**Supporting Information**

**Synthesis of** **4-Functionalized Pyrazoles via Oxidative** **Thio/selenocyanation Mediated by PhICl2 and NH4SCN/KSeCN**

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**I. General information**

1H and 13C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 oC. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. Chemical shifts were expressed in parts per million (*δ*) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J*, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectrometer. Melting points were determined with a Micromelting point apparatus. TLC plates were visualized by exposure to ultraviolet light.

Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 oC) for 3 h before used. The starting materials **1** [1] were prepared according to literature methods.Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE).

**II. Experimental Procedures**

**1.** **General procedure for the preparation of 4- thio/selenocyanated pyrazoles**



General Procedure A: Under N2 atmosphere, to a solution of NH4SCN (2.0 mmol) in toluene (5 mL) was added PhICl2 (2.0 mmol) at 0 ℃. The mixture was stirred for 30 min. Then substrate **1** (1.0 mmol) was added to this solution in one portion and the reaction mixture was stirred for about 8 h until the completion of the starting material (monitored by TLC). Then the reaction mixture was washed with water (10 mL), extracted with DCM (3 x 10 mL). The combined organic layers were dried with MgSO4 and concentrated in *vacuo*., and the residue was purified by flash column chromatography to afford the corresponding 4-thiocyanated pyrazoles **2**.



General Procedure B: Under N2 atmosphere, to a solution of KSeCN (2.0 mmol) in toluene (5 mL) was added PhICl2 (2.0 mmol) at 0 ℃. The mixture was stirred for 30 min. Then substrate **1** (1.0 mmol) was added to this solution in one portion and the reaction mixture was stirred for about 8 h until the completion of the starting material (monitored by TLC). Then the reaction mixture was washed with water (10 mL), extracted with DCM (3 x 10 mL). The combined organic layers were dried with MgSO4 and concentrated in *vacuo*., and the residue was purified by flash column chromatography to afford the corresponding 4-selenocyanated pyrazoles **3**.

**2. General procedure for the gram-scale synthesis of 2a, 3a.**

General Procedure for the gram-scale synthesis of **2a**: Under N2 atmosphere, to a solution of NH4SCN (20.0 mmol) in toluene (20 mL) was added PhICl2 (20.0 mmol) at 0 ℃. The mixture was stirred for 1 h, and then substrate **1a** (10.0 mmol) was added to this solution in one portion and the reaction mixture was stirred for about 10 h until the completion of the starting material (monitored by TLC). Then the reaction mixture was washed with water (30 mL), extracted with DCM (5 x 15 mL). The combined organic layers were dried with MgSO4 and concentrated in *vacuo*., and the residue was purified by flash column chromatography to afford the corresponding desired product **2a** (2.02 g, 88%).

General Procedure for the gram-scale synthesis of **3a**: Under N2 atmosphere, to a solution of KSeCN (20.0 mmol) in toluene (20 mL) was added PhICl2 (20.0 mmol) at 0 ℃. The mixture was stirred for 1 h. Then substrate **1a** (10.0 mmol) was added to this solution in one portion and the reaction mixture was stirred for about 10 h until the completion of the starting material (monitored by TLC). Then the reaction mixture was washed with water (30 mL), extracted with DCM (5 x 15 mL). The combined organic layers were dried with MgSO4 and concentrated in *vacuo*., and the residue was purified by flash column chromatography to afford the corresponding desired product **3a** (2.21 g, 80%).

**III. Spectroscopic Data**

**3,5-Dimethyl-1-phenyl-4-thiocyanato-1*H*-pyrazole** **(2a)**

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According to the procedure A, **2a** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (208.6 mg, yield: 91%). mp: 99-100 °C. 1H NMR (400 MHz, CDCl3) δ 7.54 – 7.45 (m, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.41 – 7.37 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.0, 144.3, 139.1, 129.4, 128.6, 125.0, 110.9, 96.6, 12.0, 11.5. HRMS (ESI) calcd for C12H11N3NaS+ [M + Na+] 252.0566, found252.0570.

**3,5-Dimethyl-4-thiocyanato-1-(*p*-tolyl)-1*H*-pyrazole (2b)**

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According to the procedure A, **2b** was purified by silica gel chromatography (10% EtOAc/petroleum ether). A white solid (218.9 mg, yield: 90%). mp: 87-88 °C. 1H NMR (400 MHz, CDCl3) δ 7.28 – 7.26 (m, 4H), 2.42 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H).13C NMR (101 MHz, CDCl3) δ 151.8, 144.3, 138.7, 136.6, 129.9, 124.8, 111.0, 96.2, 21.2, 12.0, 11.5. HRMS (ESI) calcd for C13H13N3NaS+ [M + Na+] 266.0722, found266.0727.

**3,5-Dimethyl-4-thiocyanato-1-(*o*-tolyl)-1*H*-pyrazole (2c)**

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According to the procedure A, **2c** was purified by silica gel chromatography (10% EtOAc/PE). Yellow oil (221.4 mg, yield: 91%). 1H NMR (400 MHz, CDCl3) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 9.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 2.36 (d, *J* = 3.7 Hz, 9H). 13C NMR (101 MHz, CDCl3) δ 151.9, 144.3, 139.7, 139.0, 129.4, 129.1, 125.7, 121.9, 110.9, 96.4, 21.3, 12.0, 11.5. HRMS (ESI) calcd for C13H13N3NaS+ [M + Na+] 266.0722, found266.0727.

**3,5-Dimethyl-4-thiocyanato-1-(*m*-tolyl)-1*H*-pyrazole (2d)**

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According to the procedure A, **2d** was purified by silica gel chromatography (10% EtOAc/PE). Yellow oil (218.9 mg, yield: 90%). 1H NMR (400 MHz, CDCl3) δ 7.43 – 7.28 (m, 3H), 7.19 (dd, *J* = 7.7, 1.1 Hz, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 2.05 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 151.7, 145.2, 137.8, 135.8, 131.2, 129.9, 127.5, 126.9, 111.0, 95.2, 17.2, 12.1, 10.6. HRMS (ESI) calcd for C13H13N3NaS+ [M + Na+] 266.0722, found266.0725.

**1-(4-Methoxyphenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole** **(2e)**



According to the procedure A, **2e** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (207.4 mg, yield: 80%). mp: 104-105 °C. 1H NMR (400 MHz, CDCl3) δ 7.33 – 7.27 (m, 2H), 7.01 – 6.96 (m, 2H), 3.86 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.7, 151.7, 144.5, 132.0, 126.5, 114.5, 111.0, 95.9, 55.6, 12.0, 11.4. HRMS (ESI) calcd for C13H13N3NaOS+ [M + Na+] 282.0672, found282.0676.

**1-(4-Fluorophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole** **(2f)**

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According to the procedure A, **2f** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (225 .0 mg, yield: 91%). mp: 81-82 °C. 1H NMR (400 MHz, CDCl3) δ 7.41 – 7.35 (m, 2H), 7.24 – 7.15 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 162.4 (d, *J*C-F = 250.0 Hz), 152.1, 144.5, 135.2 (d, *J*C-F = 3.0 Hz), 127.0 (d, *J*C-F = 8.1 Hz), 116.4 (d, *J*C-F = 23.2 Hz), 110.7, 96.8, 12.0, 11.4. HRMS (ESI) calcd for C12H10FN3NaS+ [M + Na+] 270.0472, found270.0476.

**1-(4-Fluorophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazol** **(2g)**

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According to the procedure A, **2g** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (226.8 mg, yield: 86%). mp: 95-98 °C. 1H NMR (400 MHz, CDCl3) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.3, 144.4, 137.5, 134.5, 129.6, 126.1, 110.7, 97.2, 12.0, 11.6. HRMS (ESI) calcd for C12H10ClN3NaS+ [M + Na+] 252.0566, found252.0570.

**1-(4-Bromophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole** **(2h)**

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According to the procedure A, **2h** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (271.2 mg, yield: 88%). mp: 111-113 °C. 1H NMR (400 MHz, CDCl3) δ 7.66 – 7.61 (m, 2H), 7.32 – 7.28 (m, 2H), 2.44 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.4, 144.4, 138.0, 132.6, 126.4, 122.4, 110.6, 97.3, 12.0, 11.6. HRMS (ESI) calcd for C12H10BrN3NaS+ [M + Na+] 329.9671, found329.9676.

**1-(4-Iodophenyl)-3,5-dimethyl-4-thiocyanato-1*H*-pyrazole** **(2i)**

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According to the procedure A, **2i** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (284.1 mg, yield: 80%). mp: 103-105 °C. 1H NMR (400 MHz, CDCl3) δ 7.86 – 7.80 (m, 2H), 7.19 – 7.15 (m, 2H), 2.44 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.4, 144.3, 138.7, 138.5, 126.5, 110.6, 97.3, 93.8, 12.0, 11.6. HRMS (ESI) calcd for C12H10IN3NaS+ [M + Na+] 377.9532, found377.9537.

**3,5-Dimethyl-4-thiocyanato-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole** **(2j)**

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According to the procedure A, **2j** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (276.4 mg, yield: 93%). mp: 67-70 °C. 1H NMR (400 MHz, CDCl3) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 2.50 (s, 3H), 2.44 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.7, 144.5, 141.8, 130.4 (q, 2*J*C-F = 33.0 Hz), 126.7, 124.8, 122.3, 110.5, 98.1, 12.1, 11.8. HRMS (ESI) calcd for C13H10F3N3NaS+ [M + Na+] 320.0440, found320.0445.

**3,5-Dimethyl-1-(4-nitrophenyl)-4-thiocyanato-1*H*-pyrazole** **(2k)**

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According to the procedure A, **2k** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (170.0 mg, yield: 62%). mp: 80-82 °C. 1H NMR (400 MHz, CDCl3) δ 8.41 – 8.35 (m, 2H), 7.69 – 7.64 (m, 2H), 2.56 (s, 3H), 2.45 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.3, 146.8, 144.6, 143.9, 125.0, 124.6, 110.2, 99.3, 12.1, 12.1. HRMS (ESI) calcd for C12H10N4NaO2S+ [M + Na+] 297.0417, found297.0420.

**3-Methyl-1,5-diphenyl-4-thiocyanato-1*H*-pyrazole** **(2l)**

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According to the procedure A, **2l** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (174.8 mg, yield: 60%). mp: 50-54 °C. 1H NMR (400 MHz, CDCl3) δ 7.46 – 7.38 (m, 3H), 7.34 – 7.25 (m, 5H), 7.24 – 7.18 (m, 2H), 2.54 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.8, 147.0, 139.2, 130.0, 129.7, 129.1, 128.8, 128.1, 127.9, 124.9, 111.2, 97.7, 12.2.HRMS (ESI) calcd for C17H13N3NaS+ [M + Na+] 314.0722, found314.0726.

**5-(4-Methoxyphenyl)-3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol** **(2m)**

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According to the procedure A, **2m** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (298.9 mg, yield: 93%). mp: 95-98 °C. 1H NMR (400 MHz, CDCl3) δ 7.32 (q, *J* = 5.5 Hz, 3H), 7.25 – 7.17 (m, 4H), 6.95 – 6.90 (m, 2H), 3.84 (s, 3H), 2.53 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 160.5, 152.7, 147.0, 139.4, 131.3, 129.1, 128.0, 125.0, 119.9, 114.3, 111.4, 97.3, 55.3, 12.2. HRMS (ESI) calcd for C18H15N3NaOS+ [M + Na+] 344.0828, found344.0820.

**1,3,5-Triphenyl-4-thiocyanato-1*H*-pyrazole** **(2n)**

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According to the procedure A, **2n** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (141.37 mg, yield: 40%). mp: 110-112 °C. 1H NMR (400 MHz, CDCl3) δ 8.04 – 7.96 (m, 2H), 7.58 – 7.45 (m, 6H), 7.40 – 7.31 (m, 7H). 13C NMR (101 MHz, CDCl3) δ 154.3, 148.6, 139.2, 131.0, 130.2, 129.9, 129.2, 129.1, 128.9, 128.7, 128.5, 128.3, 127.8, 125.0, 111.8, 96.7. HRMS (ESI) calcd for C22H15N3NaS+ [M + Na+] 376.0879, found376.0875.

**1-(*tert*-Butyl)-3-methyl-5-phenyl-4-thiocyanato-1*H*-pyrazole** **(2o)**

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According to the procedure A, **2o** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (173.68 mg, yield: 64%). mp: 99-100 °C. 1H NMR (400 MHz, CDCl3) δ 7.52 – 7.46 (m, 3H), 7.33 – 7.29 (m, 2H), 2.42 (s, 3H), 1.43 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 149.1, 147.5, 131.2, 130.4, 129.6, 128.4, 111.6, 97.9, 62.7, 30.9, 12.1. HRMS (ESI) calcd for C15H17N3NaS+ [M + Na+] 294.1035, found294.1039.

**3-Methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-ol (2p)**



According to the procedure A, **2p** was purified by silica gel chromatography (1% MeOH/CH2Cl2). A white solid (170.46 mg, yield: 80%). mp: 110-112 °C. 1H NMR (400 MHz, CHCl3) δ 7.38 – 7.34 (m, 2H), 7.28 – 7.18 (m, 4H), 2.33 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 156.2, 142.7, 134.3, 131.6, 126.4, 117.4, 17.4.

**3,5-Dimethyl-1-phenyl-4-((trifluoromethyl)thio)-1*H*-pyrazole (2q)**



Following the reported procedure [2] , **2r** was purified by silica gel chromatography (10% EtOAc/PE).Colorless oil (171.54 mg, yield: 63%). 1H NMR (400 MHz, CDCl3) δ 7.51 – 7.38 (m, 5H), 2.40 (s, 3H), 2.39 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.8, 145.9, 139.4, 129.5 (q, *J*C-F = 311.08 Hz), 129.3, 128.3, 124.9, 99.2, 11.9, 11.4. HRMS (ESI) calcd for C12H11F3N2NaS+ [M + Na+] 295.0487, found 295.0485.

**3,5-Dimethyl-4-(methylthio)-1-phenyl-1*H*-pyrazole** **(2r)**

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Following the reported procedure [2] : According to the procedure A, **2q** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (122.25 mg, yield: 56%). mp: 95-96 °C. 1H NMR (400 MHz, CDCl3) δ 7.47 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.32 (m, 1H), 2.38 (s, 6H), 2.20 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.2, 142.6, 139.9, 129.1, 127.6, 124.7, 110.9, 19.9, 12.2, 11.6. HRMS (ESI) calcd for C12H14N2NaS+ [M + Na+] 241.0770, found241.0773.

**3,5-Dimethyl-1-phenyl -4-selenocyanato-1*H*-pyrazole** **(3a)**

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According to the procedure B, **3a** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (226.5 mg, yield: 82%). mp: 82-84 °C. 1H NMR (400 MHz, CDCl3) δ 7.50 (t, *J* = 7.4 Hz, 2H), 7.46 – 7.37 (m, 3H), 2.45 (d, *J* = 6.1 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 152.4, 144.6, 139.2, 129.4, 128.6, 125.1, 100.9, 94.7, 12.9, 12.4. HRMS (ESI) calcd for C12H11N3NaSe+ [M + Na+] 300.0010, found300.0018.

**3,5-Dimethyl-4-** **selenocyanato-1-(*p*-tolyl)-1*H*-pyrazole** **(3b)**

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According to the procedure B, **3b** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (252.5 mg, yield: 87%). mp: 77-79 °C. 1H NMR (400 MHz, CDCl3) δ 7.28 (s, 4H), 2.47 – 2.40 (m, 9H). 13C NMR (101 MHz, CDCl3) δ 152.1, 144.6, 138.7, 136.7, 129.9, 124.9, 101.0, 94.4, 21.2, 12.8, 12.3. HRMS (ESI) calcd for C13H13N3NaSe+ [M + Na+] 314.0167, found314.0170.

**3,5-Dimethyl-4-selenocyanato-1-(*o*-tolyl)-1*H*-pyrazole** **(3c)**

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According to the procedure B, **3c** was purified by silica gel chromatography (15% EtOAc/PE). Yellow oil (258.3 mg, yield: 89%). 1H NMR (400 MHz, CDCl3) δ 7.38 – 7.33 (m, 1H), 7.25 – 7.21 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.2, 144.5, 139.6, 139.1, 129.4, 129.0, 125.8, 122.0, 101.0, 94.5, 21.4, 12.9, 12.4. HRMS (ESI) calcd for C13H13N3NaSe+ [M + Na+] 314.0167, found314.0163.

**3,5-Dimethyl-4-selenocyanato-1-(*m*-tolyl)-1*H*-pyrazole** **(3d)**

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According to the procedure B, **3d** was purified by silica gel chromatography (15% EtOAc/PE). Yellow oil (261.2 mg, yield: 90%). 1H NMR (400 MHz, CDCl3) δ 7.41 – 7.27 (m, 3H), 7.19 (dd, *J* = 7.7, 1.0 Hz, 1H), 2.43 (s, 3H), 2.23 (s, 3H), 2.04 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.1, 145.5, 138.0, 135.8, 131.2, 129.8, 127.5, 126.9, 101.1, 93.1, 17.2, 12.9, 11.4. HRMS (ESI) calcd for C13H13N3NaSe+ [M + Na+] 314.0167, found314.0162.

**1-(4-Methoxyphenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazole** **(3e)**

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According to the procedure B, **3e** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (225.0 mg, yield: 80%). mp: 82-85 °C. 1H NMR (400 MHz, CDCl3) δ 7.33 – 7.28 (m, 2H), 7.01 – 6.96 (m, 2H), 3.86 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.6, 152.0, 144.7, 132.3, 126.6, 114.4, 101.0, 94.0, 55.6, 12.8, 12.2. HRMS (ESI) calcd for C13H13N3NaOSe+ [M + Na+] 330.0116, found330.0110.

**1-(4-Fluorophenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazol** **(3f)**

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According to the procedure B, **3f** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (232.4 mg, yield: 79%). mp: 75-77 °C. 1H NMR (400 MHz, CDCl3) δ 7.38 (ddt, *J* = 7.9, 5.3, 2.6 Hz, 2H), 7.22 – 7.15 (m, 2H), 2.43 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 162.3 (d, *J*C-F = 250.2 Hz), 152.4, 144.7, 135.3 (d, *J*C-F = 3.2 Hz), 127.1 (d, *J*C-F = 8.8 Hz), 116.4 (d, *J*C-F = 23.1 Hz), 100.8, 94.8, 12.8, 12.3. HRMS (ESI) calcd for C12H10FN3NaSe+ [M + Na+] 317.9916, found317.9910.

**1-(4-Chlorophenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazole** **(3g)**

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According to the procedure B, **3g** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (279.6 mg, yield: 90%). mp: 95-98 °C. 1H NMR (400 MHz, CDCl3) δ 7.51 – 7.45 (m, 2H), 7.41 – 7.33 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.7, 144.6, 137.7, 134.4, 129.6, 126.2, 100.7, 95.2, 12.9, 12.4. HRMS (ESI) calcd for C12H10ClN3NaSe+ [M + Na+] 333.9621, found323.9626.

**1-(4-Bromophenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazole** **(3h)**

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According to the procedure B, **3h** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (269.9 mg, yield: 76%). mp: 96-98 °C. 1H NMR (400 MHz, CDCl3) δ 7.65 – 7.61 (m, 2H), 7.34 – 7.28 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.7, 144.6, 138.2, 132.5, 126.4, 122.4, 100.7, 95.3, 12.9, 12.5. HRMS (ESI) calcd for C12H10BrN3NaSe+ [M + Na+] 377.9116, found377.9110.

**1-(4-Iodophenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazole** **(3i)**

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According to the procedure B, **3i** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (301.6 mg, yield: 75%). mp: 85-87 °C. 1H NMR (400 MHz, CDCl3) δ 7.86 – 7.80 (m, 2H), 7.20 – 7.13 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.7, 144.6, 138.9, 138.5, 126.6, 100.7, 95.4, 93.7, 12.9, 12.5. HRMS (ESI) calcd for C12H10IN3NaSe+ [M + Na+] 425.8977, found425.8974.

**3,5-Dimethyl-4-selenocyanato-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (3j)**

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According to the procedure B, **3j** was purified by silica gel chromatography (15% EtOAc/PE). A yellow solid (285.7 mg, yield: 83%). mp: 92-95 °C. 1H NMR (400 MHz, CDCl3) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 2.52 (s, 3H), 2.44 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.1, 144.7, 142.0, 130.4 (q, *J*C-F = 33.1 Hz), 126.6 (q, *J*C-F = 3.7 Hz), 124.94 (q, *J*C-F = 273.3 Hz), 124.9, 100.6, 96.1, 12.9, 12.7. HRMS (ESI) calcd for C13H10F3N3NaSe+ [M + Na+] 367.9884, found367.9880.

**3,5-Dimethyl-1-(4-nitrophenyl)-4-selenocyanato-1*H*-pyrazole** **(3k)**

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According to the procedure B, **3k** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (183.1 mg, yield: 57%). mp: 140-142 °C. 1H NMR (400 MHz, CDCl3) δ 8.41 – 8.36 (m, 2H), 7.69 – 7.65 (m, 2H), 2.58 (s, 3H), 2.46 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.7, 146.8, 144.9, 144.0, 124.9, 124.7, 100.3, 97.3, 13.0, 12.9. HRMS (ESI) calcd for C12H10N4NaO2Se+ [M + Na+] 344.9861, found344.9868.

**1-(3,5-Dichlorophenyl)-3,5-dimethyl-4-selenocyanato-1*H*-pyrazole** **(3l)**

****

According to the procedure B, **3l** was purified by silica gel chromatography (15% EtOAc/PE). A yellow solid (296.8 mg, yield: 82%). mp: 104-106 °C. 1H NMR (400 MHz, CDCl3) δ 7.42 (t, *J* = 1.8 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 2H), 2.51 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.2, 144.7, 140.7, 135.7, 128.5, 123.3, 100.4, 96.2, 12.9, 12.7. HRMS (ESI) calcd for C12H9Cl2N3NaSe+ [M + Na+] 367.9231, found367.9235.

**2-(3,5-Dimethyl-4-selenocyanato-1*H*-pyrazol-1-yl)pyrazine (3m)**

****

According to the procedure B, **3m** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (239.2 mg, yield: 86%). mp: 95-98 °C. 1H NMR (400 MHz, CDCl3) δ 9.25 (d, *J* = 1.2 Hz, 1H), 8.52 (d, *J* = 2.5 Hz, 1H), 8.40 (dd, *J* = 2.4, 1.5 Hz, 1H), 2.83 (s, 3H), 2.47 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.7, 149.0, 147.0, 142.1, 141.2, 138.6, 100.3, 98.4, 14.3, 13.1. HRMS (ESI) calcd for C10H9N5NaSe+ [M + Na+] 301.9915, found301.9918.

**1,3,5-Triphenyl-4-selenocyanato-1*H*-pyrazole** **(3n)**

****

According to the procedure B, **3n** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (168.1 mg, yield: 42%). mp: 99-100 °C. 1H NMR (400 MHz, CDCl3) δ 7.97 – 7.92 (m, 2H), 7.56 – 7.41 (m, 6H), 7.40 – 7.28 (m, 7H). 13C NMR (101 MHz, CDCl3) δ 154.9, 149.0, 139.3, 131.5, 130.4, 129.7, 129.1, 129.0, 128.8, 128.8, 128.6, 128.2, 125.0, 102.0, 94.3. HRMS (ESI) calcd for C22H15N3NaSe+ [M + Na+] 424.0323, found424.0326.

**1-(*tert*-Butyl)-5-(4-methoxyphenyl)-3-methyl-4-selenocyanato-1*H*-pyrazole (3o)**

****

According to the procedure B, **3o** was purified by silica gel chromatography (15% EtOAc/PE). A white solid (206.9 mg, yield: 65%). mp: 97-99 °C. 1H NMR (400 MHz, CDCl3) δ 7.50 – 7.45 (m, 3H), 7.32 – 7.26 (m, 2H), 2.42 (s, 3H), 1.43 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 149.3, 147.8, 132.1, 130.5, 129.4, 128.3, 101.8, 96.2, 62.5, 31.0, 12.9. HRMS (ESI) calcd for C15H17N3NaSe+ [M + Na+] 342.0480, found342.0485.

**3,5-Dimethyl-1-phenyl-4-((trifluoromethyl)selanyl)-1*H*-pyrazole** **(3p)**

****

Following the reported procedure [2], **3p** was purified by silica gel chromatography (20% EtOAc/PE). A white solid (191.5 mg, yield: 60%). mp: 89-91 °C. 1H NMR (400 MHz, CDCl3) δ 7.53 – 7.37 (m, 5H), 2.43 (s, 3H), 2.41 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 153.6, 145.5, 139.6, 129.2, 128.2, 123.5, 112.4 (q, *J* = 335.2 Hz), 97.8, 12.7, 12.3. HRMS (ESI) calcd for C12H11F3N2NaSe+ [M + Na+] 342.9932, found342.9936.

**3,5-Dimethyl-4-(methylselanyl)-1-phenyl-1*H*-pyrazole (3q)**

****

Following the reported procedure [3], **3q** was purified by silica gel chromatography (20% EtOAc/PE). A white solid (164.4 mg, yield: 62%). mp: 100-102 °C. 1H NMR (400 MHz, CDCl3) δ 7.46 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.42 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.39 – 7.33 (m, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.06 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 152.5, 142.9, 139.9, 129.1, 127.7, 124.8, 104.3, 13.0, 12.5, 8.8. HRMS (ESI) calcd for C12H14N2NaSe+ [M + Na+] 289.0214, found289.0218.

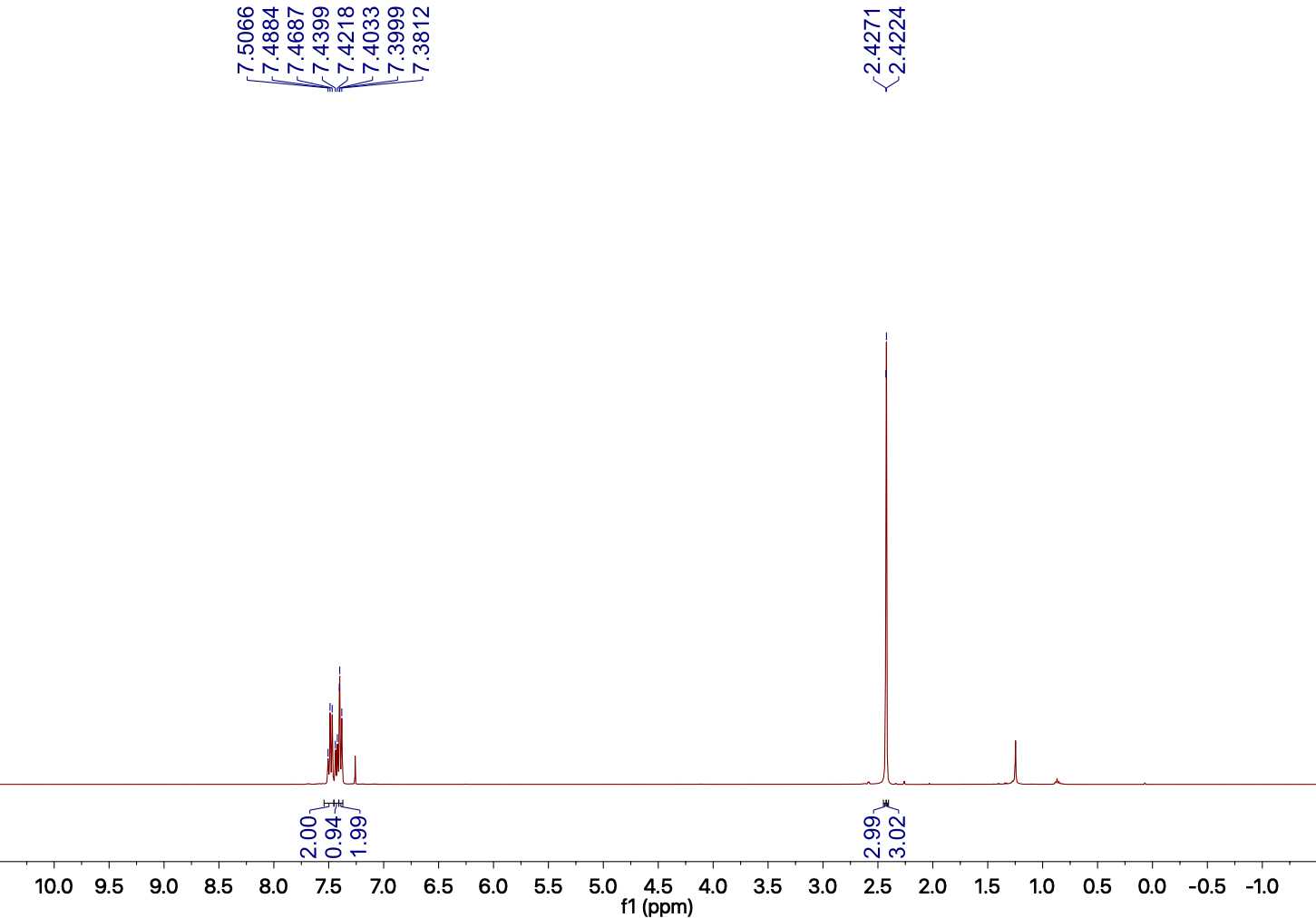
**IV. References**

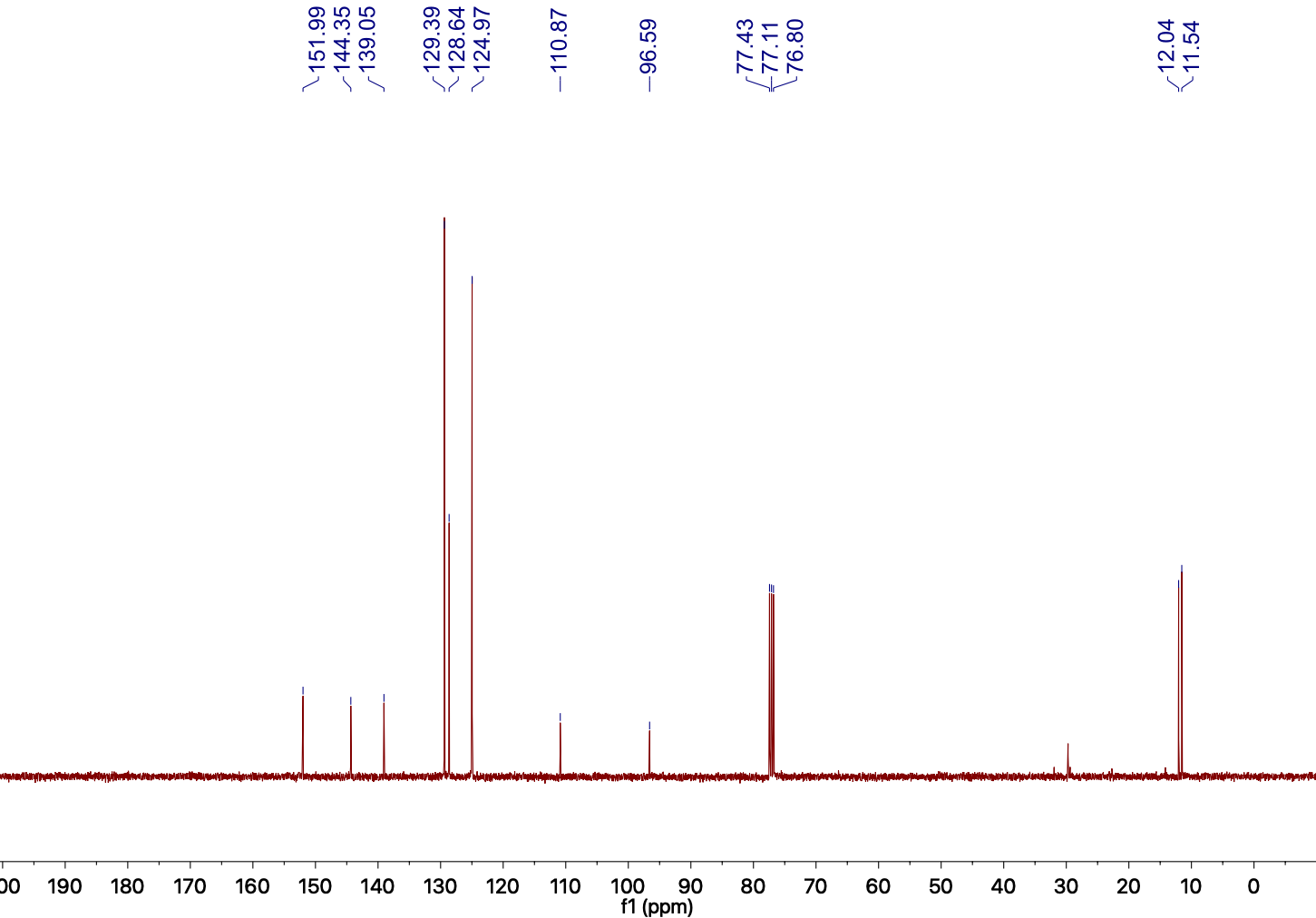
[1] Reddy, S. C.; Devi V. M.; Sunitha, M. Nagaraj, A. *Chem. Pharm. Bull.* **2010**, *58*, 1622-1626.

