Oxidative nucleophilic aromatic amination of nitrobenzenes

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Supplementary information

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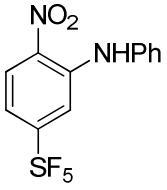
General information

NMR chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz and referenced to residual signals of solvents or internal standards: $CDCl_3$ δ_H = 7.26, δ_C = 77.16; Me_4Si δ_H = 0.00; $CFCl_3$ δ_F = 0.00. ^{13}C and ^{19}F NMR spectra were ^1H decoupled. GCMS spectra were recorded on a gas chromatograph coupled with a quadrupole mass-selective electron impact (EI) detector (70 eV). High-resolution mass spectra (HRMS) were recorded on a gas chromatograph coupled with a orthogonal acceleration time-of-flight detector using EI ionization or an FT mass spectrometer using electrospray (ESI) ionization. Infrared spectra were measured on a FT-IR instrument. Purification of the products was performed by flash chromatography using silica gel 60. Dry solvents if used were obtained the following way: Et_2O and THF were distilled over Na/benzophenone and kept over activated 3Å molecular sieves, hexane and DMF were dried using activated 3Å molecular sieves. PE refers to petroleum ether of boiling point range 40-60°C.

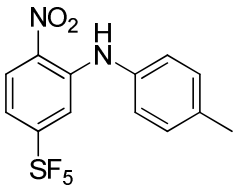
Synthesis of 2-nitro-*N*-aryl-5-(pentafluorosulfanyl)anilines (2), general procedure. A solution of *n*-BuLi (2.5 M, 1.29 mL, 3.21 mmol, 4 equiv.) in hexanes was added to a solution of arylamine (3.21 mmol, 4 equiv.) in dry THF (5 mL) cooled to -78°C under argon. After stirring the mixture for 1 min the resulting solution was added via syringe over 1 min to a solution of 4-nitro-1-(pentafluorosulfanyl)benzene (**1**) (200 mg, 0.803 mmol, 1 equiv.) in dry THF (10 mL) cooled to -110°C to -120°C (liquid N_2/EtOH) under argon. The resulting mixture was stirred at this temperature for 10 min, followed by the addition of $KMnO_4$ (216 mg, 1.36 mmol, 1.7 equiv.) and liquid NH_3 (3-5 mL). The cooling bath was removed and after 5 min. of stirring, solid NH_4Cl (1 g) was carefully added, the mixture was slowly warmed to rt and excess of ammonia was allowed to boil off. Water was carefully added, the reaction mixture was filtered through filter paper under vacuum and solid on filter washed with several portions of EtOAc. The filtrate was extracted with EtOAc, combined organic phase was washed with water, brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. Purification using flash chromatography (silica gel, PE–acetone) provided pure product **2**.

*2-Nitro-5-(pentafluorosulfanyl)-N-phenylaniline (**2a**).* Orange solid (199 mg, 73% yield);



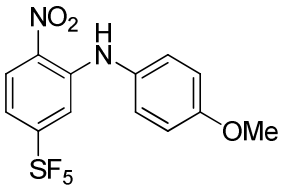
R_f 0.55 (PE-acetone, 95:5); m.p. 80-81°C; IR (film) ν_{max} (cm^{-1}) 3357, 1621, 1597, 1578, 1499, 1490, 1432, 1345, 1171, 1158, 1077, 1027, 846, 753, 600; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.51 (1H, br s), 8.28 (1H, d, J = 9.3 Hz), 7.62 (1H, d, J = 2.3 Hz), 7.47 (2H, dt, J = 7.5, 2.0 Hz), 7.31 (1H, dt, J = 7.5, 0.6 Hz), 7.29-7.26 (2H, m), 7.11 (1H, dd, J = 9.3, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.62 (quint, J = 18.8 Hz), 142.90, 137.68, 133.80, 130.31 (2C), 127.51, 126.83, 124.36 (2C), 114.67 (quint, J = 5.1 Hz), 114.43 (quint, J = 4.5 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.96-80.36 (1F, m), 60.88 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 340 (100%) $[M]^+$, 323 (8), 310 (13), 306 (22), 295 (12), 293 (14), 198 (15), 185 (14), 168 (12), 167 (46), 166 (23), 139 (16), 77 (21), 51 (11); HRMS (ESI) *m/z* Calcd for $C_{12}H_8F_5N_2O_2S$ $[M - H]^+$: 339.0232; Found: 339.0230.

*2-Nitro-5-(pentafluorosulfanyl)-N-p-tolylaniline (**2b**).* Orange solid (207 mg, 73% yield);



R_f 0.63 (PE-acetone, 95:5); m.p. 89-90°C; IR (film) ν_{max} (cm^{-1}) 3357, 3034, 2960, 1623, 1610, 1578, 1513, 1491, 1422, 1381, 1343, 1322, 1212, 1173, 1083, 1019, 950, 845, 824, 806, 753, 718, 688, 600, 583, 567; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.47 (1H, br s), 8.27 (1H, d, J = 9.4 Hz), 7.55 (1H, d, J = 2.3 Hz), 7.27 (2H, d, J = 8.1 Hz), 7.15 (2H, d, J = 8.1 Hz), 7.07 (1H, dd, J = 9.4, 2.3 Hz), 2.40 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.65 (quint, J = 18.9 Hz), 143.45, 136.98, 134.88, 133.45, 130.90 (2C), 127.48, 124.67 (2C), 114.64 (quint, J = 5.0 Hz), 114.01 (quint, J = 4.8 Hz), 21.18; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.08-80.48 (1F, m), 60.85 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 354 (100%) $[M]^+$, 320 (14), 307 (16), 198 (10), 181 (26), 180 (34), 91 (10); HRMS (ESI) *m/z* Calcd for $C_{13}H_{10}F_5N_2O_2S$ $[M - H]^+$: 353.0387; Found: 353.0386.

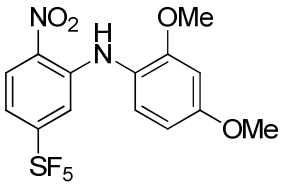
*N-(4-methyxyphenyl)-2-nitro-5-(pentafluorosulfanyl)aniline (**2c**).* Red solid (208 mg, 70% yield);



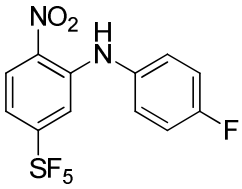
R_f 0.45 (PE-acetone, 95:5); m.p. 78-79°C; IR (film) ν_{max} (cm^{-1}) 3357, 1621, 1577, 1511, 1490, 1343, 1259, 1247, 845, 753, 600; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.42 (1H, br s), 8.27 (1H, d, J = 9.4 Hz), 7.41 (1H, d, J = 2.3 Hz), 7.19 (2H, ddd, J = 9.0, 3.4, 0.5 Hz), 7.05 (1H, dd, J = 9.4, 2.3 Hz), 6.99 (2H, dd, J = 9.0, 3.4 Hz), 3.86 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.68 (quint, J = 18.8 Hz), 158.65, 144.15,

133.10, 130.03, 127.45, 126.94 (2C), 115.50 (2C), 114.42 (quint, J = 5.0 Hz), 113.68 (quint, J = 4.4 Hz), 55.64; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.11-80.51 (1F, m), 61.03 (4F, d, J = 150.4 Hz); GCMS (EI) *m/z* 370 (100%) $[M]^+$, 355 (31), 336 (24), 308 (13), 185 (10), 182 (12), 154 (9); HRMS (ESI) *m/z* Calcd for $C_{13}H_{10}F_5N_2O_3S$ $[M + H]^+$: 369.0338; Found: 369.0334.

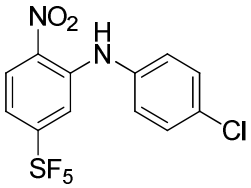
*2,4-Dimethoxy-N-(2-nitro-5-pentafluorosulfanyl)aniline (**2d**).* Red solid (189 mg, 59% yield); R_f 0.31 (PE-acetone, 95:5); m.p. 75-76°C; IR (film) ν_{max} (cm^{-1}) 3360, 2840, 1623, 1578, 1513, 1490, 1440, 1345, 1261, 846, 815, 600; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.28 (1H, br s), 8.25 (1H, d, J = 9.4 Hz), 7.29 (1H, d, J = 2.4 Hz), 7.19 (1H, d, J = 8.6 Hz), 7.03 (1H, dd, J = 9.4, 2.4 Hz), 6.59 (1H, d, J = 2.6 Hz), 6.55 (1H, dd, J = 8.6, 2.6 Hz), 3.87 (3H, s), 3.80 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.76, 158.46 (quint, J = 18.3 Hz), 154.85, 143.83, 133.25, 127.24, 126.70, 118.98, 114.90 (quint, J = 5.1 Hz), 113.44 (quint, J = 4.4 Hz), 104.77, 99.93, 55.73, 55.67; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 82.45-80.85 (1F, m), 60.85 (4F, d, J = 150.4 Hz); GCMS (EI) *m/z* 400 (100%) $[M]^+$, 385 (15), 339 (15), 338 (13), 337 (17), 336 (12), 324 (11), 153 (25); HRMS (ESI) *m/z* Calcd for $C_{14}H_{13}F_5N_2O_4S$ $[M + Na]^+$: 423.0408; Found: 423.0406.



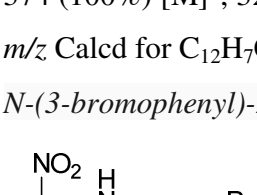
*N-(4-fluorophenyl)-2-nitro-5-(pentafluorosulfanyl)aniline (**2e**).* Orange solid (189 mg, 66% yield); R_f 0.45 (PE-acetone, 95:5); m.p. 106-107°C; IR (film) ν_{max} (cm^{-1}) 3368, 3355, 1624, 1614, 1578, 1536, 1511, 1490, 1348, 1328, 1259, 833, 808, 600; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.41 (1H, br s), 8.29 (1H, d, J = 9.3 Hz), 7.44 (1H, d, J = 2.3 Hz), 7.29-7.23 (2H, m), 7.19 (1H, d, J = 8.1 Hz), 7.17 (1H, d, J = 8.1 Hz), 7.11 (1H, dd, J = 9.3, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.30 (d, J = 247.4 Hz), 158.72 (quint, J = 18.5 Hz), 143.39, 133.63, 133.55 (d, J = 3.2 Hz), 127.55, 127.04 (2C, d, J = 8.5 Hz), 117.33 (2C, d, J = 22.6 Hz), 114.43 (quint, J = 4.6 Hz), 114.28 (quint, J = 5.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.87-80.27 (1F, m), 60.85 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 358 (100%) $[M]^+$, 324 (13), 311 (22), 216 (15), 203 (14), 185 (47), 184 (26), 157 (13), 95 (14), 75 (10); HRMS (ESI) *m/z* Calcd for $C_{12}H_7F_6S$ $[M - H]^+$: 357.0127; Found: 357.0130.



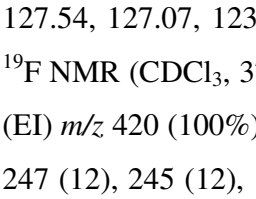
N-(4-chlorophenyl)-2-nitro-5-(pentafluorosulfanyl)aniline ***(2f)***. Red solid (215 mg, 72% yield); R_f 0.44 (PE-acetone, 95:5); m.p. 90-91°C; IR (film) ν_{max} (cm^{-1}) 3354, 1620, 1593, 1575, 1535, 1495, 1342, 1263, 848, 830, 601, 509; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.42 (1H, br s), 8.29 (1H, d, J = 9.3 Hz), 7.55 (1H, d, J = 2.3 Hz), 7.44 (2H, dd, J = 8.6, 2.1 Hz), 7.22 (2H, dd, J = 8.6, 2.1 Hz), 7.15 (1H, dd, J = 9.3, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.67 (quint, J = 18.9 Hz), 142.51, 136.32, 134.09, 132.24, 130.50 (2C), 127.60, 125.65 (2C), 114.92 (quint, J = 4.5 Hz), 114.51 (quint, J = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.78-80.18 (1F, m), 60.9 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 374 (100%) $[M]^+$, 327 (12), 201 (28), 200 (11), 166 (16), 111 (10), 75 (12); HRMS (ESI) *m/z* Calcd for $C_{12}H_7ClF_5N_2O_2S$ $[M - H]^+$: 372.9842; Found: 372.9840.



N-(3-bromophenyl)-2-nitro-5-(pentafluorosulfanyl)aniline ***(2g)***. Yellow amorphous solid (195 mg, 58% yield); R_f 0.44 (PE-acetone, 95:5); IR (film) ν_{max} (cm^{-1}) 3353, 1620, 1586, 1571, 1494, 1478, 1427, 1343, 1263, 845, 601; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.43 (1H, br s), 8.29 (1H, d, J = 9.3 Hz), 7.63 (1H, d, J = 2.3 Hz), 7.46-7.41 (2H, m), 7.33 (1H, t, J = 7.9 Hz), 7.22 (1H, ddd, J = 7.9, 1.8, 0.5 Hz), 7.17 (1H, dd, J = 9.3, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.58 (quint, J = 18.7 Hz), 141.96, 139.27, 134.39, 131.44, 129.62, 127.54, 127.07, 123.74, 122.34, 115.29 (quint, J = 4.5 Hz), 114.75 (quint, J = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.71-80.10 (1F, m), 61.00 (4F, d, J = 150.6 Hz); GCMS (EI) *m/z* 420 (100%) $[M + 1]^+$, 419 (14), 418 (97), 386 (11), 384 (11), 294 (14), 293 (22), 247 (12), 245 (12), 185 (24), 184 (19), 166 (27), 165 (14), 164 (17), 157 (16), 155 (13), 140 (10), 139 (20), 76 (13), 75 (16), 63 (15); HRMS (ESI) *m/z* Calcd for $C_{12}H_7BrF_5N_2O_2S$ $[M - H]^+$: 416.9337; Found: 416.9334.

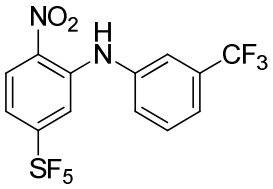


N-(4-iodophenyl)-2-nitro-5-(pentafluorosulfanyl)aniline ***(2h)***. Orange solid (255 mg, 68% yield); R_f 0.45 (PE-acetone, 95:5); m.p. 89-90°C; IR (film) ν_{max} (cm^{-1}) 3351, 1618, 1583, 1535, 1499, 1494, 1390, 1342, 1262, 1007, 848, 601; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.40 (1H, br s), 8.29 (1H, d, J = 9.3 Hz), 7.78 (2H, dd, J = 8.6, 2.8 Hz), 7.60 (1H, d, J = 2.3 Hz), 7.16 (1H, dd, J = 9.3, 2.3 Hz), 7.03 (2H, dd, J = 8.6, 2.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.64 (quint, J = 19.1 Hz), 142.08, 139.38 (2C), 137.61, 134.29, 127.61, 125.80



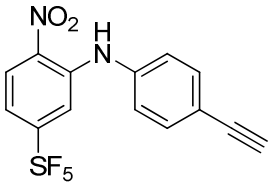
(2C), 115.11 (quint, J = 4.4 Hz), 114.62 (quint, J = 5.0 Hz), 90.58; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.76-80.16 (1F, m), 61.00 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 466 (100%) $[M]^+$, 432 (8), 185 (15), 166 (14), 139 (10), 76 (10); HRMS (ESI) *m/z* Calcd for $C_{12}H_7F_5IN_2O_2S$ $[M - H]^+$: 464.9199; Found: 464.9196.

2-Nitro-5-(pentafluorosulfanyl)-N-(3-(trifluoromethyl)phenyl)aniline ***(2i)***. Yellow



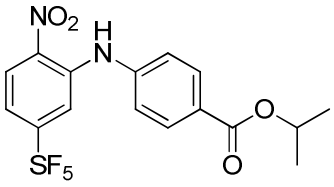
amorphous solid (196 mg, 60% yield); R_f 0.44 (PE-acetone, 95:5); IR (film) ν_{max} (cm^{-1}) 3358, 1622, 1614, 1597, 1502, 1462, 1328, 1265, 1132, 847, 754, 602; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.49 (1H, br s), 8.32 (1H, d, J = 9.3 Hz), 7.64 (1H, d, J = 2.3 Hz), 7.59 (1H, d, J = 7.7 Hz), 7.57-5.53 (2H, m), 7.47 (1H, d, J = 7.7 Hz), 7.21 (1H, dd, J = 9.3, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.64 (quint, J = 18.9 Hz), 141.76, 138.70, 134.70, 132.90 (q, J = 32.9 Hz), 130.94, 127.66, 126.82, 123.60 (q, J = 272.6 Hz), 123.06 (q, J = 3.8 Hz), 120.61 (q, J = 3.8 Hz), 115.65 (quint, J = 4.5 Hz), 114.68 (quint, J = 5.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.54-79.84 (1F, m), 60.95 (4F, d, J = 150.5 Hz), -63.53 (3F, s); GCMS (EI) *m/z* 408 (100%) $[M]^+$, 374 (13), 361 (15), 253 (11), 235 (47), 234 (19); HRMS (ESI) *m/z* Calcd for $C_{13}H_7F_8N_2O_2S$ $[M - H]^+$: 407.0106; Found: 407.0102.

N-(4-ethynylphenyl)-2-nitro-5-(pentafluorosulfanyl)aniline ***(2j)***. Red solid (227 mg, 78%



yield); R_f 0.44 (PE-acetone, 95:5); m.p. 122-123°C; IR (film) ν_{max} (cm^{-1}) 3352, 3296, 2109, 1621, 1602, 1582, 1535, 1509, 1492, 1343, 1263, 1119, 840, 811, 722, 601; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.48 (1H, br s), 8.29 (1H, d, J = 9.3 Hz), 7.67 (1H, d, J = 2.3 Hz), 7.58 (2H, dd, J = 8.6, 2.3 Hz), 7.23 (2H, dd, J = 8.6, 2.3 Hz), 7.17 (1H, dd, J = 9.3, 2.3 Hz), 3.14 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.58 (quint, J = 18.6 Hz), 141.80, 138.27, 134.48, 134.09 (2C), 127.59, 123.28 (2C), 120.10, 115.28 (quint, J = 4.5 Hz), 114.92 (quint, J = 5.0 Hz), 82.81, 78.24; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.73-80.13 (1F, m), 60.96 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 364 (100%) $[M]^+$, 330 (9), 315 (15), 191 (30), 190 (22), 163 (10); HRMS (ESI) *m/z* Calcd for $C_{14}H_8F_5N_2O_2S$ $[M - H]^+$: 363.0232; Found: 363.0229.

Isopropyl-4-[2-nitro-5-(pentafluorosulfanyl)phenylamino]benzoate ***(2k)***. Yellow



amorphous solid (120 mg, 35% yield); R_f 0.34 (PE-acetone, 95:5); IR (film) ν_{max} (cm^{-1}) 3352, 1713, 1621, 1603, 1577,

1512, 1493, 1469, 1388, 1378, 1343, 1279, 1103, 845, 601; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.52 (1H, br s), 8.31 (1H, d, J = 9.3 Hz), 8.12 (1H, dt, J = 8.7, 2.4 Hz), 7.79 (2H, d, J = 2.3 Hz), 7.31 (2H, dt, J = 8.7, 2.4 Hz), 7.22 (1H, dd, J = 9.3, 2.3 Hz), 5.27 (1H, sept, J = 6.2 Hz), 1.39 (6H, d, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.27, 158.51 (quint, J = 18.9 Hz), 142.07, 141.09, 135.06, 131.77 (2C), 128.29, 127.59, 122.02 (2C), 115.88 (quint, J = 4.5 Hz), 115.29 (quint, J = 4.8 Hz), 68.80, 22.09 (2C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.63-80.02 (1F, m), 61.02 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 426 (100%) $[M]^+$, 385 (12), 384 (71), 368 (20), 367 (82), 351 (10), 337 (11), 320 (16), 295 (10), 211 (10), 167 (16), 166 (17), 164 (10), 139 (12); HRMS (ESI) *m/z* Calcd for $C_{16}H_{14}F_5N_2O_4S$ $[M - H]^+$: 425.0600; Found: 425.0596.

