Supporting Online Material for

A Strategy to Aminate Pyridines, Diazines and Pharmaceuticals via Heterocyclic Phosphonium Salts.

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1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on a Varian 400 MR spectrometer (400 MHz), an Agilent Inova 400 (400 MHz) spectrometer, an Agilent Inova 500 (500 MHz) spectrometer or a Bruker AV-111 400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), $(CD_3)_2SO$ (2.50 ppm), CD_3OD (3.31 ppm) or CD_3CN (1.94 ppm) and coupling constants (*J*) are quoted in Hertz (Hz). Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants, proton assignment). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity was reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextet, sp = septet, m = multiplet, br = broad. Where coincident coupling constants have been observed, the apparent (app) multiplicity of the proton resonance has been reported. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at ambient temperature on Varian 400 MR spectrometer (100 MHz), an Agilent Inova 400 (100 MHz) spectrometer, an Agilent Inova 500 (125 MHz) spectrometer or a Bruker AV-111 400 (100 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.1 ppm relative to the residual solvent peaks in $CDCl_3$ (77.00 ppm), C_6D_6 (128.06 ppm), $(CD_3)_2SO$ (39.51 ppm), CD_3OD (49.00 ppm) or CD_3CN (1.32 ppm). DEPT135, NOE experiments and 2-dimensional experiments (COSY, HMBC and HSQC) were used to support assignments where appropriate.

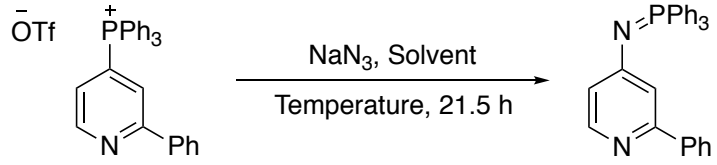
Low-resolution mass spectra (LRMS) were measured on an Agilent 6310 Quadrupole Mass Spectrometer. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer as either solids or neat films, either through direct application or deposited in $CHCl_3$, with absorptions reported in wavenumbers (cm^{-1}).

Analytical thin layer chromatography (TLC) was performed using pre-coated Merck glass-backed silica gel plates (Silicagel 60 F254) or foil-backed basic aluminum oxide plates (Baker-flex 4467). Flash column chromatography was undertaken on Fluka or Material Harvest silica gel (230–400 mesh) or Sigma-Aldrich aluminum oxide (activated, basic) under a positive pressure of air. Preparative thin layer chromatography was performed using pre-coated Silicycle glass-backed silica gel plates (Siliaplate 60Å, 20 cm×20 cm, 2000 μm, TLG–R10011B–353). Visualization was achieved using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate.

Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods.[1] 1,2-Dichloroethane (DCE), 1,4-dioxane, chloroform, chlorobenzene and acetone were purchased anhydrous from Sigma Aldrich chemical company. All reagents were purchased at the highest commercial quality and used without further purification. Reactions were carried out under an atmosphere of nitrogen unless otherwise stated. All reactions were monitored by TLC, ^{1}H NMR spectra taken from reaction samples, gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS) using an Agilent 5977A fitted with an Agilent J&W HP-5ms Ultra Inert Column (30 m, 0.25 mm, 0.25 μm film) for MS analysis and an Agilent J&W VF-5ms column (10 m, 0.15 mm, 0.15 μm film) for FID analysis or liquid chromatography mass spectrometry (LCMS) using an Agilent 6310 Quadrupole Mass Spectrometer. Melting points (mp) were recorded using a Büchi B-450 melting point apparatus and are reported uncorrected.

PPh_3 (99%) was purchased from Oakwood Chemical and is most effective when crushed to a powder before use. Tf_2O (99%) was purchased from Oakwood Chemical and used without further purification and was routinely stored in a –20 ºC fridge. NEt_3 and DBU were distilled before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were used without further purification. ACS reagent grade DMSO (≥99.9%) was purchased from Sigma Aldrich, distilled, and stored under nitrogen atmosphere in a –20 ºC fridge. ReagentPlus grade sodium azide (≥99.5%) was purchased from Sigma Aldrich and used without further purification.

2. Optimization of Reaction Conditions

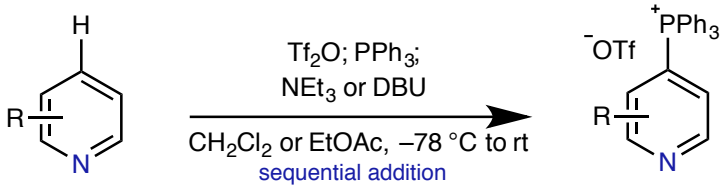


entry	equivalents of NaN_3	Concentration (M)	solvent	Temperature (ºC)	% yield*
1	1.0	1.0	DMSO	100	39
2	1.0	1.0	DMSO	110	51
3	1.0	1.0	DMSO	120	81
4	1.0	1.0	DMSO	130	74
5	1.0	1.0	DMSO	140	79
6	0.8	1.0	DMSO	120	70
8	1.25	1.0	DMSO	120	88
9	1.5	1.0	DMSO	120	84
10	2.0	1.0	DMSO	120	85
11	1.25	0.25	DMSO	120	72
12	1.25	0.5	DMSO	120	79
13	1.25	0.75	DMSO	120	86
15	**1.25**	**1.5**	**DMSO**	**120**	**91**
16	1.25	2.0	DMSO	120	88
17	1.25	3.0	DMSO	120	84
18	1.25	4.0	DMSO	120	80
19	1.25	5.0	DMSO	120	77
21	1.25	1.5	DMF	120	66
22	1.25	1.5	NMP	120	68
23	1.25	1.5	DCE	80	0

*^{1}H NMR yields shown using 1,3,5-trimethoxybenzene as an internal standard

3. Preparation of Heterocyclic Phosphonium Salts

General Procedure A



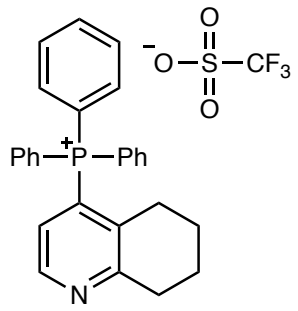
An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) or EtOAc (0.4 M) was added, the reaction vessel cooled to –78 ºC, and Tf_2O (1.0 equiv) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before PPh_3 (1.1 equiv) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and was stirred for a further 30 minutes at –78 ºC. The stated organic base (NEt_3 or DBU, 1.0 equiv) was added dropwise via syringe, the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 minutes). The reaction mixture was quenched with H_2O (approximately the same volume as CH_2Cl_2) and the mixture was transferred to a separatory funnel. The mixture was diluted with CH_2Cl_2 and the resulting organic layer was washed three times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Approximately 2-10 mL (depending on the scale of the reaction) of CH_2Cl_2 was added to reaction mixture and was then added dropwise to an excess of chilled Et_2O (0 ºC). The flask was then placed in a –20 ºC refrigerator for approximately 1 h. The resulting suspension was filtered on a frit, the solid washed with chilled Et_2O (0 ºC), and dried *in vacuo* to provide the pure phosphonium salt.

Notes.

1) PPh_3 was crushed into a powder prior to use.
2) Certain substrates require longer periods for the precipitation step and specific cases are indicated below.
3) In a small number of cases, residual CH_2Cl_2 can become trapped in the phosphonium salt products. In these cases, heating the salts under vacuum (50-100 ºC) removed the solvent.
4) In order to evaluate regioselectivity from the crude reaction mixtures, a duplicate reaction was

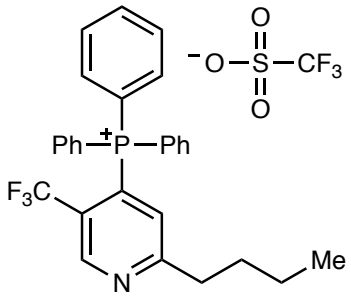
performed and aliquots taken after addition of the organic base and warming to room temperature. These aliquots were concentrated *in vacuo* and analyzed by ^{1}H and ^{31}P NMR.

Triphenyl(5,6,7,8-tetrahydroquinolin-4-yl)phosphonium trifluoromethanesulfonate (1a)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.74 (1H, app t, *J* = 5.1 Hz), 8.07-7.93 (3H, m), 7.92-7.71 (12H, m), 6.94 (1H, dd, *J* = 15.3, 5.1 Hz), 3.12-2.97 (2H, m), 2.21-2.04 (2H, m), 1.84-1.71(2H, m), 1.60-1.44 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.25 (d, *J* = 8.4 Hz), 148.20 (d, *J* = 11.4 Hz), 135.48 (d, *J* = 7.6 Hz), 135.27 (d, *J* = 3.1 Hz), 134.06 (d, *J* = 10.7 Hz), 130.50 (d, *J* = 13.0 Hz), 126.18 (d, *J* = 9.9 Hz), 125.51 (d, *J* = 82.4 Hz), 120.40 (q, *J* = 322.0 Hz), 116.34 (d, *J* = 87.7 Hz), 32.01 (d, *J* = 2.3 Hz), 29.66 (d, *J* = 5.3 Hz), 21.03, 20.54. The spectroscopic data is in agreement with our reported synthesis.[2]

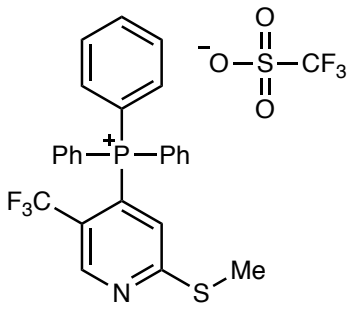
(2-Butyl-5-(trifluoromethyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1b)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$): 9.16 (1H, d, *J* = 6.8 Hz), 7.92–7.87 (3H, m), 7.80–7.76 (6H, m), 7.73–7.67 (6H, m), 7.18 (1H, d, *J* = 17.2 Hz), 2.93 (2H, t, *J* = 7.6 Hz,

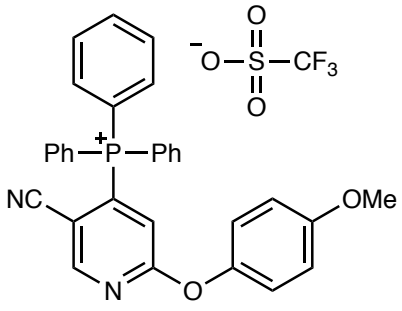
H_6), 1.69–1.62 (2H, m), 1.37–1.27 (2H, m), 0.88 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 169.99 (d, J = 9.7 Hz), 150.06 (m), 135.96 (d, J = 3.1 Hz), 134.41 (d, J = 10.4 Hz), 130.74 (d, J = 13.0 Hz), 129.77 (d, J = 8.5 Hz), 125.90 (d, J = 80.1, 1.0 Hz), 124.42 (qd, J = 33.1, 4.0 Hz), 122.49 (qd, J = 275.1, 2.9 Hz), 120.76 (q, J = 321.2 Hz), 116.40 (d, J = 90.4 Hz), 37.93, 30.35, 22.11, 13.63; ^{19}F NMR (365 MHz, $CDCl_3$): –78.27, –53.55; ^{31}P NMR (162 MHz, $CDCl_3$): 27.4 (d, J = 2.3 Hz). The spectroscopic data is in agreement with our reported synthesis.[2]

(2-(Methylthio)-5-(trifluoromethyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1c)



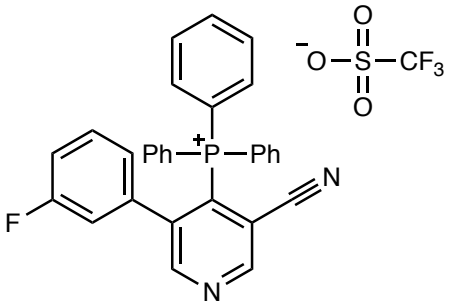
Prepared according to general procedure A using 2-(methylthio)-5-(trifluoromethyl)pyridine (850 mg, 4.40 mmol), Tf_2O (0.74 mL, 4.40 mmol), PPh_3 (1.27 g, 4.84 mmol), DBU (0.66 mL, 4.40 mmol) and CH_2Cl_2 (45 mL). After the purification procedure, the title compound was isolated as a white solid (1.34 g, 2.22 mmol, 51% yield). mp 183-184 ºC; IR ν_{max}/cm^{-1} (film): 3062, 3006, 1570, 1443, 1438, 1271, 1262, 1155, 1140, 1128, 1109, 1029, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, d, J = 6.8 Hz), 7.94-7.85 (3H, m), 7.83-7.74 (6H, m), 7.72-7.62 (6H, m), 7.00 (1H, d, J = 17.1 Hz), 2.56 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.71 (d, J = 10.3 Hz), 150.40-150.08 (m), 136.09 (d, J = 3.1 Hz), 134.45 (d, J = 10.6 Hz), 130.83 (d, J = 13.4 Hz), 128.61 (d, J = 9.5 Hz), 125.29 (d, J = 79.0 Hz), 122.74 (qd, J = 274.4, 2.1 Hz), 121.14 (qd, J = 33.7, 4.0 Hz), 120.85 (q, J = 321.2 Hz), 116.28 (d, J = 89.9 Hz), 13.64; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –53.37, –78.18; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 27.57; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 454.2, $C_{25}H_{20}F_3NPS^+$ requires 454.1.

(5-Cyano-2-(4-methoxyphenoxy)pyridin-4-yl)triphenylphosphonium (1d)



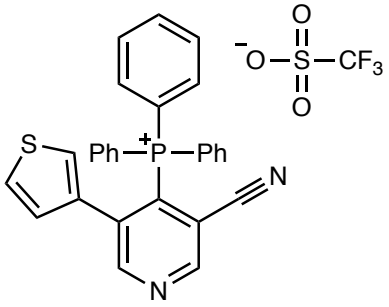
Prepared according to general procedure A using 6-(4-methoxyphenoxy)nicotinonitrile (1.23 g, 5.44 mmol), Tf_2O (0.91 mL, 5.44 mmol), PPh_3 (1.57 g, 5.98 mmol), DBU (0.81 mL, 5.44 mmol) and CH_2Cl_2 (60 mL). After the purification procedure, the title compound was isolated as a yellow solid (1.28 g, 2.01 mmol, 45% yield). mp 112-114 ºC; IR ν_{max}/cm^{-1} (film): 3061, 2989, 2226, 1575, 1502, 1467, 1438, 1357, 1261, 1236, 1223, 1147, 1106, 1029; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.63 (1H, d, *J* = 6.0 Hz), 7.96-7.71 (15H, m), 7.15 (2H, d, *J* = 8.9 Hz), 6.98 (1H, d, *J* = 16.0 Hz), 6.87 (2H, d, *J* = 8.9 Hz), 3.76 (3H, s); ^{13}C NMR (100 MHz, CDCl3) δ: 166.57 (d, *J* = 14.6 Hz), 157.51, 155.51 (d, *J* = 7.5 Hz), 145.30, 136.30 (d, *J* = 3.1 Hz), 134.75 (d, *J* = 10.8 Hz), 133.60 (d, *J* = 83.8 Hz), 131.00 (d, *J* = 13.4 Hz), 122.41, 120.76 (q, *J* = 321.3 Hz), 120.74 (d, *J* = 9.5 Hz), 114.77, 114.46 (d, *J* = 90.0 Hz), 114.06 (d, *J* = 4.5 Hz), 104.60 (d, *J* = 4.2 Hz), 55.49; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.10; ^{31}P NMR (162 MHz, $CDCl_3$) δ:22.91; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 487.3, $C_{31}H_{24}N_2O_2P^+$ requires 487.2.

(3-Cyano-5-(3-fluorophenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1e)



Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (1H, dd, *J* = 4.9, 1.2 Hz), 8.83 (1H, dd, *J* = 5.5, 1.1 Hz), 7.92-7.44 (15H, m), 7.02-6.92 (1H, m), 6.84-6.73 (2H, m), 6.70 (1H, d, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.59 (d, *J* = 247.8 Hz), 152.82, 147.29, 140.07, 137.63 (d, *J* = 7.9 Hz), 135.63, 130.31 (d, *J* = 8.4 Hz), 128.95, 128.72, 127.93, 125.41 (d, *J* = 3.1 Hz), 116.68 (d, *J*, 22.5 Hz), 115.98 (d, *J* = 21.0 Hz), 115.08. The spectroscopic data is in agreement with our reported synthesis.[3]

(3-Cyano-5-(thiophen-3-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1f)



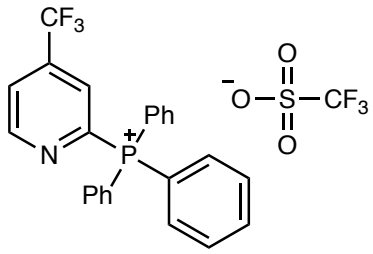
Major

11.4:1 Mixture of Regioisomers

Prepared according to general procedure A using 5-(thiophen-3-yl)nicotinonitrile (1.86 g, 10.00 mmol), Tf_2O (1.68 mL, 10.00 mmol), PPh_3 (2.88 g, 11.00 mmol), DBU (1.49 mL, 10.00 mmol) and CH_2Cl_2 (100 mL). After the purification procedure, the title compound (11.4:1 mixture of regioisomers as determined

by ^{1}H NMR)* was isolated as a white solid (3.73 g, 6.25 mmol, 63% yield). Mixture of isomers, IR ν_{max}/cm^{-1} (film): 3066, 2227, 1586, 1441, 1261, 1223, 1149, 1102, 1079, 1030, 996, 720; Major isomer, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.45 (1H, d, *J* = 5.0 Hz), 9.07 (1H, d, *J* = 5.5 Hz), 7.98-7.84 (9H, m), 7.77-7.67 (6H, m), 7.21-7.16 (1H, m), 7.13 (1H, br s), 6.57 (1H, d, *J* = 4.9 Hz); Major isomer, ^{13}C NMR† (100 MHz, DMSO-d_6) δ: 157.02 (d, *J* = 6.9 Hz), 154.74 (d, *J* = 5.8 Hz), 140.22 (d, *J* = 5.5 Hz), 135.30 (d, *J* = 3.0 Hz), 134.48 (d, *J* = 10.8 Hz), 130.35 (d, *J* = 13.3 Hz), 128.47, 128.33 (d, *J* = 84.5 Hz), 128.27, 127.78, 120.69 (q, *J* = 322.4 Hz), 117.00 (d, *J* = 88.5 Hz), 113.91 (d, *J* = 6.0 Hz), 113.21 (d, *J* = 4.4 Hz); Both isomers, ^{19}F NMR (365 MHz, DMSO-d_6) δ: –77.67; Major isomer, ^{31}P NMR (162 MHz, DMSO-d_6) δ: 20.26; Minor isomer, ^{31}P NMR (162 MHz, DMSO-d_6) δ: 19.73; *m*/*z* LRMS (ESI + APCI) found $[M - OTf]^+$ 447.3, $C_{28}H_{20}N_2PS^+$ requires 447.1.

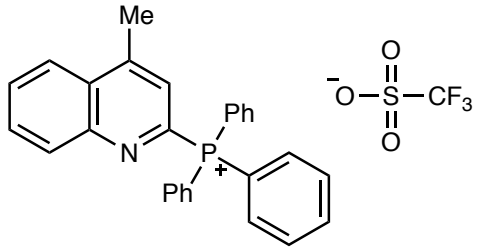
Triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (1g)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, CDCl3) δ: 9.33 (1H, d, *J* = 2.8 Hz), 8.02 (1H, m), 7.92 (3H, m), 7.82–7.69 (13H, m); ^{13}C NMR (100 MHz, CDCl3) δ: 154.20 (d, *J* = 19.9 Hz), 147.00 (d, *J* = 121.0 Hz), 139.92 (qd, *J* = 35.8 Hz, 11.3 Hz), 136.02 (d, *J* = 2.9 Hz), 134.55 (d, *J* = 10.2 Hz), 130.70 (d, *J* = 13.1 Hz), 126.05 (dq, *J* = 25.9, 3.6 Hz), 124.36 (m), 121.47 (qd, *J* = 274.1, 3.0 Hz), 120.70 (q, *J* = 320.5 Hz), 115.93 (d, *J* = 90.0 Hz). The spectroscopic data is in agreement with our reported synthesis.[2]

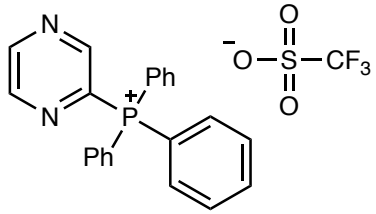
* In a separate reaction, the reaction mixture was concentrated *in vacuo* and the crude regiomeric ratio was 7.4:1.4:1 determined by analysis of the crude ^{1}H NMR spectrum.
† 1 ^{13}C resonance cannot be clearly identified from the mixture.

(4-Methylquinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate (1h)



Prepared according to general procedure A (except that the reaction was warmed to -50 °C before the addition of PPh_3 and was stirred at -50 °C for 30 minutes) using 4-methylquinoline (793 μL, 6.00 mmol), Tf_2O (1.01 mL, 6.00 mmol), PPh_3 (1.73 g, 6.60 mmol), DBU (0.90 mL, 6.00 mmol) and CH_2Cl_2 (60 mL). After the purification procedure, the title compound was isolated as a white solid (2.18 g, 3.94 mmol, 66% yield). mp 171-174 ºC; IR ν_{max}/cm^{-1} (film): 3067, 2989, 1576, 1439, 1259, 1223, 1144, 1109, 1028, 997, 765, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.12 (2H, m), 7.94-7.65 (17H, m), 7.53, (1H, d, J = 4.6 Hz), 2.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.52 (d, J = 10.6 Hz), 148.50 (d, J = 22.6 Hz), 144.376 (d, J = 117.2 Hz), 135.63 (d, J = 3.1 Hz), 134.60 (d, J = 10.1 Hz), 131.63, 130.63 (d, J = 1.2 Hz), 130.49 (d, J = 12.9 Hz), 130.39, 128.77, 125.14 (d, J = 26.4 Hz), 124.43 (d, J = 1.3 Hz), 120.83 (q, J = 321.2 Hz), 117.30 (d, J = 88.2 Hz), 19.18 (d, J = 1.5 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.07; ^{31}P NMR (162 MHz, $CDCl_3$) δ:14.41; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 404.3, $C_{28}H_{23}NP^+$ requires 404.2.

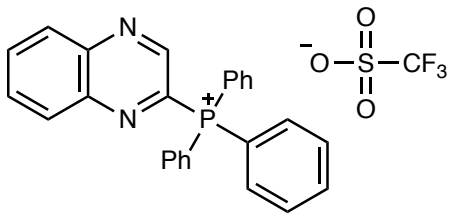
Triphenyl(pyrazin-2-yl)phosphonium trifluoromethanesulfonate (1i)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, CDCl3) δ: 9.09 (1H, br s), 9.06 (1H, br s), 8.86 (1H, br s), 7.91 (3H, m), 7.82– 7.71 (12H, m); ^{13}C NMR (100 MHz, CDCl3) δ: 149.72 (d, J =

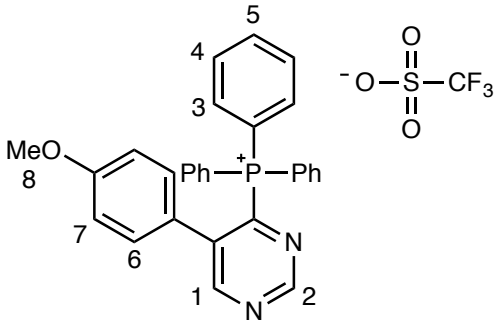
24.0 Hz), 149.51 (d, J = 3.4 Hz), 147.25 (d, J = 14.7 Hz), 141.37 (d, J = 115.4 Hz), 136.02 (d, J = 3.1 Hz), 134.54 (d, J = 10.4 Hz), 130.71 (d, J = 13.1 Hz), 120.69 (q, J = 321.1 Hz), 115.71 (d, J = 89.3 Hz). The spectroscopic data is in agreement with our reported synthesis.[2]

Triphenyl(quinoxalin-2-yl)phosphonium (1j)

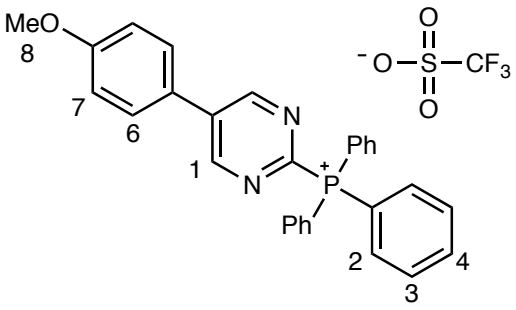


Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, s), 8.27-8.22 (2H, m), 8.09-8.01 (2H, m), 7.93-7.90 (3H, m), 7.79-7.72 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.86 (d, J = 25.4 Hz), 143.38 (d, J = 2.8 Hz), 142.70 (d, J = 17.3 Hz), 140.83 (d, J = 111.6 Hz), 136.16 (d, J = 3.1 Hz), 134.98, 134.66 (d, J = 10.5 Hz), 133.08, 130.86 (d, J = 13.0 Hz), 130.19 (d, J = 2.0 Hz), 129.85 (d, J = 2.3 Hz), 120.76 (q, J = 319.5 Hz), 116.03 (d, J = 88.1 Hz). The spectroscopic data is in agreement with our reported synthesis.[3]

(5-(4-Methoxyphenyl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1k)



Major



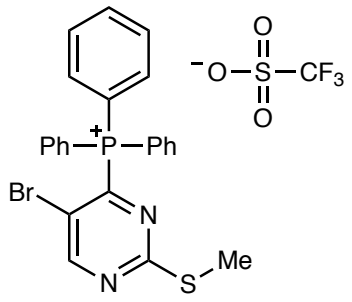
Minor

24:1 Mixture of Regioisomers

Prepared according to our previous report.[2] Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.44 (1H, s, H_2), 8.98 (1H, d, J = 9.0 Hz, H_1), 7.80-7.70 (3H, m, H_5), 7.67-7.56 (12H, m, H_3 and H_4), 6.91 (2H, d, J

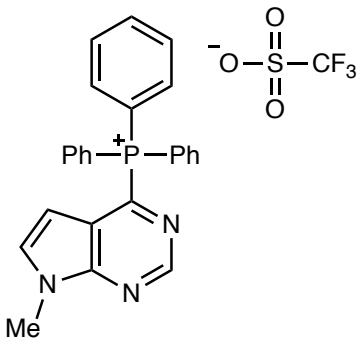
= 8.7 Hz, H_6), 6.55 (2H, d, *J* = 8.7 Hz, H_7), 3.72 (3H, s, H_8); Minor isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.23 (2H, s, H_1), 7.80-7.70 (3H, m, H_4), 7.70 (2H, d, *J* = 8.7 Hz, H_5), 7.67-7.56 (12H, m, H_2 and H_3), 7.09 (2H, d, *J* = 8.6 Hz, H_6), 3.88 (3H, s, H_7); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.84 (d, *J* = 5.3 Hz), 160.53, 156.97 (d, *J* = 16.8 Hz), 149.74 (d, *J* = 114.5 Hz), 142.72 (d, *J* = 19.2 Hz), 135.22 (d, *J* = 3.1 Hz), 134.67 (d, *J* = 10.2 Hz), 130.60, 130.25 (d, *J* = 13.1 Hz), 123.61, 120.82 (q, *J* = 321.3 Hz), 117.10 (d, *J* = 88.6 Hz), 114.37, 55.42; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.01; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ; 17.84; *m/z* LRMS (ESI + APCI) found $[M–OTf]^+$ 447.2, $C_{29}H_{24}N_2OP^+$ requires 447.2. The spectroscopic data is in agreement with our reported synthesis.[2]

(5-Bromo-2-(methylthio)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1l)



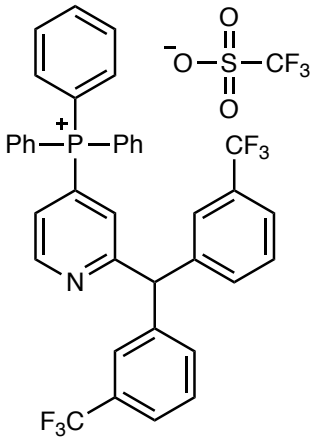
Prepared according to general procedure A using 5-bromo-2-(methylthio)pyrimidine (820 mg, 4.00 mmol), Tf_2O (0.67 mL, 4.00 mmol), PPh_3 (1.15 g, 4.40 mmol), DBU (0.60 mL, 4.00 mmol) and EtOAc (10 mL). After the purification procedure, the title compound was isolated as a white solid (1.51 g, 2.45 mmol, 61% yield). mp 168-169 ºC; IR ν_{max}/cm^{-1} (film): 3058, 2989, 1530, 1442, 1379, 1261, 1220, 1201, 1184, 1162, 1107, 1027, 724; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (1H, d, *J* = 7.9 Hz), 7.97-7.85 (3H, m), 7.83-7.66 (12H, m), 2.15 (3H, s); ^{13}C NMR (100 MHz, CDCl3) δ: 173.86 (d, *J* = 17.2 Hz), 161.98 (d, *J* = 4.1 Hz), 151.47 (d, *J* = 118.7 Hz), 136.06 (d, *J* = 3.1 Hz), 134.75 (d, *J* = 10.4 Hz), 130.74 (d, *J* = 13.3 Hz), 120.86 (q, *J* = 321.2 Hz), 120.85 (d, *J* = 17.1 Hz), 115.00 (d, *J* = 89.9 Hz), 14.43; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.08; ^{31}P NMR (162 MHz, $CDCl_3$) δ:24.37; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 465.2, $C_{23}H_{19}BrN_2PS^+$ requires 465.0.

(7-Methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1m)



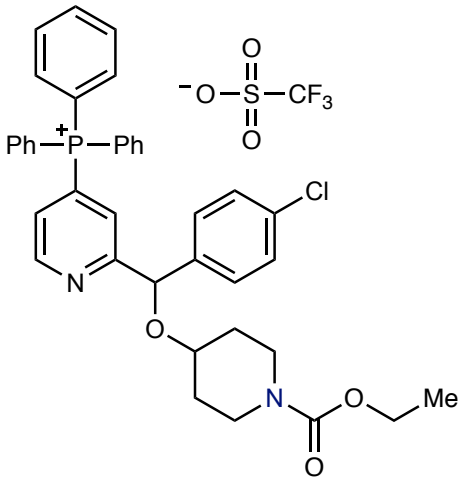
Prepared according to general procedure A using 7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (592 mg, 4.45 mmol), Tf_2O (0.75 mL, 4.45 mmol), PPh_3 (1.28 g, 4.89 mmol), DBU (0.67 mL, 4.45 mmol) and CH_2Cl_2 (45 mL). After the purification procedure, the title compound was isolated as a purple crystalline solid (0.57 g, 1.05 mmol, 24% yield); mp 184-189 ºC; IR ν_{max}/cm^{-1} (film): 3061, 2972, 1539, 1514, 1436, 1407, 1335, 1263, 1240, 1225, 1139, 1108, 1099, 1030, 728; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.12 (1H, s), 7.99-7.86 (3H, m), 7.81-7.66 (12H, m), 7.63 (1H, d, J = 3.6 Hz), 5.31(1H, d, J = 3.6 Hz), 3.98 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.64 (d, J = 9.9 Hz), 150.62 (d, J = 18.5 Hz), 142.07 (d, J = 118.7 Hz), 136.55, 136.04 (d, J = 3.1 Hz), 134.83 (d, J = 10.3 Hz), 130.63 (d, J = 13.0 Hz), 123.49 (d, J = 24.4 Hz), 120.88 (q, J = 321.0 Hz), 116.67 (d, J = 88.7), 98.28, 31.65; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; ^{31}P NMR (162 MHz, $CDCl_3$) δ:13.29; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 394.3, $C_{25}H_{21}N_3P^+$ requires 394.2.

(2-(Bis(3-(trifluoromethyl)phenyl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1n)



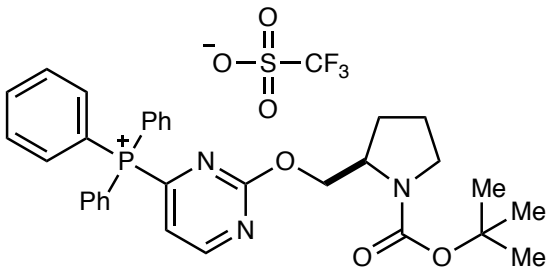
Prepared according to general procedure A (except the reaction was warmed to –30 ºC before the addition of triphenylphosphine and the reaction was then stirred at –30 ºC for 30 minutes instead –78 ºC) using 2-(bis(3-(trifluoromethyl)phenyl)methyl)pyridine (762 mg, 2.00 mmol), Tf_2O (336 μL, 2.00 mmol), PPh_3 (576 mg, 2.10 mmol), DBU (299 μL, 2.0 mmol) and CH_2Cl_2 (20 mL). After the purification procedure, the title compound was isolated as a pale orange solid (1.37 g, 1.73 mmol, 87% yield). mp 64-69 ºC; IR ν_{max}/cm^{-1} (film): 3065, 1577, 1439, 1327, 1259, 1224, 1153, 1109, 1075, 1029, 725, 636; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, app t, *J* = 5.1 Hz), 7.91-7.80 (3H, m), 7.78-7.66 (6H, m), 7.63-7.37 (15H, m), 7.29 (1H, d, *J* = 13.8 Hz), 5.97 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.02 (d, *J* = 9.8), 151.56 (d, *J* = 10.4 Hz), 141.69, 136.10 (d, *J* = 3.1 Hz), 134.31 (d, *J* = 10.5 Hz), 132.90 (d, *J* = 1.1 Hz), 130.89 (d, *J* = 13.1 Hz), 130.73 (q, *J* = 32.2 Hz), 129.99, 129.57 (d, *J* = 83.7 Hz), 126.99 (d, *J* = 8.7 Hz), 125.65-125.39 (2C, m), 124.04 (q, *J* = 3.8 Hz), 123.83 (q, *J* = 272.5 Hz), 120.78 (q, *J* = 321.2 Hz), 115.44 (d, *J* = 89.5 Hz), 57.75; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.46, –78.13; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.38; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 642.4, $C_{38}H_{27}F_6NP^+$ requires 642.2.

(2-((4-Chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl) triphenylphosphonium trifluoromethanesulfonate (1o)



Prepared according to general procedure A (except that the reaction was warmed to –50 °C before the addition of PPh_3 and was stirred at –50 °C for 30 minutes) using ethyl 4-((4-chlorophenyl)(pyridin-2-yl)methoxy)piperidine-1-carboxylate (750 mg, 2.00 mmol), Tf_2O (0.34 mL, 2.00 mmol), PPh_3 (0.58 g, 2.20 mmol), DBU (0.30 mL, 2.00 mmol) and CH_2Cl_2 (20 mL). After the purification procedure, the title compound was isolated as a white solid (1.15 g, 1.47 mmol, 73% yield). mp 95-98 ºC; IR ν_{max}/cm^{-1} (film): 3063, 2928, 1686, 1438, 1382, 1261, 1223, 1146, 1108, 1084, 1029, 636; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (1H, t, *J* = 5.1 Hz), 7.94-7.86 (3H, m), 7.82-7.73 (6H, m), 7.71-7.59 (7H, m), 7.49 (1H, ddd, *J* = 12.6, 5.0, 1.1 Hz), 7.34-7.25 (4H, m), 5.71 (1H, s), 4.11 (2H, q, *J* = 7.1 Hz), 3.70-3.60 (1H, m), 3.55-3.42 (2H, m), 3.25-3.12 (2H, m), 1.79-1.56 (2H, m), 1.54-1.37 (2H, m), 1.25 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.37 (d, *J* = 9.6 Hz), 155.43, 151.10 (d, *J* =10.5 Hz), 138.68, 136.16 (d, *J* = 3.1 Hz), 134.53 (d, *J* = 10.5 Hz), 134.01, 130.95 (d, *J* = 13.1 Hz), 129.28 (d, *J* = 84.1 Hz), 128.81, 128.47, 125.92 (d, *J* = 8.4 Hz), 123.86 (d, *J* = 9.1 Hz), 120.83 (q, *J* = 321.2 Hz), 115.80 (d, *J* = 89.4 Hz), 79.94, 72.82, 61.29, 40.69 (rot), 40.66, 31.29, 30.35 (rot), 14.68; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; ^{31}P NMR (162 MHz, $CDCl_3$) δ:22.67; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 635.3, $C_{38}H_{37}ClN_2O_3P^+$ requires 635.2.

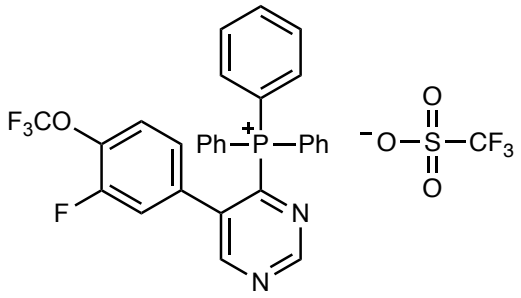
(*R*)-(2-((1-(*Tert*-butoxycarbonyl)pyrrolidin-2-yl)methoxy)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1p)



An oven dried round bottom flask equipped with a stir bar was charged with *tert*-butyl (*R*)-2-((pyrimidin-2-yloxy)methyl)pyrrolidine-1-carboxylate (249 mg, 0.89 mmol) and PPh_3 (257 mg, 0.98 mmol). The round bottom flask was placed under a nitrogen atmosphere, EtOAc (4.5 mL) was added, and the reaction vessel was cooled to –50 ºC before Tf_2O (150 μL, 0.89 mmol) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before DBU (133 μL, 0.89 mmol) was added dropwise via syringe, the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 minutes). The reaction mixture was quenched with H_2O (approximately the same volume as CH_2Cl_2) and the mixture was transferred to a separatory funnel. The mixture was diluted with CH_2Cl_2 and the resulting organic layer was washed three times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Approximately 2 mL of CH_2Cl_2 was added to reaction mixture and was then added dropwise to an excess of chilled Et_2O (0 ºC). The flask was then placed in a –20 ºC refrigerator for approximately 4.5 h. The resulting suspension was filtered on a frit, the solid washed with chilled Et_2O (0 ºC), and dried *in vacuo* to provide the pure phosphonium salt. After the purification procedure, the title compound was isolated as a white solid (471 mg, 0.68 mmol, 77% yield). mp 51-54 ºC; IR ν_{max}/cm^{-1} (film): 3064, 2976, 1684, 1560, 1544, 1424, 1393, 1367, 1260, 1149, 1029, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91, (1H, dd, *J* = 8.2, 4.8 Hz), 7.90-7.80 (3H, m), 7.77-7.59 (12H, m), 7.49 (1H, br s), 4.45-4.30 (1H, m), 4.29-4.15 (1H, m), 4.14-4.03 (1H, m), 3.29 (2H, s), 2.05-1.69 (4H, m), 1.43-1.24 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.06 (d, *J* = 19.3 Hz), 163.16 (d, *J* = 8.6 Hz), 156.69-154.78 (m), 154.63-153.87 (m), 135.97 (d, *J* = 2.9 Hz), 134.58 (d, *J* = 10.3 Hz), 130.56 (d, *J* = 13.1 Hz), 121.43 (d, *J* = 19.9 Hz), 120.60 (q, *J* = 321.2 Hz), 115.05 (d, *J* = 88.9 Hz), 79.63-78.90 (m), 68.93 (rot), 68.55, 55.20, 46.64, 46.23 (rot), 28.72-27.47 (2C, m), 23.47-22.71 (rot); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.17; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.10; *m/z* LRMS

(ESI + APCI) found $[M - OTf]^+$ 540.4, $C_{32}H_{35}N_3O_3P^+$ requires 540.2.

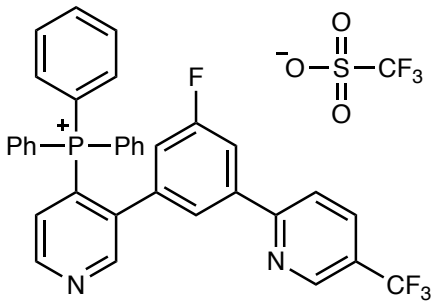
(5-(3-Fluoro-4-(trifluoromethoxy)phenyl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1q)



An oven dried round bottom flask equipped with a stir bar was charged with 5-(3-fluoro-4-(trifluoromethoxy)phenyl)pyrimidine (307 mg, 1.19 mmol) and PPh_3 (344 mg, 1.31 mmol). The round bottom flask was placed under a nitrogen atmosphere, EtOAc (6 mL) was added, and the reaction vessel was cooled to –50 ºC before Tf_2O (200 μL, 1.19 mmol) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before DBU (178 μL, 1.19 mmol) was added dropwise via syringe, the cooling bath was removed and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 minutes). The reaction mixture was quenched with H_2O (approximately the same volume as CH_2Cl_2) and the mixture was transferred to a separatory funnel. The mixture was diluted with CH_2Cl_2 and the resulting organic layer was washed six times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Approximately 2 mL of CH_2Cl_2 was added to the crude mixture which was then added dropwise to an excess of 1:1 Et_2O:hexanes to give a fine suspension. The flask was then placed in a –20 ºC refrigerator until a viscous oil settled at the bottom of the flask. The excess solvent was poured off and additional 1:1 Et_2O:hexanes was added, the mixture was stirred and decanted. This process was repeated twice more, and the resulting viscous oil was concentrated *in vacuo* to give the pure phosphonium salt as a tan solid (538 g, 0.81 mmol, 68% yield). mp 61-65 ºC; IR ν_{max}/cm^{-1} (film): 3065, 1624, 1439, 1400, 1257, 1217, 1147, 721, 636; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.50 (1H, s), 8.90 (1H, d, *J* = 8.8 Hz), 7.82-7.51 (16H, m), 6.98, (1H, d, *J* = 8.6 Hz), 6.35 (1H, d, *J* = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.00 (d, *J* = 5.3 Hz), 158.21 (d, *J* = 248.49 Hz), 157.73 (d, *J* = 16.6 Hz), 151.69 (d, *J* = 116.9 Hz), 150.75 (dd, *J* = 10.8, 1.6 Hz), 135.26 (d, *J* = 3.0 Hz), 135.04, 134.85 (d, *J* = 10.3 Hz), 132.95 (d, *J* = 2.4 Hz), 129.93 (d, *J* = 13.2 Hz), 120.54 (q, *J* = 321.1 Hz),

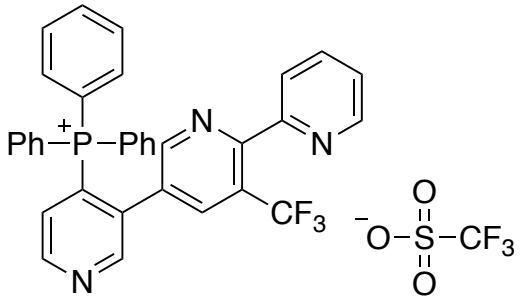
119.84 (q, J = 259.5 Hz), 118.78 (d, J = 15.1 Hz), 117.36. 116.46 (d, J = 88.8), 107.87 (d, J = 25.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.70, –78.30, –107.25 (t, J = 10.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.12; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 519.3, $C_{29}H_{20}F_4N_2OP^+$ requires 519.1.

(3-(3-Fluoro-5-(5-(trifluoromethyl)pyridin-2-yl)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1r)



Prepared according to general procedure A using 2-(3-fluoro-5-(pyridin-3-yl)phenyl)-5-(trifluoromethyl)pyridine (1.27 g, 4.00 mmol), Tf_2O (0.67 mL, 4.00 mmol), PPh_3 (1.15 g, 4.40 mmol), DBU (0.60 mL, 4.00 mmol) and CH_2Cl_2 (40 mL). After the purification procedure, the title compound was isolated as a white solid (1.92 g, 2.64 mmol, 66% yield). mp 209-211 ºC; IR ν_{max}/cm^{-1} (film): 3067, 1595, 1445, 1439, 1328, 1262, 1138, 1124, 1110, 1101, 1082, 1030, 719, 636; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (1H, app t, J = 4.8 Hz), 8.78 (1H, d, J = 6.8 Hz), 8.72 (1H, br s), 7.98 (1H, dd, J = 8.3, 1.8 Hz), 7.77-7.56 (17H, m), 7.51-7.42 (2H, m), 6.53 (1H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.25 (d, J = 249.6 Hz), 156.95, 153.34, 150.62 (d, J = 10.3 Hz), 146.22 (q, J = 4.1 Hz), 139.97 (d, J = 8.1 Hz), 139.84 (dd, J = 6.7, 2.1 Hz), 137.12 (dd, J = 8.3, 4.2 Hz), 135.42 (d, J = 3.1 Hz),134.66-134.28 (2C, m), 130.65 (d, J = 13.1 Hz), 128.45 (d, J = 9.3 Hz), 126.68 (d, J = 83.3 Hz), 125.79 (q, J = 33.2 Hz), 124.82-124.63 (m), 123.41 (q, J = 272.3 Hz), 120.81 (q, J = 321.0 Hz), 120.50, 117.49 (d, J = 23.1 Hz), 116.89 (d, J = 88.8 Hz), 114.59 (d, J = 23.0 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.35, –78.20, –110.86; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.30; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 579.2, $C_{35}H_{24}F_4N_2P^+$ requires 579.2.

Triphenyl(3'-(trifluoromethyl)-[2,2':5',3''-terpyridin]-4''-yl)phosphonium trifluoromethanesulfonate (1s)

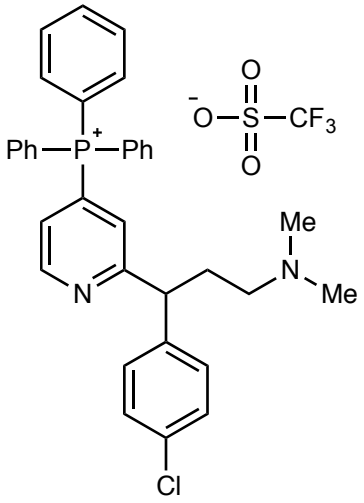


13.4:1:1 Mixture of Regioisomers

Prepared according to general procedure A (except that the reaction was warmed to –30 °C before the addition of PPh_3 and was stirred at –30 °C for 30 minutes) using 3'-(trifluoromethyl)-2,2':5',3''-terpyridine (407 mg, 1.35 mmol), Tf_2O (0.23 mL, 1.35 mmol), PPh_3 (0.39 g, 1.49 mmol), DBU (0.20 mL, 1.35 mmol) and CH_2Cl_2 (13.5 mL). After the purification procedure, the title compound (13.4:1:1 mixture of regioisomers determined by ^{31}P NMR)[‡] was isolated as a white solid (0.75 g, 1.06 mmol, 78% yield). Mixture of isomers, IR ν_{max}/cm^{-1} (film): 3064, 1588, 1438, 1262, 1224, 1141, 1108, 1030, 721; Major Isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.08 (1H, app t, *J* = 4.7 Hz), 8.79 (1H, d, *J* = 6.8 Hz), 8.70 (1H, d, *J* = 4.7 Hz), 8.27 (1H, d, *J* = 1.7 Hz), 7.87-7.58 (18H, m), 7.55 (1H, d, *J* = 7.8 Hz), 7.39 (1H, dd, *J* = 7.8, 4.7 Hz); Major Isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.12, 155.29, 153.09 (d, J = 7.3 Hz), 151.27 (d, J = 9.9 Hz), 150.97, 150.56, 148.83, 136.40, 136.24-136.07(m), 135.86 (d, J = 6.5 Hz), 135.65 (d, J = 2.8 Hz), 134.18 (d, J = 10.3 Hz), 130.70 (d, J = 13.0 Hz), 128.73 (d, J = 9.0 Hz), 127.45 (d, J = 83.1 Hz), 123.95 (q, J = 33.8 Hz), 123.77, 123.39, 122.19 (q, J = 273.7 Hz), 120.57 (q, J = 321.3 Hz), 116.19 (d, J = 88.6 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.97, –78.20; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.05; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 562.2, $C_{34}H_{24}F_3N_3P^+$ requires 562.2.

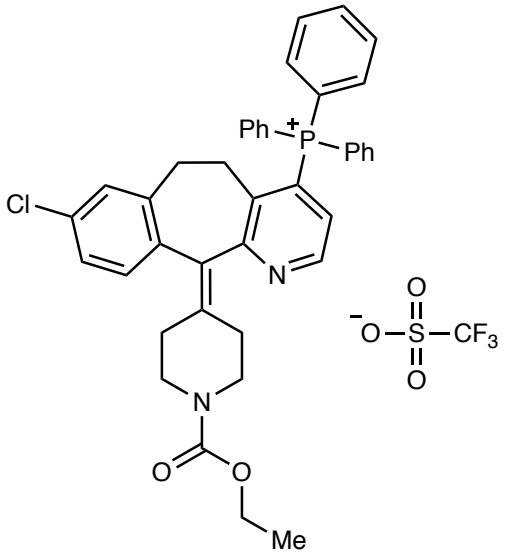
[‡] The crude regiomeric ratio was determined prior to precipitation by taking a portion of the crude mixture, concentrating *in vacuo* and analyzing by ^{31}P NMR to be 9.6:1.3:1.

(2-(1-(4-chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1t)



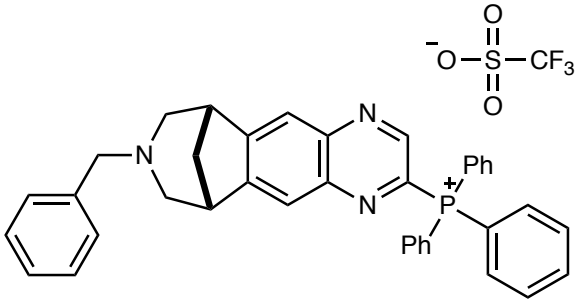
Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (1H, app t, J = 5.1 Hz, H_1), 7.93-7.86 (3H, m, H_6), 7.80-7.70 (6H, m, H_5), 7.61-7.50 (6H, m, H_4), 7.39 (1H, ddd, J = 12.8, 5.1, 1.5 Hz, H_2), 7.25-7.16 (5H, m, H_3, H_7, and H_8), 4.28 (1H, app t, J = 6.8 Hz, H_9), 2.56-2.43 (1H, m, H_{10}), 2.32-2.11 (9H, m, H_{10}, H_{11}, and H_{12}); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.55 (d, J = 9.9 Hz), 150.97 (d, J = 9.9 Hz), 140.26, 135.82 (d, J = 3.1 Hz), 134.02 (d, J = 10.7 Hz), 132.25, 130.61 (d, J = 13.0 Hz), 128.92 (d, J = 85.5 Hz), 128.75, 127.92, 126.26 (d, J = 8.4 Hz), 124.42 (d, J = 7.6 Hz), 120.46 (q, J = 321.2 Hz), 115.31 (d, J = 89.3 Hz), 56.73, 49.77, 44.88, 31.99. The spectroscopic data is in agreement with our reported synthesis.[2]

(8-Chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5Hbenzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1u)



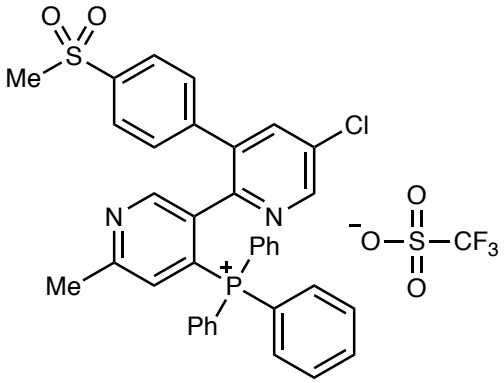
Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, app t, *J* = 5.0 Hz), 7.97-7.87 (3H, m), 7.86-7.74 (6H, m), 7.73-7.60 (6H, m), 7.16-7.01 (3H, m), 6.71 (1H, s), 4.14 (2H, q, *J* = 7.0 Hz), 3.84-3.61 (2H, m), 3.45- 3.20 (3H, m), 2.75 (1H, dt, *J* = 17.4, 4.7 Hz), 2.58 (1H, dt, *J* = 14.9, 4.7 Hz), 2.53-2.30 (3H, m), 2.26-2.09 (1H, m), 1.60-1.43 (1H, m), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.64 (d, *J* = 8.3 Hz), 155.37, 149.08 (d, *J* = 11.4 Hz), 139.23, 136.84, 136.66 (d, *J* = 6.8 Hz), 136.06 (d, *J* = 3.1 Hz), 134.21 (d, *J* = 10.7 Hz), 133.95, 133.57, 132.37, 131.58, 131.13 (d, *J* = 13.0 Hz), 129.85, 127.22 (d, *J* = 10.0 Hz), 127.01 (d, *J* = 82.2 Hz), 126.43, 120.78 (q, *J* = 321.3 Hz), 116.42 (d, *J* = 88.5 Hz), 61.39, 44.65, 44.41, 30.74, 30.46, 30.39, 29.39, 14.59. The spectroscopic data is in agreement with our reported synthesis.[2]

((6*S*,10*R*)-8-Benzyl-7,8,9,10-tetrahydro-6*H*-6,10-methanoazepino[4,5-*g*]quinoxalin-2-yl)triphenylphosphonium (1v)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (1H, s), 8.10-7.72 (17H, m), 7.20-7.05 (3H, m), 6.92-6.80 (2H, m), 3.55-3.27 (4H, m), 3.03-2.87 (2H, m), 2.66-2.42 (2H, m), 2.29-2.15 (1H, m), 1.87 (1H, d, *J* = 10.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.90 (d, *J* = 23.5 Hz), 144.21, 143.45 (d, *J* = 16.9 Hz), 137.51 (br s), 136.00 (d, *J* = 2.9 Hz), 134.55 (d, *J* = 10.9 Hz), 130.72 (d, *J* = 13.0 Hz), 129.20-126.21 (3C, m,), 120.69 (br s), 120.67 (q, *J* = 321.5 Hz), 116.42 (d, *J* = 88.3 Hz), 61.29, 57.90-56.06 (2C, m), 43.14-40.43 (3C, m). The spectroscopic data is in agreement with our reported synthesis.[2]

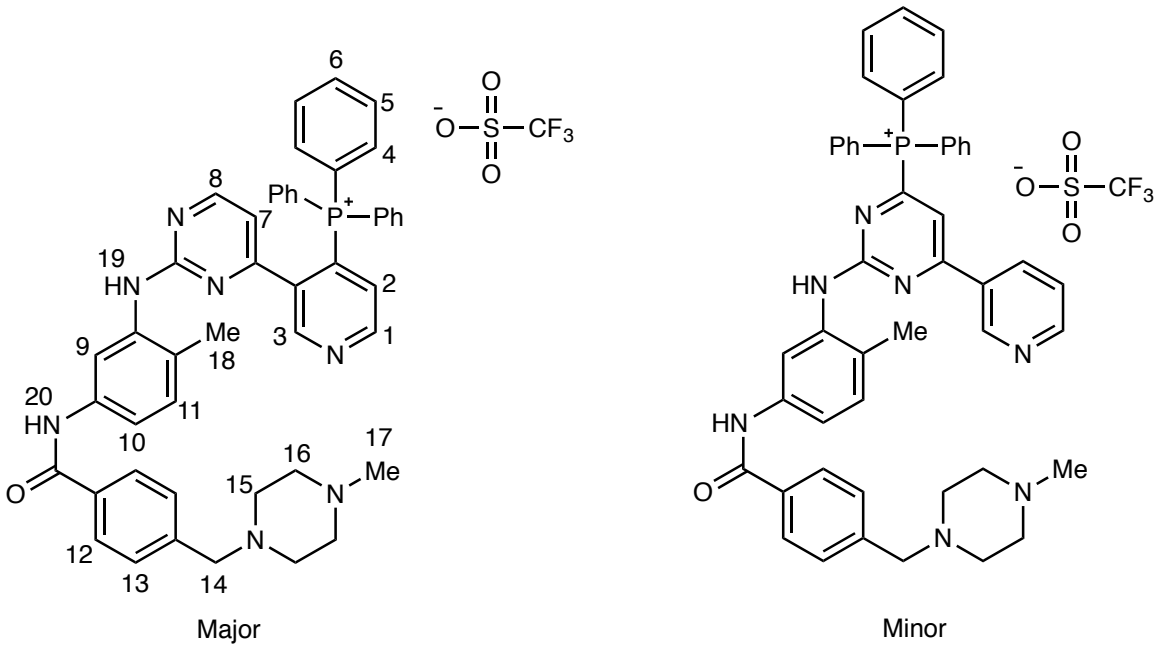
(5-Chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)triphenylphosphonium trifluoromethanesulfonate (1w)



Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (1H, d, *J* = 7.1 Hz), 8.10 (2H, d, *J* = 8.2 Hz), 7.86-7.62 (16H, m), 7.51-7.45 (3H, m), 7.20 (1H, d, *J* = 16.5 Hz), 3.14 (3H, s),

2.54 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.84 (d, *J* = 11.2 Hz), 152.42 (d, *J* = 7.3 Hz), 147.53 (d, *J* = 2.2 Hz), 146.09, 141.53, 141.02, 138.92, 135.62, 134.84 (d, *J* = 2.9 Hz), 134.17 (d, *J* = 10.0 Hz), 133.29 (d, *J* = 3.6 Hz), 132.10, 130.76 (d, *J* = 10.2 Hz), 130.03 (d, *J* = 13.1 Hz), 129.86, 128.55, 128.19 (d, *J* = 86.2 Hz), 120.77 (q, *J* = 321.1 Hz), 119.34 (d, *J* = 91.8 Hz), 43.96, 24.55. The spectroscopic data is in agreement with our reported synthesis.[3]

(3-(2-((2-Methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate and (2-((2-Methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)-6-(pyridin-3-yl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1x)



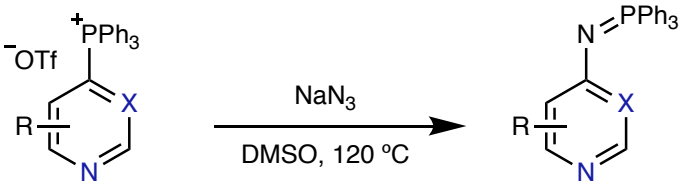
20:1 Mixture of Regioisomers

Prepared according to our previous report.[4] Major isomer, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.14 (1H, s, H_{20}), 9.55 (1H, d, *J* = 6.7 Hz, H_3), 9.09 (1H, app t, *J* = 4.6 Hz, H_1), 8.31 (1H, d, *J* = 5.1 Hz, H_8), 8.00-7.55 (18H, m, H_4, H_5, H_6, H_9, and H_{12}), 7.52-7.20 (5H, m, H_2, H_7, H_{10}, and H_{13}), 7.08 (1H, d, *J* = 8.3 Hz, H_{11}), 6.10 (1H, br, H_{19}), 3.55 (2H, s, H_{14}), 2.70-2.13 (11H, m, H_{15}, H_{16}, and H_{18}), 1.74 (3H, s, H_{17}); Major isomer, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.15, 159.79, 159.72 (d, *J* = 2.0 Hz), 158.29, 152.67 (d, *J* = 11.4 Hz), 151.77 (d, *J* = 6.8 Hz), 141.14 (br), 137.28, 136.16, 135.81 (d, *J* = 3.8 Hz),

134.70 (d, J = 2.3 Hz), 133.91 (d, J = 10.0 Hz), 130.75 (d, J = 10.2 Hz), 129.96, 129.95 (d, J = 13.4 Hz), 128.74, 127.70, 125.67 (d, J = 86.2 Hz), 125.48, 120.67 (q, J = 322.8 Hz), 119.54 (d, J = 92.3 Hz), 117.03, 117.00, 115.56, 110.34, 60.65, 53.15, 50.09, 43.09, 16.99. The spectroscopic data is in agreement with our reported synthesis.[4]

4. Preparation of Heterocyclic Iminophosphoranes

General procedure B

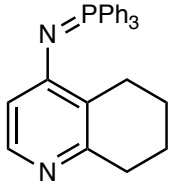


Care should be taken when handling sodium azide. We recommend conducting these reactions behind a blast shield. For proper storage, handling, and waste protocols, see the CDC's International Chemical Safety Card.[*]

An oven-dried 8 mL vial equipped with a stir bar and septa cap was charged with the phosphonium salt (1.0 equiv), sodium azide (1.25 equiv), and placed under a nitrogen atmosphere. DMSO (1.5 M) was added, the cap was wrapped with parafilm and the reaction mixture was heated for the stated time at 120 ºC. The reaction was cooled to room temperature, diluted with EtOAc and a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted a further three times with EtOAc and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography under the stated conditions to provide the iminophosphorane product.

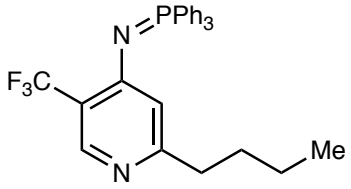
[*] Center for Disease Control and Prevention: Sodium Azide International Chemical Safety Card. https://www.cdc.gov/niosh/ipcsneng/neng0950.html (accessed Apr 4, 2018).

1,1,1-triphenyl-N-(5,6,7,8-tetrahydroquinolin-4-yl)- λ^5-phosphanimine (2a)



Prepared according to general procedure B using triphenyl(5,6,7,8-tetrahydroquinolin-4-yl)phosphonium trifluoromethanesulfonate (272 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 23 h. Flash column chromatography (basic alumina: 50% EtOAc in Hexanes) afforded the title compound as a light brown crystalline solid (174 mg, 0.43 mmol, 85% yield). mp 77-80 ºC; IR ν_{max}/cm^{-1} (film): 3084, 3051, 2989, 2954, 1442, 1439, 1270, 1260, 1221, 1145, 1106, 1029, 758, 723; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (1H, d, *J* = 6.5 Hz), 7.74-7.59 (9H, m), 7.53 (6H, td, *J* = 7.7, 3.2 Hz), 6.02 (1H, d, *J* = 6.5 Hz), 2.98-2.84 (4H, m), 1.91-1.80 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.54, 154.56, 143.78, 132.46 (d, *J* = 9.9 Hz), 132.21 (d, *J* = 2.9 Hz), 129.87 (d, *J* = 100.3 Hz), 128.86 (d, *J* = 12.2 Hz), 127.44 (d, *J* = 23.6 Hz), 113.09 (d, *J* = 11.2 Hz), 31.69, 24.94, 23.01, 22.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 6.85; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 409.4, $C_{27}H_{26}N_2P^+$ requires 409.2.

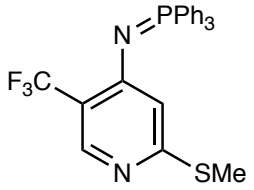
N-(2-butyl-5-(trifluoromethyl)pyridin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2b)



Prepared according to general procedure B using (2-butyl-5-(trifluoromethyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (307 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 21.25 h. Flash column chromatography (basic alumina: 30% EtOAc in hexanes) afforded the title compound as a white solid (214 mg, 0.45 mmol, 89% yield). mp 145-147 ºC; IR ν_{max}/cm^{-1} (film): 3075, 2963, 2927, 1592, 1520, 1491, 1484, 1442, 1434, 1324, 1200, 1182, 1108, 1057, 1024, 718, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (1H, d, *J* = 2.4 Hz), 7.77 (6H, dd, *J* = 8.2, 7.2

Hz), 7.58 (3H, td, *J* = 7.7, 1.6 Hz), 7.49 (6H, td, *J* = 7.7, 3.0 Hz), 6.03 (1H, s), 2.37 (2H, t, *J* = 7.5 Hz), 1.33 (2H, pent, *J* = 7.5 Hz), 1.11 (2H, pent, *J* = 7.6 Hz), 0.77 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.45, 157.38, 147.18 (qd, *J* = 6.0, 2.5 Hz), 132.44 (d, *J* = 10.0 Hz), 132.21 (d, *J* = 2.9 Hz), 129.38 (d, *J* = 101.7 Hz), 128.81 (d, *J* = 12.3 Hz), 125.35 (q, *J* = 272.3 Hz), 118.45-117.19 (m), 115.05 (d, *J* = 11.8 Hz), 37.56, 31.18, 21.97, 13.79; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.27; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 6.25; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 479.3, $C_{28}H_{27}F_3N_2P^+$ requires 479.2.

N-(2-(methylthio)-5-(trifluoromethyl)pyridin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2c)

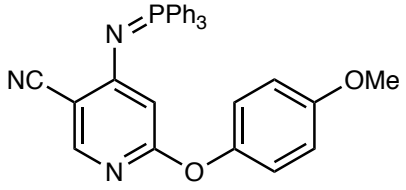


Prepared according to general procedure B using (2-(methylthio)-5-(trifluoromethyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (301 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 6 h. Flash column chromatography (silica gel: 30% EtOAc in hexanes) afforded the title compound as a white solid (219 mg, 0.47 mmol, 93% yield). mp 172-174 ºC; IR ν_{max}/cm^{-1} (film): 2989, 2901, 1578, 1569, 1516, 1468, 1434, 1418, 1326, 1103, 1058, 1019, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (1H, d, *J* = 2.5 Hz), 7.80-7.72 (6H, m), 7.59 (3H, tdd, *J* = 6.7, 1.7, 1.4 Hz), 7.54-7.47 (6H, m), 5.99 (1H, s), 2.15 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.87, 156.89, 147.19 (qd, *J* = 6.2, 2.5 Hz), 132.47 (d, *J* = 10.1 Hz), 132.38 (d, *J* = 3.0 Hz), 129.21 (d, *J* = 101.3 Hz), 128.94 (d, *J* = 12.4 Hz), 125.25 (q, *J* = 272.2 Hz), 117.11 (qd, *J* = 27.4, 23.2 Hz), 111.68 (d, *J* = 12.0 Hz), 13.29; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.23; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 6.45; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 469.2, $C_{25}H_{21}F_3N_2PS^+$ requires 469.1.

N-(2-(methylthio)-5-(trifluoromethyl)pyridin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2c) (Large Scale Procedure)

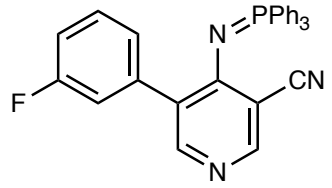
An oven-dried 8 mL vial equipped with a stir bar and septa cap was charged with (2-(methylthio)-5-(trifluoromethyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (603 mg, 1.00 mmol), sodium azide (81 mg, 1.25 mmol), and placed under a nitrogen atmosphere. DMSO (1.5 M) was added, the cap was wrapped with parafilm and the reaction mixture was heated for 15 h at 120 ºC. The reaction was cooled to room temperature, diluted with EtOAc and a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted a further three times with EtOAc and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel: 30% EtOAc in hexanes) which afforded the title compound as a white solid (421 mg, 0.90 mmol, 90% yield).

6-(4-methoxyphenoxy)-4-((triphenyl- λ^5-phosphaneylidene)amino)nicotinonitrile (2d)



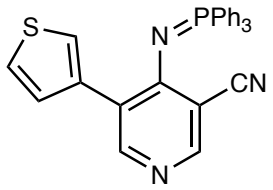
Prepared according to general procedure B using (5-cyano-2-(4-methoxyphenoxy)pyridin-4-yl)triphenylphosphonium (318 mg, 0.50 mmol), sodium azide (41 mg, 0.625 mmol) and DMSO (0.33 mL) for 8 h. Flash column chromatography (silica gel: 50% EtOAc in hexanes) afforded the title compound as a yellow solid (112 mg, 0.22 mmol, 45% yield). mp 212-214 ºC; IR ν_{max}/cm^{-1} (film): 2989, 2214, 1582, 1502, 1471, 1418, 1206, 1176, 1105, 1033; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (1H, d, *J* = 2.6 Hz), 7.74-7.67 (6H, m), 7.59 (3H, tdd, *J* = 7.3, 2.0, 1.9 Hz), 7.52-7.44 (6H, m), 6.85-6.80 (2H, m), 6.79-6.74 (2H, m), 5.55 (1H, s), 3.79 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.02, 163.28, 156.51, 153.08 (d, *J* = 2.4 Hz), 146.82, 132.56, 132.54 (d, *J* = 10.0 Hz), 129.00 (d, *J* = 12.4 Hz), 128.07 (d, *J* = 101.1 Hz), 122.26, 118.63, 114.56, 102.15, (d, *J* = 26.4 Hz), 99.39 (d, *J* = 11.9 Hz), 55.54; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 9.18; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 502.3, $C_{31}H_{25}N_3O_2P^+$ requires 502.2.

5-(3-fluorophenyl)-4-((triphenyl- λ^5-phosphaneylidene)amino)nicotinonitrile (2e)



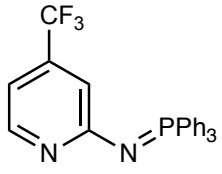
Prepared according to general procedure B using (3-cyano-5-(3-fluorophenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (304 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 23.75 h. Flash column chromatography (basic alumina: 20% EtOAc in hexanes) afforded the title compound as a yellow amorphous solid (208 mg, 0.44 mmol, 88% yield). mp 43-45 ºC; IR ν_{max}/cm^{-1} (film): 3058, 3012, 2919, 2220, 1614, 1582, 1565, 1468, 1434, 1254, 1198, 1149, 1109, 1043, 908, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (1H, s), 8.22 (1H, d, *J* = 1.7 Hz), 7.55-7.34 (9H, m), 7.39 (6H, td, *J* = 7.7, 3.4 Hz), 7.21 (1H, m), 7.08 (1H, d, *J* = 7.6 Hz), 6.97 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.34 (d, *J* = 245.8 Hz), 157.63 (d, *J* = 2.2 Hz), 154.08 (d, *J* = 0.9 Hz), 151.84, 139.90 (d, *J* = 8.1 Hz), 133.05 (d, *J* = 12.0 Hz), 132.40 (d, *J* = 10.55 Hz), 132.02 (d, *J* = 3.0 Hz), 130.08 (d, *J* = 105.3 Hz), 129.44 (d, *J* = 8.4 Hz), 128.55 (d, *J* = 12.7 Hz), 125.53 (d, *J* = 2.9 Hz), 119.1 (d, *J* = 1.0 Hz), 116.95 (d, *J* = 21.6 Hz), 113.94 (d, *J* = 21.0 Hz), 105.22 (d, *J* = 7.0 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –113.76; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 4.88; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 474.3, $C_{30}H_{22}FN_3P^+$ requires 474.2.

