Palladium-Catalyzed Amination of Unprotected Halo-7-azaindoles

Jaclyn L. Henderson, Sarah M. McDermott, Stephen L. Buchwald*

Department of Chemistry, Massachusetts Institute of Technology

Cambridge, MA 02139

sbuchwal@mit.edu

General Reagent Information: All reactions were set up in the air and carried out in screw-cap test-tubes with Teflon seals under an atmosphere of argon. Flash chromatography was performed using a) silica gel from American International Chemical or b) a Biotage Isolera instrument with prepacked 10 g silica cartridges. LiHMDS solutions in THF and toluene were purchased from Aldrich in Sure-Seal bottles and used as received. The *tert*-butanol, toluene and 1,4-dioxane were purchased from Aldrich Chemical Co. in Sure-Seal bottles and used as received. $Pd(OAc)_2$ was a gift from BASF. All heteroaryl halides and amines were purchased from Aldrich, Alfa, Matrix or Frontier and used as supplied without further purification. Anhydrous cesium carbonate was a gift from Chemetall and the anhydrous tribasic potassium phosphate, as well as the potassium carbonate were purchased from Fluka Chemical Co. The bases were stored in a nitrogen- filled glovebox and removed in small quantities and stored on the bench for up to two weeks. Ligands (**L1** and **L5**) and precatalysts (**P1** – **P5**) were synthesized using literature procedures,[1,2] or purchased from Strem (**L2 - L4**).

General Analytical Information. Isolated yields are quoted for compounds of greater than 95% purity as determined by LCMS and ^{1}H NMR. All yields reported are for an average of two experiments. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, melting point, and in many cases, elemental analysis. Nuclear Magnetic Resonance spectra were recorded on a Bruker DRX 400 spectrometer operating at 400 MHz in deuterochloroform, deuterodimethylsulfoxide or deuteromethanol. ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 100 MHz. ^{19}F NMR spectra (where applicable), were recorded on a Bruker DRX 400 spectrometer

operating at 400 MHz. Chemical shifts are quoted relative to residual solvent [7.26 ppm (^{1}H) and 77.0 ppm (^{13}C) for $CHCl_3$, 2.54 ppm (^{1}H) and 39.5 ppm (^{13}C) for DMSO, 3.31 ppm (^{1}H) and 49.0 ppm (^{13}C) for MeOH] and coupling constants (*J*) are given in Hz to the nearest 0.5 Hz. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet and br broad. NMR spectra were acquired at 300 K unless otherwise indicated. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer as thin films on KBr plates. Selected absorption maxima (υmax) are reported in wavenumbers (cm^{-1}). Melting points were determined on an SRS EZ-Melt MPA-120 and are uncorrected. Elemental analyses were performed by Atlantic Microlabs.

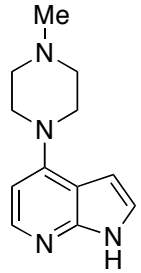
General Procedure A: Secondary amines

A screw-cap test-tube, equipped with a magnetic stir bar, was charged with RuPhos (**L1**) (2.3 mg, 1 mol %) and RuPhos precatalyst (**P1**) (3.6 mg, 1 mol %). The vial was sealed with a teflon screw-cap, then evacuated and backfilled with argon. LiHMDS (1M in THF) was added *via* syringe, followed by the heteroaryl halide (0.5 mmol) and amine (0.6 mmol, 1.2 equiv.) (heteroaryl halides or amines that were solids at room temperature were added with the catalyst). The reaction mixture was heated at 65 ˚C for 4 h. The solution was allowed to cool to room temperature, then quenched by the addition of 1M HCl (1 mL), diluted with EtOAc and poured into sat. $NaHCO_3$. After extracting with 3 portions of EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$, then concentrated. The crude product was purified on a Biotage Isolera system (10 g column), by flash column chromatography or by trituration.

General Procedure B: Primary amines

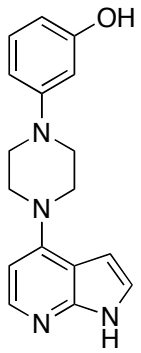
A screw-cap test-tube, equipped with a magnetic stir bar, was charged with BrettPhos (**L3**) (2.8 mg, 1 mol %) and BrettPhos precatalyst (**P3**) (4.0 mg, 1 mol %). The vial was sealed with a teflon screw-cap, evacuated and backfilled with argon. LiHMDS (1M in THF) was added *via* syringe, followed by the heteroaryl halide (0.5 mmol) and amine (0.6 mmol, 1.2 equiv.) (heteroaryl halides or amines that were solids at room temperature were added with the catalyst.) The reaction mixture was heated at 65 ˚C for 4 h. The

solution was allowed to cool to room temperature, quenched by the addition of 1M HCl (1 ml), diluted with EtOAc and poured into sat. $NaHCO_3$. After extracting with 3 portions of EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$, then concentrated. The crude product was purified on a Biotage Isolera system (10 g column), by flash column chromatography or by trituration.



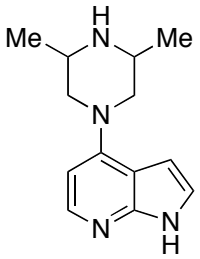
4-(4-Methylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1a)

A screw-cap test-tube, equipped with a magnetic stir bar, was charged with RuPhos (**L1**) (1.1 mg, 0.5 mol %), RuPhos precatalyst (**P1**) (1.8 mg, 0.5 mol %) and 4-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg, 0.5 mmol). The vial was sealed with a teflon screw-cap, evacuated and filled with argon. LiHMDS (1.2 mL, 2.4 quiv. 1M in THF) was added via syringe, followed by *N*-methyl piperazine (66 μL, 0.6 mmol, 1.2 equiv.). The reaction mixture was heated at 65 ˚C for 30 min. The solution was allowed to cool to room temperature, then quenched by the addition of 1 mL HCl (1M), diluted with EtOAc and poured into sat. $NaHCO_3$. After extracting with 3 portions of EtOAc, the combined organics were washed with brine, dried over $MgSO_4$, then concentrated. The crude product was purified *via* chromatography on silica (5% 2M NH_3 in MeOH/DCM) to provide the title compound as a light yellow solid, 101 mg, 94%. m.p. 169 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.38 (s, 1H), 7.89 (d, J = 5.4 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.37 (dd, *J* = 18.4, 4.5 Hz, 2H), 3.46-3.12 (m, 4H), 2.44 (dd, *J* = 6.8, 3.1 Hz, 4H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.72, 150.47, 143.66, 122.20, 110.73, 101.85, 99.95, 55.06, 49.26, 46.29 ppm. IR (KBr disc, cm-1): 3409, 2940, 2835, 2788, 1597, 1578, 1449, 1372, 1330, 1253, 1141, 1108, 1020, 1009, 899, 824, 813, 786, 718, 642.



3-(4-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)piperazin-1-yl)phenol (1b)

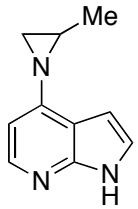
Following general procedure A using 4-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 3-(piperazin-1-yl)phenol (107 mg) and LiHMDS (1.7 mL, 3.4 equiv.). The crude product was purified *via* trituration with EtOAc, to provide the title compound as a yellow powder 135 mg, 92%. m.p. 217 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.51 (s, 1H), 9.26 (s, 1H), 8.02 (d, *J* = 5.4 Hz, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.06 (t, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.48 (dd, *J* = 10.3, 3.6 Hz, 2H), 6.42 (d, *J* = 1.9 Hz, 1H), 6.30 (dd, *J* = 7.9, 1.7 Hz, 1H), 3.62 - 3.49 (m, 5H), 3.37 - 3.25 (m, 5H), 3.19 (dd, *J* = 19.1, 5.1 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 158.19, 152.34, 150.60, 149.95, 143.85, 129.67, 122.49, 109.87, 106.69, 106.42, 102.55, 101.45, 99.62, 48.68, 48.23 ppm. IR (KBr disc, cm^{-1}): 3325, 2921, 2827, 1653, 1576, 1559, 1507, 1498, 1457, 1247, 1191, 996, 975.



4-(3,5-Dimethylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1c)

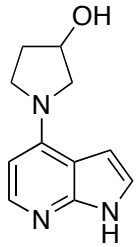
Following general procedure A using 4-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg), 2,6-dimethylpiperazine (68 mg) and LiHMDS (1.7 mL, 3.4 equiv.). The crude product was purified *via* trituration with EtOAc, to provide the title compound as a cream solid, 114 mg, 99%. m.p. 200 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.43 (s, 1H), 7.92 (d, *J* = 5.4 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 6.44 (d, *J* = 3.5 Hz, 1H), 6.39 (d, *J* = 5.5 Hz, 1H), 3.79 (d,

J = 11.1 Hz, 2H), 3.03 - 2.86 (m, 2H), 2.45 (t, *J* = 11.1 Hz, 2H), 1.06 (d, *J* = 6.3 Hz, 6H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 150.50, 150.01, 143.83, 122.25, 109.67, 101.44, 99.67, 55.15, 50.24, 18.92 ppm. IR (KBr disc, cm^{-1}): 3396, 3259, 2970, 1585, 1513, 1452, 1382, 1325, 1262, 1228, 1159, 1088, 1056, 889, 842, 781. Anal. Calcd for $C_{13}H_{18}N_4$: C, 67.80; H, 7.88; Found: C, 67.33; H, 8.01.



4-(2-Methylaziridin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1d)

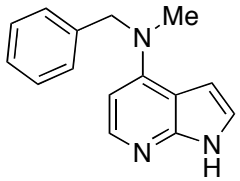
Following general procedure A using 4-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg), 2-methylaziridine (53 μL) and LiHMDS (1.2 mL, 2.4 equiv.). This compound was purified by applying the reaction directly to silica (no work-up) as it is somewhat unstable to HCl. The crude product was purified *via* chromatography on silica (3% MeOH/DCM), to provide the title compound as a light yellow powder, 78 mg, 91%. m.p. 155 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.41 (s, 1H), 8.17 (d, *J* = 5.3 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 6.61 (d, *J* = 5.3 Hz, 1H), 6.57 (d, *J* = 3.4 Hz, 1H), 2.50 - 2.35 (m, 1H), 2.30 (d, *J* = 6.1 Hz, 1H), 2.22 (d, *J* = 3.4 Hz, 1H), 1.49 (d, *J* = 5.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.17, 150.09, 143.19, 123.64, 114.09, 106.49, 98.03, 35.00, 34.71, 18.30 ppm. IR (KBr disc, cm^{-1}): 3134, 2991, 1586, 1499, 1415, 1350, 1217, 1052, 877, 822, 789, 721. Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; Found: C, 69.09; H, 6.45.



1-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)pyrrolidin-3-ol (1e)

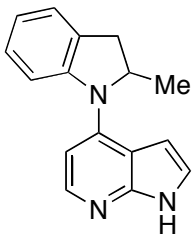
Following general procedure A using 4-chloro-1H-pyrrolo[2,3-b]pyridine (76 mg), pyrrolidin-3-ol (49 μL) and LiHMDS (1.7 mL, 3.4 equiv.). The crude product was

purified *via* trituration with EtOAc, to provide the title compound as a light yellow solid, 65 mg, 64%. m.p. 166 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.20 (s, 1H), 7.77 (d, *J* = 5.5 Hz, 1H), 7.18 - 6.83 (m, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 5.96 (d, *J* = 5.6 Hz, 1H), 5.03 (s, 1H), 3.81 - 3.50 (m, 3H), 3.50 - 3.22 (m, 2H), 2.17 - 1.69 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 149.80, 147.30, 143.80, 120.38, 106.99, 100.55, 97.78, 69.12, 57.32, 46.83, 33.52 ppm. IR (KBr disc, cm^{-1}): 3198, 2919, 2850, 1589, 1506, 1474, 1427, 1377, 1265, 1217, 1178, 1102, 980, 916, 770, 699.



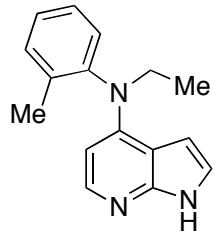
_N_-Benzyl-_N_-methyl-1_H_-pyrrolo[2,3-_b_]pyridin-4-amine (1f)

Following general procedure A using 4-chloro-1H-pyrrolo[2,3-b]pyridine (76 mg), *N*-methylbenzylamine (77 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica eluting with 5% MeOH/DCM, to provide the title compound as a light yellow solid, 114 mg, 96%. m.p. 168 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.20 (d, *J* = 69.9 Hz, 1H), 7.80 (t, *J* = 14.3 Hz, 1H), 7.38 - 7.29 (m, 3H), 7.24 (dd, *J* = 9.2, 3.9 Hz, 4H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.39 (d, *J* = 3.6 Hz, 1H), 6.20 (d, *J* = 5.6 Hz, 1H), 4.80 (s, 3H), 3.17 (s, 4H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 150.12, 149.64, 143.83, 138.73, 128.60, 126.87, 126.57, 121.13, 107.24, 100.49, 98.93, 56.10. IR (KBr disc, cm^{-1}): 3083, 1593, 1577, 1523, 1450, 1413, 1376, 1358, 1326, 1204, 1049, 926, 843, 726, 668. Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; Found: C, 75.66; H, 6.32.



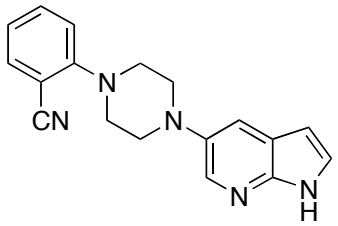
4-(2-Methylindolin-1-yl)-1_H_-pyrrolo[2,3-b]pyridine (1g)

Following general procedure A using 4-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg), 2-methylindoline (78 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 2% MeOH/DCM, to provide the title compound as a lilac solid, 116 mg, 93%. m.p. 194 °C. ^{1}H NMR (400 MHz, DMSO) δ: 11.58 (s, 1H), 8.06 (d, *J* = 5.3 Hz, 1H), 7.30 (s, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 5.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 2H), 6.23 (d, *J* = 2.5 Hz, 1H), 4.72 (m, 1H), 3.31 (m, 1H), 2.74 (dd, *J* = 15.7, 7.2 Hz, 1H), 1.20 (d, *J* = 6.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 150.48, 146.70, 143.50, 142.37, 129.97, 126.76, 124.97, 123.75, 119.58, 112.61, 109.84, 105.88, 99.92, 58.59, 36.68, 19.89 ppm. IR (KBr disc, cm^{-1}): 3131, 2928, 1576, 1504, 1481, 1458, 1362, 1283, 1112, 894, 794, 742. Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; Found: C, 76.82; H, 6.16.



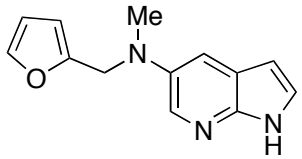
_N_-Ethyl-_N_-(_o_-tolyl)-1_H_-pyrrolo[2,3-b]pyridin-4-amine (1h)

Following general procedure A using 4-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg), N-ethyl-2-methylaniline (86 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 3% MeOH in DCM, to provide the title compound as a cream solid, 84 mg, 67%. m.p. 217 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.16 (s, 1H), 8.04 (d, *J* = 5.8 Hz, 1H), 7.44-7.10 (m, 4H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.42-6.10 (m, 1H), 4.95 (s, 1H), 3.90 (dd, *J* = 38.1, 6.9 Hz, 2H), 2.13 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.05, 148.44, 144.77, 143.25, 137.47, 131.39, 129.97, 127.62, 127.20, 120.65, 108.04, 100.42, 98.57, 47.16, 17.97, 12.61 ppm. IR (KBr disc, cm^{-1}): 3021, 3005, 1570, 1540, 1507, 1457, 1329, 820, 727, 668. Anal. Calcd for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82; Found: C, 76.32; 6.64.



2-(4-(1*H*-Pyrrolo[2,3-b]pyridin-5-yl)piperazin-1-yl)benzonitrile (2a)

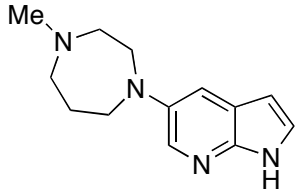
Following general procedure A using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 2-(piperazin-1-yl)benzonitrile (112 mg), RuPhos (**L1**) (4.6 mg, 2 mol %), RuPhos precatalyst (**P1**) (7.2 mg, 2 mol %) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 2% MeOH in DCM, to provide the title compound as a yellow powder, 142 mg, 94%. m.p. 213 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.41 (s, 1H), 8.13 (d, *J* = 2.6 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.68-7.60 (m, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.44-7.32 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.34 (dd, *J* = 3.3, 1.9 Hz, 1H), 3.38-3.31 (m, 4H), 3.27 (d, *J* = 3.6 Hz, 4H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 155.19, 144.25, 141.97, 136.14, 134.44, 134.33, 126.36, 122.20, 119.49, 119.22, 118.29, 115.48, 104.90, 99.38, 51.38, 51.00 ppm. IR (KBr disc, cm^{-1}): 3125, 2807, 2219, 1593, 1488, 1446, 1380. 1338, 1225, 1168, 1040, 982, 934, 884, 762, 738. Anal. Calcd for $C_{18}H_{17}N_5$: C, 71.27; H, 5.65; Found: C, 71.10; H, 5.69.



***N*-(Furan-2-ylmethyl)-*N*-methyl-1*H*-pyrrolo[2,3-b]pyridin-5-amine (2b)**

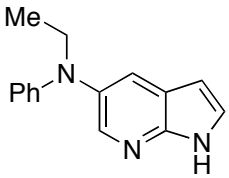
Following general procedure A using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 1-(furan-2-yl)-N-methylmethanamine (70 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 3% MeOH in DCM, to provide the title compound as a pale yellow solid, 103 mg, 91%. m.p. 84 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.57 (s, 1H), 8.21 (d, *J* = 2.6 Hz, 1H), 7.50 (d, *J* = 2.7 Hz, 1H), 7.38 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.35 (dd, *J* = 3.1, 2.1 Hz, 1H), 6.41 (dd, *J* = 3.3, 1.4 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.21-6.09 (m, 1H), 4.44 (s, 2H), 2.97 (s, 3H)

ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.11, 144.14, 142.06, 141.40, 134.08, 126.00, 120.60, 115.27, 110.22, 108.00, 99.76, 52.49, 39.78 ppm. IR (KBr disc, cm^{-1}): 3133, 3024, 2873, 1604, 1577, 1491, 1455, 1406, 1357, 1278, 1153, 1100, 725, 699. Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; Found: C, 68.46; H, 5.76.



5-(4-Methyl-1,4-diazepan-1-yl)-1H-pyrrolo[2,3-b]pyridine (2c)

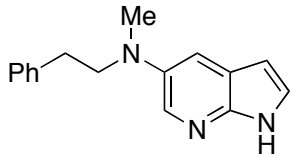
Following general procedure A using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 1-methyl-1,4-diazepane (75 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica (5% 2M NH_3 in MeOH/DCM), to provide the title compound as a yellow gum, 98 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.13 (s, 1H), 7.98 (d, *J* = 2.7 Hz, 1H), 7.25 (dd, *J* = 6.1, 3.0 Hz, 2H), 6.31 (dd, *J* = 3.3, 1.7 Hz, 1H), 3.64 - 3.53 (m, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.75 (dd, *J* = 5.6, 4.0 Hz, 2H), 2.57 (dd, *J* = 6.4, 4.6 Hz, 2H), 2.37 (s, 3H), 2.09 - 1.92 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.00, 141.44, 131.13, 125.77, 120.74, 111.34, 99.39, 58.33, 57.12, 50.21, 49.45, 46.77, 27.98 ppm. IR (KBr disc, cm^{-1}): 3194, 2937, 1606, 1573, 1493, 1462, 1384, 1282, 1164, 1119, 889, 730, 427.



***N*-Ethyl-*N*-phenyl-1*H*-pyrrolo[2,3-b]pyridin-5-amine (2d)**

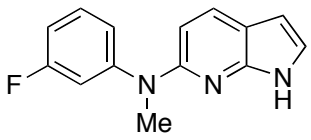
Following general procedure A using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), N-ethylaniline (76 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 4% MeOH/DCM, to provide the title compound as a lilac solid, 110 mg, 93%. m.p. 112 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.89 (s, 1H), 8.28 (d, *J* = 2.3 Hz, 1H), 7.87 (d, *J* = 2.3 Hz, 1H), 7.53 - 7.37 (m, 1H), 7.27 - 7.12 (m, 2H), 6.85 - 6.69 (m, 3H), 6.52 (dd, *J* = 3.4, 1.6 Hz, 1H), 3.83 (q, *J* = 7.1 Hz,

2H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.25, 146.83, 143.29, 136.75, 129.17, 128.57, 126.53, 121.41, 117.51, 114.45, 100.71, 47.11, 12.74 ppm. IR (KBr disc, cm^{-1}): 3123, 2966, 1595, 1499, 1371, 1281, 1262, 1175, 1065, 895, 749, 729, 695, 589, 475. Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; Found: C, 75.64; H, 6.41.



***N*-Methyl-*N*-phenethyl-1*H*-pyrrolo[2,3-b]pyridin-5-amine (2e)**

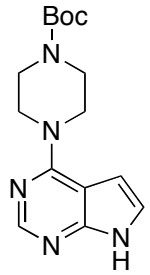
Following general procedure A using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), N-methyl-2-phenylethylamine (87 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 2% MeOH in DCM, to provide the title compound as a yellow solid, 119 mg, 95%. m.p. 81 – 82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.60 (s, 1H), 8.17 (d, J = 2.6 Hz, 1H), 7.48 (d, J = 2.7 Hz, 1H), 7.43 - 7.33 (m, 3H), 7.32 - 7.23 (m, 3H), 6.48 (dd, J = 3.3, 1.6 Hz, 1H), 3.64 (dd, J = 8.7, 6.9 Hz, 2H), 3.00 (s, 3H), 2.97 - 2.90 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.71, 141.05, 139.96, 133.08, 128.86, 128.55, 126.21, 125.98, 120.82, 113.98, 99.59, 56.96, 39.91, 32.82 ppm. IR (KBr disc, cm^{-1}): 3140, 1506, 1490, 1405, 1385, 1146, 1013, 730. Anal. Calcd for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82; Found: C, 76.46; H, 6.70.



***N*-(3-Fluorophenyl)-*N*-methyl-1*H*-pyrrolo[2,3-b]pyridin-6-amine (2f)**

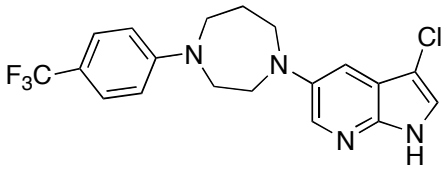
Following general procedure A using 6-chloro-1H-pyrrolo[2,3-b]pyridine (76 mg), 3-fluoro-N-methylaniline (68 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica, eluting with 5% MeOH in DCM, to provide the title compound as a lilac solid, 113 mg, 94%. m.p. 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.13 (s, 1H), 7.86 - 7.71 (m, 1H), 7.33 - 7.14 (m, 1H), 7.01 - 6.96 (m, 1H), 6.93 (dt, J = 11.3, 2.3 Hz, 1H), 6.89 (dt, J = 6.2, 3.1 Hz, 1H), 6.79 - 6.67 (m, 2H), 6.38

(dd, J = 3.5, 2.0 Hz, 1H), 3.56 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.49 (d, J = 244.7 Hz),154.19, 149.56 (d, J = 10.0 Hz), 147.50, 130.63, 130.21 (d, J = 9.7 Hz), 122.92, 116.94, 114.74, 108.89 (d, J = 21.2 Hz), 108.40 (d, J = 23.9 Hz).107.66, 100.69, 39.09 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.1 ppm. IR (KBr disc, cm^{-1}): 3172, 1607, 1578, 1490, 1431, 1361, 1290, 1257, 1191, 1122, 1000, 898, 812, 762, 705. Anal. Calcd for $C_{14}H_{12}FN_3$: C, 69.70; H, 5.01; Found: C, 69.70; H, 5.06.



***tert*-Butyl 4-(7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)piperazine-1-carboxylate (2g)**

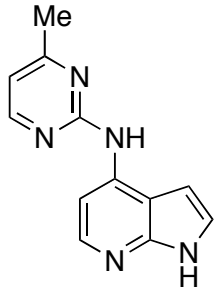
Following general procedure A using 4-chloro-7*H*-pyrrolo[2,3-d]pyrimidine (77 mg), *tert*-butyl piperazine-1-carboxylate (112 mg) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* trituration with DCM, to provide the title compound as a yellow solid, 150 mg, 99%. m.p. 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.68 (s, 1H), 8.56-8.13 (m, 1H), 7.13 (t, J = 10.2 Hz, 1H), 6.50 (dd, J = 35.5, 6.0 Hz, 1H), 4.14-3.76 (m, 4H), 3.57 (m, 4H), 1.45 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.05, 154.79, 152.21, 150.45, 121.29, 103.12, 100.89, 80.14, 45.29, 43.90, 42.73, 28.43 ppm. IR (KBr disc, cm^{-1}): 3109, 2976, 2859, 1689, 1593, 1571, 1481, 1425, 1363, 1262, 1178, 1013, 914, 821, 724. Anal. Calcd for $C_{15}H_{21}N_5O_2$: C, 59.39; H, 6.98; Found: C, 59.41; H, 7.00.



3-Chloro-5-(4-(4-(trifluoromethyl)phenyl)-1,4-diazepan-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (2h)

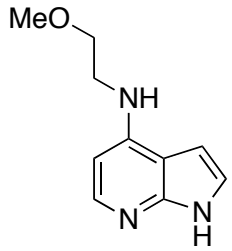
Following general procedure A using 5-bromo-3-chloro-1*H*-pyrrolo[2,3-b]pyridine (116 mg), 1-(4-(trifluoromethyl)phenyl)-1,4-diazepane (147 mg) and LiHMDS (1.2 mL, 2.4

equiv.). The crude product was purified *via* trituration with DCM/MeOH, to provide the title compound as a yellow solid, 136 mg, 69%. m.p. 196 ˚C. Note: This compound is sparingly soluble in organic solvents and requires the sample to be heated in DMSO in order ensure sufficient solubility for NMR anlyses. ^{1}H NMR (400 MHz, DMSO) δ: 11.54 (d, *J* = 2.3 Hz, 1H), 8.02 (d, *J* = 2.7 Hz, 1H), 7.48 (d, *J* = 2.8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 2.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 - 3.57 (m, 4H), 3.44 (dd, *J* = 12.7, 6.4 Hz, 4H), 2.11 - 1.83 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 150.54, 140.87, 139.61, 132.57, 126.95, 124.42, 123.53, 117.94, 115.70, 115.38, 111.38, 106.68, 100.86, 48.67, 48.36, 48.20, 47.60, 23.88 ppm. ^{19}F NMR (376 MHz, DMSO) δ: -59.22 ppm. IR (KBr disc, cm^{-1}): 3116, 1615, 1528, 1497, 1403, 1325, 1197, 1164, 1100, 1068, 1013, 929, 814.



