Supporting Online Material for

Site–Selective Switching Strategies to Functionalize Polyazines

Ryan D. Dolewski, Patrick J. Fricke, and Andrew McNally*

Department of Chemistry, Colorado State University,
Fort Collins, Colorado 80523, United States.
*andy.mcnally@colostate.edu

Table of Contents

1. General Information *S2*

2. Acetyl and Triflyl Pyridinium Formation of 1h *S4*

3. Rapid Interconversion of 1q Tf salt isomers *S5*

4. Preparation of Heterocyclic Phosphonium Salt Precursors *S6*

5. Preparation of Heterocyclic Phosphonium Salts *S23*

6. Preparation of Derivatized Polyazaarenes *S79*

7. References *S90*

8. ^{1}H, ^{13}C, ^{19}F and ^{31}P Spectra *S91*

1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on either a Bruker Ultrashield–400 (400 MHz) spectrometer, a Varian 400 MR (400 MHz) spectrometer or an Agilent Inova 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). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity 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 either a Bruker Ultrashield–400 (400 MHz) spectrometer, a Varian 400 MR spectrometer (100 MHz) or an Agilent Inova 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 $CDCl_3$ (77.0 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. Infared (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}).

Specific optical rotation measurements were obtained from $CHCl_3$ solutions having concentrations of 10 mg/mL (example 2o) using a Rudolph Research Analytical Autopol III automatic polarimeter operating at 589 nm.

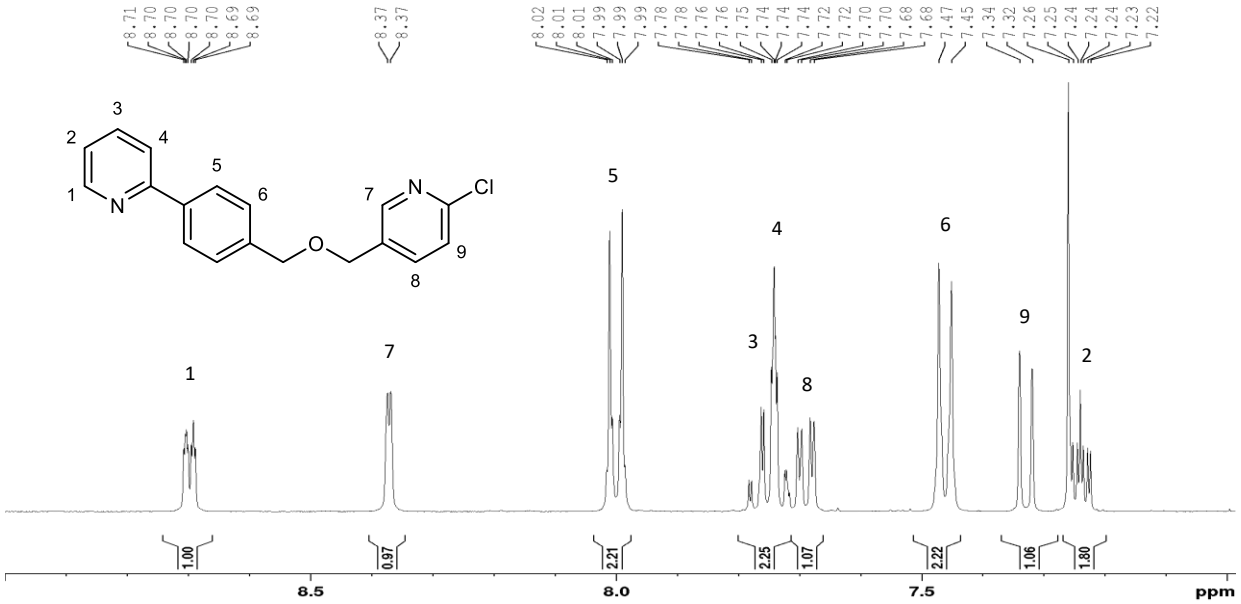
Analytical thin layer chromatography (TLC) was performed using pre–coated Merck glass backed silica gel plates (Silicagel 60 F254). Flash column chromatography was undertaken on Fluka or Material Harvest silica gel (230–400 mesh) under a positive pressure of air. Visualization was

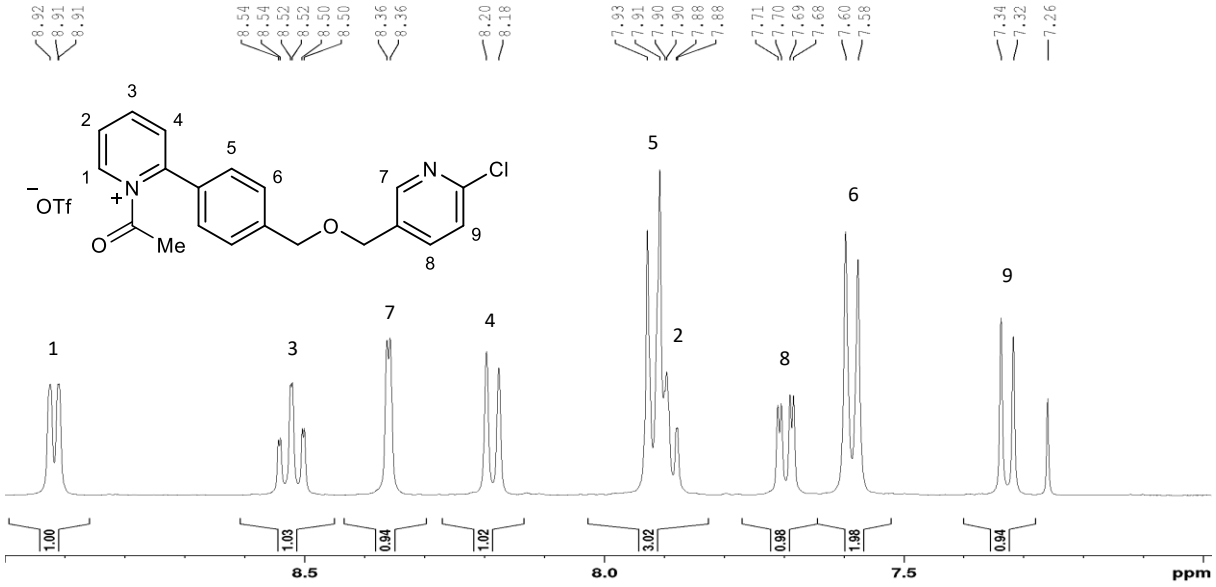
achieved using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate.

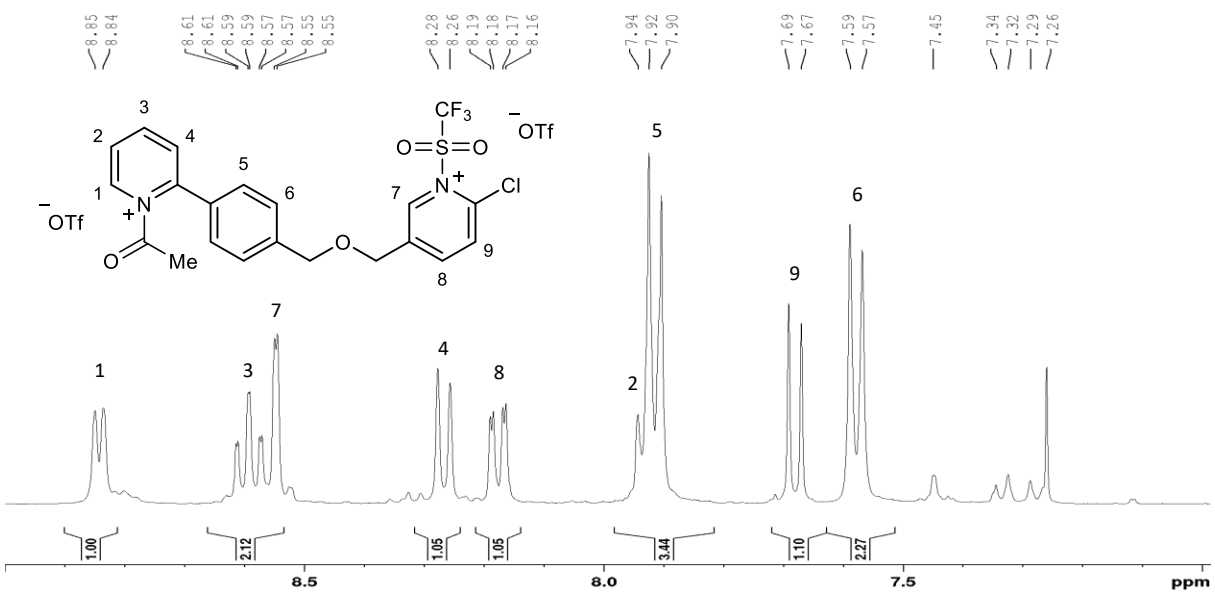
Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods.[1] Ethyl acetate (EtOAc), 1,2–Dichloroethane (DCE), 1,4–dioxane, chloroform, chlorobenzene and acetone were purchased anhydrous from Sigma Aldrich chemical company. All reagents 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 but was routinely stored in a –20 ºC fridge. NEt_3 and DBU were distilled before use. Acetyl chloride (98%) was purchased from Sigma Aldrich chemical company and was used without further purification but was routinely stored in a –20 ºC fridge. Silver trifluoromethanesulfonate (>99%) was purchased from Sigma Aldrich chemical company and was stored inside a glovebox. NaH (60% in mineral oil) was purchased from Sigma Aldrich and was typically distributed into vials and stored in a desiccator. K_2CO_3 was purchased from Sigma Aldrich chemical company, stored in a desiccator, and is most effective when crushed to a powder before use.

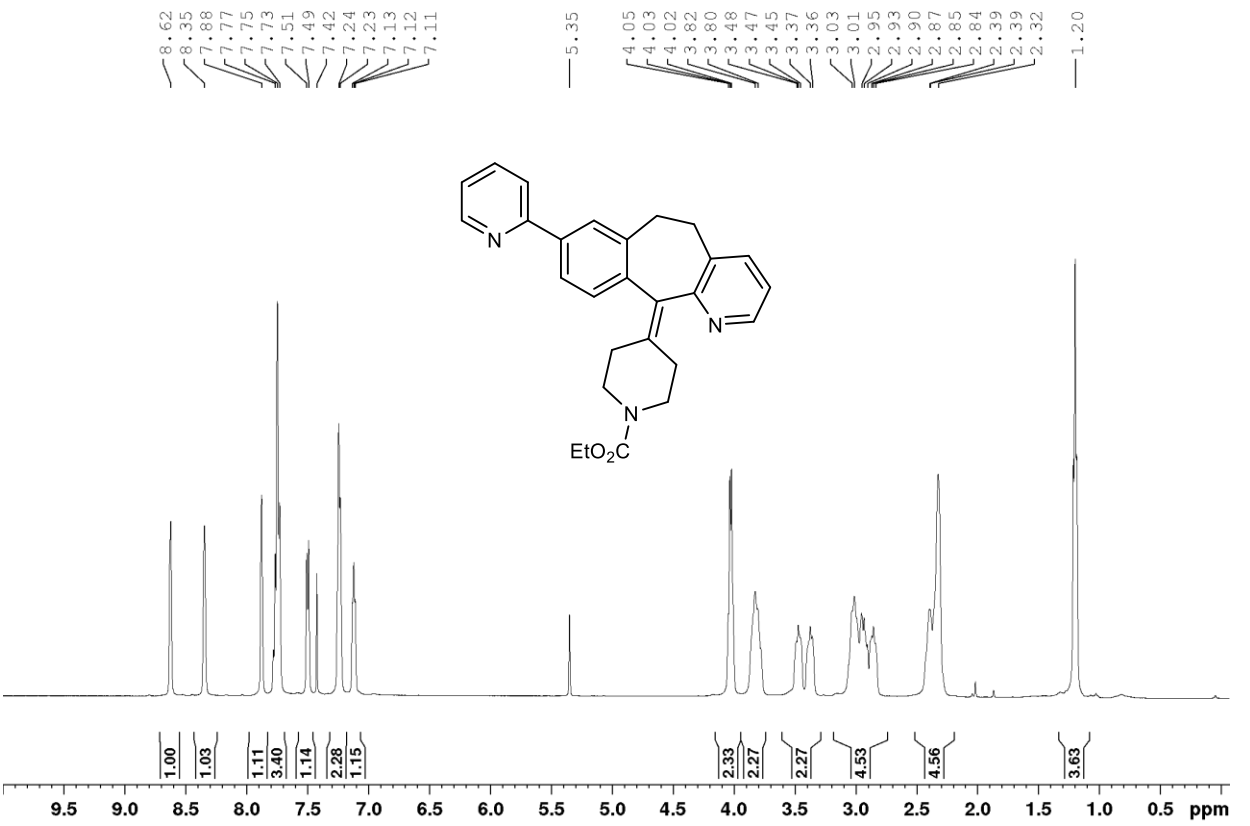
2. Acetyl and Triflyl Pyridinium Formation of 1h

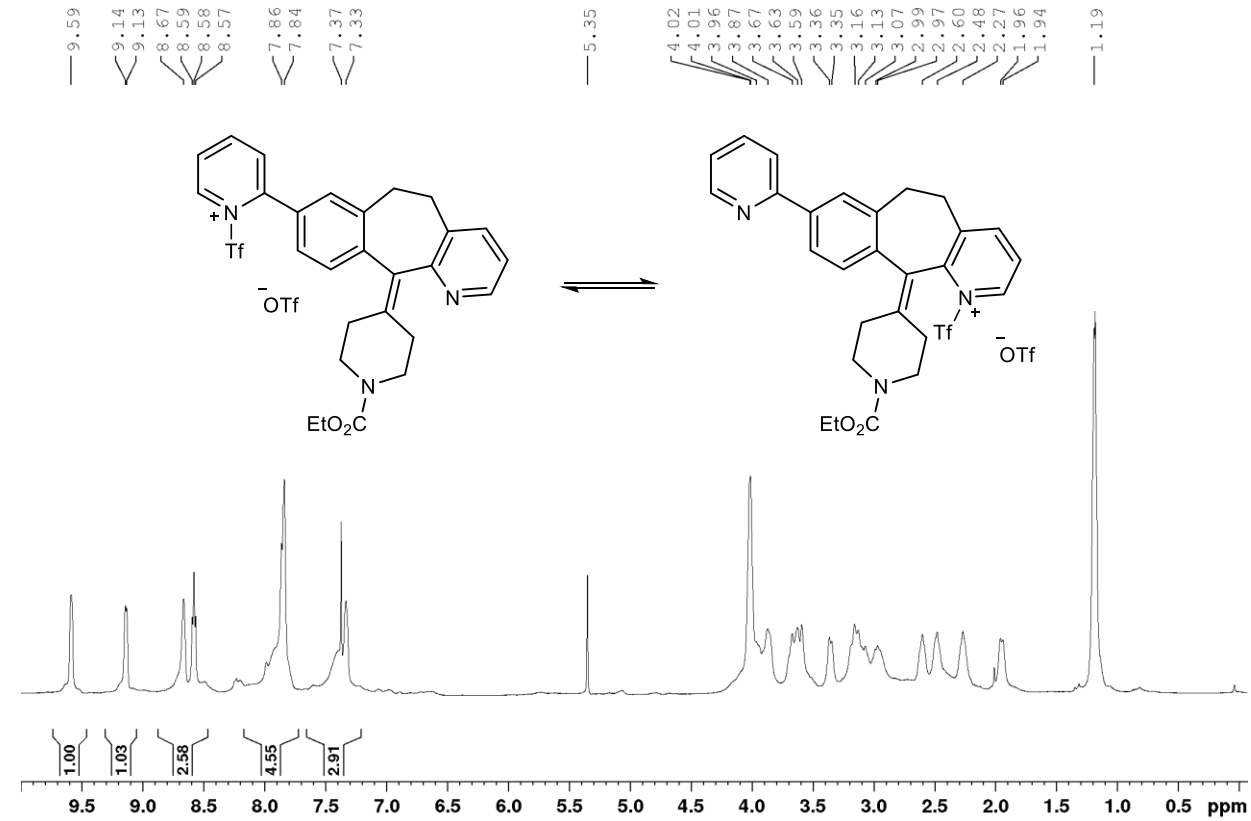






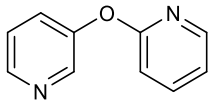
3. Rapid Interconversion of 1q Tf salt isomers





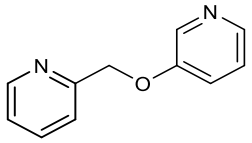
3. Preparation of Heterocyclic Phosphonium Salt Precursors

2–(pyridin–3–yloxy)pyridine



An oven dried 25 mL round bottom flask was charged with 3–hydroxypyridine (476 mg, 5.00 mmol), cobalt(II) acetylacetoneate (129 mg, 0.50 mmol), copper(I) iodide (95 mg, 0.50 mmol) and cesium carbonate (3.25 g, 10.00 mmol), and NMP (15 mL). To the reaction flask, 2–bromopyridine (477 μL, 5.00 mmol) was added and the mixture was stirred at 110 °C overnight. The reaction was cooled to room temperature, diluted with EtOAc (25 mL) and quenched with water (50 mL). The organic layer was separated, and aqueous layer was extracted with EtOAc (3 x 25 mL). The organic extracts were collected, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 50% EtOAc in hexanes) to provide the title compound as a yellow oil (482 mg, 2.80 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (1H, d, *J* = 2.7 Hz), 8.45 (1H, d, *J* = 4.6 Hz), 8.16 (1H, dd, *J* = 4.1, 0.9 Hz), 7.73 (1H, td, *J* = 8.2, 1.0 Hz), 7.53–7.50 (1H, m), 7.35 (1H, dd, *J* = 8.3, 4.7 Hz), 7.05–7.02 (1H, m), 6.98 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.6, 150.4, 147.2, 145.4, 143.4, 139.5, 128.4, 123.7, 118.9, 111.5. The spectroscopic data is in agreement with a reported synthesis.[2]

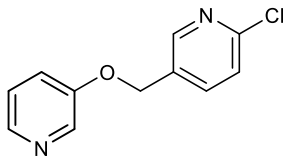
2–((pyridin–3–yloxy)methyl)pyridine



An oven dried 250 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (4 mL). The mixture was cooled to 0 °C and a mixture of 3–hydroxypyridine (523 mg, 5.50 mmol) in DMF (8 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled to 0 °C. A solution

of 2–(chloromethyl)pyridine hydrogen chloride (820 mg, 5.00 mmol) in DMF (13 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours before being quenched with water (25 mL) and diluted with CH_2Cl_2 (25 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with a saturated solution of brine (5 x), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 3.5% MeOH in CH_2Cl_2) to provide title compound as a yellow solid (373 mg, 2.00 mmol, 40% yield). 29–30 ºC IR ν_{max}/cm^{-1} (film): 3056, 3013, 2921, 1591, 1573, 1475, 1434, 1429, 1272, 1225, 1188, 1050, 797, 757, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (1H, d, *J* = 4.8 Hz), 8.41 (1H, d, *J* = 2.8 Hz), 8.23 (1H, dd, *J* = 4.6, 1.5 Hz), 7.72 (1H, dt, *J* = 7.7, 1.7 Hz), 7.50 (1H, d, *J* = 7.8 Hz), 7.29–7.19 (3H, m), 5.24 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3, 154.5, 149.4, 142.5, 138.5, 136.9, 123.8, 122.9, 121.3, 121.2, 70.8; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 187.1, $C_{11}H_{11}N_2O^+$ requires 187.1.

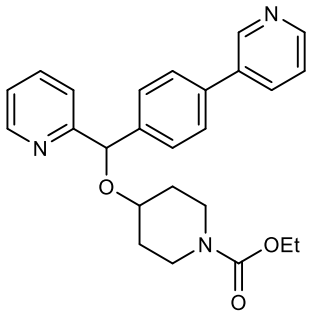
2–chloro–5–((pyridin–3–yloxy)methyl)pyridine



An oven dried 1 L round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 2.1 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (67 mL) and THF (200 mL). The mixture was cooled to 0 °C and a mixture of 3–hydroxypyridine (1.90 g, 20.00 mmol) in THF (20 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 1 hour before being cooled to 0 °C. A solution of 2–chloro–5–(chloromethyl)pyridine (3.40 g, 21.00 mmol) in DMF (20 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (100 mL) and diluted with EtOAc (100 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic extracts were dried

($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 4% MeOH in CH_2Cl_2) to provide the title compound as a brown solid (1.97 g, 8.93 mmol, 45% yield). mp 43–45 ºC; IR n_{max}/cm^{-1} (film): 3065, 3006, 2913, 1577, 1459, 1401, 1272, 1233, 1207, 1100, 1060, 1023, 819, 792, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, d, *J* = 1.8 Hz), 8.39 (1H, s), 8.29 (1H, t, *J* = 5.7 Hz), 7.76 (1H, dd, *J* = 8.2, 2.2 Hz), 7.39 (1H, d, *J* = 8.2 Hz), 7.32–7.21 (2H, m), 5.11 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.3, 151.5, 148.7, 143.0, 138.0, 130.7, 124.3, 123.9, 121.5, 67.0; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 221.1, $C_{11}H_9ClN_2O^+$ requires 221.0.

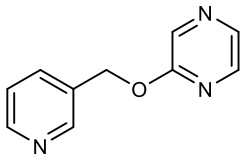
Ethyl 4–(pyridin–2–yl(4–(pyridin–3–yl)phenyl)methoxy)piperidine–1–carboxylate



An oven dried 50 mL Schlenk flask was charged with ethyl 4–((4–chlorophenyl)(pyridin–2–yl)methoxy)piperidine–1–carboxylate (1.46 g, 3.50 mmol), 3–pyridylboronic acid (473 mg, 3.85 mmol), $Pd_2(dba)_3$ (64 mg, 0.07 mmol), and tricyclohexylphosphine (47 mg, 0.17 mmol). The flask was subjected to five cycles of vacuum/nitrogen backfill before the addition of 1,4–dioxane (4.69 mL) and aqueous K_3PO_4 (1.27 M, 4.69 mL, 5.95 mmol). The Schlenk flask was sealed and heated at 100 °C for 18 hours. The reaction mixture was cooled to room temperature, filtered through a pad of silica gel (washing with EtOAc) and the filtrate concentrated *in vacuo*. The aqueous residue was then extracted with EtOAc (3 x 20 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel, gradient elution: 75% EtOAc in hexanes to 100% EtOAc) to provide the title compound as a colorless oil (1.01 g, 2.42 mmol, 69% yield). IR ν_{max}/cm^{-1} (film): 3052, 2981, 2927, 2867, 1690, 1579, 1432, 1228, 1095, 1026, 729; ^{1}H NMR (400 MHz,

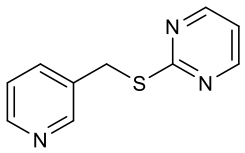
$CDCl_3$) δ: 8.81 (1H, d, *J* = 2.0 Hz), 8.56 (1H, d, *J* = 4.7 Hz), 8.53 (1H, d, *J* = 4.2 Hz), 7.82 (1H, d, *J* = 8.0 Hz), 7.70 (1H, td, *J* = 7.7, 1.4 Hz), 7.61–7.50 (5H, m), 7.33 (1H, dd, *J* = 7.9, 4.8 Hz), 7.17 (1H, m), 5.70 (1H, s), 4.11 (2H, q, *J* = 7.1 Hz), 3.78 (2H, br), 3.68 (1H, app. sept), 3.21 (2H, m), 1.86 (2H, m), 1.70 (2H, m), 1.24 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0, 155.4, 148.9, 148.4, 148.2, 141.5, 137.0, 136.9, 136.1, 134.1, 127.4, 127.1, 123.4, 122.4, 120.6, 81.3, 72.5, 61.2, 41.0 (d, *J* = 4.6 Hz), 31.0, 14.6. *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 418.3, $C_{25}H_{28}N_3O_3^+$ requires 418.2.

2–(pyridin–3–ylmethoxy)pyrazine



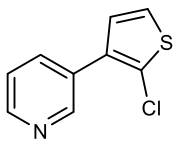
An oven–dried 100 mL round bottomed flask was charged with 3–pyridylmethanol (2.92 mL, 30.00 mmol), 2–chloropyrazine (893 µL, 10.00 mmol) and DMF (15 mL). The solution was cooled to 0 °C before sodium hydride (60% dispersion in mineral oil, 3.0 equiv) was added in one portion. The reaction mixture was warmed to room temperature and allowed to stir overnight at 70 °C. The mixture was cooled to room temperature, quenched with water (20 mL) and diluted with EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 30% EtOAc in hexanes) to provide the title compound as a light yellow solid (1.39 g, 7.43 mmol, 74% yield). mp 43–45 ºC; IR n_{max}/cm^{-1} (film): 3059, 2992, 1579, 1531, 1427, 1284, 1006, 711; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (1H, d, *J* = 1.5 Hz), 8.59 (1H, dd, *J* = 4.8, 1.5 Hz), 8.28 (1H, d, *J* = 1.2), 8.16 (1H, d, *J* = 2.8 Hz), 8.10–8.07 (1H, m), 7.79 (1H, d, *J* = 7.8 Hz), 7.31 (1H, dd, *J* = 7.8, 4.9 Hz) 5.41 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.54, 149.68, 149.54, 140.36, 137.05, 135.97, 135.81, 131.90, 123.37, 65.26; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 188.1, $C_{10}H_{10}N_3O^+$ requires 188.1.

2–((pyridin–3–ylmethyl)thio)pyrimidine



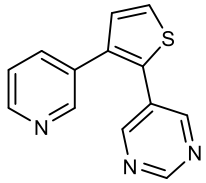
An oven dried 50 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 1.1 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DME (12 mL). The reaction mixture was cooled to 0 °C and a solution of pyridin–3–ylmethanethiol (814 mg, 6.50 mmol) in DME (3 mL) was added dropwise over 10 minutes. The reaction mixture stirred for 30 minutes at 0 °C before a solution of 2–chloropyrimidine (677 mg, 5.91 mmol) in DME (5 mL) was added dropwise over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 1 hour. The mixture was quenched with water (10 mL) and diluted with EtOAc (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 70% EtOAc in hexanes) to provide the title compound as a white solid (1.01 g, 4.97 mmol, 84% yield). mp 46–48 ºC; IR ν_{max}/cm^{-1} (film): 3030, 2966, 2923, 1562, 1547, 1377, 1201, 1181, 748, 711, 629; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, d, *J* = 4.9 Hz), 8.52 (2H, d, *J* = 4.8 Hz), 8.47 (1H, d, *J* = 4.6 Hz), 7.76 (1H, d, *J* = 7.8 Hz), 7.22 (1H, dd, *J* = 7.9, 4.9 Hz), 6.98 (1H, t, *J* = 4.9 Hz), 4.38 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 157.3, 150.3, 148.4, 136.4, 133.7, 123.3, 116.8, 32.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 204.1, $C_{10}H_{10}N_3S^+$ requires 204.1.

3–(2–chlorothiophen–3–yl)pyridine



An oven dried 500 mL round bottom flask was charged with a solution of 3–bromo–2–chlorothiophene (2.73 mL, 25.00 mmol) in toluene (175 mL), followed by an aqueous solution of Na_2CO_3 (80 mL, 2.0 M) and an ethanolic solution (80 mL) of 3–pyridinylbornonic acid (4.61 g, 37.50 mmol). After 10 minutes of stirring at room temperature, $Pd(PPh_3)_4$ (1.16 g, 1.00 mmol) was added to the reaction flask. The mixture was then deoxygenated under reduced pressure and flushed with nitrogen (3 cycles) before heating under reflux overnight. After cooling to room temperature, EtOAc (100 mL) and water (100 mL) were added and the organic phase was separated. The aqueous phase was extracted with EtOAc (2 x 100 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 20% EtOAc in hexanes) to provide the title compound as a yellow oil (2.64 g, 13.50 mmol, 54% yield). IR ν_{max}/cm^{-1} (film): 3106, 3033, 1570, 1476, 1021, 873, 710, 635; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (1H, d, *J* = 1.7 Hz), 8.59 (1H, dd, *J* = 4.8, 1.6 Hz), 7.90 (1H, dt, *J* = 7.9, 2.0 Hz), 7.36 (1H, ddd, *J* = 7.9, 4.9, 0.7 Hz), 7.20 (1H, d, *J* = 5.8 Hz), 7.07 (1H, d, *J* = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 148.6, 135.5, 134.8, 130.1, 127.8, 126.2, 123.4, 123.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 196.1, $C_9H_7ClNS^+$ requires 196.0.

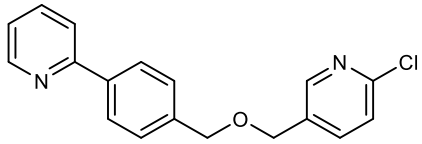
5–(3–(pyridin–3–yl)thiophen–2–yl)pyrimidine



An oven dried 100 mL Schlenk flask was charged with a solution of 3–(2–chlorothiophen–3–yl)pyridine (1.37 g, 7.00 mmol), pyrimidine–5–boronic acid (1.04 g, 8.40 mmol), and $Pd(OAc)_2$ (63 mg, 0.28 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill before being taken into glovebox. XPhos (160 mg, 0.34 mmol) was added, the flask then sealed and taken out of glovebox. Degassed *n*–BuOH (39 mL) was added to the flask before stirring the reaction mixture at room temperature for 15 minutes. An aqueous solution of cesium hydroxide monohydrate (1.22 M, 9.78 mL) was added to the mixture, the Schlenk flask sealed, and heated to

80 °C overnight. The reaction mixture was cooled to room temperature, filtered through a pad of silica gel (washing with EtOAc) and the filtrate concentrated *in vacuo*. The aqueous residue was then extracted with EtOAc (3 x 20 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 50% EtOAc in hexanes) to provide the title compound as a white solid (919 mg, 3.84 mmol, 55% yield). mp 82–85 ºC; IR ν_{max}/cm^{-1} (film): 3029, 3032, 1548, 1440, 1379, 1188, 879, 722; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.12 (1H, s), 8.65 (2H, s), 8.61–8.53 (2H, m), 7.61–7.52 (2H, m), 7.32–7.22 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 156.3, 149.7, 148.8, 137.0, 136.0, 131.6, 131.1, 130.4, 128.4, 127.2, 123.5; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 240.1, $C_{13}H_{10}N_3S^+$ requires 240.1.

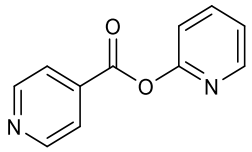
2–chloro–5–(((4–(pyridin–2–yl)benzyl)oxy)methyl)pyridine



An oven dried 1 L round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 2.1 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (106 mL) and THF (318 mL). The mixture was cooled to 0 °C and a mixture of (4–(pyridin–2–yl)phenyl)methanol (5.89 g, 31.80 mmol) in THF (20 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 1 hour before being cooled to 0 °C. A solution of 2–chloro–5–(chloromethyl)pyridine (5.41 g, 33.40 mmol) in DMF (20 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (100 mL) and diluted with EtOAc (100 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 25% EtOAc in hexanes) to provide the title compound as a light yellow solid (6.91 g, 22.20 mmol, 70% yield). mp 96–98 ºC; IR ν_{max}/cm^{-1} (film): 3050, 3006, 2921, 2856, 1586, 1566, 1460, 1094, 776, 743; ^1H NMR (400 MHz, $CDCl_3$)

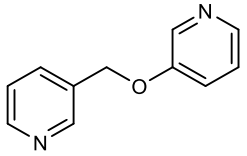
δ: 8.69 (1H, d, *J* = 4.9 Hz), 8.37 (1H, d, *J* = 2.4 Hz), 8.00 (2H, d, *J* = 8.2 Hz), 7.80–7.63 (3H, m), 7.45 (2H, d, *J* = 8.1 Hz), 7.31 (1H, d, *J* = 8.2 Hz), 7.25–7.20 (1H, m), 4.63 (2H, s), 4.55 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 150.7, 149.6, 148.8, 139.1, 138.2, 138.2, 136.7, 132.6, 128.1, 127.0, 124.1, 122.1, 120. 4, 72.3, 68.6; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 311.2, $C_{18}H_{16}ClN_2O^+$ requires 311.1.

Pyridin–2–yl isonicotinate



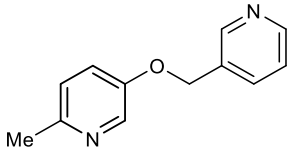
An oven dried 25 mL round bottom flask was charged with isonicotinoyl chloride hydrogen chloride (2.67 g, 15.00 mmol), 4–(dimethylamino)pyridine (660 mg, 5.40 mmol) and 2–hydroxypyridine (1.71 g, 18.00 mmol). THF (45 mL) was added to the reaction flask and triethylamine (6.3 mL, 45.00 mmol) was added dropwise over 5 minutes before heating the mixture at reflux overnight. The reaction cooled to room temperature and diluted with EtOAc (25 mL) and quenched with water (25 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified through a plug of silica eluting with 100% EtOAc to provide the title compound as a white solid (532 mg, 2.66 mmol, 18% yield). mp 86–88 ºC; IR ν_{max}/cm^{-1} (film): 3056, 3030, 1737, 1594, 1412, 1274, 1196, 1088; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (2H, d, *J* = 6.0 Hz), 8.48 (1H, dd, *J* = 4.9, 1.4 Hz), 8.03 (2H, d, *J* = 6.0 Hz), 7.90–7.86 (1H, m), 7.34–7.31 (1H, m), 7.24–7.22 (1H, d, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.3, 157.5, 150.7, 148.7, 139.7, 136.3, 123.1, 122.5, 116.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 201.1, $C_{11}H_9N_2O_2^+$ requires 201.1.

3–(pyridin–3–ylmethoxy)pyridine



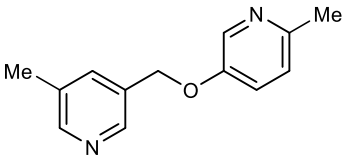
An oven dried 250 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv) and the flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (8 mL). The mixture was cooled to 0 °C and a mixture of 3–hydroxypyridine (1.14 g, 12.00 mmol) in DMF (20 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled to 0 °C. A solution of 3–(chloromethyl)pyridine hydrogen chloride (1.97 g, 12.00 mmol) in DMF (32 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of brine (5 x 25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 2.5% MeOH in CH_2Cl_2) to provide the title compound as a colorless oil (1.16 g, 6.25 mmol, 52% yield). IR ν_{max}/cm^{-1} (film): 3033, 2918, 2850, 1573, 1475, 1423, 1261, 1225, 1012; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, s), 8.61 (1H, d, *J* = 4.7 Hz), 8.40 (1H, s), 8.26 (1H, d, *J* = 4.1 Hz), 7.78 (1H, d, *J* = 7.8 Hz), 7.36–7.32 (1H, m), 7.28–7.22 (2H, m), 5.13 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 149.7, 149.0, 142.8, 138.1, 135.2, 131.7, 123.9, 123.5, 121.5, 67.8; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 187.1, $C_{11}H_{11}N_2O^+$ requires 187.1.

2–methyl–5–(pyridin–3–ylmethoxy)pyridine



An oven dried 100 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv) and the flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (4 mL). The mixture was cooled to 0 °C and a mixture of 5–hydroxy–2–methylpyridine (798 mg, 7.32 mmol) in DMF (10 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled to 0 °C. A solution of 3–(chloromethyl)pyridine hydrogen chloride (1.00 g, 6.10 mmol) in DMF (16.5 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of brine (5 x 25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 4% MeOH in CH_2Cl_2) to provide the title compound as a white amorphous solid (714 mg, 3.57 mmol, 59% yield). IR ν_{max}/cm^{-1} (film): 3035, 2918, 2881, 1569, 1483, 1243, 1215, 1025, 1005; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.67 (1H, s), 8.59 (1H, d, *J* = 4.4 Hz), 8.26 (1H, s), 7.76 (1H, d, *J* = 7.8 Hz), 7.33–7.30 (1H, m), 7.18–7.14 (1H, m), 7.07 (1H, d, *J* = 8.6), 5.08 (2H, s), 2.48 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 151.1, 149.6, 149.6, 148.9, 136.8, 135.1, 131.9, 123.4, 122.3, 67.9, 23.3; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 201.1, $C_{12}H_{13}N_2O^+$ requires 201.1.

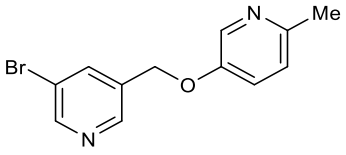
2–methyl–5–((5–methypyridin–3–yl)methoxy)pyridine



An oven dried 100 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv) and the flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (6 mL). The mixture was cooled to 0 °C and a mixture of 5–hydroxy–2–methylpyridine (1.10 g, 10.11 mmol) in DMF (14 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled

to 0 °C. A solution of 3–(chloromethyl)–5–methylpyridine hydrogen chloride (1.50 g, 8.42 mmol) in DMF (22.5 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of brine (5 x 25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 6% MeOH in CH_2Cl_2) to provide the title compound as a white solid (1.37 g, 6.42 mmol, 76% yield). mp 81–83 ºC; IR ν_{max}/cm^{-1} (film): 3070, 2948, 2918, 1569, 1483, 1380, 1267, 1215, 1025; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, s), 8.42 (1H, s), 8.26 (1H, d, *J* = 2.8 Hz), 7.59 (1H, s), 7.17 (1H, dd, *J* = 5.7, 2.8 Hz), 7.07 (1H, d, *J* = 8.4 Hz), 5.05 (2H, s), 2.49 (3H, s), 2.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 151.1, 150.2, 146.1, 136.9, 135.7, 133.1, 131.3, 123.3, 122.4, 67.9, 23.3, 18.3; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 215.2, $C_{13}H_{15}N_2O^+$ requires 215.1.

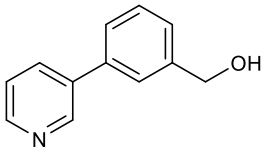
5–((5–bromopyridin–3–ly)methoxy)–2–methylpyridine



An oven dried 50 mL round bottom flask was charged with 4–dimethylaminopyridine (611 mg, 5.00 mmol) and subjected to three cycles of vacuum/nitrogen backfill before addition of CH_2Cl_2 (17 mL). The mixture was then cooled to 0 °C, 5–bromo–3–pyridinemethanol (1.13 mL, 10.00 mmol) was added dropwise, followed by adding 4–toluenesulfonyl chloride (2.38 g, 12.50 mmol) portion wise over 10 minutes. Triethylamine (2.10 mL, 15.00 mmol) was then added dropwise and the reaction was allowed to stir at room temperature for 6 hours, before being diluted with CH_2Cl_2 (25 mL) and quenched with 1 M HCl (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude mixture was carried onto the next reaction without

further purification. An oven dried 100 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of DMF (4 mL). The mixture was cooled to 0 °C and a mixture of 5–hydroxy–2–methylpyridine (707 mg, 6.48 mmol) in DMF (9 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled to 0 °C. A solution of the crude material in DMF (14.5 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of brine (5 x 25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 4% MeOH in CH_2Cl_2) to provide the title compound as a yellow oil (1.08 g, 3.85 mmol, 39% yield). IR ν_{max}/cm^{-1} (film): 3042, 3019, 2922, 1587,1494, 1265, 528; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (1H, d, *J* = 2.2 Hz), 8.58 (1H, d, *J* = 1.6 Hz), 8.26 (1H, d, *J* = 2.9 Hz), 7.94 (1H, t, *J* = 1.9 Hz), 7.17 (1H, dd, *J* = 8.5, 2.9 Hz), 7.09 (1H, d, *J* = 8.5 Hz), 5.08 (2H, s), 2.50 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 151.5, 150.7, 146.8, 137.6, 136.7, 133.7, 123.5, 122.5, 120.9, 67.1, 23.4; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 279.0, $C_{12}H_{12}BrN_2O^+$ requires 279.0.

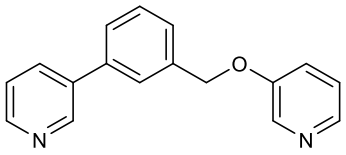
(3–(pyridin–3–yl)phenyl)methanol



An oven dried 50 mL round bottom flask was charged with $Pd(OAc)_2$ (225 mg, 1.00 mmol), PPh_3 (682 mg, 2.60 mmol) and aq. Na_2CO_3 (14.2 mL, 28.40 mmol, 2.0 M) and subjected to three cycles of vacuum/nitrogen backfill before H_2O (10 mL) was added. A solution of 3–hydroxymethylphenylboronic acid (3.28 g, 21.60 mmol) and 3–bromopyridine (1.93 mL, 20.00 mmol) in propanol (38 mL) was added to the reaction mixture and the resulting suspension was

allowed to stir at 95°C for 12 hours. The reaction mixture was diluted with EtOAc (75 mL) and quenched with water (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The organic layers were combined, washed with 1:1 saturated aqueous solution of $NaHCO_3$ (2 x 50 mL), and once with a saturated solution of brine (50 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 80% EtOAc in Hexanes) to provide the title compound as a clear–yellow oil (2.50 g, 13.52 mmol, 68% yield). IR ν_{max}/cm^{-1} (film): 3226, 3035, 2858, 1606, 1589, 1571, 1401, 1023; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.83 (1H, d, *J* = 2.1 Hz), 8.59 (1H, dd, *J* = 4.8, 1.5 Hz), 7.88 (1H, dt, *J* = 8.0, 2.3 Hz), 7.60 (1H, s), 7.52–7.34 (4H, m), 4.80 (2H, s), 2.07 (1H, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 147.3, 142.5, 137.1, 136.4, 134.4, 128.8, 126.4, 125.4, 125.1, 123.4, 63.9; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 186.2, $C_{12}H_{12}NO^+$ requires 186.1.

3–((3–(pyridin–3–yl)benzyl)oxy)pyridine

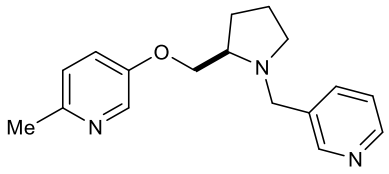


An oven dried 50 mL round bottom flask was charged with 4–dimethylaminopyridine (99 mg, 0.81 mmol) and (3–(pyridin–3–yl)phenyl)methanol (1.50 g, 8.11 mmol) and subjected to three cycles of vacuum/nitrogen backfill, before CH_2Cl_2 (13 mL) was added. The mixture was cooled to 0 °C and 4–toluenesulfonyl chloride (2.32 g, 12.15 mmol) was added over 10 minutes. NEt_3 (2.69 mL, 12.15 mmol) was then added dropwise and the reaction was allowed to stir at room temperature for 6 hours. The mixture was diluted with CH_2Cl_2 (25 mL) and quenched with 0.3 M HCl (25 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude mixture was carried onto the next reaction without further purification. An oven dried 100 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 3.3 equiv). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition

of DMF (4 mL). The mixture was cooled to 0 °C and a mixture of 3–hydroxypyridine (585 mg, 6.15 mmol) in DMF (10 mL) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 30 minutes before being cooled to 0 °C. A solution of the crude material in DMF (14 mL) was then added dropwise to the reaction mixture over 10 minutes. The reaction mixture was warmed to room temperature and allowed to stir for 12 hours. The mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of brine (5 x 25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 3% MeOH in CH_2Cl_2) to provide the title compound as a yellow oil (332 mg, 1.27 mmol, 16% yield). IR ν_{max}/cm^{-1} (film): 3032, 2923, 2873, 1572, 1473, 1424, 1259, 1226, 1021; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (1H, d, *J* = 2.2 Hz), 8.61 (1H, dd, *J* = 4.8, 1.2 Hz), 8.42 (1H, d, *J* = 2.8 Hz), 8.25 (1H, d, *J* = 4.5 Hz), 7.88 (1H, dt, *J* = 7.9, 1.8 Hz), 7.65 (1H, s), 7.57–7.46 (3H, m), 7.37 (1H, dd, *J* = 7.8, 4.8 Hz), 7.30–7.21 (2H, m), 5.19 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$)

δ: 154.6, 148.6, 148.2, 142.4, 138.2, 138.1, 137.0, 136.0, 134.2, 129.3, 127.0, 126.9, 126.0, 123.7, 123.4, 121.4, 69.9; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 263.1, $C_{17}H_{15}N_2O^+$ requires 263.1.

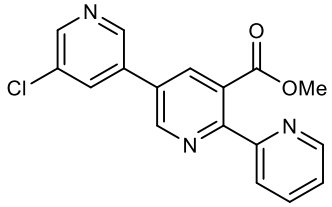
(R)–2–methyl–5–((1–(pyridin–3–ylmethyl)pyrrolidin–2–yl)methoxy)pyridine



An oven dried 500 mL round bottom flask was charged with PPh_3 (12.77 g, 48.70 mmol) and a stir bar, and subjected to three cycles of vacuum/nitrogen backfill. THF (203 mL) was then added to the flask and diethyazodiethylcarboxylate (7.67 mL, 48.7 mmol) was added dropwise over 20 minutes. The solution was allowed to stir for 30 minutes before Boc–D–prolinol (6.53 g, 32.4 mmol) was added in one portion. The solution stirred for 20 minutes and then 3–hydroxypyridine (5.31 g, 48.70 mmol) was added and the reaction mixture stirred for 36 hours. The mixture was

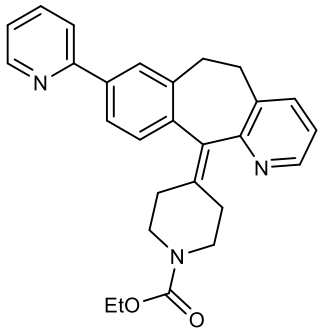
diluted with CH_2Cl_2 (100 mL) and quenched with water (100 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 50% EtOAc in hexanes) to provide a mixture of the Boc–protected 2–methyl–5–(pyrrolidin–2–ylmethoxy)pyridine and diethyl 1,2–hydrazinedicarboxylate (10.84 g). The mixture was transferred to a 300 mL round bottom flask equipped with a stir bar and diluted with CH_2Cl_2 (112 mL). Trifluoroacetic acid (31 mL) was added dropwise over 20 minutes and the solution stirred overnight. The solution was quenched with a saturated aqueous solution of NH_4OH (20 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The organic layer was washed with a saturated solution of brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The mixture was purified through flash chromatography (silica gel: 8% MeOH in CH_2Cl_2) to provide 2–methyl–5–(pyrrolidin–2–ylmethoxy)pyridine (1.52 g, 7.37 mmol, 25% yield). In a separate 50 mL round bottom flask, 3–pyridinecarboxaldehyde (675 mL, 7.19 mmol) and a stir bar were added and subjected to three cycles of vacuum/nitrogen backfills before MeOH (19 mL) and aq. acetic acid (0.96 mL, 7.20 mmol, 7.5 M) were added. The 2–methyl–5–((1–methylpyrrolidin–2–yl)methoxy)pyridine (1.52 g, 7.9 mmol) was added, followed by sodium triacetoxyborohydride (1.52 g, 7.19 mmol). The reaction was allowed to stir for 5 hours before being quenched with a saturated aqueous solution of NH_4Cl (40 mL) and diluted with CH_2Cl_2 (50 mL). The organic phase was separated from the aqueous layer and extracted with CH_2Cl_2 (3 x 50 mL). The aqueous layer was neutralized with a saturated aqueous solution of K_2CO_3 and was then extracted with CH_2Cl_2 (3 x 50 mL). The organic extracts were combined, dried ($MgSO_4$), and concentrated *in vacuo.* The mixture was purified by flash chromatography (silica gel: 2% MeOH in CH_2Cl_2 to 6% MeOH in CH_2Cl_2) to provide the title compound as a yellow oil (1.07 g, 3.77 mmol, 52% yield). IR ν_{max}/cm^{-1} (film): 3025, 2960, 2920, 2072, 2788, 1572, 1494, 1483, 1424, 1266, 1240, 1211, 1026, 714; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, s), 8.48 (1H, s), 8.15 (1H, d, J = 1.9 Hz), 7.65 (1H, d, J = 7.6 Hz), 7.22–7.19 (1H, m), 7.07–7.01 (2H, m), 4.13 (1H, d, J = 13.4 Hz), 3.96–3.84 (2H, m), 3.52 (1H, d, J = 13.4 Hz), 3.03–2.92 (2H, m), 2.46 (3H, s), 2.30 (1H, q, J = 8.5 Hz), 2.05–2.00 (1H, m), 1.76–1.73 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 150.3, 150.0, 148.3, 136.6, 136.3, 134.9, 123.2 (2C), 121.8, 71.9, 62.3, 56.9, 54.5, 28.4, 23.2, 23.0; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 284.2, $C_{17}H_{22}N_3O^+$ requires 284.2; Specific Rotation $[\alpha]_D^{22}$ +53.52 (*c* 1.00, $CHCl_3$).

3–(2–chlorothiophen–3–yl)pyridine



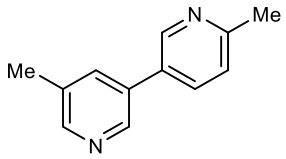
An oven dried 25 mL round bottom flask was charged with methyl 5',6–dichloro–[3,3'–bipyridine]–5–carboxylate (608 mg, 2.15 mmol) before the flask was subjected to three cycles of vacuum/nitrogen backfill. Degassed DMF (11 mL) was added to the flask followed by 2–(tributylstannyl)pyridine (975 μL, 3.01 mmol), cesium fluoride (980 mg, 6.45 mmol), CuI (82 mg, 0.43 mmol), $Pd(PPh_3)_4$ (248 mg, 0.22 mmol) in that order. The mixture was then deoxygenated under reduced pressure and flushed with nitrogen (3 cycles) before heating at 80 °C for 2 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (25 mL) and filtered through a short pad of Celite. The organic filtrate was washed with water (25 mL x 5) and a saturated solution of brine (25 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel, gradient elution: 25% EtOAc in hexanes to 50% EtOAc in hexanes) to provide the title compound as a white solid (303 mg, 0.93 mmol, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (1H, d, J = 2.0 Hz), 8.79 (1H, d, J = 1.5 Hz), 8.66 (1H, d, J = 2.0 Hz), 8.63 (1H, d, J = 4.6 Hz), 8.23 (1H, d, J = 7.9 Hz), 8.12 (1H, d, J = 2.0 Hz), 7.94 (1H, s), 7.85 (1H, t, J = 7.9 Hz), 7.34 (1H, dd, J = 7.3, 4.9 Hz), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.0, 155.2, 155.1, 148.6, 148.6, 148.2, 145.7, 136.8, 135.2, 134.0, 133.4, 132.6, 131.1, 128.8, 124.0, 122.7, 52.5. The spectroscopic data is in agreement with a reported synthesis.[3]

Ethyl 4–(8–(pyridin–2–yl)–5,6–dihydro–11H–benzo[5,6]cyclohepta[1,2–b]pyridin–11–ylidene)piperidine–1–carboxylate



An oven dried 50 mL Schlenk flask was charged with loratadine (ethyl 4–(8–chloro–5,6–dihydro–11H–benzo[5,6]cyclohepta[1,2–b]pyridin–11–ylidene)piperidine–1–carboxylate) (766 mg, 2.00 mmol), $Pd_2(dba)_3$ (183 mg, 0.20 mmol), tri–tert–butylphosphonium tetrafluoroborate (116 mg, 0.40 mmol), and cesium fluoride (668 mg, 4.40 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill before the addition of 1,4–dioxane (17 mL) and 2–(tributylstannyl)pyridine (971 µL, 3.00 mmol). The Schlenk flask was sealed and heated at 100 °C for 12 hours. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel (washing with EtOAc). The filtrate was washed with water (3 x 20 mL) and a saturated aqueous solution of brine (20 mL). The organic extract was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 30% EtOAc in hexanes) to provide the title compound as a white amorphous solid (660 mg, 1.55 mmol, 78% yield). IR ν_{max}/cm^{-1} (film): 3029, 2979, 2914, 2856, 1690, 1586, 1228, 1113, 996, 908, 723,; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.66 (1H, d, *J* = 4.7 Hz), 8.40 (1H, dd, *J* = 4.9, 1.4 Hz), 7.87 (1H, d, *J* = 1.5 Hz), 7.77–7.67 (3H, m), 7.44 (1H, dd, *J* = 7.6, 1.3 Hz), 7.30 (1H, d, *J* = 7.9 Hz), 7.23–7.17 (1H, m), 7.08 (1H, dd, *J* = 7.7, 4.8 Hz), 4.13 (2H, q, *J* = 7.1 Hz), 3.82 (2H, br), 3.58–3.31 (2H , m), 3.24–3.06 (2H, m), 3.01–2.82 (2H, m), 2.60–2.27 (4H, m), 1.25, (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 157.1, 155.5, 149.6, 146.6, 140.0, 138.5, 138.2, 137.4, 137.1, 136.7, 135.0, 133.6, 129.6, 127.6, 124.5, 122.1, 122.0, 120.4, 61.2, 44.8, 31.9, 31.7, 30.6 (d, *J* = 25.6 Hz), 14.6; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 426.3, $C_{27}H_{28}N_3O_2^+$ requires 426.2.

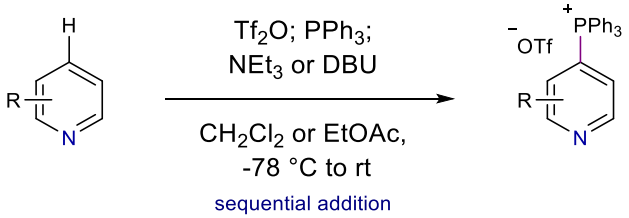
5,6'–dimethyl–3,3'–bipyridine



An oven dried 250 mL round bottom flask was charged with (6–methylpyrid–3–yl)boronic acid (1.00 g, 7.3 mmol) and $Pd(PPh_3)_4$ (734 mg, 0.64 mmol), before adding toluene (51 mL) and degassed ethanol (51 mL). 3–bromo–5–methylpyridine (0.74 mL, 6.40 mmol) and aq. Na_2CO_3 (6.7 mL, 13.40 mmol, 2.0 M) were added to the reaction mixture before heating to 110°C and stirring overnight. The solution was cooled to room temperature, diluted with CH_2Cl_2 (50 mL) and quenched with water (50 mL). The organic phase was separated from the aqueous layer and extracted with CH_2Cl_2 (3 x 50 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 4% MeOH in CH_2Cl_2) to provide the title compound as a white solid (761 mg, 4.10 mmol, 65% yield); mp 69–74 ºC; IR ν_{max}/cm^{-1} (film): 3020, 2990, 2919, 1598, 1494, 1433, 1385; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, d, *J* = 2.2 Hz), 8.61 (1H, d, *J* = 2.0 Hz), 8.45 (1H, d, *J* = 1.3 Hz), 7.75 (1H, dd, *J* = 8.0, 2.4 Hz), 7.64 (1H, m), 7.24 (1H, d, *J* = 8.0 Hz), 2.60 (3H, s), 2.40 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 149.5, 147.4, 145.2, 134.6, 134.6, 133.2, 133.0, 130.6, 123.2, 24.1, 13.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 185.2, $C_{12}H_{13}N_2^+$ requires 185.1.

4. Preparation of Heterocyclic Phosphonium Salts

General Procedure A

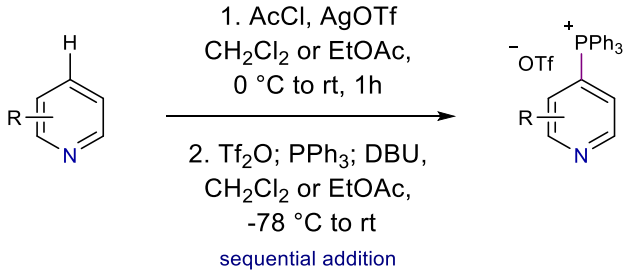


An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O (1.0 equiv) was added dropwise 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 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* to approximately 2–10 mL (depending on the scale of the reaction). An excess of chilled Et_2O (0 ºC) was added to the concentrated solution that was then placed in a –20 ºC refrigerator for approximately 1 hour. 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.

General Procedure B (Acylation–Blocking Conditions)



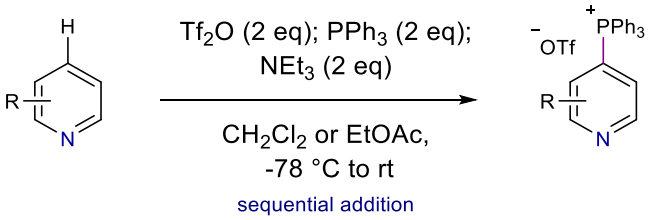
An oven dried 8 mL vial (≤ 0.50 mmol scale) or a round bottom flask (> 0.50 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and silver trifluormethanesulfonate (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 or EtOAc (0.1 M) was added, the reaction vessel cooled to 0 ºC and acetyl chloride (1.0 equiv) was added dropwise over 5 minutes. The reaction was warmed to room temperature and stirred* for 1 hour before cooling to –78 ºC. Tf_2O (1.0 equiv) was added dropwise over 5 minutes and the reaction mixture 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. 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 pyridine (2.0 equiv) and H_2O (approximately the same volume as CH_2Cl_2) and the suspension was allowed to stir for 30 minutes before being filtered through a pad of Celite (rinsed with CH_2Cl_2). The filtrate was transferred to a separatory funnel and the organic layer was washed three times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo* to approximately 2–10 mL (depending on the scale of the reaction). An excess of chilled Et_2O (0 ºC) was added to the concentrated solution that was then placed in a –20 ºC refrigerator for approximately 1 hour. 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.