N-(2-nitro-5-(pentafluorosulfanyl)phenyl)naphthalen-1-amine ***(2l)***. Yellow solid (173 mg, 55% yield); R_f 0.52 (PE-acetone, 95:5); m.p. 115-116°C; IR (film) ν_{max} (cm^{-1}) 3348, 3062, 1618, 1597, 1577, 1509, 1490, 1410, 1397, 1339, 1319, 1245, 1170, 1160, 1017, 955, 845, 816, 791, 779, 753, 736, 688, 669, 600, 578; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.80 (1H, br s), 8.34 (1H, d, J = 9.4 Hz), 7.98-7.93 (2H, m), 7.89 (1H, d, J = 8.1 Hz), 7.61-7.56 (2H, m), 7.54 (1H, d, J = 7.3 Hz), 7.50 (1H, dt, J = 7.3, 1.1 Hz), 7.30 (1H, d, J = 2.3 Hz), 7.10 (1H, dd, J = 9.4, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.73 (quint, J = 18.6 Hz), 144.16, 134.76, 133.51, 133.47, 129.65, 128.92, 128.20, 127.45, 127.38, 127.15, 125.93, 123.14, 122.01, 114.95 (quint, J = 5.0 Hz), 114.22 (quint, J = 4.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.85-80.25 (1F, m), 60.84 (4F, d, J = 150.5 Hz); GCMS (EI) *m/z* 390 (100%) $[M]^+$, 356 (28), 344 (11), 343 (13), 248 (19), 235 (13), 234 (11), 218 (10), 217 (32), 216 (25), 215 (14), 214 (12), 189 (10), 127 (16); HRMS (ESI) *m/z* Calcd for $C_{16}H_{10}F_5N_2O_2S$ $[M - H]^+$: 389.0378; Found: 389.0381.

Synthesis of 2-nitro-5-trifluormethyl-diphenylamine (3). Synthetized according to general procedure for **2** from *n*-BuLi solution (3.21 mmol), aniline (3.21 mmol), and 1-nitro-4-(trifluoromethyl)benzene (0.803 mmol) providing after flash chromatography **3** as an orange solid (145 mg 64% yield); R_f 0.68 (PE-acetone, 95:5); m.p. 72-73°C; IR (film) ν_{max} (cm^{-1}) 3355, 1631, 1598, 1592, 1528, 1499, 1493, 1462, 1347, 1120, 771, 760, 740, 696; ^{1}H NMR ($CDCl_3$,

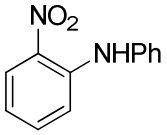
400 MHz) δ 9.55 (1H, br s), 8.32 (1H, dq, J = 8.9, 0.4 Hz), 7.50-7.43 (3H, m), 7.33-7.27 (3H, m), 6.97 (1H, ddd, J = 8.9, 1.9, 0.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.17, 137.84, 137.05 (q, J = 32.9 Hz), 134.48, 130.24 (2C), 127.92, 126.73, 124.72 (2C), 122.90 (q, J = 273.6 Hz), 113.59 (q, J = 4.2 Hz), 113.44 (q, J = 3.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -64.59 (s); GCMS (EI) *m/z* 282 (100%) $[M]^+$, 265 (14), 249 (16), 248 (32), 237 (31), 236 (14), 235 (54), 216 (15), 167 (29), 166 (14), 77 (17), 51 (13); HRMS (ESI) *m/z* Calcd for $C_{13}H_8F_3N_2O_2$ $[M - H]^+$: 281.0543; Found: 281.0540.

Synthesis of 4-nitro-3-phenylaminobenzonitrile (4). Synthetized according to general procedure for **2** from *n*-BuLi solution (3.21 mmol), aniline (3.21 mmol), and 4-nitrobenzonitrile (0.803 mmol) providing after flash chromatography **4** as a red solid (138 mg, 72% yield); R_f 0.34 (PE-acetone, 95:5); m.p. 135-136°C; IR (film) ν_{max} (cm^{-1}) 3350, 2235, 1615, 1596, 1574, 1498, 1484, 1339, 1261, 1065, 1027, 756, 697; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.48 (1H, br s), 8.29 (1H, d, J = 8.8 Hz), 7.51-7.46 (2H, m), 7.43 (1H, d, J = 1.7 Hz), 7.35 (1H, tt, J = 7.5, 1.5 Hz), 7.29-7.25 (2H, m), 6.97 (1H, dd, J = 8.8, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.27, 137.34, 134.56, 130.34 (2C), 127.86, 127.18, 125.15 (2C), 120.65, 119.08, 119.01, 117.25; GCMS (EI) *m/z* 239 (100%) $[M]^+$, 222 (15), 206 (17), 205 (49), 204 (10), 194 (44), 193 (29), 192 (89), 191 (16); HRMS (ESI) *m/z* Calcd for $C_{13}H_8N_3O$ $[M - H]^+$: 238.0622; Found: 238.0620.

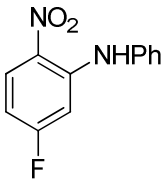
Synthesis of 4-nitro-*N*-phenylaniline (5).[1] Synthetized according to general procedure for **2** from *n*-BuLi solution (3.21 mmol), aniline (3.21 mmol), and 1,4-dinitrobenzene (0.803 mmol) providing after flash chromatography **5** as a yellow solid (147 mg, 85% yield); R_f 0.11 (PE-acetone, 95:5); m.p. 130-131°C; IR (film) ν_{max} (cm^{-1}) 3340, 1604, 1584, 1540, 1502, 1497, 1484, 1467, 1319, 1299, 841, 748; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (2H, dd, J = 9.3, 2.1 Hz), 7.42-7.36 (2H, m), 7.21 (2H, dd, J = 7.4, 1.1 Hz), 7.17 (1H, tt, J = 7.4, 1.1 Hz), 6.91 (2H, dd, J = 9.3, 2.1 Hz), 6.30 (1H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.43, 139.65, 139.59, 129.79 (2C), 126.33 (2C), 124.70, 121.99 (2C), 113.75 (2C); GCMS (EI) *m/z* 214 (100%)

$[M]^+$, 184 (33), 168 (29), 167 (92), 166 (17), 77 (12); HRMS (ESI) *m/z* Calcd for $C_{12}H_9N_2O_2$ $[M - H]^+$: 213.0669; Found: 213.0669.

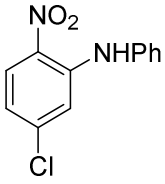
Synthesis of 2-nitro-*N*-phenylaniline (6).[2] Synthetized according to general procedure for **2** from *n*-BuLi solution (3.21 mmol), aniline (3.21 mmol), and 1,2-dinitrobenzene (0.803 mmol) providing after flash chromatography **6** as an orange solid (154 mg, 90% yield); R_f 0.57 (PE-acetone, 95:5); m.p. 78-79°C; IR (film) ν_{max} (cm^{-1}) 3351, 1618, 1596, 1500, 1459, 1348, 1039, 1028, 779, 753, 739, 691; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.49 (1H, br s), 8.20 (1H, dd, J = 8.6, 1.6 Hz), 7.45-7.38 (2H, m), 7.36 (1H, dt, J = 8.6, 1.6 Hz), 7.30-7.26 (2H, m), 7.25-7.20 (2H, m), 6.77 (1H, dt, J = 6.9, 1.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.12, 138.76, 135.74, 133.26, 129.79 (2C), 126.71, 125.71, 124.41 (2C), 117.17, 116.10; GCMS (EI) *m/z* 214 (100%) $[M]^+$, 197 (12), 181 (13), 180 (32), 169 (29), 168 (27), 167 (93), 166 (26), 140 (10), 139 (14), 77 (18), 51 (16); HRMS (ESI) *m/z* Calcd for $C_{12}H_{10}N_2O_2$ $[M + Na]^+$: 237.0634; Found: 237.0635.



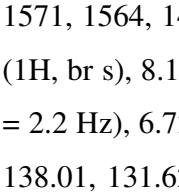
Synthesis of 5-fluoro-2-nitro-*N*-phenylaniline (7).[3] Synthetized according to general procedure for **2** from *n*-BuLi solution (3.21 mmol), aniline (3.21 mmol), and 1-fluoro-4-nitrobenzene (0.803 mmol) providing after flash chromatography **7** as a yellow solid (114 mg, 61% yield) or from 1,3-difluoro-4-nitrobenzene (0.803 mmol) in 59% yield; R_f 0.57 (PE-acetone, 95:5); m.p. 98–99°C; IR (film) ν_{max} (cm^{-1}) 3328, 1626, 1591, 1506, 1464, 1417, 1342, 775, 735, 698; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.64 (1H, br s), 8.27 (1H, dd, J = 9.5, 6.1 Hz), 7.48-7.42 (2H, m), 7.32-7.27 (3H, m), 6.80 (1H, dd, J = 11.4, 2.6 Hz), 6.47 (1H, dt, J = 9.5, 2.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.40 (d, J = 256.3 Hz), 145.75 (d, J = 13.2 Hz), 138.07, 130.09 (2C), 130.00, 129.88, 126.62, 125.06 (2C), 106.09 (d, J = 24.8 Hz), 101.50 (d, J = 27.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -99.94 (m); GCMS (EI) *m/z* 232 (100%) $[M]^+$, 215 (12), 199 (15), 198 (41), 187 (32), 186 (24), 185 (79), 184 (23), 157 (10), 77 (15), 51 (13); HRMS (ESI) *m/z* Calcd for $C_{12}H_9FN_2O_2$ $[M + Na]^+$: 255.0540; Found: 255.0541.



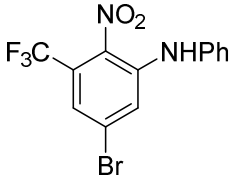
Synthesis of 5-chloro-2-nitro-*N*-phenylaniline (8).[4] Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), and 1-chloro-4-nitrobenzene (1 mmol) at -78°C providing after flash chromatography **8** as a orange solid (122 mg, 49% yield); R_f 0.42 (hexane-CH_2Cl_2, 90:10); m.p. 186–187°C; IR (film) ν_{max} (cm^{-1}) 3331, 1612, 1595, 1571, 1564, 1495, 1484, 1338, 1246, 936, 747, 710; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.55 (1H, br s), 8.16 (1H, d, J = 9.1 Hz), 7.48-7.44 (2H, m), 7.32-7.27 (3H, m), 7.15 (1H, d, J = 2.2 Hz), 6.72 (1H, dd, J = 9.1, 2.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.09, 142.65, 138.01, 131.62, 130.14 (2C), 128.26, 126.61, 125.04 (2C), 118.04, 115.33; GCMS (EI) *m/z* 250 (33%) $[M]^+$, 248 (100) $[M]^+$, 214 (51), 203 (35), 201 (35), 167 (57), 166 (45), 139 (19), 77 (31); HRMS (ESI) *m/z* Calcd for $C_{12}H_9ClN_2O_2$ $[M]^+$: 248.0353; Found: 248.0348.



Synthesis of 5-bromo-2-nitro-*N*-phenylaniline (9).[5] Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), and 1-bromo-4-nitrobenzene (1 mmol) at -78°C providing after flash chromatography **9** as a orange solid (123 mg, 42% yield); R_f 0.44 (hexane-CH_2Cl_2, 90:10); m.p. 202–203°C; IR (film) ν_{max} (cm^{-1}) 3352, 1610, 1594, 1566, 1498, 1484, 1335, 1251, 1066, 918, 795; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.52 (1H, br s), 8.07 (1H, d, J = 9.1 Hz), 7.50-7.42 (2H, m), 7.33 (1H, d, J = 2.1 Hz), 7.32-7.27 (3H, m), 6.87 (1H, dd, J = 9.1, 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.97, 137.97, 132.02, 131.39, 130.13 (2C), 128.11, 126.58, 124.97 (2C), 120.87, 118.44; GCMS (EI) *m/z* 294 (91%) $[M]^+$, 292 (93) $[M]^+$, 260 (43), 258 (41), 247 (39), 167 (100), 166 (59), 139 (39), 77 (59), 51 (44); HRMS (ESI⁻) *m/z* Calcd for $C_{12}H_9BrN_2O_2$ $[M - H]^-$: 290.9775; Found: 290.9775.

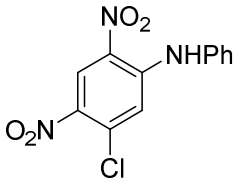


Synthesis of 5-bromo-2-nitro-*N*-phenyl-3-(trifluoromethyl)aniline (12). Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), and 4-bromo-1-nitro-2-(trifluoromethyl)benzene (1 mmol) providing after flash chromatography **12** as a yellow solid (169 mg, 47% yield); R_f 0.55 (hexane-CH_2Cl_2-EtOAc, 75:20:5); m.p.

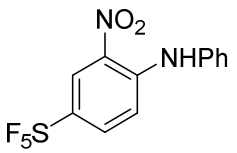


209-210°C; IR (film) ν_{max} (cm^{-1}) 3399, 1592, 1544, 1502, 1435, 1326, 1297, 1180, 1169, 1159, 961, 857, 706, 659; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.52 (1H, d, J = 1.9 Hz), 7.49 (1H, br s), 7.43 (2H, t, J = 7.6 Hz), 7.29 (1H, d, J = 1.6 Hz), 7.25 (1H, t, J = 7.5 Hz), 7.18 (2H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.24, 138.25, 133.98, 130.27 (2C), 127.08(q, J = 33.8 Hz), 127.02, 126.02 , 123.32 (2C), 123.02, 121.60 (q, J = 274.4 Hz), 120.80 (q, J = 5.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -59.83 (s); GCMS (EI) *m/z* 362 (99%) $[M]^+$, 360 (99) $[M]^+$, 235 (100), 199 (15), 198 (41), 187 (32), 186 (24), 185 (79), 184 (23), 157 (10), 77 (15), 51 (13); HRMS (EI) *m/z* Calcd for $C_{13}H_8BrF_3N_2O_2$ $[M]^+$: 359.9721; Found: 359.9728.

Synthesis of 5-chloro-2,4-dinitro-*N*-phenylaniline (13).[6] Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), and 1-chloro-2,4-dinitrobenzene (1 mmol) at -78°C providing after flash chromatography **13** as a orange solid (149 mg, 51% yield); R_f 0.37 (hexane-CH_2Cl_2-EtOAc, 75:20:5); m.p. 132-133°C; IR (film) ν_{max} (cm^{-1}) 3342, 1618, 1593, 1576, 1496, 1350, 1332, 1285, 1141, 987; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.84 (1H, br s), 9.07 (1H, s), 7.53 (2H, t, J = 7.8 Hz), 7.41 (1H, t, J = 7.5 Hz), 7.31 (2H, d, J = 7.5 Hz), 7. 17 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.73, 136.38 (2C), 135.81(2C), 130.58 (2C), 128.22, 126.82, 125.67 (2C), 118.05; GCMS (EI) *m/z* 295 (35%) $[M]^+$, 293 (100) $[M]^+$, 230 (20), 202 (21), 201 (21), 166 (40), 139 (21), 77 (20), 51 (11); HRMS (EI) *m/z* Calcd for $C_{13}H_8ClN_3O_4$ $[M]^+$: 293.0203; Found: 293.0201.

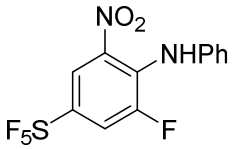


Synthesis of 2-nitro-4-(pentafluorosulfanyl)-*N*-phenylaniline (14). Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), 1-nitro-3-(pentafluorosulfanyl)benzene (1 mmol) providing after flash chromatography **14** as a orange solid (241 mg, 71% yield); R_f 0.50 (hexane-CH_2Cl_2-EtOAc, 75:20:5); m.p. 217-218°C; IR (film) ν_{max} (cm^{-1}) 3353, 2927, 1622, 1596, 1573, 1508, 1357, 1272, 914,857, 837, 597; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.72 (1H, br s), 8.66 (1H, d, J = 2.6 Hz), 7.66 (1H, dd, J = 9.5, 2.7 Hz), 7.48 (2H, m), 7.34 (1H, tt, J = 8.4, 6.8 Hz), 7.29 (2H, m), 7.15 (1H, d, J = 9.6 Hz);



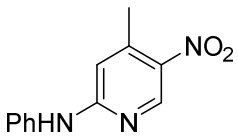
^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.98, 142.45 (quint, J = 19.9 Hz), 137.32, 132.53 (quint, J = 4.5 Hz), 130.92, 130.24 (2C), 127.32, 125.62 (quint, J = 5.0 Hz), 125.45 (2C), 115.87; ^{19}F NMR ($CDCl_3$, 376 MHz) δ 83.66 (1F, m), 63.45 (4F, d, J = 151.1 Hz); GCMS (EI) *m/z* 340 (100%) $[M]^+$, 323 (13), 306 (12), 293 (17), 185 (21), 167 (43), 139 (16), 77 (16); HRMS (EI) *m/z* Calcd for $C_{12}H_9F_5N_2O_2S$ $[M]^+$: 340.0305; Found: 340.0306.

Synthesis of 2-fluoro-6-nitro-4-(pentafluorosulfanyl)-*N*-phenylaniline (15).



Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), 1-fluoro-3-nitro-5-(pentafluorosulfanyl)benzene (1 mmol) providing after flash chromatography **15** as a orange solid (250 mg, 70% yield); R_f 0.48 (hexane-CH_2Cl_2-EtOAc, 75:20:5); m.p. 163-164°C; IR (film) ν_{max} (cm^{-1}) 3413, 1598, 1513, 1500, 1261, 1106, 923, 858, 842, 602; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.28 (1H, br s), 8.49 (1H, t, J = 2.2 Hz), 7.64 (1H, dd, J = 12.2, 2.6 Hz), 7.37 (2H, t, J = 7.9 Hz), 7.23 (1H, t, J = 7.5 Hz), 7.12 (2H, dd, J = 6.9, 2.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.39, 150.85, 141.92 (m), 139.41 (d, J = 3.3 Hz), 135.46, 133.95 (d, J = 11.7 Hz), 129.16 (2C), 125.84, 122.25 (2C), 120.96 (m), 119.74 (dt, J = 25.1, 4.5 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ 81.80 (1F, m), 63.45 (4F, d, J = 151.6 Hz), -110.58 (1F, d, J = 12.1 Hz); GCMS (EI) *m/z* 358 (100%) $[M]^+$, 313(25), 203(19), 185(41), 146(16), 77(8); HRMS (EI) *m/z* Calcd for $C_{12}H_8F_6N_2O_2S$ $[M]^+$: 358.0211; Found: 358.0209.

Synthesis of 4-methyl-5-nitro-*N*-phenylpyridin-2-amine (16).[7] Synthetized according to general procedure for **2** from *n*-BuLi solution (4 mmol), aniline (4 mmol), and 4-methyl-3-nitropyridine (1 mmol) at -78°C providing after flash chromatography **16** as a orange solid (158 mg, 69% yield)



R_f 0.24 (hexane-CH_2Cl_2-EtOAc, 20:75:5); m.p. 110-111°C; IR (film) ν_{max} (cm^{-1}) 3404, 1613, 1557, 1499, 1450, 1336, 1279, 697; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.92 (1H, s), 7.47-7.20 (1H, br s), 7.35 (2H, t, J = 7.3 Hz), 7.27 (2H, d, J = 7.3 Hz), 7.14 (1H, t, J = 7.2 Hz), 6.60 (1H, s), 2.52 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.86, 148.24, 146.09, 138.32, 129.82 (2C), 125.49, 122.68 (2C), 108.67, 21.81; GCMS (EI) *m/z* 229 (81%)

$[M]^+$, 228 (100), 182 (41), 156 (12), 128 (14) 77 (20); HRMS (EI) *m/z* Calcd for $C_{12}H_{11}N_3O_2$ $[M]^+$: 229.0851; Found: 229.0850.