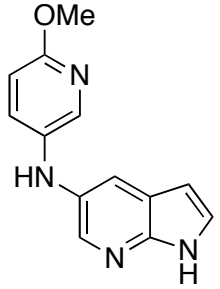
***N*-(4-Methylpyrimidin-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3a)**

Following general procedure B using 4-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 2-amino-4-methylpyrimidine (66 mg) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* trituration with EtOAc, to provide the title compound as a yellow powder, 105 mg, 93%. m.p. 232 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.49 (s, 1H), 9.77 (s, 1H), 8.49 (d, *J* = 5.0 Hz, 1H), 8.13 (dd, *J* = 24.0, 5.5 Hz, 2H), 7.43 - 7.17 (m, 1H), 7.17 - 6.99 (m, 1H), 6.92 (d, *J* = 5.0 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (101 MHz; DMSO): δ: 167.8, 159.9, 157.6, 149.5, 143.5, 139.9, 122.9, 113.2, 110.1, 103.8, 98.6, 23.7 ppm. IR (KBr disc, cm^{-1}): 3255, 3189, 3106, 1614, 1562, 1404, 1343, 1322, 1089, 838, 730, 556, 546. Anal. Calcd for $C_{12}H_{11}N_5$: C, 63.99; H, 4.92; Found: C, 63.61; H, 5.07.



***N*-(2-Methoxyethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3b)**

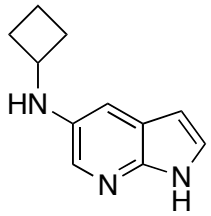
Following general procedure B using 4-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (76 mg), 2-methoxyethanamine (51 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* trituration with EtOAc to provide the title compound as a light yellow powder, 94 mg, 99%. m.p. 136 ˚C; ^{1}H NMR (400 MHz, MeOD) δ: 7.81 (d, *J* = 5.7 Hz, 1H), 7.04 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 0.5 Hz, 1H), 6.20 (d, *J* = 5.7 Hz, 1H), 3.67 - 3.51 (m, 2H), 3.45 (t, *J* = 5.6 Hz, 2H), 3.35 (d, *J* = 0.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.03, 149.23, 144.74, 122.03, 109.26, 98.69, 96.91, 72.01, 59.05, 43.34 ppm. IR (KBr disc, cm^{-1}): 3329, 1594, 1337, 1195, 1075, 897, 839, 802, 717, 640. Anal. Calcd for $C_{10}H_{13}N_3O$: C, 62.81; H, 6.85; Found C, 62.70; H, 6.85.



***N*-(6-Methoxypyridin-3-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-amine (3c)**

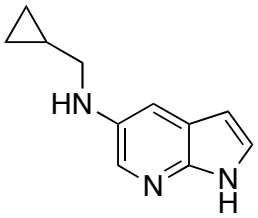
Following general procedure B using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), 5-amino-2-methoxypyridine (74 mg) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica (3% MeOH/DCM), to provide the title compound as a dark brown crystalline solid, 93 mg, 77%. m.p. 164 ˚C. ^{1}H NMR (400 MHz, DMSO) δ: 11.41 (s, 1H), 7.97 (d, *J* = 2.5 Hz, 1H), 7.83 (d, *J* = 2.9 Hz, 1H), 7.67 (s, 1H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.43 - 7.23 (m, 2H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.27 (dd, *J* = 3.3, 1.9 Hz, 1H), 3.73 (s, 4H) ppm. ^{13}C NMR (101 MHz, DMSO) δ: 157.97, 145.01, 136.90, 136.77, 134.54, 134.17, 128.97, 126.98, 120.20, 116.84, 110.96, 99.70, 53.40

ppm. IR (KBr disc, cm^{-1}): 3387, 1582, 1489, 1402, 1341, 1271, 1030, 884, 818, 721. Anal. Calcd for $C_{13}H_{12}N_4O$: C, 64.99; H, 5.03; Found: C, 64.57; H, 5.03.



***N*-Cyclobutyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3d)**

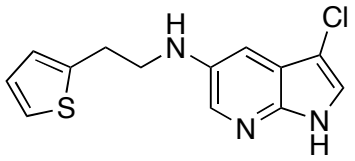
Following general procedure B using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), cyclobutylamine (60 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica (2% MeOH/DCM), to provide the title compound as a light yellow powder, 82 mg, 88%: m.p. 109 ˚C. ^{1}H NMR (400 MHz, MeOD) δ: 7.75 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J* = 9.8, 3.0 Hz, 2H), 6.29 (d, *J* = 3.4 Hz, 1H), 4.00 - 3.71 (m, 1H), 2.49 - 2.22 (m, 2H), 2.00 - 1.58 (m, 4H) ppm. ^{13}C NMR (101 MHz, MeOD) δ: 144.20, 139.71, 133.61, 127.12, 122.70, 114.19, 100.52, 51.63, 31.66, 16.02 ppm. IR (KBr disc, cm^{-1}): 3148, 2979, 1583, 1469, 1384, 1322, 1265, 1170, 863, 726, 668. Anal. Calcd for $C_{11}H_{13}N_3$; C, 70.56; H, 7.00; Found: C, 70.31; H, 7.11.



***N*-(Cyclopropylmethyl)-1*H*-pyrrolo[2,3-b]pyridin-5-amine (3e)**

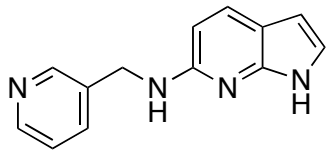
Following general procedure B using 5-bromo-1*H*-pyrrolo[2,3-b]pyridine (98 mg), cyclopropylmethanamine (51 μL) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica (3% 2M NH_3 in MeOH/DCM), to provide the title compound as a light grey powder, 93 mg, 99%. m.p. 80 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.03 (s, 1H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.40 - 6.96 (m, 2H), 6.32 (dd, *J* = 3.3, 1.7 Hz, 1H), 3.81 (s, 1H), 2.98 (d, *J* = 6.9 Hz, 2H), 1.24 - 0.97 (m, 1H), 0.62 - 0.41 (m, 2H), 0.35 - 0.08 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.61, 139.36, 132.37,

125.53, 120.59, 111.58, 99.29, 50.54, 10.92, 3.40 ppm. IR (KBr disc, cm^{-1}): 3146, 3004, 1540, 1465, 1400, 1320, 1166, 890, 725. Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; Found: C, 70.04; H, 6.96.



3-Chloro-*N*-(2-(thiophen-2-yl)ethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-amine (3f)

Following general procedure B using 3-chloro-5-bromo-1*H*-pyrrolo[2,3-b]pyridine (116 mg), 2-(thiophen-2-yl)ethylamine (74 mg) and LiHMDS (1.2 mL, 2.4 equiv The crude product was purified *via* chromatography on silica (3% MeOH/DCM), to provide the title compound as a dark brown solid, 133 mg, 96%. m.p. 104 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.39 (s, 1H), 7.81 (d, *J* = 2.6 Hz, 1H), 7.21 - 7.14 (m, 2H), 7.13 (t, *J* = 4.0 Hz, 1H), 6.95 (dt, *J* = 10.1, 5.0 Hz, 1H), 6.90 - 6.82 (m, 1H), 3.67 (dd, *J* = 18.0, 11.7 Hz, 1H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.16 (t, *J* = 6.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.81, 141.60, 139.19, 133.60, 127.13, 125.53, 124.11, 122.35, 118.68, 108.67, 102.83, 46.20, 29.61 ppm. IR (KBr disc, cm^{-1}): 3390, 3122, 3015, 2945, 2850, 1613, 1583, 1515, 1471, 1397, 1325, 1252, 1234, 1088, 1013, 850, 761, 698. Anal. Calcd for $C_{13}H_{12}ClN_3S$: C, 56.21; H, 4.35; Found: C, 56.27; H, 4.40.



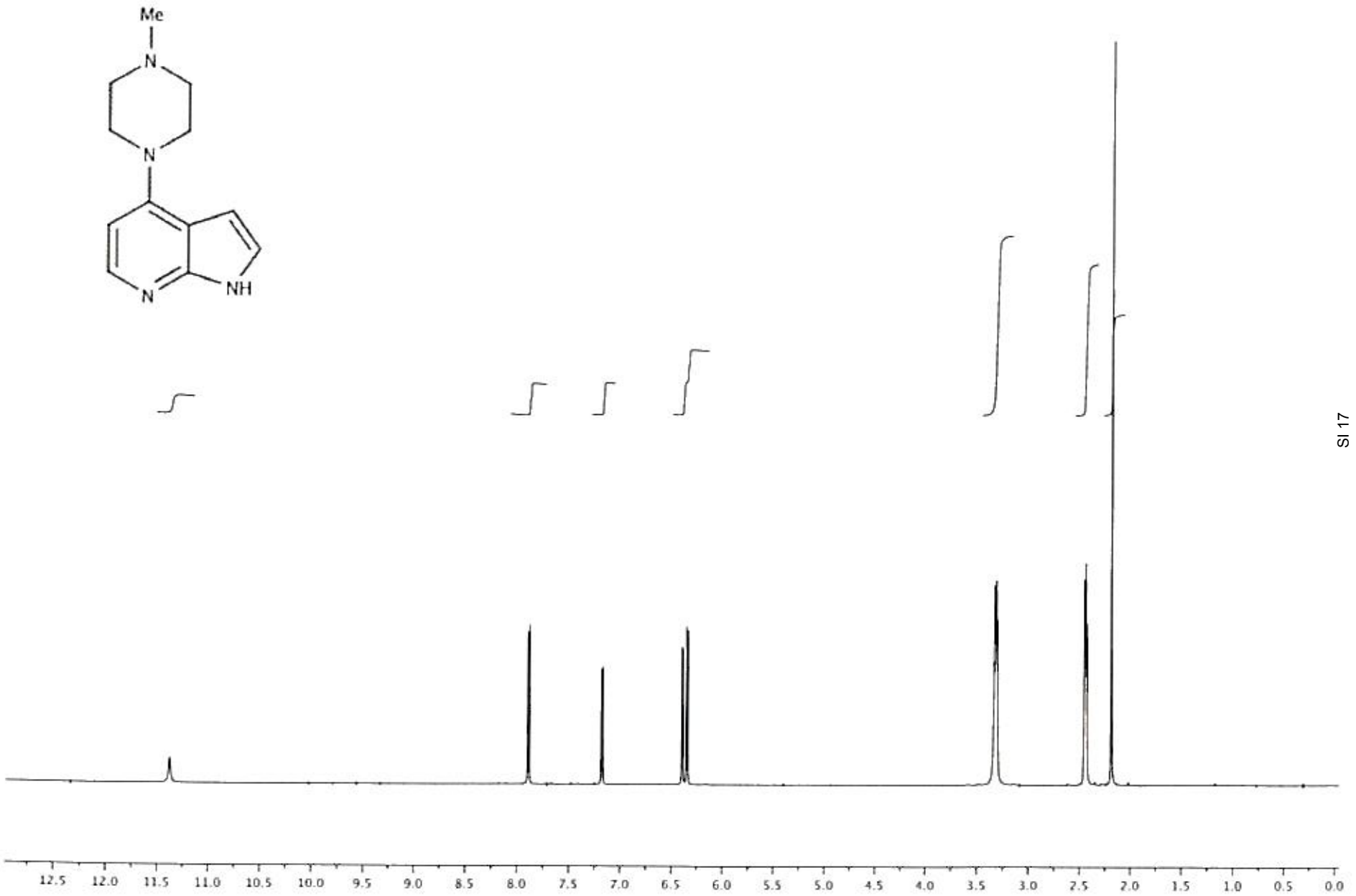
***N*-(Pyridin-3-ylmethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-6-amine (3g)**

Following general procedure B using 6-chloro-1*H*-pyrrolo[2,3-b]pyridine (76 mg), 3-picolylamine (61 μL, purified by distillation) and LiHMDS (1.2 mL, 2.4 equiv.). The crude product was purified *via* chromatography on silica (3% 2M NH_3 in MeOH/DCM), to provide the title compound as a dark purple solid, 94 mg, 84%. m.p. 104 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.09 (d, *J* = 46.8 Hz, 1H), 8.60 (d, *J* = 1.7 Hz, 1H), 8.46 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.63 (dd, *J* = 14.2, 8.1 Hz, 2H), 7.13 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.86 (dd,

J = 3.3, 2.3 Hz, 1H), 6.36 - 6.11 (m, 2H), 5.16 (d, J = 74.3 Hz, 1H), 4.54 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.69, 148.96, 148.19, 147.44, 135.30, 135.17, 130.87, 123.32, 120.18, 111.99, 102.49, 100.91, 43.71 ppm. IR (KBr disc, cm^{-1}): 3242, 1611, 1582, 1522, 1426, 1348, 1295. 1246, 1125, 1030, 801, 710.

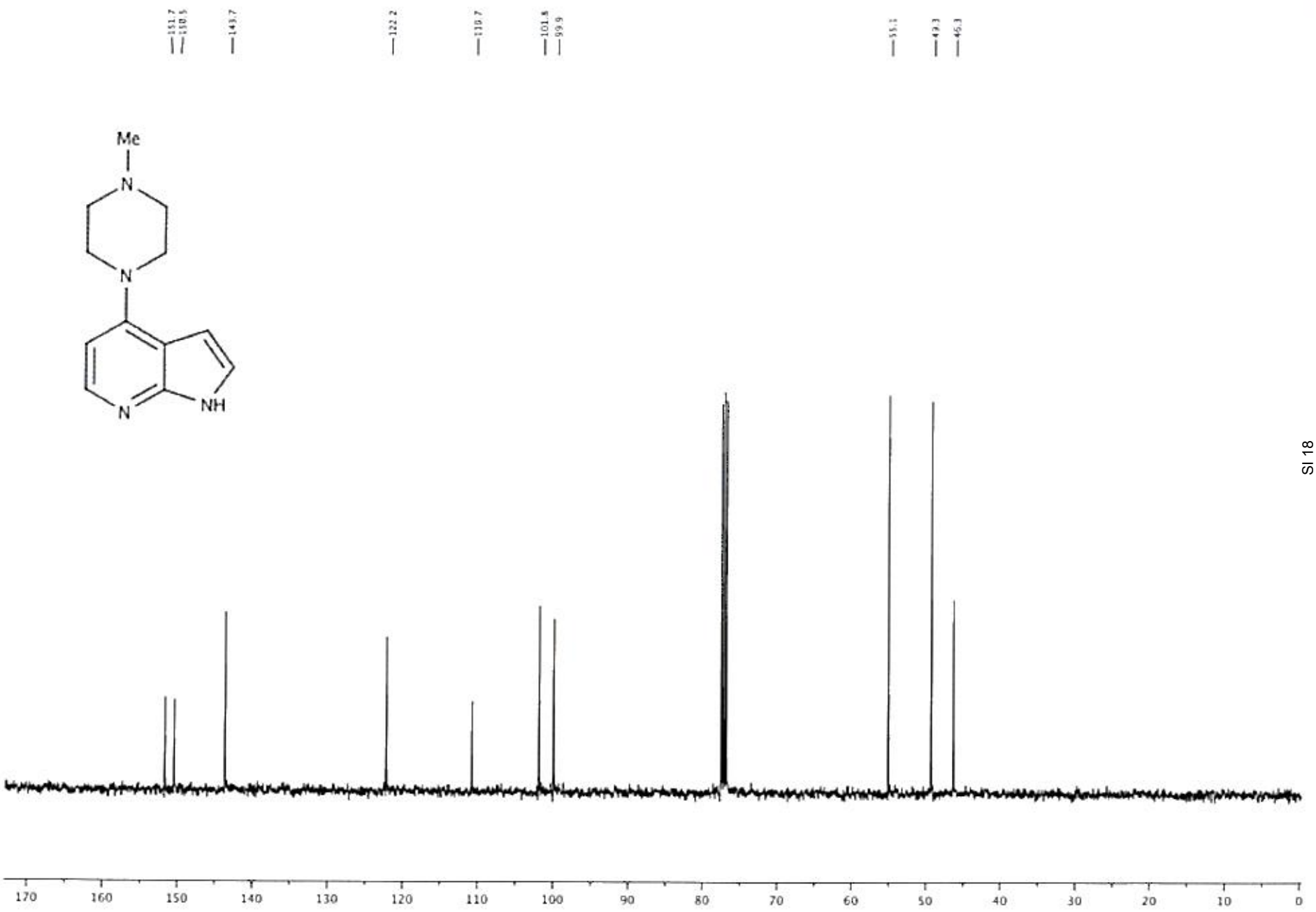
(1) Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 13552-13554.

(2) Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 6686-6687.



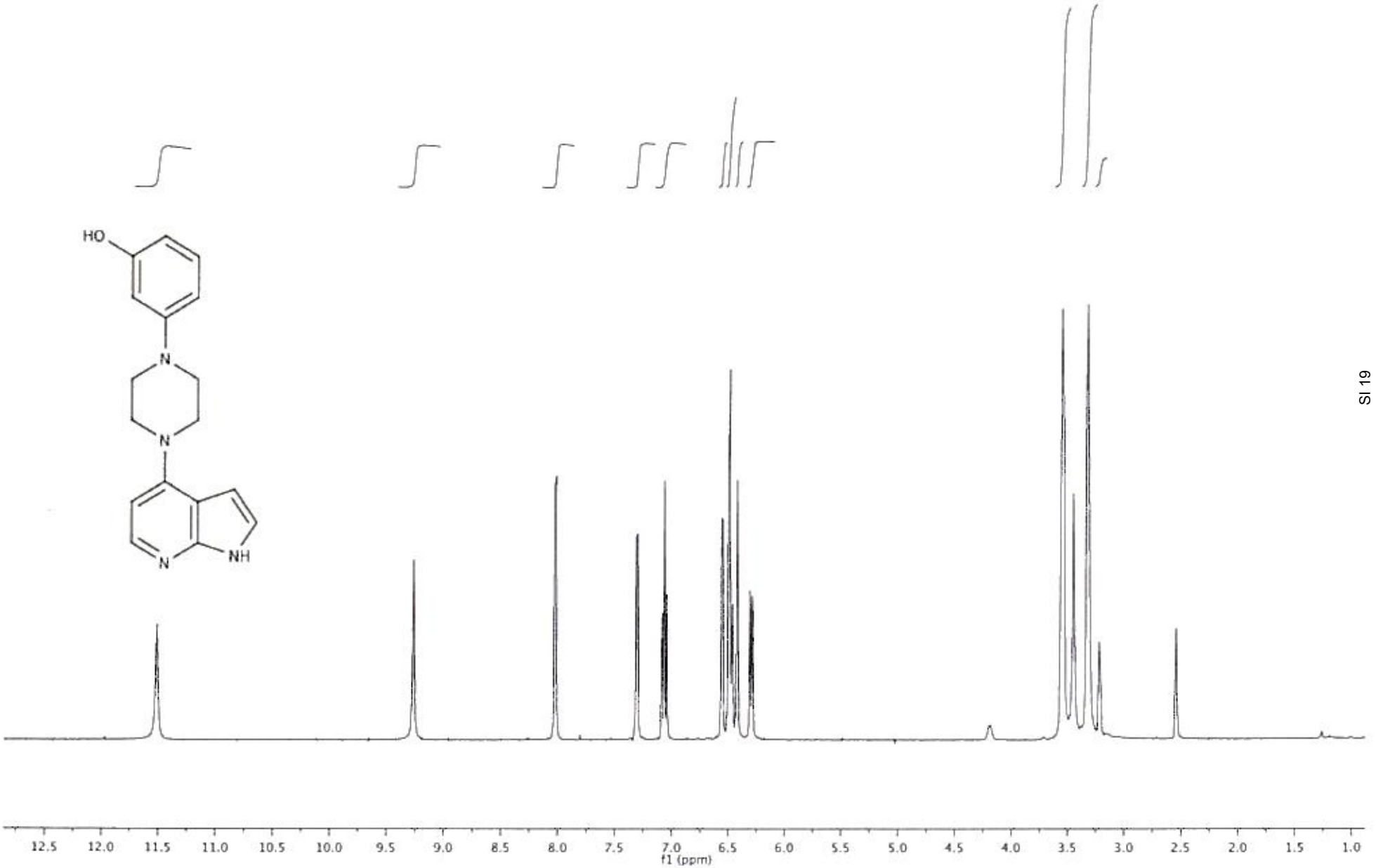
4-(4-Methylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1a)

^{1}H NMR in $CDCl_3$



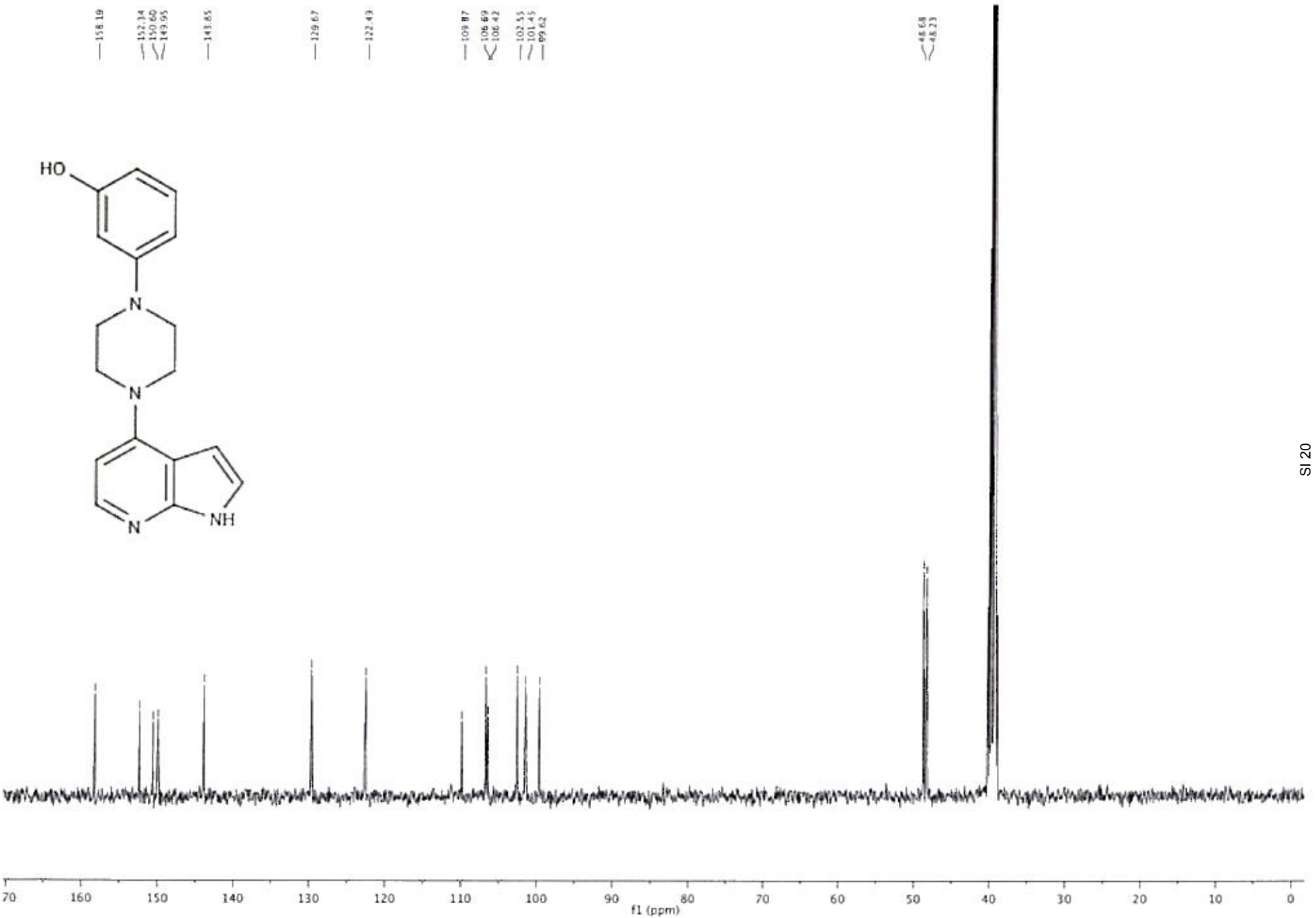
4-(4-Methylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1a)

