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Synthesis of 5-methyl-4-polyfluoroaryl-1,3-thiazol-2-amines

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Table of Contents

1. General Information

^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H and 282.4 MHz ^{19}F) and on a Bruker Avance 400 spectrometer (400 MHz for ^{1}H and 376.4 MHz for ^{19}F) in CCl_4–$CDCl_3$ mixture. The chemical shifts in the ^{19}F NMR spectra are given relative to CCl_3F (with C_6F_6 as internal standard, δ = –162.9), while those in the ^{1}H NMR spectra are given relative to the residual signal from $CHCl_3$ (δ 7.26). ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100.6 MHz), a Bruker DRX 500 (125.7 MHz), and a Bruker Avance 600 (150.9 MHz) spectrometers in $(CD_3)_2SO$ (for compounds **2**, **4**, in $CDCl_3$), the chemical shifts are given relative to the central signal of the solvent (δ 39.5 for $(CD_3)_2SO$ and δ 77.2 for $CDCl_3$). IR and UV spectra were recorded on a Bruker Vector 27 FTIR spectrometer and an Agilent Cary 5000 spectrophotometer, respectively. High-resolution mass spectra were obtained on a Thermo Electron Corporation DFS instrument (EI, 70 eV). Gas chromatography analysis was performed on an LKhM-72 gas chromatograph equipped with a packed column (length 2 m, inner diameter 4 mm, Chromosorb WAW-DMCS bulk packing impregnated with liquid stationary phase (dimethylpolysiloxane VS-1, 15% of Chromosorb WAW-DMCS w/w) and a thermal conductivity detector. Helium was used as the carrier gas (60 mL min^{-1}). The evaporator temperature was 280 °C and the initial temperature of the column was 50 °C (heating to 280 °C at 10 °C min^{-1}). Melting points were measured on a Kofler hot-stage apparatus.

The starting ketones were obtained according to the literature: (1) A. S. Vinogradov *et al*., *Russ. J. Org. Chem*., 2010, **46**, 344 (*Zh. Org. Khim*., 2010, **46**, 352) and (2) A. S. Vinogradov et al., *Chem. Sustainable Dev*., 2023, **31**, 632.

2. Experimental Procedures

2.1. The reactions of 1-(pentafluorophenyl)propane-1-one (1) with bromine.

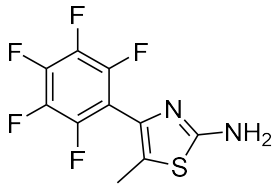
a) Bromine (1.76 g, 11 mmol) was added to a solution of ketone **1** (2.24 g, 10 mmol) in diethyl ether (20 ml). The resulting mixture was stirred at 25 °C for 5 days and analyzed by ^{19}F NMR spectroscopy. The mixture contained ketone **1** and bromo ketone **2** in the 50:50 ratio.

b) Bromine (1.76 g, 11 mmol) was added to a solution of ketone **1** (2.24 g, 10 mmol) in acetic acid (10 ml). The resulting mixture was stirred at 25 °C for 2 days and analyzed by ^{19}F NMR spectroscopy. The mixture contained bromo ketone **2** (^{19}F NMR (282.4 MHz, AcOH+$CDCl_3$), δ: -160.8 (m, 2F, F-3,5), -149.5 (tt, 1F, F-4, $^3J_{FF}$ = 20.5, $^4J_{FF}$ = 3.5 Hz), -140.8 (m, 2F, F-2, F-6)) and dibromo ketone **3** (^{19}F NMR (282.4 MHz, AcOH+$CDCl_3$), δ: -160.4 (m, 2F, F-3,5), -150.4 (tt, 1F, F-4, $^3J_{FF}$ = 20.5, $^4J_{FF}$ = 3.5 Hz), -134.5 (m, 2F, F-2, F-6)) in the 94:6 ratio.

c) Bromine (1.76 g, 11 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **1** (2.24 g, 10 mmol) in $CHCl_3$ (20 ml). The resulting mixture was stirred at 25 °C for 2 days and analyzed by ^{19}F NMR spectroscopy. The mixture contained only bromo ketone **2**. The reaction mixture was evaporated under reduced pressure (25 °C / 30 Torr). The residue was washed with H_2O (50 ml), the organic phase separated and dried over $MgSO_4$. After vacuum distillation 2.47 g (82% yield) of bromo ketone **2** was obtained with 99.8% purity (GC). Light yellow liquid. Bp 56-60 °C (3 Torr). IR (film), ν, cm^{-1}: 2983, 2933, 2871, 2096, 1722, 1650, 1521, 1502, 1446, 1411, 1334, 1187, 1143, 1095, 1068, 1029, 987, 845, 684. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 218 (3.69), 238 (3.70). ^{1}H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 1.91 (d, 3H, CH_3, $^3J_{HH}$ = 6.5 Hz), 4.91 (q, 1H, CH, $^3J_{HH}$ = 6.5 Hz). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$), δ: 19.2 (s, CH_3), 47.9 (t, CH, J_{CF} = 2.5 Hz), 113.1 (tm, C-1, $^2J_{CF}$ = 19.0 Hz), 137.8 (dm, C-F, $^1J_{CF}$ = 253.0 Hz), 143.3 (dm, C-F, $^1J_{CF}$ = 255.0 Hz), 144.5 (dm, C-F, $^1J_{CF}$ = 249.0 Hz), 187.4 (s, C=O). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -160.9 (m, 2F, F-3,5), -149.9 (tt, 1F, F-4, $^3J_{FF}$ = 20.5, $^4J_{FF}$ = 3.5 Hz), -141.5 (m, 2F, F-2,6). HRMS (ESI), *m/z*: 301.9358 (calc. for $C_9H_4BrF_5O$, *m/z*: 301.9360). Found, %: C, 35.90; H, 1.74; Br, 25.91, F, 31.20. Calc. for $C_9H_4BrF_5O$, %: C, 35.67; H, 1.33; Br, 26.37, F, 31.35.

2.2. Synthesis of 5-methyl-4-polyfluoroaryl-1,3-thiazol-2-amines.

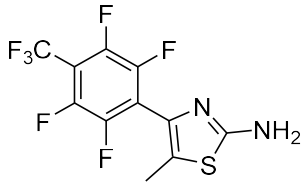
2.2.1. 5-Methyl-4-pentafluorophenyl-1,3-thiazol-2-amine (4).



a) Thiourea (1.60 g, 21 mmol) was added to a solution of bromo ketone **2** (6.06 g, 20 mmol) in ethanol (60 ml). The resulting mixture was stirred at 80 ºC for 1 h, then cooled to room temperature, and the solvent was removed under reduced pressure (30 Torr). The residue was quenched with saturated solution of $NaHCO_3$ (80 ml), the precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 4.48 g (80%) of thiazole **4**. Yellow powder. Mp 166-168 ºC. IR (KBr), ν, cm^{-1}: 3488, 3286, 3124, 2950, 2725, 1633, 1575, 1523, 1496, 1430, 1336, 1135, 1095, 1049, 979, 900, 748. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 256 (3.89). ^1H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 2.19 (s, 3H, CH_3), 5.27 (br. s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$), δ: 11.9 (s, CH_3), 110.0 (t, C-1, $^2J_{CF}$ = 19.0 Hz), 124.3 (s, C-S), 131.5 (s, C-N), 137.9 (dm, C-F, $^1J_{CF}$ = 253.0 Hz), 141.2 (dm, C-F, $^1J_{CF}$ = 255.0 Hz), 144.8 (dm, C-F, $^1J_{CF}$ = 249.0 Hz), 165.6 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -163.3 (m, 2F, F-3,5), -155.7 (t, 1F, F-4, $^3J_{FF}$ = 21 Hz), -140.6 (m, 2F, F-2,6). HRMS (ESI), *m/z*: 280.0085 (calc. for $C_{10}H_5F_5N_2S$, *m/z*: 280.0088). Found (%): C, 42.78; H, 1.71; F, 34.21; N, 10.02; S, 11.36. Calc. for $C_{10}H_5F_5N_2S$ (%): C, 42.86; H, 1.80; F, 33.90; N, 10.00; S, 11.44.

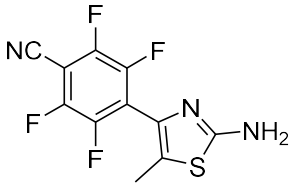
b) Bromine (1.76 g, 11 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **1** (2.24 g, 10 mmol) in $CHCl_3$ (20 ml). The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was evaporated under reduced pressure (25ºC / 30 Torr), then ethanol (15 ml) and thiourea (0.80 g, 10.5 mmol) were added to the residue. The mixture was stirred at 80 ºC for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 2.35 g (84%) of thiazole **4**.

2.2.2. 5-Methyl-4-[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]-1,3-thiazol-2-amine (10).



Bromine (0.88 g, 5.50 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **5** (1.37 g, 5.00 mmol) in $CHCl_3$ (20 ml). The resulting mixture was stirred at room temperature for 24 h. The mixture was evaporated under reduced pressure (25°C / 30 Torr), then ethanol (15 ml) and thiourea (0.40 g, 5.25 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to obtained 1.52 g (92%) of thiazole **10**. Yellow powder. Mp 122-124 °C. IR (KBr), ν, $см^{-1}$: 3454, 3434, 3301, 3147, 2958, 2929, 2736, 1641, 1560, 1538, 1459, 1326, 1238, 1174, 1099, 962, 759. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 257 (3.95), 307 (3.62). ^{1}H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 2.23 (s, 3H, CH_3), 5.37 (br. s, 2H, NH_2). $^{13}C\{^1H\}$ NMR [150.9 MHz, $(CD_3)_2SO$], δ: 11.3 (s, CH_3), 107.5 (qt, C-4, $^2J_{CF}$ = 34.0 Hz, $^2J_{CF}$ = 12.5 Hz), 119.9 (t, C-1, $^2J_{CF}$ = 18.0 Hz), 121.0 (q, CF_3, $^1J_{CF}$ = 274.0 Hz), 122.9 (s, C-S), 130.7 (s, C-N), 144.0 (dm, C-F, $^1J_{CF}$ = 256.5 Hz), 144.3 (dm, C-F, $^1J_{CF}$ = 248.0 Hz), 166.4 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -141.8 (m, 2F), -138.7 (m, 2F), -57.6 (t, 3F, CF_3, $^4J_{FF}$ = 22 Hz). HRMS (ESI), *m/z*: 330.0053 (calc. for $C_{11}H_5F_7N_2S$, *m/z*: 330.0056). Found, %: C, 40.12; H, 1.44; F, 40.00; N, 7.89; S, 10.24. Calc. for $C_{11}H_5F_7N_2S$, %: C, 40.01; H, 1.53; F, 40.27; N, 8.48; S, 9.71.

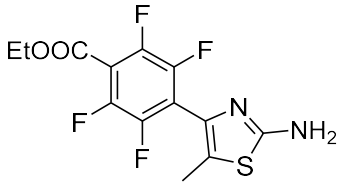
2.2.3. 5-Methyl-4-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,3-thiazol-2-amine (11).



Bromine (0.18 g, 1.14 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **6** (0.24 g, 1.04 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 2 days. The mixture was evaporated under reduced pressure (25°C / 30 Torr), then ethanol (5 ml) and thiourea (0.08 g, 1.10 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 0.27 g

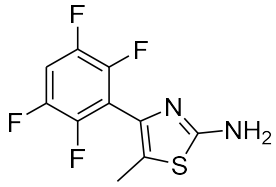
(90%) of thiazole **11**. Yellow powder. Mp 193-195 °C. IR (KBr), ν, см$^{-1}$: 3438, 3411, 3322, 3193, 2962, 2927, 2738, 2248, 1646, 1554, 1484, 1336, 1174, 985, 746. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 237 (4.31), 297 (3.57), 339 (3.63). ^{1}H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 2.24 (s, 3H, CH_3), 4.85 (br. s, 2H, NH_2). ^{13}C{^{1}H} NMR [125.7 MHz, $(CD_3)_2SO$], δ: 11.4 (s, CH_3), 92.9 (t, C-4, $^2J_{CF}$ = 17.0 Hz), 108.4 (s, CN), 121.5 (t, C-1, $^2J_{CF}$ = 18.0 Hz), 123.4 (s, C-S), 130.7 (s, C-N), 143.7 (dm, C-F, $^1J_{CF}$ = 247.5 Hz), 147.1 (dm, C-F, $^1J_{CF}$ = 258.0 Hz), 166.3 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -137.4 (m, 2F), -134.1 (m, 2F). HRMS (ESI), *m/z*: 287.0131 (calc. for $C_{11}H_5F_4N_3S$, *m/z*: 287.0135). Found, %: C, 46.36; H, 1.77; F, 26.06; N, 14.38; S, 11.34. Calc. for $C_{11}H_5F_4N_3S$, %: C, 46.00; H, 1.75; F, 26.46; N, 14.63; S, 11.16.

2.2.4. 5-Methyl-4-(4-ethoxycarbonyl-2,3,5,6-tetrafluorophenyl)-1,3-thiazol-2-amine (12).



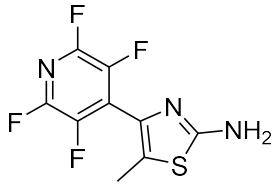
Bromine (0.44 g, 2.75 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **7** (0.70 g, 2.50 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 2 days. The mixture was evaporated under reduced pressure (25°C / 30 Torr), then ethanol (10 ml) and thiourea (0.2 g, 2.63 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 0.78 g (93%) of thiazole **12**. Yellow powder. Mp 105-107 °C. IR (KBr), ν, см$^{-1}$: 3432, 3311, 3174, 2995, 2946, 2734, 1716, 1641, 1537, 1467, 1365, 1328, 1282, 1213, 1027, 987, 734. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 225 (4.18). ^{1}H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 1.44 (t, 3H, $\underline{CH_3}CH_2$, $^3J_{HH}$ = 7.30 Hz), 2.21 (s, 3H, CH_3), 4.46 (q, 2H, $CH_3\underline{CH_2}$, $^3J_{HH}$ = 7.30 Hz), 5.41 (br. s, 2H, NH_2). ^{13}C{^{1}H} NMR [125.7 MHz, $(CD_3)_2SO$], δ: 11.3 (s, CH_3), 13.9 (s, CH_3), 62.8 (s, CH_2), 111.6 (t, C-4, $^2J_{CF}$ = 16.0 Hz), 118.4 (t, C-1, $^2J_{CF}$ = 17.5 Hz), 122.4 (s, C-S), 131.2 (s, C-N), 143.2 (dm, C-F, $^1J_{CF}$ = 245.5 Hz), 142.9 (dm, C-F, $^1J_{CF}$ = 246.5 Hz), 159.1 (s, C=O), 166.2 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -141.3 (m, 2F), -140.0 (m, 2F). HRMS (ESI), *m/z*: 334.0393 (calc. for $C_{13}H_{10}F_4N_2O_2S$, *m/z*: 334.0394). Found, %: C, 46.17; H, 2.80; F, 23.04; N, 7.93; S, 10.03. Calc. for $C_{13}H_{10}F_4N_2O_2S$, %: C, 46.71; H, 3.02; F, 22.73; N, 8.38; S, 9.59.

2.2.5. 5-Methyl-4-(2,3,5,6-tetrafluorophenyl)-1,3-thiazol-2-amine (13).



Bromine (0.88 g, 5.50 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **8** (1.03 g, 5.00 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 2 days. The mixture was evaporated under reduced pressure (25°C / 30 Torr), then ethanol (15 ml) and thiourea (0.40 g, 5.25 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 1.23 g (94%) of thiazole **13**. Light-beige powder. Mp 148-150 °C. IR (KBr), ν, $см^{-1}$: 3494, 3295, 3120, 2952, 2726, 1639, 1610, 1540, 1490, 1388, 1322, 1170, 1091, 935, 835, 763, 711. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 258 (3.92). ^1H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 2.21 (s, 3H, CH_3), 5.28 (br. s, 2H, NH_2), 7.07 (m, 1H, C_6F_4H). $^{13}C\{^1H\}$ NMR [100.6 MHz, $(CD_3)_2SO$], δ: 11.3 (s, CH_3), 106.5 (t, C-4, $^2J_{CF}$ = 23.5 Hz), 115.8 (t, C-1, $^2J_{CF}$ = 18.0 Hz), 121.3 (s, C-S), 131.9 (s, C-N), 143.8 (dm, C-F, $^1J_{CF}$ = 245.5 Hz), 145.8 (dm, C-F, $^1J_{CF}$ = 245.5 Hz), 166.2 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -141.1 (m, 2F), -140.3 (m, 2F). HRMS (ESI), *m/z*: 262.0187 (calc. for $C_{10}H_6F_4N_2S$, *m/z*: 262.0182). Found, %: C, 45.48; H, 2.25; F, 29.02; N, 10.70; S, 12.66. Calc. for $C_{10}H_6F_4N_2S$, %: C, 45.80; H, 2.31; F, 28.98; N, 10.68; S, 12.23.

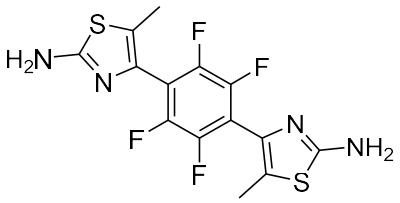
2.2.5. 5-Methyl-4-(2,3,5,6-tetrafluoropyridin-4-yl)-1,3-thiazol-2-amine (14).



Bromine (0.46 g, 2.87 mmol) and 2-3 drops of acetic acid were added to a solution of ketone **9** (0.54 g, 2.56 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 2 days. The mixture was evaporated under reduced pressure (25 °C / 30 Torr), then ethanol (10 ml) and thiourea (0.21 g, 2.74 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 0.59 g (86%) of thiazole **14**. Light-yellow powder. Mp 175-177 °C. IR (KBr), ν, $см^{-1}$: 3454, 3434, 3301, 3147, 2958, 2929, 2736, 1641, 1560, 1538, 1459, 1326, 1238, 1174, 1099, 962, 759. UV

(EtOH), $\lambda_{max.}$, nm (lg ε): 225 (3.94), 258 (3.97), 315 (3.53). ^{1}H NMR (300 MHz, CCl_4+$CDCl_3$), δ: 2.27 (s, 3H, CH_3), 4.96 (br. s, 2H, NH_2). $^{13}C\{^{1}H\}$ NMR [125.7 MHz, $(CD_3)_2SO$], δ: 11.4 (s, CH_3), 123.8 (s, C-S), 128.4 (t, C-4, $^{2}J_{CF}$ = 16.0 Hz), 130.8 (s, C-N), 139.5 (dm, C-F, $^{1}J_{CF}$ = 256.5 Hz), 143.2 (dm, C-F, $^{1}J_{CF}$ = 241.5 Hz), 166.5 (s, C-NH_2). ^{19}F NMR (282.4 MHz, CCl_4+$CDCl_3$), δ: -142.2 (m, 2F, F-3,5), -91.8 (m, 2F, F-2,6). HRMS (ESI), *m/z*: 263.0130 (calc. for $C_9H_5F_4N_3S$, *m/z*: 263.0135). Found, %: C, 40.97; H, 1.72; F, 28.98; N, 15.70; S, 12.01. Calc. for $C_9H_5F_4N_3S$, %: C, 41.07; H, 1.91; F, 28.87; N, 15.96; S, 12.18.

2.2.6. 4,4′-(2,3,5,6-Tetrafluoro-1,4-phenylene)bis(5-methyl-1,3-thiazol-2-amine) (16).



Bromine (0.84 g, 5.25 mmol) and 2-3 drops of acetic acid were added to a solution of diketone **15** (0.66 g, 2.50 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 2 days. The mixture was evaporated under reduced pressure (25°C / 30 Torr), then ethanol (15 ml) and thiourea (0.40 g, 5.25 mmol) were added to the residue. The mixture was stirred at 80 °C for 1 h, cooled to room temperature and quenched with saturated solution of $NaHCO_3$ (80 ml). The precipitate formed was filtered off, washed with water (200 ml) and air dried to yield 0.82 (87%) of bis(thiazole) **16**. Light-beige powder. Mp 295-296 °C. IR (KBr), ν, $см^{-1}$: 3454, 3263, 3162, 3110, 2927, 2854, 2703, 1619, 1542, 1517, 1483, 1461, 1336, 1170, 1105, 975, 728. UV (EtOH), $\lambda_{max.}$, nm (lg ε): 225 (4.34), 256 (4.24), 304 (3.89). ^{1}H NMR [300 MHz, $(CD_3)_2SO$], δ: 2.12 (s, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR [125.7 MHz, $(CD_3)_2SO$], δ: 11.6 (s, CH_3), 114.7 (m, C-1,4), 121.5 (s, C-S), 131.9 (s, C-N), 143.9 (dm, C-F, $^{1}J_{CF}$ = 256.5 Hz), 166.1 (s, C-NH_2). ^{19}F NMR [282.4 MHz, $(CD_3)_2SO$], δ: -141.3 (m, 4F, C_6F_4). HRMS (ESI), *m/z*: 374.0273 (calc. for $C_{14}H_{10}F_4N_4S_2$, *m/z*: 374.0278).

The crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from the solution of compound **16** in DMF.

3. Crystallographic Data.

XRD data for compound **16** (solvate with DMF) were obtained on a Bruker Kappa Apex II CCD diffractometer using *φ, ω* scans of narrow (0.5°) frames with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the *SHELX-97* programs set.[1] The H atoms positions were calculated with the riding model. Absorption

corrections were applied empirically using *SADABS* programs. Compound **16** (solvate with DMF) is triclinic, space group *P*–1, a = 6.1778(4), b = 7.2790(4), c = 14.9148(8) Å, α = 81.614(2), β = 88.460(2), γ = 70.306(3)°, V = 624.53(6) Å^3, Z = 1, $C_{20}H_{24}F_4N_6O_2S_2$, d_{calc} = 1.384 g cm^3, μ = 0.272 mm^{-1}, F(000) = 270, crystal size 0.06 × 0.50 × 0.90 mm^3, independent reflections 2884 (R_{int} = 0.037), wR_2 = 0.1438, S = 1.03 for all reflections (R = 0.0436 for 2351 reflections $F > 4\sigma$). Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles are available as CCDC 2308048 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The unit cell contains one crystallographically independent half of a molecule of **16** and one molecule of DMF.

The obtained crystal structures were analyzed for short contacts between non-bonded atoms using the *PLATON* program.[2] Molecular structure of compound **16** and the selective bond lengths are illustrated in Figure 1 (the molecule is located at the symmetry center). The bond lengths and bond angles are the same as the statistical means.[3] According to the X-ray diffraction data the thiazole ring and the phenyl ring of **16** are perfectly planar in the crystal. The standard deviations from the mean plane are 0.001 Å for both. The plane of the thiazole ring is turned out of the phenyl plane by 59.4(1)°.

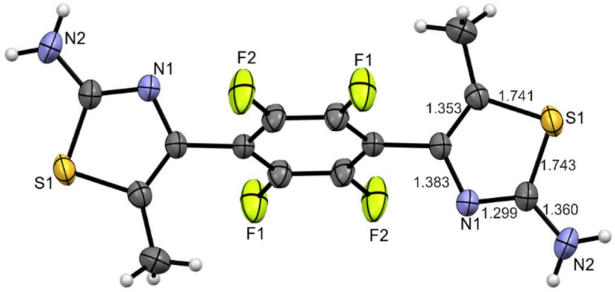


Figure S1. Molecular structure of compound **16** and the selective bond lengths.

The crystal structures solvate is stabilized by the hydrogen bonds N-H...O and C-H...F types (the parameters of H-bond are given in Table 1), they lead to formation of 2D networks.

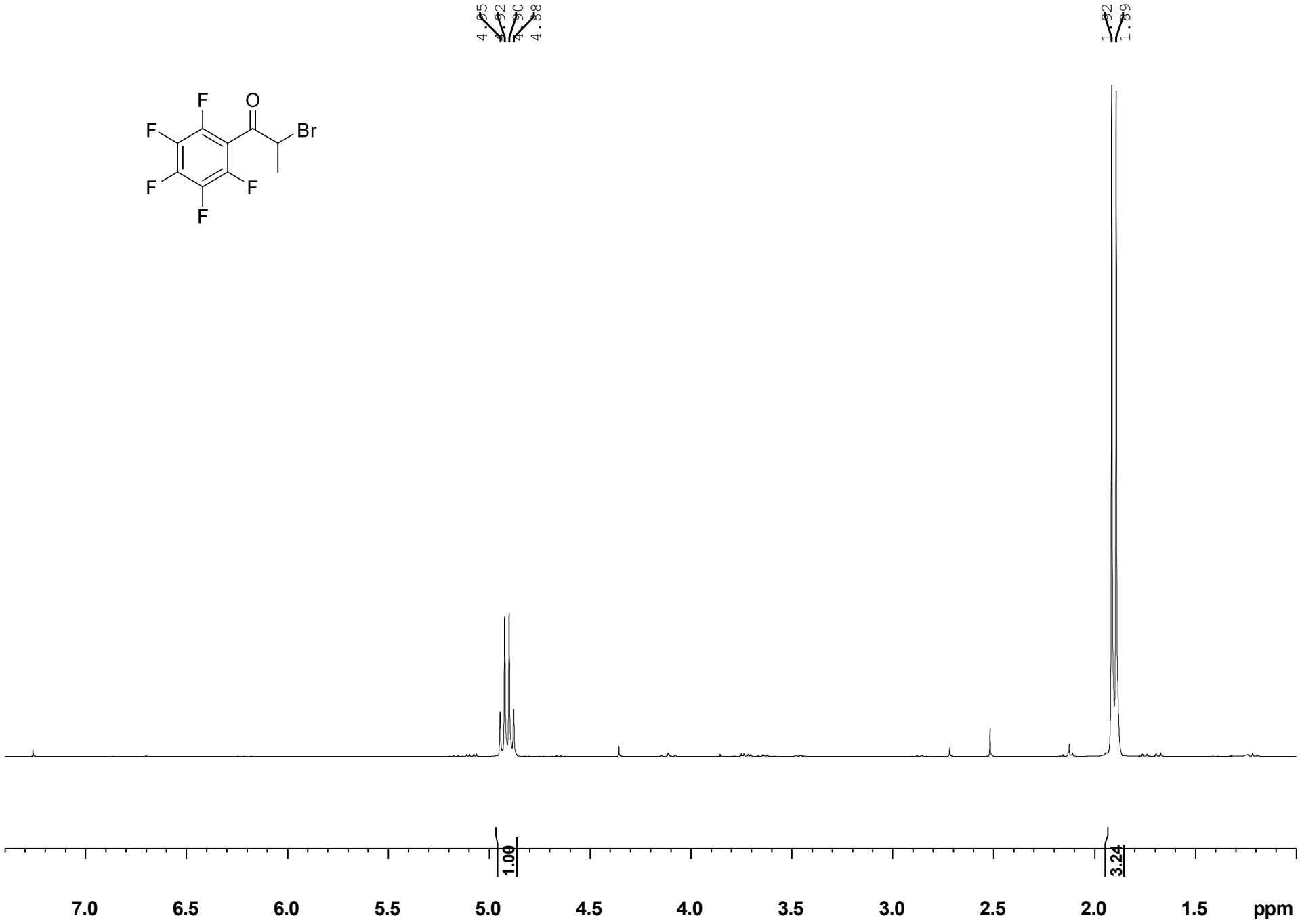
Table S1. Parameters of H-bond for solvate.

H-bond	D-H, Å	H…A, Å	D…A, Å	D-H…A, °
N2-H2A…O1	0.86	2.26	2.991(3)	143
N2-H2B…O1	0.86	2.08	2.891(3)	157
C12-H…F2	0.96	2.55	3.483(3)	165

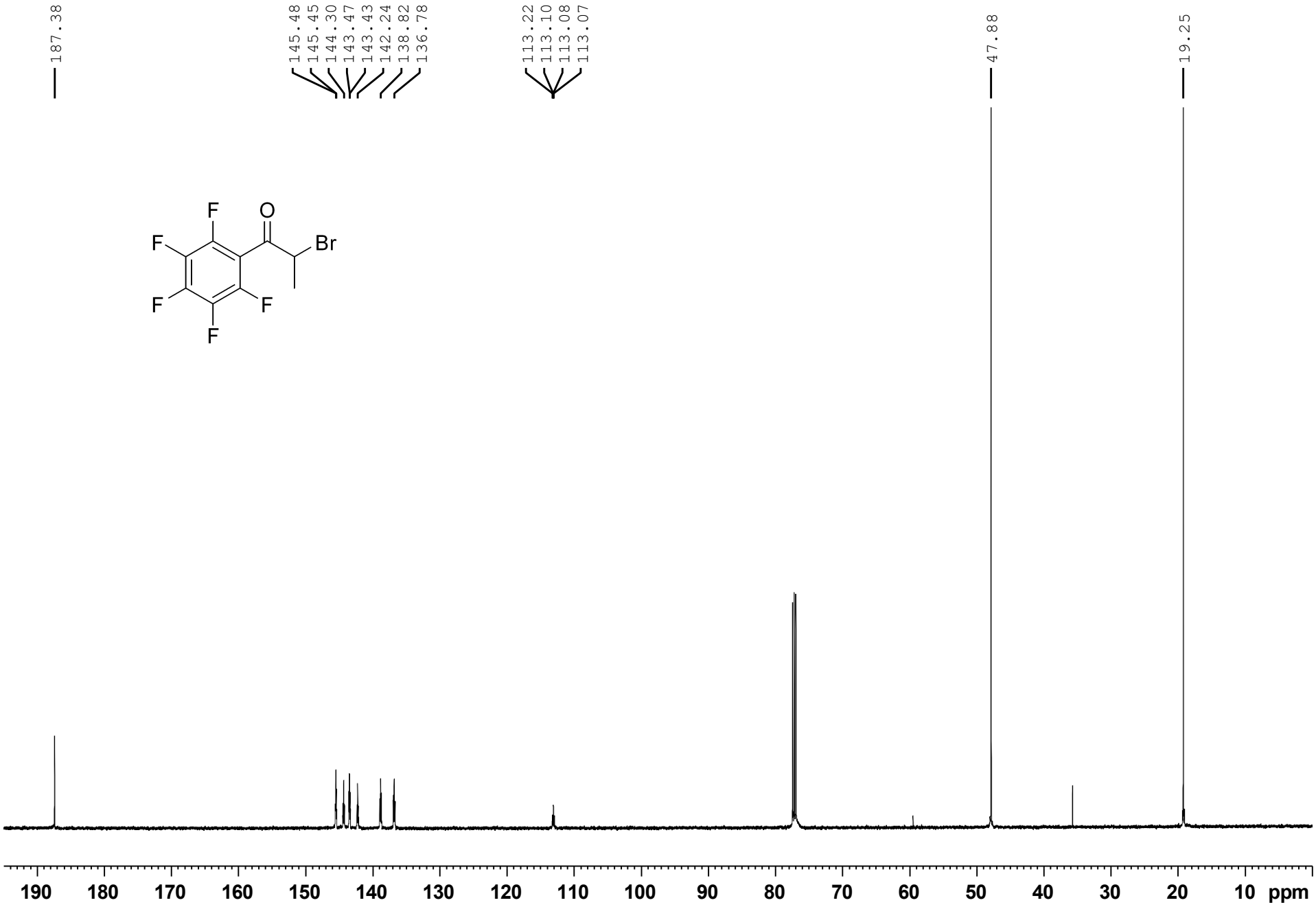
S1 G. M. Sheldrick, *SHELX-97 – Programs for Crystal Structure Analysis (Release 97-2)*. University of Göttingen, Germany, 1997.

S2 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

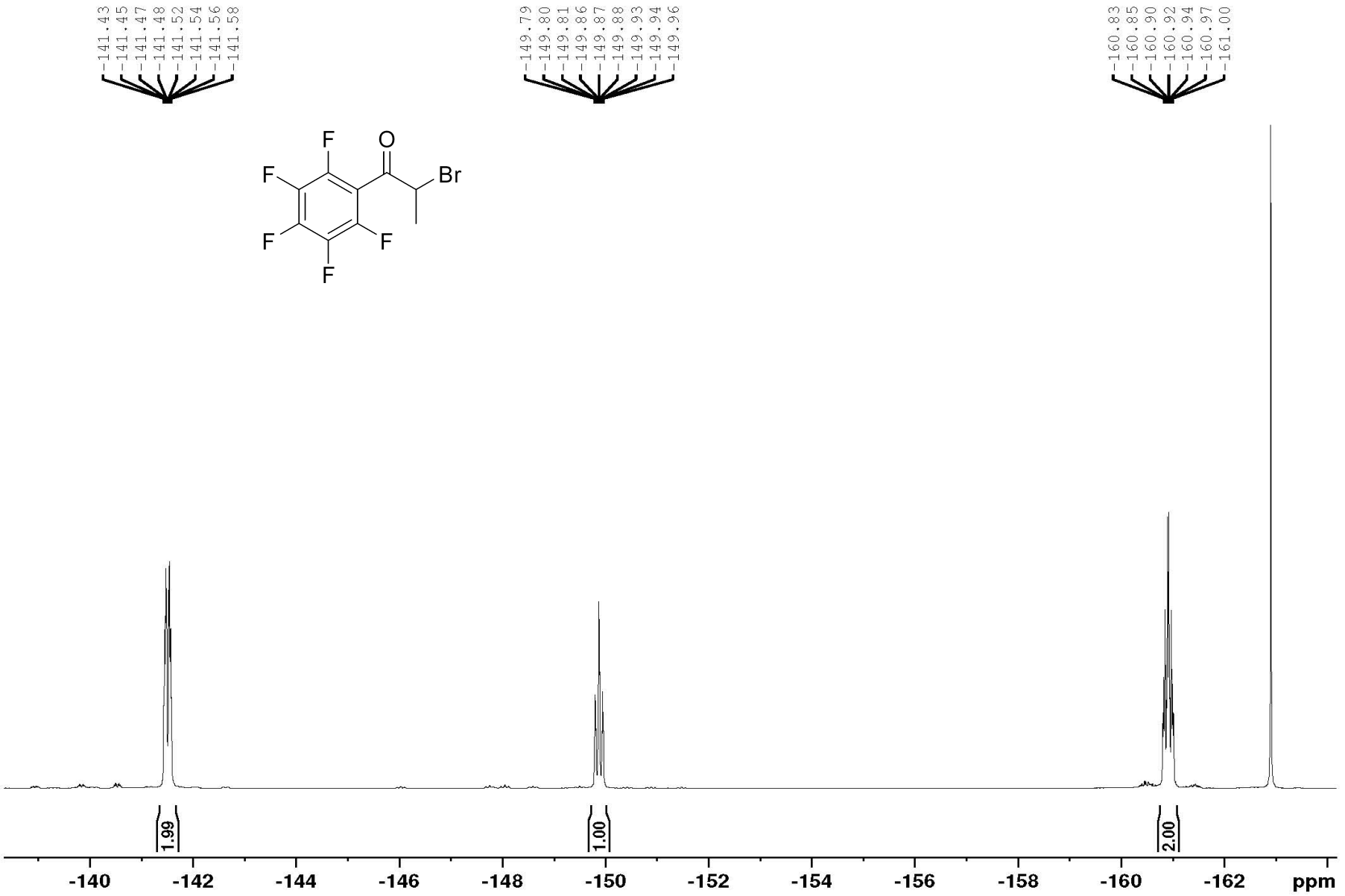
S3 F. H. Allen, O. Kenard, D. G. Watson, L. Bramer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.


4.65
4.62
4.60
4.58
1.92
1.89
F
O
F
Br
F
F
F
1.00
3.24
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

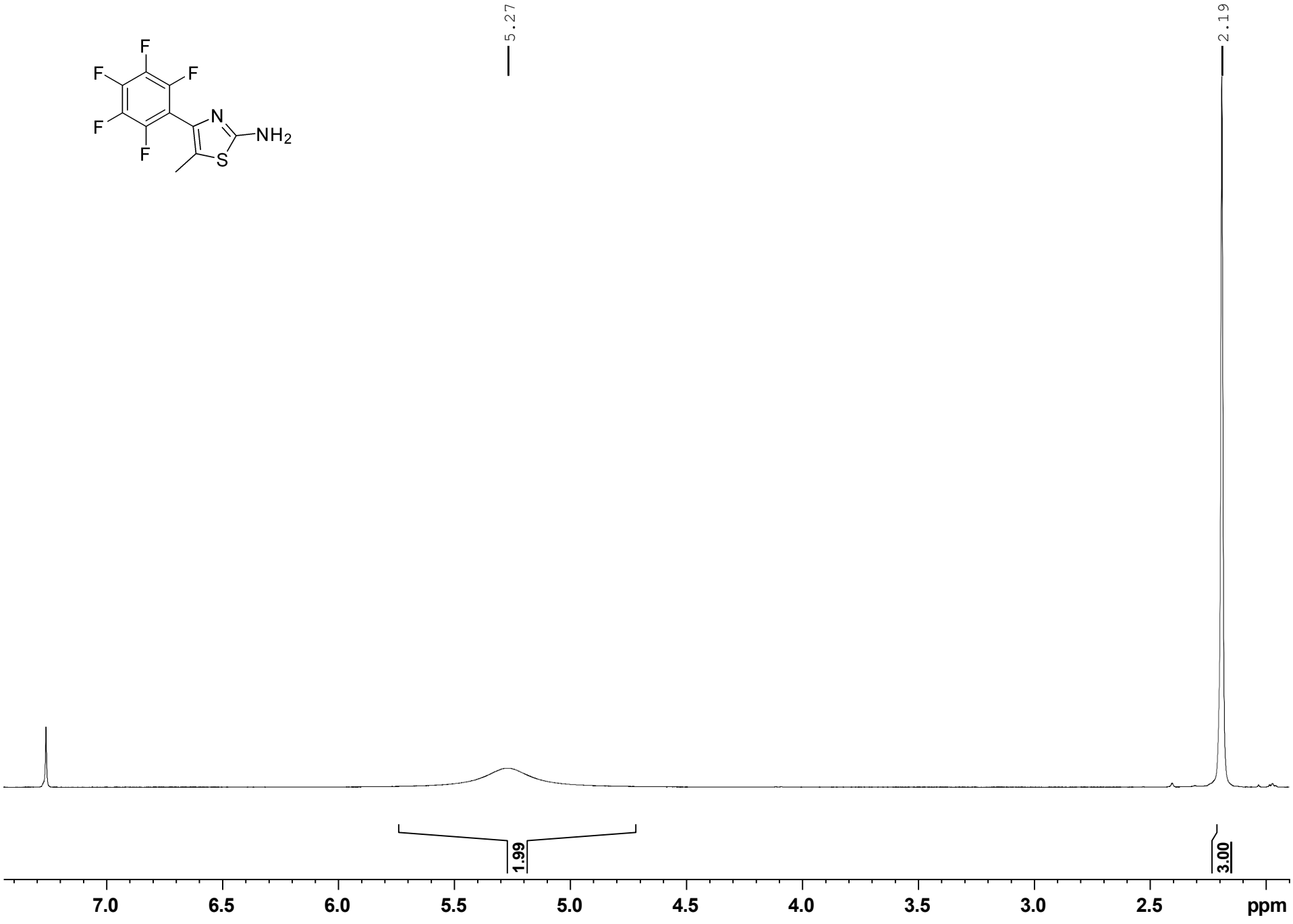
^{13}C NMR spectrum of 2-bromo-1-(pentafluorophenyl)propan-1-one (**2**)



^{19}F NMR spectrum of 2-bromo-1-(pentafluorophenyl)propan-1-one (**2**)



^{1}H NMR spectrum of 5-methyl-4-pentafluorophenyl-1,3-thiazol-2-amine (**4**)



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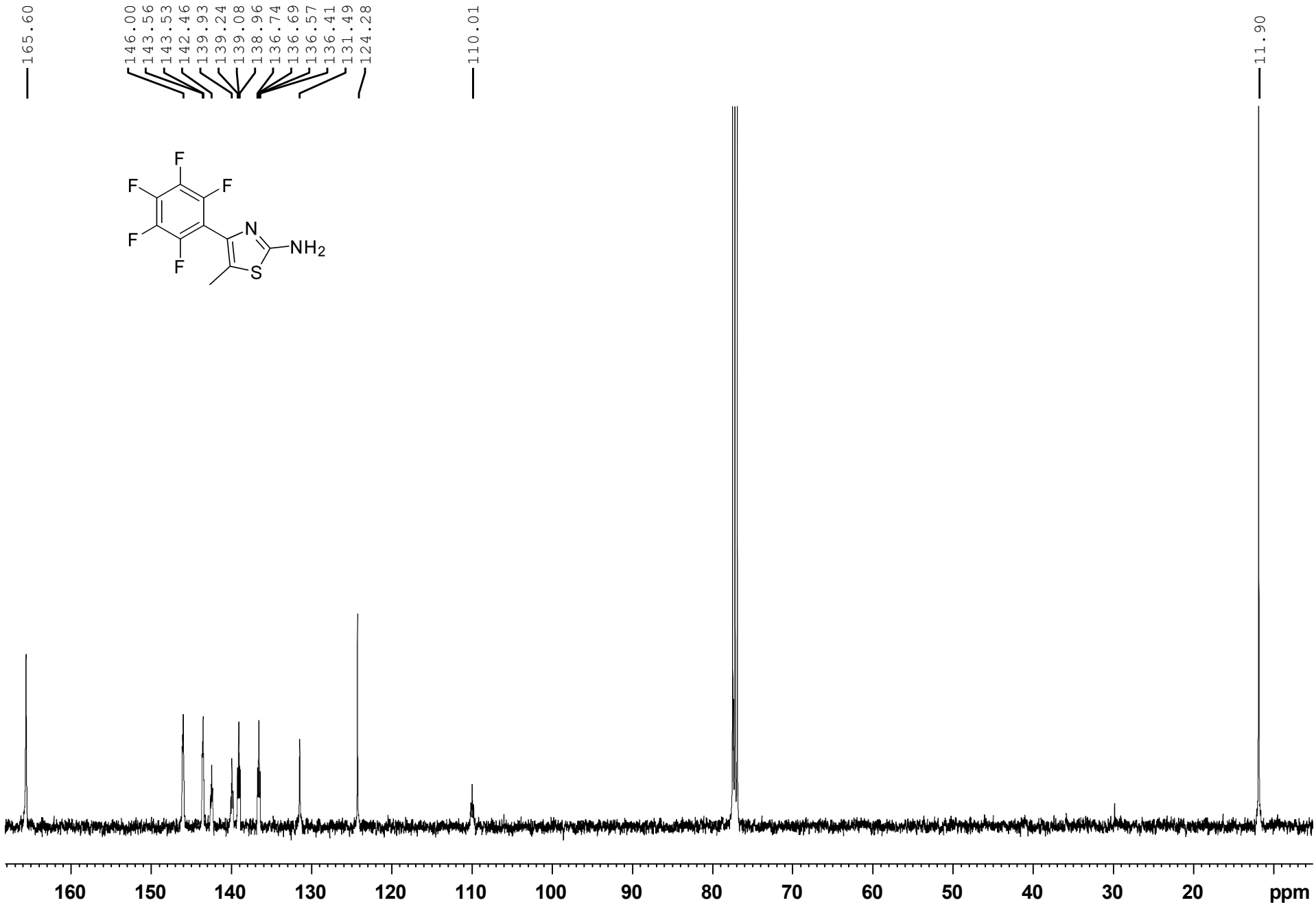

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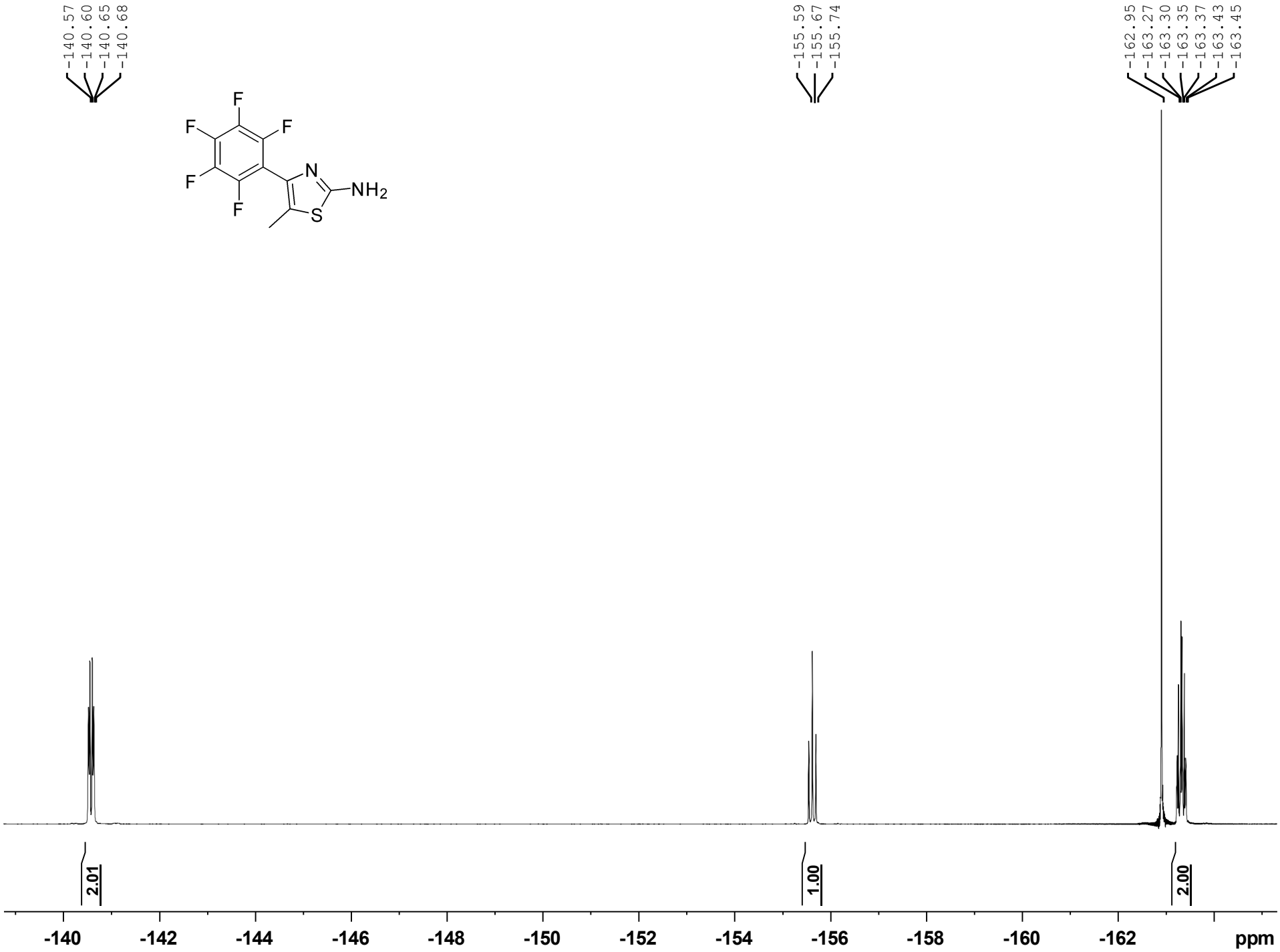
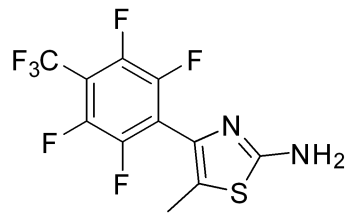


^{1}H NMR spectrum of 5-methyl-4-[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]-1,3-thiazol-2-amine (**10**)



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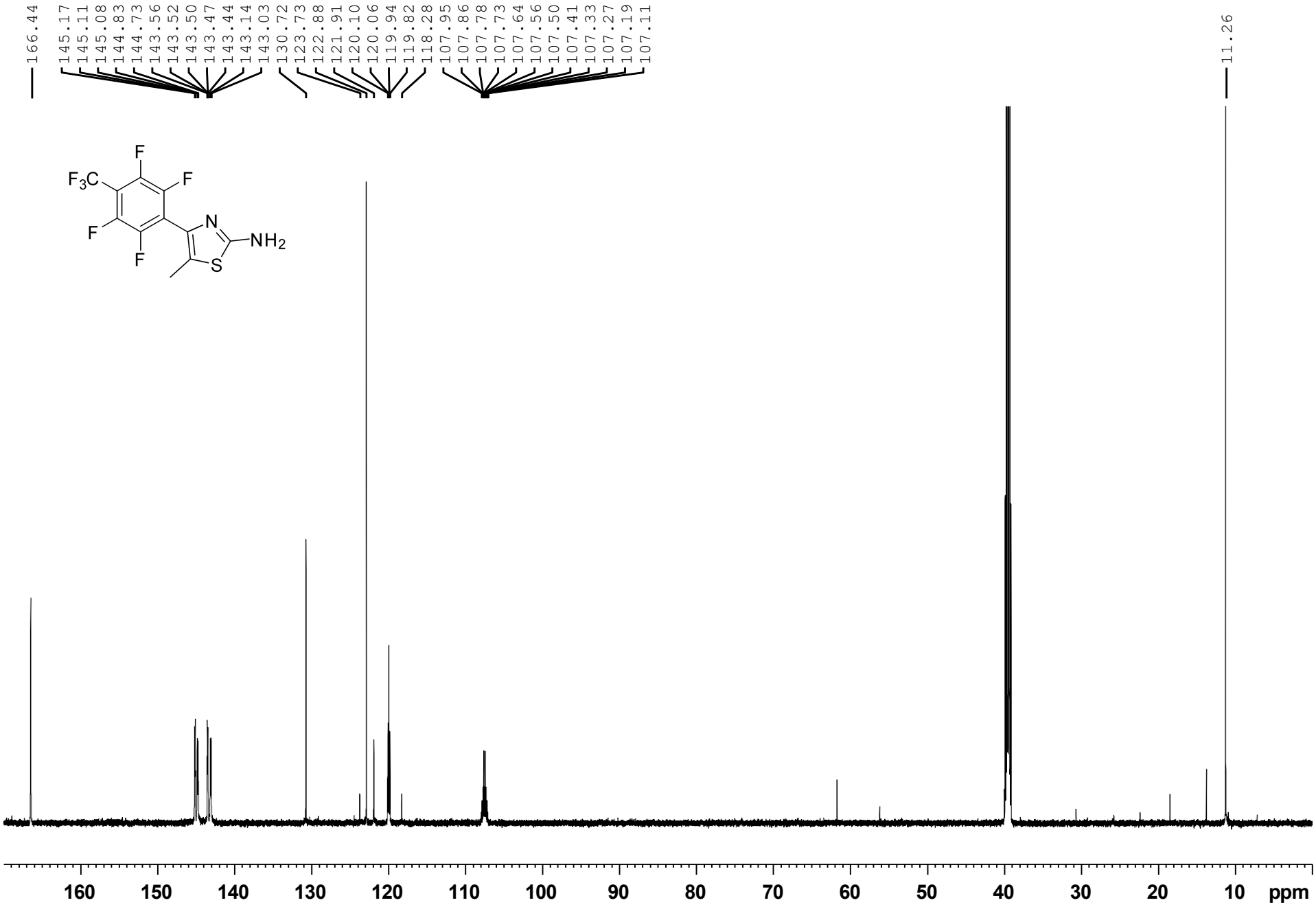

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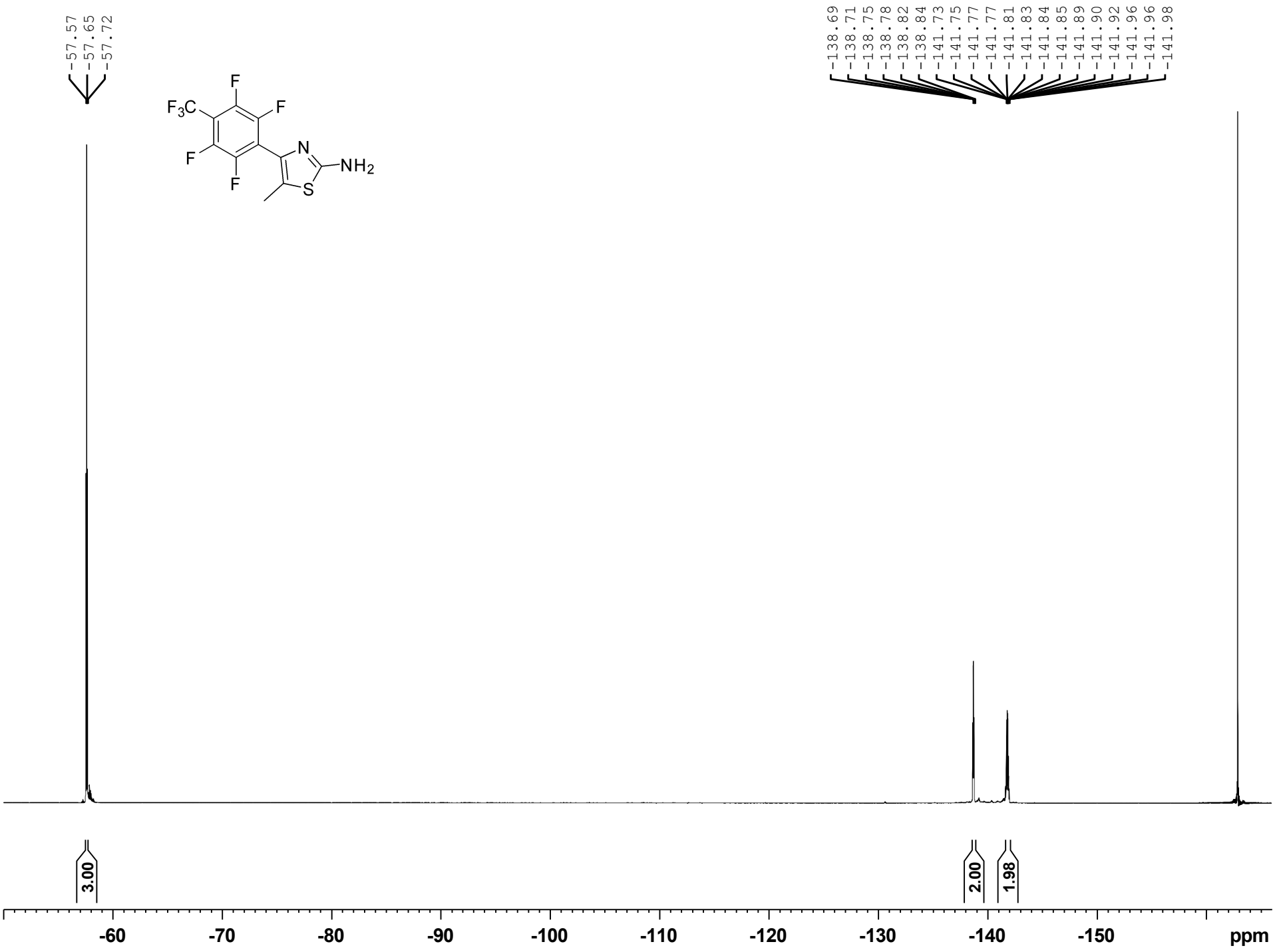
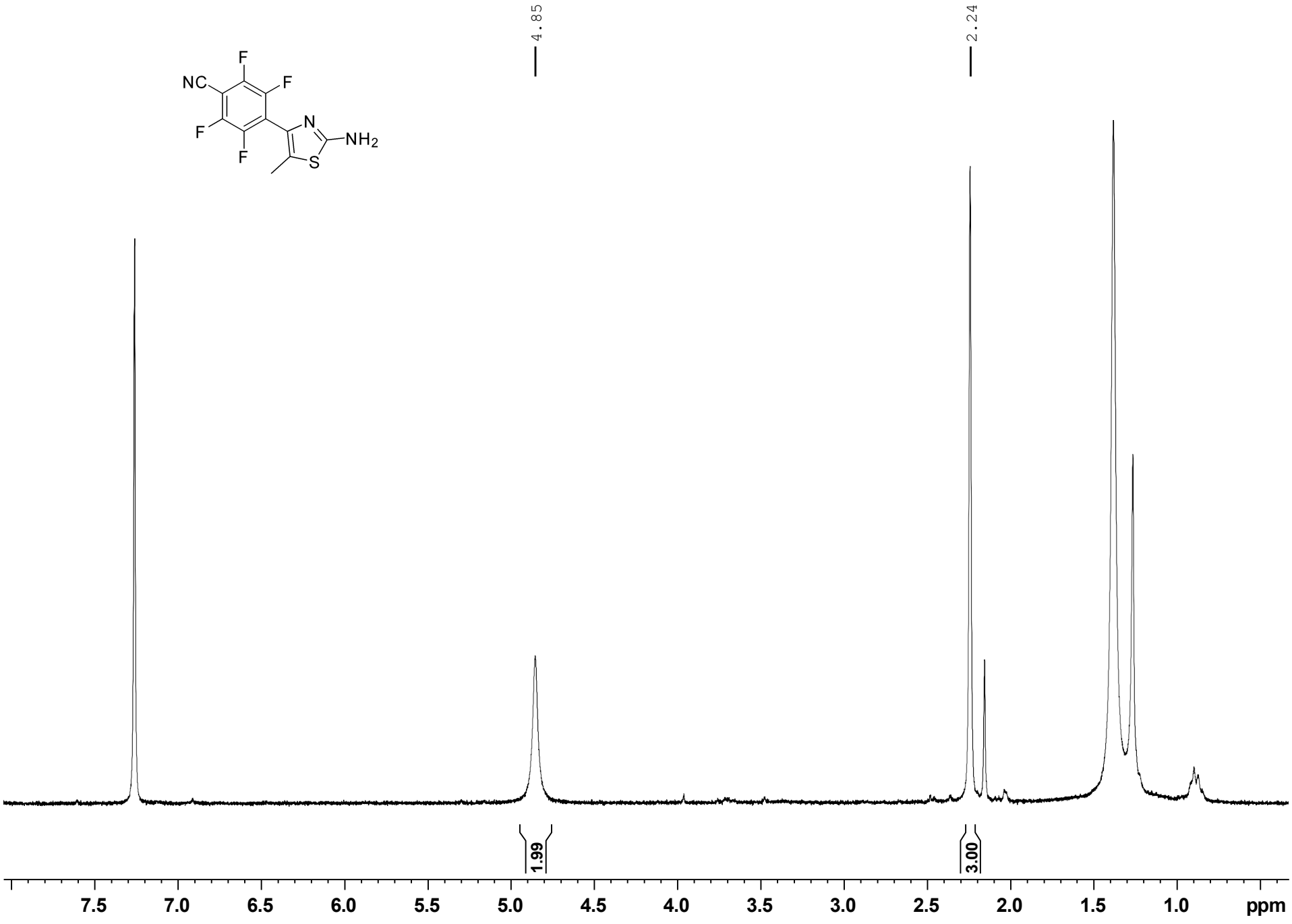


^{1}H NMR spectrum of 5-methyl-4-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,3-thiazol-2-amine (**11**)



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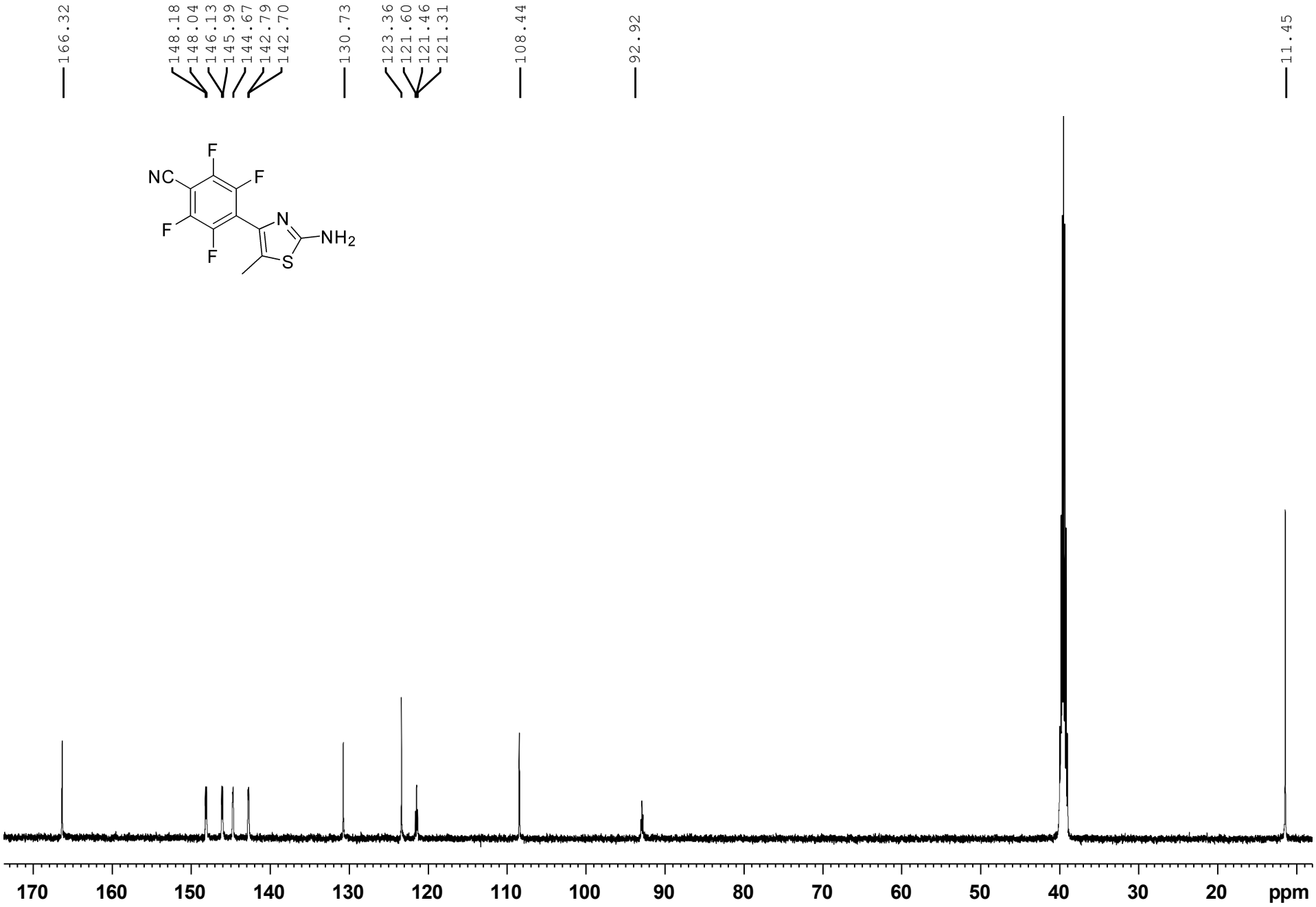

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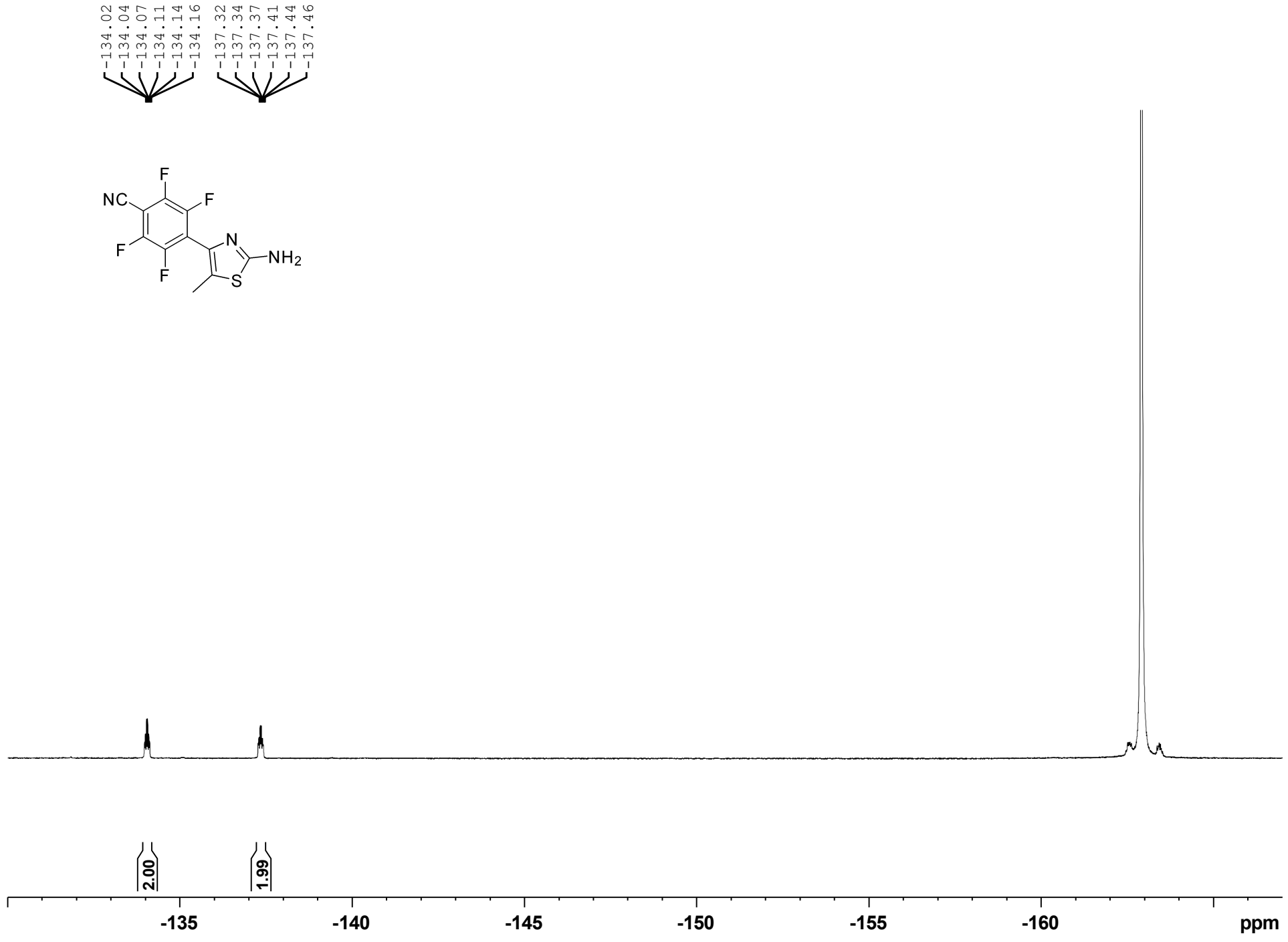
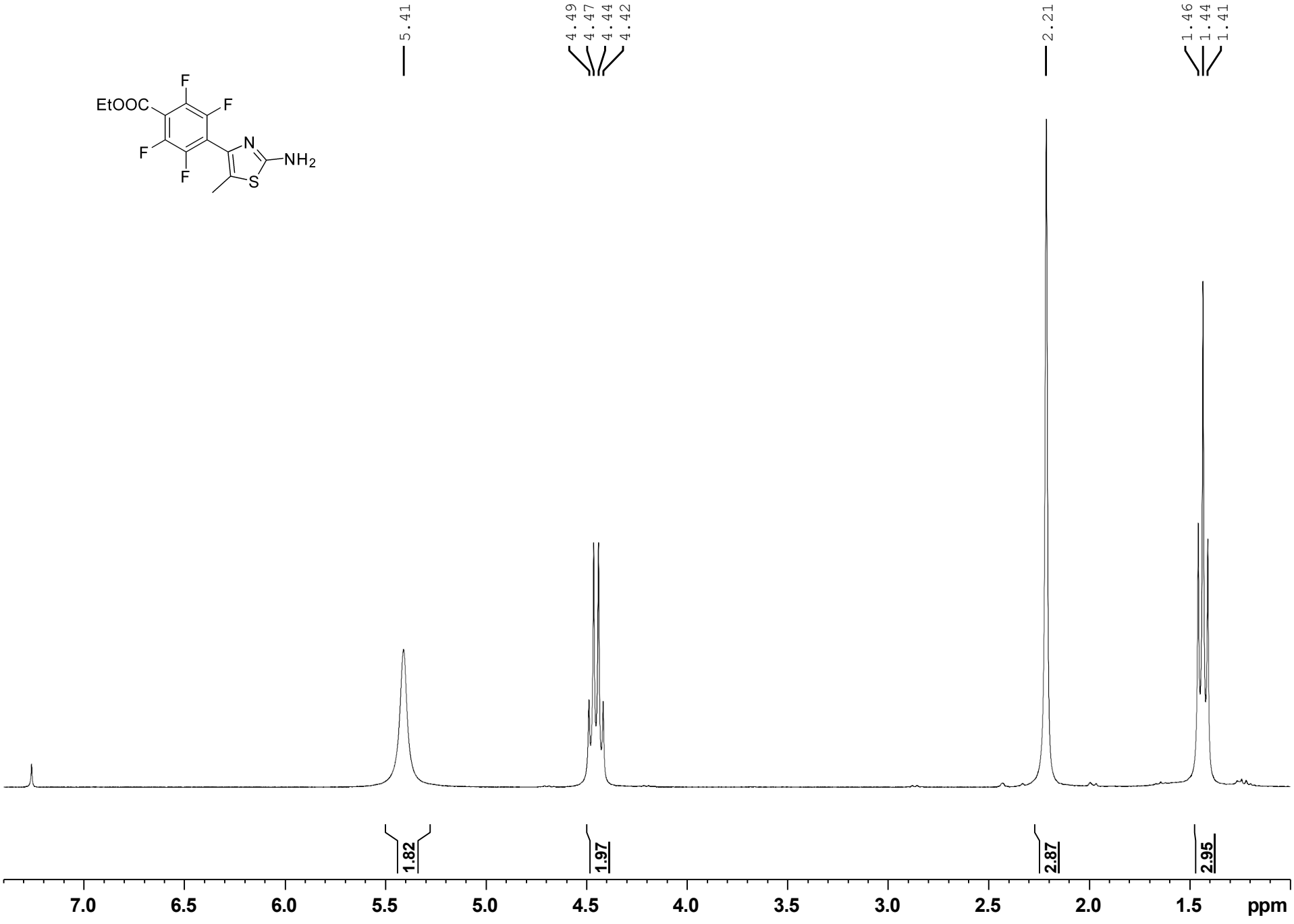


^{1}H NMR spectrum of 5-methyl-4-(4-ethoxycarbonyl-2,3,5,6-tetrafluorophenyl)-1,3-thiazol-2-amine (**12**)



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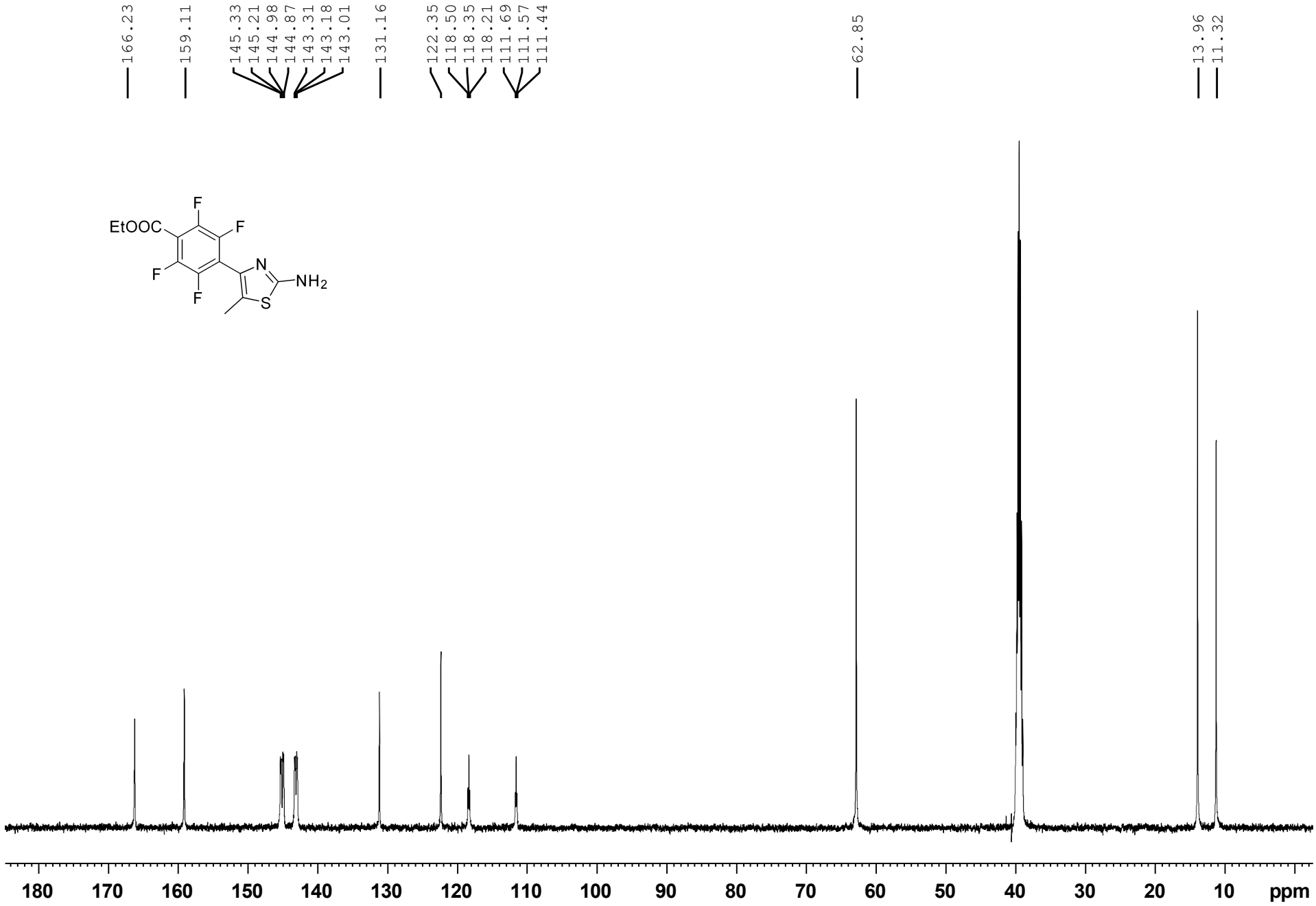

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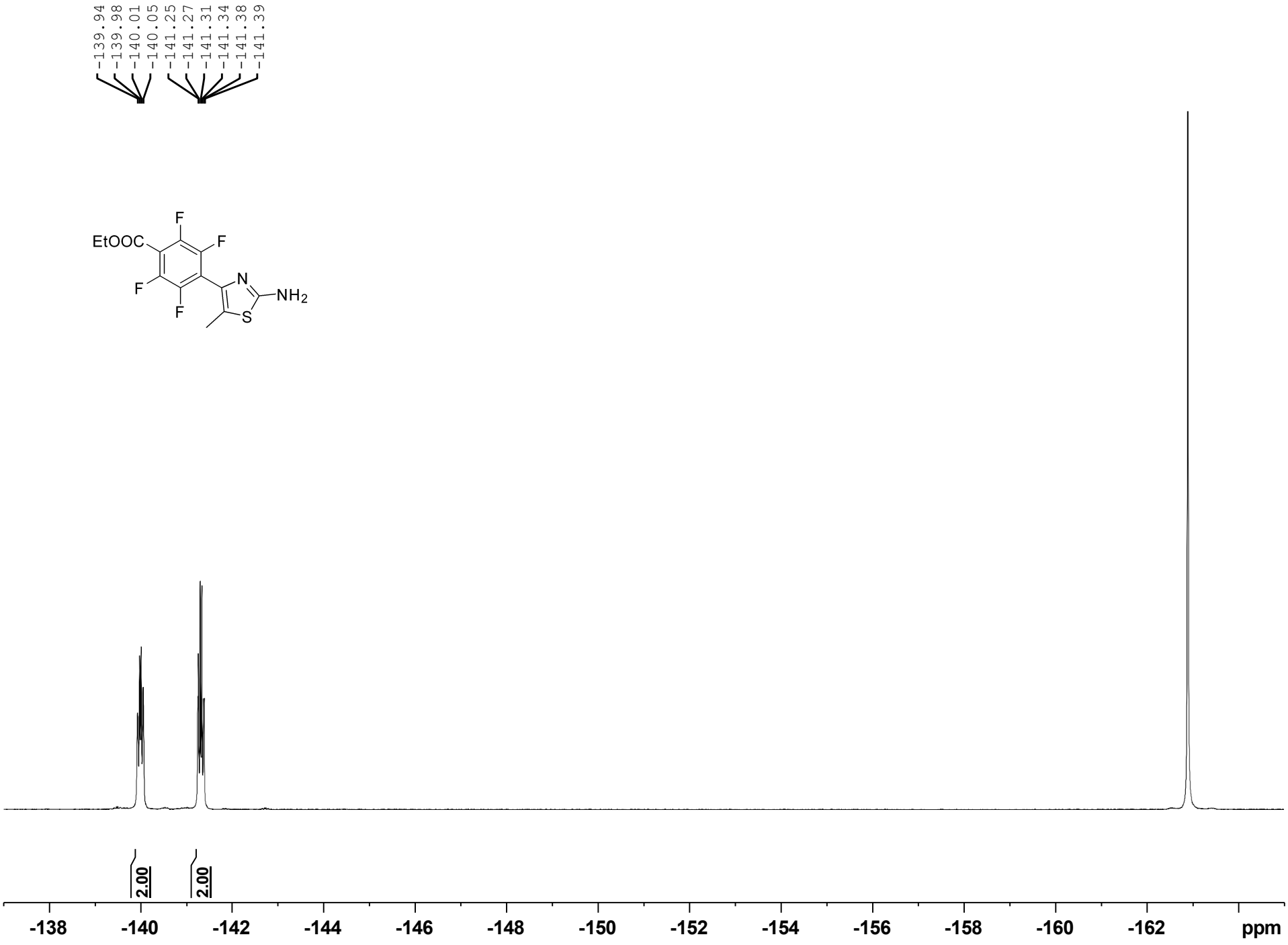

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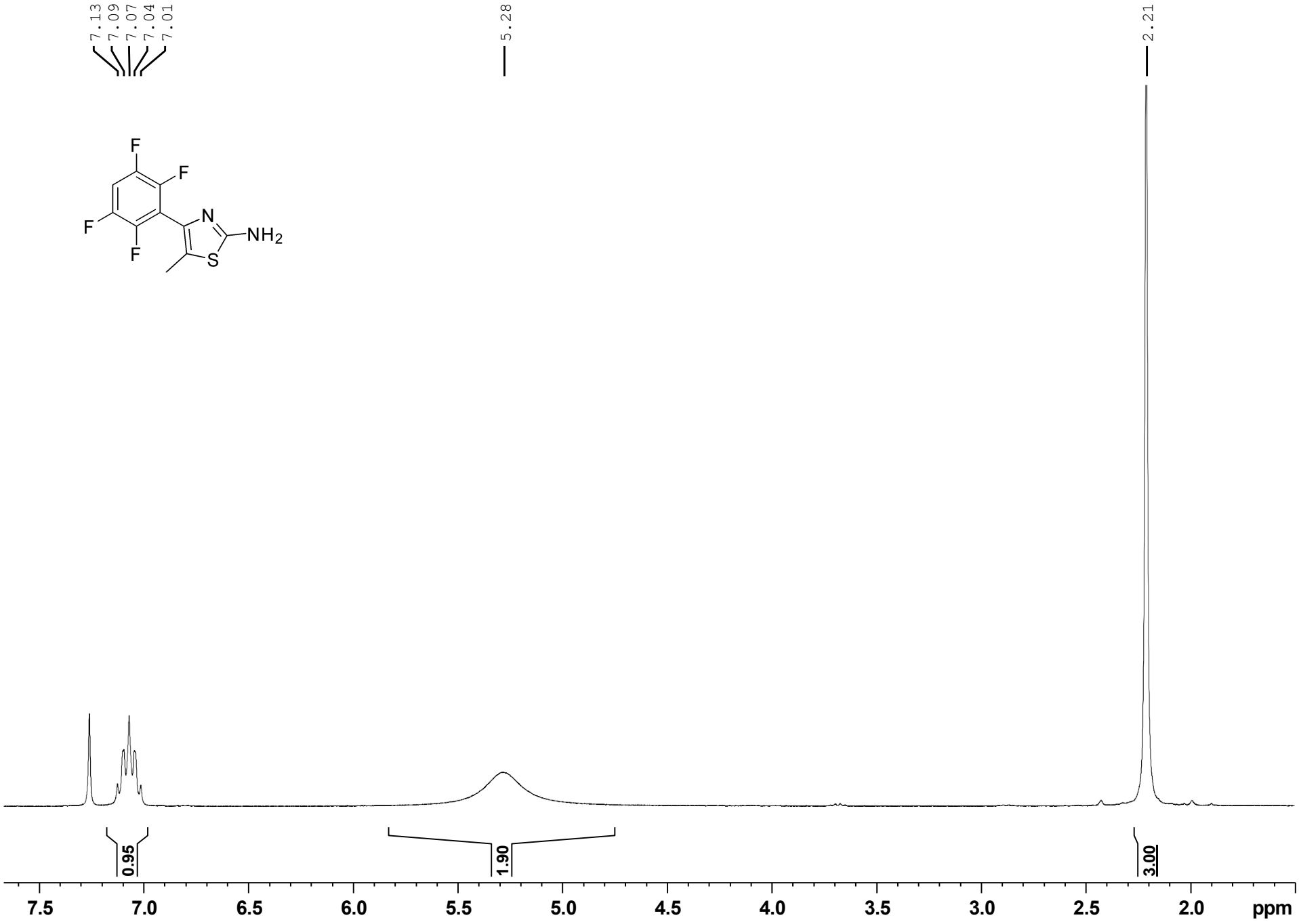

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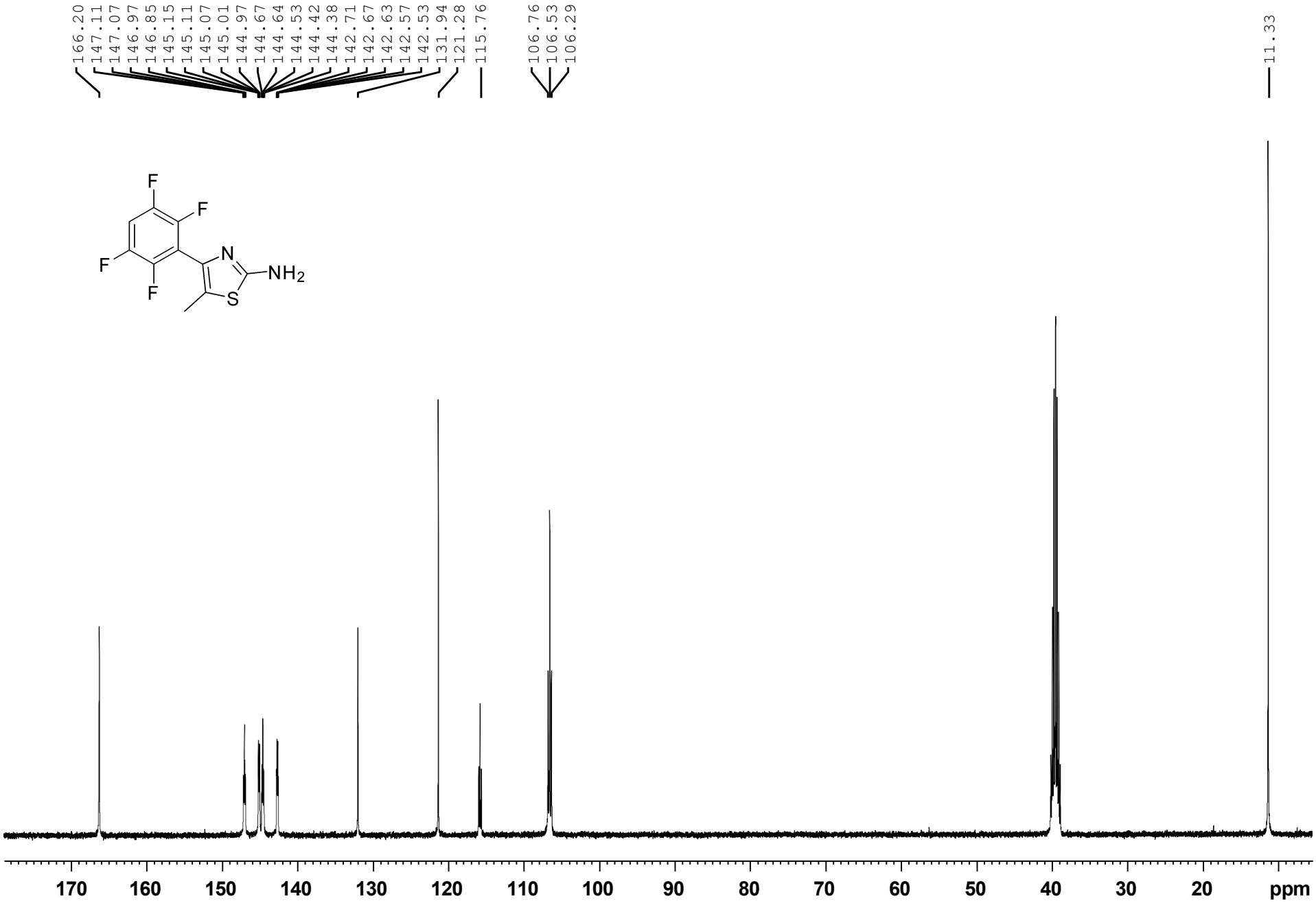

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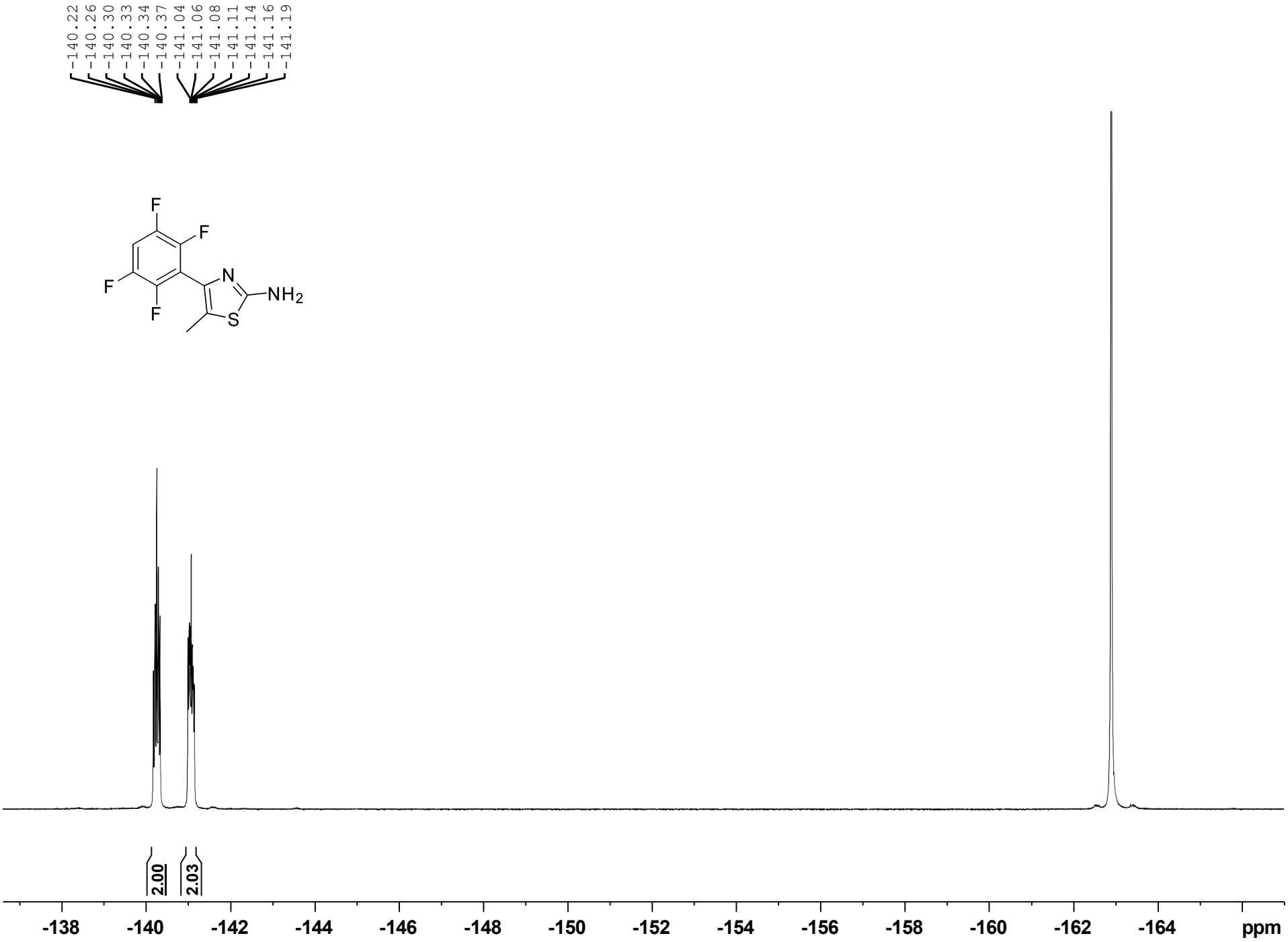

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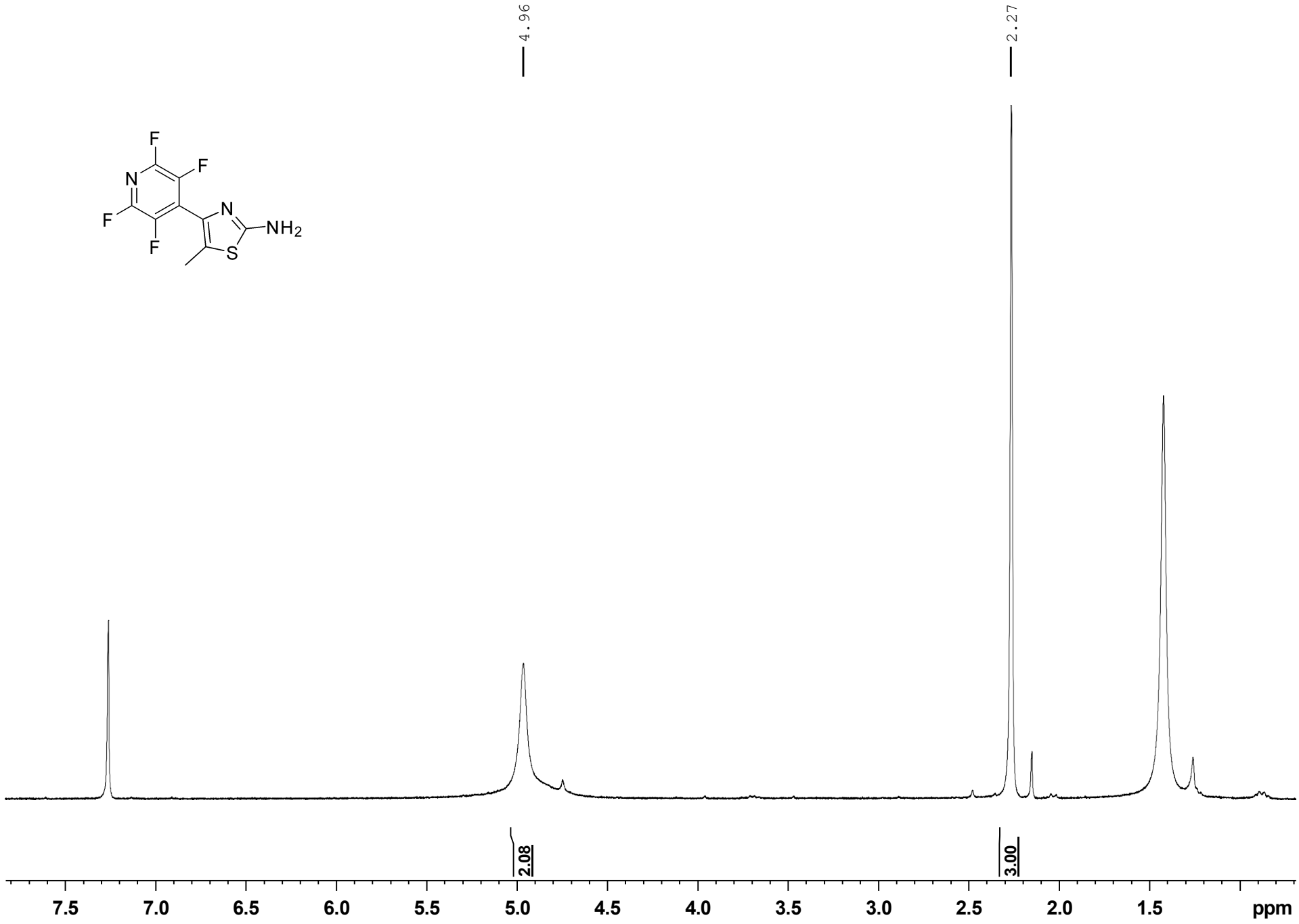

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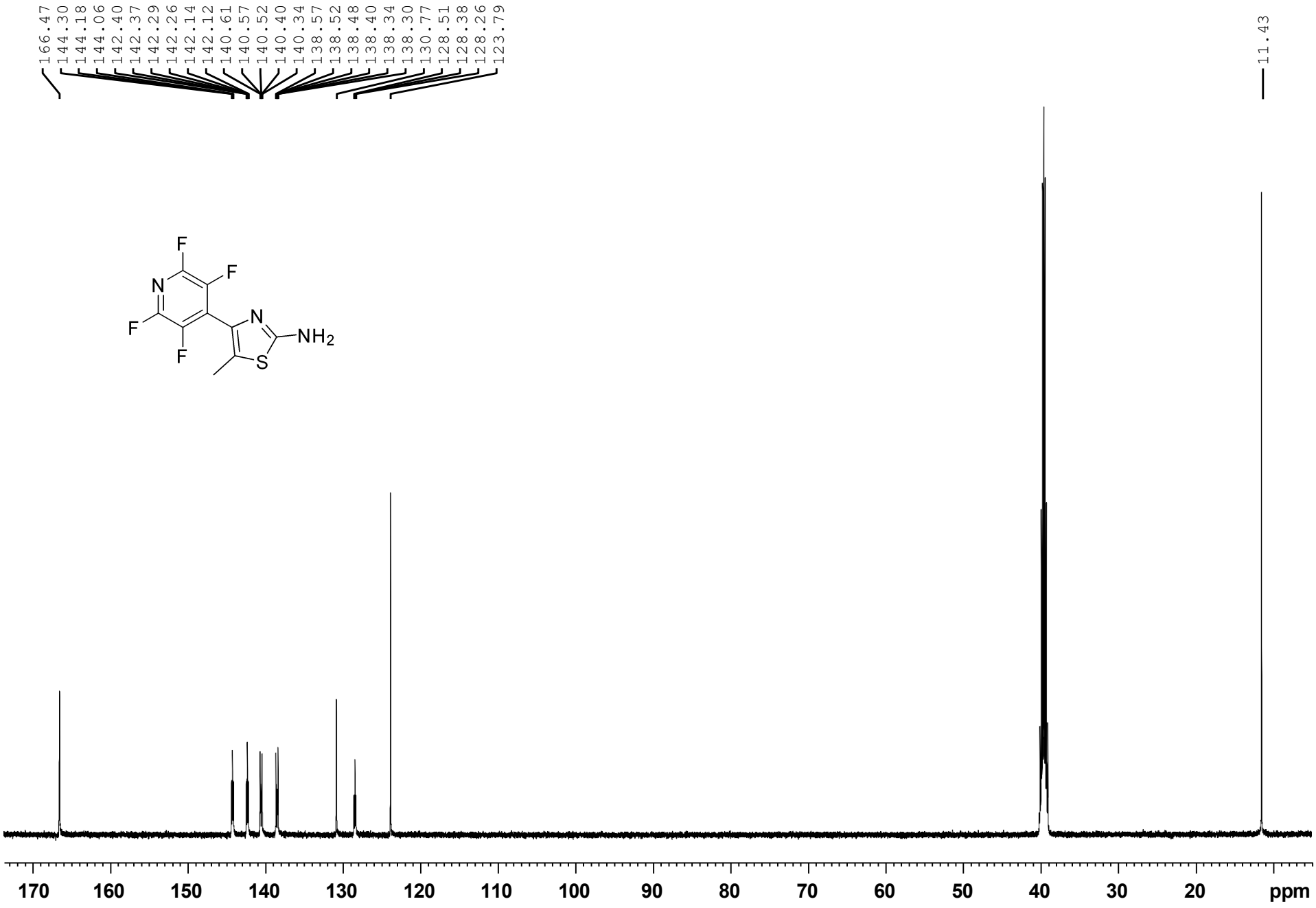

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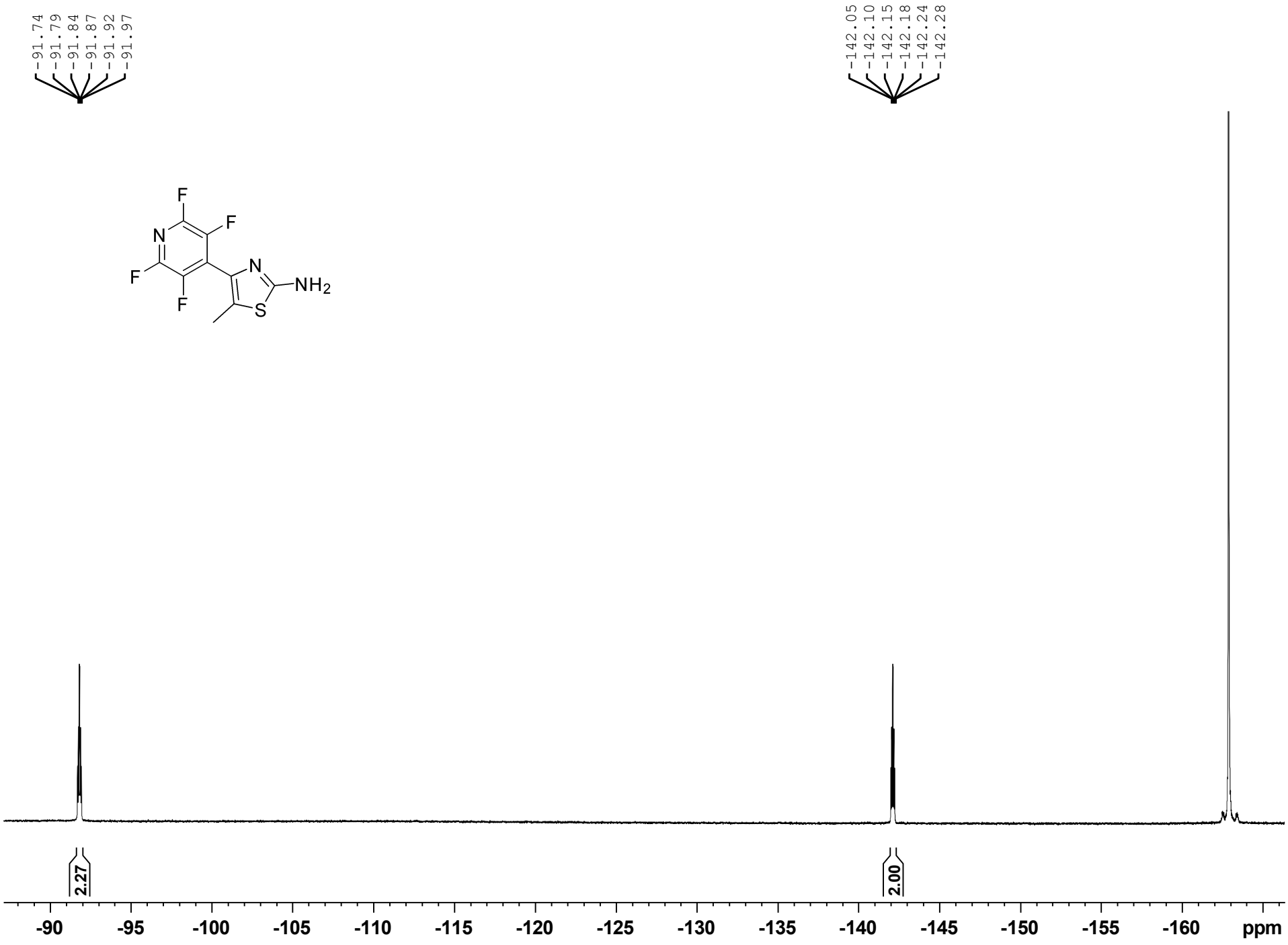

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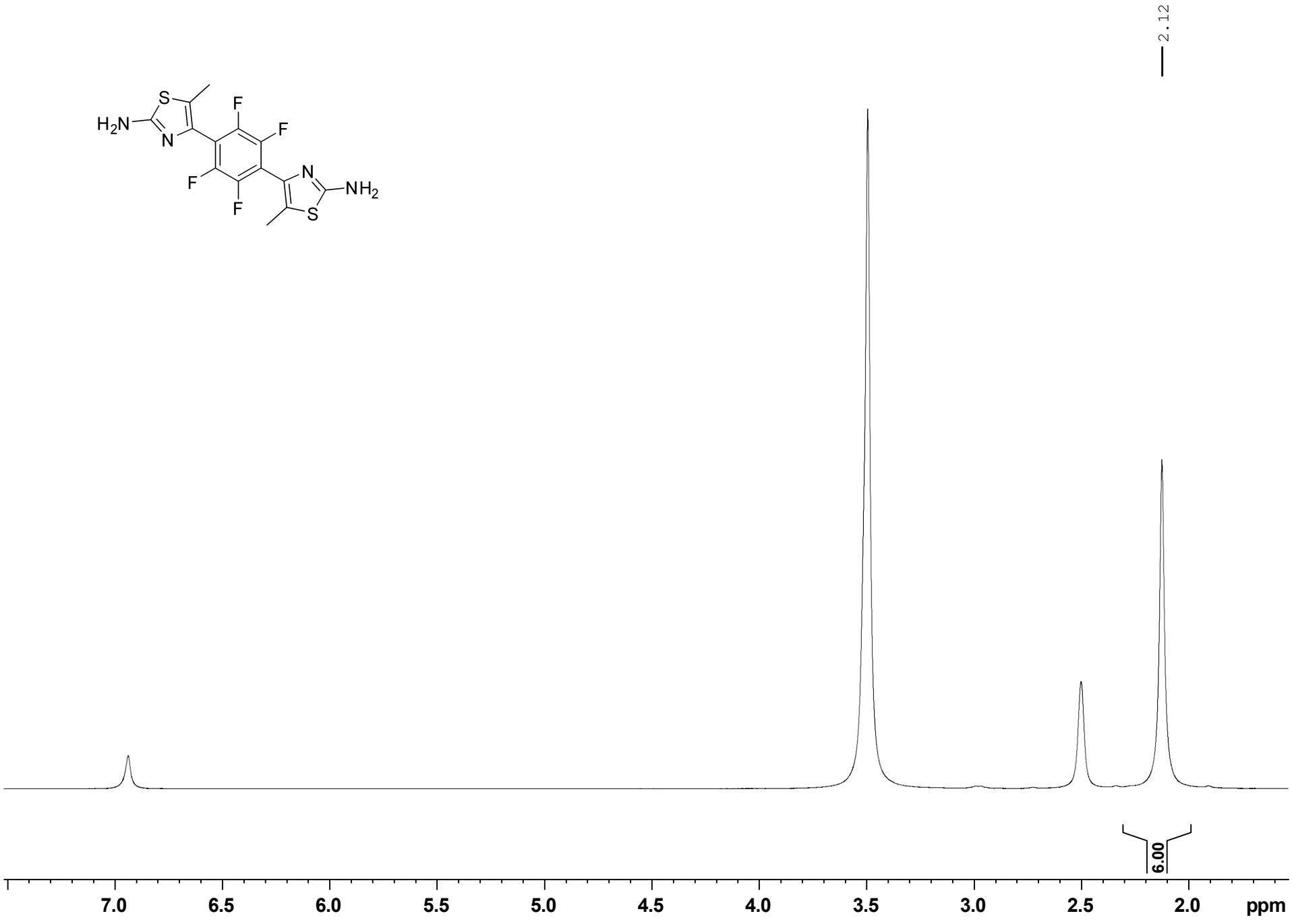

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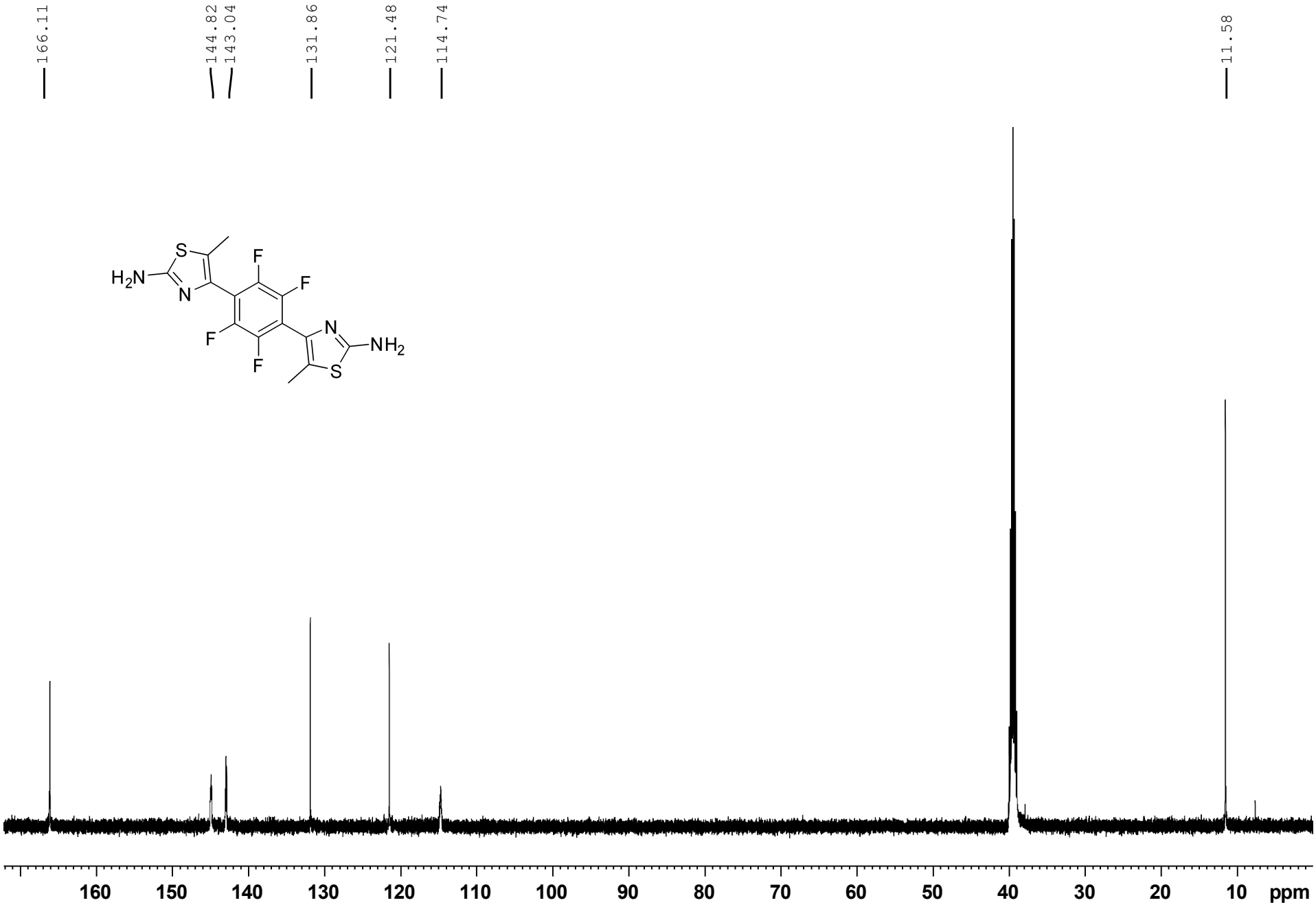

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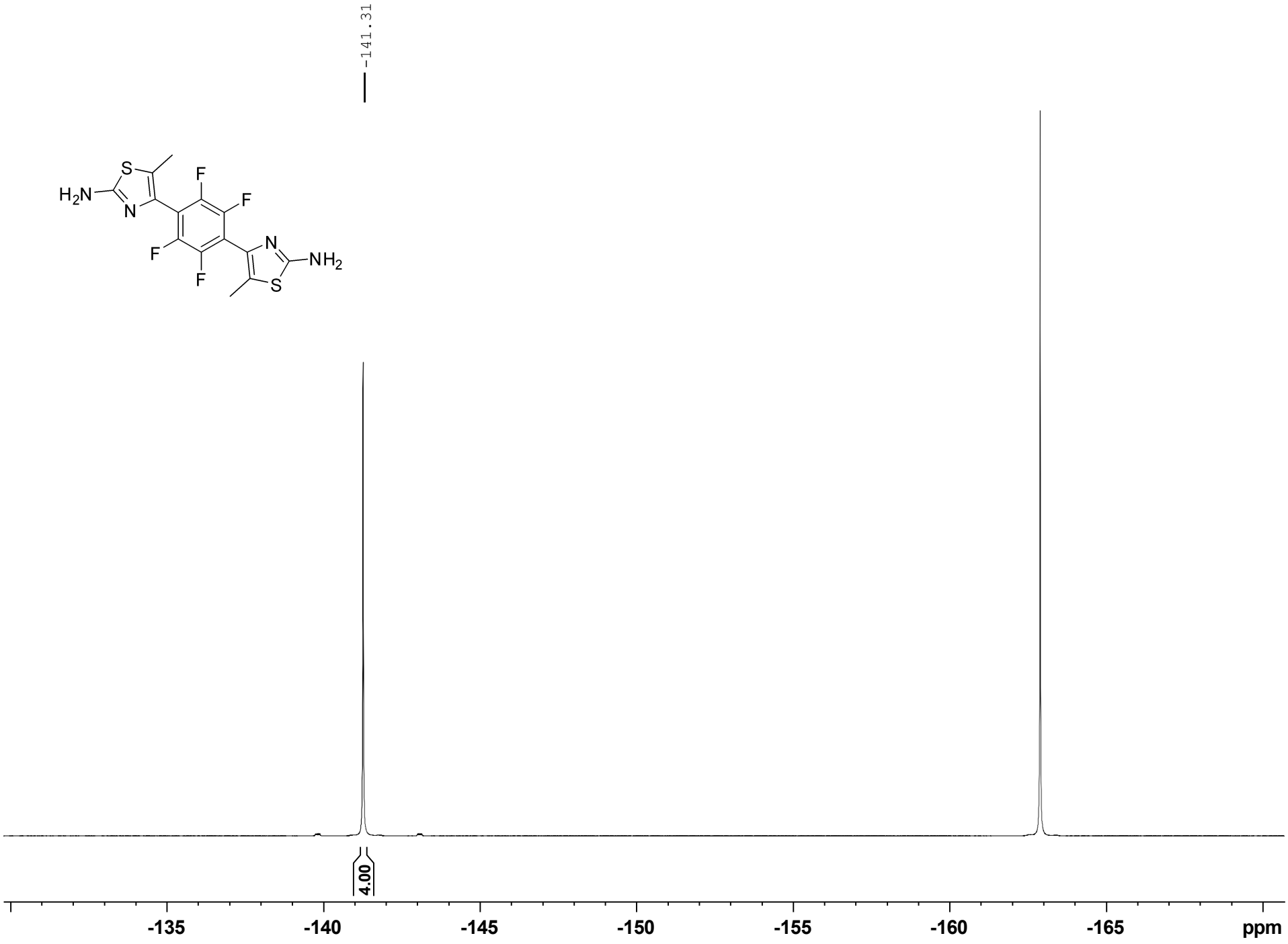

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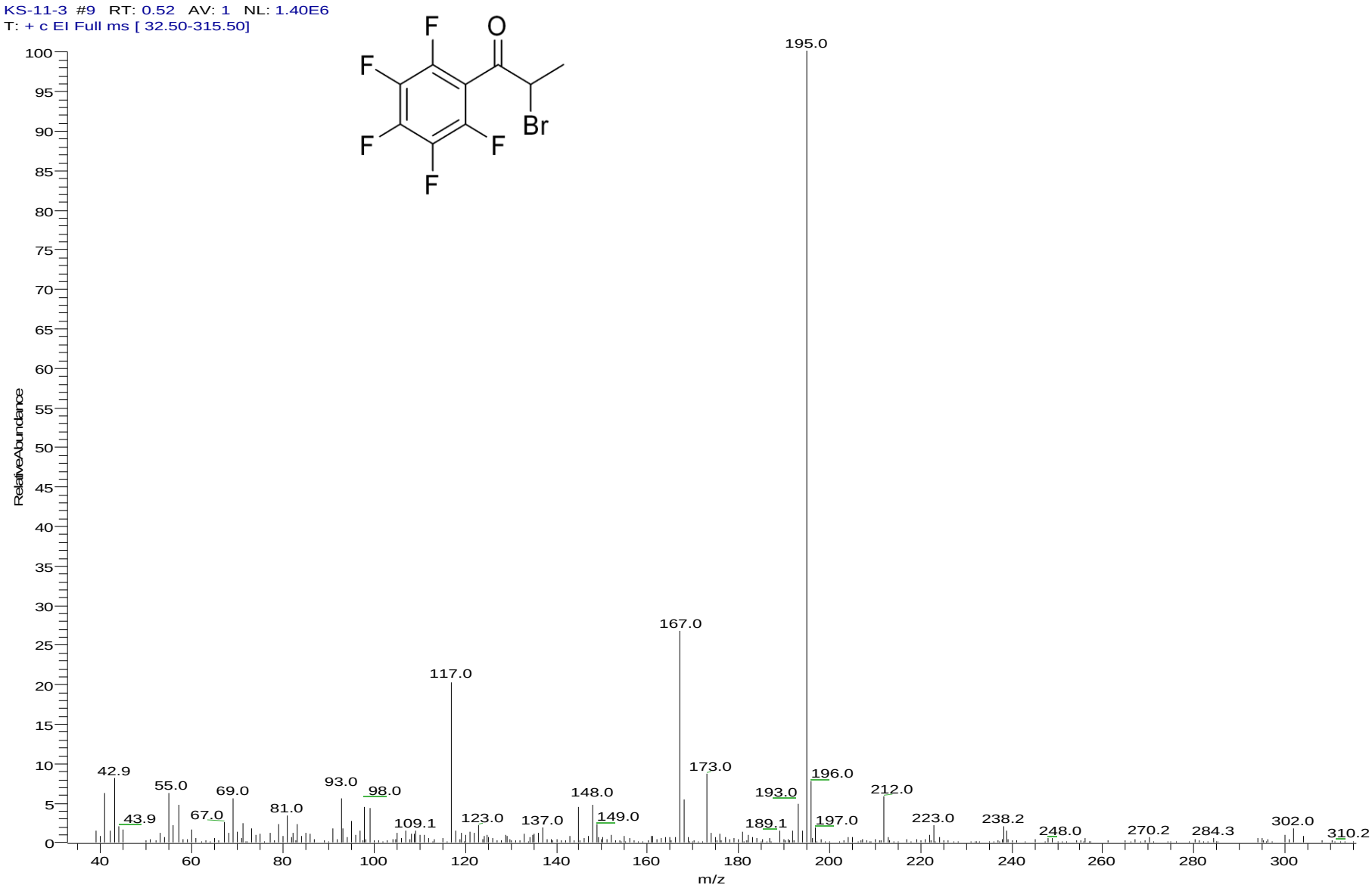

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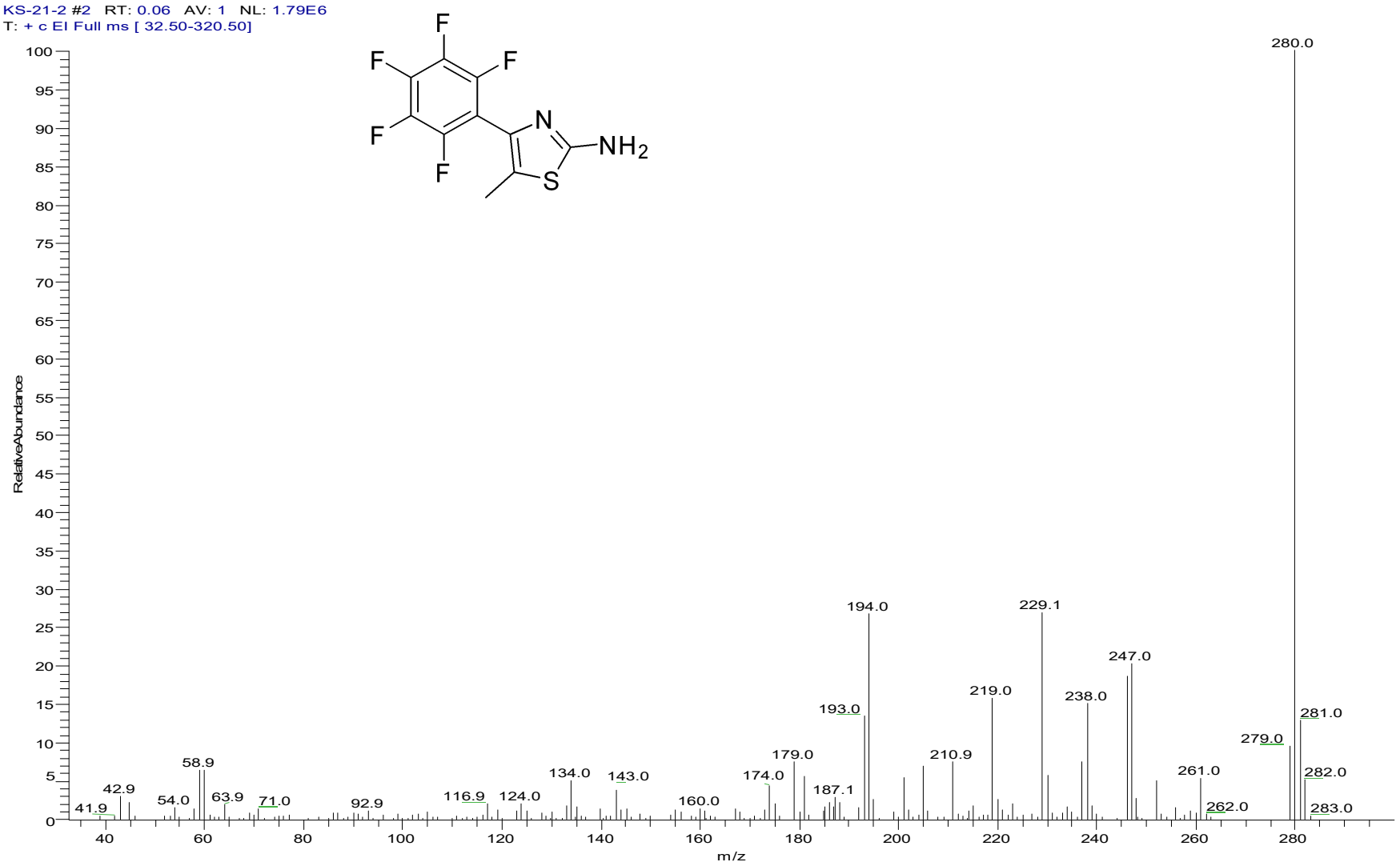

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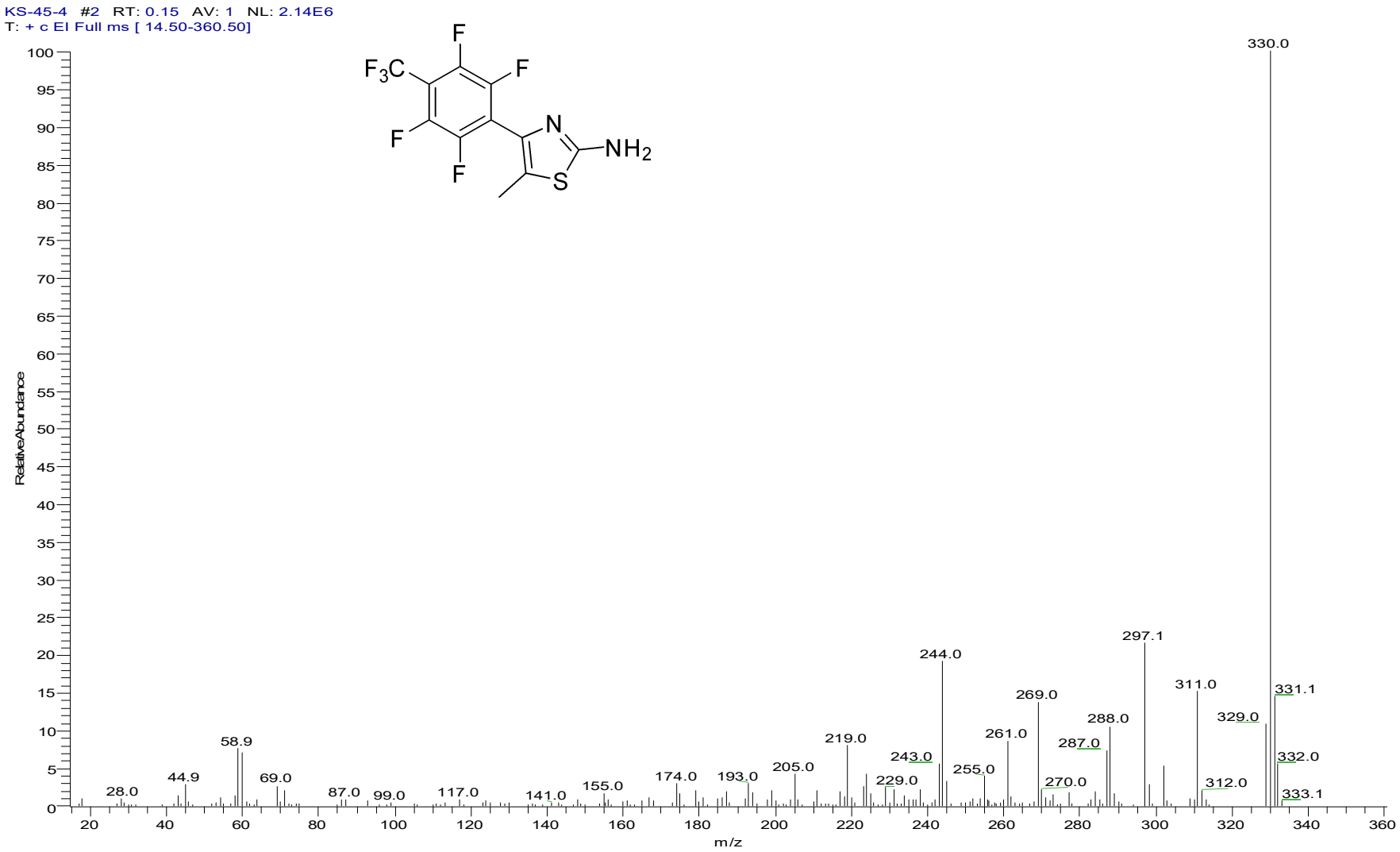

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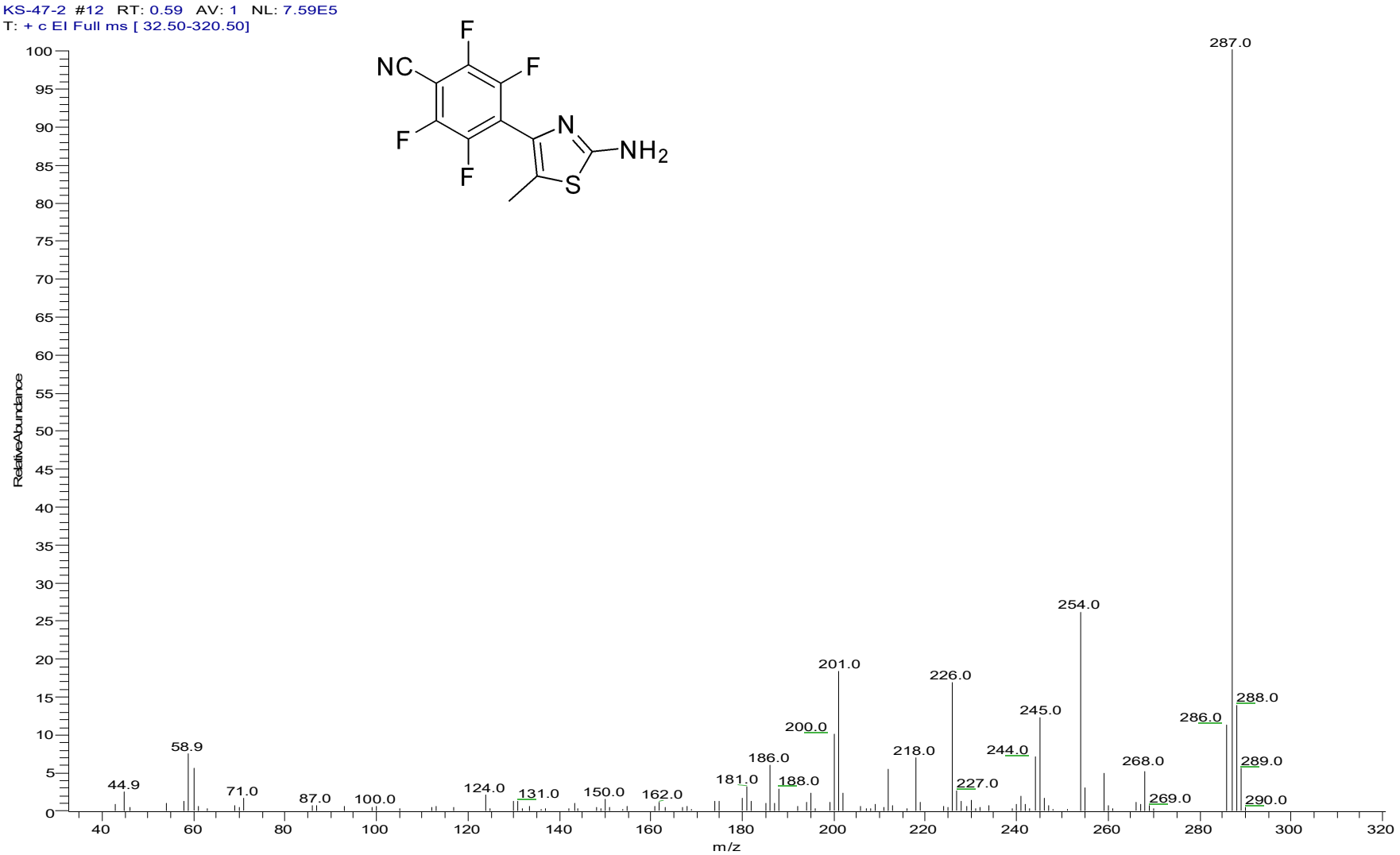

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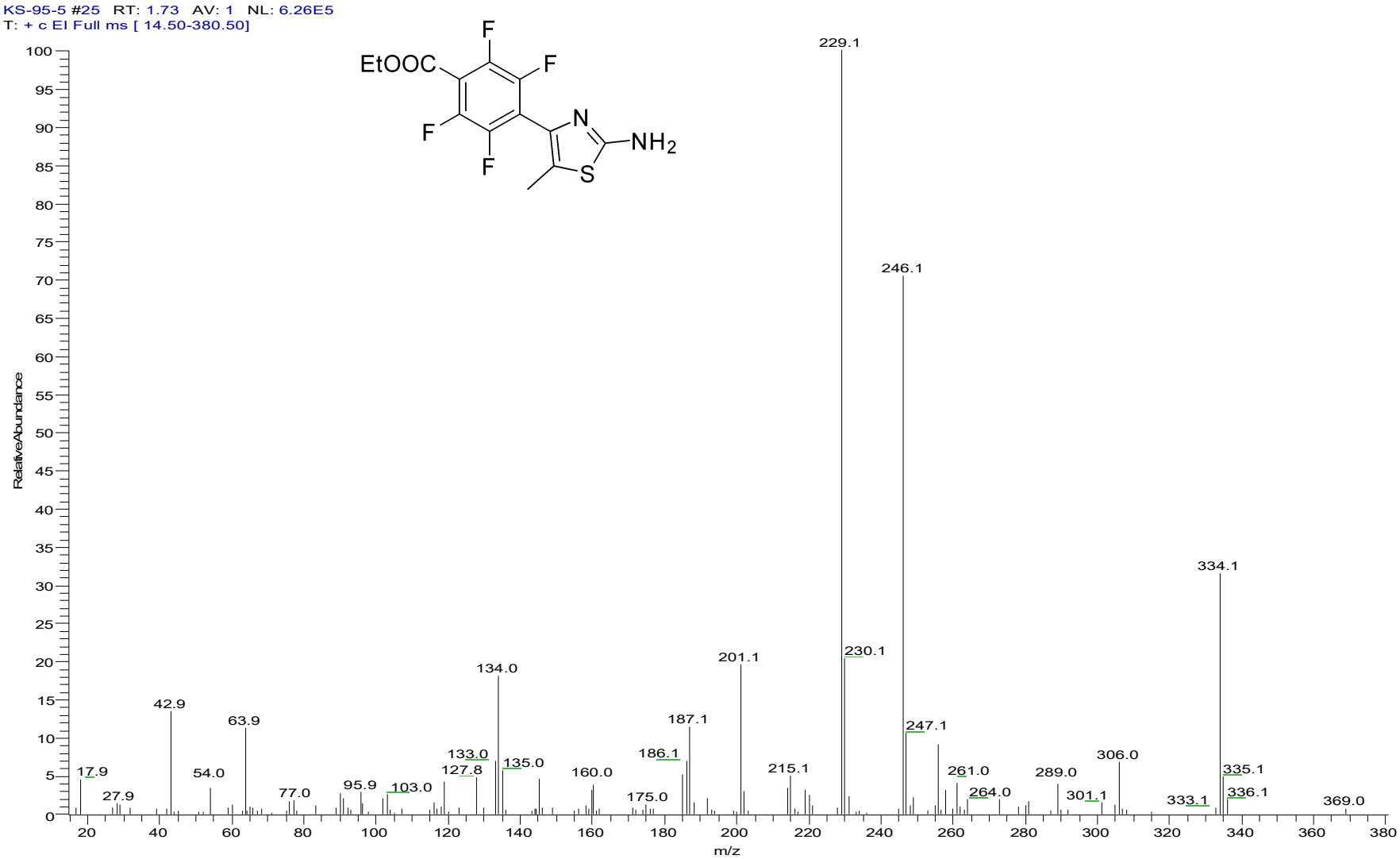

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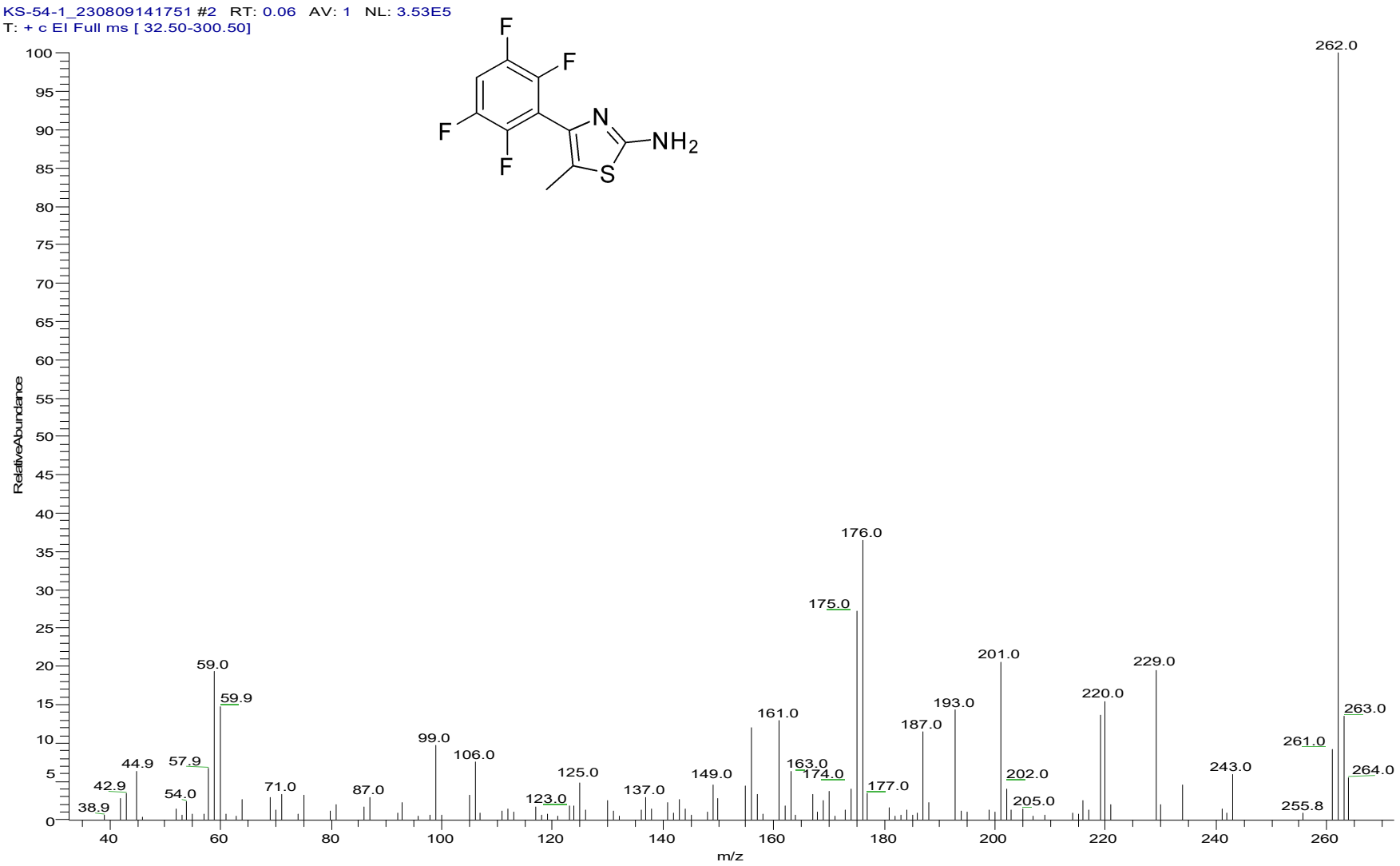

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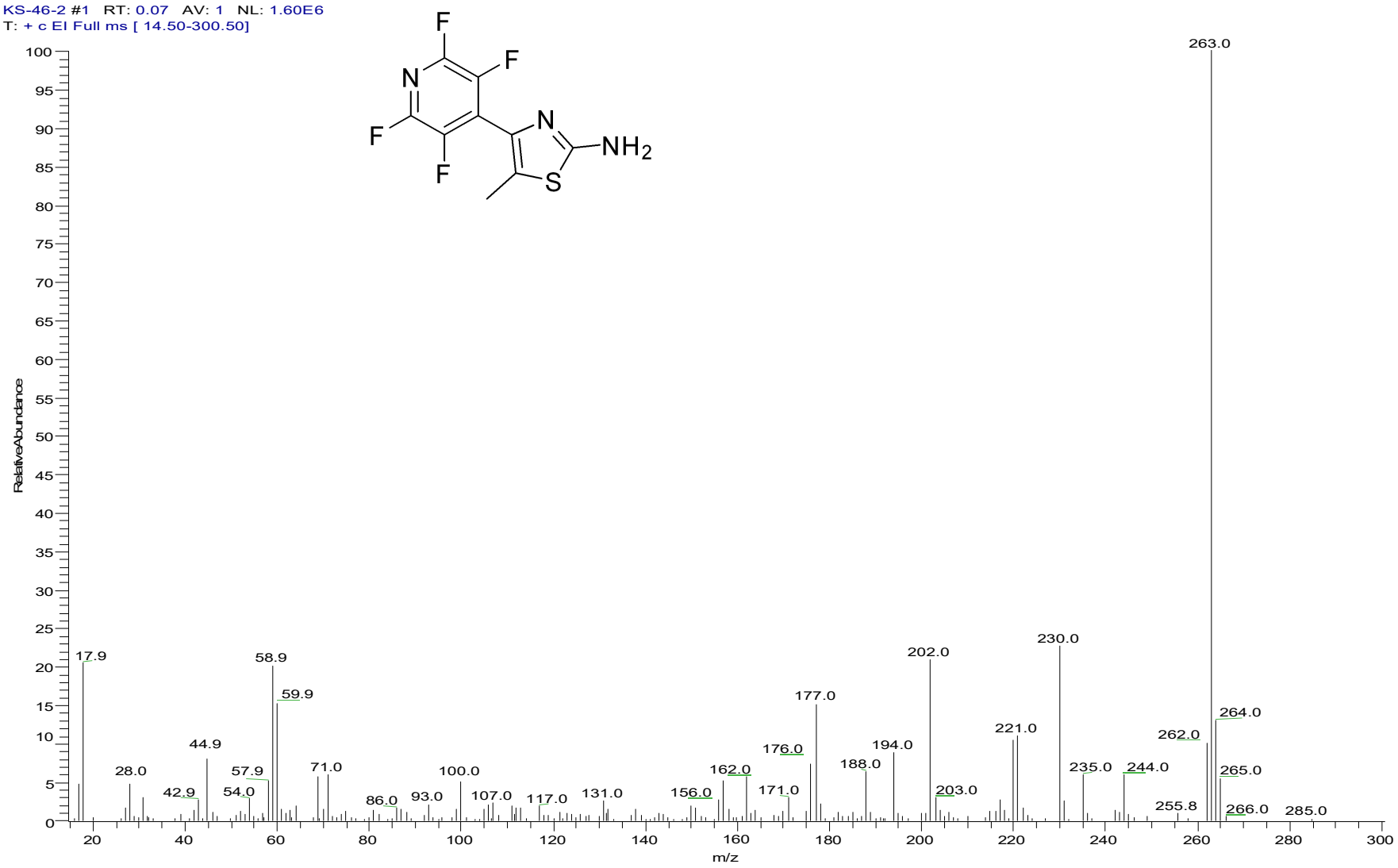

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