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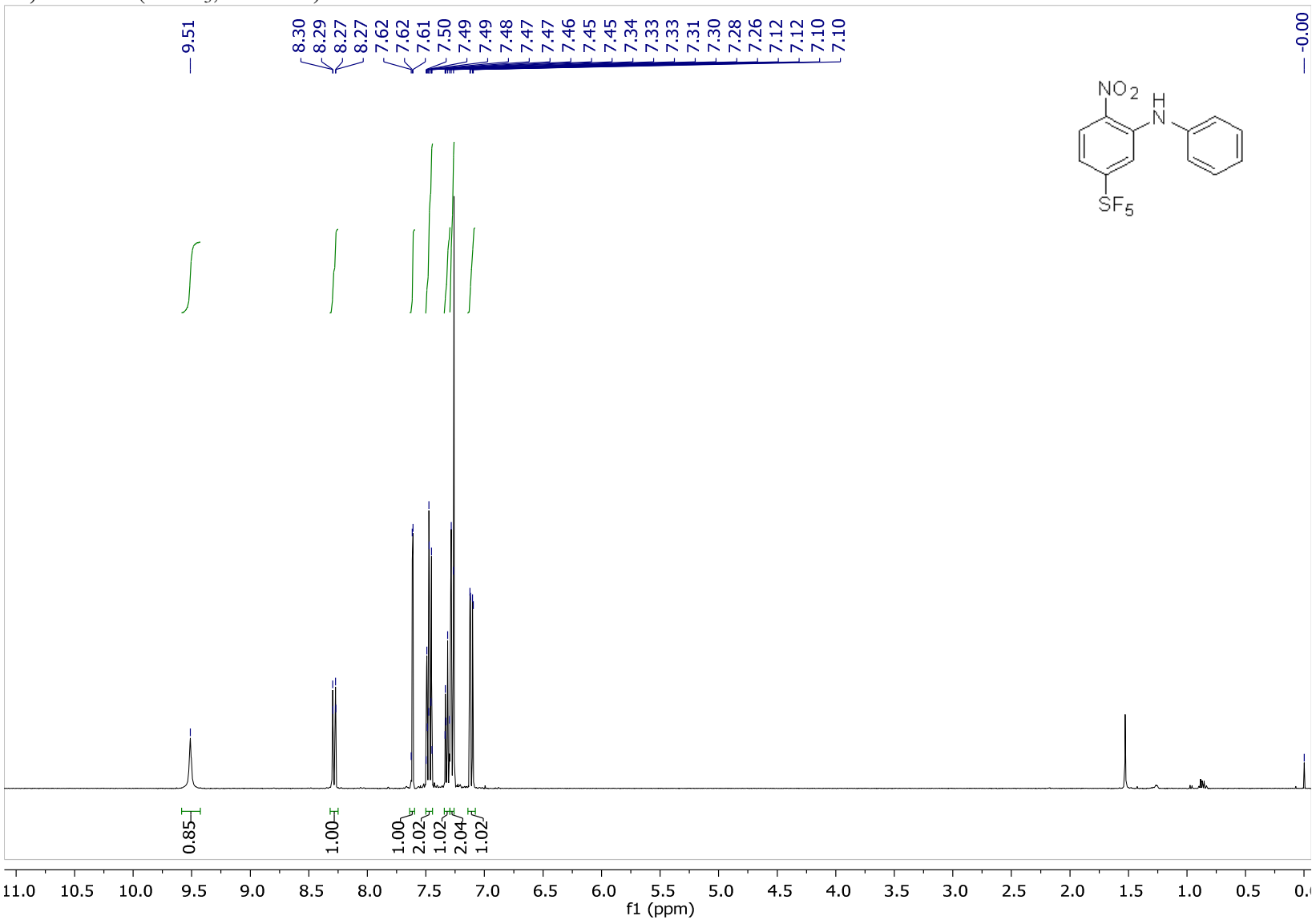
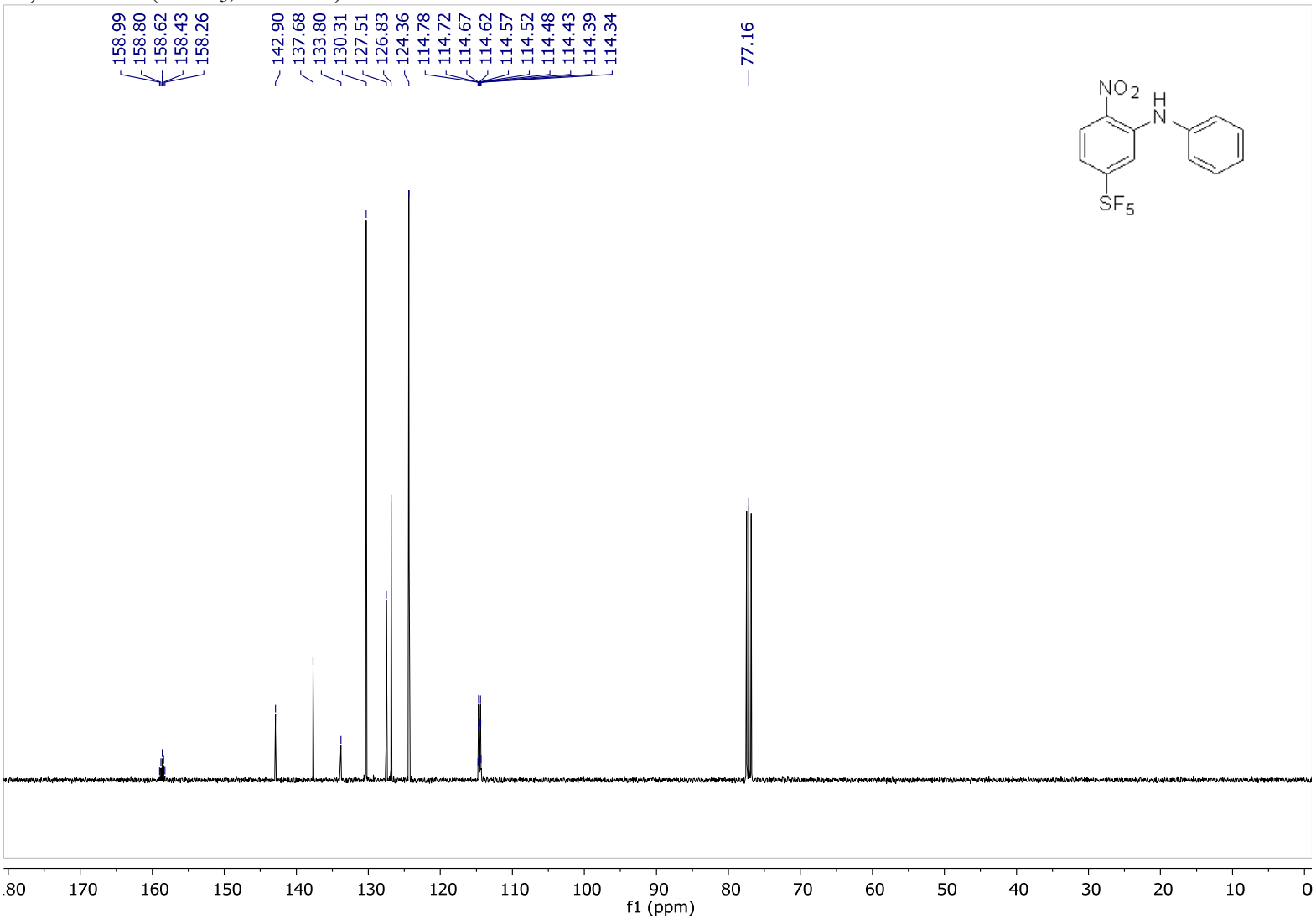
Copies of ^{1}H and ^{13}C NMR spectra

2a, ^{1}H NMR ($CDCl_3$, 400MHz)



2a, ^{13}C NMR ($CDCl_3$, 100MHz)



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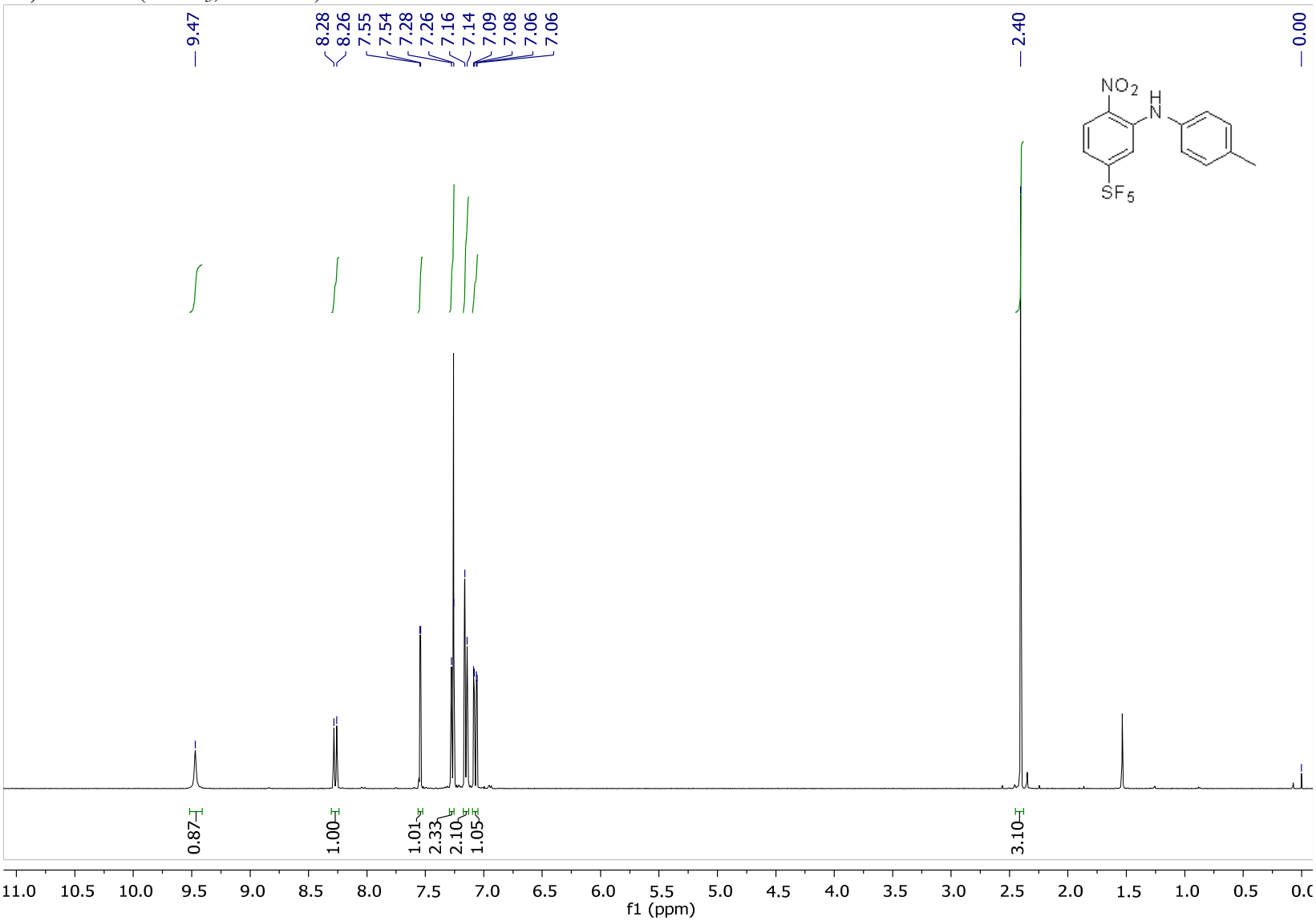

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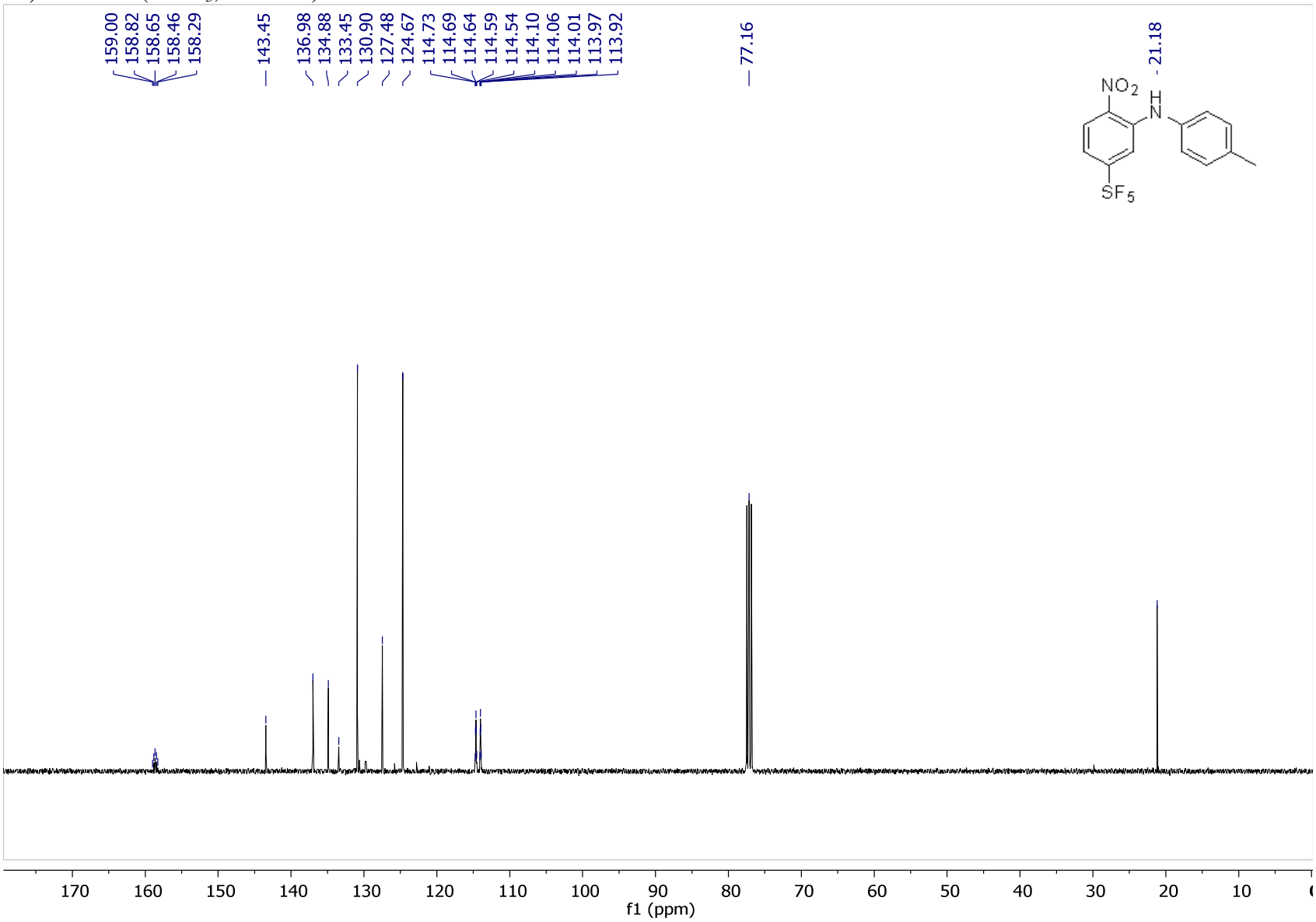

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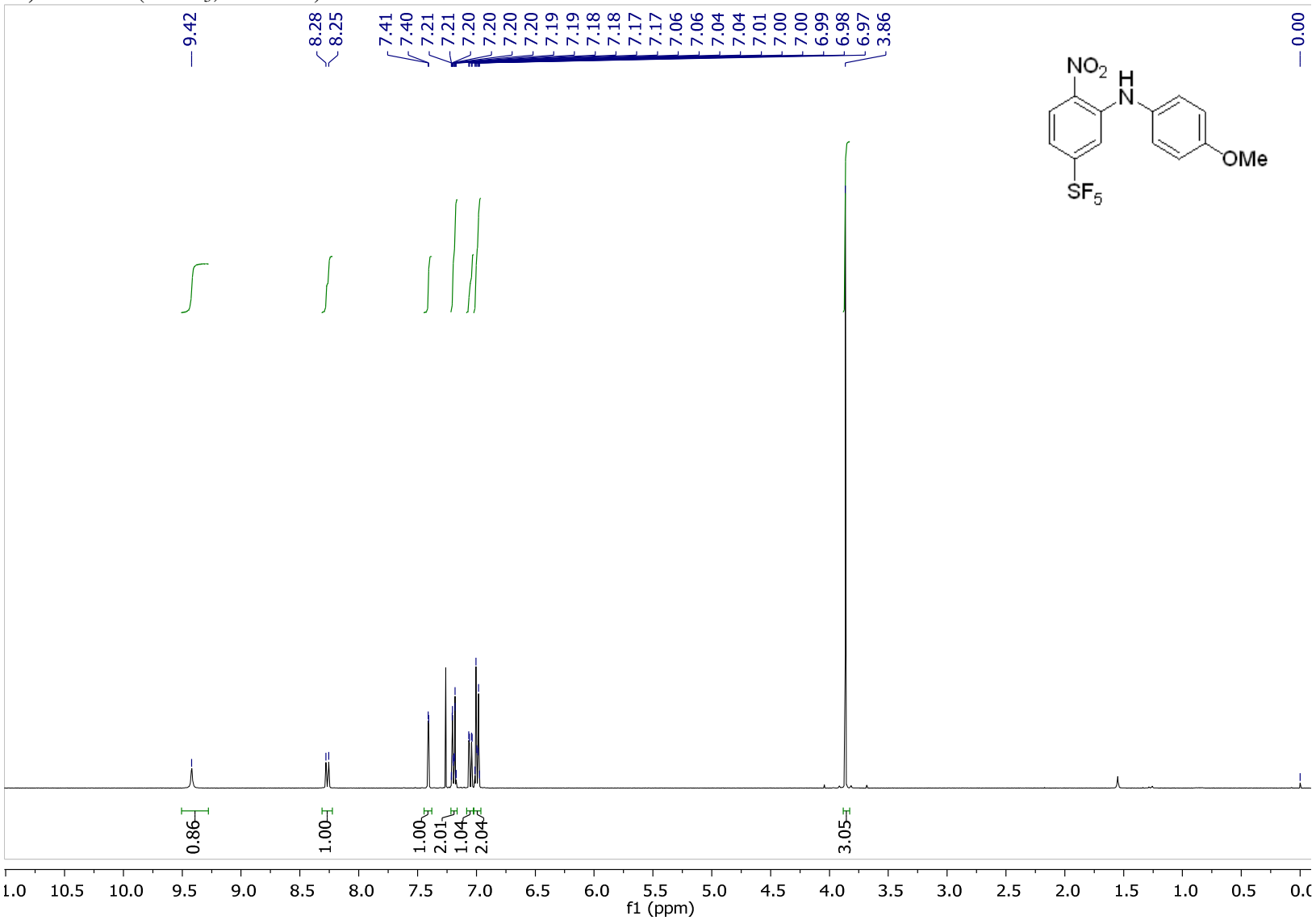

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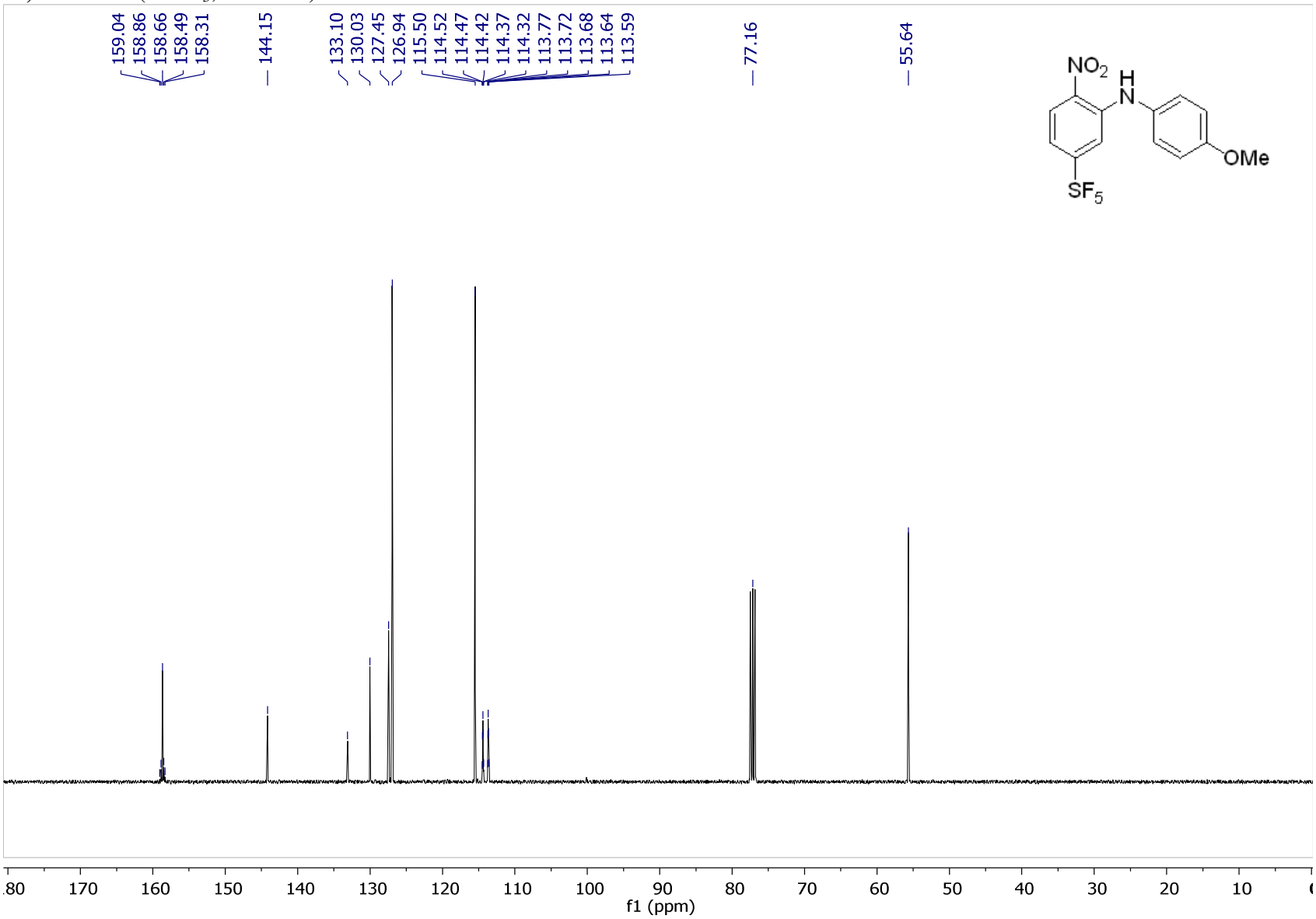