^{13}C NMR in $CDCl_3$



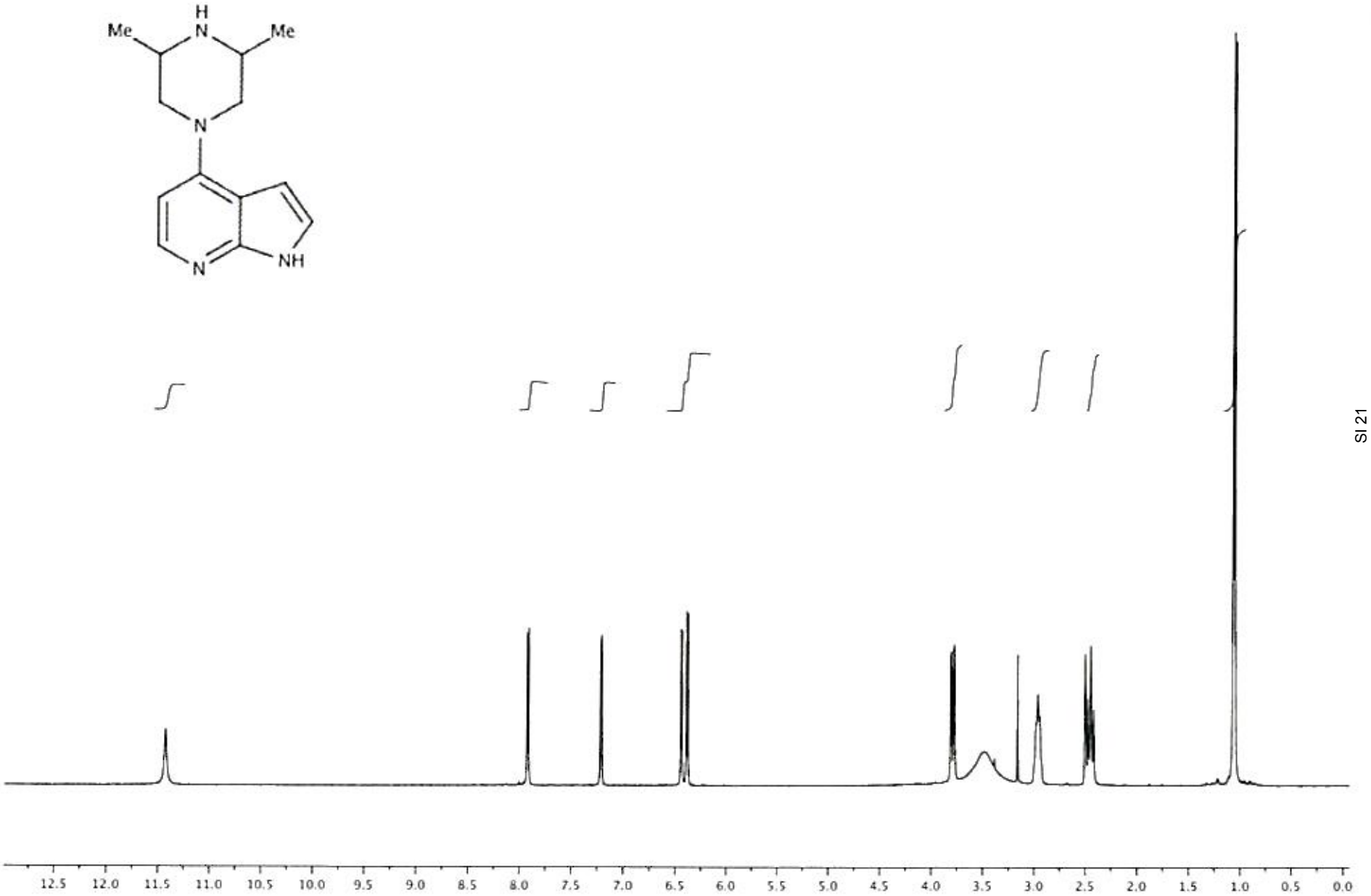
3-(4-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)piperazin-1-yl)phenol (1b)

^{1}H NMR in DMSO



3-(4-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)piperazin-1-yl)phenol (1b)

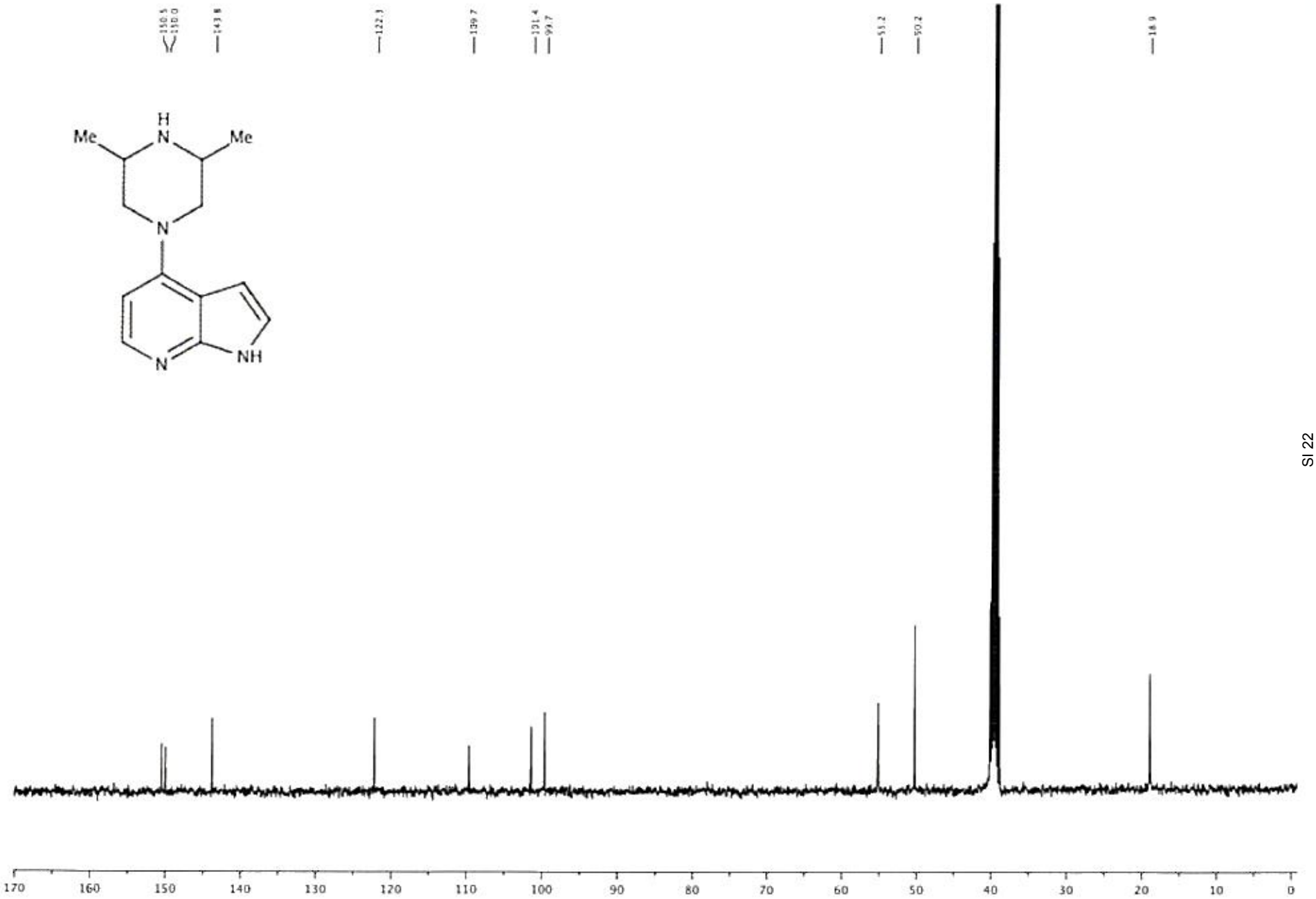
^{13}C NMR in DMSO



SI 21

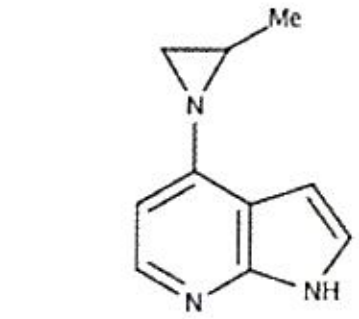
4-(3,5-Dimethylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1c)

^{1}H NMR in DMSO



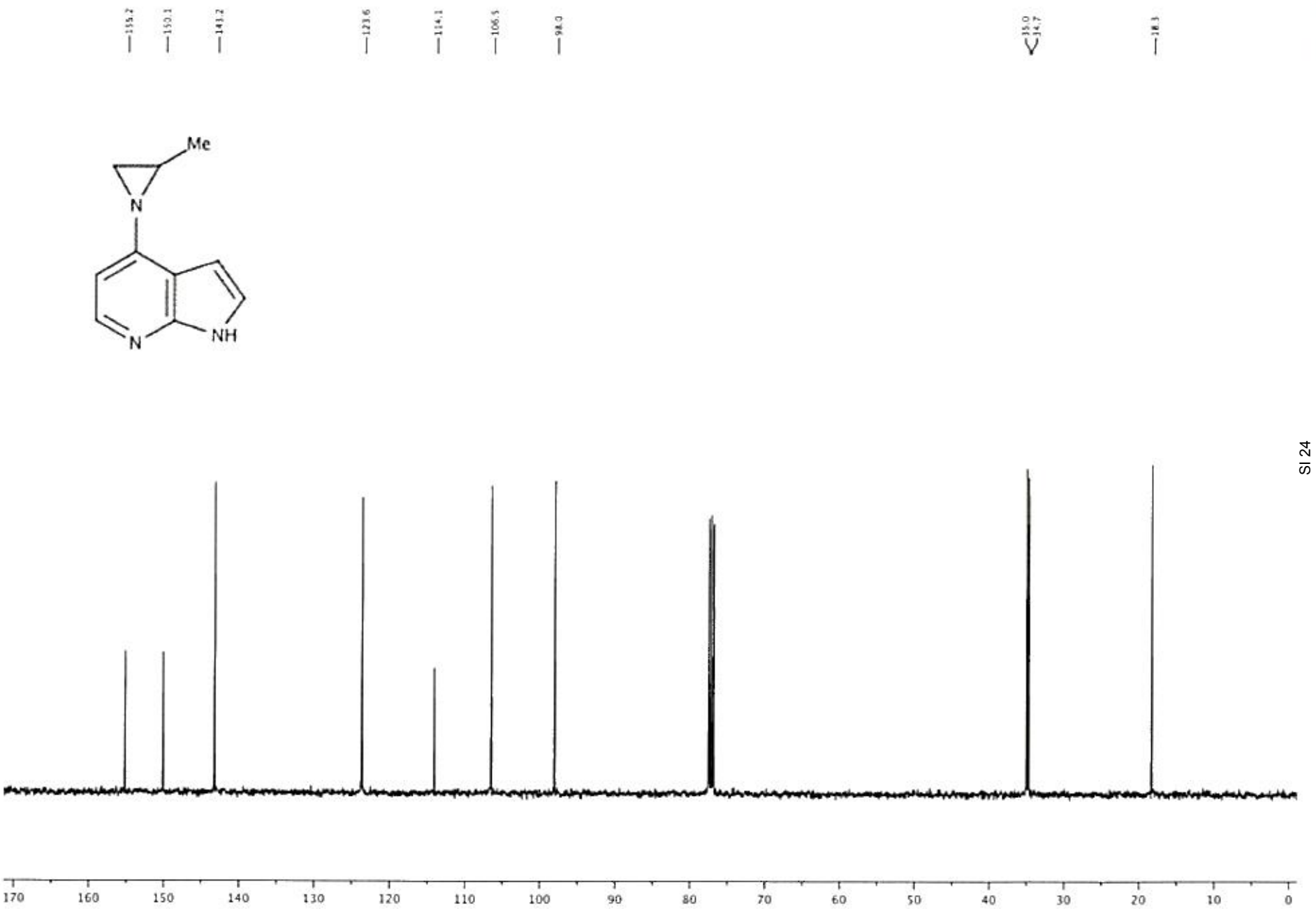
4-(3,5-Dimethylpiperazin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1c)

^{13}C NMR in DMSO



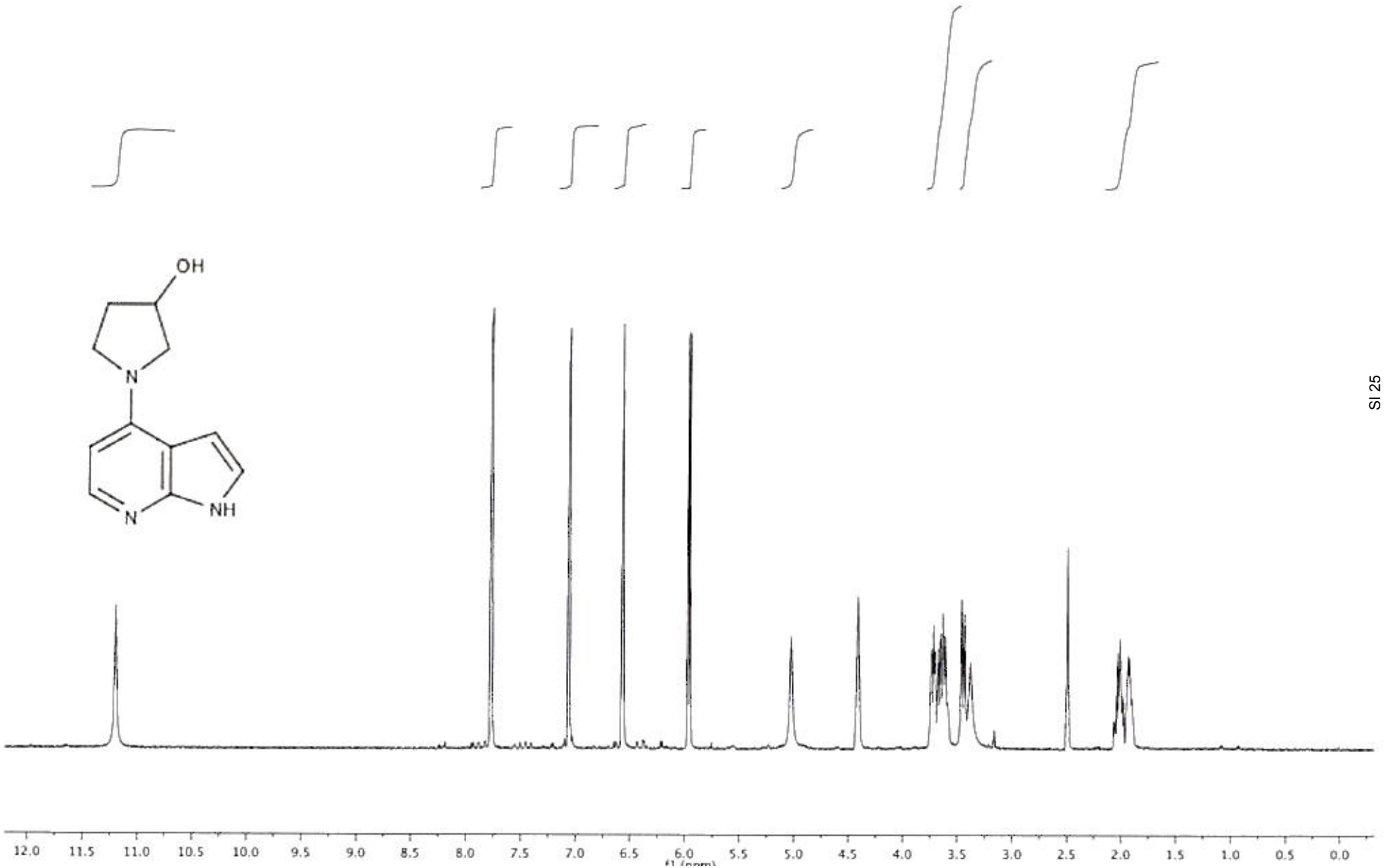
4-(2-Methylaziridin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1d)

^{1}H NMR in $CDCl_3$



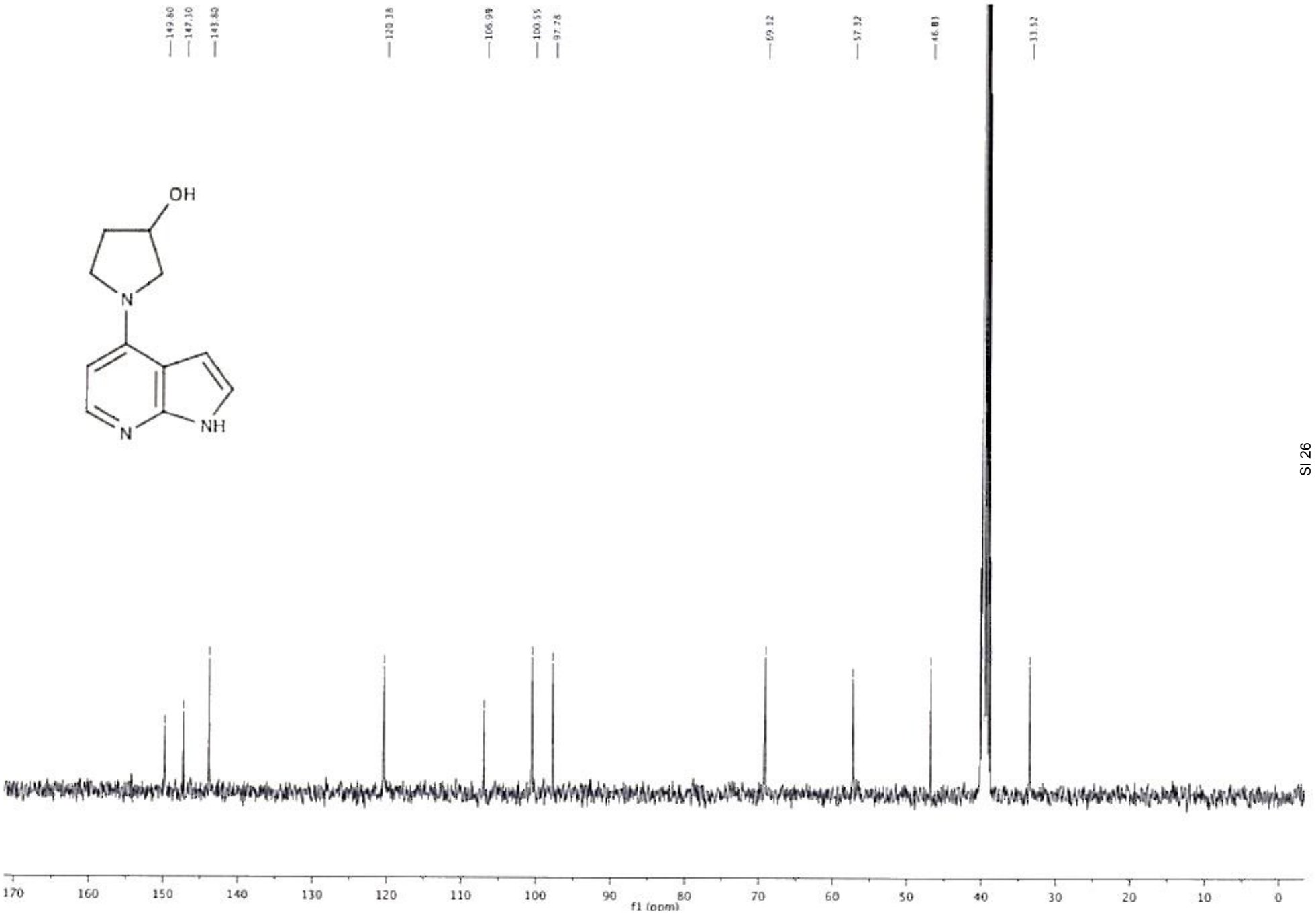
4-(2-Methylaziridin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1d)

^{13}C NMR in $CDCl_3$



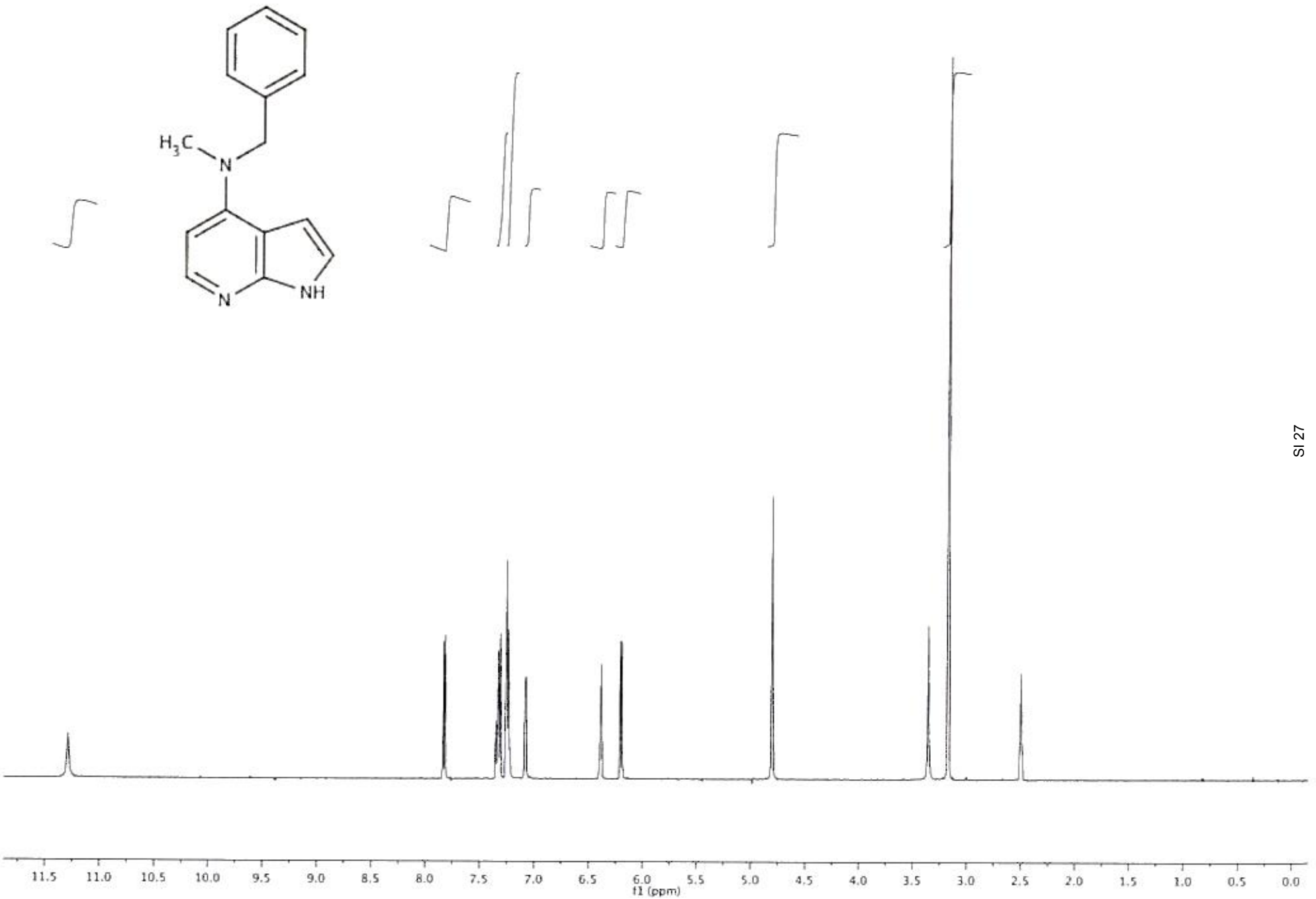
1-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)pyrrolidin-3-ol (1e)

^{1}H NMR in DMSO



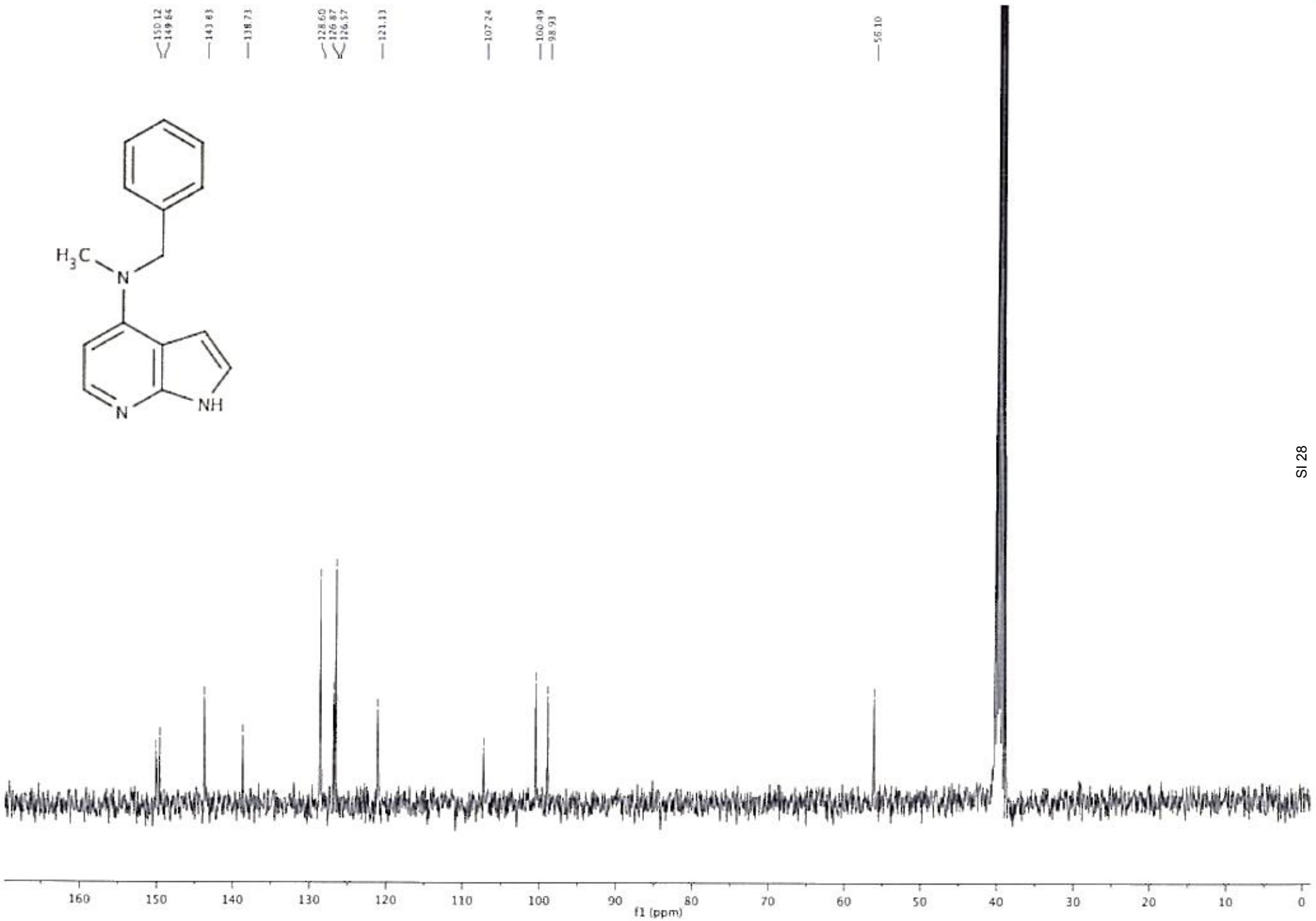
1-(1*H*-Pyrrolo[2,3-b]pyridin-4-yl)pyrrolidin-3-ol (1e)

^{13}C NMR in DMSO



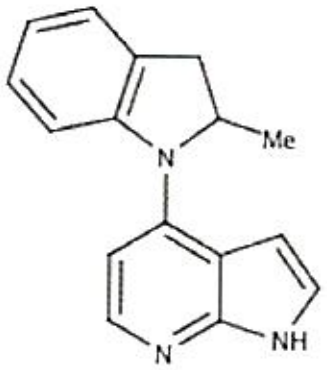
***N*-Benzyl-*N*-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (1f)**

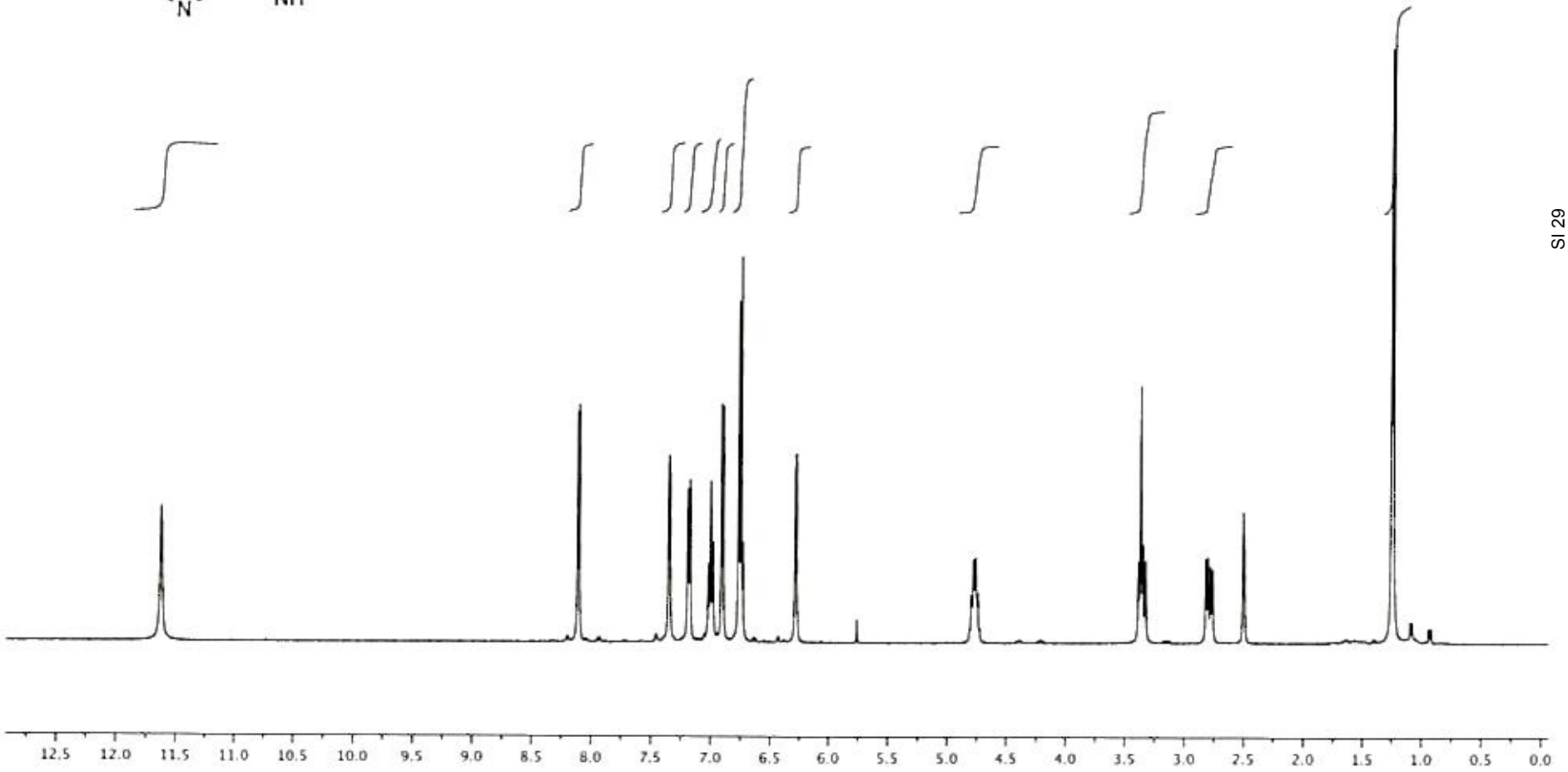
^{1}H NMR in DMSO



_N_-Benzyl-_N_-methyl-1_H_-pyrrolo[2,3-_b_]pyridin-4-amine (1f)

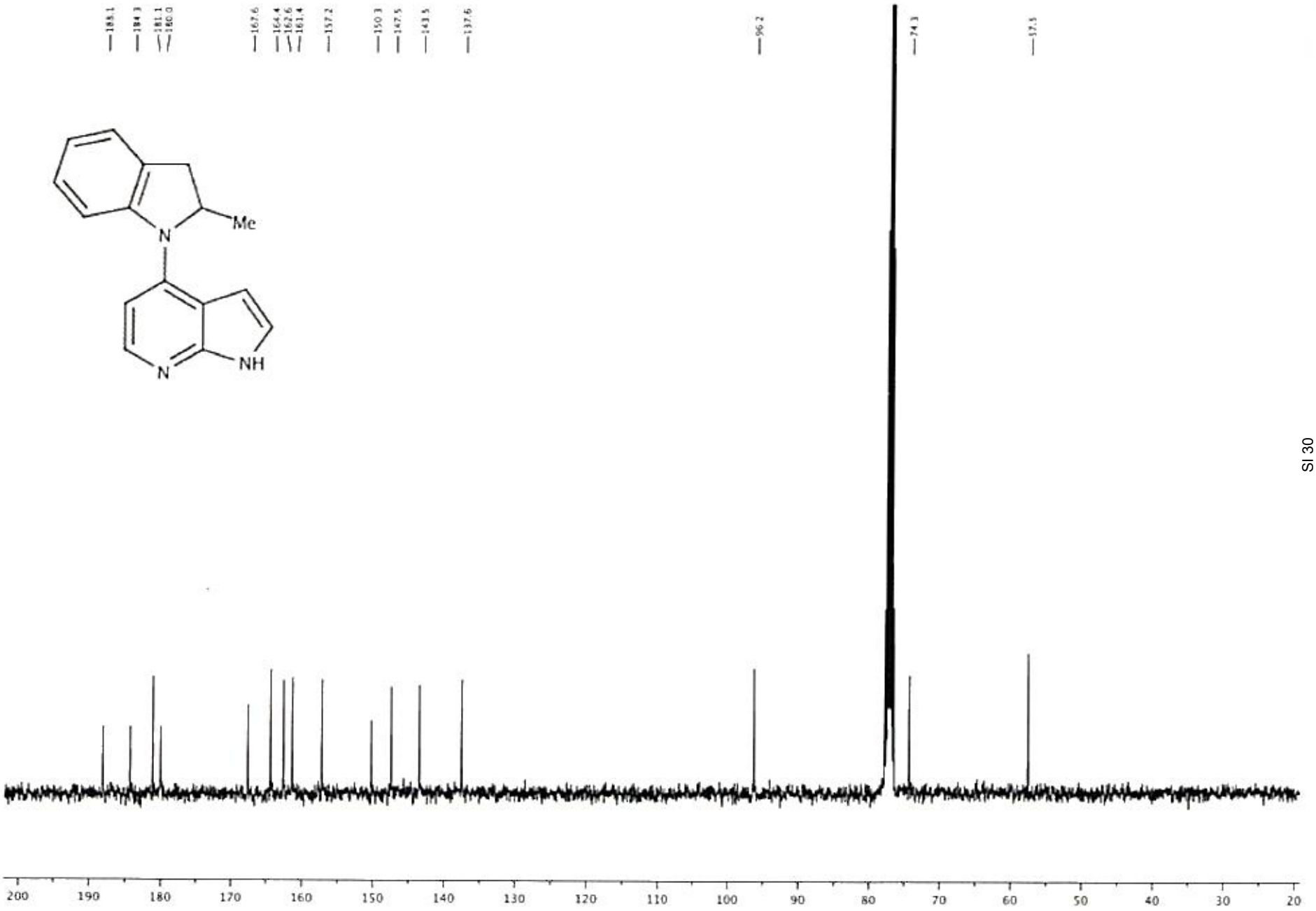
^{13}C NMR in DMSO





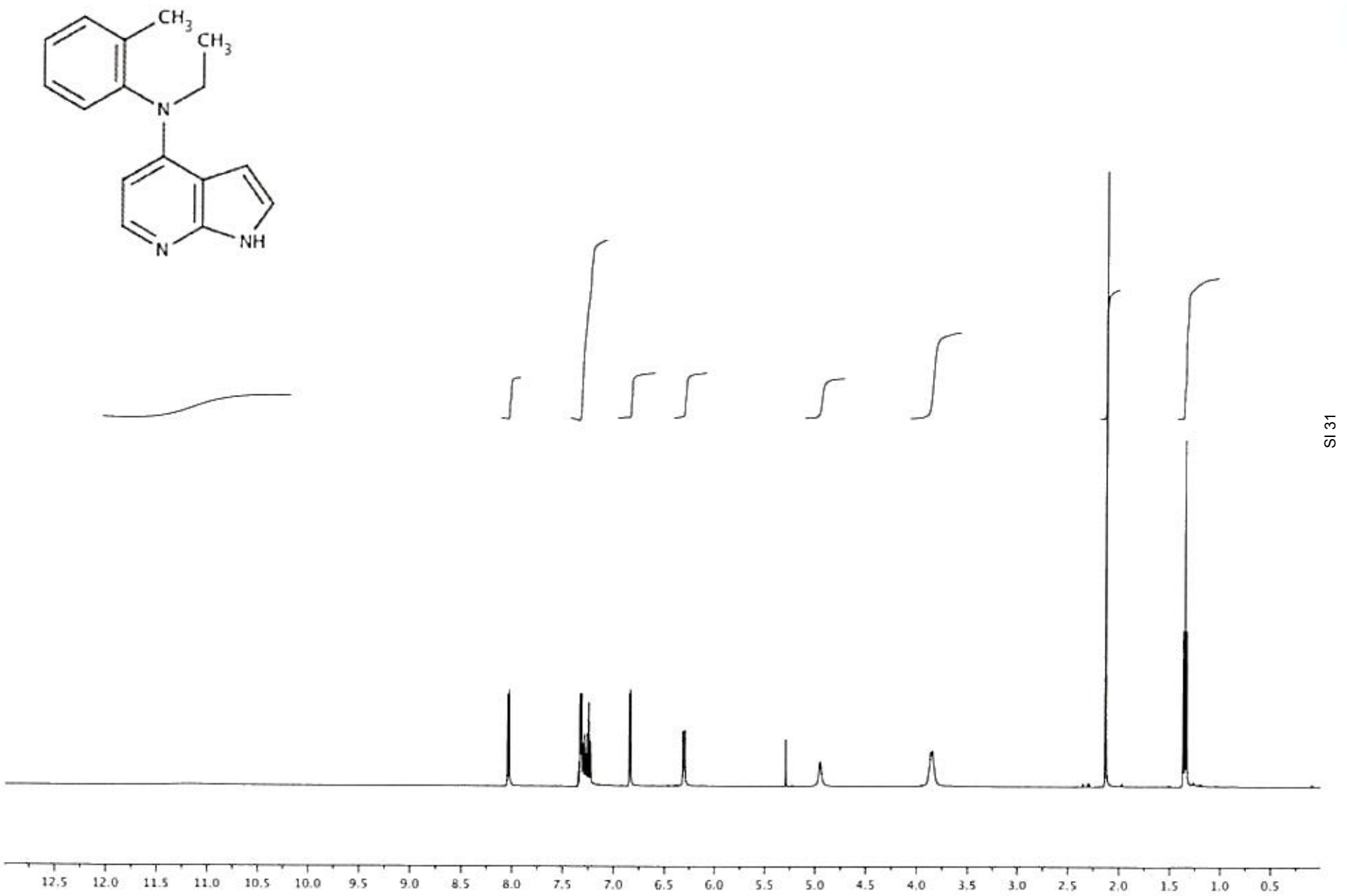
4-(2-Methylindolin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1g)

^{1}H NMR in $CDCl_3$



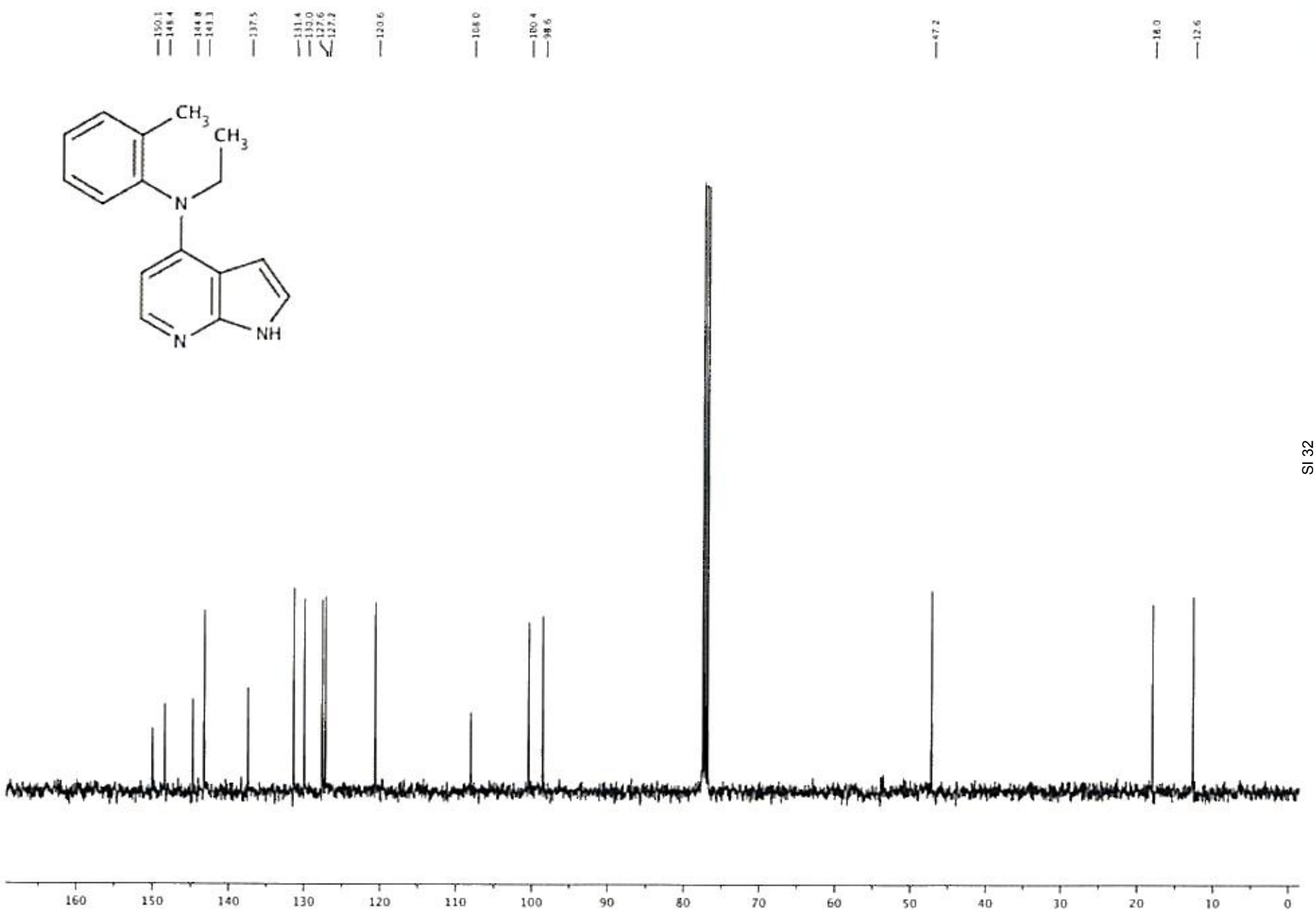
4-(2-Methylindolin-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (1g)

^{13}C NMR in $CDCl_3$



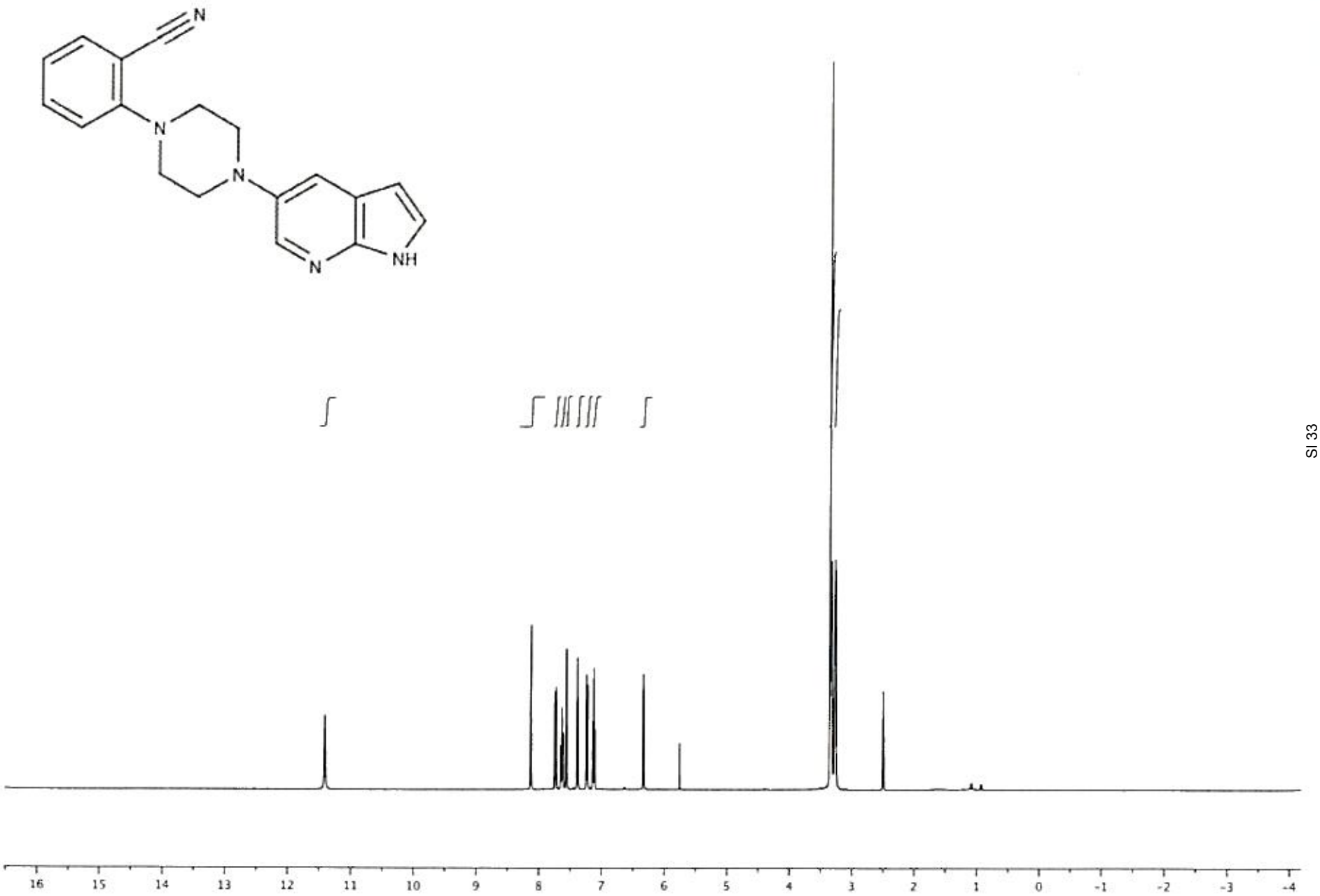
_N_-Ethyl-_N_-(_o_-tolyl)-1_H_-pyrrolo[2,3-b]pyridin-4-amine (1h)

^{1}H NMR in $CDCl_3$



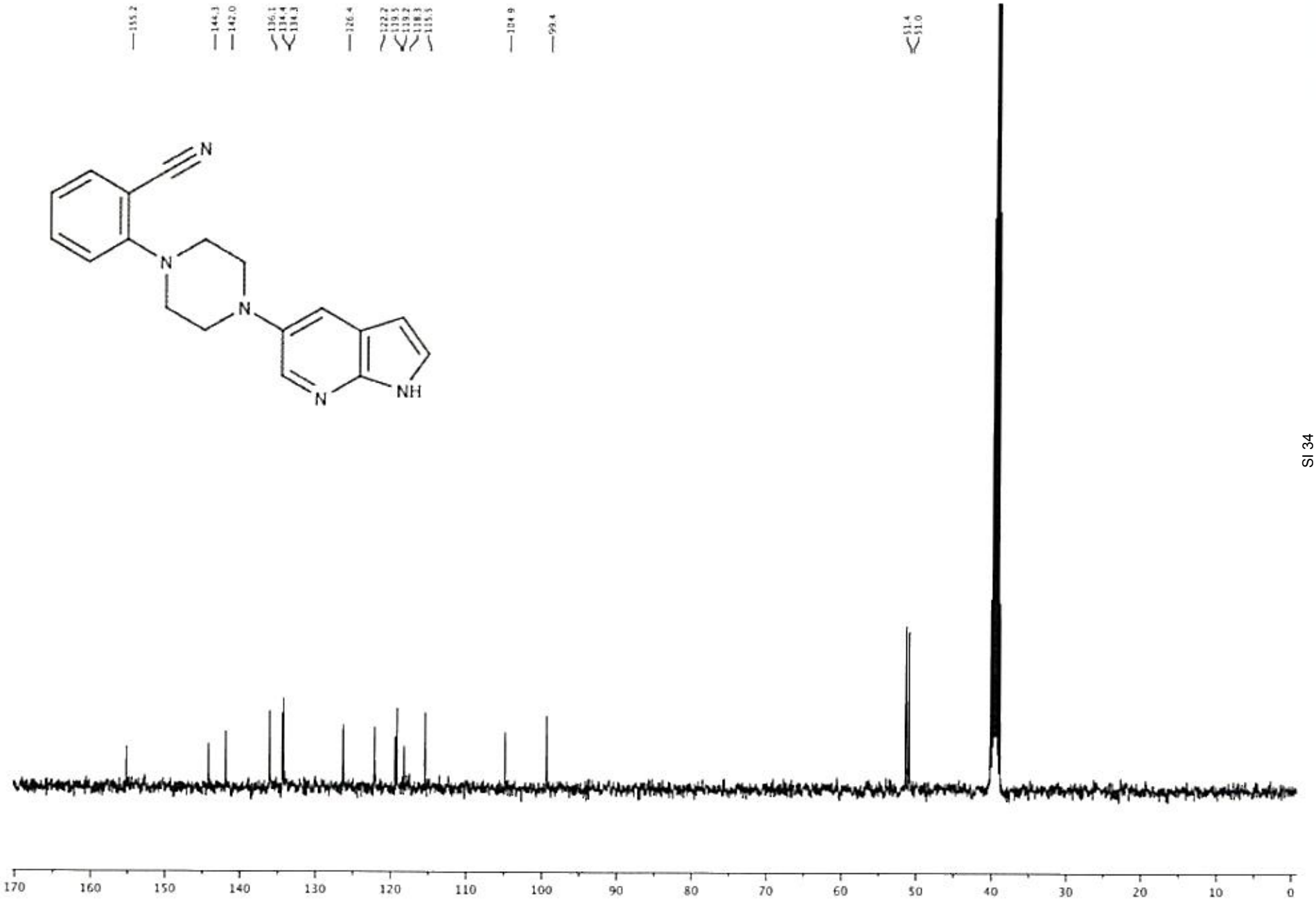
_N_-Ethyl-_N_-(_o_-tolyl)-1_H_-pyrrolo[2,3-b]pyridin-4-amine (1h)

^{13}C NMR in $CDCl_3$



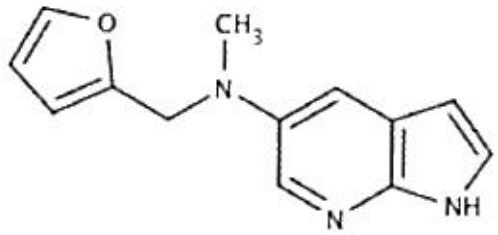
2-(4-(1*H*-Pyrrolo[2,3-b]pyridin-5-yl)piperazin-1-yl)benzonitrile (2a)

^{1}H NMR in DMSO



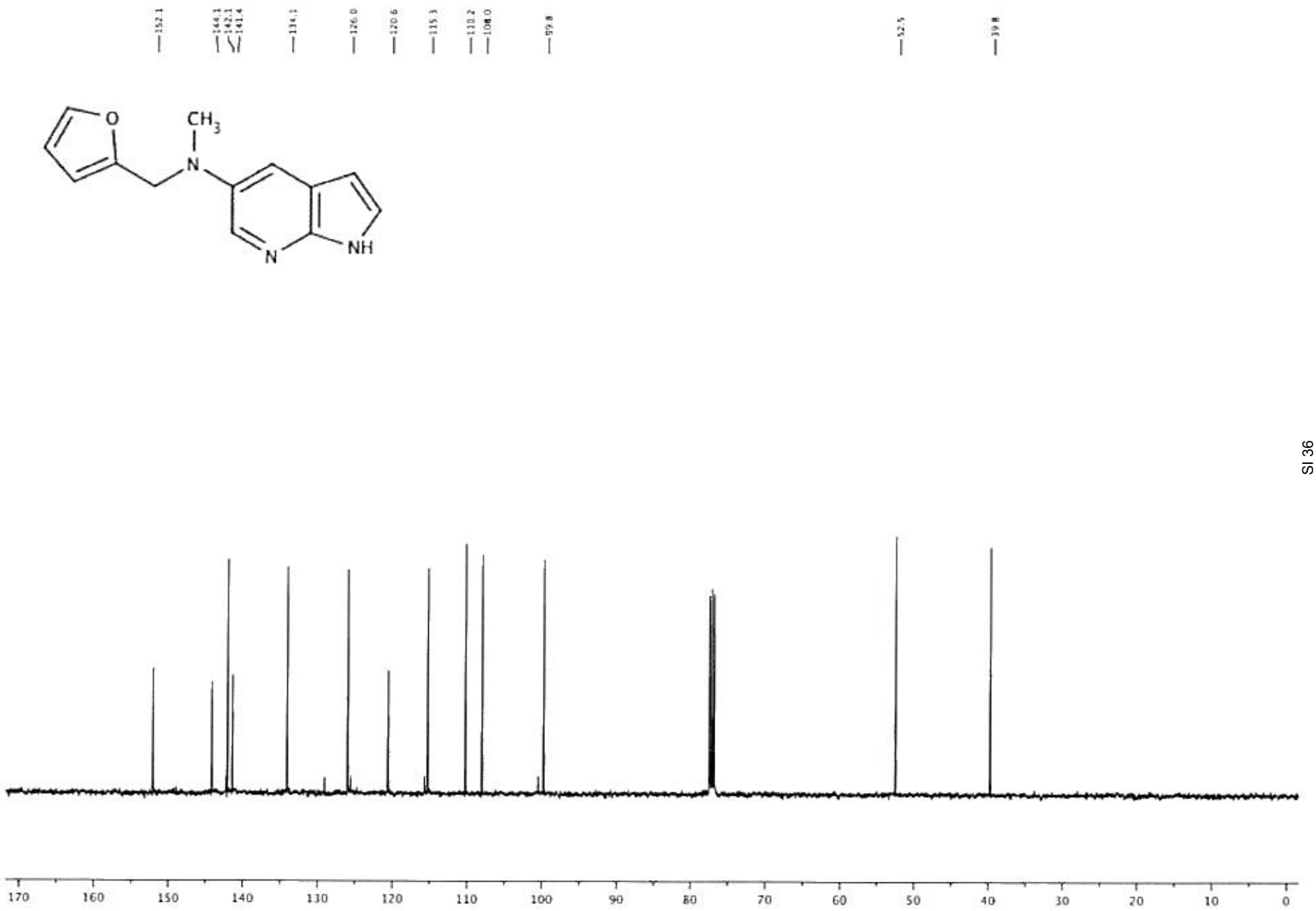
2-(4-(1*H*-Pyrrolo[2,3-b]pyridin-5-yl)piperazin-1-yl)benzonitrile (2a)

^{13}C NMR in DMSO



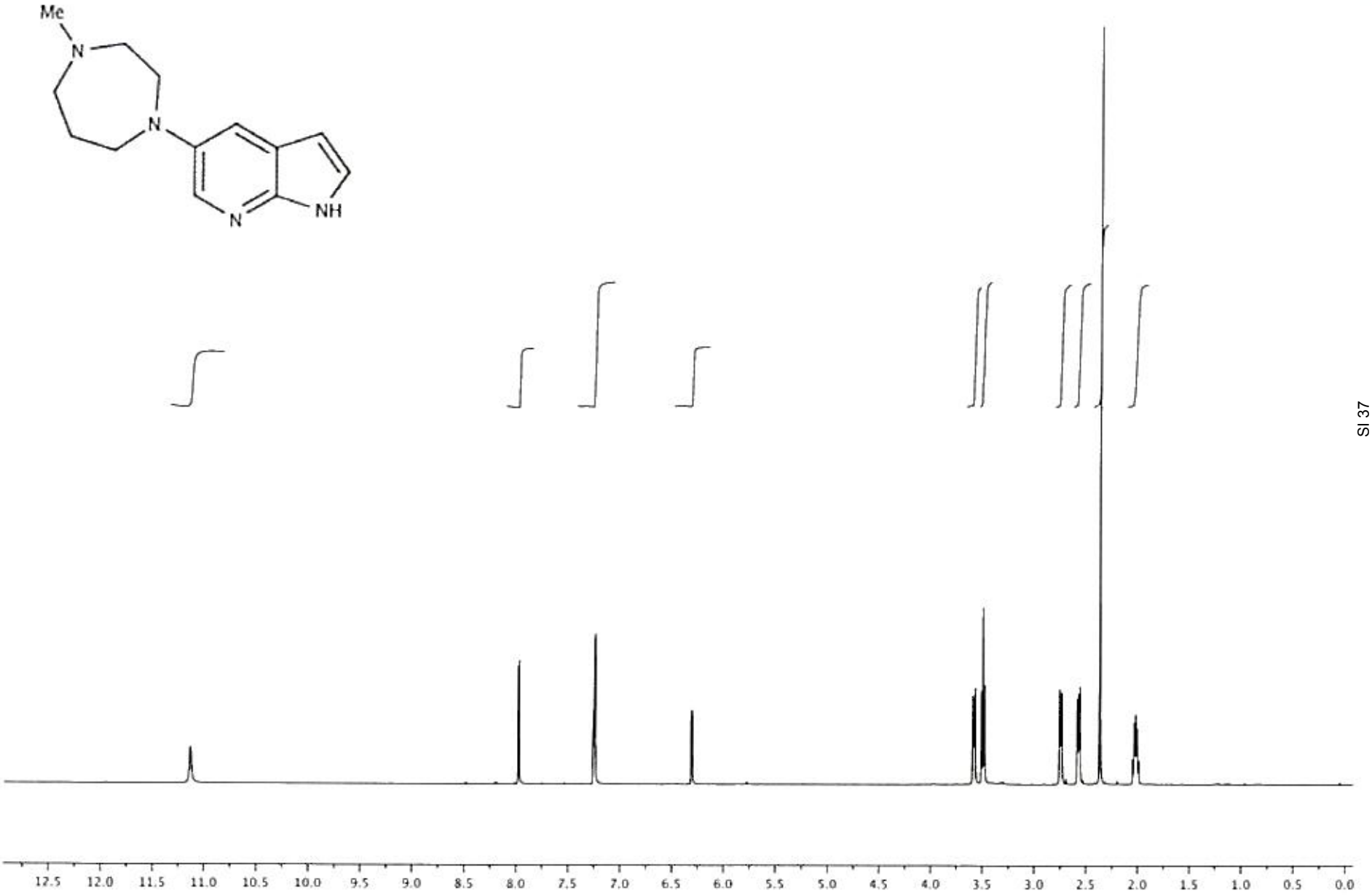
_N_-(Furan-2-ylmethyl)-_N_-methyl-1_H_-pyrrolo[2,3-b]pyridin-5-amine (2b)

^{1}H NMR in $CDCl_3$



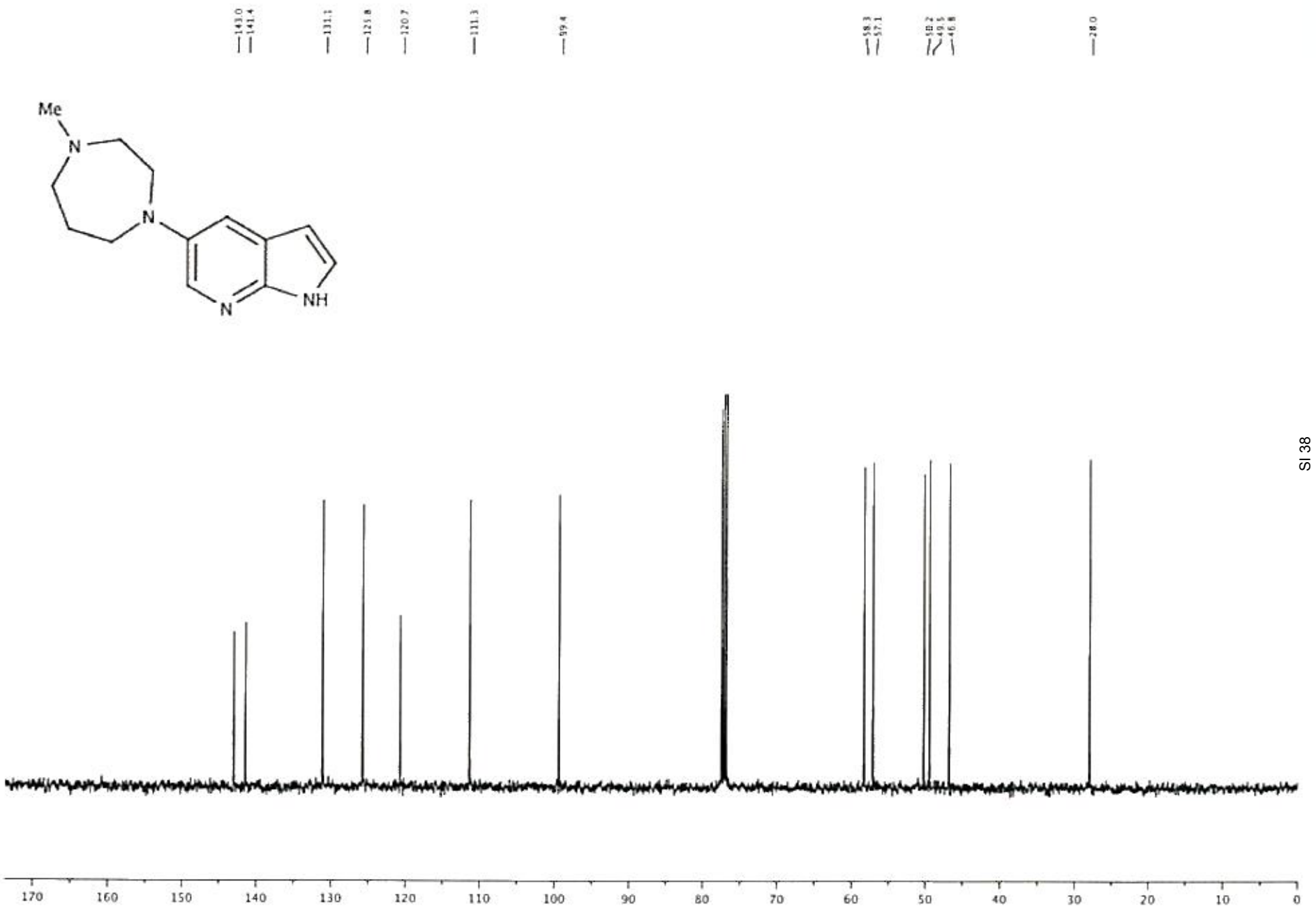
_N_-(Furan-2-ylmethyl)-_N_-methyl-1_H_-pyrrolo[2,3-b]pyridin-5-amine (2b)

^{13}C NMR in $CDCl_3$



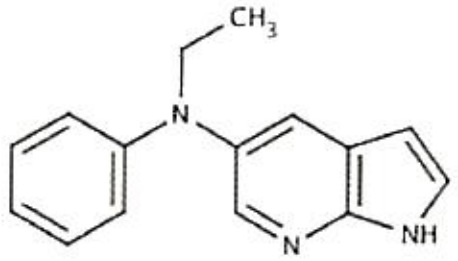
5-(4-Methyl-1,4-diazepan-1-yl)-1H-pyrrolo[2,3-b]pyridine (2c)

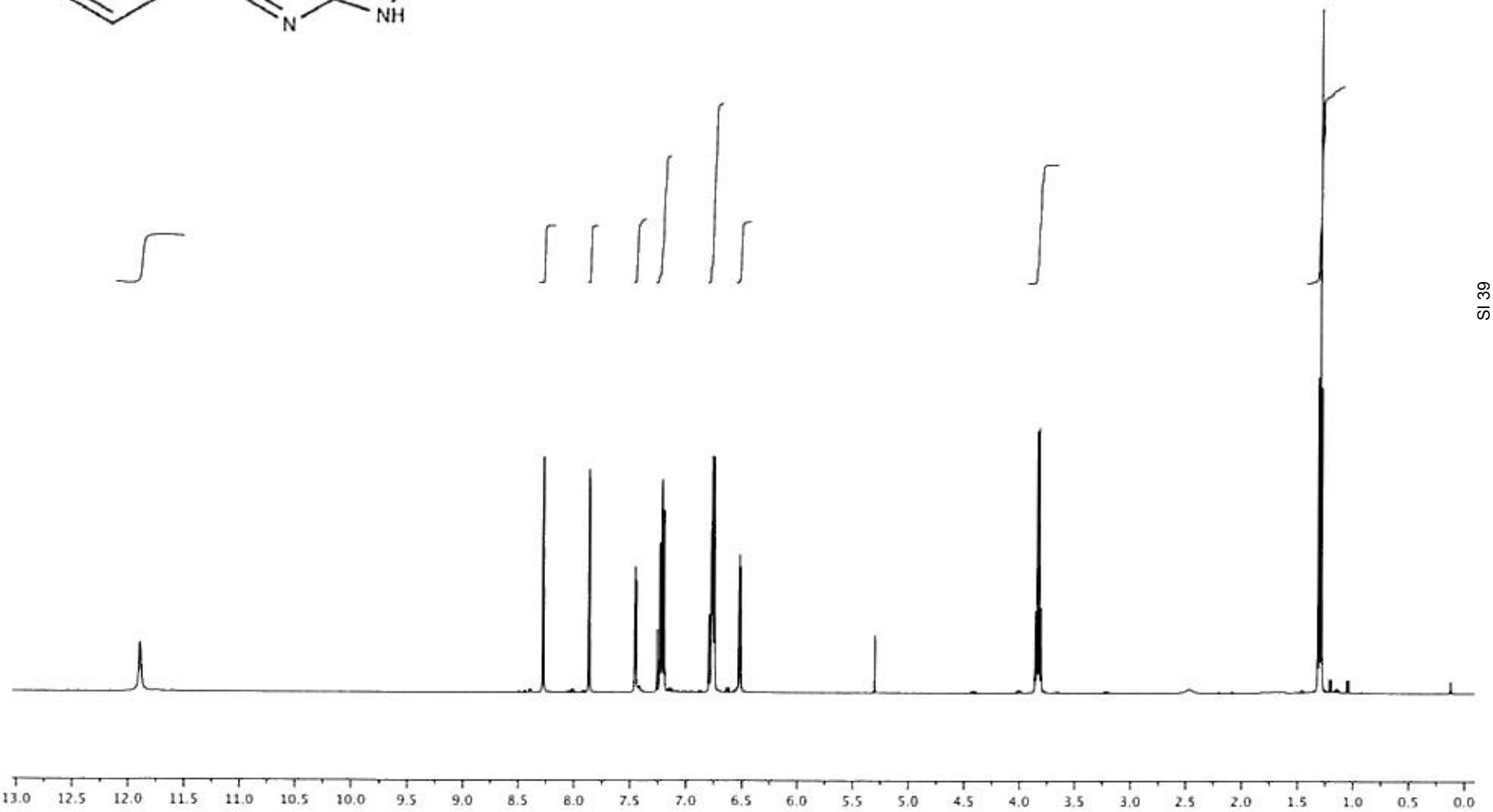
^{1}H NMR in $CDCl_3$



5-(4-Methyl-1,4-diazepan-1-yl)-1H-pyrrolo[2,3-b]pyridine (2c)

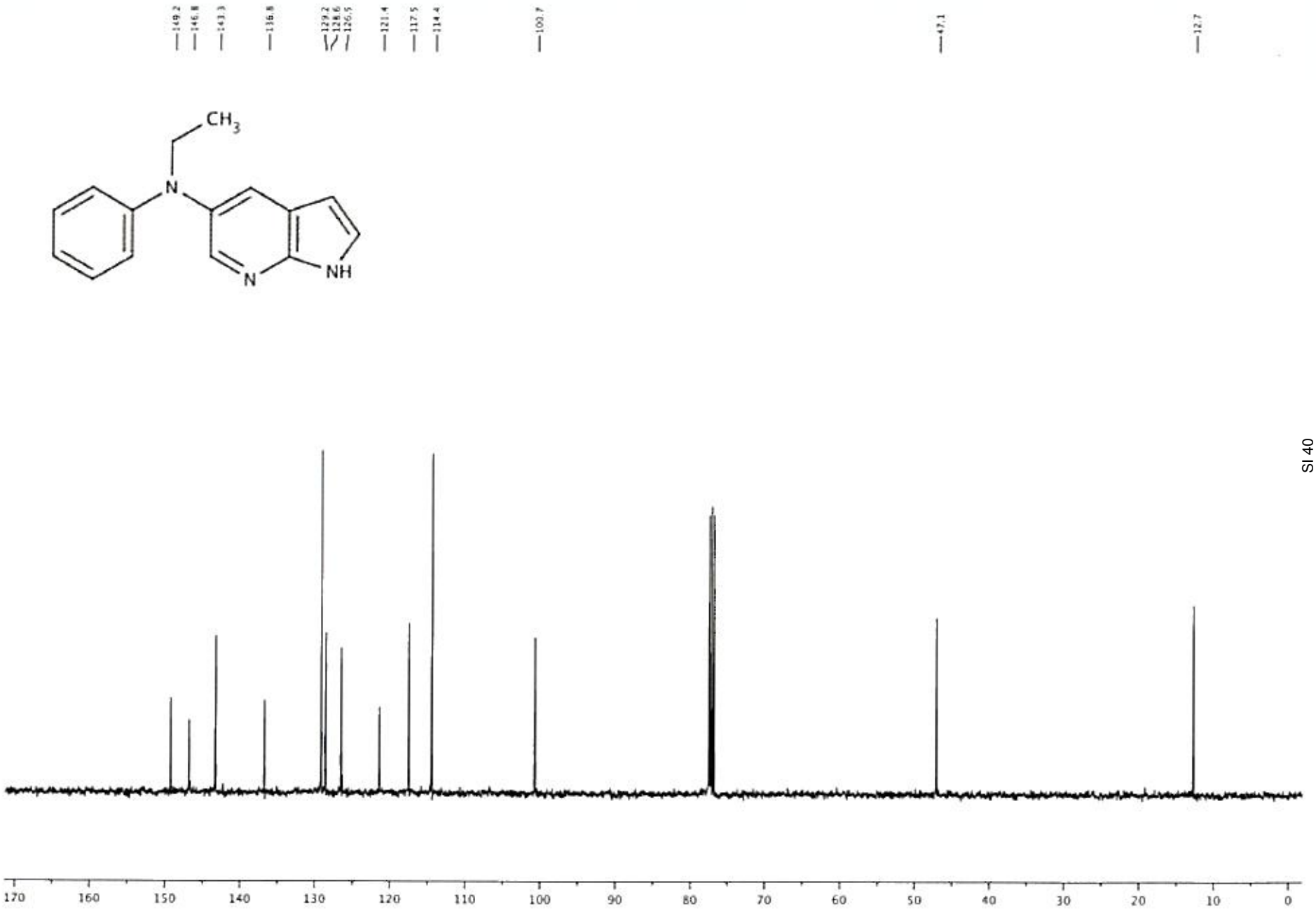
^{13}C NMR in $CDCl_3$





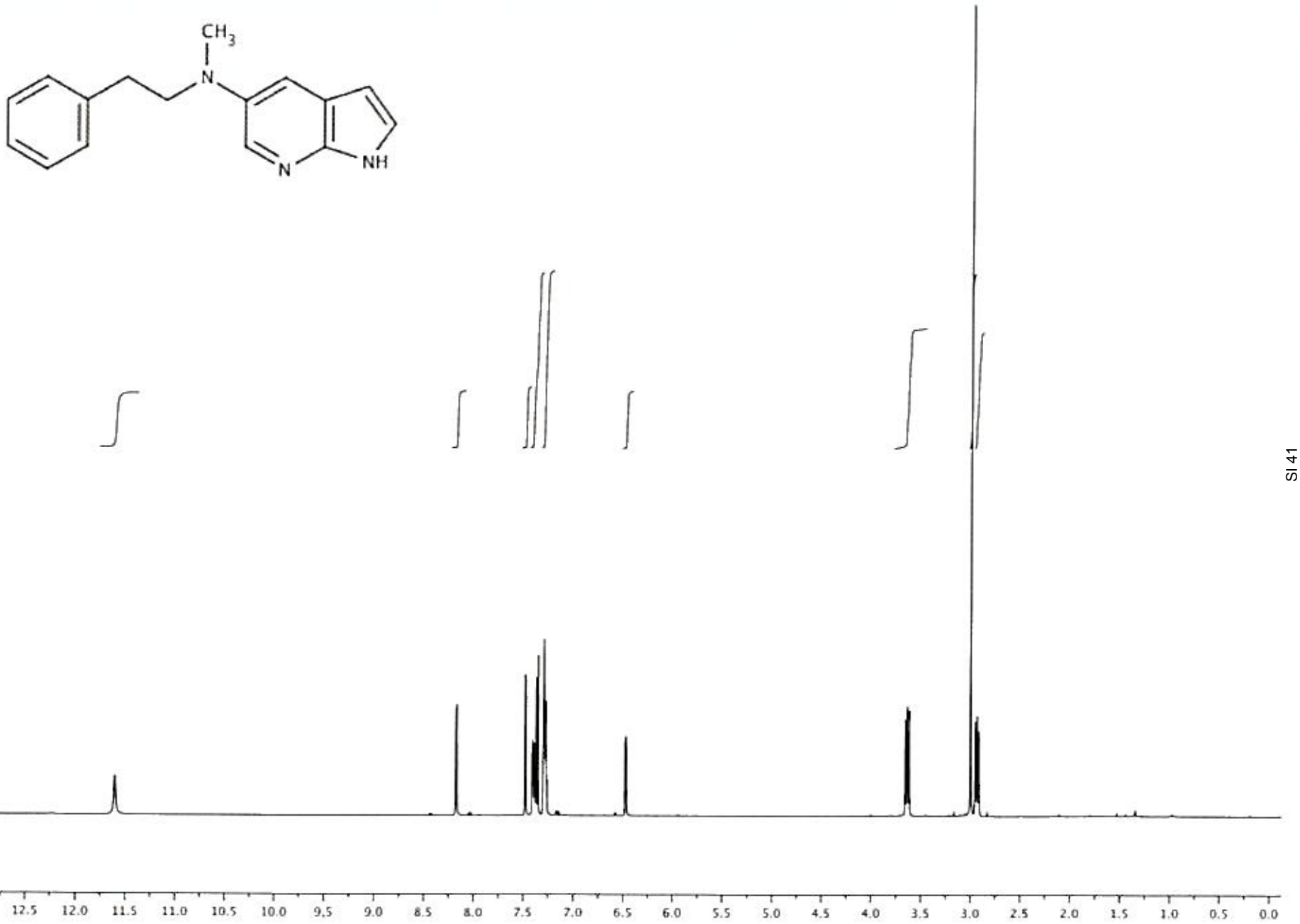
***N*-Ethyl-*N*-phenyl-1*H*-pyrrolo[2,3-b]pyridin-5-amine (2d)**

^{1}H NMR in $CDCl_3$



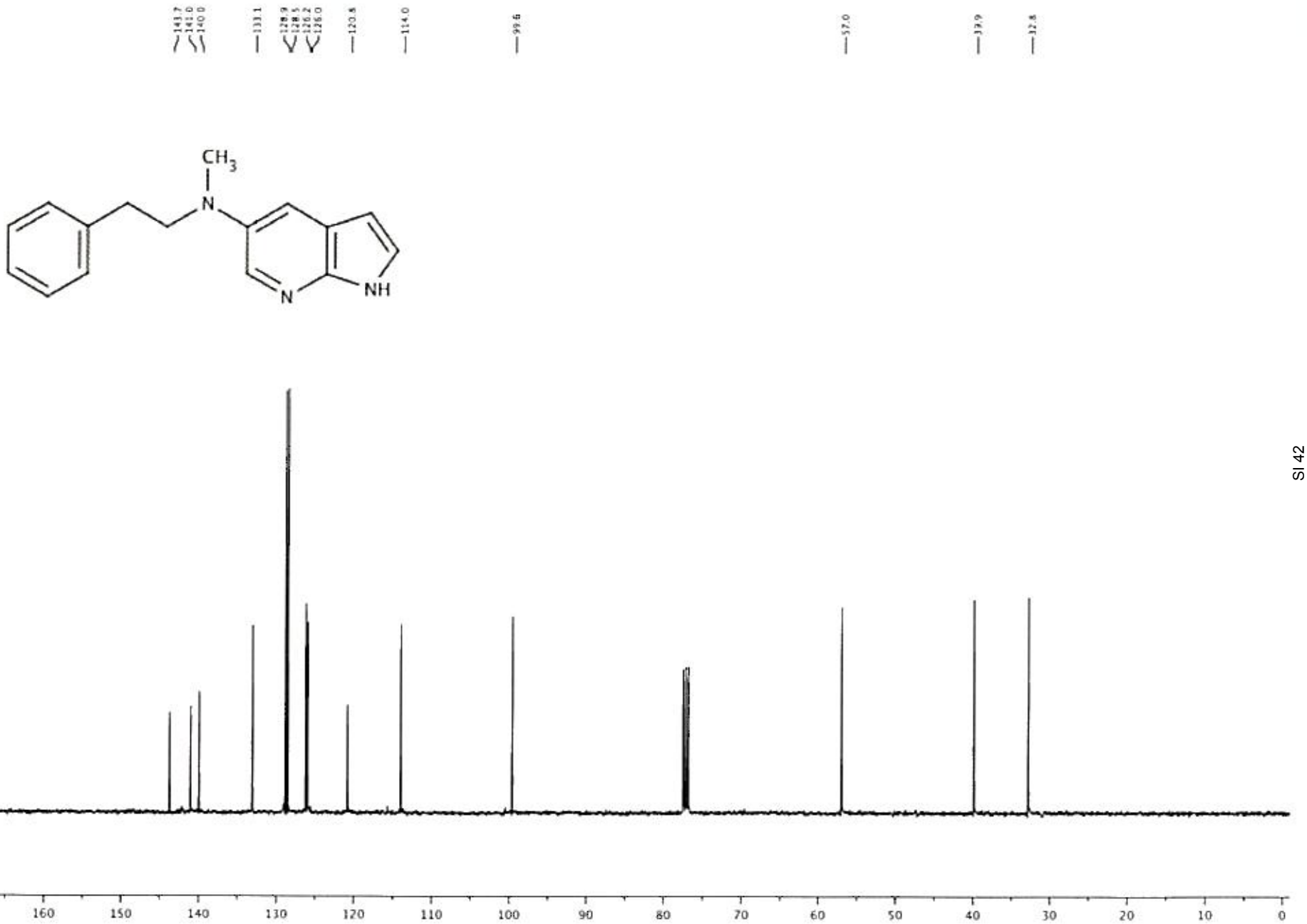
_N_-Ethyl-_N_-phenyl-1_H_-pyrrolo[2,3-b]pyridin-5-amine (2d)

^{13}C NMR in $CDCl_3$



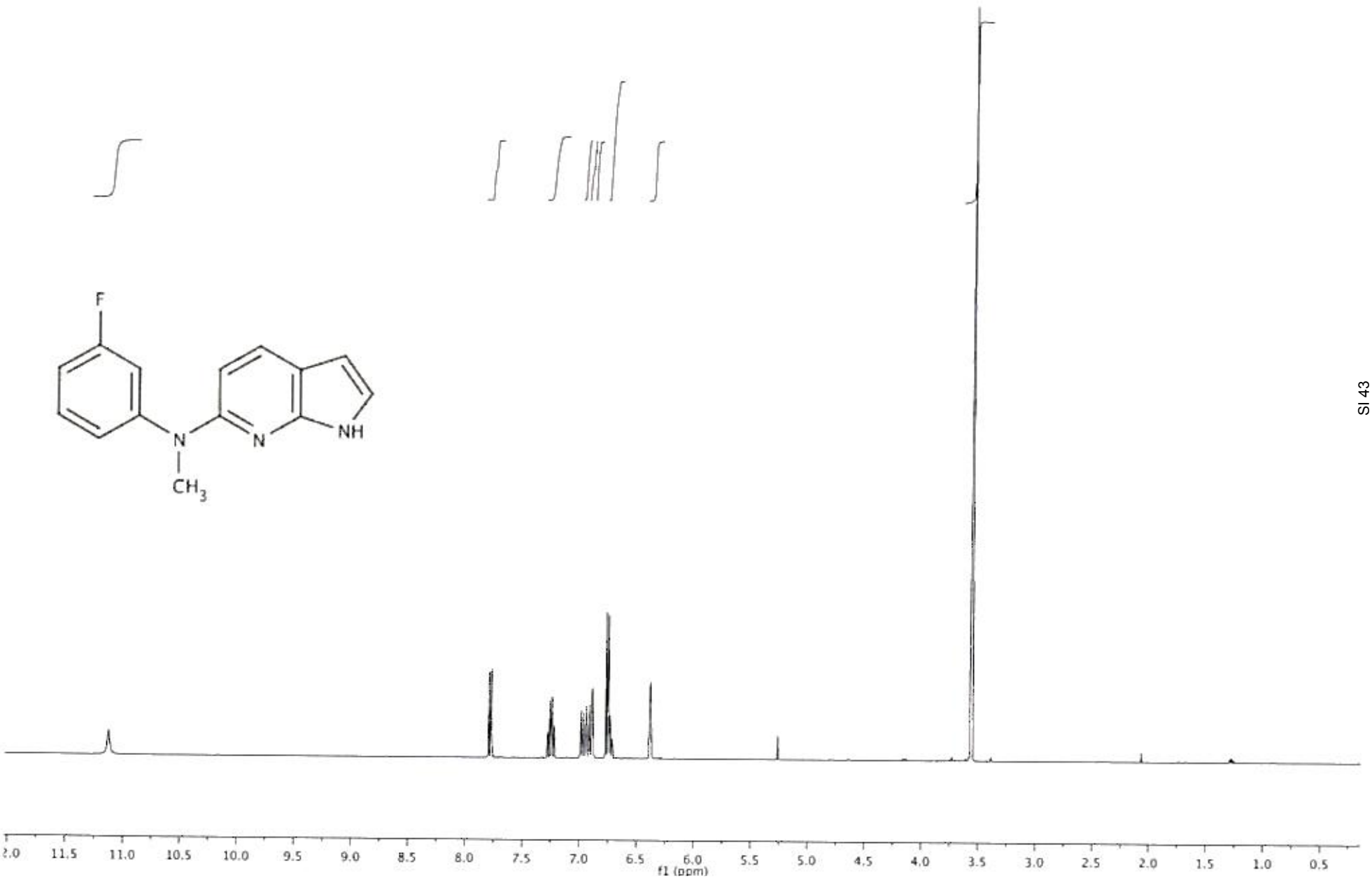
_N_-Methyl-_N_-phenethyl-1_H_-pyrrolo[2,3-b]pyridin-5-amine (2e)

^{1}H NMR in $CDCl_3$



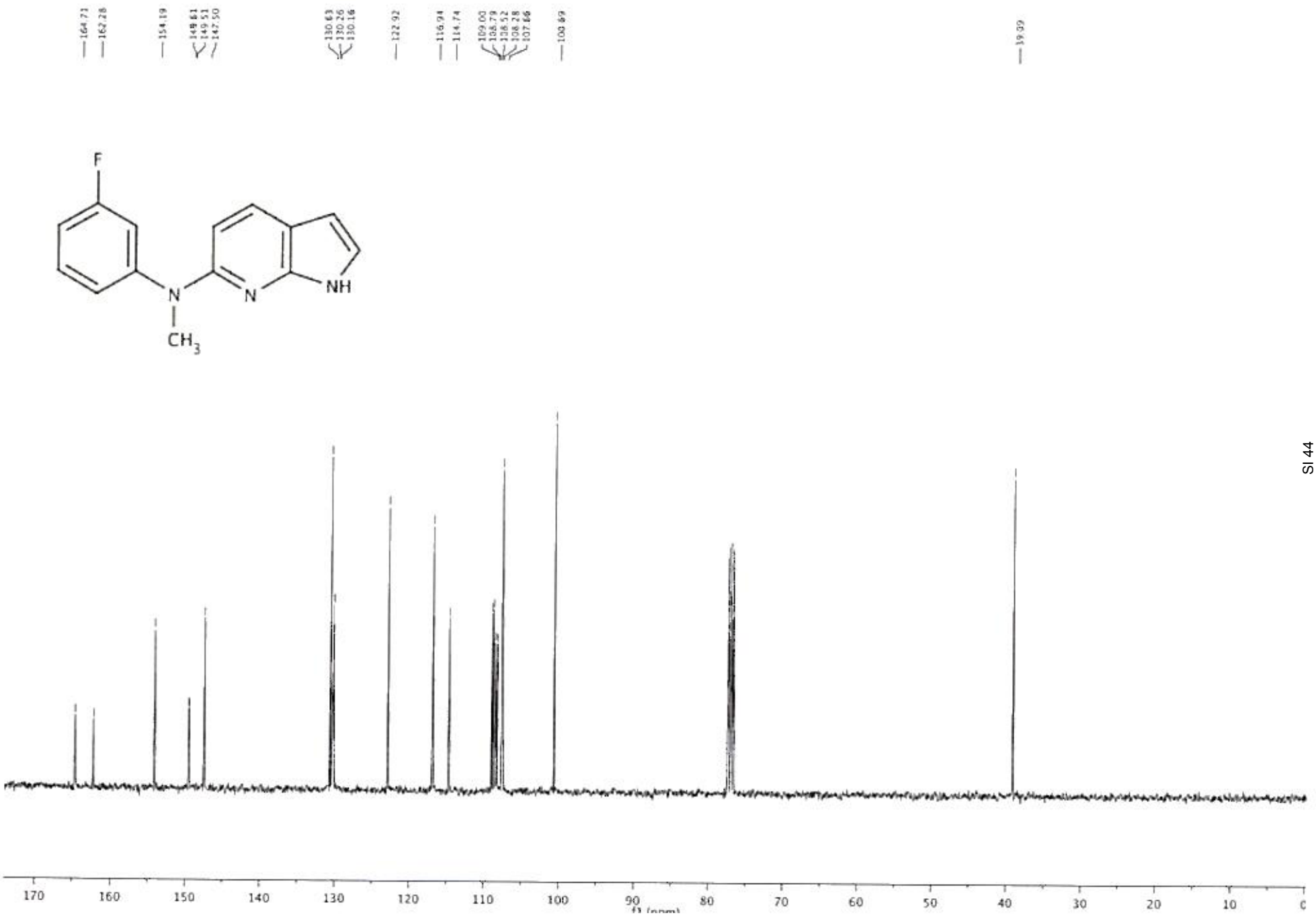
***N*-Methyl-*N*-phenethyl-1*H*-pyrrolo[2,3-b]pyridin-5-amine (2e)**

^{13}C NMR in $CDCl_3$



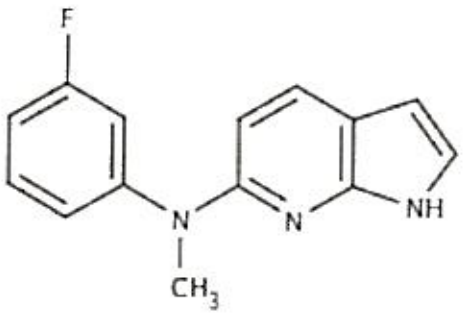
***N*-(3-Fluorophenyl)-*N*-methyl-1*H*-pyrrolo[2,3-b]pyridin-6-amine (2f)**

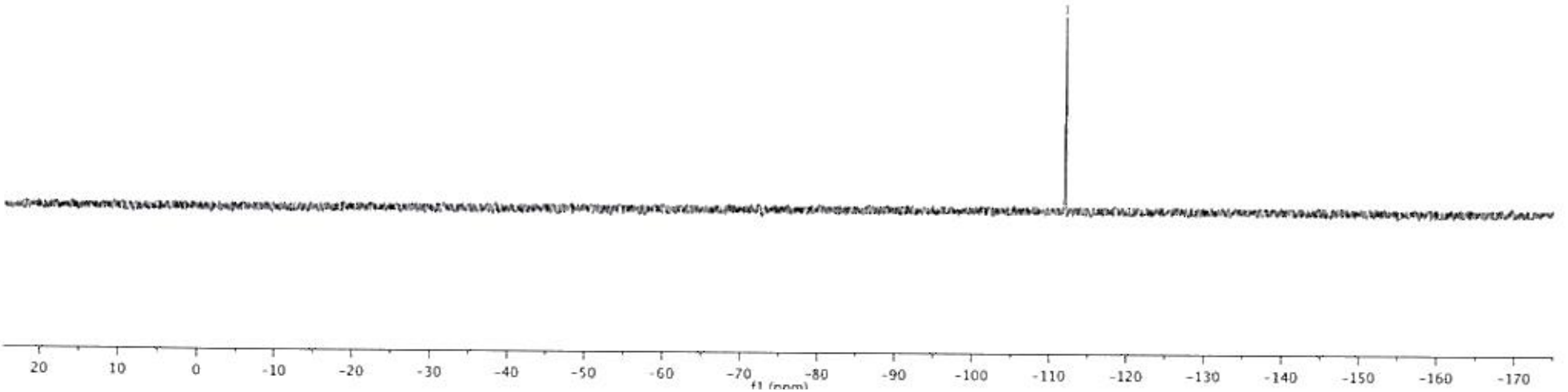
^{1}H NMR in $CDCl_3$



_N_-(3-Fluorophenyl)-_N_-methyl-1_H_-pyrrolo[2,3-b]pyridin-6-amine (2f)

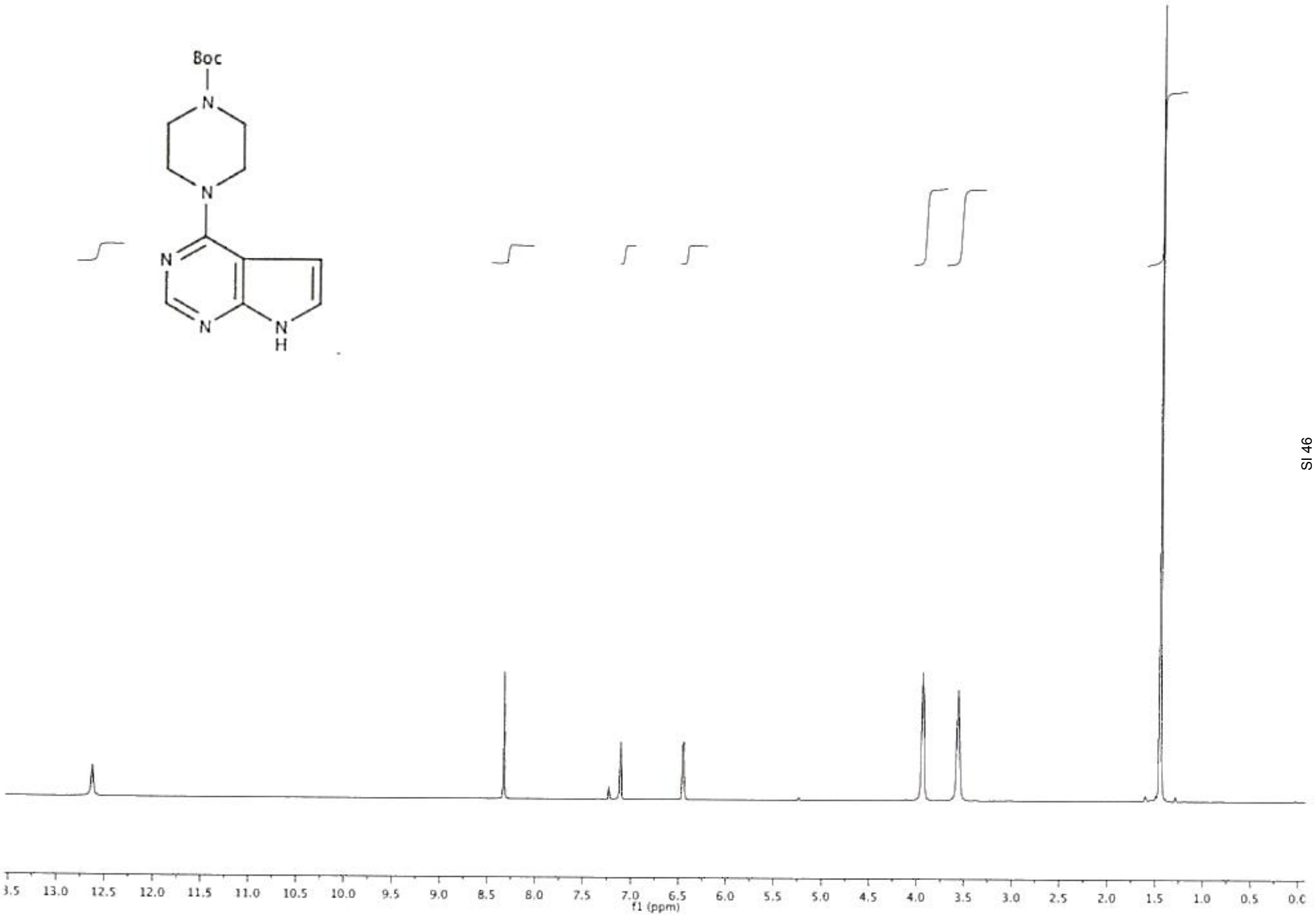
^{13}C NMR in $CDCl_3$





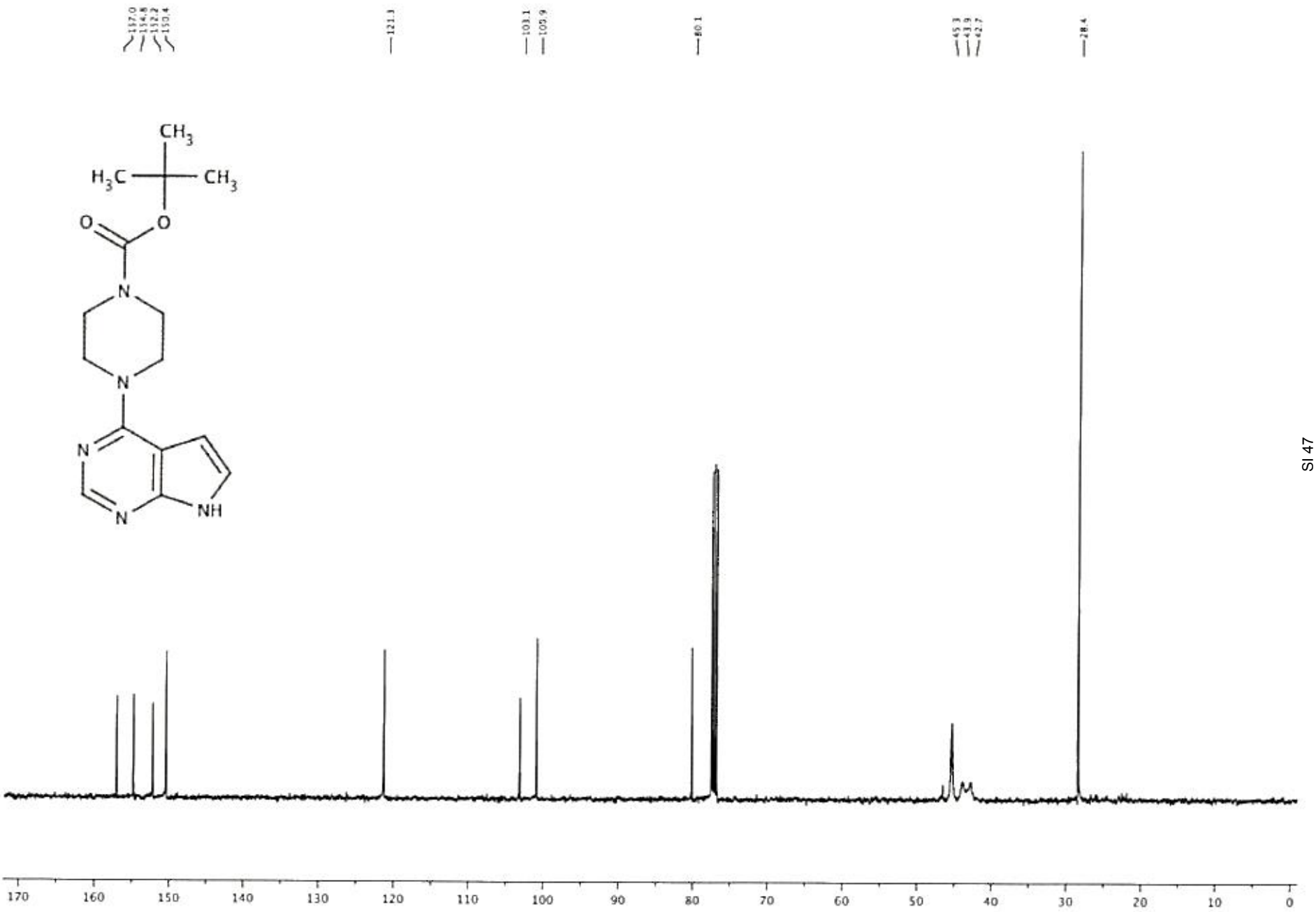
_N_-(3-Fluorophenyl)-_N_-methyl-1_H_-pyrrolo[2,3-b]pyridin-6-amine (2f)

^{19}F NMR in $CDCl_3$



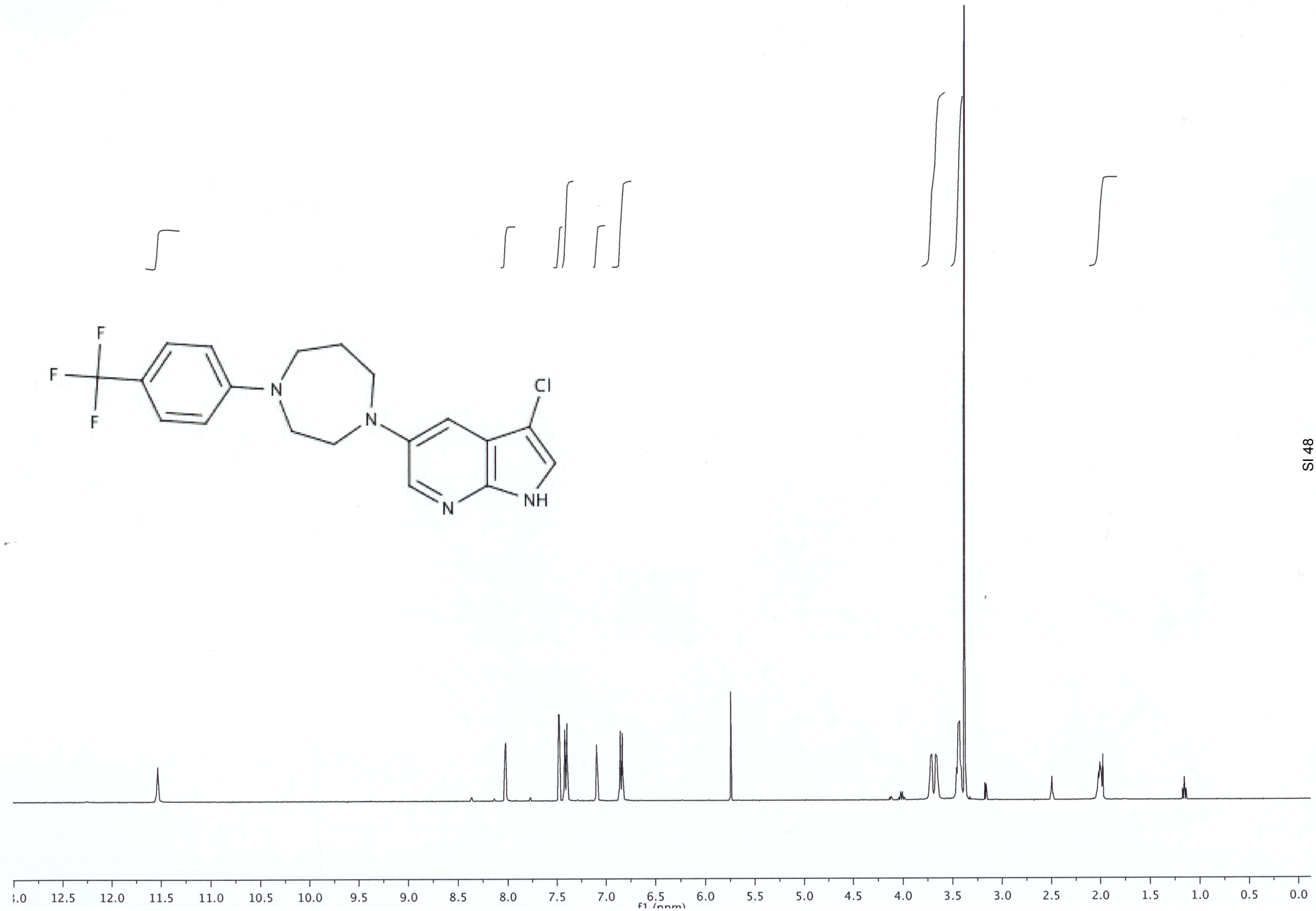
***tert*-Butyl 4-(7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)piperazine-1-carboxylate (2g)**

^{1}H NMR in $CDCl_3$



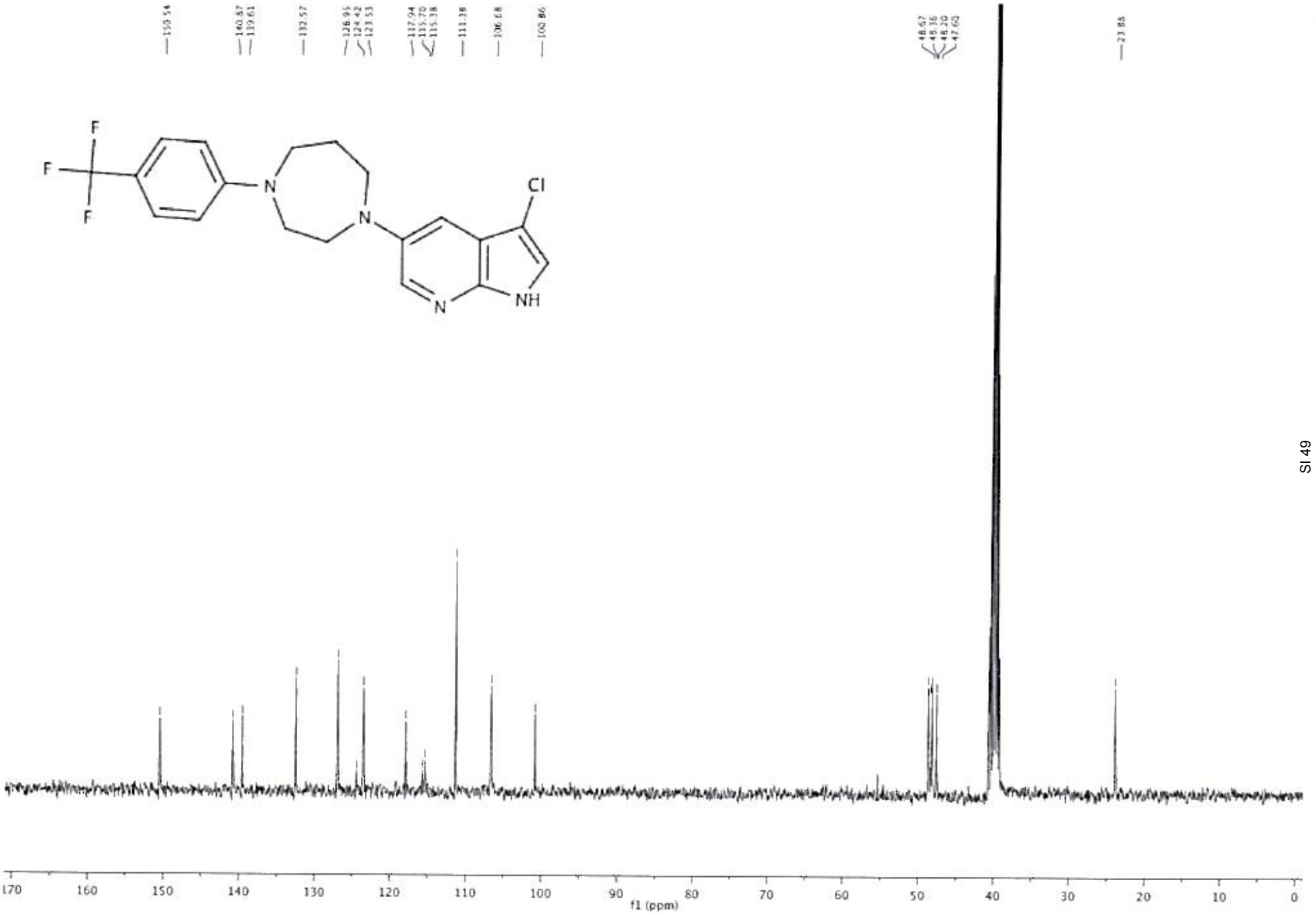
***tert*-Butyl 4-(7*H*-pyrrolo[2,3-d]pyrimidin-4-yl)piperazine-1-carboxylate (2g)**

^{13}C NMR in $CDCl_3$



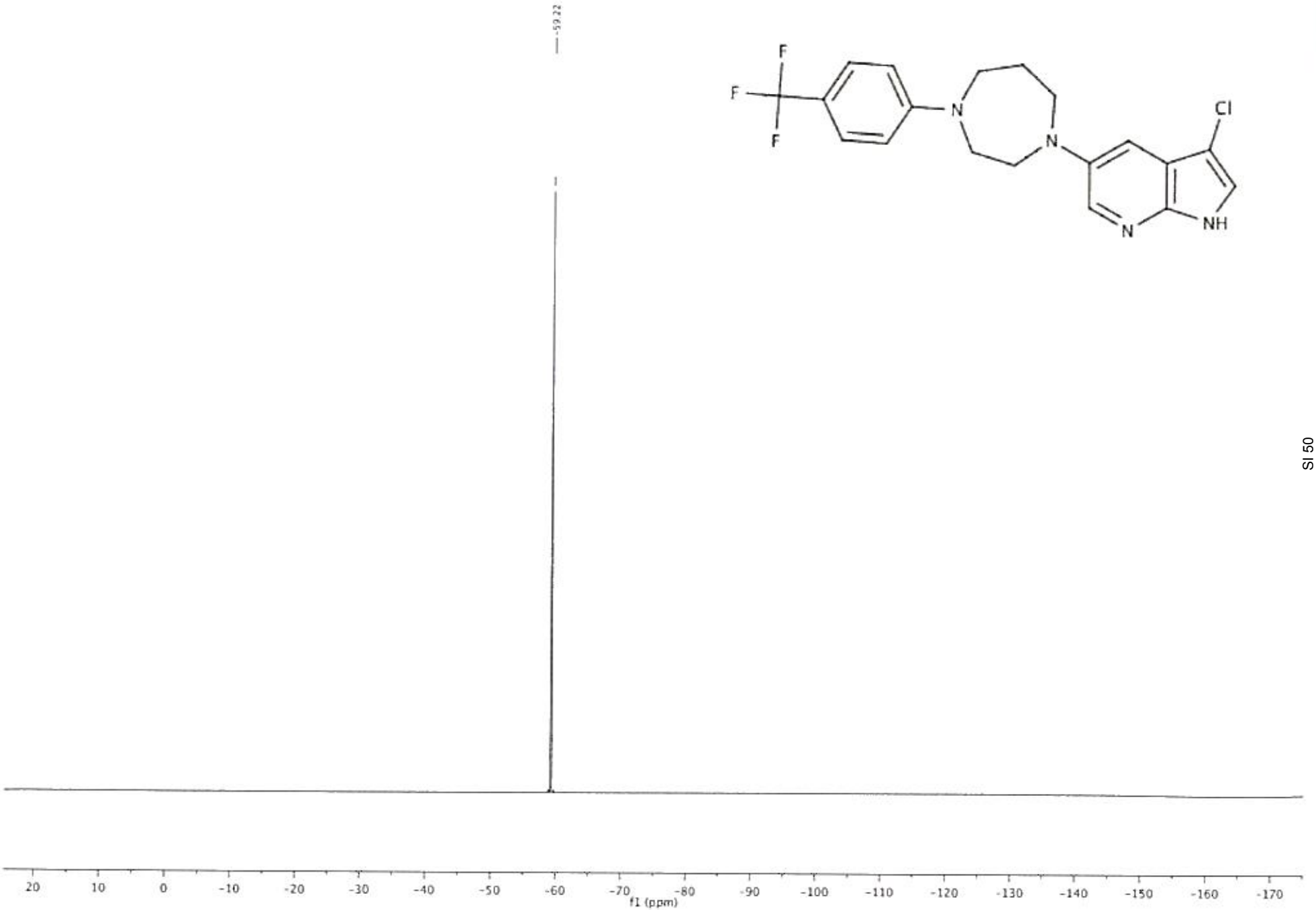
3-Chloro-5-(4-(4-(trifluoromethyl)phenyl)-1,4-diazepan-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (2h)

^{1}H NMR in DMSO - NMR sample heated (prior to acquisition) to improve solubility



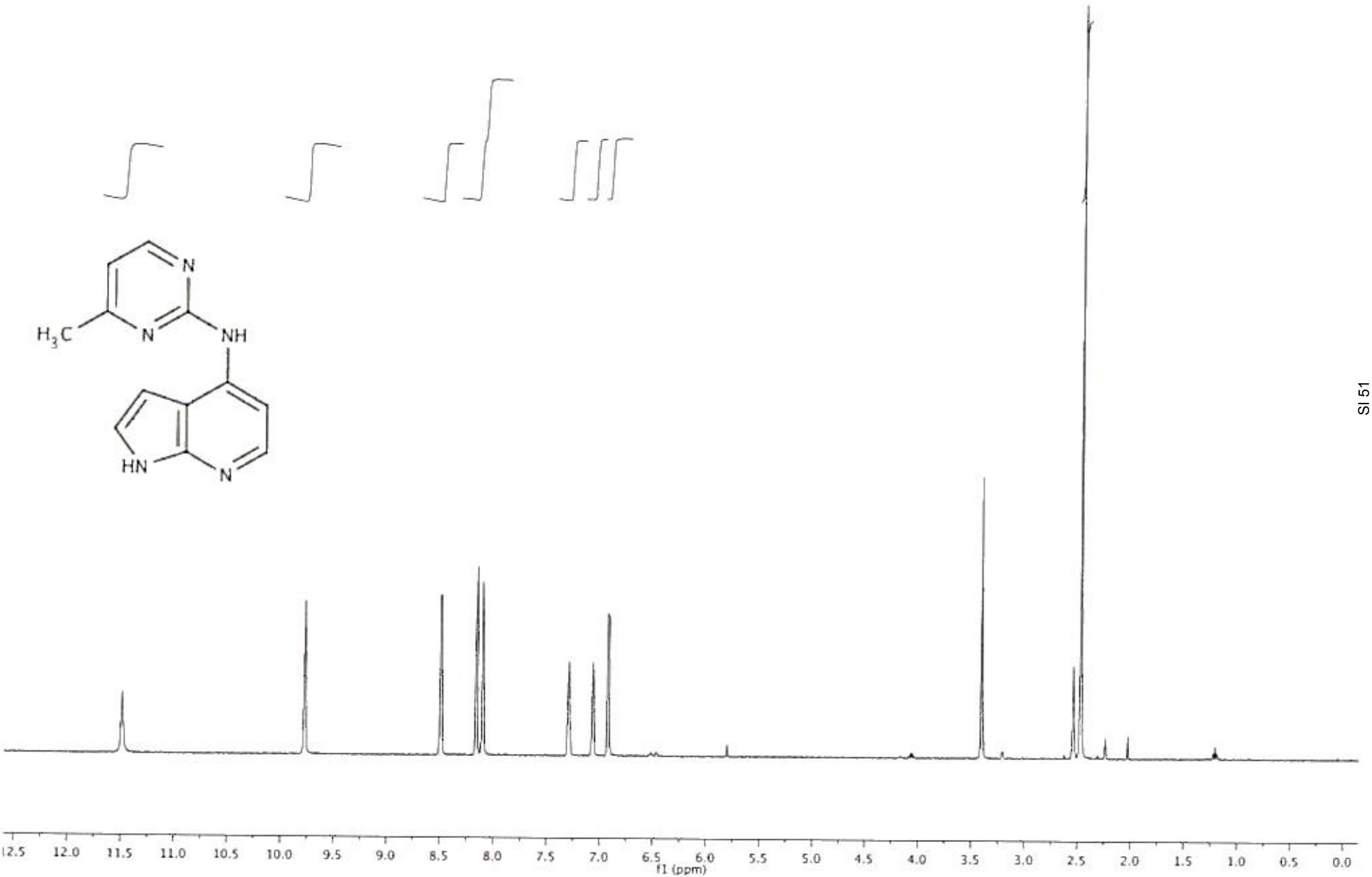
3-Chloro-5-(4-(4-(trifluoromethyl)phenyl)-1,4-diazepan-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (2h)

^{13}C NMR in DMSO



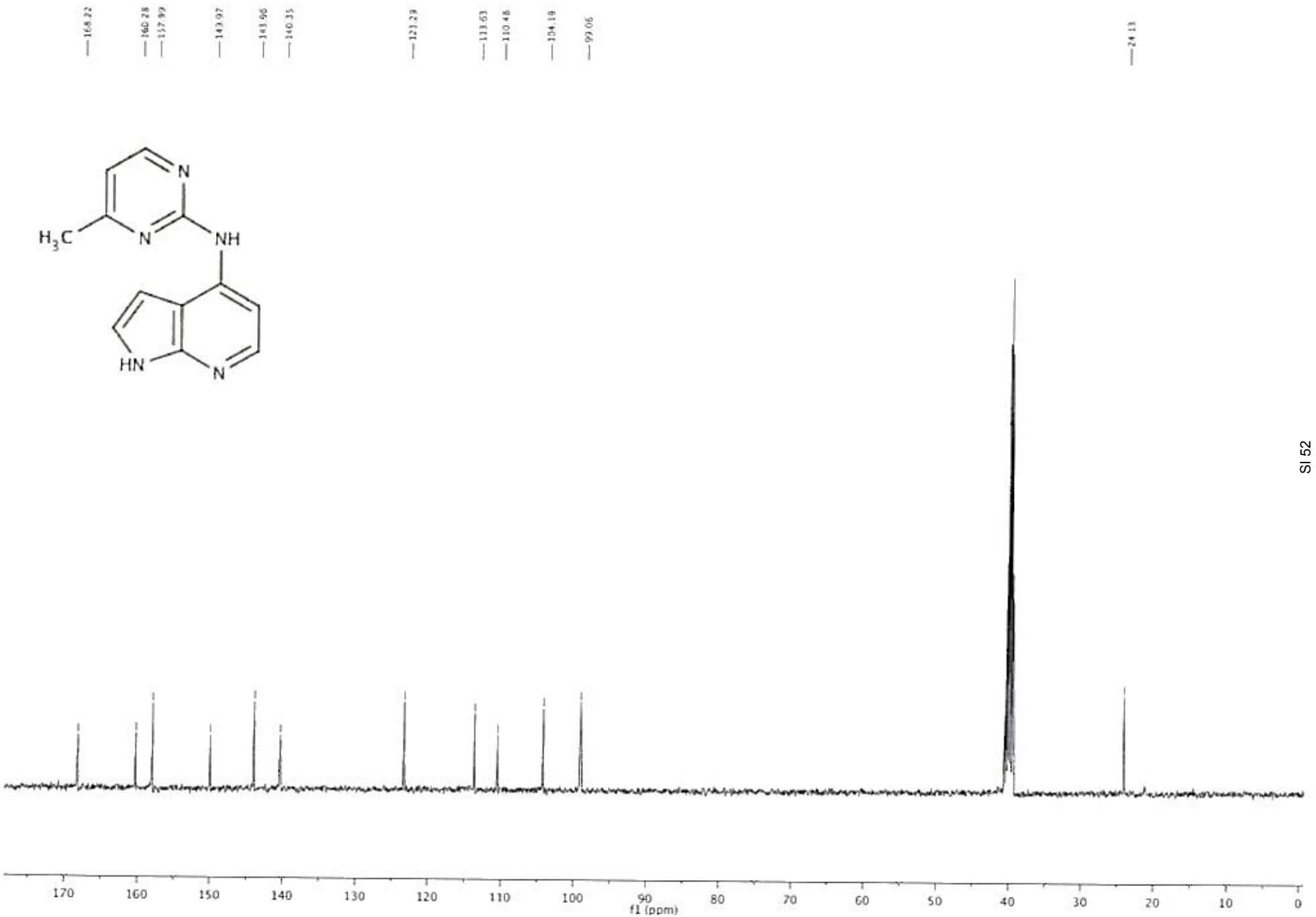
3-Chloro-5-(4-(4-(trifluoromethyl)phenyl)-1,4-diazepan-1-yl)-1*H*-pyrrolo[2,3-b]pyridine (2h)

^{19}F NMR in DMSO



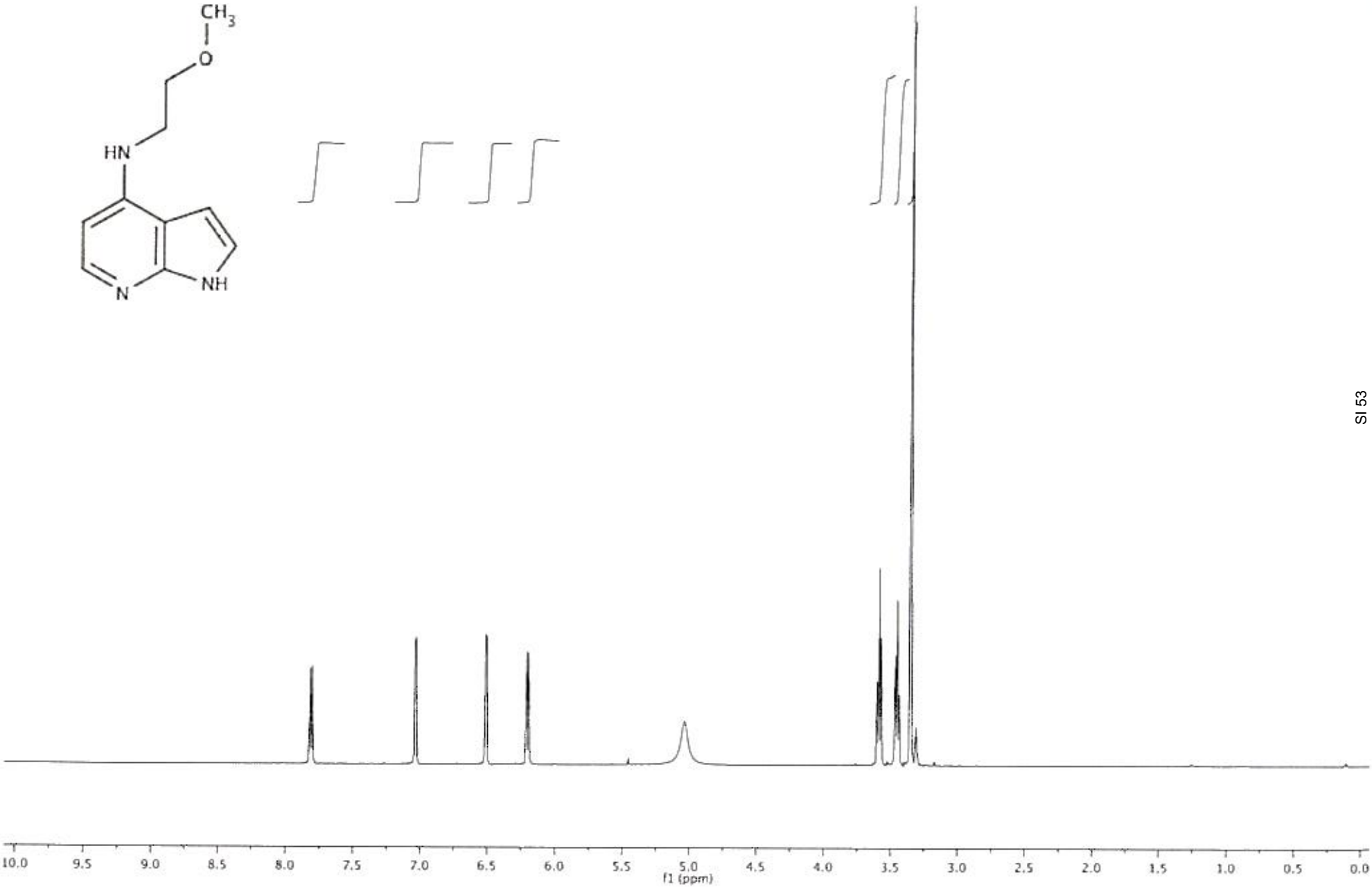
***N*-(4-Methylpyrimidin-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3a)**

^{1}H NMR in DMSO



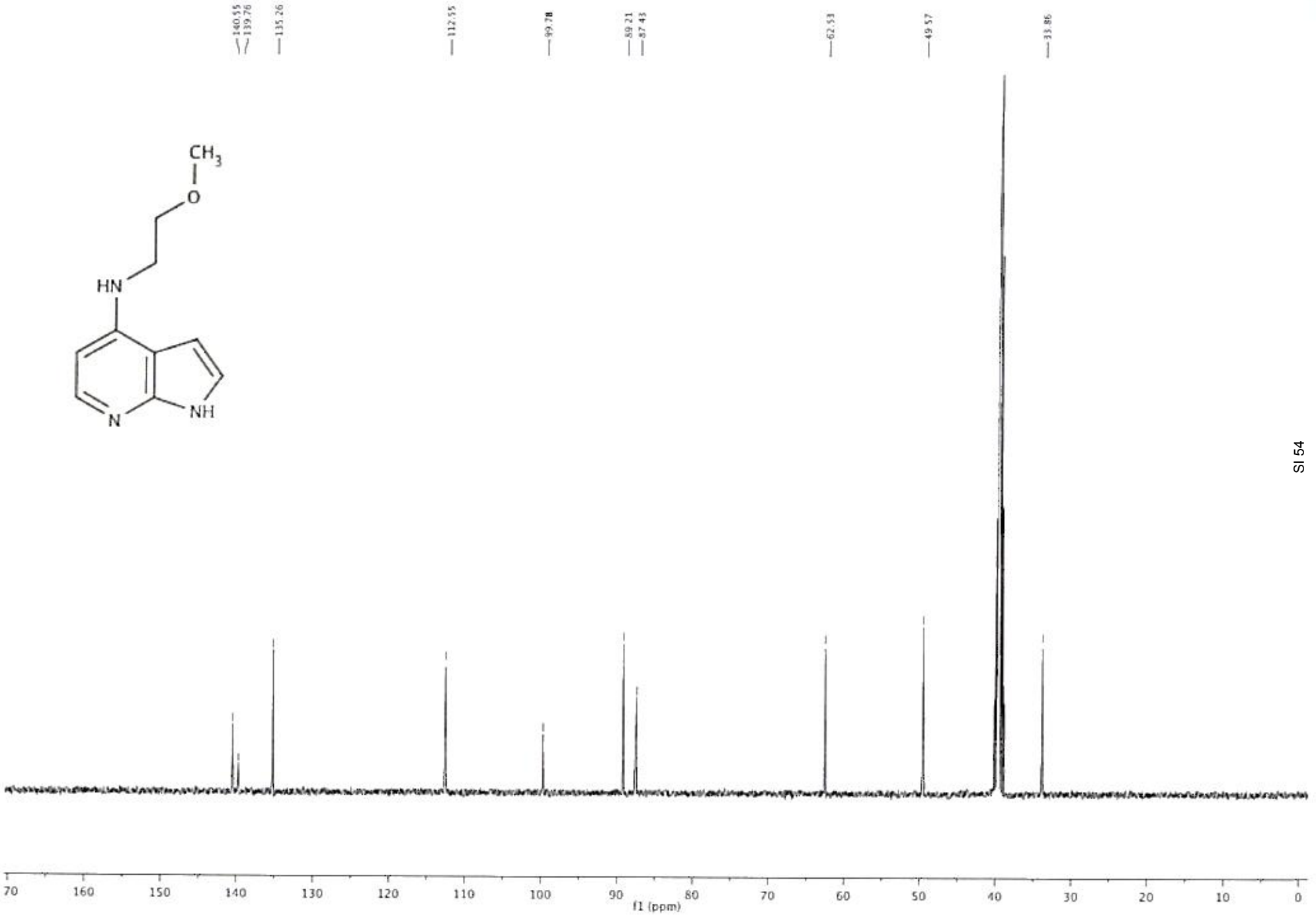
***N*-(4-Methylpyrimidin-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3a)**

^{13}C NMR in DMSO



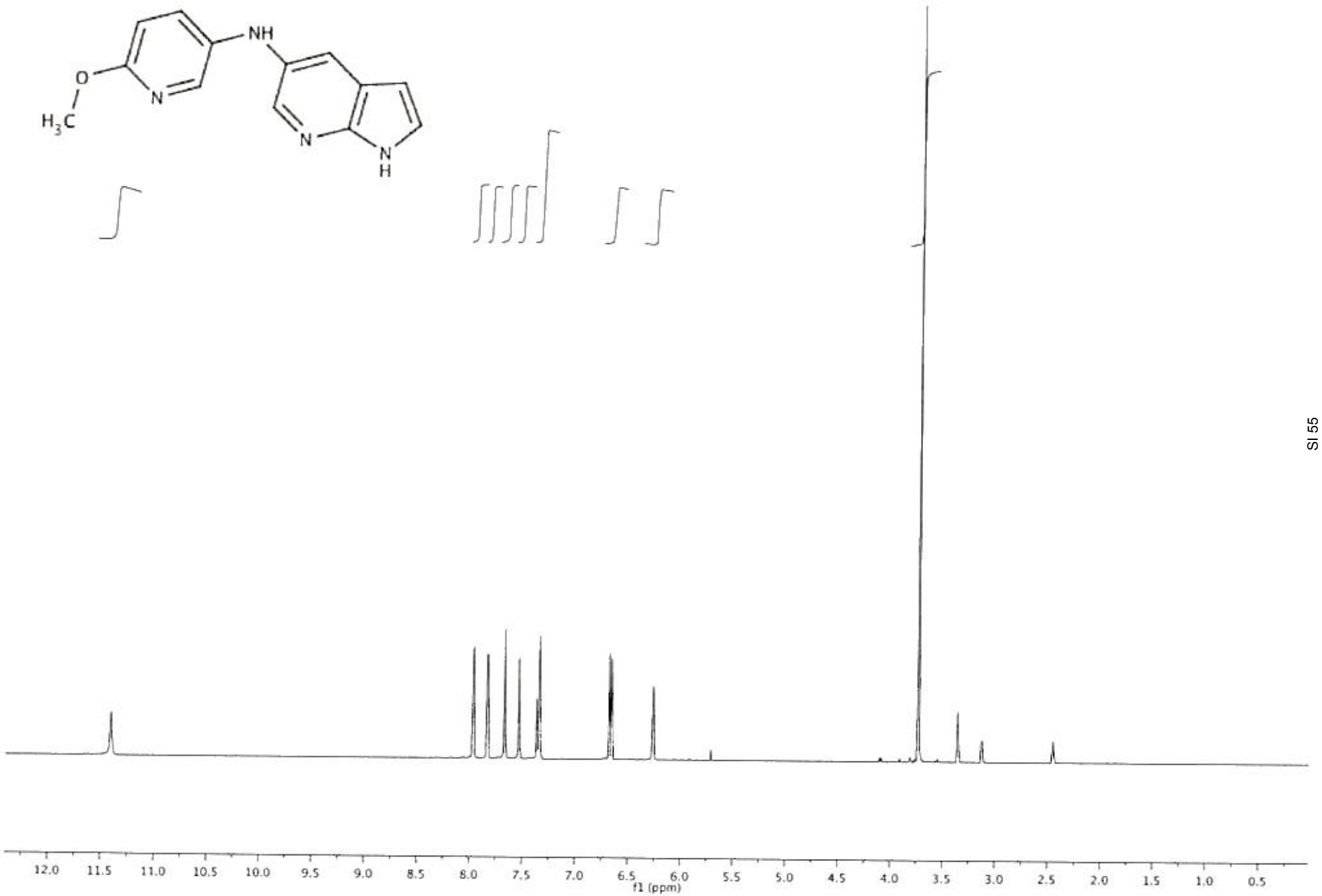
_N_-(2-Methoxyethyl)-1_H_-pyrrolo[2,3-_b_]pyridin-4-amine (3b)

^{1}H NMR in MeOD



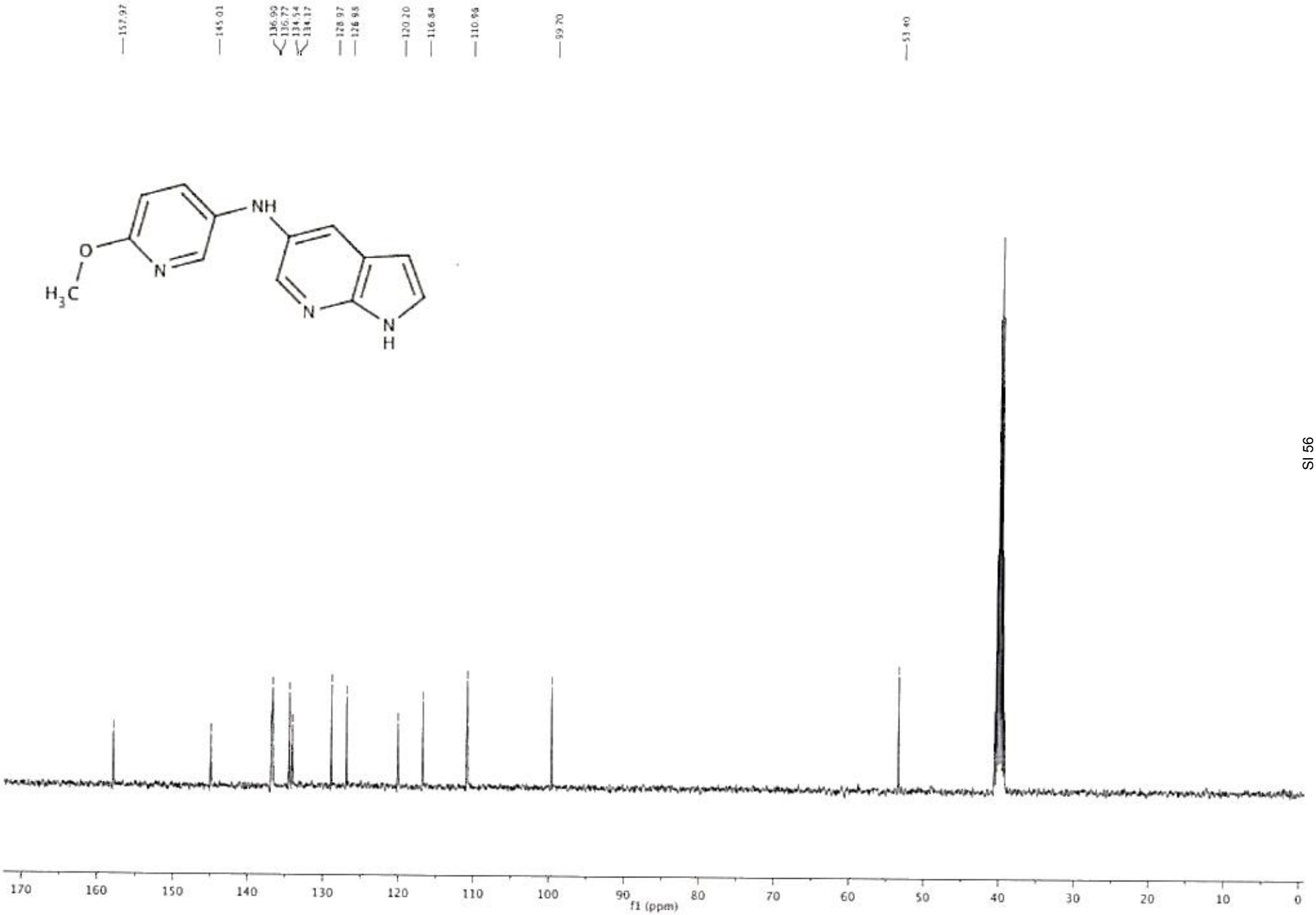
_N_-(2-Methoxyethyl)-1_H_-pyrrolo[2,3-_b_]pyridin-4-amine (3b)

^{13}C NMR in DMSO



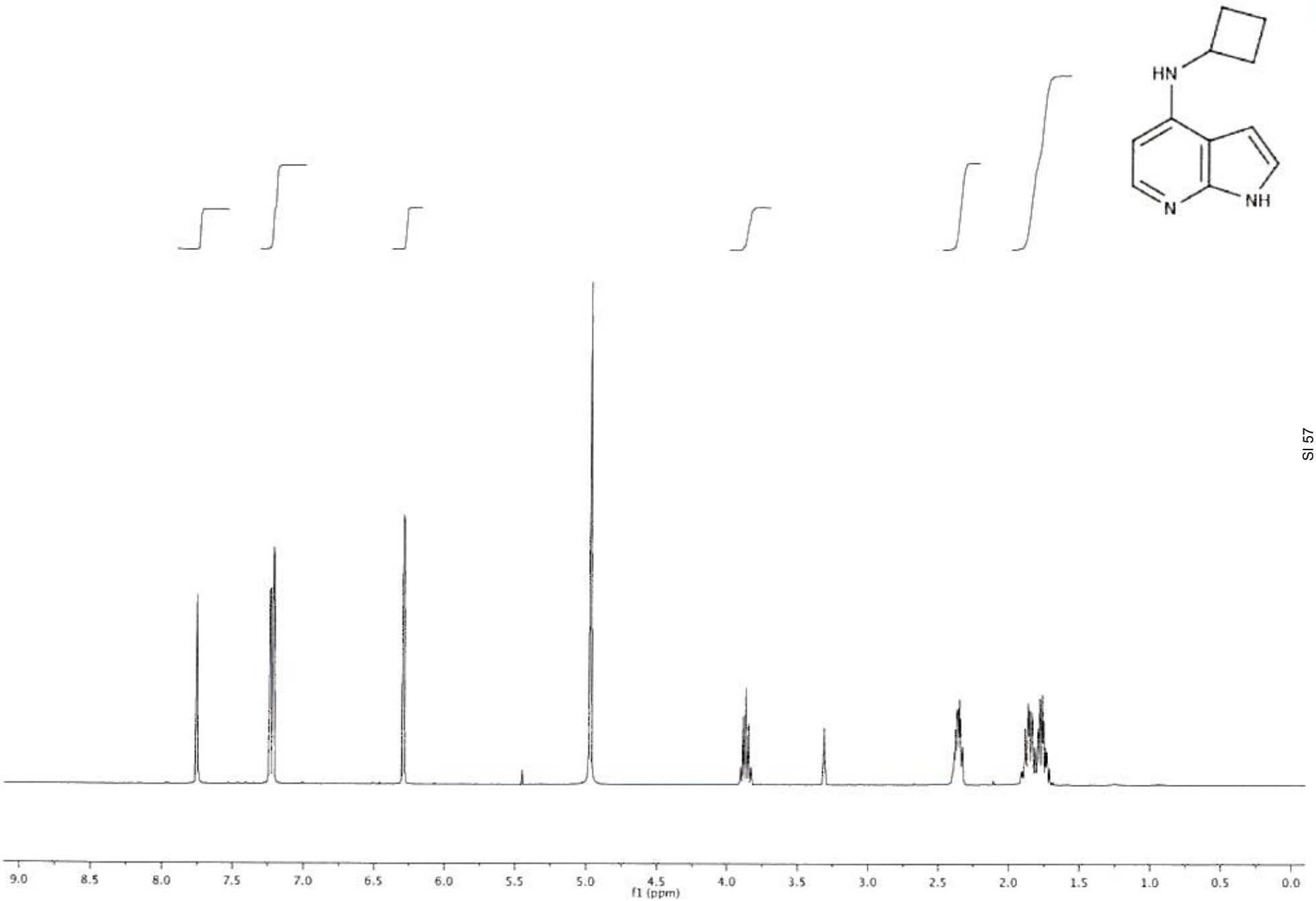
_N_-(6-Methoxypyridin-3-yl)-1_H_-pyrrolo[2,3-_b_]pyridin-5-amine (3c)

^{1}H NMR in DMSO



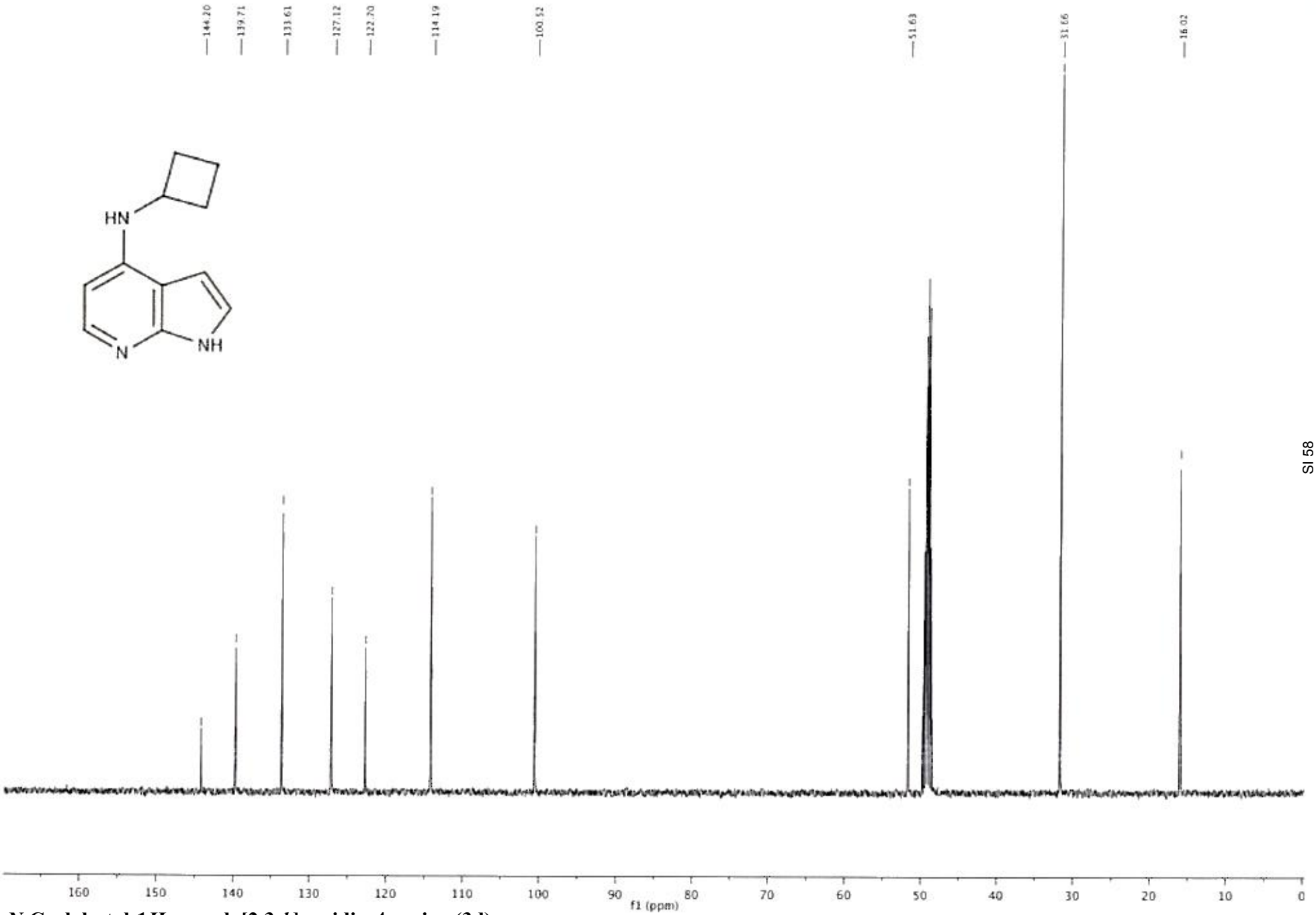
***N*-(6-Methoxypyridin-3-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-amine (3c)**

^{13}C NMR in DMSO



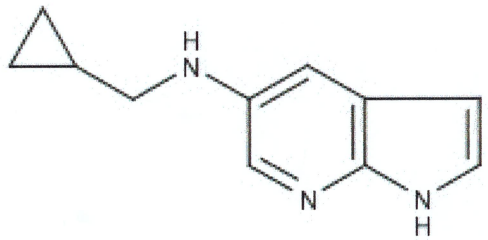
***N*-Cyclobutyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3d)**

^{1}H NMR in MeOD



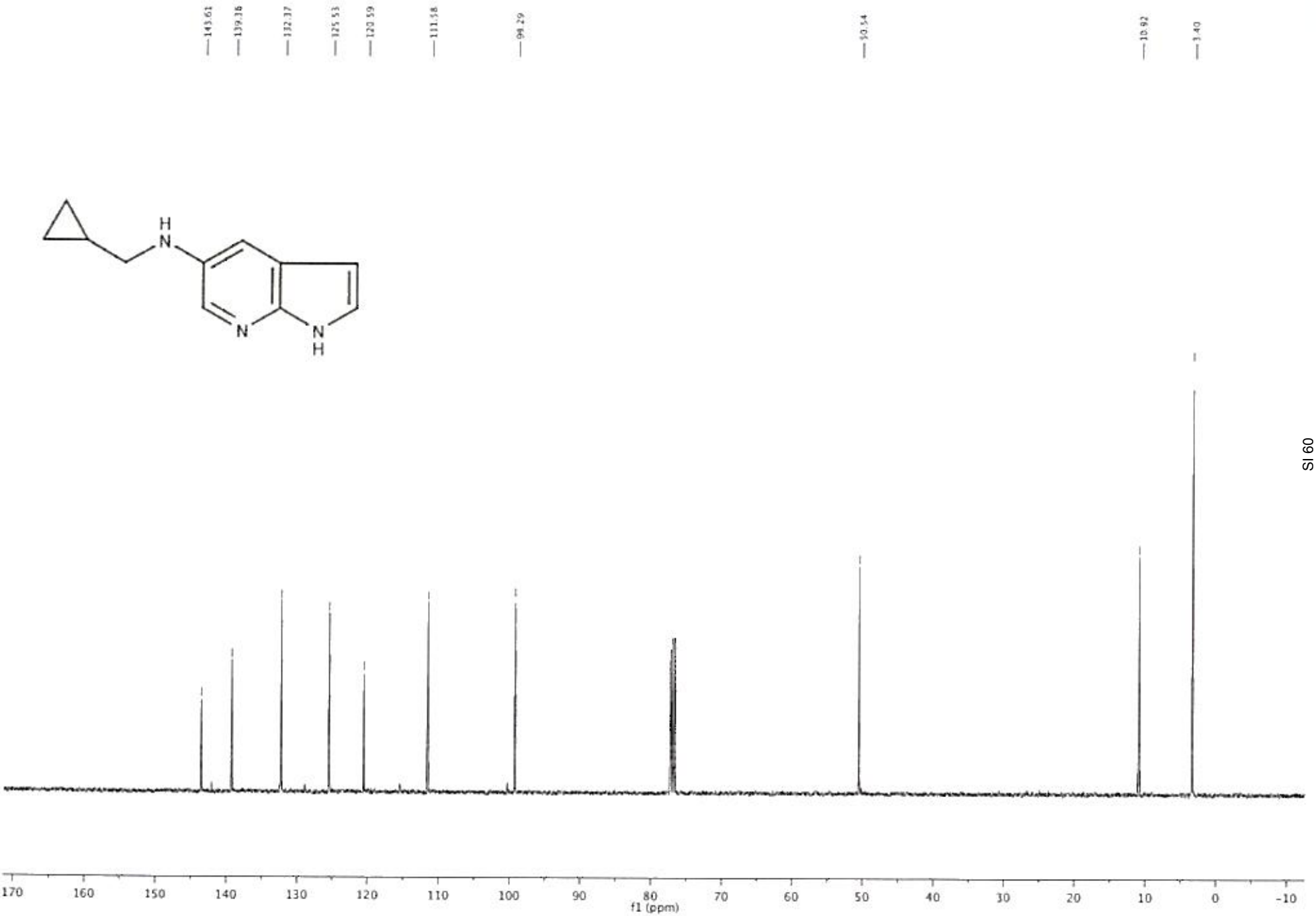
***N*-Cyclobutyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3d)**

^{13}C NMR in MeOD



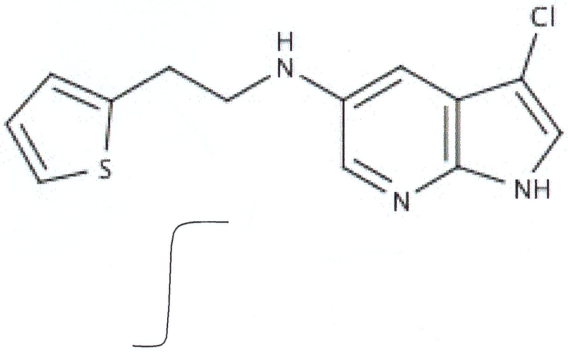
_N_-(Cyclopropylmethyl)-1_H_-pyrrolo[2,3-b]pyridin-5-amine (3e)

^{1}H NMR in $CDCl_3$



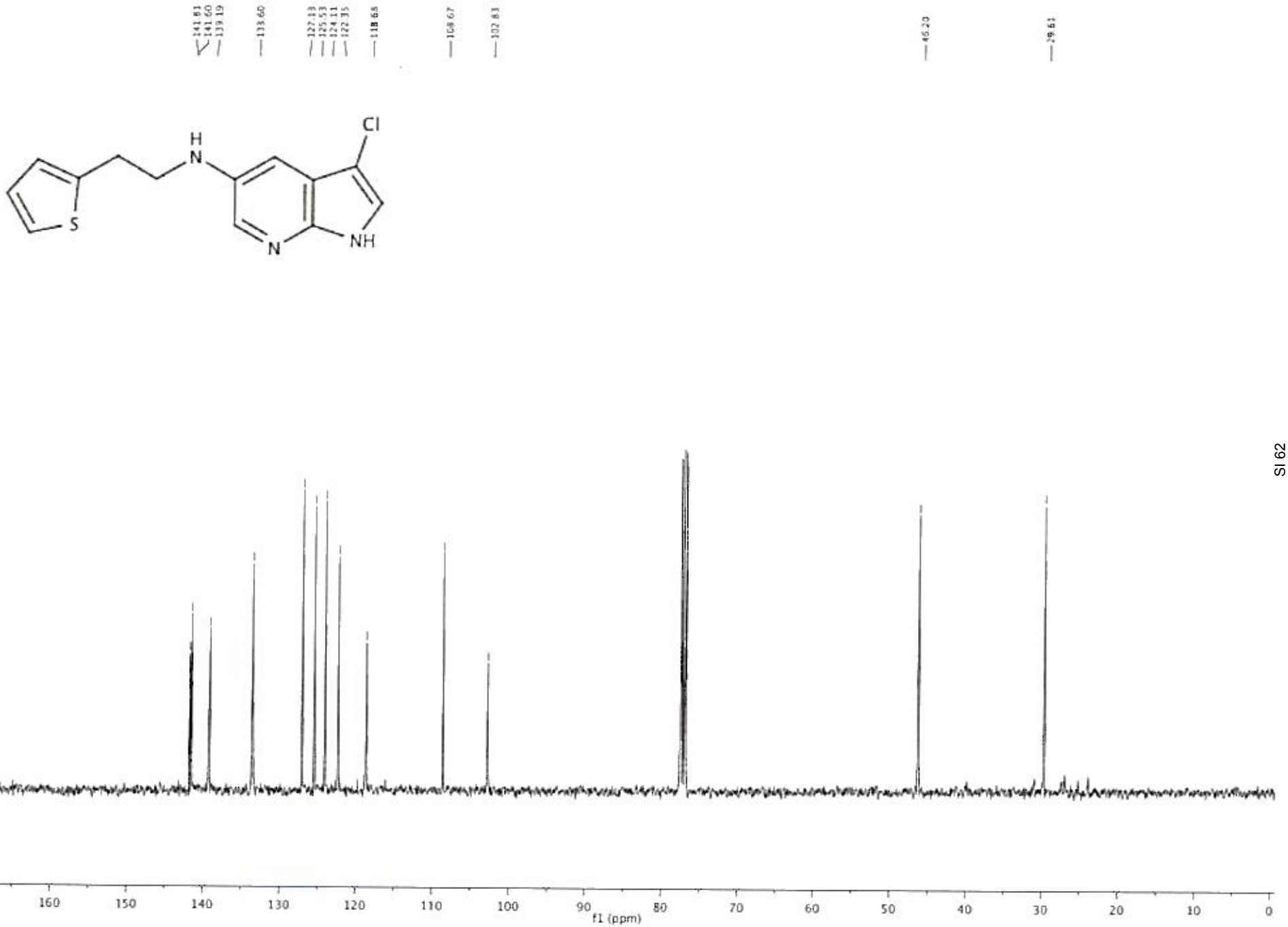
_N_-(Cyclopropylmethyl)-1_H_-pyrrolo[2,3-b]pyridin-5-amine (3e)

^{13}C NMR in $CDCl_3$



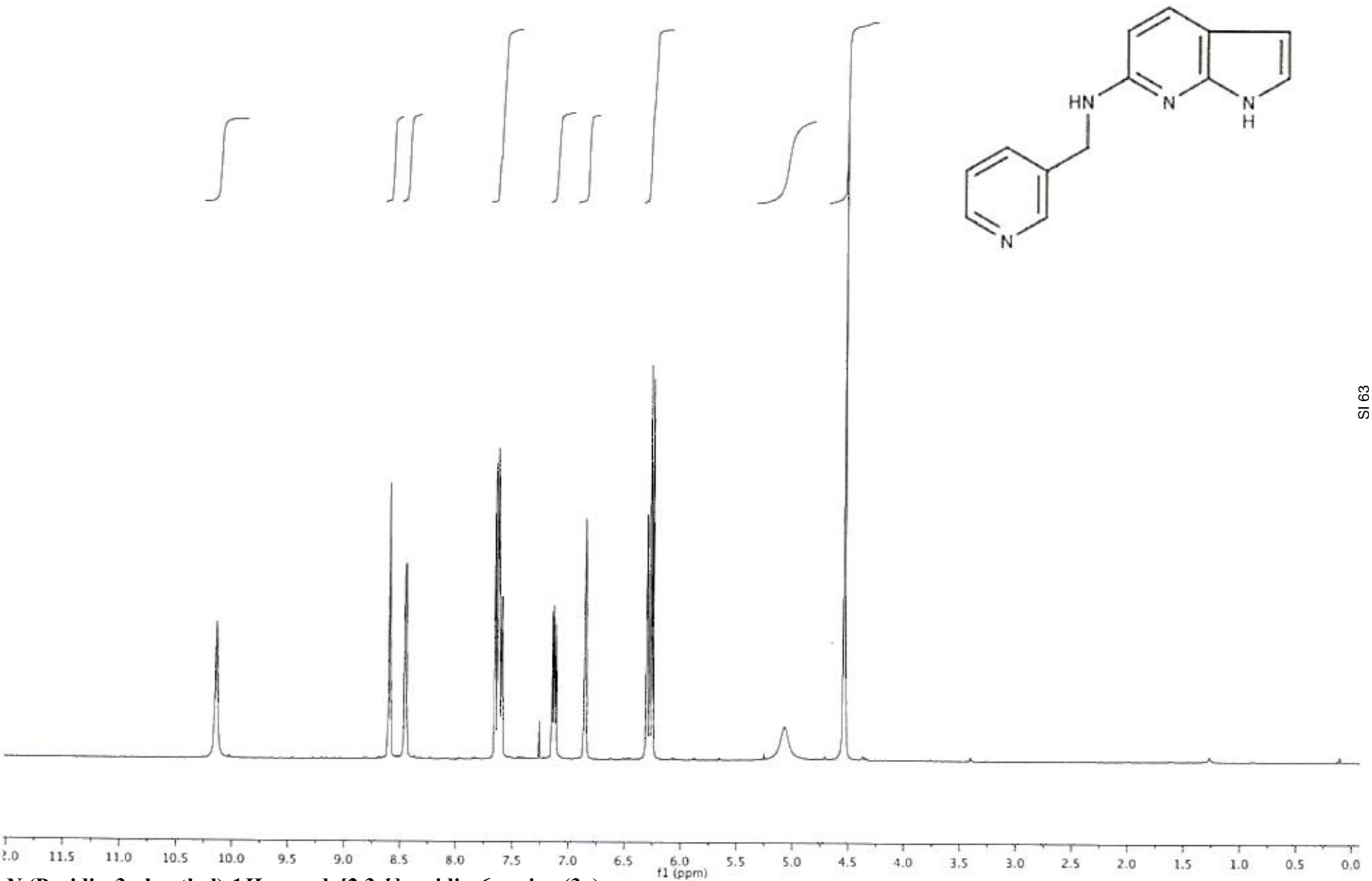
3-Chloro-*N*-(2-(thiophen-2-yl)ethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-amine (3f)

^{1}H NMR in $CDCl_3$



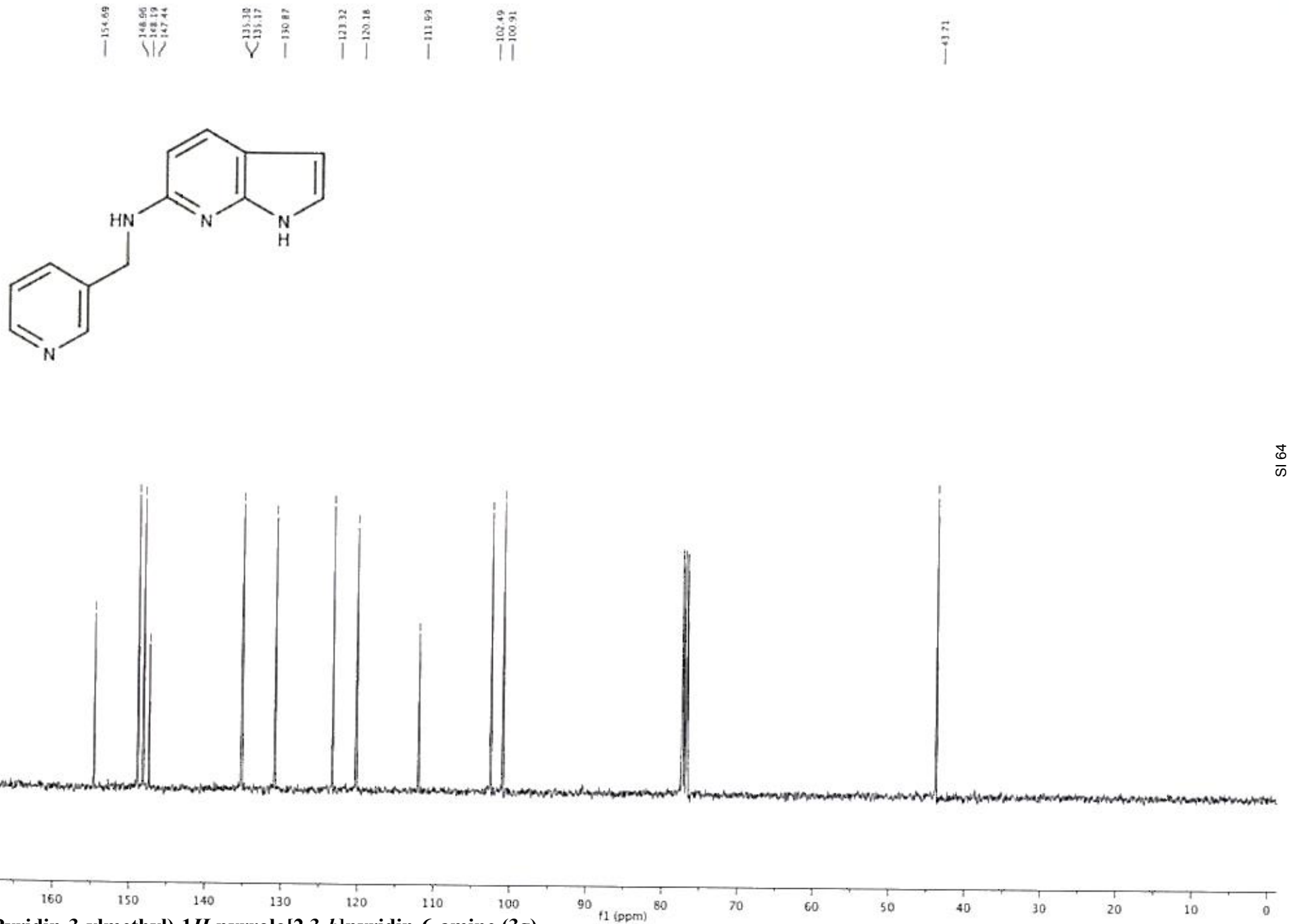
3-Chloro-*N*-(2-(thiophen-2-yl)ethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-amine (3f)

^{13}C NMR in $CDCl_3$



_N_-(Pyridin-3-ylmethyl)-1_H_-pyrrolo[2,3-_b_]pyridin-6-amine (3g)

^{1}H NMR in $CDCl_3$



***N*-(Pyridin-3-ylmethyl)-1*H*-pyrrolo[2,3-*b*]pyridin-6-amine (3g)**

^{13}C NMR in $CDCl_3$