1. General consideration

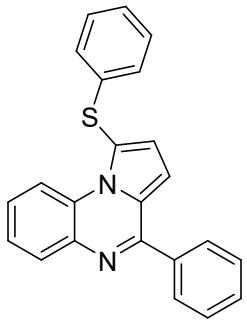
All chemicals were obtained commercially from Sigma-Aldrich, Bidepharm, AK Scientific, Energy Chemicals, and were used without further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm and film thickness = 0.25 μm). The GC yield was calculated using diphenyl ether as internal standard. Gas chromatography – mass spectrometry (GC-MS) analyses were performed using a Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm and film thickness = 0.25 μm). Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded on Bruker AV 500 or 600 spectrometers using residual $CHCl_3$ or TMS as reference. Silica gel (230-400 mesh or 37-63 μm) was obtained from HiMedia and Merck. Thin layer chromatography (TLC) was observed under the wavelengths of 254 nm and 365 nm.

2. General procedure

To an 8-mL reaction tube equipped with a magnetic stir bar was added a 4-substituted pyrrolo[1,2-*a*]quinoxaline derivative (0.1 mmol), a diaryl disulfide derivative (0.05-0.075 mmol), KI (8.3 mg, 0.05 mmol), $CuCl_2$ (4.1 mg, 0.03 mmol), and DMSO (1 mL). The mixture was then stirred at 120 °C for 24 h. After the reaction finished, it was cooled to room temperature, quenched with brine (5 mL), and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography with suitable eluents to obtain the sulfenylation products.

3. Characterization of unknown compounds

4-Phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3aa)



Following the general procedure, using 4-phenylpyrrolo[1,2-*a*]quinoxaline (24.4 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes 2:1) afforded a yellow oil (25.5 mg, 73% yield).

R_f = 0.23 (eluent toluene/hexanes 2:1).

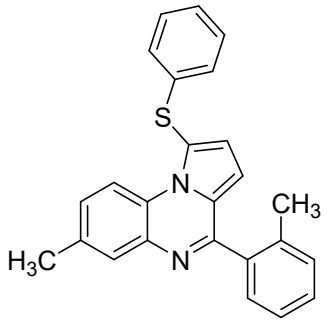
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.45 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.58 – 7.52 (m, 3H), 7.43 (ddd, *J* = 8.0, 7.1, 1.4 Hz, 1H), 7.38 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.16 (d, *J* = 4.1 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.08 – 7.05 (m, 2H), 7.04 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.21, 138.00, 137.45, 137.28, 130.16, 129.87, 129.62, 129.41, 129.27, 128.78, 128.64, 127.37, 126.63, 126.26, 126.11, 125.64, 118.01, 116.42, 108.89.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{17}N_2S^+$: 353.1107; found: 353.1114.

For 5 mmol scale, 1,23 g (70% yield) of the product was obtained after column chromatography.

7-Methyl-1-(phenylthio)-4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline (3ba)



Following the general procedure, using 7-methyl-4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline (27.2 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 30:50:1) afforded a yellow oil (24.5 mg, 65% yield).

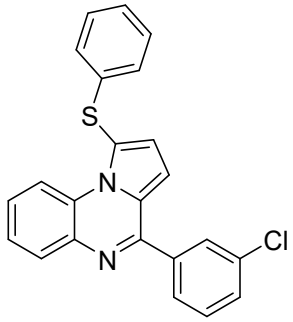
R_f = 0.3 (toluene/hexanes/ethyl acetate 30:50:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.32 (d, *J* = 8.8 Hz, 1H), 7.82 (dd, *J* = 2.2, 1.0 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 (ddd, *J* = 7.6, 1.5, 0.7 Hz, 1H), 7.32 (tdd, *J* = 7.4, 1.5, 0.7 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.13 (ddt, *J* = 7.9, 6.8, 1.2 Hz, 1H), 7.08 (d, *J* = 4.1 Hz, 1H), 7.07 – 7.05 (m, 2H), 6.58 (d, *J* = 4.1 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 155.17, 137.58, 137.10, 136.53, 135.45, 130.77, 130.21, 129.88, 129.38, 129.09, 129.00, 128.63, 127.23, 126.24, 126.20, 126.03, 125.68, 116.12, 108.59, 20.91, 19.73. Two carbon signals could not be located.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{21}N_2S^+$: 381.1420; found: 381.1425.

4-(3-Chlorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ca)



Following the general procedure, using 4-(3-chlorophenyl)pyrrolo[1,2-*a*]quinoxaline (27.9 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes/dichloromethane 200:200:1) afforded a light-yellow oil (22.4 mg, 58% yield).

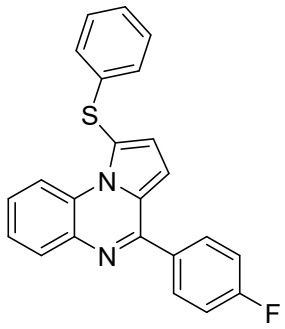
R_f = 0.29 (toluene/hexanes/ethyl acetate 200:200:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.46 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.96 (t, *J* = 1.9 Hz, 1H), 7.85 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 7.24 – 7.21 (m, 2H), 7.18 (d, *J* = 4.1 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.08 – 7.05 (m, 2H), 7.03 (d, *J* = 4.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 152.66, 139.69, 137.25, 137.08, 134.72, 130.23, 129.96, 129.91, 129.44, 129.29, 129.23, 128.92, 127.72, 126.93, 126.71, 126.31, 126.20, 125.77, 116.46, 108.64. One carbon signal could not be located.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}{}^{35}ClN_2S^+$: 387.0717; found: 387.0726.

4-(4-Fluorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3da)



Following the general procedure, using 4-(4-fluorophenyl)pyrrolo[1,2-*a*]quinoxaline (26.2 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent hexanes/toluene/ethyl acetate 70:30:1) afforded a white amorphous solid (19.8 mg, 53% yield).

R_f = 0.23 (hexanes/toluene/ethyl acetate 70:30:1)

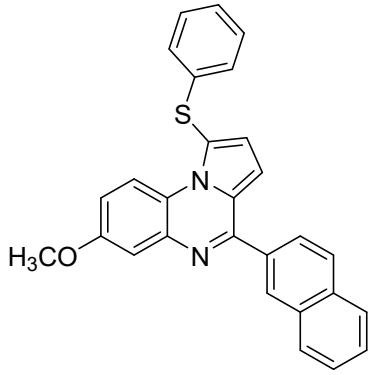
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.45 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.98 – 7.94 (m, 2H), 7.44 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 1H), 7.39 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.26 – 7.21 (m, 4H), 7.17 (d, *J* = 4.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.09 – 7.05 (m, 2H), 7.01 (d, *J* = 4.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.84 (d, *J* = 249.6 Hz), 153.06, 137.34, 137.17, 130.73 (d, *J* = 8.5 Hz), 130.11, 129.42, 129.22, 127.48, 126.66, 126.27, 126.16, 125.71, 116.44, 115.70 (d, *J* = 21.6 Hz), 108.67. Three carbon signals could not be located.

^{19}F NMR (565 MHz, $CDCl_3$, ppm) δ -110.91 – -110.96 (m, 1F).

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}FN_2S^+$: 371.1013; found: 371.1018.

7-Methoxy-4-(naphthalen-2-yl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ea)



Following the general procedure, using 7-methoxy-4-(naphthalen-2-yl)pyrrolo[1,2-*a*]quinoxaline (32.4 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 30:30:1) afforded a yellow oil (28.8 mg, 67% yield).

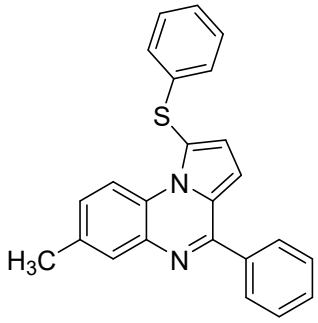
R_f = 0.31 (toluene/hexanes/ethyl acetate 20:20:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.39 (d, *J* = 9.4 Hz, 1H), 8.46 (dd, *J* = 1.7, 0.8 Hz, 1H), 8.06 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.02 (dt, *J* = 8.3, 0.7 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.95 – 7.92 (m, 1H), 7.60 – 7.54 (m, 2H), 7.54 (d, *J* = 3.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.15 (d, *J* = 4.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.09 (d, *J* = 4.2 Hz, 1H), 7.07 – 7.05 (m, 2H), 7.01 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 154.49, 138.83, 137.50, 135.44, 133.15, 129.41, 129.39, 128.72, 128.58, 128.43, 127.83, 126.99, 126.52, 126.20, 126.15, 126.10, 126.07, 123.57, 117.49, 117.27, 116.41, 111.31, 108.66, 55.63. Two carbon signals could not be located.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{21}N_2OS^+$: 433.1369; found: 433.1378.

7-Methyl-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3fa)



Following the general procedure, using 7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline (25.8 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by

column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 50:50:1) afforded a light-yellow solid (27.8 mg, 76 % yield).

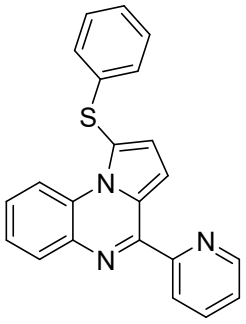
R_f = 0.29 (toluene/hexane/ethyl acetate 30:30:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.32 (d, *J* = 8.7 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.84 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.24 – 7.18 (m, 3H), 7.15 – 7.10 (m, 2H), 7.06 – 7.03 (m, 2H), 7.02 (d, *J* = 4.2 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 154.13, 138.14, 137.64, 137.32, 135.46, 129.95, 129.78, 129.52, 129.37, 128.77, 128.61, 128.58, 127.10, 126.35, 126.13, 126.00, 117.41, 116.09, 108.61, 20.90.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{19}N_2S^+$: 367.1263; found: 367.1265.

1-(Phenylthio)-4-(pyridin-2-yl)pyrrolo[1,2-*a*]quinoxaline (3ga)



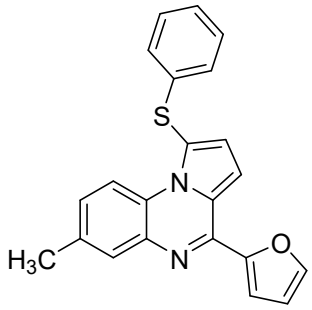
Following the general procedure, using 4-(pyridin-2-yl)pyrrolo[1,2-*a*]quinoxaline (24.5 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 20:10:1) afforded a yellow solid (21.7 mg, 61% yield).

R_f = 0.20 (ethyl acetate/hexanes 1:15).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.50 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.82 – 8.80 (m, 1H), 8.38 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.06 – 8.03 (m, 1H), 7.92 (td, *J* = 7.7, 1.8 Hz, 1H), 7.83 (d, *J* = 4.2 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.24 (d, *J* = 4.2 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.11 (ddt, *J* = 7.9, 6.8, 1.2 Hz, 1H), 7.06 – 7.03 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 156.33, 150.94, 148.84, 137.61, 136.90, 136.83, 130.37, 129.75, 129.35, 129.01, 127.91, 127.32, 126.10, 125.98, 125.50, 124.37, 123.78, 117.46, 116.46, 110.44.

4-(Furan-2-yl)-7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ha)



Following the general procedure, using 4-(furan-2-yl)-7-methylpyrrolo[1,2-*a*]quinoxaline (24.8 mg, 0.1 mmol) and diphenyl disulfide (16.4 mg, 0.075 mmol). Purification by column chromatography on silica gel (eluent ethyl acetate/hexanes 1:50) afforded a brown solid (22.2 mg, 63% yield).

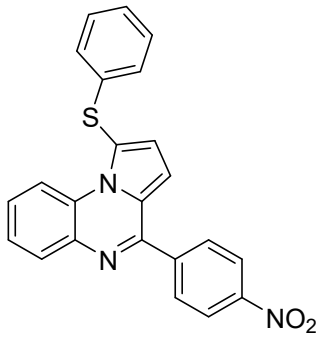
R_f = 0.22 (ethyl acetate/hexanes 1:50).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.31 (d, *J* = 8.7 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.72 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.56 (d, *J* = 4.2 Hz, 1H), 7.39 (d, *J* = 3.5 Hz, 1H), 7.22 – 7.15 (m, 4H), 7.12 – 7.08 (m, 1H), 7.03 – 7.00 (m, 2H), 6.65 (dd, *J* = 3.5, 1.7 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 152.17, 144.42, 143.09, 137.63, 136.86, 135.49, 129.65, 129.35, 128.51, 127.36, 127.01, 126.70, 126.07, 125.98, 117.28, 116.05, 112.86, 112.03, 108.30, 20.86.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{17}N_2OS^+$: 357.1056; found: 357.1055.

4-(4-Nitrophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ia)



Following the general procedure, using 4-(4-nitrophenyl)pyrrolo[1,2-*a*]quinoxaline (28.9 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol),. Purification by column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 10:20:1) afforded a yellow oil (18.1 mg, 46% yield).

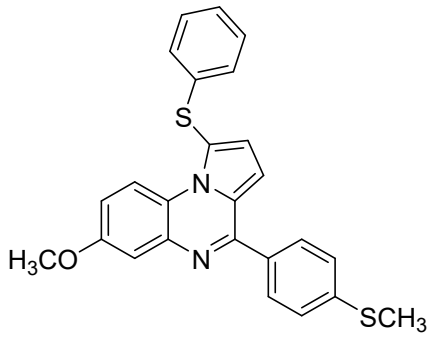
R_f = 0.37 (toluene/hexanes/ethyl acetate 20:20:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.50 – 9.46 (m, 1H), 8.44 – 8.40 (m, 2H), 8.18 – 8.13 (m, 2H), 8.06 – 8.01 (m, 1H), 7.50 – 7.42 (m, 2H), 7.26 – 7.21 (m, 2H), 7.20 (d, *J* = 4.2 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.08 (dt, *J* = 7.9, 1.1 Hz, 2H), 7.00 (d, *J* = 4.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 151.70, 148.67, 144.05, 137.02, 136.98, 130.42, 129.84, 129.48, 129.31, 128.90, 128.23, 126.79, 126.44, 126.34, 125.96, 123.88, 119.04, 116.57, 108.32.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}N_3O_2S^+$: 398.0958; found: 398.0959.

7-Methoxy-4-(4-(methylthio)phenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ja)



Following the general procedure, using 7-methoxy-4-(4-(methylthio)phenyl) pyrrolo[1,2-*a*]quinoxaline (32.0 mg, 0.1 mmol) and phenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes/ethyl acetate 15:15:1) afforded a yellow solid (25.1 mg, 59% yield).

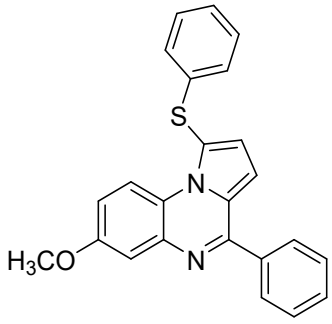
R_f = 0.26 (toluene/hexanes/ethyl acetate 15:15:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.35 (d, *J* = 9.4 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.48 (d, *J* = 3.0 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.10 (m, 2H), 7.05 – 7.01 (m, 3H), 6.98 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.88 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 157.13, 153.89, 141.09, 138.74, 137.48, 134.65, 129.39, 129.14, 129.12, 126.18, 126.13, 126.11, 126.05, 123.50, 117.44, 117.21, 116.26, 111.23, 108.40, 55.61, 15.54.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{21}N_2OS_2^+$: 429.1090; found: 429.1097.

7-Methoxy-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ka)



Following the general procedure, using 7-methoxy-4-phenylpyrrolo[1,2-*a*]quinoxaline (27.4 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent toluene/hexanes 5:1) afforded a yellow oil (18.3 mg, 48% yield).

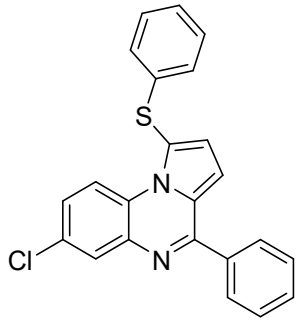
R_f = 0.26 (toluene/hexanes/ethyl acetate 20:10:1)

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.36 (d, *J* = 9.4 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.58 – 7.51 (m, 3H), 7.50 (d, *J* = 3.0 Hz, 1H), 7.21 (ddt, *J* = 8.6, 7.5, 1.7 Hz, 2H), 7.14 – 7.10 (m, 2H), 7.06 – 7.03 (m, 2H), 7.01 (d, *J* = 4.2 Hz, 1H), 6.99 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 157.14, 154.57, 138.74, 138.07, 137.49, 129.83, 129.39, 129.25, 128.76, 128.63, 126.16, 126.09, 126.05, 123.57, 117.45, 117.26, 116.33, 111.35, 108.60, 55.60.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{19}N_2OS^+$: 383.1213; found: 383.1215.

7-Chloro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3la)



Following the general procedure, using 7-chloro-4-phenylpyrrolo[1,2-*a*]quinoxaline (27.9 mg, 0.1 mmol) and diphenyl disulfide (16.2 mg, 0.075 mmol). Purification by column chromatography on silica gel (hexanes/toluene/ethyl acetate 50:10:1) afforded a yellow oil (18.7 mg, 47% yield).

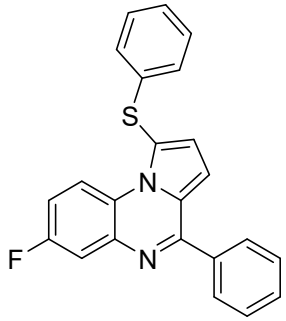
R_f = 0.34 (hexanes/toluene/ethyl acetate 50:10:1)

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.39 (d, *J* = 9.2 Hz, 1H), 8.01 (d, *J* = 2.5 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.58 – 7.52 (m, 3H), 7.32 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.17 (d, *J* = 4.2 Hz, 1H), 7.14 (tt, *J* = 4.5, 1.2 Hz, 1H), 7.06 (d, *J* = 4.2 Hz, 1H), 7.05 – 7.02 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 155.26, 138.44, 137.67, 136.86, 130.83, 130.15, 129.52, 129.42, 129.36, 128.78, 128.69, 127.77, 127.24, 126.80, 126.34, 126.27, 118.45, 117.61, 109.39.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}{}^{35}ClN_2S^+$: 387.0717; found: 387.0725.

7-Fluoro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline (3ma)



Following the general procedure, using 7-fluoro-4-phenylpyrrolo[1,2-*a*]quinoxaline (26.2 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (ethyl acetate/hexanes 1:35) afforded a yellow oil (13.9 mg, 41% yield).

R_f = 0.23 (ethyl acetate/hexanes 1:50).

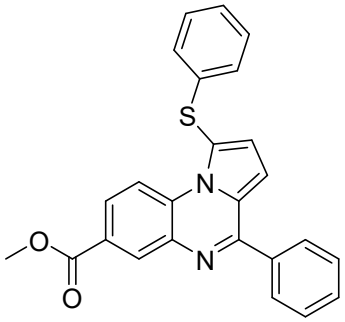
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.43 (dd, *J* = 9.4, 5.3 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.70 (dd, *J* = 9.3, 3.0 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.24 – 7.21 (m, 2H), 7.16 (d, *J* = 4.2 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.06 – 7.03 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 159.80 (d, *J* = 245.6 Hz), 155.33, 138.9 (d, *J* = 11.5 Hz), 137.71, 136.97, 130.11, 129.49, 129.33, 128.78, 128.68, 126.51, 126.28, 126.23, 125.84, 118.16, 117.85 (d, *J* = 8.7 Hz), 115.19 (d, *J* = 22.2 Hz), 114.92 (d, *J* = 23.5 Hz), 109.23.

^{19}F NMR (565 MHz, $CDCl_3$, ppm) δ -115.98 – -116.02 (m, 1F).

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}FN_2S^+$: 371.1013; found: 371.1018.

Methyl 4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline-7-carboxylate (3na)



Following the general procedure, using methyl 4-phenylpyrrolo[1,2-*a*]quinoxaline-7-carboxylate (30.2 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent ethyl acetate/hexanes 1:35) afforded a yellow oil (13.9 mg, 34% yield).

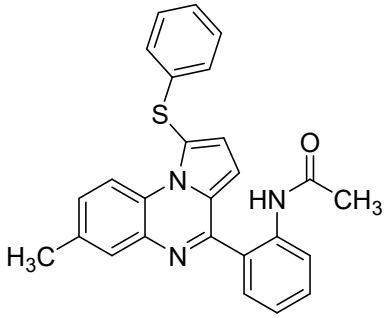
R_f = 0.26 (ethyl acetate/hexanes/toluene 1:10:40).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.50 (d, *J* = 8.9 Hz, 1H), 8.72 (d, *J* = 2.1 Hz, 1H), 8.03 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.60 – 7.53 (m, 3H), 7.25 – 7.21 (m, 3H), 7.16 – 7.12 (m, 1H), 7.09 (d, *J* = 4.1 Hz, 1H), 7.08 – 7.05 (m, 2H), 3.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 166.35, 154.99, 137.60, 136.90, 136.72, 132.17, 131.92, 130.16, 129.69, 129.52, 128.77, 128.70, 127.96, 127.33, 127.20, 126.44, 126.42, 119.10, 116.45, 109.60, 52.27.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{19}N_2O_2S^+$: 411.1162; found: 411.1170.

_N_-(2-(7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl)acetamide (3oa)



Following the general procedure, using methyl *N*-(2-(7-methylpyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl)acetamide (31.5 mg, 0.1 mmol) and phenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent ethyl acetate/dichloromethane/toluene 1:2:8) afforded a yellow solid (26.6 mg, 64% yield).

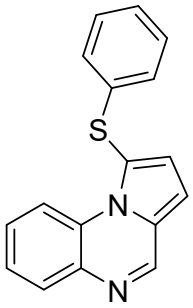
R_f = 0.23 (ethyl acetate/dichloromethane/toluene 1:2:8)

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 10.66 (s, 1H), 9.34 (d, *J* = 8.7 Hz, 1H), 8.50 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.71 (dd, 1H), 7.50 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.28 – 7.20 (m, 4H), 7.17 – 7.13 (m, 2H), 7.10 – 7.07 (m, 2H), 7.04 (d, *J* = 4.2 Hz, 1H), 2.47 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 168.31, 152.86, 137.16, 137.13, 135.99, 135.90, 130.68, 129.90, 129.47, 129.46, 129.15, 128.90, 126.93, 126.49, 126.44, 126.27, 123.02, 122.46, 118.63, 116.48, 109.97, 25.08, 20.93.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{22}N_3OS^+$: 424.1478; found: 424.1483.

1-(Phenylthio)pyrrolo[1,2-*a*]quinoxaline (3pa)



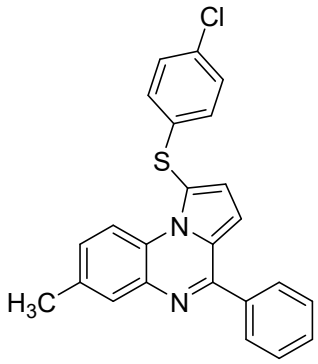
Following the general procedure, using pyrrolo[1,2-*a*]quinoxaline (16.8 mg, 0.1 mmol) and diphenyl disulfide (10.9 mg, 0.05 mmol). Purification by column chromatography on silica gel (ethyl acetate/hexanes 1:7) afforded a light-yellow solid (5.9 mg, 20% yield).

R_f = 0.23 (ethyl acetate/hexanes 1:7).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.41 – 9.38 (m, 1H), 8.82 (s, 1H), 7.95 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.23 – 7.18 (m, 2H), 7.16 (d, *J* = 4.1 Hz, 1H), 7.11 (ddt, *J* = 7.9, 6.8, 1.2 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.97 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.44, 137.34, 137.12, 130.48, 130.13, 130.04, 129.39, 127.71, 126.59, 126.19, 126.11, 125.56, 117.60, 116.59, 107.41.

1-((4-Chlorophenyl)thio)-7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline (3qb)



Following the general procedure, using 7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline (25.8 mg, 0.1 mmol) and bis(4-chlorophenyl) disulfide (21.5 mg, 0.075 mmol). Purification by column chromatography on silica gel (hexanes/toluene/ethyl acetate 50:10:1) afforded a yellow solid (26.0 mg, 66% yield).

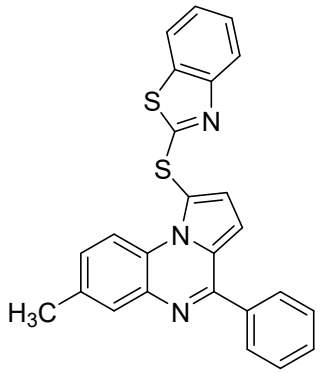
R_f = 0.23 (hexanes/toluene/ethyl acetate 50:10:1).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.26 (d, *J* = 8.7 Hz, 1H), 7.94 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.86 – 7.83 (m, 1H), 7.57 – 7.53 (m, 3H), 7.21 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 4.2 Hz, 1H), 7.02 (d, *J* = 4.2 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 154.14, 138.04, 137.31, 136.23, 135.63, 131.98, 130.09, 129.84, 129.67, 129.51, 128.75, 128.70, 128.63, 127.34, 126.98, 126.48, 116.67, 115.83, 108.67, 20.91.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{18}{}^{35}ClN_2S^+$: 401.0874; found: 401.0875.

