Supporting Information

Cycloadditions of 1,2,3-Triazines Bearing C5-Electron Donating Substituents: Robust Pyrimidine Synthesis

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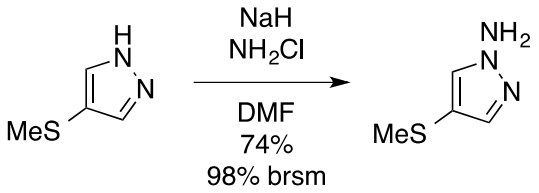
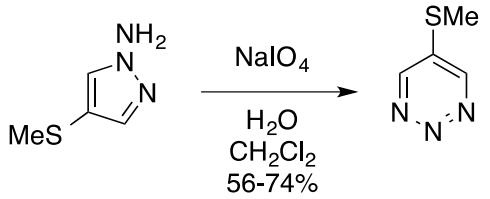
I. General Methods

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). Melting points were obtained using a Mel-Temp II apparatus and are uncorrected. ^{1}H and ^{13}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. 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.

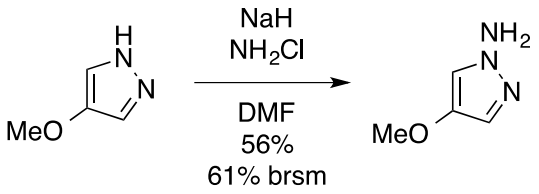
II. Synthesis of Substituted 1,2,3-Triazines



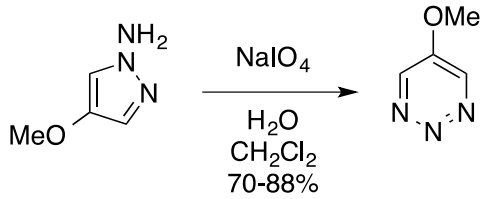
4-(Methylthio)-1*H*-pyrazol-1-amine (14). A solution of 4-(methylthio)-1*H*-pyrazole[1] (2.75 g, 24.1 mmol) in DMF (50 mL) at 0 °C was treated with sodium hydride (60% in mineral oil) (1.16 g, 28.9 mmol). The reaction mixture was warmed to 23 °C, stirred for 30 min at room temperature, and then treated with a 0.15 M solution of monochloramine[2] in diethyl ether (241 mL, 36.2 mmol). The reaction mixture was stirred at room temperature for 5 min. After 5 min, saturated aqueous $Na_2S_2O_3$ (100 mL), H_2O (100 mL), and EtOAc (500 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 200 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated on a rotary evaporator. Flash chromatography (SiO_2, 50% EtOAc/hexanes) provided a clear oil containing the product (**14,** 2.30 g, 74%, 98% brsm) and starting material (**11**, 678 mg) as an inseparable mixture. For **14**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.43 (d, *J* = 1.0 Hz, 1H), 7.38 (d, *J* = 1.0 Hz, 1H), 5.30 (bs, 2H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.3, 131.9, 112.2, 21.3; HRESI-TOF *m/z* 130.0434 ($C_4H_7N_3S$ + H^+ requires 130.0433).



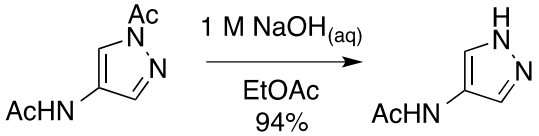
5-(Methylthio)-1,2,3-triazine (17). In a separatory funnel under an atmosphere of air, a solution containing a mixture of aminopyrazole **14** (2.30 g, 17.8 mmol) and pyrazole **11** (678 mg, 5.94 mmol) in CH_2Cl_2/water (1:1, 760 mL) was treated with $NaIO_4$ (7.63 g, 35.6 mmol) and shaken vigorously for 5 min, venting occasionally. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated on a rotary evaporator. Flash chromatography (SiO_2, 70–100% Et_2O/hexanes gradient elution) provided **17** as a light yellow crystalline solid (1.26 g, 56%; typically 56–74%): mp 93–94 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.86 (s, 2H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 146.2, 137.6, 12.9; IR (film) ν_{max} 3097, 3009, 2929, 1516, 1489, 1433, 1359, 1320, 1194, 1159, 1018, 991, 964, 940, 897, 758, 708, 659 cm^{-1}; HRESI-TOF *m/z* 128.0278 ($C_4H_5N_3S$ + H^+ requires 128.0277). 5-(Methylthio)-1,2,3-triazine (**17**) is a light yellow, crystalline solid that is sensitive to nucleophiles including water, methanol, and pyrrolidine, the latter of which consumes **17** in 4 h when present in slight excess. The material can be stored under an inert atmosphere on the bench for up to one month or at –20 °C indefinitely without significant decomposition.



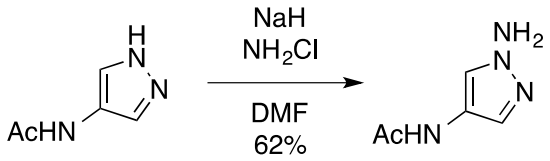
4-Methoxy-1*H*-pyrazol-1-amine (15). A solution of 4-methoxy-1*H*-pyrazole[3] (100 mg, 1.02 mmol) in DMF 2.1 mL) at 0 °C was treated with sodium hydride (60% in mineral oil) (50 mg, 1.22 mmol). The reaction mixture was warmed to 23 °C, stirred for 30 min at room temperature, and then treated with a 0.15 M solution of monochloramine[2] in diethyl ether (12.2 mL, 1.83 mmol). The reaction mixture was stirred at room temperature for 5 min. After 5 min, saturated aqueous $Na_2S_2O_3$ (10 mL), H_2O (10 mL), and EtOAc (50 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated on a rotary evaporator. Flash chromatography (SiO_2, 40–50% EtOAc/hexanes gradient elution) provided a yellow oil containing the product (**15,** 65 mg, 56%, 61% brsm) and starting material (**12**, 7 mg) as an inseparable mixture. For **15**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.07 (d, *J* = 1.2 Hz, 1H), 7.05 (d, *J* = 1.2 Hz, 1H), 5.42 (bs, 2H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 145.2, 124.3, 114.8, 60.0; IR (film) ν_{max} 3319, 3198, 2936, 2833, 1634, 1571, 1453, 1404, 1346, 1284, 1206, 1155, 1042, 980, 812, 745, 647, 611 cm^{-1}; HRESI-TOF *m/z* 114.0681 ($C_4H_7N_3O$ + H^+ requires 114.0662).



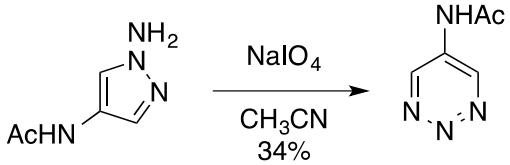
5-Methoxy-1,2,3-triazine (18). In a separatory funnel under an atmosphere of air, a solution of **15** (2.31 g, 20.4 mmol) in CH_2Cl_2/water (1:1, 860 mL) was treated with $NaIO_4$ (8.75 g, 40.8 mmol) and shaken vigorously for 5 min, venting occasionally. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated on a rotary evaporator. Flash chromatography (SiO_2, EtOAc) provided **18** as a light yellow crystalline solid (1.59 g, 70%; typically 70–88%): mp 43–45 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.76 (s, 2H), 4.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.2, 138.6, 56.2; IR (film) ν_{max} 3044, 2999, 2950, 1556, 1537, 1459, 1386, 1355, 1289, 1200, 1073, 1053, 989, 956, 913, 826, 762, 652, 566 cm^{-1}; HRESI-TOF *m/z* 112.0505 ($C_4H_5N_3O$ + H^+ requires 112.0505). 5-Methoxy-1,2,3-triazine (**18**) is a light yellow, crystalline solid that exhibits a chemical stability similar to methylthioether **17**.



***N*-(1*H*-Pyrazol-4-yl)acetamide (13).**[4,5,6] In a separatory funnel under an atmosphere of air, a solution of *N*-(1-acetyl-1*H*-pyrazol-4-yl)acetamide[4,5] (**S1**, 1.00 g, 5.98 mmol) in EtOAc (100 mL) was treated with 1 M NaOH(aq) (20 mL) and shaken vigorously for 5 min, venting occasionally. The combined organic and aqueous layers were concentrated on a rotary evaporator. The resulting residue was azeotroped with toluene. Flash chromatography (SiO_2, 10% MeOH/EtOAc) provided **13** as a pink powder (706 mg, 94%): mp 193–195 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 7.72 (s, 2H), 2.08 (s, 3H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 176.0, 139.6, 130.8, 128.3, 32.4; IR (film) ν_{max} 3203, 3040, 2948, 1650, 1583, 1484, 1396, 1321, 1285, 1132, 1021, 996, 964, 930, 864, 840, 769, 599, 570 cm^{-1}; HRESI-TOF *m/z* 126.0662 ($C_5H_7N_3O$ + H^+ requires 126.0662).

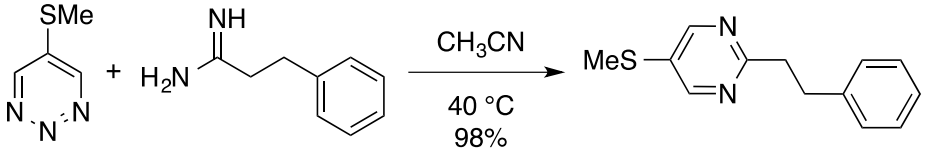


***N*-(1-Amino-1*H*-pyrazol-4-yl)acetamide (16).** A solution of **13** (500 mg, 4.00 mmol) in DMF (40 mL) was treated with sodium hydride (60% in mineral oil) (192 mg, 4.80 mmol). The reaction mixture was stirred for 5 min at room temperature, and then treated with a 0.15 M solution of monochloramine[2] in diethyl ether (40 mL, 6.00 mmol). The reaction mixture was stirred at room temperature for 5 min. After 5 min, saturated aqueous $Na_2S_2O_3$ (100 mL), H_2O (100 mL), and EtOAc (200 mL) were added to the reaction mixture. The combined organic and aqueous layers were concentrated on a rotary evaporator. The resulting residue was azeotroped with toluene. Flash chromatography (SiO_2, 0–10% MeOH/EtOAc gradient elution) provided **16** as an off white solid (346 mg, 62%). An analytically pure sample was obtained by preparatory TLC (10% MeOH/EtOAc): mp 149–151 °C; ^{1}H NMR (DMF-d_7, 600 MHz) δ 9.90 (bs, 1H), 7.73 (d, J = 1.0 Hz, 1H), 7.25 (d, J = 1.0 Hz, 1H), 6.41 (bs, 2H), 2.02 (s, 3H); ^{13}C NMR (DMF-d_7, 150 MHz) δ 167.6, 127.1, 121.9, 120.6, 23.4; IR (film) ν_{max} 3334, 3257, 3189, 3146, 3084, 2857, 1645, 1586, 1463, 1394, 1283, 1226, 1176, 1019, 991, 848, 821, 739, 595, 563 cm^{-1}; HRESI-TOF *m/z* 141.0770 ($C_5H_8N_4O$ + H^+ requires 141.0771).

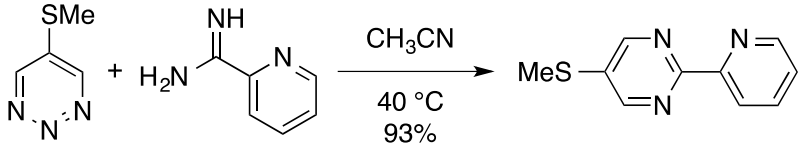


5-(*N*-Acetylamino)-1,2,3-triazine (19). In a sealed tube, a solution of **16** (1.00 g, 7.14 mmol) in CH_3CN (1 L) was treated with $NaIO_4$ (30.5 g, 143 mmol). The reaction mixture was sonicated for 16 h at a temperature ranging from 0–55 °C. After 16 h, the suspension was filtered through Celite and concentrated on a rotary evaporator. Flash chromatography (SiO_2, 5–10% MeOH/CH_2Cl_2 gradient elution) provided **19** as a red solid (338 mg, 34%); mp 155 °C (evolution of gas), 170–172 °C (decomposition); ^{1}H NMR (CD_3OD, 600 MHz) δ 9.40 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 173.0, 141.3, 133.7, 24.1; IR (film) ν_{max} 3124, 3011, 2923, 1709, 1554, 1439, 1417, 1383, 1312, 1235, 1077, 1037. 995, 968, 935, 603, 574 cm^{-1}; HRESI-TOF *m/z* 139.0614 ($C_5H_6N_4O$ + H^+ requires 139.0614). 1,2,3-Triazine **19** is a rust colored powder that displays markedly reduced sensitivity to nucleophiles compared with 1,2,3-triazines **17** and **18**. In fact, its chromatographic purification involves elution with 10% MeOH/CH_2Cl_2, an eluent incompatible with 1,2,3-triazines **17** and **18**.

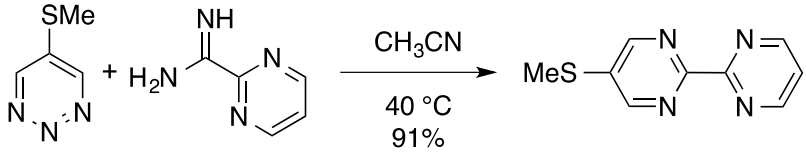
III. Reaction of 1,2,3-Triazines with Amidines



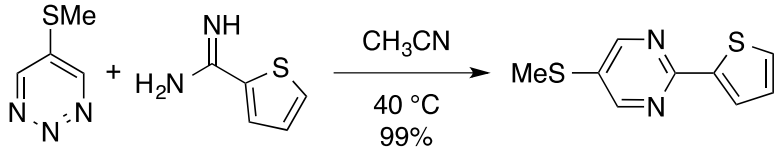
5-(Methylthio)-2-phenethylpyrimidine (21a). A 0.15 M solution of amidine **20a** (16.1 mg, 0.109 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (20.7 mg, 0.163 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21a** as a pale yellow oil (24.6 mg, 98%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.57 (s, 2H), 7.29–7.23 (m, 4H), 7.20–7.17 (m, 1H), 3.25 (dd, *J* = 9.7, 6.4 Hz, 2H), 3.14 (dd, *J* = 9.8, 6.4 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.7, 155.9, 146.1, 141.6, 131.2, 128.7, 126.3, 40.8, 34.9, 16.5; IR (film) ν_{max} 3018, 2925, 1534, 1433, 1368, 1288, 1225, 1161, 1117, 1030, 791, 743, 705, 664 cm^{-1}; HRESI-TOF *m/z* 231.0950 ($C_{13}H_{14}N_2S + H^+$ requires 231.0950).



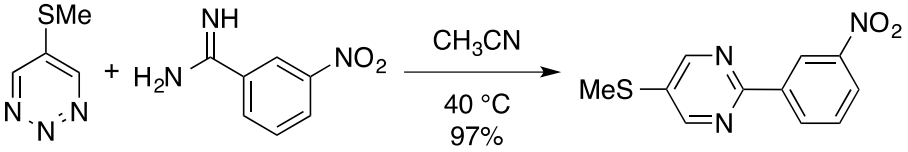
5-(Methylthio)-2-(pyridin-2-yl)pyrimidine (21b). A 0.15 M solution of amidine **20b** (7.3 mg, 0.060 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (12.0 mg, 0.091 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 10% MeOH/EtOAc) to provide **21b** as a tan solid (11.1 mg, 93%): mp 102–104 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.79 (s, 2H), 8.70 (d, *J* = 4.7 Hz, 1H), 8.49 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.97 (td, *J* = 7.8, 1.7 Hz, 1H), 7.51 (ddt, *J* = 7.3, 4.8, 0.9 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 160.6, 155.7, 155.2, 150.5, 138.9, 136.3, 126.4, 124.5, 14.8; IR (film) ν_{max} 3052, 3001, 2920, 1524, 1417, 1371, 1134, 750, 643 cm^{-1}; HRESI-TOF *m/z* 204.0592 ($C_{10}H_9N_3S + H^+$ requires 204.0590).



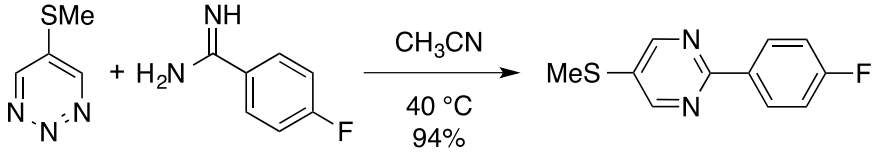
5-(Methylthio)-2,2'-bipyrimidine (21c). A 0.15 M solution of amidine **20c** (5.3 mg, 0.043 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (8.2 mg, 0.065 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 10% MeOH/EtOAc) to provide the **21c** as a dark green solid (8.1 mg, 91%): mp 134 °C (decomposition); ^{1}H NMR (CD_3OD, 600 MHz) δ 9.01 (d, *J* = 4.9 Hz, 2H), 8.86 (s, 2H), 7.62 (t, *J* = 4.9 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 162.6, 159.3, 159.0, 155.4, 138.6, 123.3, 14.4; IR (film) ν_{max} 2922, 1557, 1524, 1402, 1371, 1150, 766, 643, 628 cm^{-1}; HRESI-TOF *m/z* 205.0541 ($C_9H_8N_4S + H^+$ requires 205.0542).



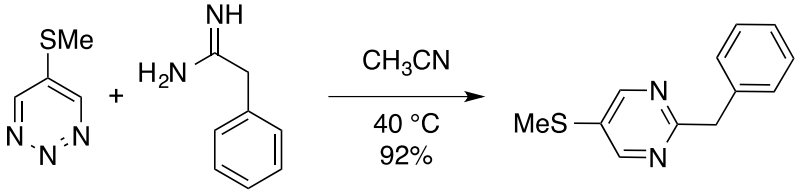
5-(Methylthio)-2-(thiophen-2-yl)pyrimidine (21d). A 0.15 M solution of amidine **20d** (4.5 mg, 0.036 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (6.8 mg, 0.054 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21d** as a yellow crystalline solid (7.4 mg, 99%): mp 70–72 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.59 (s, 2H), 7.96 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.46 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.0, 156.0, 143.1, 131.1, 130.0, 129.1, 128.7, 16.9; IR (film) ν_{max} 3076, 2917, 2852, 1516, 1434, 1409, 1126, 854, 785, 717, 635 cm^{-1}; HRESI-TOF *m/z* 209.0203 ($C_9H_8N_2S_2 + H^+$ requires 209.0202).



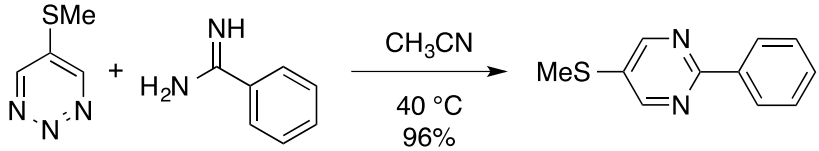
5-(Methylthio)-2-(3-nitrophenyl)pyrimidine (21e). A 0.15 M solution of amidine **20e** (9.5 mg, 0.057 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (10.9 mg, 0.086 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21e** as a light yellow powder (13.7 mg, 97%): mp 142–144 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.26 (t, *J* = 2.0 Hz, 1H), 8.74 (dt, *J* = 7.8, 1.4 Hz, 1H), 8.69 (s, 2H), 8.30 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.4, 155.2, 149.1, 139.3, 133.8, 133.7, 129.9, 125.2, 123.2, 15.8; IR (film) ν_{max} 3038, 2922, 2852, 1520, 1419, 1347, 1138, 790, 729 cm^{-1}; HRESI-TOF *m/z* 248.0488 ($C_{11}H_9N_3O_2S$ + H^+ requires 248.0488).



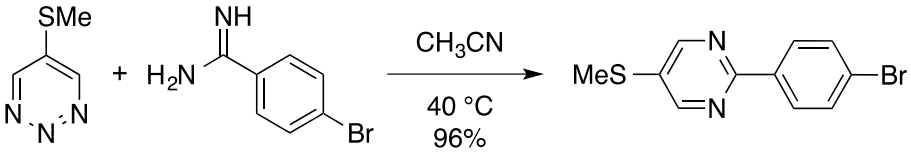
2-(4-Fluorophenyl)-5-(methylthio)pyrimidine (21f). A 0.15 M solution of amidine **20f** (7.9 mg, 0.058 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (11.0 mg, 0.086 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21f** as a white crystalline solid (11.9 mg, 94%): mp 76–77 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.66 (s, 2H), 8.41 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 164.9 (d, *J* = 250 Hz, 1C), 161.1 (s, 1C), 155.8 (s, 2C), 133.7 (d, *J* = 3 Hz, 1C), 131.8 (s, 1C), 130.3 (d, *J* = 10 Hz, 2C), 115.9 (d, *J* = 22 Hz, 2C), 16.4 (s, 1C); IR (film) ν_{max} 2923, 1598, 1059, 1422, 1372, 1211, 1149, 1131, 846, 784, 617 cm^{-1}; HRESI-TOF *m/z* 221.0541 ($C_{11}H_9FN_2S$ + H^+ requires 221.0543).



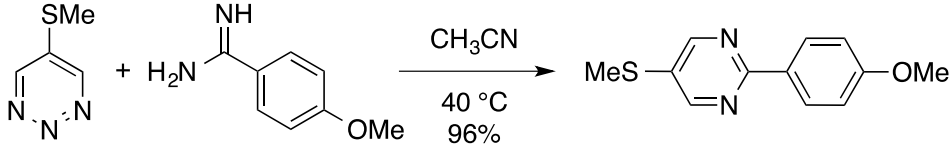
2-Benzyl-5-(methylthio)pyrimidine (21g). A 0.15 M solution of amidine **20g** (7.2 mg, 0.054 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (10.3 mg, 0.081 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21g** as a white solid (10.7 mg, 92%): mp 53–55 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.57 (s, 2H), 7.35–7.34 (m, 2H), 7.30 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.23–7.21 (m, 1H), 4.26 (s, 2H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.3, 156.1, 138.5, 131.4, 129.4, 128.9, 127.0, 45.8, 16.4; IR (film) ν_{max} 2919, 1535, 1494, 1426, 1376, 1120, 1028, 749, 699, 671, 646, 585 cm^{-1}; HRESI-TOF *m/z* 217.0794 ($C_{12}H_{12}N_2S$ + H^+ requires 217.0794).



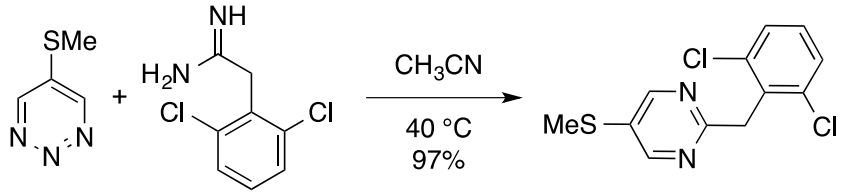
5-(Methylthio)-2-phenylpyrimidine (21h). A 0.15 M solution of amidine **20h** (7.9 mg, 0.065 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (12.5 mg, 0.098 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21h** as a white powder (12.7 mg, 96%): mp 40–41 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.68 (s, 2H), 8.41–8.40 (m, 2H), 7.49–4.46 (m, 3H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 161.9, 155.7, 137.4, 131.9, 130.9, 128.9, 128.2, 16.3; IR (film) ν_{max} 3027, 2919, 1526, 1423, 1369, 1127, 917, 736, 682, 646 cm^{-1}; HRESI-TOF *m/z* 203.0638 ($C_{11}H_{10}N_2S$ + H^+ requires 203.0637).



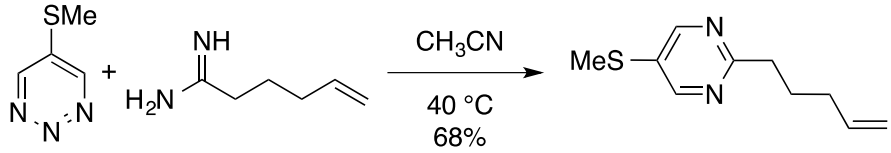
2-(4-Bromophenyl)-5-(methylthio)pyrimidine (21i). A 0.15 M solution of amidine **20i** (4.7 mg, 0.024 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (4.5 mg, 0.035 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21i** as a white crystalline solid (6.5 mg, 96%): mp 130–132 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.66 (s, 2H), 8.28 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 161.0, 155.6, 136.4, 132.4, 132.1, 129.8, 125.7, 16.2; IR (film) ν_{max} 2921, 2852, 1521, 1425, 1374, 1128, 1002, 839, 778, 647 cm^{-1}; HRESI-TOF *m/z* 280.9745 ($C_{11}H_9BrN_2S$ + H^+ requires 280.9743).



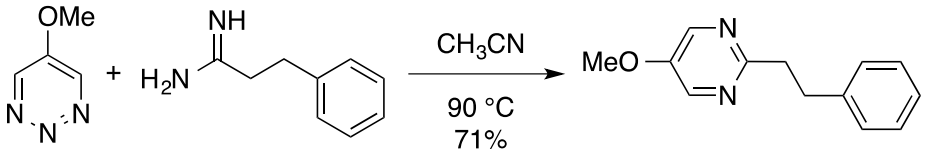
2-(4-Methoxyphenyl)-5-(methylthio)pyrimidine (21j). A 0.15 M solution of amidine **20j** (9.9 mg, 0.066 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (12.6 mg, 0.099 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21j** as a white crystalline solid (14.8 mg, 96%): mp 100–101 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.65 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.2, 162.0, 156.2, 130.7, 130.1, 129.9, 114.3, 55.7, 16.8; IR (film) ν_{max} 2920, 2837, 1604, 1514, 1422, 1234, 1164, 1017, 841, 786, 647, 618 cm^{-1}; HRESI-TOF *m/z* 233.0745 ($C_{12}H_{12}N_2OS$ + H^+ requires 233.0743).



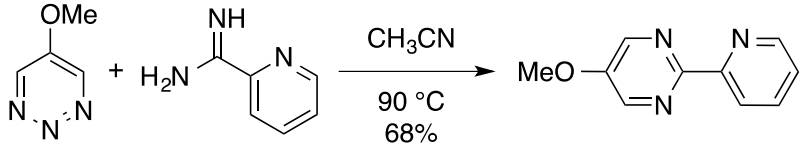
2-(2,6-Dichlorobenzyl)-5-(methylthio)pyrimidine (21k). A 0.15 M solution of amidine **20k** (13.0 mg, 0.064 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (12.3 mg, 0.096 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21k** as a light yellow crystalline solid (17.8 mg, 97%): mp 86–87 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.54 (s, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.17 (t, *J* = 8.1 Hz, 1H), 4.66 (s, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 165.0, 155.9, 136.7, 134.7, 131.4, 128.9, 128.4, 40.6, 16.3; IR (film) ν_{max} 2916, 1561, 1531, 1427, 1372, 1180, 1116, 1081, 934, 778, 758, 725, 645, 622 cm^{-1}; HRESI-TOF *m/z* 285.0015 ($C_{12}H_{10}Cl_2N_2S$ + H^+ requires 285.0014).



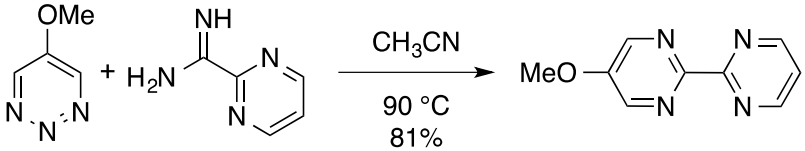
5-(Methylthio)-2-(pent-4-en-1-yl)pyrimidine (21l). A 0.15 M solution of amidine **20l** (7.4 mg, 0.066 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (12.5 mg, 0.098 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **21l** as an orange oil (8.6 mg, 68%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.56 (s, 2H), 5.84 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.05–4.96 (m, 2H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.51 (s, 3H), 2.14 (q, *J* = 6.9 Hz, 2H), 1.91 (p, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.6, 156.0, 138.5, 130.9, 115.3, 38.6, 33.7, 28.2, 16.9; IR (film) ν_{max} 2922, 2856, 1639, 1559, 1527, 1426, 1369, 1122, 1027, 910, 642 cm^{-1}; HRESI-TOF *m/z* 195.0950 ($C_{10}H_{14}N_2S$ + H^+ requires 195.0950).



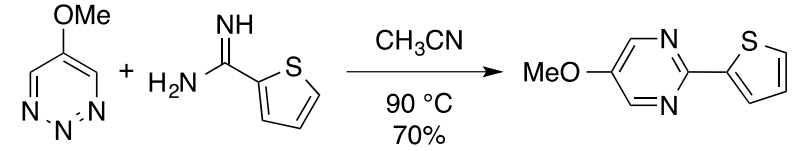
5-Methoxy-2-phenethylpyrimidine (22a). A 0.15 M solution of amidine **20a** (8.7 mg, 0.059 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (9.8 mg, 0.088 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22a** as a yellow oil (8.9 mg, 71%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.35 (s, 2H), 7.29–7.23 (m, 4H), 7.18 (ddt, *J* = 8.6, 6.6, 1.5 Hz, 1H), 3.23 (ddd, *J* = 8.5, 6.5, 0.9 Hz, 2H), 3.13 (dd, *J* = 9.9, 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 163.1, 151.9, 143.6, 141.8, 128.7, 127.8, 126.3, 56.2, 40.5, 35.3; IR (film) ν_{max} 3026, 2927, 2839, 1553, 1454, 1430, 1270, 1016, 698 cm^{-1}; HRESI-TOF *m/z* 215.1179 ($C_{13}H_{14}N_2O$ + H^+ requires 215.1179).



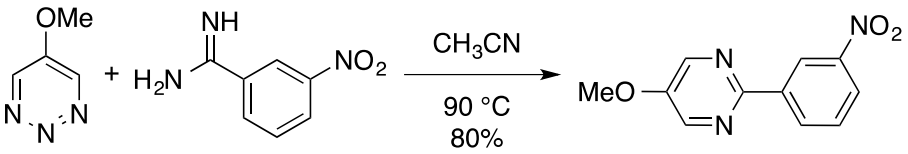
5-Methoxy-2-(pyridin-2-yl)pyrimidine (22b). A 0.15 M solution of amidine **20b** (13.3 mg, 0.11 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (18.3 mg, 0.17 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by reverse phase preparative TLC (SiO_2 RP-18, 20% MeOH/CH_3CN) to provide **22b** as a light orange powder (14.0 mg, 68%): mp 96–98 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.68 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.62 (s, 2H), 8.43 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.95 (td, *J* = 7.8, 1.8 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 157.0, 155.4, 154.9, 150.3, 144.9, 138.8, 125.8, 124.1, 56.9; IR (film) ν_{max} 3031, 2921, 2850, 1580, 1548, 1423, 1395, 1276, 1002, 753, 640, 594 cm^{-1}; HRESI-TOF *m/z* 188.0818 ($C_{10}H_9N_3O$ + H^+ requires 188.0818).



