Supporting Information for

Construction of multiple bonds via a domino reaction of trifluoroacetimidoyl nitriles with *in-situ* generated bis-nucleophiles

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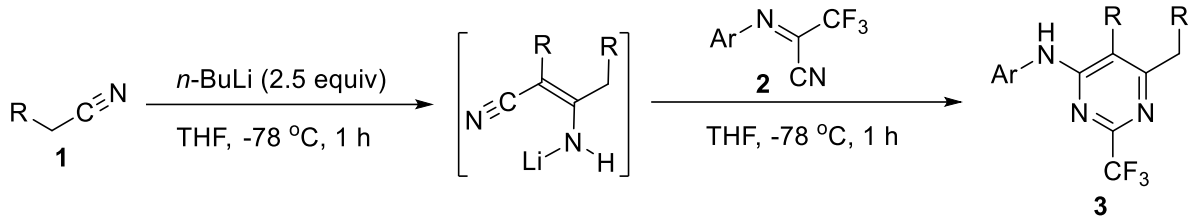
Table of contents

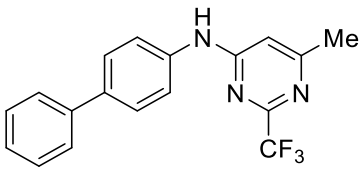
1. General information

All manipulations were carried out under argon atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (THF, Et_2O, 1,4-dioxane, toluene, *n*-hexane) or calcium hydride (dichloromethane, MeCN, DCE). Other chemicals were obtained from commercial sources, and were used without further purification. Chemical shifts (δ, ppm) in the ^1H NMR spectra were recorded using TMS as internal standard or internally referenced to $CHCl_3$ (δ = 7.26 ppm). Chemical shifts in ^{13}C NMR spectra were internally $CHCl_3$ (δ = 77.16 ppm).

2. General procedure for the double addition/double rearrangement domino reaction



Under argon atmosphere, *n*-BuLi (0.5 mmol, 2.5 M in THF, 0.2 mL) was added dropwise to the THF (1 mL) solution of alkyl nitriles (2 mmol) or alkyl dinitrtiles (1 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour. Then the THF solution of trifluoroacetimidoyl nitriles (0.2 mmol) was added to the above reaction mixture. After 1 hour, the reaction was quenched with water and extracted with EtOAc (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the desired products **3**.



***N*-([1,1'-Biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3a)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 54 mg (82%) of the title compound **3a**.

Physical state: white solid.

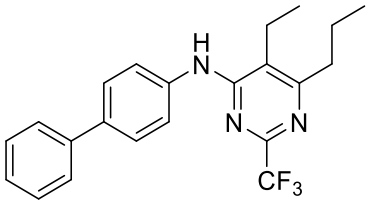
Mp: 137-139 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.63 (d, J = 8.52 Hz, 2H), 7.59 (d, J = 7.12 Hz, 2H), 7.43-7.47 (m, 2H), 7.41 (d, J = 8.48 Hz, 2H), 7.36 (t, J = 7.32 Hz, 1H), 7.17 (s, 1H), 6.67 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.6, 161.7, 156.5 (q, J_{C-F} = 35.7 Hz), 140.2, 138.7, 136.6, 129.0, 128.4, 127.6, 127.0, 123.0, 119.7 (q, J_{C-F} = 276.0 Hz), 104.3, 24.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.0.

HRMS (EI, TOF): calcd for $C_{18}H_{14}F_3N_3^+$ $[M]^+$: 329.1140, found: 329.1141.



***N*-([1,1'-Biphenyl]-4-yl)-5-ethyl-6-propyl-2-(trifluoromethyl)pyrimidin-4-amine (3b)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 10:1 petroleum ether:EtOAc) afforded 35 mg (46%) of the title compound **3b**.

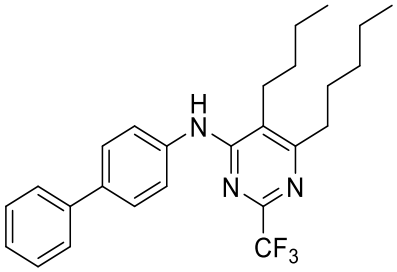
Physical state: pale brown oil.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.57-7.61 (m, 4H), 7.51 (d, J = 8.64 Hz, 2H), 7.43-7.47 (m, 2H), 7.36 (t, J = 7.36 Hz, 1H), 6.92 (s, 1H), 2.44 (t, J = 7.44 Hz, 2H), 2.05 (q, J = 7.52 Hz, 2H), 1.60-1.67 (m, 2H), 1.09 (t, J = 7.52 Hz, 3H), 0.99 (t, J = 7.32 Hz, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 166.9, 158.4, 153.3 (q, J_{C-F} = 35.7 Hz), 140.6, 138.0, 136.7, 128.9, 127.7, 127.2, 126.9, 120.9, 119.9 (q, J_{C-F} = 275.8 Hz), 118.8, 36.7, 22.7, 19.1, 14.3, 12.5.

^{19}F NMR (565 MHz, $CDCl_3$, 25 ºC) δ -70.8.

HRMS (EI, TOF): calcd for $C_{22}H_{22}F_3N_3^+$ $[M]^+$: 385.1766, found: 385.1769.



***N*-([1,1'-Biphenyl]-4-yl)-5-butyl-6-pentyl-2-(trifluoromethyl)pyrimidin-4-amine (3c)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 10:1 petroleum ether:EtOAc) afforded 46 mg (52%) of the title compound **3c**.

Physical state: white solid.

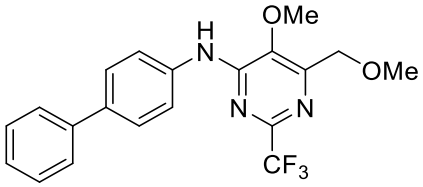
Mp: 112-114 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.75 (d, J = 8.64 Hz, 2H), 7.59-7.62 (m, 4H), 7.42-7.46 (m, 2H), 7.33 (t, J = 7.32 Hz, 1H), 6.70 (s, 1H), 2.75 (t, J = 7.92 Hz, 2H), 2.64 (t, J = 7.12 Hz, 2H),1.68-1.75 (m, 2H), 1.50-1.64 (m, 4H), 1.35-1.43 (m, 4H), 1.04 (t, J = 7.16 Hz, 3H), 0.92 (t, J = 6.92 Hz, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.4, 158.5, 153.3 (q, J_{C-F} = 35.7 Hz), 140.6, 138.0, 136.7, 128.9, 127.8, 127.2, 126.9, 120.8, 120.0 (q, J_{C-F} = 276.0 Hz), 117.7, 34.9, 32.0, 30.3, 29.0, 25.6, 23.1, 22.7, 14.1, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -70.8.

HRMS (EI, TOF): calcd for $C_{26}H_{30}F_3N_3^+$ $[M]^+$: 441.2392, found: 441.2397.



***N*-([1,1'-Biphenyl]-4-yl)-5-methoxy-6-(methoxymethyl)-2-(trifluoromethyl)pyrimidin-4-amine (3d)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 5:1 petroleum ether:EtOAc) afforded 61 mg (78%) of the title compound **3d**.

Physical state: white solid.

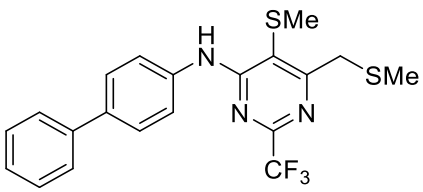
Mp: 135-137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.56-7.58 (m, 4H), 7.42-7.46 (m, 4H), 7.35 (t, J = 7.20 Hz, 1H), 7.06 (s, 1H), 4.15 (s, 2H), 3.66 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 140.7 (q, J_{C-F} = 33.0 Hz), 140.2, 139.7, 138.8, 135.8, 129.0, 127.7, 127.6, 127.0, 122.6, 117.4 (q, J_{C-F} = 286.0 Hz), 116.9, 114.0, 71.2, 58.8, 58.6.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -69.2.

HRMS (EI, TOF): calcd for $C_{20}H_{18}F_3N_3O_2^+$ $[M]^+$: 389.1351, found: 389.1352.



***N*-([1,1'-Biphenyl]-4-yl)-5-(methylthio)-6-((methylthio)methyl)-2-(trifluoromethyl)pyrimidin-4-amine (3e)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 5:1 petroleum ether:EtOAc) afforded 41 mg (49%) of the title compound **3e**.

Physical state: white solid.

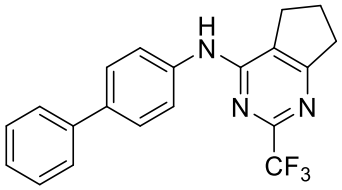
Mp: 139-141 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 8.53 (s, 1H), 7.81 (d, J = 8.68 Hz, 2H), 7.65 (d, J = 8.48 Hz, 2H), 7.61 (d, J = 7.20 Hz, 2H), 7.45 (t, J = 7.40 Hz, 2H), 7.35 (t, J = 7.32 Hz, 1H), 4.00 (s, 2H), 2.40 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 170.9, 161.0, 154.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 140.4, 137.3, 137.3, 129.0, 127.8, 127.4, 127.0, 120.8, 119.6 (q, $J_{C\text{-}F}$ = 276.2 Hz), 113.9, 37.8, 18.1, 16.0.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.2.

HRMS (EI, TOF): calcd for $C_{20}H_{18}F_3N_3S_2^+$ $[M]^+$: 421.0894, found: 421.0892.



***N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidin-4-amine (3f)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 47 mg (66%) of the title compound **3f**.

Physical state: white solid.

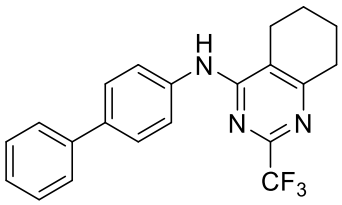
Mp: 172-174 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.70 (d, J = 8.64 Hz, 2H), 7.59 (d, J = 8.60 Hz, 4H), 7.41-7.45 (m, 2H), 7.33 (t, J = 7.32 Hz, 1H), 6.53 (s, 1H), 3.01 (t, J = 7.72 Hz, 2H), 2.78 (t, J = 7.36 Hz, 2H), 2.15-2.23 (m, 2H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 173.4, 156.6, 155.1 (q, $J_{C\text{-}F}$ = 35.4 Hz), 140.4, 137.6, 136.9, 130.0, 127.7, 127.3, 126.9, 120.9, 120.1 (q, $J_{C\text{-}F}$ = 275.5 Hz), 119.5, 34.3, 27.2, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -70.2.

HRMS (EI, TOF): calcd for $C_{20}H_{16}F_3N_3^+$ $[M]^+$: 355.1296, found: 355.1297.



***N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-5,6,7,8-tetrahydroquinazolin-4-amine (3g)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 62 mg (84%) of the title compound **3g**.

Physical state: white solid.

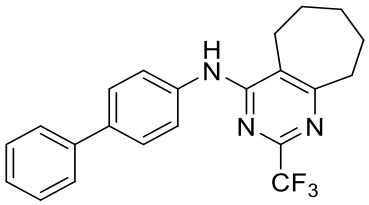
Mp: 150-152 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.72 (d, J = 8.68 Hz, 2H), 7.58 (d, J = 8.32 Hz, 4H), 7.40-7.44 (m, 2H), 7.32 (t, J = 7.36 Hz, 1H), 6.56 (s, 1H), 2.81 (t, J = 6.16 Hz, 2H), 2.49 (t, J = 5.60 Hz, 2H), 1.82-1.94 (m, 4H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 164.1, 158.4, 152.9 (q, J_{C-F} = 35.8 Hz), 140.4, 137.7, 136.6, 128.9, 127.6, 127.2, 126.8, 120.8, 120.0 (q, J_{C-F} = 275.5 Hz), 115.0, 32.1, 22.5, 21.9, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -70.6.

HRMS (EI, TOF): calcd for $C_{21}H_{18}F_3N_3^+$ $[M]^+$: 369.1453, found: 369.1454.



***N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrimidin-4-amine (3h)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel gel, 3:1 petroleum ether:EtOAc) afforded 42 mg (55%) of the title compound **3h**.

Physical state: white solid.

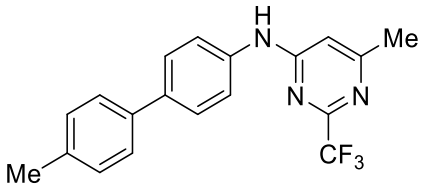
Mp: 130-132 ℃.

^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 7.71 (d, J = 8.64 Hz, 2H), 7.60 (d, J = 8.52 Hz, 4H), 7.41-7.45 (m, 2H), 7.31-7.35 (m, 1H), 6.82 (s, 1H), 3.01 (t, J = 5.70 Hz, 2H), 2.73 (t, J = 5.46 Hz, 2H), 1.91-1.95 (m, 2H), 1.73-7.75 (m, 4H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 170.6, 157.6, 152.9 (q, J_{C-F} = 35.8 Hz), 140.6, 138.0, 136.6, 129.9, 127.7, 127.2, 126.9, 120.8, 120.0, 119.9 (q, J_{C-F} = 275.6 Hz), 38.2, 31.9, 26.0, 25.4.

^{19}F NMR (565 MHz, $CDCl_3$, 25 °C): δ -70.7.

HRMS (EI, TOF): calcd for $C_{22}H_{20}F_3N_3^+$ $[M]^+$: 383.1609, found: 383.1610.



6-Methyl-N-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3i)

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 50 mg (70%) of the title compound **3i**.

Physical state: white solid.

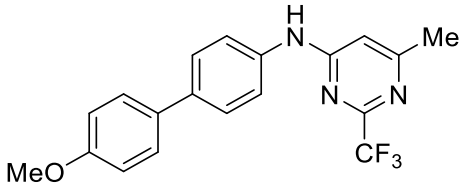
Mp: 143-145 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.61 (d, J = 8.52 Hz, 2H), 7.49 (d, J = 8.12 Hz, 2H), 7.38 (d, J = 8.44 Hz, 2H), 7.26 (d, J = 8.00 Hz, 2H), 7.12 (s, 1H), 6.66 (s, 1H), 2.44 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.6, 161.8, 156.8 (q, J_{C-F} = 35.5 Hz), 138.7, 137.5, 137.3, 136.3, 129.8, 128.2, 126.8, 123.1, 119.7 (q, J_{C-F} = 276.0 Hz), 104.1, 24.2, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.1.

HRMS (EI, TOF): calcd for $C_{19}H_{16}F_3N_3^+$ $[M]^+$: 343.1296, found: 343.1299.



***N*-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3j)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(4'-methoxy-[1,1'-biphenyl]-4-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 50 mg (71%) of the title compound **3j**.

Physical state: white solid.

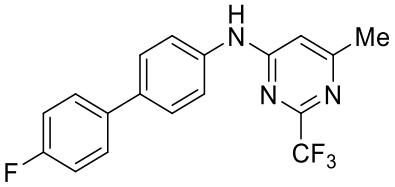
Mp: 137-139 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.59 (d, J = 8.48 Hz, 2H), 7.53 (d, J = 8.72 Hz, 2H), 7.37 (d, J = 8.44 Hz, 2H), 7.09 (s, 1H), 6.99 (d, J = 8.72 Hz, 2H), 6.66 (s, 1H), 3.86 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.6, 161.8, 156.5 (q, J_{C-F} = 35.3 Hz), 138.5, 135.9, 132.7, 128.1, 127.9, 123.3, 119.7 (q, J_{C-F} = 275.8 Hz), 114.5, 104.1, 55.5, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.1.

HRMS (EI, TOF): calcd for $C_{19}H_{16}F_3N_3O^+$ $[M]^+$: 359.1245, found: 359.1244.



***N*-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3k)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(4'-fluoro-[1,1'-biphenyl]-4-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 54 mg (77%) of the title compound **3k**.

Physical state: white solid.

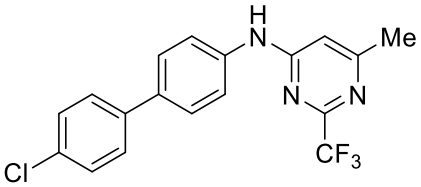
Mp: 121-123 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.58 (d, J = 8.44 Hz, 2H), 7.54 (dd, J_1 = 8.72 Hz, J_2 = 5.32 Hz, 2H), 7.42 (d, J = 8.44 Hz, 2H), 7.12-7.16 (m, 3H), 6.68 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.6, 162.6 (d, J_{C-F} = 246.8 Hz), 161.4, 156.5 (q, J_{C-F} = 35.7 Hz), 137.6, 136.7, 136.4 (d, J_{C-F} = 3.0 Hz), 128.6 (d, J_{C-F} = 8.1 Hz), 128.2, 123.0, 119.7 (q, J_{C-F} = 276.0 Hz), 115.9 (d, J_{C-F} = 21.6 Hz),104.3, 24.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.1 (s, 3F), -115.3 (s, 1F).

HRMS (EI, TOF): calcd for $C_{18}H_{13}F_4N_3^+$ $[M]^+$: 347.1046, found: 347.1047.



***N*-(4'-Chloro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3l)**

Following general procedure on 0.2 mmol scale with **(***E*)-*N*-(4'-chloro-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 61 mg (84%) of the title compound **3l**.

Physical state: white solid.

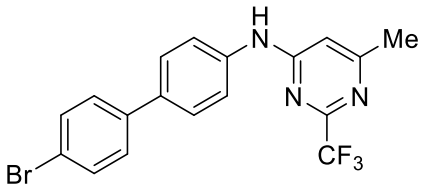
Mp: 126-128 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.49 (d, J = 8.56 Hz, 2H), 7.41 (d, J = 8.56 Hz, 2H), 7.35 (d, J = 8.52 Hz, 2H), 7.31 (d, J = 8.56 Hz, 2H), 7.16 (s, 1H), 6.57 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 1676, 161.6, 156.4 (q, J_{C-F} = 35.5 Hz), 138.6, 137.1, 137.0, 133.6, 129.1, 128.2, 128.2, 122.8, 119.7 (q, J_{C-F} = 276.0 Hz), 104.5, 24.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.0.

HRMS (EI, TOF): calcd for $C_{18}H_{13}ClF_3N_3^+$ $[M]^+$: 363.0750, found: 363.0752.



***N*-(4'-Bromo-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3m)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 65 mg (79%) of the title compound **3m**.

Physical state: white solid.

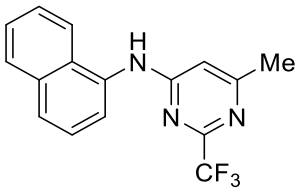
Mp: 127-129 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.56-7.60 (m, 4H), 7.43-7.46 (m, 4H),7.14 (s, 1H), 6.68 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.7, 161.6, 156.5 (q, J_{C-F} = 35.4 Hz), 139.1, 137.2, 137.1, 132.1, 128.6, 128.2, 122.9, 121.8, 119.7 (q, J_{C-F} = 275.9 Hz), 104.4, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.1.

HRMS (EI, TOF): calcd for $C_{18}H_{13}BrF_3N_3^+$ $[M]^+$: 407.0245, found: 407.0244.



6-Methyl-*N*-(naphthalen-1-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3n)

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(naphthalen-1-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 45 mg (74%) of the title compound **3n**.

Physical state: white solid.

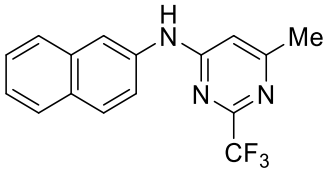
Mp: 135-137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.96-7.96 (m, 2H), 7.89 (d, J = 7.72 Hz, 1H), 7.50-7.60 (m, 4H), 7.33 (s, 1H), 6.23 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 137.8, 163.5, 156.5 (q, J_{C-F} = 35.4 Hz), 134.8, 132.7, 129.9, 128.8, 128.3, 127.3, 127.0, 125.9, 123.9, 122.2, 119.8 (q, J_{C-F} = 276.0 Hz), 103.6, 24.2.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.0.

HRMS (EI, TOF): calcd for $C_{16}H_{12}F_3N_3^+$ $[M]^+$: 303.0983, found: 303.0981.



6-Methyl-*N*-(naphthalen-2-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3o)

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(naphthalen-1-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 35 mg (58%) of the title compound **3o**.

Physical state: white solid.

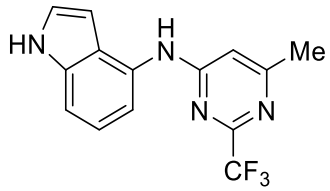
Mp: 135-136 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.88 (d, J = 8.72 Hz, 1H), 7.83-7.85 (m, 2H), 7.81 (d, J = 7.96 Hz, 1H), 7.46-7.54 (m, 2H), 7.39 (dd, J_1 = 8.72 Hz, J_2 = 2.16 Hz, 1H), 7.25 (s, 1H), 6.68 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.7, 161.9, 156.5 (q, J_{C-F} = 35.6 Hz), 134.8, 134.0, 131.4, 129.8, 127.9, 127.6, 127.1, 126.0, 122.2, 120.2, 119.7 (q, J_{C-F} = 276.04 Hz), 104.2, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.1.

HRMS (EI, TOF): calcd for $C_{16}H_{12}F_3N_3^+$ $[M]^+$: 303.0983, found: 303.0985.



***N*-(6-Methyl-2-(trifluoromethyl)pyrimidin-4-yl)-1*H*-indol-4-amine (3p)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(1*H*-indol-4-yl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 35 mg (60%) of the title compound **3p**.

Physical state: pale yellow solid.

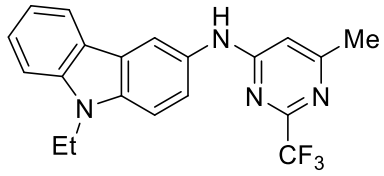
Mp: 133-134 ℃.

^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 8.50 (s, 1H), 7.37 (d, J = 8.16 Hz, 1H), 7.25-7.26 (m, 2H), 7.23 (d, J = 7.92 Hz, 1H), 7.12 (d, J = 7.44 Hz, 1H), 6.56 (s, 1H),6.45 (t, J = 2.10 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.4, 161.4, 156.4 (q, $J_{C\text{-}F}$ = 35.3 Hz), 137.3, 129.0, 125.0, 123.5, 122.6, 119.8 (q, $J_{C\text{-}F}$ = 276.0 Hz), 115.1, 110.0, 110.0, 100.0, 24.2.

^{19}F NMR (565 MHz, $CDCl_3$, 25 ºC) δ -71.0.

HRMS (EI, TOF): calcd for $C_{14}H_{11}F_3N_4^+$ $[M]^+$: 292.0936, found: 292.0937.



9-Ethyl-*N*-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)-9*H*-carbazol-3-amine (3q)

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(9-ethyl-9*H*-carbazol-3-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 59 mg (80%) of the title compound **3q**.

Physical state: white solid.

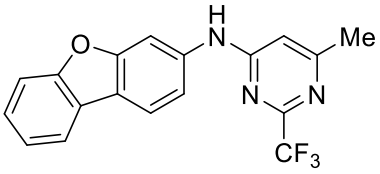
Mp: 158-159 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.97 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 1.00 Hz, 1H),7.40-7.44 (m, 1H),7.35 (d, J = 8.32 Hz, 2H), 7.25 (dd, J_1 = 8.56 Hz, J_2 = 1.92 Hz, 1H), 7.14-7.18 (m, 1H), 7.13 (s, 1H), 6.35 (s, 1H), 4.29 (q, J = 7.24 Hz, 2H), 2.27 (s, 3H),1.36 (t, J = 7.20 Hz, 3H).

^{13}C NMR (376 MHz, $CDCl_3$, 25 ºC): δ 167.3, 161.5, 156.4 (q, $J_{C\text{-}F}$ = 35.3 Hz), 128.1, 126.6, 123.8, 123.5, 122.4, 120.7, 119.8 (q, $J_{C\text{-}F}$ = 276.0 Hz), 119.4, 117.6, 109.5, 109.0, 103.2, 37.9, 24.2, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.0.

HRMS (EI, TOF): calcd for $C_{20}H_{17}F_3N_4^+$ $[M]^+$: 370.1405, found: 370.1404.



***N*-(Dibenzo[*b*,*d*]furan-3-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3r)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(dibenzo[*b*,*d*]furan-3-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 10:1 petroleum ether:EtOAc) afforded 35 mg (52%) of the title compound **3r**.

Physical state: white solid.

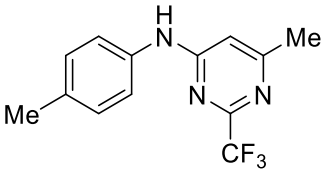
Mp: 165-166 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.94 (d, J = 8.20 Hz, 1H), 7.93 (dd, J_1 = 7.56 Hz, J_2 = 0.56 Hz, 1H), 7.70 (d, J = 0.92 Hz, 1H), 7.58 (d, J = 8.20 Hz, 2H), 7.45-7.49 (m, 1H), 7.35-7.39 (m, 1H), 7.25 (dd, J_1 = 8.28 Hz, J_2 = 1.88 Hz, 1H), 7.19 (s, 1H), 6.70 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.8, 161.8, 156.8, 156.6 (q, $J_{C\text{-}F}$ = 35.5 Hz), 136.6, 127.3, 123.8, 123.3, 122.1, 121. 6, 120.6, 119.7 (q, $J_{C\text{-}F}$ = 276.1 Hz), 117.9, 111.8, 106.3, 104.3, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.1.

HRMS (EI, TOF): calcd for $C_{18}H_{12}F_3N_3O^+$ $[M]^+$: 343.0932, found: 343.0934.



6-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)pyrimidin-4-amine (3s)

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(*p*-tolyl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 73 mg (90%) of the title compound **3s**.

Physical state: white solid.

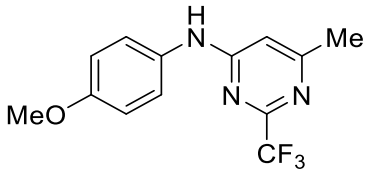
Mp: 124-126 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.18-7.23 (m, 5H), 6.56 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.3, 162.2, 156.4 (q, J_{C-F} = 35.3 Hz), 136.0, 134.5, 130.4, 123.5, 119.7 (q, J_{C-F} = 275.9 Hz), 103.7, 24.1 (d, J = 1.9 Hz), 24.0 (d, J = 1.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.1.

HRMS (EI, TOF): calcd for $C_{13}H_{12}F_3N_3^+$ $[M]^+$: 267.0983, found: 267.0982.



***N*-(4-Methoxyphenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3t)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 46 mg (82%) of the title compound **3t**.

Physical state: white solid.

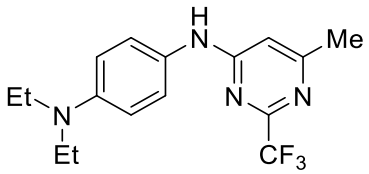
Mp: 115-116 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.22 (d, J = 8.80 Hz, 2H), 7.04 (s, 1H), 6.96 (d, J = 8.88 Hz, 2H), 6.44 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.3, 162.8, 158.2, 156.4 (q, J_{C-F} = 35.4 Hz), 129.8, 126.1, 119.7 (q, J_{C-F} = 275.9 Hz), 115.1, 103.3, 55.6, 24.2.

^{19}F NMR ($CDCl_3$, 376 MHz, 25 °C) δ -71.1.

HRMS (EI, TOF): calcd for $C_{13}H_{12}F_3N_3O^+$ $[M]^+$: 283.0932, found: 283.0934.



***N*^{1},*N*^{1}-Diethyl-*N*^{4}-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)benzene-1,4-diamine (3u)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(4-(diethylamino)phenyl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 49 mg (76%) of the title compound **3u**.

Physical state: white solid.

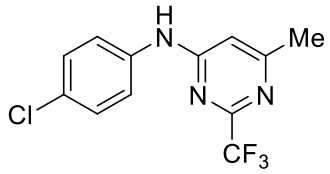
Mp: 130-132 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.09 (d, J = 8.80 Hz, 2H), 6.94 (s, 1H), 6.69 (d, J =9.00 Hz, 2H), 6.41 (s, 1H), 3.38 (q, J = 7.04 Hz, 4H), 2.37 (s, 3H), 1.19 (t, J = 7.04 Hz, 6H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.0, 163.4, 156.3 (q, J_{C-F} = 35.2 Hz), 146.8, 126.8, 124.3, 119.8 (q, J_{C-F} = 275.9 Hz), 112.3,103.0, 44.6, 24.2, 12.6.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.2.

HRMS (EI, TOF): calcd for $C_{16}H_{19}F_3N_4^+$ $[M]^+$: 324.1562, found: 324.1561.



***N*-(4-Chlorophenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3v)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(4-chlorophenyl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 37 mg (63%) of the title compound **3v**.

Physical state: white solid.

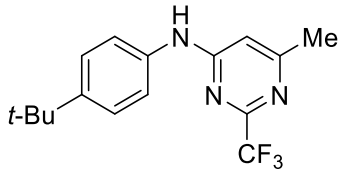
Mp: 122-124 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.38 (d, J = 8.84 Hz, 2H), 7.32 (d, J = 8.80 Hz, 2H), 6.99 (s, 1H), 6.58 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 167.8, 161.6, 156.5 (q, J_{C-F} = 35.8 Hz), 136.1, 131.0, 129.9, 124.0, 119.6 (q, J_{C-F} = 275.8 Hz), 104.4, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -71.2.

HRMS (EI, TOF): calcd for $C_{12}H_9ClF_3N_3^+$ $[M]^+$: 287.0437, found: 287.0438.



***N*-(4-(*tert*-Butyl)phenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3w)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(4-(*tert*-butyl)phenyl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 52 mg (84%) of the title compound **3w**.

Physical state: white solid.

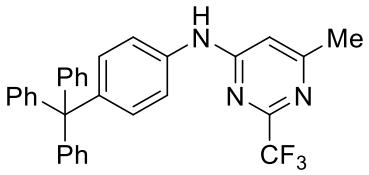
Mp: 116-118 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.43 (d, J = 8.60 Hz, 2H), 7.25 (d, J = 8.52 Hz, 2H), 7.10 (s, 1H),6.62 (s, 1H), 2.42 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.4, 162.1, 156.4 (q, $J_{C\text{-}F}$ = 35.6 Hz), 149.2, 126.7, 123.0, 119.7 (q, $J_{C\text{-}F}$ = 276.0 Hz), 103.8, 34.7, 31.4, 24.2 (d, J = 2.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.1.

HRMS (EI, TOF): calcd for $C_{16}H_{18}F_3N_3^+$ $[M]^+$: 309.1453, found: 309.1455.



6-Methyl-2-(trifluoromethyl)-*N*-(4-tritylphenyl)pyrimidin-4-amine (3x)

Following general procedure on 0.2 mmol scale with (*E*)-*N*-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 38 mg (48%) of the title compound **3x**.

Physical state: white solid.

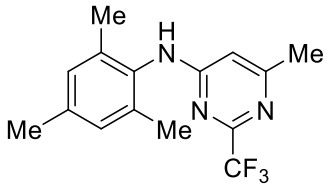
Mp: 151-153 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.18-7.29 (m, 19H), 7.03 (s, 1H), 6.67 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.6, 161.5, 156.5 (q, $J_{C\text{-}F}$ = 35.7 Hz), 146.6, 144.3, 135.2, 132.5, 131.2, 127.7, 126.2, 123.8, 121.2, 119.7 (q, $J_{C\text{-}F}$ = 276.0 Hz), 104.2, 64.8, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.1.

HRMS (EI, TOF): calcd for $C_{31}H_{24}F_3N_3^+$ $[M]^+$: 495.1922, found: 495.1923.



***N*-Mesityl-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3y)**

Following general procedure on 0.2 mmol scale with (*E*)-2,2,2-trifluoro-*N*-mesitylacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 35 mg (59%) of the title compound **3y**.

Physical state: white solid.

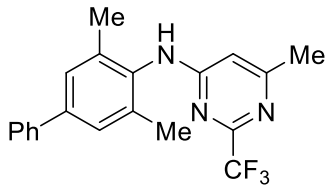
Mp: 127-129 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 6.99 (s, 2H), 6.63 (s, 1), 5.83 (s, 1H), 2.35 (s, 3), 2.33 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.7, 163.1, 156.5 (q, J_{C-F} = 34.4 Hz), 138.3, 136.6, 130.9, 129.7, 119.8 (q, J_{C-F} = 275.8 Hz), 102.2, 24.2, 21.1, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.1.

HRMS (EI, TOF): calcd for $C_{15}H_{16}F_3N_3^+$ $[M]^+$: 295.1296, found: 295.1298.



***N*-(3,5-Dimethyl-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3z)**

Following general procedure on 0.2 mmol scale with (*E*)-*N*-(3,5-dimethyl-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 46 mg (64%) of the title compound **3z**.

Physical state: white solid.

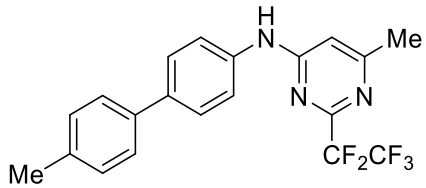
Mp: 134-136 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.60 (d, J = 7.08 Hz, 2H), 7.44-7.48 (m, 2H), 7.39 (s, 2H), 7.38 (t, J = 7.40 Hz, 1H), 6.79 (s, 1H), 5.92 (s, 1H), 2.38 (s, 3H), 2.28 (s, 6H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC): δ 167.8, 162.9, 156.5 (q, J_{C-F} = 35.3 Hz), 141.3, 140.3, 137.1, 132.8, 129.0, 127.8, 127.2, 122.1, 119.8 (q, J_{C-F} = 275.9 Hz), 102.4, 24.2, 18.6.

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -71.0.

HRMS (EI, TOF): calcd for $C_{20}H_{18}F_3N_3^+$ $[M]^+$: 357.1453, found: 357.1454.



6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(perfluoroethyl)pyrimidin-4-amine (3aa)

Following general procedure on 0.2 mmol scale with (*E*)-2,2,3,3,3-pentafluoro-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)propanimidoyl cyanide. Purification by column chromatography (silica gel, 3:1 petroleum ether:EtOAc) afforded 64 mg (63%) of the title compound **3aa**.

Physical state: white solid.

Mp: 126-128 ℃.

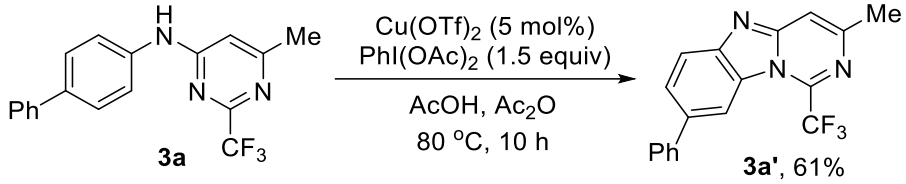
^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.62 (d, J = 8.52 Hz, 2H), 7.49 (d, J = 8.08 Hz, 2H), 7.40 (d, J = 8.44 Hz, 2H), 7.26 (d, J = 8.64 Hz, 2H), 7.05 (s, 1H), 6.67 (s, 1H), 2.45 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC, CF_2CF_3- signal is not assigned): δ 167.6, 161.6, 156.6 (t, $J_{C\text{-}F}$ = 24.8 Hz), 138.6, 137.5, 137.3, 136.3, 129.8, 128.1, 126.8, 123.0, 104.2, 24.3 (d, J = 2.5 Hz), 21.2 (d, J = 2.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) δ -82.2 (s, 3F), 118.1 (s, 2F).

HRMS (EI, TOF): calcd for $C_{20}H_{16}F_5N_3^+$ $[M]^+$: 393.1264, found: 393.1263.

3. Transformation of product 3a



In a 10 mL sealed tube, **3a** (0.2 mmol), $Cu(OTf)_2$ (4 mg, 0.01 mmol), $PhI(OAc)_2$ (97 mg, 0.3 mmol), then AcOH (1.5 mL), Ac_2O (1.5 mL) were added and the reaction mixture was stired at 80 ℃ for 12 hours. The resulting mixture was cooled to room temperature. After which the mixture was then diluted with brine (10 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by column chromatography on silica gel (PE/EA = 3:1) to give 3-Methyl-8-phenyl-1-(trifluoromethyl)benzo[4,5]imidazo[1,2-c]pyrimidine (**3a'**, 40 mg, 61%).

3-Methyl-8-phenyl-1-(trifluoromethyl)benzo[4,5]imidazo[1,2-*c*]pyrimidine (3a')

Physical state: pale yellow solid.

Mp: 151-153 ℃.

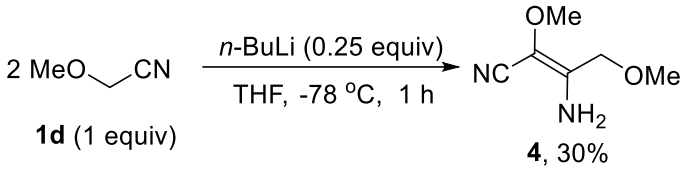
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.33 (s, 1H), 8.02 (d, J = 8.52 Hz, 1H), 7.88 (dd, J_1 = 8.56 Hz, J_2 = 1.36 Hz, 1H), 7.68 (d, J = 7.36Hz, 2H),, 7.50-7.54 (m, 3H), 7.41 (t, J = 7.36 Hz, 1H),2.66 (s, 3H).

^{13}C NMR (150.6 MHz, $CDCl_3$, 25 °C): δ 150.7, 149.6, 144.6, 141.1, 137.2, 136.9 (q, J_{C-F} = 39.9 Hz), 129.1, 127.7, 127.6, 127.4, 126.5, 120.5, 118.5 (q, J_{C-F} = 275.7 Hz), 113.1 (q, J_{C-F} = 6.5 Hz), 112.7, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) δ -69.1.

HRMS (EI, TOF): calcd for $C_{18}H_{12}F_3N_3^+$ $[M]^+$: 327.0983, found: 327.0984.

4. Mechanistic studies for the double addition/double rearrangement domino reaction



Under argon atmosphere, *n*-BuLi (2 mmol, 2.5 M in THF, 0.8 mL) was added dropwise to the THF (1 mL) solution of 2-methoxyacetonitrile (**1d**, 8 mmol, 569 mg) at -78 °C. The reaction mixture was stirred at -78 °C . After 1 hour, the reaction was quenched with water and extracted with EA (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the desired products **4** (171 mg) in 30% yield.

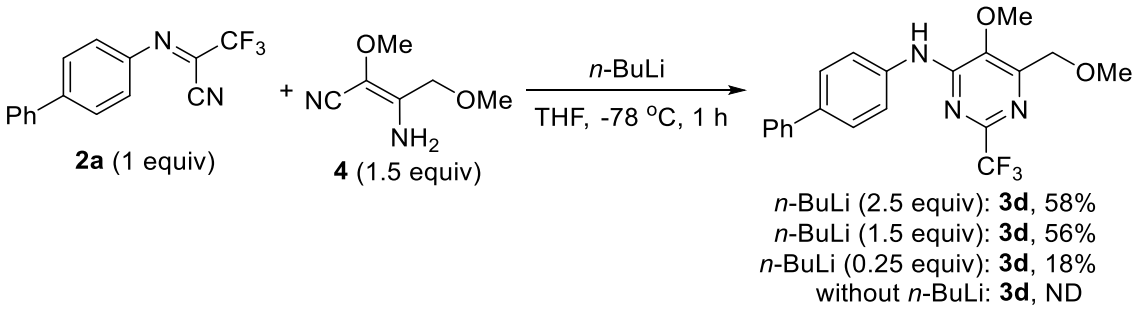
Physical state: pale yellow oil.

(*E*)-3-Amino-2,4-dimethoxybut-2-enenitrile (4)

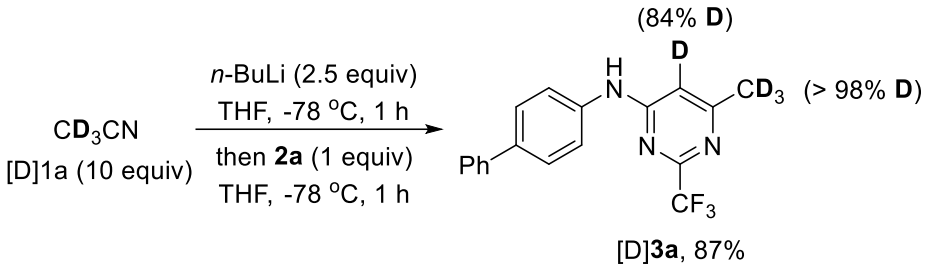
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.50 (br, 2H), 4.12 (s, 2H), 3.65 (s, 3H), 3.37 (s, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 142.9, 116.2, 107.8, 68.4, 59.1, 58.3.

HRMS (EI, TOF): calcd for $C_6H_{10}N_2O_2^+$ $[M]^+$: 142.0742, found: 142.0743.



Under argon atmosphere, *n*-BuLi (0.5 mmol, 2.5 M in THF, 0.2 mL) was added dropwise to the THF (1 mL) solution of **4** (0.3 mmol, 43 mg) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour. Then the THF solution of **2a** (0.2 mmol, 55 mg) was added to the above reaction mixture. After 1 hour, the reaction was quenched with water and extracted with EA (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The purification was performed by flash column chromatography on silica gel (silica gel gel, 3:1 petroleum ether:EtOAc) to afford the desired products **3d** (45 mg, 58%).



Under argon atmosphere, *n*-BuLi (0.5 mmol, 2.5 M in THF, 0.2 mL) was added dropwise to the THF (1 mL) solution of CD_3CN (2 mmol, 88 mg) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour. Then the THF solution of **2a** (0.2 mmol, 55 mg) was added to the above reaction mixture. After 1 hour, the reaction was quenched with water and extracted with EA (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the desired products [D]**3a** (58 mg, 87%). Deuterated ratio of [D]**3a** was determined by ^{1}H NMR (Figure S1).

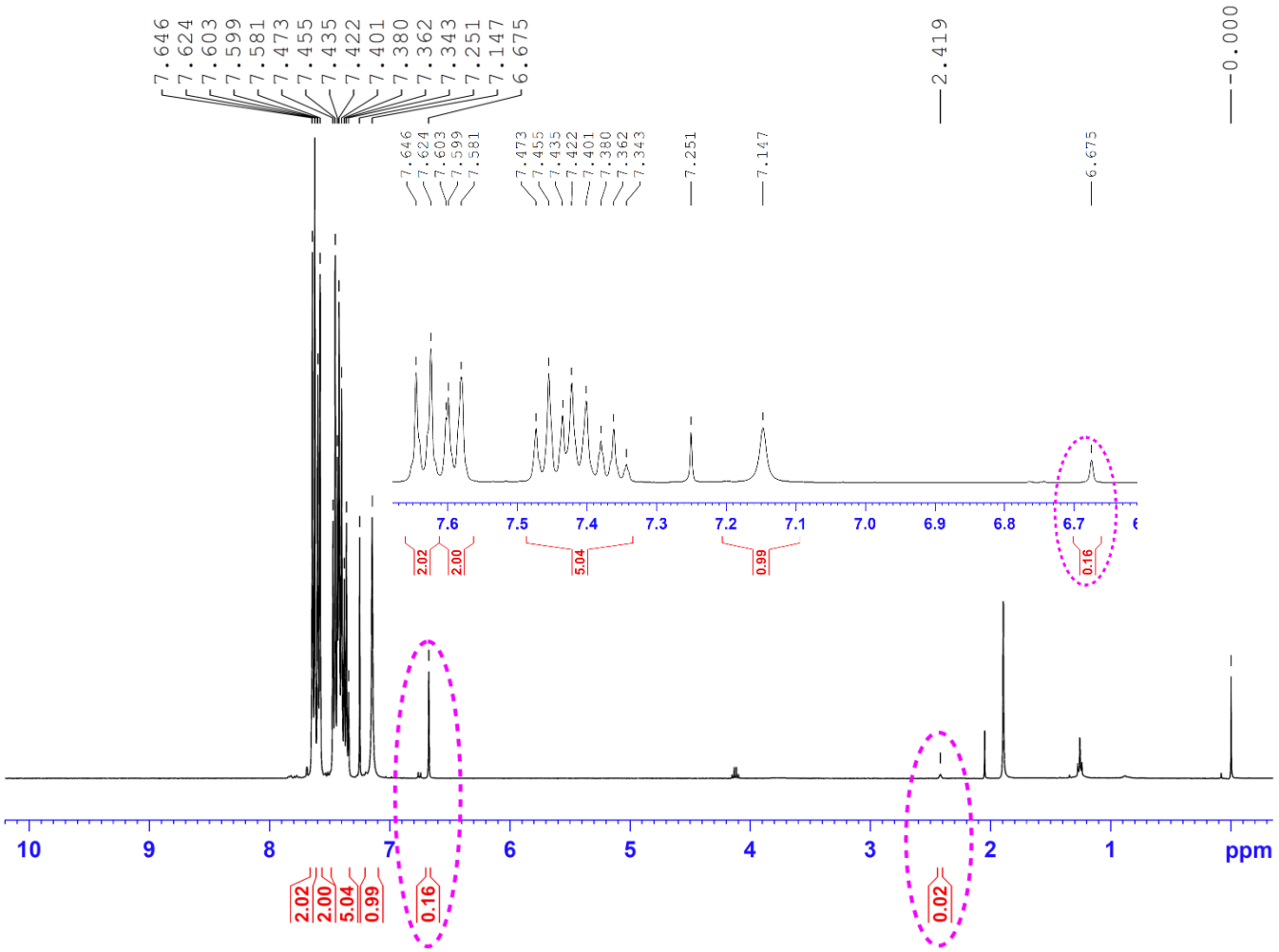
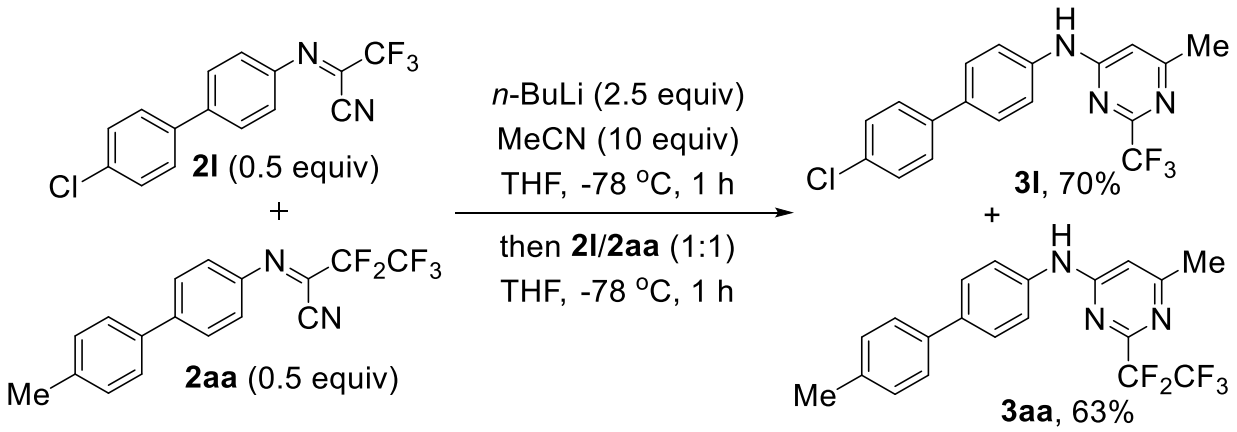


Figure S1. ^{1}H NMR spectra analysis of deuterated products [D]**3a.**



Under argon atmosphere, *n*-BuLi (0.5 mmol, 2.5 M in THF, 0.2 mL) was added dropwise to the THF (1 mL) solution of MeCN (2 mmol, 88 mg) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour. Then the THF solution of **2l** (0.1 mmol, 31 mg) and **2aa** (0.1 mmol, 34 mg) was added to the above reaction mixture. After 1 hour, the reaction was quenched with water and extracted with EA (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the corresponding products **3l** (25 mg, 70%) and **3aa** (25 mg, 63%).

5. DFT calculations for the double rearrangement in the domino reaction

All the DFT calculations were carried out using the GAUSSIAN 09 package [1]. Geometry optimization and energy calculations were performed with WB97XD [2]. The 6-31G basis set was used for all atoms [3-5]. All the reactants and products are calculated with no imaginary frequency and transition state structures have only one imaginary frequency. Solvation energy corrections were calculated using the SMD model with THF as the solvent [6-10]. Computed structures are illustrated using CYLVIEW [11].

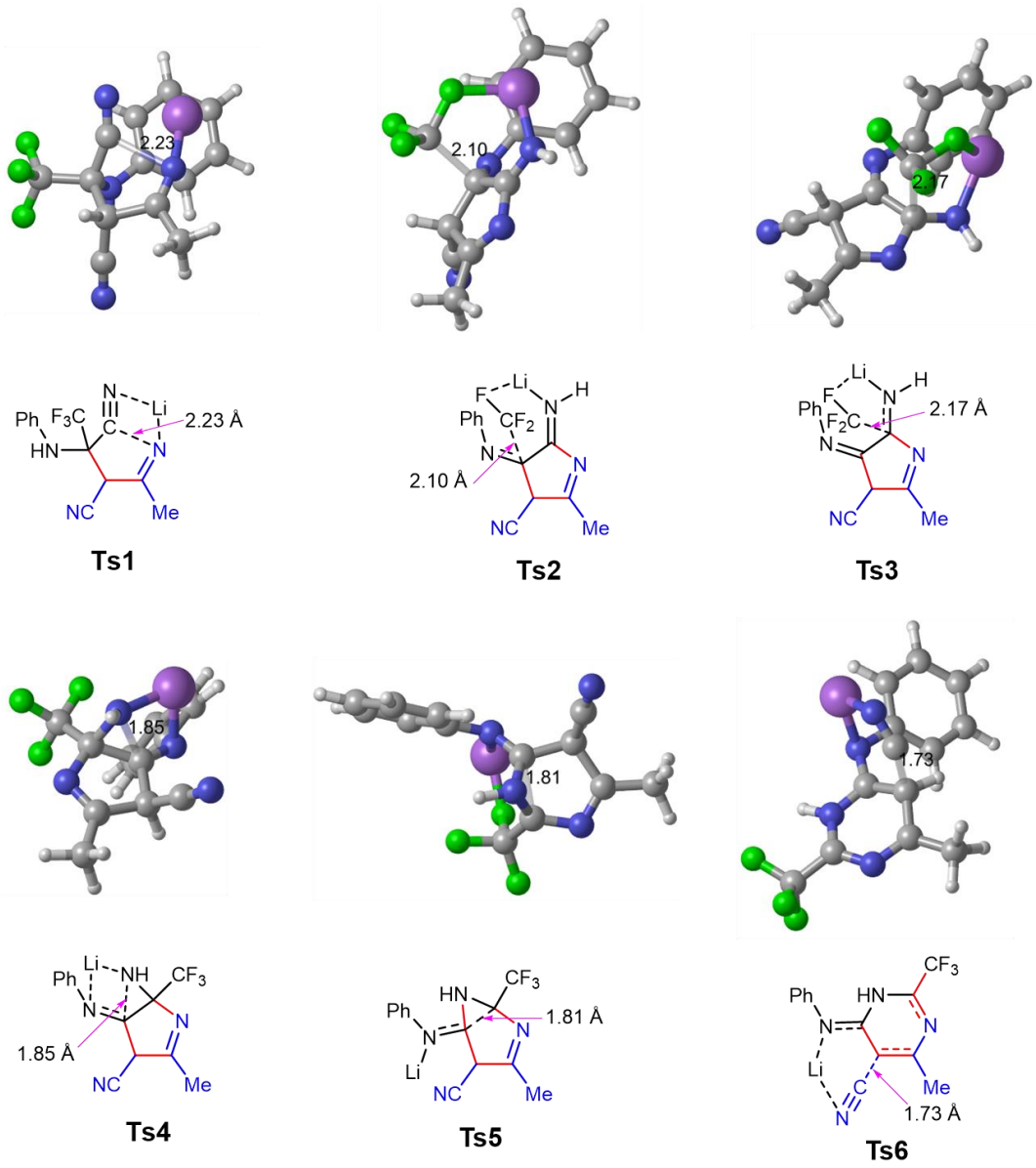


Figure S2. The geometry information of transition states **Ts1-Ts6**. The values for bond lengths are given by angstrom.

Table S1. Energies, enthalpies, and free energies (in Hartree) of the structures calculated at the WB97XD/LANL2DZ-6-31G (SMD THF).

