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Synthesis of 2-amino-3,6-di(het)arylpyridines from 5-cyano-3,6-di(het)aryl-1,2,4-triazines and arylhydrazines *via* the S_N^{ipso}/*aza*-Diels–Alder reaction sequence

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Experimental part

All reagents were purchased from commercial sources and used without further purification. Silica gel 60 (Kieselgel 60, 230-400 mesh) was used for the column chromatography. NMR spectra were recorded on a Bruker Avance (600 MHz and 400 MHz) spectrometers, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. Mass spectra were recorded on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics) with electrospray ionization. Elemental analyses were performed on a PE 2400 II CHN-analyzer (Perkin Elmer). A thick-walled glass reactor (Sigma-Aldrich) was used to carry out the aza-Diels–Alder reactions at elevated pressure. The starting 5-cyano-1,2,4-triazines **2a-c,g,**[S1] **2e,**[S2] **2f,**[S3] **2j**[S4] and compounds **1c,d,i**[S5] were prepared as described.

Compounds **1a,b,e-h**[S5] and **2h**, **5**[S1] were synthesized by the method described for the similar compounds.

3-(2,4-Difluorophenyl)-6-(p-tolyl)-1,2,4-triazine-5-carbonitrile **(2h).** M.p. 159 °C. Yield 400 mg (1.30 mmol, 62%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.50 (s, 3H, Me), 7.00 – 7.15 (m, 2H, $C_6H_3F_2$), 7.42 – 7.49 (m, 2H, Tol), 8.01 – 8.03 (m, 2H, Tol), 8.28 – 8.38 (m, 1H, $C_6H_3F_2$). **^{19}F NMR** ($CDCl_3$, δ, ppm, J, Hz): -106.11 (m, 1F, F-2($C_6H_3F_2$)), -102.69 (d, 1F, J = 11.3, F-4($C_6H_3F_2$)). **ESI-MS,** m/z: 309.10 $[M+H]^+$. Calculated for **$C_{17}H_{10}F_2N_4$**: C 66.23, H 3.27, N 18.17. Found: C 66.35, H 3.24, N 18.09.

5-(2-Phenylhydrazinyl)-3-(pyridin-2-yl)-6-(p-tolyl)-1,2,4-triazine **(1a)**. M.p. 194-196 °C. Yield 300 mg (0.85 mmol, 85%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.44 (s, 3H, Me), 6.78 – 6.81 (m, 1H, Ph), 7.09 – 7.11 (m, 2H, Ph), 7.23 – 7.25 (m, 2H, Ph), 7.27 – 7.29 (m, 2H, Tol), 7.51 (ddd, 1H, ^{3}J = 7.6, ^{3}J = 4.8, ^{4}J = 1.2, H-5(Py)), 7.94 (ddd, 1H, ^{3}J = 7.7, ^{3}J = 7.7, H-4(Py)), 8.05 – 8.07 (m, 2H, Tol), 8.40 – 8.42 (m, 1H, H-3(Py)), 8.65 – 8.67 (m, 1H, H-6(Py)), 8.82 (br. s, 1H, NH), 10.52 (br. s, 1H, NH). **^{13}C NMR** ($CDCl_3$, δ, ppm): 21.5, 112.8, 119.0, 121.8, 126.6, 128.6, 128.9, 129.2, 130.6, 134.8, 137.3, 140.2, 145.2, 147.9, 148.8, 148.9, 149.8. **ESI-MS,** m/z: 355.42 $[M+H]^+$. Calculated for **$C_{21}H_{18}N_6$**: C 71.17, H 5.12, N 23.71. Found: C 71.23, H 5.07, N 23.70.

6-Phenyl-5-(2-phenylhydrazinyl)-3-(pyridin-2-yl)-1,2,4-triazine **(1b)**. M.p. 165-167 °C. Yield 280 mg (0.82 mmol, 82%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 6.78 – 6.81 (m, 1H, Ph), 7.09 – 7.11 (m, 2H, Ph), 7.23 – 7.26 (m, 2H, Ph), 7.46 – 7.50 (m, 3H, Ph), 7.51 (ddd, 1H, ^{3}J = 7.6, ^{3}J = 4.8, ^{4}J = 1.2, H-5(Py)), 7.94 (ddd, 1H, ^{3}J = 7.6, ^{3}J = 7.6, ^{4}J = 1.8, H-4(Py)), 8.13 – 8.16 (m, 2H, Ph), 8.40 – 8.42 (m, 1H, H-3(Py)), 8.65 – 8.67 (m, 1H, 6-Py), 8.82 (br. s, 1H, NH), 10.55 (br. s, 1H, NH). **^{13}C**

NMR ($CDCl_3$, δ, ppm): 112.8, 119.1, 121.9, 126.6, 127.9, 129.0, 129.2, 130.1, 133.5, 134.8, 137.3, 145.1, 147.8, 148.9, 149.1, 149.9. **ESI-MS,** m/z: 341.14 $[M+H]^+$. Calculated for **$C_{20}H_{16}N_6$**: C 70.57, H 4.74, N 24.69. Found: C 70.52, H 4.78, N 24.70.

5-[2-(4-Fluorophenyl)hydrazinyl]-3-(furan-2-yl)-6-phenyl-1,2,4-triazine (**1e**). M.p. 202-204 °C. Yield 271 mg (0.78 mmol, 77%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 6.62 – 6.68 (m, 1H, H-4 (fur)), 6.89 – 7.02 (m, 4H, C_6H_4F), 7.30 – 7.34 (m, 1H, H-3 (fur)), 7.42 – 7.49 (m, 3H, Ph), 7.58 – 7.61 (m, 1H, H-5 (fur)), 8.03 – 8.08 (m, 2H, Ph), 8.63 and 9.22 (both br.s, 1H, NH-NH). **^{19}F NMR** ($CDCl_3$, δ, ppm): -126.15 (s, 1F, C_6H_4F). **^{13}C NMR** ($CDCl_3$, δ, ppm, J, Hz): 112.8, 113.5 (d, J = 7.6), 114.4, 115.6 (d, J = 22.9), 127.9, 128.9, 130.1, 133.4, 133.9, 141.5 (d, J = 1.6), 145.0, 145.0, 145.3, 149.0, 156.8 (d, J = 236.4). **ESI-MS**, m/z: 348.13 $[M+H]^+$. Calculated for **$C_{19}H_{14}FN_5O$**: C 65.70, H 4.06, N 20.16. Found: C 65.82, H 3.94, N 20.22.

6-Phenyl-3-(thiophen-2-yl)-5-(2-p-tolylhydrazinyl)-1,2,4-triazine **(1f)**. M.p. 226-228 °C. Yield 273 mg (0.76 mmol, 76%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.27 (s, 3H, Me), 7.00 and 7.06 (both m, 2H, $C_6\underline{H}_4Me$), 7.15-7.19 (m, 1H, H-4(thienyl)), 7.43-7.51 (m, 3H, Ph), 7.52-7.56 and 7.60-7.64 (both m, 1H, H-3(thienyl) and H-5(thienyl)), 8.06-8.11 (m, 2H, Ph), 8.71 and 9.09 (both br.s, 1H, NH-NH). **^{13}C NMR** ($CDCl_3$, δ, ppm): 20.6, 112.8, 127.3, 127.9, 128.1, 128.3, 128.7, 129.0, 129.7, 130.0, 131.1, 133.4, 135.0, 142.7, 148.1, 148.9. **ESI-MS**, m/z: 360.13 $[M+H]^+$. Calculated for **$C_{20}H_{17}N_5S$**: C 66.83, H 4.77, N 19.48. Found: C 66.95, H 4.85, N 19.69.

5-[2-(4-Fluorophenyl)hydrazinyl]-3-methyl-6-phenyl-1,2,4-triazine **(1g)**. M.p. > 250 °C. Yield 236 mg (0.80 mmol, 80%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.16 (s, 3H, Me), 6.87-6.99 (m, 4H, C_6H_4F), 7.40-7.48 (m, 3H, Ph), 7.97-8.04 (m, 2H, Ph), 8.57-8.67 (m, 2H, NHNH). **^{19}F NMR** ($CDCl_3$, δ, ppm): -126.33 (s, 1F, C_6H_4F). **^{13}C NMR** ($CDCl_3$, δ, ppm, J, Hz): 20.0, 113.4 (d, J = 7.2), 115.6 (d, J = 21.6), 127.9, 128.8, 130.0, 133.3, 134.2, 141.6, 148.6, 154.1, 156.7 (d, J = 236.8). **ESI-MS**, m/z: 296.13 $[M+H]^+$. Calculated for **$C_{16}H_{14}FN_5$**: C 65.07, H 4.78, N 23.71. Found: C 65.19, H 4.89, N 23.65.

3-(2,4-Difluorophenyl)-5-(2-phenylhydrazinyl)-6-p-tolyl-1,2,4-triazine **(1h)**. M.p. 230-232 °C. Yield 315 mg (0.81 mmol, 81%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.44 (s, 3H, Me), 6.77-6.83 (s, 1H, Ph), 6.94-7.01 (m, 1H, CH($C_6H_3F_2$)), 7.06-7.16 (m, 3H, Ph, CH($C_6H_3F_2$)), 7.21-7.30 (m, 4H, Ph, Tol), 8.01-8.06 (m, 2H, Tol), 8.29-8.37 (m, 1H, CH($C_6H_3F_2$)), 8.73 (br. s, 1H, PhNHN$\underline{H}$), 9.49-9.55 (m, 1H, PhN$\underline{H}$NH). **^{19}F NMR** ($CDCl_3$, δ, ppm, J, Hz): -109.33 (m, 1F, F-2($C_6H_3F_2$)), -102.28 (d, 1F, J = 10.8, F-4($C_6H_3F_2$)). **^{13}C NMR** ($CDCl_3$, δ, ppm, J, Hz): 21.5, 104.9 (dd, J = 26.2, 26.2), 112.8, 113.0 (dd, J = 21.6, 3.4), 114.7 (dd, J = 3.4, 3.4), 119.2, 128.6, 128.9, 129.2, 130.2, 132.4 (dd, J = 10.6, 3.4), 133.7, 140.4, 145.0, 148.8, 149.1, 161.4 (J = 251.6, 12.5), 165.2 (J = 256.8, 13.5). **ESI-MS**, m/z: 390.15 $[M+H]^+$. Calculated for **$C_{22}H_{17}F_2N_5$**: C 67.86, H 4.40, N 17.98. Found: C 67.76, H 4.52, N 17.85.

6-Phenyl-3-p-tolyl-1,2,4-triazin-5-amine (**5**). M.p. 208-210 °C. Yield 170 mg (0.65 mmol, 65%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.44 (s, 3H, Me), 5.30 (br. s, 2H, NH_2), 7.29-7.33 (m, 2H, Tol), 7.51-7.59 (m, 3H, Ph), 7.76-7.80 (m, 2H, Ph), 8.36-8.39 (m, 2H, Tol). **^{13}C NMR** ($CDCl_3$, δ, ppm, J, Hz): 21.5, 128.1, 128.1, 129.3 (2C), 129.9, 132.6, 134.0, 141.4, 145.9, 153.8, 161.4. **ESI-MS**, m/z: 263.13 $[M+H]^+$. Calculated for **$C_{16}H_{14}N_4$**: C 73.26, H 5.38, N 21.36. Found: C 73.13, H 5.22, N 21.49.

*General procedure for synthesis of 3,6-diarylpyridin-2-amines **(4a-d)***.

To a suspension of the corresponding 1,2,4-triazine **1** (0.3 mmol) in *o*-dichlorobenzene (10 ml) 2,5-nonbornadiene (0.2 ml, 1.97 mmol) was added. The resulting mixture was stirred in a thick-walled glass reactor (autoclave) at 215 °C for 10 h under argon atmosphere. The solvent was removed under reduced pressure. The reaction product was isolated by column chromatography (silica gel, eluent: DCM/EtOAc, 7:3, unless indicated otherwise).

5-(p-Tolyl)-[2,2'-bipyridin]-6-amine **(4a)**. M.p. 136-138 °C. Yield 41 mg (0.16 mmol, 52%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.40 (s, 3H, Me), 4.71 (br. s, 2H, NH_2), 7.22 – 7.27 (m, 3H, Tol, H-5′(Py)), 7.38 – 7.41 (m, 2H, Tol), 7.50 (d, 1H, ^{3}J = 7.8, H-3(Py)), 7.76 (ddd, 1H, ^{3}J = 7.6, ^{3}J = 7.6, ^{4}J = 1.8, H-4′ (Py)), 7.80 (d, 1H, ^{3}J = 7.8, H-4(Py)), 8.29 – 8.31 (m, 1H, H-3′(Py)), 8.65 – 8.68 (m, 1H, H-6′(Py)). **^{13}C NMR**, ($CDCl_3$, δ, ppm): 21.1, 112.0, 120.8, 122.2, 123.1, 128.4 (2C), 129.6 (2C), 134.9, 136.6, 137.5, 138.6, 149.0, 153.2, 155.4, 156.1. **ESI-MS**, m/z: 262.13 $[M+H]^+$. Calculated for **$C_{17}H_{15}N_3$**: C 78.13, H 5.79, N 16.08. Found: C 78.06, H 5.82, N 16.12.

5-Phenyl-[2,2'-bipyridin]-6-amine **(4b)**. M.p. 122-124 °C. Yield 44 mg (0.22 mmol, 58%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.69 (br. s, 2H, NH_2), 7.25 – 7.29 (m, 1H, H-5′(Py)), 7.35 – 7.41 (m, 1H, Ph), 7.45 – 7.53 (m, 5H, Ph, H-3(Py)), 7.78 (ddd, 1H, ^{3}J = 7.6, ^{3}J = 7.6, ^{4}J = 1.8, H-4′(Py)), 7.82 (d, 1H, ^{3}J = 8.0, H-4(Py)), 8.29 – 8.33 (m, 1H, H-3′(Py)), 8.66 – 8.69 (m, 1H, H-6′(Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 118.8, 121.1, 122.6, 123.4, 127.9, 128.4 (2C), 129.0 (2C), 136.7, 137.1, 139.2, 149.1, 152.1, 154.7, 155.0. **ESI-MS**, m/z: 248.11 $[M+H]^+$. Calculated for **$C_{16}H_{13}N_3$**: C 77.71, H 5.30, N 16.99. Found: C 77.78, H 5.25, N 16.97.

Procedure for synthesis from **2d**. The mixture of 5-cyano-1,2,4-triazine **2d** (86 mg, 0.3 mmol) and the phenylhydrazine (34 mg, 0.03 ml, 0.32 mmol) was stirred at 150 °C for 8 h in argon atmosphere. The resulting mixture was suspended in *o*-dichlorobenzene (10 ml), 2,5-nonbornadiene (0.2 ml, 1.97 mmol) was added, and the suspension was stirred in a thick-walled glass reactor (autoclave) at 215 °C for 10 h under argon atmosphere, then the solvent was removed under at a reduced pressure. The reaction product was isolated by column chromatography (silica gel, eluent: DCM/EtOAc, 9:1). Yield 61 mg (0.23 mmol, 75%).

3,6-Di-p-tolylpyridin-2-amine **(4c)**. M.p. 146-148 °C. Synthesized from **1c**: yield 69 mg (0.25 mmol, 84%). Synthesized from **1d**: eluent - DCM/EtOAc, 9:1; yield 44 mg (0.15 mmol, 53%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.40 and 2.42 (both, s, 3H, Me), 4.67 (br. s, 2H, NH_2), 7.16 (d, ^{3}J = 7.6, H-5(Py), 7.24 – 7.31 (m, 4H, Tol), 7.37 – 7.43 (m, 3H, H-4(Py), Tol), 7.86 – 7.91 (m, 2H, Tol). **^{13}C NMR** ($CDCl_3$, δ, ppm): 21.3, 21.4, 110.6, 127.0, 128.0, 128.0, 128.4, 129.3, 129.8, 129.9, 130.0, 130.2, 138.8, 140.8, 154.7. **ESI-MS**, m/z: 274.15 $[M+H]^+$. Calculated for **$C_{19}H_{18}N_2$**: C 83.18, H 6.61, N 10.21. Found: C 83.21, H 6.54, 10.25.

6-(Furan-2-yl)-3-phenylpyridin-2-amine (**4e**). M.p. 83 °C. Yield 21 mg (0.09 mmol, 30%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 4.68 (br. s, 2H, NH_2), 6.49-6.53 (m, 1H, H-4(fur)), 6.94-6.97 (m, 1H, H-3(fur)), 7.16 (d, 1H, ^{3}J = 7.6, H-5(Py)), 7.34-7.39 (m, 1H, Ph), 7.41 (d, 1H, ^{3}J = 7.6, H-4(Py)), 7.43-7.50 (m, 4H, Ph), 7.50-7.53 (m, 1H, H-3(fur)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 108.3, 109.6, 111.9, 120.6, 127.8, 128.7, 129.1, 138.0, 138.5, 143.1, 146.7, 153.6, 155.5. **ESI-MS**, m/z: 237.10 $[M+H]^+$. Calculated for **$C_{15}H_{12}N_2O$**: C 76.25, H 5.12, N 11.86. Found: C 76.38, H 5.25, N 11.72.

3-Phenyl-6-(thiophen-2-yl)pyridin-2-amine (**4f**). M.p. 67 °C. Yield 26 mg (0.10 mmol, 34%). **^{1}H NMR** (600 MHz, $CDCl_3$, δ, ppm, J, Hz): 4.66 (br. s, 2H, NH_2), 7.09 (dd, 1H, ^3J = 5.2, 3.6, H-4(thienyl), 7.14 (d, 1H, ^3J = 7.8, H-5(Py)), 7.35 (dd, 1H, ^3J = 5.2, ^4J = 1.2, H-3(thienyl)), 7.36-7.39 (m, 1H, Ph), 7.38 (d, 1H, ^3J = 7.8, H-4(Py)), 7.44-7.49 (m, 4H, Ph), 7.56 (dd, 1H, ^3J = 3.6, ^4J = 1.2, H-3(thienyl)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 109.8, 120.3, 124.2, 126.9, 127.7, 127.9, 128.7, 129.1, 138.1, 138.5, 145.0, 150.2, 155.4. **ESI-MS**, m/z: 253.08 $[M+H]^+$. Calculated for **$C_{15}H_{12}N_2S$**: C 71.40, H 4.79, N 11.10. Found: C 71.23, H 4.87, N 11.26.

6-Methyl-3-phenylpyridin-2-amine (**4g**). M.p. 75 °C. Yield 29 mg (0.17 mmol, 57%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.42 (s, 3H, Me), 4.59 (br. s, 2H, NH_2), 6.61 (d, 1H, ^3J = 7.8, H-5(Py), 7.27 (d, 1H, ^3J = 7.8, H-4(Py), 7.31-7.38 (m, 1H, Ph), 7.40-7.47 (m, 4H, Ph). **^{13}C NMR** ($CDCl_3$, δ, ppm): 23.9, 113.8, 118.9, 127.6, 128.8, 129.1, 138.3, 138.4, 155.2, 156.0. **ESI-MS**, m/z: 170.10 $[M+H]^+$. Calculated for **$C_{12}H_{11}N$**: C 78.23, H 6.57, N 15.21. Found: C 78.11, H 6.42, N 15.38.