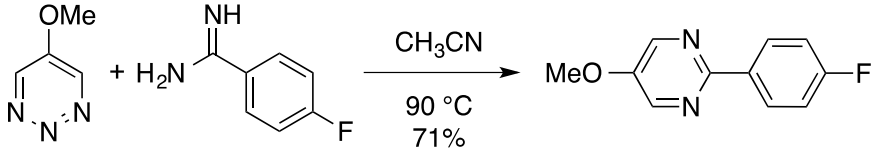
5-Methoxy-2,2'-bipyrimidine (22c). A 0.15 M solution of amidine **20c** (8.3 mg, 0.068 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (11.3 mg, 0.10 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by reverse phase preparative TLC (SiO_2 RP-18, 20% MeOH/CH_3CN) to provide **22c** as a white powder (10.4 mg, 81%): mp 153–155 °C (decomposition); ^{1}H NMR (CD_3OD, 600 MHz) δ 8.99 (d, *J* = 4.9 Hz, 2H), 8.70 (s, 2H), 7.60 (t, *J* = 4.9 Hz, 1H), 4.07 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 162.5, 159.2, 155.8, 155.4, 145.1, 122.9, 57.1; IR (film) ν_{max} 3036, 2998, 2943, 2851, 1540, 1410, 1388, 1009, 766, 638, 605 cm^{-1}; HRESI-TOF *m/z* 189.0771 ($C_9H_8N_4O$ + H^+ requires 189.0771).



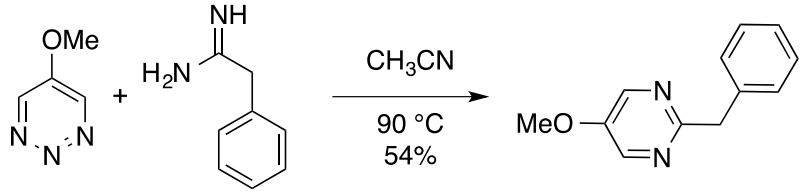
5-Methoxy-2-(thiophen-2-yl)pyrimidine (22d). A 0.15 M solution of amidine **20d** (10.9 mg, 0.086 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (14.4 mg, 0.13 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22d** as a yellow crystalline solid (11.6 mg, 70%): mp 84–87 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.38 (s, 2H), 7.86 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.3, 151.8, 143.8, 143.3, 128.8, 128.6, 127.8, 56.4; IR (film) ν_{max} 3106, 3038, 2917, 2847, 1551, 1455, 1440, 1417, 1392, 1280, 1203, 1020, 910, 854, 782, 706, 631, 591 cm^{-1}; HRESI-TOF *m/z* 193.0430 ($C_9H_8N_2OS$ + H^+ requires 193.0430).



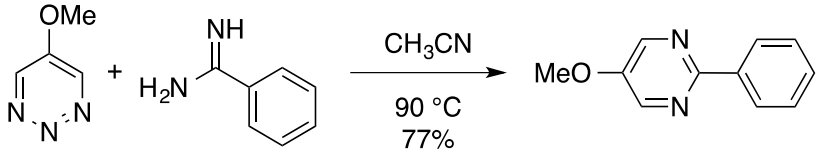
5-Methoxy-2-(3-nitrophenyl)pyrimidine (22e). A 0.15 M solution of amidine **20e** (9.4 mg, 0.057 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (9.5 mg, 0.085 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22e** as a light yellow powder (10.5 mg, 80%): mp 146–149 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.24 (t, *J* = 2.0 Hz, 1H), 8.70 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 8.51 (s, 2H), 8.28 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.8, 153.0, 149.2, 143.9, 139.6, 133.5, 129.8, 124.6, 123.0, 56.5; IR (film) ν_{max} 3082, 2940, 2843, 1521, 1452, 1428, 1352, 1287, 1009, 908, 789, 723, 667, 588 cm^{-1}; HRESI-TOF *m/z* 232.0717 ($C_{11}H_9N_3O_3$ + H^+ requires 232.0717).



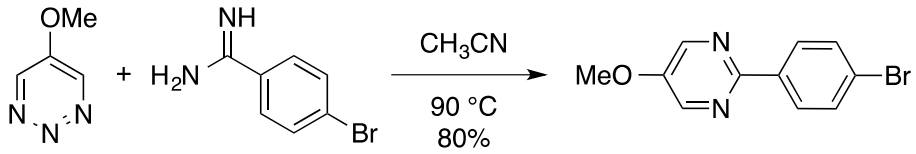
2-(4-Fluorophenyl)-5-methoxypyrimidine (22f). A 0.15 M solution of amidine **20f** (8.5 mg, 0.062 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (10.3 mg, 0.092 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22f** as a white powder (9.0 mg, 71%): mp 118–120 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.45 (s, 2H), 8.36–8.33 (m, 2H), 7.16–7.11 (m, 2H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 164.5 (d, *J* = 249 Hz, 1C), 157.4 (s, 1C), 152.3 (s, 1C), 143.7 (s, 2C), 134.0 (d, *J* = 3 Hz, 1C), 129.89 (d, *J* = 9 Hz, 2C), 115.8 (d, *J* = 22 Hz, 2C), 56.4 (s, 1C); IR (film) ν_{max} 2921, 2847, 1601, 1547, 1510, 1452, 1429, 1389, 1275, 1208, 1151, 1013, 847, 783, 556 cm^{-1}; HRESI-TOF *m/z* 205.0772 ($C_{11}H_9FN_2O$ + H^+ requires 205.0772).



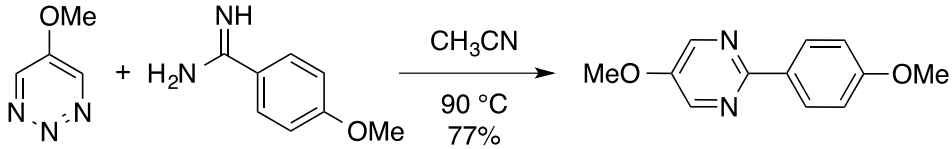
2-Benzyl-5-methoxypyrimidine (22g). A 0.15 M solution of amidine **20g** (8.0 mg, 0.059 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (9.9 mg, 0.089 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22g** as a yellow oil (6.4 mg, 54%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.35 (s, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 4.25 (s, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.7, 151.9, 143.8, 139.1, 129.3, 128.9, 126.8, 56.2, 45.3; IR (film) ν_{max} 3026, 2934, 2851, 1551, 1431, 1284, 1017, 753, 724, 695, 594, 548 cm^{-1}; HRESI-TOF *m/z* 201.1022 ($C_{12}H_{12}N_2O$ + H^+ requires 201.1022).



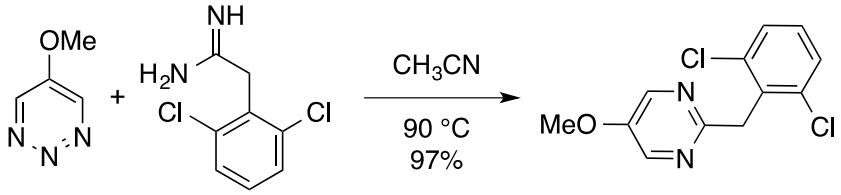
5-Methoxy-2-phenylpyrimidine (22h). A 0.15 M solution of amidine **20h** (14.7 mg, 0.12 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (20.4 mg, 0.18 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide the **22h** as a light yellow crystalline solid (17.5 mg, 77%): mp 47–49 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.48 (s, 2H), 8.36–8.33 (m, 2H), 7.49–4.42 (m, 3H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 158.2, 152.3, 143.7, 137.8, 130.1, 128.9, 127.9, 56.3; IR (film) ν_{max} 3017, 2938, 2839, 1549, 1449, 1428, 1277, 1011, 911, 741, 695, 642, 587 cm^{-1}; HRESI-TOF *m/z* 187.0866 ($C_{11}H_{10}N_2O$ + H^+ requires 187.0866).



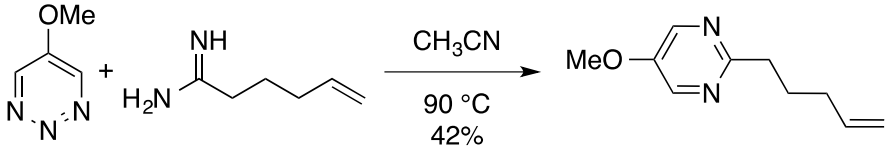
2-(4-Bromophenyl)-5-methoxypyrimidine (22i). A 0.15 M solution of amidine **20i** (5.4 mg, 0.027 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (4.5 mg, 0.040 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22i** as a white powder (5.7 mg, 80%): mp 145–147 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.46 (s, 2H), 8.24–8.22 (m, 2H), 7.60–7.58 (m, 2H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.3, 152.5, 143.8, 136.7, 132.1, 129.5, 124.8, 56.4; IR (film) ν_{max} 3018, 2920, 2848, 1588, 1574, 1545, 1453, 1429, 1385, 1276, 1061, 1006, 843, 776, 730, 643 cm^{-1}; HRESI-TOF *m/z* 264.9971 ($C_{11}H_9BrN_2O$ + H^+ requires 264.9971).



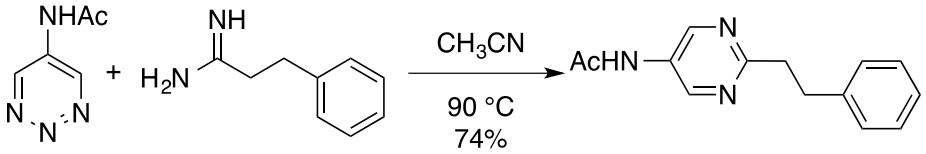
2-(4-Methoxyphenyl)-5-methoxypyrimidine (22j). A 0.15 M solution of amidine **20j** (12.7 mg, 0.085 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (14.1 mg, 0.13 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22j** as a white powder (14.1 mg, 77%): mp 111–114 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.43 (s, 2H), 8.31–8.28 (m, 2H), 6.99–6.95 (m, 2H), 3.94 (s, 3H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 161.5, 158.2, 151.8, 143.7, 130.6, 129.4, 114.2, 56.3, 55.7; IR (film) ν_{max} 3036, 2946, 2841, 1606, 1544, 1414, 1389, 1270, 1246, 1233, 1165, 1006, 841, 784, 563 cm^{-1}; HRESI-TOF *m/z* 217.0971 ($C_{12}H_{12}N_2O_2$ + H^+ requires 217.0971).



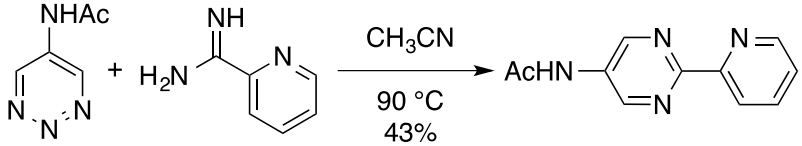
2-(2,6-Dichlorobenzyl)-5-methoxypyrimidine (22k). A 0.15 M solution of amidine **20k** (17.9 mg, 0.088 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (14.7 mg, 0.13 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22k** as an orange oil (23.0 mg, 97%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.32 (s, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 4.63 (s, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 160.4, 151.8, 143.8, 136.7, 135.2, 128.7, 128.4, 56.2, 40.2; IR (film) ν_{max} 3036, 3017, 2970, 2935, 1553, 1450, 1416, 1278, 1175, 1016, 931, 761, 732, 564 cm^{-1}; HRESI-TOF *m/z* 269.0244 ($C_{12}H_{10}Cl_2N_2O$ + H^+ requires 269.0243).



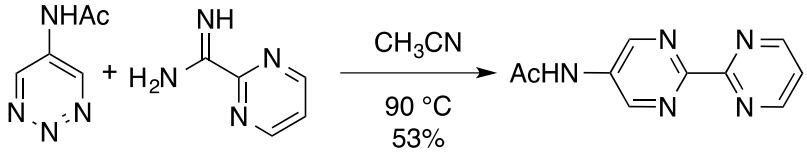
5-Methoxy-2-(pent-4-en-1-yl)pyrimidine (22l). A 0.15 M solution of amidine **20l** (6.2 mg, 0.055 mmol) in CH_3CN was treated with 1,2,3-triazine **18** (9.2 mg, 0.083 mmol). The reaction mixture was heated to 90 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **22l** as a yellow oil (4.1 mg, 42%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.33 (s, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.02 (dd, *J* = 17.1, 2.1 Hz, 1H), 4.96 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.89 (s, 3H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.89 (p, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 164.0, 151.8, 143.6, 138.7, 115.2, 56.2, 38.2, 33.7, 28.4; IR (film) ν_{max} 2931, 2839, 1552, 1455, 1430, 1270, 1016, 907, 637 cm^{-1}; HRESI-TOF *m/z* 179.1179 ($C_{10}H_{14}N_2O$ + H^+ requires 179.1179).



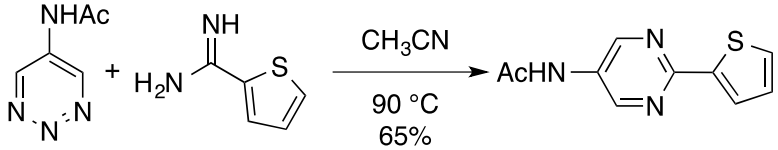
***N*-(2-Phenethylpyrimidin-5-yl)acetamide (23a).** A 0.15 M solution of amidine **20a** (12.3 mg, 0.083 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (17.2 mg, 0.13 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23a** as a white crystalline solid (14.8 mg, 74%): mp 104–106 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.92 (s, 2H), 7.24–7.21 (m, 2H), 7.18–7.12 (m, 3H), 3.19–3.16 (m, 2H), 3.10–3.07 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 165.9, 149.0, 142.4, 133.6, 129.4, 129.4, 127.8, 41.2, 35.8, 23.5; IR (film) ν_{max} 3285, 3032, 1645, 1451, 1379, 696 cm^{-1}; HRESI-TOF *m/z* 242.1288 ($C_{14}H_{15}N_3O$ + H^+ requires 242.1288).



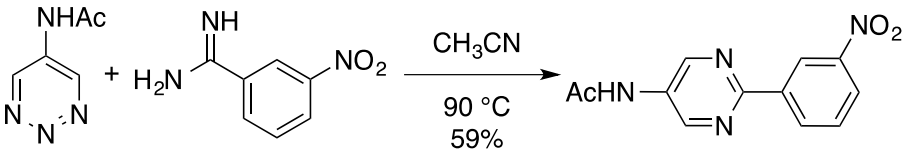
***N*-(2-(Pyridin-2-yl)pyrimidin-5-yl)acetamide (23b).** A 0.15 M solution of amidine **20b** (9.6 mg, 0.079 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (16.4 mg, 0.12 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by reverse phase PTLC (SiO_2 RP-18, 20% MeOH/CH_2Cl_2) to provide **23b** as a white solid (7.3 mg, 43%): ^{1}H NMR (CD_3OD, 600 MHz) δ 9.18 (s, 2H), 8.71 (d, *J* = 4.5 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.00 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.2, 158.9, 155.1, 150.3, 149.1, 139.0, 135.3, 126.2, 124.4, 23.7; IR (film) ν_{max} 3224, 3065, 2928, 1681, 1580, 1523, 1427, 1377, 1287, 759 cm^{-1}; HRESI-TOF *m/z* 215.0927 ($C_{11}H_{10}N_4O$ + H^+ requires 215.0927).



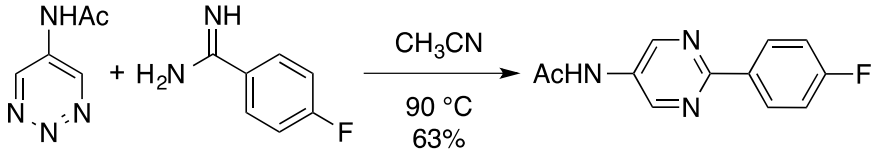
***N*-([2,2'-Bipyrimidin]-5-yl)acetamide (23c).** A 0.15 M solution of amidine **20c** (6.6 mg, 0.054 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (11.1 mg, 0.080 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by reverse phase PTLC (SiO_2 RP-18, 20% MeOH/CH_2Cl_2) to provide **23c** as a white solid (6.1 mg, 53%): mp >250 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 9.26 (s, 2H), 9.00 (d, *J* = 4.9 Hz, 2H), 7.61 (t, *J* = 4.9 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.3, 162.4, 159.3, 157.2, 148.9, 136.5, 123.1, 23.7; IR (film) ν_{max} 3341, 3027, 1681, 1565, 1469, 1411, 1372, 1351, 1335, 973, 762, 644 cm^{-1}; HRESI-TOF *m/z* 216.0880 ($C_{10}H_9N_5O$ + H^+ requires 216.0880).



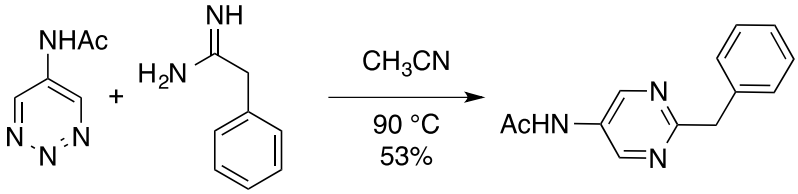
***N*-(2-(Thiophen-2-yl)pyrimidin-5-yl)acetamide (23d).** A 0.15 M solution of amidine **20d** (5.0 mg, 0.040 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (8.2 mg, 0.059 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23d** as a light orange solid (5.6 mg, 65%): mp 194–196 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.94 (s, 2H), 7.89 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.0, 157.8, 149.1, 143.9, 133.3, 130.5, 129.2, 129.2, 23.6; IR (film) ν_{max} 3075, 1618, 1528, 1445, 1346, 1215, 973, 857, 785, 737, 636 cm^{-1}; HRESI-TOF *m/z* 220.0539 ($C_{10}H_9N_3OS$ + H^+ requires 220.0539).



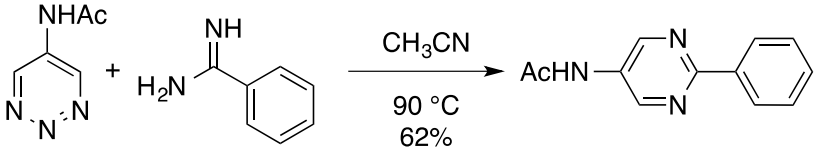
***N*-(2-(3-Nitrophenyl)pyrimidin-5-yl)acetamide (23e).** A 0.15 M solution of amidine **20e** (6.9 mg, 0.042 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (8.7 mg, 0.063 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23e** as a light orange solid (6.4 mg, 59%): mp 208–210 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 9.19 (t, *J* = 2.0 Hz, 1H), 9.13 (s, 2H), 8.76 (dt, *J* = 7.9, 1.4 Hz, 1H), 8.32 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.2, 158.4, 150.2, 149.1, 140.4, 134.8, 134.4, 131.0, 125.6, 123.2, 23.6; IR (film) ν_{max} 1646, 1530, 1435, 1346, 914, 796, 817 cm^{-1}; HRESI-TOF *m/z* 259.0826 ($C_{12}H_{10}N_4O_3$ + H^+ requires 259.0826).



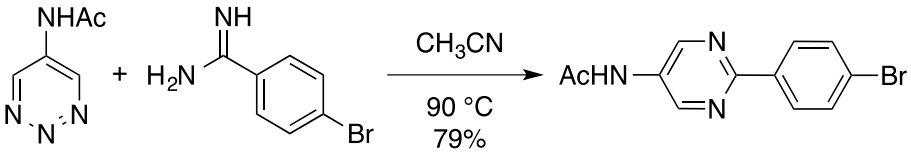
***N*-(2-(4-Fluorophenyl)pyrimidin-5-yl)acetamide (23f).** A 0.15 M solution of amidine **20f** (7.6 mg, 0.055 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (11.3 mg, 0.082 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23f** as a colorless solid (8.0 mg, 63%): mp 244–247 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 9.04 (s, 2H), 8.40–8.36 (m, 2H), 7.21–7.17 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1 (s, 1C), 165.8 (d, *J* = 250 Hz, 1C), 159.9 (s, 1C), 149.2 (s, 2C), 134.9 (d, *J* = 3 Hz, 1C), 133.8 (s, 1C), 131.0 (d, *J* = 9 Hz, 2C), 116.3 (d, *J* = 23 Hz, 2C), 23.6 (s, 1C); IR (film) ν_{max} 1646, 1599, 1454, 1361, 1219, 847, 789, 607 cm^{-1}; HRESI-TOF *m/z* 232.0881 ($C_{12}H_{10}FN_3O$ + H^+ requires 232.0881).



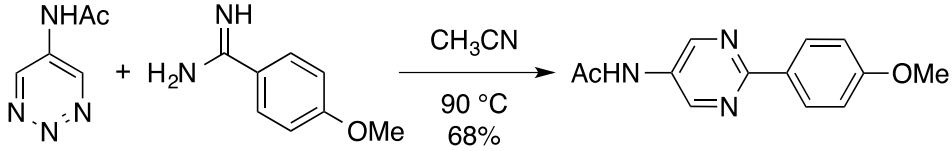
***N*-(2-Benzylpyrimidin-5-yl)acetamide (23g).** A 0.15 M solution of amidine **20g** (4.6 mg, 0.035 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (7.2 mg, 0.052 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23g** as a light yellow solid (4.1 mg, 53%): mp 104–106 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.93 (s, 2H), 7.31–7.17 (m, 5H), 4.20 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 165.5, 149.3, 139.6, 133.7, 129.9, 129.5, 127.6, 45.6, 23.5; IR (film) ν_{max} 3228, 3151, 3062, 3028, 2924, 1702, 1585, 1525, 1531, 1445, 1424, 1373, 1285, 1236, 696 cm^{-1}; HRESI-TOF *m/z* 228.1131 ($C_{13}H_{13}N_3O$ + H^+ requires 228.1131).



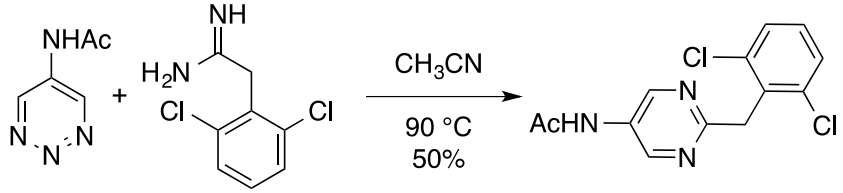
***N*-(2-Phenylpyrimidin-5-yl)acetamide (23h).** A 0.15 M solution of amidine **20h** (12.5 mg, 0.10 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (21.5 mg, 0.16 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23h** as a colorless solid (13.7 mg, 62%): mp 204–206 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 9.05 (s, 2H), 8.34–8.30 (m, 2H), 7.48–4.40 (m, 3H), 2.19 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 170.2, 158.9, 147.3, 136.6, 132.0, 129.5, 127.7, 126.9, 21.7; IR (film) ν_{max} 1647, 1444, 1414, 1375, 1359, 948, 922, 738, 687, 648, 607 cm^{-1}; HRESI-TOF *m/z* 214.0975 ($C_{12}H_{11}N_3O$ + H^+ requires 214.0975).



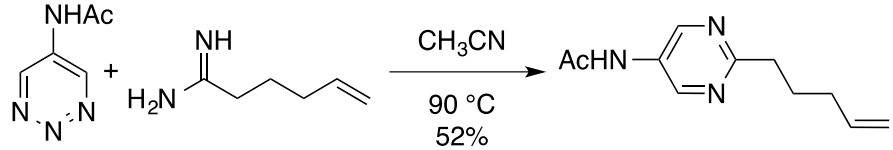
***N*-(2-(4-Bromophenyl)pyrimidin-5-yl)acetamide (23i).** A 0.15 M solution of amidine **20i** (7.3 mg, 0.037 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (7.6 mg, 0.055 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23i** as a white solid (8.5 mg, 79%): mp >250 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 9.05 (s, 2H), 8.27–8.23 (m, 2H), 7.66–7.62 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 159.8, 149.1, 137.7, 134.1, 132.8, 130.5, 125.8, 23.6; IR (film) ν_{max} 1650, 1454, 1359, 1069, 1007, 843, 785, 648, 569 cm^{-1}; HRESI-TOF *m/z* 292.0080 ($C_{12}H_{10}BrN_3O$ + H^+ requires 292.0080).



***N*-(2-(4-Methoxyphenyl)pyrimidin-5-yl)acetamide (23j).** A 0.15 M solution of amidine **20j** (7.5 mg, 0.050 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (10.28 mg, 0.074 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23j** as a light orange crystalline solid (8.2 mg, 68%): mp 214–216 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.99 (s, 2H), 8.28–8.26 (m, 2H), 7.02–7.00 (m, 2H), 3.86 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 163.2, 160.9, 149.2, 133.2, 131.0, 130.4, 114.9, 55.8, 23.6; IR (film) ν_{max} 1683, 1422, 1347, 1252, 1169, 1016, 847, 790 cm^{-1}; HRESI-TOF *m/z* 244.1080 ($C_{13}H_{13}N_3O_2$ + H^+ requires 244.1080).

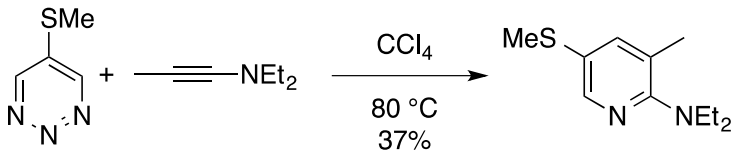


***N*-(2-(2,6-Dichlorobenzyl)pyrimidin-5-yl)acetamide (23k).** A 0.15 M solution of amidine **20k** (12.7 mg, 0.062 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (12.9 mg, 0.094 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23k** as a colorless solid (9.2 mg, 50%): mp 240–242 °C; ^{1}H NMR (CD_3OD, 600 MHz) δ 8.88 (s, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.27 (dd, *J* = 8.5, 7.7 Hz, 1H), 4.62 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 163.3, 149.2, 137.5, 135.4, 133.6, 130.0, 129.3, 40.6, 23.5; IR (film) ν_{max} 1682, 1444, 1372, 1357, 941, 777, 654 cm^{-1}; HRESI-TOF *m/z* 296.0352 ($C_{13}H_{11}Cl_2N_3O$ + H^+ requires 296.0352).

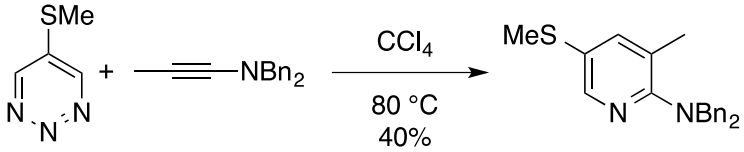


***N*-(2-(Pent-4-en-1-yl)pyrimidin-5-yl)acetamide (23l).** A 0.15 M solution of amidine **20l** (4.6 mg, 0.041 mmol) in CH_3CN was treated with 1,2,3-triazine **19** (8.5 mg, 0.062 mmol). The reaction mixture was heated to 90 °C and stirred for 72 h, at which time the mixture was purified by PTLC (SiO_2, 10% MeOH/CH_2Cl_2) to provide **23l** as a colorless oil (4.4 mg, 52%): ^{1}H NMR (CD_3OD, 600 MHz) δ 8.92 (s, 2H), 5.83 (dtt, *J* = 17.4, 10.7, 6.7 Hz, 1H), 5.04–4.95 (m, 2H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.11 (p, *J* = 7.2 Hz, 2H), 1.88 (p, *J* = 7.6 Hz, 2H); ^{13}C NMR (CD_3OD, 150 MHz) δ 172.1, 166.7, 149.1, 139.3, 133.5, 115.5, 38.7, 34.4, 29.1, 23.5; IR (film) ν_{max} 3234, 3077, 2929, 1669, 1588, 1523, 1446, 1380, 1289, 012, 647, 603 cm^{-1}; HRESI-TOF *m/z* 206.1288 ($C_{11}H_{15}N_3O$ + H^+ requires 206.1288).

IV. Reaction of 1,2,3-Triazines with Ynamines

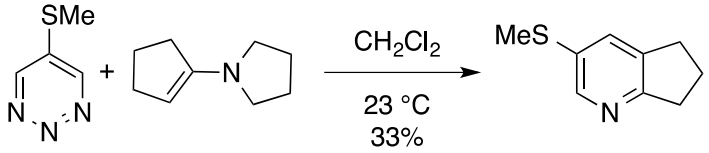


2-Diethylamino-3-methyl-5-(methylthio)pyridine (27a). A 0.15 M solution of ynamine **26a**[8] (11.5 mg, 0.10 mmol) in CCl_4 was treated with 1,2,3-triazine **17** (19.7 mg, 0.16 mmol). The reaction mixture was heated to 80 °C and stirred for 24 h, at which time the mixture was purified by PTLC (SiO_2, 60% CH_2Cl_2/hexanes) to provide **27a** as a light yellow film (8.1 mg, 37%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 2.5 Hz, 1H), 3.18 (q, *J* = 7.1 Hz, 4H), 2.44 (s, 3H), 2.24 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 160.3, 145.4, 140.7, 126.4, 126.3, 45.4, 19.2, 18.4, 13.5; IR (film) ν_{max} 2966, 2919, 2867, 1469, 1422, 1376, 1354, 1254, 1139, 885, 790, 766, 643, 579 cm^{-1}; HRESI-TOF *m/z* 211.1263 ($C_{11}H_{18}N_2S$ + H^+ requires 211.1263).



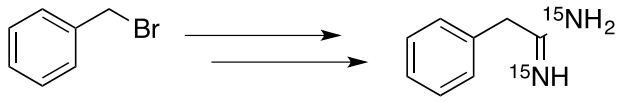
2-Dibenzylamino-3-methyl-5-(methylthio)pyridine (27b). A 0.15 M solution of ynamine **26b**[8] (7.2 mg, 0.031 mmol) in CCl_4 was treated with 1,2,3-triazine **17** (5.8 mg, 0.046 mmol). The reaction mixture was heated to 80 °C and stirred for 24 h, at which time the mixture was purified by PTLC (SiO_2, 50% CH_2Cl_2/hexanes) to provide **27b** as a light yellow film (4.1 mg, 40%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.29–7.25 (m, 8H), 7.23–7.20 (m, 2H), 4.31 (s, 4H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.9, 145.1, 140.4, 139.3, 128.6, 127.7, 127.2, 127.1, 126.2, 54.9, 19.1, 17.9; IR (film) ν_{max} 3028, 2920, 1451, 1422, 1219, 1027, 952, 738, 696 cm^{-1}; HRESI-TOF *m/z* 355.1576 ($C_{21}H_{22}N_2S$ + H^+ requires 355.1576).

V. Reaction of 1,2,3-Triazines with Enamines

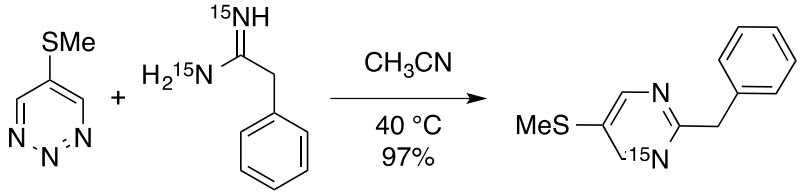


3-(Methylthio)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (29). A 0.15 M solution of enamine **28** (10.0 mg, 0.073 mmol) in CH_2Cl_2 was treated successively with crushed 4 Å molecular sieves (spatula tip, ~15 mg) and 1,2,3-triazine **17** (13.9 mg, 0.11 mmol). The reaction mixture was stirred at 23 °C for 18 h, at which time the mixture was filtered through Celite, concentrated, and purified by PTLC (SiO_2, 60% EtOAc/hexanes) to provide **29** as a light yellow film (4.0 mg, 33%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.28 (s, 1H), 7.44 (s, 1H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.48 (s, 3H), 2.13 (p, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 163.6, 147.1, 137.7, 132.3, 132.2, 34.1, 31.0, 23.7, 17.4; IR (film) ν_{max} 2953, 2920, 1553, 1453, 1433, 1212, 902, 716 cm^{-1}; HRESI-TOF *m/z* 166.0686 ($C_9H_{11}NS$ + H^+ requires 166.0685).