Structures	E_{gas}	G_{gas}	E_{sol}	G_{sol}	Imaginary Frequency
LiCN	-100.3163148	-100.330597	-100.4065115	-100.4207937	-
B	-1026.8899947	-1026.720651	-1027.4190573	-1027.2497136	-
C	-1026.909536	-1026.737466	-1027.447953	-1027.275881	-
D	-1026.8997637	-1026.727111	-1027.444823	-1027.2721703	-
E	-1026.8896324	-1026.724526	-1027.4173244	-1027.252218	-
F	-1026.9067257	-1026.735736	-1027.4431067	-1027.272117	-
G	-1026.8925912	-1026.719592	-1027.4083113	-1027.2353121	-
H	-1026.9079579	-1026.738158	-1027.4496922	-1027.2798923	-
I	-926.5770108	-926.411286	-927.0564089	-926.8906841	-
Ts1	-1026.8896914	-1026.719816	-1027.4186097	-1027.2487343	-104.38
Ts2	-1026.8788834	-1026.710298	-1027.4141741	-1027.2455887	-211.54
Ts3	-1026.8803241	-1026.712048	-1027.4103399	-1027.2420638	-198.33
Ts4	-1026.8702807	-1026.698988	-1027.4165646	-1027.2452719	-241.69
Ts5	-1026.8617964	-1026.691371	-1027.4031761	-1027.2327507	-446.28
Ts6	-1026.8860206	-1026.715088	-1027.4218309	-1027.2508983	-400.29

Table S2. The ΔE_{gas}, ΔG_{gas}, ΔE_{sol}, and ΔG_{sol} (kcal/mol) of the species for the double rearrangement in the domino reaction

Structures	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}	ΔG_{sol}
B	0.0	0.0	0.0	0.0
C	-12.3	-10.5	-18.1	-16.4
D	-6.1	-4.1	-16.2	-14.1
E	0.23	-8.9	1.1	-1.6
F	-10.5	-9.5	-15.1	-14.0
G	-1.6	0.7	6.7	9.0
H	-11.3	-11.0	-19.2	-18.9
I	-2.1	-13.3	-27.5	-38.7
Ts1	0.0	0.5	0.3	0.6
Ts2	7.0	6.5	3.1	2.6
Ts3	6.1	5.4	5.5	4.8
Ts4	12.4	13.6	1.6	2.8
Ts5	17.7	18.4	10.0	10.6
Ts6	2.5	3.5	-1.7	-0.7

WB97XD geometries for all the optimized compounds and transition states

LiCN

Li	0.00000000	0.00000000	-2.08404700
C	0.00000000	0.00000000	-0.15433400
N	0.00000000	0.00000000	1.02544900

B

N	0.31705600	1.81400200	-1.26063400
C	-0.85409000	2.04787600	-0.88088800
C	-1.62077000	3.34970800	-0.97950500
H	-1.03570100	4.05840800	-1.56781700
H	-2.59606000	3.20317500	-1.46101700
H	-1.80580200	3.78027700	0.01199300
C	-1.72453100	0.86621000	-0.22683800
H	-2.57223700	0.65936600	-0.89262700
C	-2.23271300	1.27866900	1.07530300
N	-2.57493200	1.68093400	2.11821100
C	-0.81881500	-0.39868400	-0.12421700
N	0.14311100	-0.28117300	0.96708200
C	-1.66634800	-1.66955400	0.11524900
F	-0.88626300	-2.81087300	0.10169200
F	-2.30951800	-1.62491200	1.33602300
F	-2.64108600	-1.82682300	-0.86018100

C	-0.13750300	-0.57956500	-1.43417500
N	0.31432700	-1.02165100	-2.42353400
C	1.53794700	-0.20531600	0.76787500
C	2.23729900	-1.24541500	0.13383700
C	2.23848100	0.94662300	1.16961900
C	3.59988800	-1.10341300	-0.14920700
H	1.71542200	-2.15512000	-0.13501700
C	3.60566500	1.06717600	0.91459100
H	1.69577500	1.76140400	1.63647800
C	4.28982300	0.05168100	0.23397500
H	4.12301200	-1.90928800	-0.65204800
H	4.13019600	1.96326000	1.22741400
H	5.34825300	0.15297400	0.02252100
H	-0.21043400	0.24879900	1.75286800
Li	1.87214900	0.93982100	-1.54738200

C

C	-0.41752400	-0.51256000	1.37854200
C	-2.39405700	-1.32286000	0.60381600
C	-2.18151300	-0.07753300	-0.29267200
C	-0.72525100	0.31863100	0.03895900
H	-2.88674100	0.69427200	0.04748500
C	-0.62895900	1.80906100	0.33321000
F	0.67208100	2.19440700	0.72667600
F	-1.48121300	2.23945000	1.33048700
F	-0.90144300	2.59356000	-0.79095600
N	0.20599200	-0.03669800	-1.02623700
H	0.04107300	0.43406200	-1.90810700
C	1.56751500	-0.36684900	-0.76611100
C	1.90497200	-1.63796100	-0.27918100
C	2.58510800	0.58291200	-0.96774500
C	3.22798000	-1.93828200	0.04582900
H	1.11845700	-2.36658100	-0.12747200
C	3.91538700	0.27364800	-0.65506200
H	2.32898400	1.56201600	-1.36002600
C	4.23650200	-0.98372900	-0.13173700
H	3.47026100	-2.91720200	0.44338000
H	4.69341400	1.01057900	-0.82483500
H	5.26419700	-1.22270300	0.11857000
N	-1.49105400	-1.50037300	1.49364800
C	-2.43697200	-0.32059400	-1.70780900
N	-2.64746200	-0.51978500	-2.83872500
C	-3.60273600	-2.17511500	0.43174300
H	-3.60392600	-2.65024100	-0.55640400
H	-3.62115500	-2.94833100	1.20058600

H	-4.51760400	-1.57423200	0.50363100
N	0.58824800	-0.37462400	2.09649400
Li	2.07180800	0.61978200	1.60012600

D

C	0.62436000	-0.57406100	-1.31205900
C	2.60830500	-1.10417200	-0.49206200
C	2.17644500	0.08289300	0.37993500
C	0.67918800	0.26364700	-0.02195200
H	2.78557900	0.94789600	0.07816400
C	0.42619200	1.75108900	-0.36375000
F	-0.84829300	1.95157200	-0.96044000
F	1.33294500	2.25872100	-1.29878100
F	0.46572100	2.58293900	0.72785400
N	-0.13997200	-0.32296500	0.98613200
C	-1.50769500	-0.48202500	0.76452600
C	-2.03544200	-1.72215700	0.31514500
C	-2.44636000	0.56176200	0.99626300
C	-3.39655300	-1.88552800	0.04214400
H	-1.33832700	-2.54075900	0.17343600
C	-3.80667200	0.39743500	0.71831800
H	-2.07935100	1.49913100	1.39835100
C	-4.29071600	-0.82075700	0.21853300
H	-3.76231600	-2.84515900	-0.31009200
H	-4.49430200	1.21663300	0.90495300
H	-5.34654200	-0.94725000	0.00612300
N	1.76513200	-1.41442000	-1.42391800
C	2.39251500	-0.14306200	1.80477900
N	2.68712400	-0.32562300	2.91833000
C	3.89852300	-1.80351900	-0.28202300
H	3.89101500	-2.31174300	0.68949600
H	4.06501200	-2.53660900	-1.07166000
H	4.72737700	-1.08688900	-0.26013700
N	-0.39250900	-0.64135700	-2.09838300
Li	-2.02881600	0.20649600	-1.42807500
H	-0.28600100	-1.35255100	-2.82402100

E

C	-0.71158400	-0.24467500	1.32012600
C	-2.84913300	-0.49621600	0.76351200
C	-2.12239100	-0.61180300	-0.58039600
C	-0.66897400	-0.63370600	-0.13222500
H	-2.27611700	0.31790900	-1.14968400
C	-0.52021500	2.29617800	-0.31202300
F	0.95226400	2.48636700	0.38636600

F	-1.00254000	3.60955800	-0.12760100
F	-0.06870900	2.32191900	-1.68295100
N	0.28965600	-0.97784800	-0.88882900
C	1.65042100	-0.97477100	-0.49474700
C	2.18235400	-1.99025900	0.31145200
C	2.47618300	0.05211100	-0.97945800
C	3.52795000	-1.94714900	0.67475300
H	1.53911000	-2.79163100	0.65733500
C	3.82068600	0.09279200	-0.59175600
H	2.05486300	0.80861900	-1.63235800
C	4.34932600	-0.90070500	0.23917900
H	3.93532400	-2.72976400	1.30547200
H	4.45348700	0.89450500	-0.95704800
H	5.39370000	-0.87026200	0.52855900
N	-2.05806200	-0.29730400	1.77301000
C	-2.54403100	-1.75592700	-1.37728200
N	-2.90326000	-2.67907500	-1.99299900
C	-4.32398900	-0.57131600	0.88076800
H	-4.62322400	-0.48365600	1.92535800
H	-4.78687700	0.23841700	0.30391300
H	-4.69638500	-1.51566000	0.46769100
N	0.28040900	0.09236200	2.05612600
Li	1.74026000	1.06895100	1.13060200
H	-0.00462400	0.30981700	3.01405800

F

C	0.69816000	-0.69703000	0.60539800
C	2.77643400	0.28682600	0.45589900
C	1.98802500	1.01664500	-0.63654900
C	0.56877000	0.55591000	-0.32175600
H	2.28629900	0.61764000	-1.61776800
N	-0.44170400	1.23392000	-0.67961600
C	-1.78374200	0.95011700	-0.37317000
C	-2.40593000	1.66142700	0.67053500
C	-2.52503100	0.01811300	-1.11537700
C	-3.72822200	1.38009600	1.01294800
H	-1.82612700	2.38892600	1.22459900
C	-3.85632400	-0.25051800	-0.77000600
H	-2.05428900	-0.50393300	-1.93808500
C	-4.45906100	0.41259800	0.30355300
H	-4.19217800	1.91638100	1.83331200
H	-4.41693800	-0.98003100	-1.34402500
H	-5.48818100	0.20095900	0.56995500
N	2.11000900	-0.61674200	1.08111100
C	2.16993100	2.46301900	-0.64483600

N	2.33713400	3.61756600	-0.62904600
C	4.20362900	0.59895800	0.73833400
H	4.31462800	1.63862400	1.06679800
H	4.57893500	-0.06751000	1.51592800
H	4.80982000	0.47590200	-0.16669100
N	-0.26668400	-0.73977800	1.64403500
Li	-2.04999500	-0.83730500	1.29757400
H	0.20470700	-0.94156200	2.52343200
C	0.63761000	-1.98463700	-0.25902900
F	-0.67114600	-2.23492200	-0.69435300
F	1.40627800	-1.89303400	-1.43093400
F	1.04892700	-3.11286600	0.40626300

G

C	1.45766800	0.64028700	-0.09370900
C	1.90368100	-1.24320500	1.02853800
C	0.76243100	-1.66764500	0.08936800
C	0.43243300	-0.37116800	-0.69790900
H	-0.11696900	-1.97561400	0.67050800
N	2.25195700	-0.00262300	0.92520000
C	1.15703900	-2.75618600	-0.79642100
N	1.51409400	-3.60235500	-1.51762200
C	2.53807200	-2.19449300	1.97823700
H	3.01414000	-3.02216000	1.43978000
H	3.28979500	-1.67770900	2.57629600
H	1.78248100	-2.62989200	2.64238900
N	1.57357100	0.16754900	-1.48614100
C	1.25715800	2.10116200	0.06800900
F	0.45976100	2.60422300	-0.98610800
F	0.61874900	2.42811000	1.24166800
F	2.43389500	2.83086000	0.01947500
N	-0.79690200	-0.11317900	-1.27730100
C	-1.93523700	-0.14568000	-0.46874200
C	-3.19695900	-0.25552200	-1.09194600
C	-1.90547200	-0.04304400	0.94029700
C	-4.36892800	-0.26600600	-0.34315200
H	-3.22833000	-0.35235800	-2.17286200
C	-3.08802500	-0.06081700	1.68514800
H	-0.96145000	0.10345400	1.45867800
C	-4.32710500	-0.17434000	1.05486000
H	-5.32502400	-0.35611200	-0.84996300
H	-3.03484600	0.03061900	2.76607200
H	-5.24320000	-0.18650900	1.63521700
Li	-0.02698500	1.06804300	-2.52722000
H	2.37313400	-0.43239500	-1.68419500

H

C	1.77265900	-0.77881500	-0.19637400
C	2.28776200	1.40376200	0.33389500
C	1.17616900	1.79564000	-0.65513700
C	0.00908200	0.84634600	-0.42699100
H	1.55681400	1.64313700	-1.68790400
N	-1.24193000	1.31559900	-0.31691500
N	2.58725700	0.13495600	0.37566400
C	0.68259100	3.15822000	-0.53671600
N	0.11975400	4.17838600	-0.42994800
C	3.11075200	2.45406300	1.00976400
H	3.90754900	1.96169700	1.57126900
H	3.57193100	3.14639200	0.28916500
H	2.52093800	3.05718200	1.71253100
N	0.39737000	-0.42639200	-0.36547100
C	2.02884500	-2.19222000	-0.03477800
F	3.35296300	-2.55235500	-0.17717400
F	1.63774900	-2.76344900	1.23071300
F	1.26248000	-2.95361400	-0.94945400
Li	-1.77114600	3.12428000	-0.29898800
C	-2.31328100	0.39863200	-0.08142600
C	-3.01646200	0.45851300	1.13067100
C	-2.71557400	-0.52389300	-1.06167300
C	-4.10739100	-0.38416700	1.35717600
H	-2.68099900	1.14614800	1.90233700
C	-3.79996300	-1.37086200	-0.82666400
H	-2.18259600	-0.56245500	-2.00734000
C	-4.50117800	-1.30219200	0.38084500
H	-4.63850200	-0.33320500	2.30180000
H	-4.09901500	-2.08292100	-1.58841800
H	-5.34226100	-1.96248800	0.56059600
H	-0.30037800	-1.15757500	-0.29269900

I

C	-2.38939600	-1.83743600	0.07218800
C	-1.67359400	0.34753300	-0.10228400
C	0.02030900	-1.37437000	0.07148300
C	-1.10858200	-2.28332200	0.13317400
H	-0.87230600	-3.33480400	0.22739200
C	-3.59378900	-2.72120300	0.11910400
H	-4.24144300	-2.42834100	0.95173600
H	-4.17732400	-2.60628500	-0.80039000
H	-3.31584000	-3.77095400	0.23487200
N	-2.67710900	-0.46276200	-0.04173100

N	-0.36051900	-0.01930800	-0.05648300
C	-1.95109700	1.82919500	-0.14193200
F	-3.08763500	2.14505300	-0.83380400
F	-2.07713500	2.34699200	1.14212000
F	-0.88572700	2.50885800	-0.73447100
N	1.24412800	-1.78424000	0.10351700
C	2.33192400	-0.87571400	0.08148200
C	3.26211900	-0.95483400	-0.96515000
C	2.53675600	0.05577600	1.11486600
C	4.36325100	-0.09892600	-0.99110400
H	3.11031400	-1.69580400	-1.74224400
C	3.64431800	0.90599000	1.08415400
H	1.84412600	0.08823100	1.95128400
C	4.55843600	0.83674300	0.02988700
H	5.07517700	-0.16637400	-1.80718300
H	3.79524200	1.61798300	1.88909500
H	5.41749100	1.49835600	0.00824100
H	0.36961100	0.67746300	-0.14974300

Ts1

N	0.40681700	-1.54571900	1.42863800
C	-0.68381400	-1.98093300	0.98133800
C	-1.22595500	-3.38642200	1.08321400
H	-2.23281200	-3.38981600	1.51945700
H	-1.29618900	-3.85785300	0.09581200
H	-0.56329300	-3.98156200	1.71329500
C	-1.65630700	-0.95683200	0.24382700
H	-2.53732000	-0.80000800	0.87994600
C	-2.08909300	-1.48726200	-1.04270200
N	-2.37013000	-1.96432100	-2.07178300
C	-0.85996700	0.37260000	0.09847500
N	0.10367400	0.30829800	-0.99665500
C	-1.80307500	1.56349700	-0.15374900
F	-1.12355400	2.76346300	-0.18595000
F	-2.46057100	1.43017000	-1.36596800
F	-2.77776200	1.66427900	0.82938400
C	-0.16211400	0.60585100	1.40006000
N	0.25084000	1.22887000	2.31770400
C	1.50274200	0.25407500	-0.79508000
C	2.18304300	1.31786400	-0.17969500
C	2.22361400	-0.88724600	-1.18319900
C	3.54807500	1.20413800	0.10720900
H	1.64345700	2.22251000	0.07106400
C	3.59253500	-0.97876600	-0.92985700
H	1.69612400	-1.71709300	-1.64176700

C	4.25811900	0.05608100	-0.26212100
H	4.05828300	2.02892200	0.59310800
H	4.13360600	-1.86925200	-1.23040200
H	5.31870900	-0.02295600	-0.05103000
H	-0.23792600	-0.19186000	-1.80691200
Li	1.85637000	-0.50399800	1.80286600

Ts2

C	-0.67661400	0.14971100	-1.31876100
C	-2.77496300	0.59174200	-0.74402800
C	-2.08154200	0.41680200	0.61239400
C	-0.61543700	0.19390100	0.19601500
H	-2.48564700	-0.46670800	1.12200100
C	-0.54453500	-1.90265100	0.33007400
F	0.76636400	-2.34659300	-0.25762300
F	-1.45446400	-2.82064300	-0.23749900
F	-0.41047500	-2.29344800	1.66741600
N	0.33251100	0.71893600	0.93395500
C	1.67624200	0.76238300	0.53009100
C	2.16766200	1.76022300	-0.33539900
C	2.57805500	-0.20468000	1.02557600
C	3.50413200	1.75682700	-0.73522600
H	1.48380500	2.52061900	-0.69549200
C	3.91573400	-0.20600200	0.61279900
H	2.21094400	-0.94314800	1.72930900
C	4.38348800	0.76664400	-0.27835300
H	3.86205000	2.52835600	-1.40905100
H	4.59344100	-0.95909700	1.00183600
H	5.42126200	0.76810800	-0.59263400
N	-1.99108600	0.45034800	-1.76891100
C	-2.27955100	1.57747000	1.47620300
N	-2.49820000	2.50856300	2.14366000
C	-4.22380800	0.88337600	-0.85959700
H	-4.47024600	1.80768600	-0.32457500
H	-4.50716500	0.98147000	-1.90779100
H	-4.80796100	0.07786300	-0.39893300
N	0.29336200	-0.15293900	-2.10103900
Li	1.80761800	-0.99703800	-1.17028900
H	0.03454400	-0.12669500	-3.08882500

Ts3

C	0.66968100	-0.31023700	1.00636100
C	2.81673000	0.21317400	0.58353500
C	2.05706200	0.86288100	-0.58101800
C	0.60978600	0.66845200	-0.14400000

H	2.22530200	0.27084900	-1.49400200
C	0.53682200	-1.99161700	-0.35488200
F	-0.90995600	-2.35477200	-0.12610700
F	1.19299100	-3.17857200	-0.01806000
F	0.59079800	-1.93440100	-1.77491300
N	-0.36261600	1.25483900	-0.71326200
C	-1.71822100	1.04070600	-0.37473800
C	-2.33244400	1.75833200	0.66280900
C	-2.46346500	0.11802000	-1.12684500
C	-3.66584300	1.50599000	0.98272900
H	-1.74824400	2.47081400	1.23218300
C	-3.80030200	-0.13235200	-0.79275600
H	-1.98533300	-0.40954400	-1.94363900
C	-4.40372700	0.55188000	0.26815800
H	-4.12991000	2.04895700	1.79864900
H	-4.36658200	-0.85471400	-1.37054300
H	-5.44010100	0.36058800	0.52229100
N	2.05819600	-0.42715200	1.40602600
C	2.43520700	2.24576500	-0.84046600
N	2.76167500	3.35026100	-1.02585300
C	4.29440300	0.29174600	0.70812200
H	4.62049800	-0.24851800	1.59752900
H	4.77456000	-0.14734300	-0.17460600
H	4.62364300	1.33495200	0.77344300
N	-0.30805300	-0.50489400	1.86368700
Li	-1.91032900	-1.10311900	0.97348000
H	0.03410200	-0.95479600	2.71374800

Ts4

C	0.96230900	-0.79955300	0.38109700
C	2.70580300	-0.11652800	-0.87038900
C	1.91239100	1.17301600	-0.62303500
C	0.65476100	0.65819200	0.09684500
H	1.59485900	1.61542500	-1.57734100
N	-0.42043000	1.41645500	0.30926800
C	-1.72893000	1.06147200	-0.07272400
C	-2.80664900	1.54675100	0.68741000
C	-2.00641500	0.30008800	-1.22151200
C	-4.12052400	1.24299000	0.33554000
H	-2.60266600	2.18858600	1.54157700
C	-3.32211200	-0.00743500	-1.56448800
H	-1.18991800	-0.04980900	-1.84546400
C	-4.38801500	0.45509200	-0.78806500
H	-4.93847800	1.62513700	0.93810600
H	-3.51488700	-0.60792100	-2.44782800

H	-5.41023100	0.21616400	-1.05963400
N	2.16458800	-1.17386800	-0.37051500
C	2.64899300	2.17568700	0.13596100
N	3.23169000	2.95226200	0.78418700
C	3.98081900	-0.12614100	-1.63536400
H	4.73901200	0.48029100	-1.12602800
H	4.34828900	-1.14857700	-1.73218400
H	3.83580900	0.30261500	-2.63357100
N	1.23763900	-0.14968200	1.66089800
Li	-0.05341600	1.15341500	2.22445600
H	2.23351900	-0.20692500	1.88685100
C	-0.01673800	-1.93928000	0.44473100
F	-1.16075500	-1.59687500	1.14922100
F	-0.40775900	-2.36665700	-0.81294400
F	0.53700000	-3.02952300	1.09252800

Ts5

C	-1.34679100	0.78176900	0.65737200
C	-2.89138400	-0.66769200	-0.06776300
C	-1.62277100	-1.32723200	-0.63729700
C	-0.40575700	-0.51535400	-0.17518900
H	-1.67188900	-1.30672400	-1.73505200
N	0.64768000	-0.31927400	-0.99764800
C	1.95975600	-0.39859000	-0.47524400
C	2.97387100	0.37976500	-1.05995700
C	2.31201200	-1.27238400	0.57219800
C	4.28826800	0.31136800	-0.60228200
H	2.73568000	1.04501200	-1.88909100
C	3.62833100	-1.33426600	1.03013600
H	1.56294800	-1.93430400	0.99827700
C	4.62374500	-0.54108400	0.45315300
H	5.05143800	0.92556200	-1.06913700
H	3.87906300	-2.01948600	1.83352000
H	5.64545400	-0.59503100	0.81185900
N	-2.72427200	0.46601000	0.52385100
C	-1.47450600	-2.71831800	-0.21559700
N	-1.36449000	-3.83027000	0.12181900
C	-4.22708000	-1.29388900	-0.26707300
H	-4.38906000	-1.54740300	-1.32142300
H	-4.30649000	-2.22364700	0.30834400
H	-5.00638600	-0.60664800	0.06576000
N	-0.49167000	-0.25957200	1.22670300
C	-0.91074100	2.10365700	0.40369100
F	-0.67471600	2.37580800	-1.18935000
F	-1.76192000	3.13527800	0.65157700

F	0.35913500	2.40287600	0.84747300
H	0.35011100	0.04468700	1.71059500
Li	0.31139500	1.18252700	-2.10696400

Ts6

C	2.26267500	0.08744500	0.11946600
C	1.09307000	-1.89260100	0.23076400
C	-0.12710200	-1.24476400	-0.24557200
C	-0.12895500	0.23194100	-0.05373800
H	-1.04594600	-1.72771000	0.08362200
N	-1.18320100	1.04621000	-0.29960300
C	-2.47235700	0.71850100	0.15019700
C	-3.56880500	1.32902400	-0.49552700
C	-2.74224600	-0.15282300	1.22629000
C	-4.87947000	1.03438700	-0.12564100
H	-3.38614100	2.09787700	-1.24779600
C	-4.05674500	-0.44170500	1.59124600
H	-1.92062400	-0.56512700	1.80429300
C	-5.13449900	0.13326100	0.91171800
H	-5.70339500	1.52065900	-0.63792400
H	-4.24008800	-1.11393400	2.42361900
H	-6.15348900	-0.09667700	1.20109700
N	2.24416100	-1.22526300	0.29366500
C	-0.41112800	-1.34821400	-1.95224000
N	-0.82640300	-0.69365400	-2.84288900
C	1.09310900	-3.37688600	0.37525600
H	2.06812600	-3.72326600	0.72172200
H	0.32162500	-3.71797400	1.07620000
H	0.87743300	-3.84778000	-0.59894000
N	1.08559300	0.80398200	0.03200800
C	3.51382800	0.84415300	0.28679000
F	3.86824800	1.07948800	1.62754900
F	4.60774100	0.24040000	-0.29175400
F	3.38307400	2.12710100	-0.27700600
H	1.10058200	1.81811100	0.06263600
Li	-1.51298900	1.09455500	-2.27131900

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6. Crystal data and structure refinement of product 3m

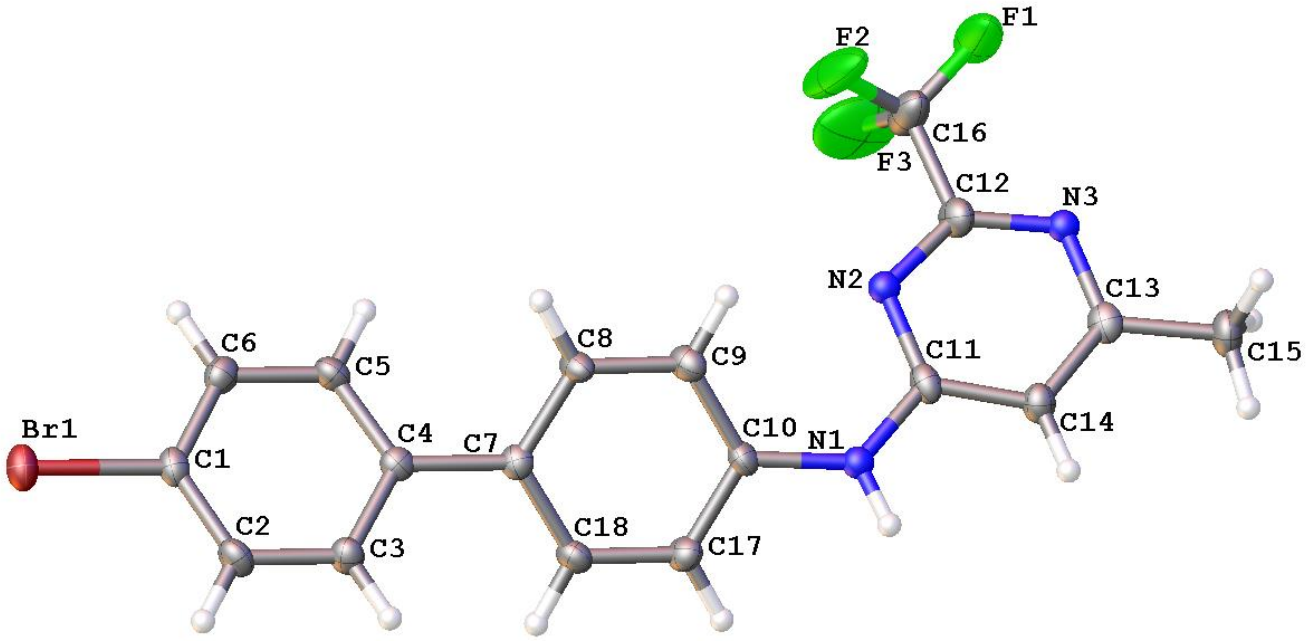


Figure S3. Crystal data and structure refinement of product **3m**.

Table S3. Crystal data and structure refinement for **3m**.

Identification code	**3m**	
CCDC	1956510	
Empirical formula	$C_{18}H_{13}BrF_3N_3$	
Formula weight	408.21	
Temperature	170.15 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 23.6780(5) Å	= 90 °.
	b = 11.5222(2) Å	= 113.6610(10) °.
	c = 26.8116(6) Å	= 90 °.
Volume	6699.9(2) $Å^3$	
Z	16	
Density (calculated)	1.619 Mg/m^3	

Absorption coefficient	2.513 mm^{-1}
F(000)	3264
Crystal size	0.08 x 0.05 x 0.03 mm^3
Theta range for data collection	3.131 to 55.025 °.
Index ranges	-28<=h<=28, -14<=k<=10, -32<=l<=32
Reflections collected	69365
Independent reflections	12722 [R(int) = 0.0797]
Completeness to theta = 53.594 °	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5507
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12722 / 6 / 905
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1043
R indices (all data)	R1 = 0.1058, wR2 = 0.1248
Extinction coefficient	n/a
Largest diff. peak and hole	0.966 and -0.750 e.$Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3m**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7582(1)	4293(1)	2470(1)	42(1)
F(1)	5106(2)	12519(5)	4512(1)	128(2)
F(2)	5705(2)	11574(5)	4269(2)	141(2)
F(3)	4945(3)	10801(5)	4302(2)	161(3)
N(1)	4559(2)	10969(3)	2316(2)	36(1)

N(2)	4859(2)	11407(3)	3233(2)	36(1)
N(3)	4361(2)	12938(3)	3510(2)	36(1)
C(1)	7020(2)	5485(4)	2448(2)	31(1)
C(2)	6593(2)	5869(4)	1954(2)	36(1)
C(3)	6194(2)	6755(4)	1940(2)	34(1)
C(4)	6210(2)	7263(4)	2419(2)	29(1)
C(5)	6644(2)	6850(4)	2911(2)	34(1)
C(6)	7048(2)	5973(4)	2926(2)	35(1)
C(7)	5785(2)	8226(4)	2400(2)	29(1)
C(8)	5958(2)	9100(4)	2788(2)	31(1)
C(9)	5563(2)	9990(4)	2779(2)	36(1)
C(10)	4973(2)	10042(4)	2368(2)	29(1)
C(11)	4503(2)	11631(4)	2711(2)	34(1)
C(12)	4753(2)	12071(5)	3587(2)	40(1)
C(13)	4015(2)	13183(4)	2976(2)	34(1)
C(14)	4074(2)	12550(4)	2566(2)	35(1)
C(15)	3582(2)	14193(4)	2873(2)	46(1)
C(16)	5127(3)	11770(7)	4169(2)	66(2)
C(17)	4795(2)	9184(4)	1978(2)	35(1)
C(18)	5188(2)	8293(4)	1991(2)	33(1)
Br(2)	2572(1)	6861(1)	2603(1)	50(1)
F(4)	-1858(2)	-1438(4)	495(1)	93(1)
F(5)	-1041(2)	-513(5)	676(1)	118(2)
F(6)	-1777(3)	271(4)	779(2)	132(2)
N(4)	-84(2)	-242(3)	2652(2)	36(1)
N(5)	-754(2)	-538(3)	1758(2)	34(1)
N(6)	-1571(2)	-1928(3)	1532(2)	36(1)
C(19)	2082(2)	5544(4)	2581(2)	34(1)
C(20)	2124(2)	5052(4)	3064(2)	34(1)
C(21)	1776(2)	4071(4)	3043(2)	31(1)

C(22)	1384(2)	3584(4)	2545(2)	27(1)
C(23)	1351(2)	4117(4)	2070(2)	35(1)
C(24)	1698(2)	5094(4)	2084(2)	36(1)
C(25)	1014(2)	2544(4)	2539(2)	26(1)
C(26)	1226(2)	1726(4)	2953(2)	32(1)
C(27)	868(2)	799(4)	2975(2)	31(1)
C(28)	274(2)	662(4)	2573(2)	26(1)
C(29)	-580(2)	-801(4)	2282(2)	32(1)
C(30)	-1243(2)	-1113(4)	1424(2)	37(1)
C(31)	-1385(2)	-2196(4)	2065(2)	33(1)
C(32)	-892(2)	-1645(4)	2452(2)	34(1)
C(33)	-1747(2)	-3107(4)	2209(2)	41(1)
C(34)	-1474(3)	-734(6)	839(2)	57(2)
C(35)	61(2)	1444(4)	2146(2)	33(1)
C(36)	425(2)	2372(4)	2131(2)	33(1)
Br(3)	3515(1)	11511(1)	813(1)	55(1)
F(7)	5993(1)	3278(2)	490(1)	54(1)
F(8)	6625(1)	1898(3)	674(2)	76(1)
F(9)	6559(2)	2907(4)	1309(1)	92(1)
N(7)	7251(2)	6803(3)	816(2)	36(1)
N(8)	6904(2)	4902(3)	804(1)	28(1)
N(9)	7546(2)	3303(3)	794(2)	32(1)
C(37)	4205(2)	10784(4)	746(2)	37(1)
C(38)	4104(2)	9919(4)	371(2)	38(1)
C(39)	4600(2)	9305(4)	359(2)	33(1)
C(40)	5200(2)	9545(4)	720(2)	29(1)
C(41)	5288(2)	10472(4)	1076(2)	41(1)
C(42)	4792(2)	11098(4)	1086(2)	44(1)
C(43)	5726(2)	8827(4)	729(2)	29(1)
C(44)	5637(2)	7726(4)	495(2)	29(1)

C(45)	6122(2)	7029(4)	518(2)	31(1)
C(46)	6727(2)	7422(4)	785(2)	30(1)
C(47)	7340(2)	5639(4)	804(2)	28(1)
C(48)	7047(2)	3793(4)	800(2)	29(1)
C(49)	7983(2)	4061(4)	788(2)	33(1)
C(50)	7898(2)	5232(4)	796(2)	35(1)
C(51)	8550(2)	3548(5)	762(2)	43(1)
C(52)	6564(2)	2961(4)	822(2)	37(1)
C(53)	6819(2)	8525(4)	1013(2)	38(1)
C(54)	6334(2)	9207(4)	992(2)	38(1)
Br(4)	4940(1)	4444(1)	807(1)	52(1)
F(10)	1888(2)	13890(4)	1069(2)	124(2)
F(11)	2409(2)	12583(4)	1008(3)	140(2)
F(12)	1810(2)	13325(5)	325(2)	151(2)
N(10)	1180(2)	9126(3)	748(2)	35(1)
N(11)	1510(2)	11044(3)	753(2)	31(1)
N(12)	845(2)	12625(3)	740(2)	35(1)
C(55)	4212(2)	5280(4)	714(2)	34(1)
C(56)	4243(2)	6468(4)	768(2)	34(1)
C(57)	3728(2)	7079(4)	731(2)	32(1)
C(58)	3170(2)	6521(4)	634(2)	29(1)
C(59)	3149(2)	5324(4)	563(2)	32(1)
C(60)	3668(2)	4702(4)	603(2)	36(1)
C(61)	2635(2)	7189(4)	633(2)	28(1)
C(62)	2230(2)	6722(4)	836(2)	33(1)
C(63)	1759(2)	7368(4)	871(2)	36(1)
C(64)	1675(2)	8522(4)	704(2)	30(1)
C(65)	1074(2)	10289(4)	742(2)	31(1)
C(66)	1362(2)	12150(4)	760(2)	33(1)
C(67)	403(2)	11849(4)	712(2)	35(1)

C(68)	503(2)	10681(4)	721(2)	36(1)
C(69)	-206(2)	12352(5)	652(2)	47(1)
C(70)	1853(2)	12997(5)	782(2)	44(1)
C(71)	2068(2)	9000(4)	487(2)	31(1)
C(72)	2536(2)	8332(4)	451(2)	32(1)

Table S5. Bond lengths [Å] and angles [ᵊ] for **3m**.

Br(1)-C(1)	1.896(4)
F(1)-C(16)	1.278(7)
F(2)-C(16)	1.302(7)
F(3)-C(16)	1.298(8)
N(1)-H(1)	0.8800
N(1)-C(10)	1.418(5)
N(1)-C(11)	1.356(5)
N(2)-C(11)	1.337(6)
N(2)-C(12)	1.320(6)
N(3)-C(12)	1.322(6)
N(3)-C(13)	1.363(6)
C(1)-C(2)	1.377(6)
C(1)-C(6)	1.376(6)
C(2)-H(2)	0.9500
C(2)-C(3)	1.382(6)
C(3)-H(3)	0.9500
C(3)-C(4)	1.397(6)
C(4)-C(5)	1.390(6)
C(4)-C(7)	1.486(6)
C(5)-H(5)	0.9500
C(5)-C(6)	1.380(6)

C(6)-H(6)	0.9500
C(7)-C(8)	1.387(6)
C(7)-C(18)	1.402(6)
C(8)-H(8)	0.9500
C(8)-C(9)	1.380(6)
C(9)-H(9)	0.9500
C(9)-C(10)	1.391(6)
C(10)-C(17)	1.377(6)
C(11)-C(14)	1.409(6)
C(12)-C(16)	1.494(7)
C(13)-C(14)	1.373(6)
C(13)-C(15)	1.501(6)
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(17)-H(17)	0.9500
C(17)-C(18)	1.376(6)
C(18)-H(18)	0.9500
Br(2)-C(19)	1.898(4)
F(4)-C(34)	1.288(6)
F(5)-C(34)	1.291(6)
F(6)-C(34)	1.337(7)
N(4)-H(4)	0.8800
N(4)-C(28)	1.412(5)
N(4)-C(29)	1.357(5)
N(5)-C(29)	1.332(6)
N(5)-C(30)	1.324(5)
N(6)-C(30)	1.322(6)
N(6)-C(31)	1.353(6)

C(19)-C(20)	1.381(6)
C(19)-C(24)	1.378(6)
C(20)-H(20)	0.9500
C(20)-C(21)	1.386(6)
C(21)-H(21)	0.9500
C(21)-C(22)	1.401(6)
C(22)-C(23)	1.388(6)
C(22)-C(25)	1.482(6)
C(23)-H(23)	0.9500
C(23)-C(24)	1.386(6)
C(24)-H(24)	0.9500
C(25)-C(26)	1.386(6)
C(25)-C(36)	1.399(6)
C(26)-H(26)	0.9500
C(26)-C(27)	1.380(6)
C(27)-H(27)	0.9500
C(27)-C(28)	1.397(6)
C(28)-C(35)	1.382(6)
C(29)-C(32)	1.402(6)
C(30)-C(34)	1.503(7)
C(31)-C(32)	1.369(6)
C(31)-C(33)	1.500(6)
C(32)-H(32)	0.9500
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(35)-H(35)	0.9500
C(35)-C(36)	1.385(6)
C(36)-H(36)	0.9500
Br(3)-C(37)	1.907(4)

F(7)-C(52)	1.338(5)
F(8)-C(52)	1.314(5)
F(9)-C(52)	1.312(5)
N(7)-H(7)	0.8800
N(7)-C(46)	1.404(5)
N(7)-C(47)	1.359(5)
N(8)-C(47)	1.337(5)
N(8)-C(48)	1.323(5)
N(9)-C(48)	1.315(5)
N(9)-C(49)	1.359(6)
C(37)-C(38)	1.365(7)
C(37)-C(42)	1.371(7)
C(38)-H(38)	0.9500
C(38)-C(39)	1.382(6)
C(39)-H(39)	0.9500
C(39)-C(40)	1.388(6)
C(40)-C(41)	1.391(6)
C(40)-C(43)	1.488(6)
C(41)-H(41)	0.9500
C(41)-C(42)	1.388(7)
C(42)-H(42)	0.9500
C(43)-C(44)	1.393(6)
C(43)-C(54)	1.394(6)
C(44)-H(44)	0.9500
C(44)-C(45)	1.382(6)
C(45)-H(45)	0.9500
C(45)-C(46)	1.394(6)
C(46)-C(53)	1.389(6)
C(47)-C(50)	1.410(6)
C(48)-C(52)	1.512(6)

C(49)-C(50)	1.366(6)
C(49)-C(51)	1.492(6)
C(50)-H(50)	0.9500
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(53)-H(53)	0.9500
C(53)-C(54)	1.375(6)
C(54)-H(54)	0.9500
Br(4)-C(55)	1.902(4)
F(10)-C(70)	1.269(6)
F(11)-C(70)	1.299(6)
F(12)-C(70)	1.246(6)
N(10)-H(10)	0.8800
N(10)-C(64)	1.409(5)
N(10)-C(65)	1.362(6)
N(11)-C(65)	1.342(5)
N(11)-C(66)	1.324(6)
N(12)-C(66)	1.323(5)
N(12)-C(67)	1.356(6)
C(55)-C(56)	1.376(7)
C(55)-C(60)	1.372(6)
C(56)-H(56)	0.9500
C(56)-C(57)	1.378(6)
C(57)-H(57)	0.9500
C(57)-C(58)	1.396(6)
C(58)-C(59)	1.390(6)
C(58)-C(61)	1.482(6)
C(59)-H(59)	0.9500
C(59)-C(60)	1.389(6)

C(60)-H(60)	0.9500
C(61)-C(62)	1.387(6)
C(61)-C(72)	1.391(6)
C(62)-H(62)	0.9500
C(62)-C(63)	1.374(6)
C(63)-H(63)	0.9500
C(63)-C(64)	1.392(6)
C(64)-C(71)	1.393(6)
C(65)-C(68)	1.406(6)
C(66)-C(70)	1.500(6)
C(67)-C(68)	1.364(6)
C(67)-C(69)	1.502(6)
C(68)-H(68)	0.9500
C(69)-H(69A)	0.9800
C(69)-H(69B)	0.9800
C(69)-H(69C)	0.9800
C(71)-H(71)	0.9500
C(71)-C(72)	1.384(6)
C(72)-H(72)	0.9500

C(10)-N(1)-H(1)	115.6
C(11)-N(1)-H(1)	115.6
C(11)-N(1)-C(10)	128.8(4)
C(12)-N(2)-C(11)	114.6(4)
C(12)-N(3)-C(13)	114.1(4)
C(2)-C(1)-Br(1)	119.8(3)
C(6)-C(1)-Br(1)	119.7(4)
C(6)-C(1)-C(2)	120.5(4)
C(1)-C(2)-H(2)	120.2
C(1)-C(2)-C(3)	119.5(4)

C(3)-C(2)-H(2)	120.2
C(2)-C(3)-H(3)	119.4
C(2)-C(3)-C(4)	121.2(4)
C(4)-C(3)-H(3)	119.4
C(3)-C(4)-C(7)	120.8(4)
C(5)-C(4)-C(3)	117.8(4)
C(5)-C(4)-C(7)	121.4(4)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-C(4)	121.2(4)
C(6)-C(5)-H(5)	119.4
C(1)-C(6)-C(5)	119.9(4)
C(1)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(8)-C(7)-C(4)	121.6(4)
C(8)-C(7)-C(18)	116.7(4)
C(18)-C(7)-C(4)	121.7(4)
C(7)-C(8)-H(8)	118.9
C(9)-C(8)-C(7)	122.1(4)
C(9)-C(8)-H(8)	118.9
C(8)-C(9)-H(9)	119.9
C(8)-C(9)-C(10)	120.3(4)
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-N(1)	123.1(4)
C(17)-C(10)-N(1)	118.5(4)
C(17)-C(10)-C(9)	118.3(4)
N(1)-C(11)-C(14)	119.5(4)
N(2)-C(11)-N(1)	119.4(4)
N(2)-C(11)-C(14)	121.1(4)
N(2)-C(12)-N(3)	130.6(5)
N(2)-C(12)-C(16)	114.3(4)

N(3)-C(12)-C(16)	115.1(4)
N(3)-C(13)-C(14)	121.3(4)
N(3)-C(13)-C(15)	115.7(4)
C(14)-C(13)-C(15)	123.0(5)
C(11)-C(14)-H(14)	120.9
C(13)-C(14)-C(11)	118.1(5)
C(13)-C(14)-H(14)	120.9
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
F(1)-C(16)-F(2)	108.1(6)
F(1)-C(16)-F(3)	105.6(6)
F(1)-C(16)-C(12)	114.6(5)
F(2)-C(16)-C(12)	112.9(5)
F(3)-C(16)-F(2)	103.4(6)
F(3)-C(16)-C(12)	111.3(6)
C(10)-C(17)-H(17)	119.4
C(18)-C(17)-C(10)	121.3(4)
C(18)-C(17)-H(17)	119.4
C(7)-C(18)-H(18)	119.4
C(17)-C(18)-C(7)	121.3(4)
C(17)-C(18)-H(18)	119.4
C(28)-N(4)-H(4)	115.3
C(29)-N(4)-H(4)	115.3
C(29)-N(4)-C(28)	129.5(4)
C(30)-N(5)-C(29)	114.6(4)
C(30)-N(6)-C(31)	115.1(4)

C(20)-C(19)-Br(2)	119.1(4)
C(24)-C(19)-Br(2)	119.2(4)
C(24)-C(19)-C(20)	121.7(4)
C(19)-C(20)-H(20)	120.7
C(19)-C(20)-C(21)	118.5(4)
C(21)-C(20)-H(20)	120.7
C(20)-C(21)-H(21)	119.3
C(20)-C(21)-C(22)	121.4(4)
C(22)-C(21)-H(21)	119.3
C(21)-C(22)-C(25)	119.8(4)
C(23)-C(22)-C(21)	118.0(4)
C(23)-C(22)-C(25)	122.2(4)
C(22)-C(23)-H(23)	119.3
C(24)-C(23)-C(22)	121.3(4)
C(24)-C(23)-H(23)	119.3
C(19)-C(24)-C(23)	119.0(4)
C(19)-C(24)-H(24)	120.5
C(23)-C(24)-H(24)	120.5
C(26)-C(25)-C(22)	121.2(4)
C(26)-C(25)-C(36)	117.2(4)
C(36)-C(25)-C(22)	121.5(4)
C(25)-C(26)-H(26)	119.0
C(27)-C(26)-C(25)	121.9(4)
C(27)-C(26)-H(26)	119.0
C(26)-C(27)-H(27)	120.0
C(26)-C(27)-C(28)	120.0(4)
C(28)-C(27)-H(27)	120.0
C(27)-C(28)-N(4)	116.6(4)
C(35)-C(28)-N(4)	124.3(4)
C(35)-C(28)-C(27)	119.0(4)

N(4)-C(29)-C(32)	120.3(4)
N(5)-C(29)-N(4)	118.2(4)
N(5)-C(29)-C(32)	121.4(4)
N(5)-C(30)-C(34)	114.4(4)
N(6)-C(30)-N(5)	129.7(5)
N(6)-C(30)-C(34)	115.8(4)
N(6)-C(31)-C(32)	120.8(4)
N(6)-C(31)-C(33)	117.1(4)
C(32)-C(31)-C(33)	122.2(4)
C(29)-C(32)-H(32)	120.8
C(31)-C(32)-C(29)	118.4(4)
C(31)-C(32)-H(32)	120.8
C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
F(4)-C(34)-F(5)	108.0(5)
F(4)-C(34)-F(6)	105.6(5)
F(4)-C(34)-C(30)	114.8(5)
F(5)-C(34)-F(6)	104.4(5)
F(5)-C(34)-C(30)	113.9(5)
F(6)-C(34)-C(30)	109.3(5)
C(28)-C(35)-H(35)	119.9
C(28)-C(35)-C(36)	120.2(4)
C(36)-C(35)-H(35)	119.9
C(25)-C(36)-H(36)	119.2
C(35)-C(36)-C(25)	121.5(4)
C(35)-C(36)-H(36)	119.2

C(46)-N(7)-H(7)	115.0
C(47)-N(7)-H(7)	115.0
C(47)-N(7)-C(46)	129.9(4)
C(48)-N(8)-C(47)	114.3(4)
C(48)-N(9)-C(49)	114.6(4)
C(38)-C(37)-Br(3)	119.1(4)
C(38)-C(37)-C(42)	120.9(4)
C(42)-C(37)-Br(3)	119.9(4)
C(37)-C(38)-H(38)	120.3
C(37)-C(38)-C(39)	119.5(5)
C(39)-C(38)-H(38)	120.3
C(38)-C(39)-H(39)	119.3
C(38)-C(39)-C(40)	121.5(4)
C(40)-C(39)-H(39)	119.3
C(39)-C(40)-C(41)	117.4(4)
C(39)-C(40)-C(43)	121.1(4)
C(41)-C(40)-C(43)	121.4(4)
C(40)-C(41)-H(41)	119.4
C(42)-C(41)-C(40)	121.2(5)
C(42)-C(41)-H(41)	119.4
C(37)-C(42)-C(41)	119.3(5)
C(37)-C(42)-H(42)	120.4
C(41)-C(42)-H(42)	120.4
C(44)-C(43)-C(40)	121.6(4)
C(44)-C(43)-C(54)	116.9(4)
C(54)-C(43)-C(40)	121.4(4)
C(43)-C(44)-H(44)	118.8
C(45)-C(44)-C(43)	122.4(4)
C(45)-C(44)-H(44)	118.8
C(44)-C(45)-H(45)	120.0

C(44)-C(45)-C(46)	119.9(4)
C(46)-C(45)-H(45)	120.0
C(45)-C(46)-N(7)	124.5(4)
C(53)-C(46)-N(7)	117.4(4)
C(53)-C(46)-C(45)	118.1(4)
N(7)-C(47)-C(50)	118.9(4)
N(8)-C(47)-N(7)	120.0(4)
N(8)-C(47)-C(50)	121.1(4)
N(8)-C(48)-C(52)	114.2(4)
N(9)-C(48)-N(8)	130.5(4)
N(9)-C(48)-C(52)	115.2(4)
N(9)-C(49)-C(50)	121.1(4)
N(9)-C(49)-C(51)	116.7(4)
C(50)-C(49)-C(51)	122.3(4)
C(47)-C(50)-H(50)	120.8
C(49)-C(50)-C(47)	118.3(4)
C(49)-C(50)-H(50)	120.8
C(49)-C(51)-H(51A)	109.5
C(49)-C(51)-H(51B)	109.5
C(49)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
F(7)-C(52)-C(48)	112.3(4)
F(8)-C(52)-F(7)	104.9(4)
F(8)-C(52)-C(48)	113.7(4)
F(9)-C(52)-F(7)	105.3(4)
F(9)-C(52)-F(8)	107.7(4)
F(9)-C(52)-C(48)	112.4(4)
C(46)-C(53)-H(53)	119.2

C(54)-C(53)-C(46)	121.6(4)
C(54)-C(53)-H(53)	119.2
C(43)-C(54)-H(54)	119.4
C(53)-C(54)-C(43)	121.1(4)
C(53)-C(54)-H(54)	119.4
C(64)-N(10)-H(10)	115.1
C(65)-N(10)-H(10)	115.1
C(65)-N(10)-C(64)	129.8(4)
C(66)-N(11)-C(65)	114.7(4)
C(66)-N(12)-C(67)	114.2(4)
C(56)-C(55)-Br(4)	118.8(3)
C(60)-C(55)-Br(4)	120.4(4)
C(60)-C(55)-C(56)	120.8(4)
C(55)-C(56)-H(56)	120.3
C(55)-C(56)-C(57)	119.5(4)
C(57)-C(56)-H(56)	120.3
C(56)-C(57)-H(57)	119.3
C(56)-C(57)-C(58)	121.5(4)
C(58)-C(57)-H(57)	119.3
C(57)-C(58)-C(61)	120.4(4)
C(59)-C(58)-C(57)	117.5(4)
C(59)-C(58)-C(61)	122.1(4)
C(58)-C(59)-H(59)	119.4
C(60)-C(59)-C(58)	121.3(4)
C(60)-C(59)-H(59)	119.4
C(55)-C(60)-C(59)	119.4(4)
C(55)-C(60)-H(60)	120.3
C(59)-C(60)-H(60)	120.3
C(62)-C(61)-C(58)	121.5(4)
C(62)-C(61)-C(72)	117.3(4)

C(72)-C(61)-C(58)	121.1(4)
C(61)-C(62)-H(62)	119.2
C(63)-C(62)-C(61)	121.6(4)
C(63)-C(62)-H(62)	119.2
C(62)-C(63)-H(63)	119.6
C(62)-C(63)-C(64)	120.7(4)
C(64)-C(63)-H(63)	119.6
C(63)-C(64)-N(10)	117.5(4)
C(63)-C(64)-C(71)	118.6(4)
C(71)-C(64)-N(10)	123.9(4)
N(10)-C(65)-C(68)	119.0(4)
N(11)-C(65)-N(10)	120.1(4)
N(11)-C(65)-C(68)	120.9(4)
N(11)-C(66)-C(70)	114.9(4)
N(12)-C(66)-N(11)	130.1(4)
N(12)-C(66)-C(70)	115.0(4)
N(12)-C(67)-C(68)	121.7(4)
N(12)-C(67)-C(69)	115.9(4)
C(68)-C(67)-C(69)	122.4(4)
C(65)-C(68)-H(68)	120.8
C(67)-C(68)-C(65)	118.3(4)
C(67)-C(68)-H(68)	120.8
C(67)-C(69)-H(69A)	109.5
C(67)-C(69)-H(69B)	109.5
C(67)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
F(10)-C(70)-F(11)	102.0(5)
F(10)-C(70)-C(66)	114.3(4)

F(11)-C(70)-C(66)	113.7(5)
F(12)-C(70)-F(10)	108.1(5)
F(12)-C(70)-F(11)	103.8(5)
F(12)-C(70)-C(66)	113.7(5)
C(64)-C(71)-H(71)	120.1
C(72)-C(71)-C(64)	119.8(4)
C(72)-C(71)-H(71)	120.1
C(61)-C(72)-H(72)	119.0
C(71)-C(72)-C(61)	121.9(4)
C(71)-C(72)-H(72)	119.0

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3m**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2} U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	42(1)	32(1)	60(1)	4(1)	28(1)	6(1)
F(1)	141(4)	176(5)	41(2)	-18(3)	10(2)	103(4)
F(2)	76(3)	265(7)	58(3)	-23(3)	0(2)	92(4)
F(3)	232(7)	150(5)	65(3)	52(3)	21(4)	-3(5)
N(1)	38(2)	34(2)	35(2)	-2(2)	15(2)	9(2)
N(2)	31(2)	45(3)	37(2)	-3(2)	17(2)	9(2)
N(3)	32(2)	37(3)	43(3)	-4(2)	19(2)	2(2)
C(1)	30(2)	25(3)	44(3)	0(2)	22(2)	-1(2)
C(2)	46(3)	34(3)	37(3)	-5(2)	25(2)	0(2)
C(3)	38(3)	36(3)	33(3)	2(2)	20(2)	3(2)
C(4)	31(2)	29(3)	32(3)	1(2)	17(2)	-4(2)

C(5)	41(3)	34(3)	32(3)	-5(2)	19(2)	-2(2)
C(6)	34(3)	32(3)	38(3)	6(2)	14(2)	1(2)
C(7)	25(2)	32(3)	34(3)	1(2)	17(2)	-2(2)
C(8)	23(2)	37(3)	34(3)	-10(2)	12(2)	-4(2)
C(9)	32(3)	41(3)	40(3)	-8(2)	20(2)	-4(2)
C(10)	31(2)	24(3)	35(3)	-4(2)	17(2)	-2(2)
C(11)	32(3)	28(3)	49(3)	-5(2)	25(2)	-2(2)
C(12)	33(3)	48(3)	44(3)	-3(3)	21(2)	6(2)
C(13)	30(2)	35(3)	48(3)	0(2)	25(2)	-3(2)
C(14)	36(3)	33(3)	41(3)	4(2)	21(2)	4(2)
C(15)	49(3)	38(3)	56(3)	4(3)	28(3)	14(3)
C(16)	63(4)	92(6)	41(4)	4(4)	20(3)	38(4)
C(17)	27(2)	42(3)	36(3)	-1(2)	13(2)	2(2)
C(18)	36(3)	35(3)	30(3)	-6(2)	17(2)	-3(2)
Br(2)	42(1)	35(1)	80(1)	4(1)	31(1)	-9(1)
F(4)	105(3)	112(3)	43(2)	-11(2)	8(2)	-72(3)
F(5)	86(3)	217(5)	48(2)	7(3)	22(2)	-80(3)
F(6)	216(6)	97(4)	54(3)	23(2)	23(3)	42(4)
N(4)	37(2)	37(2)	32(2)	1(2)	11(2)	-10(2)
N(5)	30(2)	38(2)	35(2)	-5(2)	14(2)	-13(2)
N(6)	29(2)	36(2)	44(3)	-2(2)	15(2)	-8(2)
C(19)	26(2)	27(3)	52(3)	0(2)	19(2)	-1(2)
C(20)	25(2)	31(3)	46(3)	-4(2)	12(2)	-5(2)
C(21)	28(2)	34(3)	31(3)	2(2)	13(2)	-1(2)
C(22)	22(2)	27(3)	35(3)	-1(2)	13(2)	0(2)
C(23)	35(3)	34(3)	36(3)	-2(2)	14(2)	-1(2)
C(24)	43(3)	28(3)	42(3)	6(2)	24(2)	2(2)
C(25)	22(2)	28(3)	27(2)	-4(2)	9(2)	-3(2)
C(26)	22(2)	40(3)	31(3)	-1(2)	9(2)	-5(2)
C(27)	28(2)	37(3)	26(2)	2(2)	8(2)	-1(2)