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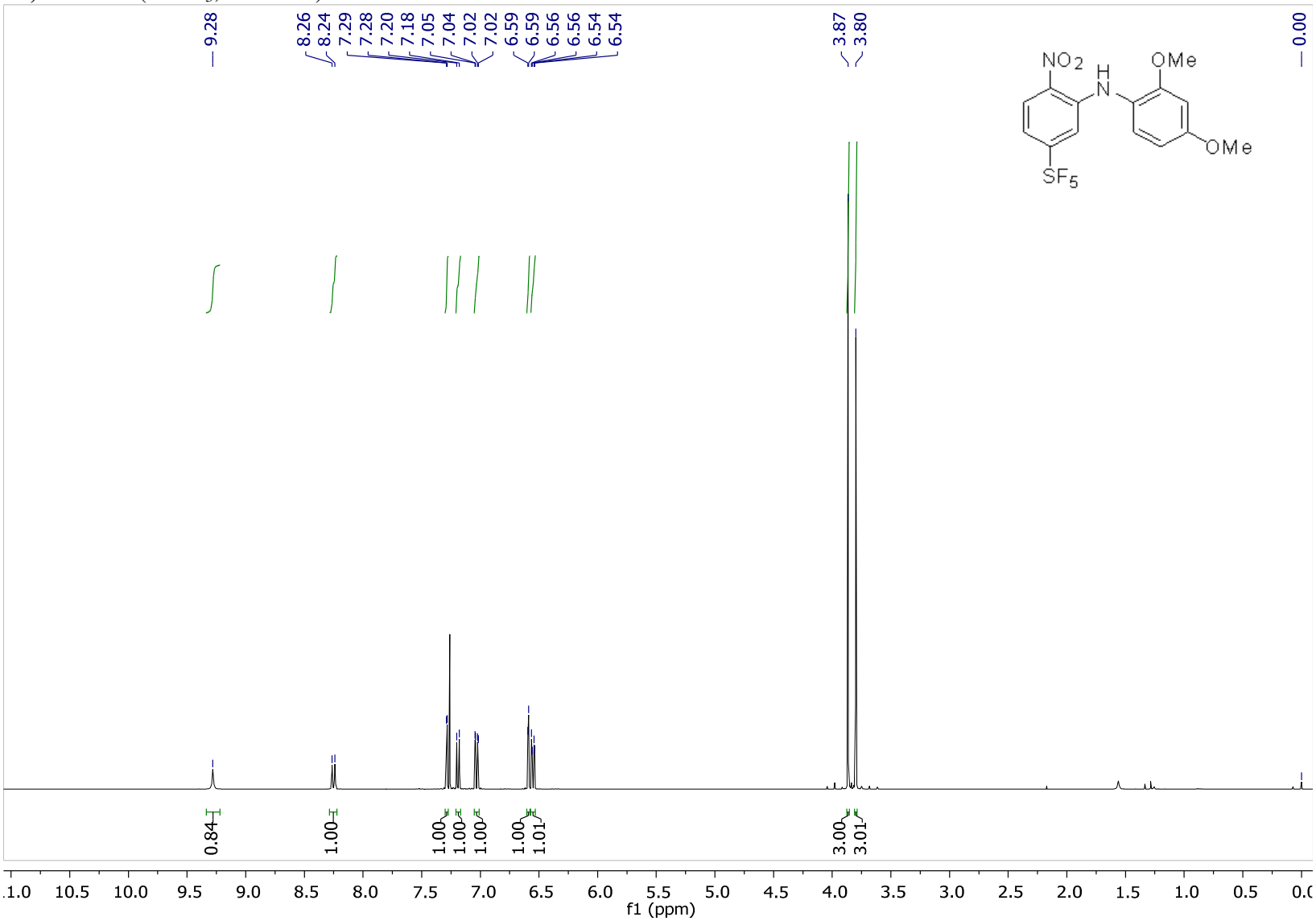

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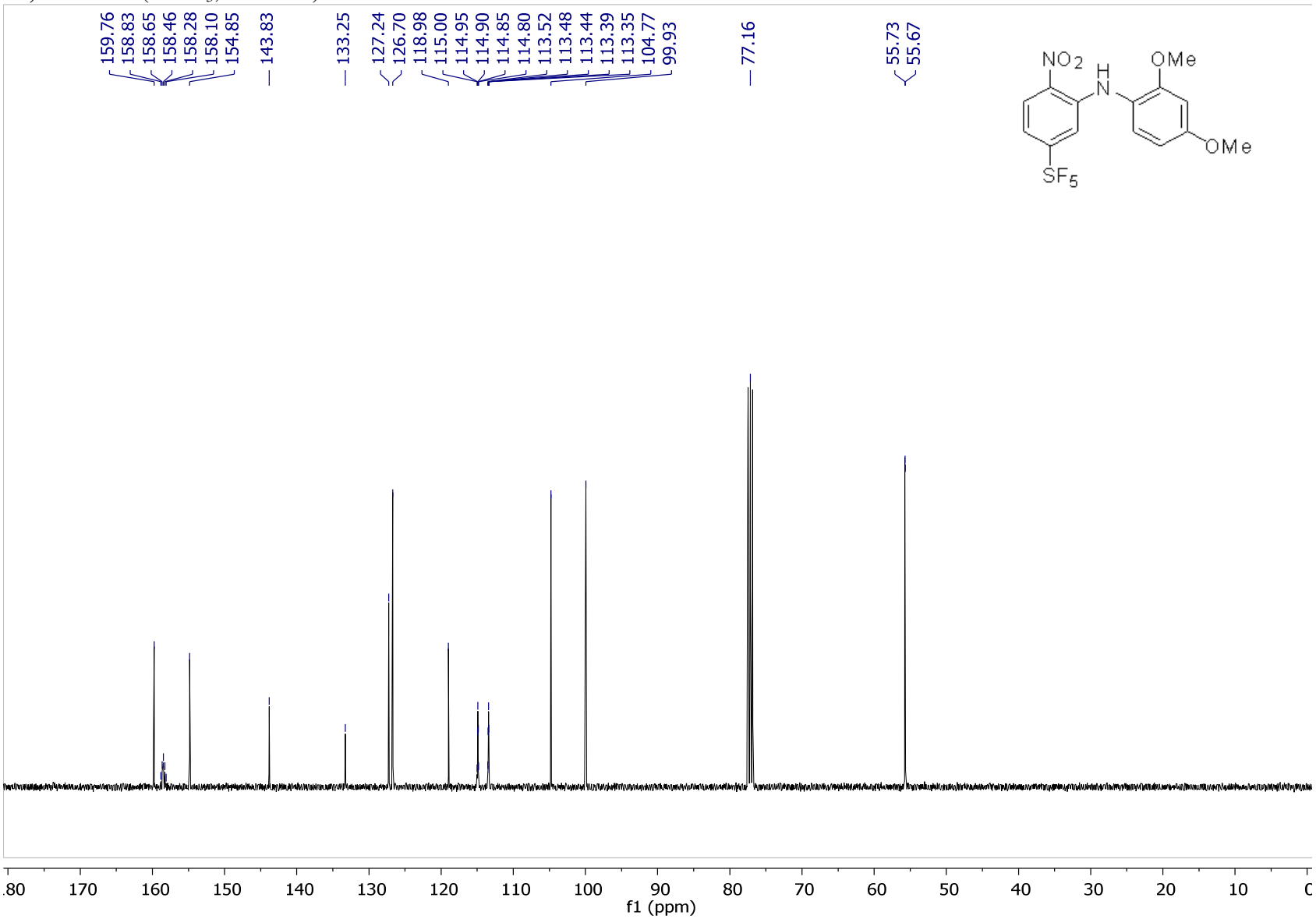

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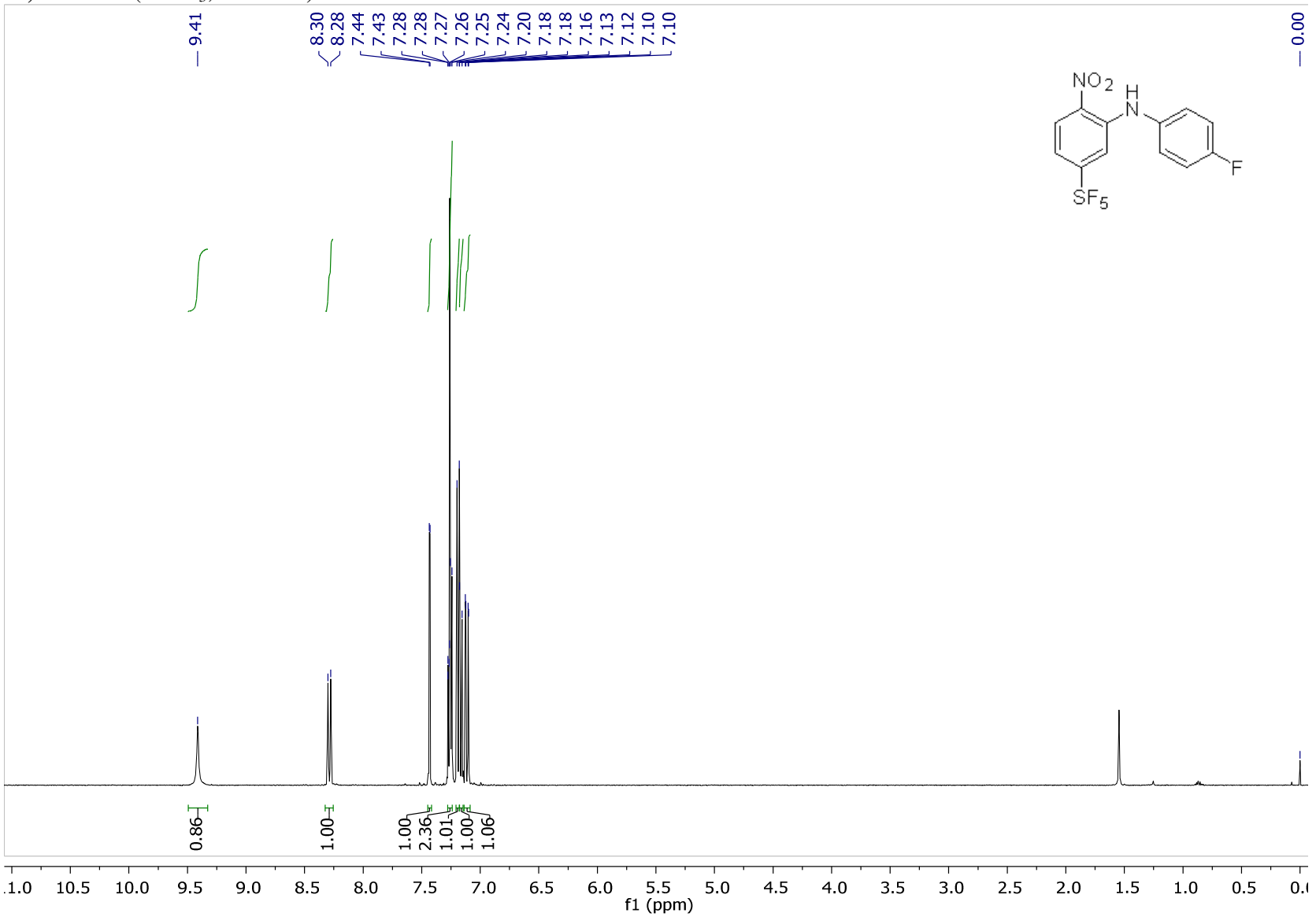

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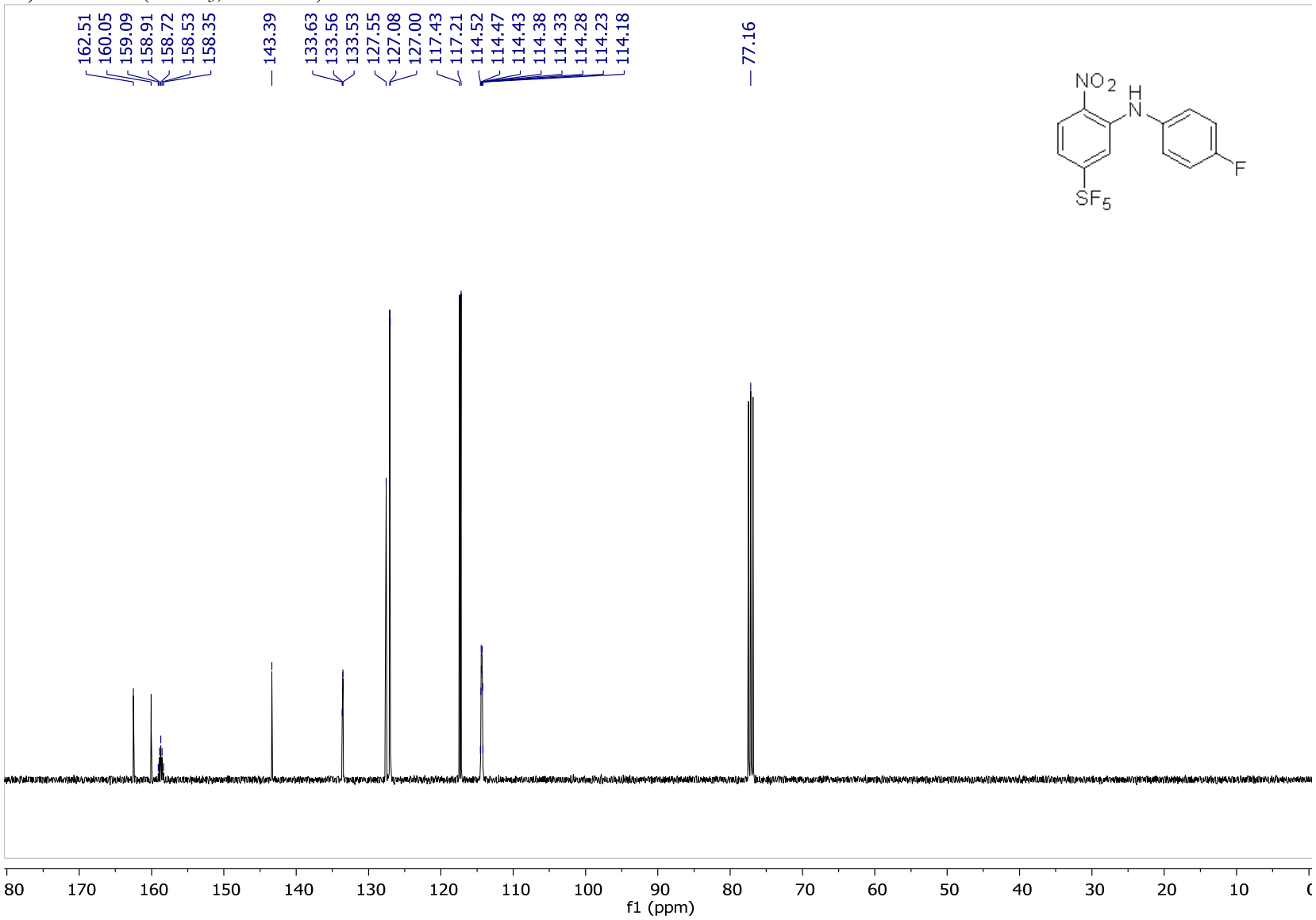

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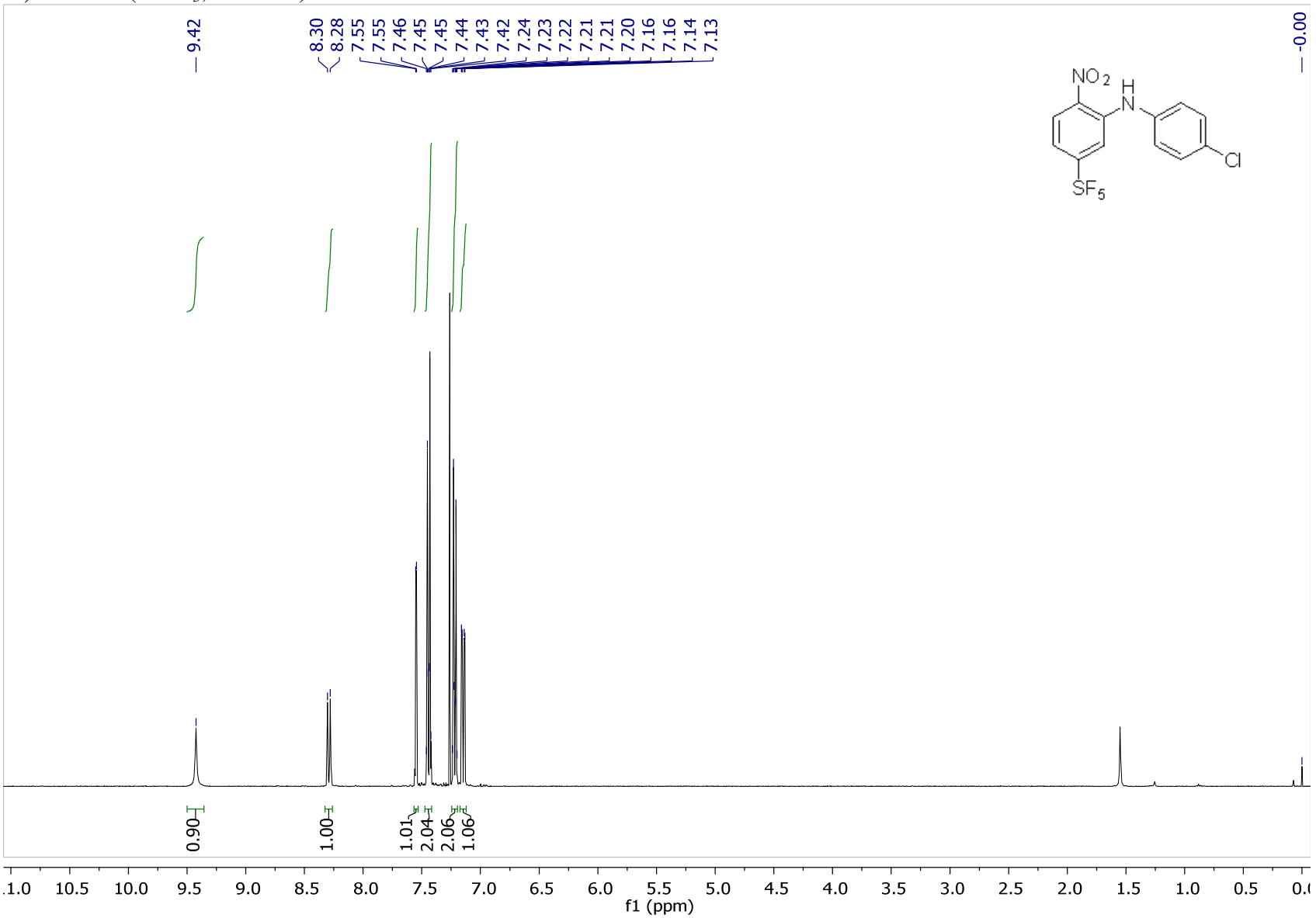