5-(thiophen-3-yl)-4-((triphenyl- λ^5-phosphaneylidene) amino)nicotinonitrile (2f)



Prepared according to general procedure B using (3-cyano-5-(thiophen-3-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (298 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 21 h. Flash column chromatography (basic alumina: 50% EtOAc in hexanes) afforded the title compound as a yellow oil (164 mg, 0.35 mmol, 71% yield). IR ν_{max}/cm^{-1} (film): 3058, 3011, 2218, 1566, 1464, 1435, 1372, 1245, 1152, 1108, 1043, 1025, 748, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34, (1H, d, *J* = 1.8 Hz), 8.32 (1H, s), 7.58-7.48 (9H, m), 7.42 (6H, td, *J* = 7.5, 3.3 Hz), 7.25 (1H, dd, *J* = 3.0, 1.7 Hz), 7.22 (1H, dd, *J* = 5.0, 3.0 Hz), 7.17 (1H, dd, *J* = 5.0, 1.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.61 (d, *J* = 1.8 Hz), 153.67 (d, *J* = 1.0 Hz), 151.83, 137.77, 132.51 (d, *J* = 10.6 Hz), 132.03 (d, *J* = 2.9 Hz), 130.31 (d, *J* = 105.2 Hz), 129.42, 129.31, 128.56 (d, *J* = 12.8 Hz), 124.53, 123.73, 119.28 (d, *J* = 0.8 Hz), 104.76 (d, *J* = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 5.00; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 462.2, $C_{28}H_{21}N_3PS^+$ requires 462.1.

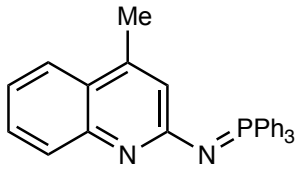
1,1,1-triphenyl-N-(4-(trifluoromethyl)pyridin-2-yl)- λ^5-phosphanimine (2g)



Prepared according to general procedure B using triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (279 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 25 h. Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the title compound as a pale yellow solid (186 mg, 0.44 mmol, 88% yield). mp 159-160 ºC; IR ν_{max}/cm^{-1} (film): 3055, 2995, 1595, 1546, 1469, 1422,1335, 1305, 1271, 1162, 1128, 1111, 1073, 1034, 1022, 998, 720,

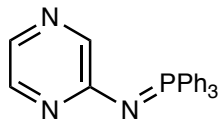
690; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89, (1H, d, *J* = 5.4 Hz), 7.81 (6H, m), 7.52 (3H, td, *J* = 7.5, 1.4 Hz), 7.13 (1H, s), 7.44 (6H, td, *J* = 7.8, 2.9 Hz), 6.60 (1H, d, *J* = 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.25 (d, *J* = 6.3 Hz), 147.97, 138.73 (qd, *J* = 32.7, 5.3 Hz), 133.08 (d, *J* = 9.7 Hz), 131.69 (d, *J* = 2.9 Hz), 129.61 (d, *J* = 100.1 Hz), 128.7 (d, *J* = 12.2 Hz), 123.52 (qd, *J* = 272.9, 1.5 Hz), 113.42 (dq, *J* = 26.0, 4.0 Hz), 107.10 (q, *J* = 3.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –65.10; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 14.85; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 423.3 $C_{24}H_{19}F_3N_2P^+$ requires 423.1.

N-(4-methylquinolin-2-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2h)



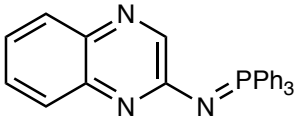
Prepared according to general procedure B using (4-methylquinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate (277 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 22.67 h. Flash column chromatography (basic alumina: 25% EtOAc in hexanes) afforded the title compound as a yellow solid (277 mg, 0.33 mmol, 66% yield). mp 193-195 ºC; IR ν_{max}/cm^{-1} (film): 3077, 3046, 2989, 1602, 1541, 1456, 1438, 1386, 1355, 1321, 1308, 1243, 1206, 1188, 1108, 1073, 1058, 914, 854, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.85 (6H, m), 7.70 (1H, d, *J* = 8.2 Hz), 7.53-7.46 (3H, m), 7.41 (6H, td, *J* = 7.7, 2.9 Hz), 7.36-7.24 (2H, m), 7.11 (1H, ddd, *J* = 8.1, 6.7, 1.5 Hz), 7.05 (1H, s), 2.52 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.64 (d, *J* = 6.8 Hz), 147.96, 143.38 (d, *J* = 4.8 Hz), 133.29 (d, *J* = 9.5 Hz), 131.40 (d, *J* = 2.8 Hz), 130.12 (d, *J* = 99.3 Hz), 128.17 (d, *J* = 12.1 Hz), 127.85, 126.13, 123.68, 123.25, 120.87, 120.55 (d, *J* = 25.1 Hz), 18.42 (d, *J* = 0.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.97; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 419.3, $C_{28}H_{24}N_2P^+$ requires 419.2.

1,1,1-triphenyl-N-(pyrazin-2-yl)- λ^5-phosphanimine (2i)



Prepared according to general procedure B using triphenyl(pyrazin-2-yl)phosphonium trifluoromethanesulfonate (245 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 21.5 h. Flash column chromatography (silica gel: 30% EtOAc in hexanes) afforded the title compound as a brown solid (98 mg, 0.28 mmol, 55% yield). mp 174-176 ºC; IR ν_{max}/cm^{-1} (film): 3061, 1573, 1492, 1471, 1435, 1410, 1344, 1109, 996, 718, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (1H, s), 7.80 (6H, dd, *J* = 8.3, 7.2 Hz), 7.70-7.64 (2H, m), 7.53 (3H, td, *J* = 7.8, 1.6 Hz), 7.44 (6H, td, *J* = 7.6, 2.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.19 (d, *J* = 6.4 Hz), 141.89 (d, *J* = 25.8 Hz), 140.99, 131.82 (d, *J* = 2.9 Hz), 133.02 (d, *J* = 9.8 Hz), 131.82 (d, *J* = 2.9 Hz), 129.34 (d, *J* = 100.1 Hz), 128.44 (d, *J* = 12.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.85; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 356.2, $C_{22}H_{19}N_3P^+$ requires 356.1.

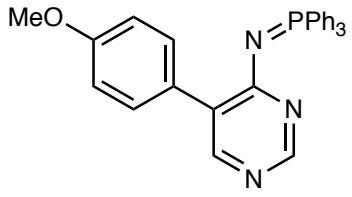
1,1,1-triphenyl-N-(quinoxalin-2-yl)- λ^5-phosphanimine (2j)



Prepared according to general procedure B using triphenyl(quinoxalin-2-yl)phosphonium (270 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 22.5 h. Flash column chromatography (basic alumina: 30% EtOAc in hexanes) afforded the title compound as a yellow solid (172 mg, 0.42 mmol, 85% yield). mp 125-128 ºC; IR ν_{max}/cm^{-1} (film): 3061, 2989, 1534, 1437, 1432, 1407, 1375, 1352, 1305, 1237, 1106, 1033, 1023, 1011, 946, 904, 728, 720.3, 687; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (1H, s), 7.93-7.85 (6H, m), 7.80 (1H, dd, *J* = 8.1, 1.4 Hz), 7.54 (3H, tdd, *J* = 6.7, 1.7, 1.4 Hz), 7.49-7.42 (6H, m), 7.37 (1H, ddd, *J* = 8.3, 6.8, 1.4 Hz), 7.31-7.22 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.17 (d, *J* = 6.7 Hz), 147.00 (d, *J* = 26.8 Hz), 142.21, 136.82, 133.21 (d, *J* = 9.8 Hz),

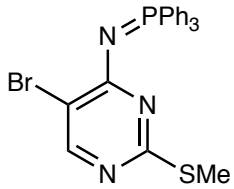
131.41 (d, J = 2.9 Hz), 129.34-128.22 (4C, m), 125.80, 123.30; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.83; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 406.2, $C_{26}H_{21}N_3P^+$ requires 406.2.

N-(5-(4-methoxyphenyl)pyrimidin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2k)



Prepared according to general procedure B using 5-(4-methoxyphenyl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (298 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 21.75 h. Flash column chromatography (basic alumina: 75% EtOAc in hexanes) afforded the title compound as a yellow solid (201 mg, 0.43 mmol, 87% yield). mp 139-141 ºC; IR ν_{max}/cm^{-1} (film): 3058, 2989, 1578, 1567, 1517, 1506, 1451, 1432, 1411, 1391, 1354, 1293, 1239, 1176, 1116, 1108, 1101, 1028, 1018, 824, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.18 (2H, m), 7.88-7.76 (8H, m), 7.52 (3H, td, J = 7.7, 1.5 Hz), 7.43 (6H, td, J = 7.7, 2.9 Hz), 7.01 (2H, d, J = 8.6 Hz), 3.59 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.22 (d, J = 6.7 Hz), 158.59, 155.84, 153.10 (d, J = 3.0 Hz), 133.04 (d, J = 9.8 Hz), 131.67 (d, J = 2.8 Hz), 130.38, 129.65, 129.07 (d, J = 100.4 Hz), 128.22 (d, J = 12.2 Hz), 125.47 (d, J = 22.0 Hz), 113.11, 55.12; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.78; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 462.3, $C_{29}H_{25}N_3OP^+$ requires 462.2.

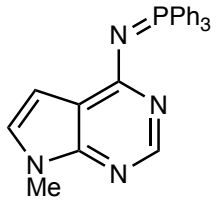
N-(5-bromo-2-(methylthio)pyrimidin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2l)



Prepared according to general procedure B using (5-bromo-2-(methylthio)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (308 mg, 0.50 mmol), sodium azide (41 mg, 0.63

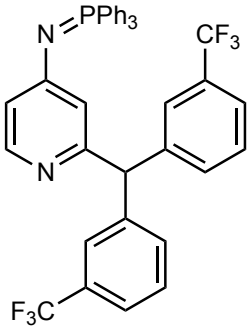
mmol) and DMSO (0.33 mL) for 18 h. Flash column chromatography (basic alumina: 30% EtOAc in hexanes) afforded the title compound as a white solid (235 mg, 0.49 mmol, 98% yield). mp 176-178 ºC; IR ν_{max}/cm^{-1} (film): 3061, 2989, 1541, 1495, 1482, 1426, 1350, 1316, 1301, 1174, 1109, 1061, 1028, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (1H, d, *J* = 2.9 Hz), 7.82-7.74 (6H, m), 7.57 (3H, tdd, *J* = 7.2, 1.6, 1.4 Hz), 7.51-7.44 (6H, m), 1.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.16, (d, *J* = 0.5 Hz), 163.96, (d, *J* = 4.6 Hz), 155.57 (d, *J* = 2.6 Hz), 132.88 (d, *J* = 10.0 Hz), 132.17 (d, *J* = 2.9 Hz), 128.54 (d, *J* = 12.4 Hz), 128.38 (d, *J* = 101.2 Hz), 109.14 (d, *J* = 26.2 Hz), 13.50; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 480.1, $C_{23}H_{20}BrN_3PS^+$ requires 480.0.

N-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)-1,1,1-triphenyl- λ^5-phosphanimine (2m)



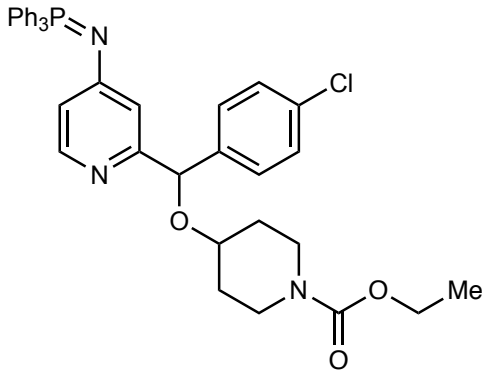
Prepared according to general procedure B using (7-methyl-*7H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (272 mg, 0.50 mmol), sodium azide (41 mg, 0.63 mmol) and DMSO (0.33 mL) for 8 h. Flash column chromatography (basic alumina: 50% EtOAc in hexanes) afforded the title compound as a yellow solid (108 mg, 0.26 mmol, 53% yield). mp 236-238 ºC; IR ν_{max}/cm^{-1} (film): 3051, 2919, 2850, 1567, 1555, 1482, 1443, 1431, 1375, 1334, 1293, 1245, 1107, 1063, 715; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (1H, s), 7.92-7.84 (6H, m), 7.52 (3H, tdd, *J* = 7.6, 1.6, 1.4 Hz), 7.47-7.40 (6H, m), 6.86 (1H, d, *J* = 3.4 Hz), 6.75 (1H, d, *J* = 3.4 Hz), 3.76 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.46 (d, *J* = 6.9 Hz), 151.14, 150.62 (d, *J* = 5.3 Hz), 133.42 (d, *J* = 9.8 Hz), 131.68 (d, *J* = 2.9 Hz), 129.65 (d, *J* = 100.0 Hz), 128.29 (d, *J* = 12.2 Hz), 123.90, 111.16 (d, *J* = 25.2 Hz), 99.94, 31.08; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.13; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 409.3, $C_{25}H_{22}N_4P^+$ requires 409.2.

***N*-(2-(bis(3-(trifluoromethyl)phenyl)methyl)-5-methylpyridin-4-yl)-1,1,1-triphenyl-λ^5-phosphanimine (2n)**



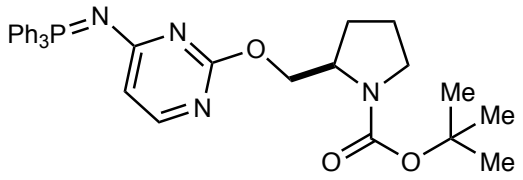
Prepared according to general procedure B (except the reaction was diluted and extracted with CH_2Cl_2 instead of EtOAc during the workup) using **(**2-(bis(3-(trifluoromethyl)phenyl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (198 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 17 h. Flash column chromatography (silica gel was packed in hexanes and neutralized with NEt_3 then: 40% EtOAc, 1% NEt_3 in hexanes to 60% EtOAc, 1% NEt_3 in hexanes) afforded the title compound as a white solid (122 mg, 0.19 mmol, 74% yield). mp 44-46 ºC; IR ν_{max}/cm^{-1} (film): 3058, 2989, 1582, 1477, 1438, 1352, 1327, 1157, 1115, 1074, 1049, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (1H, d, *J* = 5.5 Hz), 7.58-7.48 (6H, m), 7.47-7.39 (3H, m), 7.39-7.26 (8H, m), 7.24-7.14 (4H, m), 7.10-7.00 (2H, m), 6.52 (1H, dd, *J* = 5.5, 1.8 Hz), 6.11 (1H, s), 5.45 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.55 (d, *J* = 1.5 Hz), 159.53 (d, *J* = 2.5 Hz), 149.62 (d, *J* = 2.2 Hz), 143.32, 132.67, (d, *J* = 0.9 Hz), 132.37 (d, *J* = 9.8 Hz), 132.17 (d, *J* = 2.8 Hz), 130.49 (q, *J* = 32.0 Hz), 129.06 (d, *J* = 99.4 Hz), 128.78 (d, *J* = 12.1 Hz), 128.67, 125.82 (q, *J* = 3.8 Hz), 124.06 (q, *J* = 272.4, Hz), 123.32 (q, *J* = 3.8 Hz), 118.41 (d, *J* = 18.1 Hz), 117.66 (d, *J* = 21.0 Hz), 58.75; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.41; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 8.97; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 657.3, $C_{38}H_{28}F_6N_2P^+$ requires 657.2.

Ethyl 4-((4-chlorophenyl)(4-((triphenyl-λ^5-phosphaneylidene)amino)pyridin-2-yl)methoxy)piperidine-1-carboxylate (2o)



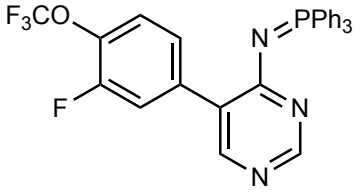
Prepared according to general procedure B using (2-((4-chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl) triphenylphosphonium trifluoromethanesulfonate (196 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 24.75 h. Flash column chromatography (silica gel, gradient elution: 2% MeOH in CH_2Cl_2 to 4% MeOH in CH_2Cl_2) afforded the title compound as a light yellow oil (110 mg, 0.17 mmol, 68% yield). IR ν_{max}/cm^{-1} (film): 3057, 2928, 1692, 1585, 1477, 1437, 1354, 1230, 1108, 1088, 1028, 752, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (1H, d, *J* = 5.7 Hz), 7.73-7.64 (6H, m), 7.62-7.55 (3H, m), 7.52-7.43 (6H, m), 7.20-7.14 (4H, m), 6.68 (1H, d, *J* = 1.8 Hz), 6.60 (1H, dd, *J* = 5.8, 1.9 Hz), 5.46 (1H, s), 4.11 (2H, q, *J* = 7.1 Hz), 3.64-3.47 (3H, m), 3.21-3.04 (2H, m), 1.78-1.67 (1H, m), 1.61-1.35 (3H, m), 1.24 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.11, 159.51, 155.42, 146.62, 140.10, 132.98, 132.57-132.30 (2C, m), 128.93 (d, *J* = 12.2 Hz), 128.76 (d, J = 99.6 Hz), 128.27, 128.07, 118.42 (d, *J* = 22.15), 114.54 (d, *J* = 18.4 Hz), 79.76, 72.12, 61.13, 40.87, 40.83 (rot), 30.89 (rot), 30.80, 14.66; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 650.3, $C_{38}H_{38}ClN_3O_3P^+$ requires 650.2.

***Tert*-butyl (*R*)-2-(((4-((triphenyl-λ^5-phosphaneylidene)amino)pyrimidin-2-yl)oxy)methyl)pyrrolidine-1-carboxylate (2p)**



Prepared according to general procedure B (except the reaction was diluted and extracted with CH_2Cl_2 instead of EtOAc during the workup) using triphenyl(5,6,7,8-tetrahydroquinolin-4-yl)phosphonium trifluoromethanesulfonate (172 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 12 h. Flash column chromatography (silica gel, gradient elution: 1% MeOH in CH_2Cl_2 to 2.5% MeOH in CH_2Cl_2) afforded the title compound as an off white solid (125 mg, 0.23 mmol, 90% yield). mp 156-159 ºC; IR ν_{max}/cm^{-1} (film): 3052, 2997, 2980, 1681, 1578, 1571, 15.27, 1456, 1446, 1440, 1435, 1400, 1360, 1344, 1330, 1282, 1111, 1036, 942, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.84 (1H, m), 7.77-7.59 (6H, m), 7.56-7.46 (3H, m), 7.45-7.34 (6H, m), 6.52-6.39 (1H, m), 3.92-3.79 (1H, m), 3.74-3.45 (1H, m), 3.39-2.80 (3H, m), 1.83-1.25 (13H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.25 (rot), 170.17, 163.97, 156.53, 156.29 (rot), 154.15, 133.08-132.40 (m), 131.84 (d, J = 2.6 Hz), 129.59-128.19 (2C, m), 108.16 (d, J = 23.9 Hz), 78.97, 78.64 (rot), 65.97, 55.61 (rot), 55.42, 46.58 (rot), 46.01, 28.64-27.56 (2C, m), 23.56 (rot), 22.22; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.17; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.78; *m*/*z* LRMS (ESI + APCI) found $[M+H]^+$ 555.4, $C_{32}H_{36}N_4O_3P^+$ requires 555.3.

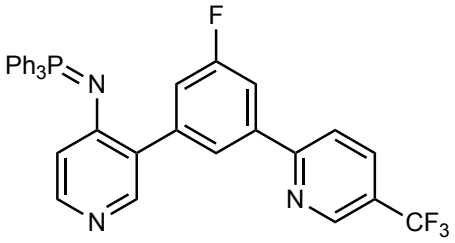
***N*-(5-(3-fluoro-4-(trifluoromethoxy)phenyl)pyrimidin-4-yl)-1,1,1-triphenyl-λ^5-phosphanimine (2q)**



Prepared according to general procedure B (except the reaction was diluted and extracted with CH_2Cl_2 instead of EtOAc during the workup) using (*R*)-(2-((1-(*tert*-butoxycarbonyl)pyrrolidin-2-

yl)methoxy)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (167 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 8 h. Flash column chromatography (silica gel was packed in hexanes and neutralized with NEt_3 then: 50% EtOAc in hexanes to 55% EtOAc in hexanes) afforded the title compound as a off-white solid (126 mg, 0.24 mmol, 95% yield). mp 44-47 ºC; IR ν_{max}/cm^{-1} (film): 3057, 3010, 1571, 1516, 1450, 1435, 1419, 1398, 1250, 1214, 1168, 1106, 1020, 997, 716, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (1H, s), 8.20 (1H, br s), 7.85-7.66 (7H, m), 7.57-7.47 (3H, m), 7.47-7.37 (6H, m), 7.19-7.05 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.55 (d, *J* = 5.9 Hz), 160.27 (d, *J* = 250.8 Hz), 157.50, 154.42, 148.68 (dd, *J* = 11.0, 2.1 Hz), 133.04 (d, *J* = 9.8 Hz), 132.80 (d, *J* = 5.1 Hz), 131.91 (d, *J* = 2.8 Hz), 128.82 (d, *J* = 100.9 Hz), 128.37 (d, *J* = 12.2 Hz), 124.45 (d, *J* = 15.3 Hz), 120.46 (d, *J* = 23.3 Hz), 120.42 (q, *J* = 257.7 Hz), 115.95 (d, *J* = 3.2 Hz), 100.87 (d, *J* = 26.5 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.99, –108.65 (t, *J* = 9.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.32; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 534.3, $C_{29}H_{21}F_4N_3OP^+$ requires 534.1

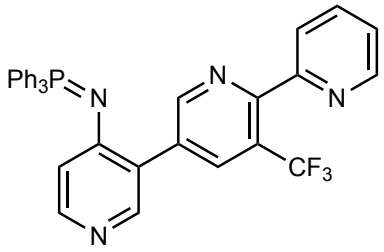
_N_-(3-(3-fluoro-5-(5-(trifluoromethyl)pyridin-2-yl)phenyl)pyridin-4-yl)-1,1,1-triphenyl-λ^5-phosphanimine (2r)



Prepared according to general procedure B using (3-(3-Fluoro-5-(5-(trifluoromethyl)pyridin-2-yl)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (182 mg, 0.25 mmol), sodium azide (20 mg, mmol) and DMSO (0.17 mL) for 8 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3, gradient elution: 50% EtOAc in hexanes to 75% EtOAc in hexanes) afforded the title compound as a white solid (104 mg, 0.17 mmol, 70% yield). mp 80-83 ºC; IR ν_{max}/cm^{-1} (film): 3056, 2989, 2925, 1579, 1484, 1401, 1355, 1327, 1131, 1108, 1082, 1040, 753, 718, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94-8.91 (1H, m), 8.38 (1H, d, *J* = 2.9 Hz), 8.18 (1H, t, *J* = 1.5 Hz), 7.95-7.89 (2H, m), 7.82-7.75 (2H, m), 7.70-7.60 (7H, m), 7.57-7.49 (3H, m), 7.41 (6H, td, *J* = 7.8, 3.0 Hz), 6.33 (1H, d, *J* = 5.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.95 (d, *J* = 244.1 Hz), 159.74 (q, *J* = 1.6

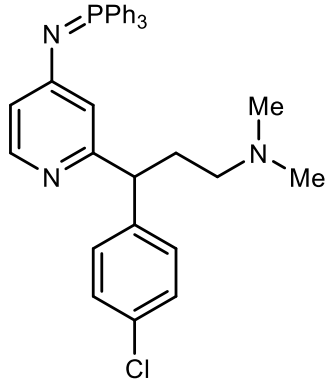
Hz), 155.86, 150.02 (d, J = 2.2 Hz), 148.93, 146.54 (q, J = 4.1 Hz), 141.80 (d, J = 8.5 Hz), 139.00 (d, J = 8.2 Hz), 133.89 (q, J = 3.5 Hz), 132.45 (d, J = 10.0 Hz), 132.17 (d, J = 2.9 Hz), 130.41, 129.69 (d, J = 100.5 Hz), 128.82 (d, J = 12.2 Hz), 125.00 (q, J = 33.1 Hz), 124.69 (d, J = 2.4 Hz), 123.68 (q, J = 272.1 Hz), 119.93, 118.75 (d, J = 22.1 Hz), 116.89 (d, J = 11.1 Hz), 112.10 (d, J = 23.3 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.25, –114.34; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 6.60; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 594.3, $C_{35}H_{25}F_4N_3P^+$ requires 594.2.

1,1,1-Triphenyl-*N*-(3'-(trifluoromethyl)-[2,2':5',3''-terpyridin]-4''-yl)-λ^5-phosphanimine (2s)



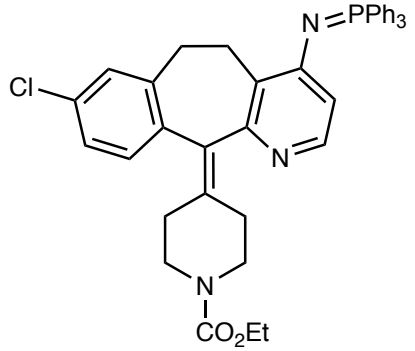
Prepared according to general procedure B using triphenyl(3'-(trifluoromethyl)-[2,2':5',3''-terpyridin]-4''-yl)phosphonium trifluoromethanesulfonate (178 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 20 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3, gradient elution: 100% EtOAc to 5% MeOH in CH_2Cl_2) afforded the title compound as a light yellow oil (108 mg, 0.19 mmol, 75% yield). IR ν_{max}/cm^{-1} (film): 3055, 2989, 2928, 1580, 1489, 1476, 1452, 1439, 1419, 1386, 1355, 1331, 1133, 1109, 1036, 753, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (1H, d, J = 1.7 Hz), 8.80 (1H, d, J = 1.9 Hz), 8.75 (1H, ddd, J = 4.9, 1.7, 0.9 Hz), 8.38 (1H, d, J = 2.6 Hz), 7.95 (1H, d, J = 5.7 Hz), 7.85 (1H, ddd, J = 9.5, 7.5, 1.8 Hz), 7.74 (1H, d, J = 7.8 Hz), 7.71-7.63 (6H, m), 7.60-7.54 (3H, m), 7.48 (6H, td, J = 7.6, 3.1 Hz), 7.38, (1H, ddd, J = 7.5, 4.9, 1.2 Hz), 6.34 (1H, d, J = 5.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.29, 156.49, 153.96 (q, J = 1.6 Hz), 151.86, 149.98 (d, J = 2.4 Hz), 149.62, 149.01, 136.70 (q, J = 5.0 Hz), 136.29, 134.19, 132.49-132.31 (2C, m), 129.20 (d, J = 100.36 Hz), 128.97 (d, J = 12.2 Hz), 126.61 (d, J = 23.7 Hz), 123.90 (q, J = 273.4 Hz), 123.84 (q, J = 32.3 Hz), 123.80 (d, J = 1.3 Hz), 123.27, 116.75 (d, J = 12.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.33; ^{31}P NMR (162 MHz, $CDCl_3$) δ:8.68; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 577.3, $C_{34}H_{25}F_3N_4P^+$ requires 577.2.

3-(4-Chlorophenyl)-N,N-dimethyl-3-(4-((triphenyl-λ5-phosphanylidene)amino)pyridin-2-yl)propan-1-amine (2t)



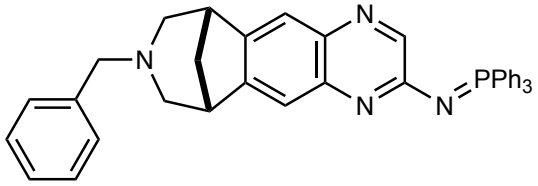
Prepared according to general procedure B using (2-(1-(4-chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (137 mg, 0.20 mmol), sodium azide (16 mg, 0.25 mmol) and DMSO (0.13 mL) for 20.5 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3, gradient elution: 5% MeOH in CH_2Cl_2 to 5% MeOH in CH_2Cl_2 with 1% NH_4OH) afforded the title compound as a Yellow Oil (31 mg, 0.06 mmol, 28% yield). IR ν_{max}/cm^{-1} (film): 3057, 2938, 2857, 2815, 2766, 1582, 1475, 1437, 1351, 1180, 1107, 1043, 1026, 1014, 750; (400 MHz, $CDCl_3$) δ: 8.00 (1H, d, J = 5.6 Hz), 7.70-7.60 (6H, m), 7.59-7.51 (3H, m), 7.49-7.40 (6H, m), 7.16-7.06 (4H, m), 6.45 (1H, d, J = 5.6 Hz), 6.40 (1H, s), 3.81 (1H, t, J = 7.3 Hz), 2.33-2.06 (9H, m), 2.02-1.90 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.63, 159.23, 148.81, 142.46, 132.49 (d, J = 9.8 Hz), 132.13 (d, J = 2.8 Hz), 131.56, 129.47 (d, J = 99.3 Hz), 129.41, 128.80 (d, J = 12.1 Hz), 128.24, 117.00 (d, J = 19.1 Hz), 116.89 (d, J = 19.7 Hz), 57.95, 50.69, 45.44, 32.55; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 8.10; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 550.3, $C_{34}H_{34}ClN_3P^+$ requires 550.2.

Ethyl 4-(8-chloro-4-((triphenyl-λ^5-phosphaneylidene)amino)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (2u)



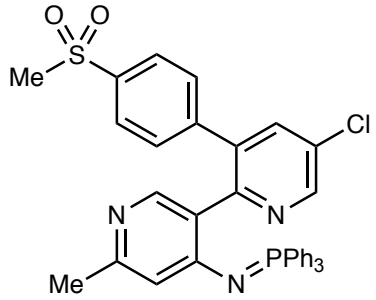
Prepared according to general procedure B using (8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5Hbenzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (198 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 15.25 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3: 6% MeOH in CH_2Cl_2) followed by filtration through a neutralized plug of silica (NEt_3) eluting with 5% MeOH in hexanes afforded the title compound as a yellow crystalline solid (68 mg, 0.10 mmol, 41% yield). mp 166-170 ºC; IR ν_{max}/cm^{-1} (film): 3054, 2989, 2912, 1693, 1560, 1465, 1434, 1367, 1339, 1230, 1121, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (1H, d, *J* = 5.6 Hz), 7.75-7.66 (6H, m), 7.57 (3H, td, *J* = 7.2, 1.6 Hz), 7.48 (6H, td, *J* = 7.7, 3.0 Hz), 7.19 (1H, s), 7.13-7.10 (2H, m), 6.08 (1H, dd, *J* = 5.6, 0.9 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 3.84 (2H, br s,), 3.44-3.26 (3H, m), 3.12-3.00 (2H, m), 2.91-2.81 (1H, m), 2.81-2.37 (2H, m), 2.34-2.25 (2H, m), 1.24 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.57 (br), 155.24, 147.49 (br), 141.55 (br), 140.21, 138.19 (br), 137.80, 133.20, 133.03 (d, *J* = 2.6 Hz), 132.28 (d, *J* = 10.1 Hz), 130.11, 129.26 (d, *J* = 12.4 Hz), 128.41 (d, *J* = 23.71 Hz), 128.12, 127.56 (d, *J* = 101.6 Hz), 127.50 (br), 126.31, 113.16 (d, *J* =12.3 Hz), 61.16, 45.57, 44.05, 43.97, 31.06, 30.51, 28.15, 14.57; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 5.25; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 658.3, $C_{40}H_{38}ClN_3O_2P^+$ requires 658.2.

***N*-((6*S*,10*R*)-8-benzyl-7,8,9,10-tetrahydro-6*H*-6,10-methanoazepino[4,5-*g*]quinoxalin-2-yl)-1,1,1-triphenyl-λ^5-phosphanimine (2v)**



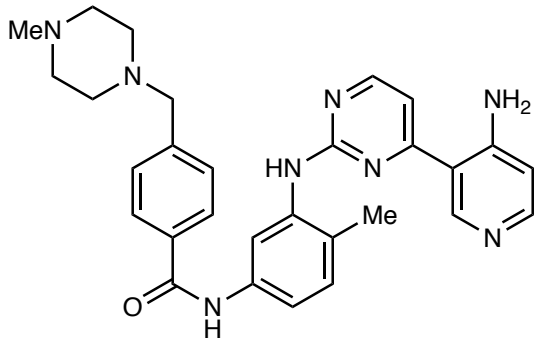
Prepared according to general procedure B using ((6*S*,10*R*)-8-benzyl-7,8,9,10-tetrahydro-6*H*-6,10-methanoazepino[4,5-*g*]quinoxalin-2-yl)triphenylphosphonium trifluoromethanesulfonate (178 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 42.25 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3: 40% EtOAc in hexanes) followed by filtration through a neutralized plug of silica (NEt_3) eluting with 20% EtOAc in hexanes to afford the title compound as a dark yellow oil (73 mg, 0.13 mmol, 51% yield). IR ν_{max}/cm^{-1} (film): 3059, 2945, 2787, 1532, 1467, 1438, 1389, 1303, 1216, 1108, 951, 906, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (1H, s), 7.98-7.85 (6H, m), 7.59-7.51 (4H, m), 7.46 (6H, td, *J* = 7.6, 2.8 Hz), 7.16-7.04 (4H, m), 6.86 (2H, d, *J* = 6.7 Hz), 3.47 (2H, s), 3.19 (1H, m), 3.10 (1H, m), 2.91 (1H, dd, *J* = 10.3, 2.4 Hz), 2.85 (1H, dd, *J* = 10.3, 2.5 Hz), 2.51 (1H, d, *J* = 9.9 Hz), 2.44 (1H, d, *J* = 10.0 Hz), 2.25-2.16 (1H, m), 1.17 (1H, d, *J* = 10.5 Hz); ^{13}C NMR of this compound is poorly resolved, containing several broad and overlapping peaks (see S172); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.75; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 577.3, $C_{38}H_{34}N_4P^+$ requires 577.3.

***N*-(5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)-1,1,1-triphenyl-λ^5-phosphanimine (2w)**



Prepared according to general procedure B using (5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)triphenylphosphonium trifluoromethanesulfonate (192 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol) and DMSO (0.17 mL) for 39.75 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3: 5% MeOH in CH_2Cl_2) afforded the title compound as a yellow crystalline solid (94 mg, 0.15 mmol, 60% yield). mp 116-120 ºC; IR ν_{max}/cm^{-1} (film): 3055, 2989, 2923, 1589, 1494, 1438, 1413, 1312, 1150, 1109, 719; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, d, *J* = 2.3 Hz), 8.34 (1H, d, *J* = 3.0 Hz), 7.64 (1H, d, *J* = 2.3 Hz), 7.59-7.50 (5H, m), 7.41 (6H, td, *J* = 7.9, 3.0 Hz), 7.24-7.16 (8H, m), 5.78 (1H, s), 2.99 (3H, s), 2.15 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.41, 156.47, 154.99, 148.79, 147.48, 144.96, 139.05, 137.40, 136.08, 132.27, (d, *J* = 2.9 Hz), 132.14 (d, *J* = 10.0 Hz), 130.15, 129.50, 129.00 (d, *J* = 100.4 Hz), 128.75 (d, *J* = 12.2 Hz), 128.19 (d, *J* = 24.8 Hz), 126.85, 115.06 (d, *J* = 11.3 Hz), 44.48, 23.83; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 6.76; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 634.2, $C_{36}H_{30}ClN_3O_2PS^+$ requires 634.2

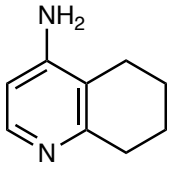
***N*-(3-((4-(4-aminopyridin-3-yl)pyrimidin-2-yl)amino)-4-methylphenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide (2x)**



An 8 mL vial equipped with a screw cap and septa was charged with (3-(2-((2-methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate and (2-((2-Methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)-6-(pyridin-3-yl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (20:1 mixture of regioisomers, 90 mg, 0.10 mmol), sodium azide (8 mg, 0.13 mmol) and DMSO (0.07 mL) and heated for 13.75 h at 100 ºC. The reaction was cooled to room temperature and an additional 70 μL of DMSO and 20 μL of H_2O were added and the mixture stirred for 52 h. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3, gradient elution: 10% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2 with 1% NEt_3) afforded the title compound as a dark yellow solid (20 mg, 0.04 mmol, 40% yield). mp 226-229 ºC; IR ν_{max}/cm^{-1} (film): 3285, 2935, 2804, 1609, 1562, 1530, 1507, 1457, 1290, 1241, 1211, 1163, 1139, 1053, 1010, 816; ^1H NMR (400 MHz, CD_3OD) δ: 8.62 (1H, br s), 8.30 (1H, d, *J* = 5.6 Hz), 7.88-7.81(3H, m), 7.76 (1H, d, *J* = 2.0 Hz), 7.53 (1H, dd, *J* = 8.3, 2.1 Hz), 7.42 (2H, d, *J* = 8.2 Hz), 7.24 (1H, d, *J* = 8.3 Hz), 7.19 (1H, d, *J* = 5.6 Hz), 6.56 (1H, d, *J* = 6.0 Hz), 3.55 (2H, s), 2.46 (8H, br s), 2.26-2.19 (6H, m); ^{13}C NMR (100 MHz CD_3OD) δ: 168.55, 166.56, 162.09, 159.23, 156.38, 150.48, 149.65, 142.96, 139.05, 138.48, 135.31, 131.88, 131.61, 130.55, 128.67, 120.32, 119.87, 114.44, 112.52, 107.48, 63.27, 55.74, 53.59, 45.98, 17.84; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 509.3, $C_{29}H_{33}N_8O^+$ requires 509.3

5. Derivatization Reactions

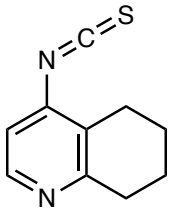
5,6,7,8-Tetrahydroquinolin-4-amine (3aa)



An 8mL vial equipped with a screw cap and septa was charged with 1,1,1-triphenyl-*N*-(5,6,7,8-tetrahydroquinolin-4-yl)- λ^5-phosphanimine (204 mg, 0.5 mmol) and 0.5 mL of a 9:1 mixture of DMF/H_2O. The vial was sealed and heated at 100 ºC for 44 h before the reaction was loaded directly onto a silica gel column. Flash column chromatography (silica gel packed in hexanes and neutralized with NEt_3, gradient elution: 5% MeOH in CH_2Cl_2 to 1% MeOH in basified[§] CH_2Cl_2 to 2.5% MeOH in basified CH_2Cl_2 followed by filtration through a plug of basic alumina by gradient elution: 1% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2) followed by filtration through a plug of basic alumnia eluting with 5% MeOH in CH_2Cl_2 to afford the title compound as a white crystalline solid (61 mg, 0.41 mmol, 83% yield). mp 121-125 ºC; IR ν_{max}/cm^{-1} (film): 3329, 3190, 2930, 1637, 1589, 1481, 1452, 1351, 1164, 1066, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (1H, d, *J* = 5.3 Hz), 6.33 (1H, d, *J* = 5.4 Hz), 4.16 (2H, br s), 2.84-2.72 (2H, m), 2.44-2.31 (2H, m), 1.88-172 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.86, 150.90, 146.59, 115.71, 106.98, 32.65, 22.79, 22.67, 22.39; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 149.2, $C_9H_{13}N_2^+$ requires 149.1.

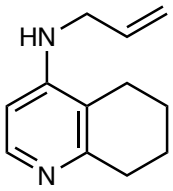
[§] CH_2Cl_2 was basified by shaking in a seperatory funnel with aqueous ammonium hydroxide.

4-Isothiocyanato-5,6,7,8-tetrahydroquinoline (3ab)



An 8 mL vial equipped with a screw cap and septa was charged with 1,1,1-triphenyl-*N*-(5,6,7,8-tetrahydroquinolin-4-yl)-λ^5-phosphanimine (102 mg, 0.25 mmol), carbon disulfide (375 μL) and toluene (1.25 mL). The vial was sealed and heated at 100 ºC for 64 h until consumption of starting material was observed by LCMS analysis. The reaction mixture was cooled to room temperature, concentrated *in vacuo* and the crude material was directly purified by flash column chromatography (silica gel: 10% EtOAc in hexanes) to afford title compound as a yellow oil (24 mg, 0.13 mmol, 50% yield). IR ν_{max}/cm^{-1} (film): 2938, 2052, 1566, 1460, 1437, 1408, 1066, 832, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (1H, d, *J* = 5.2 Hz), 6.90 (1H, d, *J* = 5.2 Hz), 2.95-2.87 (2H, m), 2.83-2.75 (2H, m), 1.93-1.80 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.73, 147.49, 138.95, 138.35, 128.59, 117.42, 32.70, 24.90, 22.51, 22.03; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 191.1, $C_{10}H_{11}N_2S^+$ requires 191.1

***N*-allyl-5,6,7,8-tetrahydroquinolin-4-amine (3ac)**

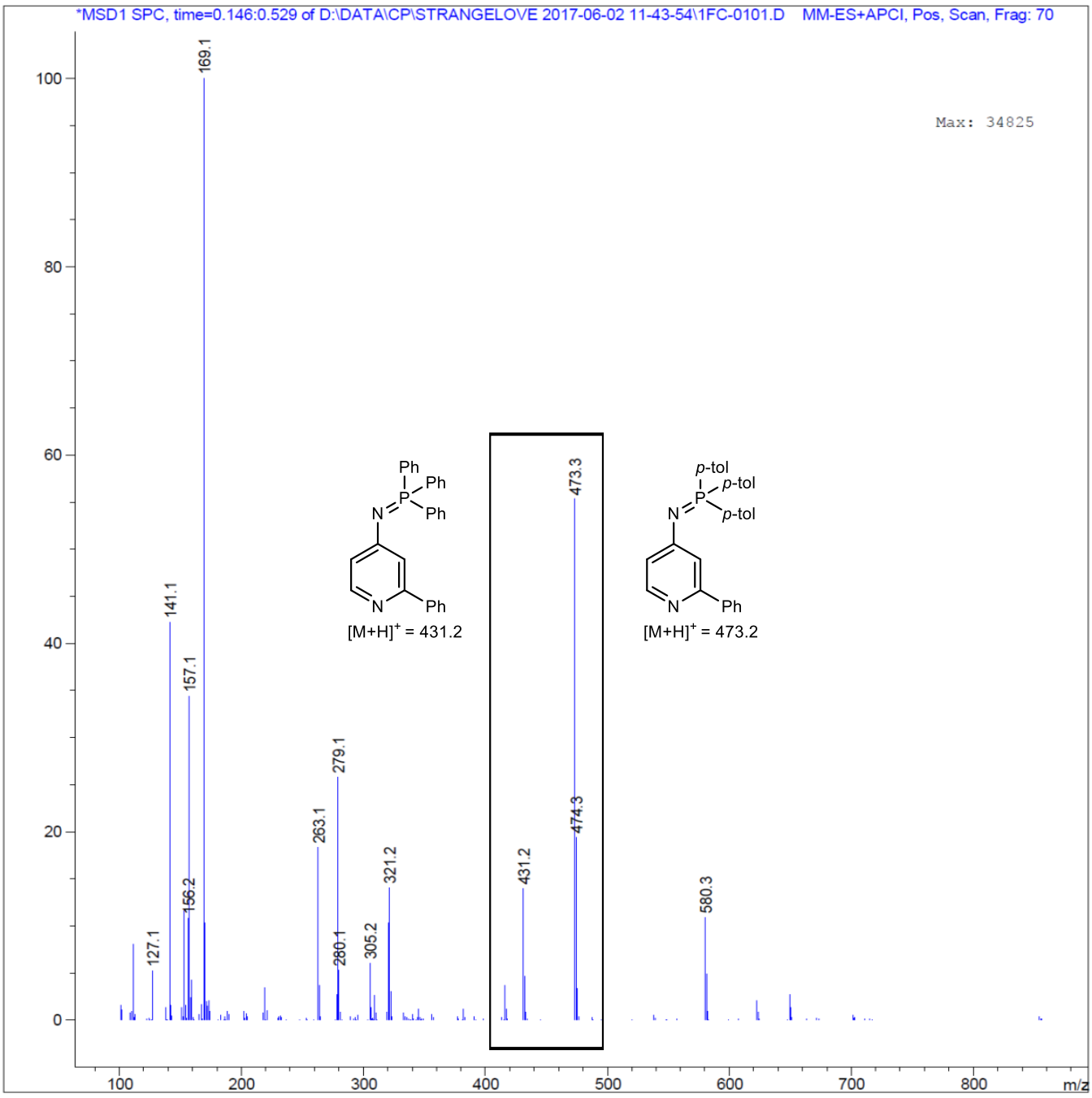


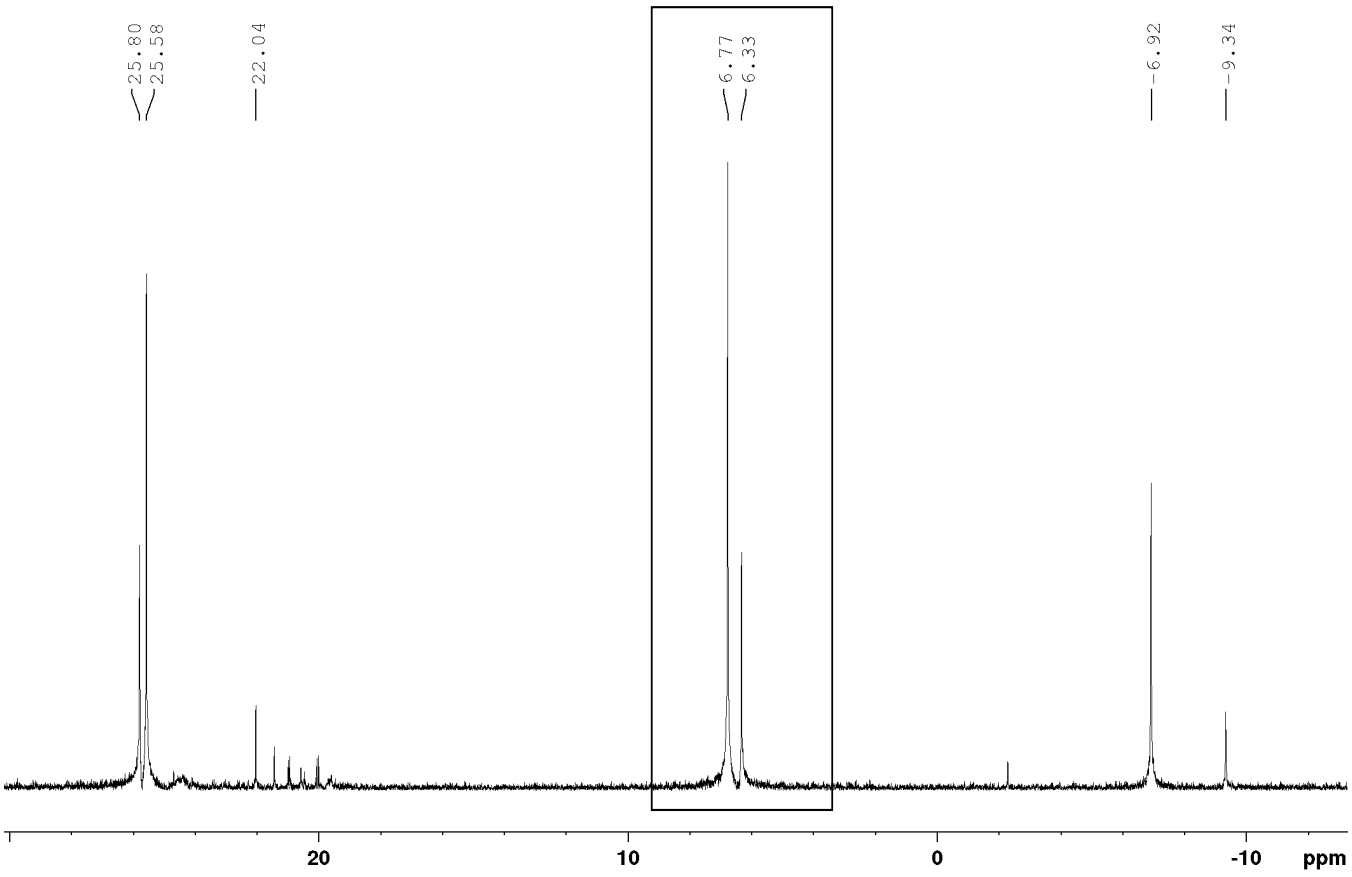
An 8 mL vial equipped with a screw cap and septa was charged with 1,1,1-triphenyl-*N*-(5,6,7,8-tetrahydroquinolin-4-yl)-λ^5-phosphanimine (102 mg, 0.25 mmol), allyl iodide (34 μl, 0.38 mmol) and MeCN (3.33 mL). The vial was sealed and heated at 90 ºC for 41 h before additional allyl iodide (34 μl, 0.38 mmol) was added. The reaction was heated at 90 ^{o}C for a further 21 h before being concentrated *in vacuo*, dissolved in MeOH (2 mL) and added to a chilled (0 ^{o}C) solution of MeOH (15 mL) and acetyl

chloride (0.35 mL, 5.0 mmol). The reaction mixture was stirred for 1 h at room temperature and then concentrated *in vacuo*. The crude material was directly purified by flash column chromatography (neutral alumina activated, gradient elution: 1% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2 with 1% NEt_3) followed by filtration through a plug of activated basic alumina eluting with 10% MeOH in CH_2Cl_2. A second round of flash column chromatography (neutral alumina activated, gradient elution: 1% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2) provided the title compound as a yellow solid (44 mg, 0.23 mmol, 94% yield). mp 204-206 ºC; IR ν_{max}/cm^{-1} (film): 3291, 3157, 2939, 1639, 1500, 1450, 1428, 1214, 1182, 845; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (1H, d, J = 7.2 Hz), 6.81 (1H, d, J = 7.2 Hz), 6.11-6.00 (1H, m), 5.34 (1H, d, J = 10.5), 5.00 (1H, d, J = 17.2 Hz), 4.87-4.80 (2H, m), 2.93-2.85 (2H, m), 2.54-2.46 (2H, m), 1.96-1.82 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.22, 151.62, 143.15, 133.27, 119.47, 118.76, 108.64, 57.06, 27.40, 24.27, 22.43, 21.70; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 189.1, $C_{12}H_{17}N_2^+$ requires 189.1

6. Phosphine Competition Experiment

The reaction was conducted in accordance with general experimental B using Triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate, except that tri-*p*-tolylphosphane (76 mg, 0.25 mmol) was also added at the start of the reaction. After the work up procedure, the reaction was analyzed by ^{31}P NMR and LCMS analysis.


*MSD1 SPC, time=0.146:0.529 of D:\DATA\CP\STRANGELOVE 2017-06-02 11-43-54\1FC-0101.D MM-ES+APCI, Pos, Scan, Frag: 70
Max: 34825
169.1
141.1
157.1
156.2
127.1
263.1
279.1
280.1
305.2
321.2
431.2
473.3
474.3
580.3
Ph
Ph
Ph
N
P
N
Ph
[M+H]+ = 431.2
p-tol
p-tol
p-tol
N
P
N
Ph
[M+H]+ = 473.2
100
80
60
40
20
0
100
200
300
400
500
600
700
800
m/z



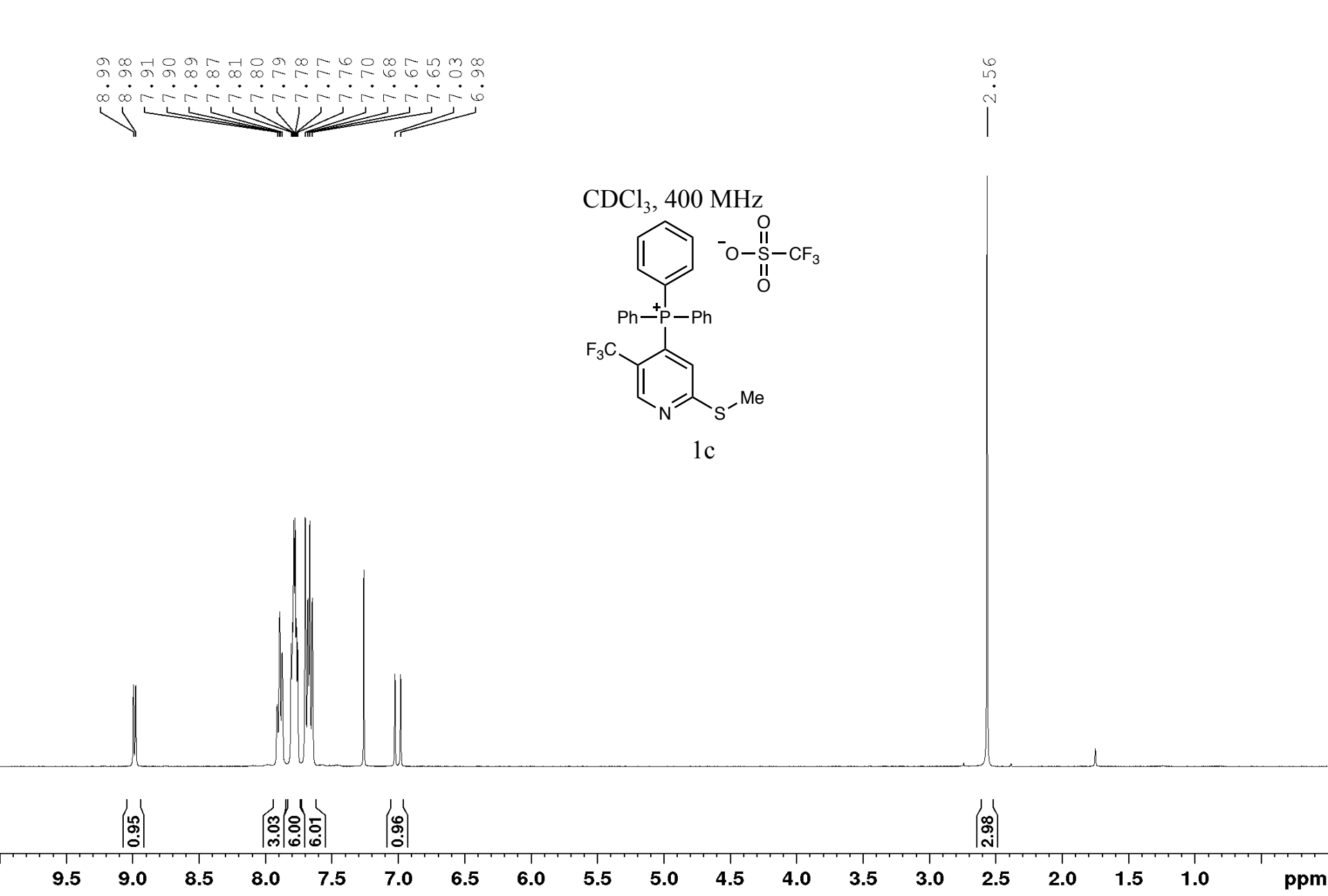
7. References

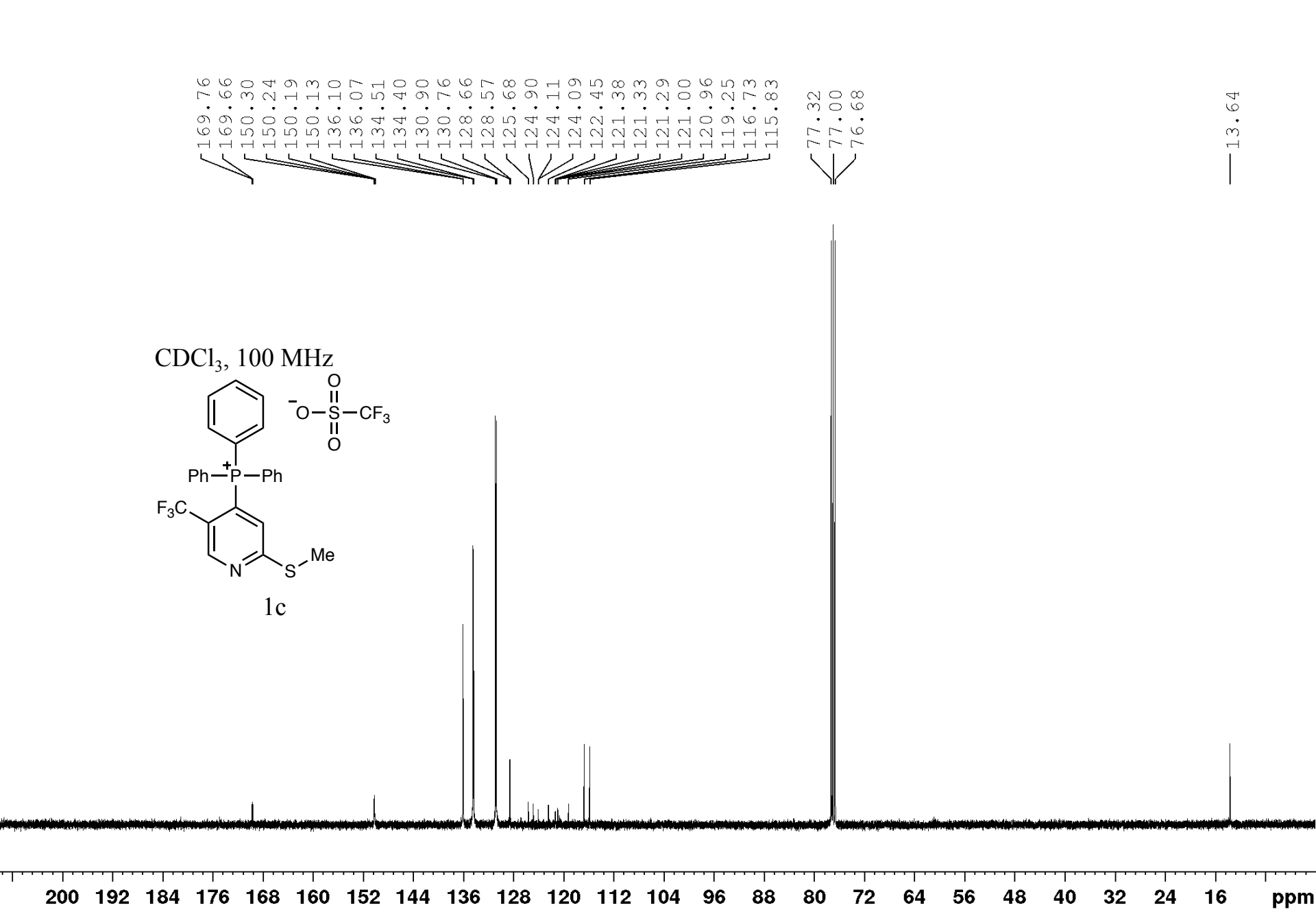
S1. D. D. Perrin, W. L. F. Amarego, Purification of Laboratory Chemicals (Pergamon, Press, Oxford. ed. 3, 1988).

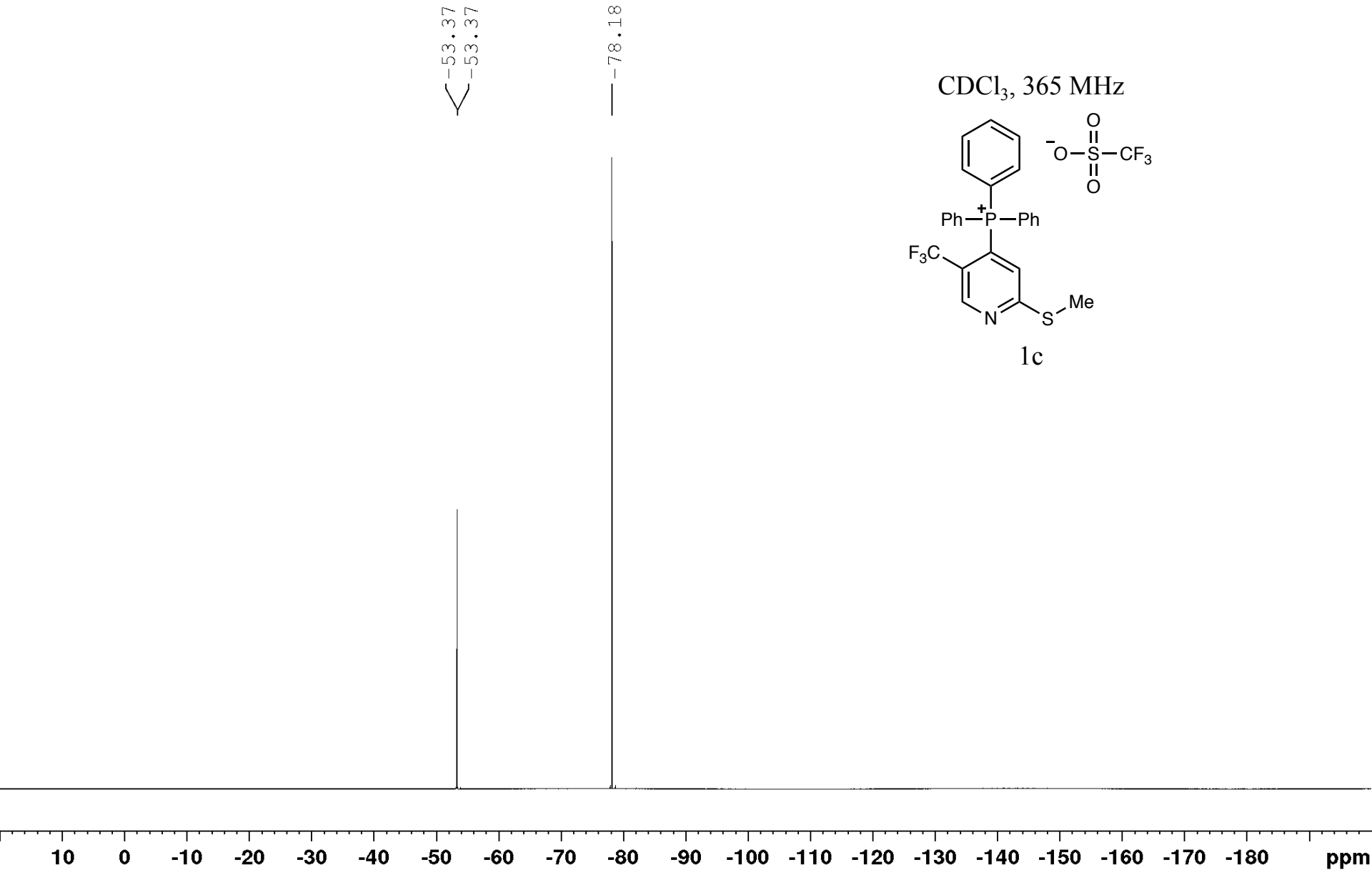
S2. Hilton, M.; Dolewski, R.; McNally, A. Selective Functionalization of Pyridines via Heterocyclic Phosphonium Salts. *J. Am. Chem. Soc*., 2016, 138 (42), pp 13806–13809.