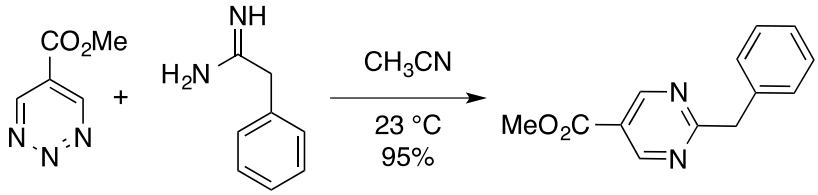
VI. Labeling Study



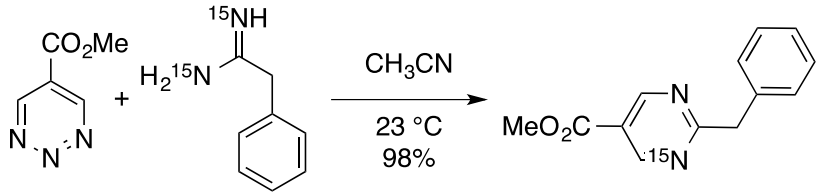
2-Phenylacetimidamide-$^{15}N_2$ (^{15}N-20g). Compound **^{15}N-20g** was prepared as described elsewhere.[9]



2-Benzyl-5-(methylthio)pyrimidine-^{15}N (24). A 0.15 M solution of amidine **^{15}N-20g** (10.0 mg, 0.073 mmol) in CH_3CN was treated with 1,2,3-triazine **17** (14.0 mg, 0.11 mmol). The reaction mixture was heated to 40 °C and stirred for 24 h, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **24** as a white solid (15.4 mg, 97%): mp 53–55 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.57 (s, 2H), 7.35–7.34 (m, 2H), 7.30 (dd, J = 8.5, 6.8 Hz, 2H), 7.23–7.21 (m, 1H), 4.26 (s, 2H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 167.3, 156.1, 138.5, 131.4, 129.4, 128.9, 127.0, 45.8, 16.4; IR (film) ν_{max} 2919, 1535, 1494, 1426, 1376, 1120, 1028, 749, 699, 671, 646, 585 cm^{-1}; HRESI-TOF *m/z* 218.0776 ($C_{12}H_{12}N^{15}NS$ + H^+ requires 218.0765).



Methyl 2-benzylpyrimidine-5-carboxylate (S2). A 0.15 M solution of amidine **20g** (10.0 mg, 0.073 mmol) in CH_3CN was treated with 1,2,3-triazine **4** (15.3 mg, 0.11 mmol). The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **S2** as a white solid (16.0 mg, 95%): mp 81–83 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.20 (s, 2H), 7.37–7.35 (m, 2H), 7.32–7.30 (m, 2H), 7.25–7.22 (m, 1H), 4.36 (s, 2H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.7, 164.6, 158.8, 137.7, 129.5, 129.0, 127.2, 121.8, 52.9, 46.5; IR (film) ν_{max} 1719, 1579, 1419, 1290, 1270, 1192, 1028, 746, 699, 582 cm^{-1}; HRESI-TOF *m/z* 229.0970 ($C_{13}H_{12}N_2O_2$ + H^+ requires 229.0971).



Methyl 2-benzylpyrimidine-5-carboxylate-^{15}N (26). A 0.15 M solution of amidine **^{15}N-20g** (10.0 mg, 0.073 mmol) in CH_3CN was treated with 1,2,3-triazine **4** (15.3 mg, 0.11 mmol). The reaction mixture was stirred at 23 °C for 10 min, at which time the mixture was purified by flash chromatography (SiO_2, 20% EtOAc/hexanes) to provide **26** as a white solid (16.4 mg, 98%): mp 81–83 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.20 (s, 2H), 7.37–7.35 (m, 2H), 7.32–7.30 (m, 2H), 7.25–7.22 (m, 1H), 4.36 (s, 2H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.7, 164.6, 158.8, 137.7, 129.5, 129.0, 127.2, 121.8, 52.9, 46.5; IR (film) ν_{max} 1719, 1579, 1419, 1290, 1270, 1192, 1028, 746, 699, 582 cm^{-1}; HRESI-TOF *m/z* 230.0946 ($C_{13}H_{12}N^{15}NO_2$ + H^+ requires 230.0942).