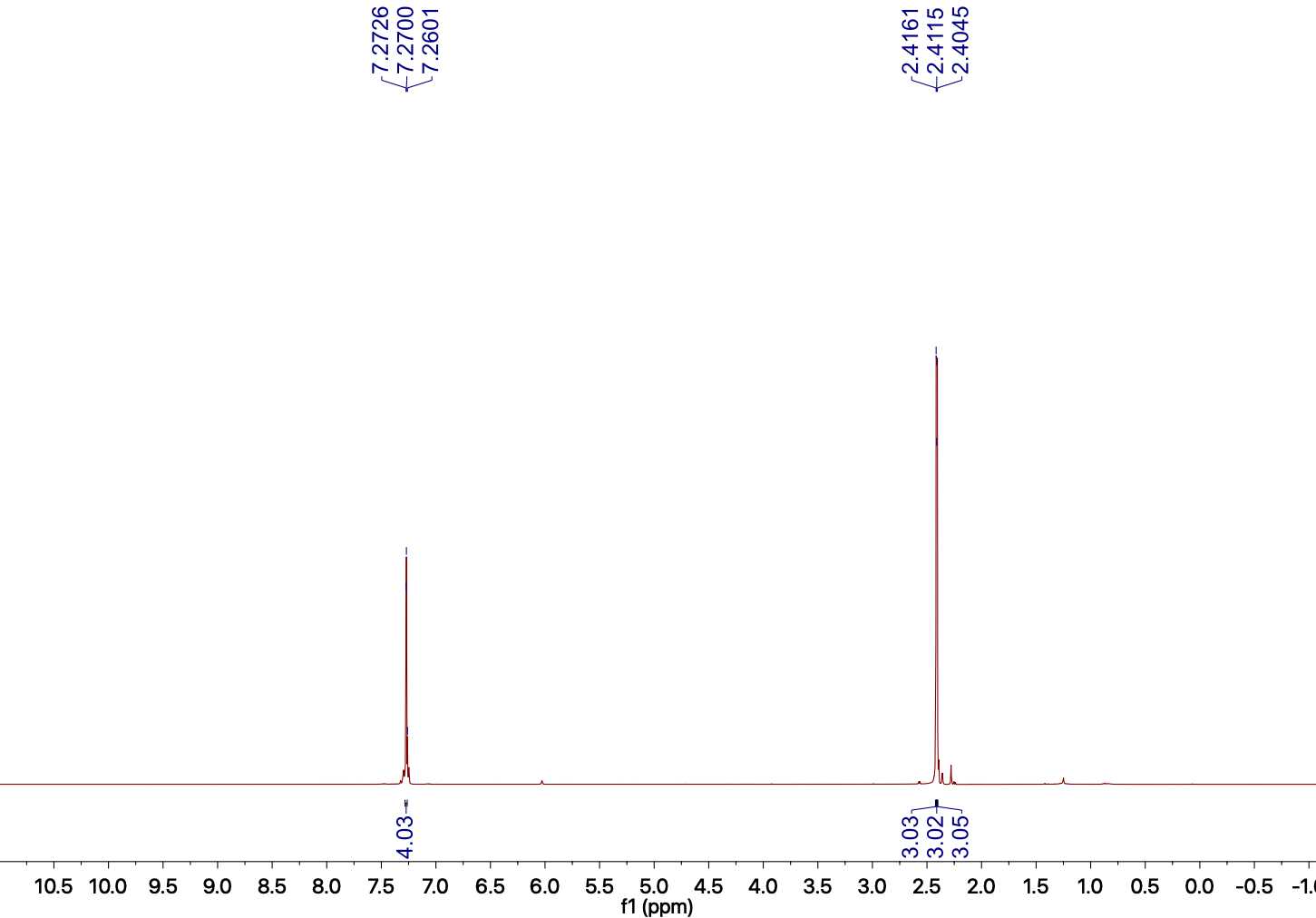
[2] R. Adams, H. B. Bramlet, F. H. Tendick, *J. Am. Chem. Soc.* **1920**, *42*, 2369-2374.

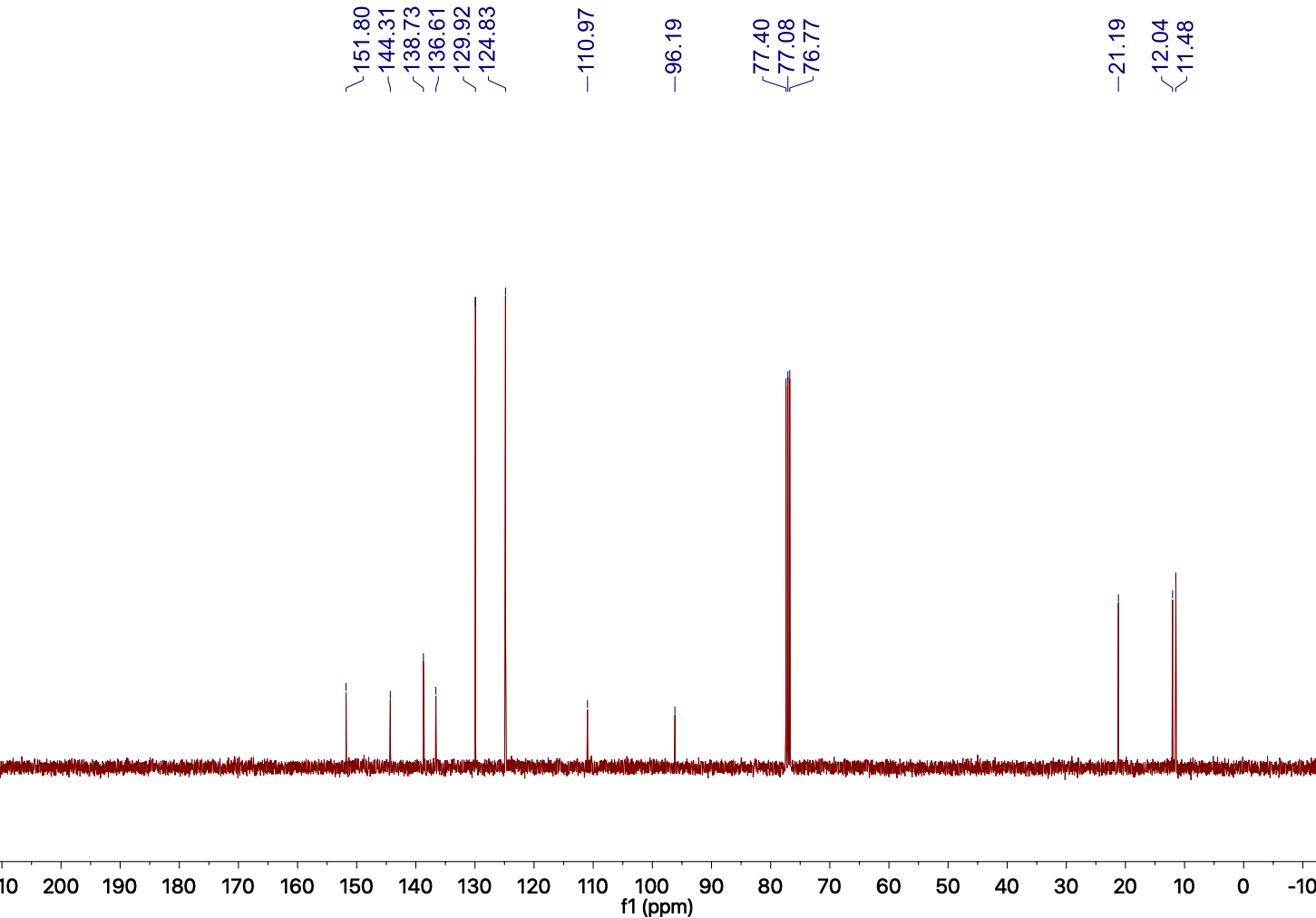
[3] Jouvin, K.; Matheis, C.; Goossen, L. J. *Chem. Eur. J.* **2015**, *21*, 14324-14327.