S3. Anderson, R.; Jett, B.; McNally, A. Selective Formation of Heteroaryl Thioethers via a Phosphonium Ion Coupling Reaction. *Tetrahedron*, 2017, https://doi.org/10.1016/j.tet.2017.12.040

S4. Koniarczyk, J.; Hesk, D.; Overgard, A.; Davies, I.W.; McNally, A. A General Strategy for Site-Selective Incorporation of Deuterium and Tritium into Pyridines, Diazines and Pharmaceuticals, *J. Am. Chem. Soc.*, 2018, doi.org/10.1021/jacs.7b11710


8.99
8.98
7.91
7.90
7.89
7.87
7.81
7.80
7.79
7.78
7.77
7.76
7.70
7.68
7.67
7.65
7.03
6.98
2.56
CDCl3, 400 MHz
Ph
P
Ph
F3C
N
S
Me
O
S
CF3
1c
0.95
3.03
6.00
6.01
0.96
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


169.76
169.66
150.30
150.24
150.19
150.13
136.10
136.07
134.51
134.40
130.90
130.76
128.66
128.57
125.68
124.90
124.11
124.09
122.45
121.38
121.33
121.29
121.00
120.96
119.25
116.73
115.83
77.32
77.00
76.68
13.64
CDCl3, 100 MHz
O
O−S−CF3
O
Ph−P−Ph
F3C
N
S
Me
1c
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm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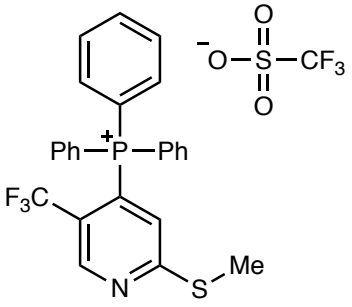
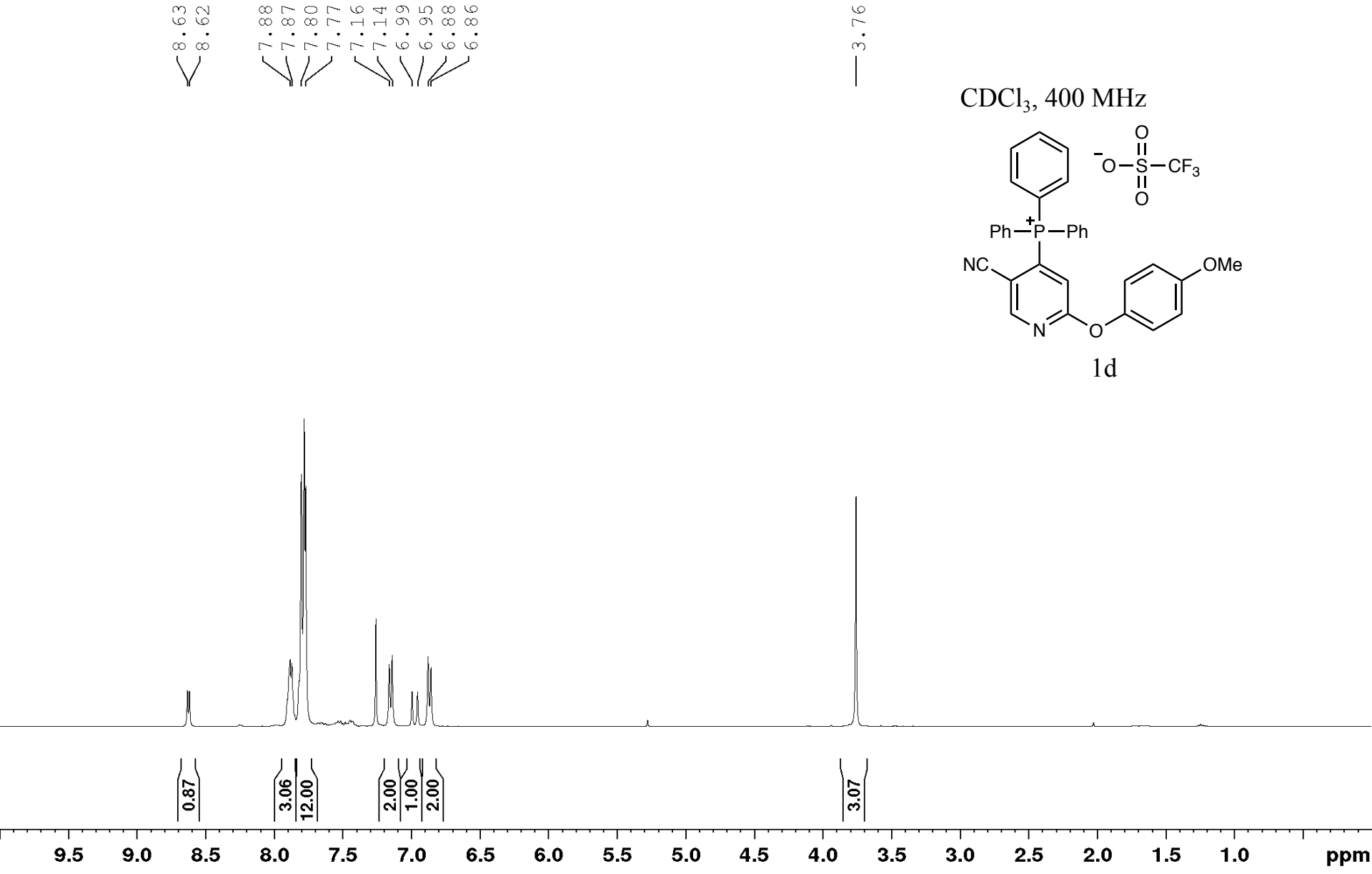
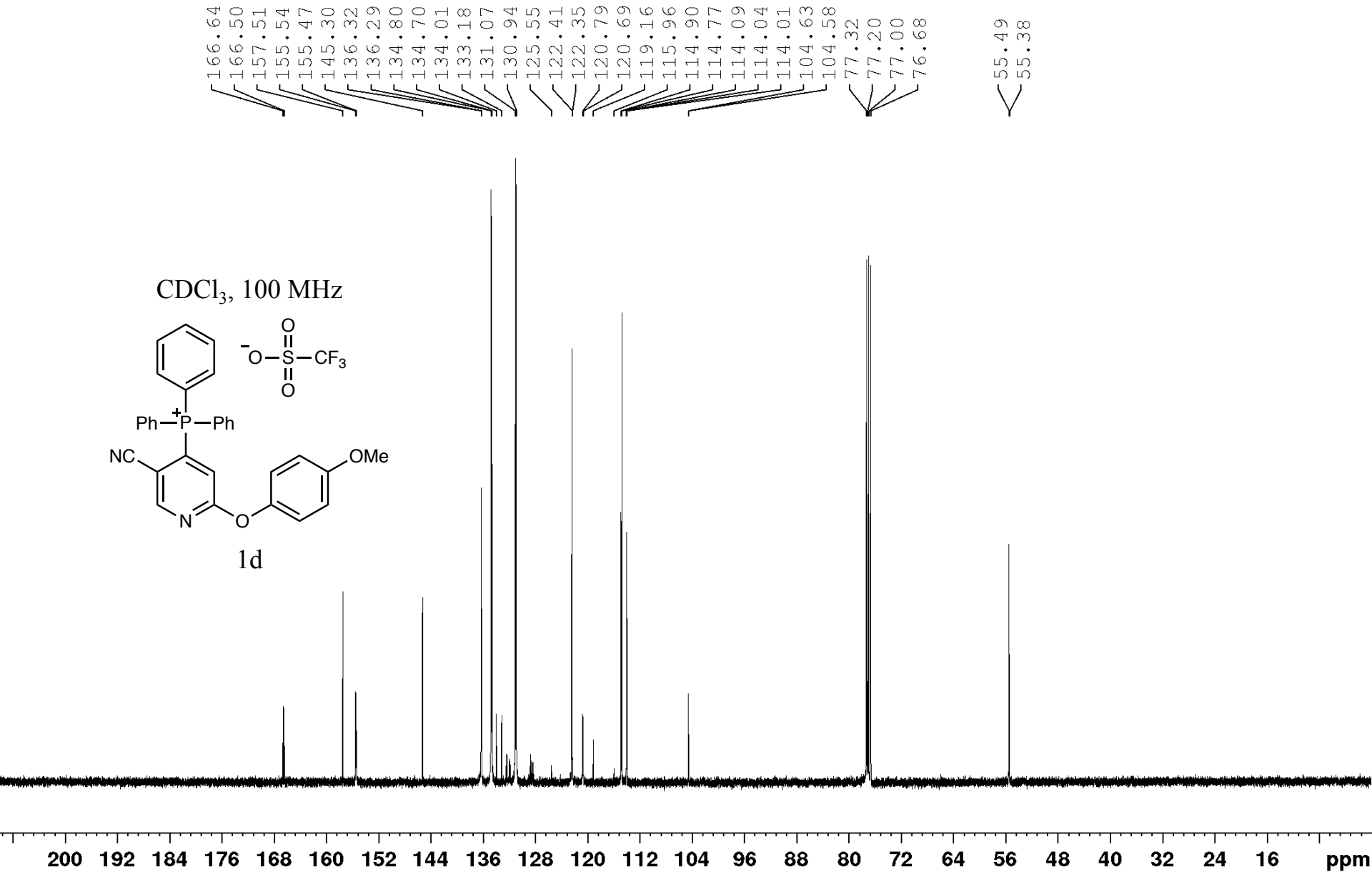
-53.37
-78.18
CDCl3, 365 MHz
Ph
P
Ph
F3C
N
S
Me
O
O
S
CF3
O
1c
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

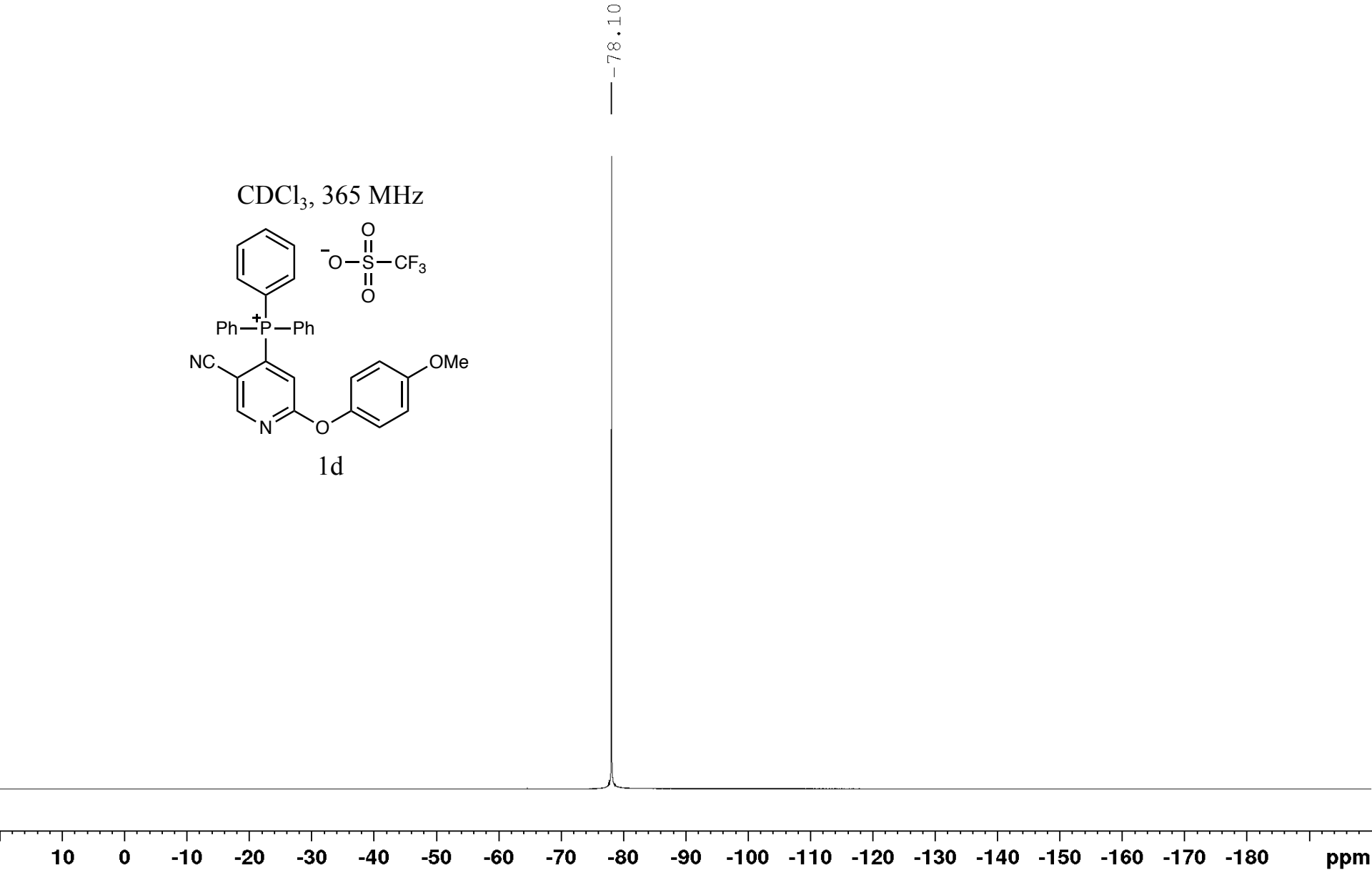
$CDCl_3$, 162 MHz



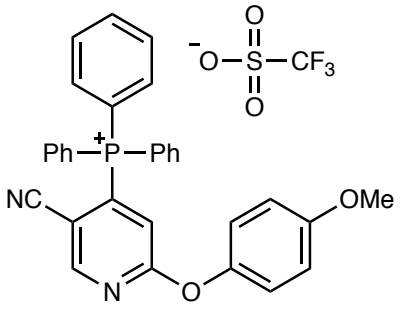
1c


8.63
8.62
7.88
7.87
7.80
7.77
7.16
7.14
6.99
6.95
6.88
6.86
3.76
CDCl3, 400 MHz
Ph
P
Ph
NC
OMe
N
O
O
O
O
S
CF3
1d
0.87
3.06
12.00
2.00
1.00
2.00
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

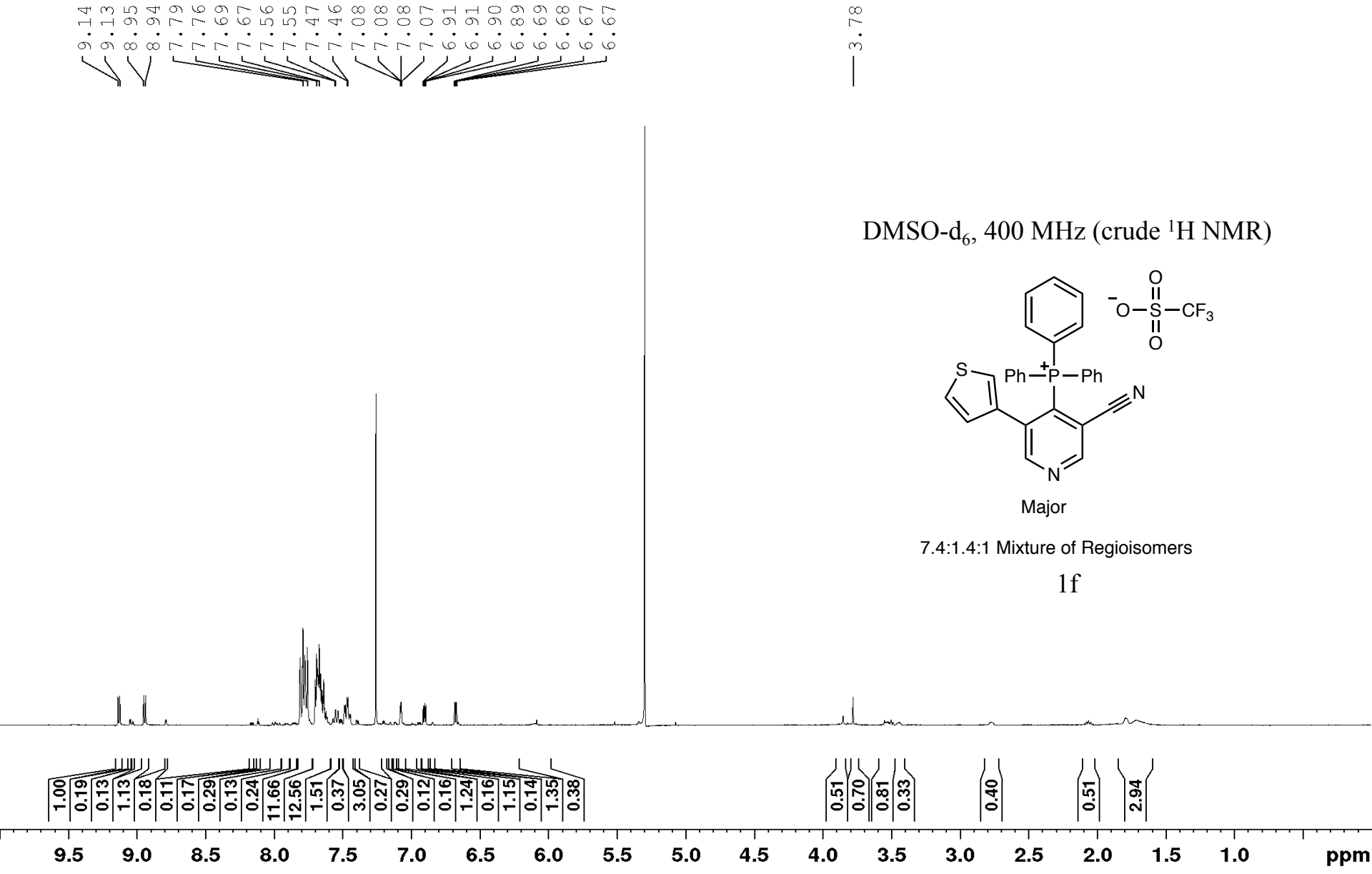

166.64
166.50
157.51
155.54
155.47
145.30
136.32
136.29
134.80
134.70
134.01
133.18
131.07
130.94
125.55
122.41
122.35
120.79
120.69
119.16
115.96
114.90
114.77
114.09
114.04
114.01
104.63
104.58
77.32
77.20
77.00
76.68
55.49
55.38
CDCl3, 100 MHz
Ph
P
Ph
NC
OMe
N
O
O
O
S
CF3
1d
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm


-78.10
CDCl3, 365 MHz
Ph
P
Ph
NC
OMe
N
O
O
S
CF3
1d
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz



1d



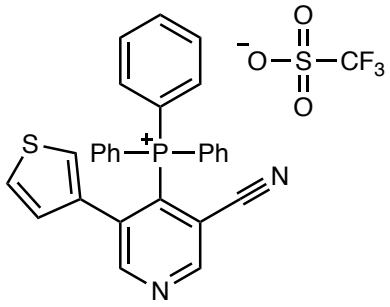
DMSO-d_6, 400 MHz (crude ^{1}H NMR)

Major

7.4:1.4:1 Mixture of Regioisomers

1f

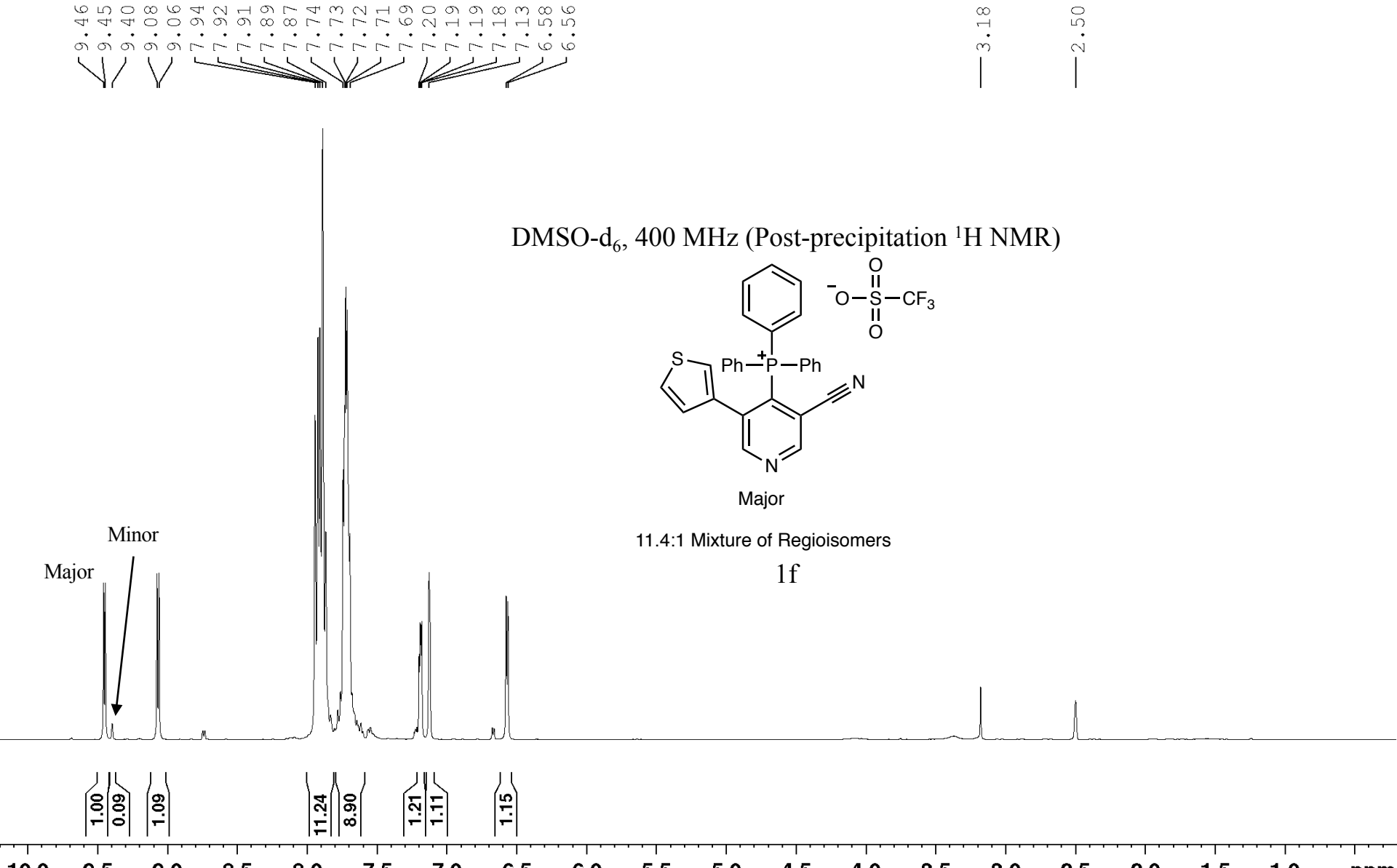
DMSO-d_6, 400 MHz (crude ^{1}H NMR)



Major

7.4:1.4:1 Mixture of Regioisomers

1f


9.46
9.45
9.40
9.08
9.06
7.94
7.92
7.91
7.89
7.87
7.74
7.73
7.72
7.71
7.69
7.20
7.19
7.19
7.18
7.13
6.58
6.56
3.18
2.50
DMSO-d6, 400 MHz (Post-precipitation 1H NMR)
Major
11.4:1 Mixture of Regioisomers
1f
Minor
Major
1.00
0.09
1.09
11.24
8.90
1.21
1.11
1.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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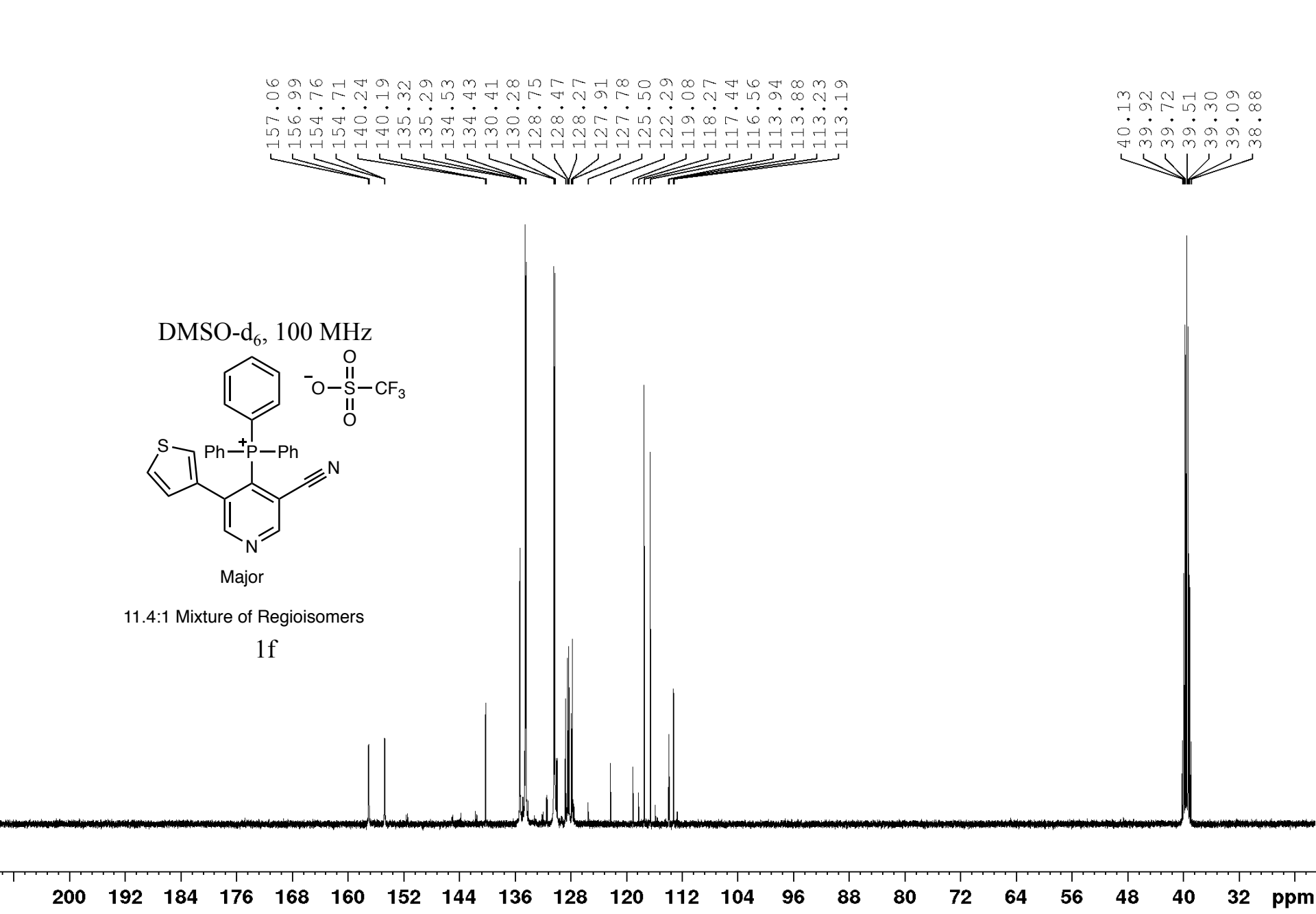
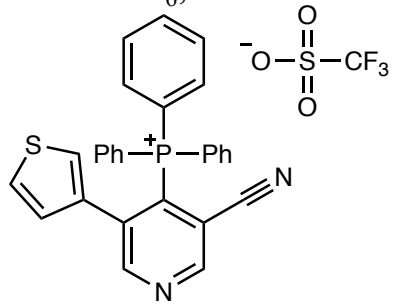
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


157.06
156.99
154.76
154.71
140.24
140.19
135.32
135.29
134.53
134.43
130.41
130.28
128.75
128.47
128.27
127.91
127.78
125.50
122.29
119.08
118.27
117.44
116.56
113.94
113.88
113.23
113.19
40.13
39.92
39.72
39.51
39.30
39.09
38.88
DMSO-d6, 100 MHz
Major
11.4:1 Mixture of Regioisomers
1f
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
ppm

DMSO-d_6, 365 MHz

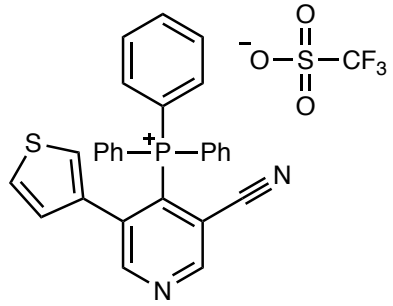


Major

11.4:1 Mixture of Regioisomers

1f

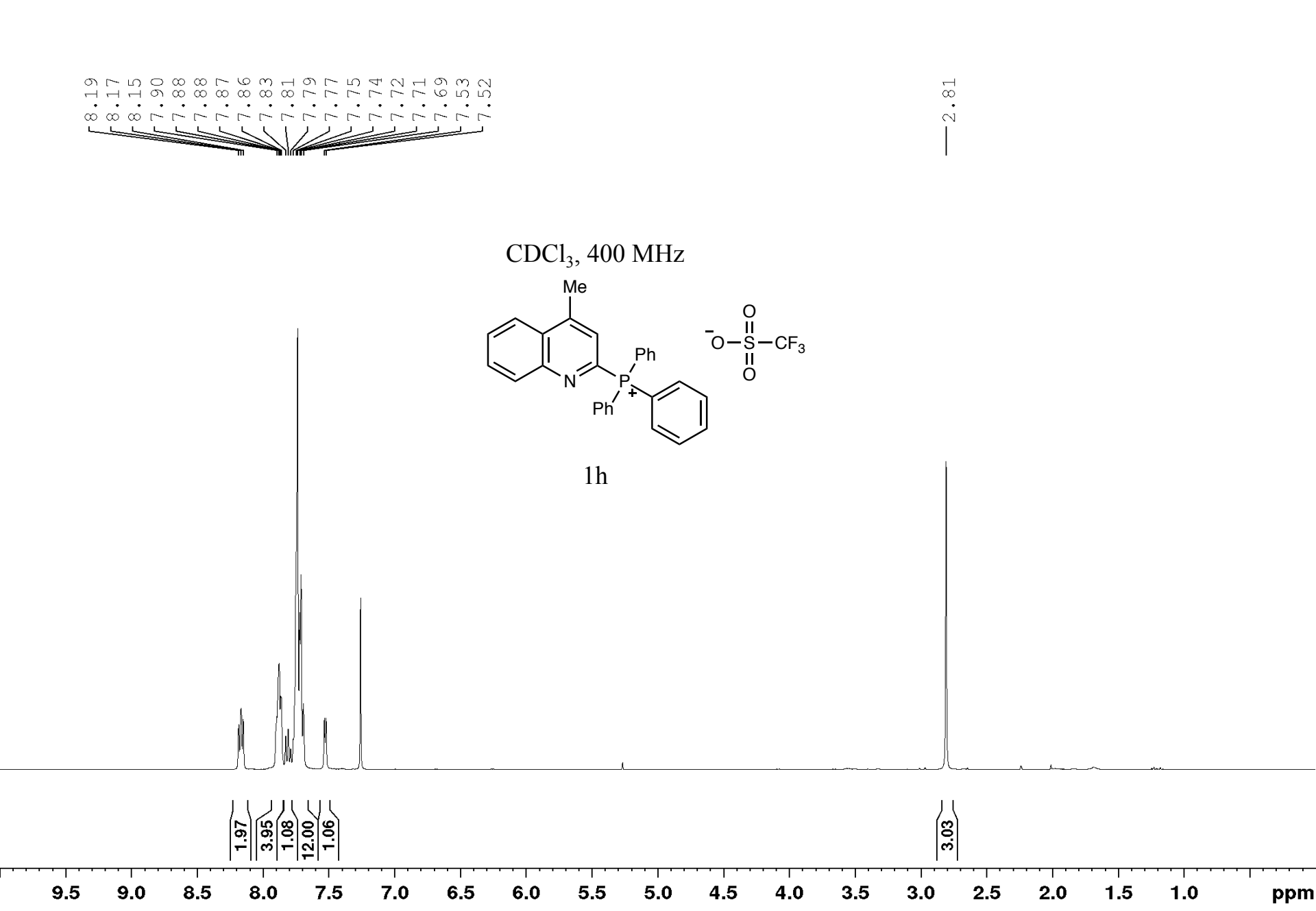
DMSO-d_6, 162MHz



Major

11.4:1 Mixture of Regioisomers

1f


8.19
8.17
8.15
7.90
7.88
7.88
7.87
7.86
7.83
7.81
7.79
7.77
7.75
7.74
7.72
7.71
7.69
7.53
7.52
2.81
CDCl3, 400 MHz
Me
Ph
Ph
N
P
O
O
S
O
CF3
1h
1.97
3.95
1.08
12.00
1.06
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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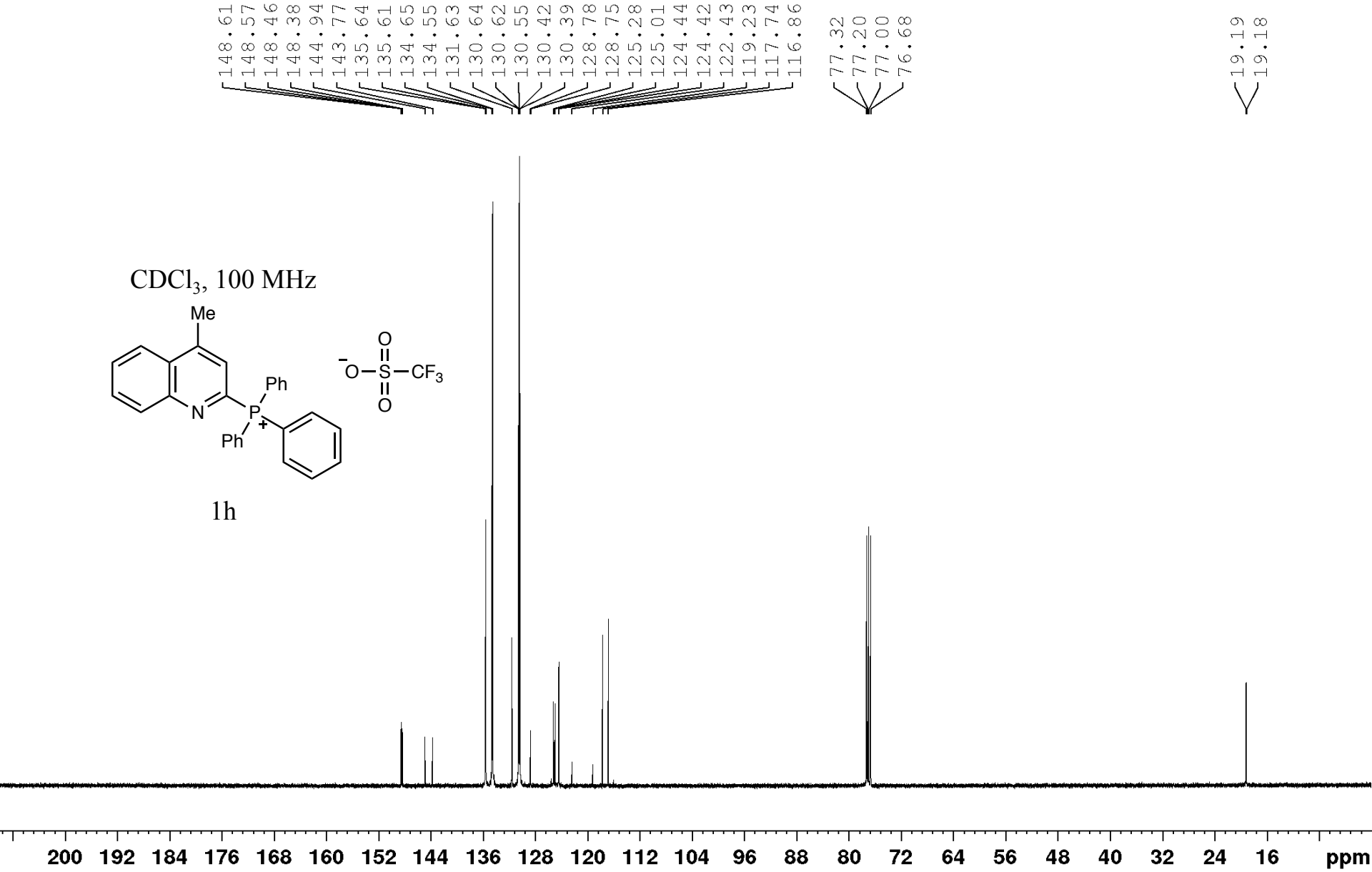
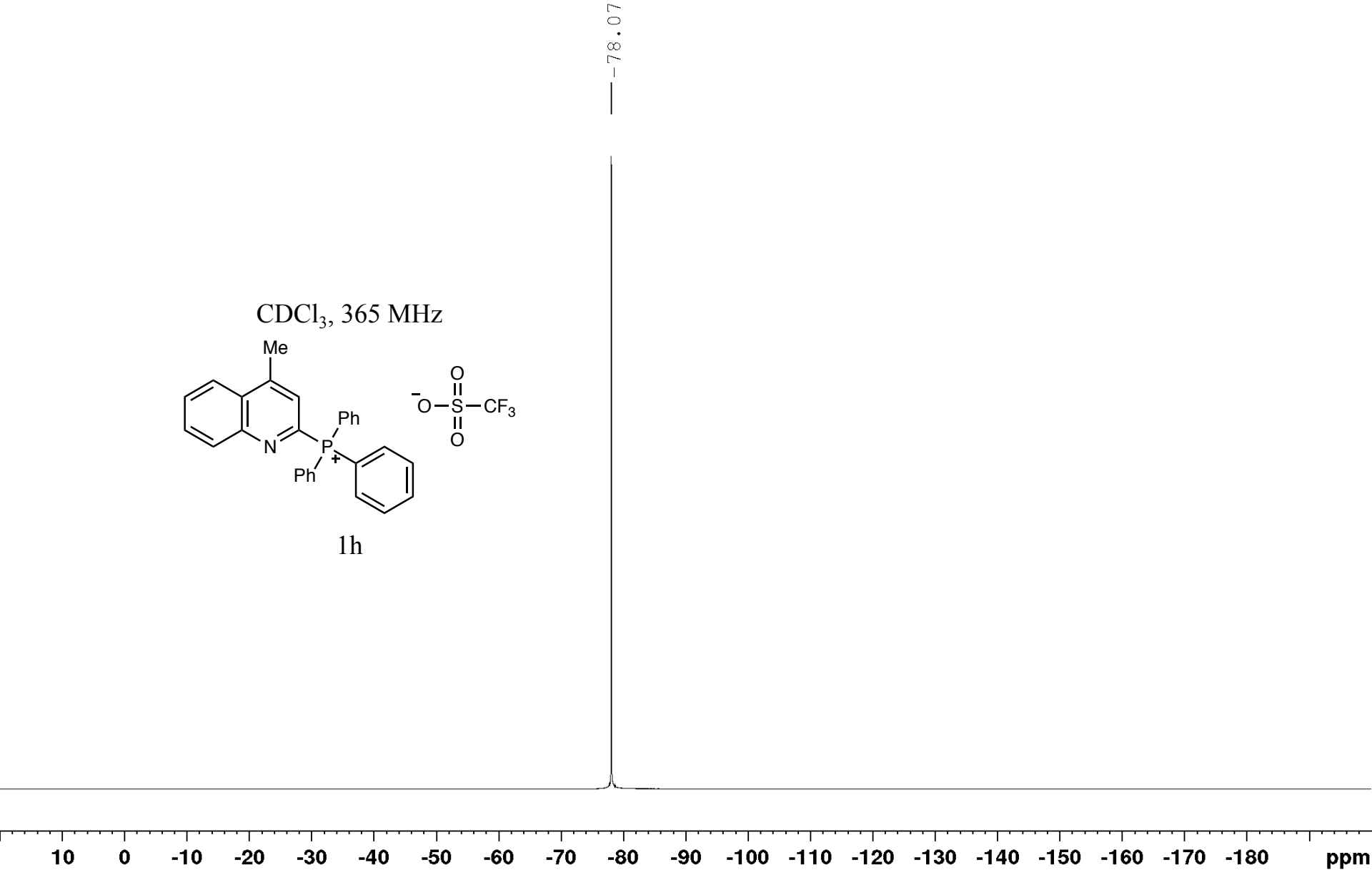
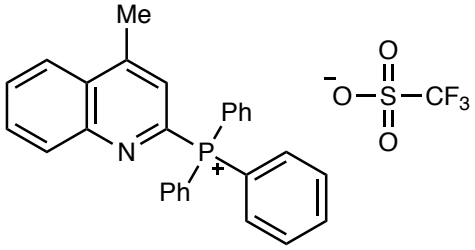
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

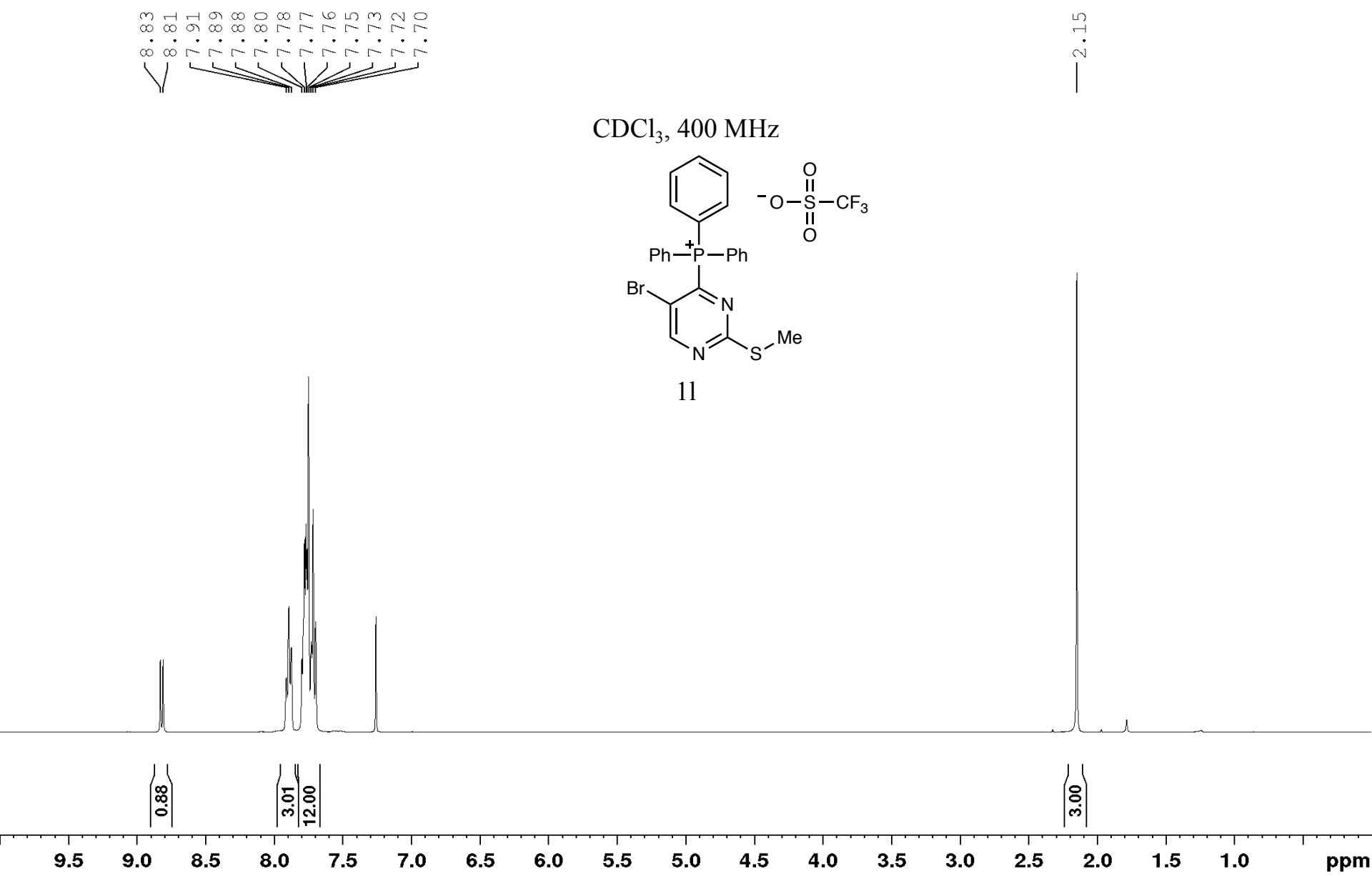

148.61
148.57
148.46
148.38
144.94
143.77
135.64
135.61
134.65
134.55
131.63
130.64
130.62
130.55
130.42
130.39
128.78
128.75
125.28
125.01
124.44
124.42
122.43
119.23
117.74
116.86
77.32
77.20
77.00
76.68
19.19
19.18
CDCl3, 100 MHz
Me
Ph
Ph
N
P
O
S
CF3
1h
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-78.07
CDCl3, 365 MHz
Me
Ph
Ph
N
P
O
S
CF3
1h
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

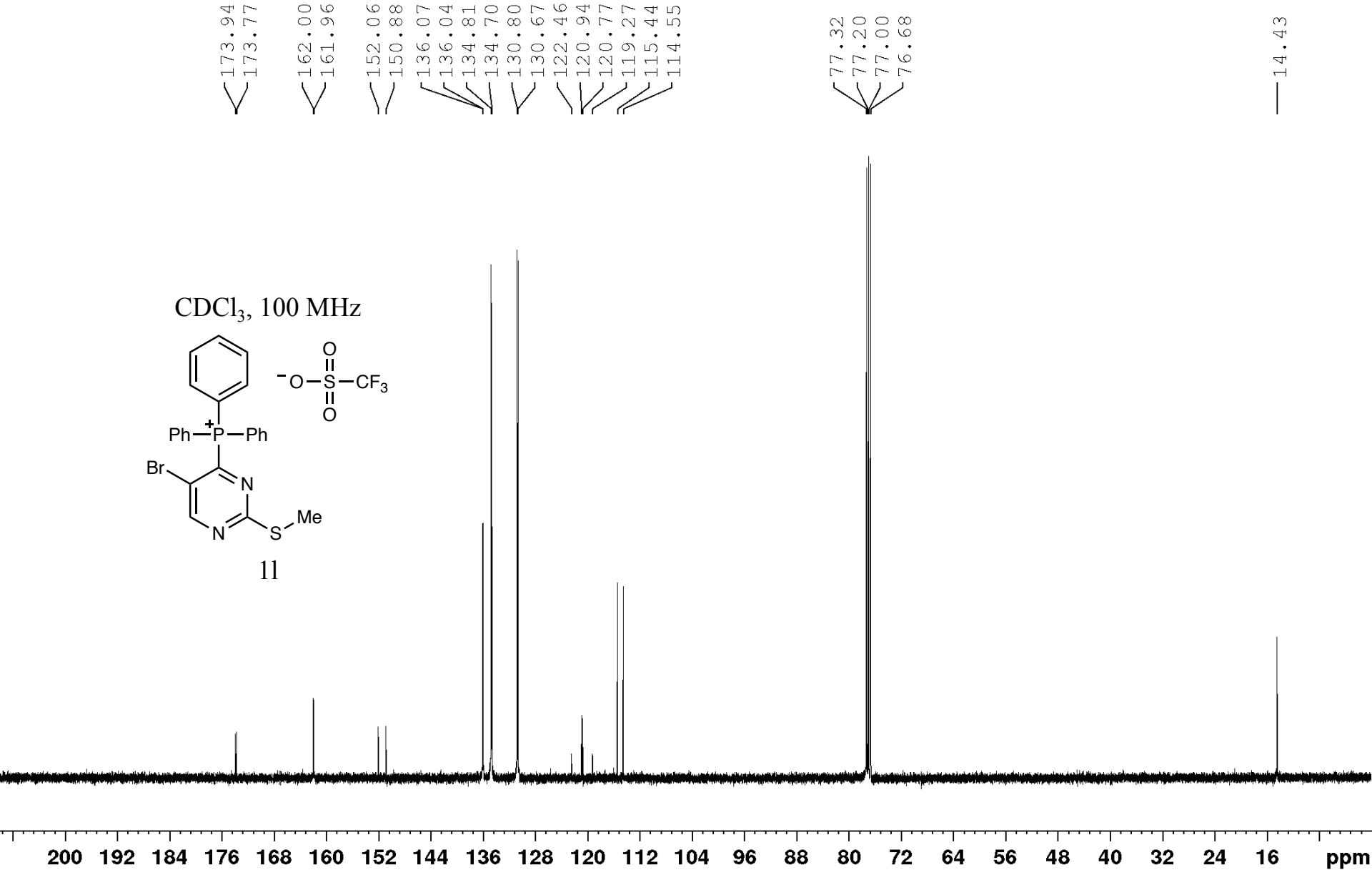


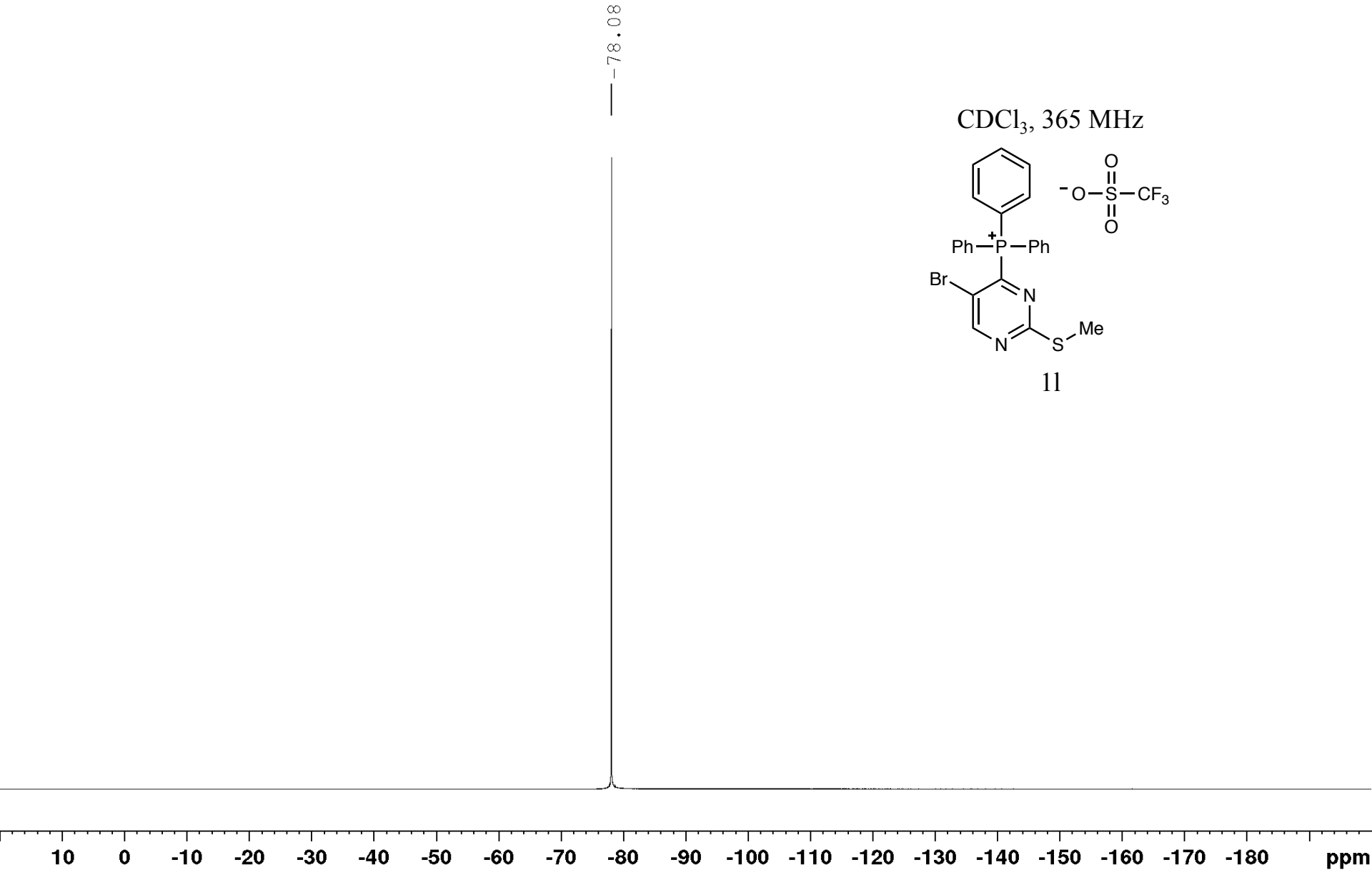
1h



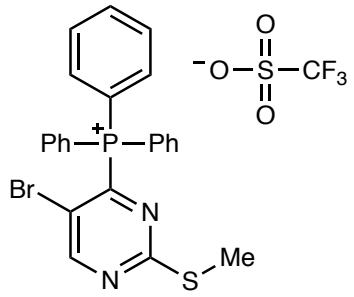
$CDCl_3$, 400 MHz

11

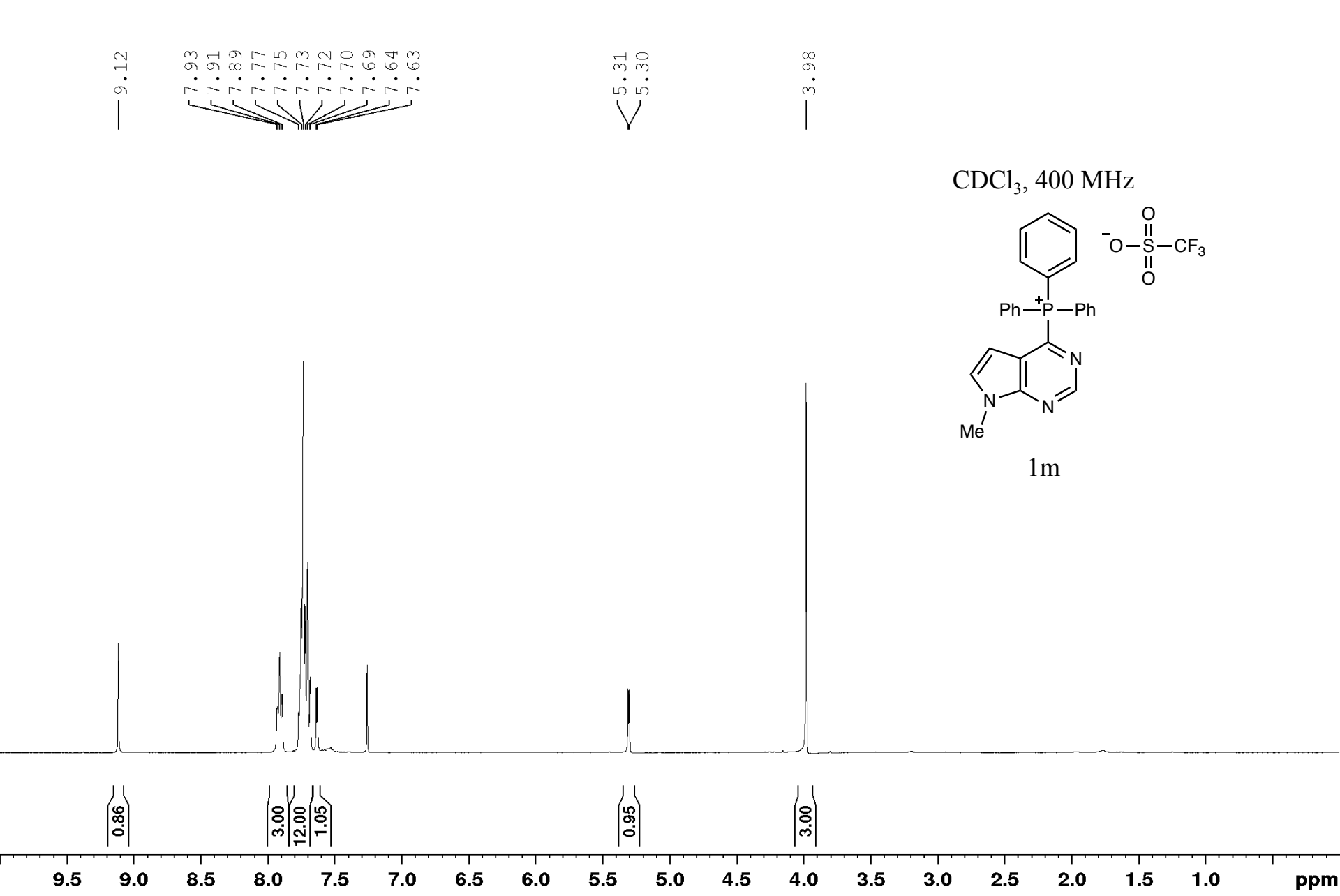

173.94
173.77
162.00
161.96
152.06
150.88
136.07
136.04
134.81
134.70
130.80
130.67
122.46
120.94
120.77
119.27
115.44
114.55
77.32
77.20
77.00
76.68
14.43
CDCl3, 100 MHz
Ph
P
Ph
Br
N
N
S
Me
O
O
S
O
CF3
11
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

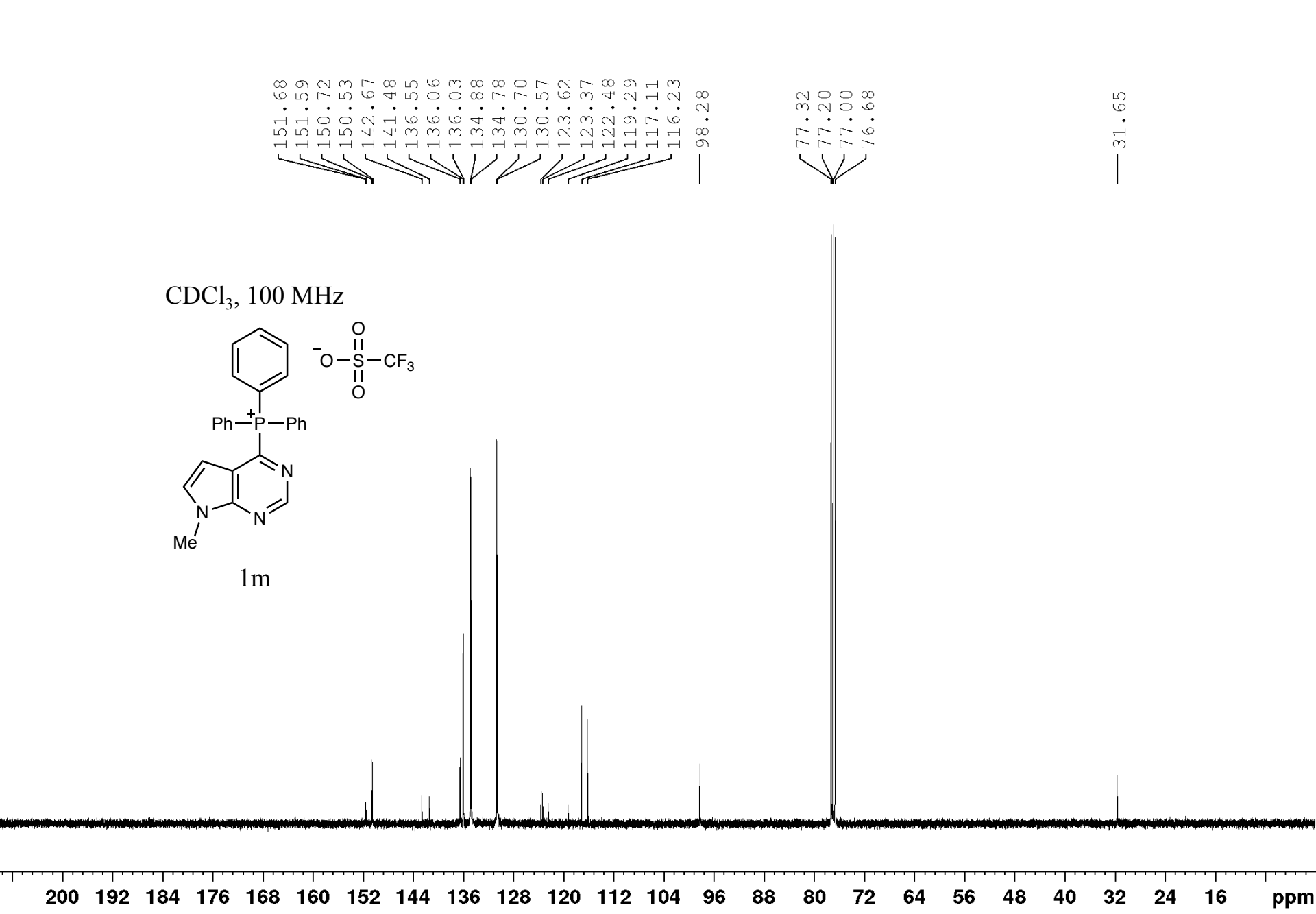

-78.08
CDCl3, 365 MHz
Ph
P
Ph
Br
N
N
S
Me
O
O
O
O
CF3
11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

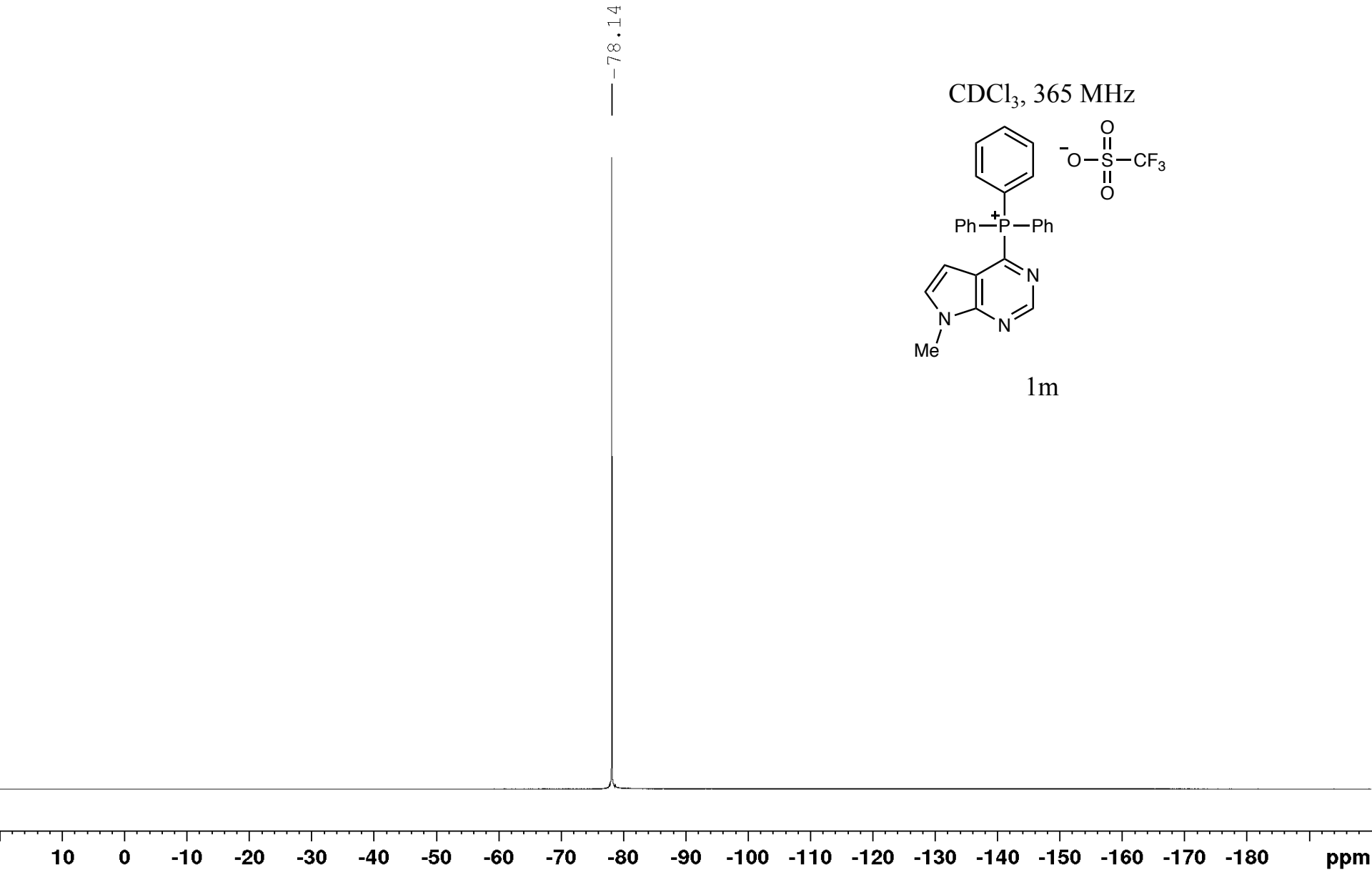
$CDCl_3$, 162 MHz



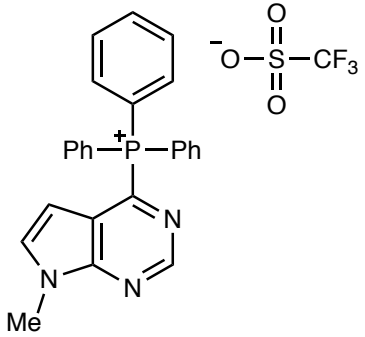
11


9.12
7.93
7.91
7.89
7.77
7.75
7.73
7.72
7.70
7.69
7.64
7.63
5.31
5.30
3.98
CDCl3, 400 MHz
Ph
P
Ph
O
O
S
CF3
O
N
N
N
Me
1m
0.86
3.00
12.00
1.05
0.95
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

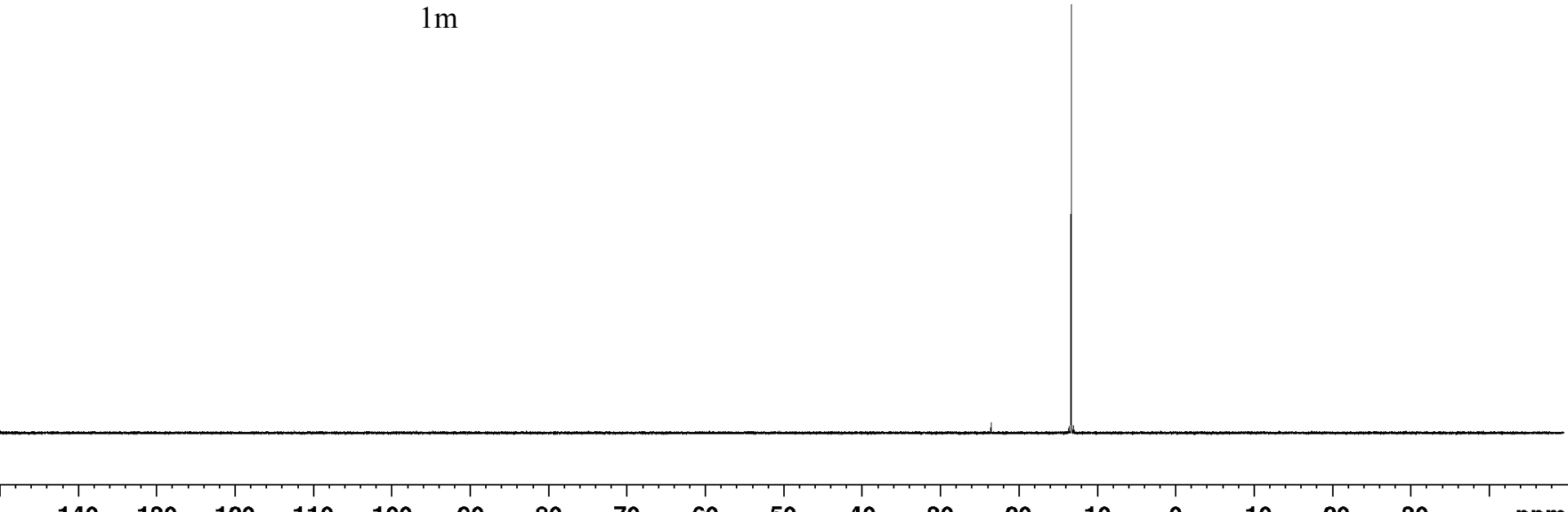

151.68
151.59
150.72
150.53
142.67
141.48
136.55
136.06
136.03
134.88
134.78
130.70
130.57
123.62
123.37
122.48
119.29
117.11
116.23
98.28
77.32
77.20
77.00
76.68
31.65
CDCl3, 100 MHz
Ph
P
Ph
N
N
N
Me
O
S
CF3
1m
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

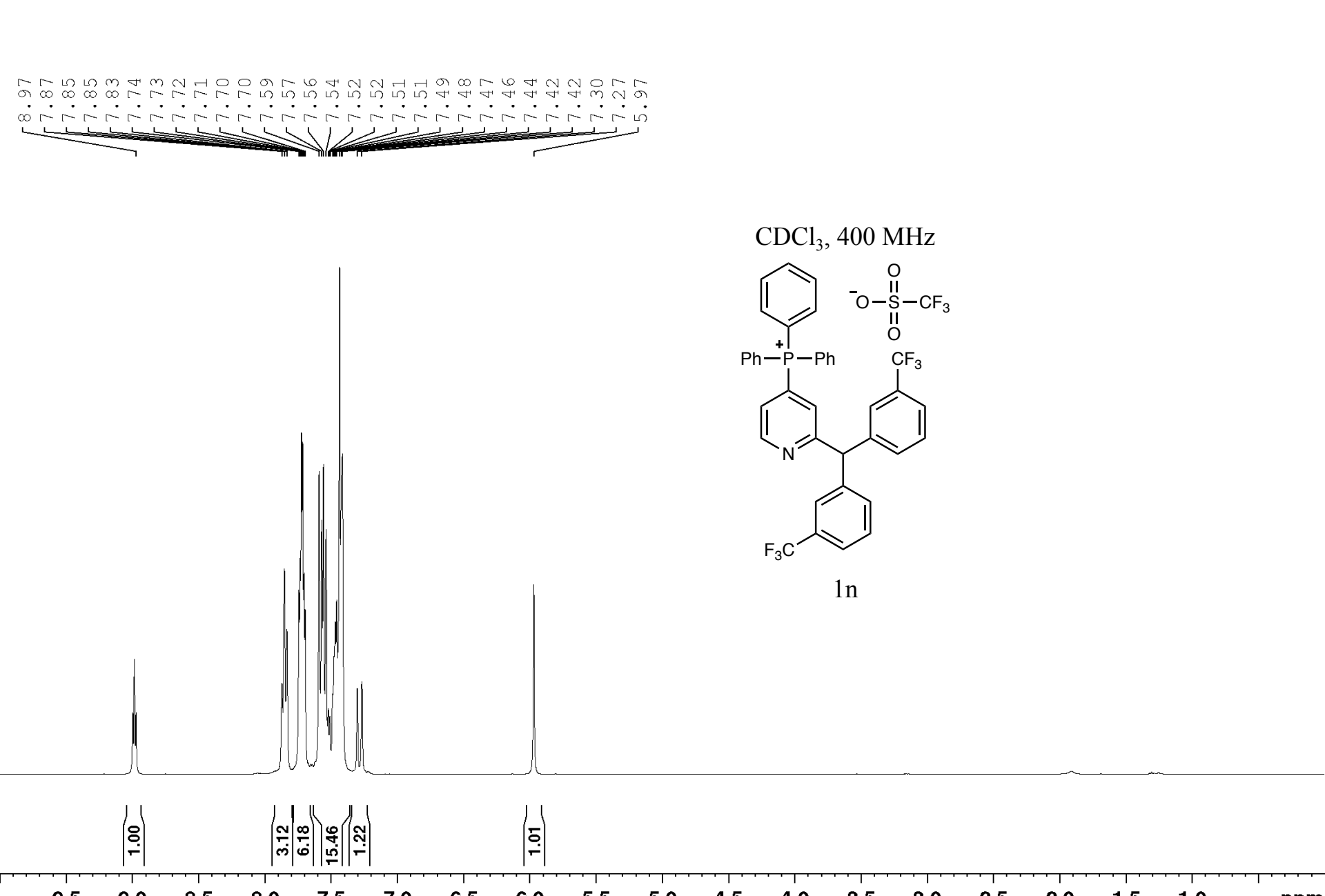

-78.14
CDCl3, 365 MHz
Ph
P
Ph
N
N
N
Me
O
O
S
CF3
O
1m
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