* Uniformed stirring is important for the reaction; the reaction vessel was placed directly on the middle of the stir plate and the mixture stirred at 1400–2000 rpms for the duration of the reaction.

1) Silver trifluoromethanesulfonate was taken fresh from a glovebox before each reaction.
2) PPh_3 was crushed into a powder prior to use.
3) Certain substrates require longer periods for the precipitation step and specific cases are indicated below.
4) 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.
5) 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.

General Procedure C (Base–Switching Conditions)



An oven dried 8 mL vial (≤ 0.50 mmol scale) or a round bottom flask (> 0.50 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 or EtOAc (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O (2.0 equiv) was added dropwise over 5 minutes. The reaction was stirred[†] for 30 minutes before PPh_3 (2.0 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. NEt_3, (2.0 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 CH_2Cl_2 and the resulting organic layer was washed

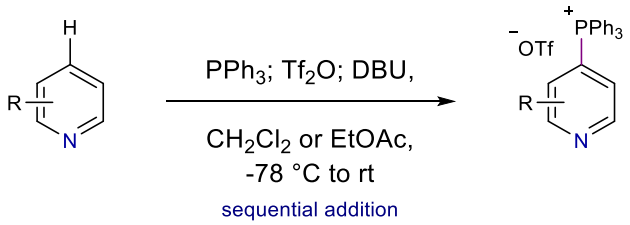
[†] Uniformed stirring is important for the reaction; the reaction vessel was placed directly on the middle of the stir plate and the mixture stirred at 1400–2000 rpms for the duration of the reaction.

at least five times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo* to approximately 2–10 mL (depending on the scale of the reaction). An excess of chilled Et_2O (0 ºC) was added to the concentrated solution that was then placed in a –20 ºC refrigerator for approximately 1 hour. 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 contain residual protonated NEt_3 after the precipitation step. In these cases, the phosphonium salt is diluted with CH_2Cl_2 and washed with H_2O until the protonated NEt_3 disappears.
3) Certain substrates require longer periods for the precipitation step and specific cases are indicated below.
4) 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.
5) 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 ^1H and ^{31}P NMR.

General Procedure D (Reverse Order of Reagent Addition)



An oven dried 8 mL vial (≤ 0.50 mmol scale) or a round bottom flask (> 0.50 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and PPh_3 (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O

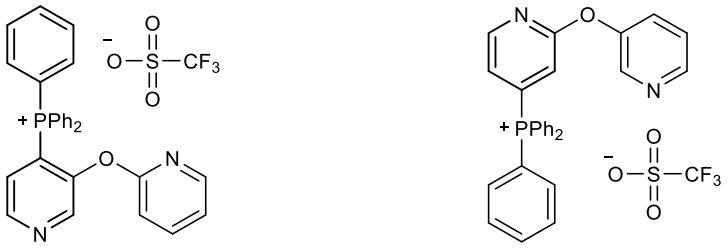
(1.0 equiv) was added dropwise over 5 minutes. The reaction was stirred[‡] for 1 hour before DBU (1.0 equiv) was added dropwise via syringe, the cooling bath removed and the reaction warmed to room temperature while stirring (approximately 15–30 minutes). The reaction mixture was quenched with H_2O (approximately the same volume as CH_2Cl_2) and the mixture was transferred to a separatory funnel. The mixture was diluted 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* to approximately 2–10 mL (depending on the scale of the reaction). An excess of chilled Et_2O (0 ºC) was added to the concentrated solution that was then placed in a –20 ºC refrigerator for approximately 1 hour. 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.

[‡] Uniformed stirring is important for the reaction; the reaction vessel was placed directly on the middle of the stir plate and the mixture stirred at 1400–2000 rpms for the duration of the reaction.

Triphenyl(3–(pyridin–2–yloxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2a)

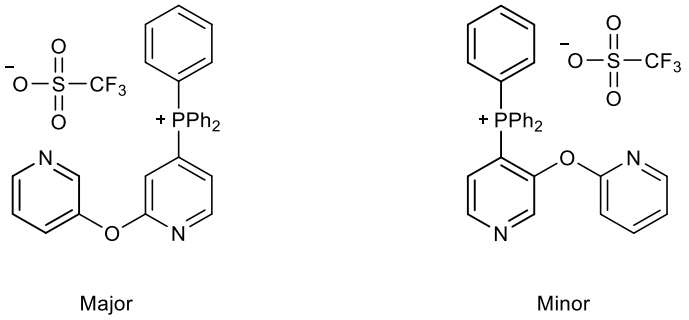


Major Minor

>20:1(Major:Minor) Mixture of Isomers

Prepared according to general procedure A using 2–(pyridin–3yloxy)pyridine (183 mg, 1.06 mmol), Tf_2O (179 μL, 1.06 mmol), PPh_3 (306 mg, 1.17 mmol), DBU (159 μL, 1.06 mmol) and CH_2Cl_2 (10.6 mL). After the purification procedure, the title compound was isolated as a white solid (498 mg, 0.85 mmol, 81% yield). mp 149–158 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3063, 1601, 1589, 1437, 1269, 1221, 1140, 1031; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.91 (1H, app d, *J* = 6.2 Hz), 8.76 (1H, app t, *J* = 8.8 Hz), 7.98 (1H, dd, *J* = 4.8, 1.8 Hz), 7.83–7.64 (15H, m), 7.55–7.51 (1H, m), 7.30 (1H, dd, *J* = 14.2, 5.0 Hz), 7.02 (1H, dd, *J* = 7.2, 5.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 151.1, 146.6, 146.4 (d, *J* = 10.1 Hz), 146.3 (d, *J* = 4.4 Hz), 140.4, 135.6 (d, *J* = 3.1 Hz), 133.9 (d, *J* = 11.0 Hz), 130.6 (d, *J* = 13.4 Hz), 127.6 (d, *J* = 7.0 Hz), 120.9, 120.7 (q, *J* = 320.3 Hz), 119.6 (d, *J* = 86.1 Hz), 115.7 (d, *J* = 91.4 Hz), 111.2; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.13; *m/z* LRMS (ESI + APCI) found $[M – OTf]^+$ 433.2, $C_{28}H_{22}N_2OP^+$ requires 433.1.

Triphenyl(2–(pyridin–3–yloxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2a)

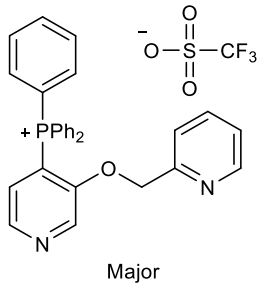


Major Minor

17:1:1:1 (Major:Minor:Undefined phosphonium isomers) Mixture of Isomers

Prepared according to general procedure B (except that the phosphine was stirred for 6 hours at –50 ºC instead of 30 minutes at –78 ºC) using 2–(pyridin–3yloxy)pyridine (86 mg, 0.50 mmol), silver trifluormethanesulfonate (129 mg, 0.50 mmol), acetyl chloride (36 μL, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), PPh_3 (145 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol), pyridine (81 μL, 1.00 mmol), and EtOAc (5.0 mL). After the purification procedure, the title compound was isolated as a brown solid (113 mg, 0.19 mmol, 39% combined yield).; Both isomers, IR ν_{max}/cm^{-1} (film): 3064, 1588, 1439, 1382, 1260, 1222, 1108, 1030, 906, 734, 689, 647; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.49–8.46 (3H, m), 7.93–7.62 (16H, m), 7.37 (1H, dd, *J* = 8.2, 4.7 Hz), 7.30 (1H, dd, *J* = 11.9, 5.2 Hz), 7.12 (1H, d, *J* = 14.5 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.4 (d, *J* = 15.9 Hz), 149.8 (d, *J* = 12.1 Hz), 149.2, 146.4, 143.3, 136.2 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 10.6 Hz), 132.2 (d, *J* = 84.5 Hz), 130.9 (d, *J* = 13.1 Hz), 126.4, 124.1, 121.6 (d, *J* = 8.3 Hz), 120.7 (q, *J* = 321.2 Hz), 116.5 (d, *J* = 10.3 Hz), 115.4 (d, *J* = 89.5 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.39; Minor isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.97, 21.17, 21.00; *m/z* LRMS (ESI + APCI) found $[M – OTf]^+$ 433.2, $C_{28}H_{22}N_2OP^+$ requires 433.1.

Triphenyl(3–(pyridin–2–ylmethoxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2b)

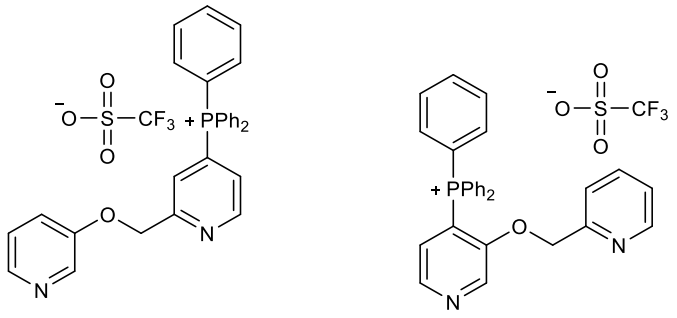


Major

>20:1 (Major:Minor) (Minor is a 2-position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure D using 2–((pyridin–3–yloxy)methyl)pyridine (31 mg, 0.17 mmol), Tf_2O (29 μL, 0.17 mmol), PPh_3 (45 mg, 0.17 mmol), DBU (26 μL, 0.17 mmol), and EtOAc (1.7 mL). After the purification procedure, the title compound was isolated as a white solid (103 mg, 0.17 mmol, >99% combined yield). mp: 40–45 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3060, 1483, 1438, 1414, 1260, 1223, 1151, 1107, 1030, 911, 722, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.78 (1H, app d, *J* = 6.7 Hz), 8.52 (1H, app t, *J* = 4.4 Hz), 8.37 (1H, d, *J* = 4.4 Hz), 7.84–7.80 (3H, m), 7.71–7.66 (6H, m), 7.60–7.55 (6H, m), 7.47 (1H, td. *J* = 7.7, 1.6 Hz), 7.14 (1H, dd, *J* = 7.0, 4.9 Hz), 7.07 (1H, dd, *J* = 15.2, 4.4 Hz), 6.57 (1H, d, *J* = 7.8 Hz), 5.15 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 152.9, 149.0, 143.9 (d, *J* = 10.9 Hz), 137.1 (d, *J* = 4.4 Hz), 136.8, 135.5 (d, *J* = 3.0 Hz), 133.8 (d, *J* = 10.8 Hz), 130.5 (d, *J* = 13.4 Hz), 127.9 (d, *J* = 7.0 Hz), 123.4, 122.0, 120.7 (q, *J* = 321.3 Hz), 116.1 (d, *J* = 91.4 Hz), 115.0 (d, *J* = 86.6 Hz), 72.3; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.55; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.44; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 447.2, $C_{29}H_{24}N_2OP^+$ requires 447.2.

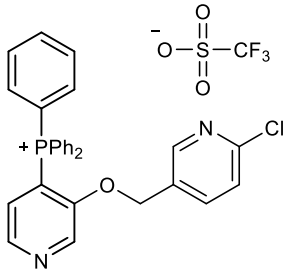
Triphenyl(2–((pyridin–3–yloxy)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2b)



11:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure B using 2–((pyridin–3–yloxy)methyl)pyridine (19 mg, 0.10 mmol), silver trifluormethanesulfonate (27 mg, 0.10 mmol), acetyl chloride (8 μL, 0.10 mmol), Tf_2O (18 μL, 0.11 mmol), PPh_3 (30 mg, 0.11 mmol), DBU (16 μL, 0.11 mmol), pyridine (17 μL, 0.20 mmol), and EtOAc (1 mL). After the purification procedure, the title compound was isolated as a brown solid (22 mg, 0.037 mmol, 37% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3062, 1585, 1575, 1439, 1260, 1224, 1154, 1108, 1030, 908, 723, 689, 635; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.03 (1H, app t, *J* = 5.0 Hz), 8.23 (2H, bs), 7.92–7.57 (17H, m), 7.23 (2H, s), 5.38 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1 (d, *J* = 10.2 Hz), 153.8, 151.6 (d, *J* = 10.4 Hz), 142.8, 138.4, 136.2 (d, *J* = 2.9 Hz), 134.5 (d, *J* = 10.4 Hz), 131.0 (d, *J* = 13.1 Hz), 129.3 (d, *J* = 84.3 Hz), 126.5 (d, *J* = 8.4 Hz), 124.5 (d, *J* = 8.9 Hz), 124.1, 121.2, 120.8 (q, *J* = 321.0 Hz), 115.6 (d, *J* = 89.5 Hz), 69.8; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.18; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.95; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.64; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 447.2, $C_{29}H_{24}N_2OP^+$ requires 447.2.

Triphenyl(3–(pyridin–2–yloxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2c)

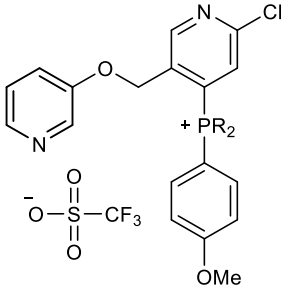


Major

20:1:1 (Major:Unidentified phosphonium isomers) Mixture of Isomers

Prepared according to general procedure A using 2–chloro–5–((pyridin–3–yloxy)methyl)pyridine (110 mg, 0.50 mmol), Tf_2O (84 μL, 0.50 mmol), PPh_3 (144 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5 mL). After the purification procedure, the title compound was isolated as a white solid (265 mg, 0.42 mmol, 84% yield). All isomers, IR ν_{max}/cm^{-1} (film): 3059, 2924, 1570, 1438, 1414, 1261, 1105, 1029, 721, 689, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.92 (1H, d, *J* = 6.7 Hz), 8.54 (1H, app t, *J* = 4.3 Hz), 7.94–7.47 (16H, m), 7.38 (1H, dd, *J* = 8.2, 2.4 Hz), 7.08 (2H, d, *J* = 8.2 Hz), 7.02 (1H, dd, *J* = 14.6, 4.9 Hz), 5.30 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 151.2, 149.0, 143.9 (d, *J* = 11.0 Hz), 139.2, 137.3 (d *J* = 4.3 Hz), 135.5 (d, *J* = 2.9 Hz), 133.7 (d, *J* = 10.7 Hz), 130.9 (d, *J* = 13.0 Hz), 128.6, 127.7 (d, *J* = 6.9 Hz), 123.9, 120.7 (q, *J* = 321.1 Hz), 116.1 (d, *J* = 91.3 Hz), 114.6 (d, *J* = 87.1 Hz), 68.6; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.18; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.54; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.22, 18.53; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 481.2, $C_{29}H_{23}ClN_2OP^+$ requires 482.1.

Triphenyl(2–(pyridin–3–yloxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2c)

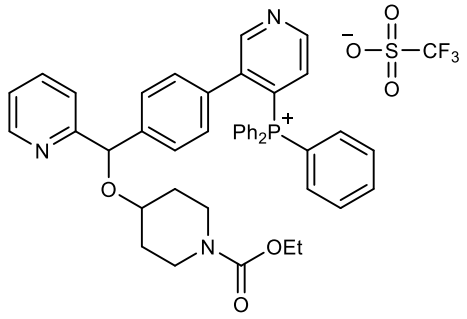


Major

12.8:2.2:2.2 (Major:Unidentified phosphonium isomers) Mixture of Isomers

Prepared according to general procedure B (except that tris(4–methoxyphenyl)phosphine was used instead of triphenylphosphine) using 2–chloro–5–((pyridin–3–yloxy)methyl)pyridine (55 mg, 0.25 mmol), silver trifluormethanesulfonate (64 mg, 0.25 mmol), acetyl chloride (18 μL, 0.25 mmol), Tf_2O (42 μL, 0.25 mmol), tris(4–methoxyphenyl)phosphine (97 mg, 0.28 mmol), DBU (37 μL, 0.25 mmol), pyridine (40 μL, 0.50 mmol), and EtOAc (2.5 mL). After the purification procedure, the title compound was isolated as a brown solid (79 mg, 0.11 mmol, 44% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3061, 2916, 1438, 1398, 1260, 1152, 1108, 1030, 908, 722, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.90 (1H, d, J = 6.3 Hz), 8.11 (1H, d, J = 3.8 Hz), 7.86–6.71 (16H, m), 4.80 (2H, s), 3.91 (9H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2 (d, J = 2.7 Hz), 153.7 (d, J = 9.1 Hz), 153.5 (d, J = 15.1 Hz), 148.9, 142.5, 137.3, 136.1 (d, J = 12.2 Hz), 133.2 (d, J = 5.6 Hz), 132.2 (d, J = 81.7 Hz), 129.2 (d, J = 11.0 Hz), 124.0 (br), 120.7 (q, J = 321.0 Hz), 119.1, 116.4 (d, J = 14.4 Hz), 106.1 (d, J = 98.8 Hz), 65.3 (d, J = 2.5 Hz), 56.0; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.19; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.17; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.56, 19.42, 19.20; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 571.2, $C_{28}H_{22}N_2OP^+$ requires 571.2.

(3–(4–(((1–(ethoxycarbonyl)piperidin–4–yl)oxy)(pyridin–2–yl)methyl)phenyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2d)

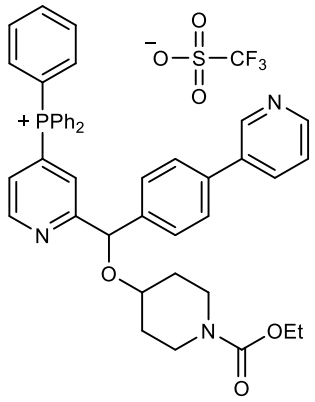


Major

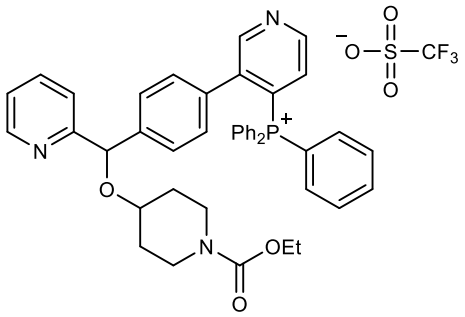
5.9:2.2:1 (Major:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using ethyl 4–(pyridin–2–yl(4–(pyridin–3–yl)phenyl)methoxy)piperidine–1–carboxylate (42 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (29 mg, 0.11 mmol), DBU (15 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (1 mL) to afford the title compound (combined ^{1}H NMR yield: 73%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99-8.89 (1H, m), 8.75 (1H, d, *J* = 6.8 Hz), 8.64 (1H, d, *J* = 5.3 Hz), 8.09-7.14 (19H, m), 7.09 (2H, d, *J* = 8.0 Hz), 6.71 (2H, d, *J* = 8.1 Hz), 5.59 (1H, s), 4.19-4.03 (2H, m), 3.84-3.66 (2H, m), 3.60-3.37 (1H, m), 3.29-3.01 (2H, m), 1.92-1.51 (4H, m), 1.33-1.15 (3H, m); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.45; Other phosphonium isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.61 (d, *J* = 19.9 Hz); *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 678.3, $C_{43}H_{41}N_3O_3P^+$ requires 678.3.

(2–(((1–(ethoxycarbonyl)piperidin–4–yl)oxy)(4–(pyridin–3–yl)phenyl)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2d)



Major

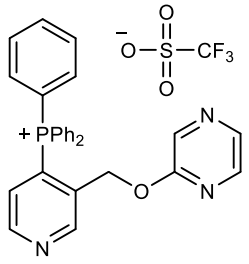


Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure B using acetyl chloride (14 μL, 0.20 mmol), silver trifluoromethanesulfonate (51 mg, 0.40 mmol), ethyl 4–(pyridin–2–yl(4–(pyridin–3–yl)phenyl)methoxy)piperidine–1–carboxylate (83 mg, 0.20 mmol), Tf_2O (34 μL, 0.20 mmol), PPh_3 (58 mg, 0.22 mmol), DBU (30 μL, 0.20 mmol) and CH_2Cl_2 (2.0 mL). After the purification procedure, the title compound was isolated as an off–white solid (62 mg, 0.075 mmol, 37% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3009, 2930, 1685, 1437, 1264, 1225, 1108, 1030, 747; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.94 (1H, app t, *J* = 5.0 Hz), 8.82 (1H, br), 8.59 (1H, br), 7.99–7.43 (22H, m), 7.38 (1H, br s), 5.81 (1H, s), 4.13 (2H, q, *J* = 7.1 Hz), 3.83–3.62 (1H, m), 3.60–3.38 (2H, m), 3.31–3.10 (2H, m), 1.98–1.36 (4H, m), 1.26 (3H, t, *J* = 7.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5 (d, *J* = 9.6 Hz), 155.4, 151.1 (d, *J* = 10.5 Hz), 148.4, 147.9, 140.0, 137.6, 136.2 (d, *J* = 2.9 Hz), 135.9, 134.4 (d, *J* = 10.5 Hz), 130.9 (d, *J* = 13.1 Hz), 130.5, 129.2 (d, *J* = 83.8 Hz), 127.8, 127.3, 125.8 (d, *J* = 8.1 Hz), 123.9–123.5 (2C, m), 120.8 (q, *J* = 321.2 Hz), 115.7 (d, *J* = 89.4 Hz), 80.2, 72.6, 61.2, 40.6 (d, *J* = 5.6 Hz), 30.7 (d, *J* = 103.8 Hz), 14.6; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.16; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.69; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.46; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 678.3, $C_{43}H_{41}N_3O_3P^+$ requires 678.3.

Triphenyl(3–((pyrazin–2–yloxy)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2e)

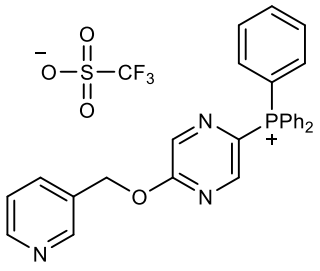


Major

10:1.4:1.2:1.2:1 (Major:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 2–(pyridin–3–ylmethoxy)pyrazine (19 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (29 mg, 0.11 mmol), DBU (15 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (1 mL) to afford the title compound (combined ^{1}H NMR yield: 58%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (1H, d, J = 6.6 Hz), 8.90 (1H, app t, J =5.6 Hz), 8.06-8.00 (1H, m), 7.86-7.30 (18H, m), 4.91 (2H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.71; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.25, 21.03, 17.74, 16.72; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 448.3, $C_{28}H_{23}N_3OP^+$ requires 448.2.

Triphenyl(5–(pyridin–3–ylmethoxy)pyrazin–2–yl)phosphonium trifluoromethanesulfonate (2e)

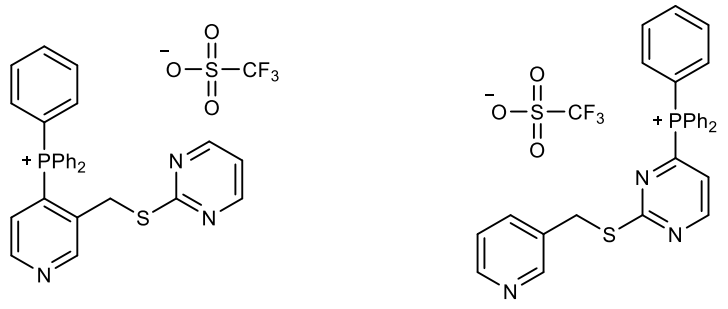


Major

>20:1:1 (Major:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure B using acetyl chloride (29 μL, 0.40 mmol), silver trifluoromethanesulfonate (103 mg, 0.40 mmol), 2–(pyridin–3–ylmethoxy)pyrazine (75 mg, 0.40 mmol), Tf_2O (68 μL, 0.40 mmol), PPh_3 (115 mg, 0.44 mmol), DBU (60 μL, 0.40 mmol) and EtOAc (4.0 mL). After the purification procedure, the title compound was isolated as an off white solid (120 mg, 0.20 mmol, 50% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3061, 3011, 1525, 1439, 1262, 1152, 1030, 748, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.66 (1H, dd, *J* = 4.1, 2.4 Hz), 8.57 (1H, dd, *J* = 1.6, 1.2 Hz), 8.48, (1H, dd, *J* = 2.4, 1.4 Hz), 8.11 (1H, d, *J* = 1.4 Hz), 7.87–7.50 (15H, m), 7.32 (1H, dt, 7.8, 1.6 Hz), 7.16 (1H, dd, *J* = 7.7, 4.8 Hz), 5.38 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9 (d, *J* = 17.8 Hz), 149.8 (2C), 147.7 (d, *J* = 3.4 Hz), 139.8 (d, *J* = 15.1 Hz), 136.8, 135.3 (d, *J* = 3.0 Hz), 134.2 (d, *J* = 10.5 Hz), 130.2 (d, *J* = 13.3 Hz), 129.6, 127.0 (d, *J* = 121.9 Hz), 123.4, 120.7 (q, *J* = 321.2 Hz), 116.3 (d, *J* = 90.8 Hz), 67.4; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.23; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.04; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 448.2, $C_{28}H_{23}N_3OP^+$ requires 448.2.

Triphenyl(3–((pyrimidin–2–ylthio)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2f)

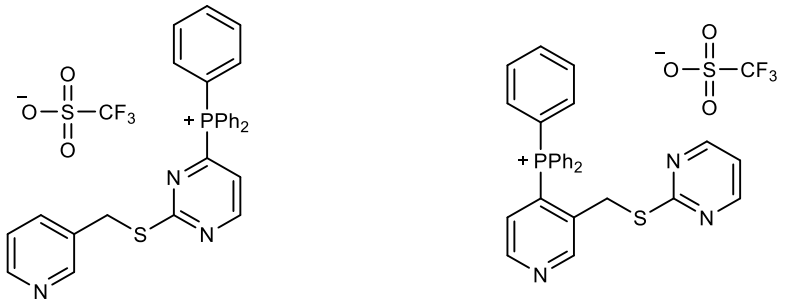


Major Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure D using 2–((pyridin–3–ylmethyl)thio)pyrimidine (102 mg, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), PPh_3 (131 mg, 0.50 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as a white solid (254 mg, 0.41 mmol, 83% combined yield). mp 75–81 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3061, 2962, 1584, 1551, 1380, 1259, 1151, 1106, 1029, 912, 721, 689; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (1H, d, *J* = 6.8 Hz), 8.84 (1H, app t, *J* = 4.4 Hz), 8.45 (2H, d, *J* = 4.8 Hz), 7.98–7.62 (15H, m), 7.17 (1H, dd, *J* = 15.2, 5.0 Hz), 7.03 (1H, t, *J* = 4.8 Hz), 4.18 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 157.5, 153.7 (d, *J* = 7.4 Hz), 150.3 (d, *J* = 10.4 Hz), 137.0 (d, *J* = 5.9 Hz), 136.1 (d, *J* = 3.0 Hz), 134.2 (d, *J* = 10.6 Hz), 131.1 (d, *J* = 13.1 Hz), 128.0 (d, *J* = 9.7 Hz), 126.1 (d, *J* = 82.6 Hz), 120.7 (q, *J* = 321.2 Hz), 117.5, 115.8 (d, *J* = 88.6 Hz), 31.7 (d, *J* = 5.1 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.10; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.42; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 464.2, $C_{28}H_{23}N_3PS^+$ requires 464.1.

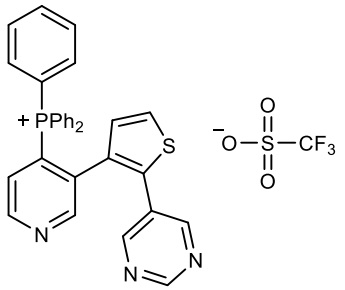
Triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2f)



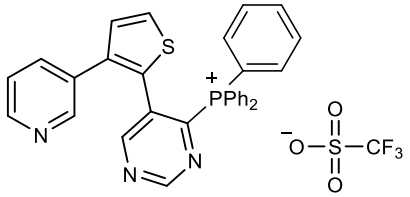
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure B using acetyl chloride (29 μL, 0.40 mmol), silver trifluoromethanesulfonate (103 mg, 0.40 mmol), 2–((pyridin–3–ylmethyl)thio)pyrimidine (81 mg, 0.40 mmol), Tf_2O (68 μL, 0.40 mmol), PPh_3 (115 mg, 0.44 mmol), DBU (60 μL, 0.40 mmol) and EtOAc (4.0 mL). After the purification procedure, the title compound was isolated as a white solid (184 mg, 0.30 mmol, 75% yield). All isomers, IR ν_{max}/cm^{-1} (film): 3061, 3030, 2985, 1528, 1438, 1260, 1149, 1009, 1029, 911, 724; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.04 (1H, dd, *J* = 7.6, 5.0 Hz), 8.54–8.35 (2H, m), 8.03–7.57 (17H, m), 7.34–7.11 (1H, m), 4.29 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7 (d, *J* = 17.6 Hz), 160.6 (d, *J* = 7.4 Hz), 154.6 (d, *J* = 111.5 Hz), 149.6, 148.6, 136.2, 136.1 (d, *J* = 2.9 Hz), 134.6 (d, *J* = 10.3 Hz), 132.2, 130.7 (d, *J* = 13.1 Hz), 123.4, 123.1 (d, *J* = 20.3 Hz), 120.7 (q, *J* = 321.1 Hz), 114.9 (d, *J* = 88.9 Hz), 32.5; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.18; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.66; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 464.2, $C_{28}H_{23}N_3PS^+$ requires 464.1.

Triphenyl(3–(2–(pyrimidin–5–yl)thiophen–3–yl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2g)



Major

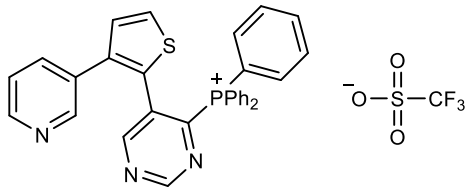


Minor

5.6:3.1:1 (Major:Unidentified phosphonium isomer:Minor) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 5–(3–(pyridin–3–yl)thiophen–2–yl)pyrimidine (72 mg, 0.30 mmol), Tf_2O (51 μL, 0.30 mmol), PPh_3 (87 mg, 0.33 mmol), DBU (45 μL, 0.30 mmol), 1,3,5-trimethoxybenzene as an internal standard (25 mg, 0.15 mmol), and CH_2Cl_2 (3 mL) to afford the title compound (combined ^{1}H NMR yield: 53%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98-8.90 (2H, m), 8.70 (1H, d, J = 6.7 Hz), 8.09 (2H, s), 7.85-7.29 (16H, m), 7.10 (1H, d, J = 5.2 Hz), 6.57 (1H, d, J = 5.2 Hz); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.75; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.21, 20.73, 18.67; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 500.1, $C_{31}H_{23}N_3PS^+$ requires 500.1.

Triphenyl(5–(3–(pyridin–3–yl)thiophen–2–yl)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2g)

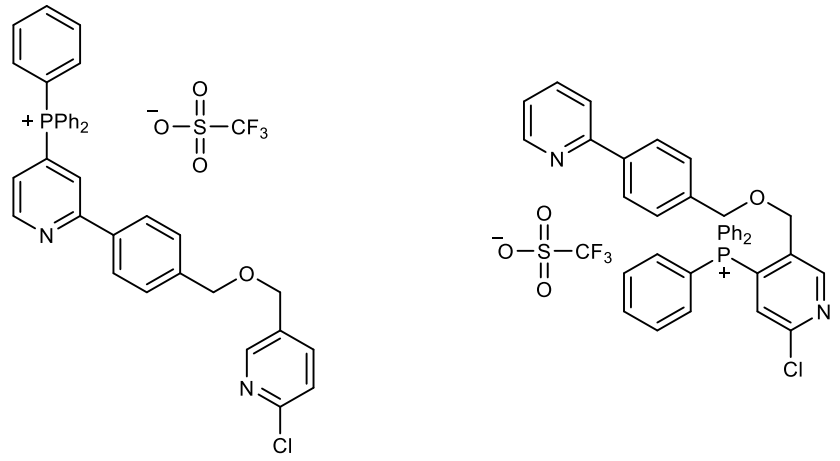


Major

>20:1 (Major:2–position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure B using acetyl chloride (11 μL, 0.15 mmol), silver trifluoromethanesulfonate (39 mg, 0.15 mmol), 5–(3–(pyridin–3–yl)thiophen–2–yl)pyrimidine (36 mg, 0.15 mmol), Tf_2O (25 μL, 0.15 mmol), PPh_3 (43 mg, 0.17 mmol), DBU (22 μL, 0.15 mmol) and CH_2Cl_2 (1.5 mL). After the purification procedure, the title compound was isolated as a yellow/orange solid (41 mg, 0.063 mmol, 42% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3062, 1438, 1261, 1153, 1106, 1030, 912, 720, 636; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.51 (1H, s), 8.97 (1H, d, *J* = 8.7 Hz), 8.45 (1H, br s), 8.19–7.15 (19H, m), 6.98 (1H, d, *J* = 5.2 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.2 (d, *J* = 5.1 Hz), 158.0 (d, *J* = 16.7 Hz), 152.6 (d, *J* = 113.3 Hz), 146.7 (2C, m), 138.8–138.2 (2C, m), 135.7, 135.5 (d, *J* = 3.1 Hz), 134.5 (d, *J* = 10.2 Hz), 132.0 (d, *J* = 9.9 Hz), 130.8, 130.3 (d, *J* = 11.9 Hz), 129.4, 128.4 (d, *J* = 11.9 Hz), 127.8, 120.7 (q, *J* = 320.5 Hz), 116.1 (d, *J* = 88.6 Hz); All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.11; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.70; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.02; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 500.1, $C_{31}H_{23}N_3PS^+$ requires 500.1.

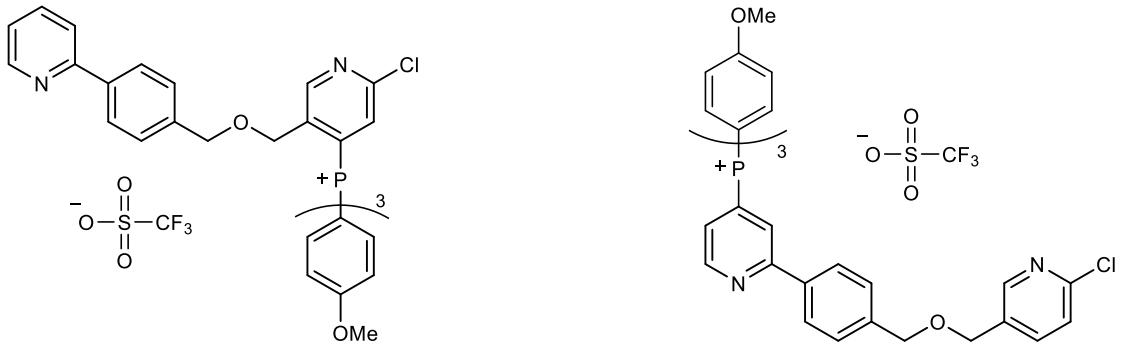
(2–(4–(((6–chloropyridin–3–yl)methoxy)methyl)phenyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2h)



19:1:1 (Major:Minor:2-position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure A using 2–chloro–5–(((4–(pyridin–2–yl)benzyl)oxy)methyl)pyridine (466 μL, 1.50 mmol), Tf_2O (253 μL, 1.50 mmol), PPh_3 (433 mg, 1.65 mmol), DBU (227 μL, 1.50 mmol) and CH_2Cl_2 (15 mL). After the purification procedure, the title compound was isolated as a white solid (957 mg, 1.33 mmol, 88% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3060, 2851, 1584, 1438, 1260, 1148, 1107, 1029, 688; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.07 (1H, app t, *J* = 5.1 Hz), 8.33 (1H, d, *J* = 2.2 Hz), 8.06–7.62 (19H, m), 7.60–7.41 (3H, m), 7.31 (1H, d, *J* = 4.1 Hz), 4.62 (2H, s), 4.54 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9 (d, *J* = 10.2 Hz), 151.7 (d, *J* = 10.6 Hz), 150.5, 148.7, 140.2, 138.3, 136.4 (d, *J* = 1.5 Hz), 136.2 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 10.4 Hz), 132.5, 131.0 (d, *J* = 13.1 Hz), 129.3 (d, *J* = 84.1 Hz), 128.3, 127.3, 125.3 (d, *J* = 8.2 Hz), 124.0, 123.2 (d, *J* = 8.6 Hz), 120.7 (q, *J* = 321.2 Hz), 115.6 (d, *J* = 89.6 Hz), 71.9, 68.7; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.10; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.83; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.79, 15.38; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 571.2, $C_{36}H_{29}ClN_2OP^+$ requires 571.2.

(2–chloro–5–(((4–(pyridin–2–yl)benzyl)oxy)methyl)pyridin–4–yl)tris(4–methoxyphenyl)phosphonium trifluoromethanesulfonate (2h)

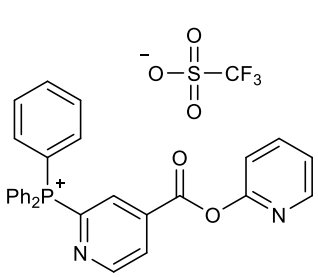


Major Minor

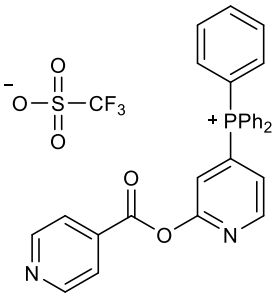
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure B (except that the phosphine was added as a solution in CH_2Cl_2 (4.5 mL) dropwise over 30 minutes) using acetyl chloride (43 μL, 0.60 mmol), silver trifluoromethanesulfonate (154 mg, 0.60 mmol), 2–chloro–5–(((4–(pyridin–2–yl)benzyl)oxy)methyl)pyridine (186 mg, 0.60 mmol), Tf_2O (101 μL, 0.60 mmol), tris(4–methoxyphenyl)phosphine (233 mg, 0.66 mmol), DBU (91 μL, 0.60 mmol) and CH_2Cl_2 (6.0 mL). After the purification procedure, the title compound was isolated as a grey solid (308 mg, 0.38 mmol, 63%). mp 81–85 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3093, 3010, 2975, 2944, 2843, 1591, 1262, 1106, 1018, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.83 (1H, d, *J* = 6.2 Hz), 8.67 (1H, d, *J* = 4.4 Hz), 7.86 (2H, d, *J* = 8.2 Hz), 7.82–7.70 (2H, m), 7.59–7.38 (6H, m), 7.31–7.11 (7H, m), 7.09–6.96 (3H, m), 4.10 (2H, s), 4.06 (2H, s), 3.87 (9H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1 (d, *J* = 2.9 Hz), 156.3, 152.7 (d, *J* = 15.3 Hz), 152.7 (d, *J* = 9.3 Hz), 149.4, 138.9, 136.8, 136.5, 135.9 (d, *J* = 12.2 Hz), 135.2 (d, *J* = 5.9 Hz), 131.5 (d, *J* = 82.2 Hz), 128.8 (d, *J* = 11.2 Hz), 128.3, 126.6, 122.2, 120.8 (q, *J* = 321.4 Hz), 120.3, 116.4 (d, *J* = 14.3 Hz), 106.5 (d, *J* =98.9 Hz), 72.9, 67.5 (d, *J* = 3.6 Hz), 55.9; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.11; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.60; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 661.3, $C_{39}H_{35}ClN_2O_4P^+$ requires 661.2.

Triphenyl(4–((pyridin–2–yloxy)carbonyl)pyridin–2–yl)phosphonium trifluoromethanesulfonate (2i)



Major

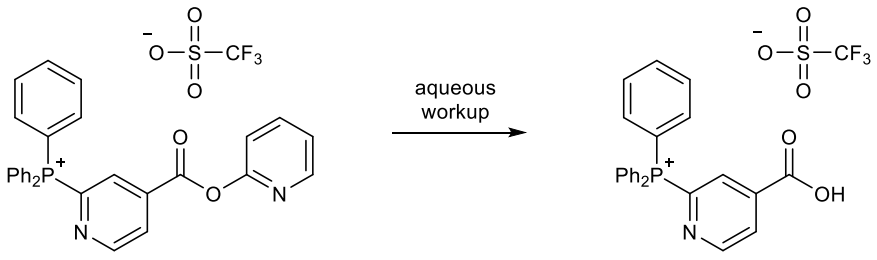


Minor

>20:1 Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture)[§] using pyridin–2–yl isonicotinate (52 mg, 0.26 mmol), Tf_2O (44 μL, 0.26 mmol), triphenylphosphine (75 mg, 0.28 mmol), DBU (39 μL, 0.26 mmol), 1,3,5-trimethoxybenzene as an internal standard (44 mg, 0.26 mmol), and CH_2Cl_2 (2.6 mL) to afford the title compound (combined ^{1}H NMR yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.23 (1H, d J = 4.8 Hz), 8.50-8.44 (1H, m), 8.39 (1H, dd, J = 4.9, 1.6 Hz), 8.36 (1H, d, J = 6.3 Hz), 7.97-7.60 (16H, m), 7.37 (1H, d, J = 8.2 Hz), 7.30 (1H, dd, J = 7.0, 5.3 Hz); Major isomer, ^{31}P NMR (162

§ ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture due to partial hydrolysis of the product during the aqueous workup.

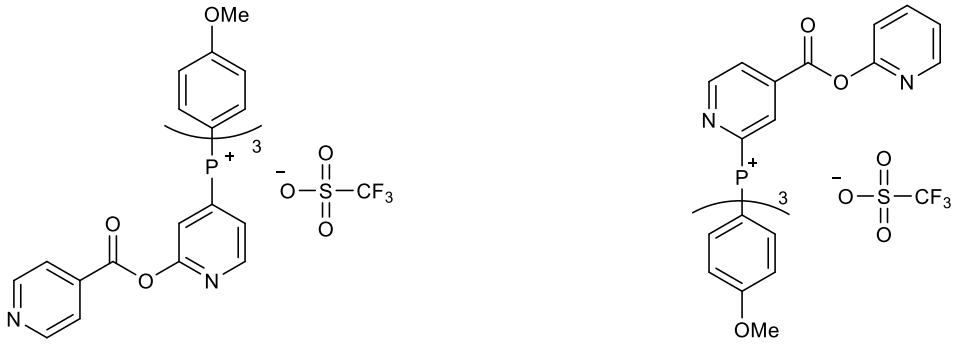


detected by LCMS

m/z LRMS (ESI + APCI) found [M - OTf]+ 384.1, $C_{24}H_{19}NO_2P^+$ requires 384.1

MHz, $CDCl_3$) δ: 16.25; Hydrolyzed product, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.73; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 461.1, $C_{29}H_{22}N_2O_2P^+$ requires 461.1.

(2–(isonicotinoyloxy)pyridin–4–yl)tris(4–methoxyphenyl)phosphonium trifluoromethanesulfonate (2i)



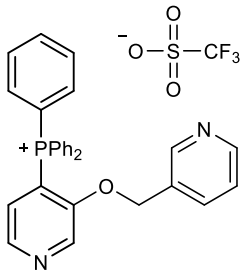
Major Minor

>20:1 (Major:Minor) Mixture of Isomers

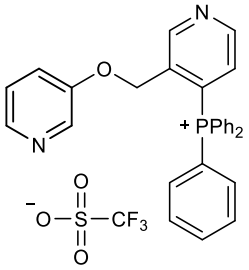
Prepared according to general procedure B using Pyridin–2–yl isonicotinate (50 mg, 0.25 mmol), silver trifluoromethanesulfonate (64 mg, 0.25 mmol), acetyl chloride (18 μL, 0.25 mmol) Tf_2O (42 μL, 0.25 mmol), tris(4–methoxyphenyl)phosphane (97 mg, 0.28 mmol), DBU (37 μL, 0.25 mmol) and EtOAc (2.5 mL). After the purification procedure, the title compound was isolated as a brown solid (76 mg, 0.11 mmol, 43% yield). mp 70–78 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3095, 2974, 2948, 1754, 1664, 1592, 1503, 1298, 1111, 1030; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.82–8.79 (3H, m), 7.98 (2H, d, *J* = 5.8 Hz), 7.61–7.22 (14H, m), 3.92 (9H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5 (d, *J* = 2.9 Hz), 163.0, 158.2 (d, *J* = 15.3 Hz), 151.0 (d, *J* = 12.1 Hz), 150.7, 136.3 (d, *J* = 12.3 Hz), 135.4, 134.9 (d, *J* = 85.2 Hz), 125.8 (d, *J* = 8.5 Hz), 123.2, 120.7 (q, *J* = 321.0 Hz), 120.2 (d, *J* = 9.9 Hz), 116.7 (d, *J* = 14.3 Hz), 105.7 (d, *J* = 98.9 Hz), 56.0; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.17; Major isomer, ^{31}P NMR

(162 MHz, $CDCl_3$) δ: 20.54; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 551.3, $C_{32}H_{28}N_2O_5P^+$ requires 551.2.

Triphenyl(3–(pyridin–3–ylmethoxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2j)



Major

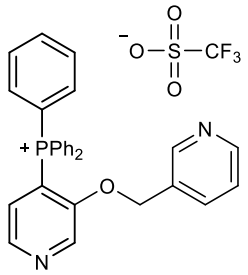


Minor

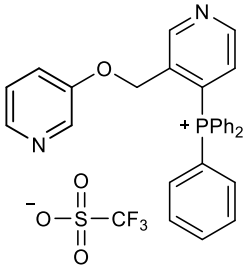
2.9:2.2:2.8 (Major:Minor:mix of 2 phosphonium isomers) Mixture of Isomers

Prepared according to general procedure A (except that ^1H NMR and ^{31}P NMR were run on the crude reaction mixture) using 3–(pyridin–3–ylmethoxy)pyridine (26 mg, 0.16 mmol), Tf_2O (26 μL, 0.16 mmol), PPh_3 (50 mg, 0.18 mmol), DBU (23 μL, 0.16 mmol), 1,3,5-trimethoxybenzene as an internal standard (27 mg, 0.16 mmol), and CH_2Cl_2 (1.6mL) to afford the title compound (combined ^1H NMR yield: 77%). Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.83 (1H, d, J = 6.7 Hz), 8.50 (1H, app t, J = 4.3 Hz), 8.34 (1H, d, J = 2.6 Hz), 7.93-7.36 (16H, m), 7.36-6.88 (3H, m), 5.08 (2H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.36; Other phosphonium isomers isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.84, 21.11, 20.90; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 447.2, $C_{29}H_{24}N_2OP^+$ requires 447.2.

Triphenyl(3–(pyridin–3–ylmethoxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2j)



Major

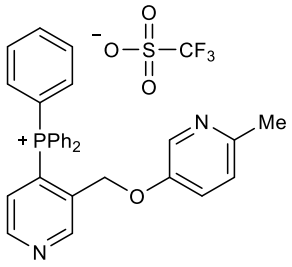


Minor

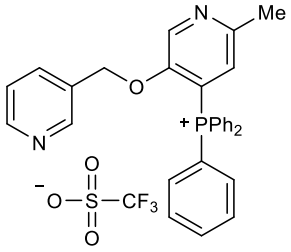
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C (except that the phosphine addition and stirring was conducted at –30 ºC instead of –78 ºC) using 3–(pyridin–3–ylmethoxy)pyridine (194 mg, 1.04 mmol), Tf_2O (352 μL, 2.09 mmol), PPh_3 (548 mg, 2.09 mmol), NEt_3 (291 μL, 2.09 mmol) and CH_2Cl_2 (10.4 mL). After the purification procedure, the title compound was isolated as a purple amorphous solid (408 mg, 4.08 mmol, 69% yield); Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 1572, 1543, 1438, 1413, 1260, 1190, 1149,1029; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.90 (1H, app d, *J* = 6.7 Hz), 8.59 (1H, app t, *J* = 4.4 Hz), 8.43 (1H, dd, *J* = 3.5, 1.2 Hz), 7.87–7.55 (16H, m), 7.30–7.28 (1H, m), 7.09 (1H, d, *J* = 4.9 Hz), 7.06 (1H, dd, *J*= 5.1, 4.8 Hz), 5.25 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.6, 149.4, 148.8, 143.7 (d, *J* = 11.0 Hz), 136.9 (d, *J* = 4.4 Hz), 135.9, 135.3 (d, *J* = 3.0 Hz), 133.5 (d, *J* = 10.9 Hz), 130.3 (d, *J* = 13.3 Hz), 129.1, 127.6 (d, *J* = 7.2 Hz), 123.1, 120.5 (q, *J* = 321.1 Hz), 115.9 (d, *J* = 91.5 Hz), 114.6 (d, *J* = 87.0 Hz), 69.3; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.42; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 447.2, $C_{29}H_{24}N_2OP^+$ requires 447.2.

(3–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2k)



Major

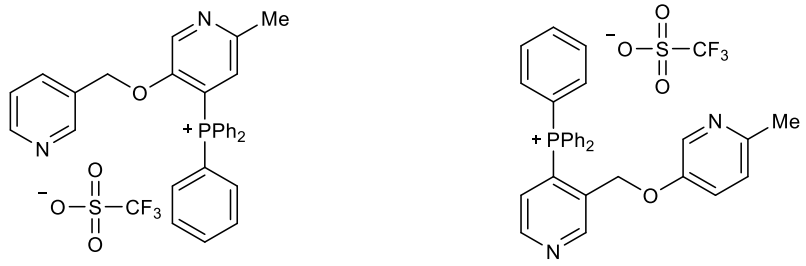


Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure A using 2–methyl–5–(pyridin–3–ylmethoxy)pyridine (111 mg, 0.55 mmol), Tf_2O (94 μL, 0.55 mmol), PPh_3 (160 mg, 0.61 mmol), DBU (83 μL, 0.55 mmol) and CH_2Cl_2 (5.6 mL). After the purification procedure, the title compound was isolated as a white solid (226 mg, 0.37 mmol, 68% yield). mp 150–160 ºC; Both isomers, IR ν_{max}/cm^{-1} (film):3059, 1586, 1573, 1484, 1438, 1259, 1153, 1105, 1029; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (1H, app d, *J* = 6.4 Hz), 8.92 (1H, app t, *J* = 4.2 Hz), 7.83–7.65 (15H, m), 7.30–7.25 (1H, m), 6.94 (1H, d, *J* = 2.5 Hz), 6.84 (1H, d, *J* =8.6 Hz), 6.46 (1H, dd, *J* = 8.5, 2.5 Hz), 4.74 (2H, s), 2.36 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7 (d, *J* = 8.1 Hz), 151.9 (d, *J* = 10.8 Hz), 151.5, 150.3, 136.1, 135.7 (d, *J* = 3.1 Hz), 134.9 (d, *J* = 5.1 Hz), 134.2 (d, *J* = 10.2 Hz), 130.6 (d, *J* = 13.0 Hz), 129.2 (d, *J* = 9.7 Hz), 126.1 (d, *J* = 82.0 Hz), 123.4, 120.7 (q, *J* = 320.9 Hz), 120.3, 116.6 (d, *J* = 90.1 Hz), 66.2, 23.2; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.18; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.99; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 461.2, $C_{30}H_{26}N_2OP^+$ requires 461.2

(2–methyl–5–(pyridin–3–ylmethoxy)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2k)

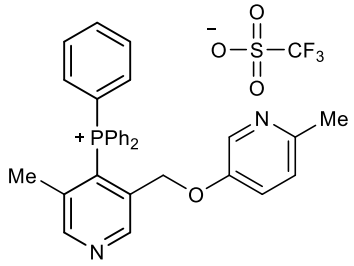


Major Minor

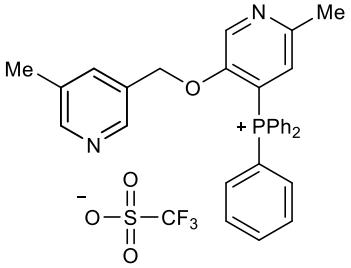
13:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C (except the phosphine was stirred for 1 hour instead of 30 minutes) using 2–methyl–5–(pyridin–3–ylmethoxy)pyridine (41 mg, 0.21 mmol), Tf_2O (70 μL, 0.41 mmol), PPh_3 (108 mg, 0.41 mmol), *N,N*–dimethylcyclohexylamine (62 μL, 0.41 mmol) and CH_2Cl_2 (2.1 mL). After the purification procedure, the title compound was isolated as a yellow solid (69 mg, 0.11 mmol, 55% yield); Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 1579, 1438, 1351, 1263, 1106, 908; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (1H, app d, *J* = 6.9 Hz), 8.42 (1H, s), 7.86–7.82 (4H, m), 7.73–7.68 (6H, m), 7.58–7.53 (6H, m), 7.24–7.22 (1H, m), 7.08 (1H, dd, *J* = 7.6, 4.8 Hz), 6.82 (1H, d, *J* = 15.1 Hz), 5.18 (2H, s), 2.53 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3 (d, *J* = 10.9 Hz), 152.7, 149.7, 148.9, 136.1 (d, *J* = 5.0 Hz), 136.0, 135.3 (d, *J* = 3.0 Hz), 133.8 (d, *J* = 10.7 Hz), 130.6 (d, *J* = 13.2 Hz), 129.4, 127.1 (d, *J* = 6.9 Hz), 123.3, 120.8 (q, *J* = 321.4 Hz), 116.2 (d, *J* = 91.4 Hz), 115.3 (d, *J* = 86.4 Hz), 69.5, 23.7; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.34; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.91; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 461.3, $C_{30}H_{26}N_2OP^+$ requires 461.2.

(3–methyl–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



Major

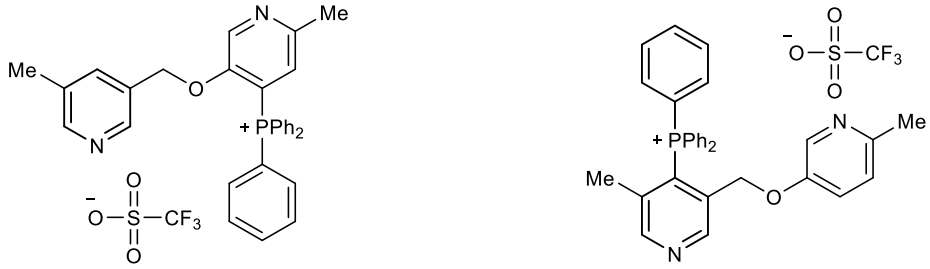


Minor

20:1:2.9 (Major:Minor:Unidentified phosphonium isomers) Mixture of Isomers

Prepared according to general procedure A (except that the Tf_2O stirred for 1 hour and phosphine stirred for 2 hours) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (107 mg, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), PPh_3 (145 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as brown oil (169 mg, 0.27 mmol, 54% yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 2958, 2923, 1572, 1482, 1438, 1261, 1030; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.84 (1H, app d, J = 6.1 Hz), 8.74 (1H, app d, J = 6.3 Hz), 7.86–7.60 (15H, m), 7.44 (1H, d, J = 3.0 Hz), 6.89 (1H, d, J = 8.5 Hz), 6.49 (1H, dd, J = 8.5, 3.0 Hz), 4.54 (2H, s), 2.42 (3H, s), 1.85 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.6 (d, J = 8.6 Hz), 152.0 (d, J = 8.4 Hz), 151.1, 150.6, 138.0 (d, J = 7.2 Hz), 136.1, 136.0, 135.2 (d, J = 3.0 Hz), 133.9 (d, J = 10.3 Hz), 130.5 (d, J = 13.1 Hz), 126.7 (d, J = 80.4 Hz), 123.2, 120.6, 120.6 (q, J = 320.9 Hz), 118.1 (d, J = 87.0 Hz), 65.7 (d, J = 4.4 Hz), 23.0, 21.4 (d, J = 5.6 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.20; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.56; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.39, 21.30, 16.43; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 475.3, $C_{31}H_{28}N_2OP^+$ requires 475.2.

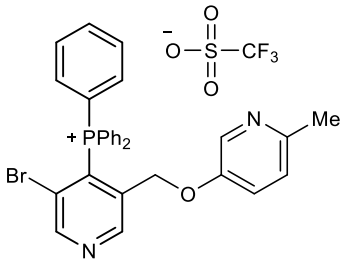
(2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C (except that 3 equivalents of NEt_3 were used instead of 1 equiv) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (107 mg, 0.50 mmol), Tf_2O (169 μL, 1.00 mmol), PPh_3 (262 mg, 1.00 mmol), NEt_3 (209 μL, 1.50 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as a brown solid (203 mg, 0.33 mmol, 65% yield). mp 65–75 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 3026, 2924, 1584, 1438, 1260, 1149, 1029; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.71 (1H, app d, *J* = 6.9 Hz), 8.26 (1H, s), 7.86–7.55 (16H, m), 6.97 (1H, s), 6.86 (1H, d, *J* = 15.1 Hz), 5.09 (2H, s), 2.54 (3H, s), 2.17 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3 (d, *J* = 11.1 Hz), 152.7, 150.3, 146.0, 136.2, 136.0 (d, *J* = 5.0 Hz), 135.4 (d, *J* = 3.1 Hz), 133.8 (d, *J* = 10.9 Hz), 132.8, 130.5 (d, *J* = 13.2 Hz), 128.8, 127.2 (d, *J* = 7.2 Hz), 120.7 (q, *J* = 321.7 Hz), 116.3 (d, *J* = 91.3 Hz), 115.3 (d, *J* = 86.6 Hz), 69.4, 23.7, 18.0; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.20; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.28; *m/z* LRMS (ESI + APCI) found $[M – OTf]^+$ 475.2, $C_{31}H_{28}N_2OP^+$ requires 475.2.

