Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information For

Synthesis of 2,4-Diarylated Pyrimidines Enabled by Ni-catalyzed C-Sulfone Bond Activation

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1. General Information

Flash column chromatography was performed using silica gel (300-400 mesh) purchased from Qindao Haiyang. $Ni(COD)_2$, $PCy_3 \cdot HBF_4$, dry THF and other dry solvents were purchased from Energy Chemicals or TCI Chemicals and used as received. Dry toluene was freshly distilled from sodium/benzophenone under N_2 atmosphere. Other ligands were purchased from Energy Chemicals, TCI Chemicals, or Sigma-Aldrich and used without further purification.

Unless otherwise noted, all reported yields of the reactions are isolated yields of purified products. NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HR-MS), and melting point (if solids). NMR spectra were recorded on a Bruker AMX 400 spectrometer and were calibrated using TMS (0.00 ppm) or residual deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; $(CD_3)_2SO$: 2.50 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR), and the tabulated data were reported in ppm. IR spectra were taken on Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). HR-MS spectra were recorded on a Waters Q-TOF Premier. Melting points (m.p.) were recorded on an INESA SGW X-4 melting point apparatus.

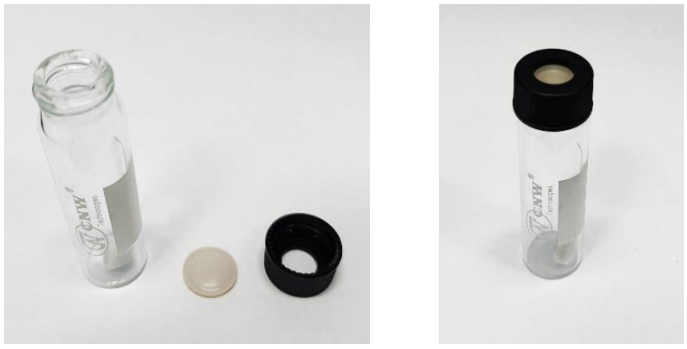
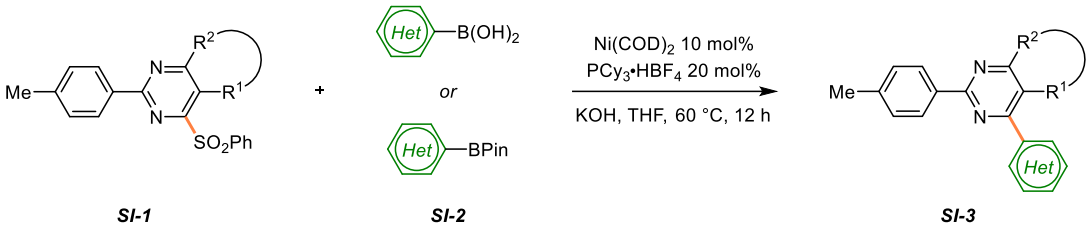


Figure S1. Reaction Vials (8 mL)

2. General Procedure for the Ni-Catalyzed Cross-Coupling Reaction



Pyrimidinyl sulfone **SI-1** (0.2 mmol, 1.0 equiv.), aryl boronic acid (or boronic acid pinacol ester) **SI-2** (0.4 mmol, 2.0 equiv.), and $Cy_3P•HBF_4$ (0.04 mmol, 20 mol%) were weighed into a dried screw-capped vial containing a magnetic stir bar. The vial was loosely capped and transferred into a nitrogen-filled glovebox. To the vial was sequentially added $Ni(COD)_2$ (0.02 mmol, 10 mol%), powderized KOH (0.4 mmol, 2.0 equiv.), and THF (0.1 M). The vial was tightly sealed with a Teflon-lined cap, and taken out of the glovebox. The mixture was stirred at 60 ºC for 12 h. After completion, the reaction was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with saturated NH_4Cl. The aqueous phase was then extracted with ethyl acetate (10 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give product **SI-3**.

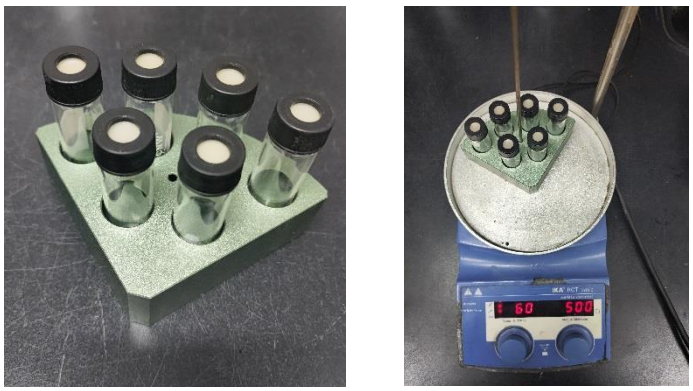
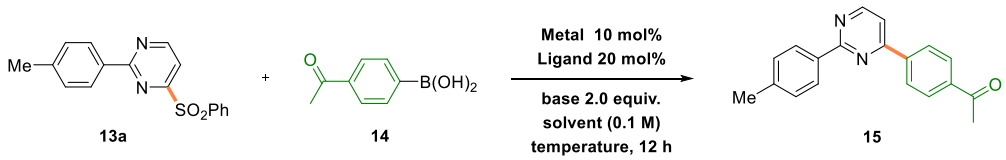


Figure S2. Reactor used in this study

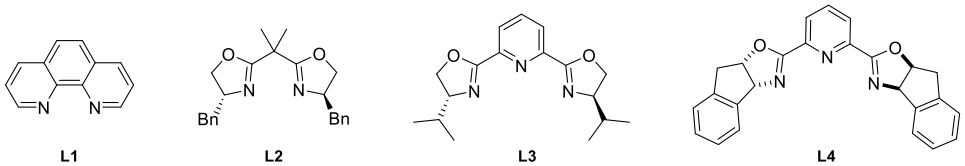
3. Condition Optimization

Table S1. Other Representative Conditions Not Listed in Table 1

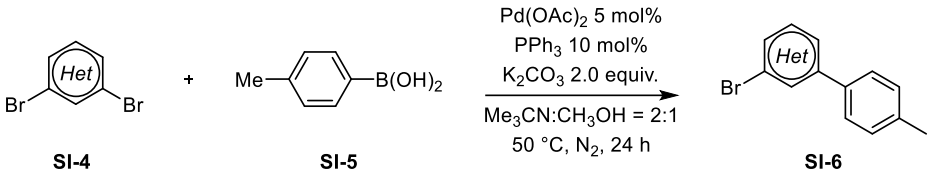


entry	Metal	Ligand	base	solvent	temperature	conversion of **13a**	yield of **15**
1	$Pd(PPh_3)_4$	–	K_2CO_3	THF	40 °C	7%	0%
2	$NiBr_2$	PPh_3	K_2CO_3	THF	40 °C	17%	0%
3	$Ni(OTf)_2$	PPh_3	K_2CO_3	THF	40 °C	22%	0%
4	$Ni(COD)_2$	PPh_3	K_2CO_3	THF	40 °C	40%	11%
5	$Ni(COD)_2$	L1	K_2CO_3	THF	40 °C	7%	0%
6	$Ni(COD)_2$	L2	K_2CO_3	THF	40 °C	10%	0%
7	$Ni(COD)_2$	L3	K_2CO_3	THF	40 °C	8%	0%
8	$Ni(COD)_2$	L4	K_2CO_3	THF	40 °C	22%	3%
9	$Ni(COD)_2$	S-Phos	K_2CO_3	THF	40 °C	43%	4%
10	$Ni(COD)_2$	RuPhos	K_2CO_3	THF	40 °C	26%	5%
11	$Ni(COD)_2$	BINAP	K_2CO_3	THF	40 °C	26%	6%
12	$Ni(COD)_2$	dppm	K_2CO_3	THF	40 °C	33%	11%
13	$Ni(COD)_2$	dpppe	K_2CO_3	THF	40 °C	96%	59%
14	$Ni(COD)_2$	PCy_3	K_2CO_3	THF	40 °C	93%	48%
15	$Ni(COD)_2$	PCy_3•HBF_4	Et_3N	THF	40 °C	48%	25%
16	$Ni(COD)_2$	PCy_3•HBF_4	K_3PO_4	THF	40 °C	59%	48%
17	$Ni(COD)_2$	PCy_3•HBF_4	Na_3PO_4	THF	40 °C	10%	8%
18	$Ni(COD)_2$	PCy_3•HBF_4	KF	THF	40 °C	40%	12%
19	$Ni(COD)_2$	PCy_3•HBF_4	*t*-BuOK	THF	40 °C	95%	37%
20[b]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	DCM	40 °C	15%	4%
21[b]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	EA	40 °C	25%	8%
22[b]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	MeCN	40 °C	40%	20%
23[b]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	dioxane	40 °C	35%	8%
24[b]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	THF	60 °C	82%	77%
25[c]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	THF	60 °C	100%	87%
26[d]	$Ni(COD)_2$	PCy_3•HBF_4	KOH	THF	60 °C	20%	0%

[a] Unless otherwise specified, Reactions in this **Table S1** were performed under a N_2 atmosphere, using **13a** (0.05 mmol, 1.0 equiv.), **14** (0.10 mmol, 2.0 equiv.), and solvent (0.5 mL) for 12 h. Yield and conversion were determined by 1H NMR using 1,3,5-trimethoxybenzene as internal standard. [b] **14** (0.075 mmol, 1.5 equiv.), and KOH (0.075 mmol, 1.5 equiv.) was used. [c] $Ni(COD)_2$ (5 mol%), and PCy_3•HBF_4 (10 mol%) was used. [d] Under air condition.

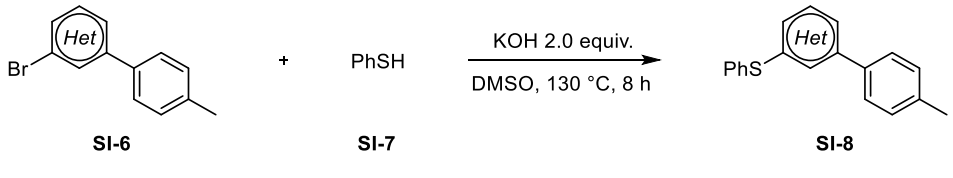


4. General Procedures for Control Experiments



The reaction was prepared according to the literature reported.[1]

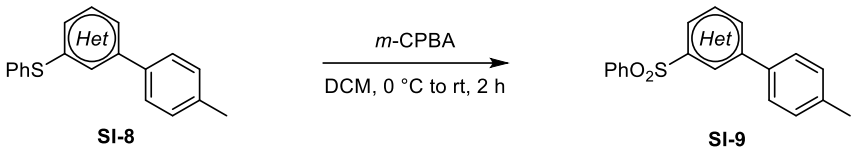
Dibromopyridine (**SI-4** 5.0 mmol), 4-tolylboronic acid (**SI-5**, 5.0 mmol, 1.0 equiv.), K_2CO_3 (5.0 mmol, 2.0 equiv.), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) were weighed into a dried 50 mL thick wall pressure bottle containing a magnetic stir bar. The bottle was then transferred into a nitrogen-filled glovebox. The reaction mixture was dissolved in dried CH_3CN/CH_3OH (2:1). The round bottom flask was tightly sealed, and taken out of the glovebox. The thick wall pressure bottle was stirred at 50 ºC under N_2 atmosphere for 24 h. After completion, the reaction mixture was cooled to room temperature and the solid was filtered off. The filtrate was then concentrated and the resulting crude product was dissolved in DCM (30 mL). The solution was washed with water (10 mL×3) and brine (10 mL×1), and dried over Na_2SO_4. Upon removal of the solvent under vacuum, the resulting residue was subjected to flash silica gel column chromatography (petroleum ether/DCM) to give the desired product **SI-6**.



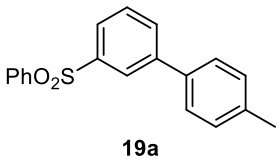
The reaction was prepared according to the literature reported.[2]

A sealable tube equipped with a magnetic stir bar was charged with the aryl bromide **SI-6** (4.0 mmol, 1.0 equiv.), KOH (8.0 mmol, 2.0 equiv.), and thiophenol **SI-7** (4.0 mmol, 1.0 equiv.). The reaction tube was loosely capped and transferred into a nitrogen-filled glovebox. Dry DMSO (10 mL) was added by syringe. The reaction tube was screw capped and put into a preheated oil bath (110-130 ºC) for 8 h. The reaction mixture was then allowed to reach room

temperature before it was treated with DCM (5 mL) and H_2O (10 mL). The aqueous phase was separated and extracted with DCM (3 x 5 mL), and the combined organic phase was washed with H_2O (10 mL×3) and brine (10 mL×1), dried with Na_2SO_4, filtered and concentrated under reduced pressure. After removal of the solvent the residue was purified by flash column chromatography on silica gel (petroleum ether/DCM) to obtain the corresponding product **SI-8**.



To a DCM solution (30 mL) of **SI-8** (4.0 mmol, 1.0 equiv.) cooled at 0 °C was added *m*-CPBA (9.6 mmol, 2.4 equiv.) dropwise over 10 min. The reaction was allowed to warm to room temperature and stirred for another 2h, and then diluted by addition of DCM. The mixture washed by sat. aq. $NaHCO_3$ (30 mL×2), and brine (10 mL×1). The mixture was extracted with DCM, and the combined organic layers were dried and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give Product **SI-9** as a white solid.

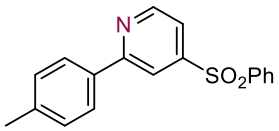


4'-methyl-3-(phenylsulfonyl)-1,1'-biphenyl (19a)

Following **General Procedure**, 1,3-dibromobenzene (5.0 mmol, 1.18 g) was used. Compound **19a** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 10/1) as a white solid (0.42 g, 3 steps yield 27%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (d, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.60–7.40 (m, 6H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 142.2, 141.7, 138.4, 136.3, 133.3, 131.6, 129.9, 129.8, 129.4, 127.7, 127.1, 126.1, 125.9, 21.2. **IR (thin film, cm^{-1})**: 3083, 2917, 1587, 1547, 1445, 1313, 1270, 1159, 1133, 1083, 987, 798, and 758 cm^{-1}. **m.p.**: 98.9–101.9 °C. **HRMS (DART-TOF)**

calculated for $C_{19}H_{17}O_2S^+$ $[M+H]^+$ m/z 309.0944, found 309.0955.

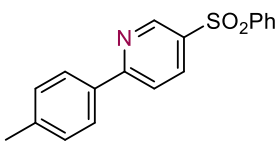


19b

4-(phenylsulfonyl)-2-(*p*-tolyl) pyridine (19b)

Following **General Procedure**, 2,4-dibromopyridine (5.0 mmol, 1.18 g) was used. Compound **19b** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 5/1) as a white solid (0.52 g, 3 steps yield 34%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.2 Hz, 1H), 8.17 (s, 1H), 8.00 (d, *J* = 6.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.74–7.60 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4, 151.0, 150.7, 140.5, 140.0, 135.0, 134.2, 129.9, 129.7, 128.2, 127.1, 118.5, 117.0, 21.5. **IR (thin film, cm^{-1})**: 3059, 2920, 1611, 1575, 1551, 1447, 1387, 1323, 1270, 1158, 1110, 1080, 1018, 818, and 758 cm^{-1}. **m.p.**: 106.8–109.8 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{16}NO_2S^+$ $[M+H]^+$ m/z 310.0896, found 310.0909.



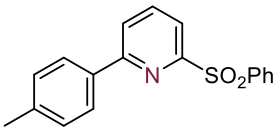
19c

5-(phenylsulfonyl)-2-(*p*-tolyl) pyridine (19c)

Following **General Procedure**, 2,5-dibromopyridine (5.0 mmol, 1.18 g) was used. Compound **19c** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 5/1) as a light yellow solid (0.22 g, 3 steps yield 14%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.4 Hz, 1H), 8.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.4, 148.9, 141.4, 141.0, 136.1, 135.9, 134.8, 133.8, 129.9, 129.7, 127.8, 127.5, 120.0, 21.5. **IR (thin film, cm^{-1})**: 3059, 2925, 1579, 1555, 1465, 1447, 1371, 1323, 1309, 1278, 1260, 1160,

1116, 1078, 1011, 815, 765, 752 and 747 cm^{-1}. **m.p.**: 177.1–180.1 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{16}NO_2S^+$ $[M+H]^+$ m/z 310.0896, found 310.0906.



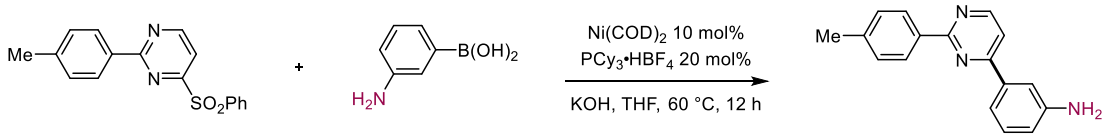
19d

2-(phenylsulfonyl)-6-(*p*-tolyl) pyridine (19d)

Following **General Procedure**, 2,6-dibromopyridine (5.0 mmol, 1.18 g) was used. Compound **19d** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 5/1) as a white solid (0.48 g, 3 steps yield 31%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 1H), 7.85–7.77 (m, 3H), 7.61–7.57 (m, 1H), 7.54–7.51 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6, 158.1, 140.4, 139.1, 138.7, 134.4, 133.7, 129.7, 129.3, 129.0, 127.0, 122.9, 119.5, 21.4. **IR (thin film, cm^{-1})**: 3062, 2917, 1595, 1472, 1446, 1304, 1270, 1154, 1105, 1074, 832, 793, 777, and 752 cm^{-1}. **m.p.**: 143.2–146.2 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{16}NO_2S^+$ $[M+H]^+$ m/z 310.0896, found 310.0897.

5. General Procedures for the Scale-Up Experiment



13a
4.5 mmol

16l
9.0 mmol

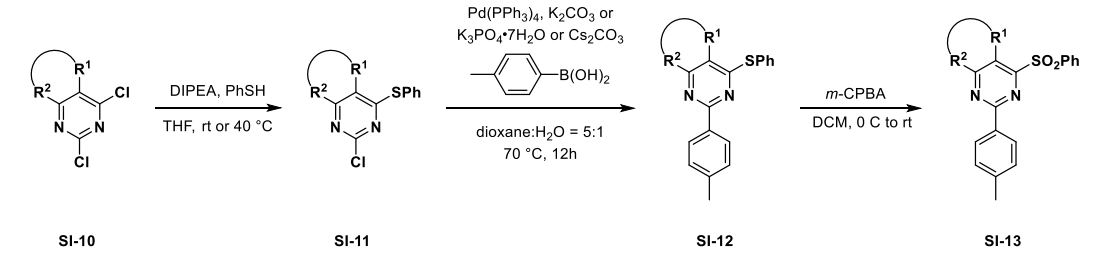
17l
0.85 g, 72% yield

To a dried 100 mL thick wall pressure bottle equipped with a stir bar was added pyrimidinyl sulfone **13a** (1.40 g, 4.5 mmol, 1.0 equiv.), 3-Aminophenylboronic acid monohydrate **16l** (1.40 g, 9.0 mmol, 2.0 equiv.), and PCy_3•HBF_4 (0.33 g, 0.9 mmol, 0.2 equiv.). The bottle was loosely capped and transferred into a nitrogen-filled glovebox. To the thick wall pressure bottle was sequentially added $Ni(COD)_2$ (0.12 g, 0.45 mmol, 0.1 equiv.), powderized KOH (0.45 g, 9.0 mmol, 2.0 equiv.), and THF (45 mL, 0.1 M). The thick wall pressure bottle

was tightly sealed, and taken out of the glovebox. The mixture was stirred at preheated oil bath (60 ºC) for 12 h. After completion, the reaction was cooled to room temperature, and removed the solvent under vacuum. The crude mixture was dissolved in EtOAc and washed with an aqueous solution of NH_4Cl (30 mL×2), $NaHCO_3$ (30 mL×1), and brine (20 mL×1). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) to give product **17l** as a white solid (0.85g, 72%).

6. General Procedures for Pyrimidinyl Sulfone Electrophiles

6.1 Procedures for the Synthesis of General Pyrimidinyl Sulfones



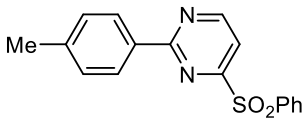
The reaction was prepared according to the literature reported.

Thiophenol (1.0 equiv.) was added dropwise to a stirred solution of DIPEA (1.2 equiv.) and 2,4-Dichloropyrimidine (**SI-10**, 1.0 equiv.) in THF at 0 ºC. The reaction mixture was heated to 50 ºC (or room temperature) overnight. After completion, the solvents were removed and the crude mixture was dissolved in EtOAc and washed with an aqueous solution of NH_4Cl (30 mL×2), $NaHCO_3$ (30 mL×1), and brine (20 mL×1). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give the crude Product **SI-11**.[3]

The crude Product **SI-11** (1.0 equiv.), 4-tolylboronic acid (1.5 equiv.), base (K_2CO_3, or Cs_2CO_3, or $K_3PO_4 \cdot 7H_2O$, 2.0equiv.), were weighed into a dried 50 mL thick wall pressure bottle containing a magnetic stir bar. The bottle was then transferred into a nitrogen-filled glovebox. To the bottle was added $Pd(PPh_3)_4$ (5 mol%) and solvent dioxane/ H_2O (5:1). The thick wall pressure bottle was tightly sealed, and taken out of the glovebox. The solution was stirred at 70 ºC under oil bath for 12 h. After completion, the reaction mixture was cooled to room

temperature and the solid was filtered off. The filtrate was then concentrated and the resulting crude product was dissolved in EtOAc (30 mL). The solution was washed with water (10 mL×3) and brine (10 mL×1), and dried over Na_2SO_4. Upon removal of the solvent under vacuum, the resulting residue was subjected to flash silica gel column chromatography (petroleum ether/EtOAc) to give the crude product **SI-12**.[4]

To a DCM solution of crude product **SI-12** (1.0 equiv.) cooled at 0 °C was added *m*-CPBA (2.4 equiv.) dropwise over 10 min. The reaction was allowed to warm to room temperature and stirred for another 2h, and then diluted by addition of DCM. The mixture washed by sat. aq. $NaHCO_3$ (30 mL×2), and brine (10 mL×1). The mixture was extracted with DCM, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give Product **SI-13** as a white solid.

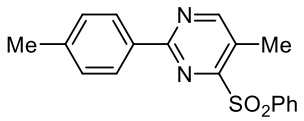


13a

4-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine (13a)

Following **General Procedure**, 2,4-dichloropyrimidine (10.0 mmol, 1.49 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use $K_3PO_4 \cdot 7H_2O$ (20.0 mmol, 6.77 g) as base. Compound **13a** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 5/1) as a white solid (1.21 g, 3 steps yield 39%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 4.8 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 8.15 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 4.8 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.0, 165.7, 160.4, 142.5, 137.5, 134.6, 133.2, 129.7, 129.6, 129.3, 128.7, 114.4, 21.7 (d, *J* = 3.8 Hz). **IR (thin film, cm^{-1})**: 3069, 3017, 2917, 1612, 1558, 1532, 1406, 1381, 1325, 1170, 1144, 751, 727, 592, and 579 cm^{-1}. **m.p.**: 149.9–152.9 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{15}N_2O_2S^+$ $[M+H]^+$ m/z 311.0849, found 311.0850.

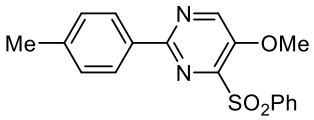


13b

5-methyl-4-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine (13b)

Following **General Procedure**, 2,4-dichloro-5-methylpyrimidine (10.0 mmol, 1.63 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use $K_3PO_4 \cdot 7H_2O$ (20.0 mmol, 6.77g) as base. Compound **13b** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 10/1) as a white solid (1.69 g, 3 steps yield 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.75 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.1, 162.3, 162.2, 141.8, 137.4, 134.2, 133.2, 130.1, 129.4, 128.9, 128.0, 125.4, 21.6 (d, *J* = 3.8 Hz), 15.2 (d, *J* = 3.6 Hz). **IR (thin film, cm^{-1})**: 3005, 2984, 1696, 1570, 1516, 1420, 1307, 1275, 1261, 1152, 1110, 763, 749, and 690 cm^{-1}. **m.p.**: 176.8–179.8 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{17}N_2O_2S^+$ $[M+H]^+$ m/z 325.1005, found 325.1012.

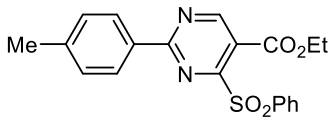


13c

5-methoxy-4-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine (13c)

Following **General Procedure**, 2,4-dichloro-5-methoxypyrimidine (10.0 mmol, 1.79 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use Cs_2CO_3 (20.0 mmol, 6.51g) as base. Compound **13c** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 5/1) as a white solid (1.09 g, 3 steps yield 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.08 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.7, 153.2, 148.4, 144.3, 141.0, 137.8, 134.2, 133.2, 130.0, 129.4, 128.9, 127.7, 57.2 (d, *J* = 5.4 Hz), 21.5 (d, *J* = 4.0 Hz). **IR (thin film, cm^{-1})**: 3050, 3008, 2946, 2865, 1554, 1414, 1318, 1276, 1195, 1139, 1082, 1005, 764, 750, 690, and 579 cm^{-1}. **m.p.**: 207.1–210.1 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{17}N_2O_3S^+$ $[M+H]^+$ m/z 341.0954, found 341.0950.

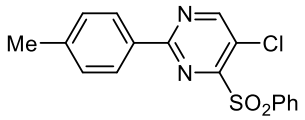


13d

ethyl 4-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine-5-carboxylate (13d)

Following **General Procedure**, ethyl 2,4-dichloropyrimidine-5-carboxylate (10.0 mmol, 2.21 g) was used and the SNAr reaction was react at room temperature. The Suzuki reaction was use $K_3PO_4 \cdot 7H_2O$ (20.0 mmol, 6.51g) as base. Compound **13d** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 10/1) as a white solid (1.11 g, 3 steps yield 29%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.12 (d, *J* = 7.2 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.56 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.5, 164.8, 163.9, 160.1, 143.4, 137.6, 134.4, 132.4, 130.2, 129.7, 129.0, 129.0, 121.0, 63.2, 21.7 (d, *J* = 3.7 Hz,), 14.1. **IR (thin film, cm^{-1})**: 3069, 2986, 1730, 1564, 1511, 1426, 1328, 1305, 1260, 1154, 793, 751, 727, and 591 cm^{-1}. **m.p.**: 92.1–95.1 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{19}N_2O_4S^+$ $[M+H]^+$ m/z 383.1060, found 383.1061.



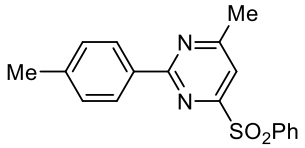
13e

5-chloro-4-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine (13e)

Following **General Procedure**, 2,4,5-trichloropyrimidine (10.0 mmol, 1.83 g) was used and the SNAr reaction was react at room temperature. The Suzuki reaction was use $K_3PO_4 \cdot 7H_2O$ (20.0 mmol, 6.51g) as base. Compound **13e** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 10/1) as a white solid (1.31 g, 3 steps yield 38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.1, 161.7, 160.5, 142.7, 136.7, 134.6, 132.2, 130.2, 129.6, 129.1, 128.5, 124.5, 21.6 (d, *J* = 3.3 Hz). **IR (thin film, cm^{-1})**: 3069, 3036, 2927, 1608, 1546, 1506, 1448, 1405, 1326, 1178, 1153, 1090, 779, 756, 727, 688, 594, and 588 cm^{-1}. **m.p.**: 187.7–

190.7 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{14}ClN_2O_2S^+$ $[M+H]^+$ m/z 345.0459, found 345.0454.

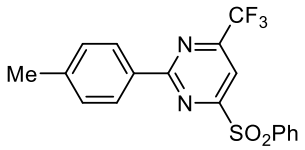


13f

4-methyl-6-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidine (13f)

Following **General Procedure**, 2,4-dichloro-6-methylpyrimidine (10.0 mmol, 1.63 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use Cs_2CO_3 (20.0 mmol, 6.51g) as base. Compound **13f** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 10/1) as a white solid (0.62 g, 3 steps yield 19%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.14 (d, *J* = 7.2 Hz, 2H), 7.77 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.67 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.1, 166.6, 165.2, 142.1, 137.7, 134.4, 133.5, 129.6, 129.4, 129.2, 128.7, 114.0, 25.0 (d, *J* = 3.2 Hz), 21.6 (d, *J* = 3.1 Hz). **IR (thin film, cm^{-1})**: 3005, 2979, 1565, 1531, 1447, 1381, 1275, 1261, 1160, 764, 750, 604, and 579 cm^{-1}. **m.p.**: 141.2–144.2 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{17}N_2O_2S^+$ $[M+H]^+$ m/z 325.1005, found 325.1010.



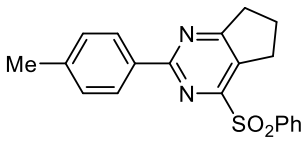
13g

4-(phenylsulfonyl)-2-(*p*-tolyl)-6-(trifluoromethyl) pyrimidine (13g)

Following **General Procedure**, 2,4-dichloro-6-(trifluoromethyl)pyrimidine (10.0 mmol, 2.17 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use Cs_2CO_3 (20.0 mmol, 6.51g) as base. Compound **13g** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 8/1) as a white solid (0.57 g, 3 steps yield 15%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 2H), 8.18–8.15 (m, 3H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 169.6, 166.6, 159.0 (q, *J* = 37.0 Hz), 140.2 (d, *J* = 702.7 Hz), 135.0, 131.9, 129.9, 129.8, 129.5, 129.1, 121.1 (d, *J* = 292.6 Hz), 120.1 (d, *J* = 822.2 Hz), 110.3 (d, *J* = 2.8 Hz), 21.7 (d, *J* = 3.0 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -69.85. **IR (thin film, cm^{-1})**: 3069, 3006, 2989, 1564, 1549, 1386, 1331, 1275, 1210, 1156, 1085, 764, 750, 595, and 579 cm^{-1}. **m.p.**: 144.3–147.3 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{14}F_3N_2O_2S^+$ $[M+H]^+$ m/z 379.0723, found 379.0728.

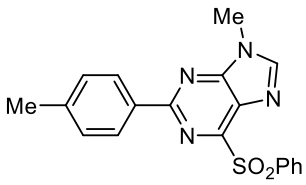


13i

4-(phenylsulfonyl)-2-(*p*-tolyl)-6, 7-dihydro-5H-cyclopenta [d] pyrimidine (13i)

Following **General Procedure**, 2,4-dichloro-6-(trifluoromethyl)pyrimidine (10.0 mmol, 1.89 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use Cs_2CO_3 (20.0 mmol, 6.51g) as base. Compound **13i** was isolated by silica gel chromatography (petroleum ether/EtOAc = 1/0 to 8/1) as a white solid (1.23 g, 3 steps yield 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 7.6 Hz, 4H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.23 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.7, 163.7, 160.6, 141.6, 138.1, 134.3, 133.7, 129.6, 129.4, 129.1, 128.4, 34.4, 29.3, 22.3, 21.6 (d, *J* = 3.5 Hz). **IR (thin film, cm^{-1})**: 3073, 2978, 1579, 1524, 1384, 1325, 1162, 1137, 1081, 775, 727, 687, and 593 cm^{-1}. **m.p.**: 188.3–191.3 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{19}N_2O_2S^+$ $[M+H]^+$ m/z 351.1162, found 351.1161.



13j

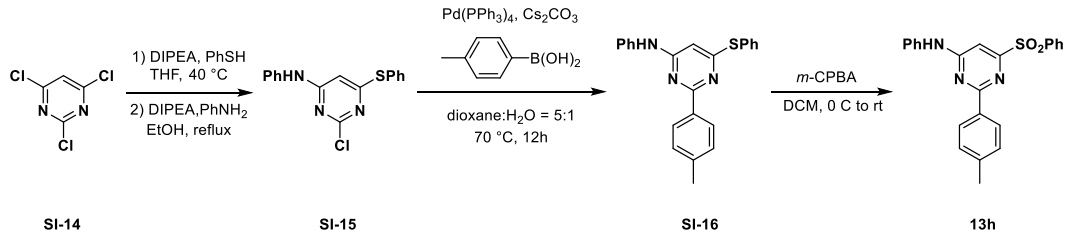
9-methyl-6-(phenylsulfonyl)-2-(*p*-tolyl)-9H-purine (13j)

Following **General Procedure**, 2,6-dichloro-9-methyl-9H-purine (10.0 mmol, 2.03 g) was used and the SNAr reaction was react at 50 ºC. The Suzuki reaction was use K_2CO_3 (20.0 mmol, 2.76 g) as base. Compound **13j** was isolated by silica gel chromatography (petroleum

ether/DCM/EtOAc = 1/0/0 to 0/4/1) as a white solid (1.53 g, 3 steps yield 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.2 Hz, 2H), 8.23–8.21 (m, 3H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 155.2, 153.1, 147.4, 142.7, 138.7, 133.9, 131.7, 131.4, 130.2, 129.7, 129.6, 129.0, 30.5, 21.8. **IR (thin film, cm^{-1})**: 3065, 3012, 2960, 1596, 1549, 1508, 1447, 1383, 1334, 1276, 1226, 1162, 1141, 1083, 763, 750, 725, 697, 685, 634, and 585 cm^{-1}. **m.p.**: 191.5–194.5 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{17}N_4O_2S^+$ $[M+H]^+$ m/z 365.1067, found 365.1064.

6.2 Procedures for the Synthesis of N-phenyl-6-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidin-4-amine (13h)



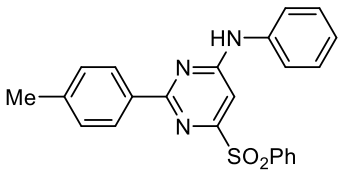
Thiophenol (1.0 equiv.) was added dropwise to a stirred solution of DIPEA (1.2 equiv.) and 2,4,6-trichloropyrimidine (**SI-14**, 1.0 equiv.) in THF at 0 ºC. The reaction mixture was heated to 50 ºC (or room temperature) overnight. After completion, the solvents were removed and the crude mixture was dissolved in EtOAc and washed with an aqueous solution of NH_4Cl (30 mL×2), $NaHCO_3$ (30 mL×1), and brine (20 mL×1). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give the crude Product.[3]

The crude Product was added to a stirred solution of DIPEA (1.2 equiv.) and aniline (1.0 equiv.) in EtOH and refluxed for 8 h. After completion, the reaction was cooled to ambient temperature and removed the solvent by evaporation. The crude mixture was dissolved in EtOAc and washed with an aqueous solution of NH_4Cl (30 mL×2), $NaHCO_3$ (30 mL×1), and brine (20 mL×1). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel

(petroleum ether/EtOAc) to give the crude Product **SI-15**.[5]

The crude Product **SI-15** (1.0 equiv.), 4-tolylboronic acid (1.5 equiv.), Cs_2CO_3 (2.0 equiv.), were weighed into a dried 50 mL thick wall pressure bottle containing a magnetic stir bar. The bottle was then transferred into a nitrogen-filled glovebox. To the bottle was added $Pd(PPh_3)_4$ (5 mmol%) and solvent dioxane/ H_2O (5:1). The thick wall pressure bottle was tightly sealed, and taken out of the glovebox. The solution was stirred at 70 ºC under oil bath for 12 h. After completion, the reaction mixture was cooled to room temperature and the solid was filtered off. The filtrate was then concentrated and the resulting crude product was dissolved in EtOAc (30 mL). The solution was washed with water (10 mL×3) and brine (10 mL×1), and dried over Na_2SO_4. Upon removal of the solvent under vacuum, the resulting residue was subjected to flash silica gel column chromatography (petroleum ether/EtOAc) to give the crude product **SI-16**.[4]

To a DCM solution of crude product **SI-16** (1.0 equiv.) cooled at 0 °C was added *m*-CPBA (2.4 equiv.) dropwise over 10 min. The reaction was allowed to warm to room temperature and stirred for another 2h, and then diluted by addition of DCM. The mixture washed by sat. aq. $NaHCO_3$ (30 mL×2), and brine (10 mL×1). The mixture was extracted with DCM, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give Product **13h** as a white solid.



13h

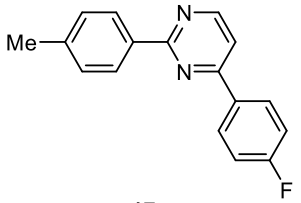
N-phenyl-6-(phenylsulfonyl)-2-(*p*-tolyl) pyrimidin-4-amine (13h)

Following **General Procedure**, 2,4,6-trichloropyrimidine (10.0 mmol, 1.83 g) was used. Compound **13h** was isolated by silica gel chromatography (petroleum ether/DCM = 1/0 to 1/1) as a white solid (1.16 g, 4 steps yield 29%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.13–8.10 (m, 4H), 7.80–7.76 (m, 3H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.36 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 2.33

(s, 3H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 164.2, 161.3, 141.4, 138.8, 137.5, 134.6, 133.7, 129.6, 129.3, 129.0, 128.9, 127.9, 123.5, 120.4, 21.0 (d, *J* = 3.5 Hz). **IR (thin film, cm^{-1})**: 3363, 3006, 2979, 1609, 1562, 1497, 1438, 1350, 1275, 1176, 1161, 764, 750, and 578 cm^{-1}. **m.p.**: 240.6–243.6 °C. **HRMS (DART-TOF)** calculated for $C_{23}H_{20}N_3O_2S^+$ $[M+H]^+$ m/z 402.1271, found 402.1271.

7. Characterization Data for Compounds in Scheme 2

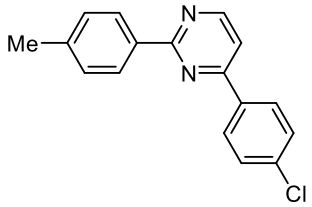


17a

4-(4-fluorophenyl)-2-(*p*-tolyl) pyrimidine (17a)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-fluorophenyl)boronic acid **16a** (56.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (49.7 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.2 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 8.21–8.13 (m, 2H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23–7.05 (m, 2H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7 (d, *J* = 249.7 Hz) 164.7, 163.5, 162.7, 157.9, 141.2, 135.3, 133.2 (d, *J* = 3.1 Hz), 129.4, 129.3, 129.2, 128.3, 116.0 (d, *J* = 78.4 Hz), 113.9, 21.6 (d, *J* = 3.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -109.59. **IR (thin film, cm^{-1})**: 2926, 2851, 1600, 1583, 1562, 1548, 1507, 1436, 1411, 1380, 1232, 1176, 1158, 949, 874, 821, 788, and 750 cm^{-1}. **m.p.**: 87.3–90.3 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{14}FN_2^+$ $[M+H]^+$ m/z 265.1136, found 265.1134.

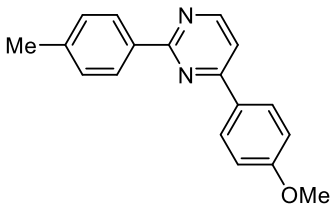


17b

4-(4-chlorophenyl)-2-(*p*-tolyl)pyrimidine (17b)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-chlorophenyl)boronic acid **16b** (62.5 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (41.8 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.2 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.50–7.46 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 162.6, 158.1, 141.2, 137.2, 135.6, 135.1, 129.4, 129.3, 128.6, 128.4, 114.0, 21.6 (d, *J* = 4.0 Hz). **IR (thin film, cm^{-1})**: 2998, 2922, 1582, 1560, 1544, 1489, 1437, 1404, 1265, 1175, 1108, 874, 817, 785, and 739 cm^{-1}. **m.p.**: 144.8–147.8 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{14}ClN_2^+$ $[M+H]^+$ m/z 281.0840, found 281.0837.



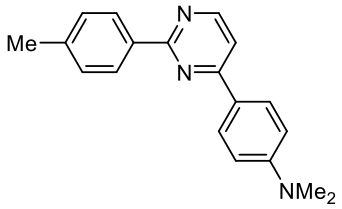
17c

4-(4-methoxyphenyl)-2-(*p*-tolyl) pyrimidine (17c)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-methoxyphenyl)boronic acid **16c** (60.8 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (55.1 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.2 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 163.3, 162.1, 157.6, 140.9, 135.4,

129.5, 129.3, 128.8, 128.3, 114.3, 113.4, 55.5 (d, *J* = 5.7 Hz), 21.6 (d, *J* = 4.4 Hz). **IR (thin film, cm^{-1})**: 2922, 2832, 1606, 1582, 1560, 1544, 1510, 1434, 1415, 1381, 1252, 1173, 822, 788, 765, and 748 cm^{-1}. **m.p.**: 115.6–118.6 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{17}N_2O^+$ $[M+H]^+$ m/z 277.1335, found 277.1333.

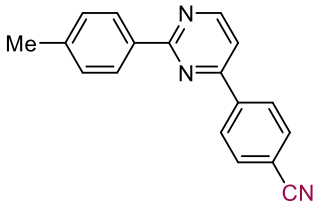


17d

N, N-dimethyl-4-(2-(*p*-tolyl) pyrimidin-4-yl) aniline (17d)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-(dimethylamino)phenyl)boronic acid **16d** (66.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (55.6 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.2 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 6H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.3, 163.7, 157.0, 152.4, 140.6, 135.8, 129.3, 128.4, 128.2, 124.2, 112.7, 111.8, 40.2 (d, *J* = 2.3 Hz), 21.6 (d, *J* = 4.4 Hz). **IR (thin film, cm^{-1})**: 2922, 2850, 2803, 1608, 1581, 1560, 1540, 1520, 1424, 1330, 1288, 1197, 1174, 947, 874, 814, 786, 764, and 750 cm^{-1}. **m.p.**: 189.1–192.1 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{20}N_3^+$ $[M+H]^+$ m/z 290.1652, found 290.1651.

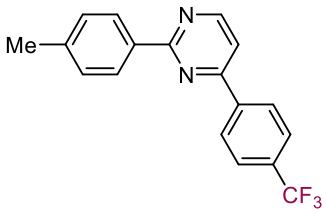


17e

4-(2-(*p*-tolyl) pyrimidin-4-yl) benzonitrile (17e)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-cyanophenyl)boronic acid **16e** (58.8 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (53.3 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.2 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.0, 161.7, 158.5, 141.5, 141.2, 134.7, 132.7, 129.5, 128.4, 127.8, 118.5, 114.6, 114.3, 21.6 (d, *J* = 4.3 Hz). **IR (thin film, cm^{-1})**: 2908, 1580, 1558, 1501, 1383, 1334, 1174, 949, 874, 819, 786, and 750 cm^{-1}. **m.p.**: 163.2–165.2 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{14}N_3^+$ $[M+H]^+$ m/z 272.1182, found 272.1181.



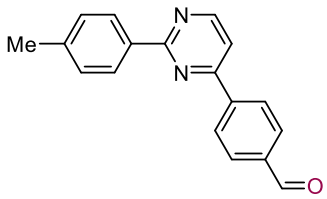
17f

2-(*p*-tolyl)-4-(4-(trifluoromethyl) phenyl) pyrimidine (17f)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-(trifluoromethyl)phenyl)boronic acid **16f** (76.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (62.0 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.2 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.0, 162.4, 158.3, 141.4, 140.5, 134.9, 132.6 (q, *J*

= 32.4 Hz), 129.5, 128.4, 127.6, 126.0 (d, *J* = 11.3 Hz), 126.0 (d, *J* = 3.8 Hz), 124.1 (d, *J* = 270.6 Hz), 124.1 (d, *J* = 812.2 Hz), 114.6, 21.6 (d, *J* = 4.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.77. **IR (thin film, cm^{-1})**: 2998, 1585, 1560, 1496, 1391, 1329, 1175, 1131, 949, 874, 826, 790, 764, and 750 cm^{-1}. **m.p.**: 155.1–158.1 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{14}F_3N_2^+$ $[M+H]^+$ m/z 315.1104, found 315.1106.

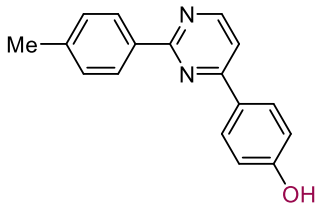


17g

4-(2-(*p*-tolyl) pyrimidin-4-yl) benzaldehyde (17g)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-formylphenyl)boronic acid **16g** (60.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (44.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.85 (d, *J* = 5.2 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 5.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.9 (d, *J* = 2.2 Hz), 165.0, 162.4, 158.3, 142.6, 141.4, 137.8, 134.9, 130.2, 129.5, 128.4, 127.9, 114.9, 21.6 (d, *J* = 3.9 Hz). **IR (thin film, cm^{-1})**: 3008, 2927, 1690, 1582, 1559, 1547, 1503, 1380, 1299, 1172, 949, 874, 817, and 784 cm^{-1}. **m.p.**: 137.9–140.9 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{15}N_2O^+$ $[M+H]^+$ m/z 275.1179, found 275.1181.

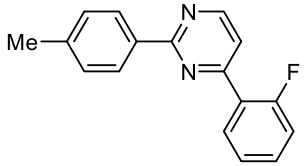


17h

4-(2-(*p*-tolyl) pyrimidin-4-yl) phenol (17h)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-hydroxyphenyl)boronic acid **16h** (55.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (45.2 mg, 78%).

^{1}H NMR (400 MHz, DMSO) δ 10.14 (s, 1H), 8.79 (d, *J* = 5.2 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 163.2, 162.8, 160.6, 158.0, 140.5, 135.0, 129.3, 128.9, 127.8, 127.0, 115.9, 113.5, 21.1 (d, *J* = 4.5 Hz). **IR (thin film, cm^{-1})**: 3309, 3012, 2932, 1584, 1560, 1545, 1509, 1386, 1276, 1265, 1172, 949, 874, 825, 764, and 749 cm^{-1}. **m.p.**: 210.3–213.3 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{15}N_2O^+$ $[M+H]^+$ m/z 263.1179, found 263.1182.



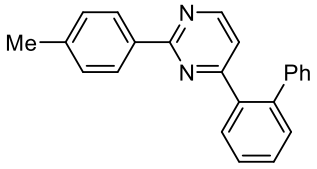
17i

4-(2-fluorophenyl)-2-(*p*-tolyl) pyrimidine (17i)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (2-fluorophenyl)boronic acid **16i** (56.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (45.7 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 5.2 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 2H), 8.36 (td, *J* = 8.0, 2.0 Hz, 1H), 7.68 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.51–7.41 (m, 1H), 7.34–7.30 (m, 3H), 7.18 (ddd, *J* = 11.6, 8.4, 1.2 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 162.9,

160.4, 160.1 (d, *J* = 2.5 Hz), 157.8, 141.1, 135.2, 132.3, 132.3, 131.1 (d, *J* = 2.5 Hz), 129.4, 128.3, 125.3 (d, *J* = 10.3 Hz), 124.8 (d, *J* = 3.5 Hz), 118.6 (d, *J* = 22.0 Hz), 116.5 (d, *J* = 22.8 Hz), 21.6 (d, *J* = 4.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.73. **IR (thin film, cm^{-1})**: 3031, 2922, 1613, 1583, 1560, 1490, 1429, 1405, 1381, 1300, 1249, 1212, 1176, 831, 792, and 759 cm^{-1}. **m.p.**: 49.4–52.4 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{14}FN_2^+$ $[M+H]^+$ m/z 265.1136, found 265.1137.

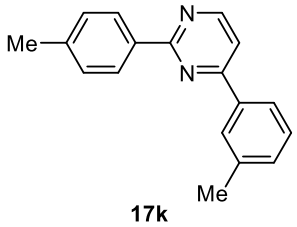


17j

4-([1,1'-biphenyl]-2-yl)-2-(*p*-tolyl) pyrimidine (17j)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), [1,1'-biphenyl]-2-ylboronic acid **16j** (79.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (57.4 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.2 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.95–7.75 (m, 1H), 7.56–7.47 (m, 2H), 7.49–7.40 (m, 1H), 7.31–7.14 (m, 7H), 6.76 (d, *J* = 5.2 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 164.7, 156.3, 141.5, 141.1, 140.9, 137.4, 135.2, 131.0, 130.7, 129.8, 129.7, 129.3, 128.4, 128.3, 127.9, 127.2, 119.5, 21.6 (d, *J* = 3.6 Hz). **IR (thin film, cm^{-1})**: 3030, 2932, 2855, 1580, 1558, 1540, 1478, 1427, 1404, 1378, 1176, 832, 795, 764, 746, and 701 cm^{-1}. **m.p.**: 78.3–81.3 °C. **HRMS (DART-TOF)** calculated for $C_{23}H_{19}N_2^+$ $[M+H]^+$ m/z 323.1543, found 323.1544.

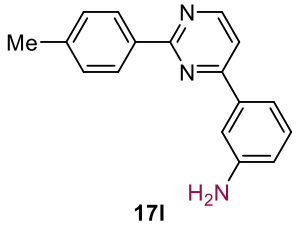


17k

4-(*m*-tolyl)-2-(*p*-tolyl) pyrimidine (17k)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), m-tolylboronic acid **16k** (54.4 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (42.8 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.2 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 2H), 8.03 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 5.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 3H), 2.48 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 164.1, 157.8, 141.0, 138.7, 137.2, 135.4, 131.8, 129.4, 128.9, 128.4, 128.0, 124.5, 114.5, 21.7, 21.6. **IR (thin film, cm^{-1})**: 2920, 2855, 1583, 1561, 1548, 1490, 1430, 1406, 1382, 1176, 949, 874, 830, 763, and 750 cm^{-1}. **m.p.**: 67.4–70.4 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{17}N_2^+$ $[M+H]^+$ m/z 261.1386, found 261.1388.



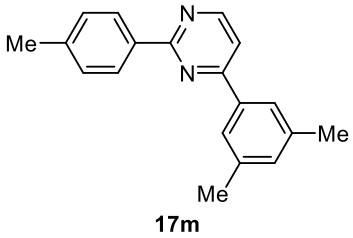
17l

3-(2-(*p*-tolyl) pyrimidin-4-yl) aniline (17l)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), 3-Aminophenylboronic acid monohydrate **16l** (62.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (42.0 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.2 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.34–7.24 (m, 3H), 6.79 (s, 1H), 3.91 (s, 2H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.6, 164.0, 157.7, 147.1, 141.0, 138.2, 135.3,

129.9, 129.4, 128.3, 117.7, 117.5, 114.5, 113.6, 21.6 (d, J = 3.7 Hz). **IR (thin film, cm^{-1})**: 3342, 2908, 1609, 1583, 1561, 1546, 1495, 1429, 1405, 1384, 1330, 1307, 1276, 1176, 949, 874, 830, 780, 765, and 750 cm^{-1}. **m.p.**: 129.4–132.4 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{16}N_3^+$ $[M+H]^+$ m/z 262.1339, found 262.1342.

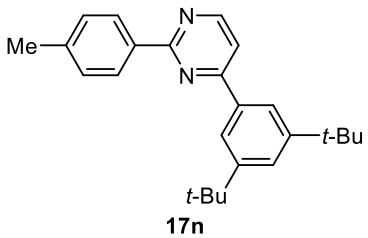


17m

4-(3, 5-dimethylphenyl)-2-(*p*-tolyl) pyrimidine (17m)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (3,5-dimethylphenyl)boronic acid **16m** (60.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (49.9 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 5.2 Hz, 1H), 8.46 (d, J = 8.0 Hz, 2H), 7.79 (s, 2H), 7.50 (d, J = 5.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.13 (s, 1H), 2.42 (s, 3H), 2.41 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 164.2, 157.7, 140.9, 138.6, 137.1, 135.4, 132.7, 129.4, 128.3, 125.1, 114.5, 21.6 (d, J = 4.0 Hz), 21.5 (d, J = 3.9 Hz). **IR (thin film, cm^{-1})**: 3032, 3011, 2919, 2855, 1582, 1561, 1546, 1423, 1405, 1376, 1329, 1306, 1276, 1175, 825, 789, 748, and 665 cm^{-1}. **m.p.**: 79.1–82.1 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{19}N_2^+$ $[M+H]^+$ m/z 275.1543, found 275.1541.



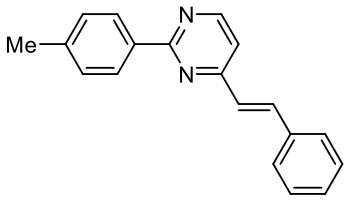
17n

4-(3,5-di-*tert*-butylphenyl)-2-(*p*-tolyl) pyrimidine (17n)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (3,5-di-tert-

butylphenyl)boronic acid **16n** (93.7 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (66.3 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.2 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.03 (s, 1H), 8.03 (s, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.42 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.1, 164.6, 157.7, 151.6, 140.9, 136.7, 135.4, 129.4, 128.3, 125.2, 121.7, 114.8, 35.2, 31.6, 21.6 (d, *J* = 4.4 Hz). **IR (thin film, cm^{-1})**: 2962, 2865, 1582, 1560, 1547, 1417, 1377, 1362, 1249, 1176, 881, 826, 791, 764, 750, and 665 cm^{-1}. **m.p.**: 125.4–128.4 °C. **HRMS (DART-TOF)** calculated for $C_{25}H_{31}N_2^+$ $[M+H]^+$ m/z 359.2482, found 359.2487.

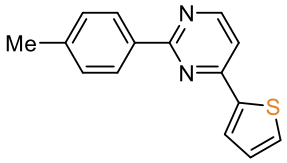


17o

(*E*)-4-styryl-2-(*p*-tolyl) pyrimidine (17o)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), trans-beta-styrylboronic acid **16o** (59.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 20:1) afforded the title product as a white solid (42.5 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.2 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16–7.03 (m, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.6, 162.4, 157.8, 141.0, 137.0, 136.0, 135.3, 129.4, 129.4, 129.0, 128.3, 127.8, 126.4, 116.2, 21.6. **IR (thin film, cm^{-1})**: 3017, 2917, 1637, 1581, 1558, 1541, 1494, 1449, 1432, 1404, 1388, 1276, 1175, 968, 873, 819, 788, 764, 751, and 690 cm^{-1}. **m.p.**: 112.5–115.5 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{17}N_2^+$ $[M+H]^+$ m/z 273.1386, found 273.1386.

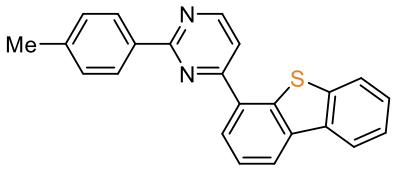


17p

4-(thiophen-2-yl)-2-(*p*-tolyl) pyrimidine (17p)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), thiophen-2-ylboronic acid **16p** (51.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 20:1) afforded the title product as a light yellow solid (48.0 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.2 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 4.4 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 159.0, 157.6, 143.1, 141.1, 134.9, 130.1, 129.4, 128.4, 128.3, 127.4, 112.6, 21.6 (d, *J* = 4.4 Hz). **IR (thin film, cm^{-1})**: 3041, 2922, 2860, 1610, 1582, 1559, 1546, 1438, 1419, 1406, 1385, 1342, 1275, 1176, 822, 785, 749, and 710 cm^{-1}. **m.p.**: 62.1–65.1 °C. **HRMS (DART-TOF)** calculated for $C_{15}H_{13}N_2S^+$ $[M+H]^+$ m/z 253.0794, found 253.0792.



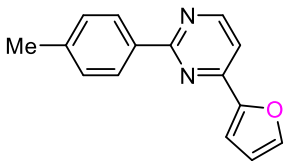
17q

4-(dibenzo [b, d] thiophen-4-yl)-2-(*p*-tolyl) pyrimidine (17q)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), 4-dibenzothiophene boronic acid **16q** (91.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a light yellow solid (66.3 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.2 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 5.2 Hz, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.50–7.40 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR (101**

MHz, $CDCl_3$) δ 164.8, 163.1, 157.5, 142.0, 141.2, 138.0, 137.6, 135.2, 134.4, 131.0, 129.5, 129.0, 127.1, 125.9, 124.5, 124.4, 123.9, 122.6, 121.4, 114.6, 21.7 (d, *J* = 4.3 Hz). **IR (thin film, cm^{-1})**: 2932, 2851, 1582, 1560, 1539, 1430, 1406, 1371, 1276, 1177, 828, 800, 785, and 750 cm^{-1}. **m.p.**: 147.6–150.6 °C. **HRMS (DART-TOF)** calculated for $C_{23}H_{17}N_2S^+$ $[M+H]^+$ m/z 353.1107, found 353.1110.

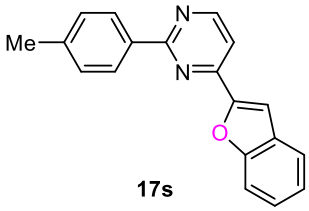


17r

4-(furan-2-yl)-2-(*p*-tolyl) pyrimidine (17r)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), furan-2-ylboronic acid **16r** (44.7 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 20:1) afforded the title product as a white solid (37.7 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.2 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.58 (dd, *J* = 3.6, 2.0 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.6, 157.8, 155.6, 152.3, 145.0, 141.0, 135.0, 129.4, 128.3, 112.6, 112.3, 112.2, 21.6 (d, *J* = 3.1 Hz). **IR (thin film, cm^{-1})**: 3031, 2927, 2855, 1600, 1557, 1479, 1428, 1393, 1368, 1223, 1176, 1006, 917, 884, 821, 787, 746, and 682 cm^{-1}. **m.p.**: 64.4–67.4 °C. **HRMS (DART-TOF)** calculated for $C_{15}H_{13}N_2O^+$ $[M+H]^+$ m/z 237.1022, found 237.1023.



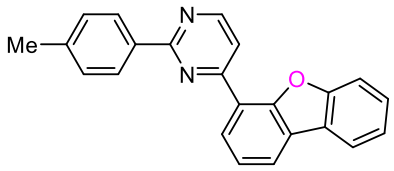
17s

4-(benzofuran-3-yl)-2-(*p*-tolyl) pyrimidine (17s)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), benzofuran-2-ylboronic acid **16s** (64.8 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7

mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 20:1) afforded the title product as a white solid (55.2 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.2 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.33–7.25 (m, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 158.2, 155.9, 155.8, 153.7, 141.2, 134.9, 129.4, 128.5, 128.4, 126.4, 123.6, 122.4, 113.3, 111.8, 108.3, 21.6 (d, *J* = 3.4 Hz). **IR (thin film, cm^{-1})**: 2916, 2865, 1604, 1560, 1530, 1450, 1391, 1178, 832, 815, 787, and 748 cm^{-1}. **m.p.**: 168.2–171.2 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{15}N_2O^+$ $[M+H]^+$ m/z 287.1179, found 287.1182.

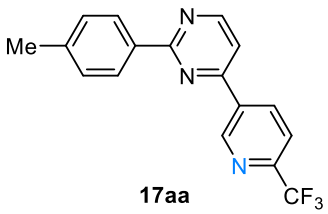


17t

4-(dibenzo [b, d] furan-4-yl)-2-(*p*-tolyl) pyrimidine (17t)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), dibenzofuran-4-ylboronic acid **16t** (84.8 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 20:1) afforded the title product as a white solid (63.5 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 5.2 Hz, 1H), 8.64 (d, *J* = 8.8 Hz, 1H), 8.48 (d, *J* = 8.8 Hz, 2H), 8.29 (d, *J* = 5.2 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 160.1, 158.0, 156.1, 154.6, 141.0, 135.4, 129.4, 128.3, 127.6, 127.3, 125.5, 123.7, 123.3, 123.2, 121.9, 120.8, 118.2, 111.9, 21.6 (d, *J* = 3.3 Hz). **IR (thin film, cm^{-1})**: 2903, 2851, 1583, 1559, 1474, 1441, 1377, 1300, 1175, 830, 802, and 754 cm^{-1}. **m.p.**: 176.4–179.4 °C. **HRMS (DART-TOF)** calculated for $C_{23}H_{17}N_2O^+$ $[M+H]^+$ m/z 337.1335, found 337.1343.

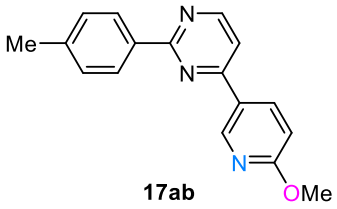


17aa

2-(*p*-tolyl)-4-(6-(trifluoromethyl) pyridin-3-yl) pyrimidine (17aa)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (6-(trifluoromethyl)pyridin-3-yl)boronic acid **16aa** (76.4 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a light yellow solid (46.3 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.90 (d, *J* = 5.1 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 160.1, 158.70, 149.7 (q, *J* = 34.4 Hz), 148.8, 141.8, 136.2, 135.5, 134.5, 129.6, 128.4, 120.7 (d, *J* = 2.9 Hz), 121.5 (d, *J* = 172.6 Hz), 114.7, 21.6 (d, *J* = 2.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -67.96. **IR (thin film, cm^{-1})**: 2993, 1585, 1559, 1492, 1399, 1341, 1276, 1178, 1134, 947, 874, 829, 790, 764, and 750 cm^{-1}. **m.p.**: 175.2–178.2 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{13}F_3N_3^+$ $[M+H]^+$ m/z 316.1056, found 316.1057.



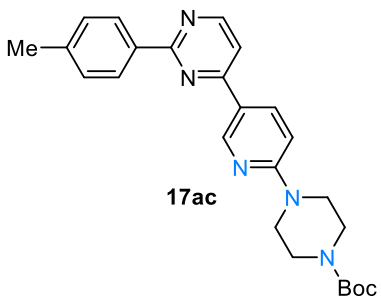
17ab

4-(6-methoxypyridin-3-yl)-2-(*p*-tolyl) pyrimidine (17ab)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (6-methoxypyridin-3-yl)boronic acid **16ab** (61.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (49.4 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.4 Hz, 1H), 8.75 (d, *J* = 5.2 Hz, 1H), 8.50–8.24 (m, 3H), 7.45 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.01 (s,

3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 164.7, 161.6, 157.8, 146.7, 141.2, 137.4, 135.1, 129.4, 128.3, 126.3, 113.3, 111.2, 53.9 (d, *J* = 4.1 Hz), 21.6 (d, *J* = 3.1 Hz). **IR (thin film, cm^{-1})**: 3005, 2841, 1603, 1562, 1543, 1495, 1438, 1394, 1358, 1276, 1260, 1174, 950, 875, 821, 785, 764, and 750 cm^{-1}. **m.p.**: 94.2–97.2 °C. **HRMS (DART-TOF)** calculated for $C_{17}H_{16}N_3O^+$ $[M+H]^+$ m/z 278.1288, found 278.1290.

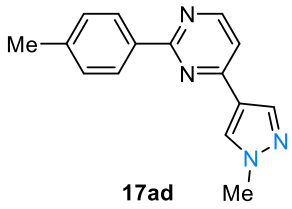


17ac

***tert*-butyl 4-(5-(2-(*p*-tolyl) pyrimidin-4-yl) pyridin-2-yl) piperazine-1-carboxylate (17ac)**

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), tert-butyl 4-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)piperazine-1-carboxylate (**16ac**) (155.7 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (79.4 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.4 Hz, 1H), 8.69 (d, *J* = 5.2 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 2H), 8.31 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 1H), 3.70–3.62 (m, 4H), 3.60–3.52 (m, 4H), 2.42 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 161.8, 160.0, 157.4, 154.8, 147.8, 140.9, 136.2, 135.3, 129.3, 128.2, 122.0, 112.5, 106.3, 80.1, 44.7, 43.3, 28.5, 21.5 (d, *J* = 3.2 Hz). **IR (thin film, cm^{-1})**: 2984, 1688, 1601, 1502, 1403, 1276, 1173, 949, 874, 818, 789, 764, and 750 cm^{-1}. **m.p.**: 189.2–192.2 °C. **HRMS (DART-TOF)** calculated for $C_{25}H_{30}N_5O_2^+$ $[M+H]^+$ m/z 432.2394, found 432.2400.

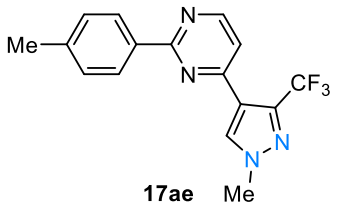


17ad

4-(1-methyl-1H-pyrazol-4-yl)-2-(*p*-tolyl) pyrimidine (17ad)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), 1-methyl-4-pyrazole boronic acid pinacol ester **16ad** (83.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (30.5 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.2 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 2H), 8.11 (s, 1H), 8.07 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 5.2 Hz, 1H), 3.97 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 158.8, 157.4, 140.9, 138.5, 135.2, 130.4, 129.3, 128.2, 122.1, 113.6, 39.4 (d, *J* = 4.1 Hz), 21.6 (d, *J* = 3.4 Hz). **IR (thin film, cm^{-1})**: 2936, 1587, 1561, 1537, 1405, 1226, 1176, 978, 950, 872, 827, 789, 765, and 750 cm^{-1}. **m.p.**: 117.2–120.2 °C. **HRMS (DART-TOF)** calculated for $C_{15}H_{15}N_4^+$ $[M+H]^+$ m/z 251.1291, found 251.1292.



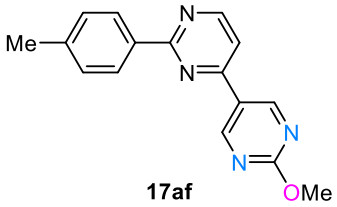
17ae

4-(1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)-2-(*p*-tolyl) pyrimidine (17ae)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)-1H-pyrazole **16ae** (110.4 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (51.2 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 5.2 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 2H), 8.14 (s, 1H), 7.32 (d, *J* = 5.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 158.0, 156.8, 141.2, 139.4 (q, *J* = 37.3 Hz), 134.9, 133.8, 129.4, 128.3,

125.4, 122.8, 120.4, 120.1, 115.4 (d, J = 2.9 Hz), 39.90, 21.59. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.37. **IR (thin film, cm^{-1})**: 2903, 1586, 1573, 1559, 1490, 1430, 1407, 1327, 1281, 1174, 1138, 1088, 825, 789, 764, and 749 cm^{-1}. **m.p.**: 109.3–112.3 °C. **HRMS (DART-TOF)** calculated for $C_{16}H_{14}F_3N_4^+$ $[M+H]^+$ m/z 319.1165, found 319.1164.

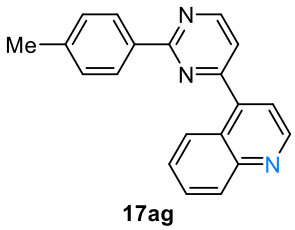


17af

2'-methoxy-2-(*p*-tolyl)-4,5'-bipyrimidine (17af)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (2-methoxypyrimidin-5-yl)boronic acid **16af** (61.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (41.2 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 2H), 8.82 (d, J = 5.2 Hz, 1H), 8.42 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 5.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 4.12 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 165.1, 159.3, 158.5, 158.3, 141.6, 134.7, 129.5, 128.4, 124.6, 113.2, 55.6 (d, J = 4.1 Hz), 21.6 (d, J = 3.3 Hz). **IR (thin film, cm^{-1})**: 2960, 2922, 1597, 1582, 1566, 1487, 1445, 1409, 1363, 1325, 1306, 1275, 1169, 1036, 949, 830, 789, 764, and 750 cm^{-1}. **m.p.**: 158.1–161.1 °C. **HRMS (DART-TOF)** calculated for $C_{16}H_{15}N_4O^+$ $[M+H]^+$ m/z 279.1240, found 279.1243.



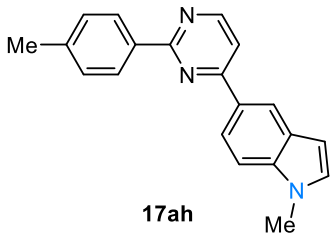
17ag

4-(2-(*p*-tolyl) pyrimidin-4-yl) quinolone (17ag)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), quinolin-4-ylboronic acid **16ag** (69.2 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was

purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (26.4 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 4.4 Hz, 1H), 8.96 (d, *J* = 5.2 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.4Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.82–7.76 (m, 1H), 7.64–7.55 (m, 2H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.0, 164.3, 158.1, 150.1, 149.1, 144.2, 141.6, 134.7, 130.2, 129.8, 129.6, 128.5, 127.6, 125.5, 125.4, 121.5, 119.2, 21.7. **IR (thin film, cm^{-1})**: 3008, 1580, 1557, 1542, 1507, 1462, 1437, 1395, 1382, 1276, 1177, 949, 874, 831, 794, 764, and 750 cm^{-1}. **m.p.**: 126.7–129.7 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{16}N_3^+$ $[M+H]^+$ m/z 298.1339, found 298.1343.

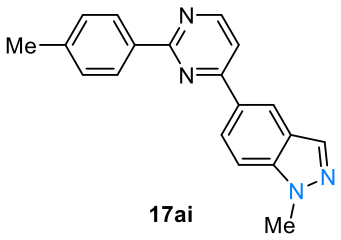


17ah

1-methyl-5-(2-(*p*-tolyl) pyrimidin-4-yl)-1H-indole (17ah)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (1-methylindol-5-yl)boronic acid **16ah** (70.0 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 8:1) afforded the title product as a white solid (45.7 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.2 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 2H), 8.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 3.2 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H), 3.76 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.0, 164.5, 157.3, 140.7, 138.5, 135.7, 130.1, 129.3, 128.9, 128.4, 128.3, 120.9, 120.7, 114.0, 109.6, 102.4, 33.1 (d, *J* = 4.1 Hz), 21.6 (d, *J* = 3.5 Hz). **IR (thin film, cm^{-1})**: 2920, 1583, 1558, 1512, 1433, 1421, 1405, 1337, 1275, 1175, 875, 831, 806, 786, 764, and 750 cm^{-1}. **m.p.**: 174.4–177.4 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{18}N_3^+$ $[M+H]^+$ m/z 300.1495, found 300.1495.



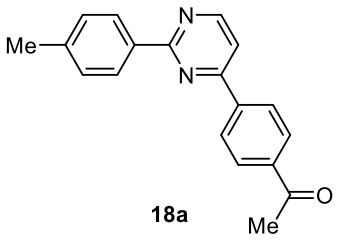
17ai

1-methyl-5-(2-(*p*-tolyl) pyrimidin-4-yl)-1H-indazole (17ai)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), 1-Methyl-1H-indazol-5-boronic acid **16ai** (70.4 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (32.0 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.2 Hz, 1H), 8.61 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.27 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.11 (s, 1H), 7.57 (d, *J* = 5.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.10 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 164.0, 157.7, 141.1, 141.0, 135.4, 134.2, 129.9, 129.4, 128.3, 125.5, 124.6, 121.0, 114.0, 109.4, 35.8 (d, *J* = 3.9 Hz), 21.6 (d, *J* = 2.9 Hz). **IR (thin film, cm^{-1})**: 3031, 2921, 1582, 1560, 1503, 1430, 1406, 1348, 1276, 1175, 1108, 949, 874, 831, 806, 786, 764, and 750 cm^{-1}. **m.p.**: 151.9–154.9 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{17}N_4^+$ $[M+H]^+$ m/z 301.1448, found 301.1444.

8. Characterization Data for Compounds in Scheme 3 and 4



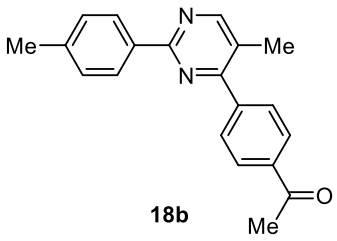
18a

1-(4-(2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18a)

Following the **General Procedure**, pyrimidinyl sulfone **13a** (62.1 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue

was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 5:1) afforded the title product as a white solid (52.6 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.2 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 2H), 8.27 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 164.9, 162.6, 158.2, 141.3 (d, *J* = 5.1 Hz), 138.7, 135.0, 129.5, 128.9, 128.4, 127.5 (d, *J* = 3.1 Hz), 114.7, 26.9 (d, *J* = 3.9 Hz), 21.6 (d, *J* = 4.0 Hz). **IR (thin film, cm^{-1})**: 3017, 2908, 1684, 1580, 1559, 1435, 1406, 1380, 1265, 1177, 957, 870, 821, 787, 764, and 750 cm^{-1}. **m.p.**: 137.8–140.8 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{17}N_2O^+$ $[M+H]^+$ m/z 289.1335, found 289.1341.

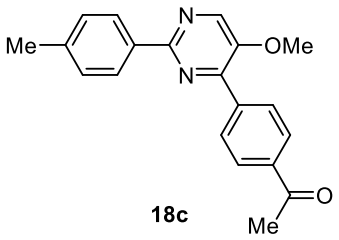


18b

1-(4-(5-methyl-2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18b)

Following the **General Procedure**, pyrimidinyl sulfone **13b** (64.9 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (35.7 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.8, 163.7, 162.8, 159.5, 143.0, 140.8, 137.4, 134.9, 129.5, 129.4, 128.4, 128.1, 125.4, 26.9, 21.6, 17.0. **IR (thin film, cm^{-1})**: 2922, 2860, 1685, 1581, 1532, 1424, 1356, 1265, 956, 873, 840, 792, and 748 cm^{-1}. **m.p.**: 144.9–147.9 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{19}N_2O^+$ $[M+H]^+$ m/z 303.1492, found 303.1498.

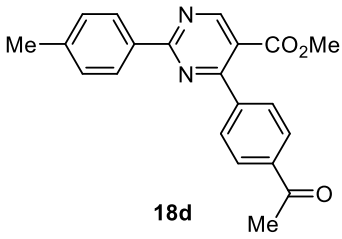


18c

1-(4-(5-methoxy-2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18c)

Following the **General Procedure**, pyrimidinyl sulfone **13c** (68.1 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 4:1) afforded the title product as a white solid (59.2 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.32 (dd, *J* = 13.2, 8.0 Hz, 4H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 157.6, 151.8, 149.9, 141.5, 140.2, 140.1, 137.7, 134.8, 130.0, 129.4, 128.1, 127.7, 56.3, 26.9, 21.5. **IR (thin film, cm^{-1})**: 2927, 2841, 1682, 1606, 1556, 1449, 1429, 1378, 1285, 1267, 1231, 1174, 1012, 957, 849, and 788 cm^{-1}. **m.p.**: 132.3–135.3 °C. **HRMS (DART-TOF)** calculated for $C_{27}H_{26}ClF_3N_3O_3^+$ $[M+H]^+$ m/z 319.1441, found 319.1449.



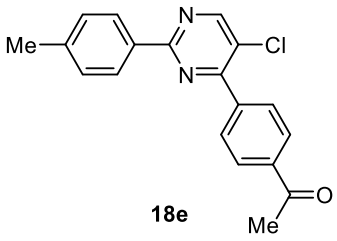
18d

ethyl 4-(4-acetylphenyl)-2-(*p*-tolyl) pyrimidine-5-carboxylate (18d)

Following the **General Procedure**, pyrimidinyl sulfone **13d** (73.7 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (60.2 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ9.21 (s, 1H), 8.45 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.26 (q, J = 7.2 Hz, 2H), 2.67 (s, 3H), 2.43

(s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 165.9, 165.7, 165.4, 159.5, 142.7, 142.5, 137.9, 133.9, 129.6, 129.4, 129.0, 128.2, 121.5, 61.9, 26.9, 21.7, 13.9. **IR (thin film, cm^{-1})**: 2998, 2922, 2846, 1721, 1686, 1572, 1556, 1527, 1426, 1363, 1266, 1176, 1134, 801, 749 and 684 cm^{-1}. **m.p.**: 109.0–112.0 °C. **HRMS (DART-TOF)** calculated for $C_{27}H_{26}ClF_3N_3O_3^+$ $[M+H]^+$ m/z 361.1547, found 361.1552.

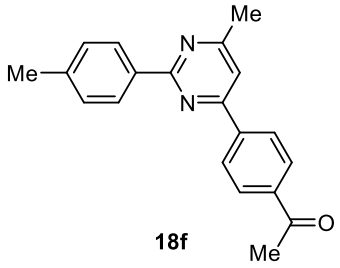


18e

1-(4-(5-chloro-2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18e)

Following the **General Procedure**, pyrimidinyl sulfone **13e** (69.0 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (22.6 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 2H), 8.08 (q, *J* = 8.4 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.67 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 162.9, 161.1, 158.1, 141.7, 140.5, 138.2, 133.8, 130.0, 129.6, 128.4, 128.3, 126.6, 26.9 (d, *J* = 5.2 Hz, 2H), 21.7 (d, *J* = 5.3 Hz). **IR (thin film, cm^{-1})**: 2913, 1689, 1584, 1496, 1412, 1330, 1175, 950, 874, 783, 678, and 662 cm^{-1}. **m.p.**: 136.9–139.9 °C. **HRMS (DART-TOF)** calculated for $C_{19}H_{16}ClN_2O^+$ $[M+H]^+$ m/z 323.0946, found 323.0945.

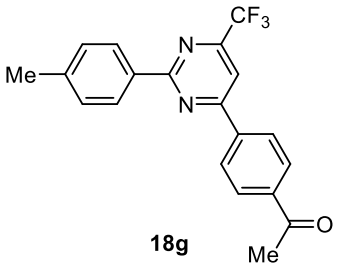


18f

1-(4-(6-methyl-2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18f)

Following the **General Procedure**, pyrimidinyl sulfone **13f** (64.9 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (47.0 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.63 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.8, 168.2, 164.6, 162.4, 141.7, 141.0, 138.5, 135.2, 129.4, 128.8, 128.4, 127.4, 114.2, 26.9 (d, *J* = 5.7 Hz), 24.7 (d, *J* = 5.6 Hz), 21.6 (d, *J* = 5.5 Hz). **IR (thin film, cm^{-1})**: 2926, 2852, 1684, 1587, 1568, 1504, 1368, 1265, 1176, 957, 837, 784, 764, and 750 cm^{-1}. **m.p.**: 164.0–167.0 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{19}N_2O^+$ $[M+H]^+$ m/z 303.1492, found 303.1489.

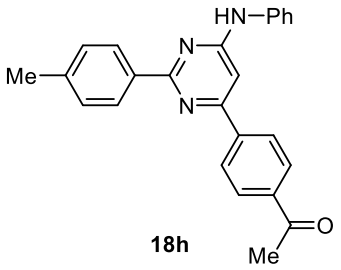


18g

1-(4-(2-(*p*-tolyl)-6-(trifluoromethyl) pyrimidin-4- yl) phenyl) ethan-1-one (18g)

Following the **General Procedure**, pyrimidinyl sulfone **13g** (75.7 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a light yellow solid (60.6 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.5, 165.7, 165.1 157.1 (q, *J* = 35.8 Hz), 142.4, 139.3 136.8 (d, *J* =640.7 Hz), 133.6, 129.6, 129.0, 128.8, 127.7, 120.9 (d, *J* = 273.9 Hz), 120.8 (d, *J* = 852.8 Hz), 110.1, 26.9 (d, *J* = 5.5 Hz), 21.7 (d, *J* = 5.5 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -69.98. **IR (thin film, cm^{-1})**: 3089, 2913, 1690, 1578, 1509, 1431, 1394, 1379, 1267, 1183, 1159, 1139, 895, 839, 786, and 750 cm^{-1}. **m.p.**: 169.4–172.4 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{16}F_3N_2O^+$ $[M+H]^+$ m/z 357.1209, found 357.1203.

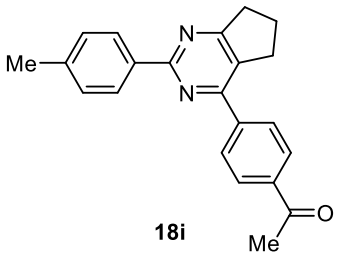


18h

1-(4-(6-(phenylamino)-2-(*p*-tolyl) pyrimidin-4-yl) phenyl) ethan-1-one (18h)

Following the **General Procedure**, pyrimidinyl sulfone **13h** (80.3 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc: DCM = 1:0:0 to 4:1:1) afforded the title product as a light yellow solid (69.8 mg, 92%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 2.64 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 197.6, 163.2, 161.4, 160.3, 141.4, 140.4, 140.0, 137.9, 135.3, 129.1, 128.9, 128.8, 127.8, 126.7, 122.4, 119.8, 101.1, 26.9 (d, *J* = 7.1 Hz), 21.0 (d, *J* = 6.5 Hz). **IR (thin film, cm^{-1})**: 3360, 3008, 1587, 1497, 1441, 1358, 1275, 1177, 949, 874, 826, 764, and 750 cm^{-1}. **m.p.**: 216.6–219.6 °C. **HRMS (DART-TOF)** calculated for $C_{25}H_{22}N_3O^+$ $[M+H]^+$ m/z 380.1757, found 380.1764.

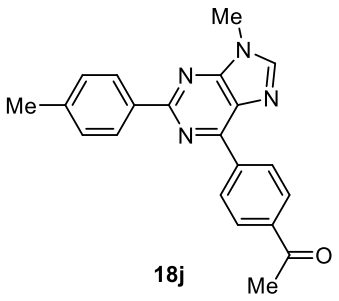


18i

1-(4-(2-(*p*-tolyl)-6, 7-dihydro-5H-cyclopenta[d]pyrimidin-4-yl) phenyl) ethan-1-one (18i)

Following the **General Procedure**, pyrimidinyl sulfone **13i** (70.1 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a light yellow solid (48.2 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 2H), 8.10 (q, *J* = 8.4 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.66 (s, 3H), 2.42 (s, 3H), 2.17 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 177.0, 163.4, 158.1, 142.6, 140.6, 137.7, 135.4, 129.3, 129.2, 129.0, 128.5, 128.2, 34.5, 30.9, 26.9 (d, *J* = 5.9 Hz), 22.9, 21.6 (d, *J* = 5.9 Hz). **IR (thin film, cm^{-1})**: 2920, 1685, 1580, 1545, 1500, 1385, 1359, 1264, 1170, 959, 867, 777, and 590 cm^{-1}. **m.p.**: 204.2–207.2 °C. **HRMS (DART-TOF)** calculated for $C_{22}H_{21}N_2O^+$ $[M+H]^+$ m/z 329.1648, found 329.1651.

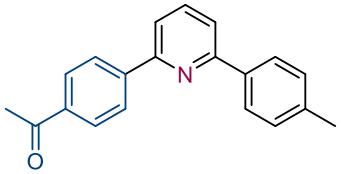


18j

1-(4-(9-methyl-2-(*p*-tolyl)-9H-purin-6-yl) phenyl) ethan-1-one (18j)

Following the **General Procedure**, pyrimidinyl sulfone **13j** (72.9 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc: DCM = 1:0:0 to 0:4:1) afforded the title product as a white solid (35.6 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.0 Hz, 2H), 8.68 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.65 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.2, 157.2, 154.1, 153.6, 145.1, 142.7, 141.5, 137.9, 133.3, 129.8, 129.7, 129.4, 128.5, 128.4, 29.7, 26.9, 21.7. **IR (thin film, cm^{-1})**: 3003, 2908, 1591, 1496, 1386, 1336, 1276, 1261, 1173, 950, 873, 764, and 750 cm^{-1}. **m.p.**: 228.4–231.4 °C. **HRMS (DART-TOF)** calculated for $C_{21}H_{19}N_4O^+$ $[M+H]^+$ m/z 343.1553, found 343.1558.



20d

1-(4-(6-(*p*-tolyl) pyridin-2-yl) phenyl) ethan-1-one (20d)

Following the **General Procedure**, pyridinyl sulfone **19d** (61.9 mg, 0.2 mmol), (4-acetylphenyl)boronic acid **14** (65.6 mg, 0.4 mmol), $Ni(COD)_2$ (5.5 mg, 0.02 mmol), $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol), KOH (22.4 mg, 0.4 mmol), and THF (2.0 mL) were used. The residue was purification by flash chromatography (SiO_2, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a white solid (41.4 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 8.05 (t, *J* = 8.4 Hz, 4H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.0, 2.8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.64 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.0, 143.9, 139.3, 137.7, 137.2, 136.5, 129.6, 128.8, 127.2, 126.9, 119.2, 118.9, 26.8, 21.4. **IR (thin film, cm^{-1})**: 3056, 2925, 1685, 1588, 1419, 1279, 1265, 1116, 893, 855, 797, 760, and 753 cm^{-1}. **m.p.**: 165.4–168.4 °C. **HRMS (DART-TOF)** calculated for $C_{20}H_{18}NO^+$ $[M+H]^+$ m/z 288.1383, found 288.1390.

9. References

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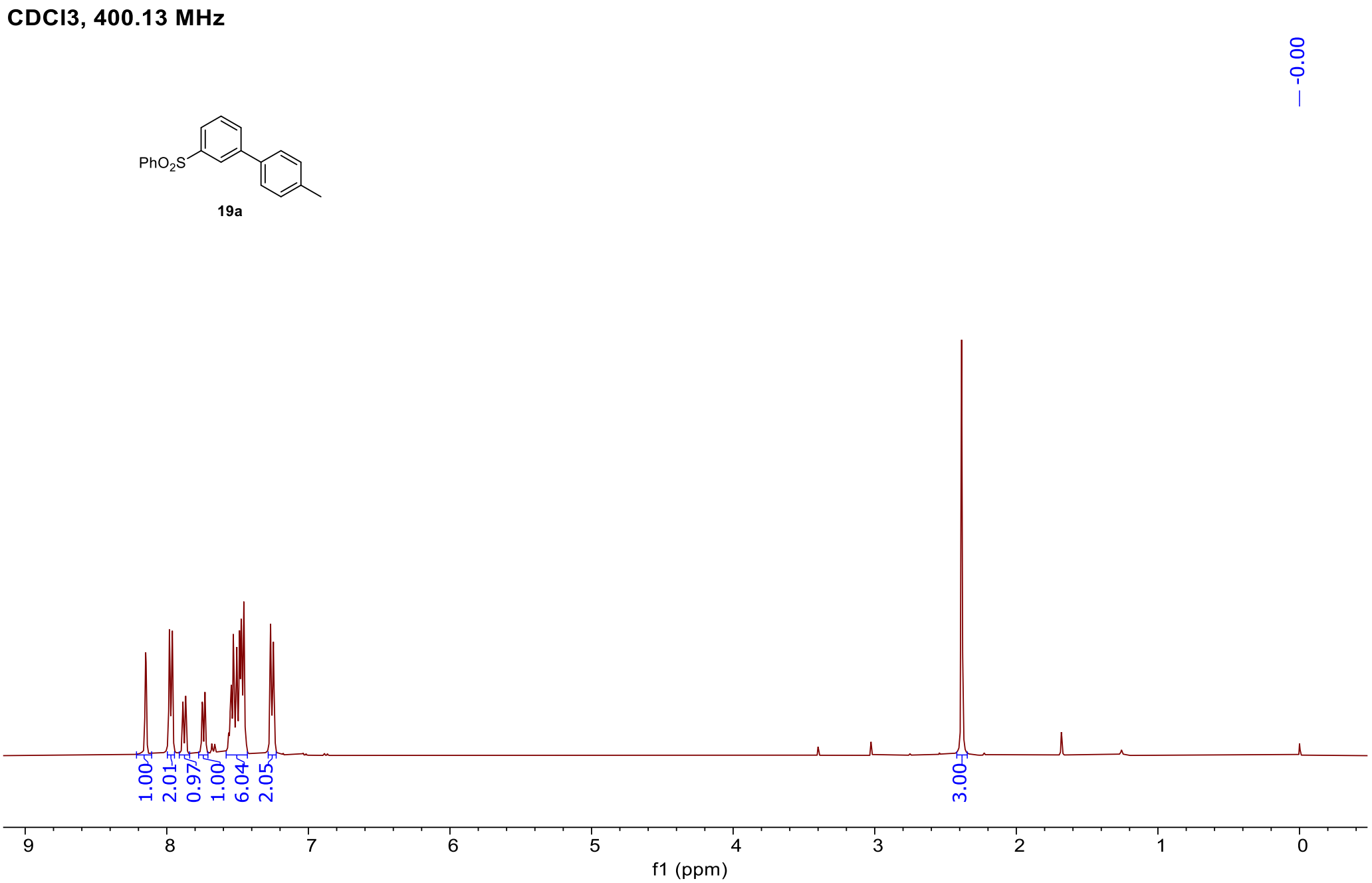
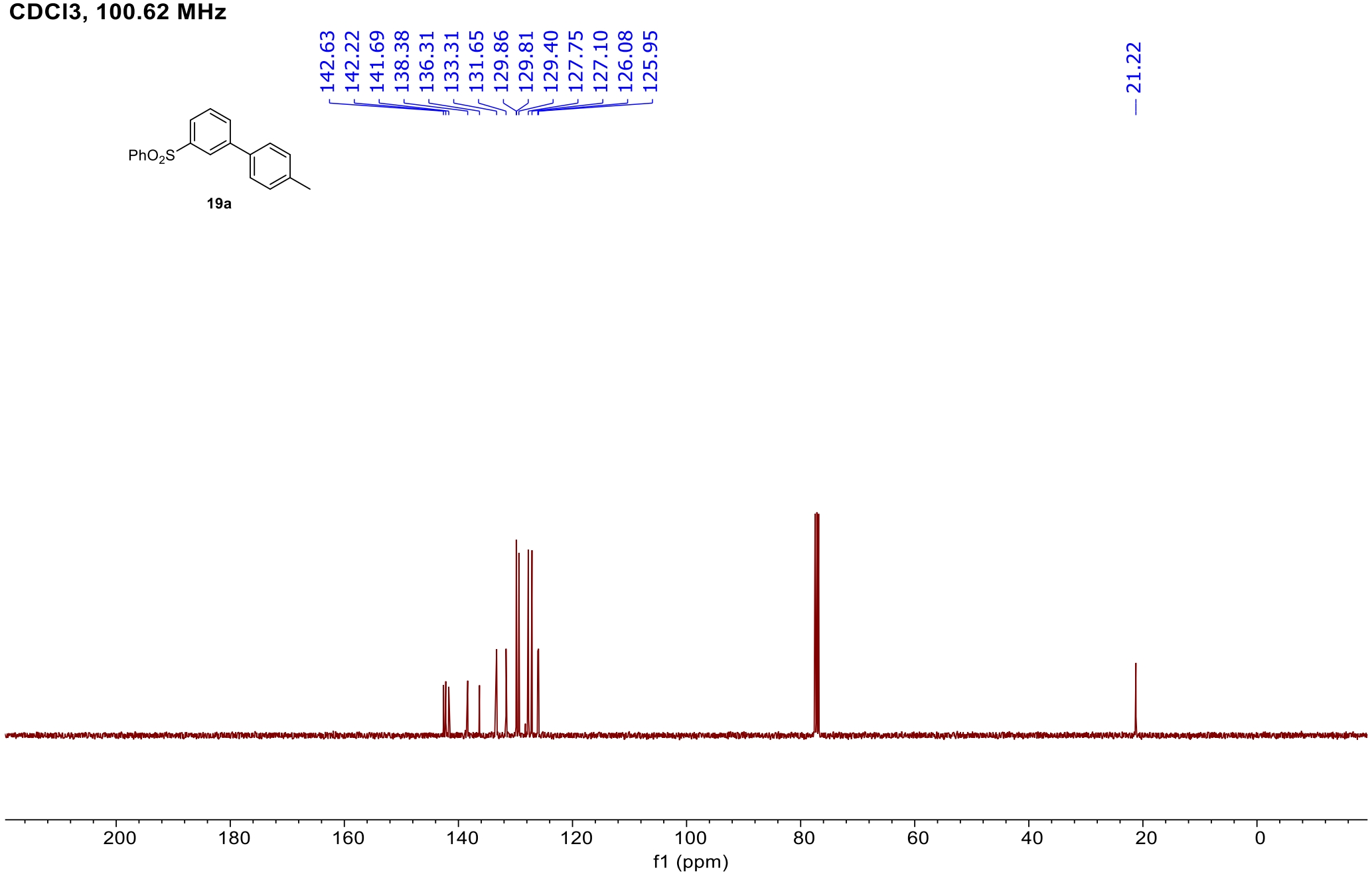
10. NMR Spectra

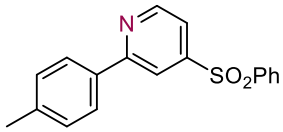


^{1}H NMR Spectrum of **19a**



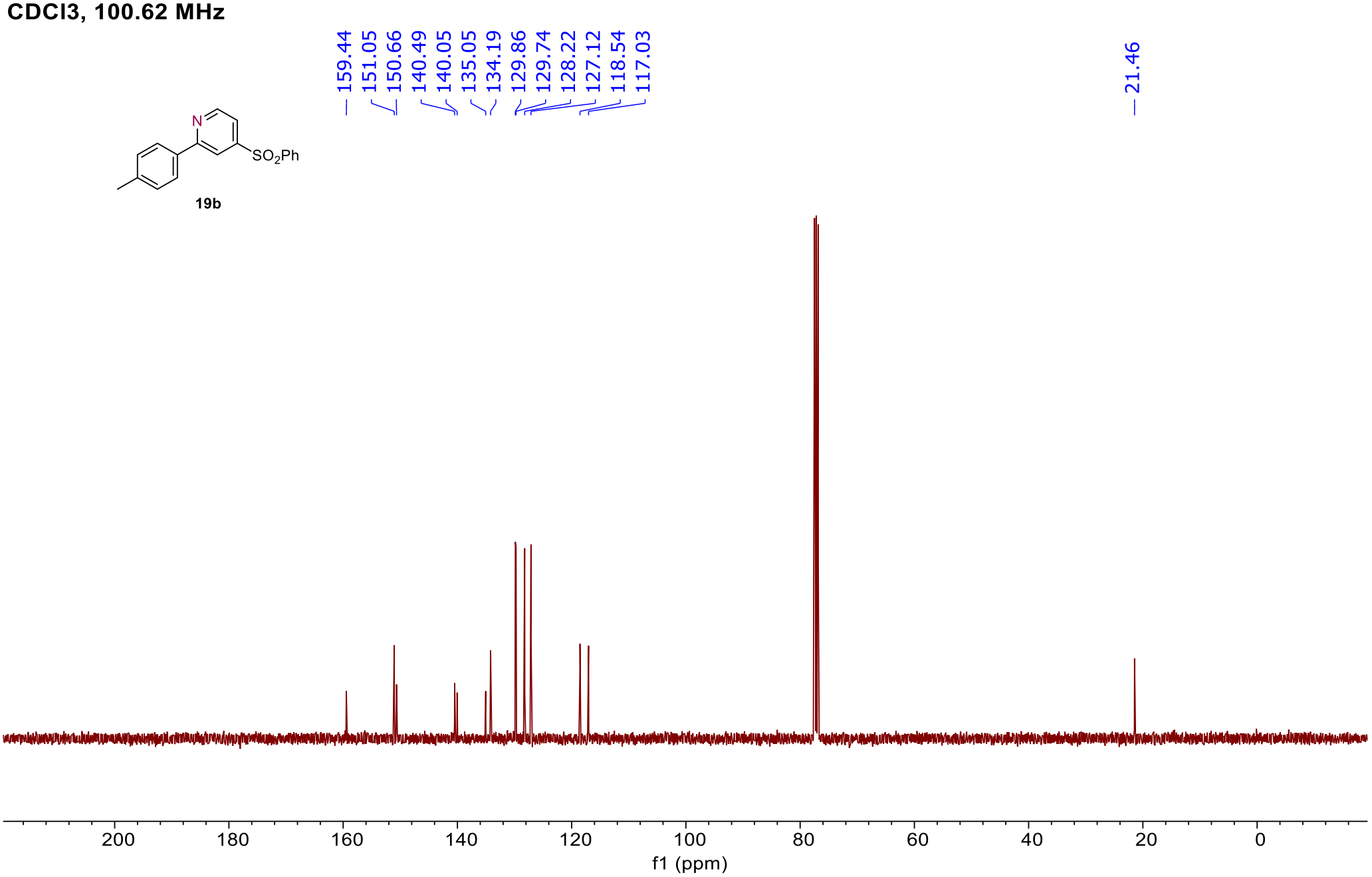
^{13}C NMR Spectrum of **19a**

CDCl3, 400.13 MHz



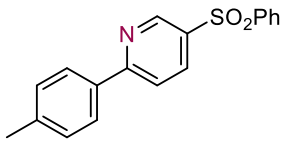
19b

^{1}H NMR Spectrum of **19b**



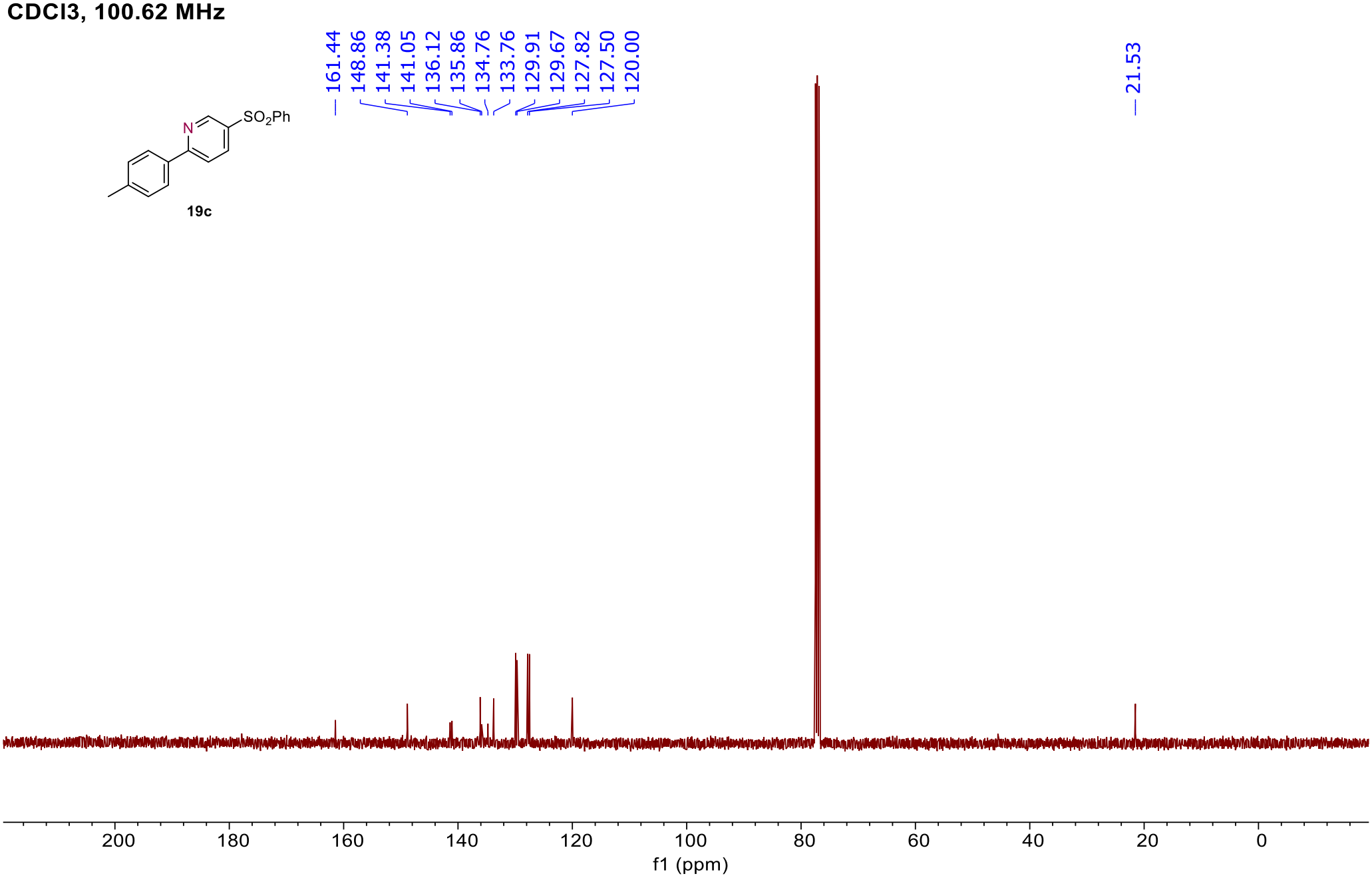
^{13}C NMR Spectrum of **19b**

CDCl3, 400.13 MHz



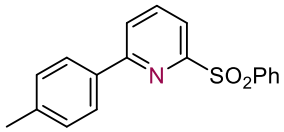
19c

^{1}H NMR Spectrum of **19c**



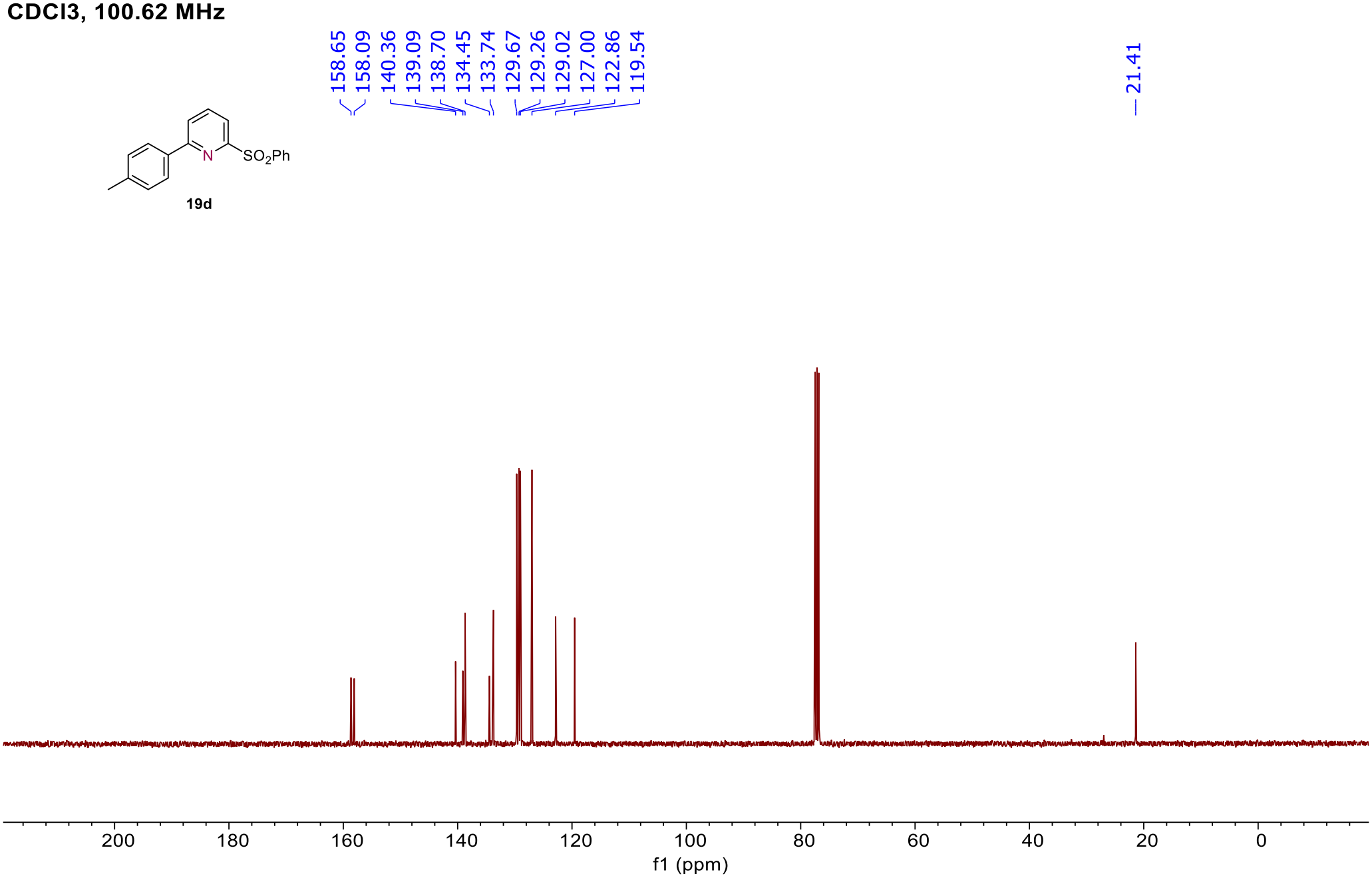
^{13}C NMR Spectrum of **19c**

CDCl3, 400.13 MHz

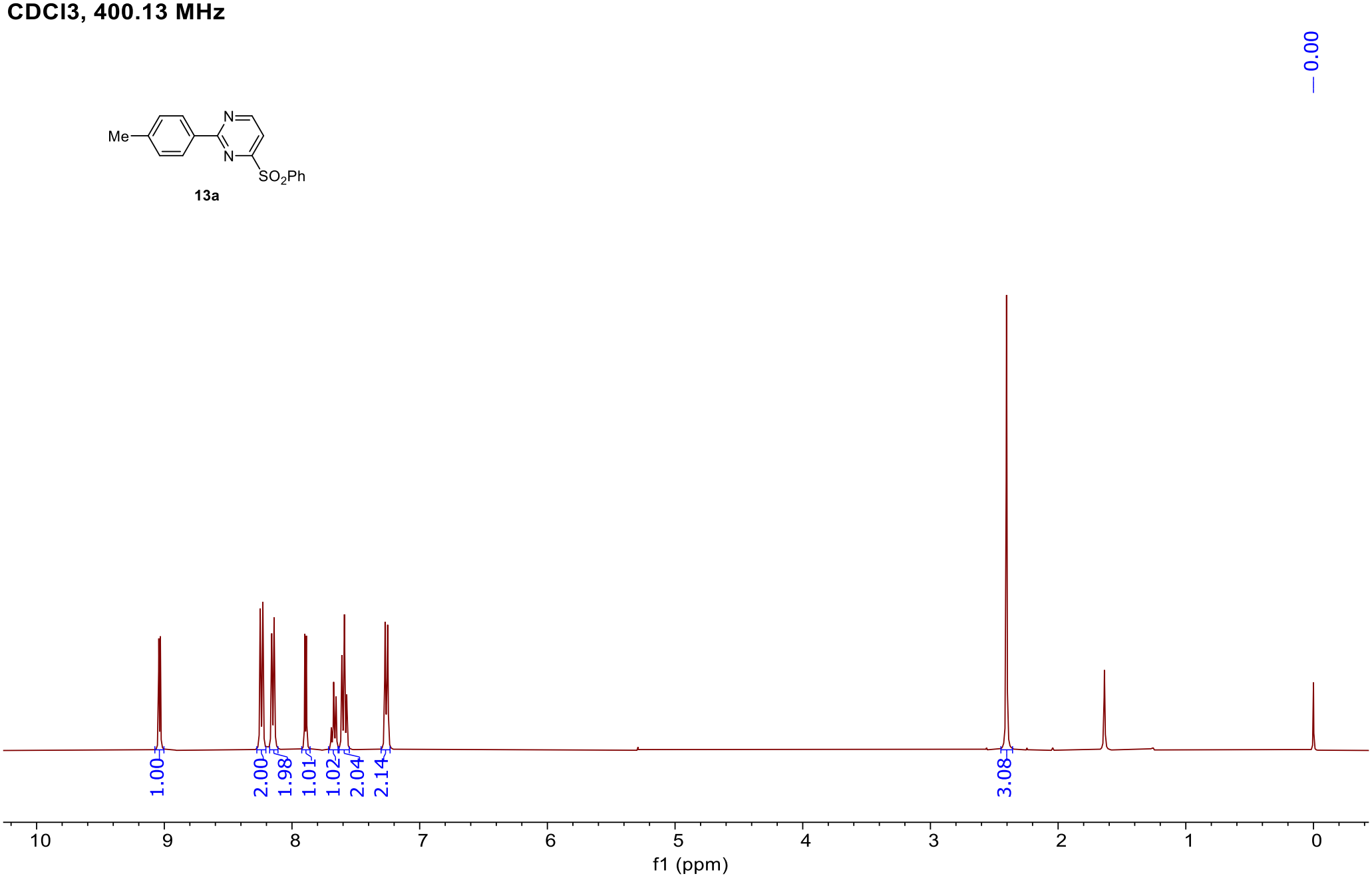


19d

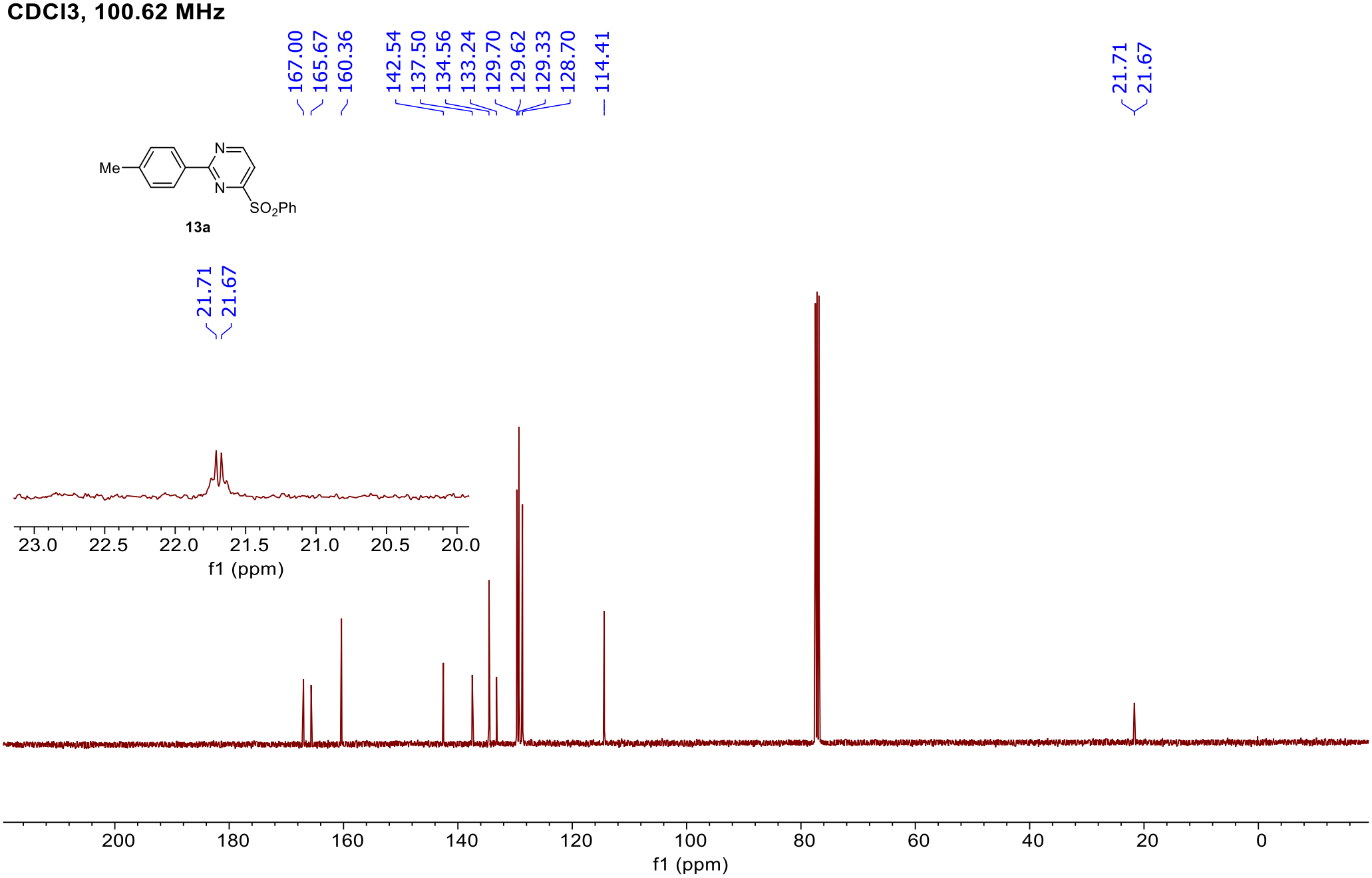
^{1}H NMR Spectrum of **19d**



^{13}C NMR Spectrum of **19d**

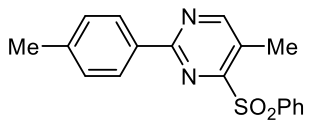


^{1}H NMR Spectrum of **13a**



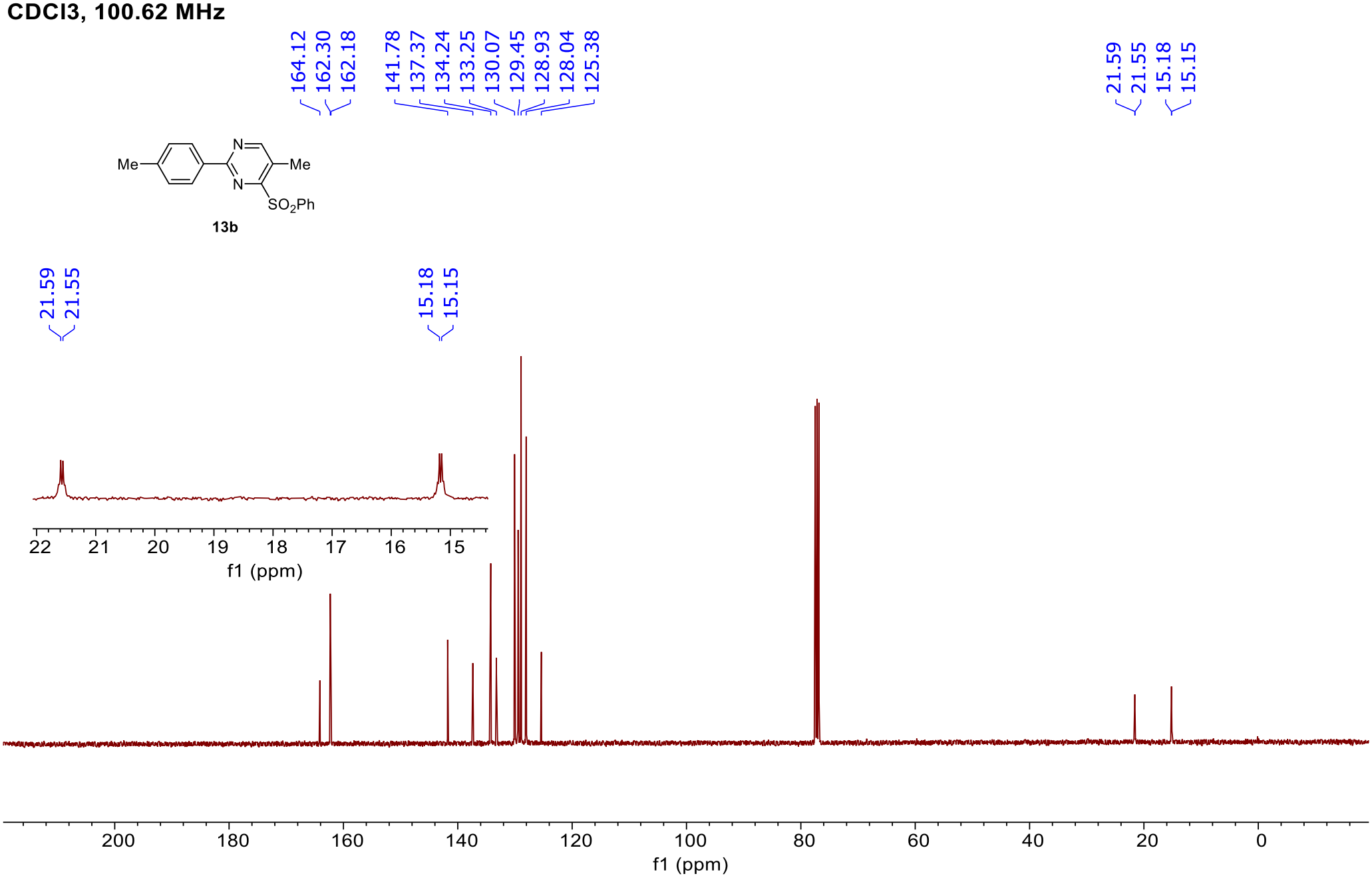
^{13}C NMR Spectrum of **13a**

CDCl3, 400.13 MHz



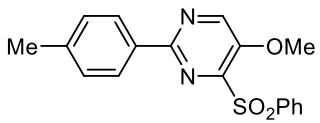
13b

^{1}H NMR Spectrum of **13b**



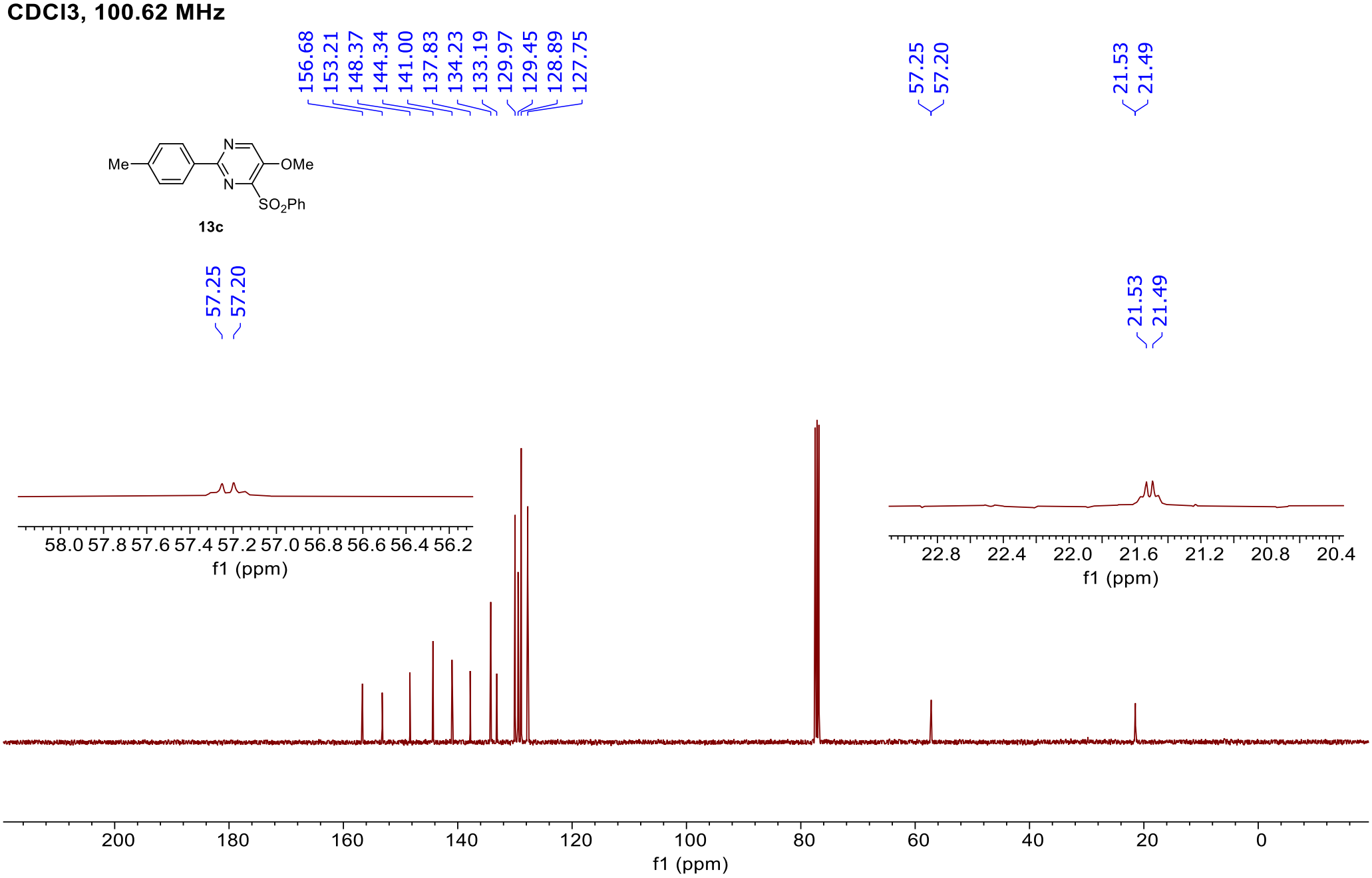
^{13}C NMR Spectrum of **13b**

CDCl3, 400.13 MHz



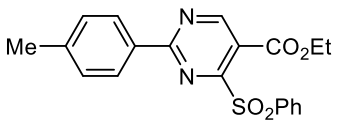
13c

^{1}H NMR Spectrum of **13c**



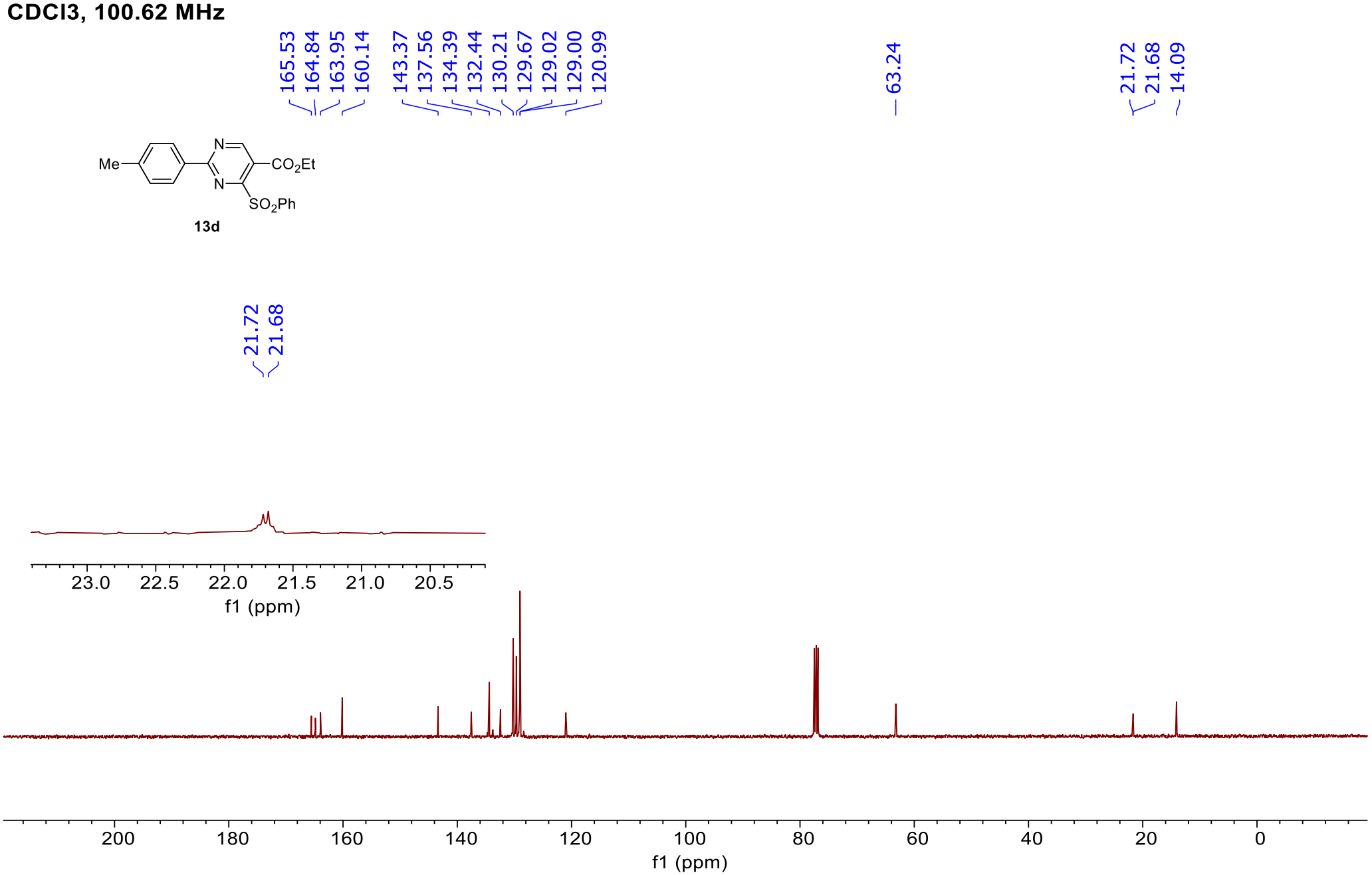
^{13}C NMR Spectrum of **13c**

CDCl3, 400.13 MHz



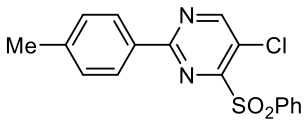
13d

^{1}H NMR Spectrum of **13d**



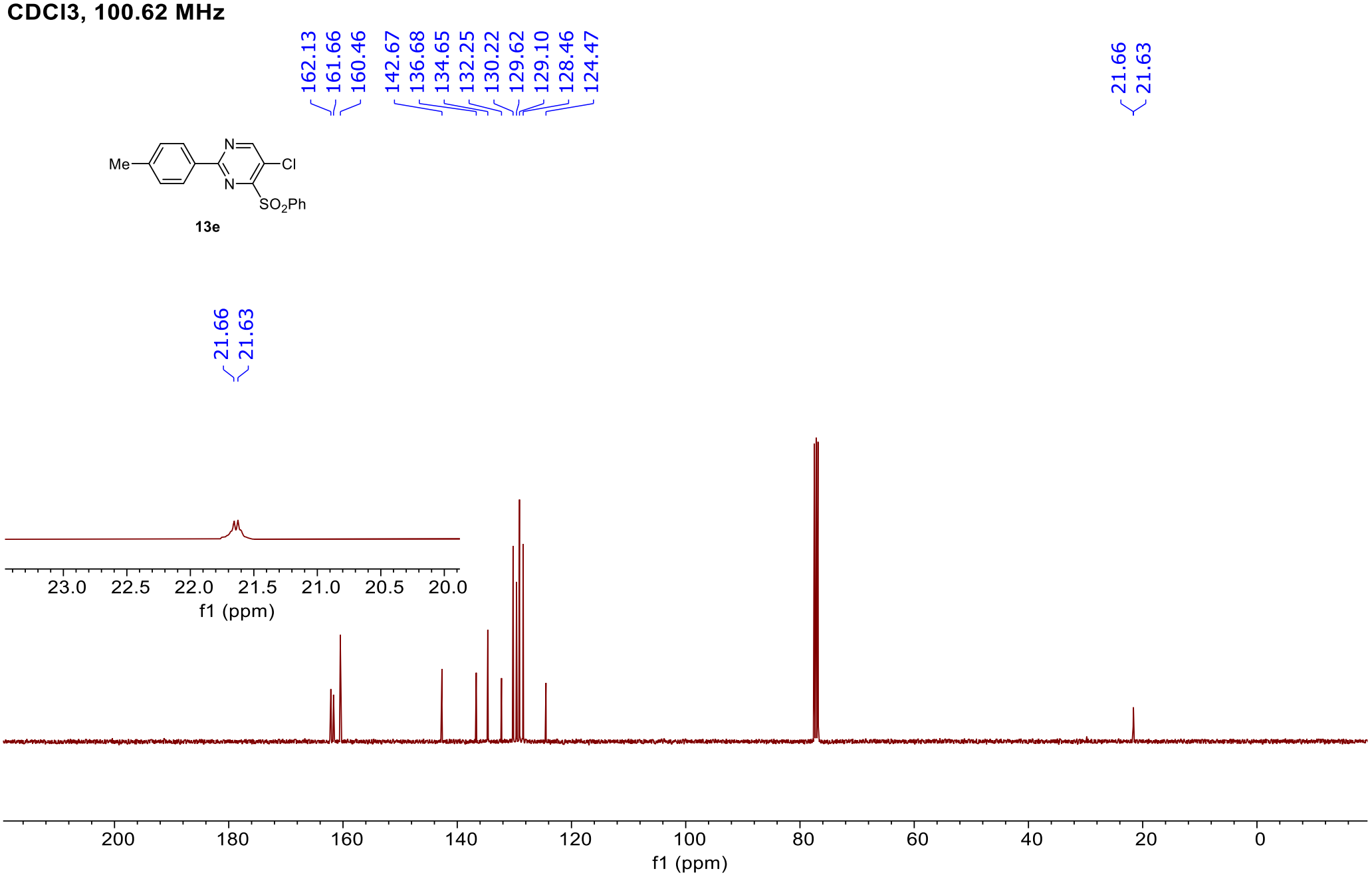
^{13}C NMR Spectrum of **13d**

CDCl3, 400.13 MHz



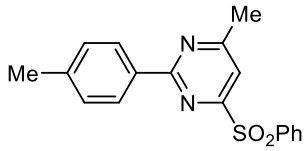
13e

^{1}H NMR Spectrum of **13e**



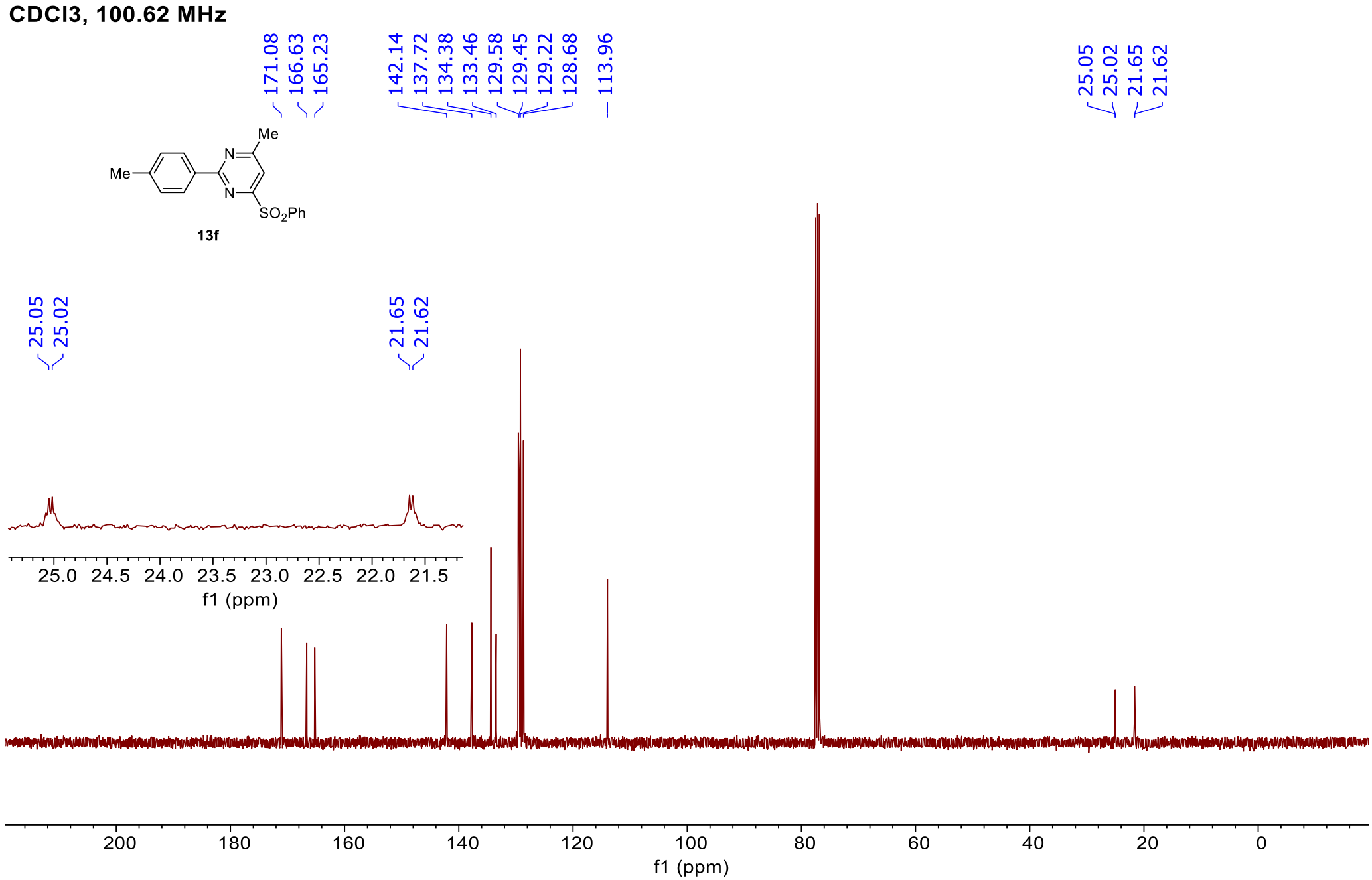
^{13}C NMR Spectrum of **13e**

CDCl3, 400.13 MHz



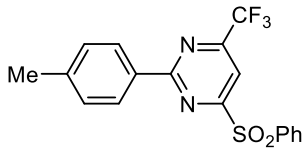
13f

^{1}H NMR Spectrum of **13f**



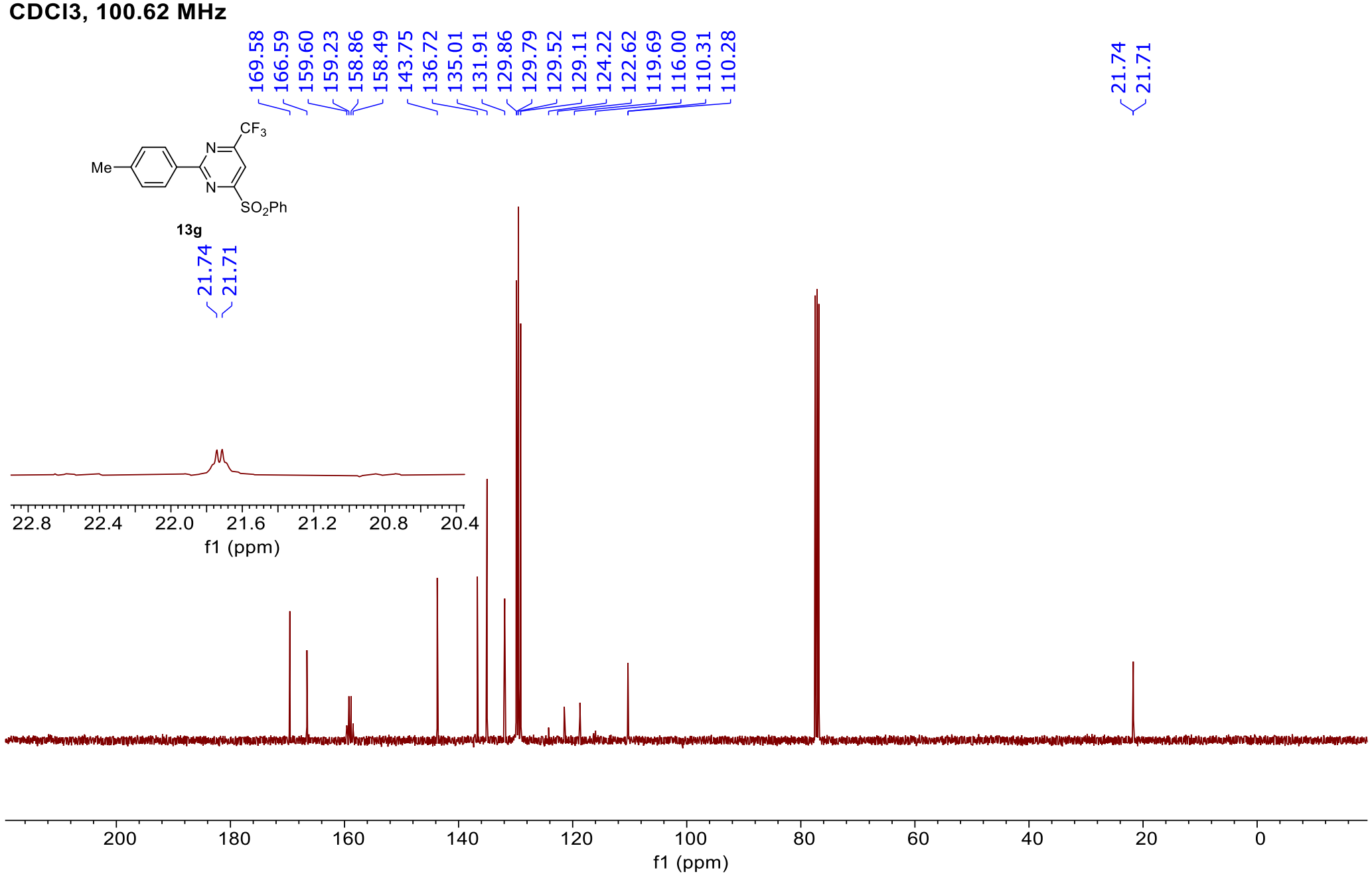
^{13}C NMR Spectrum of **13f**

CDCl3, 400.13 MHz



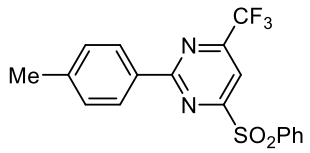
13g

^{1}H NMR Spectrum of **13g**



^{13}C NMR Spectrum of **13g**

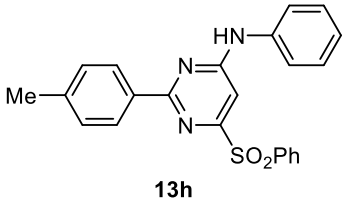
CDCl3, 376.46 MHz



13g

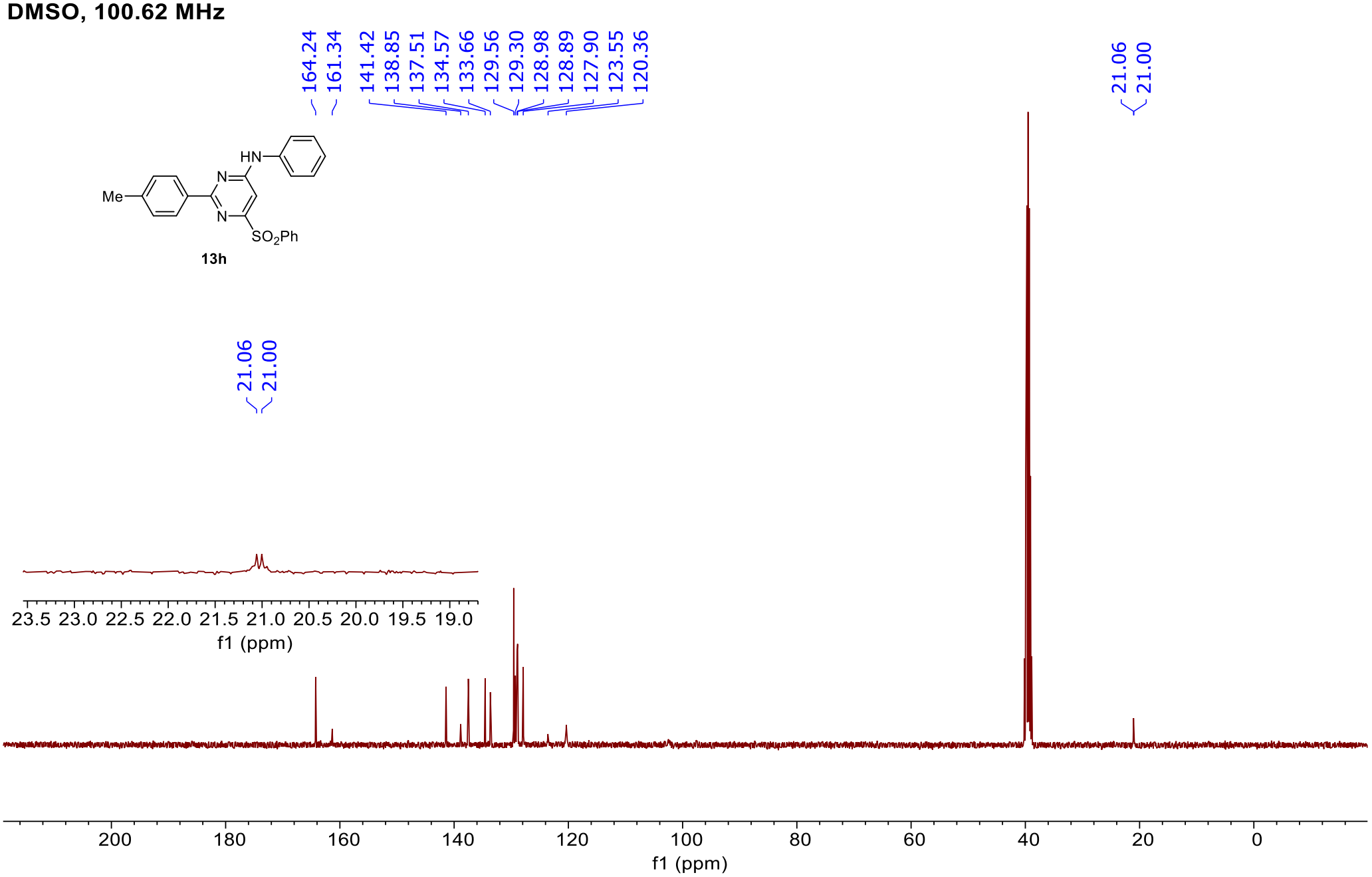
^{19}F NMR Spectrum of **13g**

DMSO, 400.13 MHz



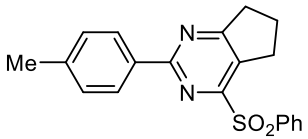
13h

^{1}H NMR Spectrum of **13h**



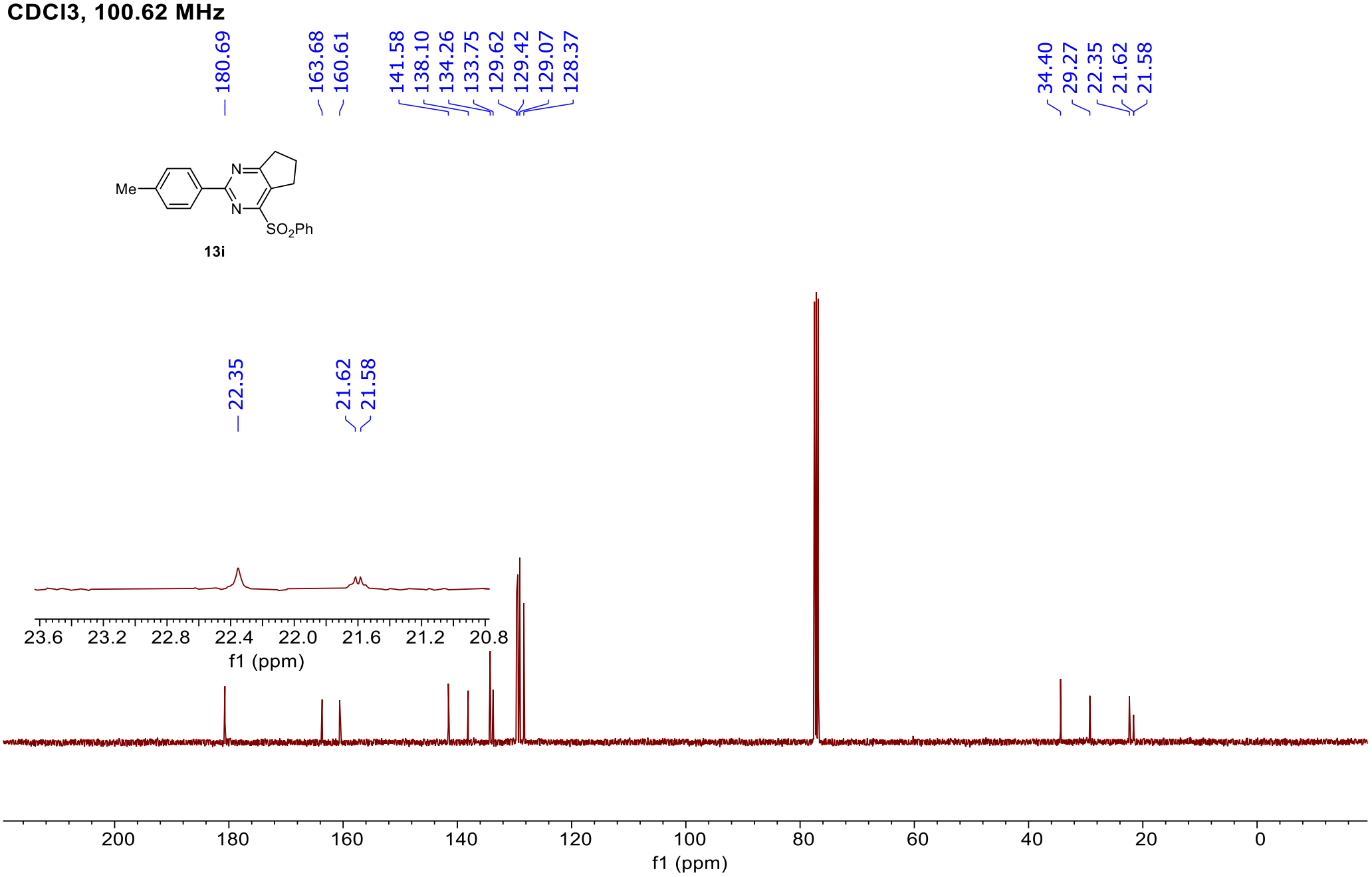
^{13}C NMR Spectrum of **13h**

CDCl3, 400.13 MHz



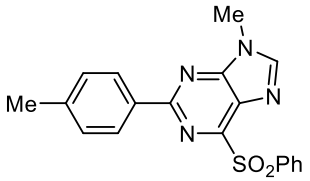
13i

^{1}H NMR Spectrum of **13i**



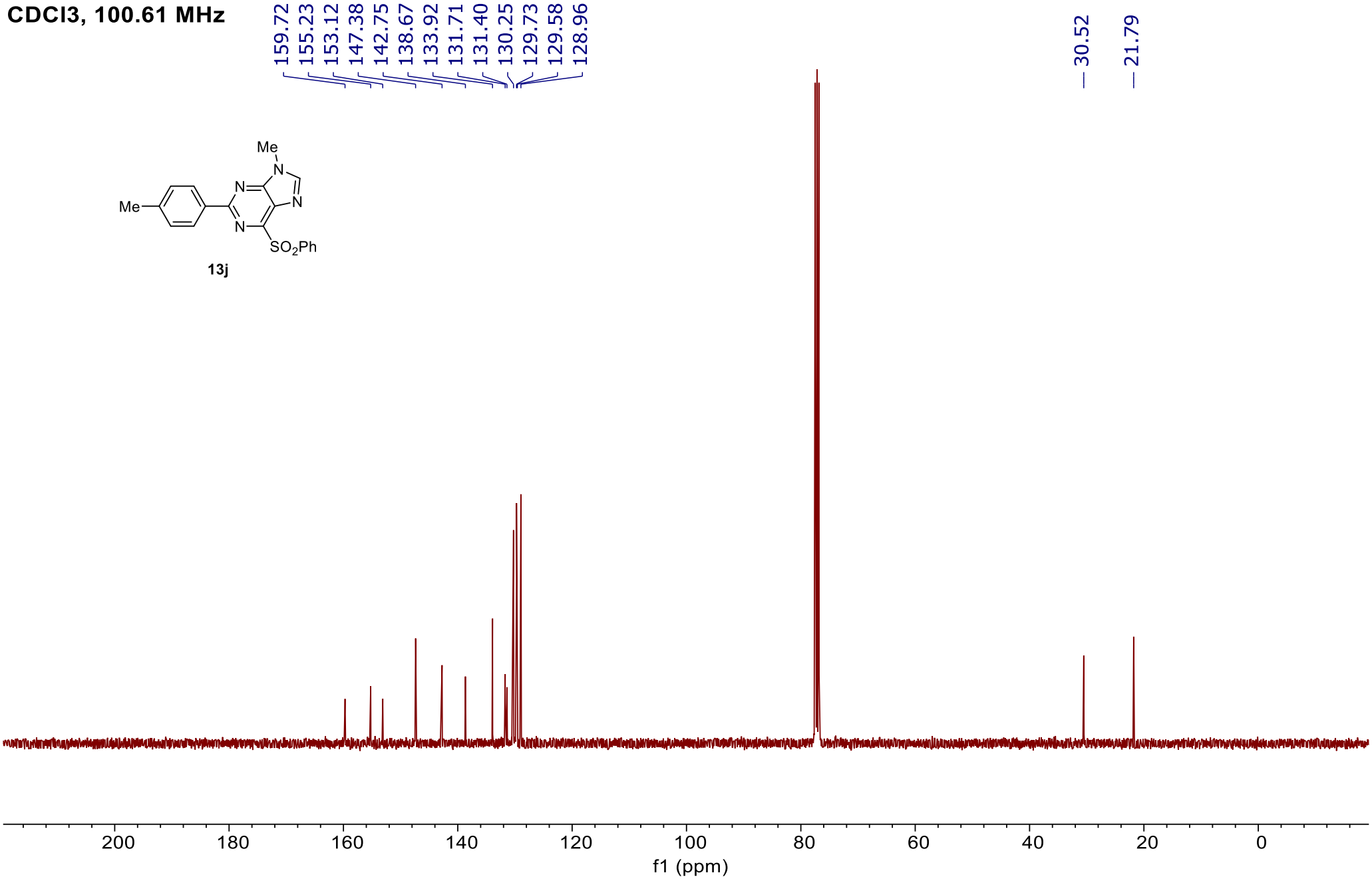
^{13}C NMR Spectrum of **13i**

CDCl3, 400.13 MHz



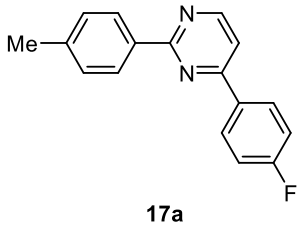
13j

^{1}H NMR Spectrum of **13j**



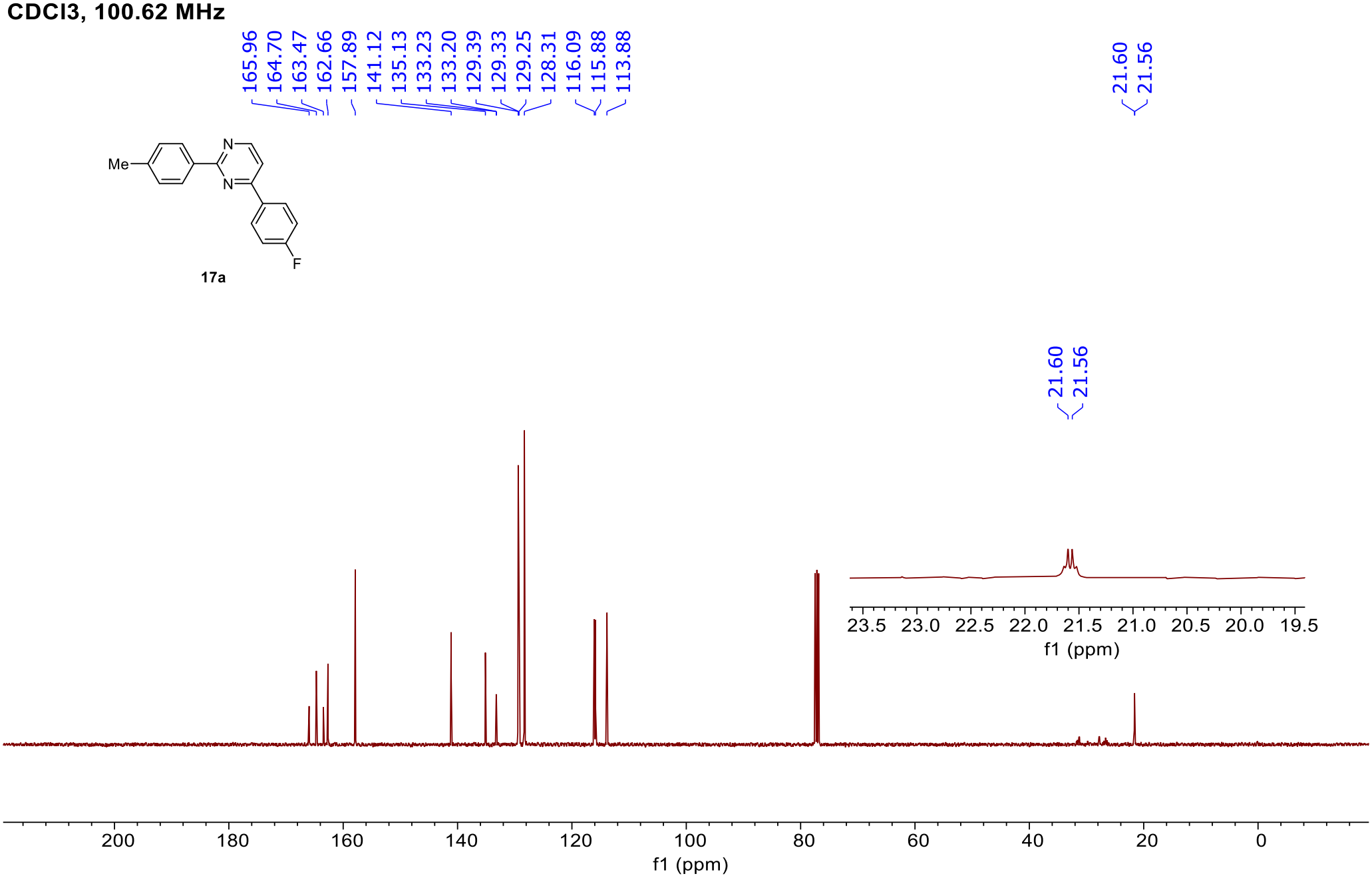
^{13}C NMR Spectrum of **13j**

CDCl3, 400.13 MHz

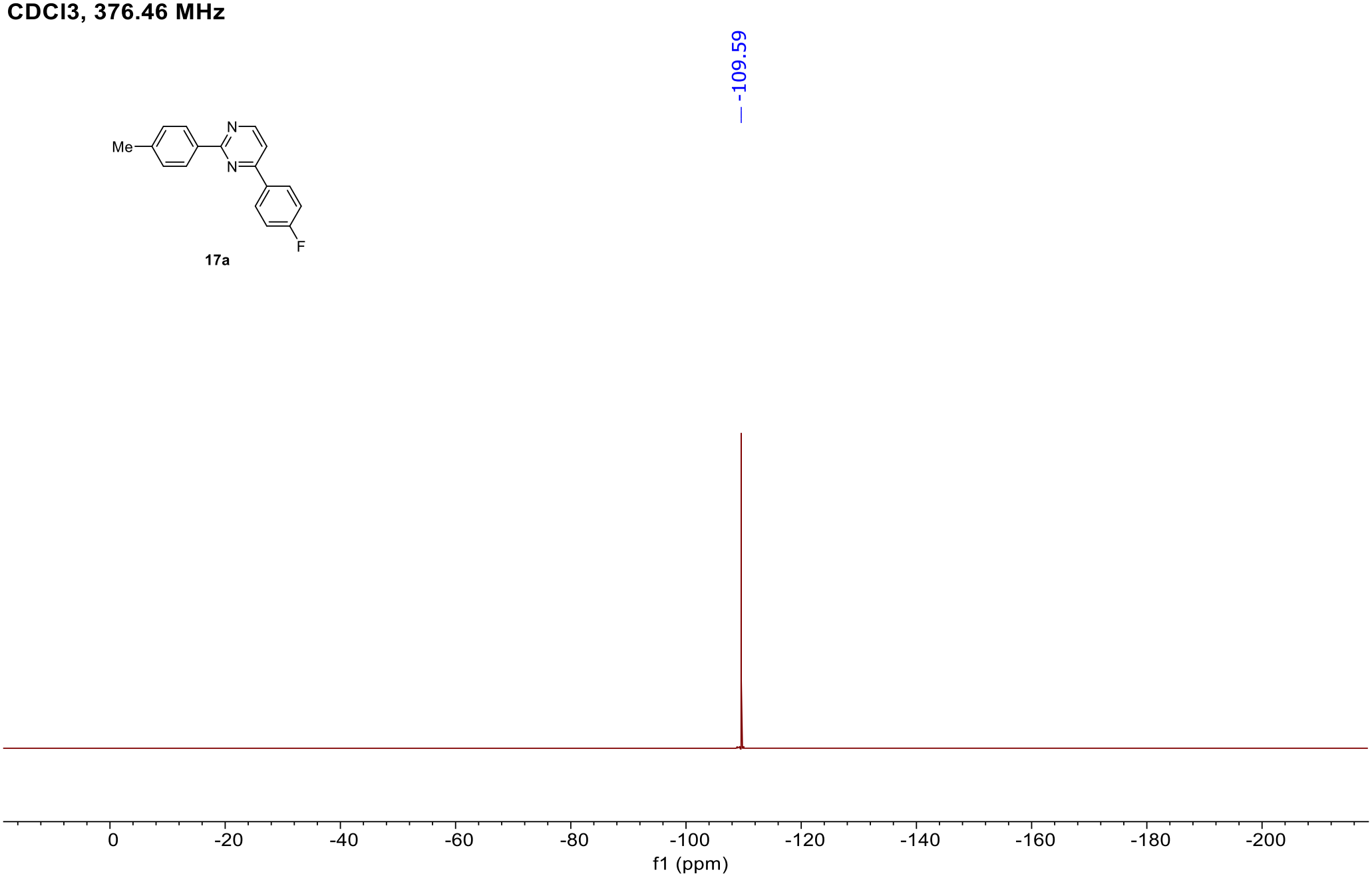


17a

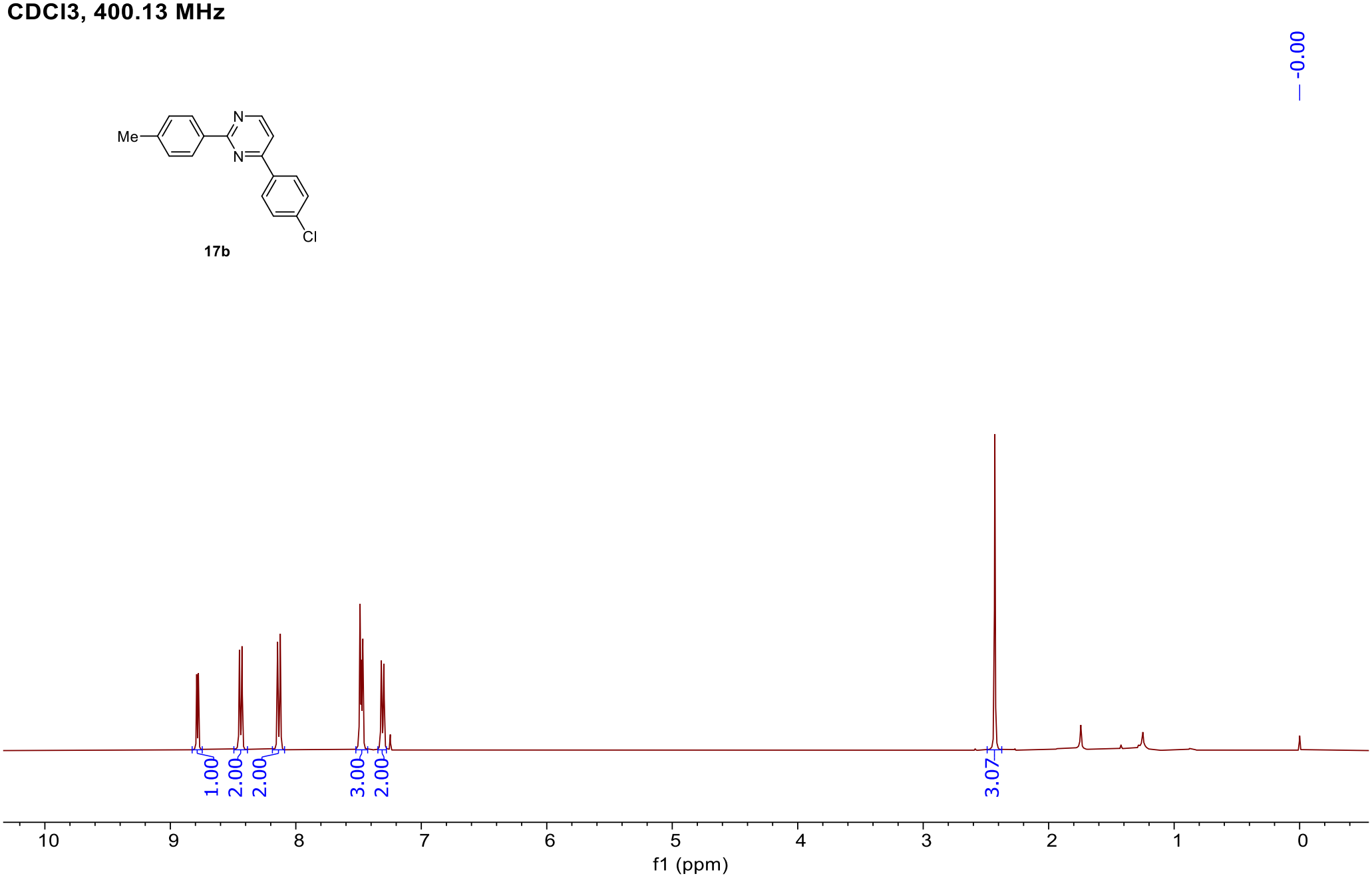
^{1}H NMR Spectrum of **17a**



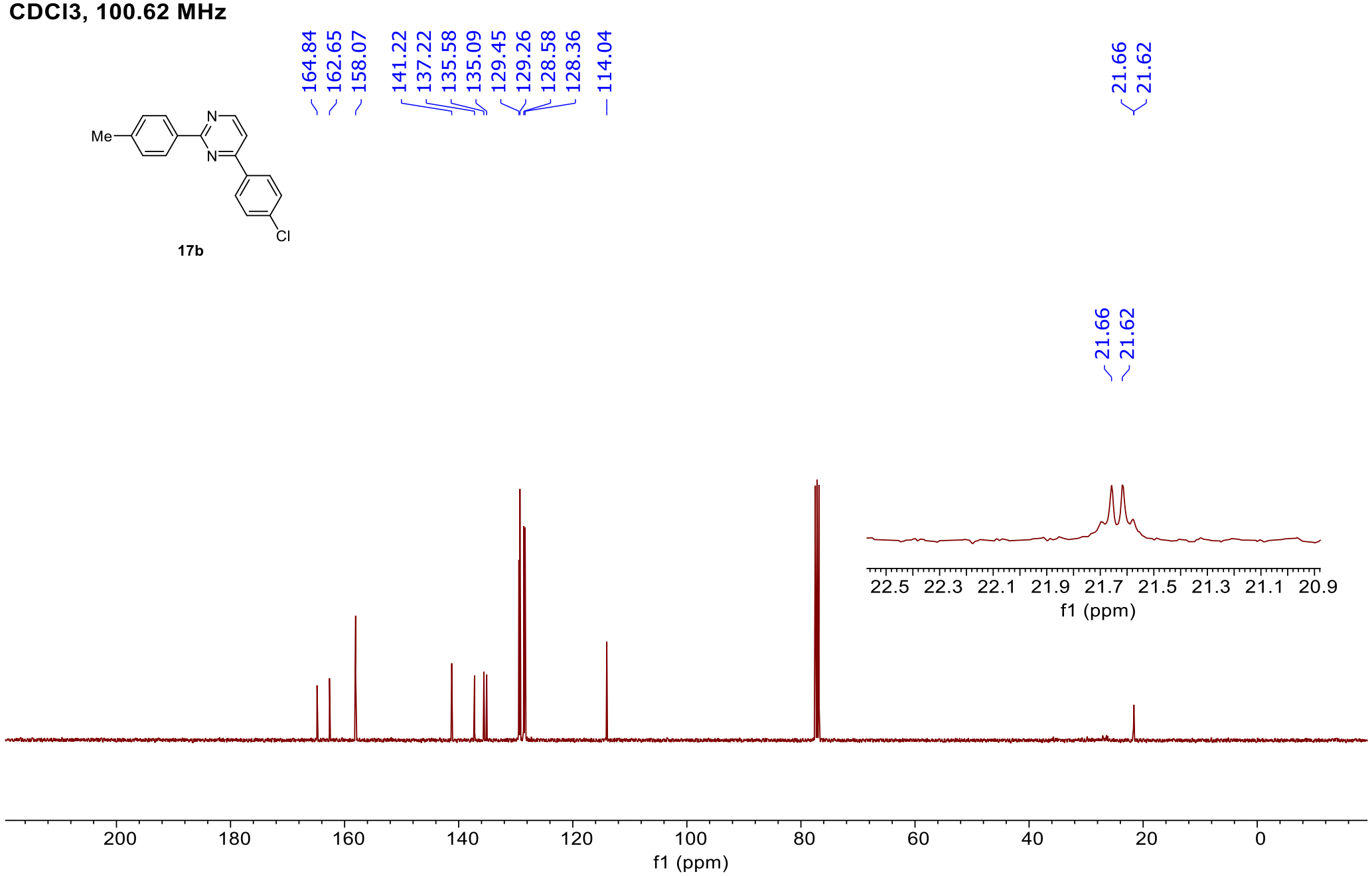
^{13}C NMR Spectrum of **17a**



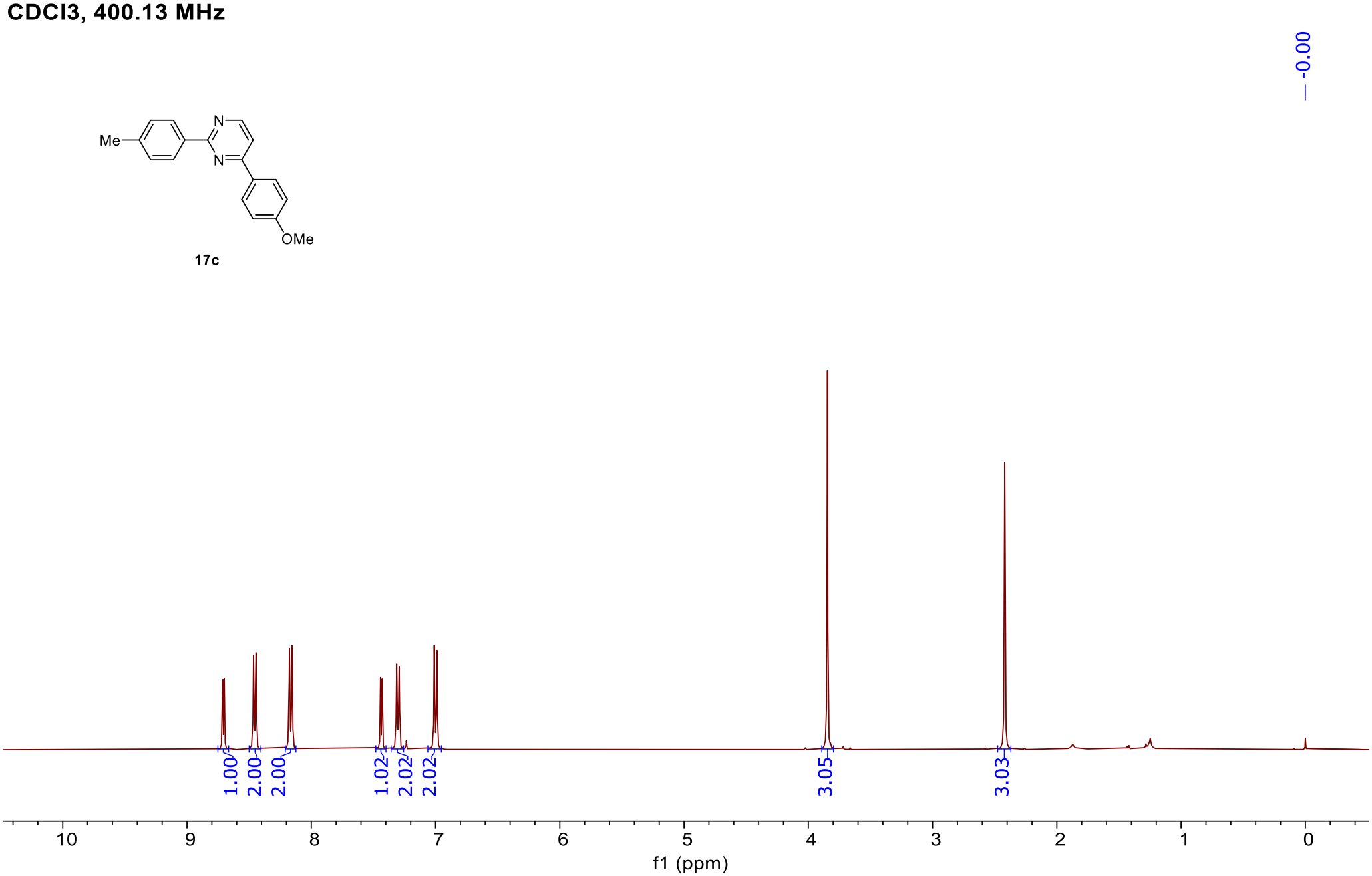
^{19}F NMR Spectrum of **17a**



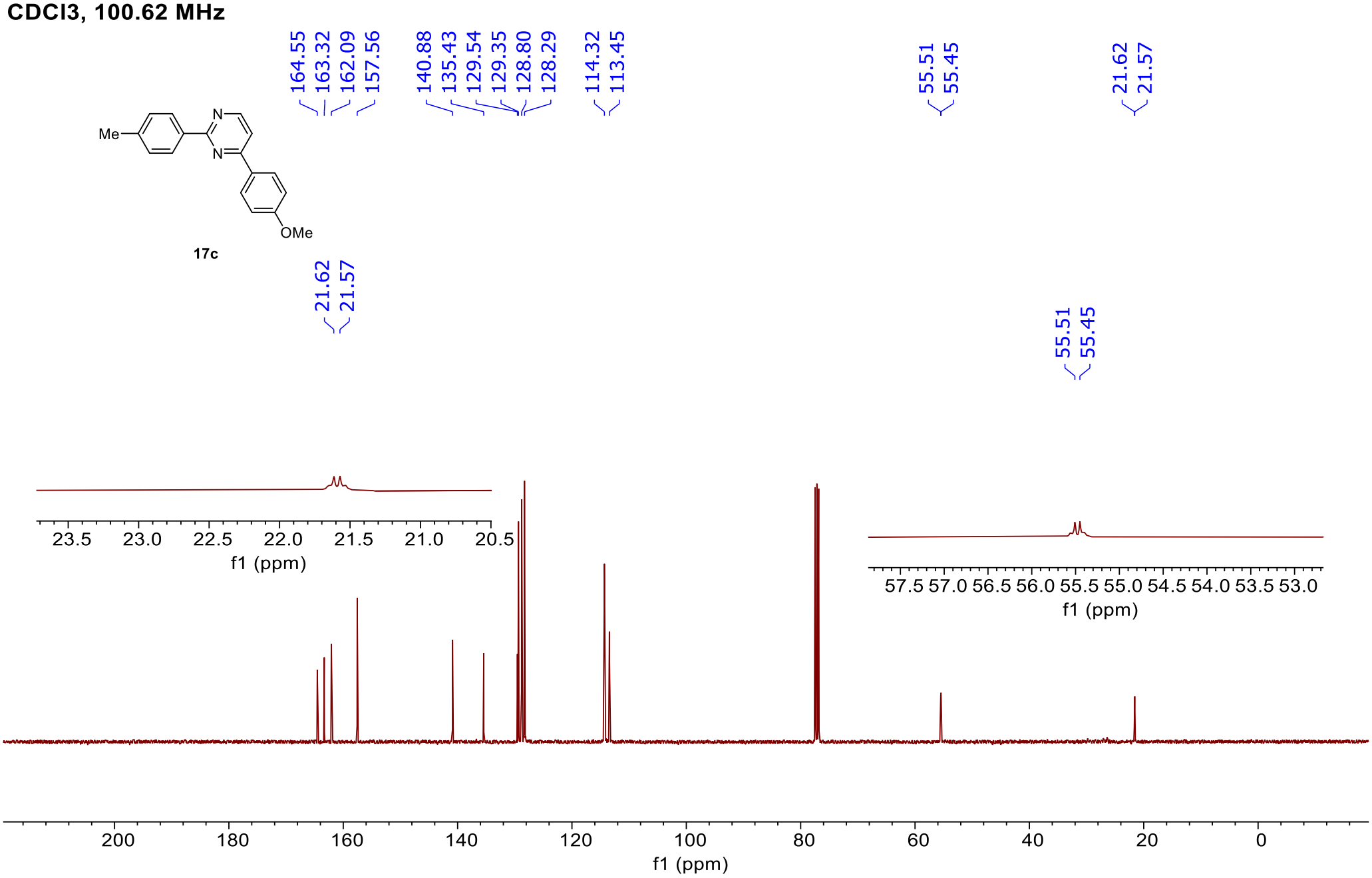
^{1}H NMR Spectrum of **17b**



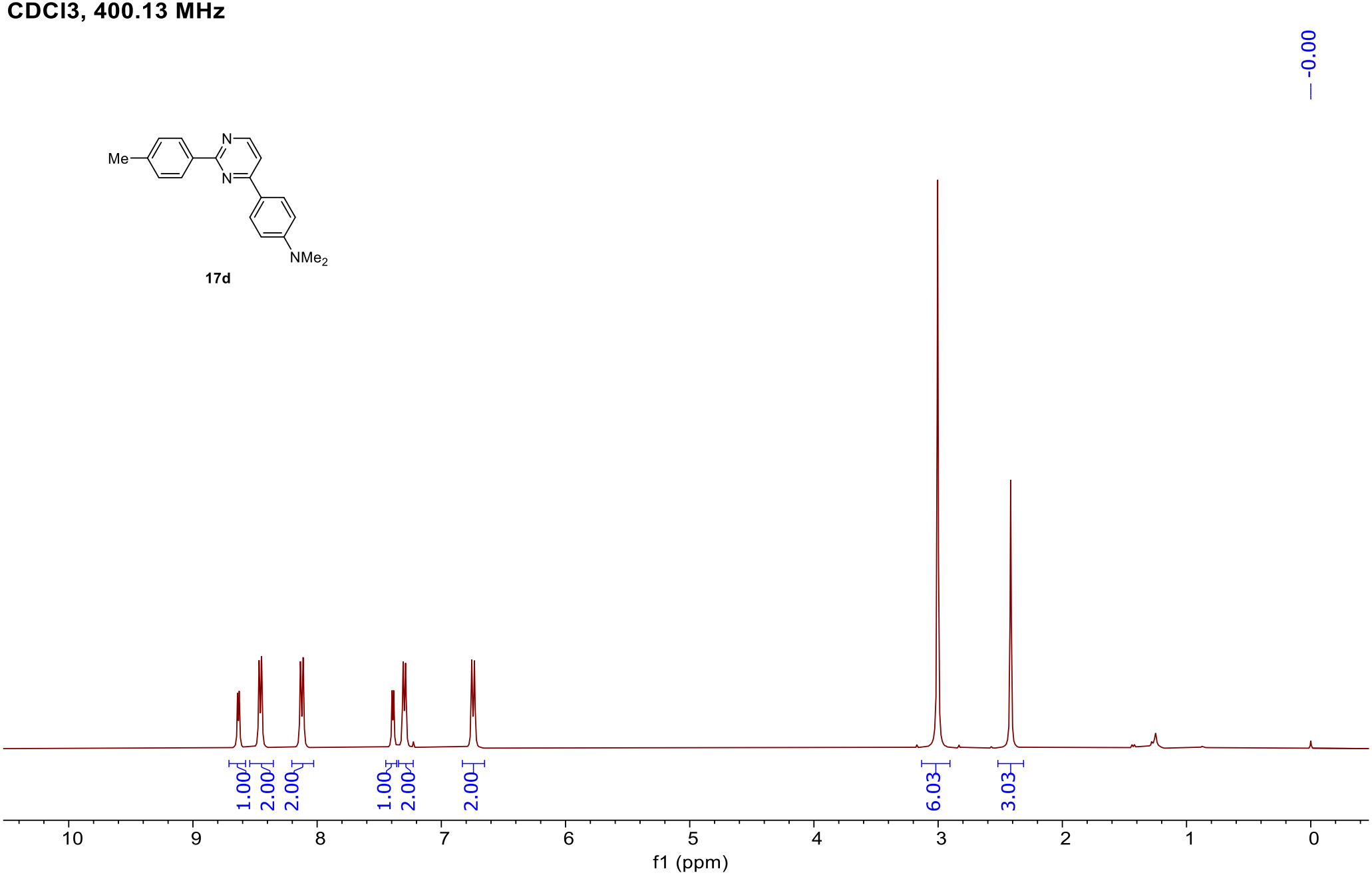
^{13}C NMR Spectrum of **17b**



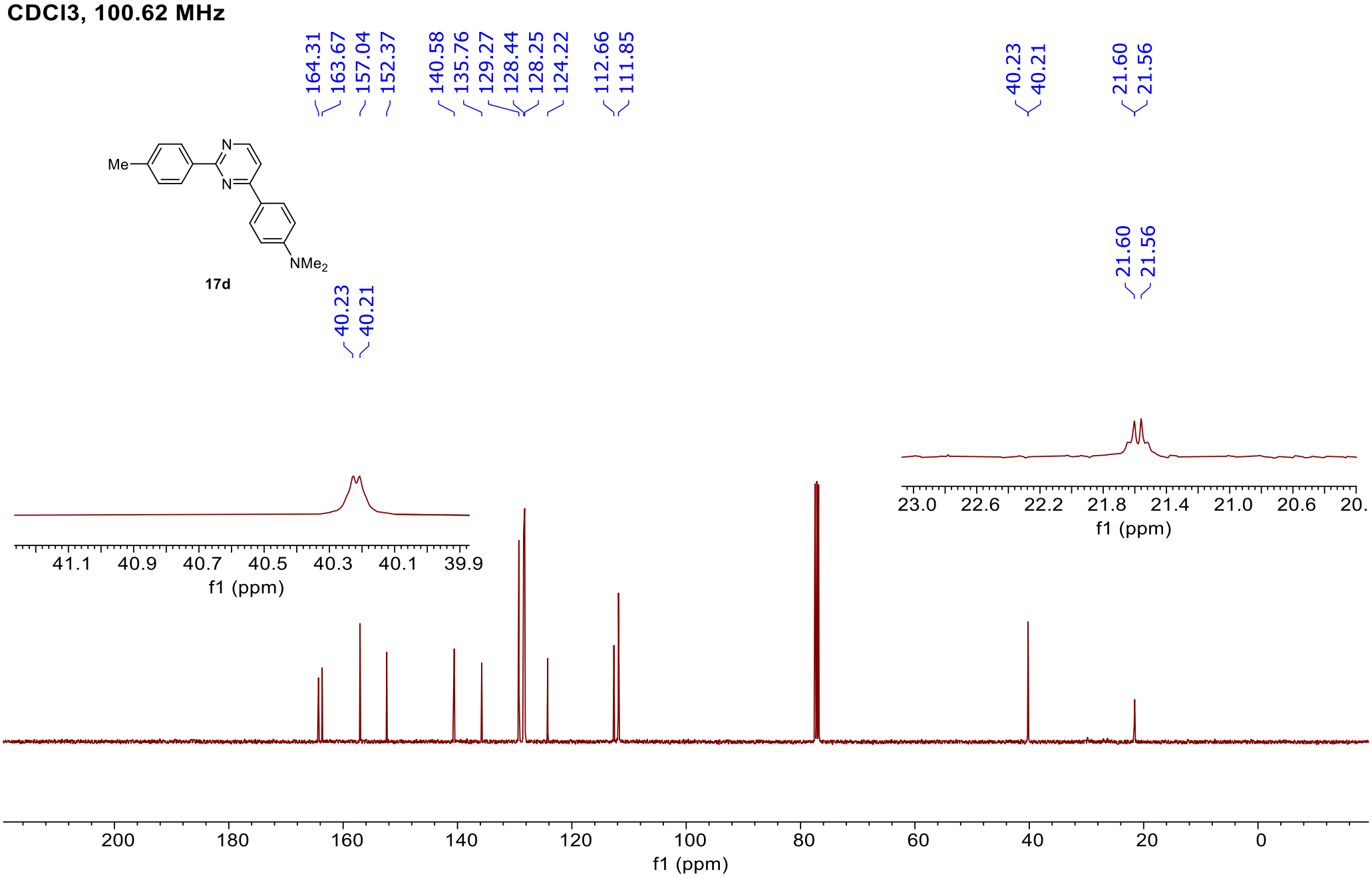
^{1}H NMR Spectrum of **17c**



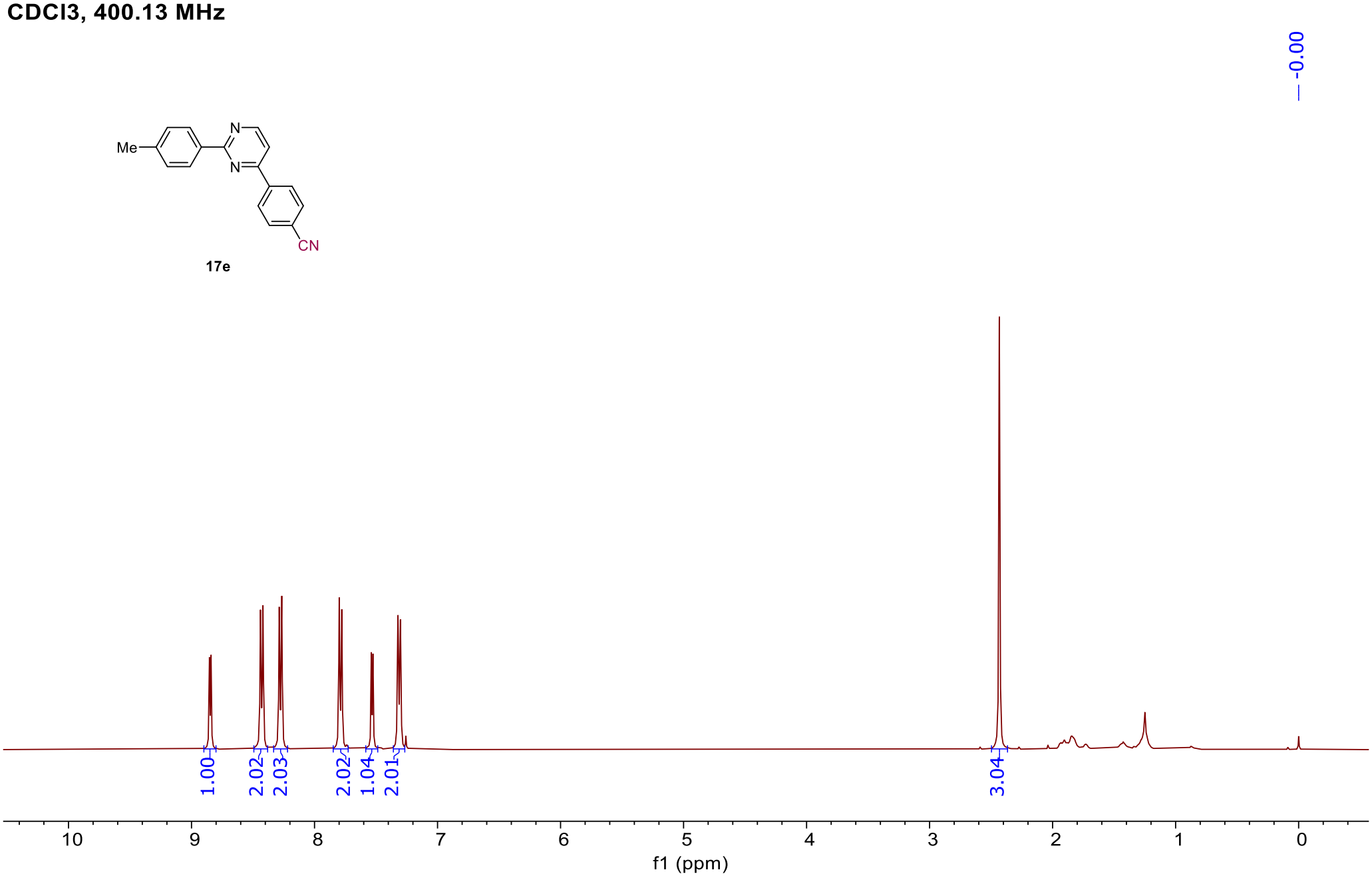
^{13}C NMR Spectrum of **17c**



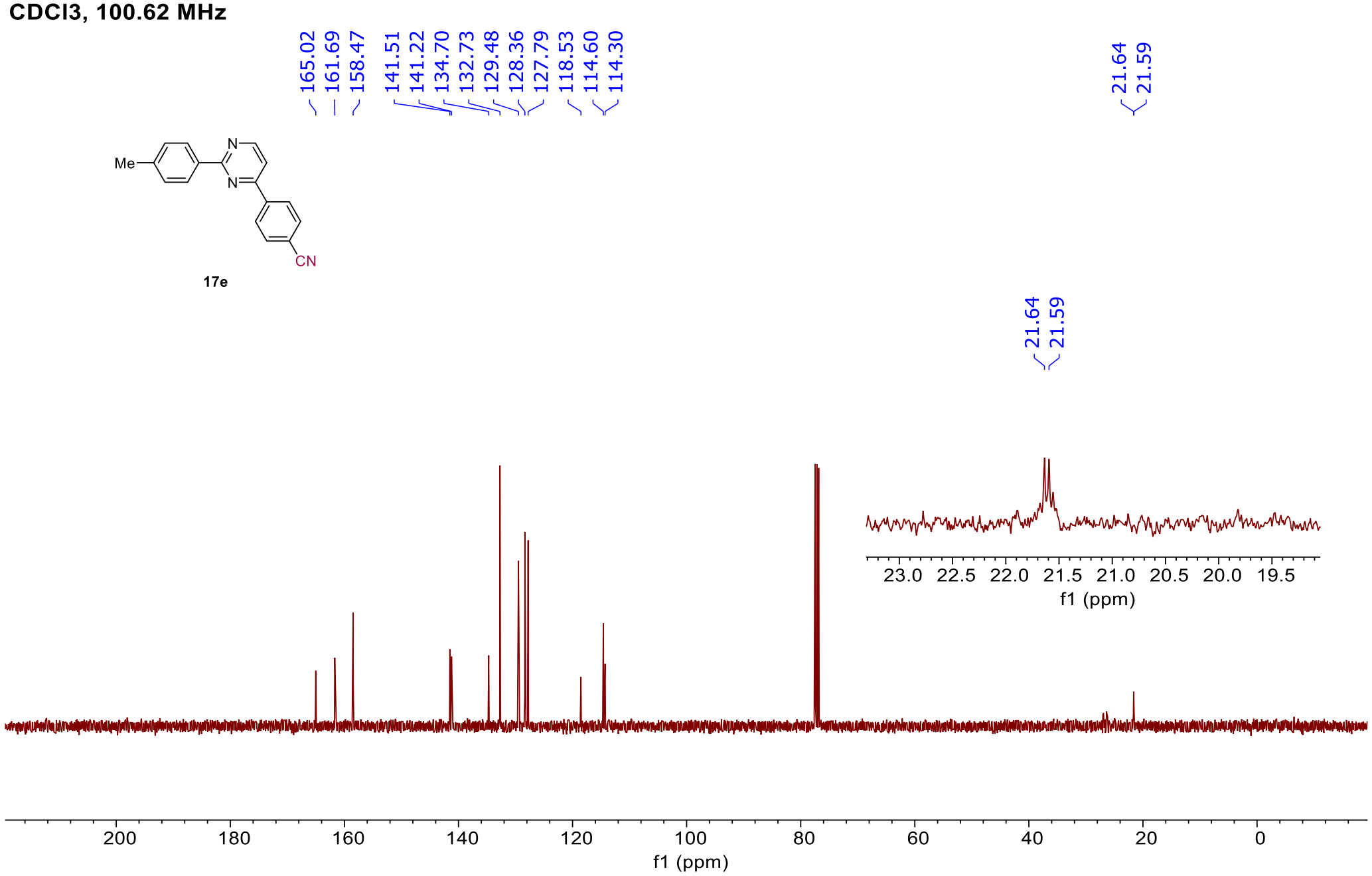
^{1}H NMR Spectrum of **17d**



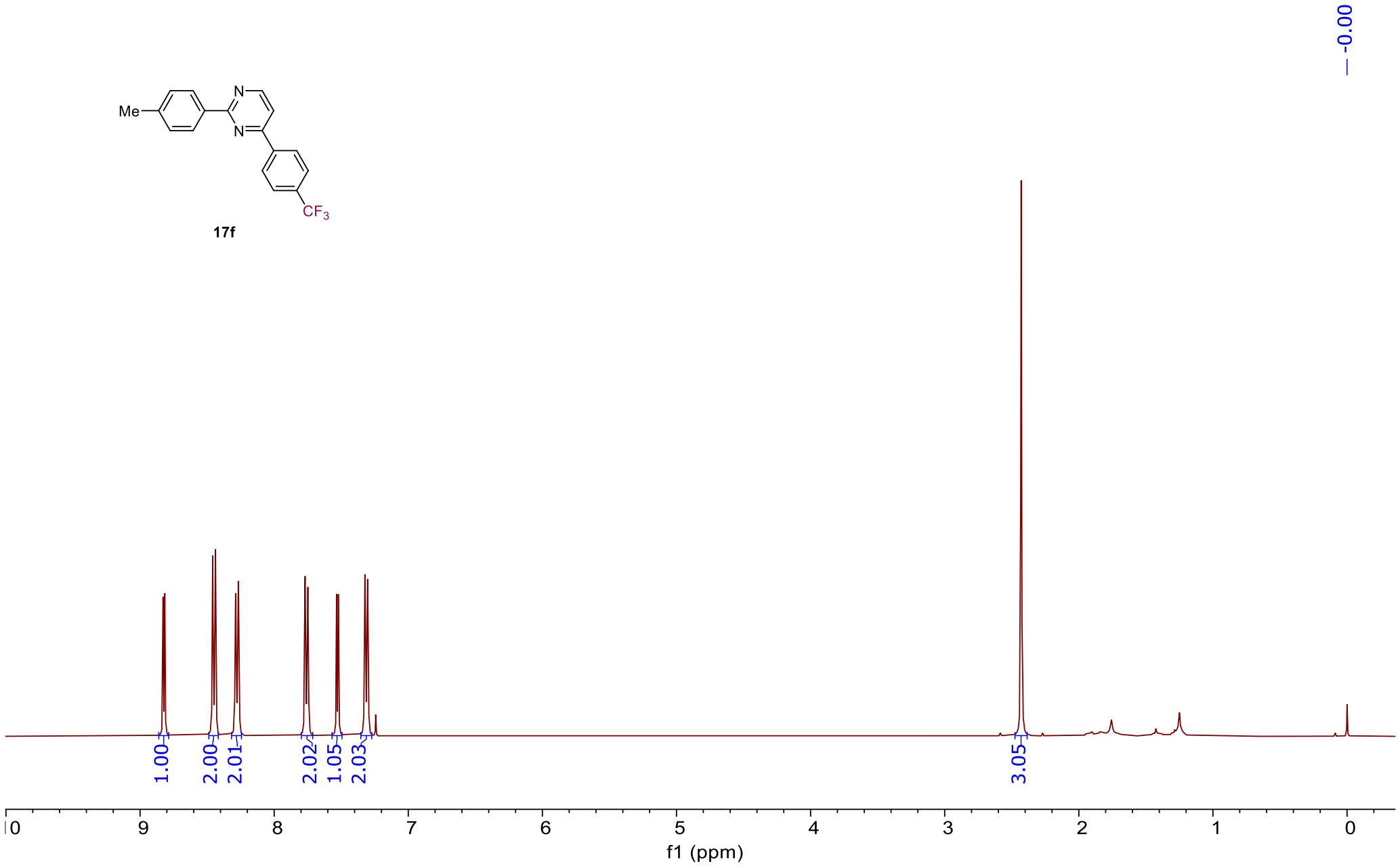
^{13}C NMR Spectrum of **17d**



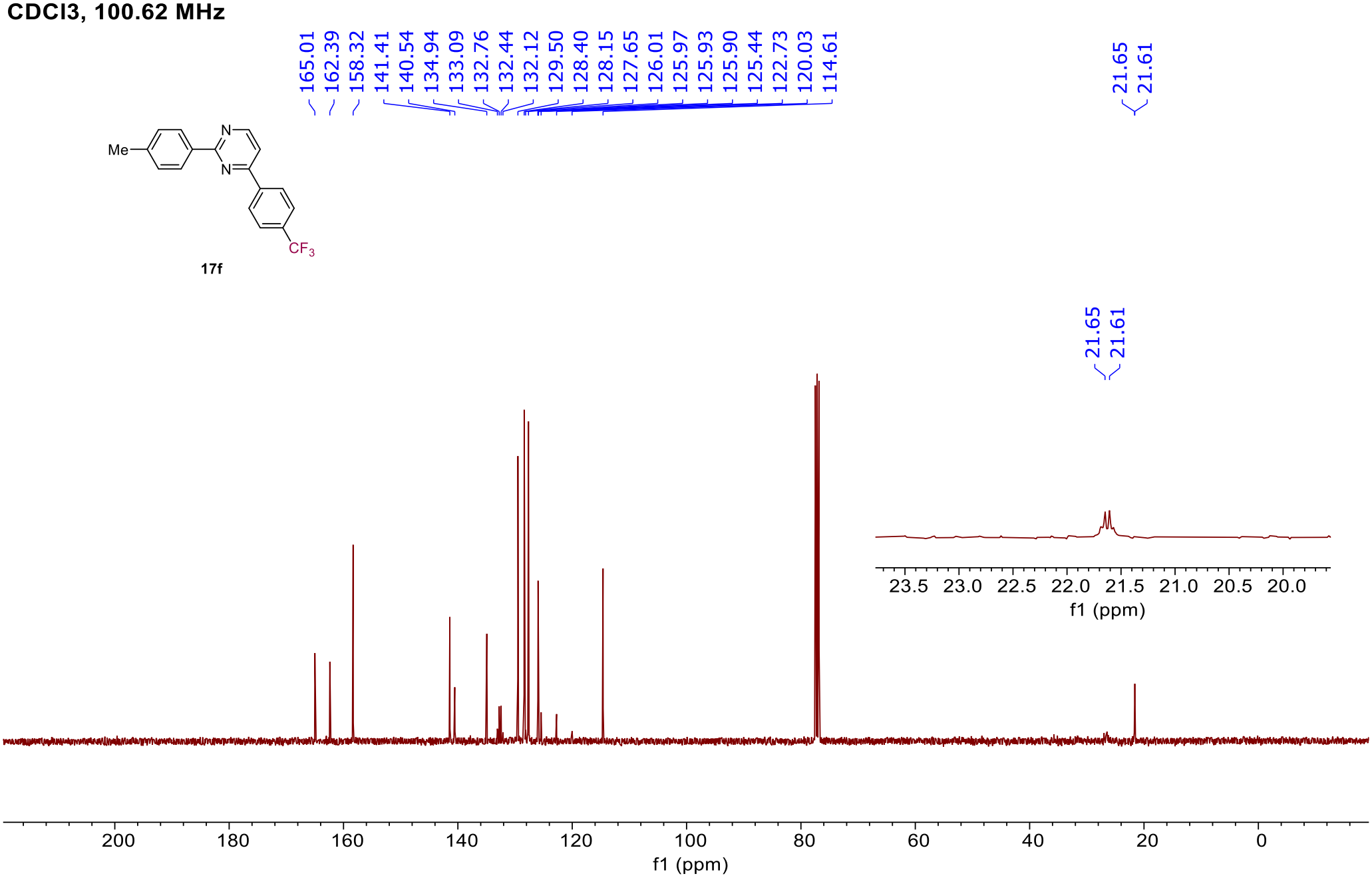
^{1}H NMR Spectrum of **17e**



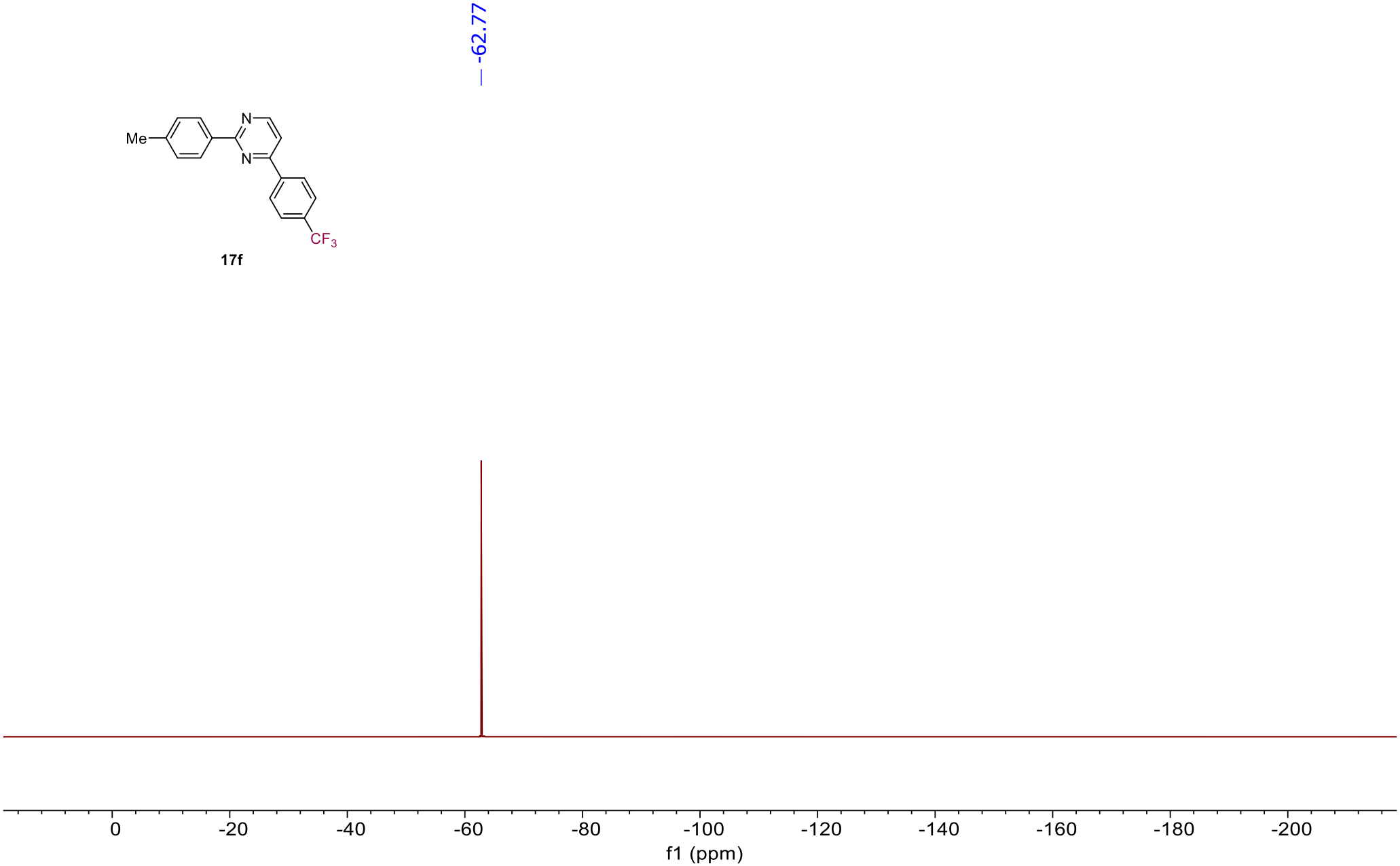
^{13}C NMR Spectrum of **17e**



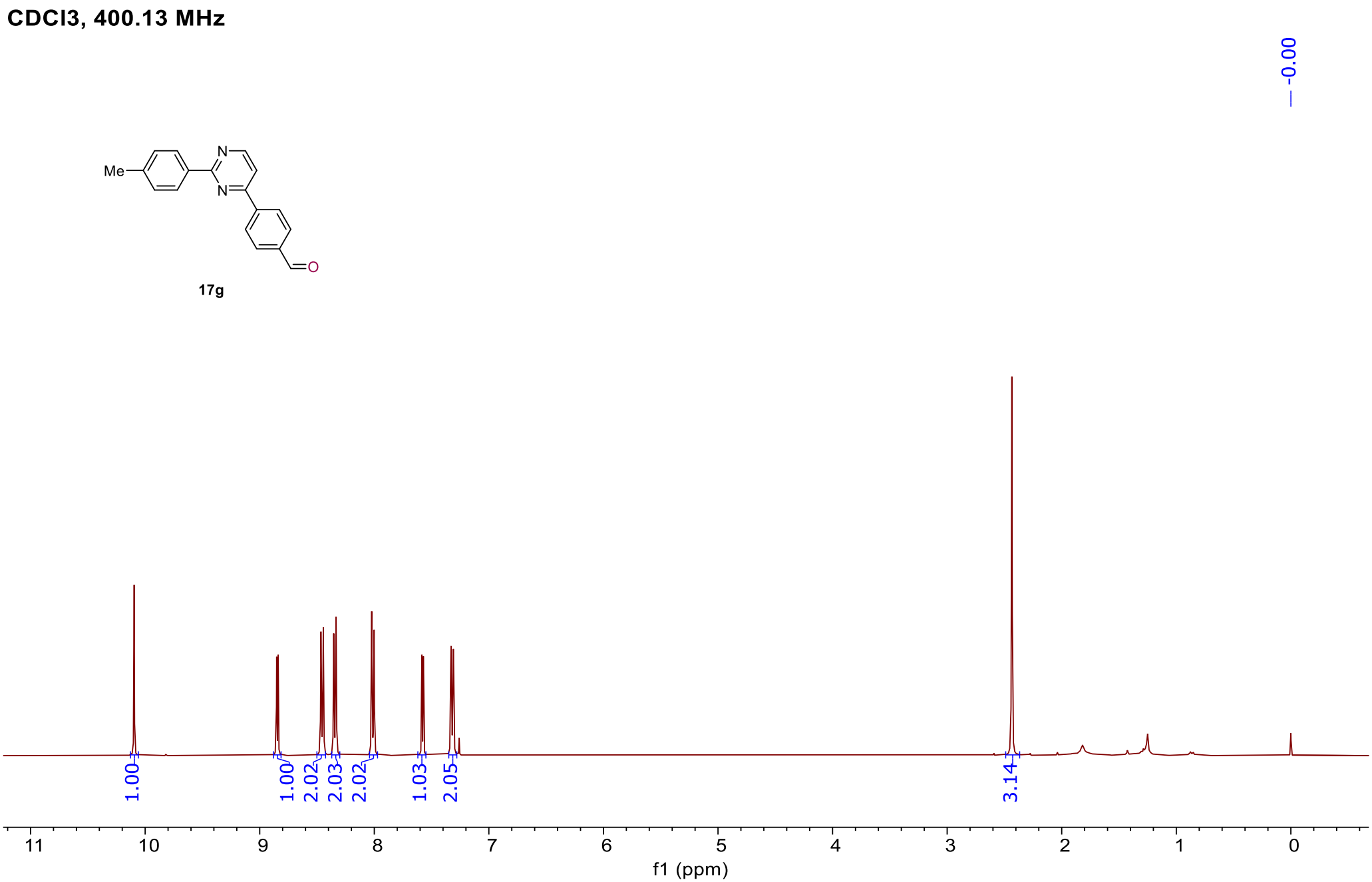
^{1}H NMR Spectrum of **17f**



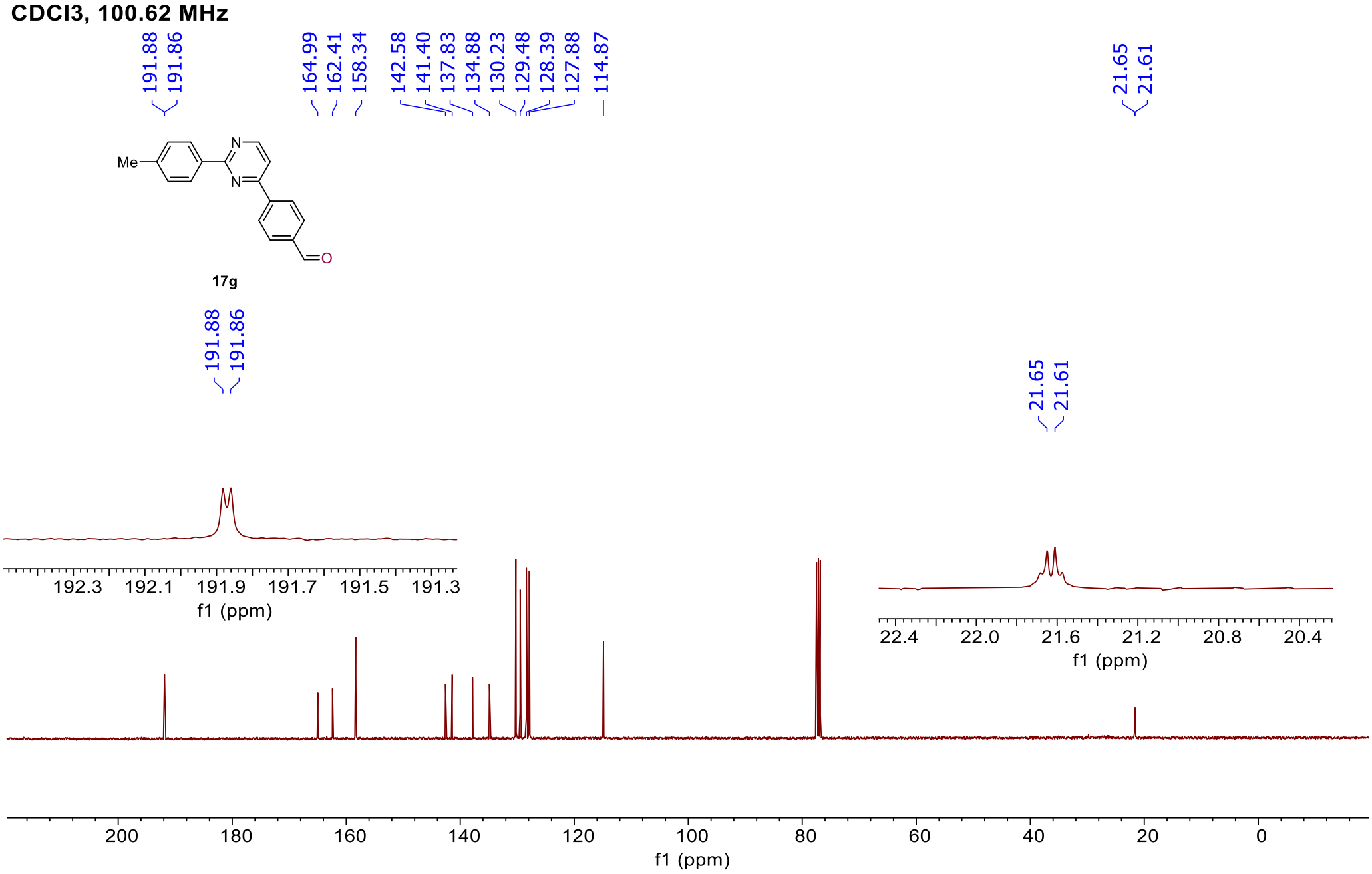
^{13}C NMR Spectrum of **17f**



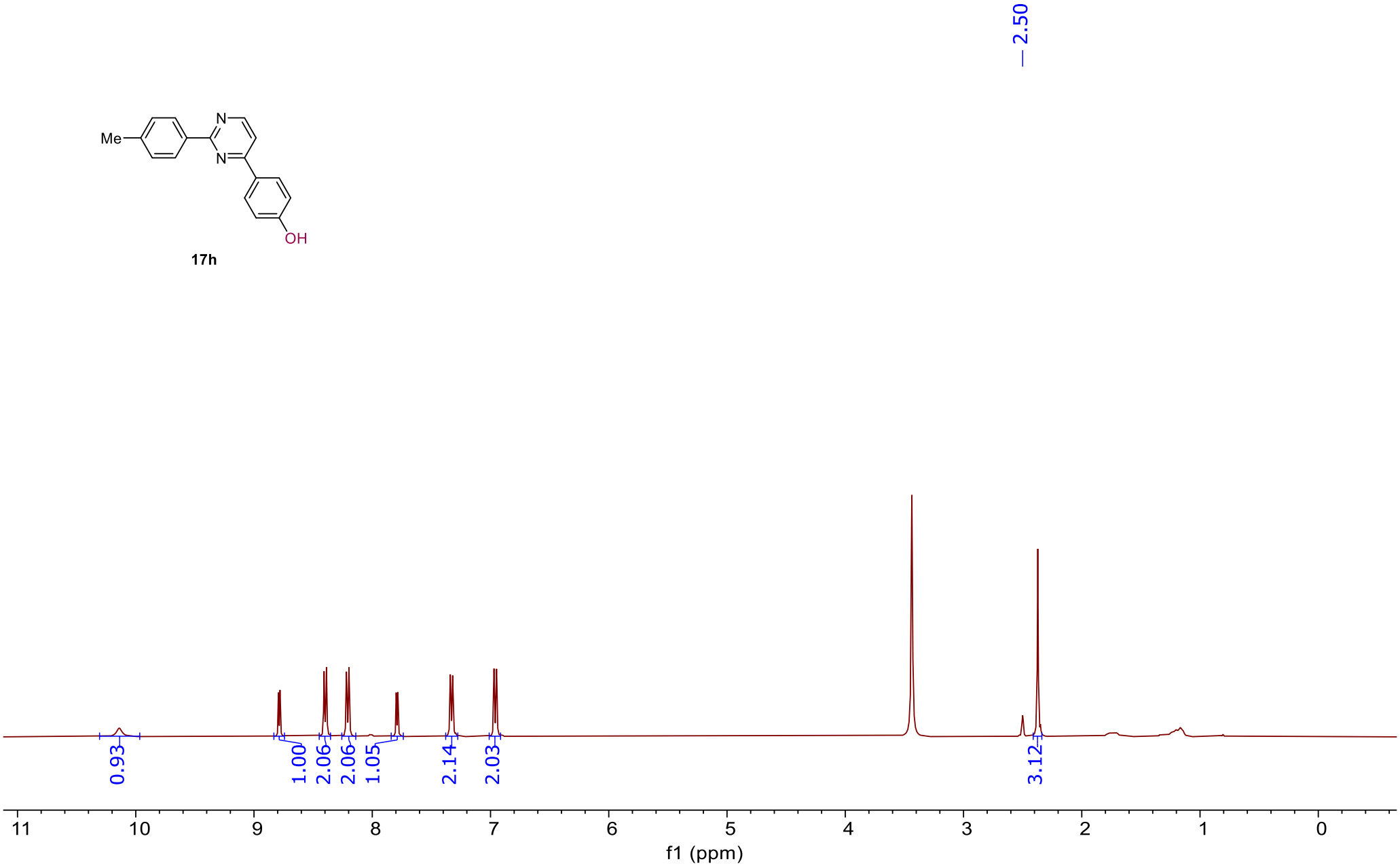
^{19}F NMR Spectrum of **17f**



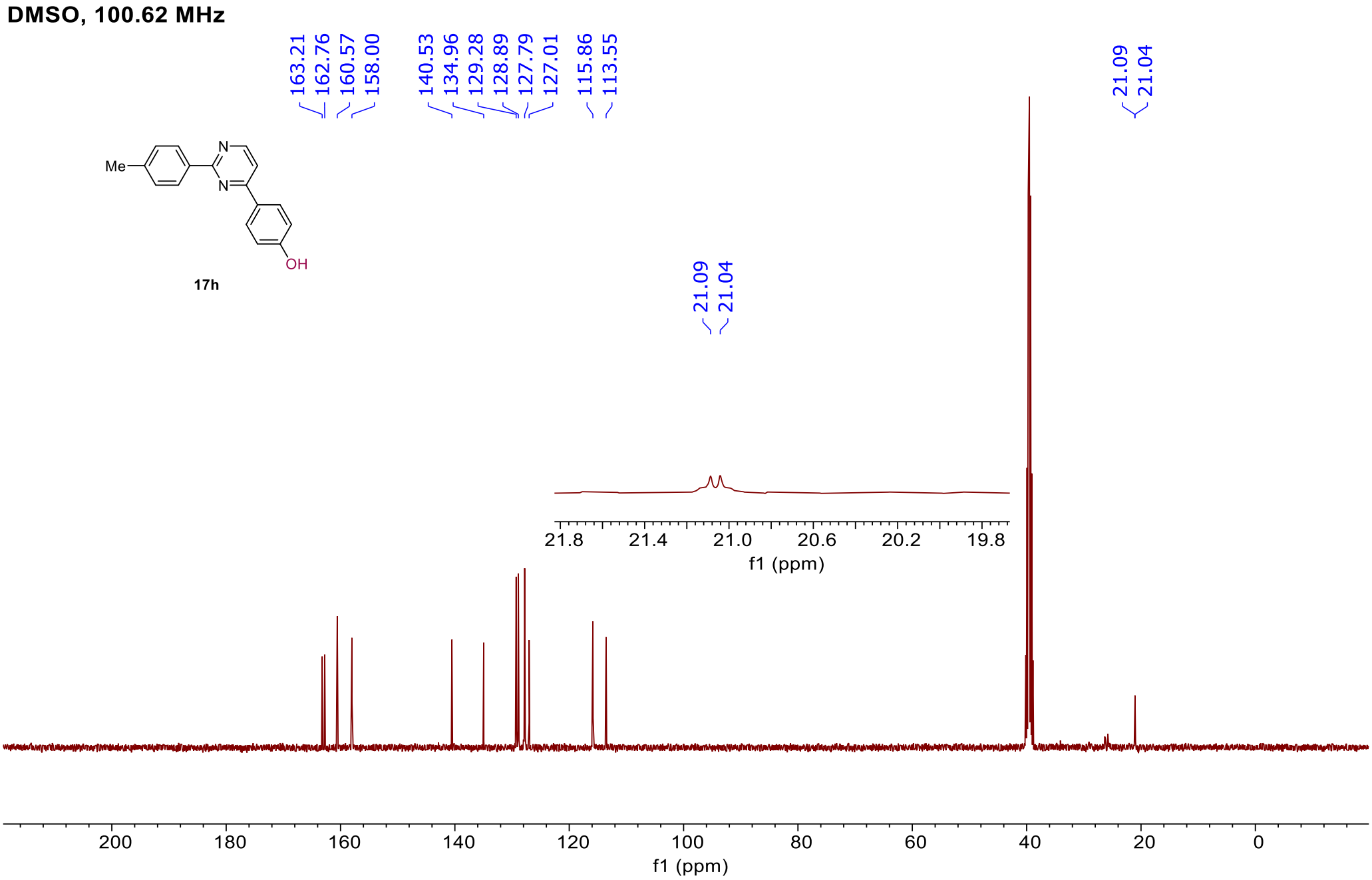
^{1}H NMR Spectrum of **17g**



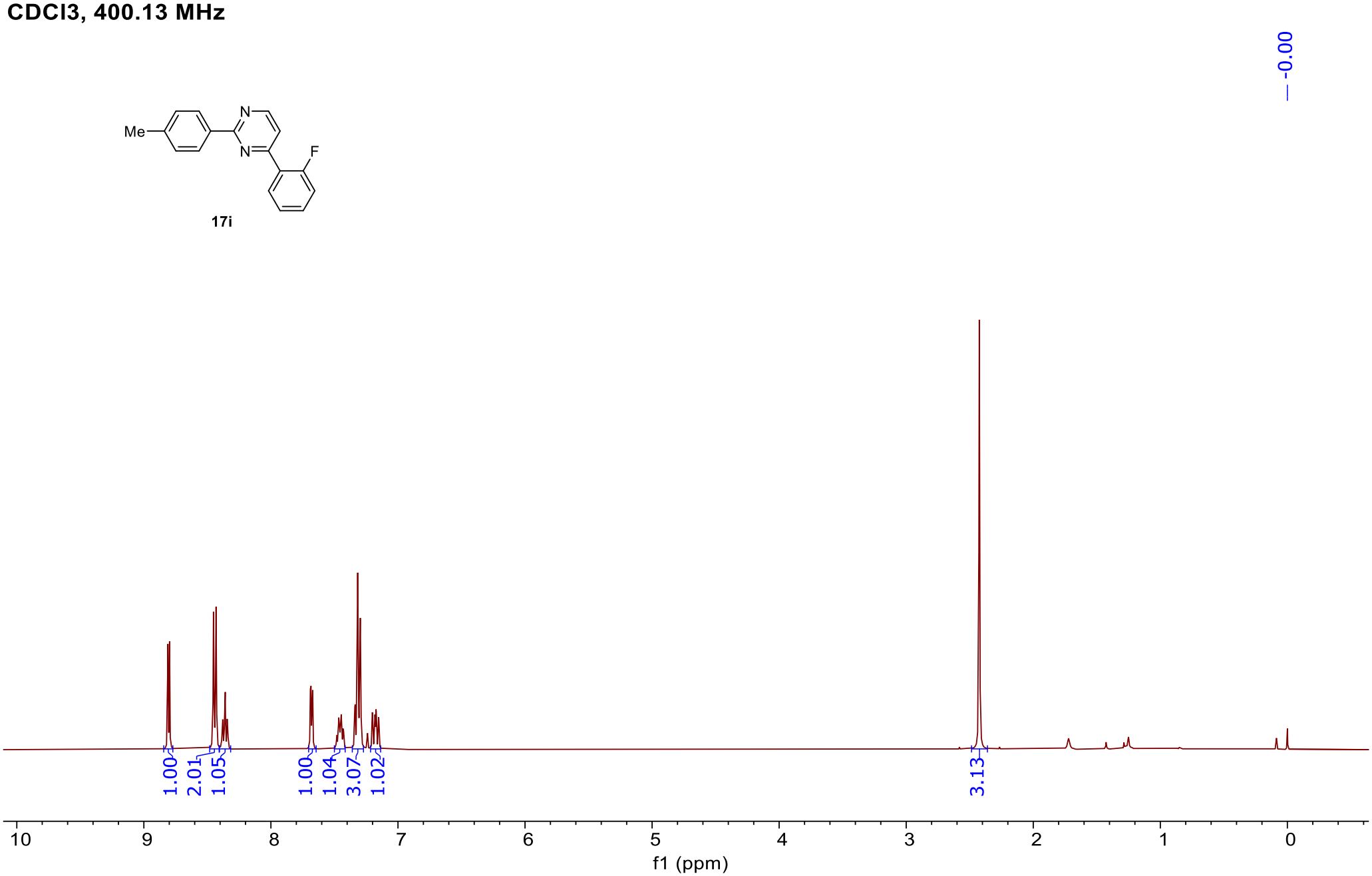
^{13}C NMR Spectrum of **17g**



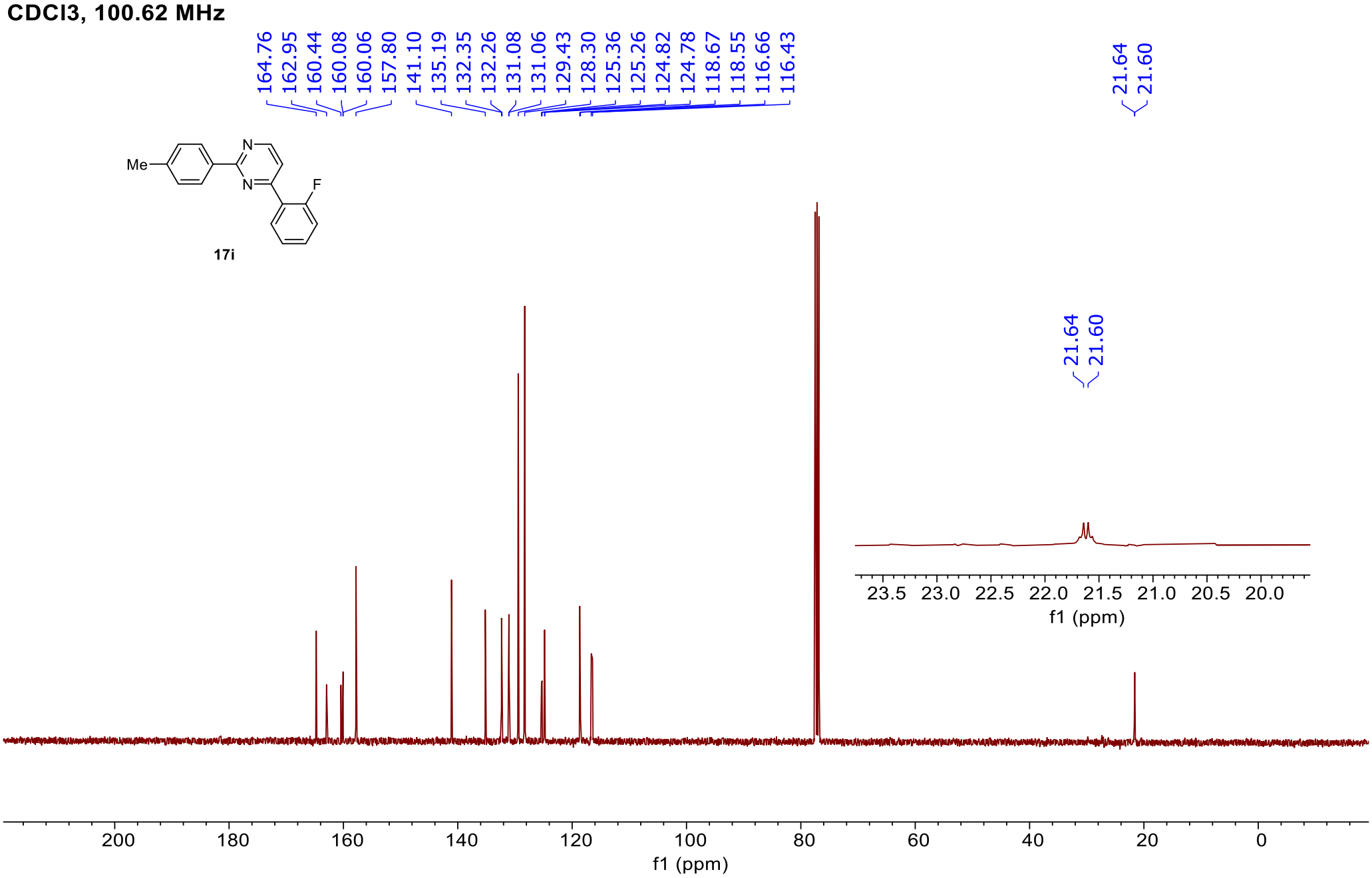
^{1}H NMR Spectrum of **17h**



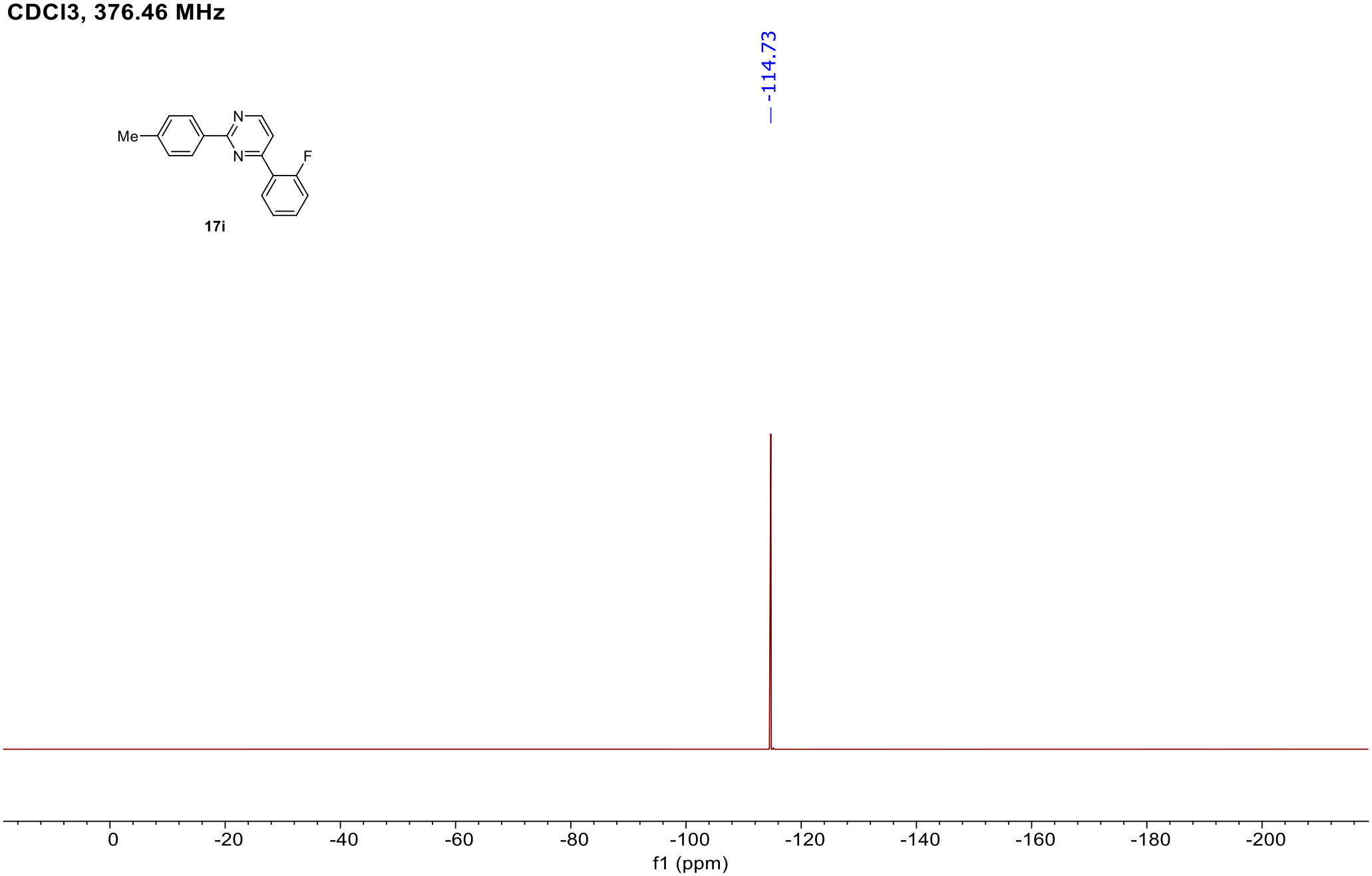
^{13}C NMR Spectrum of **17h**



^{1}H NMR Spectrum of **17i**

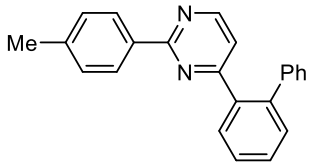


^{13}C NMR Spectrum of **17i**



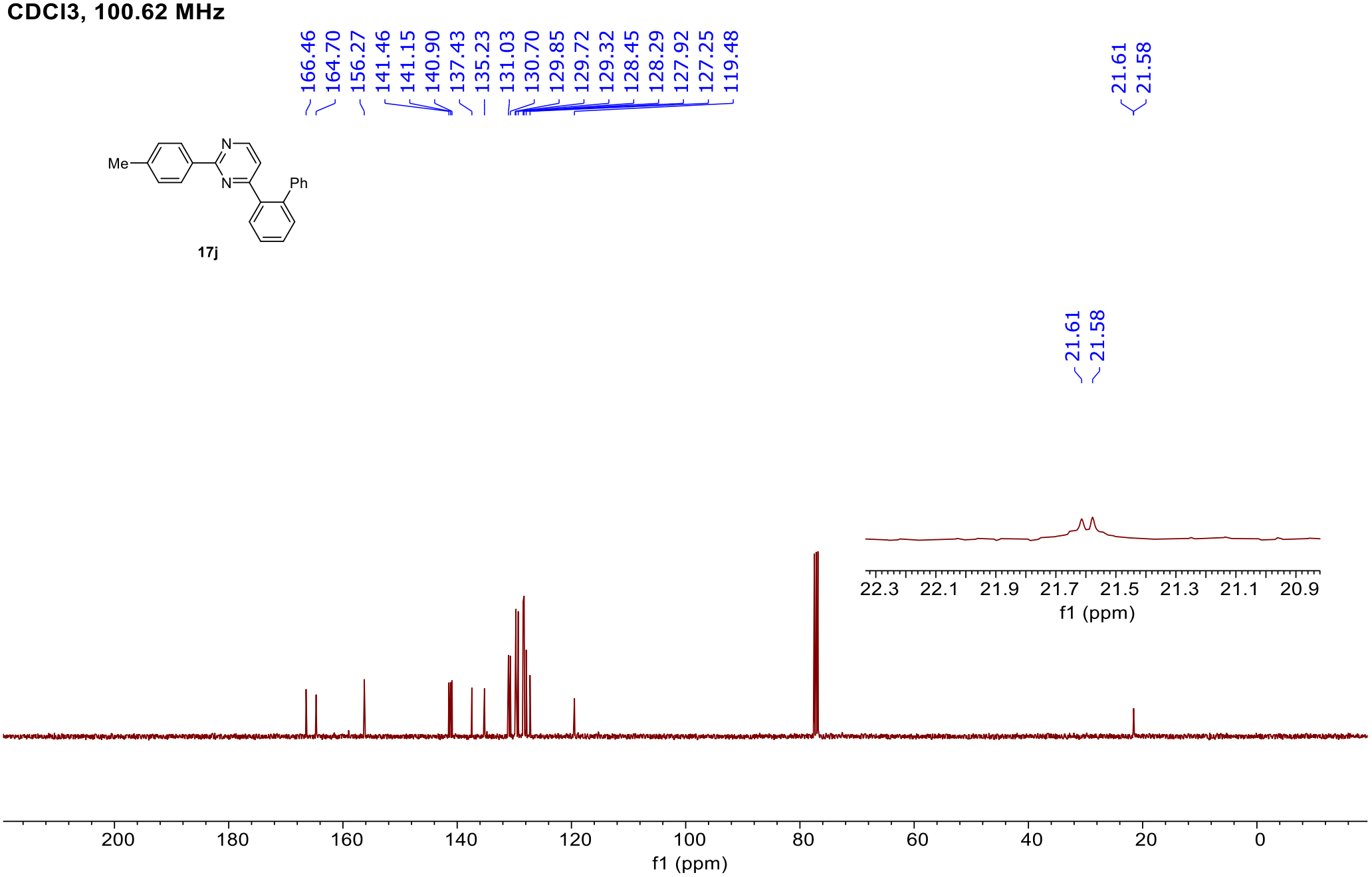
^{19}F NMR Spectrum of **17i**

CDCl3, 400.13 MHz



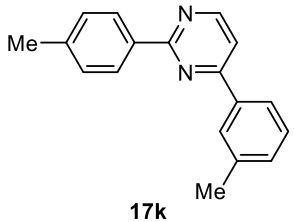
17j

^{1}H NMR Spectrum of **17j**



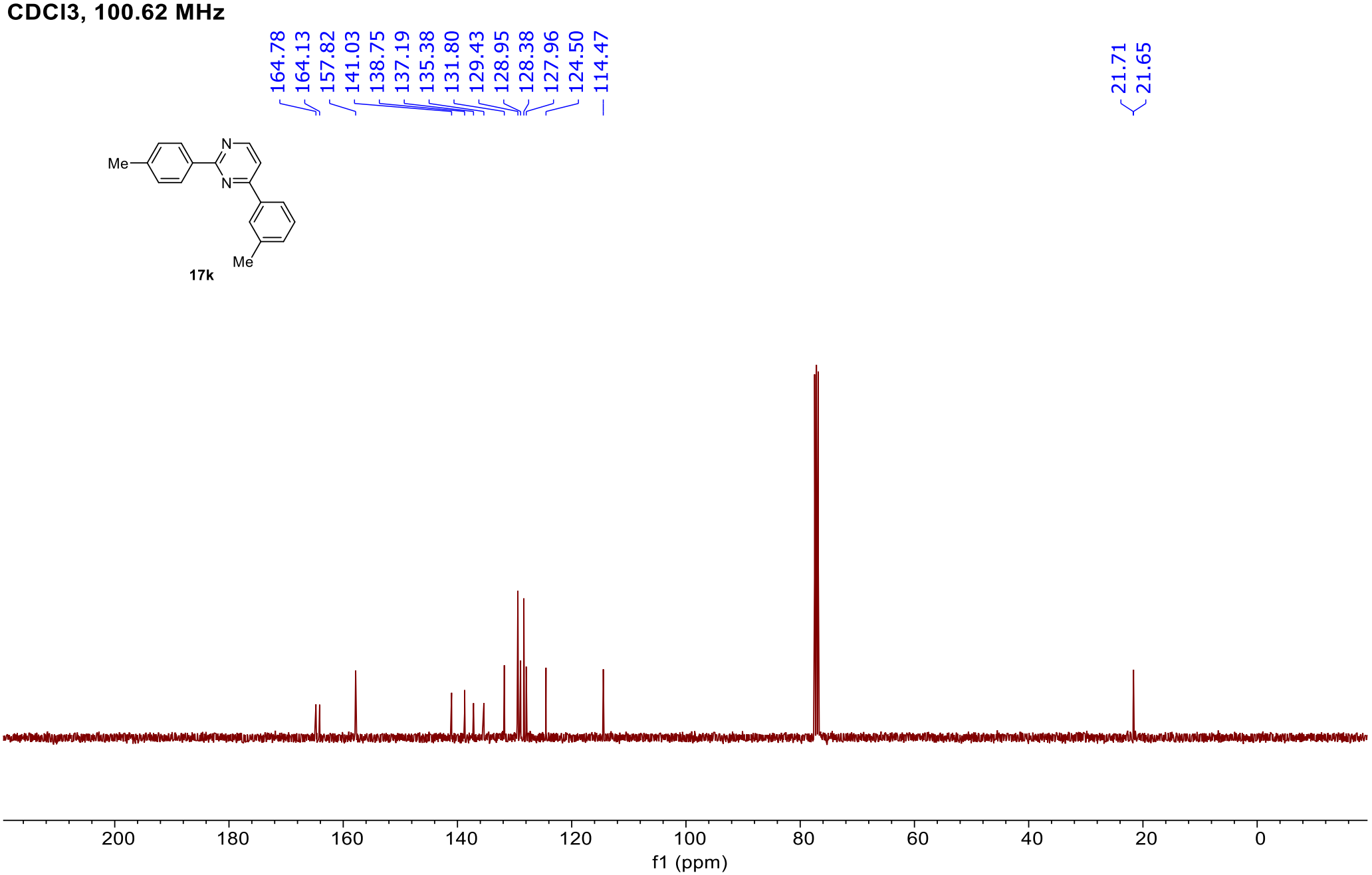
^{13}C NMR Spectrum of **17j**

CDCl3, 400.13 MHz

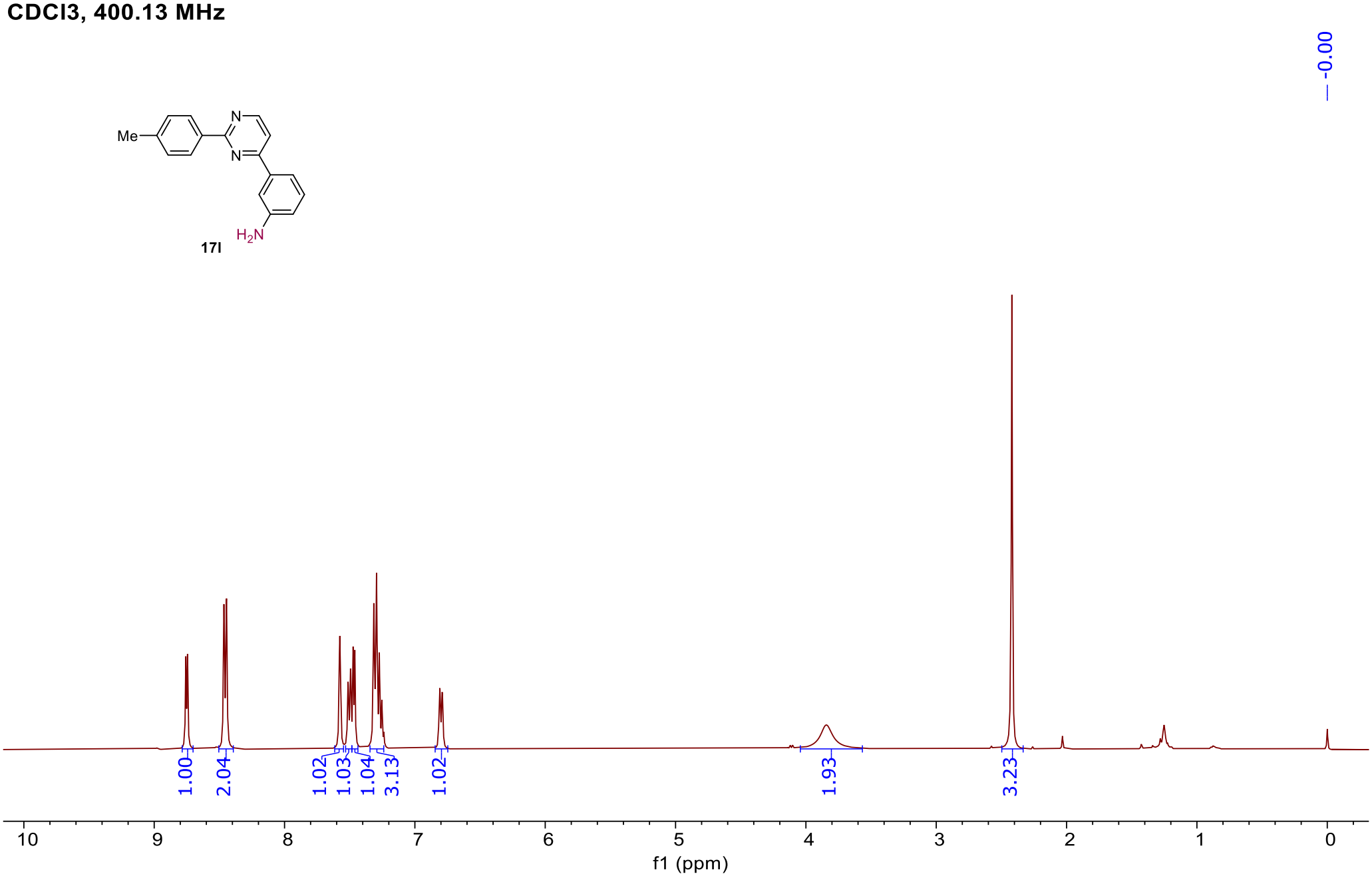


17k

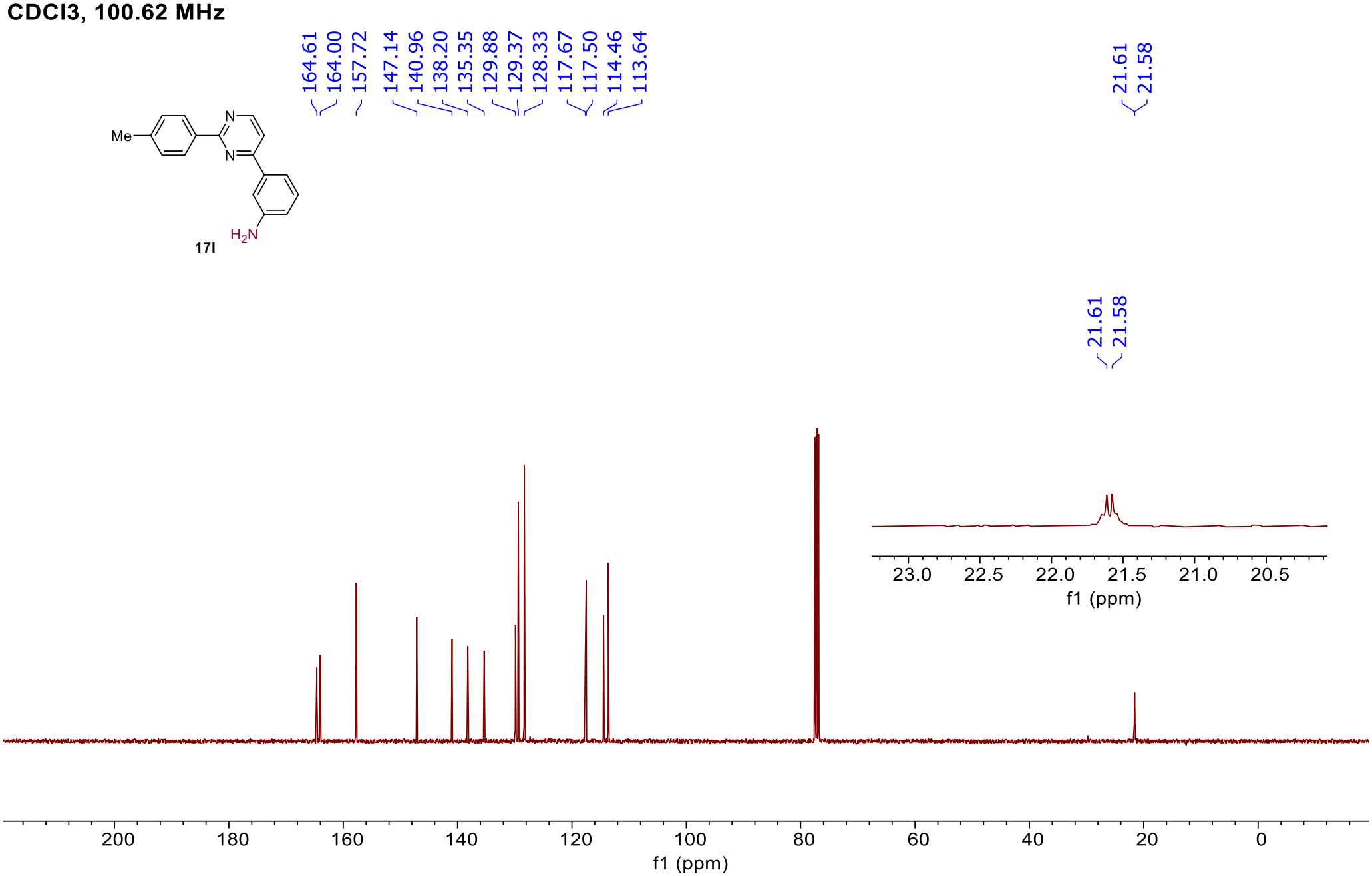
^{1}H NMR Spectrum of **17k**



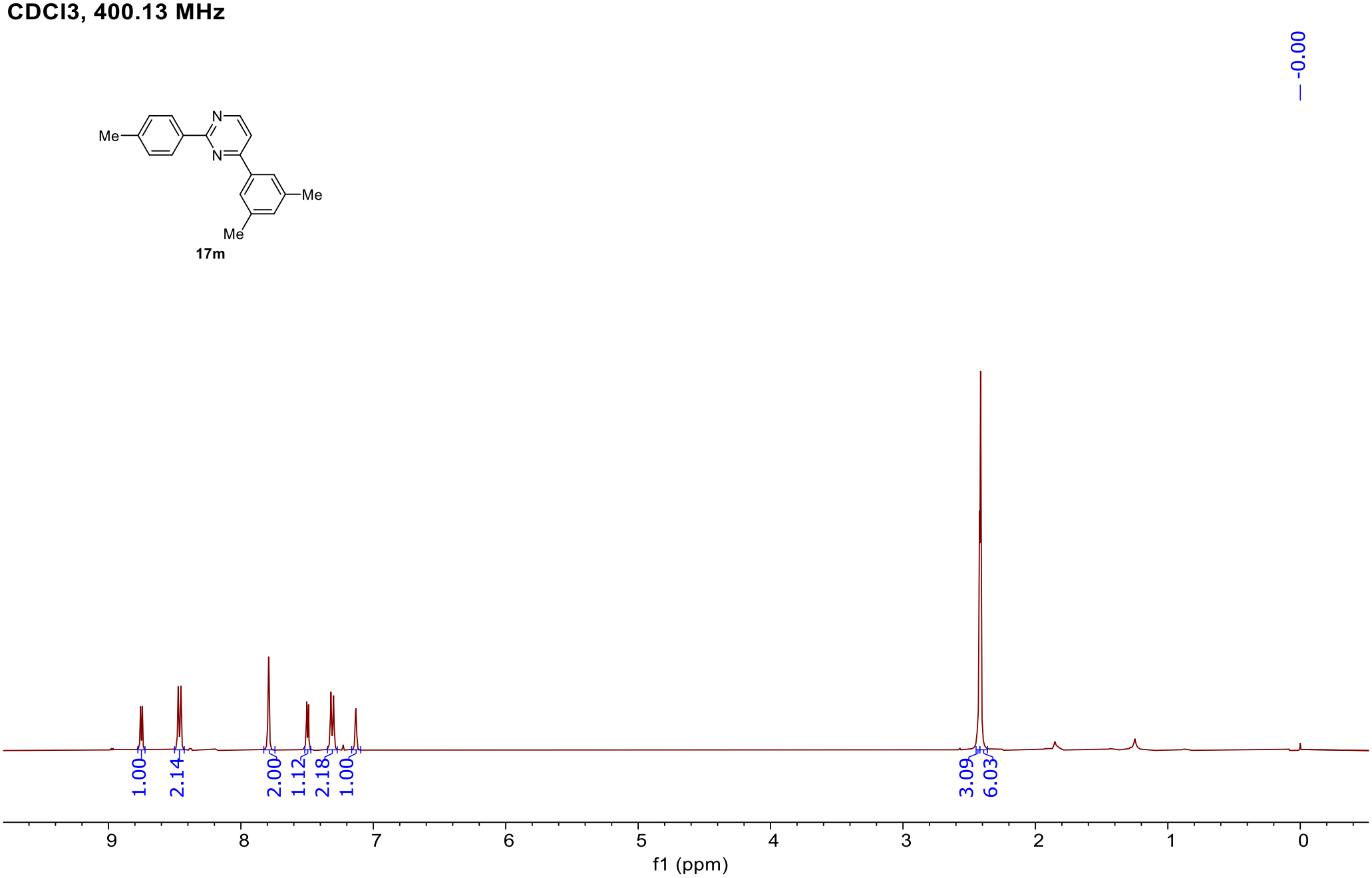
^{13}C NMR Spectrum of **17k**



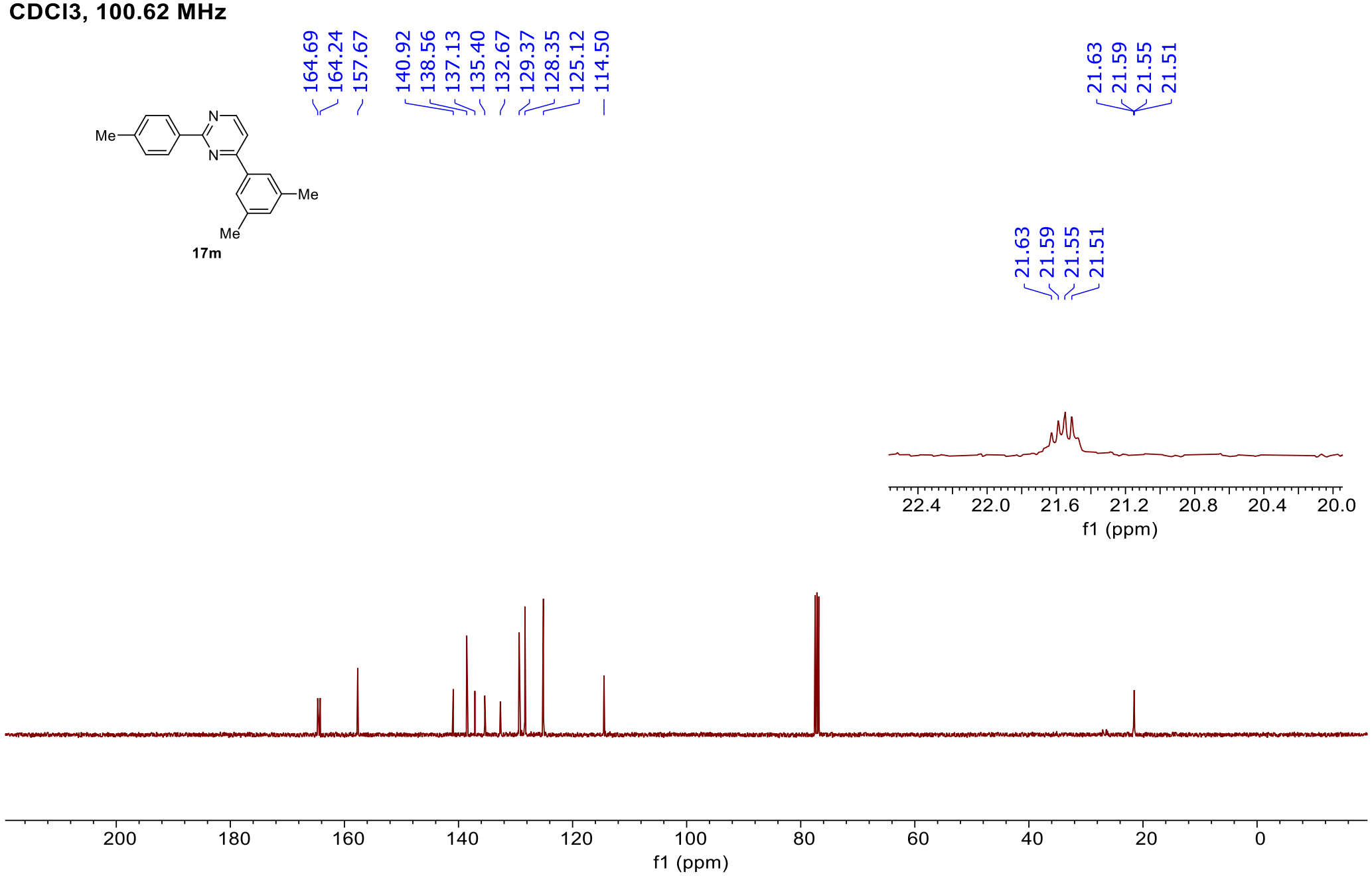
^{1}H NMR Spectrum of **17l**



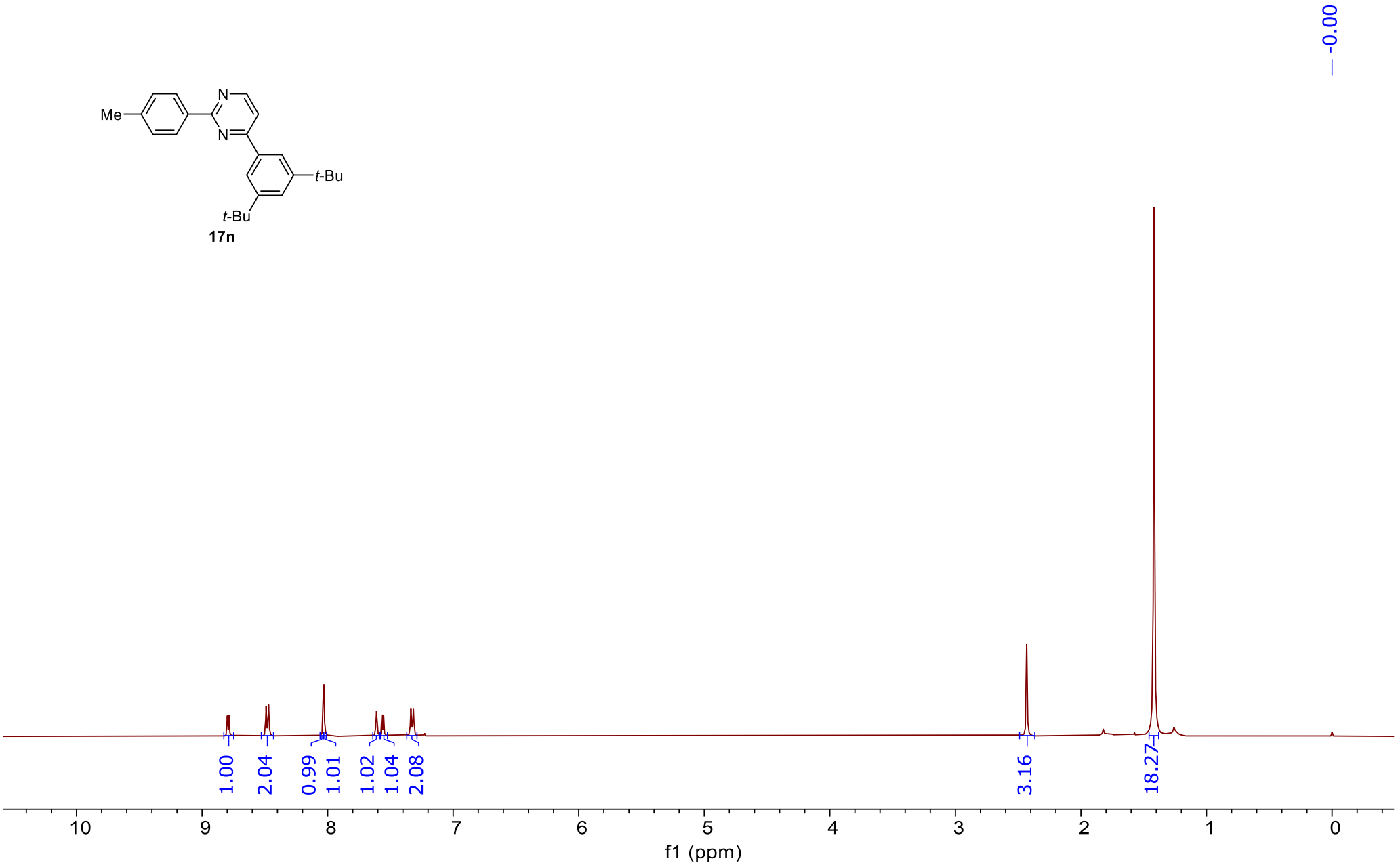
^{13}C NMR Spectrum of **17l**



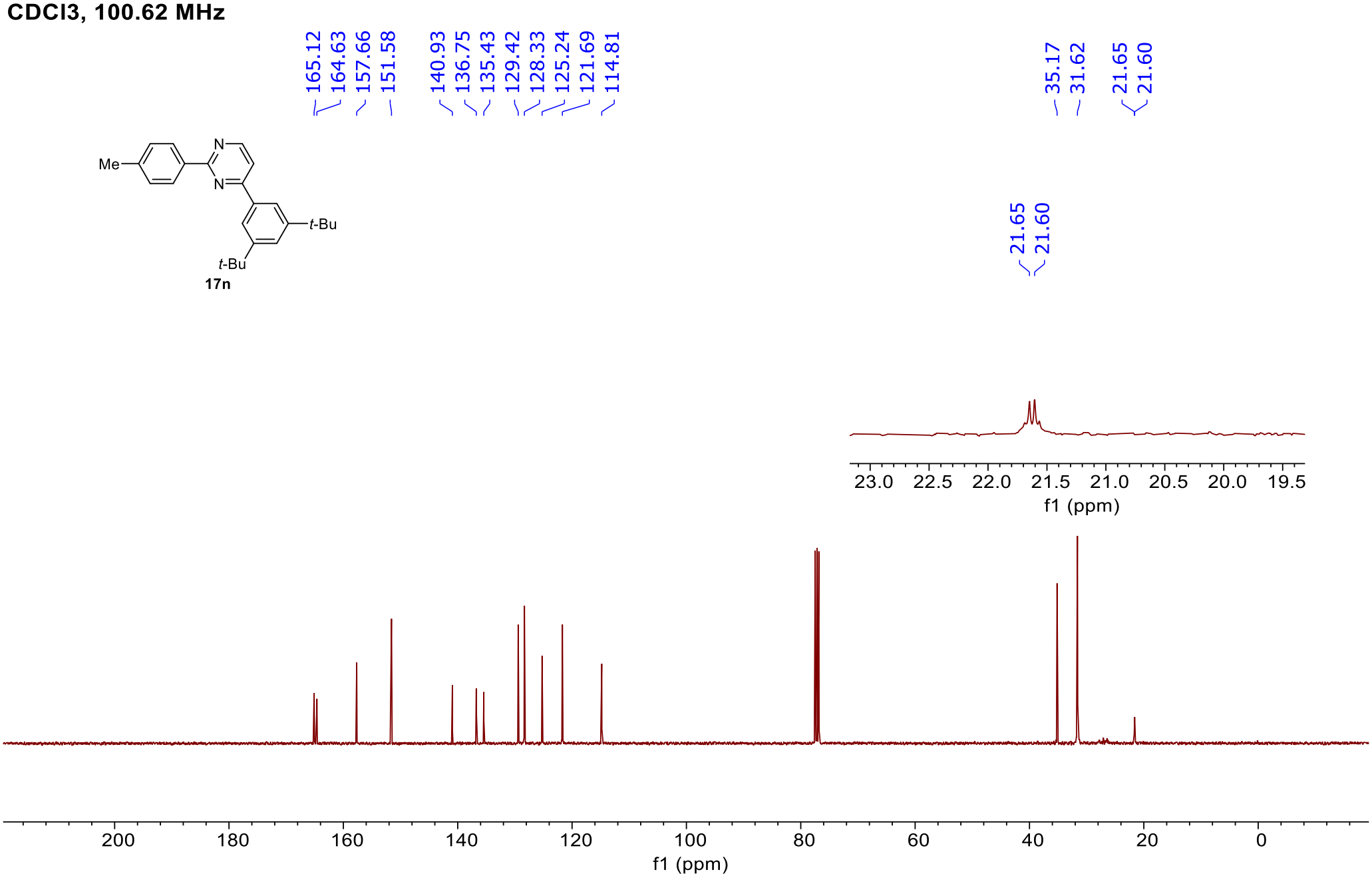
^{1}H NMR Spectrum of **17m**



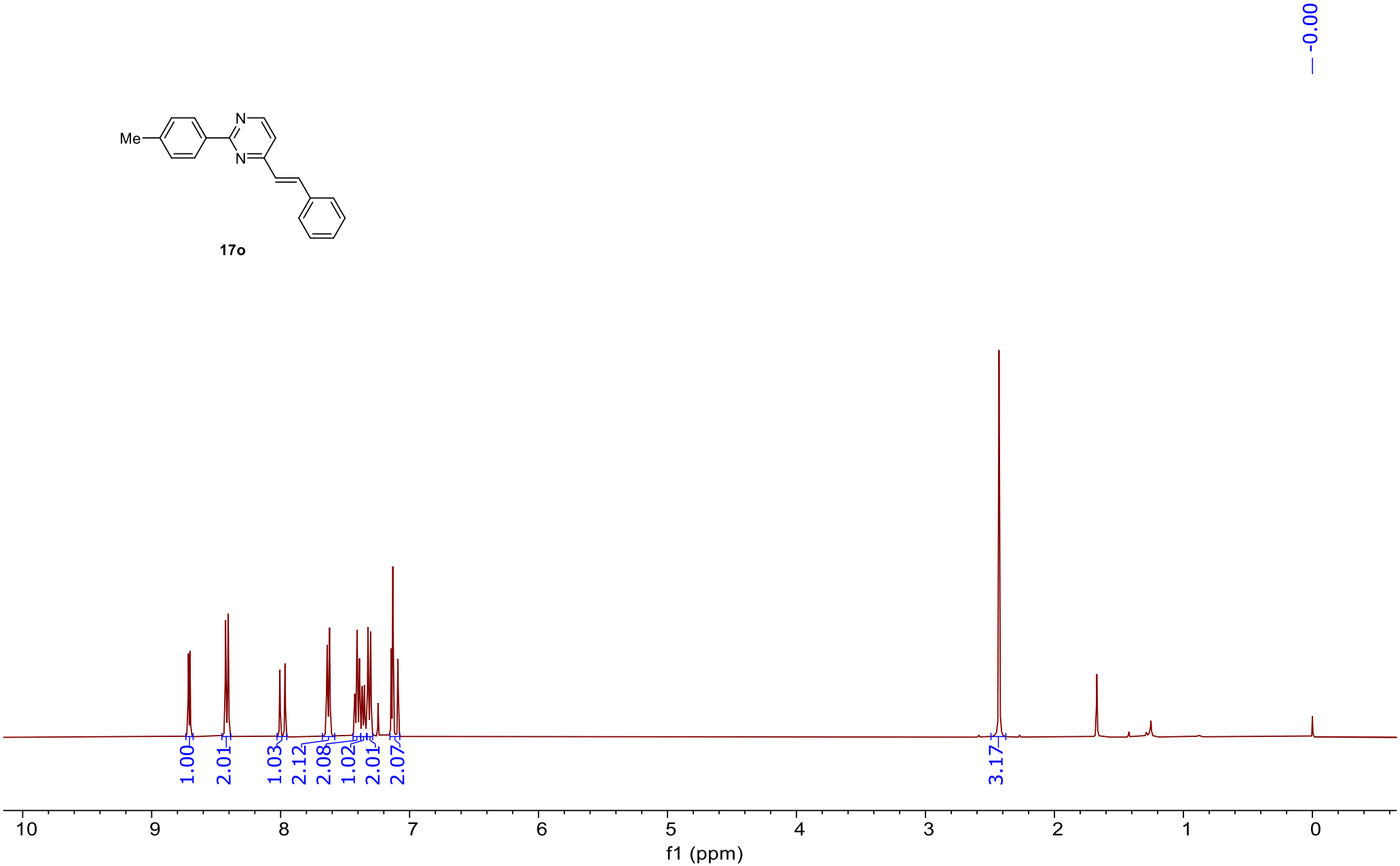
^{13}C NMR Spectrum of **17m**



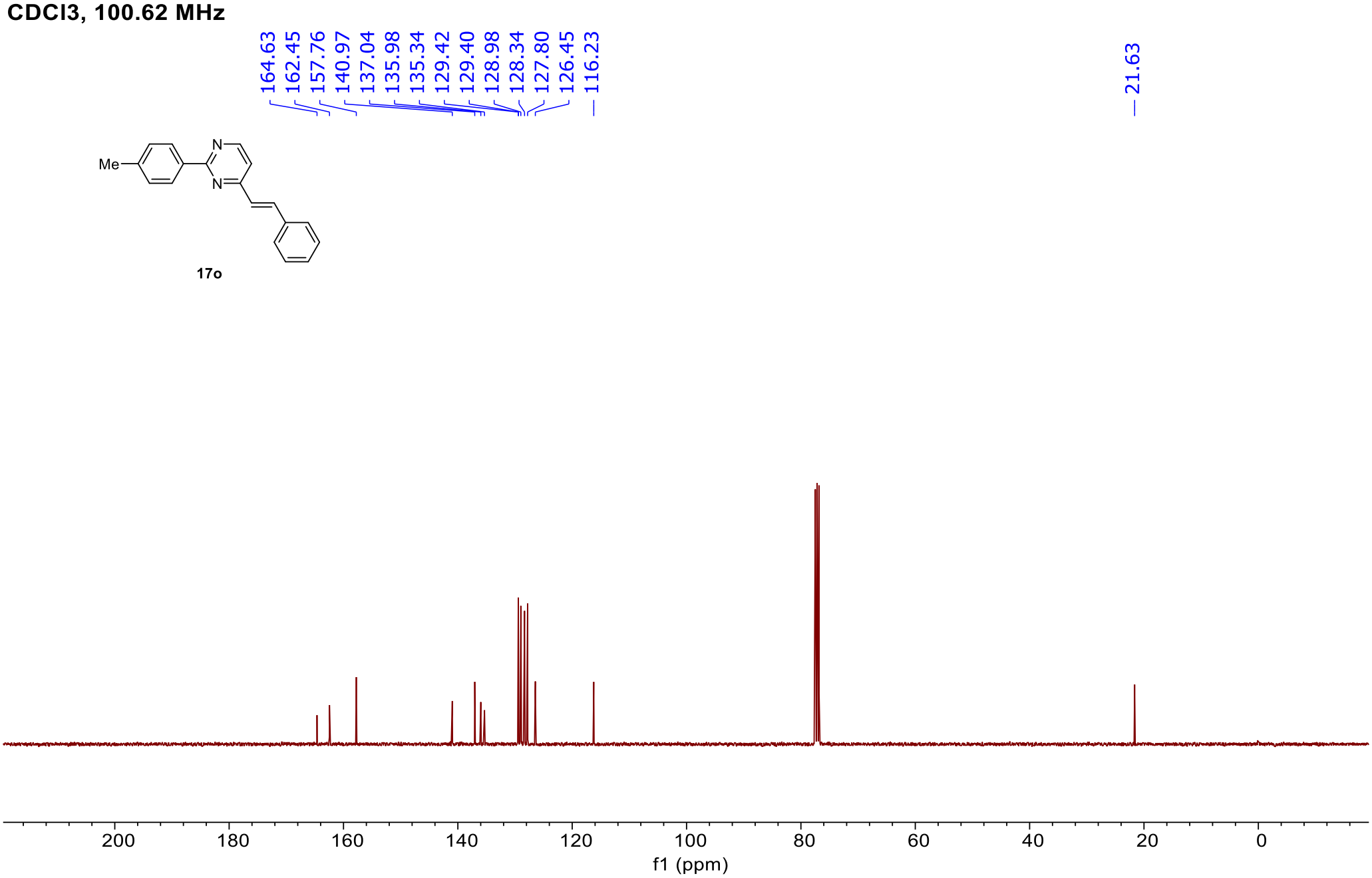
^{1}H NMR Spectrum of **17n**



^{13}C NMR Spectrum of **17n**

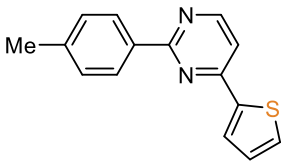


^{1}H NMR Spectrum of **17o**



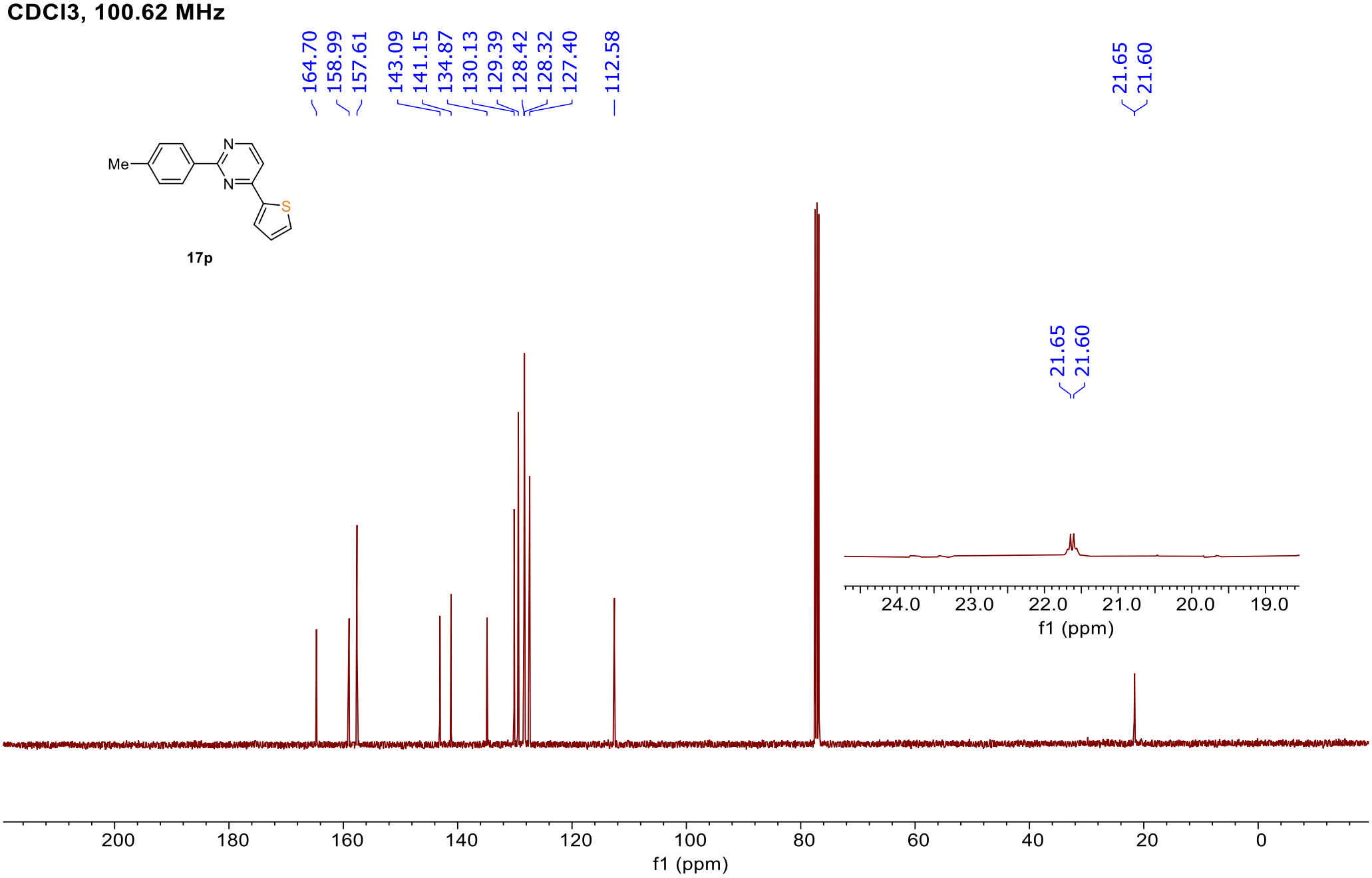
^{13}C NMR Spectrum of **17o**

CDCl3, 400.13 MHz

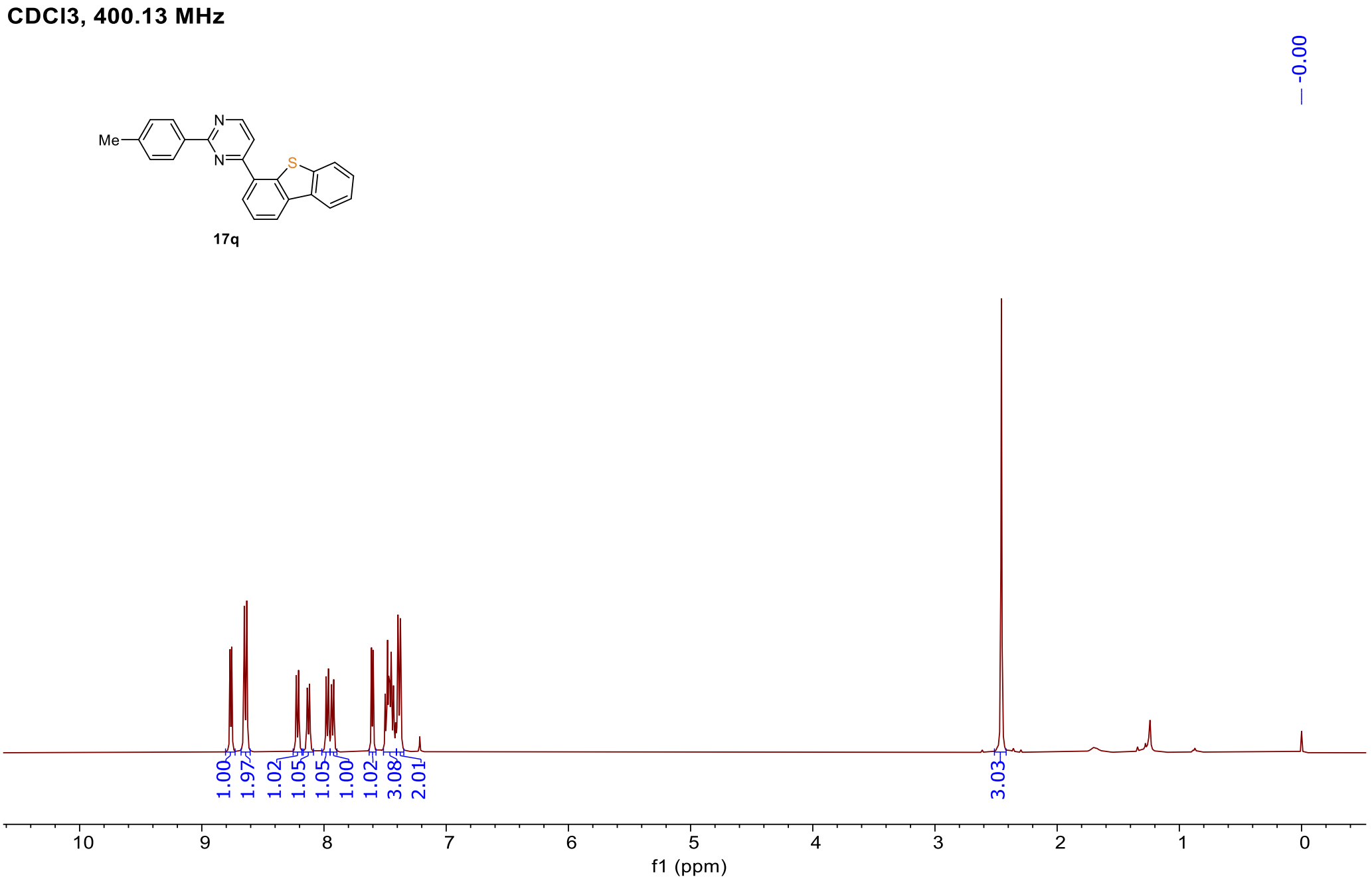


17p

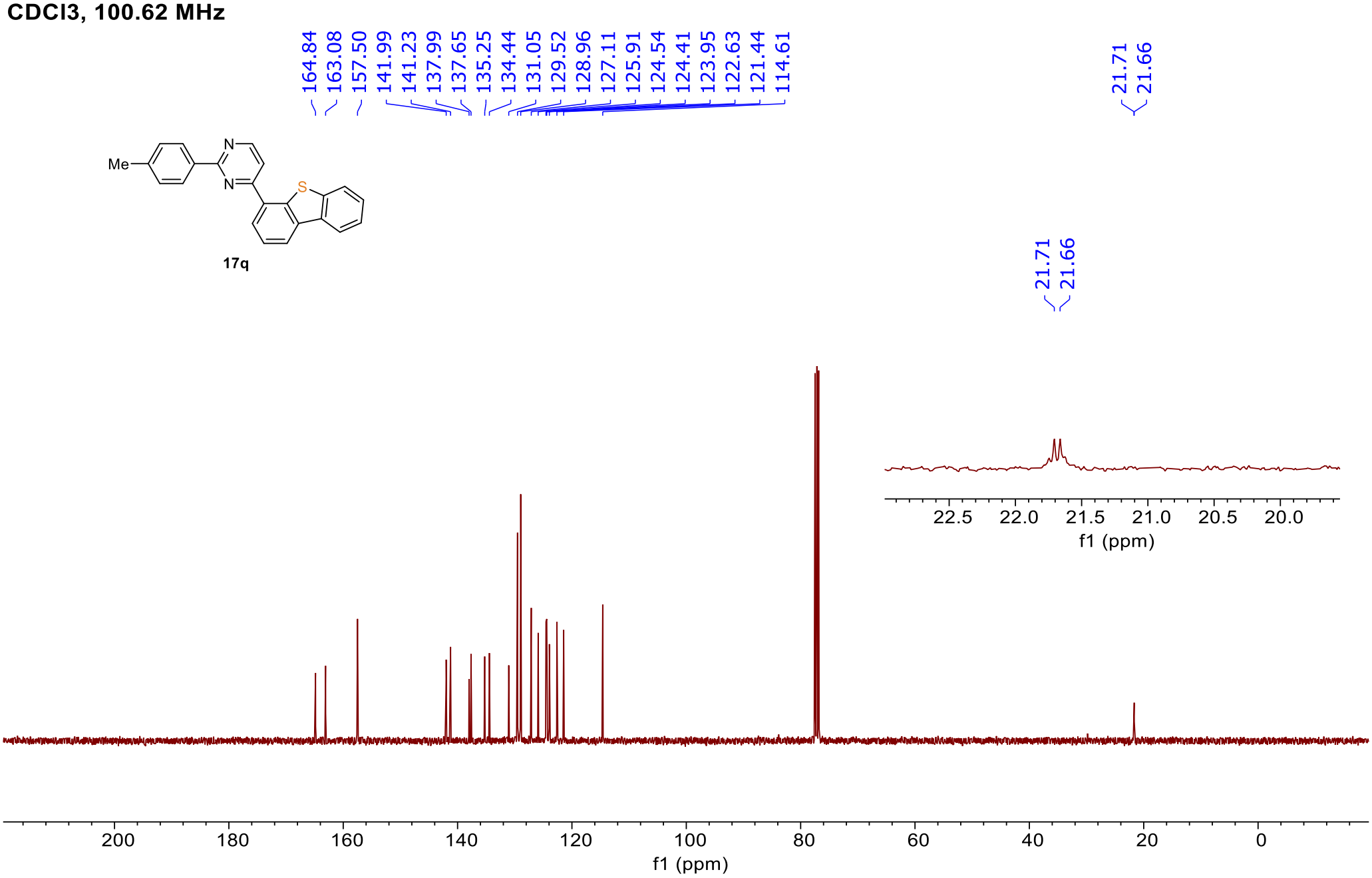
^{1}H NMR Spectrum of **17p**



^{13}C NMR Spectrum of **17p**

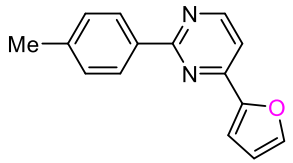


^{1}H NMR Spectrum of **17q**



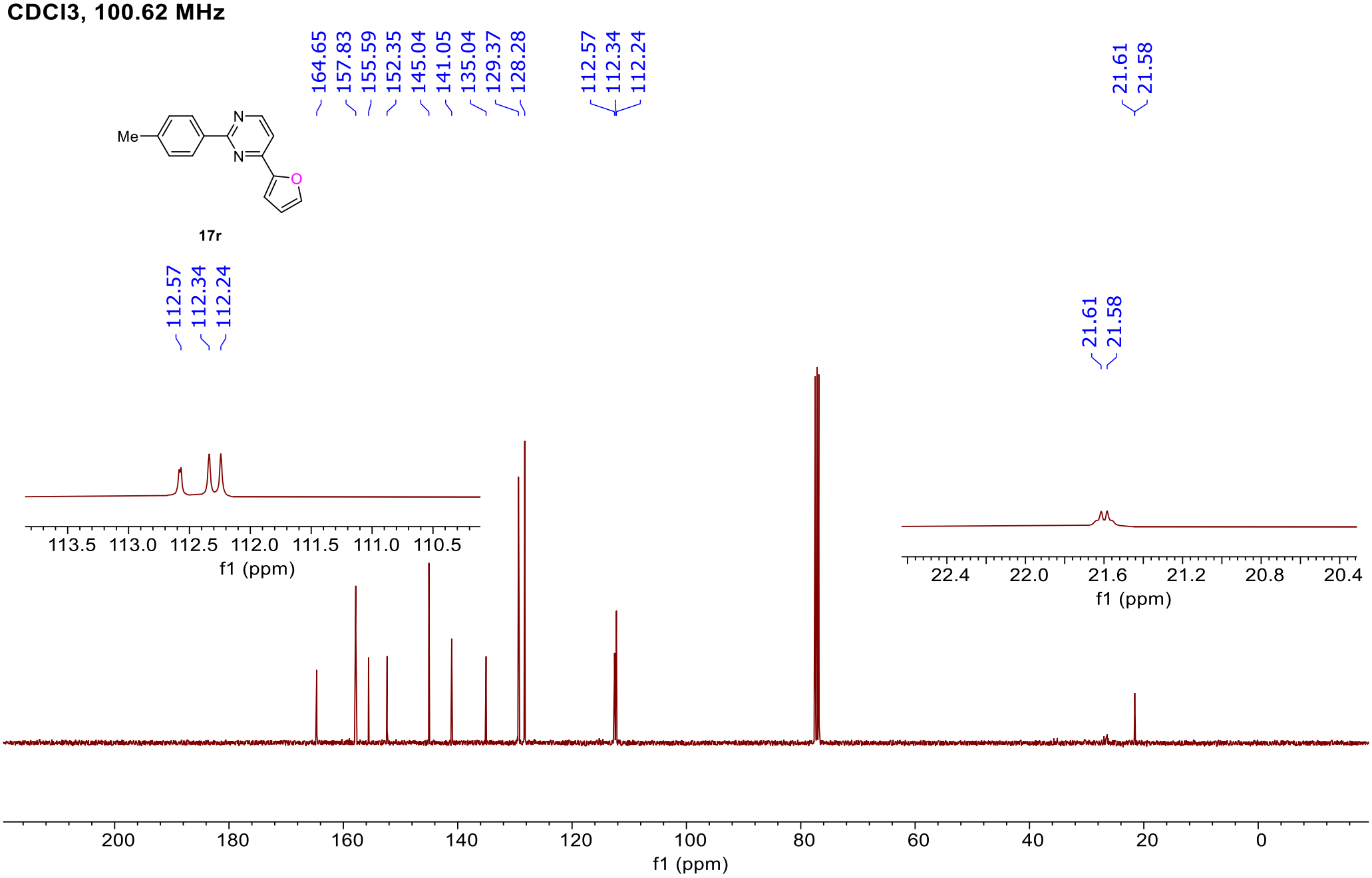
^{13}C NMR Spectrum of **17q**

CDCl3, 400.13 MHz

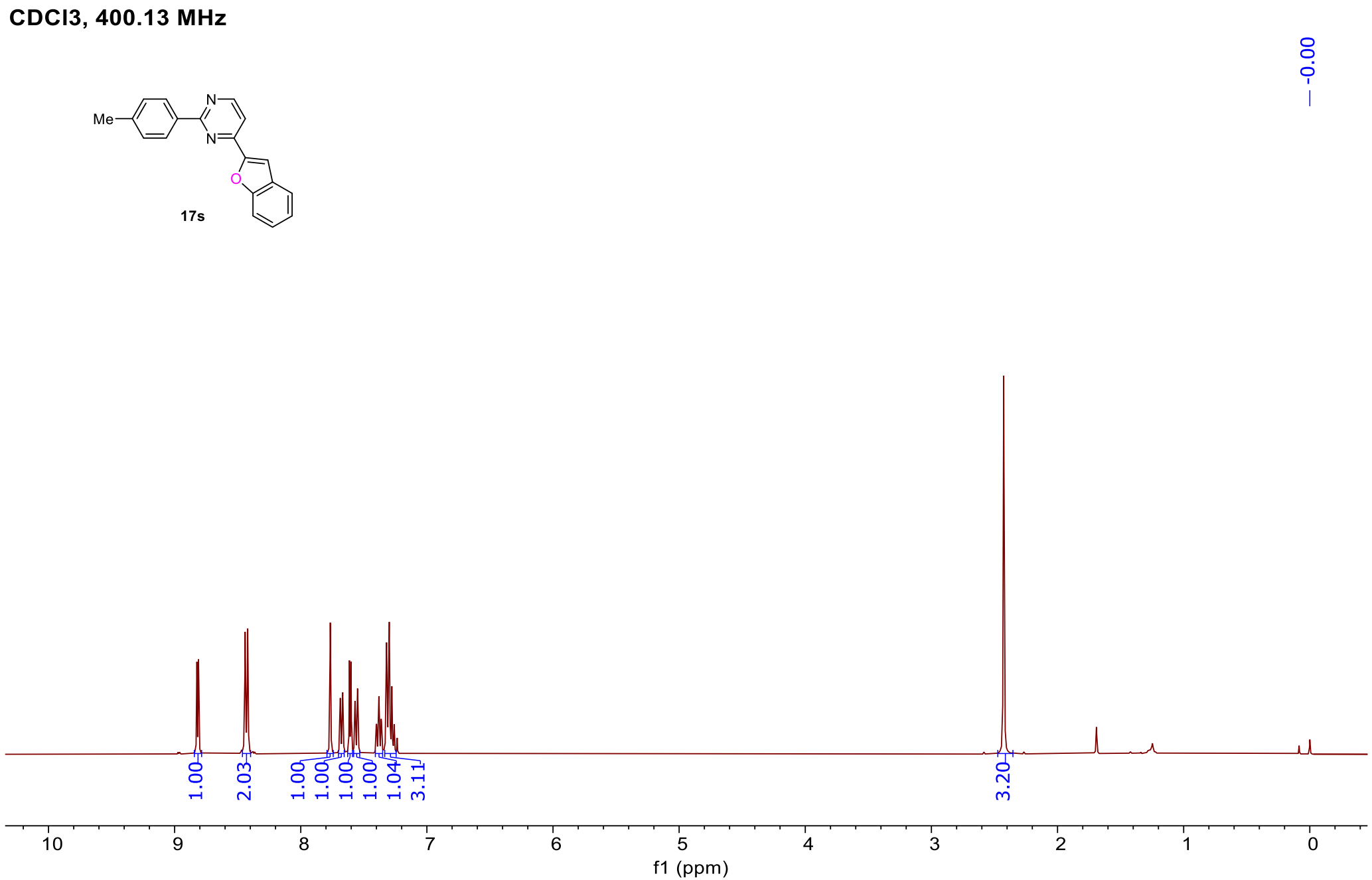


17r

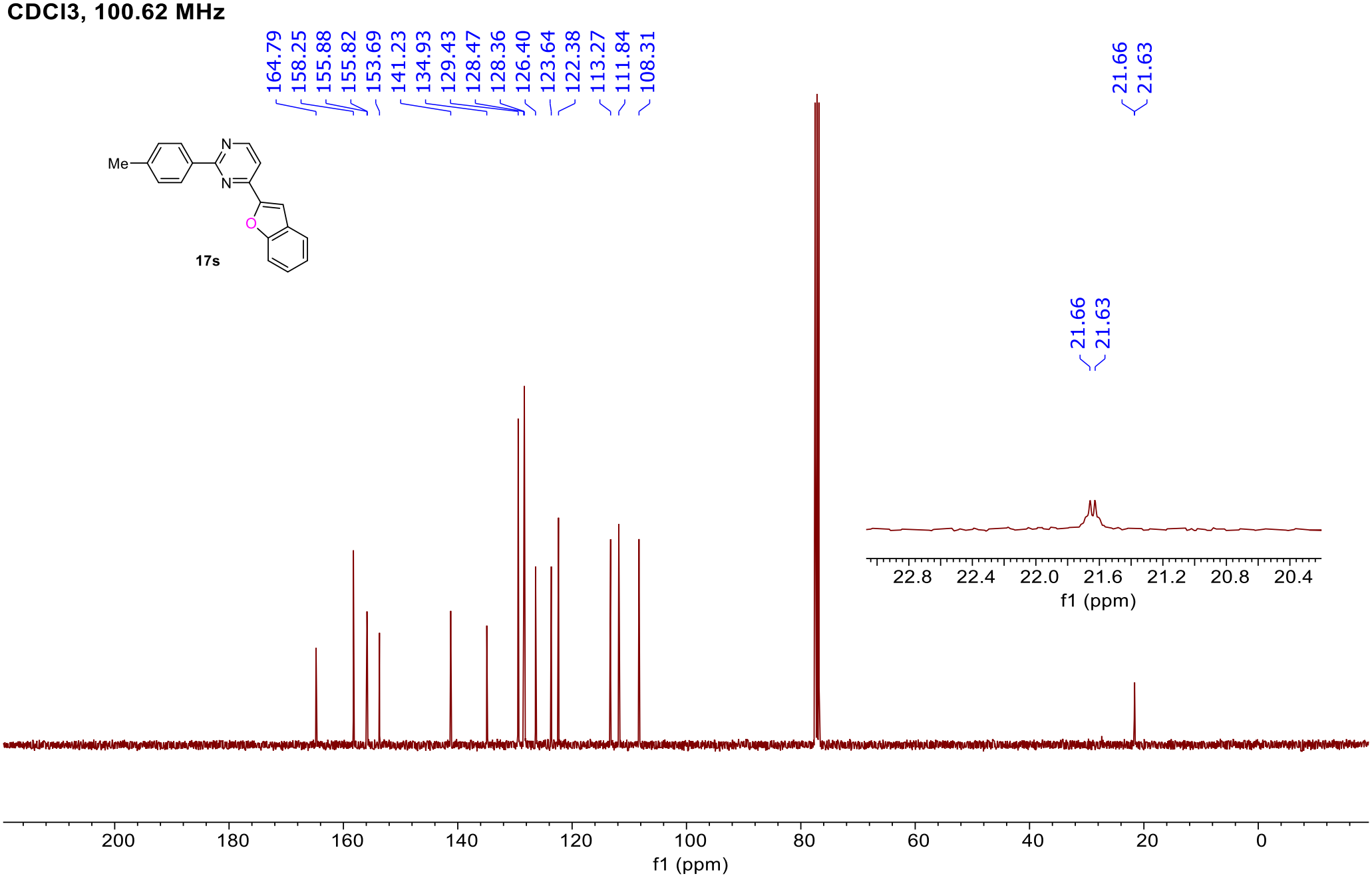
^{1}H NMR Spectrum of **17r**



^{13}C NMR Spectrum of **17r**

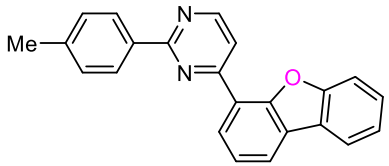


^{1}H NMR Spectrum of **17s**



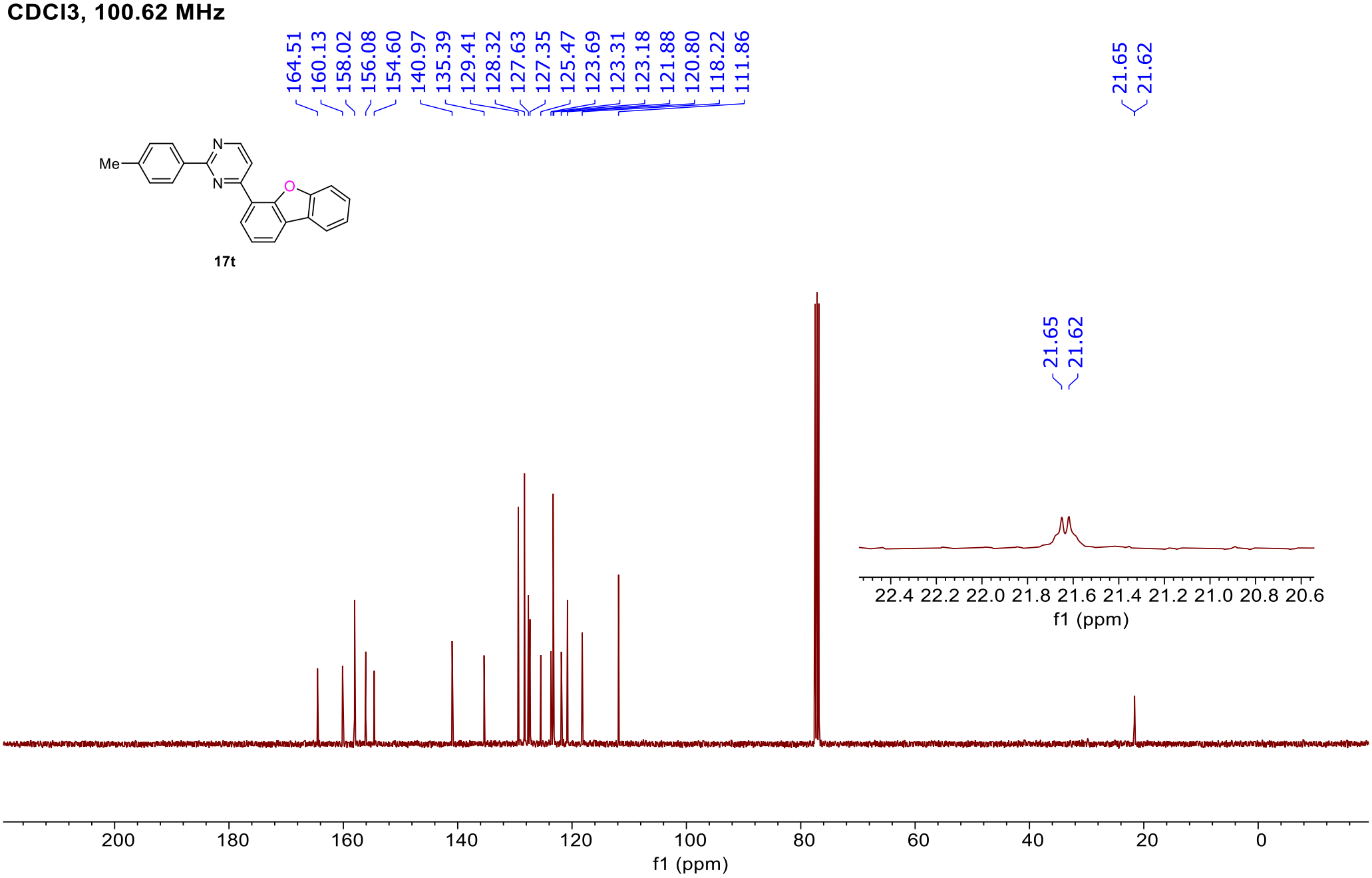
^{13}C NMR Spectrum of **17s**

CDCl3, 400.13 MHz

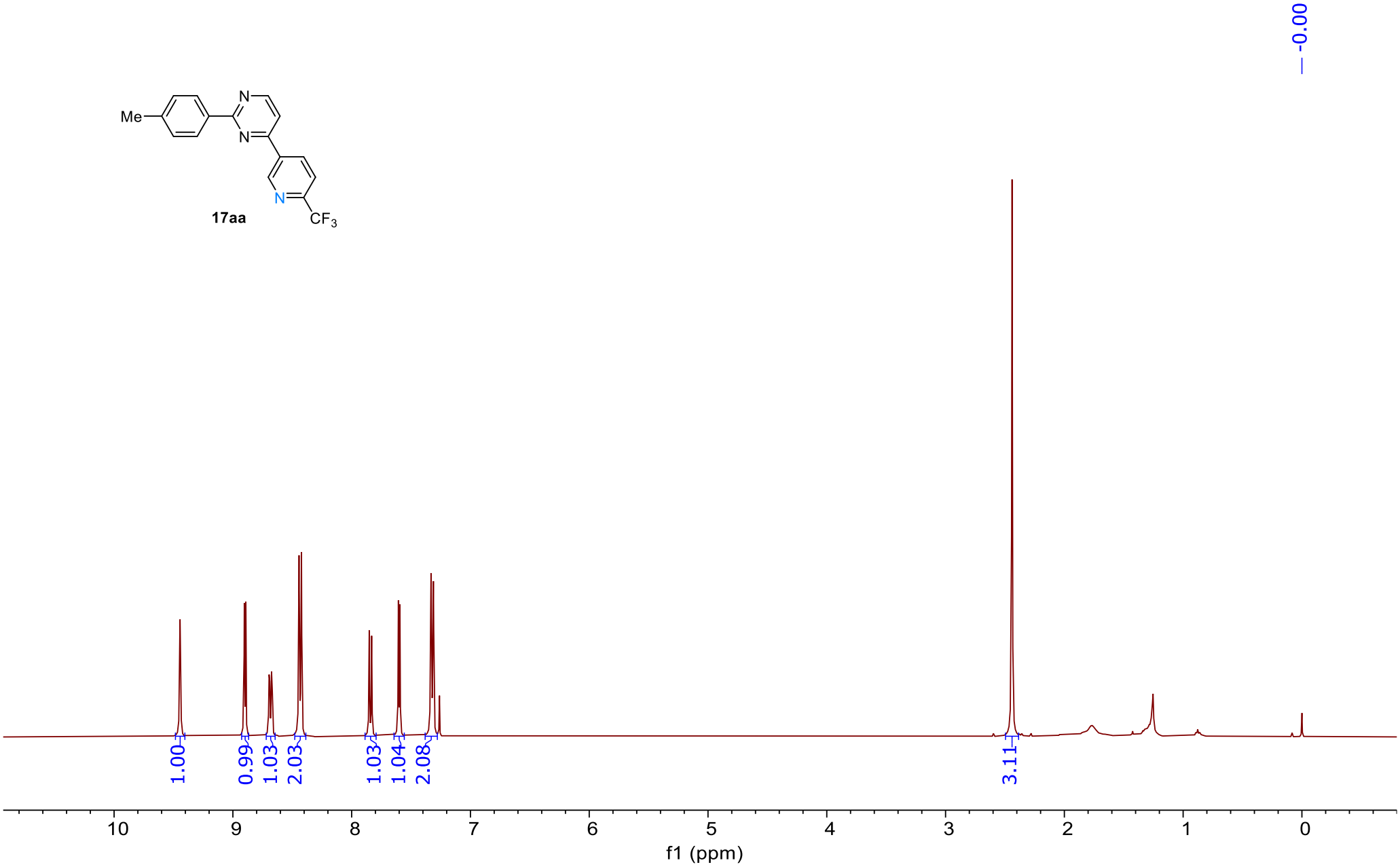


17t

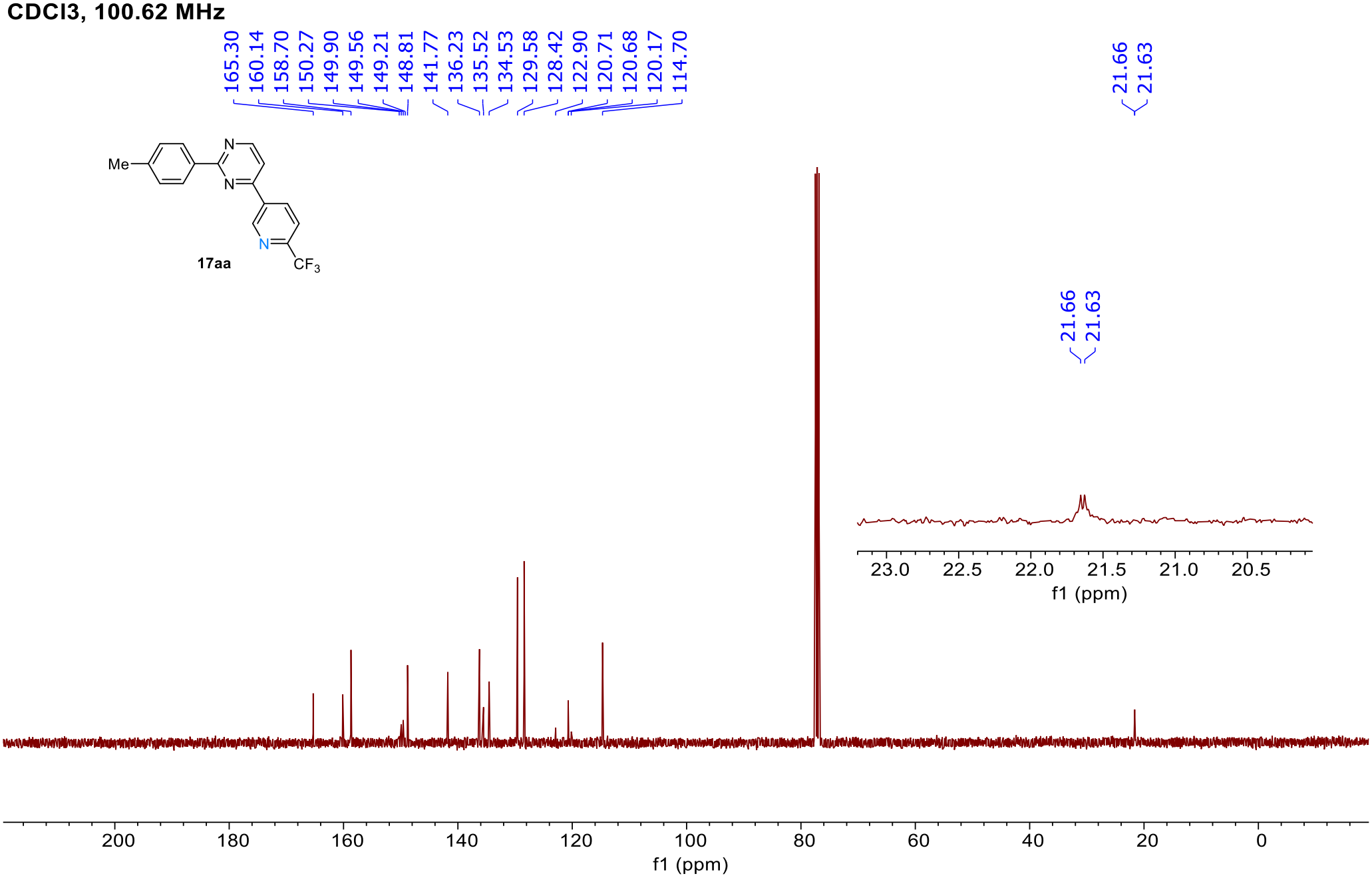
^{1}H NMR Spectrum of **17t**



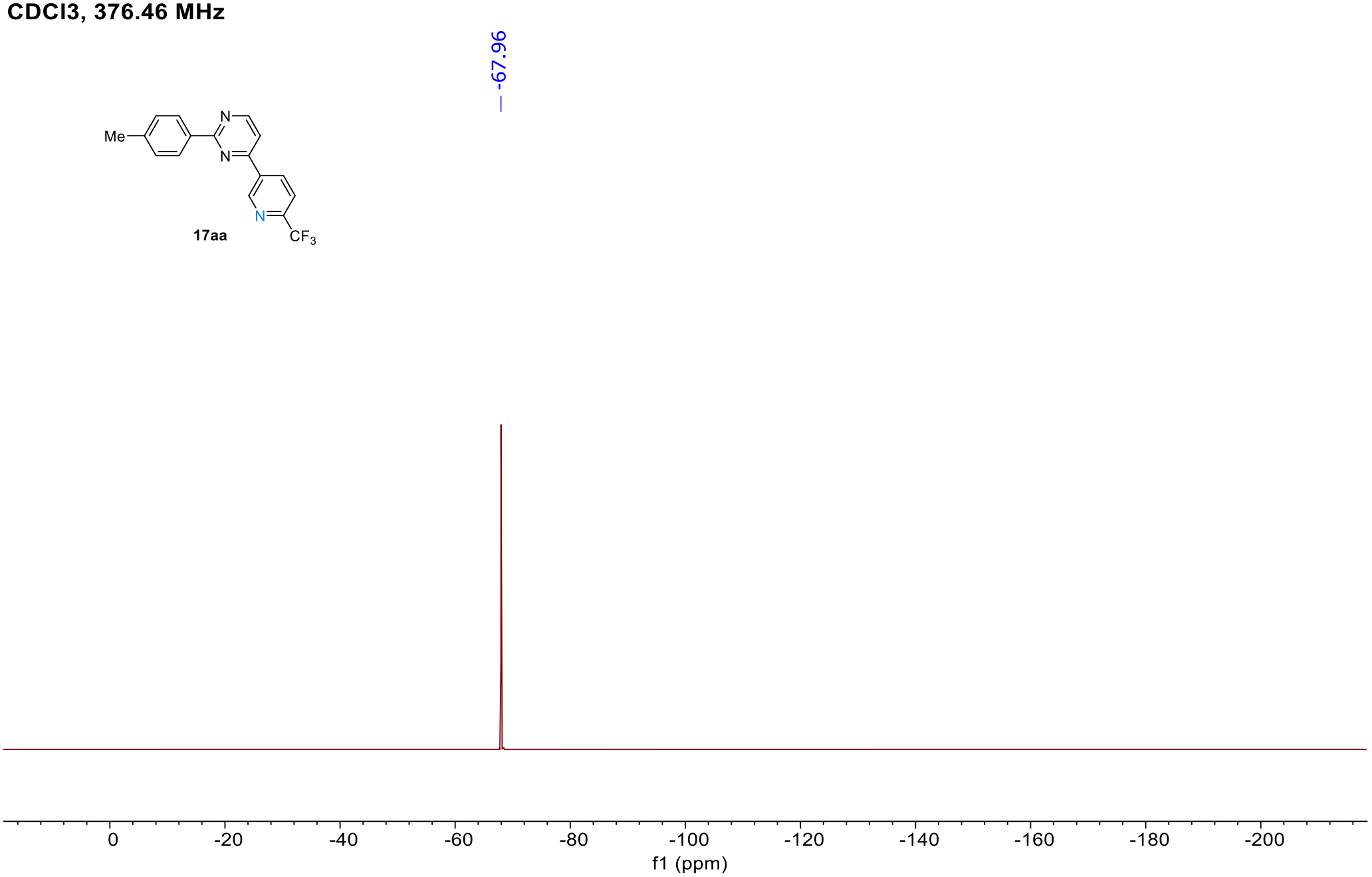
^{13}C NMR Spectrum of **17t**



^{1}H NMR Spectrum of **17aa**

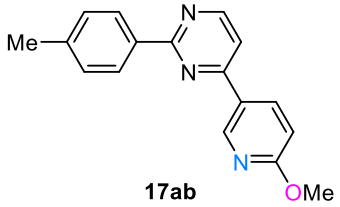


^{13}C NMR Spectrum of **17aa**



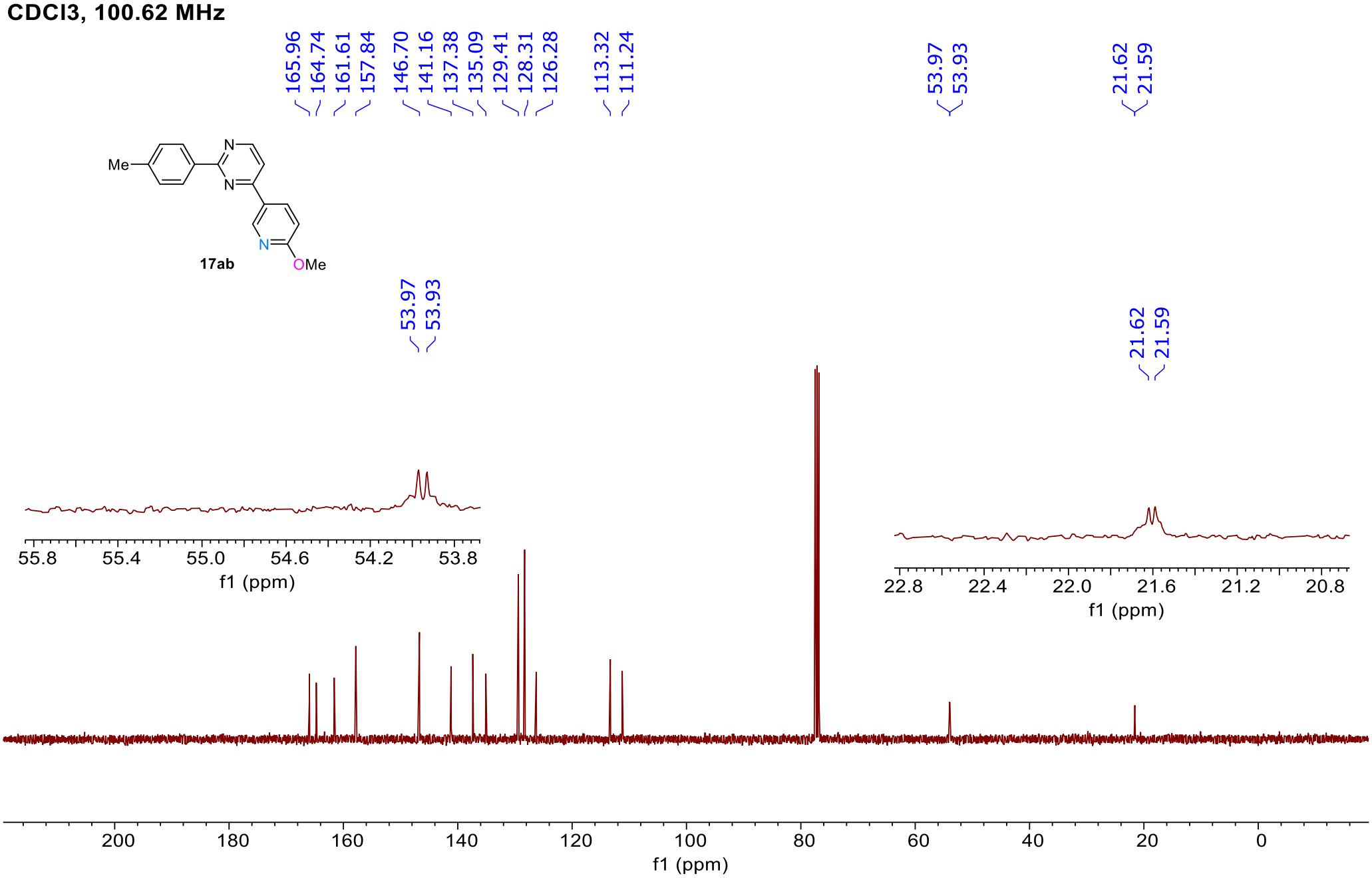
^{19}F NMR Spectrum of **17aa**

CDCl3, 400.13 MHz

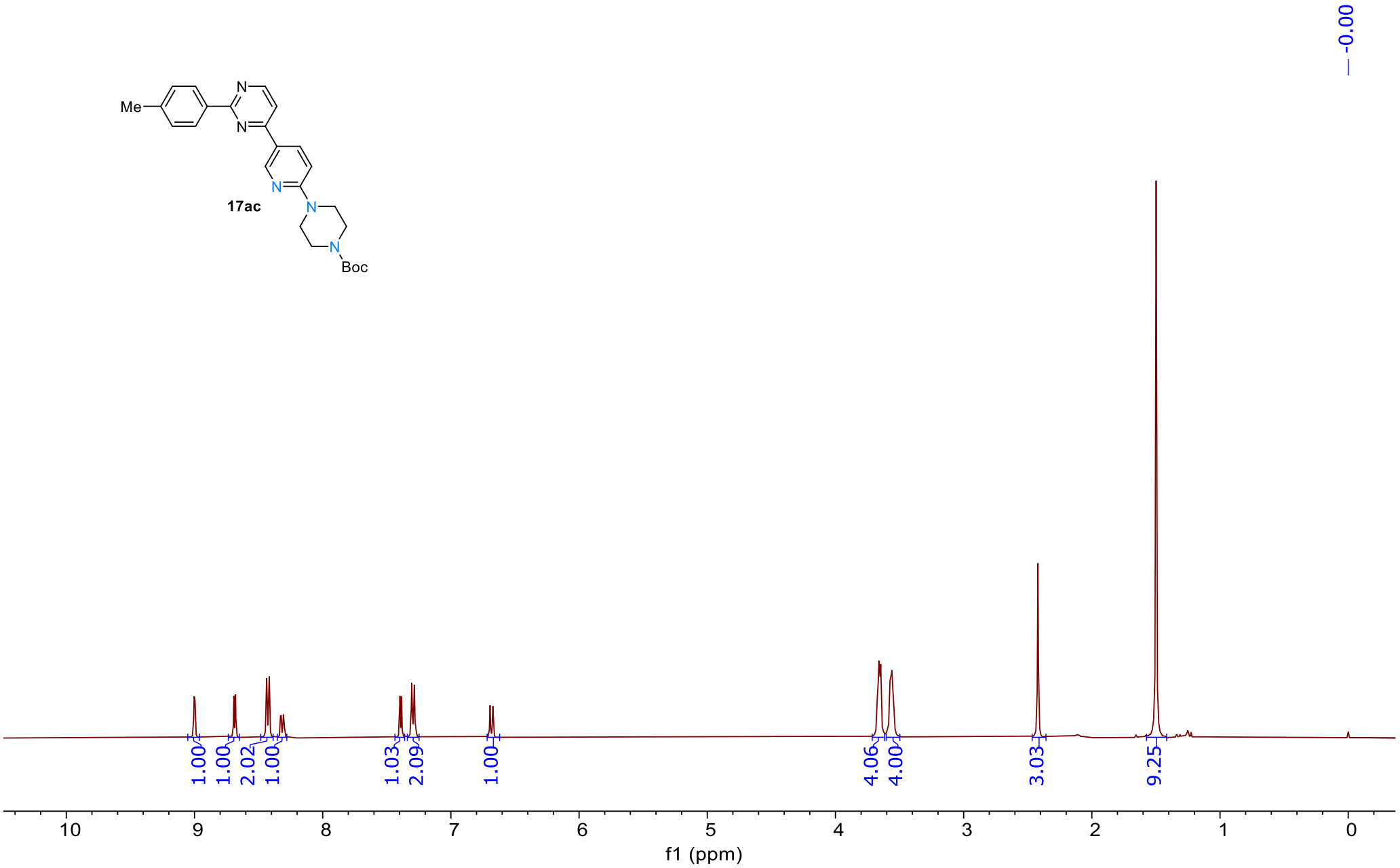


17ab

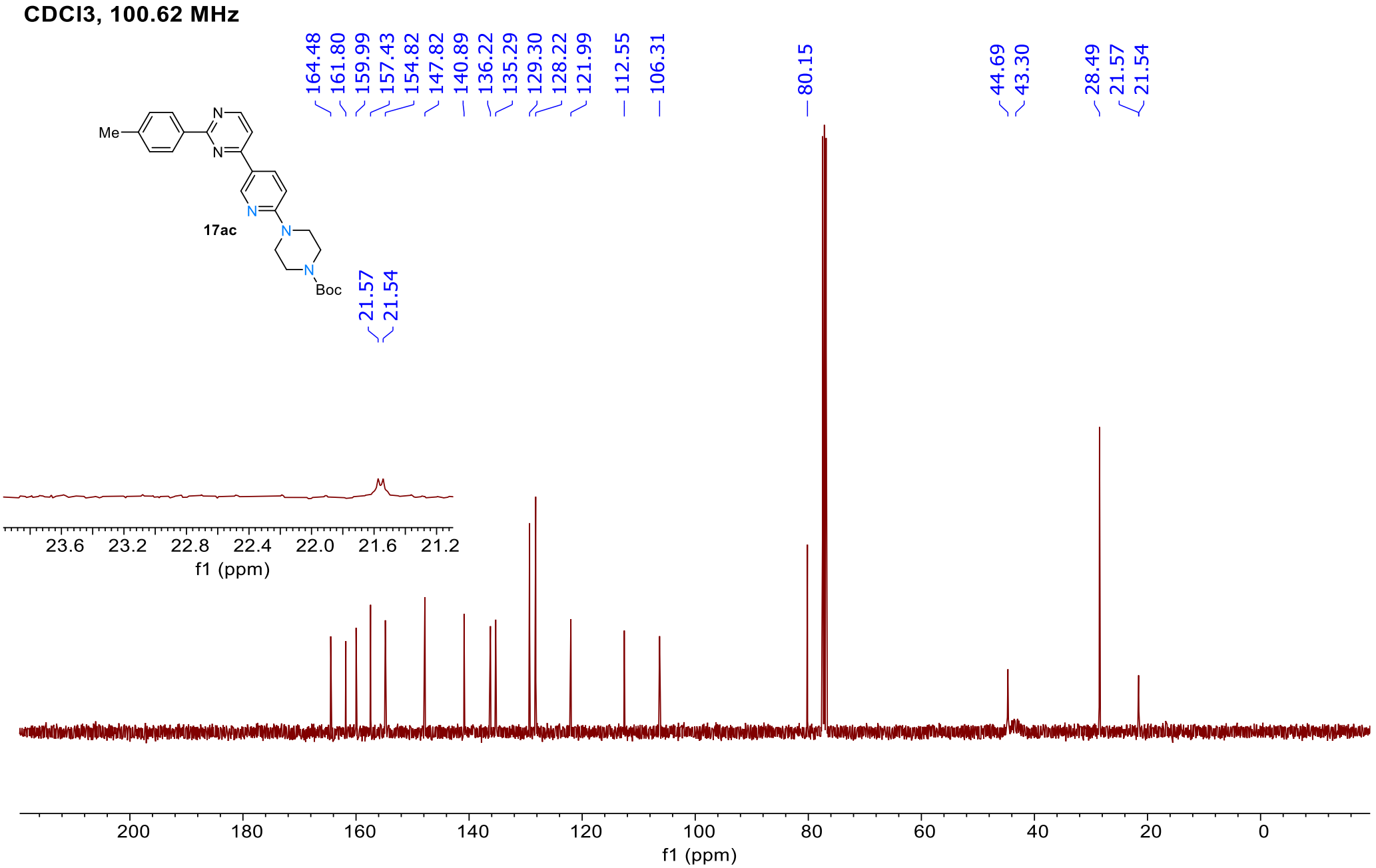
^{1}H NMR Spectrum of **17ab**



^{13}C NMR Spectrum of **17ab**

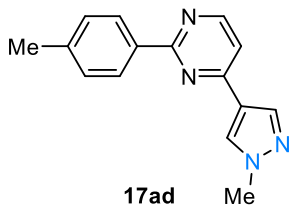


^{1}H NMR Spectrum of **17ac**



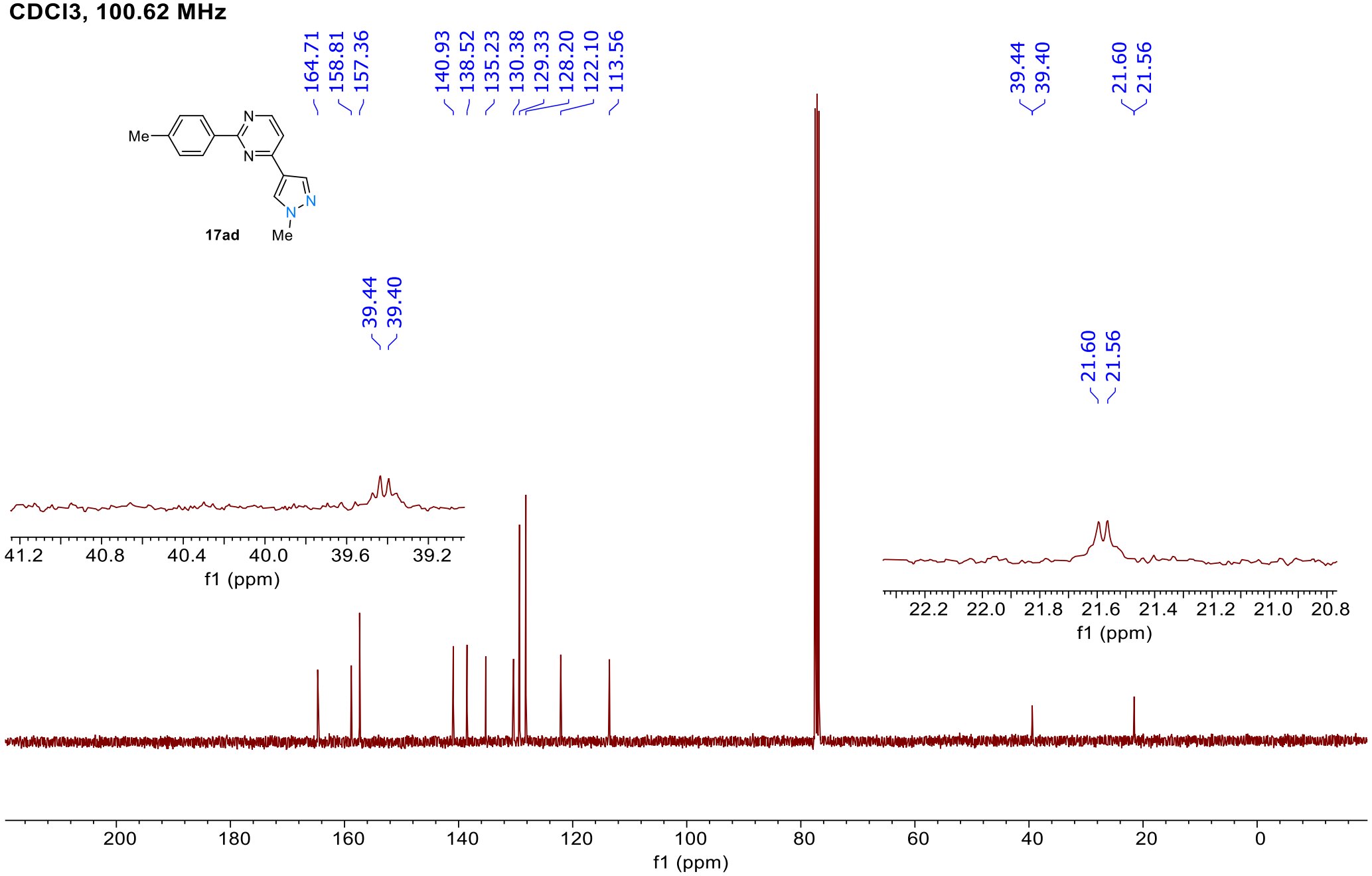
^{13}C NMR Spectrum of **17ac**

CDCl3, 400.13 MHz

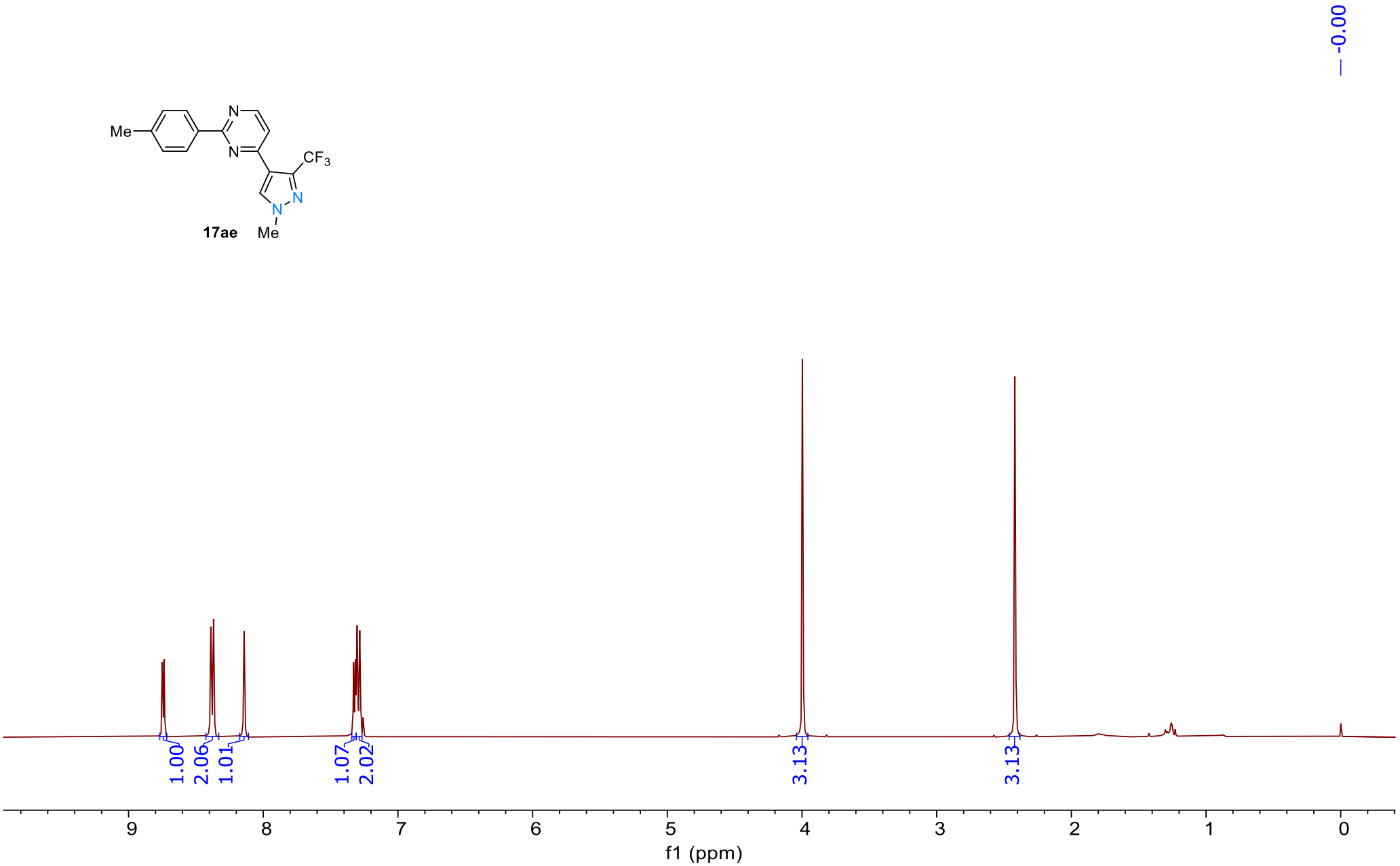


17ad

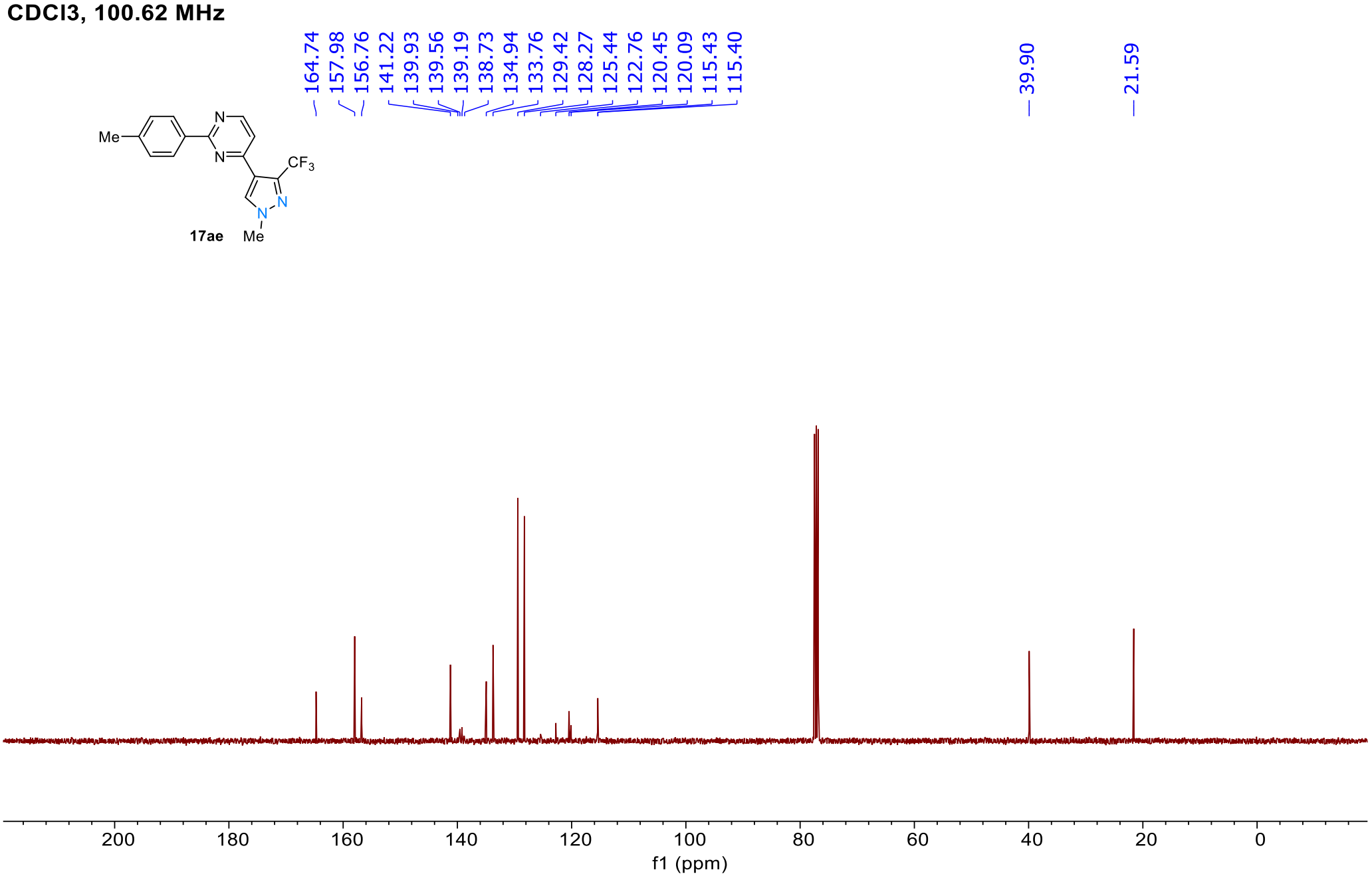
^{1}H NMR Spectrum of **17ad**



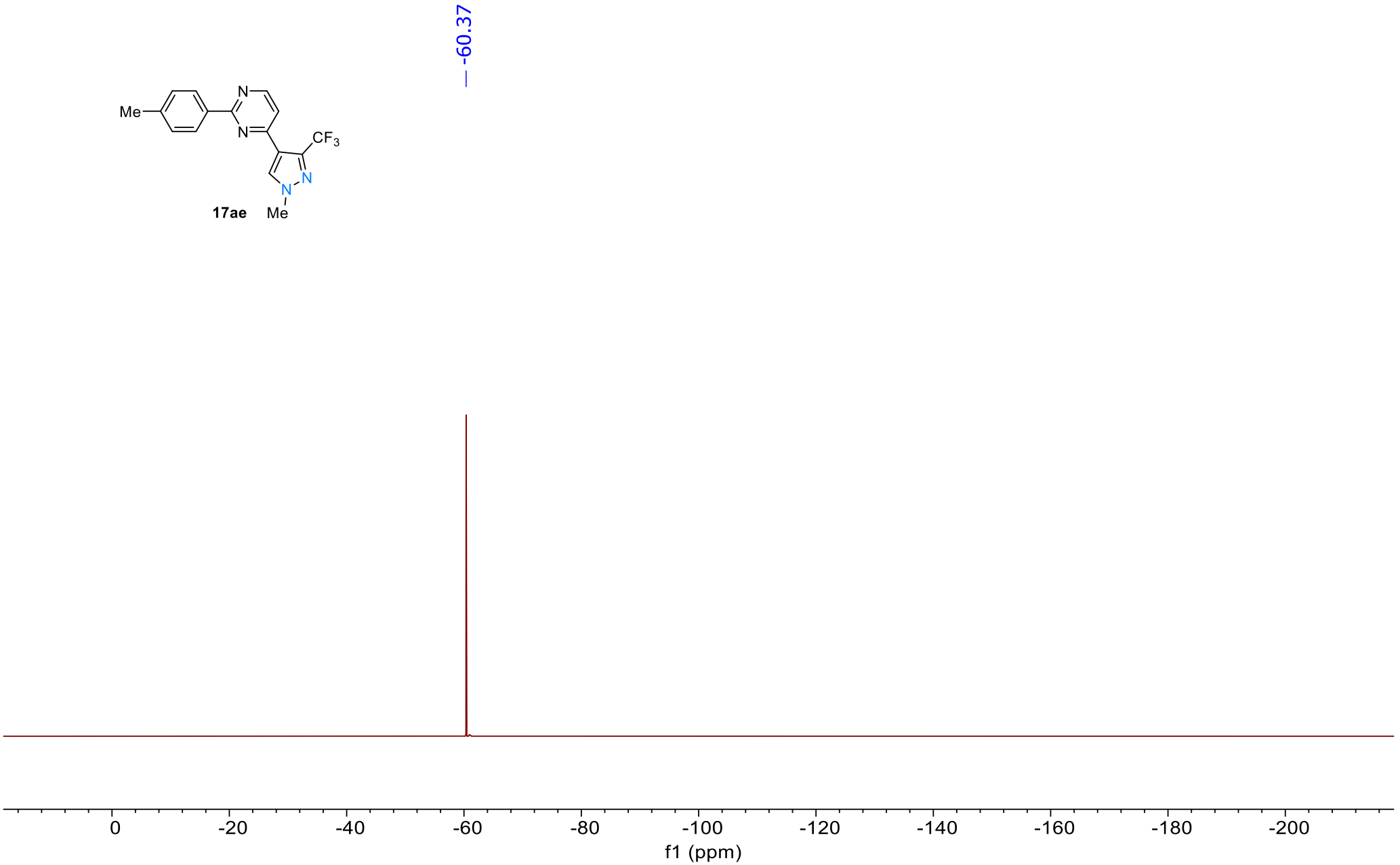
^{13}C NMR Spectrum of **17ad**



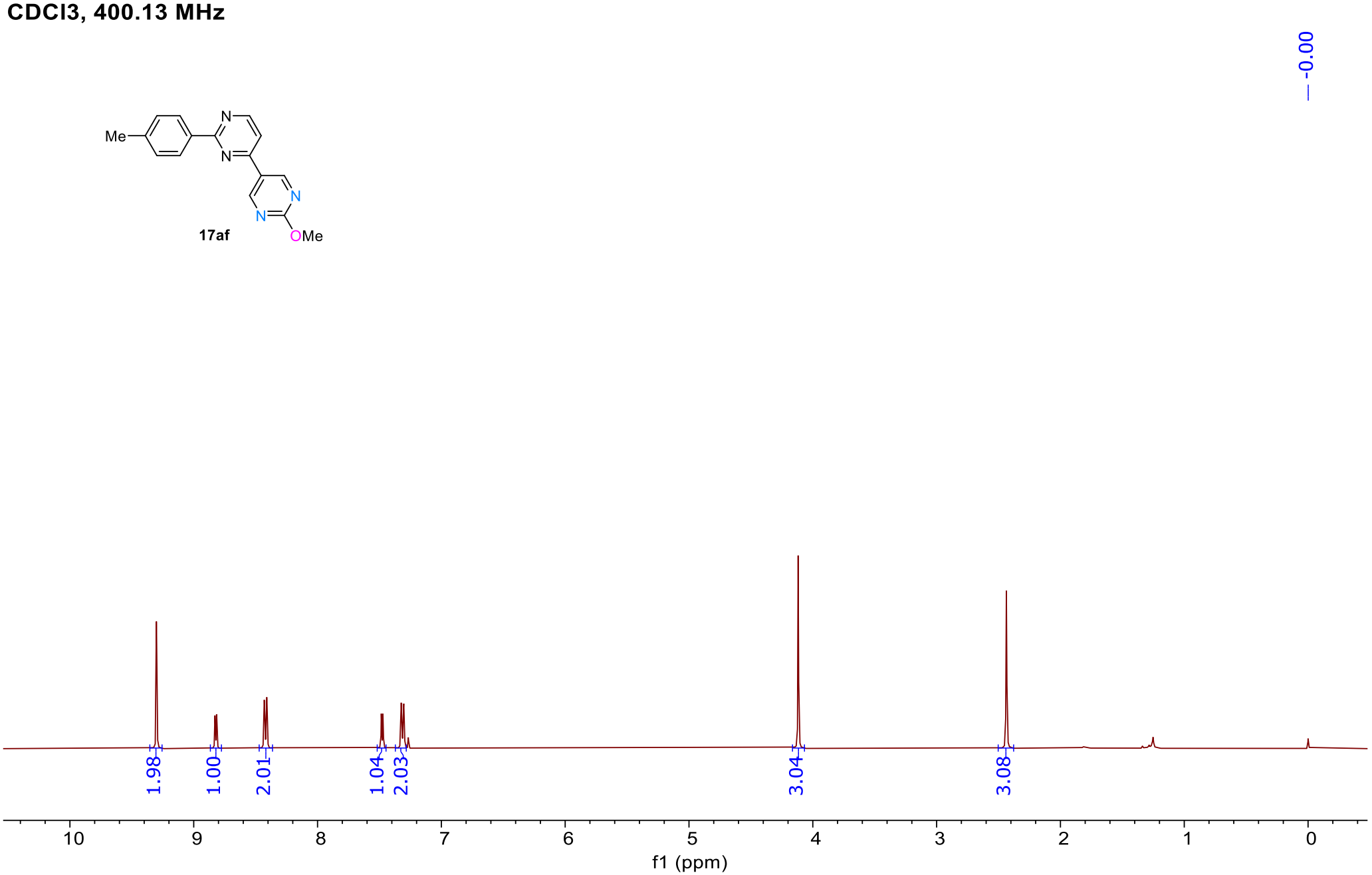
^{1}H NMR Spectrum of **17ae**



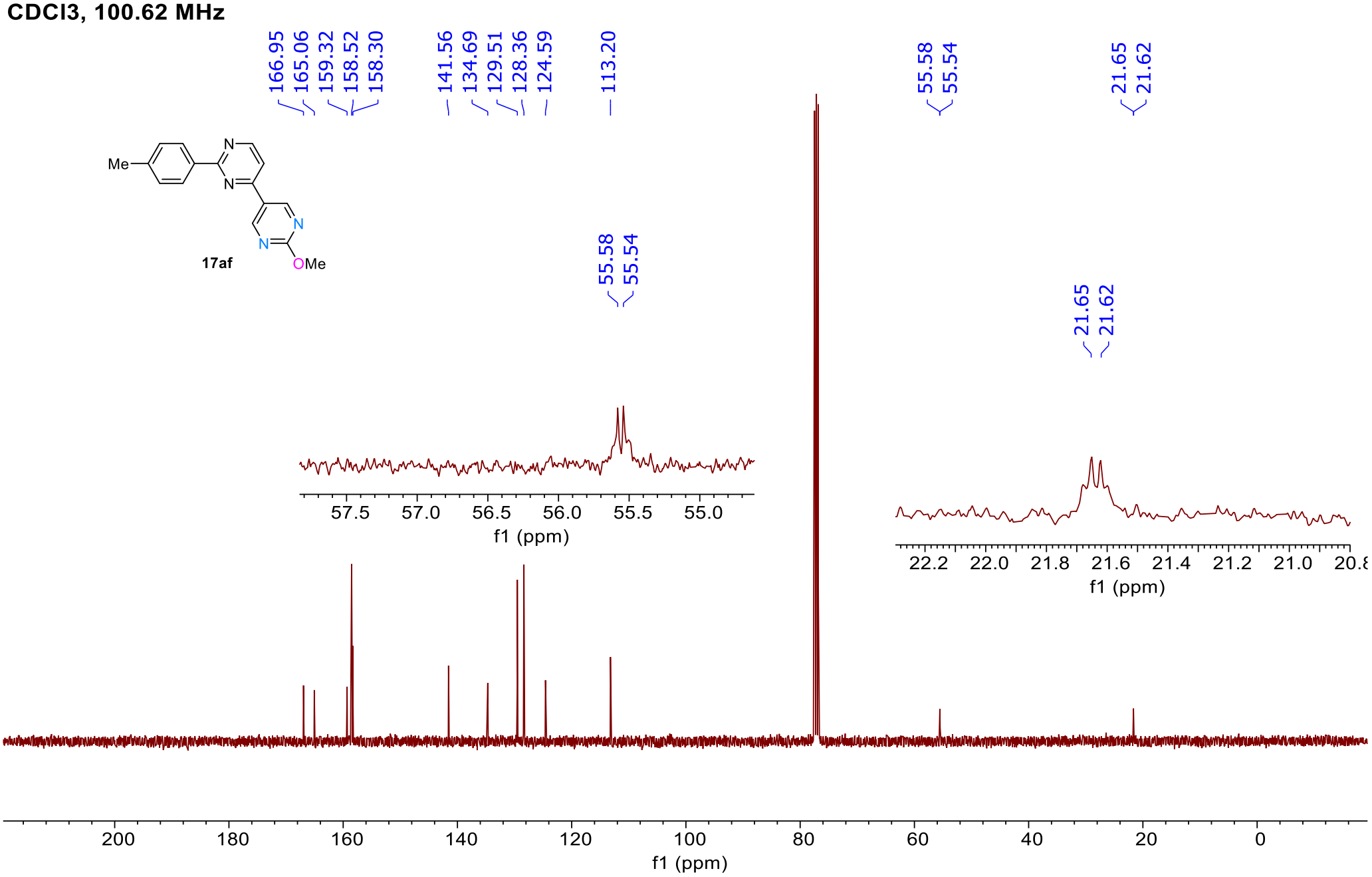
^{13}C NMR Spectrum of **17ae**



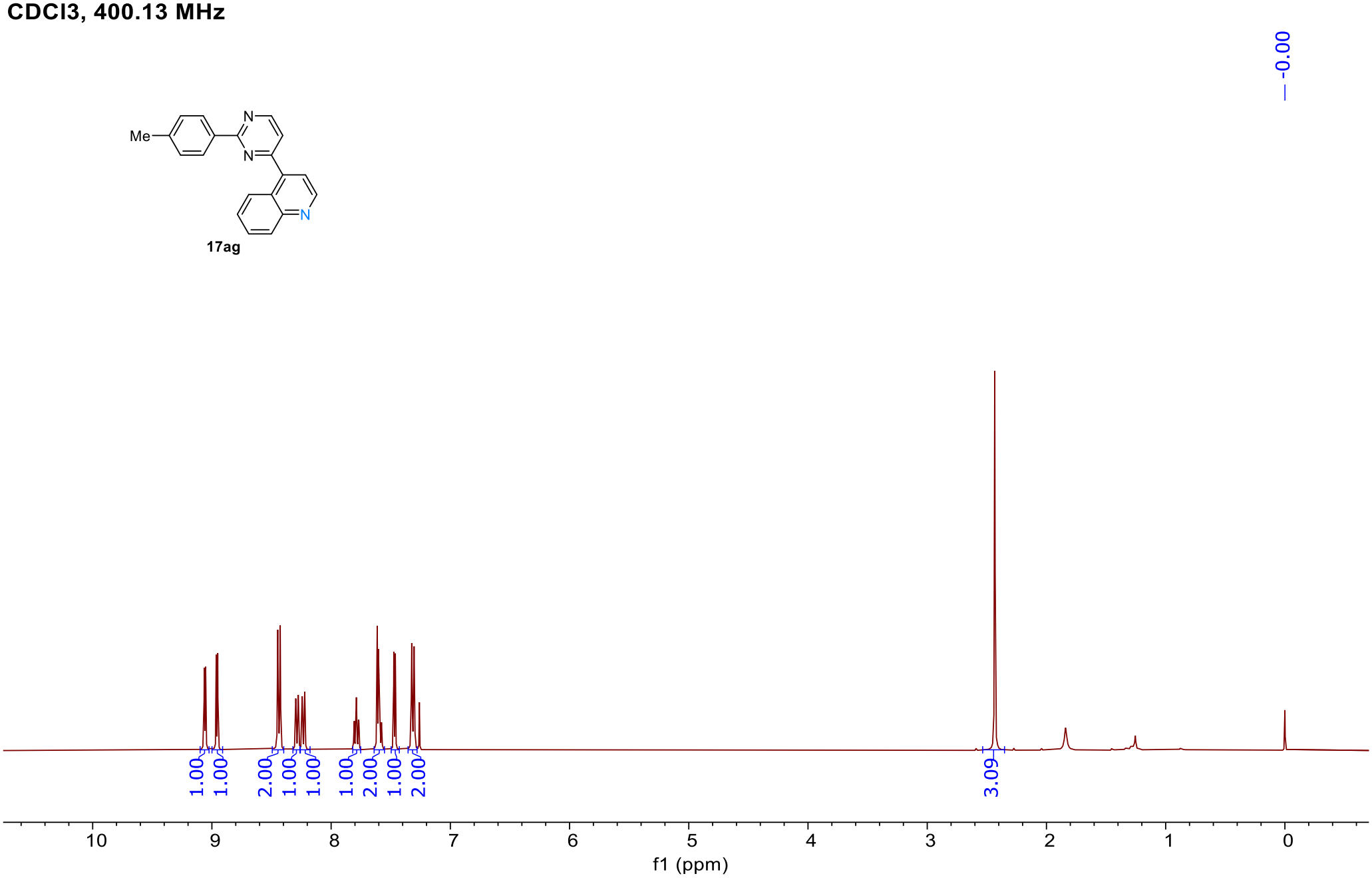
^{19}F NMR Spectrum of **17ae**



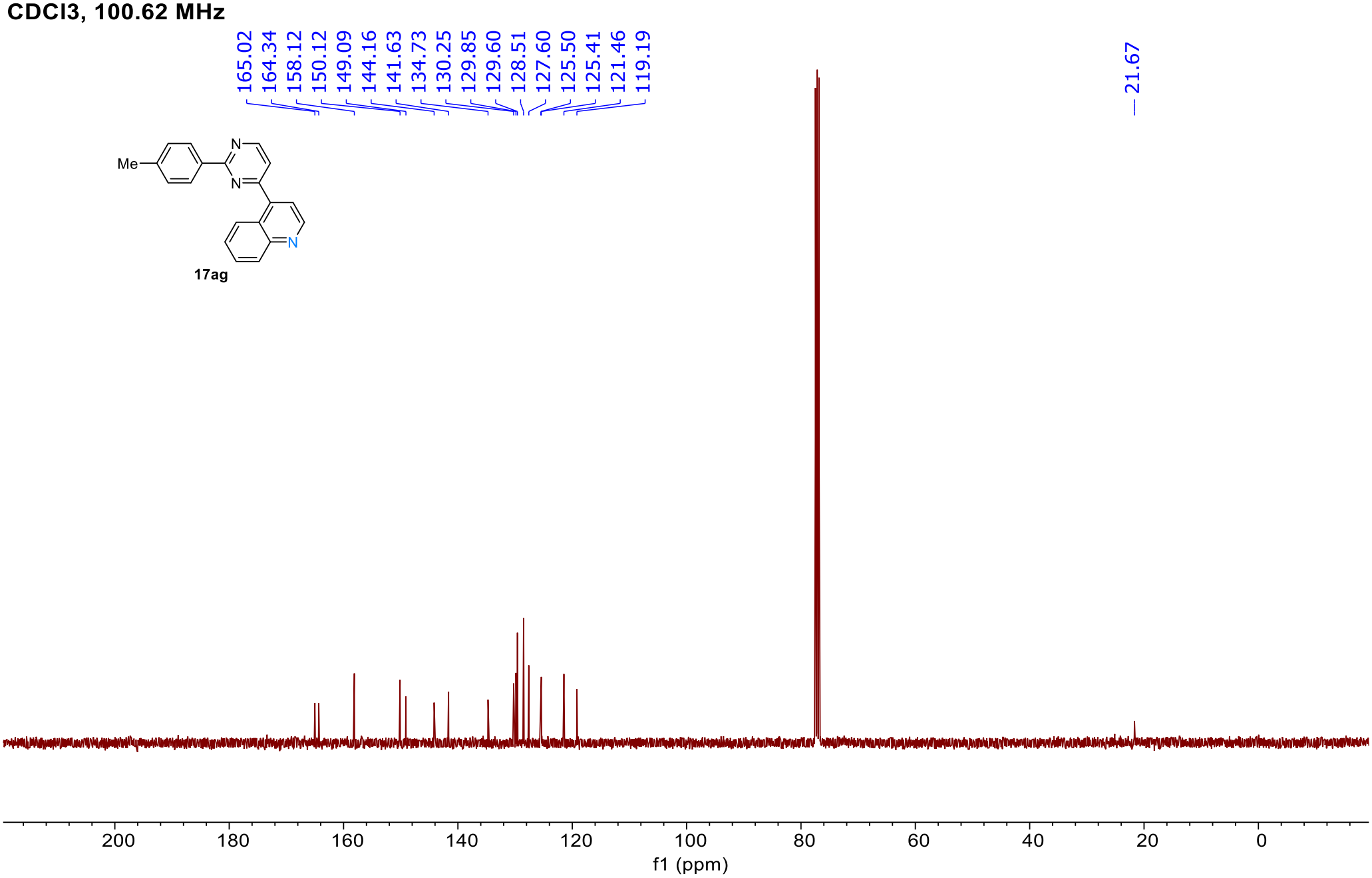
^{1}H NMR Spectrum of **17af**



^{13}C NMR Spectrum of **17af**

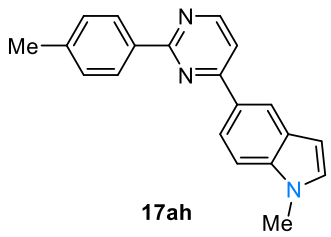


^{1}H NMR Spectrum of **17ag**



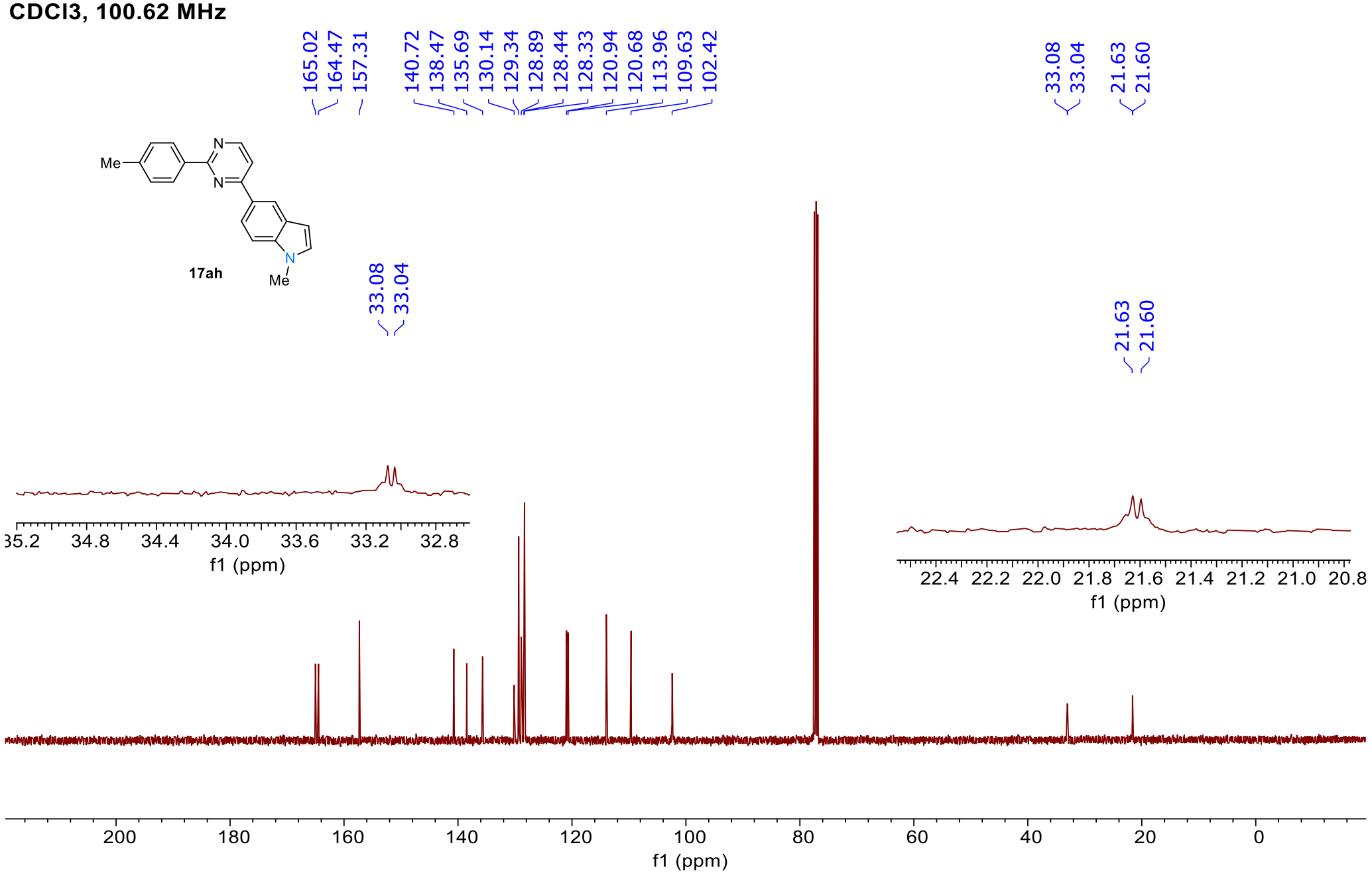
^{13}C NMR Spectrum of **17ag**

CDCl3, 400.13 MHz



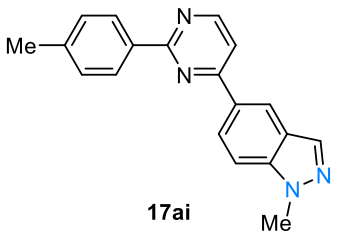
17ah

^{1}H NMR Spectrum of **17ah**



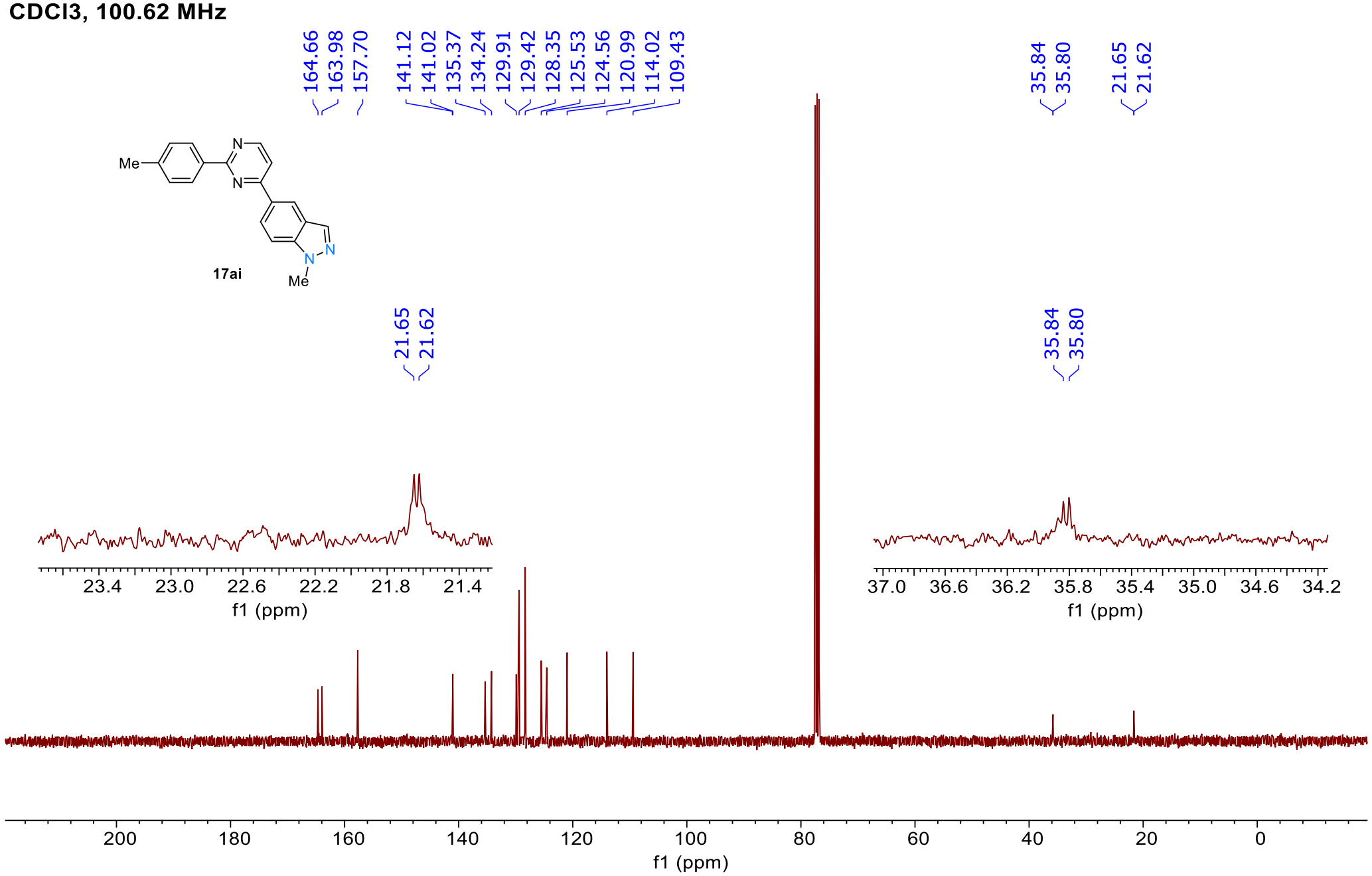
^{13}C NMR Spectrum of **17ah**

CDCl3, 400.13 MHz

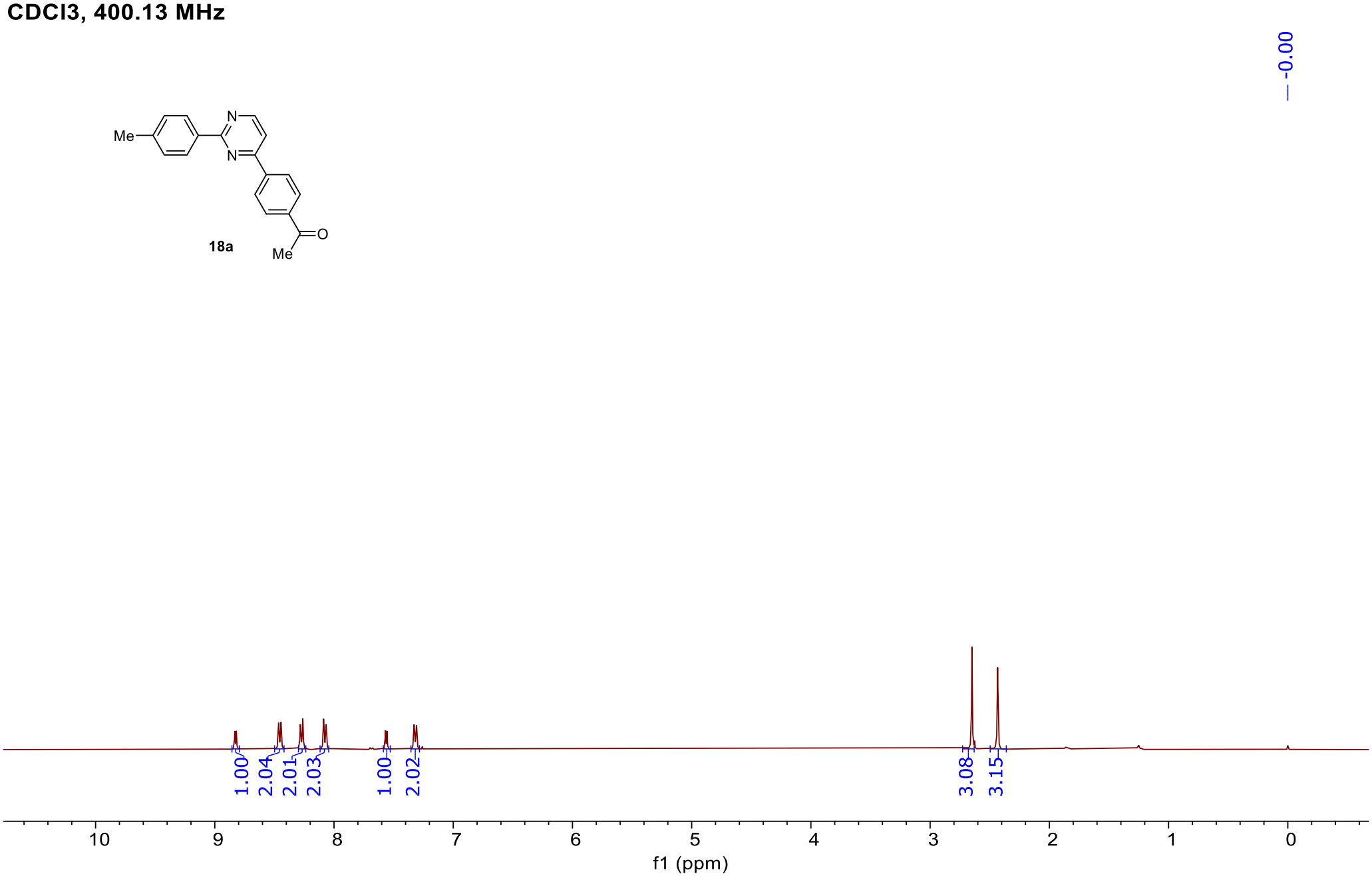


17ai

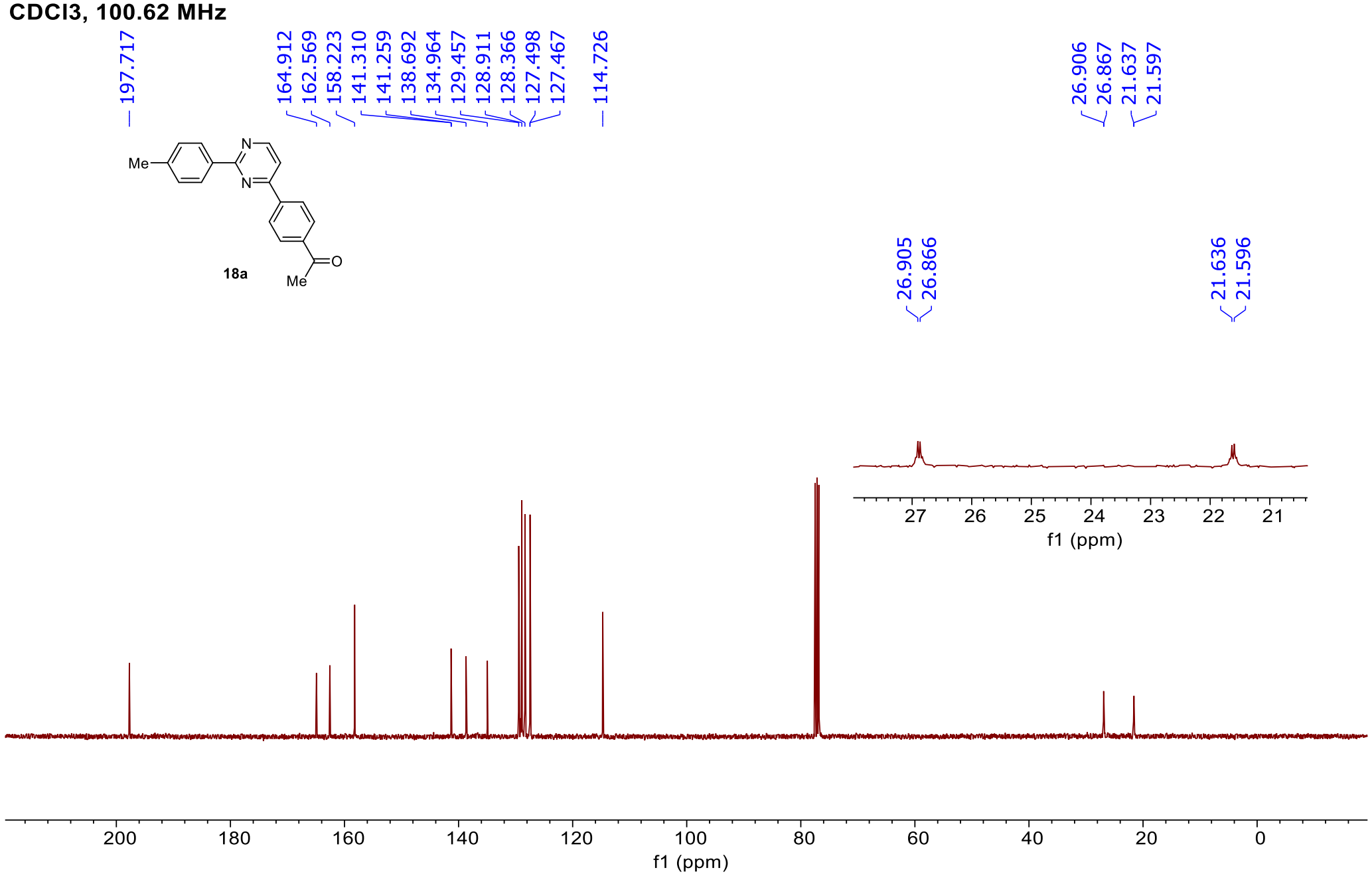
^{1}H NMR Spectrum of **17ai**



^{13}C NMR Spectrum of **17ai**

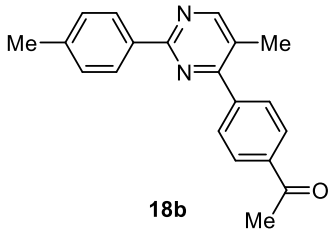


^{1}H NMR Spectrum of **18a**



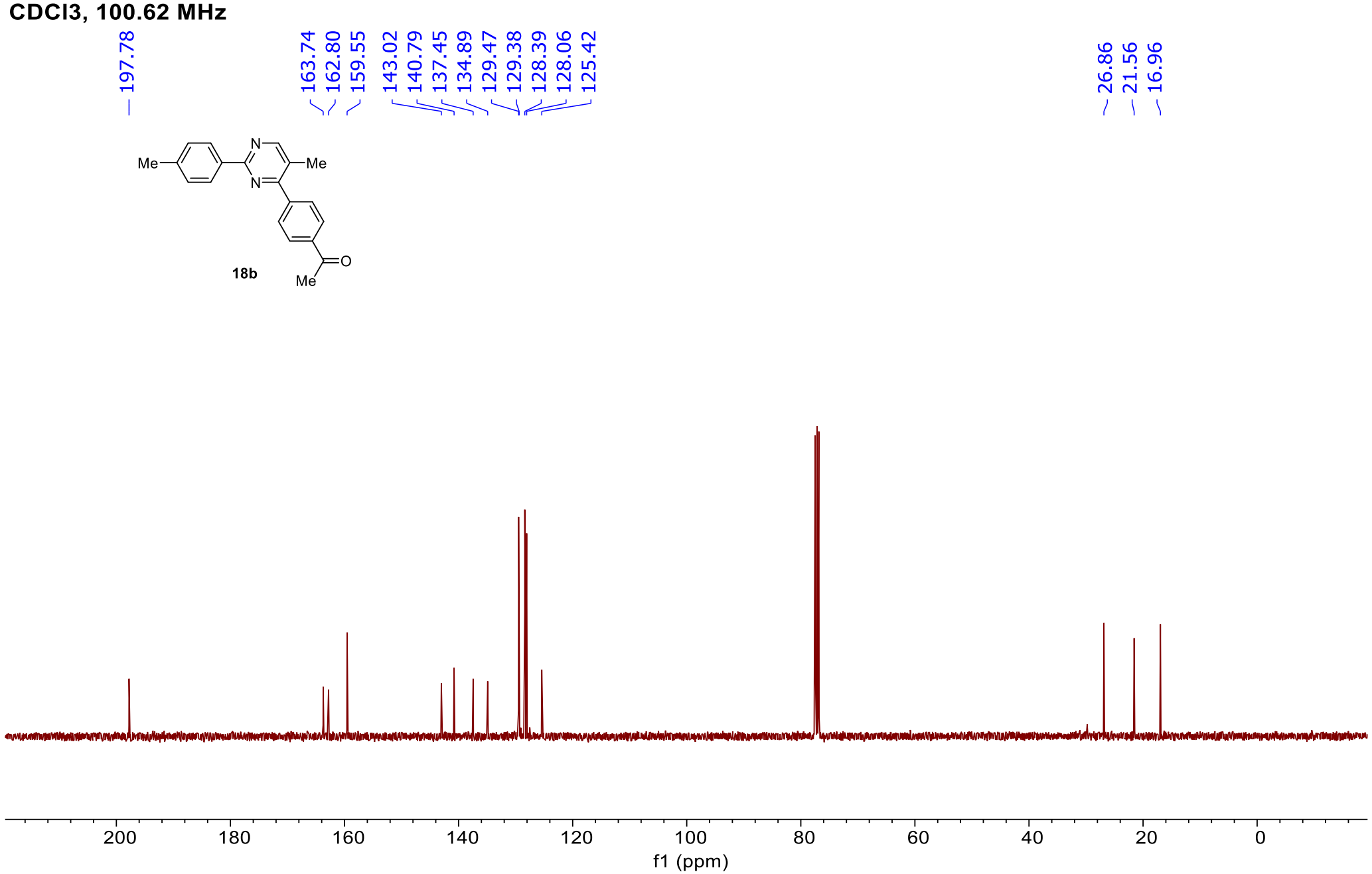
^{13}C NMR Spectrum of **18a**

CDCl3, 400.13 MHz



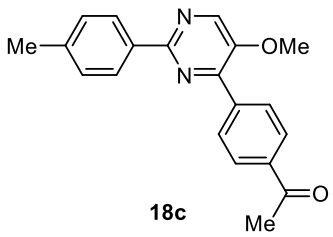
18b

^{1}H NMR Spectrum of **18b**



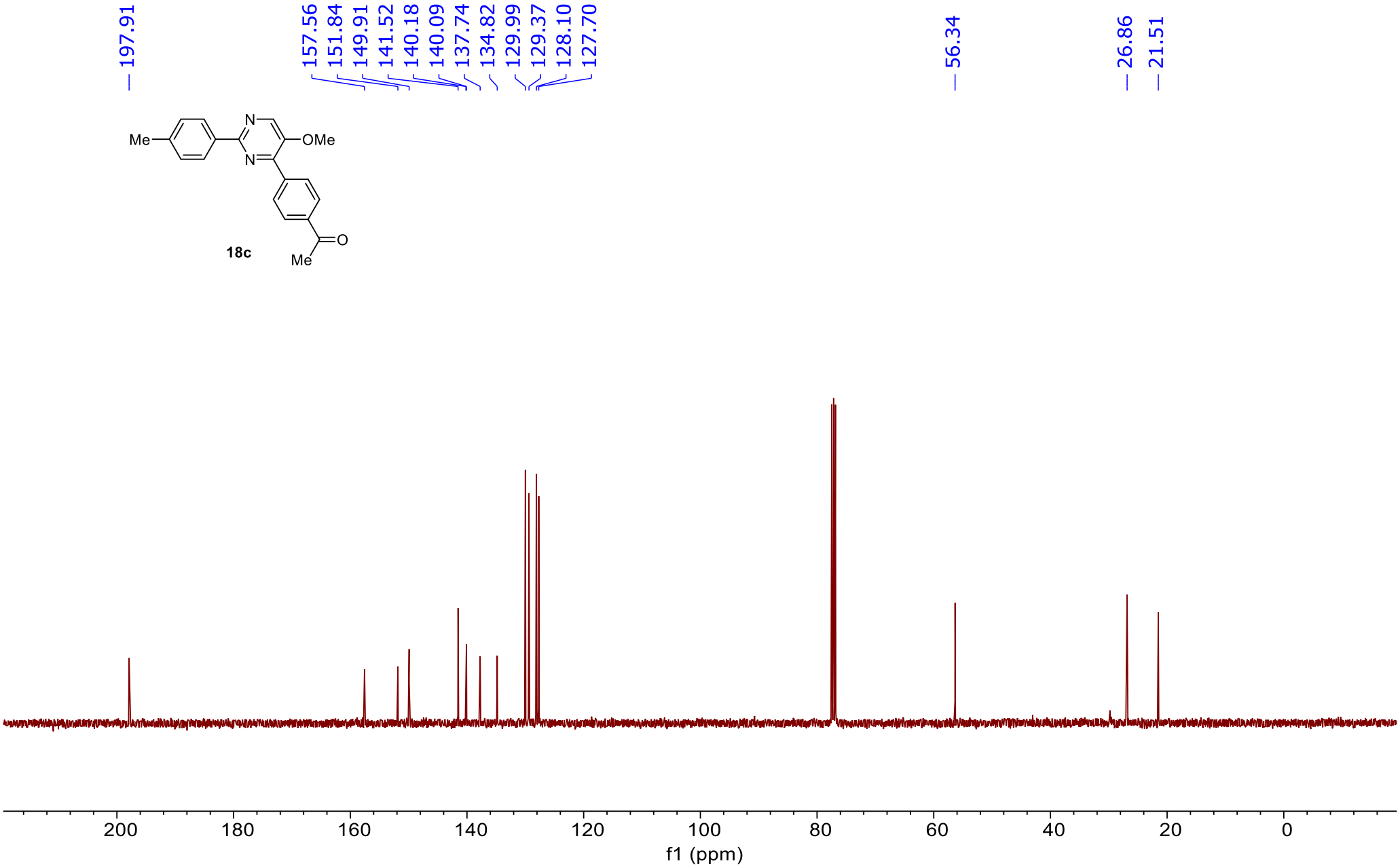
^{13}C NMR Spectrum of **18b**

CDCl3, 400.13 MHz



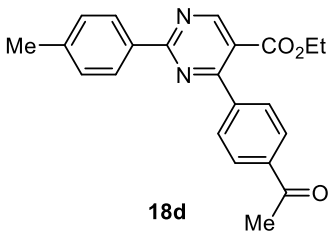
18c

^{1}H NMR Spectrum of **18c**



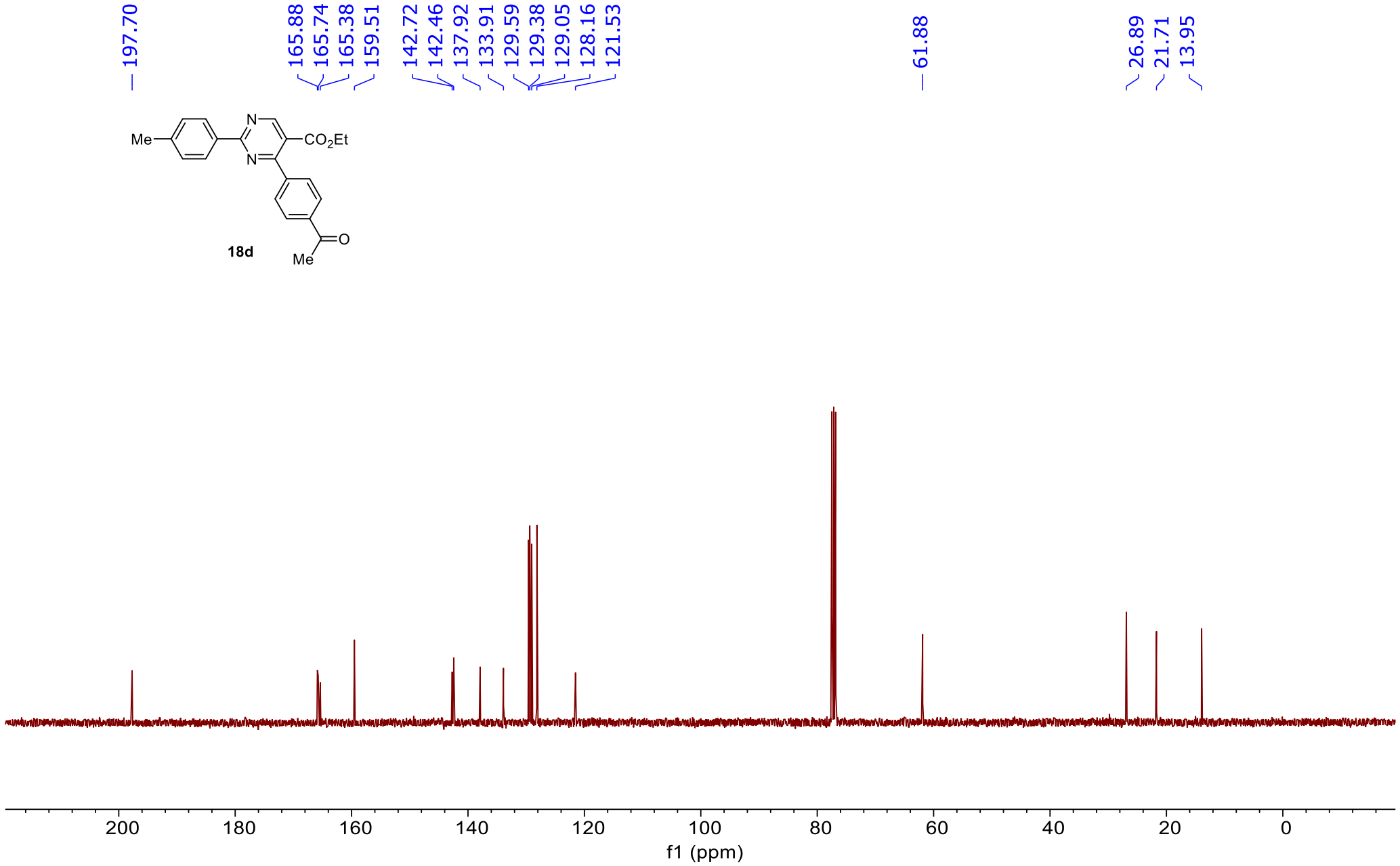
^{13}C NMR Spectrum of **18c**

CDCl3, 400.13 MHz



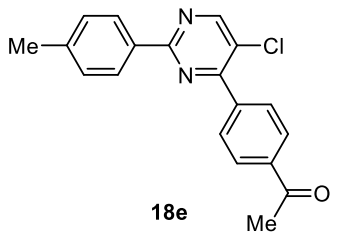
18d

^{1}H NMR Spectrum of **18d**



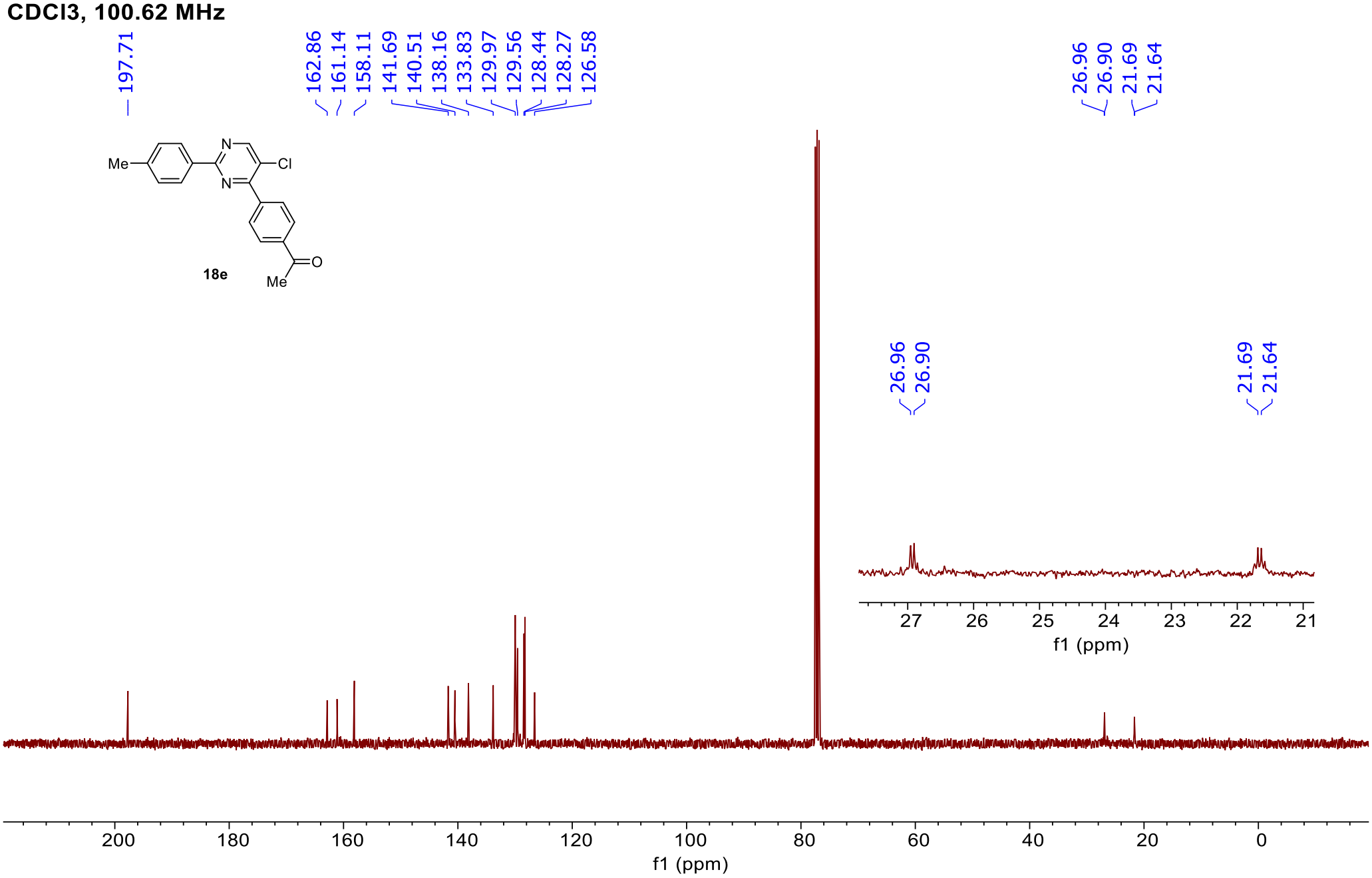
^{13}C NMR Spectrum of **18d**

CDCl3, 400.13 MHz



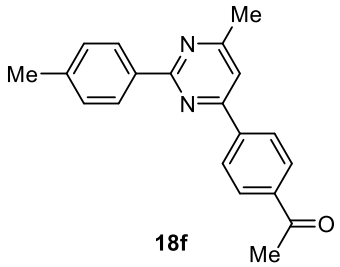
18e

^{1}H NMR Spectrum of **18e**



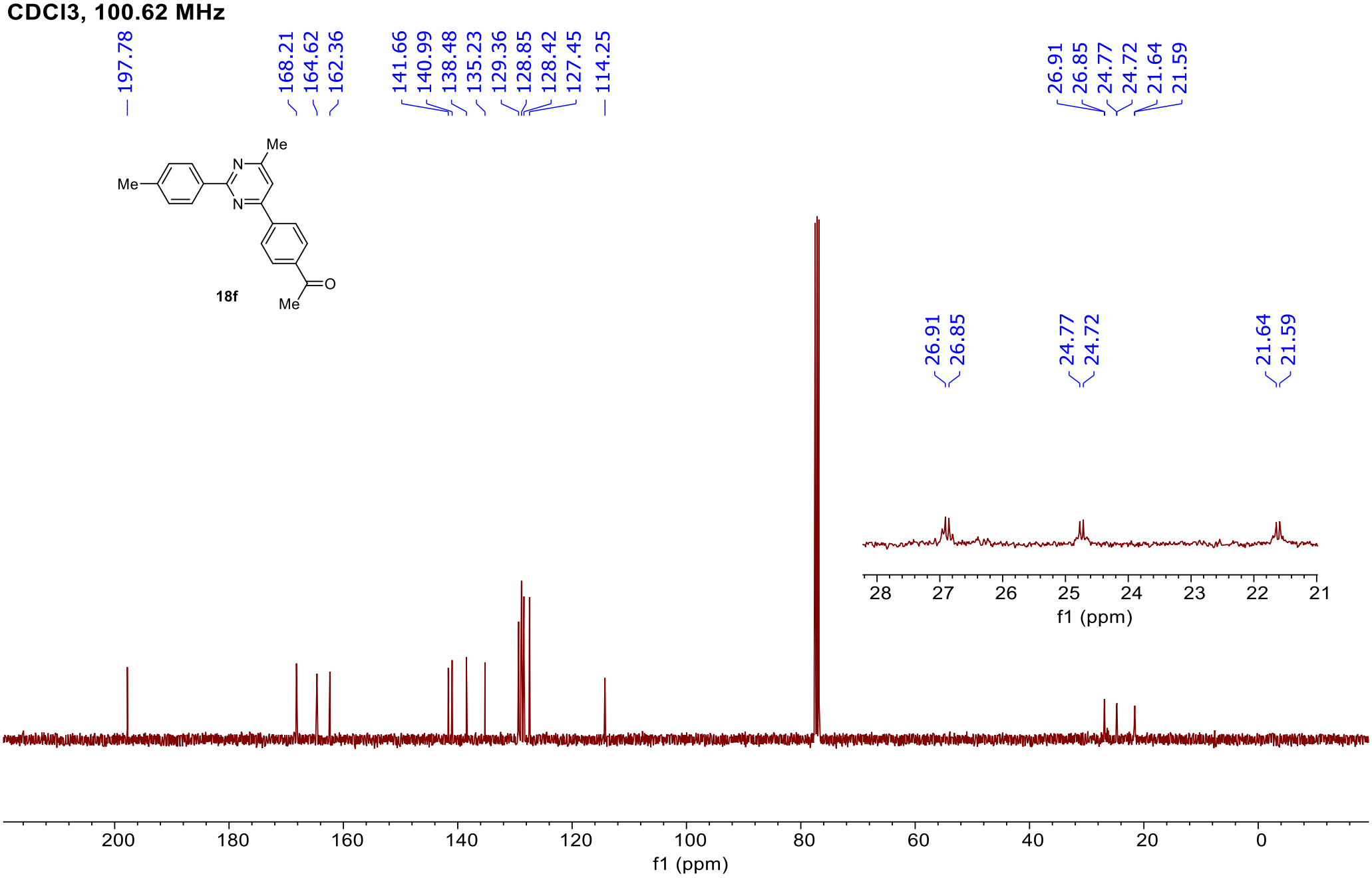
^{13}C NMR Spectrum of **18e**

CDCl3, 400.13 MHz



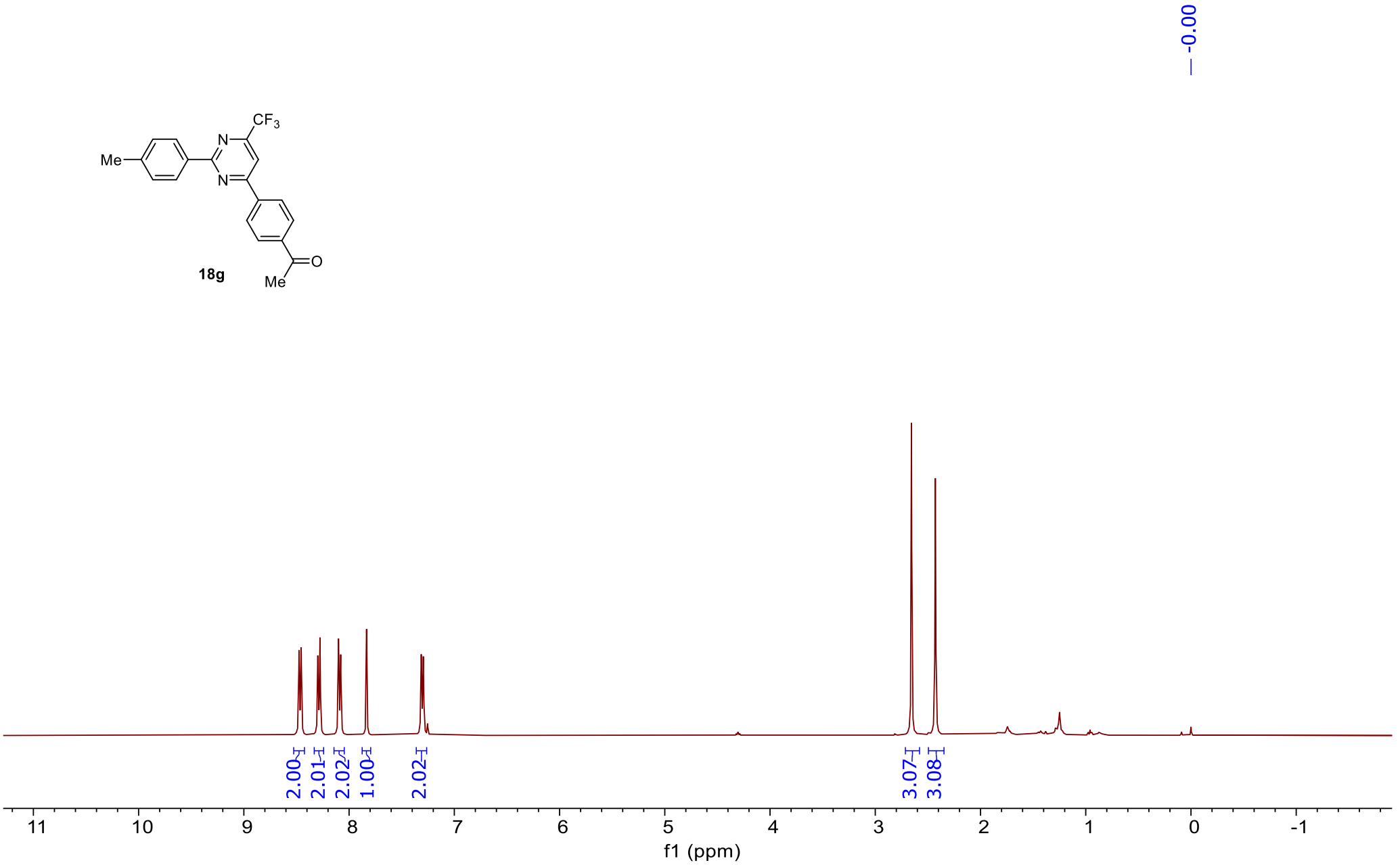
18f

^{1}H NMR Spectrum of **18f**

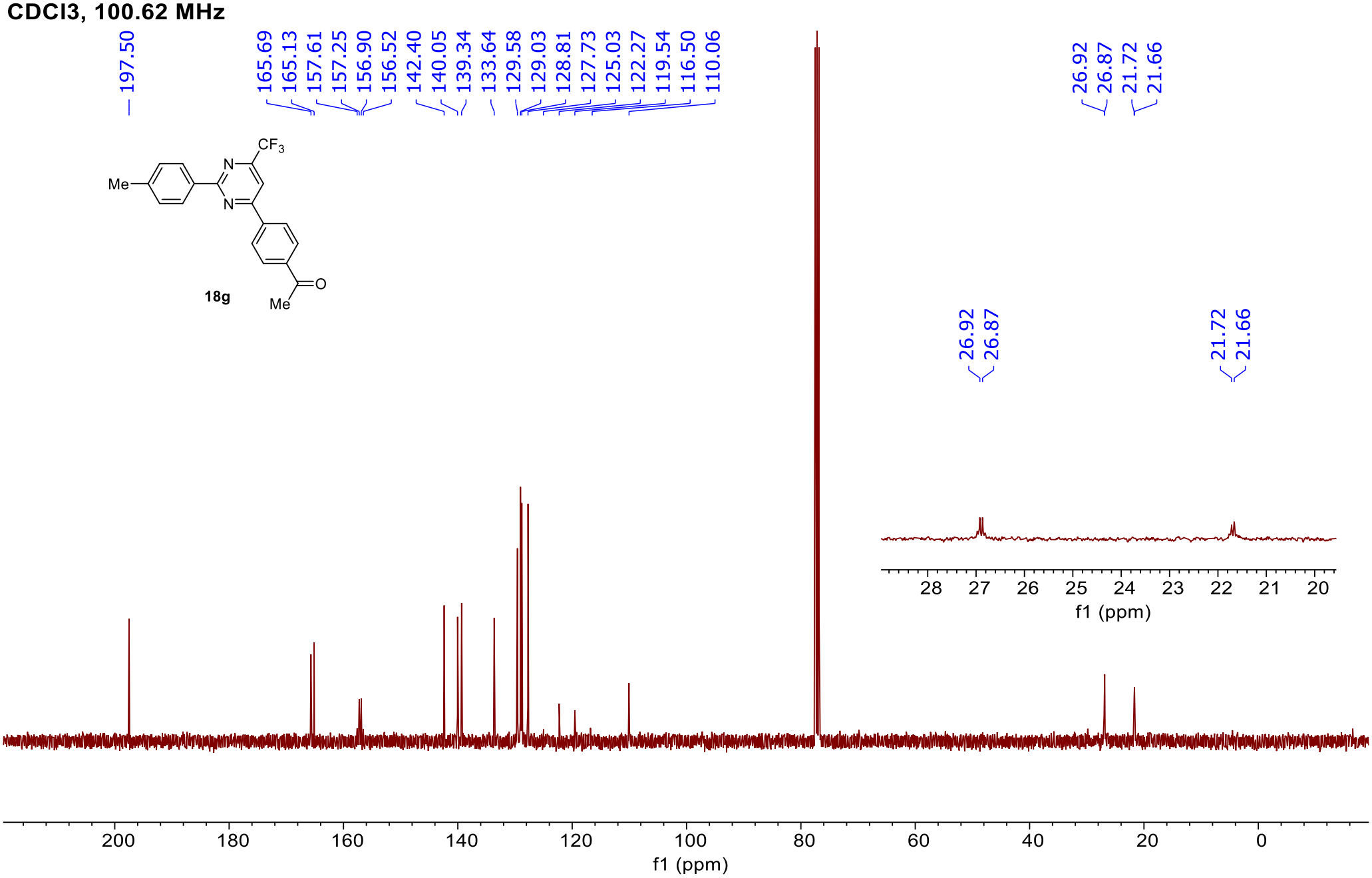


^{13}C NMR Spectrum of **18f**

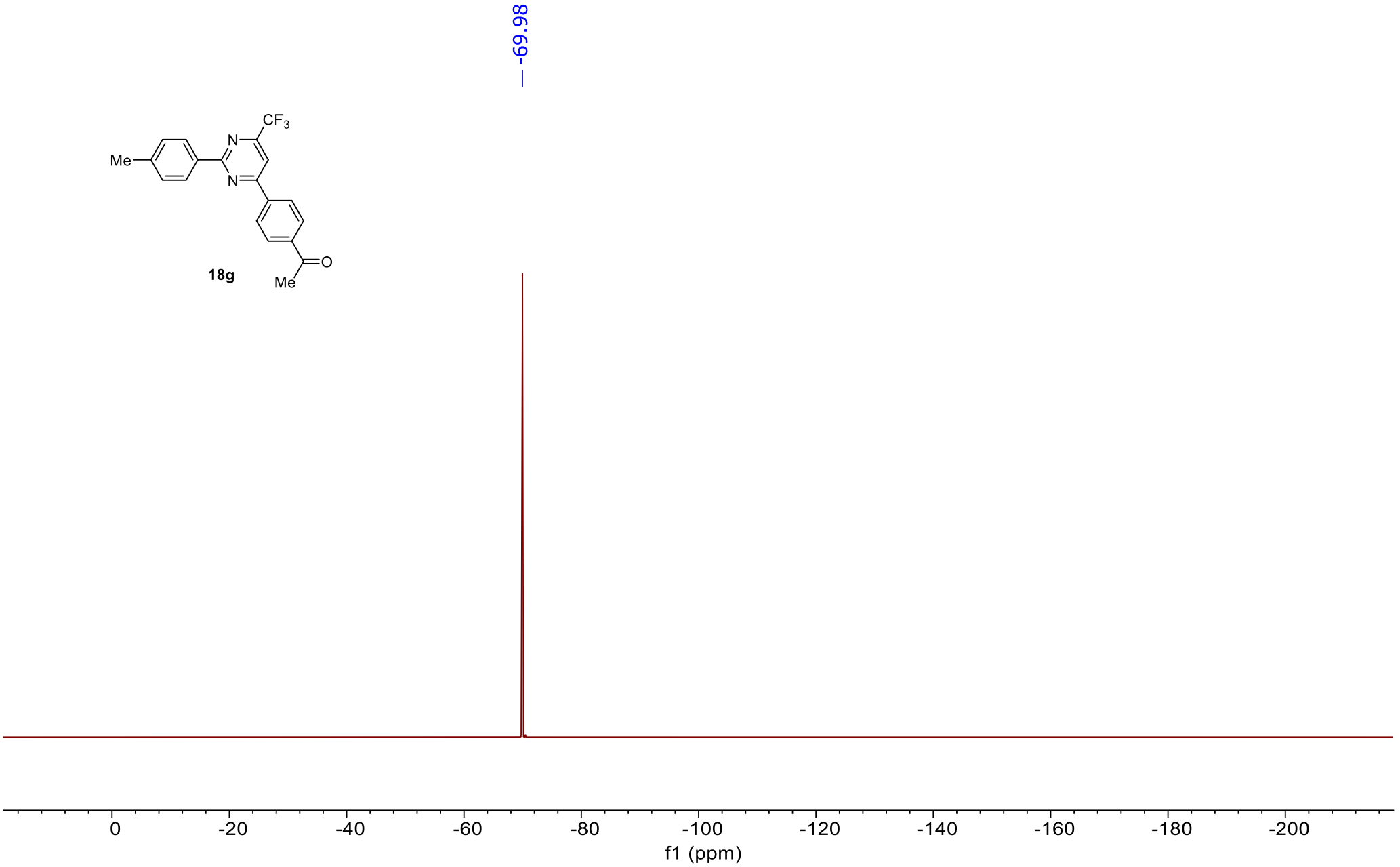
CDCl3, 400.13 MHz



^{1}H NMR Spectrum of **18g**

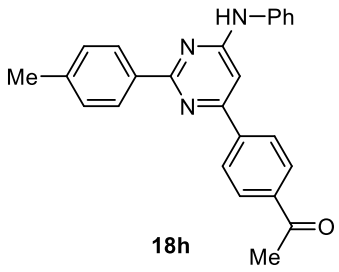


^{13}C NMR Spectrum of **18g**



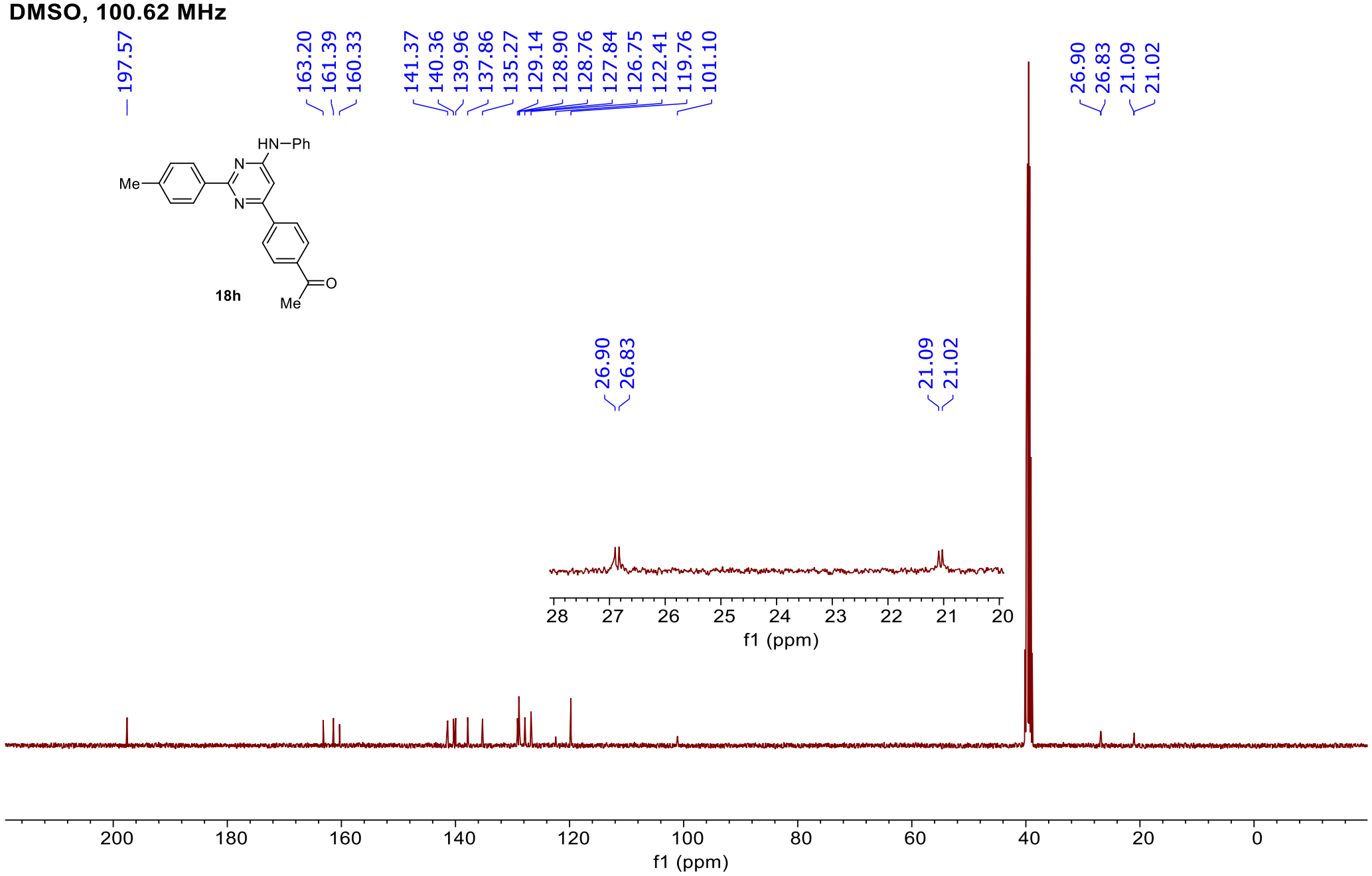
^{19}F NMR Spectrum of **18g**

DMSO, 400.13 MHz

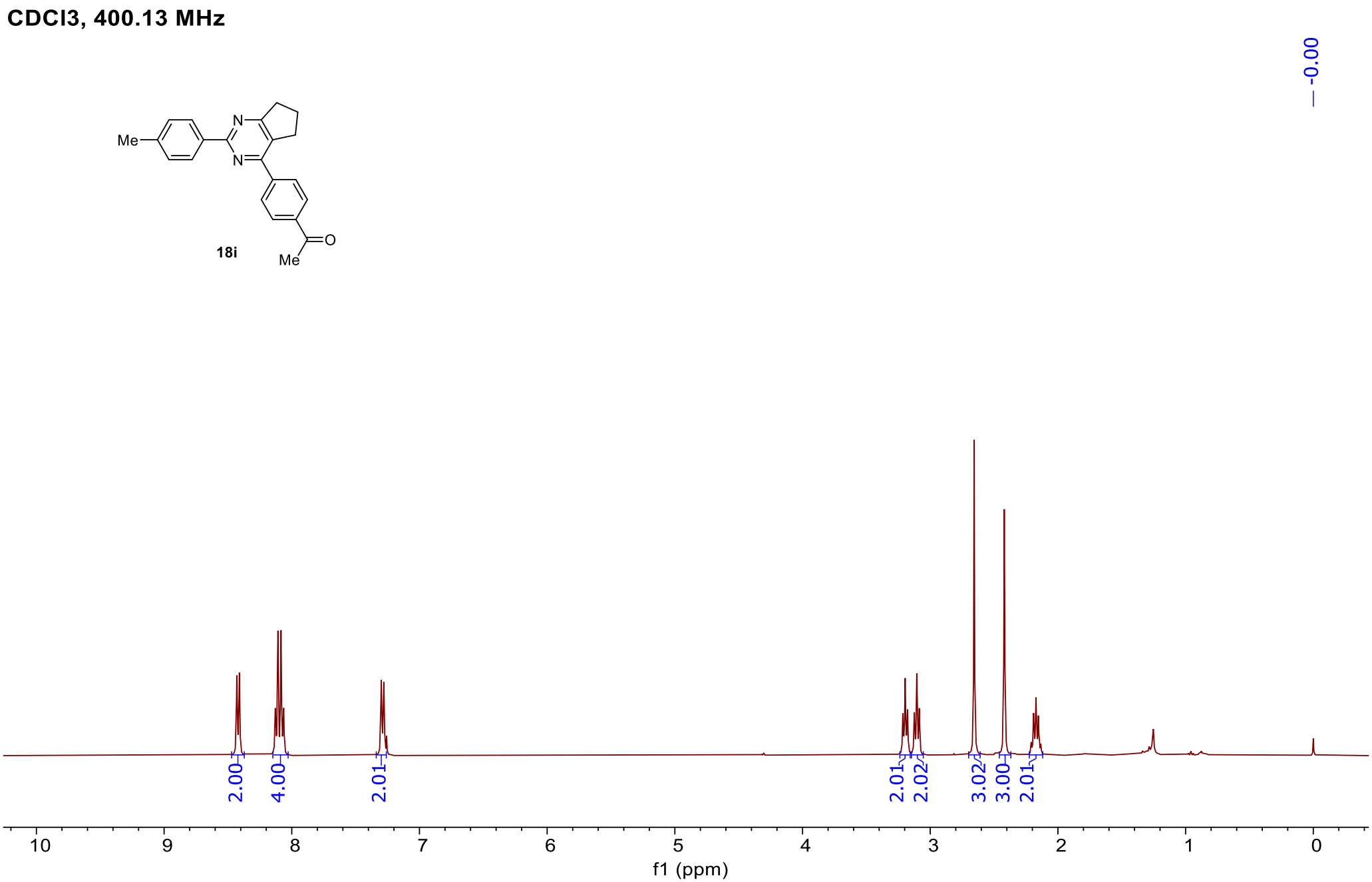


18h

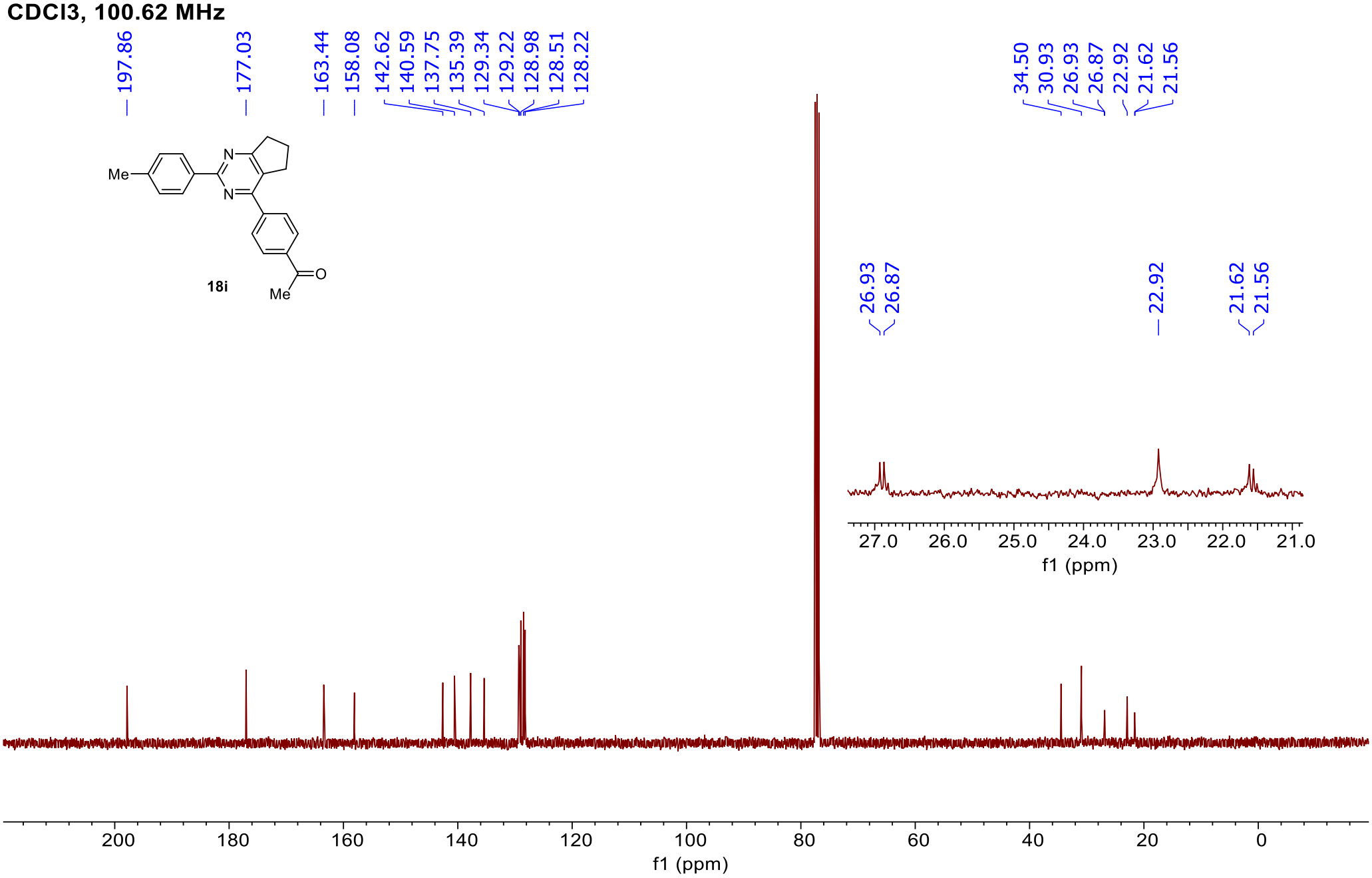
^{1}H NMR Spectrum of **18h**



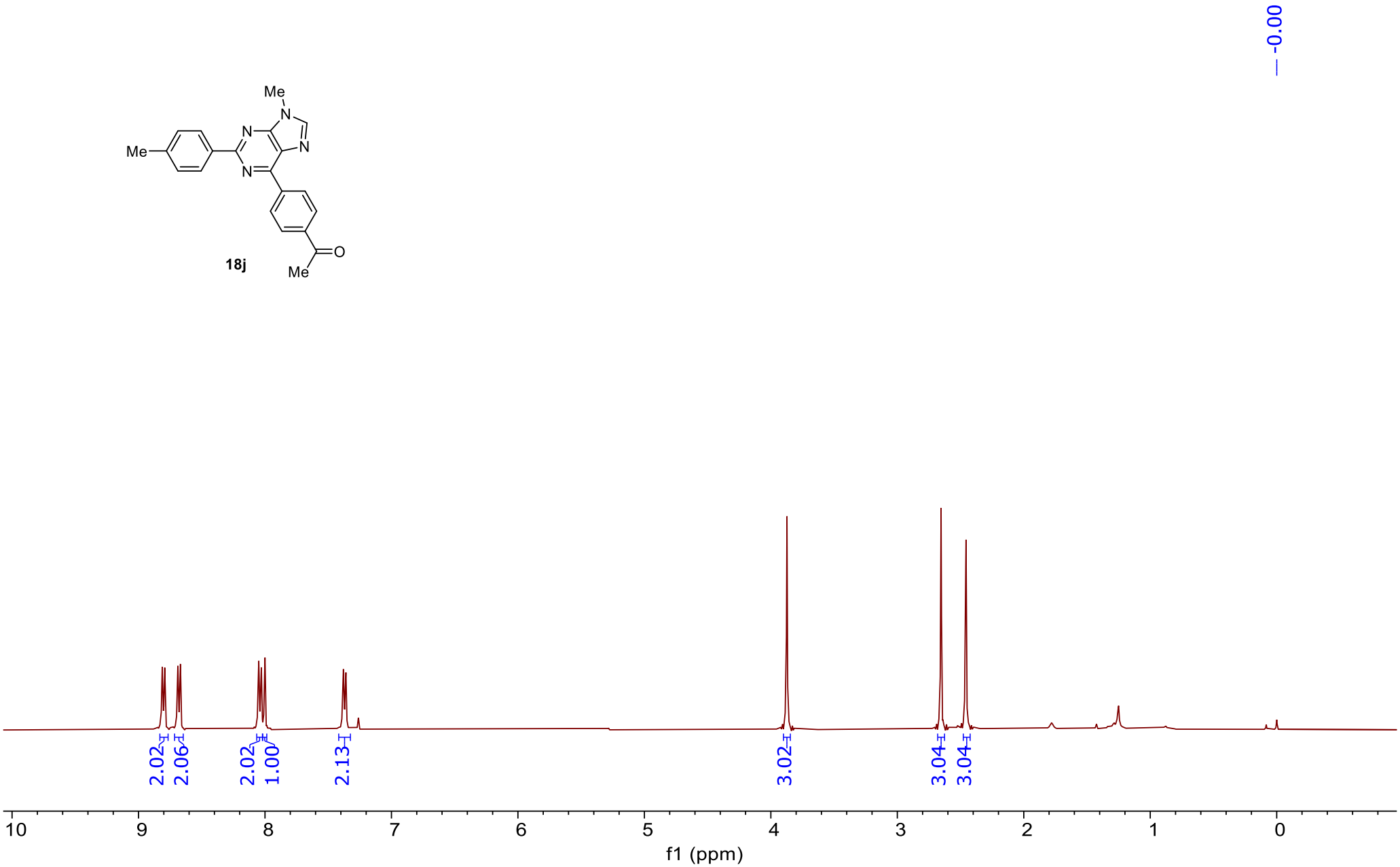
^{13}C NMR Spectrum of **18h**



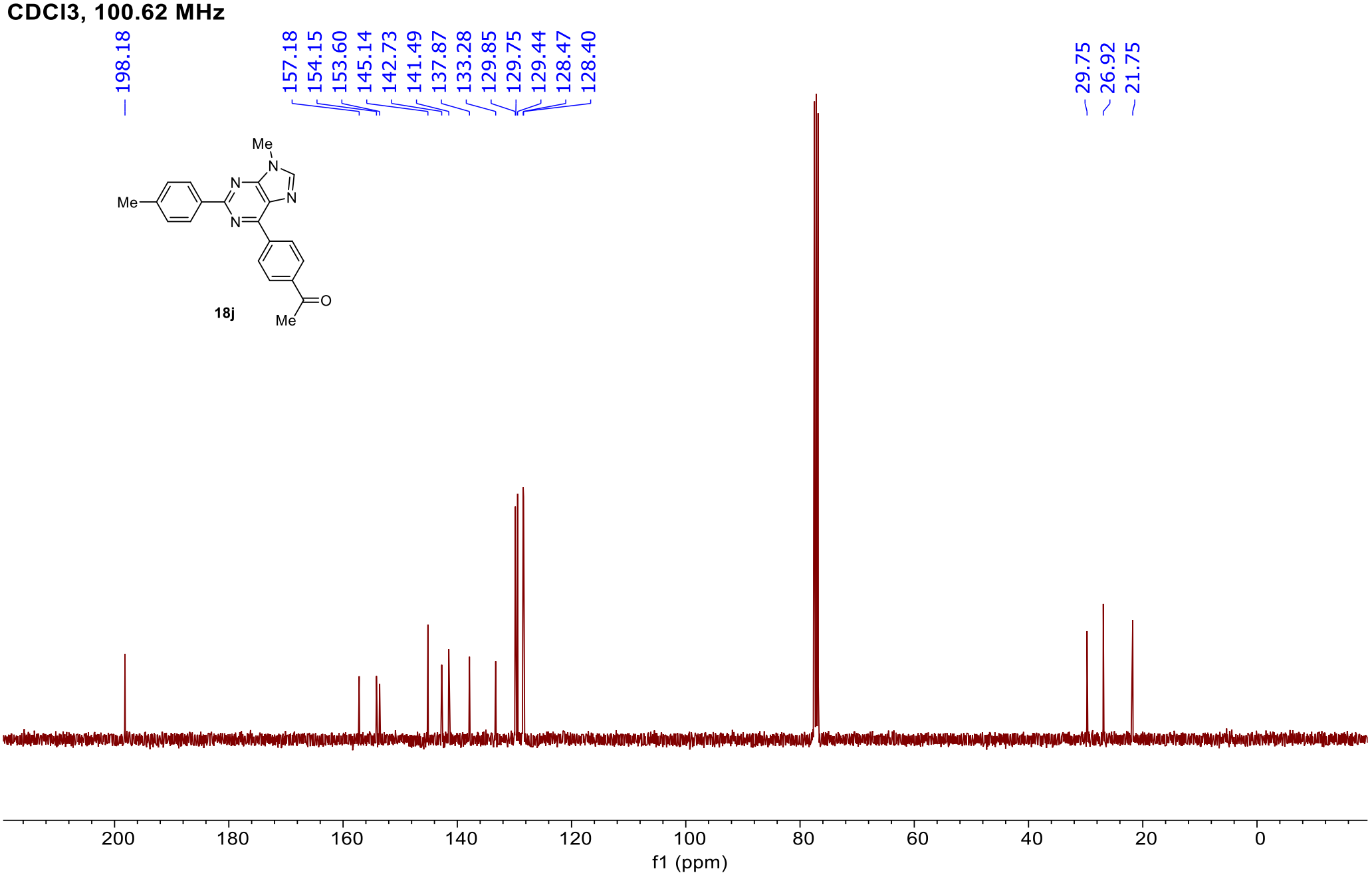
^{1}H NMR Spectrum of **18i**



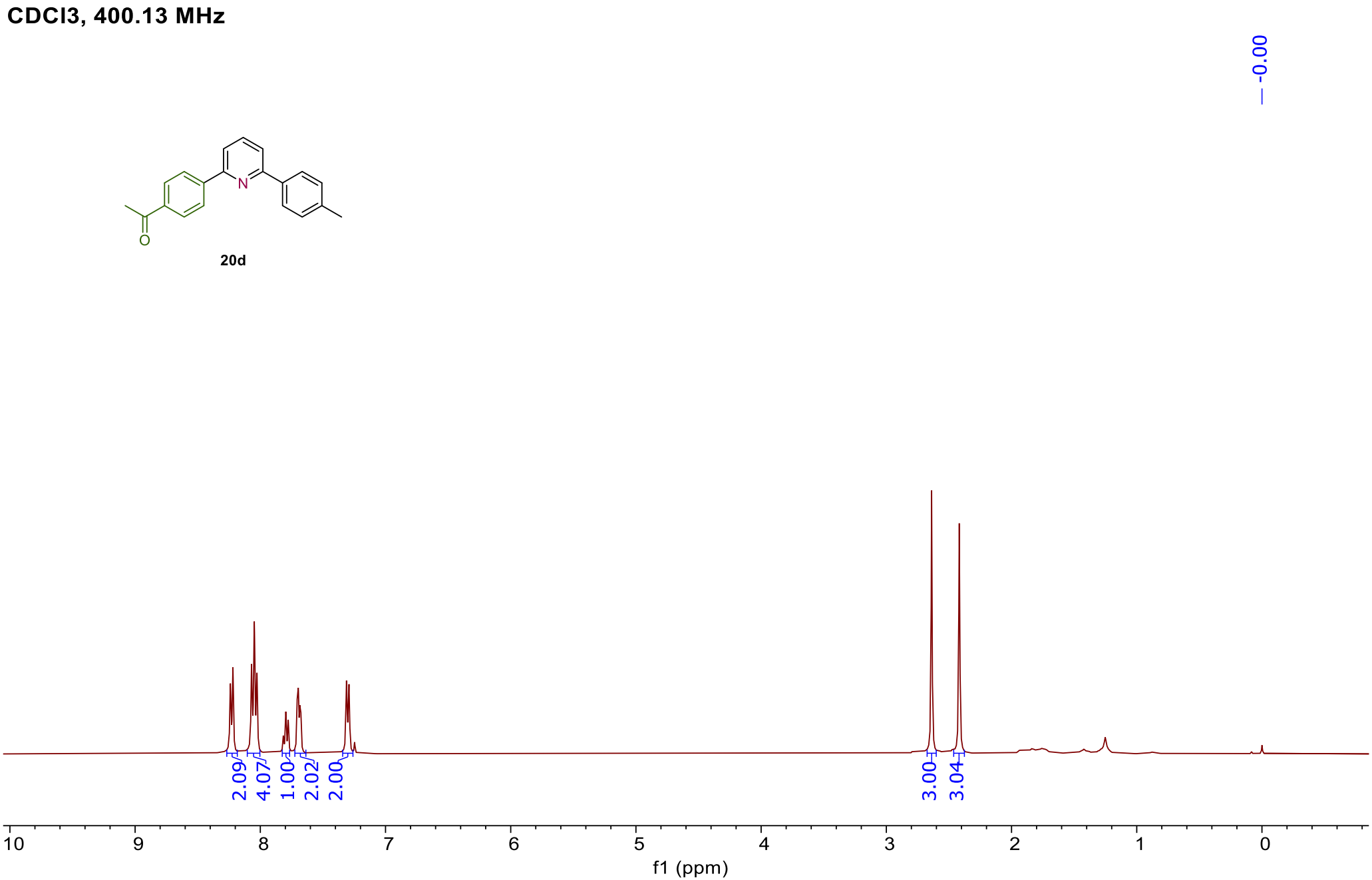
^{13}C NMR Spectrum of **18i**



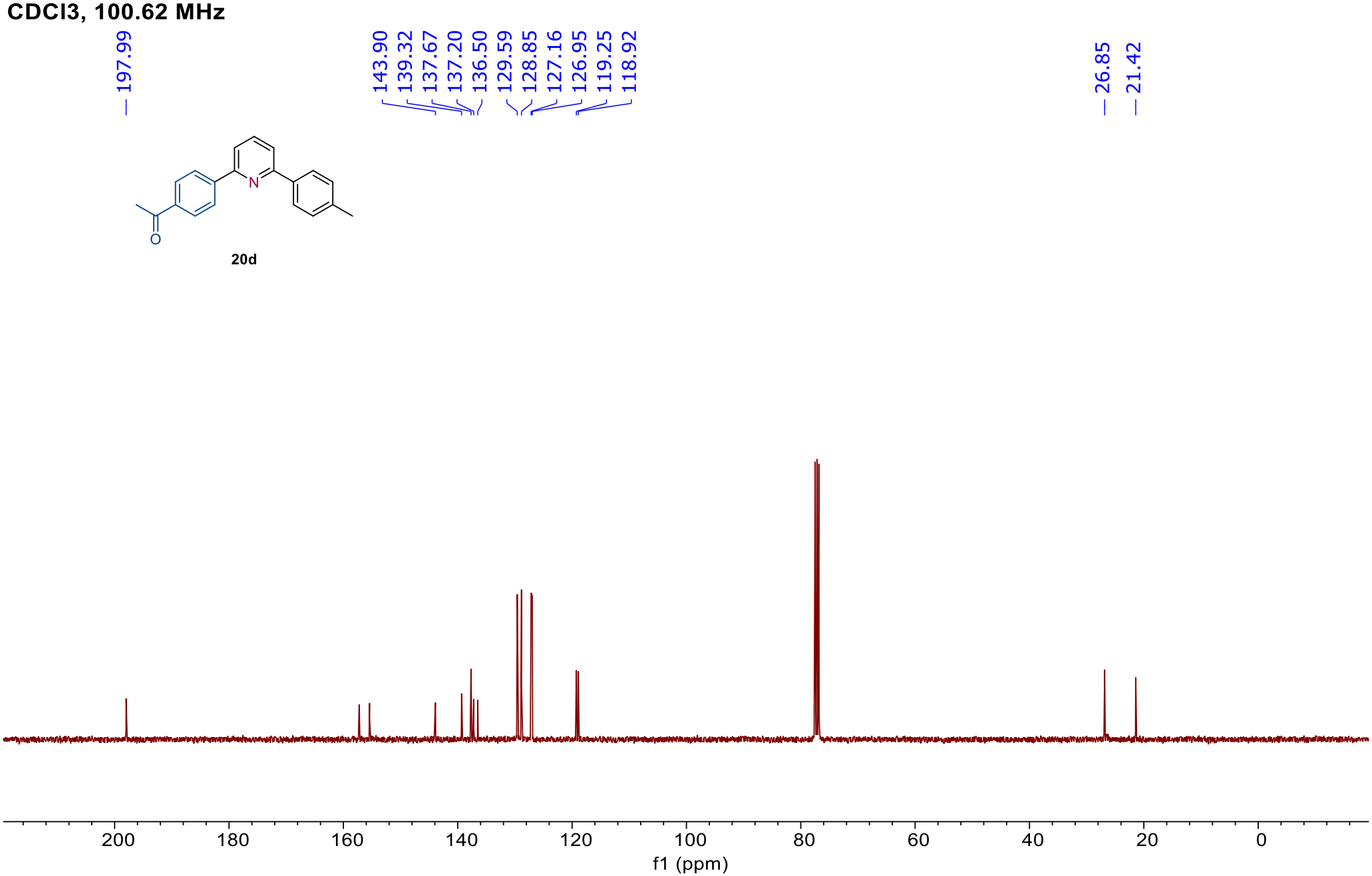
^{1}H NMR Spectrum of **18j**



^{13}C NMR Spectrum of **18j**



^{1}H NMR Spectrum of **20d**



^{13}C NMR Spectrum of **20d**