VII. References

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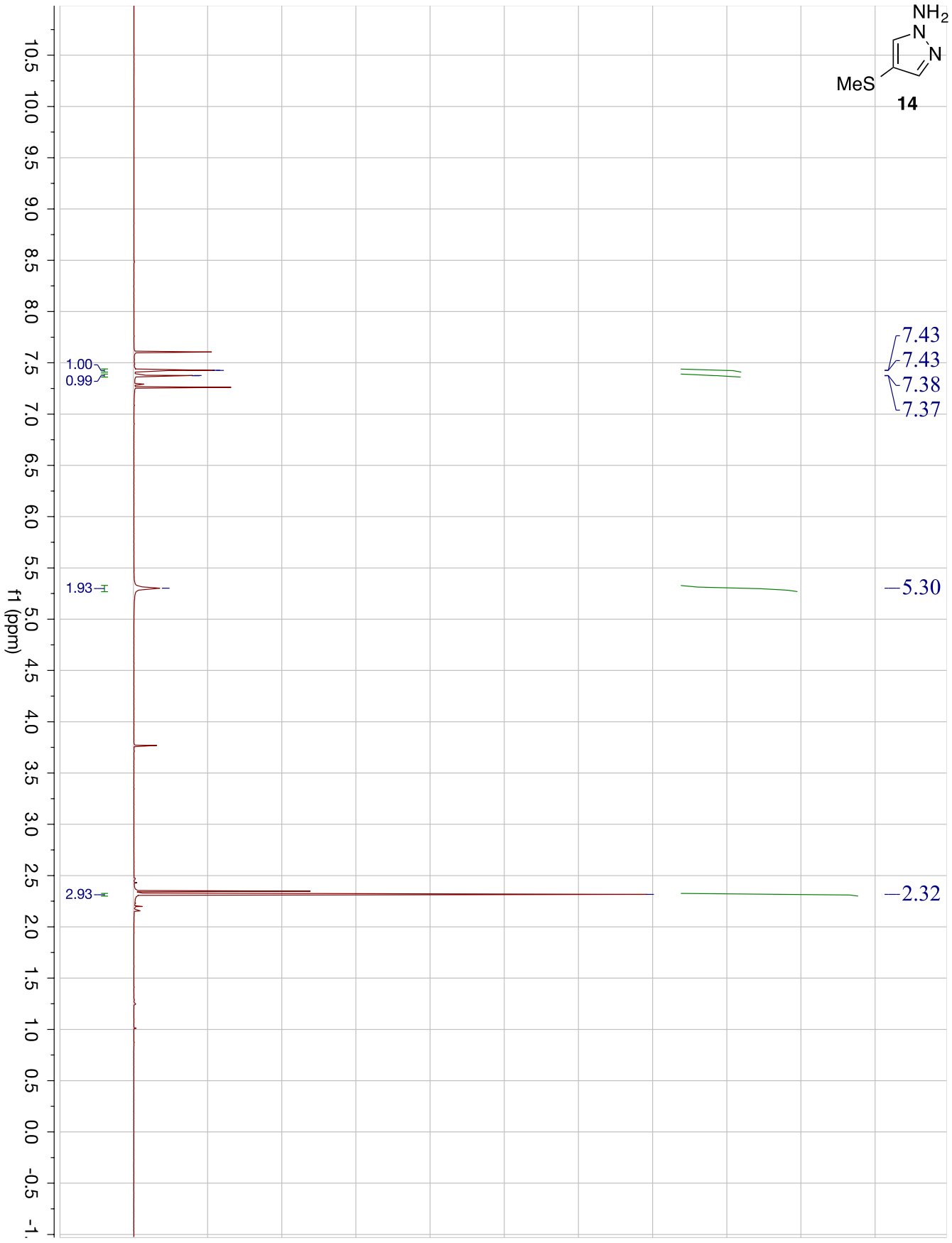
VIII. ^{1}H NMR Spectra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7.38
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2.32
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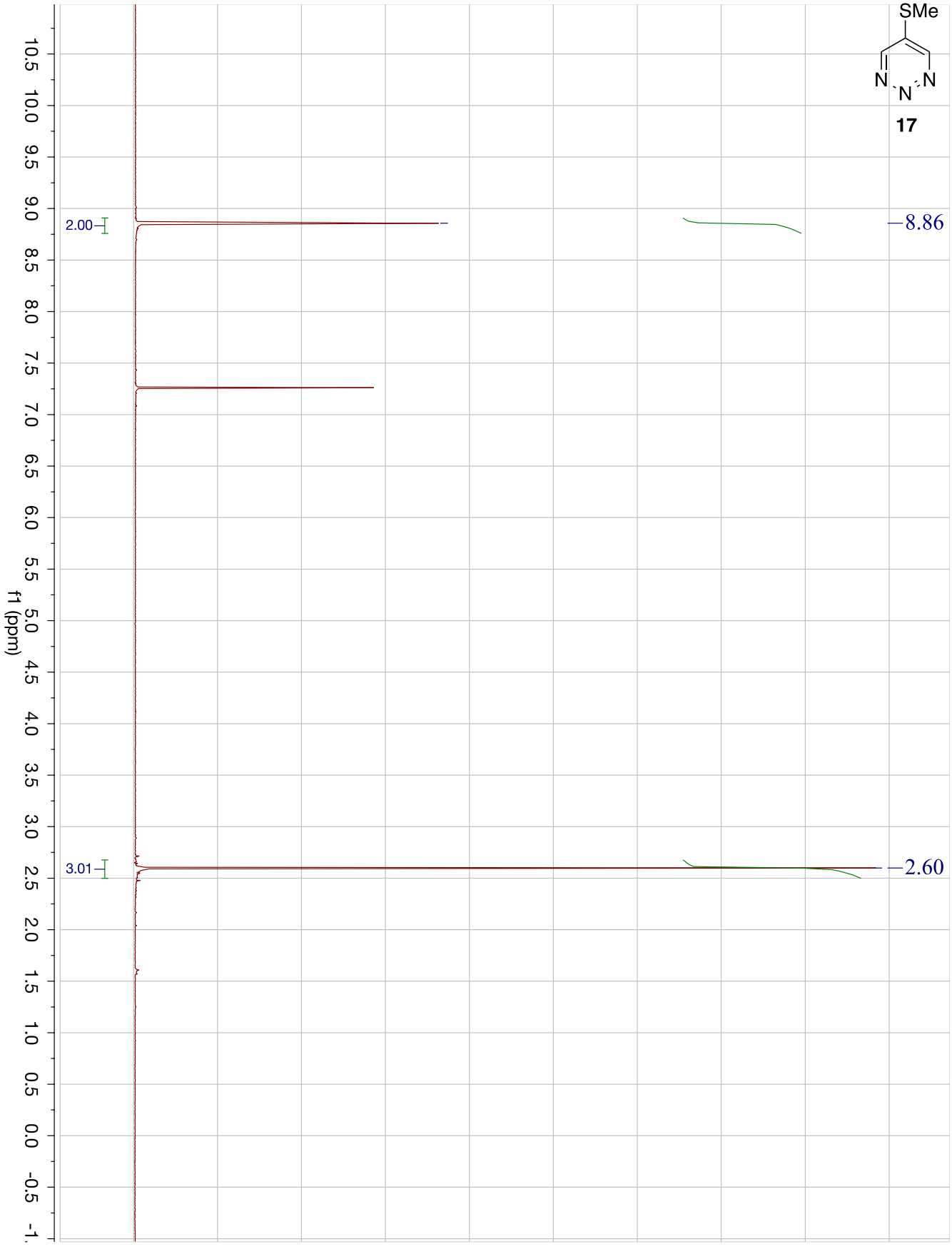
0.99
1.93
2.93
f1 (ppm)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17
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f1 (ppm)
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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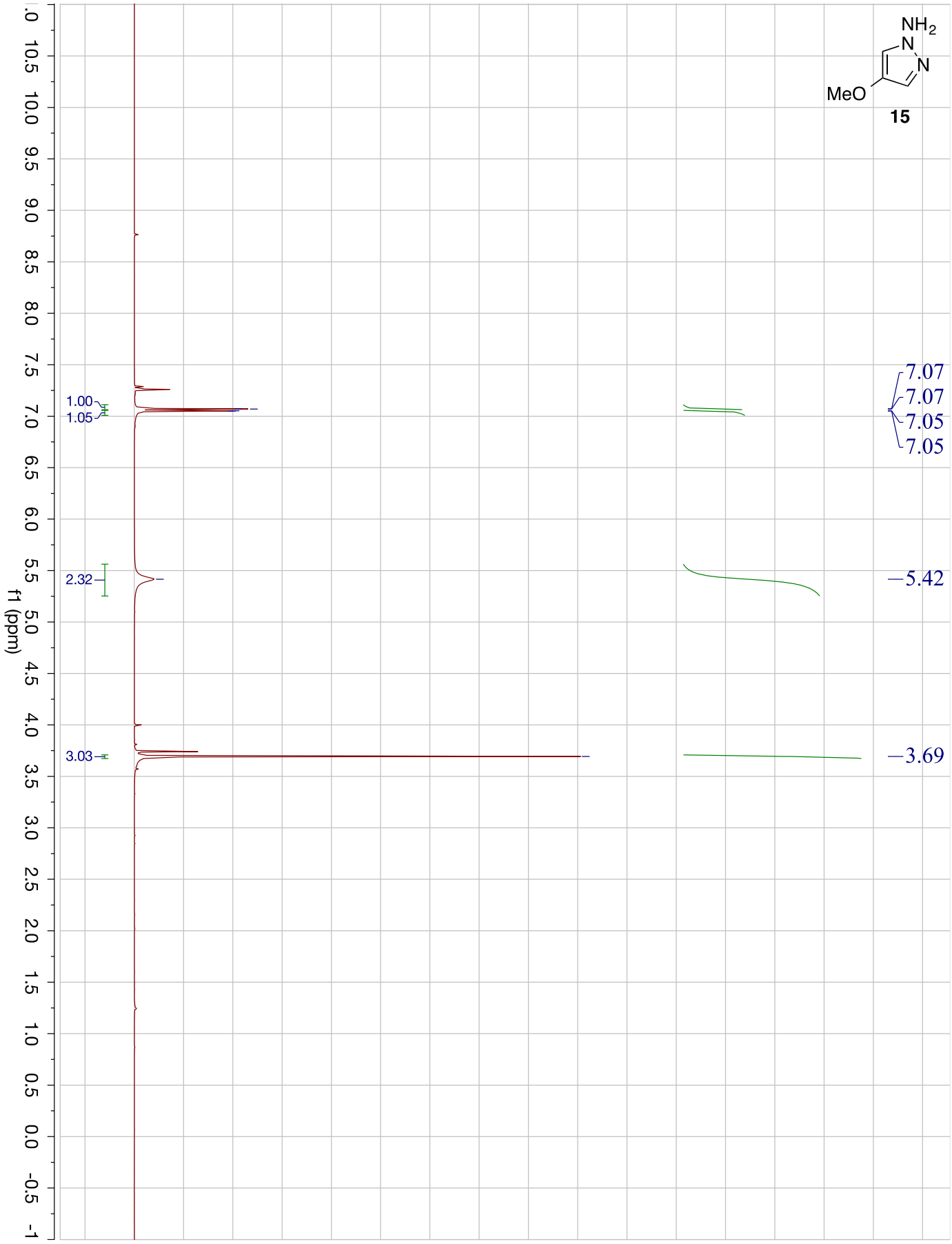
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.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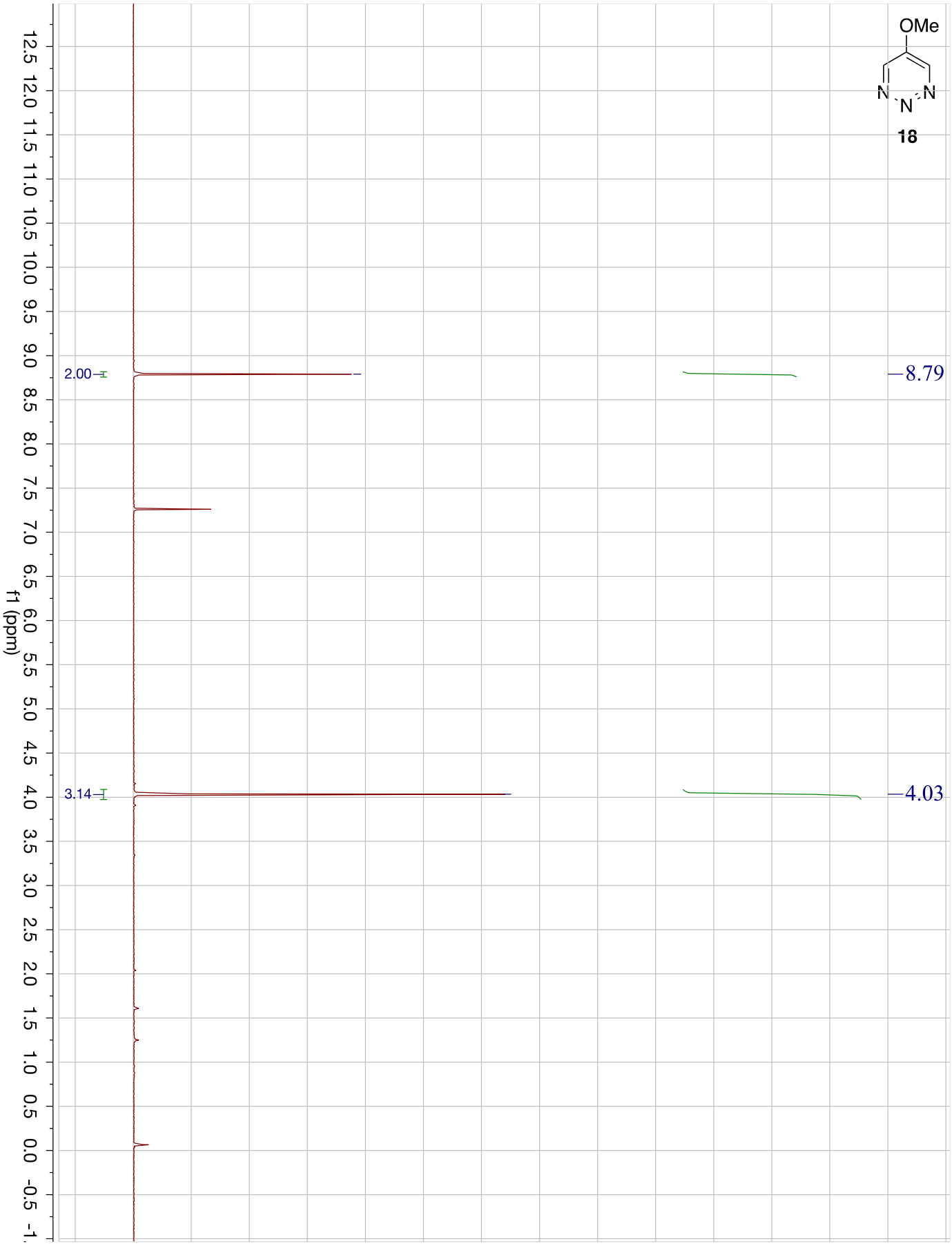
3.03
f1 (ppm)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18
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4.03
f1 (ppm)
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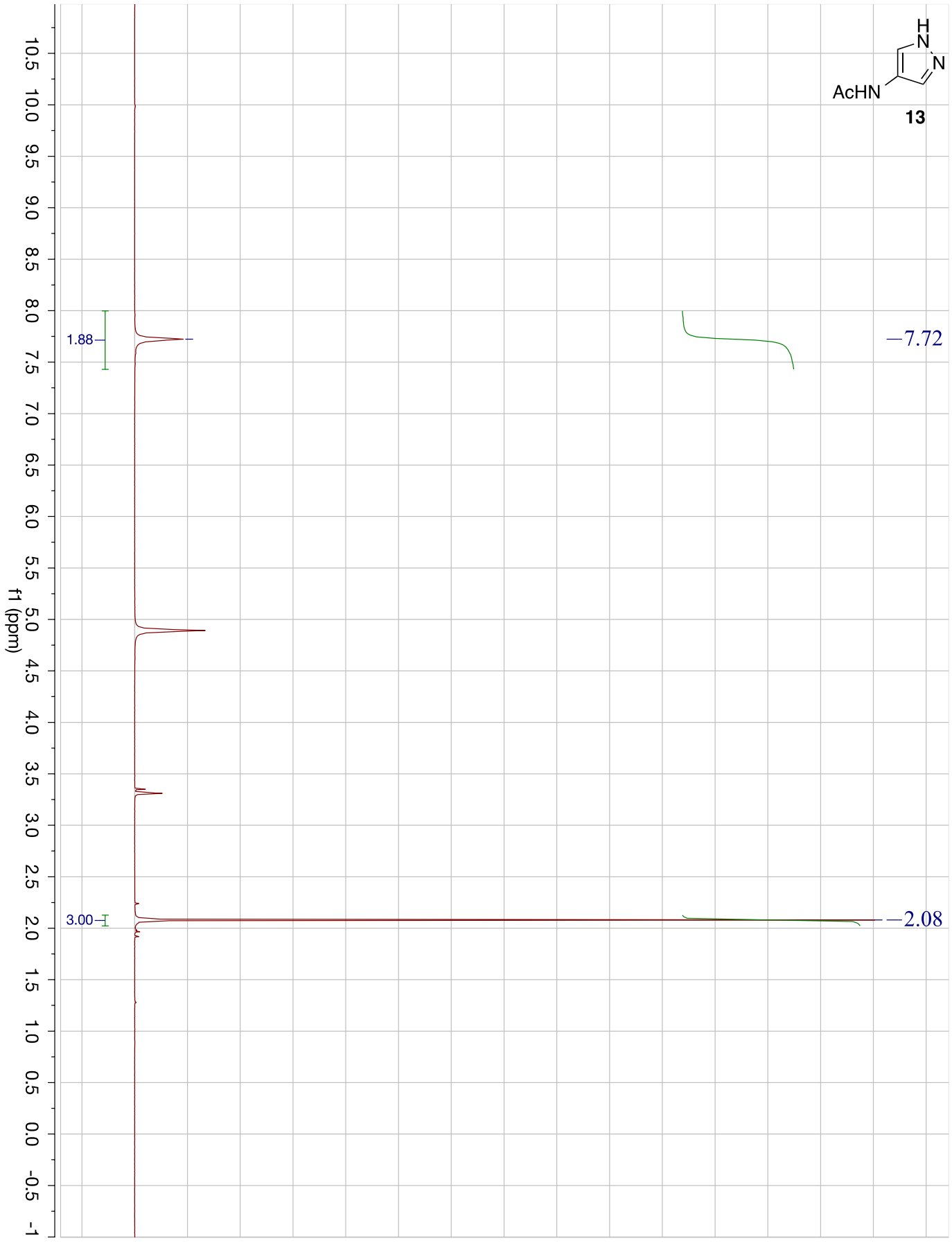
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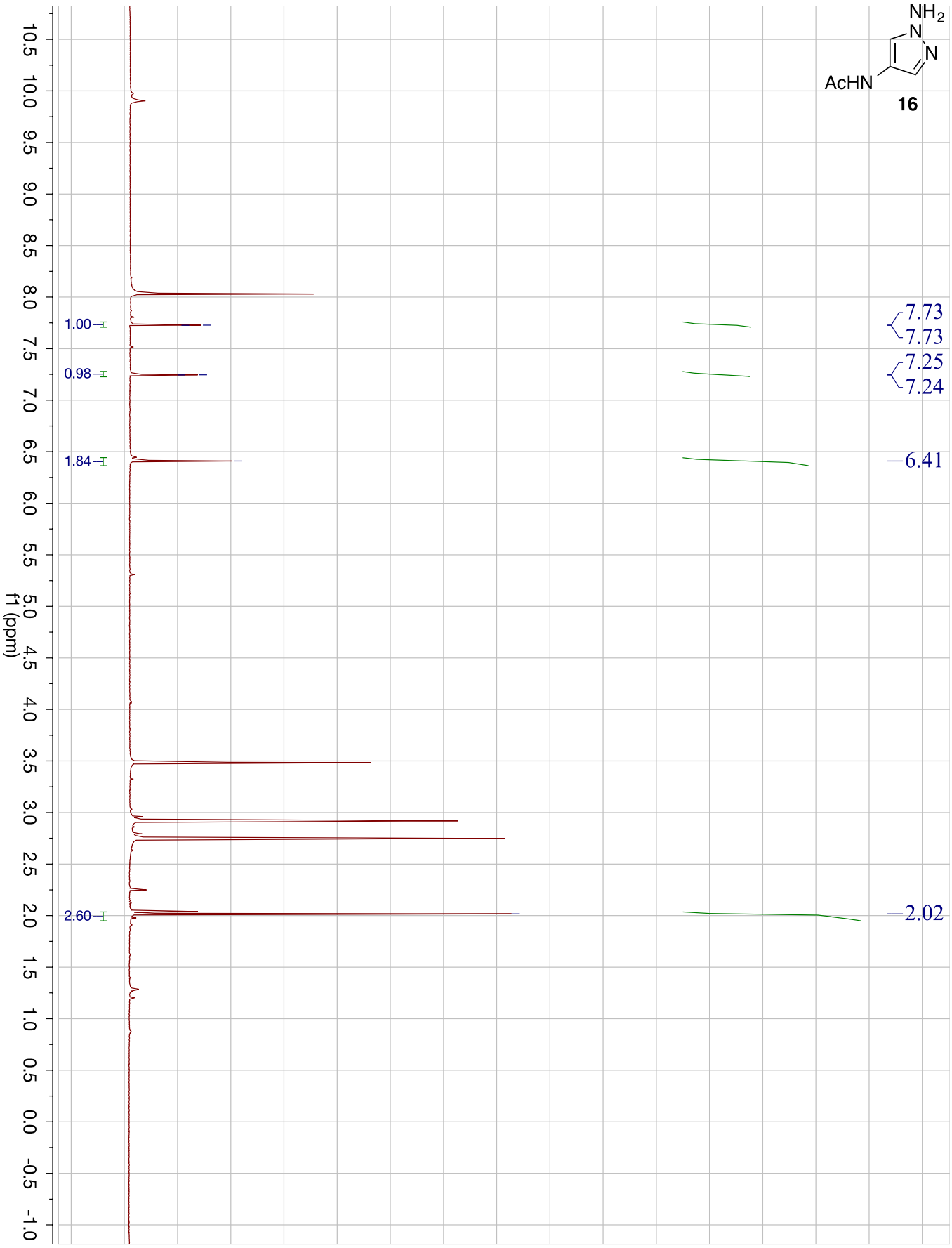
7.72
2.08
f1 (ppm)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N
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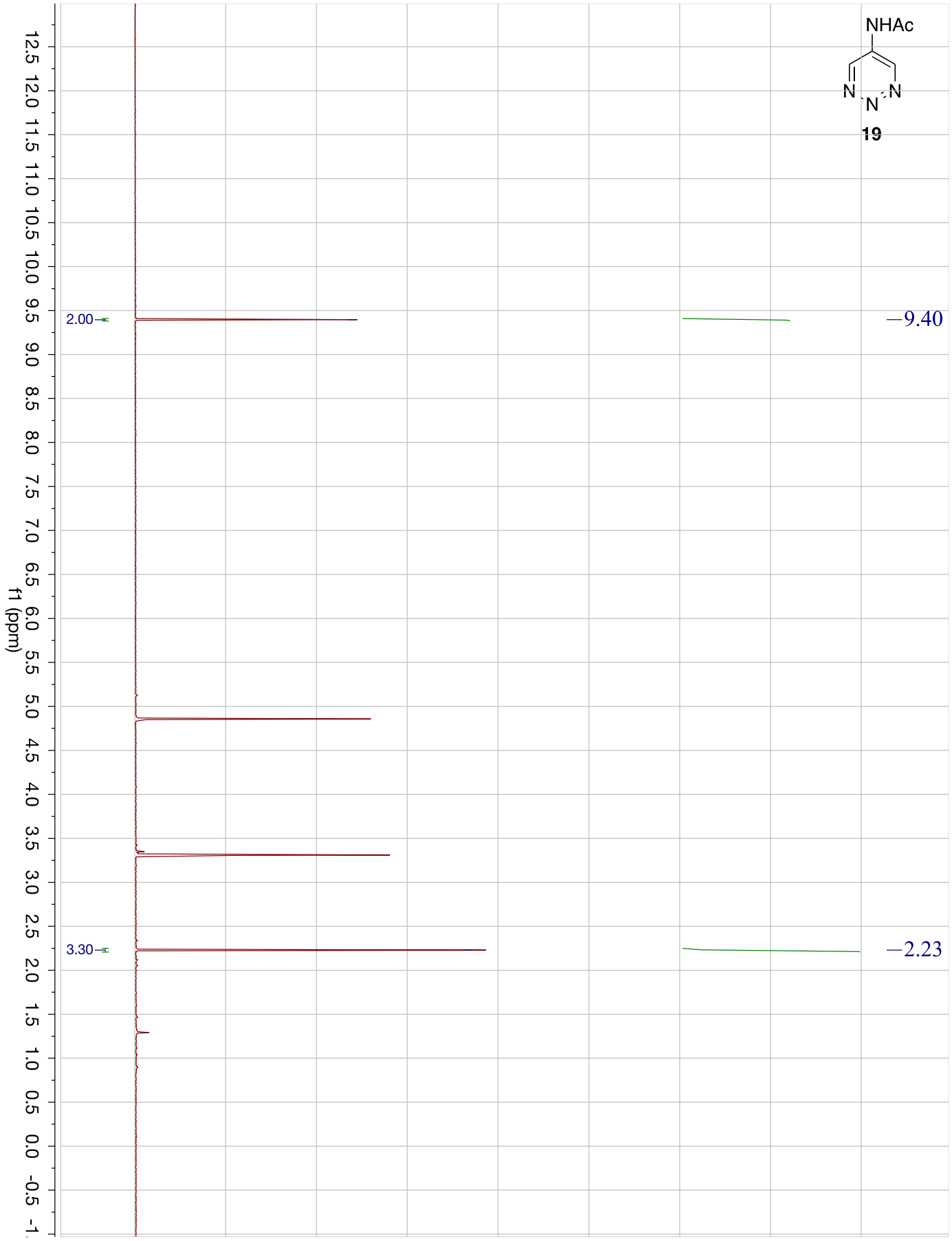
f1 (ppm)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2.23
f1 (ppm)
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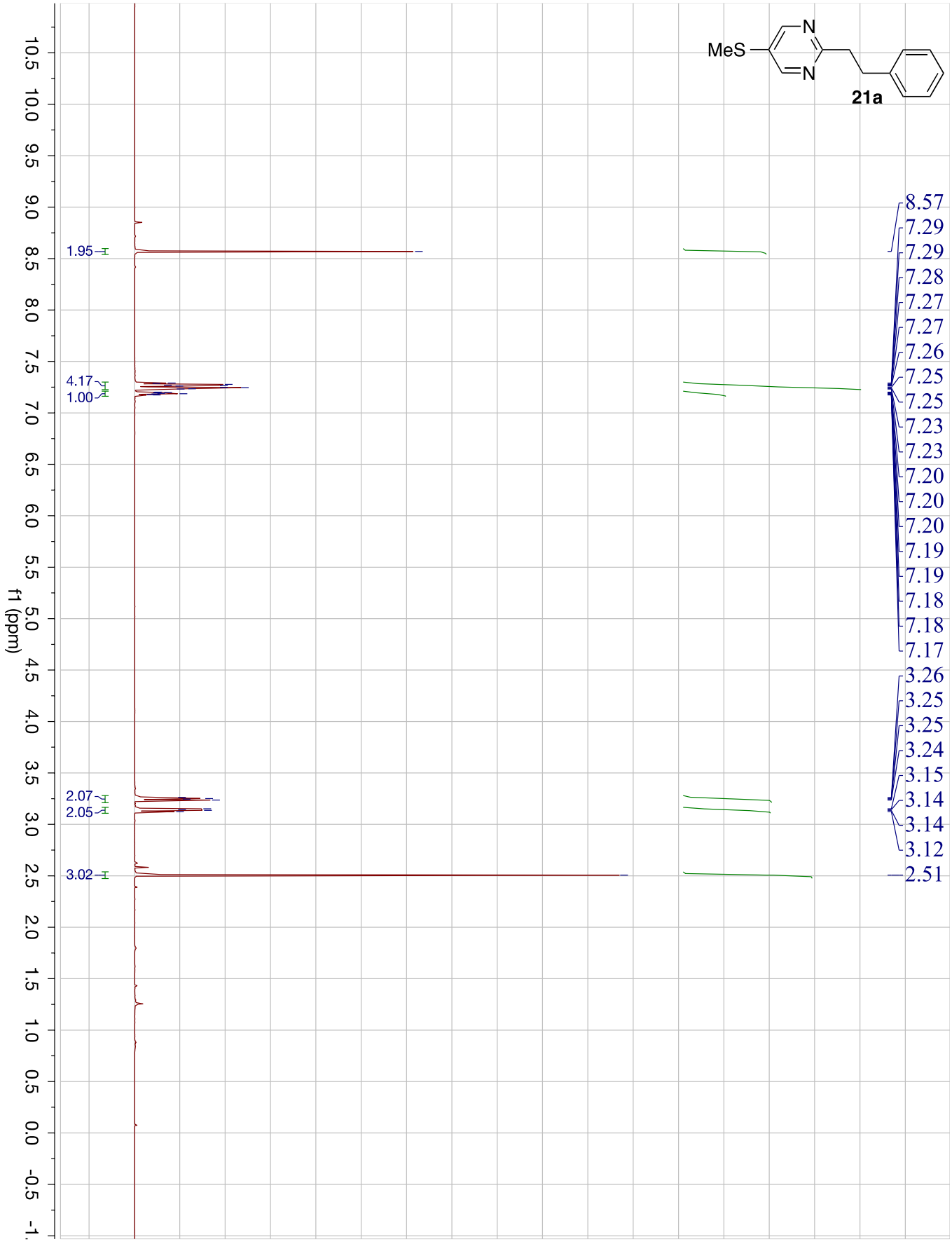
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N
21a
f1 (ppm)
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1.95
4.17
1.00
2.07
2.05
3.02
8.57
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.23
7.23
7.20
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7.19
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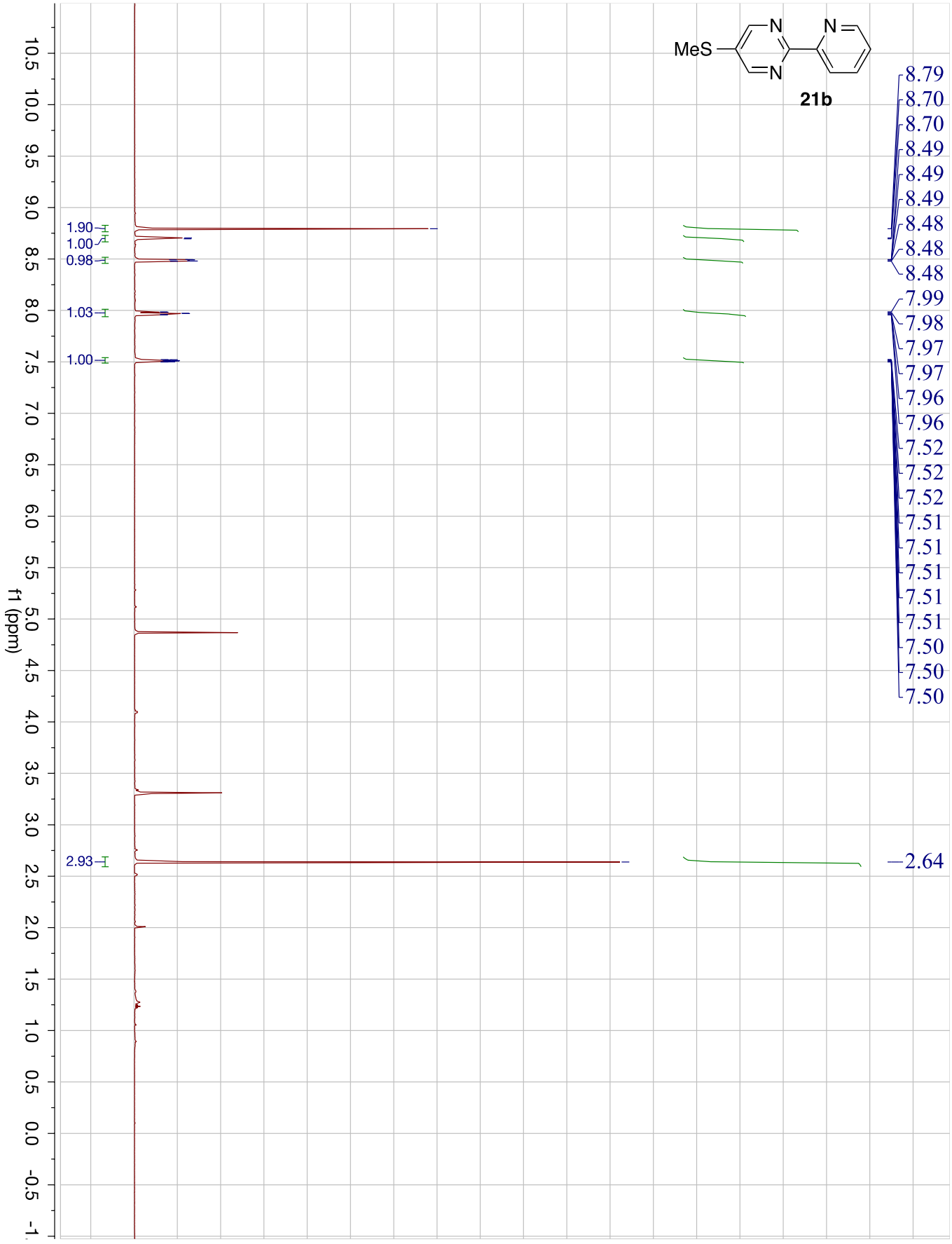
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7.52
7.51
7.51
7.51
7.51
7.51
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7.50
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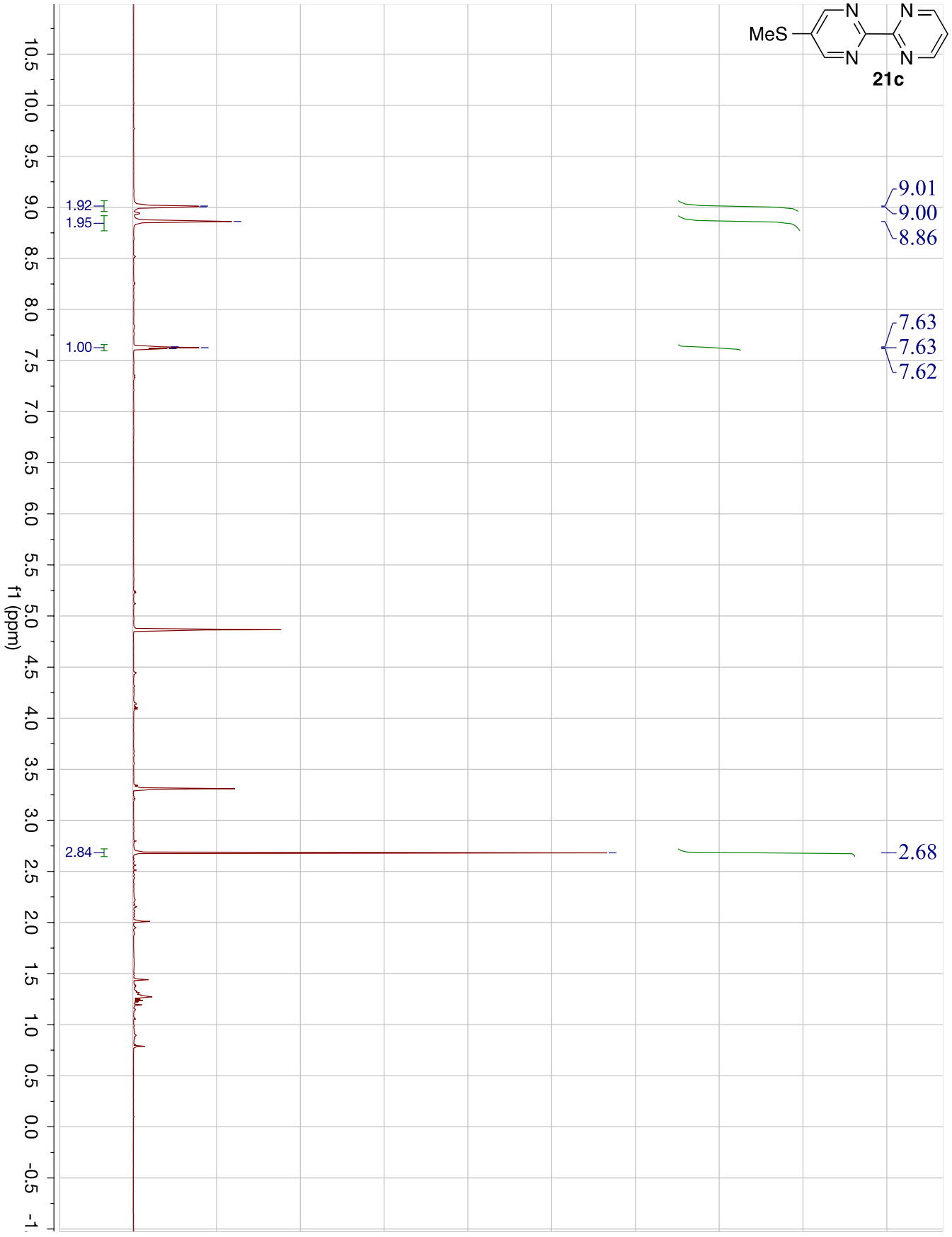
2.93
f1 (ppm)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1.00
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f1 (ppm)
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10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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3.0
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1.0
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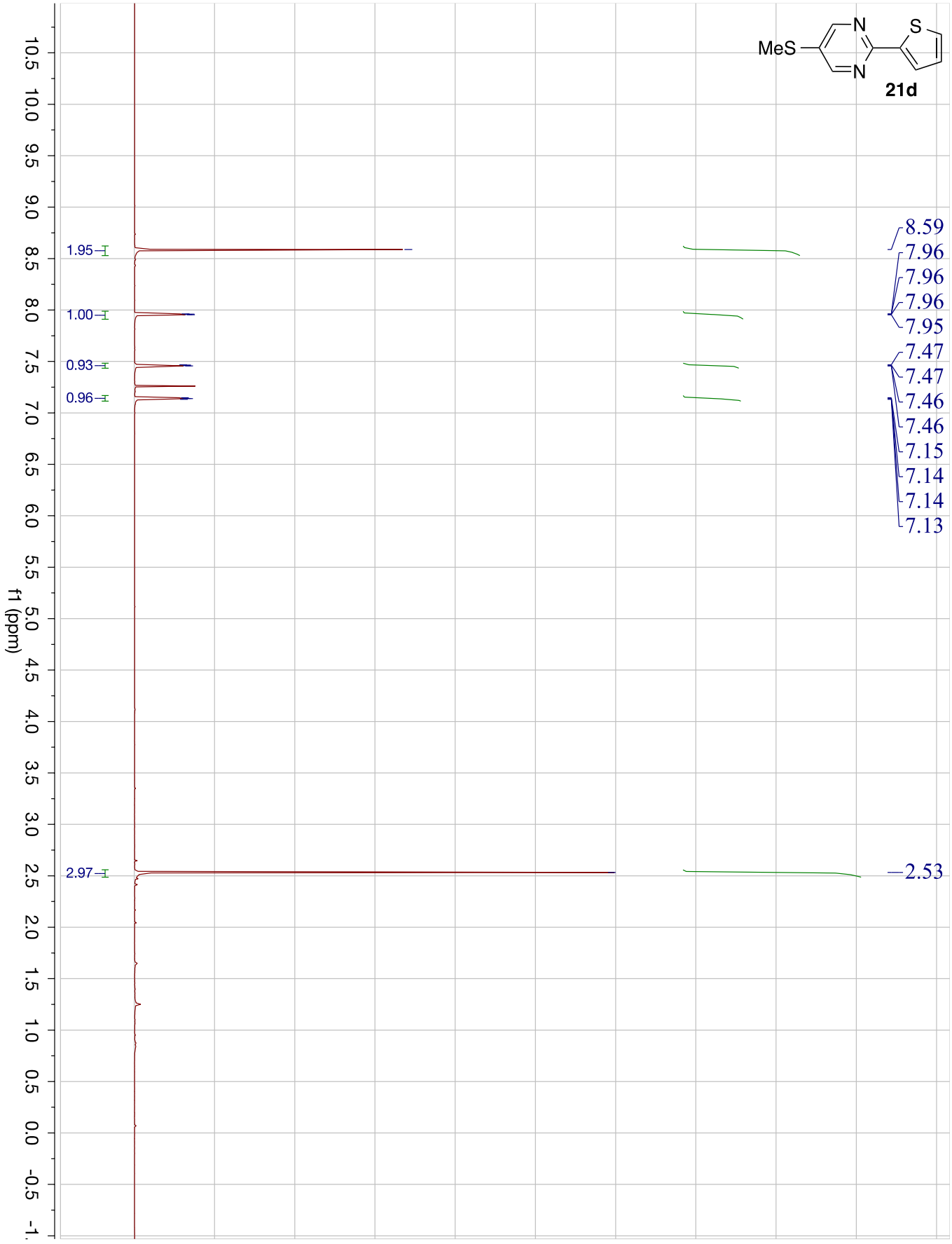
-1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7.14
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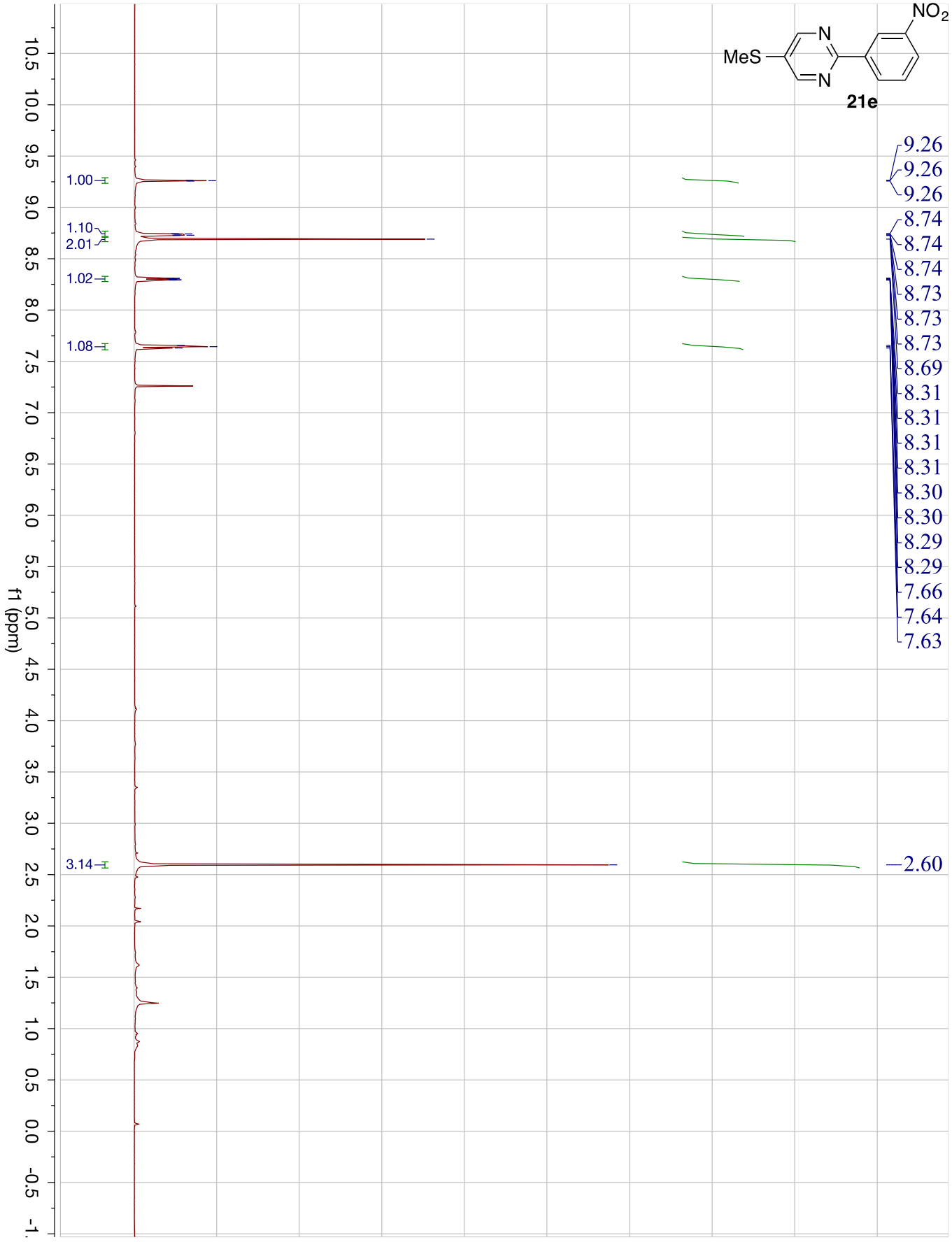
2.97
f1 (ppm)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8.31
8.31
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8.30
8.30
8.29
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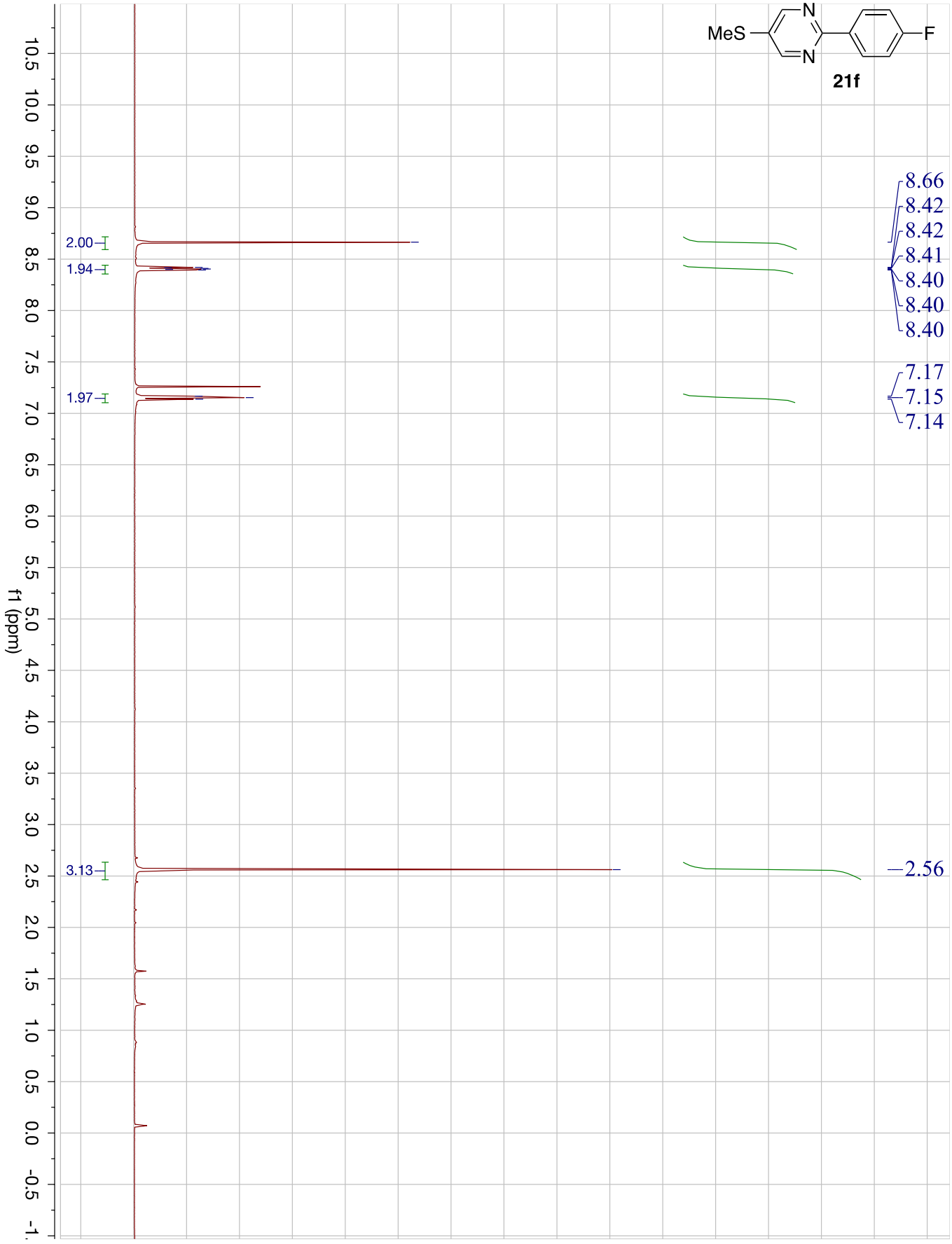
3.14
f1 (ppm)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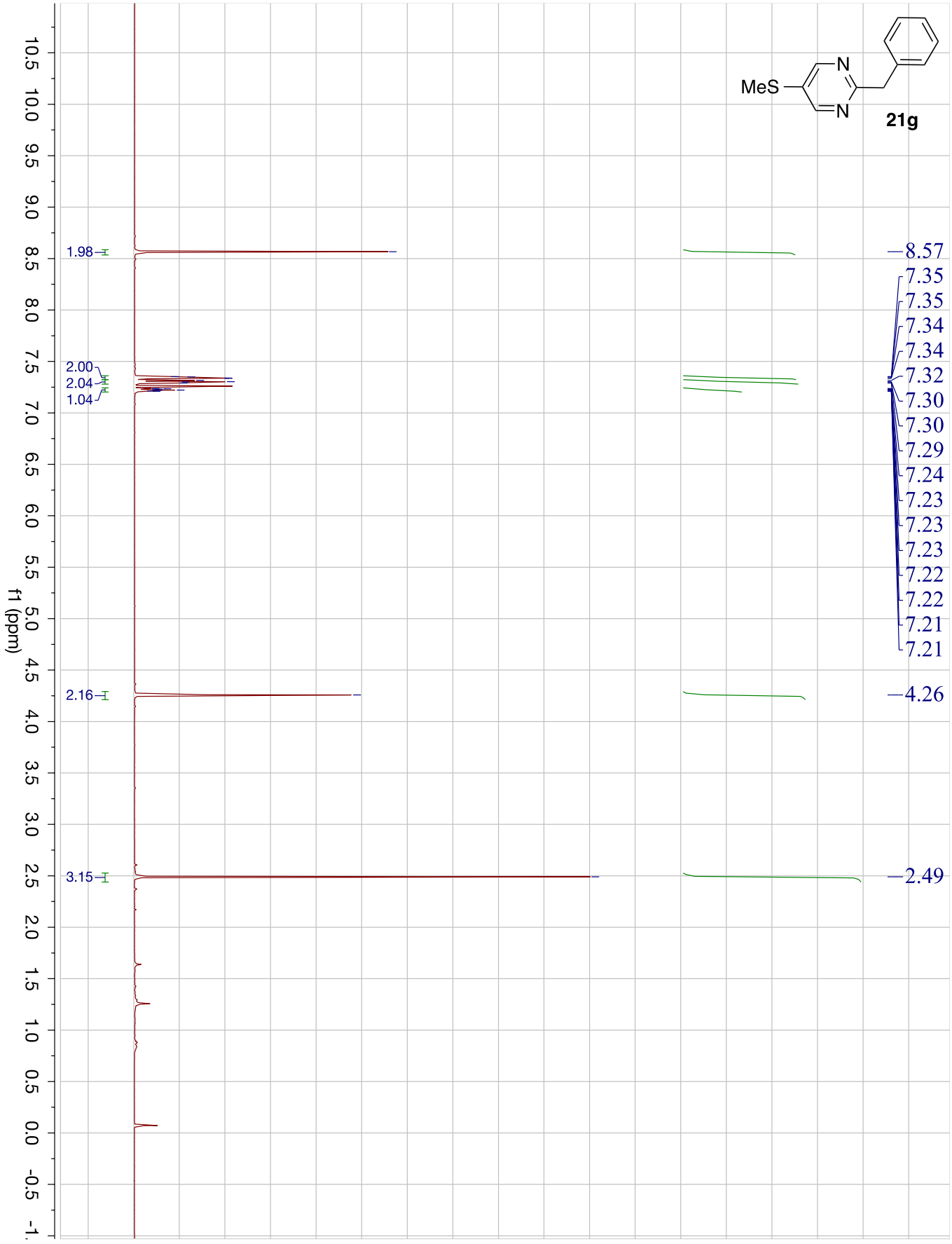
f1 (ppm)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7.32
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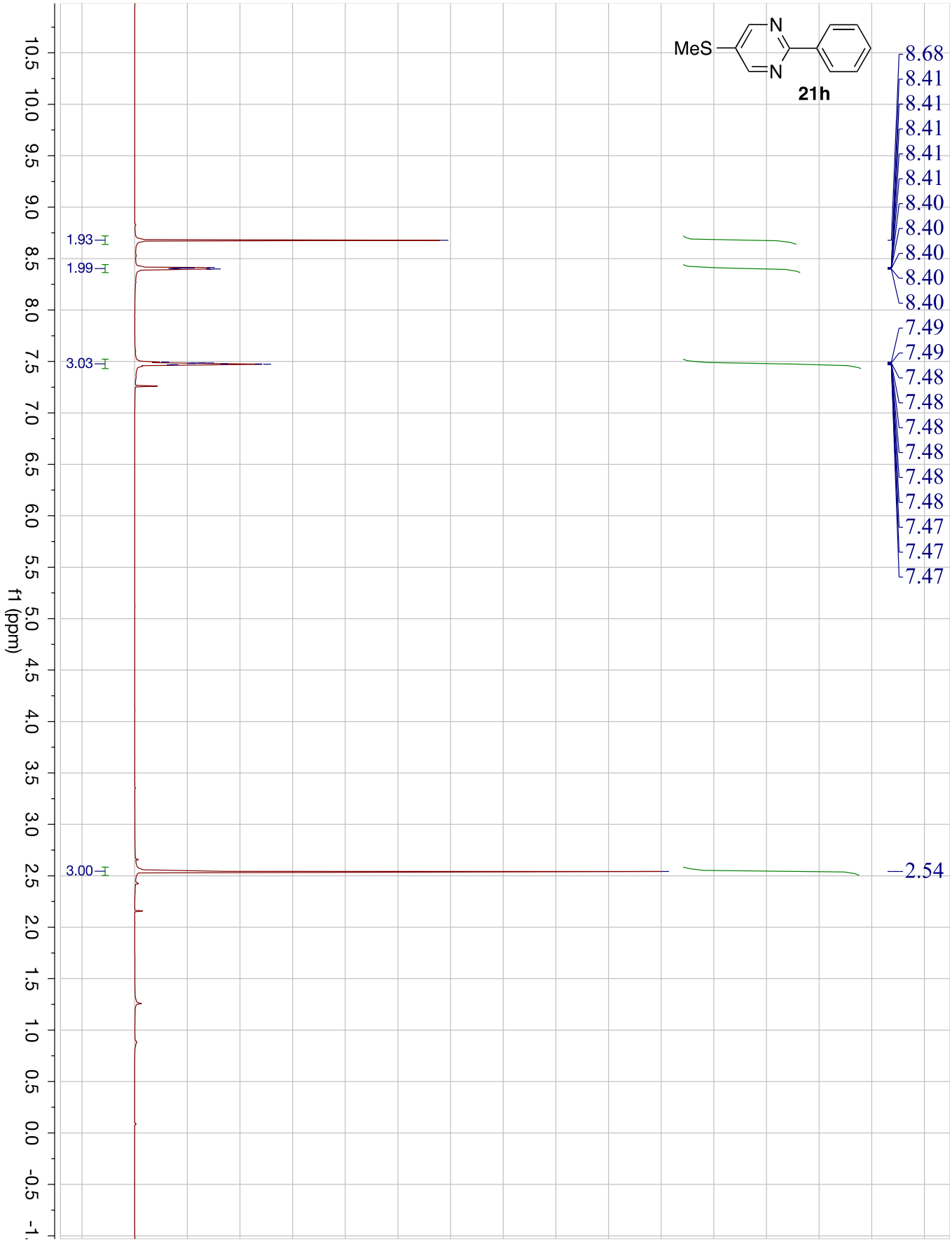
f1 (ppm)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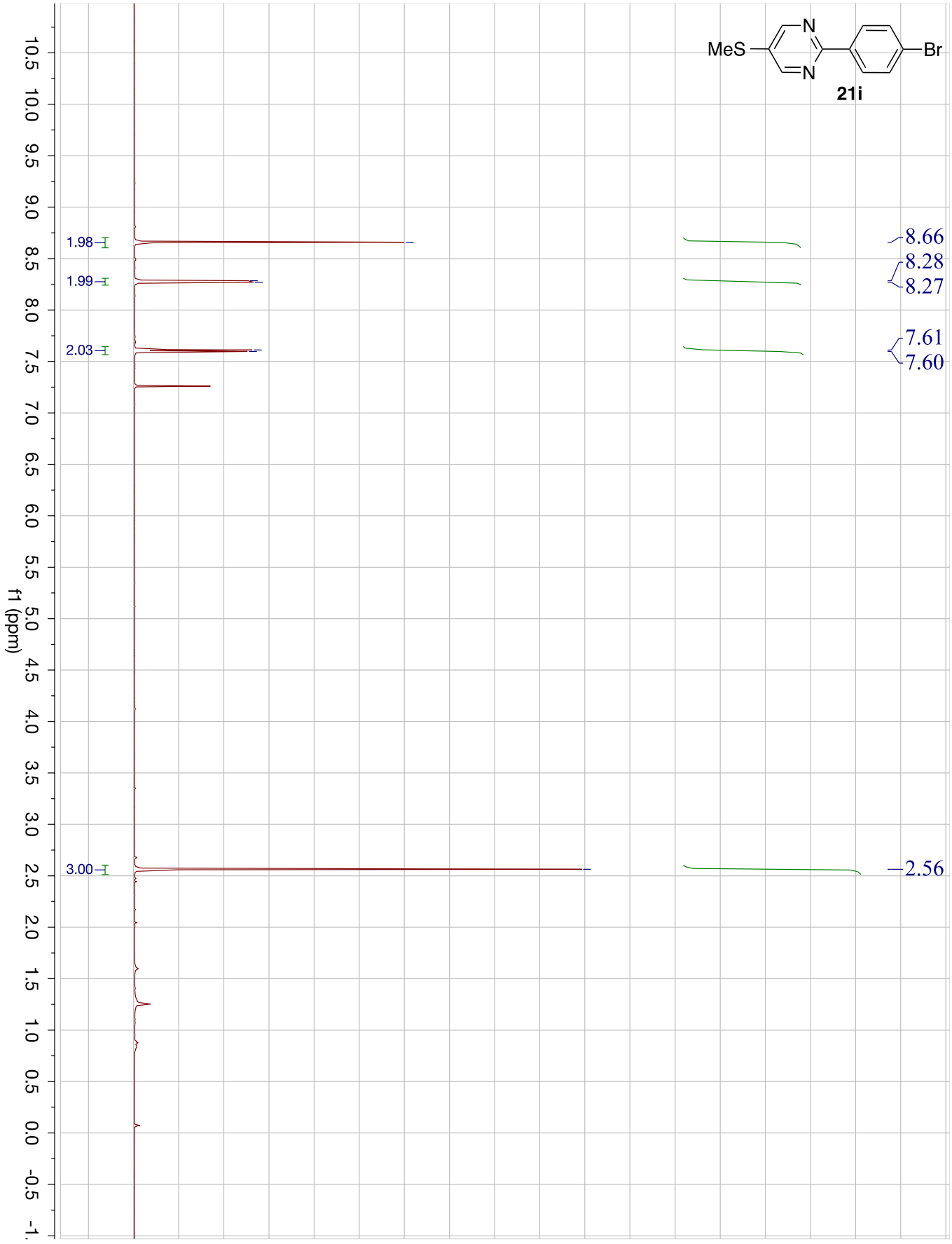
f1 (ppm)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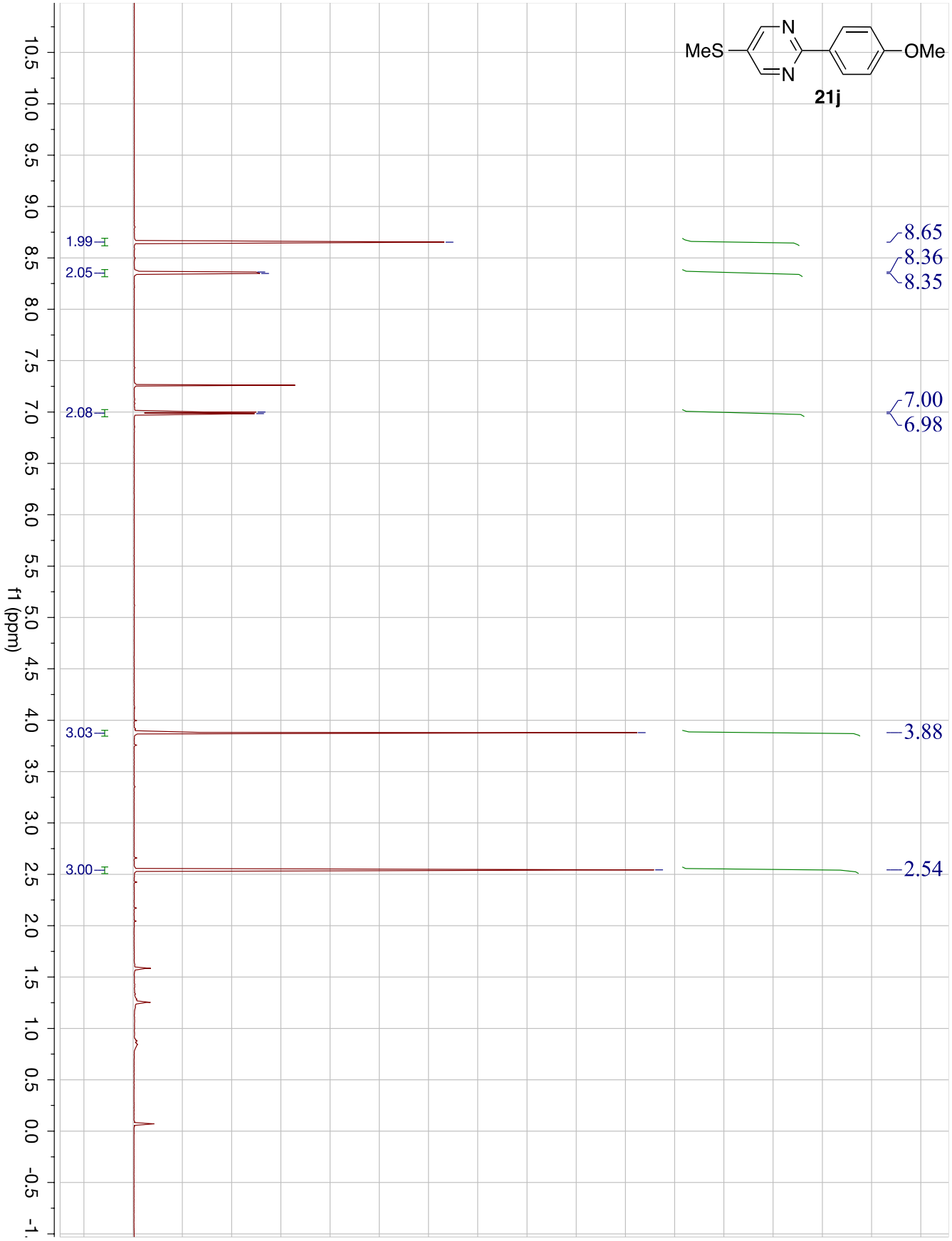
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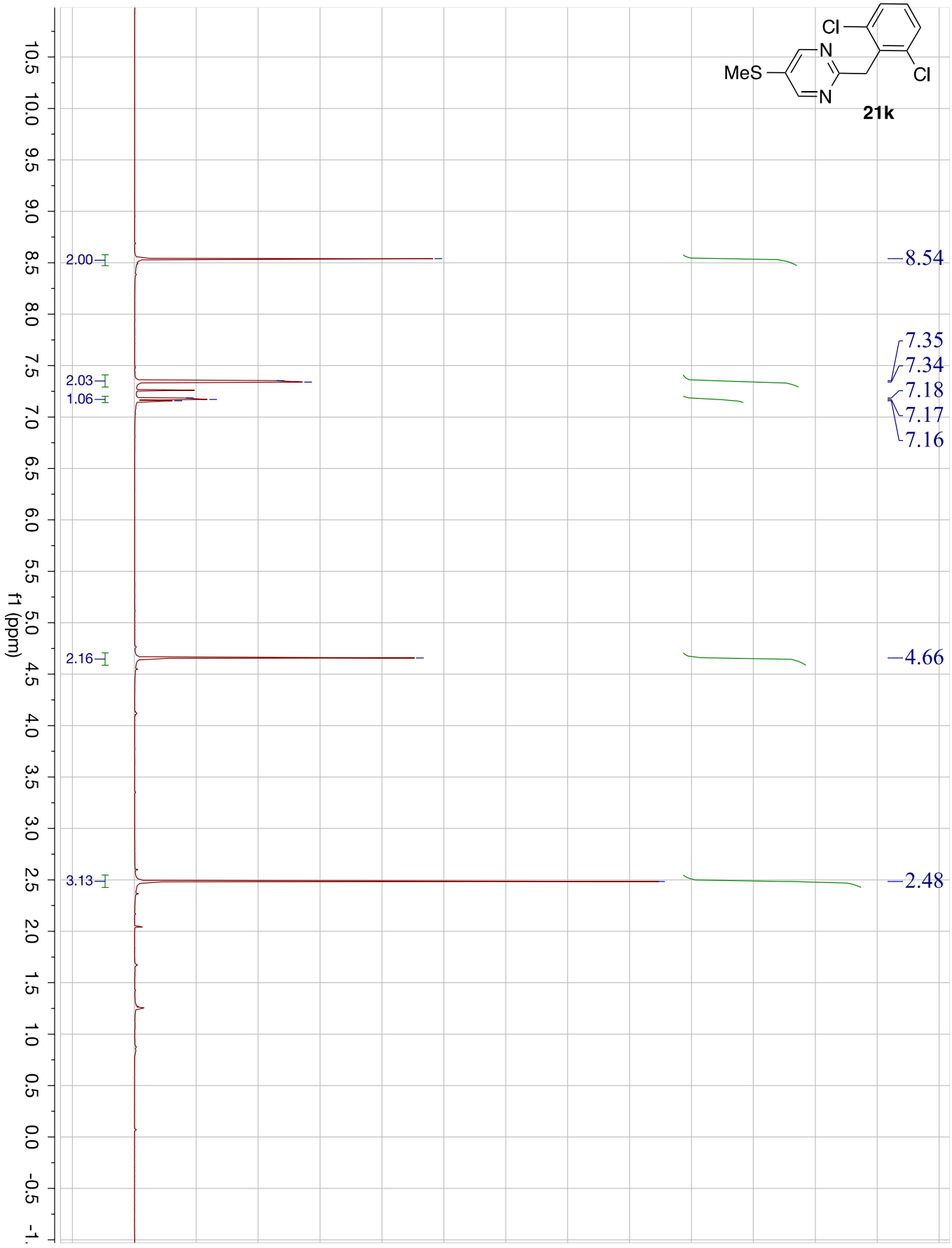
f1 (ppm)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N
MeS
N
Cl
21k
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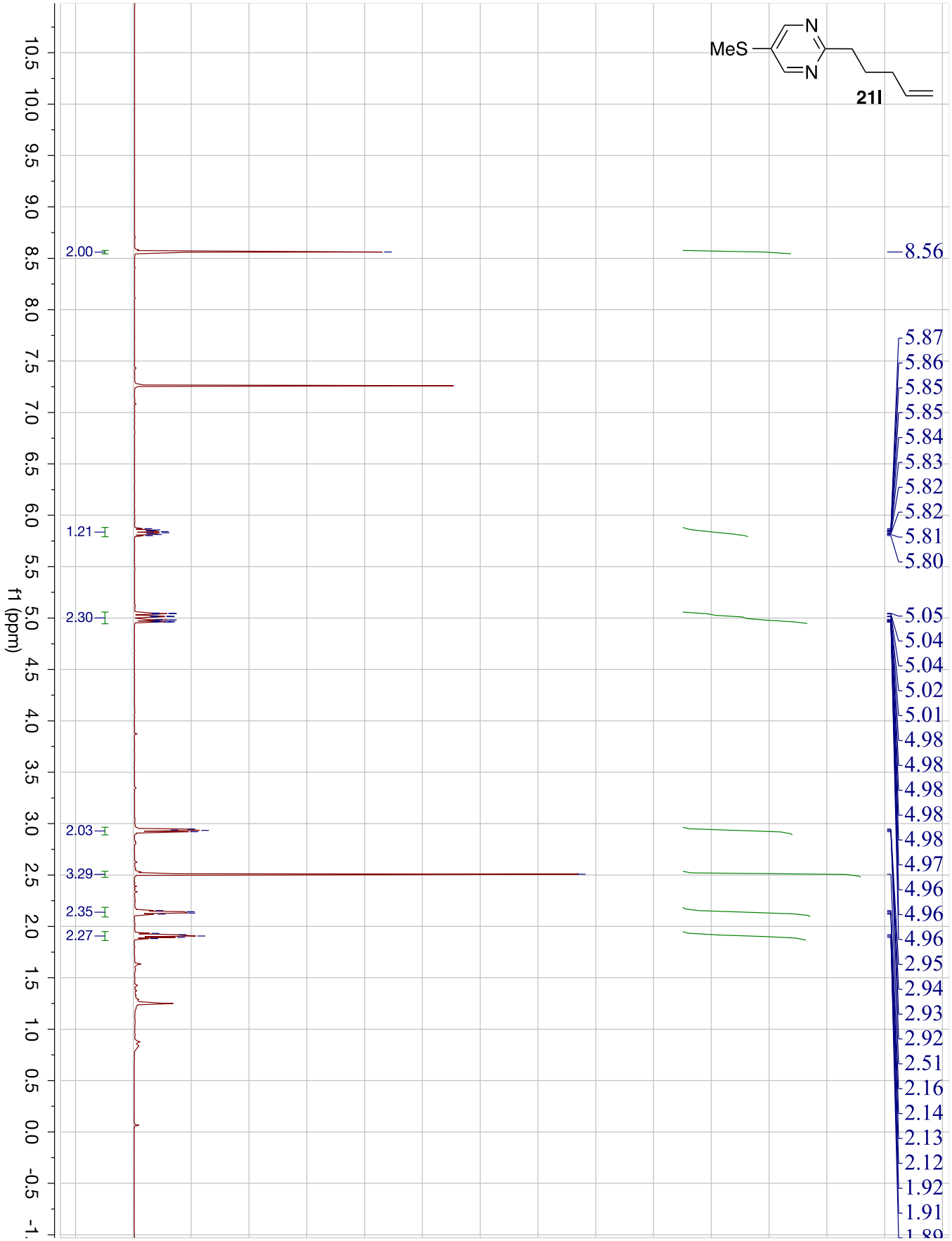
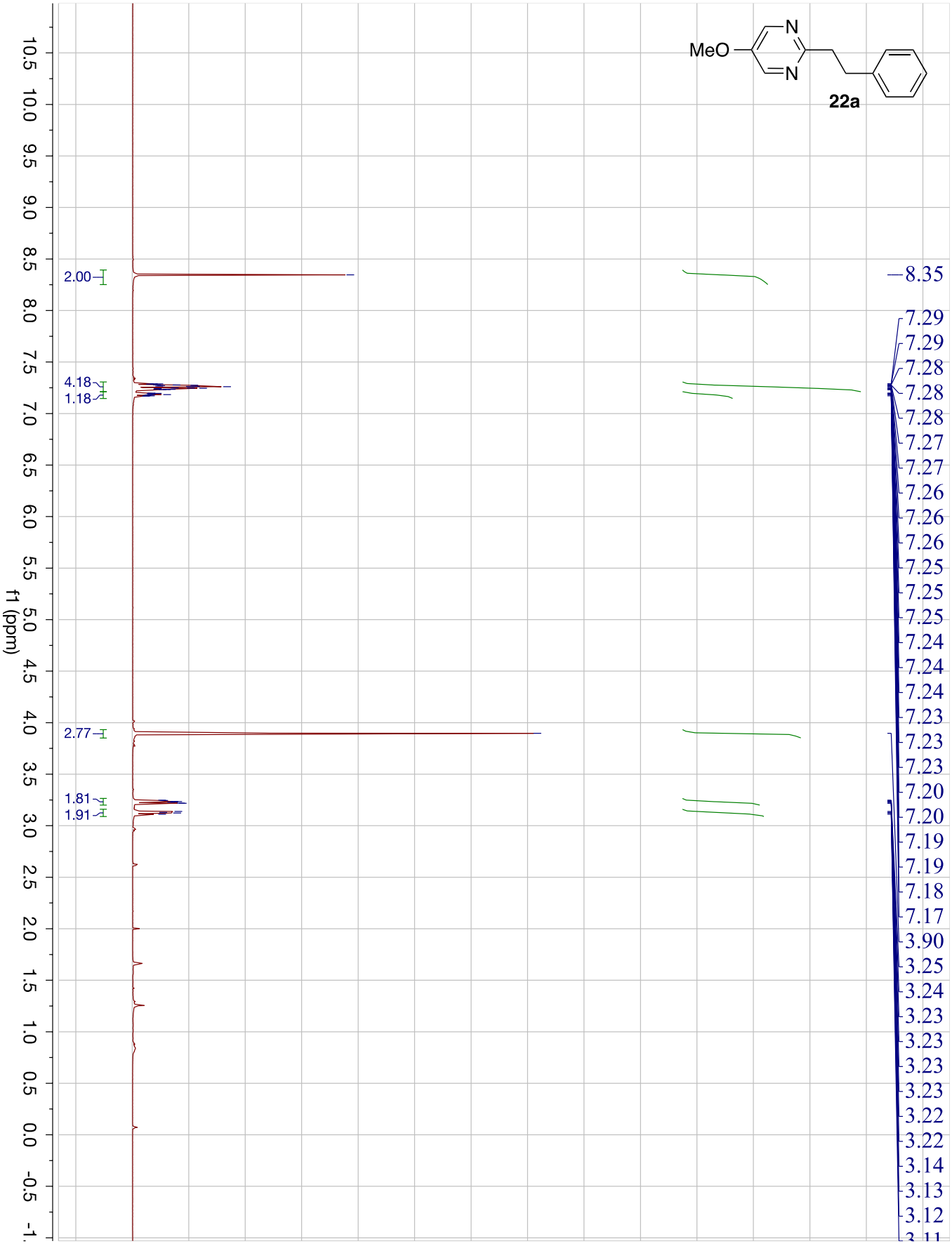
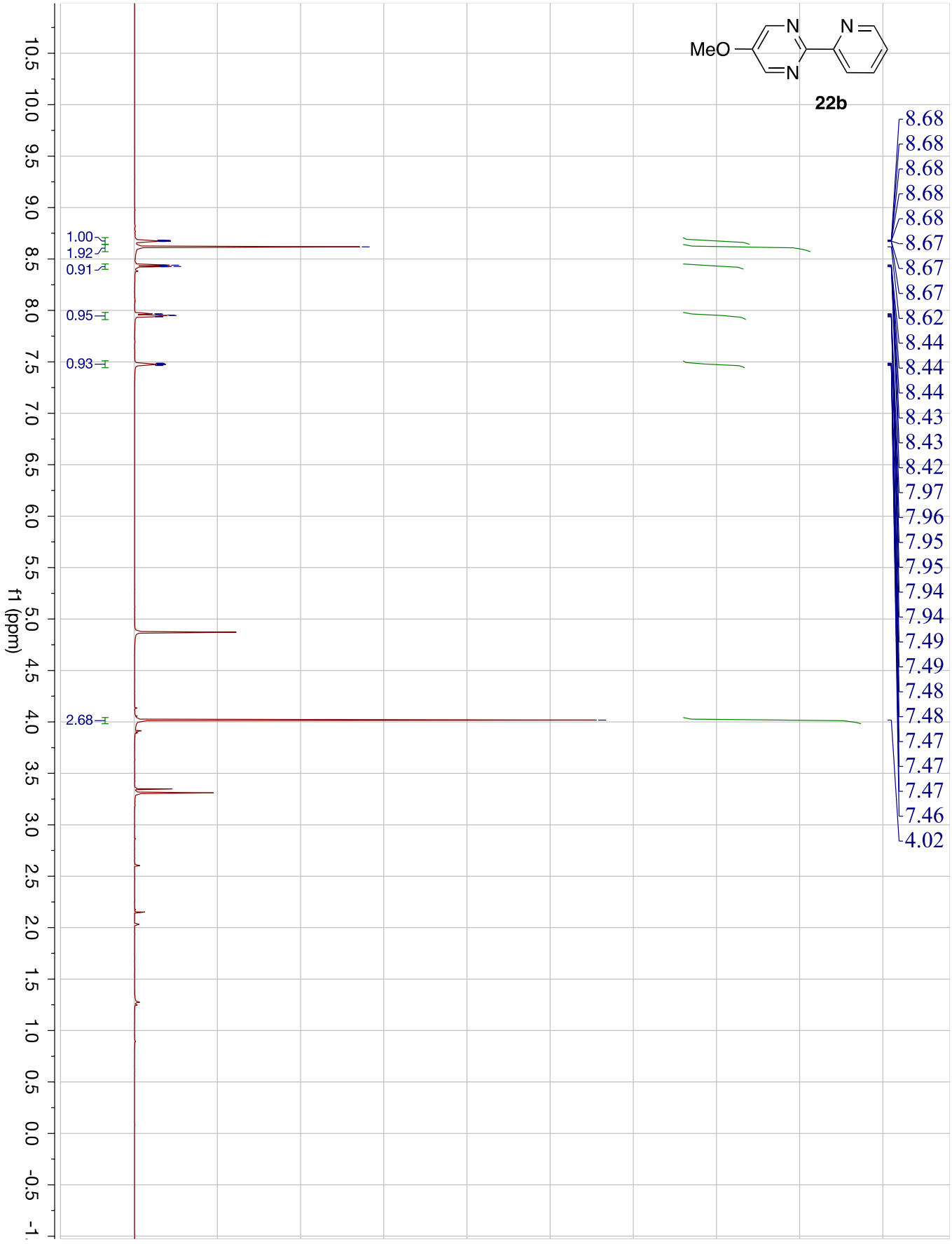
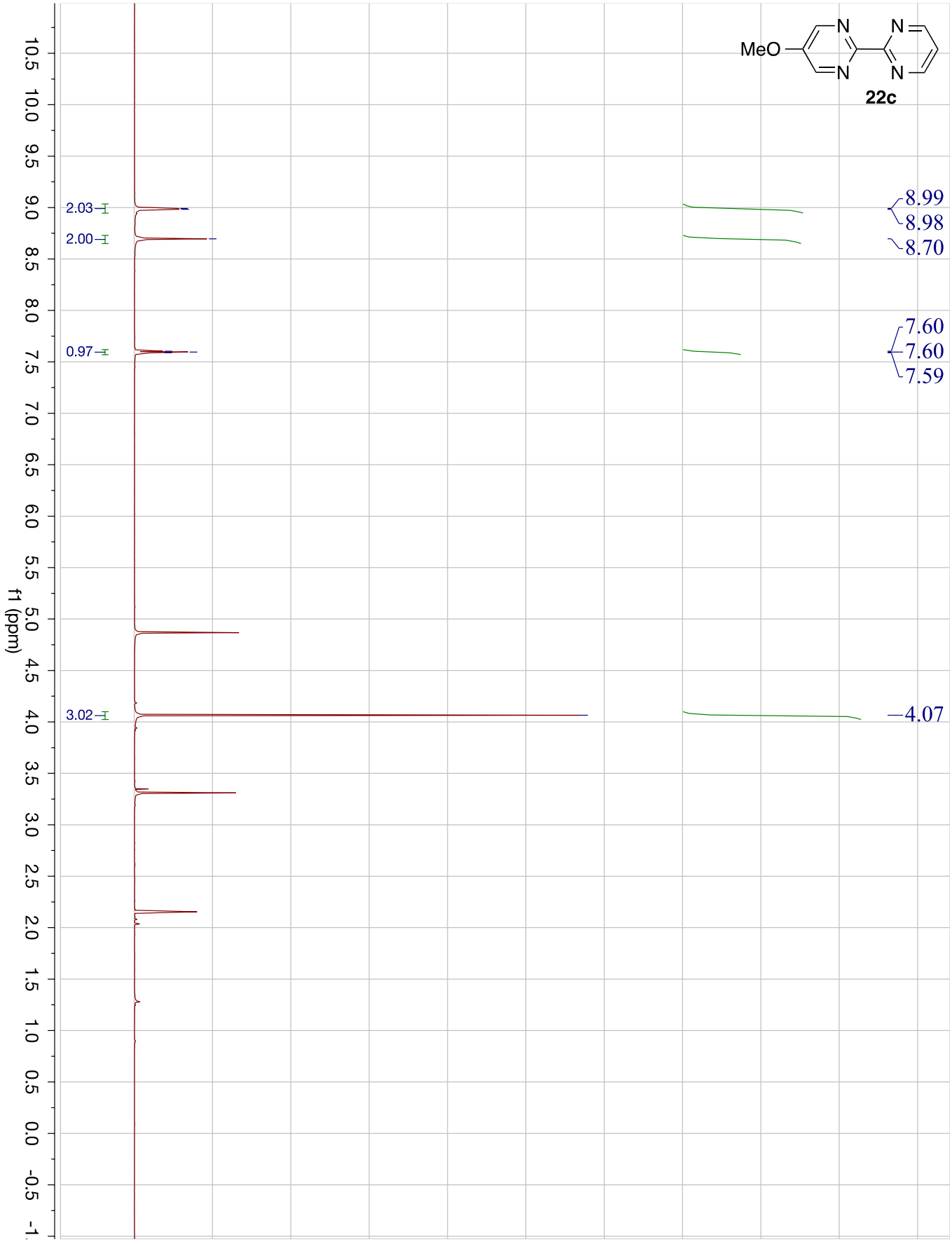
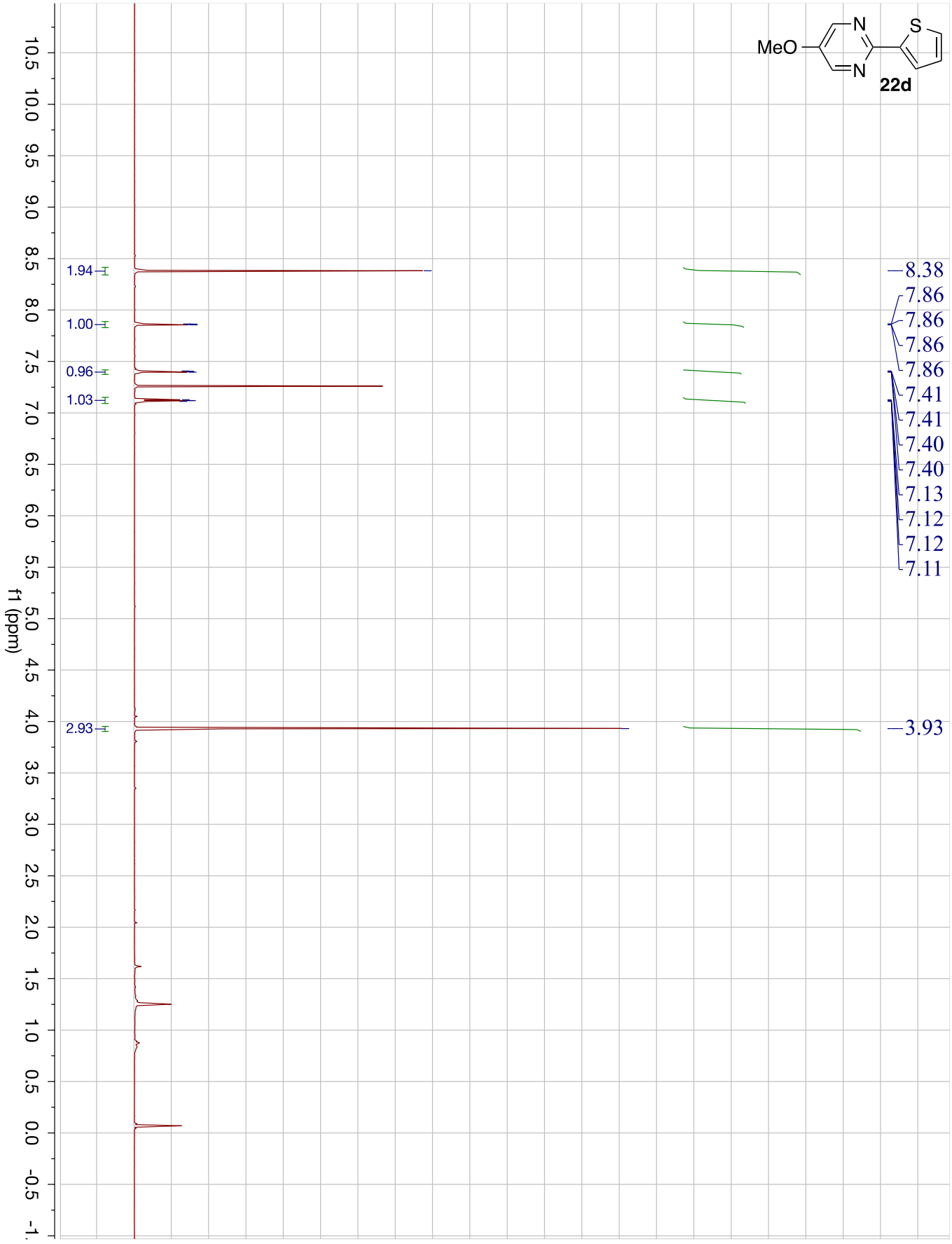
2.03
1.06
2.16
3.13
8.54
7.35
7.34
7.18
7.17
7.16
4.66
2.48
f1 (ppm)