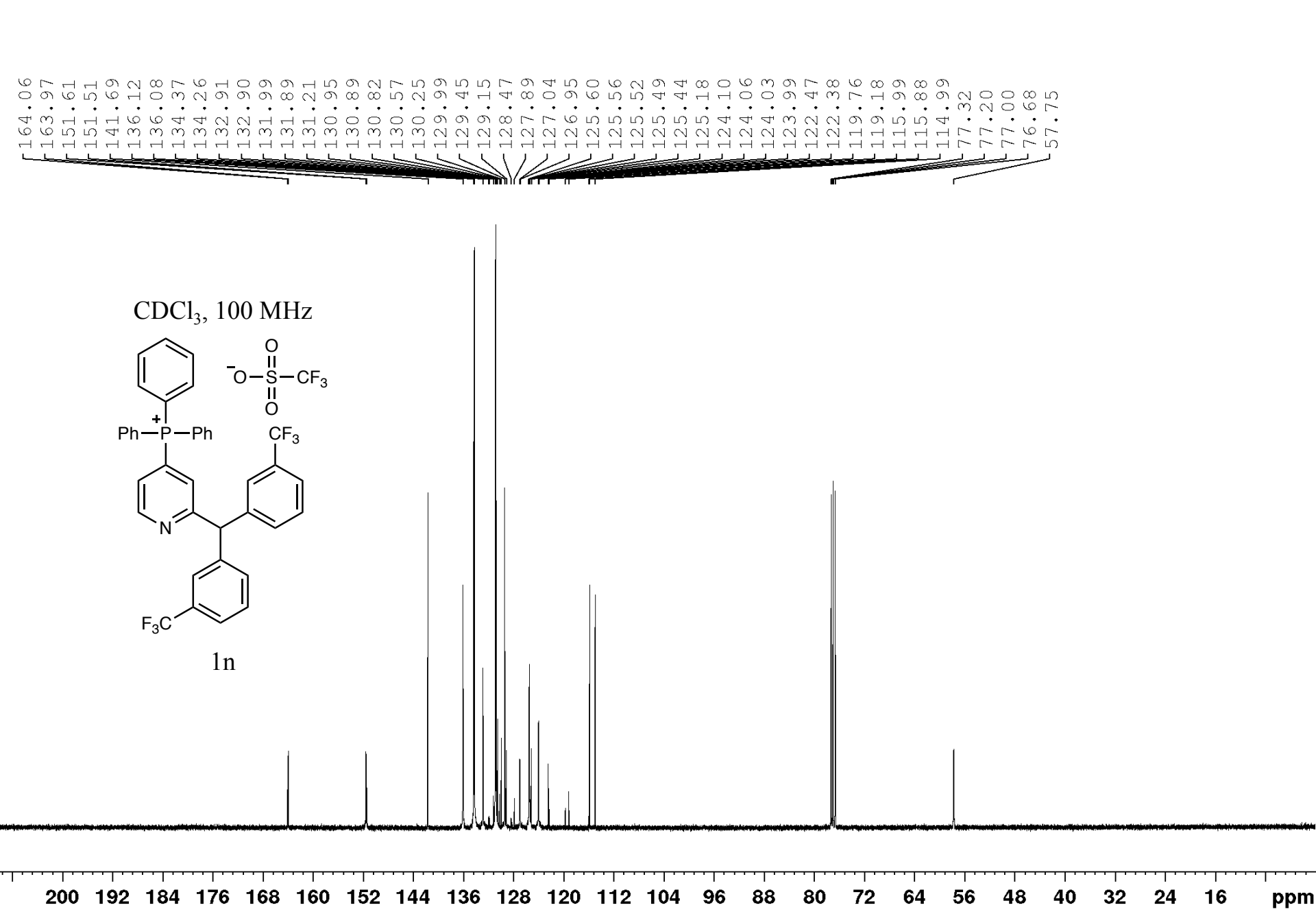
$CDCl_3$, 162 MHz



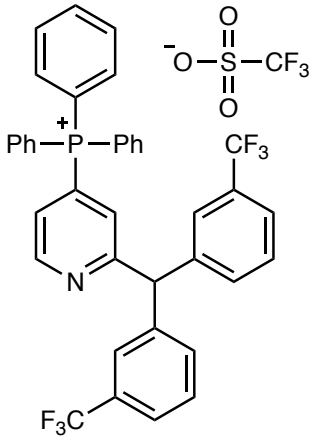
1m



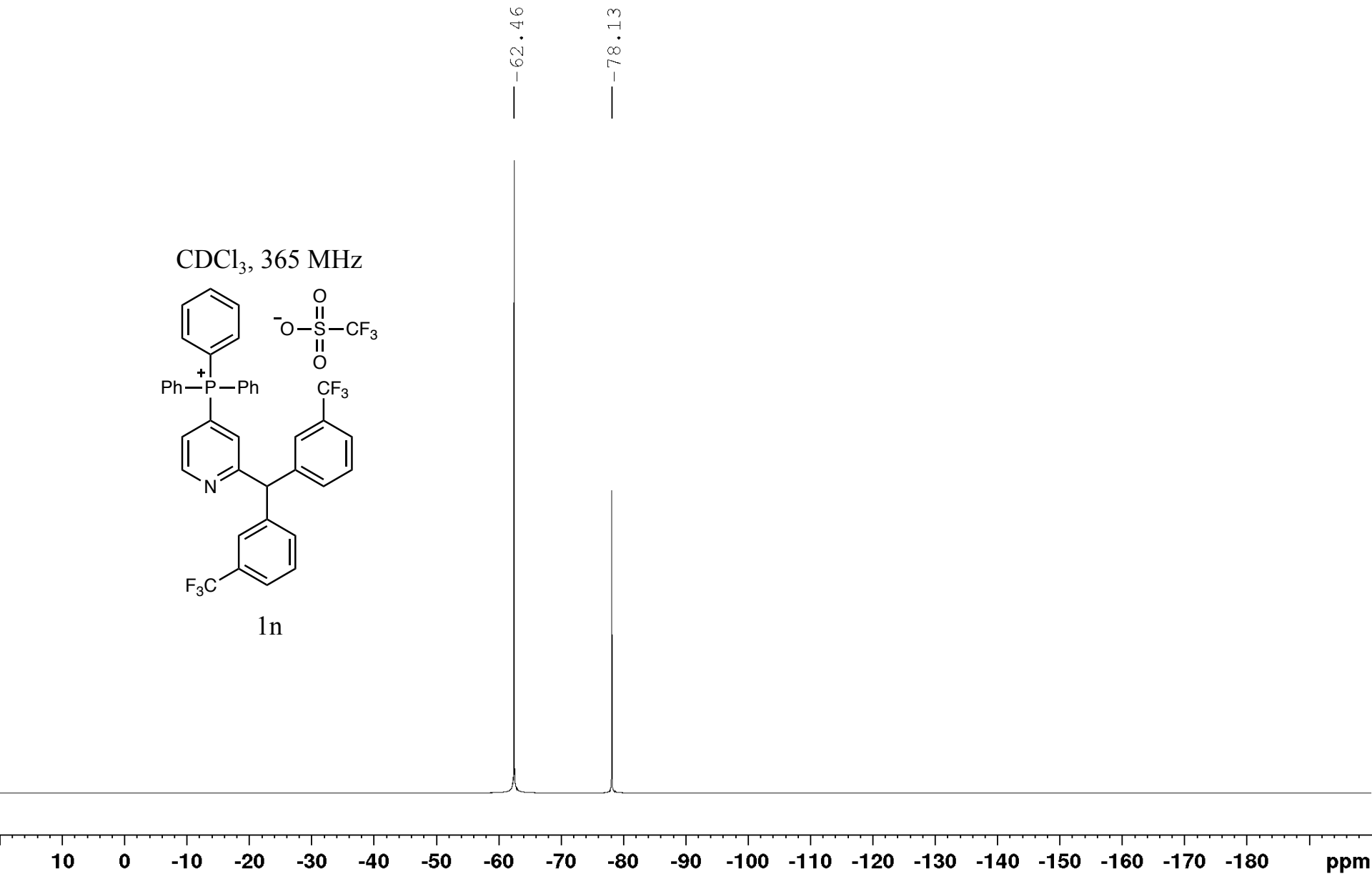

8.97
7.87
7.85
7.85
7.83
7.74
7.73
7.72
7.71
7.70
7.70
7.59
7.57
7.56
7.54
7.52
7.52
7.51
7.51
7.49
7.48
7.47
7.46
7.44
7.42
7.42
7.30
7.27
5.97
CDCl3, 400 MHz
Ph—P—Ph
CF3
F3C
N
O—S—CF3
1n
1.00
3.12
6.18
15.46
1.22
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


164.06
163.97
151.61
151.51
141.69
136.12
136.08
134.37
134.26
132.91
132.90
131.99
131.89
131.21
130.95
130.89
130.82
130.57
130.25
129.99
129.45
129.15
128.47
127.89
127.04
126.95
125.60
125.56
125.52
125.49
125.44
125.18
124.10
124.06
124.03
123.99
122.47
122.38
119.76
119.18
115.99
115.88
114.99
77.32
77.20
77.00
76.68
57.75
CDCl3, 100 MHz
1n
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

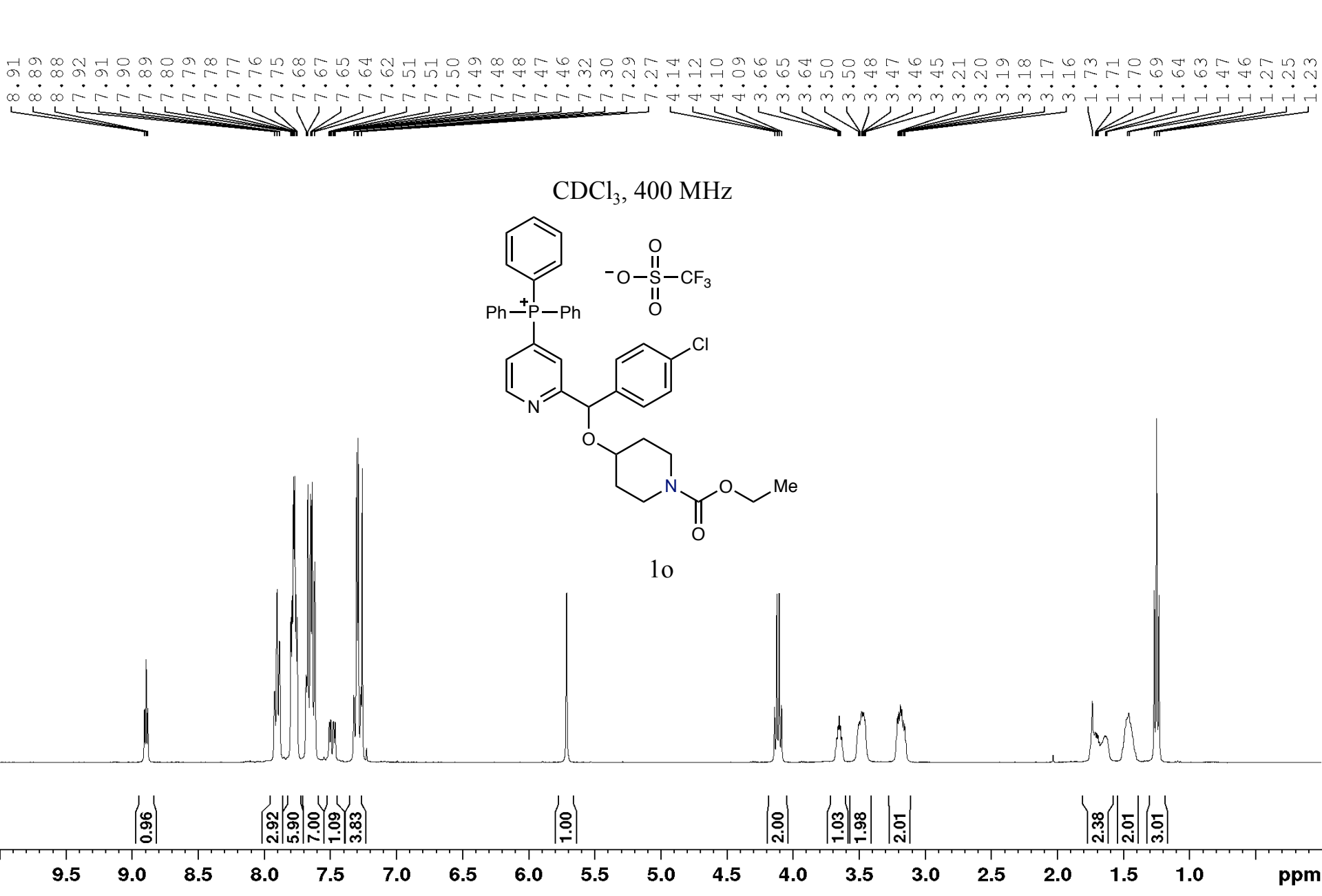
$CDCl_3$, 162 MHz



1n

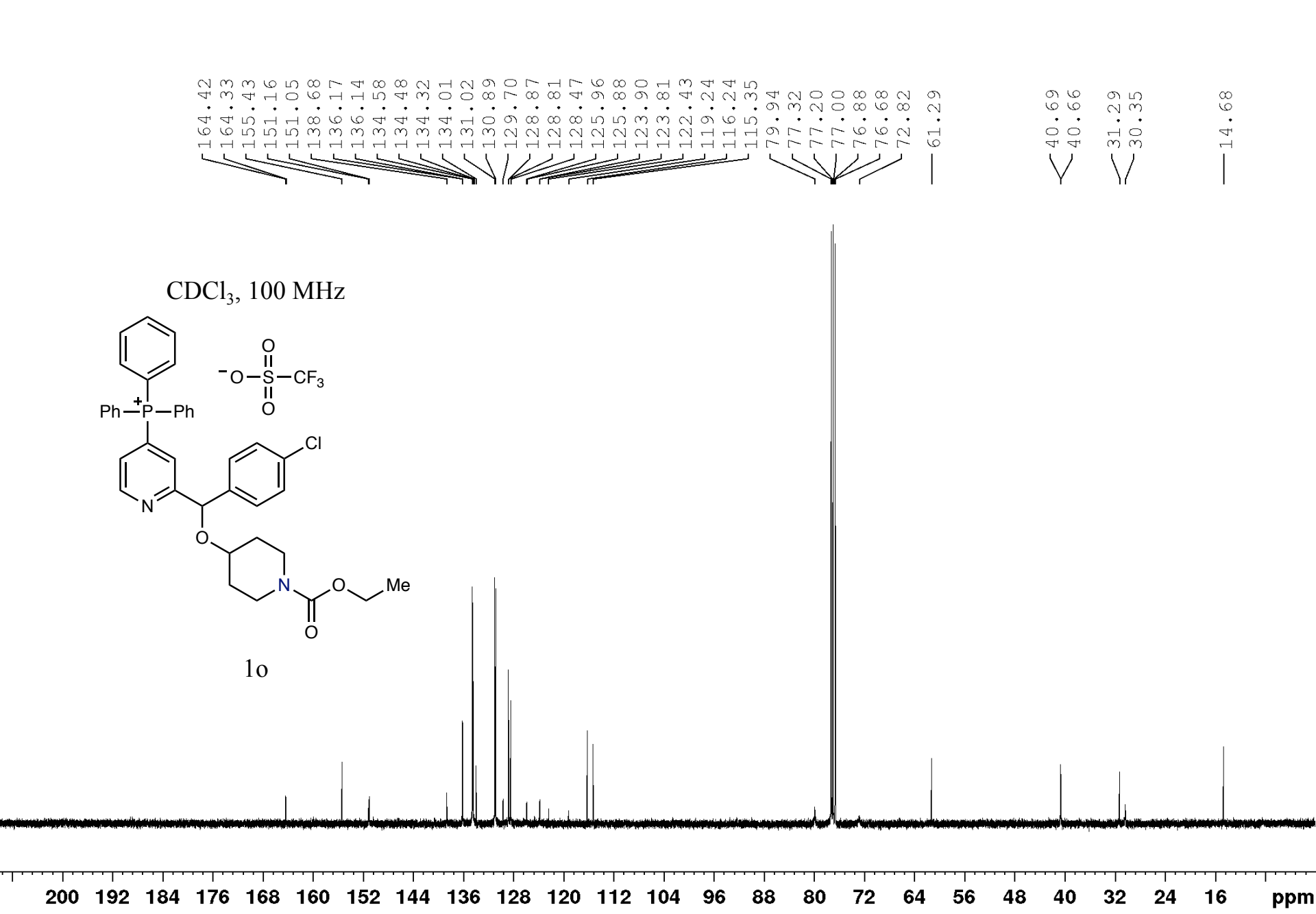

-62.46
-78.13
CDCl3, 365 MHz
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

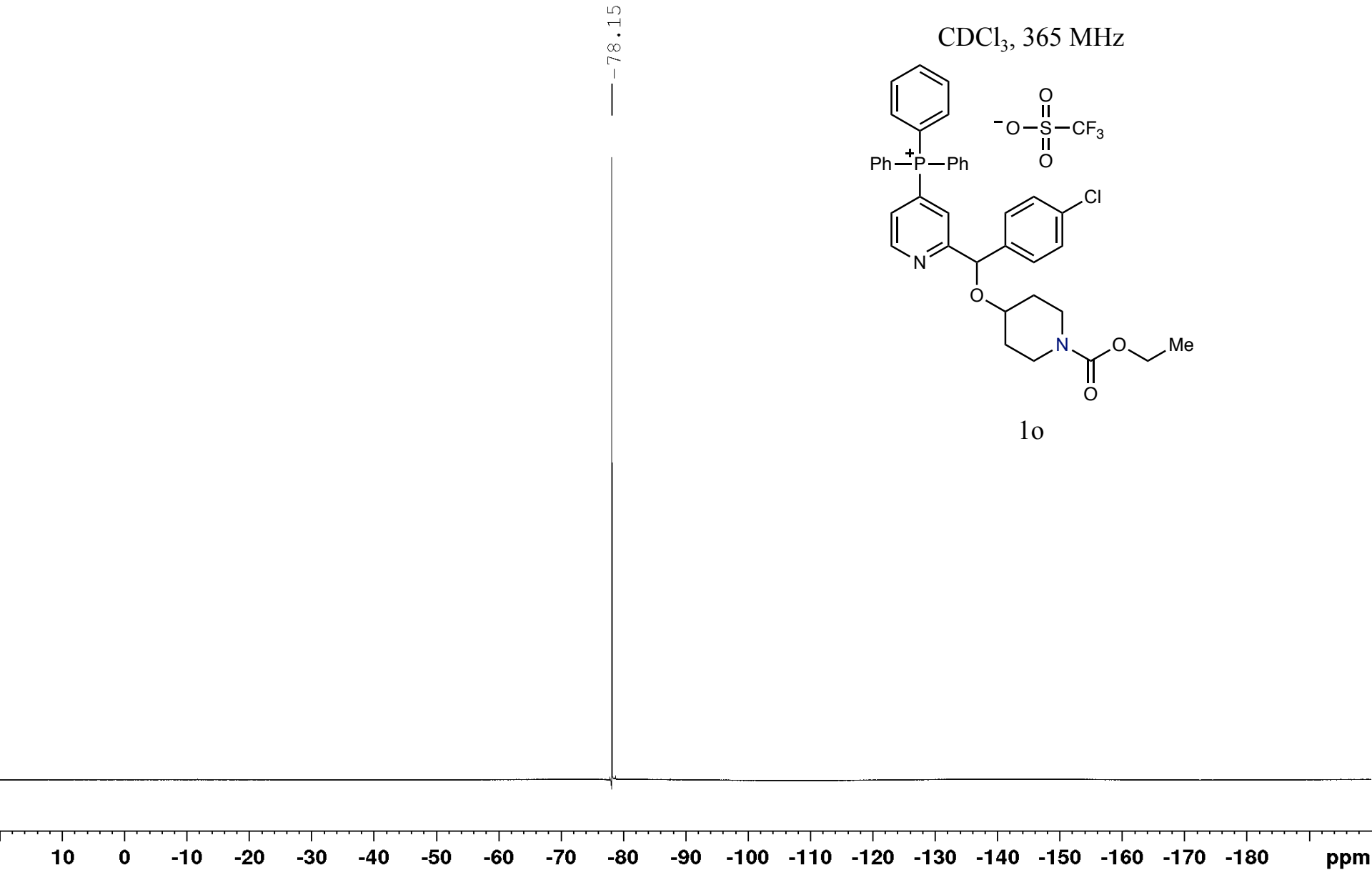
1n



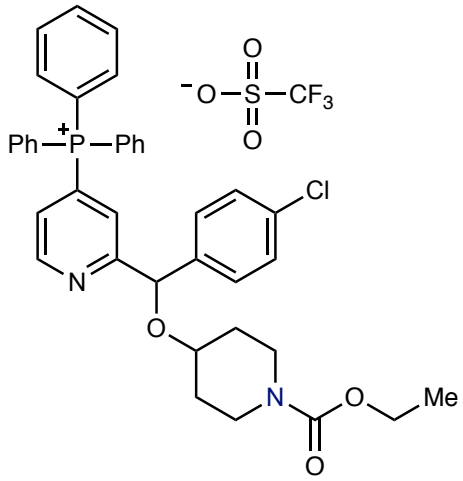
$CDCl_3$, 400 MHz

1o

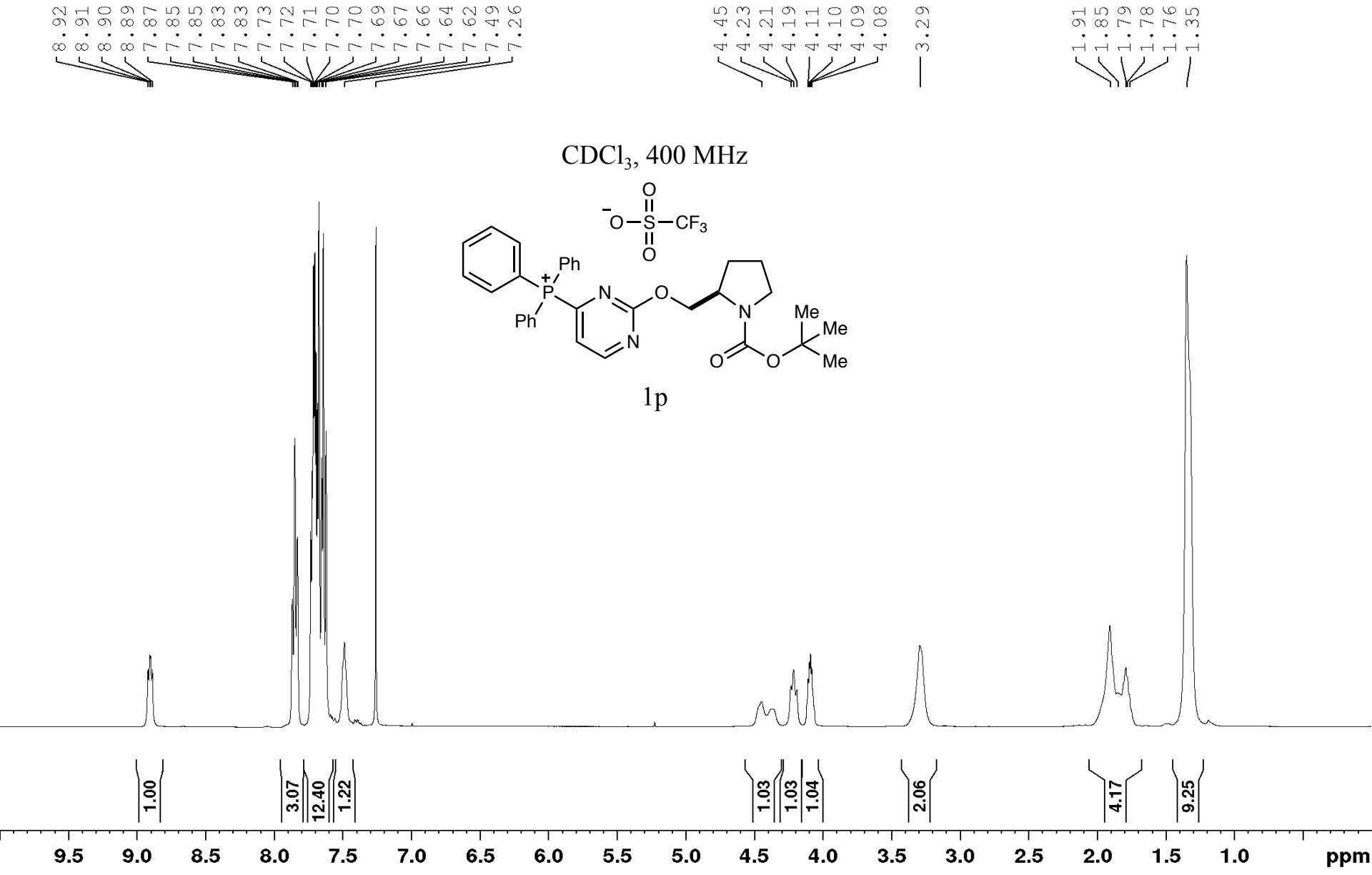

164.42
164.33
155.43
151.16
151.05
138.68
136.17
136.14
134.58
134.48
134.32
134.01
131.02
130.89
129.70
128.87
128.81
128.47
125.96
125.88
123.90
123.81
122.43
119.24
116.24
115.35
79.94
77.32
77.20
77.00
76.88
76.68
72.82
61.29
40.69
40.66
31.29
30.35
14.68
CDCl3, 100 MHz
Ph
P
Ph
O
S
CF3
Cl
N
O
N
O
O
Me
1o
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

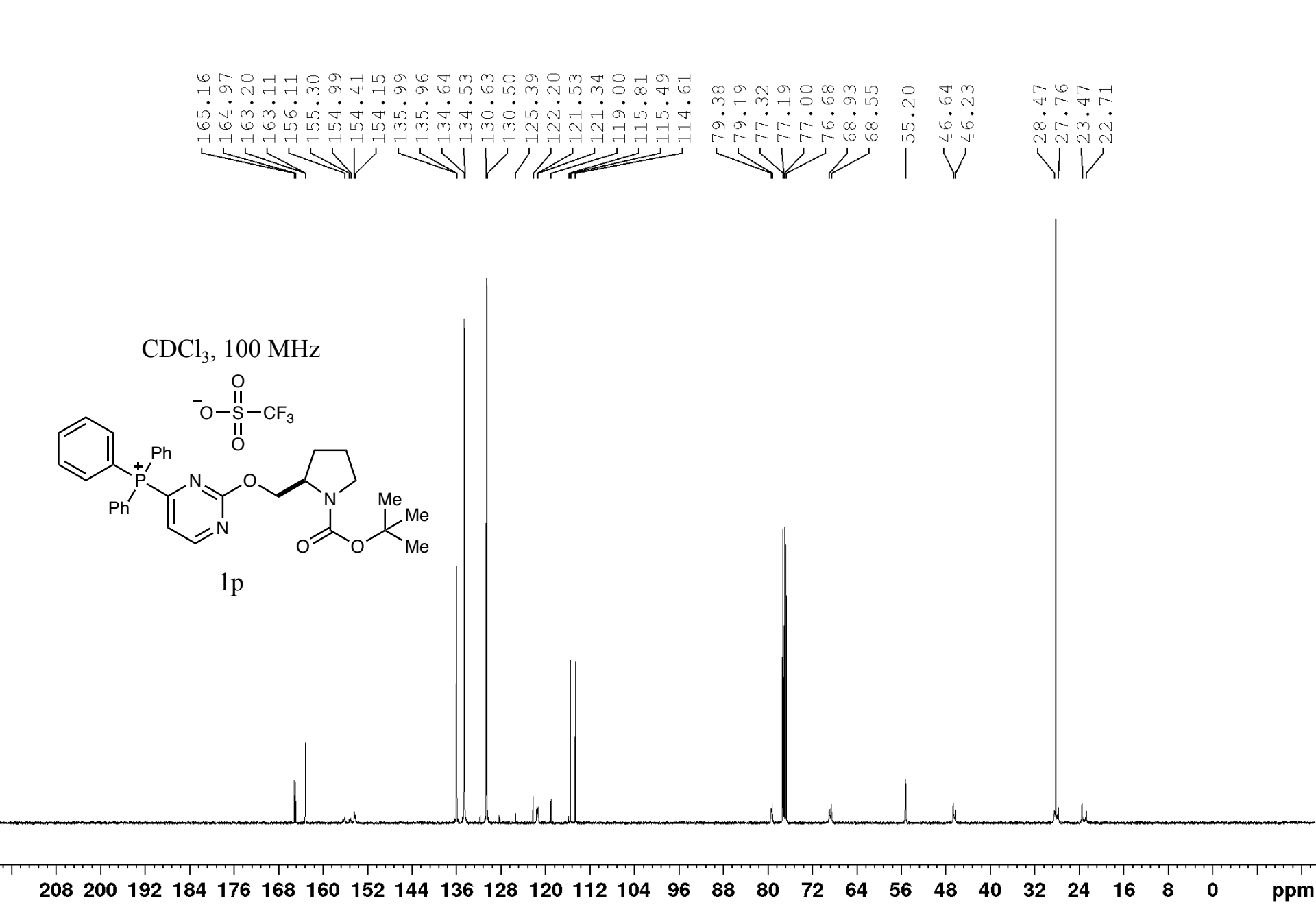

-78.15
CDCl3, 365 MHz
Ph
P
Ph
O
O
S
CF3
Cl
N
O
N
O
O
Me
1o
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

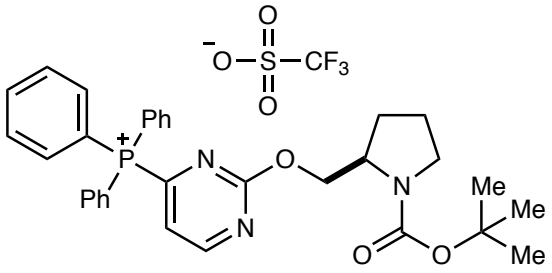


1o


8.92
8.91
8.90
8.89
7.87
7.85
7.85
7.83
7.83
7.73
7.72
7.71
7.70
7.70
7.69
7.67
7.66
7.64
7.62
7.49
7.26
4.45
4.23
4.21
4.19
4.11
4.10
4.09
4.08
3.29
1.91
1.85
1.79
1.78
1.76
1.35
CDCl3, 400 MHz
1p
1.00
3.07
12.40
1.22
1.03
1.03
1.04
2.06
4.17
9.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


165.16
164.97
163.20
163.11
156.11
155.30
154.99
154.41
154.15
135.99
135.96
134.64
134.53
130.63
130.50
125.39
122.20
121.53
121.34
119.00
115.81
115.49
114.61
79.38
79.19
77.32
77.19
77.00
76.68
68.93
68.55
55.20
46.64
46.23
28.47
27.76
23.47
22.71
CDCl3, 100 MHz
1p
208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 ppm

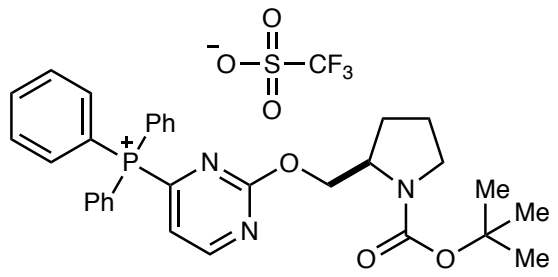
$CDCl_3$, 365 MHz



1p

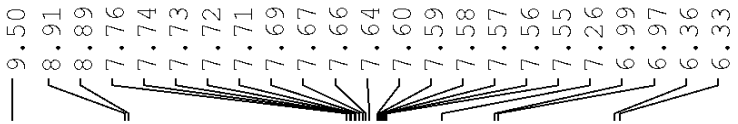
16.10

$CDCl_3$, 162 MHz

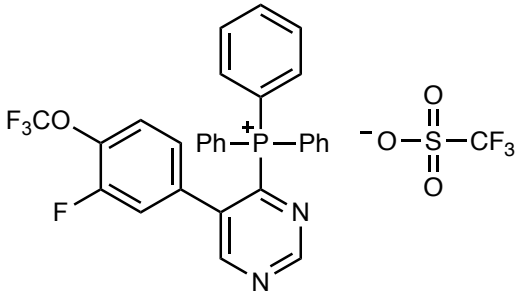


1p

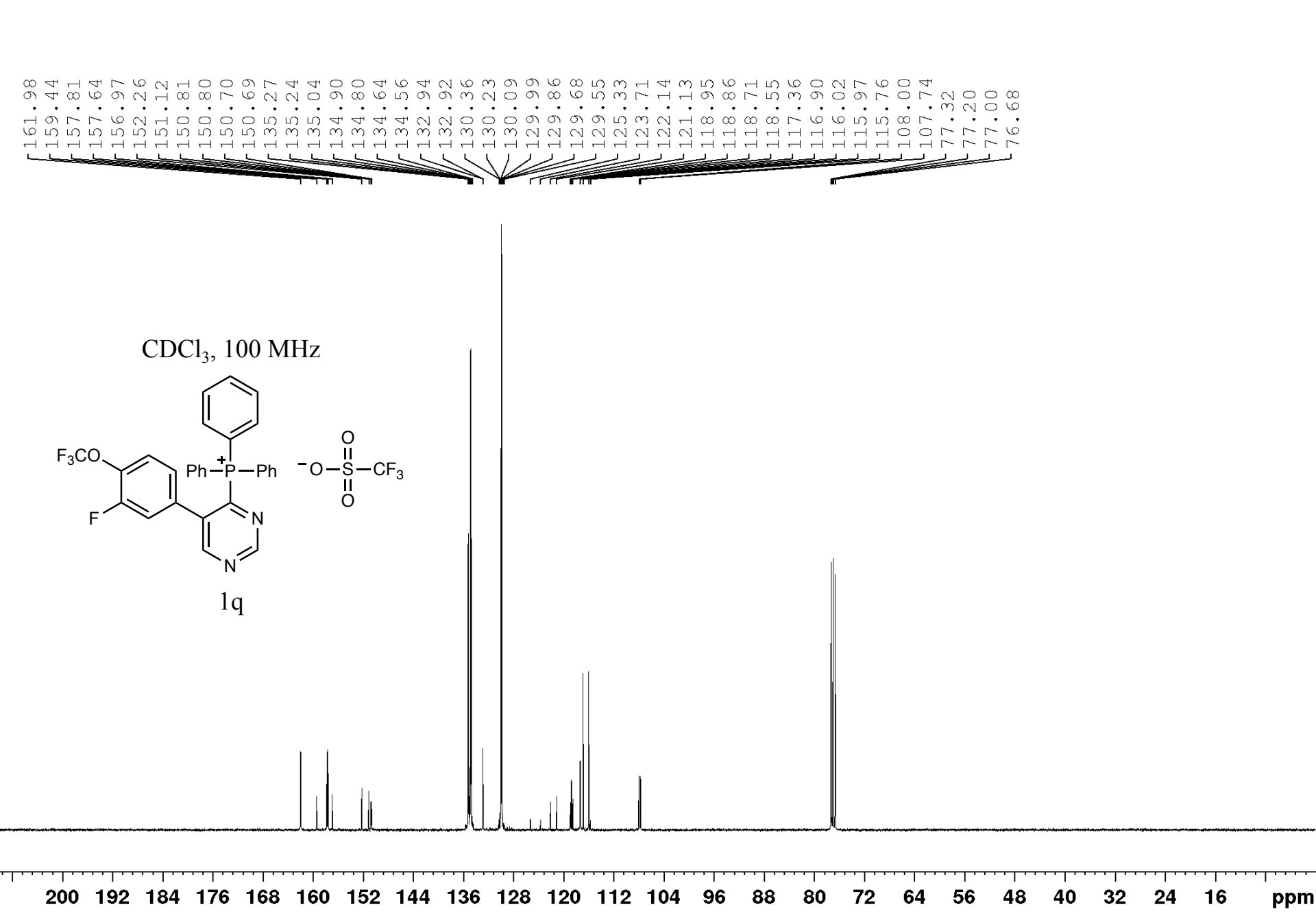
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm



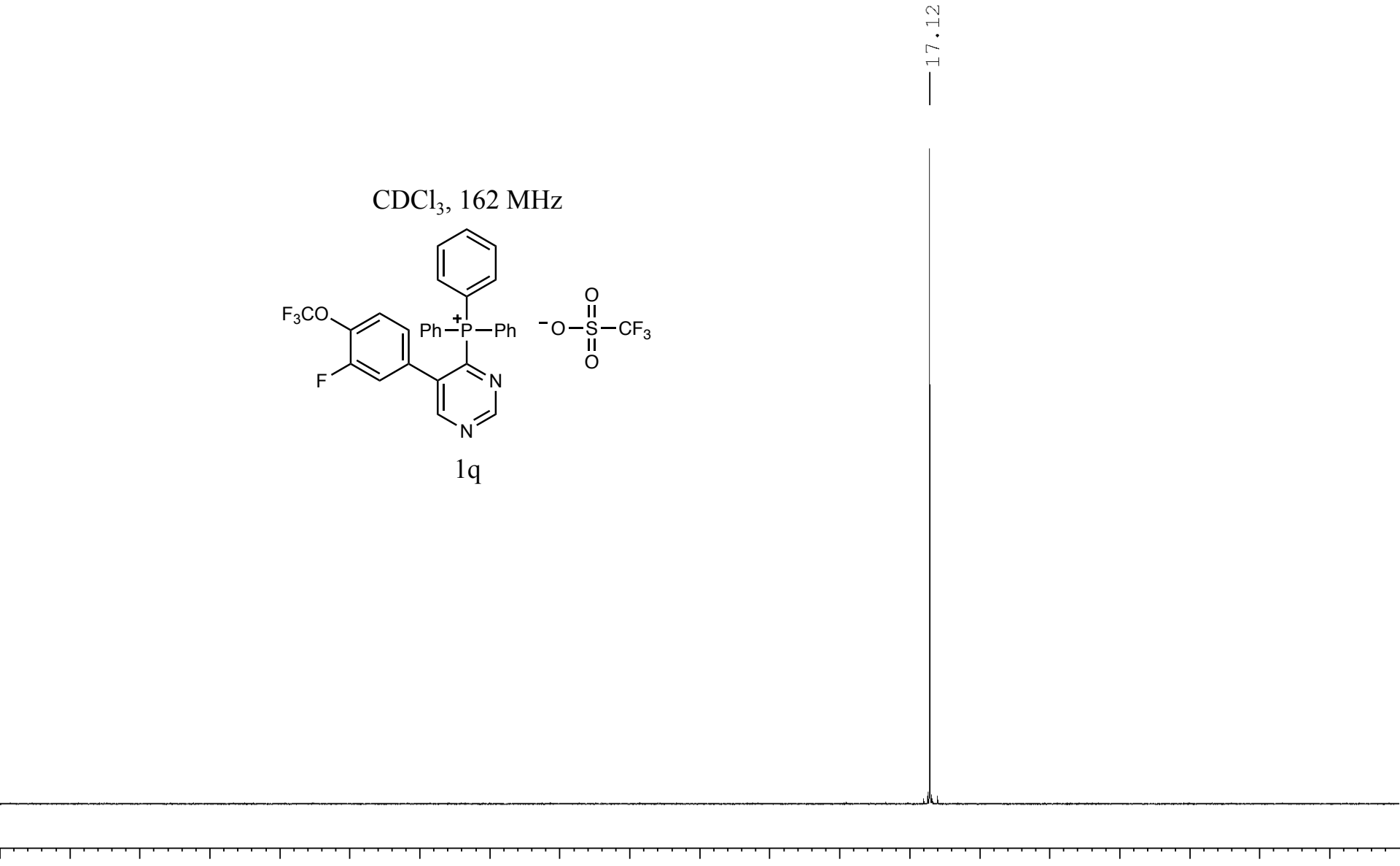
$CDCl_3$, 400 MHz

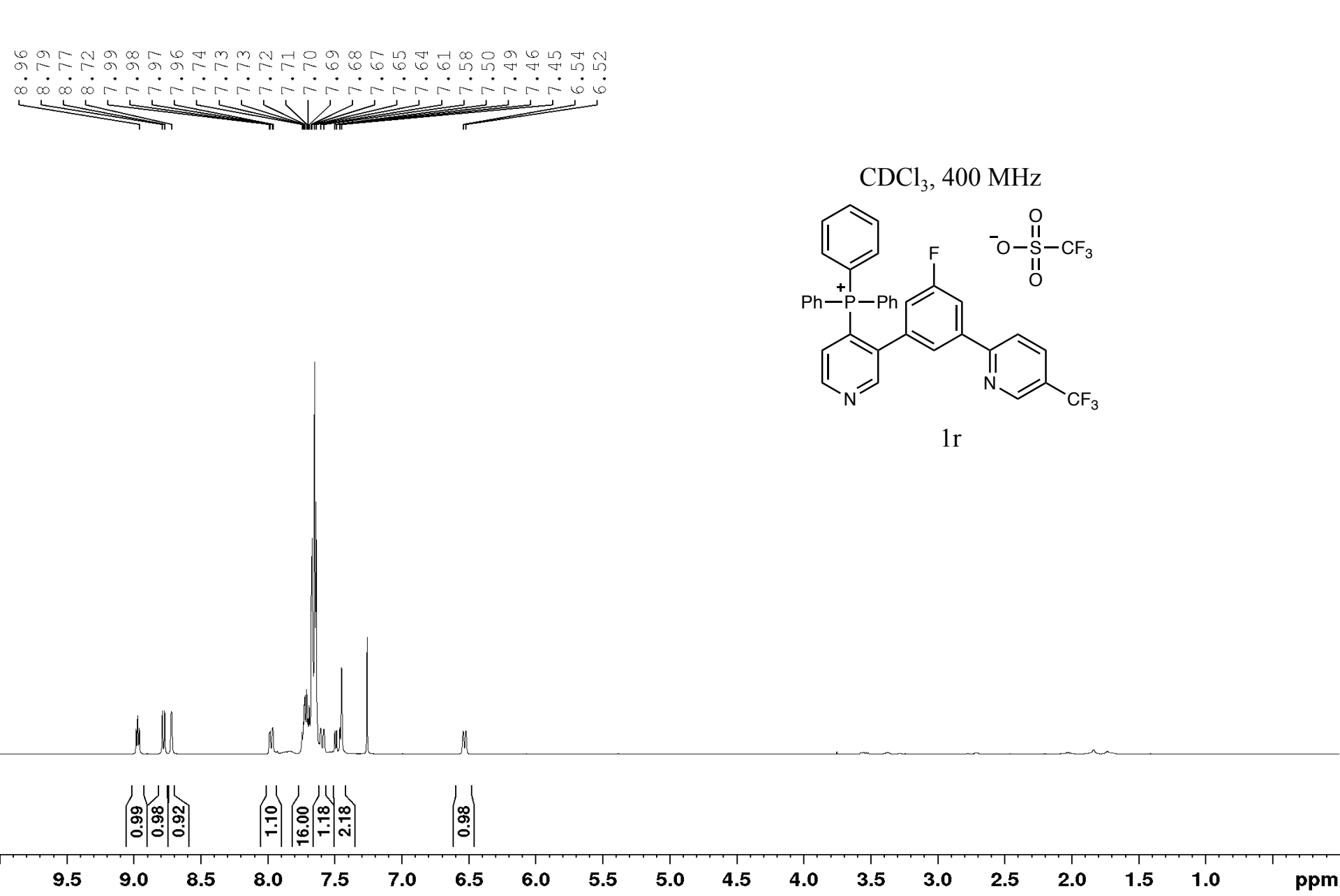


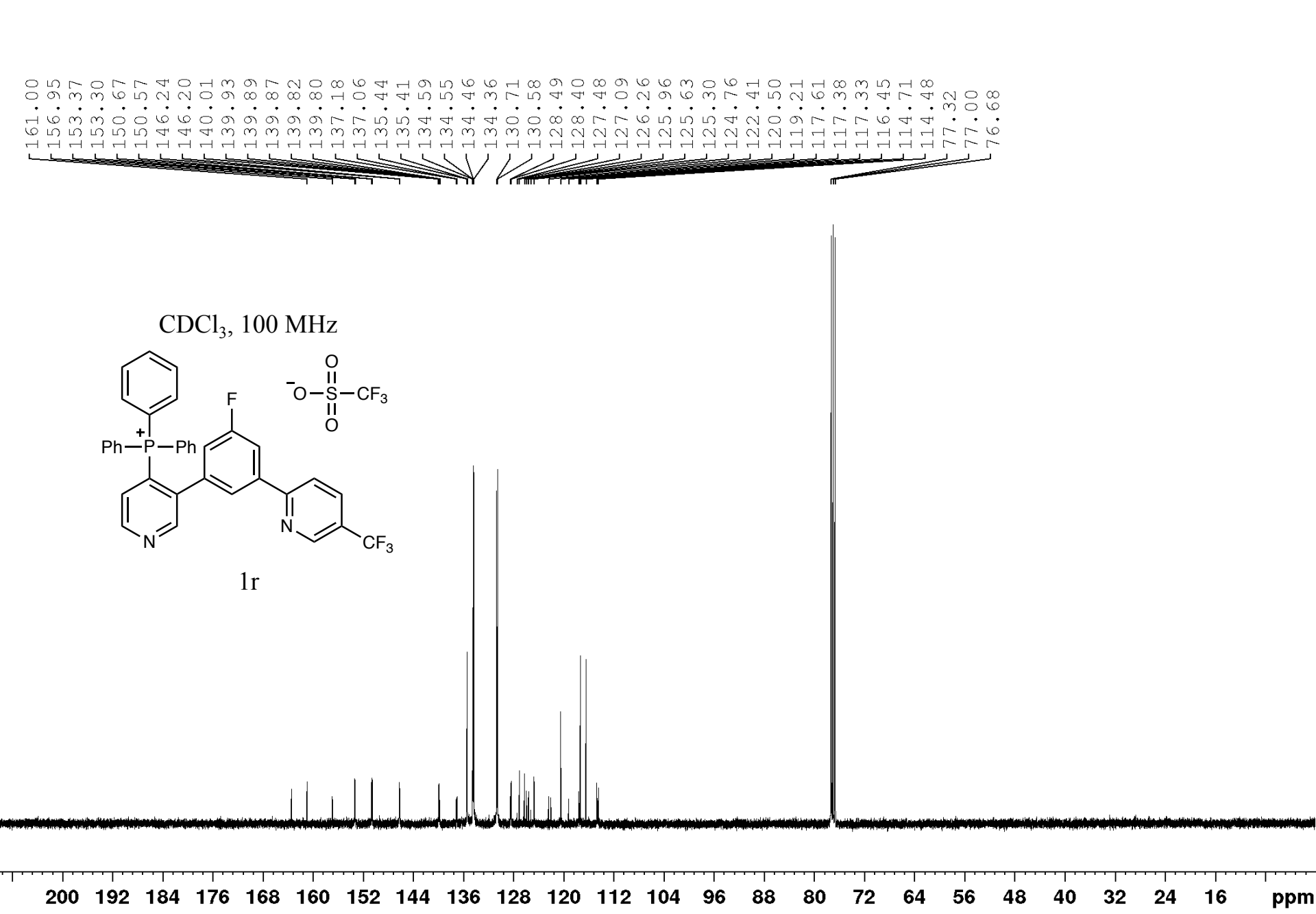
1q

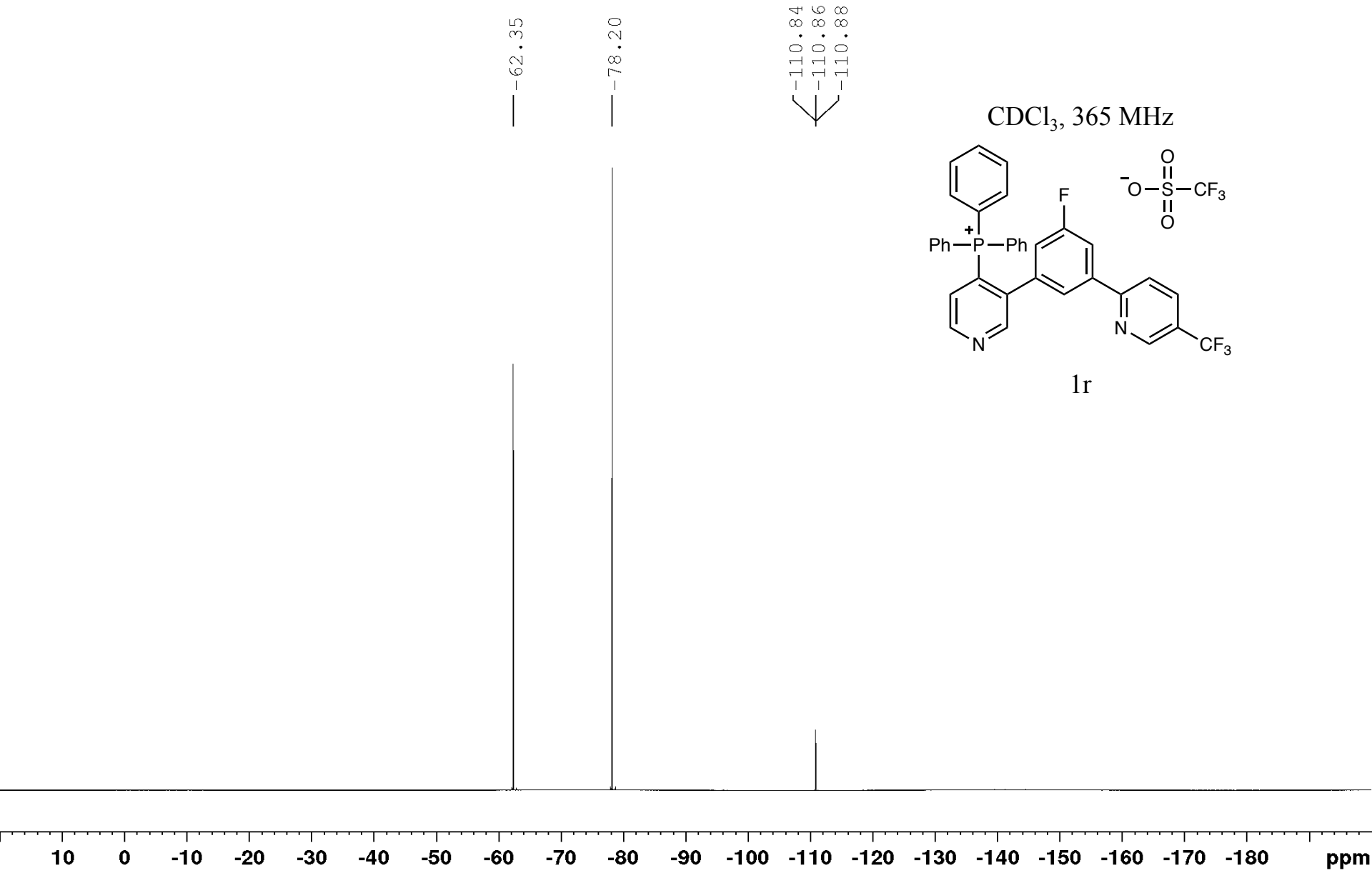

161.98
159.44
157.81
157.64
156.97
152.26
151.12
150.81
150.80
150.70
150.69
135.27
135.24
135.04
134.90
134.80
134.64
134.56
132.94
132.92
130.36
130.23
130.09
129.99
129.86
129.68
129.55
125.33
123.71
122.14
121.13
118.95
118.86
118.71
118.55
117.36
116.90
116.02
115.97
115.76
108.00
107.74
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
F3CO
Ph–P–Ph
O–S–CF3
F
N
N
1q
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-57.70
-78.30
-107.22
-107.25
-107.28
CDCl3, 365 MHz
F3CO
F
Ph
P
Ph
O
S
CF3
N
N
1q
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

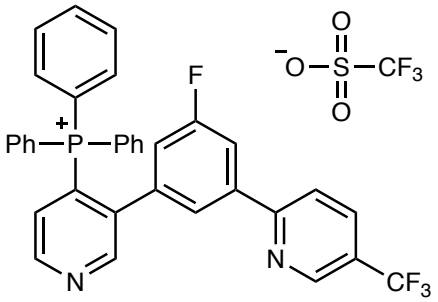

17.12
CDCl3, 162 MHz
F3CO
F
Ph
P
Ph
O
S
CF3
N
N
1q
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


8.96
8.79
8.77
8.72
7.99
7.98
7.97
7.96
7.74
7.73
7.73
7.72
7.71
7.70
7.69
7.68
7.67
7.65
7.64
7.61
7.58
7.50
7.49
7.46
7.45
6.54
6.52
CDCl3, 400 MHz
F
O
O
O
CF3
Ph
P
Ph
N
N
CF3
1r
0.99
0.98
0.92
1.10
16.00
1.18
2.18
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

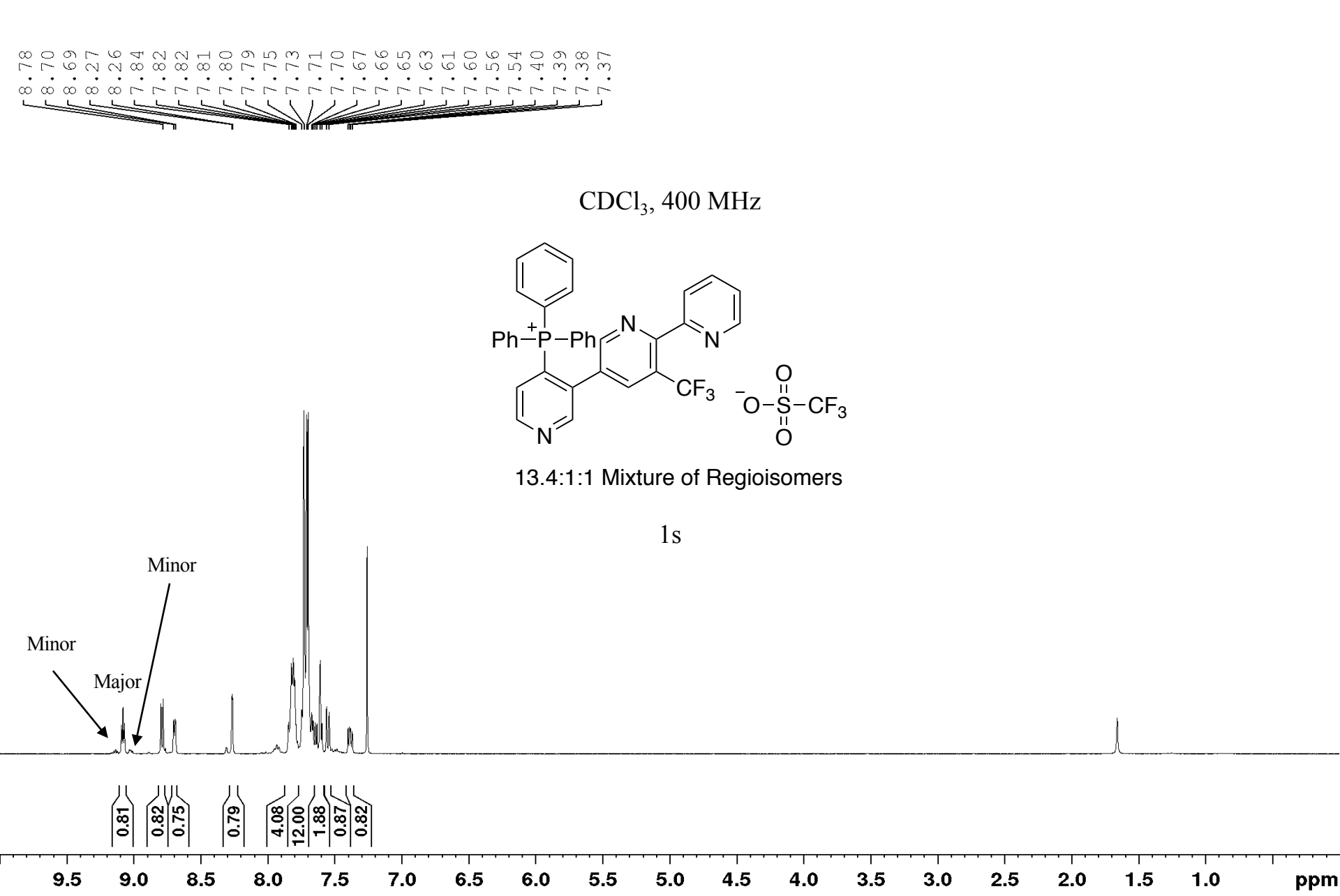

161.00
156.95
153.37
153.30
150.67
150.57
146.24
146.20
140.01
139.93
139.89
139.87
139.82
139.80
137.18
137.06
135.44
135.41
134.59
134.55
134.46
134.36
130.71
130.58
128.49
128.40
127.48
127.09
126.26
125.96
125.63
125.30
124.76
122.41
120.50
119.21
117.61
117.38
117.33
116.45
114.71
114.48
77.32
77.00
76.68
CDCl3, 100 MHz
F
O
O
S
CF3
O
Ph
P
Ph
N
N
CF3
1r
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm


-62.35
-78.20
-110.84
-110.86
-110.88
CDCl3, 365 MHz
Ph
P
Ph
F
O
S
CF3
N
N
CF3
1r
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

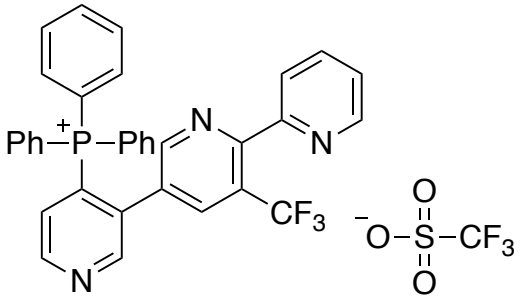


1r


8.78
8.70
8.69
8.27
8.26
7.84
7.82
7.82
7.81
7.80
7.79
7.75
7.73
7.71
7.70
7.67
7.66
7.65
7.63
7.61
7.60
7.56
7.54
7.40
7.39
7.38
7.37
CDCl3, 400 MHz
Ph
P
Ph
N
N
CF3
O
O
S
CF3
O
N
13.4:1:1 Mixture of Regioisomers
1s
Minor
Minor
Major
0.81
0.82
0.75
0.79
4.08
12.00
1.88
0.87
0.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

155.29
153.13
153.06
151.32
151.22
150.97
150.56
148.83
136.40
136.15
135.89
135.83
135.66
135.64
134.31
134.24
134.13
133.83
133.75
130.95
130.81
130.76
130.63
130.50
130.47
130.33
128.77
128.68
127.86
127.03
125.37
124.10
123.77
123.55
123.39
122.17
120.82
118.97
116.63
116.55
115.75
115.67
114.74
77.32
77.20
77.00
76.68

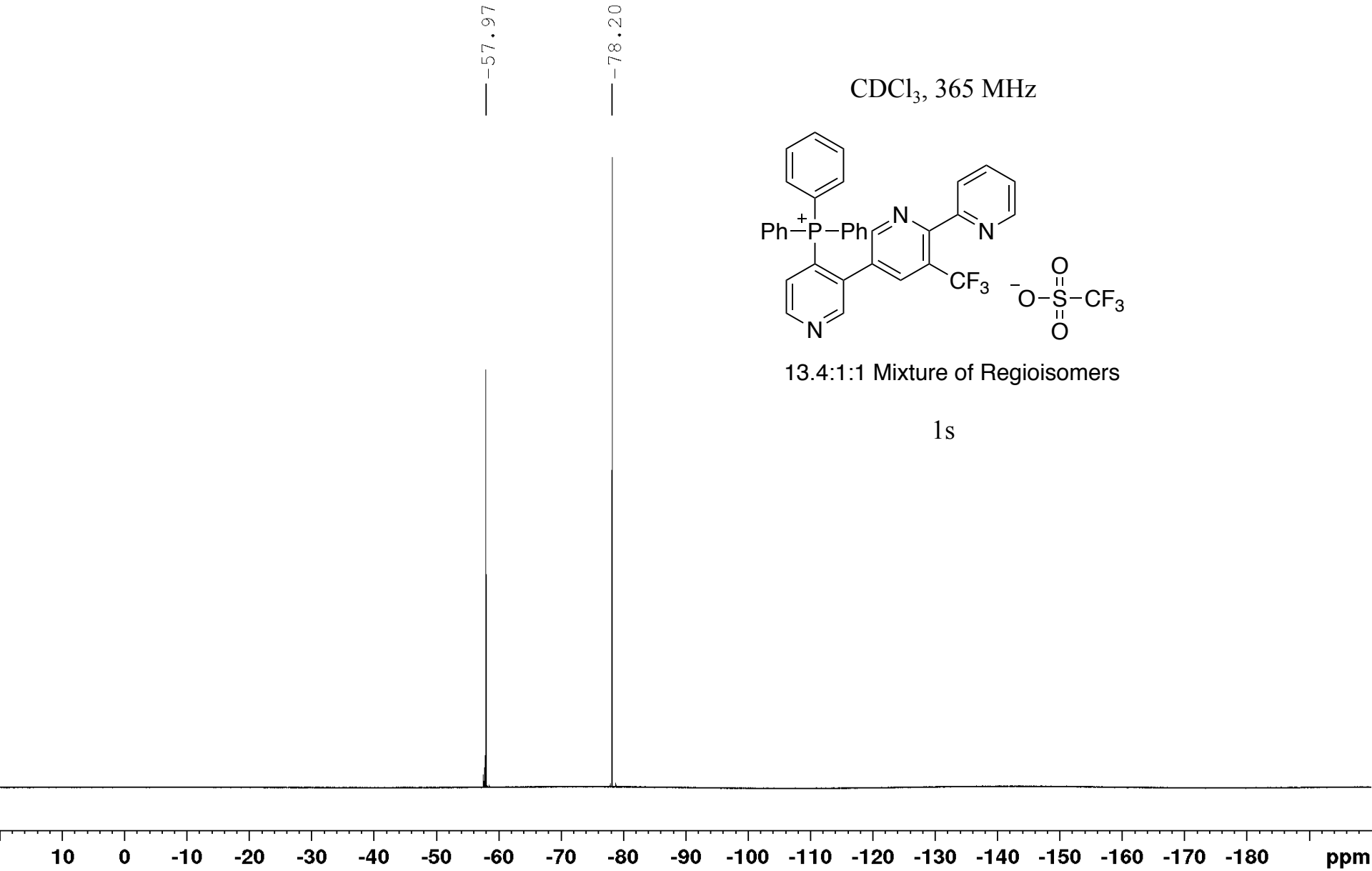
$CDCl_3$, 100 MHz



13.4:1:1 Mixture of Regioisomers

1s

200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

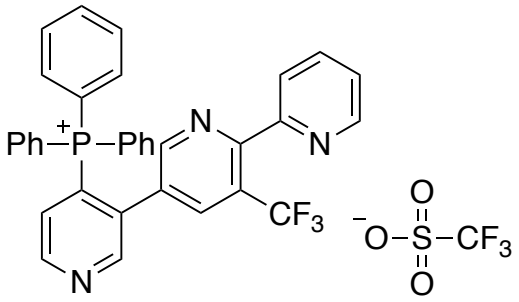


$CDCl_3$, 365 MHz

13.4:1:1 Mixture of Regioisomers

1s

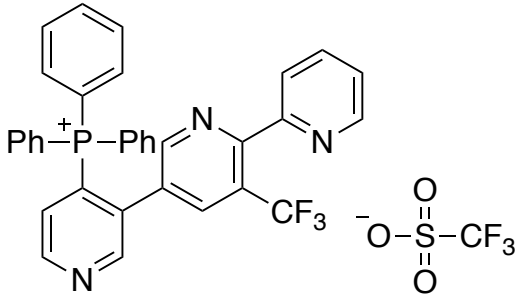
$CDCl_3$, 162 MHz (crude ^{31}P NMR)



9.6:1.3:1 Mixture of Regioisomers

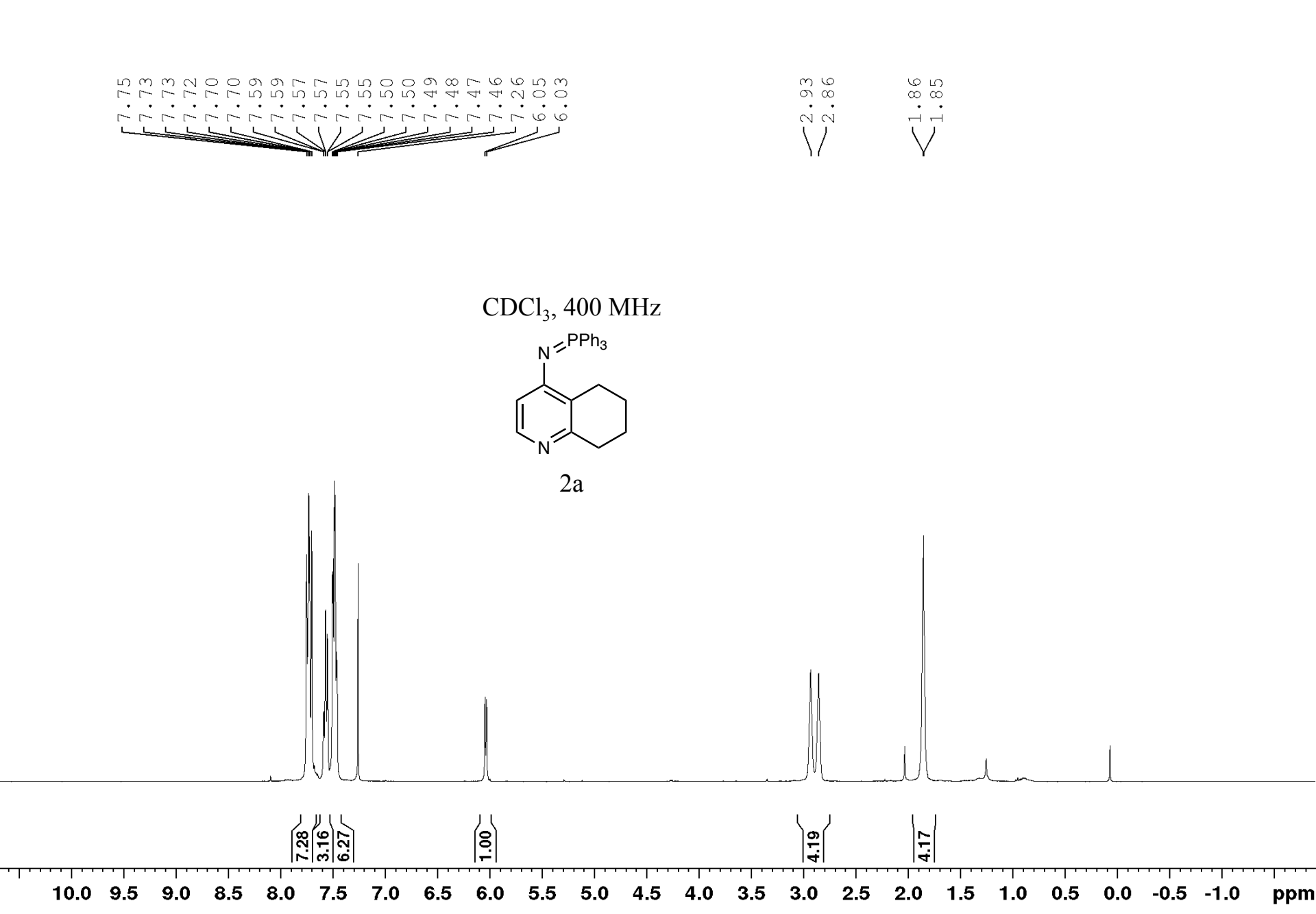
1s

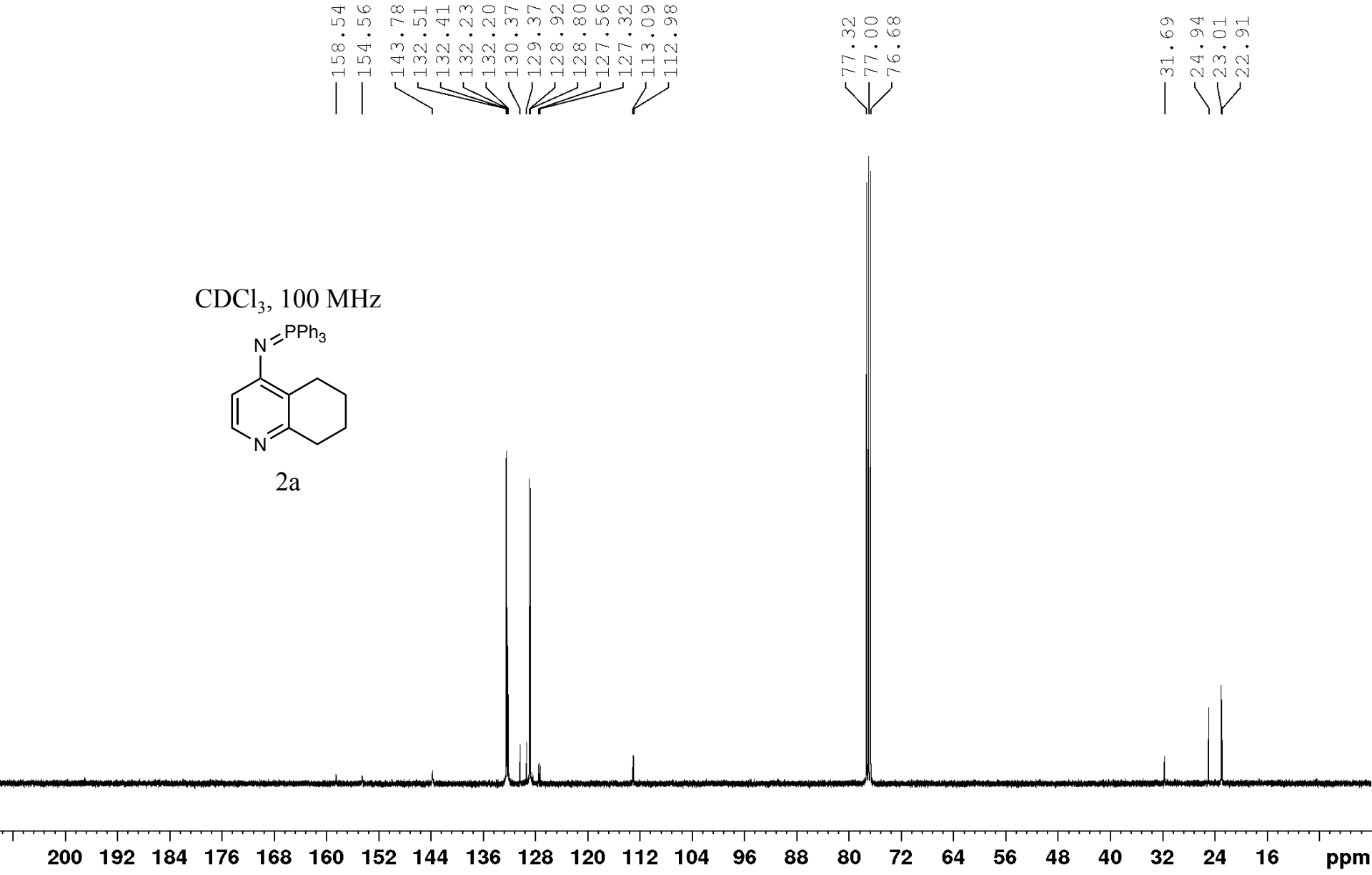
$CDCl_3$, 162 MHz (Post-precipitate ^{31}P NMR)