(3–bromo–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2m)

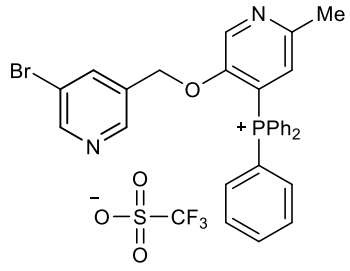


Major

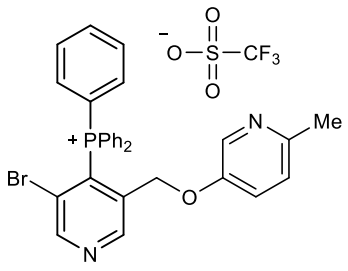
Mixture of Isomers

Prepared according to general procedure A (except that yield was not determined due to a mixture of phosphonium isomers) using 5–((5–bromopyridin–3–yl)methoxy)–2–methylpyridine (33 mg, 0.12 mmol), Tf_2O (20 μL, 0.12 mmol), PPh_3 (34 mg, 0.13 mmol), DBU (18 μL, 0.12 mmol), and CH_2Cl_2 (1.2 mL) to afford the title compound. Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.13; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.26, 21.31, 20.96; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 539.1, $C_{30}H_{25}BrN_2OP^+$ requires 539.1.

(5–((5–bromopyridin–3–yl)methoxy)–2–methylpyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2m)



Major

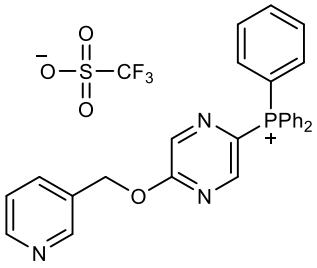


MInor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C using 5–((5–bromopyridin–3–yl)methoxy)–2–methylpyridine (191 mg, 0.68 mmol), Tf_2O (231 μL, 1.37 mmol), PPh_3 (359 mg, 1.37 mmol), NEt_3 (191 μL, 1.37 mmol) and CH_2Cl_2 (6.8 mL). After the purification procedure, the title compound was isolated as a brown solid (261 mg, 0.38 mmol, 56% yield). mp 68–75 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 2923, 1585, 1484, 1351, 1260, 1106, 1029; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.77 (1H, app d, *J* = 7.0 Hz), 8.46 (1H, d, *J* = 2.1 Hz), 7.95 (1H, s), 787–7.55 (15H, m), 7.21 (1H, t, *J* = 1.8 Hz), 6.82 (1H, d, *J* = 15.2 Hz), 5.23 (2H, s), 2.53 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2 (d, *J* = 11.1 Hz), 152.4, 150.5, 147.0, 138.0, 136.2 (d, *J* = 4.8 Hz), 135.4 (d, *J* = 3.0 Hz), 133.6 (d, *J* = 10.8 Hz), 131.3, 130.5 (d, *J* = 13.4 Hz), 126.9 (d, *J* = 7.0 Hz), 120.6 (q, *J* = 321.1 Hz), 120.0, 116.1 (d, *J* = 91.3 Hz), 115.0 (d, *J* = 86.5 Hz), 68.3, 23.6; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.20; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.31; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 539.1, $C_{30}H_{25}BrN_2OP^+$ requires 539.1.

Triphenyl(5–(pyridin–3–ylmethoxy)pyrazin–2–yl)phosphonium trifluoromethanesulfonate (2e)



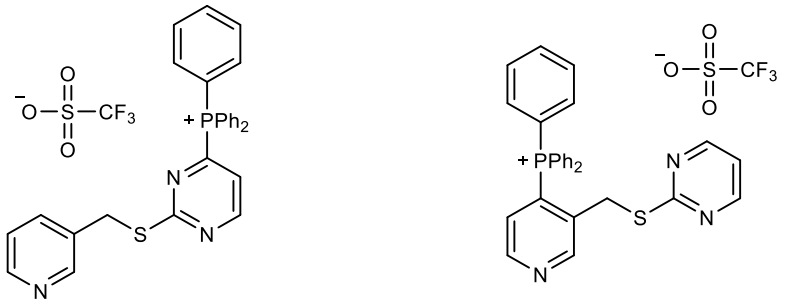
Major

>20:1 (Major:2–position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure C (except that the reaction mixture was warmed to –30 ºC prior to adding PPh_3 and remained at –30 ºC for 30 minutes before cooling down to –78 ºC for NEt_3 addition) using 2–(pyridin–3–ylmethoxy)pyrazine (75 mg, 0.40 mmol), Tf_2O (135 μL, 0.80 mmol), PPh_3 (210 mg, 0.80 mmol), NEt_3 (112 μL, 0.80 mmol) and EtOAc (4.0 mL). After the

purification procedure, the title compound was isolated as a white solid (176 mg, 0.29 mmol, 74% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3061, 2954, 1553, 1525, 1439, 1260, 1152, 1030, 723, 636; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (1H, dd, *J* = 4.1, 2.4 Hz), 8.58 (1H, m), 8.49 (1H, d, *J* = 3.7 Hz), 8.10 (1H, s), 7.94–7.49 (15H, m), 7.42 (1H, d, *J* = 7.8 Hz), 7.17 (1H, dd, *J* = 7.7, 4.9 Hz), 5.42 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0 (d, *J* = 17.9 Hz), 149.8 (2C), 147.7 (d, *J* = 3.4 Hz), 139.8 (d, *J* = 15.0 Hz), 136.8, 135.3 (d, *J* = 3.1 Hz), 134.2 (d, *J* = 10.6 Hz), 130.2 (d, *J* = 13.2 Hz), 130.0, 127.0 (d, *J* = 122.0 Hz), 123.4, 120.7 (q, *J* = 321.1 Hz), 116.3 (d, *J* = 90.8 Hz), 67.4; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.22; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.91; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 448.2, $C_{28}H_{23}N_3OP^+$ requires 448.2.

Triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2f)

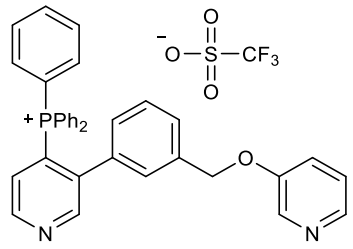


>20:1 (Major:Minor) Mixture of Isomers

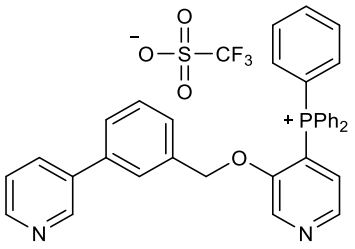
Prepared according to general procedure C using 2–((pyridin–3–ylmethyl)thio)pyrimidine (102 mg, 0.50 mmol), Tf_2O (169 μL, 1.00 mmol), PPh_3 (262 mg, 1.00 mmol), NEt_3 (139 μL, 1.00 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as a white solid (210 mg, 0.34 mmol, 68% yield). mp 157–163 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3061, 2964, 1528, 1438, 1259, 1150, 1109, 1029, 910, 724; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.03 (1H, dd, *J* = 7.6, 4.9 Hz), 8.51–8.35 (2H, m), 7.96–7.83 (3H, m), 7.82–7.58 (14H, m),

7.30–7.19 (1H, m), 4.30 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7 (d, *J* = 17.6 Hz), 160.5 (d, *J* = 7.4 Hz), 154.6 (d, *J* = 111.6 Hz), 149.5, 148.5, 136.3, 136.1 (d, *J* = 2.9 Hz), 134.6 (d, *J* = 10.3 Hz), 132.3, 130.7 (d, *J* = 13.1 Hz), 123.5, 123.1 (d, *J* = 20.2 Hz), 120.6 (q, *J* = 321.2 Hz), 114.9 (d, *J* = 88.8 Hz), 32.5; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.23; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.61; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.19; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 464.2, $C_{28}H_{23}N_3PS^+$ requires 464.1.

Triphenyl(3–((3–(pyridin–3–yl)benzyl)oxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2n)



Major

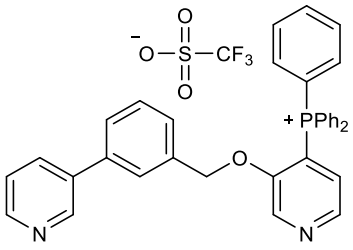


Minor

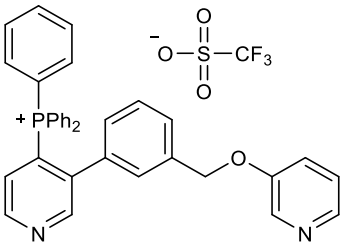
2.2:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 3–((3–(pyridin–3–yl)benzyl)oxy)pyridine (27 mg, 0.10 mmol), Tf_2O (18 μL, 0.10 mmol), PPh_3 (30 mg, 0.11 mmol), DBU (16 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (19 mg, 0.10 mmol), and CH_2Cl_2 (1 mL) to afford the title compound (combined ^{1}H NMR yield: 67%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90-8.79 (1H, m), 8.66-8.46 (3H, m), 8.05-7.12 (19H, m), 7.05 (1H, dd, *J* = 14.8, 4.7 Hz), 6.90 (1H, s), 6.80 (1H, d, *J* = 7.5 Hz), 5.17 (2H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.35; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.44; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 523.3, $C_{35}H_{28}N_2OP^+$ requires 523.3.

Triphenyl(3–((3–(pyridin–3–yl)benzyl)oxy)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2n)



Major

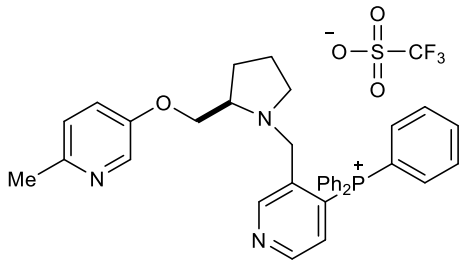


Minor

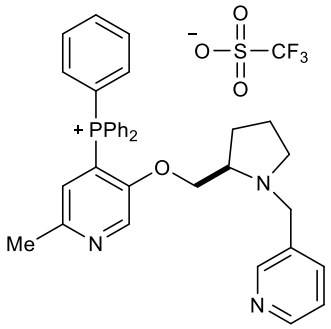
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C using 3–((3–(pyridin–3–yl)benzyl)oxy)pyridine (55 mg, 0.21 mmol), Tf_2O (71 μL, 0.42 mmol), PPh_3 (110 mg, 0.42 mmol), NEt_3 (59 μL, 0.42 mmol) and CH_2Cl_2 (2.1 mL). After the purification procedure, the title compound was isolated as a brown oil (115 mg, 0.17 mmol, 82% yield); Both isomers, IR ν_{max}/cm^{-1} (film): 3058, 2923, 1438, 1414, 1261, 1222, 1149, 1107, 1029, 980, 915, 721, 688, 635; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.86 (1H, app d, *J* = 6.7 Hz), 8.62 (1H, dd, *J* = 4.8, 1.4 Hz), 8.57 (1H, app t, *J* = 8.8 Hz), 8.54 (1H, d, *J* = 2.0 Hz), 7.75–7.53 (16H, m), 7.43–7.38 (2H, m), 7.25 (1H, t, *J* = 7.7 Hz), 7.09 (1H, dd, *J* = 14.8, 4.9 Hz), 6.91 (1H, s), 6.84 (1H, d, *J* = 7.6 Hz), 5.22 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 148.7, 147.9, 144.0 (d, *J* = 11.0 Hz), 137.9, 137.0, 137.0, 135.7, 135.4 (d, *J* = 2.9 Hz), 134.4, 133.9 (d, *J* = 10.7 Hz), 130.5 (d, *J* = 13.2 Hz), 129.3, 128.0 (d, *J* = 7.1 Hz), 127.7, 127.3, 126.6, 123.7, 120.9 (q, *J* = 321.2 Hz), 116.2 (d, *J* = 91.4 Hz), 114.9 (d, *J* = 86.9 Hz), 71.9; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.10; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.39; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 523.3, $C_{35}H_{28}N_2OP^+$ requires 523.3.

(3–((2–(((6–methylpyridin–3–yl)oxy)methyl)pyrrolidin–1–yl)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2o)



Major

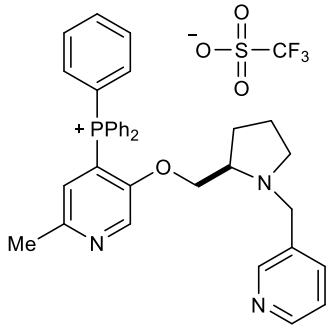


Minor

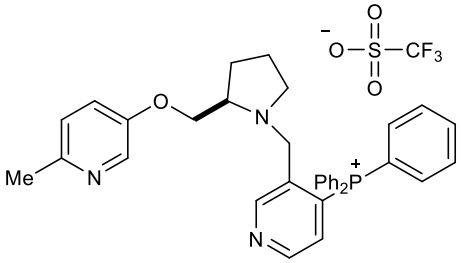
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure A using 2–methyl–5–((1–(pyridin–3–ylmethyl)pyrrolidin–2–yl)methoxy)pyridine (150 mg, 0.53 mmol), Tf_2O (89 μL, 0.53 mmol), PPh_3 (153 mg, 0.58 mmol), DBU (80 μL, 0.53 mmol) and CH_2Cl_2 (5.3 mL). After the purification procedure, the title compound was isolated as a yellow solid (227 mg, 0.33 mmol, 65% yield). mp 55–61 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3060, 2953, 2872, 2815, 1571, 1484, 1438, 1401, 1260, 1151, 1106, 909; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.39 (1H, app d, *J* = 6.7 Hz), 8.81 (1H, app t, *J* = 4.6 Hz), 7.91–7.60 (16H, m), 7.11 (1H, dd, *J* = 15.5, 5.1 Hz), 7.06 (1H, d, *J* = 8.6 Hz), 3.85 (1H, d, *J* = 16.0 Hz), 3.73–3.71 (2H, m), 3.31 (1H, d, *J* = 16.0 Hz), 2.76–2.65 (2H, m) 2,48 (3H, s), 1.88–1.79 (1H, m), 1.74–1.50 (4H, m); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9 (d, *J* = 7.9 Hz), 152.5, 150.4, 150.0 (d, *J* = 10.5 Hz), 139.0 (d, *J* = 6.2 Hz), 136.6, 135.9 (d, *J* = 2.9 Hz), 133.9 (d, *J* = 10.5 Hz), 130.9, 127.7 (d, *J* = 9.7 Hz), 125.4 (d, *J* = 81.8 Hz), 123.3, 121.4, 120.7 (q, *J* = 321.2 Hz), 116.2 (d, *J* = 88.7 Hz), 71.8, 62.1, 56.3 (d, *J* = 4.8 Hz), 53.7, 27.5, 23.1, 23.1; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.83; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 544.3, $C_{35}H_{35}N_3OP^+$ requires 544.3; Specific Rotation $[\alpha]_D^{22}$ +50.88 (*c* 1.00, $CHCl_3$).

(2–methyl–5–((1–(pyridin–3–ylmethyl)pyrrolidin–2–yl)methoxy)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2o)



Major

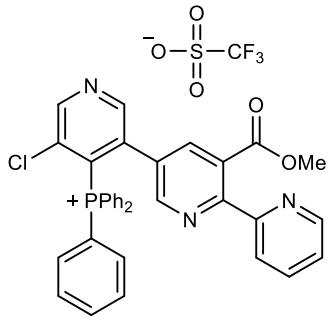


Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C using 2–methyl–5–((1–(pyridin–3–ylmethyl)pyrrolidin–2–yl)methoxy)pyridine (147.0 mg, 0.52 mmol), Tf_2O (175 μL, 1.04 mmol), PPh_3 (272.1 mg, 1.04 mmol), Et_3N (145 μL, 1.04 mmol) and CH_2Cl_2 (5.2 mL). After the purification procedure, the title compound was isolated as a brown solid (193.9 mg, 0.28 mmol, 54% yield). mp 70–78 ºC; Both isomers, IR ν_{max}/cm^{-1} (film): 3061, 2987, 2881, 1439, 1260, 1155, 1107, 1030, 907, 723, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.62 (1H, app d, *J* = 6.4 Hz), 8.47–8.46 (2H, m), 7.78–7.70 (11H, m), 7.62–7.56 (7H, m), 7.23 (1H, dd, *J* = 7.7, 4.9 Hz), 6.73 (1H, d, *J* = 15.3 Hz), 4.36 (1H, bs), 3.88 (1H, t, *J* = 7.3 Hz), 3.70 (1H, d, *J* = 12.4 Hz), 3.41 (1H, s), 2.85 (1H, s), 2.46 (5H, m), 1.54 (3H, m), 1.06 (1H, m) ; Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3 (d, *J* = 11.0 Hz), 153.2, 149.7, 148.5, 136.4, 135.9 (d, *J* = 5.1 Hz), 135.7 (d, *J* = 3.0 Hz), 133.8 (d, *J* = 10.8 Hz), 130.7 (d, *J* = 13.2 Hz), 129.9, 127.5 (d, *J* = 7.1 Hz), 123.3, 120.8 (q, *J* = 321.3 Hz), 116.5 (d, *J* = 91.0 Hz), 115.0 (d, *J* = 86.5 Hz), 72.9, 61.7, 56.9, 54.1, 28.0, 23.7, 22.8; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.42; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 544.3, $C_{35}H_{35}N_3OP^+$ requires 544.3; Specific Rotation $[\alpha]_D^{22}$ +10.26 (*c* 0.85, $CHCl_3$).

(5''–chloro–3'–(methoxycarbonyl)–[2,2':5',3''–terpyridin]–4''–yl)triphenylphosphonium trifluoromethanesulfonate (2p)

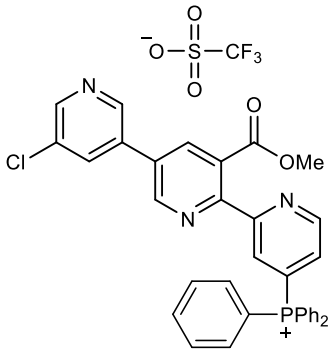


Major

10:3.1:1 (Major:Bis-phosphonium isomer:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using methyl–5''–chloro–[2,2':5',3''–terpyridine]–3'–carboxylate (16 mg, 0.05 mmol), Tf_2O (9 μL, 0.05 mmol), PPh_3 (14 mg, 0.06 mmol), DBU (8 μL, 0.05 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (0.5 mL) to afford the title compound (combined ^{1}H NMR yield: 83%). Major isomer ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.93 (1H, d, J = 5.4 Hz), 8.70-8.55 (2H, m), 8.26 (1H, d, J = 2.0 Hz), 8.02-7.50 (18H, m), 7.40-7.30 (1H, m), 3.70 (3H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.82; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.71, 22.60, 20.71, 21.67; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 586.2, $C_{35}H_{26}ClN_3O_2P^+$ requires 586.2.

(5''–chloro–3'–(methoxycarbonyl)–[2,2':5',3''–terpyridin]–4–yl)triphenylphosphonium trifluoromethanesulfonate (2p)

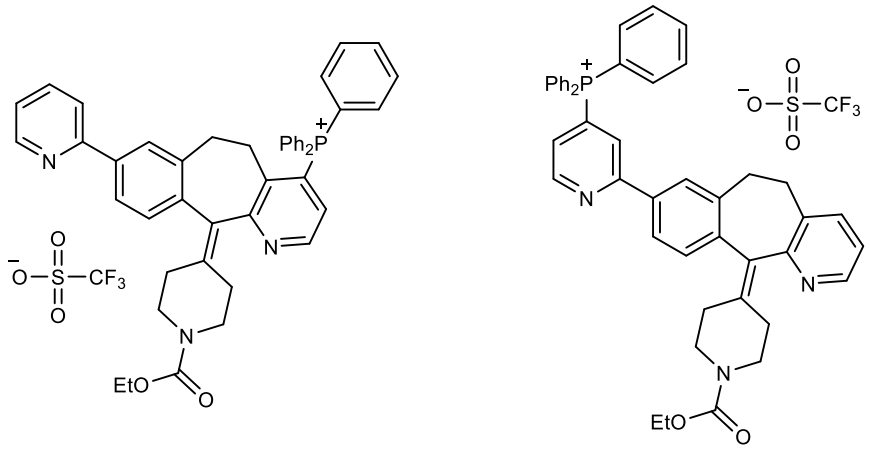


Major

>20:1 (Major:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure C (except that the reaction mixture was warmed to –50 ºC prior to adding PPh_3 and remained at –50 ºC for 1 hour before cooling down to –78 ºC for NEt_3 addition) using methyl–5''–chloro–[2,2':5',3''–terpyridine]–3'–carboxylate (65 mg, 0.20 mmol), Tf_2O (68 μL, 0.40 mmol), PPh_3 (105 mg, 0.40 mmol), NEt_3 (56 μL, 0.40 mmol) and CH_2Cl_2 (2.0 mL). After the purification procedure, the title compound was isolated as a yellow solid (132 mg, 0.18 mmol, 89% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3059, 2951, 1728, 1439, 1259, 1107, 1030, 909, 724, 646; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.07 (1H, app t, *J* = 4.8 Hz), 8.88 (1H, s), 8.76 (1H, s), 8.66 (1H, s), 8.42 (1H, d, *J* = 13.6 Hz), 8.16 (1H, d, *J* = 2.2 Hz), 8.07–7.61 (17H, m), 3.90 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 156.9 (d, *J* = 10.6 Hz), 152.3 (d, *J* = 2.0 Hz), 150.7 (d, *J* = 10.3 Hz), 148.7, 148.4, 145.5, 136.2 (d, *J* = 2.9 Hz), 135.4, 134.4 (d , *J* = 10.5 Hz), 134.0, 132.8, 132.5, 132.3, 131.0 (d, *J* = 13.0 Hz), 129.5 (d, *J* = 84.2 Hz), 129.1, 127.4 (d, *J* = 8.4 Hz), 125.7 (d, *J* = 9.3 Hz), 120.7 (q, *J* = 321.4 Hz), 115.5 (d, *J* = 89.8 Hz), 52.9; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.66; Other phosphonium isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.68; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 586.2, $C_{35}H_{26}ClN_3O_2P^+$ requires 586.2.

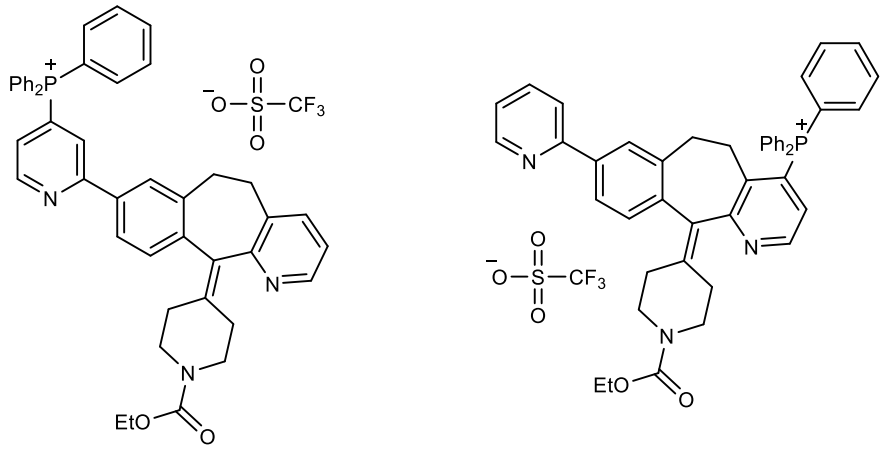
(2–(11–(1–(ethoxycarbonyl)piperidin–4–ylidene)–6,11–dihydro–5H–benzo[5,6]cyclohepta[1,2–b]pyridin–8–yl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2q)



10:3.1:1 (Major:Bis-phosphonium isomer:Minor) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using ethyl 4–(8–(pyridin–2–yl)–5,6–dihydro–11H–benzo[5,6]cyclohepta[1,2–b]pyridin–11–ylidene)piperidine–1–carboxylate (21 mg, 0.05 mmol), Tf_2O (9 μL, 0.05 mmol), PPh_3 (14 mg, 0.06 mmol), DBU (8 μL, 0.05 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (0.5 mL) to afford the title compound (combined ^{1}H NMR yield: 89%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (1H, app t, J = 4.8 Hz), 8.66-8.57 (1H, m), 8.01-7.33 (19H, m), 7.33-7.15 (2H, m), 7.02 (1H, dd, J = 14.8, 5.2 Hz), 4.20-4.02 (2H, m), 3.91-3.60 (2H, m), 3.42-3.20 (3H, m), 3.00-2.79 (1H, m), 2.65-2.05 (5H, m), 1.78-1.54 (1H, m) 1.36-1.07 (3H, m); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.24; Other phosphonium isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.79, 22.77, 21.13; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 686.4, $C_{45}H_{41}N_3O_2P^+$ requires 686.3.

(11–(1–(ethoxycarbonyl)piperidin–4–ylidene)–8–(pyridin–2–yl)–6,11–dihydro–5H–benzo[5,6]cyclohepta[1,2–b]pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2q)

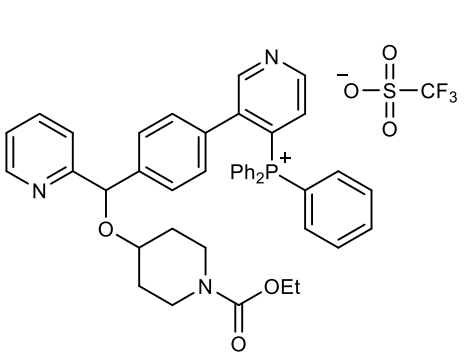


>20:1 (Major:Minor) Mixture of Isomers

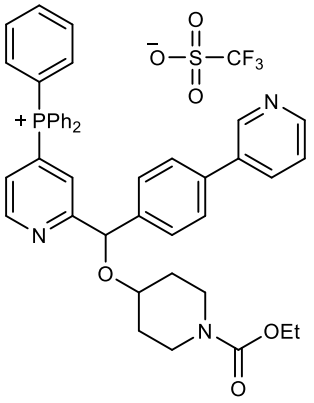
Prepared according to general procedure C using ethyl 4–(8–(pyridin–2–yl)–5,6–dihydro–11H–benzo[5,6]cyclohepta[1,2–b]pyridin–11–ylidene)piperidine–1–carboxylate (213 mg, 0.50 mmol), Tf_2O (169 μL, 1.00 mmol), PPh_3 (262 mg, 1.00 mmol), NEt_3 (139 μL, 1.00 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as a white solid (301 mg, 0.36 mmol, 72% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3060, 2982, 2910, 2868, 1686, 1437, 1260, 1223, 1109, 1030, 909, 724, 646; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.07 (1H, app t, *J* = 4.9 Hz), 8.39 (1H, dd, *J* = 5.0, 1.4 Hz), 7.98–7.89 (3H, m), 7.86 (1H, d, *J* = 1.5 Hz), 7.85–7.76 (7H, m), 7.75–7.65 (6H, m), 7.59 (1H, dd, *J* = 7.9, 1.8 Hz), 7.54–7.44 (2H, m), 7.29 (1H, d, *J* = 8.0 Hz), 7.11 (1H, dd, *J* = 7.7, 4.8 Hz), 4.13 (2H, q, *J* = 7.1 Hz), 3.94–3.69 (2H, m), 3.57–3.30 (2H, m), 3.23–3.03 (2H, m), 3.03–2.82 (2H, m), 2.61–2.24 (4H, m), 1.24 (3H, t, *J* = 7.1 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0 (d, *J* = 10.3 Hz), 151.7 (d, *J* = 11.2 Hz), 156.4, 155.4, 146.2, 141.7, 139.0, 138.0, 137.9, 136.2 (d, *J* = 2.9 Hz), 136.1 (d, *J* = 1.5 Hz), 134.5 (d, *J* = 10.7 Hz), 134.2, 133.8, 131.0 (d, *J* = 13.1 Hz), 129.9, 129.3 (d, *J* = 83.6 Hz), 125.2 (d, *J* = 8.4 Hz), 124.7, 123.2 (d, *J* = 8.8 Hz), 122.4, 120.8 (q, *J* = 320.8 Hz), 115.7 (d, *J* = 89.2 Hz), 61.2, 44.7, 31.7, 31.5, 30.7, 30.5, 14.6; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.79; Minor isomer, ^{31}P NMR

(162 MHz, $CDCl_3$) δ: 21.17; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 686.3, $C_{45}H_{41}N_3O_2P^+$ requires 686.3.

(3–(4–(((1–(ethoxycarbonyl)piperidin–4–yl)oxy)(pyridin–2–yl)methyl)phenyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2d)



Major



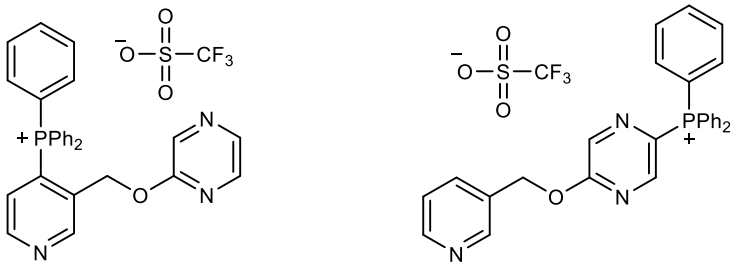
Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure D (except that Tf_2O was added at –50 ºC and stirred for 1 hour instead of at –78 ºC for 1 hour) using ethyl 4–(pyridin–2–yl(4–(pyridin–3–yl)phenyl)methoxy)piperidine–1–carboxylate (104 mg, 0.25 mmol), Tf_2O (42 μL, 0.25 mmol), PPh_3 (66 mg, 0.25 mmol), DBU (37 μL, 0.25 mmol) and CH_2Cl_2 (2.5 mL). After the purification procedure, the title compound was isolated as a light yellow solid (167 mg, 0.20 mmol, 81% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3062, 2929, 2856, 1685, 1436, 1261, 1153, 1099, 1029, 909, 724, 635; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.94 (1H, app t, *J* = 4.6 Hz), 8.72 (1H, d, *J* = 6.8 Hz), 8.58 (1H, d, *J* = 4.3 Hz), 7.93–7.17 (19H, m), 7.03 (2H, d, *J* = 8.2 Hz), 6.69 (2H, d, *J* = 8.2 Hz), 5.47 (1H, s), 4.10 (2H, q, *J* = 7.1 Hz), 3.82–3.64 (2H, m), 3.60–3.84 (1H, m), 3.27–3.07 (2H, m), 1.93–1.48 (4H, m), 1.23 (3H, t, *J* = 7.1 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.1, 155.2, 153.6 (d, *J* = 10.2 Hz), 149.8 (d, *J* = 10.2 Hz), 148.7, 142.1, 141.3 (d, *J* = 7.0 Hz), 137.0, 135.2 (d, *J* = 2.7 Hz), 134.0 (d, *J* = 10.2 Hz), 133.6 (d, *J* = 3.9 Hz), 130.3 (d, *J* = 13.0 Hz), 129.1, 128.1 (d, *J* = 9.6 Hz), 126.2, 126.1 (d, *J* = 83.2 Hz), 122.7, 120.7

(q, J = 321.2 Hz), 120.6, 116.6 (d, J = 89.0 Hz), 80.6, 72.4, 61.0, 40.7, 30.7 (d, J = 38.0 Hz), 14.4; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.11; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.45; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.49; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 678.3, $C_{43}H_{41}N_3O_3P^+$ requires 678.3.

Triphenyl(3–((pyrazin–2–yloxy)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2e)



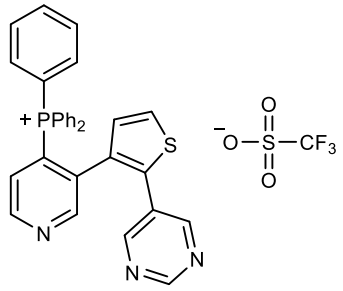
Major Minor

18.5:1:1:1 (Major:2–position phosphonium isomer:Minor:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure D using 2–(pyridin–3–ylmethoxy)pyrazine (94 mg, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), PPh_3 (131 mg, 0.50 mmol), DBU (75 μL, 0.50 mmol) and CH_2Cl_2 (5.0 mL). After the purification procedure, the title compound was isolated as a white solid (249 mg, 0.42 mmol, 83% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3063, 2903, 1585, 1484, 1259, 1152, 1030, 908, 722; Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (1H, app d, J = 6.6 Hz), 8.96 (1H, app t, J = 4.6 Hz), 8.08 (1H, d, J = 2.7 Hz), 7.91–7.58 (16H, m), 7.39 (1H, d, J = 1.2 Hz), 7.33 (1H, dd, J = 15.7, 5.1 Hz), 4.96 (2H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 152.8 (d, J = 7.8 Hz), 151.9, (d, J = 10.6 Hz), 140.3, 137.7, 135.9 (d, J = 2.9 Hz), 134.6, 134.4 (d, J = 5.8 Hz), 134.2 (d, J = 10.6 Hz), 130.7 (d, J = 13.1 Hz), 129.0 (d, J = 9.4 Hz), 126.5 (d, J = 81.5 Hz), 120.7 (q, J = 321.1 Hz), 116.1 (d, J = 89.2 Hz), 63.6 (d, J = 4.0 Hz); All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.16; Major isomer, ^{31}P NMR (162 MHz,

$CDCl_3$) δ: 22.70; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.33, 21.01, 16.64; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 448.3, $C_{28}H_{23}N_3OP^+$ requires 448.2.

Triphenyl(3–(2–(pyrimidin–5–yl)thiophen–3–yl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2g)

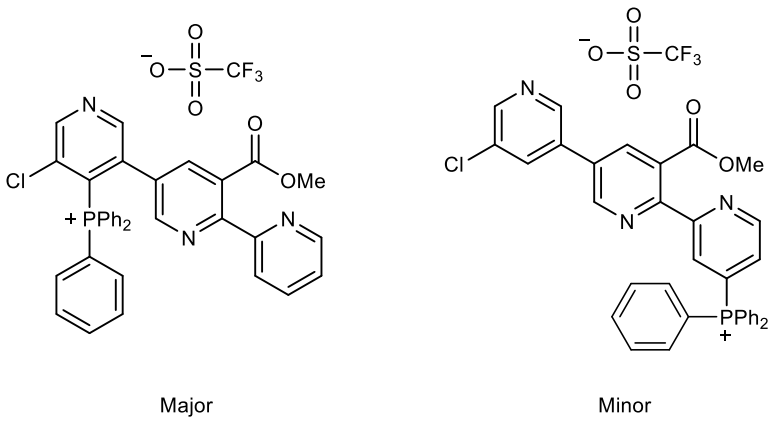


Major

17.3:1:1 (Major:Unidentified phosphonium isomer:2-position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure D using 5–(3–(pyridin–3–yl)thiophen–2–yl)pyrimidine (24 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (27 mg, 0.10 mmol), DBU (15 μL, 0.10 mmol) and CH_2Cl_2 (1.0 mL). After the purification procedure, the title compound was isolated as a yellow solid (50 mg, 0.077 mmol, 77% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3064, 2957, 2852, 1438, 1262, 1153, 1104, 1030, 721; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.19–8.91 (2H, m), 8.81 (1H, d, *J* = 6.7 Hz), 8.19 (2H, br s), 7.97–7.39 (16H, m), 7.15 (1H, d, *J* = 5.0 Hz), 6.74 (1H, d, *J* = 5.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 154.2 (d, *J* = 6.5 Hz), 154.7 (2C), 150.6 (d, *J* = 10.0 Hz), 136.2 (d, *J* = 5.7 Hz), 135.7 (d, *J* = 2.9 Hz), 134.4, 134.1 (d, *J* = 10.3 Hz), 132.7 (d, *J* = 4.2 Hz), 131.9, 130.7 (d, *J* = 13.0 Hz), 129.1 (d, *J* = 8.7 Hz), 127.9, 127.2 (d, *J* = 82.7 Hz), 120.8 (q, *J* = 321.2 Hz), 116.0 (d, *J* = 88.7 Hz); All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.14; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.79; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.32, 15.38; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 500.1, $C_{31}H_{23}N_3PS^+$ requires 500.1.

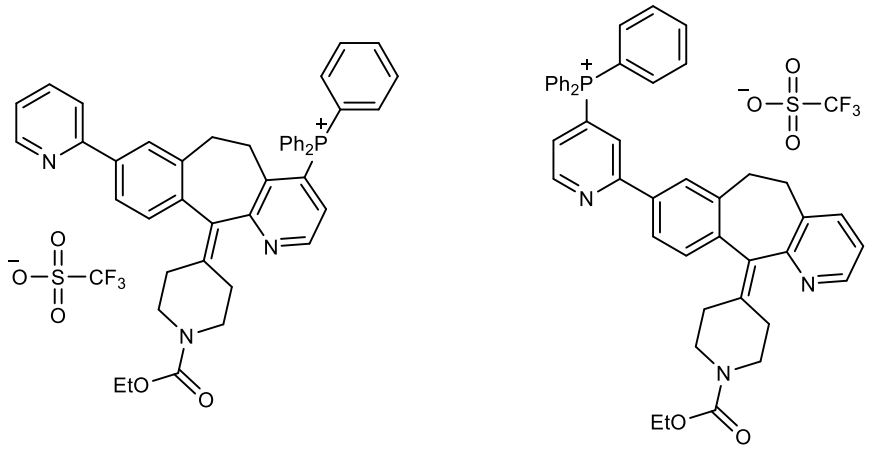
(5''–chloro–3'–(methoxycarbonyl)–[2,2':5',3''–terpyridin]–4''–yl)triphenylphosphonium trifluoromethanesulfonate (2p)



>20:1 (Major:Unidentified phosphonium isomer) Mixture of Isomers

Prepared according to general procedure D using methyl–5''–chloro–[2,2':5',3''–terpyridine]–3'–carboxylate (65 mg, 0.20 mmol), Tf_2O (34 μL, 0.20 mmol), PPh_3 (52 mg, 0.20 mmol), DBU (30 μL, 0.20 mmol) and CH_2Cl_2 (2.0 mL). After the purification procedure, the title compound was isolated as a tan solid (137 mg, 0.19 mmol, 93% combined yield). All isomers, IR ν_{max}/cm^{-1} (film): 3062, 2986, 1728, 1438, 1263, 1152, 1030, 912, 720, 636; Major isomer ^1H NMR (400 MHz, $CDCl_3$) δ: 8.96 (1H, d, *J* = 4.5 Hz), 8.70 (1H, d, *J* = 3.1 Hz), 8.61 (1H, s), 8.28 (1H, s), 8.06–7.46 (18H, m), 7.40–7.29 (1H, m), 3.74 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 155.3 (d, *J* = 2.2 Hz), 154.7, 152.4 (d, *J* = 7.2 Hz), 151.9 (d, *J* = 4.8 Hz), 149.6, 148.6, 140.7 (d, *J* = 5.7 Hz), 136.9 (d, *J* = 10.9 Hz), 136.8, 136.1 (d, *J* = 2.3 Hz), 135.4 (d, *J* = 2.7 Hz), 134.0 (d, *J* = 10.6 Hz), 130.7 (d, *J* = 13.6 Hz), 130.0, 127.5, 125.5 (d, *J* = 88.0 Hz), 124.1, 122.6, 120.8 (q, *J* = 321.4 Hz), 116.9 (d, *J* = 89.1 Hz), 52.3; All isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.17; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.78; Other phosphonium isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.65; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 586.2, $C_{35}H_{26}ClN_3O_2P^+$ requires 586.2.

(2–(11–(1–(ethoxycarbonyl)piperidin–4–ylidene)–6,11–dihydro–5H–benzo[5,6]cyclohepta[1,2–b]pyridin–8–yl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2q)

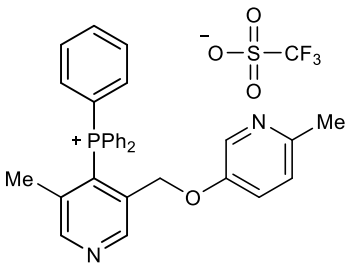


>20:1 (Major:Minor) Mixture of Isomers

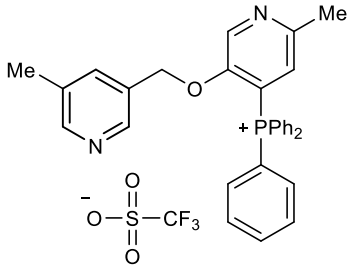
Prepared according to general procedure D using ethyl 4–(8–(pyridin–2–yl)–5,6–dihydro–11H–benzo[5,6]cyclohepta[1,2–b]pyridin–11–ylidene)piperidine–1–carboxylate (86 mg, 0.20 mmol), Tf_2O (34 μL, 0.20 mmol), PPh_3 (59 mg, 0.20 mmol), DBU (30 μL, 0.20 mmol) and CH_2Cl_2 (2.0 mL). After the purification procedure, the title compound was isolated as a yellow solid (123 mg, 0.15 mmol, 74% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3089, 2980, 1689, 1578, 1437, 1261, 1222, 1108, 1029, 726, 634; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.75 (1H, app t, *J* = 4.5 Hz), 8.67 (1H, d, *J* = 3.3 Hz), 8.06–7.56 (18H, m), 7.44 (1H, s), 7.35–7.17 (2H, m), 7.05 (1H, dd, *J* = 14.9, 5.1 Hz), 4.16 (2H, q, *J* = 7.0 Hz), 3.90–3.62 (2H, m), 3.54–3.24 (3H, m), 3.03–2.81 (1H, m), 2.74–2.35 (4H, m), 2.32–2.07 (1H, m), 1.91–1.67 (1H, m), 1.28 (3H, t, *J* = 7.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.8 (d, *J* = 8.5 Hz), 156.2, 155.4, 149.4, 149.0 (d, *J* = 11.5 Hz), 139.1–138.7 (2C), 137.2 (d, *J* = 7.1 Hz), 136.1 (d, *J* = 2.1 Hz), 135.4, 134.2 (d, *J* = 10.5 Hz), 133.2 (d, *J* = 2.1 Hz), 131.1 (d, *J* = 13.0 Hz), 130.8, 128.6, 126.8 (d, *J* = 81.4 Hz), 127.1 (d, *J* = 9.8 Hz), 124.7, 122.4, 120.8 (q, *J* = 321.3 Hz), 120.5, 116.5 (d, *J* = 88.8 Hz), 61.4, 44.7, 44.8, 30.8, 30.8, 30.5, 29.8, 14.6; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –

78.13; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.24; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.72; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 686.4, $C_{45}H_{41}N_3O_2P^+$ requires 686.3.

(3–methyl–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



Major

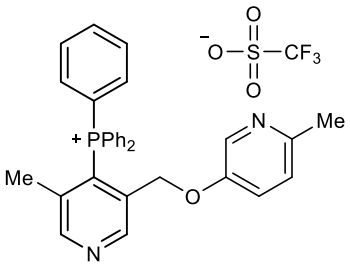


Minor

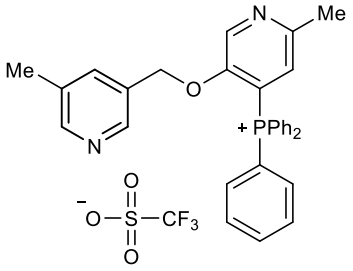
1:1.5:2 (Mixure of 2 phosphonium isomers:Major:Minor) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture and that Tf_2O stirred for 15 minutes instead of 30 minutes) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (22 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (29 mg, 0.11 mmol), DBU (15 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (0.5 mL) to afford the title compound (combined ^{1}H NMR yield: 44%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (1H, d, J = 6.0 Hz), 8.79-8.72 (1H, m), 7.94-7.33 (17H, m), 7.12-7.03 (1H, m), 6.86-6.76 (1H, m), 4.63 (1H, s), 2.22 (3H, s), 1.86 (3H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.53; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.86, 21.33, 16.43; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 475.3, $C_{31}H_{28}N_2OP^+$ requires 475.2.

(3–methyl–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



Major

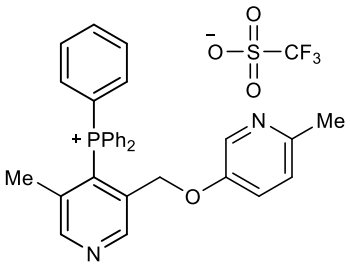


Minor

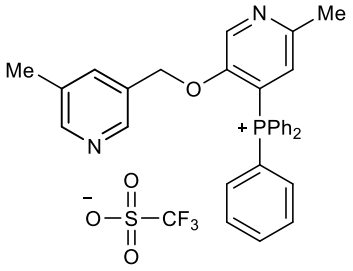
3.3:1:1 (Major:Minor:Mixture of 2 phosphonium isomers) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (22 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (29 mg, 0.11 mmol), DBU (15 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (0.5 mL) to afford the title compound (combined ^{1}H NMR yield: 52%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (1H, d, *J* = 6.0 Hz), 8.75 (1H, d, *J* = 6.2 Hz), 7.88-7.37 (16H, m), 7.03-6.92 (1H, m), 6.59 (1H, dd, *J* = 8.7, 3.0 Hz), 4.49 (2H, s), 2.43 (3H, s), 1.85 (3H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.57; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.96, 21.29, 16.41; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 475.3, $C_{31}H_{28}N_2OP^+$ requires 475.2.

(3–methyl–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



Major

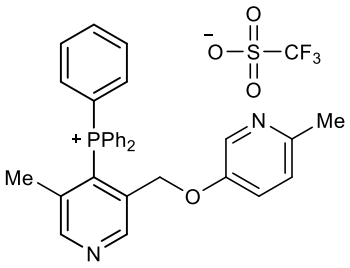


Minor

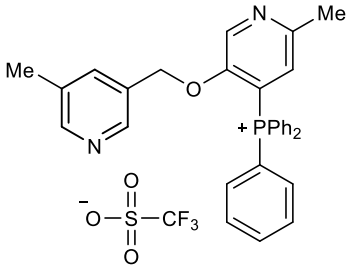
20:1:2.9 (Major:Minor:Mixture of 2 phosphonium isomers) Mixture of Isomers

Prepared according to general procedure A (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture that Tf_2O stirred for 60 minutes instead of 30 minutes) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (22 mg, 0.10 mmol), Tf_2O (17 μL, 0.10 mmol), PPh_3 (29 mg, 0.11 mmol), DBU (15 μL, 0.10 mmol), 1,3,5-trimethoxybenzene as an internal standard (17 mg, 0.10 mmol), and CH_2Cl_2 (0.5 mL) to afford the title compound (combined ^{1}H NMR yield: 72%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (1H, d, J = 6.0 Hz), 8.74 (1H, d, J = 6.2 Hz), 7.92-7.33 (16H, m), 6.88 (1H, d, J = 8.6 Hz), 6.44 (1H, dd, J = 8.6, 3.0 Hz), 4.45 (2H, s), 2.40 (3H, s), 1.85 (3H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.58; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.90, 21.28, 16.42; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 475.3, $C_{31}H_{28}N_2OP^+$ requires 475.2.

(3–methyl–5–(((6–methylpyridin–3–yl)oxy)methyl)pyridin–4–yl)triphenylphosphonium trifluoromethanesulfonate (2l)



Major

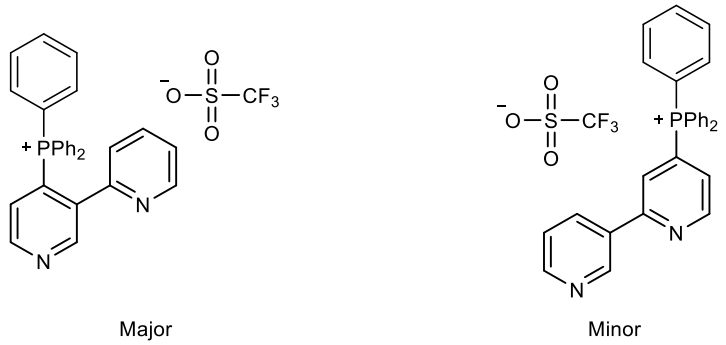


Minor

4.3:1:1.1 (Major:Minor:Mixture of 2 phosphonium isomers) Mixture of Isomers

Prepared according to general procedure D (except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 2–methyl–5–((5–methylpyridin–3–yl)methoxy)pyridine (50 mg, 0.23 mmol), Tf_2O (39 μL, 0.23 mmol), PPh_3 (60 mg, 0.23 mmol), DBU (35 μL, 0.23 mmol), 1,3,5-trimethoxybenzene as an internal standard (39 mg, 0.23 mmol), and CH_2Cl_2 (2.3 mL) to afford the title compound (combined ^{1}H NMR yield: 52%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (1H, d, *J* = 6.0 Hz), 8.70 (1H, d, *J* = 6.2 Hz), 8.08-7.17 (16H, m), 7.06-7.00 (1H, m), 6.47-6.35 (1H, m), 4.41 (2H, s), 2.31 (3H, s), 1.81 (3H, s); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.57; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.81, 21.27, 16.39; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 475.3, $C_{31}H_{28}N_2OP^+$ requires 475.2.

[2,3'–bipyridin]–4'–yltriphenylphosphonium trifluoromethanesulfonate (2r)

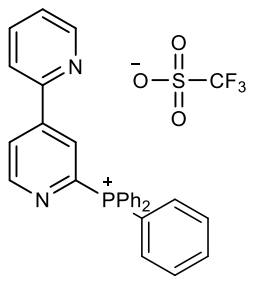


Major Minor

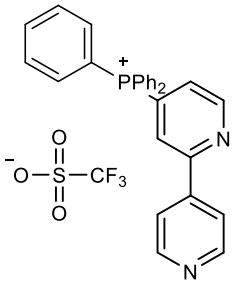
>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure A using 2,3'–bipyridine (156 mg, 1.00 mmol), Tf_2O (169 μL, 1.00 mmol), PPh_3 (288 mg, 1.10 mmol), DBU (150 μL, 1.00 mmol) and CH_2Cl_2 (10 mL). After the purification procedure, the title compound was isolated as a white amorphous solid (542 mg, 0.96 mmol, 96% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3072, 3029, 1591, 1438, 1275, 1257, 1223, 1166, 1109, 1029, 739, 659, 569; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.60 (1H, d, *J* = 6.6 Hz), 8.94 (1H, app t, *J* = 4.8 Hz), 8.06 (1H, d, *J* = 8.1 Hz), 7.85–7.46 (17H, m), 7.21 (1H, dd, *J* = 15.9, 5.1 Hz), 7.04 (1H, dd, *J* = 7.6, 5.1 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.8 (d, *J* = 11.6 Hz), 150.0 (d, *J* = 6.6 Hz), 148.3, 146.4, 138.5, 136.3, 134.2 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 9.7 Hz), 131.2 (d, *J* = 10.8 Hz), 130.1 (d, *J* = 13.3 Hz), 125.3 (d, *J* = 91.6 Hz), 125.0, 122.1 (d, *J* = 95.9 Hz), 121.4, 120.9 (q, *J* = 321.2 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.05; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 26.26; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 417.2, $C_{28}H_{22}N_2P^+$ requires 417.2.

[2,4'–bipyridin]–2'–yltriphenylphosphonium trifluoromethanesulfonate (2s)



Major

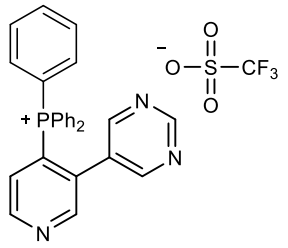


Minor

>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure D using 2,4'–bipyridine (39 mg, 0.25 mmol), Tf_2O (42 μL, 0.25 mmol), PPh_3 (66 mg, 0.25 mmol), DBU (37 μL, 0.25 mmol) and EtOAc (2.5 mL). After the purification procedure, the title compound was isolated as a grey amorphous solid (83 mg, 0.17 mmol, 59% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3064, 1583, 1437, 1261, 1150, 1030, 723, 634; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.12 (1H, d, *J* = 4.9 Hz), 8.68–8.62 (1H, m), 8.49–8.36 (2H, m), 8.08 (1H, d, *J* = 8.0 Hz), 7.97–7.85 (4H, m), 7.84–7.68 (12H, m), 7.37 (1H, ddd, *J* = 7.7, 4.8, 1.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2 (d, *J* = 20.2 Hz), 151.6 (d, *J* = 2.0 Hz), 150.1, 148.6 (d, *J* = 10.8 Hz), 145.2 (d, *J* = 120.6 Hz), 137.9, 135.7 (d, *J* = 2.9 Hz), 134.5 (d, *J* = 10.1 Hz), 130.5 (d, *J* = 13.0 Hz), 128.7 (d, *J* = 25.8 Hz), 125.4 (d, *J* = 3.4 Hz), 125.0, 120.8 (q, *J* = 321.1 Hz), 116.9 (d, *J* = 89.0 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.09; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.79; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 417.2, $C_{28}H_{22}N_2P^+$ requires 417.2.

Triphenyl(3–(pyrimidin–5–yl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2t)

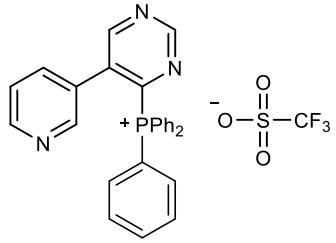


Major

>20:1 (Major:2-position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure D using 5–(pyridin–3–yl)pyrimidine (157 mg, 1.00 mmol), Tf_2O (169 μL, 1.00 mmol), PPh_3 (288 mg, 1.10 mmol), DBU (150 μL, 1.00 mmol) and EtOAc (10 mL). After the purification procedure, the title compound was isolated as a yellow amorphous solid (410 mg, 0.72 mmol, 72% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3061, 1551, 1439, 1261, 1149, 1102, 1029, 720, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.07 (1H, dd, *J* = 5.2, 4.2 Hz), 8.88 (1H, s), 8.73 (1H, d, *J* = 6.8 Hz), 8.21 (2H, s), 7.89–7.79 (3H, m), 7.83–7.65 (12H, m), 7.59 (1H, dd, *J* = 15.2, 5.0 Hz); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 156.0, 153.3 (d, *J* = 7.4 Hz), 151.6 (d, *J* = 10.2 Hz), 135.9 (d, *J* = 2.9 Hz), 134.4 (d, *J* = 10.4 Hz), 134.1 (d, *J* = 6.2 Hz), 130.9 (d, *J* = 13.1 Hz), 129.6 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 9.1 Hz), 127.3 (d, *J* = 82.9 Hz), 120.6 (q, *J* = 321.1 Hz), 116.3 (d, *J* = 88.6 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.18; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.08; Other phosphonium isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.75; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 418.2, $C_{27}H_{21}N_3P^+$ requires 418.2.

Triphenyl(5–(pyridin–3–yl)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2t)

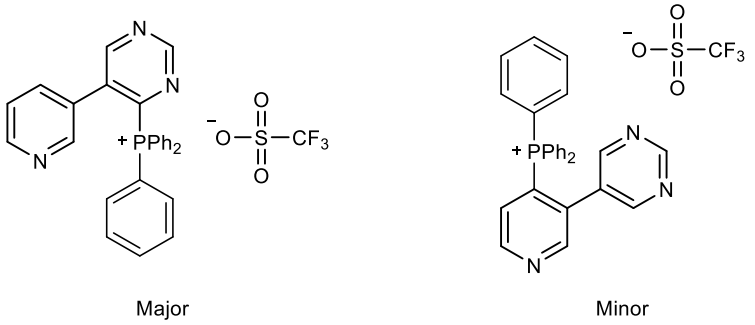


Major

7.7:1 (Major:2-position phosphonium isomer) Mixture of Isomers

Prepared according to general procedure B (except that Tf_2O was added at –30 ºC and stirred for 1 hour instead of at –78 ºC for 1 hour) using 5–(pyridin–3–yl)pyrimidine (79 mg, 0.50 mmol), silver trifluormethanesulfonate (128 mg, 0.50 mmol), acetyl chloride (36 μL, 0.50 mmol), Tf_2O (85 μL, 0.50 mmol), PPh_3 (44 mg, 0.55 mmol), DBU (75 μL, 0.50 mmol) and EtOAc (5 mL). After the purification procedure, the title compound was isolated as a yellow solid (59 mg, 0.01 mmol, 21% combined yield. Both isomers, IR ν_{max}/cm^{-1} (film): 3093, 3011, 2976, 2946, 2843, 1591, 1567, 1502, 1259, 1184, 1105, 1029, 1018, 803, 636; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.52 (1H, s), 8.96 (1H, d, *J* = 8.9 Hz), 8.35 (1H, d, *J* = 3.9 Hz), 8.10 (1H,s), 8.00–7.47 (16H, m), 7.10–7.00 (1H, m); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8 (d, *J* = 5.1 Hz), 157.7 (d, *J* = 16.8 Hz), 156.4 (d, *J* = 16.0 Hz), 150.4 (d, *J* = 114.7 Hz), 150.3, 148.5, 139.5 (d, *J* = 19.4 Hz), 136.9, 135.3 (d, *J* = 2.9 Hz), 134.7 (d, *J* = 10.2 Hz), 130.3 (d, *J* = 13.1 Hz), 123.6, 120.6 (q, *J* = 321.1 Hz), 116.6 (d, *J* = 88.5 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.25; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.87; Other phosphonium isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.96; *m/z* LRMS (ESI + APCI) found $[M – OTf]^+$ 418.2, $C_{33}H_{22}N_2O_3P^+$ requires 418.2.