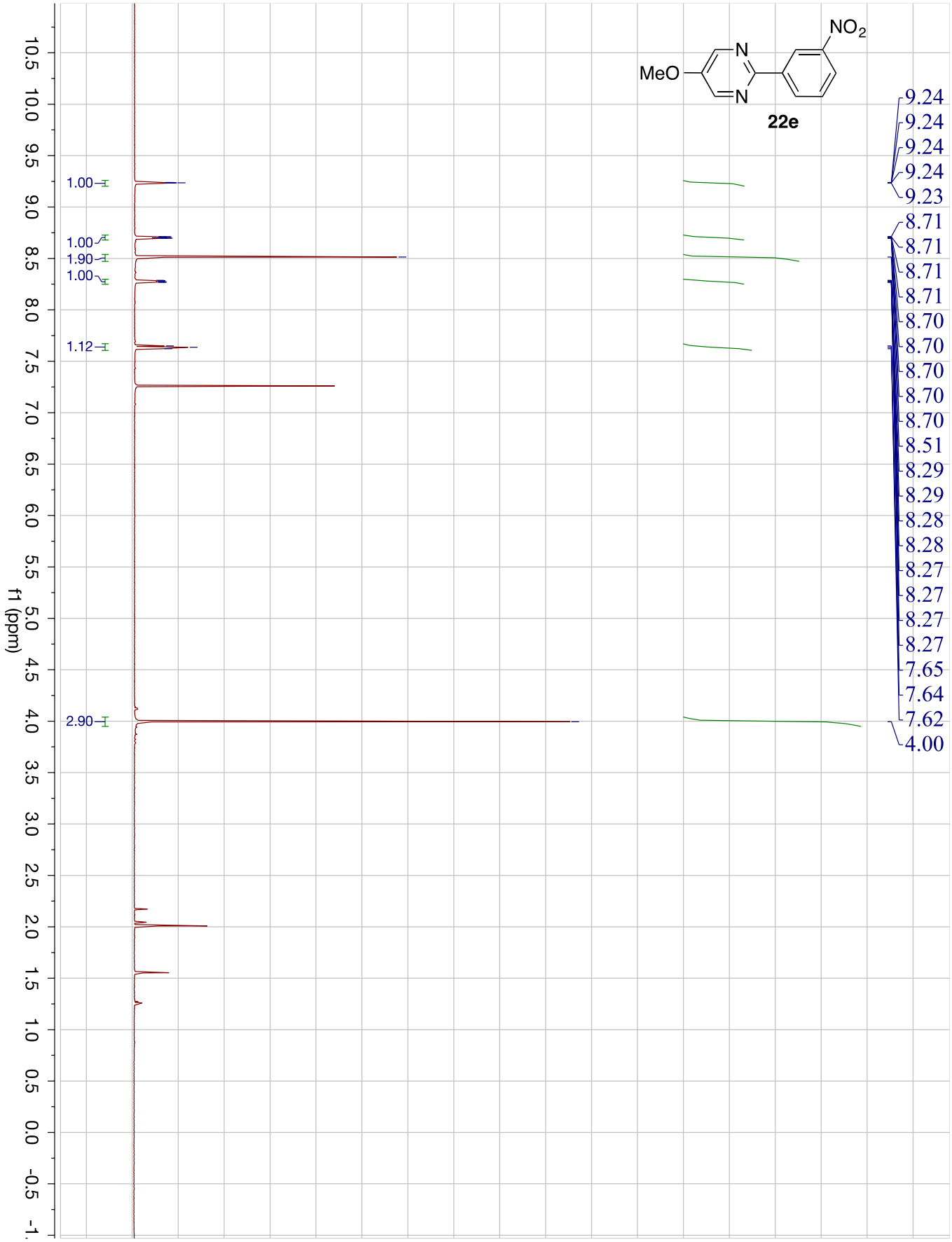

MeS
N
N
21l
f1 (ppm)
2.00
1.21
2.30
2.03
3.29
2.35
2.27
8.56
5.87
5.86
5.85
5.85
5.84
5.83
5.82
5.82
5.81
5.80
5.05
5.04
5.04
5.02
5.01
4.98
4.98
4.98
4.98
4.98
4.97
4.96
4.96
4.96
2.95
2.94
2.93
2.92
2.51
2.16
2.14
2.13
2.12
1.92
1.91