2-((7-Methyl-4-phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)benzo[*d*]thiazole (3qc)



Following the general procedure, using 7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline (25.8 mg, 0.1 mmol) and 2,2'-dithiobis(benzothiazole) (24.9 mg, 0.075 mmol). Purification by column chromatography on silica gel (eluent hexanes/toluene/ethyl acetate 30:5:1) afforded a light yellow oil (25.1 mg, 60% yield).

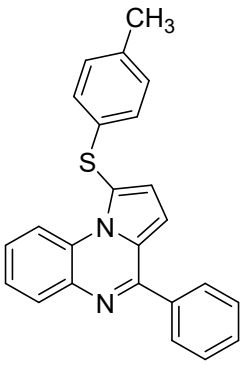
R_f = 0.34 (ethyl acetate/hexanes 1:15).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.30 (d, *J* = 8.8 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.90 (ddd, *J* = 8.3, 1.2, 0.6 Hz, 1H), 7.87 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.40 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.31 (d, *J* = 4.2 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.09 (d, *J* = 4.2 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 170.02, 154.39, 154.08, 137.88, 137.35, 136.03, 135.70, 130.38, 130.34, 129.97, 129.27, 128.82, 128.68, 127.42, 126.81, 126.27, 124.48, 122.15, 121.01, 115.61, 114.10, 108.92, 20.89.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{18}N_3S_2^+$: 424.0937, found: 424.0943.

4-Phenyl-1-(*p*-tolylthio)pyrrolo[1,2-*a*]quinoxaline (3ad)



Following the general procedure, using methyl 4-phenylpyrrolo[1,2-*a*]quinoxaline (24.4 mg, 0.1 mmol) and *p*-tolyl disulfide (12.3 mg, 0.05 mmol). Purification by column chromatography on silica gel (hexanes/toluene = 1:1) afforded a light-yellow solid (26.8 mg, 73% yield).

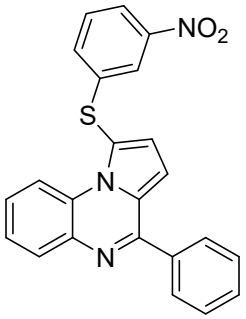
R_f = 0.23 (hexanes/toluene 1:2).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.48 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.58 – 7.52 (m, 3H), 7.46 – 7.38 (m, 2H), 7.13 (d, *J* = 4.2 Hz, 1H), 7.06 – 6.99 (m, 5H), 2.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.19, 137.96, 137.21, 136.23, 133.57, 130.19, 130.05, 129.87, 129.43, 129.29, 128.78, 128.64, 127.31, 126.79, 126.23, 125.59, 116.53, 108.92, 20.93. One carbon signal could not be located.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{19}N_2S^+$: 367.1263; found: 367.1271.

1-((3-Nitrophenyl)thio)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3ae)



Following the general procedure, using methyl 4-phenylpyrrolo[1,2-*a*]quinoxaline (24.4 mg, 0.1 mmol) and 3-nitrophenyl disulfide (15.4 mg, 0.05 mmol). Purification by column chromatography on silica gel (eluent ethyl acetate/hexanes 1:35) afforded a yellow solid (24.1 mg, 61% yield).

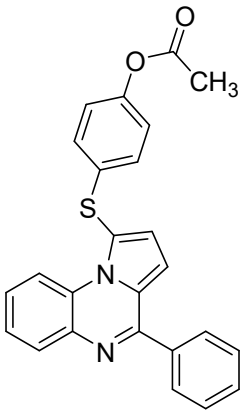
R_f = 0.23 (ethyl acetate/hexanes 1:35).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.36 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.99 – 7.94 (m, 4H), 7.60 – 7.54 (m, 3H), 7.46 (ddd, *J* = 8.1, 7.2, 1.3 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.27 – 7.22 (m, 2H), 7.09 (d, *J* = 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.30, 148.95, 140.73, 137.76, 137.34, 131.43, 130.59, 130.21, 130.18, 130.03, 129.07, 128.78, 128.71, 127.68, 127.47, 125.97, 120.94, 120.62, 115.73, 115.22, 109.18.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{16}N_3O_2S^+$: 398.0958; found: 398.0964.

4-((4-Phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)phenyl acetate (3af)



Following the general procedure, using methyl 4-phenylpyrrolo[1,2-*a*]quinoxaline (24.4 mg, 0.1 mmol) and disulfanediylbis(4,1-phenylene)diacetate (16.7 mg, 0.05 mmol). Purification by column chromatography on silica gel ethyl acetate/hexanes 1:10) afforded a yellow liquid (7.5 mg, 18% yield).

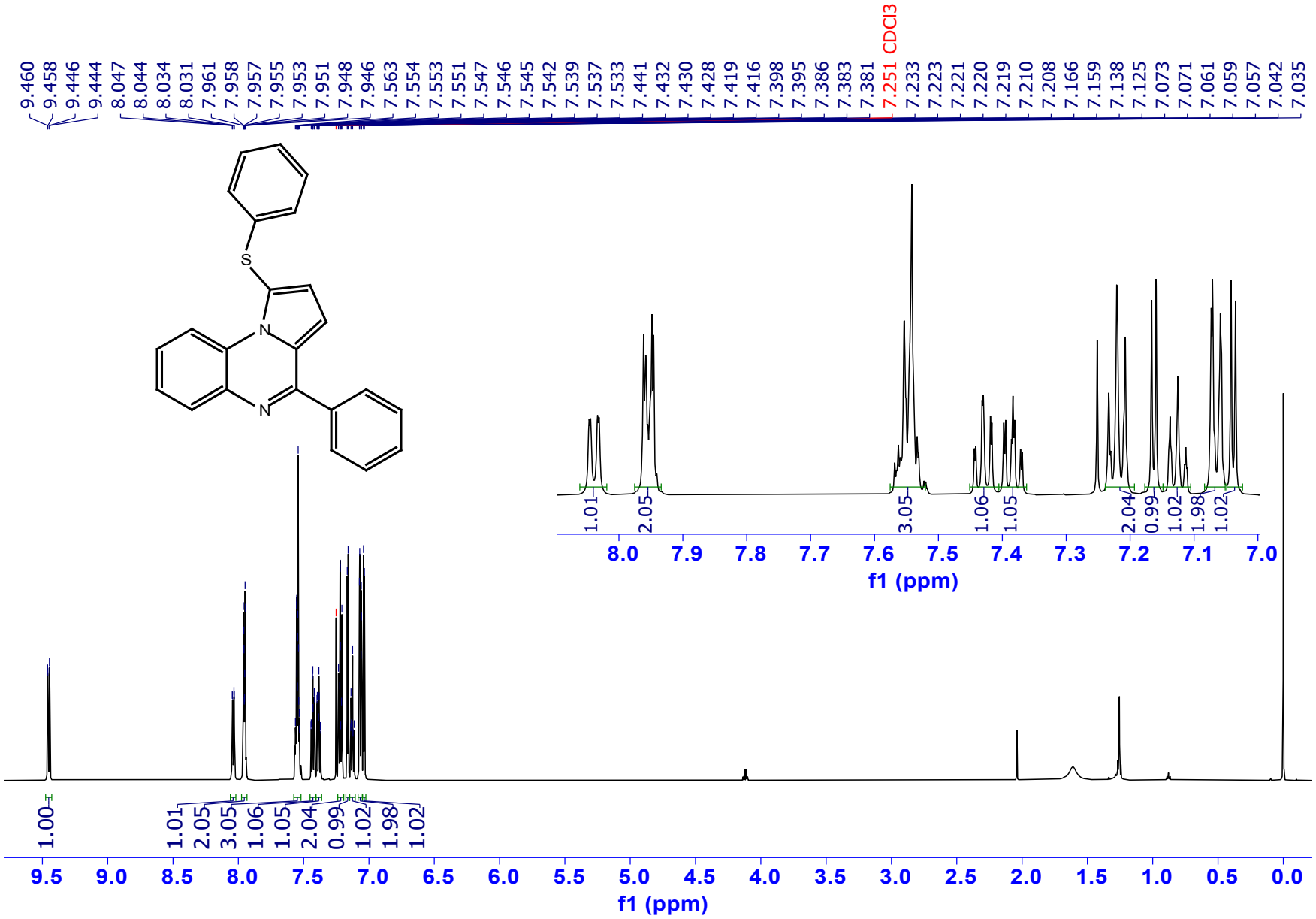
R_f = 0.26 (ethyl acetate/hexanes 1:10).

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.46 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.58 – 7.51 (m, 3H), 7.48 – 7.39 (m, 2H), 7.15 (dd, *J* = 4.2, 0.6 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.03 (dd, *J* = 4.2, 0.6 Hz, 1H), 6.99 – 6.94 (m, 2H), 2.24 (s, 3H).

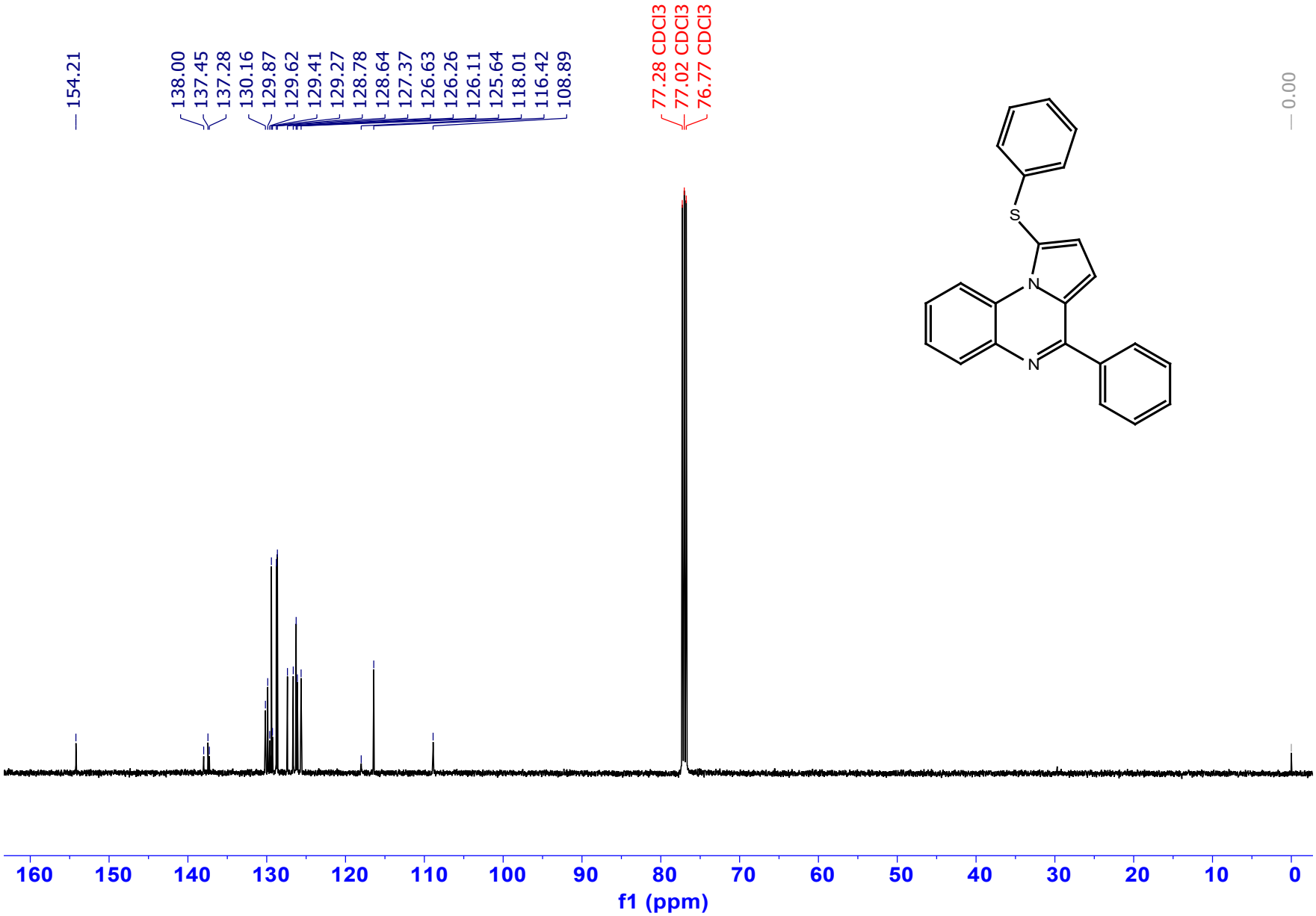
^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 169.24, 154.20, 149.17, 137.91, 137.24, 134.59, 130.22, 129.90, 129.64, 129.22, 128.77, 128.65, 127.50, 127.46, 126.62, 125.74, 122.63, 118.02, 116.30, 108.98, 21.06.

HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{19}N_2O_2S^+$: 411.1162; found: 411.1172.

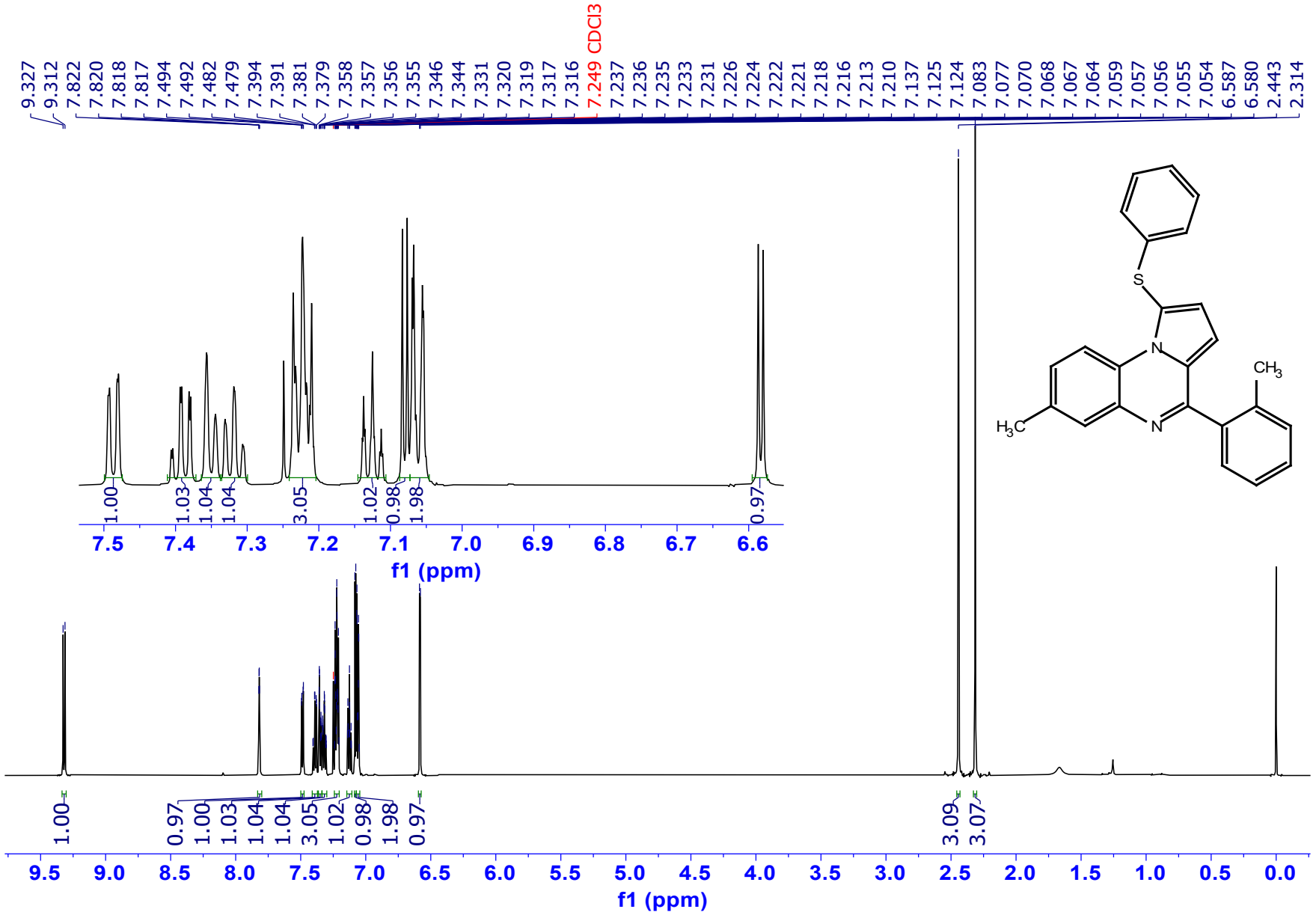
4. Copies of NMR spectra



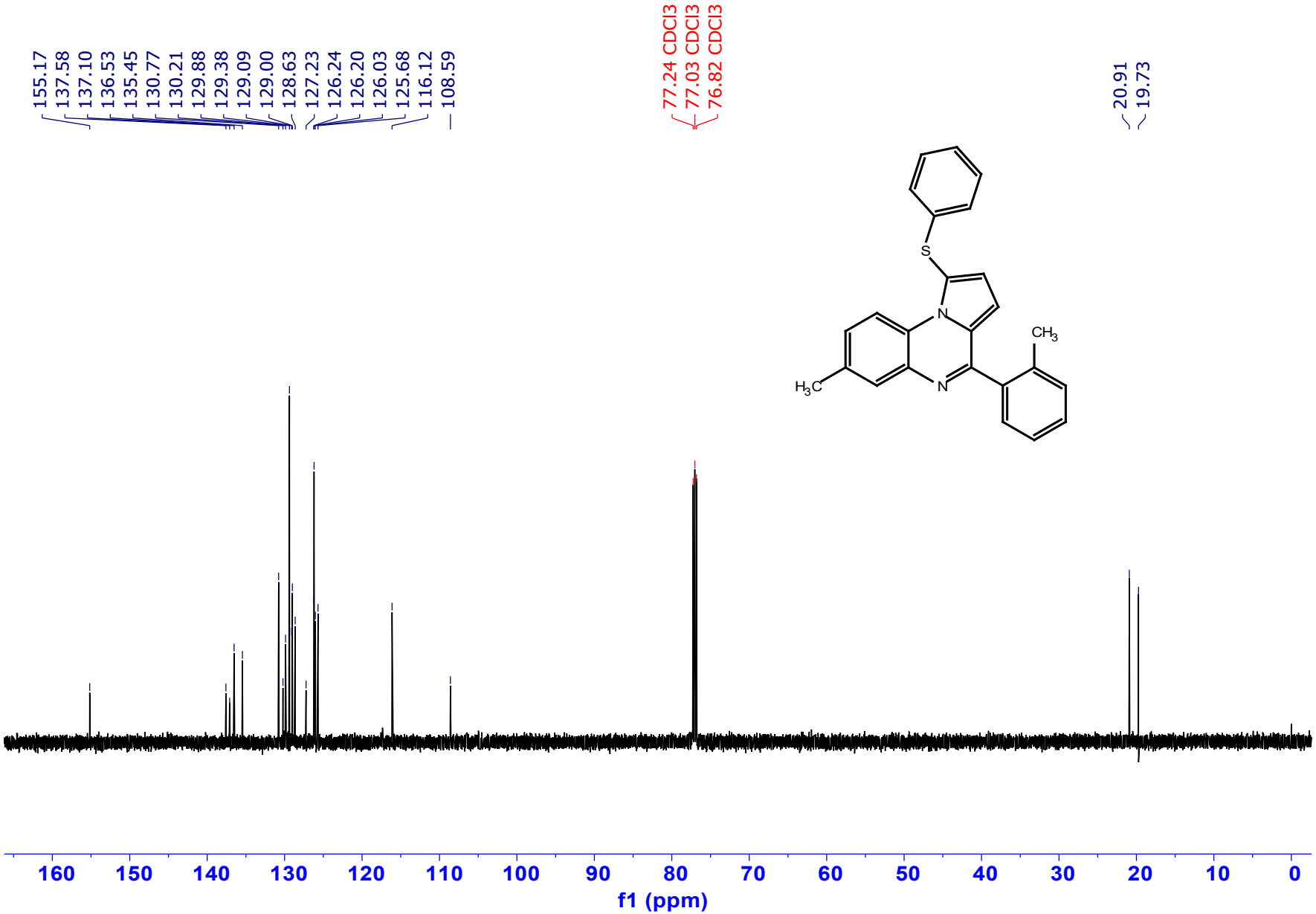
^{1}H NMR spectrum of 4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



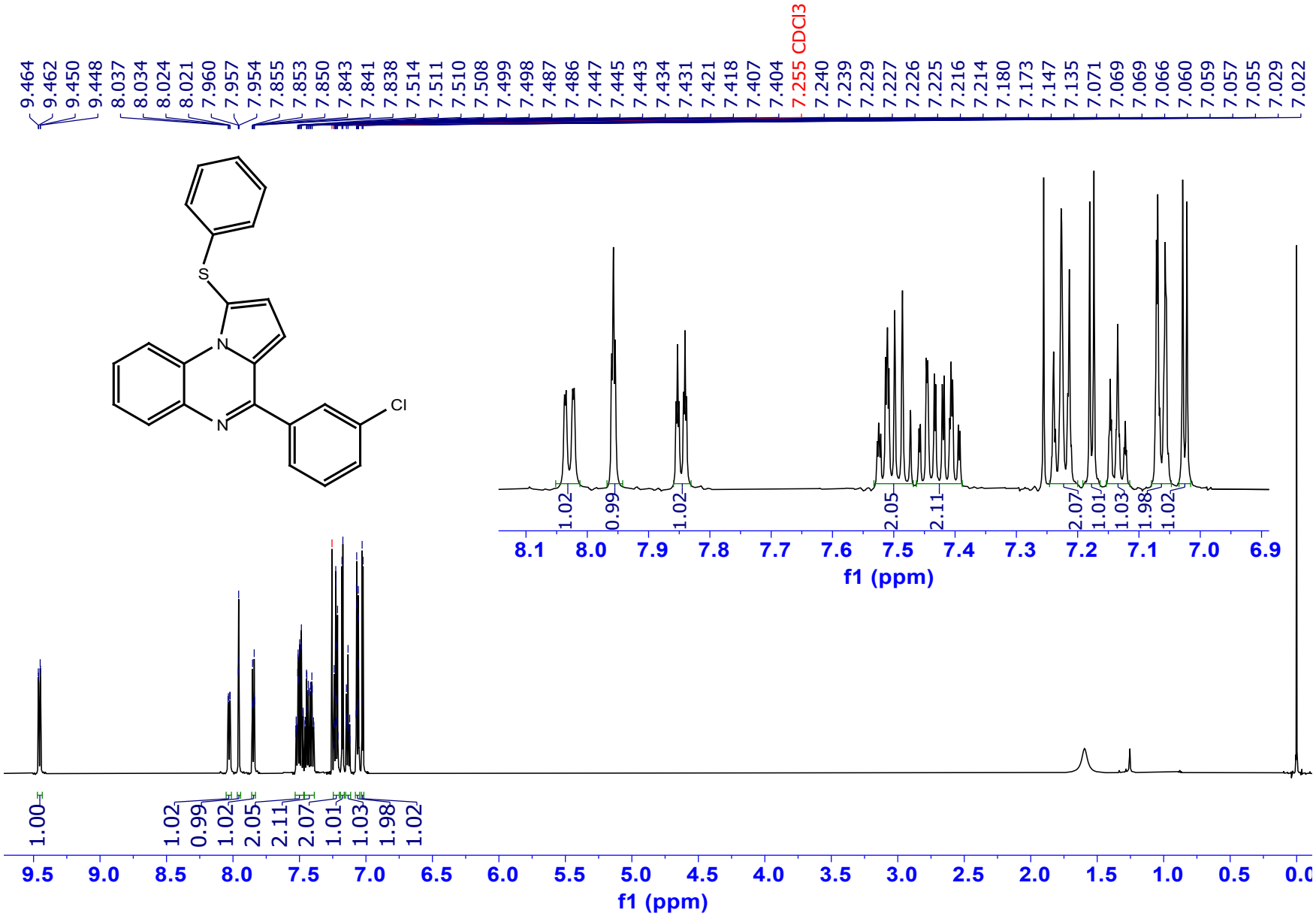
^{13}C NMR spectrum of 4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



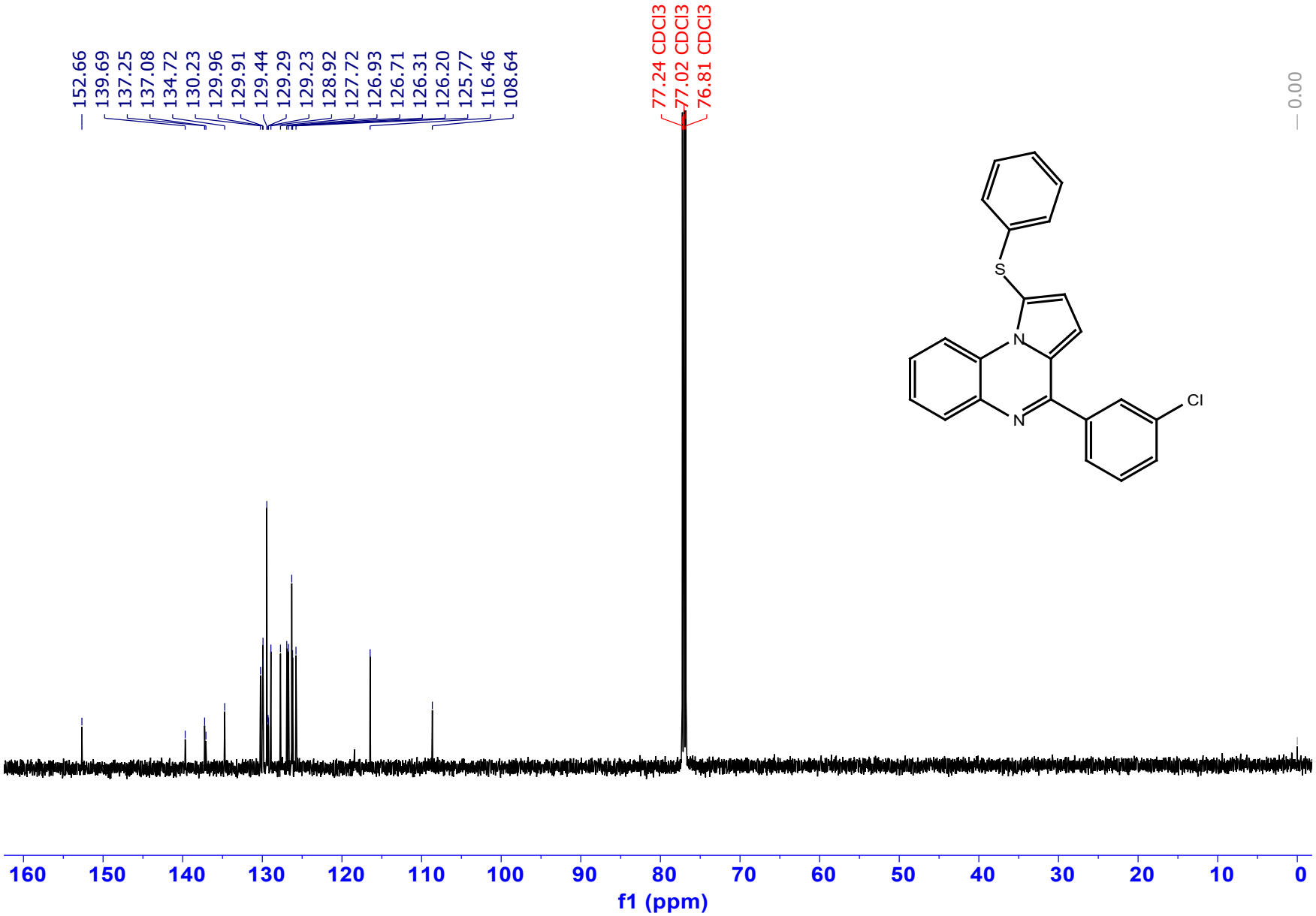
^{1}H NMR spectrum of 7-methyl-1-(phenylthio)-4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline.