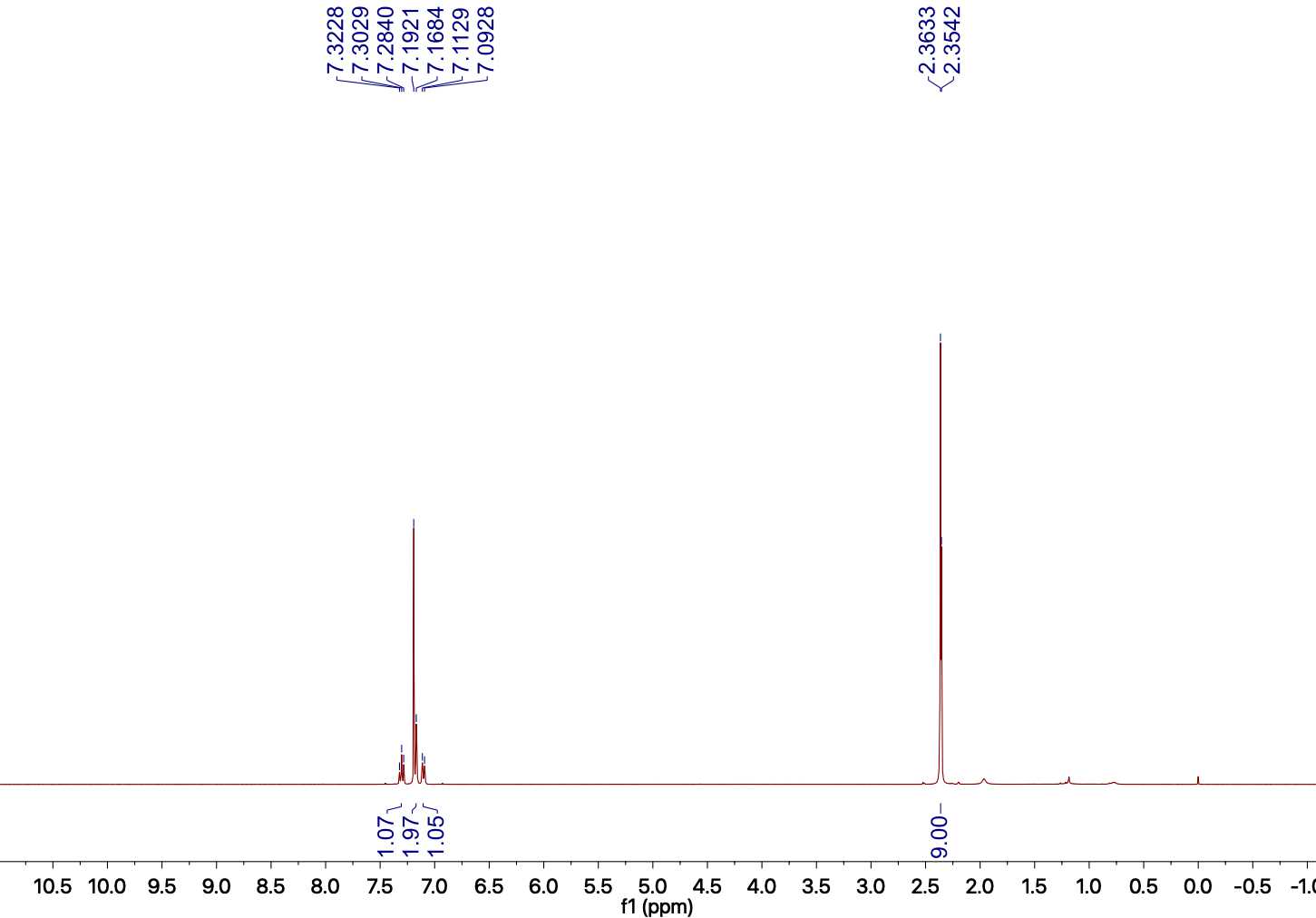
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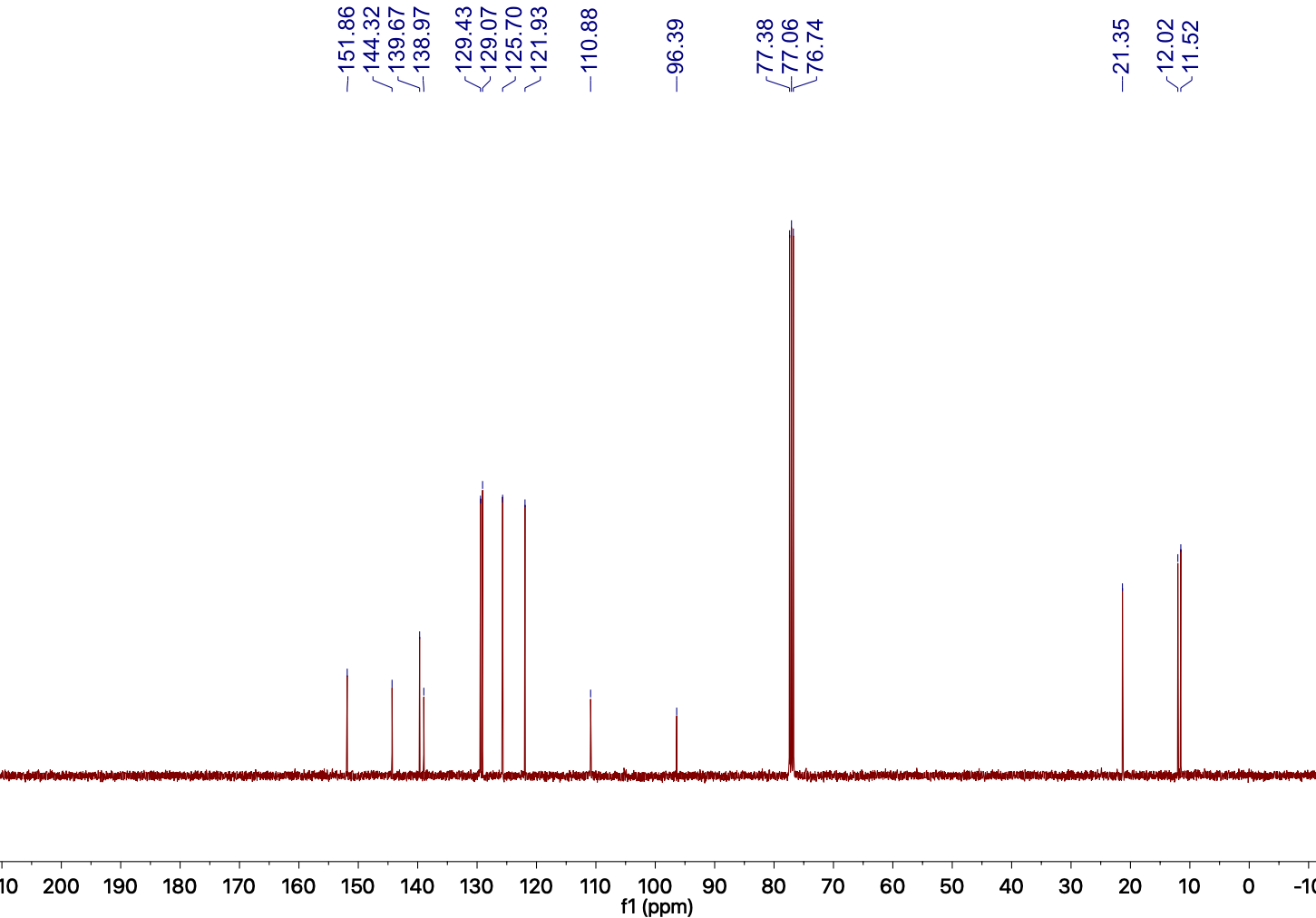
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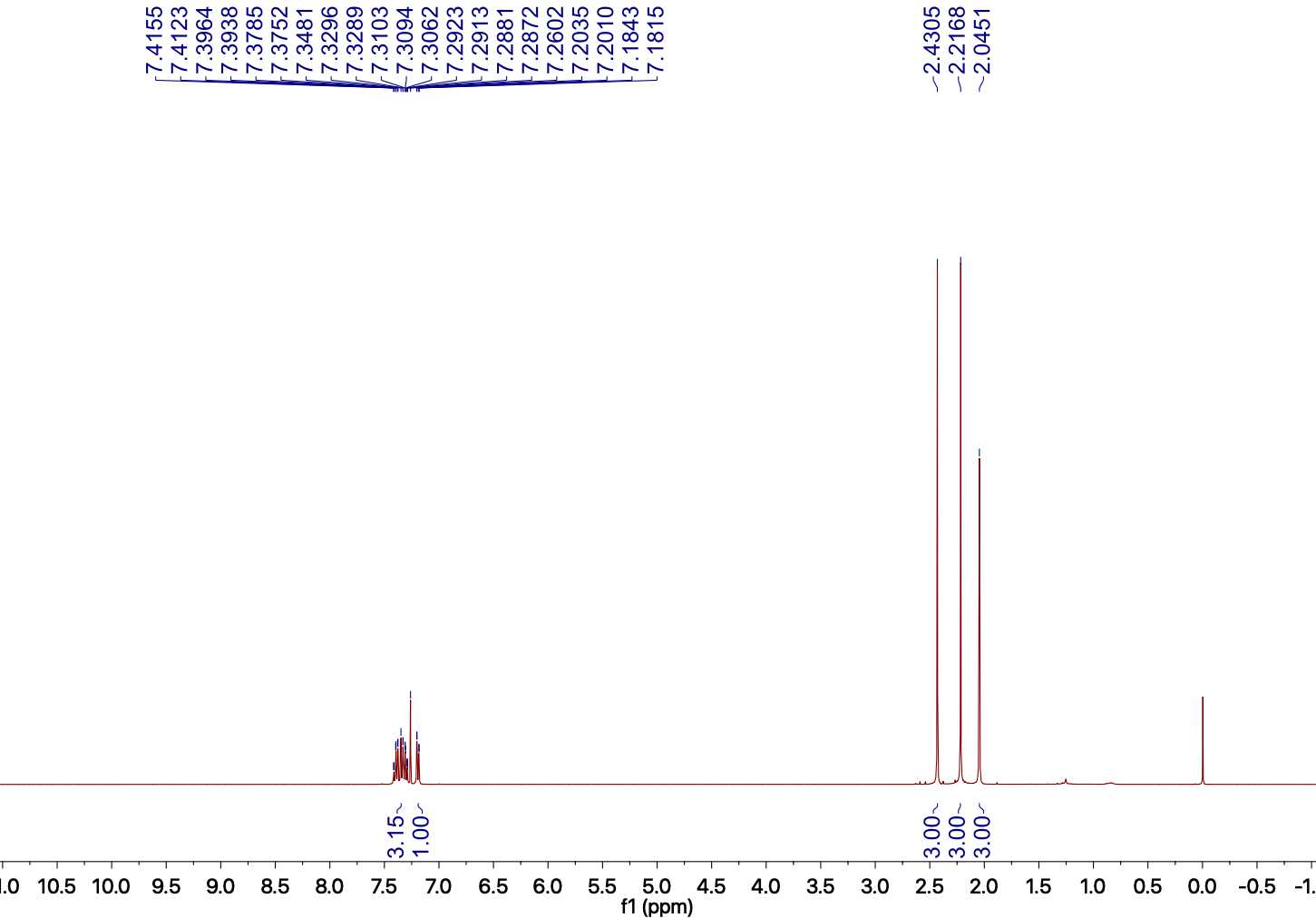
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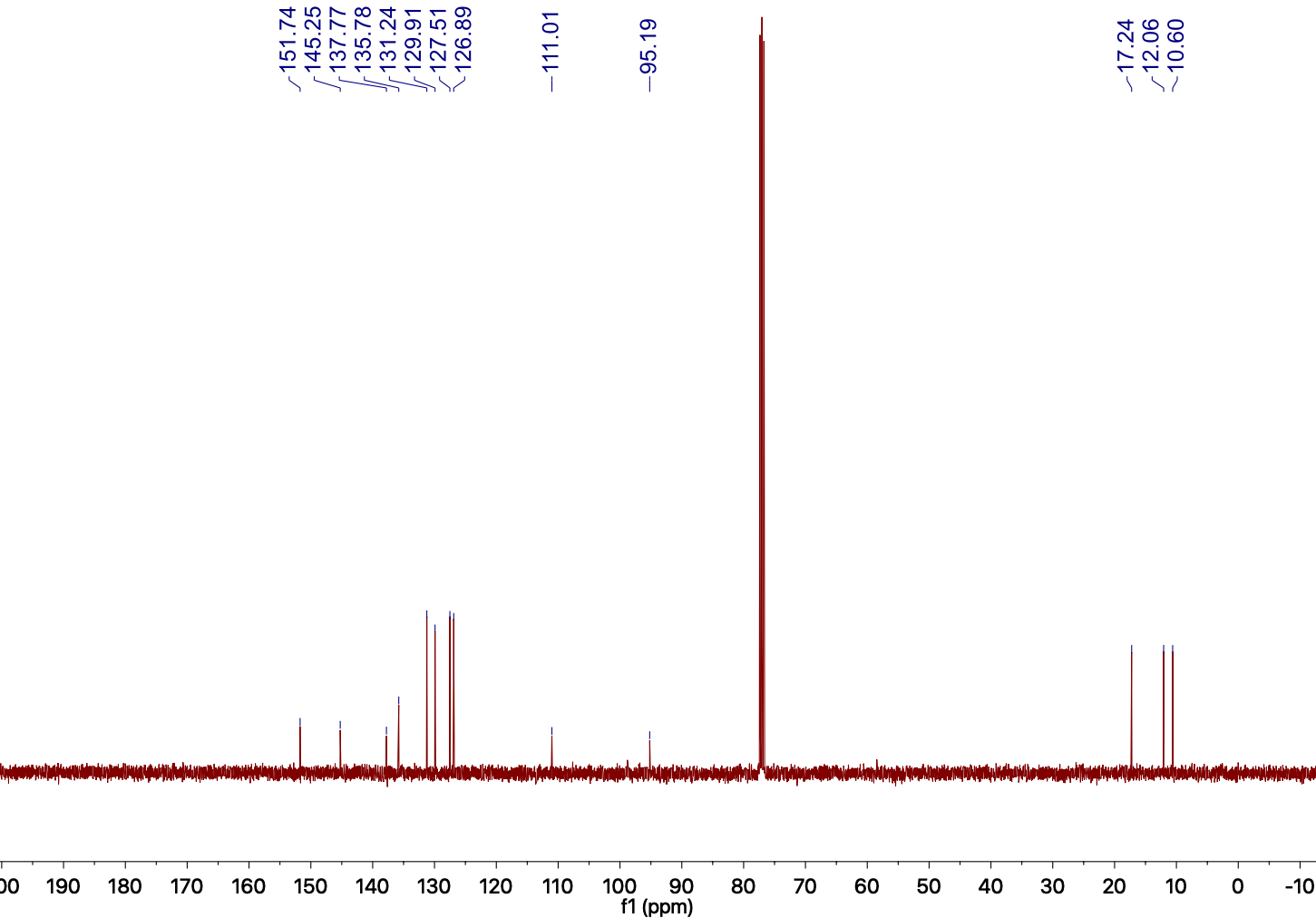
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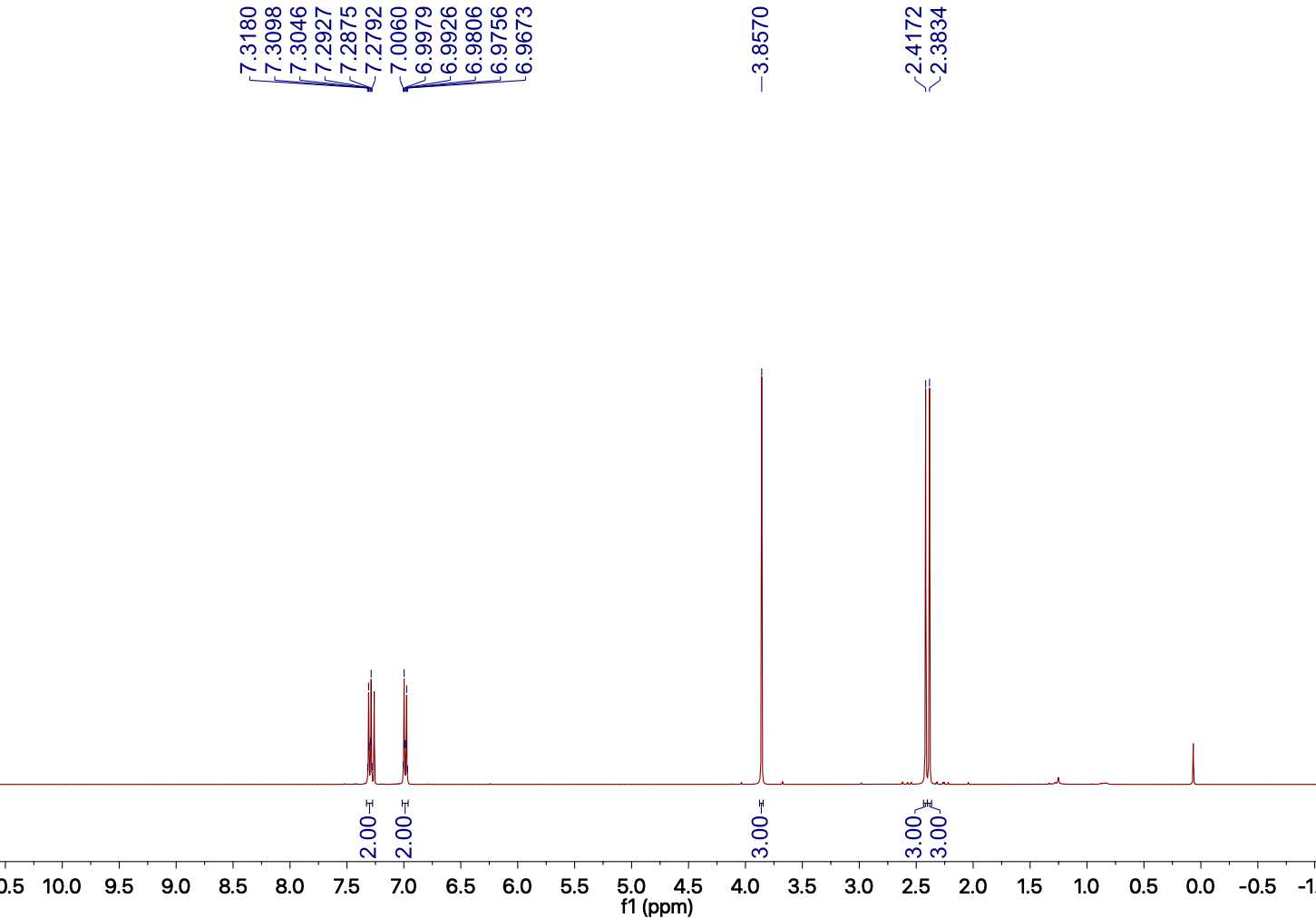
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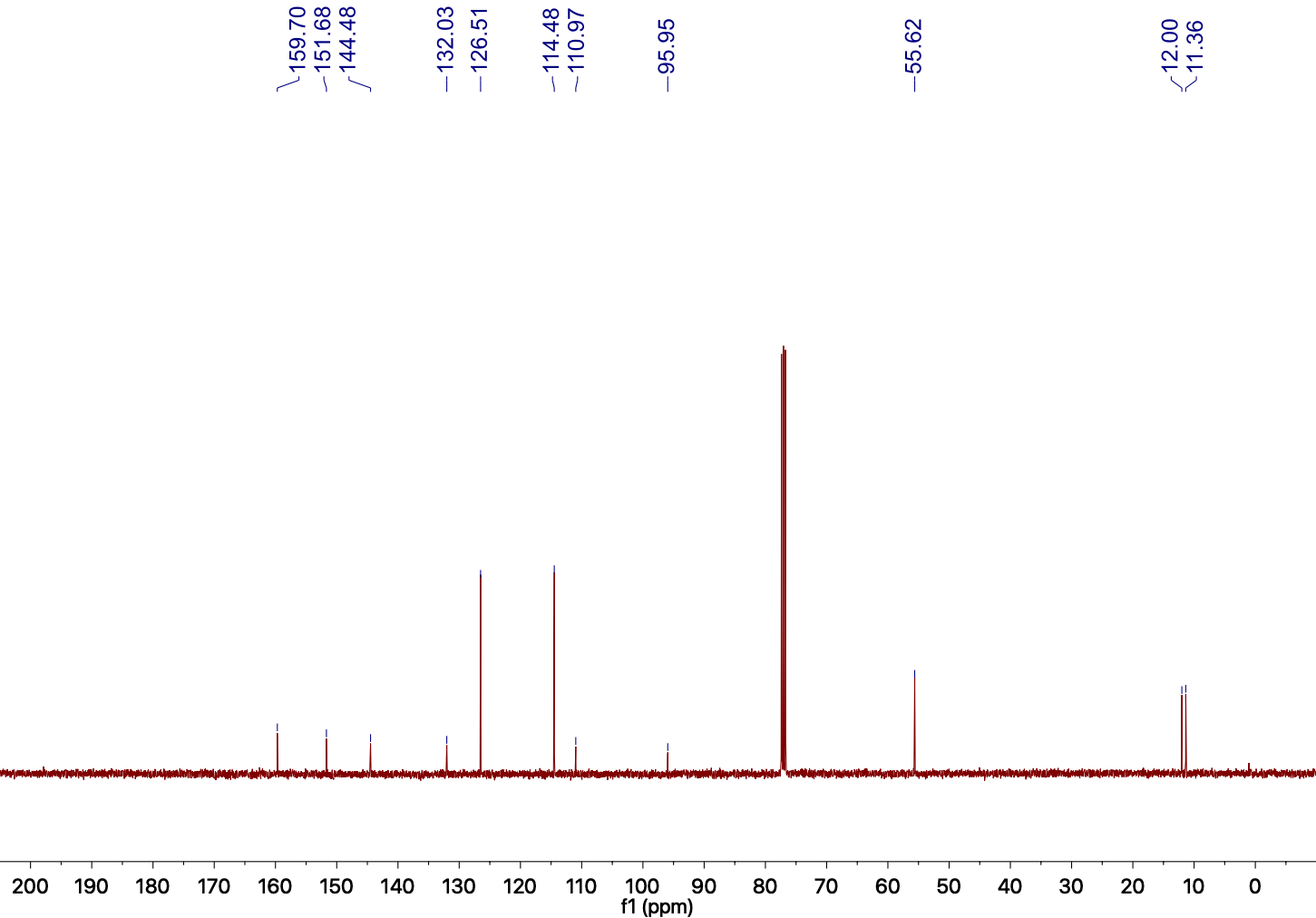
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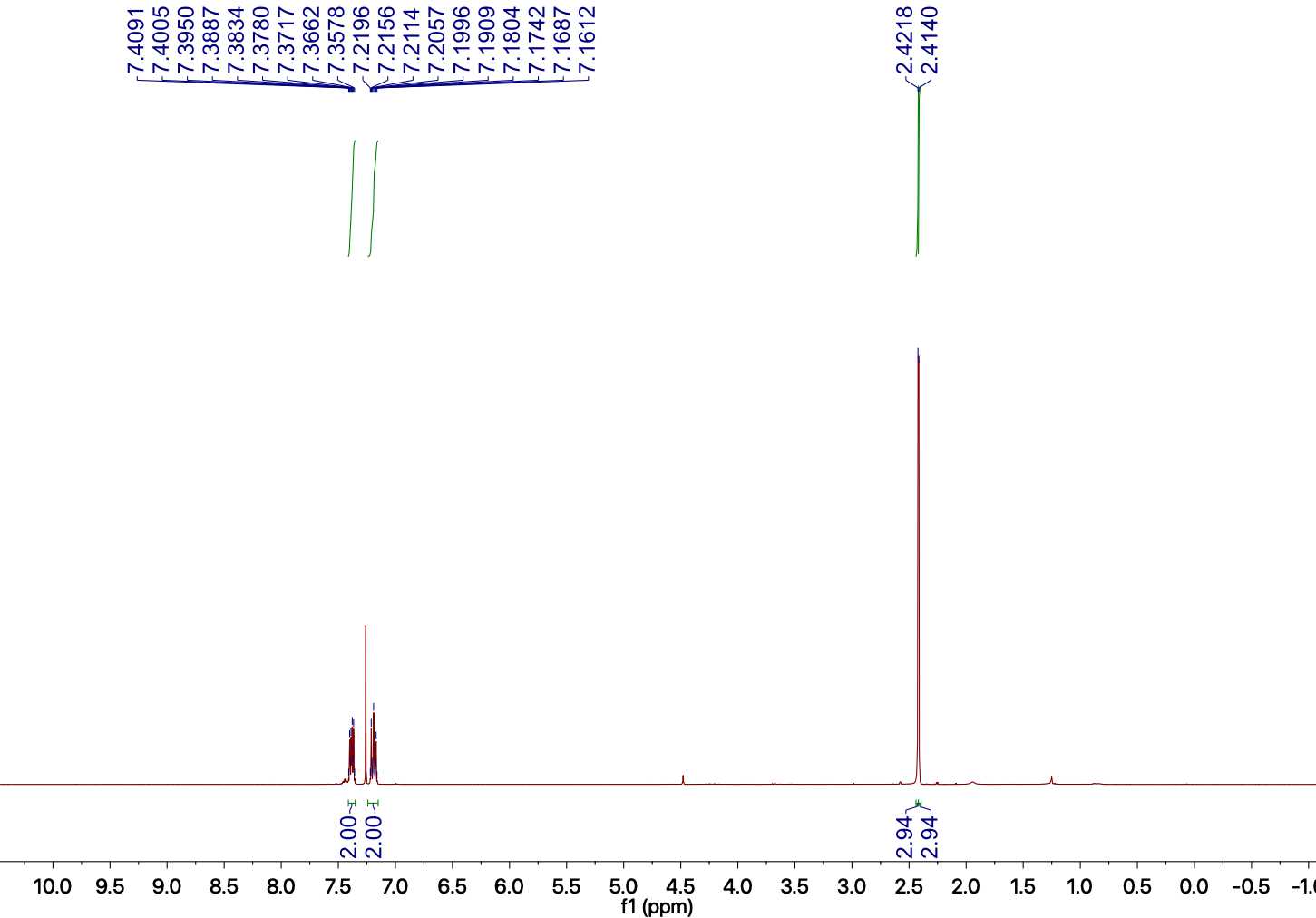
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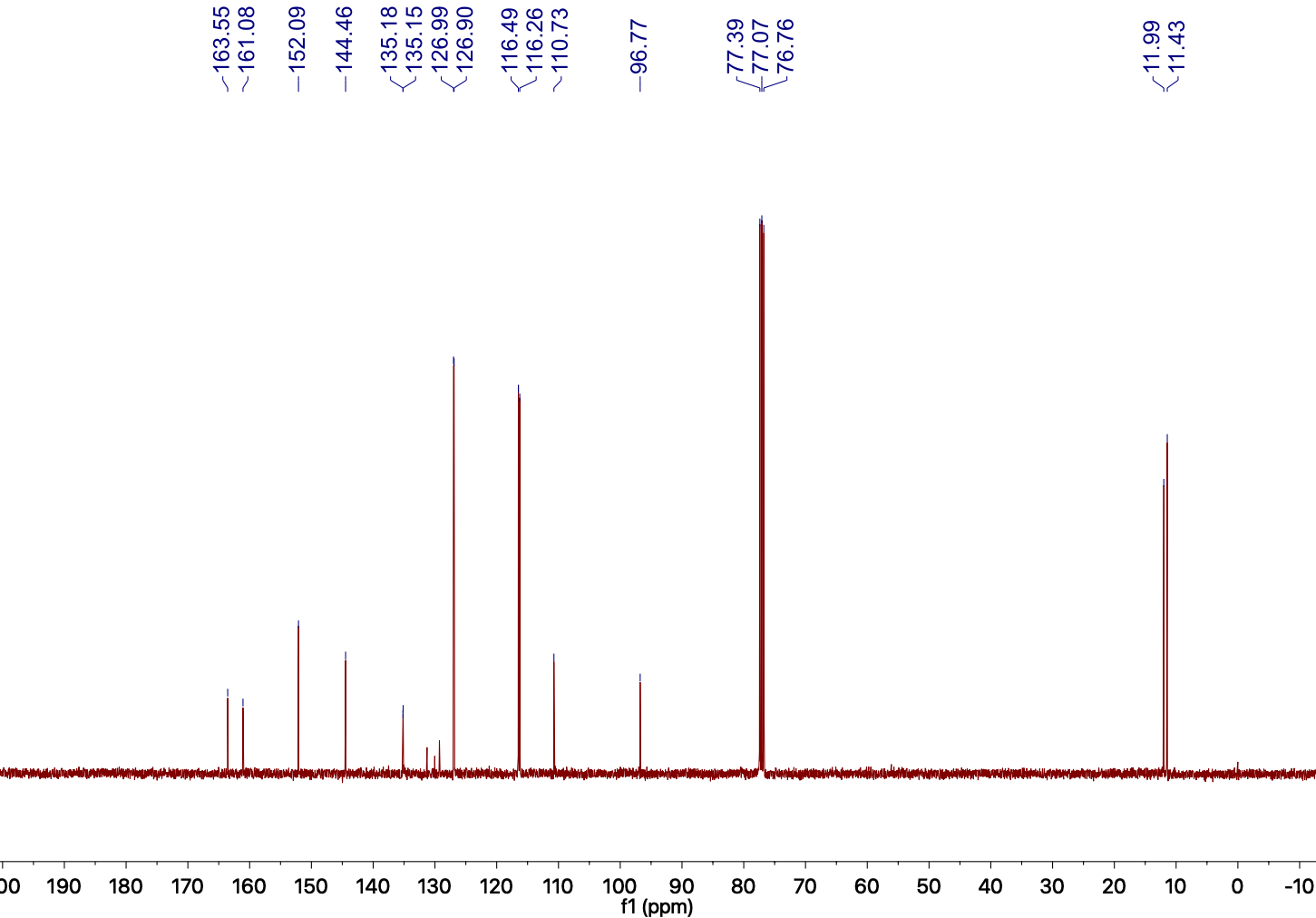
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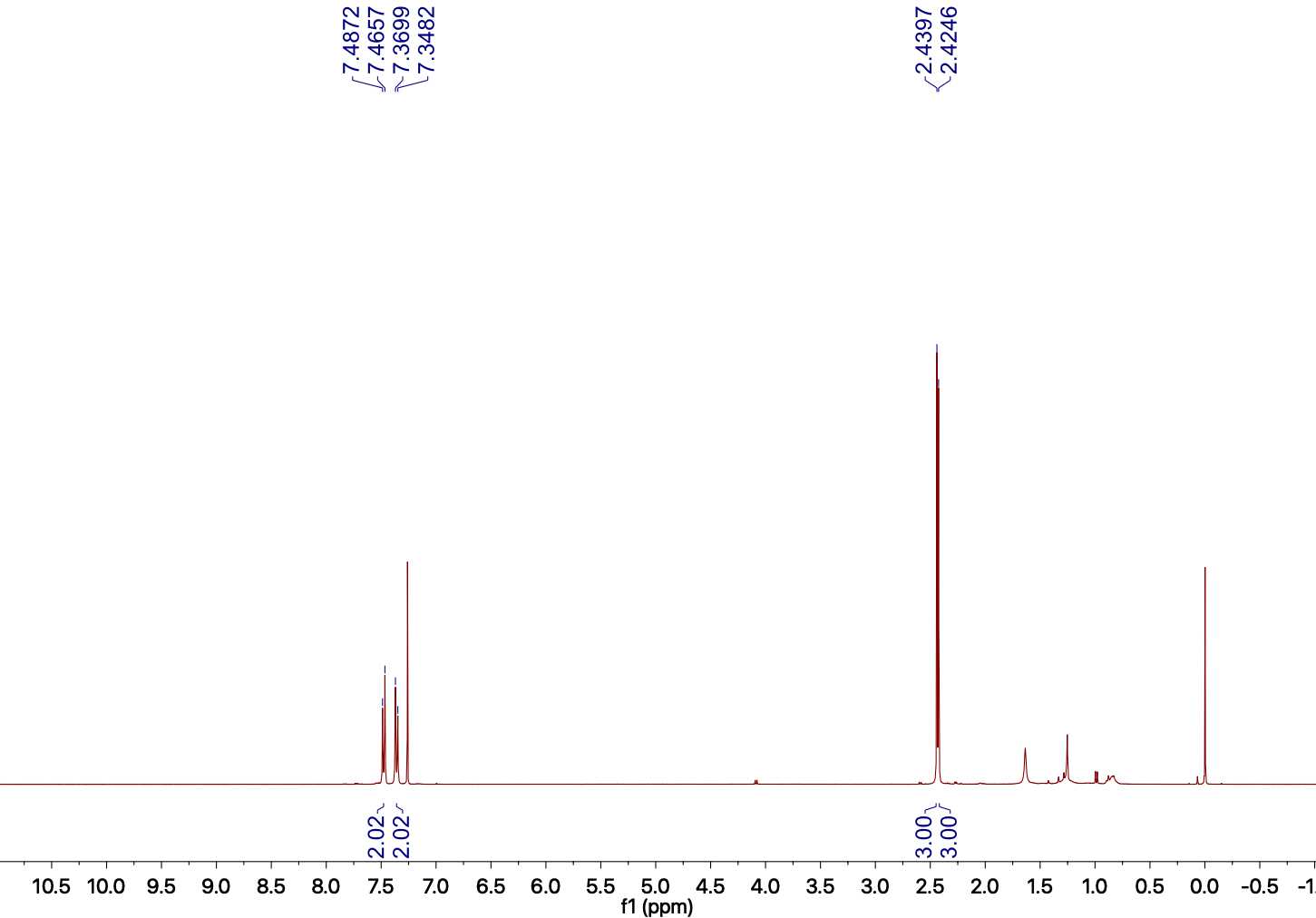
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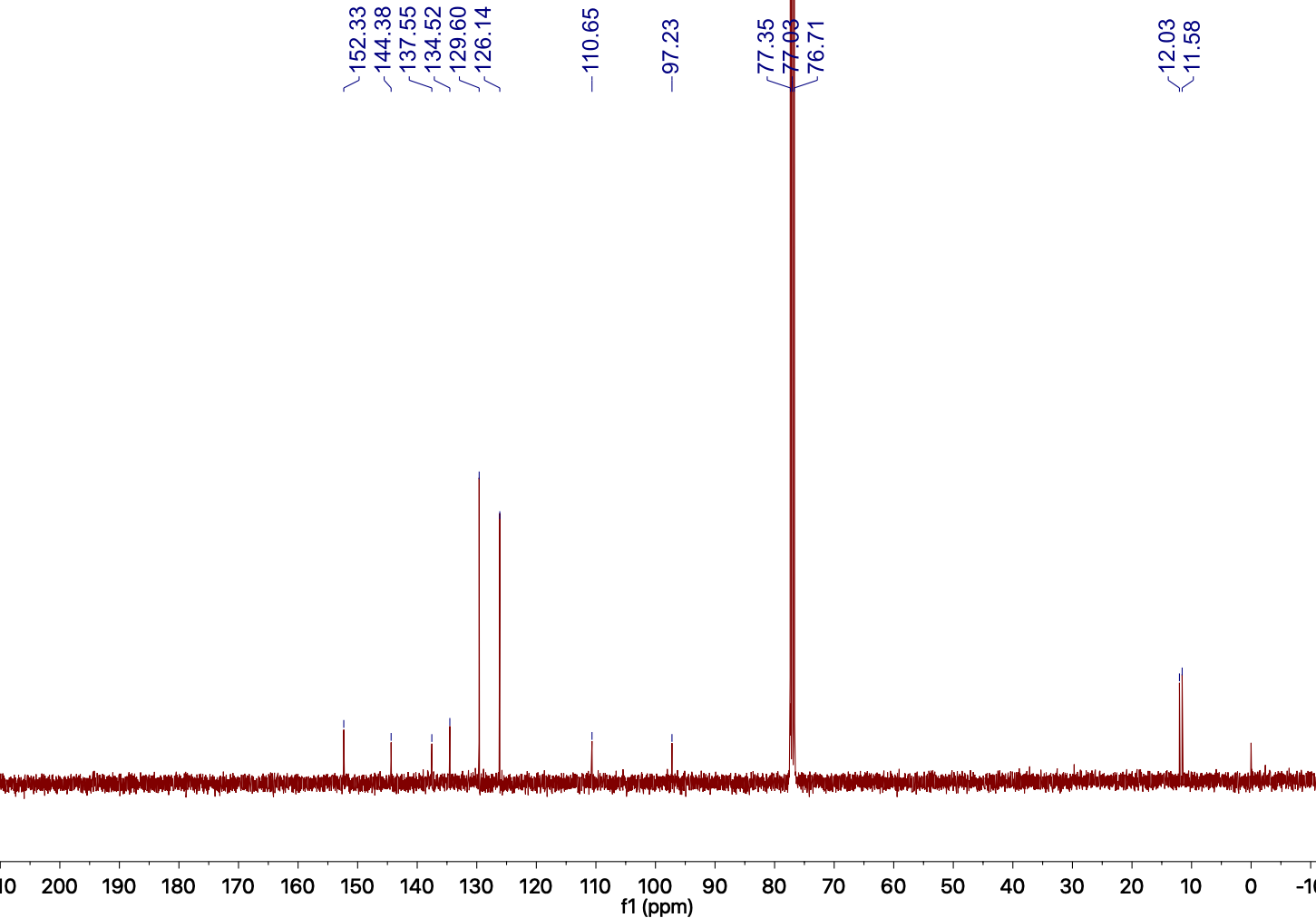
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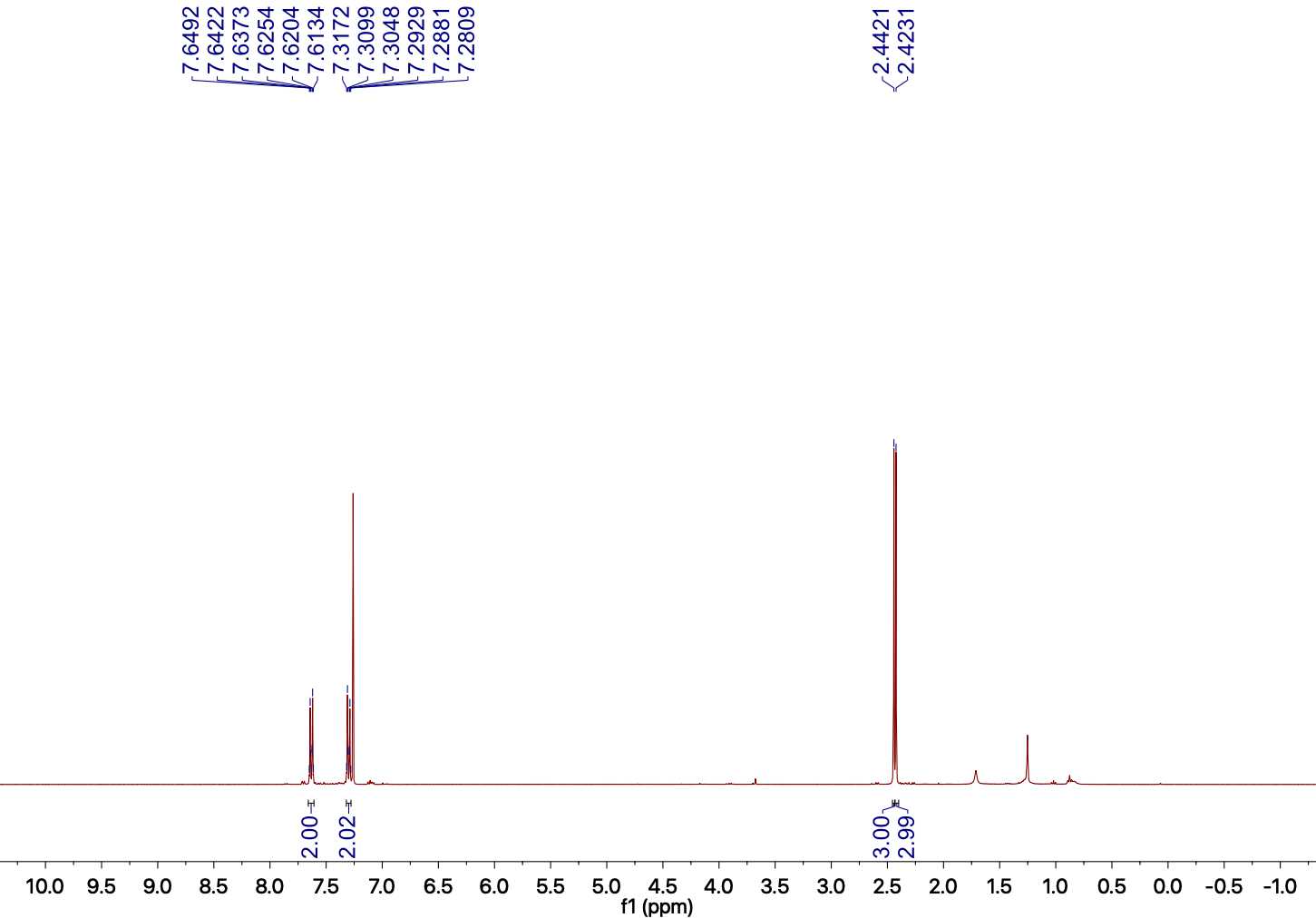
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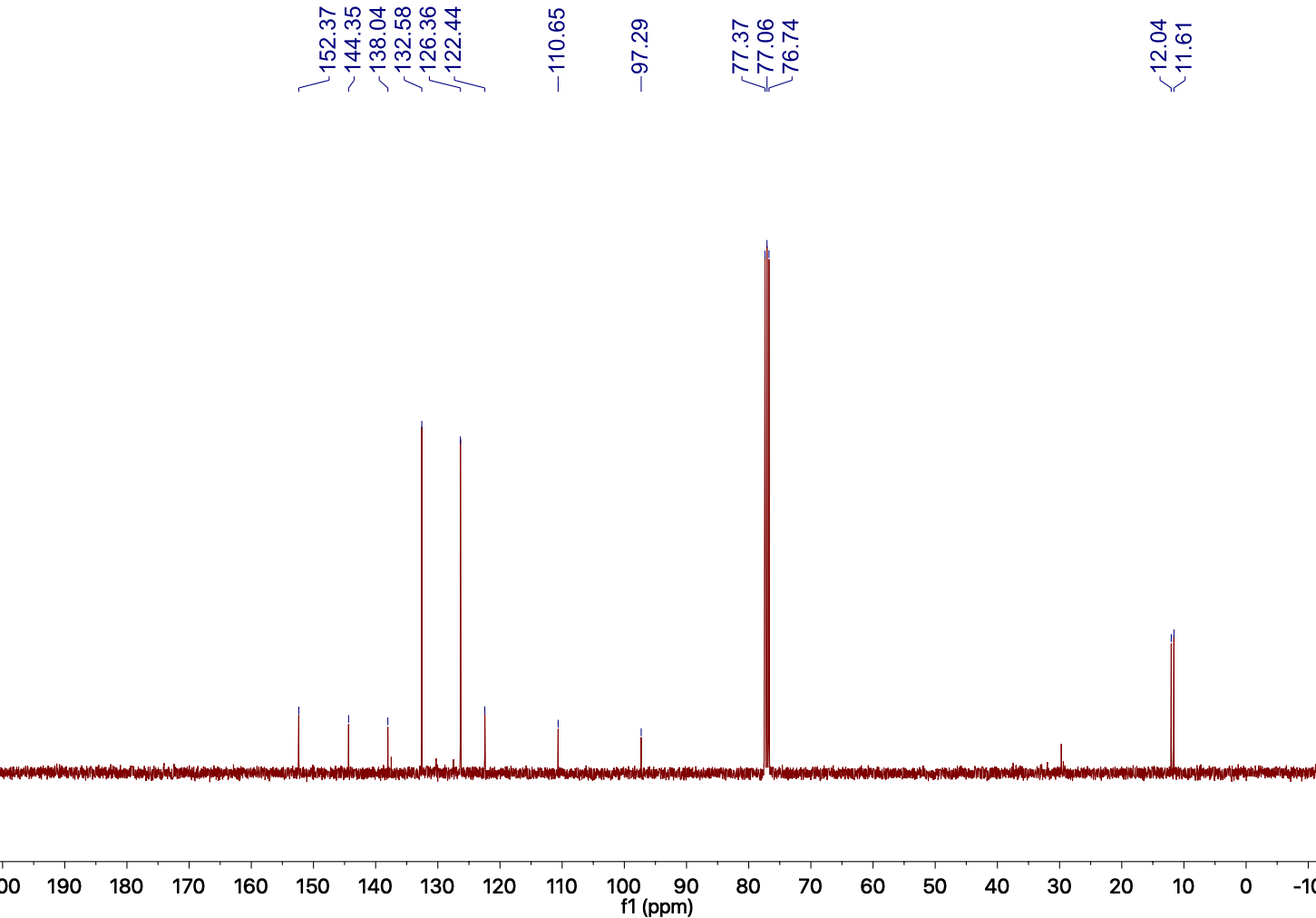
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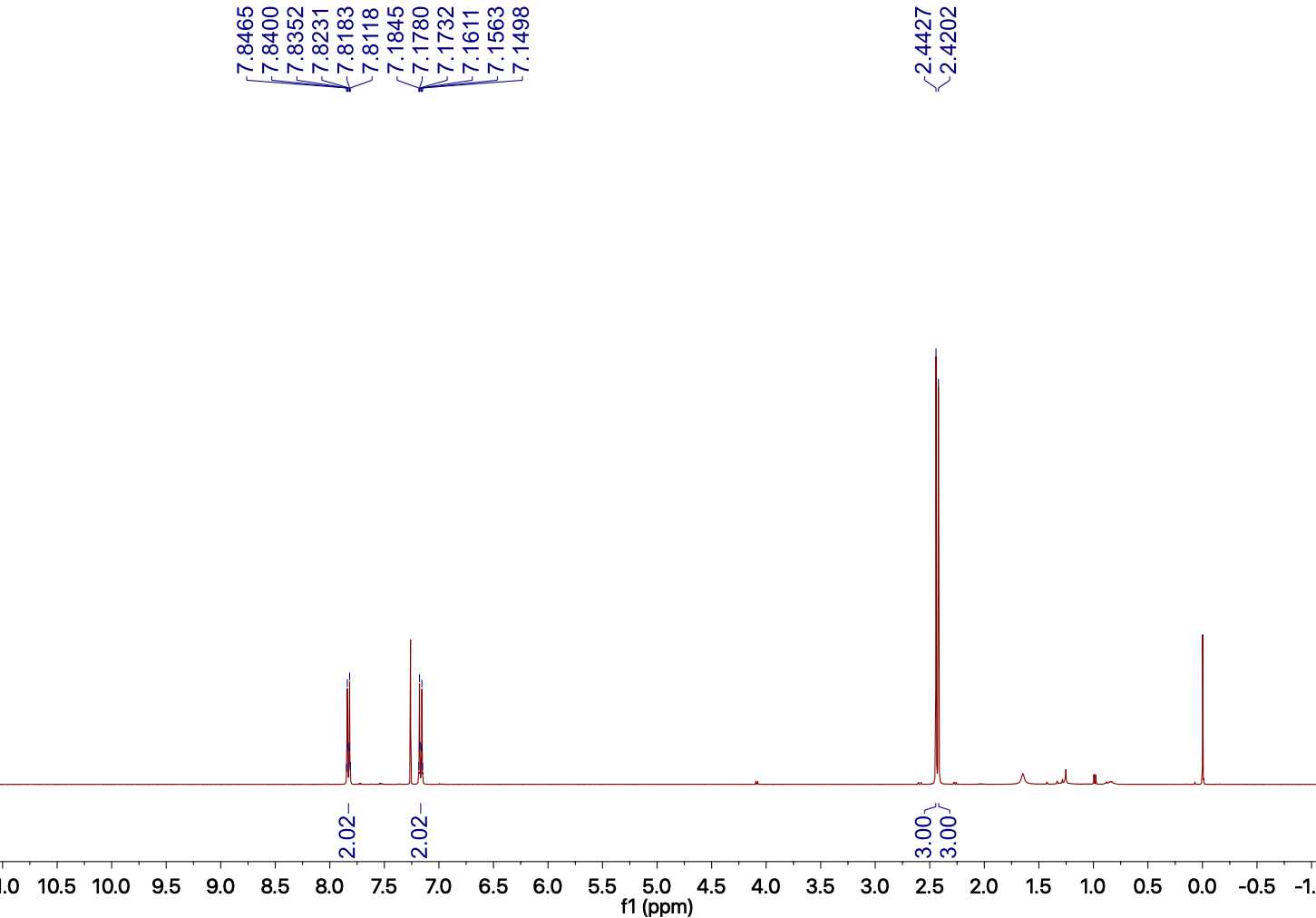
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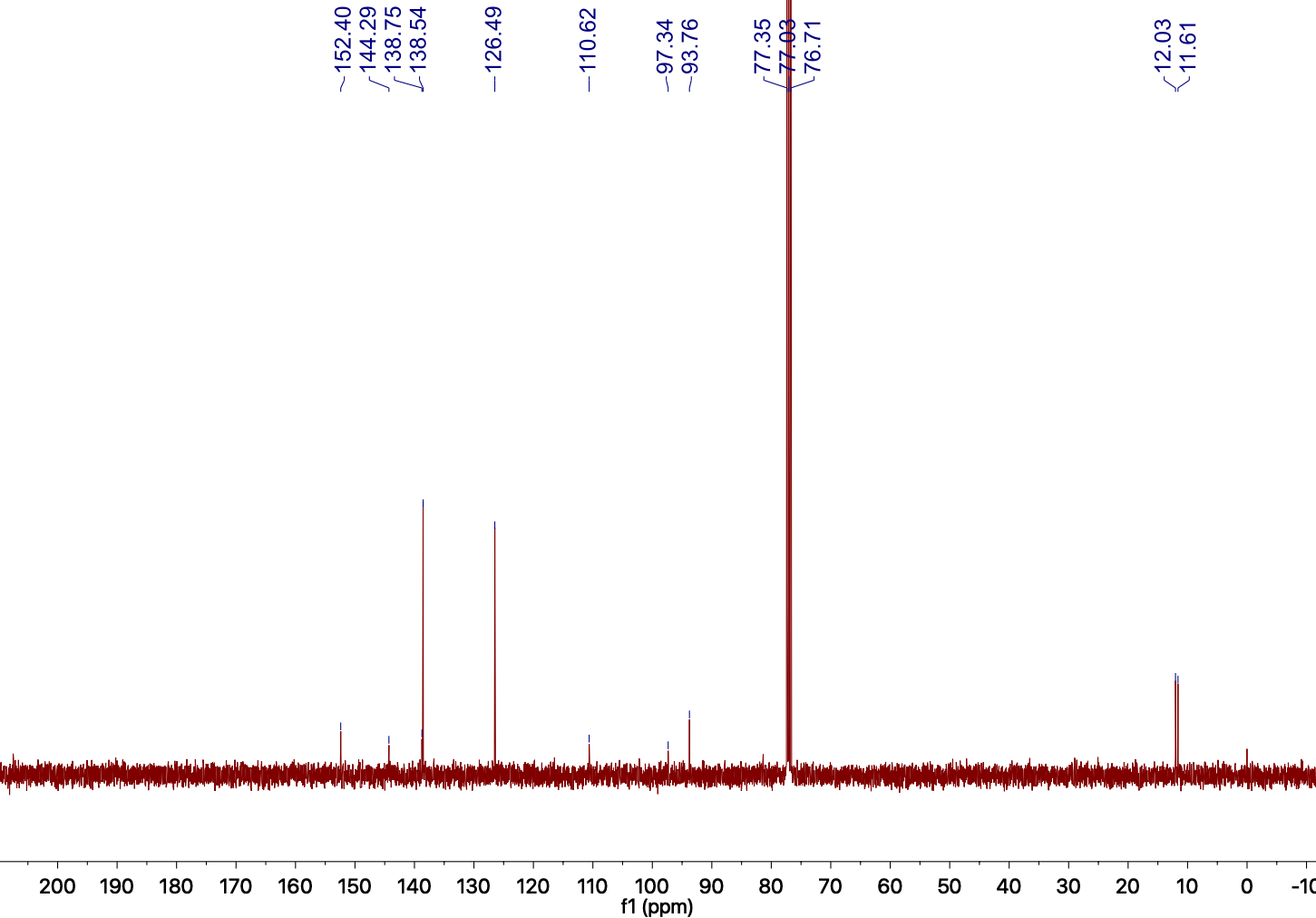
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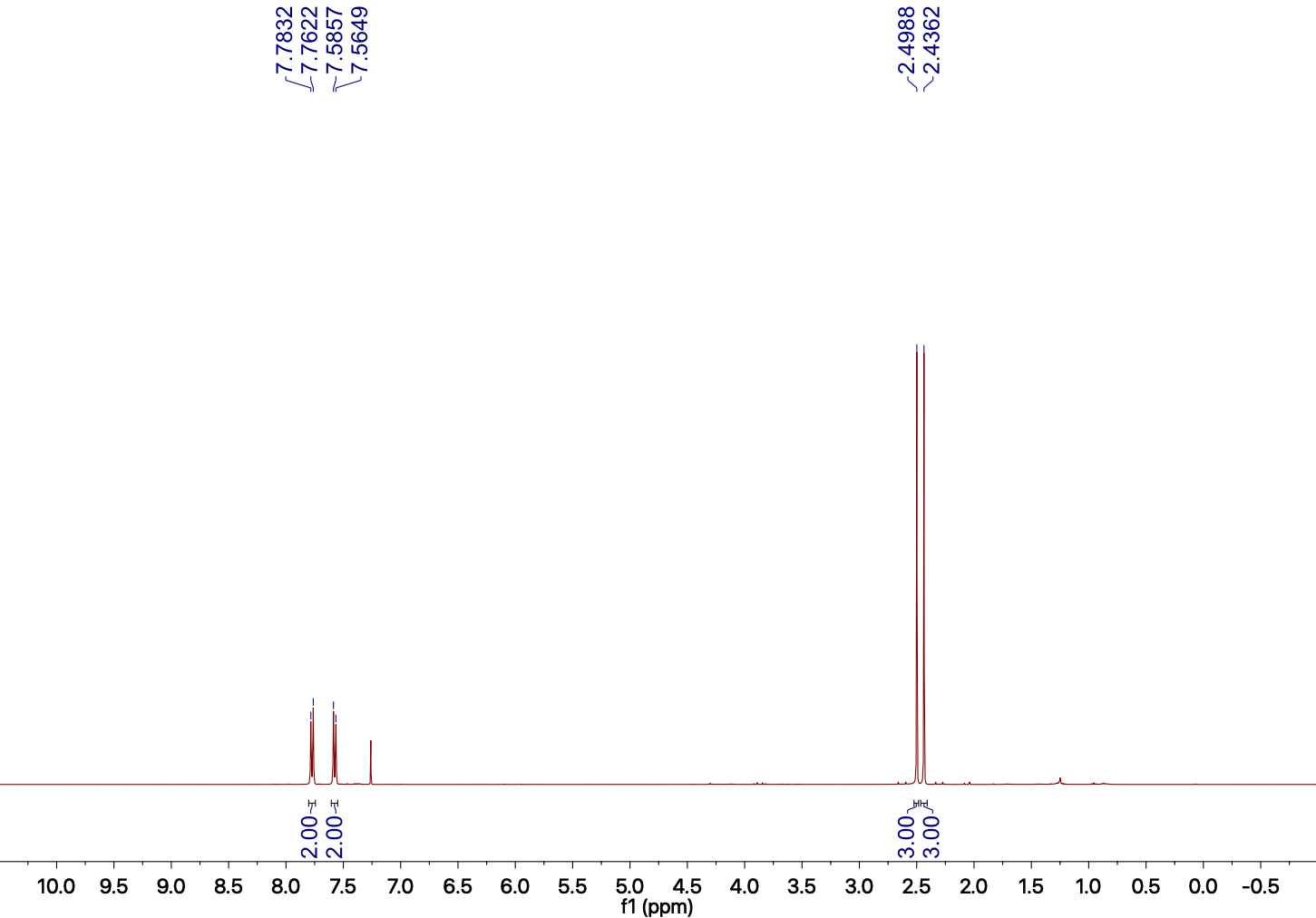
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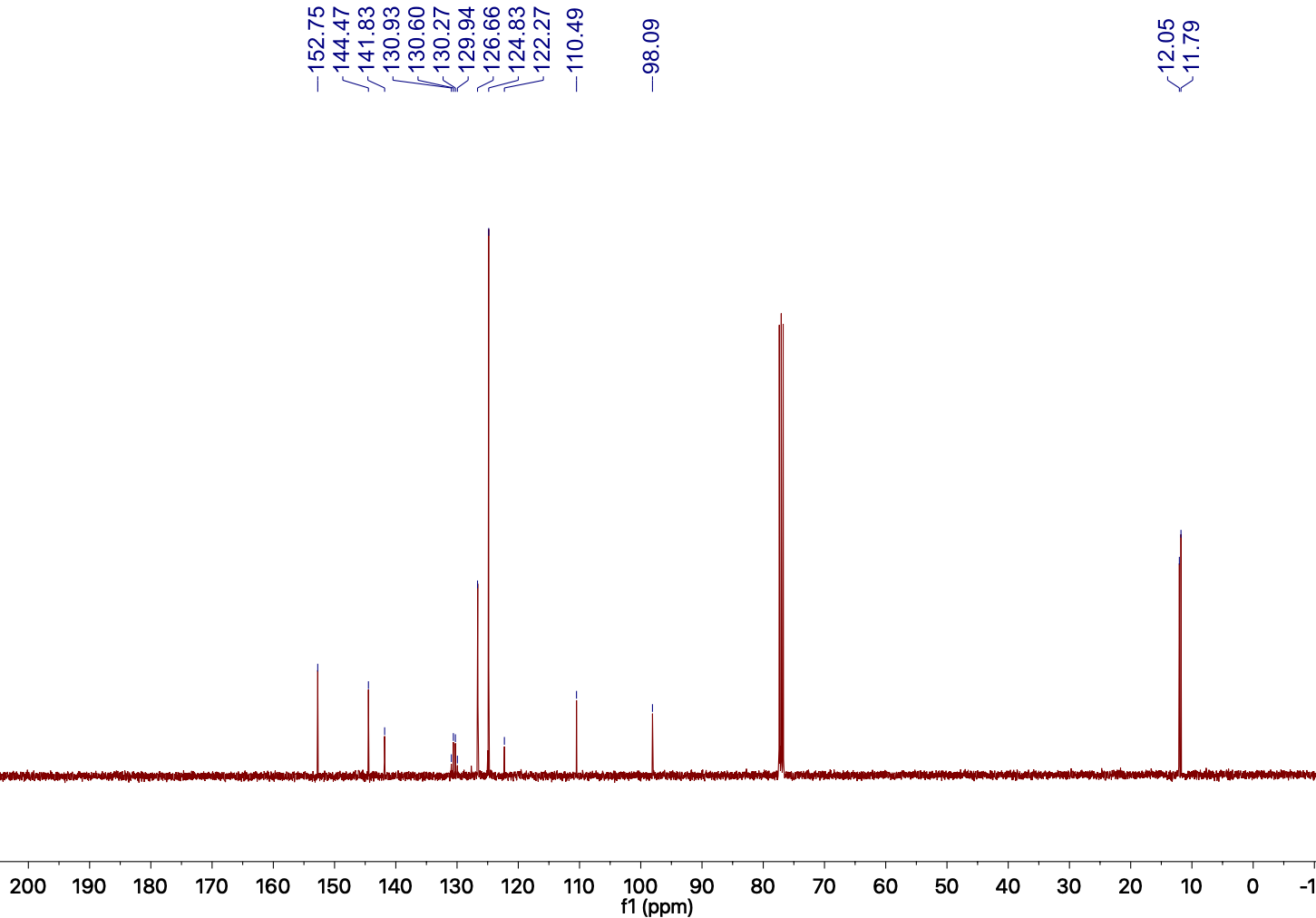
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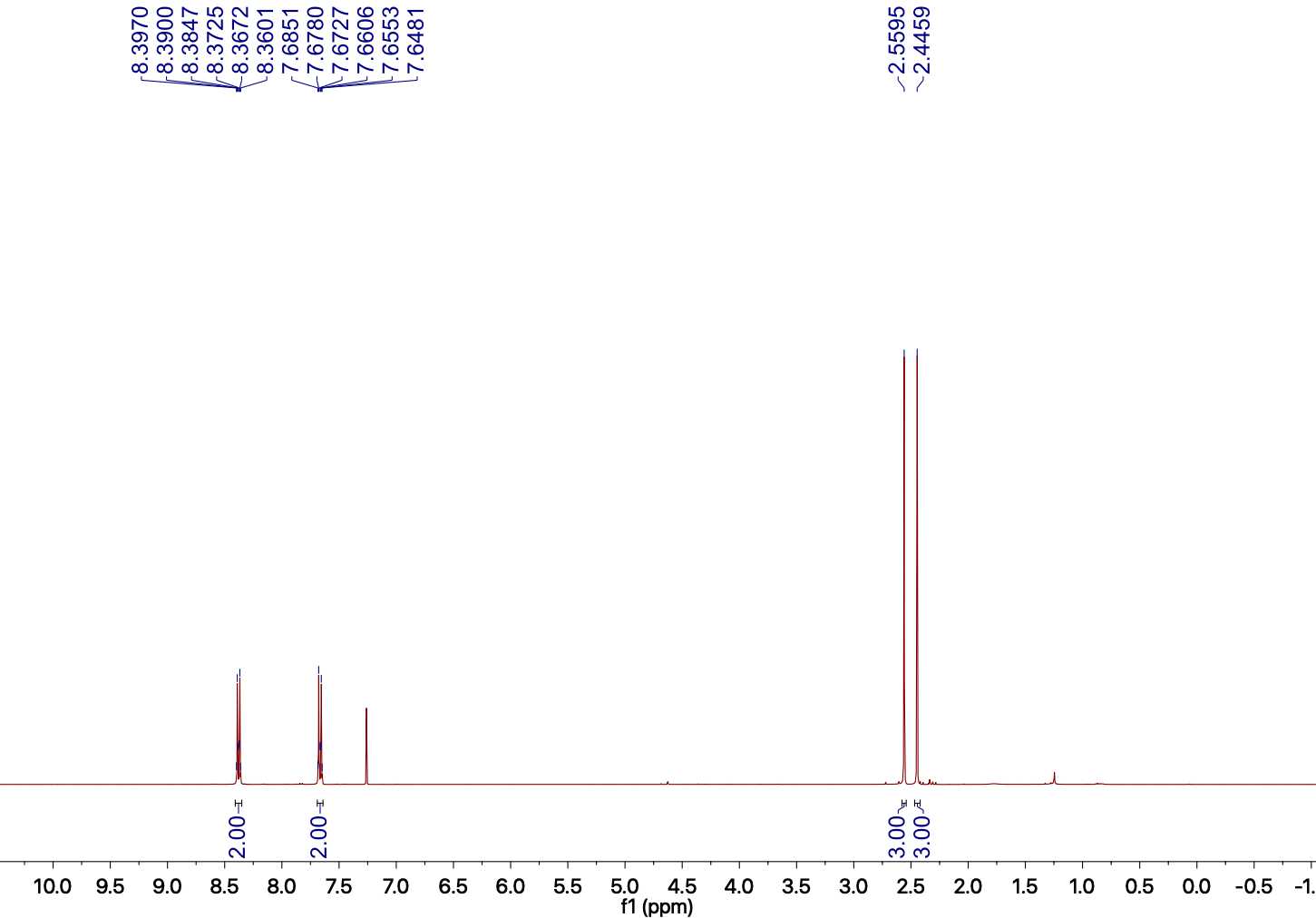
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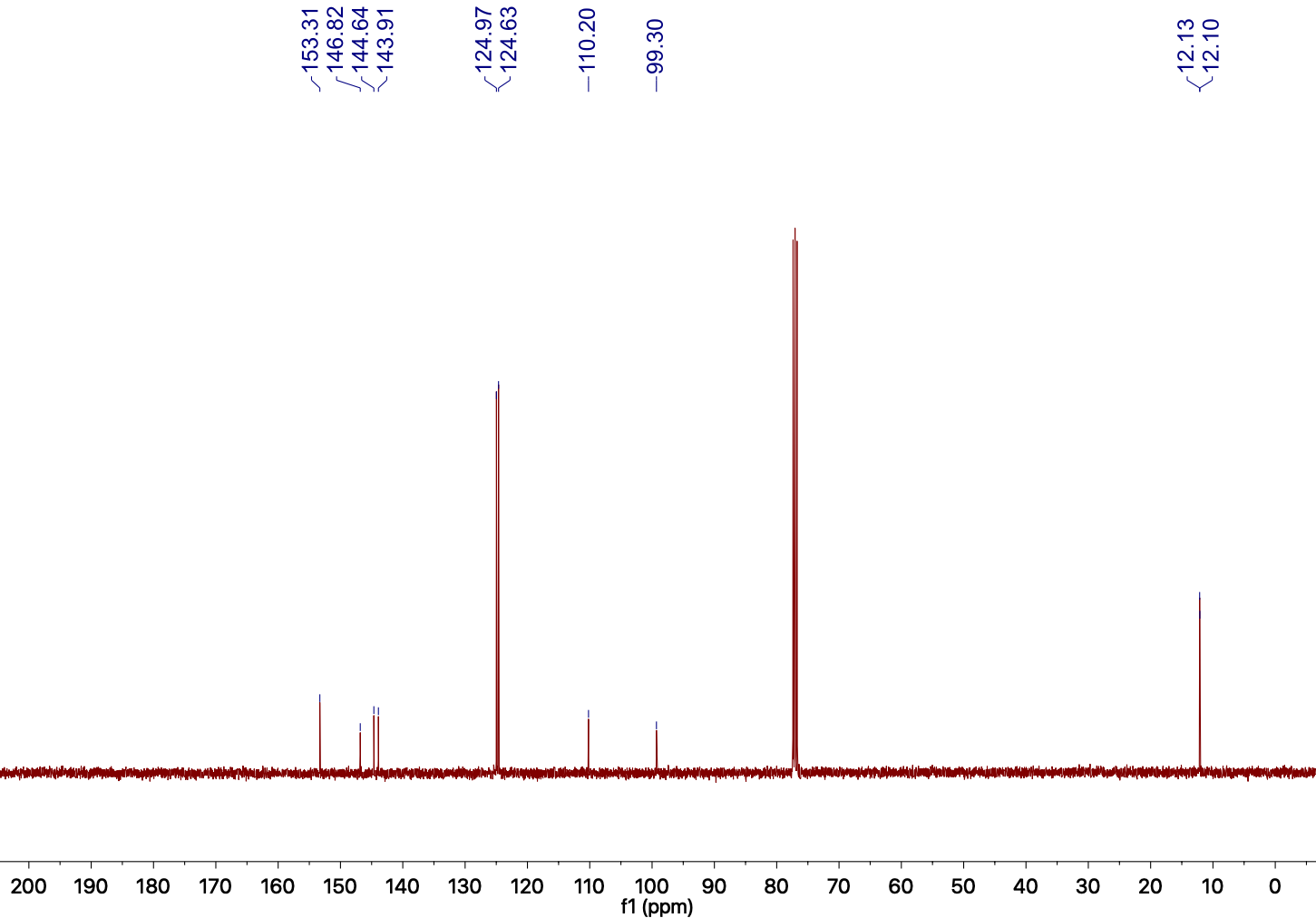
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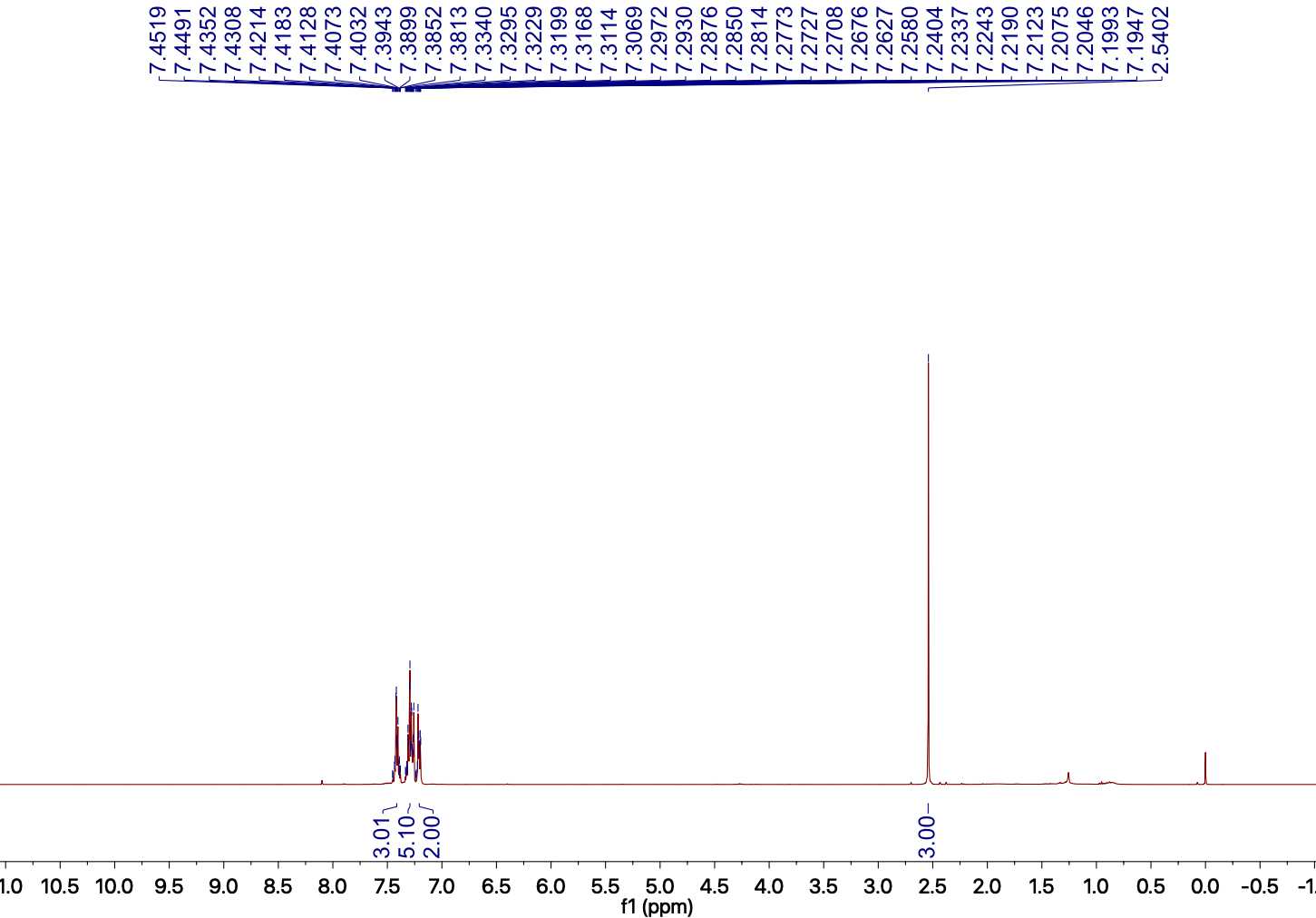
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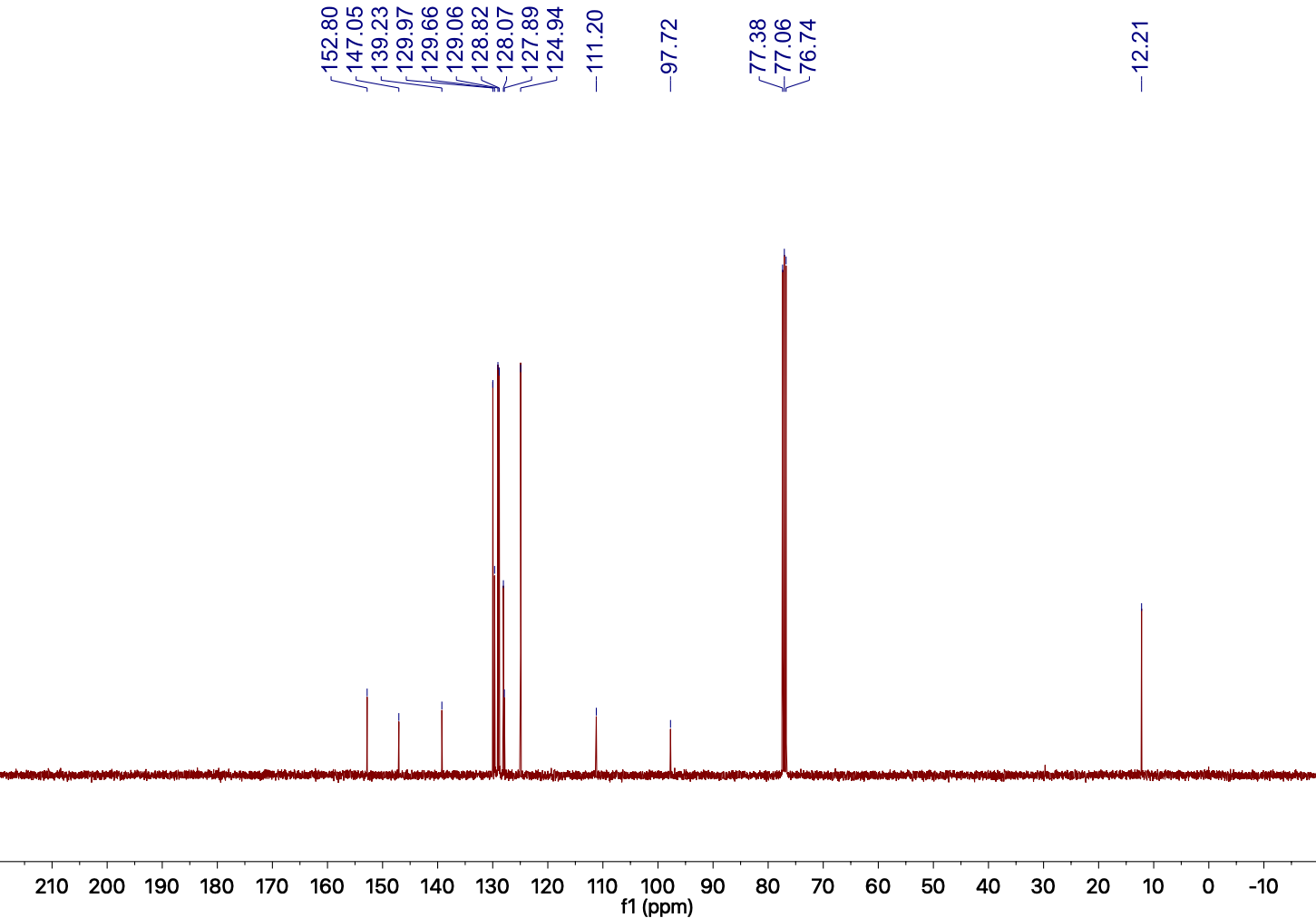
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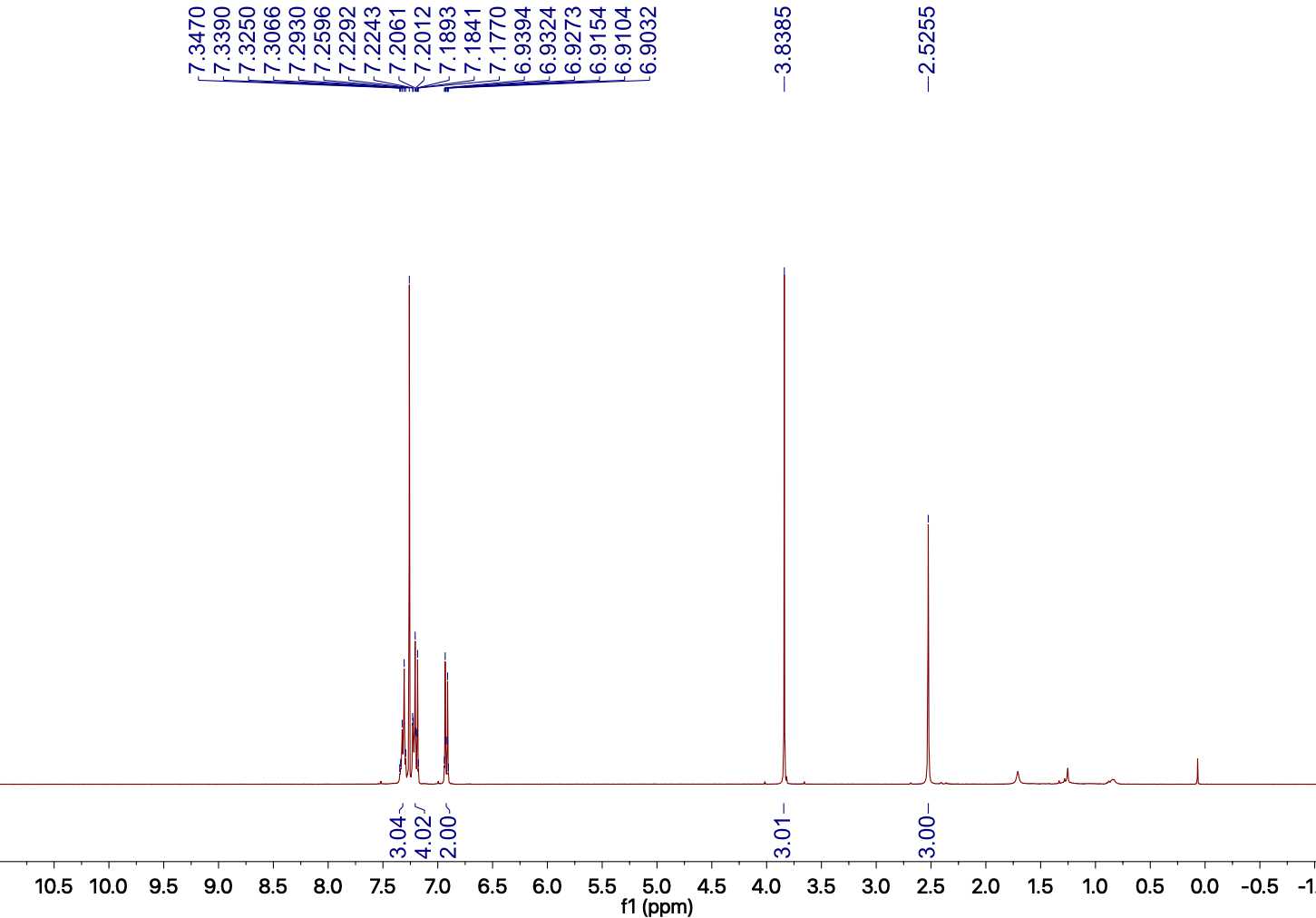
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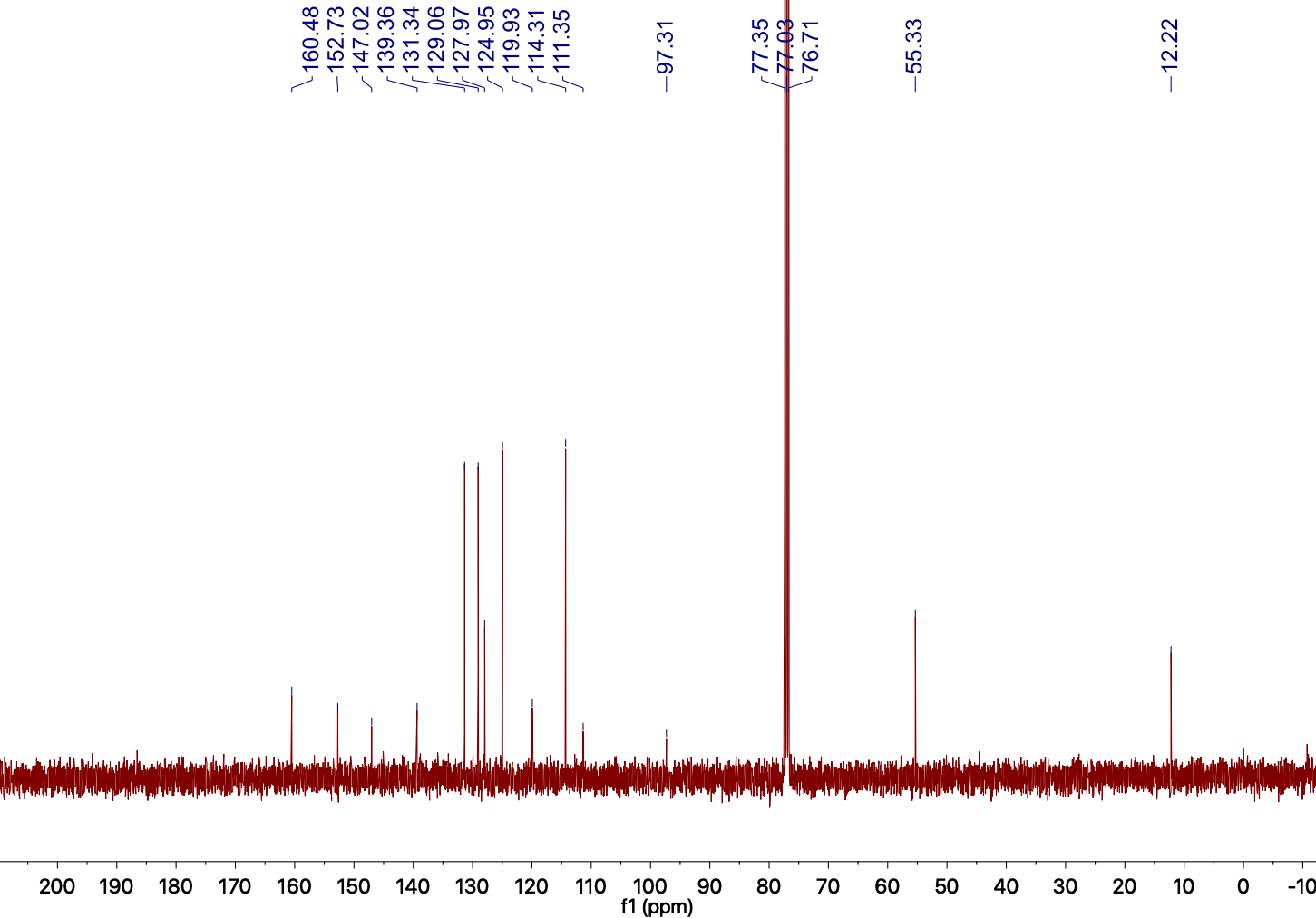
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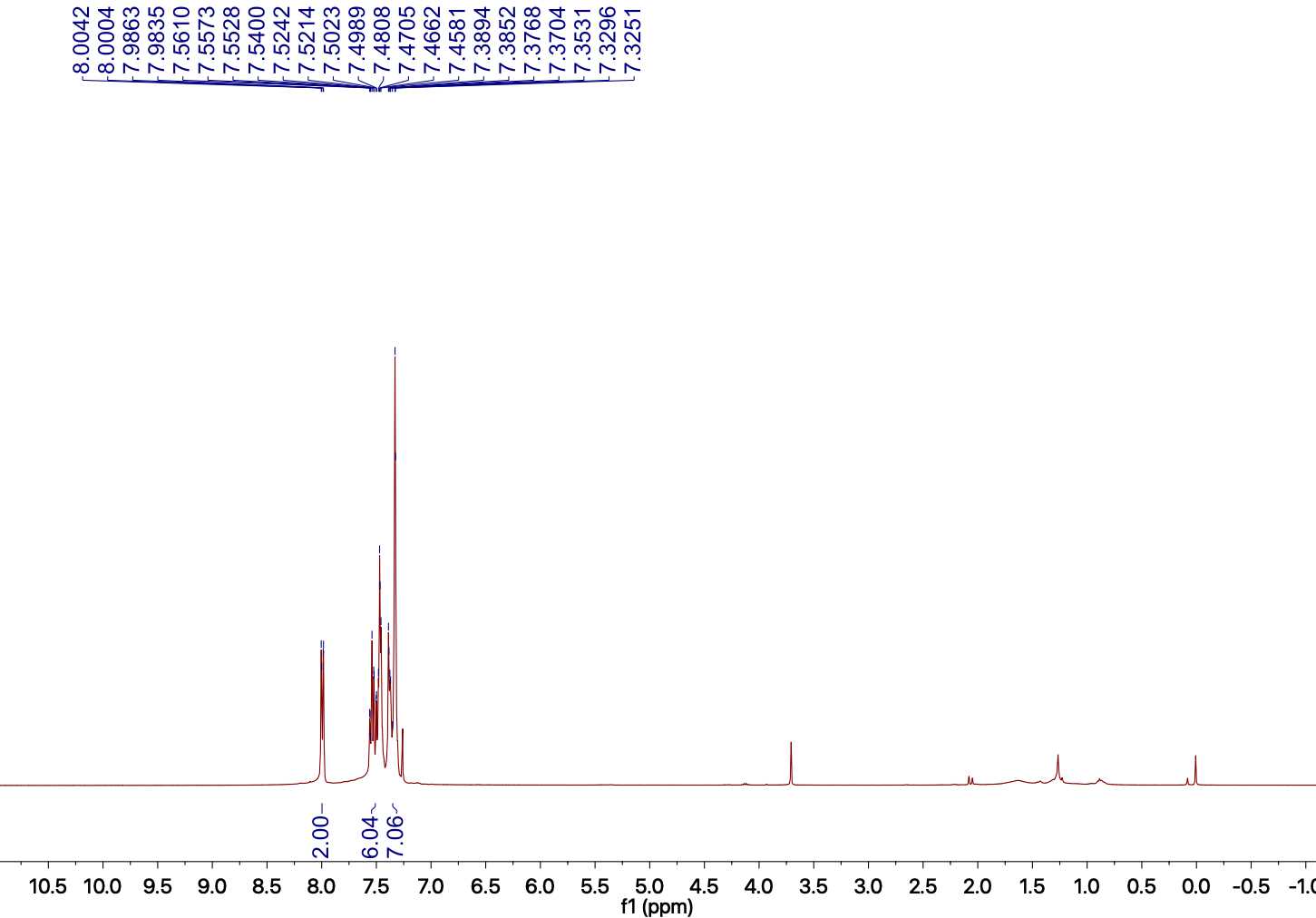
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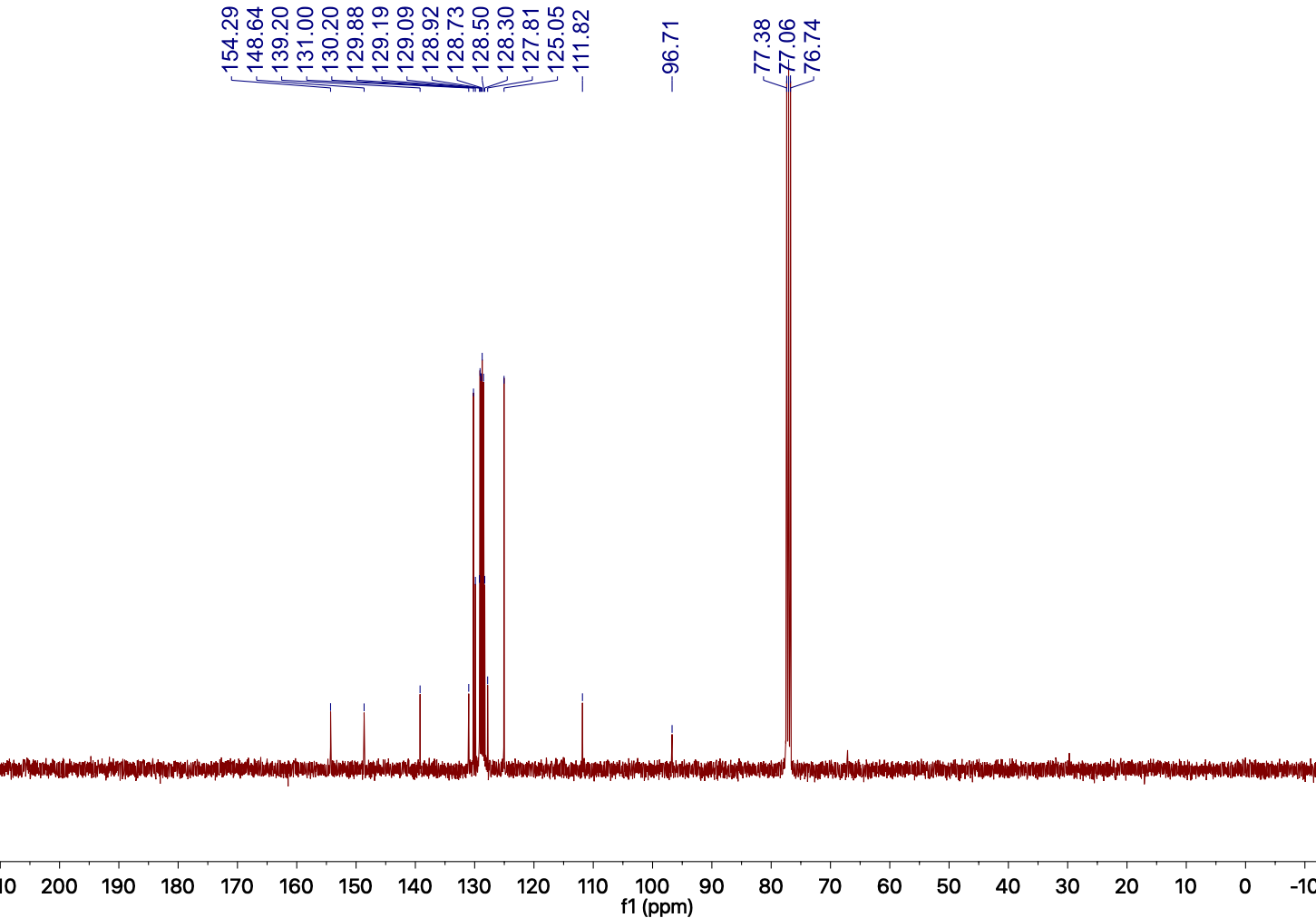
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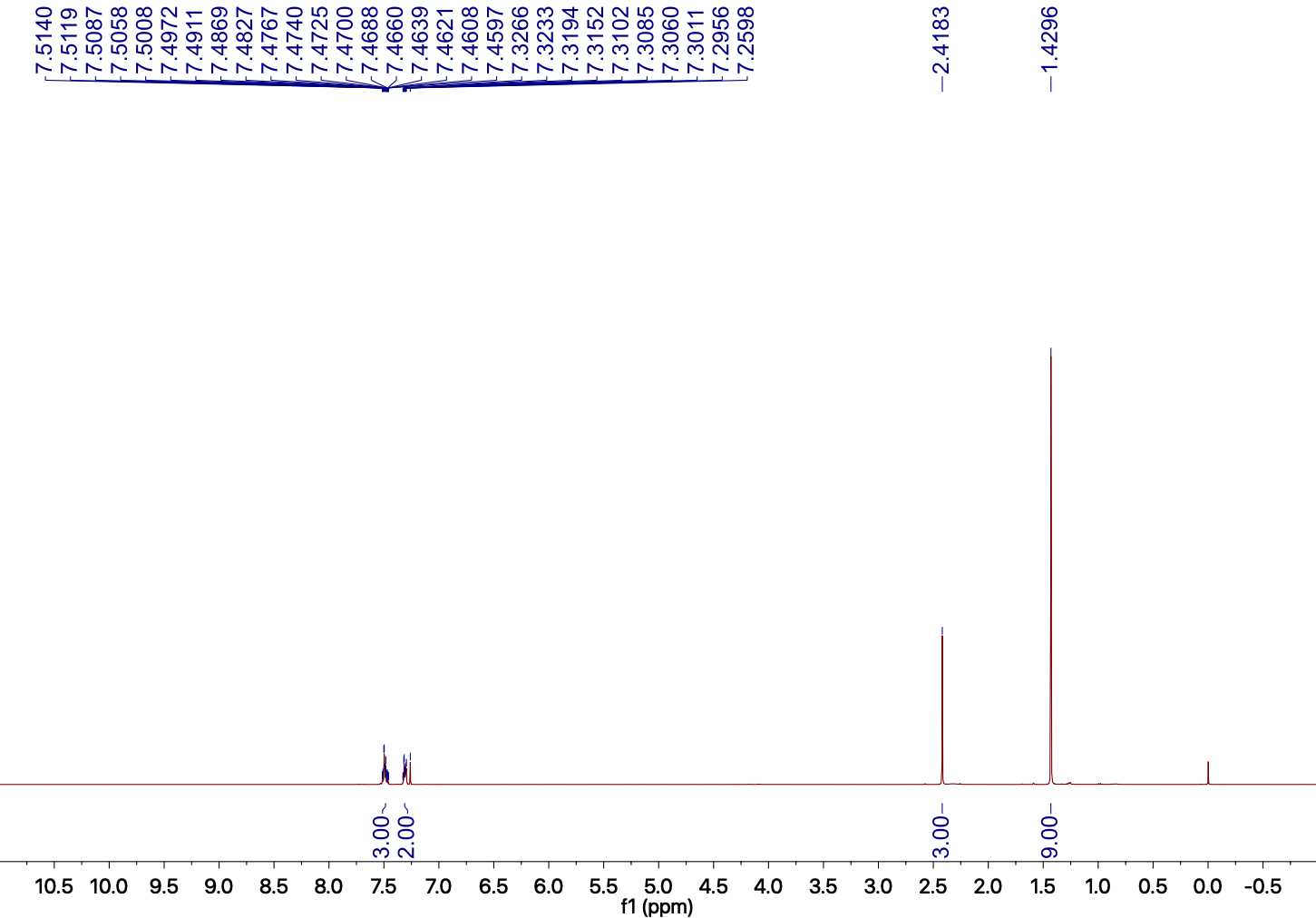
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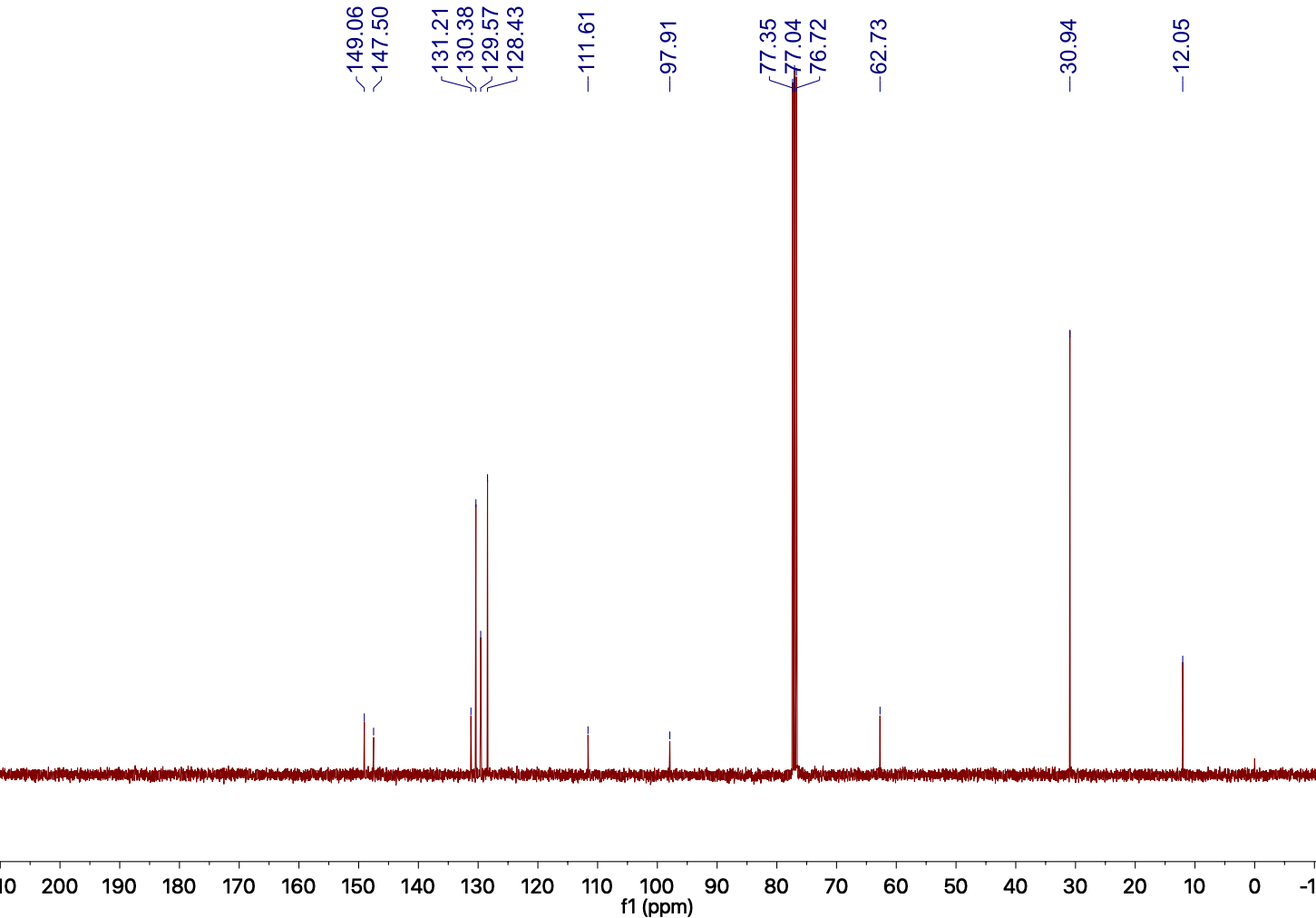
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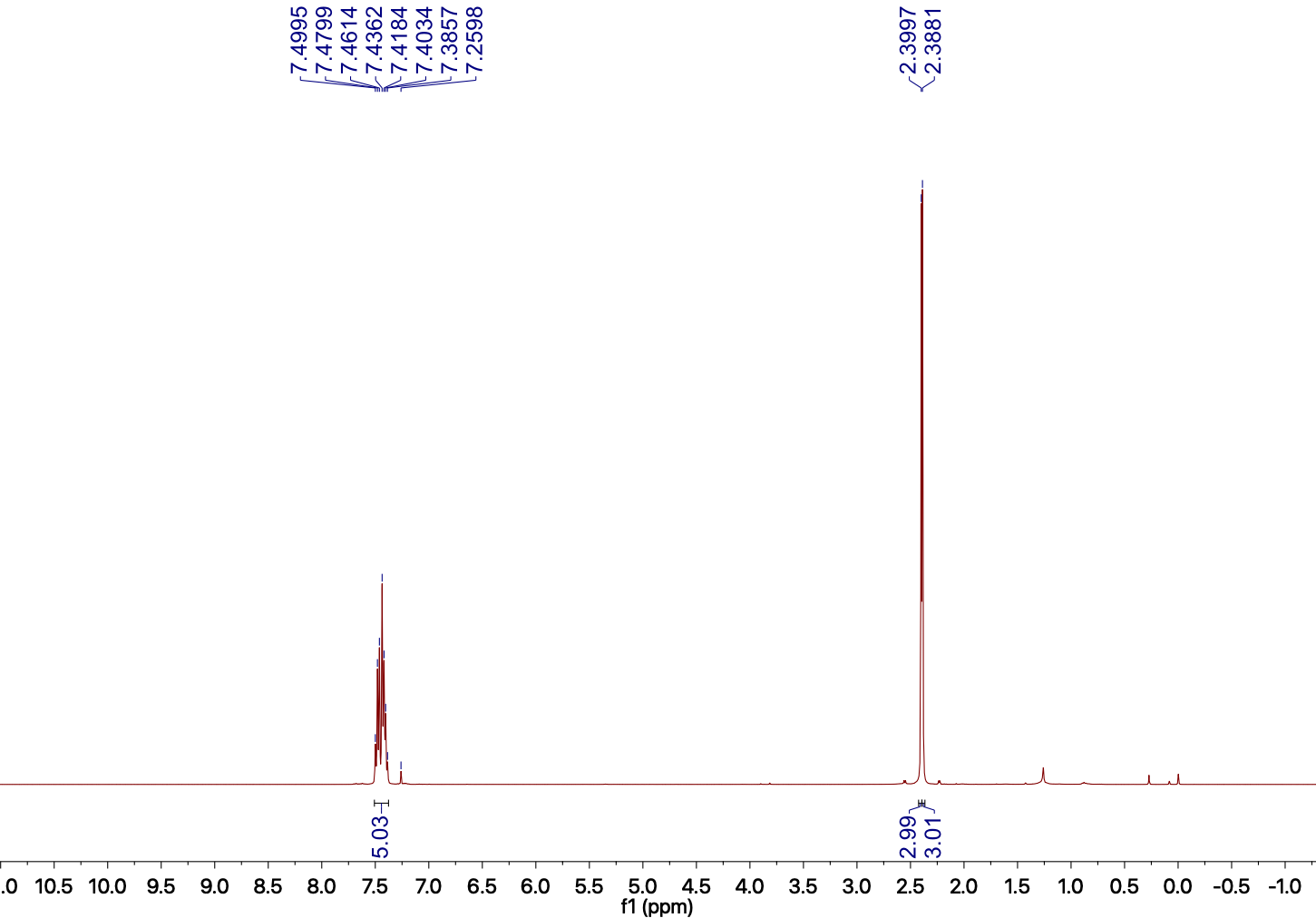
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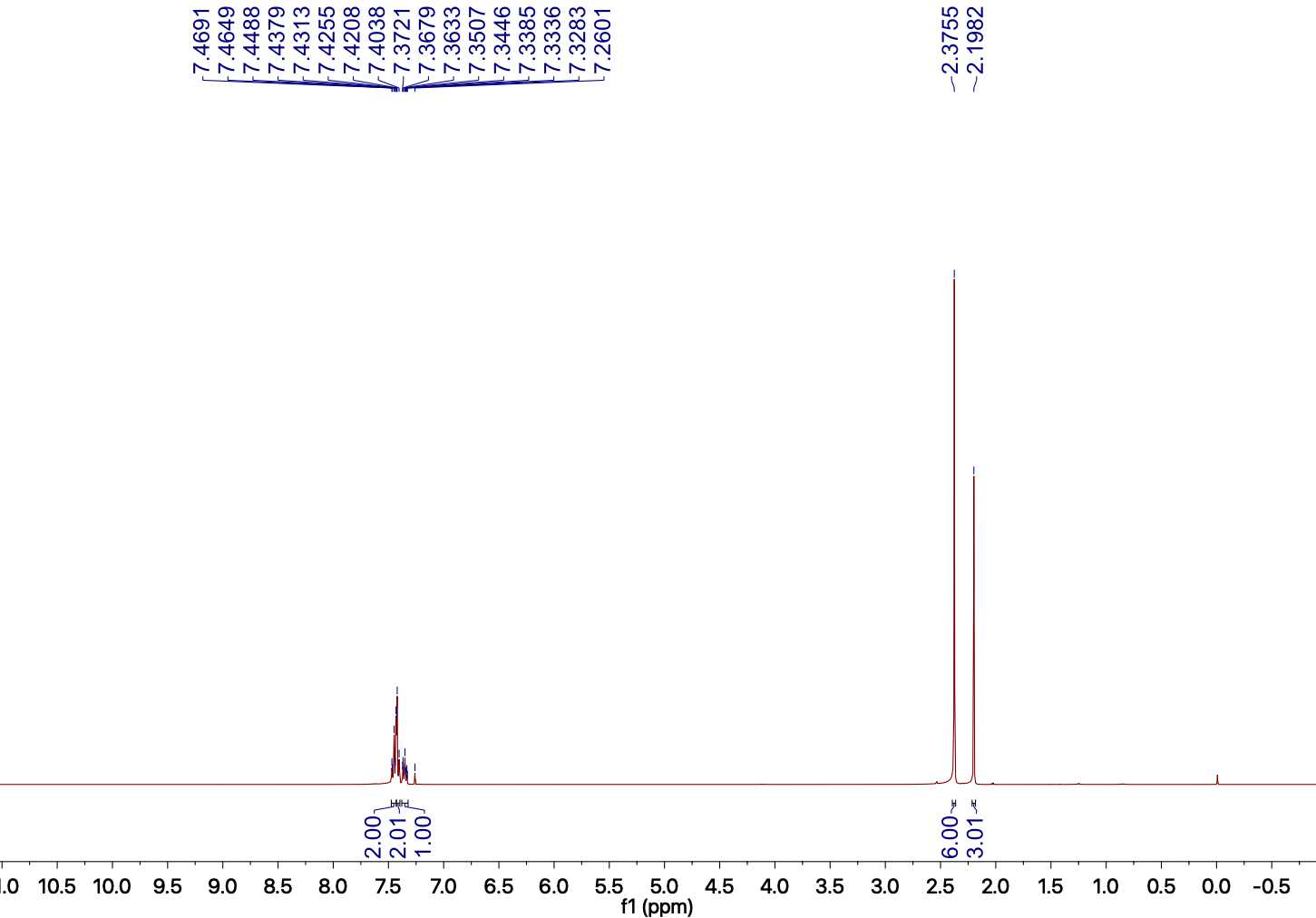
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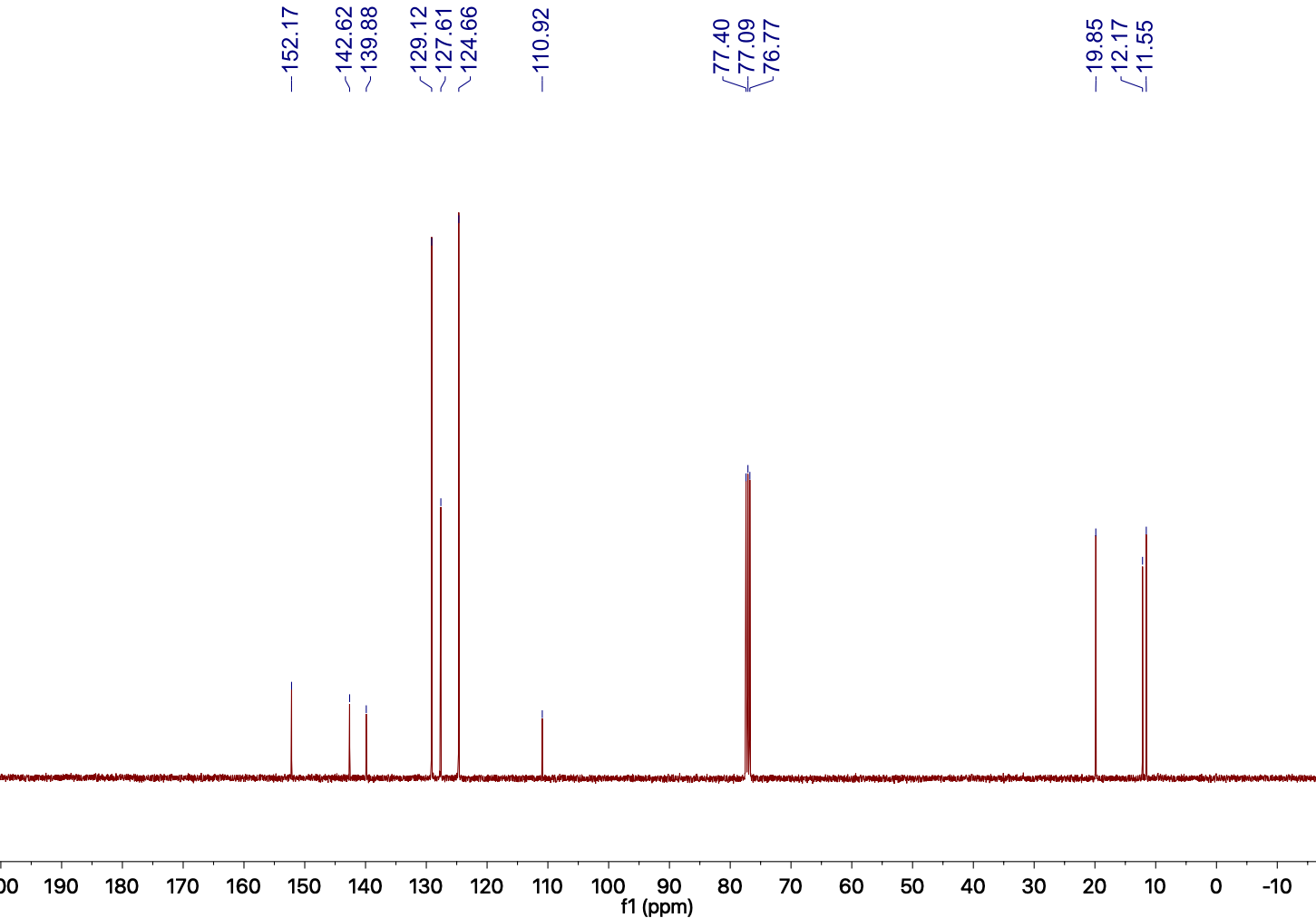
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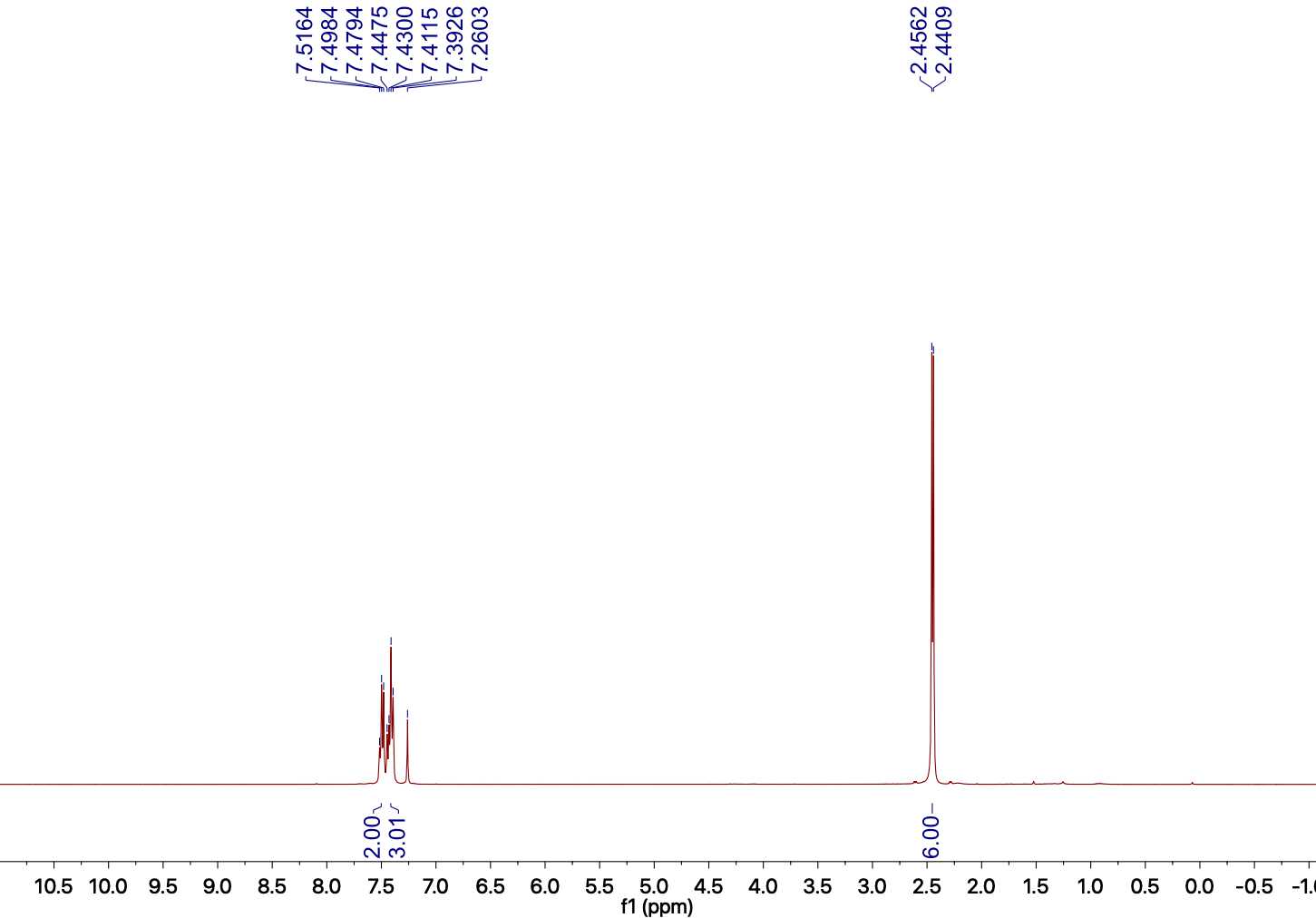
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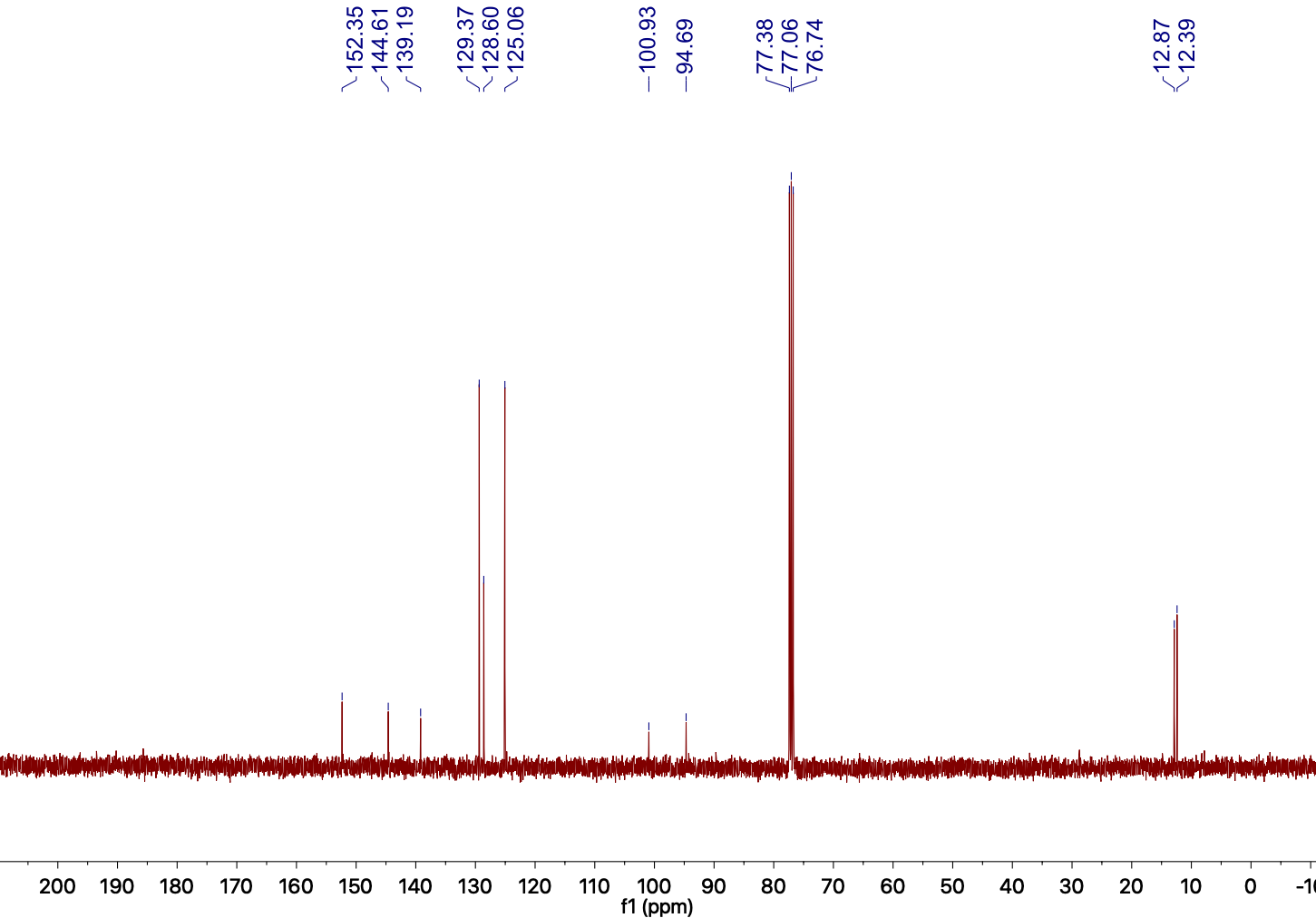
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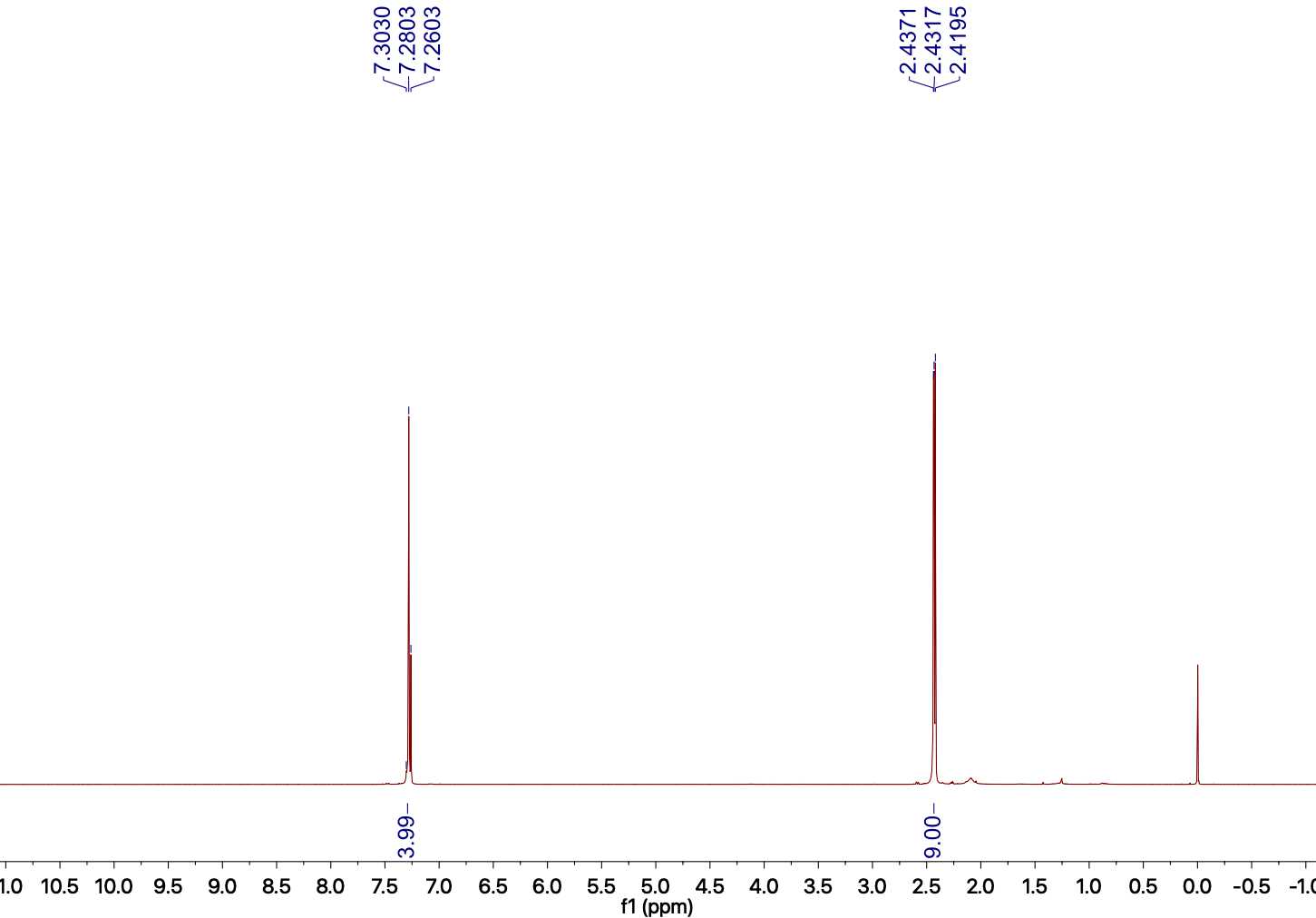
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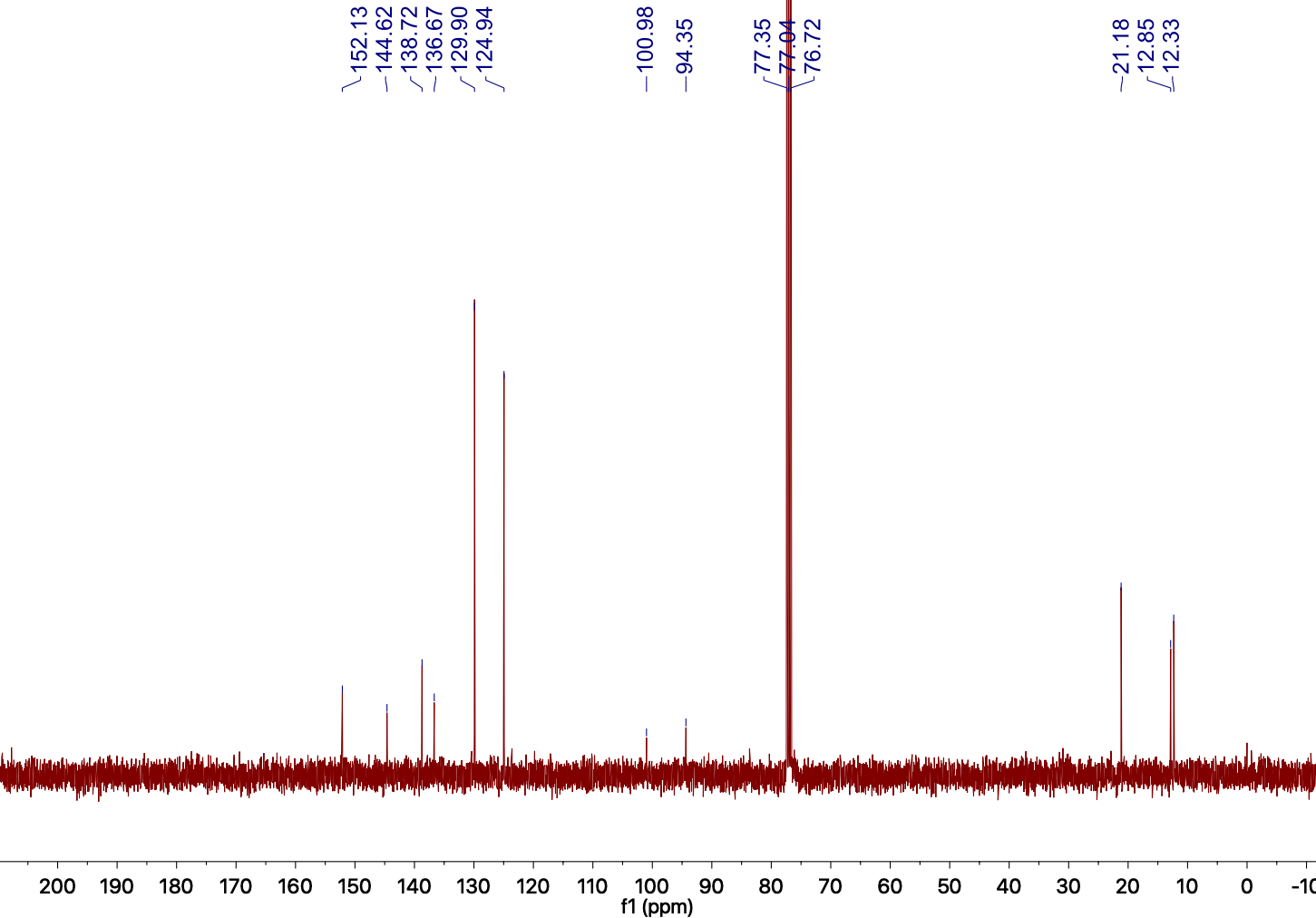
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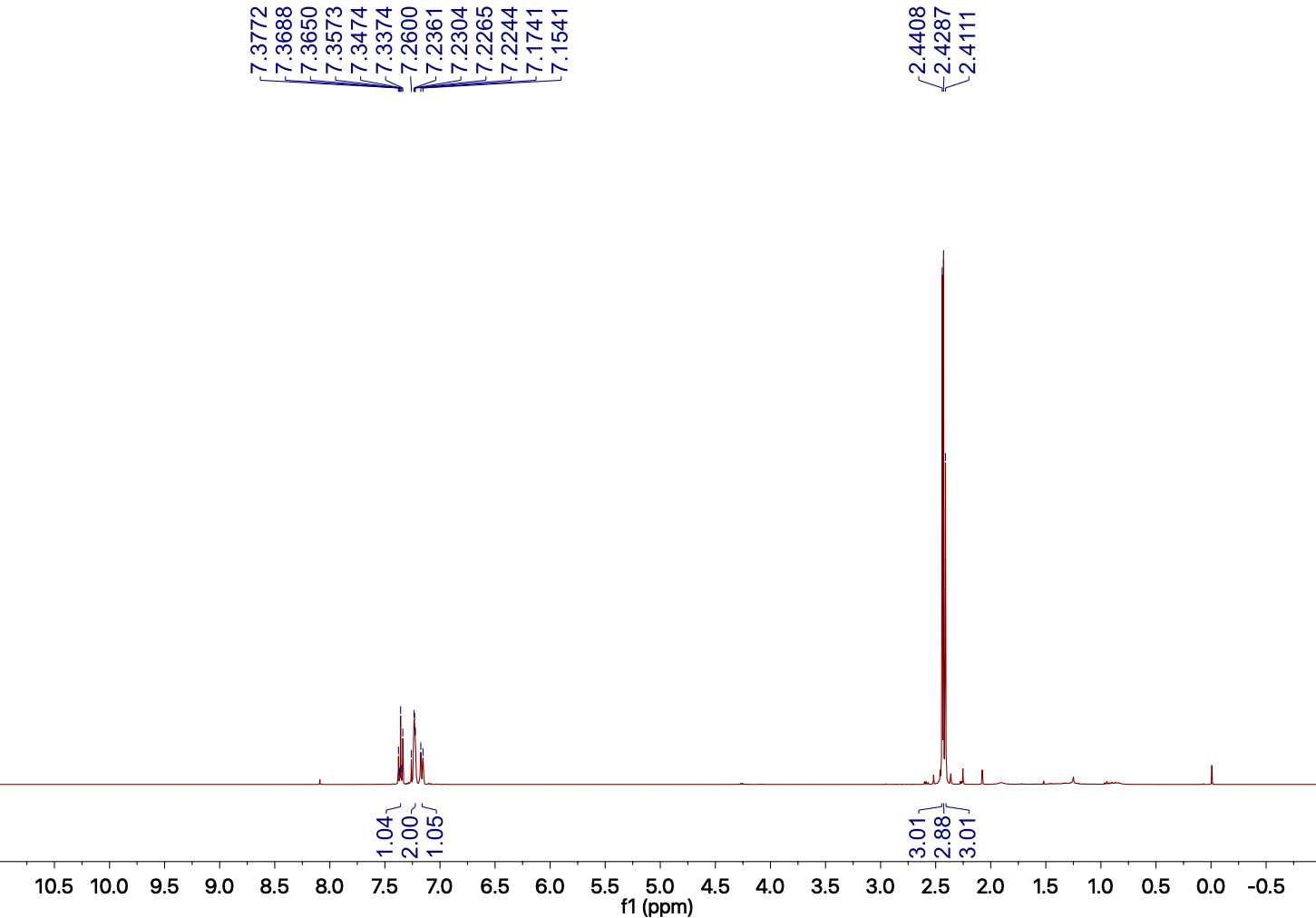
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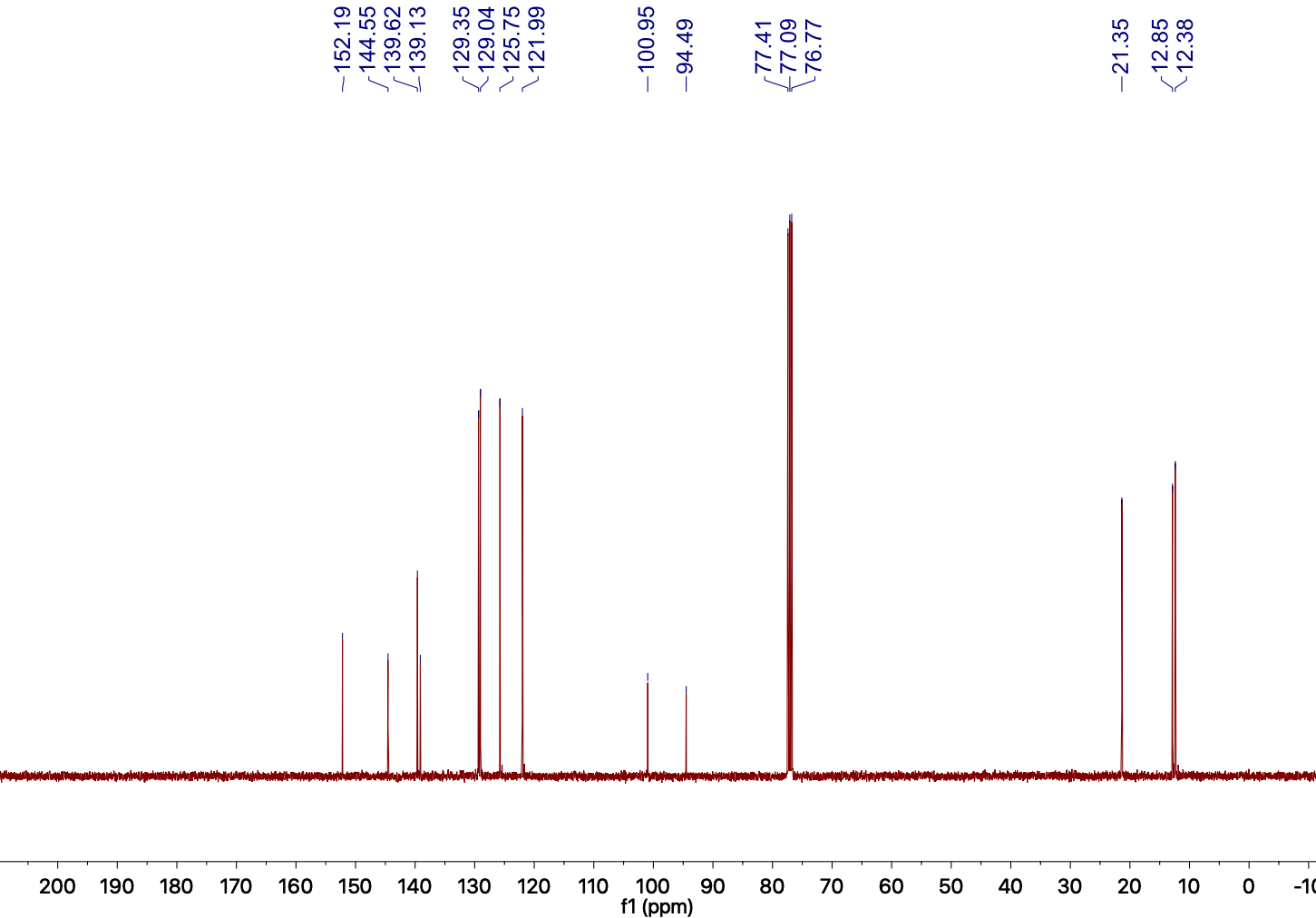
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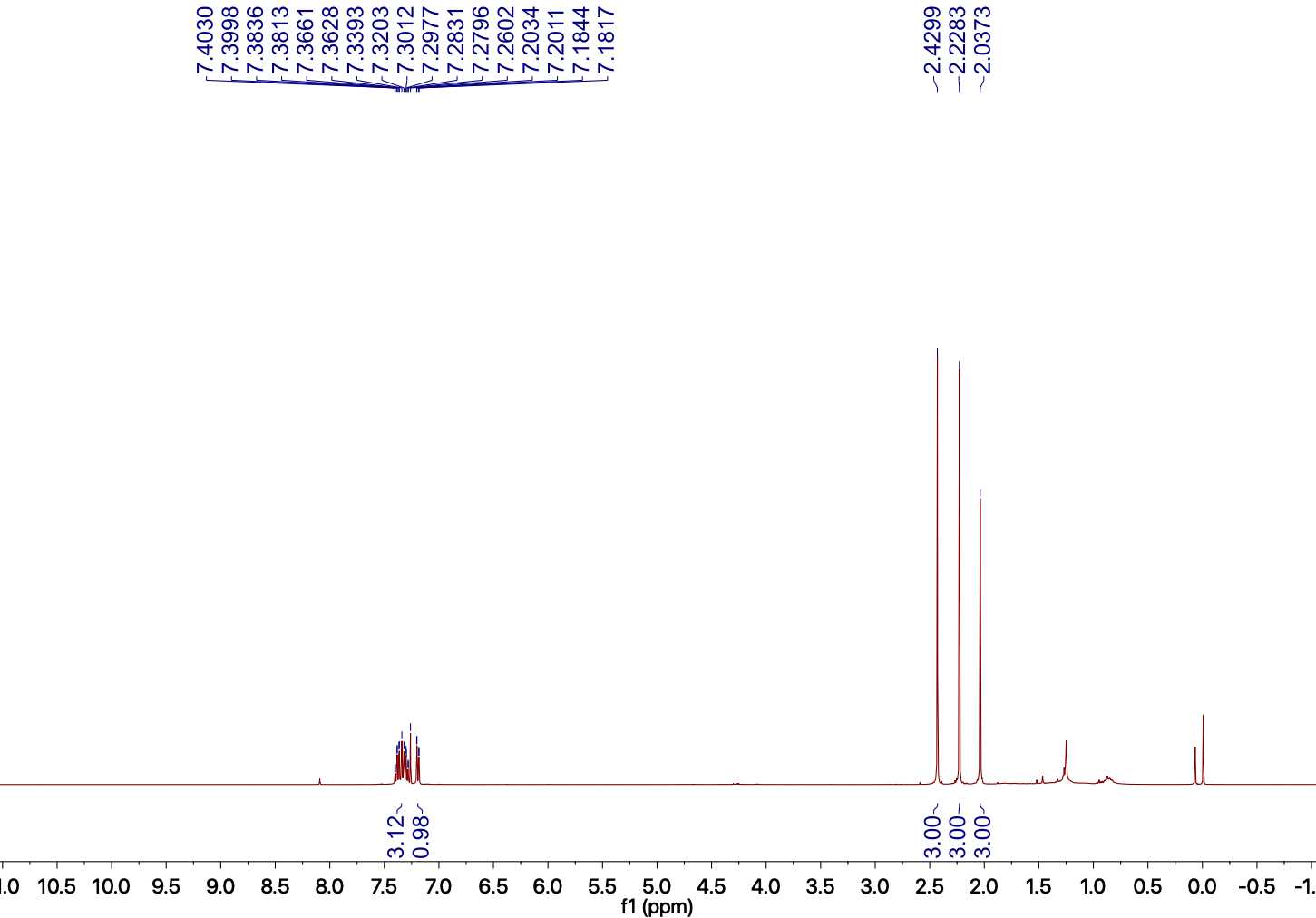
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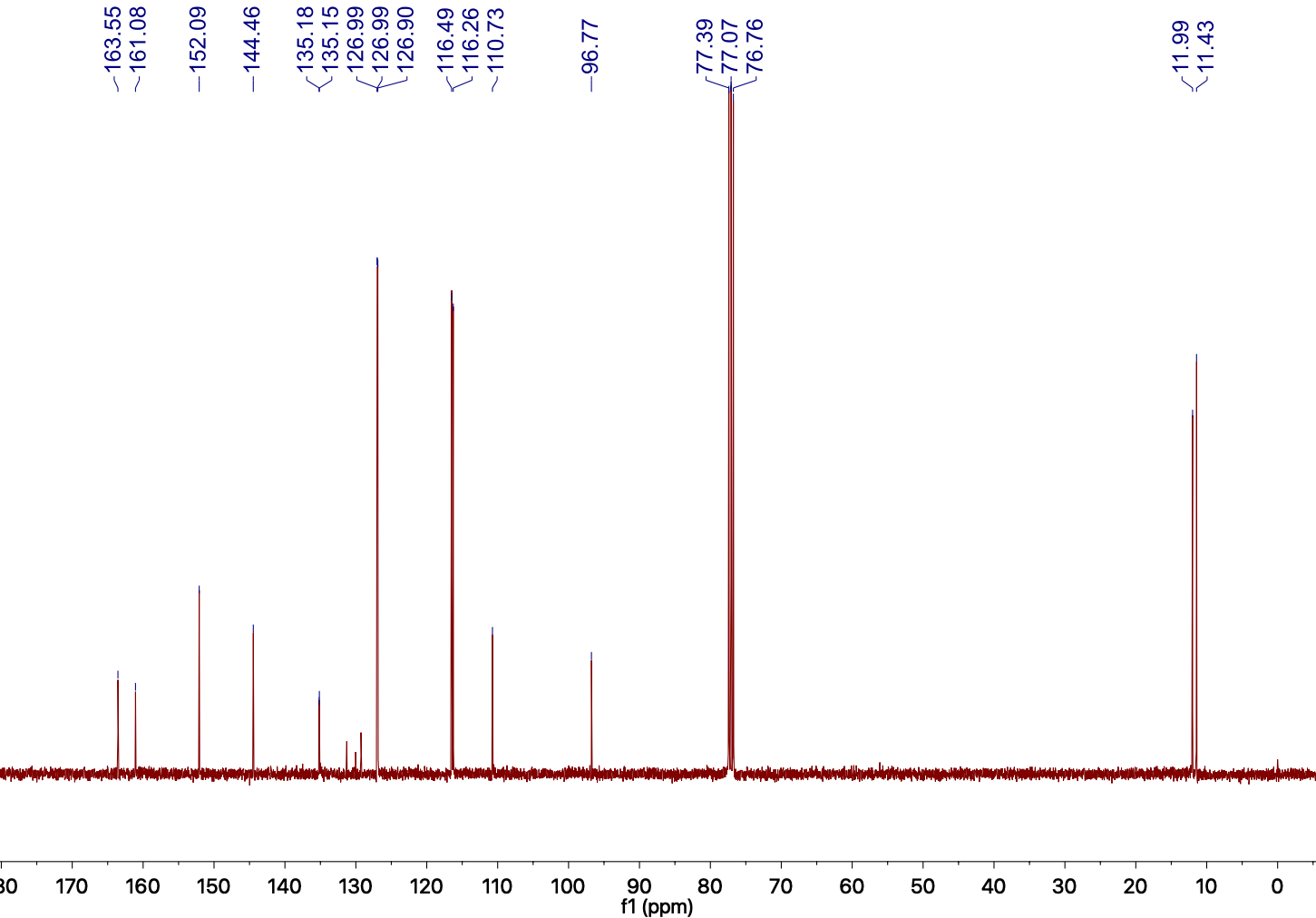
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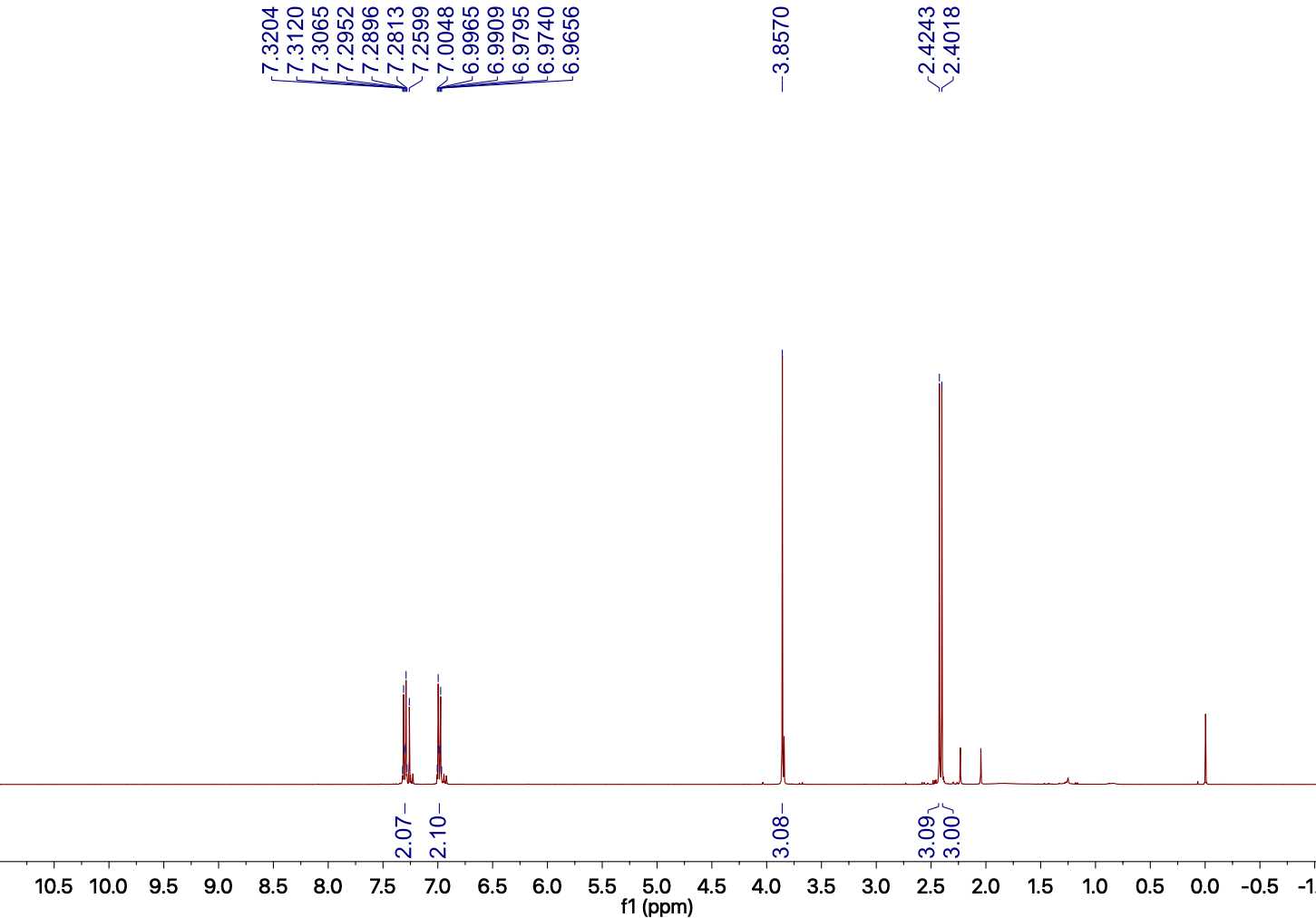
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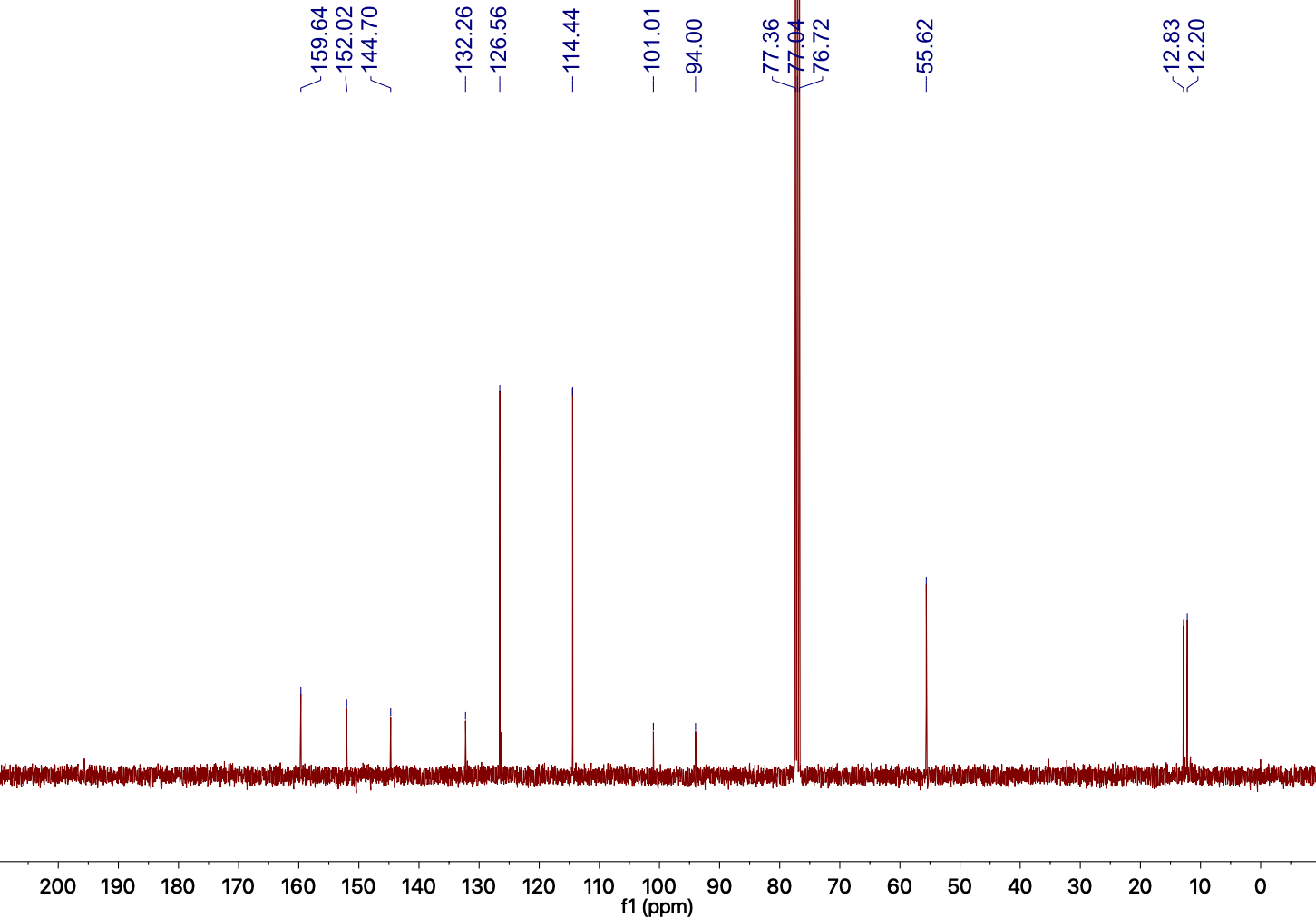
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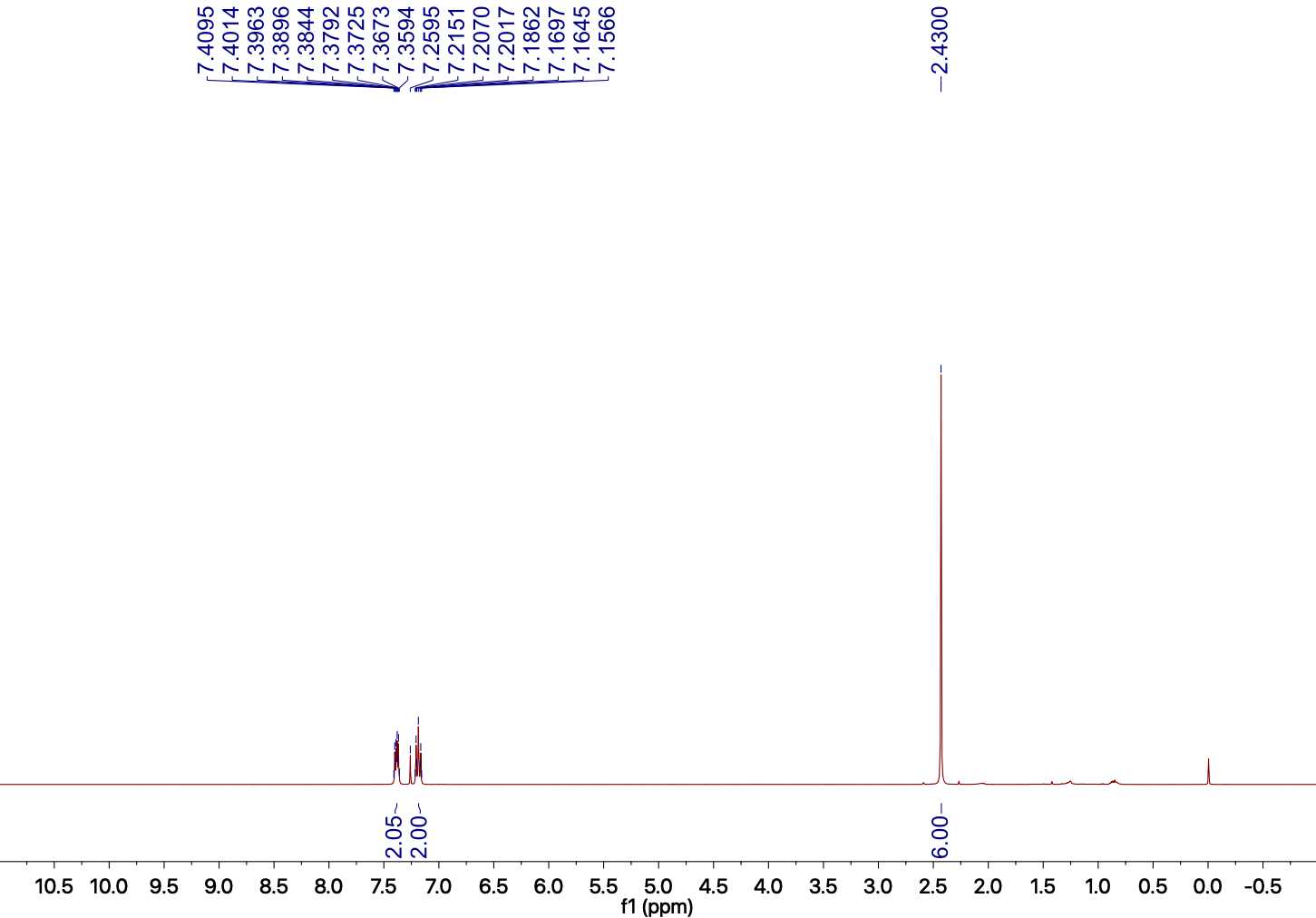
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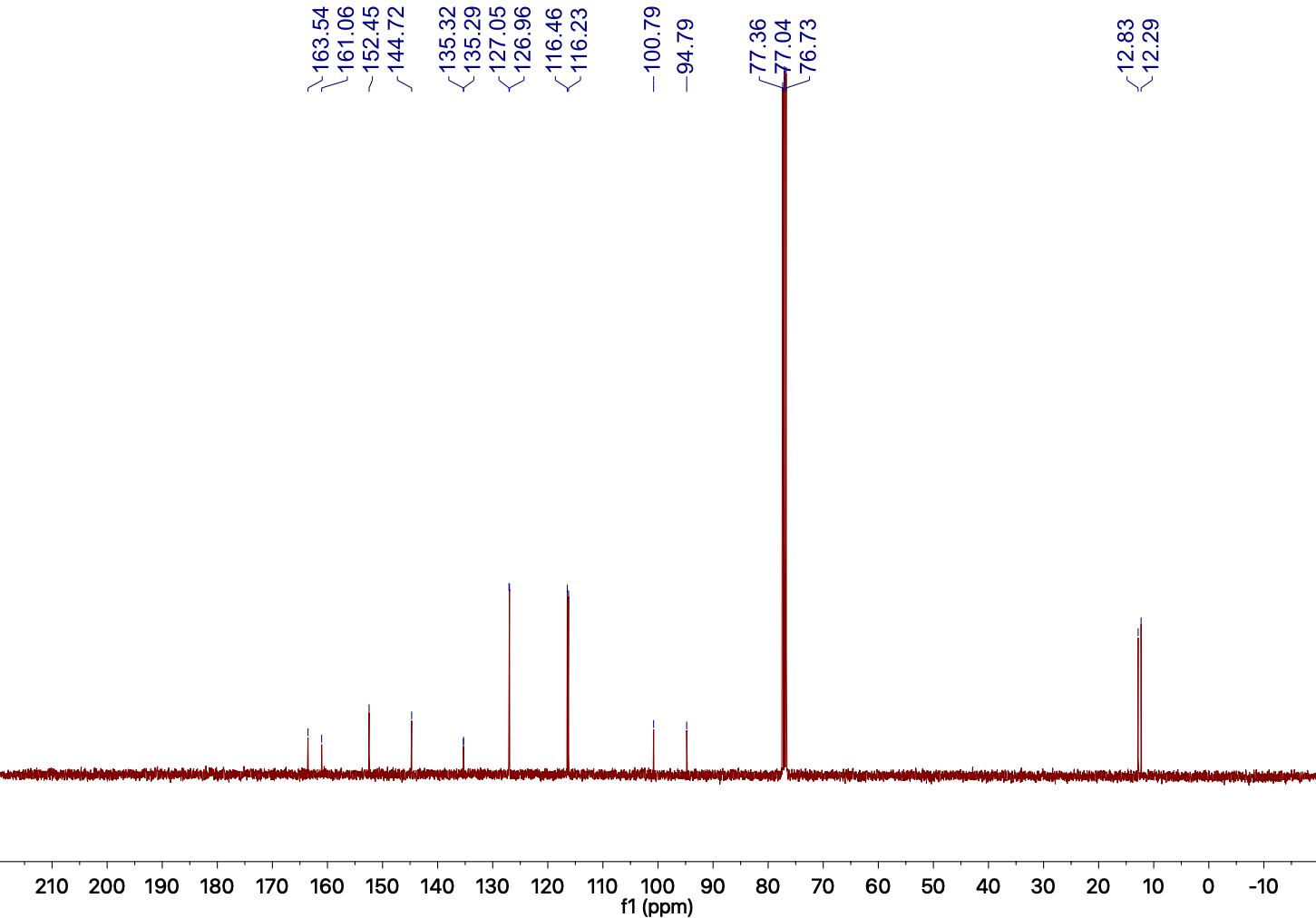
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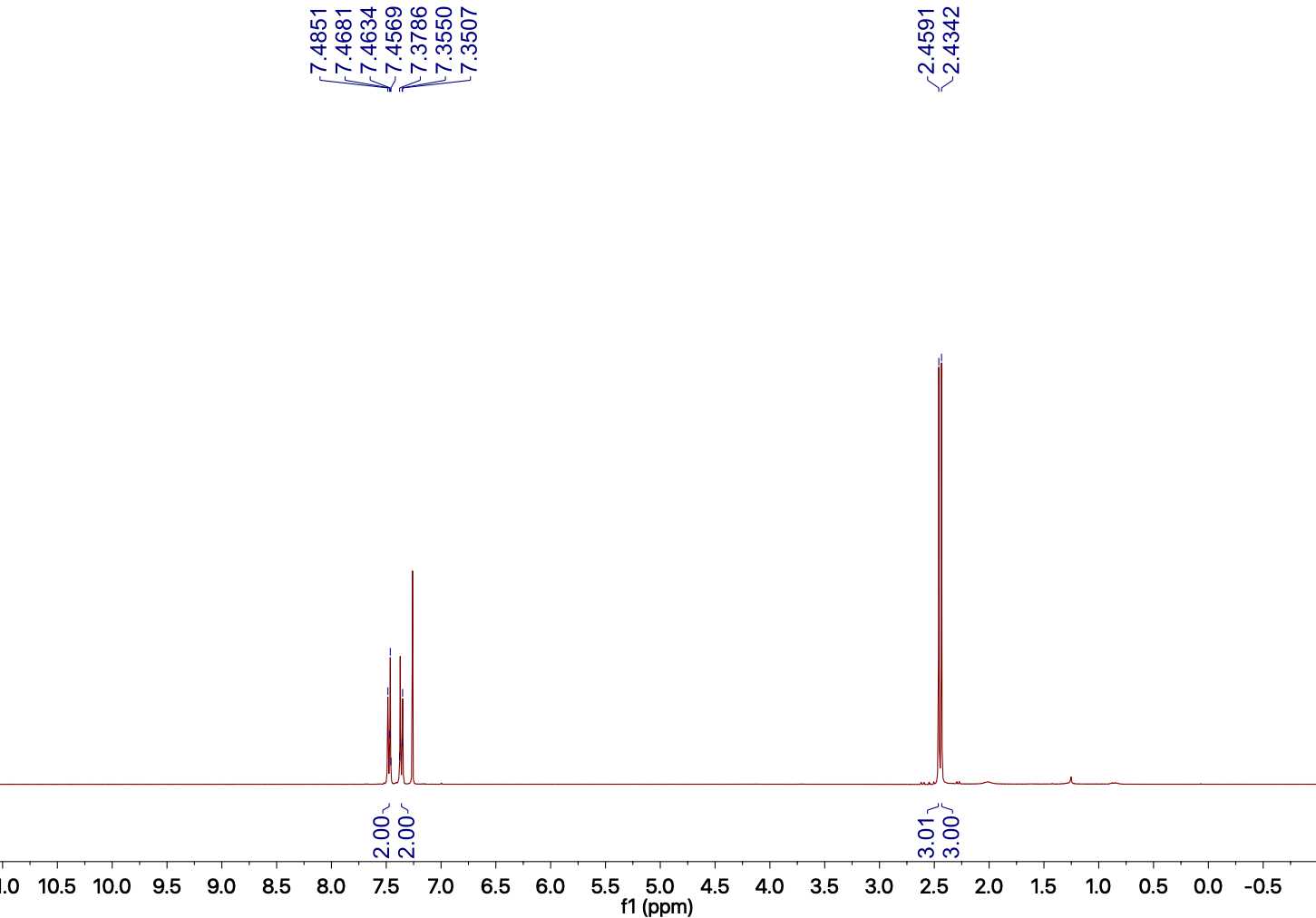
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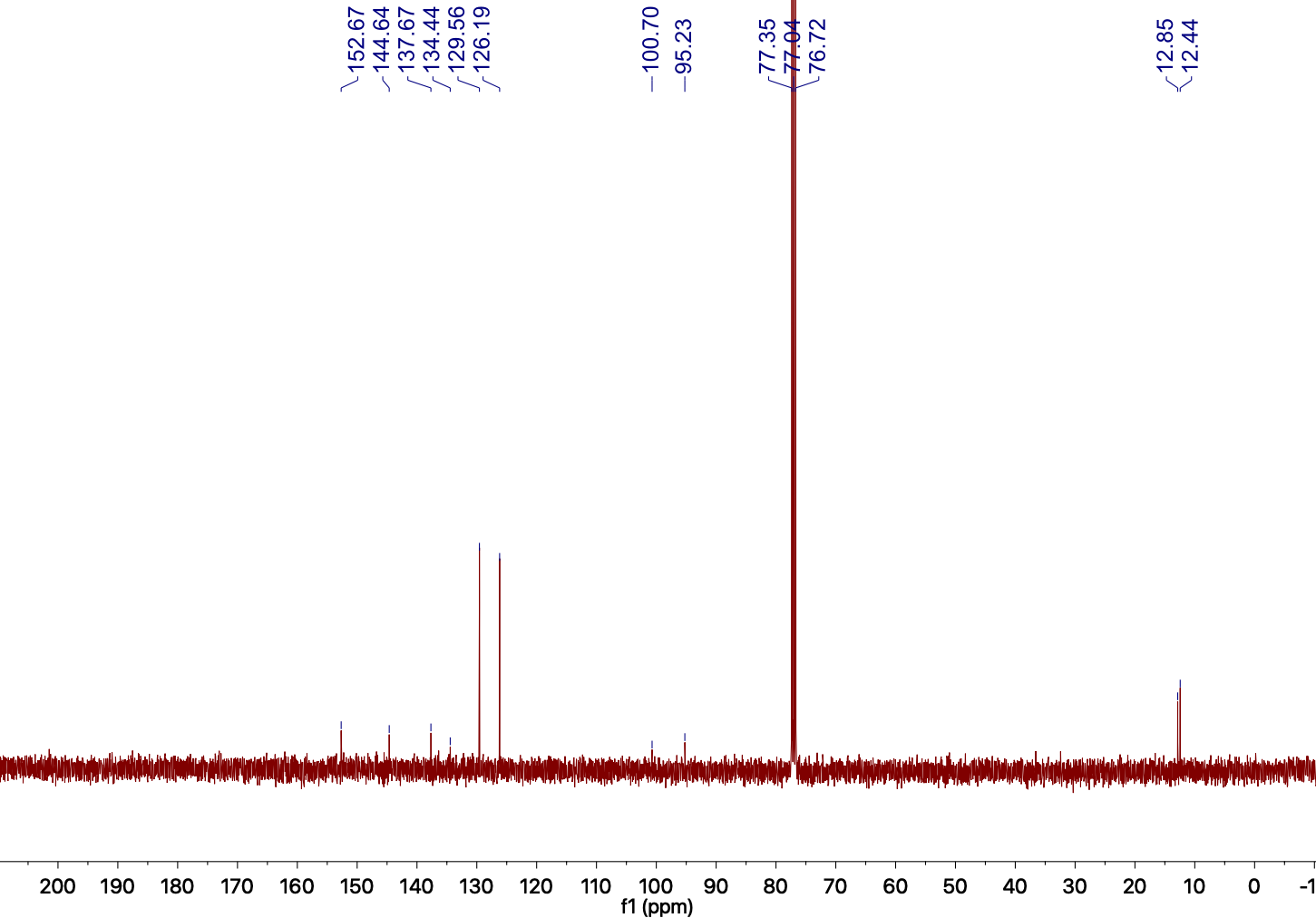
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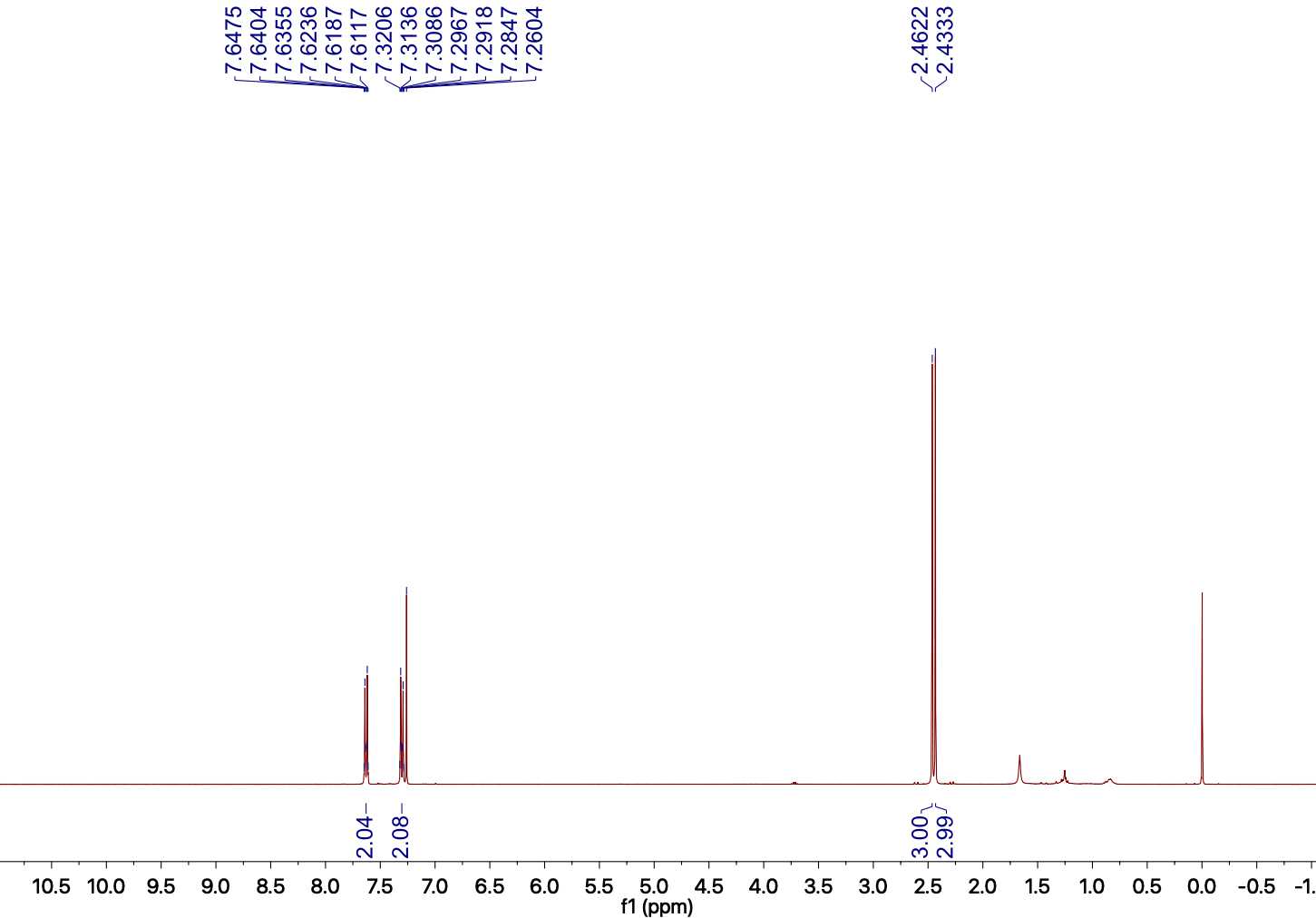
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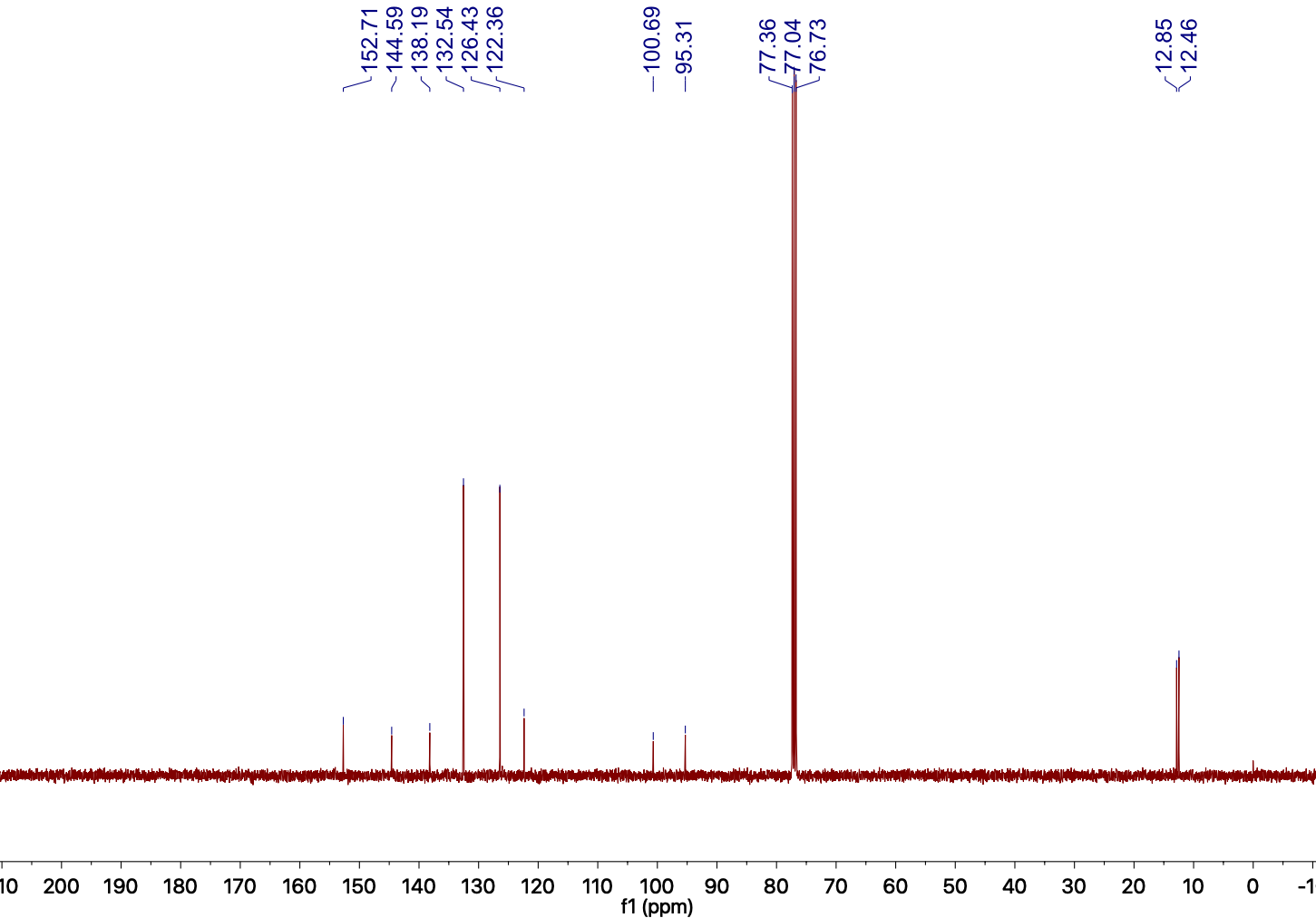
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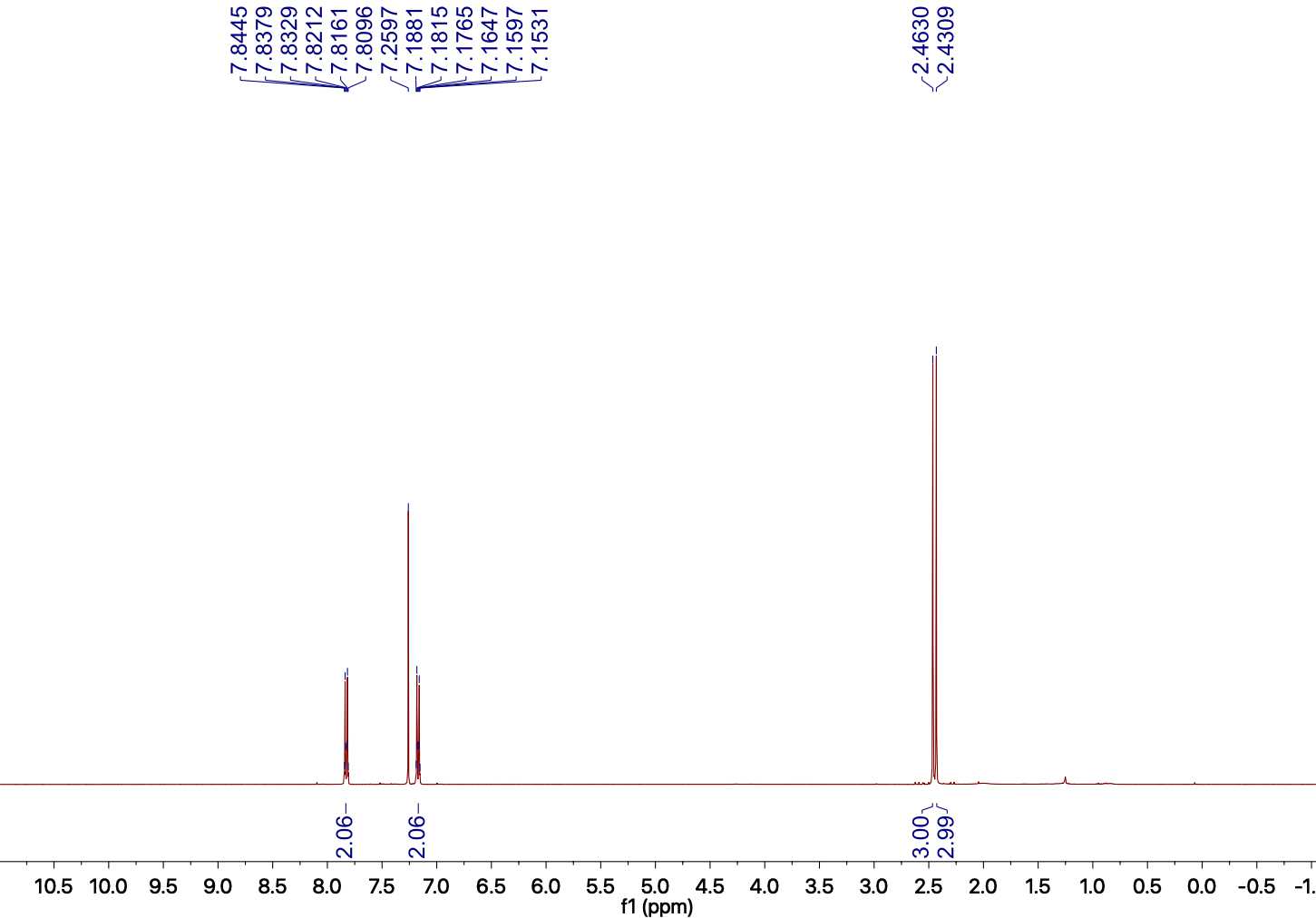
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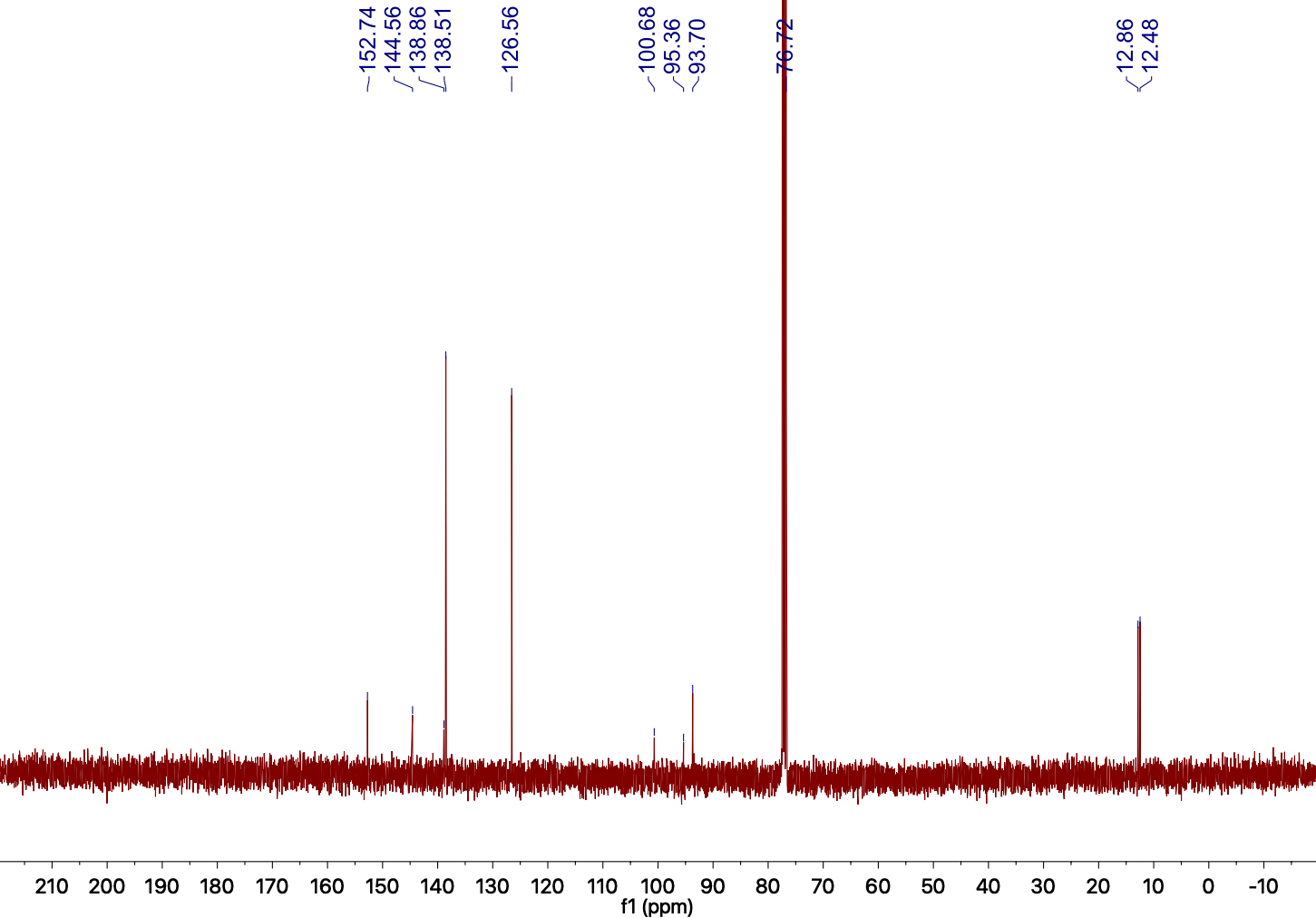
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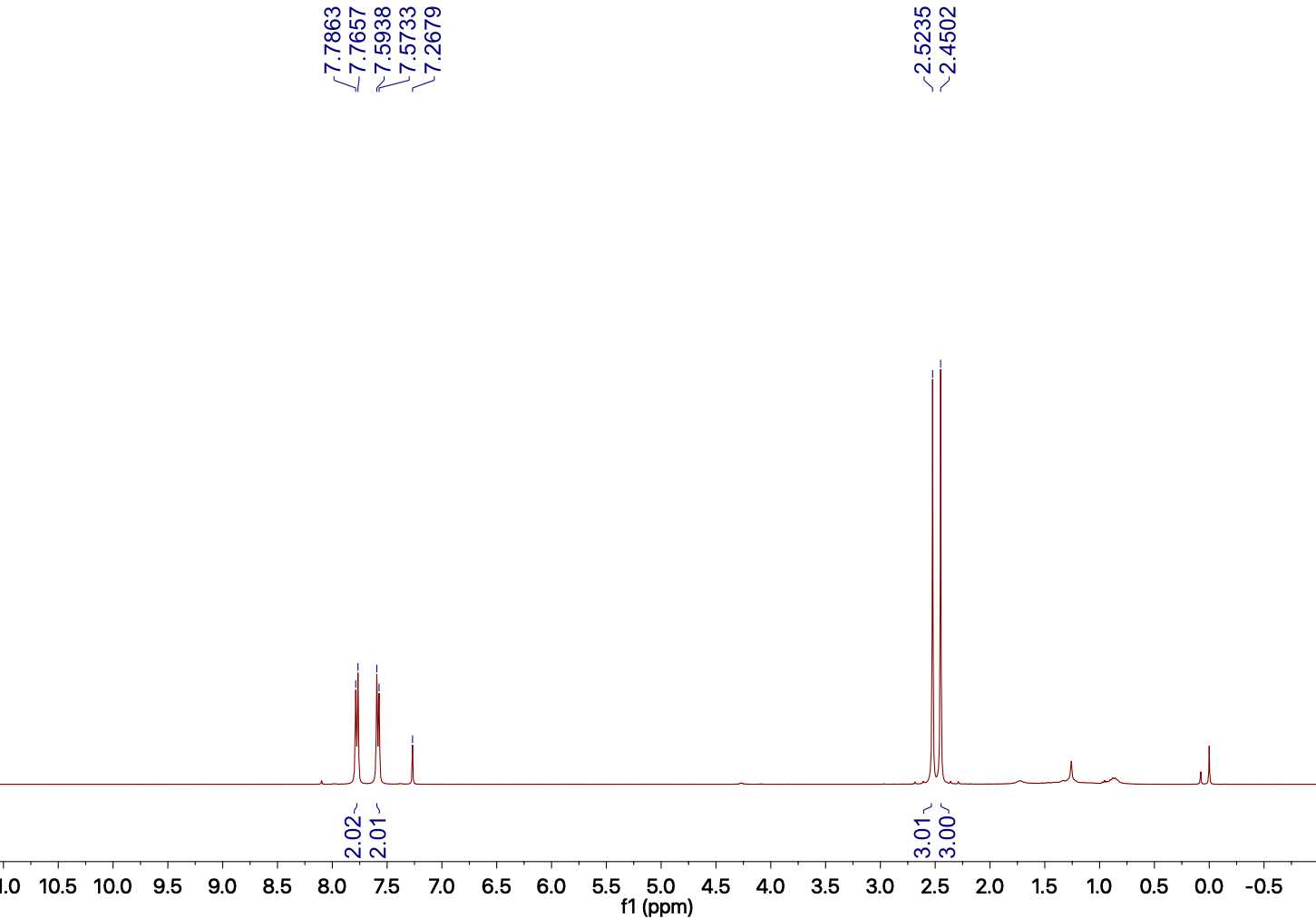
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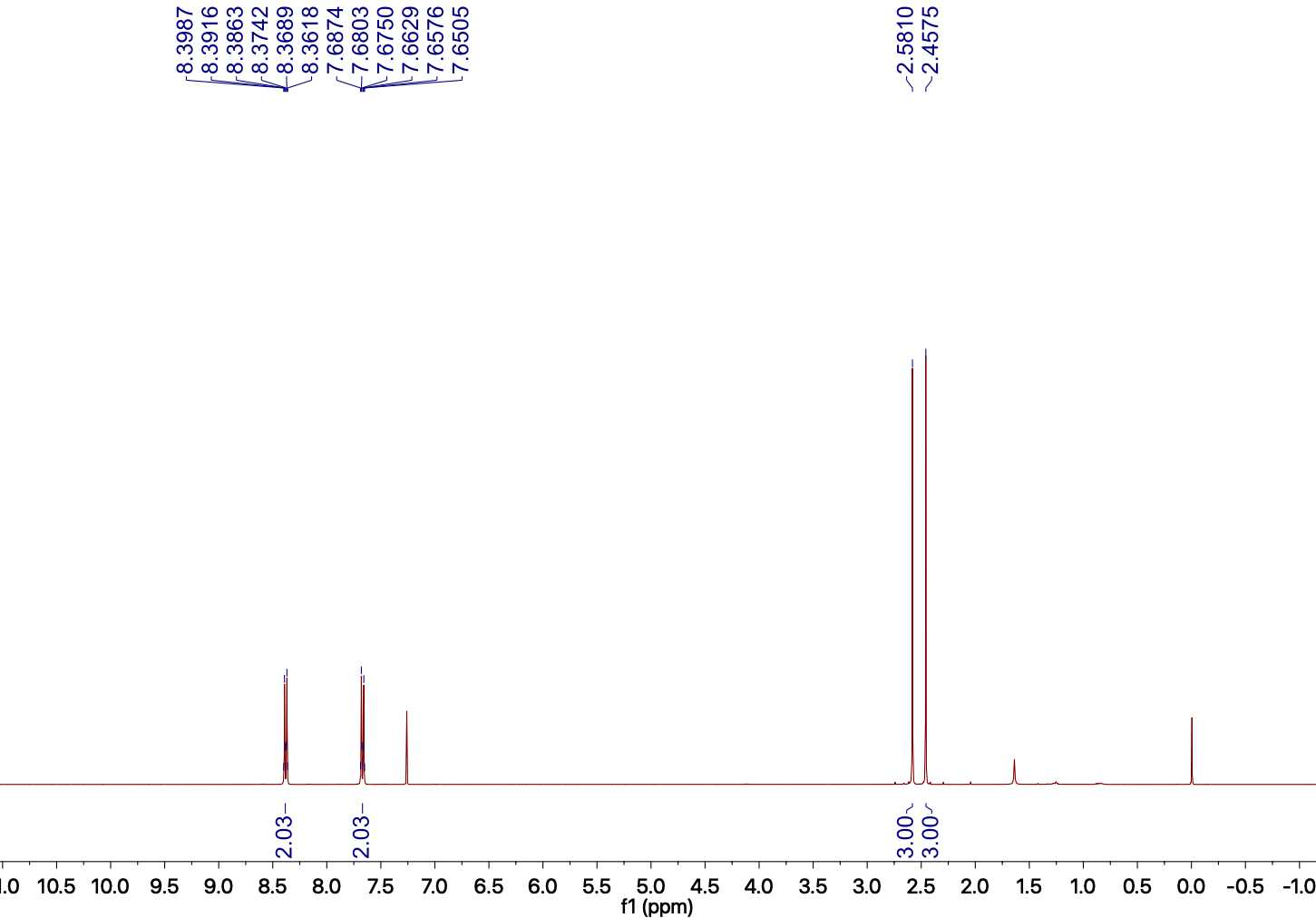
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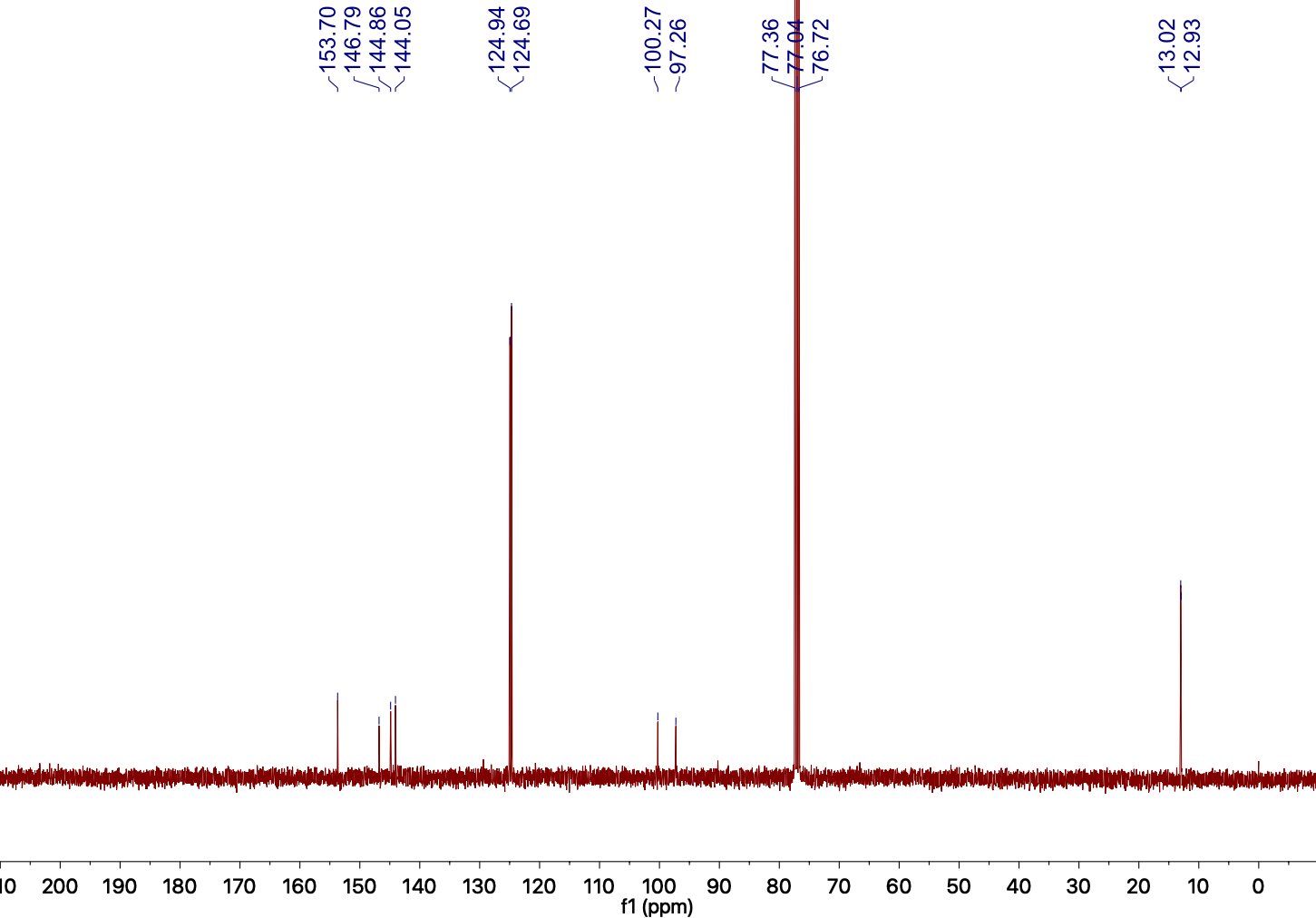
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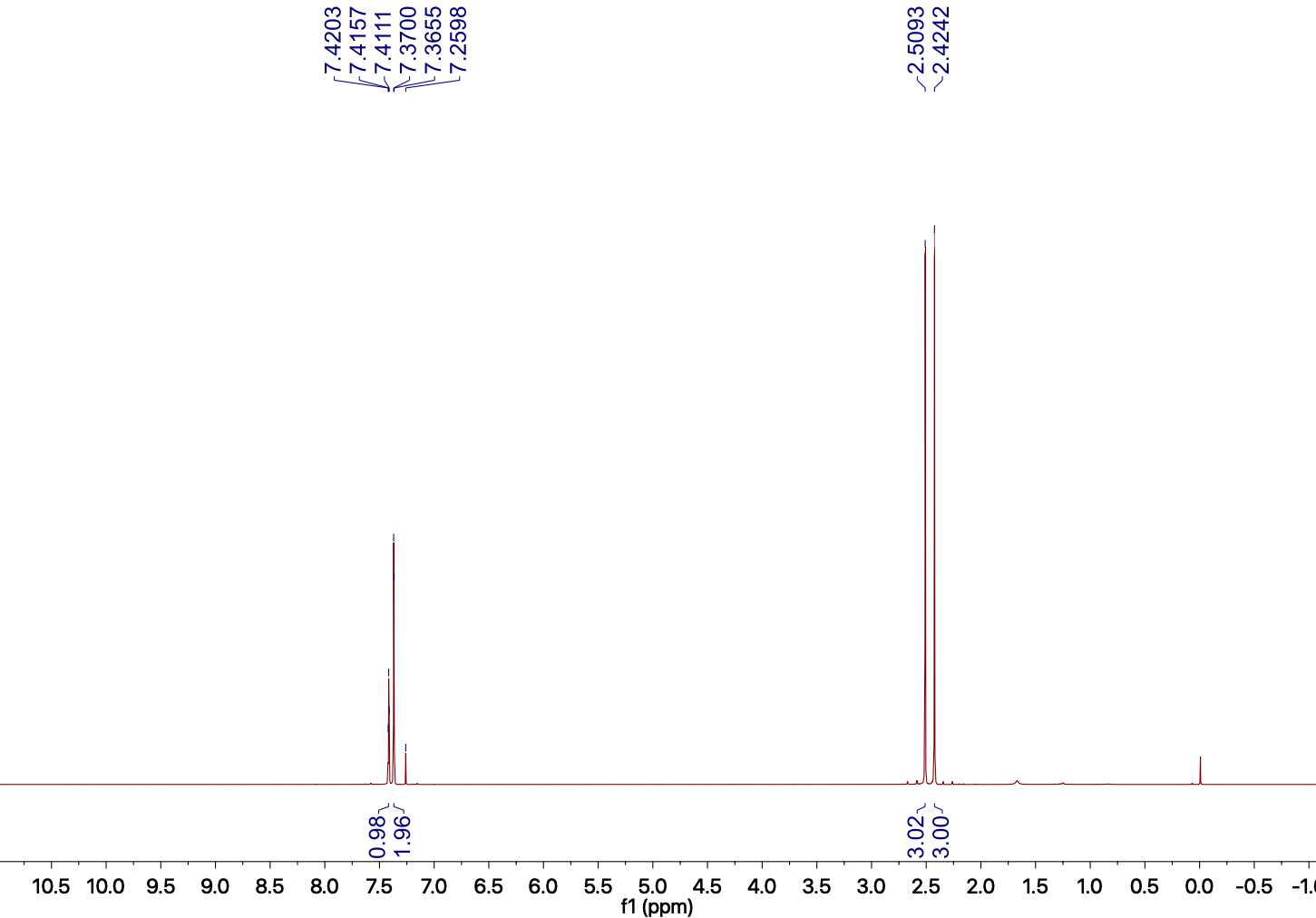
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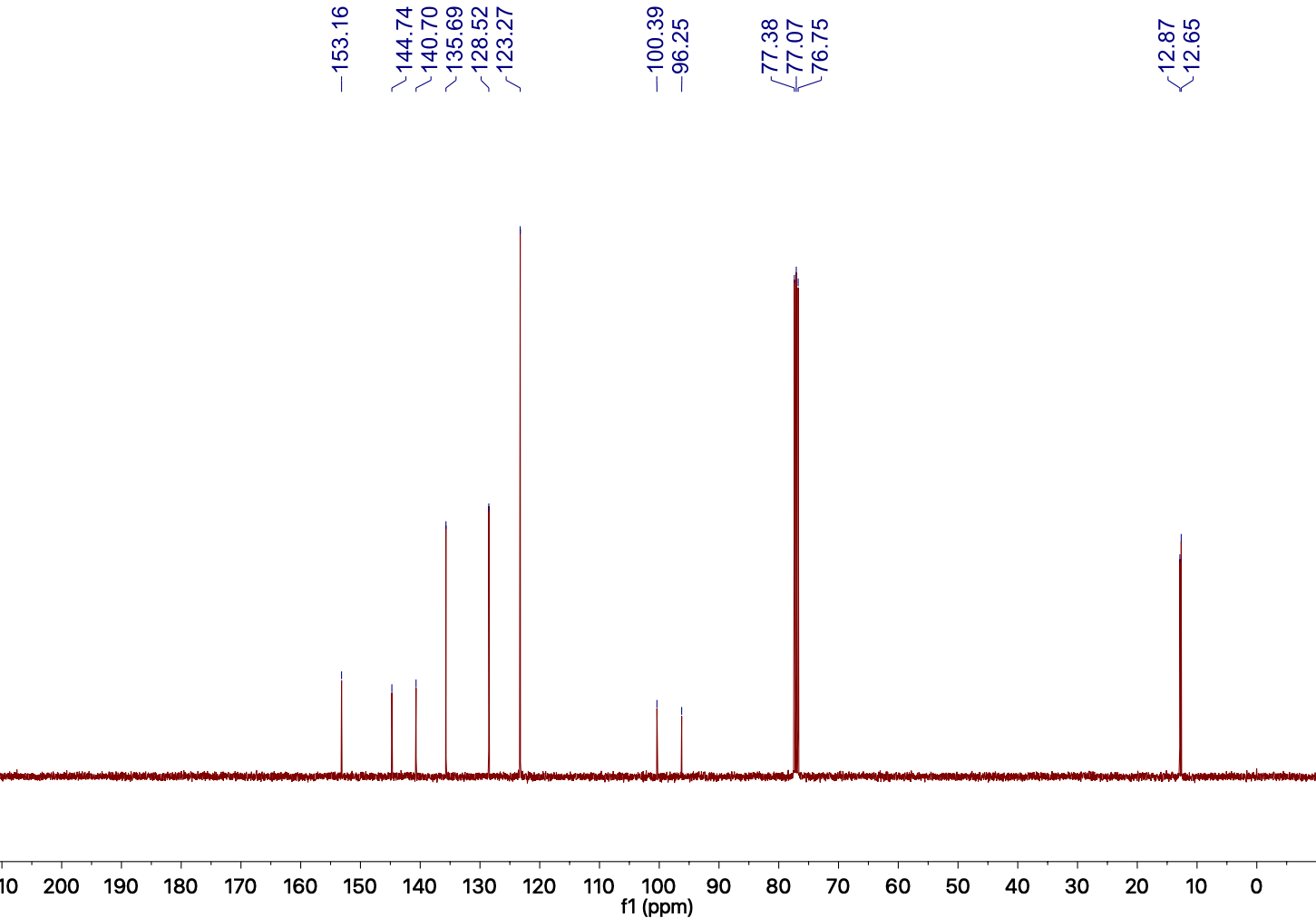
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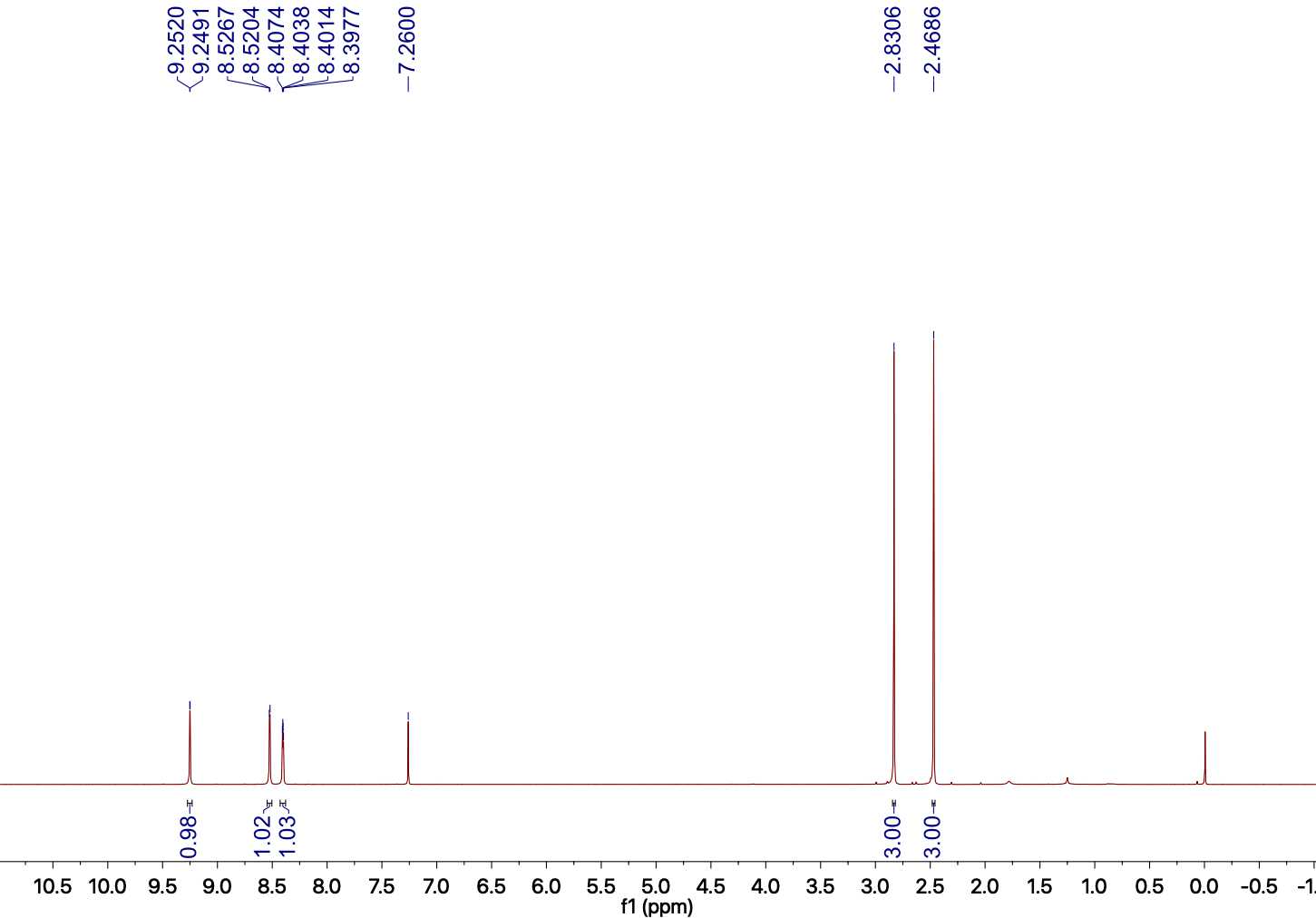
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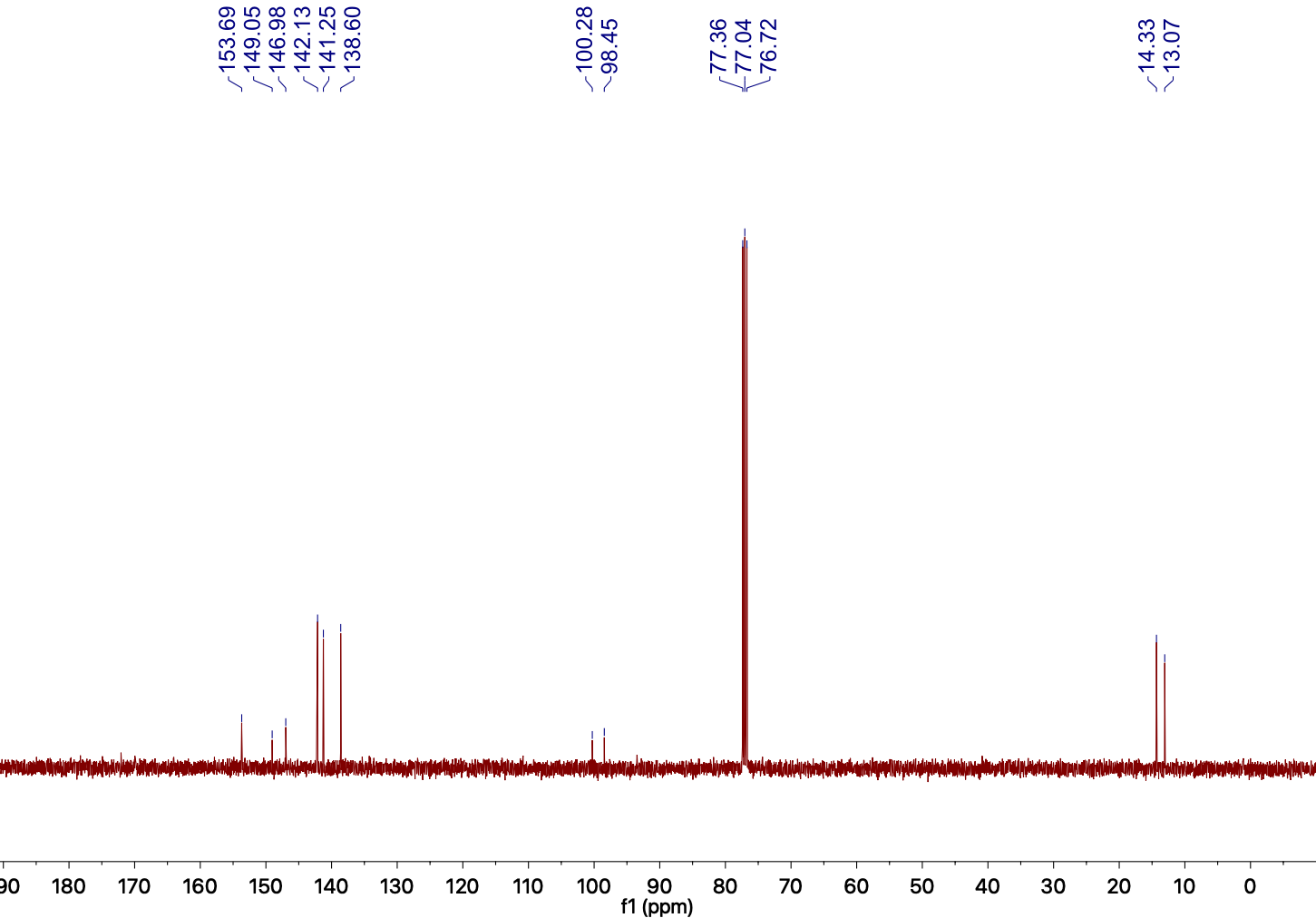
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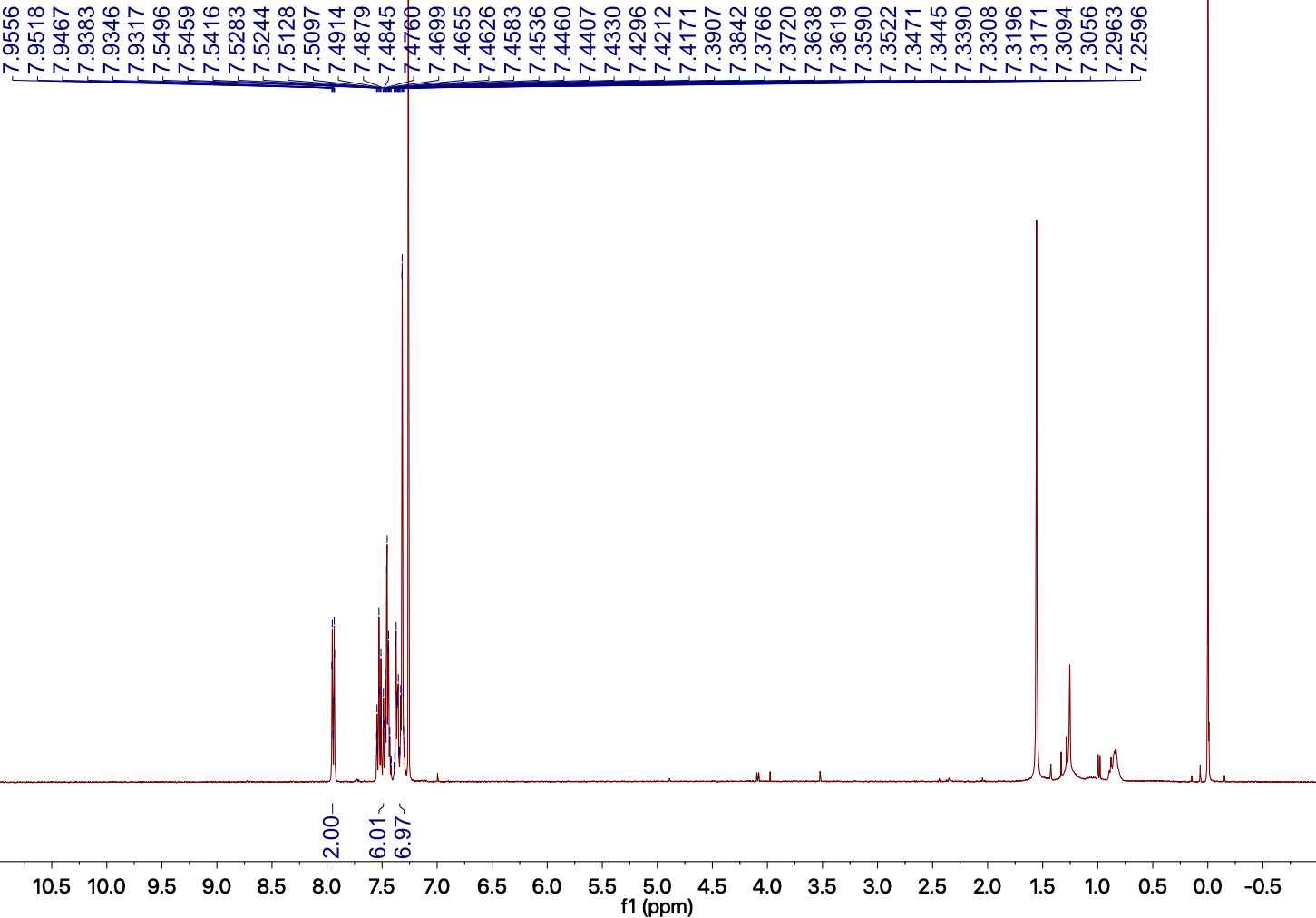
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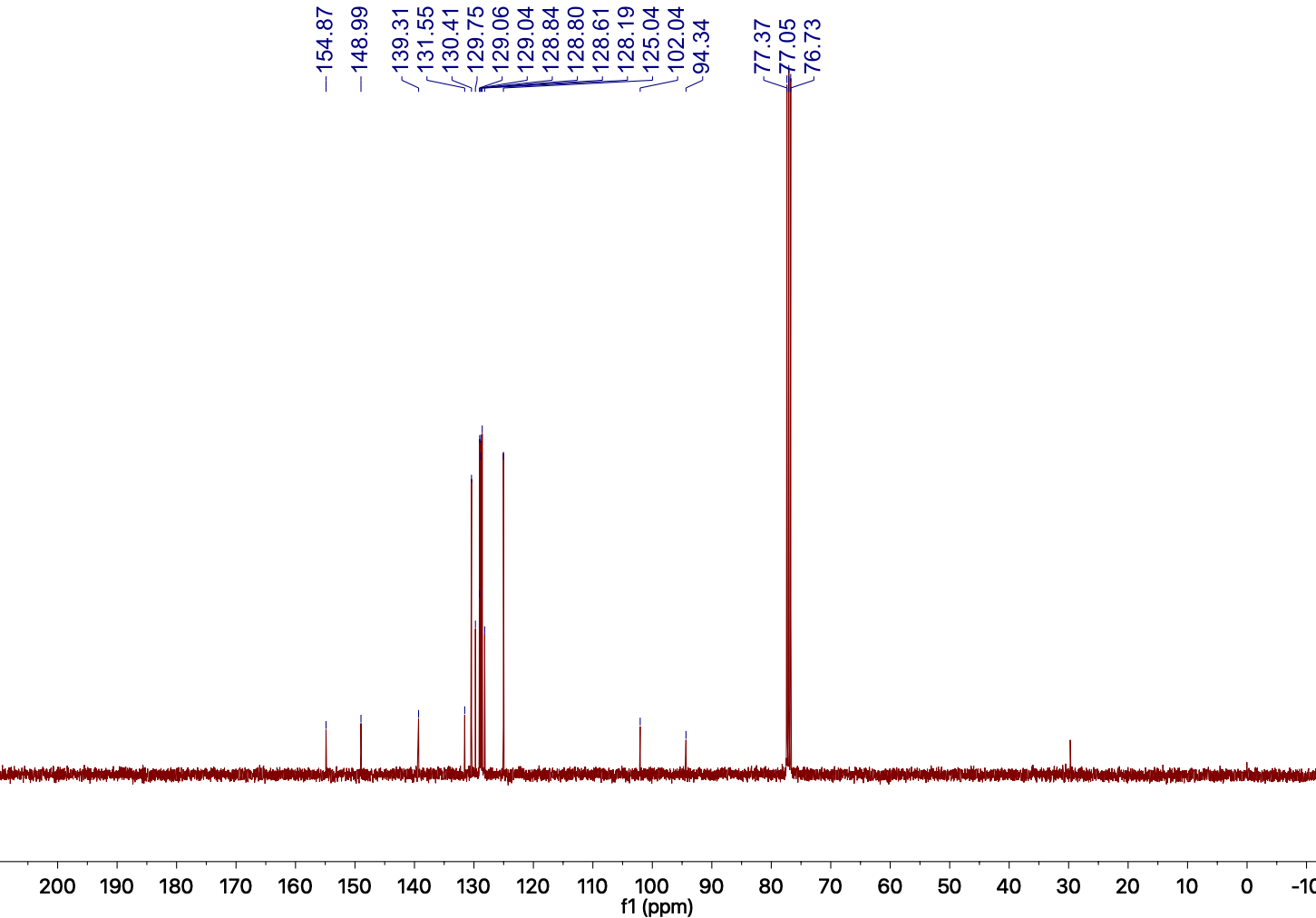
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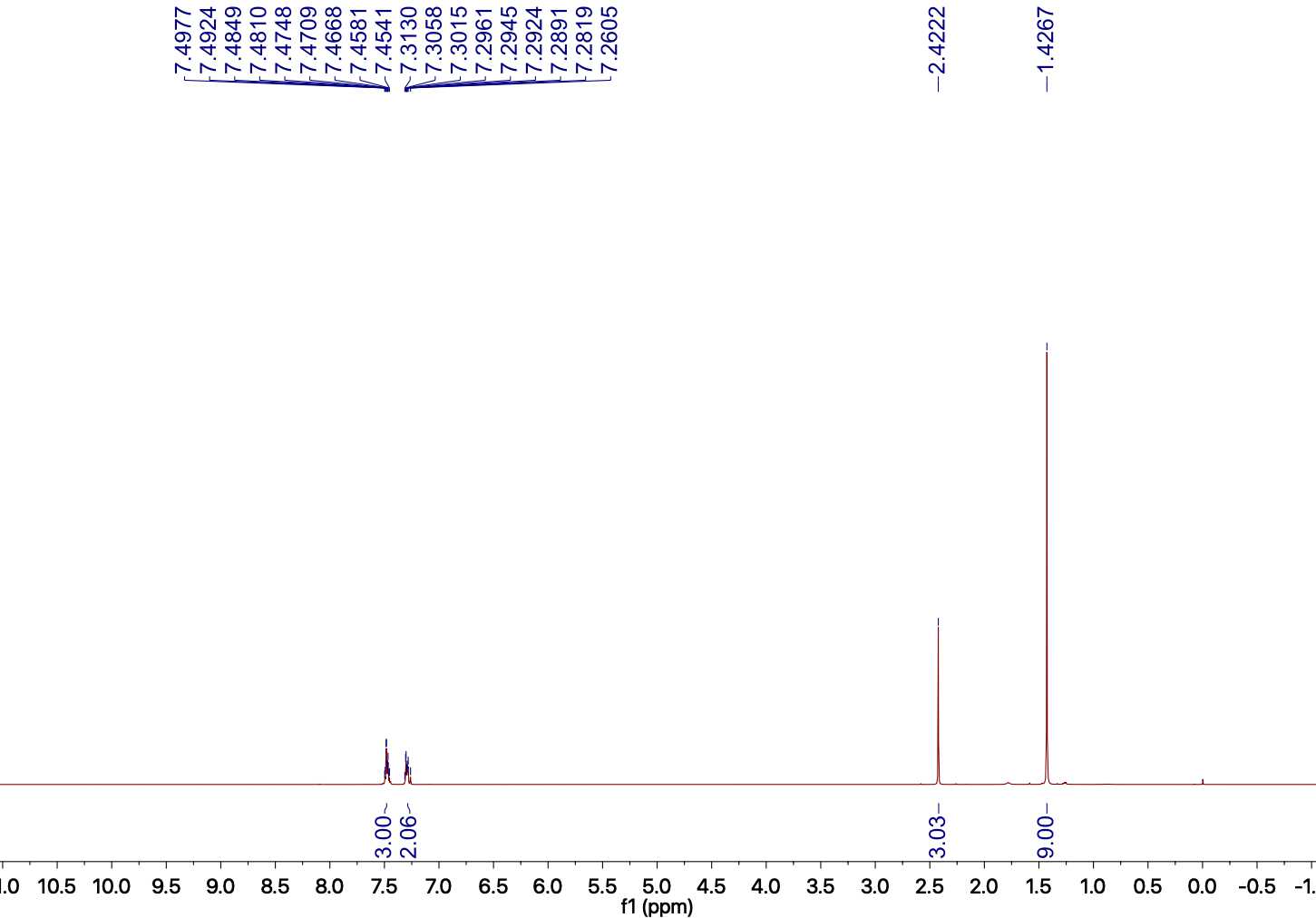
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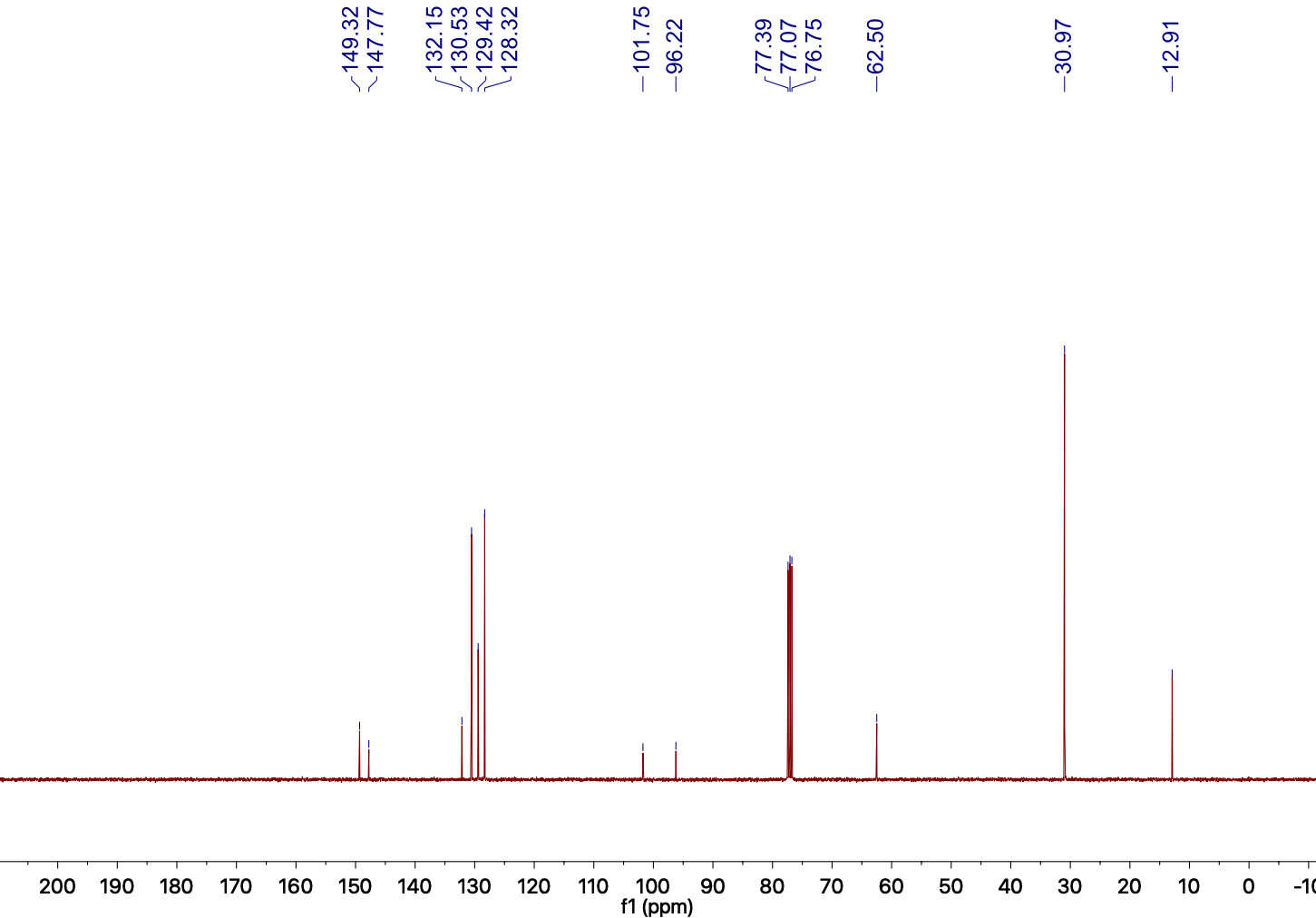
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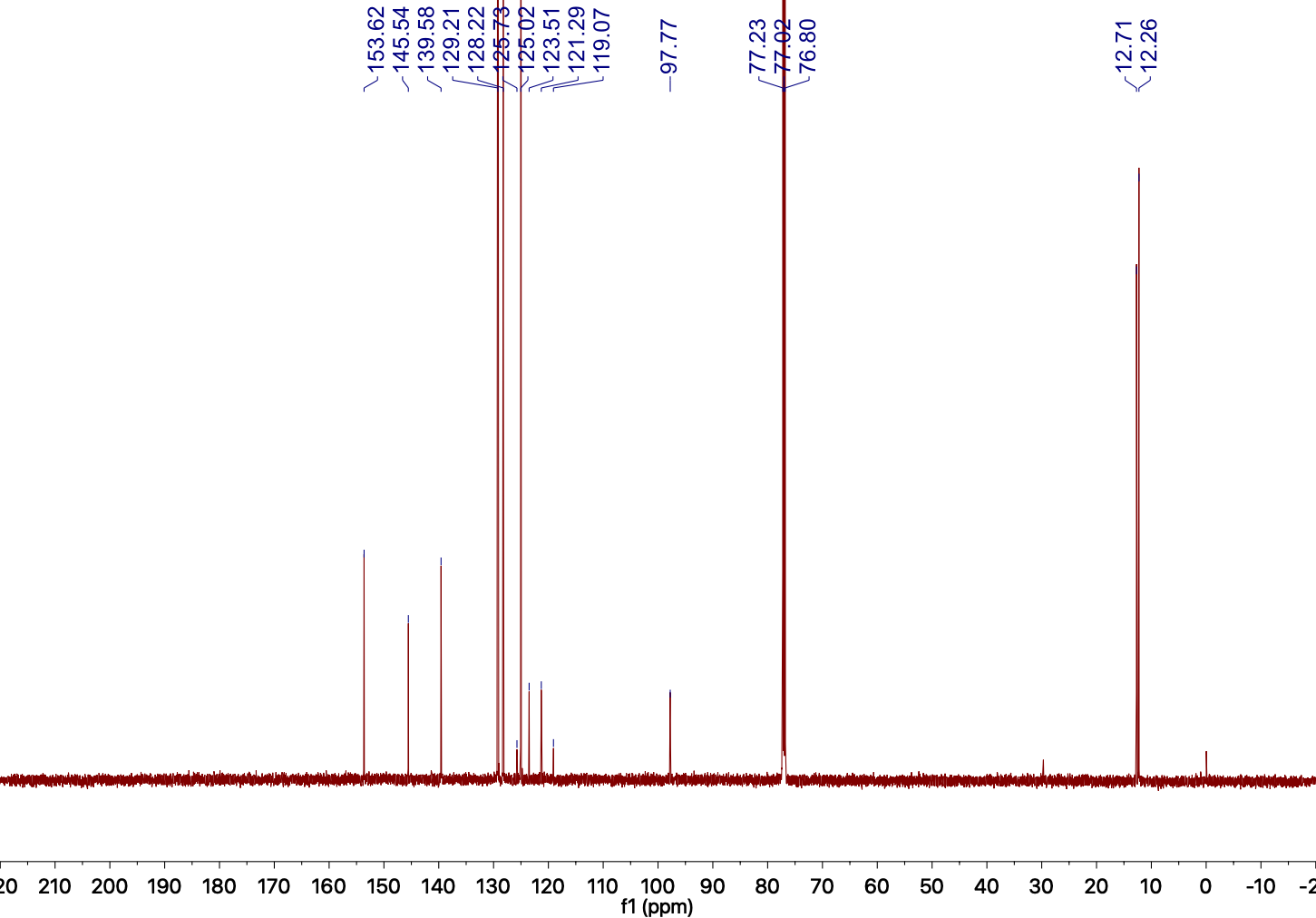
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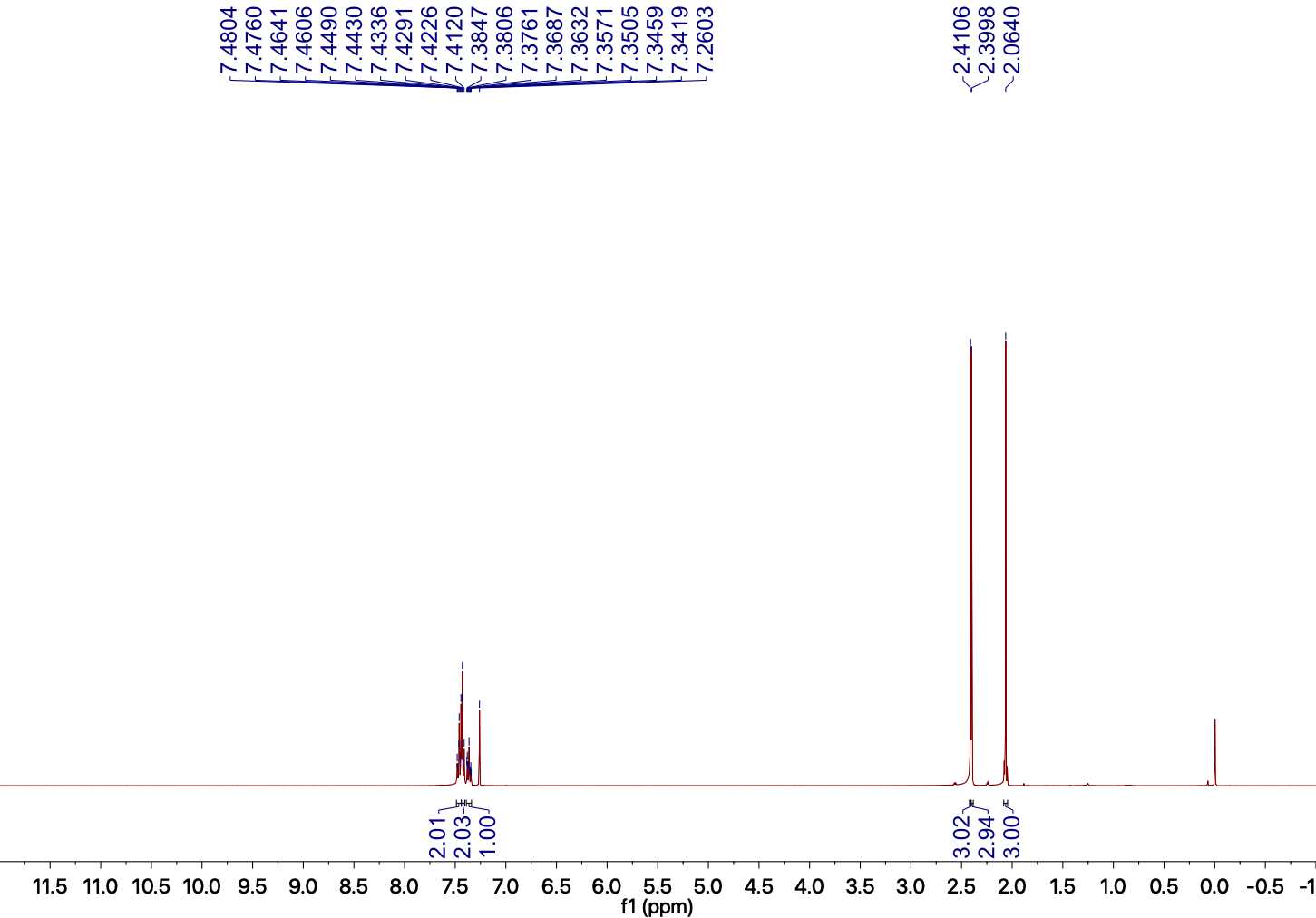
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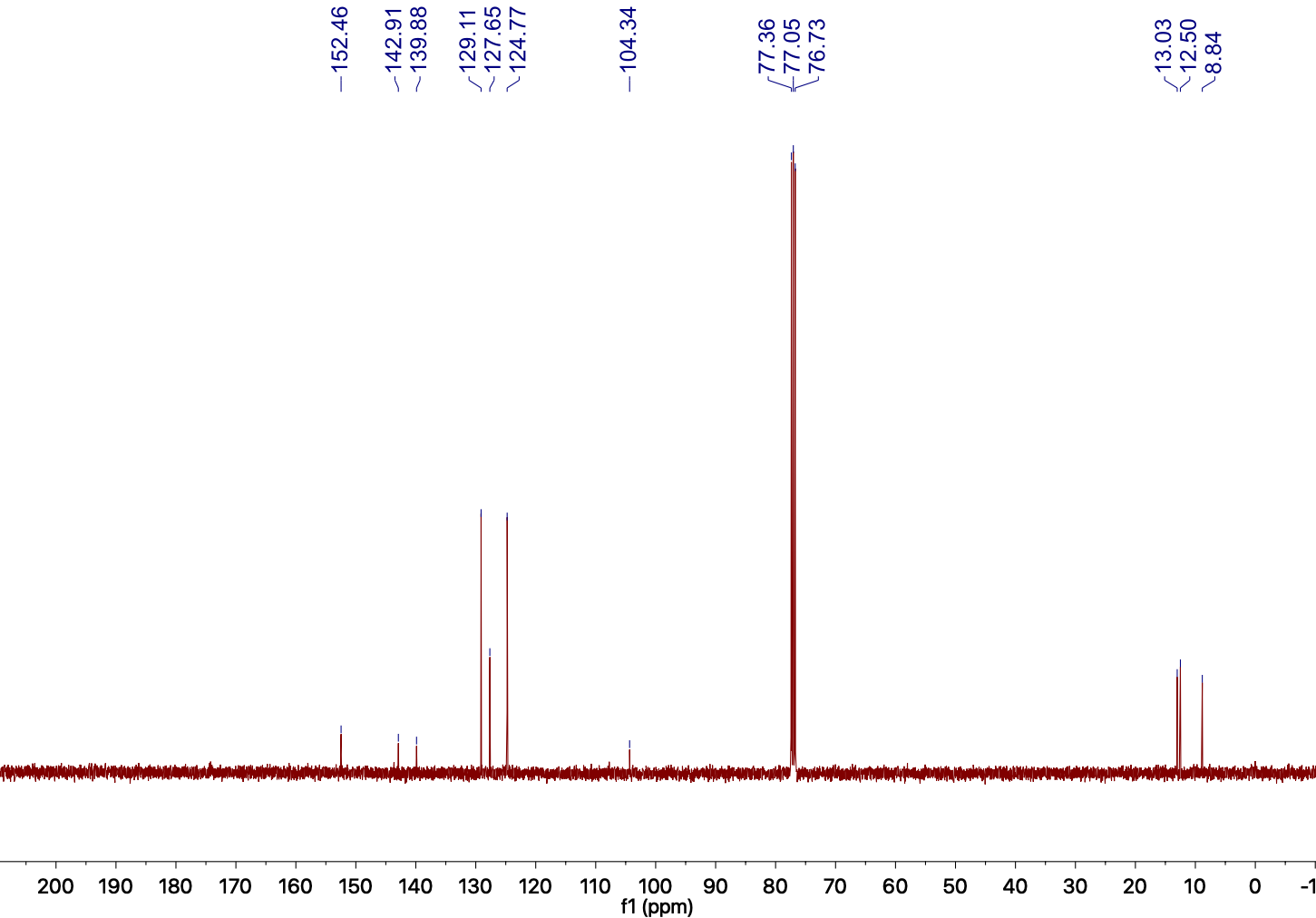
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