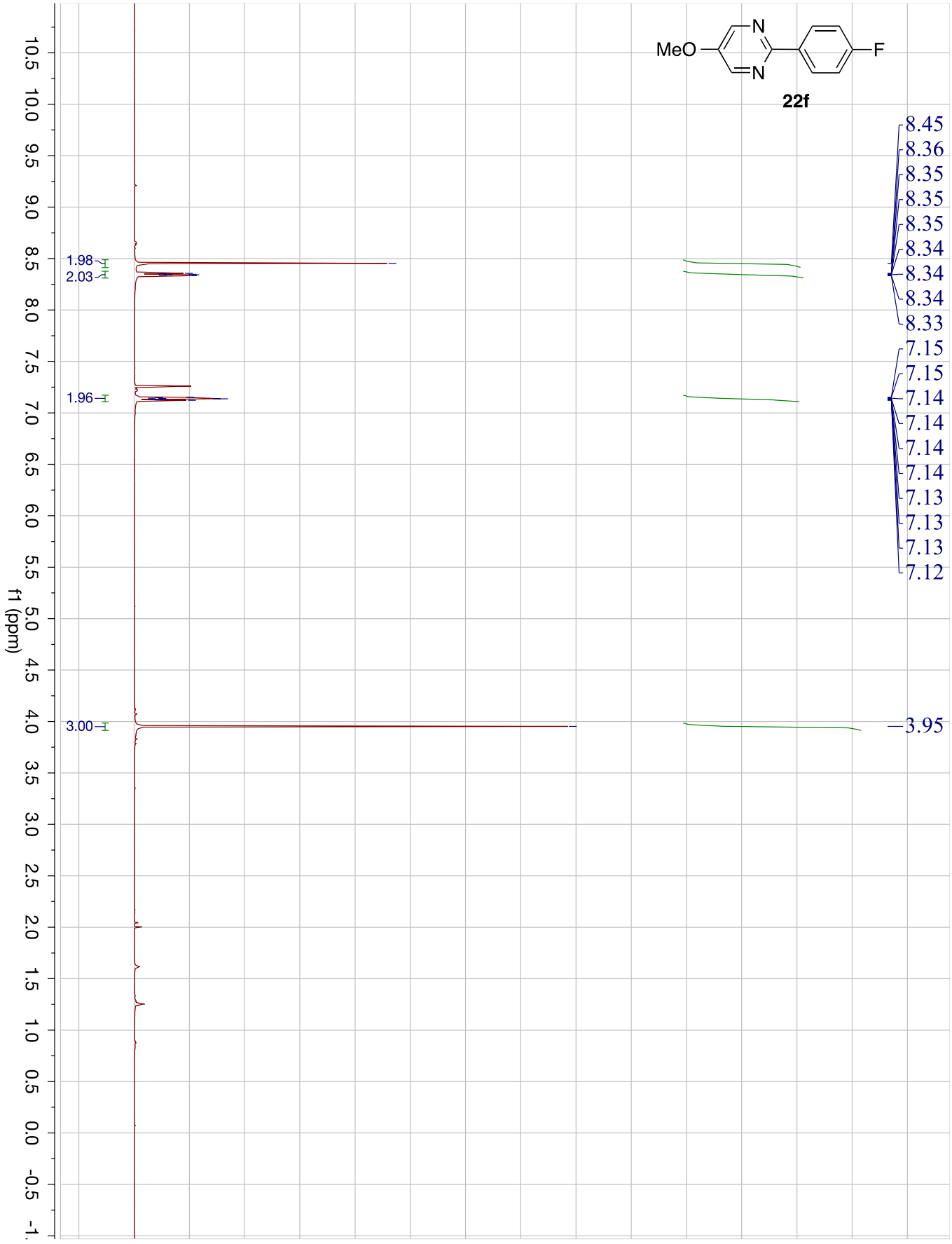

MeO
N
N
22a
f1 (ppm)
2.00
4.18
1.18
2.77
1.81
1.91
8.35
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.20
7.20
7.19
7.19
7.18
7.17
3.90
3.25
3.24
3.23
3.23
3.23
3.23
3.22
3.22
3.14
3.13
3.12

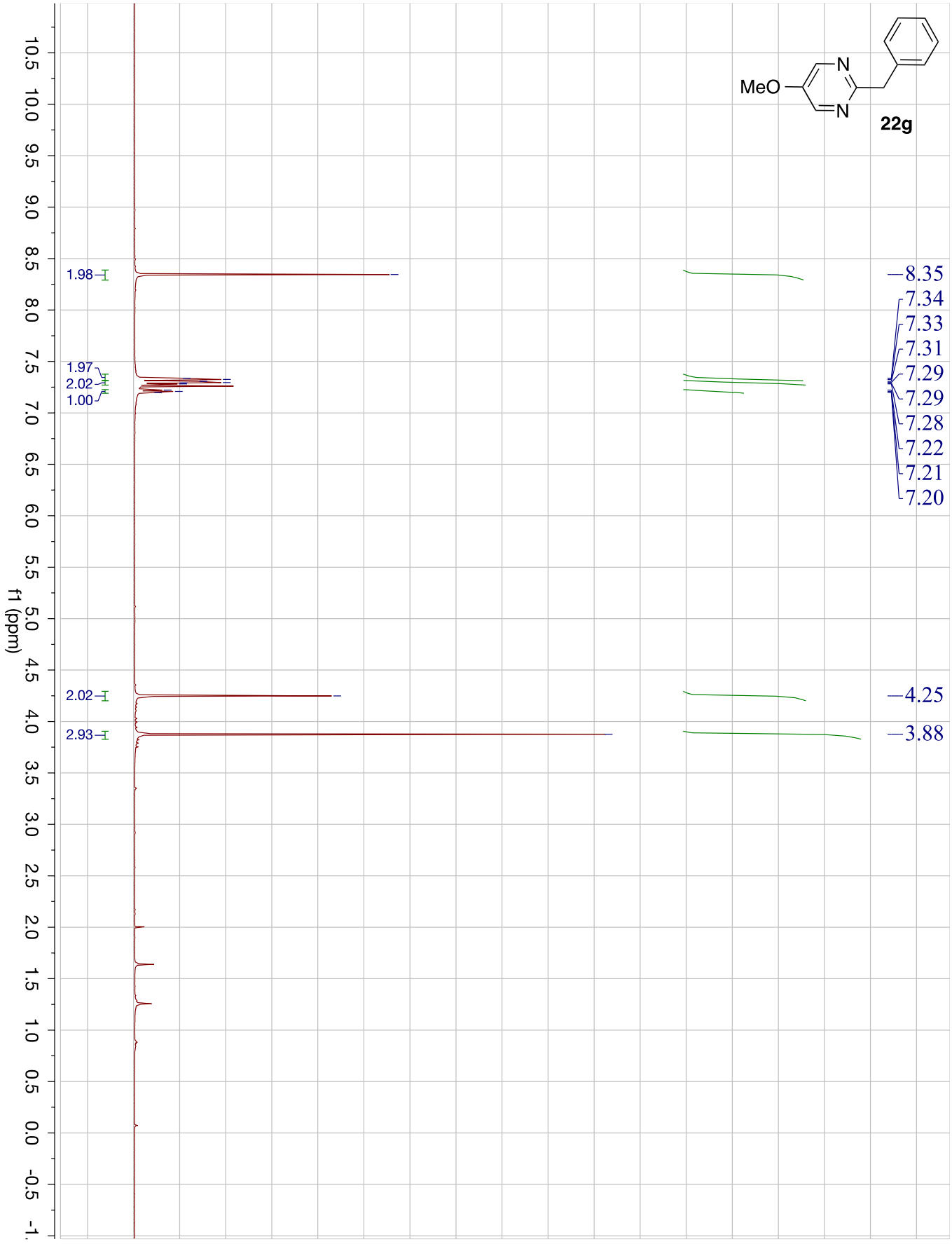

MeO
N
N
N
22b
1.00
1.92
0.91
0.95
0.93
2.68
8.68
8.68
8.68
8.68
8.68
8.67
8.67
8.67
8.62
8.44
8.44
8.44
8.43
8.43
8.42
7.97
7.96
7.95
7.95
7.94
7.94
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.46
4.02
f1 (ppm)

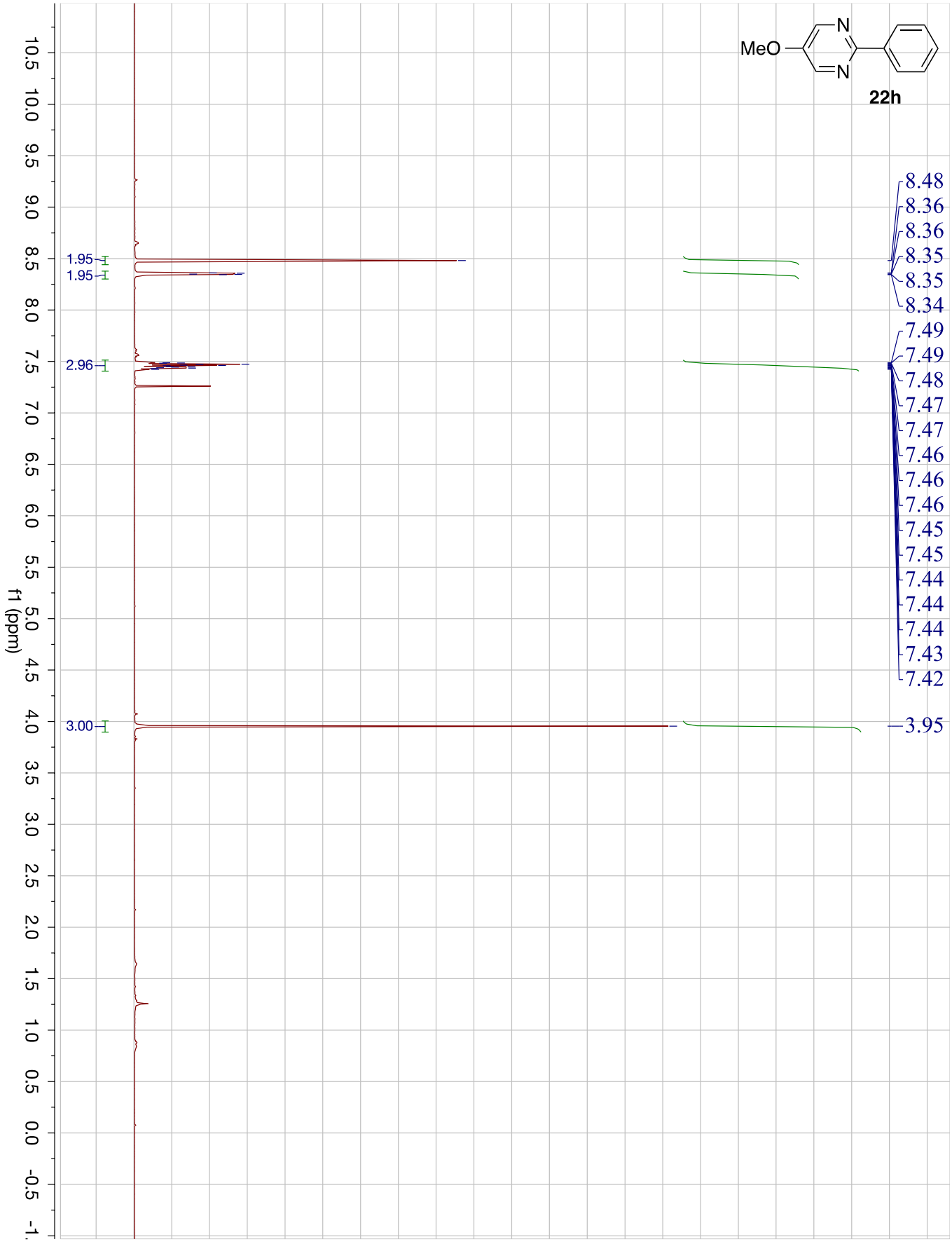

MeO
N
N
N
N
22c
8.99
8.98
8.70
7.60
7.60
7.59
4.07
2.03
2.00
0.97
3.02
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1


MeO
N
S
N
22d
1.94
1.00
0.96
1.03
2.93
8.38
7.86
7.86
7.86
7.86
7.41
7.41
7.40
7.40
7.13
7.12
7.12
7.11
3.93
f1 (ppm)


MeO
N
N
NO2
22e
9.24
9.24
9.24
9.24
9.23
8.71
8.71
8.71
8.71
8.70
8.70
8.70
8.70
8.70
8.51
8.29
8.29
8.28
8.28
8.27
8.27
8.27
8.27
7.65
7.64
7.62
4.00
1.00
1.00
1.90
1.00
1.12
2.90
f1 (ppm)


MeO
N
N
F
22f
8.45
8.36
8.35
8.35
8.35
8.34
8.34
8.34
8.33
7.15
7.15
7.14
7.14
7.14
7.14
7.13
7.13
7.13
7.12
3.95
1.98
2.03
1.96
3.00
f1 (ppm)


MeO
N
N
22g
1.98
1.97
2.02
1.00
2.02
2.93
8.35
7.34
7.33
7.31
7.29
7.29
7.28
7.22
7.21
7.20
4.25
3.88
f1 (ppm)


MeO
N
N
22h
8.48
8.36
8.36
8.35
8.35
8.34
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.45
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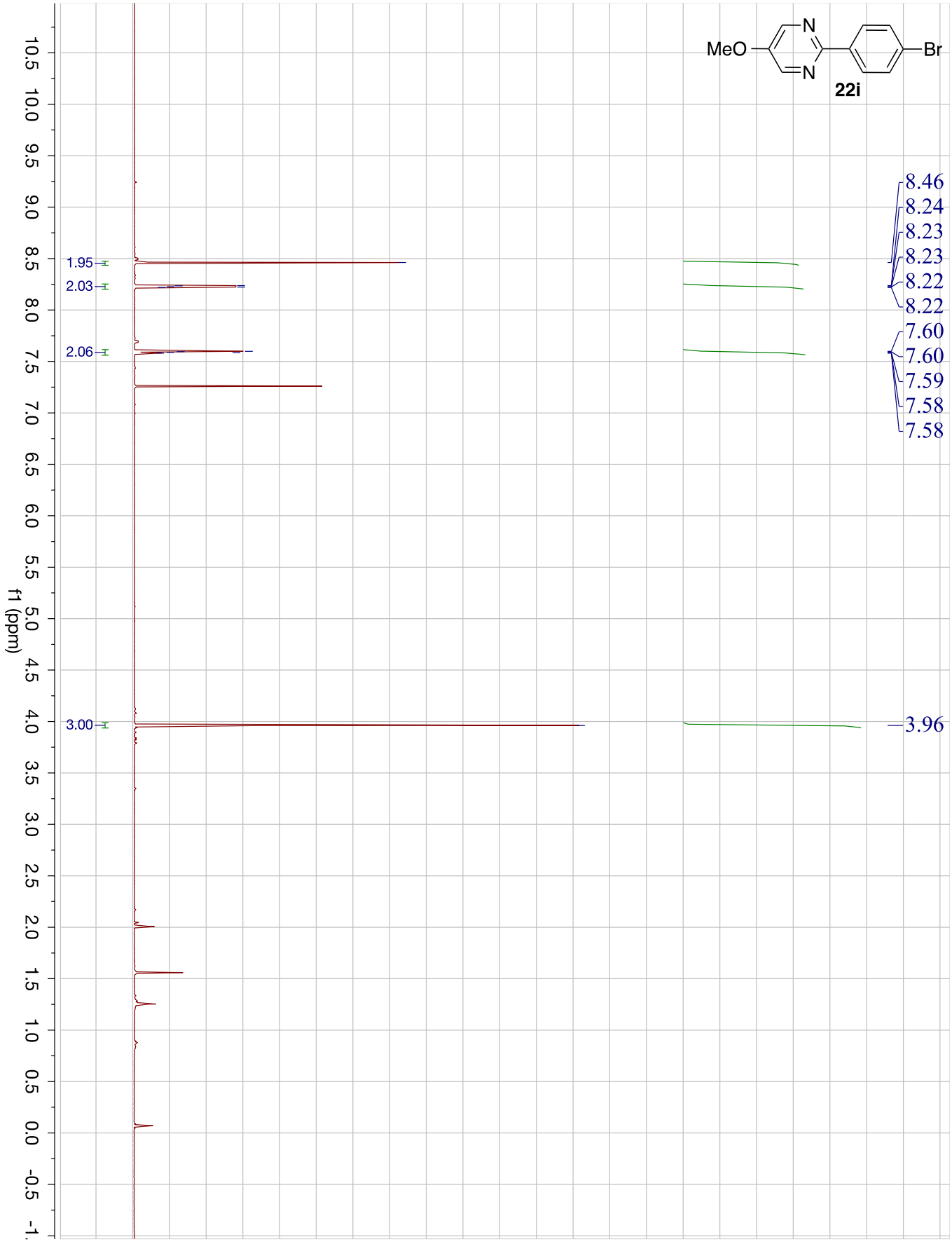
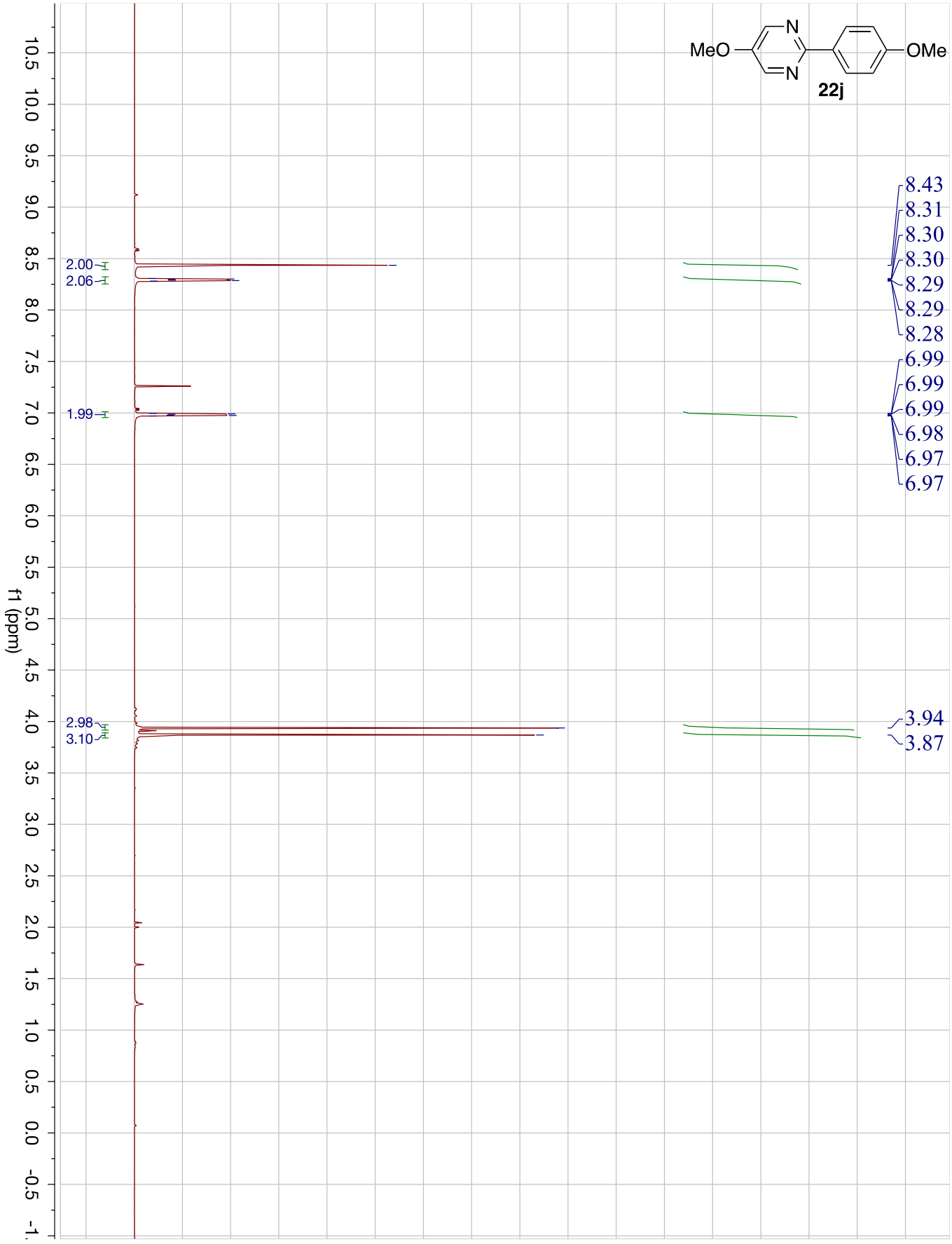
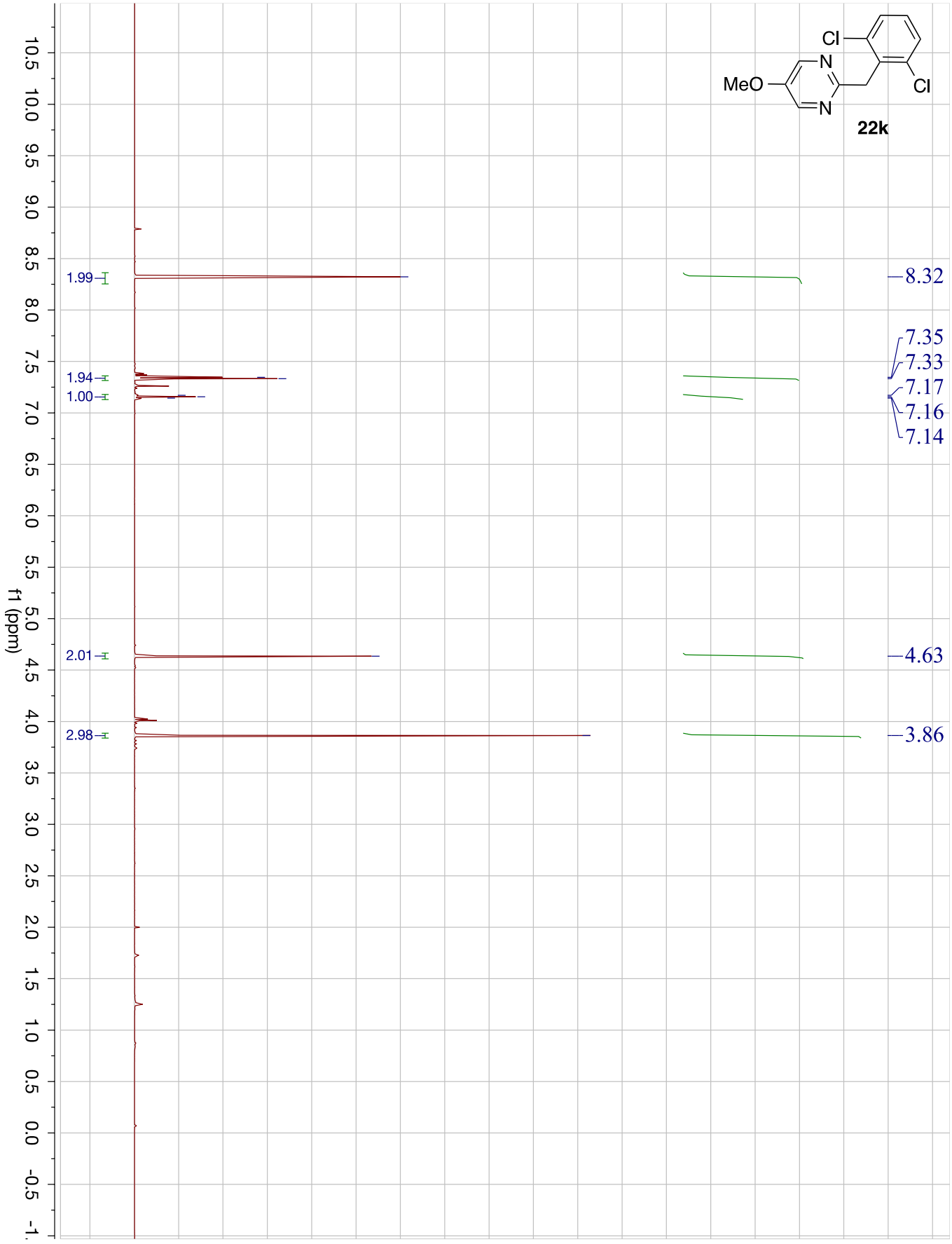
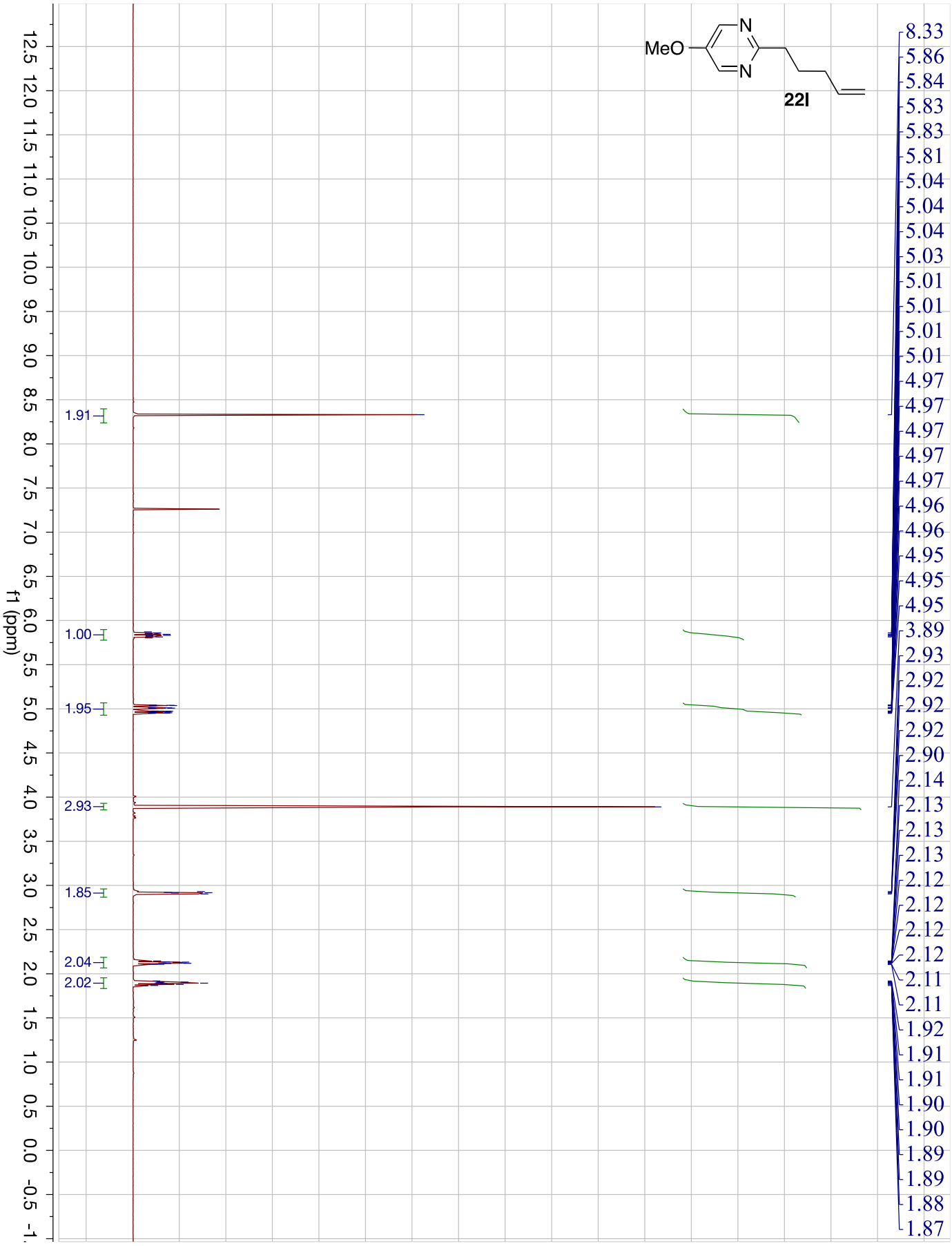
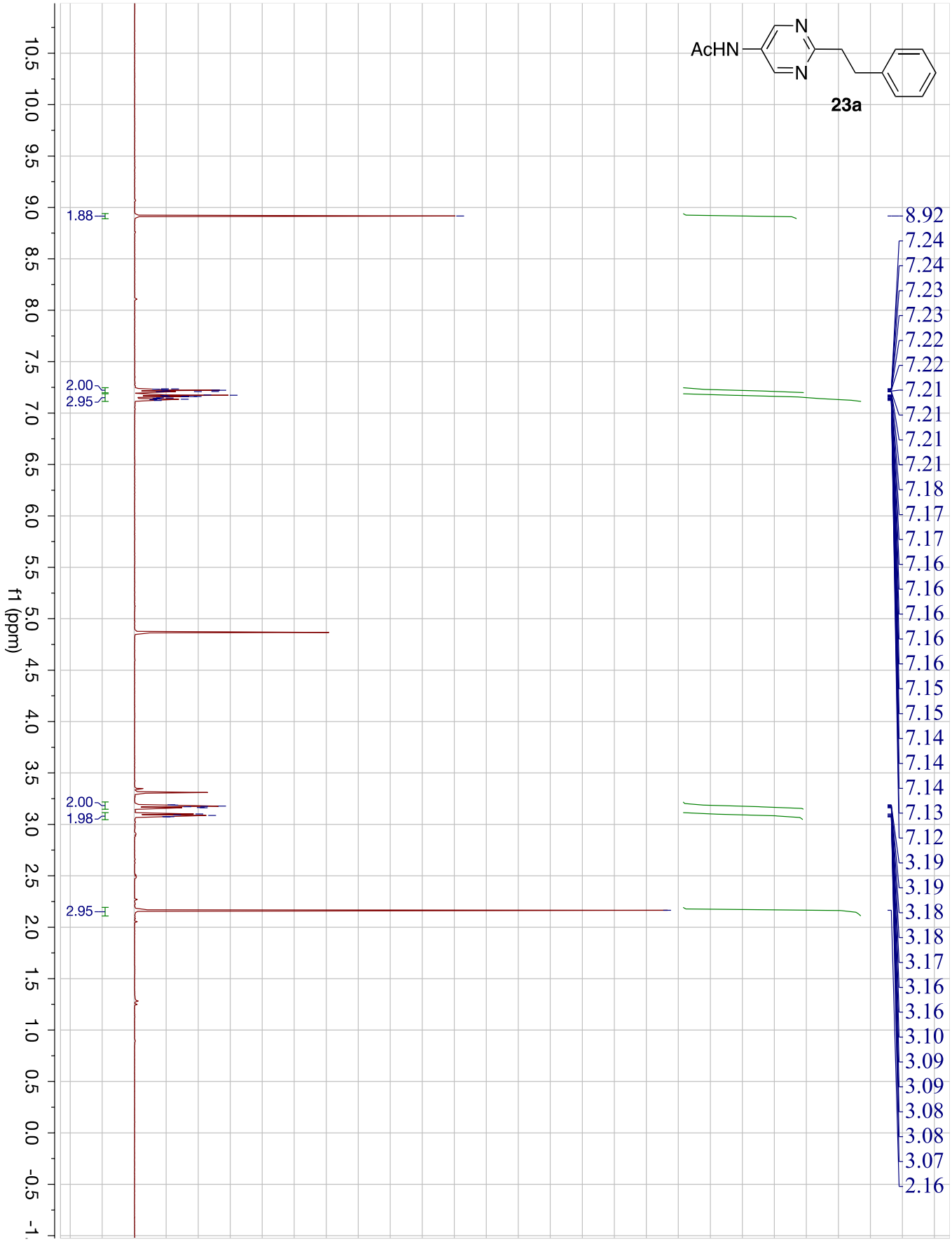
7.44
7.43
7.42
3.95
1.95
1.95
2.96
3.00
f1 (ppm)