Triphenyl(5–(pyridin–3–yl)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2t)

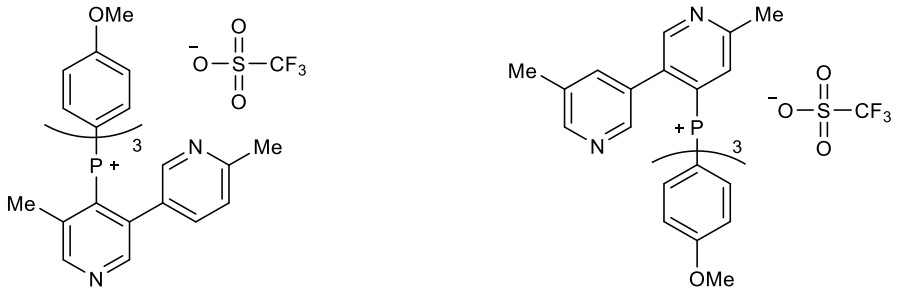


Major Minor

2:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C using except that ^{1}H NMR and ^{31}P NMR were run on the crude reaction mixture) using 5–(pyridin–3–yl)pyrimidine (16 mg, 0.10 mmol), Tf_2O (34 μL, 0.20 mmol), PPh_3 (59 mg, 0.22 mmol), DBU (30 μL, 0.20 mmol), 1,3,5-trimethoxybenzene as an internal standard (39 mg, 0.23 mmol), and EtOAc (1 mL) to afford the title compound (combined ^{1}H NMR yield: 19%). Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.42 (1H, s), 8.87 (1H, d, *J* = 8.9 Hz), 8.39-8.25 (1H, m), 7.97-7.12 (17H, m), 6.98 (1H, dd, *J* = 8.0, 4.9 Hz); Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.73; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.47; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 418.2, $C_{33}H_{22}N_2O_3P^+$ requires 418.2.

(5,6'–dimethyl–[3,3'–bipyridin]–4–yl)tris(4–methoxyphenyl)phosphonium trifluoromethanesulfonate (2u)

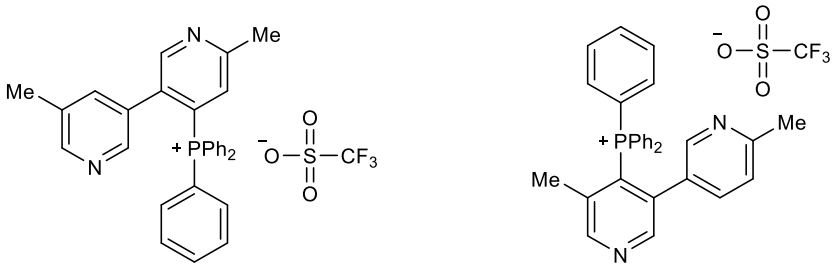


Major Minor

14:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure D using 5,6'–dimethyl–3,3'–bipyridine (47 mg, 0.26 mmol), Tf_2O (43 μL, 0.26 mmol), tris(4–methoxyphenyl)phosphine (92 mg, 0.26 mmol), DBU (39 μL, 0.26 mmol) and CH_2Cl_2 (2.6 mL). After the purification procedure, the title compound was isolated as a brown solid (83 mg, 0.12 mmol, 48% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3095, 3014, 2973, 2947, 2843, 1591, 1566, 1501, 1261, 1183, 1102, 1029; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, app d, *J* = 5.9 Hz), 8.45 (1H, app d, *J* = 5.7 Hz), 7.87 (1H, s), 7.47–7.42 (6H, m), 7.26–7.25 (1H, m), 7.09–7.06 (6H, m), 6.75 (1H, d, *J* = 8.0 Hz), 3.90 (9H, s), 2.41 (3H, s), 1.93 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1 (d, *J* = 2.9 Hz), 158.4, 153.2 (d, *J* = 8.2 Hz), 151.9 (d, *J* = 7.5 Hz), 148.2, 139.6 (d, *J* = 7.6 Hz), 137.4 (d, *J* = 7.4 Hz), 136.3, 135.6 (d, *J* = 12.0 Hz), 129.2 (d, *J* = 4.7 Hz), 127.2 (d, *J* = 83.4 Hz), 122.9, 120.8 (q, *J* = 321.2 Hz) 116.3 (d, *J* = 14.3 Hz), 108.5 (d, *J* = 96.7 Hz), 55.9, 23.9, 21.3 (d, *J* = 5.4 Hz); Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.17; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.85; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.68; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 535.3, $C_{33}H_{22}N_2O_3P^+$ requires 535.2.

(5',6–dimethyl–[3,3'–bipyridin]–4–yl)triphenylphosphonium trifluoromethanesulfonate (2u)



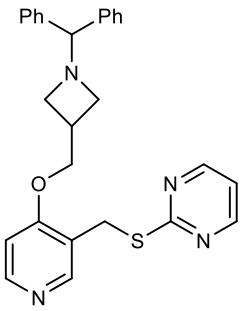
10:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure A (except that 1.75 equivalent of PPh_3 and 2 equivalents of Tf_2O and DBU were used instead of 1 equivalent of each) using 5,6'–dimethyl–3,3'–bipyridine (37 mg, 0.20 mmol), Tf_2O (68 μL, 0.40 mmol), PPh_3 (93 mg, 0.35 mmol), DBU (61 μL, 0.40

mmol) and CH_2Cl_2 (2.0 mL). After the purification procedure, the title compound was isolated as a brown solid (60 mg, 0.10 mmol, 50% combined yield). Both isomers, IR ν_{max}/cm^{-1} (film): 3060, 3026, 2923, 1572, 1438, 1260, 1151, 1103, 1029; Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 8.59 (1H, app d, *J* = 7.1 Hz), 8.12 (1H, s), 7.81–7.63 (16H, m), 7.27 (1H, d, *J* = 15.6 Hz), 6.90 (1H, s), 2.70 (3H, s), 1.98 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6 (d, *J* = 10.3 Hz), 153.0 (d, *J* = 8.3 Hz), 150.3, 146.0, 137.2, 135.4 (d, *J* = 3.0 Hz), 134.9 (d, *J* = 6.7 Hz), 134.3 (d, *J* = 10.2 Hz), 133.9 (d, *J* = 10.4 Hz), 130.8, 130.6 (d, *J* = 13.0 Hz), 127.9 (d, *J* = 9.4 Hz), 127.0 (d, *J* = 82.9 Hz), 120.8 (q, *J* = 321.1 Hz), 116.8 (d, *J* = 88.7 Hz), 24.6, 17.8; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; Major isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.23; Minor isomer, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.78; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 445.3, $C_{30}H_{26}N_2P^+$ requires 445.2.

4. Preparation of Derivatized Polyazaarenes

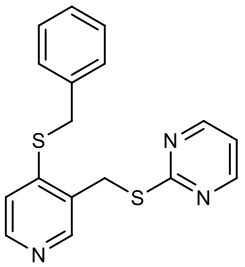
2–(((4–((1–benzhydrylazetidin–3–yl)methoxy)pyridin–3–yl)methyl)thio)pyrimidine (3a)



An oven dried 8 mL vial with a stir bar and septa cap was charged with sodium hydride (60% dispersion in mineral oil, 15 mg, 1.5 equiv) and placed under a nitrogen atmosphere. THF (250 μL) was added, the suspension was cooled to 0 ºC and a solution of (1–benzhydrylazetidin–3–yl)methanol (95 mg, 0.38 mmol) in THF (250 μL) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the septa cap was briefly removed and triphenyl(3–((pyrimidin–2–ylthio)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) was added in one portion. The reaction was subjected to three rapid cycles of

vacuum/nitrogen backfill[**], the ice bath removed and the reaction stirred for 12 hours while warming to room temperature. The reaction was quenched with H_2O (2.0 mL), the aqueous layer was separated and extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with a saturated aqueous solution of brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (neutralized silica gel: 70% EtOAc in hexanes) to afford the title compound as a yellow solid (64 mg, 0.14 mmol, 56% yield). mp 142–144 ºC; IR ν_{max}/cm^{-1} (film): 3027, 2924, 2852, 1564, 1492, 1380, 1287, 1197, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (1H, s), 8.51 (2H, d, *J* = 4.8 Hz), 8.38 (1H, d, *J* = 5.7 Hz), 7.49–7.12 (10H, m), 6.95 (1H, t, *J* = 4.8 Hz), 6.77 (1H, d, *J* = 5.7 Hz), 4.41 (3H, s), 4.20 (2H, d, *J* = 5.9 Hz), 3.34 (2H, t, *J* = 7.6 Hz), 3.13 (2H, t, *J* = 6.6 Hz), 3.04–2.88 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 162.8, 157.2, 151.1, 150.6, 142.0, 128.4, 127.4, 127.1, 122.3, 116.5, 106.6, 77.9, 69.3, 55.6, 29.1, 27.4; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 455.2, $C_{27}H_{27}N_4OS^+$ requires 455.2.

2–(((4–(benzylthio)pyridin–3–yl)methyl)thio)pyrimidine (3b)

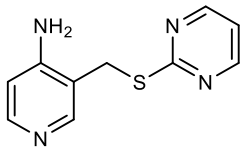


An oven dried 8 mL vial with a stir bar and septa cap was charged with sodium hydride (60% dispersion in mineral oil, 15 mg, 1.5 equiv) and placed under a nitrogen atmosphere. THF (1.0 mL) was added, the suspension was cooled to 0 ºC and benzyl mercaptan (32 μL, 0.38 mmol) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the septa cap was briefly removed and triphenyl(3–((pyrimidin–2–ylthio)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) was added in one portion. The reaction was

[**] Vacuum was applied very briefly (less than a second) using a Schlenk manifold so that negligible solvent loss occurs.

subjected to three rapid cycles of vacuum/nitrogen backfill[††], the ice bath removed and the reaction stirred for 12 hours while warming to room temperature. The reaction was quenched with H_2O (2.0 mL), the aqueous layer was separated and extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with a saturated aqueous solution of brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (neutralized silica gel: 50% EtOAc in hexanes) followed by flash chromatography (silica gel, gradient elution: 50% EtOAc/hexanes with 1% AcOH to 100% EtOAc with 3% NEt_3) to afford the title compound as a yellow oil (43 mg, 0.13 mmol, 53% yield). IR ν_{max}/cm^{-1} (film): 3029, 2924, 1563, 1547, 1378, 1193, 1181, 713; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.56 (1H, br), 8.44 (2H, d, J = 4.8 Hz), 8.22 (1H, br), 7.39–7.15 (5H, m), 7.06 (1H, d, J = 5.0 Hz), 6.88 (1H, t, J = 4.8 Hz), 4.36 (2H, s), 4.16 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.4, 157.2, 149.9, 148.3, 148.1, 135.2, 130.5, 128.8, 128.7, 127.7, 119.9, 116.6, 36.3, 30.5; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 325.1, $C_{17}H_{16}N_3S_2^+$ requires 326.1.

3–((pyrimidin–2–ylthio)methyl)pyridin–4–amine (3c)

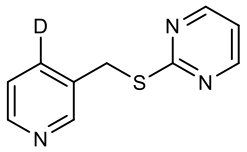


An oven dried 8 mL vial with a stir bar and septa cap was charged with triphenyl(3–((pyrimidin–2–ylthio)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol), sodium azide (20 mg, 0.31 mmol), and placed under a nitrogen atmosphere. DMSO (167 μL) was added, the cap was wrapped with parafilm and the reaction mixture was heated overnight at 120 ºC. The reaction was cooled to room temperature, diluted with EtOAc (2 mL), and a saturated aqueous solution of $NaHCO_3$ (2 mL). The aqueous layer was extracted a further three times with EtOAc (2 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo* into an oven dried 8 mL vial equipped with a stir bar. The residue was subjected to three

[††] Vacuum was applied very briefly (less than a second) using a Schlenk manifold so that negligible solvent loss occurs.

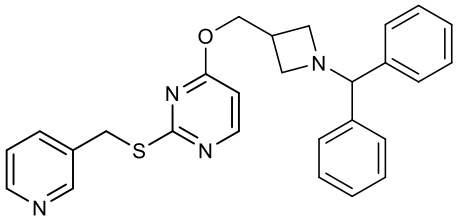
cycles of vacuum/nitrogen backfill before addition of a 9:1 solution of DMF and H_2O (250 μL). The reaction mixture was stirred at 100 ºC overnight before being cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography (neutralized silica gel, gradient elution: 3% MeOH in CH_2Cl_2 to 7.5% MeOH in CH_2Cl_2) followed by filtration through a plug of basic alumina eluting with 100% EtOAc and then 10% MeOH in CH_2Cl_2 to afford the title compound as a yellow oil (31 mg, 0.14 mmol, 57% yield). IR ν_{max}/cm^{-1} (film): 3339, 3207, 3034, 2927, 1598, 1584, 1548, 1379, 1183, 906, 727; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (2H, d, *J* = 4.8 Hz), 8.26 (1H, s), 8.11 (1H, d, *J* = 5.6 Hz), 7.01 (1H, t, *J* = 4.9 Hz), 6.50 (1H, d, *J* = 5.6 Hz), 4.89 (2H, br), 4.37 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 157.3, 151.7, 150.9, 149.0, 116.8, 116.6, 109.9, 29.7; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 219.1, $C_{10}H_{11}N_4S^+$ requires 219.1.

2–(((pyridin–3–yl–4–d)methyl)thio)pyrimidine (3d)



An oven–dried 8 mL vial equipped with a stir bar was charged with the triphenyl(3–((pyrimidin–2–ylthio)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol), K_2CO_3 (52 mg, 0.38 mmol), and placed under a nitrogen atmosphere. CD_3OD:D_2O 9:1 (750 μL) was added at room temperature and the reaction was stirred for 12 hours. The reaction mixture was diluted with CH_2Cl_2 (2 mL) and the mixture was dried (MgSO4), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, gradient elution: 50% EtOAc in hexanes with 1% AcOH to 75% EtOAc in hexanes with 3% NEt_3) to afford the title compound as a colorless oil (38 mg, 0.19 mmol, 75% yield). IR ν_{max}/cm^{-1} (film): 3659, 3589, 3034, 2956, 2921, 1564, 1548, 1381, 1203, 651; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, br), 8.60–8.43 (3H, m), 7.33–7.18 (1H, m), 6.99 (1H, t, *J* = 4.9 Hz), 4.41–4.35 (0.58H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 157.3, 150.3, 148.4, 136.1 (t, *J* = 25.3 Hz), 133.8, 123.3, 116.8, 32.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 207.1, $C_{10}H_9DN_3S^+$ requires 205.1

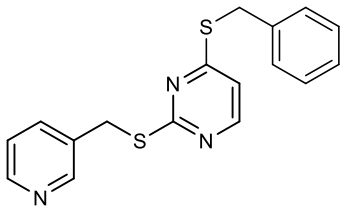
4–((1–benzhydrylazetidin–3–yl)methoxy)–2–((pyridin–3–ylmethyl)thio)pyrimidine (4a)



An oven dried 8 mL vial with a stir bar and septa cap was charged with sodium hydride (60% dispersion in mineral oil, 1.5 equiv) and placed under a nitrogen atmosphere. THF (250 μL) was added, the suspension was cooled to 0 ºC and a solution of (1–benzhydrylazetidin–3–yl)methanol (95 mg, 0.38 mmol) in THF (250 μL) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the septa cap was briefly removed and triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill[‡‡], the ice bath removed, and the reaction stirred for 12 hours while warming to room temperature. The reaction was quenched with H_2O (2.0 mL), the aqueous layer was separated and extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with a saturated aqueous solution of brine, dried ($MgSO_4$), filtered and concentrated *in vacuo.* The crude material was purified by flash chromatography (neutralized silica gel: 50% EtOAc in Hexanes to 60% EtOAc in hexanes) to provide title compound as a yellow oil (77 mg, 0.17 mmol, 68% yield); IR ν_{max}/cm^{-1} (film): 3058, 3026, 2951, 2831, 1710, 1551, 1440, 1316, 1230; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69–8.68 (1H, d, *J* = 1.7 Hz), 8.49 (1H, dd *J* = 4.7, 1.2 Hz), 8.21 (1H, d, *J* = 5.7 Hz), 7.77 (1H, dt, *J* = 7.8, 3.7 Hz), 7.41–7.39 (4H, m), 7.28–7.16 (7H, m), 6.37 (1H, d, *J* = 5.7 Hz), 4.46 (2H, d, *J* = 7.0 Hz), 4.37–4.34 (3H, m), 3.29 (2H, t, *J* = 7.5 Hz), 2.97 (2H, t, *J* = 13.1 Hz), 2.87–2.79 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 168.6, 157.1, 150.0, 148.3, 141.9, 136.2, 133.8, 128.3, 127.3, 127.0, 123.2, 104.2, 77.8, 68.6, 56.0, 32.2, 28.7; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 455.2, $C_{27}H_{27}N_4OS^+$ requires 455.2.

[‡‡] Vacuum was applied very briefly (less than a second) using a Schlenk manifold so that negligible solvent loss occurs.

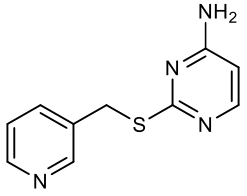
4–(benzylthio)–2–((pyridin–3–ylmethyl)thio)pyrimidine (4b)



An oven dried 8 mL vial with a stir bar and septa cap was charged with sodium hydride (60% dispersion in mineral oil, 1.1 eq) and placed under a nitrogen atmosphere. THF (1.0 mL) was added, the suspension was cooled to 0 ºC and benzyl mercaptan (32 μL, 0.28 mmol) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the septa cap was briefly removed and triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill[§§], the ice bath was removed and the reaction stirred for 12 hours while warming to room temperature. The reaction was quenched with H_2O (2.0 mL), the aqueous layer was separated and extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with a saturated aqueous solution of brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel: 50% EtOAc in Hexanes) to provide title compound as a yellow oil (66 mg, 0.20 mmol, 81% yield). IR ν_{max}/cm^{-1} (film): 3031, 2929, 1548, 1516, 1314, 904; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.66 (1H, s), 8.48 (1H, d *J* = 3.7 Hz), 8.14 (1H, d, *J* = 5.4 Hz), 7.74–7.72 (1H, m), 7.36–7.21 (6H, m), 6.82 (1H, d, *J* = 3.7 Hz), 4.38 (2H, s), 4.36 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 169.9, 154.5, 150.1, 148.5, 136.5, 136.3, 133.5, 128.8, 128.6, 127.4, 123.3, 114.4, 33.5, 32.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 326.1, $C_{17}H_{16}N_3S_2^+$ requires 326.1.

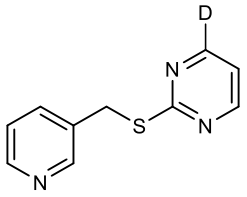
[§§] Vacuum was applied very briefly (less than a second) using a Schlenk manifold so that negligible solvent loss occurs.

4–((1–benzhydrylazetidin–3–yl)methoxy)–2–((pyridin–3–ylmethyl)thio)pyrimidine (4c)



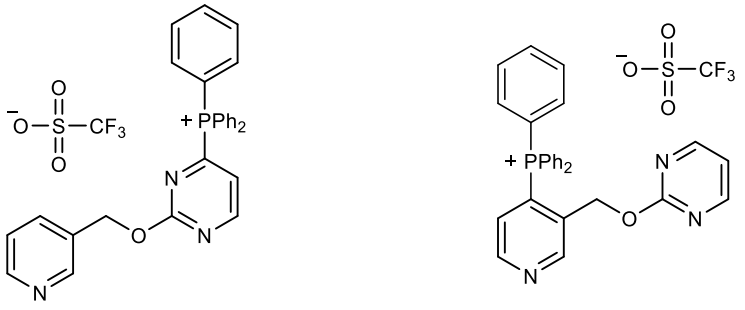
An oven dried 8 mL vial with a stir bar and septa cap was charged with triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) and sodium azide (13 mg, 0.31 mmol), and placed under a nitrogen atmosphere. DMSO (167 μL) was added, the cap was wrapped with parafilm and the reaction mixture was heated overnight at 120 ºC. The reaction was cooled to room temperature, diluted with EtOAc (2 mL), and quenched with a saturated aqueous solution of $NaHCO_3$ (2 mL). The aqueous layer was extracted a further three times with EtOAc (2 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo* into an oven dried 8 mL vial equipped with a stir bar. The residue was subjected to three cycles of vacuum/nitrogen backfill before addition of a 9:1 solution of DMF and H_2O (250 μL). The reaction mixture was stirred at 100 ºC for 44 hours before being cooled to room temperature and concentrated *in vacuo*. The solution was purified by flash chromatography (silica gel: 6% MeOH in CH_2Cl_2) to provide title compound as a white solid (36 mg, 0.16 mmol, 66% yield). mp 114–116 ºC; IR ν_{max}/cm^{-1} (film): 3303, 3147, 3029, 1641, 1580, 1540, 1478, 1354, 904; ^1H NMR (400 MHz, CDCl3) δ: 8.67 (1H, s), 8.46 (1H, d, *J* = 3.6 Hz), 8.04 (1H, d, *J* = 5.8 Hz), 7.75 (1H, dt, *J* = 7.9, 3.7 Hz), 7.22 (1H, dd, *J* = 7.8, 4.8 Hz), 6.12 (1H, d, *J* = 5.8 Hz), 4.93 (2H, br), 4.33 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 162.4, 156.0, 150.2, 148.2, 136.4, 134.3, 123.3, 101.2, 32.0; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 219.1, $C_{10}H_{11}N_4S^+$ requires 219.1.

2–((pyridin–3–ylmethyl)thio)pyrimidine–4–d (4d)



An oven dried 8 mL vial was charged with K_2CO_3 (52 mg, 0.38 mmol) and triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) and subjected to three rapid vacuum/nitrogen backfills. CD_3OD:D_2O 9:1 (750 μL) was added at room temperature and the reaction was stirred for 12 hours. The solution was then diluted with CH_2Cl_2 (2 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (neutralized silica gel: 50% EtOAc in Hexanes) to provide title compound as a yellow oil (37.6 mg, 0.19 mmol, 74% yield); IR ν_{max}/cm^{-1} (film): 3385, 3029, 2923, 1730, 1534, 1403, 1329, 1205; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.71 (1H, s), 8.53 (1H, d, J = 4.8 Hz), 8.47 (1H, d, J = 4.2 Hz), 7.77 (1H, d, J = 7.8 Hz), 7.23 (1H, dd, J = 7.8, 4.8 Hz), 6.98 (1H, d, J = 4.8 Hz), 4.38 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 157.2, 159.9 (t, J = 27.9 Hz), 150.3, 148.3, 136.3, 133.7, 123.2, 116.6, 32.2; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 205.1, $C_{10}H_9DN_3S^+$ requires 205.1.

Triphenyl(2–(pyridin–3–ylmethoxy)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (2v)

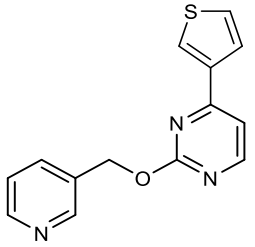


>20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure C using 2–(pyridin–3–ylmethoxy)pyrimidine (190 mg, 1.01 mmol), Tf_2O (342 μL, 2.02 mmol), PPh_3 (531 mg, 2.02 mmol), Et_3N (282 μL, 2.02 mmol) and CH_2Cl_2 (10.1 mL). After the purification procedure, the title compound was isolated as a red amorphous solid (388 mg, 0.65 mmol, 64% yield); IR ν_{max}/cm^{-1} (film): 3063, 1559, 1545, 1437, 1420, 1356, 1259, 1149, 1029, 726, 634; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.05 (1H, dd, J = 7.8, 5.0

Hz), 8.60–8.59 (2H, m), 7.91–7.67 (17H, m), 7.31 (1H, dd, *J* = 7.8, 4.7 Hz), 5.45 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.7 (d, *J* = 19.5 Hz), 163.5 (d, *J* = 8.5 Hz), 156.5, 155.4, 149.2, 136.2, 136.1 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 13.1 Hz), 123.6, 122.0 (d, *J* = 20.5 Hz), 120.7 (q, *J* = 321.1 Hz), 115.1 (d, *J* = 89.1 Hz), 67.8; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.31; *m/z* LRMS (ESI + APCI) found $[M - OTf]^+$ 448.2, $C_{28}H_{23}N_3OP^+$ requires 448.2.

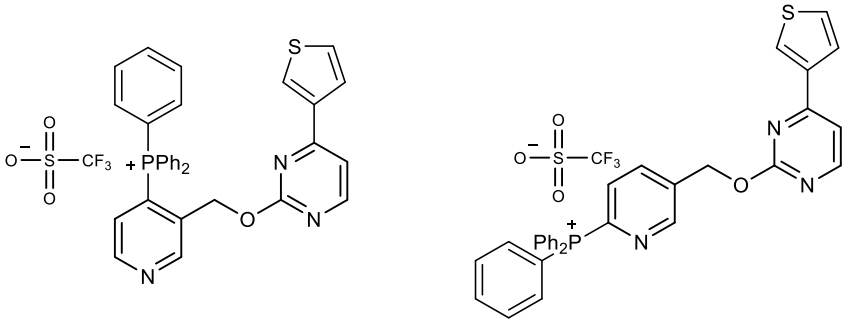
2–(pyridin–3–ylmethoxy)–4–(thiophen–3–yl)pyrimidine



An oven dried 8 mL vial was charged with triphenyl(2–((pyridin–3–ylmethyl)thio)pyrimidin–4–yl)phosphonium trifluoromethanesulfonate (152.0 mg, 0.25 mmol) and 3–thienylboronic acid (65.1 mg, 0.508 mmol) and added to a glovebox. Bis(1,5–cyclooctadiene)nickel(0) (7.0 mg, 0.025 mmol), SiPRHCl (11.0 mg, 0.025 mmol), sodium tertbutoxide (2.5 mg, 0.025 mmol), potassium phosphate tribasic (107.8 mg, 0.508 mmol) and 4A molecular sieves (170.5 mg) were added to the vial and sealed. The sealed vial was taken out of the glove box and THF (2.5 mL) was added. The solution stirred at room temperature for 20 min before being heated to 70°C for 24 hours. The solution was cooled to room temperature and quench with water. The organic layer was separated from the aqueous and the aqueous was extracted three times with CH_2Cl_2. The organic layers were combined, washed with brine once, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 100% EtOAc) followed by flash chromatography (silica gel: 90% EtOAc in Hexanes with 1% AcOH) to provide title compound as a yellow oil (33.6 mg, 0.12 mmol, 50% yield); IR ν_{max}/cm^{-1} (film): 3090, 2954, 2923, 1574, 1448, 1429, 1409, 1347, 1314, 1262, 1021, 786, 711; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (1H, s), 8.57 (1H, d, *J* = 4.8 Hz), 8.51 (1H, d, *J* = 5.2 Hz), 8.13 (1H, dd, *J* = 2.3, 1.2 Hz), 7.89 (1H, d, *J* = 7.8 Hz), 7.67 (1H, dd, *J* = 5.1, 1.1 Hz), 7.41–7.40 (1H, m), 7.32 (1H, dd, *J* = 7.8, 4.9 Hz), 7.22–7.21

(1H, m), 5.52 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 162.1, 159.8, 149.7, 149.4, 139.5, 136.0, 132.3, 127.4, 126.9, 126.0, 123.4, 111.0, 66.4; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 270.1, $C_{14}H_{12}N_3OS$ requires 270.1.

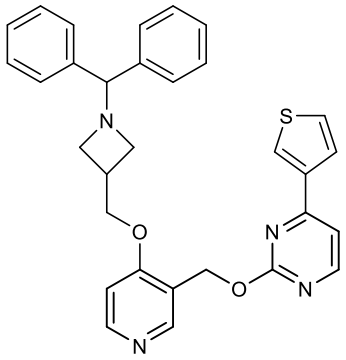
triphenyl(3–(((4–(thiophen–3–yl)pyrimidin–2–yl)oxy)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (2va)



20:1 (Major:Minor) Mixture of Isomers

Prepared according to general procedure D (except that the reaction was stirred at –50 °C) using 2–(pyridine–3–ylmethoxy)–4–(thiophen–3–yl)pyrimidine (195.7 mg, 0.73 mmol), Tf_2O (123 μL, 0.73 mmol), PPh_3 (209.6 mg, 0.80 mmol), DBU (109 μL, 0.73 mmol) and CH_2Cl_2 (7.3 mL). After the purification procedure, the title compound was isolated as white solid (445 mg, 0.66 mmol, 90% yield); IR ν_{max}/cm^{-1} (film): 3090, 3061, 1576, 1558, 1438, 1417, 1260, 1222, 1149, 1105, 1029, 721, 636; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.14 (1H, app d, *J* = 6.6 Hz), 8.91 (1H, app t, *J* = 4.6 Hz), 8.23 (1H, d, *J* = 5.2 Hz), 7.86 (1H, d, *J* = 1.5 Hz), 7.81–7.64 (15H, m), 7.40–7.35 (2H, m), 7.28 (1H, dd, *J* = 15.5, 5.0 Hz), 7.19 (1H, d, *J* = 5.2 Hz), 5.02 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.0, 161.6, 159.4, 152.9 (d, *J* = 7.7 Hz), 151.6 (d, *J* = 10.5 Hz), 138.7, 135.7 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 5.6 Hz), 134.2 (d, *J* = 10.5 Hz), 130.6 (d, *J* = 13.1 Hz), 128.7 (d, *J* = 9.3 Hz), 127.6, 126.9, 126.5 (d, *J* = 81.4 Hz), 125.7, 120.7 (q, *J* = 321.2 Hz), 116.1 (d, *J* = 89.2 Hz), 111.6, 64.6 (d, *J* = 4.2 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.04; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.73; *m/z* LRMS (ESI + APCI) found $[M – OTf]^+$ 530.2, $C_{27}H_{25}NP^+$ requires 530.1.

2–((4–((1–benzhydrylazetidin–3–yl)methoxy)pyridin–3–yl)methoxy)–4–(thiophen–3–yl)pyrimidine (6)



An oven dried 8 mL vial with a stir bar and septa cap was charged with sodium hydride (60% dispersion in mineral oil, 1.5 eq.) and placed under a nitrogen atmosphere. THF (375 μL) was added, the suspension was cooled to 0 ºC and a solution of (1–benzhydrylazetidin–3–yl)methanol (57 mg, 0.255 mmol) in THF (375 μL) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes before the septa cap was briefly removed and triphenyl(3–(((4–(thiophen–3–yl)pyrimidin–2–yl)oxy)methyl)pyridin–4–yl)phosphonium trifluoromethanesulfonate (102 mg, 0.15 mmol) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill[***], the ice bath removed, and the reaction stirred for 12 hours at 40ºC. The reaction was quenched with H_2O (2.0 mL), the aqueous layer was separated and extracted with Et_2O (10 mL x 3). The combined organic extracts were washed with a saturated aqueous solution of brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 90% EtOAc in Hexanes) to provide the title compound as a white solid (39 mg, 0.08 mmol, 50% yield); IR ν_{max}/cm^{-1} (film): 3027, 2952, 2839, 1594, 1576, 1412, 1341, 1269, 906, 727, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (1H, s), 8.47–8.46 (2H, m), 8.12 (1H, dd, *J* = 2.9, 1.2 Hz), 7.67 (1H, dd, *J* = 5.1, 1.2 Hz), 7.39–7.32 (5 H, m), 7.23–7.12 (7H, m), 6.81 (1H, d, *J* = 5.7 Hz), 5.55 (2H, s), 4.28 (1H, s), 4.18 (2H, d, *J* = 6.0 Hz), 3.26 (2H, t, *J* = 7.8 Hz), 3.05 (2H, t, *J* = 7.8 Hz), 2.88 (1H, m);^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 163.2, 162.0, 159.6, 151.6, 151.1, 141.9, 139.6, 128.3, 127.4, 127.3, 127.0, 126.7, 126.0,

[***] Vacuum was applied very briefly (less than a second) using a Schlenk manifold so that negligible solvent loss occurs.

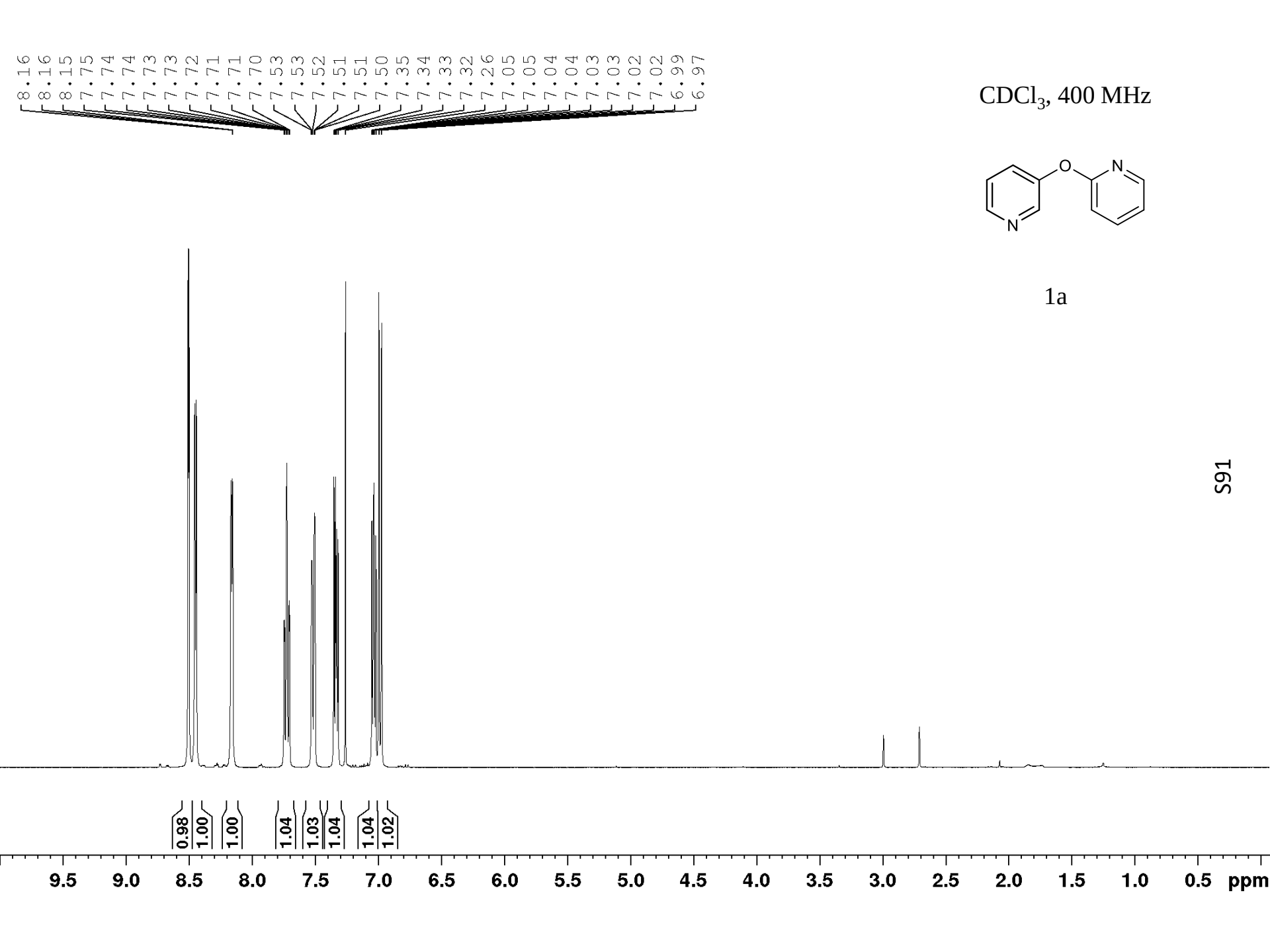
120.8, 110.8, 106.6, 77.9, 69.3, 62.4, 55.5, 29.0; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 521.3, $C_{31}H_{29}N_4O_2S^+$ requires 520.2.

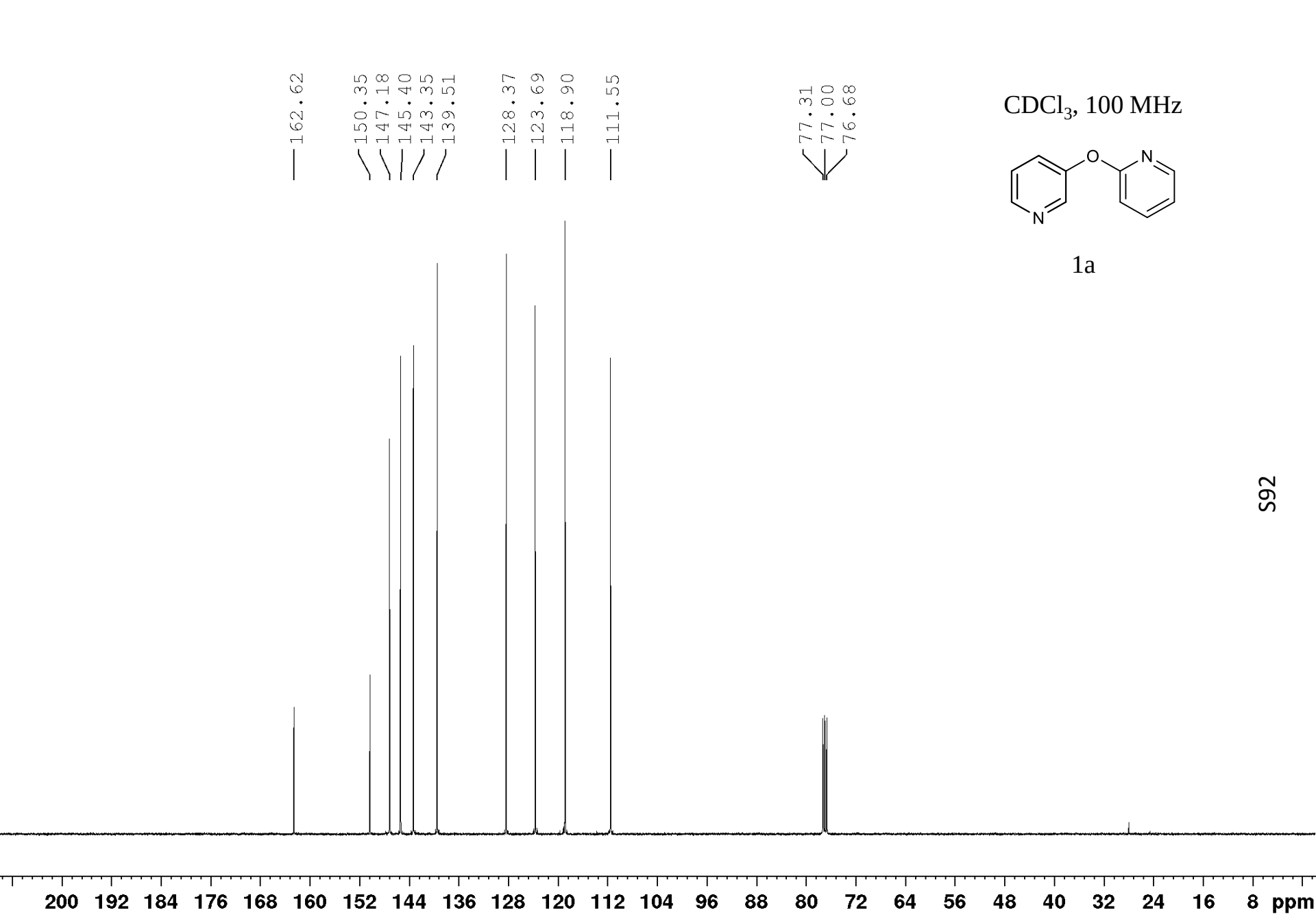
8. References

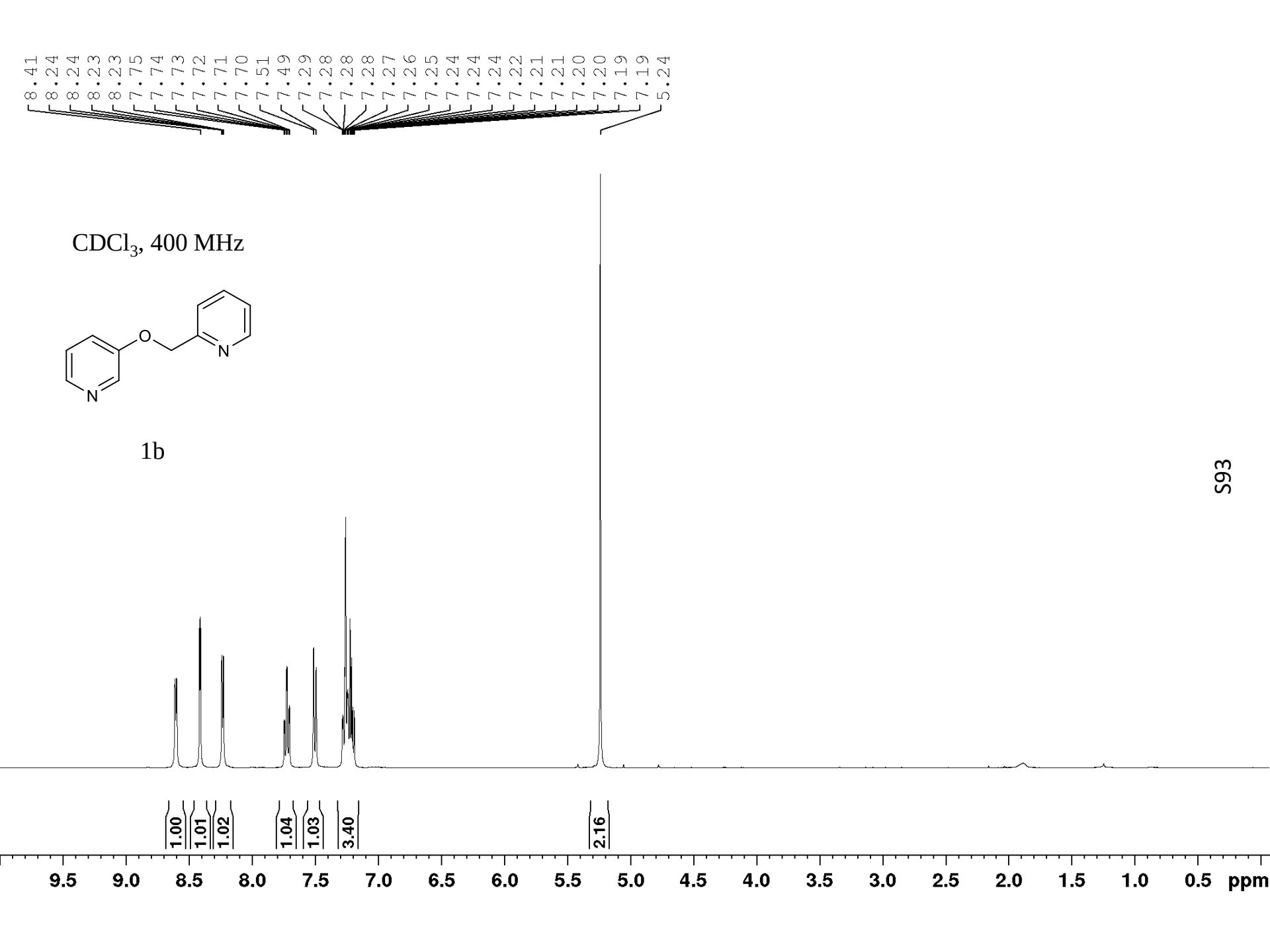
S1. D. D. Perrin, W. L. F. Amarego, Purification of Laboratory Chemicals (Pergamon, Press, Oxford. ed. 3, 1988).

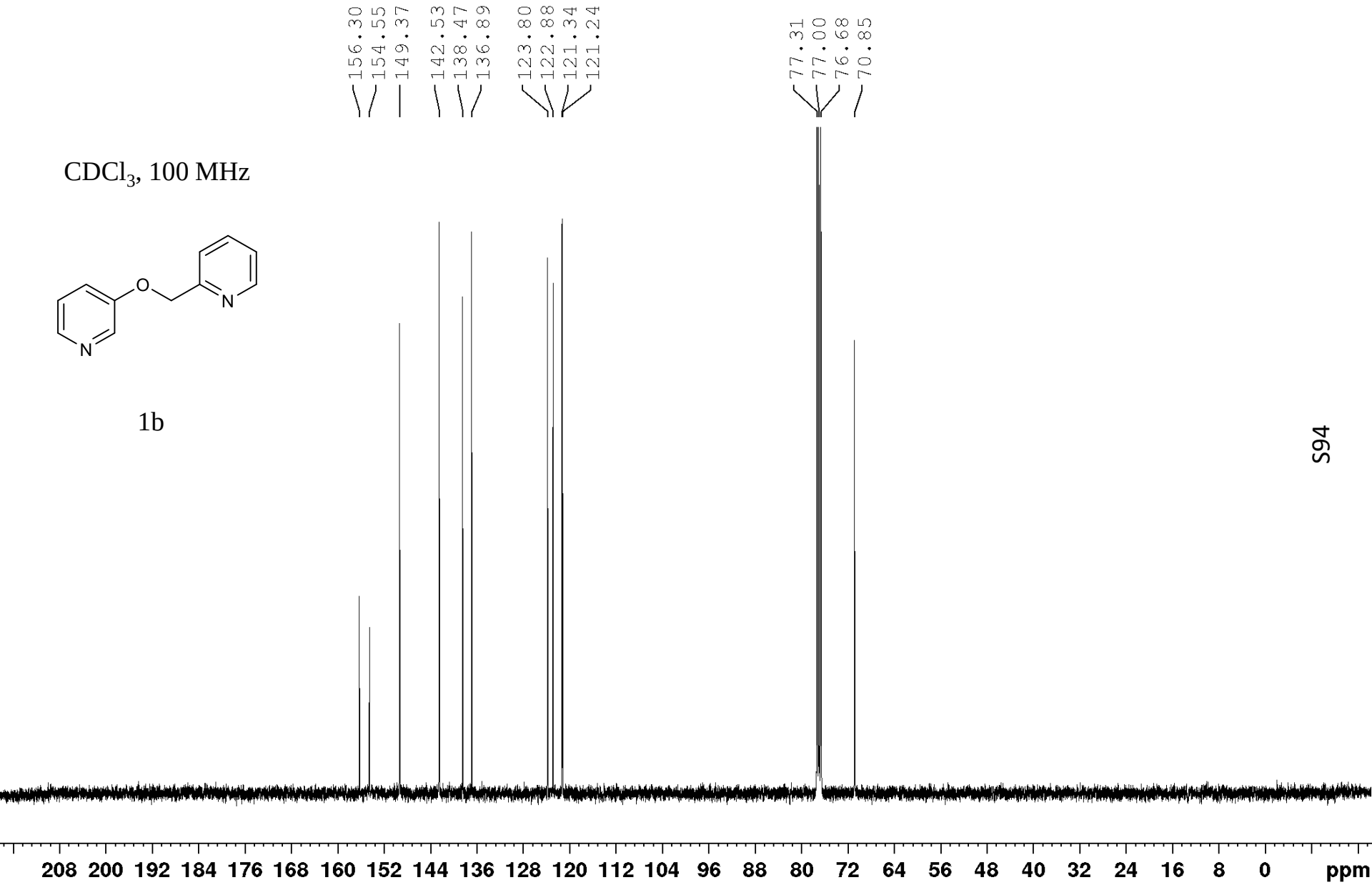
S2. Kundu, D.; Tripathy, M.; Maity, P.; Ranu, B. C. Cobalt–Catalyzed Intermolecular C(sp^2)–O Cross–Coupling. *Chem. Eur. J*. 2015, 21, pp. 8727–8732.

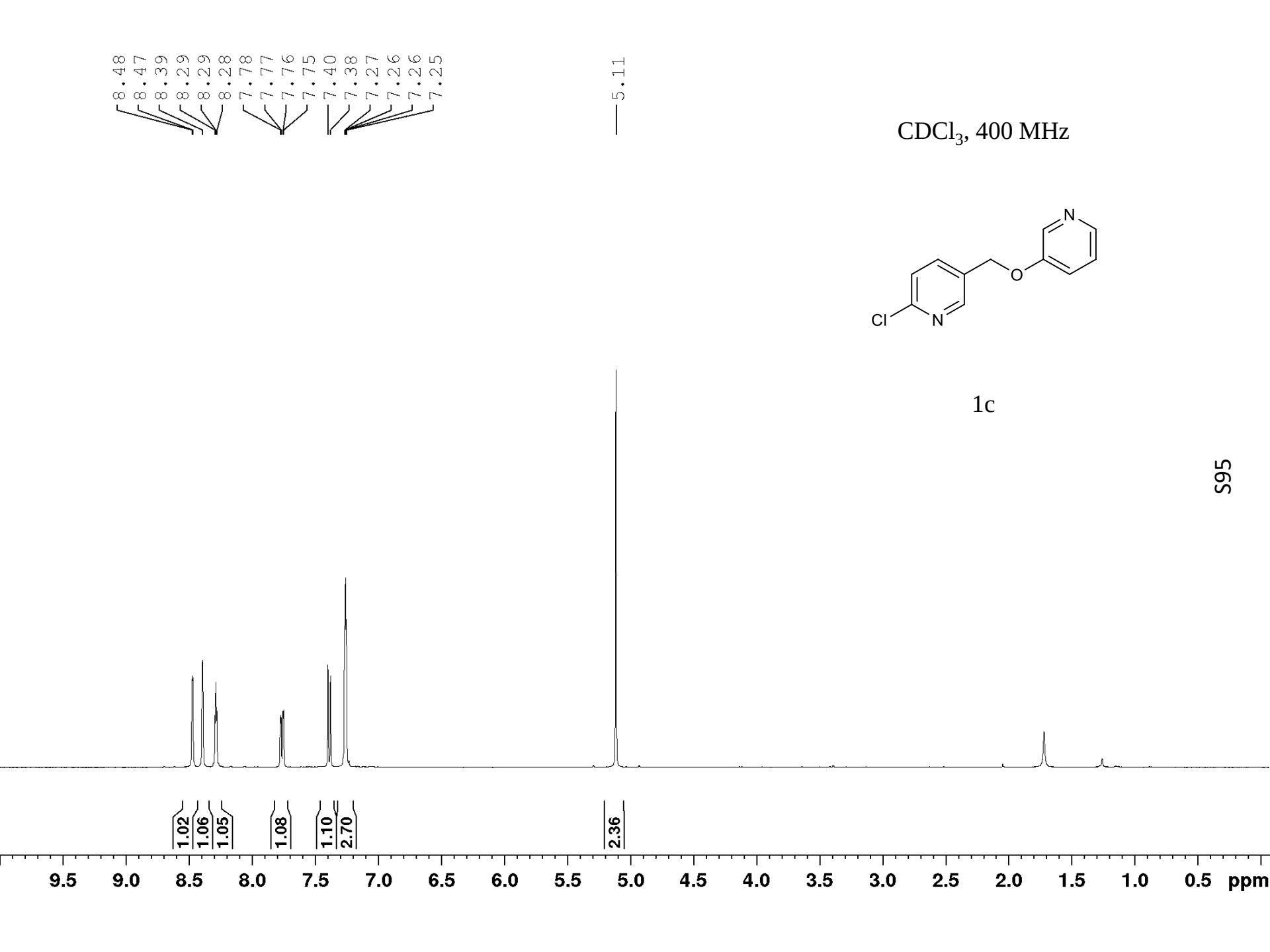
S3. Gao, M.; Wang, M.; Zheng, Q–H. Synthesis of [^{11}C]MK–1064 as a new PET radioligand for imaging of orexin–2 receptor. *Bioorg. Med. Chem. Lett*. 2016, 26, 3694–3699.