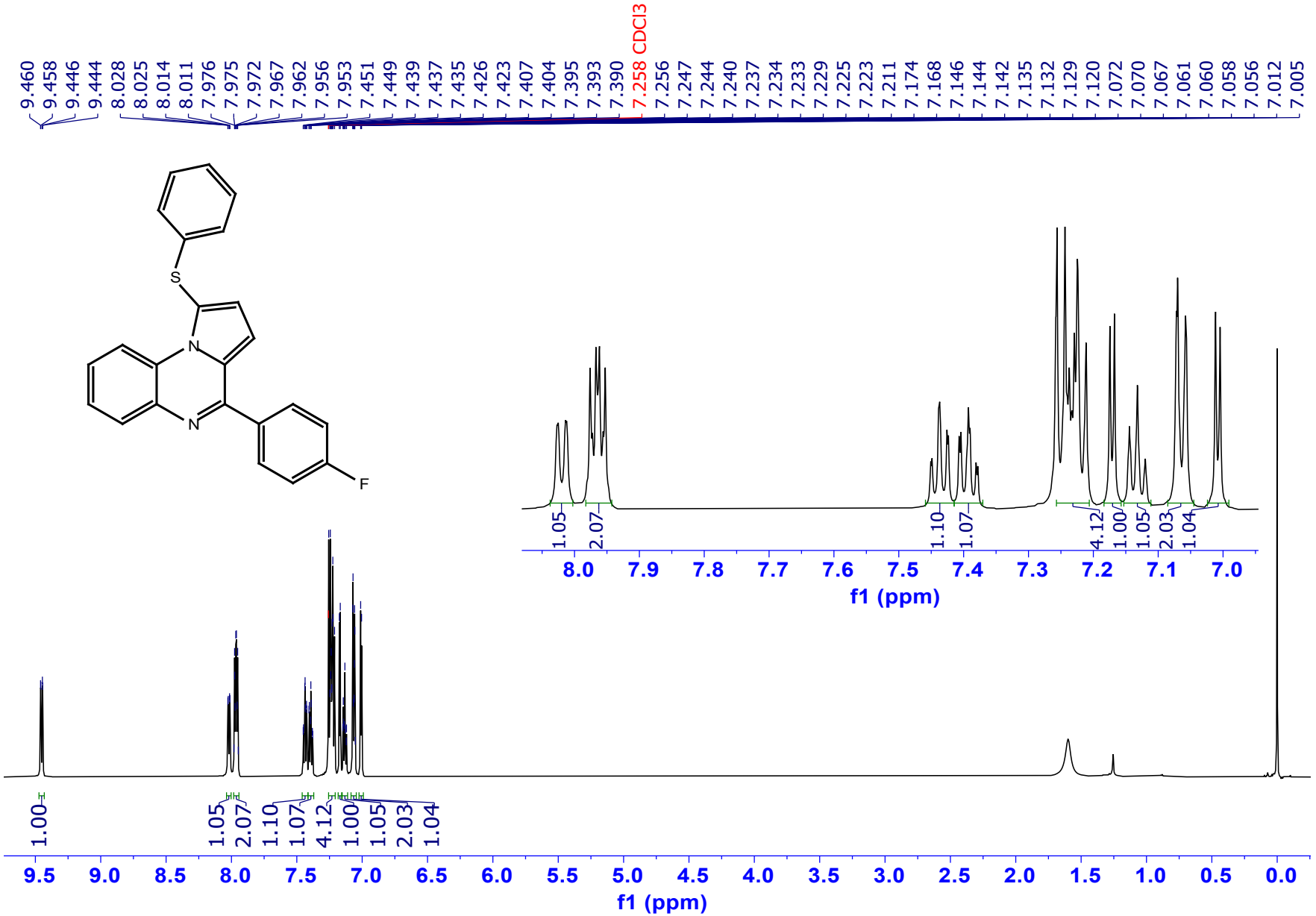
^{13}C NMR spectrum of 7-methyl-1-(phenylthio)-4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline.



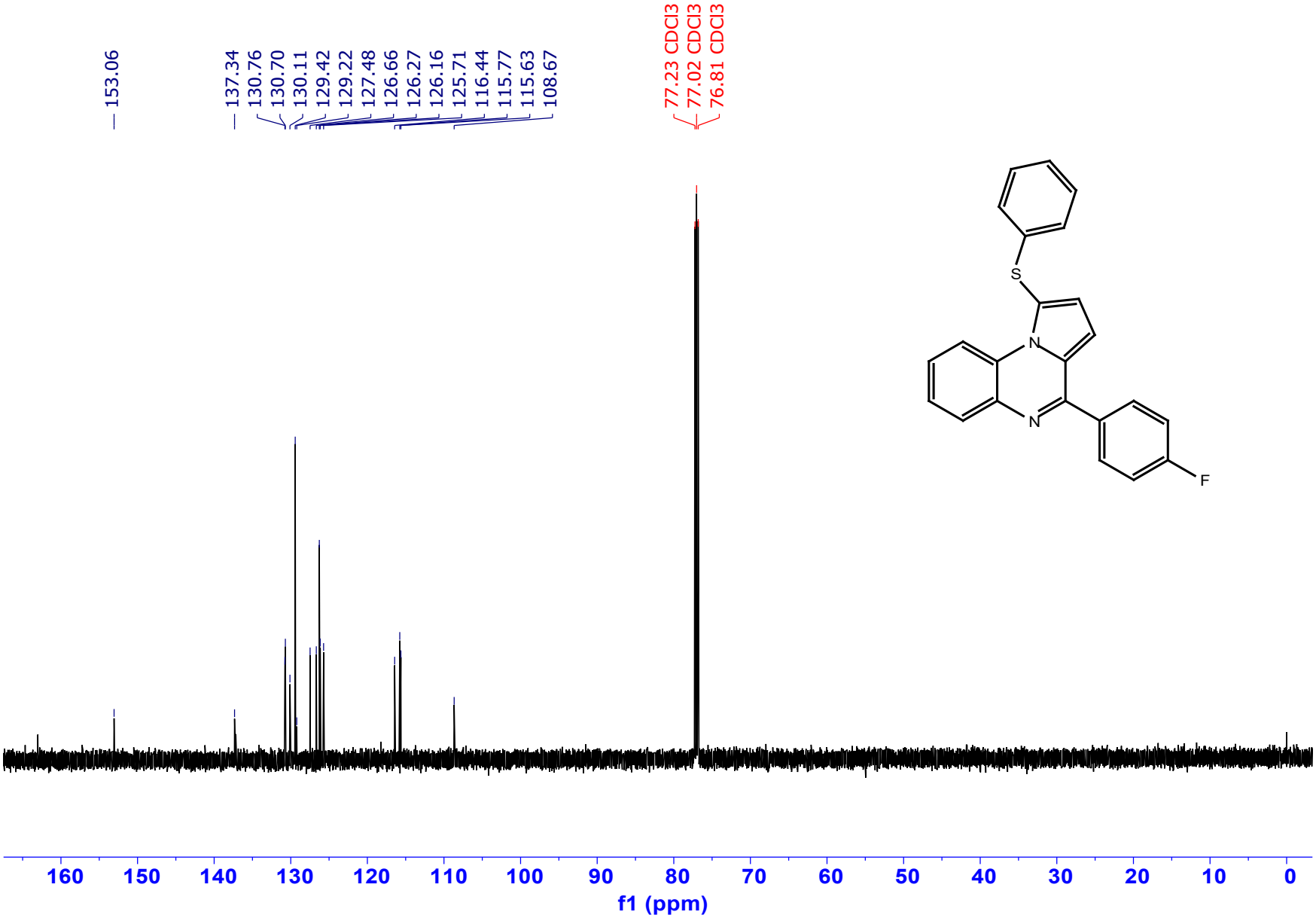
^{1}H NMR spectrum of 4-(3-chlorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



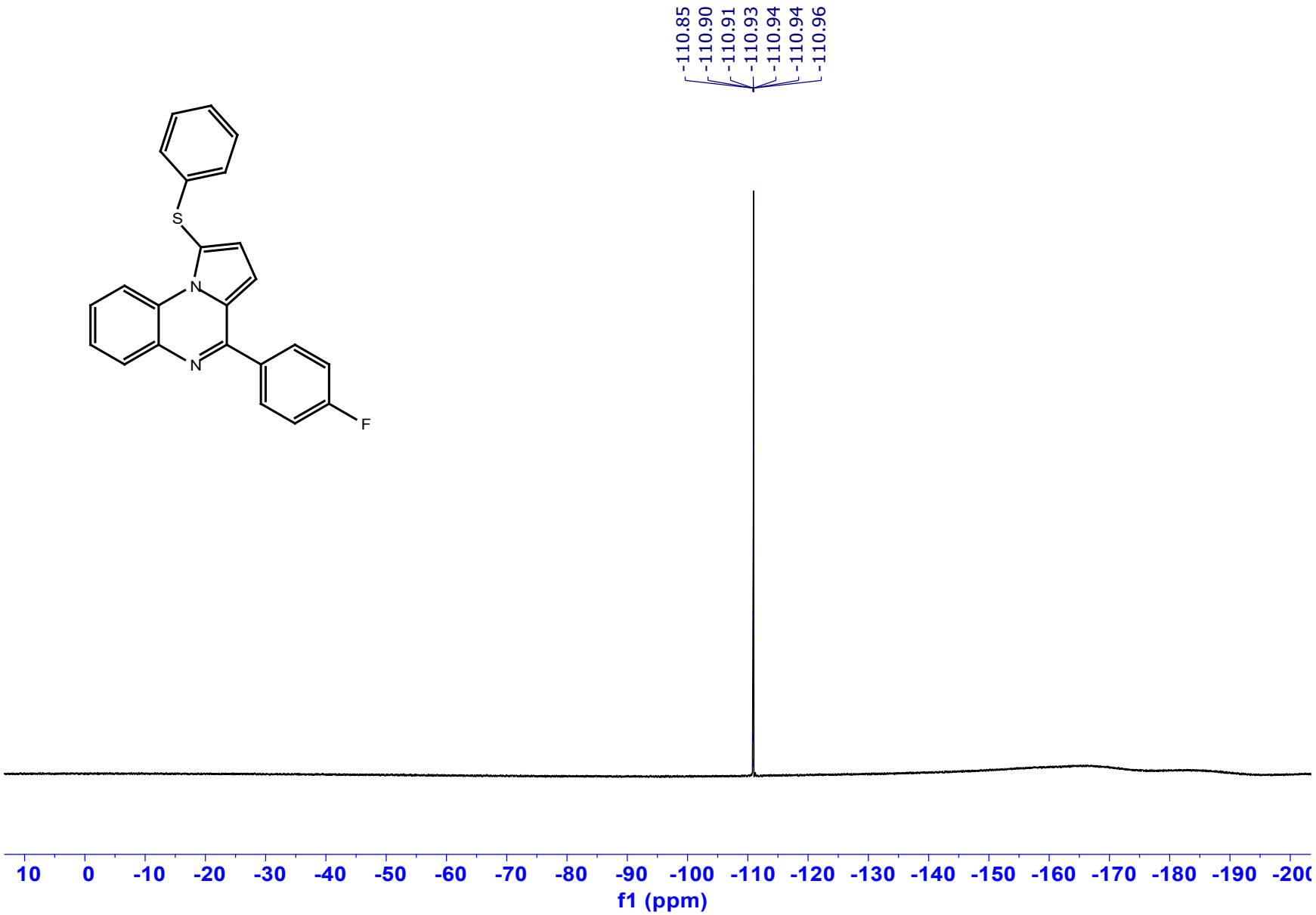
^{13}C NMR spectrum of 4-(3-chlorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



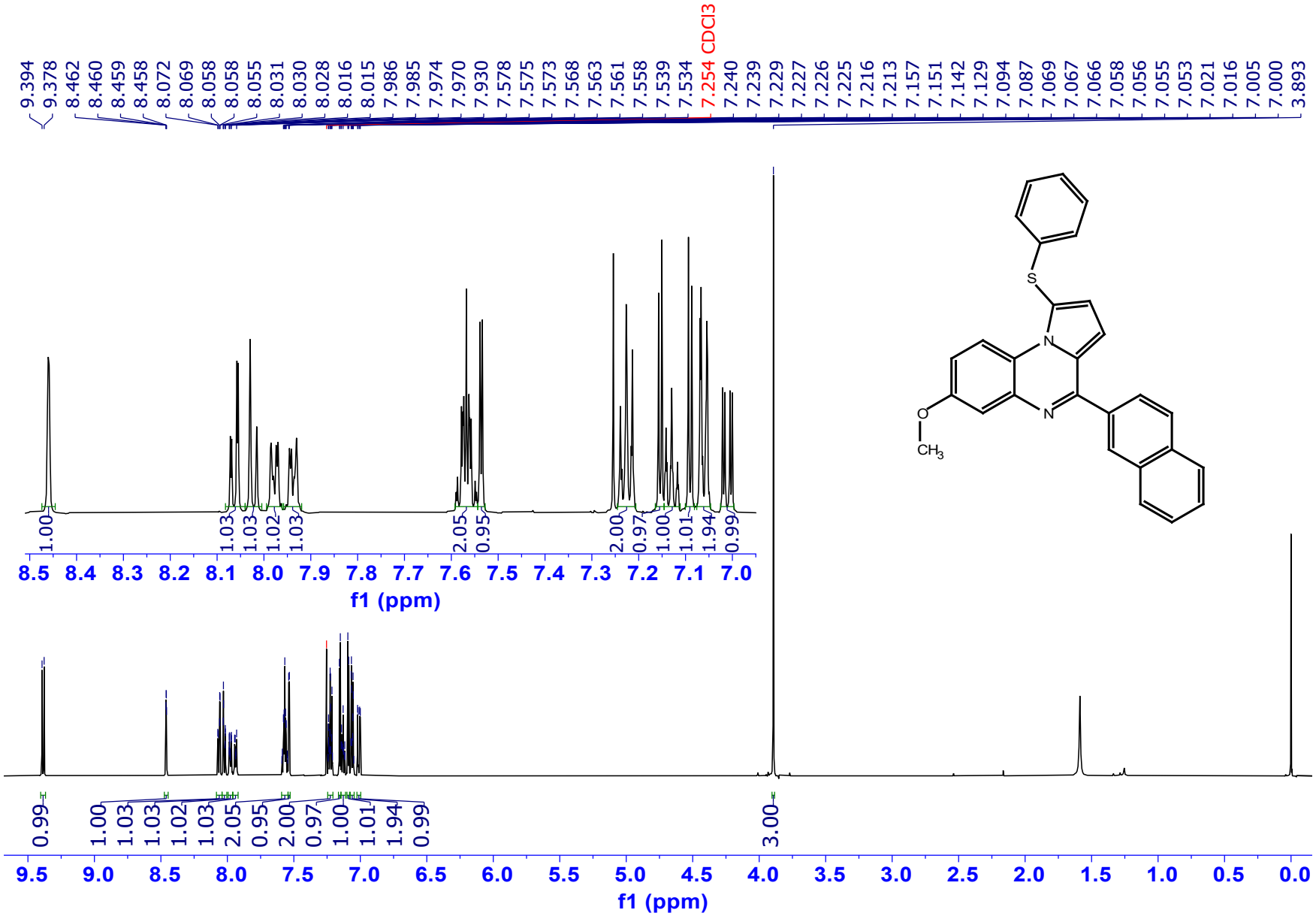
^{1}H NMR spectrum of 4-(4-fluorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



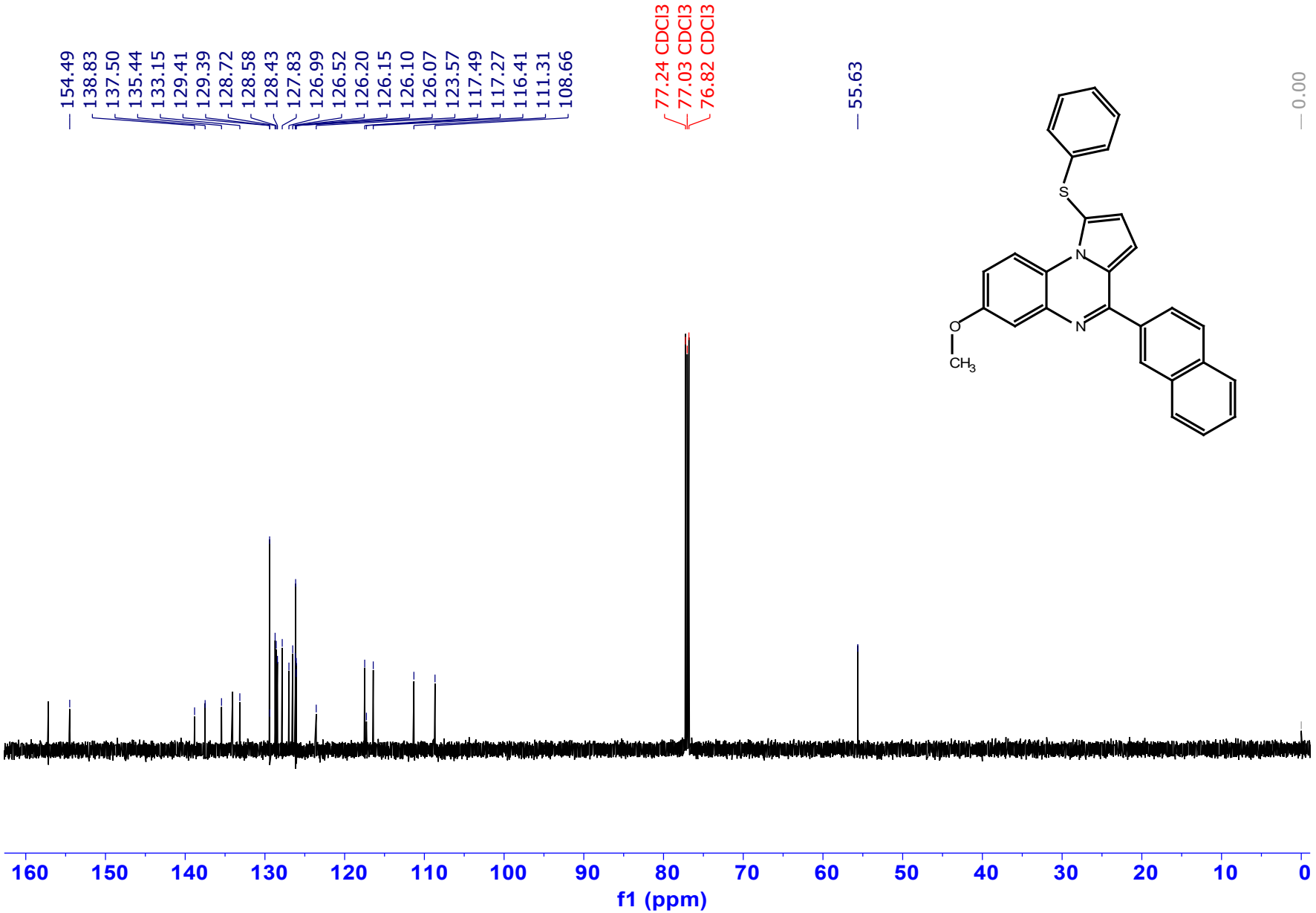
^{13}C NMR spectrum of 4-(4-fluorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



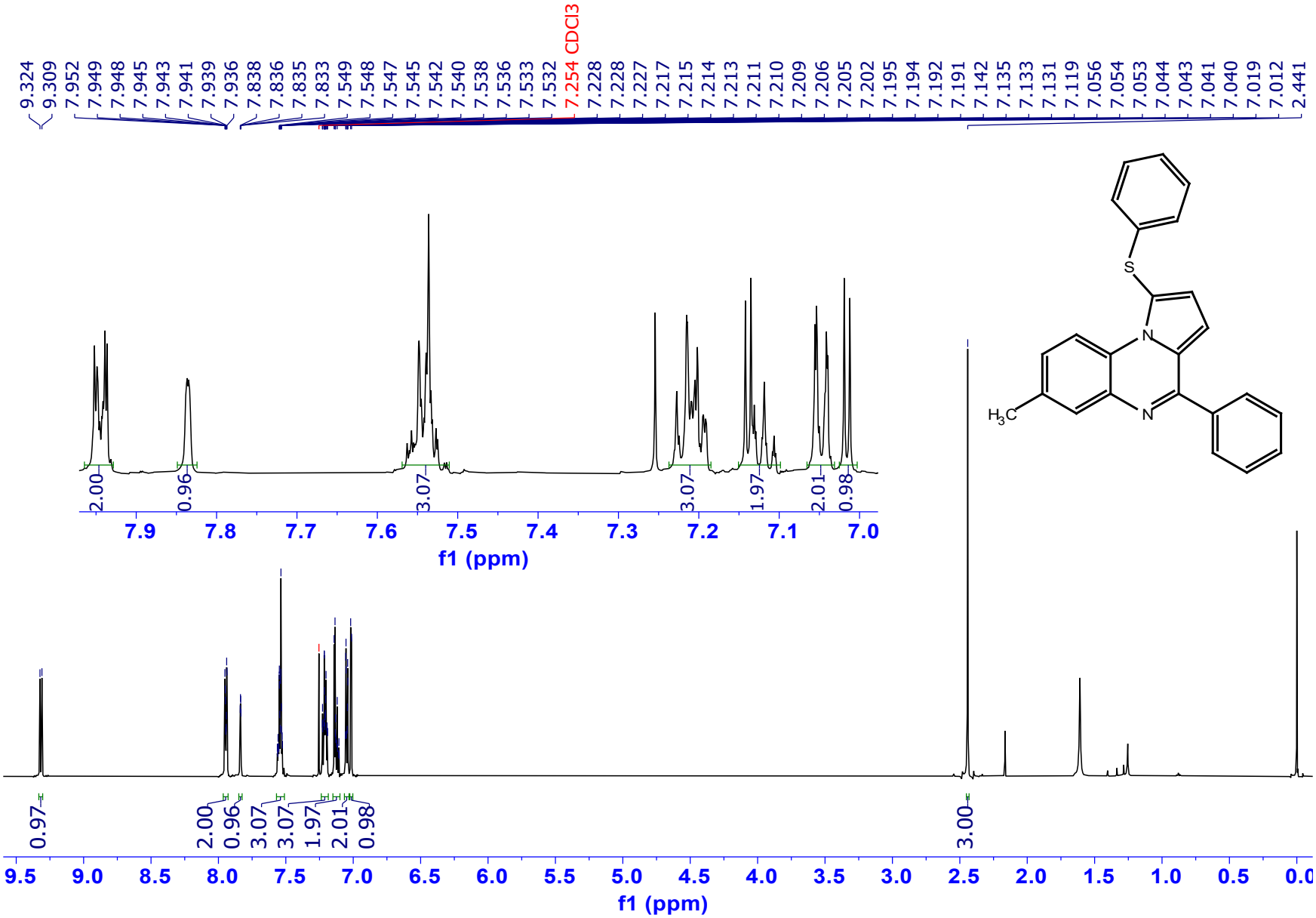
^{19}F NMR spectrum of 4-(4-fluorophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



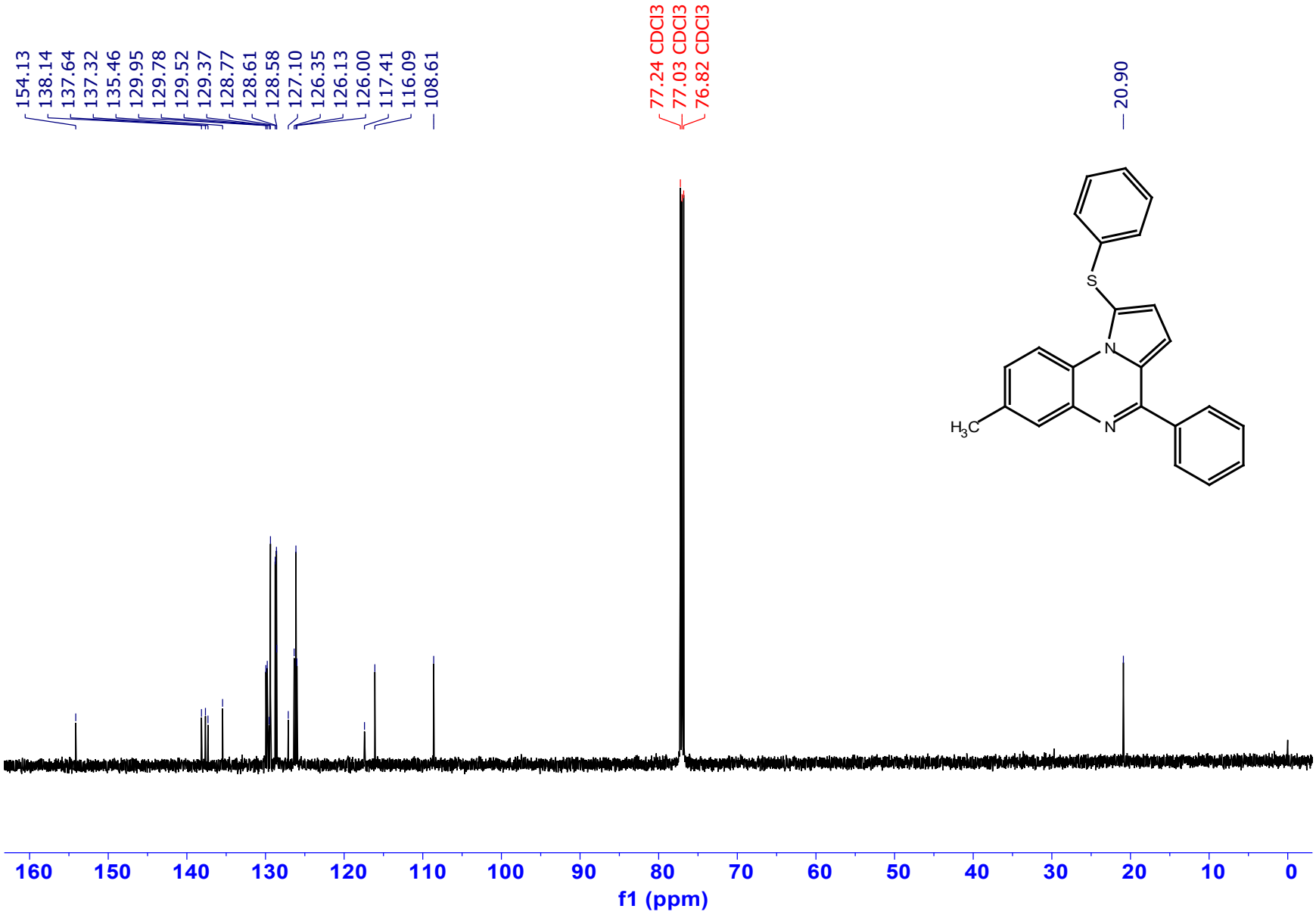
^{1}H NMR spectrum of 7-methoxy-4-(naphthalen-2-yl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



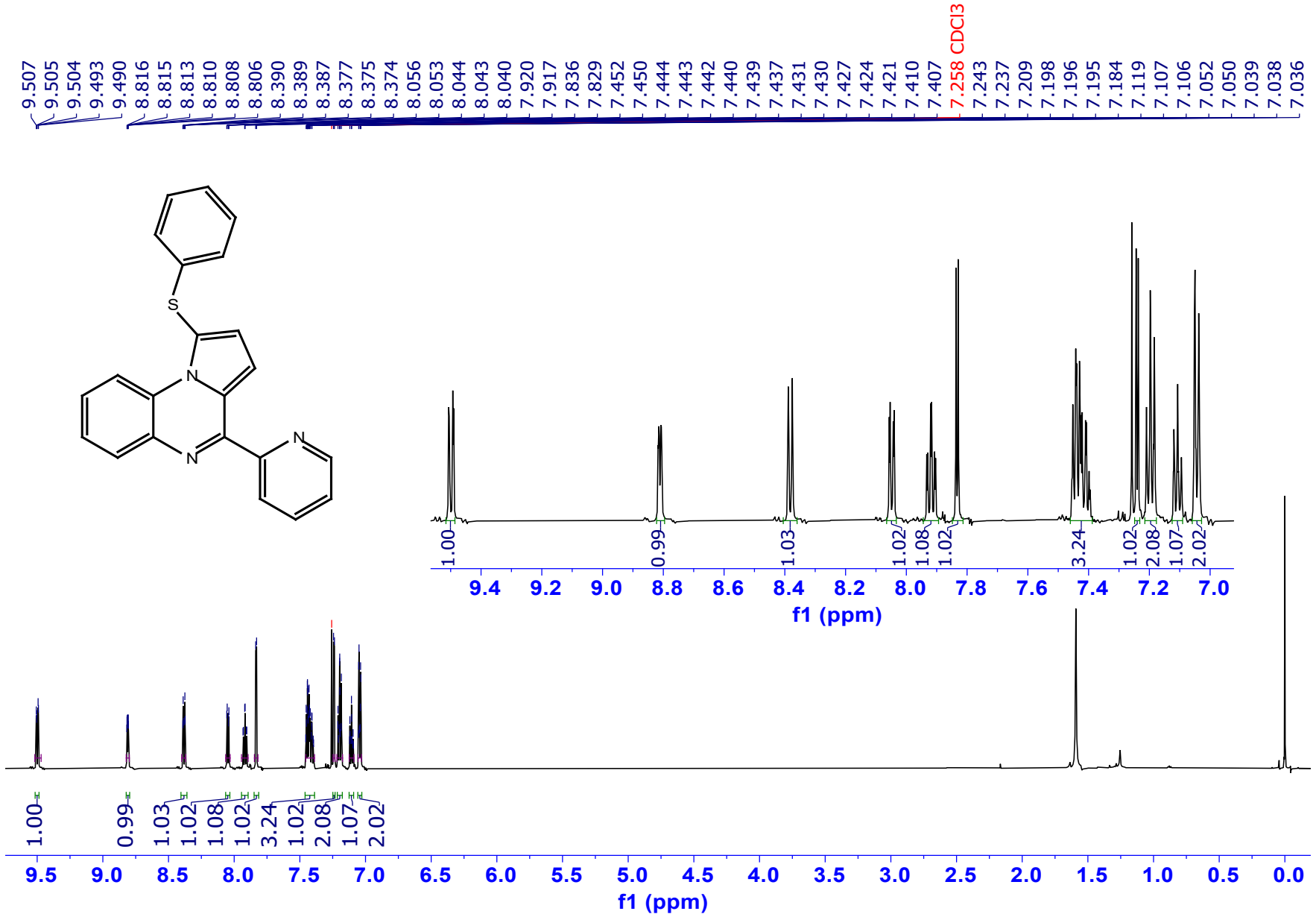
^{13}C NMR spectrum of 7-methoxy-4-(naphthalen-2-yl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



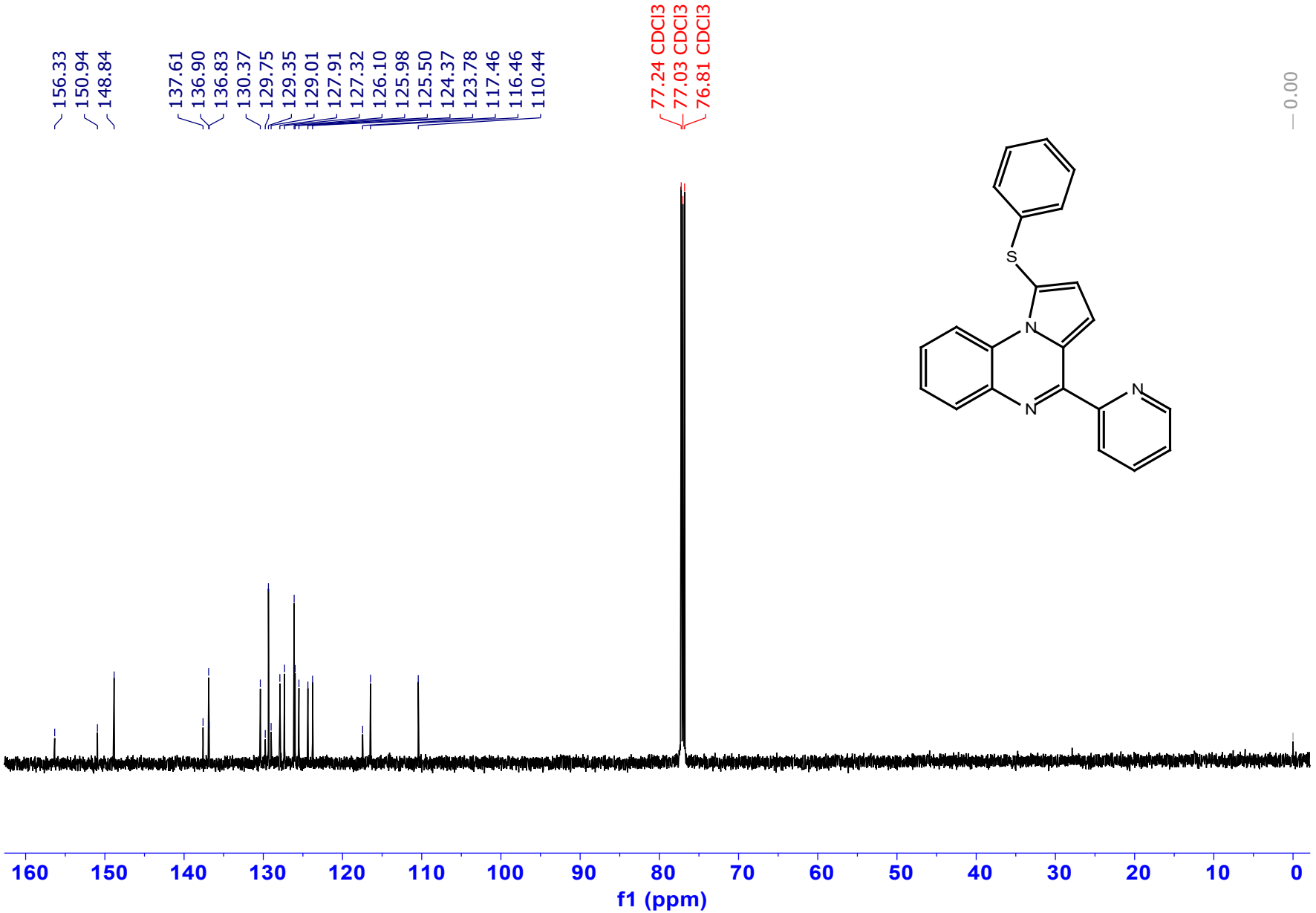
^{1}H NMR spectrum of 7-methyl-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



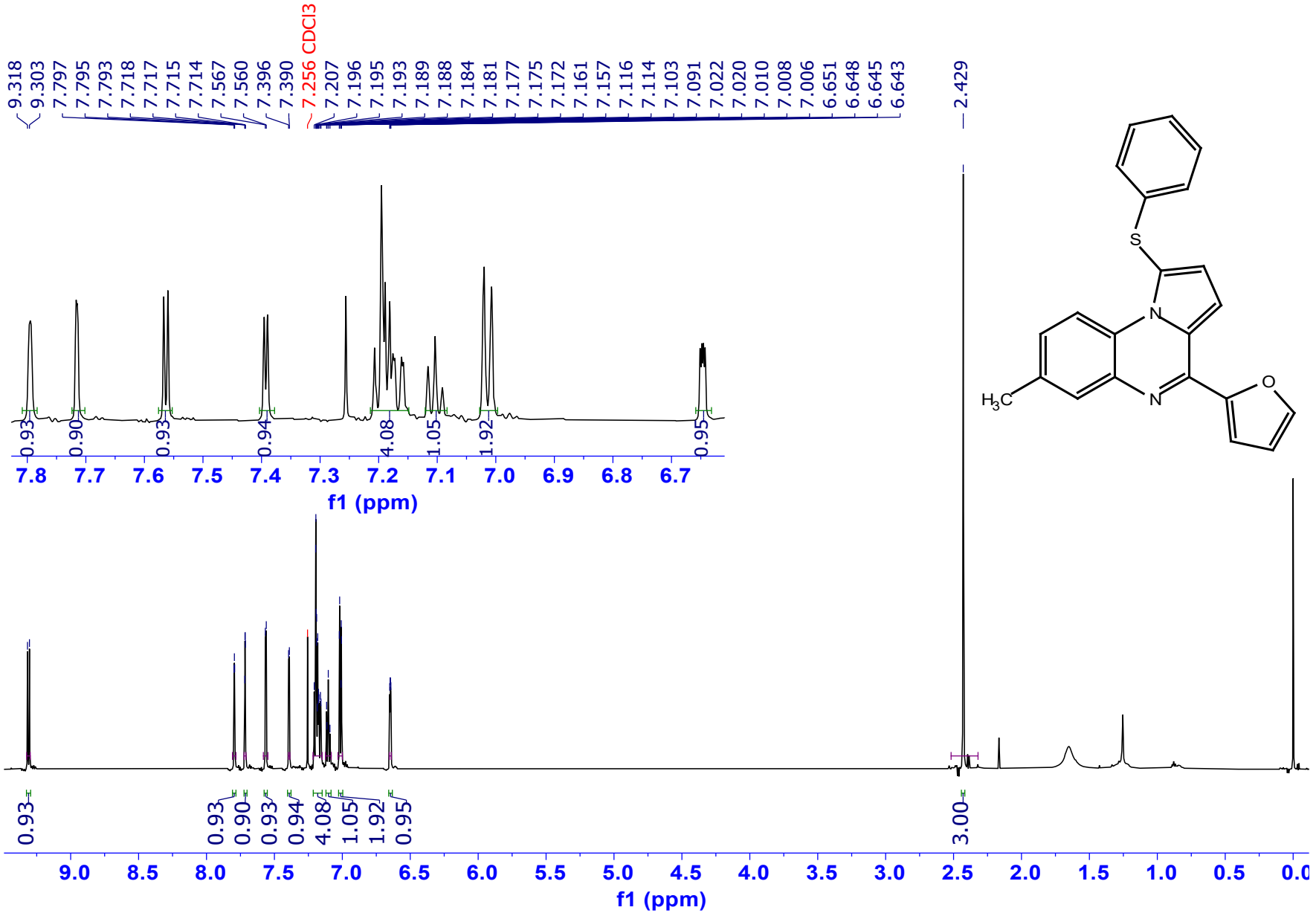
^{13}C NMR spectrum of 7-methyl-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



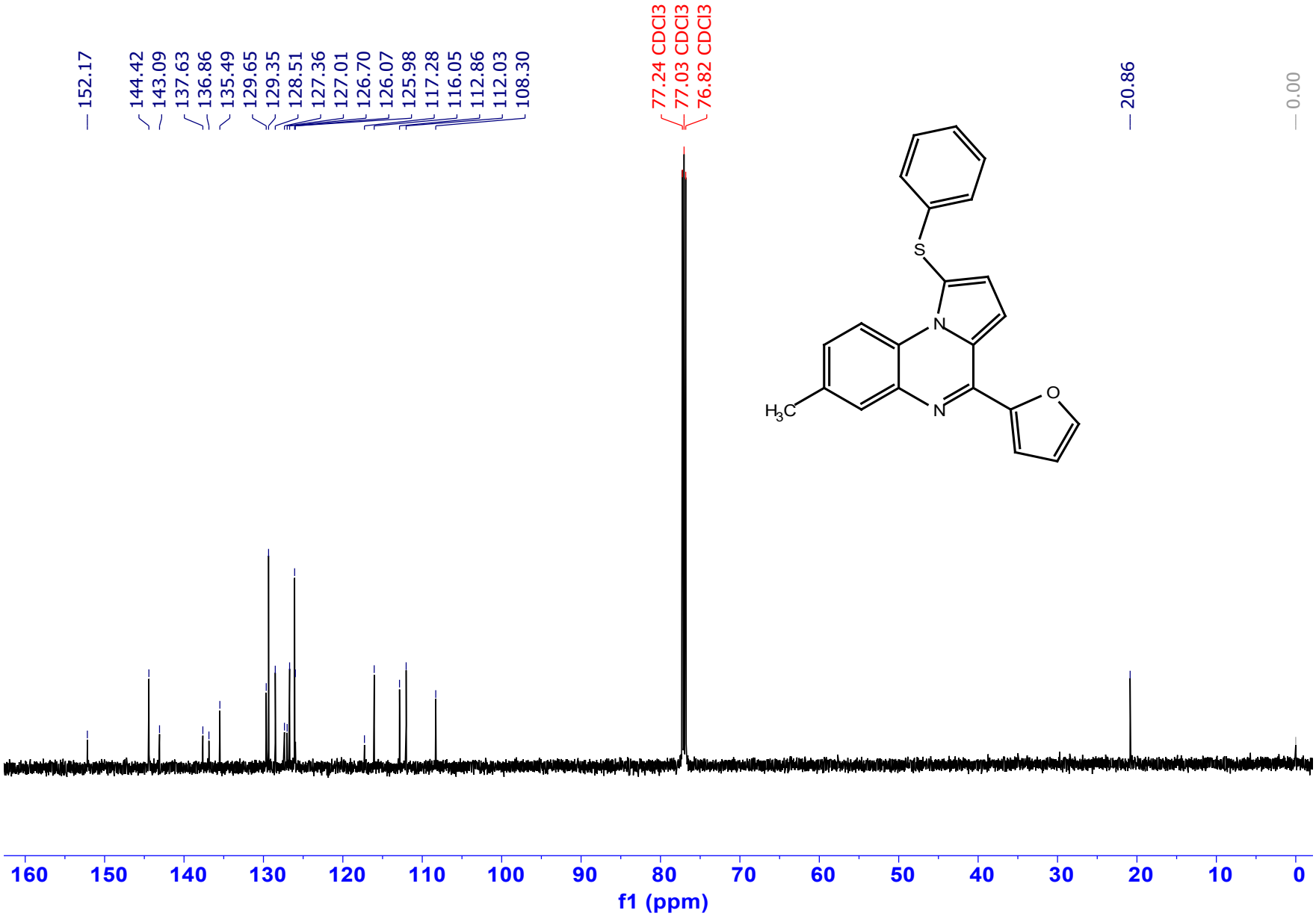
^{1}H NMR spectrum of 1-(phenylthio)-4-(pyridin-2-yl)pyrrolo[1,2-*a*]quinoxaline.



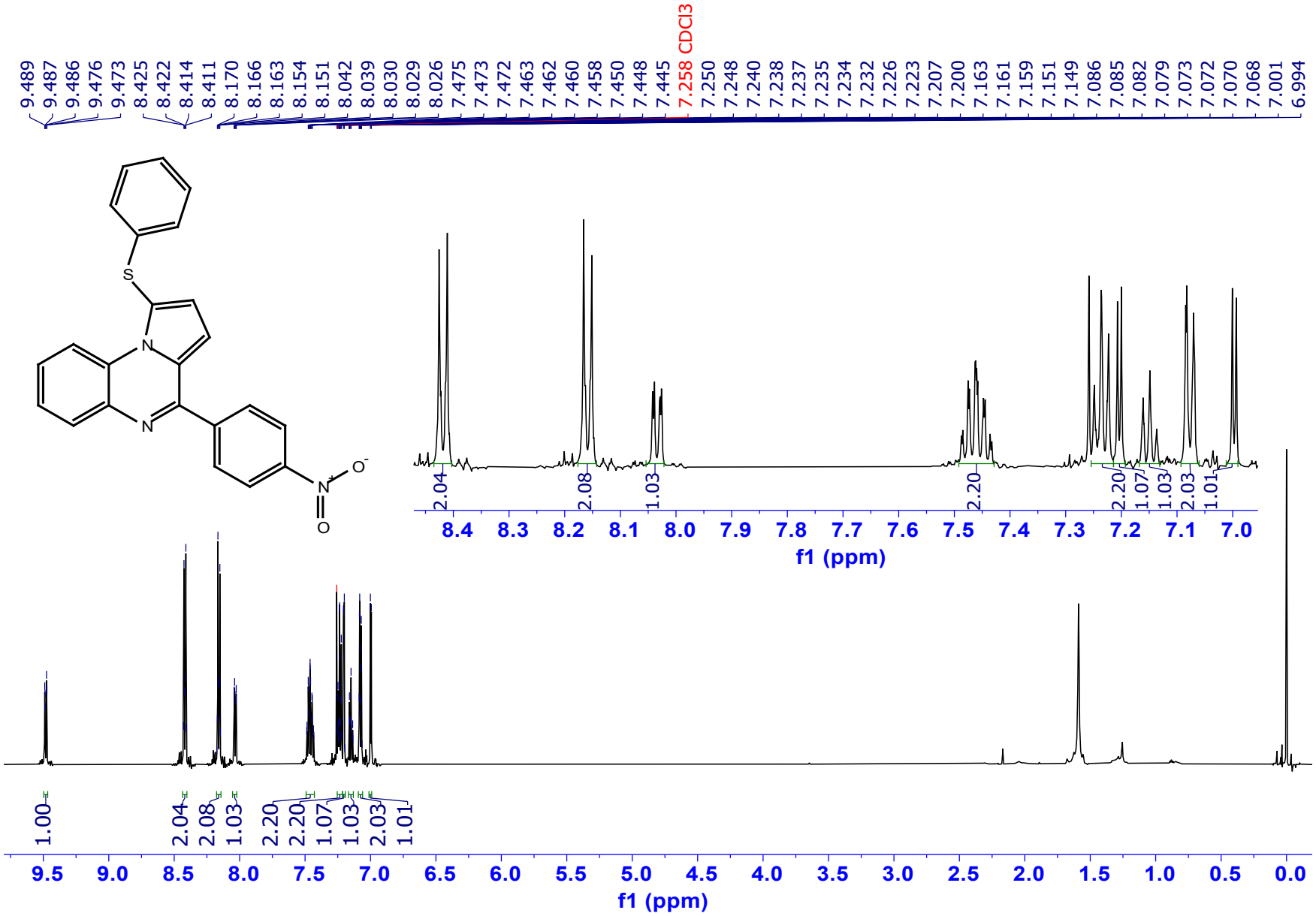
^{13}C NMR spectrum of 1-(phenylthio)-4-(pyridin-2-yl)pyrrolo[1,2-*a*]quinoxaline.



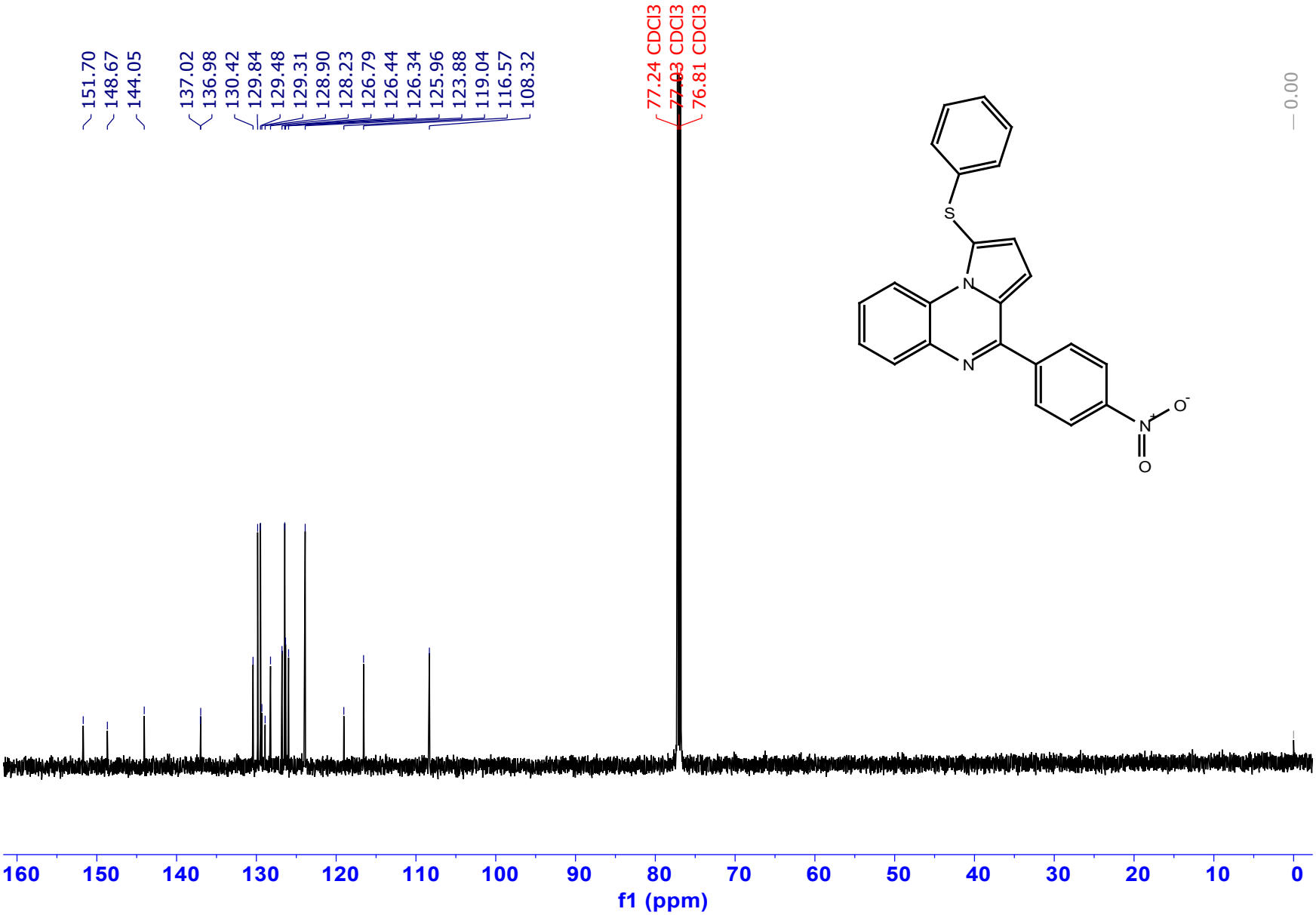
[1]H NMR spectrum of 4-(furan-2-yl)-7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



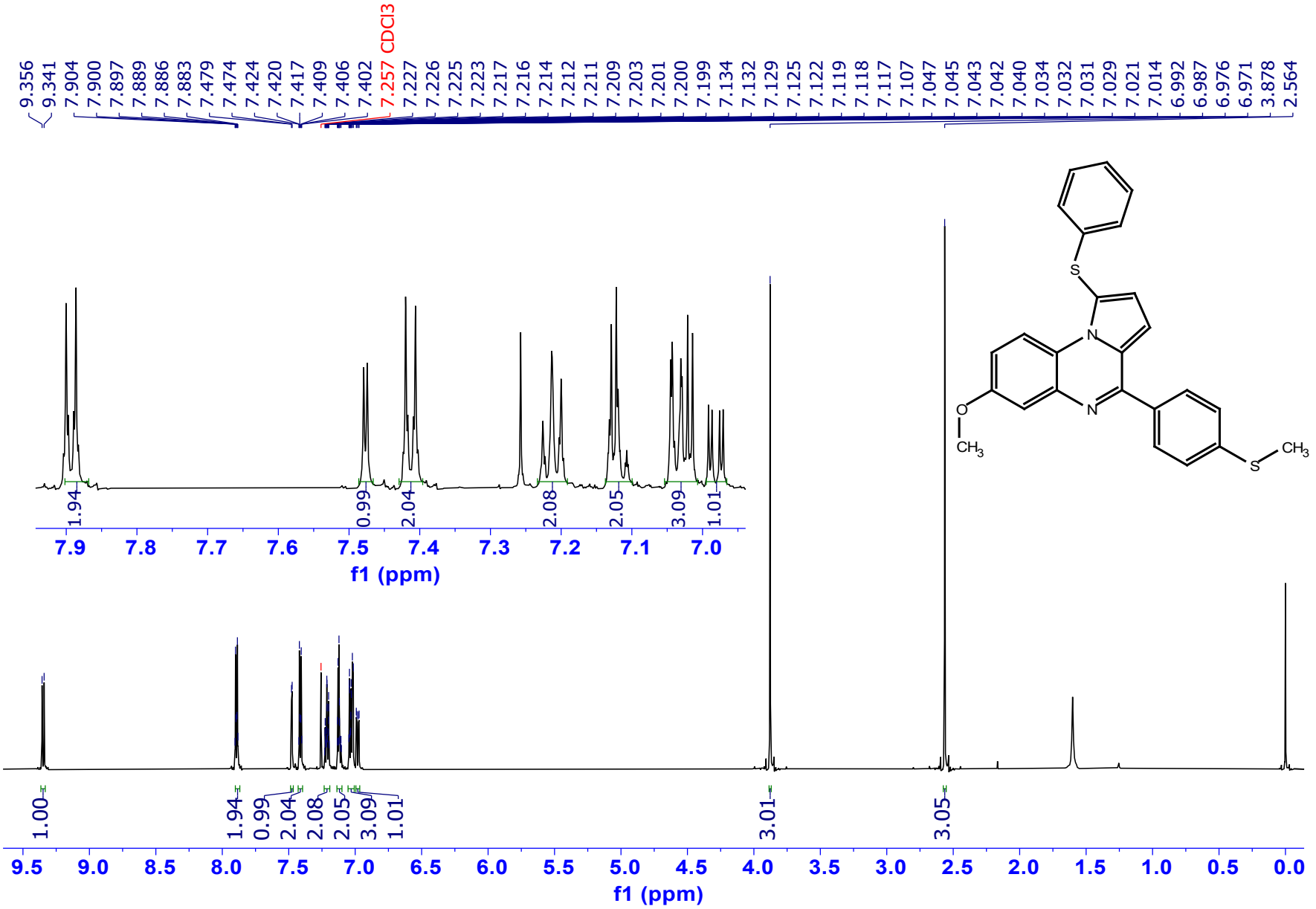
^{13}C NMR spectrum of 4-(furan-2-yl)-7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



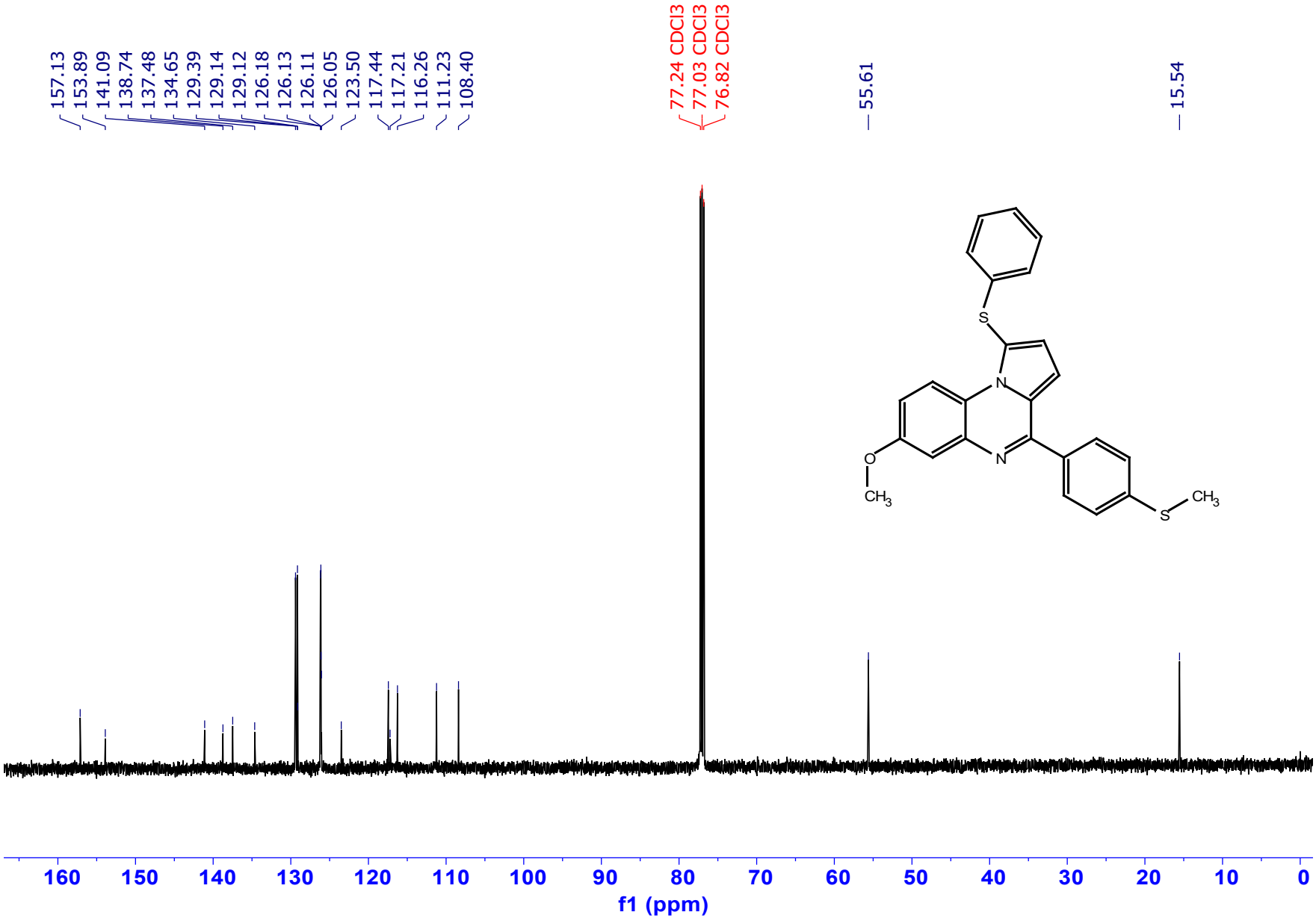
^{1}H NMR spectrum of 4-(4-nitrophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



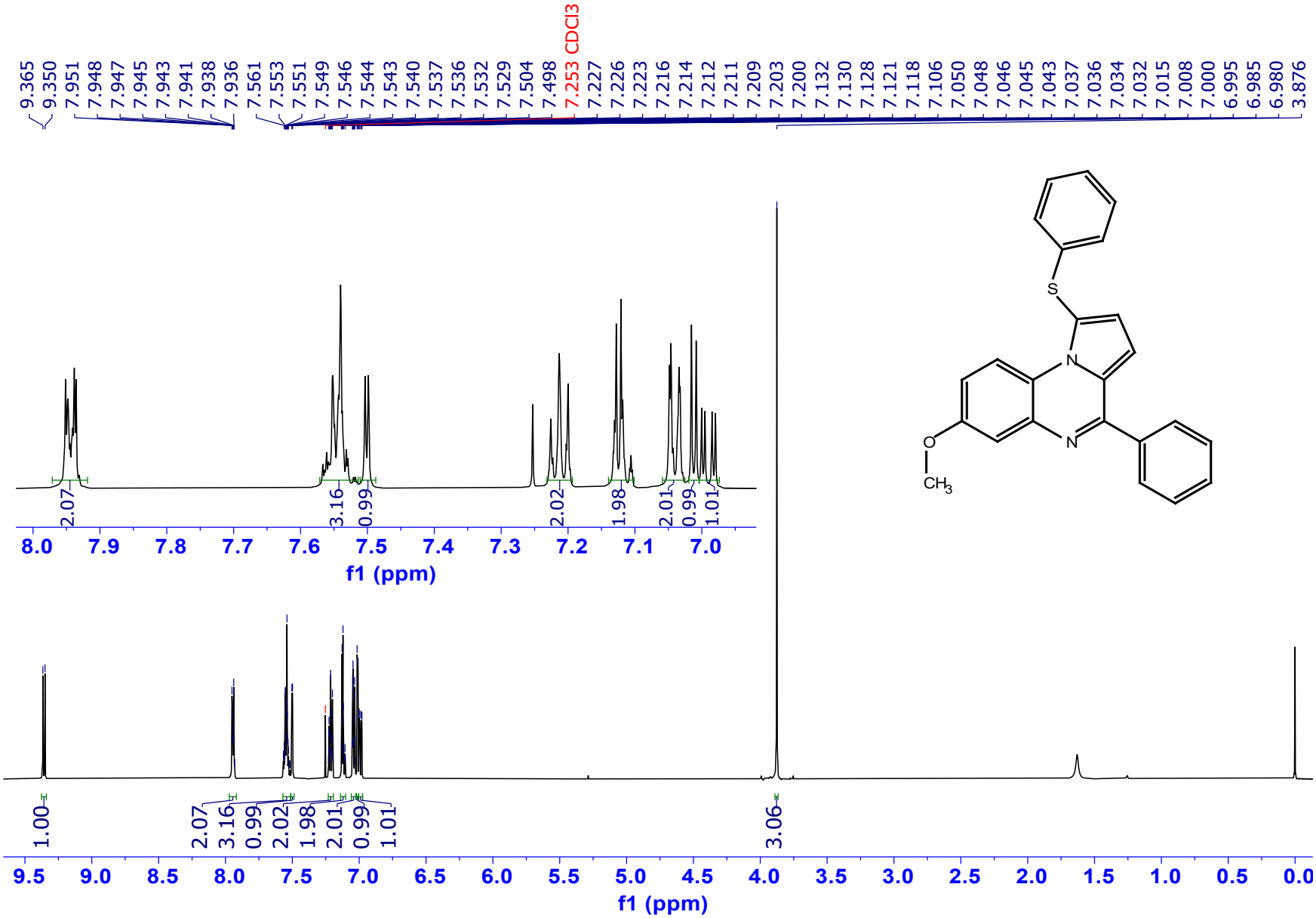
^{13}C NMR spectrum of 4-(4-nitrophenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



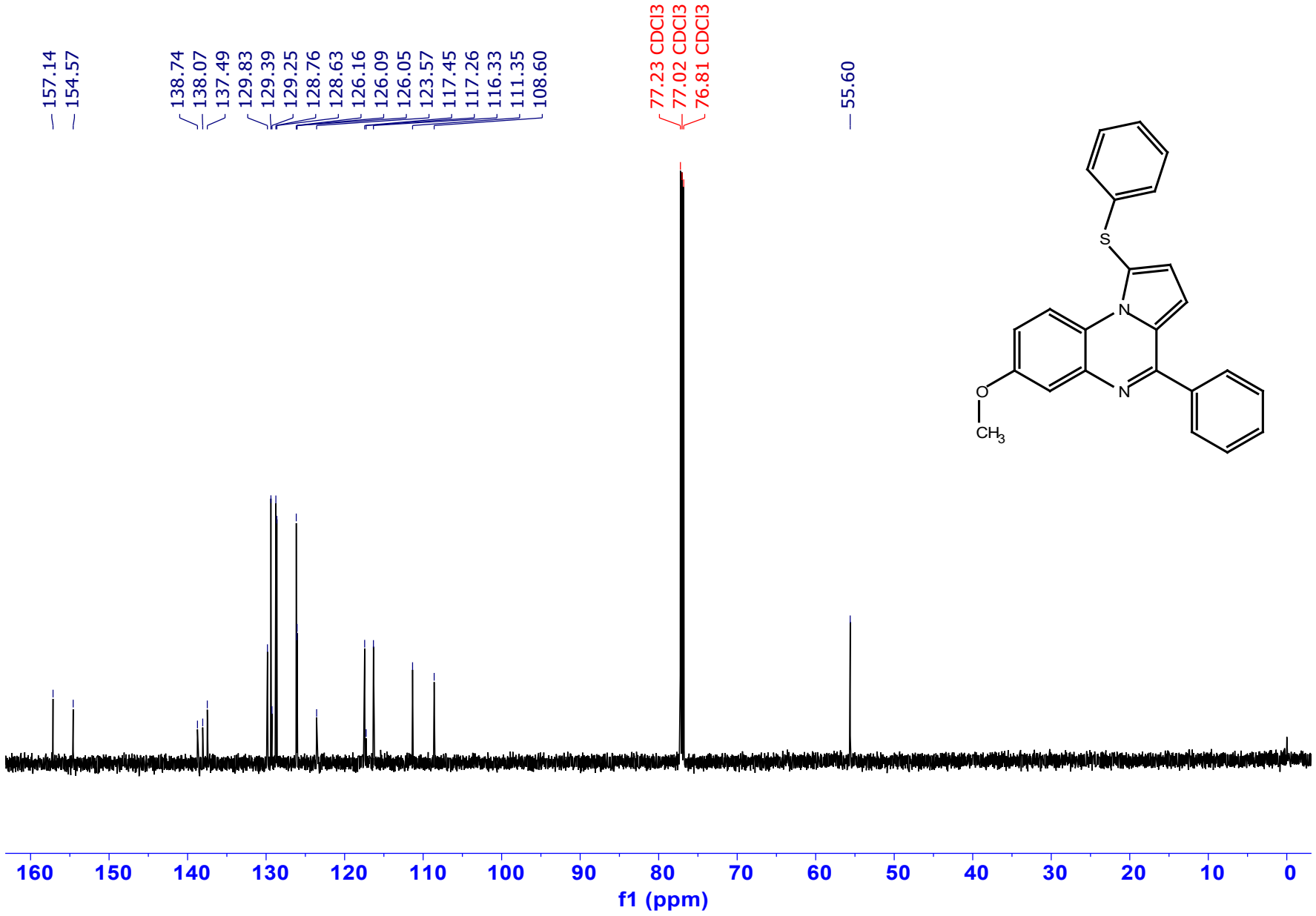
^{1}H NMR spectrum of 7-methoxy-4-(4-(methylthio)phenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



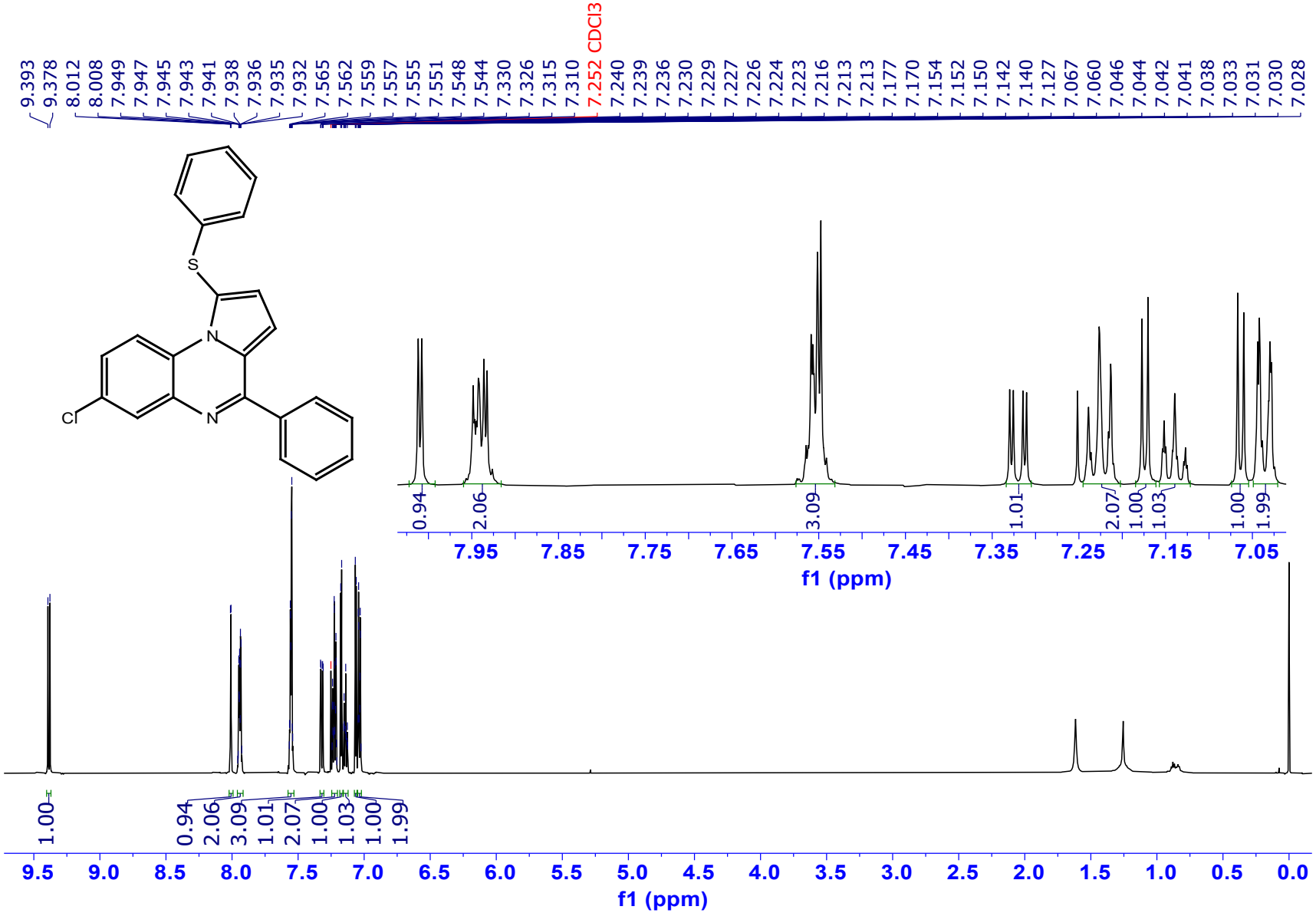
^{13}C NMR spectrum of 7-methoxy-4-(4-(methylthio)phenyl)-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



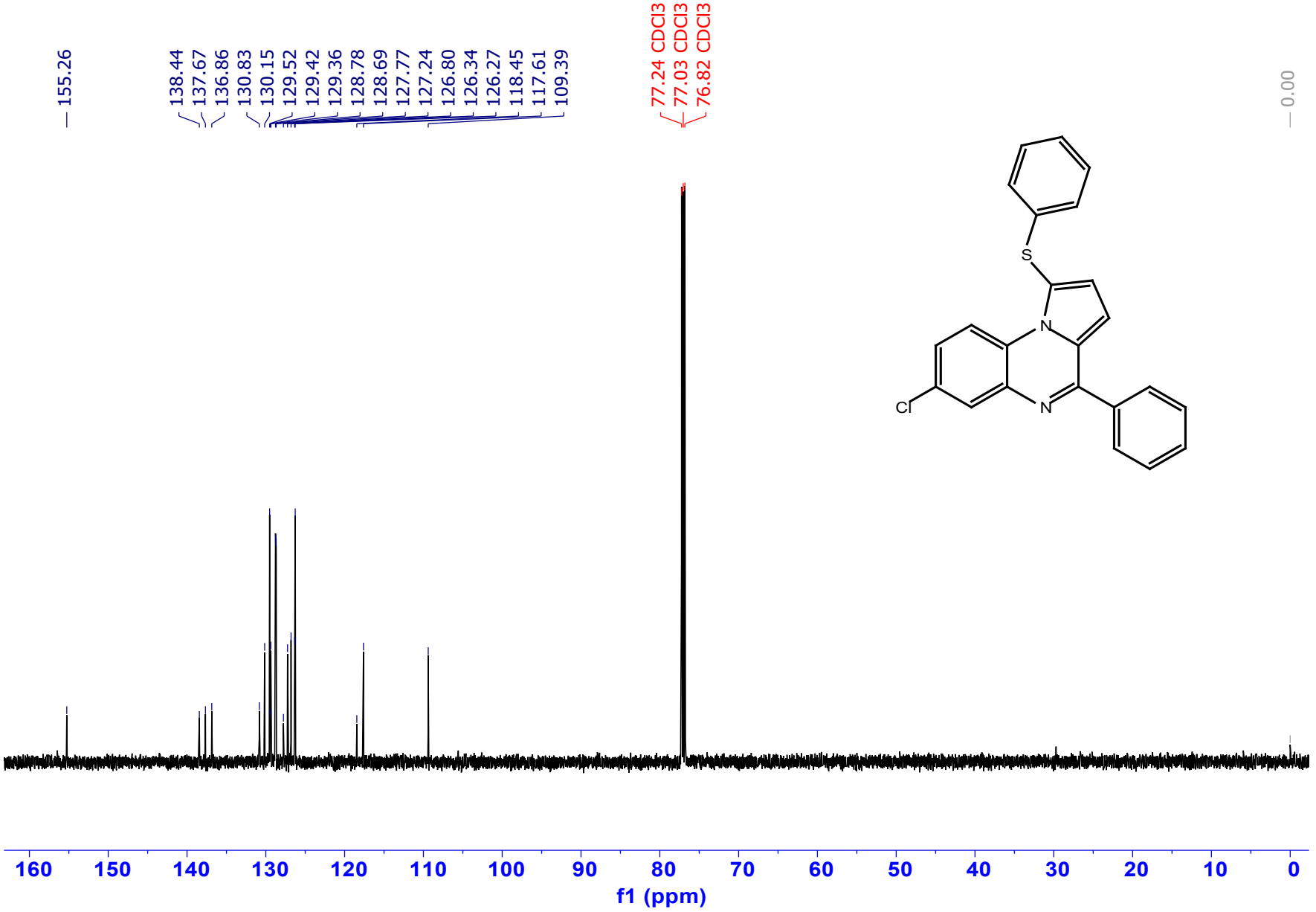
^{1}H NMR spectrum of 7-methoxy-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.


157.14
154.57
138.74
138.07
137.49
129.83
129.39
129.25
128.76
128.63
126.16
126.09
126.05
123.57
117.45
117.26
116.33
111.35
108.60
77.23 CDCl3
77.02 CDCl3
76.81 CDCl3
55.60
S
N
N
O
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

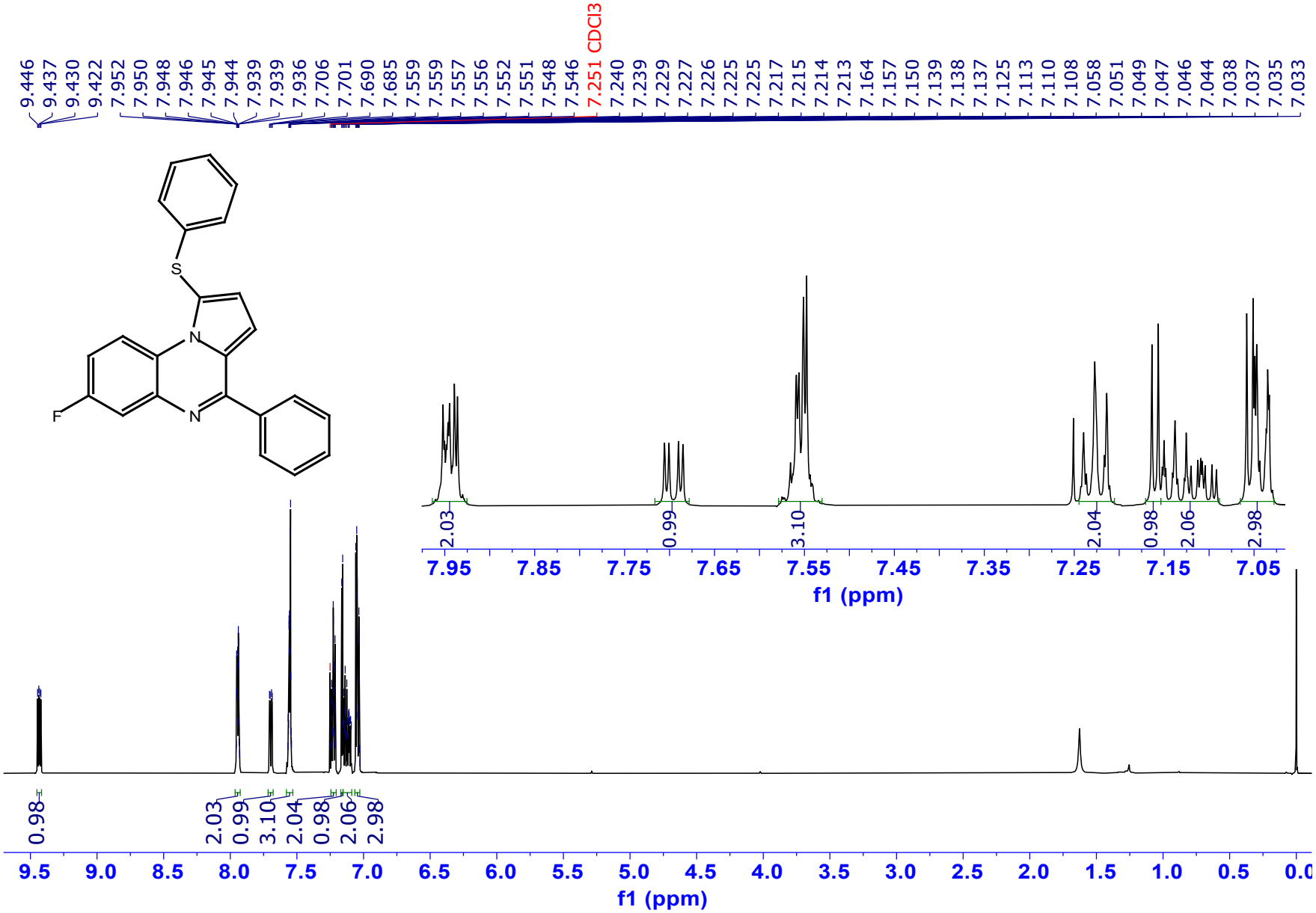
^{13}C NMR spectrum of 7-methoxy-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



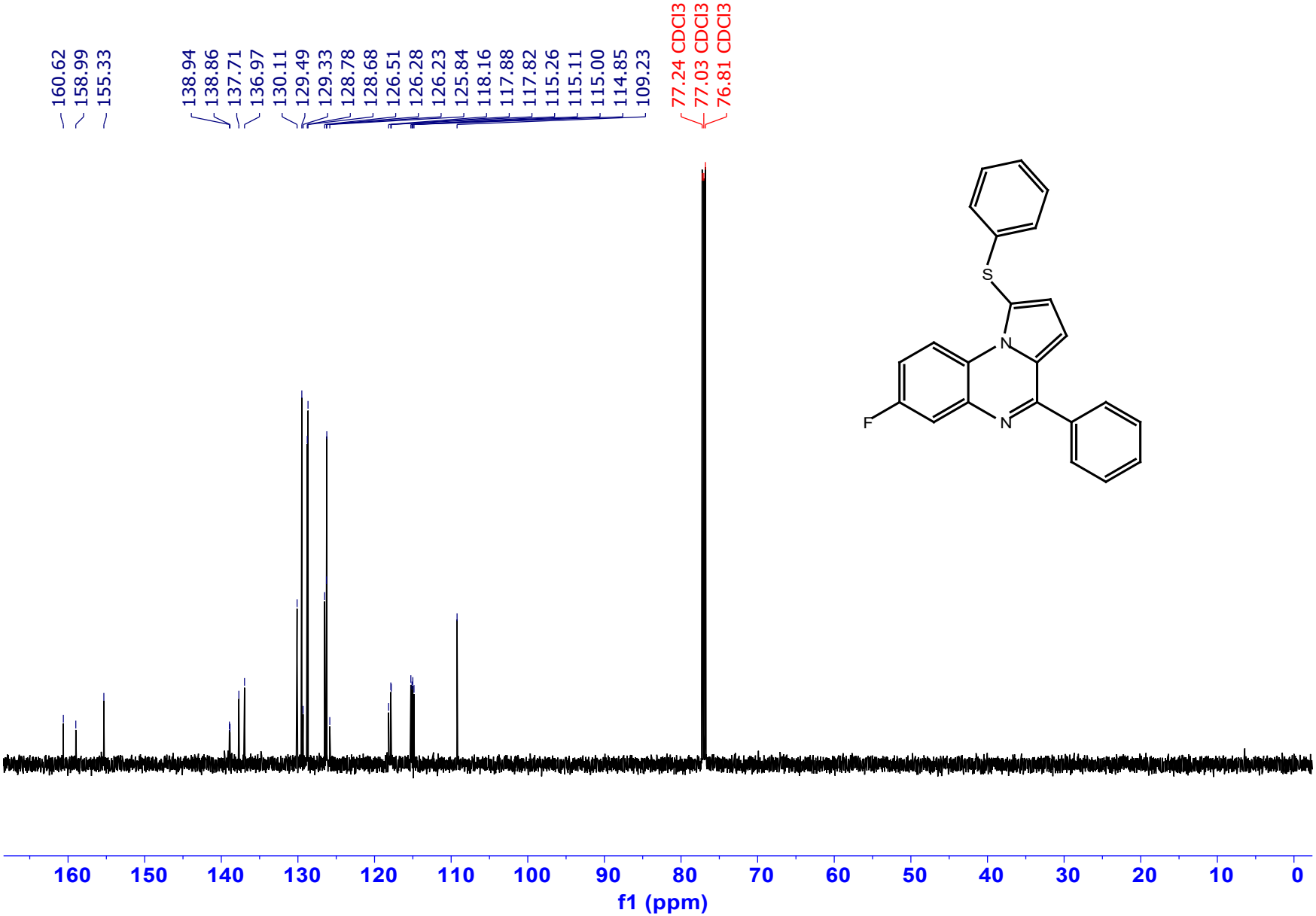
^{1}H NMR spectrum of 7-chloro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



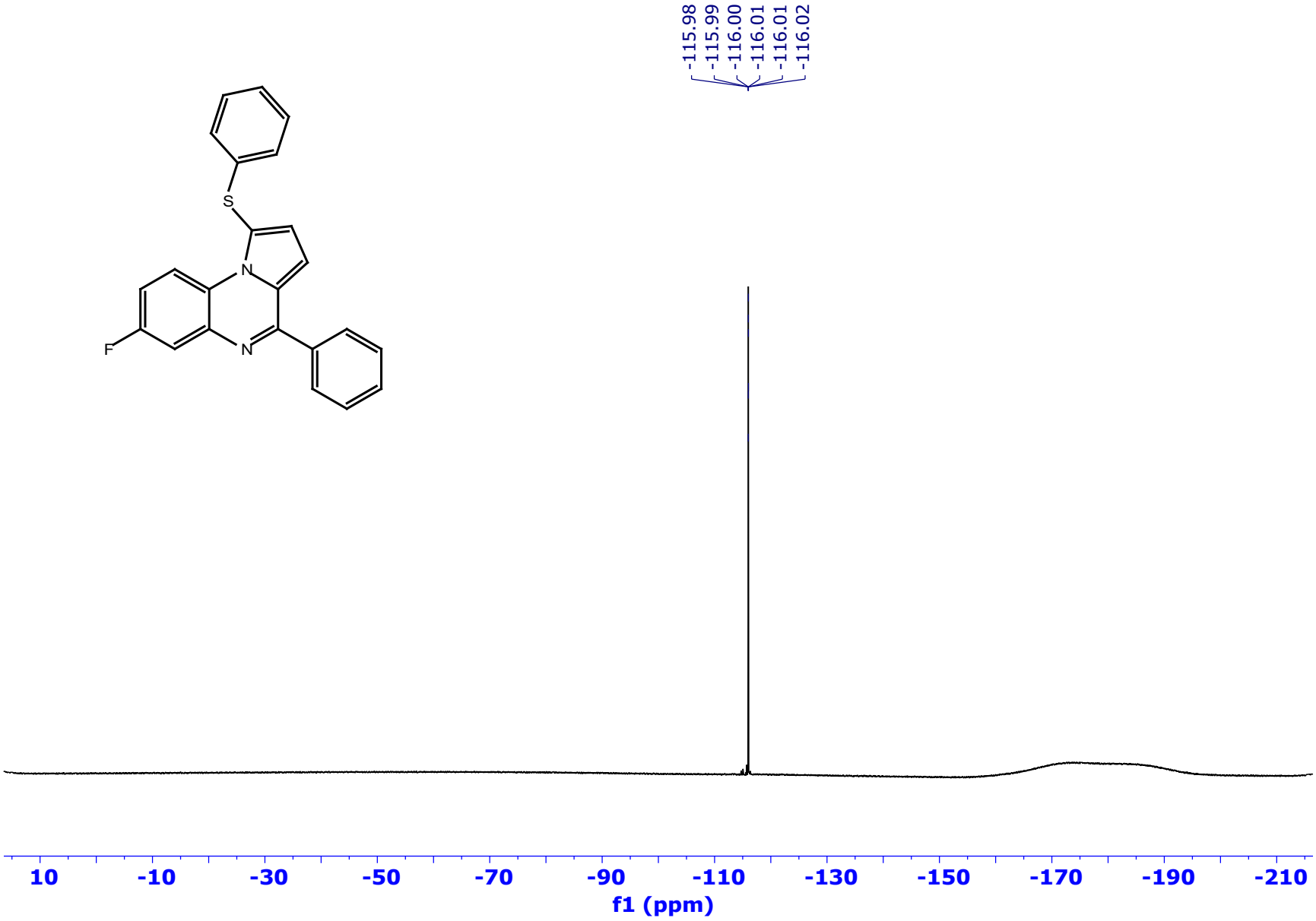
^{13}C NMR spectrum of 7-chloro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



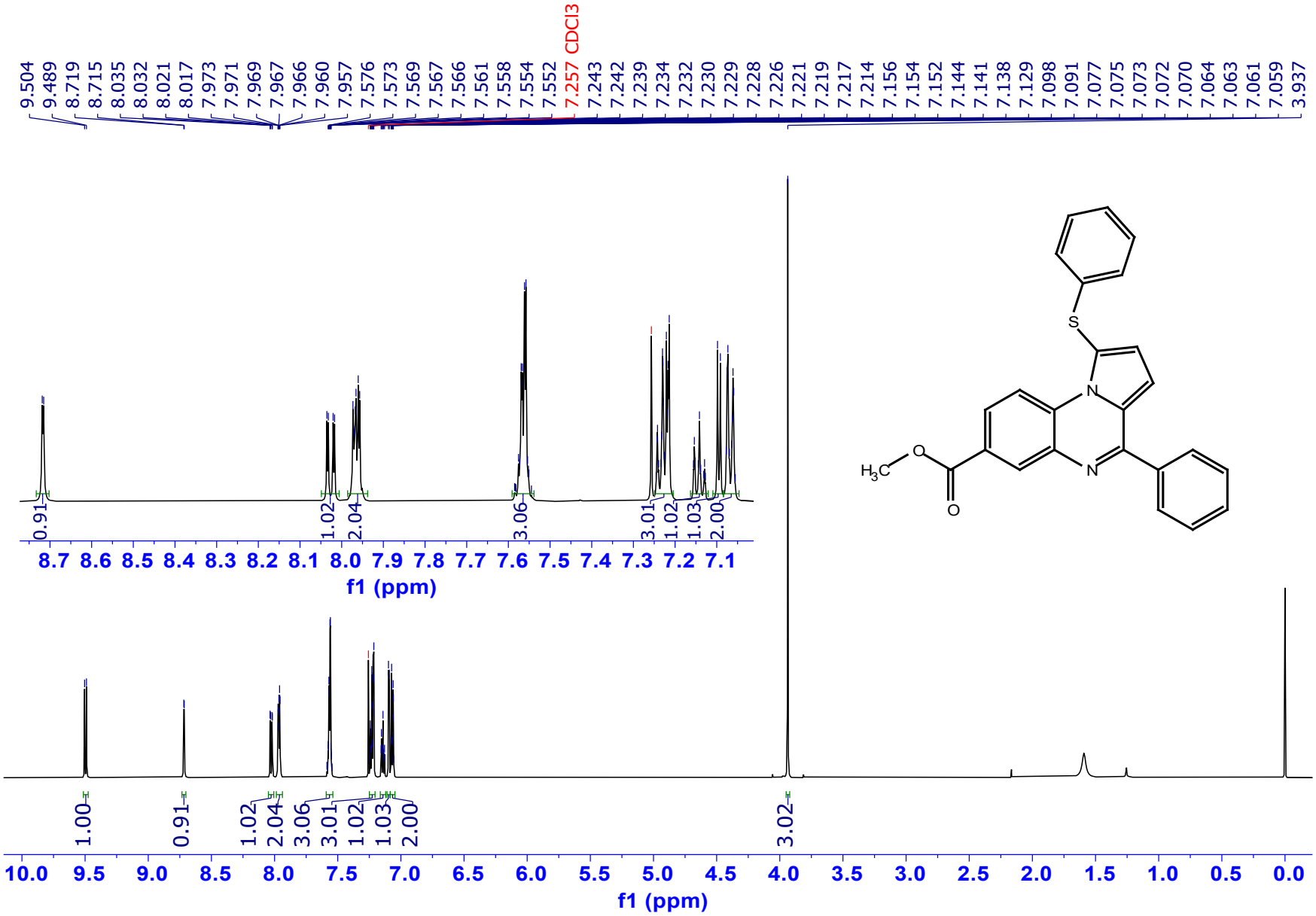
^{1}H NMR spectrum of 7-fluoro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



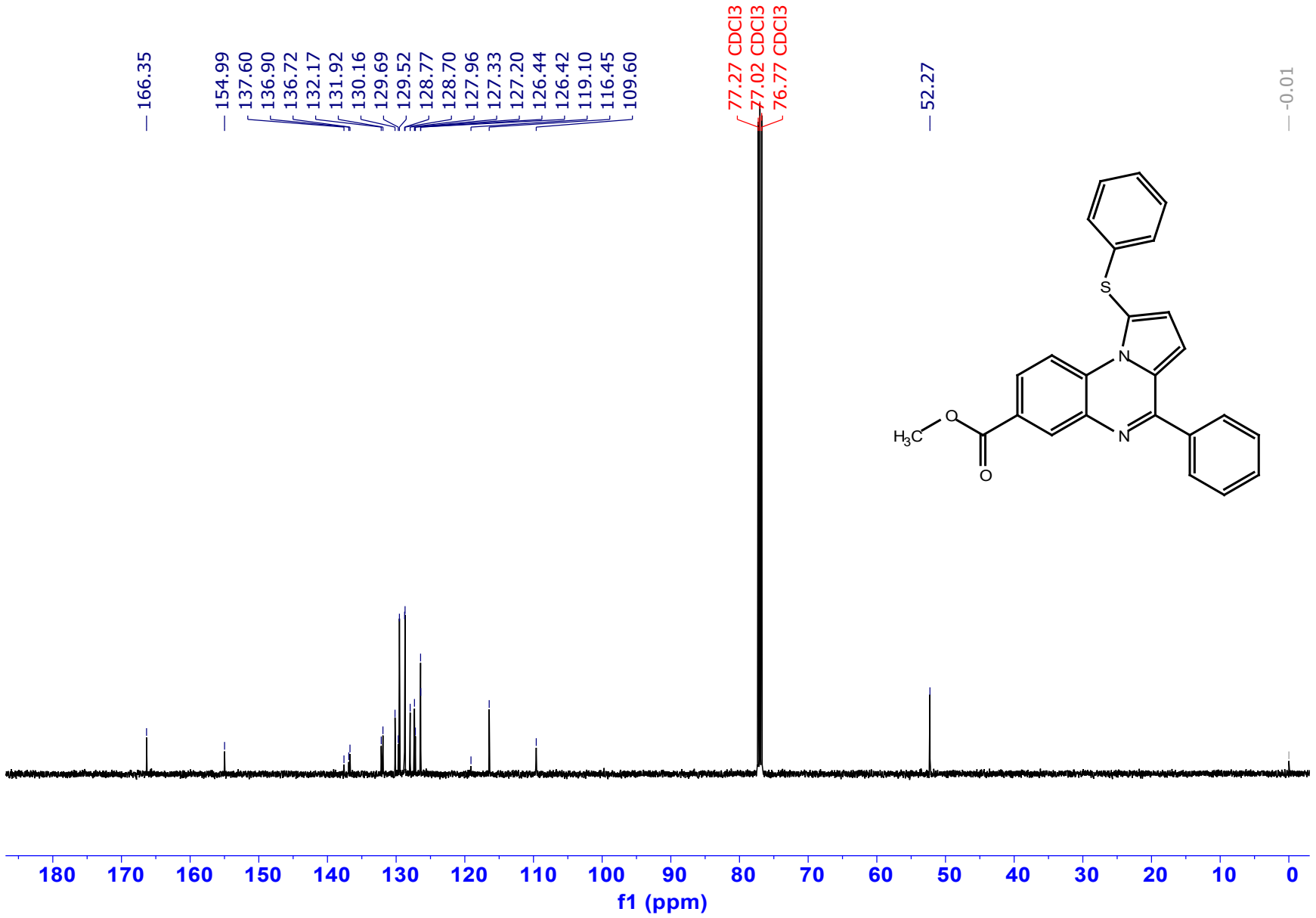
^{13}C NMR spectrum of 7-fluoro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



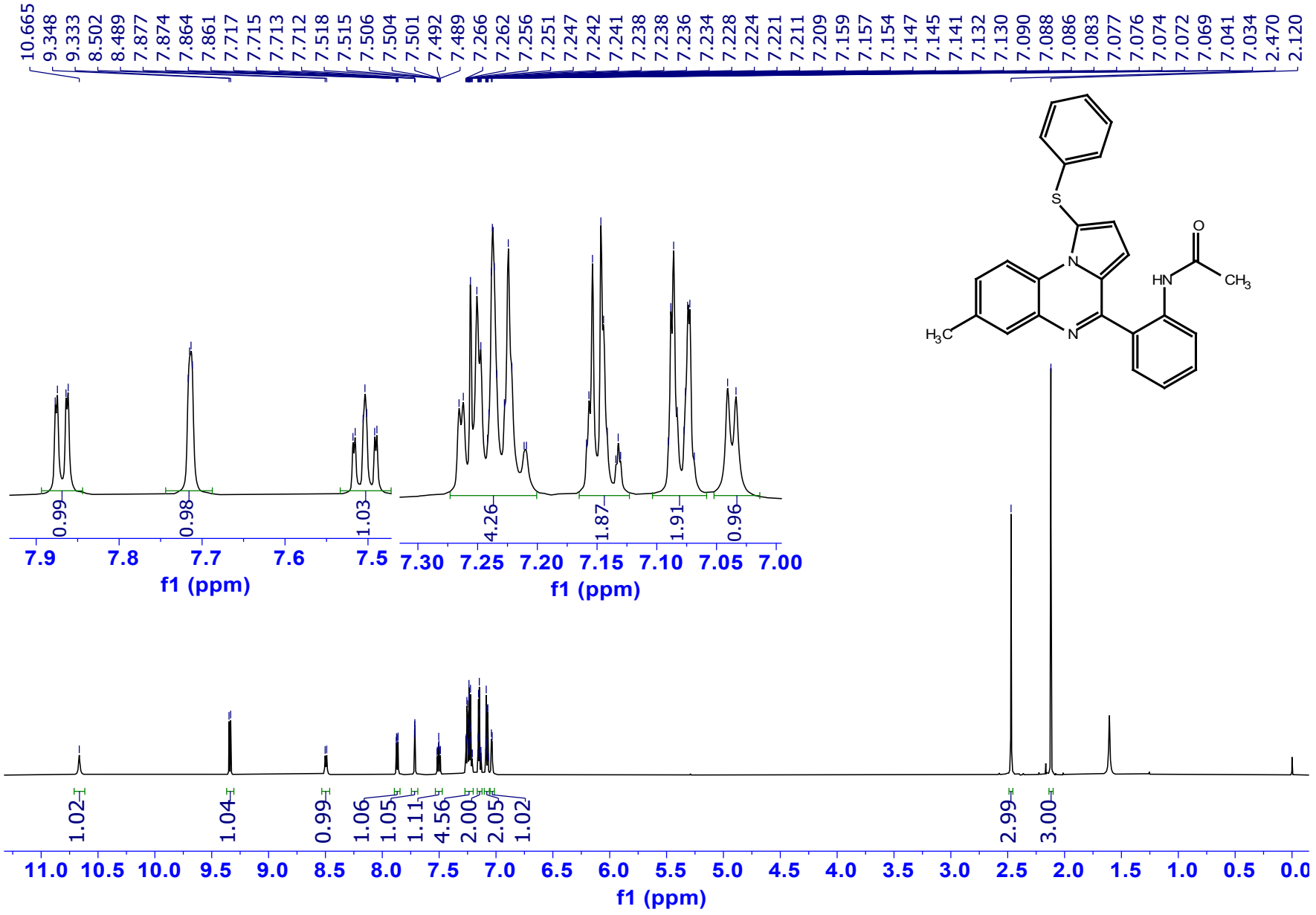
^{19}F NMR spectrum of 7-fluoro-4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



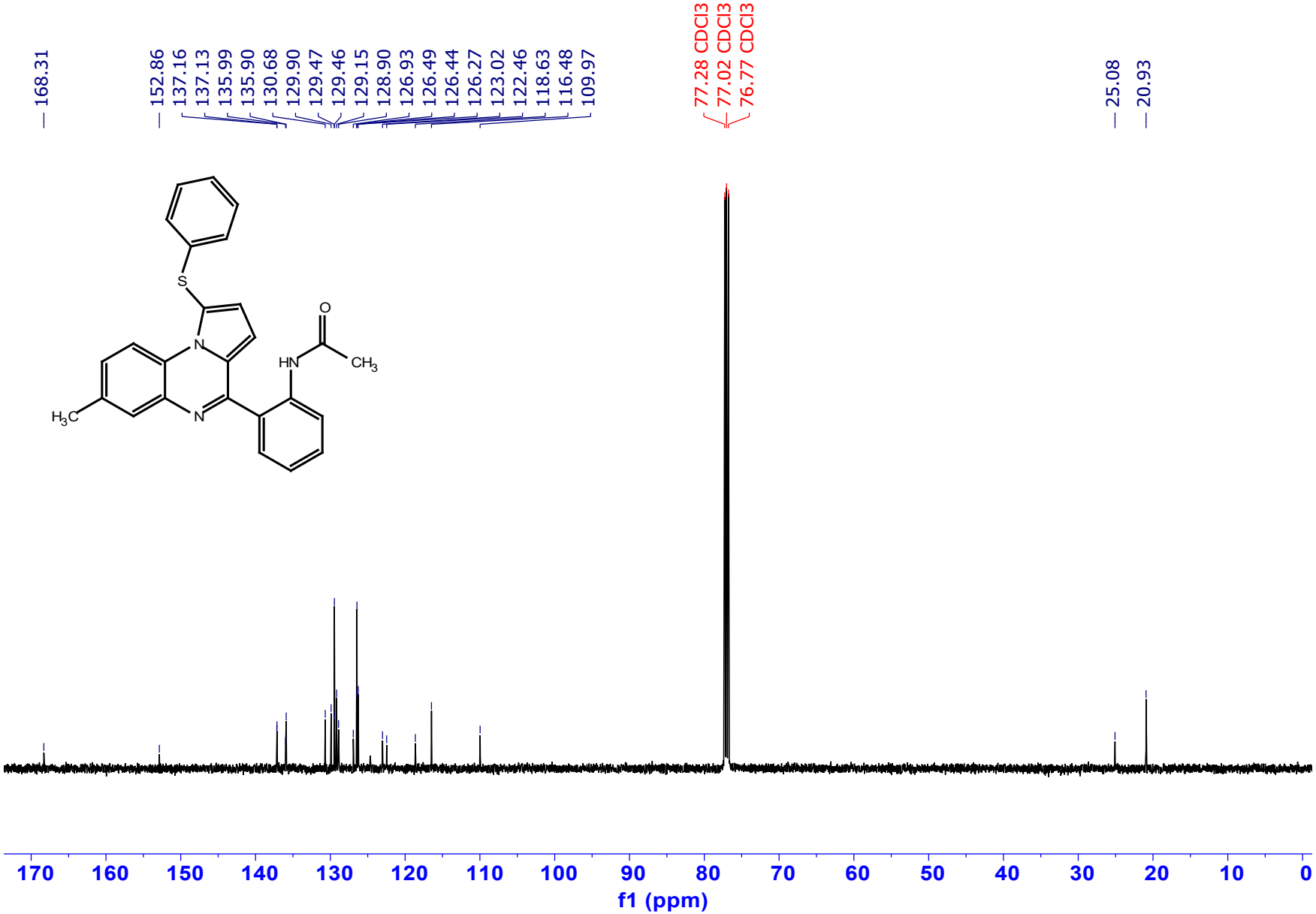
^{1}H NMR spectrum of methyl 4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline-7-carboxylate.



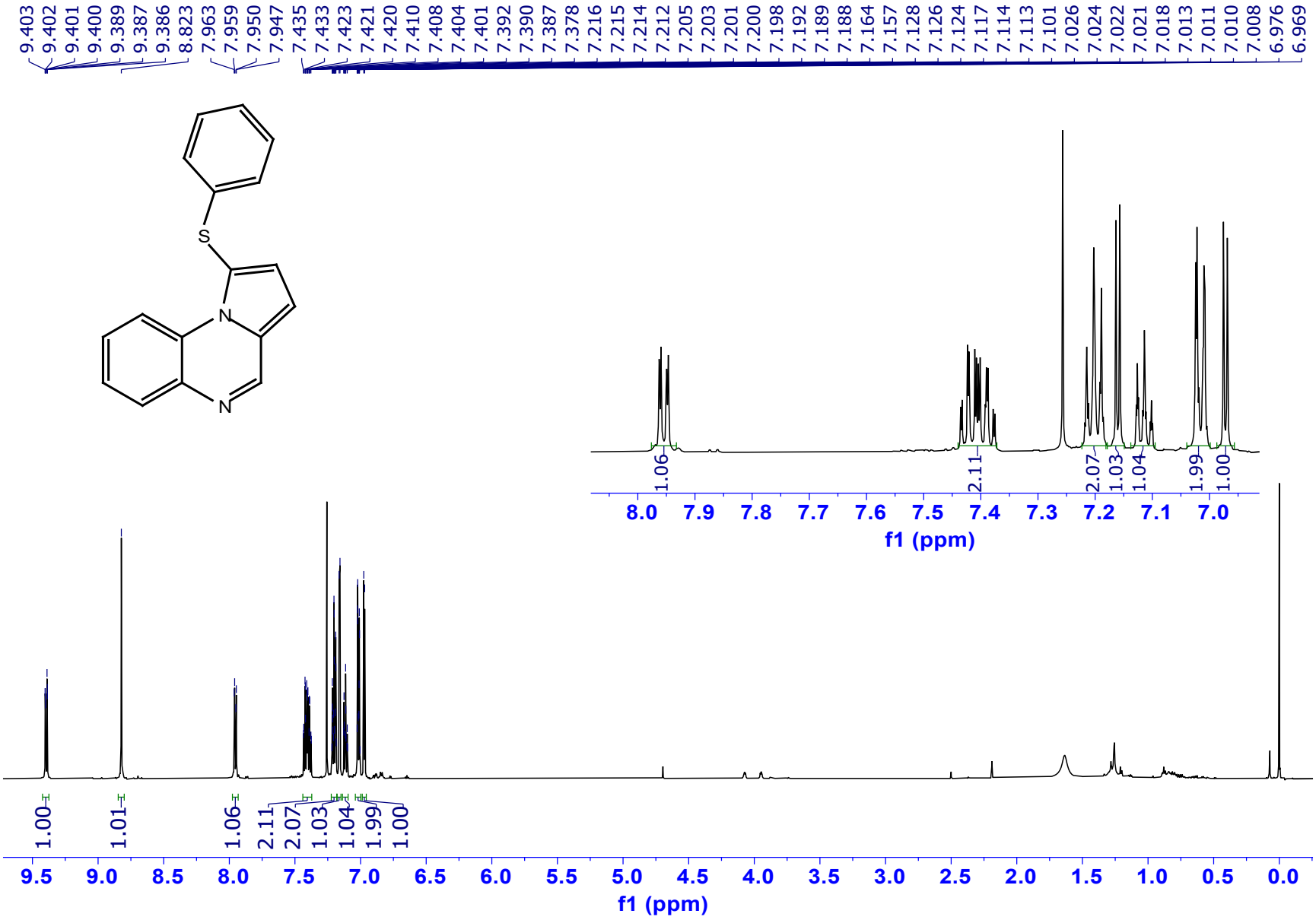
^{13}C NMR spectrum of methyl 4-phenyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline-7-carboxylate.



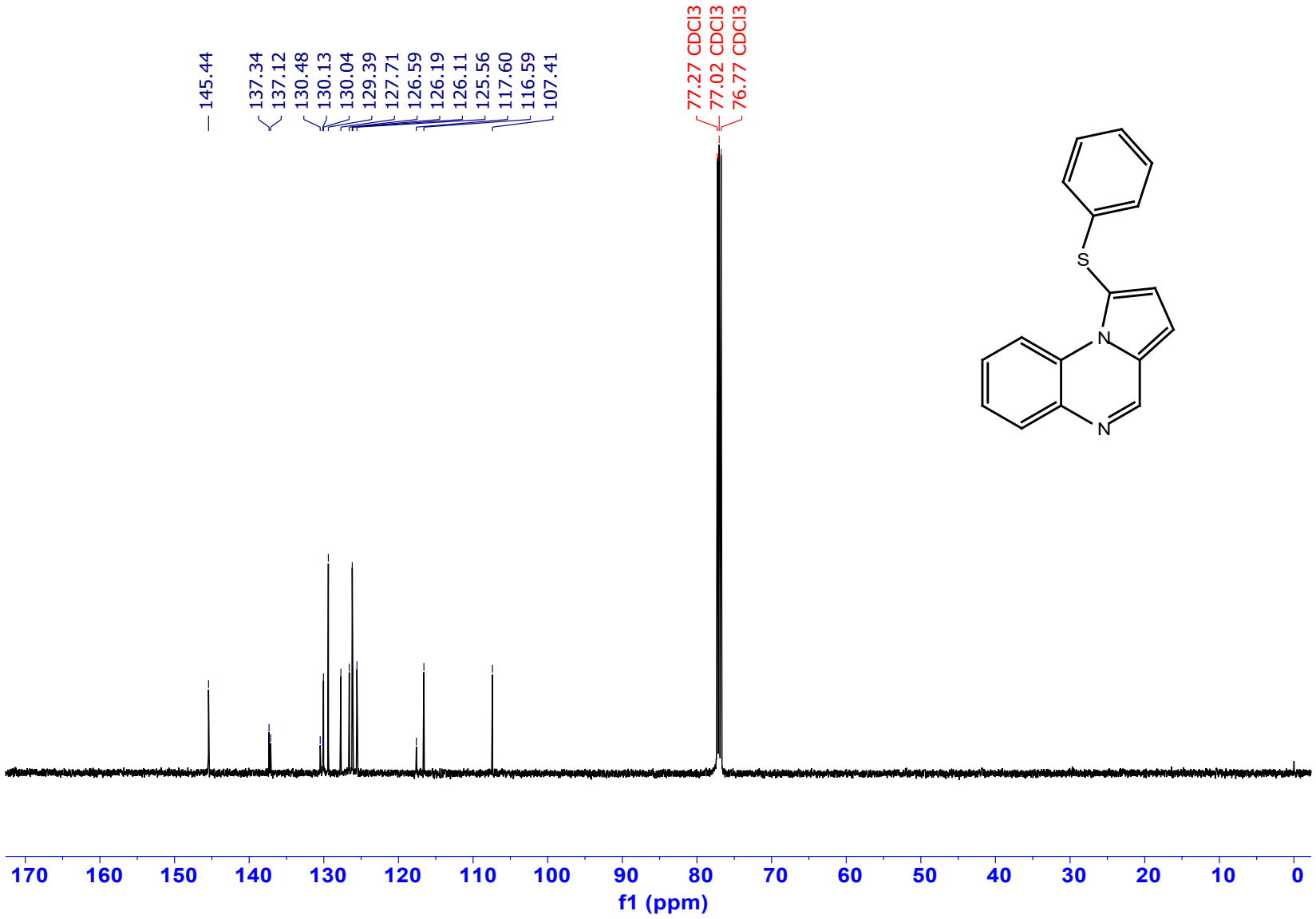
^{1}H NMR spectrum of *N*-(2-(7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl)acetamide.



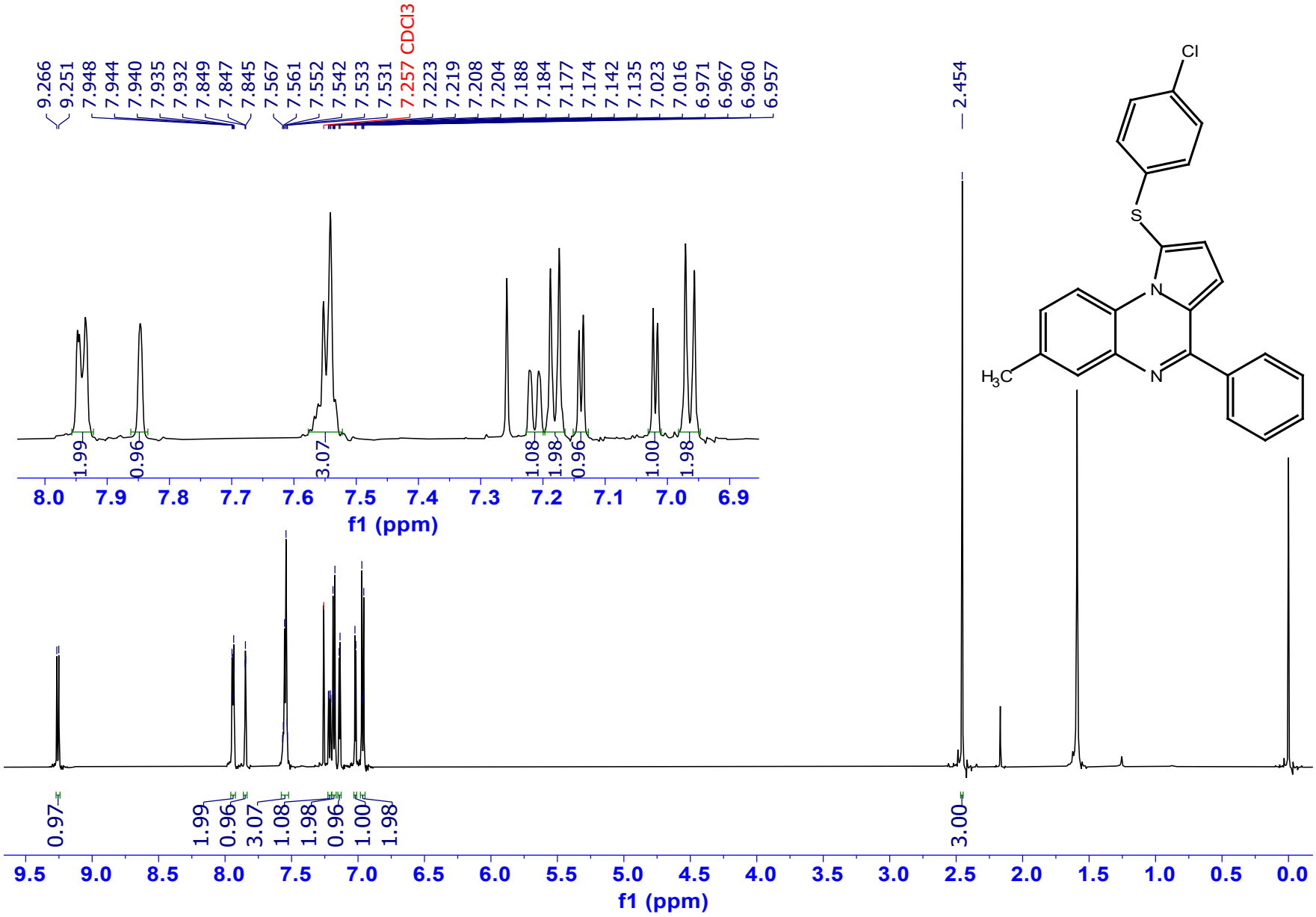
^{13}C NMR spectrum of *N*-(2-(7-methyl-1-(phenylthio)pyrrolo[1,2-*a*]quinoxalin-4-yl)phenyl)acetamide.



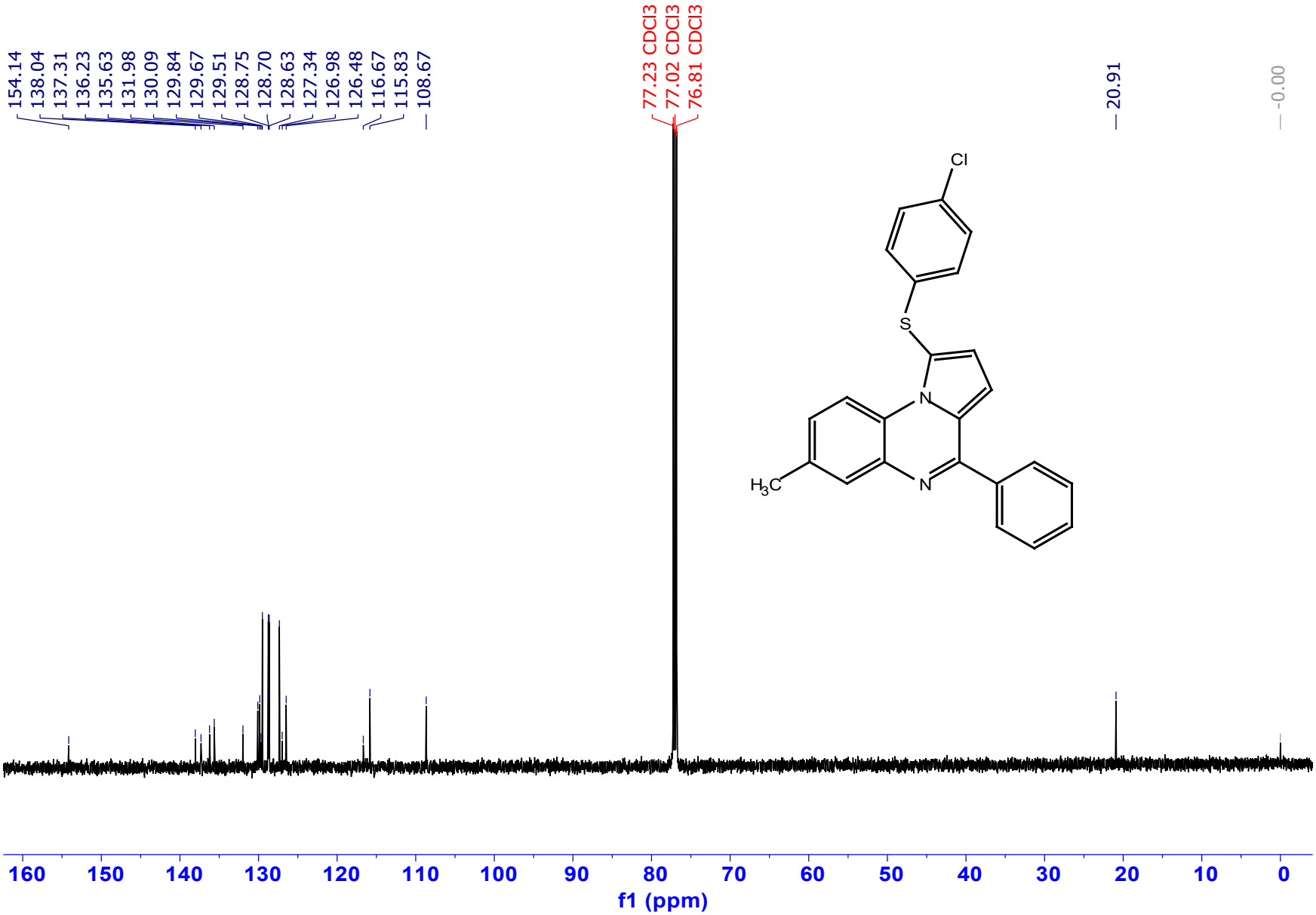
^{1}H NMR spectrum of 1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



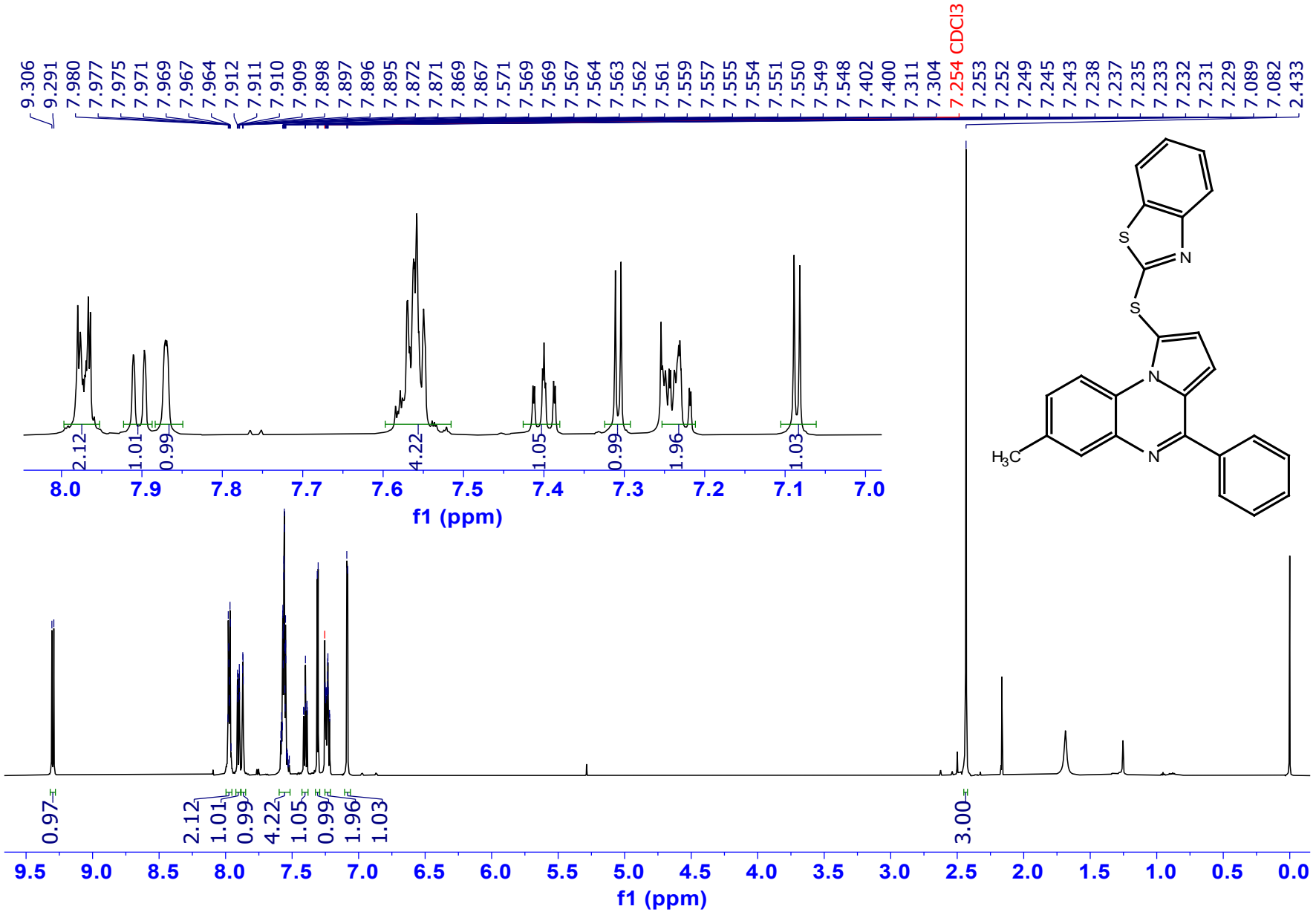
^{13}C NMR spectrum of 1-(phenylthio)pyrrolo[1,2-*a*]quinoxaline.



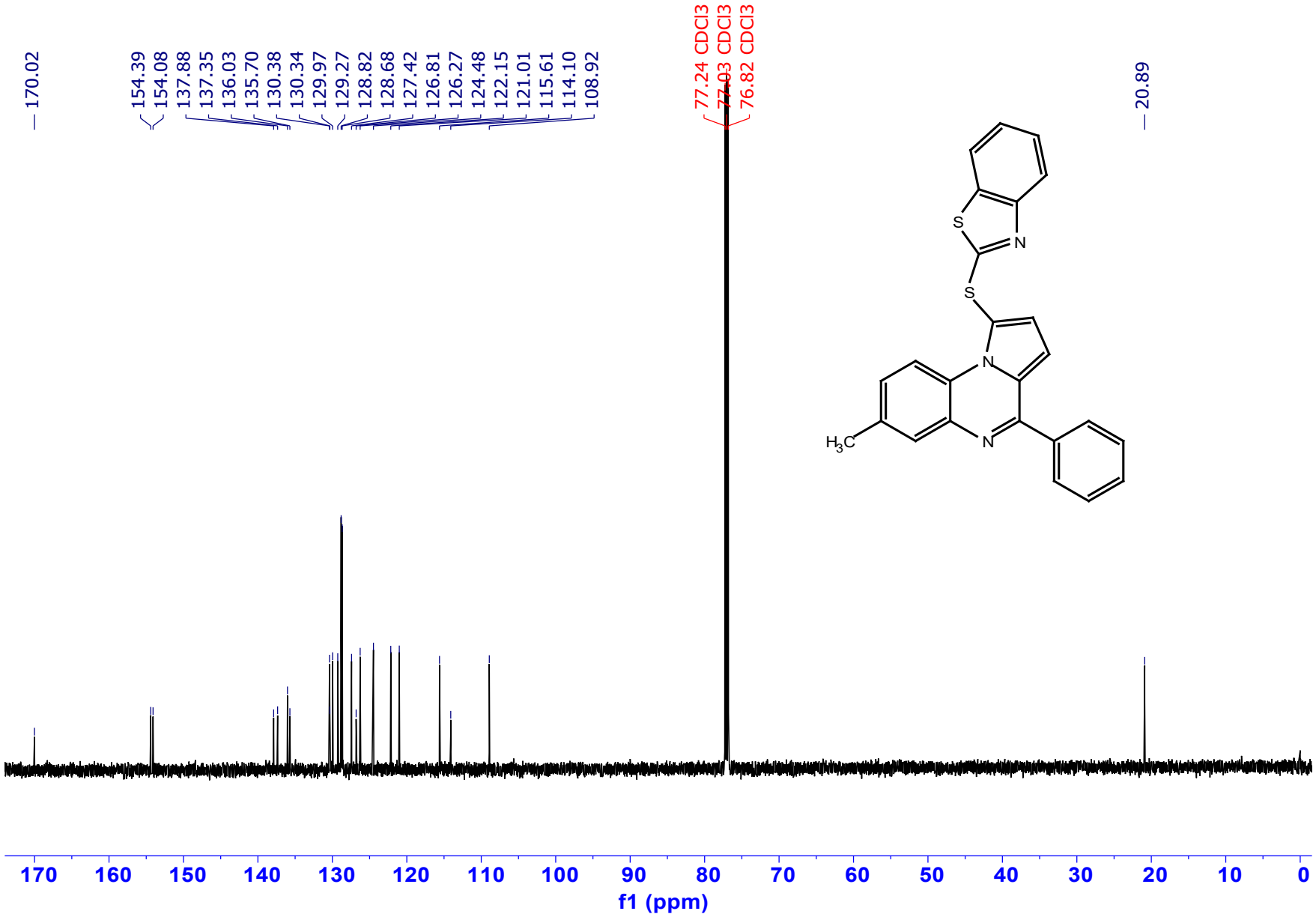
^{1}H NMR spectrum of 1-((4-chlorophenyl)thio)-7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline.



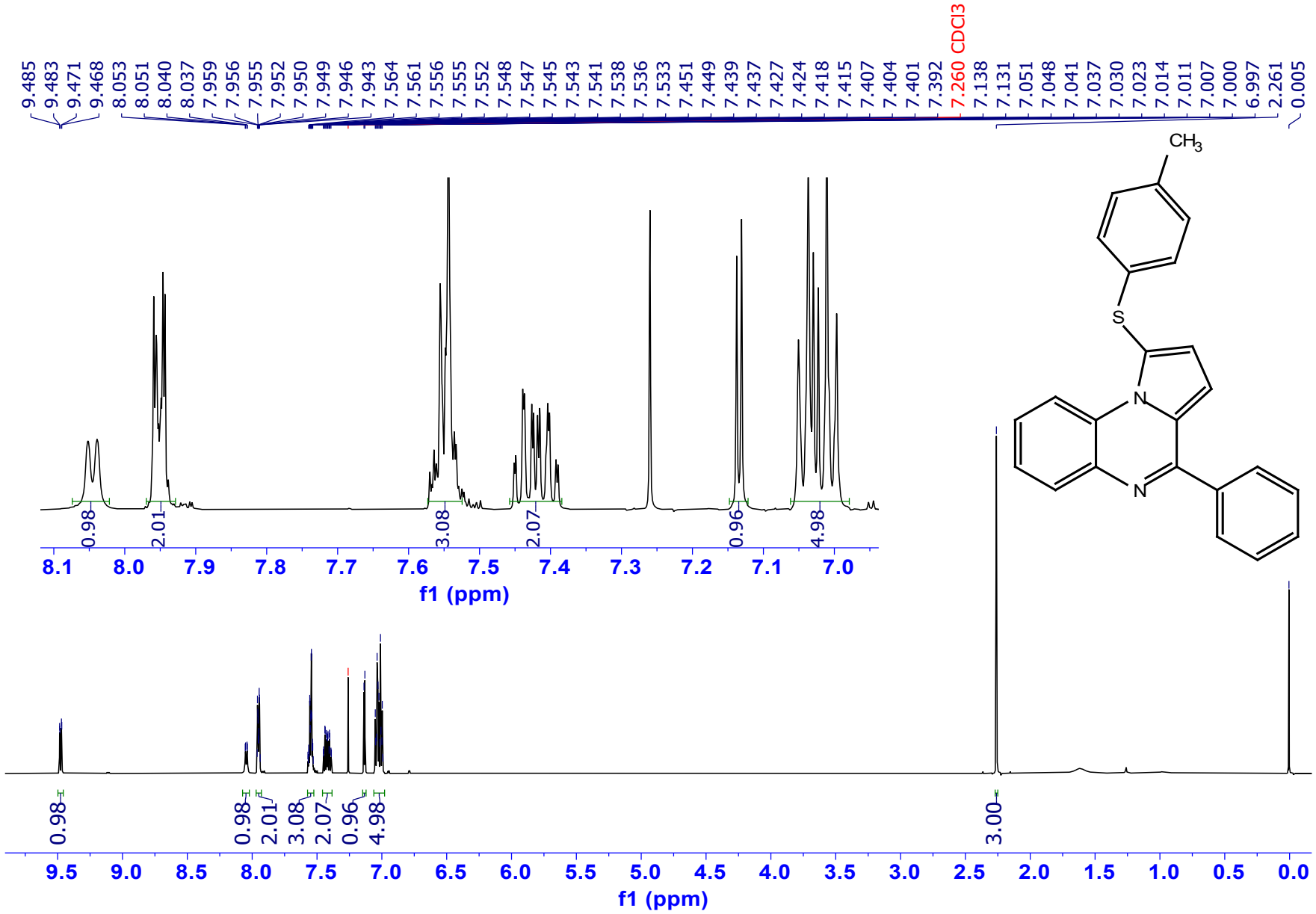
^{13}C NMR spectrum of 1-((4-chlorophenyl)thio)-7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline.



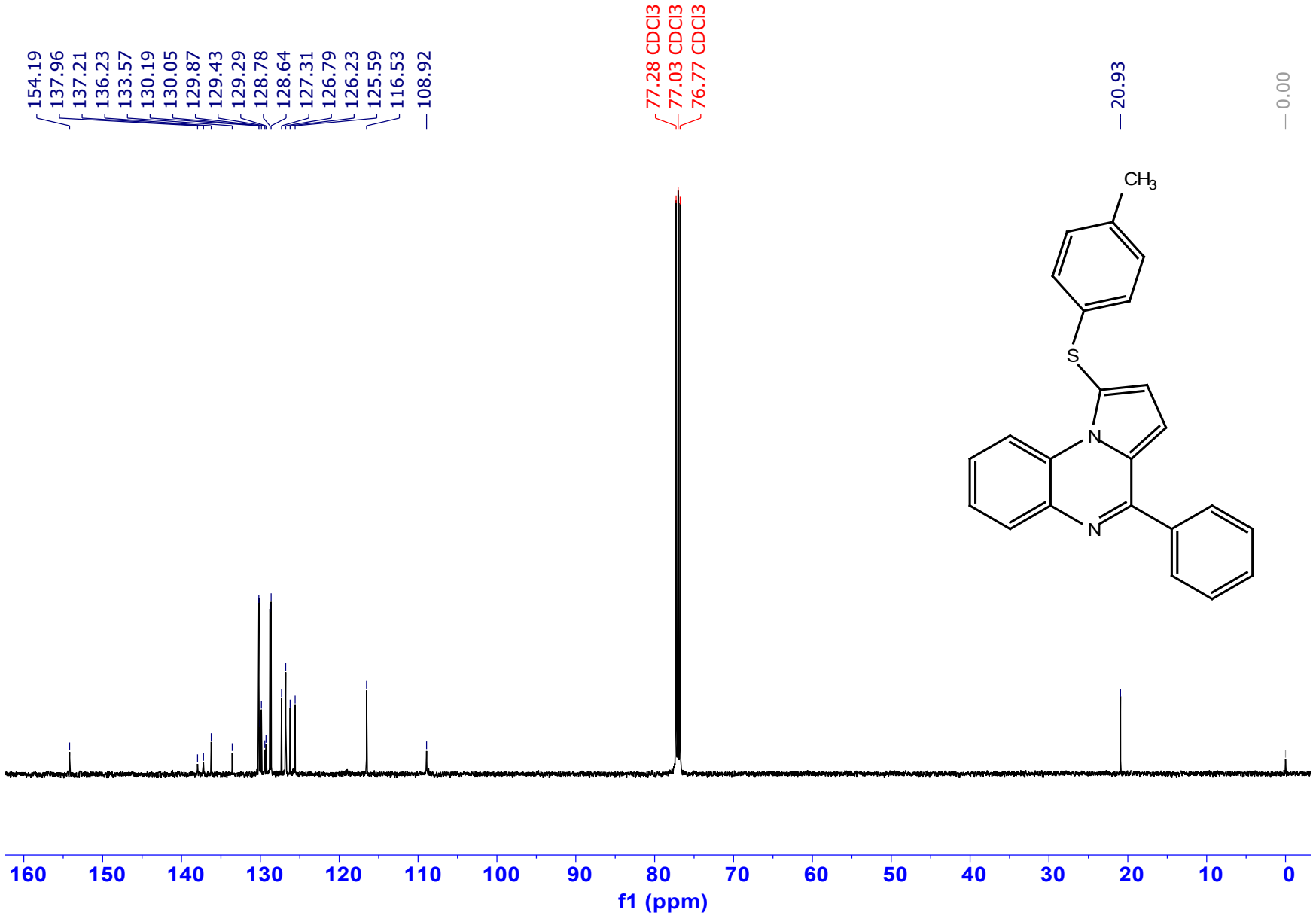
^{1}H NMR spectrum of 2-((7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)benzo[*d*]thiazole.



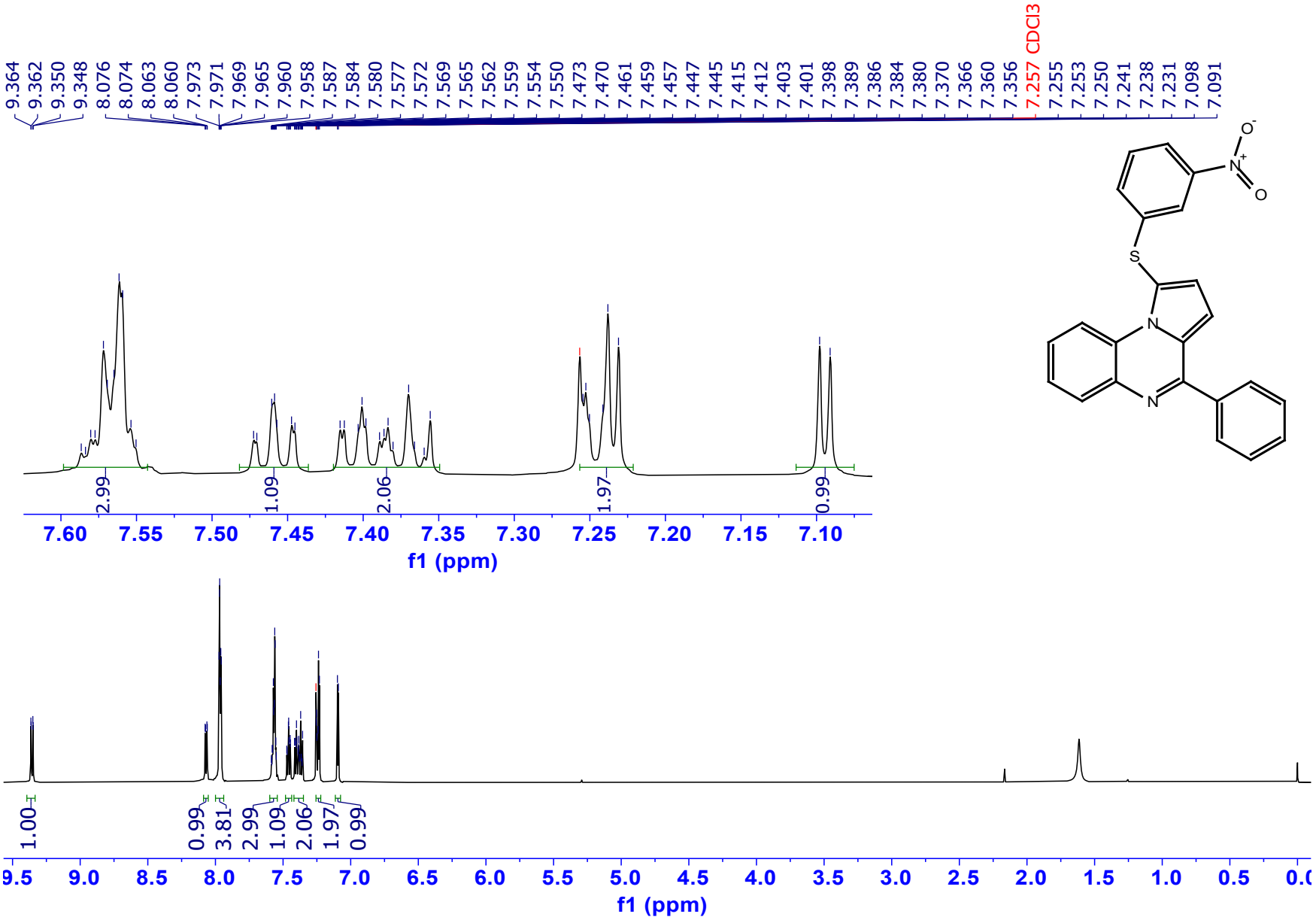
^{13}C NMR spectrum of 2-((7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)benzo[*d*]thiazole.



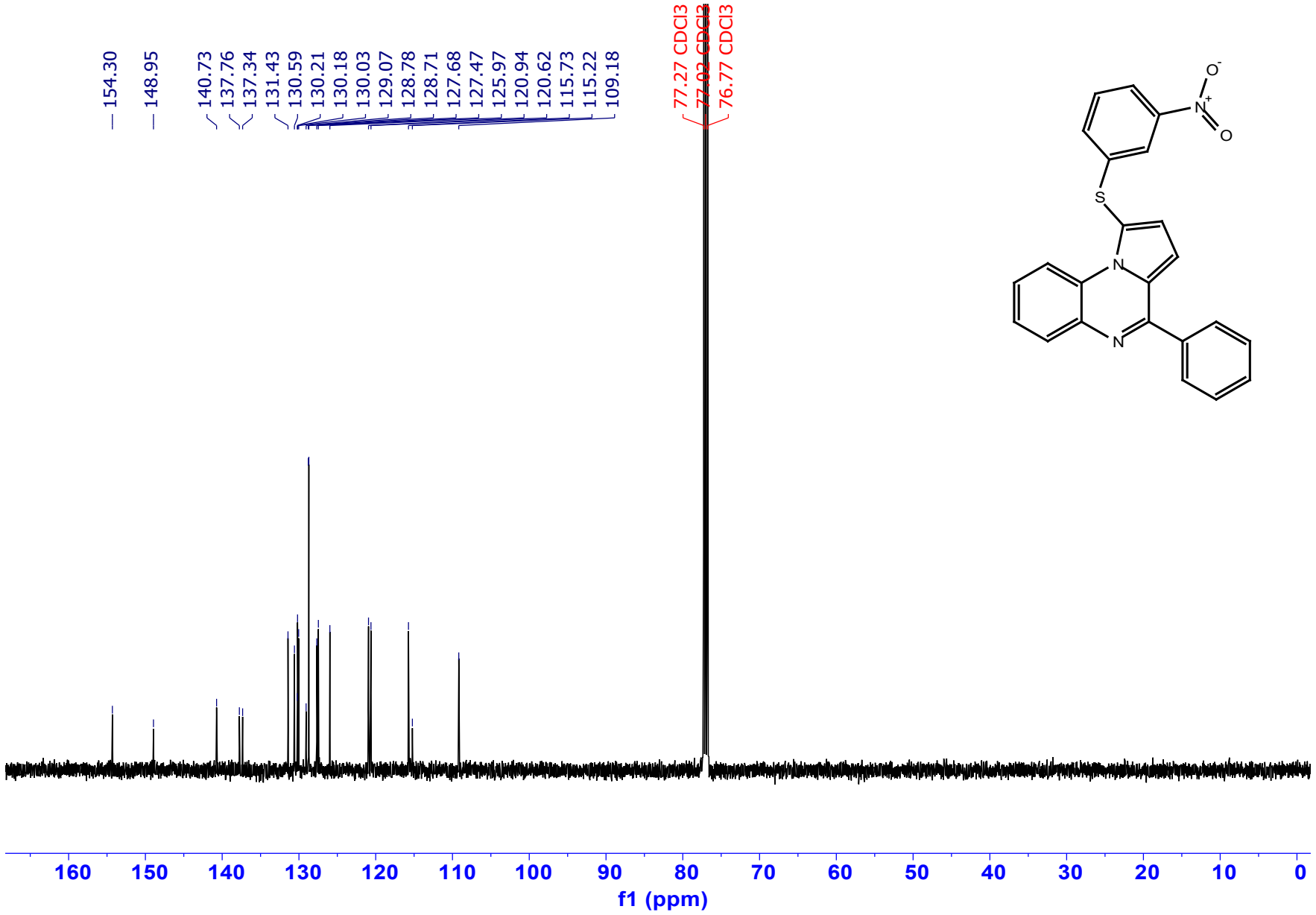
^{1}H NMR spectrum of 4-phenyl-1-(*p*-tolylthio)pyrrolo[1,2-*a*]quinoxaline.



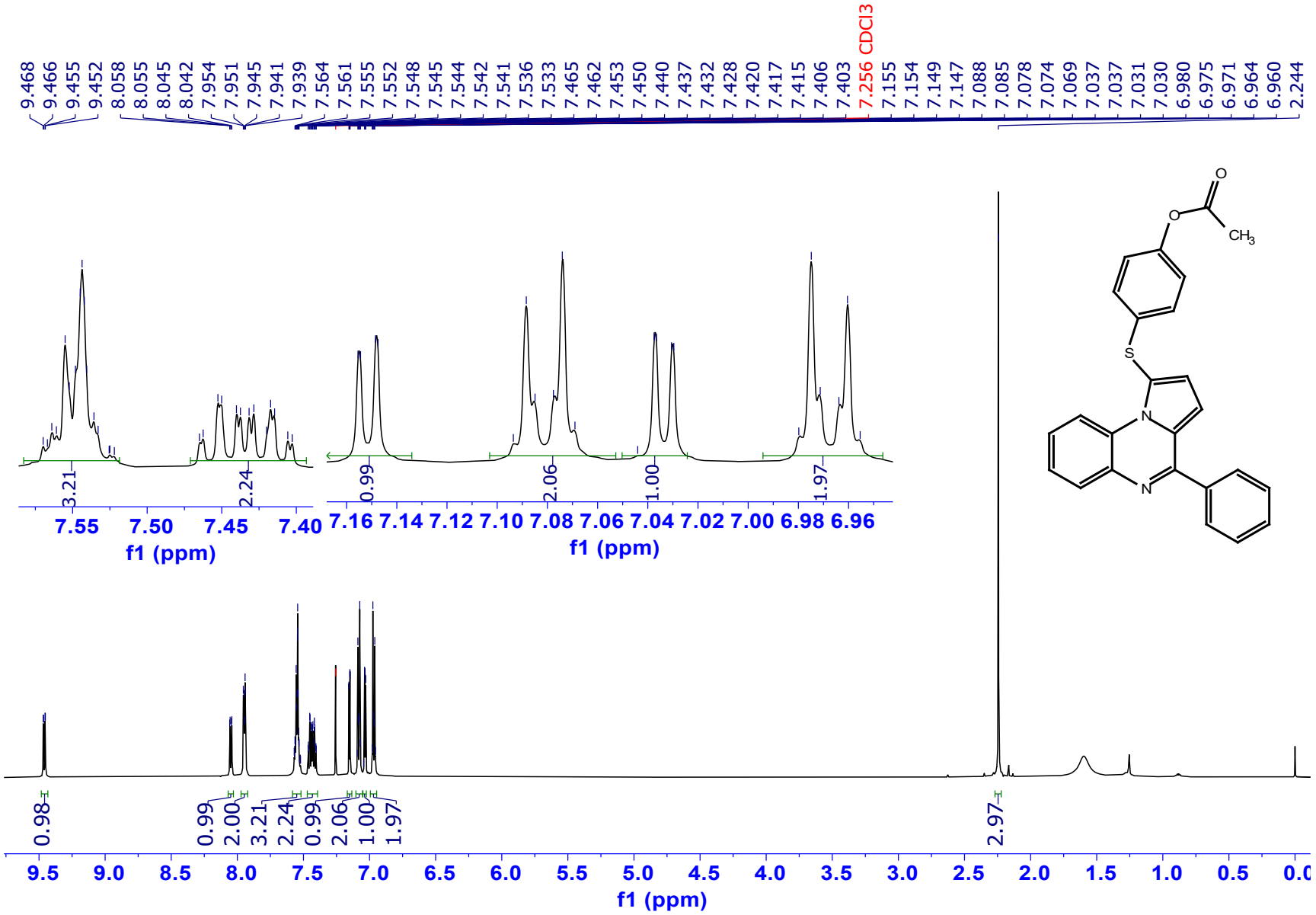
^{13}C NMR spectrum of 4-phenyl-1-(*p*-tolylthio)pyrrolo[1,2-*a*]quinoxaline.



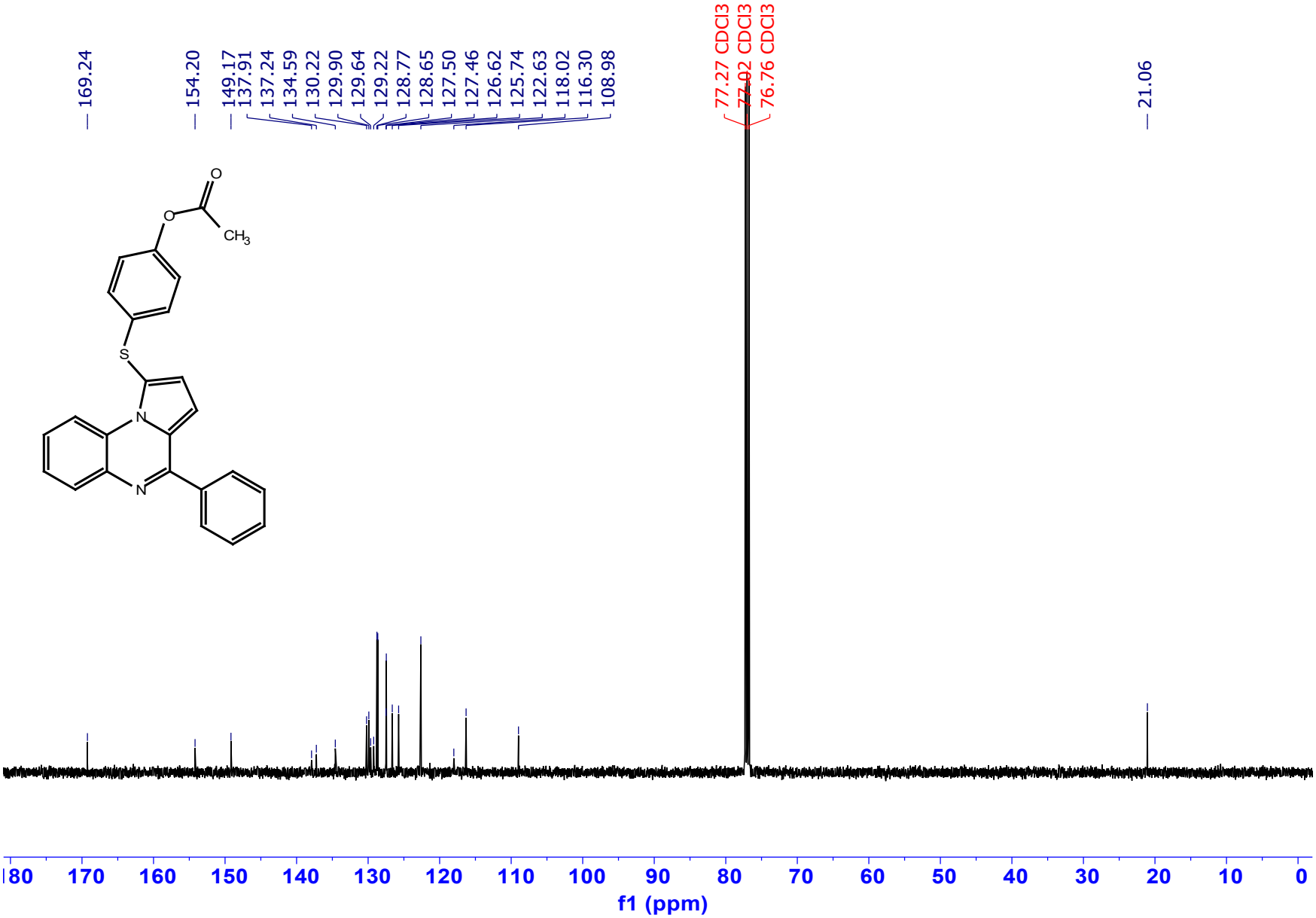
^{1}H NMR spectrum of 1-((3-nitrophenyl)thio)-4-phenylpyrrolo[1,2-*a*]quinoxaline.



^{13}C NMR spectrum of 1-((3-nitrophenyl)thio)-4-phenylpyrrolo[1,2-*a*]quinoxaline.



1H NMR spectrum of 4-((4-phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)phenyl acetate.



^{13}C NMR spectrum of 4-((4-phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)thio)phenyl acetate.