MeO
N
N
Br
22i
8.46
8.24
8.23
8.23
8.22
8.22
7.60
7.60
7.59
7.58
7.58
3.96
1.95
2.03
2.06
3.00
f1 (ppm)


MeO
N
N
OMe
22j
8.43
8.31
8.30
8.30
8.29
8.29
8.28
6.99
6.99
6.99
6.98
6.97
6.97
3.94
3.87
2.00
2.06
1.99
2.98
3.10
f1 (ppm)


Cl
N
MeO
N
Cl
22k
1.99
1.94
1.00
2.01
2.98
8.32
7.35
7.33
7.17
7.16
7.14
4.63
3.86
f1 (ppm)


MeO
N
N
22l
f1 (ppm)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
1.91
1.00
1.95
2.93
1.85
2.04
2.02
8.33
5.86
5.84
5.83
5.83
5.81
5.04
5.04
5.04
5.03
5.01
5.01
5.01
5.01
4.97
4.97
4.97
4.97
4.96
4.96
4.95
4.95
4.95
3.89
2.93
2.92
2.92
2.92
2.90
2.14
2.13
2.13
2.13
2.12
2.12
2.12
2.12
2.11
2.11
1.92
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.87


AcHN
N
N
23a
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
1.88
2.00
2.95
2.00
1.98
2.95
8.92
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.18
7.17
7.17
7.16
7.16
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.14
7.13
7.12
3.19
3.19
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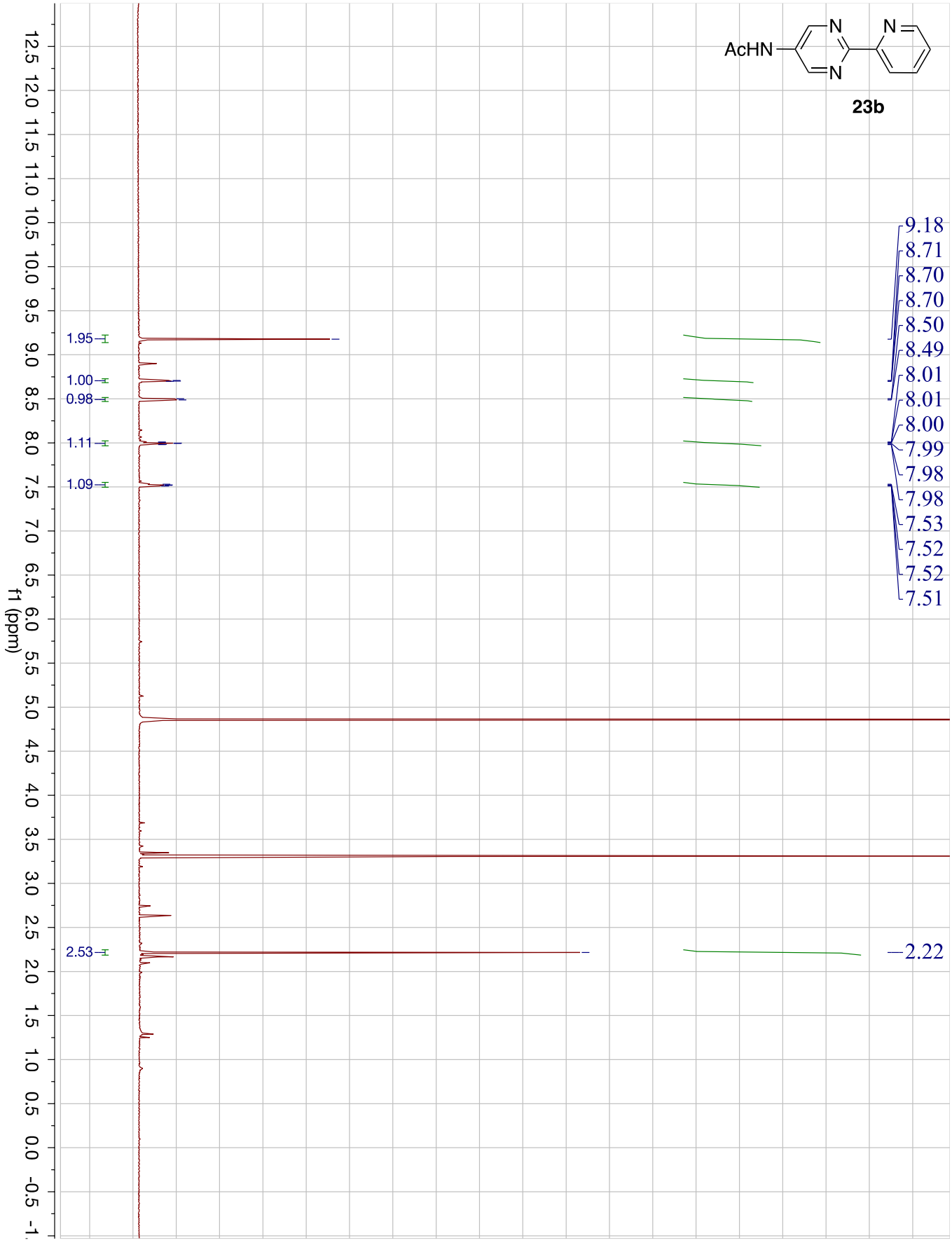
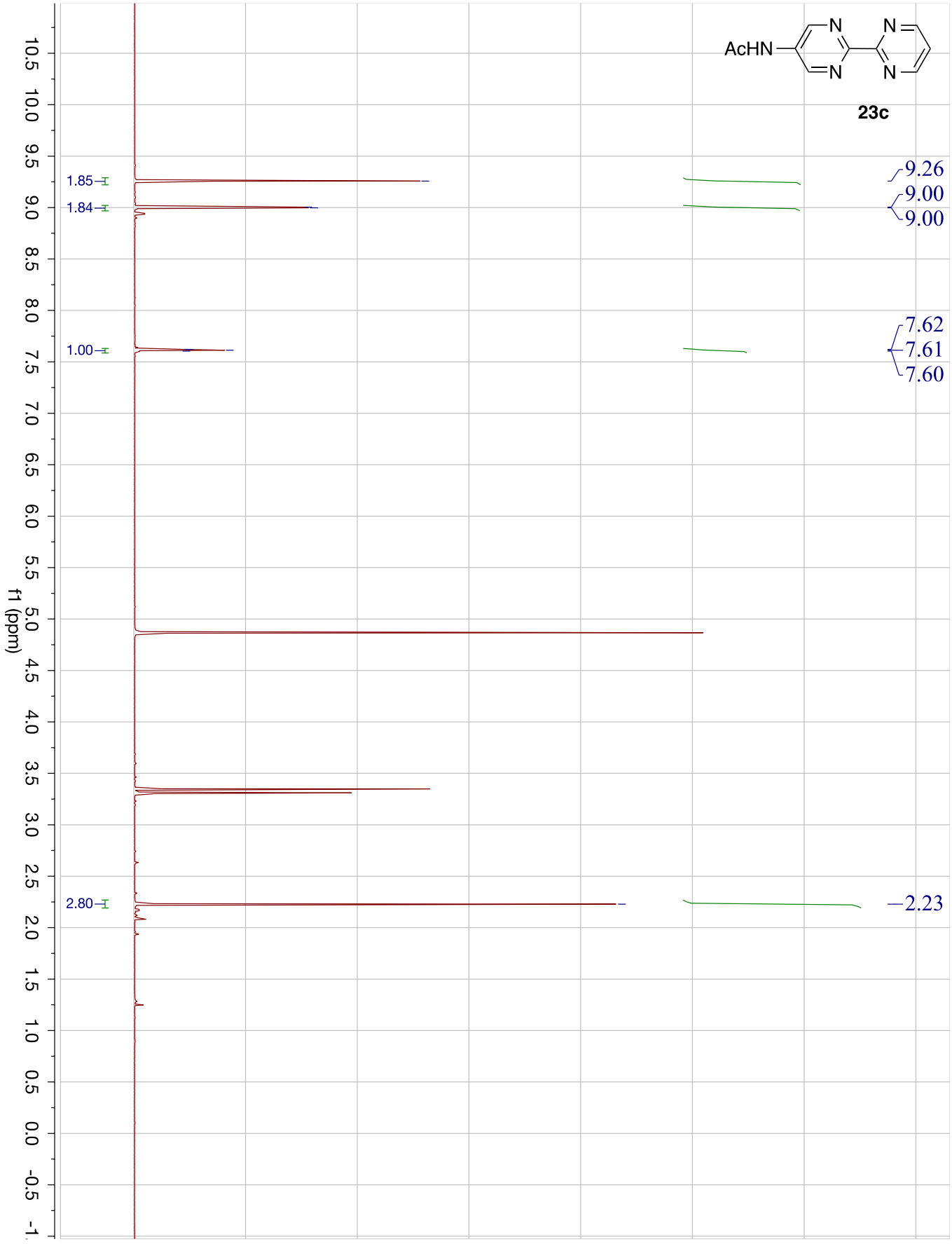
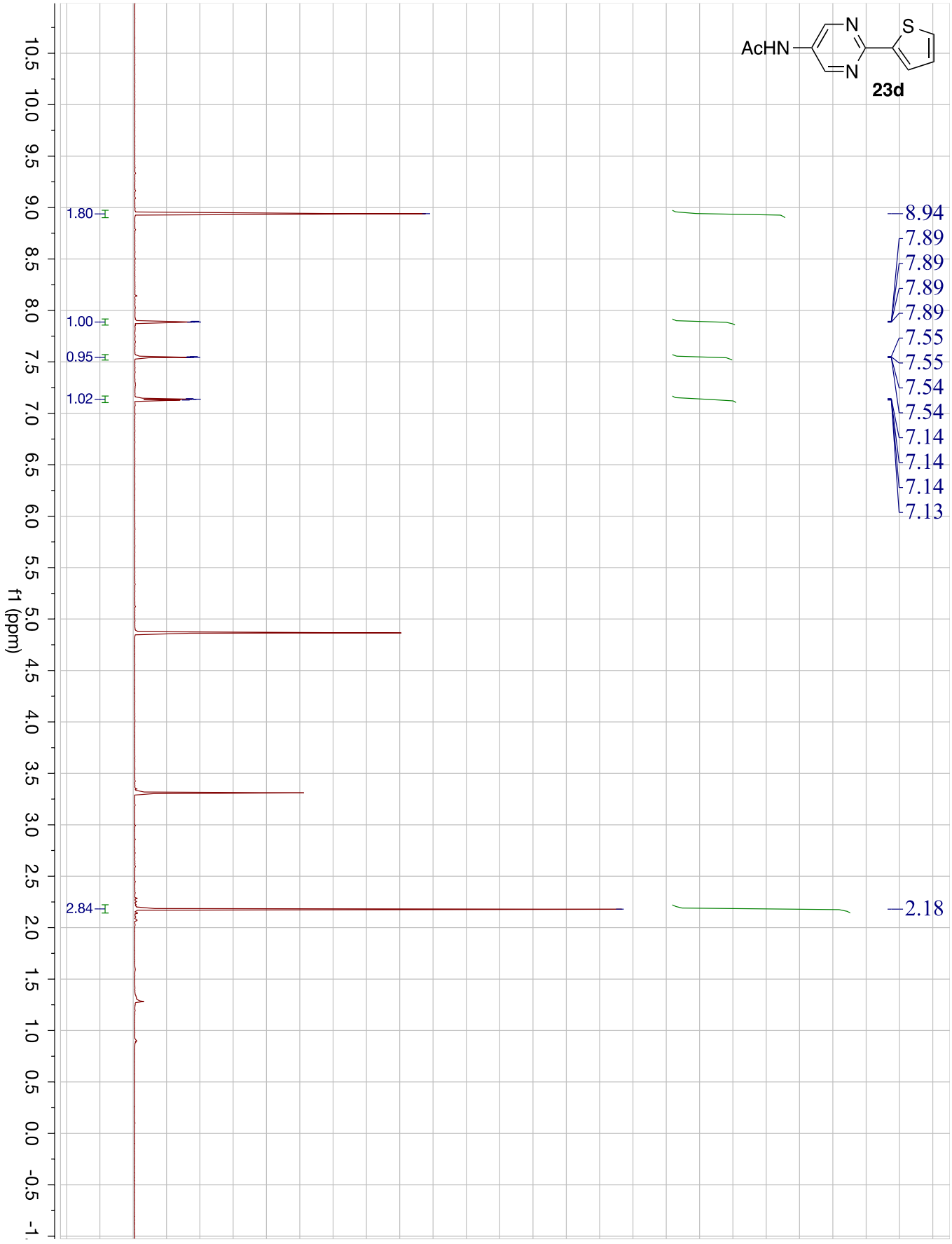
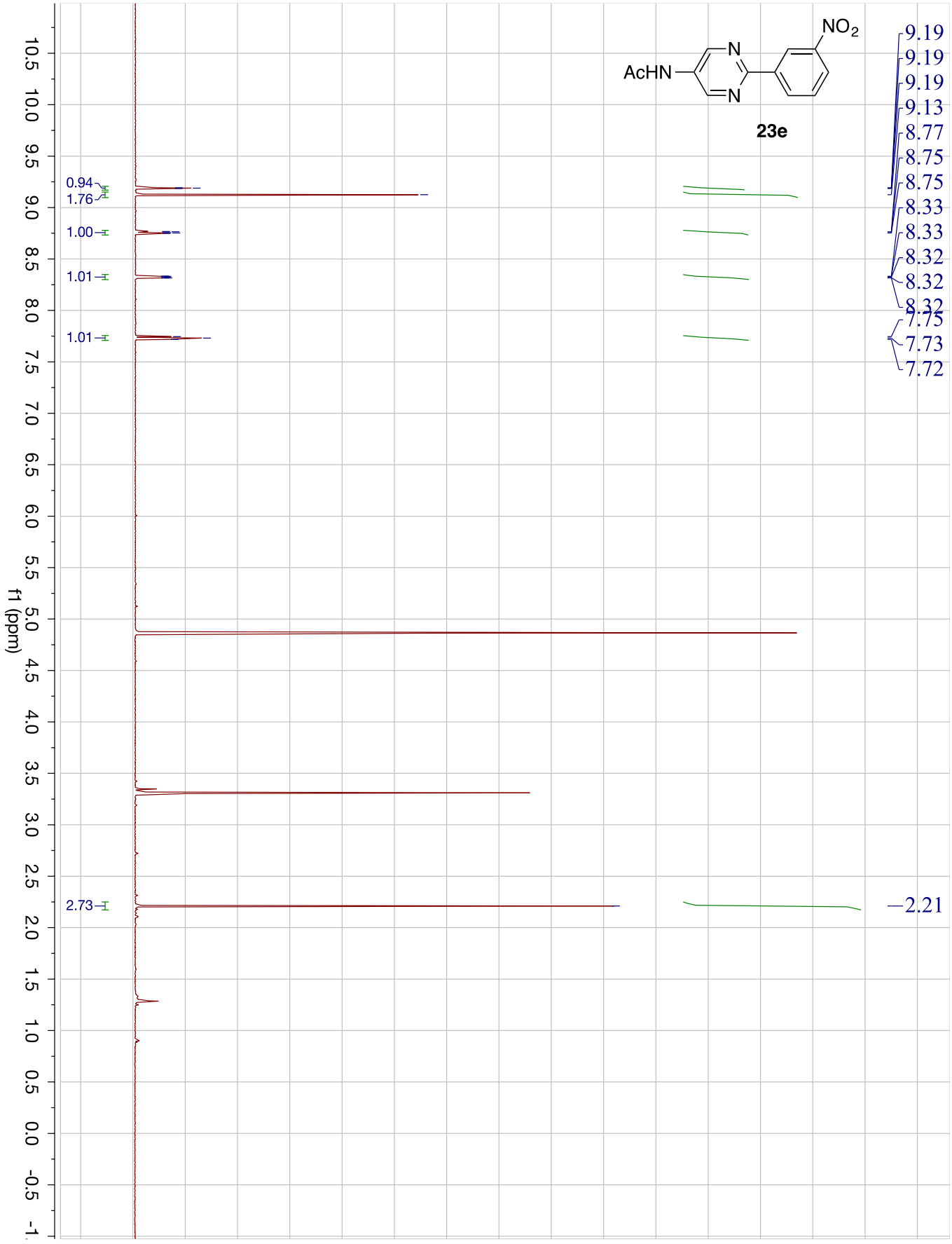
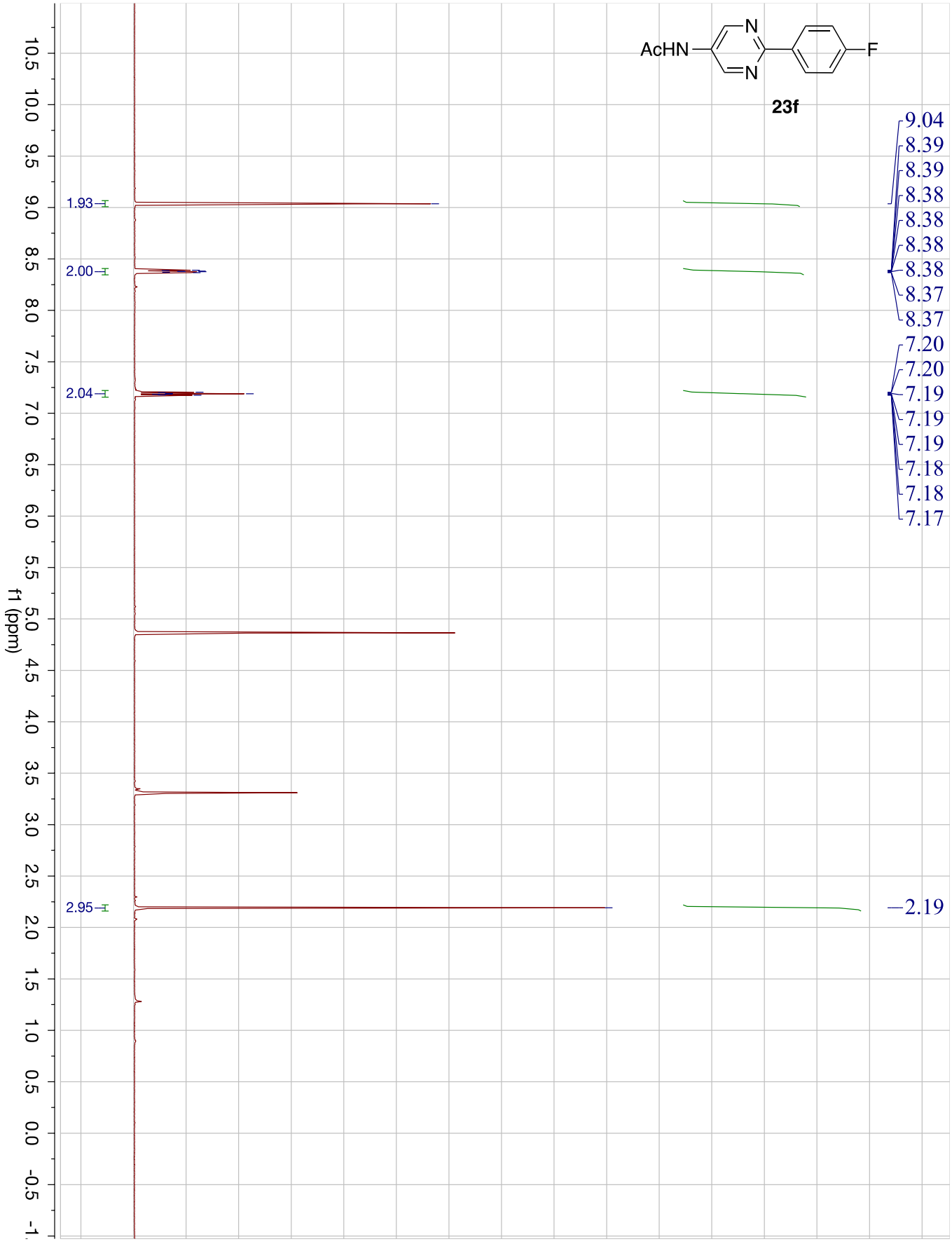
3.09
3.09
3.08
3.08
3.07
2.16

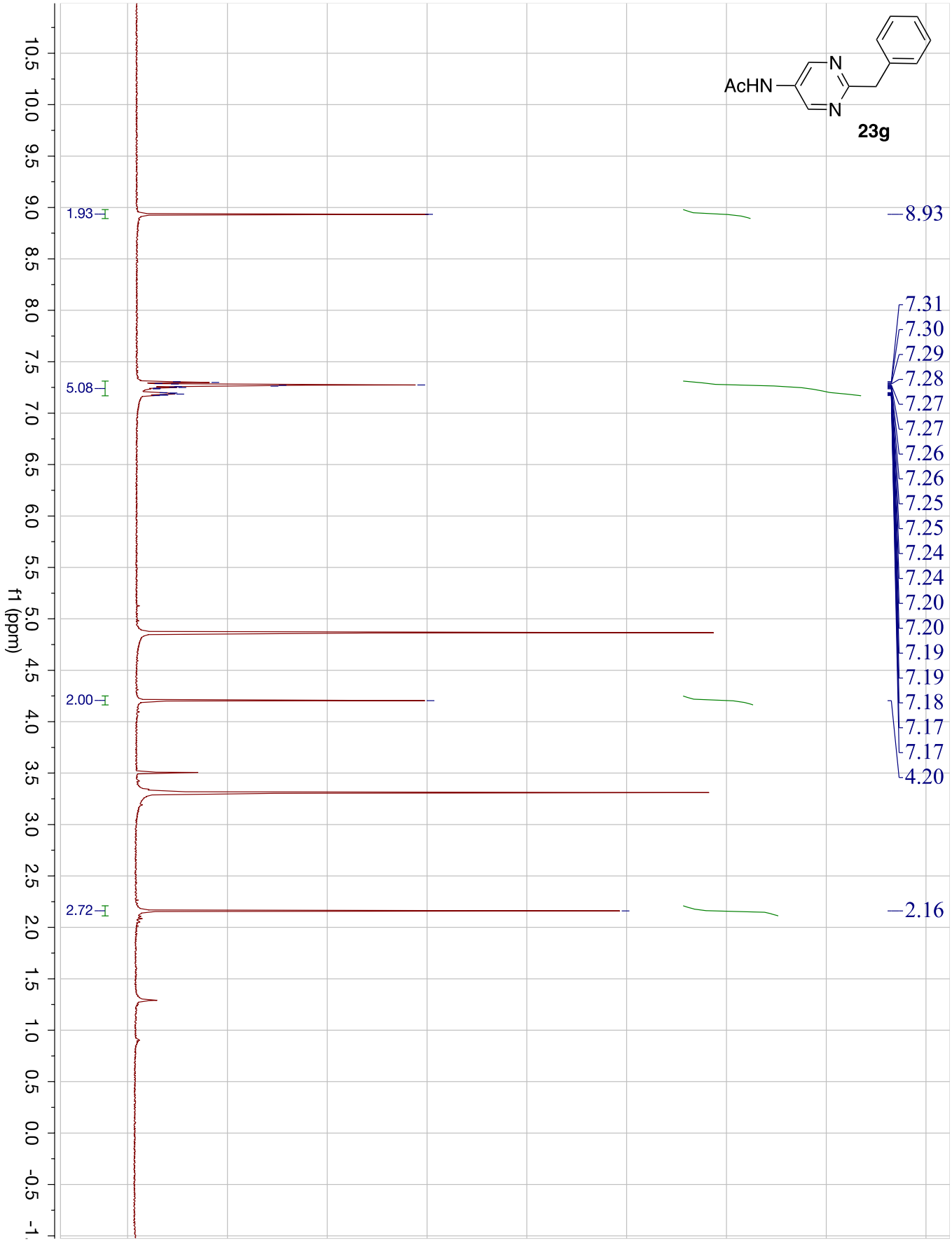

AcHN
N
N
N
23b
9.18
8.71
8.70
8.70
8.50
8.49
8.01
8.01
8.00
7.99
7.98
7.98
7.53
7.52
7.52
7.51
1.95
1.00
0.98
1.11
1.09
2.53
2.22
f1 (ppm)

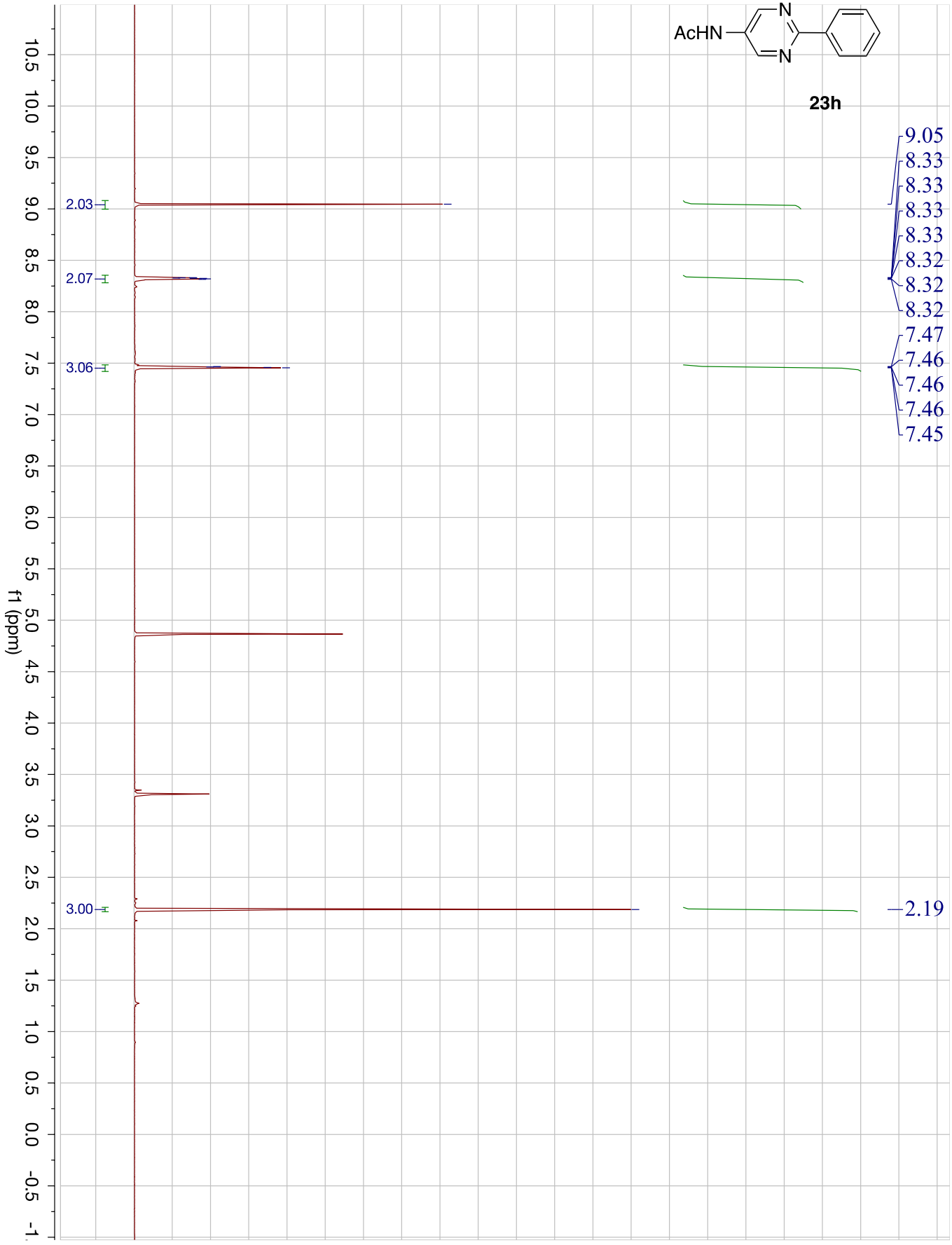

AcHN
N
N
N
N
23c
9.26
9.00
9.00
7.62
7.61
7.60
2.23
1.85
1.84
1.00
2.80
f1 (ppm)


AcHN
N
S
N
23d
1.80
1.00
0.95
1.02
2.84
8.94
7.89
7.89
7.89
7.89
7.55
7.55
7.54
7.54
7.14
7.14
7.14
7.13
2.18
f1 (ppm)


AcHN
N
N
NO2
23e
9.19
9.19
9.19
9.13
8.77
8.75
8.75
8.33
8.33
8.32
8.32
8.32
7.75
7.73
7.72
2.21
0.94
1.76
1.00
1.01
1.01
2.73
f1 (ppm)


AcHN
N
N
F
23f
9.04
8.39
8.39
8.38
8.38
8.38
8.38
8.37
8.37
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.17
2.19
1.93
2.00
2.04
2.95
f1 (ppm)


AcHN
N
N
23g
1.93
5.08
2.00
2.72
8.93
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.20
7.20
7.19
7.19
7.18
7.17
7.17
4.20
2.16
f1 (ppm)