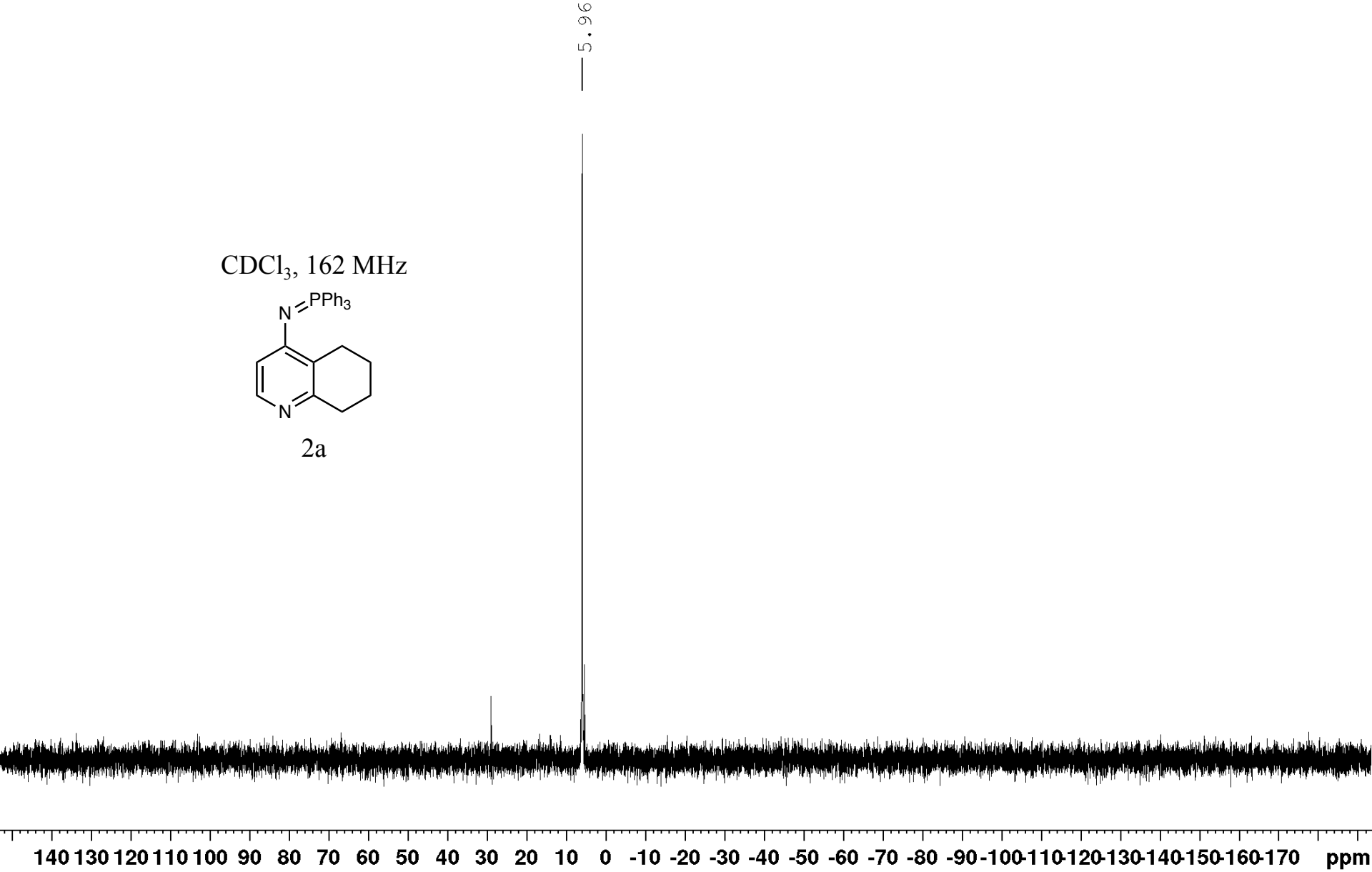


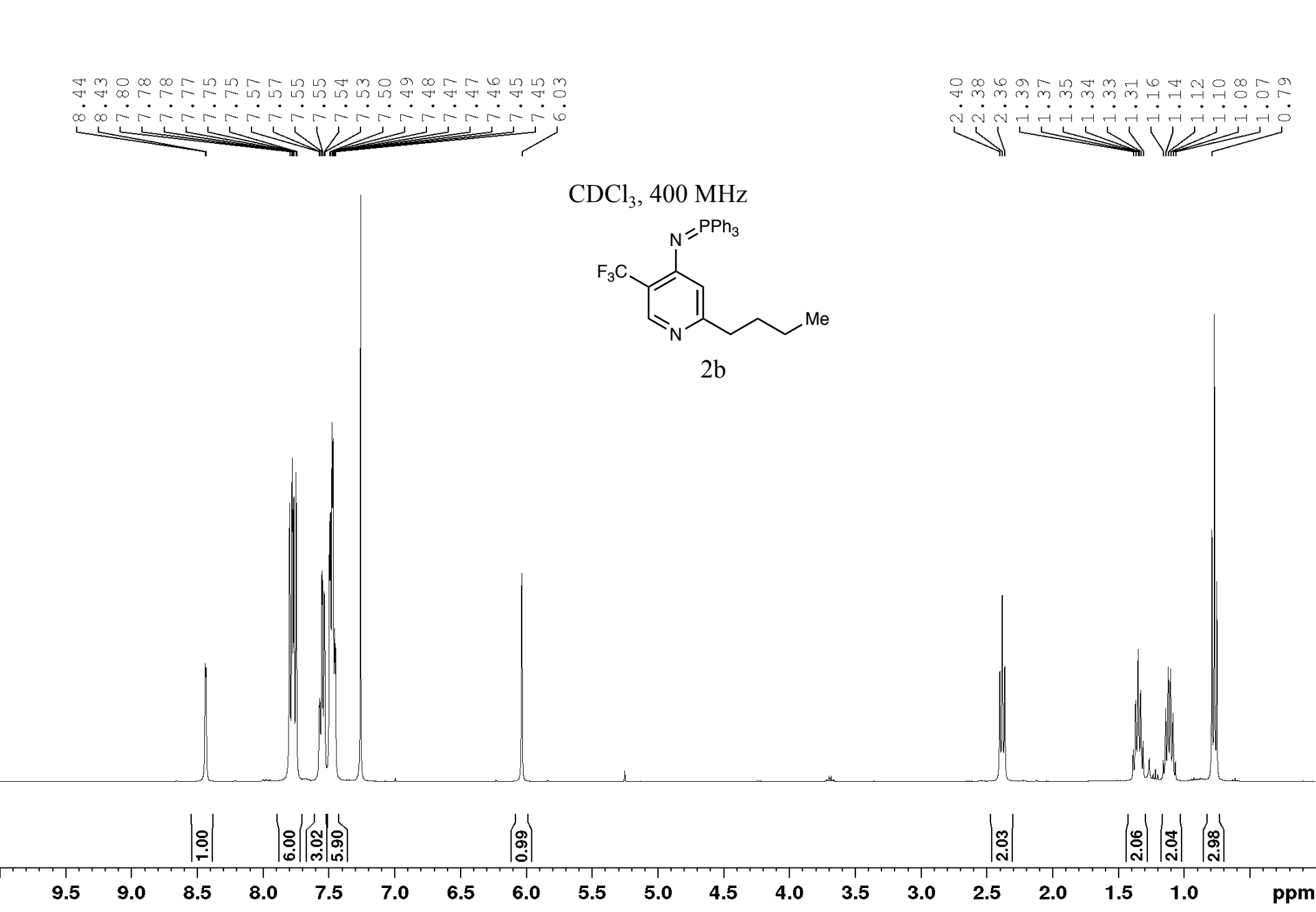
13.4:1:1 Mixture of Regioisomers

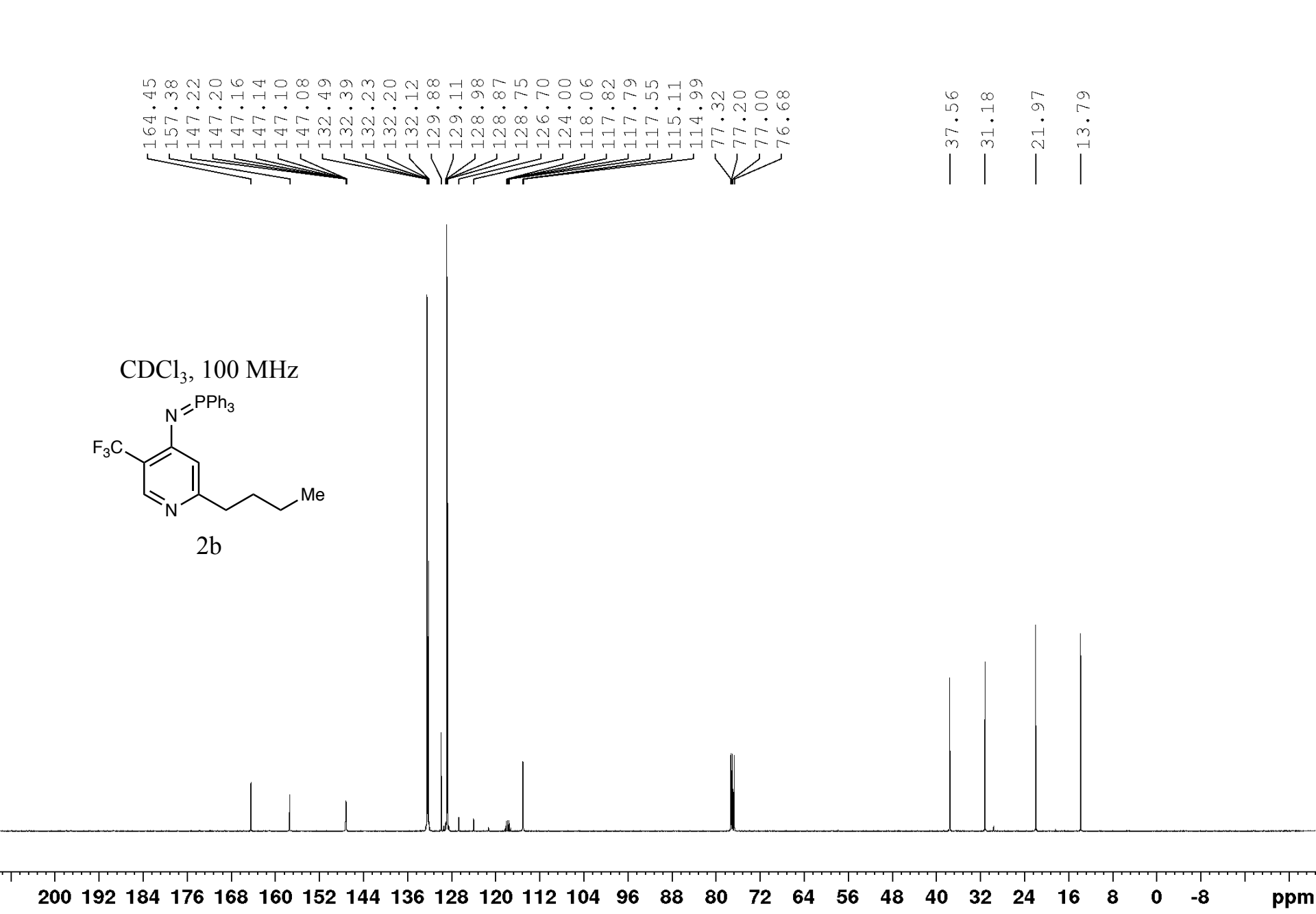
1s


7.75
7.73
7.73
7.72
7.70
7.70
7.59
7.59
7.57
7.57
7.55
7.55
7.50
7.50
7.49
7.48
7.47
7.46
7.26
6.05
6.03
2.93
2.86
1.86
1.85
CDCl3, 400 MHz
N
PPh3
N
2a
7.28
3.16
6.27
1.00
4.19
4.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm

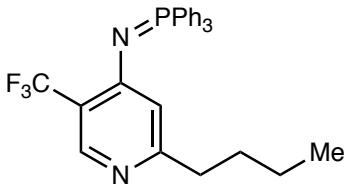

158.54
154.56
143.78
132.51
132.41
132.23
132.20
130.37
129.37
128.92
128.80
127.56
127.32
113.09
112.98
77.32
77.00
76.68
31.69
24.94
23.01
22.91
CDCl3, 100 MHz
N
PPh3
N
2a
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


5.96
CDCl3, 162 MHz
N
PPh3
N
2a
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 ppm

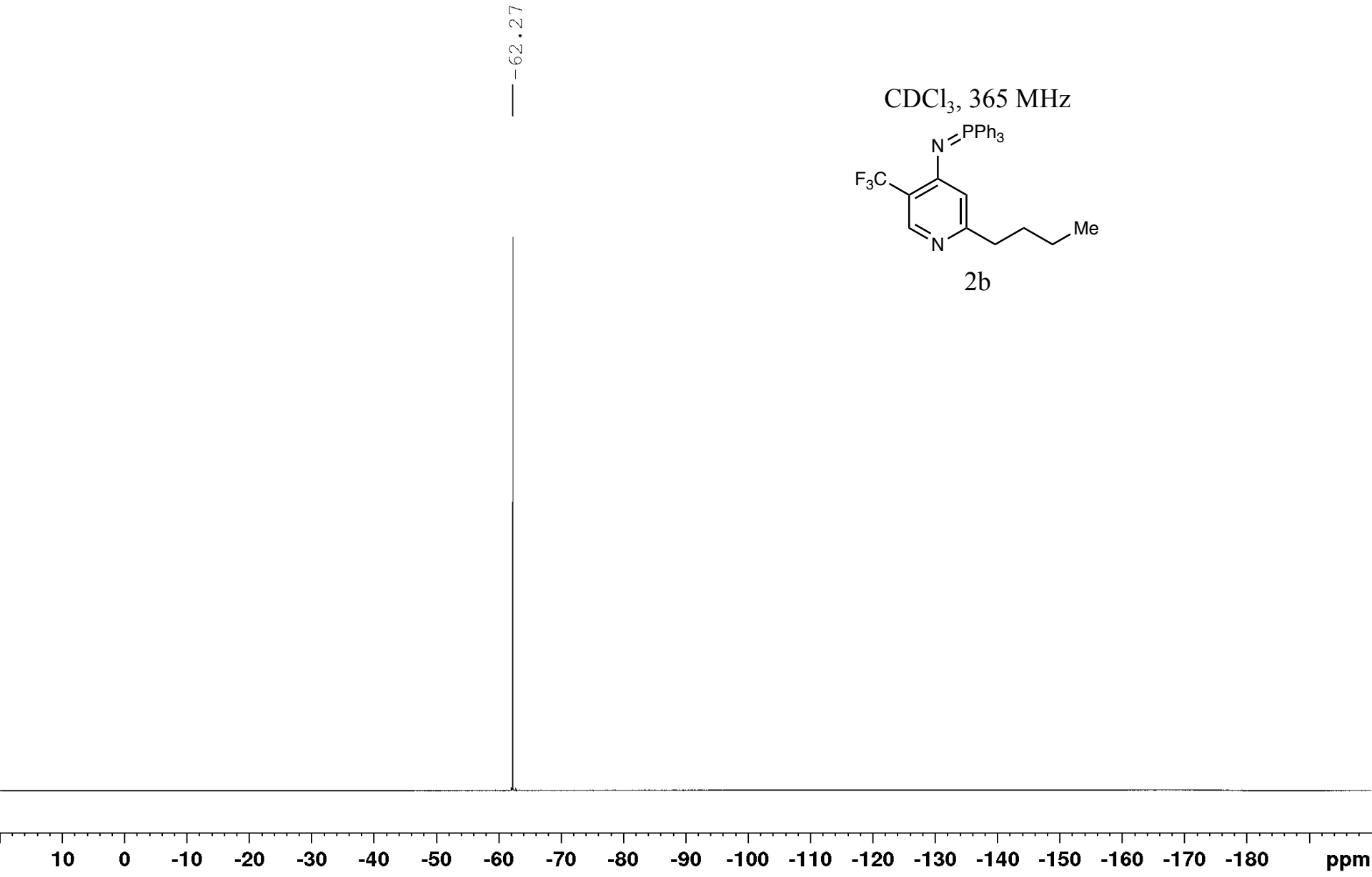

8.44
8.43
7.80
7.78
7.78
7.77
7.75
7.75
7.57
7.57
7.55
7.55
7.54
7.53
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
6.03
2.40
2.38
2.36
1.39
1.37
1.35
1.34
1.33
1.31
1.16
1.14
1.12
1.10
1.08
1.07
0.79
CDCl3, 400 MHz
N
PPh3
F3C
N
Me
2b
1.00
6.00
3.02
5.90
0.99
2.03
2.06
2.04
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

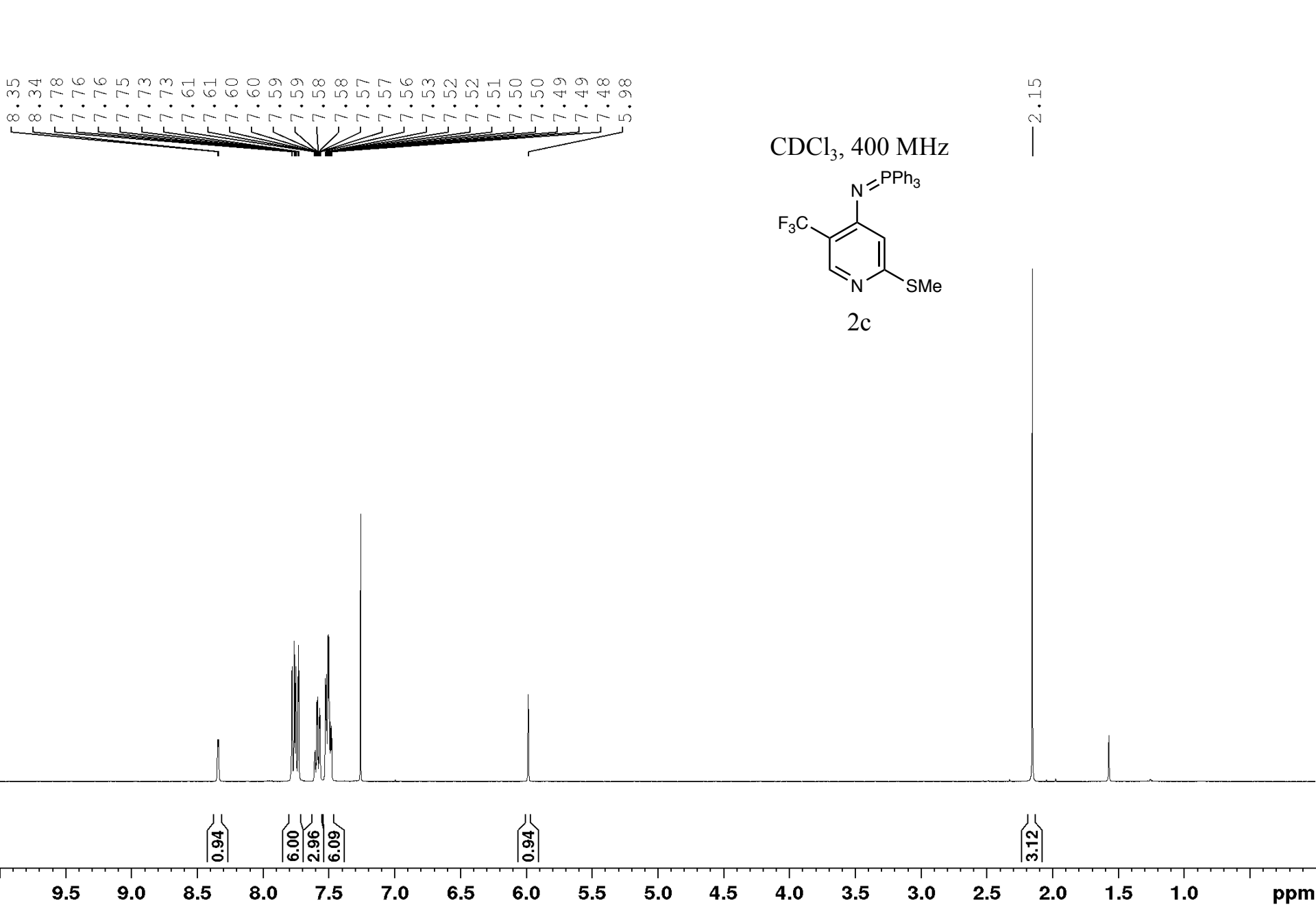

164.45
157.38
147.22
147.20
147.16
147.14
147.10
147.08
132.49
132.39
132.23
132.20
132.12
129.88
129.11
128.98
128.87
128.75
126.70
124.00
118.06
117.82
117.79
117.55
115.11
114.99
77.32
77.20
77.00
76.68
37.56
31.18
21.97
13.79
CDCl3, 100 MHz
N
PPh3
F3C
N
Me
2b
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
ppm

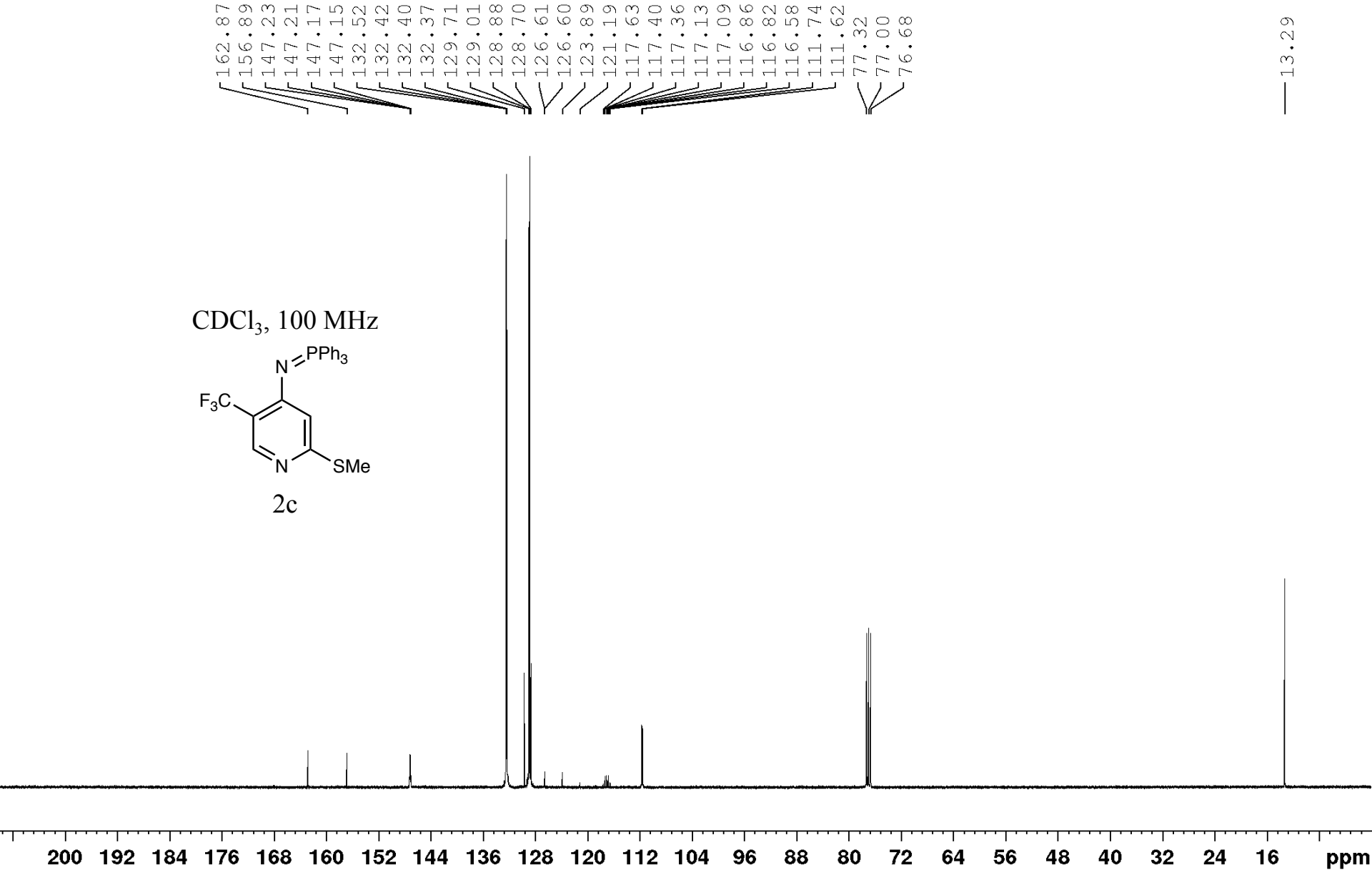
$CDCl_3$, 162 MHz

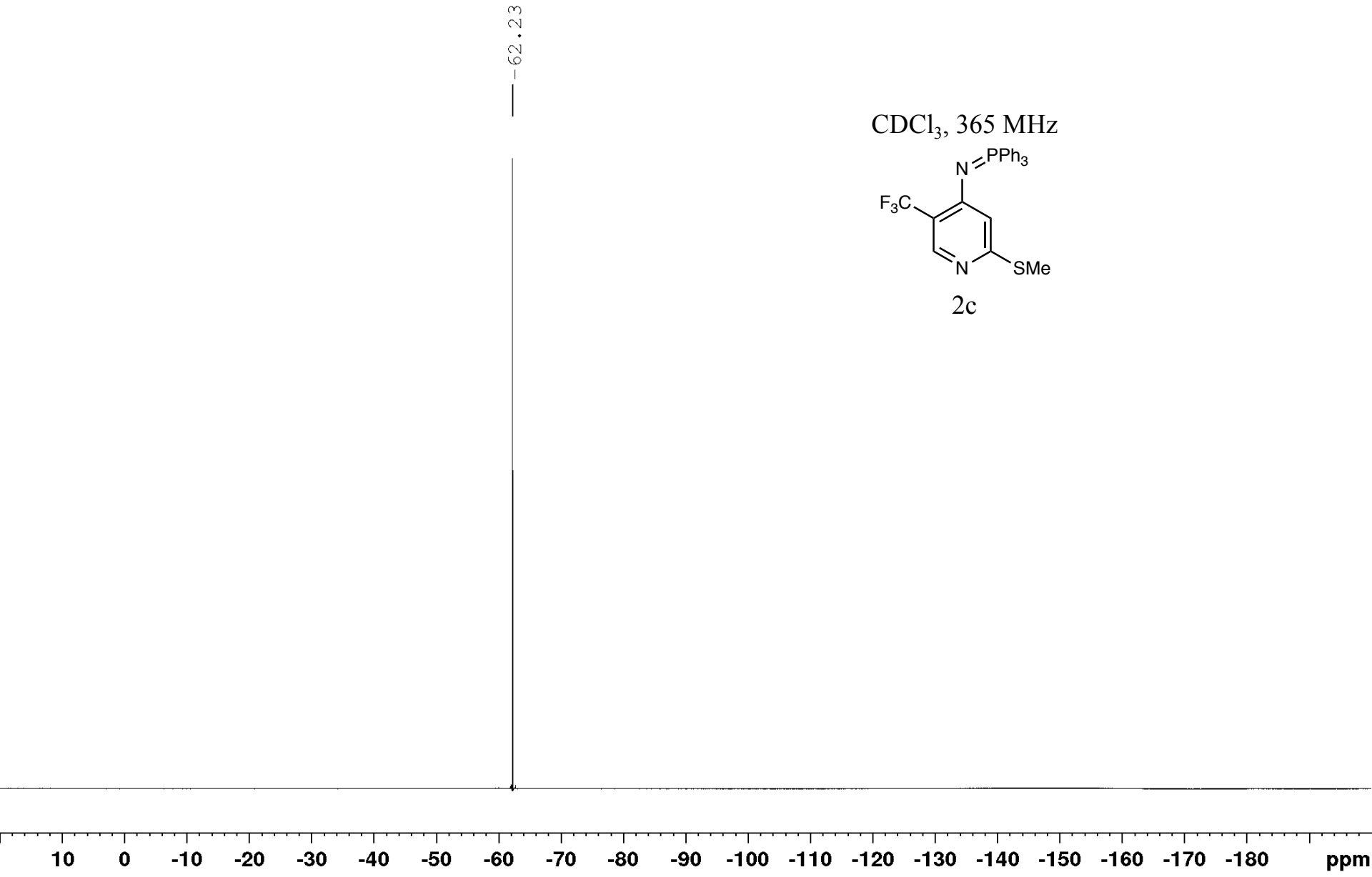


2b

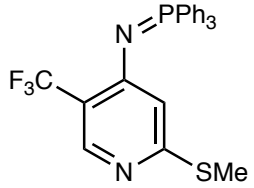

-62.27
CDCl3, 365 MHz
N
PPh3
F3C
N
Me
2b
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


8.35
8.34
7.78
7.76
7.76
7.75
7.73
7.73
7.61
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
5.98
2.15
CDCl3, 400 MHz
N
PPh3
F3C
N
SMe
2c
0.94
6.00
2.96
6.09
0.94
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

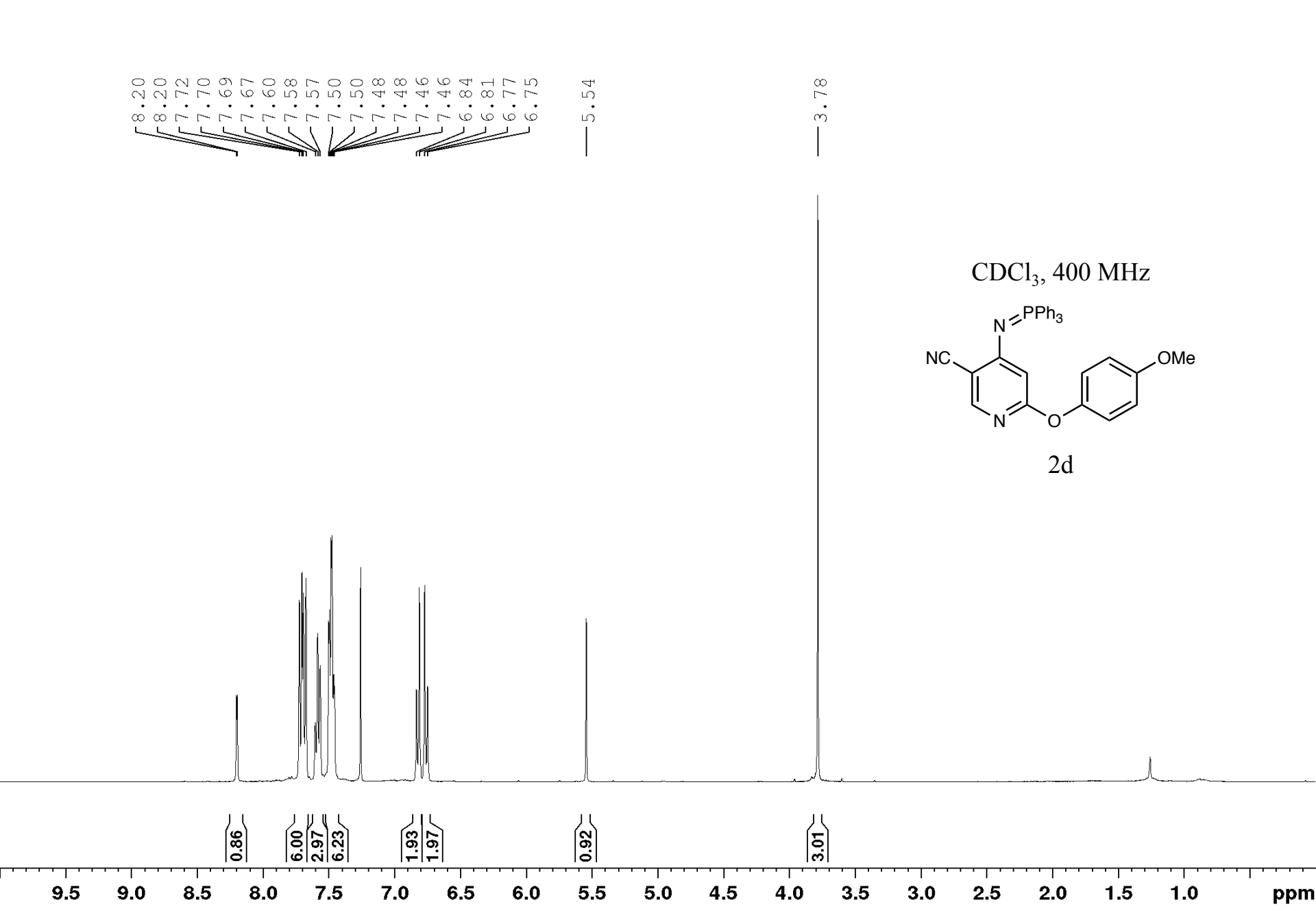

162.87
156.89
147.23
147.21
147.17
147.15
132.52
132.42
132.40
132.37
129.71
129.01
128.88
128.70
126.61
126.60
123.89
121.19
117.63
117.40
117.36
117.13
117.09
116.86
116.82
116.58
111.74
111.62
77.32
77.00
76.68
13.29
CDCl3, 100 MHz
N=PPh3
F3C
N
SMe
2c
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

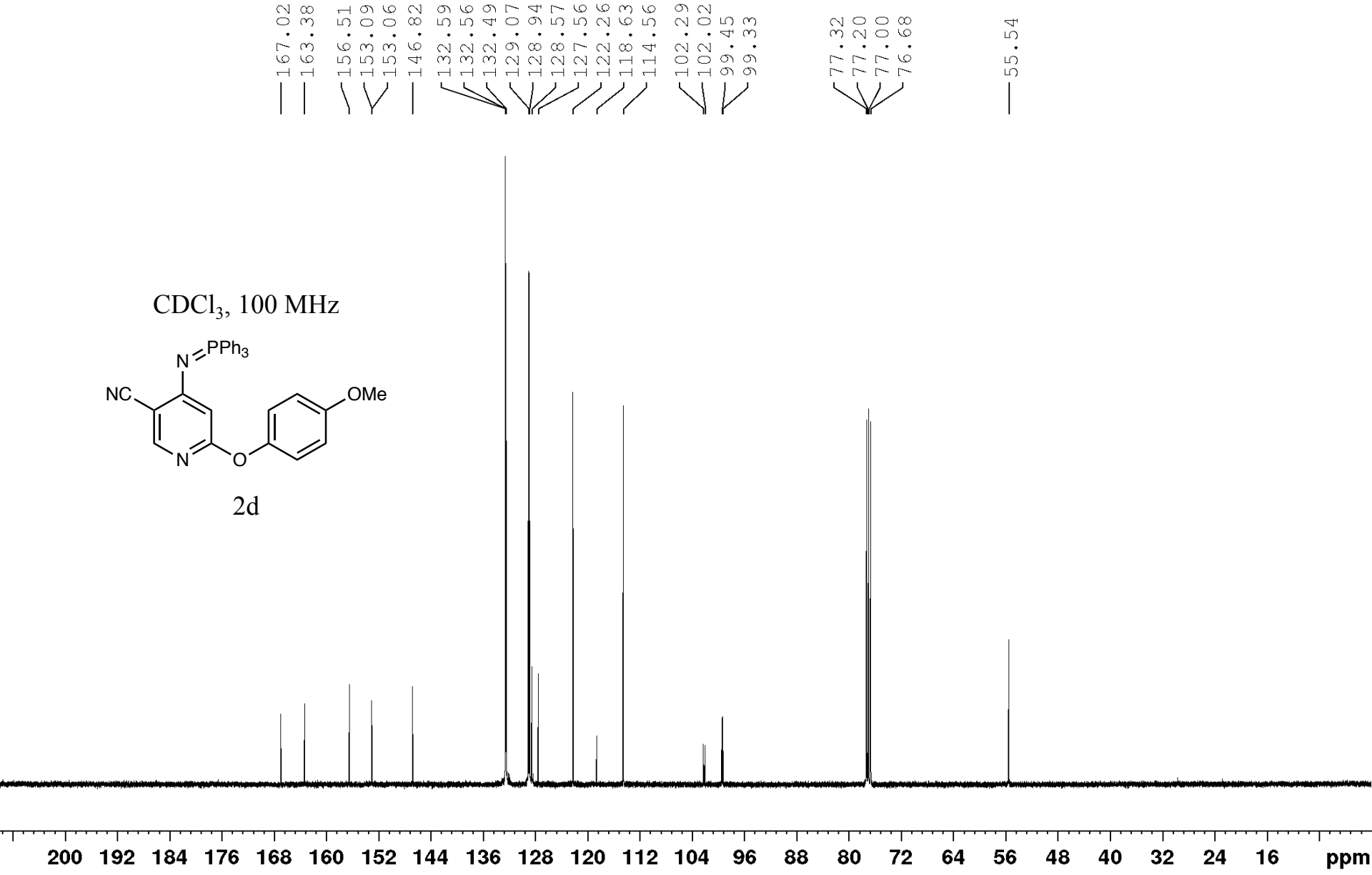

-62.23
CDCl3, 365 MHz
N
PPh3
F3C
N
SMe
2c
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

$CDCl_3$, 162 MHz

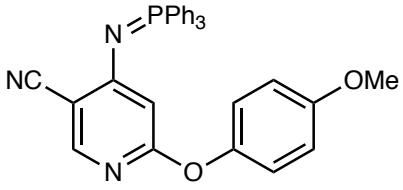


2c

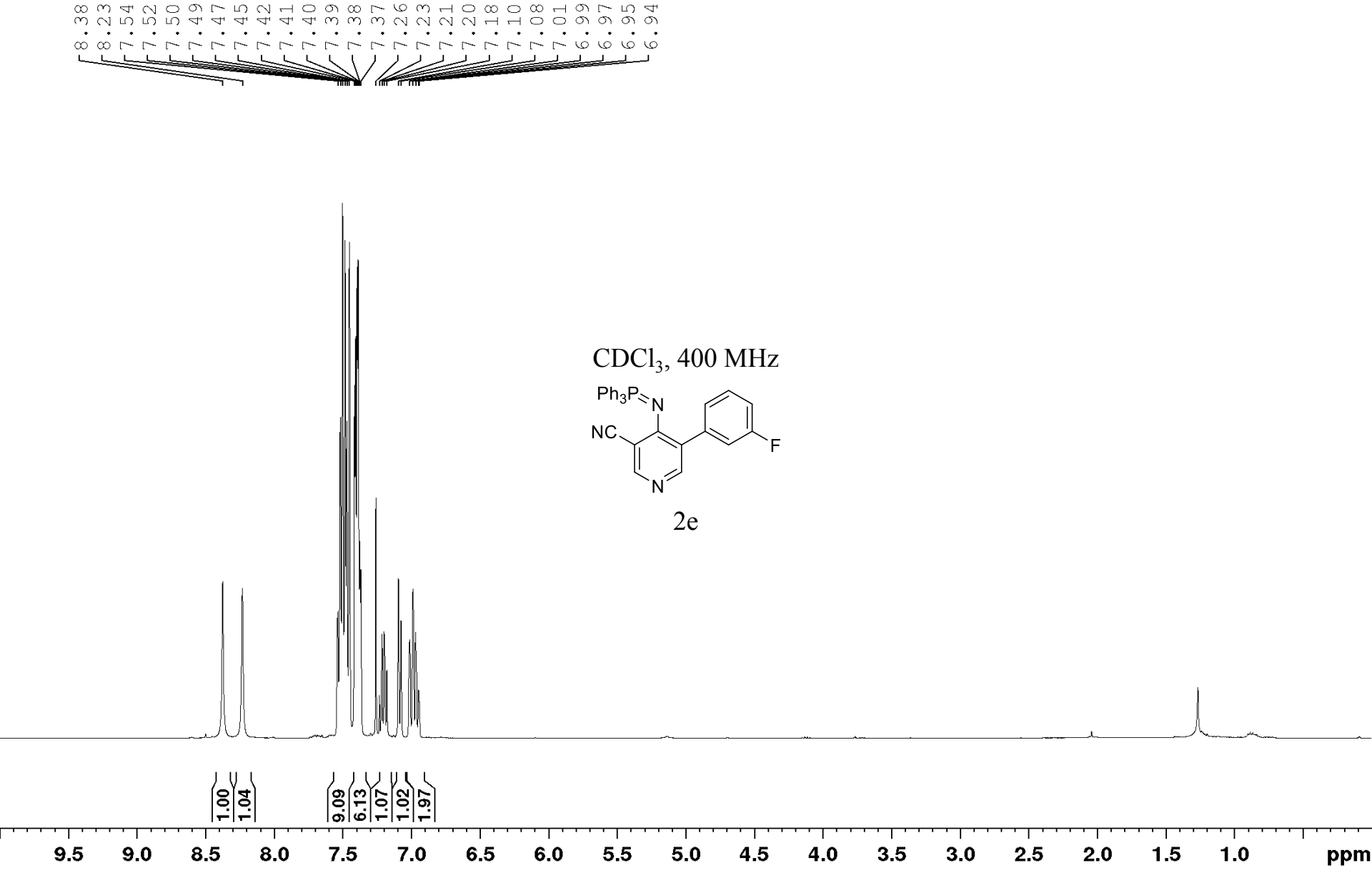

8.20
8.20
7.72
7.70
7.69
7.67
7.60
7.58
7.57
7.50
7.50
7.48
7.48
7.46
7.46
6.84
6.81
6.77
6.75
5.54
3.78
CDCl3, 400 MHz
N
PPh3
NC
OMe
N
O
2d
0.86
6.00
2.97
6.23
1.93
1.97
0.92
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

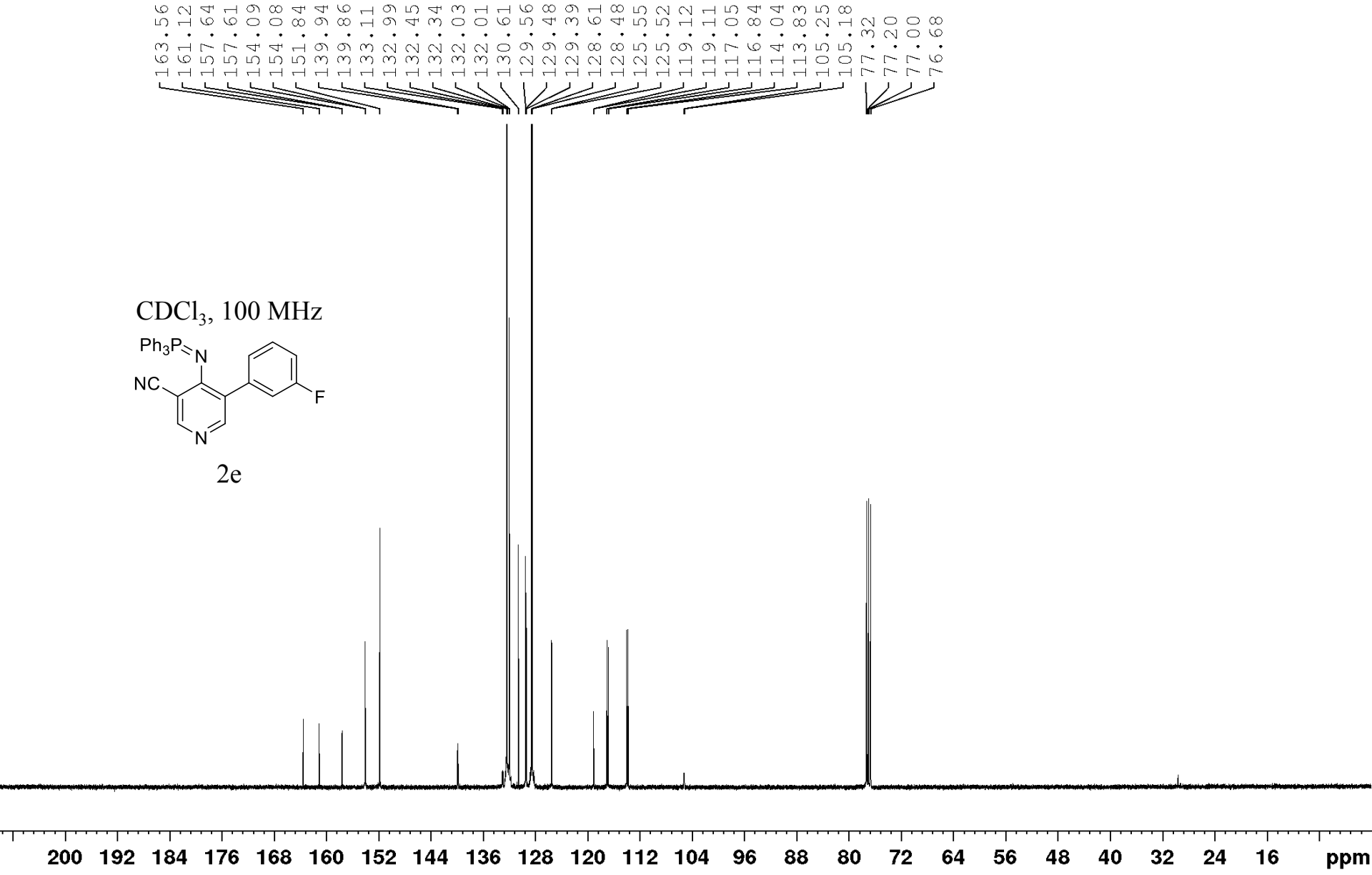

167.02
163.38
156.51
153.09
153.06
146.82
132.59
132.56
132.49
129.07
128.94
128.57
127.56
122.26
118.63
114.56
102.29
102.02
99.45
99.33
77.32
77.20
77.00
76.68
55.54
CDCl3, 100 MHz
N=PPh3
NC
OMe
N
O
2d
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

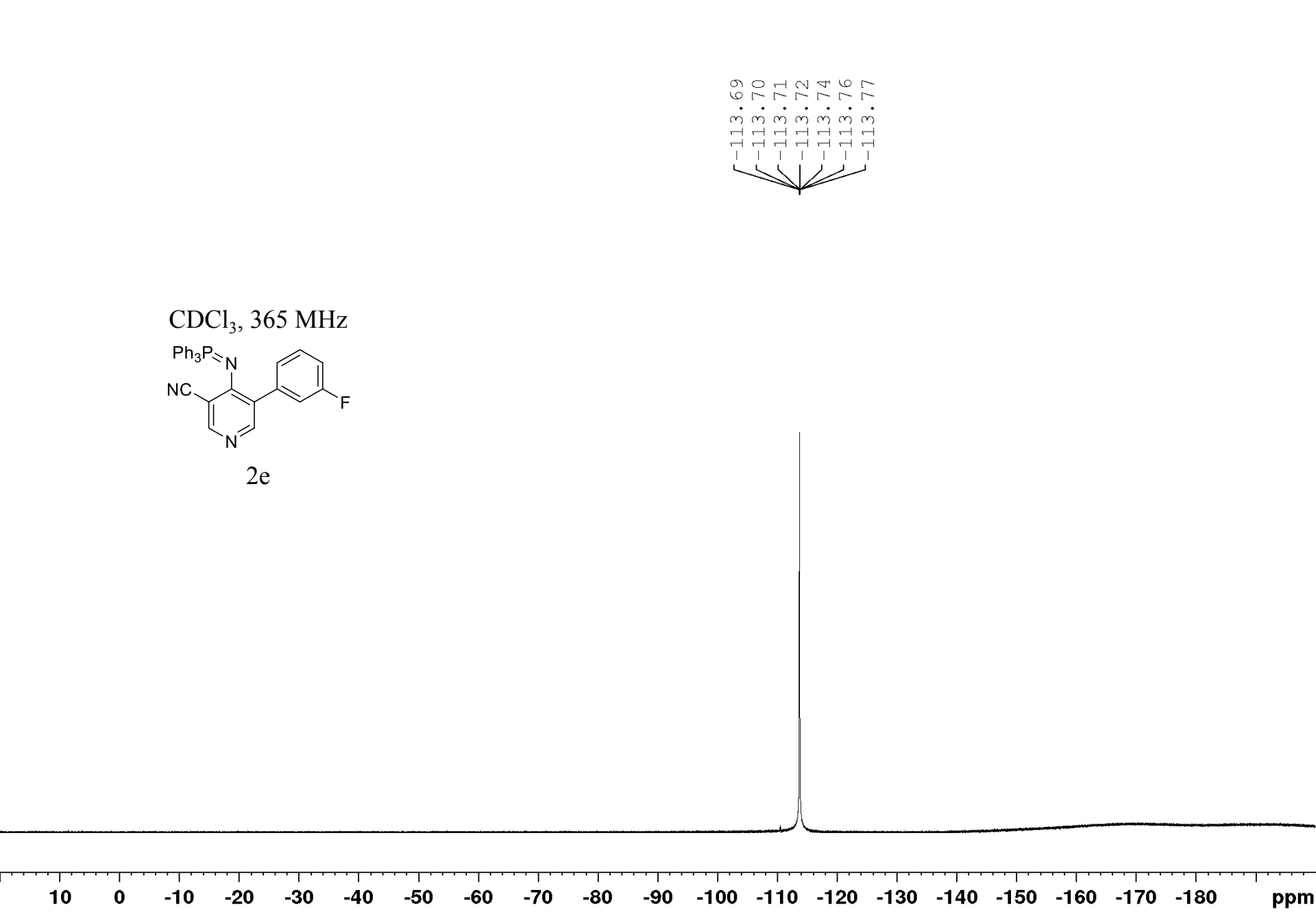
$CDCl_3$, 162 MHz

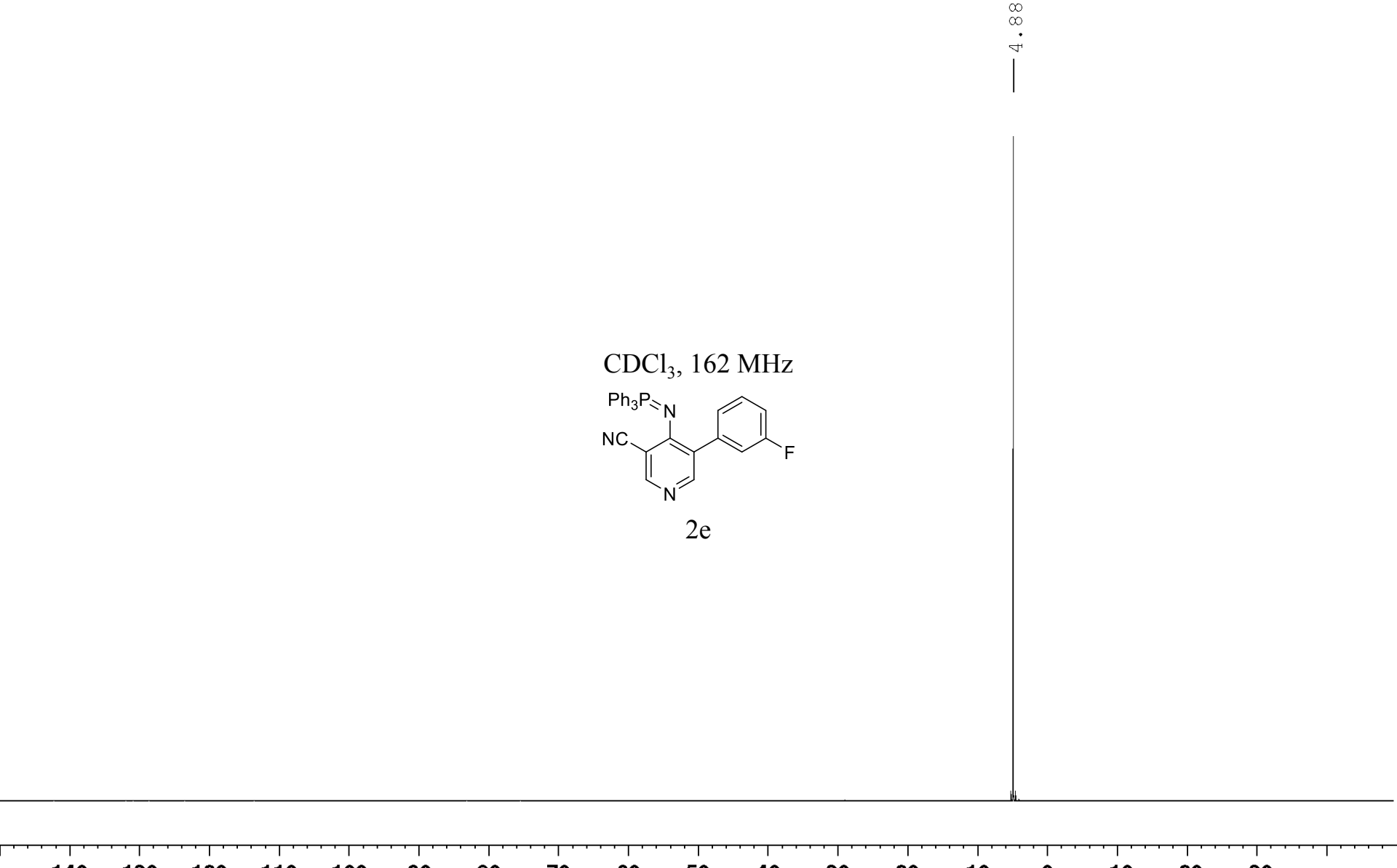


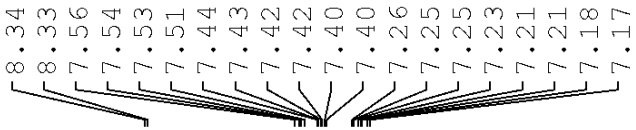
2d


8.38
8.23
7.54
7.52
7.50
7.49
7.47
7.45
7.42
7.41
7.40
7.39
7.38
7.37
7.26
7.23
7.21
7.20
7.18
7.10
7.08
7.01
6.99
6.97
6.95
6.94
CDCl3, 400 MHz
Ph3P
N
NC
F
N
2e
1.00
1.04
9.09
6.13
1.07
1.02
1.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

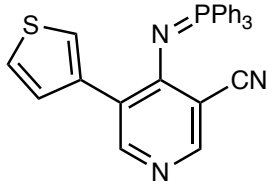

163.56
161.12
157.64
157.61
154.09
154.08
151.84
139.94
139.86
133.11
132.99
132.45
132.34
132.03
132.01
130.61
129.56
129.48
129.39
128.61
128.48
125.55
125.52
119.12
119.11
117.05
116.84
114.04
113.83
105.25
105.18
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
Ph3P=N
NC
F
N
2e
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-113.69
-113.70
-113.71
-113.72
-113.74
-113.76
-113.77
CDCl3, 365 MHz
Ph3P=N
NC
F
N
2e
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

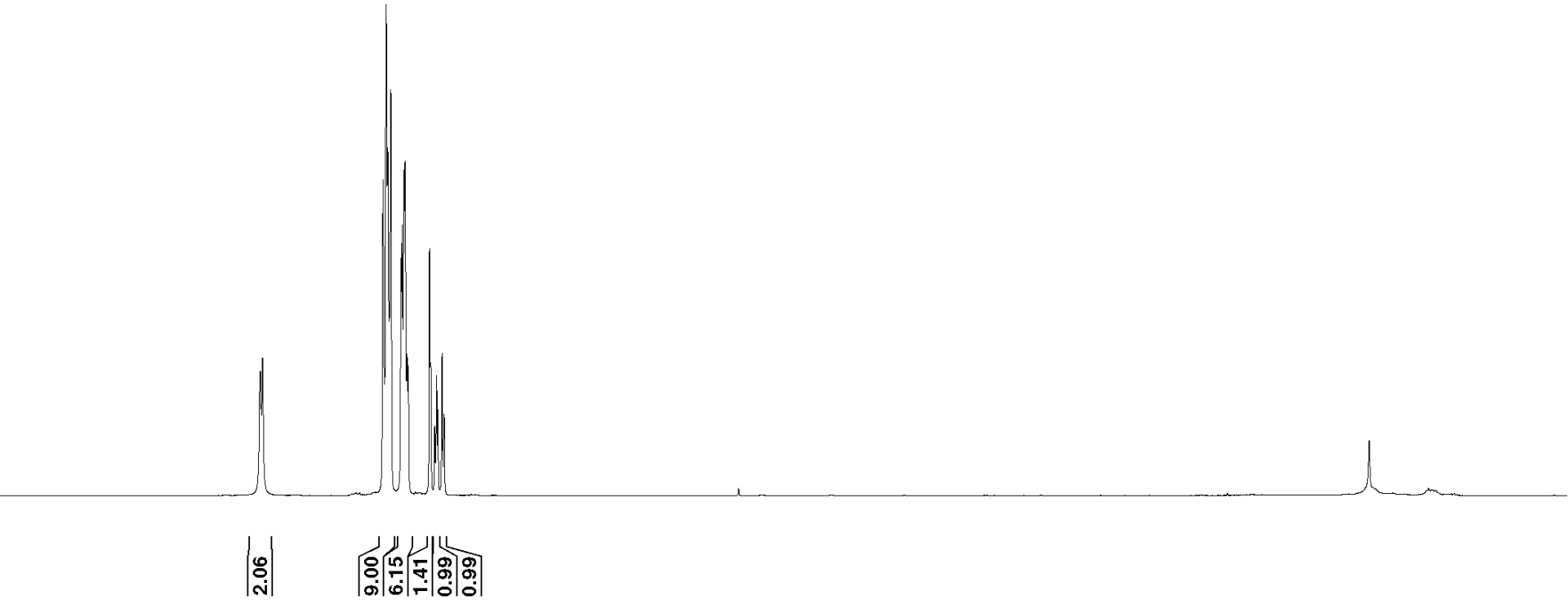

4.88
CDCl3, 162 MHz
Ph3P
N
NC
F
N
2e
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

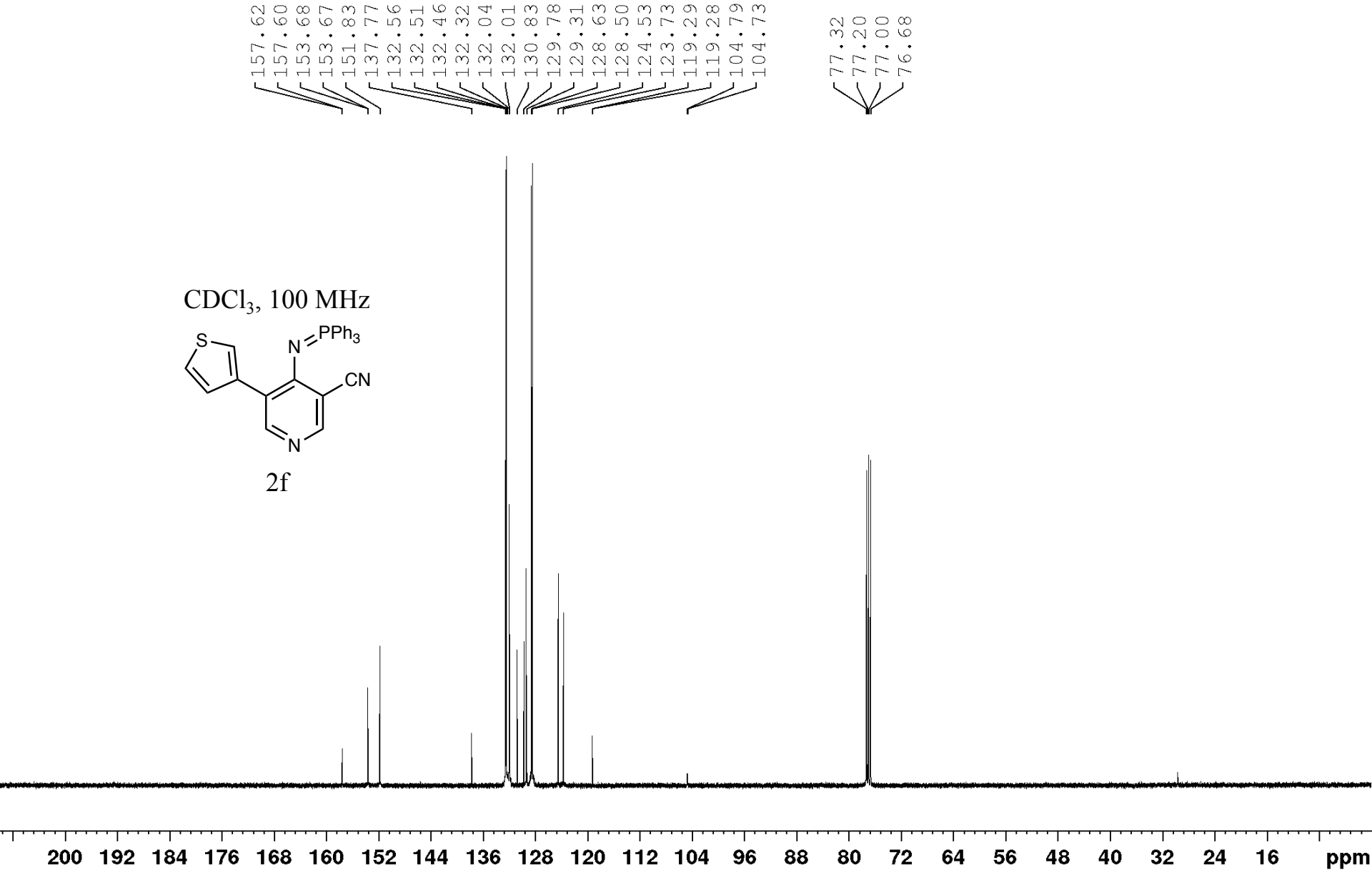


$CDCl_3$, 400 MHz

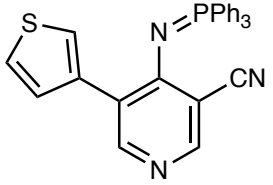


2f

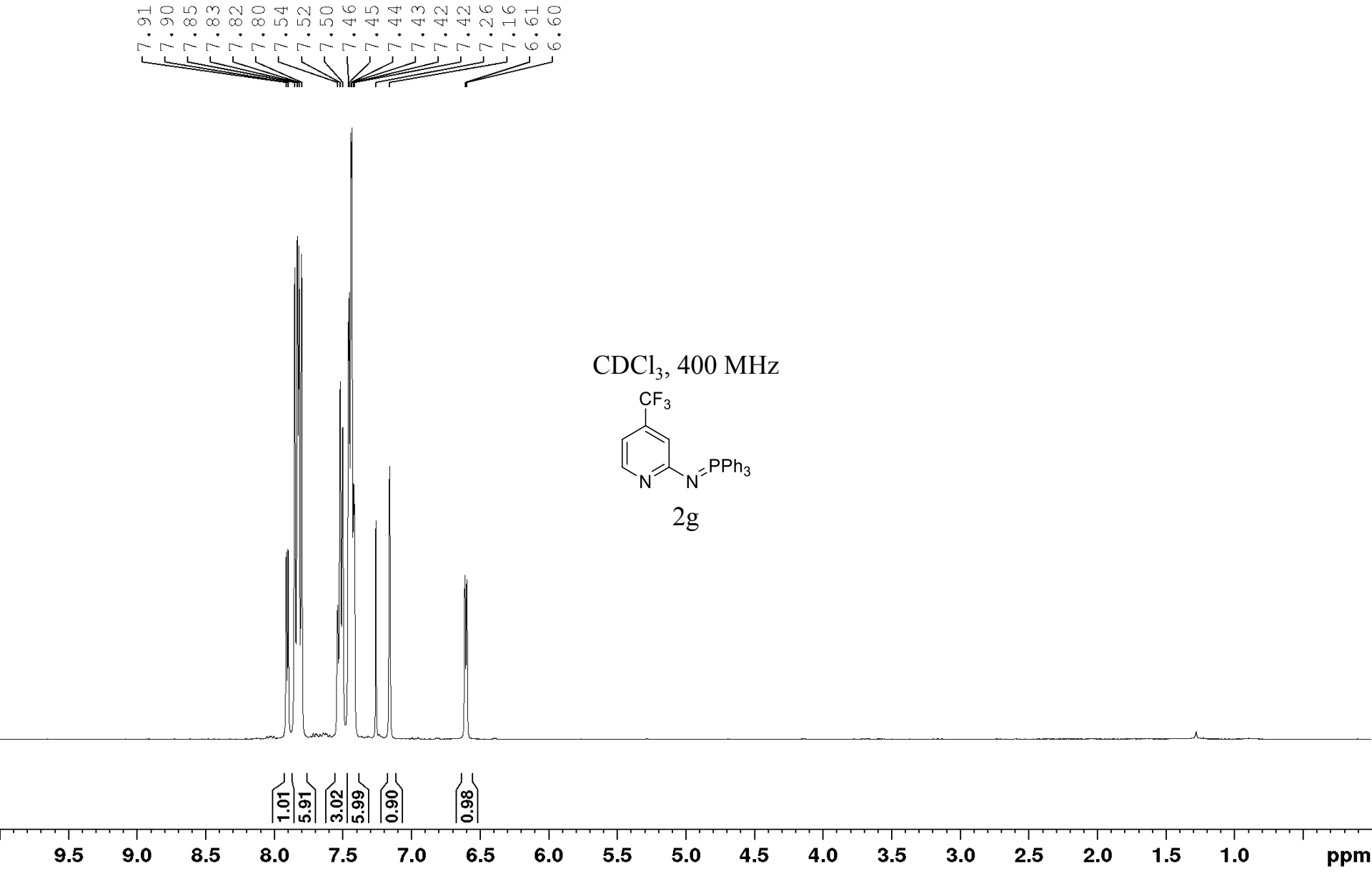


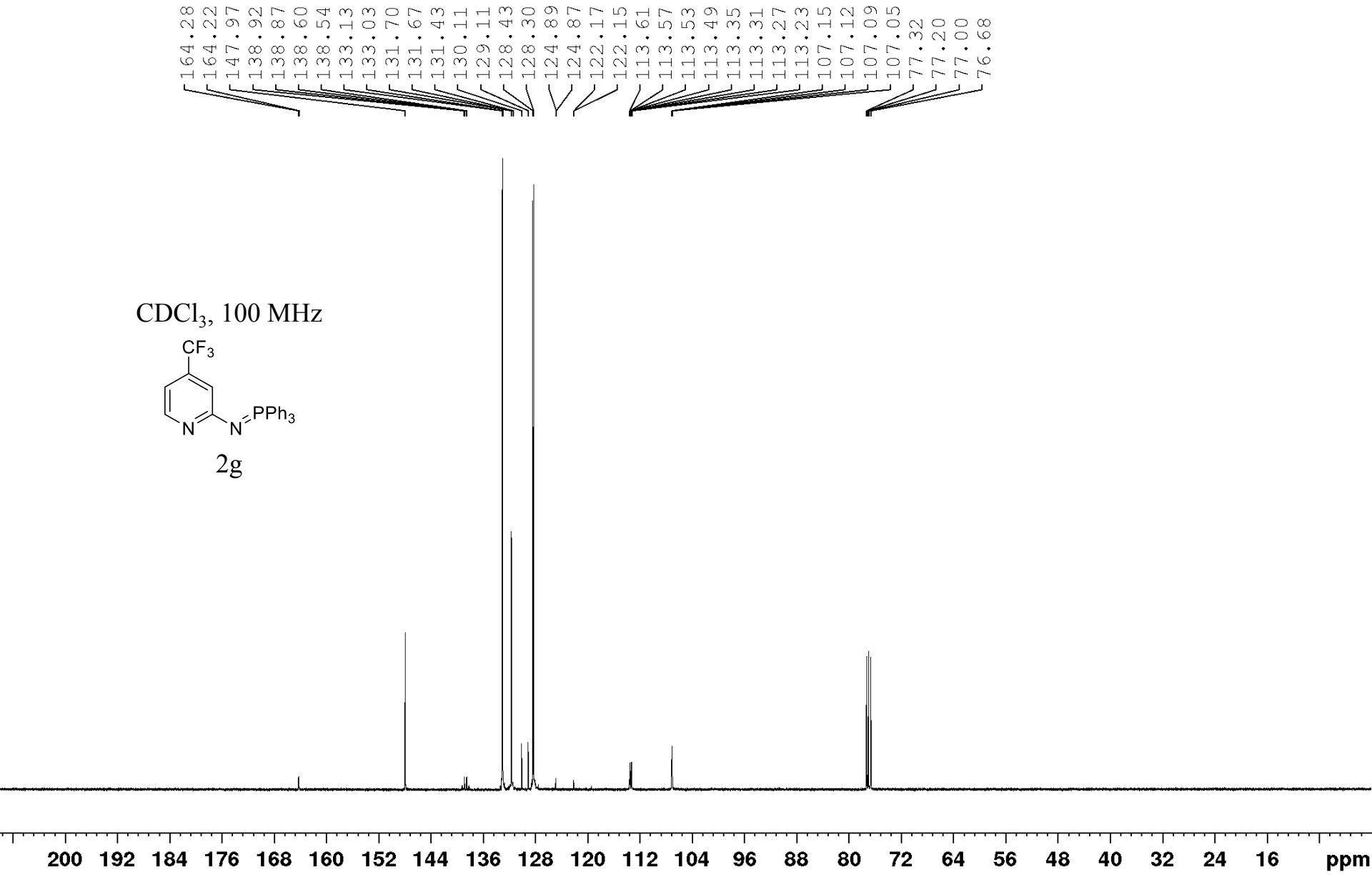

157.62
157.60
153.68
153.67
151.83
137.77
132.56
132.51
132.46
132.32
132.04
132.01
130.83
129.78
129.31
128.63
128.50
124.53
123.73
119.29
119.28
104.79
104.73
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
S
N
PPh3
CN
N
2f
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