6-(2,4-Difluorophenyl)-3-p-tolylpyridin-2-amine (**4h**). M.p. > 250 °C. Yield 60 mg (0.20 mmol, 67%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.42 (s, 3H, Me), 4.73 (br. s, 2H, NH_2), 6.85-6.93 and 6.95-7.02 (both m, 1H, $CH(C_6H_3F_2)$), 7.21 (d, 1H, ^3J = 7.2, H-5(Py), 7.27-7.31 and 7.36-7.41 (both m, 2H, Tol), 7.44 (d, 1H, ^3J = 7.2, H-4(Py), 7.09-8.04 (m, 1H, $CH(C_6H_3F_2)$). **^{19}F NMR** ($CDCl_3$, δ, ppm, J, Hz): -110.04 (m, 1F), -111.85 (m, 1F). **ESI-MS**, m/z: 297.12 $[M+H]^+$. Calculated for **$C_{18}H_{14}F_2N_2$**: C 72.96, H 4.76, N 9.45. Found: C 73.07, H 4.82, N 9.29.

3-Phenyl-6-p-tolylpyridin-2-amine (**4j**). M.p. 144 °C. Yield 16 mg (0.06 mmol, 20%). **^{1}H NMR** ($CDCl_3$, δ, ppm, J, Hz): 2.40 (s, 3H, Me), 4.68 (br. s, 2H, NH_2), 7.18 (d, 1H, J = 8.0, H-5(Py)), 7.23-7.28 (m, 2H, Tol), 7.37-7.43 (m, 1H, Ph), 7.44-7.55 (m, 5H, Ph, H-4(Py)), 7.88-7.94 (m, 2H, Tol). **^{13}C NMR** ($CDCl_3$, δ, ppm): 21.3, 111.1, 120.1, 126.7, 127.6, 128.7, 129.1, 129.3, 136.7, 138.3, 138.5, 138.6, 155.3, 155.5. **ESI-MS**, m/z: 261.14 $[M+H]^+$. Calculated for **$C_{18}H_{16}N_2$**: C 83.04, H 6.19, N 10.76. Found: C 83.13, H 6.05, N 10.62.

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Figure S1. ^{1}H NMR spectrum of compound *2h*