AcHN
N
N
23h
9.05
8.33
8.33
8.33
8.33
8.32
8.32
8.32
7.47
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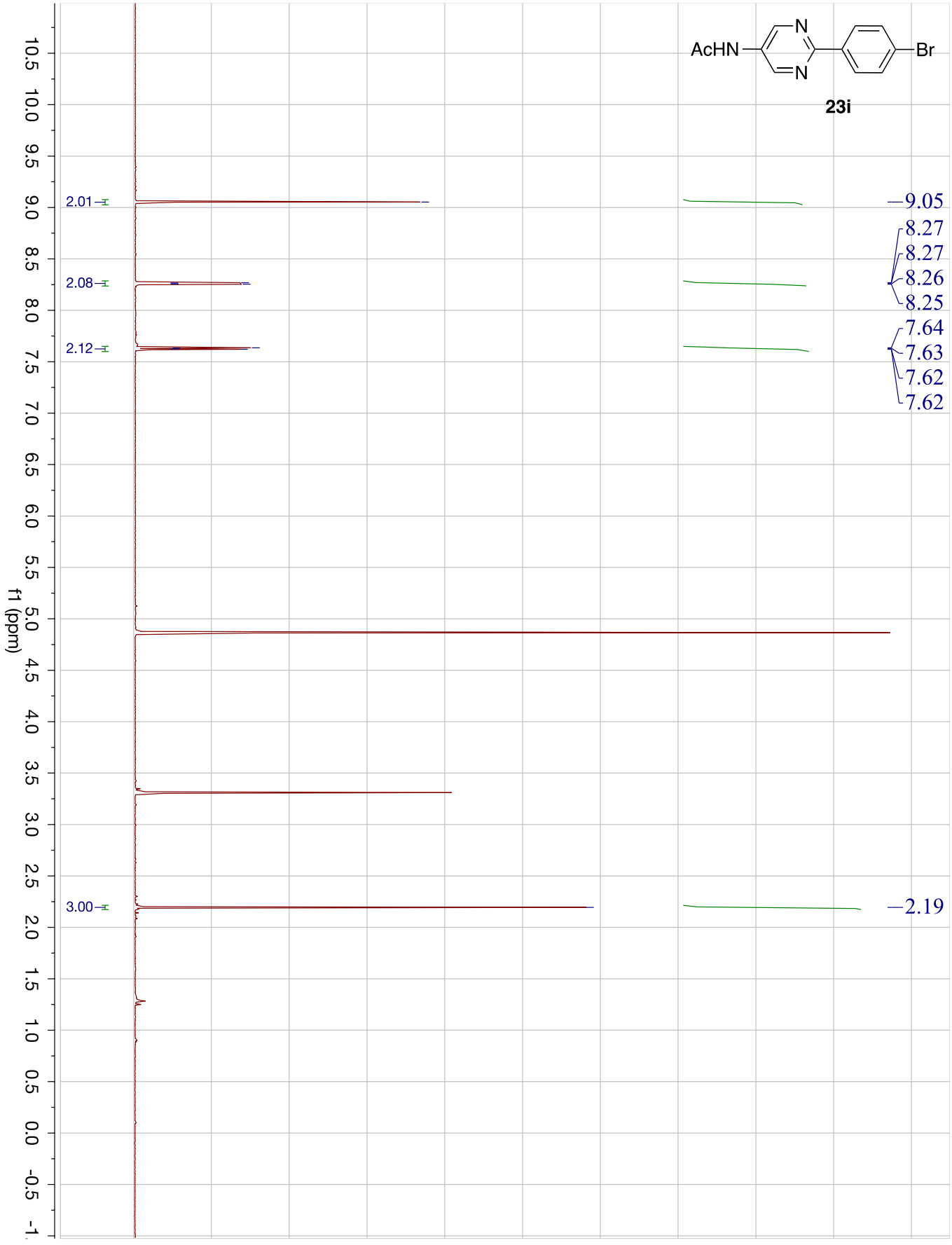
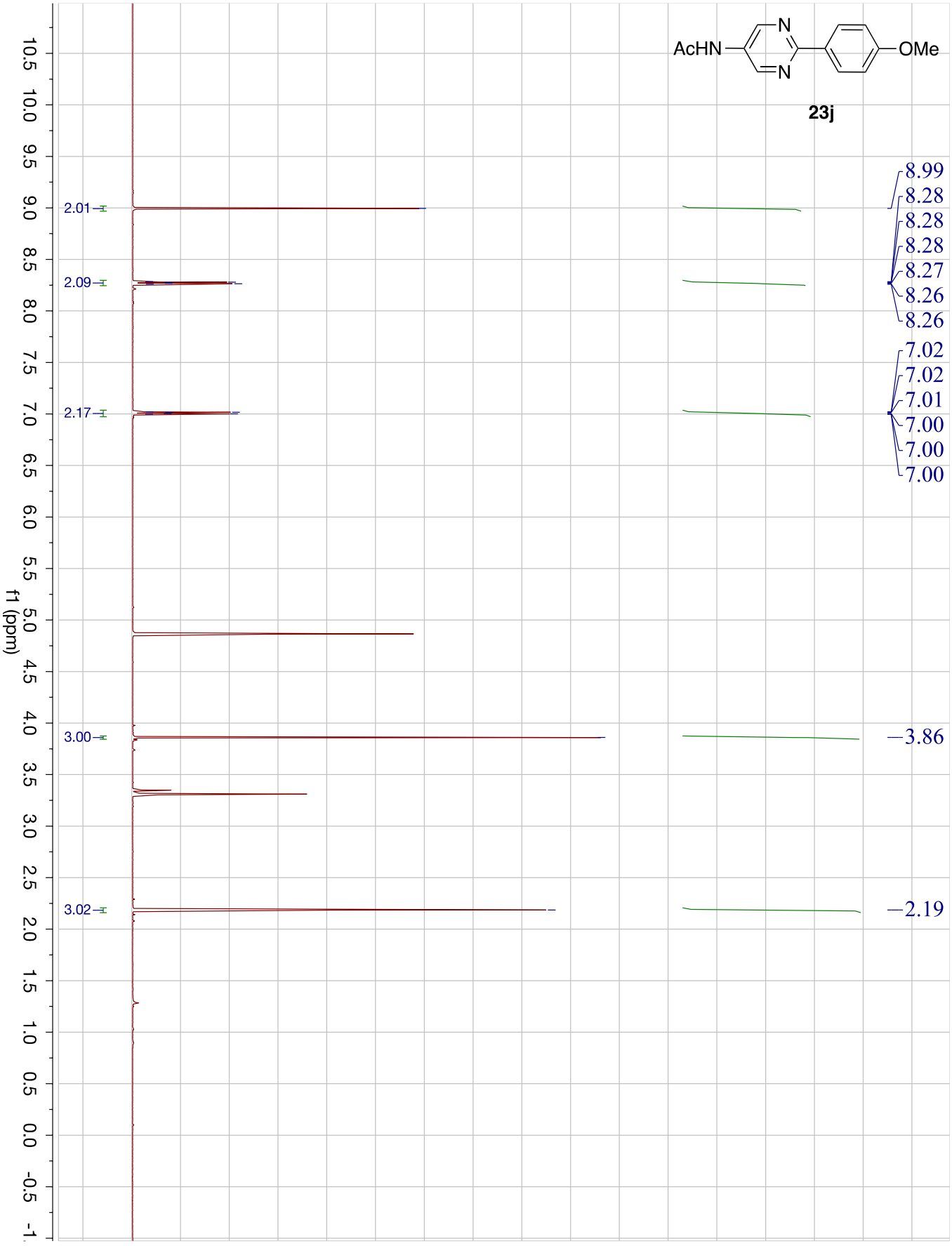
7.46
7.46
7.45
2.19
2.03
2.07
3.06
3.00
f1 (ppm)


AcHN
N
N
Br
23i
2.01
2.08
2.12
3.00
9.05
8.27
8.27
8.26
8.25
7.64
7.63
7.62
7.62
2.19
f1 (ppm)


AcHN
N
N
OMe
23j
8.99
8.28
8.28
8.28
8.27
8.26
8.26
7.02
7.02
7.01
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7.00
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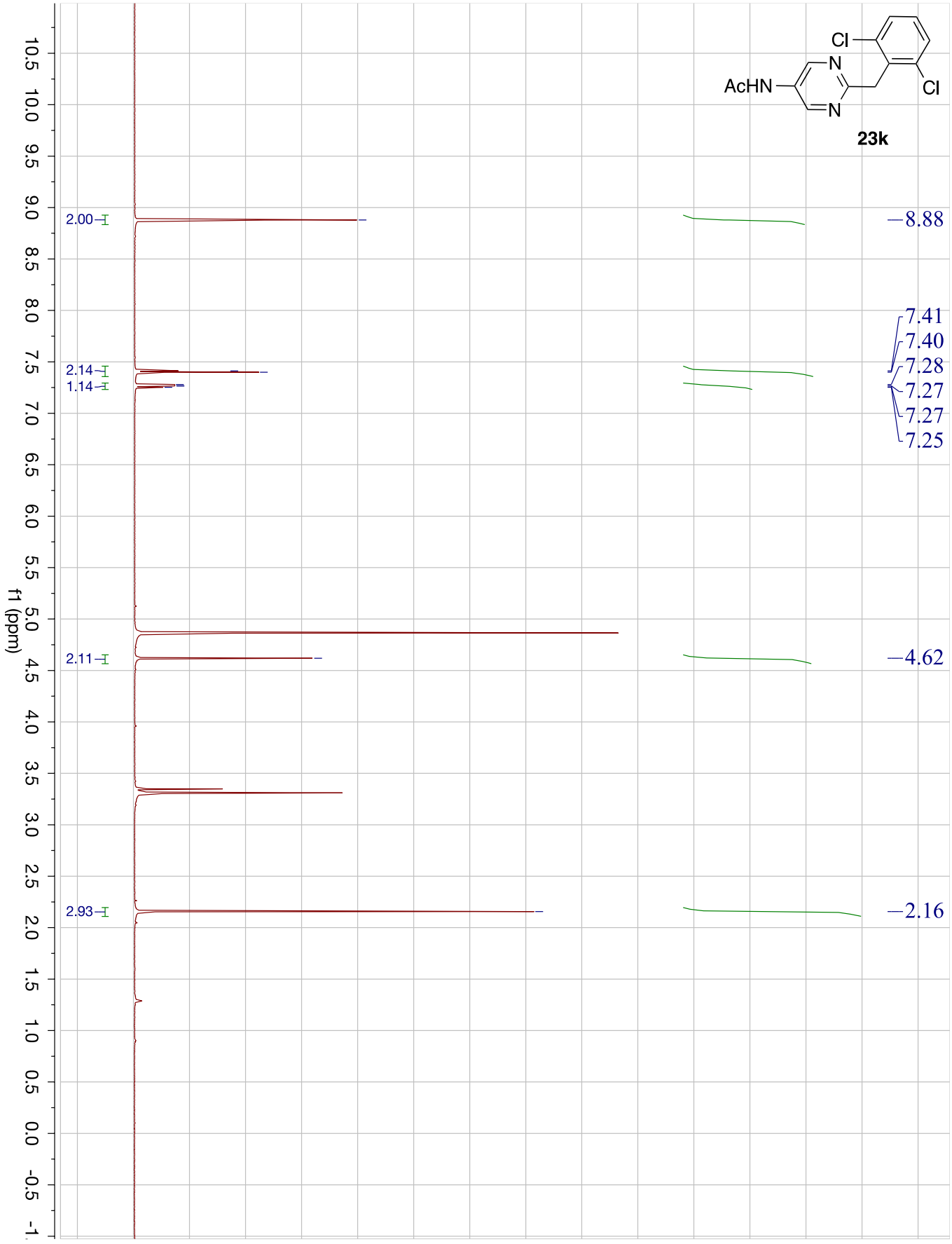
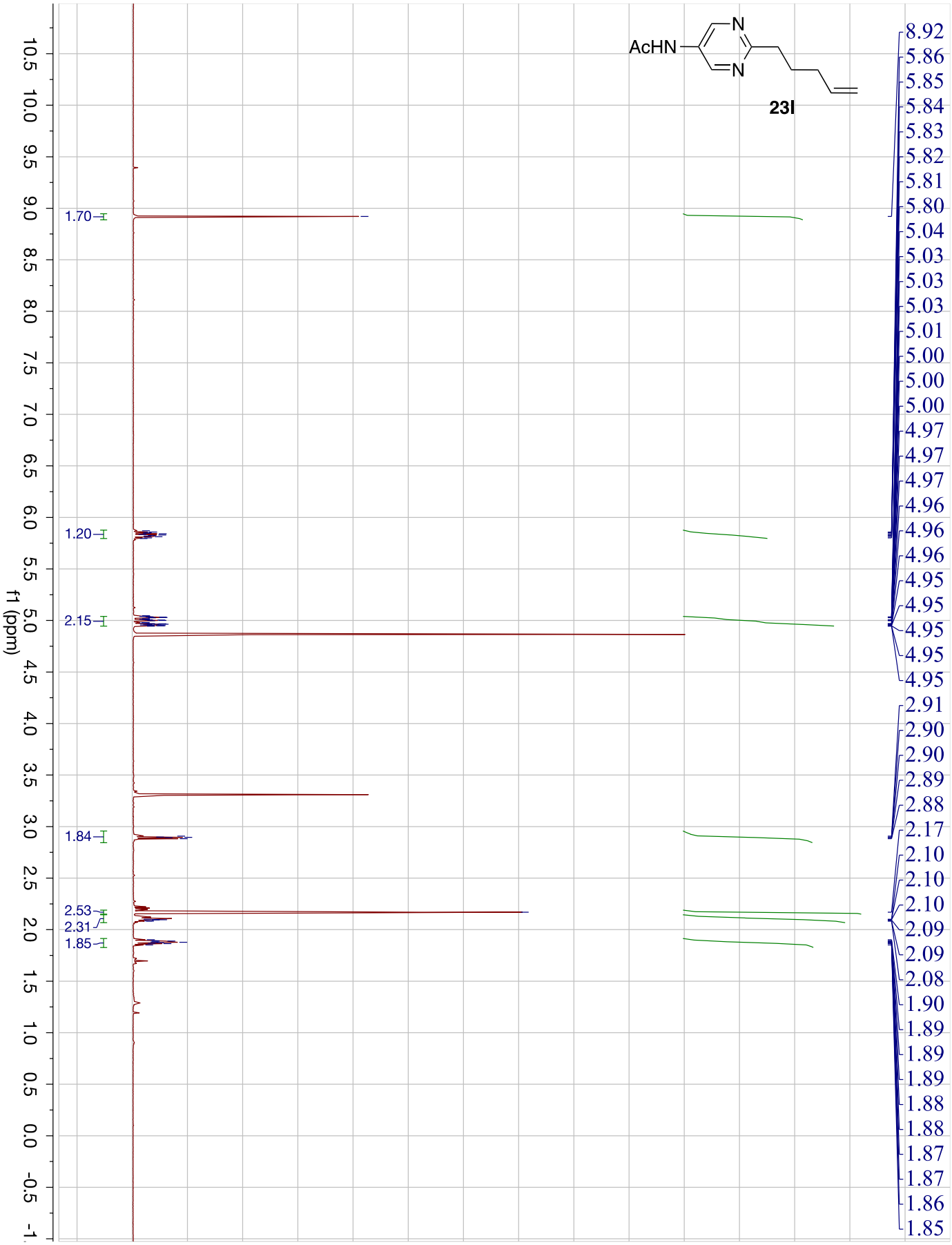
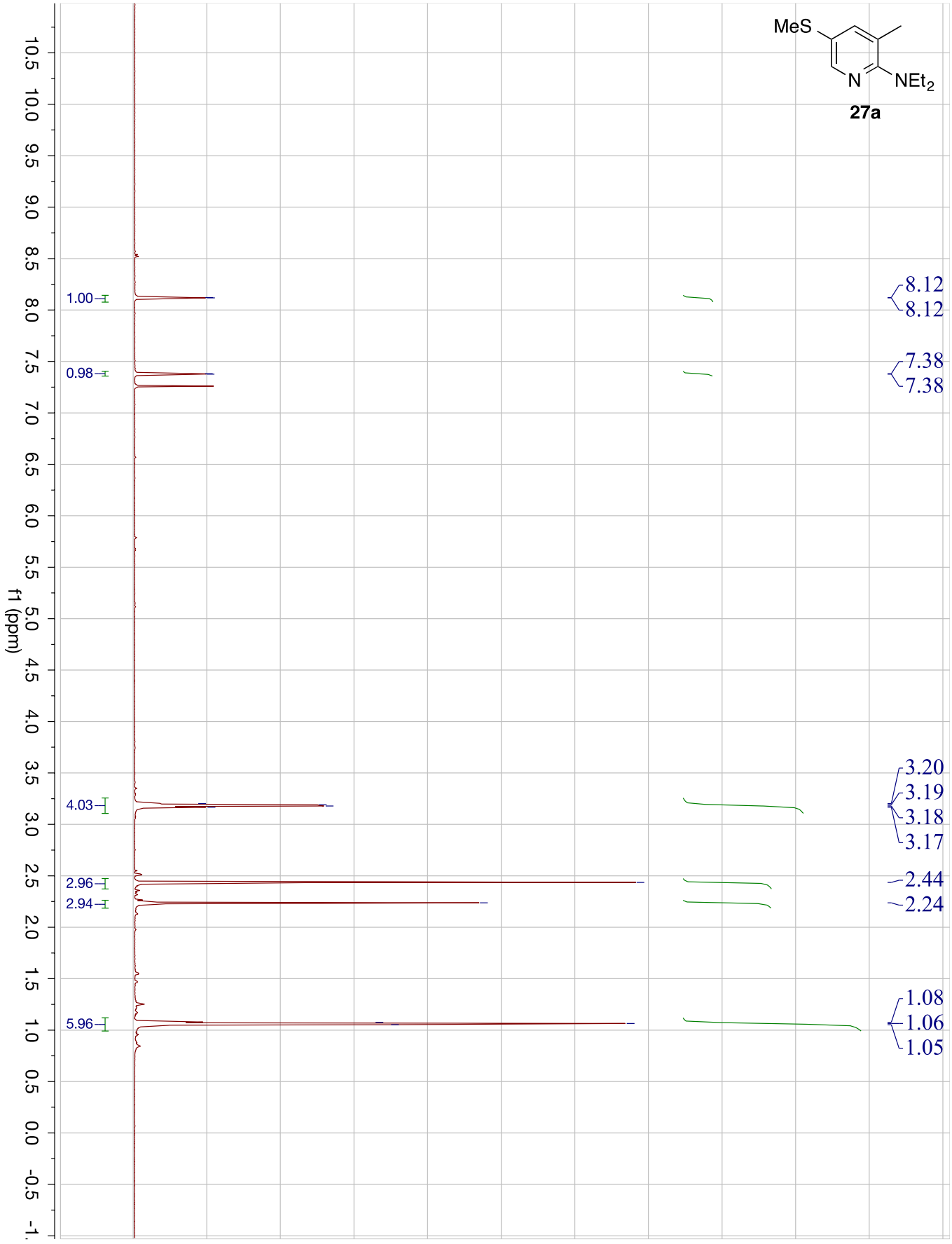
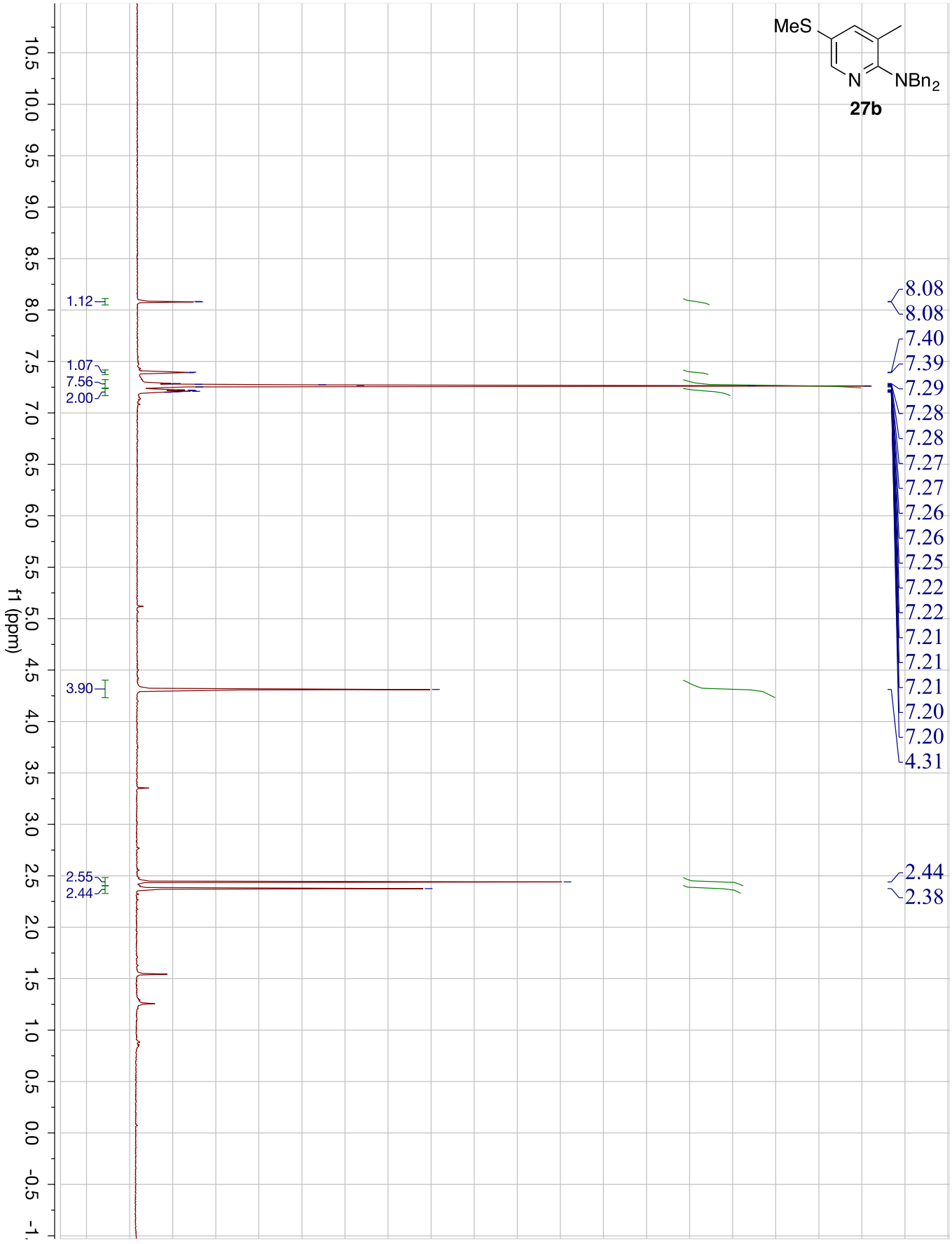
2.01
2.09
2.17
3.00
3.02
f1 (ppm)


Cl
N
AcHN
Cl
N
23k
2.00
2.14
1.14
2.11
2.93
8.88
7.41
7.40
7.28
7.27
7.27
7.25
4.62
2.16
f1 (ppm)


AcHN
N
N
23l
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
1.70
1.20
2.15
1.84
2.53
2.31
1.85
8.92
5.86
5.85
5.84
5.83
5.82
5.81
5.80
5.04
5.03
5.03
5.03
5.01
5.00
5.00
5.00
4.97
4.97
4.97
4.96
4.96
4.96
4.95
4.95
4.95
4.95
4.95
2.91
2.90
2.90
2.89
2.88
2.17
2.10
2.10
2.10
2.09
2.09
2.08
1.90
1.89
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.85


MeS
N
NEt2
27a
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
1.00
0.98
4.03
2.96
2.94
5.96
8.12
8.12
7.38
7.38
3.20
3.19
3.18
3.17
2.44
2.24
1.08
1.06
1.05


MeS
N
NBn2
27b
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
1.12
1.07
7.56
2.00
3.90
2.55
2.44
8.08
8.08
7.40
7.39
7.29
7.28
7.28
7.27
7.27
7.26
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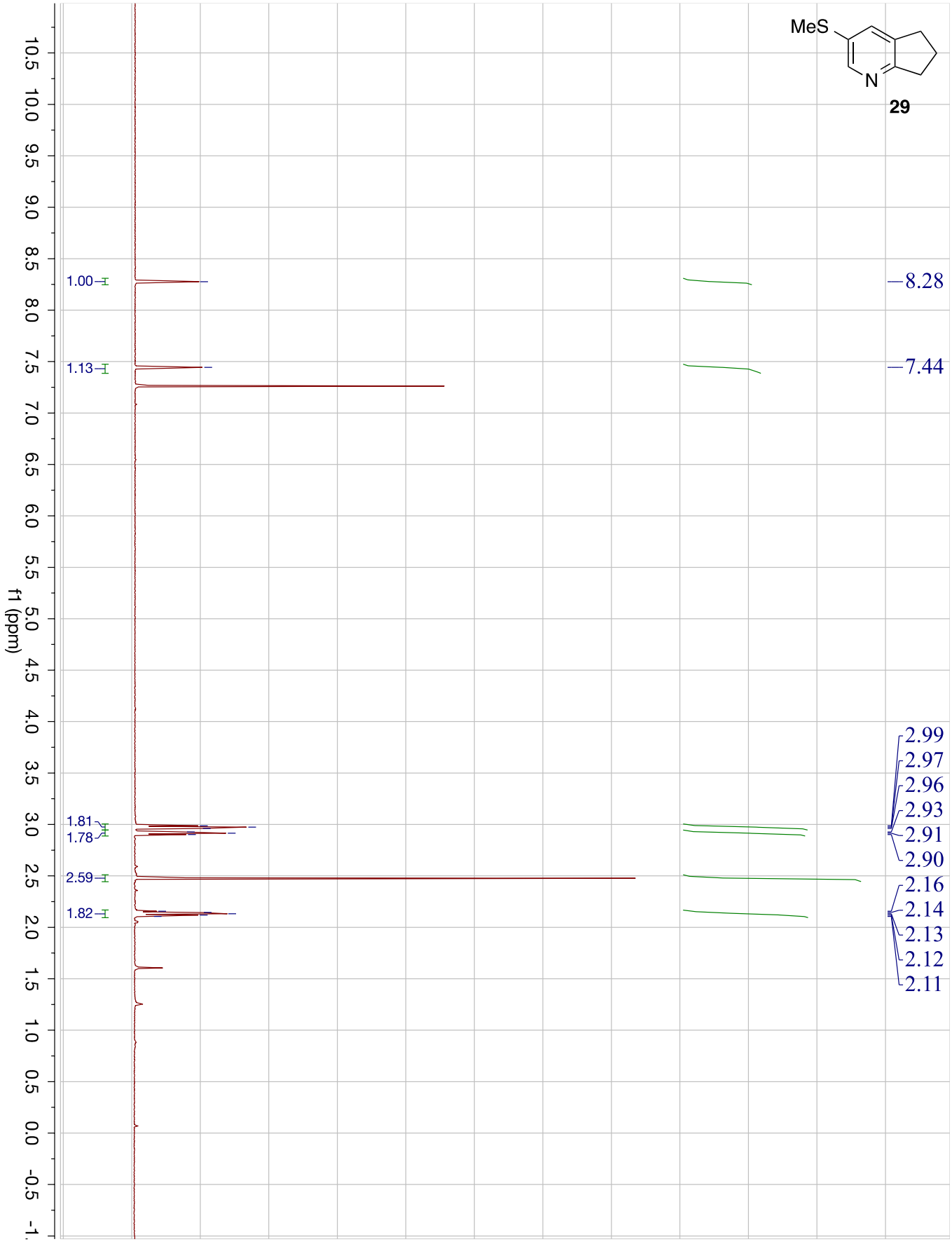
7.22
7.21
7.21
7.21
7.20
7.20
4.31
2.44
2.38


MeS
N
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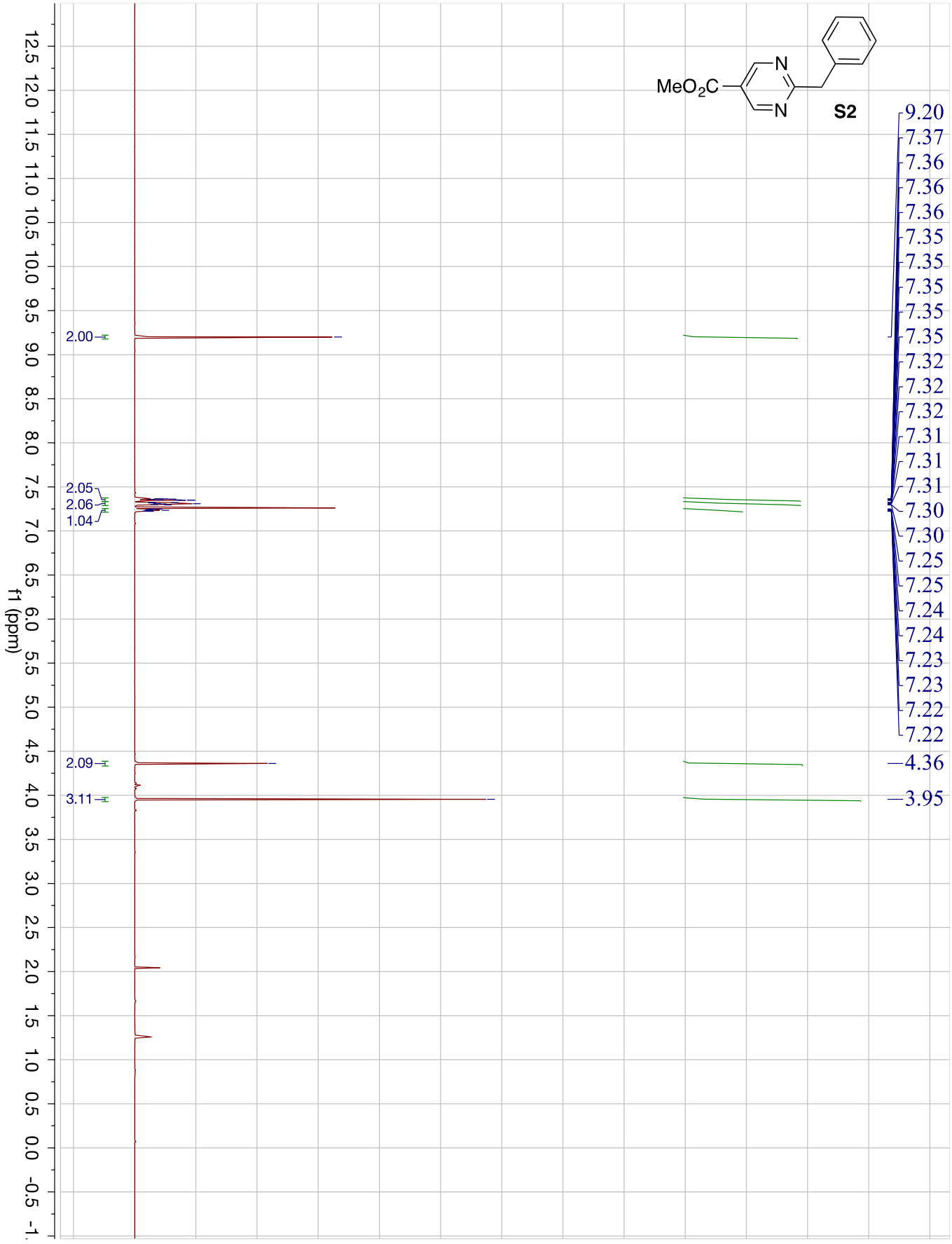
1.00
1.13
1.81
1.78
2.59
1.82
8.28
7.44
2.99
2.97
2.96
2.93
2.91
2.90
2.16
2.14
2.13
2.12
2.11
f1 (ppm)


MeO2C
N
N
S2
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7.36
7.36
7.36
7.35
7.35
7.35
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7.35
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
4.36
3.95
2.00
2.05
2.06
1.04
2.09
3.11
f1 (ppm)