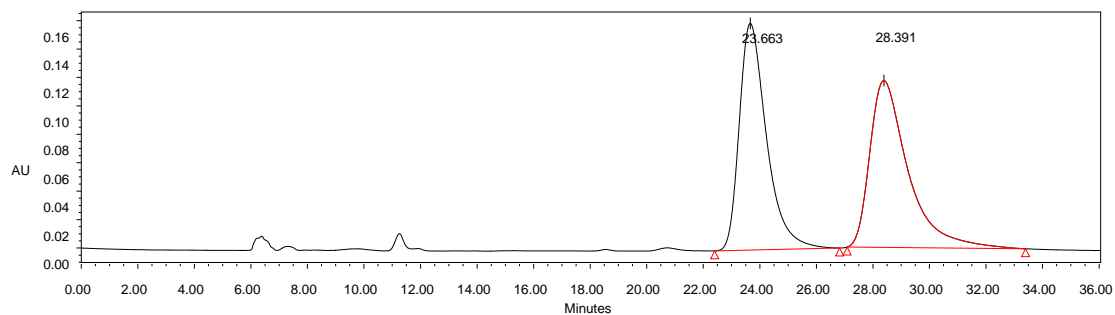
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.949	9182080	50.65	137716	bb	Unknown
2	33.173	8946114	49.35	81698	bb	Unknown



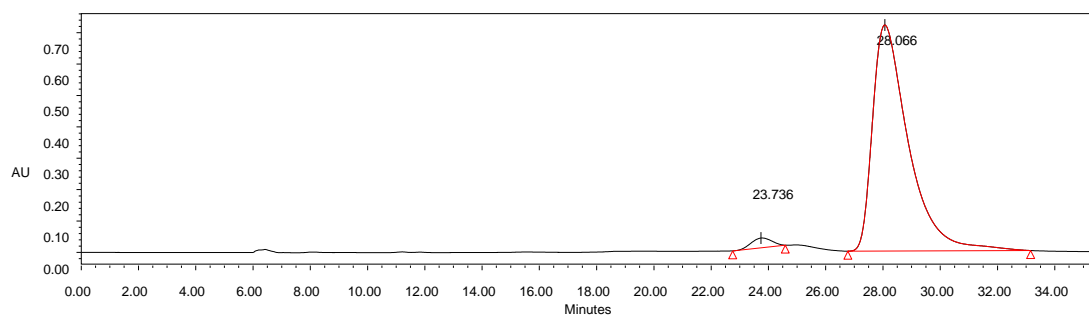
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	24.208	3239664	1.98	57740	bb	Unknown
2	31.625	160257161	98.02	1625658	bb	Unknown



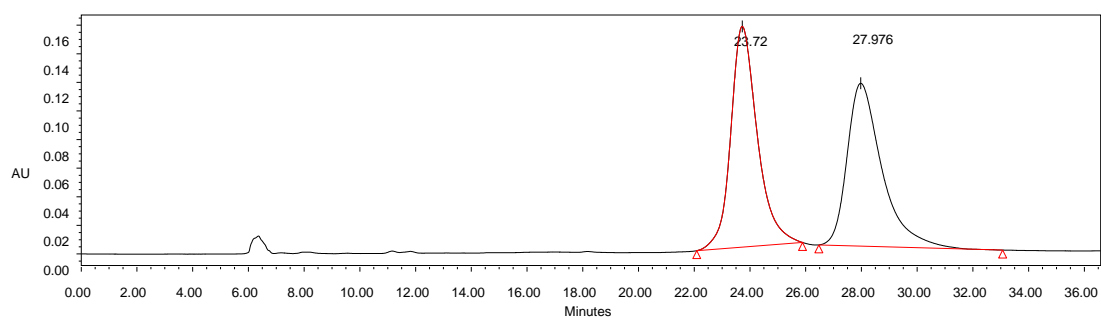
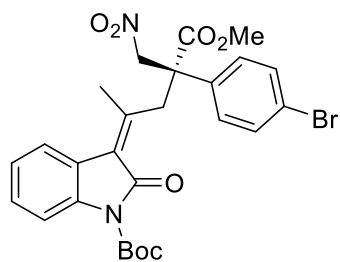
4c



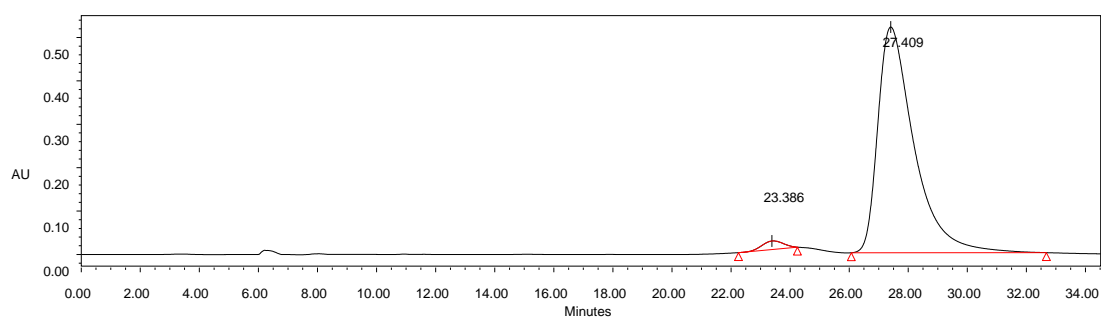
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.663	10676134	49.19	159487	bb	Unknown
2	28.391	11027032	50.81	117385	bb	Unknown



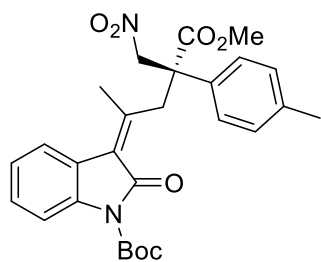
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.736	1555436	2.42	31181	bb	Unknown
2	28.066	62682534	97.58	720397	bb	Unknown



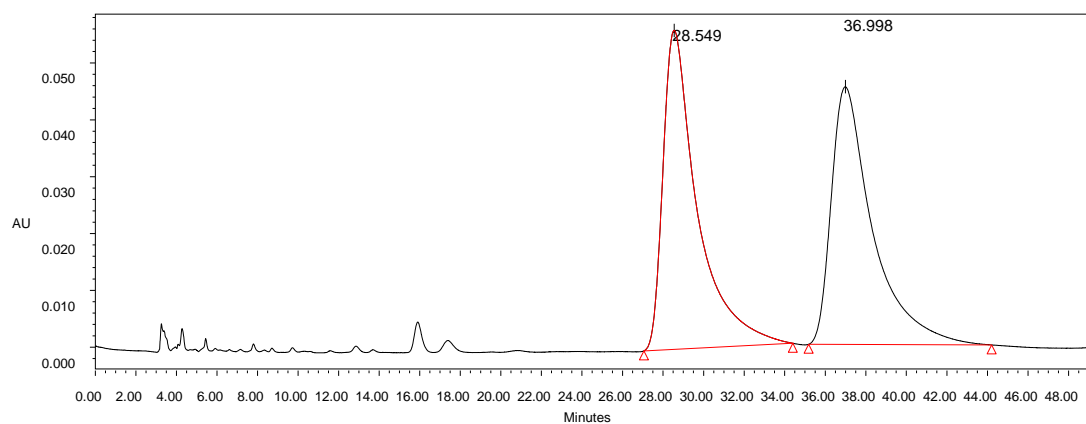
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.724	10252334	50.94	154384	bb	Unknown
2	27.976	9874652	49.06	113816	bb	Unknown



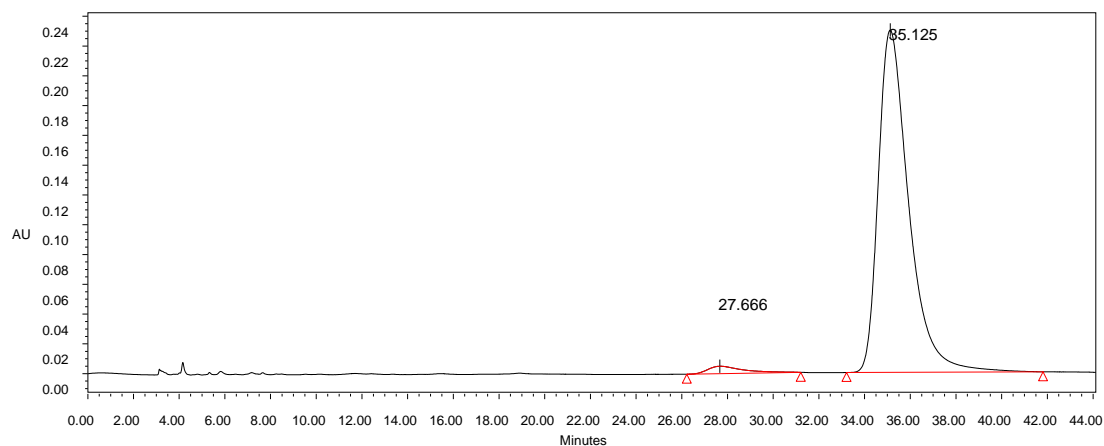
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.386	987340	2.18	19730	bb	Unknown
2	27.409	44305742	97.82	520205	bb	Unknown



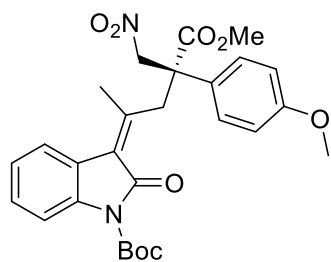
4e



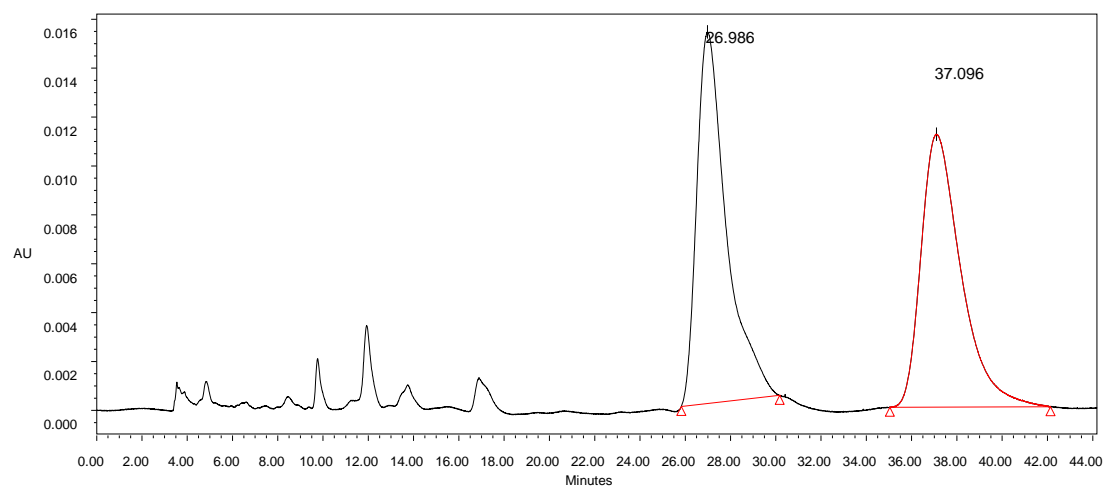
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	28.549	6590049	50.69	56100	bb	Unknown
2	36.998	6411793	49.31	45326	bb	Unknown



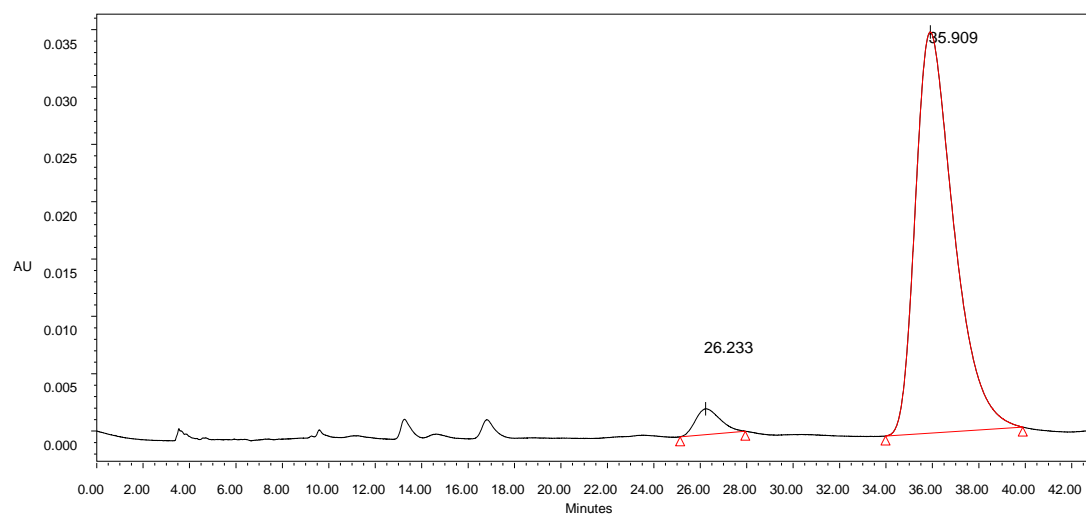
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	27.666	544395	2.49	5018	bb	Unknown
2	35.125	21349543	97.51	229867	bb	Unknown



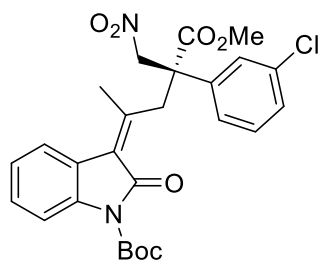
4f



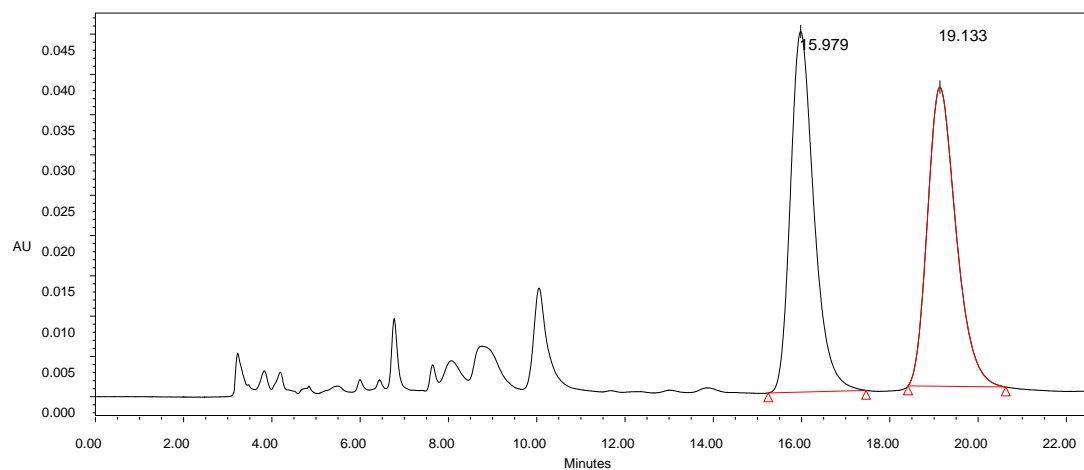
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	26.986	1385813	50.28	15201	bb	Unknown
2	37.096	1370443	49.72	11162	bb	Unknown



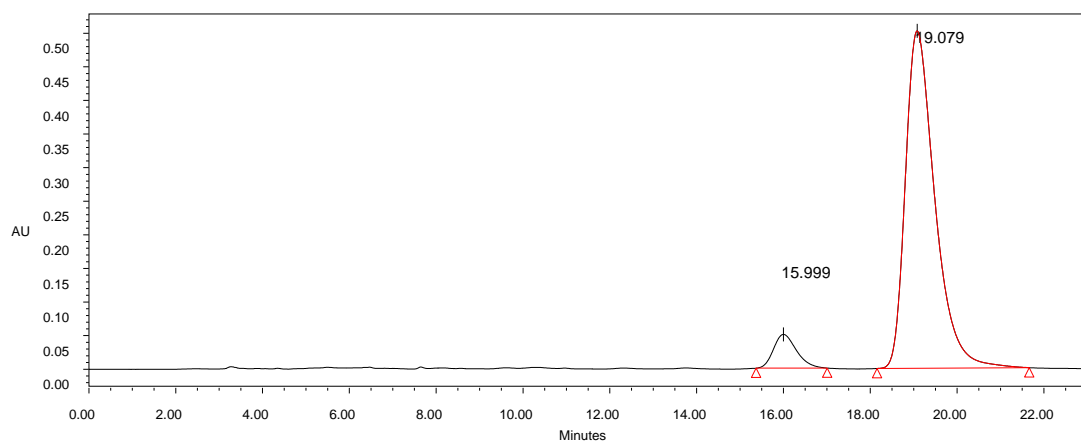
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	26.233	167276	3.98	2259	bb	Unknown
2	35.909	4032801	96.02	34975	bb	Unknown



**4g**

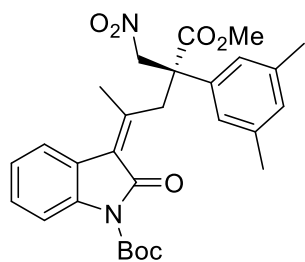


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.979	1655546	49.80	44750	bb	Unknown
2	19.133	1668782	50.20	37129	bb	Unknown

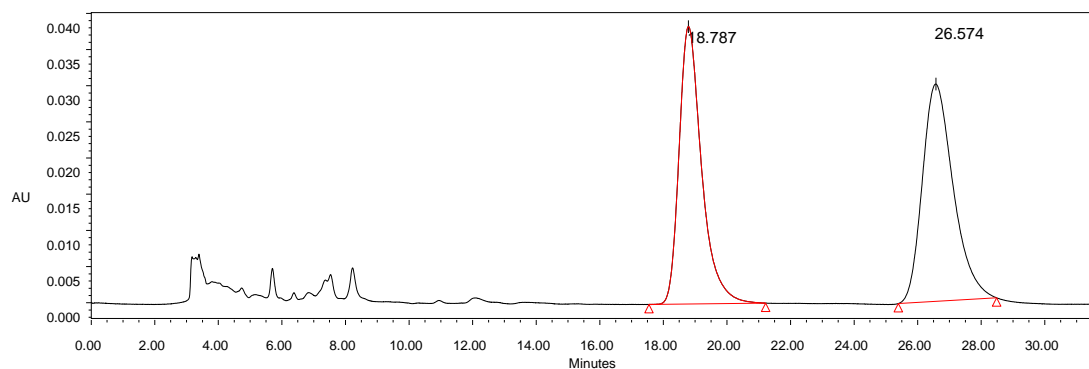


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.999	1843243	7.21	50229	bb	Unknown
2	19.079	23709372	92.79	502135	bb	Unknown

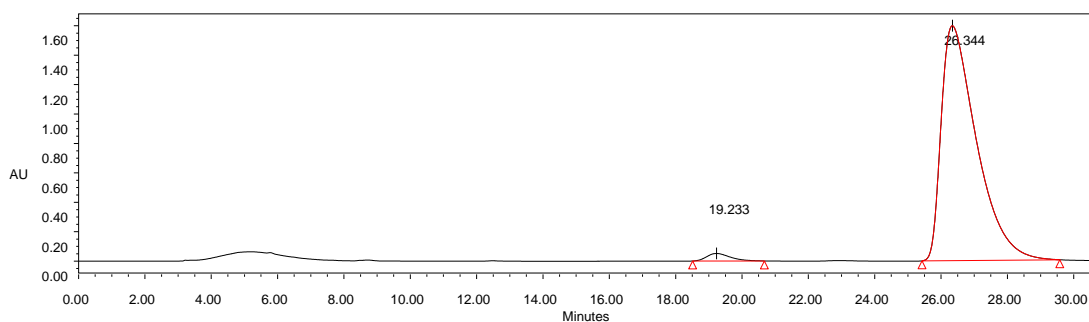




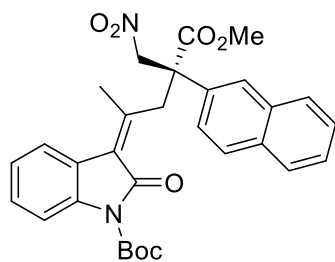
4h



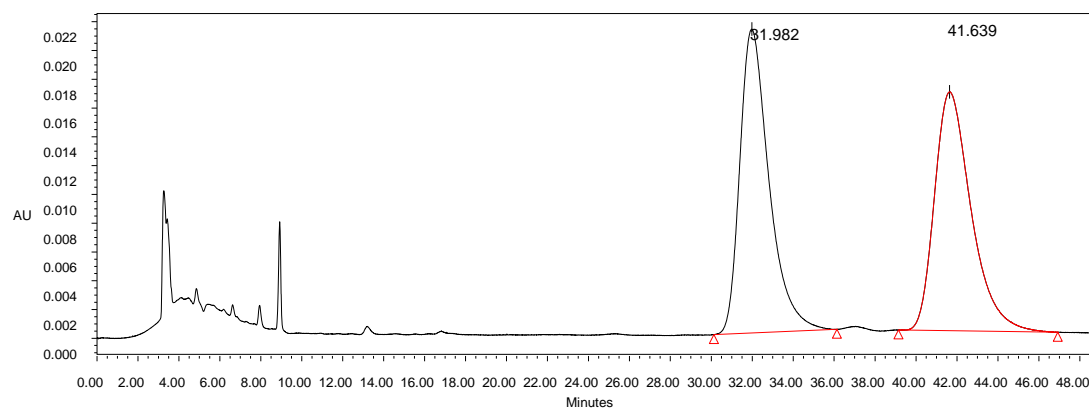
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	18.787	1887534	48.21	38345	bb	Unknown
2	26.574	2027784	51.79	30044	bb	Unknown



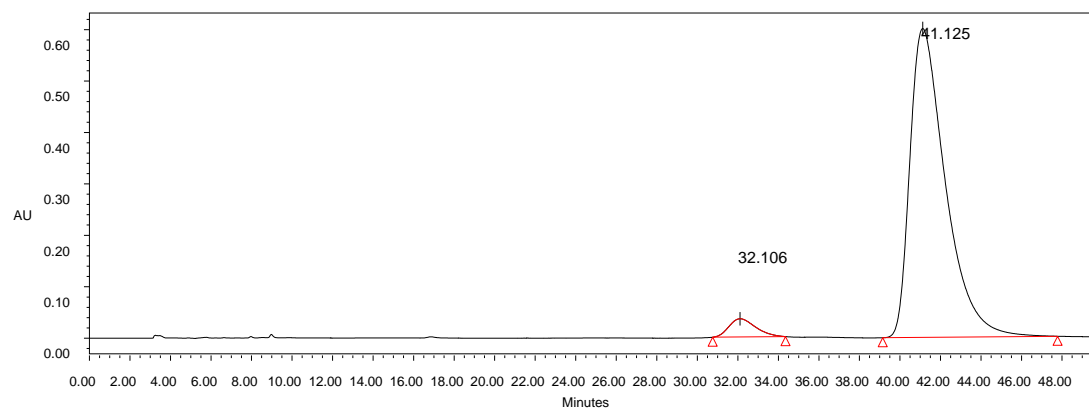
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	19.233	2513466	2.09	51300	bb	Unknown
2	26.344	117744895	97.91	1596904	bb	Unknown



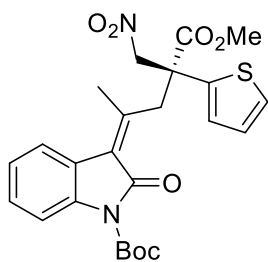
4i



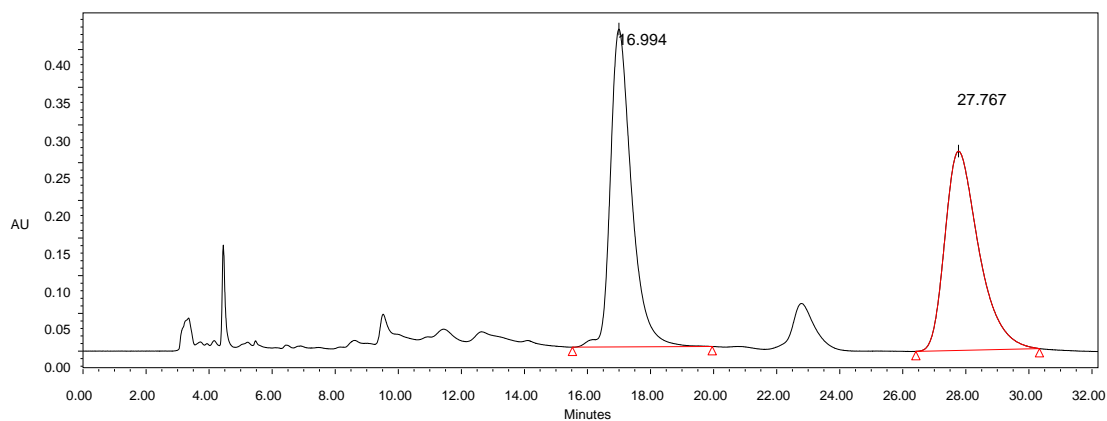
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	31.982	2091266	50.35	21118	bb	Unknown
2	41.639	2061949	49.65	16593	bb	Unknown



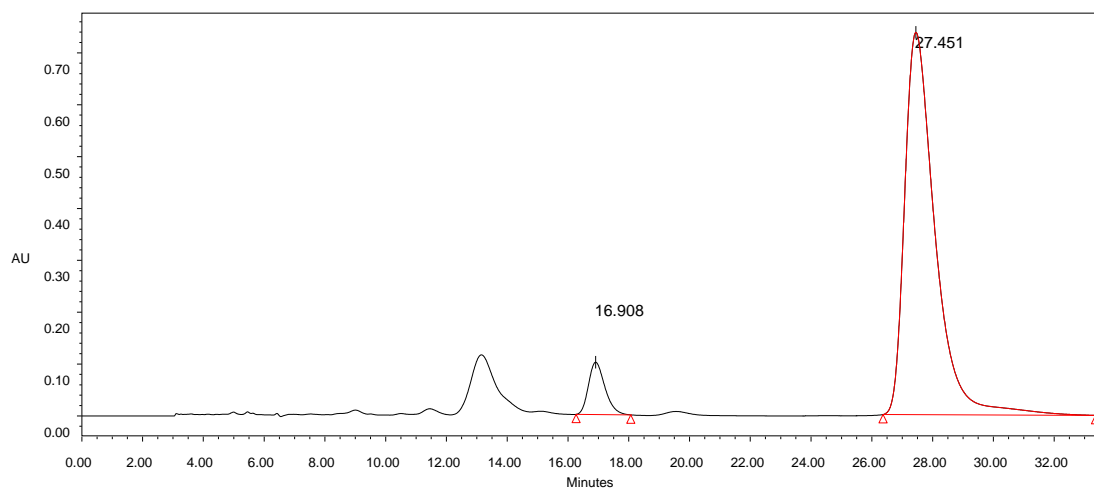
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	32.106	3245893	4.24	35463	bb	Unknown
2	41.125	73230247	95.76	600674	bb	Unknown



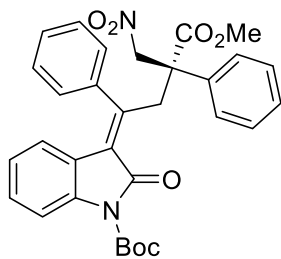
4j



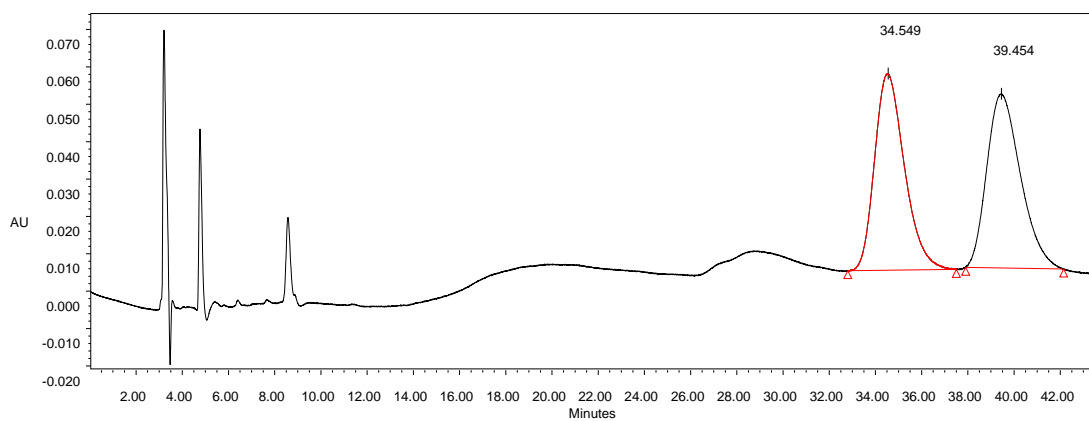
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	16.994	19697685	49.92	421824	bb	Unknown
2	27.767	19759125	50.08	264507	bb	Unknown



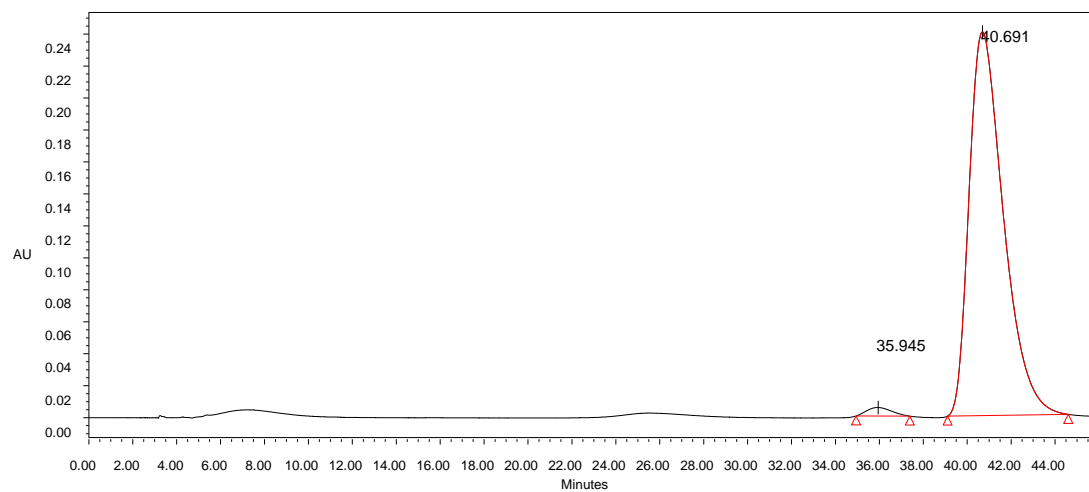
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	16.908	3802126	6.90	100996	bb	Unknown
2	27.451	51286404	93.10	737153	bb	Unknown



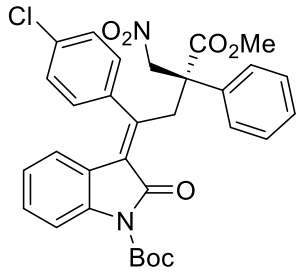
4k



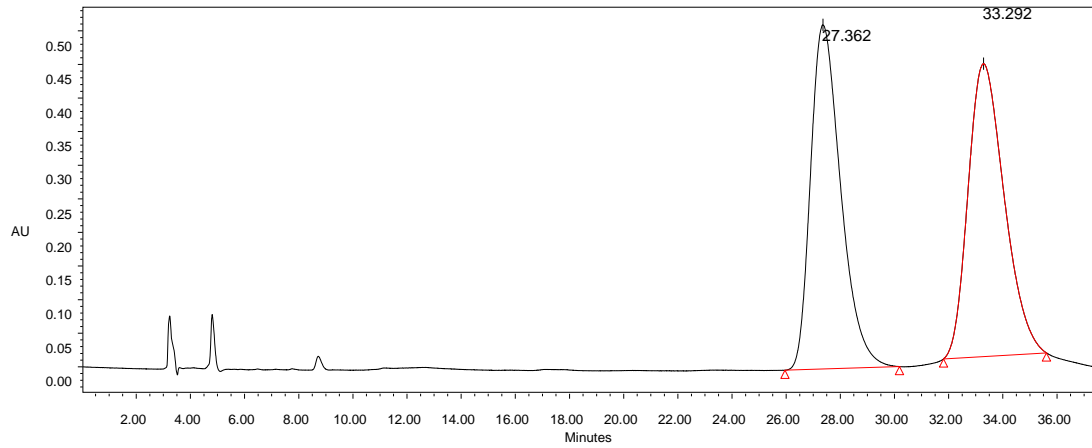
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	34.549	4726916	50.02	52589	bb	Unknown
2	39.454	4722888	49.98	46575	bb	Unknown



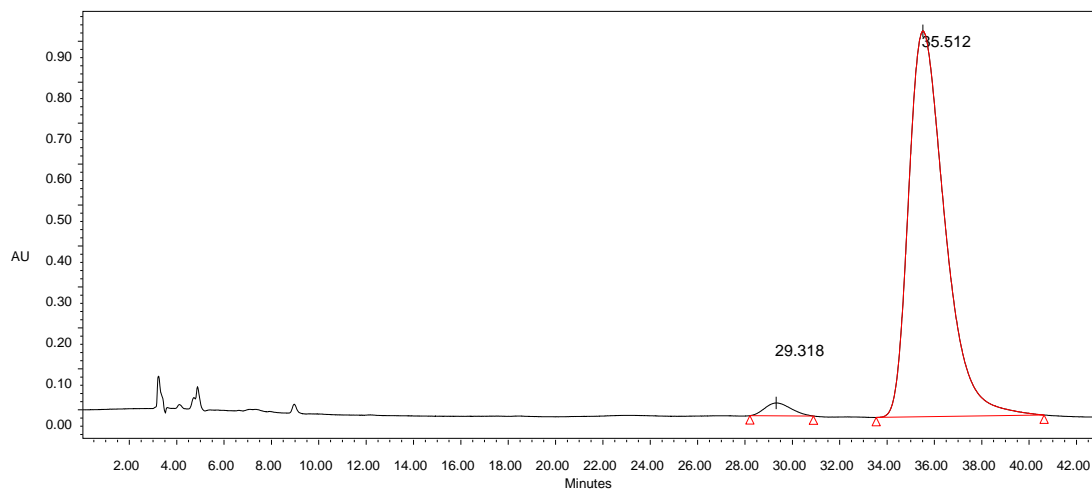
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	35.945	419989	1.58	5369	bb	Unknown
2	40.691	26110850	98.42	240099	bb	Unknown



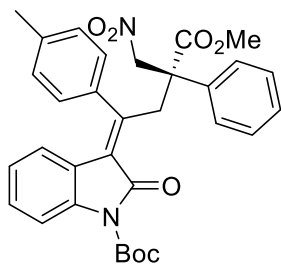
41



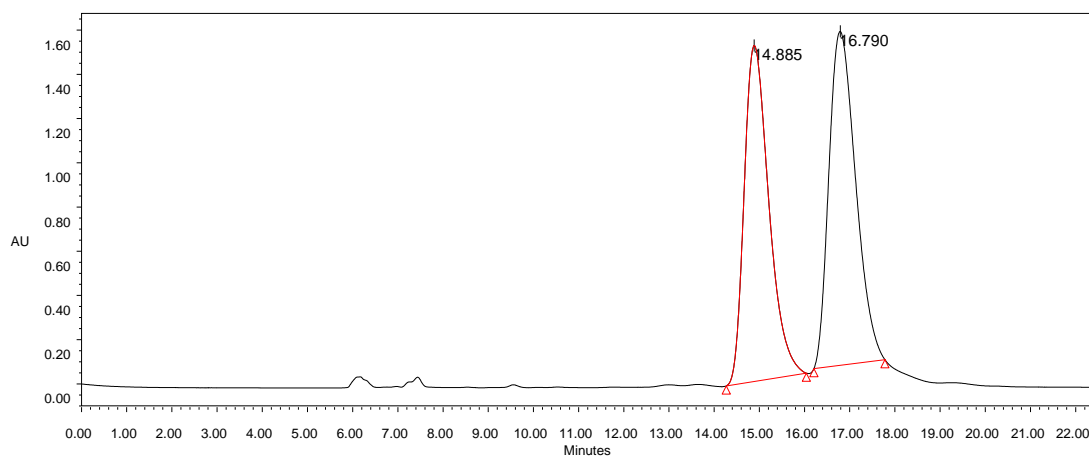
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	27.362	39660558	49.49	512108	bb	Unknown
2	33.292	40474990	50.51	436067	bb	Unknown



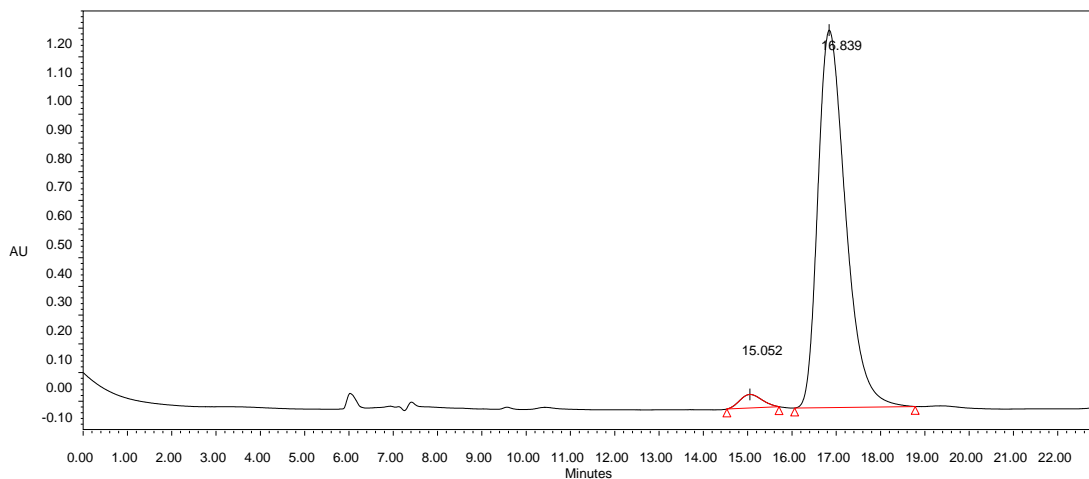
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	29.318	2407607	2.34	31356	bb	Unknown
2	35.512	100401256	97.66	942488	bb	Unknown



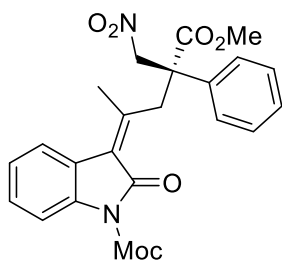
4m



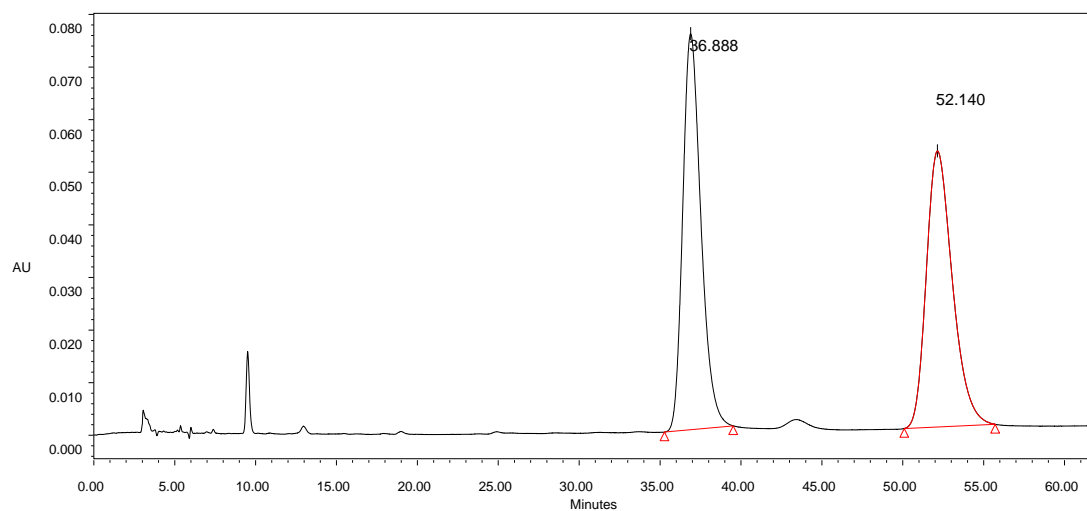
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	14.885	57816854	48.29	1519438	bb	Unknown
2	16.790	61911467	51.71	1510405	bb	Unknown



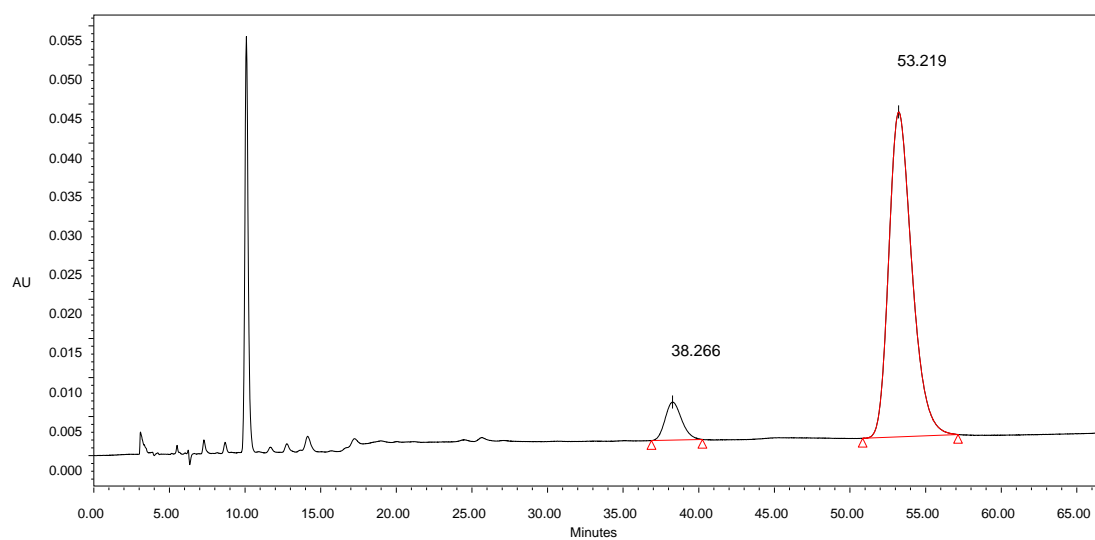
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.052	1637075	2.78	47222	bb	Unknown
2	16.839	57217215	97.22	1315281	bb	Unknown



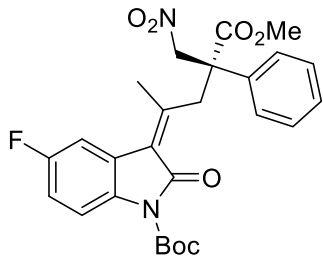
4p



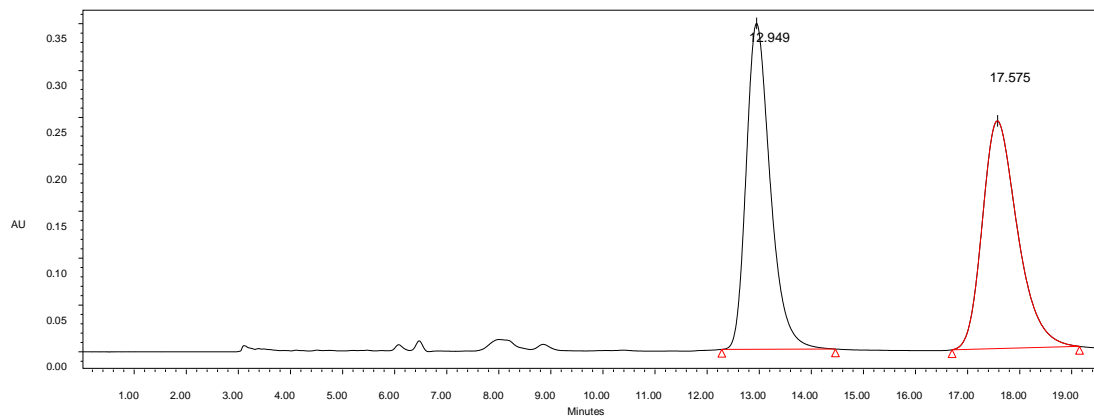
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	36.888	5916233	50.14	75286	bb	Unknown
2	52.140	5882144	49.86	52500	bb	Unknown



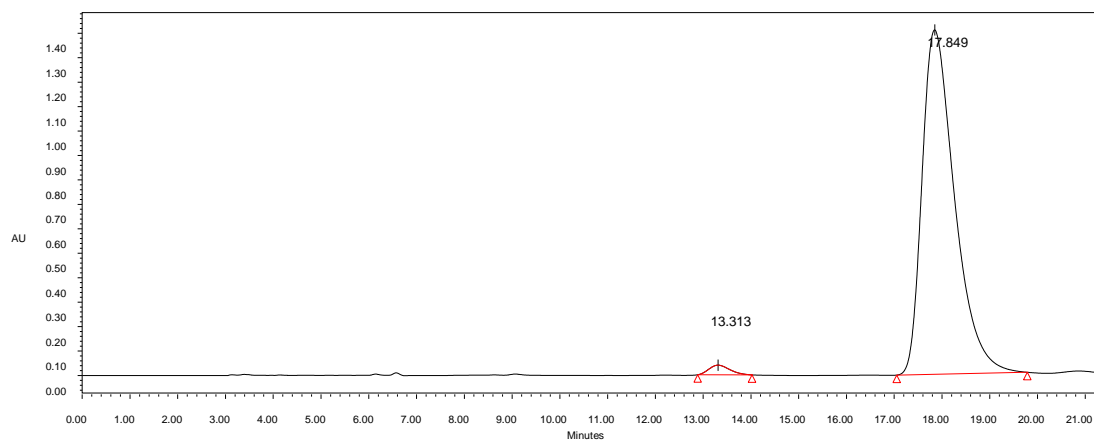
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	38.266	370100	7.69	4877	bb	Unknown
2	53.219	4444357	92.31	41595	bb	Unknown



4q

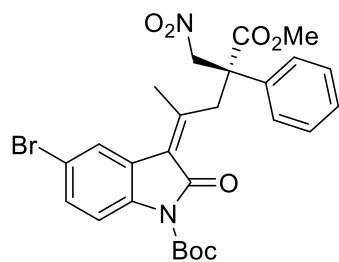


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	12.949	11172029	49.47	347688	bb	Unknown
2	17.575	11412518	50.53	242814	bb	Unknown

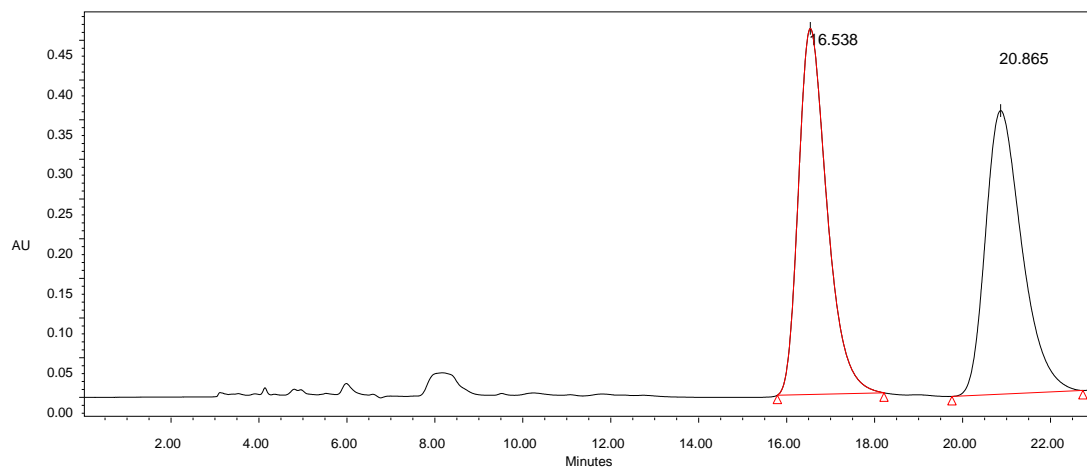


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	13.313	1192910	1.76	39372	bb	Unknown
2	17.849	66698289	98.24	1408903	bb	Unknown

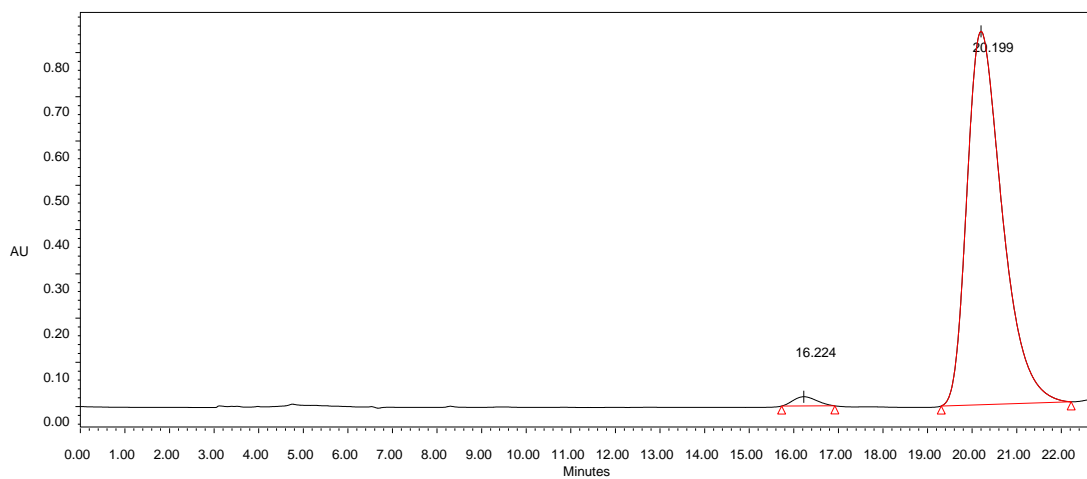




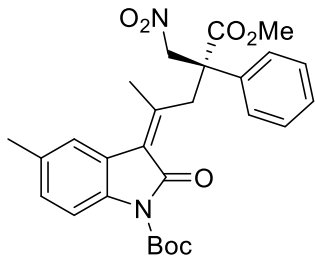
4r



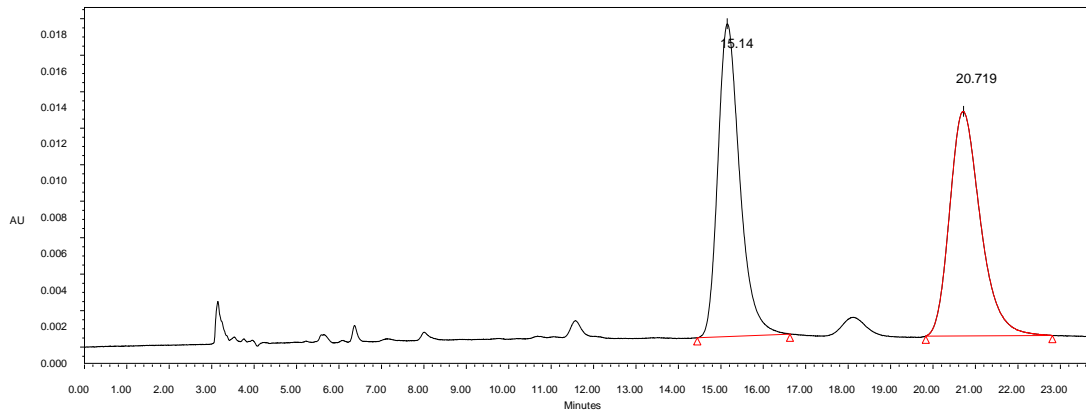
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	16.538	20869603	50.42	461322	bb	Unknown
2	20.865	20522654	49.58	357489	bb	Unknown



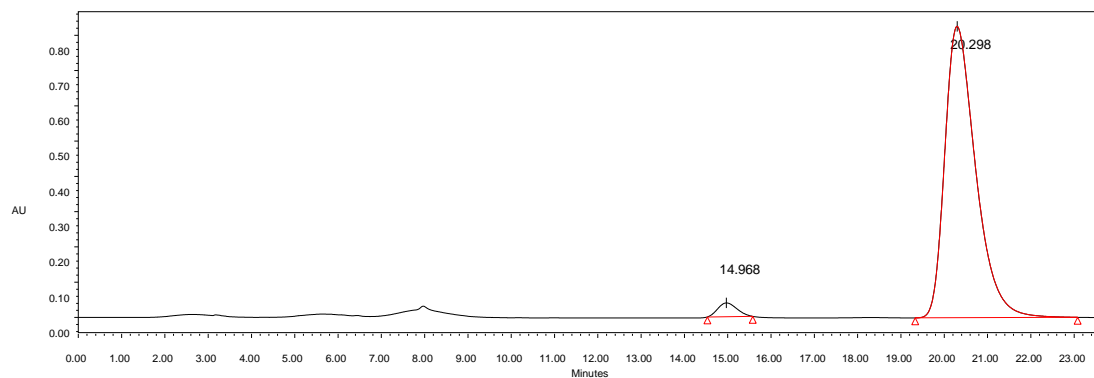
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	16.224	762256	1.61	20836	bb	Unknown
2	20.199	46477365	98.39	843651	bb	Unknown



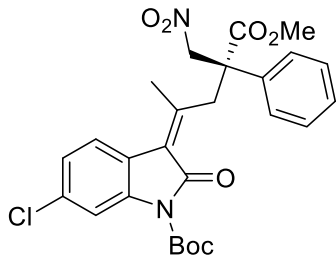
4s



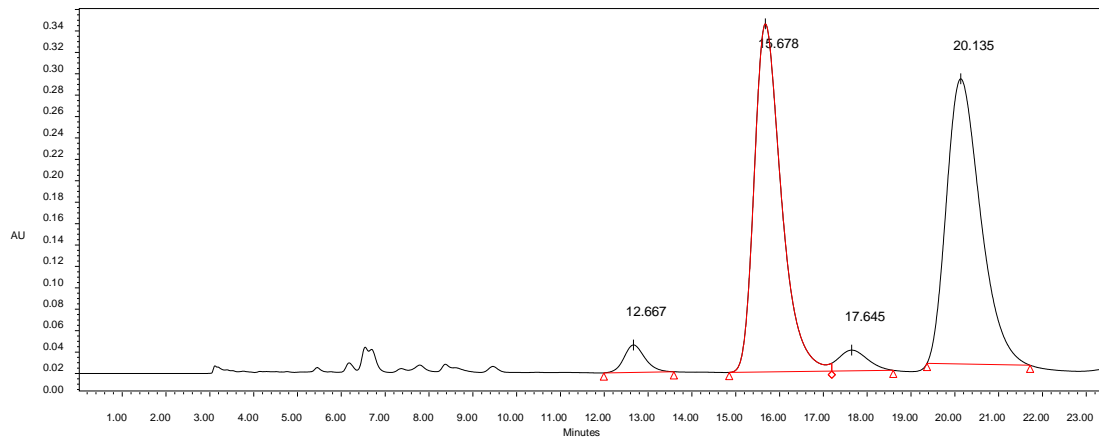
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.148	616044	49.75	17151	bb	Unknown
2	20.719	622295	50.25	12319	bb	Unknown



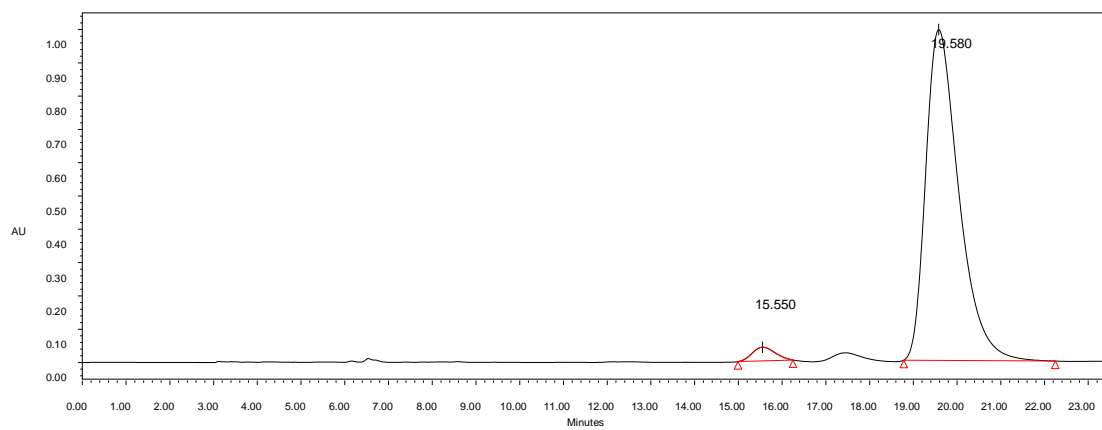
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	14.968	1193201	2.83	39124	bb	Unknown
2	20.298	40950116	97.17	826166	bb	Unknown



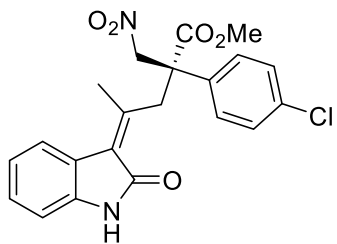
4t



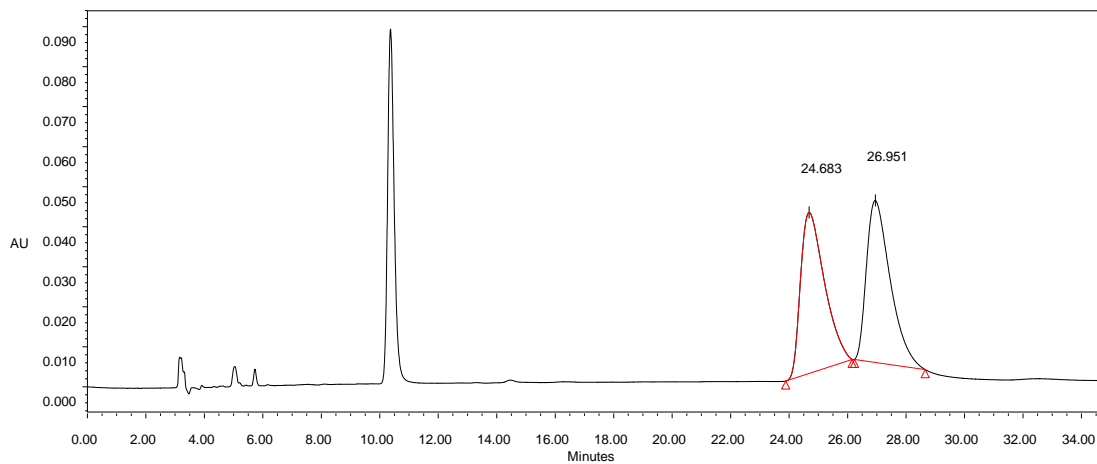
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	12.667	850646	2.82	25652	BB	Unknown
2	15.678	14037255	46.59	325215	Bv	Unknown
3	17.645	874464	2.90	19369	vb	Unknown
4	20.135	14365992	47.68	266418	bb	Unknown



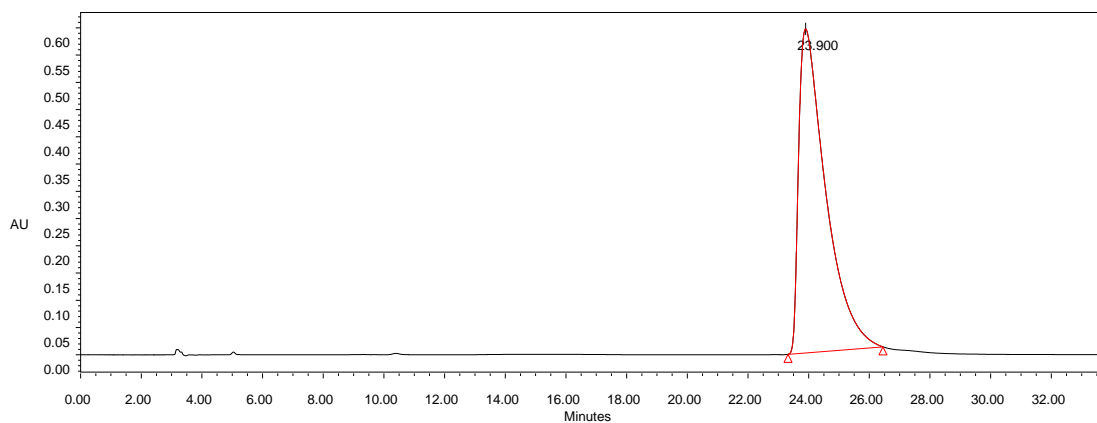
Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.550	1498731	2.79	41197	bb	Unknown
2	19.580	52257038	97.21	993875	bb	Unknown



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Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	24.683	2289977	50.02	40239	bb	Unknown
2	26.951	2288164	49.98	40476	bb	Unknown



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	23.900	36795471	99.99	594748	bb	Unknown