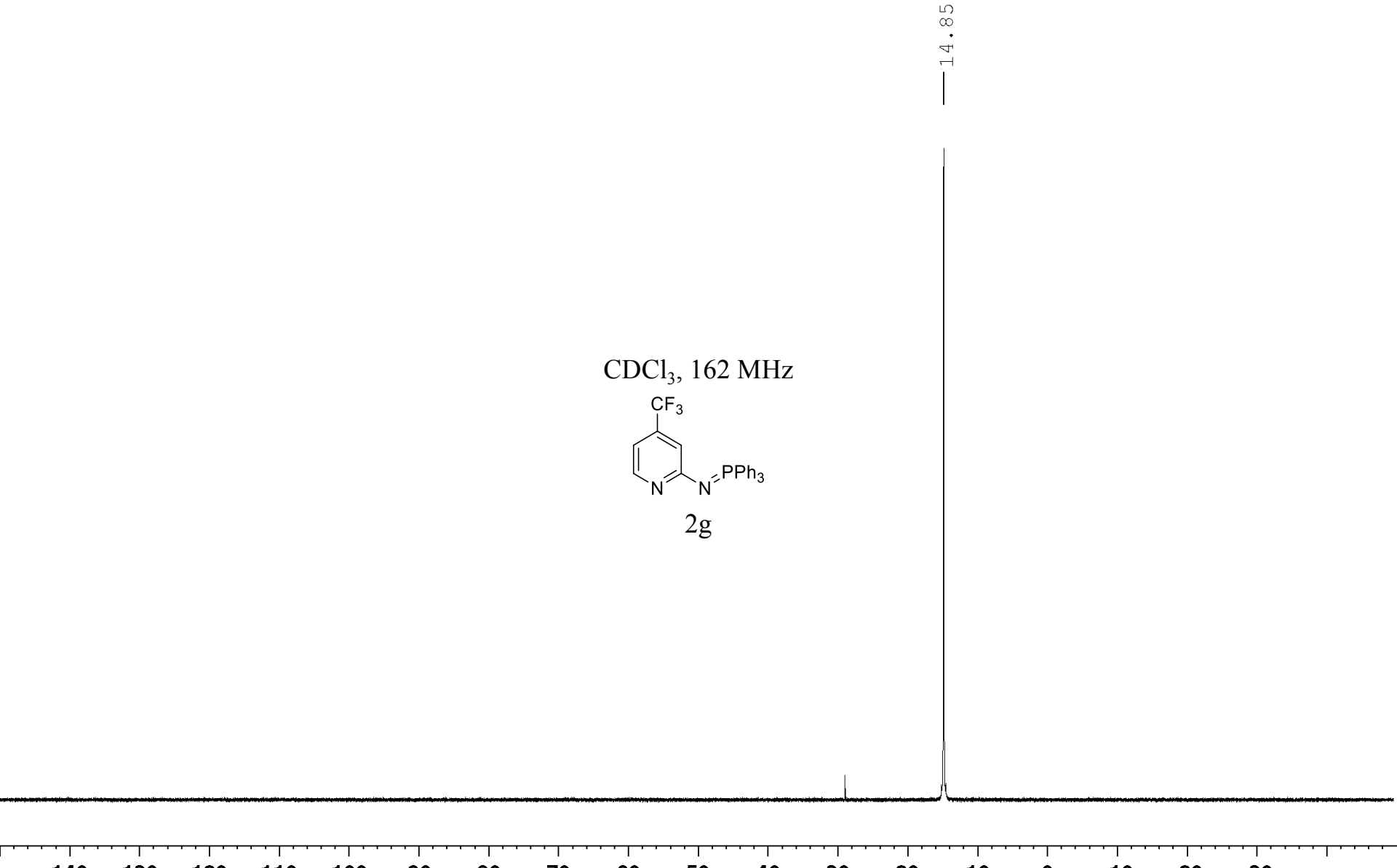
$CDCl_3$, 162 MHz

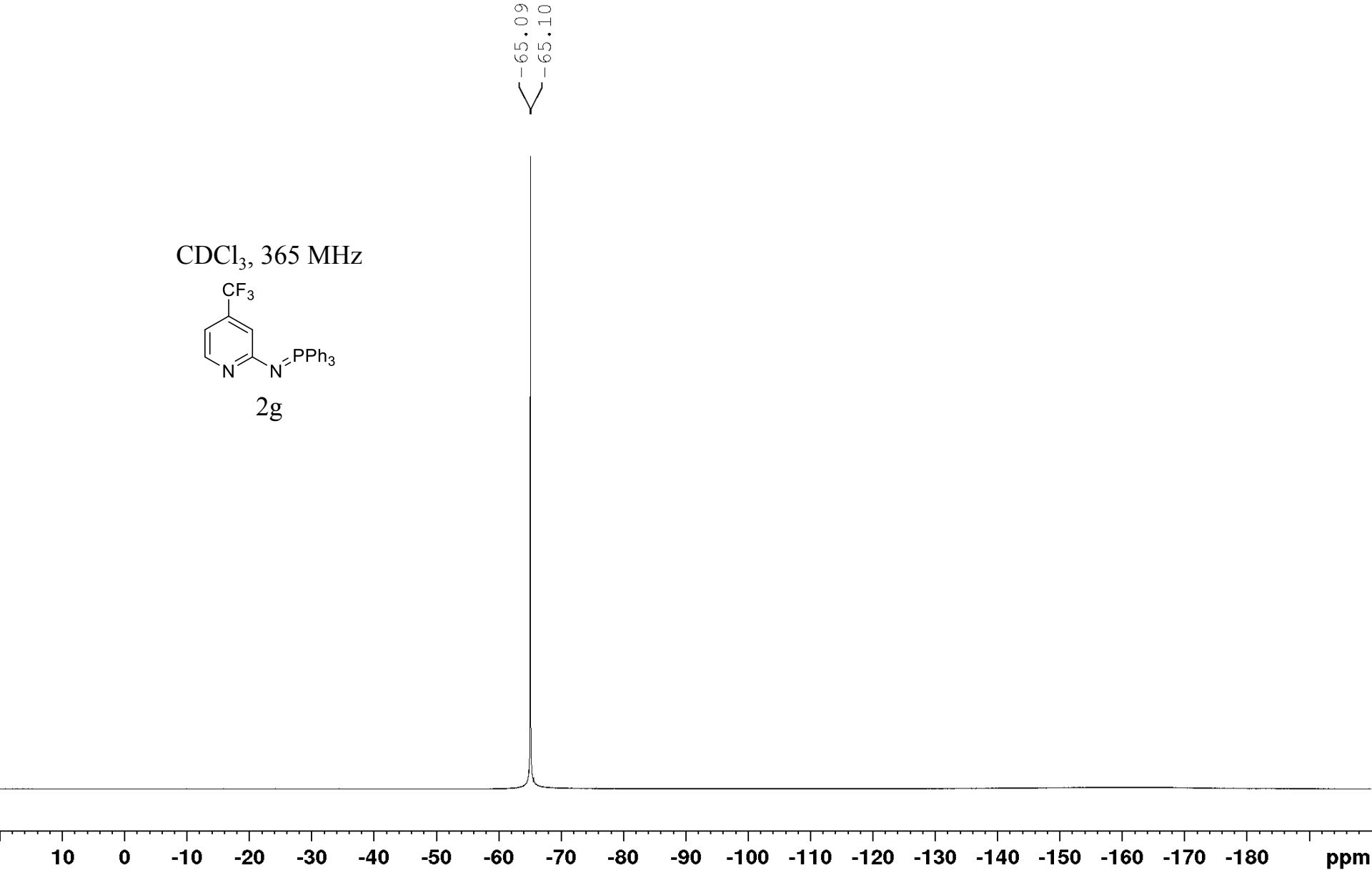


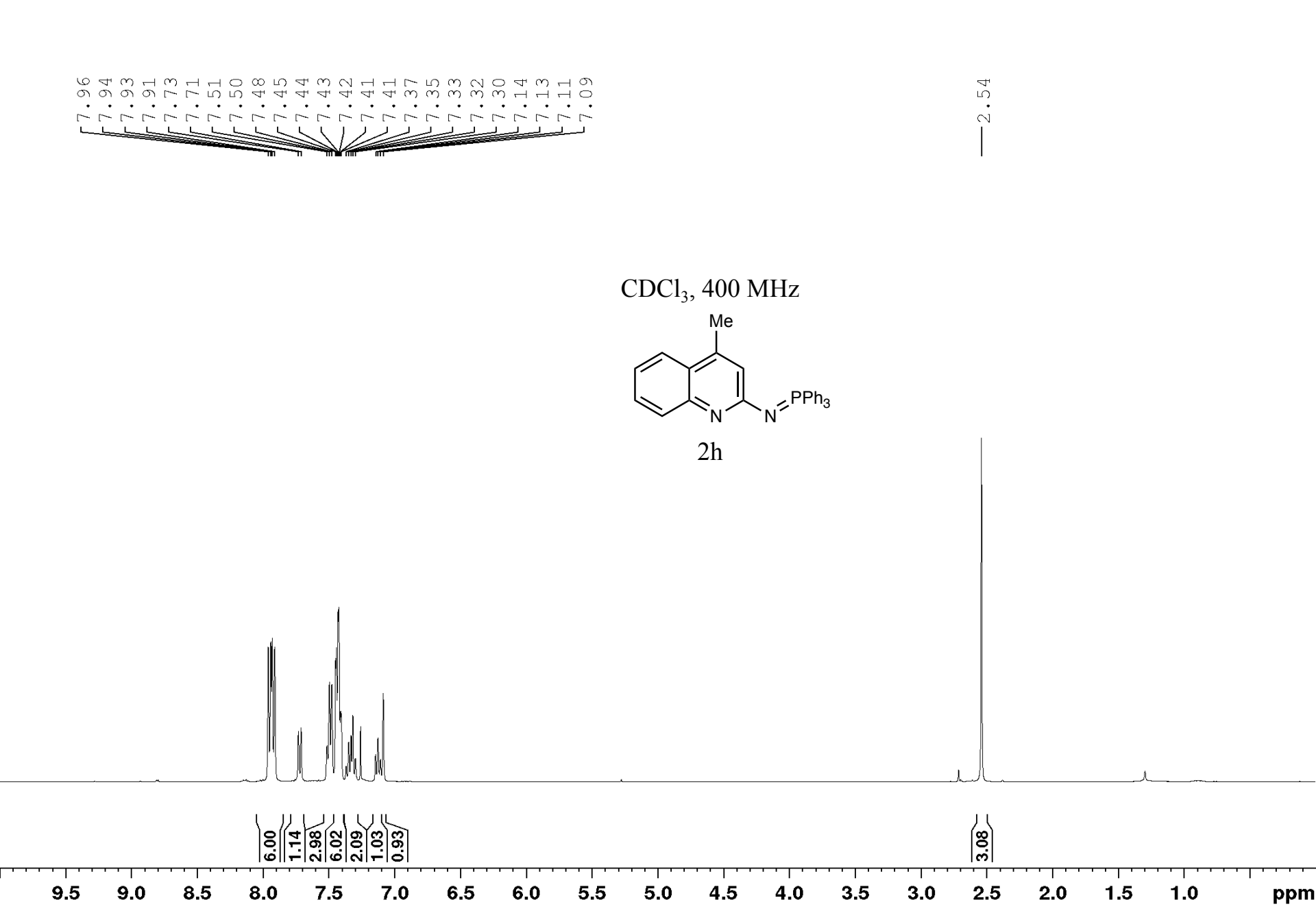
2f

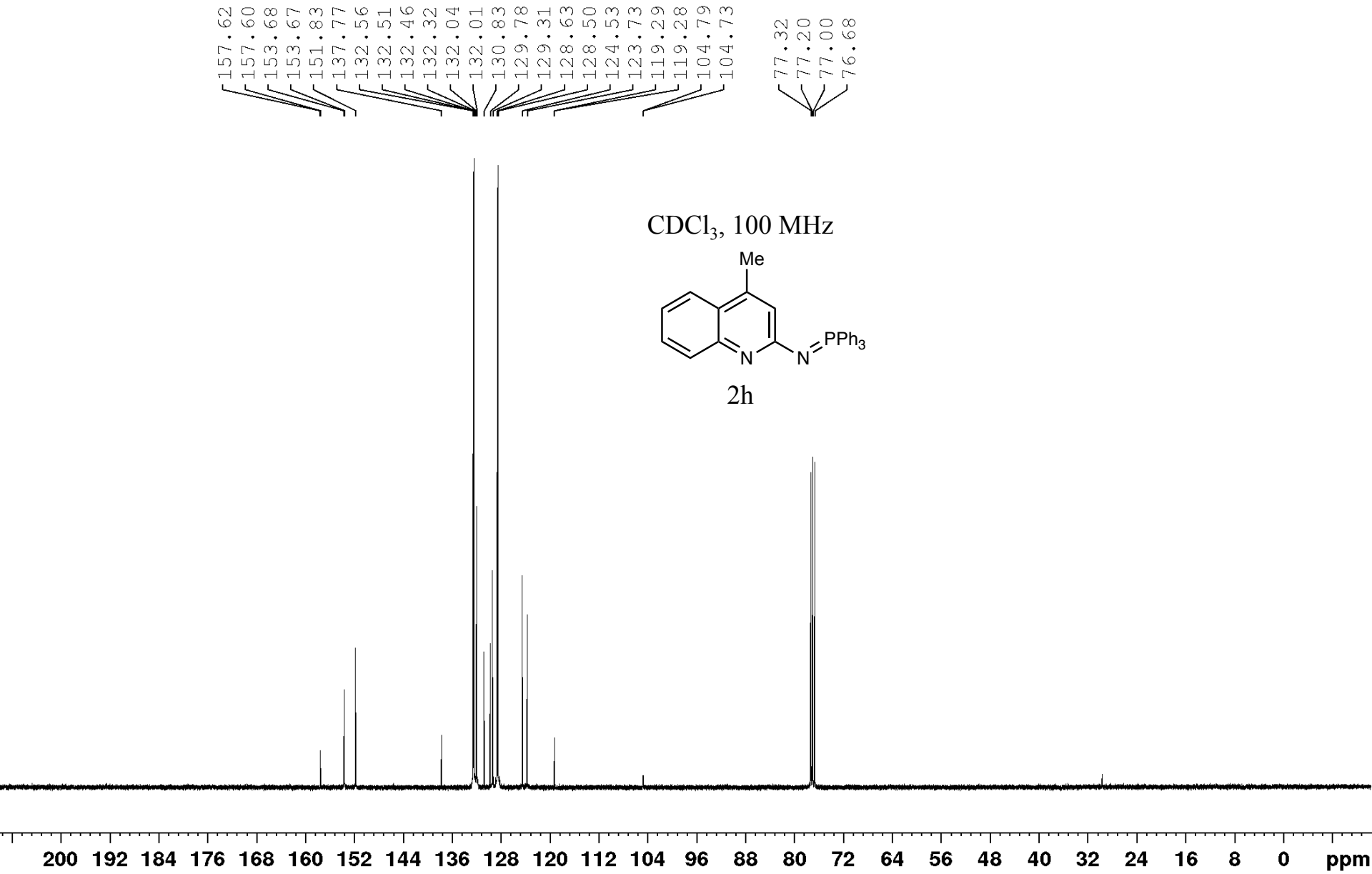

7.91
7.90
7.85
7.83
7.82
7.80
7.54
7.52
7.50
7.46
7.45
7.44
7.43
7.42
7.42
7.26
7.16
6.61
6.60
CDCl3, 400 MHz
CF3
PPh3
N
N
2g
1.01
5.91
3.02
5.99
0.90
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


164.28
164.22
147.97
138.92
138.87
138.60
138.54
133.13
133.03
131.70
131.67
131.43
130.11
129.11
128.43
128.30
124.89
124.87
122.17
122.15
113.61
113.57
113.53
113.49
113.35
113.31
113.27
113.23
107.15
107.12
107.09
107.05
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
CF3
N
N
PPh3
2g
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

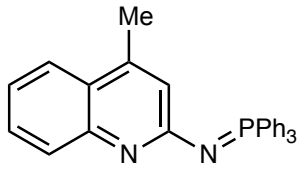

14.85
CDCl3, 162 MHz
CF3
N
N
PPh3
2g
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


-65.09
-65.10
CDCl3, 365 MHz
CF3
N
N
PPh3
2g
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


7.96
7.94
7.93
7.91
7.73
7.71
7.51
7.50
7.48
7.45
7.44
7.43
7.42
7.41
7.41
7.37
7.35
7.33
7.32
7.30
7.14
7.13
7.11
7.09
2.54
CDCl3, 400 MHz
Me
PPh3
N
N
2h
6.00
1.14
2.98
6.02
2.09
1.03
0.93
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

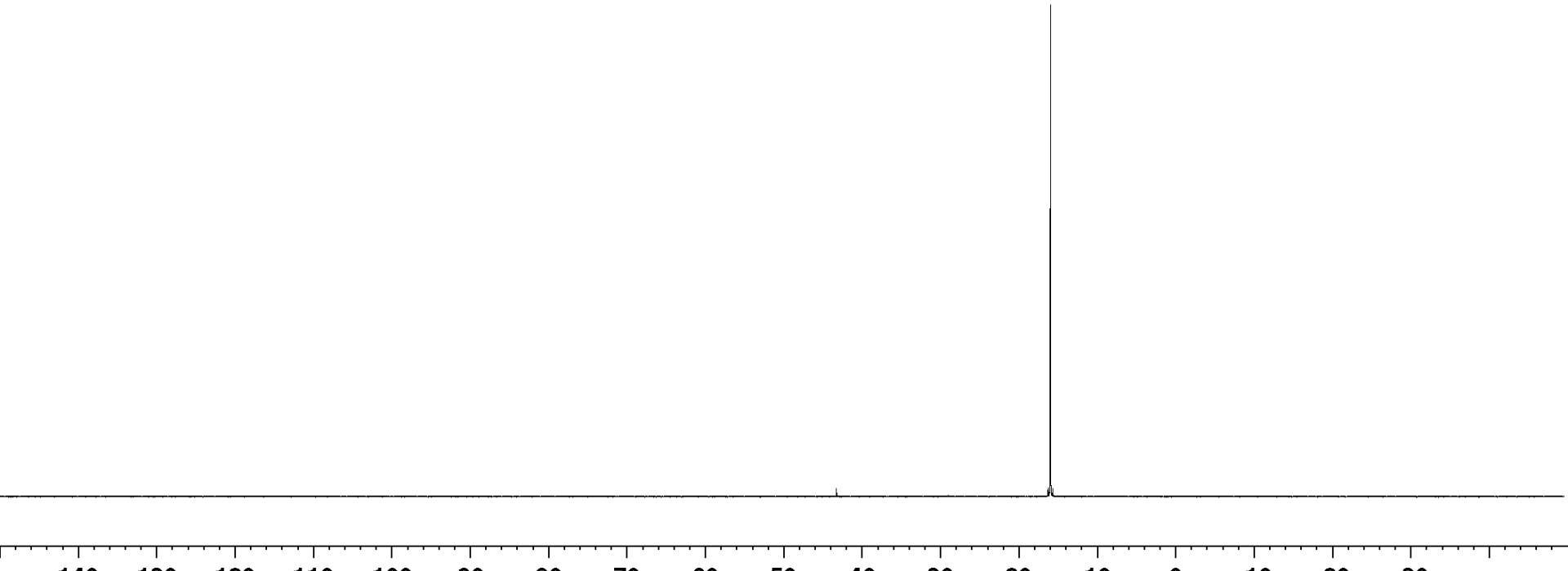

157.62
157.60
153.68
153.67
151.83
137.77
132.56
132.51
132.46
132.32
132.04
132.01
130.83
129.78
129.31
128.63
128.50
124.53
123.73
119.29
119.28
104.79
104.73
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
Me
PPh3
N
N
2h
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 ppm

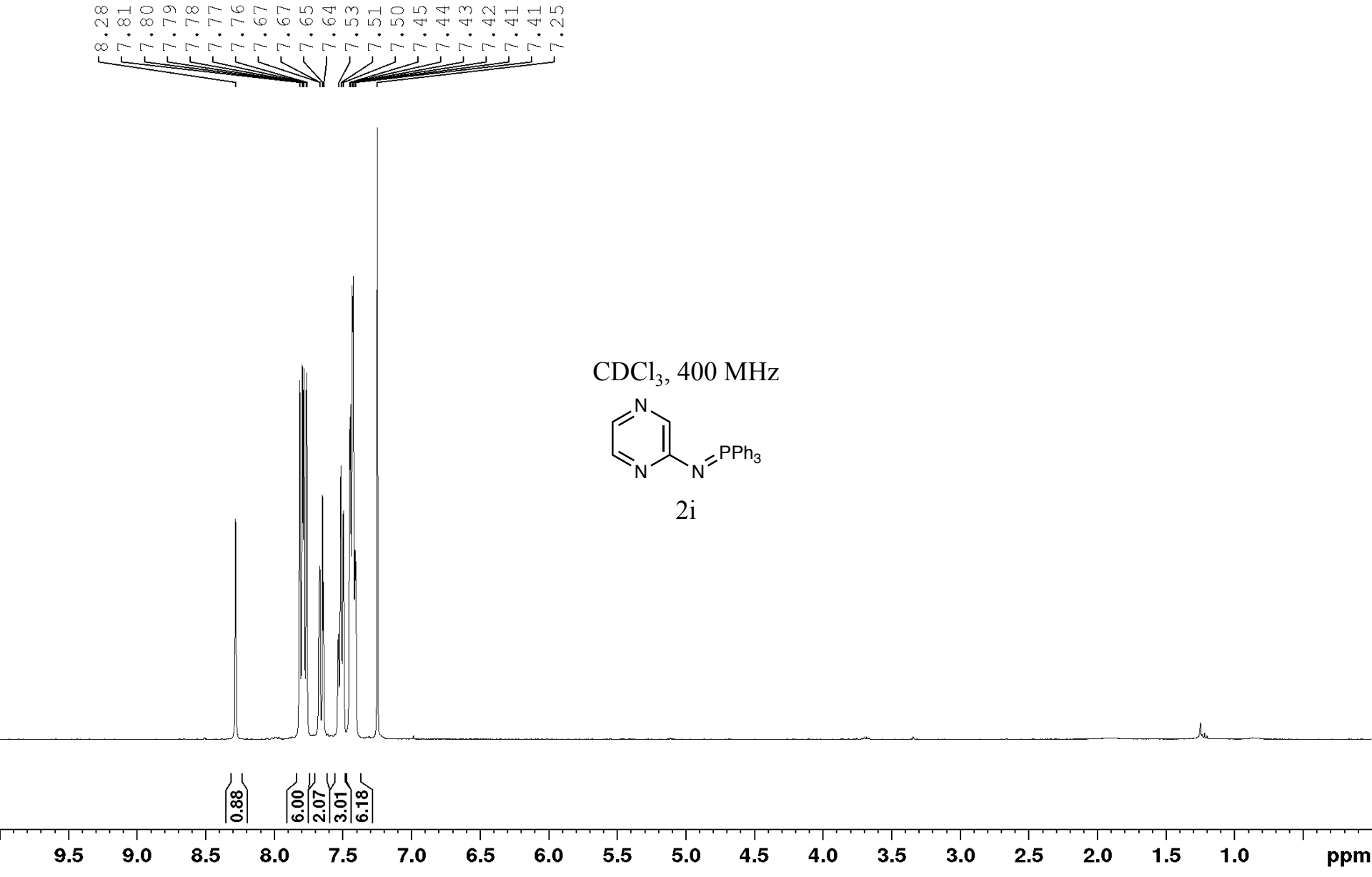
$CDCl_3$, 162 MHz

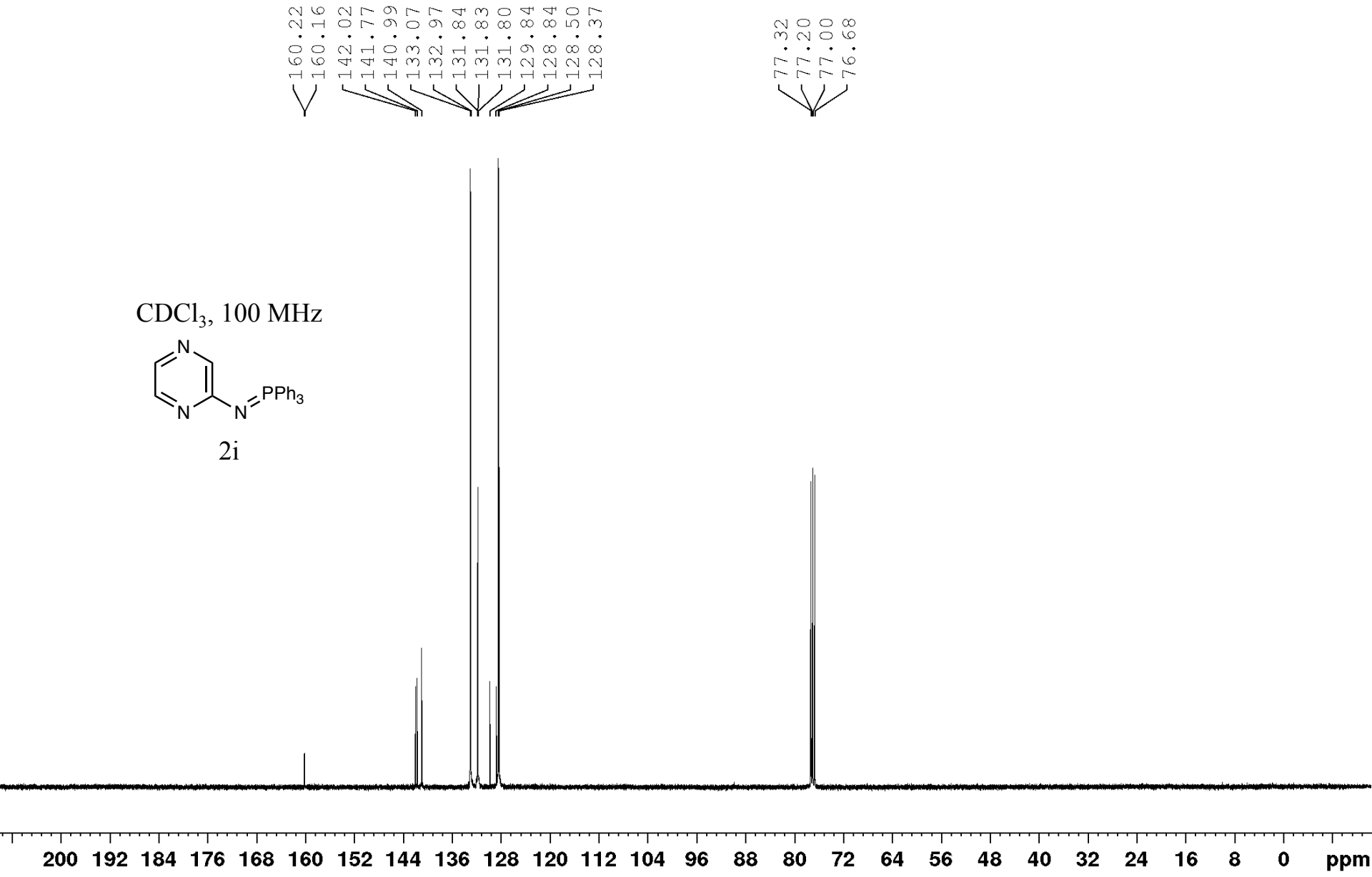


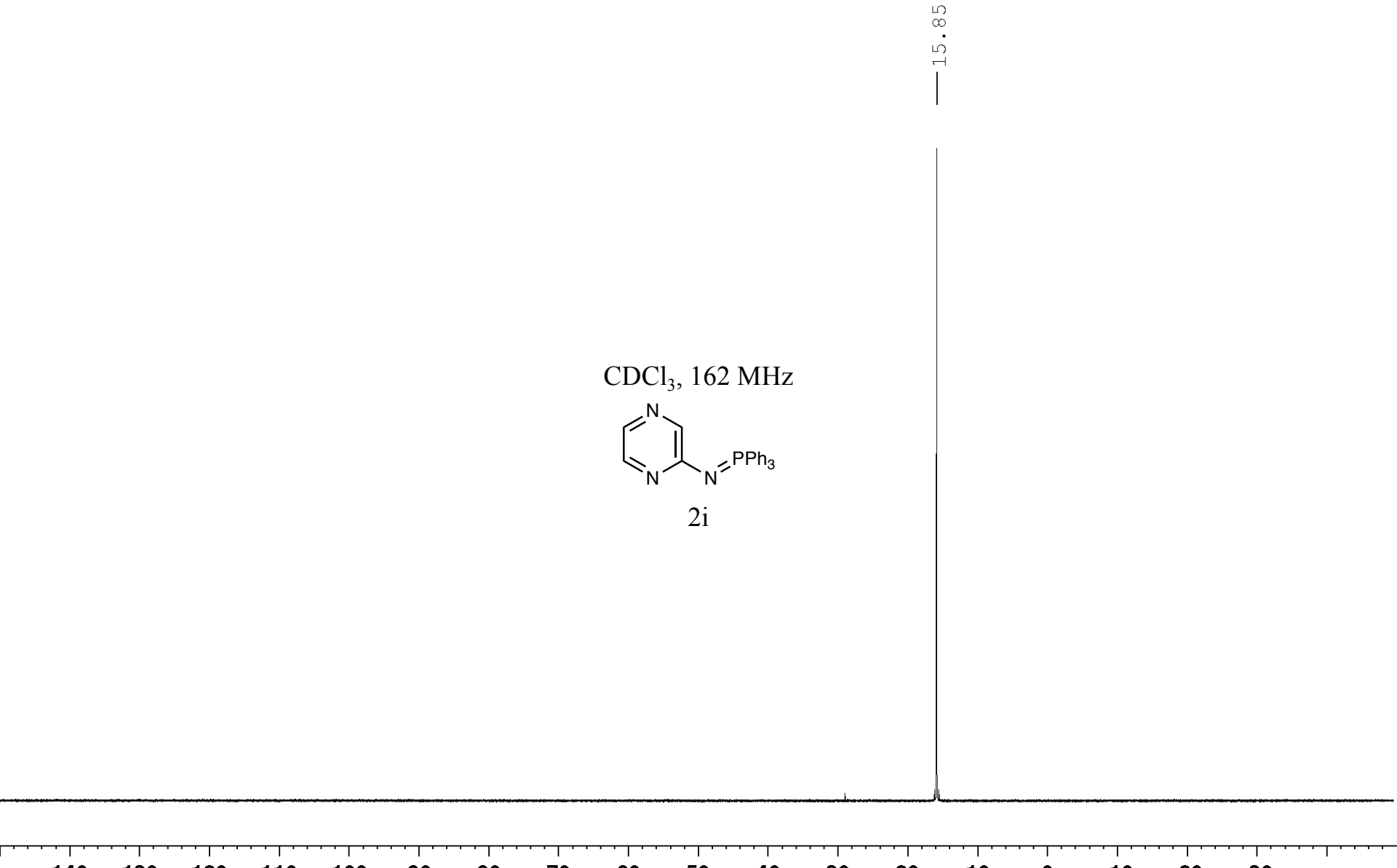
2h

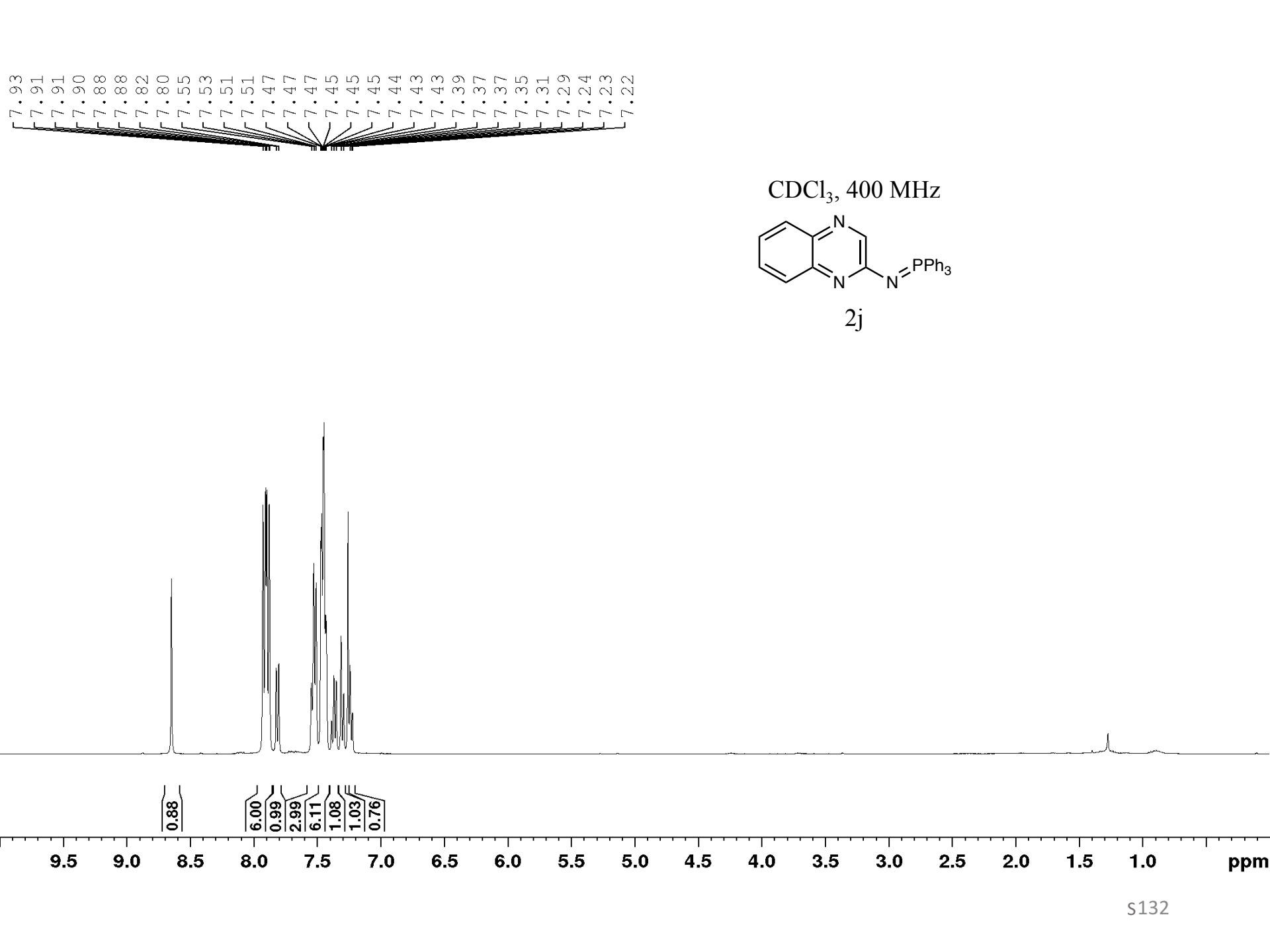
15.96

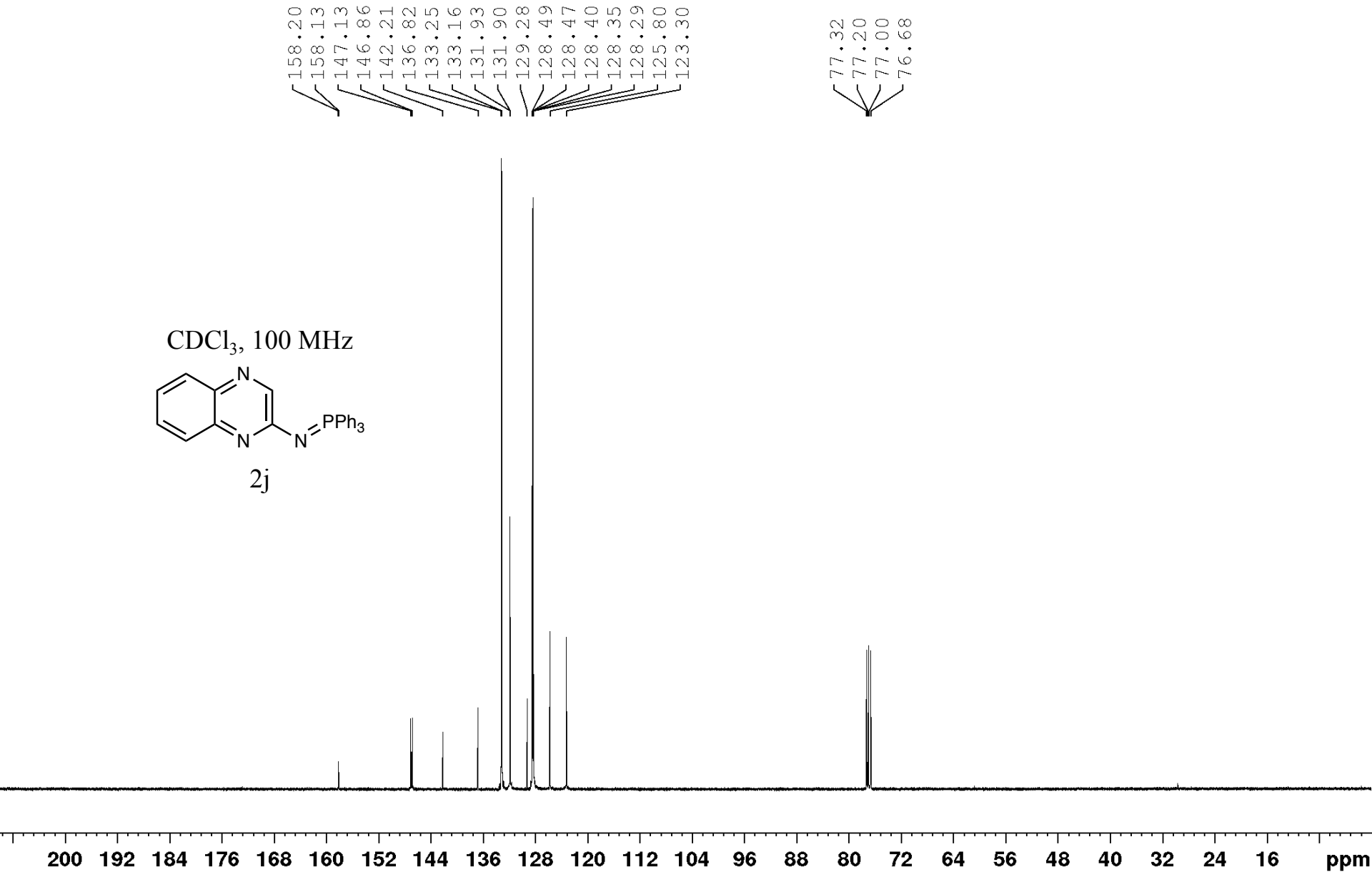



8.28
7.81
7.80
7.79
7.78
7.77
7.76
7.67
7.67
7.65
7.64
7.53
7.51
7.50
7.45
7.44
7.43
7.42
7.41
7.41
7.25
CDCl3, 400 MHz
N
N
N
PPh3
2i
0.88
6.00
2.07
3.01
6.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

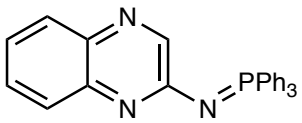

160.22
160.16
142.02
141.77
140.99
133.07
132.97
131.84
131.83
131.80
129.84
128.84
128.50
128.37
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
N
N
N
PPh3
2i
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 ppm


15.85
CDCl3, 162 MHz
N
N
N
PPh3
2i
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

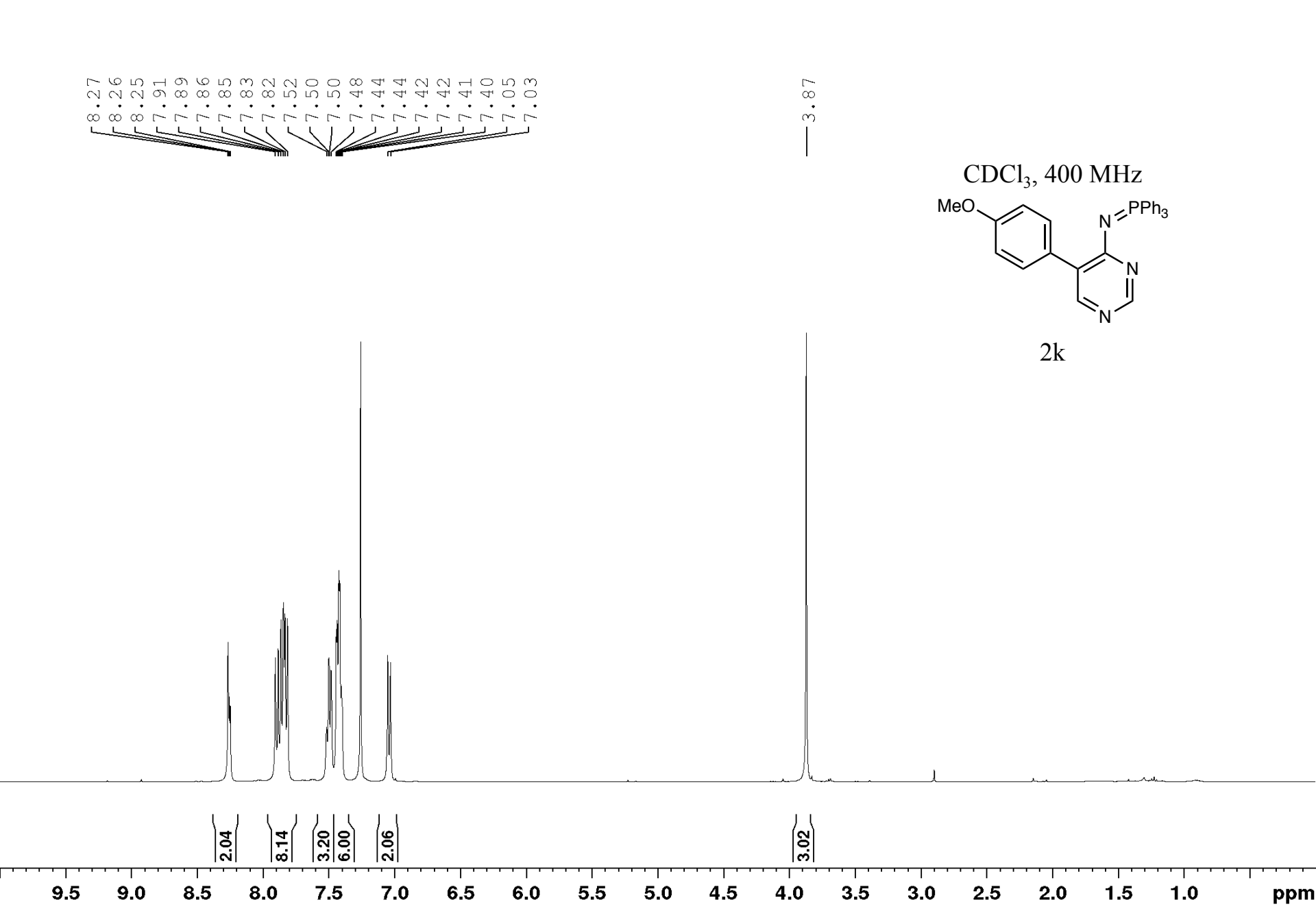

7.93
7.91
7.91
7.90
7.88
7.88
7.82
7.80
7.55
7.53
7.51
7.51
7.47
7.47
7.47
7.45
7.45
7.45
7.44
7.43
7.43
7.39
7.37
7.37
7.35
7.31
7.29
7.24
7.23
7.22
CDCl3, 400 MHz
N
N
N
PPh3
2j
0.88
6.00
0.99
2.99
6.11
1.08
1.03
0.76
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

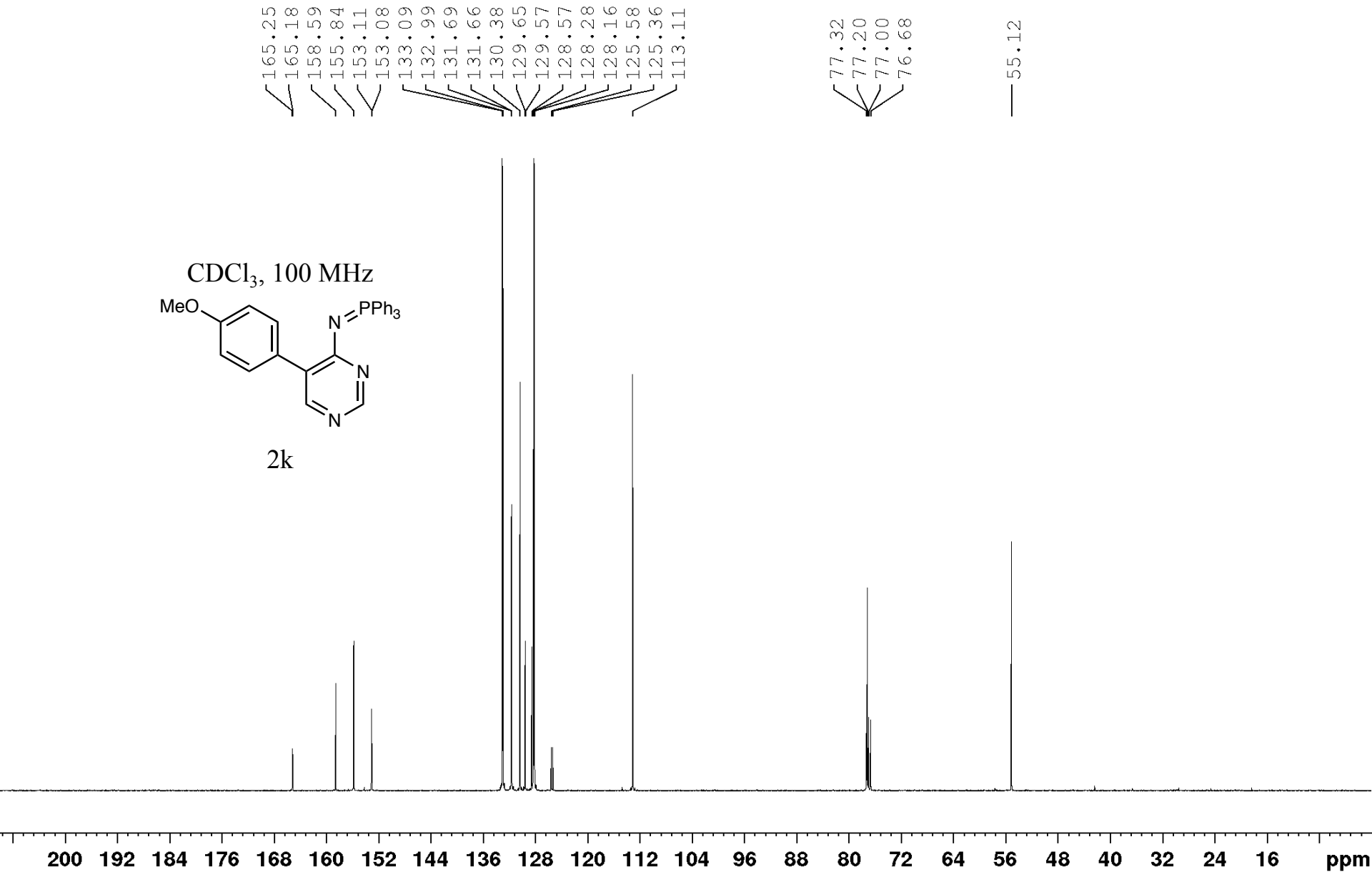

158.20
158.13
147.13
146.86
142.21
136.82
133.25
133.16
131.93
131.90
129.28
128.49
128.47
128.40
128.35
128.29
125.80
123.30
77.32
77.20
77.00
76.68
CDCl3, 100 MHz
N
N
N
PPh3
2j
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

$CDCl_3$, 162 MHz



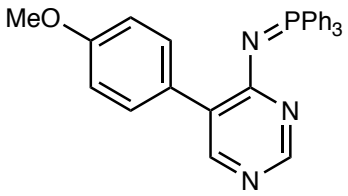
2j


8.27
8.26
8.25
7.91
7.89
7.86
7.85
7.83
7.82
7.52
7.50
7.50
7.48
7.44
7.44
7.42
7.42
7.41
7.40
7.05
7.03
3.87
CDCl3, 400 MHz
MeO
N
PPh3
N
N
2k
2.04
8.14
3.20
6.00
2.06
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


165.25
165.18
158.59
155.84
153.11
153.08
133.09
132.99
131.69
131.66
130.38
129.65
129.57
128.57
128.28
128.16
125.58
125.36
113.11
77.32
77.20
77.00
76.68
55.12
CDCl3, 100 MHz
MeO
N=PPh3
N
N
2k
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

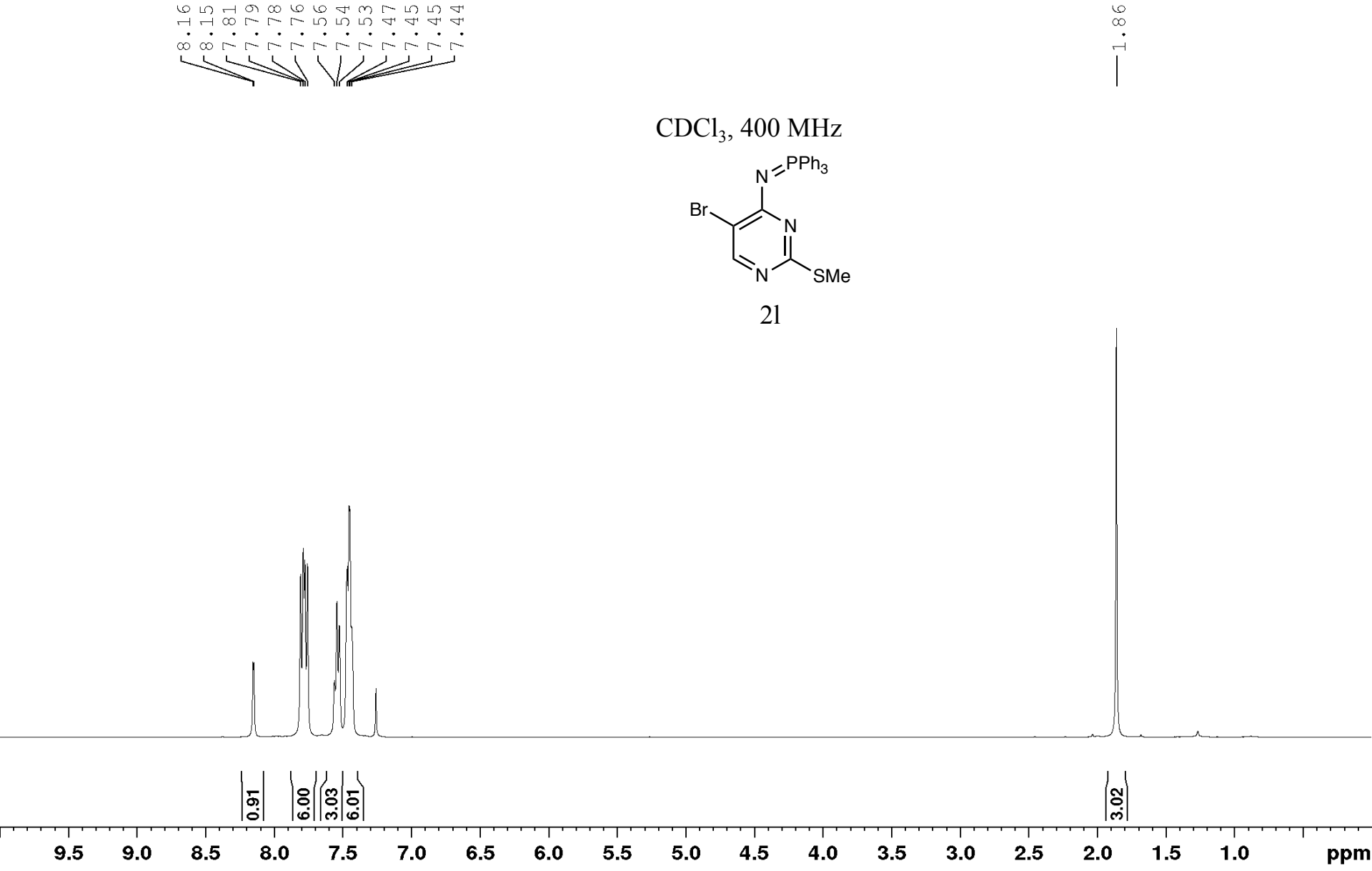
15.99

$CDCl_3$, 162 MHz

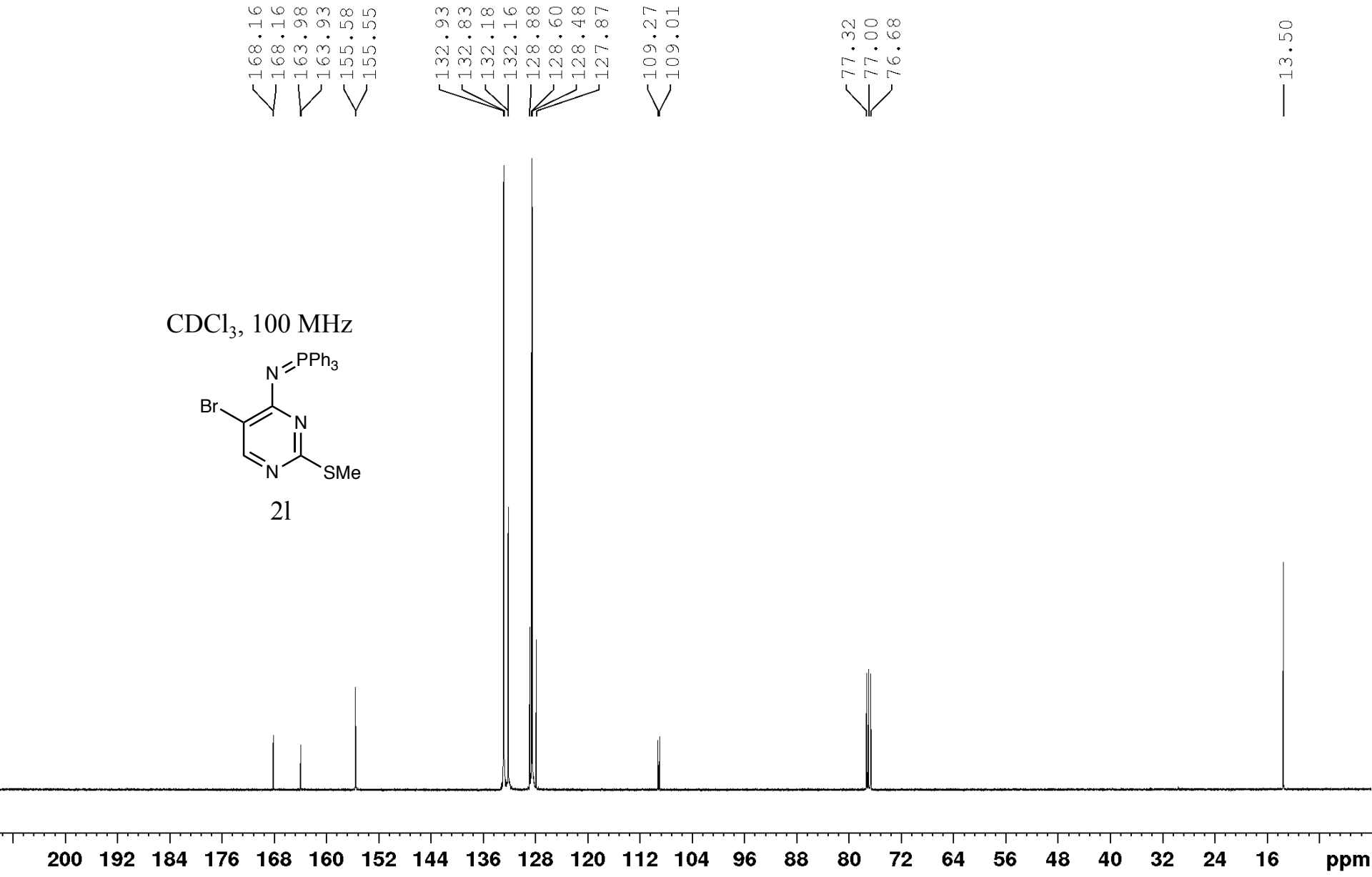


2k

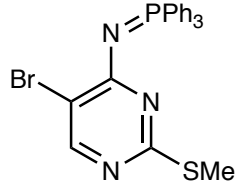
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.16
8.15
7.81
7.79
7.78
7.76
7.56
7.54
7.53
7.47
7.45
7.45
7.44
1.86
CDCl3, 400 MHz
N
PPh3
Br
N
N
SMe
0.91
6.00
3.03
6.01
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

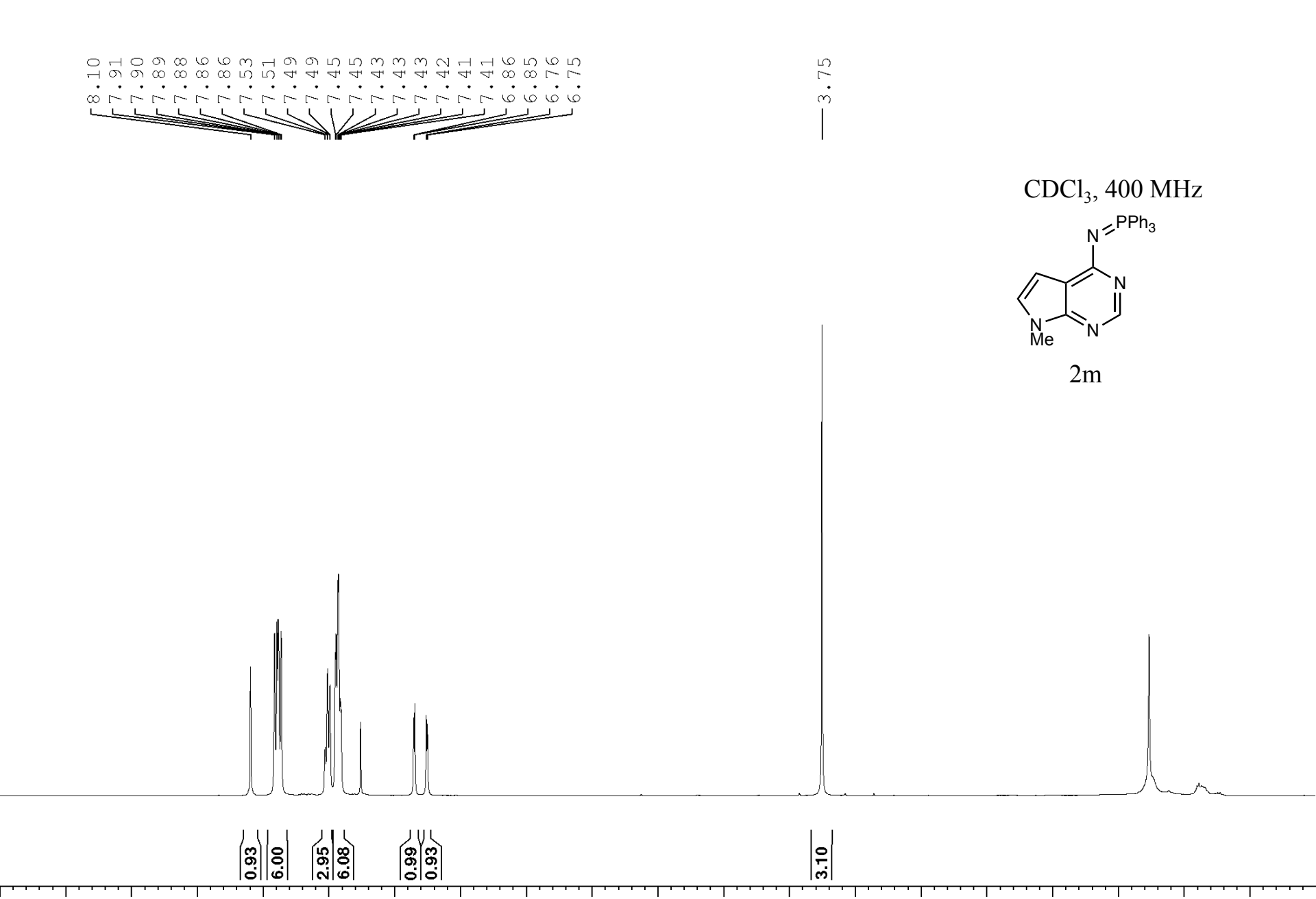
21

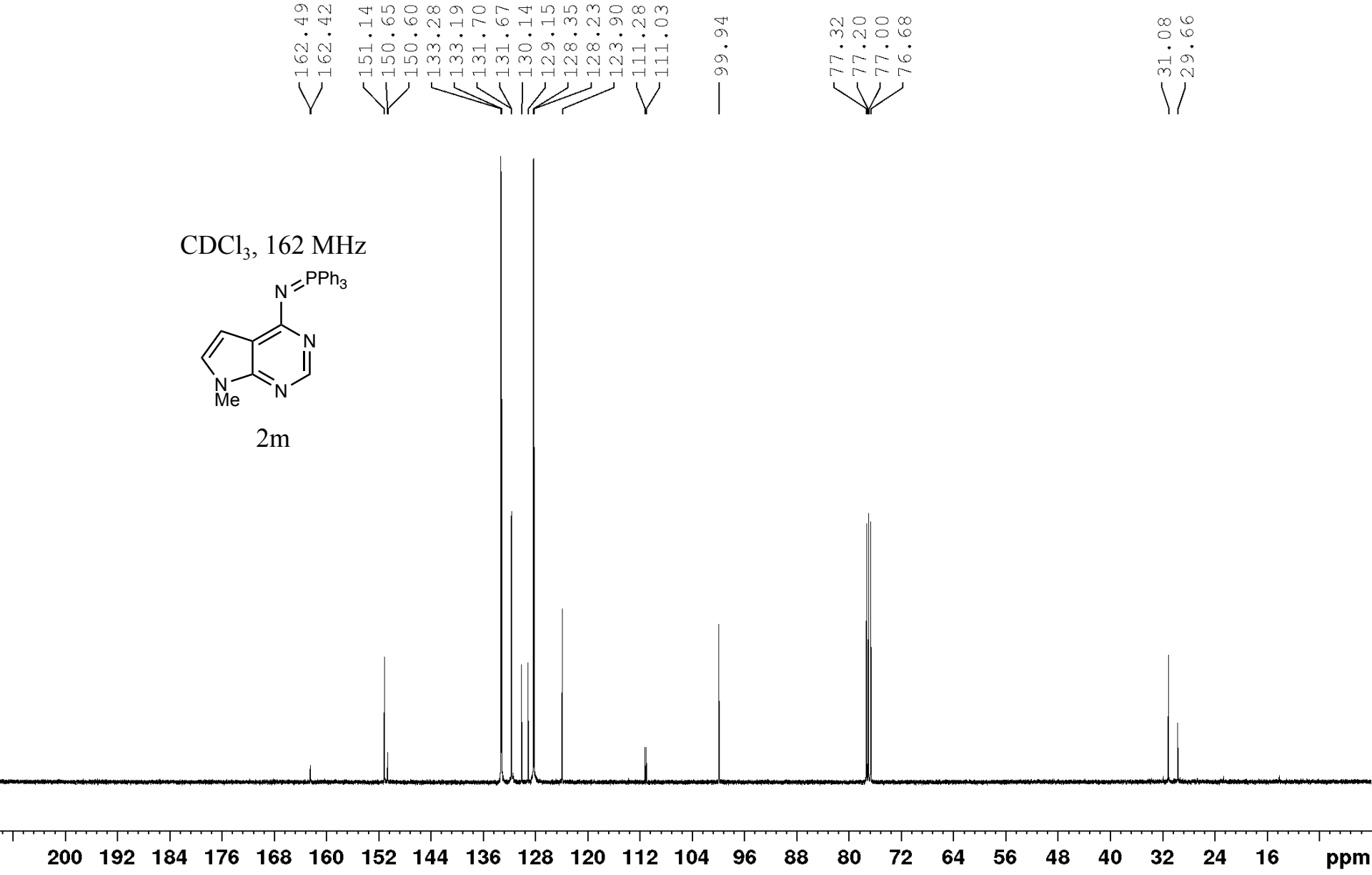

168.16
168.16
163.98
163.93
155.58
155.55
132.93
132.83
132.18
132.16
128.88
128.60
128.48
127.87
109.27
109.01
77.32
77.00
76.68
13.50
CDCl3, 100 MHz
N
PPh3
Br
N
N
SMe
2l
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

$CDCl_3$, 162 MHz

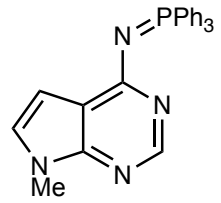


21

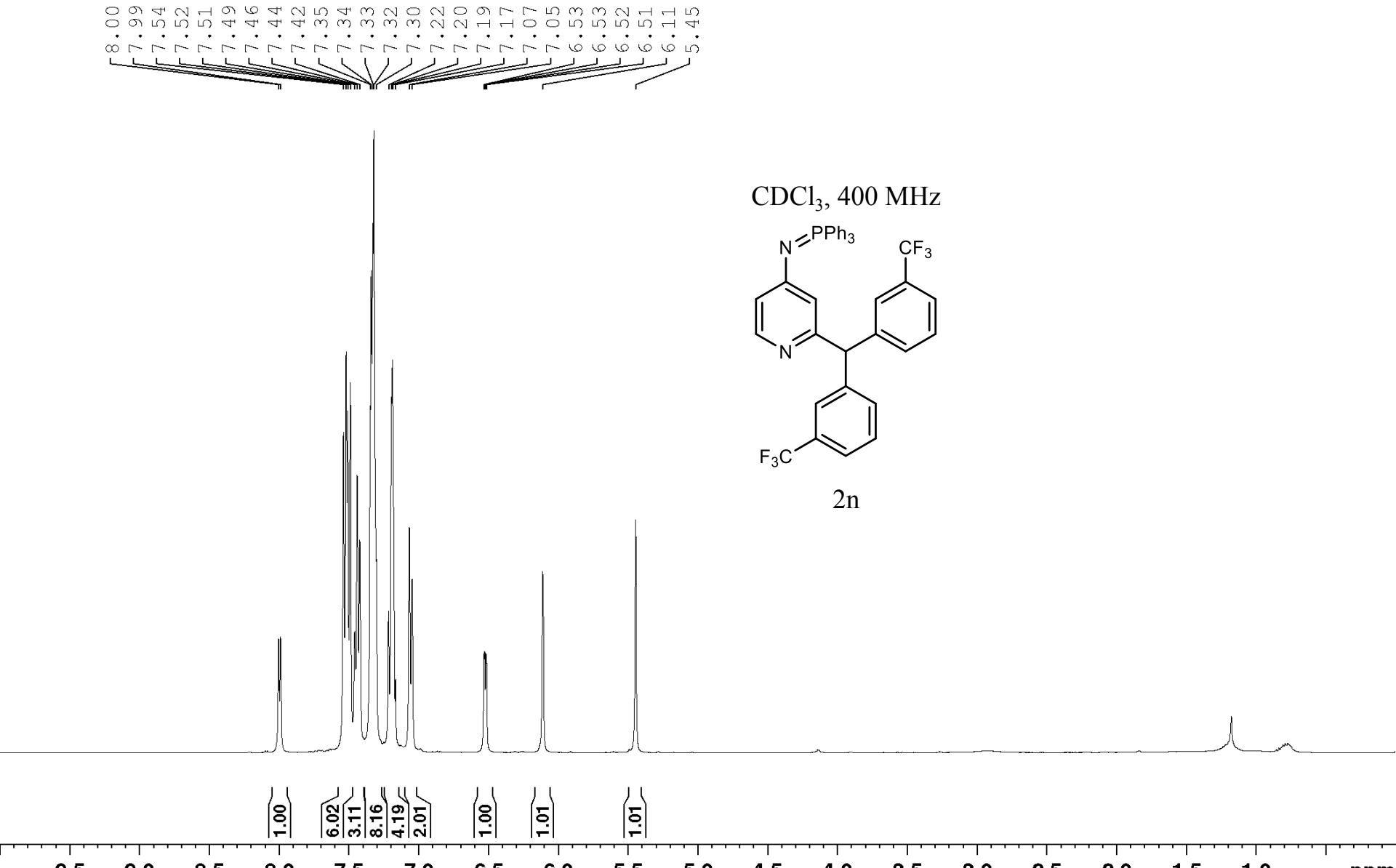

8.10
7.91
7.90
7.89
7.88
7.86
7.86
7.53
7.51
7.49
7.49
7.45
7.45
7.43
7.43
7.43
7.42
7.41
7.41
6.86
6.85
6.76
6.75
3.75
CDCl3, 400 MHz
N
PPh3
N
N
N
Me
2m
0.93
6.00
2.95
6.08
0.99
0.93
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

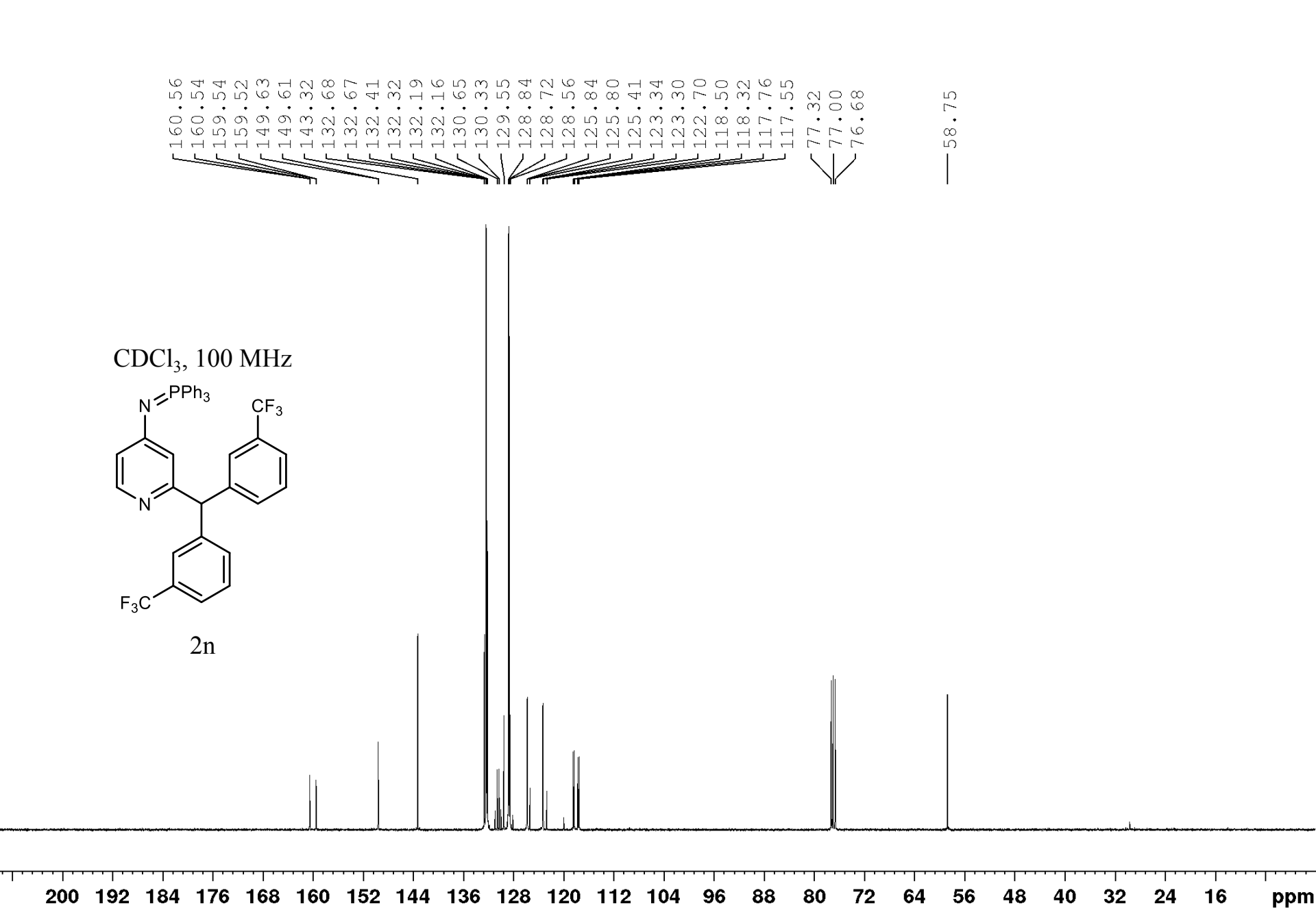

162.49
162.42
151.14
150.65
150.60
133.28
133.19
131.70
131.67
130.14
129.15
128.35
128.23
123.90
111.28
111.03
99.94
77.32
77.20
77.00
76.68
31.08
29.66
CDCl3, 162 MHz
N
PPh3
N
N
N
Me
2m
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