C(28)	25(2)	25(3)	27(2)	-5(2)	8(2)	-6(2)
C(29)	24(2)	28(3)	43(3)	-6(2)	15(2)	-5(2)
C(30)	36(3)	35(3)	41(3)	-7(2)	16(2)	-11(2)
C(31)	27(2)	20(3)	53(3)	3(2)	18(2)	0(2)
C(32)	31(2)	33(3)	37(3)	4(2)	13(2)	-3(2)
C(33)	33(3)	31(3)	58(3)	-1(3)	17(2)	-5(2)
C(34)	62(4)	60(4)	41(3)	-4(3)	13(3)	-32(3)
C(35)	27(2)	31(3)	33(3)	0(2)	4(2)	-7(2)
C(36)	36(3)	33(3)	30(3)	0(2)	12(2)	-4(2)
Br(3)	57(1)	42(1)	84(1)	7(1)	46(1)	12(1)
F(7)	34(2)	47(2)	78(2)	4(2)	21(2)	-7(1)
F(8)	56(2)	32(2)	147(3)	-12(2)	46(2)	-6(2)
F(9)	104(3)	128(3)	46(2)	-5(2)	33(2)	-73(3)
N(7)	23(2)	29(2)	57(3)	-1(2)	16(2)	-5(2)
N(8)	23(2)	29(2)	32(2)	0(2)	10(2)	0(2)
N(9)	27(2)	33(2)	35(2)	0(2)	10(2)	4(2)
C(37)	43(3)	24(3)	54(3)	7(2)	31(3)	7(2)
C(38)	38(3)	34(3)	46(3)	6(3)	22(2)	2(2)
C(39)	38(3)	26(3)	35(3)	3(2)	17(2)	3(2)
C(40)	33(2)	23(3)	32(3)	5(2)	15(2)	0(2)
C(41)	38(3)	37(3)	52(3)	-4(3)	21(2)	-2(2)
C(42)	55(3)	31(3)	55(3)	-8(3)	31(3)	-4(3)
C(43)	33(2)	25(3)	30(3)	0(2)	13(2)	-4(2)
C(44)	26(2)	30(3)	31(3)	-3(2)	10(2)	-3(2)
C(45)	29(2)	29(3)	35(3)	-6(2)	13(2)	-4(2)
C(46)	30(2)	27(3)	34(3)	1(2)	15(2)	-3(2)
C(47)	26(2)	27(3)	29(3)	0(2)	10(2)	-2(2)
C(48)	28(2)	31(3)	27(3)	0(2)	11(2)	-1(2)
C(49)	26(2)	40(3)	33(3)	-6(2)	11(2)	4(2)
C(50)	21(2)	45(3)	36(3)	-1(2)	9(2)	-7(2)

C(51)	31(3)	49(3)	51(3)	-4(3)	18(2)	7(2)
C(52)	34(3)	35(3)	46(3)	-3(2)	18(2)	-3(2)
C(53)	25(2)	27(3)	57(3)	-2(2)	8(2)	-6(2)
C(54)	37(3)	22(3)	51(3)	-3(2)	12(2)	-5(2)
Br(4)	40(1)	55(1)	59(1)	-9(1)	18(1)	13(1)
F(10)	140(4)	79(3)	217(5)	-81(3)	137(4)	-67(3)
F(11)	46(2)	71(3)	292(7)	29(4)	57(3)	-9(2)
F(12)	163(4)	214(5)	71(3)	3(3)	41(3)	-145(4)
N(10)	29(2)	28(2)	54(3)	3(2)	23(2)	-2(2)
N(11)	28(2)	32(2)	35(2)	-2(2)	15(2)	2(2)
N(12)	33(2)	36(2)	40(2)	-1(2)	18(2)	6(2)
C(55)	34(3)	37(3)	32(3)	-2(2)	14(2)	5(2)
C(56)	33(3)	43(3)	30(3)	-4(2)	17(2)	-2(2)
C(57)	36(3)	24(3)	37(3)	-1(2)	18(2)	-4(2)
C(58)	30(2)	31(3)	26(2)	0(2)	11(2)	-3(2)
C(59)	34(3)	30(3)	35(3)	-2(2)	15(2)	-4(2)
C(60)	45(3)	27(3)	39(3)	-5(2)	19(2)	1(2)
C(61)	26(2)	25(3)	29(2)	2(2)	9(2)	-3(2)
C(62)	30(2)	24(3)	45(3)	6(2)	16(2)	0(2)
C(63)	31(3)	32(3)	49(3)	7(2)	21(2)	-6(2)
C(64)	26(2)	31(3)	34(3)	1(2)	14(2)	-1(2)
C(65)	31(2)	32(3)	34(3)	3(2)	18(2)	2(2)
C(66)	35(3)	34(3)	32(3)	-1(2)	17(2)	1(2)
C(67)	27(2)	48(3)	31(3)	3(2)	12(2)	6(2)
C(68)	31(2)	37(3)	42(3)	3(2)	18(2)	-2(2)
C(69)	41(3)	53(4)	51(3)	0(3)	23(3)	12(3)
C(70)	48(3)	31(3)	68(4)	-4(3)	39(3)	-3(3)
C(71)	35(3)	24(3)	36(3)	1(2)	16(2)	-4(2)
C(72)	33(2)	32(3)	35(3)	4(2)	19(2)	-1(2)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3m**.

	x	y	z	U(eq)
H(1)	4305	11139	1980	43
H(2)	6574	5528	1625	43
H(3)	5903	7024	1599	40
H(5)	6663	7176	3242	41
H(6)	7344	5707	3265	42
H(8)	6361	9086	3070	37
H(9)	5696	10570	3054	43
H(14)	3832	12725	2195	42
H(15A)	3310	14070	3064	68
H(15B)	3333	14261	2481	68
H(15C)	3820	14907	3005	68
H(17)	4393	9207	1695	42
H(18)	5051	7713	1716	39
H(4)	31	-479	2991	43
H(20)	2385	5380	3404	41
H(21)	1805	3721	3373	37
H(23)	1084	3806	1728	42
H(24)	1673	5448	1755	43
H(26)	1630	1807	3229	38
H(27)	1026	253	3264	37
H(32)	-763	-1829	2827	41
H(33A)	-2181	-2873	2073	61
H(33B)	-1583	-3196	2606	61
H(33C)	-1714	-3847	2043	61

H(35)	-337	1344	1863	39
H(36)	272	2904	1836	40
H(7)	7570	7234	848	44
H(38)	3697	9741	122	46
H(39)	4528	8706	97	39
H(41)	5695	10681	1316	50
H(42)	4859	11737	1327	53
H(44)	5228	7444	313	35
H(45)	6044	6284	353	37
H(50)	8207	5759	797	42
H(51A)	8722	2965	1050	65
H(51B)	8855	4162	813	65
H(51C)	8444	3181	406	65
H(53)	7228	8815	1187	46
H(54)	6413	9950	1160	46
H(10)	895	8686	786	42
H(56)	4618	6864	831	41
H(57)	3752	7899	772	38
H(59)	2772	4924	485	39
H(60)	3647	3884	555	44
H(62)	2280	5937	955	39
H(63)	1488	7022	1010	43
H(68)	194	10147	714	43
H(69A)	-139	13104	838	70
H(69B)	-409	11823	814	70
H(69C)	-468	12458	265	70
H(71)	2015	9782	364	38
H(72)	2798	8664	299	38

Table S8. Torsion angles [°] for **3m**.

Br(1)-C(1)-C(2)-C(3)	-178.6(3)
Br(1)-C(1)-C(6)-C(5)	179.2(3)
N(1)-C(10)-C(17)-C(18)	176.5(4)
N(1)-C(11)-C(14)-C(13)	178.2(4)
N(2)-C(11)-C(14)-C(13)	-2.3(7)
N(2)-C(12)-C(16)-F(1)	168.8(6)
N(2)-C(12)-C(16)-F(2)	44.4(8)
N(2)-C(12)-C(16)-F(3)	-71.4(7)
N(3)-C(12)-C(16)-F(1)	-12.6(9)
N(3)-C(12)-C(16)-F(2)	-137.0(6)
N(3)-C(12)-C(16)-F(3)	107.1(6)
N(3)-C(13)-C(14)-C(11)	0.1(7)
C(1)-C(2)-C(3)-C(4)	-0.5(7)
C(2)-C(1)-C(6)-C(5)	0.4(7)
C(2)-C(3)-C(4)-C(5)	0.2(7)
C(2)-C(3)-C(4)-C(7)	179.2(4)
C(3)-C(4)-C(5)-C(6)	0.5(7)
C(3)-C(4)-C(7)-C(8)	-147.4(4)
C(3)-C(4)-C(7)-C(18)	32.9(6)
C(4)-C(5)-C(6)-C(1)	-0.7(7)
C(4)-C(7)-C(8)-C(9)	-179.1(4)
C(4)-C(7)-C(18)-C(17)	179.5(4)
C(5)-C(4)-C(7)-C(8)	31.5(6)
C(5)-C(4)-C(7)-C(18)	-148.1(4)
C(6)-C(1)-C(2)-C(3)	0.3(7)
C(7)-C(4)-C(5)-C(6)	-178.5(4)
C(7)-C(8)-C(9)-C(10)	-0.7(7)
C(8)-C(7)-C(18)-C(17)	-0.2(6)

C(8)-C(9)-C(10)-N(1)	-176.0(4)
C(8)-C(9)-C(10)-C(17)	0.4(7)
C(9)-C(10)-C(17)-C(18)	0.0(7)
C(10)-N(1)-C(11)-N(2)	-2.1(7)
C(10)-N(1)-C(11)-C(14)	177.3(4)
C(10)-C(17)-C(18)-C(7)	-0.1(7)
C(11)-N(1)-C(10)-C(9)	-31.9(7)
C(11)-N(1)-C(10)-C(17)	151.7(4)
C(11)-N(2)-C(12)-N(3)	-1.6(8)
C(11)-N(2)-C(12)-C(16)	176.6(5)
C(12)-N(2)-C(11)-N(1)	-177.6(4)
C(12)-N(2)-C(11)-C(14)	2.9(6)
C(12)-N(3)-C(13)-C(14)	1.2(6)
C(12)-N(3)-C(13)-C(15)	-177.7(4)
C(13)-N(3)-C(12)-N(2)	-0.5(7)
C(13)-N(3)-C(12)-C(16)	-178.7(5)
C(15)-C(13)-C(14)-C(11)	178.9(4)
C(18)-C(7)-C(8)-C(9)	0.6(6)
Br(2)-C(19)-C(20)-C(21)	-178.2(3)
Br(2)-C(19)-C(24)-C(23)	178.7(3)
N(4)-C(28)-C(35)-C(36)	173.7(4)
N(4)-C(29)-C(32)-C(31)	-179.3(4)
N(5)-C(29)-C(32)-C(31)	-0.3(7)
N(5)-C(30)-C(34)-F(4)	165.5(5)
N(5)-C(30)-C(34)-F(5)	40.3(7)
N(5)-C(30)-C(34)-F(6)	-76.0(6)
N(6)-C(30)-C(34)-F(4)	-17.3(8)
N(6)-C(30)-C(34)-F(5)	-142.6(5)
N(6)-C(30)-C(34)-F(6)	101.2(6)
N(6)-C(31)-C(32)-C(29)	-0.4(7)

C(19)-C(20)-C(21)-C(22)	-0.6(6)
C(20)-C(19)-C(24)-C(23)	-0.6(7)
C(20)-C(21)-C(22)-C(23)	-0.3(6)
C(20)-C(21)-C(22)-C(25)	-179.2(4)
C(21)-C(22)-C(23)-C(24)	0.7(6)
C(21)-C(22)-C(25)-C(26)	-31.0(6)
C(21)-C(22)-C(25)-C(36)	146.0(4)
C(22)-C(23)-C(24)-C(19)	-0.3(7)
C(22)-C(25)-C(26)-C(27)	175.1(4)
C(22)-C(25)-C(36)-C(35)	-175.2(4)
C(23)-C(22)-C(25)-C(26)	150.2(4)
C(23)-C(22)-C(25)-C(36)	-32.8(6)
C(24)-C(19)-C(20)-C(21)	1.0(7)
C(25)-C(22)-C(23)-C(24)	179.6(4)
C(25)-C(26)-C(27)-C(28)	0.0(7)
C(26)-C(25)-C(36)-C(35)	1.9(6)
C(26)-C(27)-C(28)-N(4)	-174.1(4)
C(26)-C(27)-C(28)-C(35)	2.2(7)
C(27)-C(28)-C(35)-C(36)	-2.4(7)
C(28)-N(4)-C(29)-N(5)	4.4(7)
C(28)-N(4)-C(29)-C(32)	-176.6(4)
C(28)-C(35)-C(36)-C(25)	0.3(7)
C(29)-N(4)-C(28)-C(27)	-158.3(4)
C(29)-N(4)-C(28)-C(35)	25.5(7)
C(29)-N(5)-C(30)-N(6)	-2.3(7)
C(29)-N(5)-C(30)-C(34)	174.4(5)
C(30)-N(5)-C(29)-N(4)	-179.5(4)
C(30)-N(5)-C(29)-C(32)	1.5(6)
C(30)-N(6)-C(31)-C(32)	-0.1(6)
C(30)-N(6)-C(31)-C(33)	179.4(4)

C(31)-N(6)-C(30)-N(5)	1.6(7)
C(31)-N(6)-C(30)-C(34)	-175.1(5)
C(33)-C(31)-C(32)-C(29)	-179.8(4)
C(36)-C(25)-C(26)-C(27)	-2.1(6)
Br(3)-C(37)-C(38)-C(39)	-173.2(3)
Br(3)-C(37)-C(42)-C(41)	172.6(4)
N(7)-C(46)-C(53)-C(54)	178.6(4)
N(7)-C(47)-C(50)-C(49)	179.6(4)
N(8)-C(47)-C(50)-C(49)	0.0(7)
N(8)-C(48)-C(52)-F(7)	43.9(6)
N(8)-C(48)-C(52)-F(8)	162.8(4)
N(8)-C(48)-C(52)-F(9)	-74.6(5)
N(9)-C(48)-C(52)-F(7)	-138.0(4)
N(9)-C(48)-C(52)-F(8)	-19.1(6)
N(9)-C(48)-C(52)-F(9)	103.6(5)
N(9)-C(49)-C(50)-C(47)	-0.8(7)
C(37)-C(38)-C(39)-C(40)	0.2(7)
C(38)-C(37)-C(42)-C(41)	-4.6(7)
C(38)-C(39)-C(40)-C(41)	-3.6(7)
C(38)-C(39)-C(40)-C(43)	175.7(4)
C(39)-C(40)-C(41)-C(42)	3.0(7)
C(39)-C(40)-C(43)-C(44)	-17.9(6)
C(39)-C(40)-C(43)-C(54)	164.7(4)
C(40)-C(41)-C(42)-C(37)	1.0(8)
C(40)-C(43)-C(44)-C(45)	-177.4(4)
C(40)-C(43)-C(54)-C(53)	178.1(4)
C(41)-C(40)-C(43)-C(44)	161.4(4)
C(41)-C(40)-C(43)-C(54)	-16.0(7)
C(42)-C(37)-C(38)-C(39)	4.0(7)
C(43)-C(40)-C(41)-C(42)	-176.4(4)

C(43)-C(44)-C(45)-C(46)	0.1(7)
C(44)-C(43)-C(54)-C(53)	0.6(7)
C(44)-C(45)-C(46)-N(7)	-177.7(4)
C(44)-C(45)-C(46)-C(53)	-1.0(7)
C(45)-C(46)-C(53)-C(54)	1.7(7)
C(46)-N(7)-C(47)-N(8)	-5.7(7)
C(46)-N(7)-C(47)-C(50)	174.7(4)
C(46)-C(53)-C(54)-C(43)	-1.5(8)
C(47)-N(7)-C(46)-C(45)	-28.0(7)
C(47)-N(7)-C(46)-C(53)	155.3(5)
C(47)-N(8)-C(48)-N(9)	-0.2(7)
C(47)-N(8)-C(48)-C(52)	177.6(4)
C(48)-N(8)-C(47)-N(7)	-179.1(4)
C(48)-N(8)-C(47)-C(50)	0.5(6)
C(48)-N(9)-C(49)-C(50)	1.0(6)
C(48)-N(9)-C(49)-C(51)	-177.9(4)
C(49)-N(9)-C(48)-N(8)	-0.5(7)
C(49)-N(9)-C(48)-C(52)	-178.3(4)
C(51)-C(49)-C(50)-C(47)	178.0(4)
C(54)-C(43)-C(44)-C(45)	0.1(7)
Br(4)-C(55)-C(56)-C(57)	-176.6(3)
Br(4)-C(55)-C(60)-C(59)	177.0(3)
N(10)-C(64)-C(71)-C(72)	-178.9(4)
N(10)-C(65)-C(68)-C(67)	-179.6(4)
N(11)-C(65)-C(68)-C(67)	0.1(7)
N(11)-C(66)-C(70)-F(10)	-143.3(5)
N(11)-C(66)-C(70)-F(11)	-26.8(7)
N(11)-C(66)-C(70)-F(12)	91.8(6)
N(12)-C(66)-C(70)-F(10)	37.9(7)
N(12)-C(66)-C(70)-F(11)	154.4(5)

N(12)-C(66)-C(70)-F(12)	-87.0(6)
N(12)-C(67)-C(68)-C(65)	-2.3(7)
C(55)-C(56)-C(57)-C(58)	-0.6(7)
C(56)-C(55)-C(60)-C(59)	-2.1(7)
C(56)-C(57)-C(58)-C(59)	-1.6(7)
C(56)-C(57)-C(58)-C(61)	175.9(4)
C(57)-C(58)-C(59)-C(60)	2.0(7)
C(57)-C(58)-C(61)-C(62)	-143.6(4)
C(57)-C(58)-C(61)-C(72)	33.2(6)
C(58)-C(59)-C(60)-C(55)	-0.2(7)
C(58)-C(61)-C(62)-C(63)	175.3(4)
C(58)-C(61)-C(72)-C(71)	-174.8(4)
C(59)-C(58)-C(61)-C(62)	33.7(7)
C(59)-C(58)-C(61)-C(72)	-149.5(4)
C(60)-C(55)-C(56)-C(57)	2.5(7)
C(61)-C(58)-C(59)-C(60)	-175.4(4)
C(61)-C(62)-C(63)-C(64)	-0.3(7)
C(62)-C(61)-C(72)-C(71)	2.2(7)
C(62)-C(63)-C(64)-N(10)	179.6(4)
C(62)-C(63)-C(64)-C(71)	1.7(7)
C(63)-C(64)-C(71)-C(72)	-1.1(7)
C(64)-N(10)-C(65)-N(11)	-8.0(7)
C(64)-N(10)-C(65)-C(68)	171.7(4)
C(64)-C(71)-C(72)-C(61)	-0.9(7)
C(65)-N(10)-C(64)-C(63)	162.6(5)
C(65)-N(10)-C(64)-C(71)	-19.6(7)
C(65)-N(11)-C(66)-N(12)	-2.4(7)
C(65)-N(11)-C(66)-C(70)	179.0(4)
C(66)-N(11)-C(65)-N(10)	-178.3(4)
C(66)-N(11)-C(65)-C(68)	2.0(6)

C(66)-N(12)-C(67)-C(68)	2.1(6)
C(66)-N(12)-C(67)-C(69)	-176.1(4)
C(67)-N(12)-C(66)-N(11)	0.4(7)
C(67)-N(12)-C(66)-C(70)	178.9(4)
C(69)-C(67)-C(68)-C(65)	175.8(4)
C(72)-C(61)-C(62)-C(63)	-1.6(7)

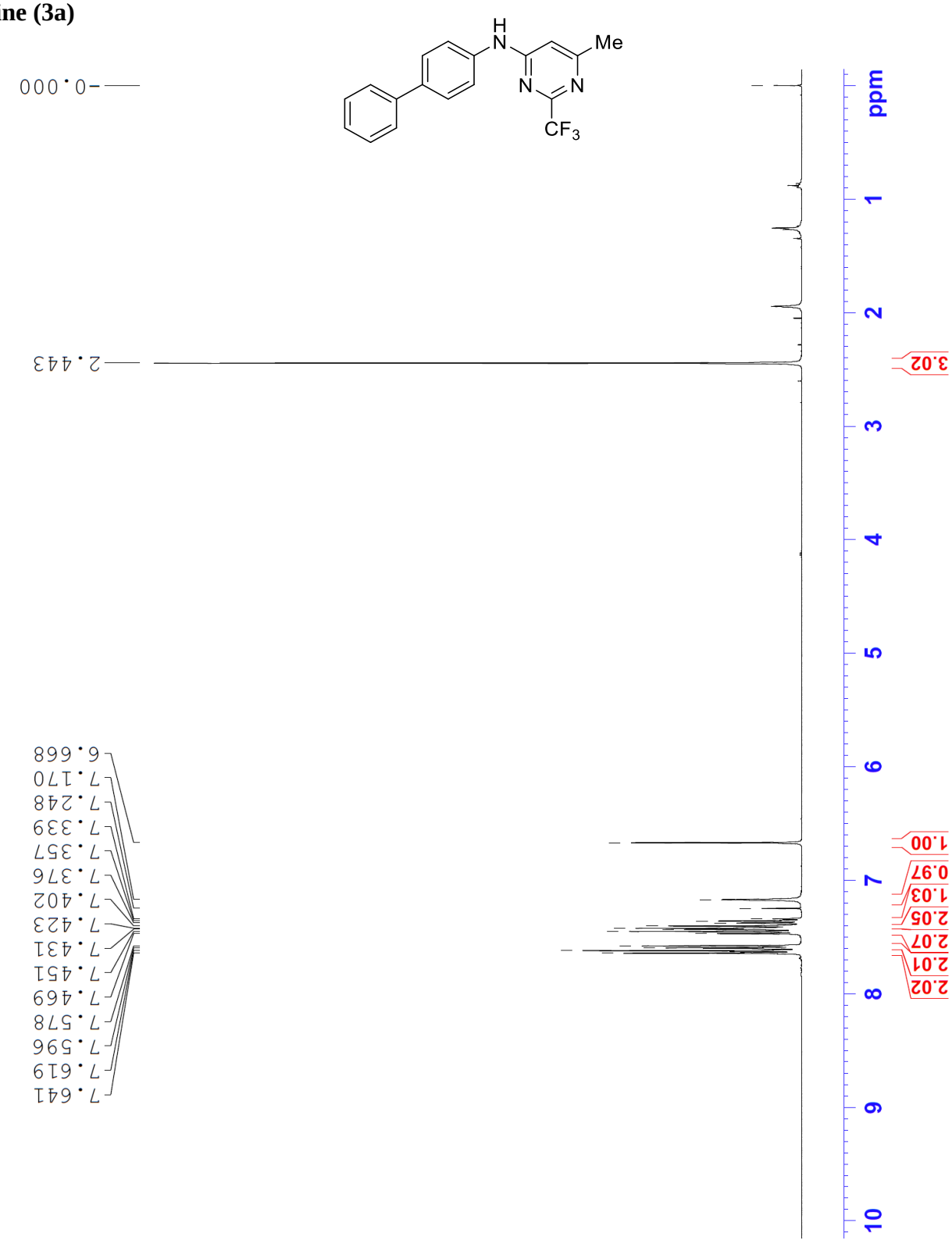
Symmetry transformations used to generate equivalent atoms:

Table S9. Hydrogen bonds for **3m** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

7. Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra

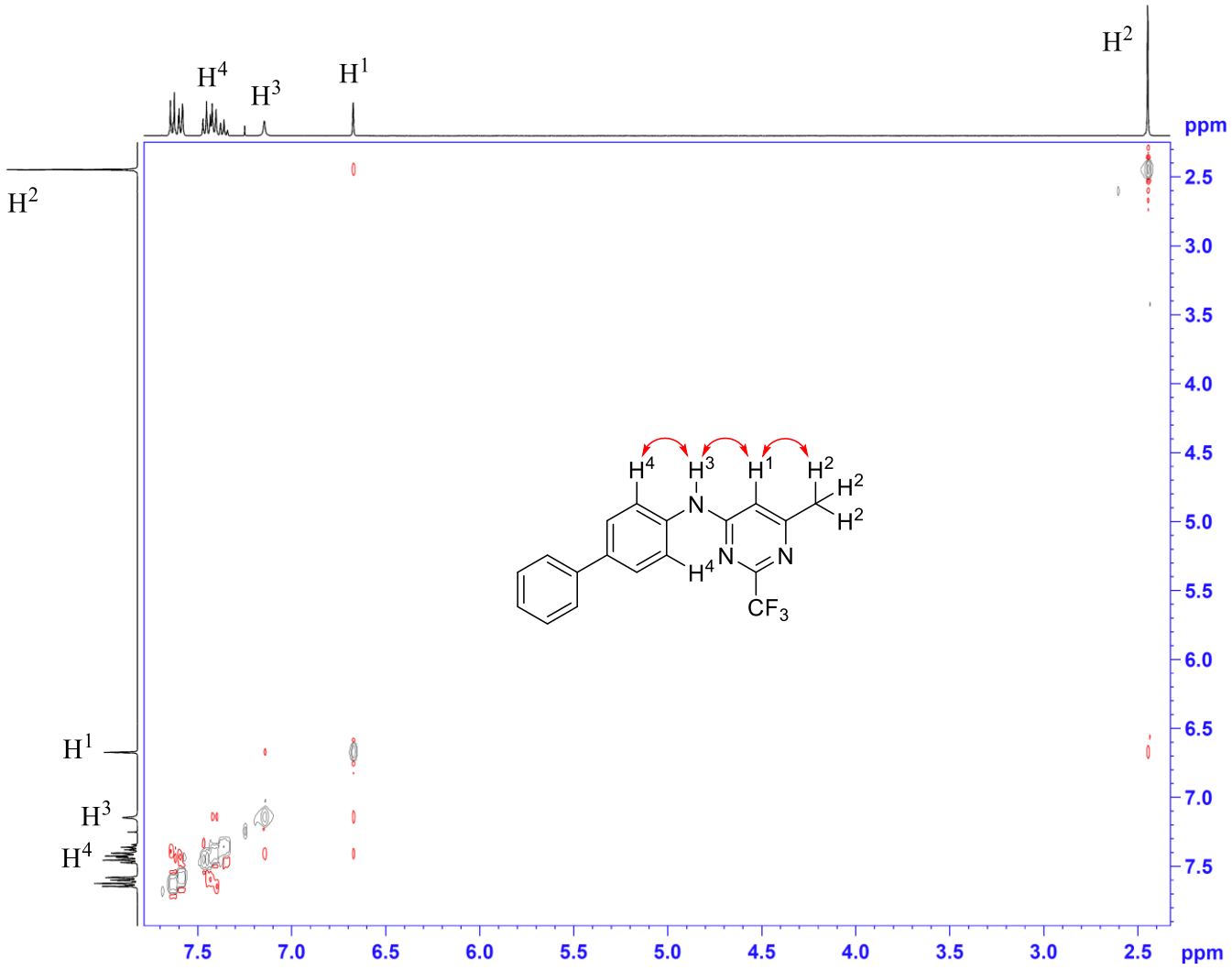
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3a)

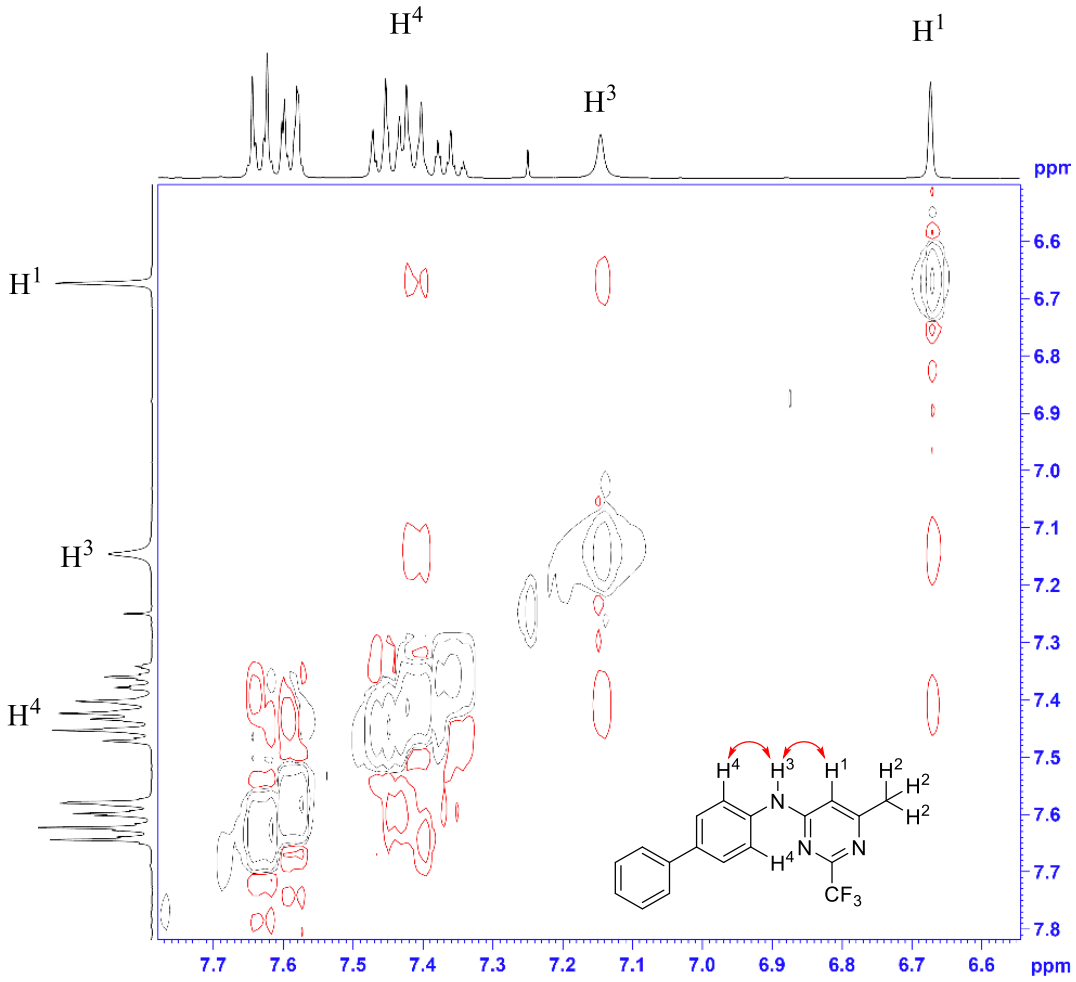


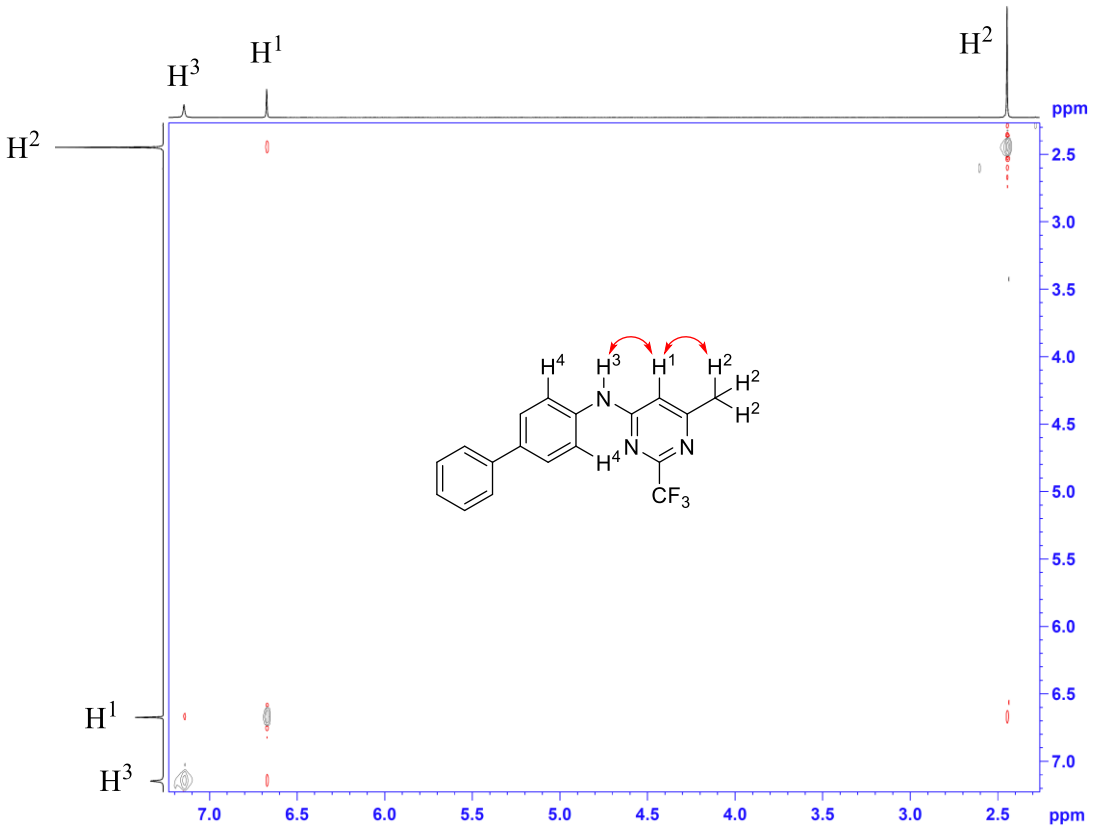
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3a)

^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3a)

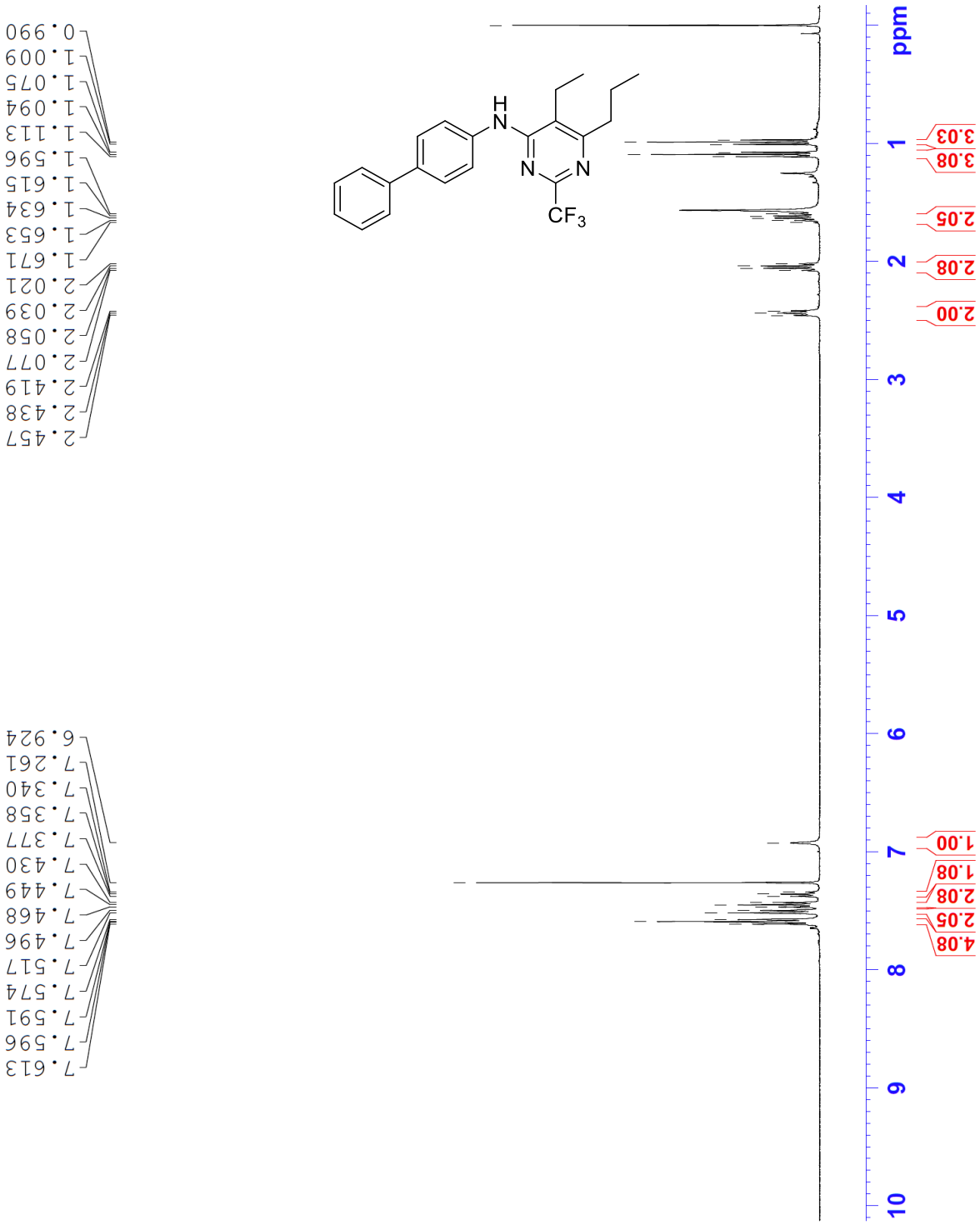
^{1}H-^{1}H NOSEY (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3a)



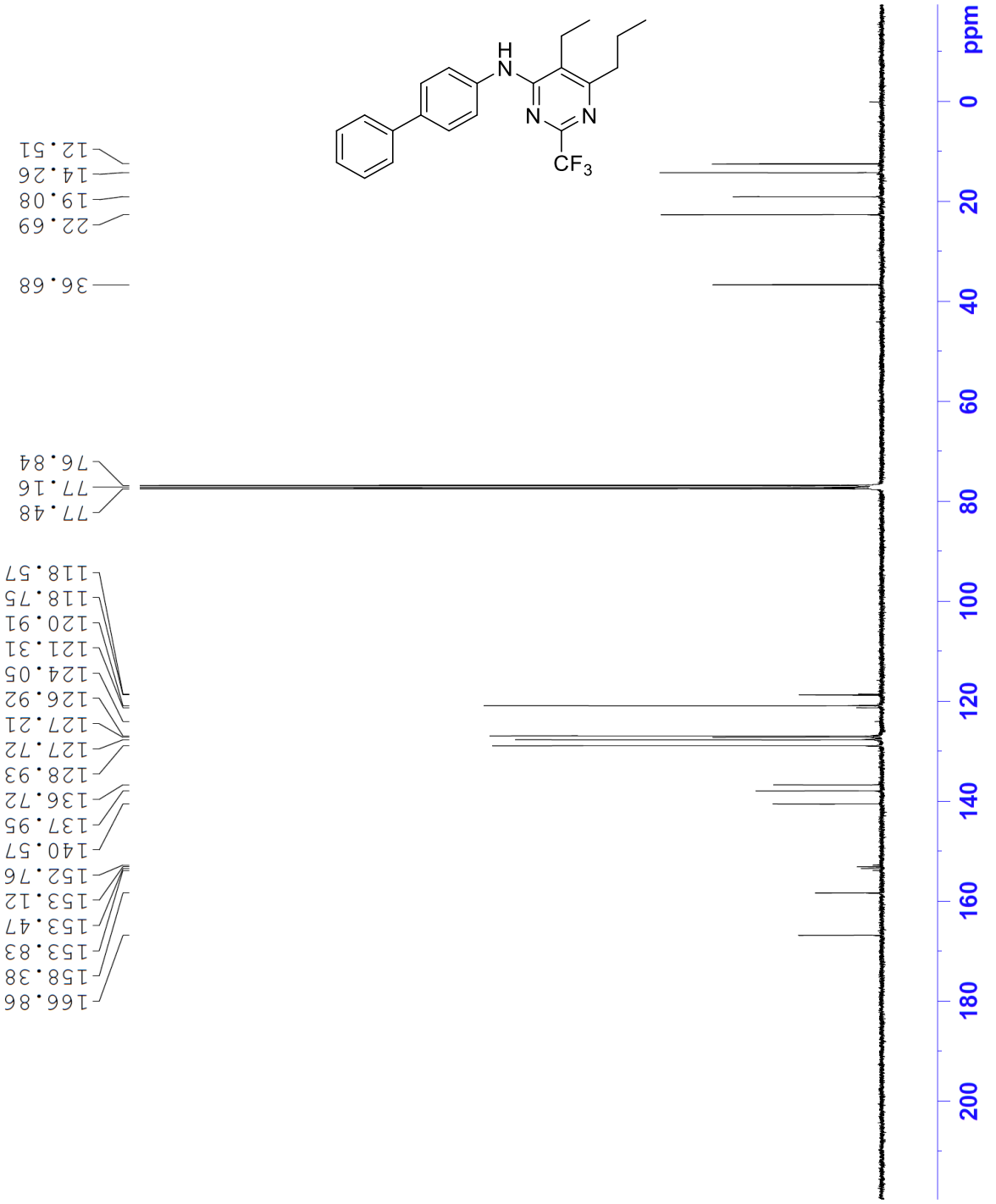

H4
H1
H3
ppm
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
H1
H3
H4
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
H4
H3
H1
H2
H2
H2
N
N
N
H4
CF3


H3
H1
H2
ppm
H2
H1
H3
H4
H3
H1
H2
H2
H2
N
N
N
H4
CF3
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

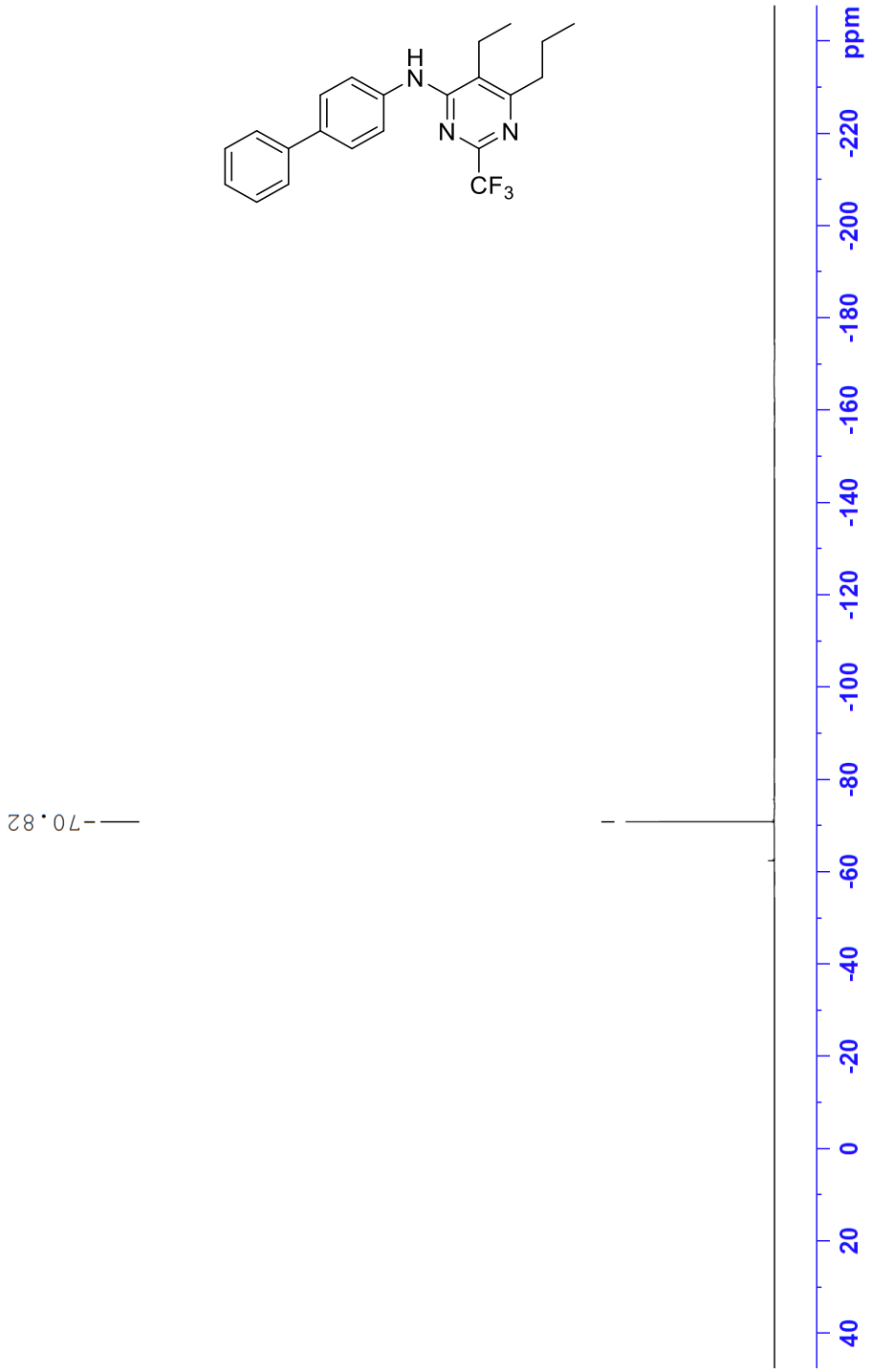
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-ethyl-6-propyl-2-(trifluoromethyl)pyrimidin-4-amine (3b)



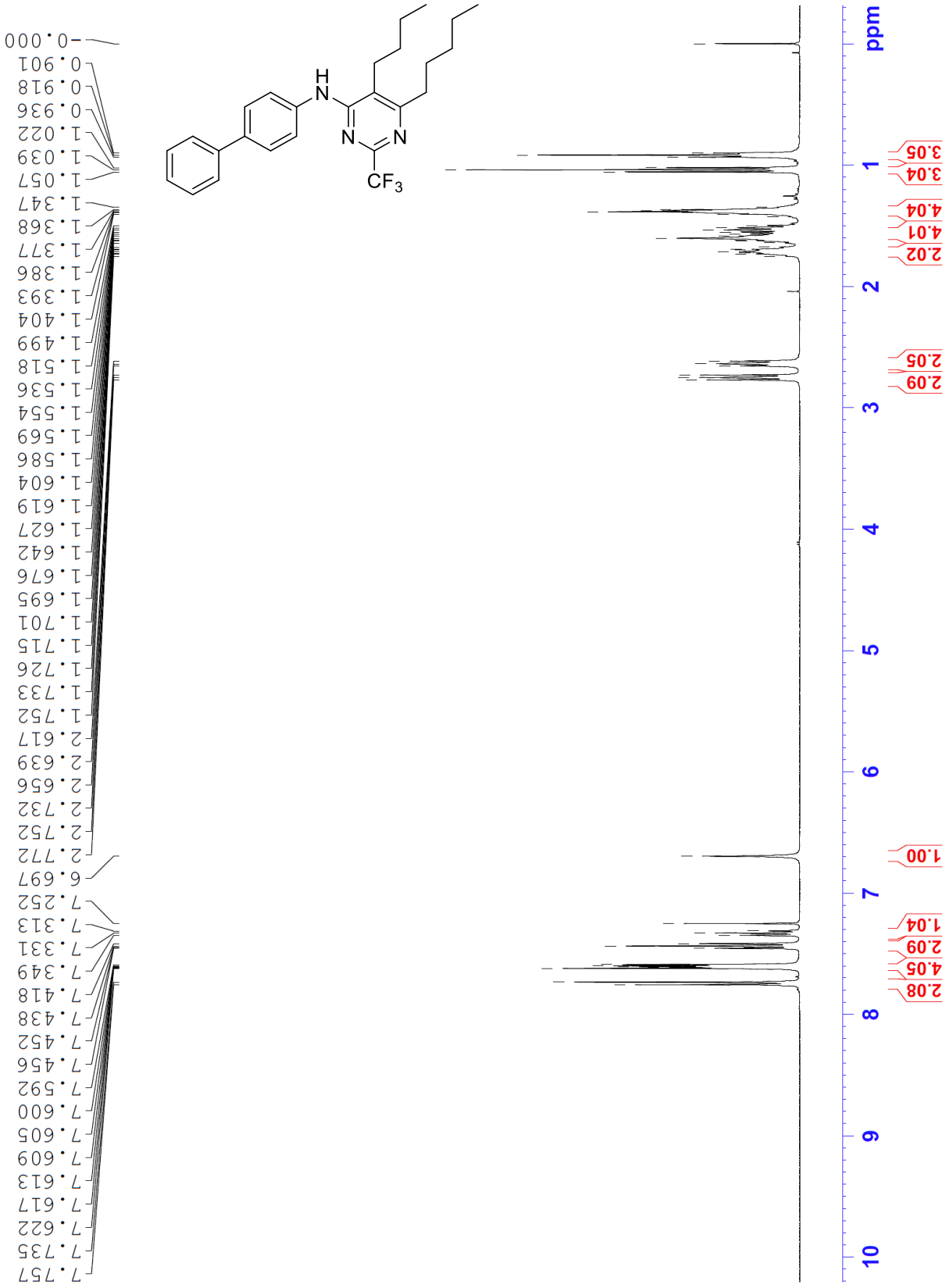
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-ethyl-6-propyl-2-(trifluoromethyl)pyrimidin-4-amine (3b)



^{19}F NMR (565 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-ethyl-6-propyl-2-(trifluoromethyl)pyrimidin-4-amine (3b)

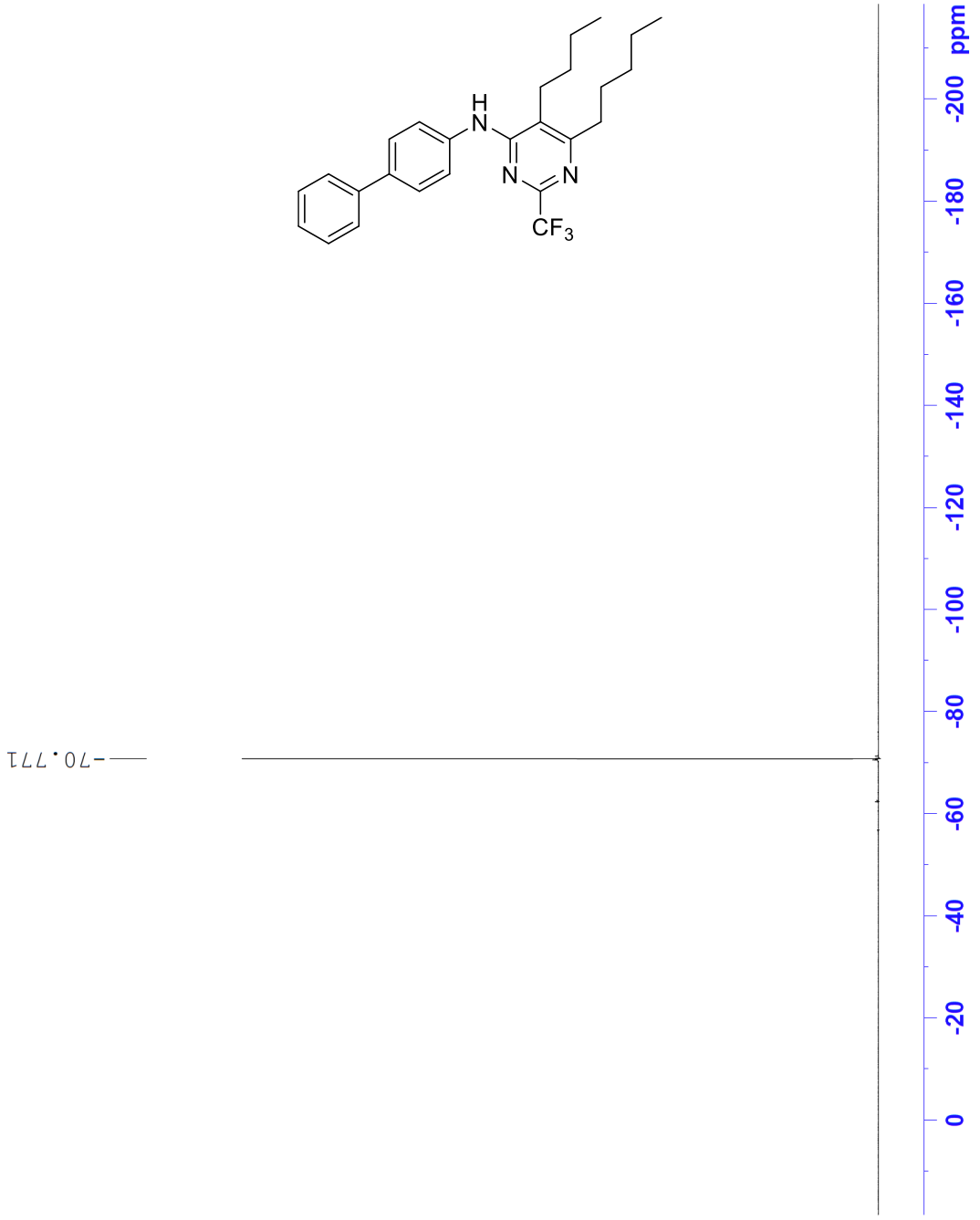


^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-butyl-6-pentyl-2-(trifluoromethyl)pyrimidin-4-amine (3c)

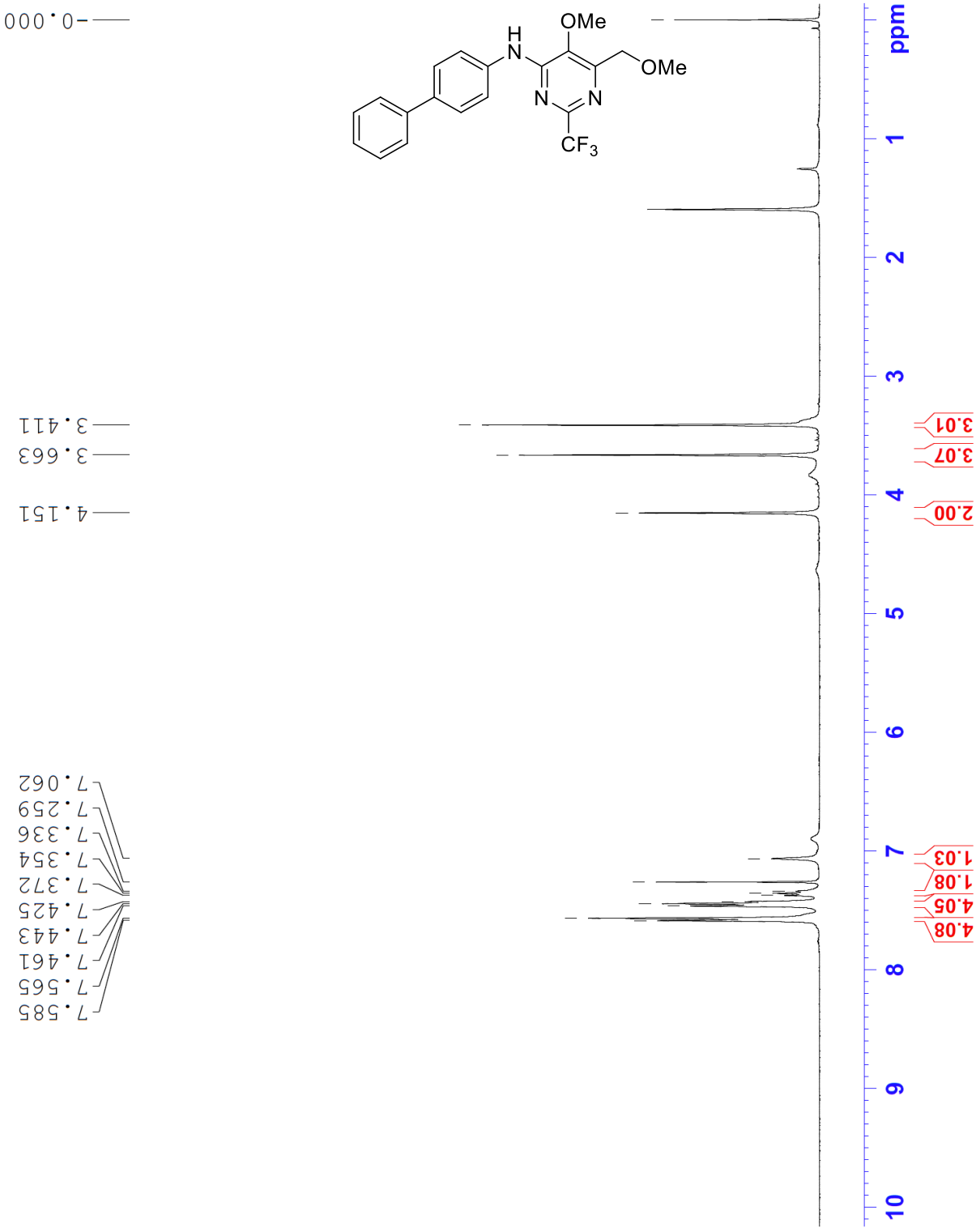


^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-butyl-6-pentyl-2-(trifluoromethyl)pyrimidin-4-amine (3c)

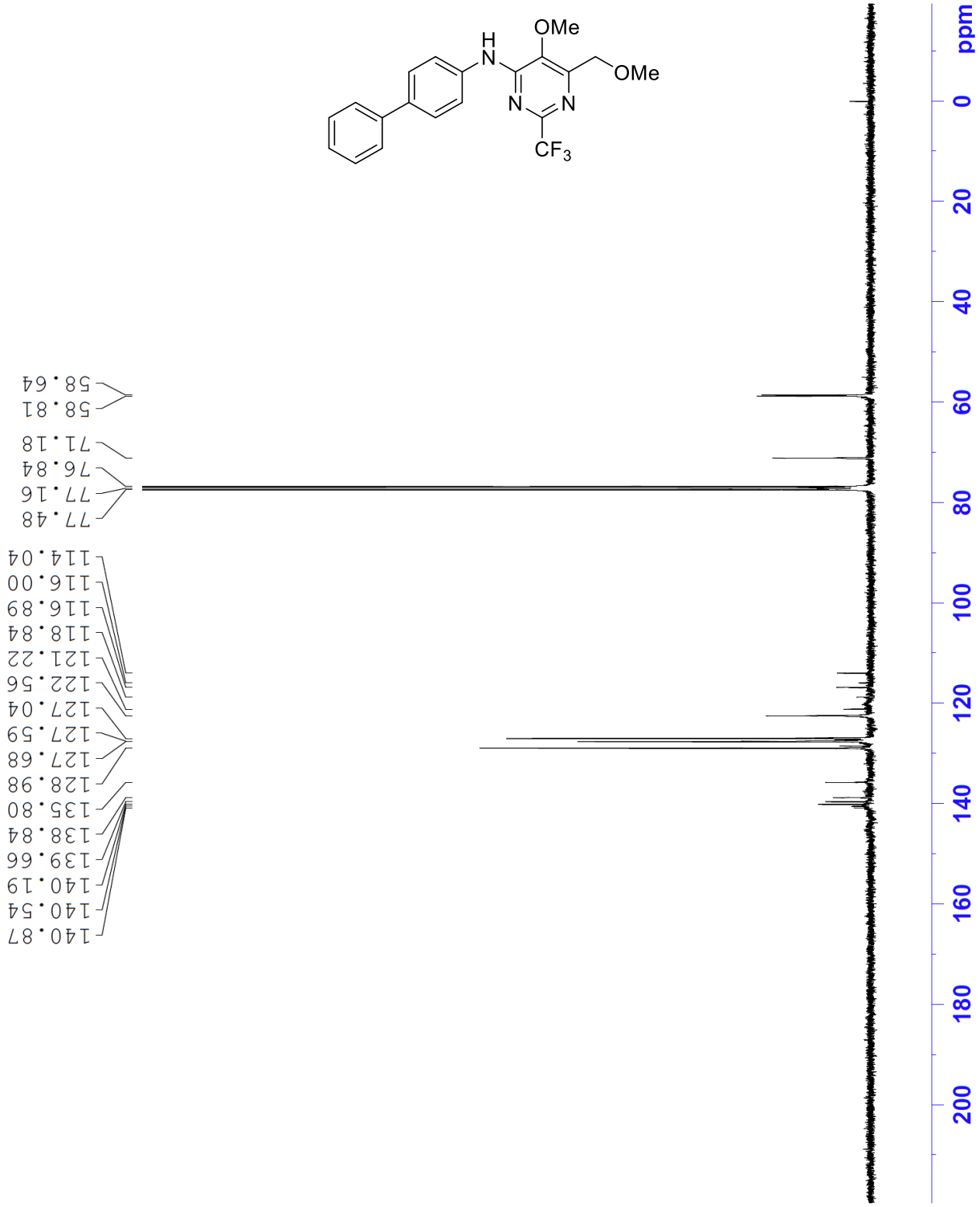
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-butyl-6-pentyl-2-(trifluoromethyl)pyrimidin-4-amine (3c)



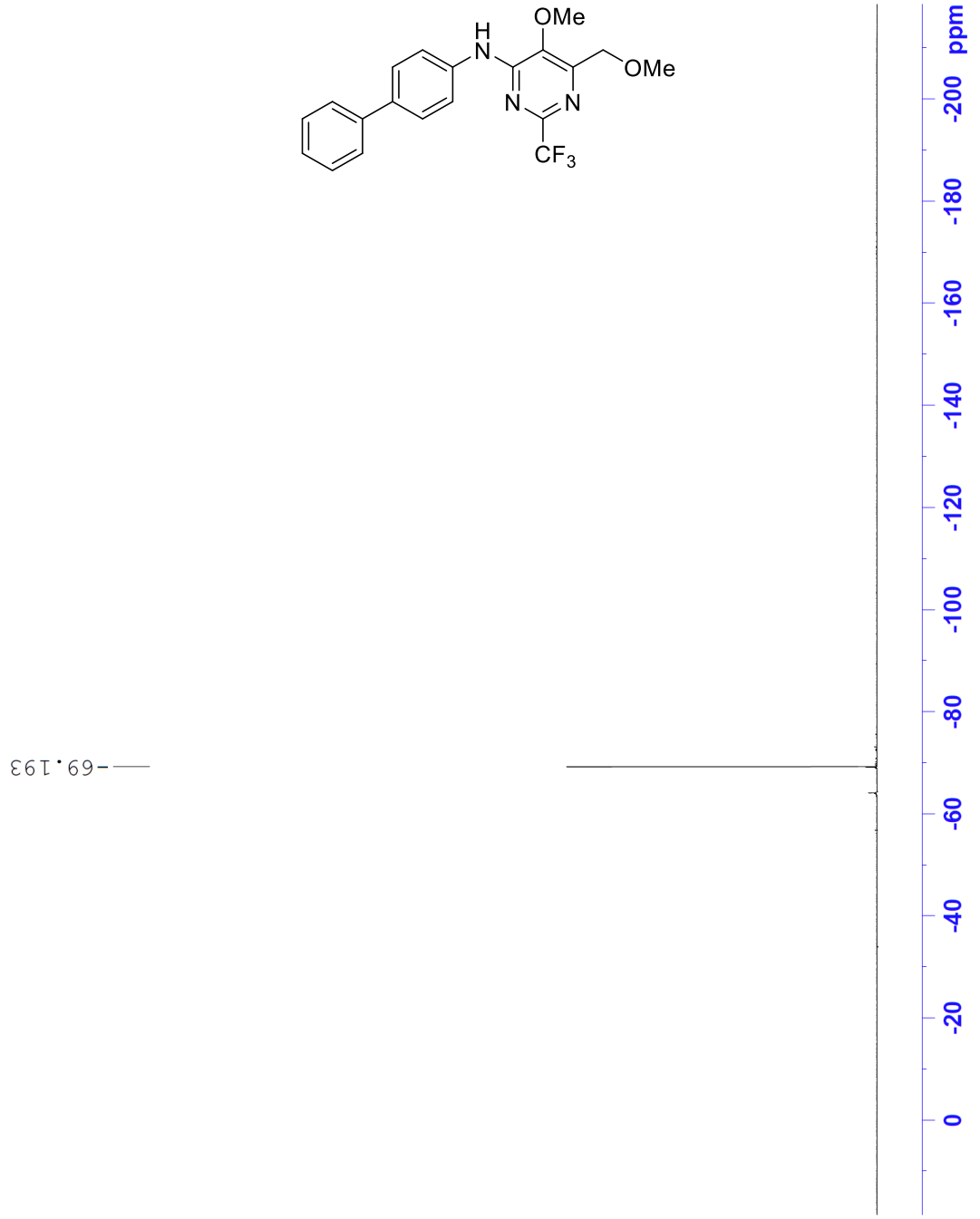
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-methoxy-6-(methoxymethyl)-2-(trifluoromethyl)pyrimidin-4-amine (3d)



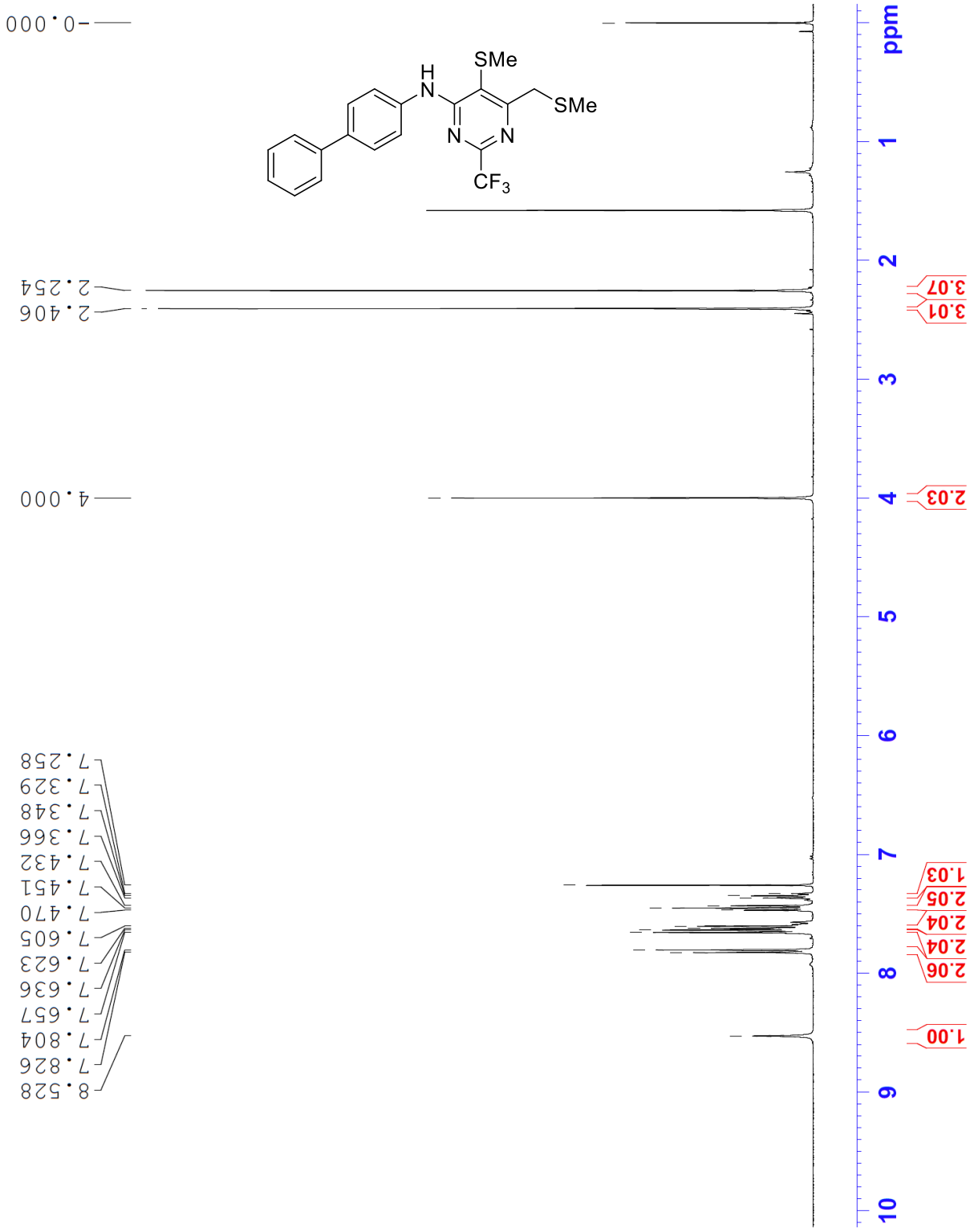
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-methoxy-6-(methoxymethyl)-2-(trifluoromethyl)pyrimidin-4-amine (3d)



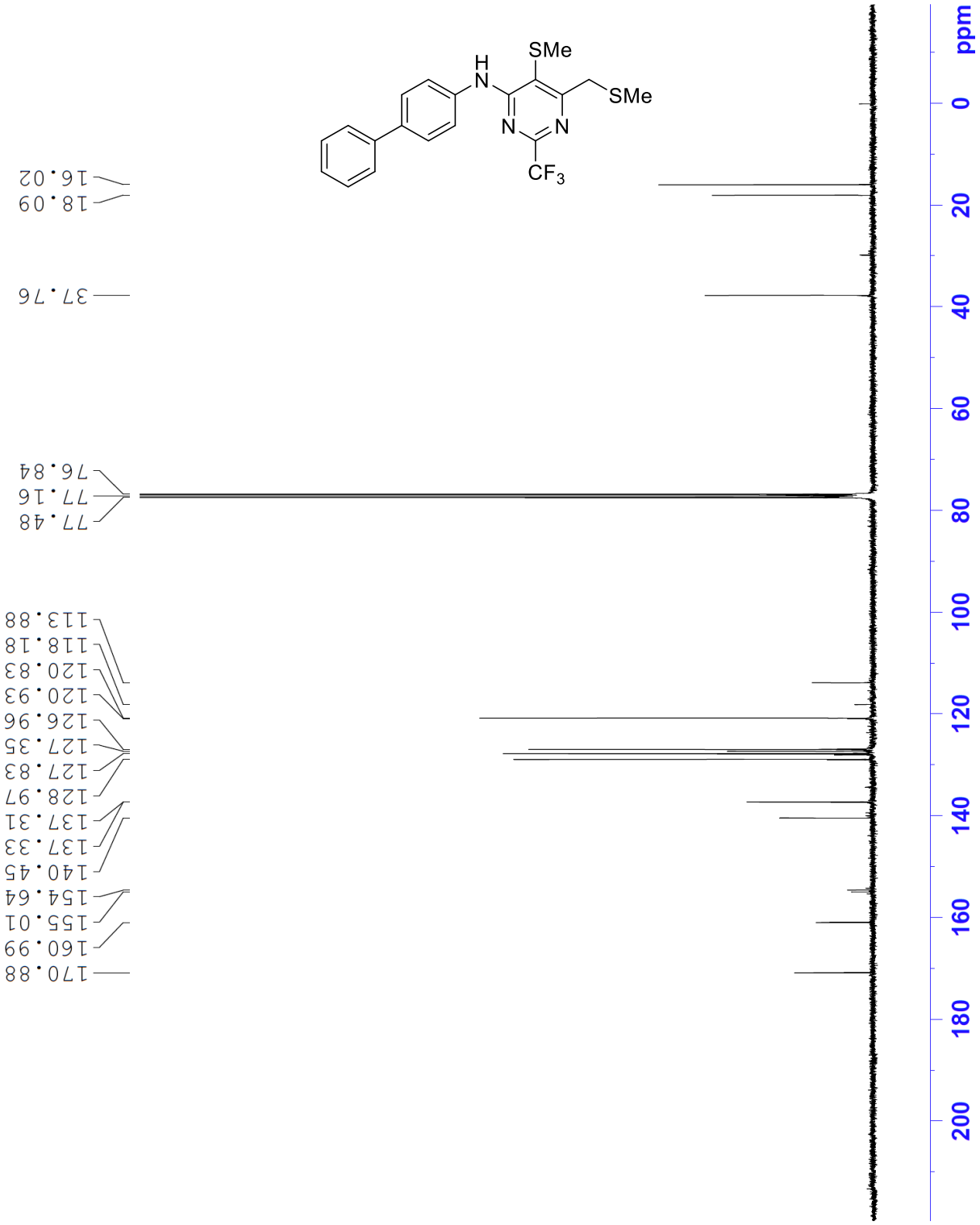
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-methoxy-6-(methoxymethyl)-2-(trifluoromethyl)pyrimidin-4-amine (3d)



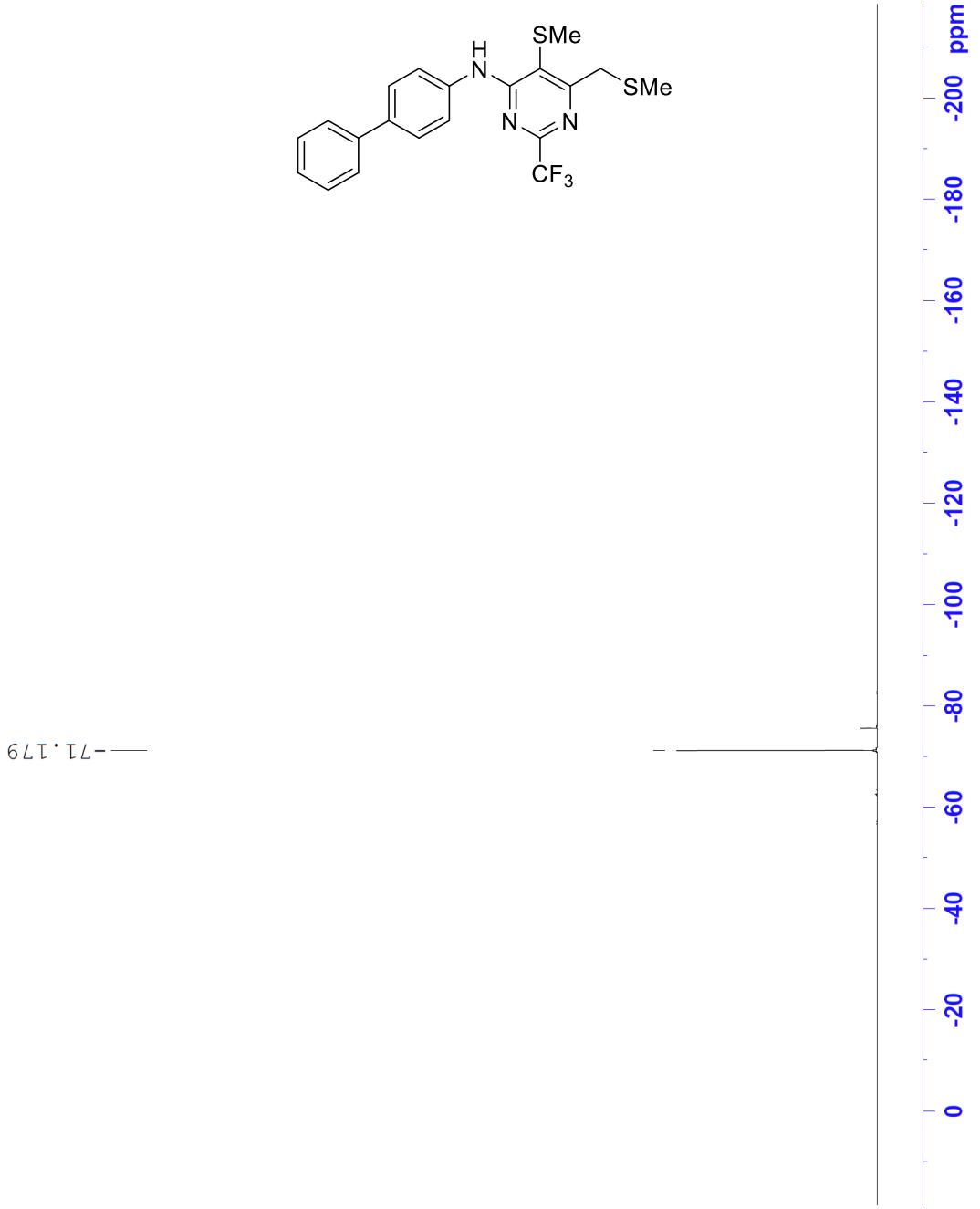
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-(methylthio)-6-((methylthio)methyl)-2-(trifluoromethyl)pyrimidin-4-amine (3e)



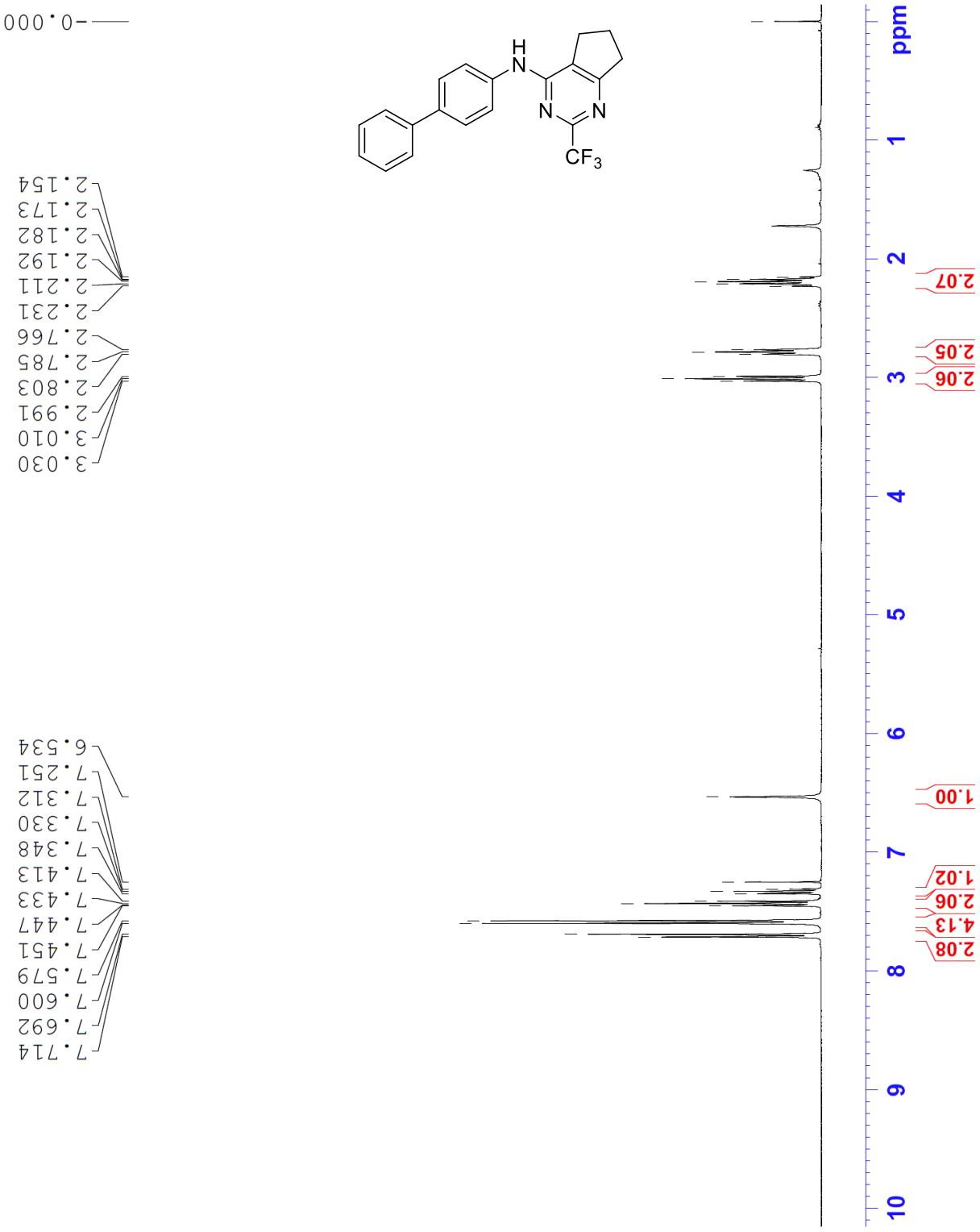
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-(methylthio)-6-((methylthio)methyl)-2-(trifluoromethyl)pyrimidin-4-amine (3e)



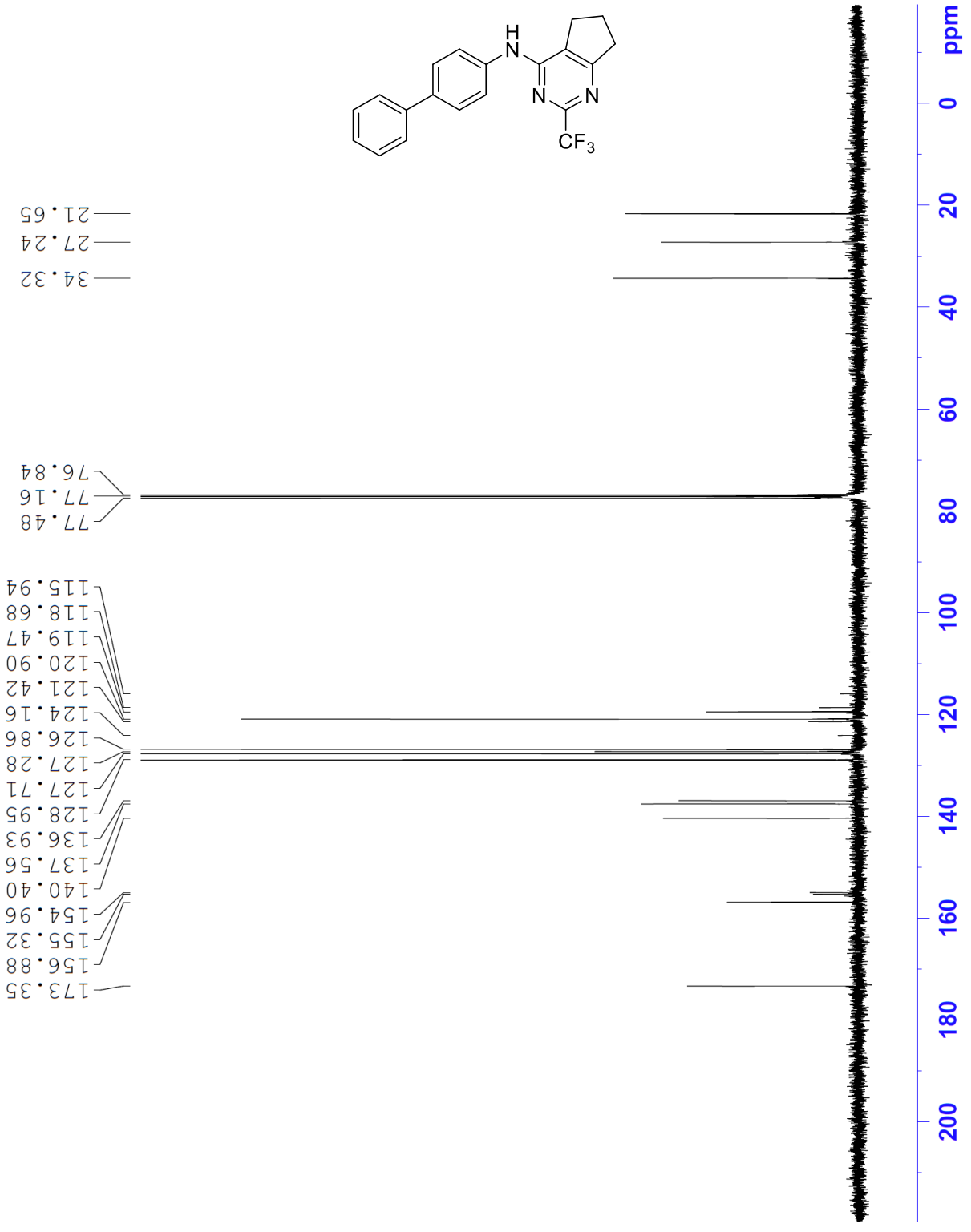
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-5-(methylthio)-6-((methylthio)methyl)-2-(trifluoromethyl)pyrimidin-4-amine (3e)



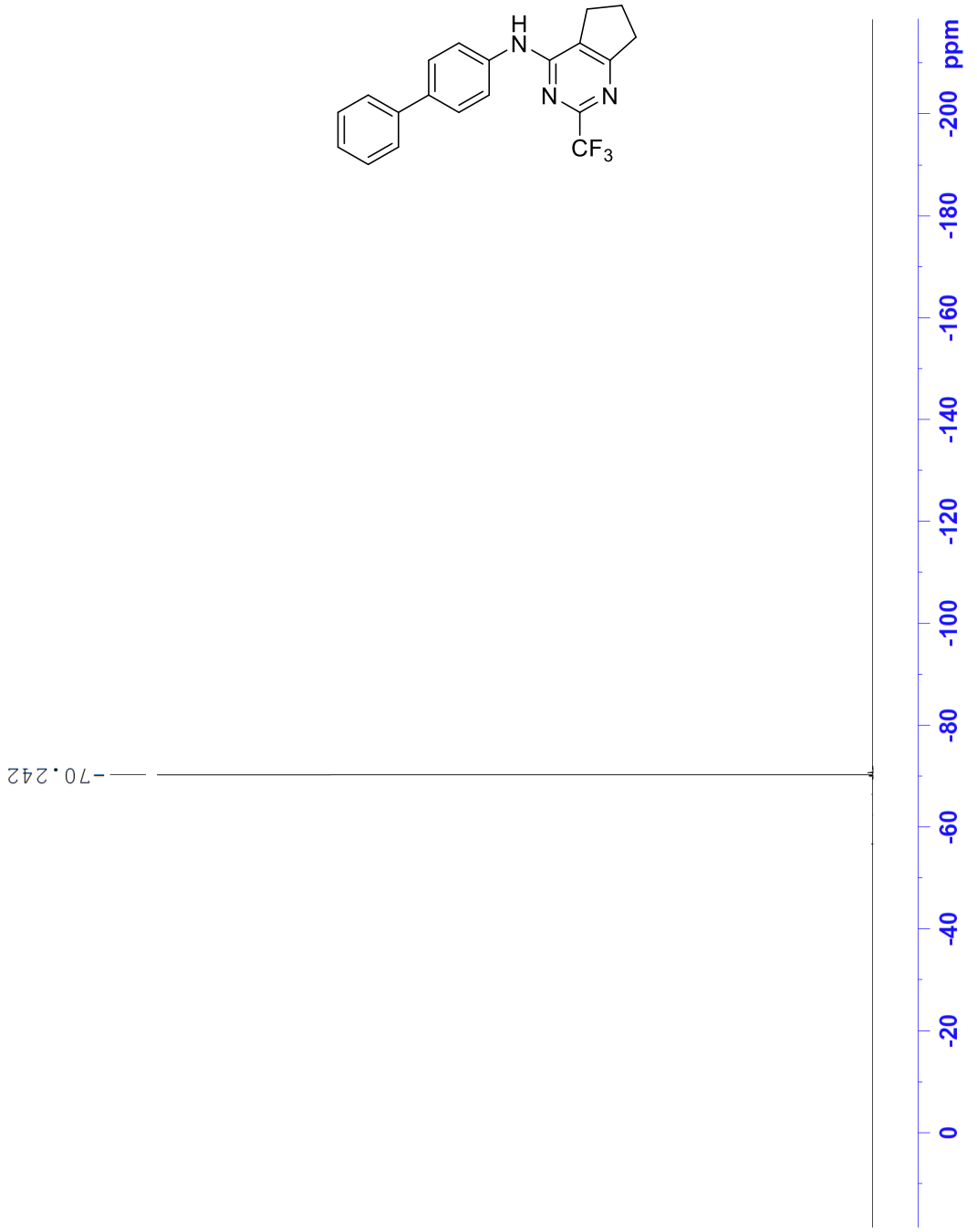
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidin-4-amine (3f)



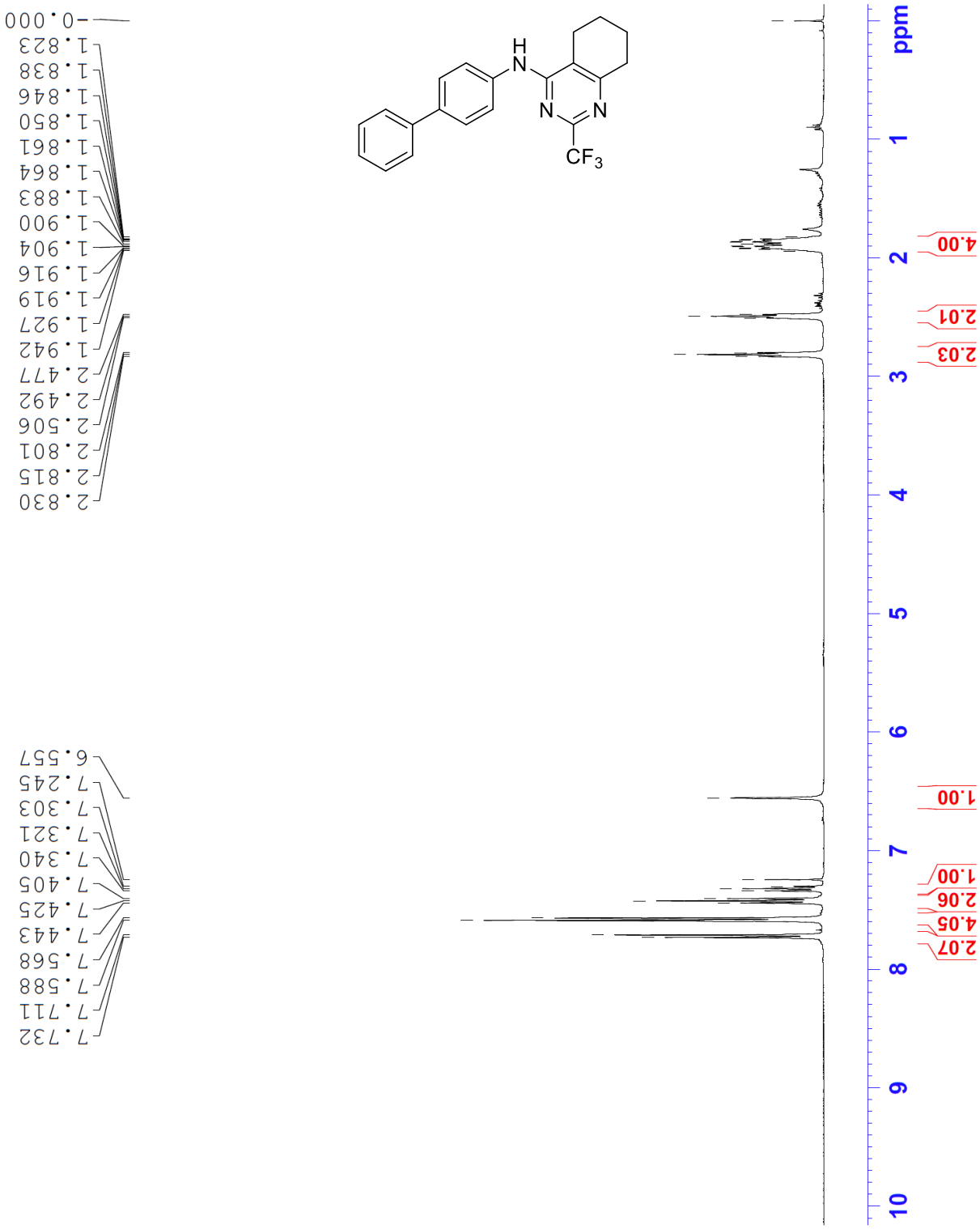
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidin-4-amine (3f)



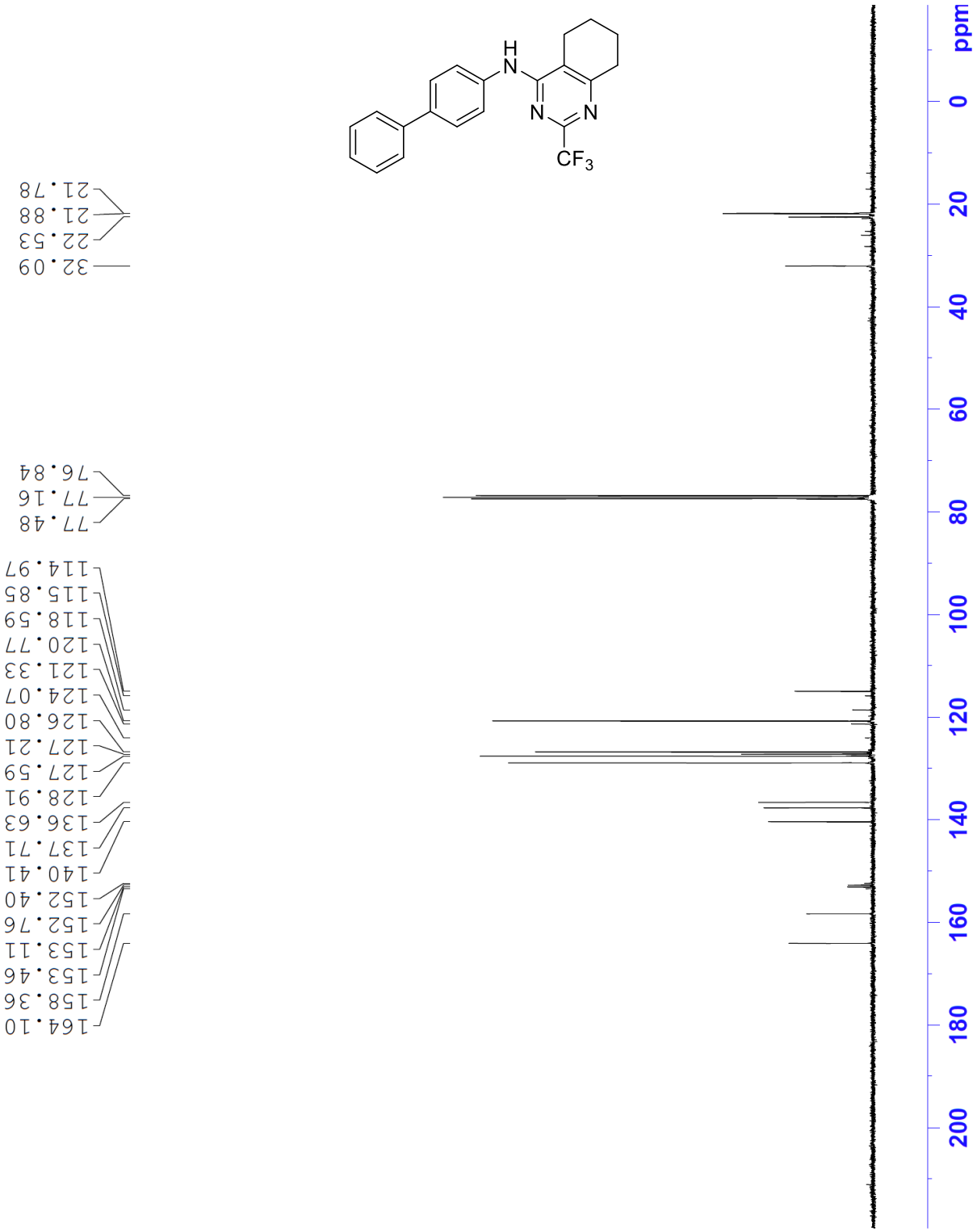
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidin-4-amine (3f)



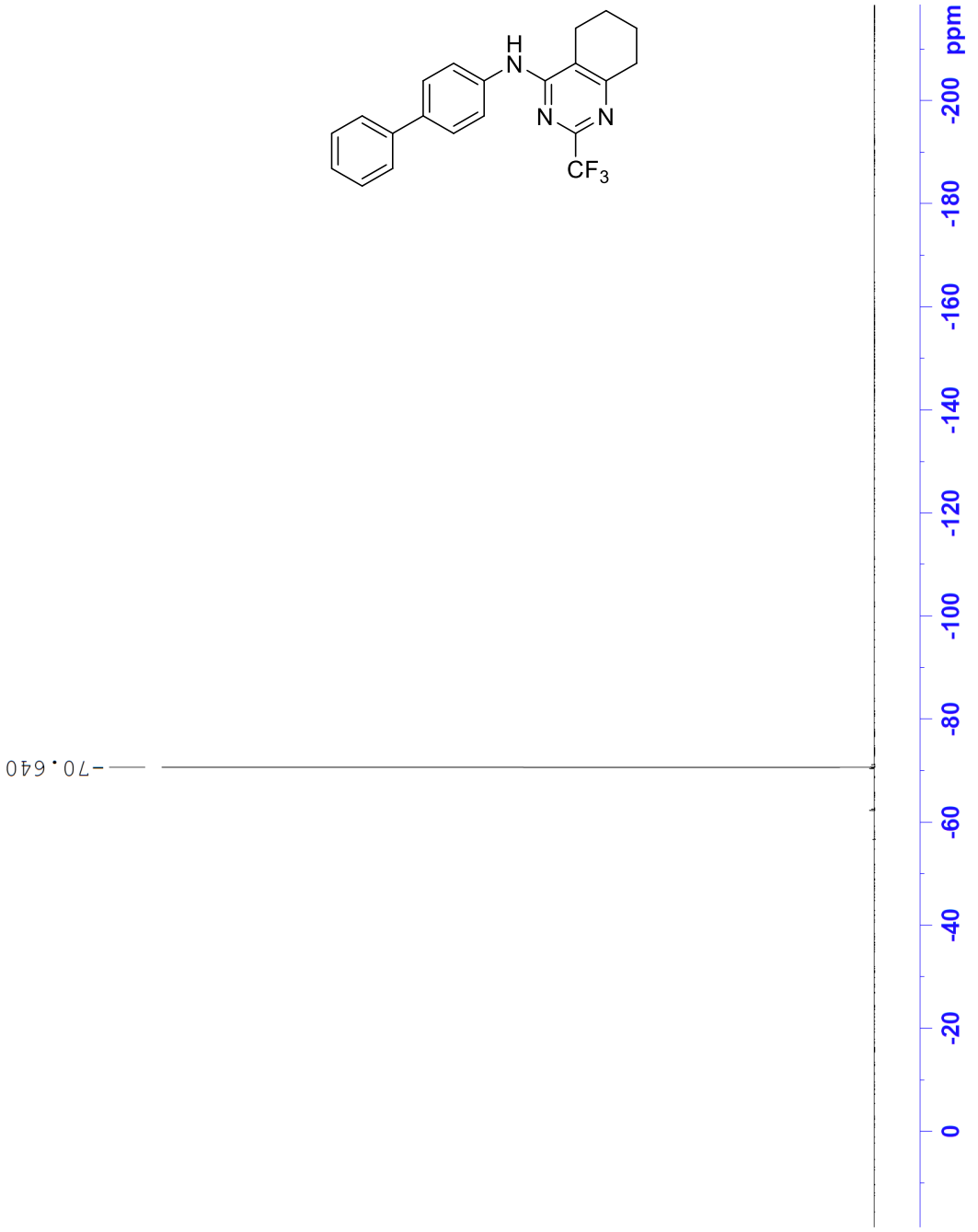
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-5,6,7,8-tetrahydroquinazolin-4-amine (3g)



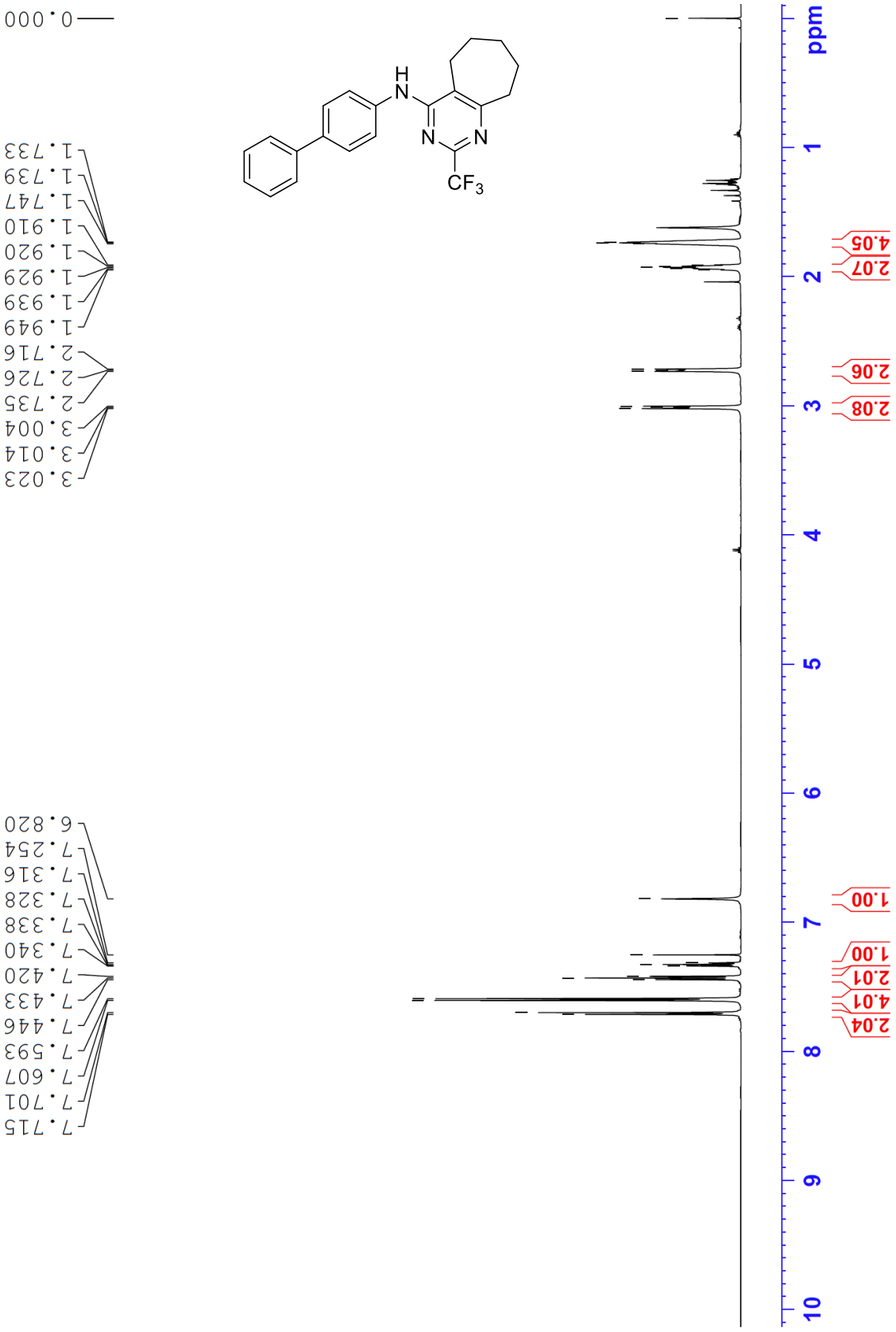
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-5,6,7,8-tetrahydroquinazolin-4-amine (3g)



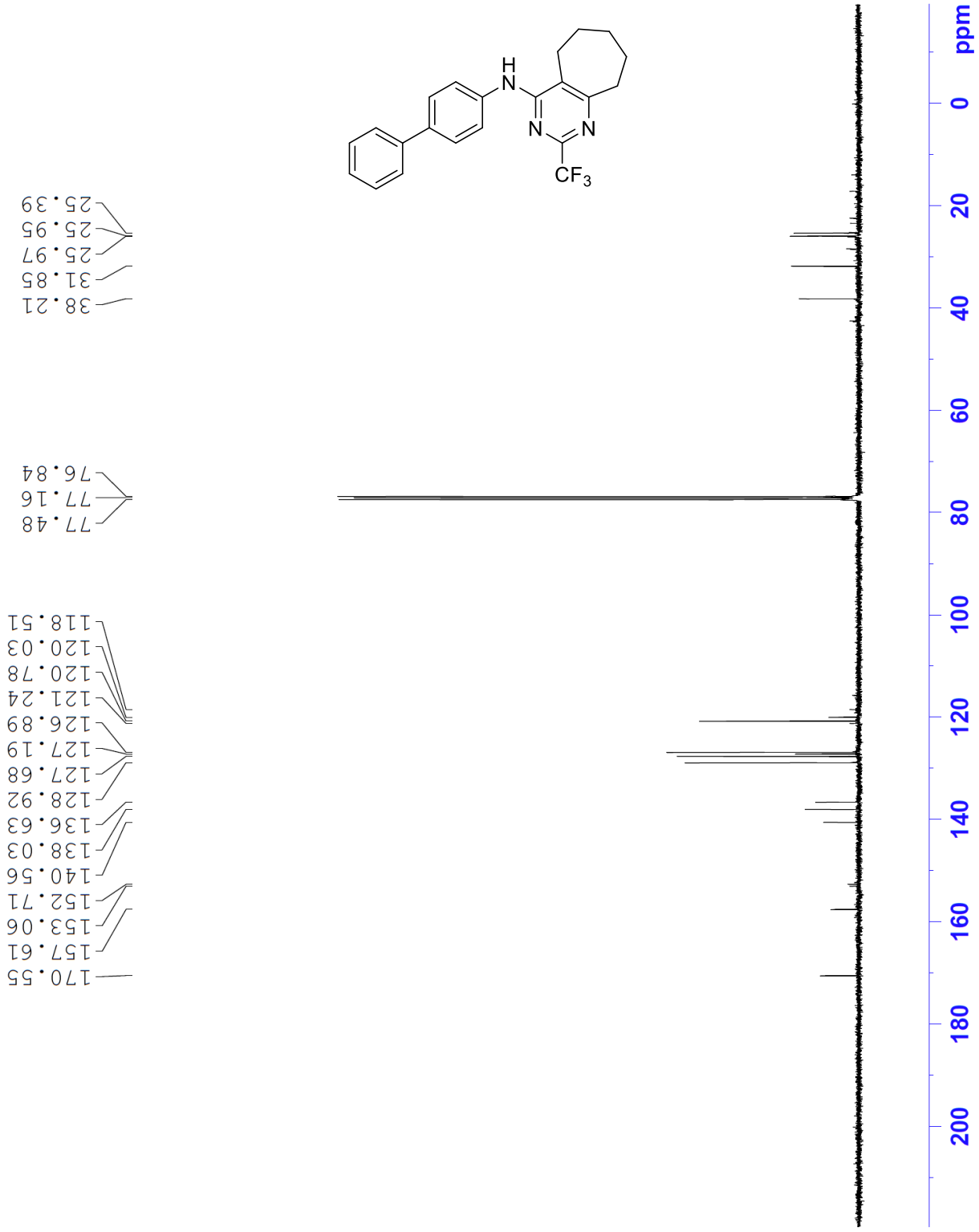
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-5,6,7,8-tetrahydroquinazolin-4-amine (3g)



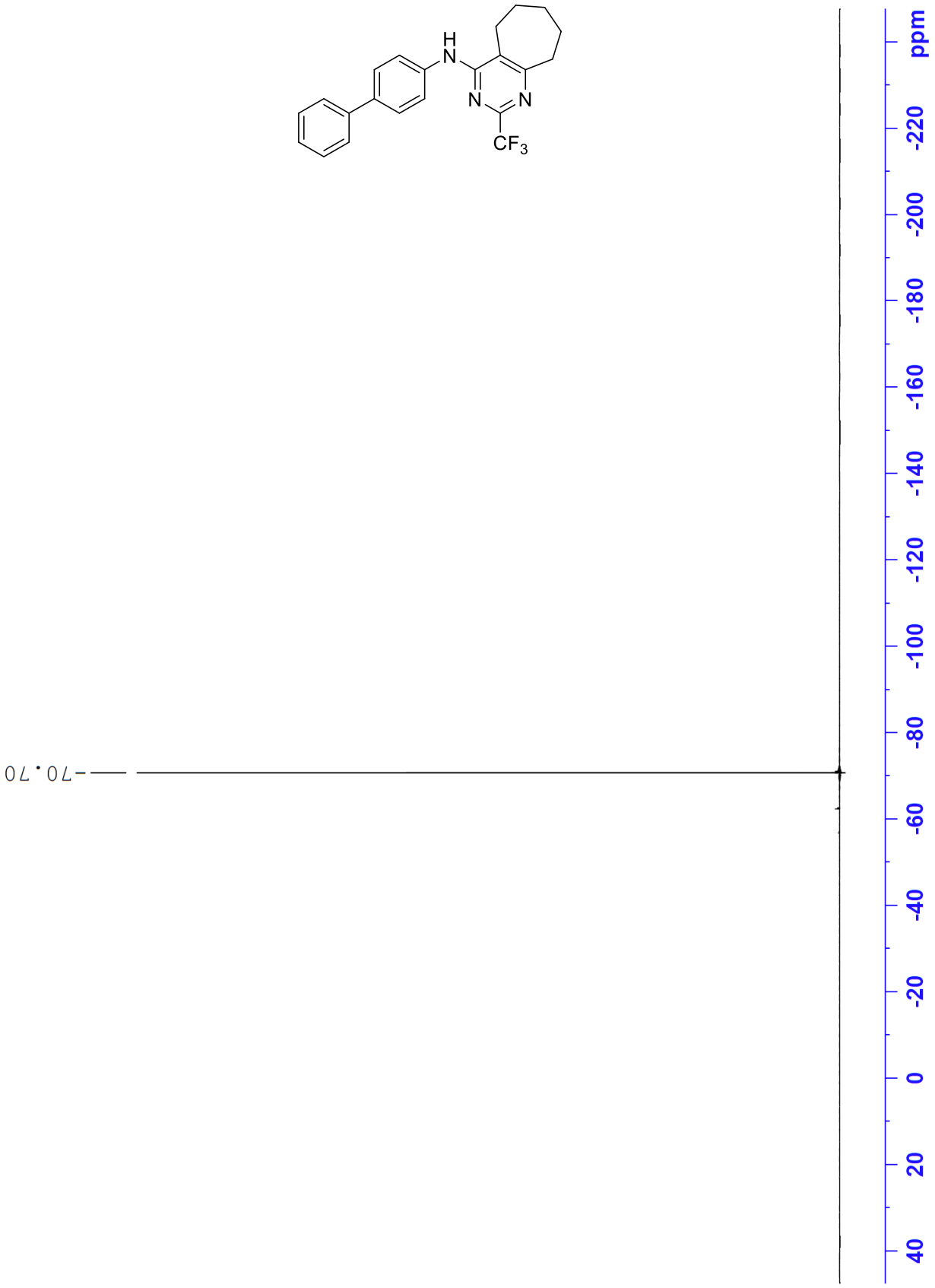
^{1}H NMR (600 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrimidin-4-amine (3h)



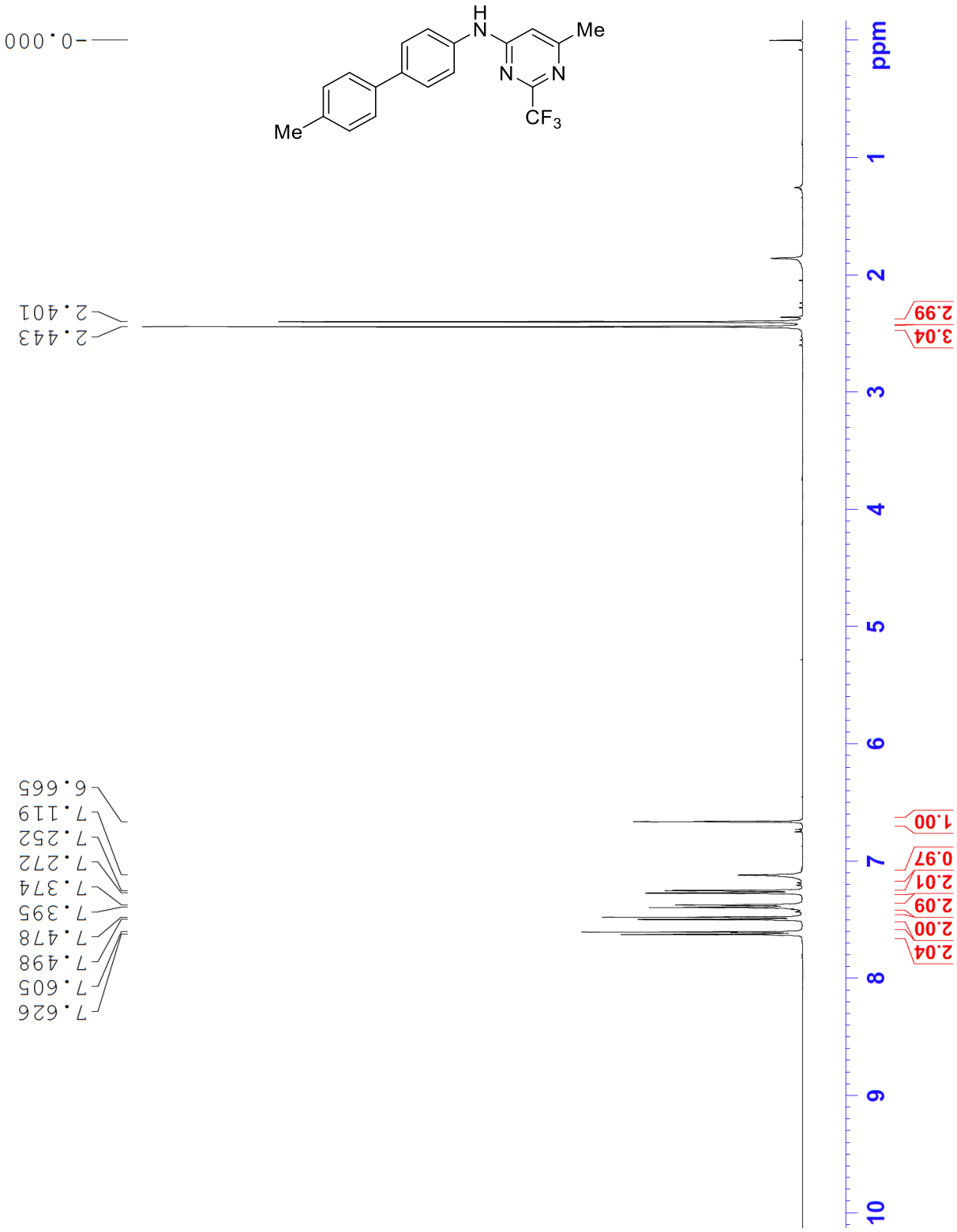
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrimidin-4-amine (3h)



^{19}F NMR (565 MHz, $CDCl_3$) of *N*-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*d*]pyrimidin-4-amine (3h)

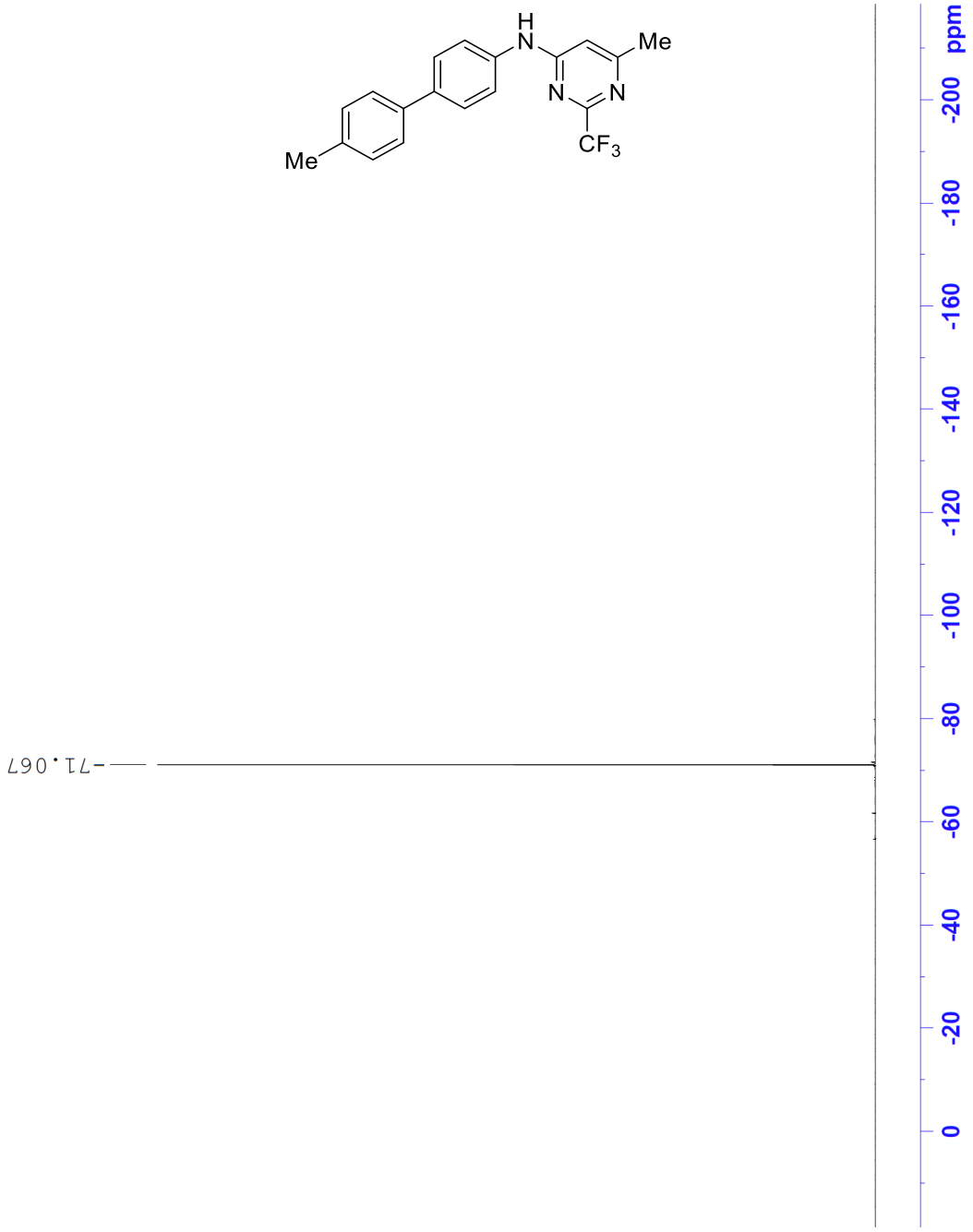


^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3i)

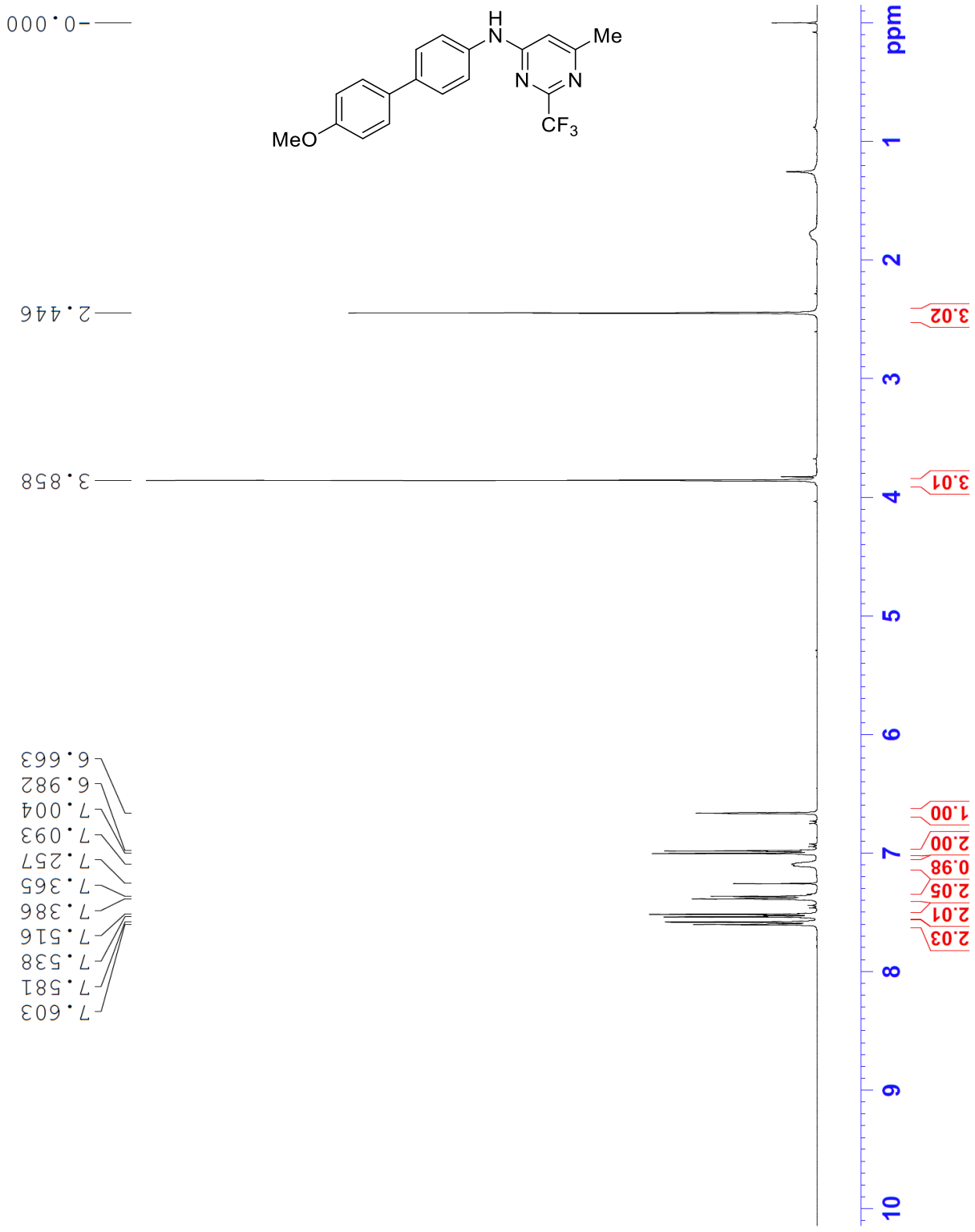


^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3i)

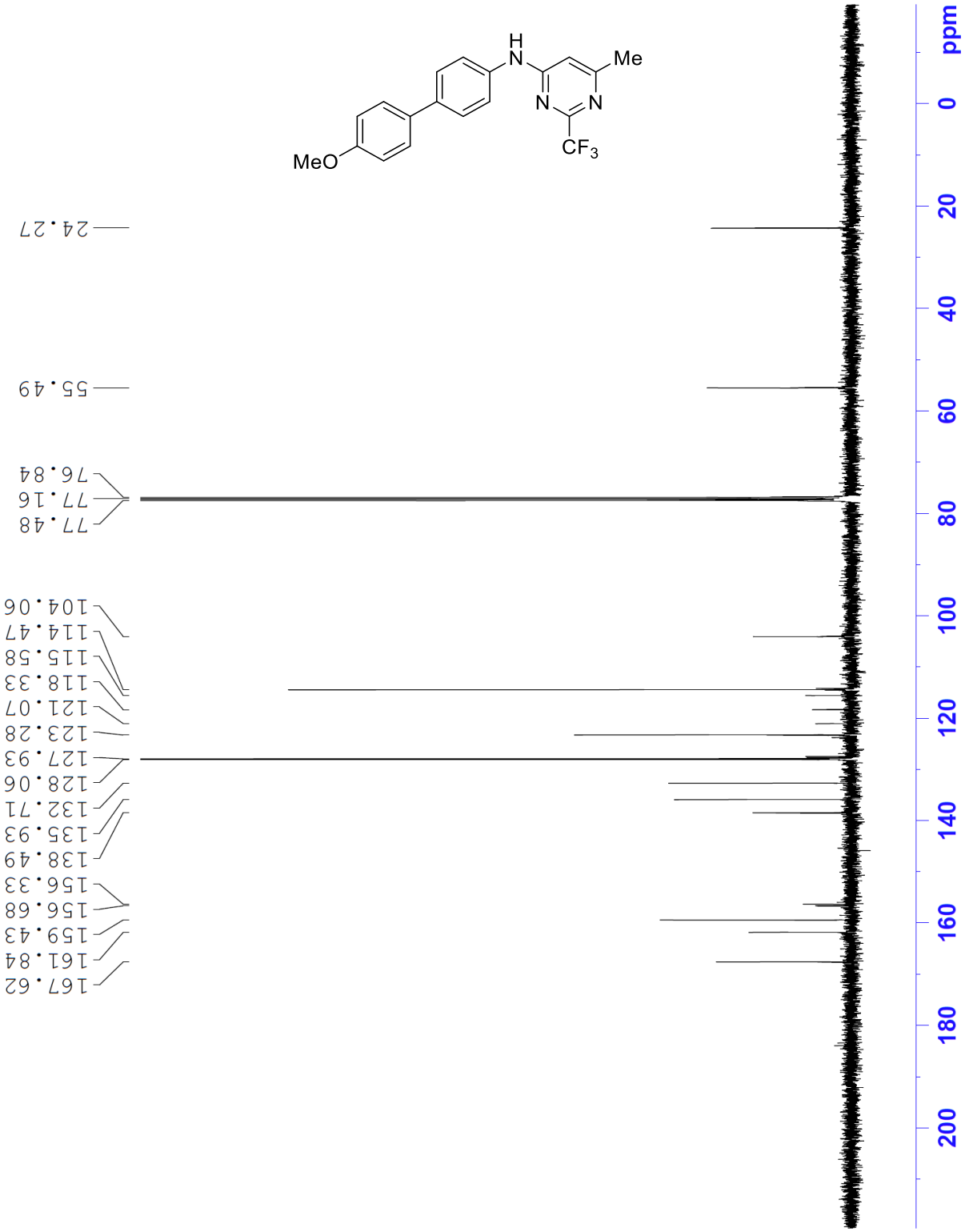
^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3i)



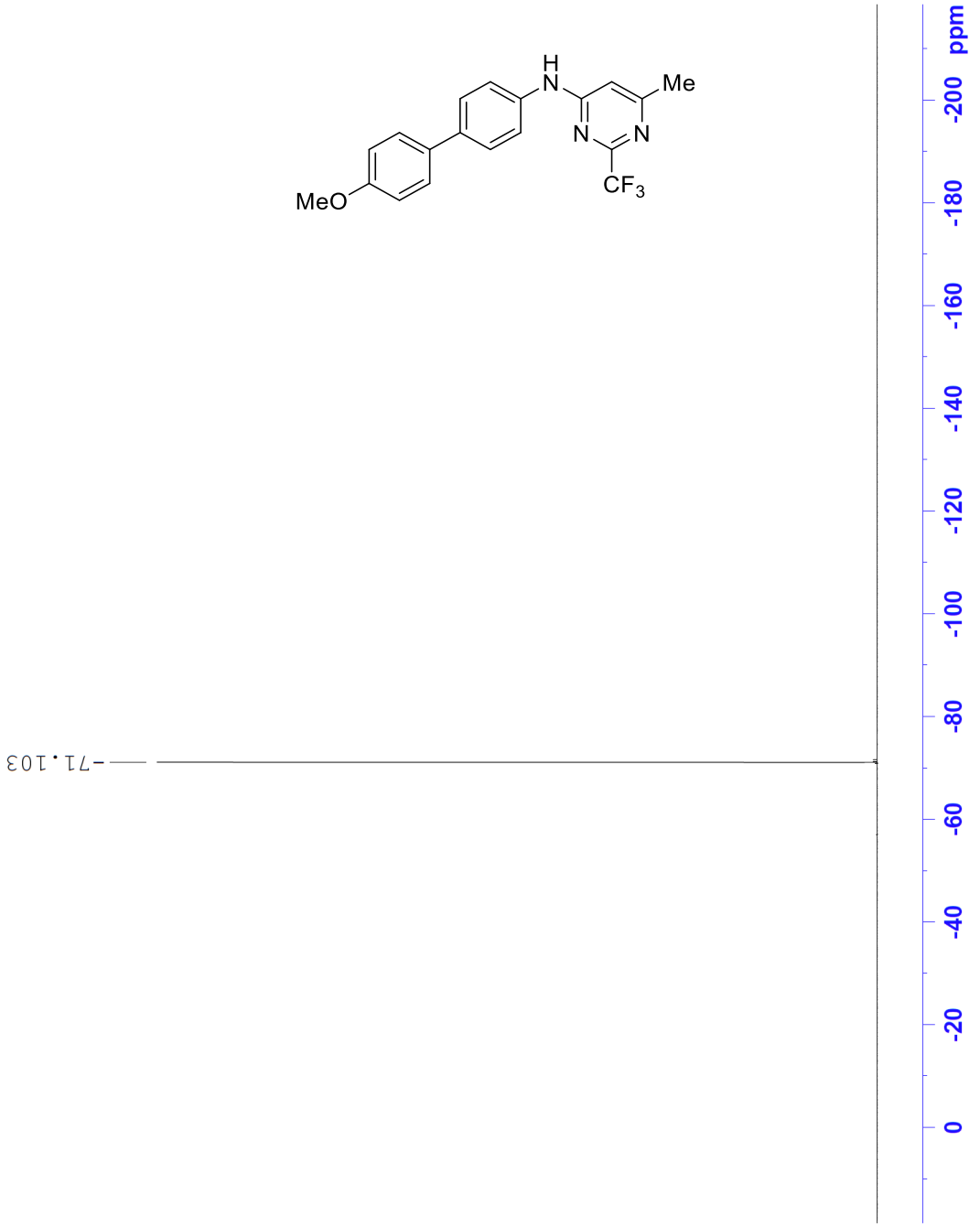
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3j)



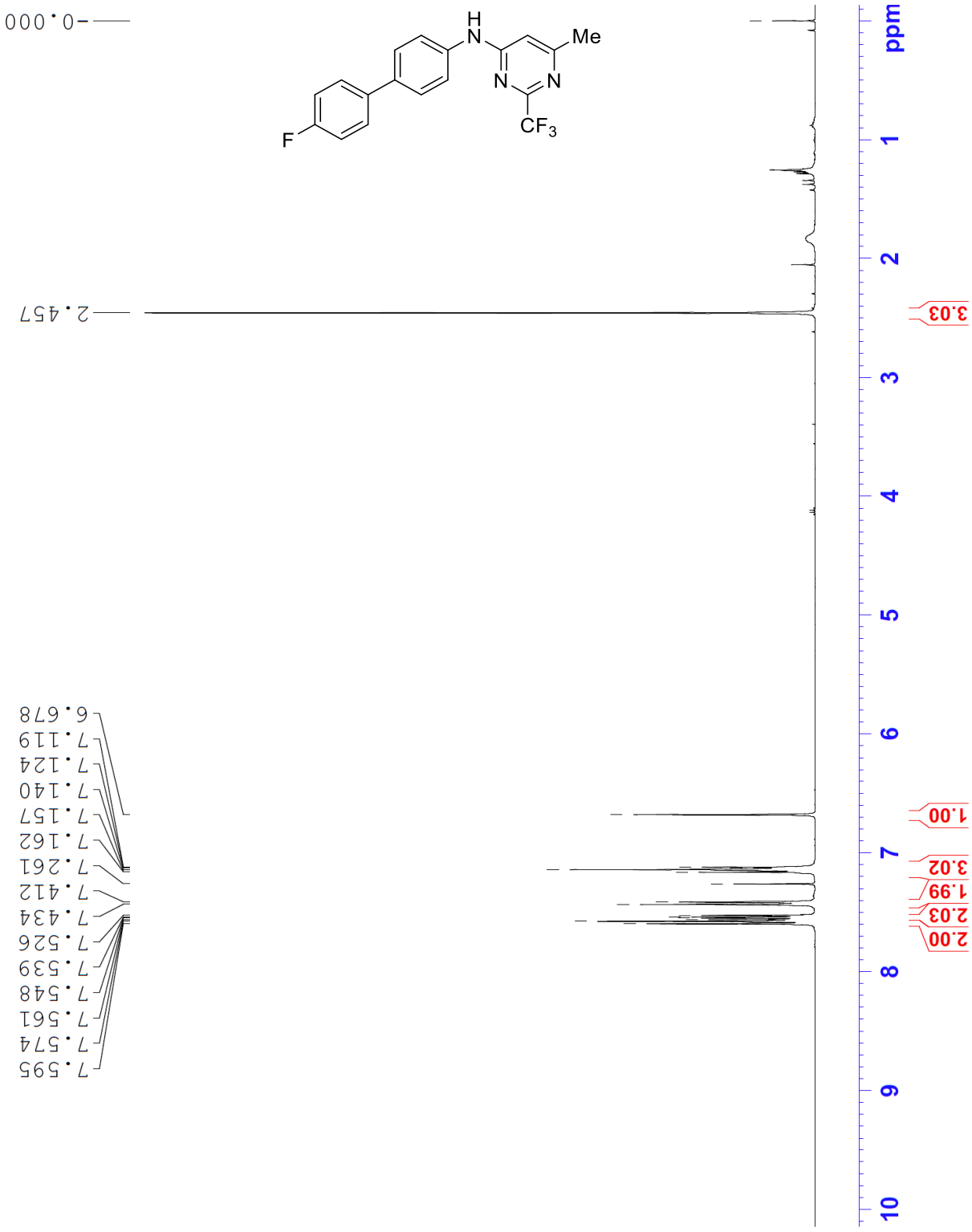
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3j)



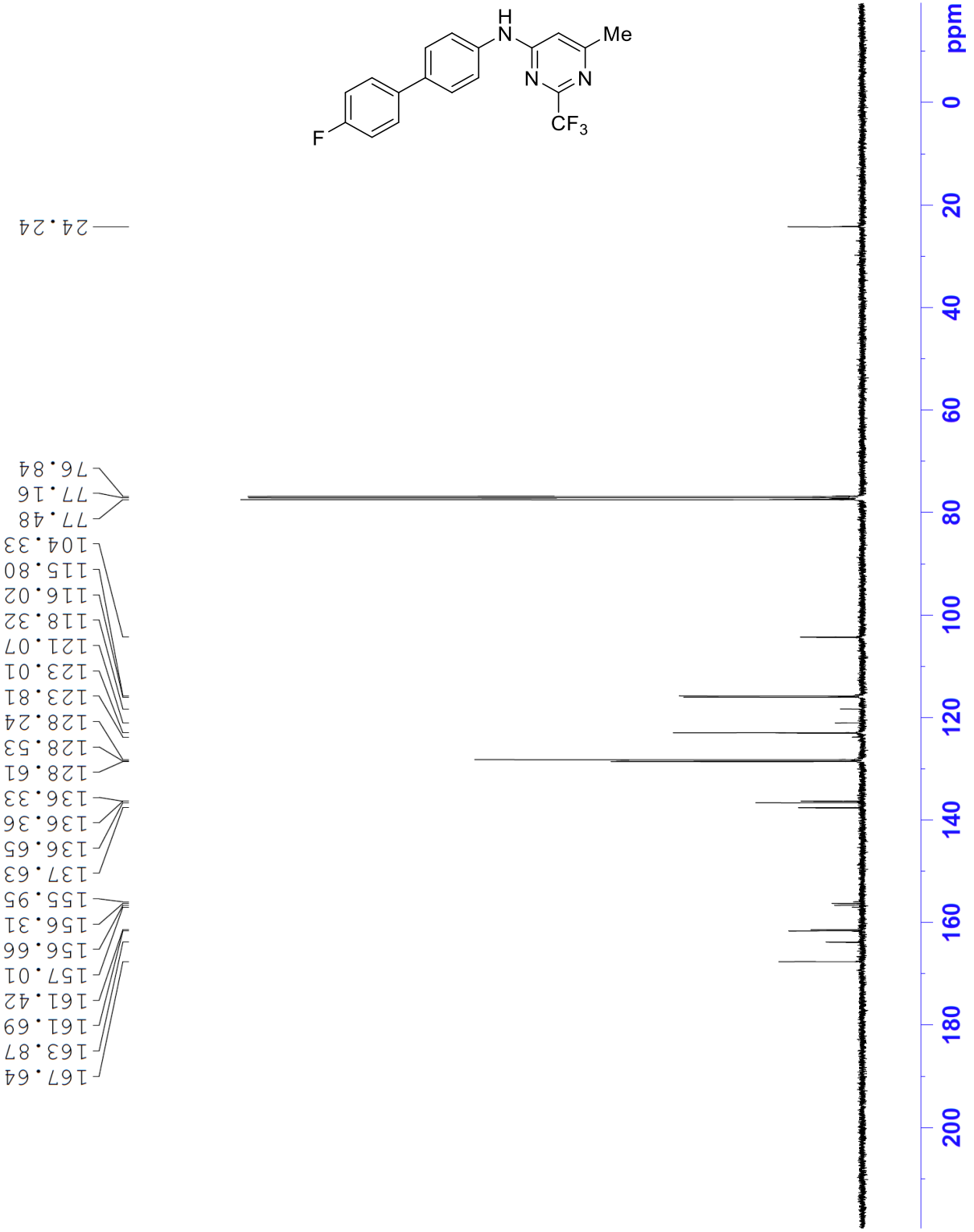
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3j)



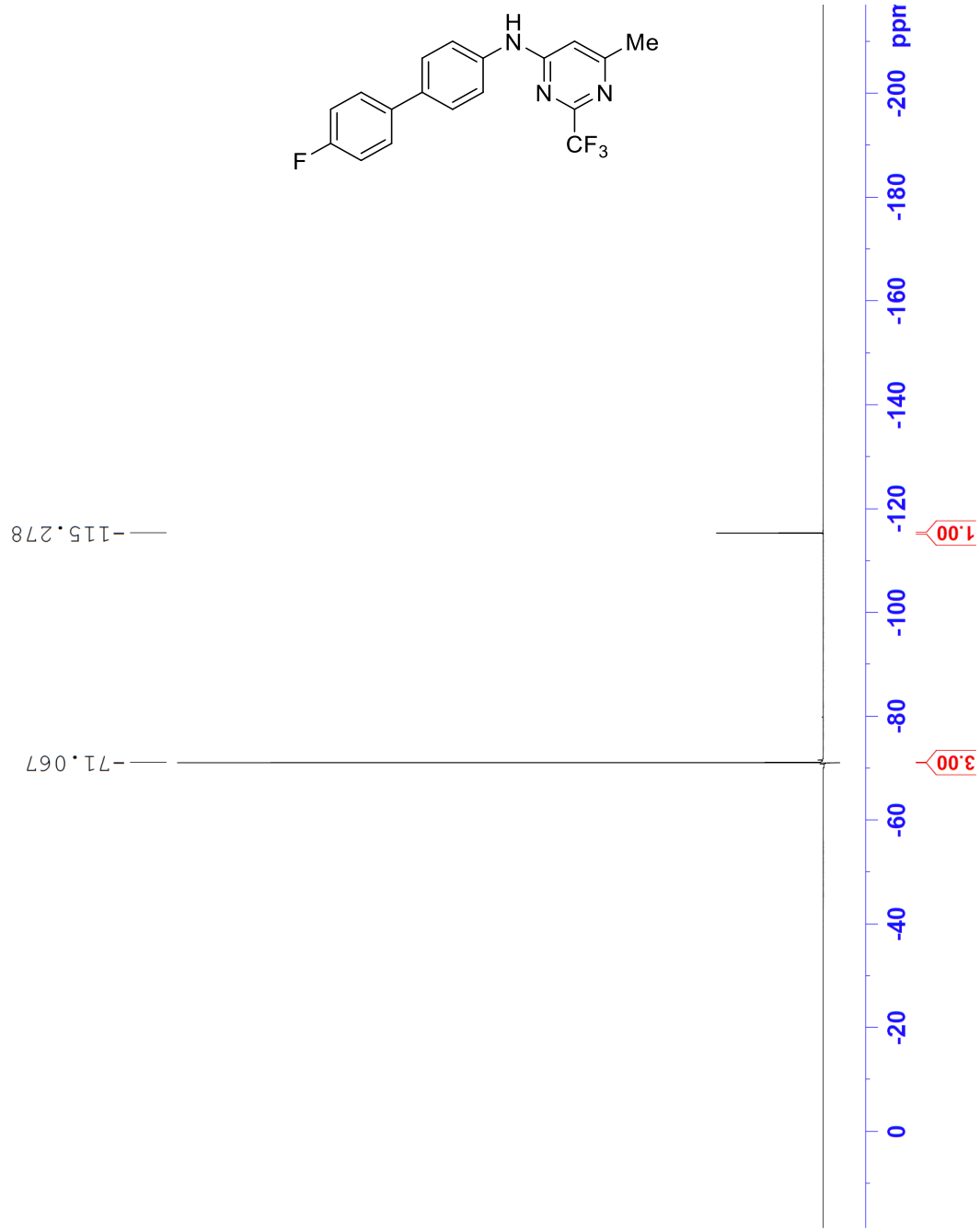
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3k)



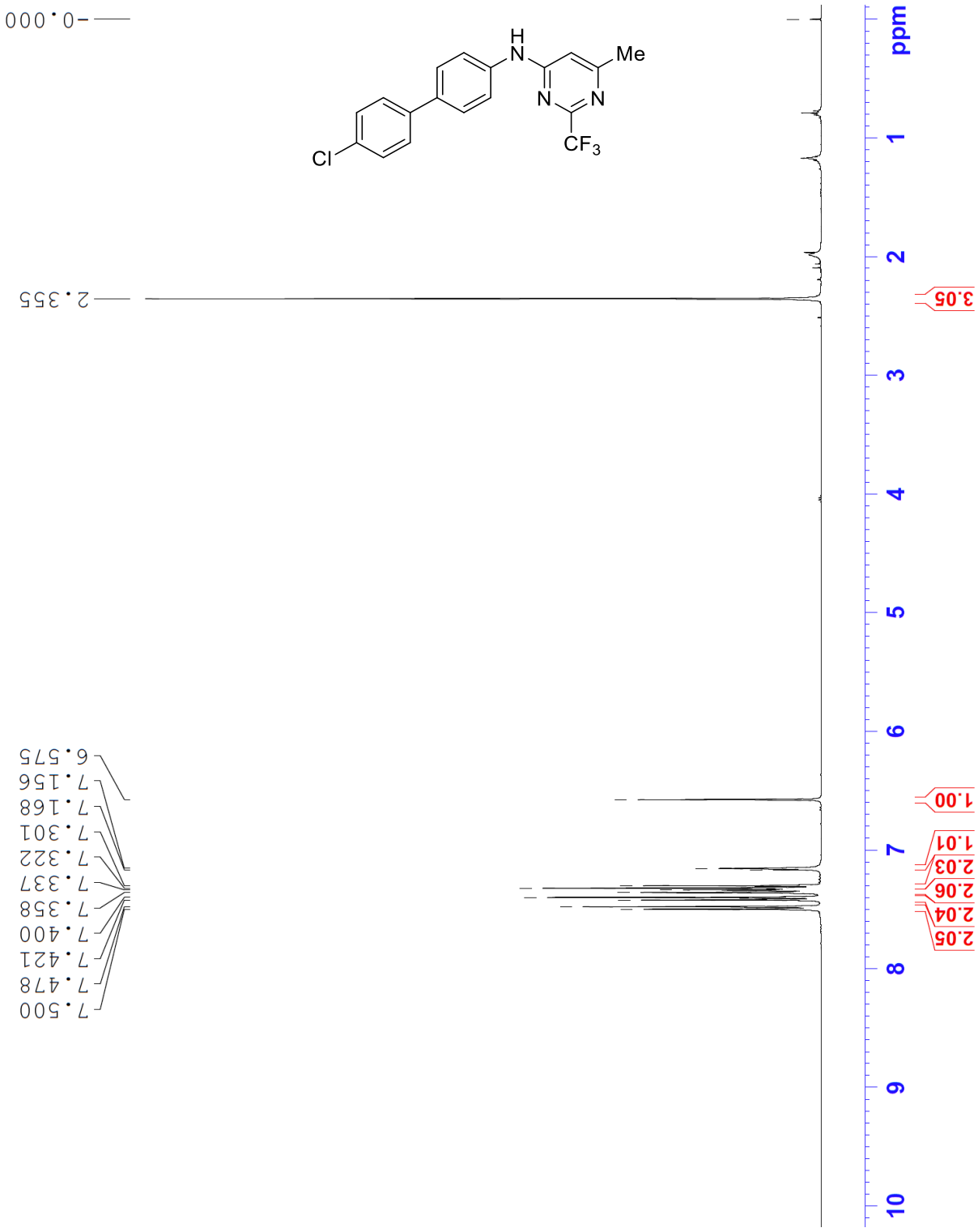
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3k)



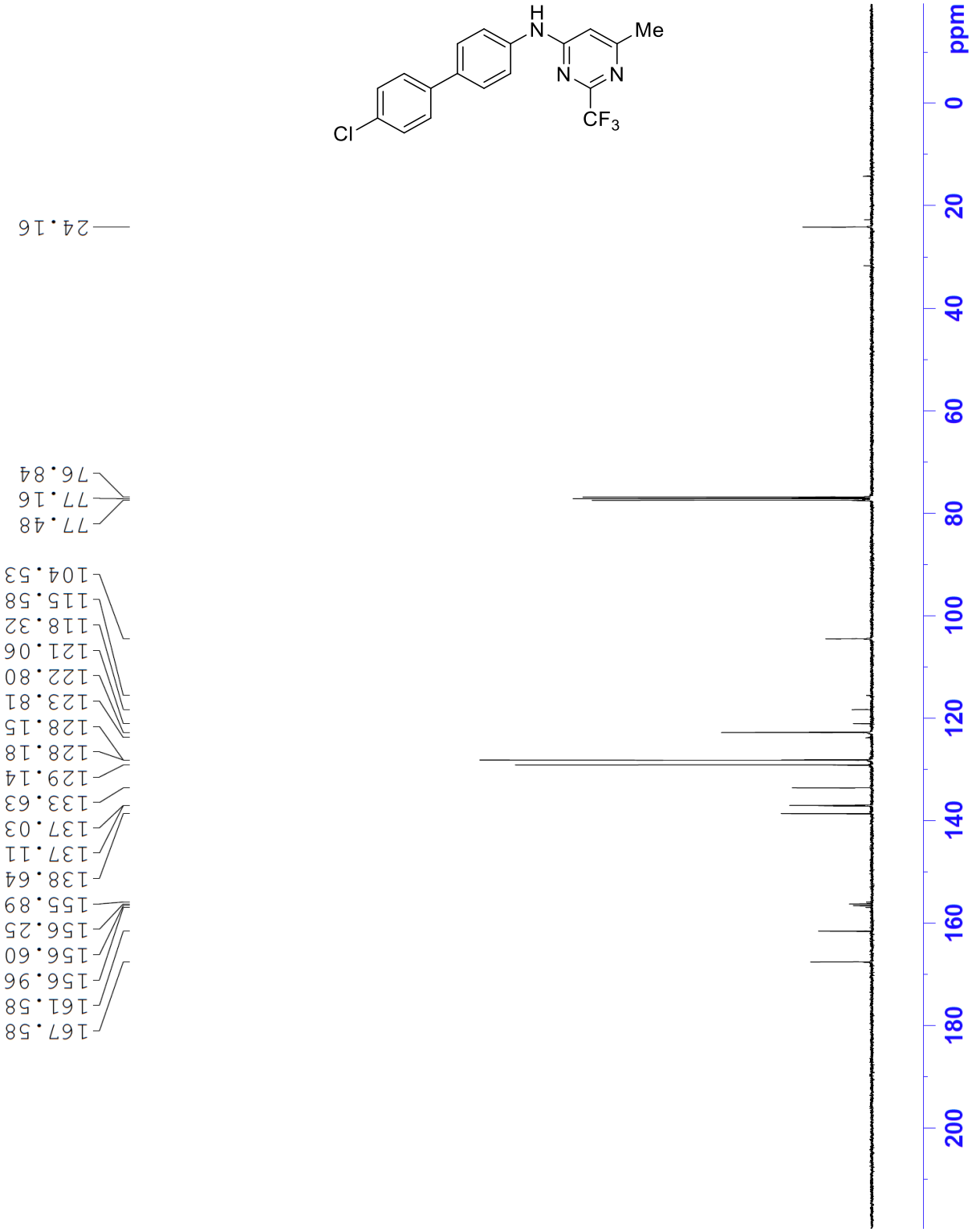
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3k)



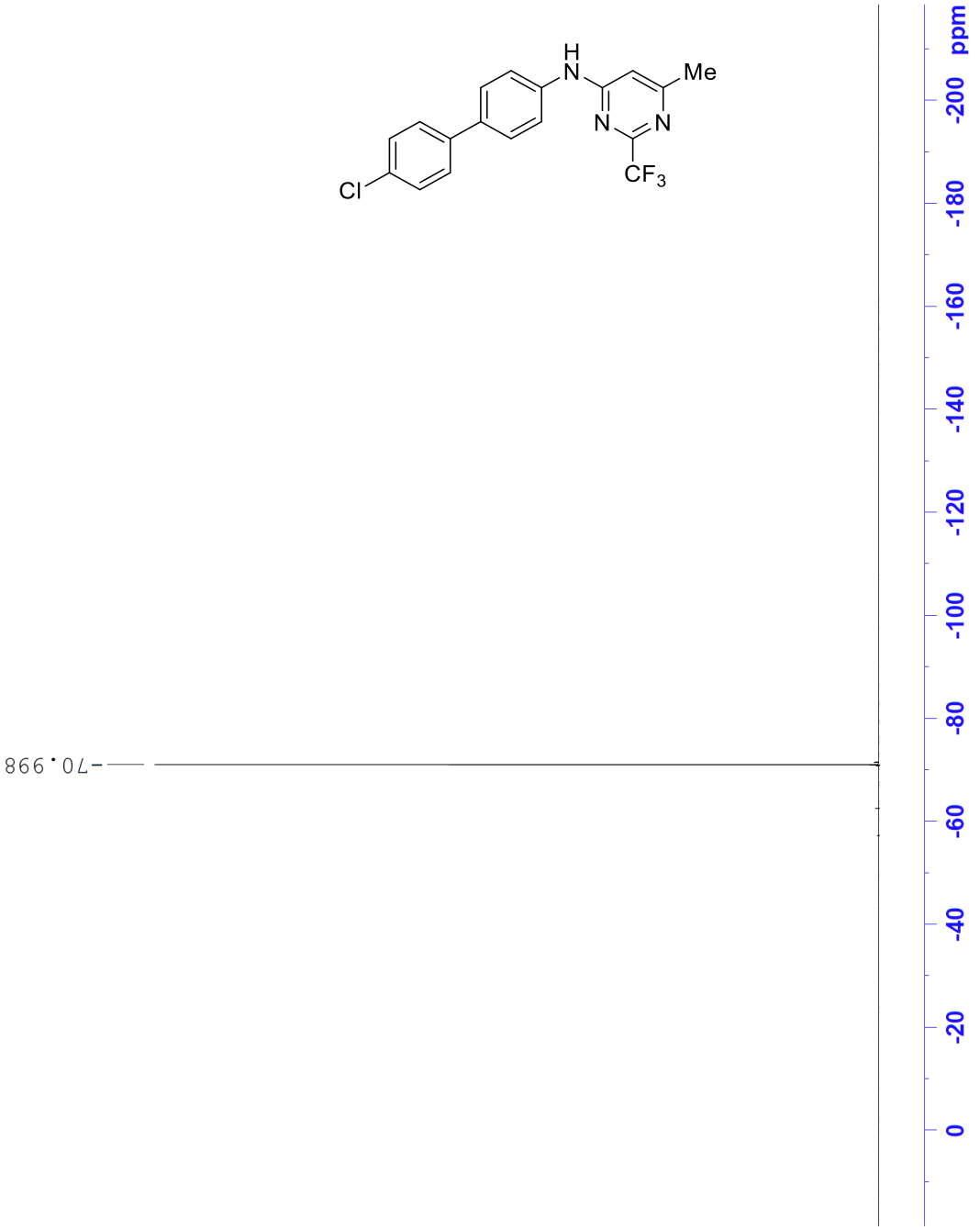
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4'-Chloro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3l)



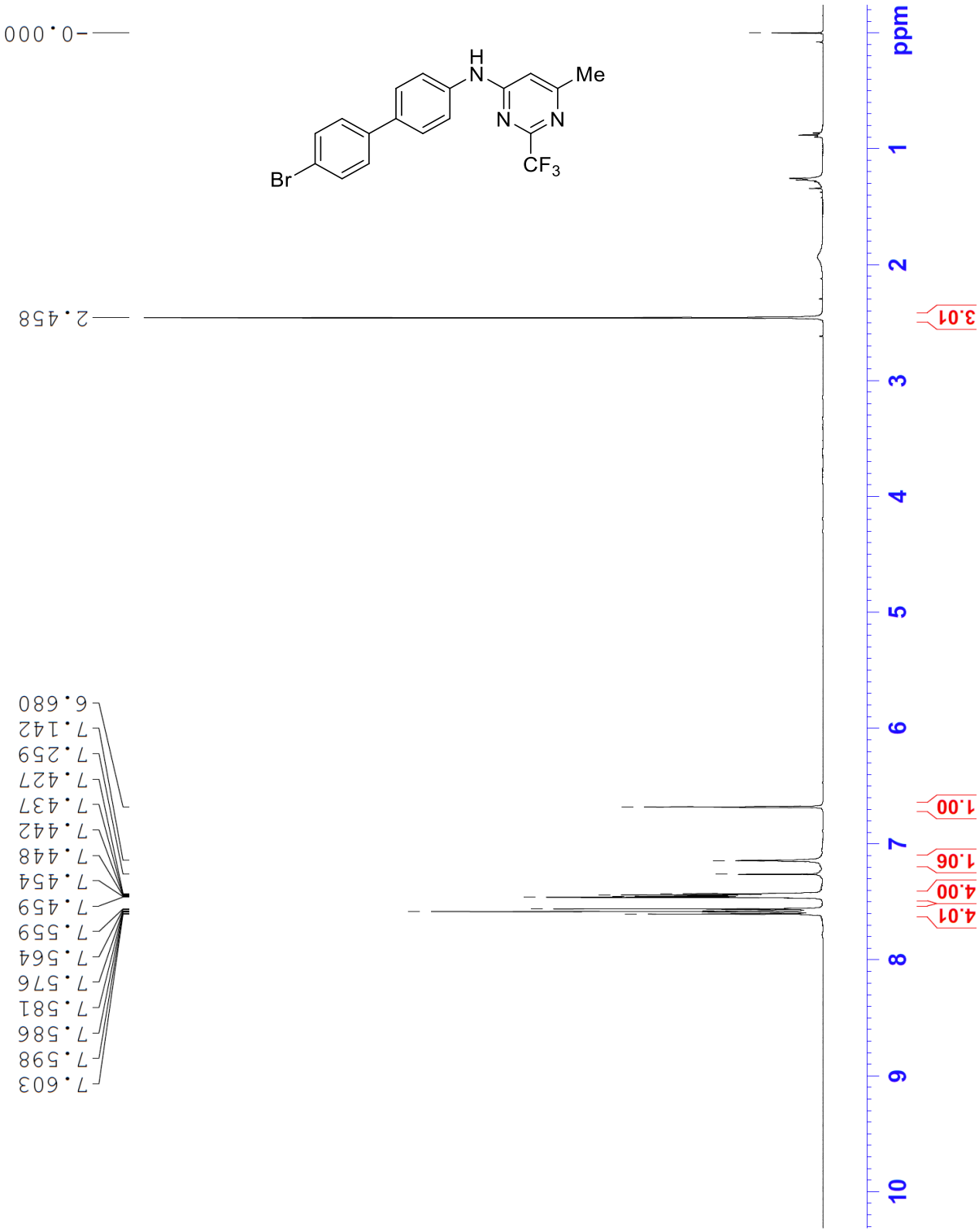
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4'-Chloro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3l)



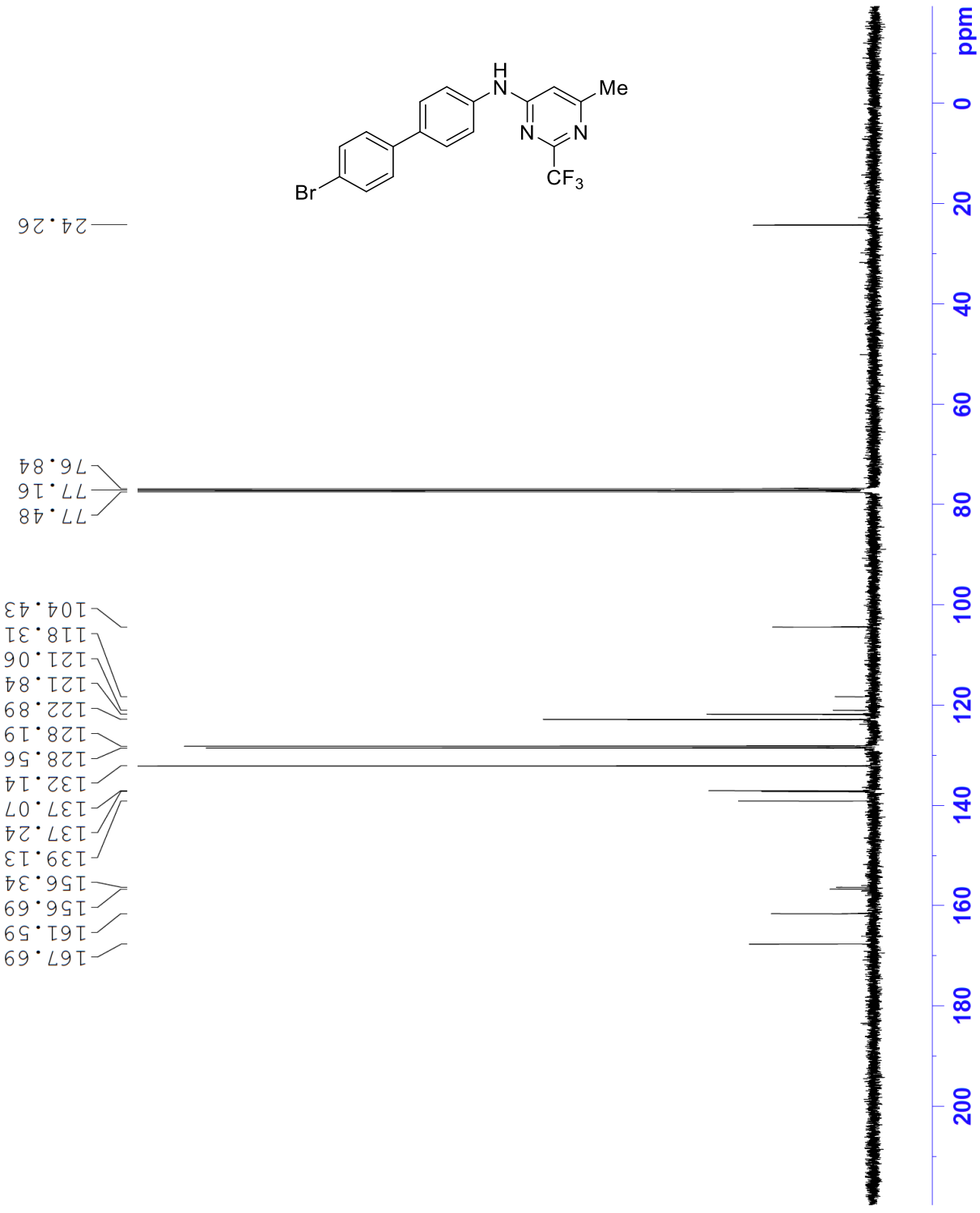
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4'-Chloro-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3l)



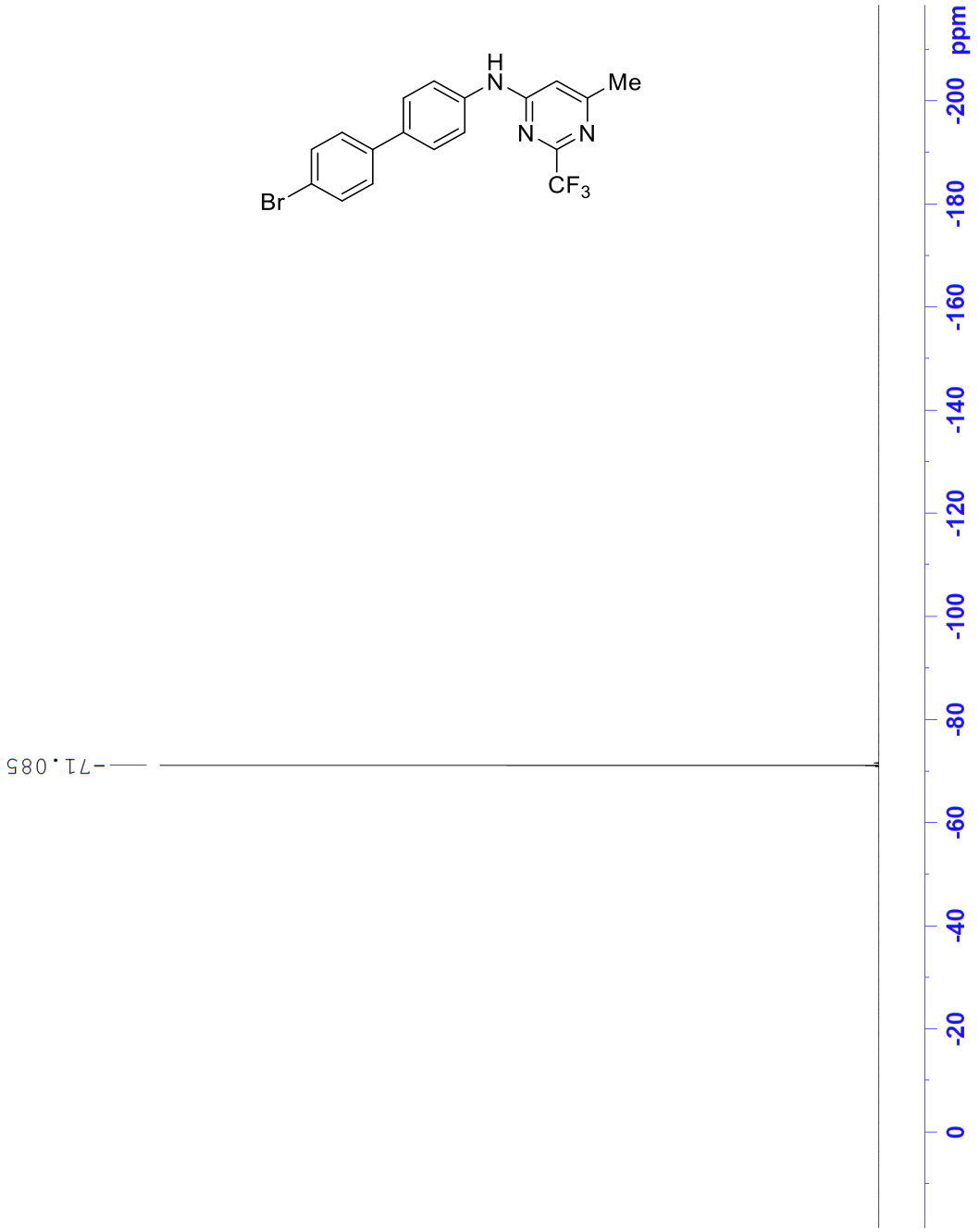
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4'-Bromo-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3m)