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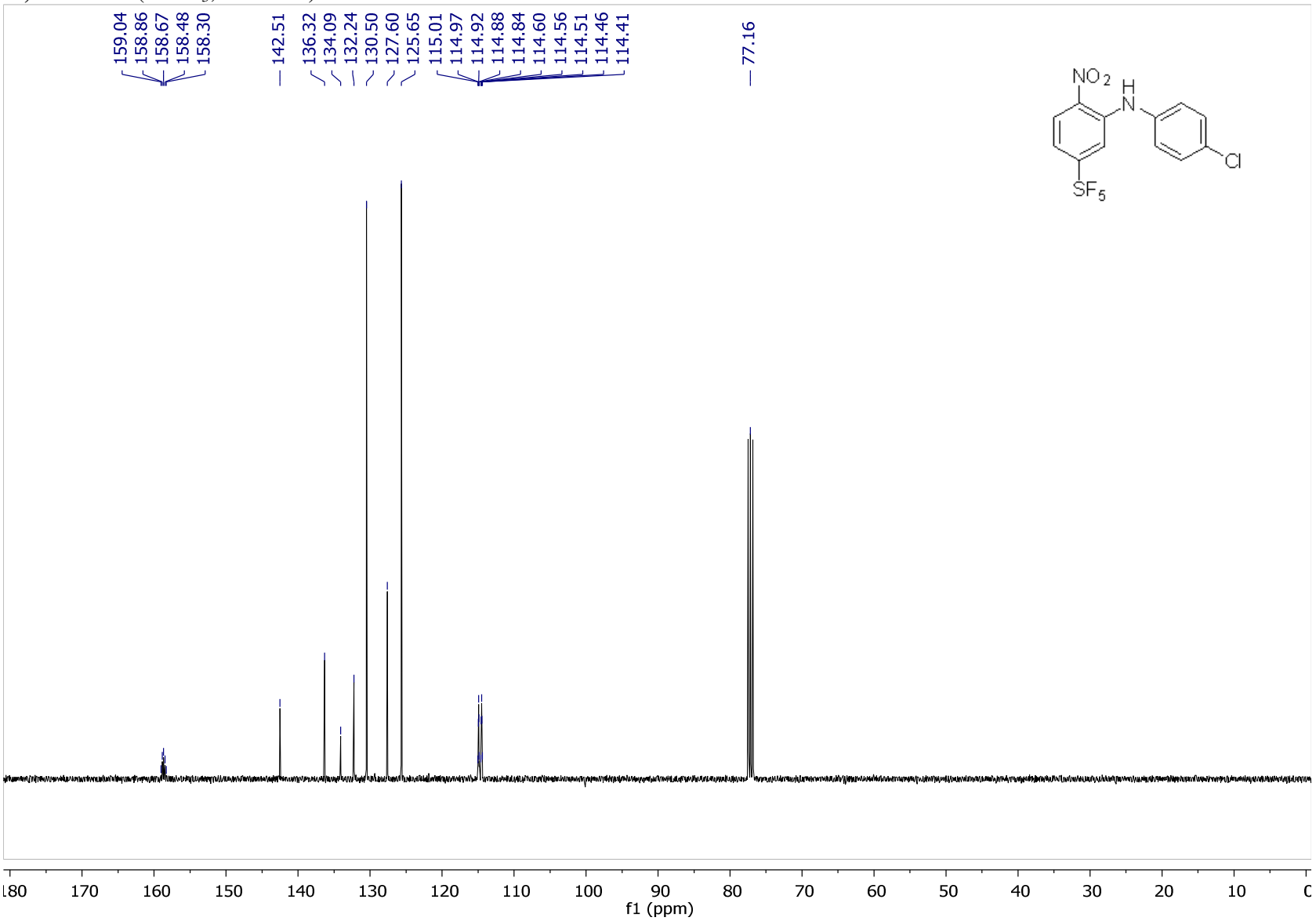

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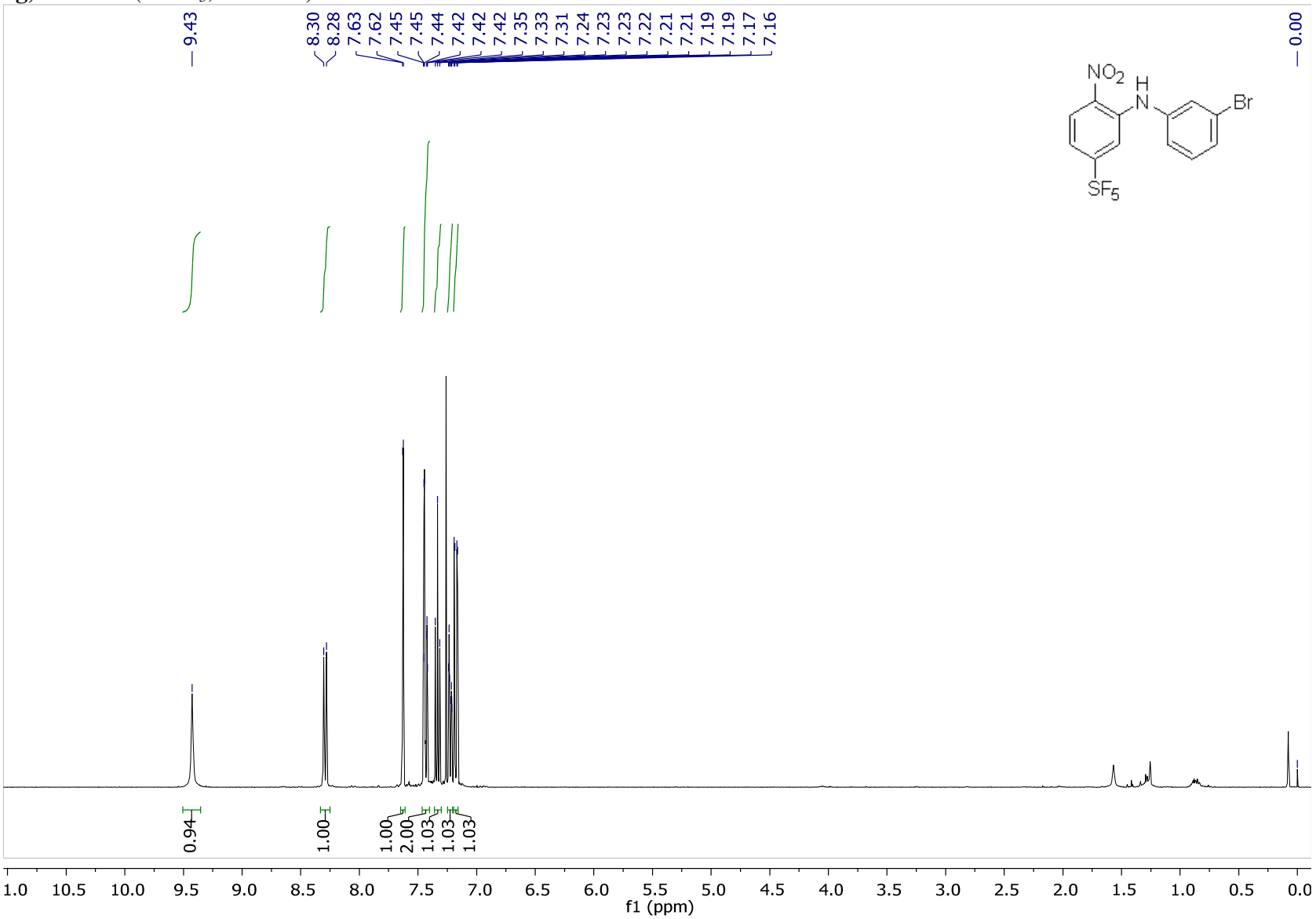

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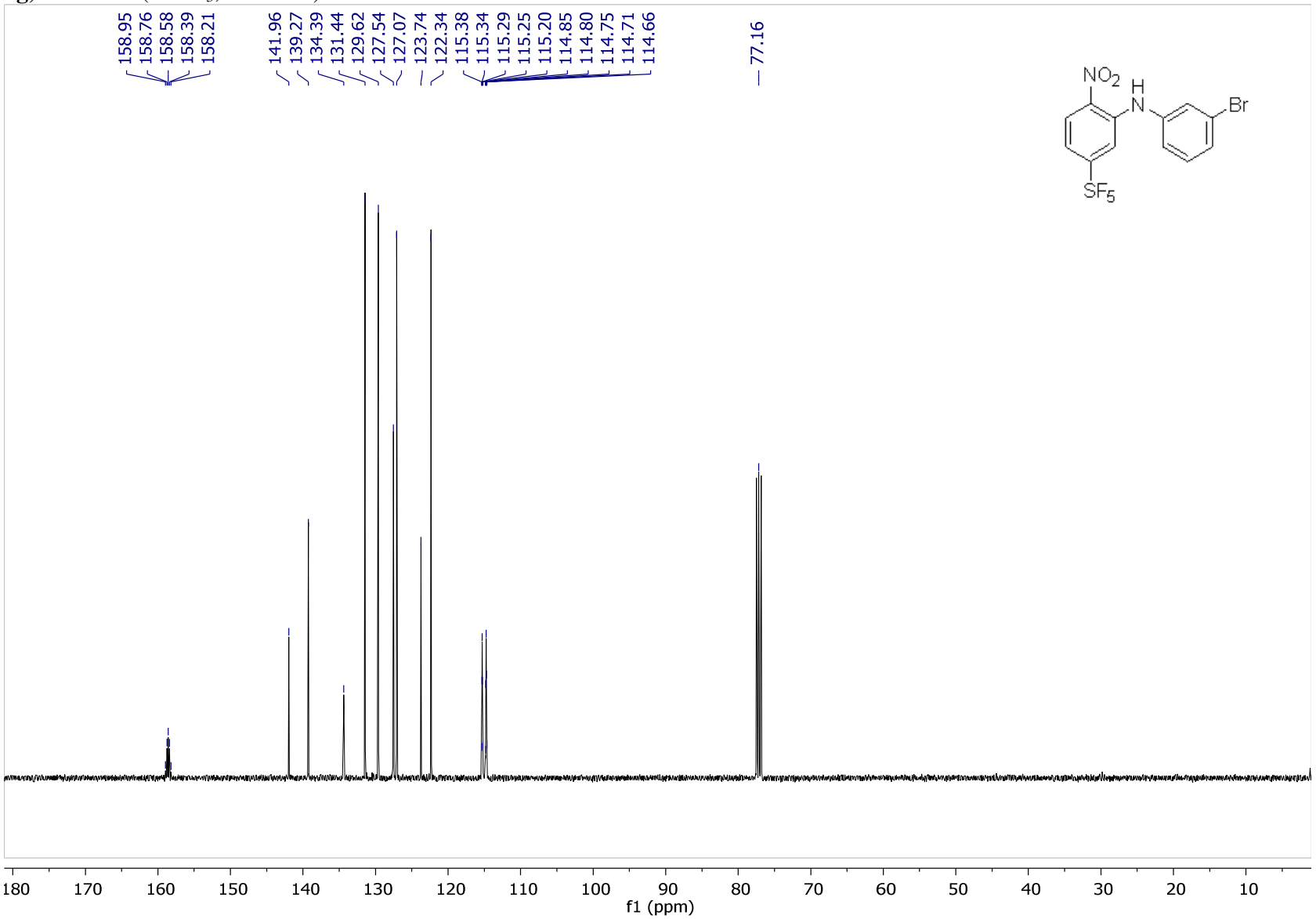

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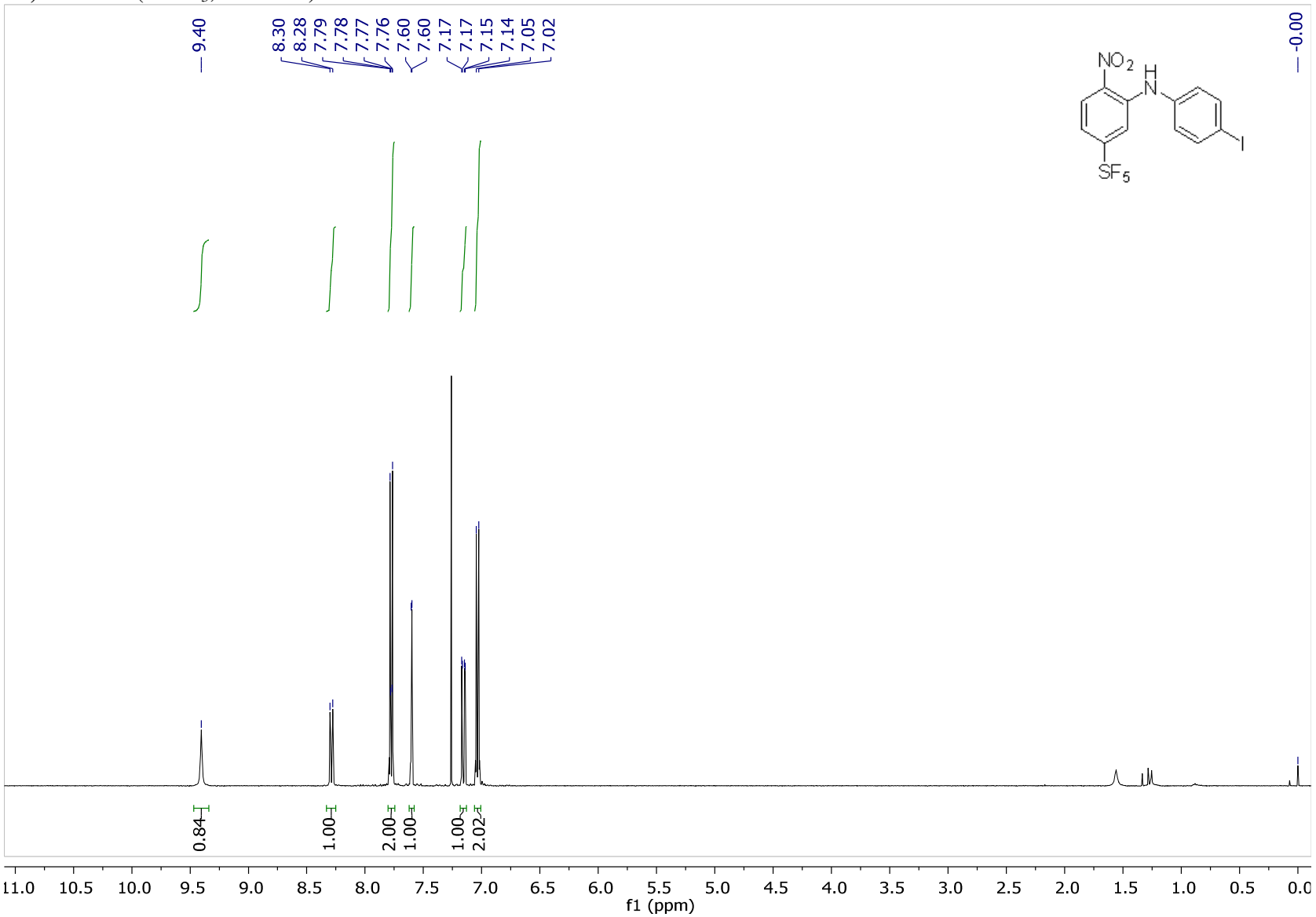

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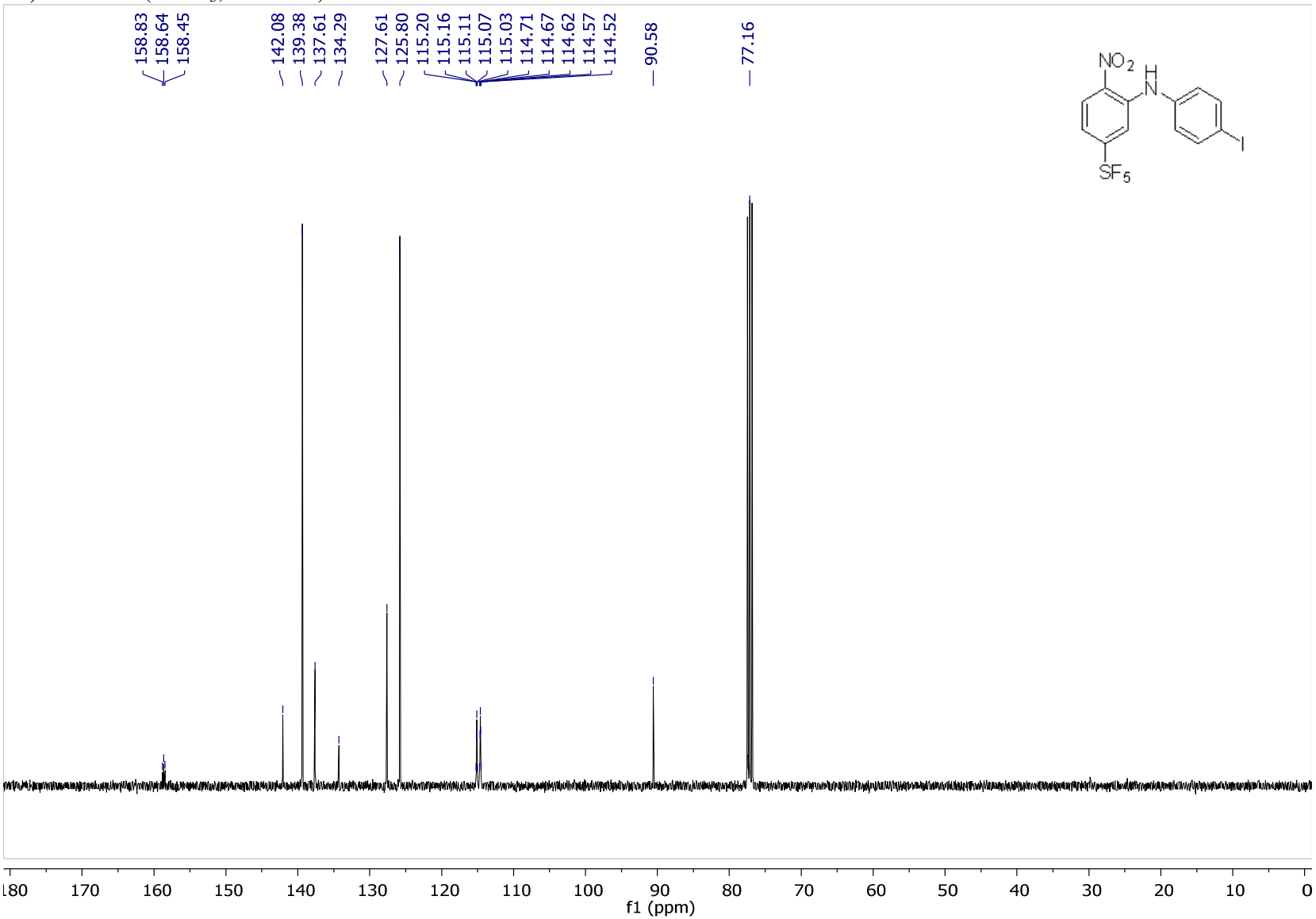

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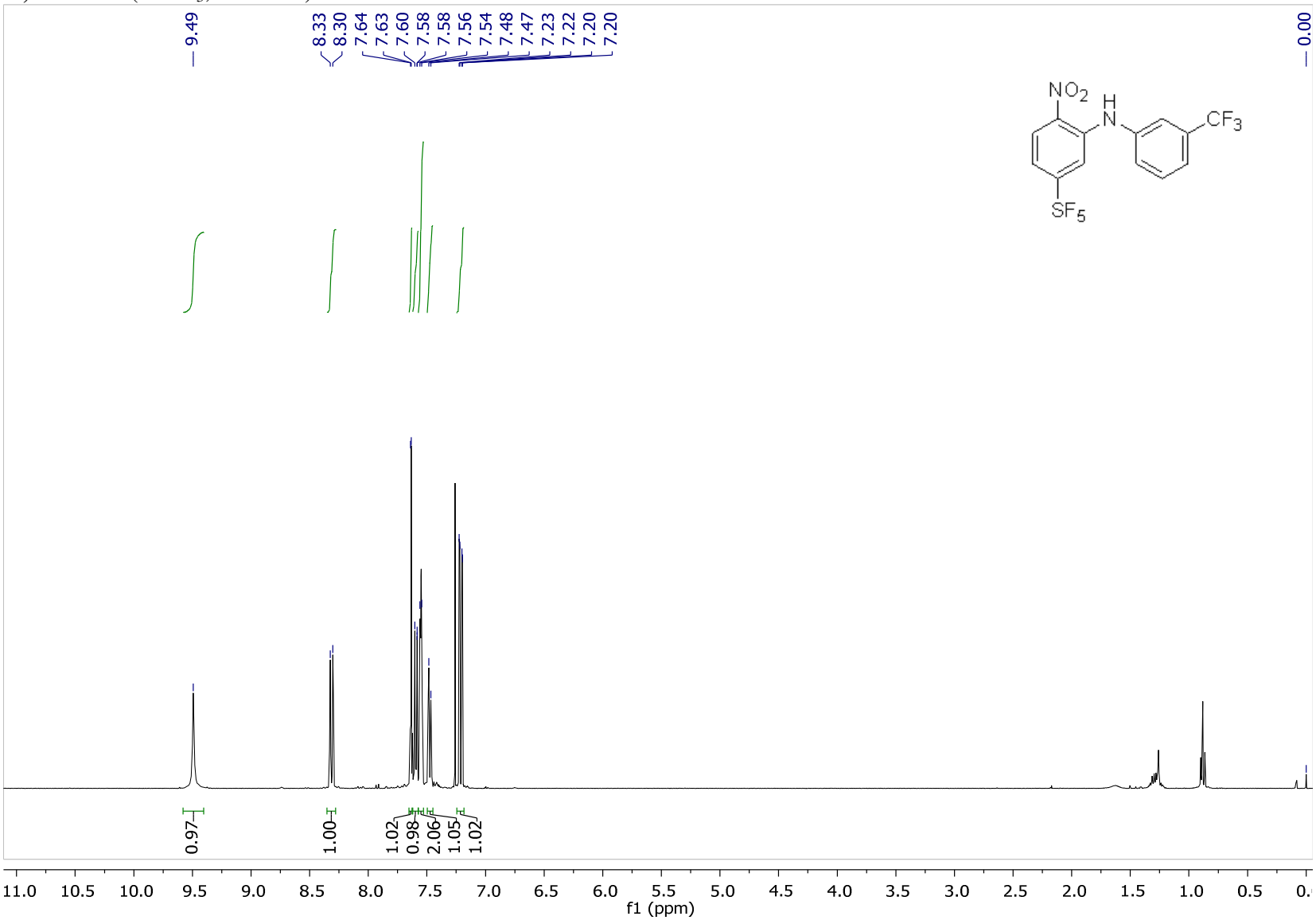

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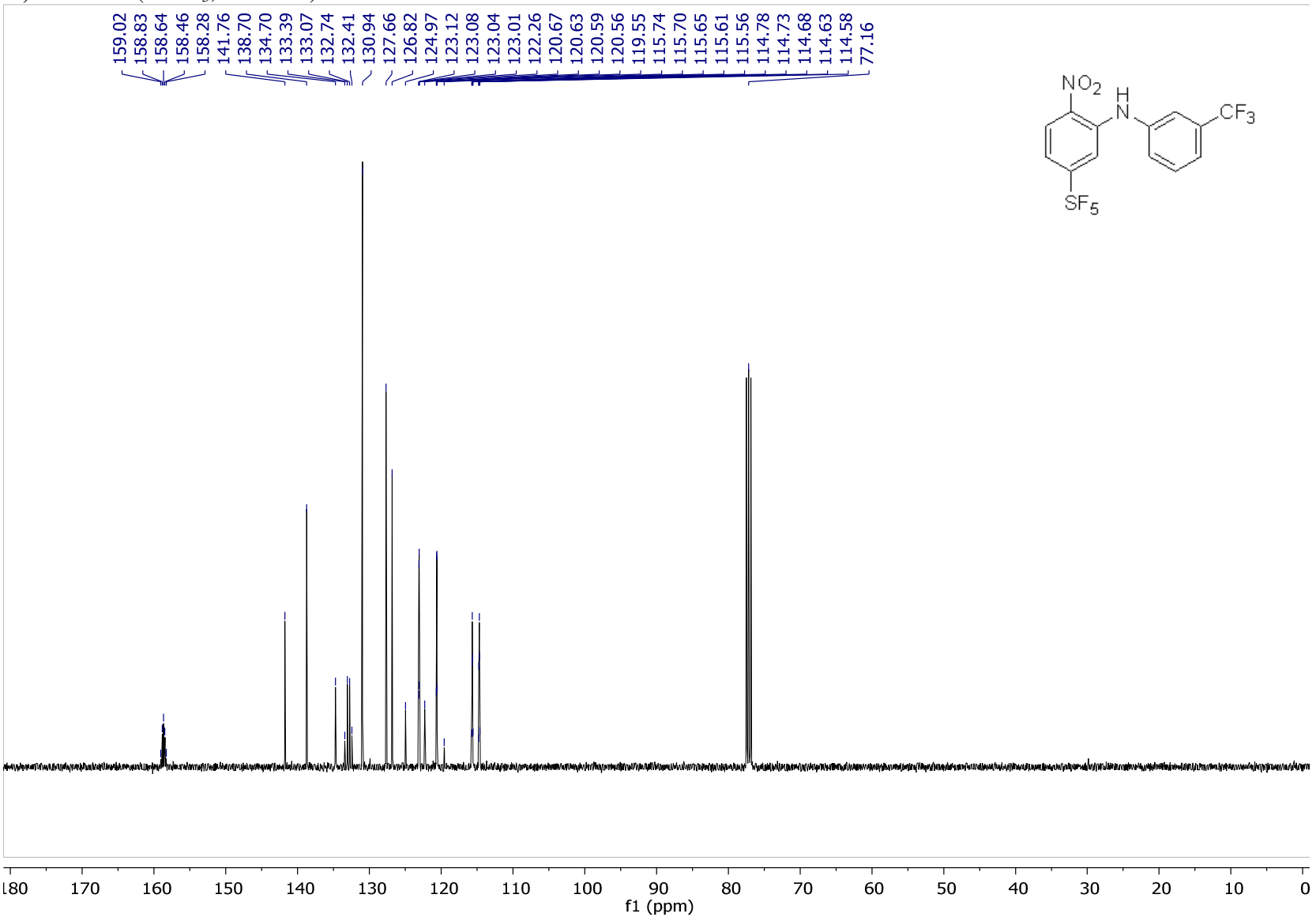

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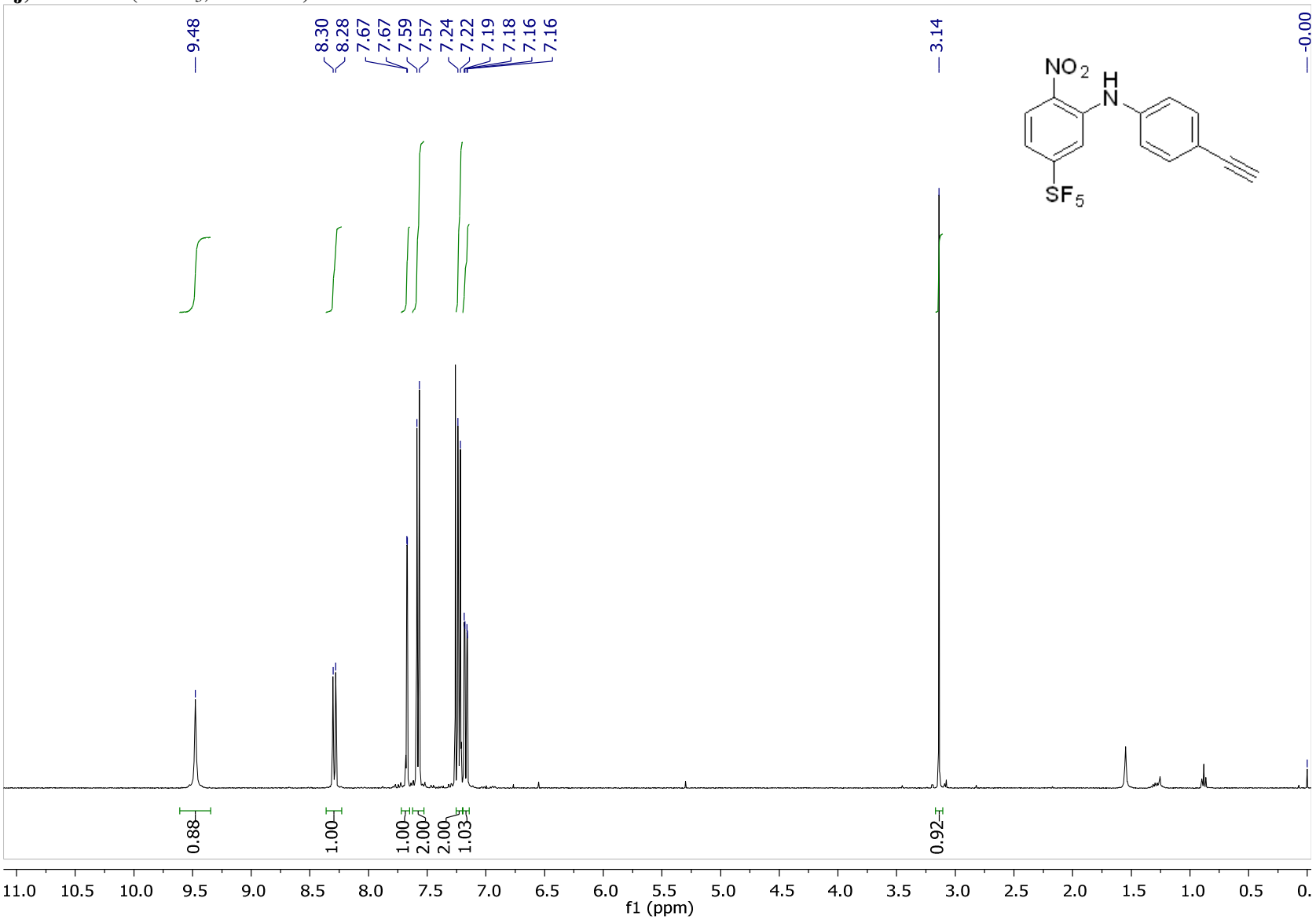

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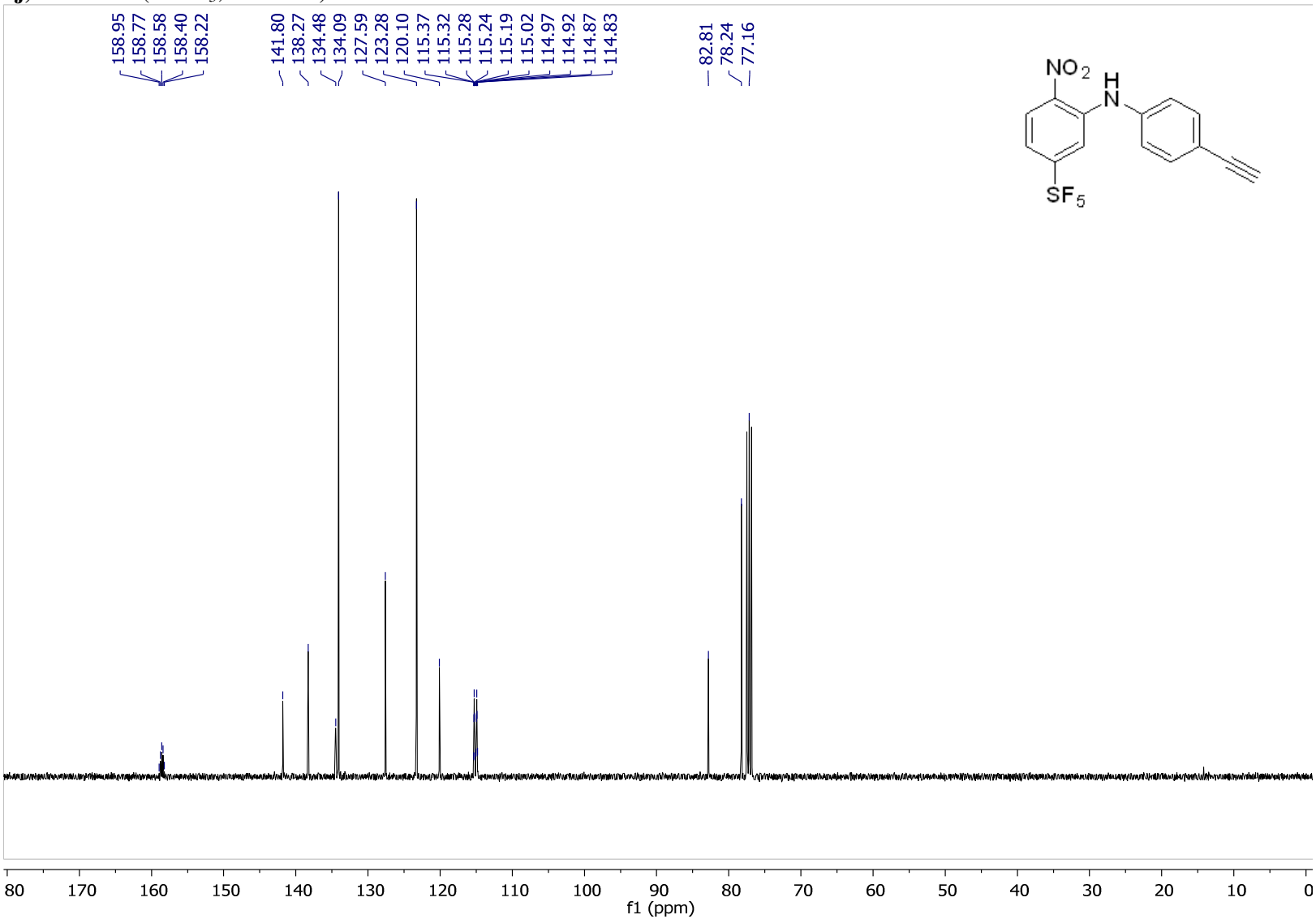

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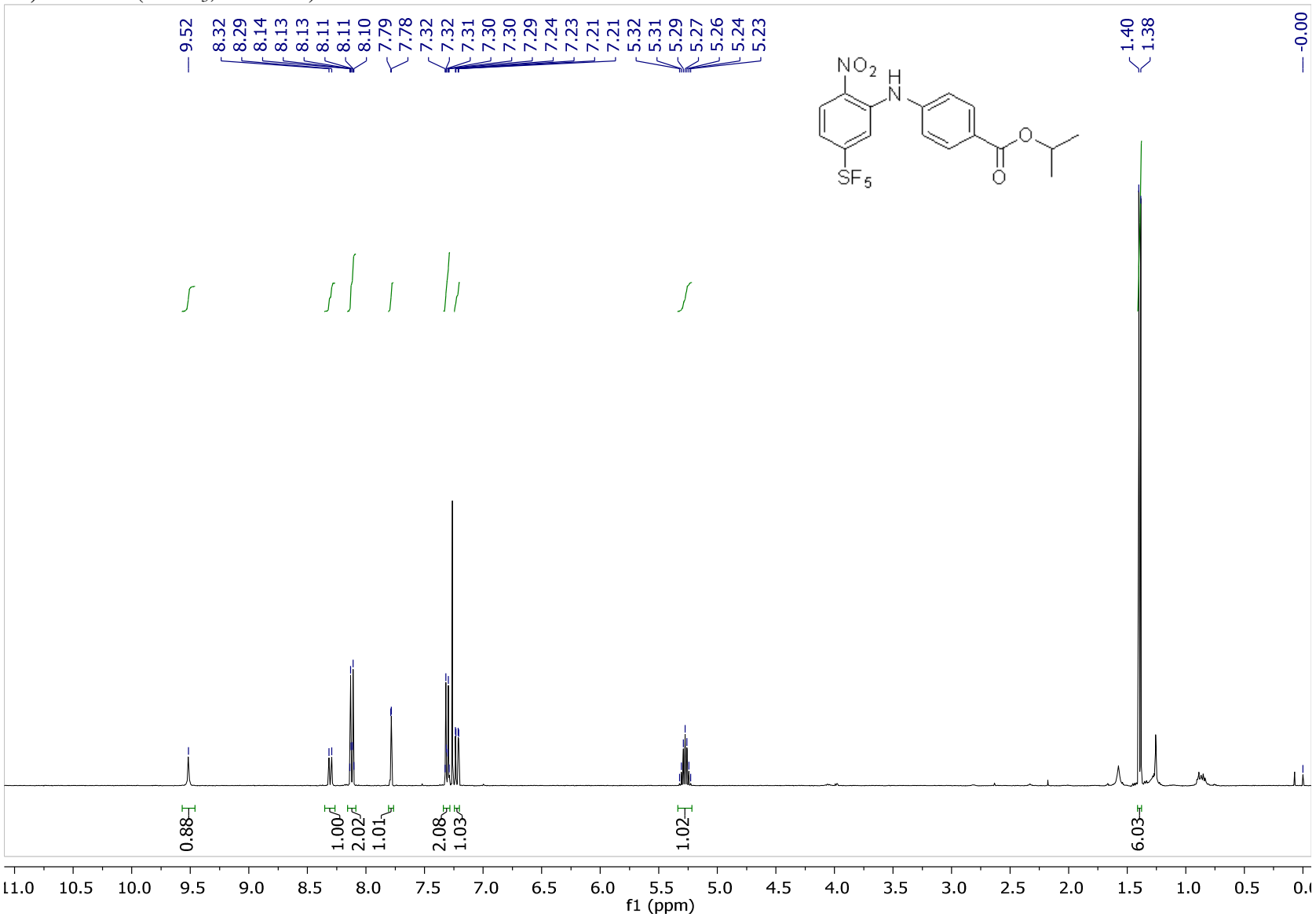

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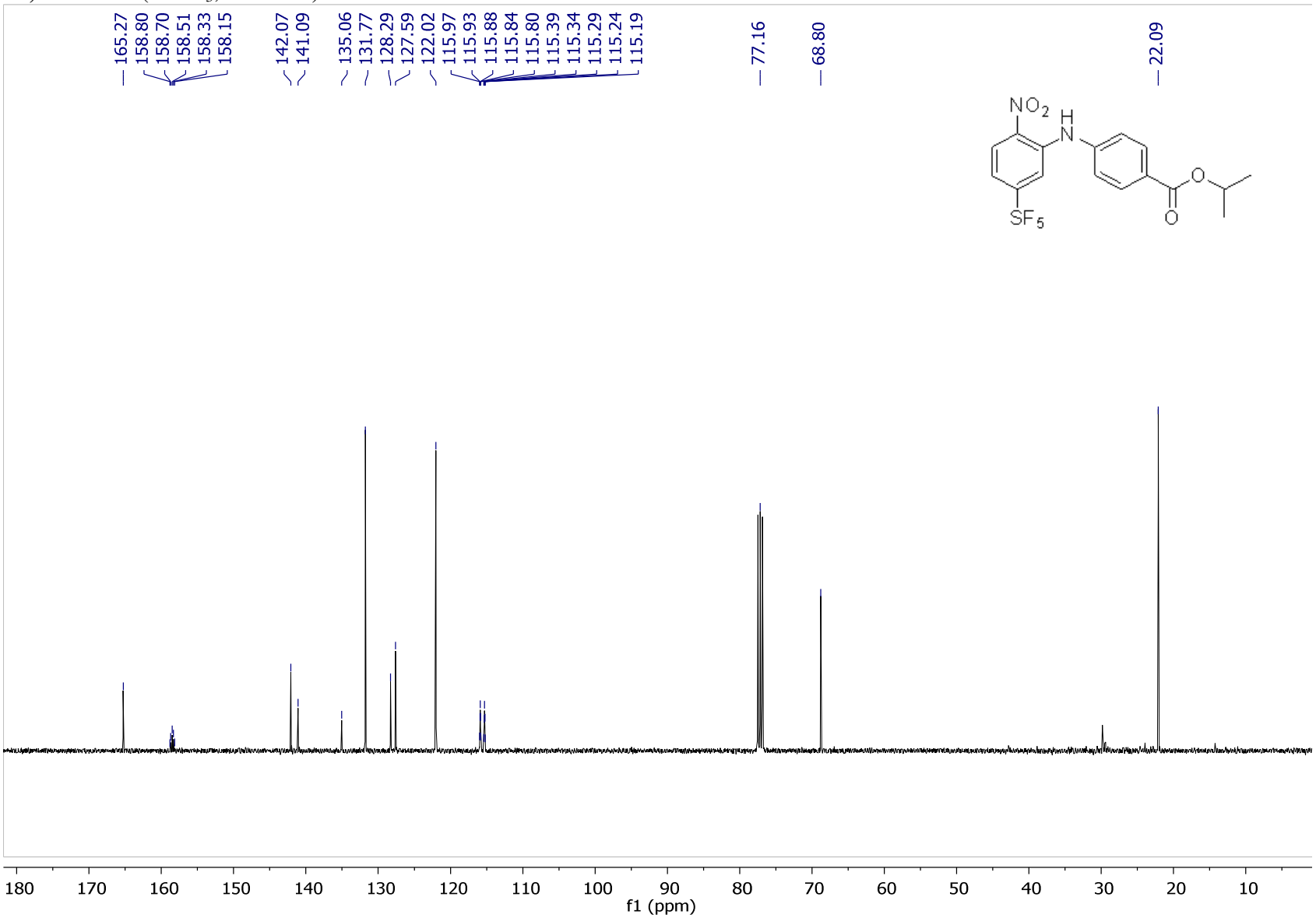

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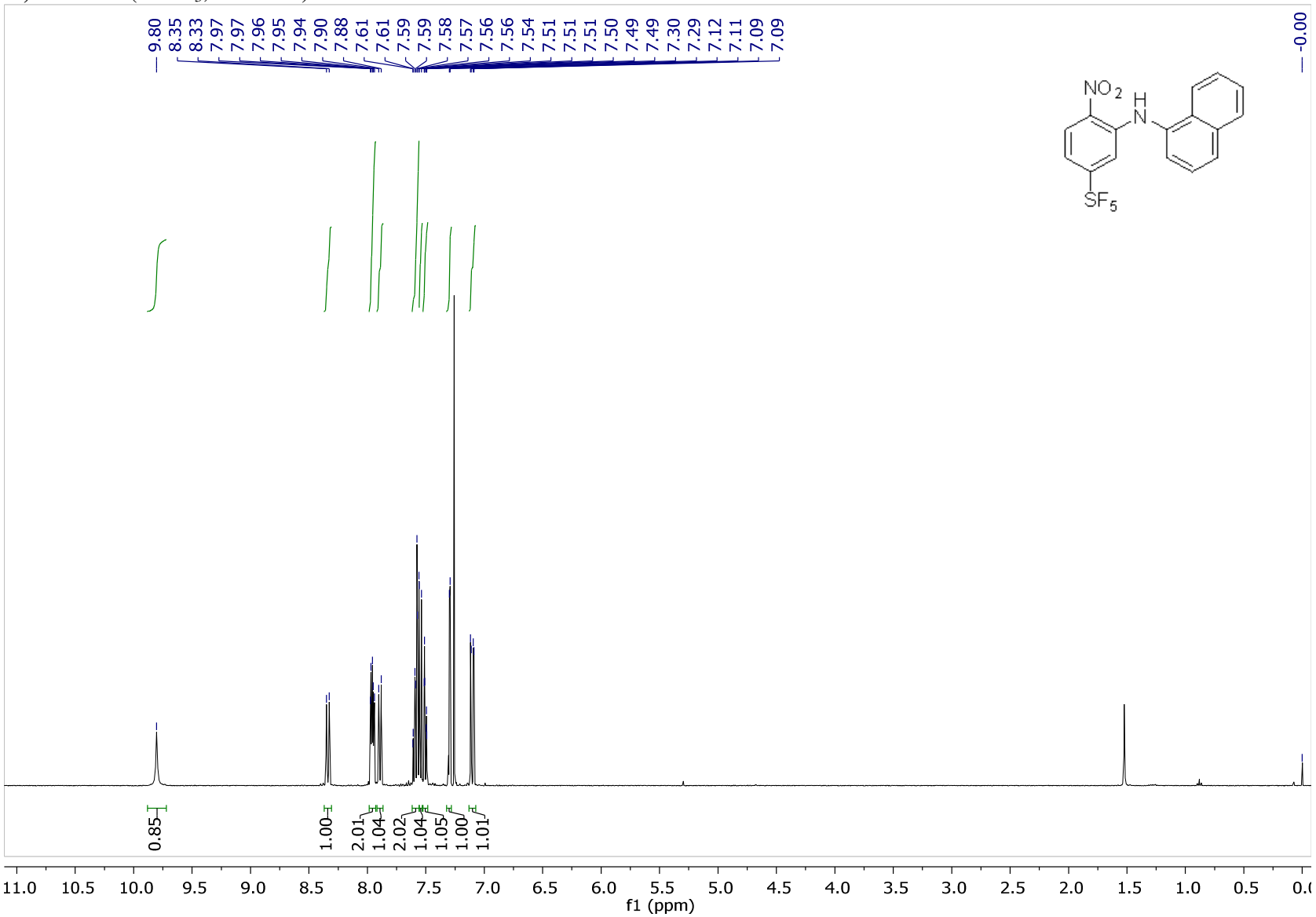

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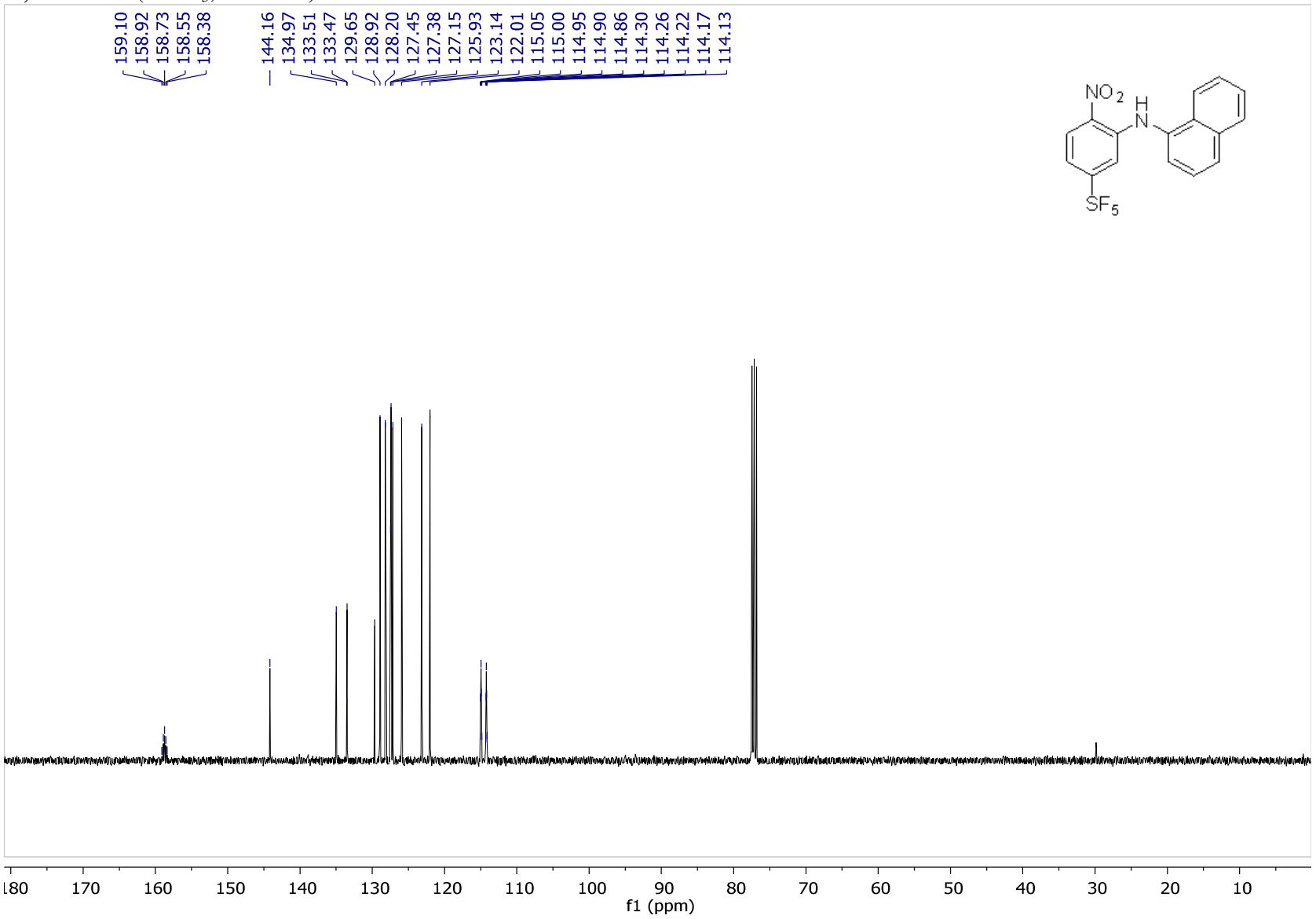

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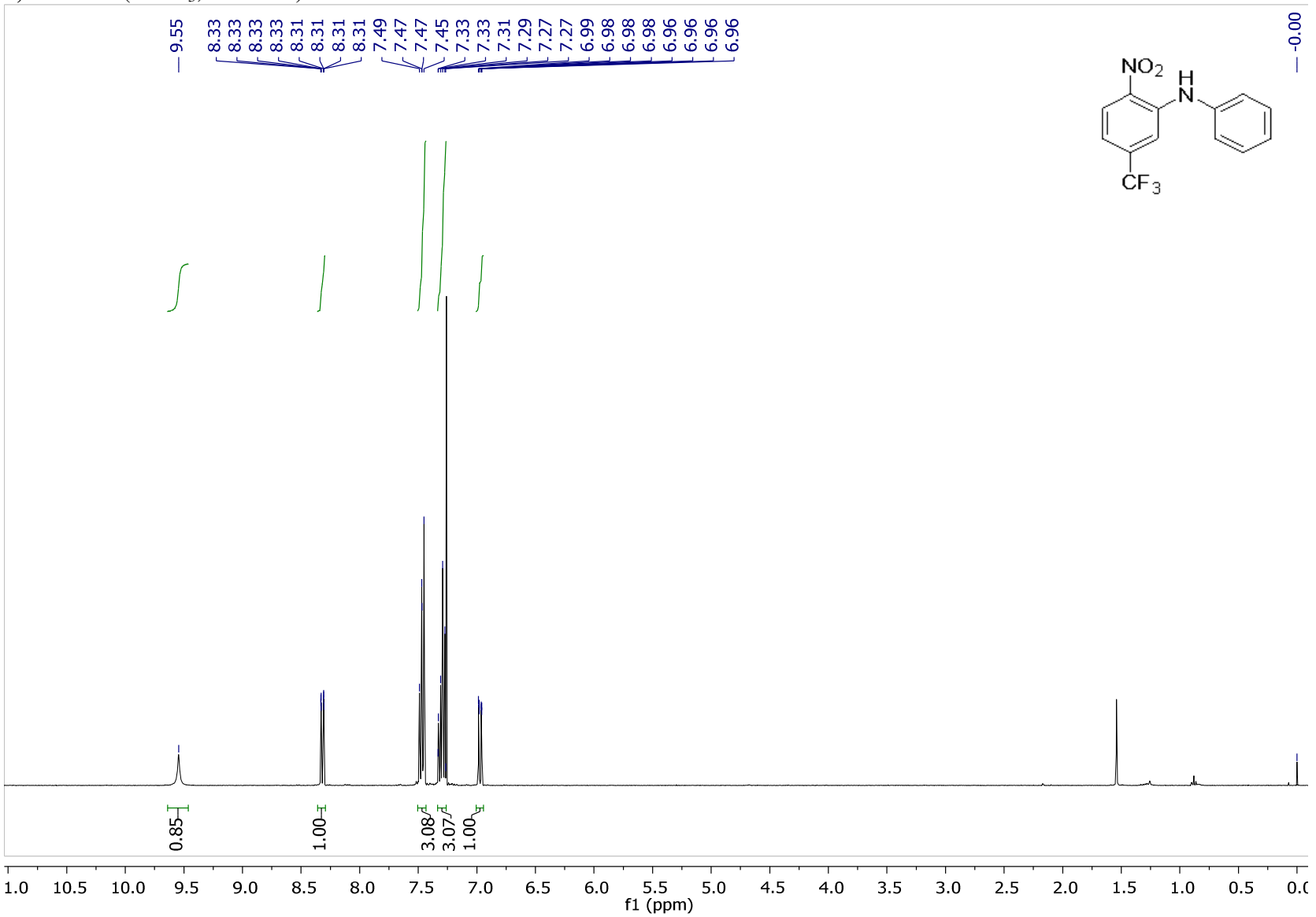

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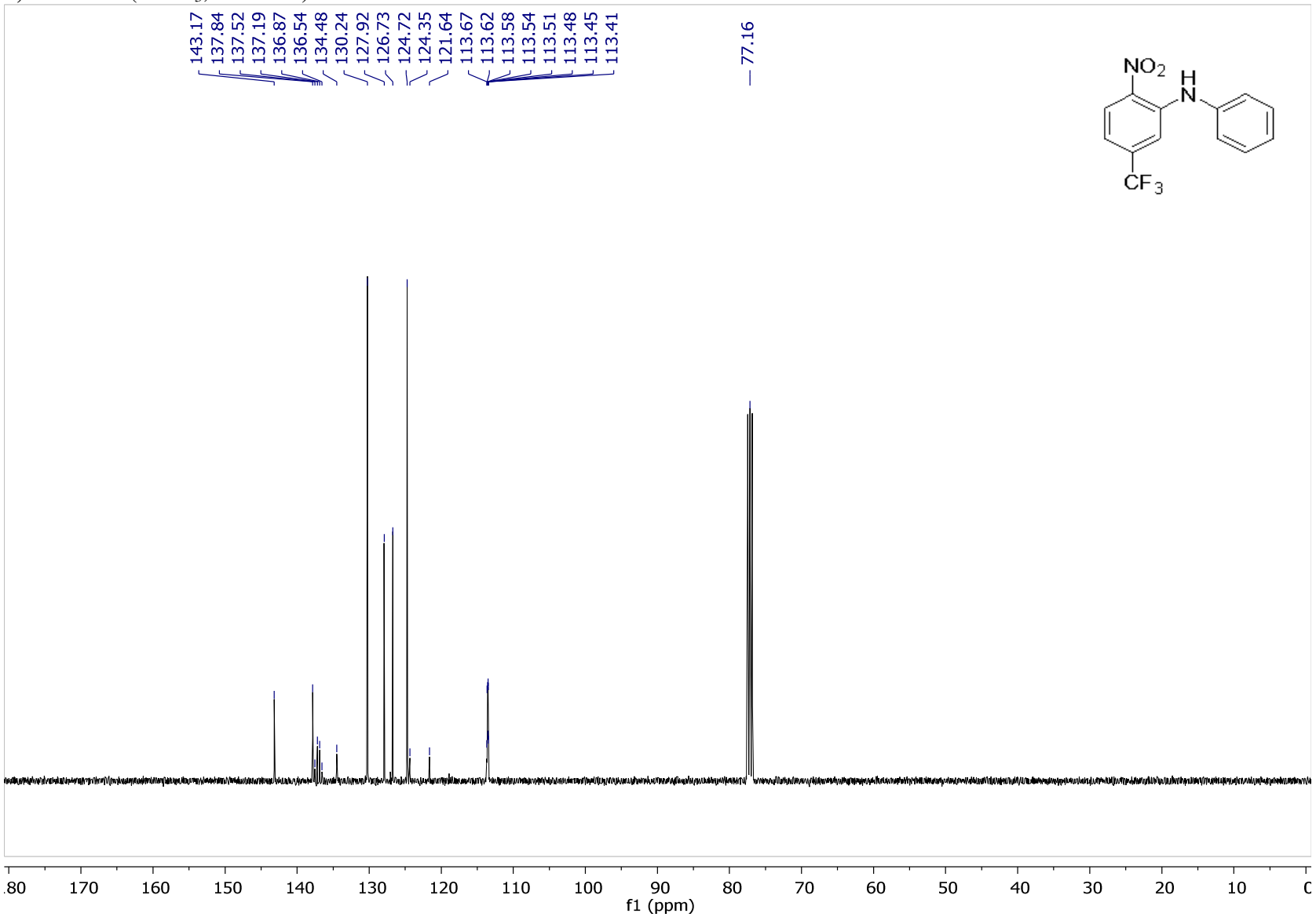

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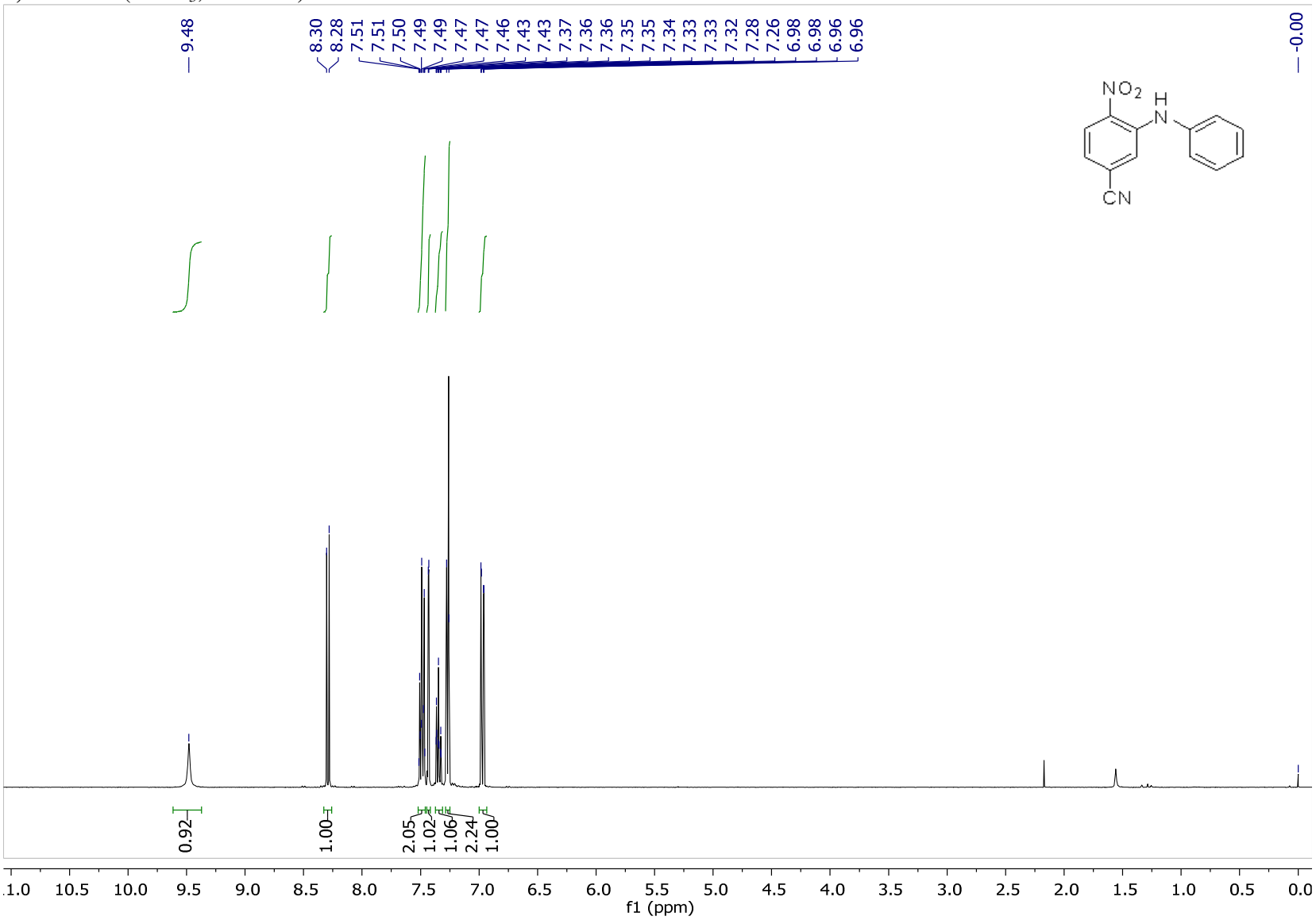
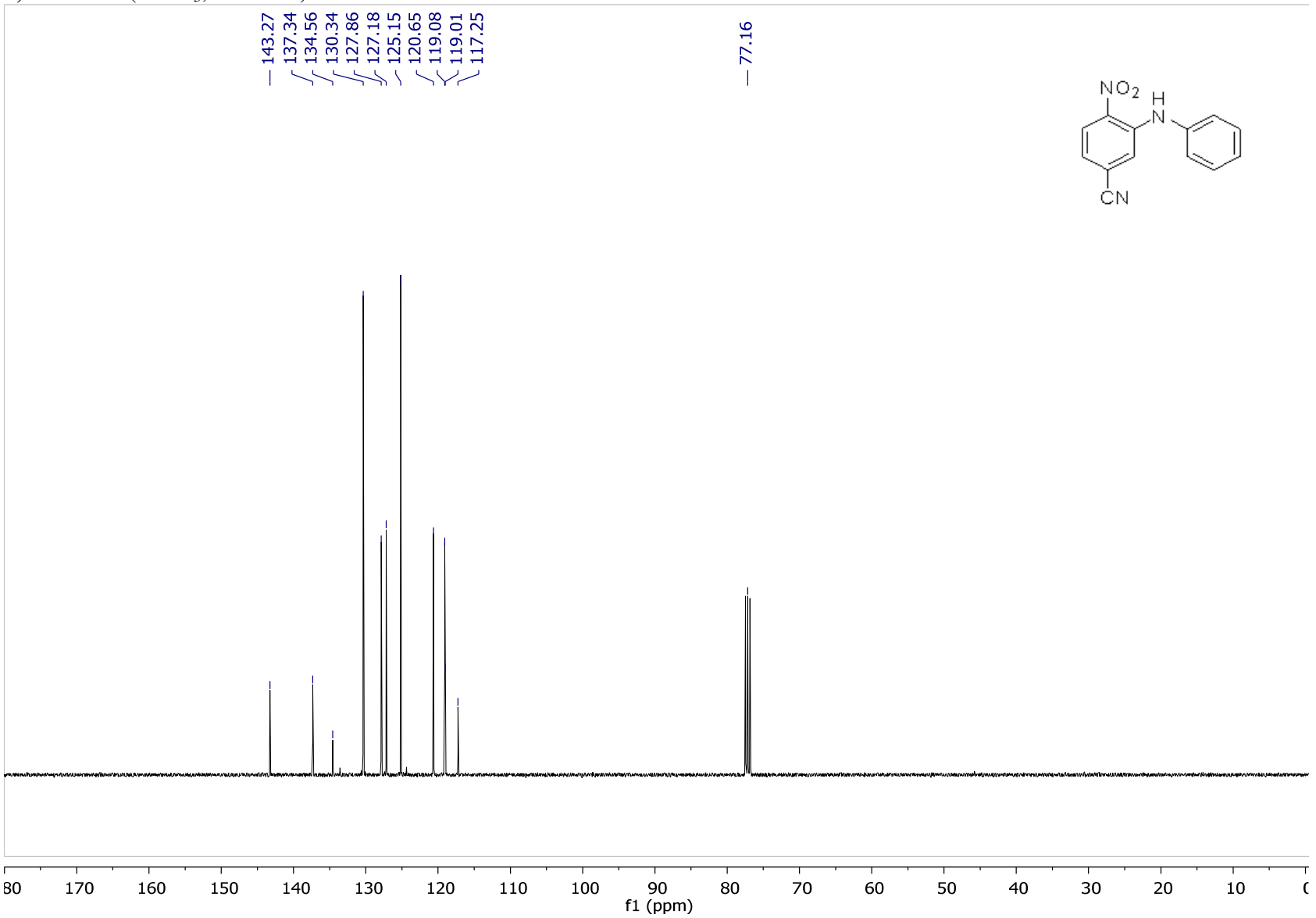


4, ^{13}C NMR ($CDCl_3$, 100MHz)



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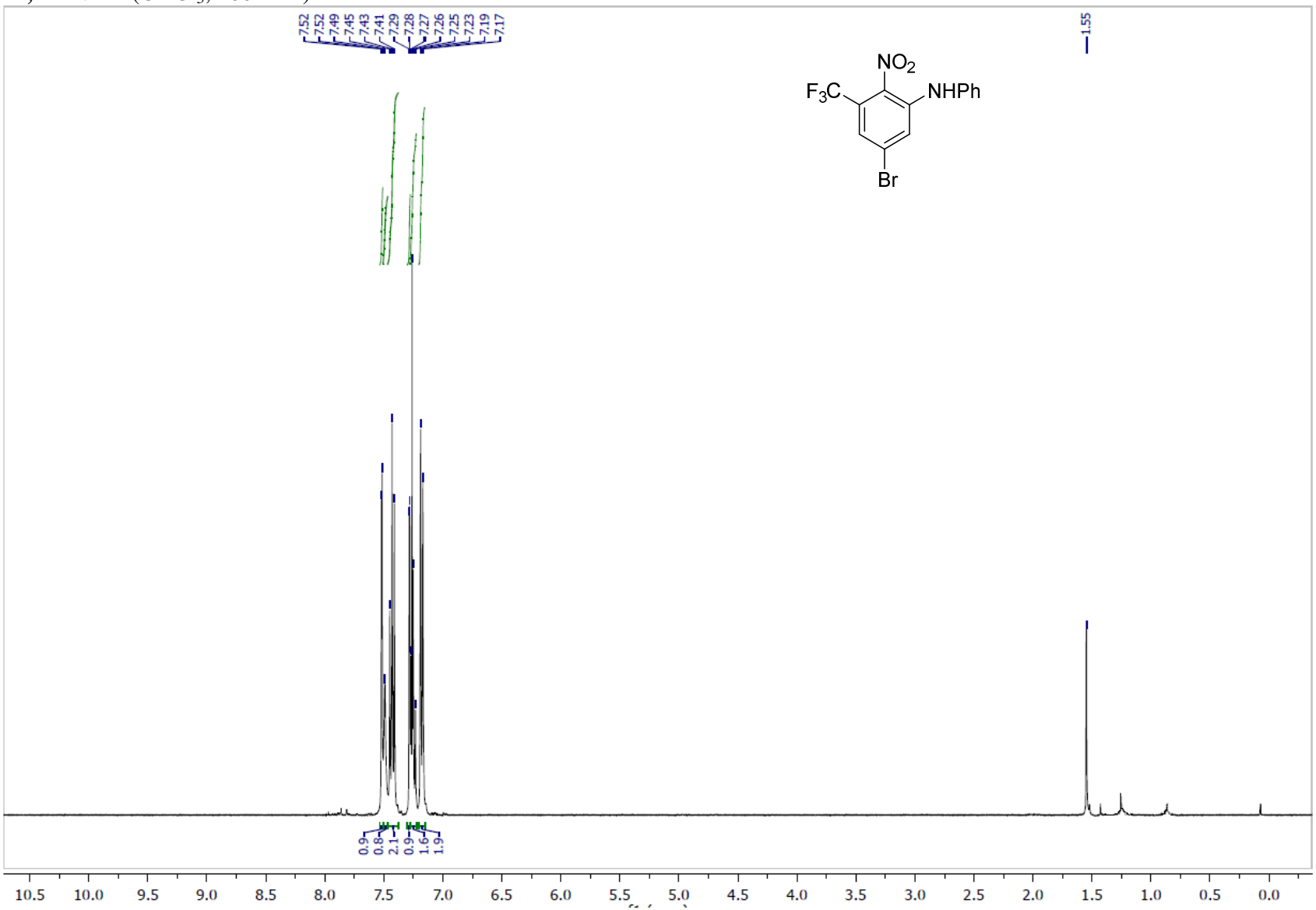
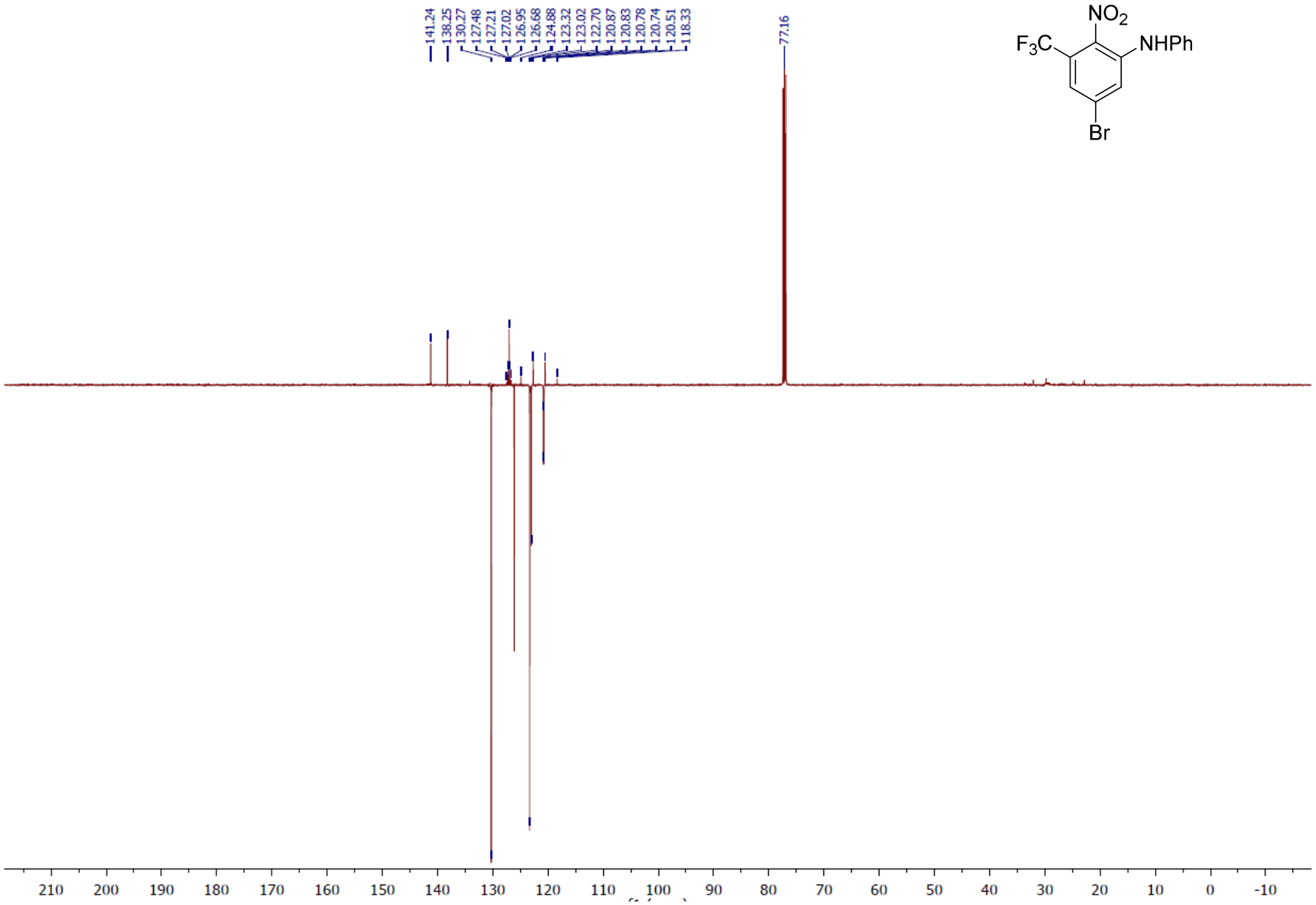


12, ^{13}C NMR ($CDCl_3$, 100MHz)



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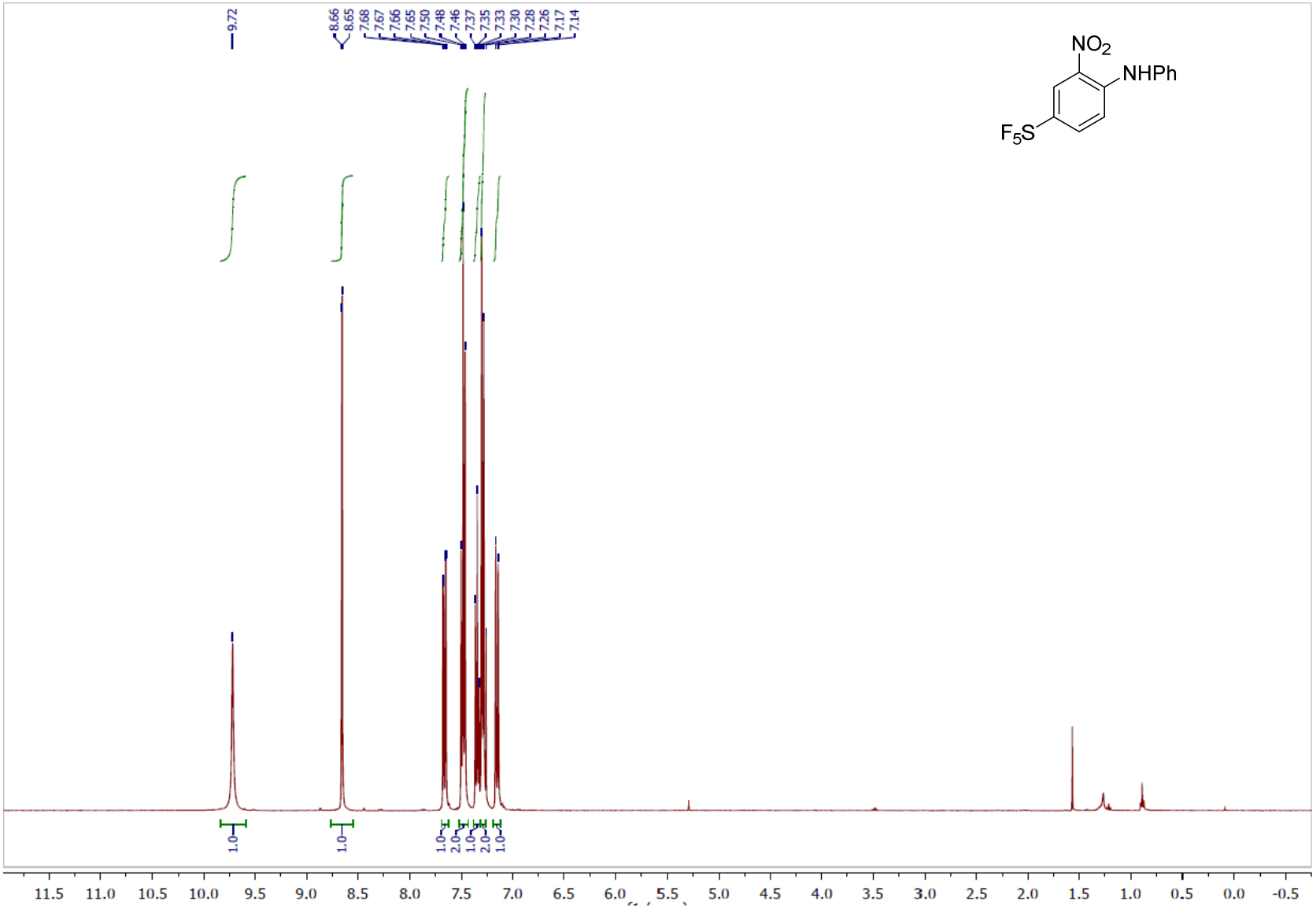

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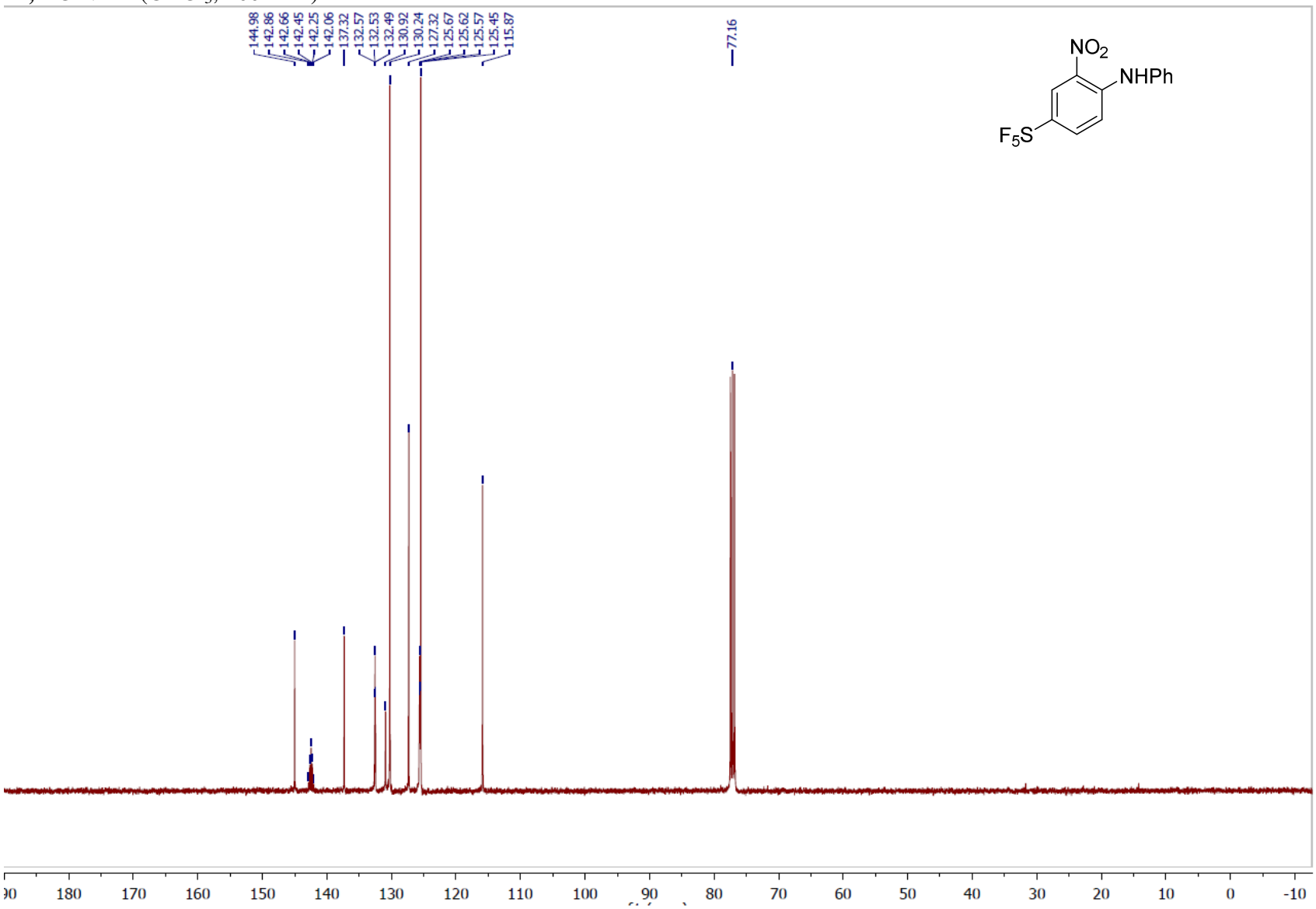

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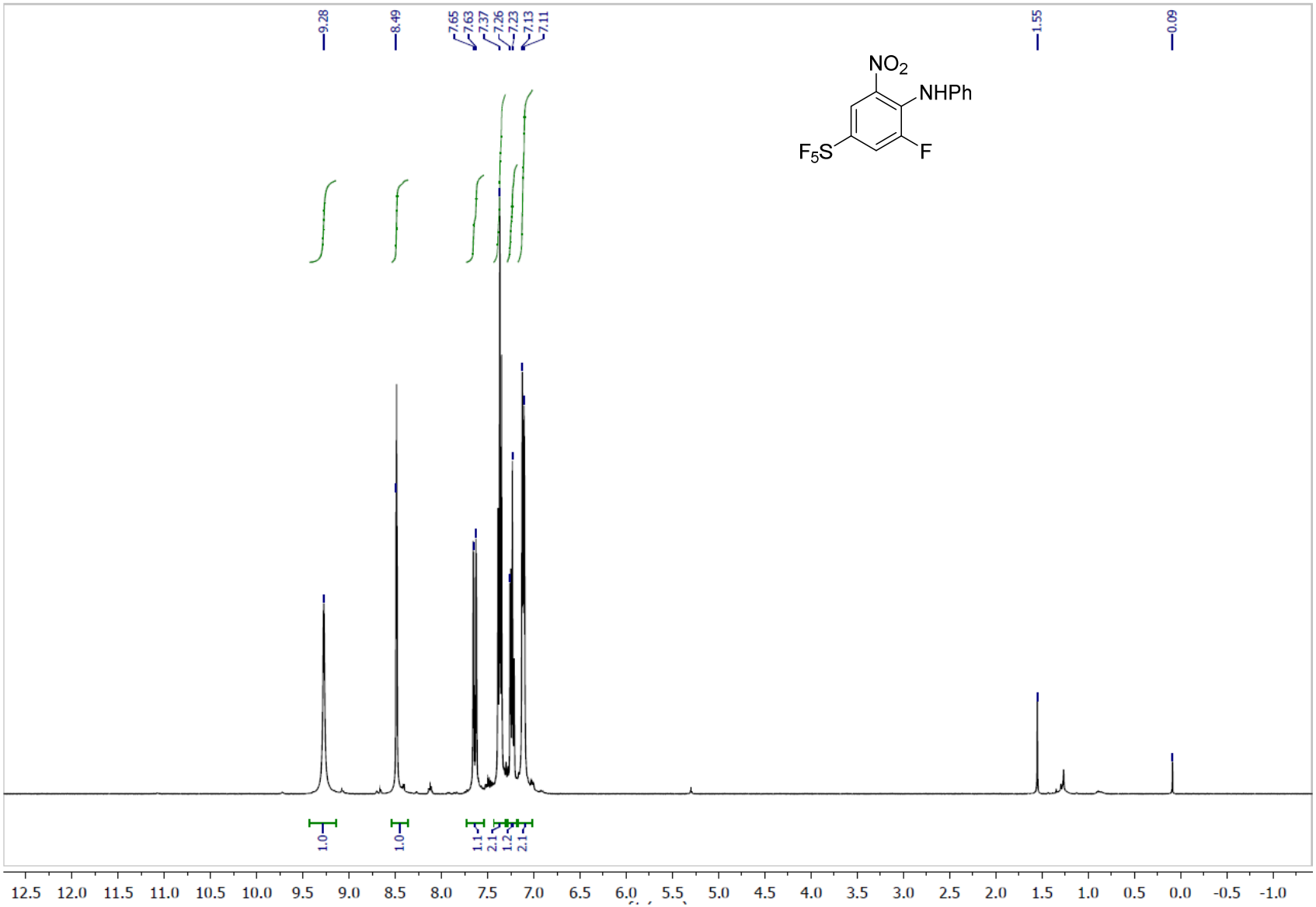

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