$CDCl_3$, 162 MHz

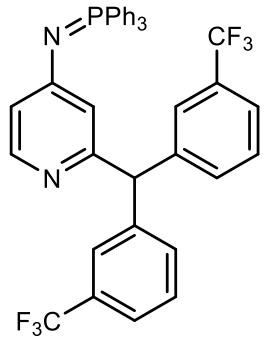


2m

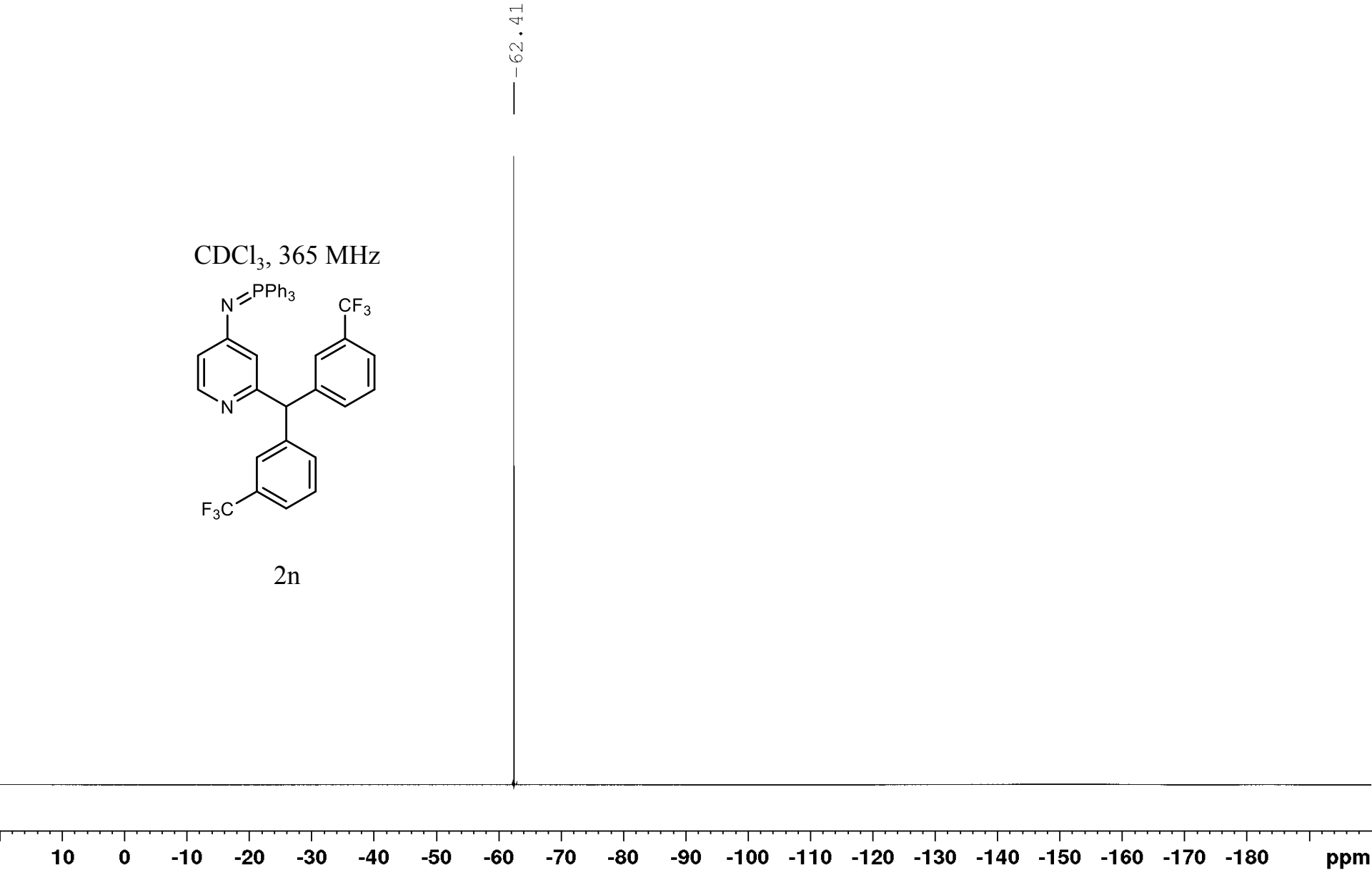

8.00
7.99
7.54
7.52
7.51
7.49
7.46
7.44
7.42
7.35
7.34
7.33
7.32
7.30
7.22
7.20
7.19
7.17
7.07
7.05
6.53
6.53
6.52
6.51
6.11
5.45
CDCl3, 400 MHz
N
PPh3
CF3
N
F3C
2n
1.00
6.02
3.11
8.16
4.19
2.01
1.00
1.01
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

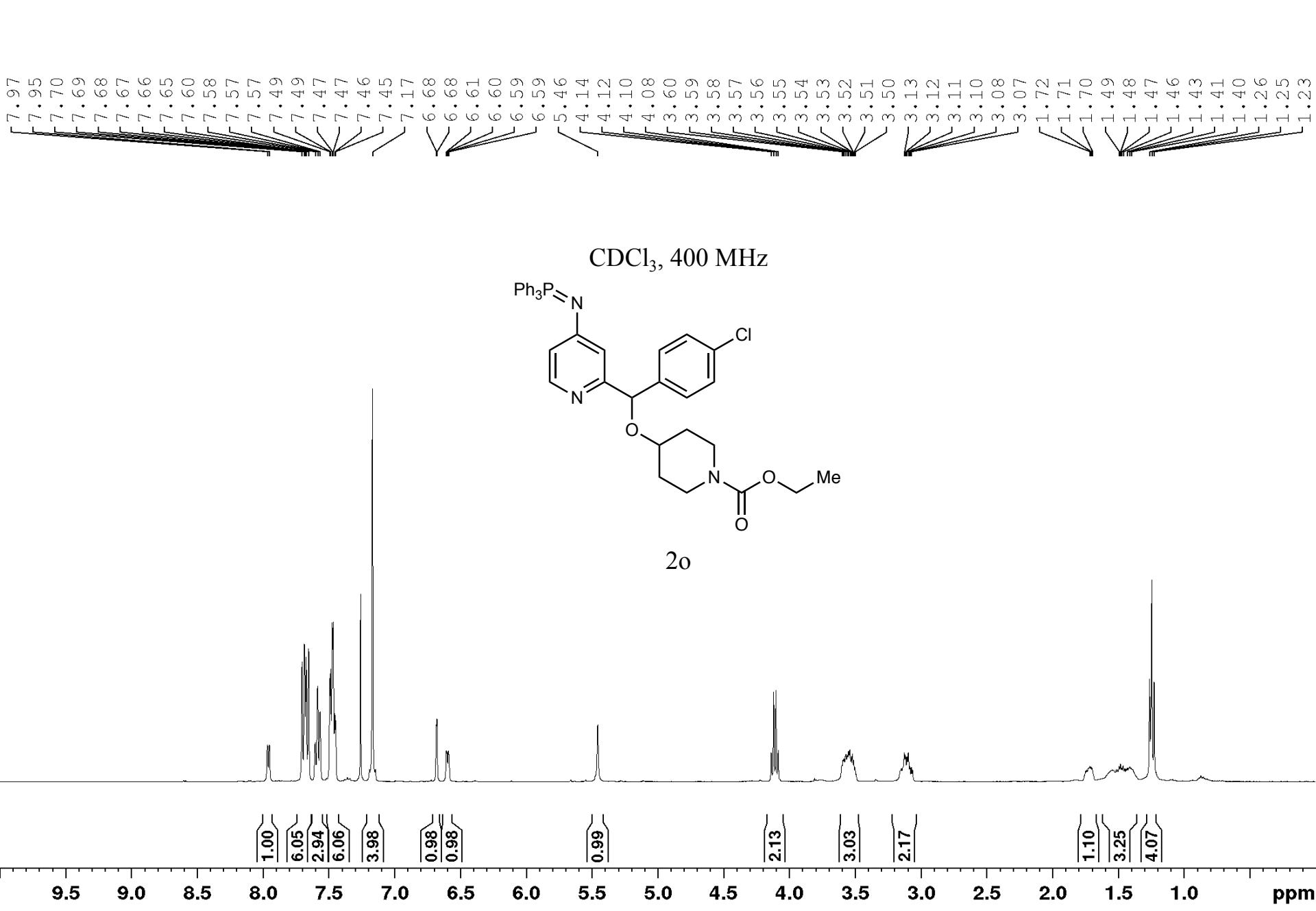

160.56
160.54
159.54
159.52
149.63
149.61
143.32
132.68
132.67
132.41
132.32
132.19
132.16
130.65
130.33
129.55
128.84
128.72
128.56
125.84
125.80
125.41
123.34
123.30
122.70
118.50
118.32
117.76
117.55
77.32
77.00
76.68
58.75
CDCl3, 100 MHz
N
PPh3
CF3
N
F3C
2n
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

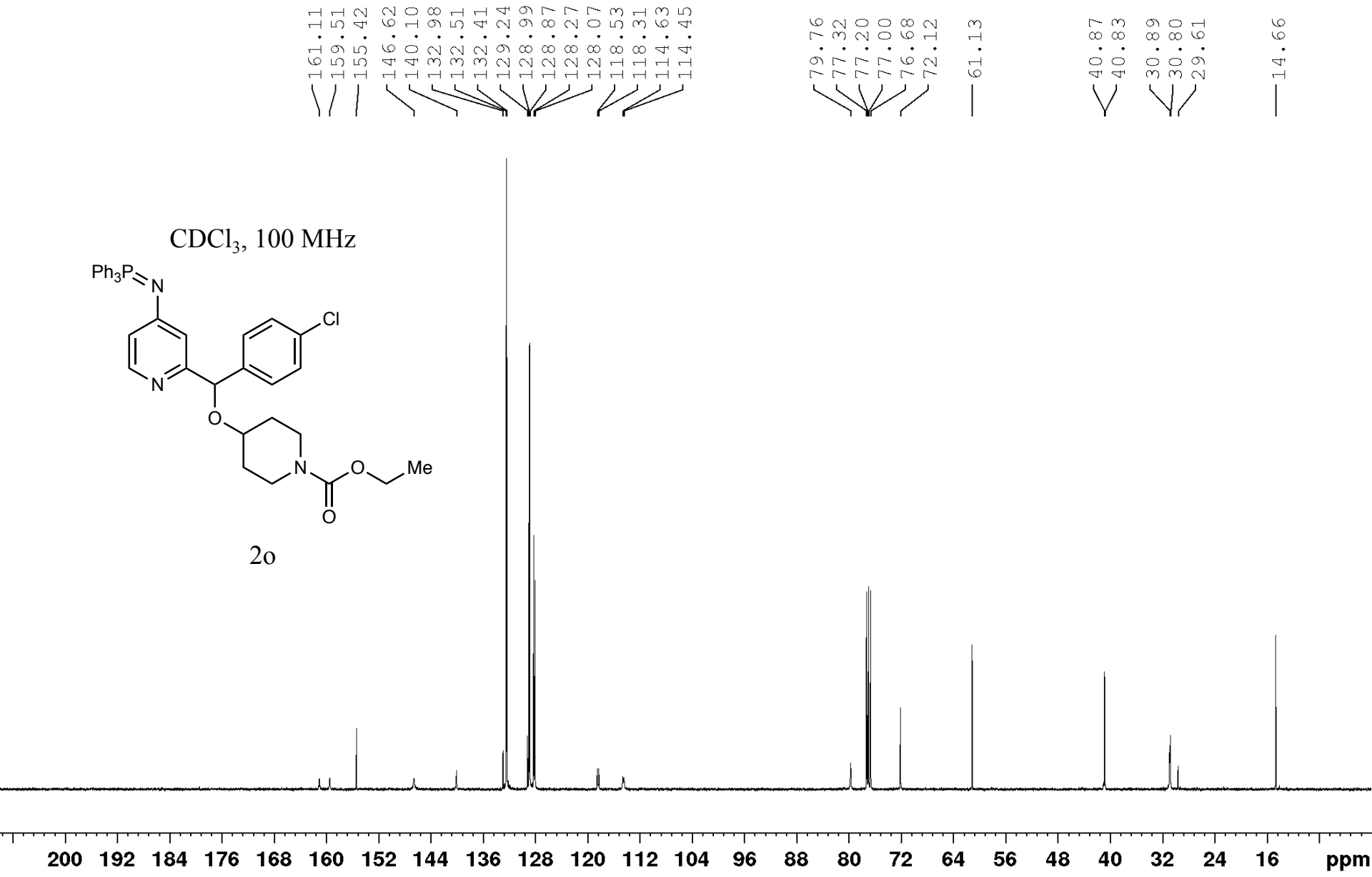
$CDCl_3$, 162 MHz



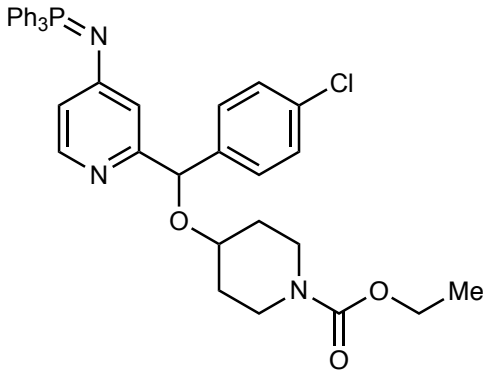
2n


-62.41
CDCl3, 365 MHz
N
PPh3
CF3
N
F3C
2n
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

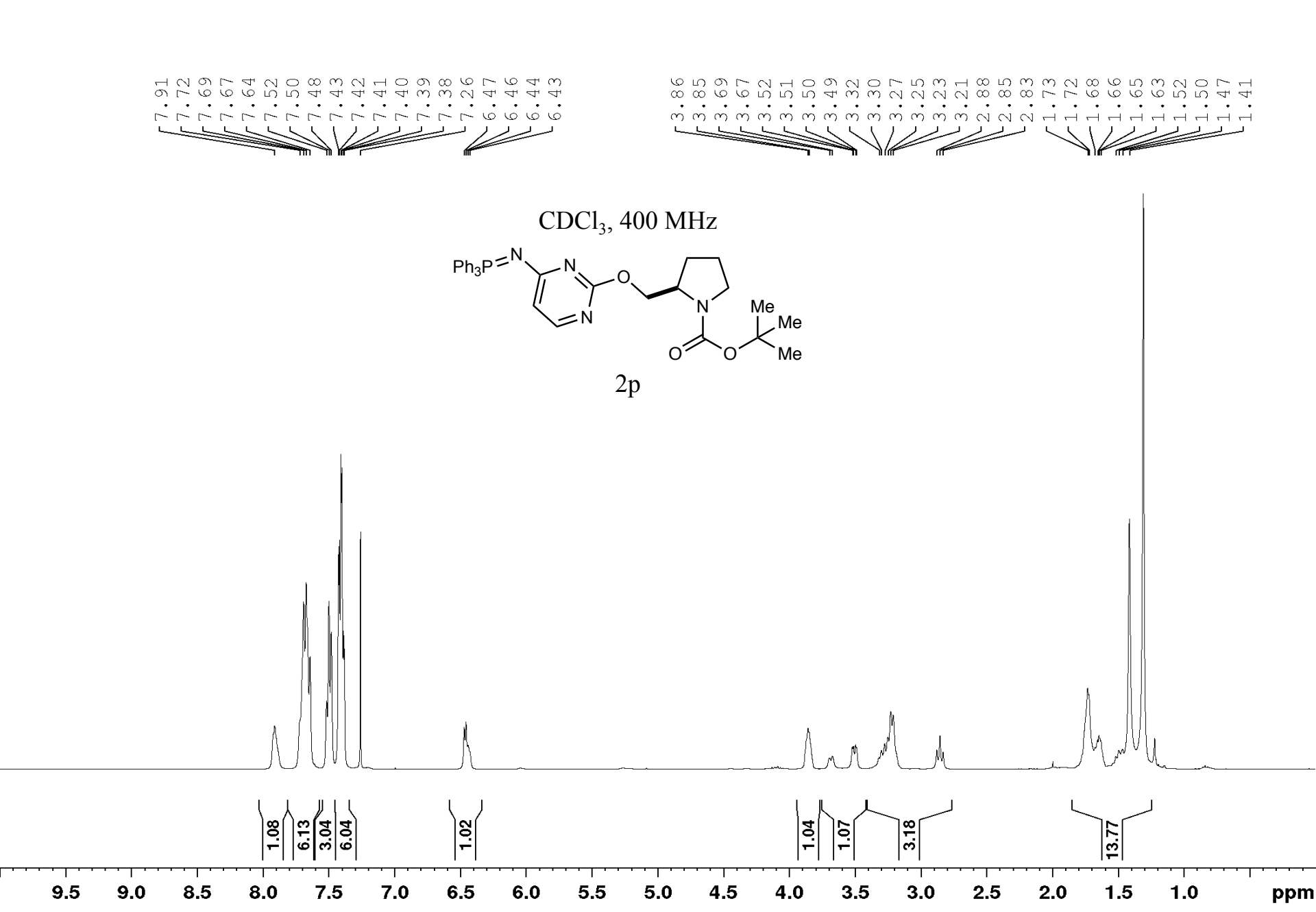

7.97
7.95
7.70
7.69
7.68
7.67
7.66
7.65
7.60
7.58
7.57
7.57
7.49
7.49
7.47
7.47
7.46
7.45
7.17
6.68
6.68
6.61
6.60
6.59
6.59
5.46
4.14
4.12
4.10
4.08
3.60
3.59
3.58
3.57
3.56
3.55
3.54
3.53
3.52
3.51
3.50
3.13
3.12
3.11
3.10
3.08
3.07
1.72
1.71
1.70
1.49
1.48
1.47
1.46
1.43
1.41
1.40
1.26
1.25
1.23
CDCl3, 400 MHz
Ph3P=N
Cl
N
O
N
O
Me
O
2o
1.00
6.05
2.94
6.06
3.98
0.98
0.98
0.99
2.13
3.03
2.17
1.10
3.25
4.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

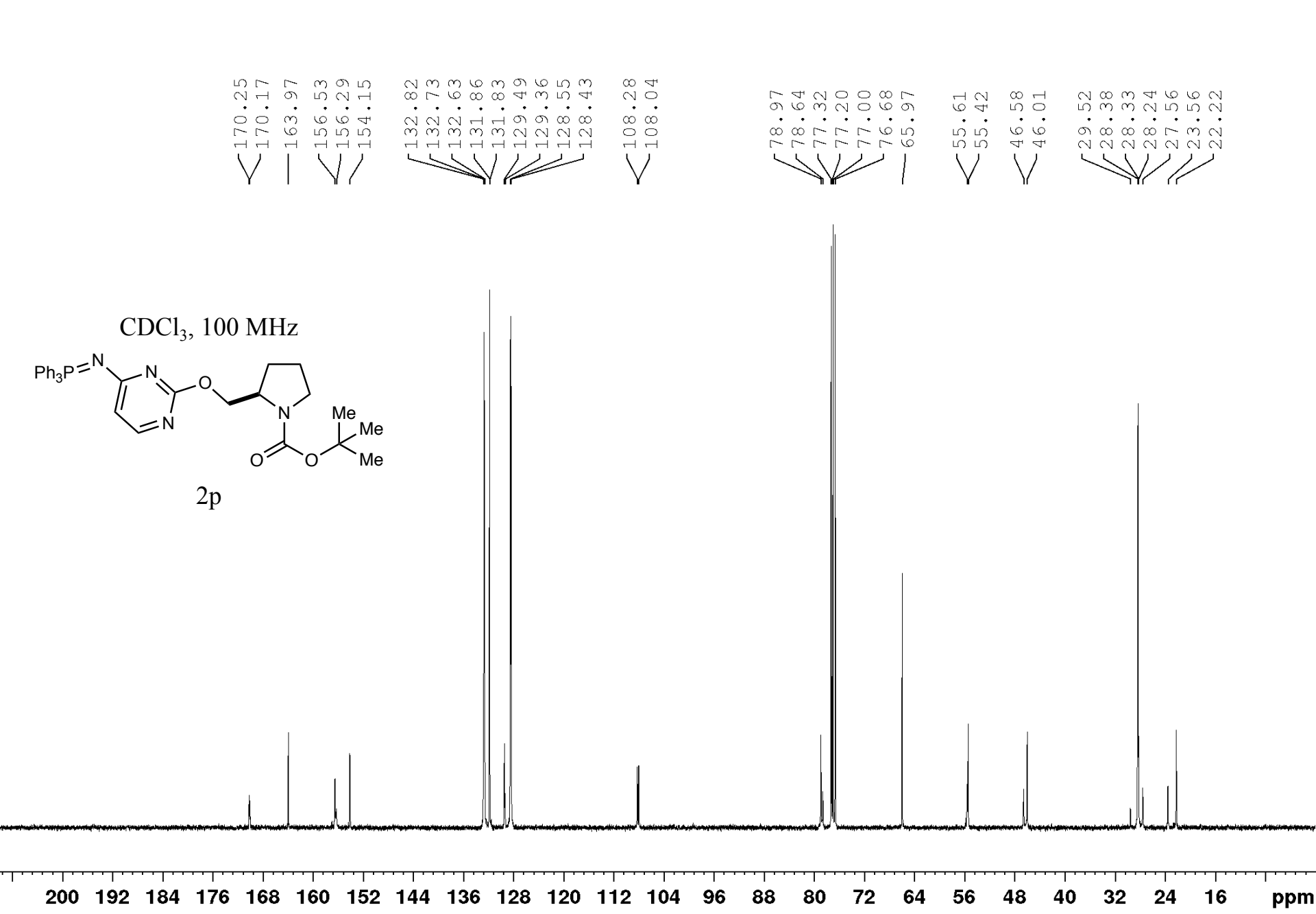

161.11
159.51
155.42
146.62
140.10
132.98
132.51
132.41
129.24
128.99
128.87
128.27
128.07
118.53
118.31
114.63
114.45
79.76
77.32
77.20
77.00
76.68
72.12
61.13
40.87
40.83
30.89
30.80
29.61
14.66
CDCl3, 100 MHz
Ph3P=N
Cl
N
O
N
O
Me
O
2o
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

$CDCl_3$, 162 MHz

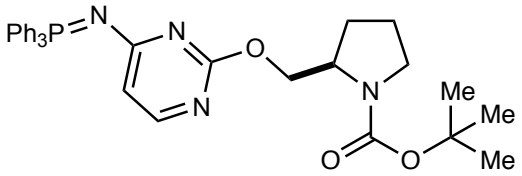


2o


7.91
7.72
7.69
7.67
7.64
7.52
7.50
7.48
7.43
7.42
7.41
7.40
7.39
7.38
7.26
6.47
6.46
6.44
6.43
3.86
3.85
3.69
3.67
3.52
3.51
3.50
3.49
3.32
3.30
3.27
3.25
3.23
3.21
2.88
2.85
2.83
1.73
1.72
1.68
1.66
1.65
1.63
1.52
1.50
1.47
1.41
CDCl3, 400 MHz
Ph3P=N
N
N
O
N
Me
Me
Me
O
O
2p
1.08
6.13
3.04
6.04
1.02
1.04
1.07
3.18
13.77
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


170.25
170.17
163.97
156.53
156.29
154.15
132.82
132.73
132.63
131.86
131.83
129.49
129.36
128.55
128.43
108.28
108.04
78.97
78.64
77.32
77.20
77.00
76.68
65.97
55.61
55.42
46.58
46.01
29.52
28.38
28.33
28.24
27.56
23.56
22.22
CDCl3, 100 MHz
Ph3P=N
N
N
O
N
Me
Me
Me
O
O
2p
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

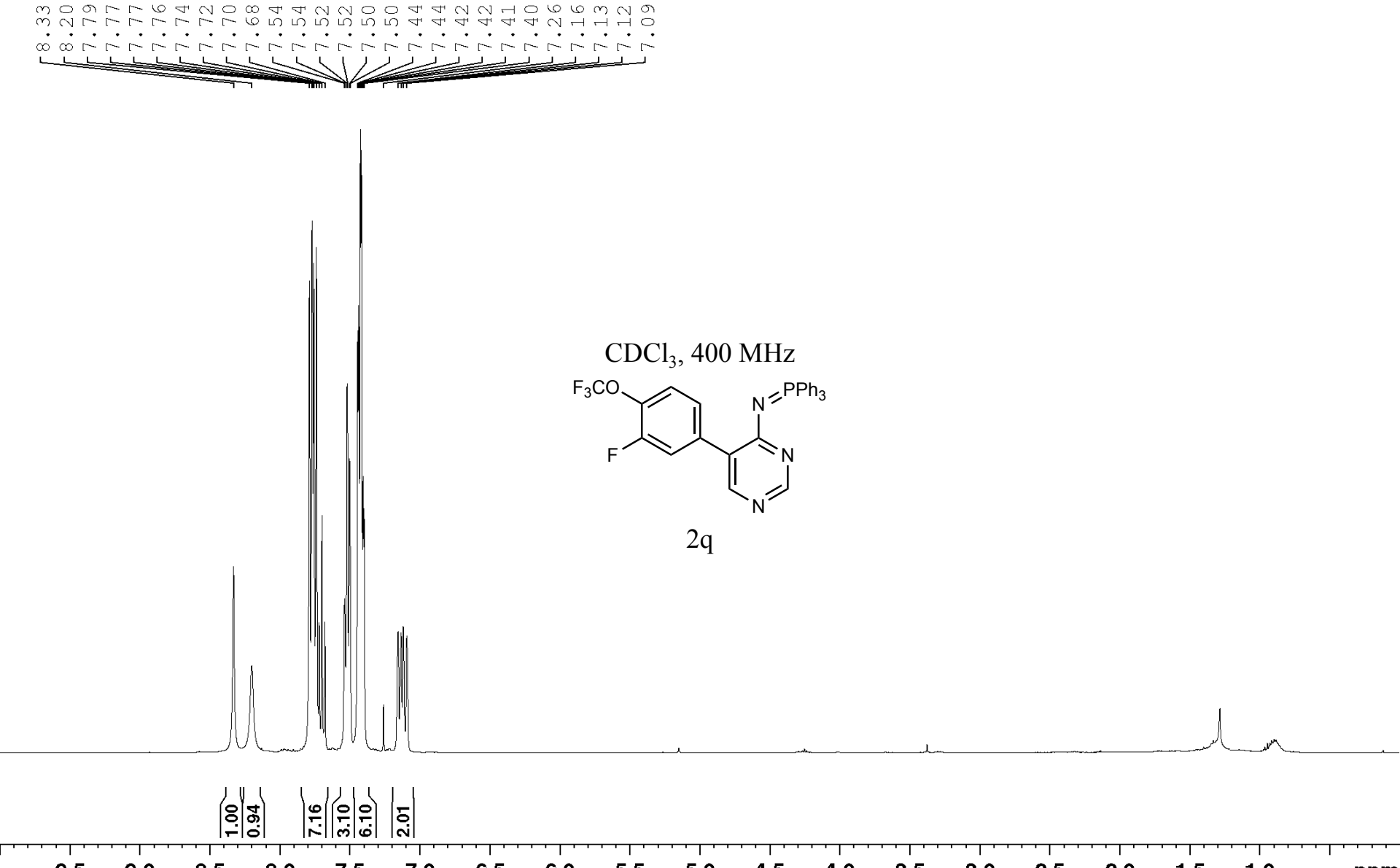
$CDCl_3$, 162 MHz

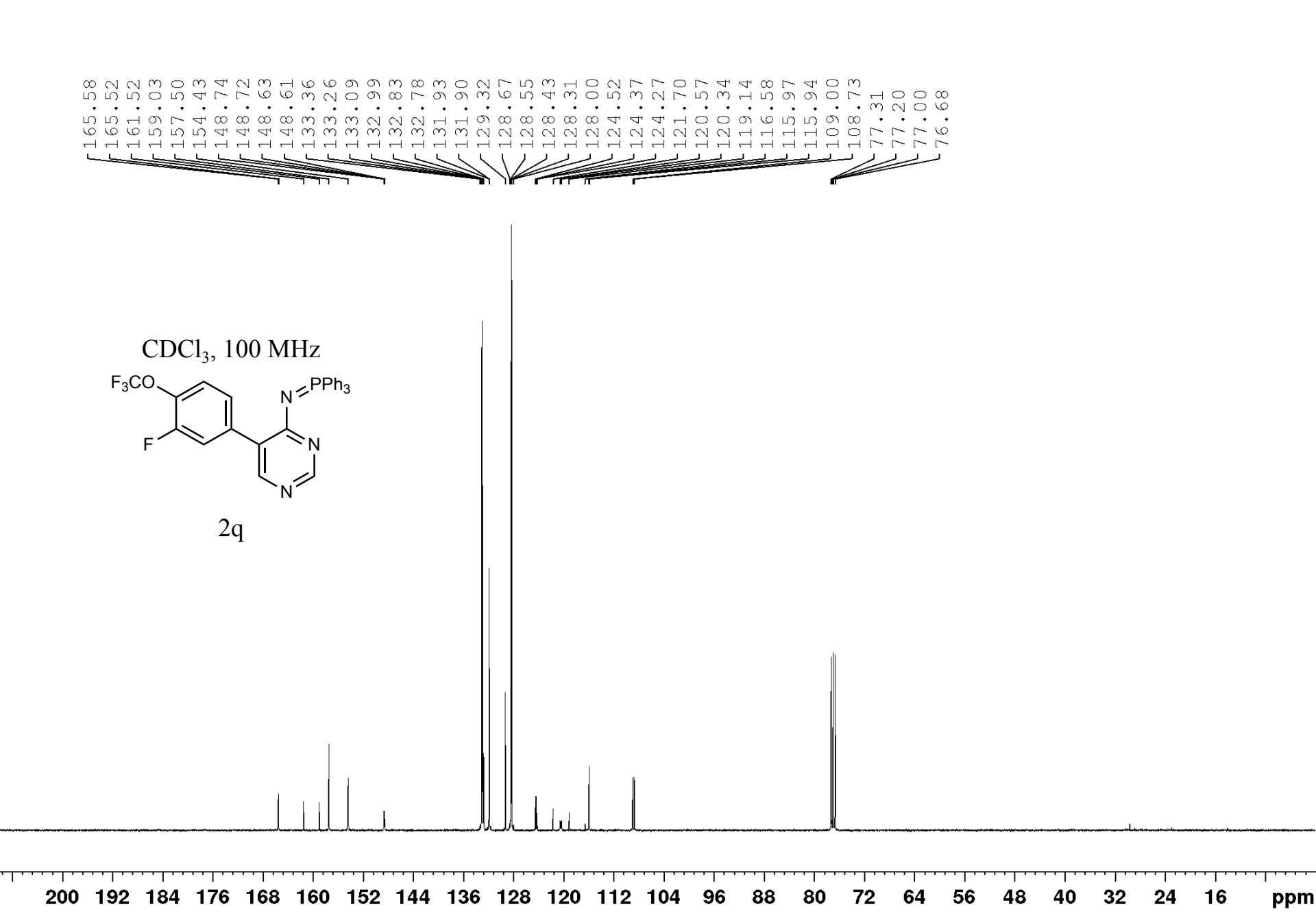


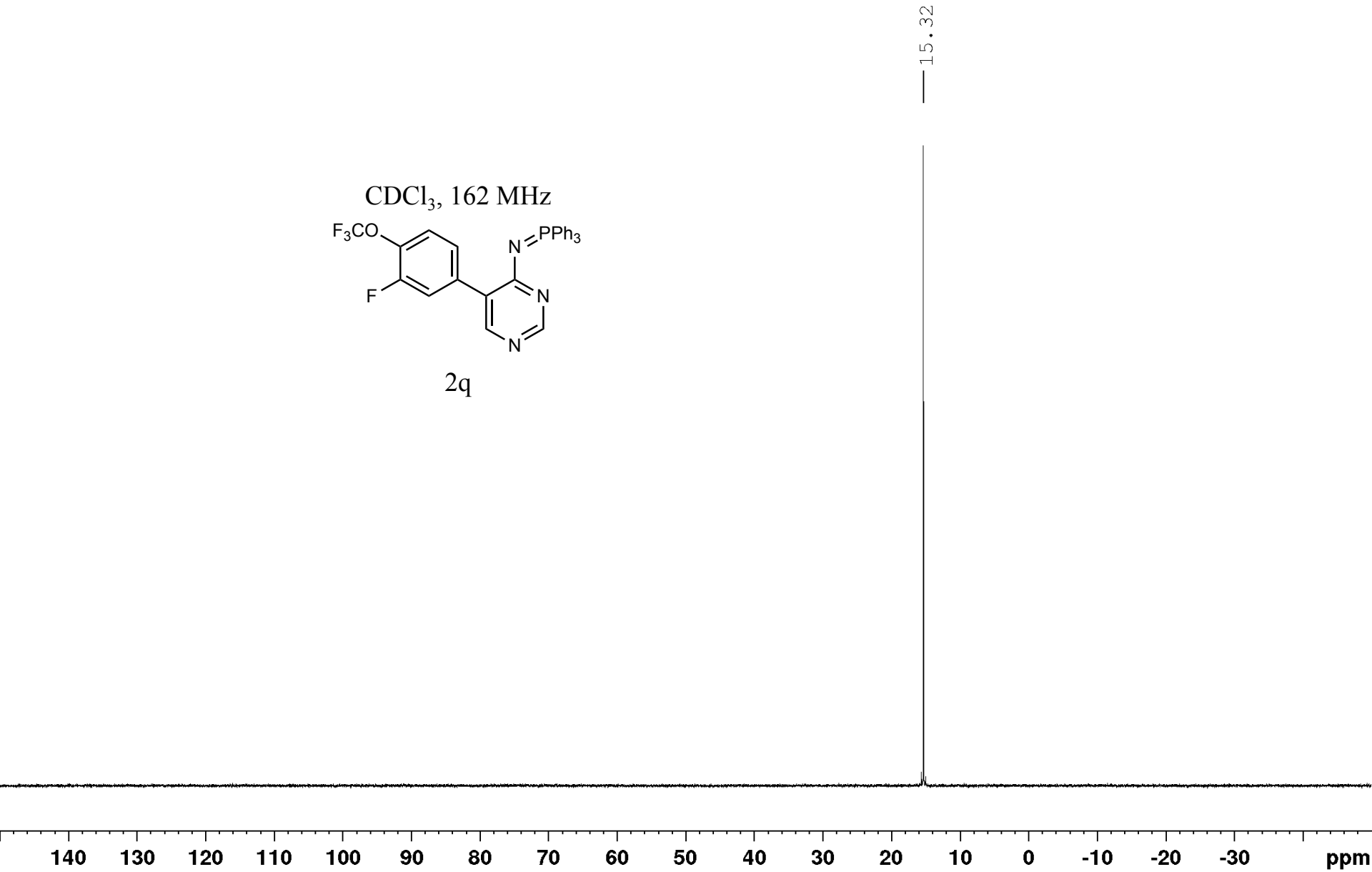
2p

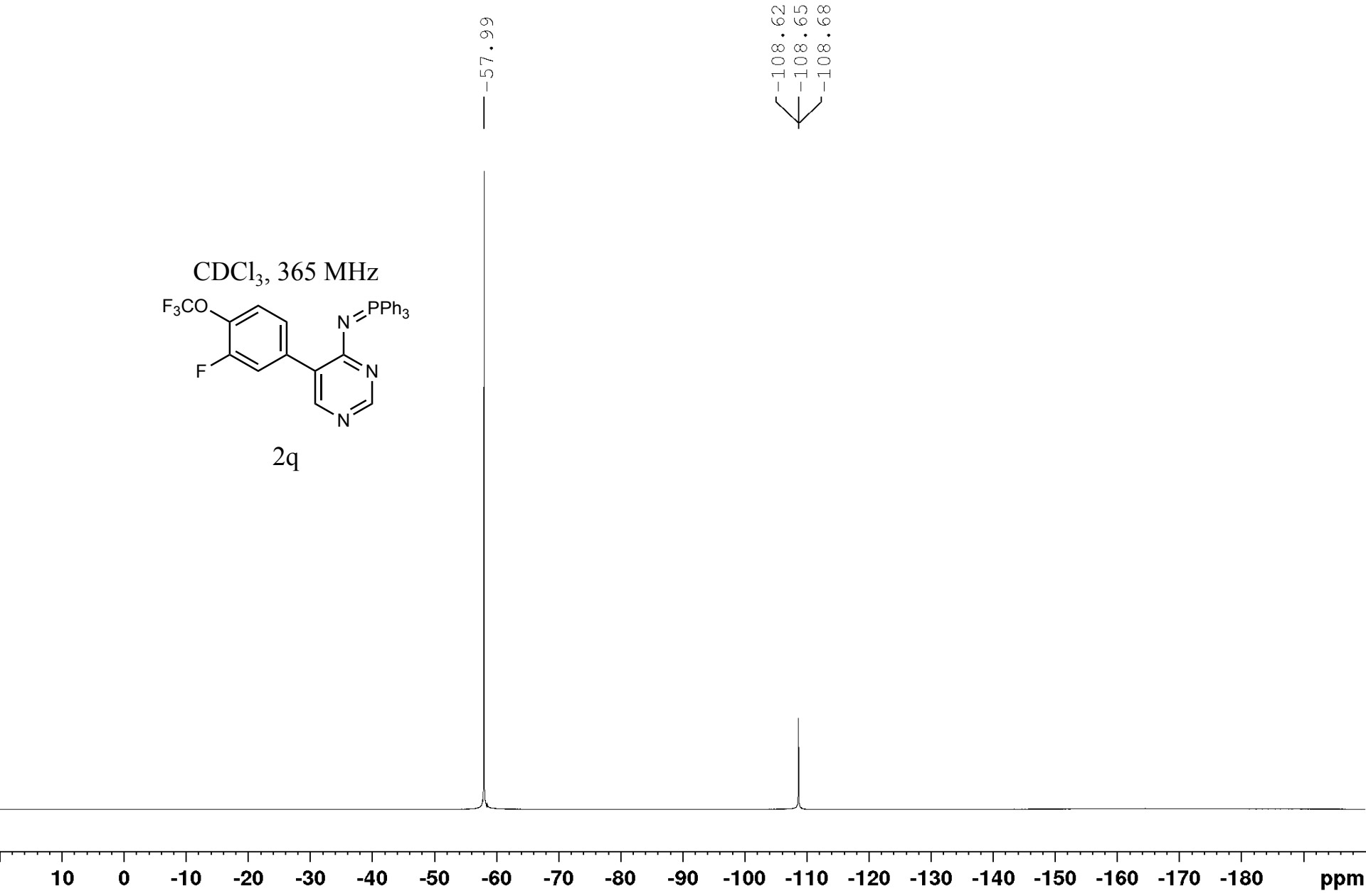
17.78

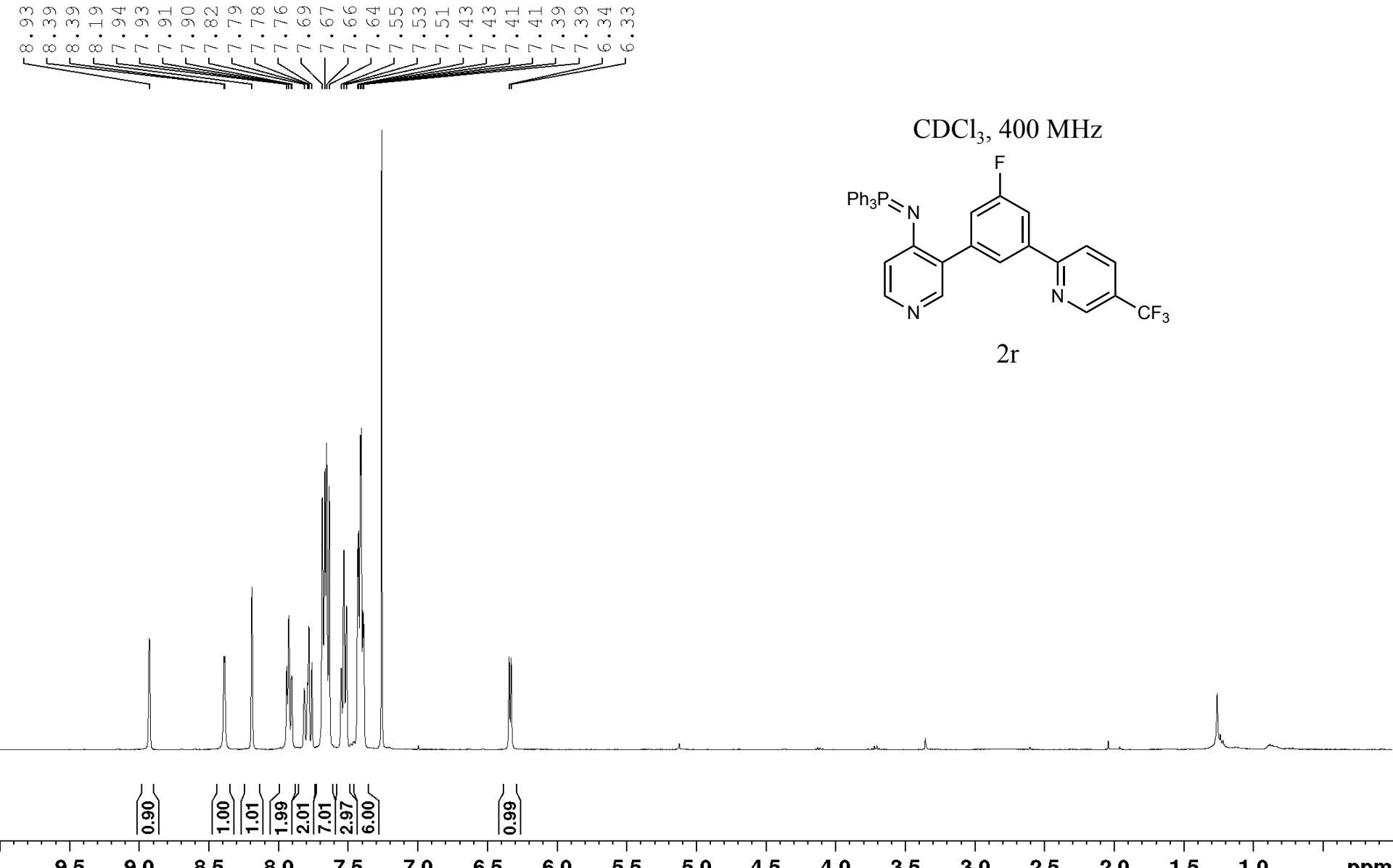
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.33
8.20
7.79
7.77
7.77
7.76
7.74
7.72
7.70
7.68
7.54
7.54
7.52
7.52
7.50
7.50
7.44
7.44
7.42
7.42
7.41
7.40
7.26
7.16
7.13
7.12
7.09
CDCl3, 400 MHz
F3CO
F
N
PPh3
N
N
2q
1.00
0.94
7.16
3.10
6.10
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


165.58
165.52
161.52
159.03
157.50
154.43
148.74
148.72
148.63
148.61
133.36
133.26
133.09
132.99
132.83
132.78
131.93
131.90
129.32
128.67
128.55
128.43
128.31
128.00
124.52
124.37
124.27
121.70
120.57
120.34
119.14
116.58
115.97
115.94
109.00
108.73
77.31
77.20
77.00
76.68
CDCl3, 100 MHz
F3CO
N=PPh3
F
N
N
2q
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


15.32
CDCl3, 162 MHz
F3CO
F
N
PPh3
N
N
2q
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


-57.99
-108.62
-108.65
-108.68
CDCl3, 365 MHz
F3CO
N=PPh3
F
N
N
2q
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

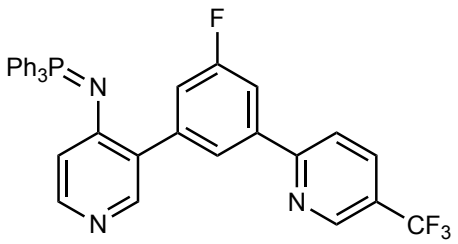


$CDCl_3$, 400 MHz

2r

159.73
159.72
155.86
150.03
150.01
148.93
146.60
146.56
146.52
146.48
141.84
141.75
139.05
138.97
133.94
133.91
133.87
133.84
132.50
132.40
132.18
132.15
130.41
130.19
129.19
128.88
128.76
127.74
125.49
125.16
125.03
124.83
124.71
124.68
124.50
122.32
119.93
119.62
118.86
118.64
116.95
116.83
112.21
111.98
77.32
77.00
76.68

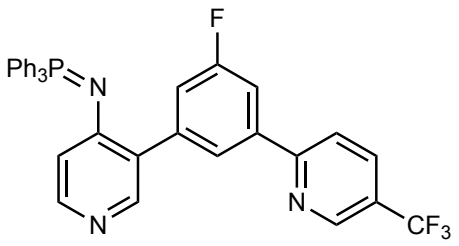
$CDCl_3$, 100 MHz



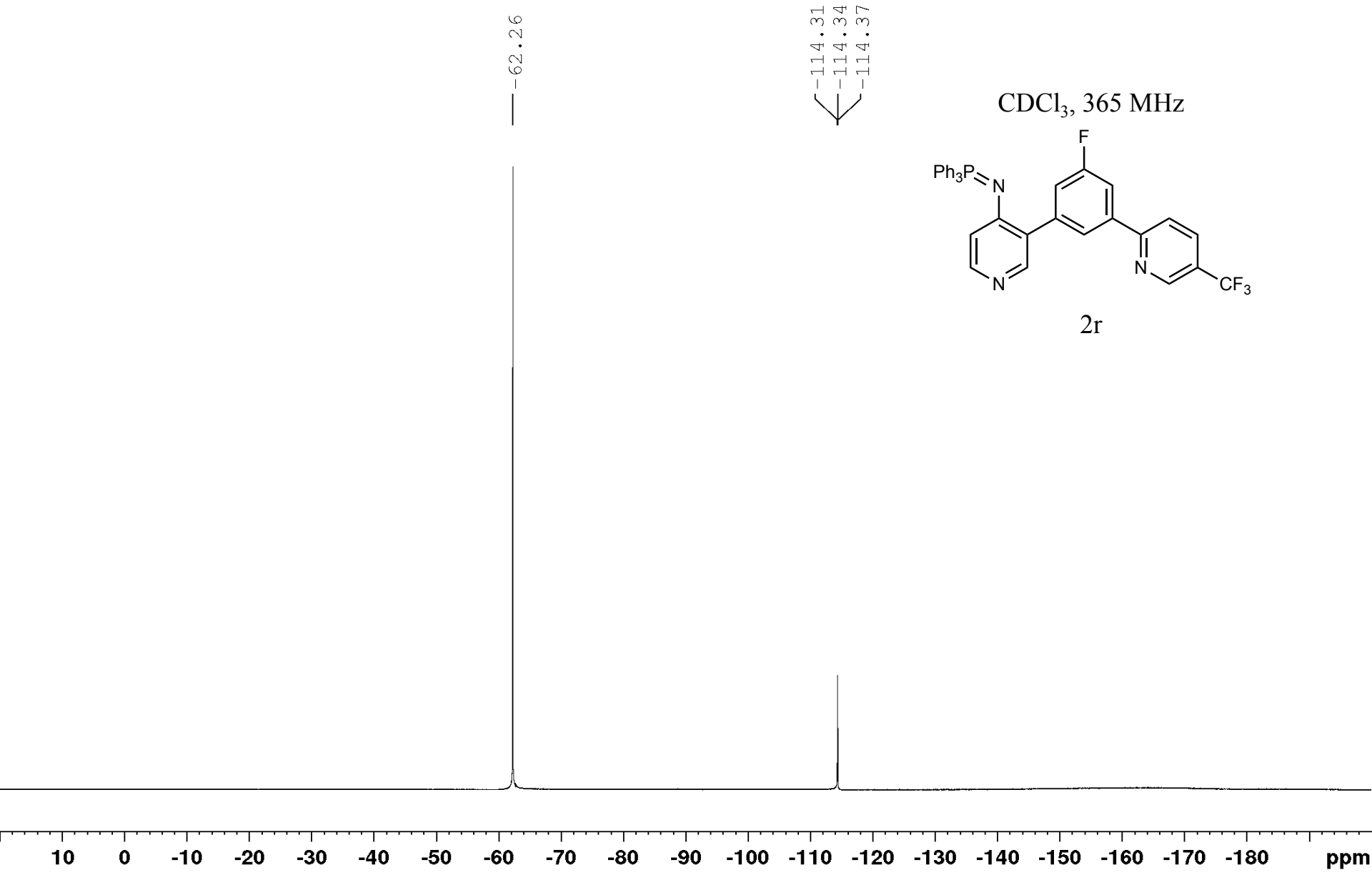
2r

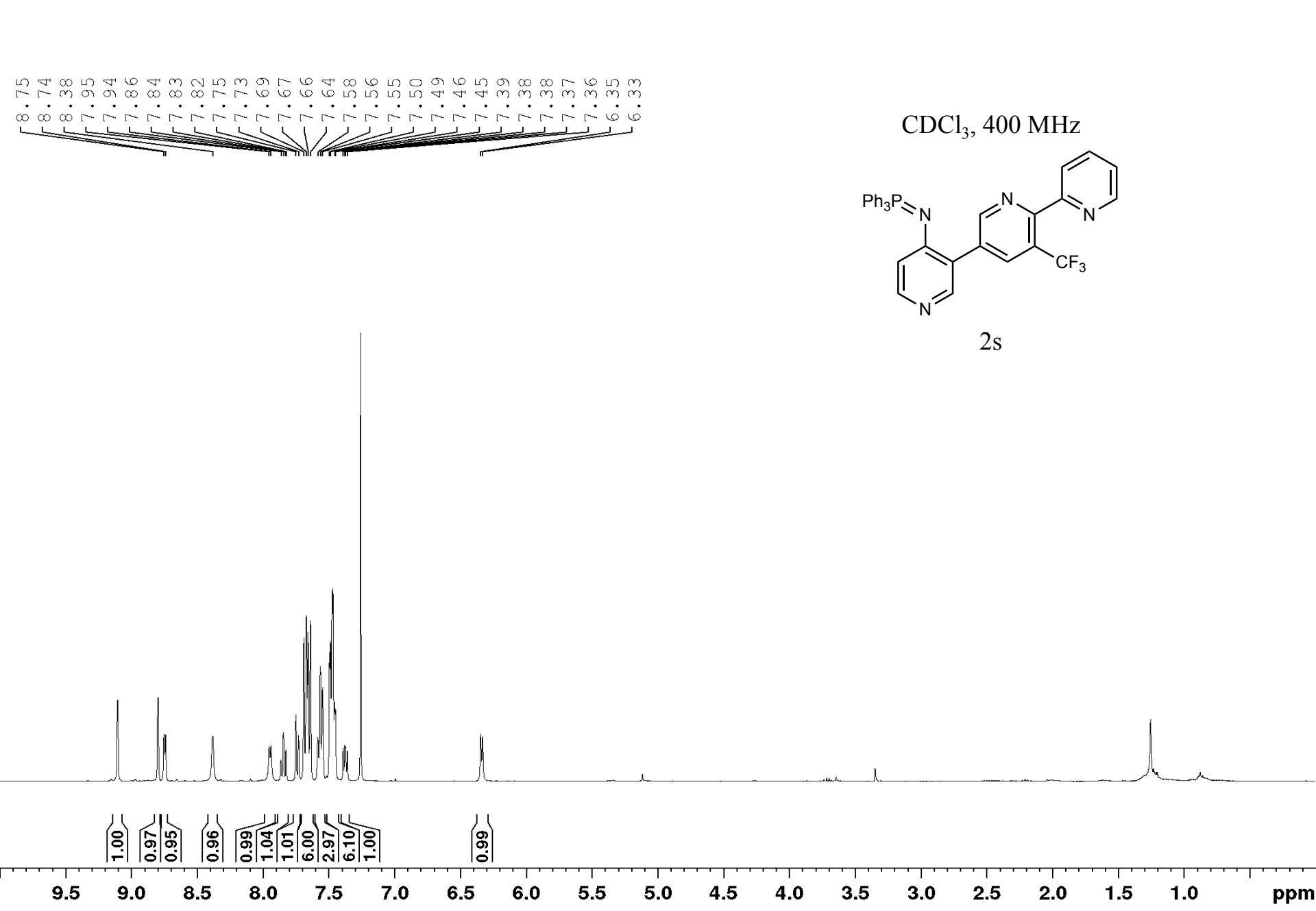
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

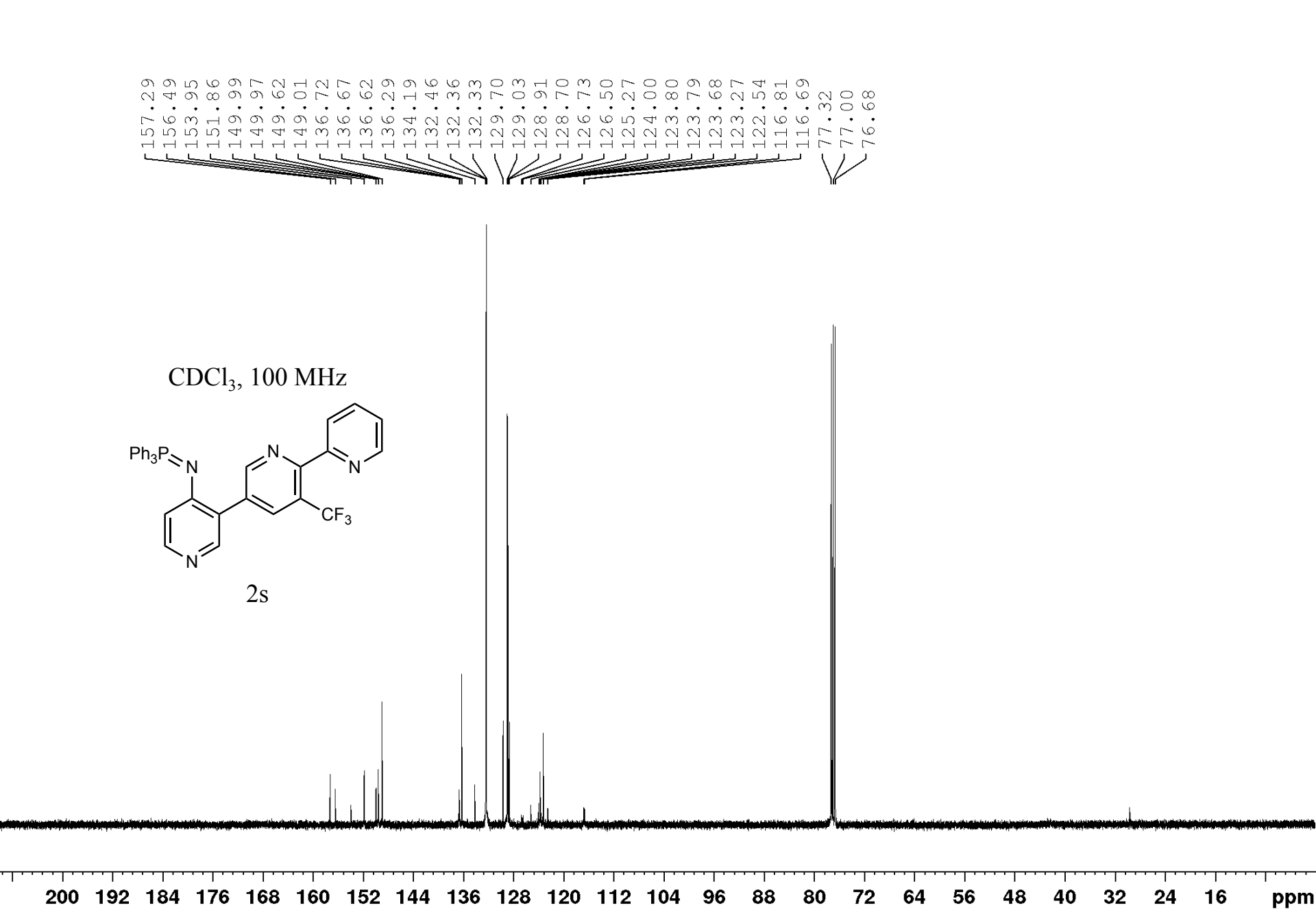
$CDCl_3$, 162 MHz



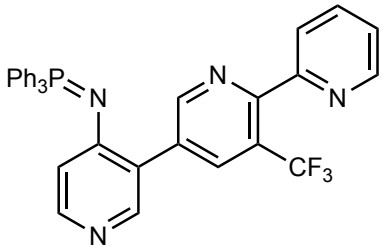
2r


-62.26
-114.31
-114.34
-114.37
CDCl3, 365 MHz
F
Ph3P=N
N
N
CF3
2r
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


8.75
8.74
8.38
7.95
7.94
7.86
7.84
7.83
7.82
7.75
7.73
7.69
7.67
7.66
7.64
7.58
7.56
7.55
7.50
7.49
7.46
7.45
7.39
7.38
7.38
7.37
7.36
6.35
6.33
CDCl3, 400 MHz
Ph3P=N
N
N
N
CF3
2s
1.00
0.97
0.95
0.96
0.99
1.04
1.01
6.00
2.97
6.10
1.00
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


157.29
156.49
153.95
151.86
149.99
149.97
149.62
149.01
136.72
136.67
136.62
136.29
134.19
132.46
132.36
132.33
129.70
129.03
128.91
128.70
126.73
126.50
125.27
124.00
123.80
123.79
123.68
123.27
122.54
116.81
116.69
77.32
77.00
76.68
CDCl3, 100 MHz
Ph3P=N
N
N
N
CF3
2s
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

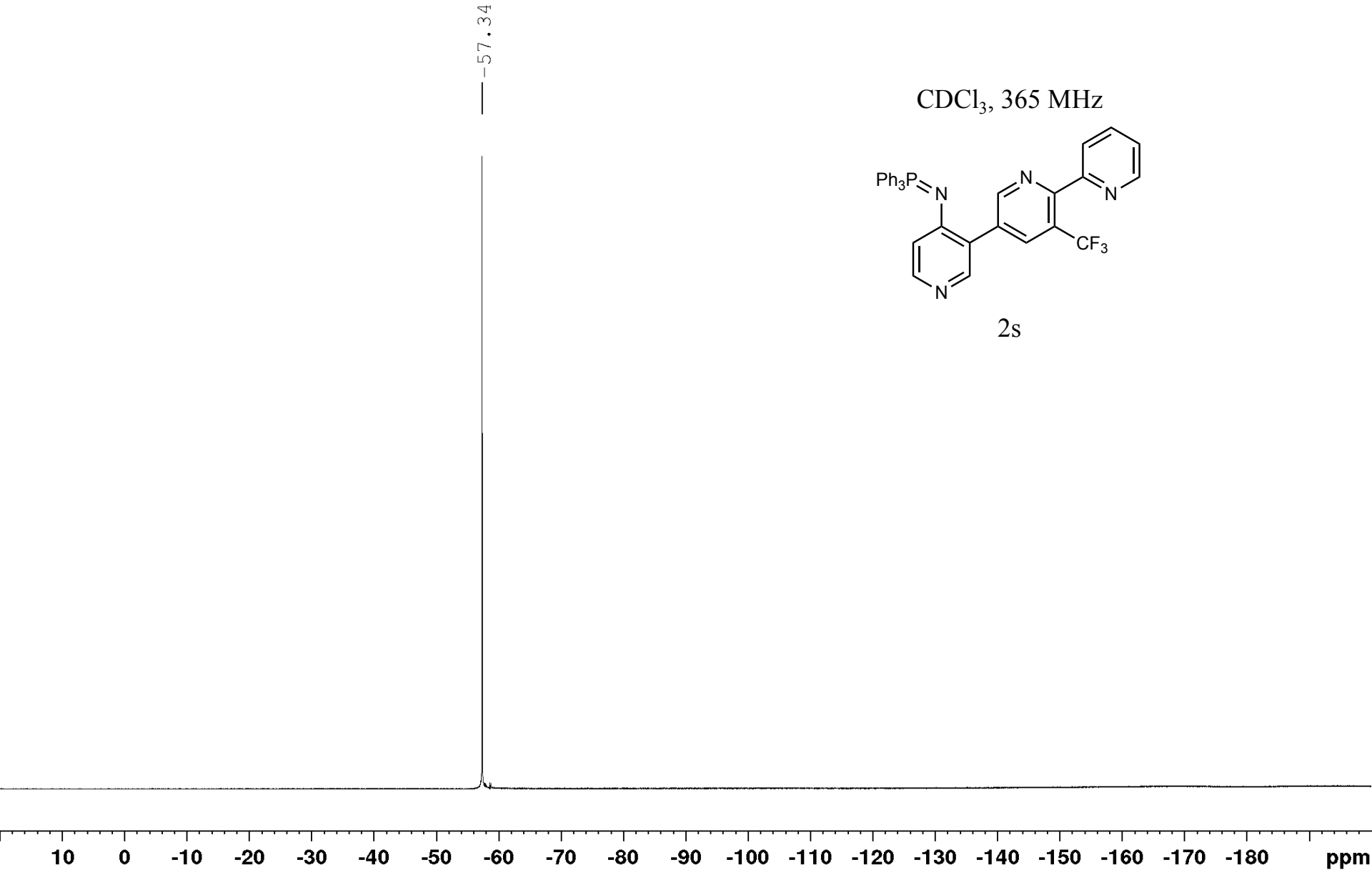
$CDCl_3$, 162 MHz

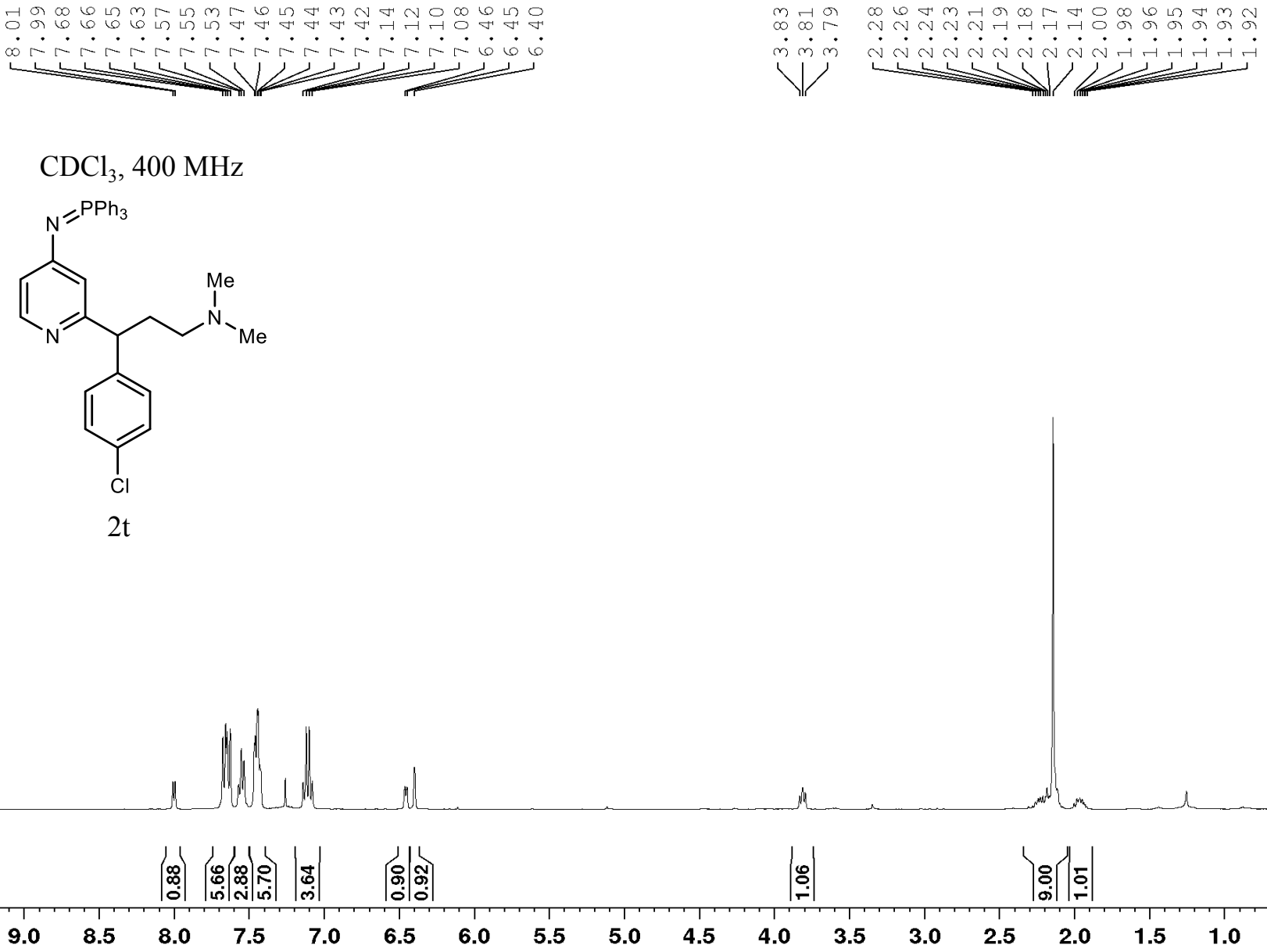


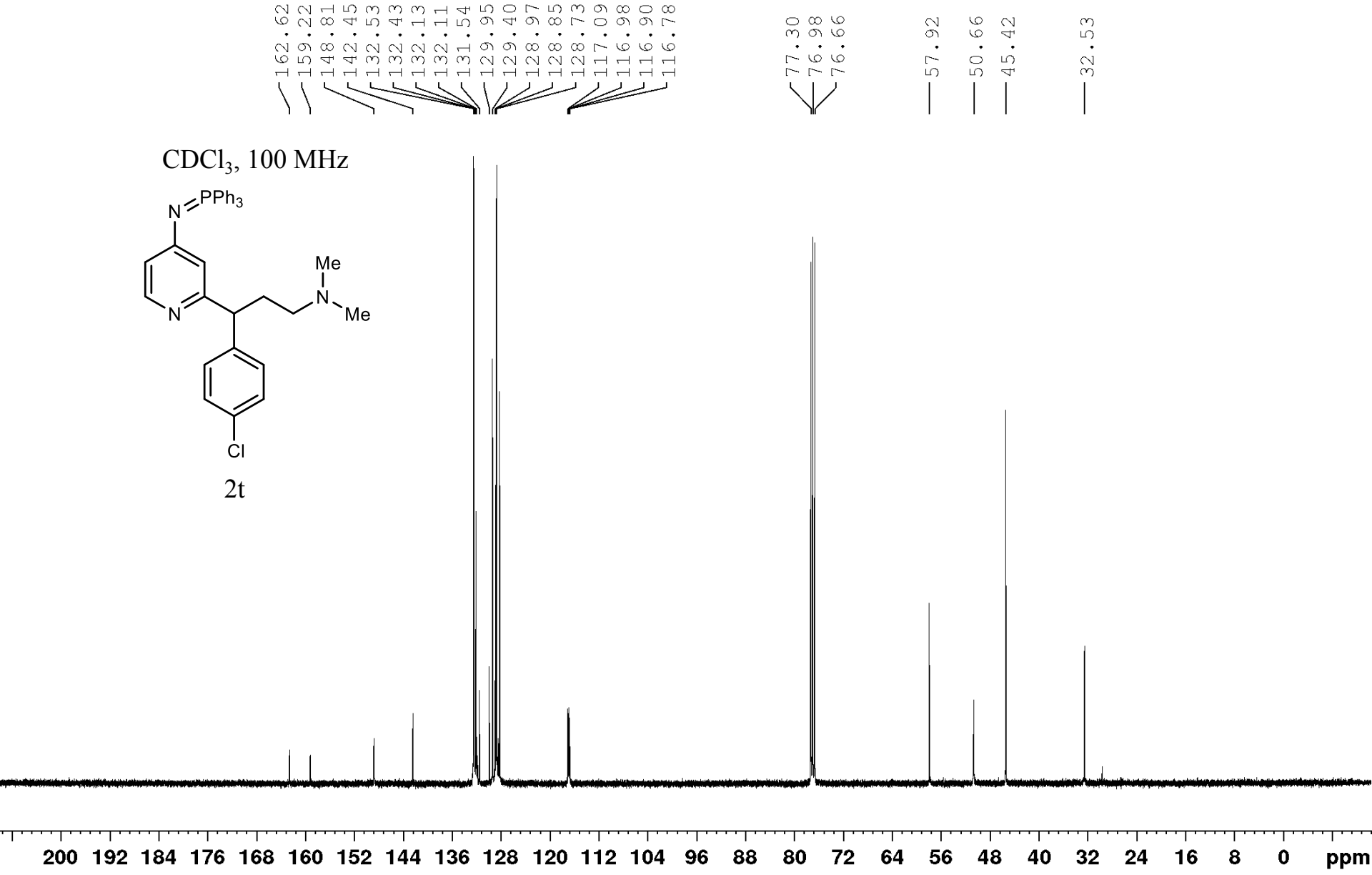
2s

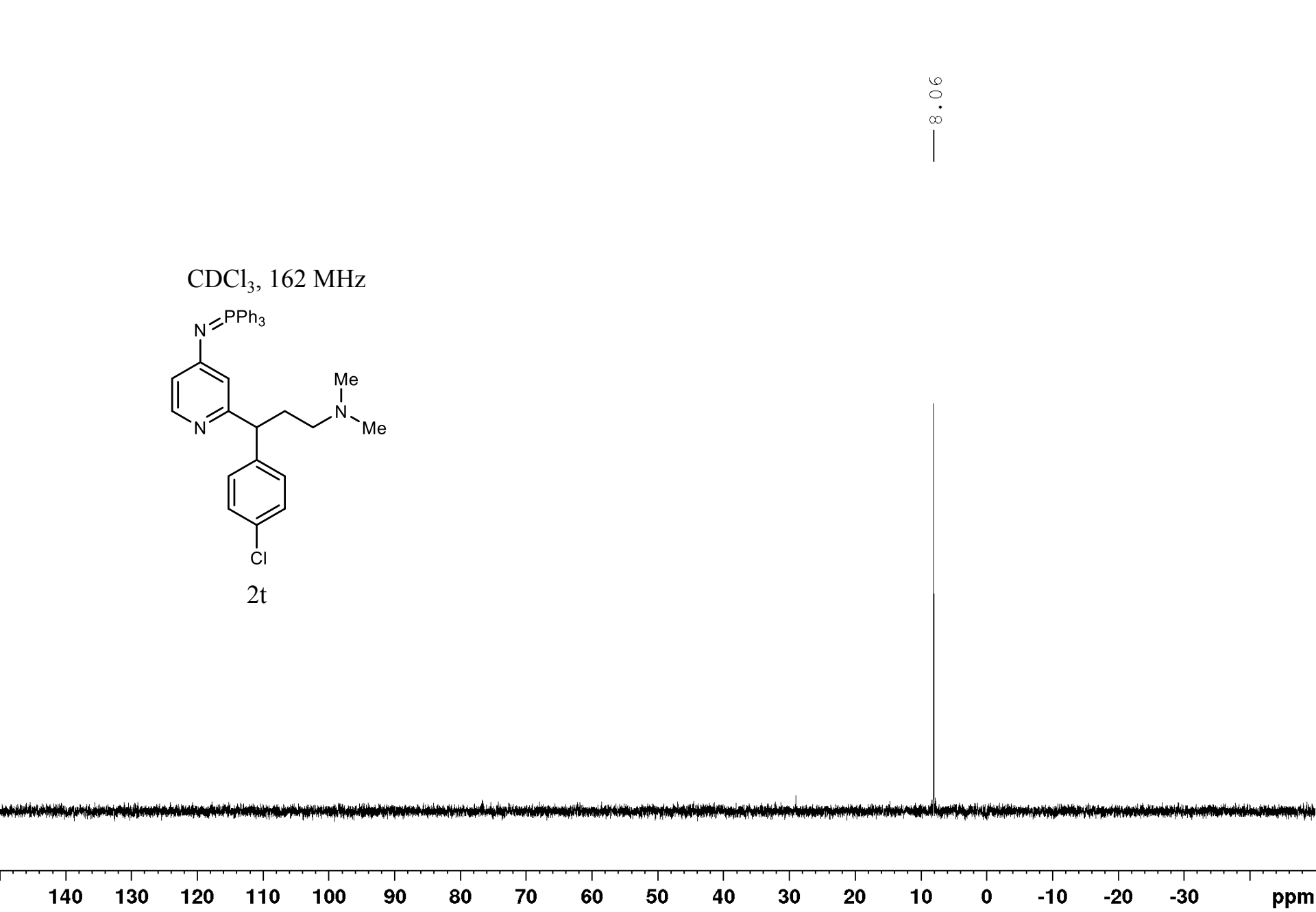
8.68

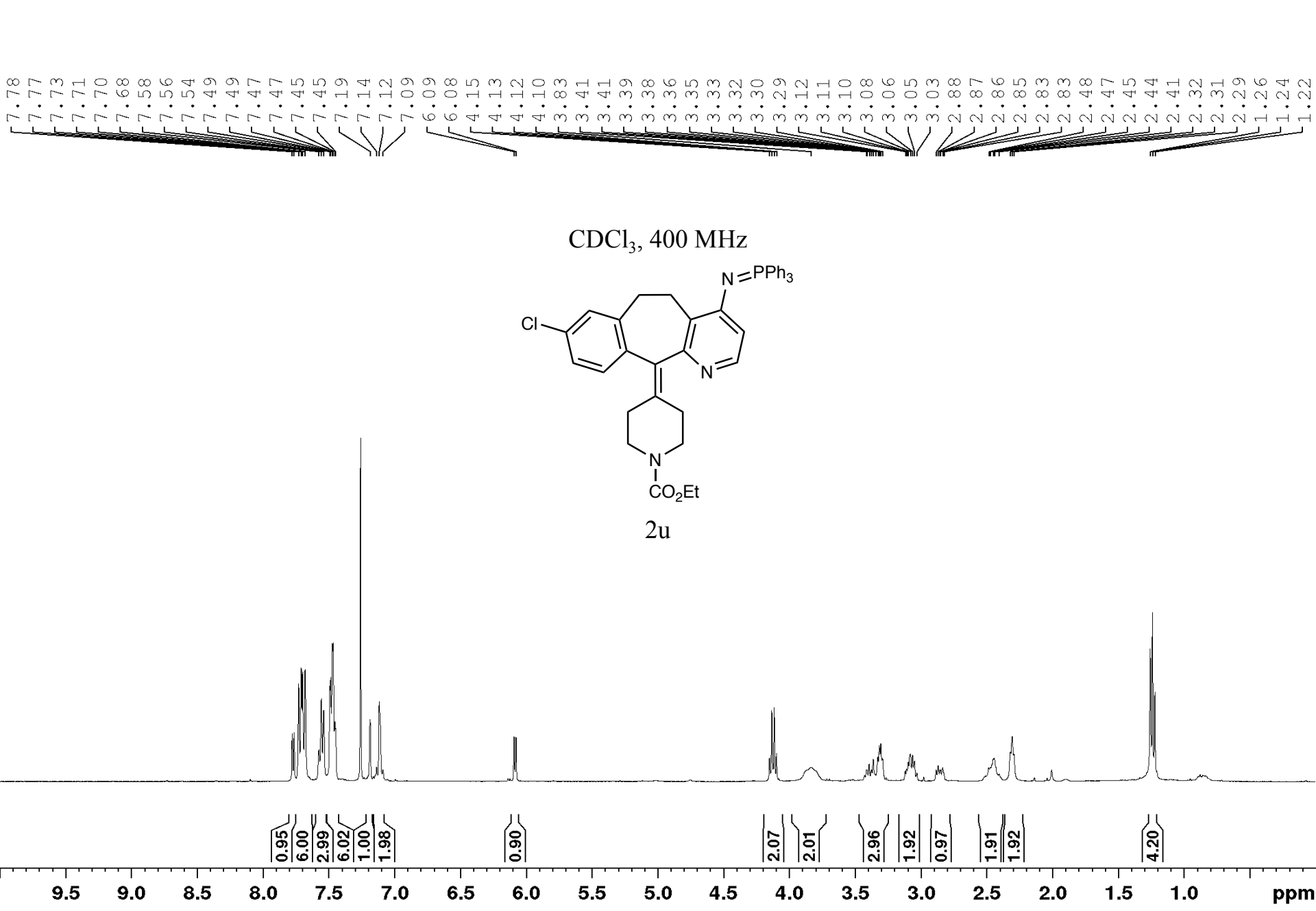
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