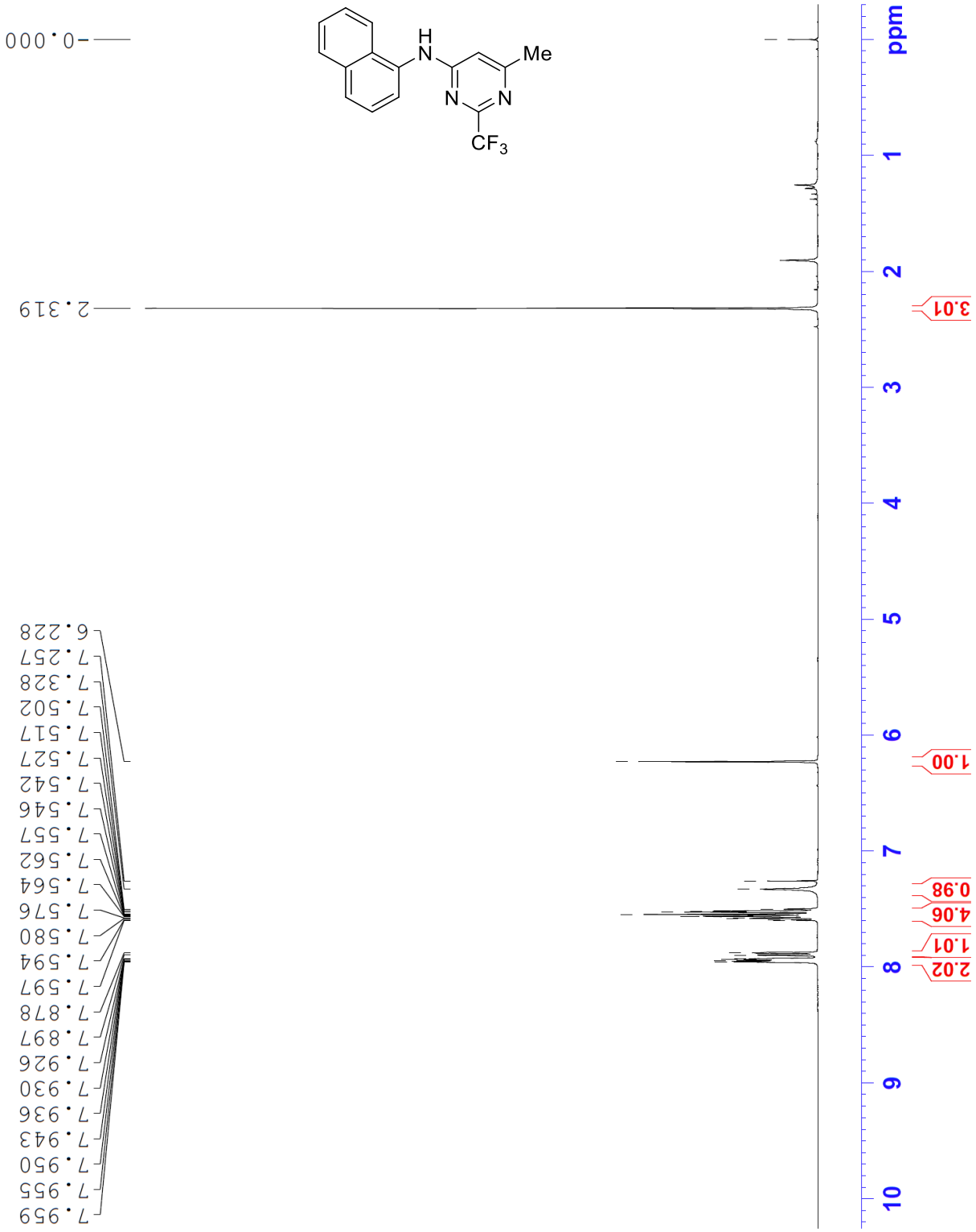
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4'-Bromo-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3m)



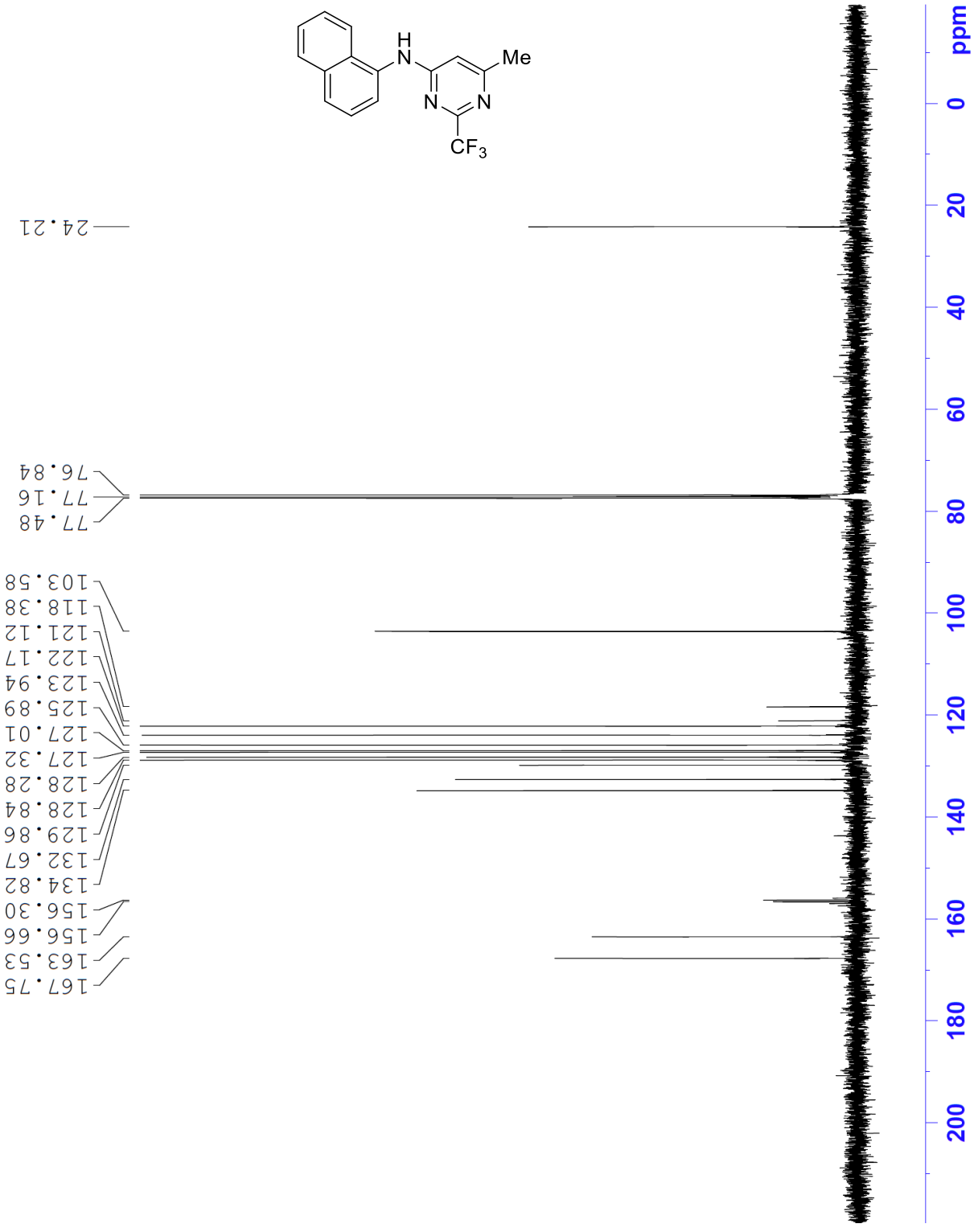
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4'-Bromo-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3m)



^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-1-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3n)

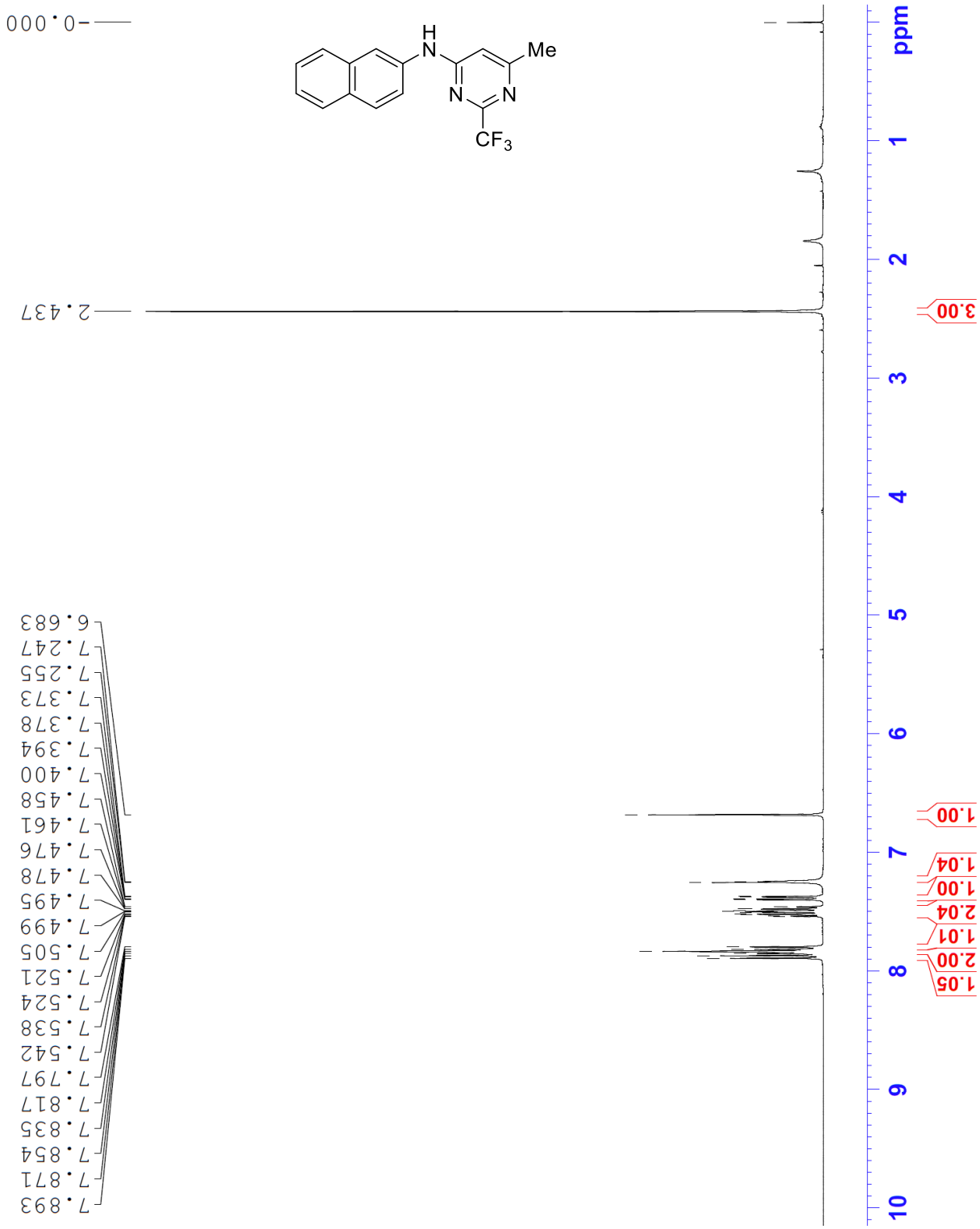


^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-1-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3n)

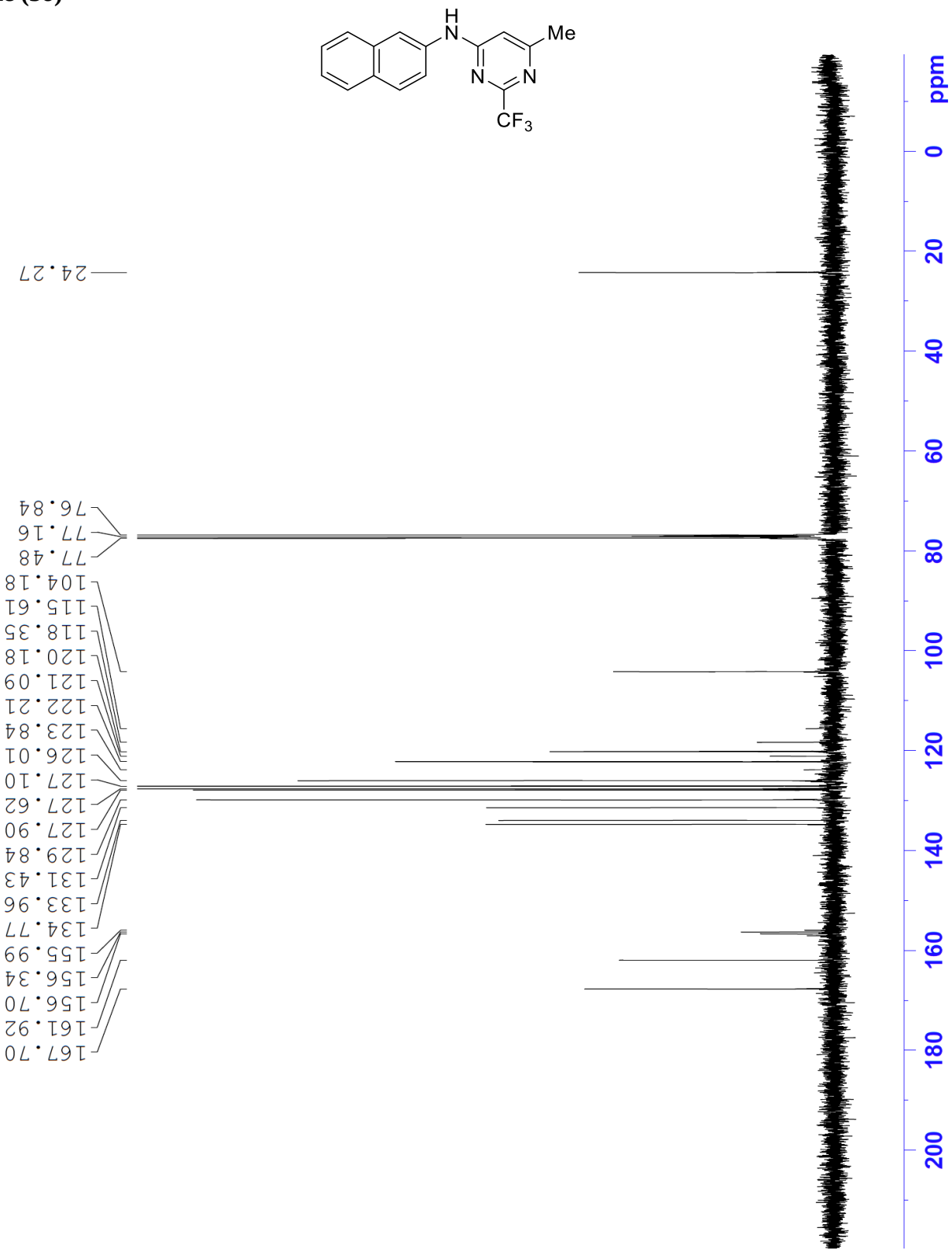


^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-1-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3n)

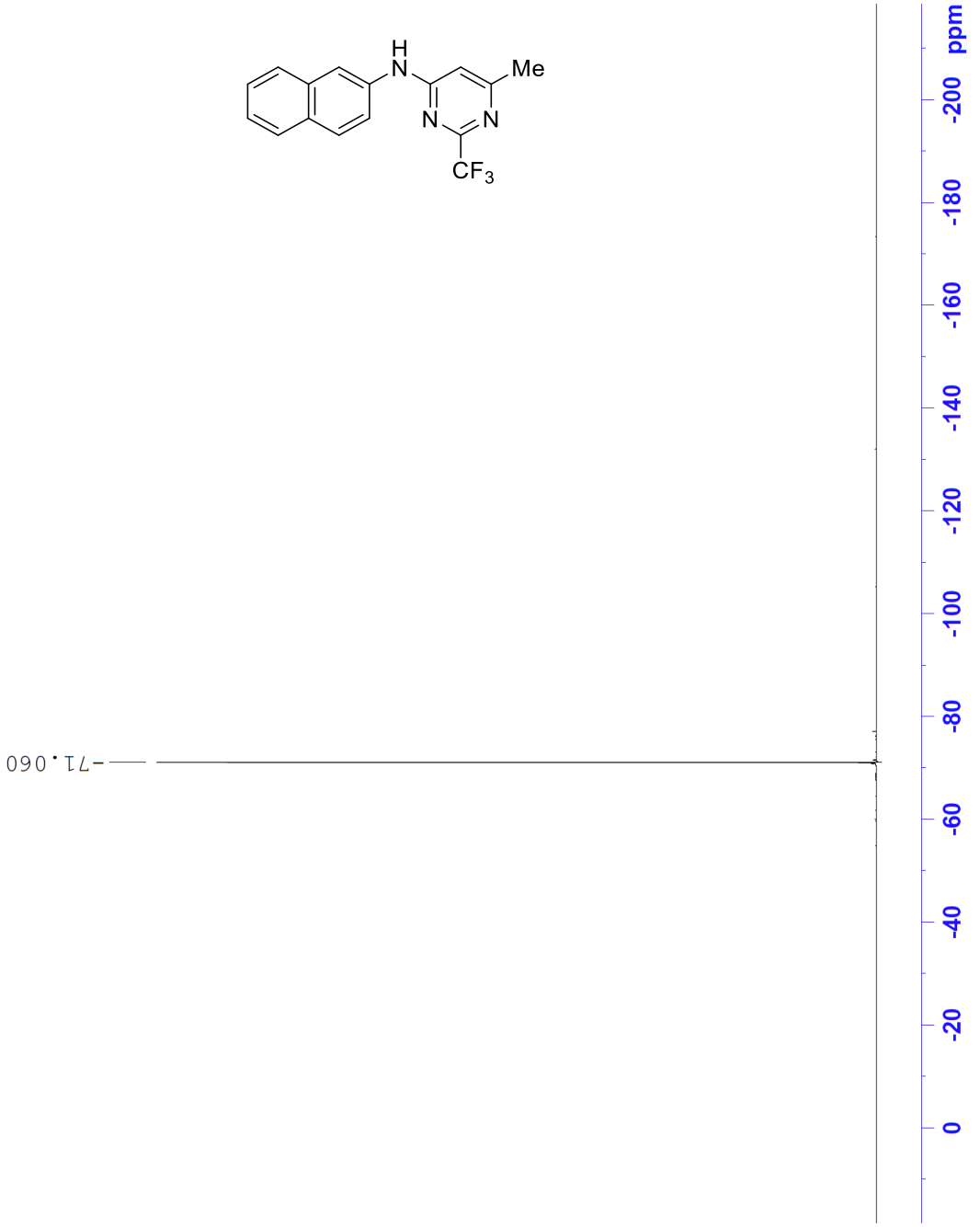
^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-2-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3o)



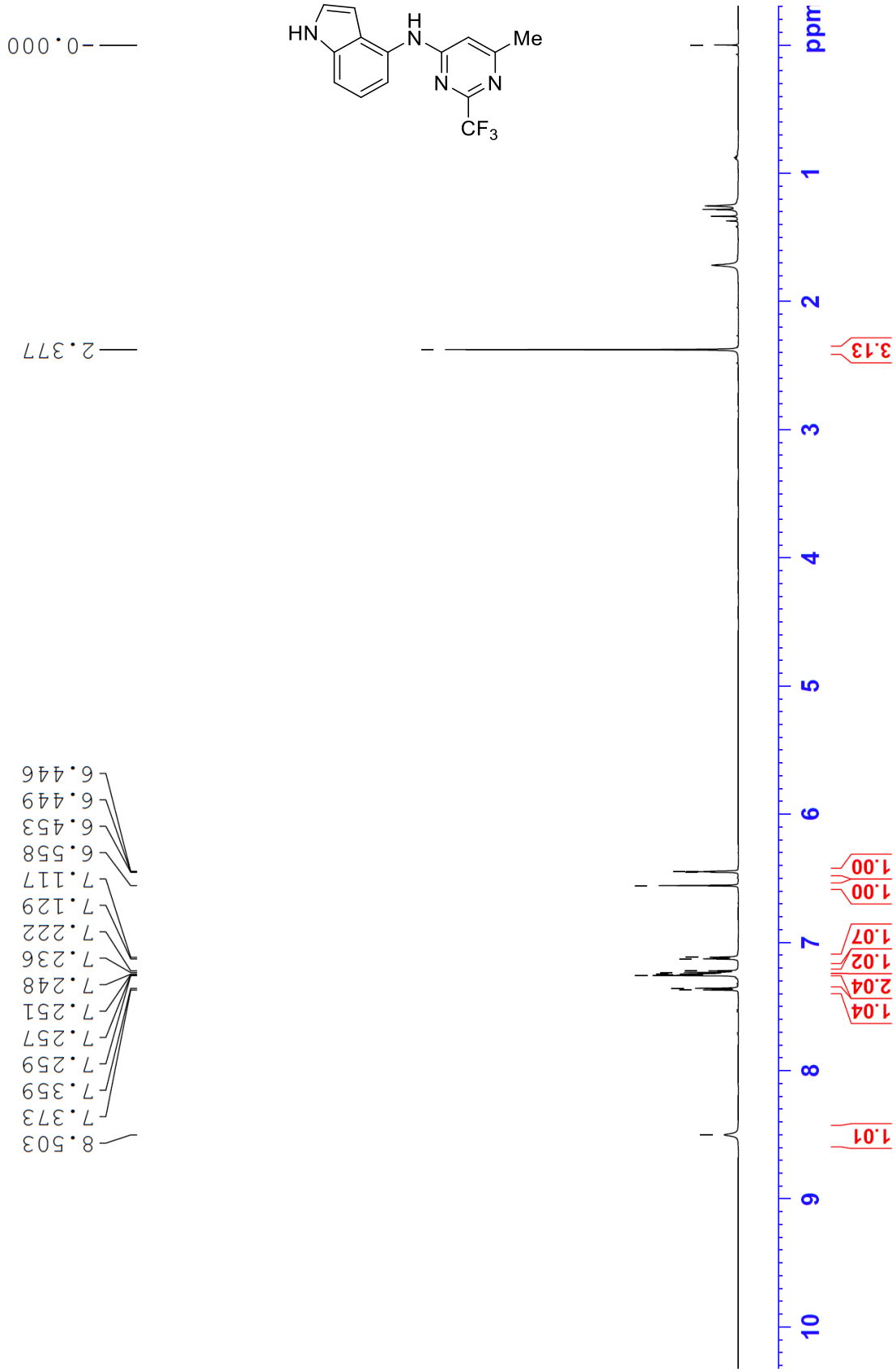
^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-2-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3o)



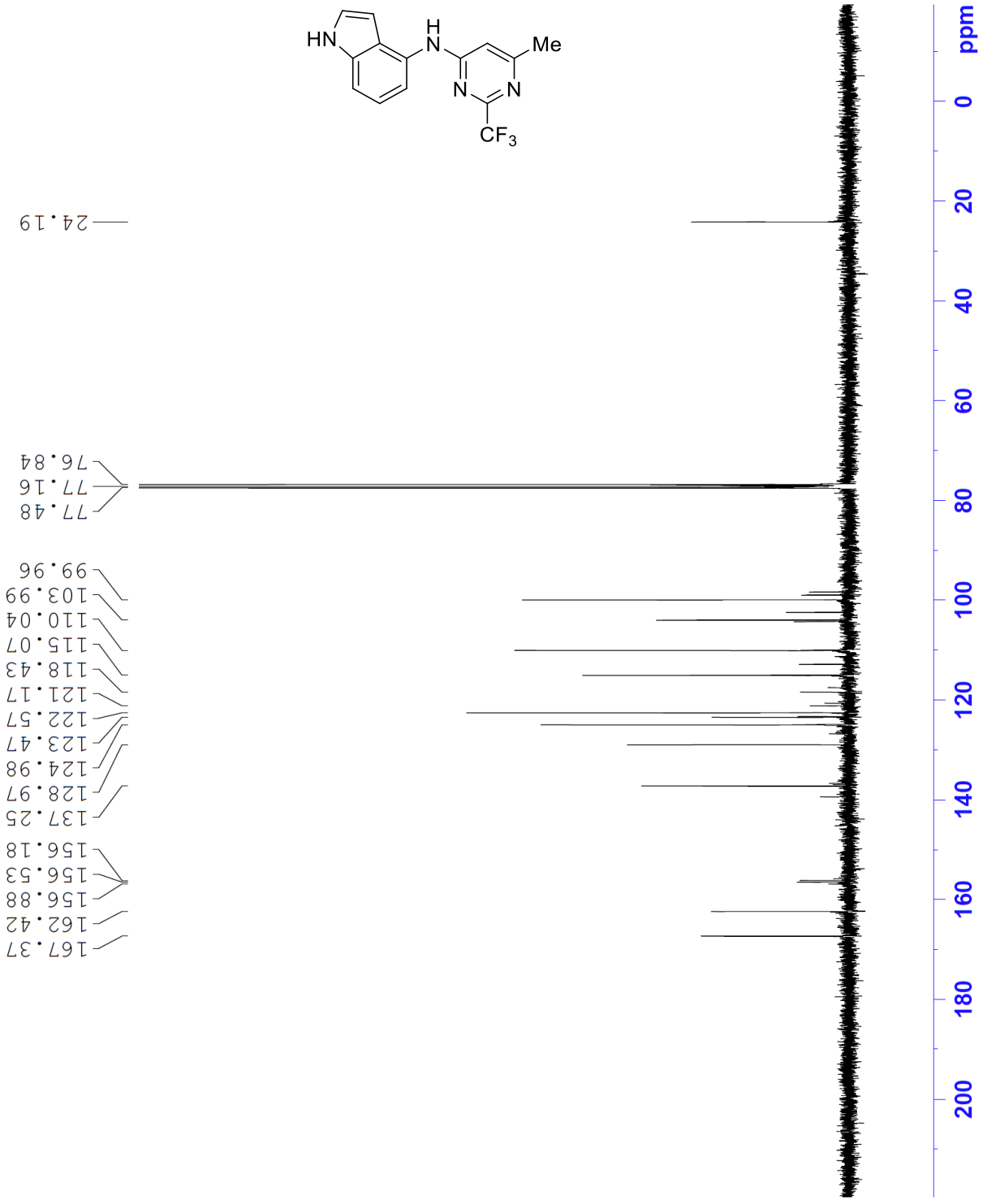
^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-*N*-(naphthalen-2-yl)-2-(trifluoromethyl)pyrimidin-4-amine (3o)



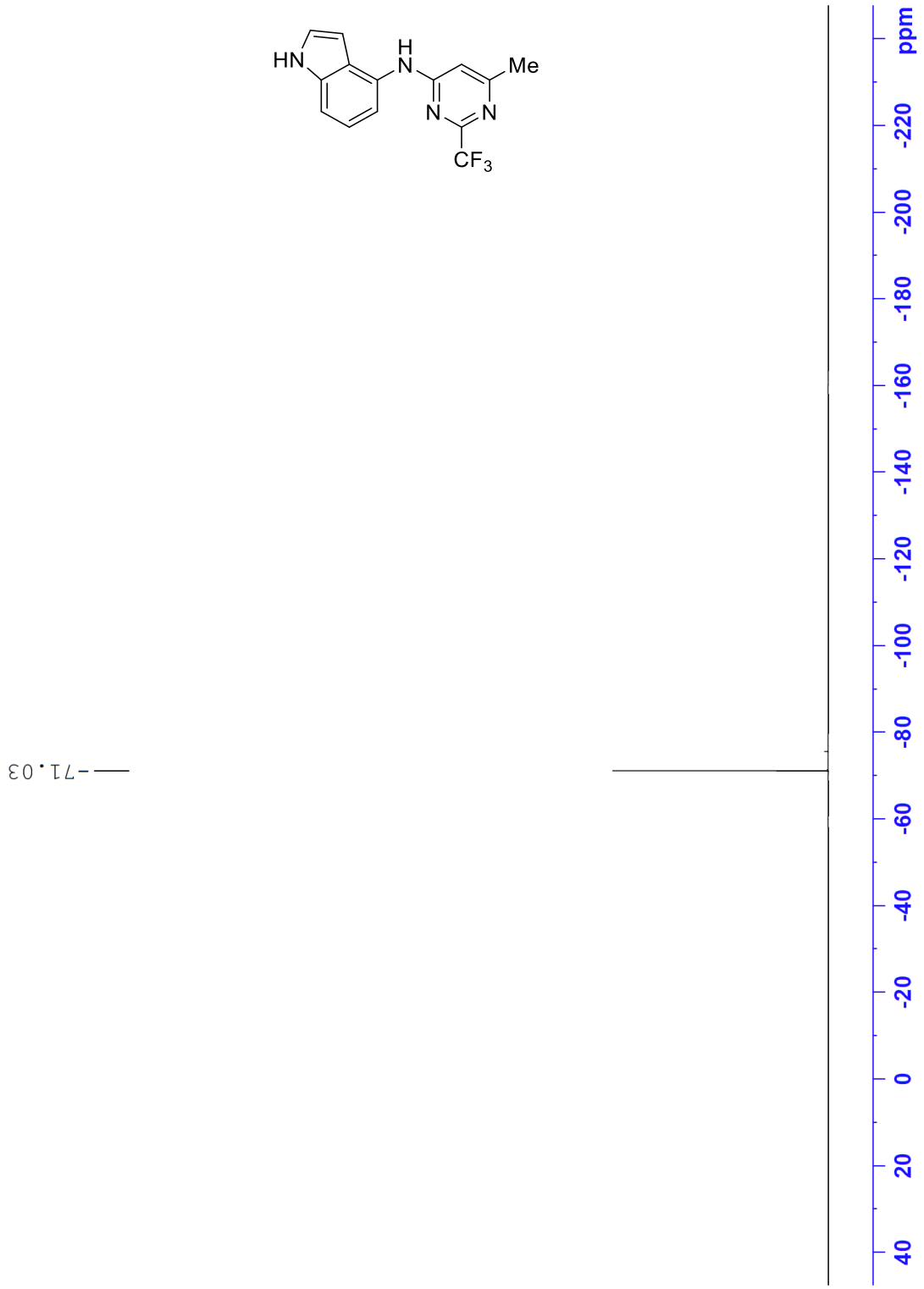
^{1}H NMR (600 MHz, $CDCl_3$) of *N*-(6-Methyl-2-(trifluoromethyl)pyrimidin-4-yl)-1*H*-indol-4-amine (3p)



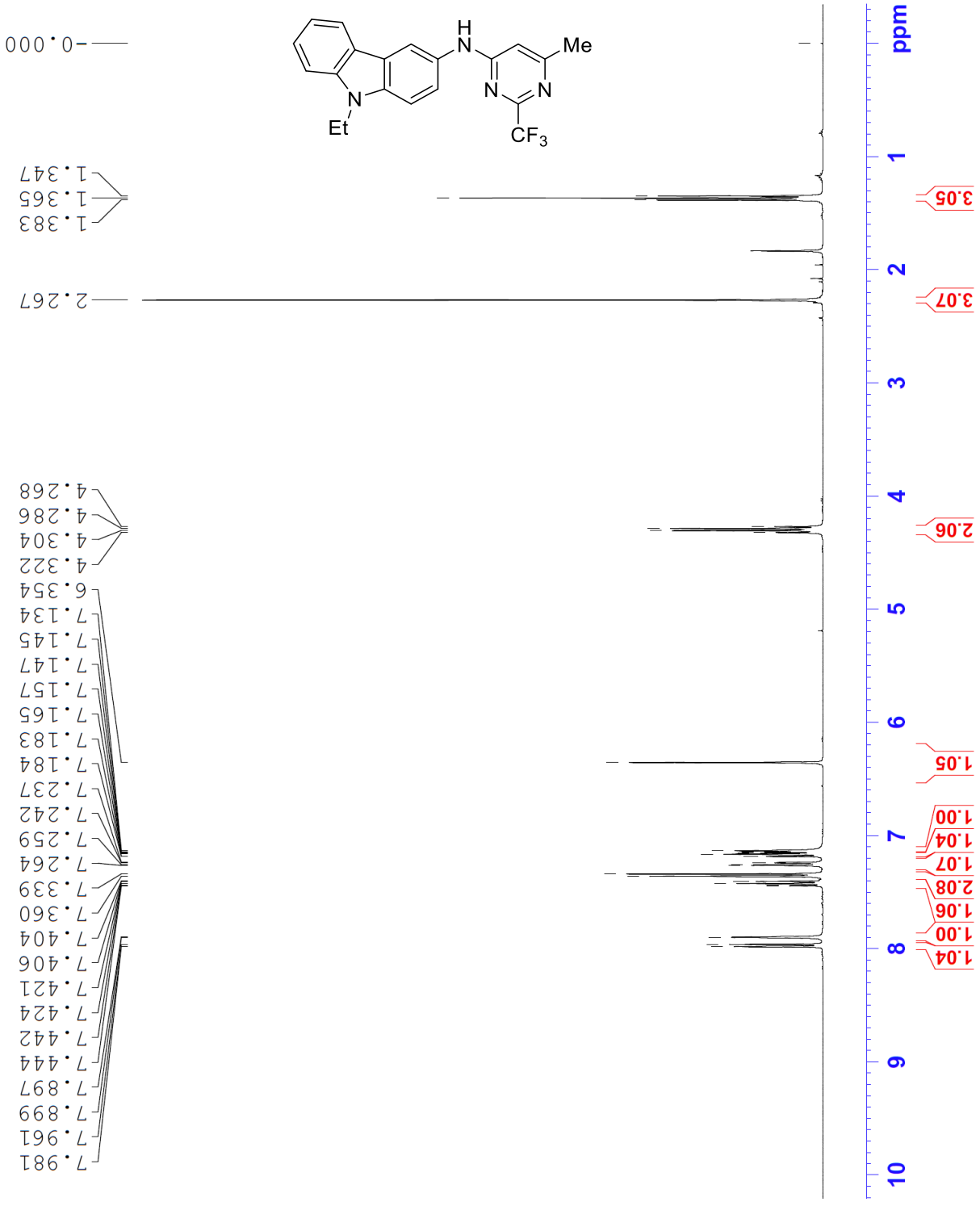
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(6-Methyl-2-(trifluoromethyl)pyrimidin-4-yl)-1*H*-indol-4-amine (3p)



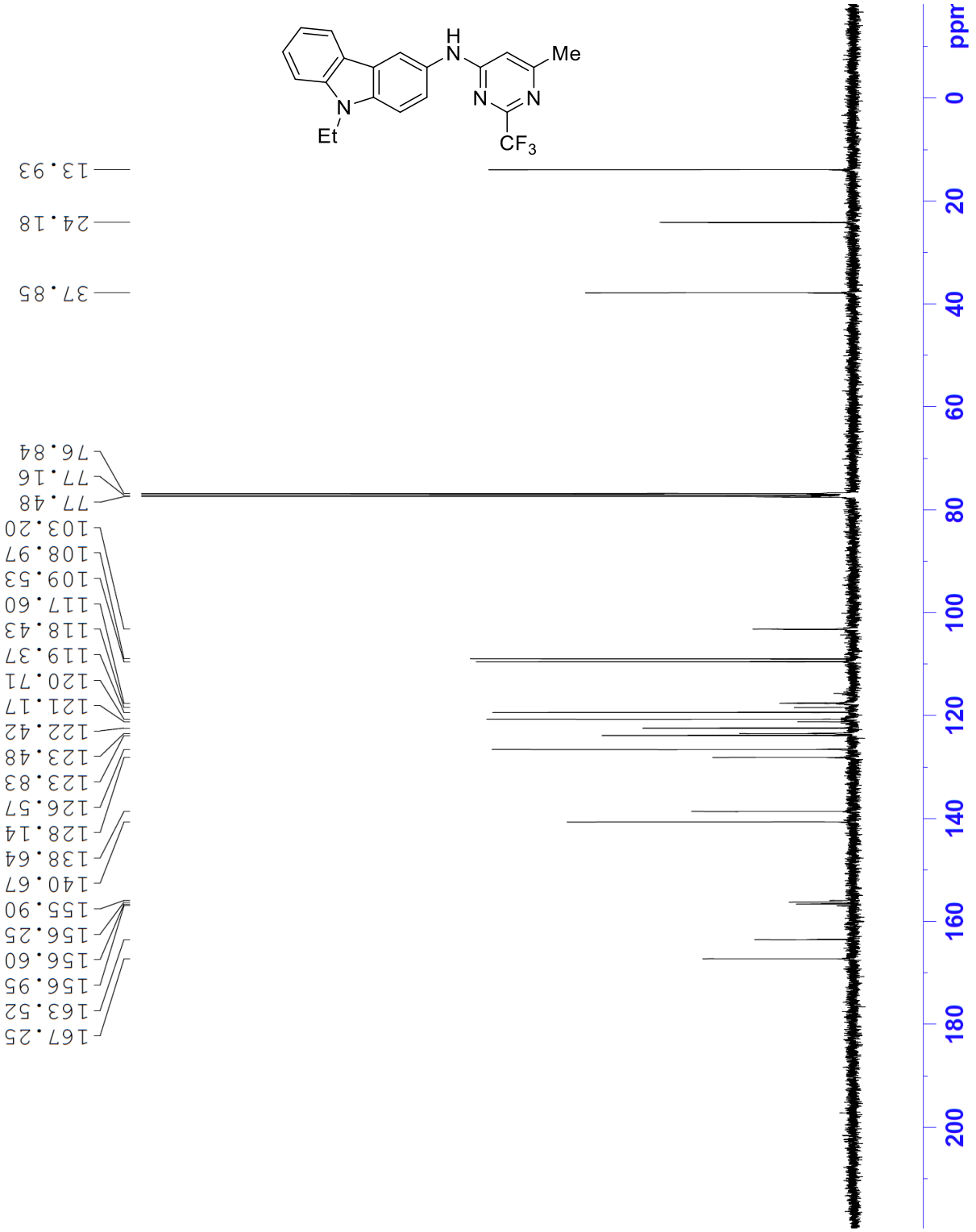
^{19}F NMR (565 MHz, $CDCl_3$) of *N*-(6-Methyl-2-(trifluoromethyl)pyrimidin-4-yl)-1*H*-indol-4-amine (3p)



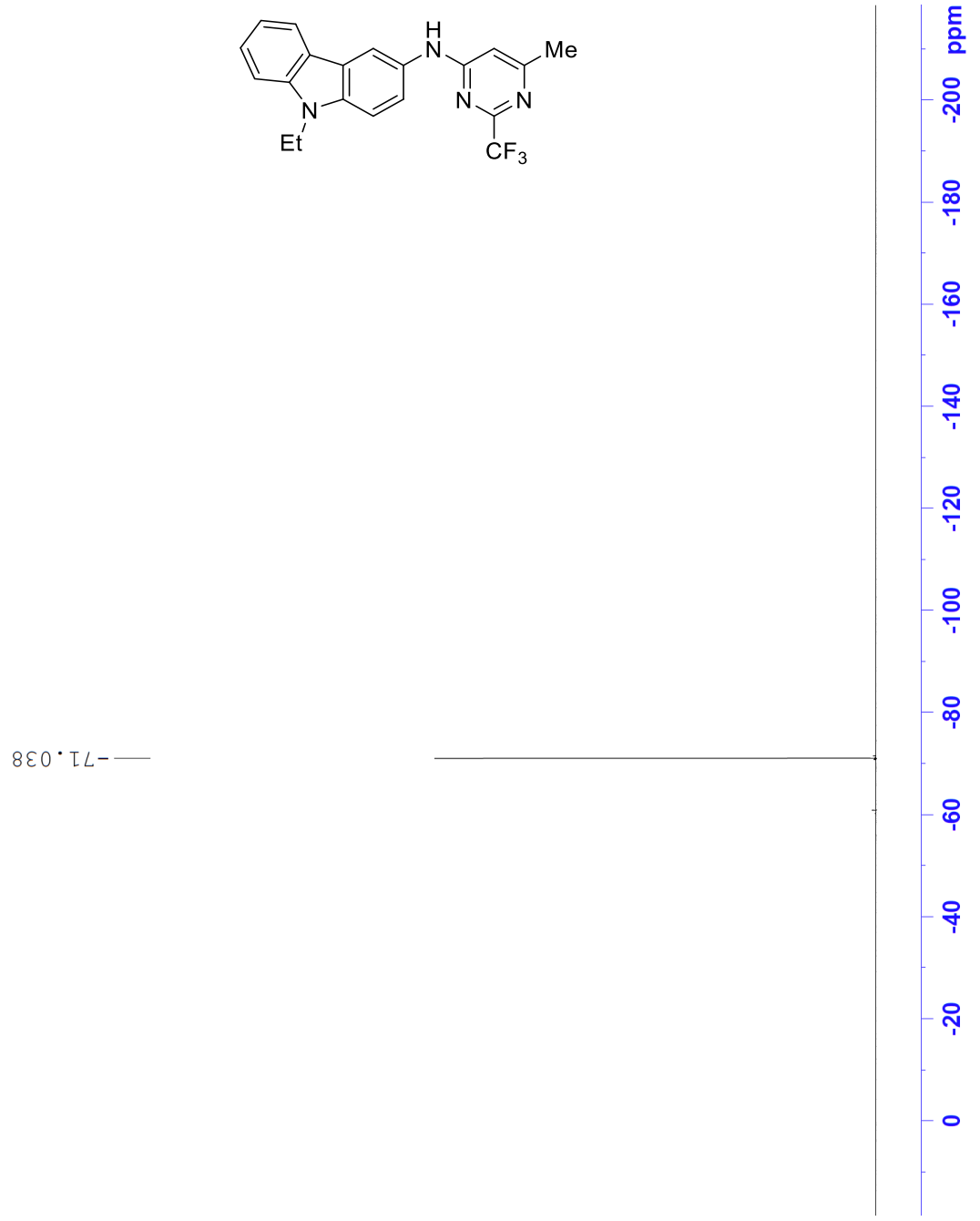
^{1}H NMR (400 MHz, $CDCl_3$) of 9-Ethyl-*N*-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)-9*H*-carbazol-3-amine (3q)



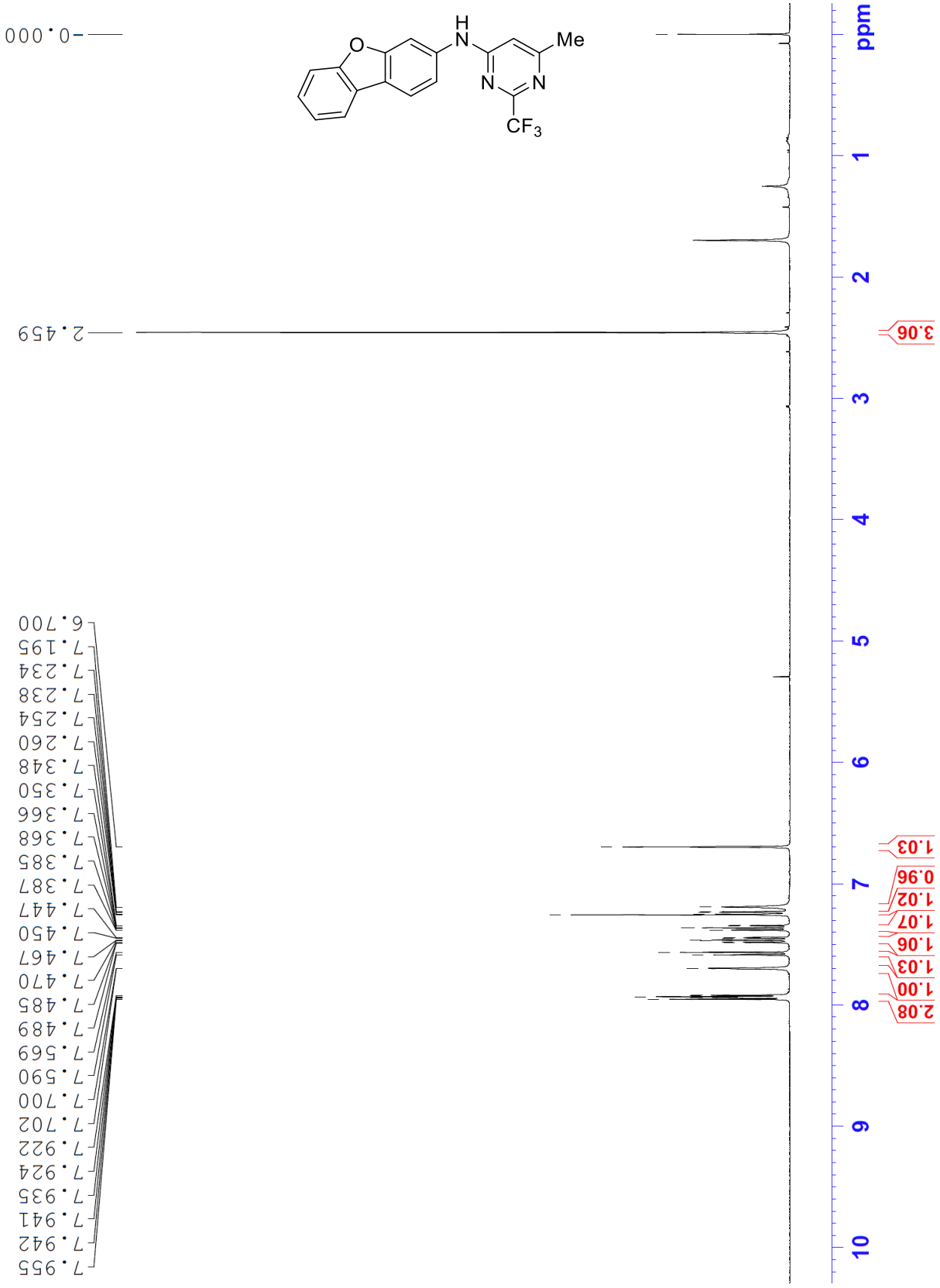
^{13}C NMR (100.6 MHz, $CDCl_3$) of 9-Ethyl-*N*-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)-9*H*-carbazol-3-amine (3q)



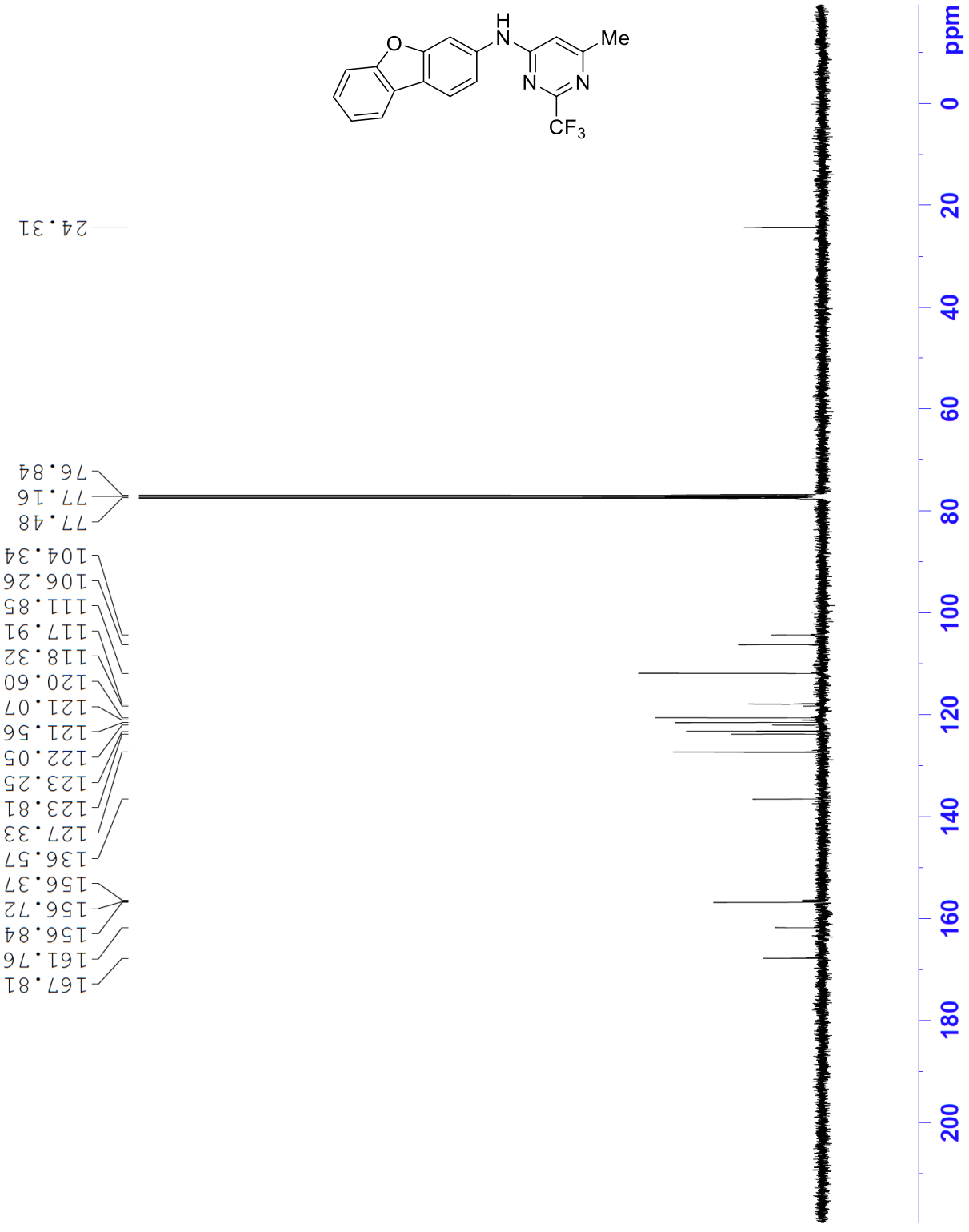
^{19}F NMR (376 MHz, $CDCl_3$) of 9-Ethyl-*N*-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)-9*H*-carbazol-3-amine (3q)



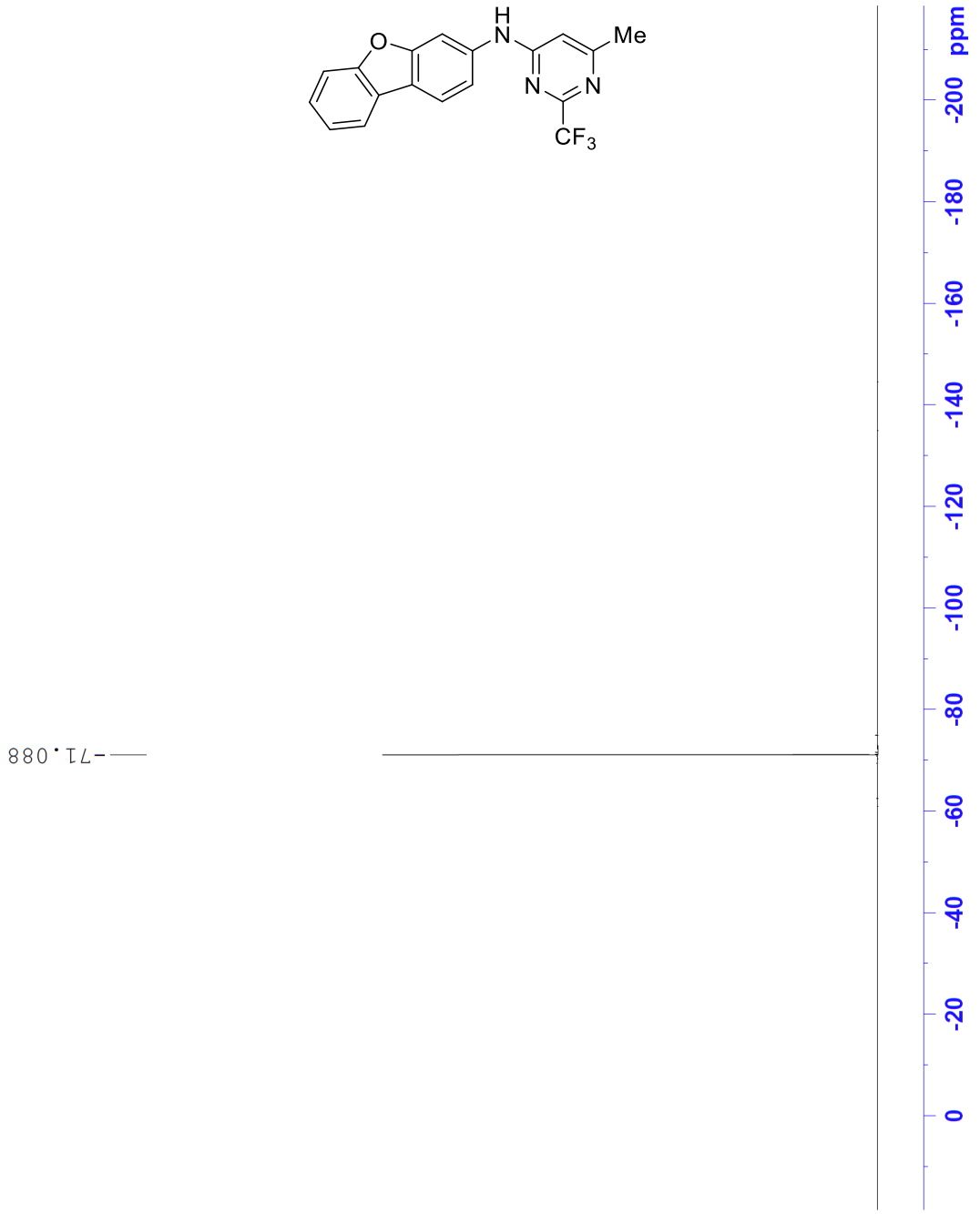
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(Dibenzo[*b*,*d*]furan-3-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3r)



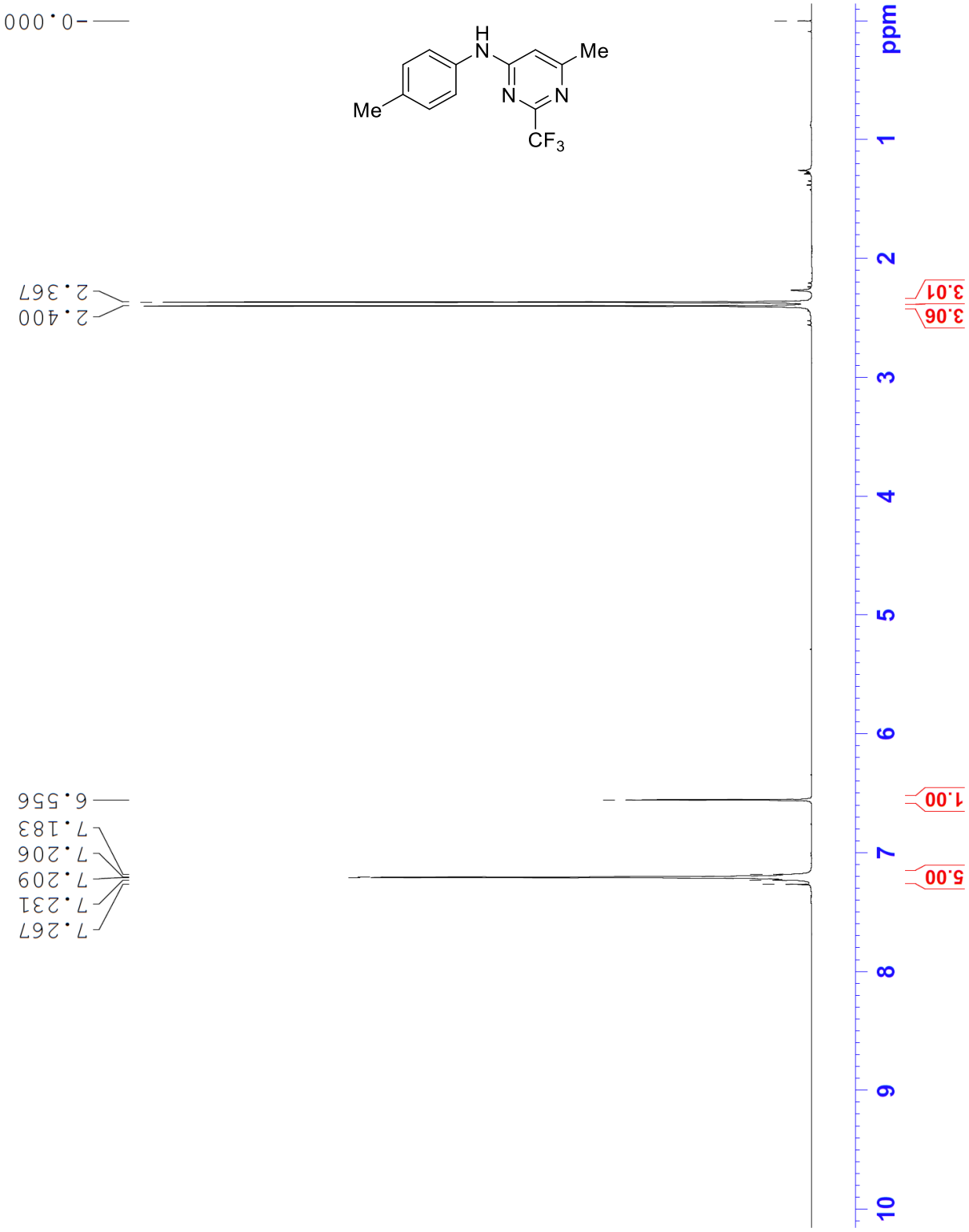
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(Dibenzo[*b*,*d*]furan-3-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3r)



^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(Dibenzo[*b*,*d*]furan-3-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3r)

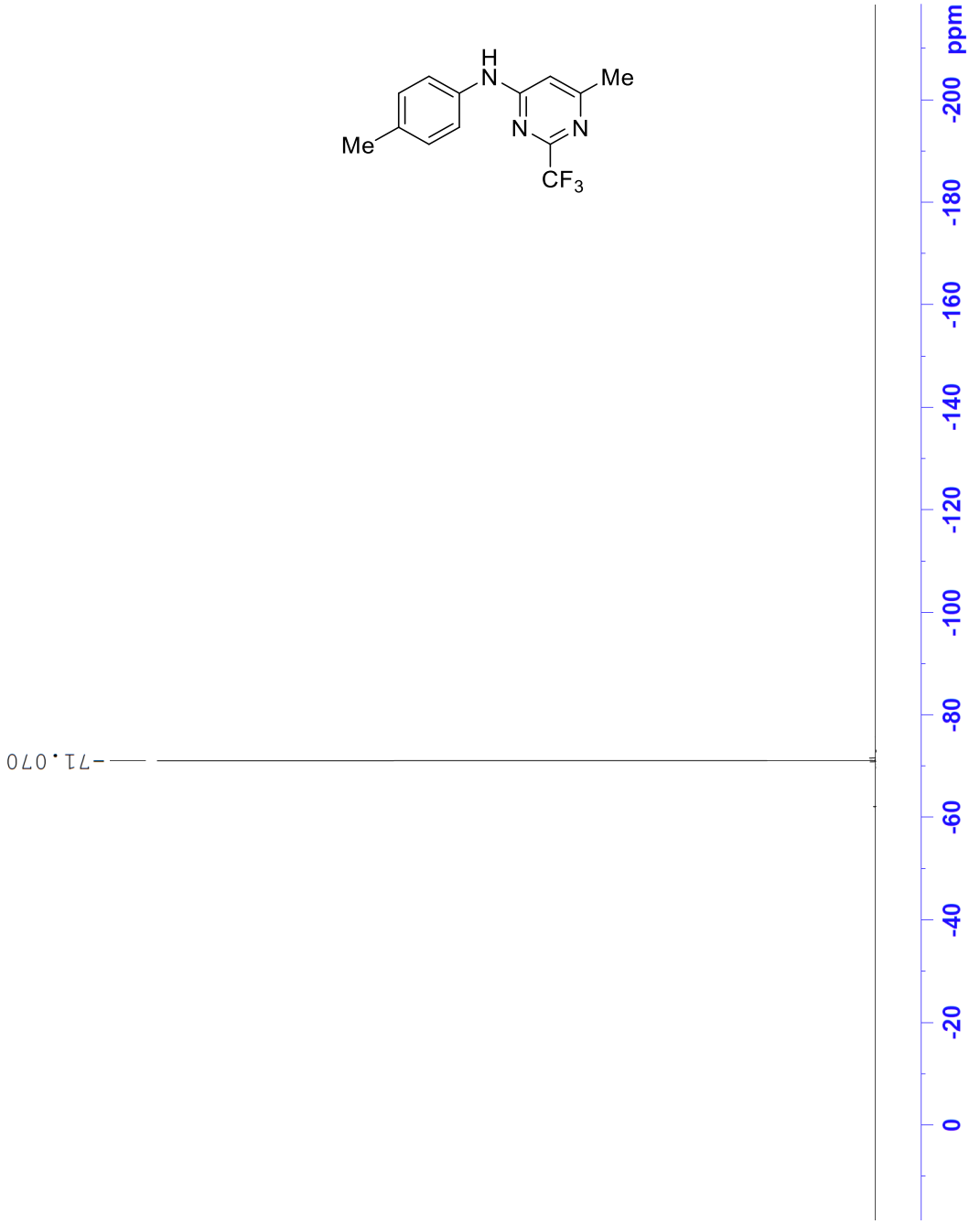


^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)pyrimidin-4-amine (3s)

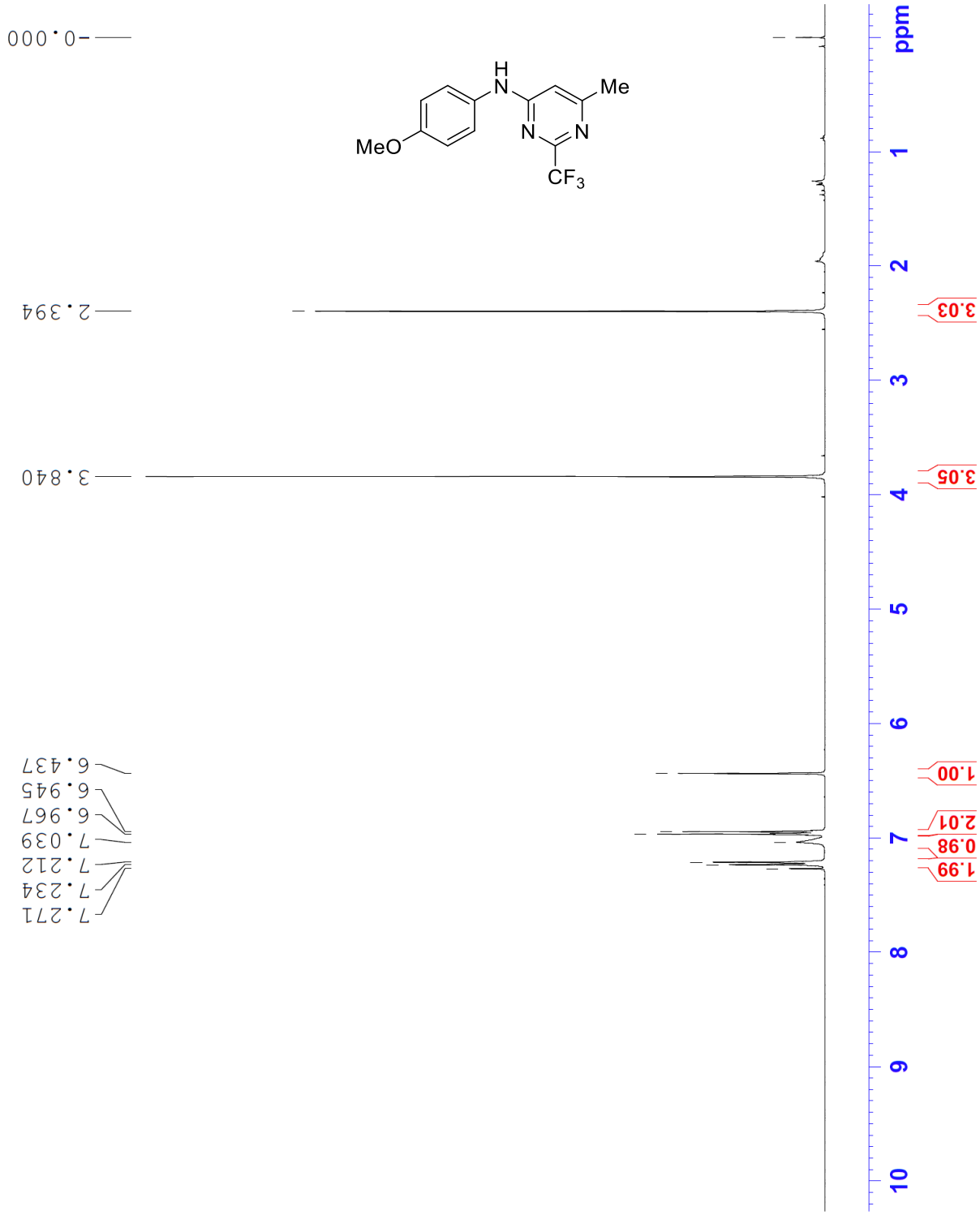


^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)pyrimidin-4-amine (3s)

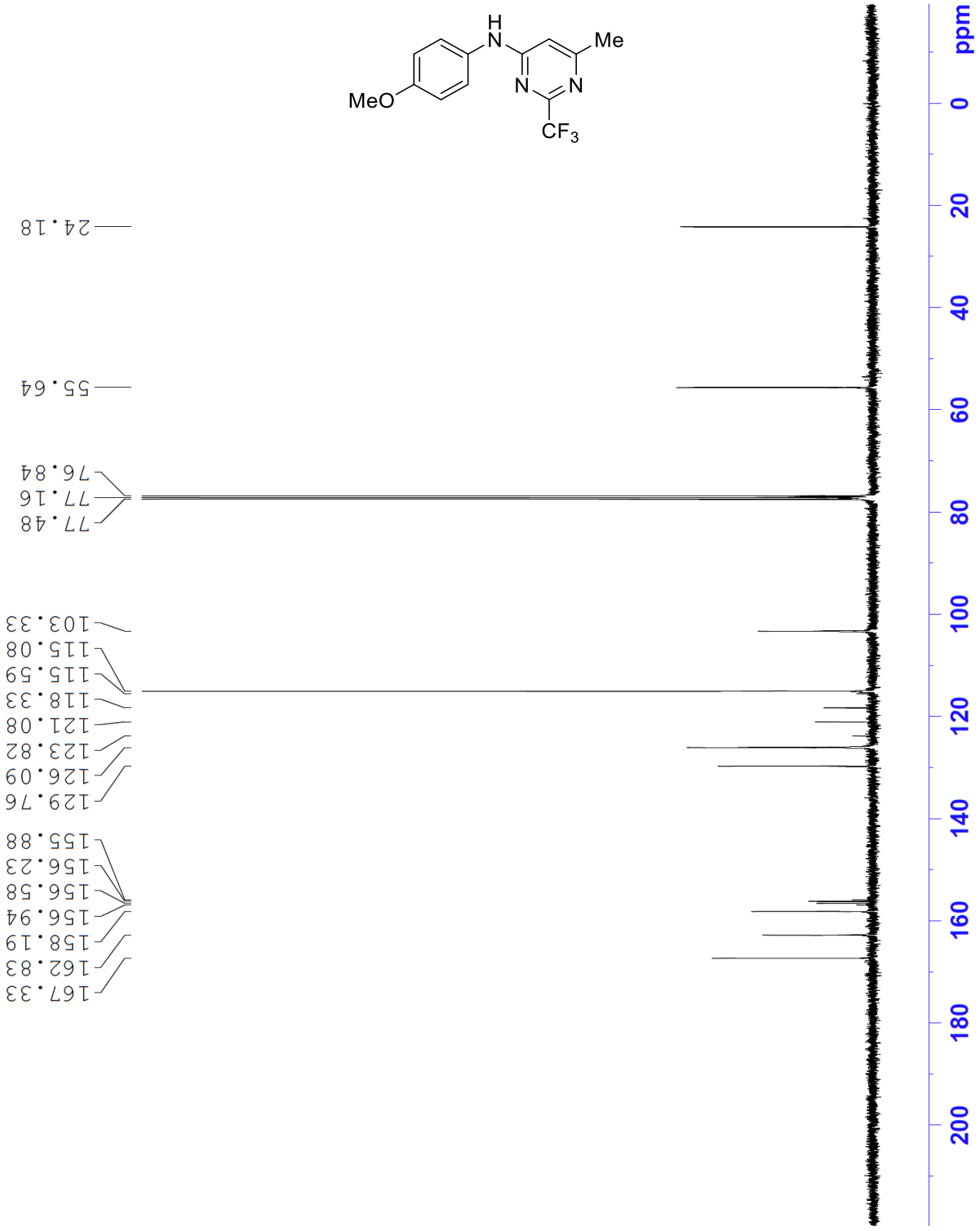
^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)pyrimidin-4-amine (3s)



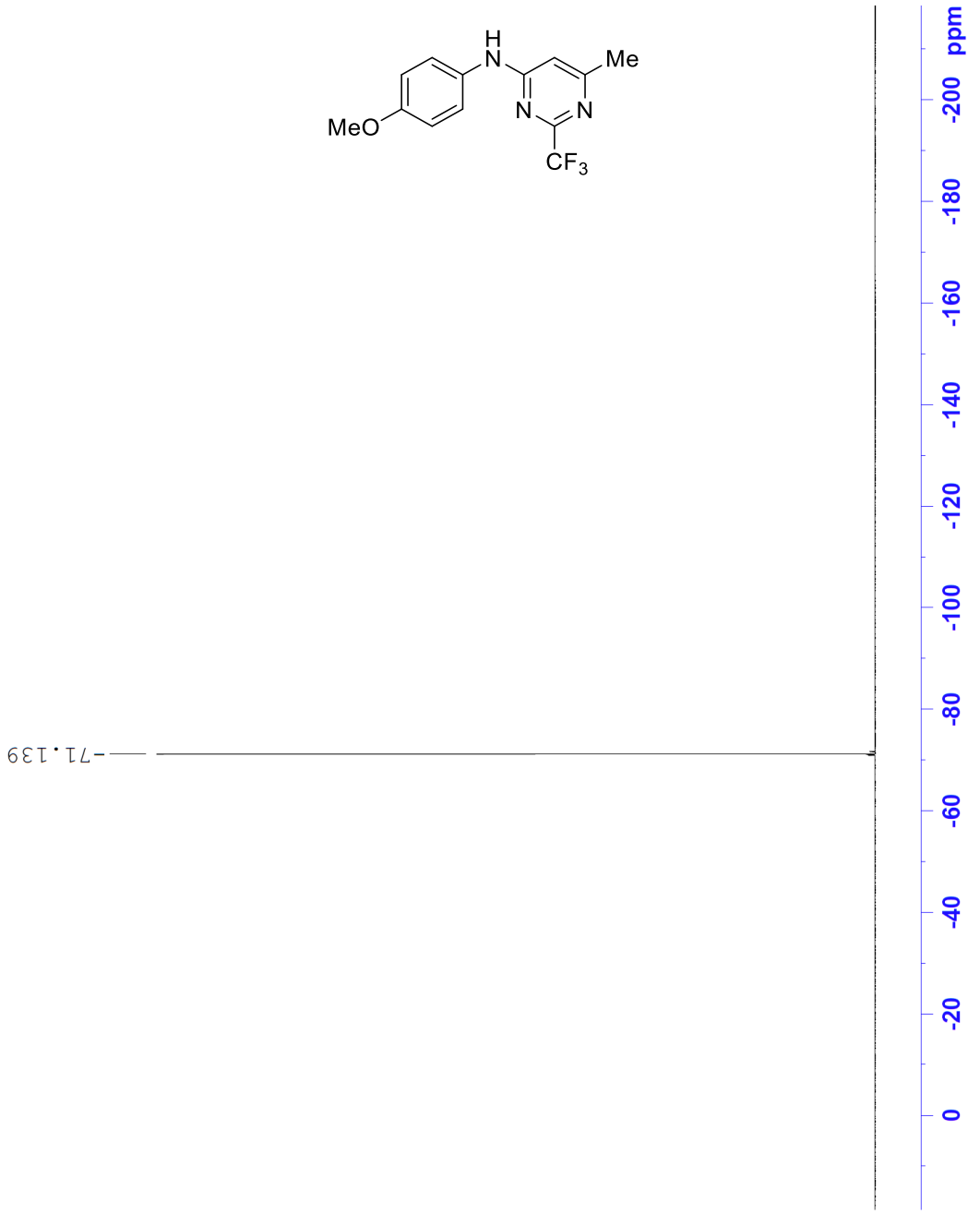
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-Methoxyphenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3t)



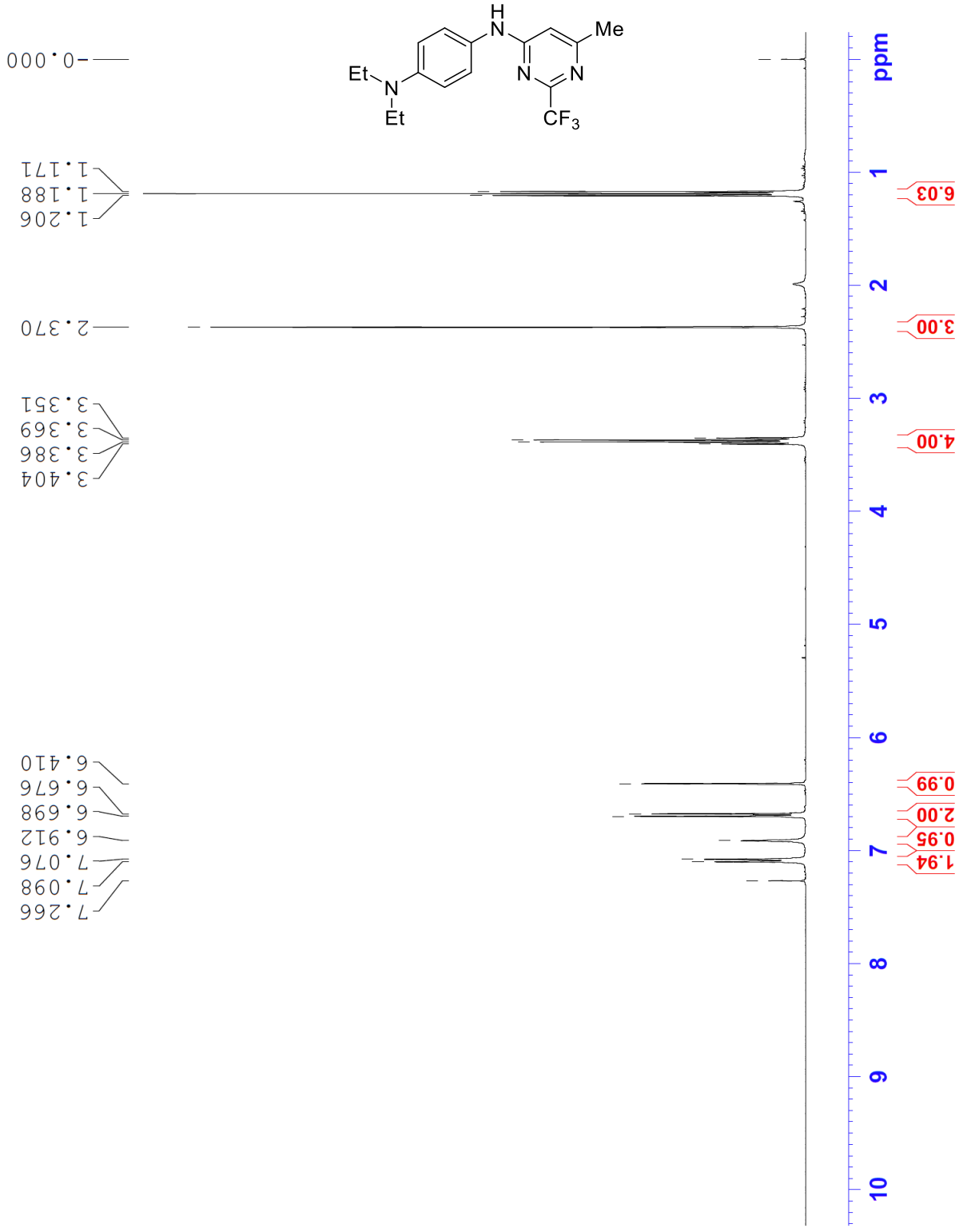
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4-Methoxyphenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3t)



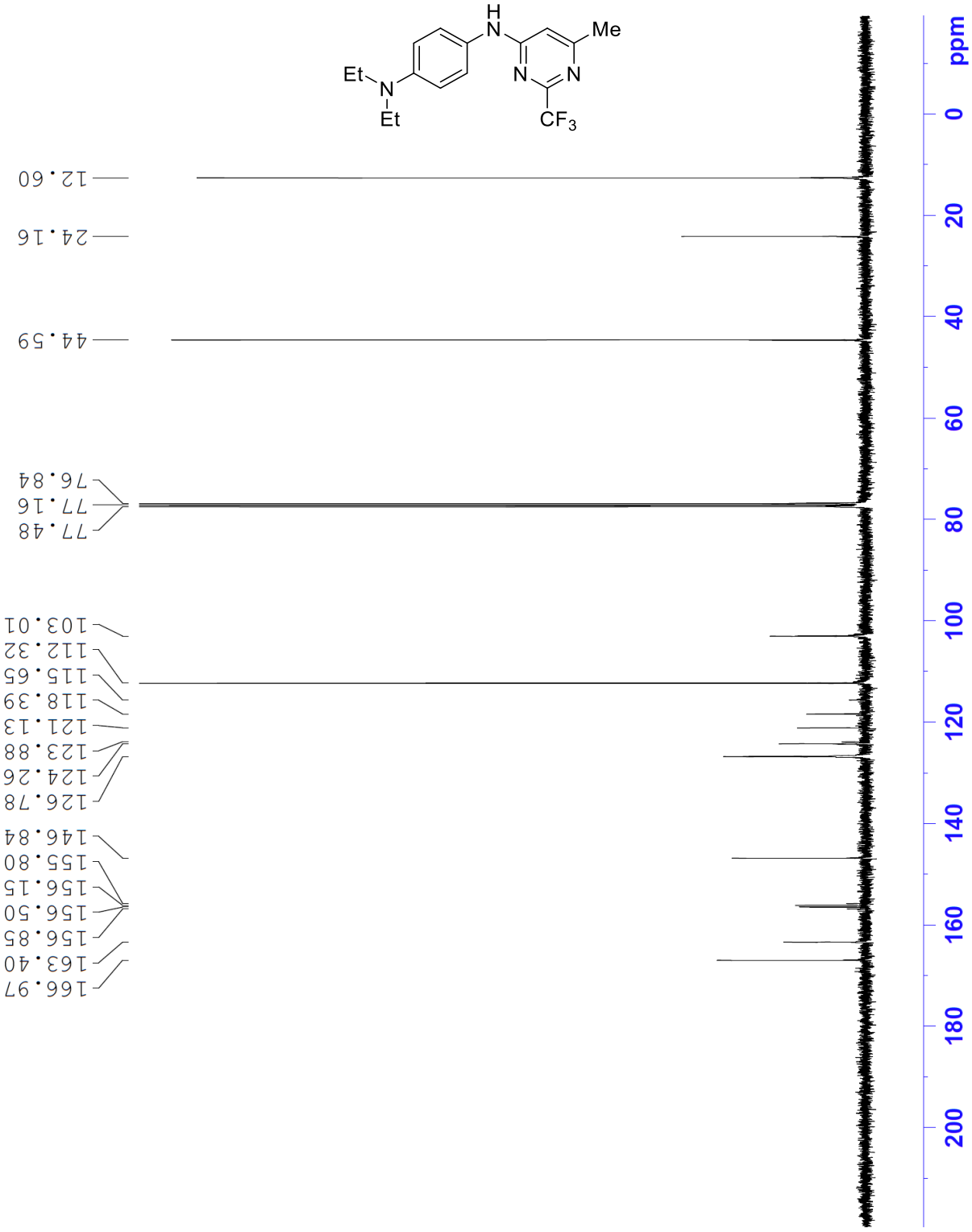
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4-Methoxyphenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3t)



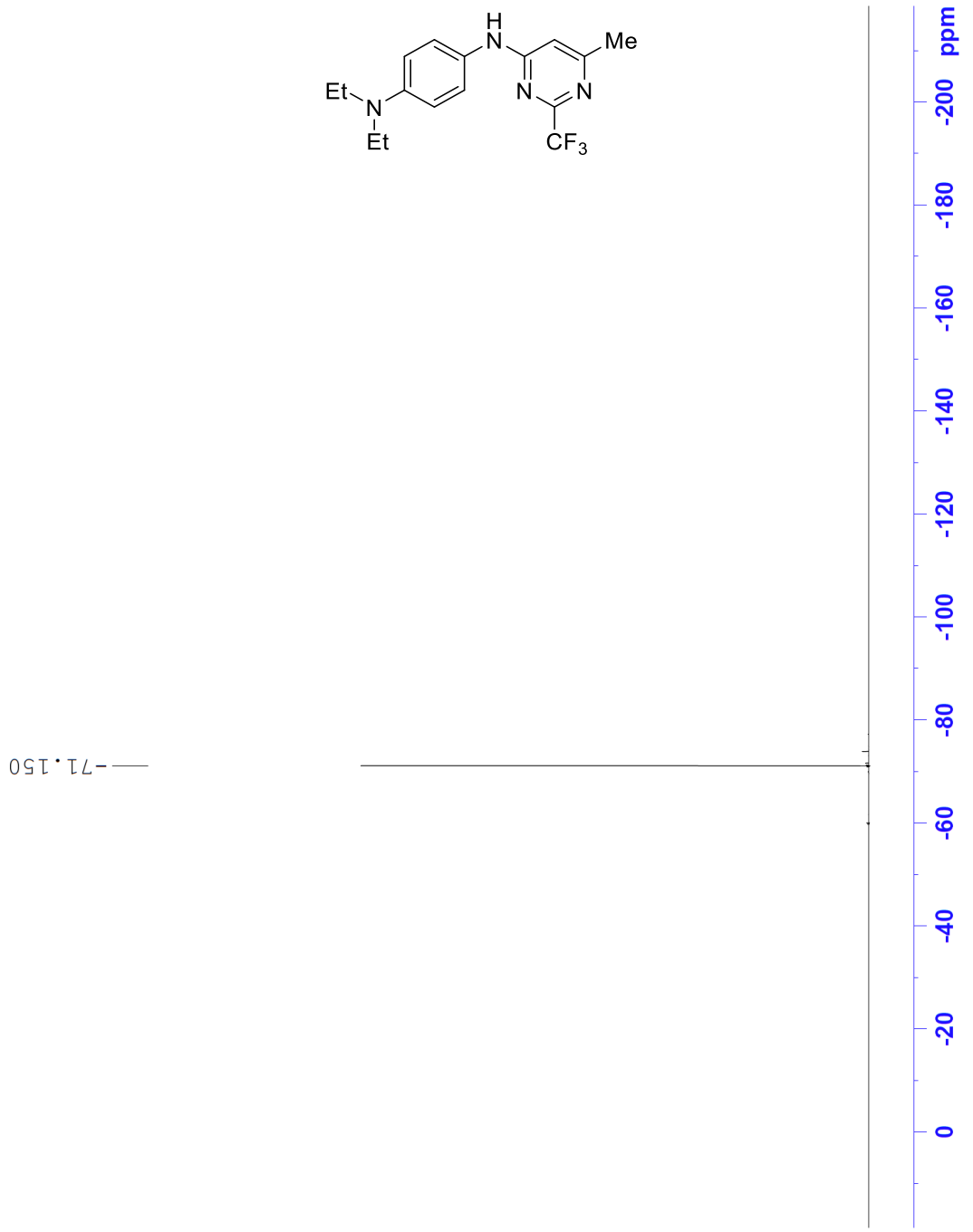
^{1}H NMR (400 MHz, $CDCl_3$) of N^1,N^1-Diethyl-N^4-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)benzene-1,4-diamine (3u)



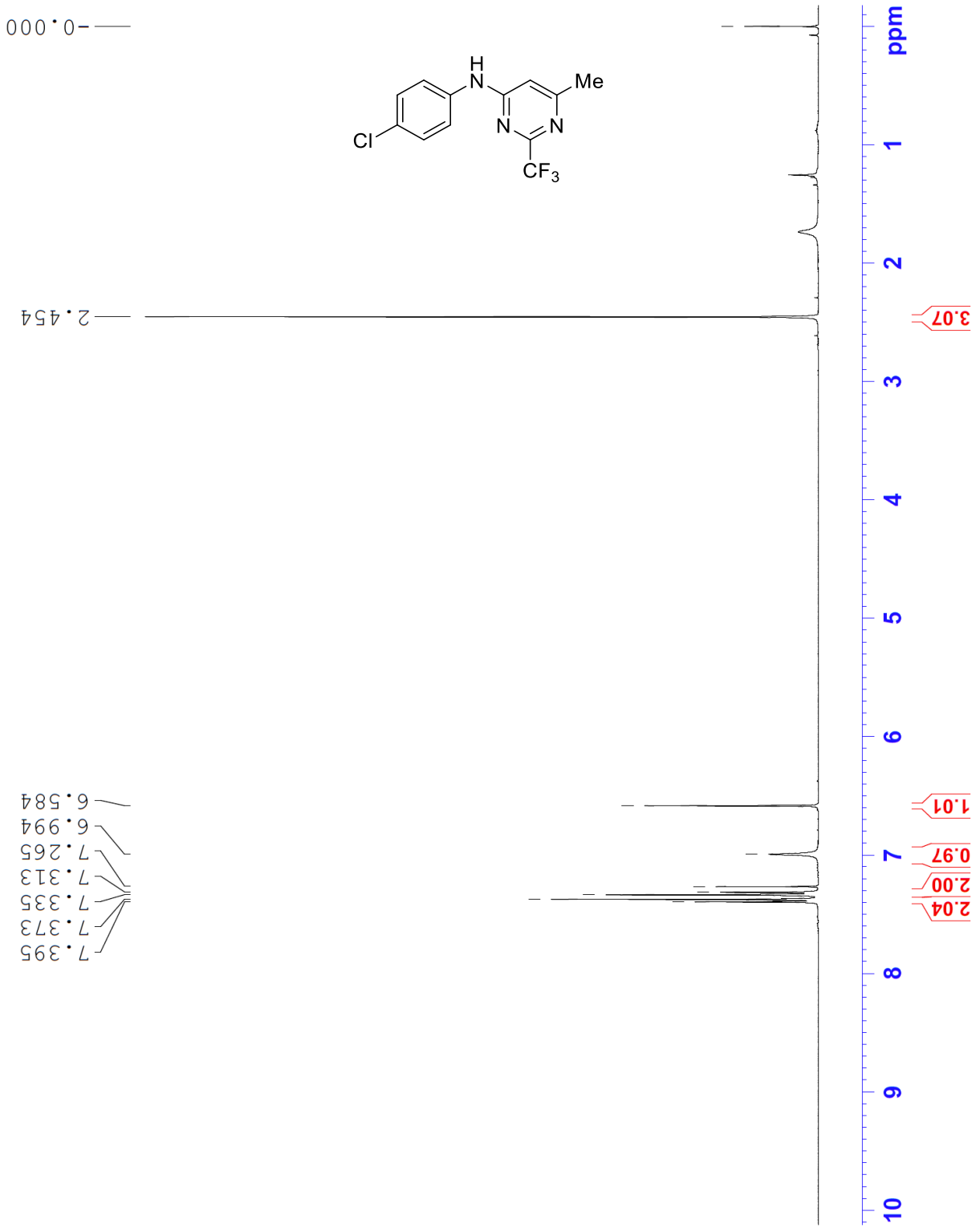
^{13}C NMR (100.6 MHz, $CDCl_3$) of N^1,N^1-Diethyl-N^4-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)benzene-1,4-diamine (3u)



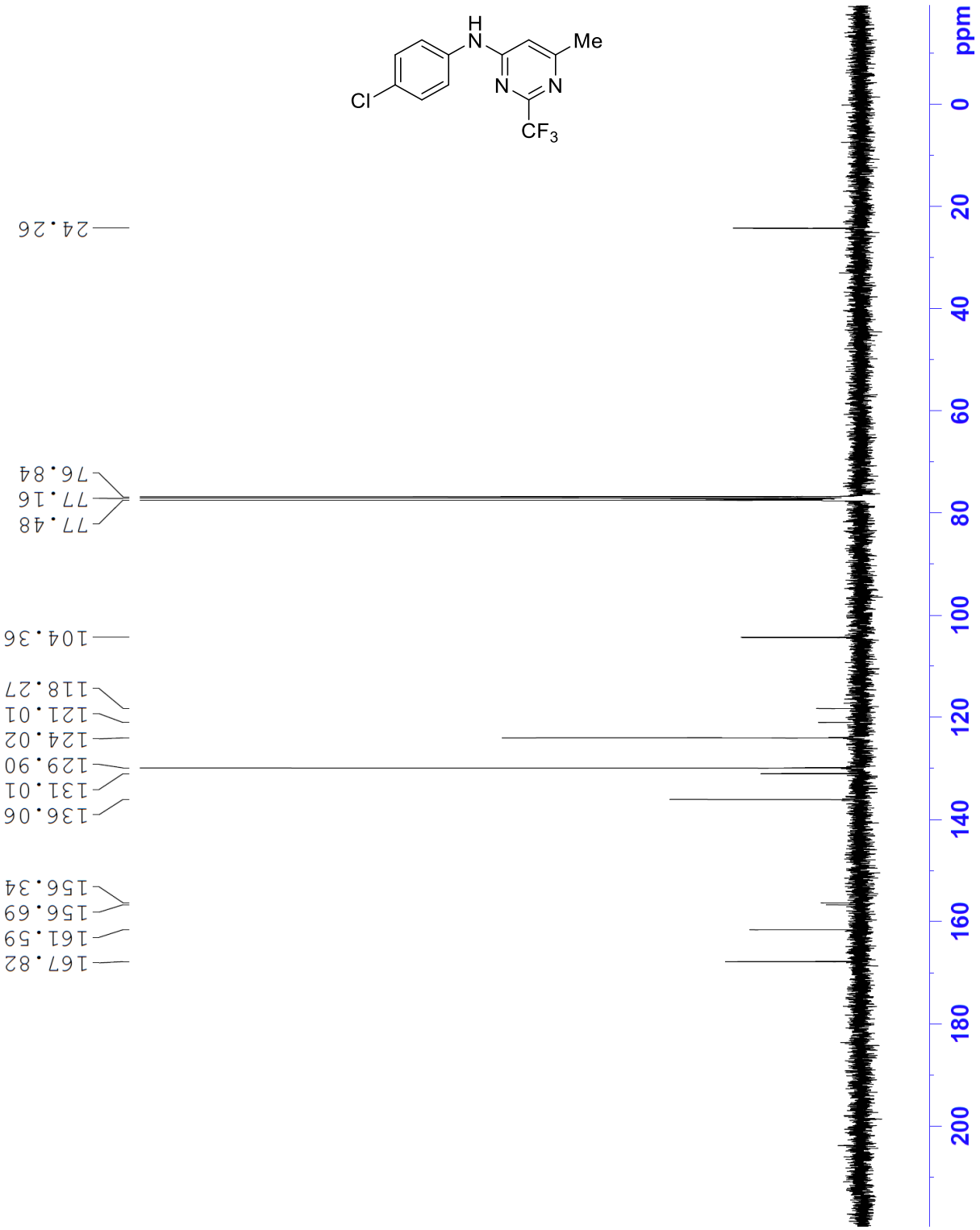
^{19}F NMR (376 MHz, $CDCl_3$) of N^1,N^1-Diethyl-N^4-(6-methyl-2-(trifluoromethyl)pyrimidin-4-yl)benzene-1,4-diamine (3u)



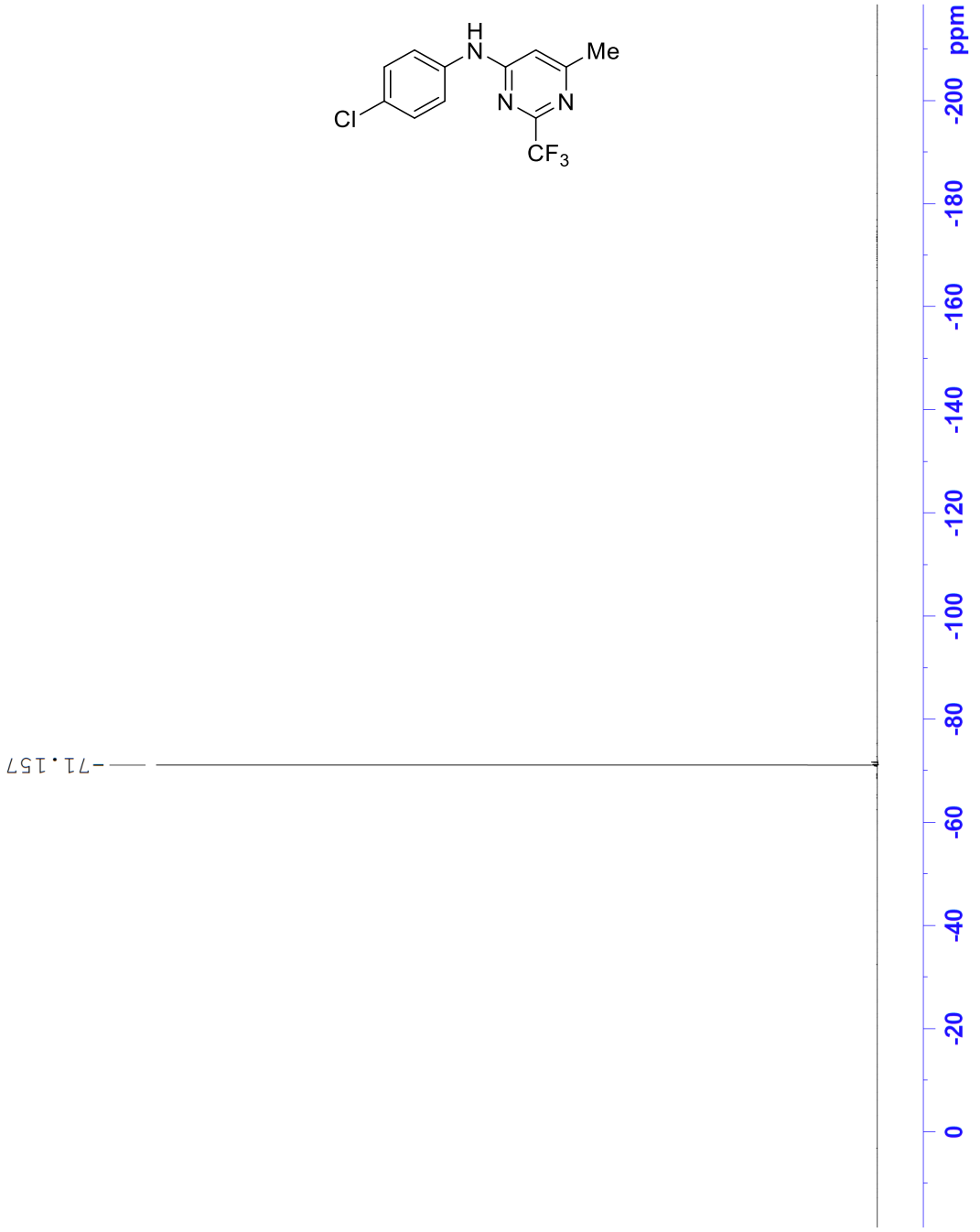
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-Chlorophenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3v)



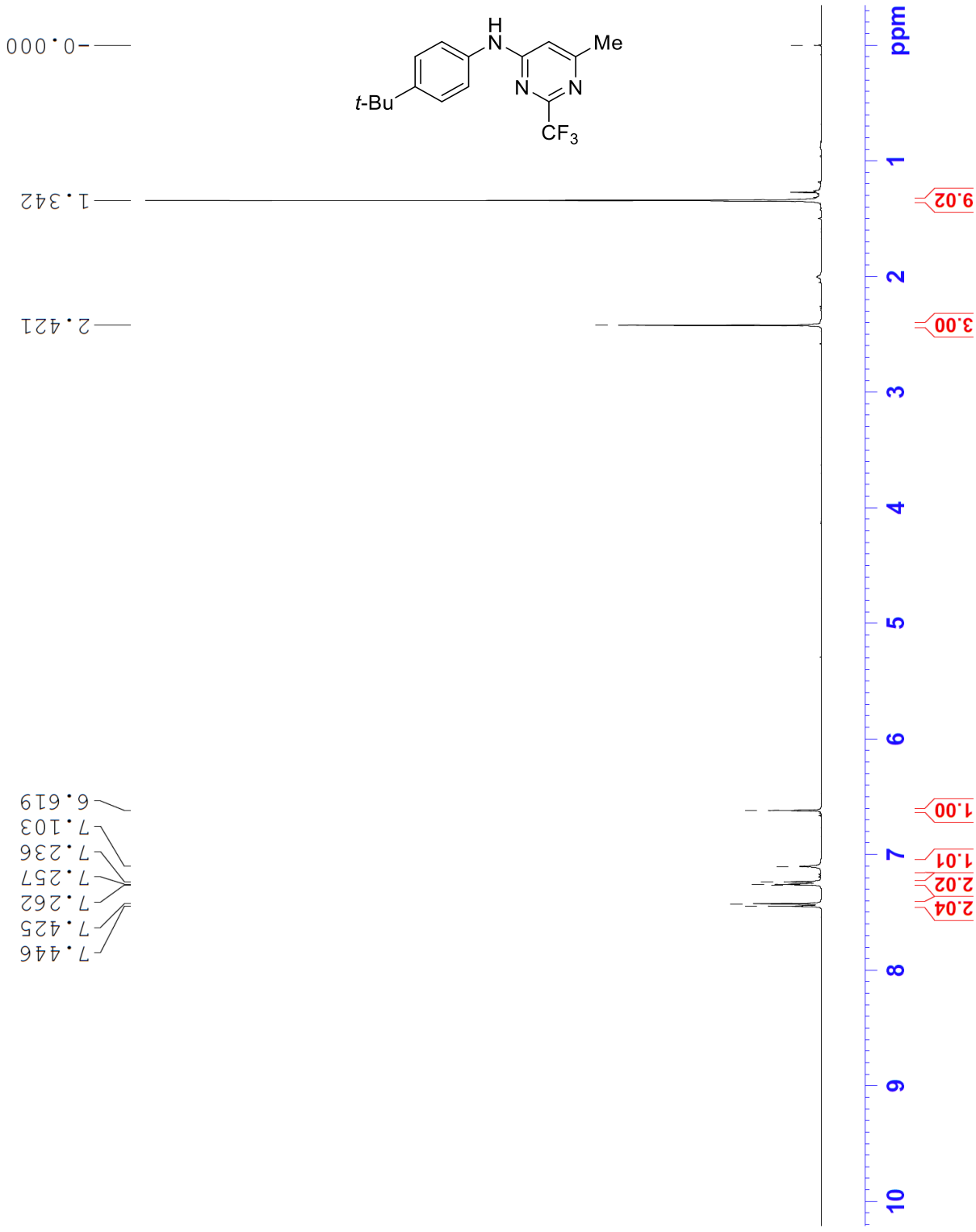
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4-Chlorophenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3v)



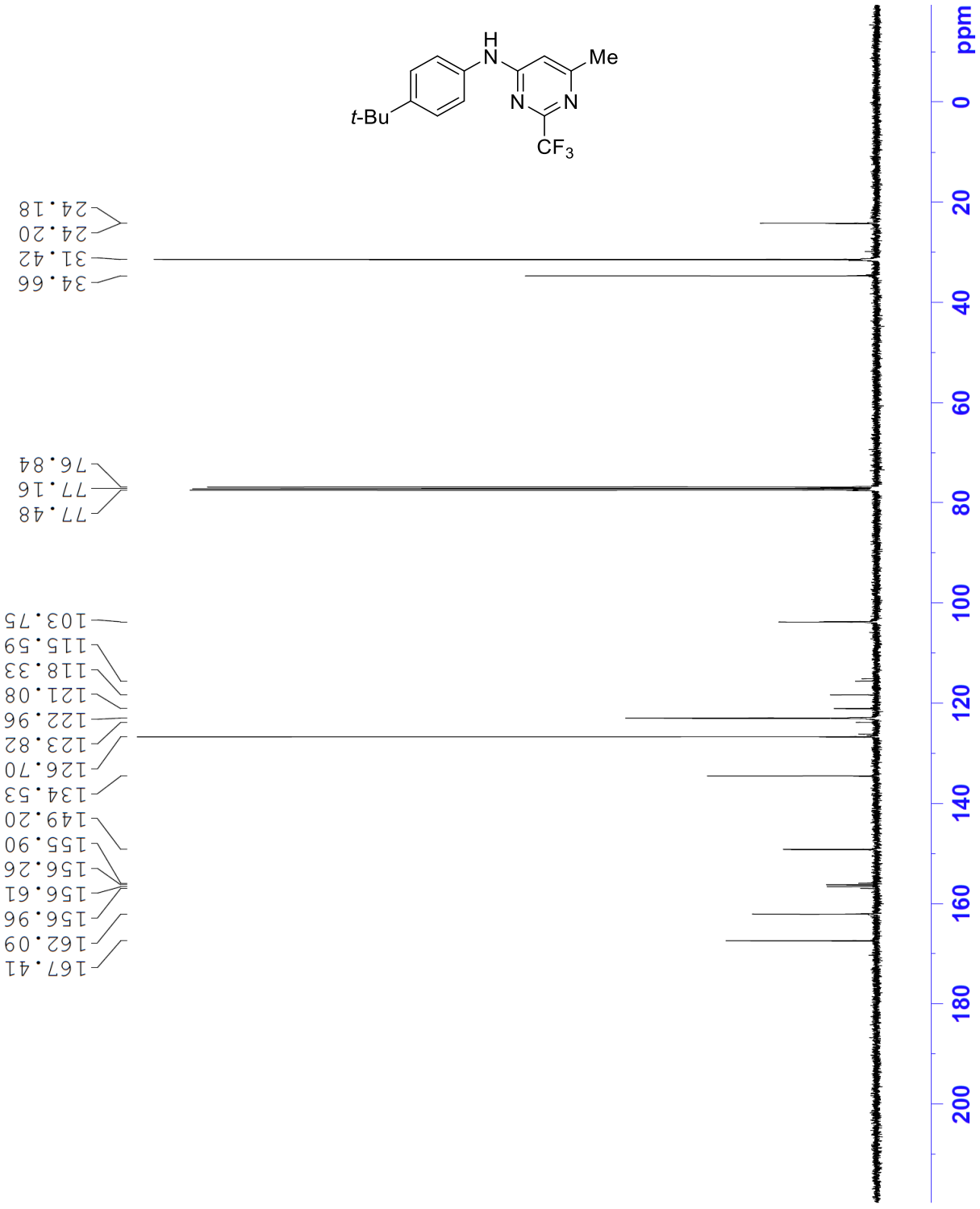
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4-Chlorophenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3v)



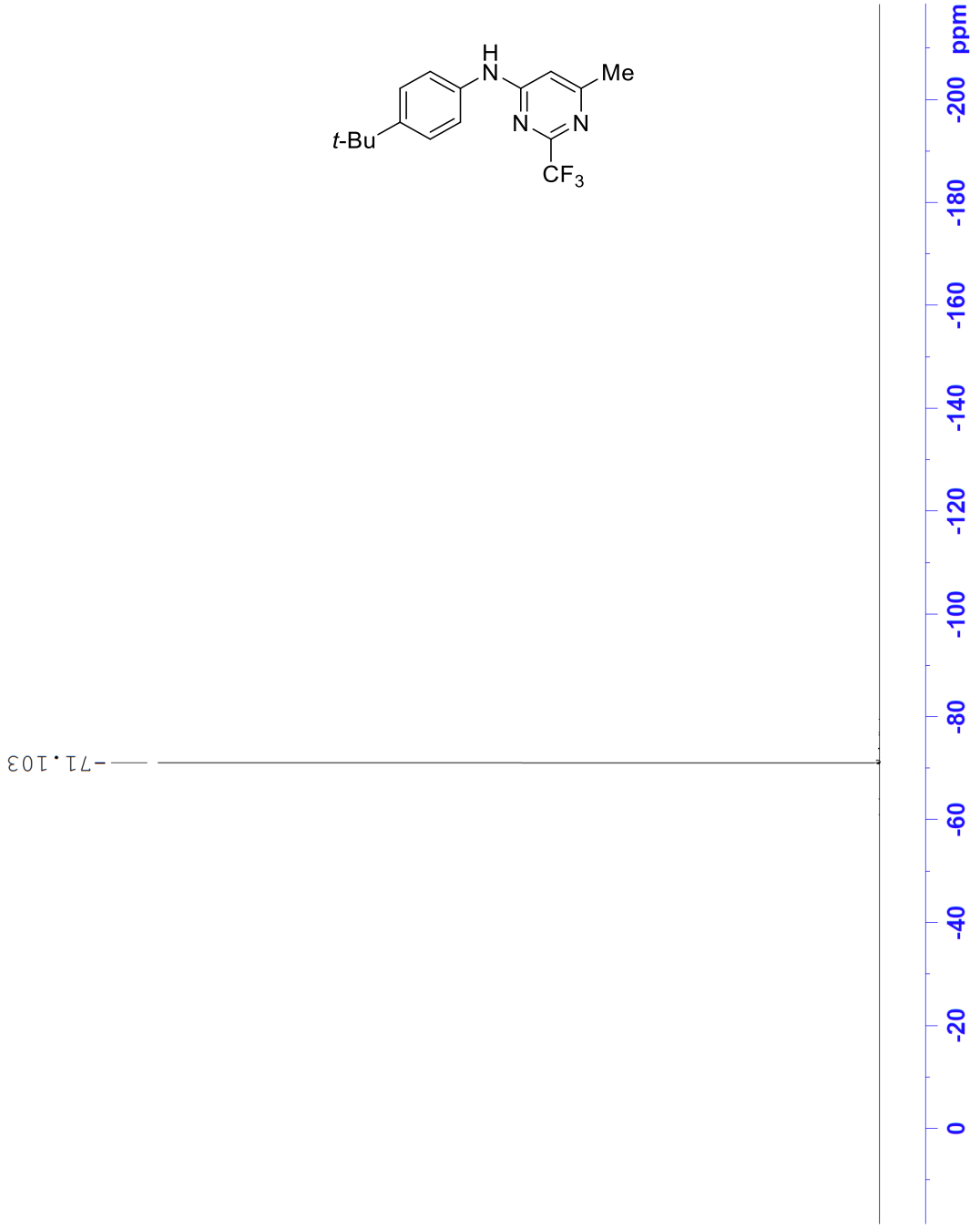
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-(*tert*-Butyl)phenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3w)



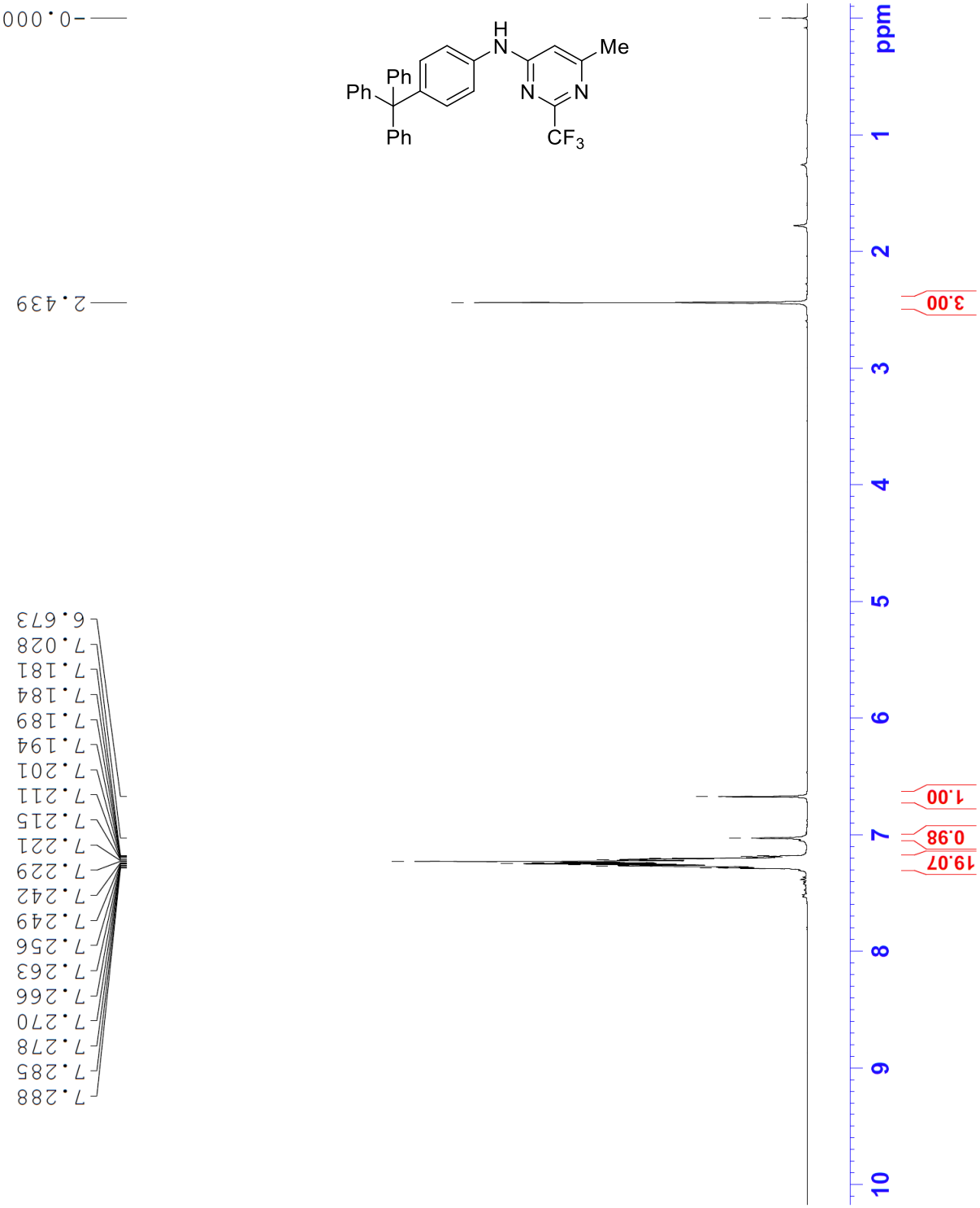
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(4-(*tert*-Butyl)phenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3w)



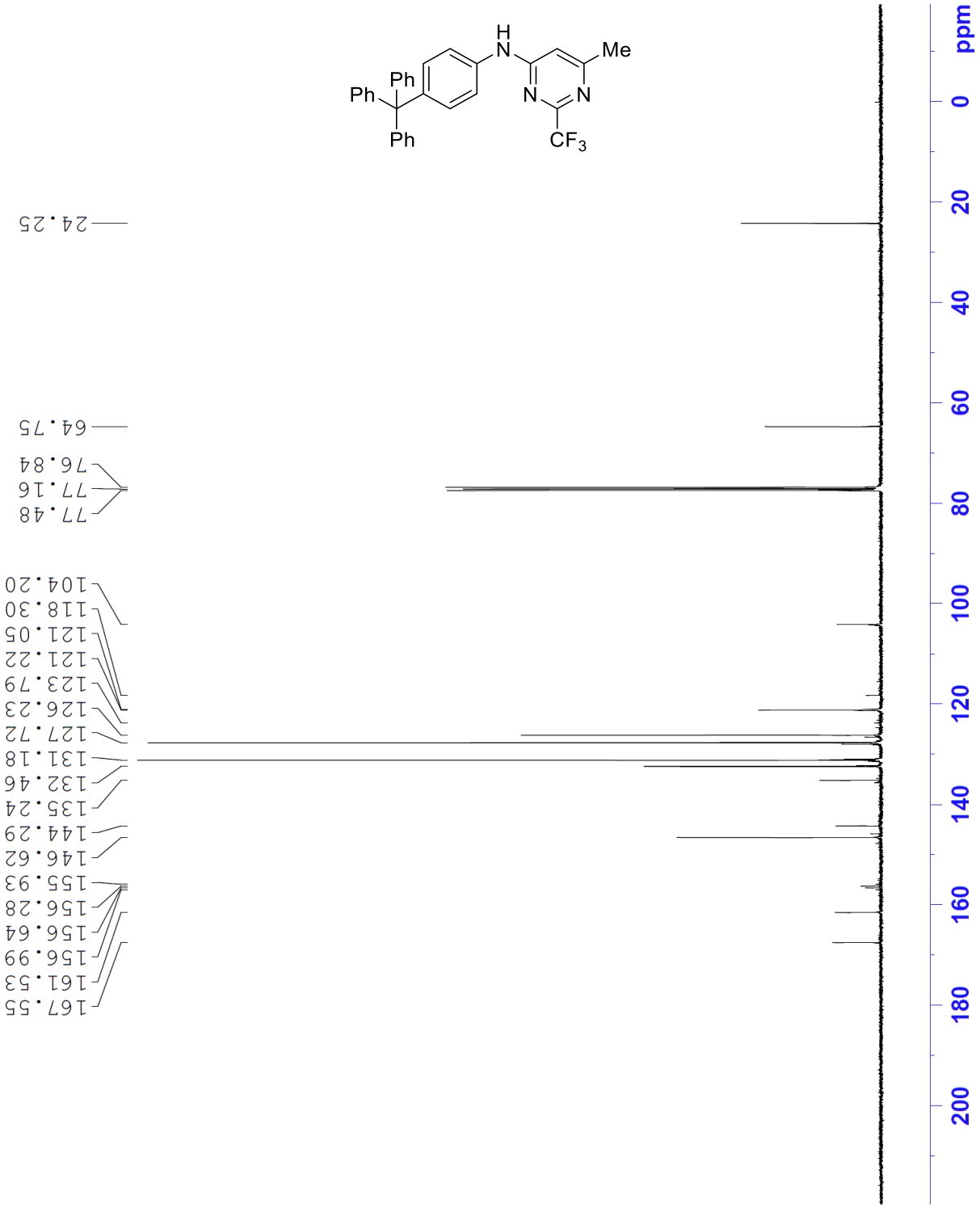
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4-(*tert*-Butyl)phenyl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3w)



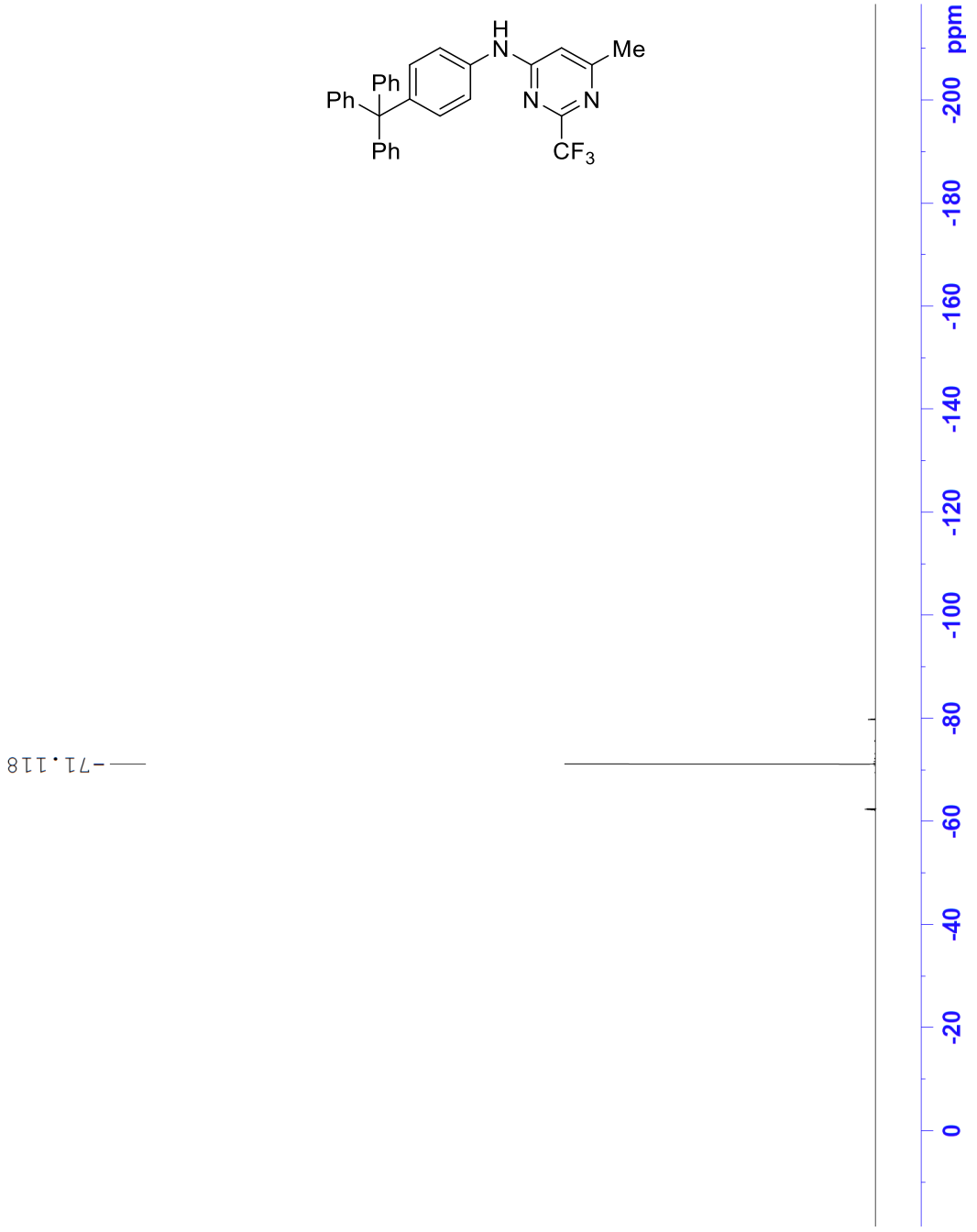
^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-2-(trifluoromethyl)-*N*-(4-tritylphenyl)pyrimidin-4-amine (3x)



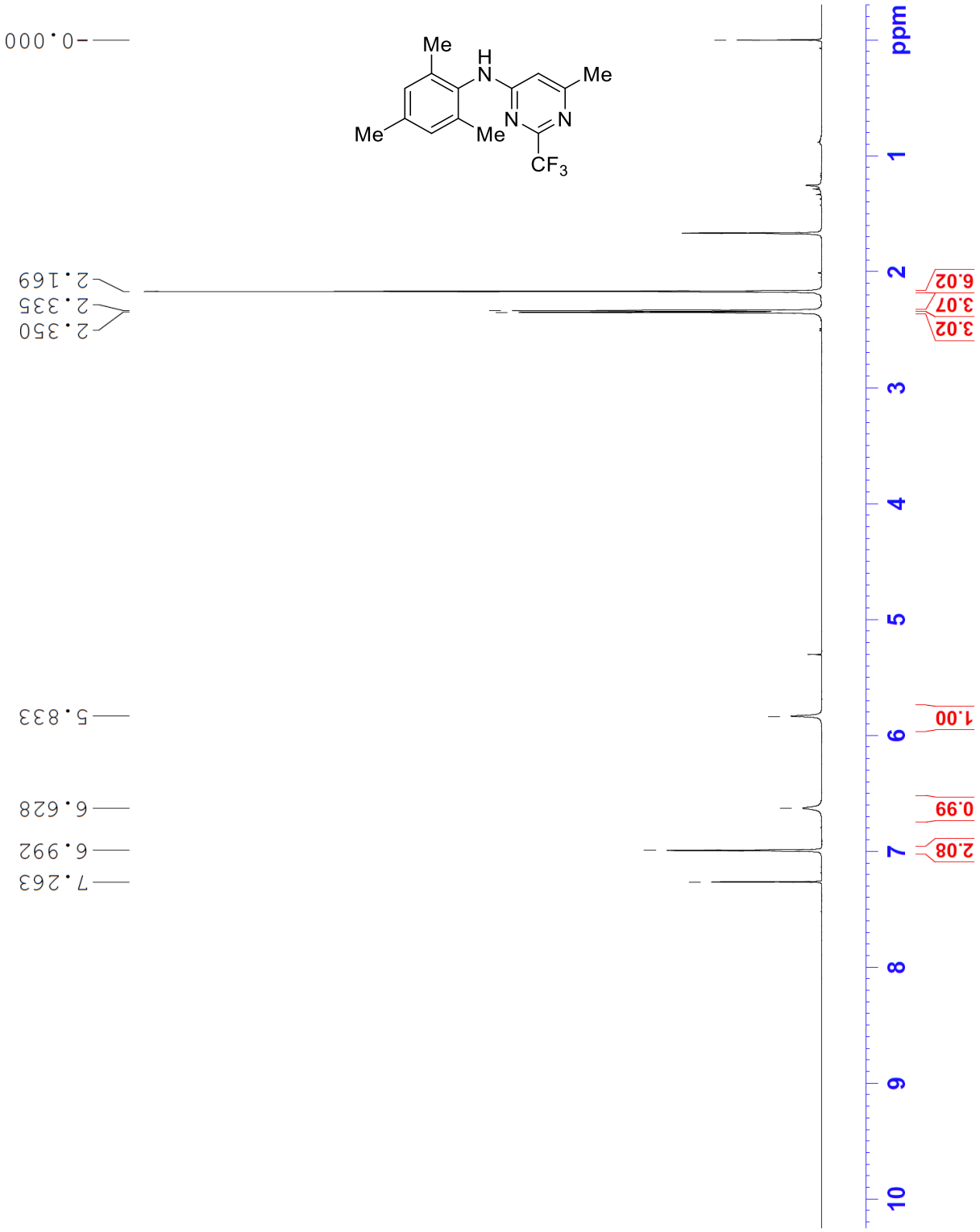
^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-2-(trifluoromethyl)-*N*-(4-tritylphenyl)pyrimidin-4-amine (3x)



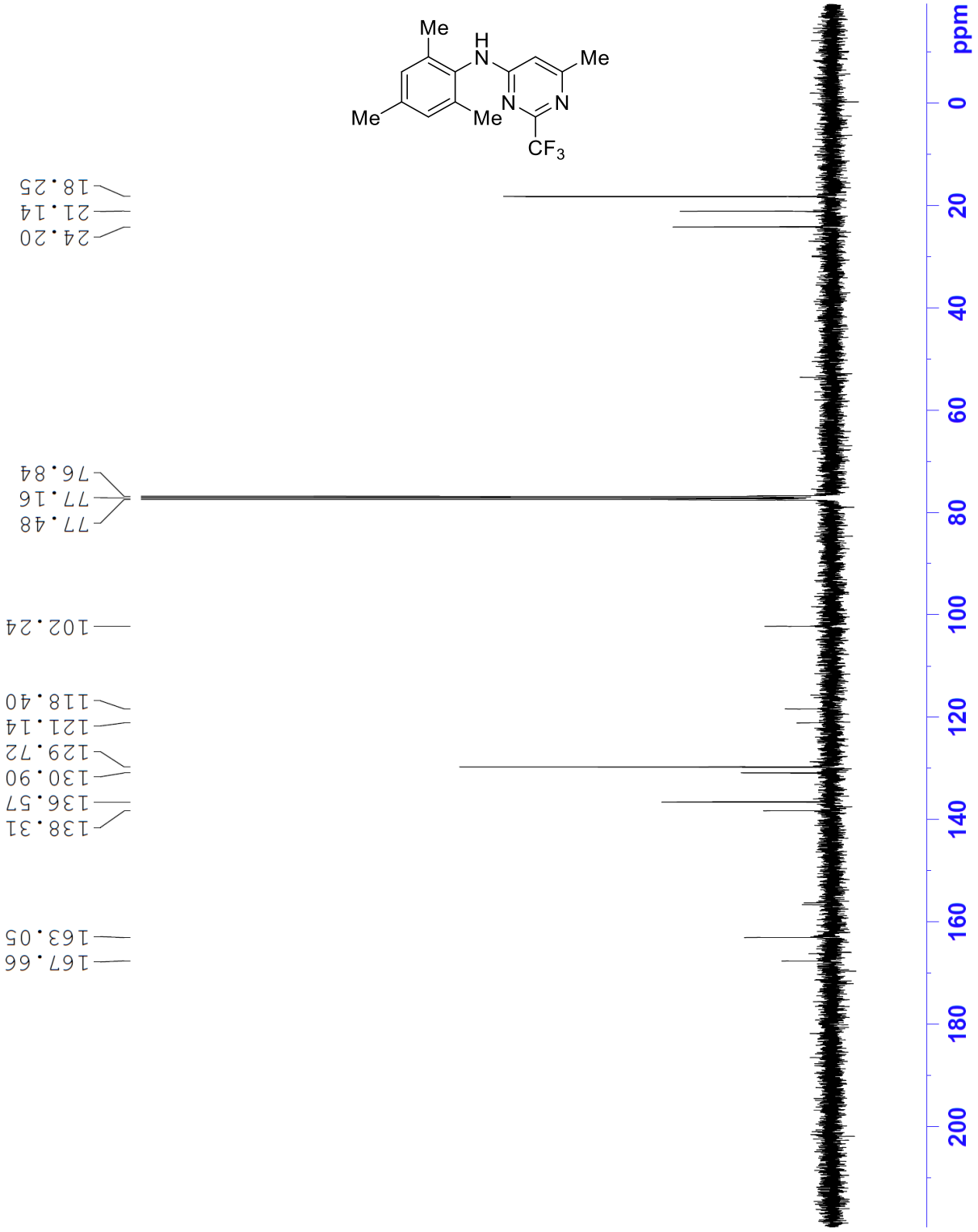
^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-2-(trifluoromethyl)-*N*-(4-tritylphenyl)pyrimidin-4-amine (3x)



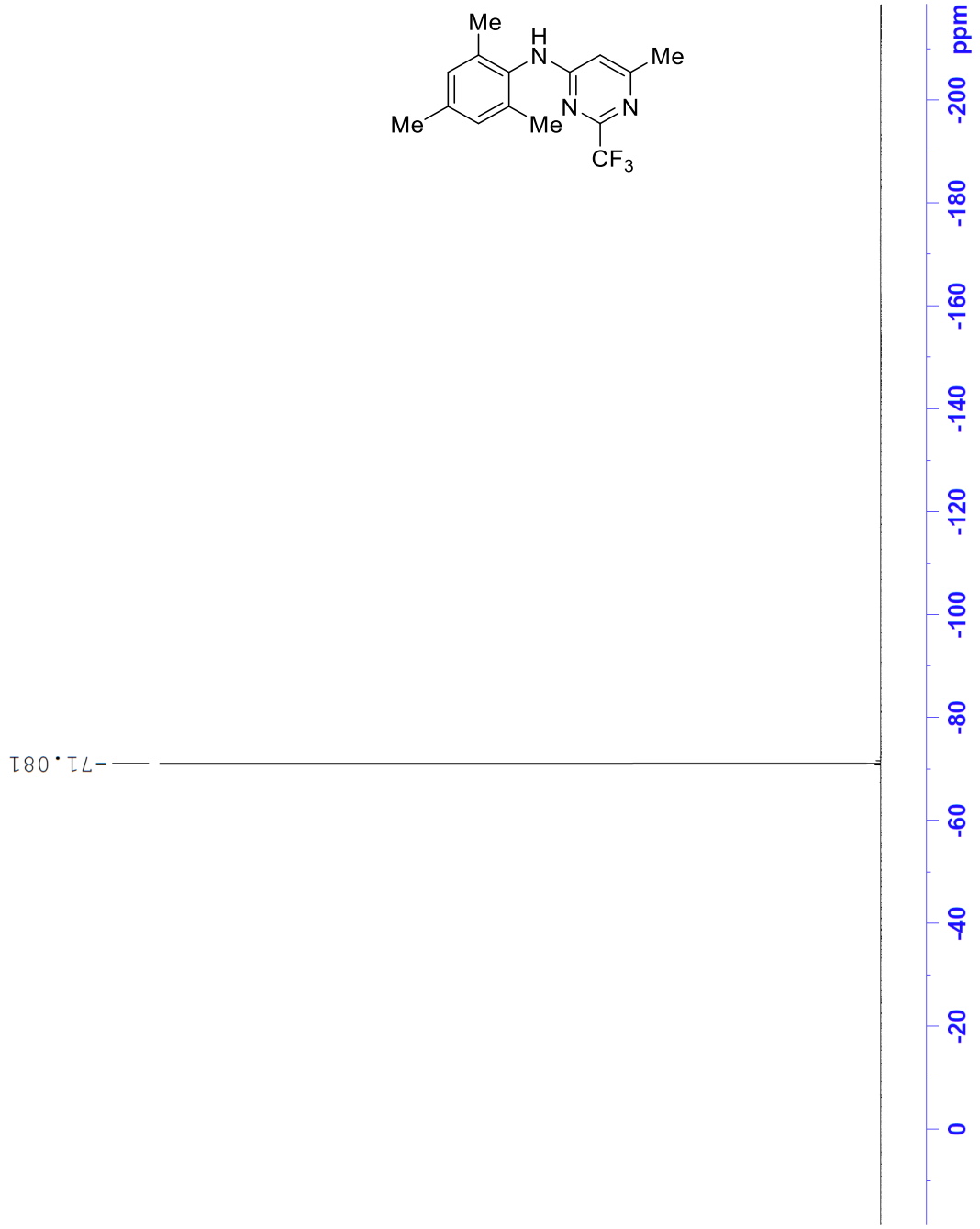
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-Mesityl-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3y)



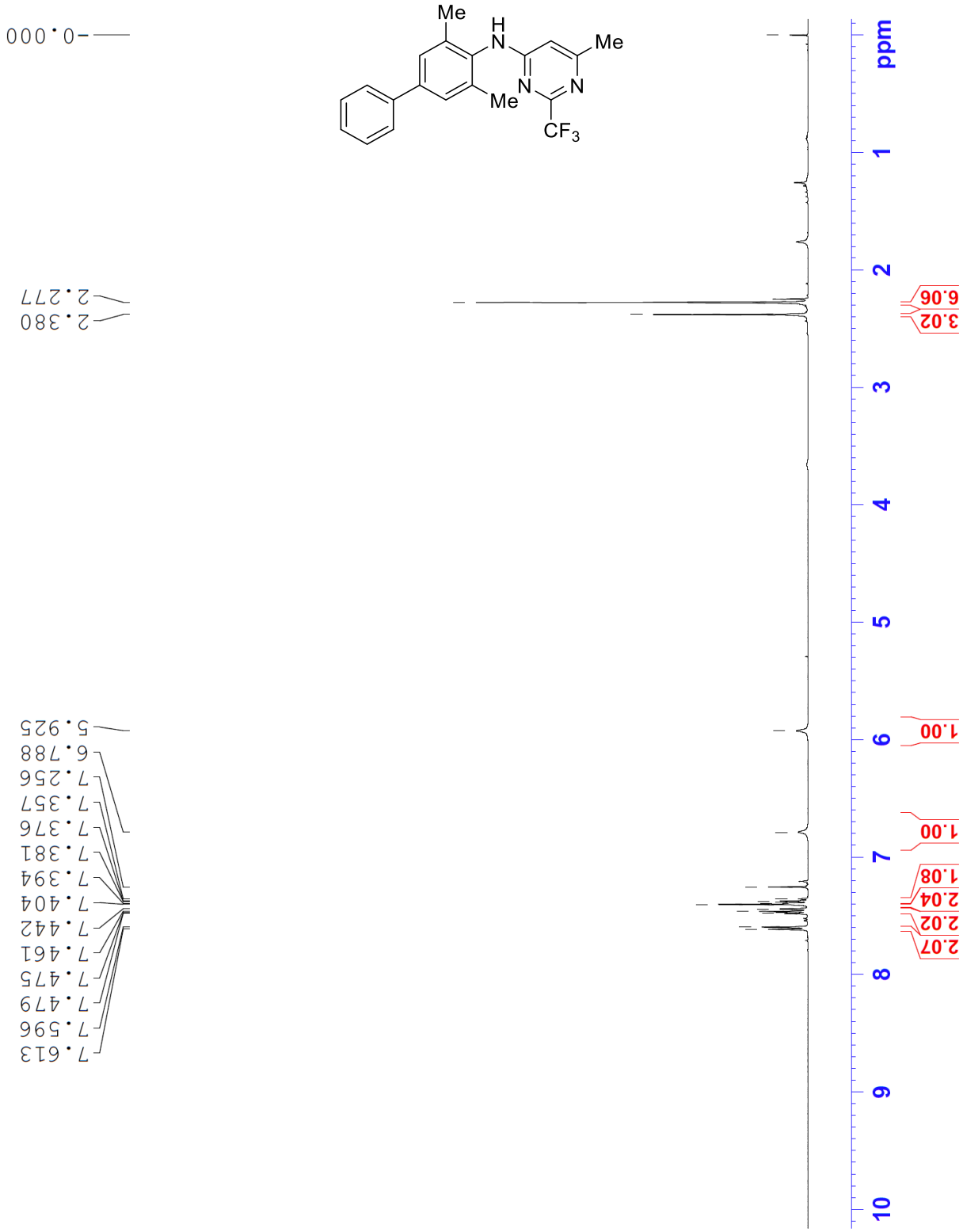
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-Mesityl-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3y)



^{19}F NMR (376 MHz, $CDCl_3$) of *N*-Mesityl-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3y)



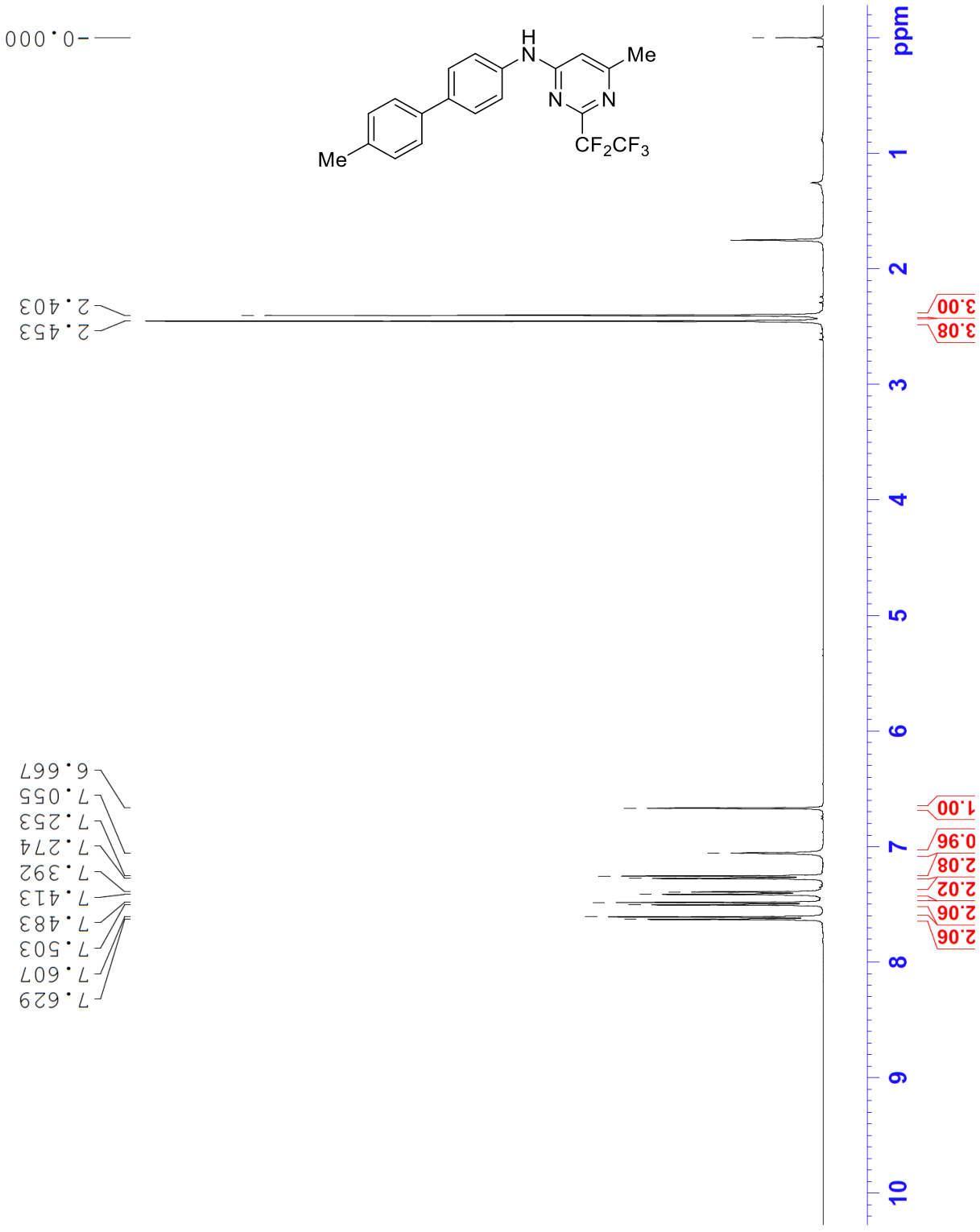
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(3,5-Dimethyl-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3z)



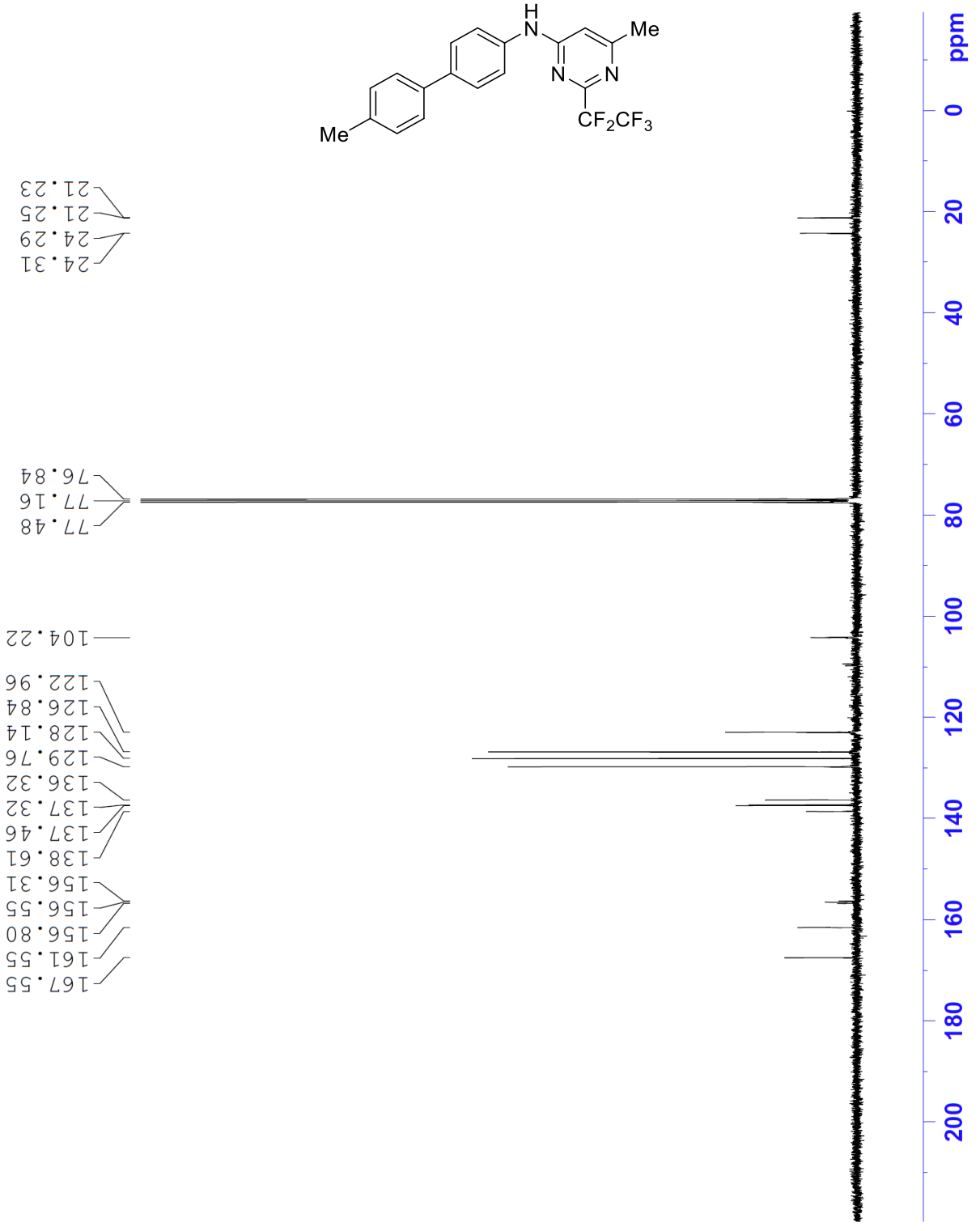
^{13}C NMR (100.6 MHz, $CDCl_3$) of *N*-(3,5-Dimethyl-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3z)

^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(3,5-Dimethyl-[1,1'-biphenyl]-4-yl)-6-methyl-2-(trifluoromethyl)pyrimidin-4-amine (3z)

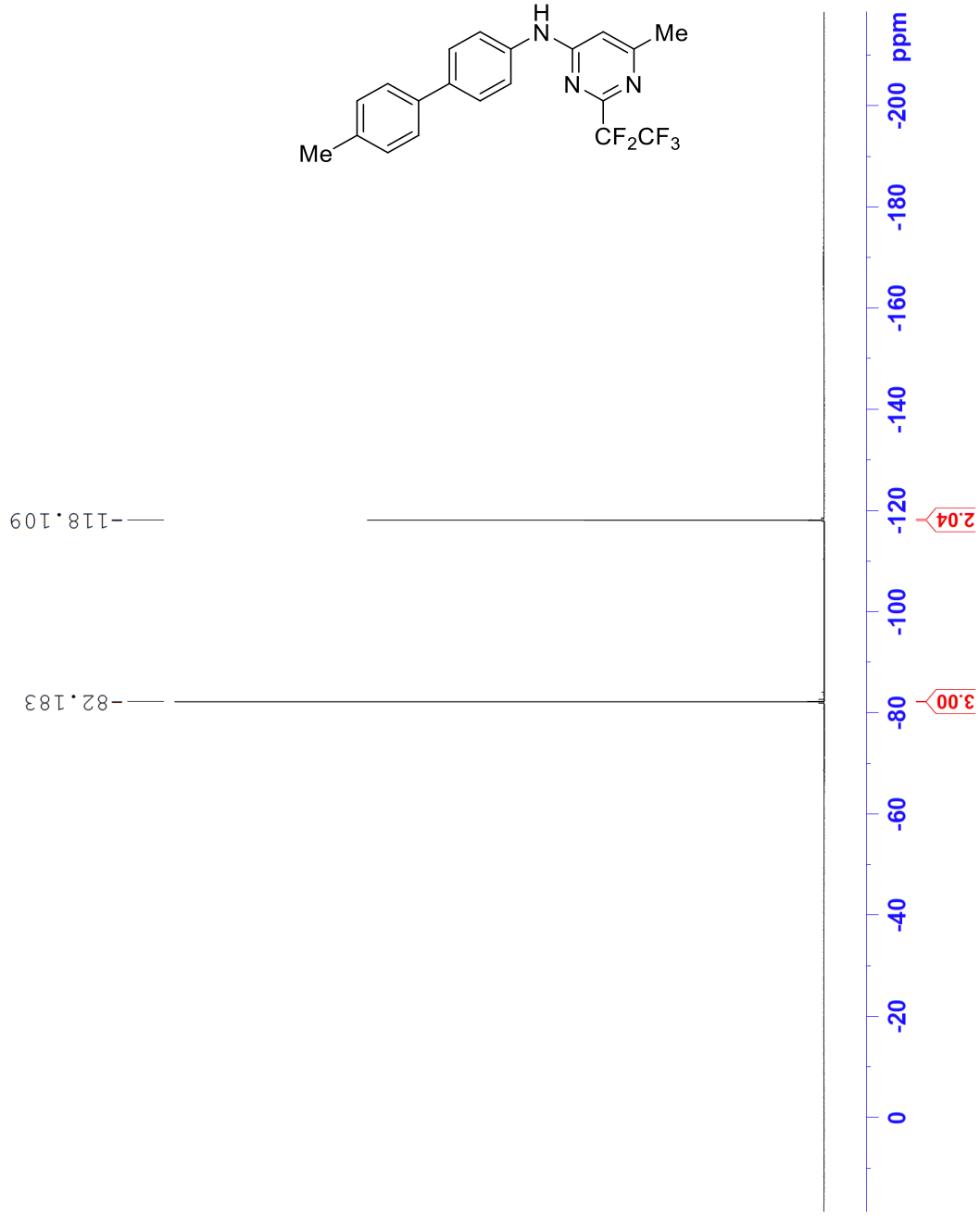
^{1}H NMR (400 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(perfluoroethyl)pyrimidin-4-amine (3aa)



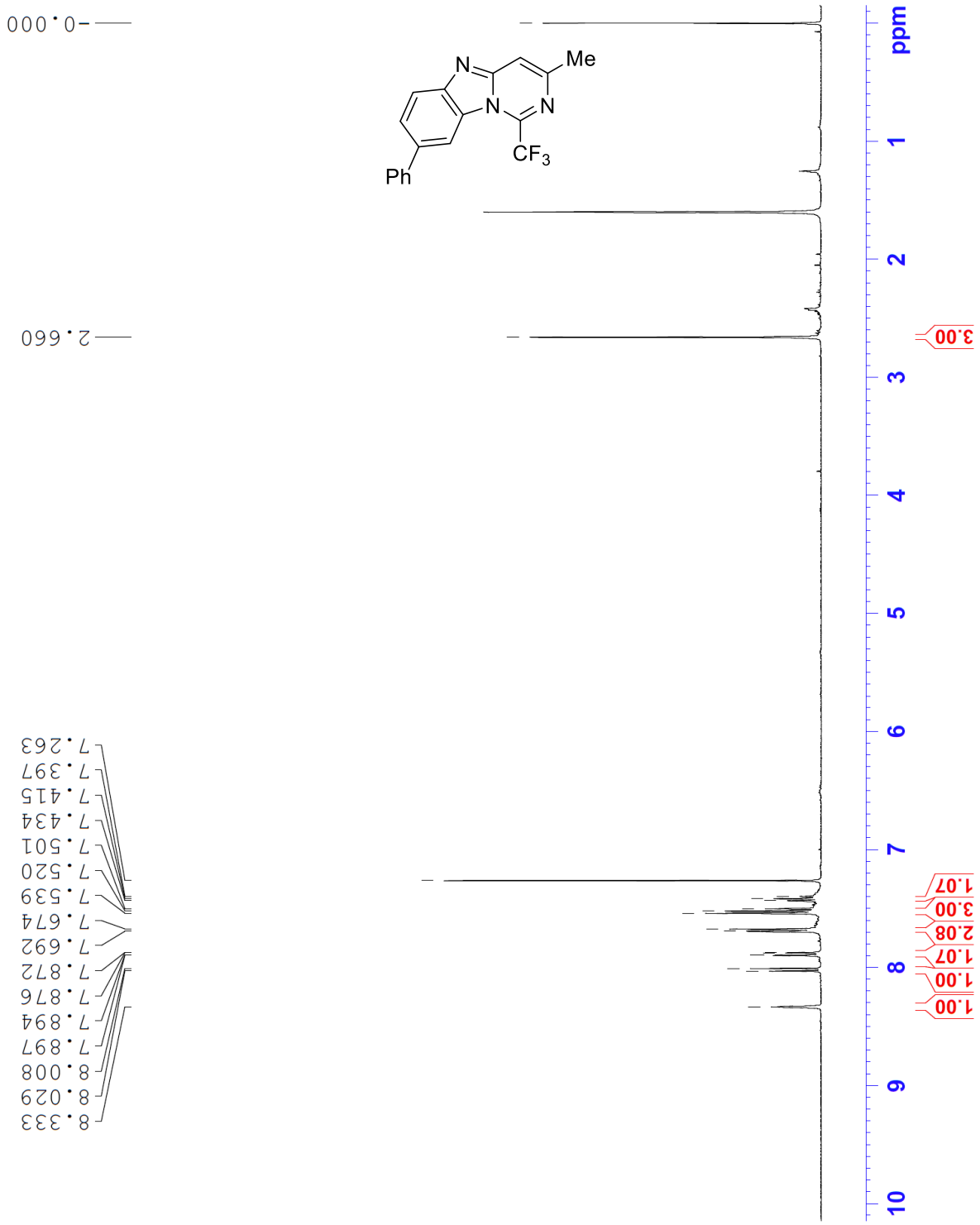
^{13}C NMR (100.6 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(perfluoroethyl)pyrimidin-4-amine (3aa)



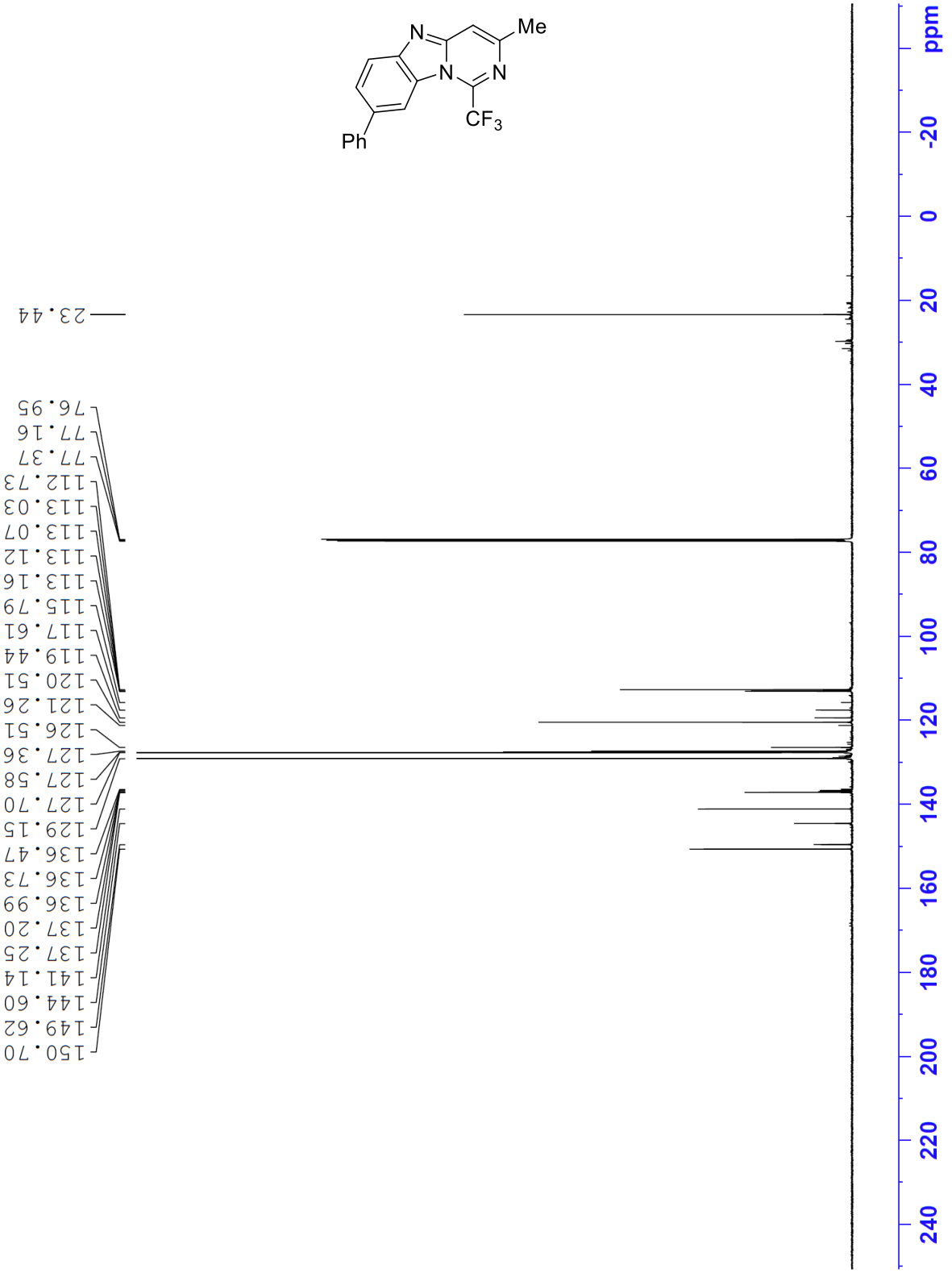
^{19}F NMR (376 MHz, $CDCl_3$) of 6-Methyl-*N*-(4'-methyl-[1,1'-biphenyl]-4-yl)-2-(perfluoroethyl)pyrimidin-4-amine (3aa)



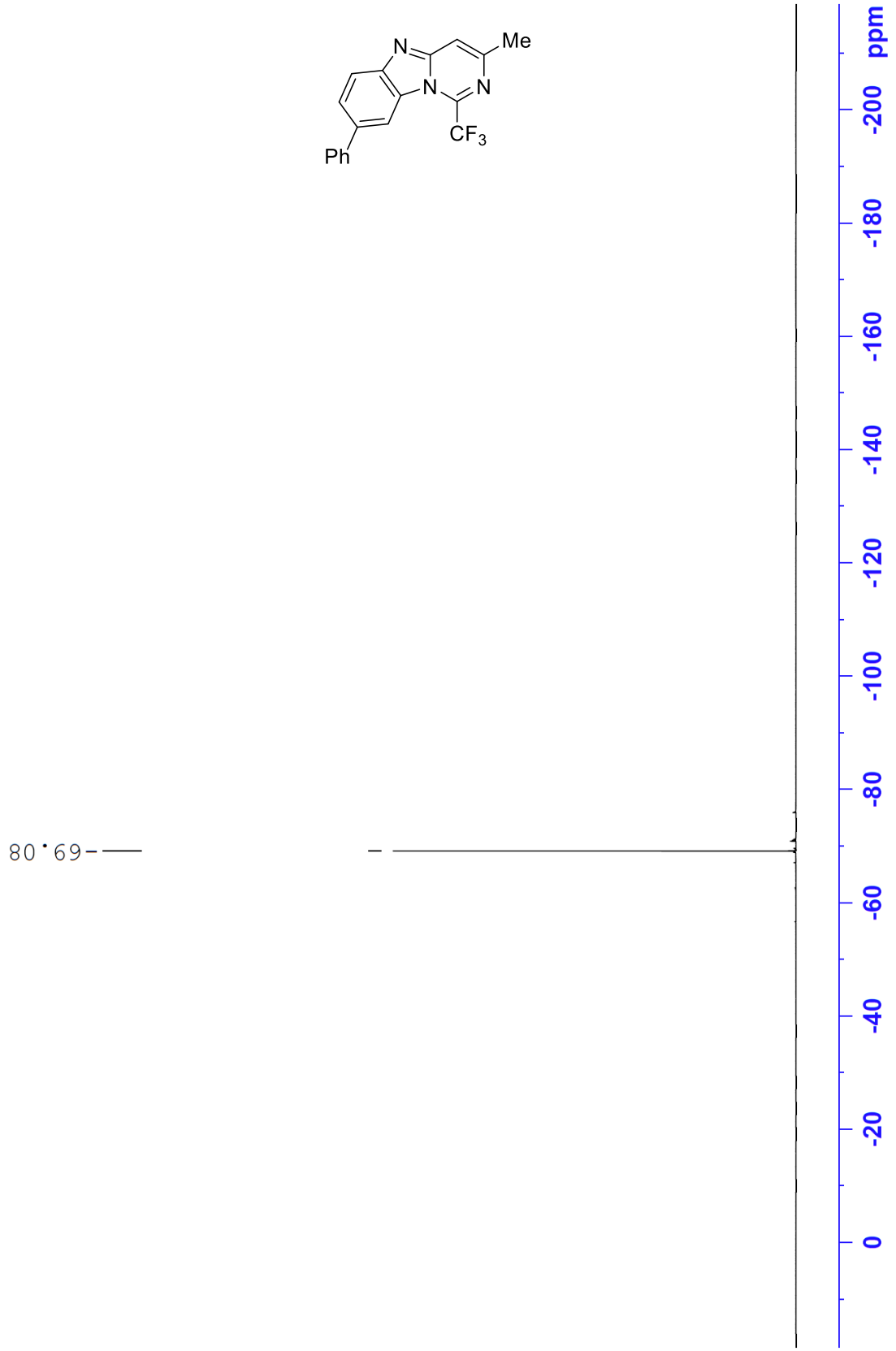
^{1}H NMR (400 MHz, $CDCl_3$) of 3-Methyl-8-phenyl-1-(trifluoromethyl)benzo[4,5]imidazo[1,2-*c*]pyrimidine (3a')



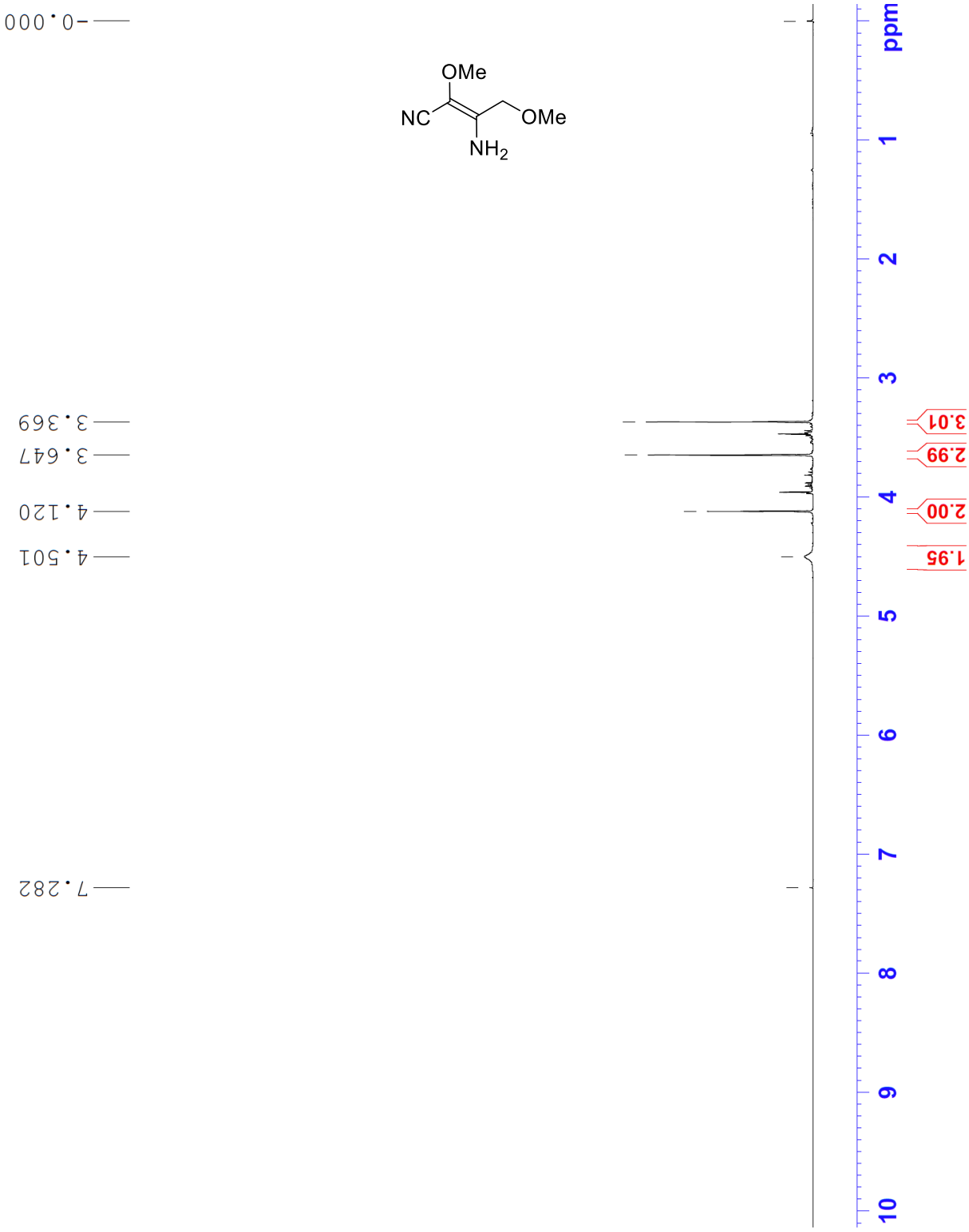
^{13}C NMR (150.9 MHz, $CDCl_3$) of 3-Methyl-8-phenyl-1-(trifluoromethyl)benzo[4,5]imidazo[1,2-*c*]pyrimidine (3a')



^{19}F NMR (376 MHz, $CDCl_3$) of 3-Methyl-8-phenyl-1-(trifluoromethyl)benzo[4,5]imidazo[1,2-*c*]pyrimidine (3a')



^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-3-Amino-2,4-dimethoxybut-2-enenitrile (4)



^{13}C NMR (100.6 MHz, $CDCl_3$) of (*E*)-3-Amino-2,4-dimethoxybut-2-enenitrile (4)