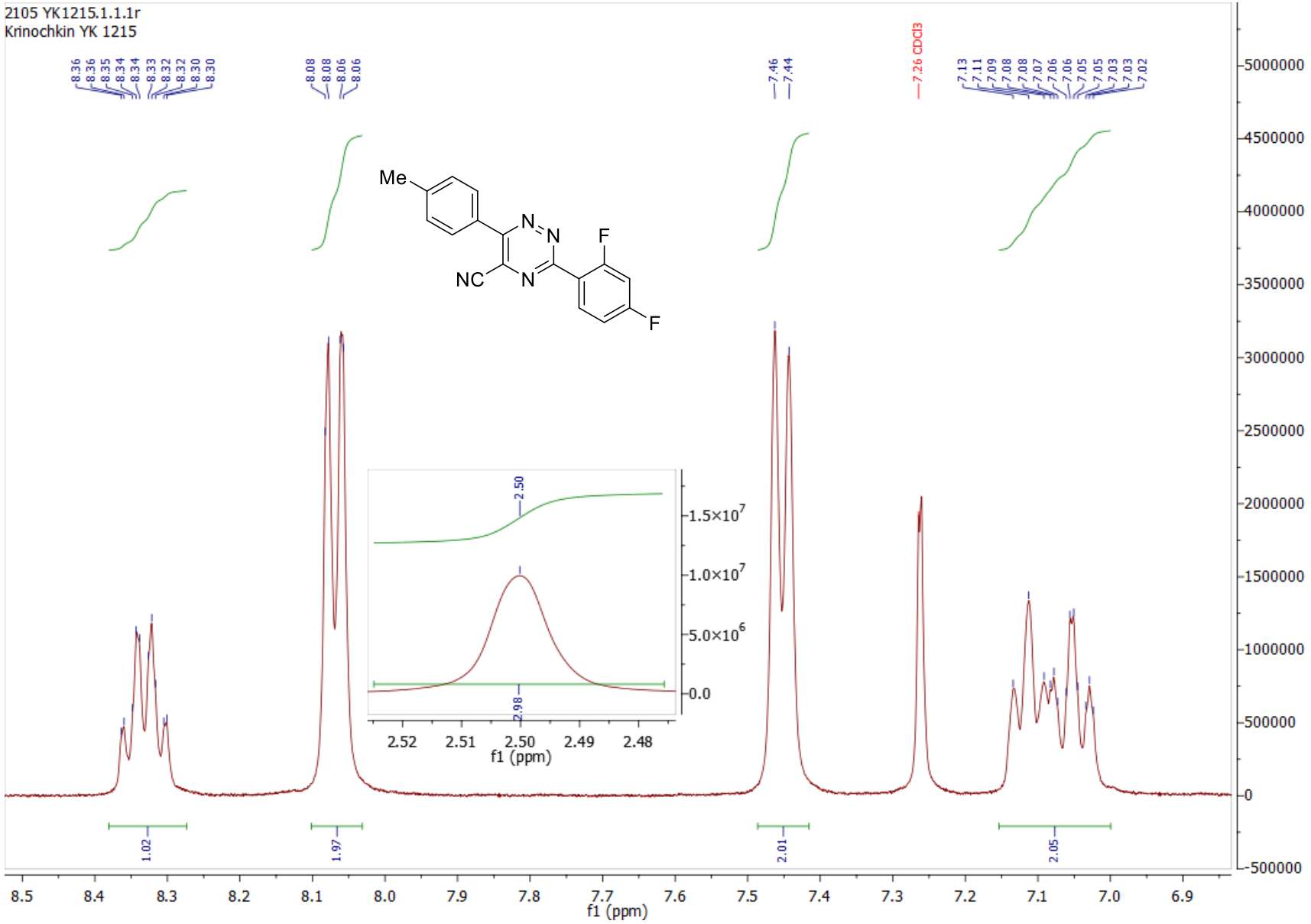

Figure S2. ^{19}F NMR spectrum of compound *2h*

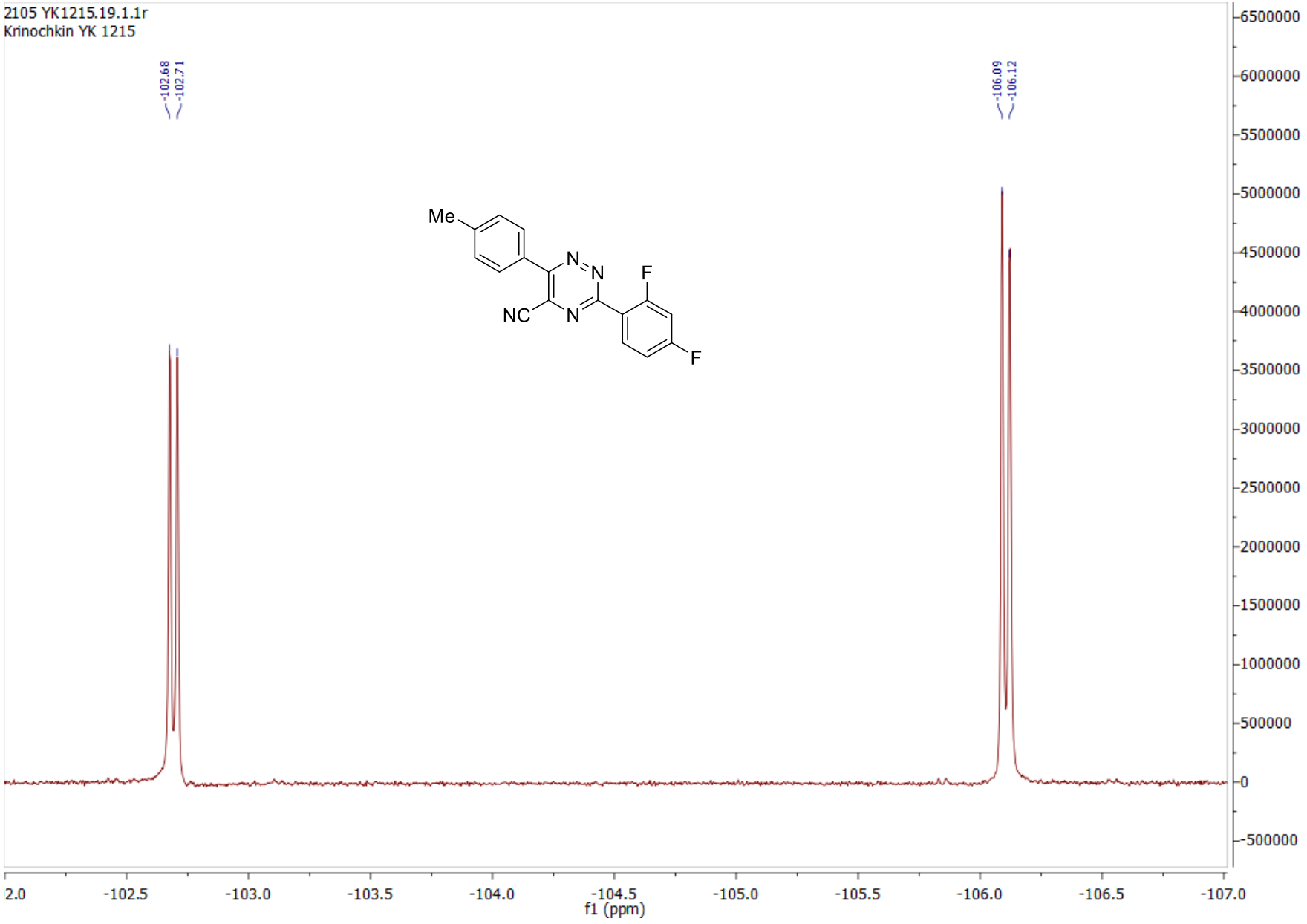

Figure S3. ^{1}H NMR Spectra of compound *1a*

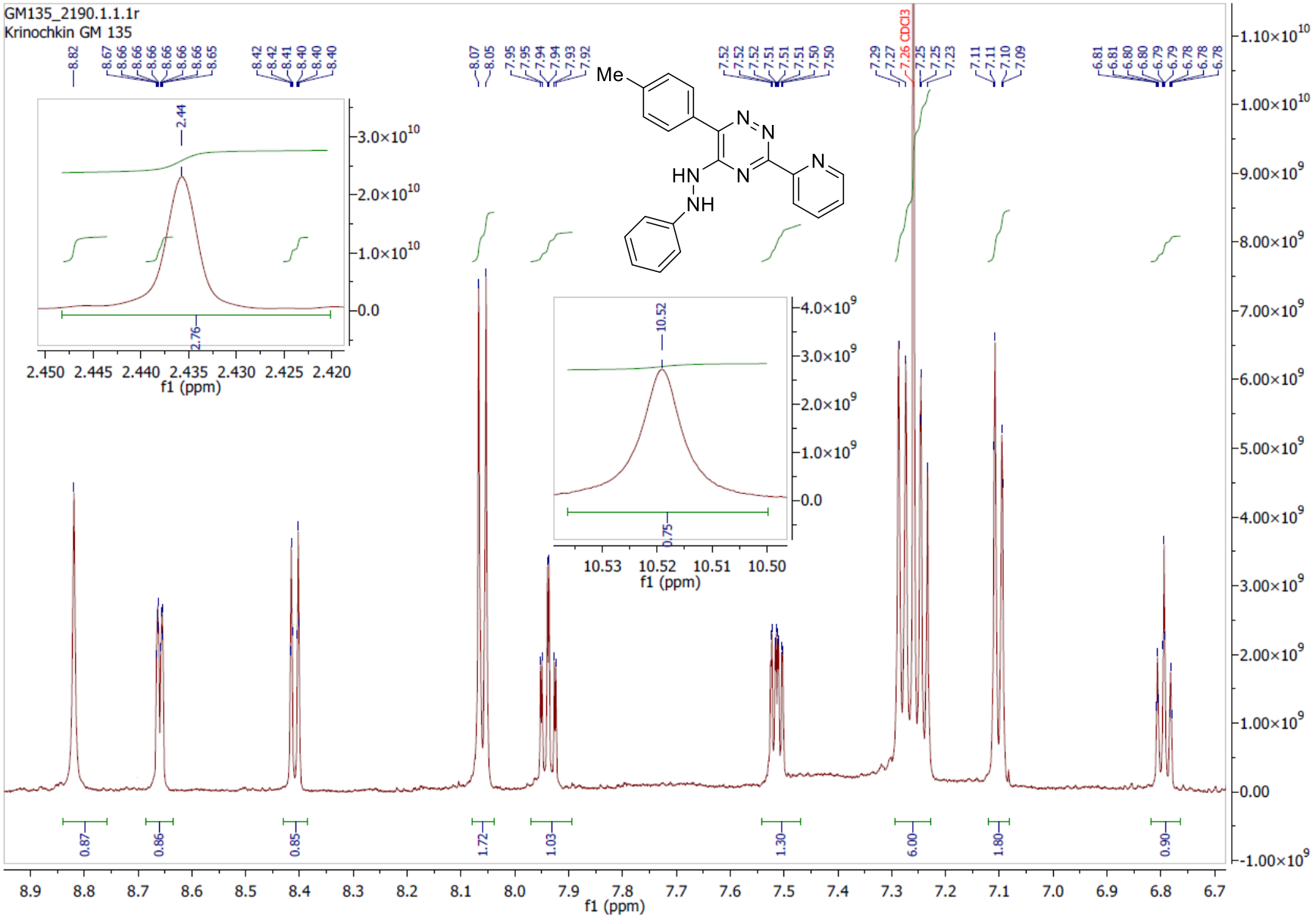

Figure S4. ^{13}C NMR spectrum of compound *1a*

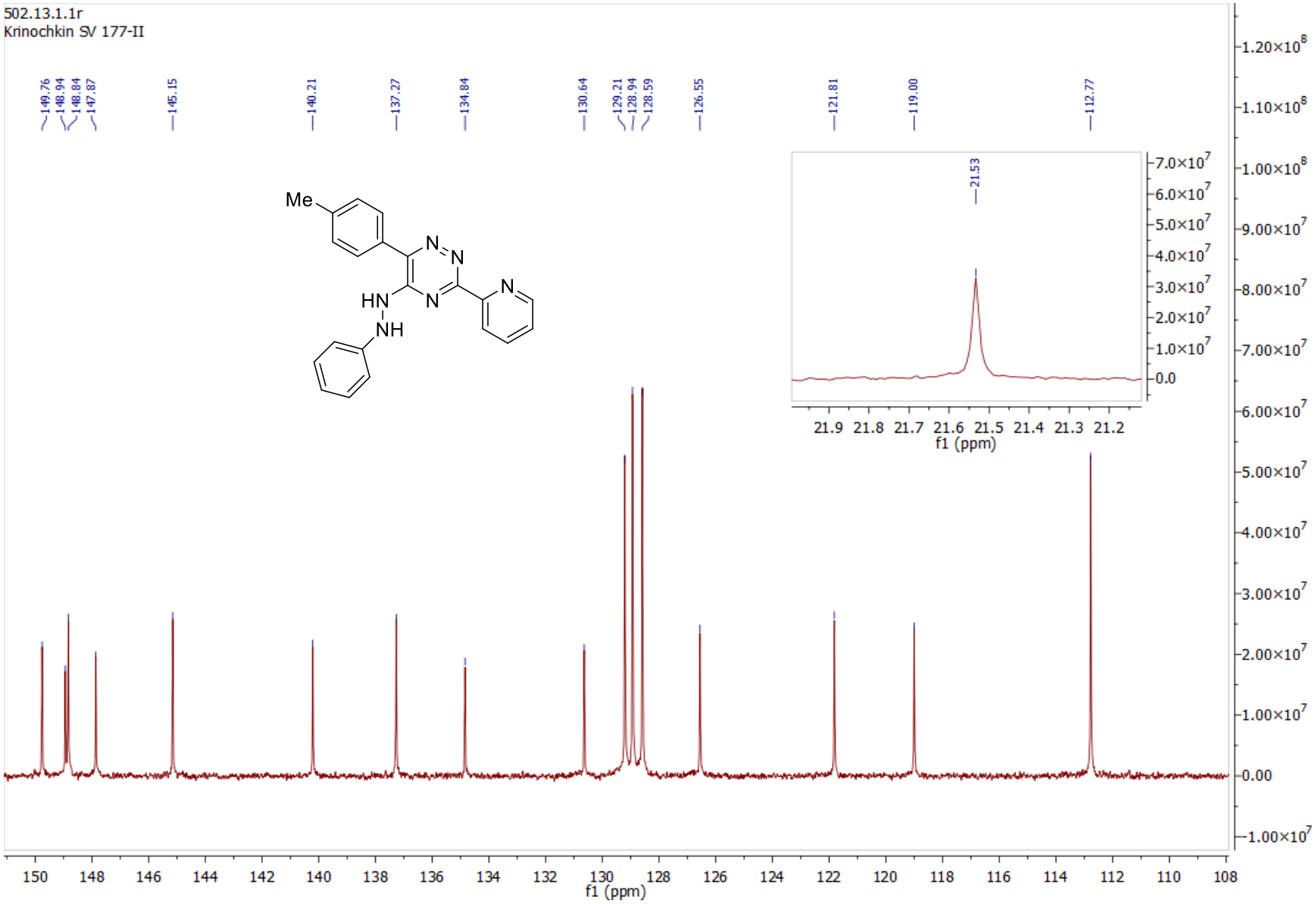

Figure S5. ^{1}H NMR spectrum of compound *1b*

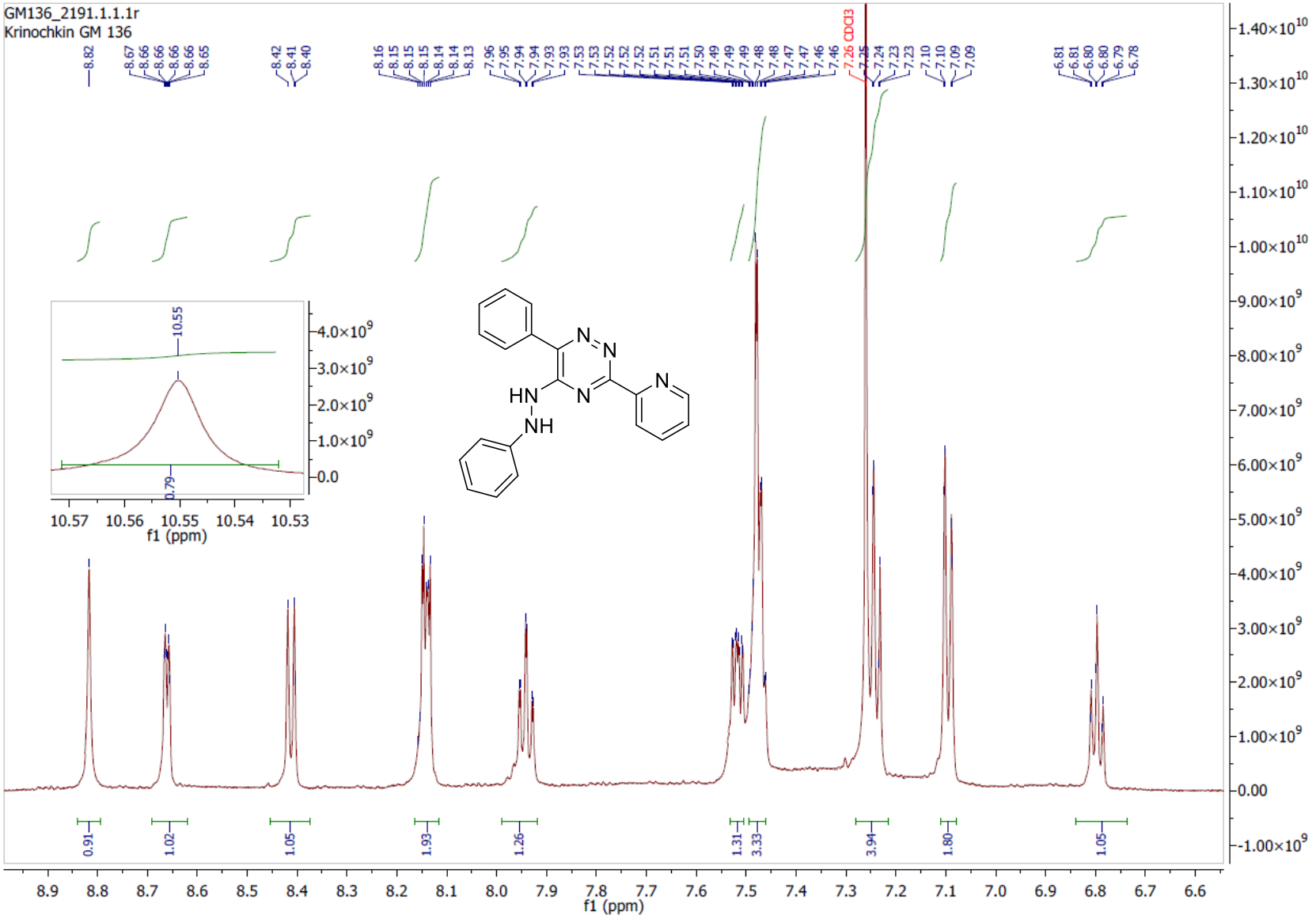

Figure S6. ^{13}C NMR spectrum of compound *1b*

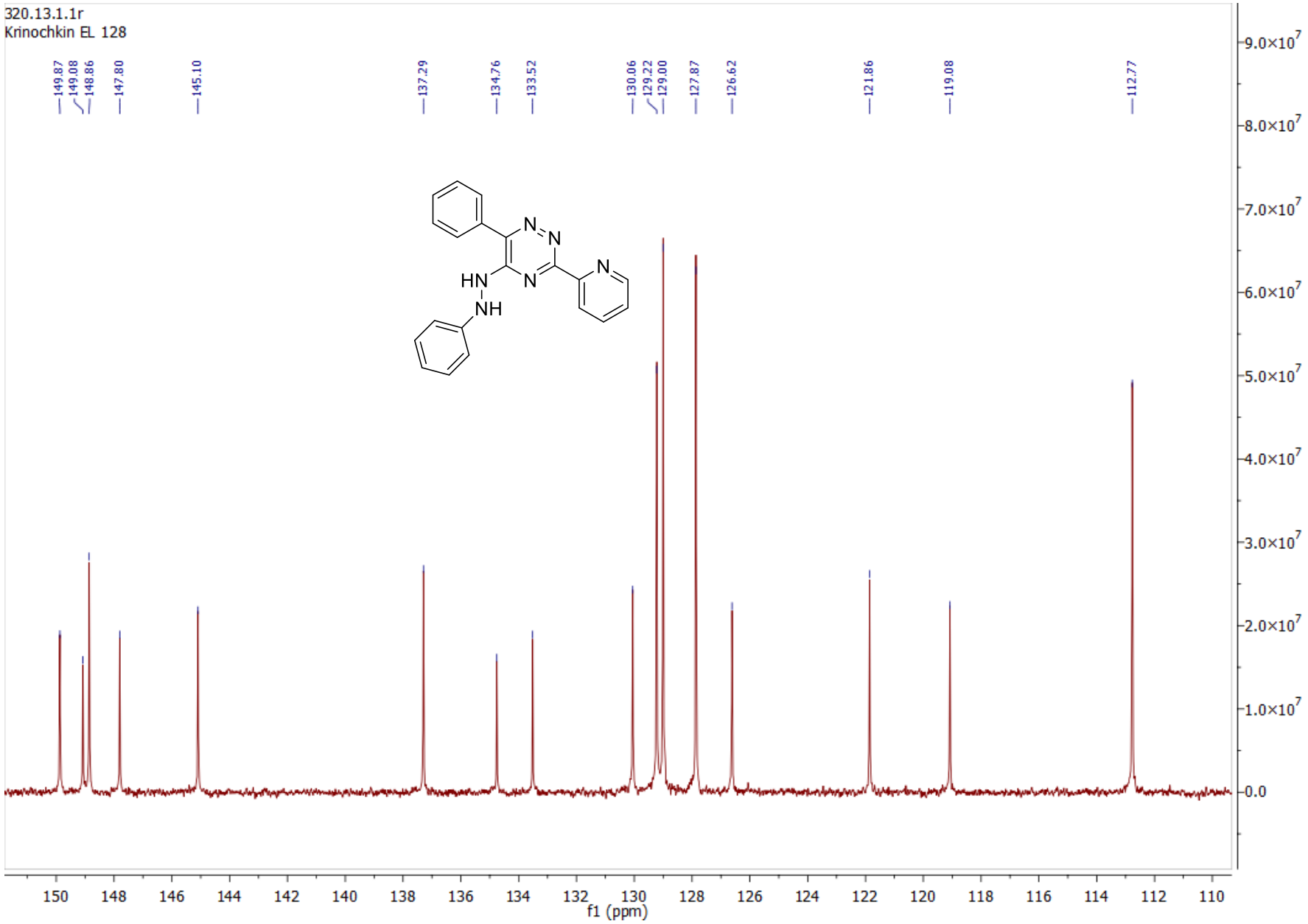