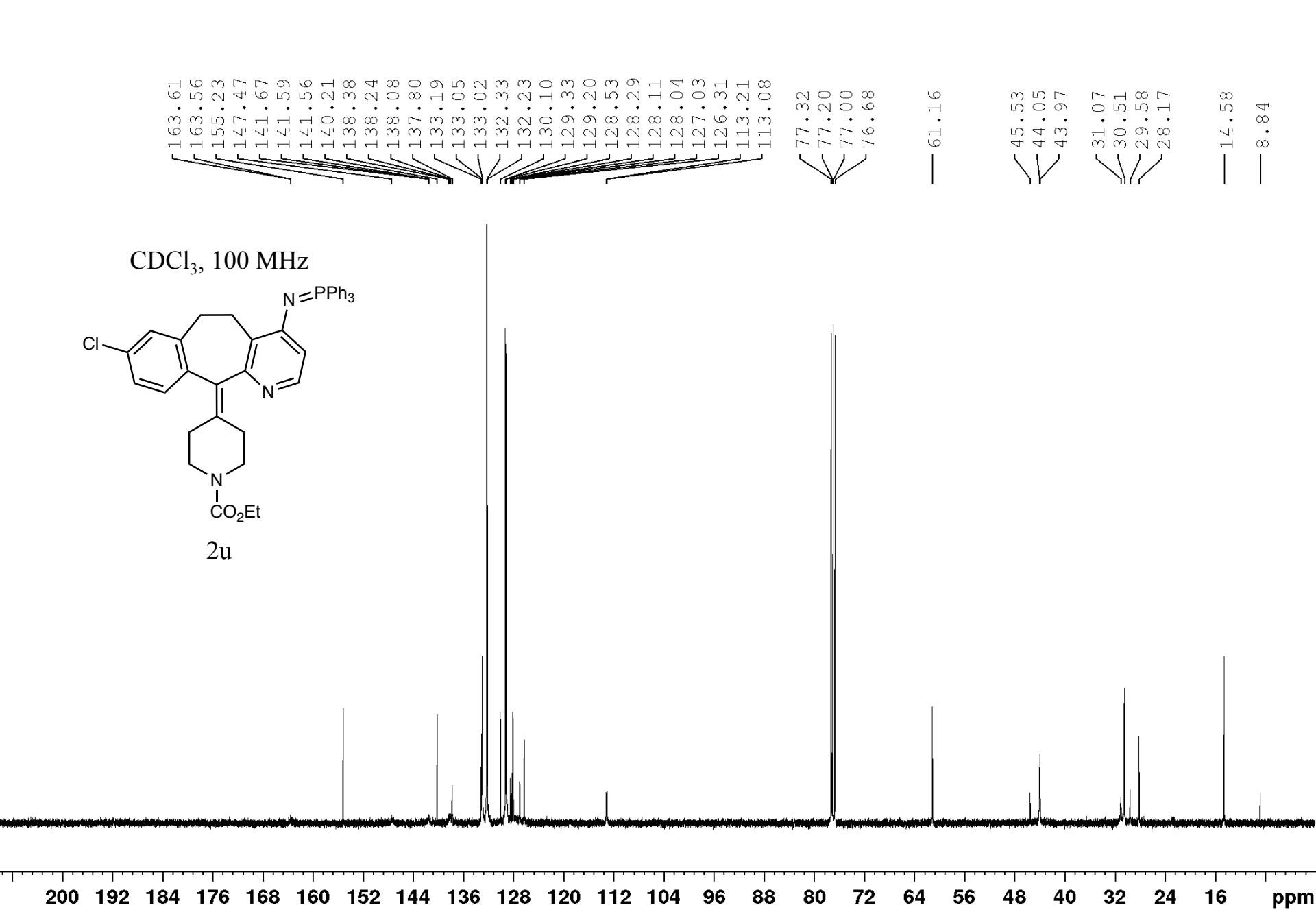

-57.34
CDCl3, 365 MHz
Ph3P=N
N
N
N
CF3
2s
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


8.01
7.99
7.68
7.66
7.65
7.63
7.57
7.55
7.53
7.47
7.46
7.45
7.44
7.43
7.42
7.14
7.12
7.10
7.08
6.46
6.45
6.40
3.83
3.81
3.79
2.28
2.26
2.24
2.23
2.21
2.19
2.18
2.17
2.14
2.00
1.98
1.96
1.95
1.94
1.93
1.92
CDCl3, 400 MHz
N
PPh3
Me
N
Me
N
Cl
2t
0.88
5.66
2.88
5.70
3.64
0.90
0.92
1.06
9.00
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

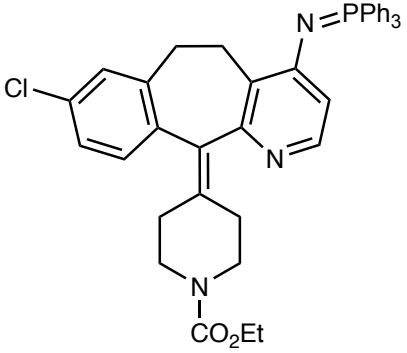

162.62
159.22
148.81
142.45
132.53
132.43
132.13
132.11
131.54
129.95
129.40
128.97
128.85
128.73
117.09
116.98
116.90
116.78
77.30
76.98
76.66
57.92
50.66
45.42
32.53
CDCl3, 100 MHz
N
PPh3
Me
N
Me
N
Cl
2t
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 ppm


8.06
CDCl3, 162 MHz
N
PPh3
Me
N
Me
N
Cl
2t
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

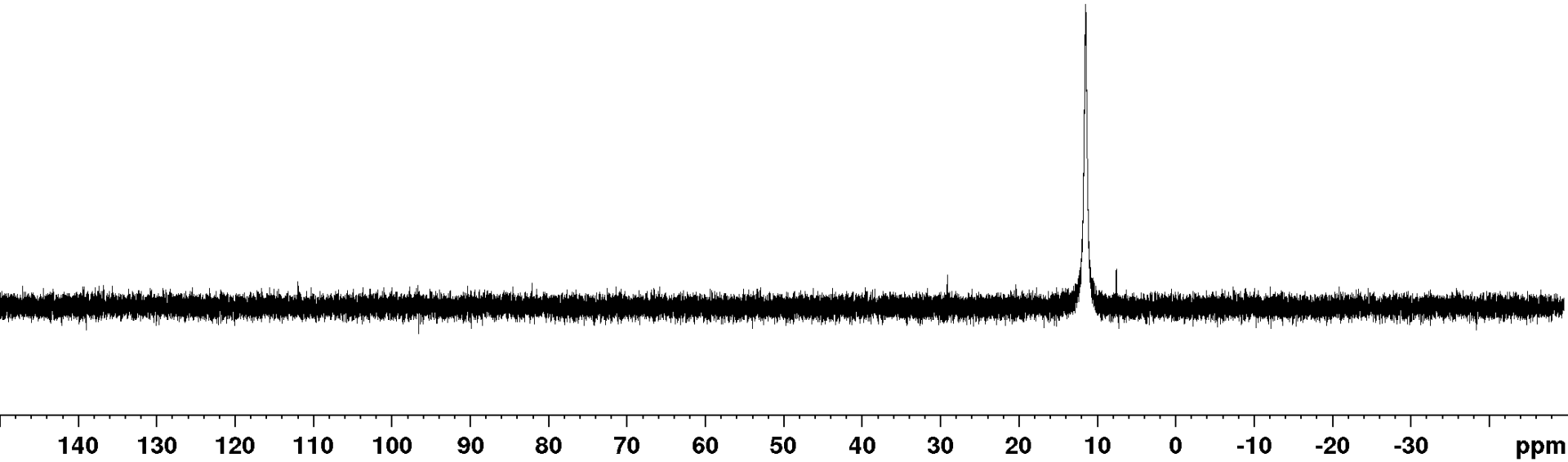

7.78
7.77
7.73
7.71
7.70
7.68
7.58
7.56
7.54
7.49
7.49
7.47
7.47
7.45
7.45
7.19
7.14
7.12
7.09
6.09
6.08
4.15
4.13
4.12
4.10
3.83
3.41
3.41
3.39
3.38
3.36
3.35
3.33
3.32
3.30
3.29
3.12
3.11
3.10
3.08
3.06
3.05
3.03
2.88
2.87
2.86
2.85
2.83
2.83
2.48
2.47
2.45
2.44
2.41
2.32
2.31
2.29
1.26
1.24
1.22
CDCl3, 400 MHz
N=PPh3
Cl
N
N
CO2Et
2u
0.95
6.00
2.99
6.02
1.00
1.98
0.90
2.07
2.01
2.96
1.92
0.97
1.91
1.92
4.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

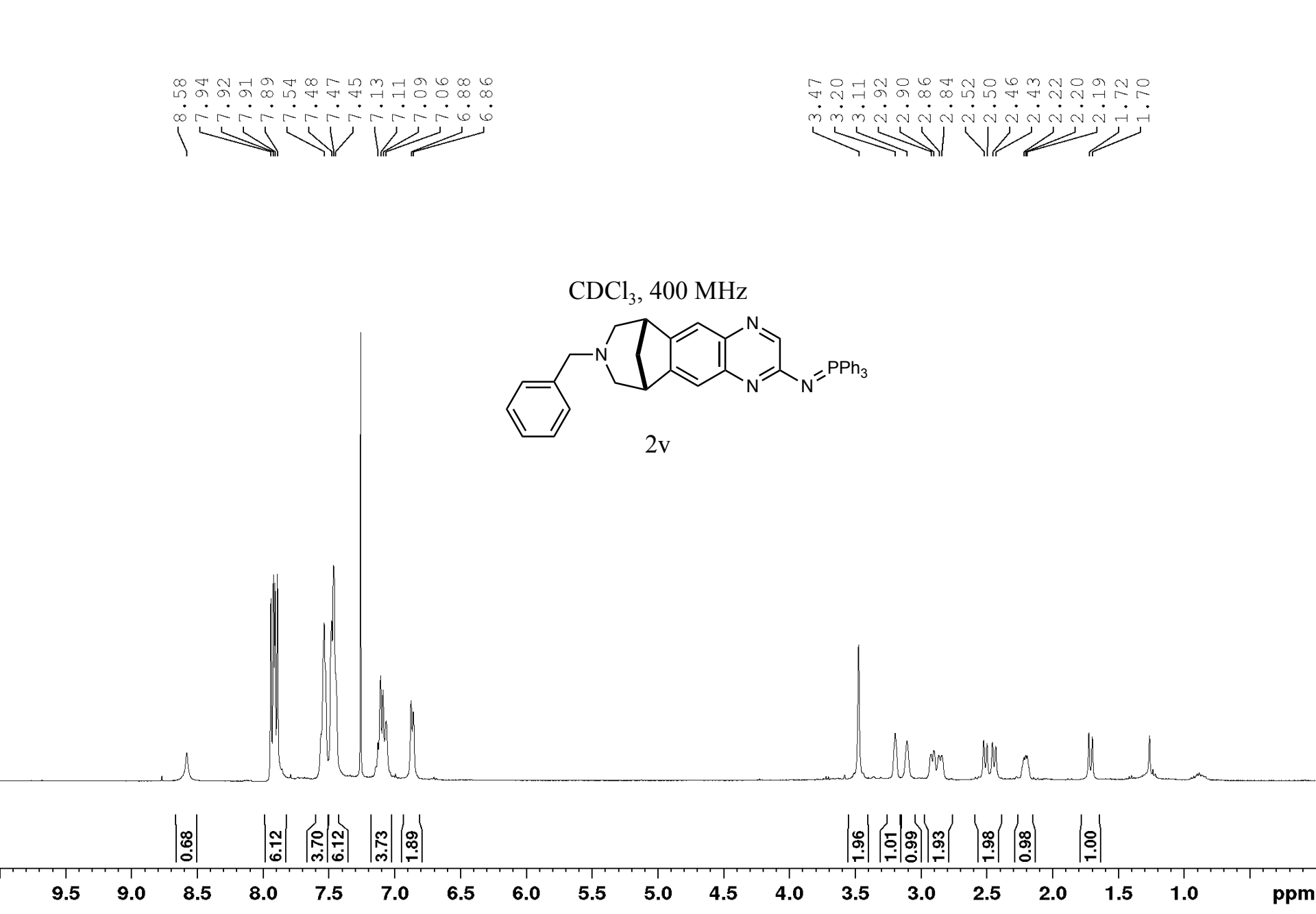

163.61
163.56
155.23
147.47
141.67
141.59
141.56
140.21
138.38
138.24
138.08
137.80
133.19
133.05
133.02
132.33
132.23
130.10
129.33
129.20
128.53
128.29
128.11
128.04
127.03
126.31
113.21
113.08
77.32
77.20
77.00
76.68
61.16
45.53
44.05
43.97
31.07
30.51
29.58
28.17
14.58
8.84
CDCl3, 100 MHz
N=PPh3
Cl
N
N
CO2Et
2u
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

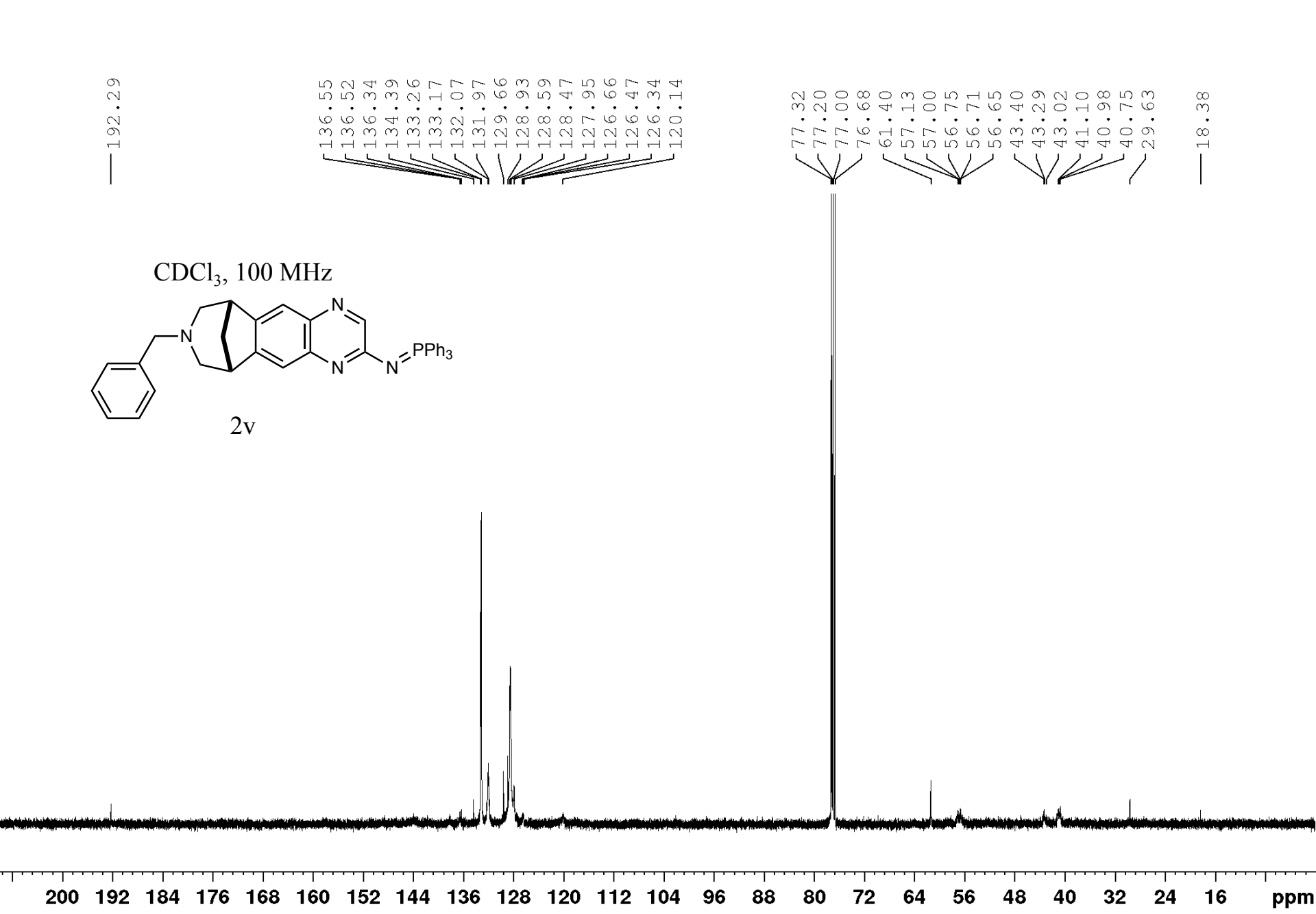
$CDCl_3$, 162 MHz



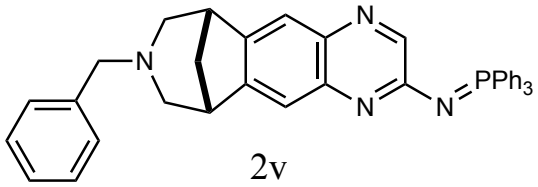
2u




8.58
7.94
7.92
7.91
7.89
7.54
7.48
7.47
7.45
7.13
7.11
7.09
7.06
6.88
6.86
3.47
3.20
3.11
2.92
2.90
2.86
2.84
2.52
2.50
2.46
2.43
2.22
2.20
2.19
1.72
1.70
CDCl3, 400 MHz
N
N
N
N
PPh3
2v
0.68
6.12
3.70
6.12
3.73
1.89
1.96
1.01
0.99
1.93
1.98
0.98
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

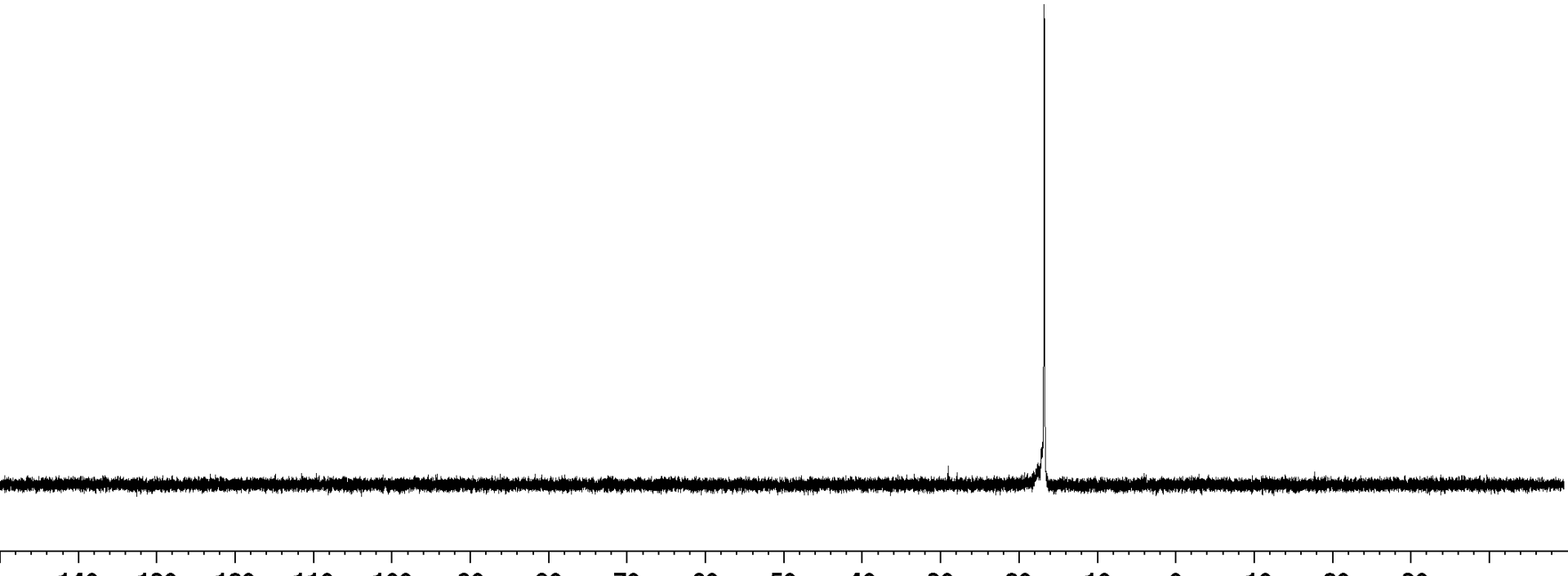

192.29
136.55
136.52
136.34
134.39
133.26
133.17
132.07
131.97
129.66
128.93
128.59
128.47
127.95
126.66
126.47
126.34
120.14
77.32
77.20
77.00
76.68
61.40
57.13
57.00
56.75
56.71
56.65
43.40
43.29
43.02
41.10
40.98
40.75
29.63
18.38
CDCl3, 100 MHz
N
N
N
N
PPh3
2v
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

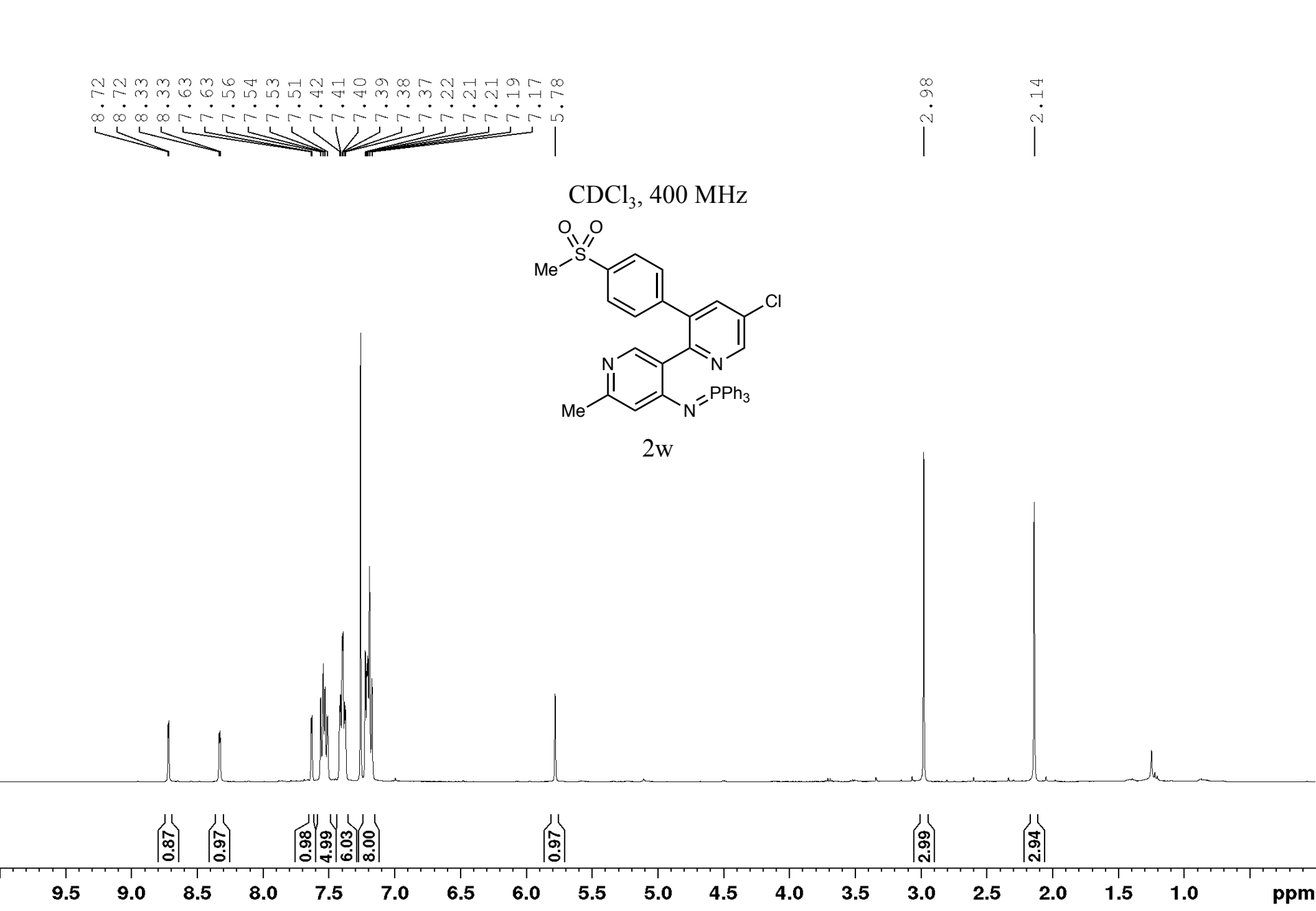
$CDCl_3$, 162 MHz

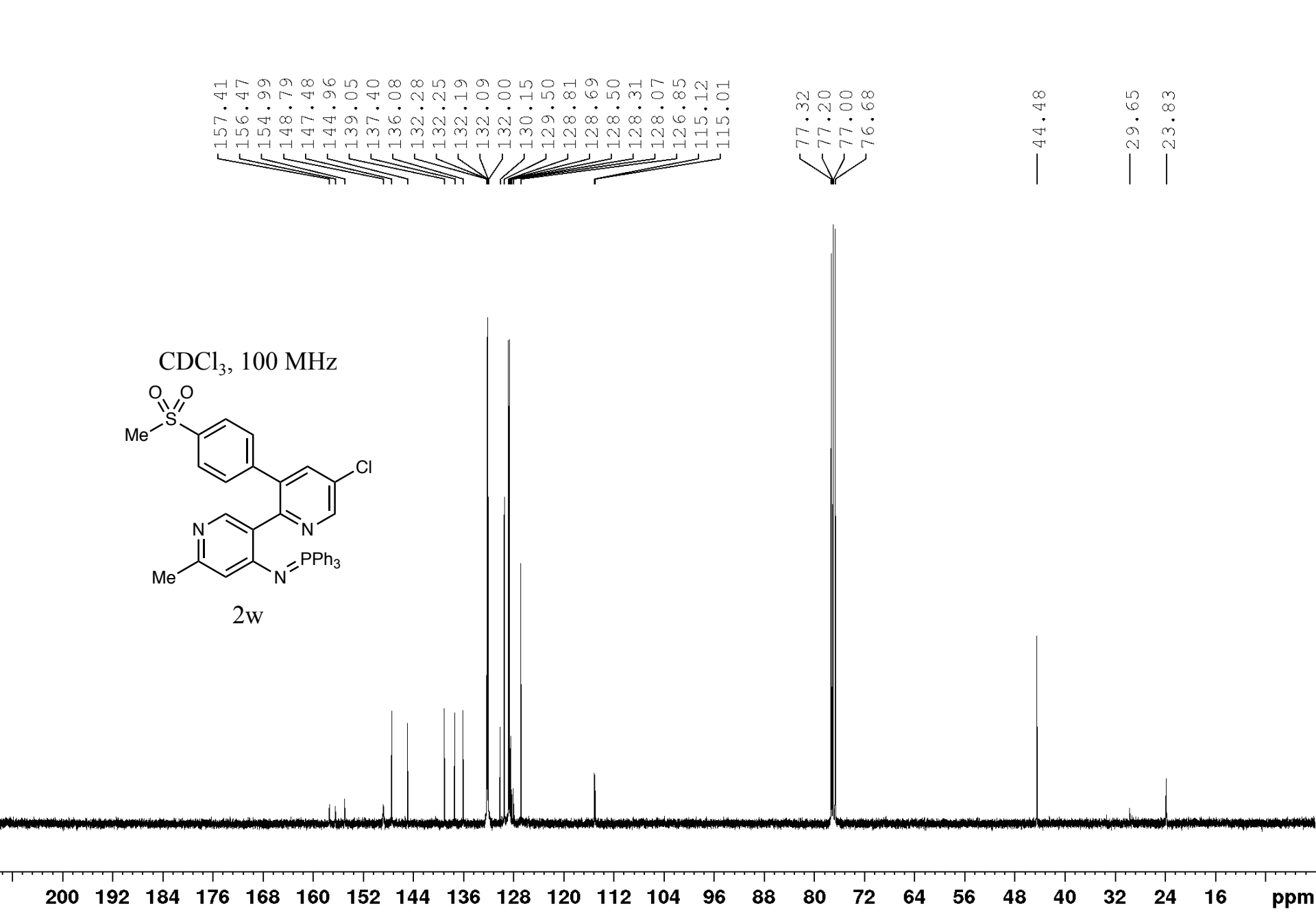


2v

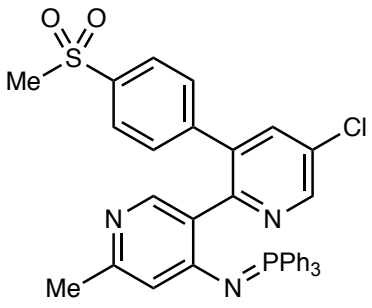
16.75




8.72
8.72
8.33
8.33
7.63
7.63
7.56
7.54
7.53
7.51
7.42
7.41
7.40
7.39
7.38
7.37
7.22
7.21
7.21
7.19
7.17
5.78
2.98
2.14
CDCl3, 400 MHz
O
O
S
Me
Cl
N
N
PPh3
Me
N
2w
0.87
0.97
0.98
4.99
6.03
8.00
0.97
2.99
2.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

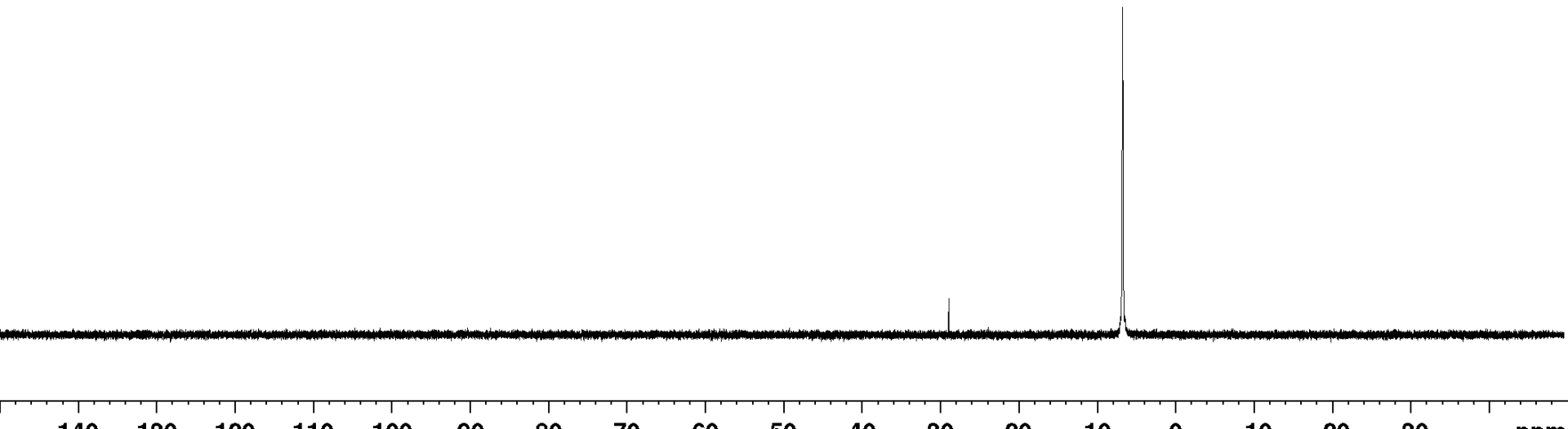

157.41
156.47
154.99
148.79
147.48
144.96
139.05
137.40
136.08
132.28
132.25
132.19
132.09
132.00
130.15
129.50
128.81
128.69
128.50
128.31
128.07
126.85
115.12
115.01
77.32
77.20
77.00
76.68
44.48
29.65
23.83
CDCl3, 100 MHz
O
O
S
Me
Cl
N
N
Me
N
PPh3
2w
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm

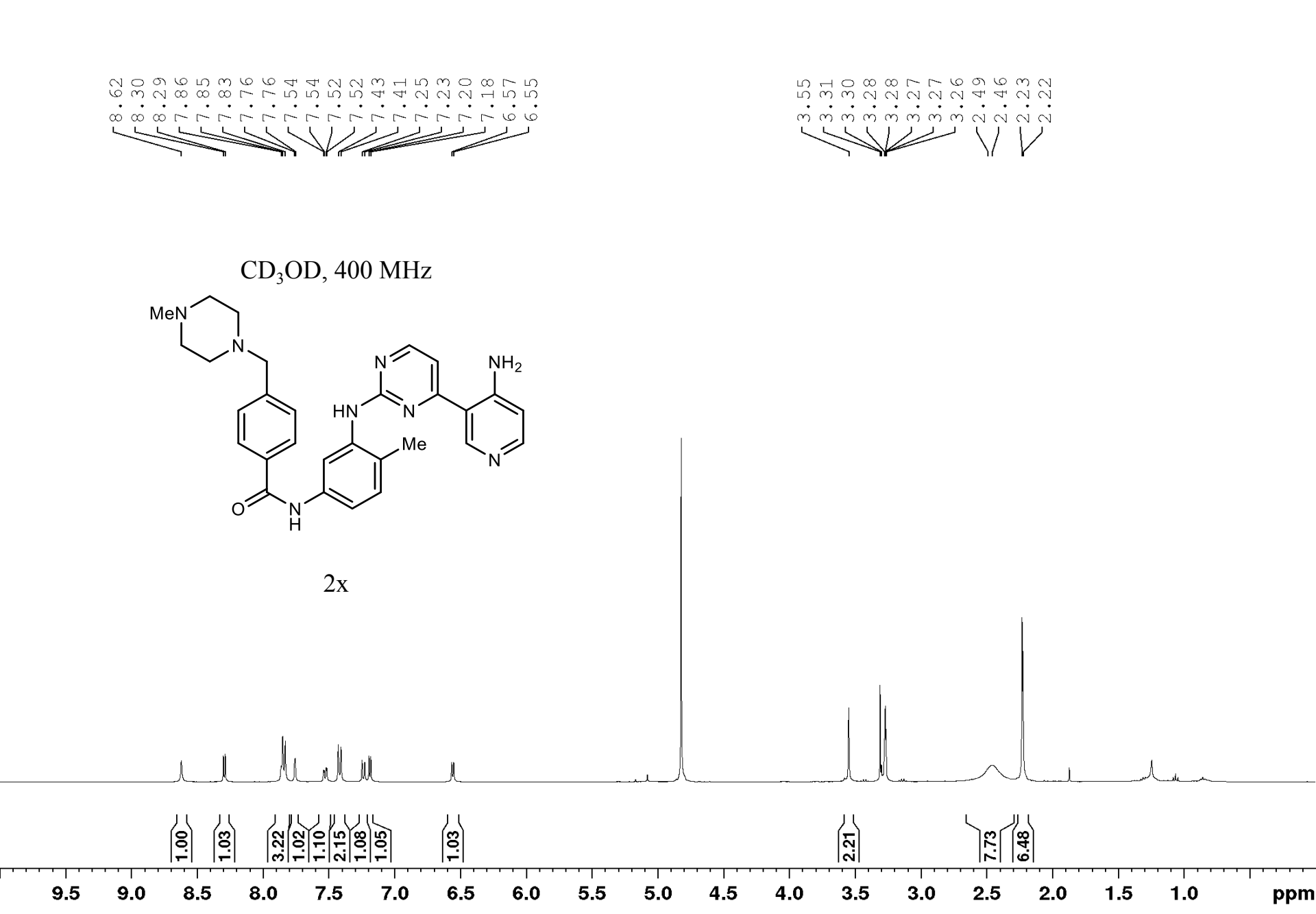
$CDCl_3$, 162 MHz

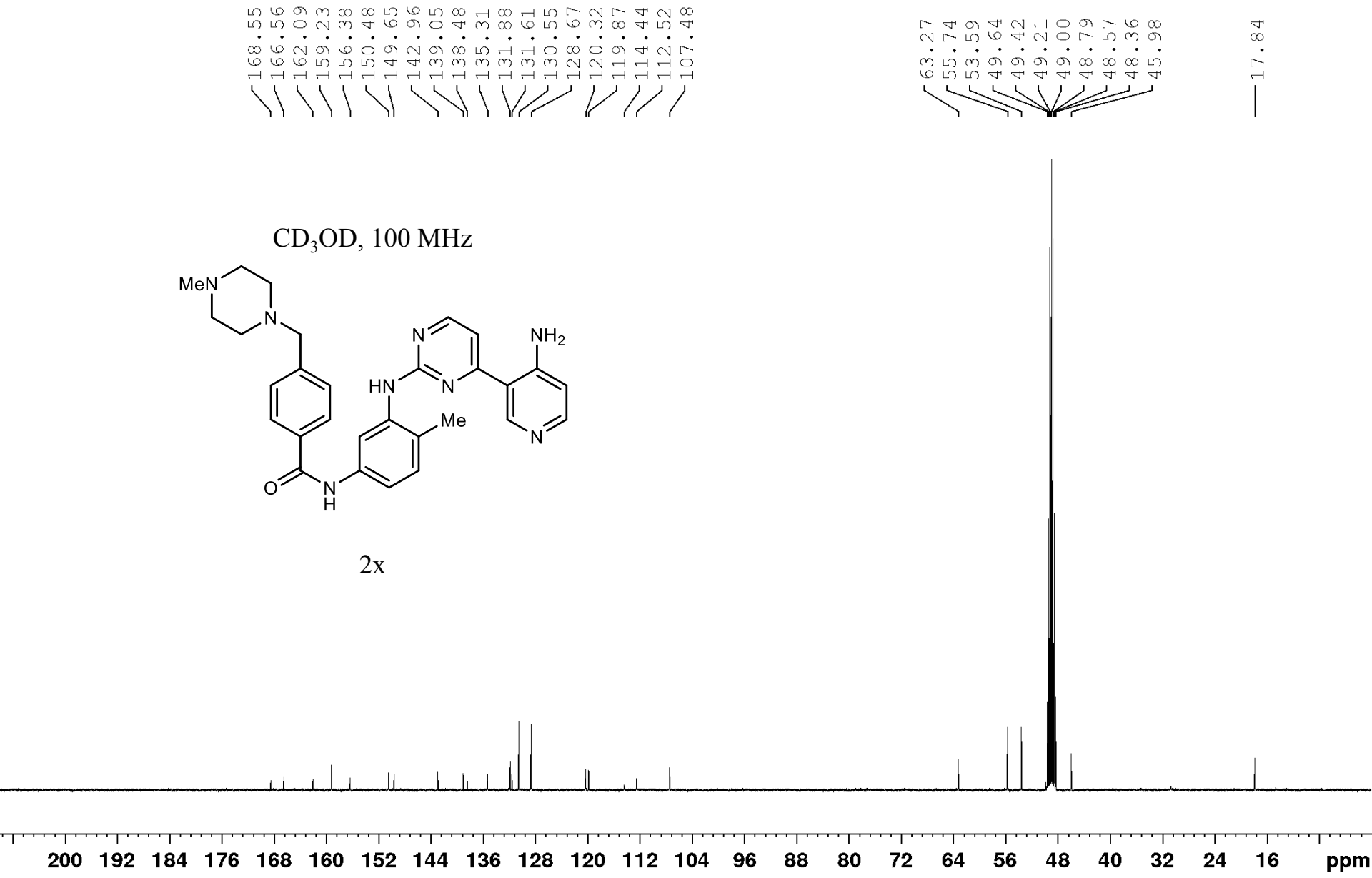


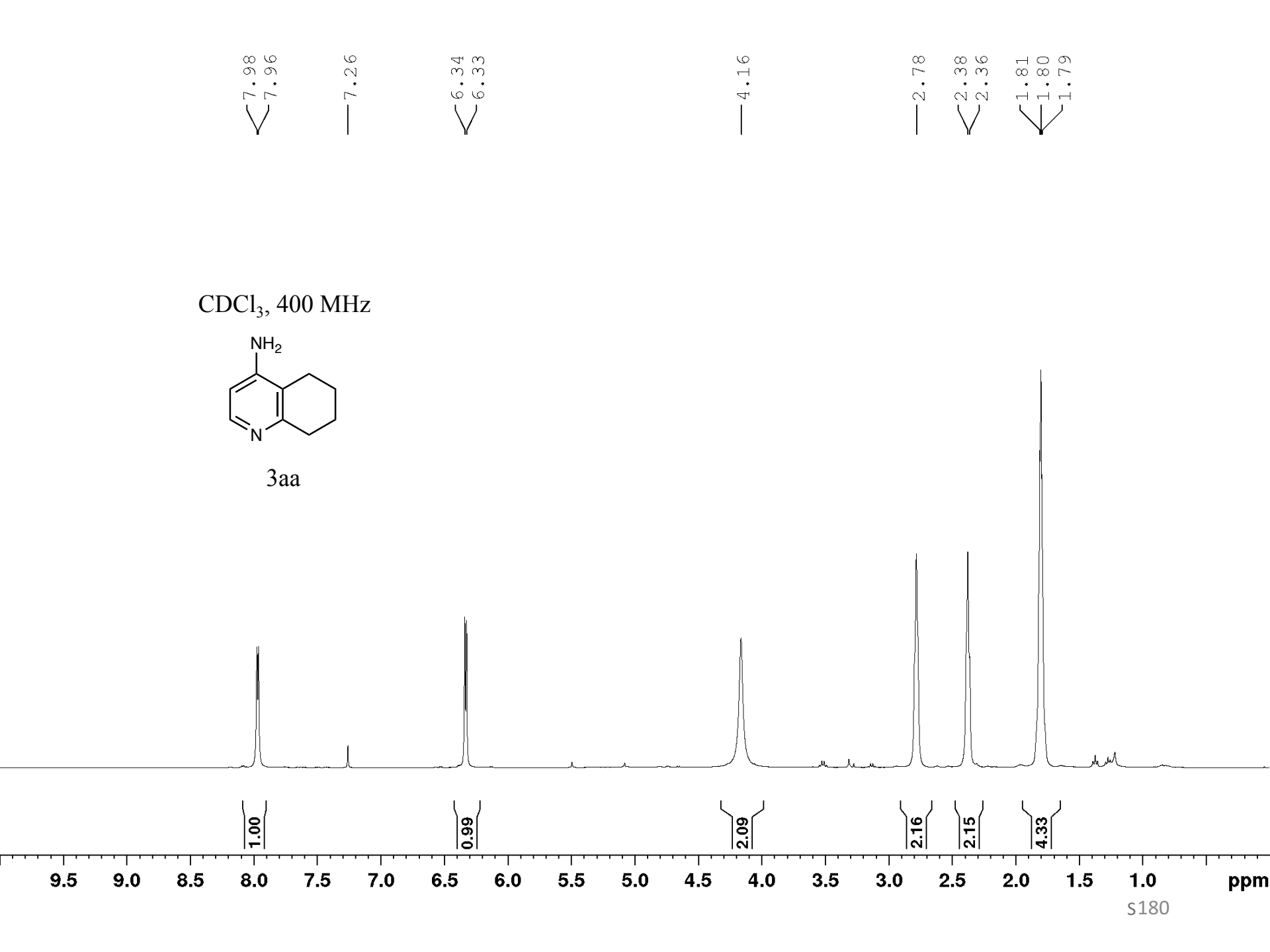
2w

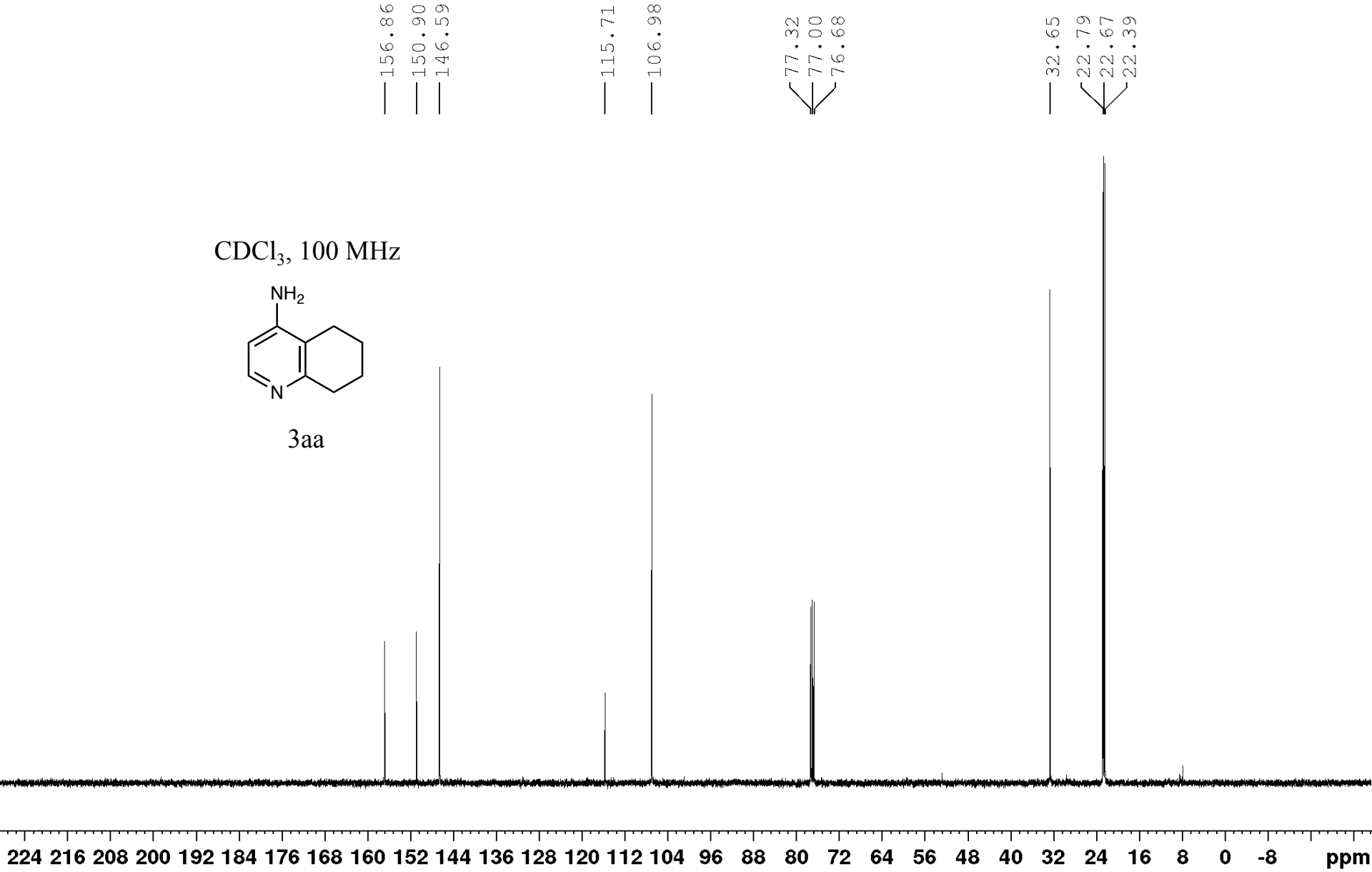
6.75




8.62
8.30
8.29
7.86
7.85
7.83
7.76
7.76
7.54
7.54
7.52
7.52
7.43
7.41
7.25
7.23
7.20
7.18
6.57
6.55
3.55
3.31
3.30
3.28
3.28
3.27
3.27
3.26
2.49
2.46
2.23
2.22
CD3OD, 400 MHz
MeN
N
HN
N
N
NH2
Me
N
O
N
H
2x
1.00
1.03
3.22
1.02
1.10
2.15
1.08
1.05
1.03
2.21
7.73
6.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

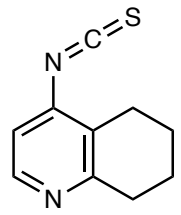

168.55
166.56
162.09
159.23
156.38
150.48
149.65
142.96
139.05
138.48
135.31
131.88
131.61
130.55
128.67
120.32
119.87
114.44
112.52
107.48
63.27
55.74
53.59
49.64
49.42
49.21
49.00
48.79
48.57
48.36
45.98
17.84
CD3OD, 100 MHz
MeN
N
HN
N
N
NH2
Me
N
O
N
H
2x
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


7.98
7.96
7.26
6.34
6.33
4.16
2.78
2.38
2.36
1.81
1.80
1.79
CDCl3, 400 MHz
NH2
N
3aa
1.00
0.99
2.09
2.16
2.15
4.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

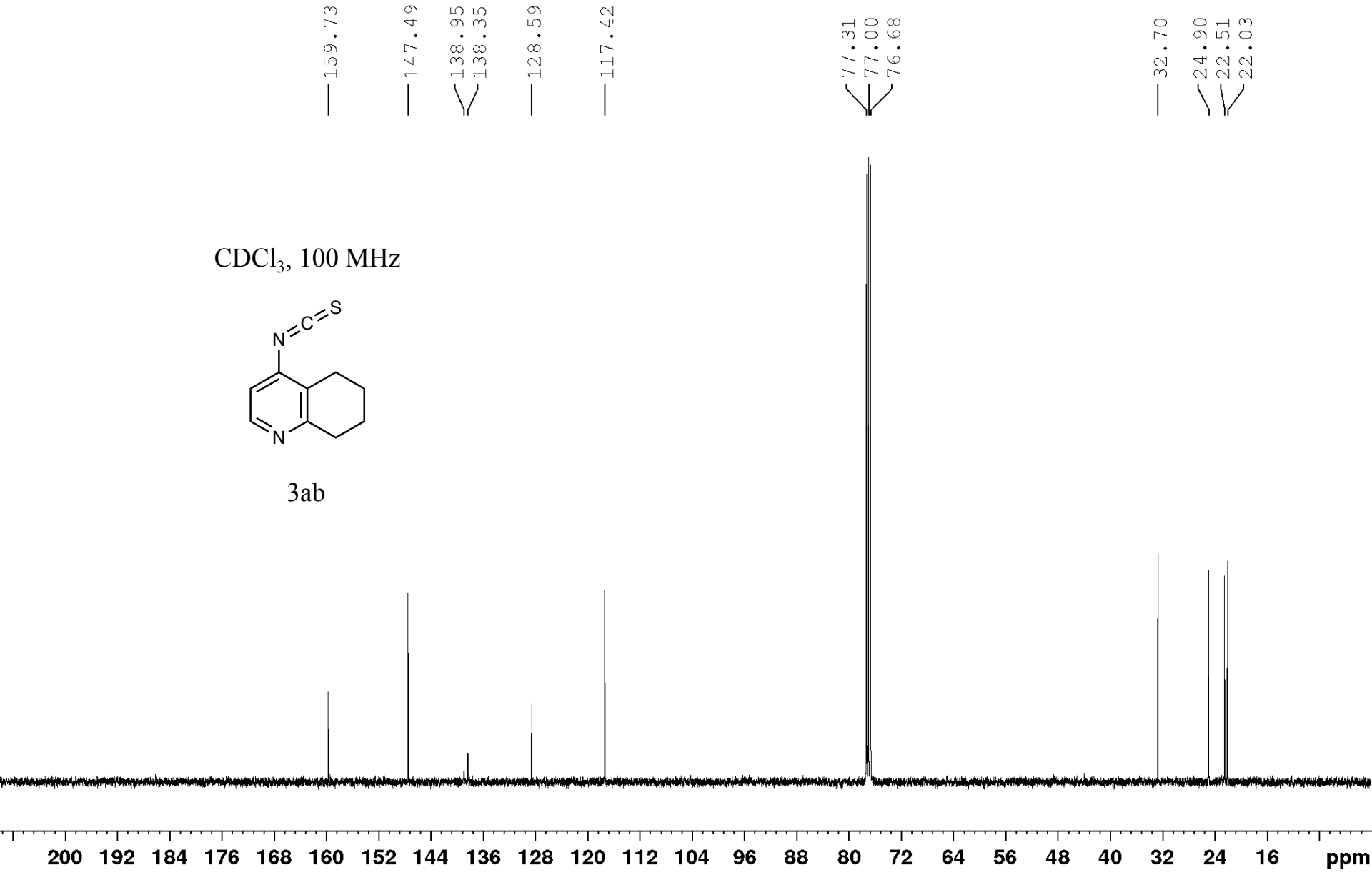

156.86
150.90
146.59
115.71
106.98
77.32
77.00
76.68
32.65
22.79
22.67
22.39
CDCl3, 100 MHz
NH2
N
3aa
224 216 208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8 ppm

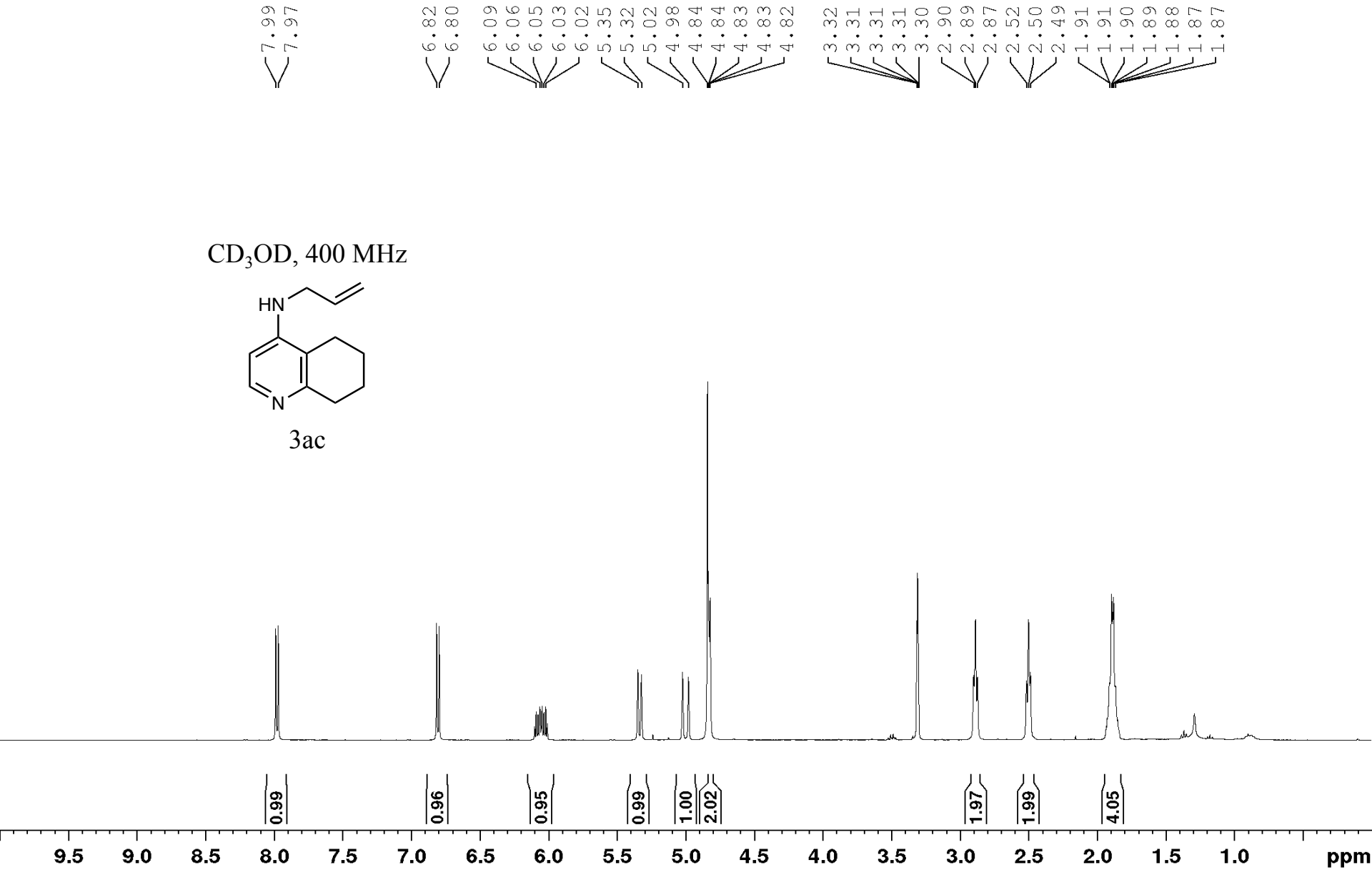
8.33
8.32
7.26
6.91
6.90
2.93
2.91
2.90
2.81
2.80
2.78
1.89
1.87
1.87
1.86
1.86
1.85

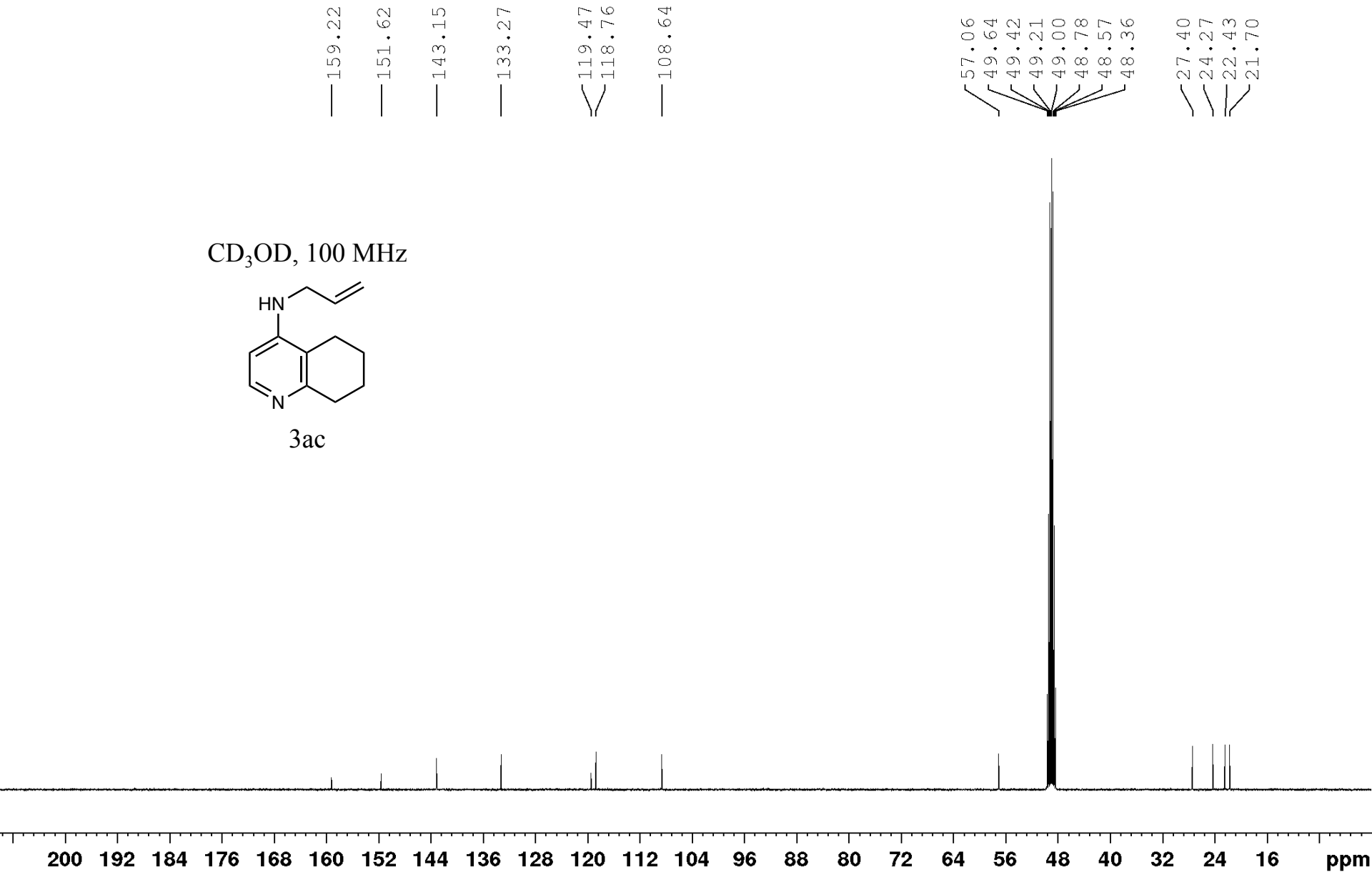
$CDCl_3$, 400 MHz



3ab


159.73
147.49
138.95
138.35
128.59
117.42
77.31
77.00
76.68
32.70
24.90
22.51
22.03
CDCl3, 100 MHz
N
C
S
N
3ab
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


7.99
7.97
6.82
6.80
6.09
6.06
6.05
6.03
6.02
5.35
5.32
5.02
4.98
4.84
4.84
4.83
4.83
4.82
3.32
3.31
3.31
3.31
3.30
2.90
2.89
2.87
2.52
2.50
2.49
1.91
1.91
1.90
1.89
1.88
1.87
1.87
CD3OD, 400 MHz
HN
N
3ac
0.99
0.96
0.95
0.99
1.00
2.02
1.97
1.99
4.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


159.22
151.62
143.15
133.27
119.47
118.76
108.64
57.06
49.64
49.42
49.21
49.00
48.78
48.57
48.36
27.40
24.27
22.43
21.70
CD3OD, 100 MHz
HN
N
3ac
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm