

## Supporting Information

### The Synthesis, Characterization, and Rapid Cycloadditions of 5-Nitro-1,2,3-Triazine

Christopher M. Glinkerman and Dale L. Boger\*

*Department of Chemistry and the Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037, United States*

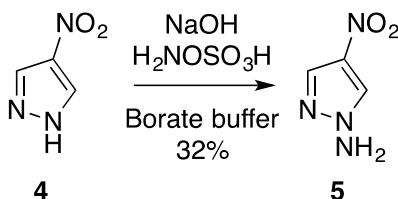
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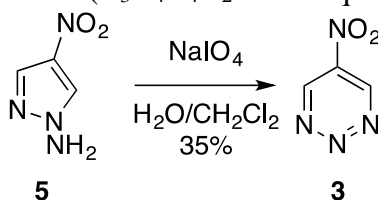
## I. General Methods

**General Methods.** All reactions were performed under nitrogen unless otherwise noted. All reagents and solvents, with the exception of amidines, were used as supplied without further purification unless otherwise noted. Amidines were purchased as their hydrochloride salts and free-based with 1 M NaOH(aq). Preparative TLC and column chromatography were conducted using Millipore SiO<sub>2</sub> 60 F<sub>254</sub> PTLC (0.5 mm) and Zeochem ZEOprep 60 ECO SiO<sub>2</sub> (40–63 μm), respectively. Analytical TLC was conducted using Millipore SiO<sub>2</sub> 60 F<sub>254</sub> TLC (0.250 mm) plates. Melting points were obtained using a Mel-Temp II apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker Avance III HD 600 MHz spectrometer equipped with either a 5 mm QCI or 5 mm CPDCH probe or a Bruker Avance III 400 MHz spectrometer equipped with a 5 mm BBFO probe. IR spectra were obtained using a Thermo Nicolet 380 FT-IR with a SmartOrbit Diamond ATR accessory. Mass spectrometric analysis was performed by direct sample injection on an Agilent G1969A ESI-TOF mass spectrometer. The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K<sub>α</sub> radiation (λ = 0.71073). Differential scanning calorimetry was performed on a Mettler DSC822e differential scanning calorimeter equipped with gold-plated sample pans. Semiempirical computational studies (AM1,<sup>1</sup> MNDO<sup>2</sup>) were conducted on energy minimized structures (MM2,<sup>3</sup> ChemBio3D<sup>4</sup>) using Molecular Orbital Package (MOPAC) 2016.<sup>5</sup>

## II. 5-Nitro-1,2,3-triazine Synthesis

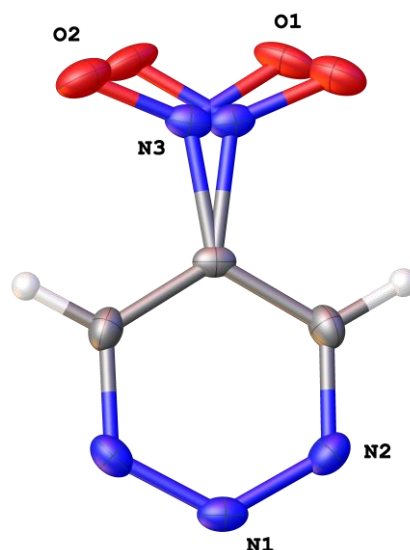


**4-Nitro-1H-pyrazol-1-amine (5).** According to the procedure of Vlnogradov et al.<sup>6</sup> borate buffer (25 mL) was pretreated with NaOH (800 mg, 20.0 mmol). After complete dissolution of the base, 4-nitropyrazole (**4**, 570 mg, 5.00 mmol) was added to the solution, followed by H<sub>2</sub>NOSO<sub>3</sub>H (1.70 g, 15.0 mmol) portionwise over 10 min. The resulting solution was heated to 60 °C for 5 h behind a blast shield. The resulting mixture was cooled and extracted (4 × 25 mL) with Et<sub>2</sub>O. The combined organic extracts were washed with aqueous 1 N NaOH (1 × 50 mL), washed with H<sub>2</sub>O (1 × 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated on a rotary evaporator. Recrystallization from H<sub>2</sub>O provided **5** as a light yellow crystalline solid (206 mg, 32%): mp 93–96 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 8.15 (s, 1H), 7.97 (s, 1H), 5.45 (bs, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 134.4, 134.1, 128.8; IR (film) ν<sub>max</sub> 3347, 3292, 3233, 3108, 1627, 1521, 1469, 1394, 1305, 1219, 1182, 975, 953, 902, 816, 754, 551 cm<sup>-1</sup>; HRESI-TOF *m/z* 129.0409 (C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub> + H<sup>+</sup> requires 129.0407).



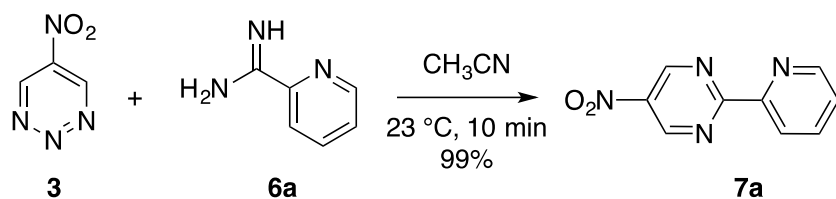
**5-Nitro-1,2,3-triazine (3).** A solution of **5**<sup>6</sup> (500 mg, 3.90 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/water (1:1, 130 mL) in a separatory funnel under an atmosphere of air was treated with NaIO<sub>4</sub> (4.17 g, 19.5 mmol) and shaken vigorously for 3 min, venting frequently. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on a rotary evaporator. Flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) provided **3** as a light yellow solid (172 mg, 35%). Differential scanning calorimetry (DSC, page S61) of **3** noted one broad exotherm (66–272 °C) with a peak heat flow at 113 °C with a total thermal potential of –4342 J/g with an onset temperature of 66 °C: mp 115 °C (decomposition); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.72 (s, 2H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 150 MHz) δ 142.3, 138.6; IR (film) ν<sub>max</sub> 3047, 1582, 1515, 1360, 1328, 939, 864, 722, 657 cm<sup>-1</sup>; HRESI-TOF *m/z* 127.0251 (C<sub>3</sub>H<sub>2</sub>N<sub>4</sub>O<sub>2</sub> + H<sup>+</sup> requires 127.0251). 5-

Nitro-1,2,3-triazine (**3**) is a light yellow, crystalline solid that is extremely sensitive to nucleophiles including water, methanol, and pyrrolidine. As a result of the compound's sensitivity, it is imperative that the organic phase of the reaction mixture be separated from the aqueous phase and thoroughly dried as rapidly as possible. In addition, column chromatography must be carried out quickly, as **3** decomposes on silica (as well as on alumina and florisil). It should be noted that **3** appears yellow in solution and, thus, column fractions containing the product can be identified visually. This is especially important as **3** decomposes on TLC. Pure 5-nitro-1,2,3-triazine (**3**) was stored under an inert atmosphere at 0 °C for eighteen weeks without significant decomposition. Despite the compound's high nitrogen content, the authors have not been able to elicit detonation through the application of shock, friction, or heat. It is recommended that those intending to work with **3** utilize all the safety precautions associated with high energy density material research. For an excellent example, see: Zhang, J.; Zhang, Q.; Vo, T. T.; Parrish, D. A.; Shreeve, J. M. *J. Am. Chem. Soc.* **2015**, *137*, 1697. The structure of **3** was confirmed in a single crystal X-ray structure determination conducted with a yellow irregular crystal obtained by slow evaporation of a saturated solution of **3** in CH<sub>2</sub>Cl<sub>2</sub>/hexanes (CCDC 1818968).

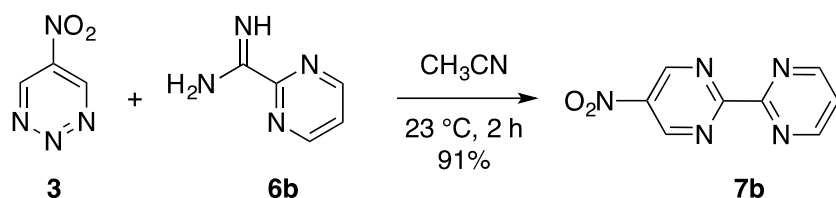


X-ray structure of 5-nitro-1,2,3-triazine (**3**).

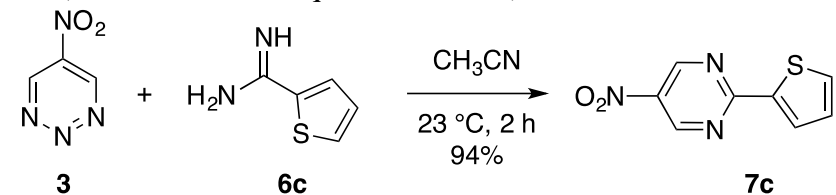
### III. Reaction of 3 with Amidines



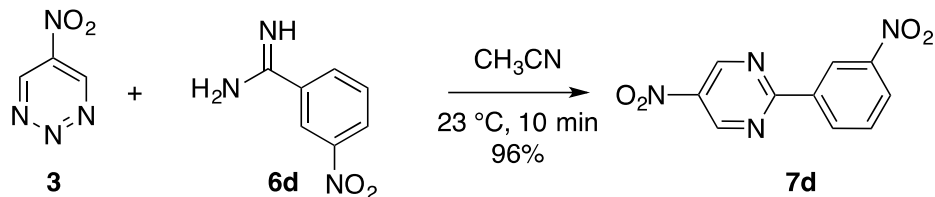
**5-Nitro-2-(pyridin-2-yl)pyrimidine (7a).** A 0.026 M solution of amidine **6a** (3.20 mg, 0.026 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by reverse phase preparative TLC (SiO<sub>2</sub> RP-18, 10% MeOH/EtOAc) to provide **7a** as a white solid<sup>7</sup> (5.32 mg, 99%): mp, slow decomposition upon heating; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz) δ 9.68 (s, 2H), 8.80 (d, *J* = 4.8 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.09 (td, *J* = 7.8, 1.7 Hz, 1H), 7.66 (m, 1H); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 150 MHz) δ 167.0, 154.6, 153.8, 151.1, 143.4, 139.4, 128.0, 126.5; IR (film) ν<sub>max</sub> 2917, 1564, 1514, 1414, 1348, 760, 536 cm<sup>-1</sup>; HRESI-TOF *m/z* 203.0564 (C<sub>9</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub> + H<sup>+</sup> requires 203.0563).



**5-Nitro-2,2'-bipyrimidine (7b).** A 0.1 M solution of amidine **6b** (7.75 mg, 0.064 mmol) in CH<sub>3</sub>CN was treated with a 0.1 M solution of 1,2,3-triazine **3** (12.0 mg, 0.095 mmol) in CH<sub>3</sub>CN. The reaction mixture was stirred at 23 °C for 2 h, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 10% MeOH/EtOAc) to provide **7b** as a white solid (11.7 mg, 91%): mp >250 °C; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 9.74 (s, 2H), 9.10 (d, *J* = 4.9 Hz, 2H), 7.74 (t, *J* = 4.9 Hz, 1H); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 150 MHz) δ 208.2, 163.6, 159.9, 157.7, 152.9, 122.3; IR (film) ν<sub>max</sub> 3033, 2920, 1582, 1554, 1507, 1403, 1356, 760, 639, 537 cm<sup>-1</sup>; HRESI-TOF *m/z* 204.0515 (C<sub>8</sub>H<sub>5</sub>N<sub>5</sub>O<sub>2</sub> + H<sup>+</sup> requires 204.0516).

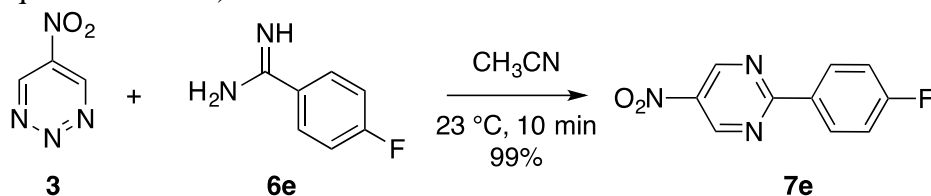


**5-Nitro-2-(thiophen-2-yl)pyrimidine (7c).** A 0.1 M solution of amidine **6c** (15.4 mg, 0.122 mmol) in CH<sub>3</sub>CN was treated with a 0.1 M solution of 1,2,3-triazine **3** (23.0 mg, 0.183 mmol) in CH<sub>3</sub>CN. The reaction mixture was stirred at 23 °C for 2 h, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7c** as a yellow solid (23.7 mg, 94%): mp >250 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.42 (s, 2H), 8.20 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.70 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.23 (dd, *J* = 5.0, 3.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 164.9, 153.3, 141.4, 139.8, 134.4, 133.2, 129.4; IR (film) ν<sub>max</sub> 1563, 1526, 1498, 1434, 1337, 850, 790, 730, 630, 532 cm<sup>-1</sup>; HRESI-TOF *m/z* 208.0176 (C<sub>8</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>S + H<sup>+</sup> requires 208.1075).

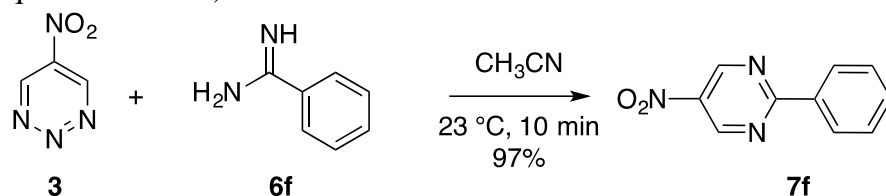


**5-Nitro-2-(3-nitrophenyl)pyrimidine (7d).** A 0.026 M solution of amidine **6d** (4.36 mg, 0.0264 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction

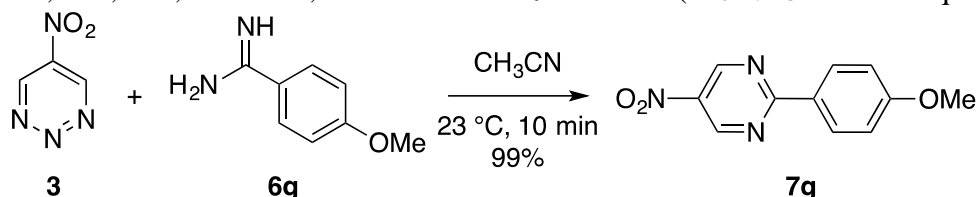
was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7d** as a white solid<sup>7</sup> (6.24 mg, 96%): mp 131–132 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.60 (s, 2H), 9.43 (t, *J* = 1.9 Hz, 1H), 8.91 (dt, *J* = 7.9, 1.3 Hz, 1H), 8.45 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 166.2, 153.3, 149.1, 141.2, 137.3, 135.2, 130.2, 127.2, 124.7; IR (film) ν<sub>max</sub> 1588, 1563, 1516, 1483, 1441, 1422, 1348, 801, 781, 739 cm<sup>-1</sup>; HRESI-TOF *m/z* 247.0461 (C<sub>10</sub>H<sub>6</sub>N<sub>4</sub>O<sub>4</sub> + H<sup>+</sup> requires 247.0462).



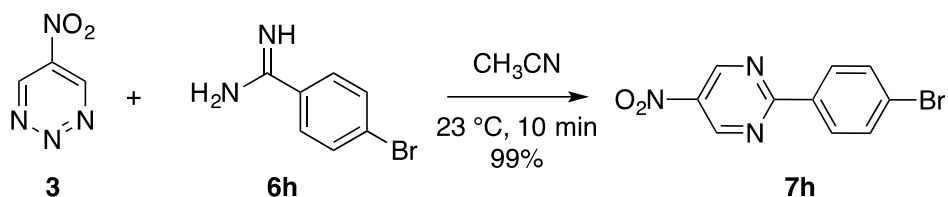
**2-(4-Fluorophenyl)-5-nitropyrimidine (7e).** A 0.026 M solution of amidine **6e** (3.65 mg, 0.0264 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7e** as a white solid<sup>7</sup> (5.77 mg, 99%): mp 147–149 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.51 (s, 2H), 8.60–8.58 (m, 2H), 7.24–7.21 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 167.6 (s, 1C), 166.3 (d, *J* = 255 Hz, 1C), 153.3 (s, 2C), 140.7 (s, 1C), 132.5 (d, *J* = 8.8 Hz, 2C), 132.1 (d, *J* = 2.4 Hz, 1C), 116.5 (d, *J* = 21.7 Hz, 2C); IR (film) ν<sub>max</sub> 1599, 1568, 1518, 1429, 1352, 1236, 859, 796 cm<sup>-1</sup>; HRESI-TOF *m/z* 220.0516 (C<sub>10</sub>H<sub>6</sub>FN<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 220.0516).



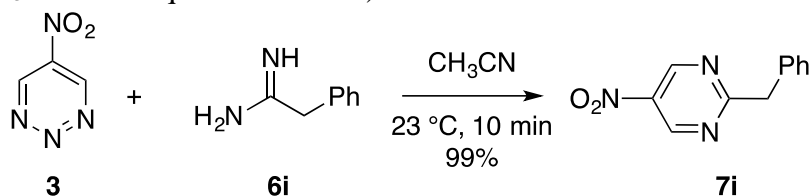
**5-Nitro-2-phenylpyrimidine (7f).** A 0.026 M solution of amidine **6f** (120.2 mg, 1.00 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (189.1 mg, 1.50 mmol) in CH<sub>3</sub>CN dropwise over 10 min. The reaction was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 10% EtOAc/hexanes) to provide **7f** as a white solid<sup>7</sup> (197.7 mg, 98%): mp 214–216 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.53 (s, 2H), 8.57–8.55 (m, 2H), 7.62–7.59 (m, 1H), 7.57–7.53 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 168.6, 153.2, 140.8, 135.8, 133.3, 130.0, 129.4; IR (film) ν<sub>max</sub> 2918, 1563, 1513, 1424, 1341, 855, 746, 691, 641, 536 cm<sup>-1</sup>; HRESI-TOF *m/z* 202.0611 (C<sub>10</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 202.0611).



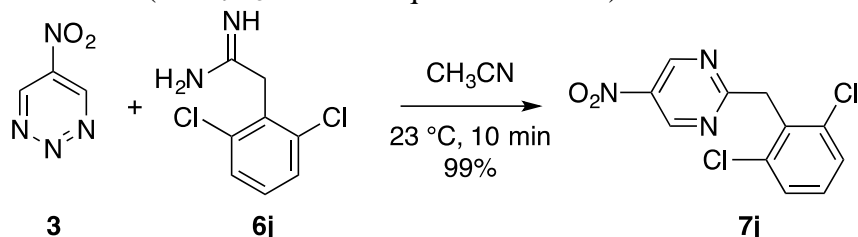
**2-(4-Methoxyphenyl)-5-nitropyrimidine (7g).** A 0.026 M solution of amidine **6g** (3.96 mg, 0.026 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7g** as a yellow solid<sup>7</sup> (6.05 mg, 99%): mp 194–195 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.46 (s, 2H), 8.53–8.51 (m, 2H), 7.05–7.02 (m, 2H), 3.92 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 168.3, 164.1, 153.2, 140.2, 132.1, 128.5, 114.8, 55.9; IR (film) ν<sub>max</sub> 1604, 1584, 1569, 1512, 1428, 1350, 1269, 794 cm<sup>-1</sup>; HRESI-TOF *m/z* 232.0717 (C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub> + H<sup>+</sup> requires 232.0717).



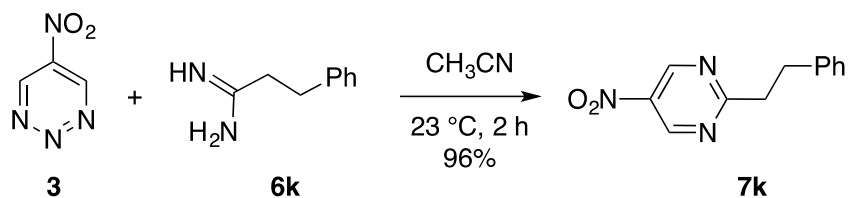
**2-(4-Bromophenyl)-5-nitropyrimidine (7h).** A 0.026 M solution of amidine **6h** (5.25 mg, 0.0264 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7h** as a white solid<sup>7</sup> (7.37 mg, 99%): mp 223–225 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.52 (s, 2H), 8.44–8.42 (m, 2H), 7.70–7.67 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 167.8, 153.3, 140.9, 134.7, 132.7, 131.5, 128.6; IR (film) ν<sub>max</sub> 1583, 1560, 1513, 1425, 1336, 851, 783, 643, 535 cm<sup>-1</sup>; HRESI-TOF *m/z* 279.9716 (C<sub>10</sub>H<sub>6</sub>BrN<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 279.9716).



**2-Benzyl-5-nitropyrimidine (7i).** A 0.026 M solution of amidine **6i** (3.54 mg, 0.0264 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7i** as a white solid<sup>7</sup> (5.66 mg, 99%): mp 98–99 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.41 (s, 2H), 7.37–7.31 (m, 4H), 7.28–7.25 (m, 1H), 4.43 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 175.4, 153.1, 141.0, 136.9, 129.6, 129.2, 127.6, 46.4; IR (film) ν<sub>max</sub> 1587, 1563, 1513, 1425, 1348, 850, 750, 699, 638, 580 cm<sup>-1</sup>; HRESI-TOF *m/z* 216.0767 (C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 216.0767).



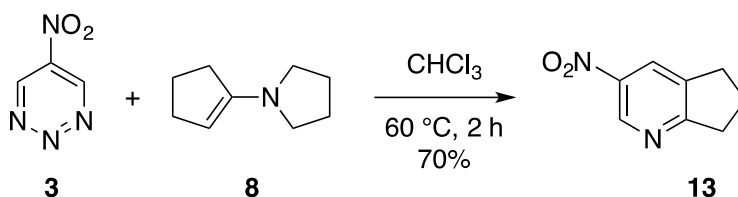
**2-(2,6-Dichlorobenzyl)-5-nitropyrimidine (7j).** A 0.026 M solution of amidine **6j** (5.37 mg, 0.0264 mmol) in CH<sub>3</sub>CN was treated with a 0.026 M solution of 1,2,3-triazine **3** (5.00 mg, 0.040 mmol) in CH<sub>3</sub>CN. The reaction was instantaneous as evidenced by the rapid evolution of N<sub>2</sub>. The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7j** as a colorless film (7.41 mg, 99%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.39 (s, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 8.1 Hz, 1H), 4.83 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 173.5, 153.0, 141.0, 136.7, 133.5, 129.5, 128.5, 41.4; IR (film) ν<sub>max</sub> 1587, 1567, 1435, 1351, 777 cm<sup>-1</sup>; HRESI-TOF *m/z* 283.9987 (C<sub>11</sub>H<sub>7</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 283.9988).



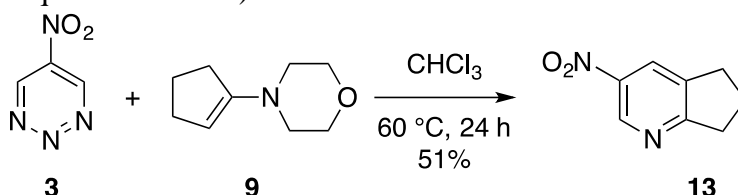
**5-Nitro-2-phenethylpyrimidine (7k).** A 0.1 M solution of amidine **6k** (14.6 mg, 0.099 mmol) in CH<sub>3</sub>CN was treated with a 0.1 M solution of 1,2,3-triazine **3** (18.6 mg, 0.148 mmol) in CH<sub>3</sub>CN. The reaction mixture was

stirred at 23 °C for 2 h, at which time the mixture was concentrated. The residue was purified by flash chromatography (SiO<sub>2</sub>, 30% EtOAc/hexanes) to provide **7k** as a white solid (21.6 mg, 96%): mp 110–112 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.40 (s, 2H), 7.30–7.27 (m, 2H), 7.23–7.19 (m, 3H), 3.45 (dd, *J* = 8.8, 7.0 Hz, 2H), 3.22 (dd, *J* = 9.0, 6.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 176.1, 152.7, 141.0, 140.7, 128.9, 128.7, 126.7, 41.4, 34.4; IR (film) ν<sub>max</sub> 2920, 1588, 1565, 1518, 1434, 1347, 852, 749, 702, 638 cm<sup>-1</sup>; HRESI-TOF *m/z* 230.0924 (C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 230.0924).

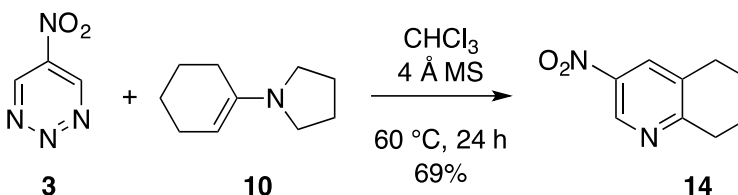
#### IV. Reaction of 3 with Enamines



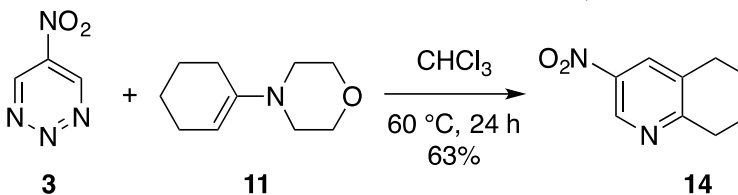
**3-Nitro-6,7-dihydro-5H-cyclopenta[b]pyridine (13).** A 0.2 M solution of enamine **8** (7.70  $\mu\text{L}$ , 0.053 mmol) in  $\text{CHCl}_3$  was treated with a 0.2 M solution of **3** (10.0 mg, 0.079 mmol) in  $\text{CHCl}_3$  at 23  $^\circ\text{C}$ . The reaction mixture was heated to 60  $^\circ\text{C}$  and stirred for 2 h. The mixture was cooled and concentrated and the residue was purified by PTLC ( $\text{SiO}_2$ , 50% EtOAc/hexanes) to provide **13** as a beige solid<sup>8</sup> (6.04 mg, 70%): mp 81–83  $^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  9.21 (d,  $J = 2.4$  Hz, 1H), 8.25 (t,  $J = 1.1$  Hz, 1H), 3.12 (t,  $J = 7.8$  Hz, 2H), 3.06 (t,  $J = 7.6$  Hz, 2H), 2.26 (p,  $J = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  173.3, 144.1, 143.8, 138.7, 127.1, 34.8, 30.8, 23.8; IR (film)  $\nu_{\text{max}}$  3060, 2921, 1585, 1512, 1397, 1346, 1319, 1259, 814, 747, 537  $\text{cm}^{-1}$ ; HRESI-TOF  $m/z$  165.0658 ( $\text{C}_8\text{H}_8\text{N}_2\text{O}_2 + \text{H}^+$  requires 165.0659).



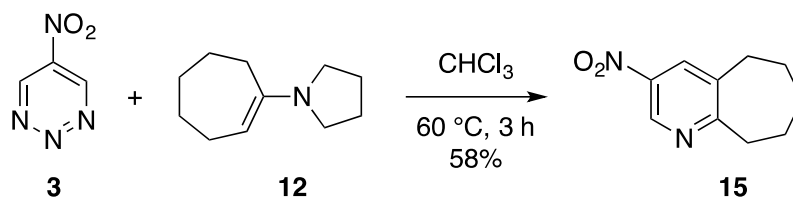
**3-Nitro-6,7-dihydro-5H-cyclopenta[b]pyridine (13).** A 0.2 M solution of enamine **9** (10.0 mg, 0.065 mmol) in  $\text{CHCl}_3$  was treated with a 0.2 M solution of **3** (12.3 mg, 0.098 mmol) in  $\text{CHCl}_3$  at 23  $^\circ\text{C}$ . The reaction mixture was heated to 60  $^\circ\text{C}$  and stirred for 24 h. The mixture was cooled and concentrated and the residue was purified by PTLC ( $\text{SiO}_2$ , 50% EtOAc/hexanes) to provide **13** as a beige solid<sup>8</sup> (5.50 mg, 51%) identical to that detailed above.



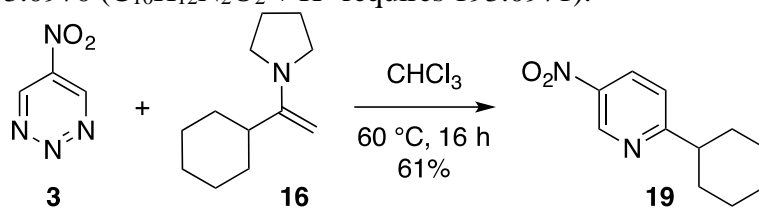
**3-Nitro-5,6,7,8-tetrahydroquinoline (14).** A 0.2 M solution of enamine **10** (8.50  $\mu\text{L}$ , 0.053 mmol) in  $\text{CHCl}_3$  was treated with crushed 4  $\text{\AA}$  molecular sieves (25 mg), then with a 0.2 M solution of **3** (10.0 mg, 0.079 mmol) in  $\text{CHCl}_3$  at 23  $^\circ\text{C}$ . The reaction mixture was heated to 60  $^\circ\text{C}$  and stirred for 24 h. The mixture was cooled and concentrated and the residue was purified by PTLC ( $\text{SiO}_2$ , 50% EtOAc/hexanes) to provide **14** as a white solid<sup>8</sup> (6.50 mg, 69%): mp 59–61  $^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  9.71 (d,  $J = 2.5$  Hz, 1H), 8.16–8.15 (m, 1H), 3.03 (t,  $J = 6.5$  Hz, 2H), 2.90 (t,  $J = 6.1$  Hz, 2H), 1.98–1.94 (m, 2H), 1.89–1.85 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  165.0, 142.7, 142.4, 133.6, 131.6, 33.3, 29.1, 22.8, 22.4; IR (film)  $\nu_{\text{max}}$  2947, 2925, 2860, 1573, 1509, 1449, 1349, 1325, 944, 918, 803, 745  $\text{cm}^{-1}$ ; HRESI-TOF  $m/z$  179.0815 ( $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2 + \text{H}^+$  requires 179.0815).



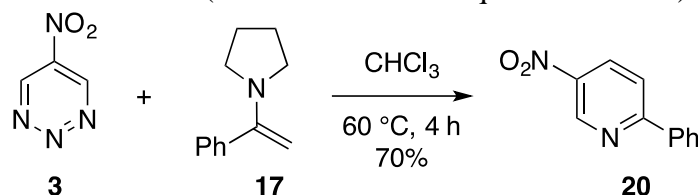
**3-Nitro-5,6,7,8-tetrahydroquinoline (14).** A 0.2 M solution of enamine **11** (10.0 mg, 0.060 mmol) in  $\text{CHCl}_3$  was treated with a 0.2 M solution of **3** (11.3 mg, 0.090 mmol) in  $\text{CHCl}_3$  at 23  $^\circ\text{C}$ . The reaction mixture was heated to 60  $^\circ\text{C}$  and stirred for 24 h. The mixture was cooled and concentrated and the residue was purified by PTLC ( $\text{SiO}_2$ , 50% EtOAc/hexanes) to provide **14** as a white solid<sup>8</sup> (6.74 mg, 63%) identical to that detailed above.



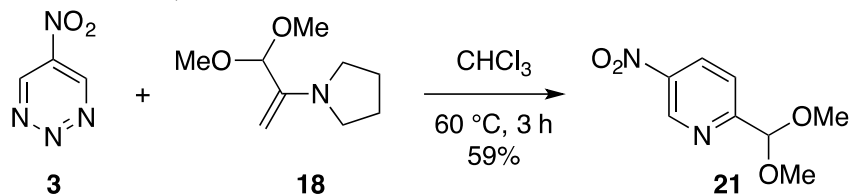
**3-Nitro-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine (15).** A 0.2 M solution of enamine **12**<sup>9</sup> (10.0 mg, 0.061 mmol) in CHCl<sub>3</sub> was treated with a 0.2 M solution of **3** (11.5 mg, 0.091 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 60 °C and stirred for 3 h. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **15** as a light orange film<sup>8</sup> (6.77 mg, 58%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.11 (d, *J* = 2.5 Hz, 1H), 8.16 (d, *J* = 2.4 Hz, 1H), 3.16 (d, *J* = 11.4 Hz, 2H), 2.90 (d, *J* = 11.3 Hz, 2H), 1.92 (p, *J* = 6.0 Hz, 2H), 1.75–1.71 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 170.7, 143.1, 142.0, 139.5, 131.0, 39.9, 35.4, 32.5, 27.8, 26.3; IR (film) ν<sub>max</sub> 2938, 2859, 1592, 1574, 1509, 1444, 1348, 1093, 797 cm<sup>-1</sup>; HRESI-TOF *m/z* 193.0970 (C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> + H<sup>+</sup> requires 193.0971).



**2-Cyclohexyl-5-nitropyridine (19).** A 0.2 M solution of enamine **16**<sup>9</sup> (10.0 mg, 0.056 mmol) in CHCl<sub>3</sub> was treated with a 0.2 M solution of **3** (10.6 mg, 0.084 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 60 °C and stirred for 16 h. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 20% EtOAc/hexanes) to provide **19** as a light yellow film (7.02 mg, 61%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.35 (dd, *J* = 2.7, 0.7 Hz, 1H), 8.38 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.34 (dd, *J* = 8.6, 0.6 Hz, 1H), 2.84 (tt, *J* = 11.9, 3.4 Hz, 1H), 1.96 (d, *J* = 13.2 Hz, 2H), 1.89 (dt, *J* = 13.3, 3.5 Hz, 2H), 1.78 (dtt, *J* = 12.9, 3.2, 1.6 Hz, 1H), 1.55 (qd, *J* = 12.6, 3.2 Hz, 2H), 1.43 (qt, *J* = 13.0, 3.4 Hz, 2H), 1.31 (tt, *J* = 12.7, 3.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 173.6, 145.0, 142.9, 131.8, 121.6, 47.1, 32.9, 26.6, 26.2; IR (film) ν<sub>max</sub> 2927, 2851, 1595, 1572, 1514, 1346, 849 cm<sup>-1</sup>; HRESI-TOF *m/z* 207.1129 (C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> + H<sup>+</sup> requires 207.1128).

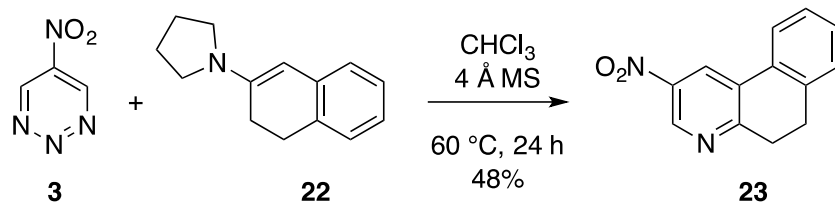


**5-Nitro-2-phenylpyridine (20).** A 0.2 M solution of enamine **17**<sup>9</sup> (10.0 mg, 0.058 mmol) in CHCl<sub>3</sub> was treated with a 0.2 M solution of **3** (10.9 mg, 0.087 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 60 °C and stirred for 4 h. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 20% EtOAc/hexanes) to provide **20** as a light yellow solid<sup>8</sup> (8.05 mg, 70%): mp 98–101 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.51 (d, *J* = 2.6 Hz, 1H), 8.54 (dd, *J* = 8.8, 2.7 Hz, 1H), 8.10–8.09 (m, 2H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.54–7.53 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 162.9, 145.6, 143.3, 137.4, 132.3, 131.3, 129.5, 128.1, 120.4; IR (film) ν<sub>max</sub> 2922, 1574, 1518, 1448, 1342, 850, 737, 685 cm<sup>-1</sup>; HRESI-TOF *m/z* 201.0660 (C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> + H<sup>+</sup> requires 201.0659).



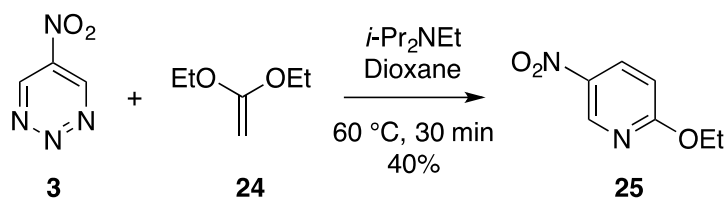
**2-(Dimethoxymethyl)-5-nitropyridine (21).** A 0.2 M solution of enamine **18**<sup>9</sup> (10.0 mg, 0.058 mmol) in CHCl<sub>3</sub> was treated with a 0.2 M solution of **3** (11.0 mg, 0.088 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 60 °C and stirred for 3 h. The mixture was cooled and concentrated and the residue was purified

by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **21** as a light orange film (6.87 mg, 59%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.43 (dd, *J* = 2.7, 0.7 Hz, 1H), 8.52 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 5.45 (s, 1H), 3.44 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 163.6, 144.9, 144.3, 132.1, 122.1, 103.4, 54.3; IR (film) ν<sub>max</sub> 2923, 1599, 1521, 1343, 1053, 863, 846, 760, 729 cm<sup>-1</sup>; HRESI-TOF *m/z* 199.0713 (C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub> + H<sup>+</sup> requires 199.0713).

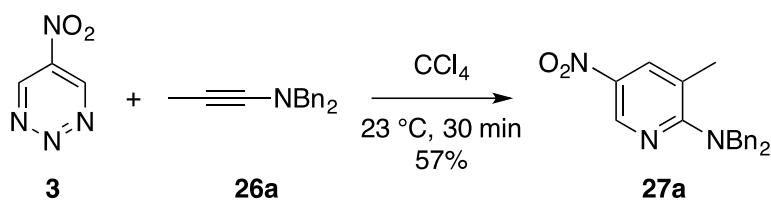


**2-Nitro-5,6-dihydrobenzof[7]quinoline (23).** A 0.2 M solution of enamine **22** (10.0 mg, 0.050 mmol) in CHCl<sub>3</sub> was treated with crushed 4 Å molecular sieves (25 mg), then with a 0.2 M solution of **3** (9.50 mg, 0.075 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 60 °C and stirred for 24 h. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **23** as an orange film (5.50 mg, 48%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.27 (d, *J* = 2.5 Hz, 1H), 8.77 (d, *J* = 2.4 Hz, 1H), 7.82 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.42 (dp, *J* = 7.4, 1.6 Hz, 2H), 7.36–7.34 (m, 1H), 3.25 (dd, *J* = 8.6, 6.2 Hz, 2H), 3.09 (dd, *J* = 8.6, 6.2 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 164.6, 145.6, 143.0, 137.2, 131.2, 131.1, 130.2, 129.0, 128.1, 125.4, 124.8, 32.3, 28.3; IR (film) ν<sub>max</sub> 3077, 2955, 1594, 1517, 1407, 1342, 806, 783, 739 cm<sup>-1</sup>; HRESI-TOF *m/z* 227.0820 (C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> + H<sup>+</sup> requires 227.0815).

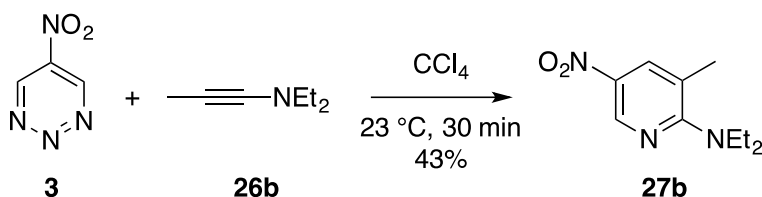
## V. Reaction of **3** with Ynamines, Ketene Acetals, and Enol Ethers



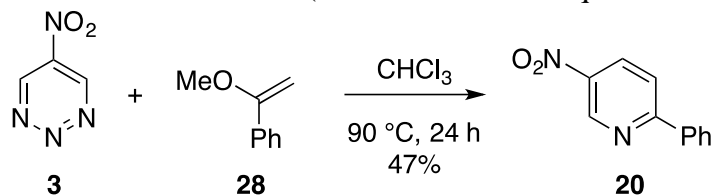
**2-Ethoxy-5-nitropyridine (25).** A 0.04 M solution of **3** (32.6 mg, 0.258 mmol) in dioxane was heated to 60 °C and treated with *i*-Pr<sub>2</sub>NEt (13.5 μL, 0.078 mmol). The resulting reaction mixture was then rapidly treated with a 0.04 M solution of 1,1-diethoxyethene (**24**, 10.0 mg, 0.086 mmol) and stirred for 30 min. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **25** as a light yellow solid<sup>10</sup> (5.73 mg, 40%): mp 65–67 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 9.06 (d, *J* = 2.9 Hz, 1H), 8.33 (dd, *J* = 9.1, 2.3 Hz, 1H), 6.79 (d, *J* = 9.1 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 167.4, 145.2, 139.6, 134.1, 111.6, 63.9, 14.7; IR (film) ν<sub>max</sub> 2923, 1736, 1604, 1577, 1347, 1272, 1024, 1006, 918, 846, 765, 682, 533 cm<sup>-1</sup>; HRESI-TOF *m/z* 169.0608 (C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub> + H<sup>+</sup> requires 169.0608).



***N,N*-Dibenzyl-3-methyl-5-nitropyridin-2-amine (27a).** A 0.001 M solution of ynamine **26a**<sup>11</sup> (14.0 mg, 0.060 mmol) in CCl<sub>4</sub> was treated with **3** (11.3 mg, 0.089 mmol). The reaction mixture was stirred at 23 °C for 30 min. The mixture was concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **27a** as a yellow film (11.3 mg, 57%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 8.98 (d, *J* = 2.7 Hz, 1H), 8.14 (d, *J* = 1.8 Hz, 1H), 7.36–7.33 (m, 4H), 7.31–7.28 (m, 2H), 7.24–7.23 (m, 4H), 4.74 (s, 4H), 2.45 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 163.8, 142.9, 138.0, 137.8, 135.7, 129.0, 127.9, 127.7, 120.1, 53.5, 21.0; IR (film) ν<sub>max</sub> 1728, 1683, 1578, 1495, 1321, 1242, 1175, 1115, 698, 552 cm<sup>-1</sup>; HRESI-TOF *m/z* 334.1550 (C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 334.1550).



***N,N*-Diethyl-3-methyl-5-nitropyridin-2-amine (27b).** A 0.01 M solution of ynamine **26b**<sup>11</sup> (10.0 mg, 0.090 mmol) in CCl<sub>4</sub> was treated with **3** (34.0 mg, 0.270 mmol). The reaction mixture was stirred at 23 °C for 30 min. The mixture was concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 50% EtOAc/hexanes) to provide **27b** as a yellow film (7.99 mg, 43%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 8.91 (dd, *J* = 2.7, 0.6 Hz, 1H), 8.02 (dd, *J* = 2.7, 0.8 Hz, 1H), 3.53 (q, *J* = 7.0 Hz, 4H), 2.36 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 163.2, 143.0, 136.6, 135.1, 119.2, 44.9, 21.3, 14.0; IR (film) ν<sub>max</sub> 2973, 2932, 1588, 1573, 1489, 1431, 1320, 1299, 1270, 1108 cm<sup>-1</sup>; HRESI-TOF *m/z* 210.1238 (C<sub>10</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> + H<sup>+</sup> requires 210.1237).



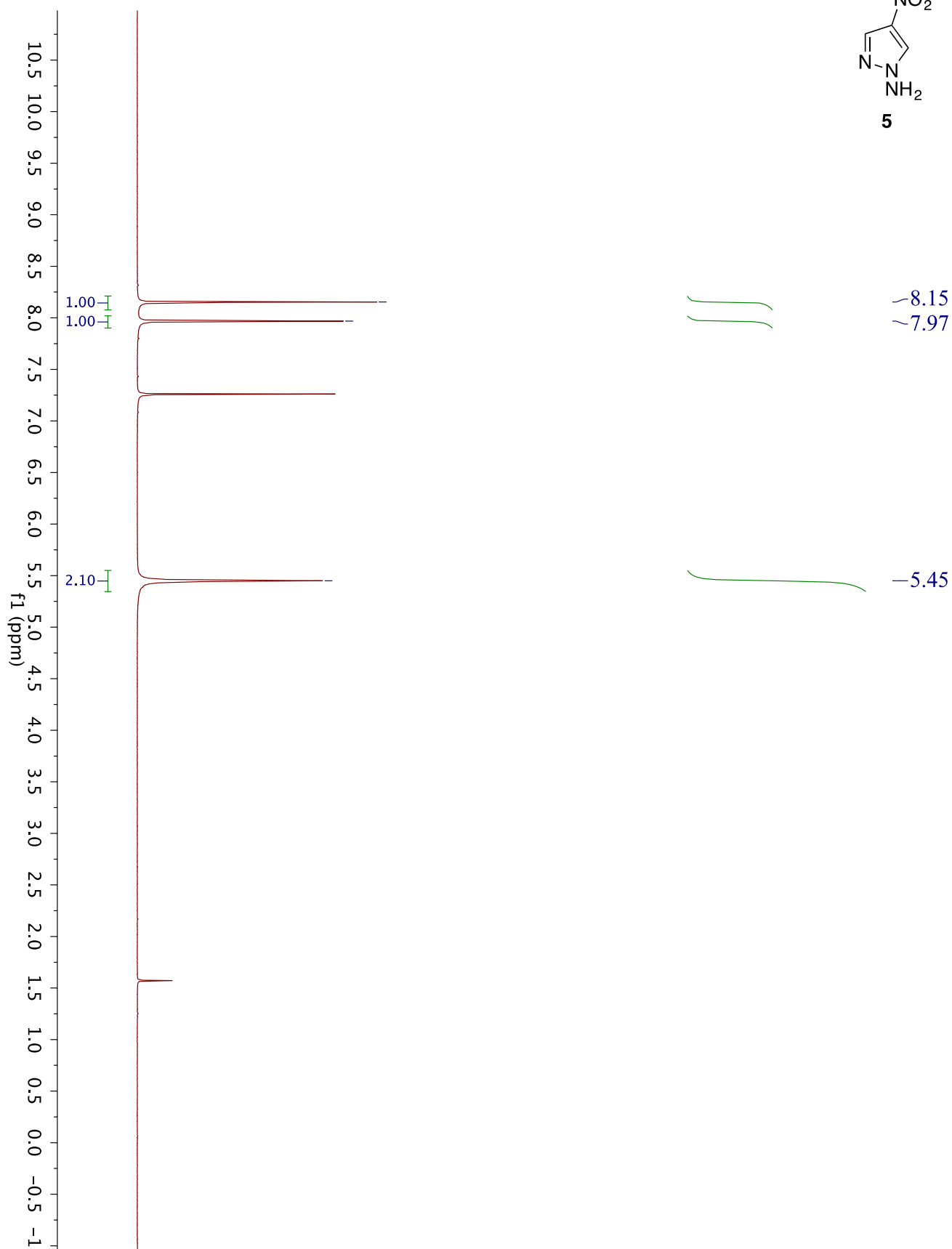
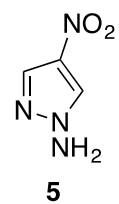
**5-Nitro-2-phenylpyridine (20).** A 0.04 M solution of enol ether **28**<sup>12</sup> (4.10 mg, 0.031 mmol) in CHCl<sub>3</sub> was treated with **3** (14.1 mg, 0.112 mmol) in CHCl<sub>3</sub> at 23 °C. The reaction mixture was heated to 90 °C and stirred

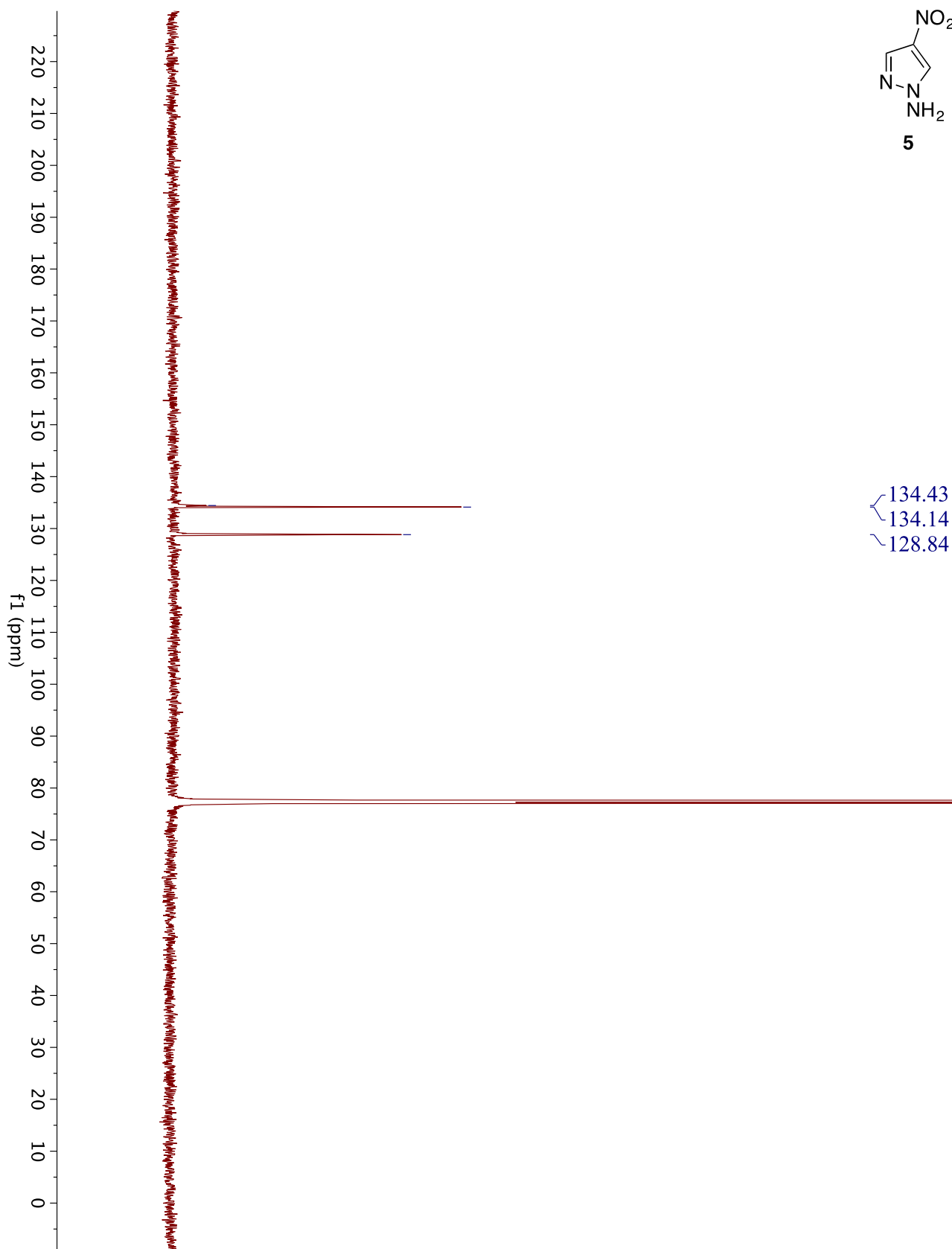
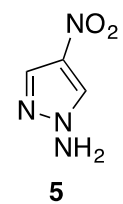
for 24 h. The mixture was cooled and concentrated and the residue was purified by PTLC (SiO<sub>2</sub>, 20% EtOAc/hexanes) to provide **20** as a light yellow solid (2.90 mg, 47%) identical to that detailed above.

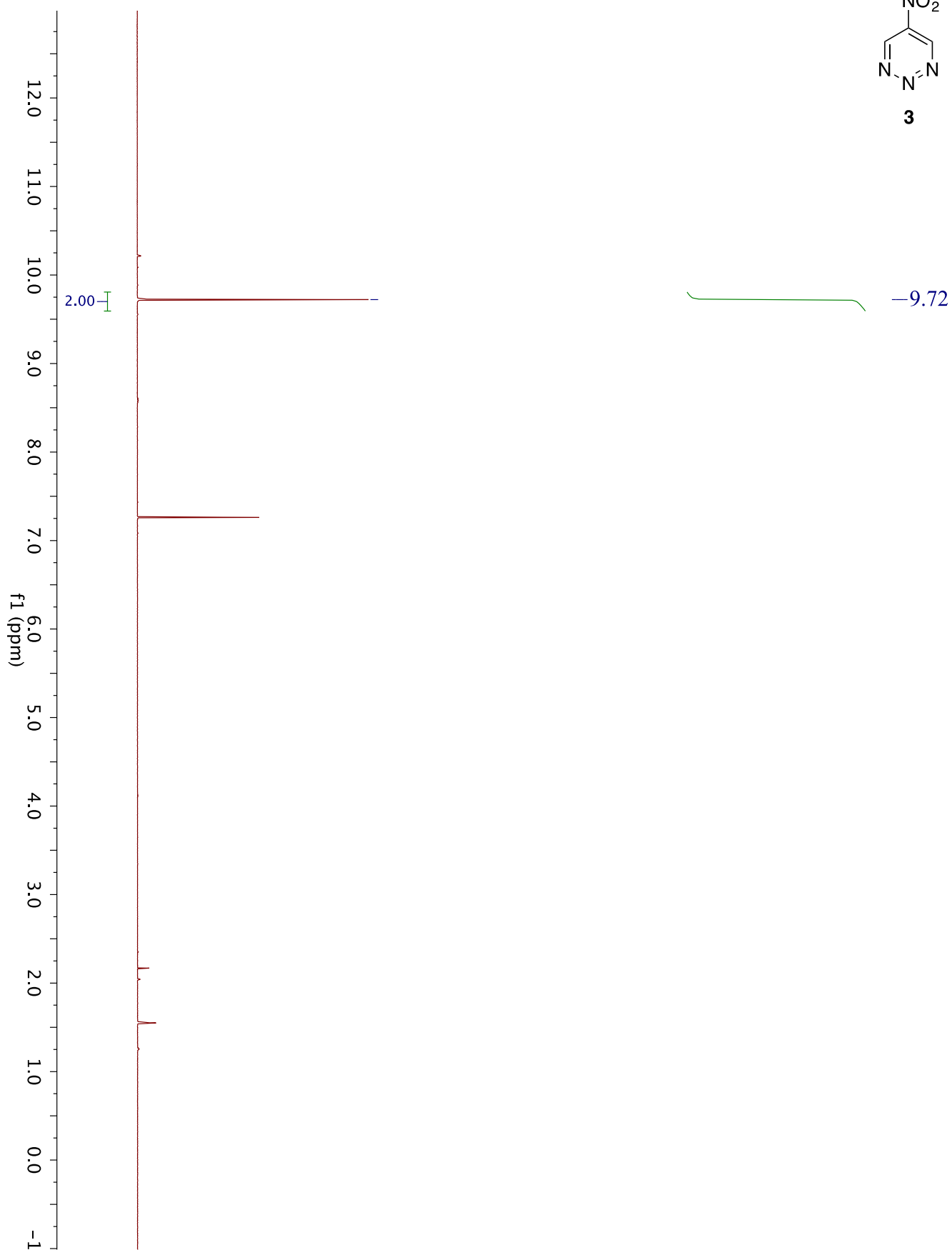
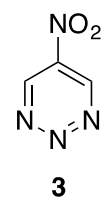
## VI. References

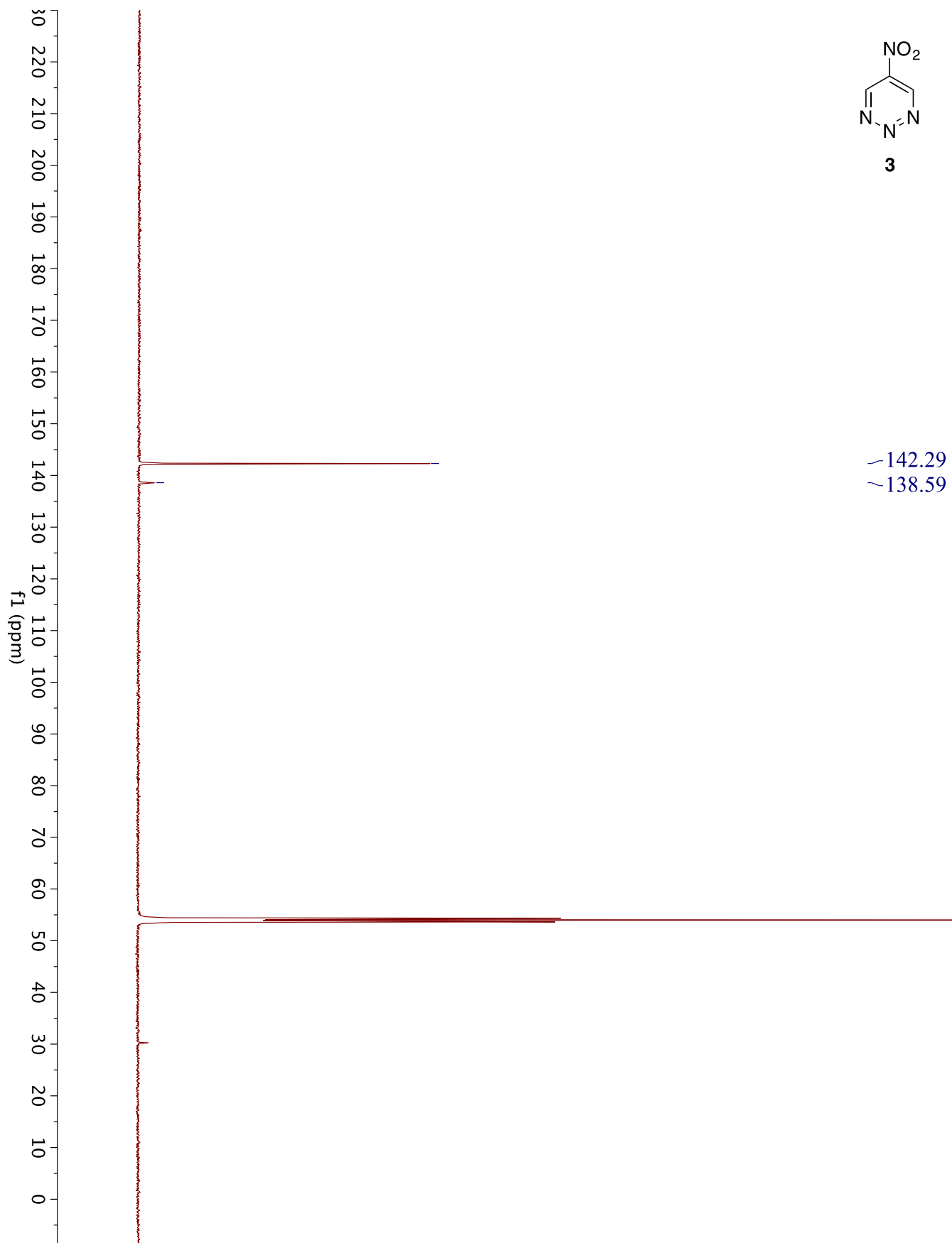
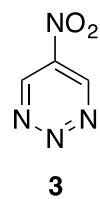
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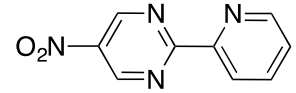
## VII. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



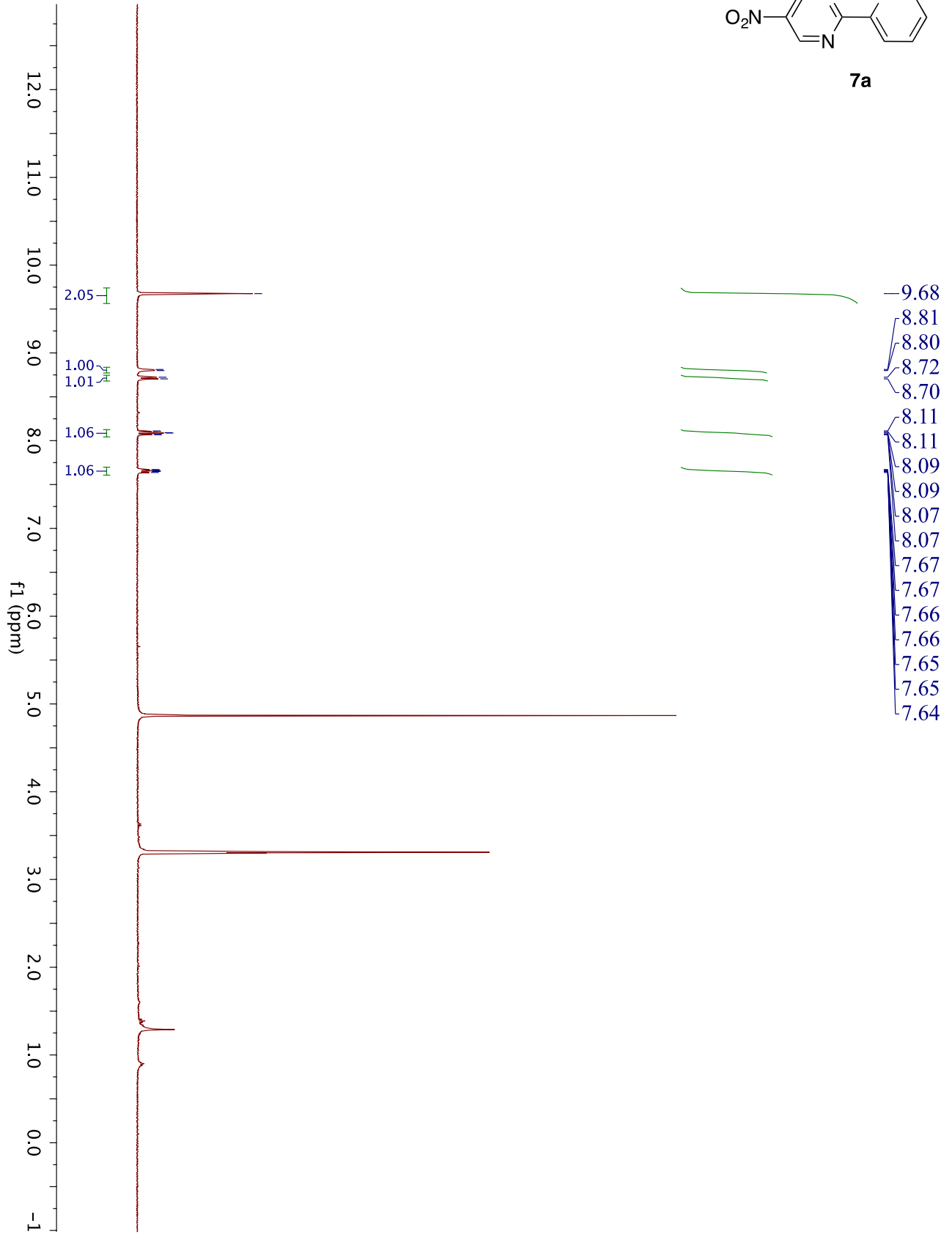


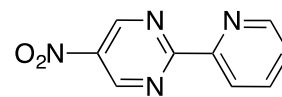




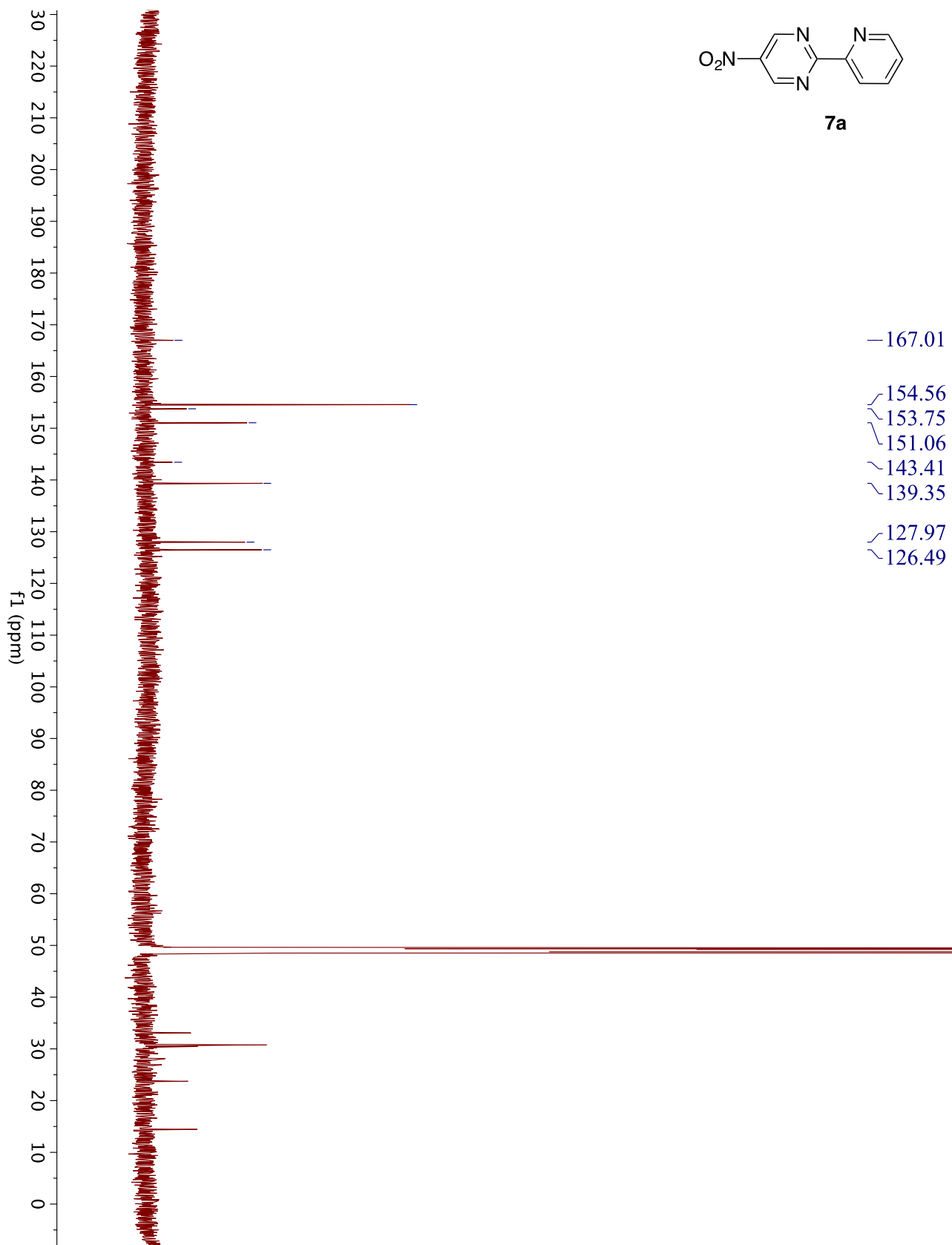


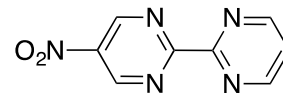
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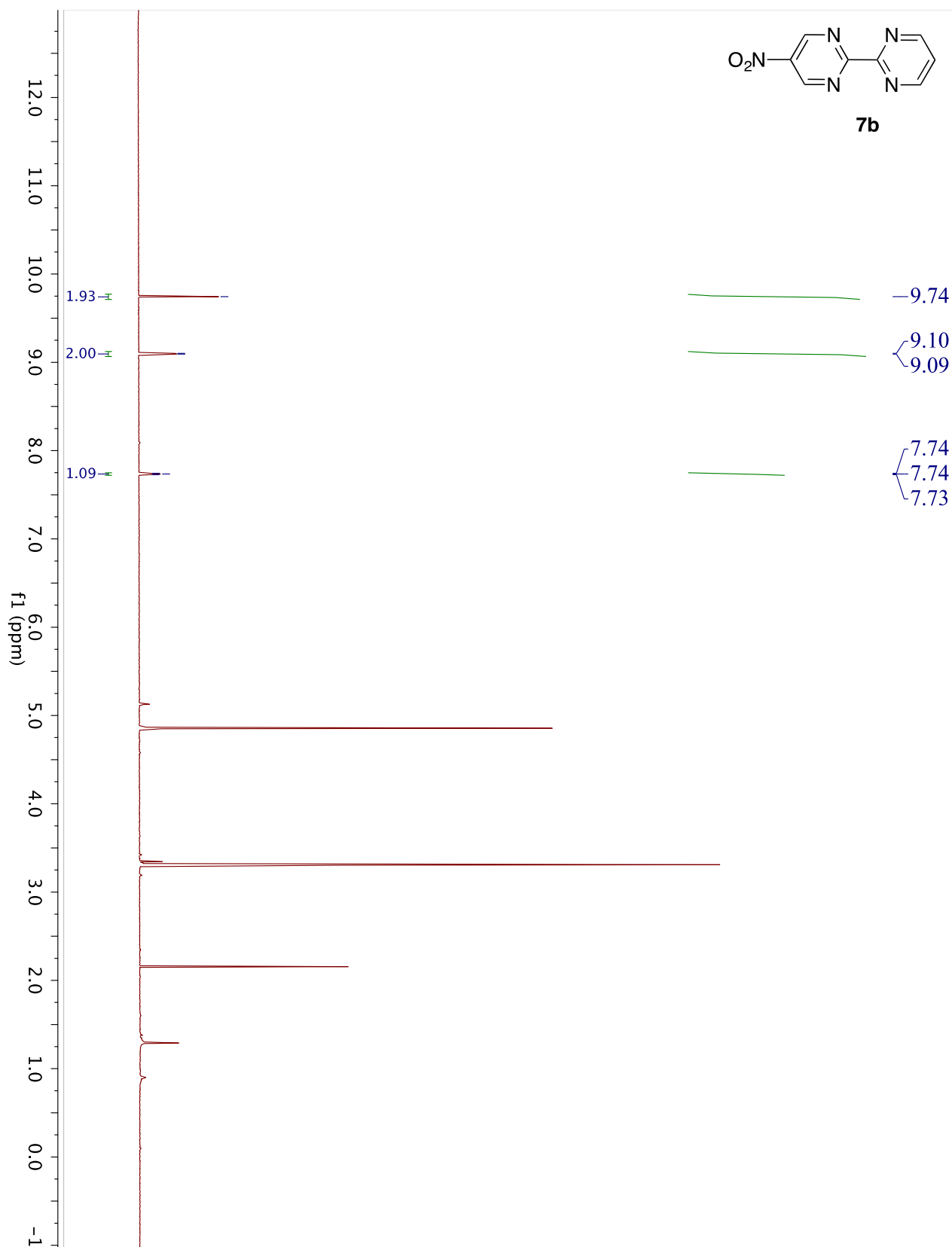


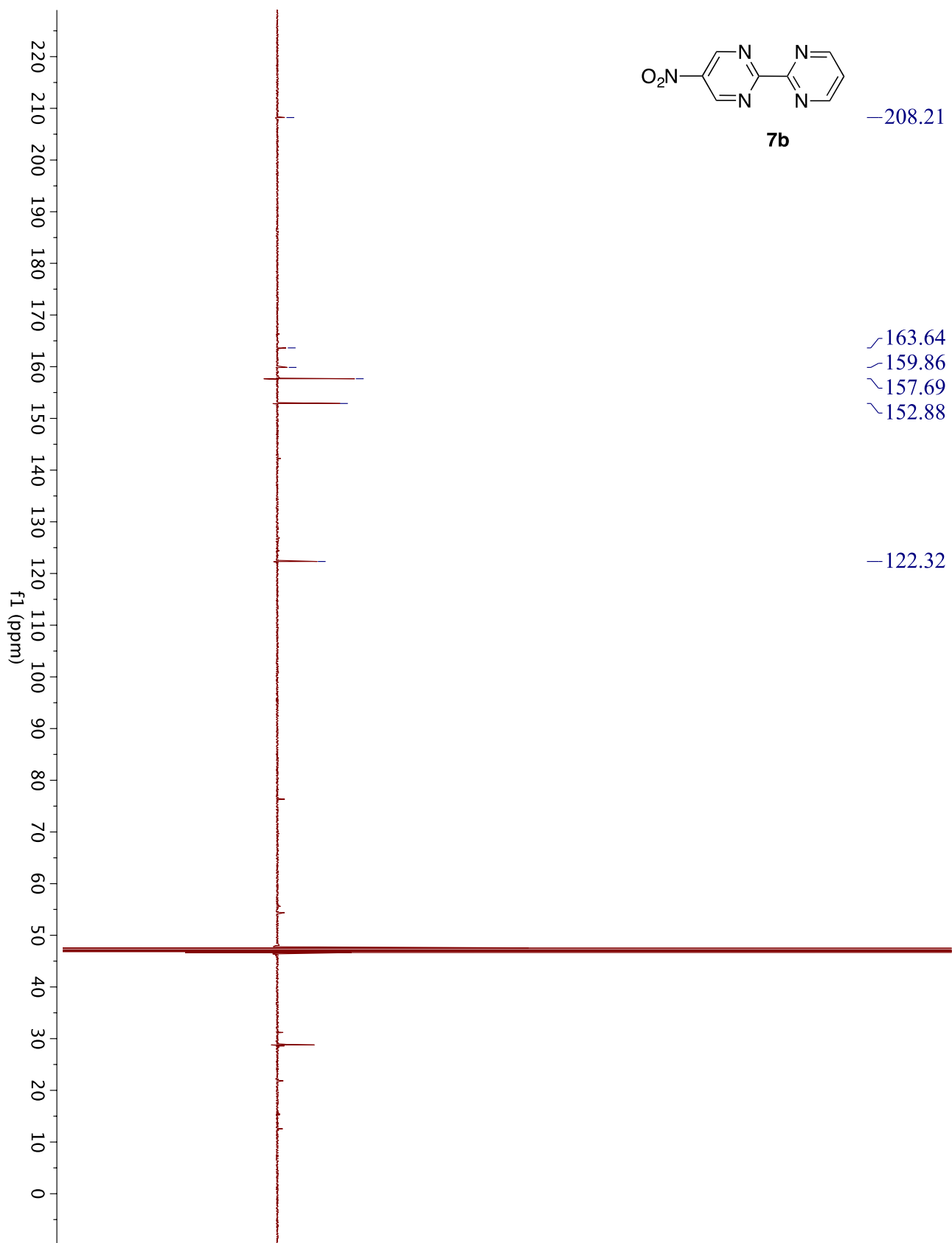
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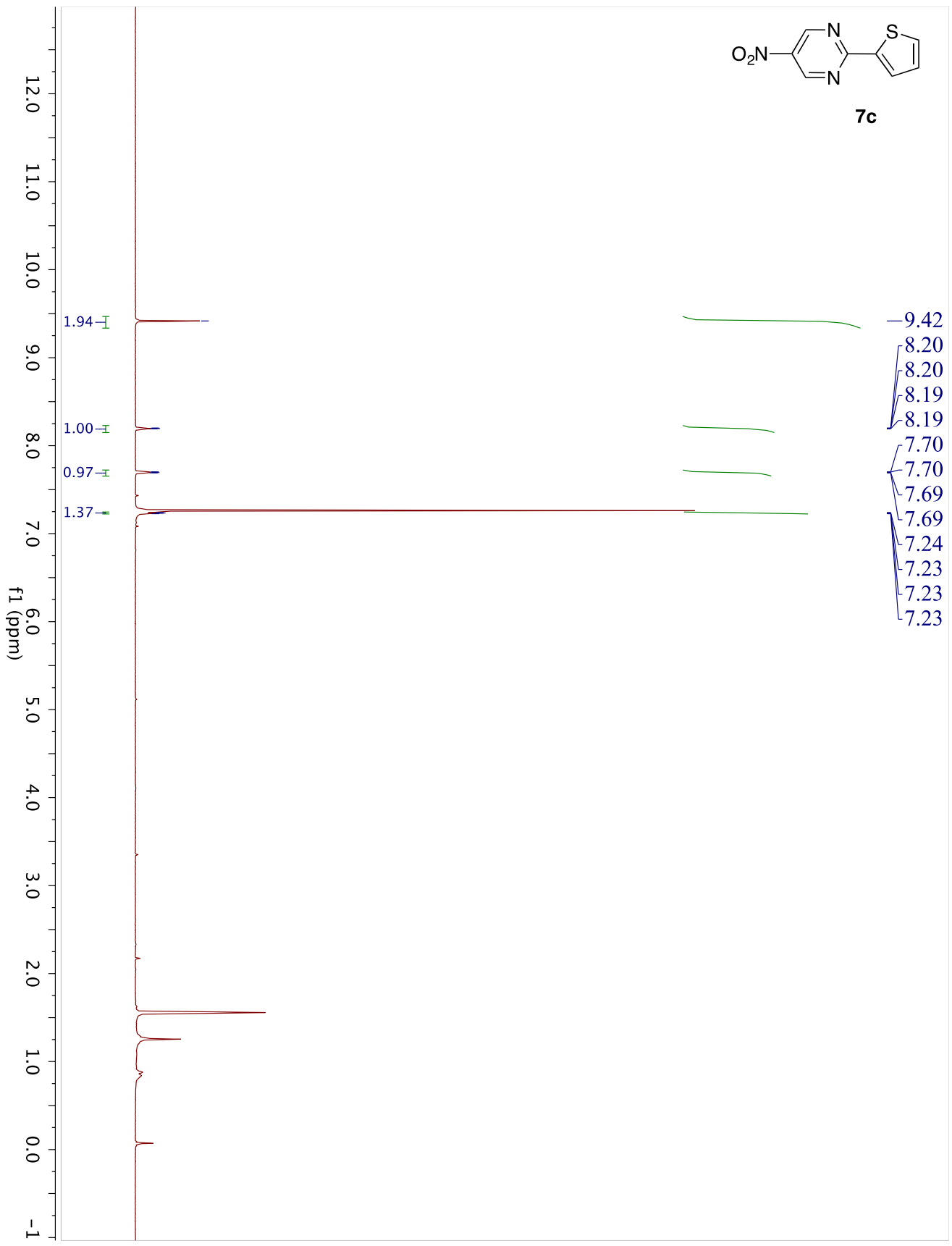


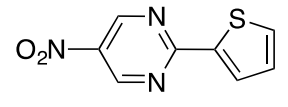


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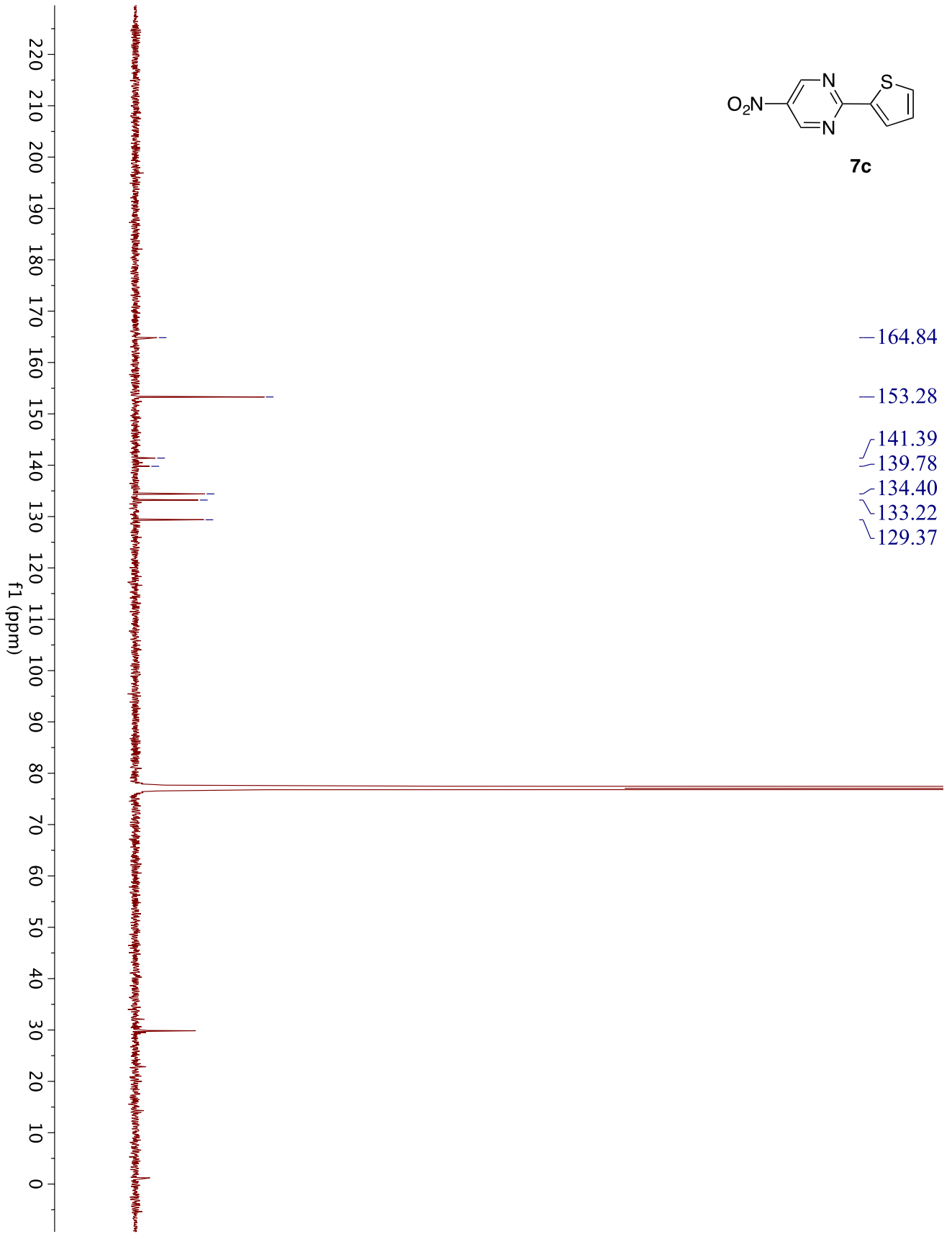


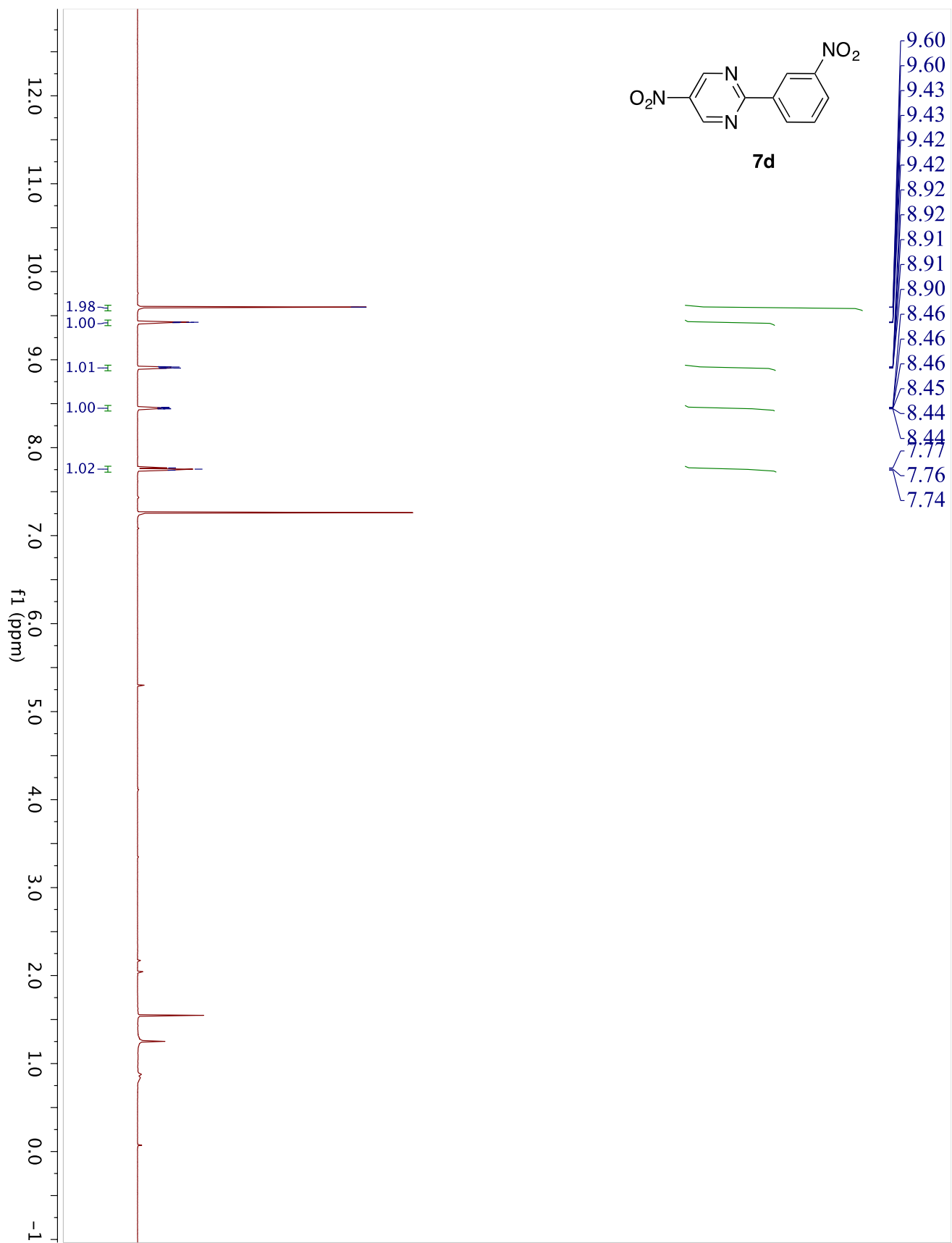


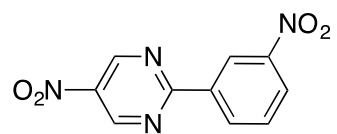


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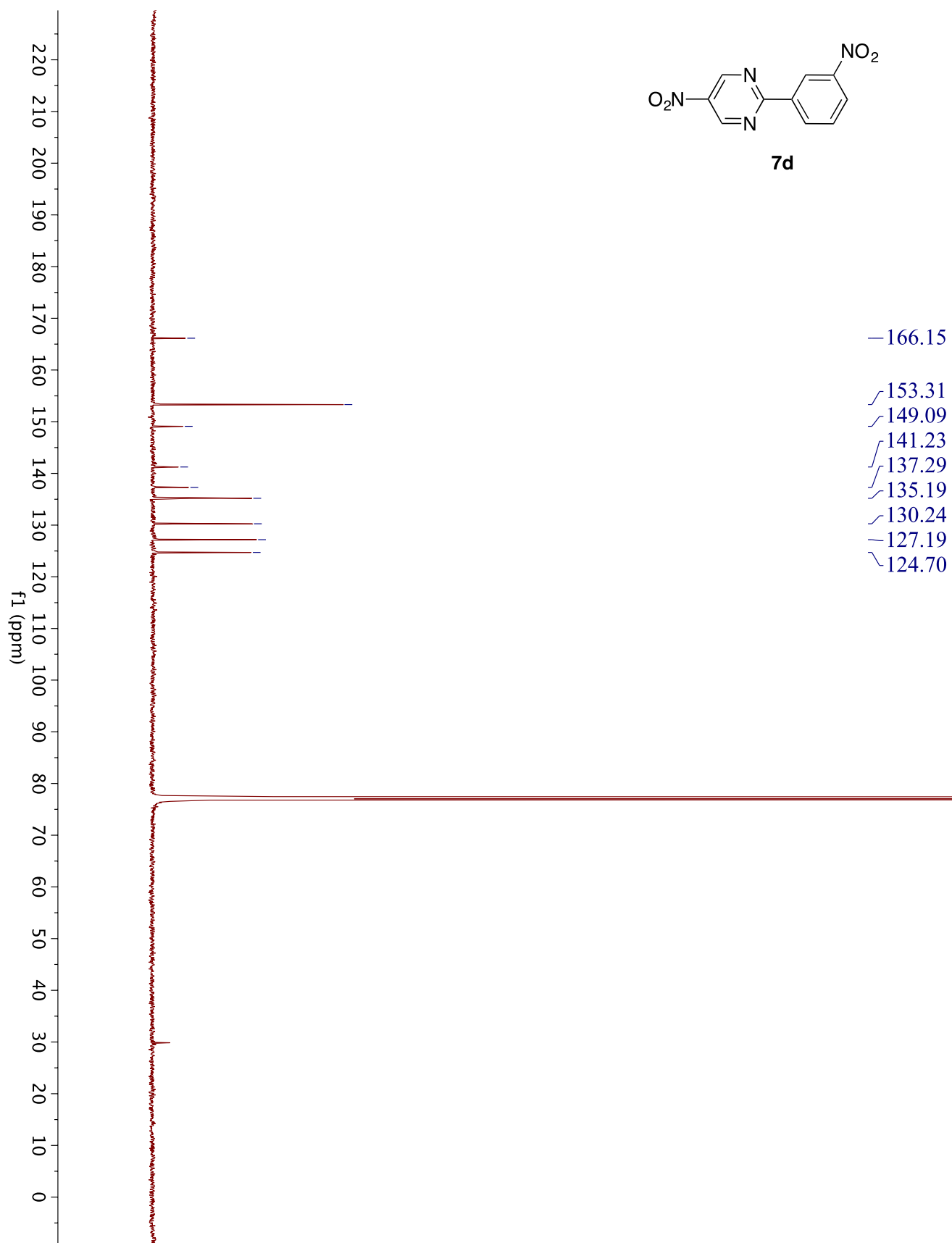
- 164.84
- 153.28
- 141.39
- 139.78
- 134.40
- 133.22
- 129.37

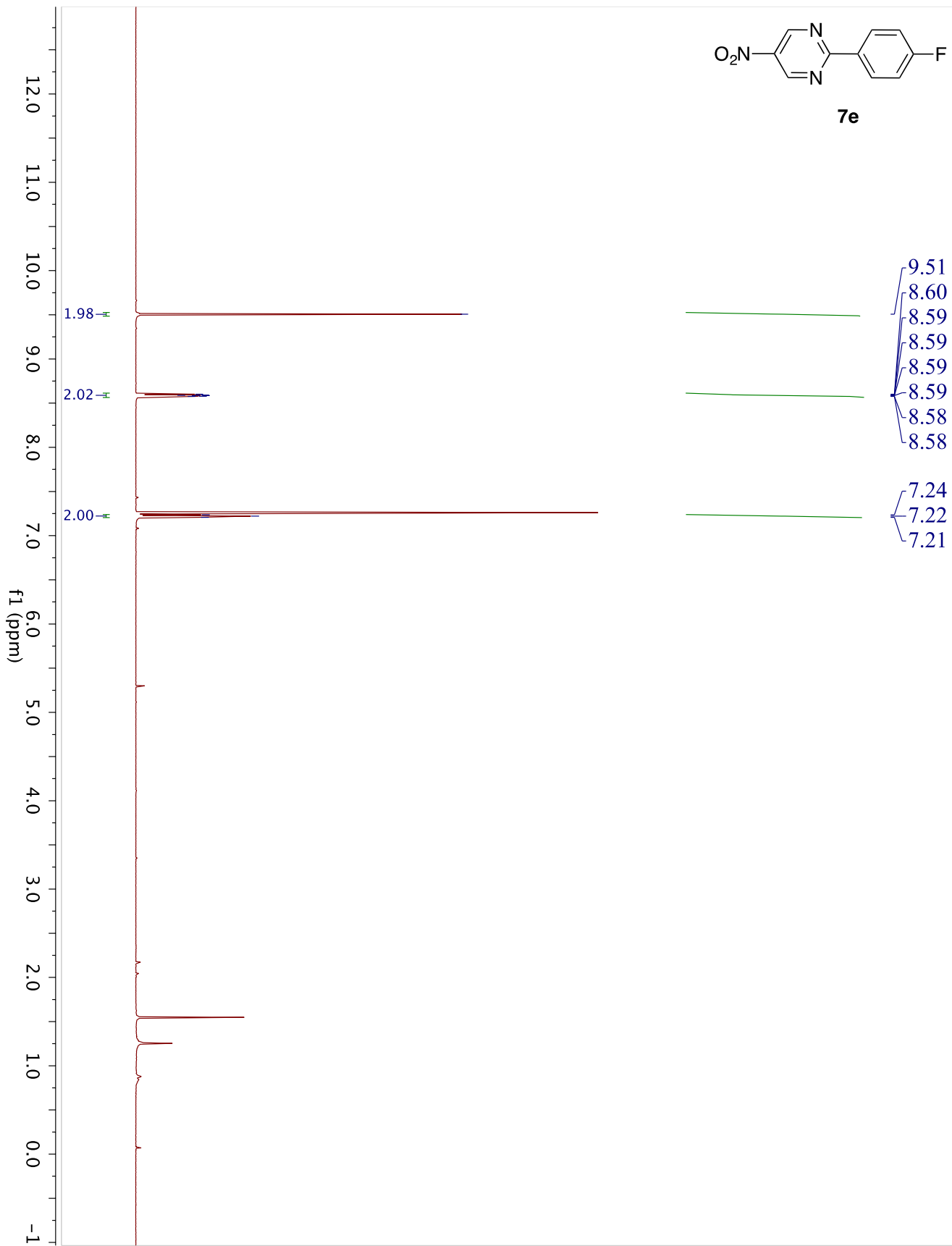


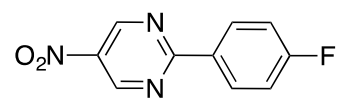




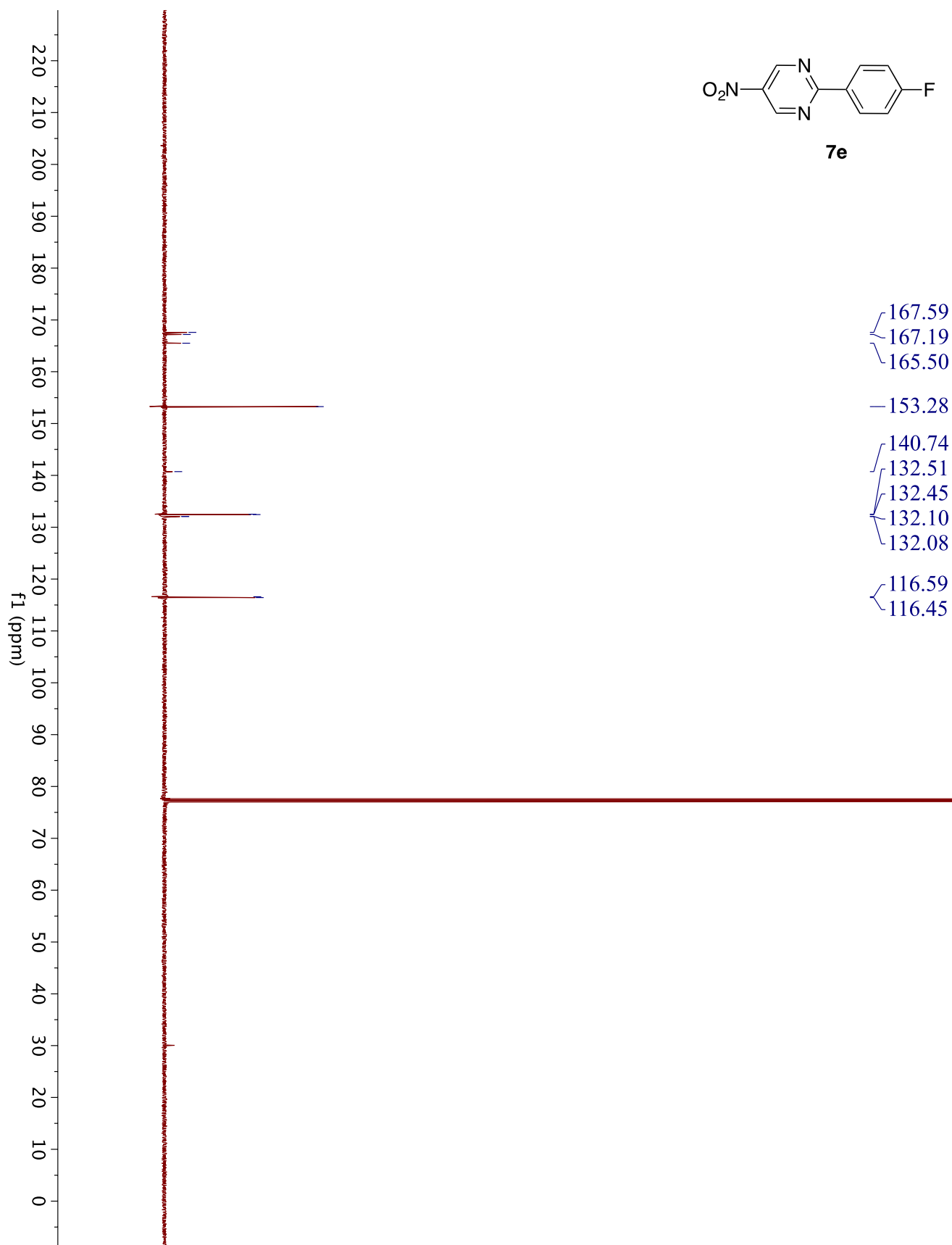
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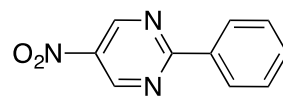




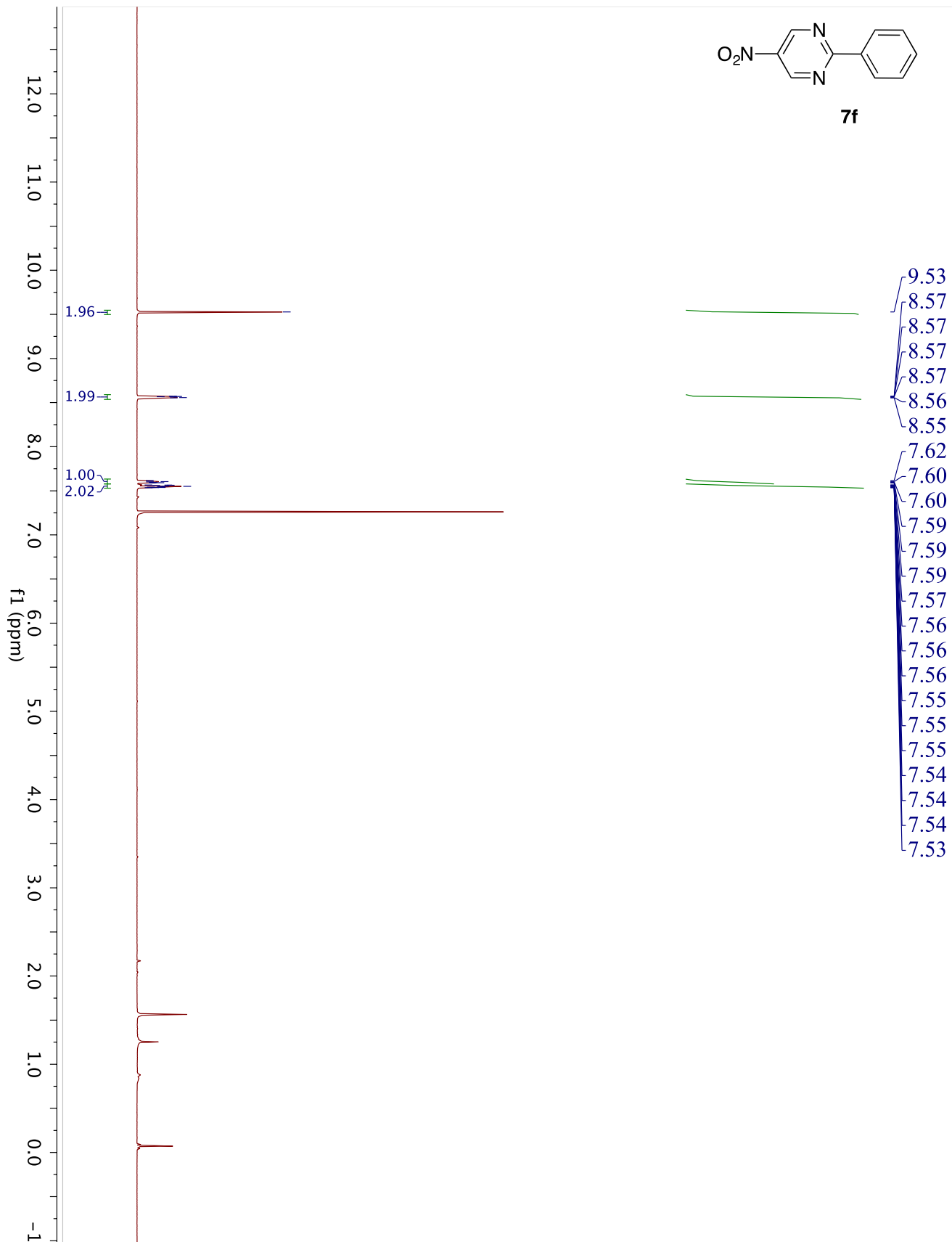


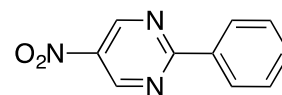
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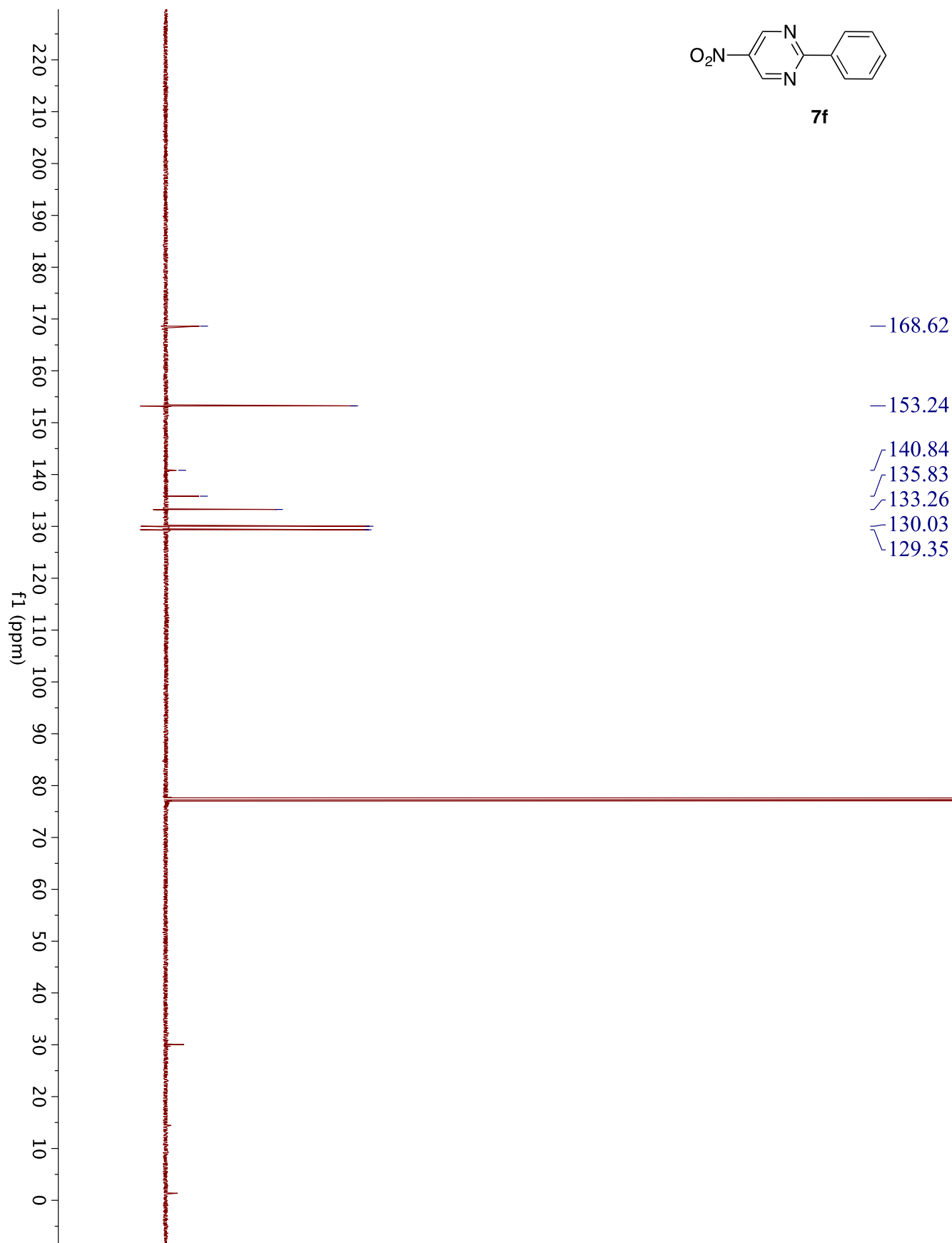


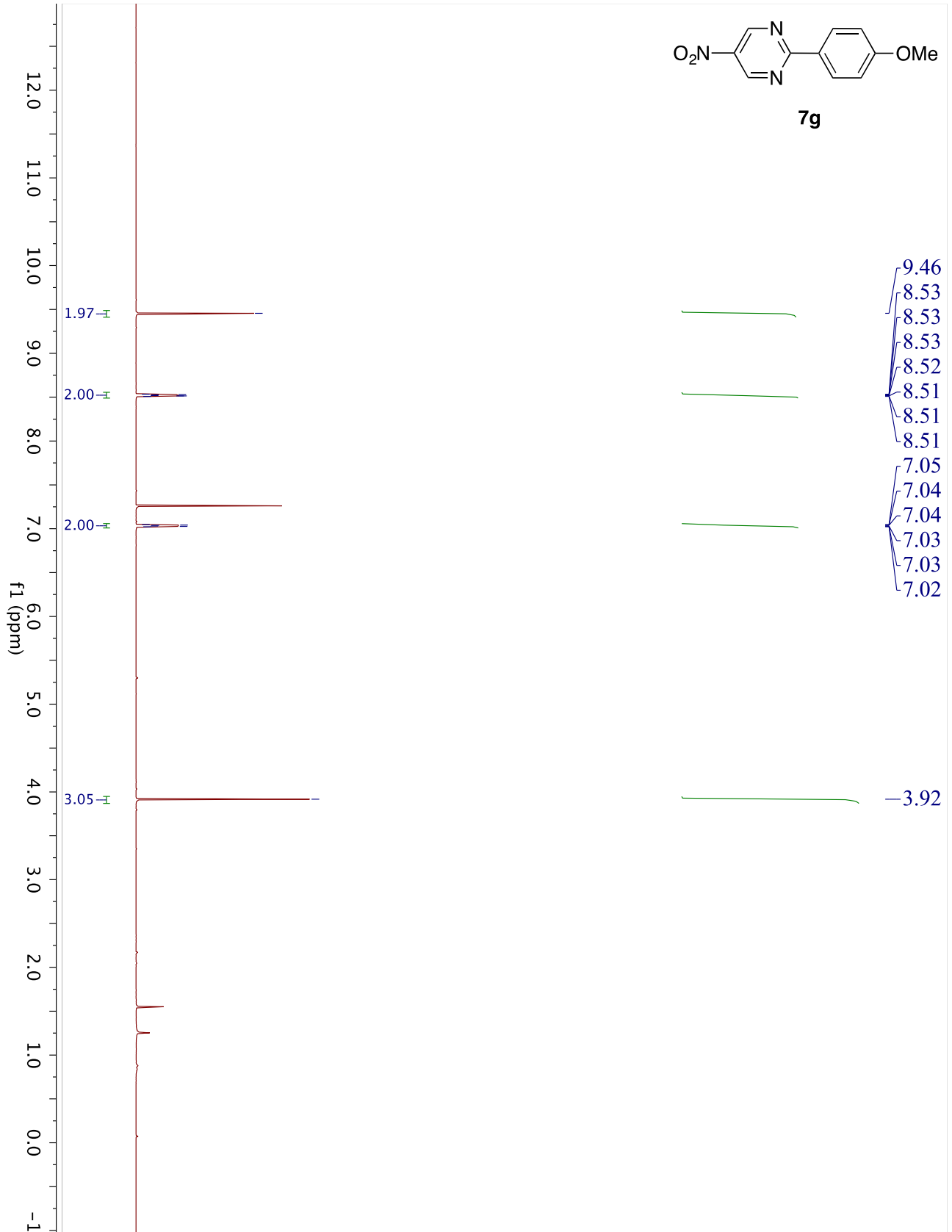
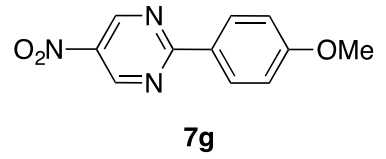
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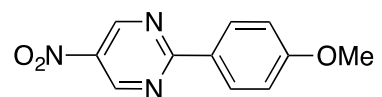




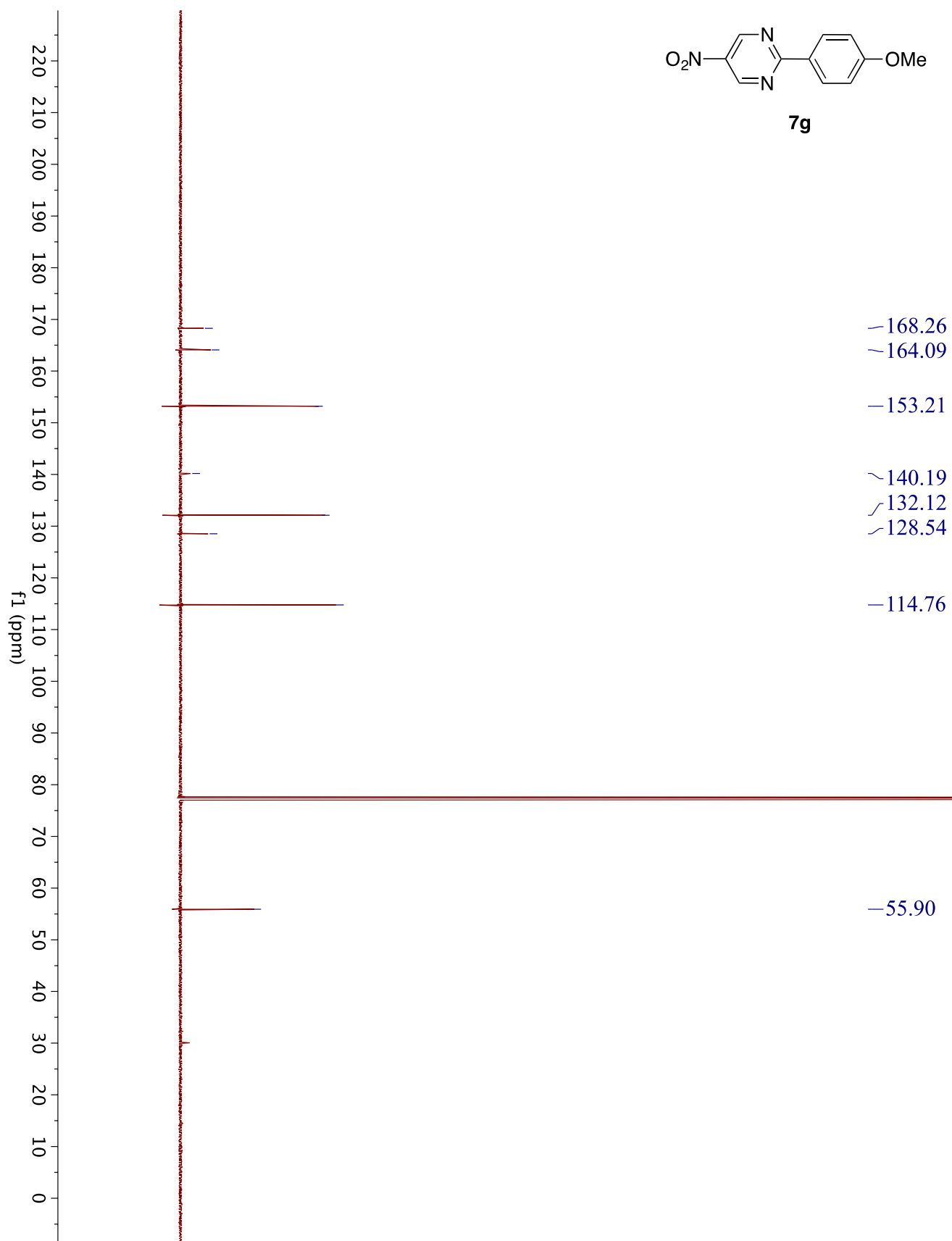
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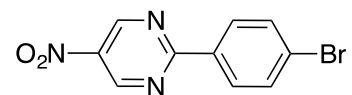




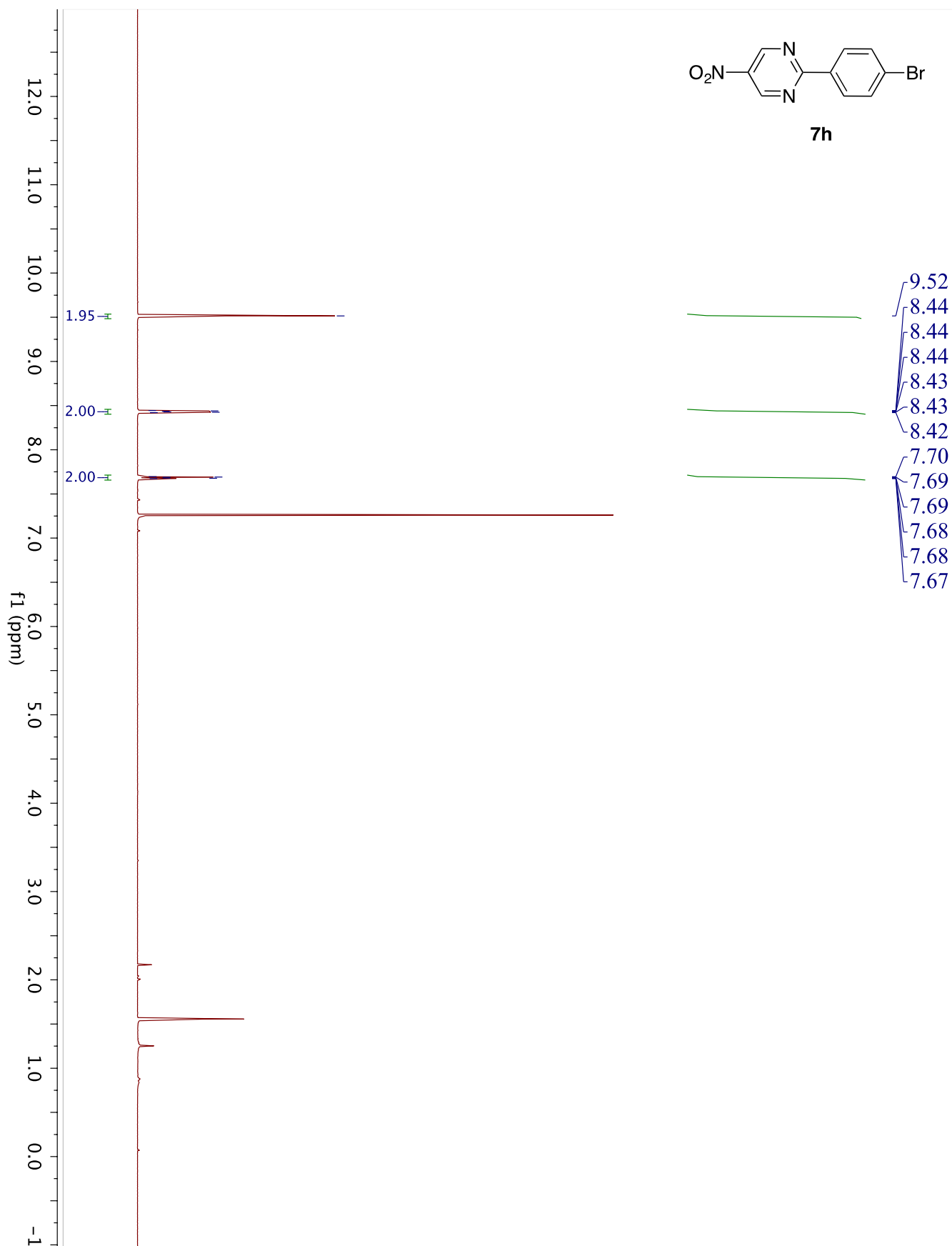


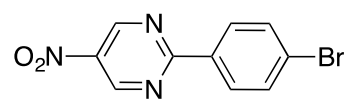
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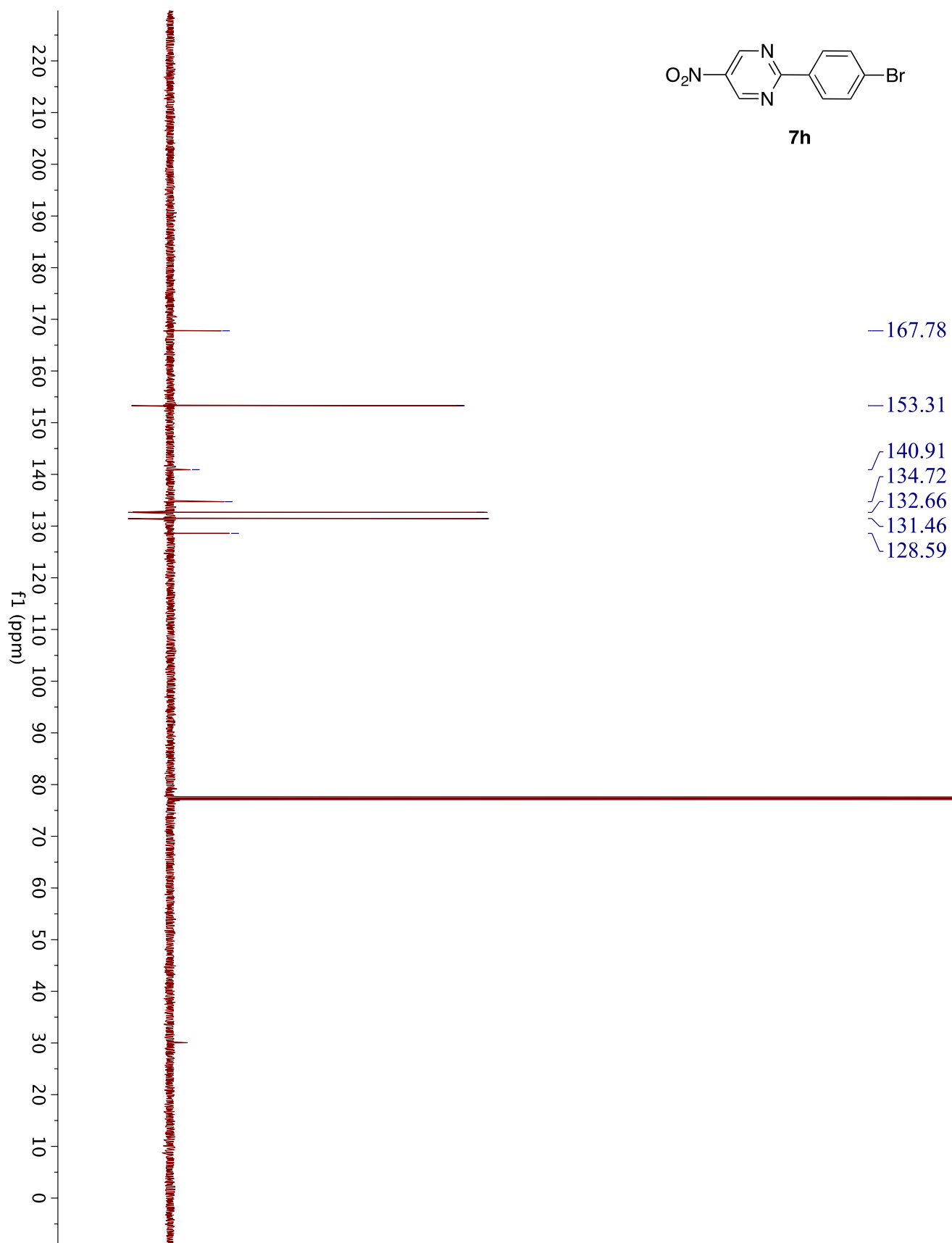


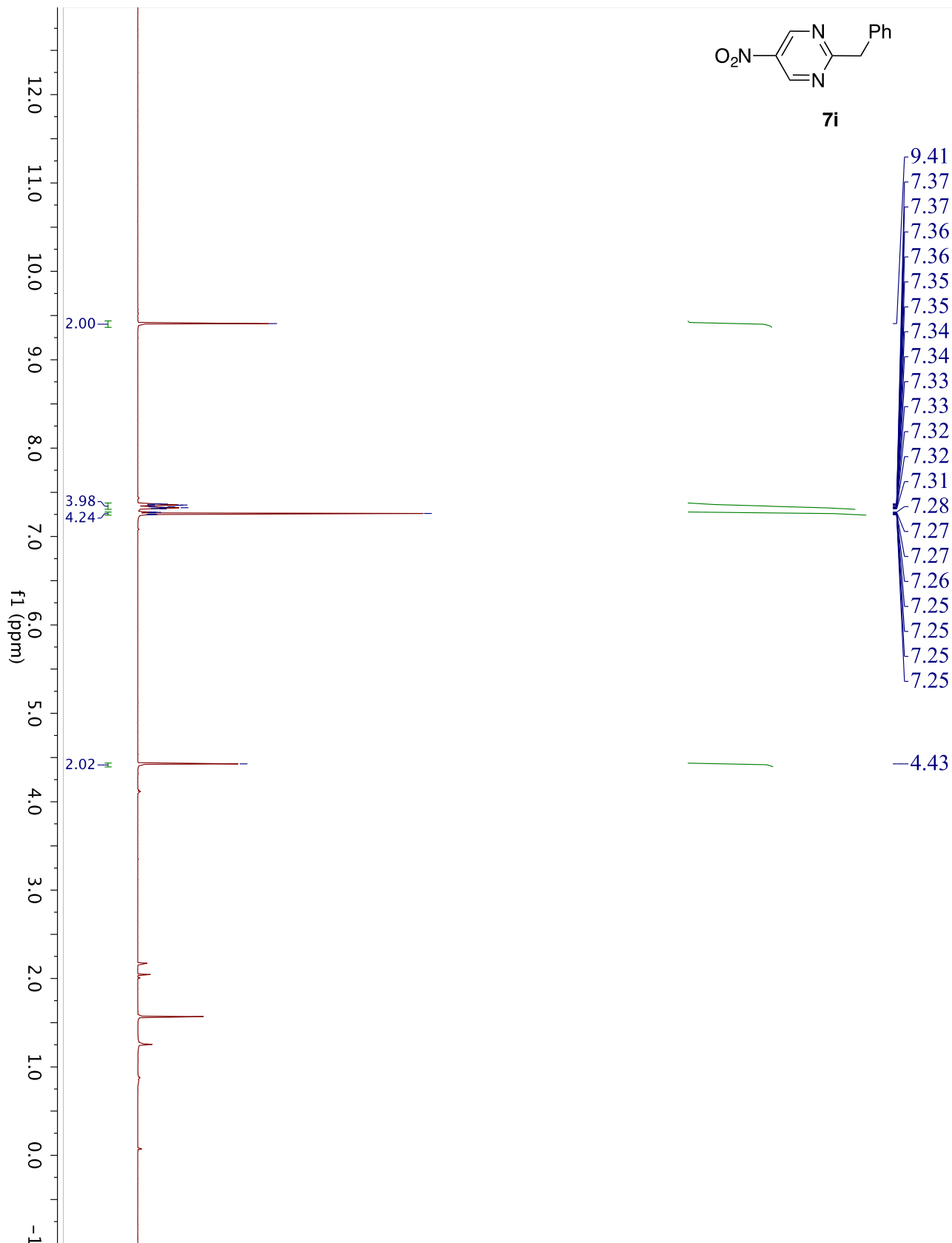
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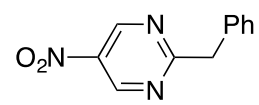




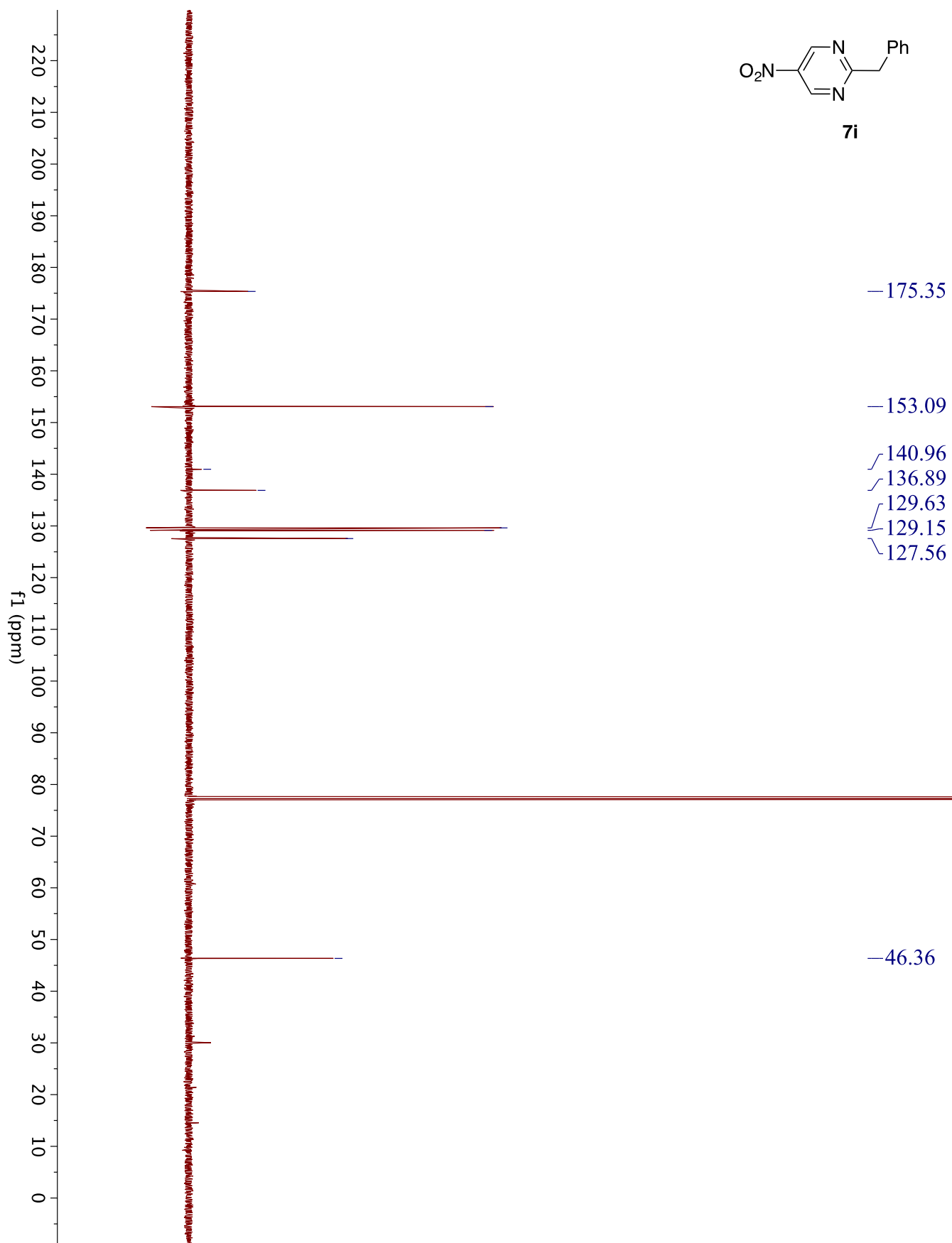
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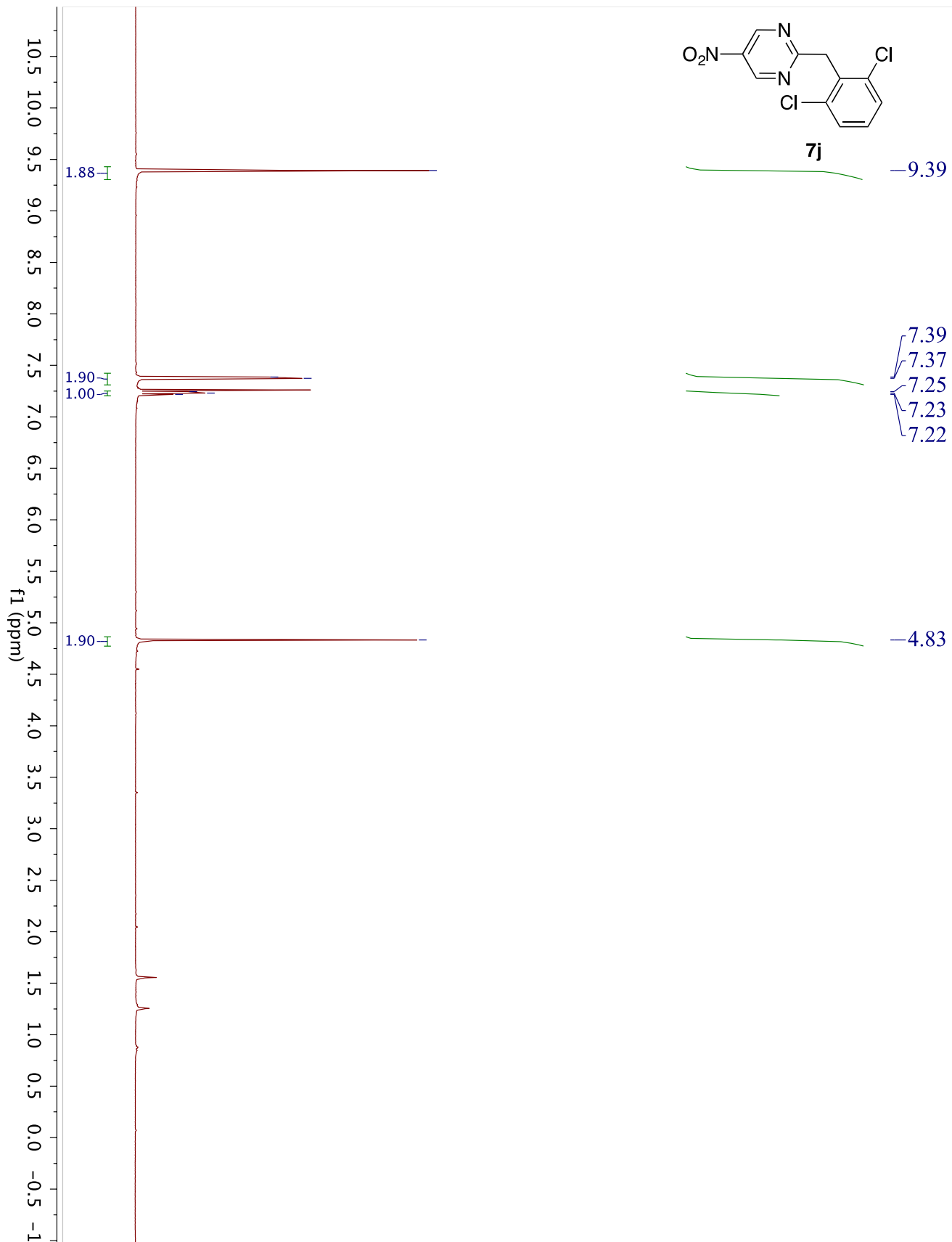


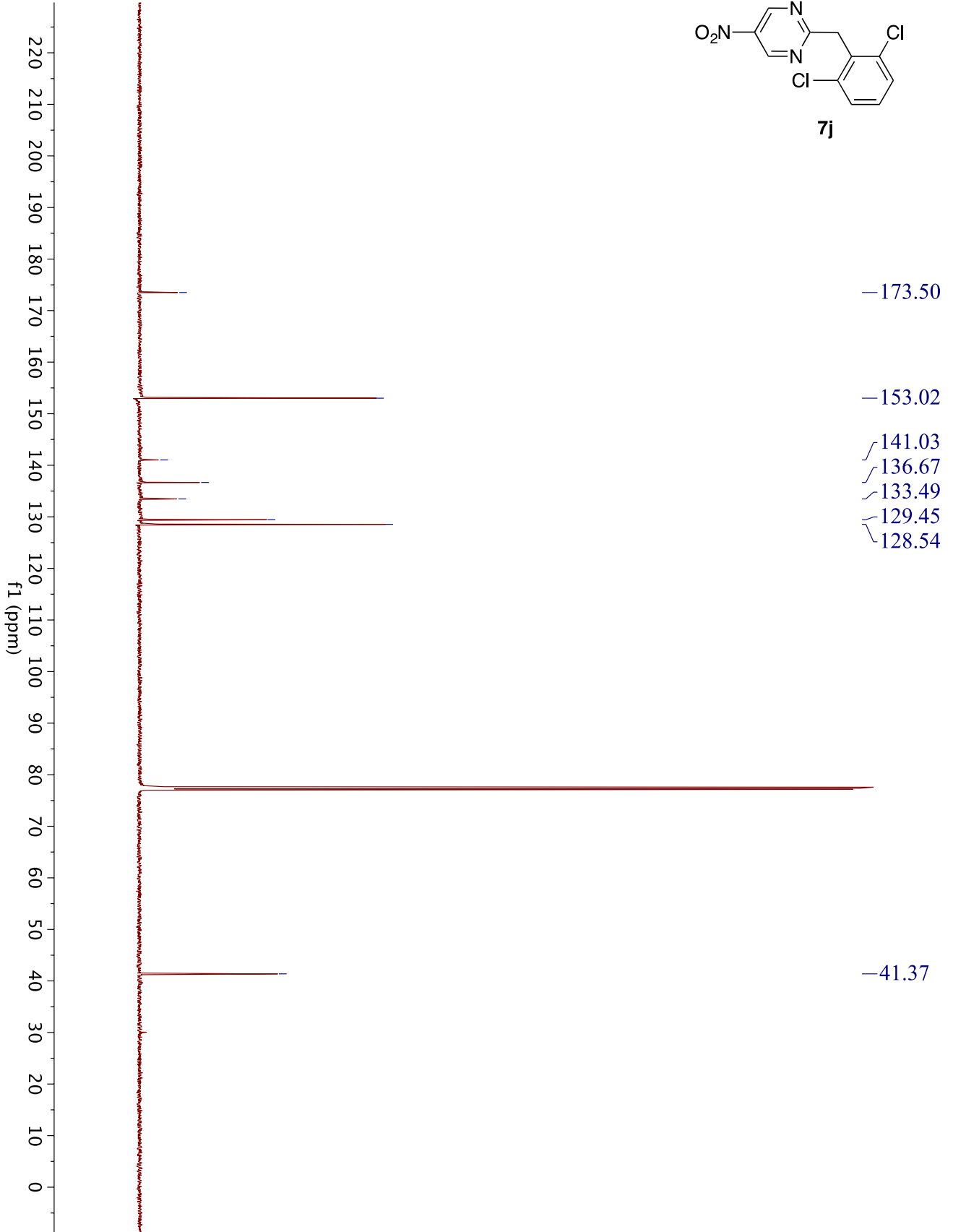
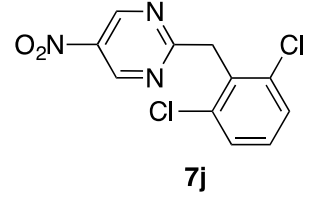


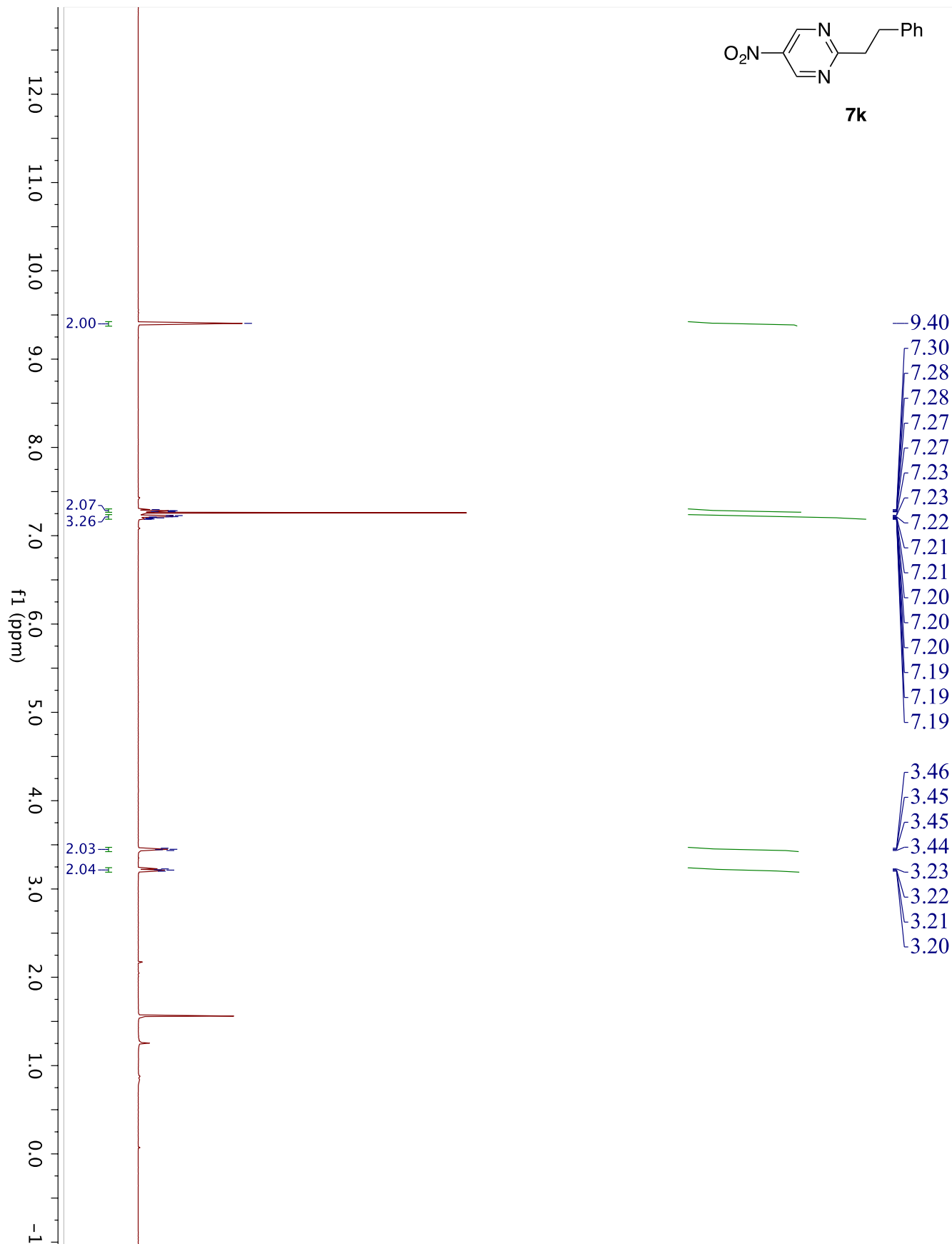


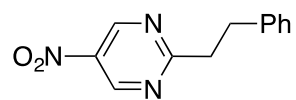
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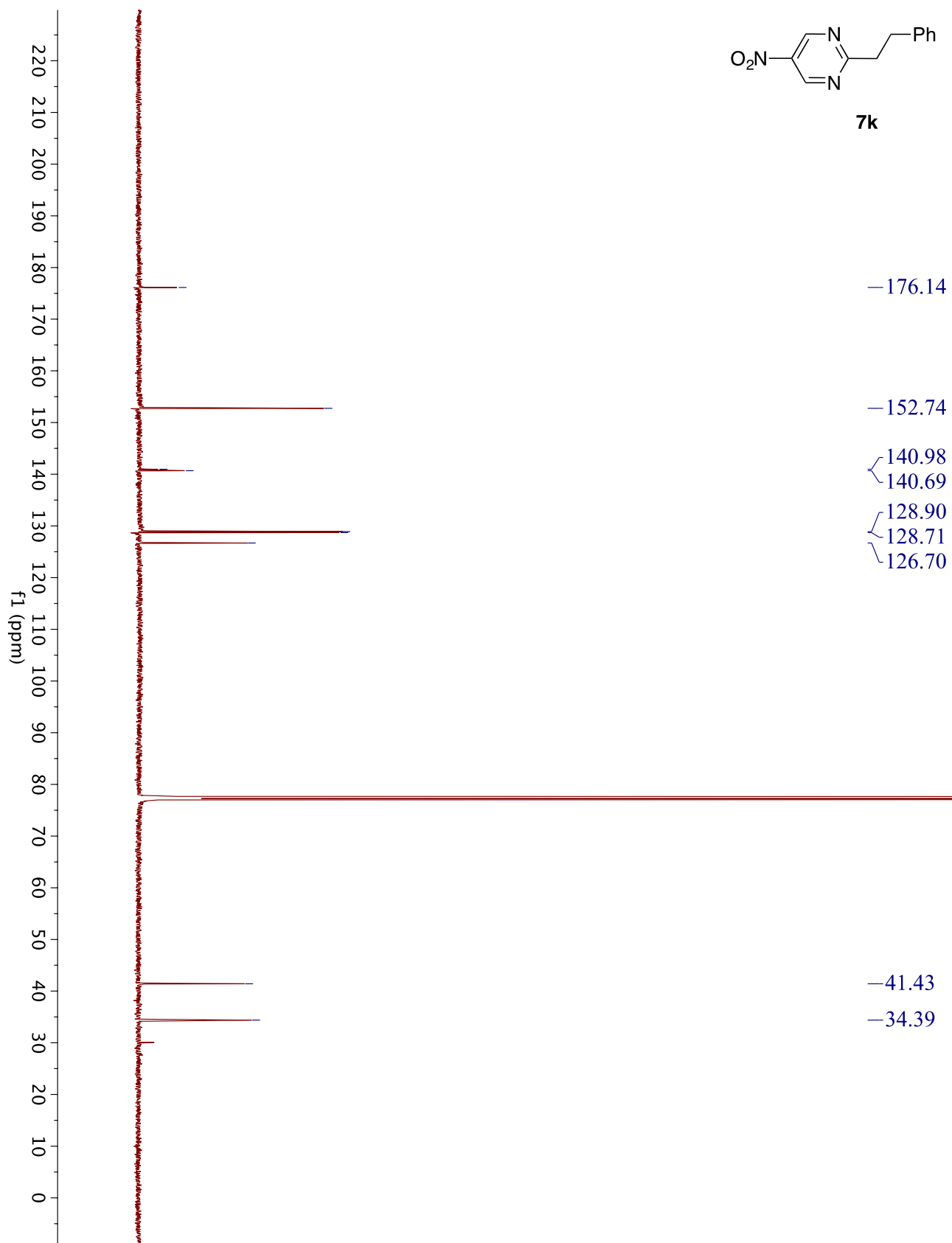


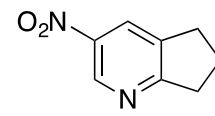




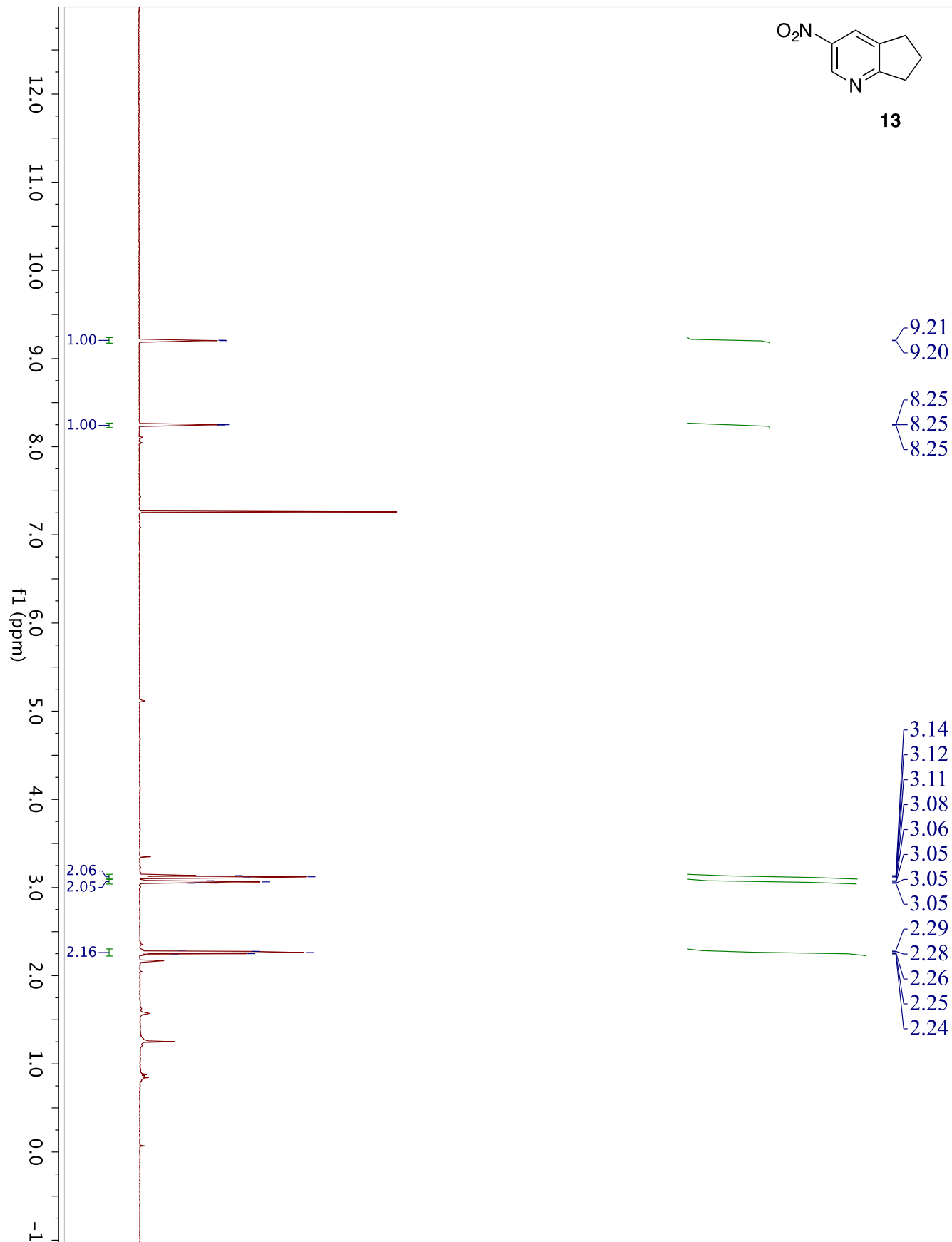


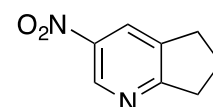
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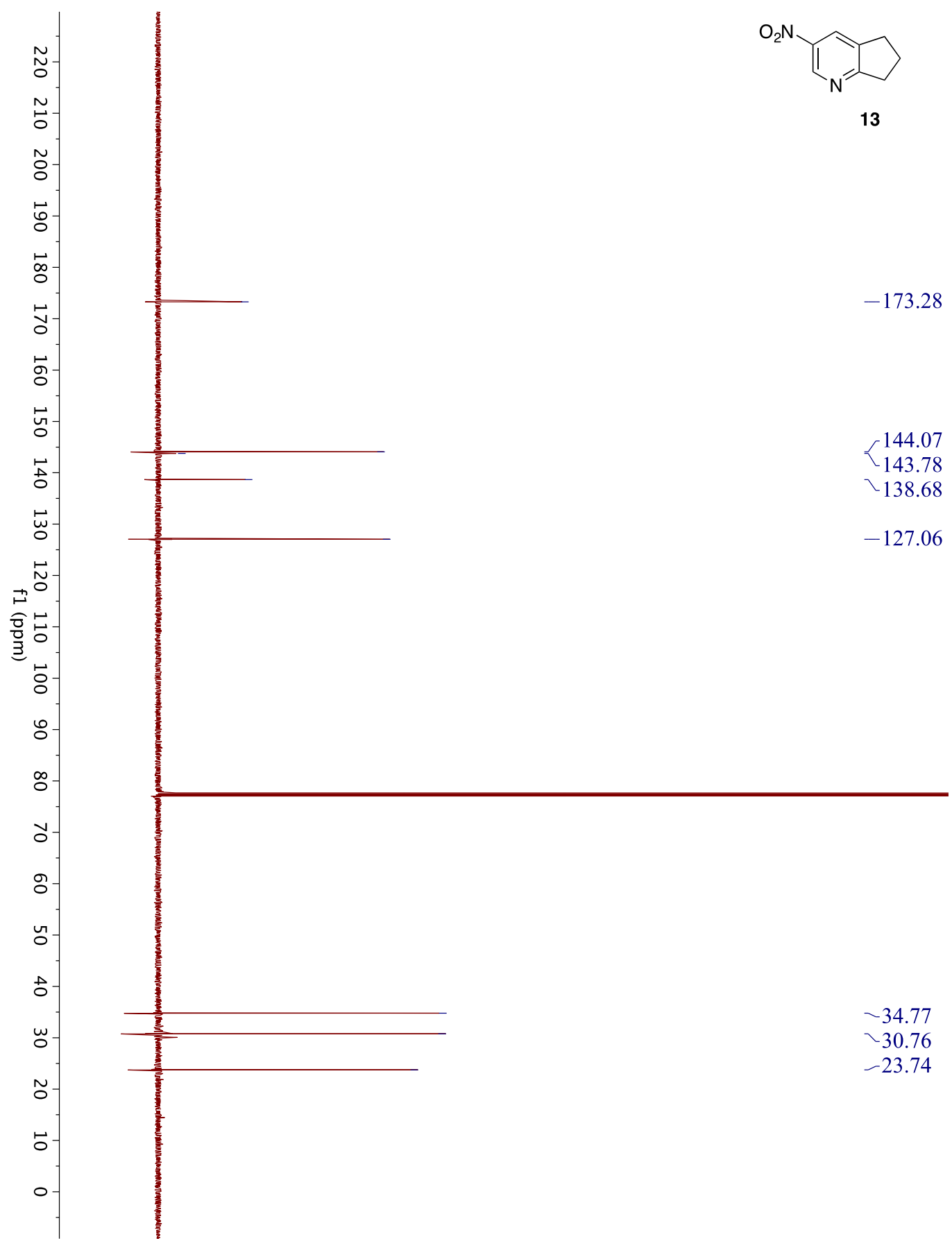


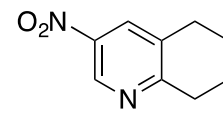
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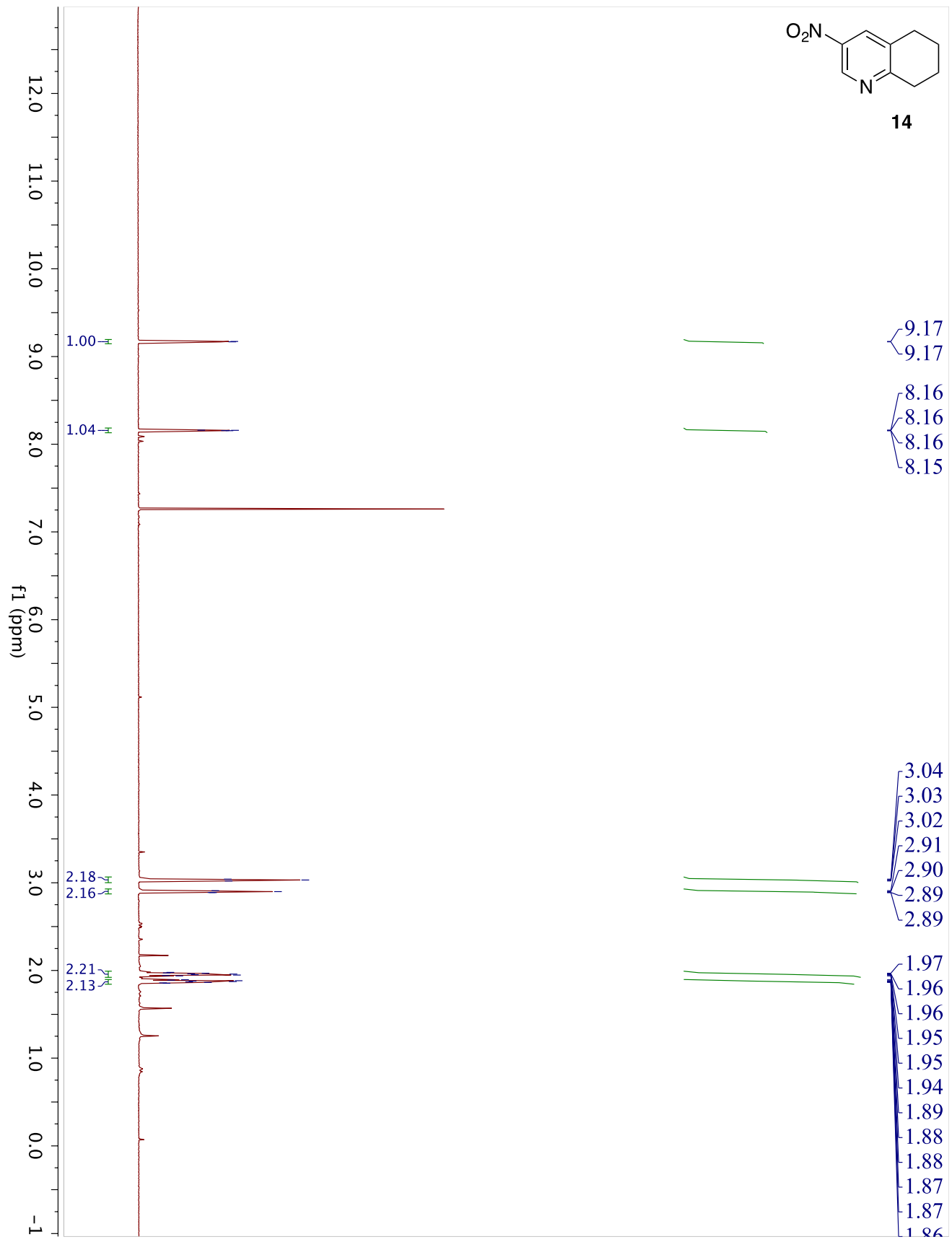


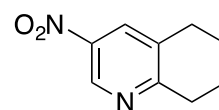
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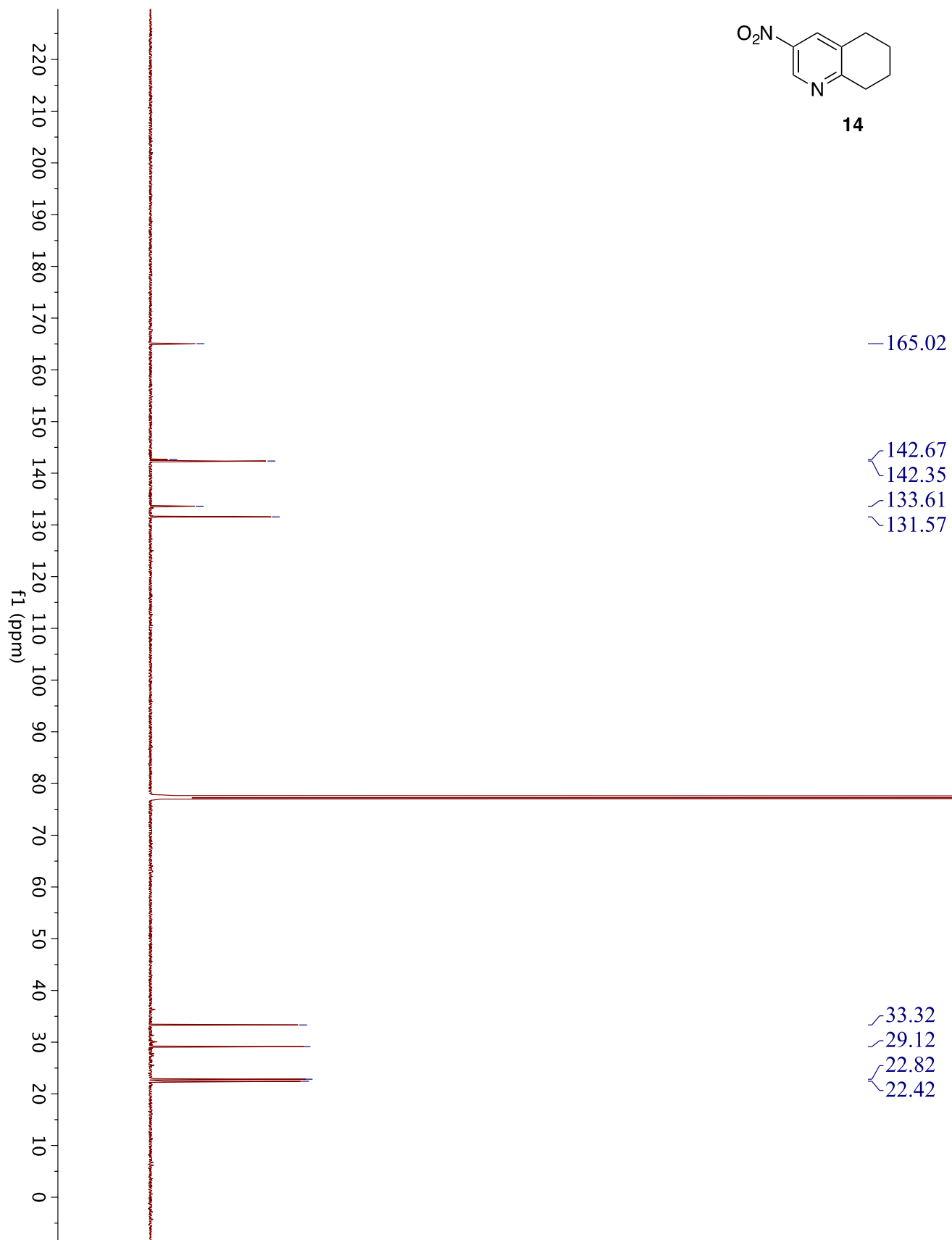


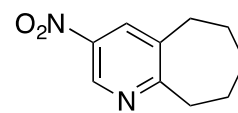
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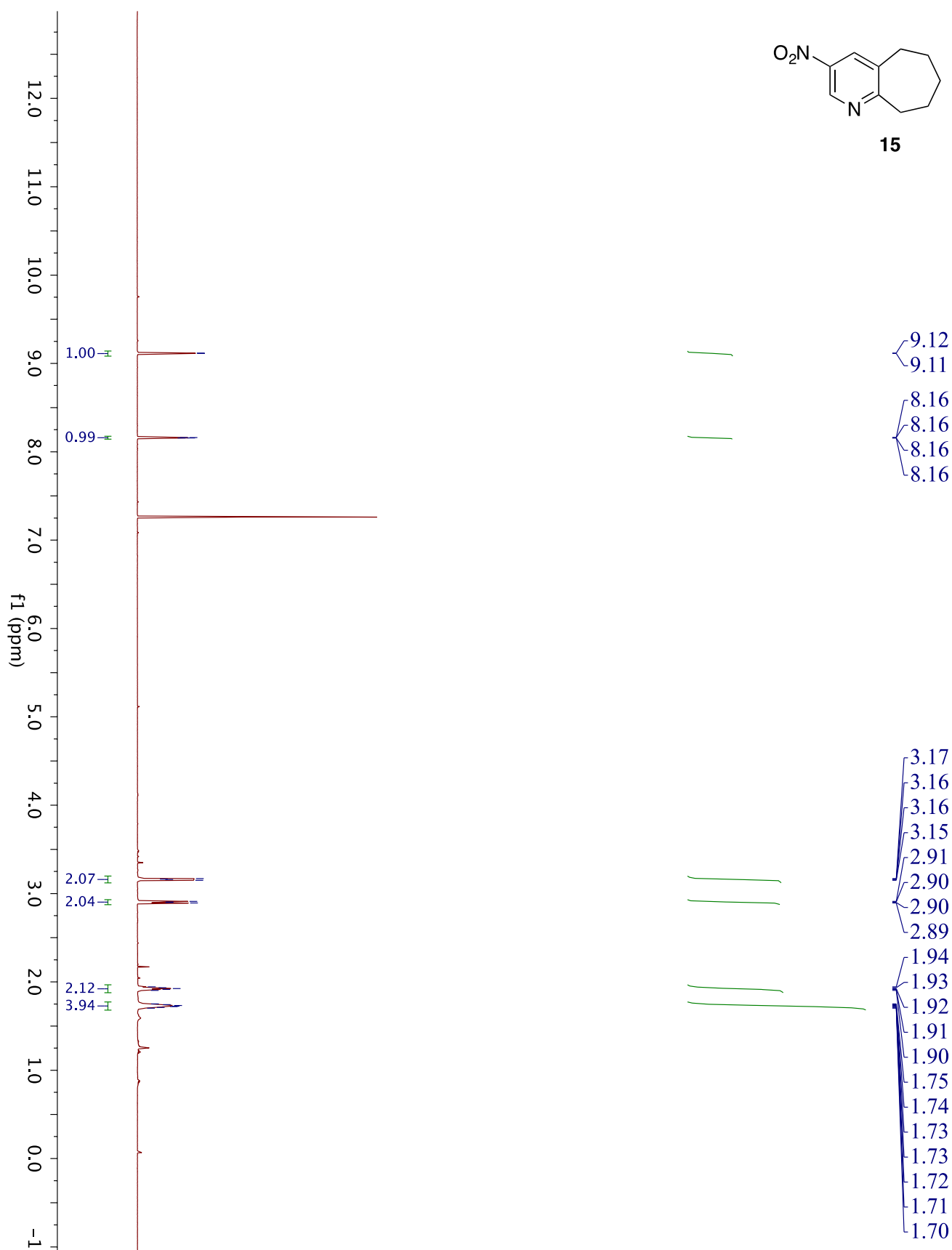


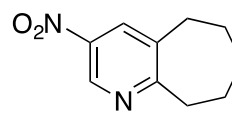
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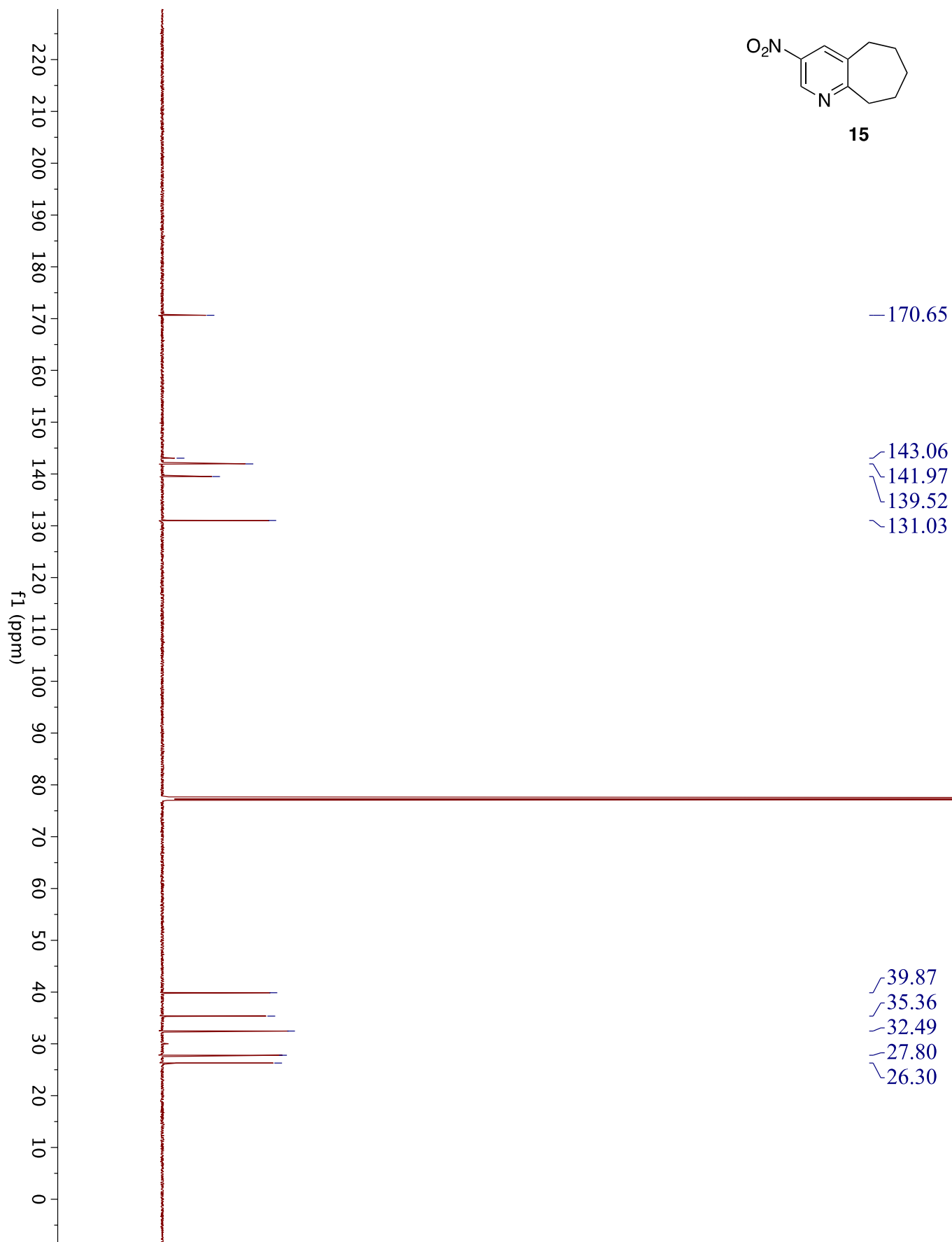


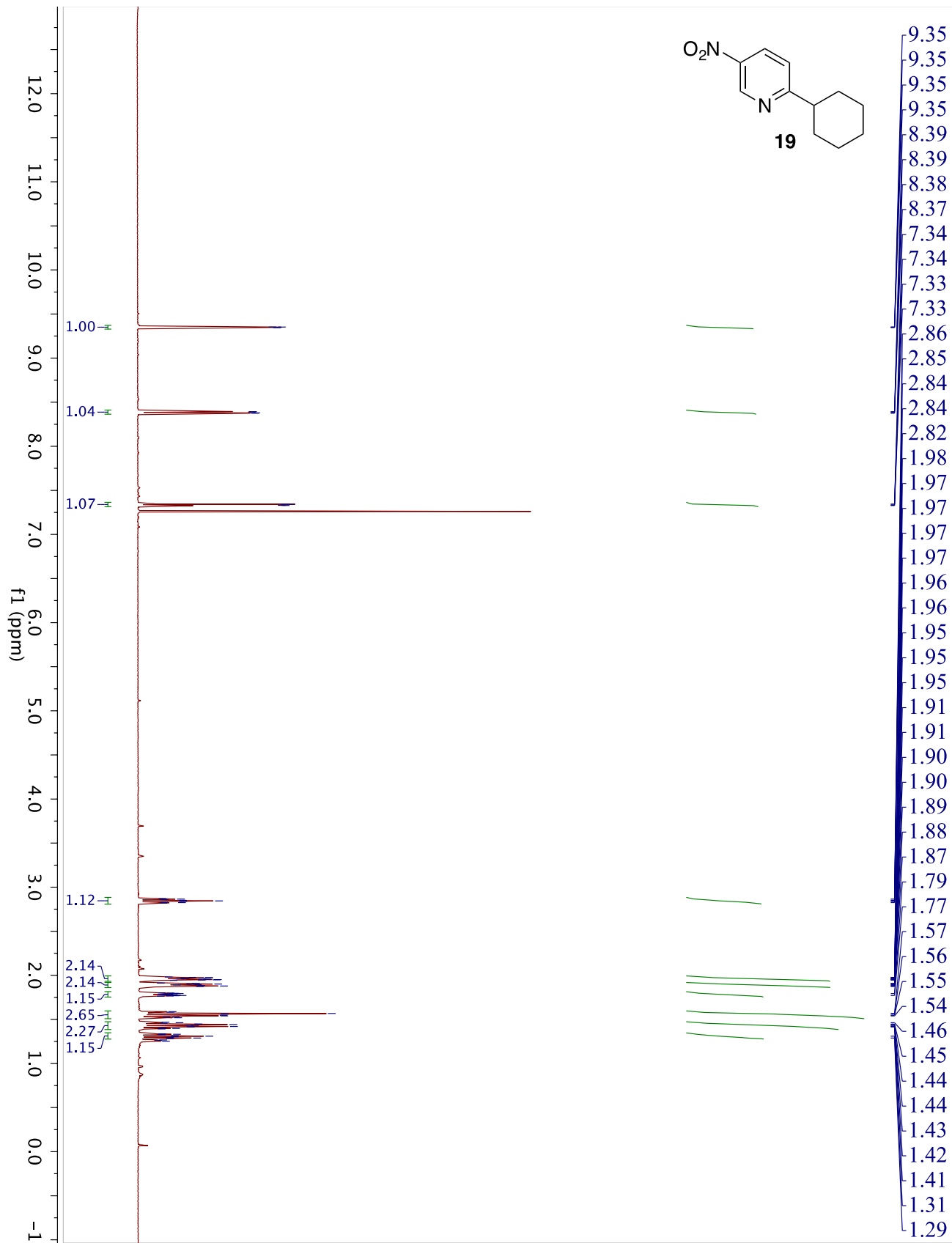
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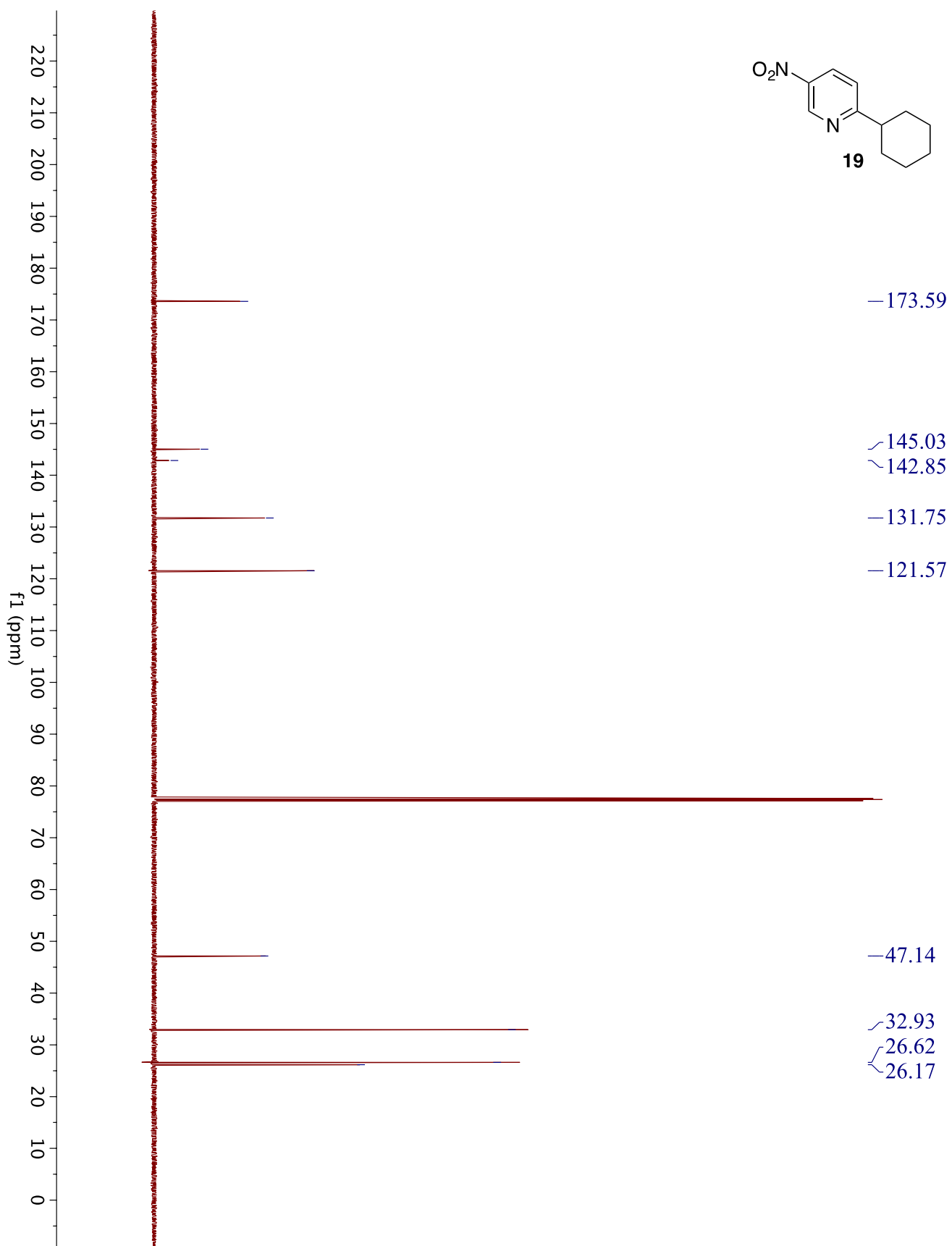
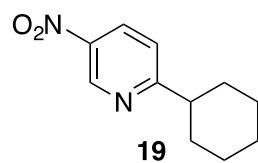


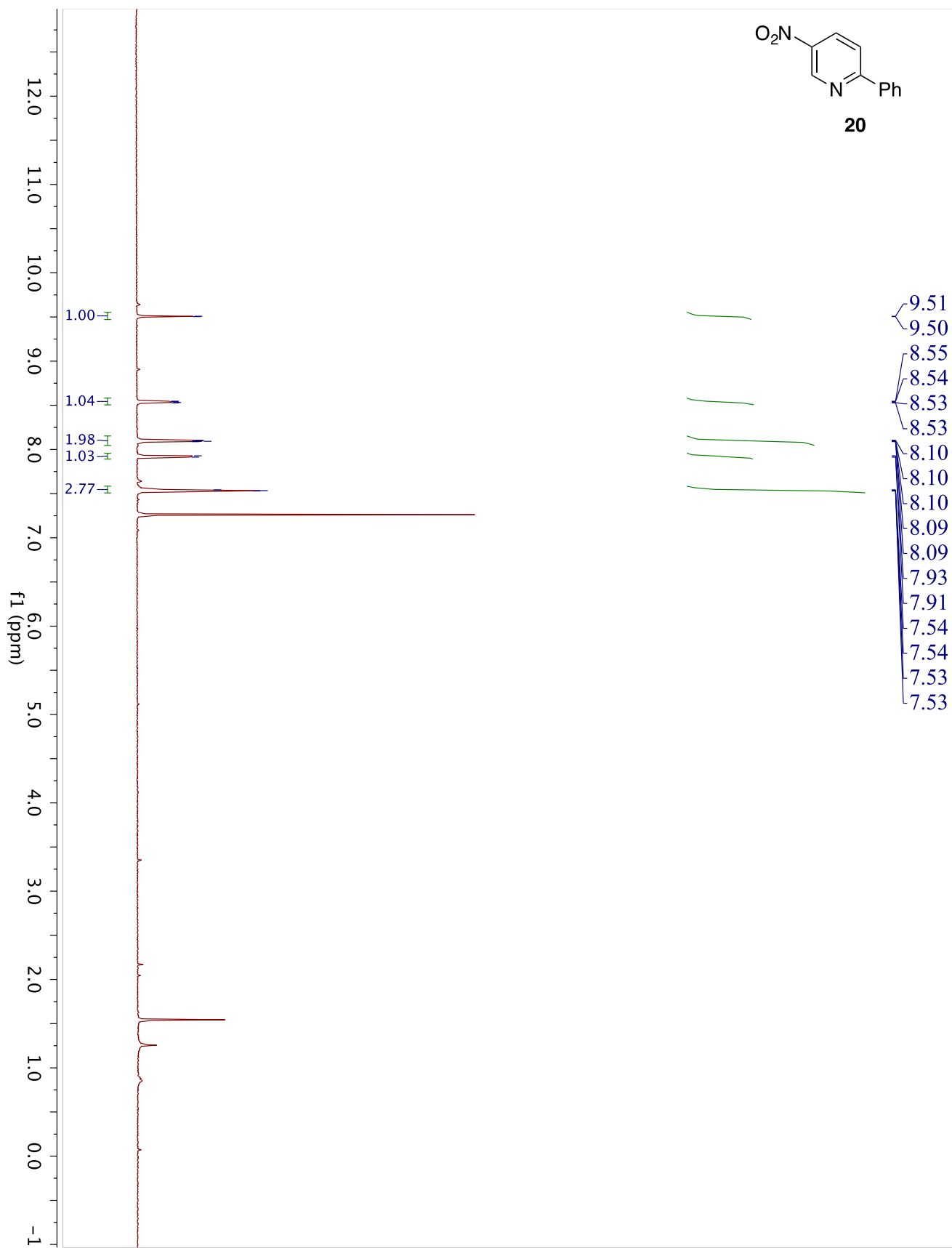
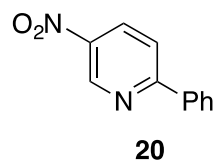


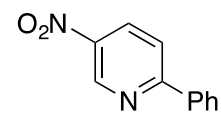
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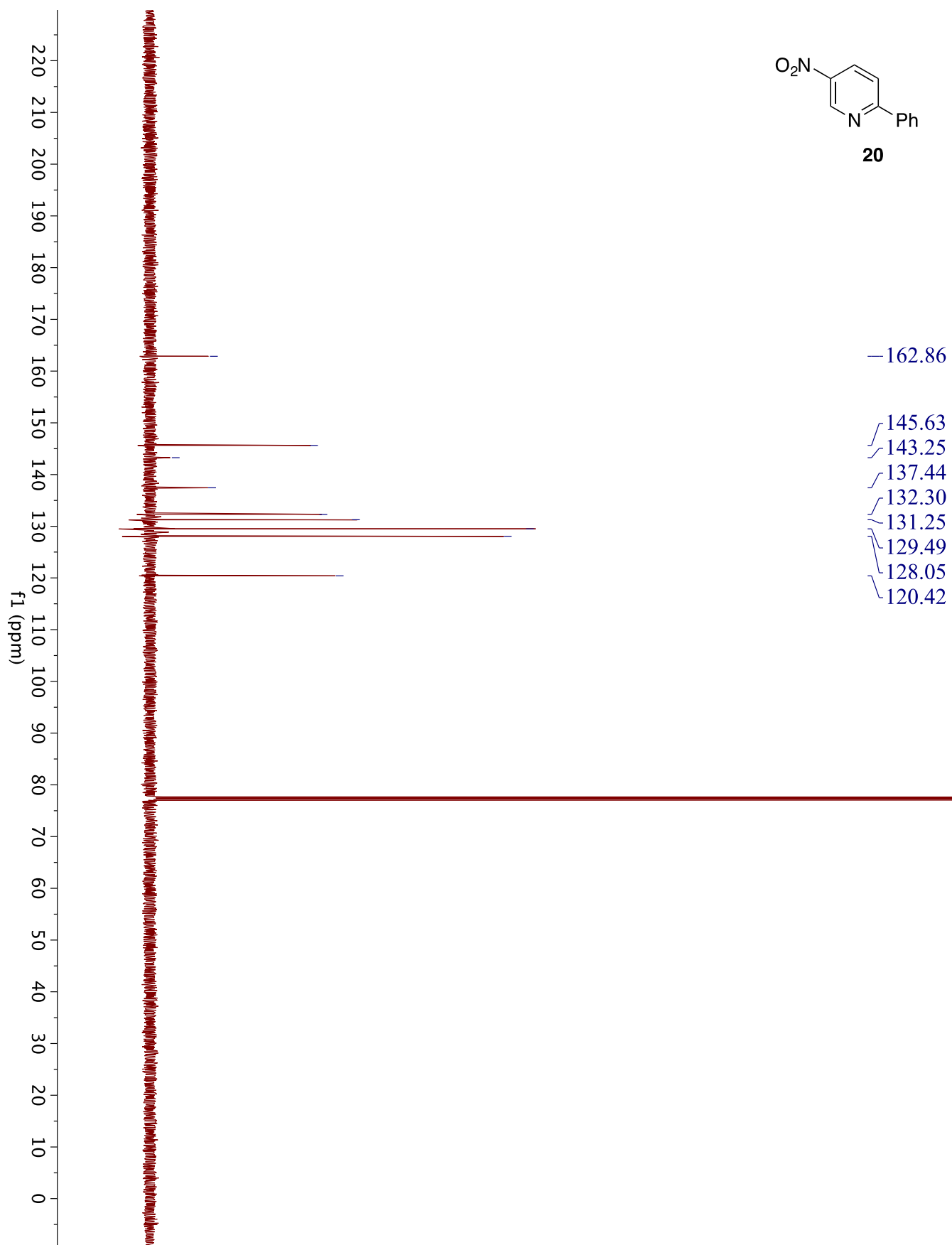


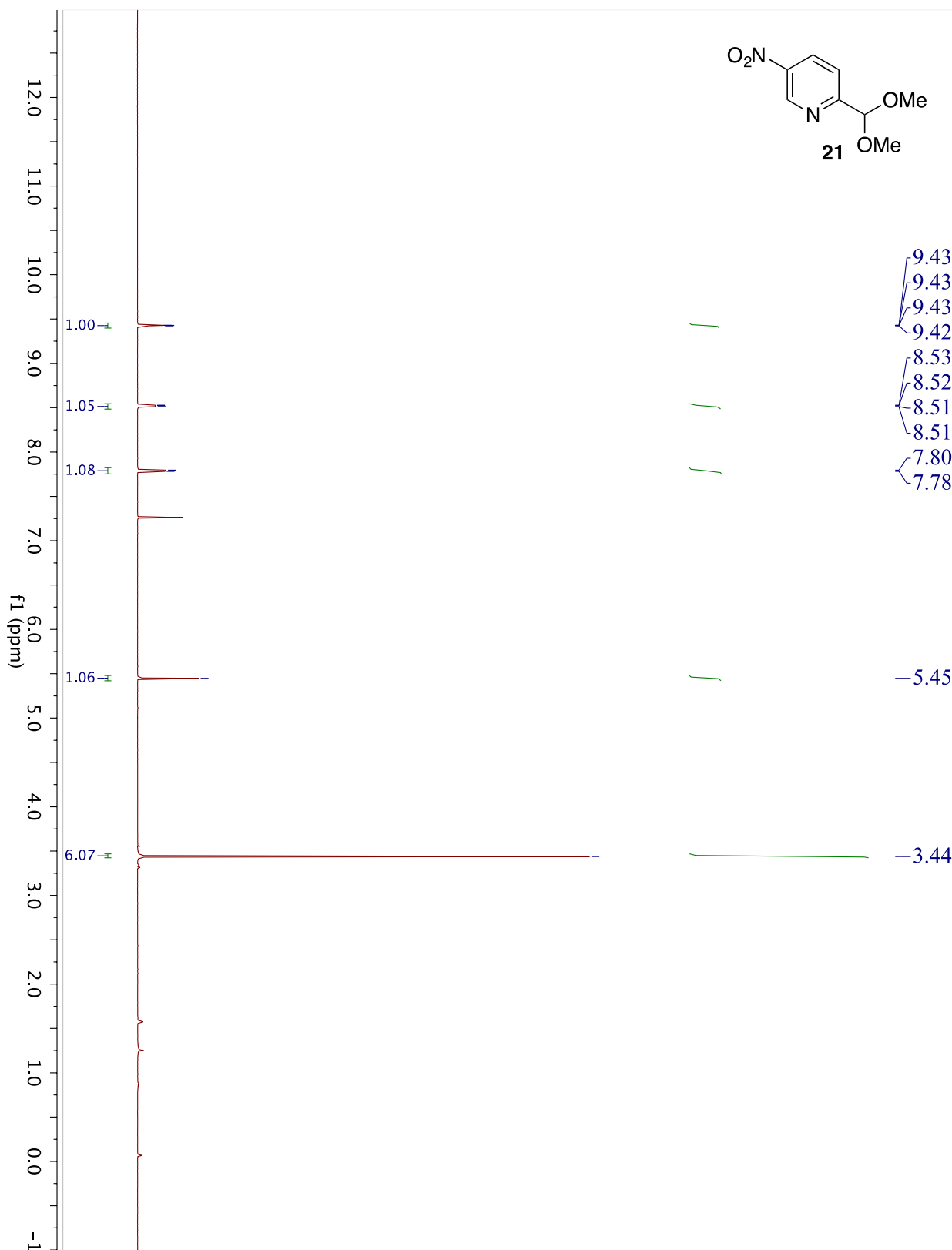


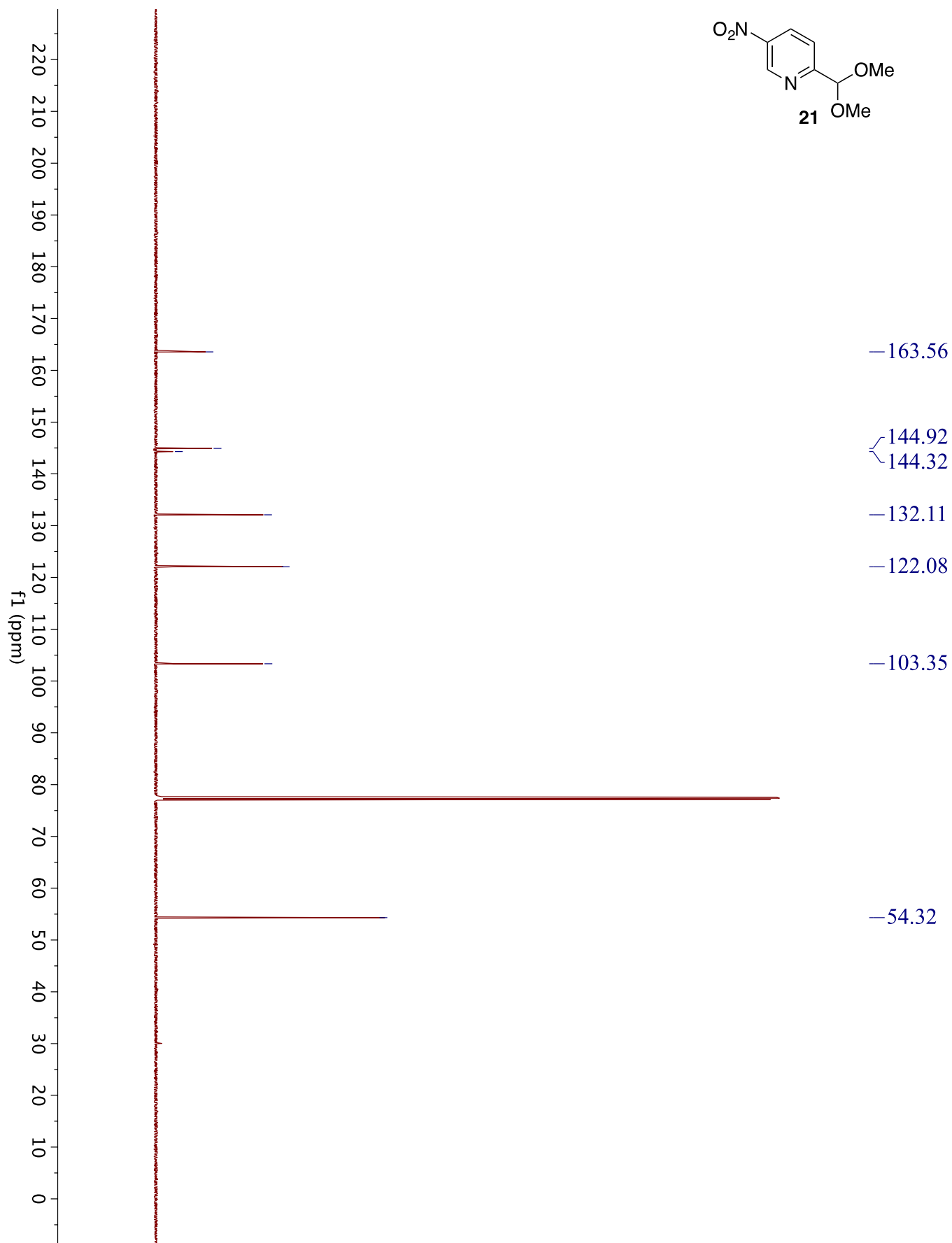
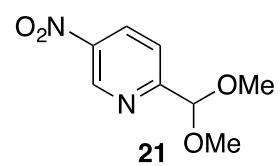


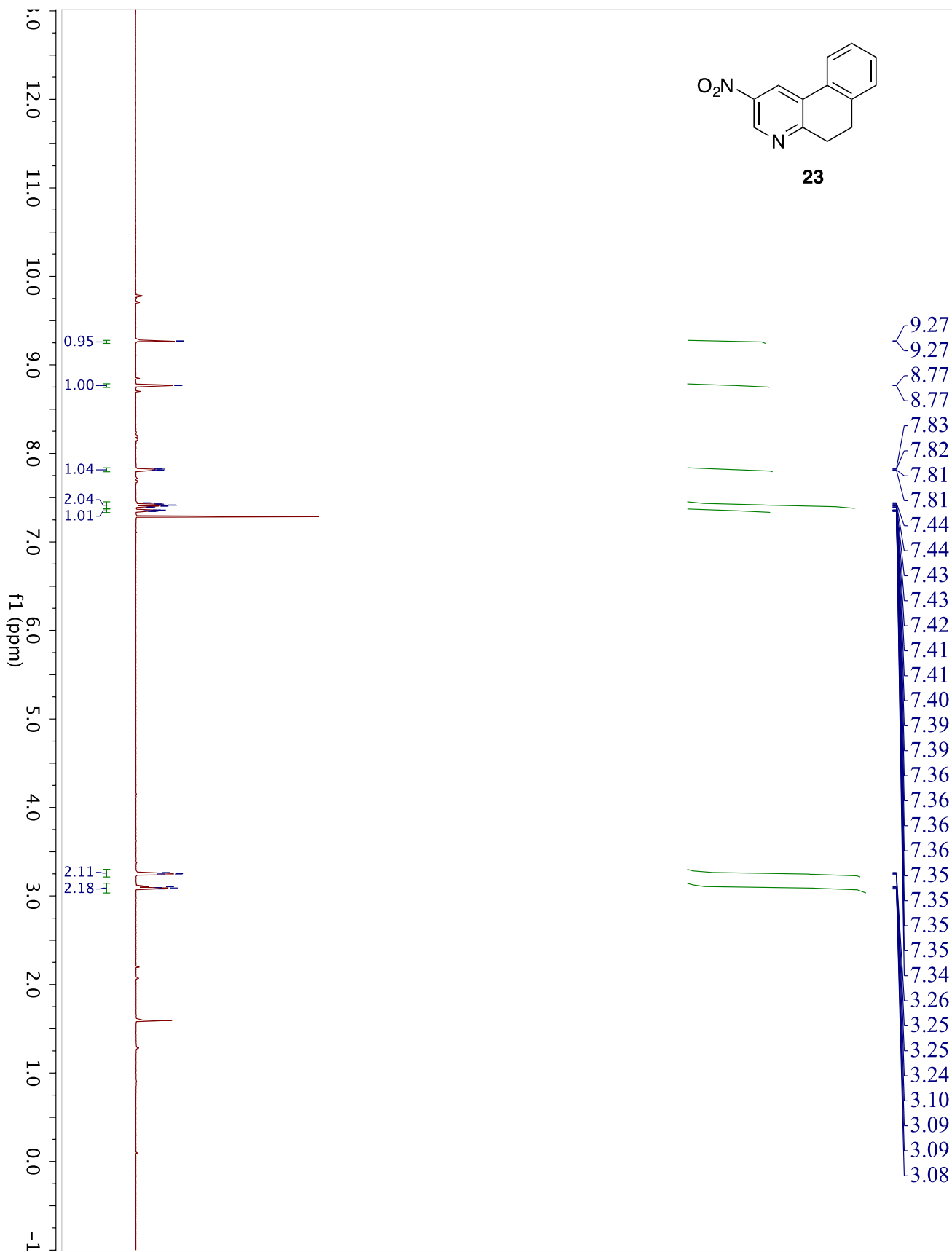


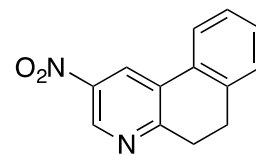
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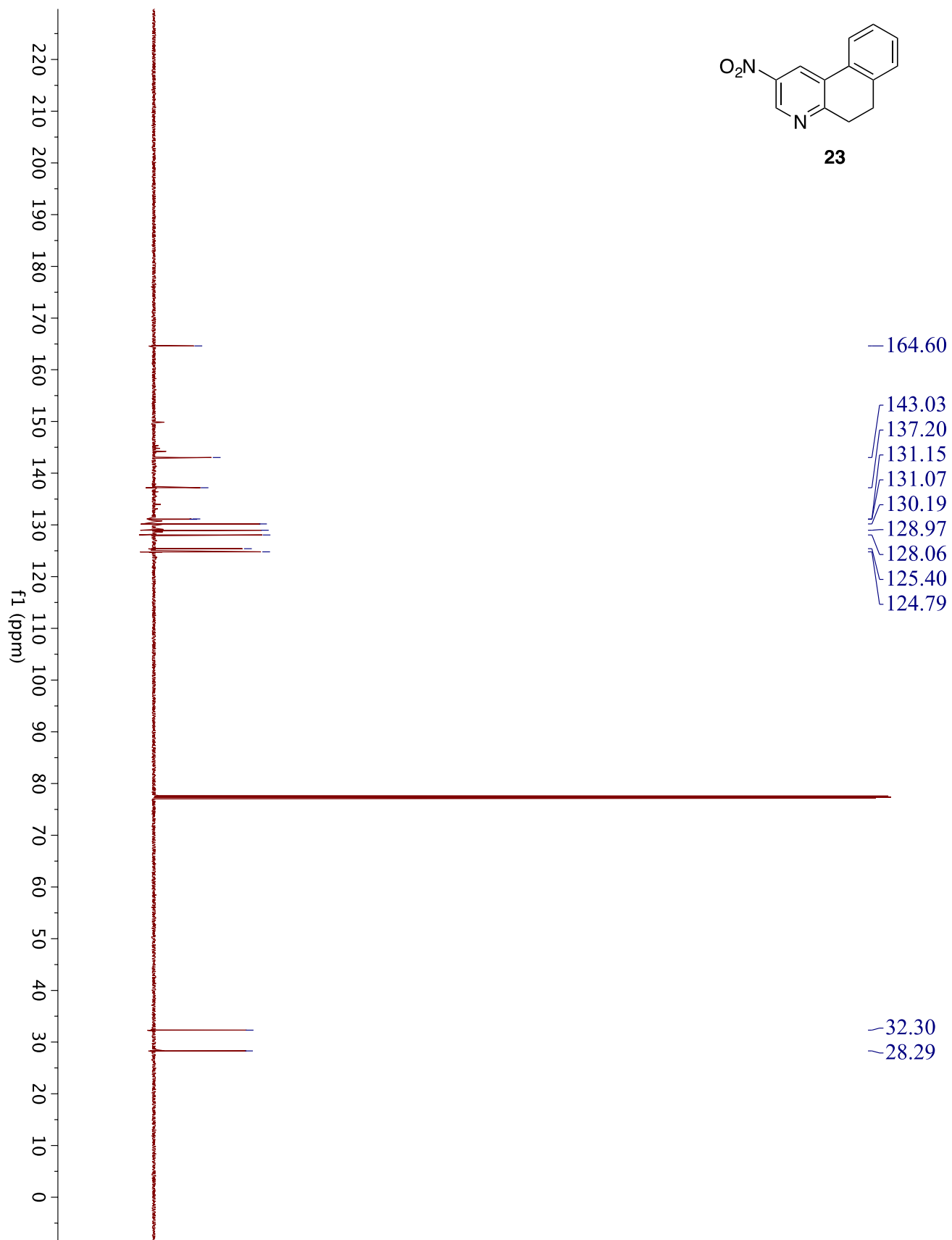


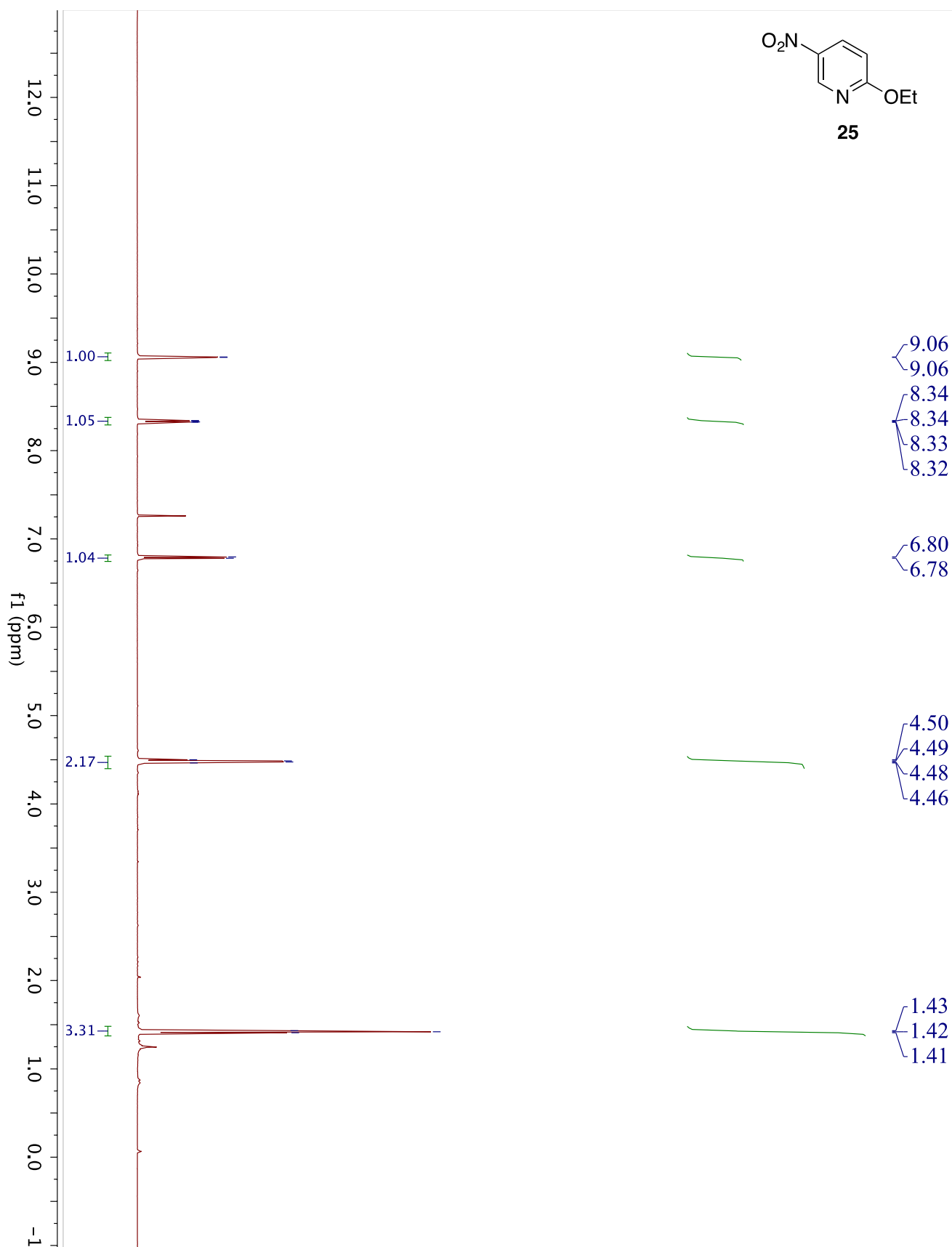
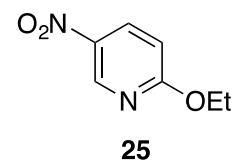


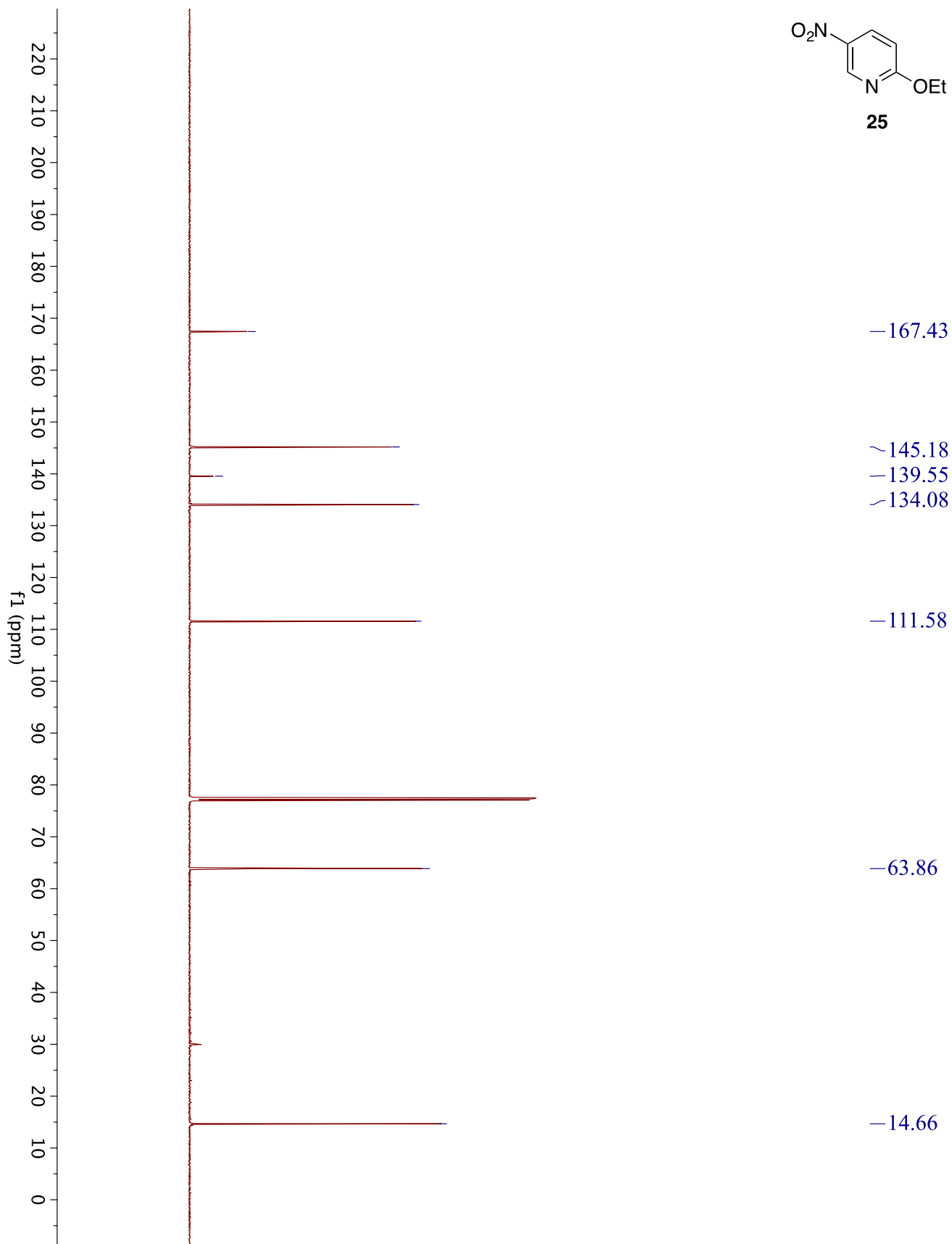
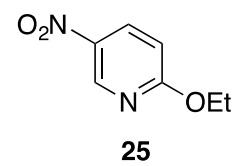


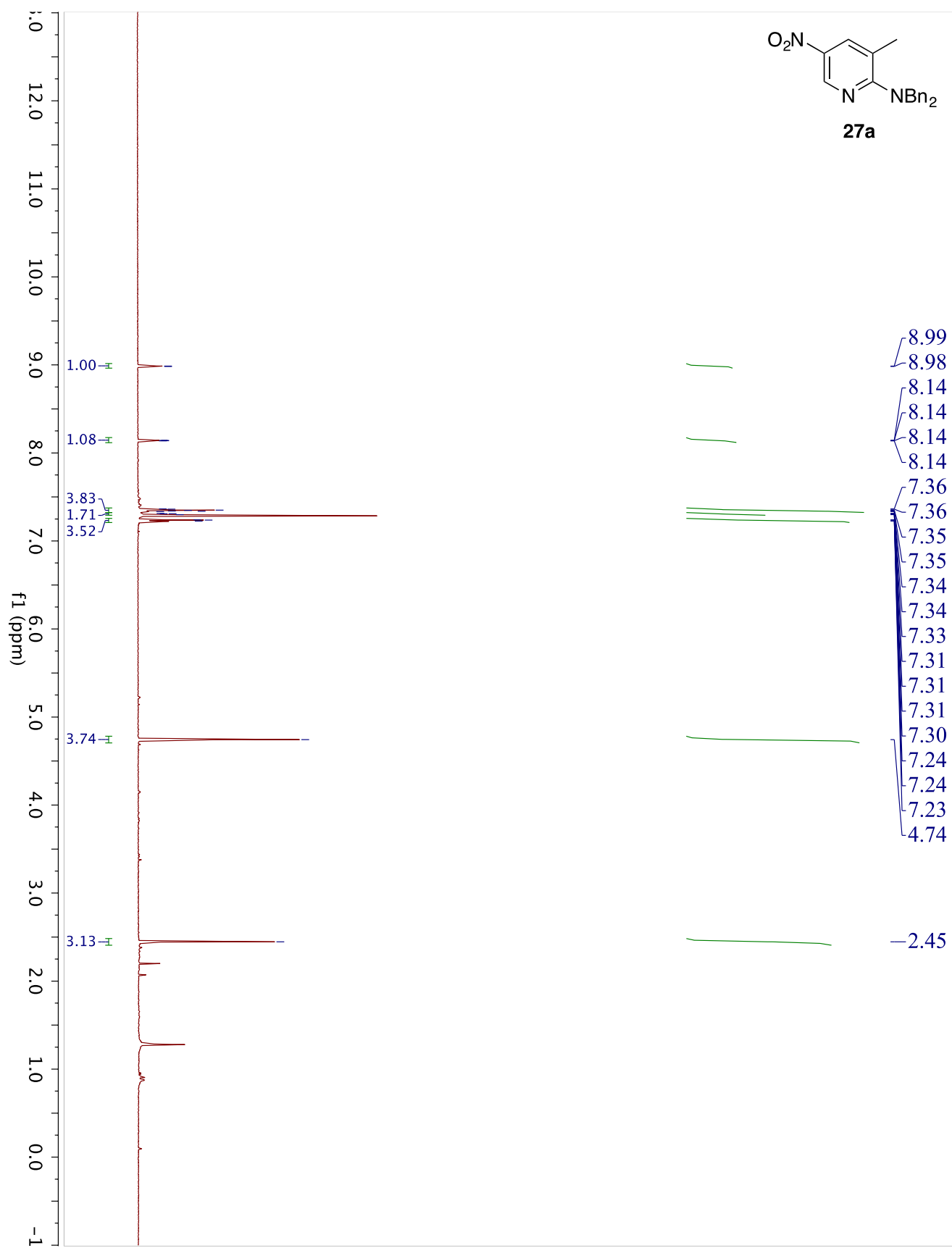
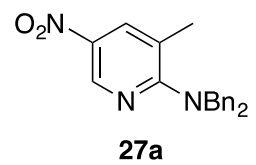


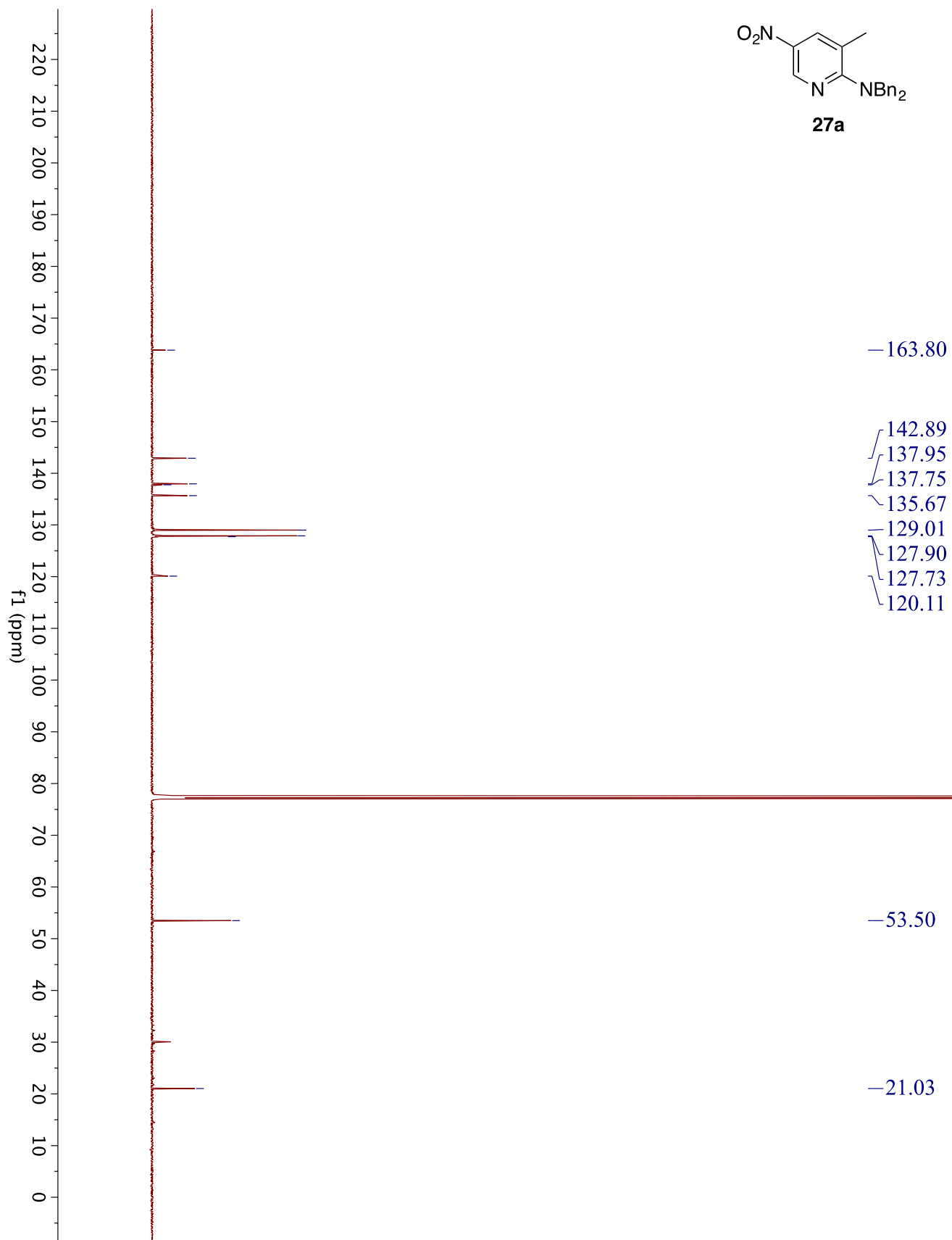
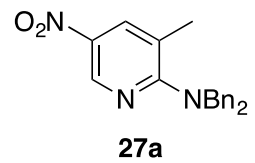
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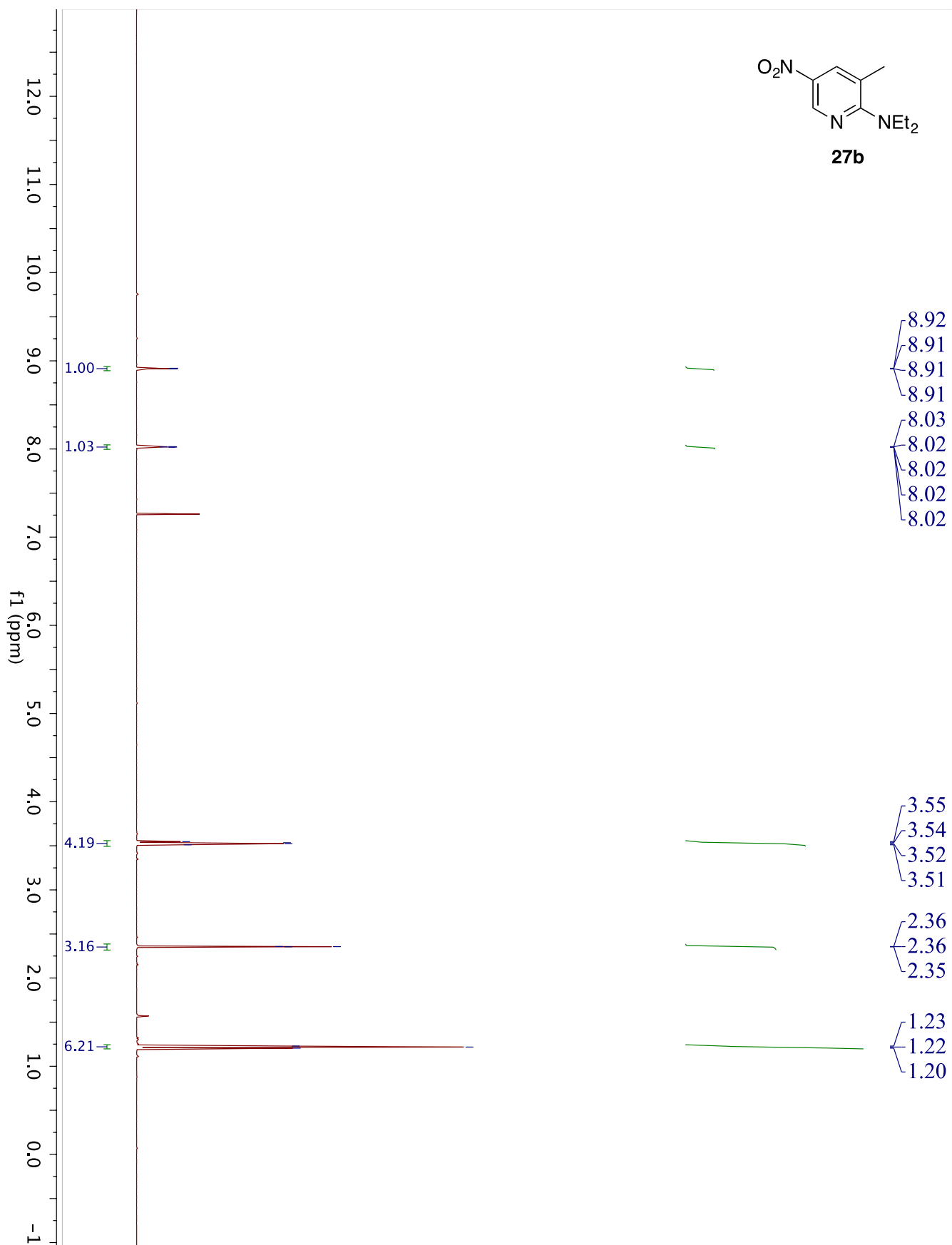
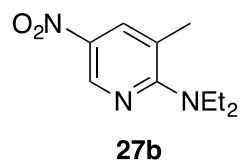


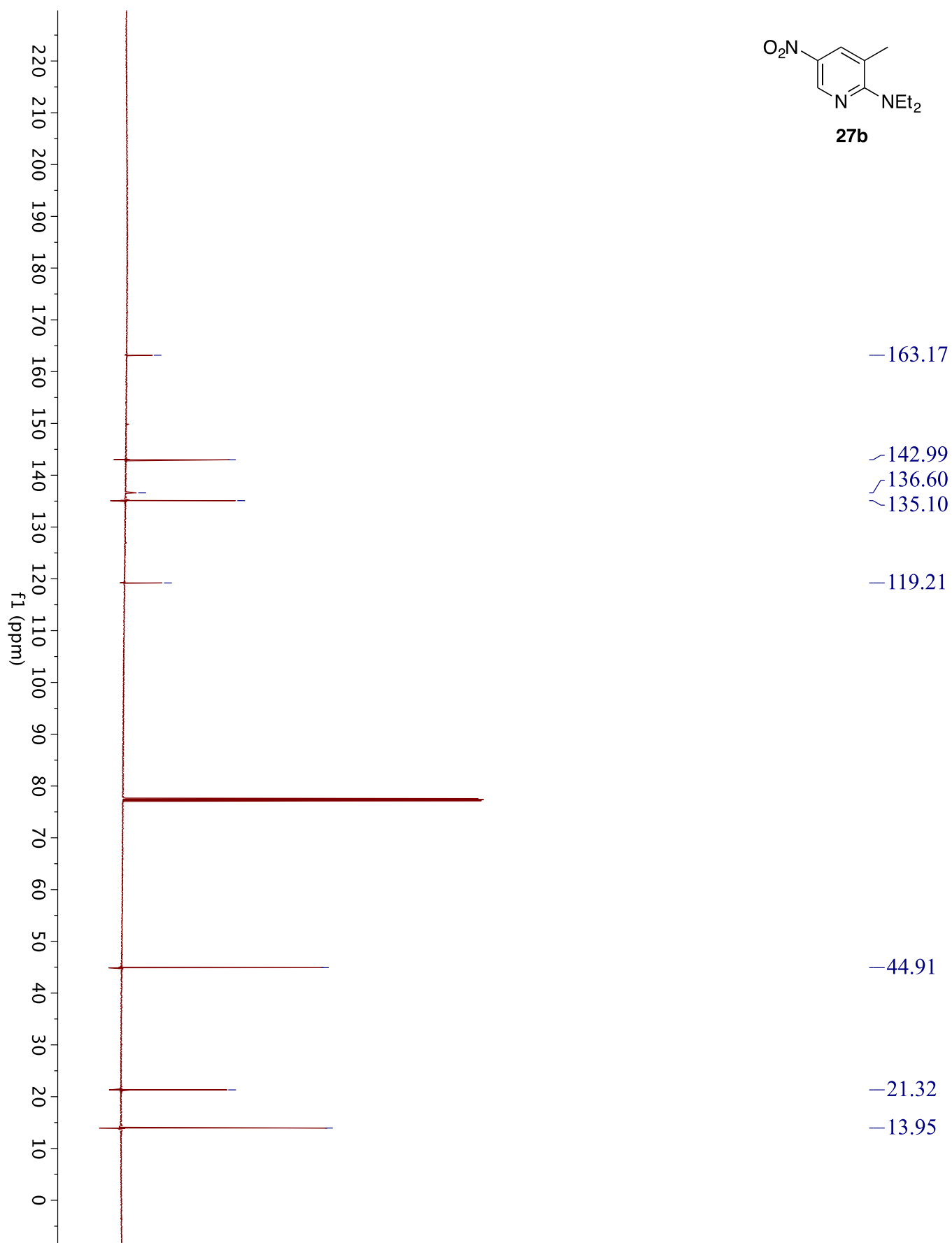
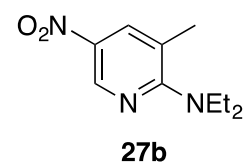












# VIII. Differential Scanning Calorimetry