Figure S7. ^{1}H NMR spectrum of compound *1e*

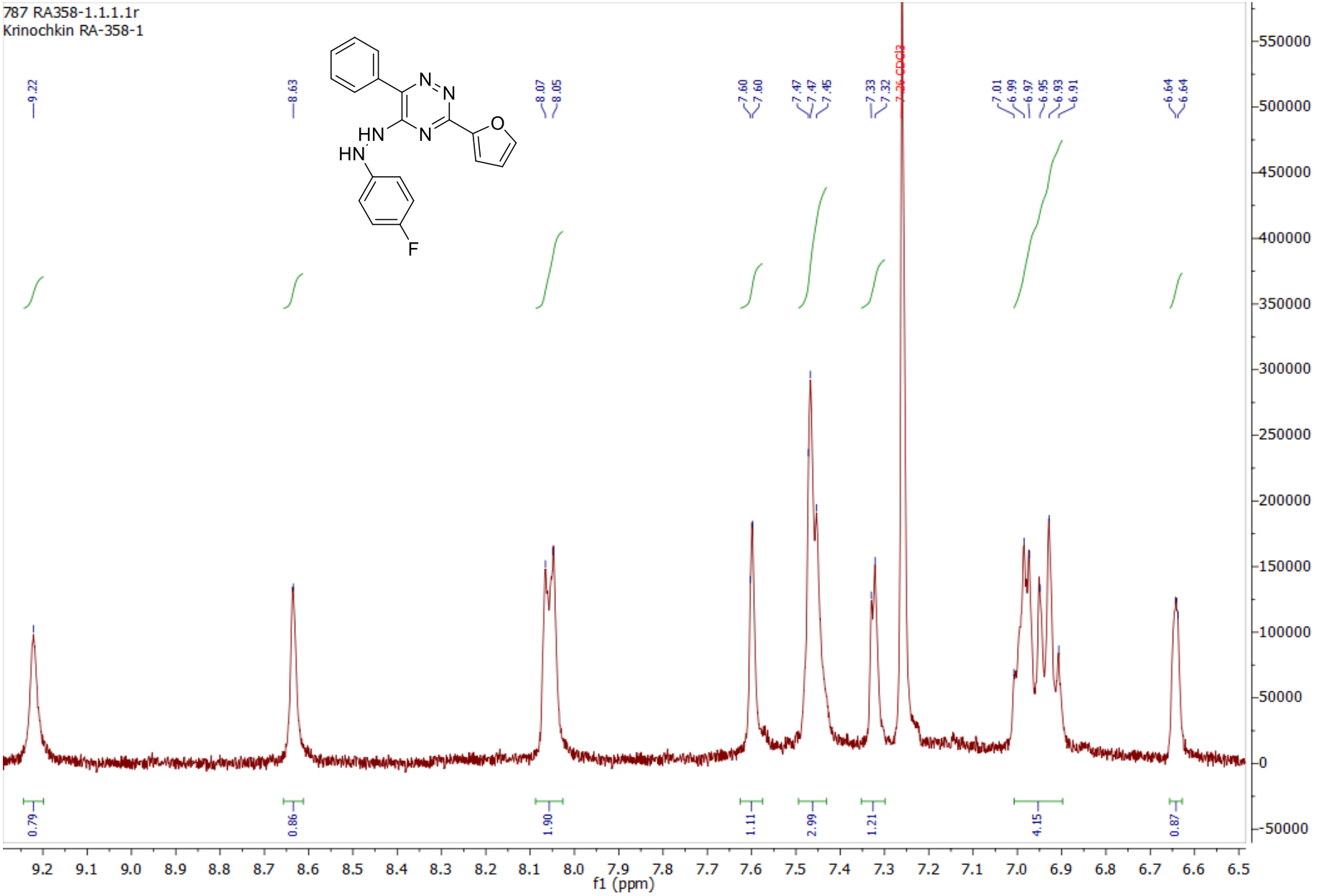

Figure S8. ^{13}C NMR spectrum of compound *1e*

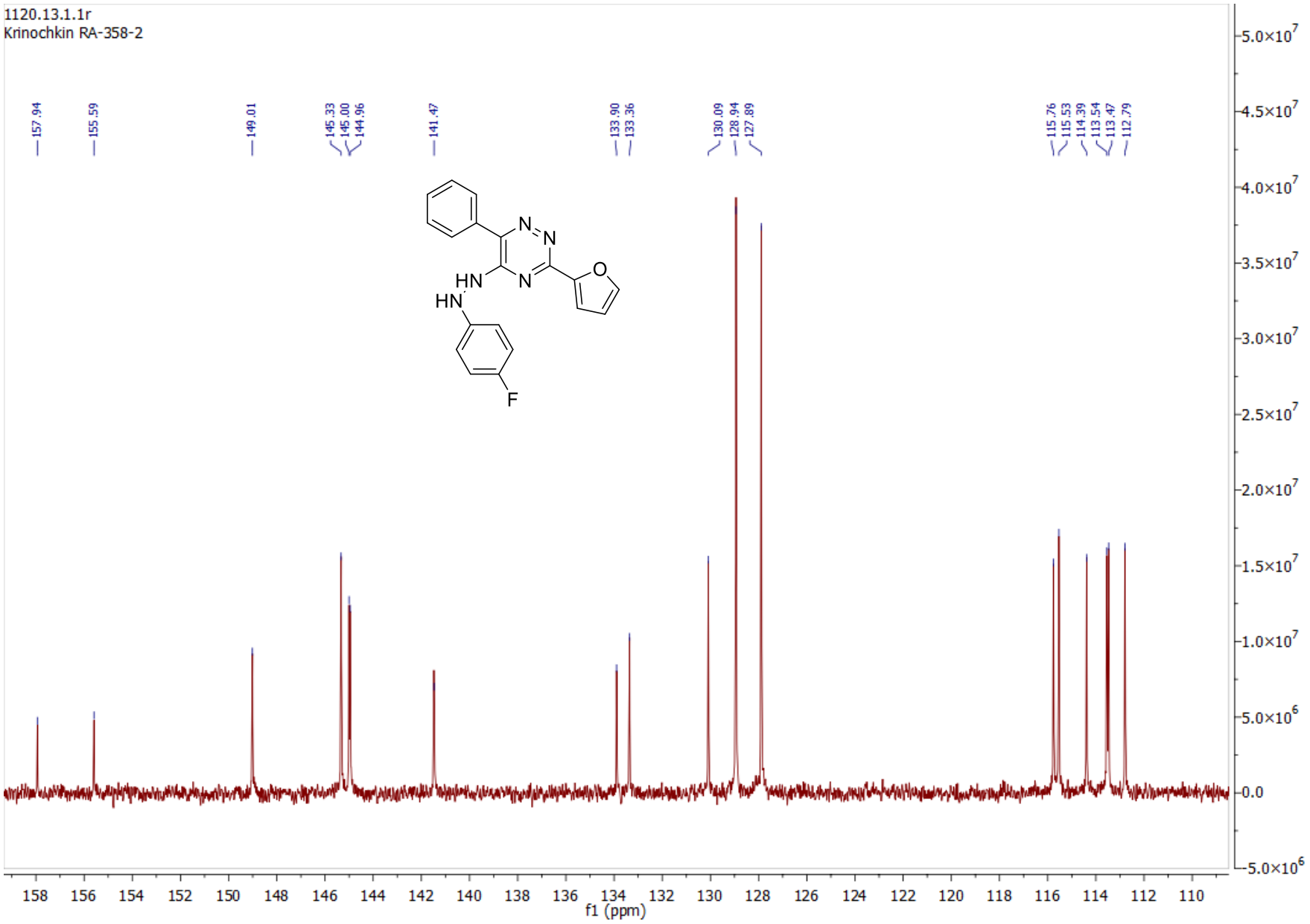

Figure S9. ^{19}F NMR spectrum of compound *1e*

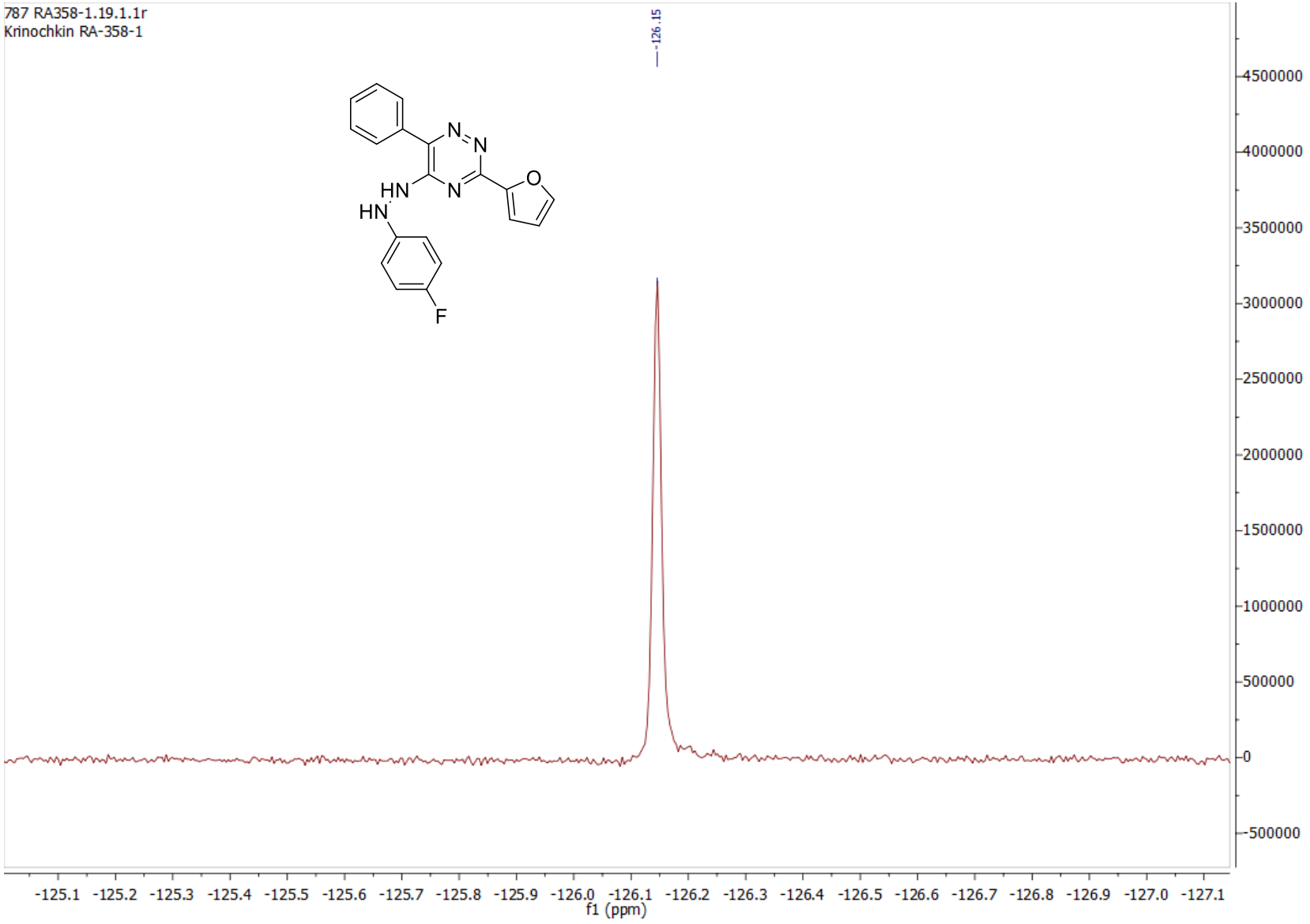

Figure S10. ^{1}H NMR spectrum of compound *1f*

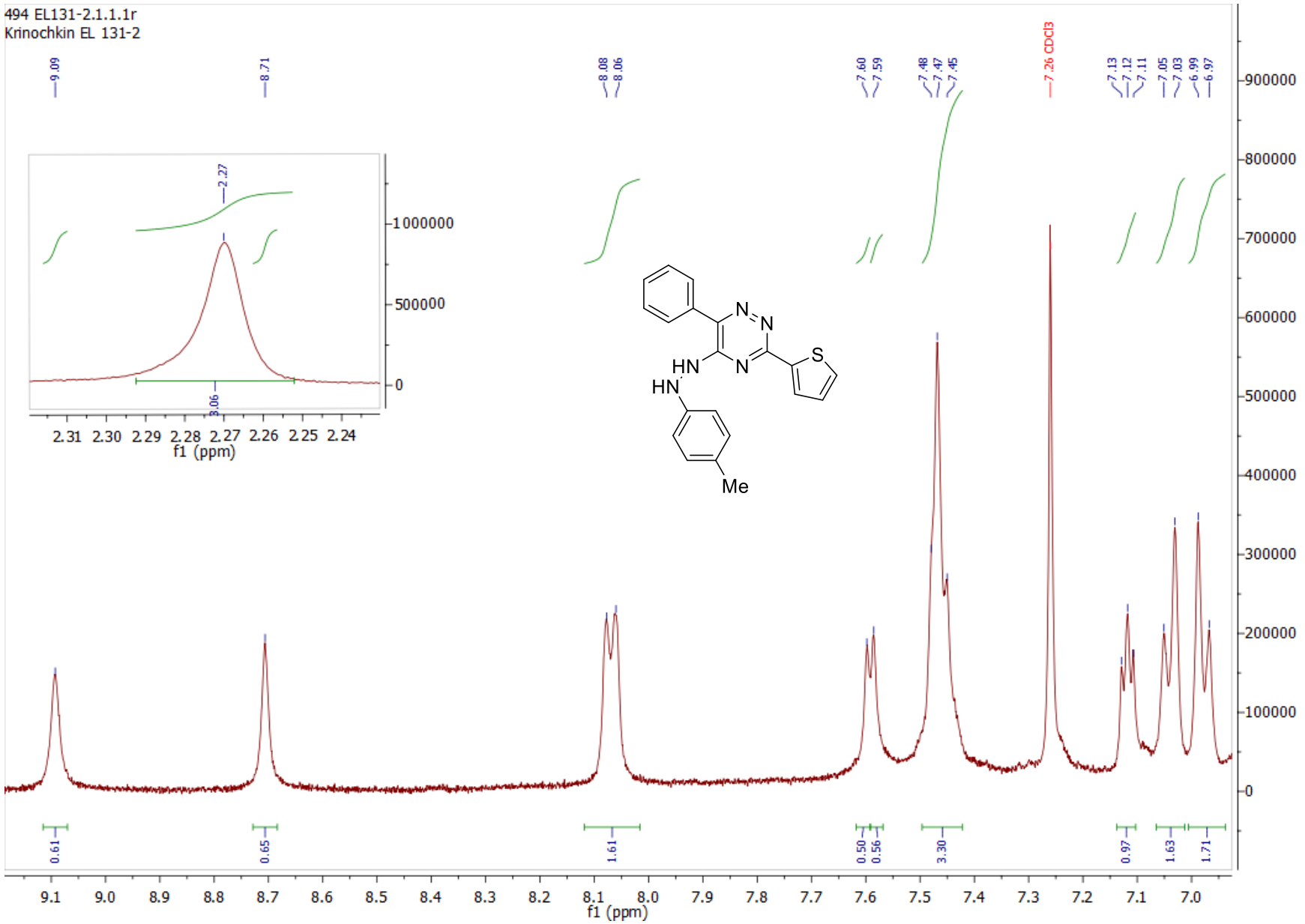

Figure S11. ^{13}C NMR spectrum of compound *1f*

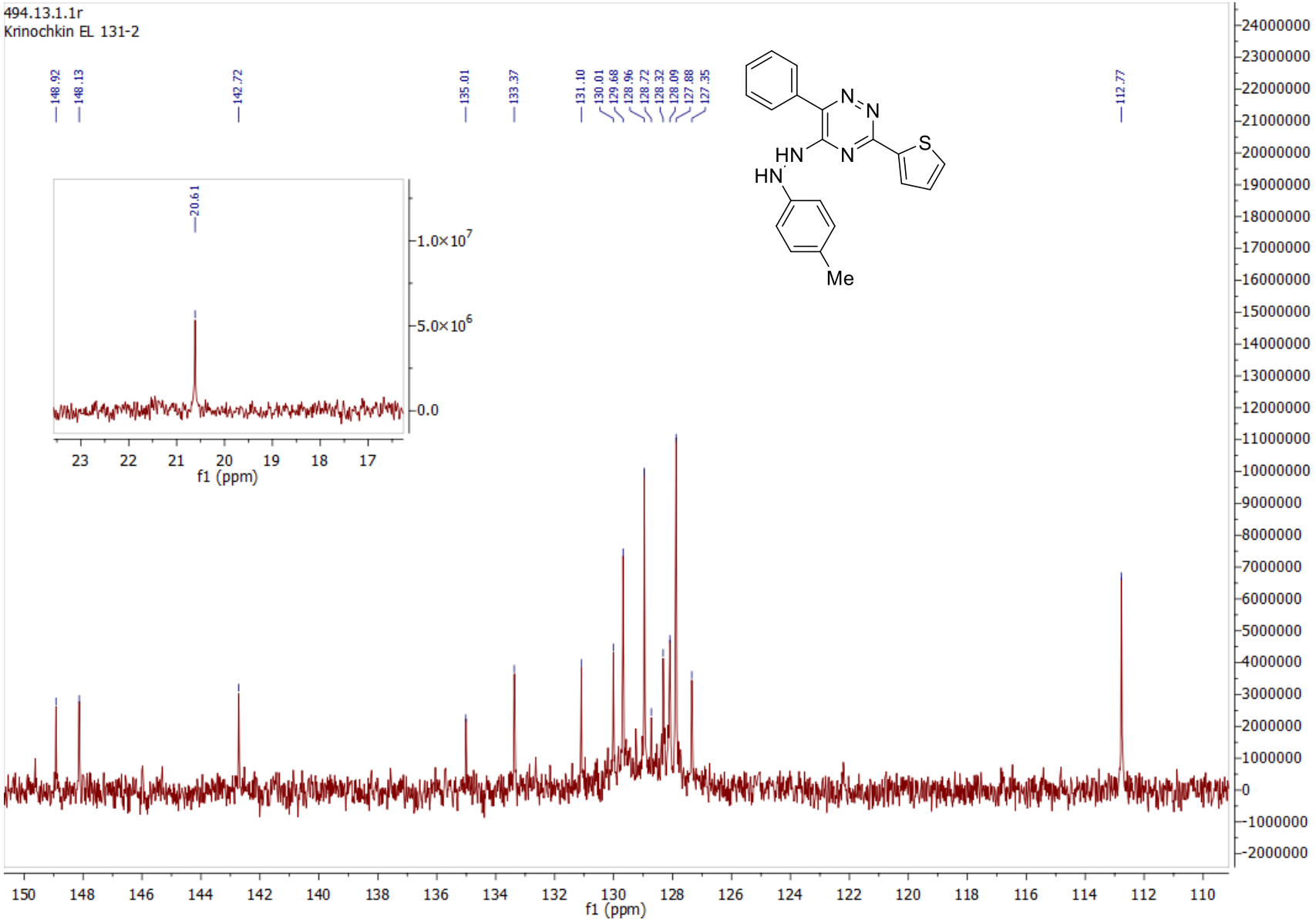

Figure S12. ^{1}H NMR spectrum of compound *1g*

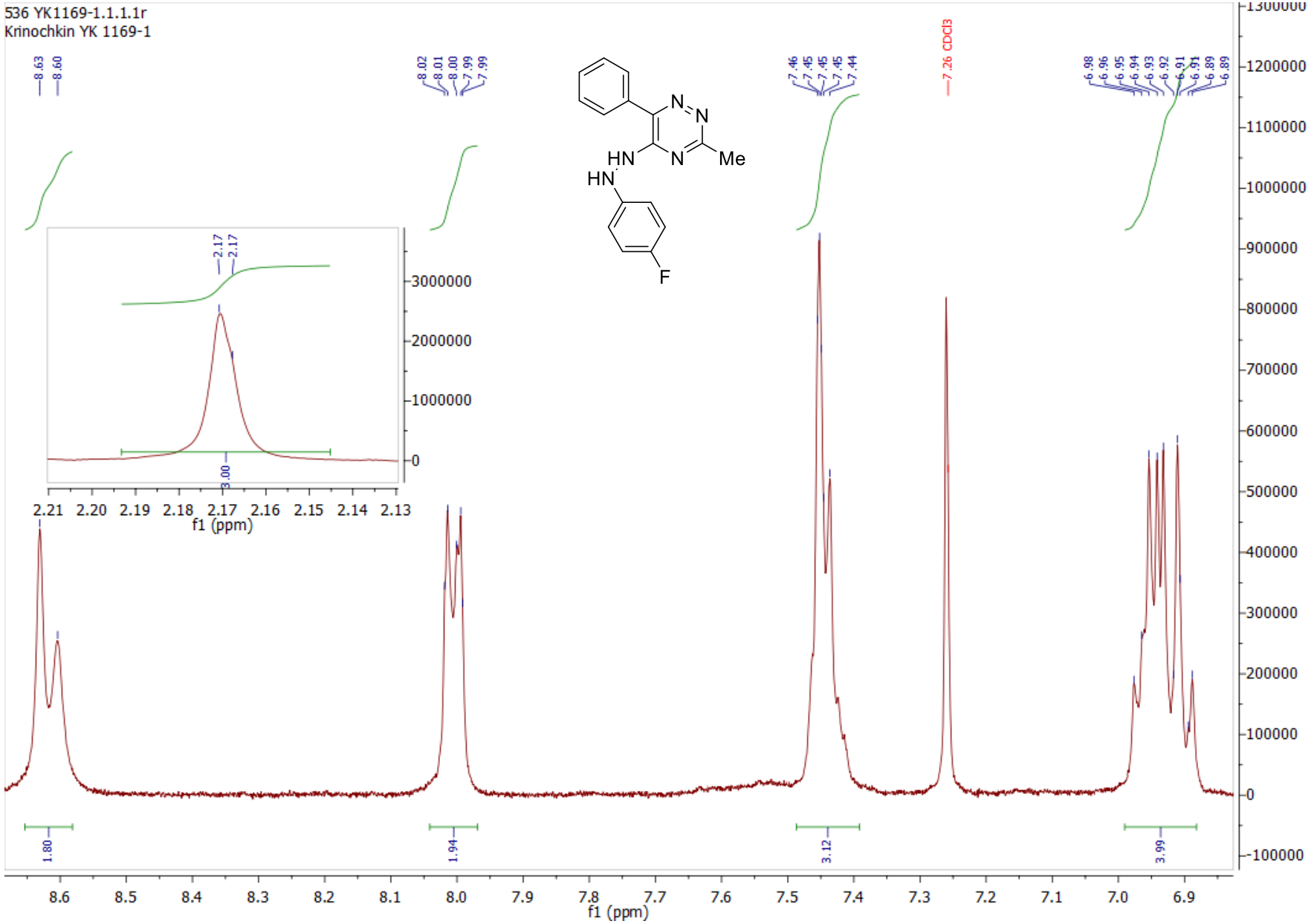

Figure S13. ^{13}C NMR spectrum of compound *1g*

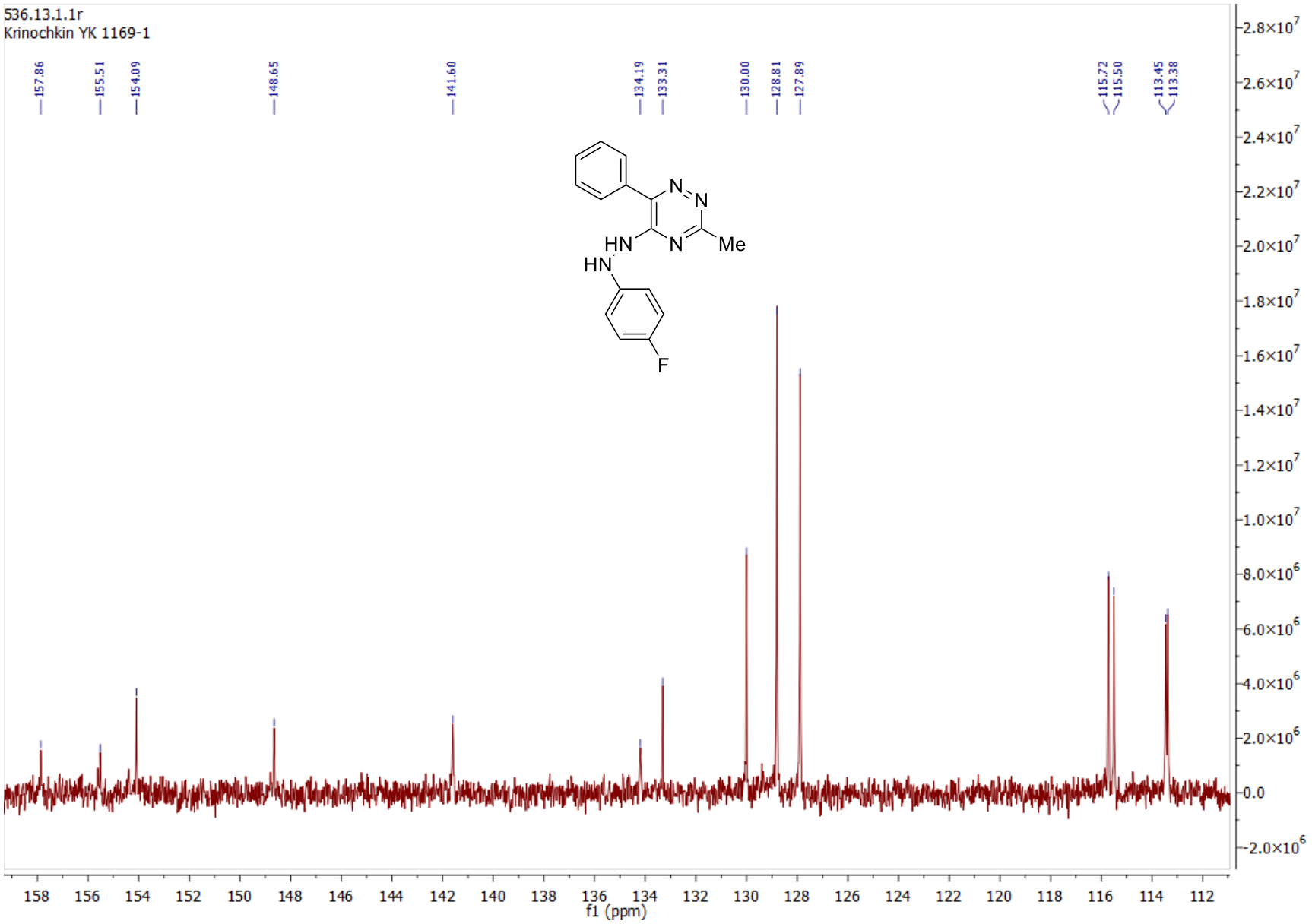

Figure S14. ^{19}F NMR spectrum of compound *1g*

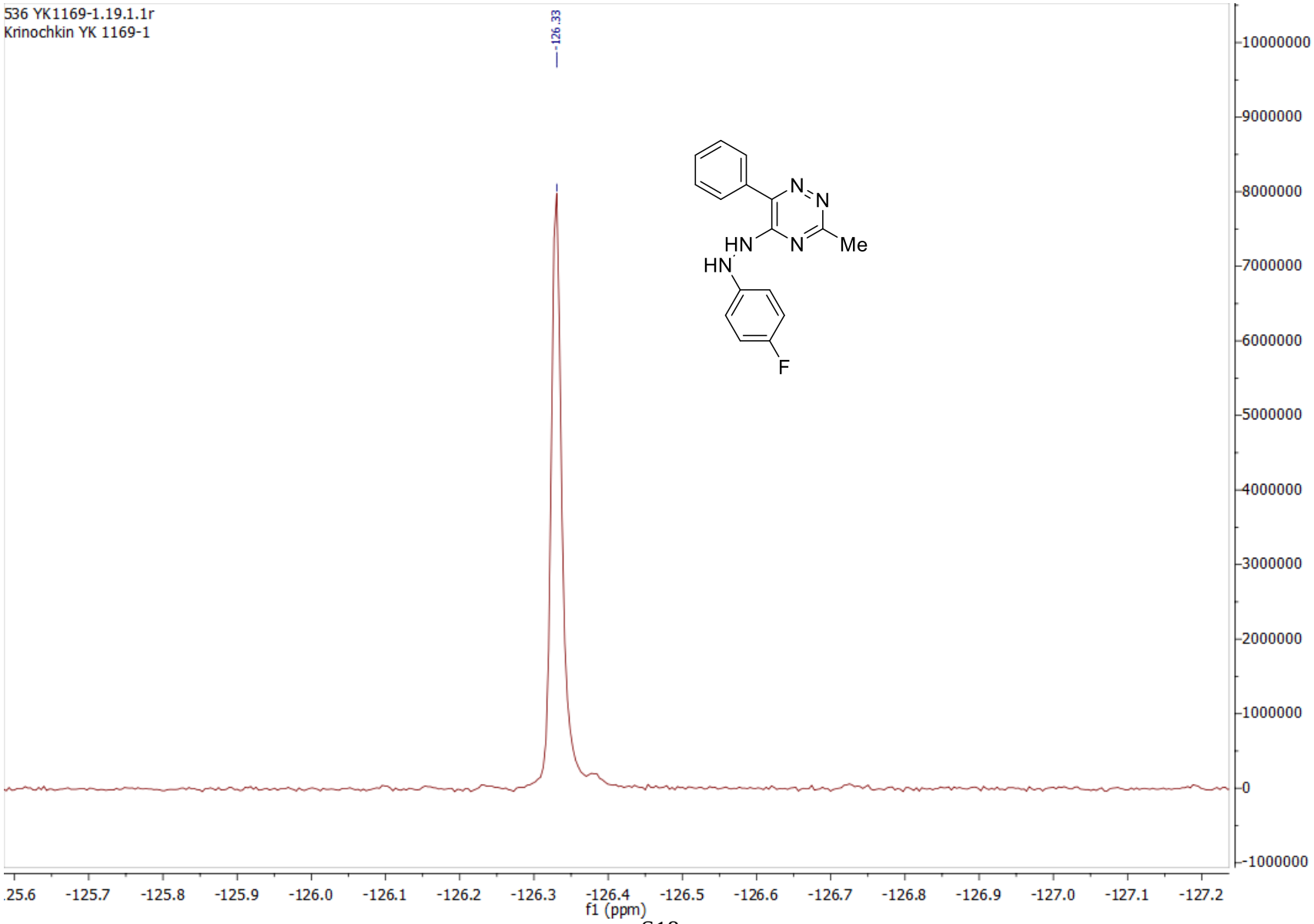

Figure S15. ^{1}H NMR spectrum of compound *1h*

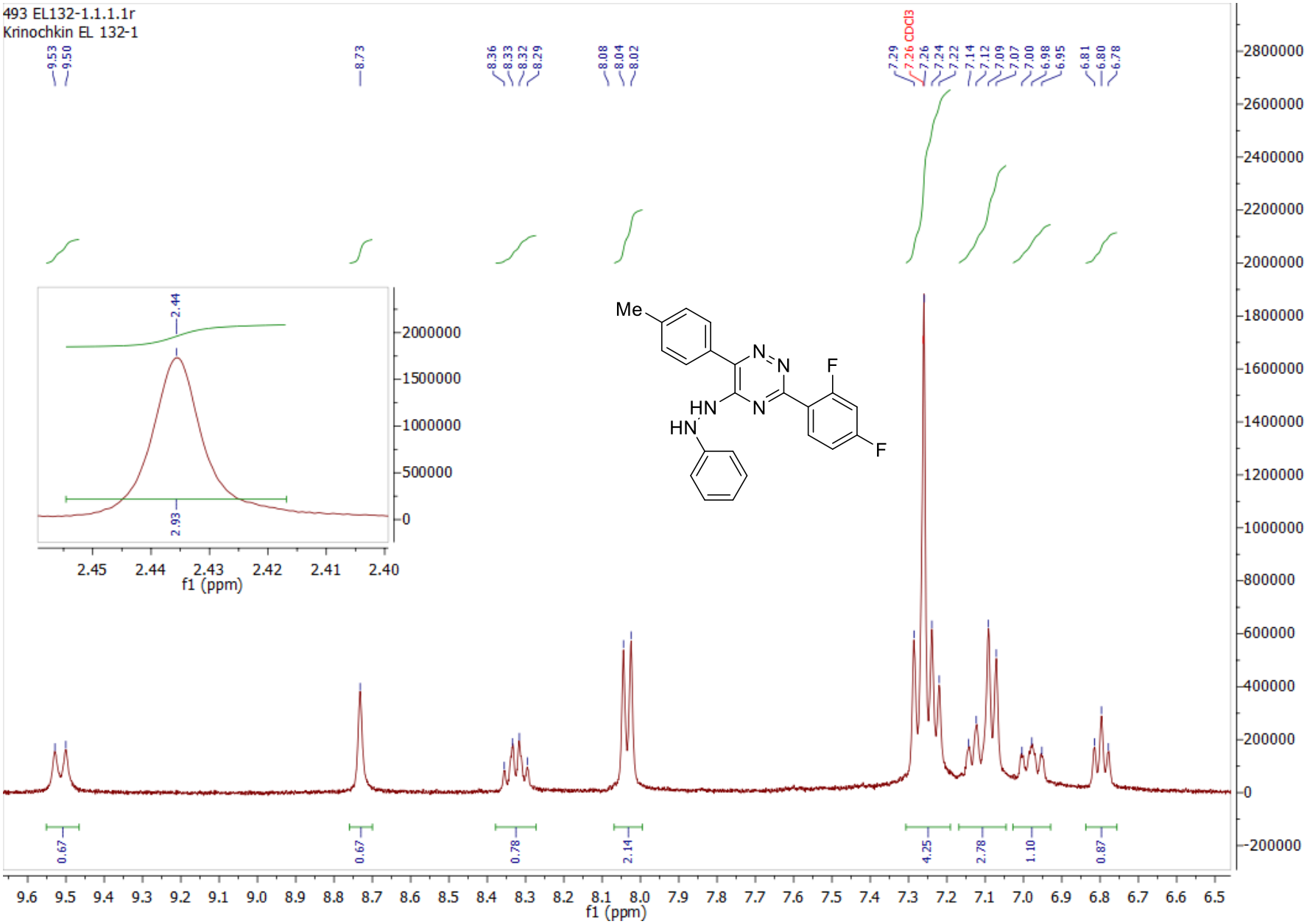

Figure S16. ^{13}C NMR spectrum of compound *1h*

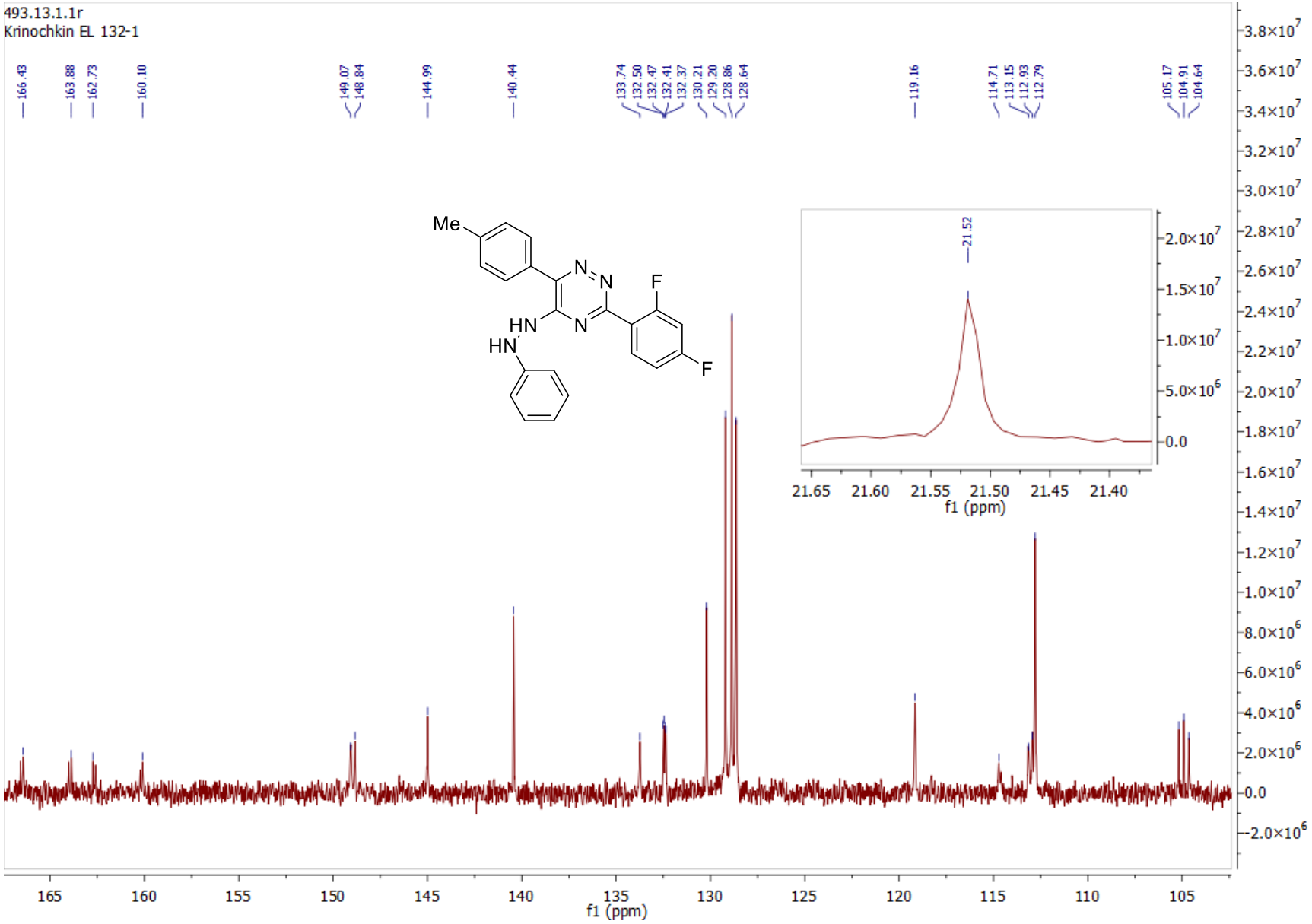

Figure S17. ^{19}F NMR spectrum of compound *1h*

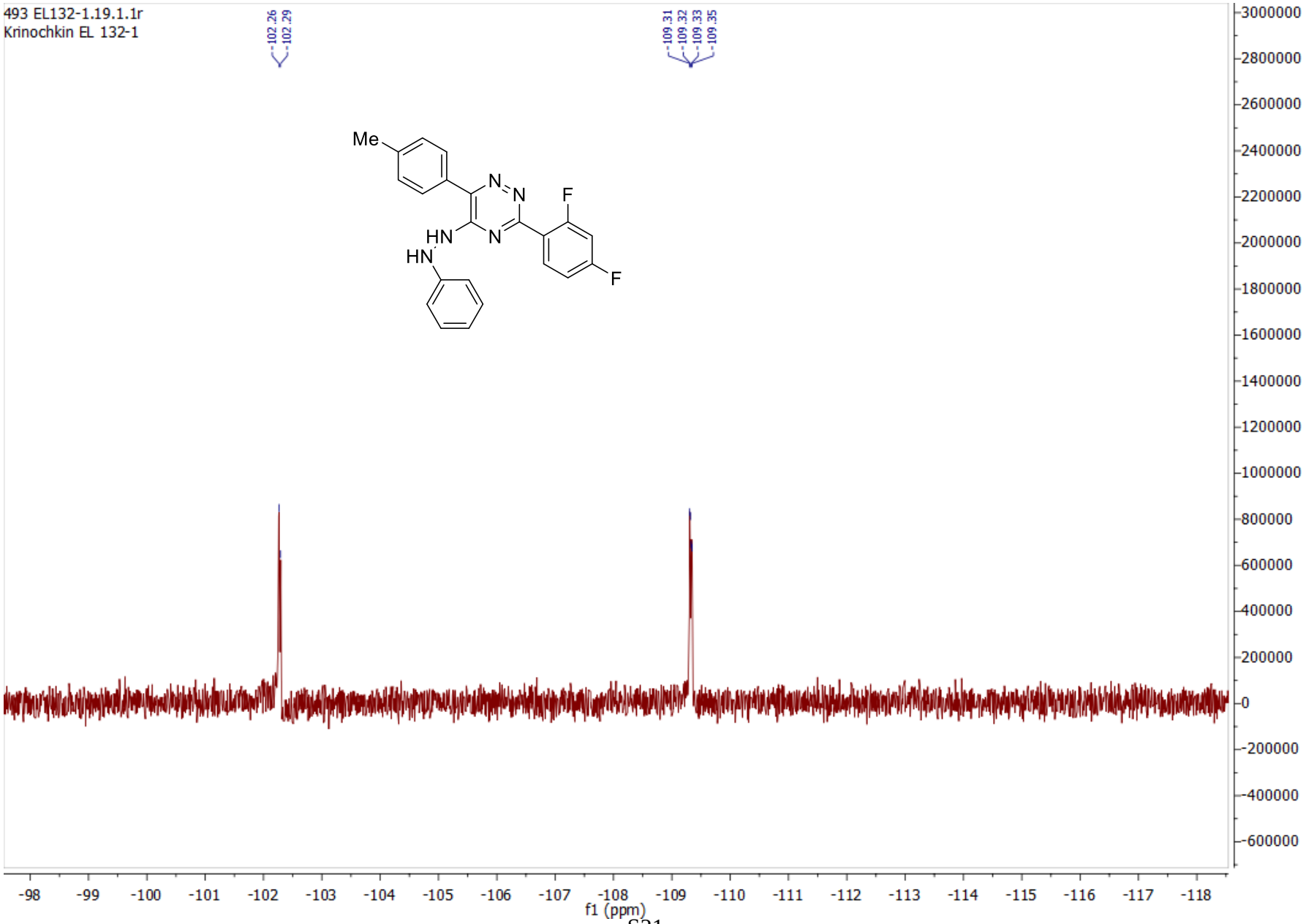

Figure S18. ^{1}H NMR spectrum of compound *5*

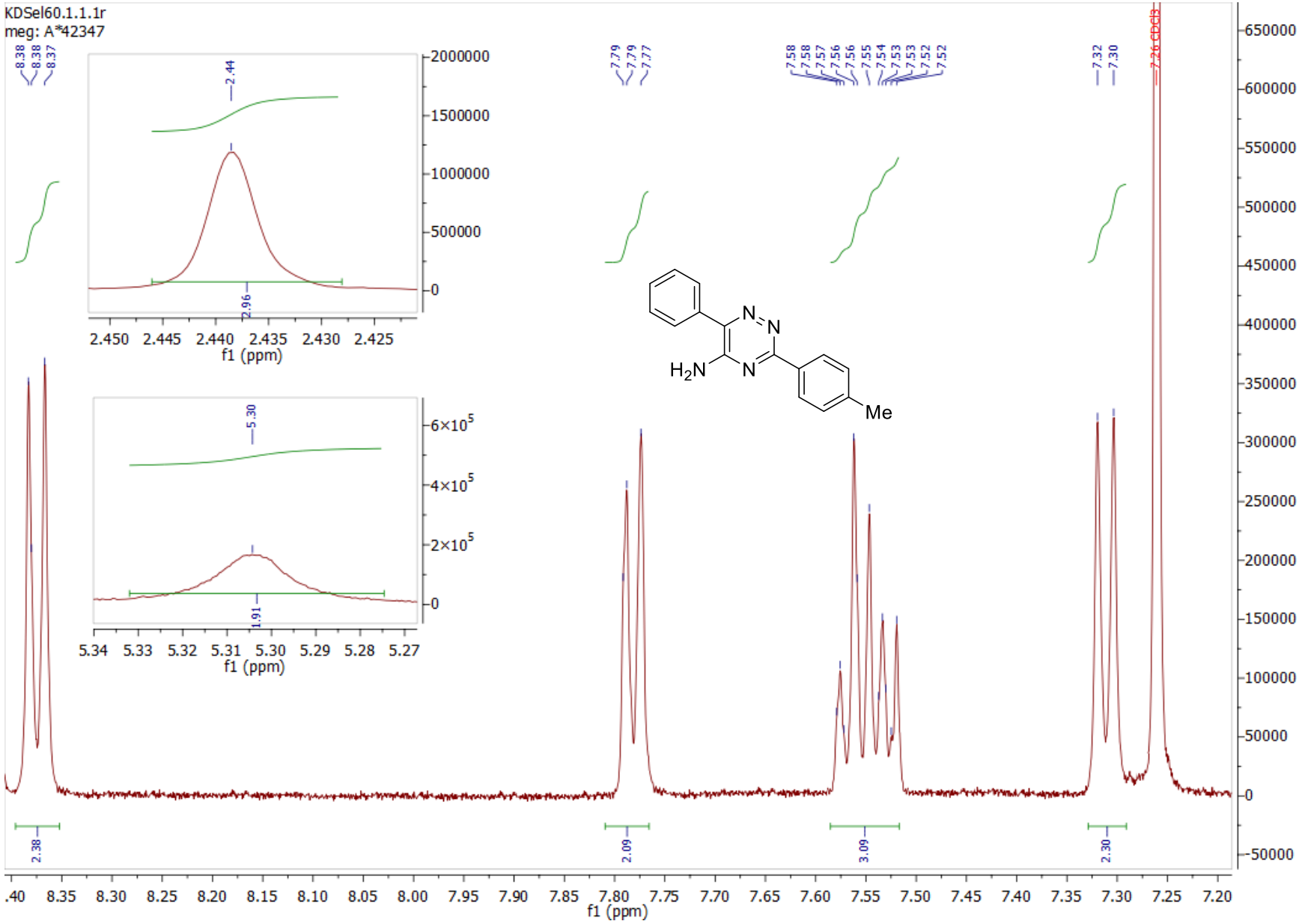

Figure S19. ^{13}C NMR spectrum of compound *5*

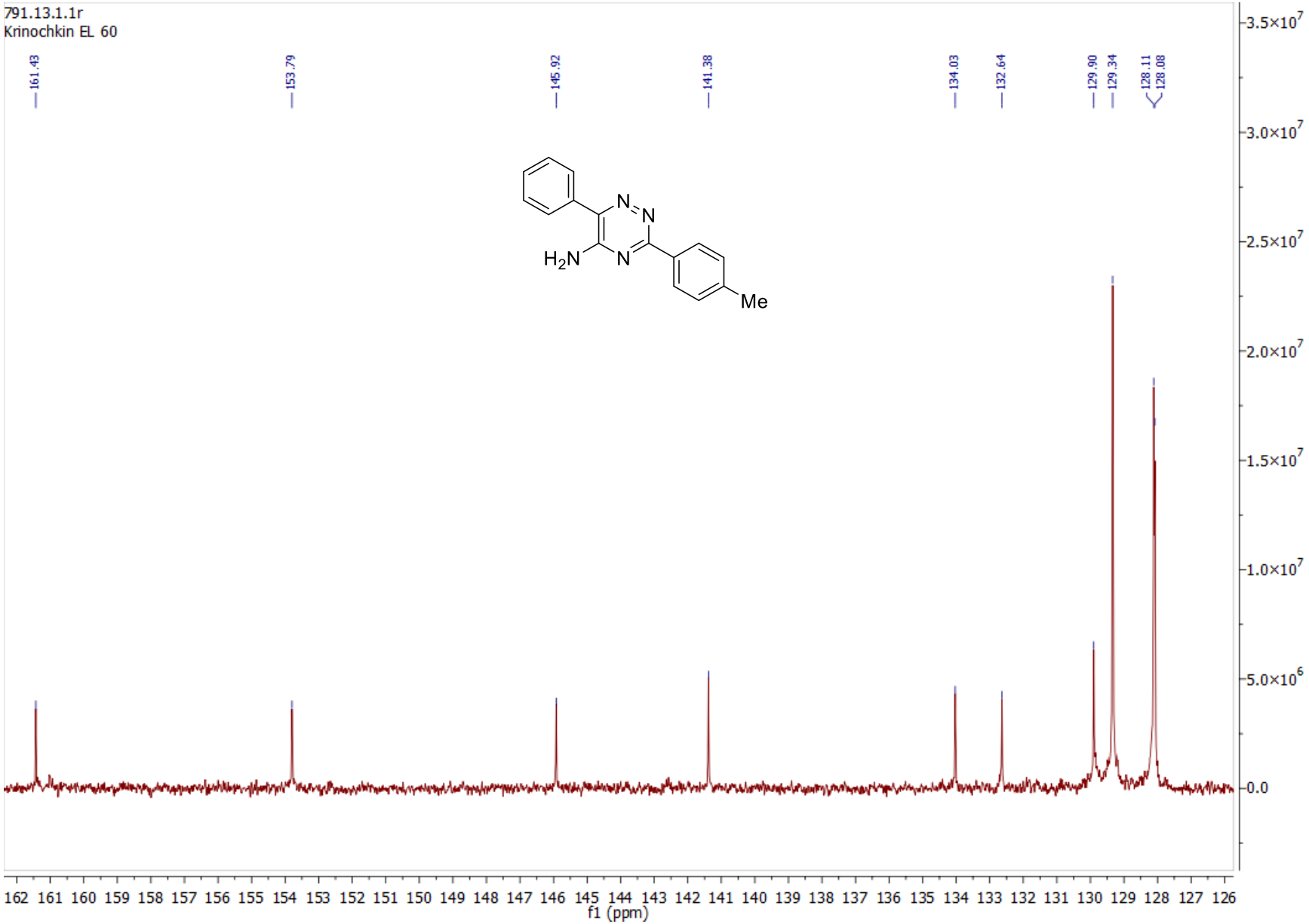

Figure S20. ^{1}H NMR spectrum of compound *4a*

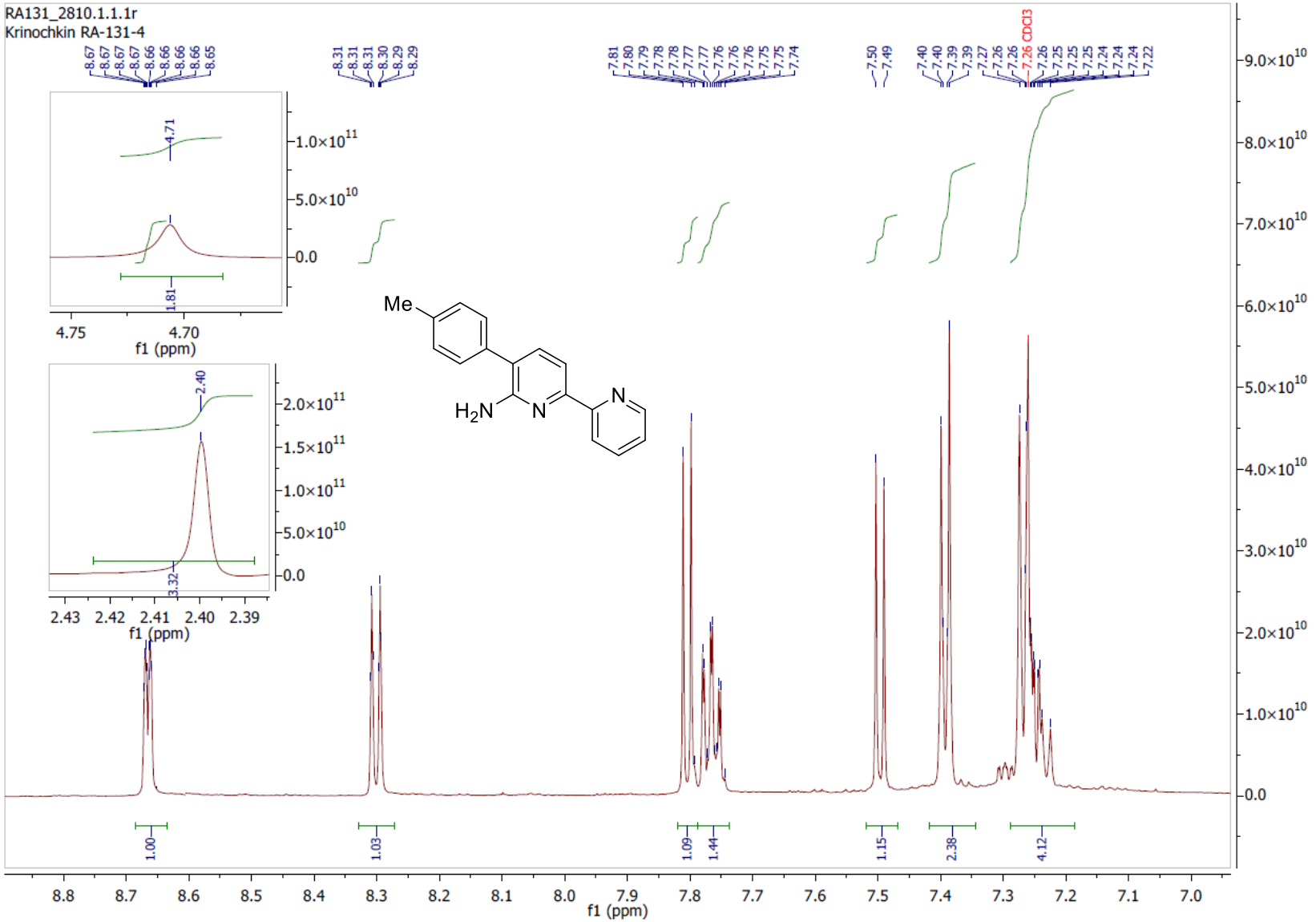

Figure S21. ^{13}C NMR spectrum of compound *4a*

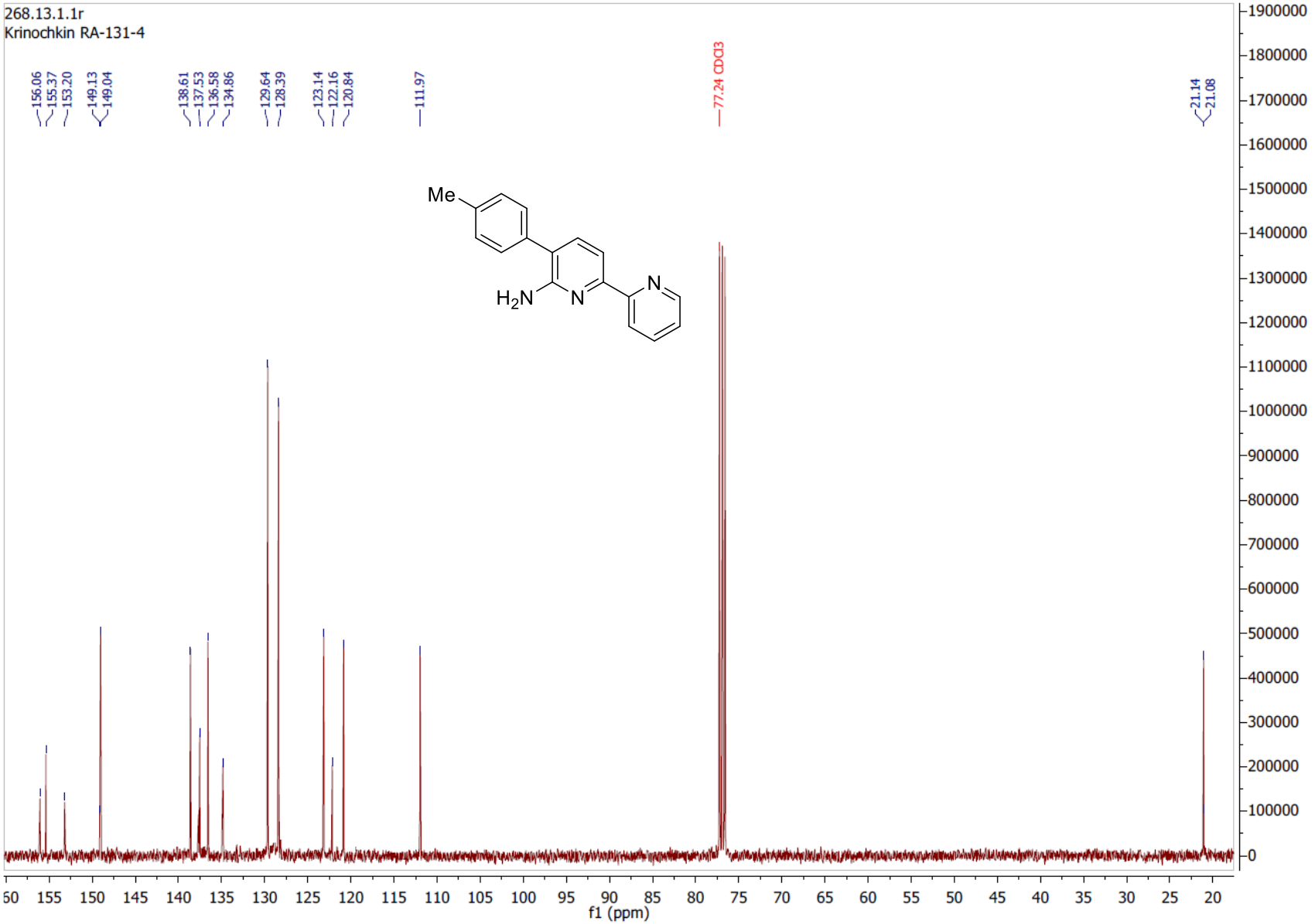

Figure S22. ^{1}H NMR spectrum of compound *4b*

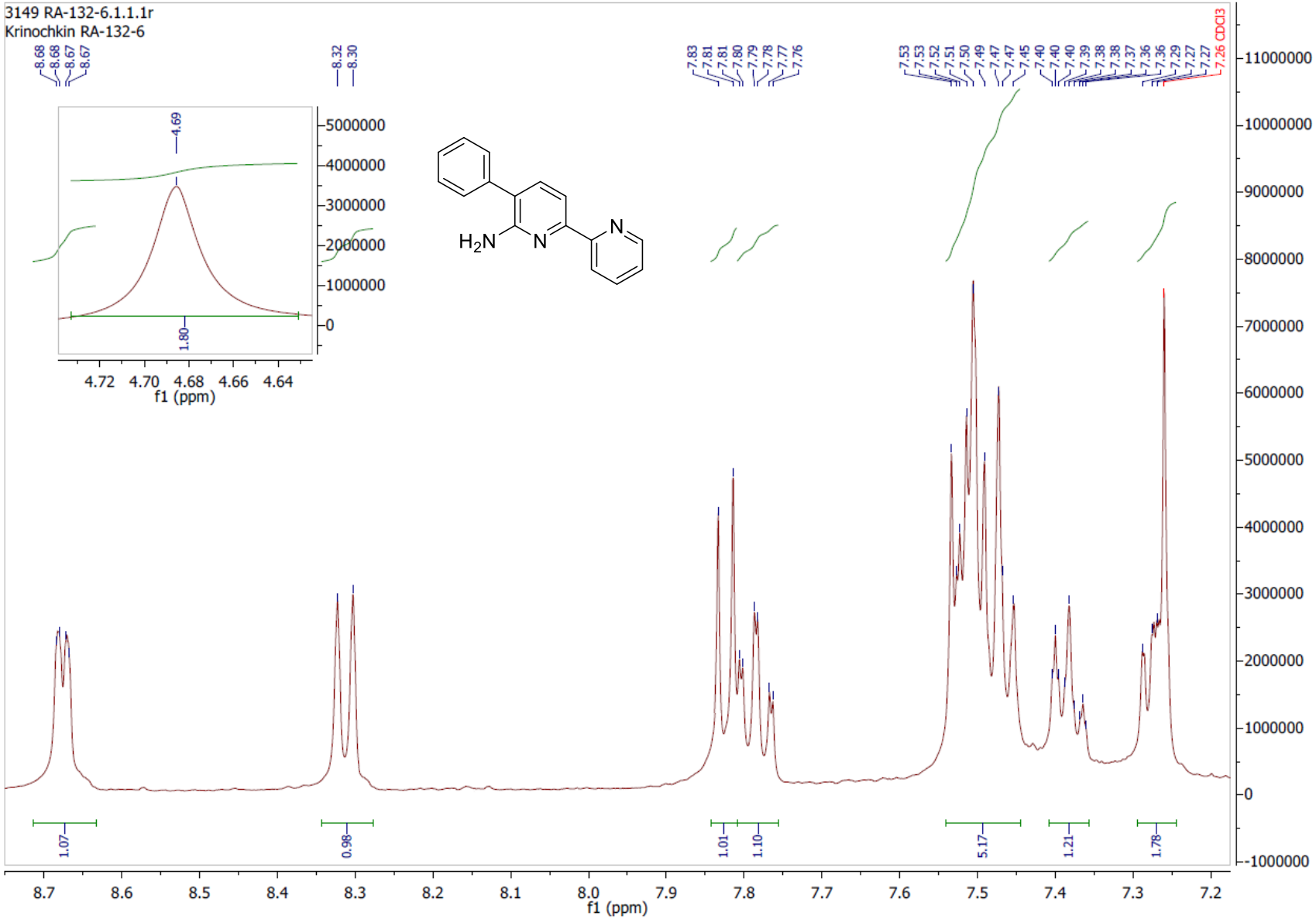

Figure S23. ^{13}C NMR spectrum of compound *4b*

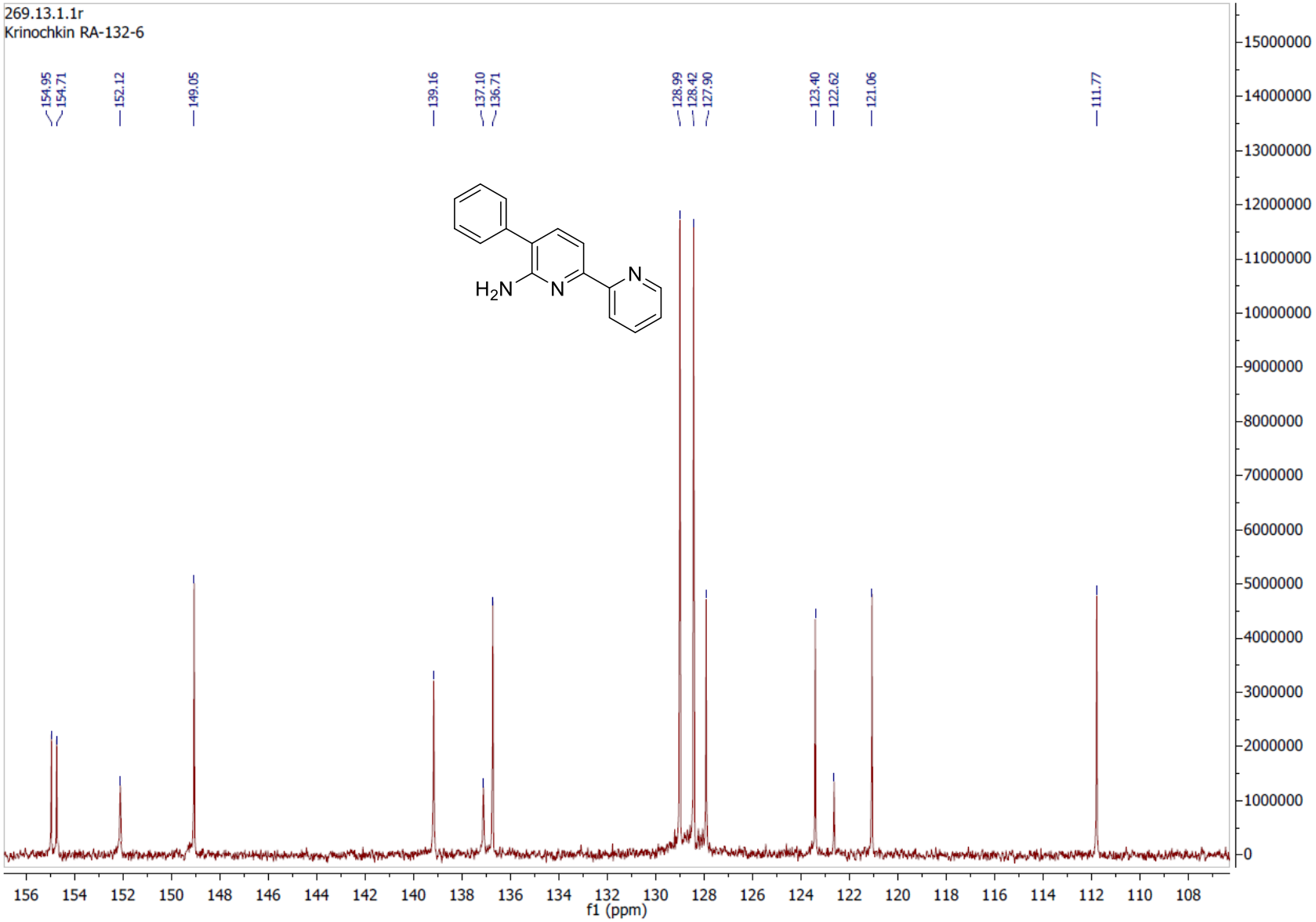

Figure S24. ^{1}H NMR spectrum of compound *4c*

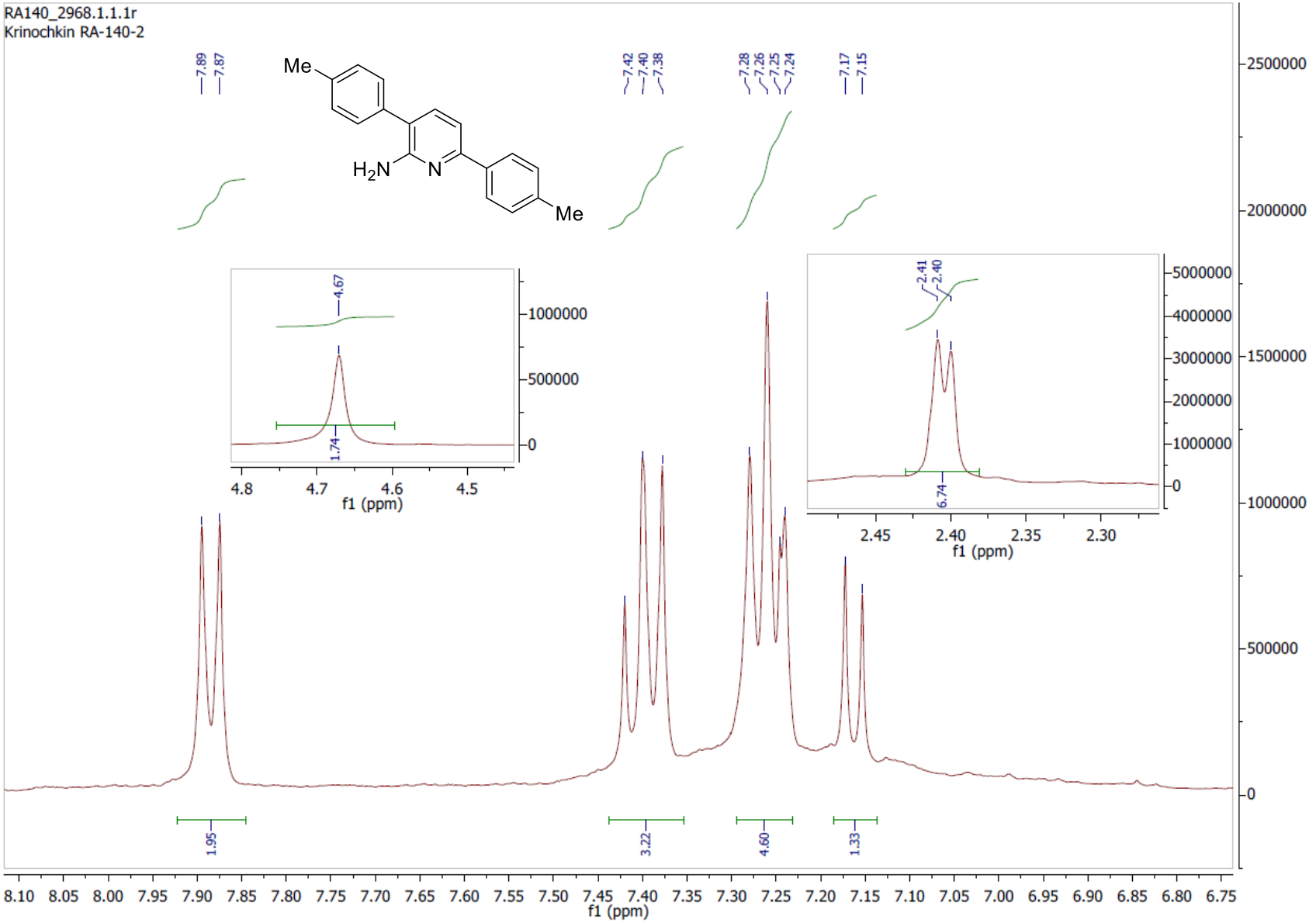

Figure S25. ^{13}C NMR spectrum of compound *4c*

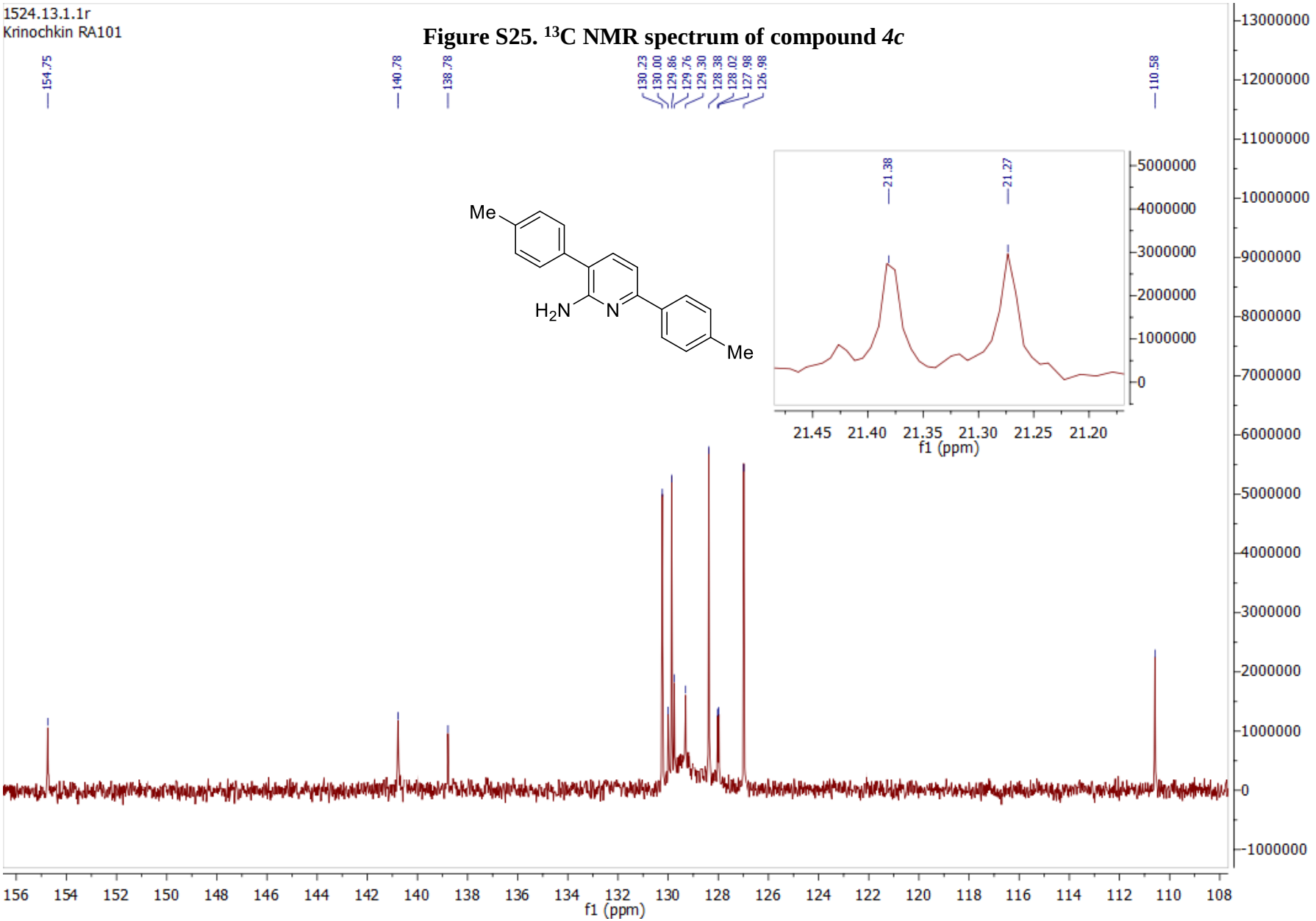

Figure S25. ^{1}H NMR spectrum of compound *4e*

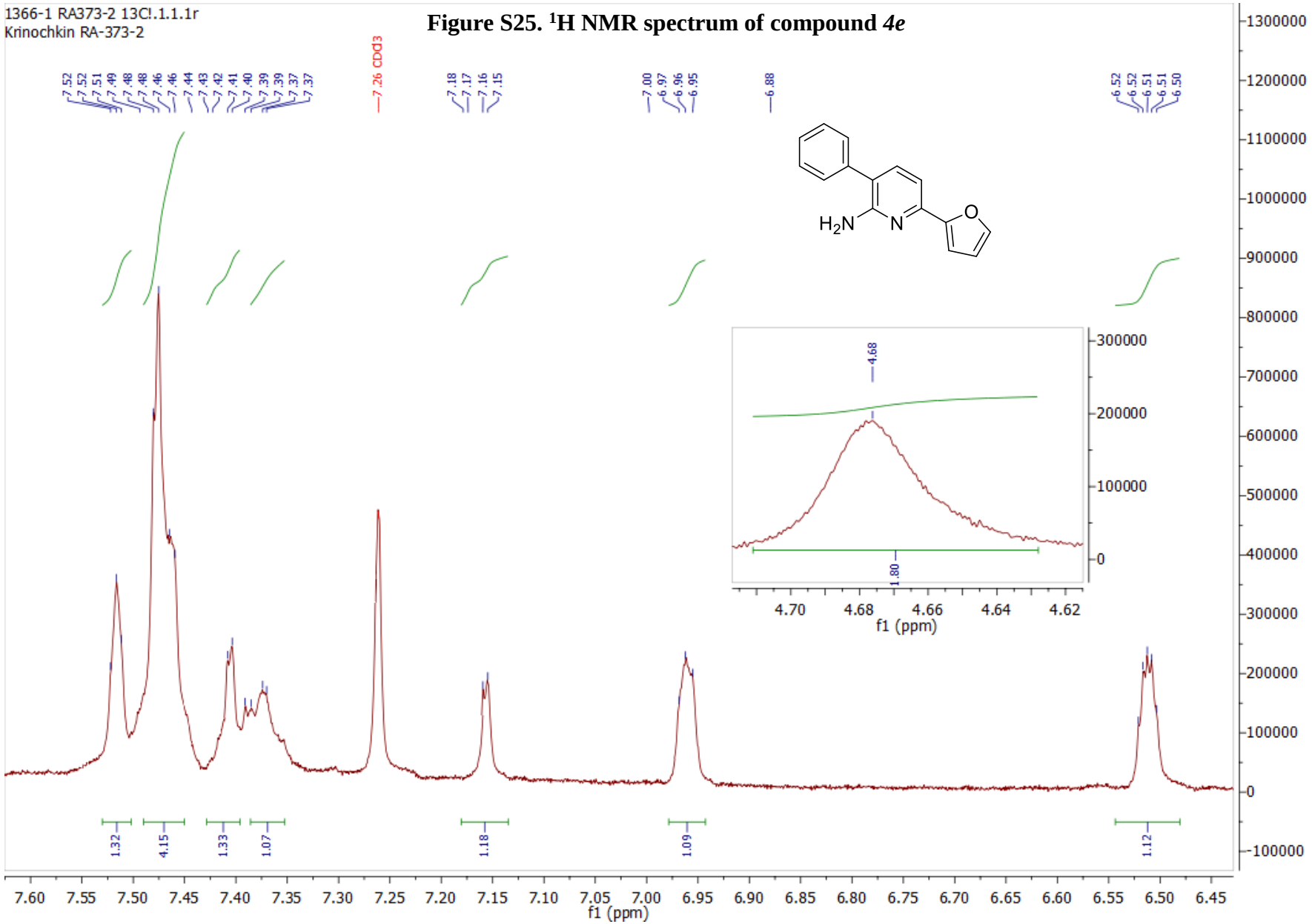

Figure S26. ^{13}C NMR spectrum of compound *4e*

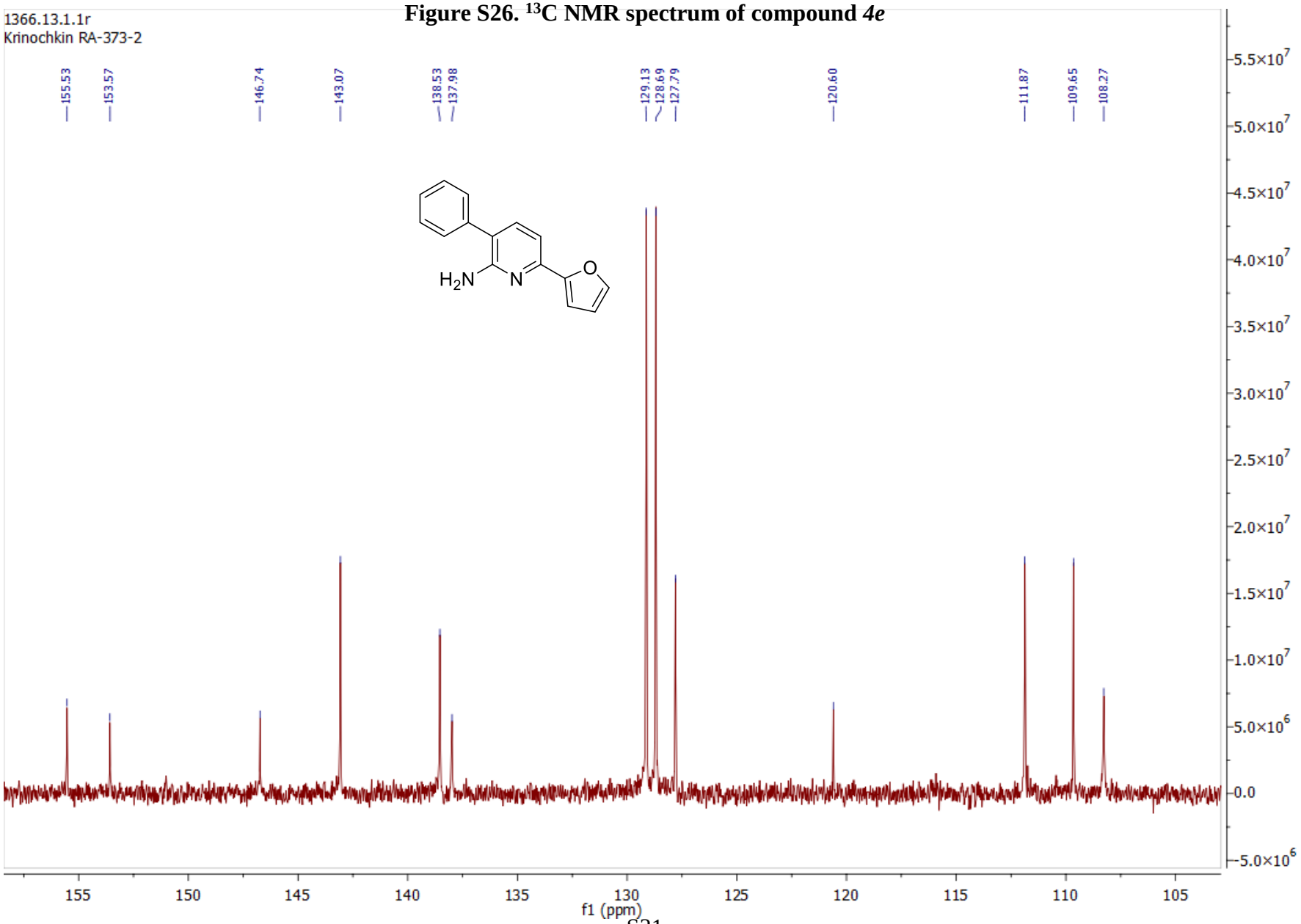

Figure S27. ^{1}H NMR spectrum of compound *4f*

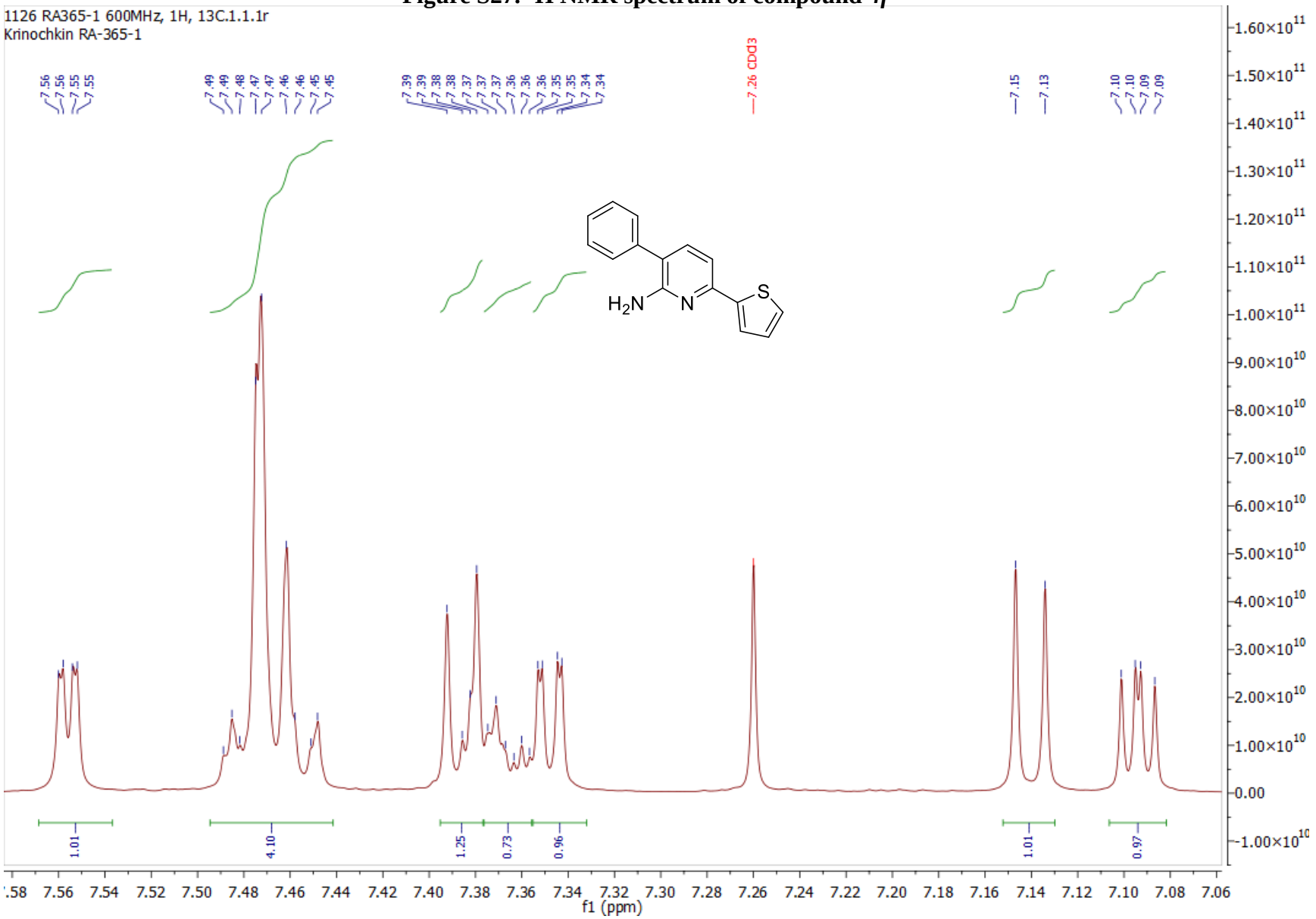

Figure S28. ^{13}C NMR spectrum of compound *4f*

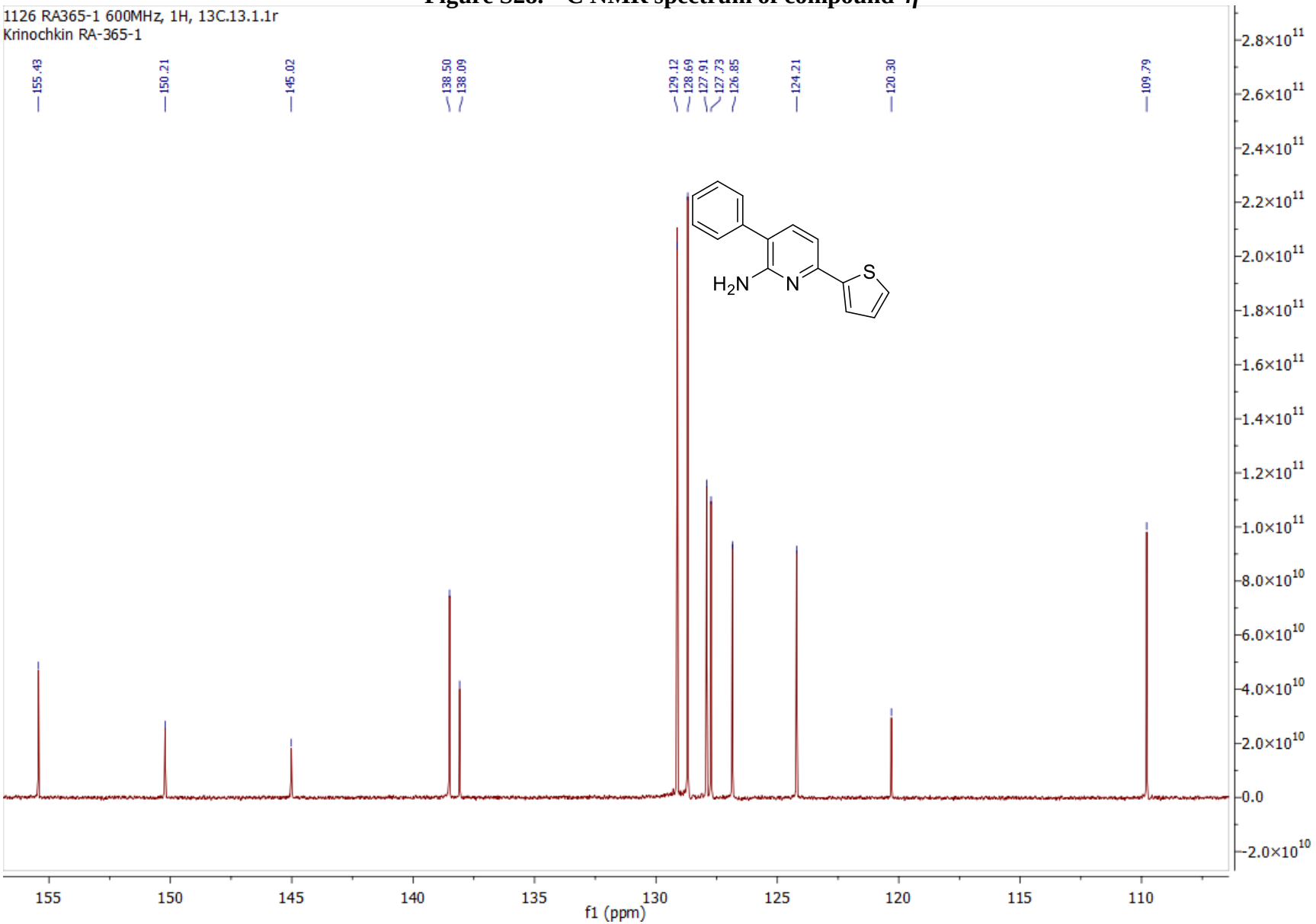

Figure S29. ^{1}H NMR spectrum of compound *4g*

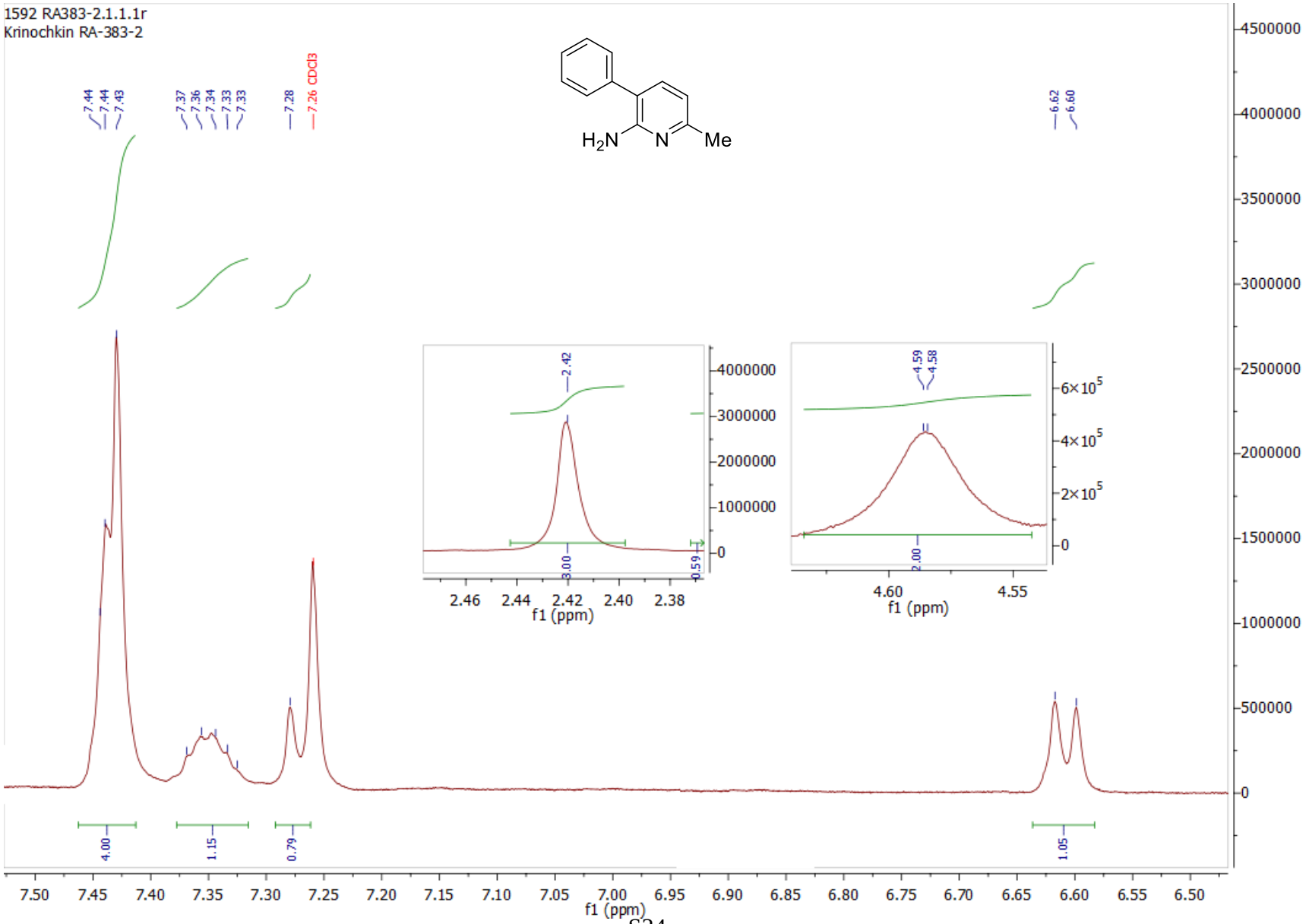

Figure S30. ^{13}C NMR spectrum of compound *4g*

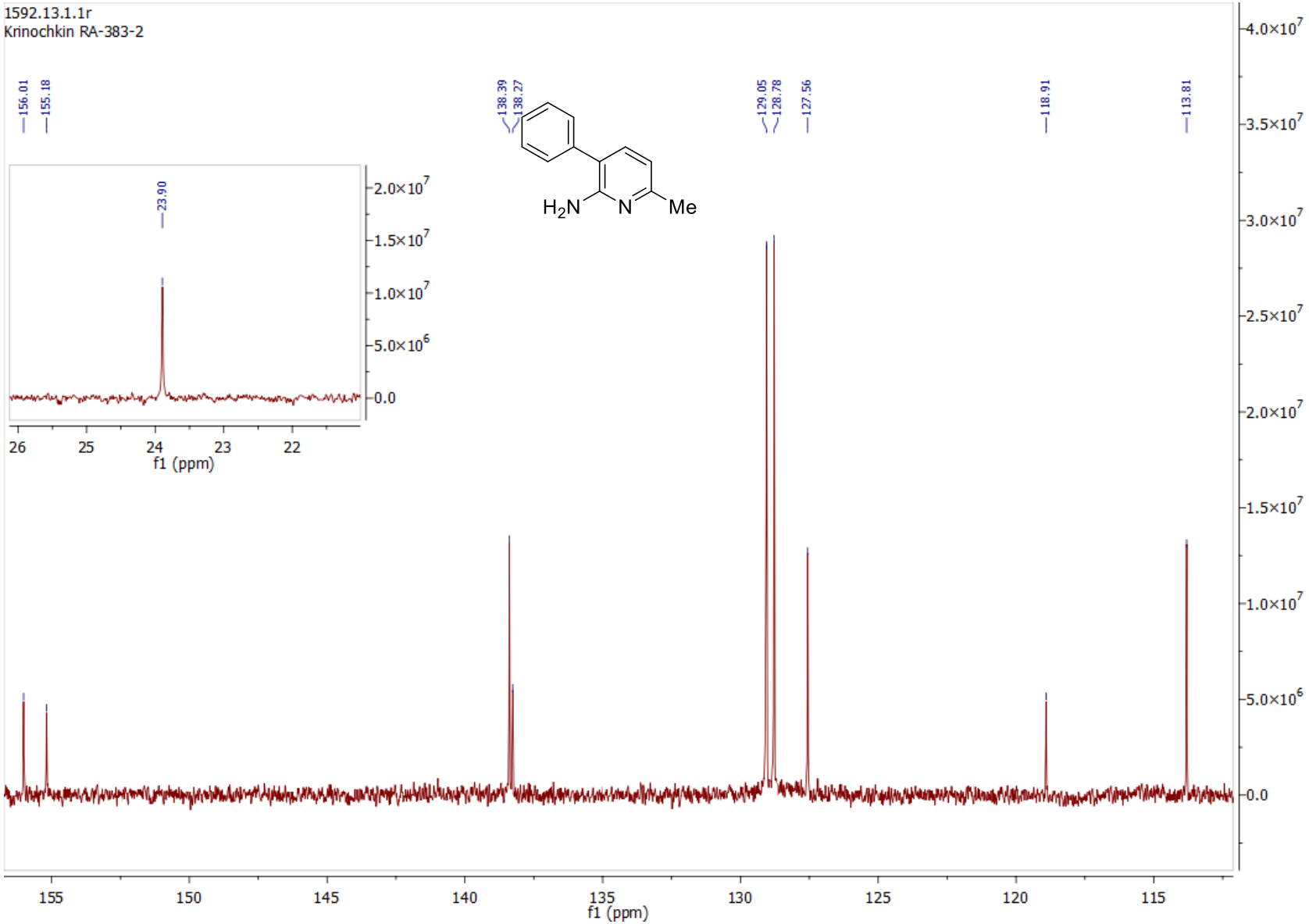

Figure S31. ^{1}H NMR spectrum of compound *4h*

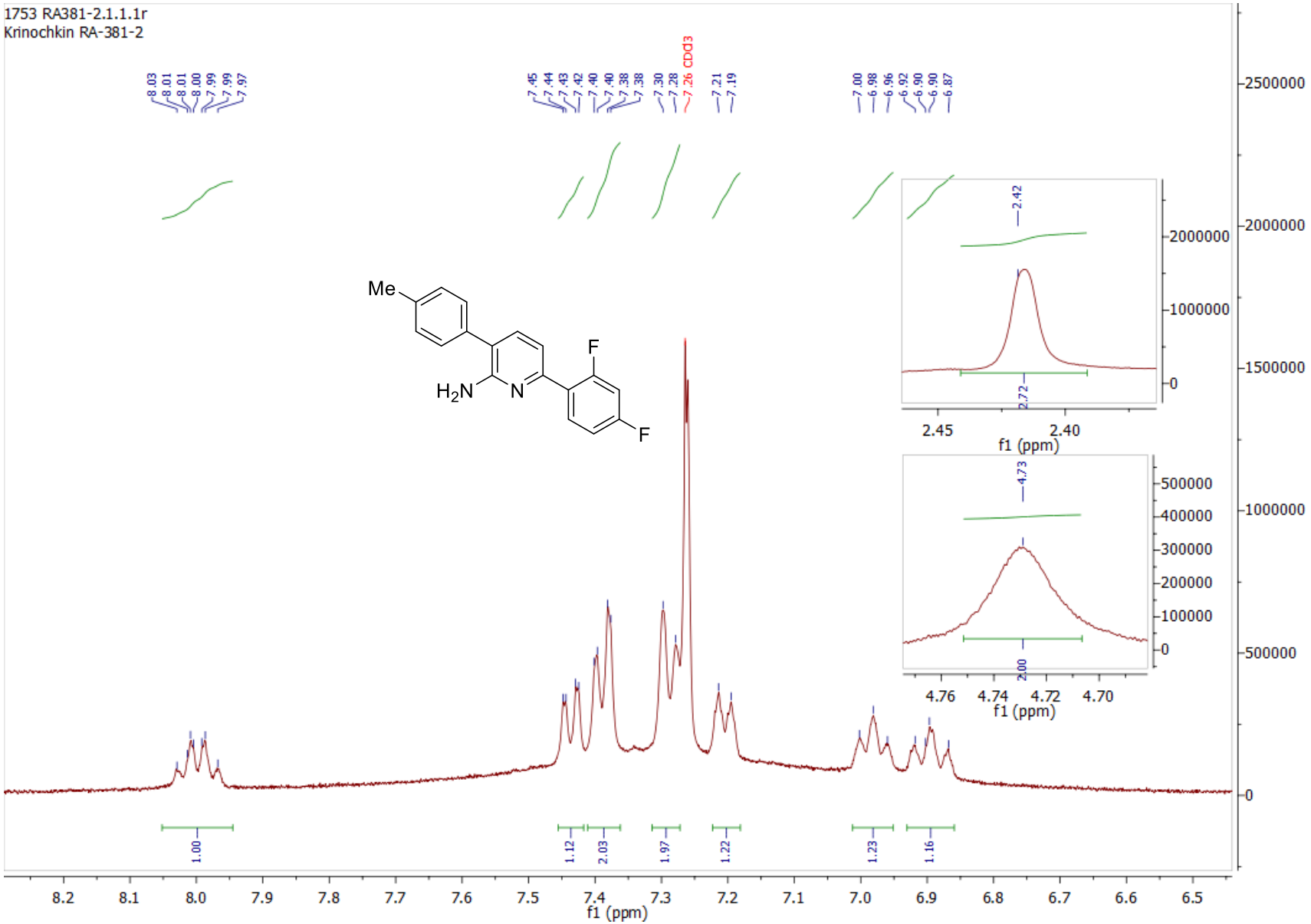

Figure S32. ^{19}F NMR spectrum of compound *4h*

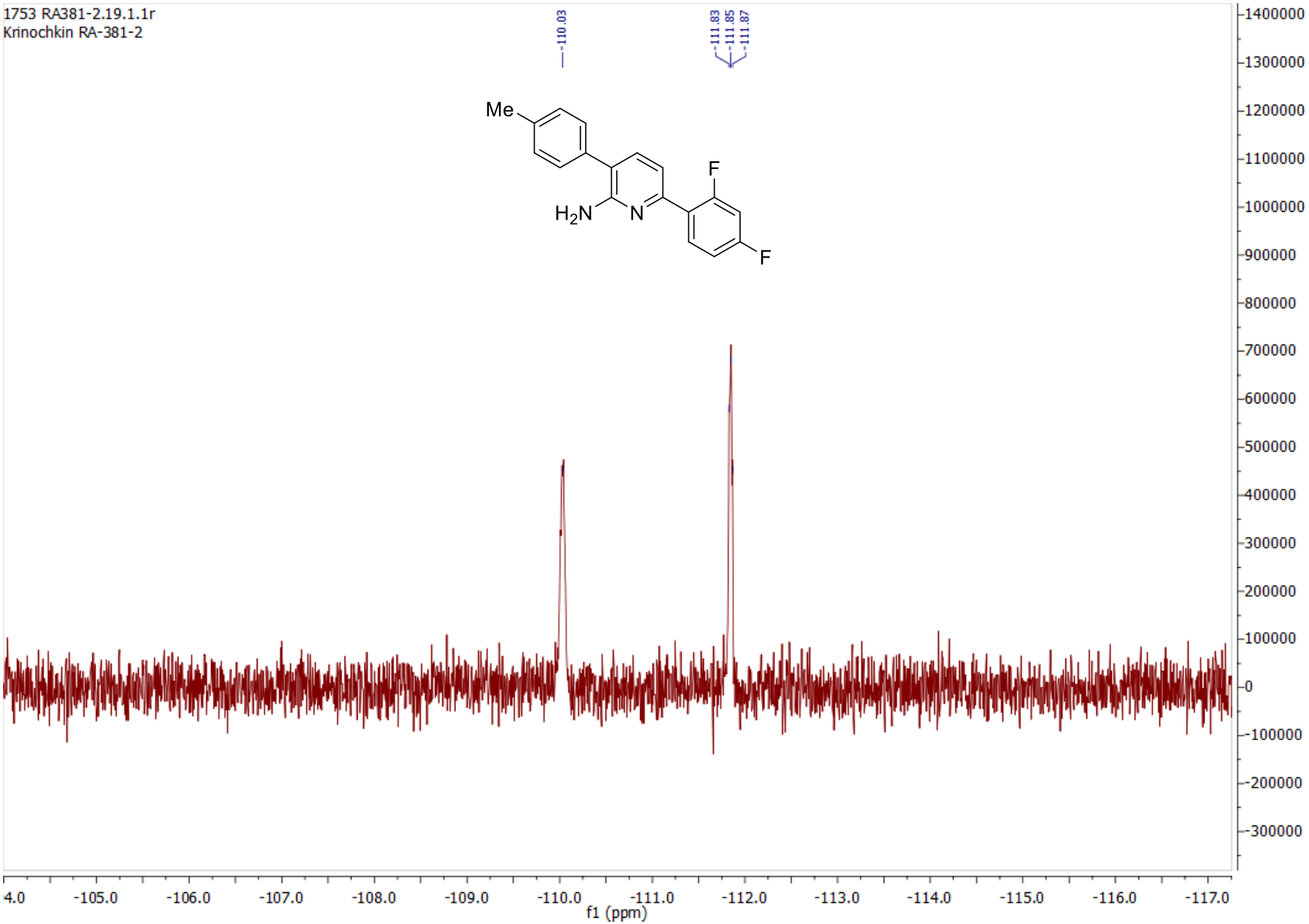

Figure S33. ^{19}H NMR spectrum of compound *4j*

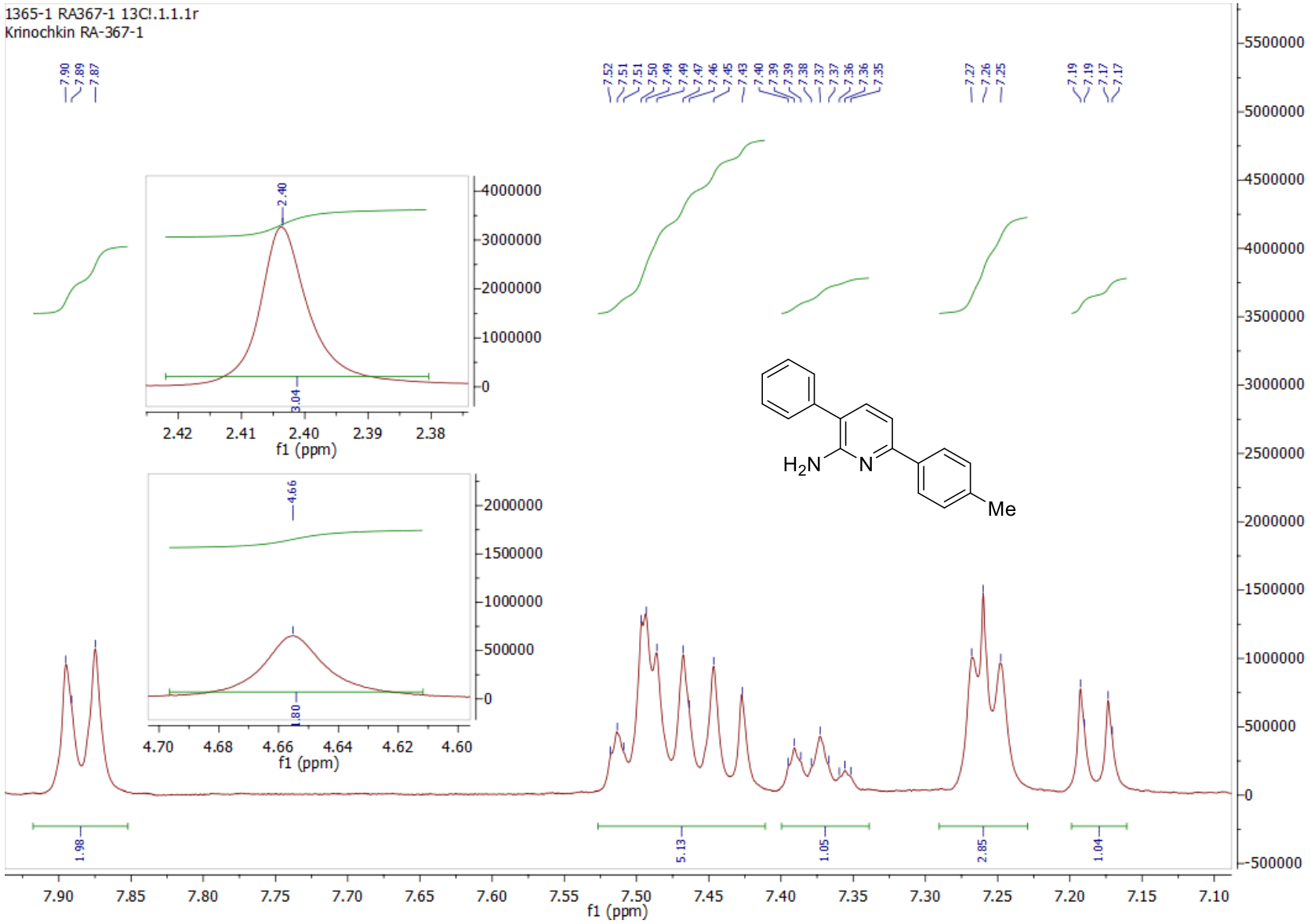

Figure S34. ^{13}C NMR spectrum of compound *4j*