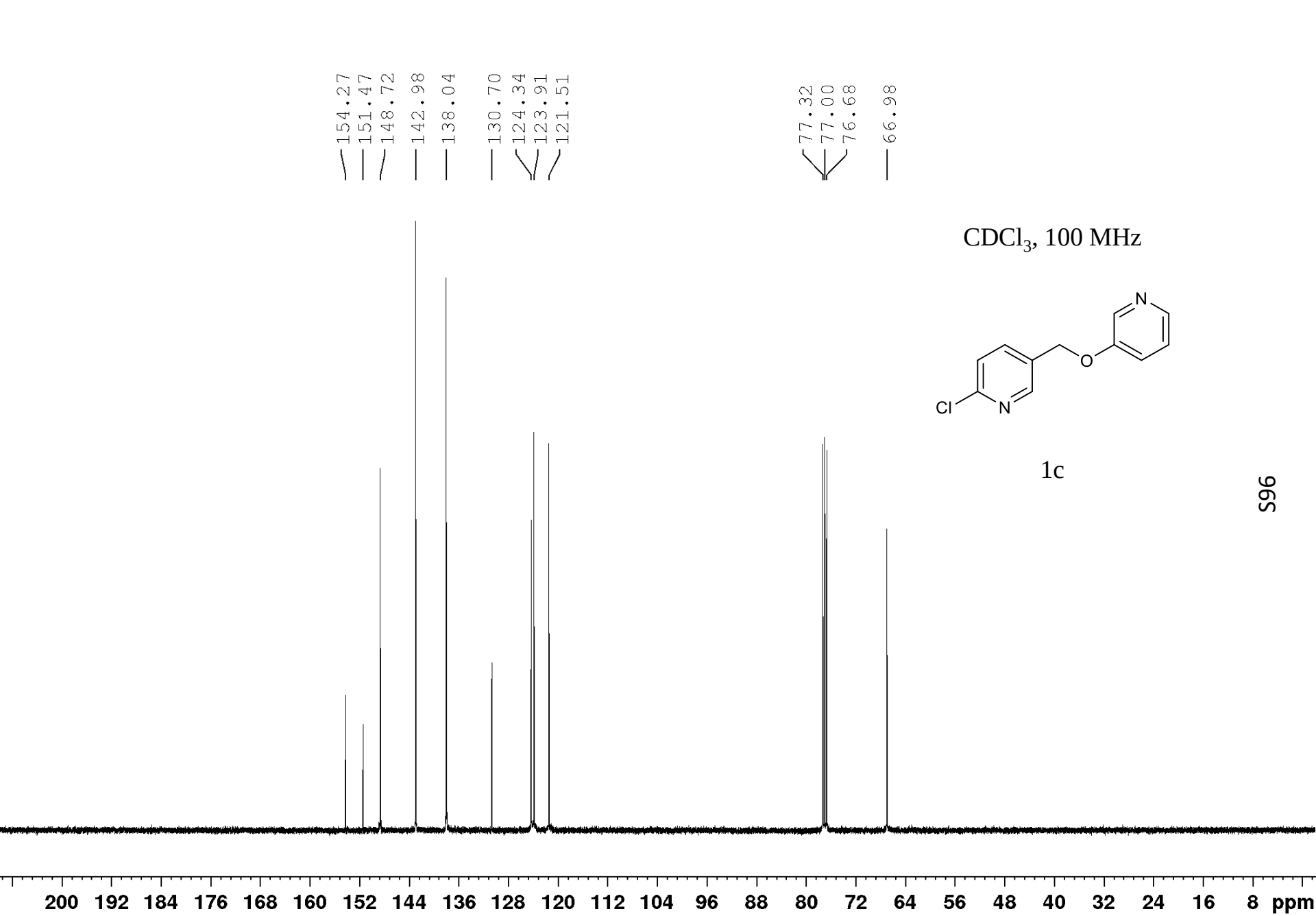

8.16
8.16
8.15
7.75
7.74
7.74
7.73
7.73
7.72
7.71
7.71
7.70
7.53
7.53
7.52
7.51
7.51
7.50
7.35
7.34
7.33
7.32
7.26
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
6.99
6.97
CDCl3, 400 MHz
O
N
N
1a
S91
0.98
1.00
1.00
1.04
1.03
1.04
1.04
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

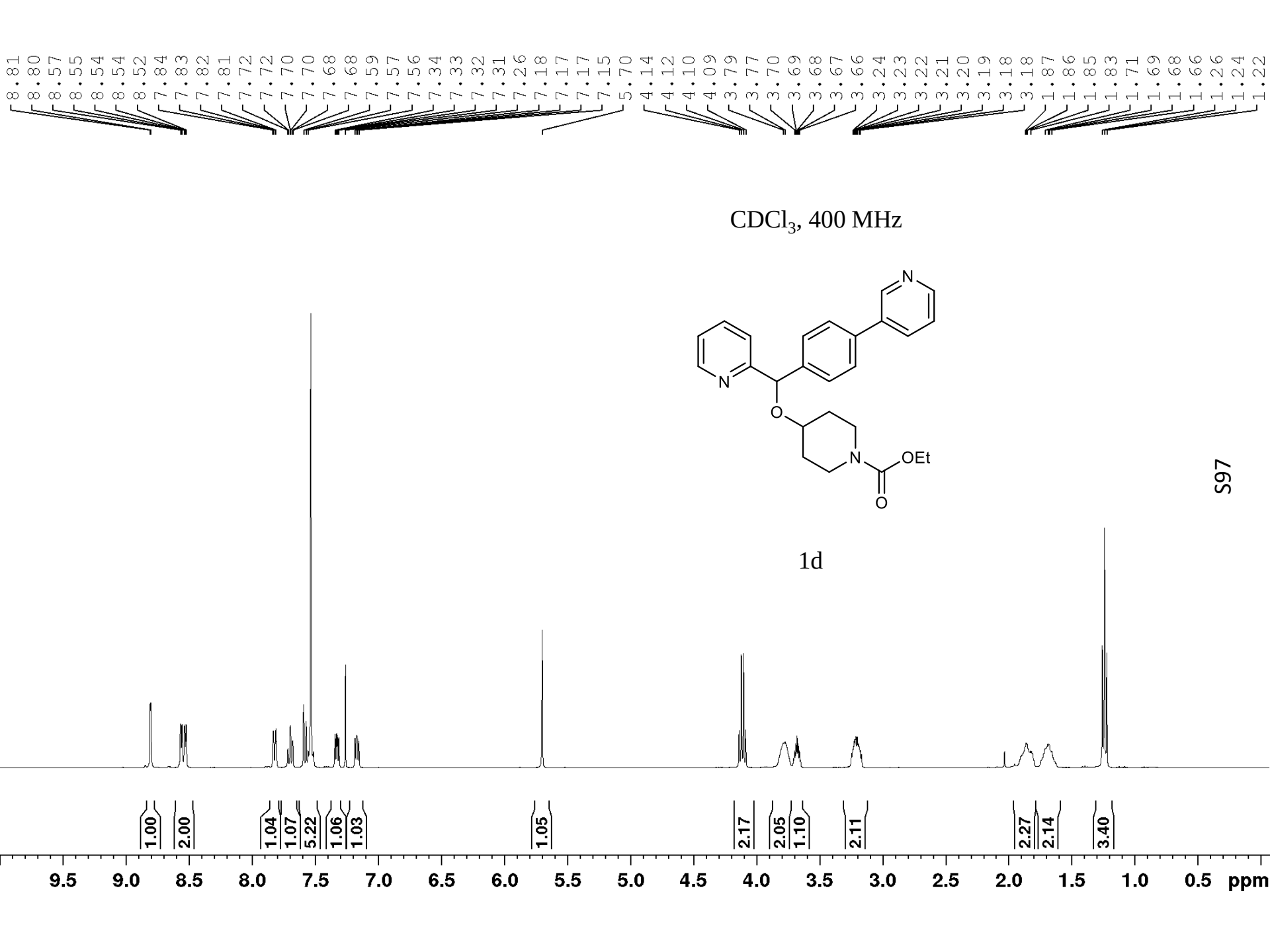

162.62
150.35
147.18
145.40
143.35
139.51
128.37
123.69
118.90
111.55
77.31
77.00
76.68
CDCl3, 100 MHz
O
N
N
1a
S92
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


8.41
8.24
8.24
8.23
8.23
7.75
7.74
7.73
7.72
7.71
7.70
7.51
7.49
7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.24
7.22
7.21
7.21
7.20
7.20
7.19
7.19
5.24
CDCl3, 400 MHz
O
N
N
1b
S93
1.00
1.01
1.02
1.04
1.03
3.40
2.16
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
ppm


156.30
154.55
149.37
142.53
138.47
136.89
123.80
122.88
121.34
121.24
77.31
77.00
76.68
70.85
CDCl3, 100 MHz
O
N
N
1b
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

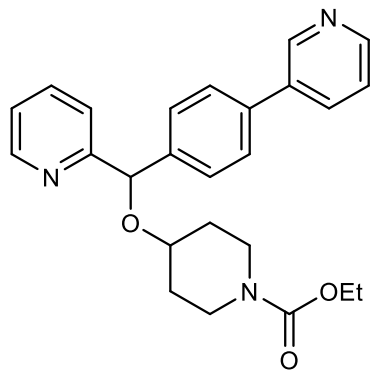

8.48
8.47
8.39
8.29
8.29
8.28
7.78
7.77
7.76
7.75
7.40
7.38
7.27
7.26
7.26
7.25
5.11
CDCl3, 400 MHz
N
O
Cl
N
1c
S95
1.02
1.06
1.05
1.08
1.10
2.70
2.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


154.27
151.47
148.72
142.98
138.04
130.70
124.34
123.91
121.51
77.32
77.00
76.68
66.98
CDCl3, 100 MHz
N
O
Cl
N
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 8 ppm


8.81
8.80
8.57
8.55
8.54
8.54
8.52
7.84
7.83
7.82
7.81
7.72
7.72
7.70
7.70
7.68
7.68
7.59
7.57
7.56
7.34
7.33
7.32
7.31
7.26
7.18
7.17
7.17
7.15
5.70
4.14
4.12
4.10
4.09
3.79
3.77
3.70
3.69
3.68
3.67
3.66
3.24
3.23
3.22
3.21
3.20
3.19
3.18
3.18
1.87
1.86
1.85
1.83
1.71
1.69
1.68
1.66
1.26
1.24
1.22
CDCl3, 400 MHz
N
N
O
N
OEt
O
1d
S97
1.00
2.00
1.04
1.07
5.22
1.06
1.03
1.05
2.17
2.05
1.10
2.11
2.27
2.14
3.40
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
ppm

161.97
155.45
148.90
148.41
148.20
141.52
137.03
136.87
136.14
134.14
127.43
127.14
123.43
122.43
120.58
81.28
77.31
77.00
76.68
72.49
61.17
41.01
40.97
31.01
14.62

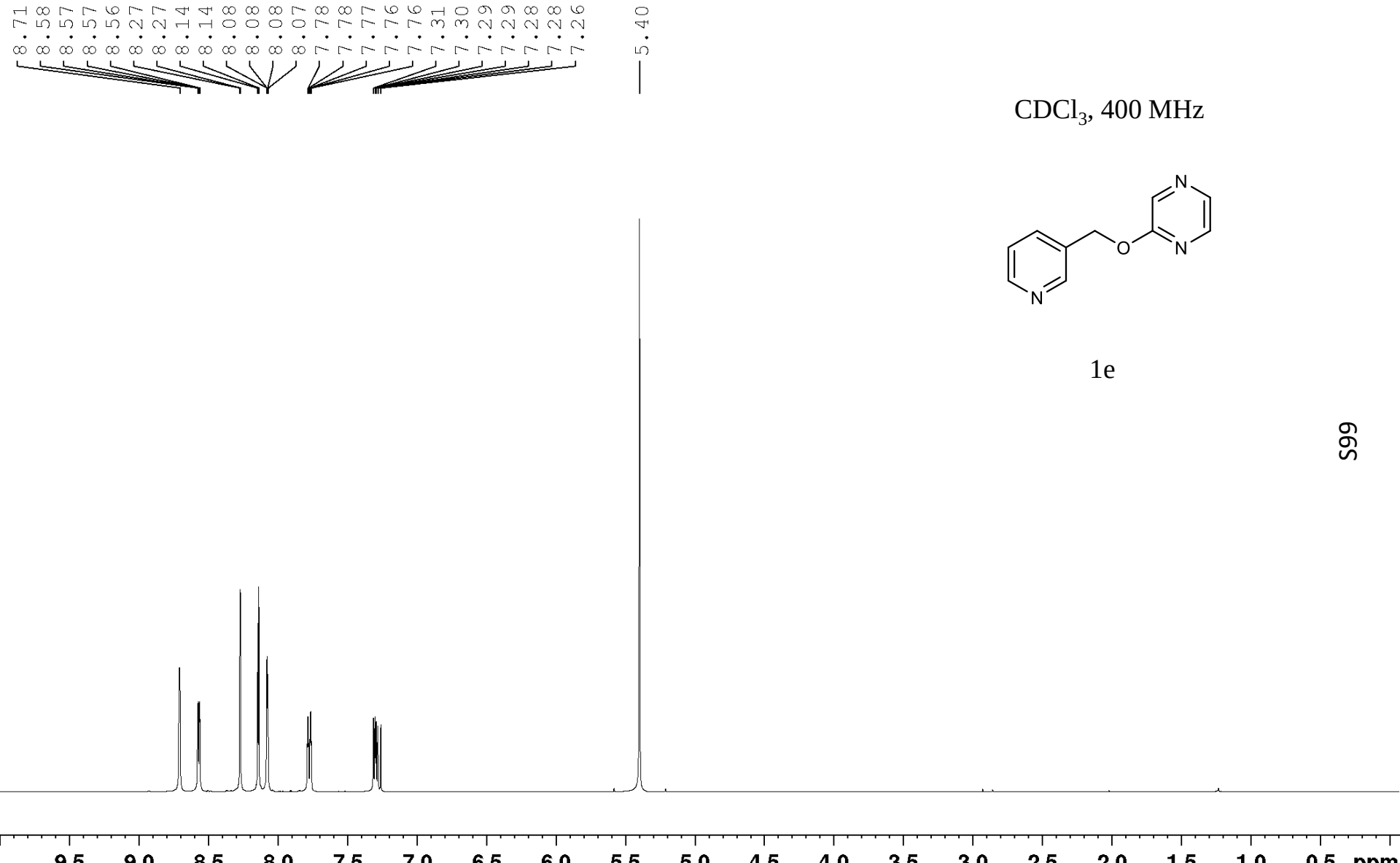
$CDCl_3$, 100 MHz

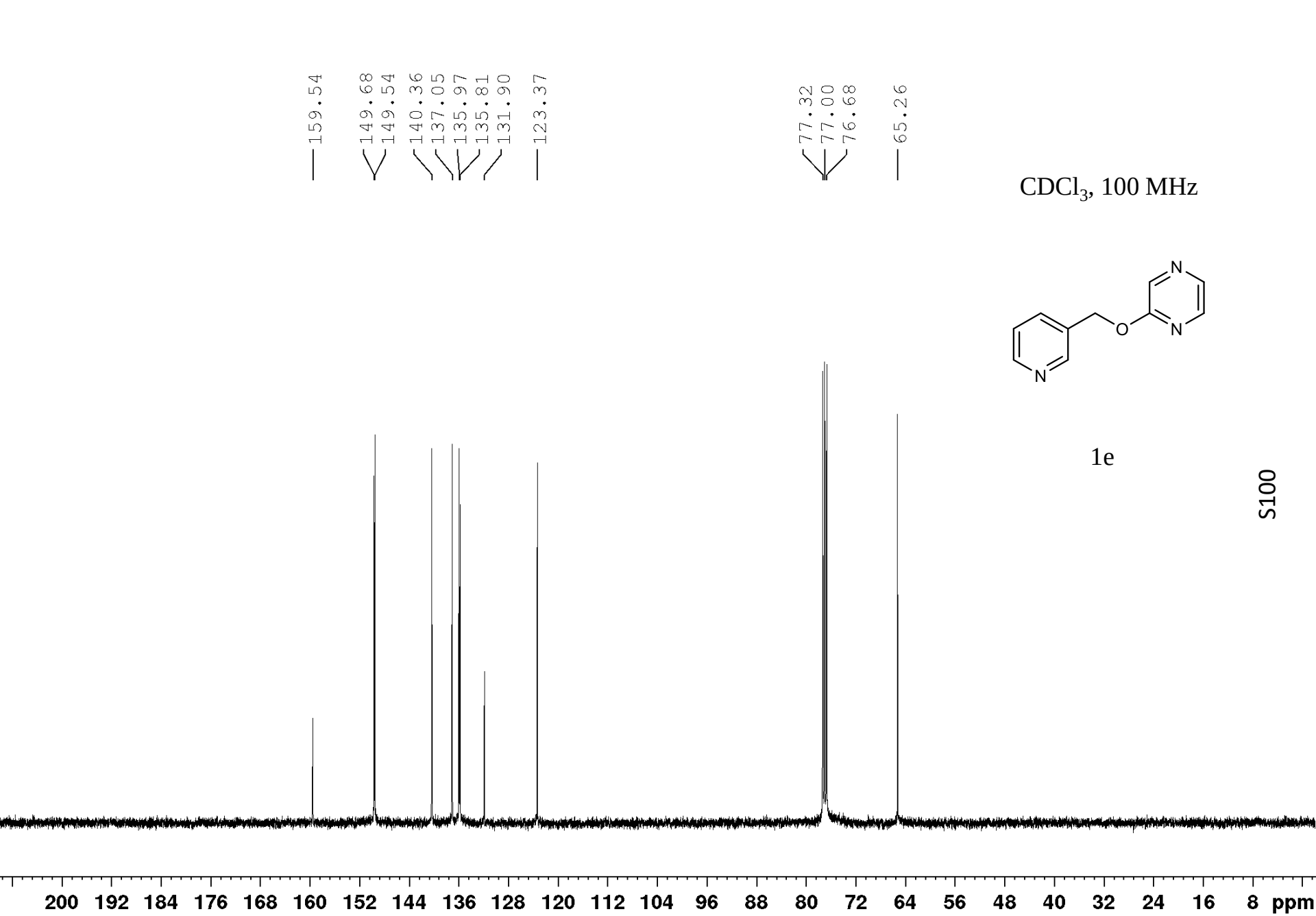


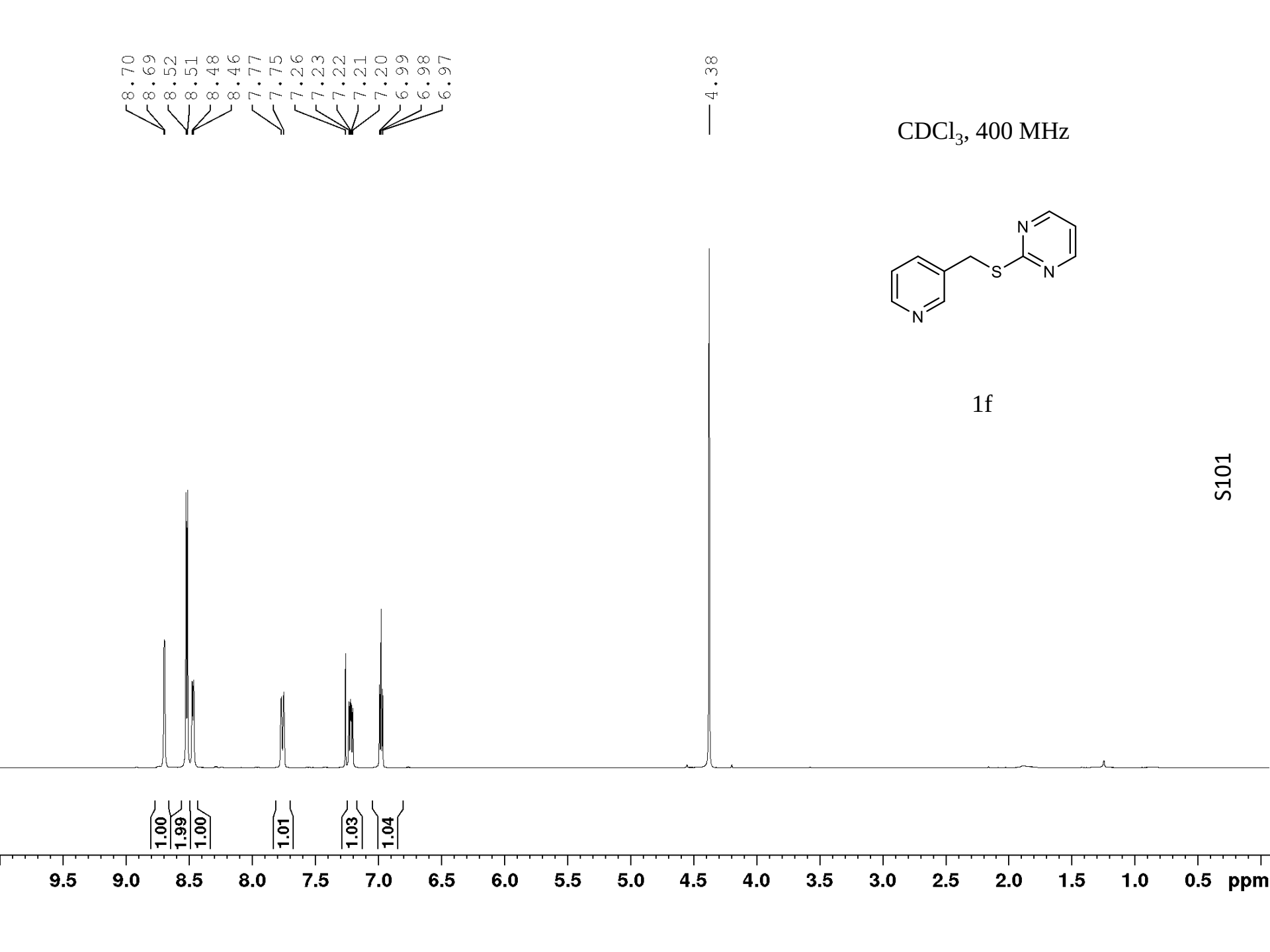
1d

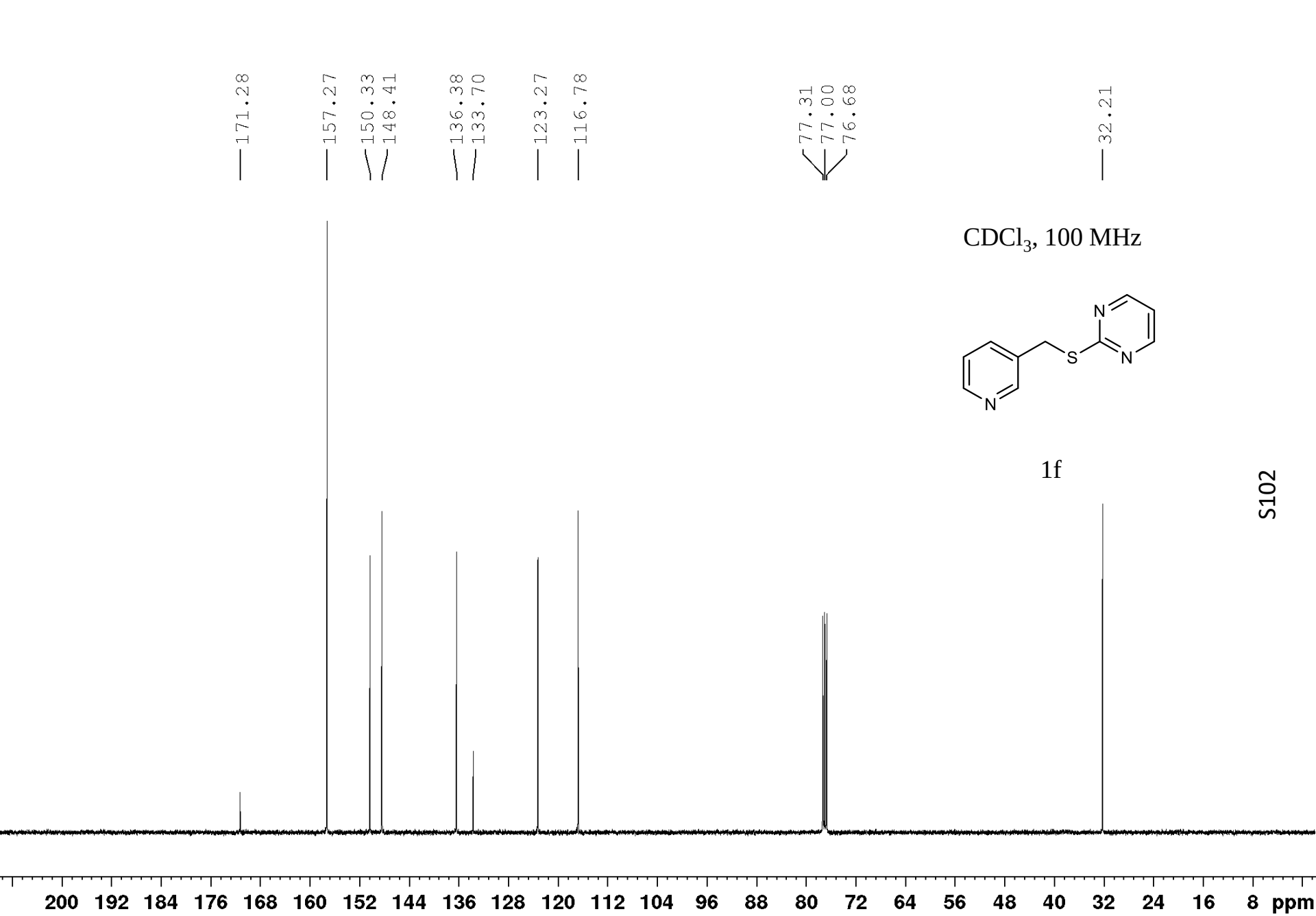
S98

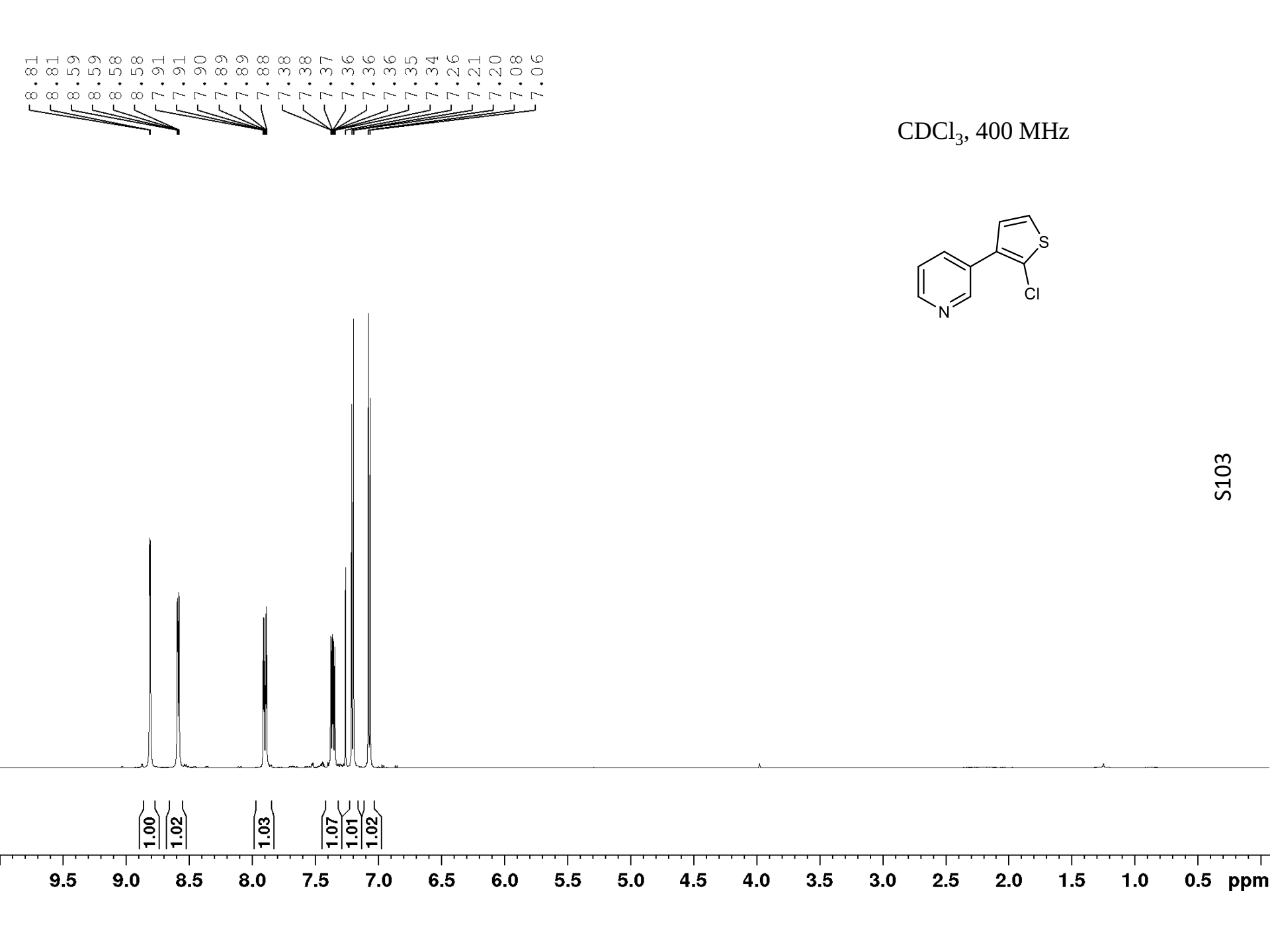
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

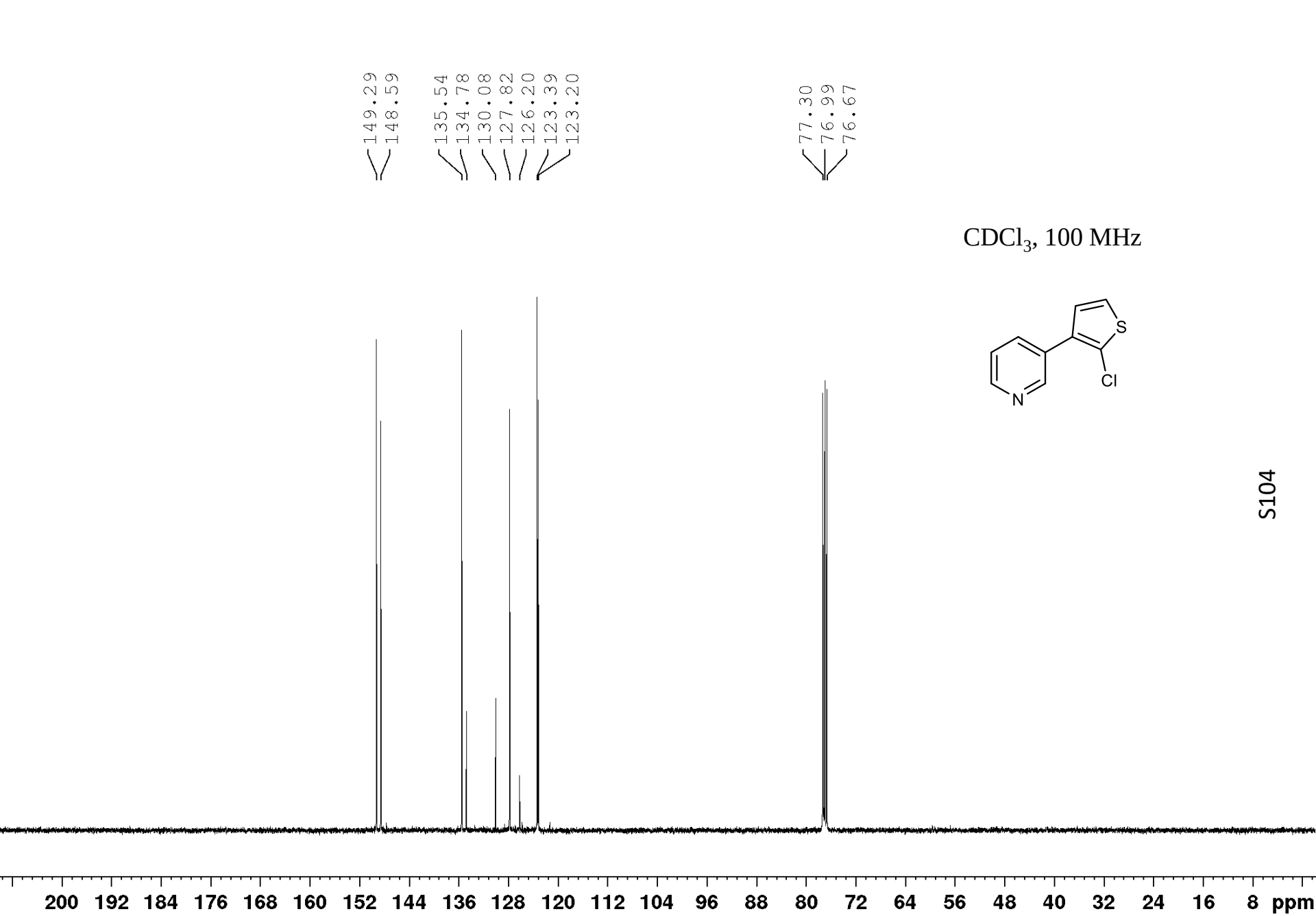

8.71
8.58
8.57
8.57
8.56
8.27
8.27
8.14
8.14
8.08
8.08
8.08
8.07
7.78
7.78
7.77
7.76
7.76
7.31
7.30
7.29
7.29
7.28
7.28
7.26
5.40
CDCl3, 400 MHz
N
O
N
N
1e
S99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

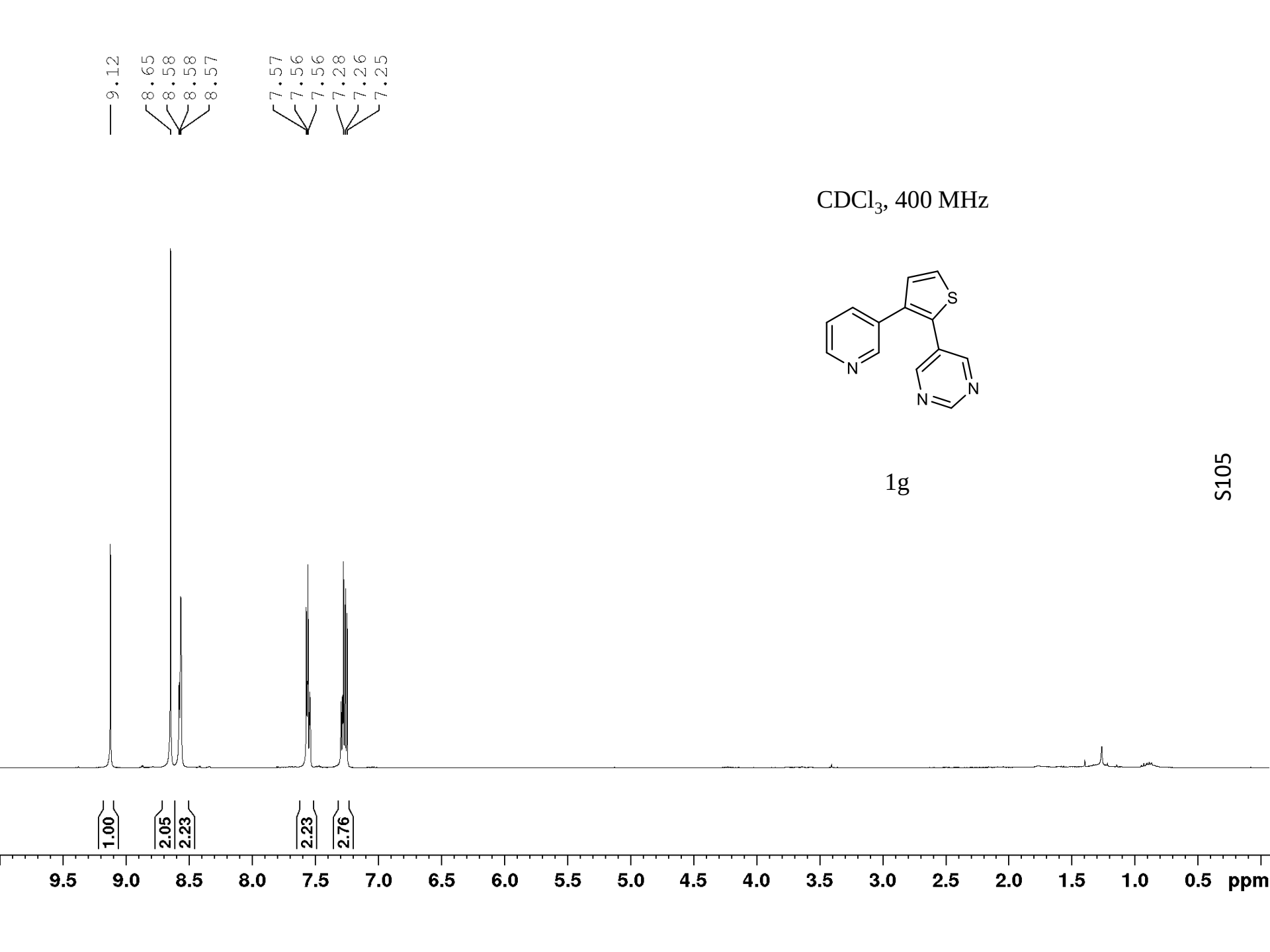

159.54
149.68
149.54
140.36
137.05
135.97
135.81
131.90
123.37
77.32
77.00
76.68
65.26
CDCl3, 100 MHz
N
O
N
N
1e
S100
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

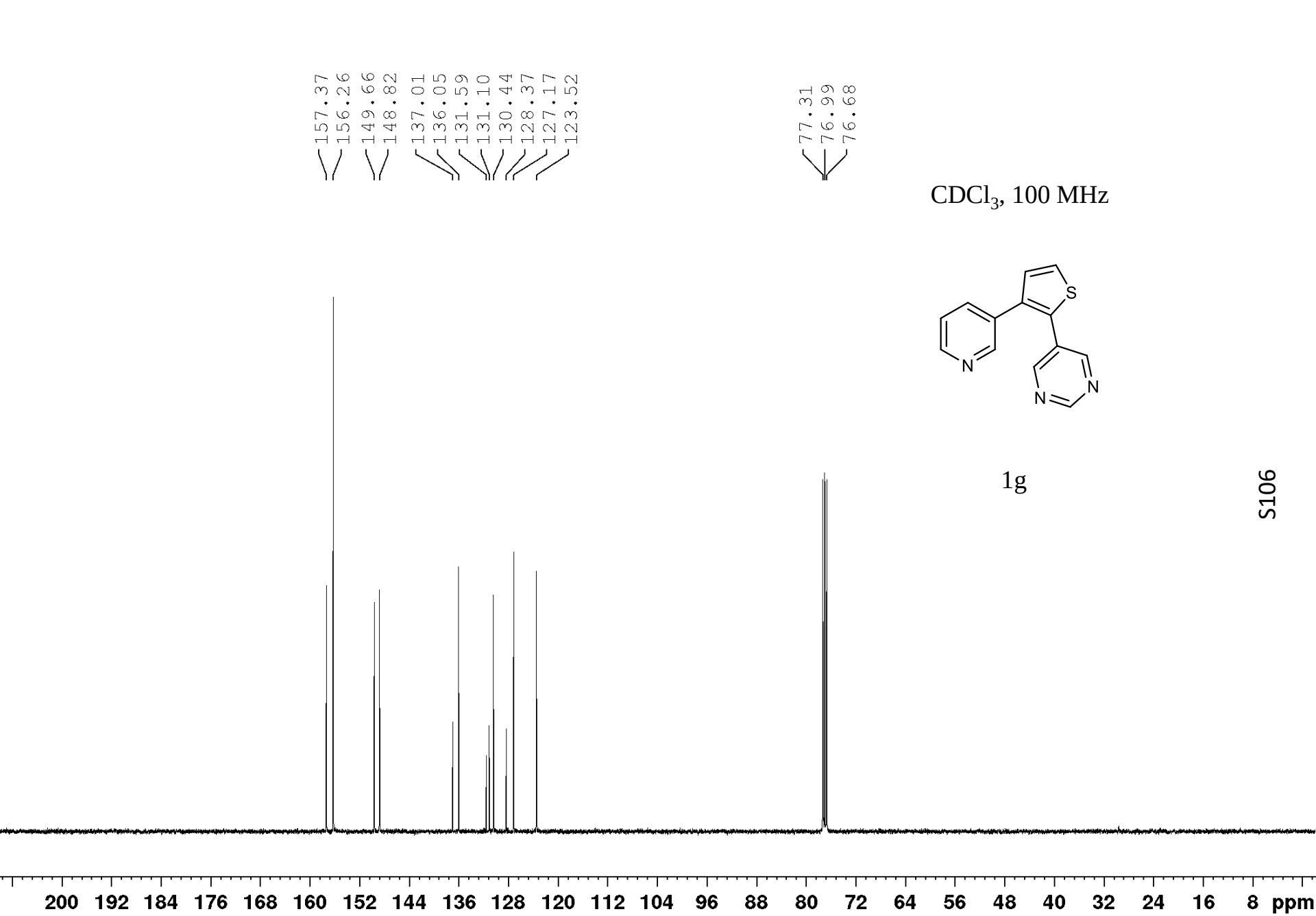

8.70
8.69
8.52
8.51
8.48
8.46
7.77
7.75
7.26
7.23
7.22
7.21
7.20
6.99
6.98
6.97
4.38
CDCl3, 400 MHz
N
S
N
N
1f
S101
1.00
1.99
1.00
1.01
1.03
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

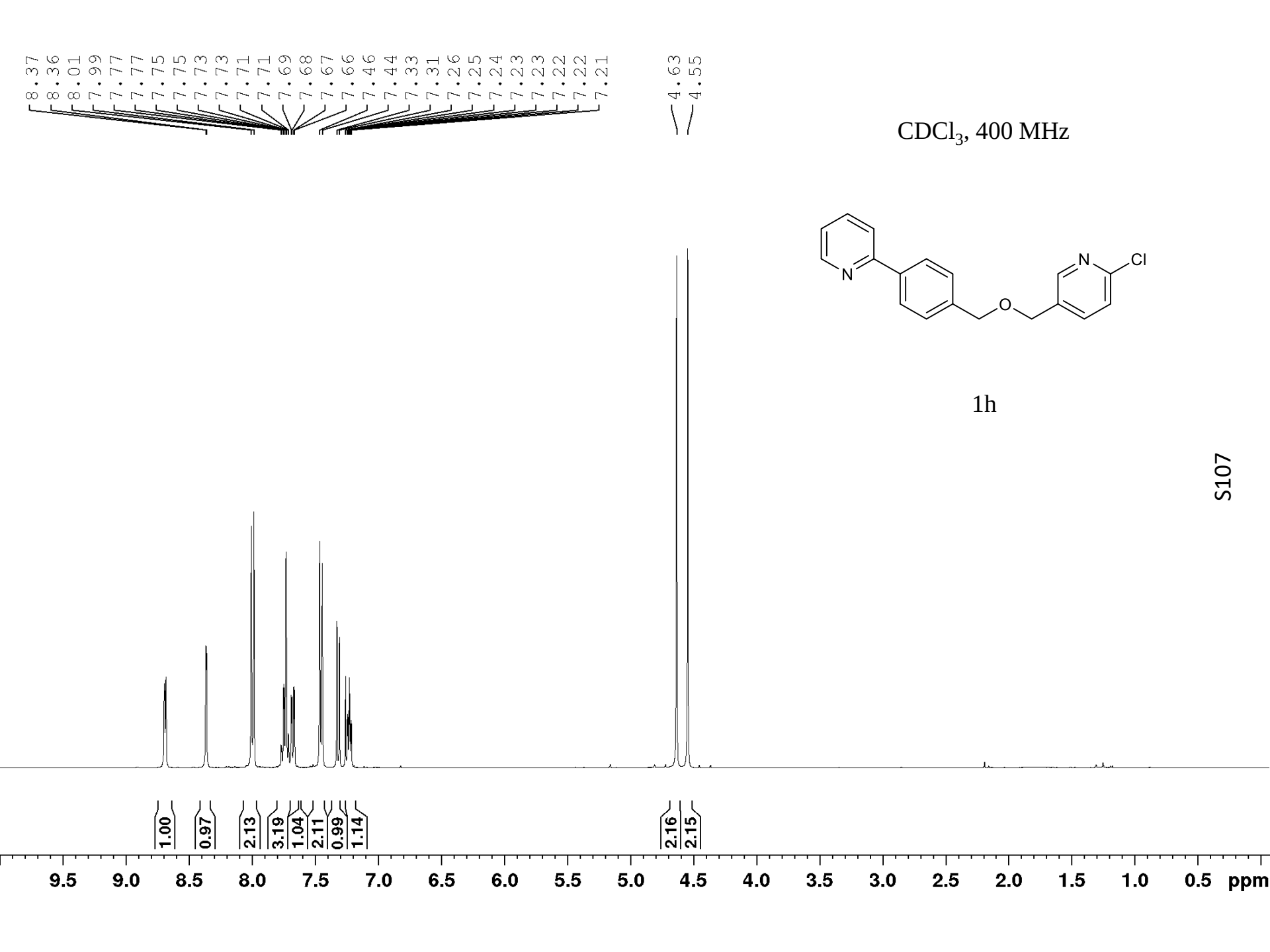

171.28
157.27
150.33
148.41
136.38
133.70
123.27
116.78
77.31
77.00
76.68
32.21
CDCl3, 100 MHz
N
S
N
N
1f
S102
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

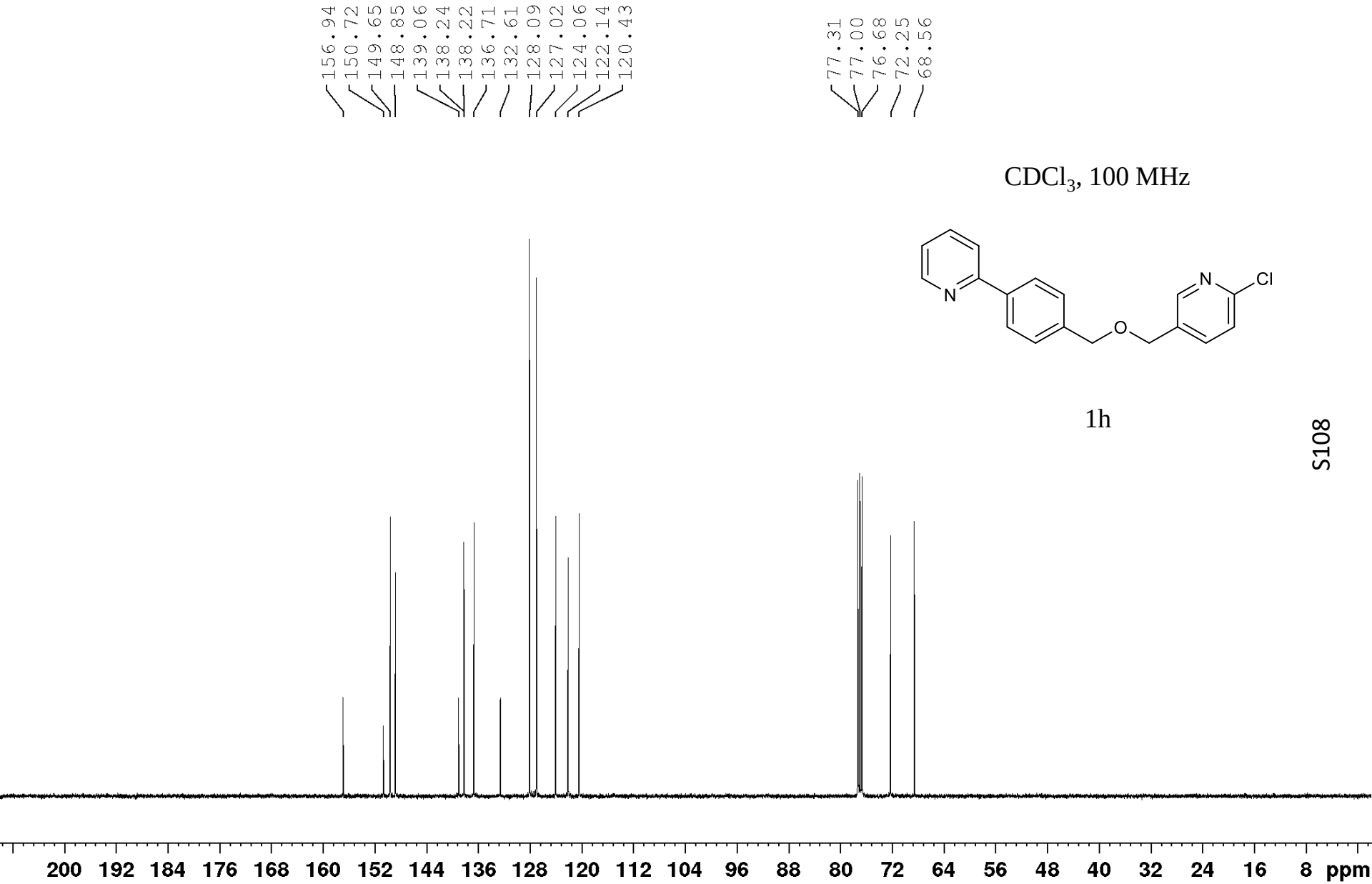

8.81
8.81
8.59
8.59
8.58
8.58
7.91
7.91
7.90
7.89
7.89
7.88
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.26
7.21
7.20
7.08
7.06
CDCl3, 400 MHz
S
Cl
N
S103
1.00
1.02
1.03
1.07
1.01
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

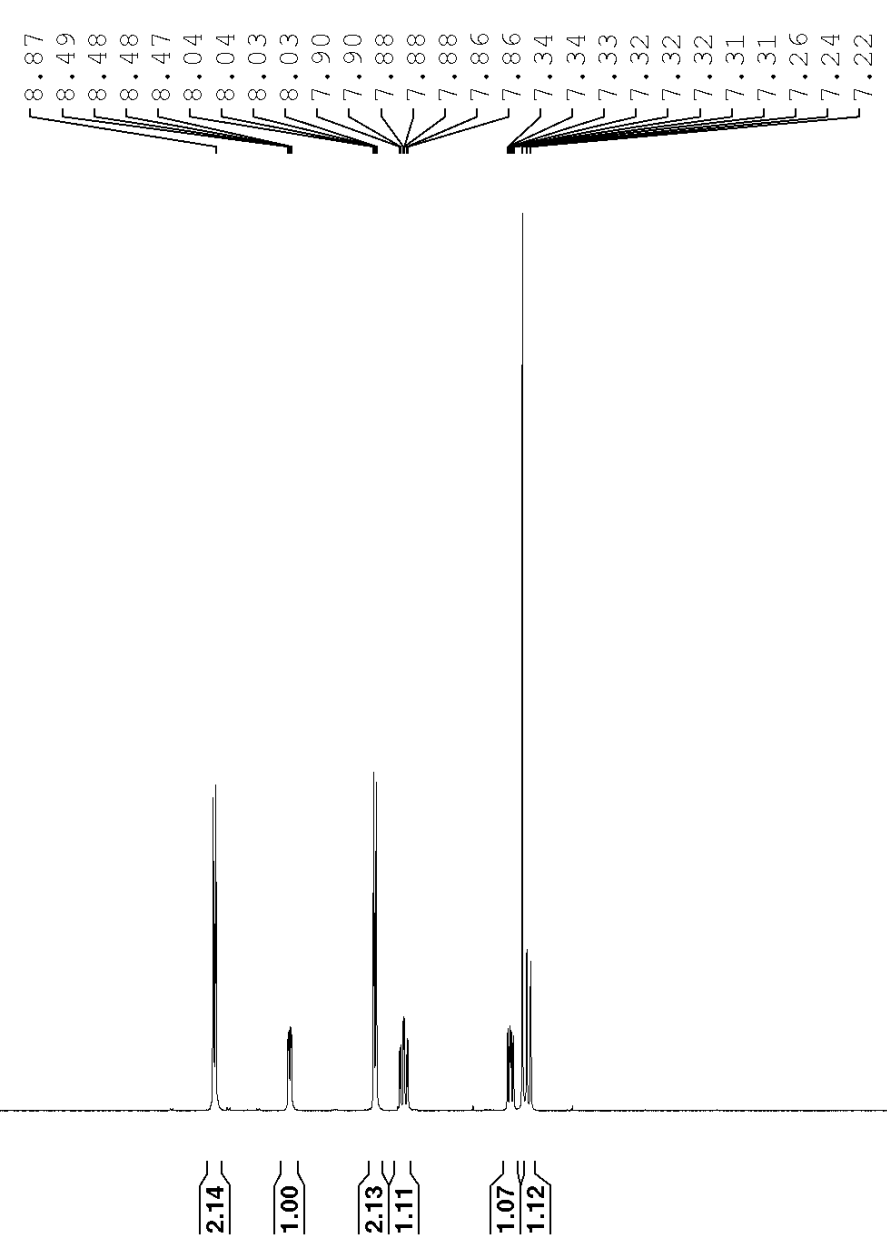

149.29
148.59
135.54
134.78
130.08
127.82
126.20
123.39
123.20
77.30
76.99
76.67
CDCl3, 100 MHz
S
Cl
N
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


9.12
8.65
8.58
8.58
8.57
7.57
7.56
7.56
7.28
7.26
7.25
CDCl3, 400 MHz
S
N
N
N
1g
S105
1.00
2.05
2.23
2.23
2.76
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
0.5
ppm

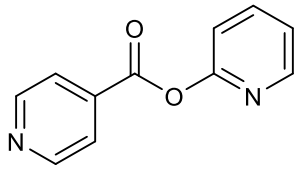

157.37
156.26
149.66
148.82
137.01
136.05
131.59
131.10
130.44
128.37
127.17
123.52
77.31
76.99
76.68
CDCl3, 100 MHz
S
N
N
N
1g
S106
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


8.37
8.36
8.01
7.99
7.77
7.77
7.75
7.75
7.73
7.73
7.71
7.71
7.69
7.68
7.67
7.66
7.46
7.44
7.33
7.31
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.21
4.63
4.55
CDCl3, 400 MHz
N
N
Cl
O
1h
S107
1.00
0.97
2.13
3.19
1.04
2.11
0.99
1.14
2.16
2.15
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
ppm

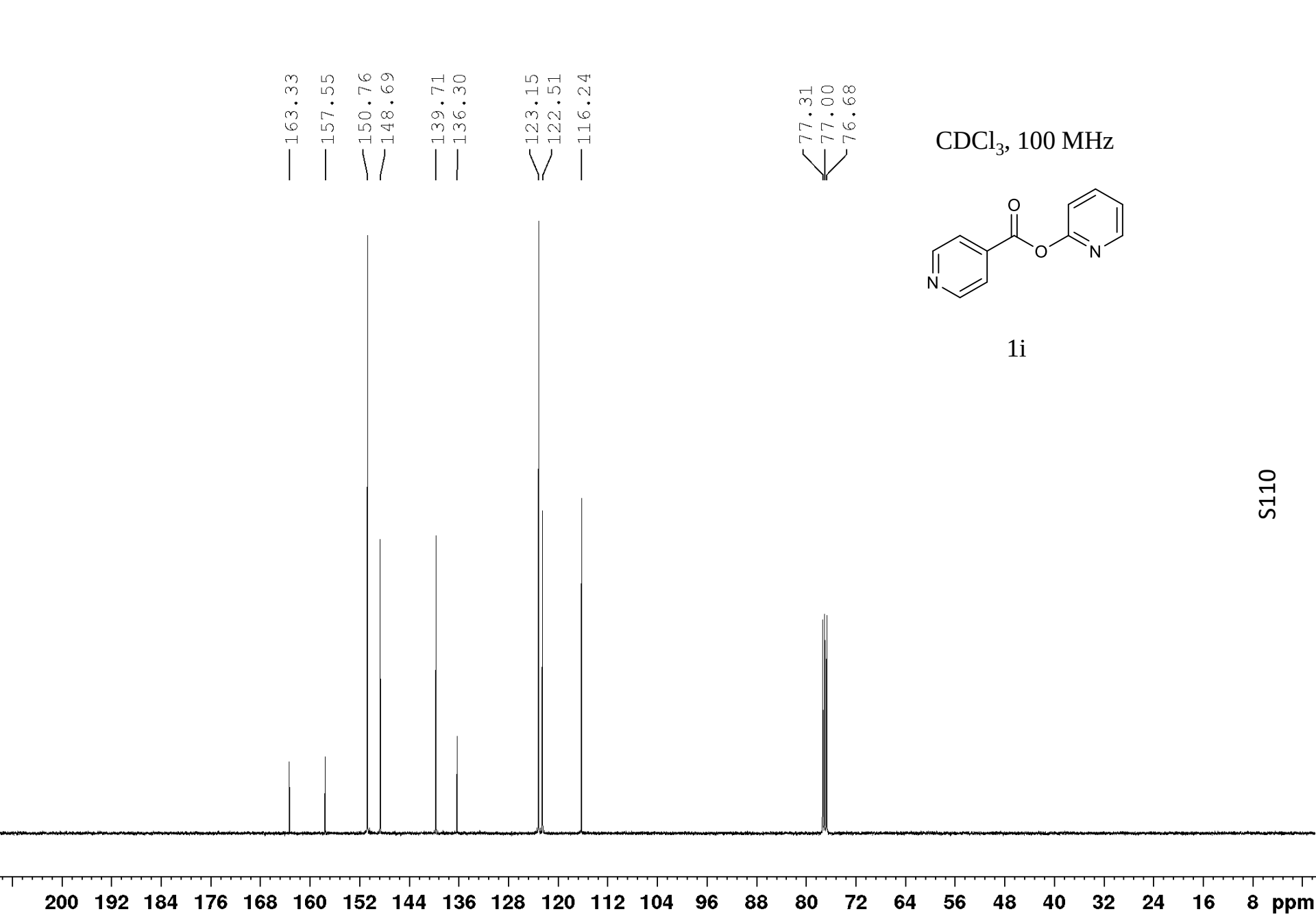

156.94
150.72
149.65
148.85
139.06
138.24
138.22
136.71
132.61
128.09
127.02
124.06
122.14
120.43
77.31
77.00
76.68
72.25
68.56
CDCl3, 100 MHz
N
O
N
Cl
1h
S108
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

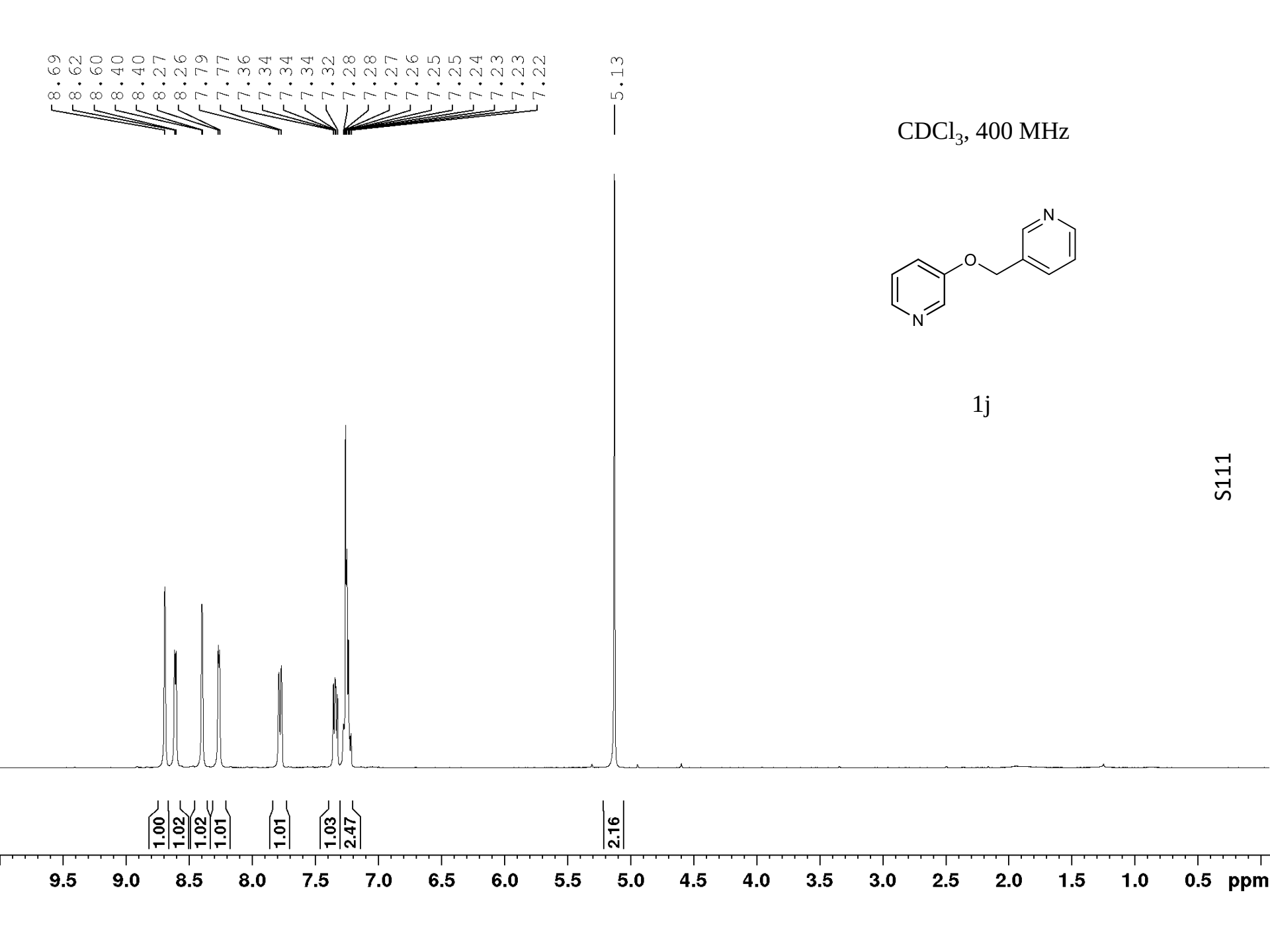


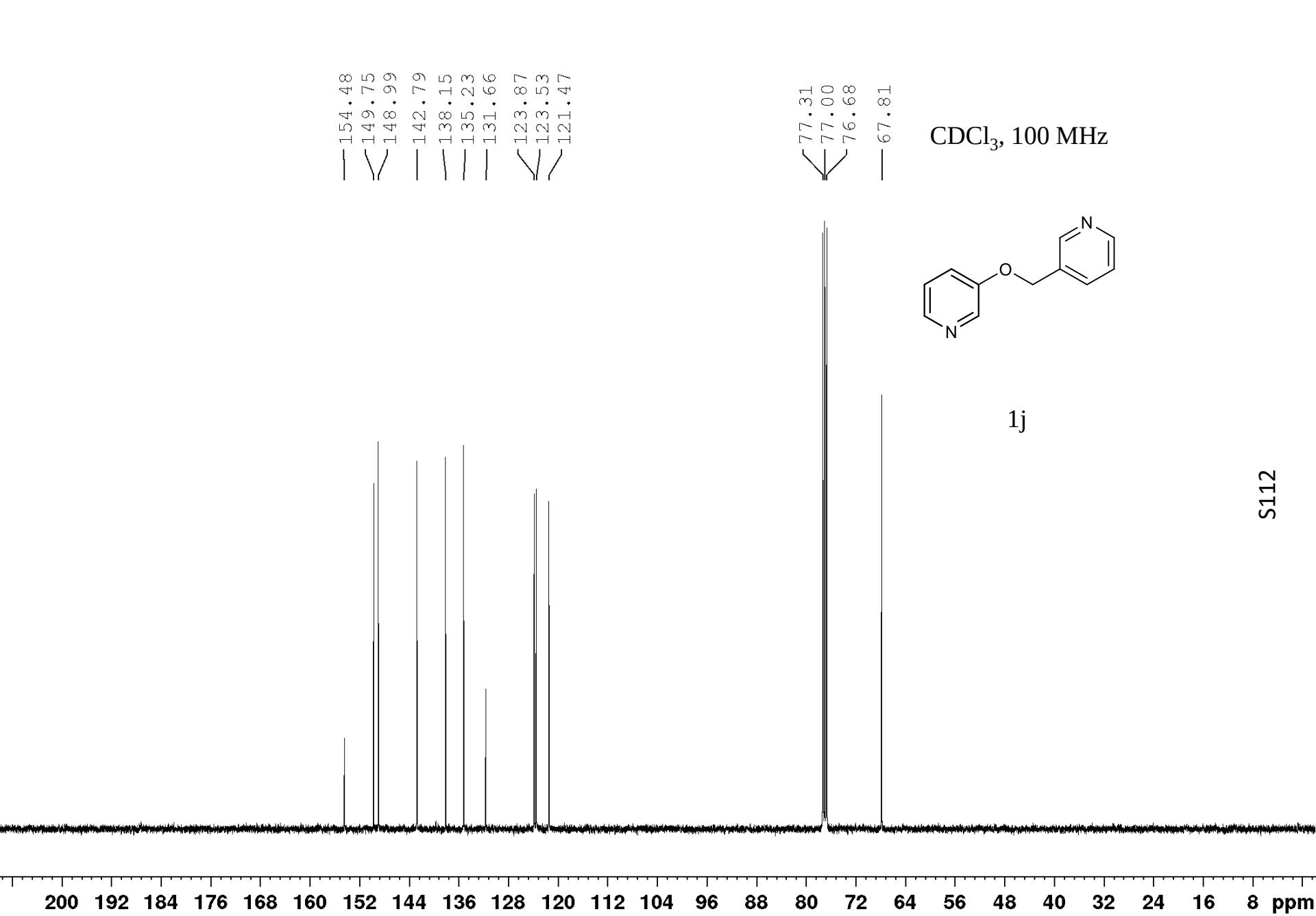
$CDCl_3$, 400 MHz

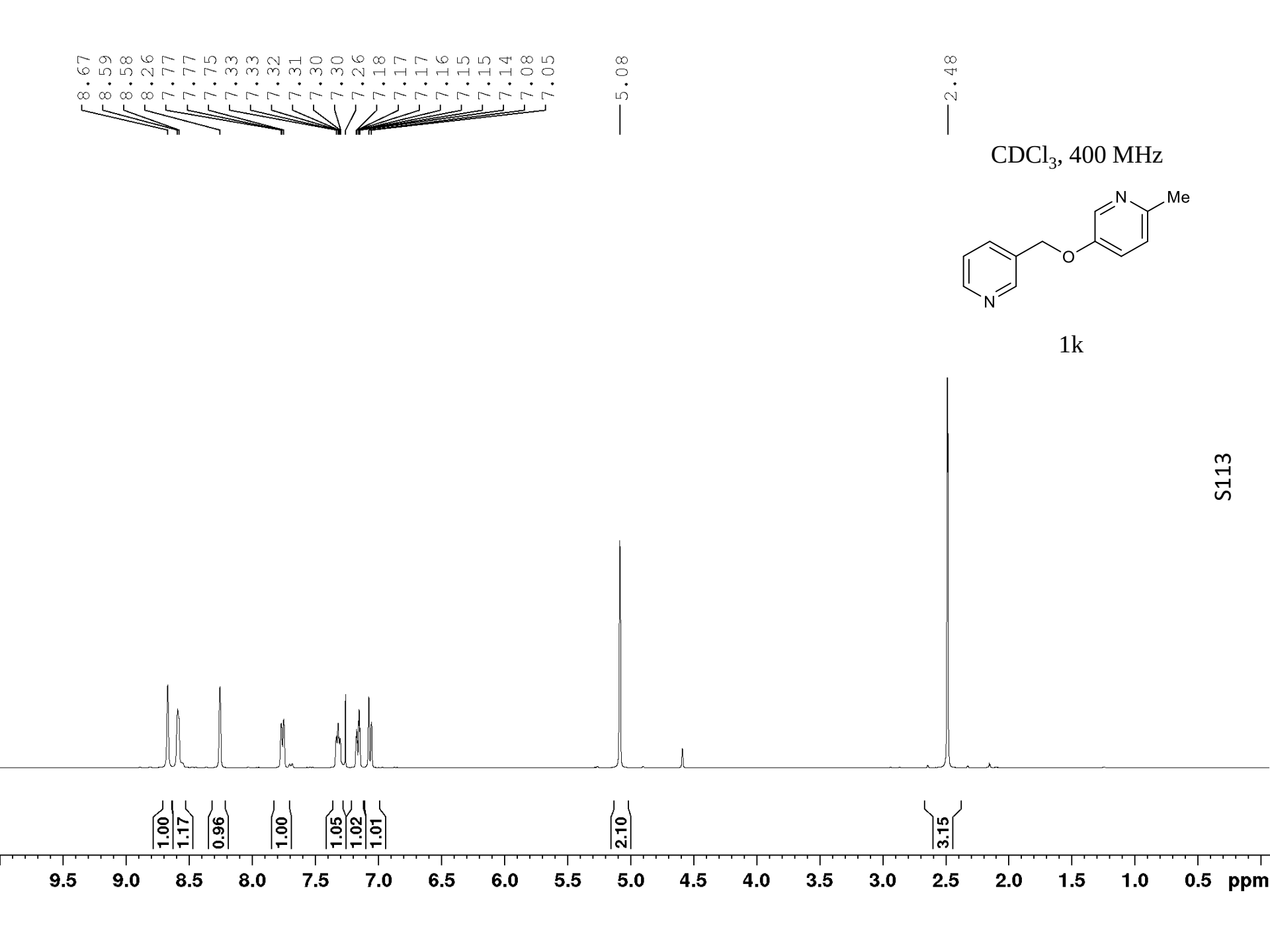


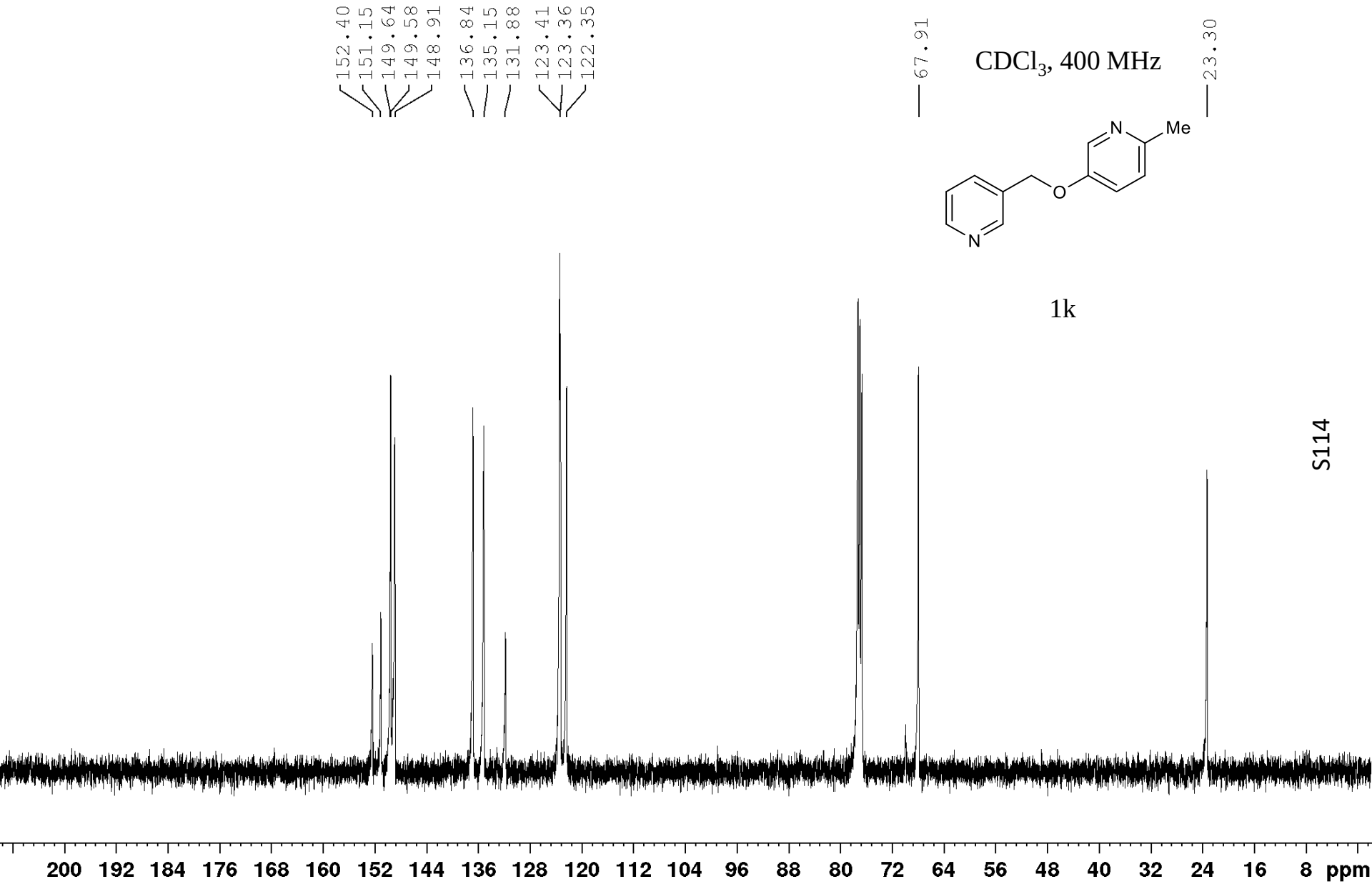
1i

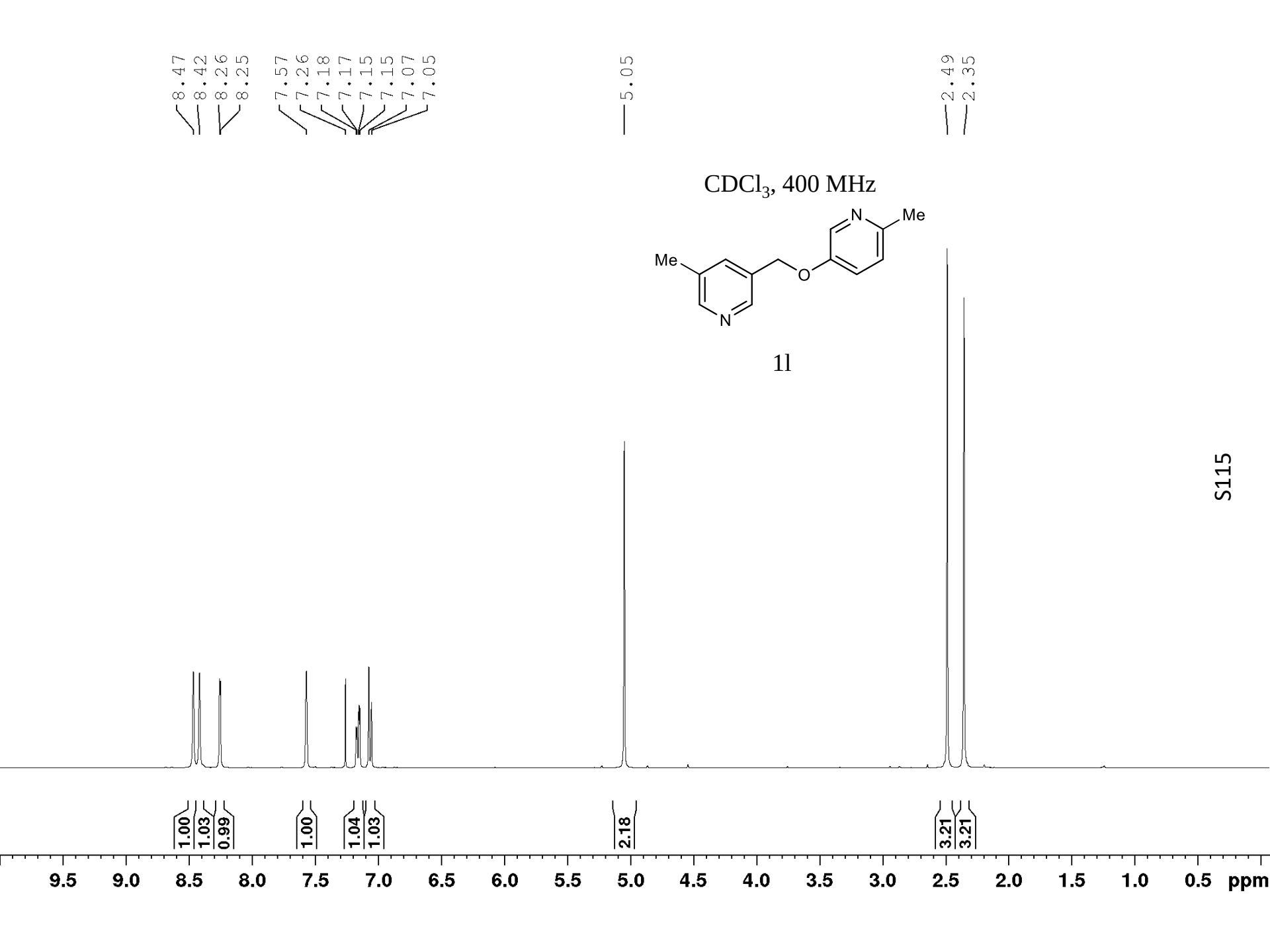

163.33
157.55
150.76
148.69
139.71
136.30
123.15
122.51
116.24
77.31
77.00
76.68
CDCl3, 100 MHz
O
O
N
N
1i
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

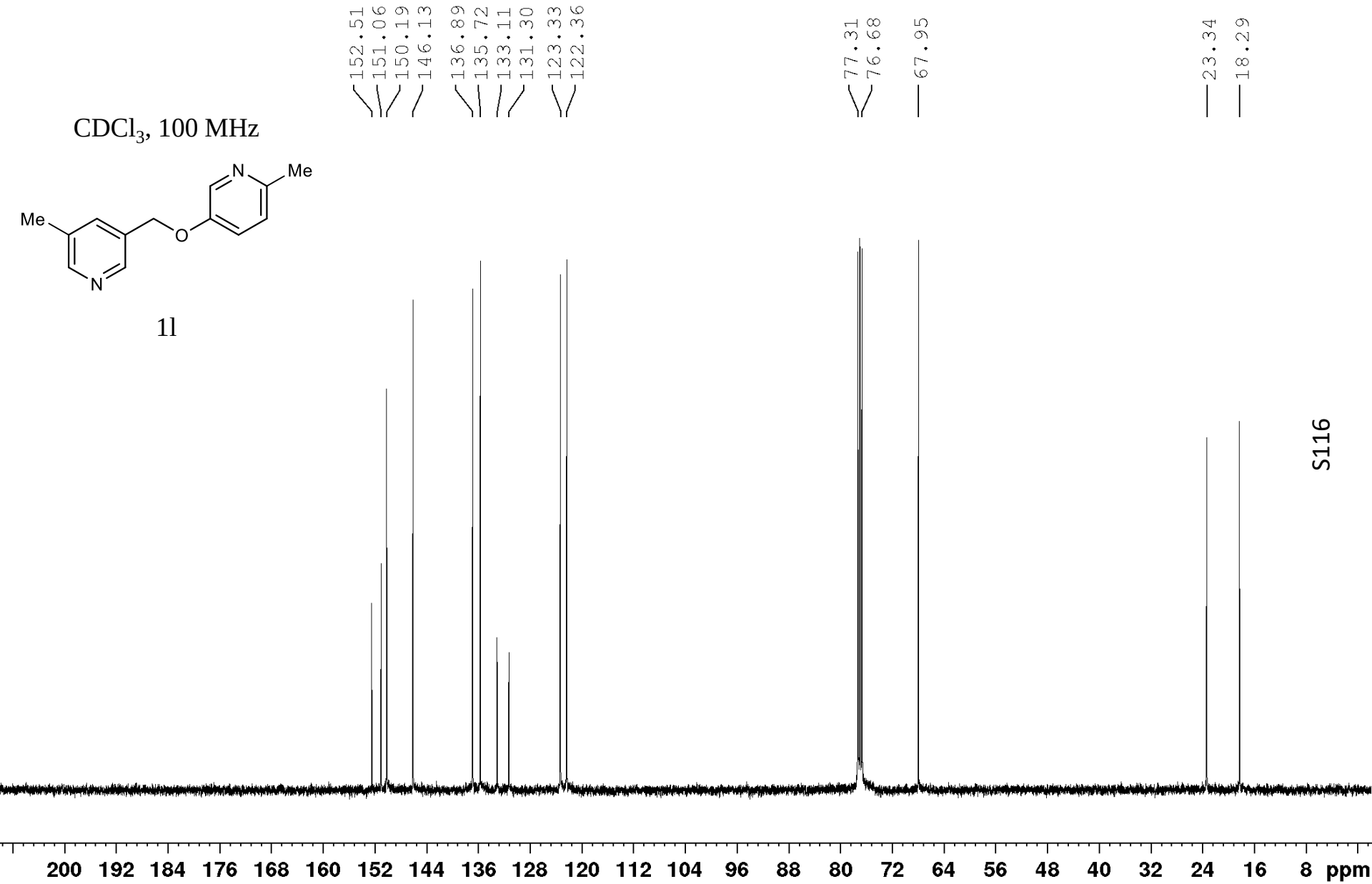

8.69
8.62
8.60
8.40
8.40
8.27
8.26
7.79
7.77
7.36
7.34
7.34
7.34
7.32
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
5.13
CDCl3, 400 MHz
N
O
N
1j
S111
1.00
1.02
1.02
1.01
1.01
1.03
2.47
2.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

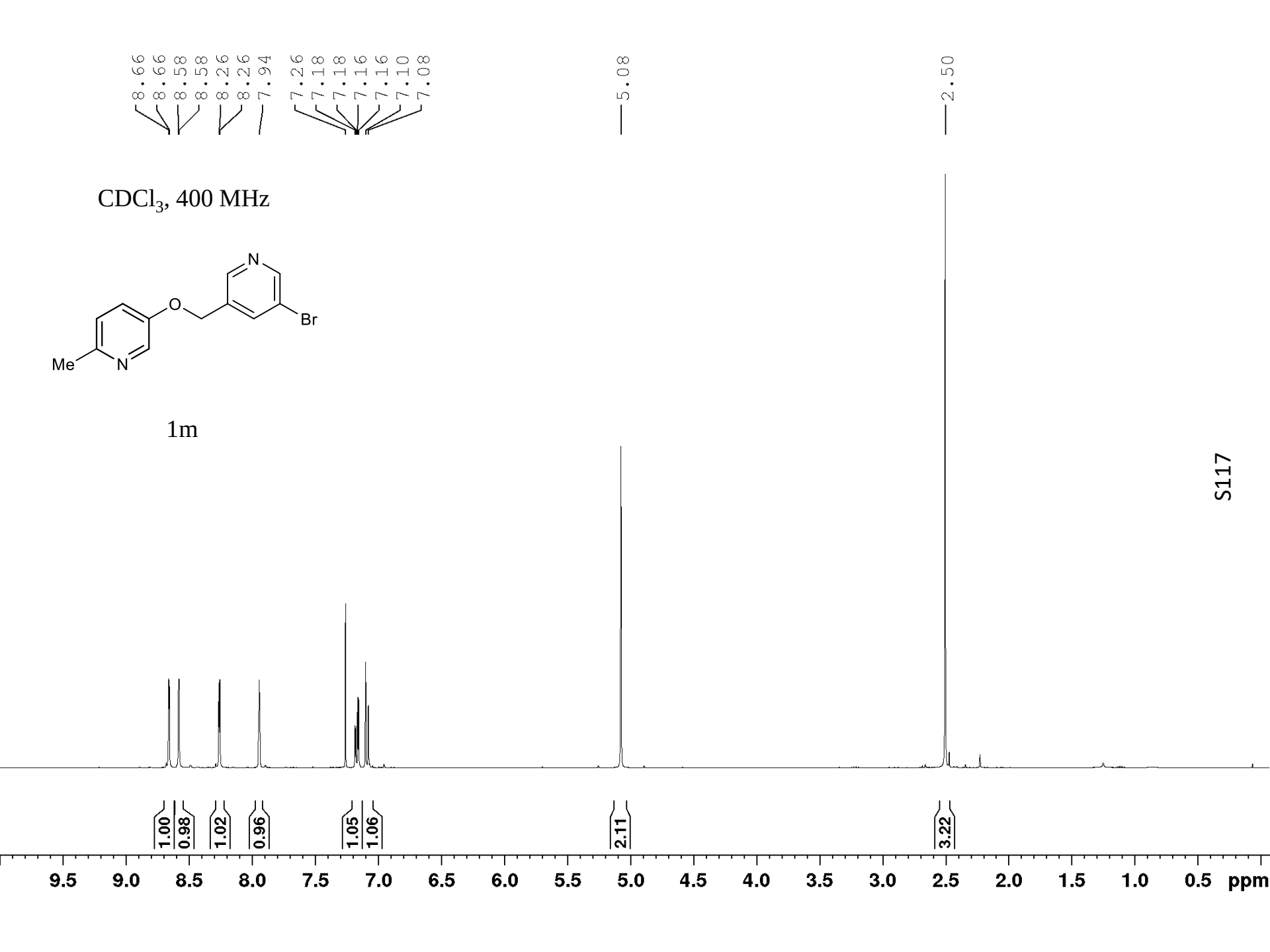

154.48
149.75
148.99
142.79
138.15
135.23
131.66
123.87
123.53
121.47
77.31
77.00
76.68
67.81
CDCl3, 100 MHz
N
O
N
1j
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

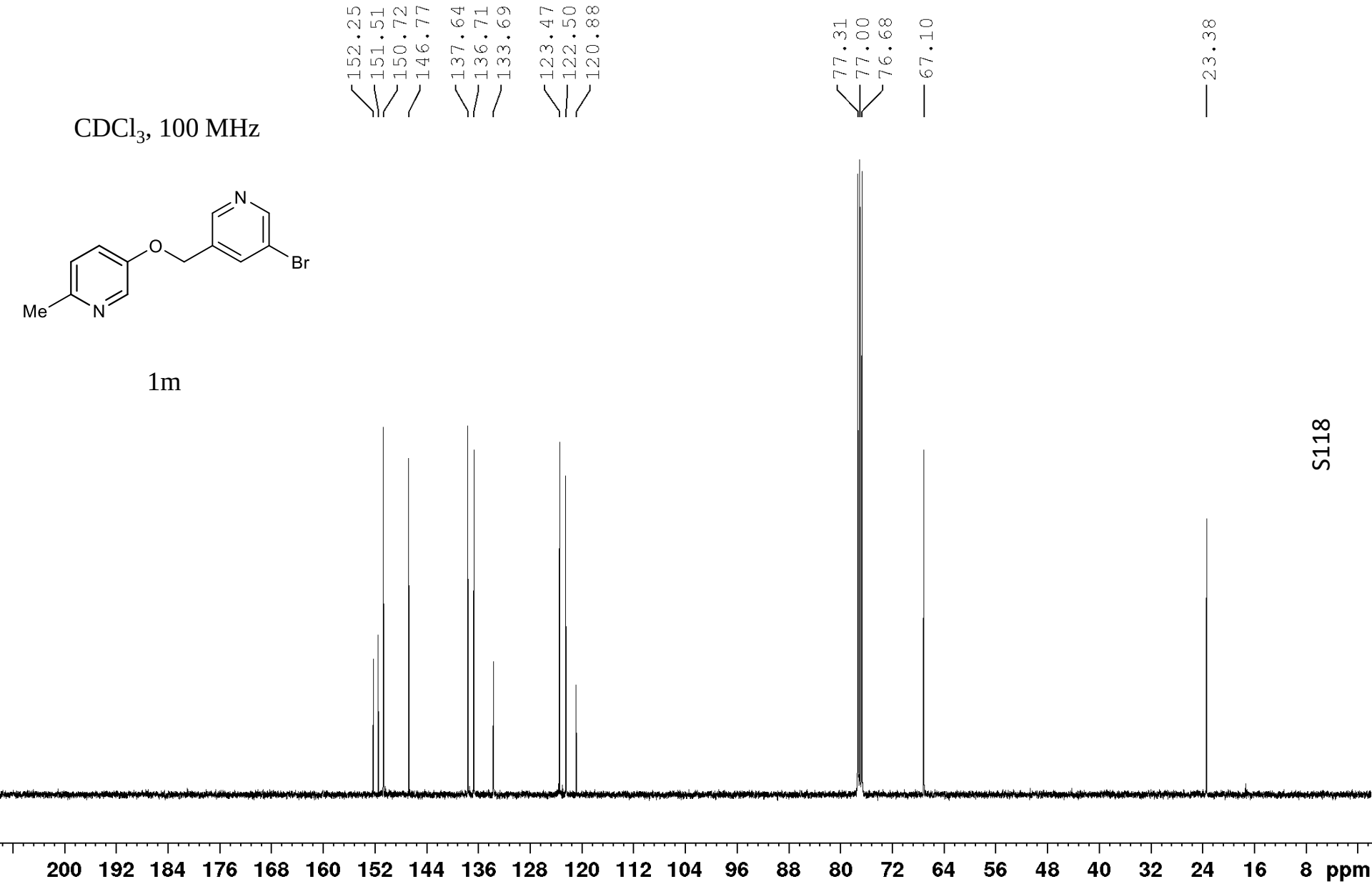

8.67
8.59
8.58
8.26
7.77
7.77
7.75
7.33
7.33
7.32
7.31
7.30
7.30
7.26
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.08
7.05
5.08
2.48
CDCl3, 400 MHz
N
Me
O
N
1k
S113
1.00
1.17
0.96
1.00
1.05
1.02
1.01
2.10
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

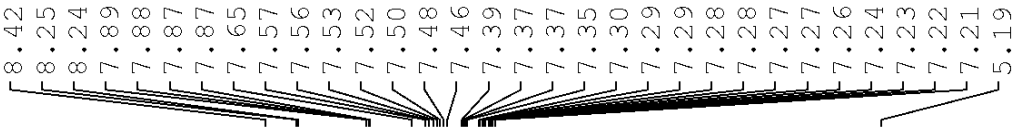

152.40
151.15
149.64
149.58
148.91
136.84
135.15
131.88
123.41
123.36
122.35
67.91
23.30
CDCl3, 400 MHz
N
Me
O
N
1k
S114
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


8.47
8.42
8.26
8.25
7.57
7.26
7.18
7.17
7.15
7.15
7.07
7.05
5.05
2.49
2.35
CDCl3, 400 MHz
N
Me
Me
O
N
1l
S115
1.00
1.03
0.99
1.00
1.04
1.03
2.18
3.21
3.21
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
ppm

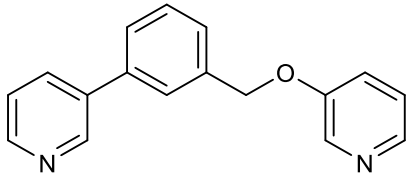

152.51
151.06
150.19
146.13
136.89
135.72
133.11
131.30
123.33
122.36
77.31
76.68
67.95
23.34
18.29
CDCl3, 100 MHz
N
Me
Me
O
N
1l
S116
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


8.66
8.66
8.58
8.58
8.26
8.26
7.94
7.26
7.18
7.18
7.16
7.16
7.10
7.08
5.08
2.50
CDCl3, 400 MHz
N
O
Br
Me
N
1m
S117
1.00
0.98
1.02
0.96
1.05
1.06
2.11
3.22
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
ppm


152.25
151.51
150.72
146.77
137.64
136.71
133.69
123.47
122.50
120.88
77.31
77.00
76.68
67.10
23.38
CDCl3, 100 MHz
N
O
Br
Me
N
1m
S118
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 ppm

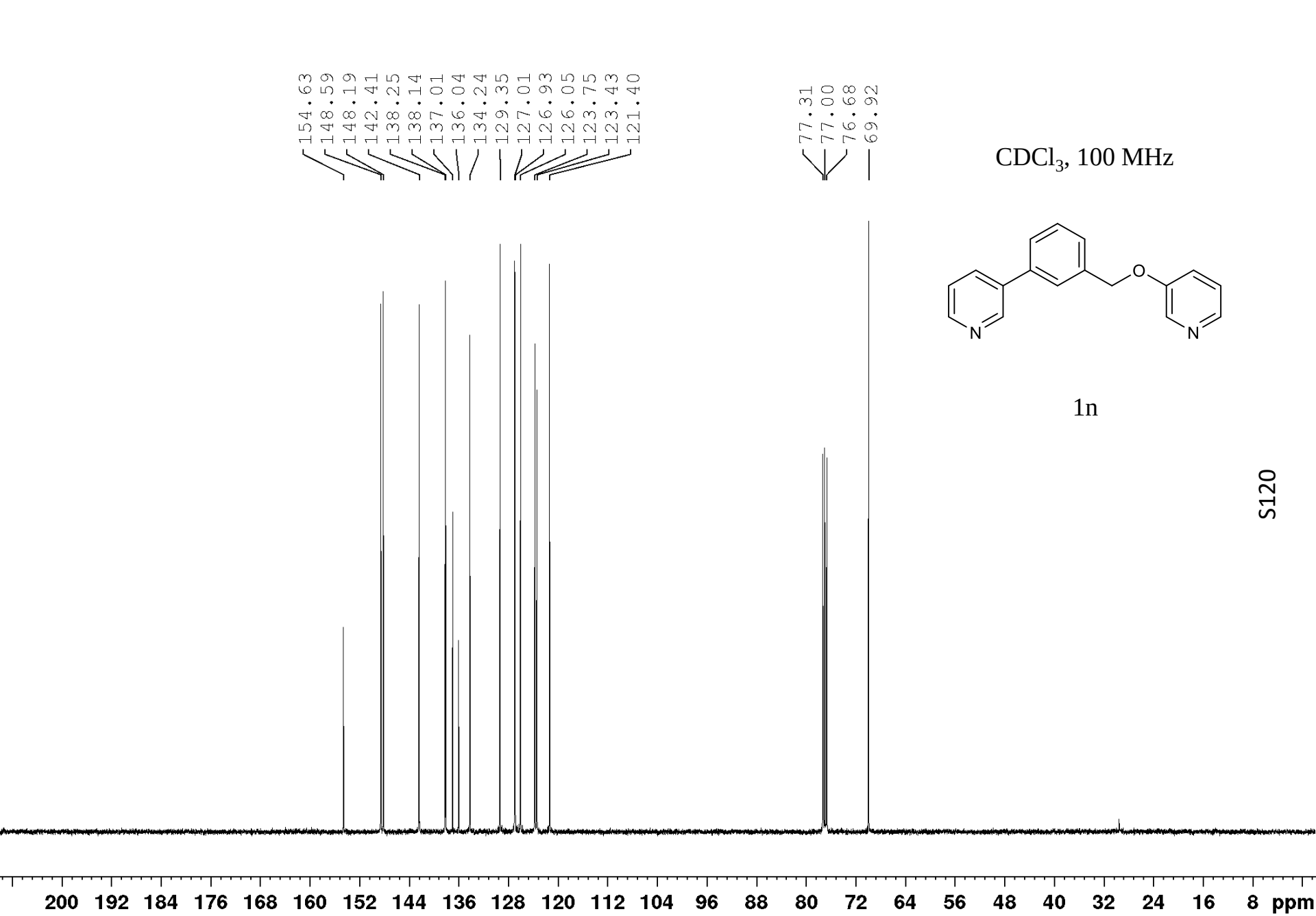


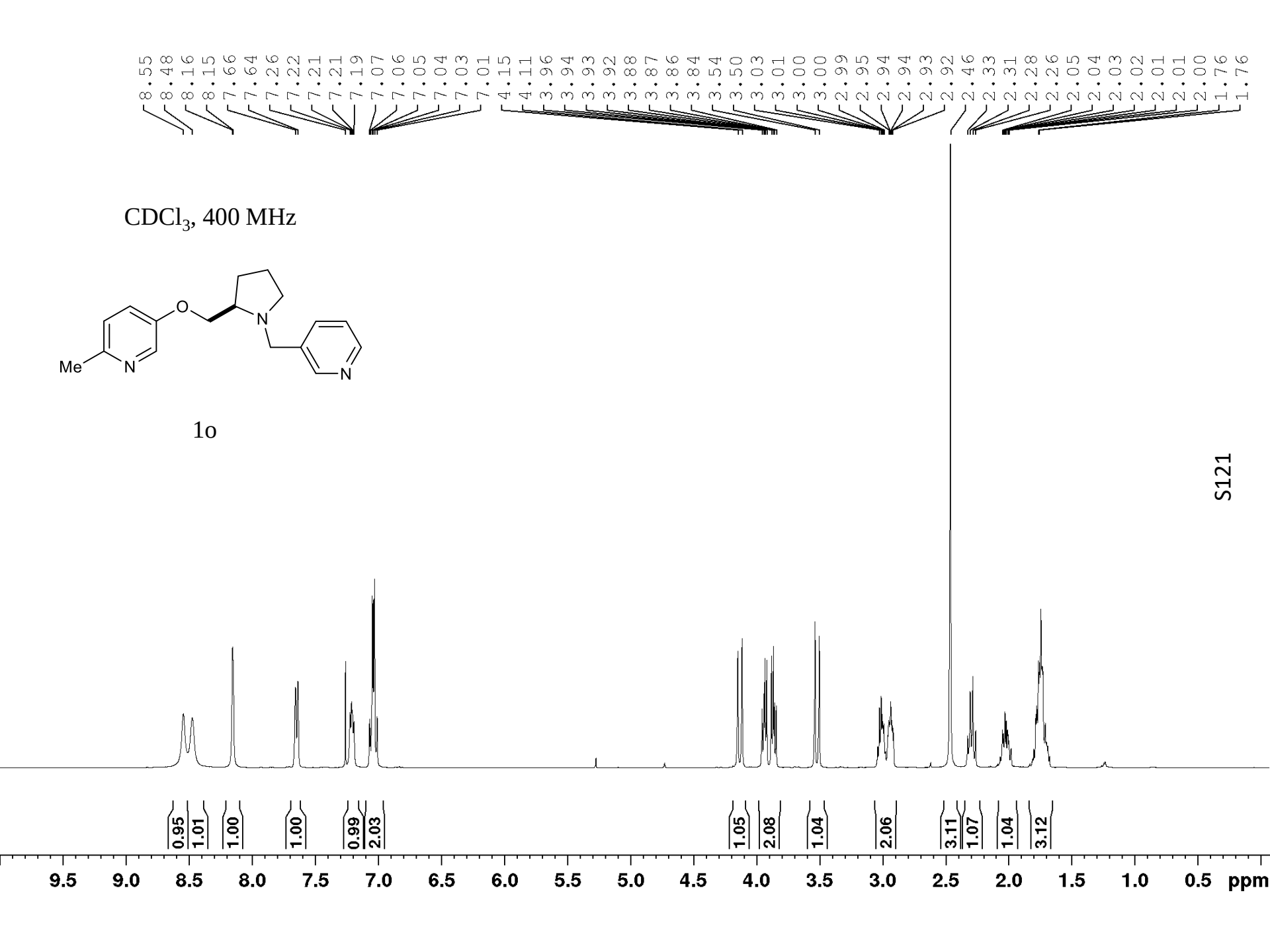
$CDCl_3$, 400 MHz

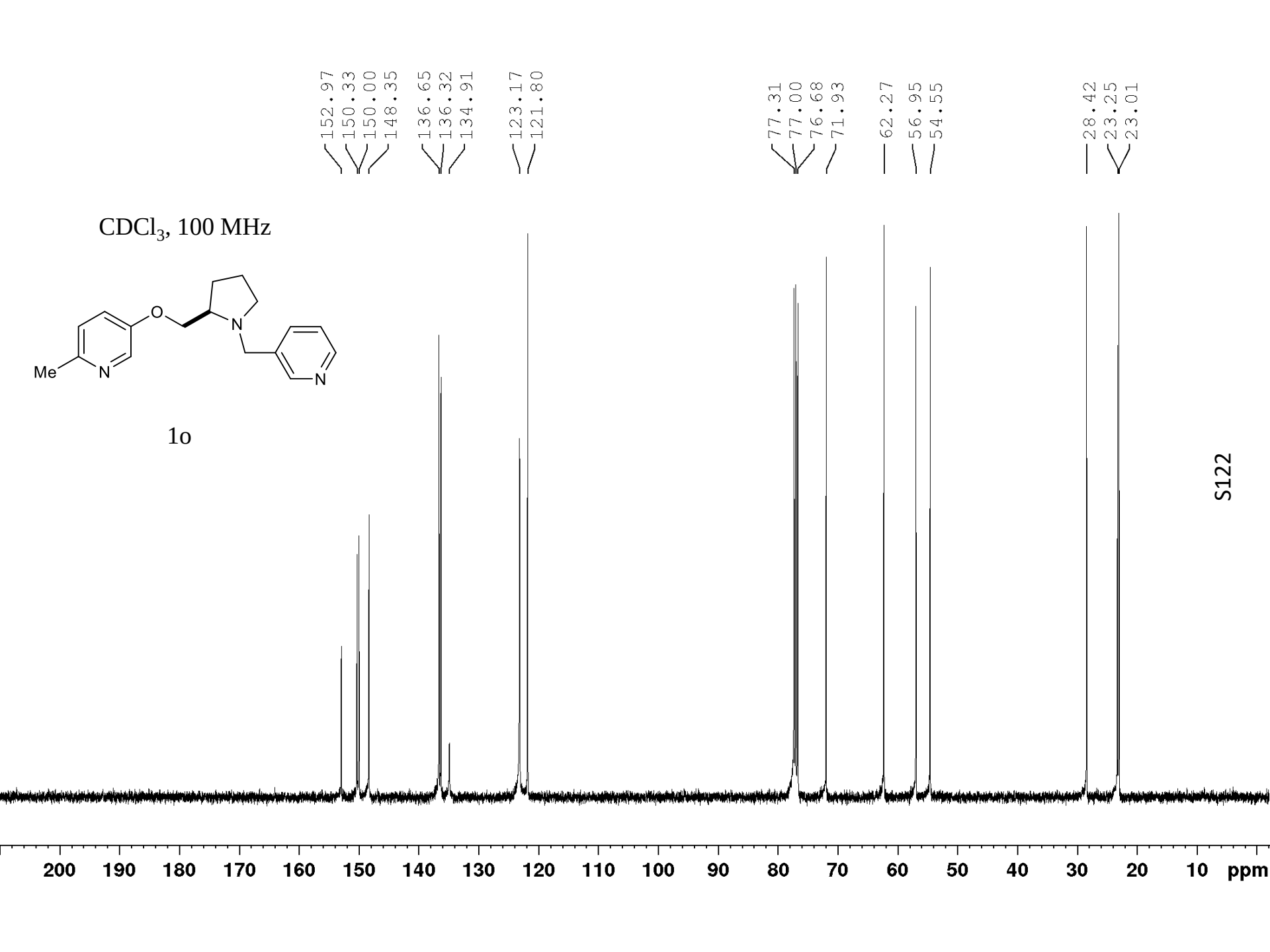


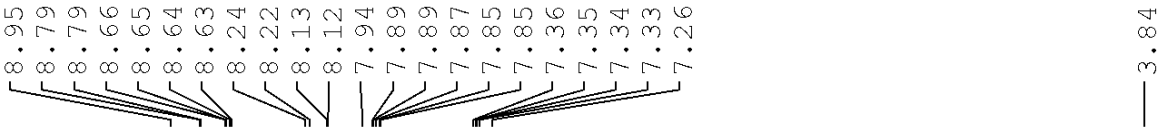
1n

S119

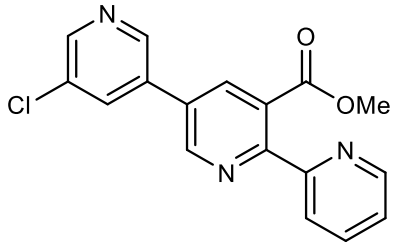

154.63
148.59
148.19
142.41
138.25
138.14
137.01
136.04
134.24
129.35
127.01
126.93
126.05
123.75
123.43
121.40
77.31
77.00
76.68
69.92
CDCl3, 100 MHz
O
N
N
1n
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


8.55
8.48
8.16
8.15
7.66
7.64
7.26
7.22
7.21
7.21
7.19
7.07
7.06
7.05
7.04
7.03
7.01
4.15
4.11
3.96
3.94
3.93
3.92
3.88
3.87
3.86
3.84
3.54
3.50
3.03
3.01
3.00
3.00
2.99
2.95
2.94
2.94
2.93
2.92
2.46
2.33
2.31
2.28
2.26
2.05
2.04
2.03
2.02
2.01
2.01
2.00
1.76
1.76
CDCl3, 400 MHz
Me
N
O
N
N
1o
S121
0.95
1.01
1.00
1.00
0.99
2.03
1.05
2.08
1.04
2.06
3.11
1.07
1.04
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
0.5
ppm


152.97
150.33
150.00
148.35
136.65
136.32
134.91
123.17
121.80
77.31
77.00
76.68
71.93
62.27
56.95
54.55
28.42
23.25
23.01
CDCl3, 100 MHz
Me
N
O
N
N
1o
S122
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

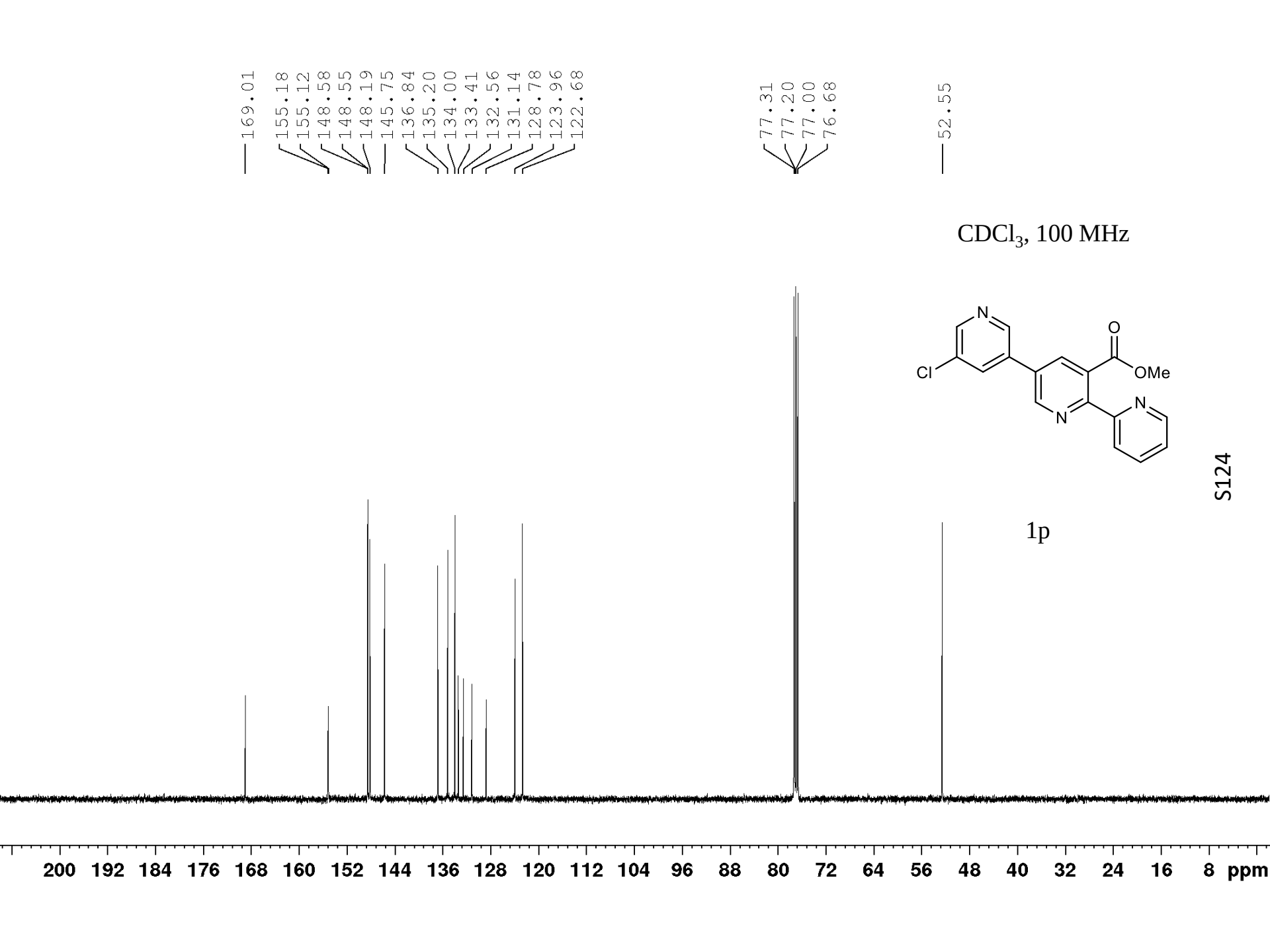


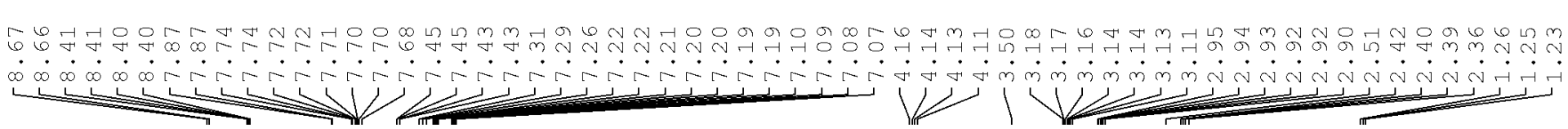
$CDCl_3$, 400 MHz



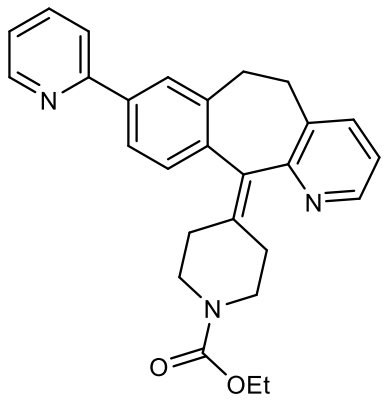
1p

S123


169.01
155.18
155.12
148.58
148.55
148.19
145.75
136.84
135.20
134.00
133.41
132.56
131.14
128.78
123.96
122.68
77.31
77.20
77.00
76.68
52.55
CDCl3, 100 MHz
N
O
Cl
OMe
N
N
1p
S124
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 ppm



$CDCl_3$, 400 MHz



1q

S125

157.21
157.07
155.47
149.59
146.56
140.05
138.47
138.23
137.45
137.09
136.68
134.98
133.63
129.64
127.56
124.47
122.11
122.01
120.36

77.31
77.20
76.99
76.68

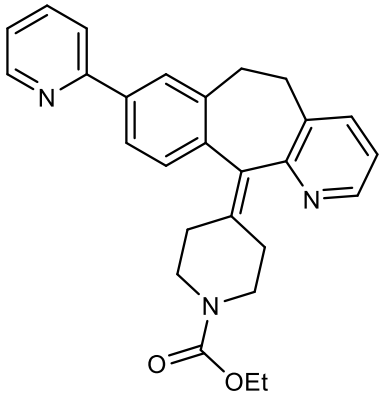
61.24

44.84

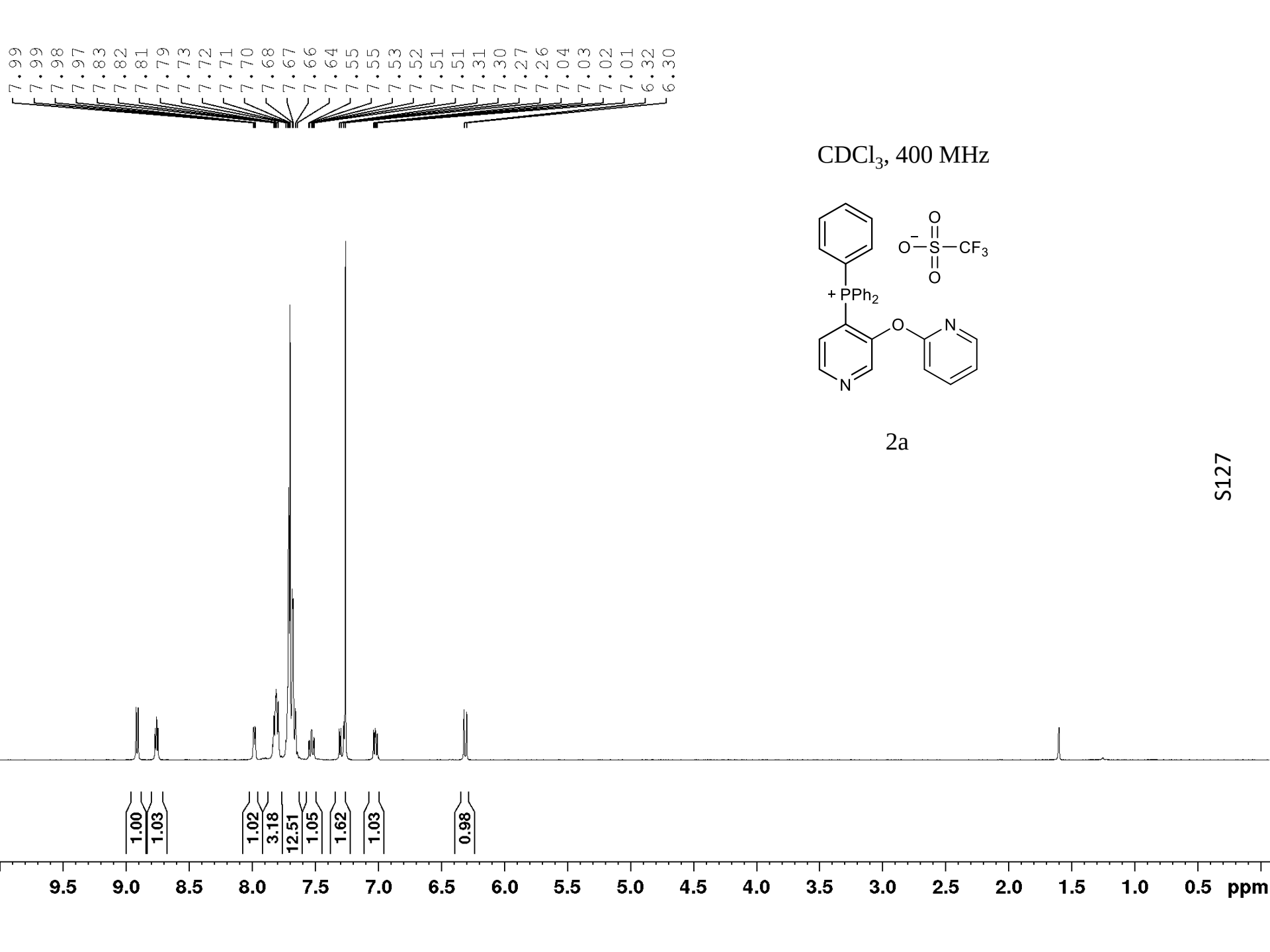
31.92
31.74
30.78
30.53

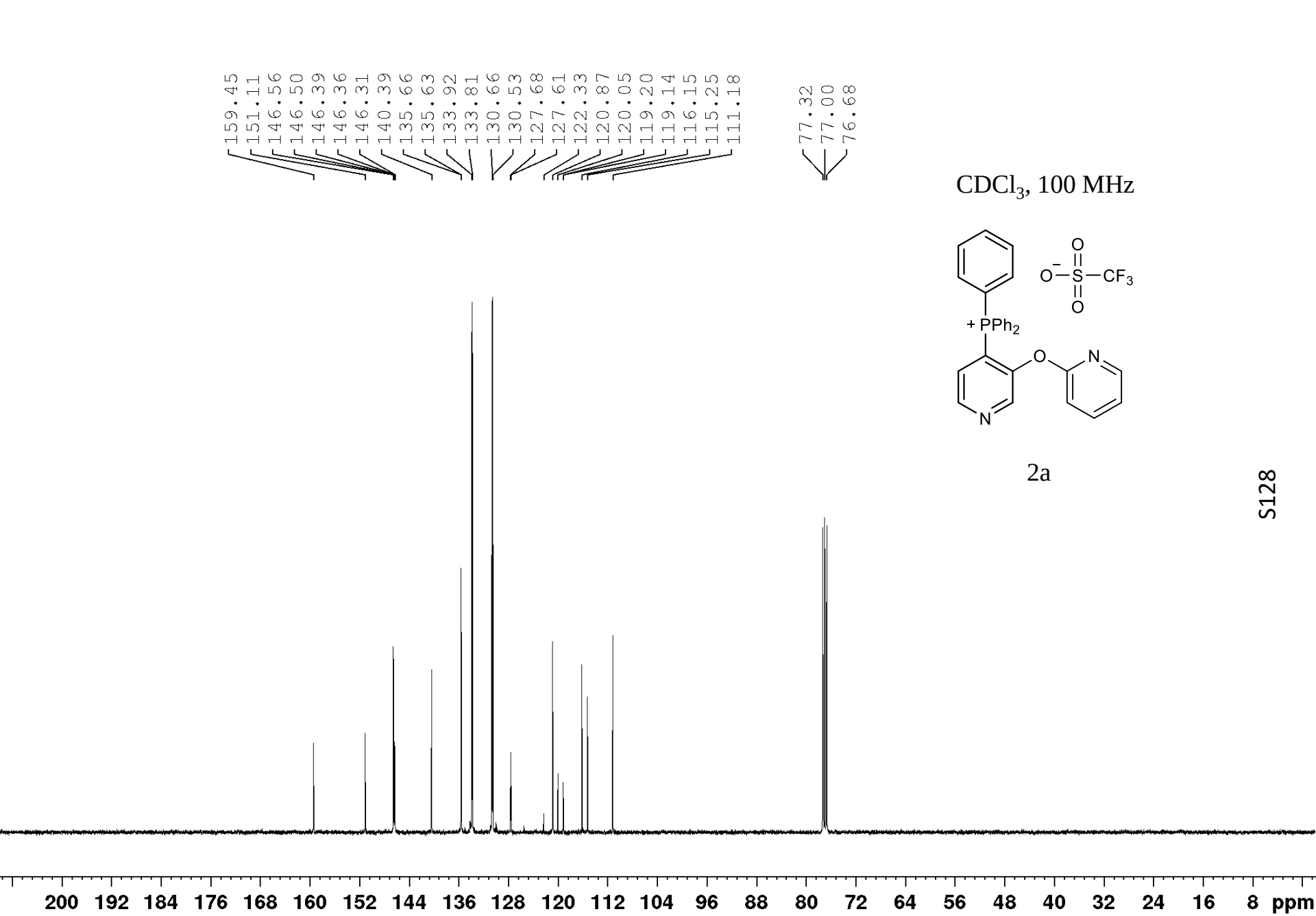
14.65

$CDCl_3$, 100 MHz



1q

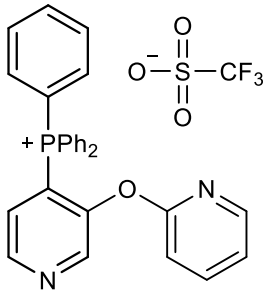

7.99
7.99
7.98
7.97
7.83
7.82
7.81
7.79
7.73
7.72
7.71
7.70
7.68
7.67
7.66
7.64
7.55
7.55
7.53
7.52
7.51
7.51
7.31
7.30
7.27
7.26
7.04
7.03
7.02
7.01
6.32
6.30
CDCl3, 400 MHz
+ PPh2
O
N
2a
1.00
1.03
1.02
3.18
12.51
1.05
1.62
1.03
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



$CDCl_3$, 100 MHz

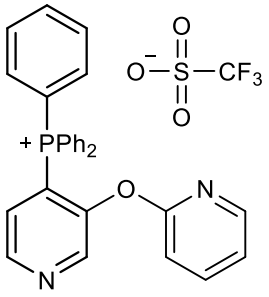
2a

$CDCl_3$, 365 MHz



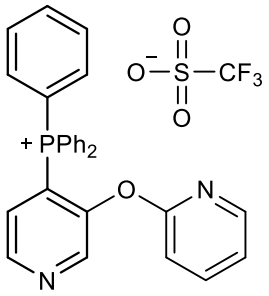
2a

$CDCl_3$, 162 MHz

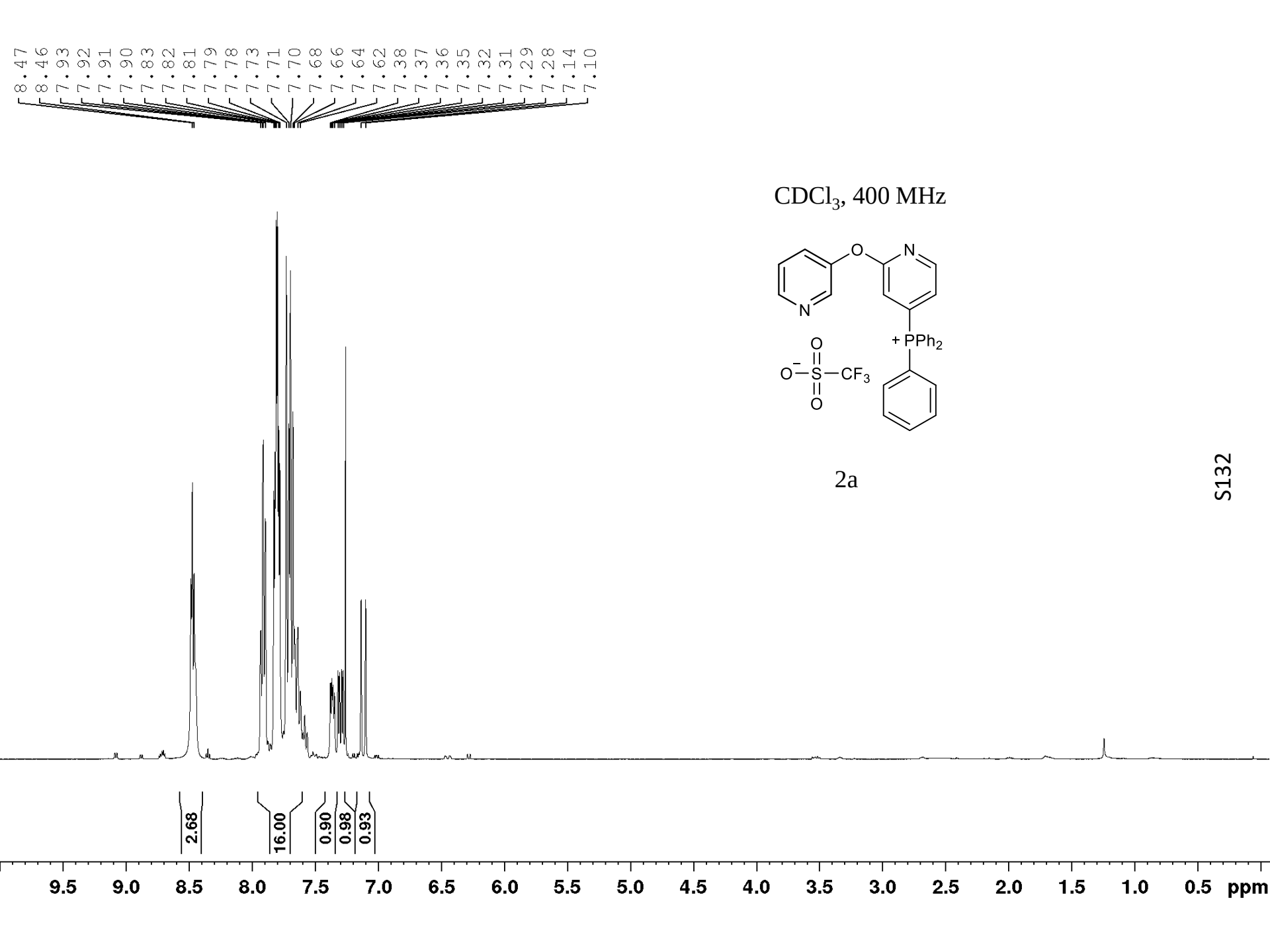


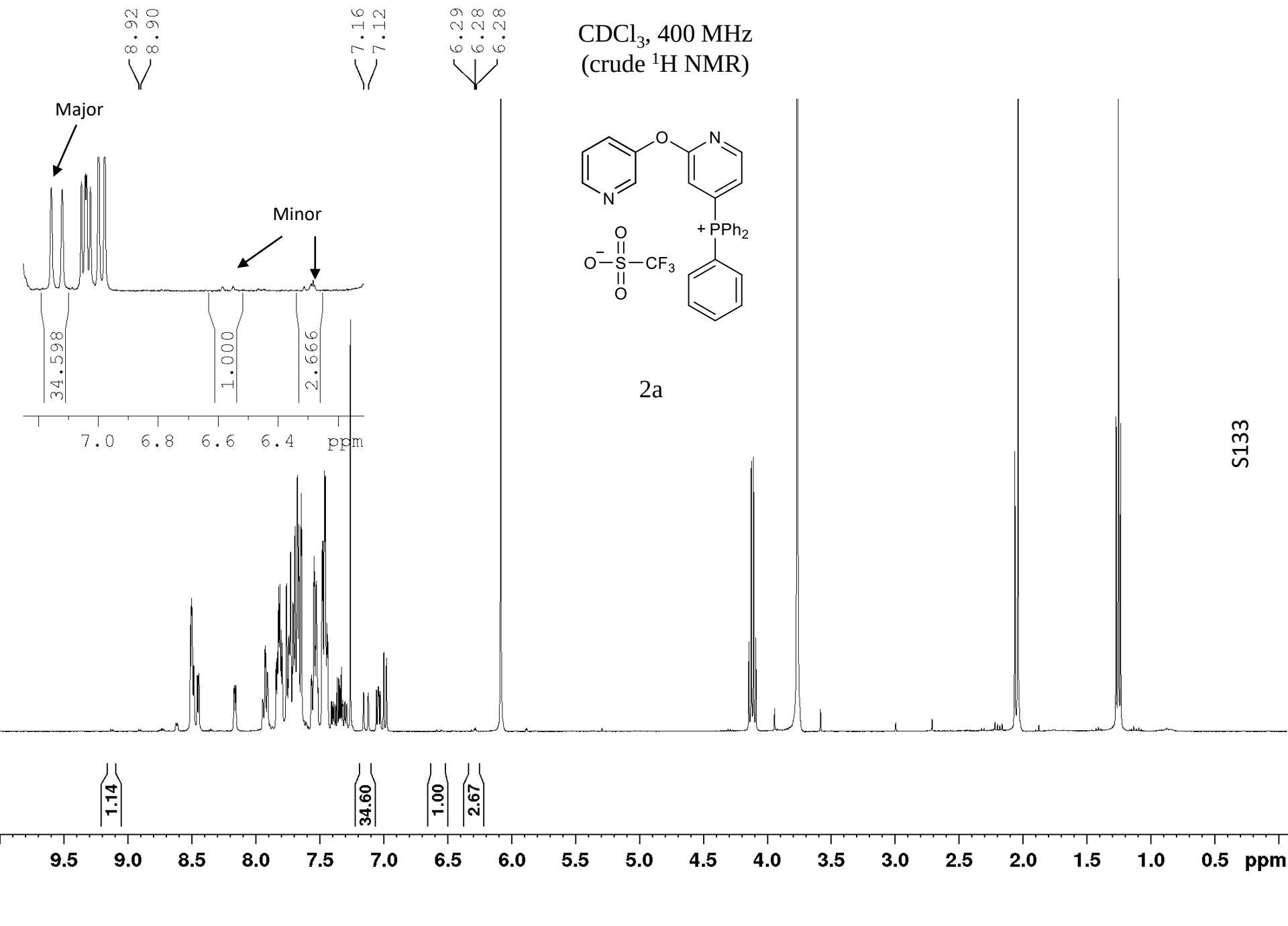
2a

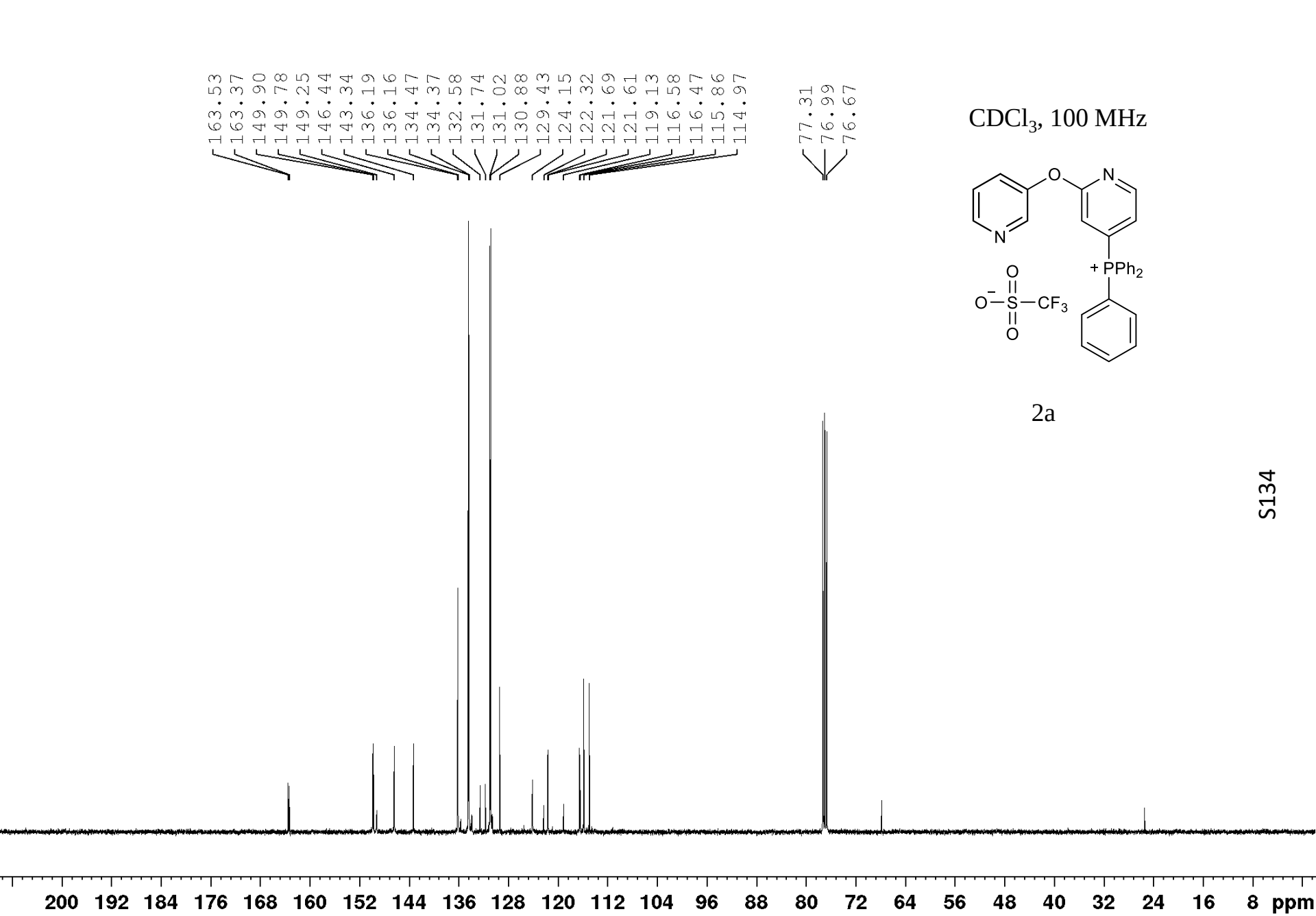
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

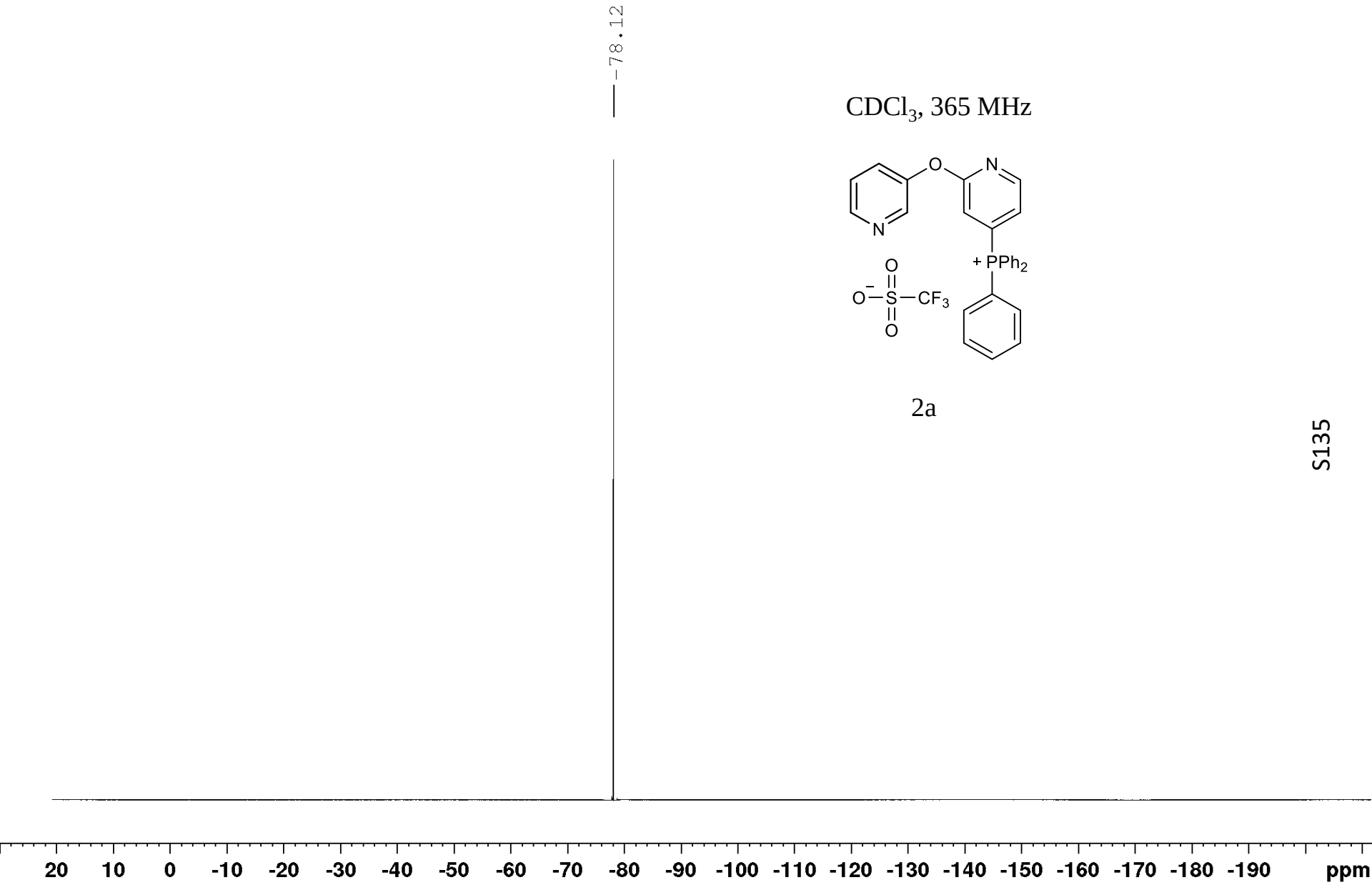


2a

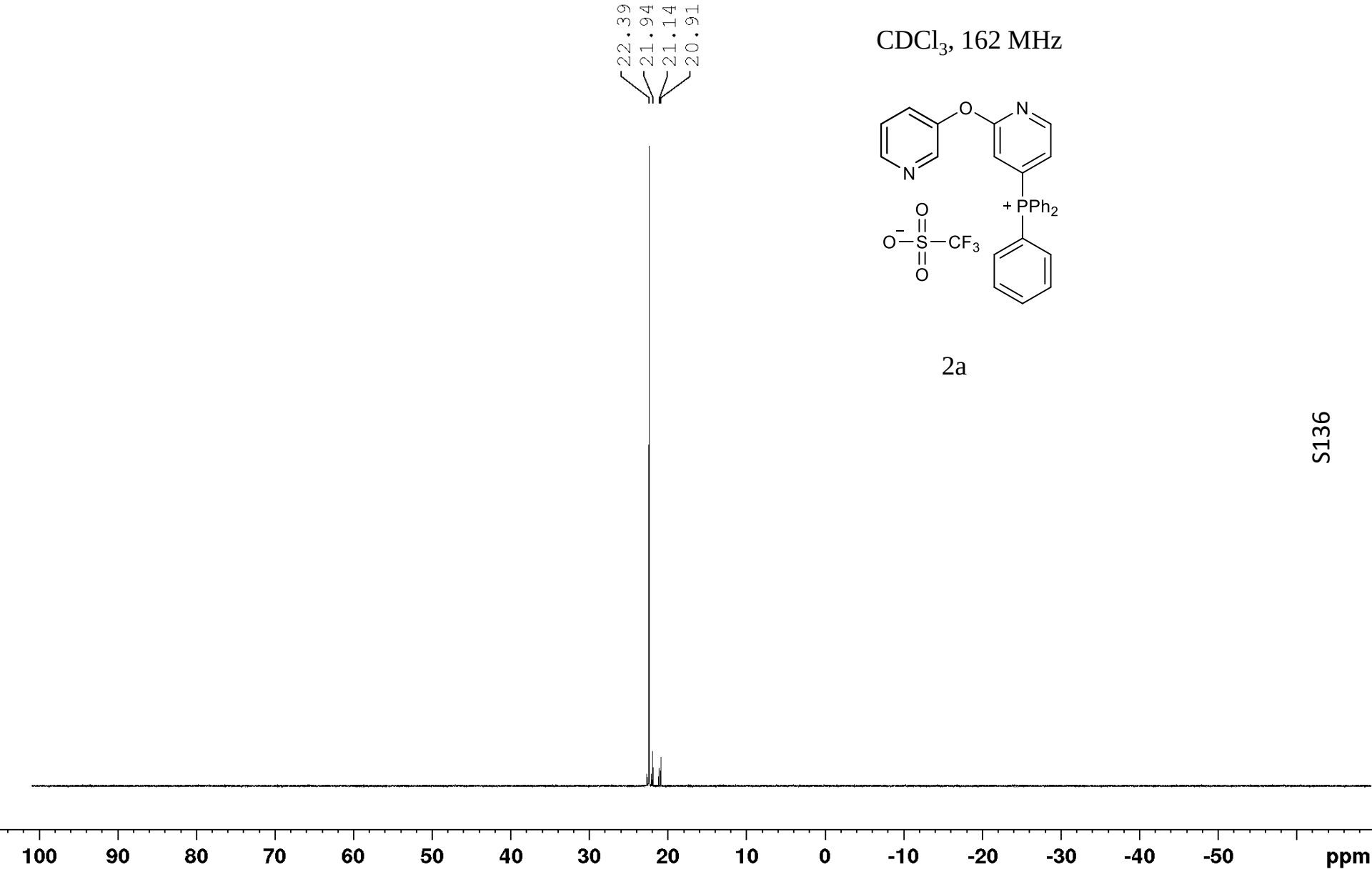

8.47
8.46
7.93
7.92
7.91
7.90
7.83
7.82
7.81
7.79
7.78
7.73
7.71
7.70
7.68
7.66
7.64
7.62
7.38
7.37
7.36
7.35
7.32
7.31
7.29
7.28
7.14
7.10
CDCl3, 400 MHz
O
N
N
+ PPh2
O
O−S−CF3
O
2a
S132
2.68
16.00
0.90
0.98
0.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


8.92
8.90
7.16
7.12
6.29
6.28
6.28
CDCl3, 400 MHz
(crude 1H NMR)
Major
Minor
34.598
1.000
2.666
7.0
6.8
6.6
6.4
ppm
O
N
N
+ PPh2
O
O−S−CF3
O
2a
S133
1.14
34.60
1.00
2.67
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
ppm

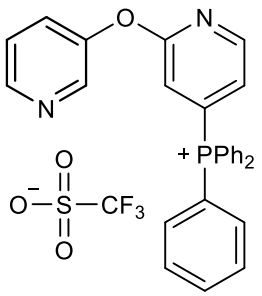

163.53
163.37
149.90
149.78
149.25
146.44
143.34
136.19
136.16
134.47
134.37
132.58
131.74
131.02
130.88
129.43
124.15
122.32
121.69
121.61
119.13
116.58
116.47
115.86
114.97
77.31
76.99
76.67
CDCl3, 100 MHz
O
N
N
+ PPh2
O
O
S
CF3
O
2a
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


-78.12
CDCl3, 365 MHz
O
N
N
+ PPh2
O
O
S
CF3
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

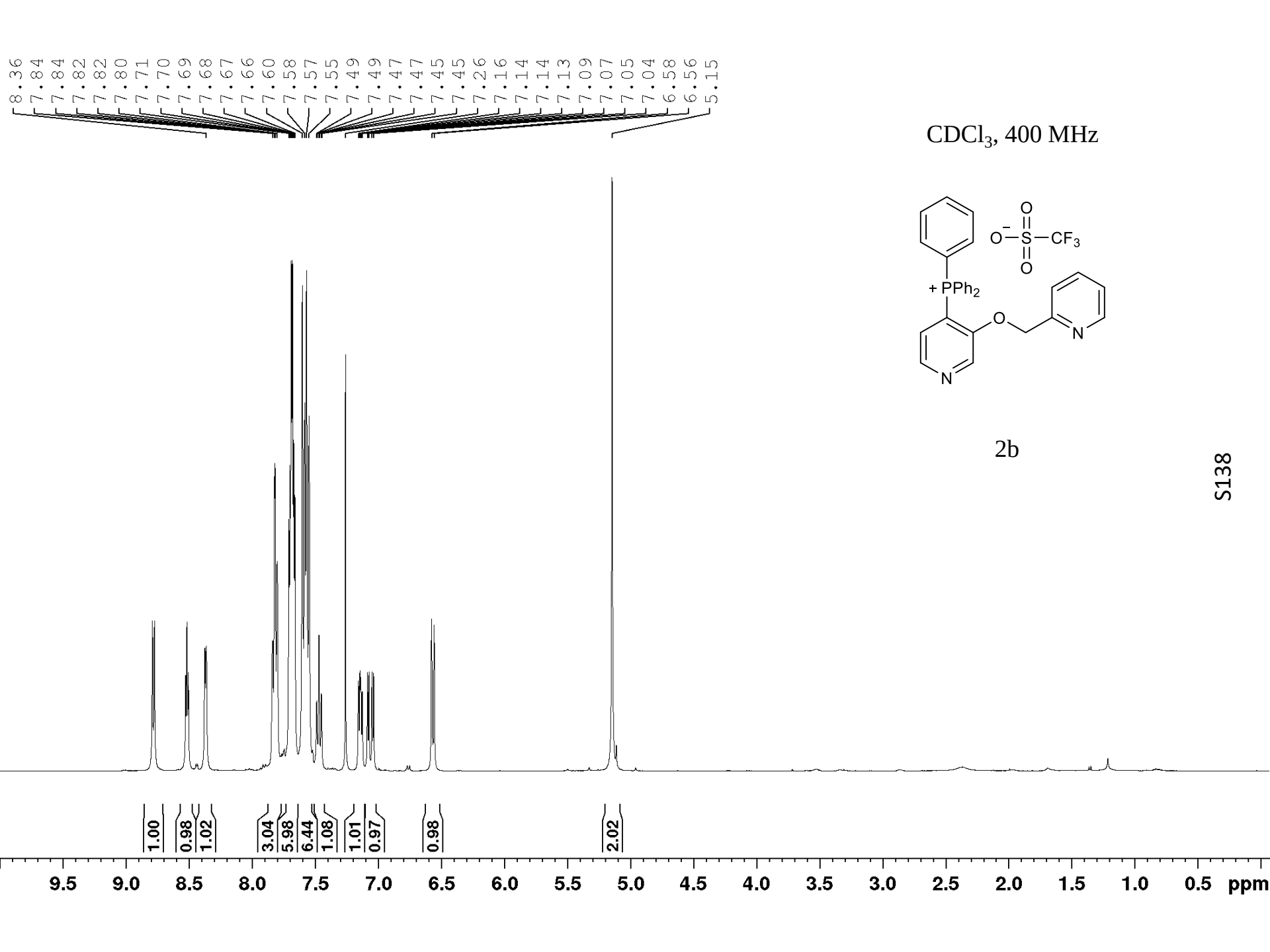
2a

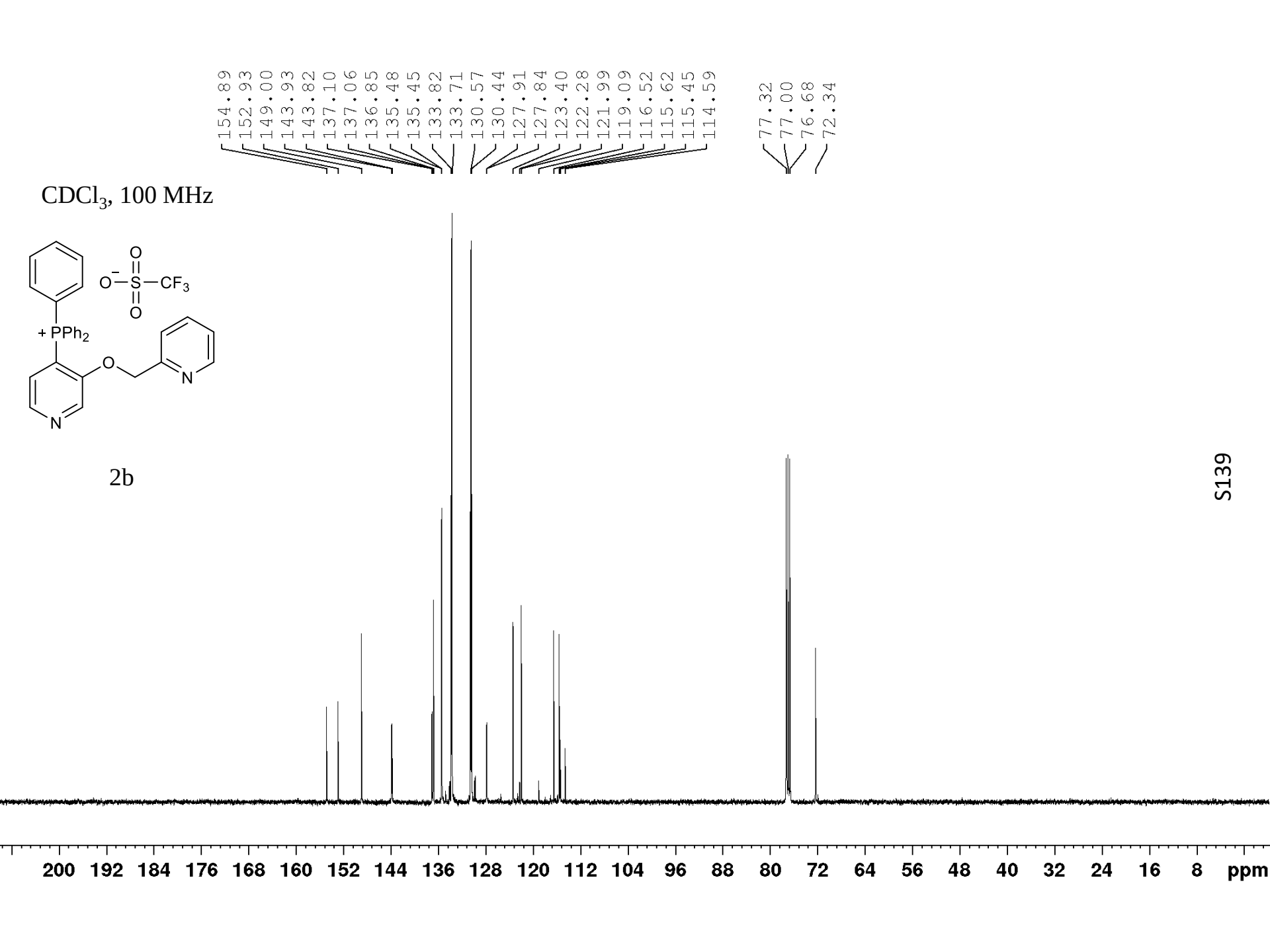

22.39
21.94
21.14
20.91
CDCl3, 162 MHz
O
N
N
+ PPh2
O
O
S
CF3
O
2a
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

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

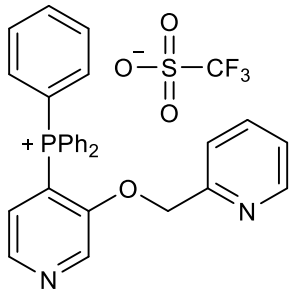


2a


8.36
7.84
7.84
7.82
7.82
7.80
7.71
7.70
7.69
7.68
7.67
7.66
7.60
7.58
7.57
7.55
7.49
7.49
7.47
7.47
7.45
7.45
7.26
7.16
7.14
7.14
7.13
7.09
7.07
7.05
7.04
6.58
6.56
5.15
CDCl3, 400 MHz
+ PPh2
O
S
CF3
N
N
2b
S138
1.00
0.98
1.02
3.04
5.98
6.44
1.08
1.01
0.97
0.98
2.02
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
0.5
ppm

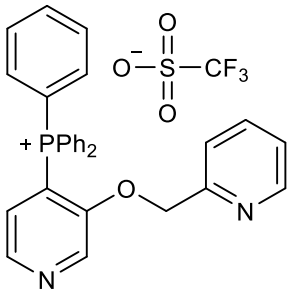

154.89
152.93
149.00
143.93
143.82
137.10
137.06
136.85
135.48
135.45
133.82
133.71
130.57
130.44
127.91
127.84
123.40
122.28
121.99
119.09
116.52
115.62
115.45
114.59
77.32
77.00
76.68
72.34
CDCl3, 100 MHz
2b
S139
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



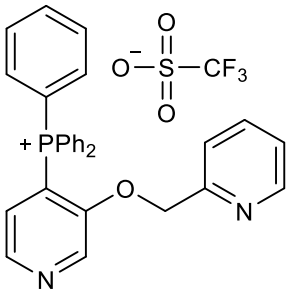
2b

$CDCl_3$, 162 MHz

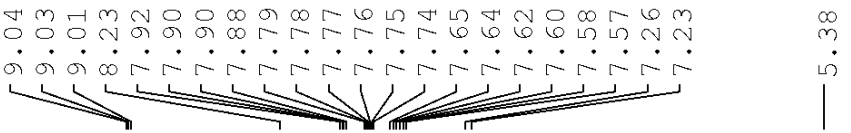


2b

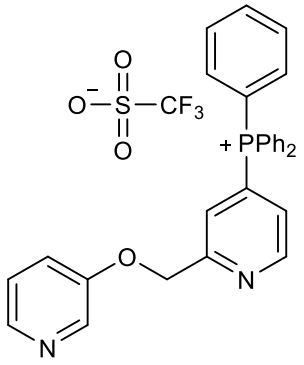
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)



2b

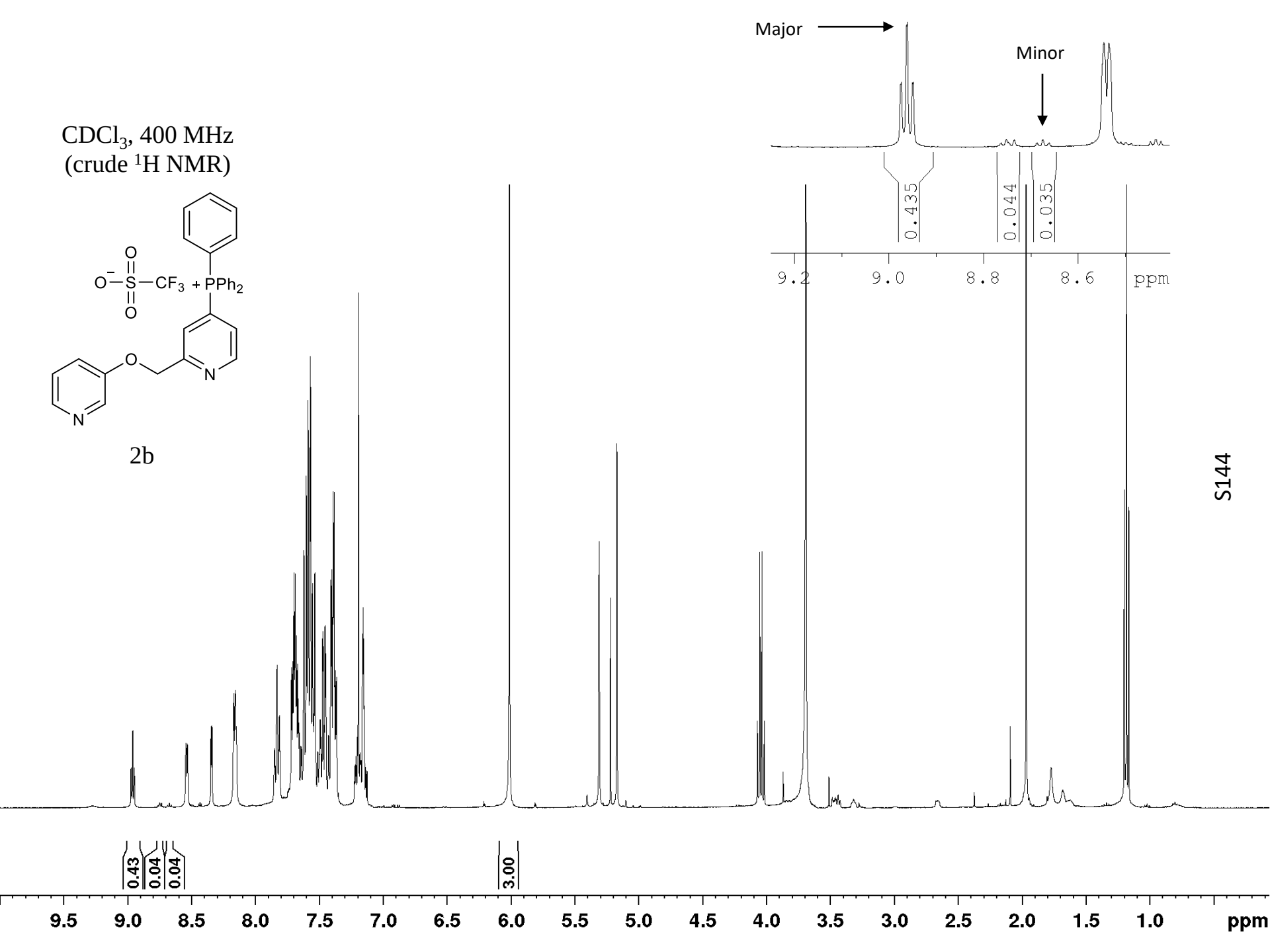


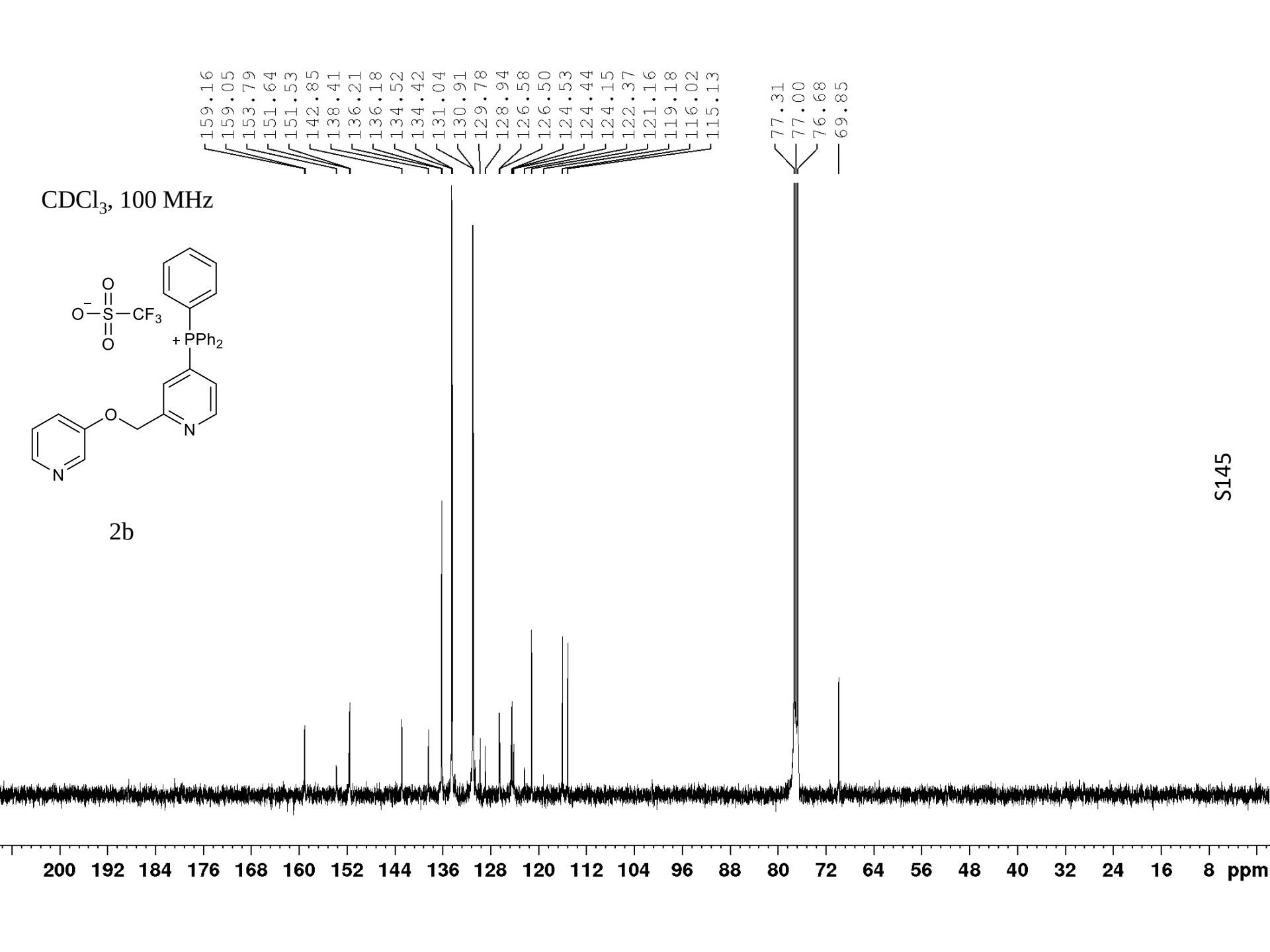
$CDCl_3$, 400 MHz



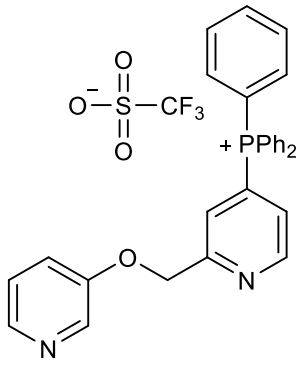
2b

S143


Major
Minor
0.435
0.044
0.035
9.2
9.0
8.8
8.6
ppm
CDCl3, 400 MHz
(crude 1H NMR)
2b
S144
0.43
0.04
0.04
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

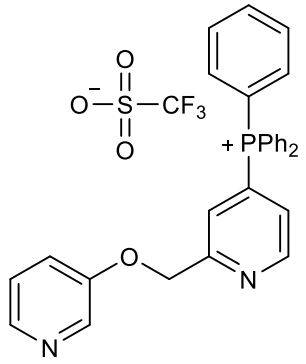

159.16
159.05
153.79
151.64
151.53
142.85
138.41
136.21
136.18
134.52
134.42
131.04
130.91
129.78
128.94
126.58
126.50
124.53
124.44
124.15
122.37
121.16
119.18
116.02
115.13
77.31
77.00
76.68
69.85
CDCl3, 100 MHz
2b
S145
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



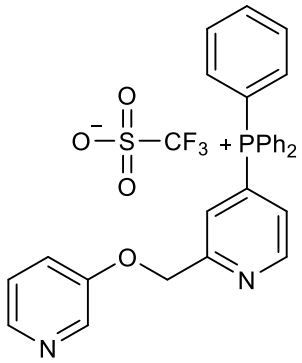
2b

$CDCl_3$, 162 MHz

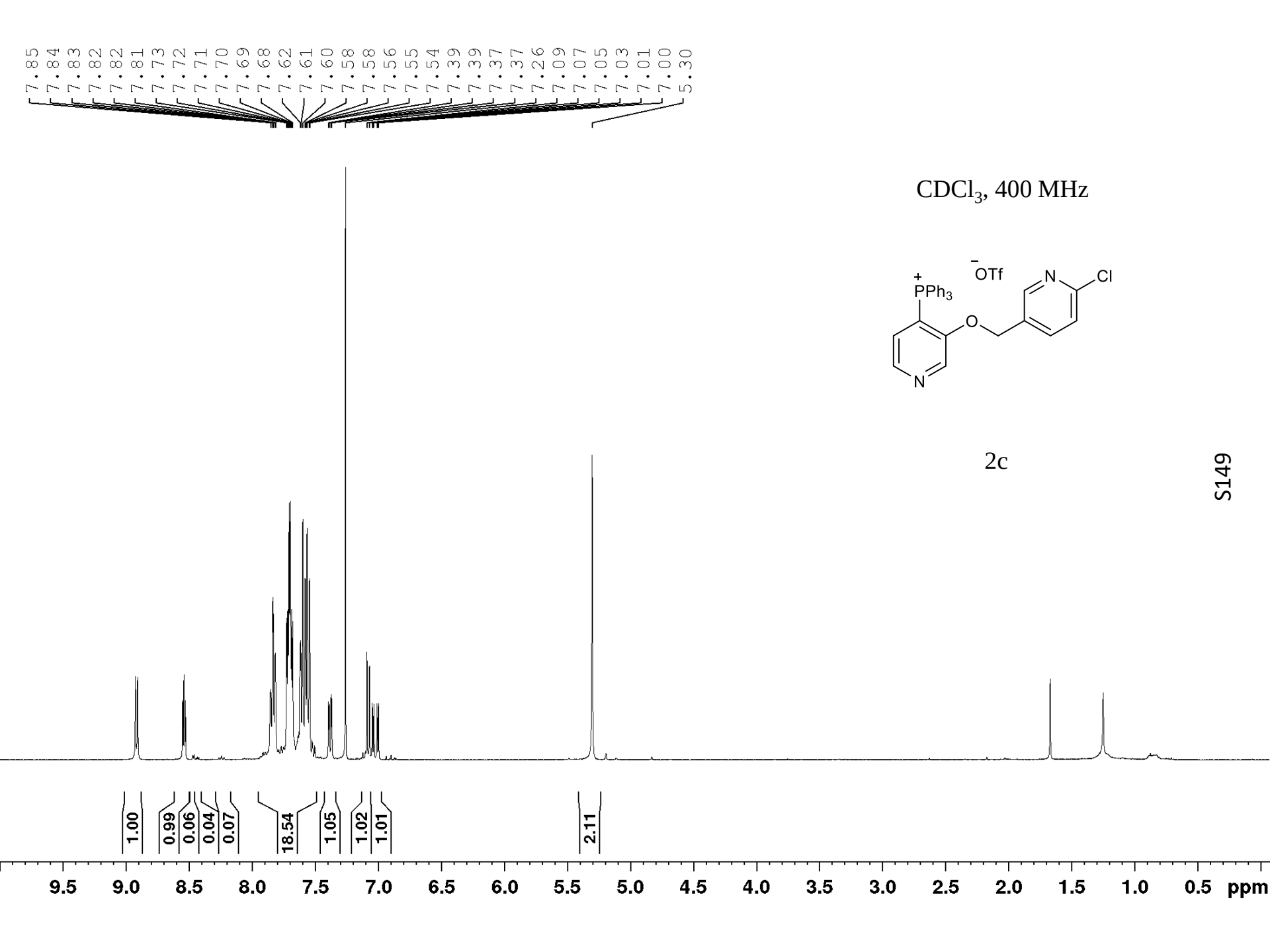


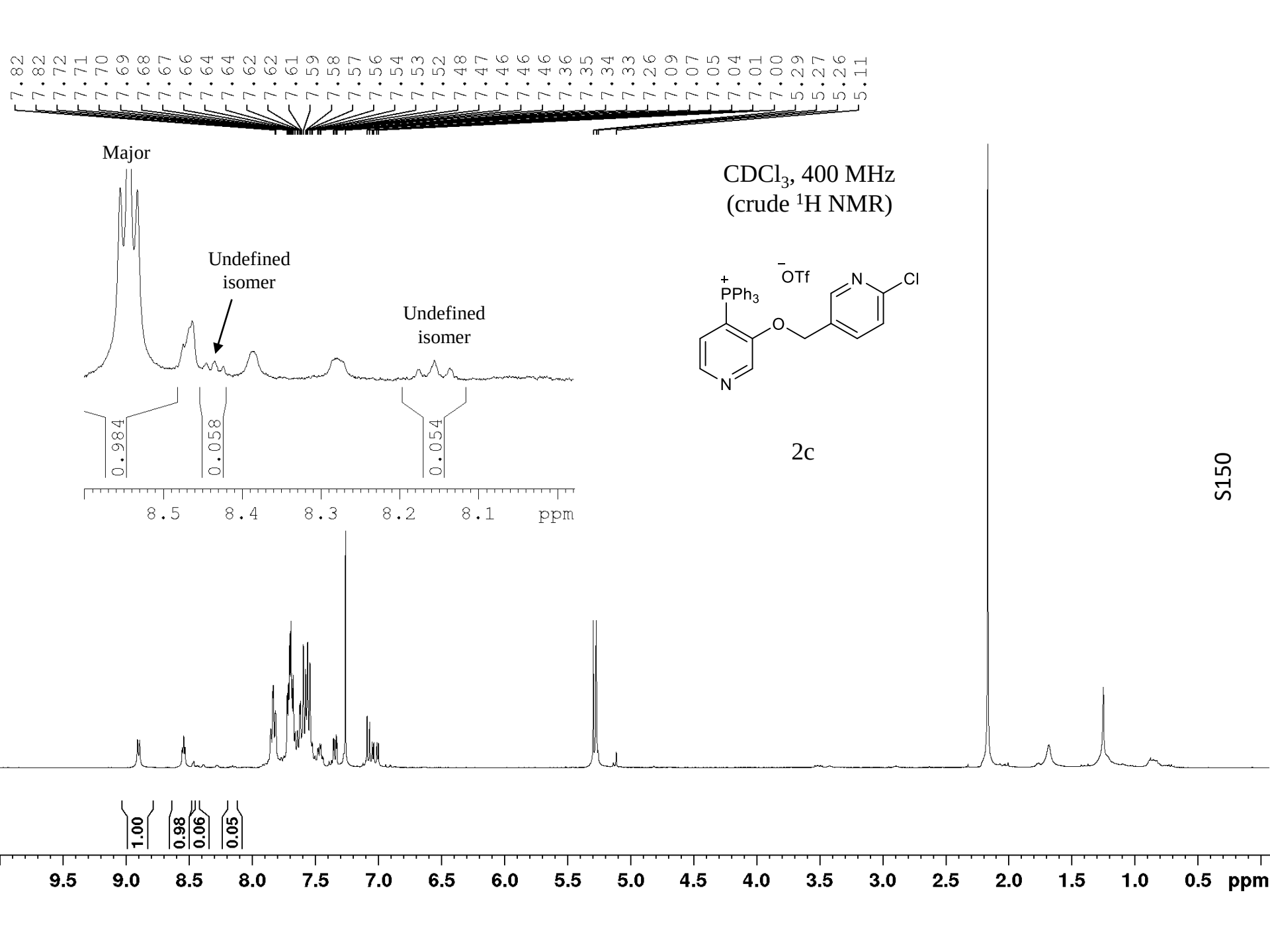
2b

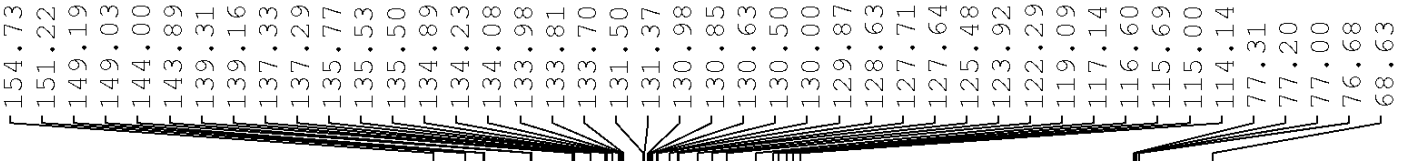
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)



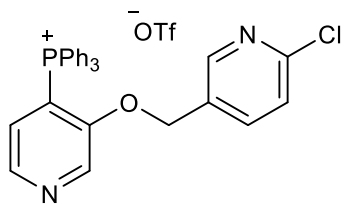
2b


7.85
7.84
7.83
7.82
7.82
7.81
7.73
7.72
7.71
7.70
7.69
7.68
7.62
7.61
7.60
7.58
7.58
7.56
7.55
7.54
7.39
7.39
7.37
7.37
7.26
7.09
7.07
7.05
7.03
7.01
7.00
5.30
CDCl3, 400 MHz
OTf
PPh3
N
Cl
O
N
2c
S149
1.00
0.99
0.06
0.04
0.07
18.54
1.05
1.02
1.01
2.11
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
ppm

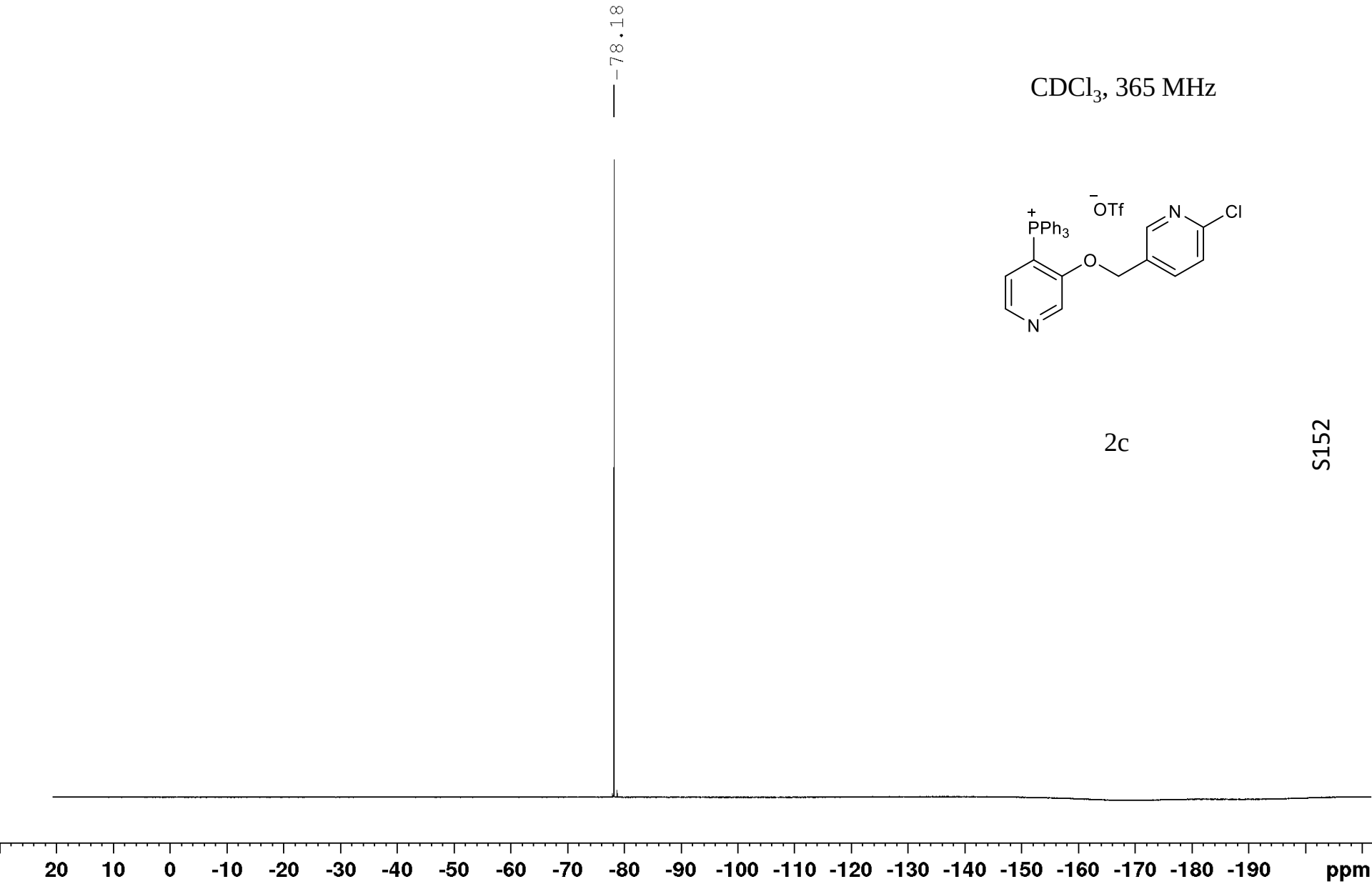

7.82 7.82 7.72 7.71 7.70 7.69 7.68 7.67 7.66 7.64 7.64 7.62 7.62 7.61 7.59 7.58 7.57 7.56 7.54 7.53 7.52 7.48 7.47 7.46 7.46 7.46 7.36 7.35 7.34 7.33 7.26 7.09 7.07 7.05 7.04 7.01 7.00 5.29 5.27 5.26 5.11
Major
Undefined isomer
Undefined isomer
0.984
0.058
0.054
8.5 8.4 8.3 8.2 8.1 ppm
CDCl3, 400 MHz
(crude 1H NMR)
OTf
PPh3
N
Cl
O
N
2c
S150
1.00
0.98
0.06
0.05
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 0.5 ppm

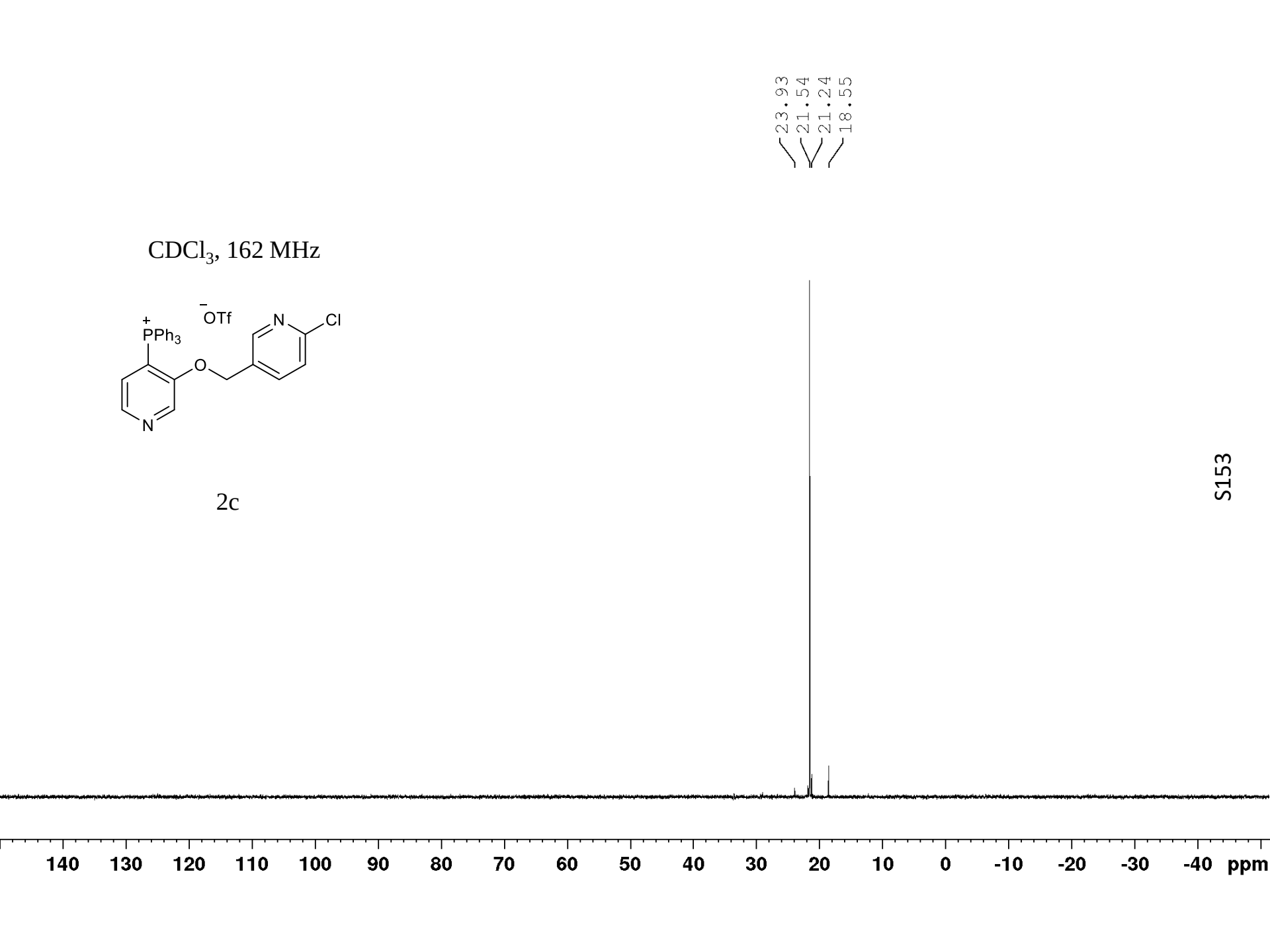


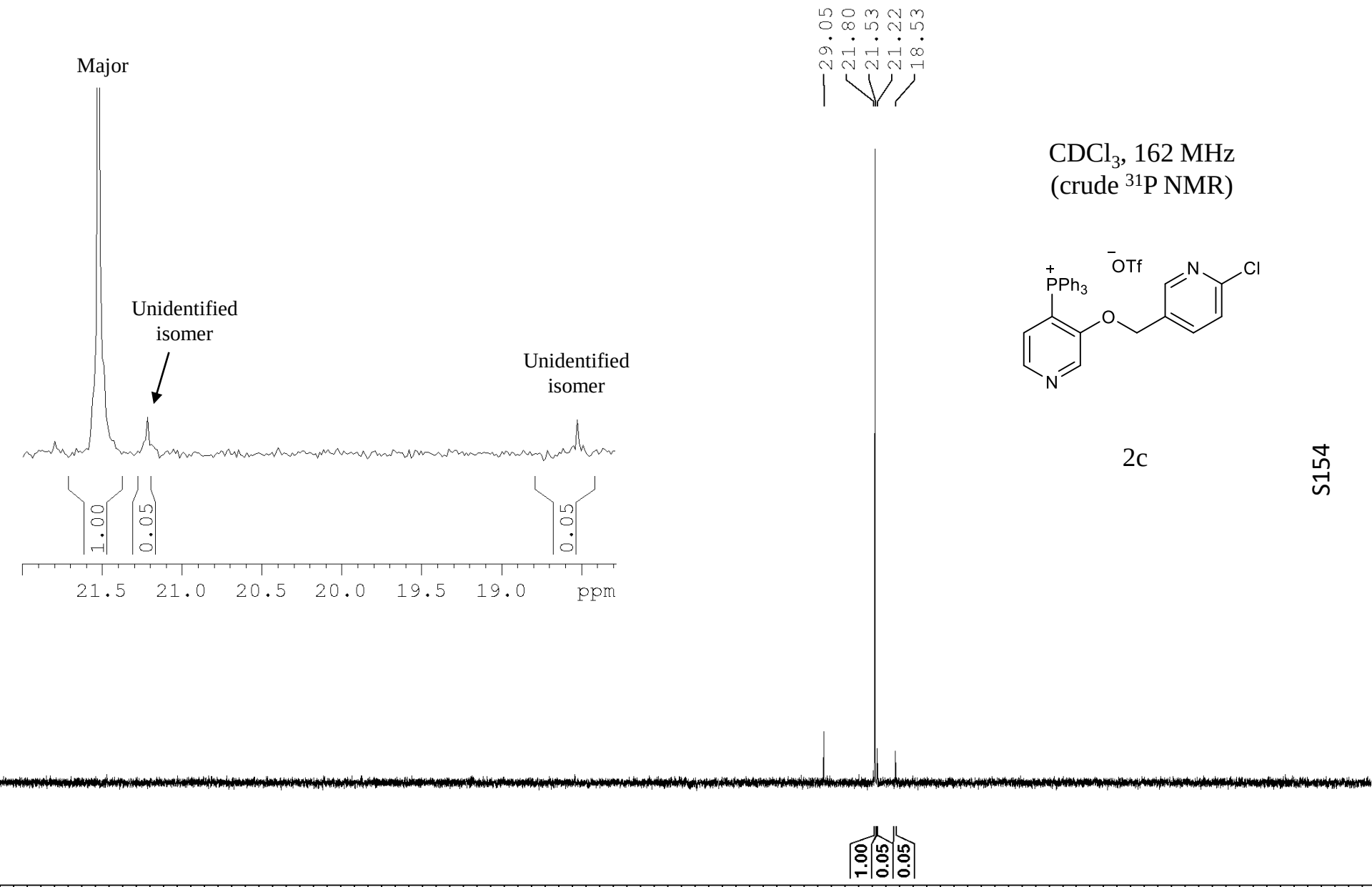
$CDCl_3$, 100 MHz



2c

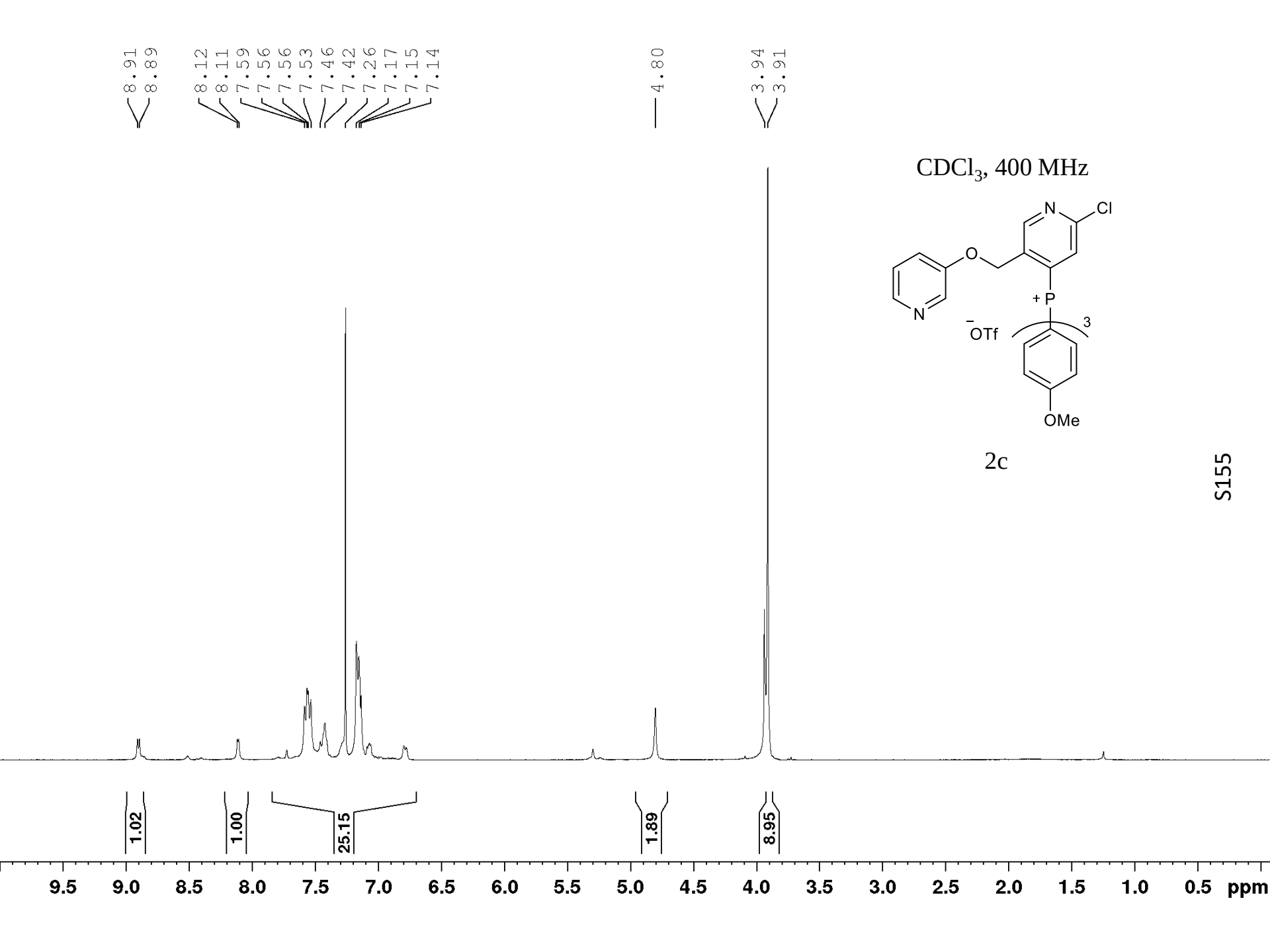

-78.18
CDCl3, 365 MHz
+
PPh3
OTf
N
Cl
O
N
2c
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

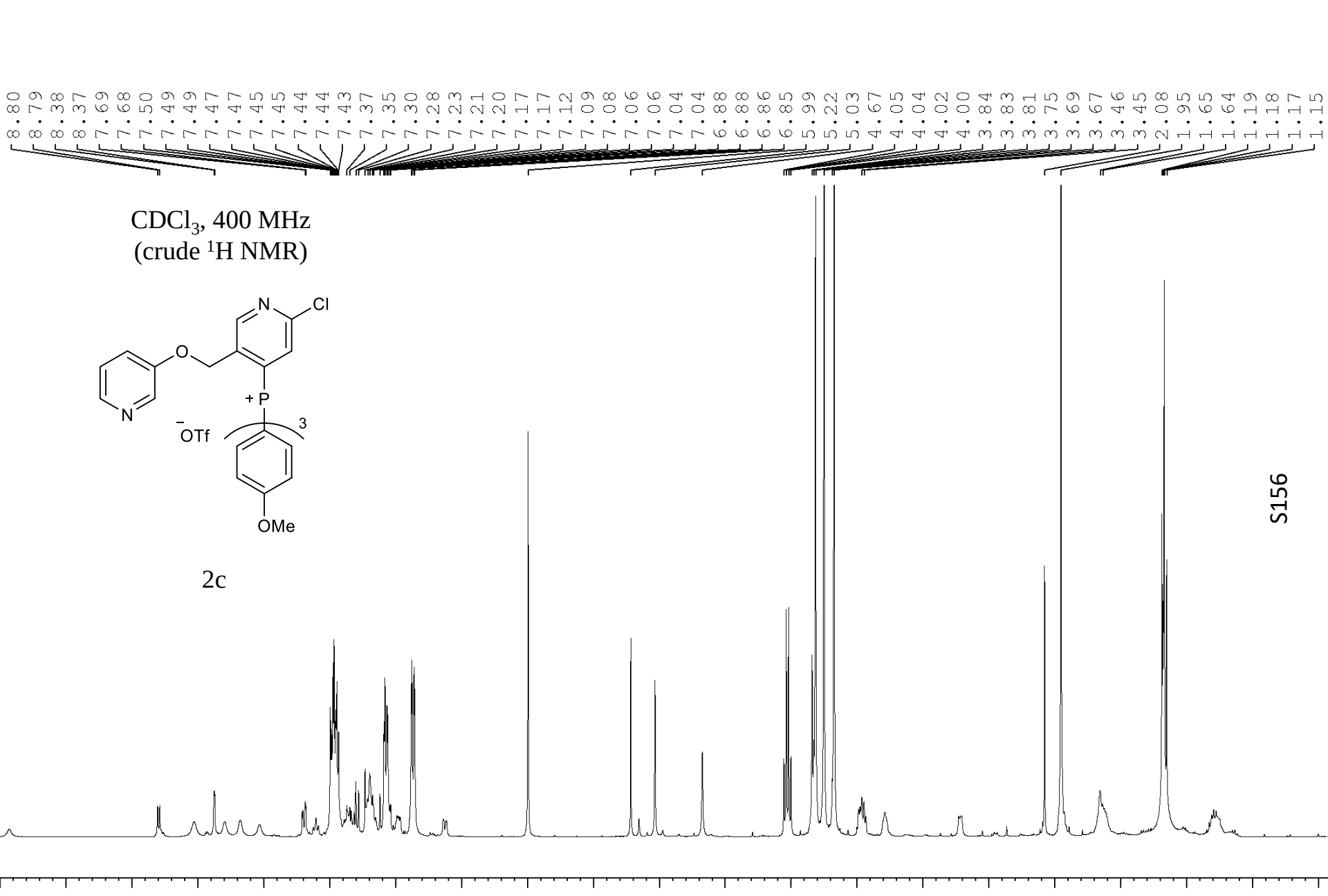

23.93
21.54
21.24
18.55
CDCl3, 162 MHz
+
PPh3
−
OTf
N
Cl
O
N
2c
S153
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

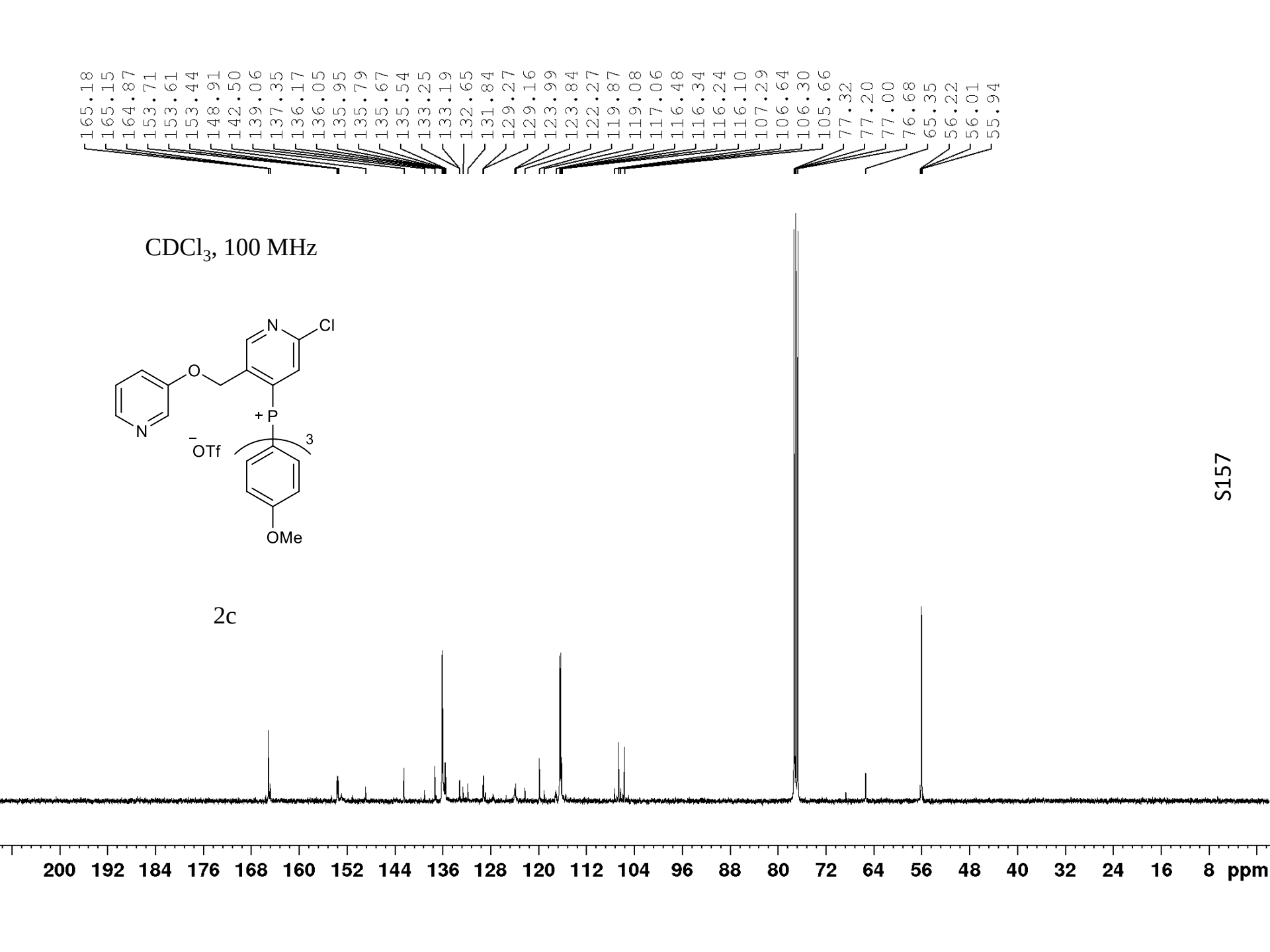


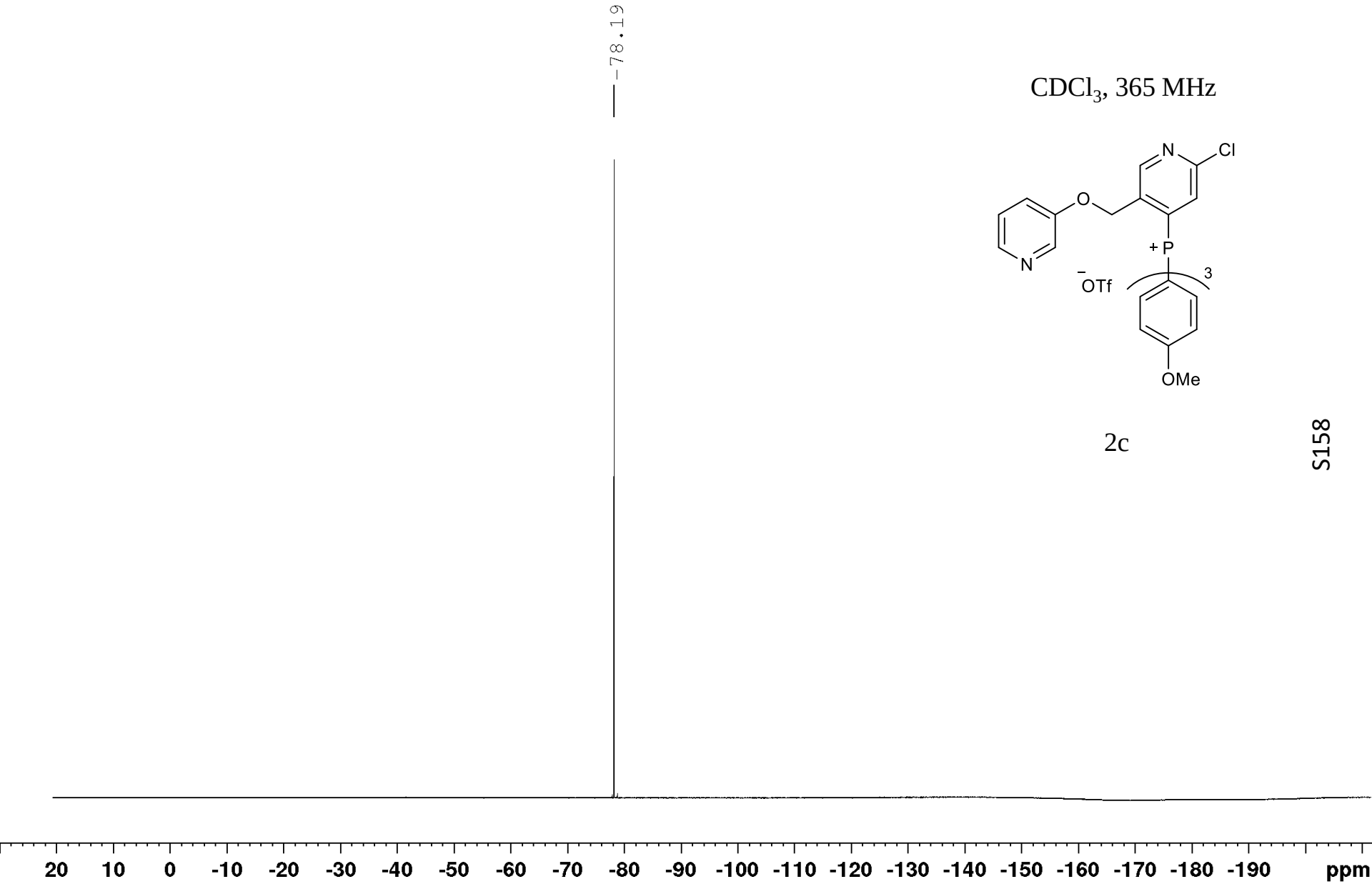
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

2c


8.91
8.89
8.12
8.11
7.59
7.56
7.56
7.53
7.46
7.42
7.26
7.17
7.15
7.14
4.80
3.94
3.91
CDCl3, 400 MHz
N
Cl
O
+ P
N
OTf
3
OMe
2c
S155
1.02
1.00
25.15
1.89
8.95
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
ppm

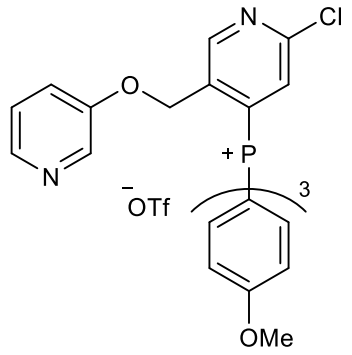

8.80
8.79
8.38
8.37
7.69
7.68
7.50
7.49
7.49
7.47
7.47
7.45
7.45
7.44
7.44
7.43
7.37
7.35
7.30
7.28
7.23
7.21
7.20
7.17
7.17
7.12
7.09
7.08
7.06
7.06
7.04
7.04
6.88
6.88
6.86
6.85
5.99
5.22
5.03
4.67
4.05
4.04
4.02
4.00
3.84
3.83
3.81
3.75
3.69
3.67
3.46
3.45
2.08
1.95
1.65
1.64
1.19
1.18
1.17
1.15
CDCl3, 400 MHz
(crude 1H NMR)
N
Cl
O
N
+ P
3
OTf
OMe
2c
S156
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
ppm


165.18
165.15
164.87
153.71
153.61
153.44
148.91
142.50
139.06
137.35
136.17
136.05
135.95
135.79
135.67
135.54
133.25
133.19
132.65
131.84
129.27
129.16
123.99
123.84
122.27
119.87
119.08
117.06
116.48
116.34
116.24
116.10
107.29
106.64
106.30
105.66
77.32
77.20
77.00
76.68
65.35
56.22
56.01
55.94
CDCl3, 100 MHz
N
Cl
O
+ P
N
OTf
3
OMe
2c
S157
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 ppm

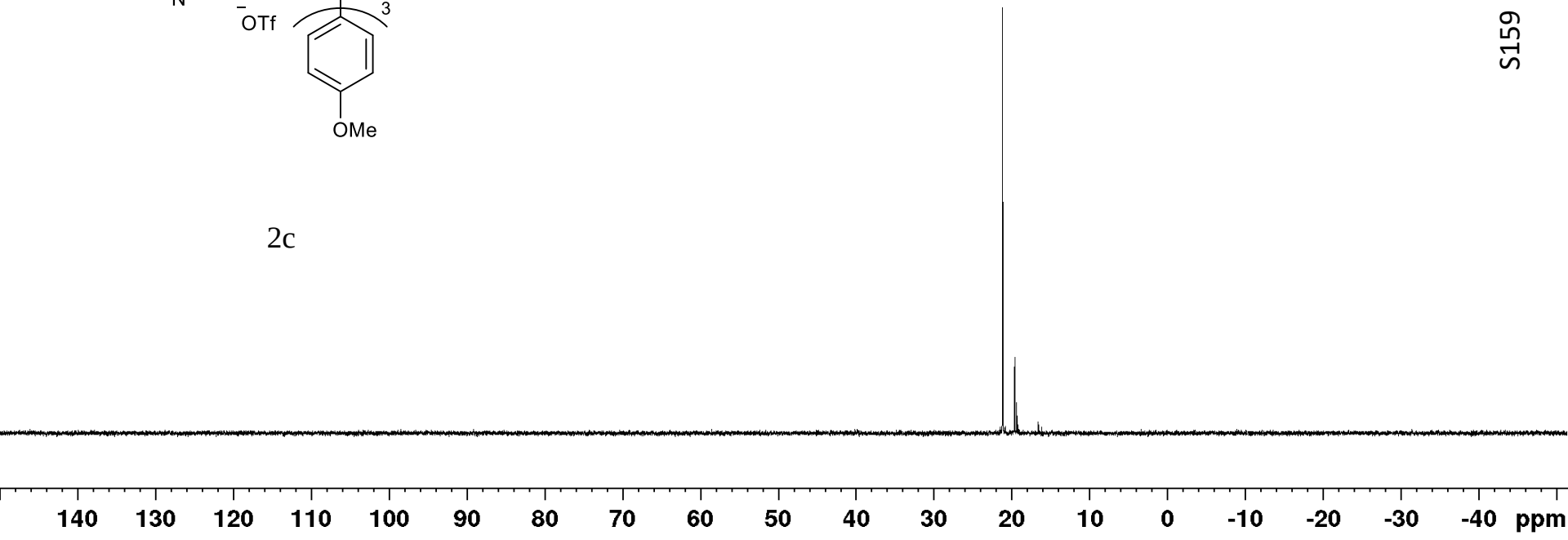

-78.19
CDCl3, 365 MHz
N
Cl
O
N
+ P
3
− OTf
OMe
2c
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

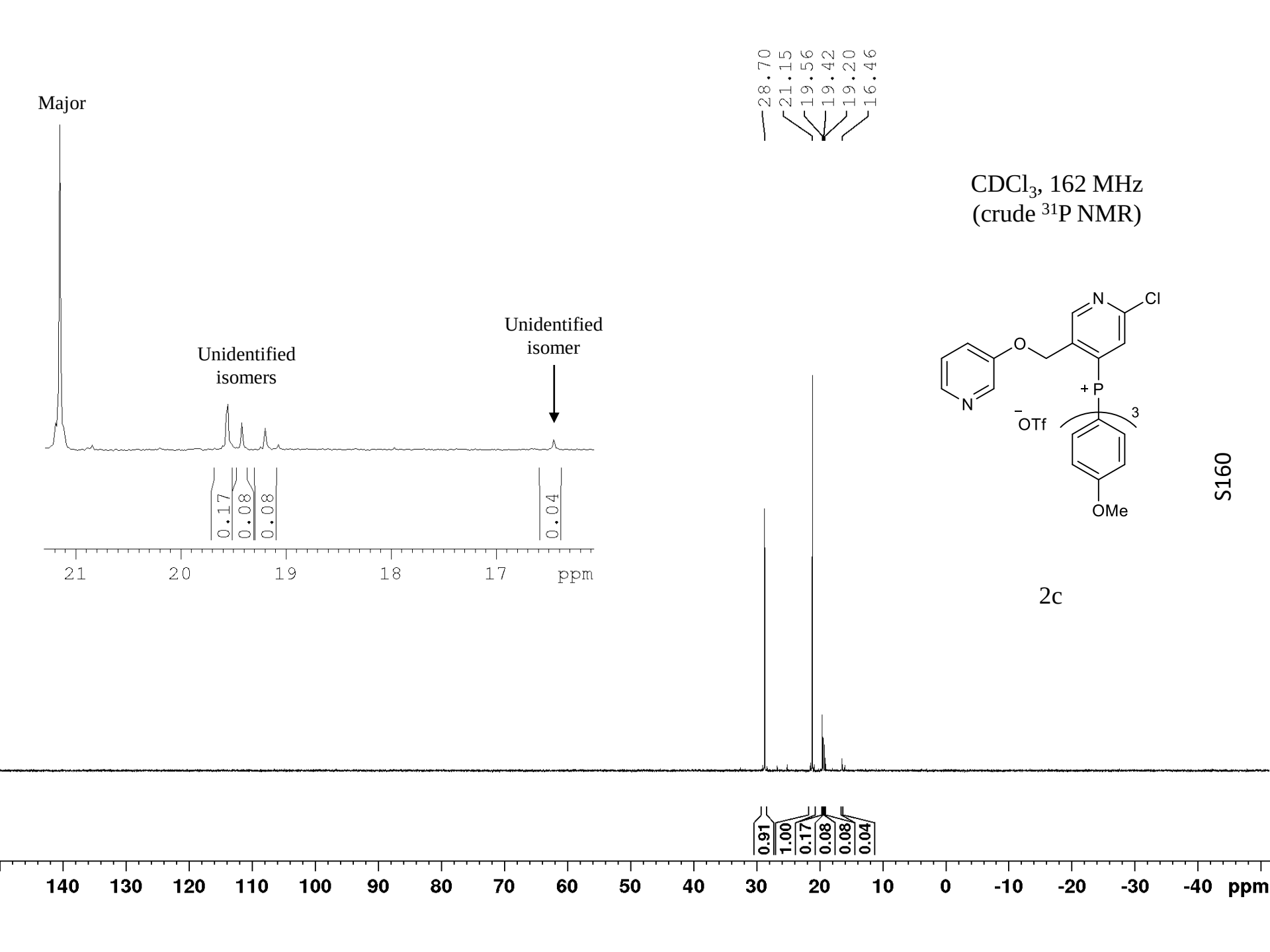
21.17
19.65
19.62
19.35
16.58

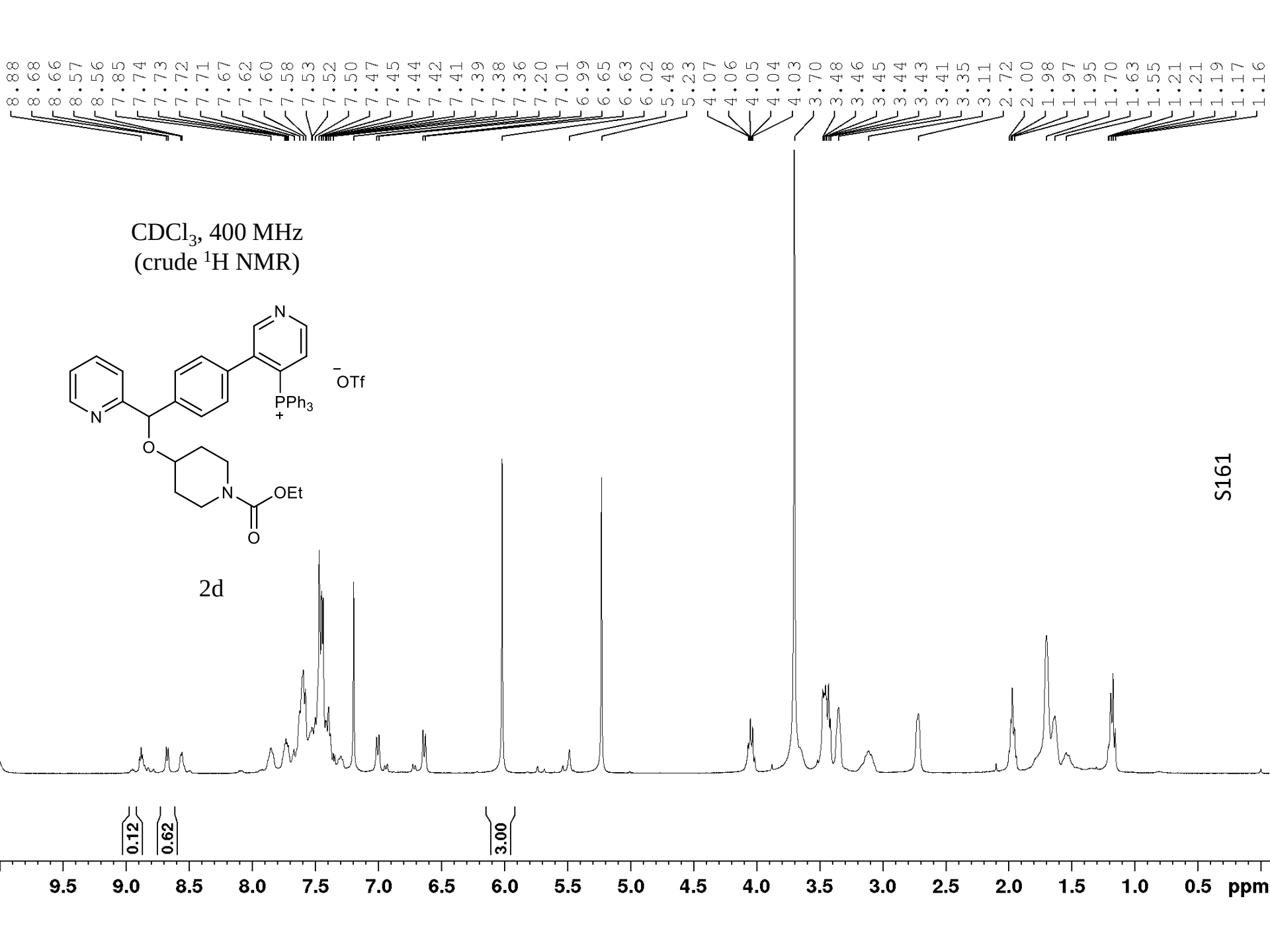
$CDCl_3$, 162 MHz

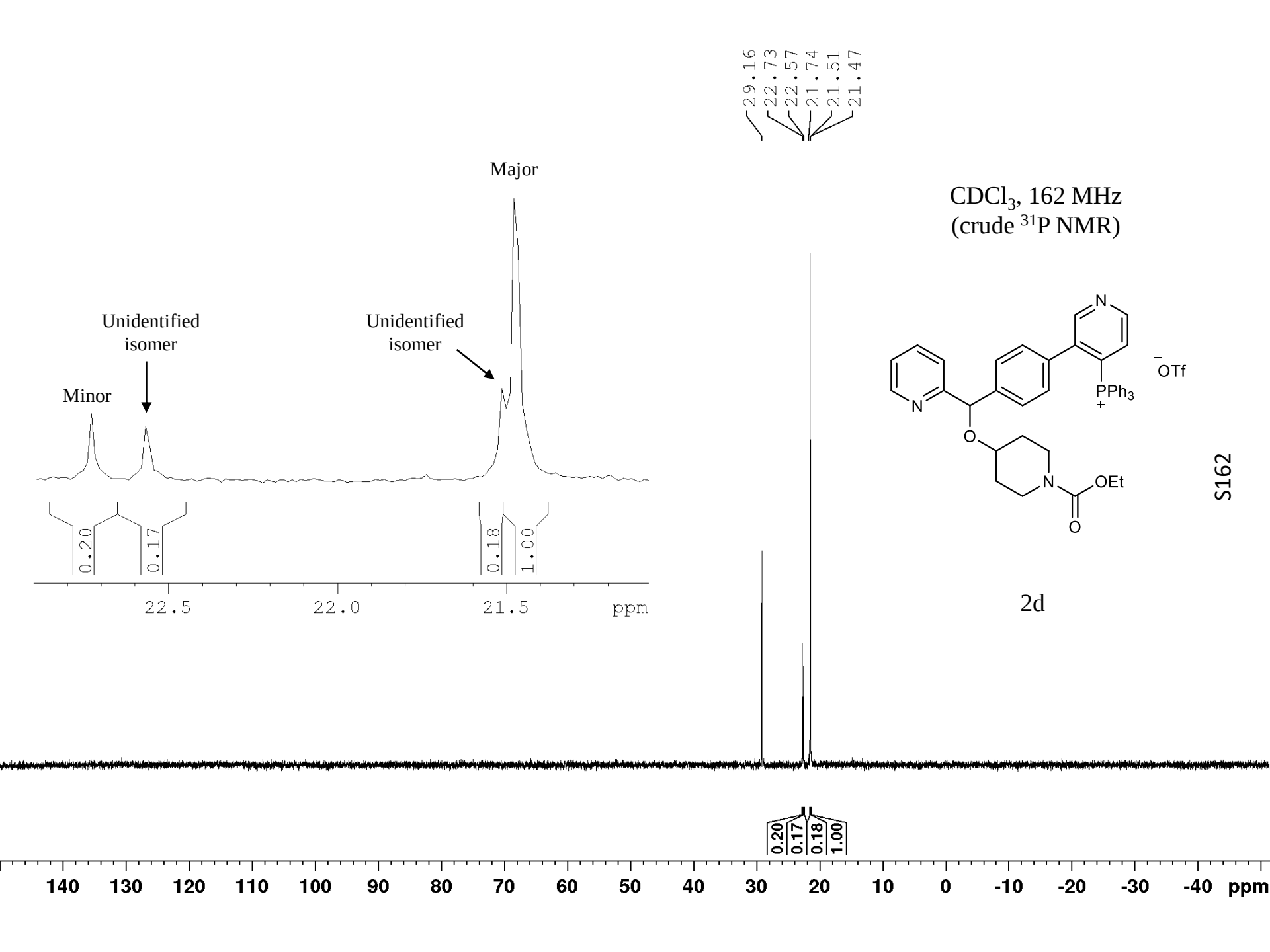


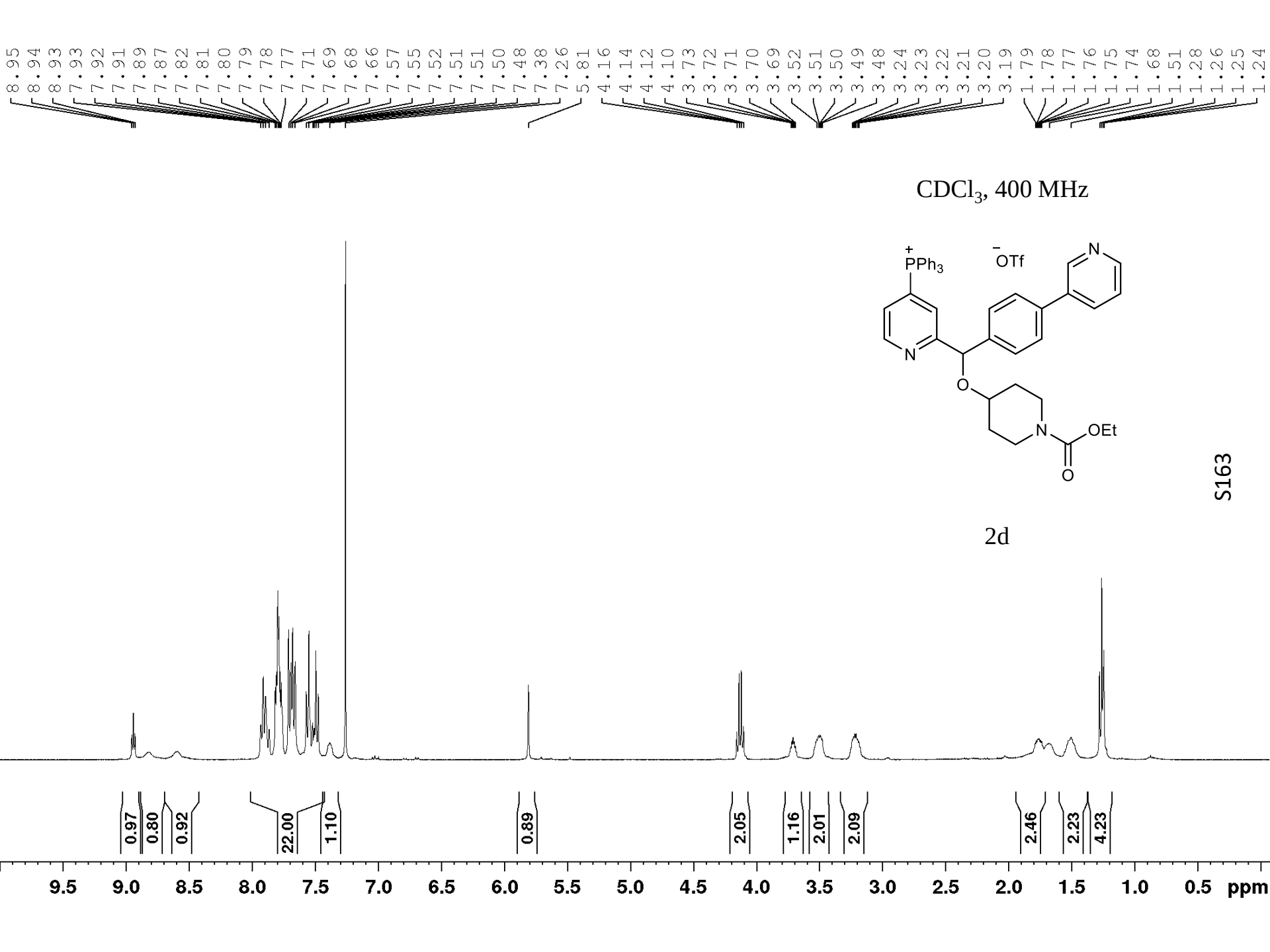
2c

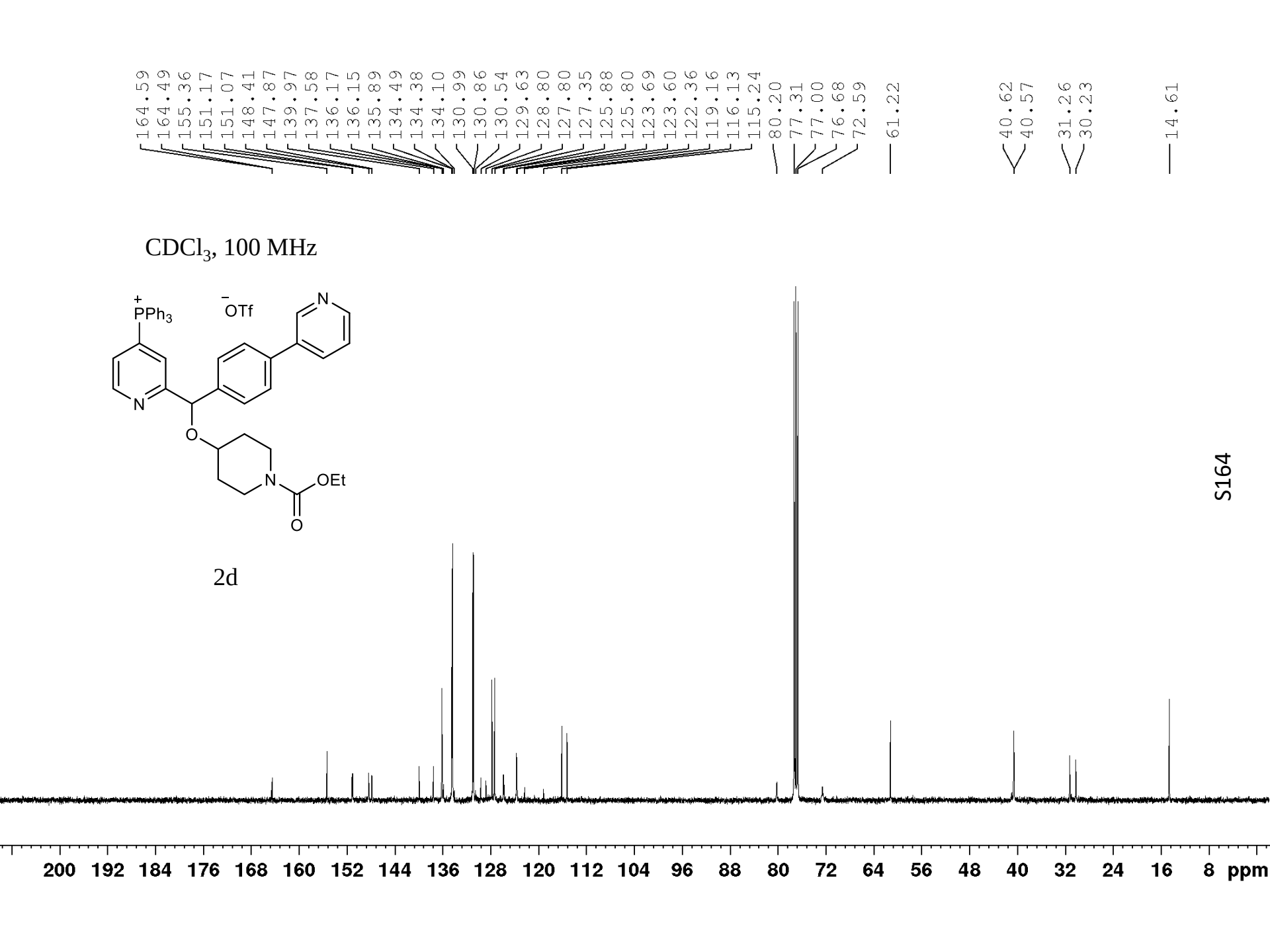


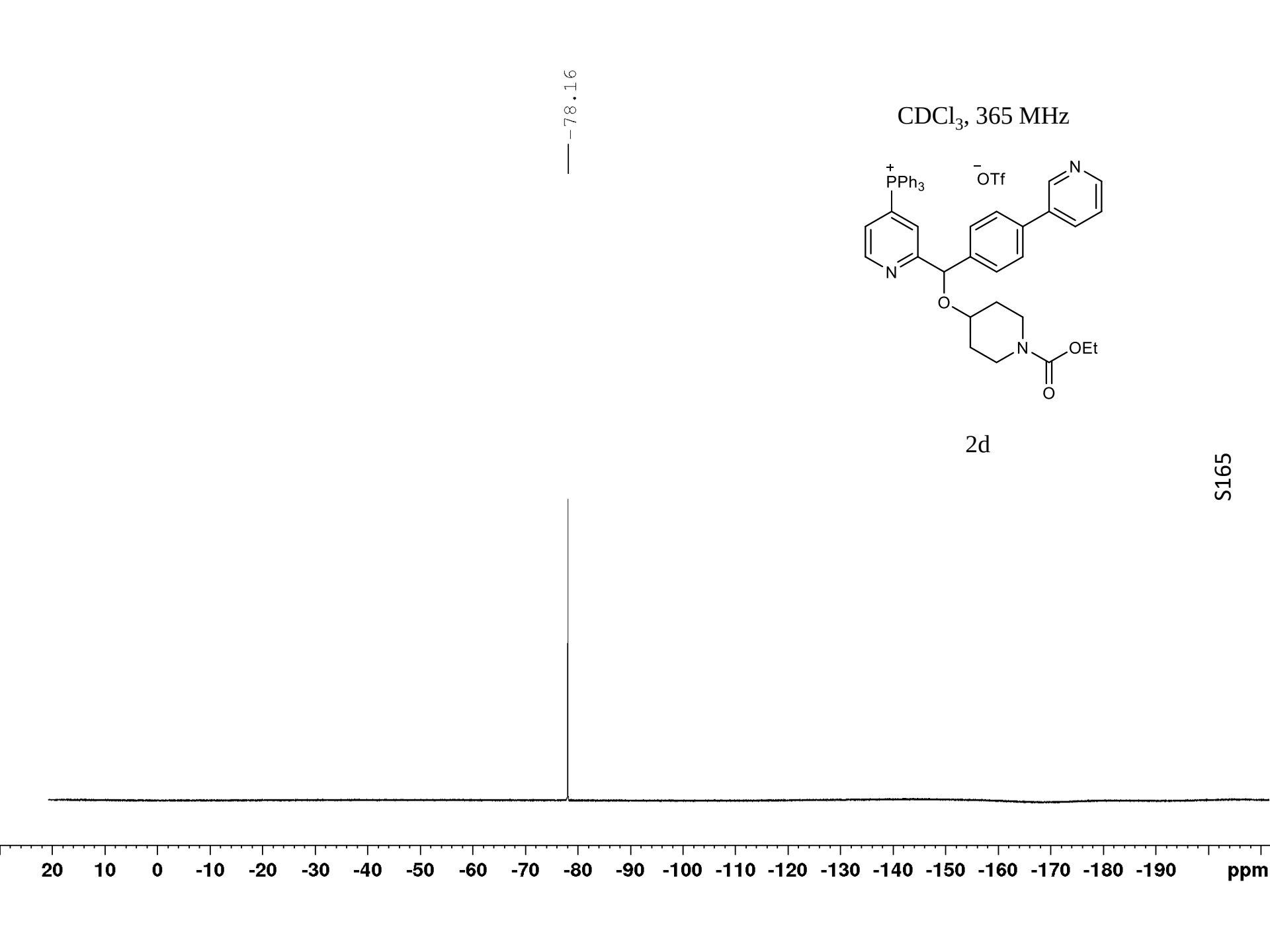

28.70
21.15
19.56
19.42
19.20
16.46
Major
Unidentified isomers
Unidentified isomer
0.17
0.08
0.08
0.04
21
20
19
18
17
ppm
CDCl3, 162 MHz
(crude 31P NMR)
N
Cl
O
N
+ P
3
OTf
OMe
2c
S160
0.91
1.00
0.17
0.08
0.08
0.04
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

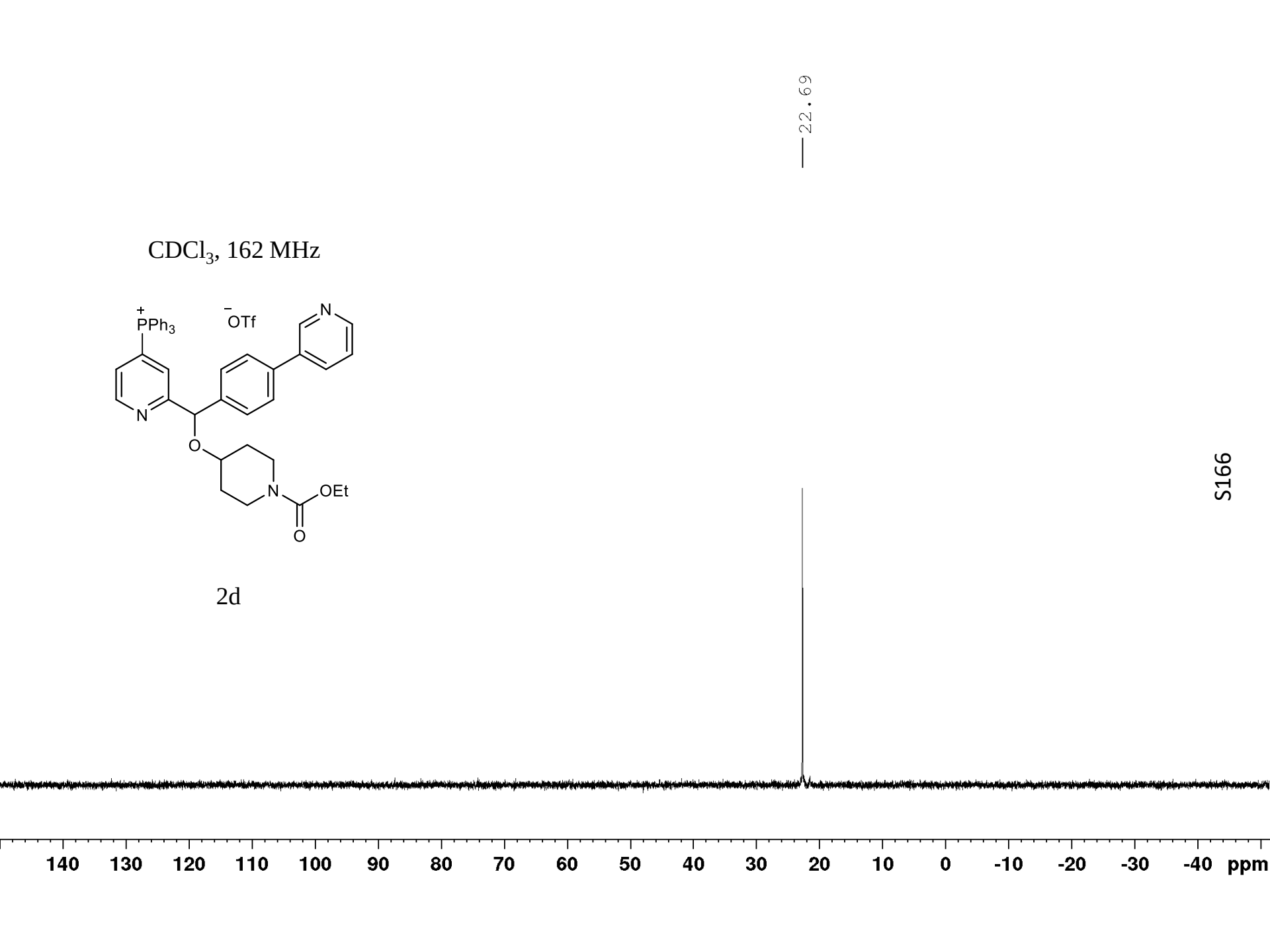

8.88
8.68
8.66
8.57
8.56
8.85
7.74
7.73
7.72
7.71
7.67
7.62
7.60
7.58
7.53
7.52
7.50
7.47
7.45
7.44
7.42
7.41
7.39
7.38
7.36
7.20
7.01
6.99
6.65
6.63
6.02
5.48
5.23
4.07
4.06
4.05
4.04
4.03
3.70
3.48
3.46
3.45
3.44
3.43
3.41
3.35
3.11
2.72
2.00
1.98
1.97
1.95
1.70
1.63
1.55
1.21
1.21
1.19
1.17
1.16
CDCl3, 400 MHz
(crude 1H NMR)
N
OTf
PPh3
+
N
O
N
OEt
O
2d
S161
0.12
0.62
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
0.5
ppm


29.16
22.73
22.57
21.74
21.51
21.47
Major
Unidentified isomer
Unidentified isomer
Minor
0.20
0.17
0.18
1.00
22.5
22.0
21.5
ppm
CDCl3, 162 MHz
(crude 31P NMR)
N
OTf
PPh3
+
N
O
N
OEt
O
2d
S162
0.20
0.17
0.18
1.00
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


8.95 8.94 8.93 7.93 7.92 7.91 7.89 7.87 7.82 7.81 7.80 7.79 7.78 7.77 7.71 7.69 7.68 7.66 7.57 7.55 7.52 7.51 7.51 7.50 7.48 7.38 7.26 5.81 4.16 4.14 4.12 4.10 3.73 3.72 3.71 3.70 3.69 3.52 3.51 3.50 3.49 3.48 3.24 3.23 3.22 3.21 3.20 3.19 1.79 1.78 1.77 1.76 1.75 1.74 1.68 1.51 1.28 1.26 1.25 1.24
CDCl3, 400 MHz
PPh3
OTf
N
N
O
N
OEt
O
S163
2d
0.97 0.80 0.92 22.00 1.10 0.89 2.05 1.16 2.01 2.09 2.46 2.23 4.23
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 ppm

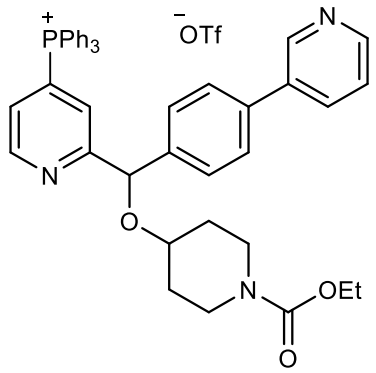

164.59
164.49
155.36
151.17
151.07
148.41
147.87
139.97
137.58
136.17
136.15
135.89
134.49
134.38
134.10
130.99
130.86
130.54
129.63
128.80
127.80
127.35
125.88
125.80
123.69
123.60
122.36
119.16
116.13
115.24
80.20
77.31
77.00
76.68
72.59
61.22
40.62
40.57
31.26
30.23
14.61
CDCl3, 100 MHz
PPh3
OTf
N
N
O
N
OEt
O
2d
S164
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 ppm


−78.16
CDCl3, 365 MHz
+
PPh3
−
OTf
N
N
O
N
OEt
O
2d
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


22.69
CDCl3, 162 MHz
PPh3
OTf
N
N
O
N
OEt
O
2d
S166
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

29.02
22.69
21.46

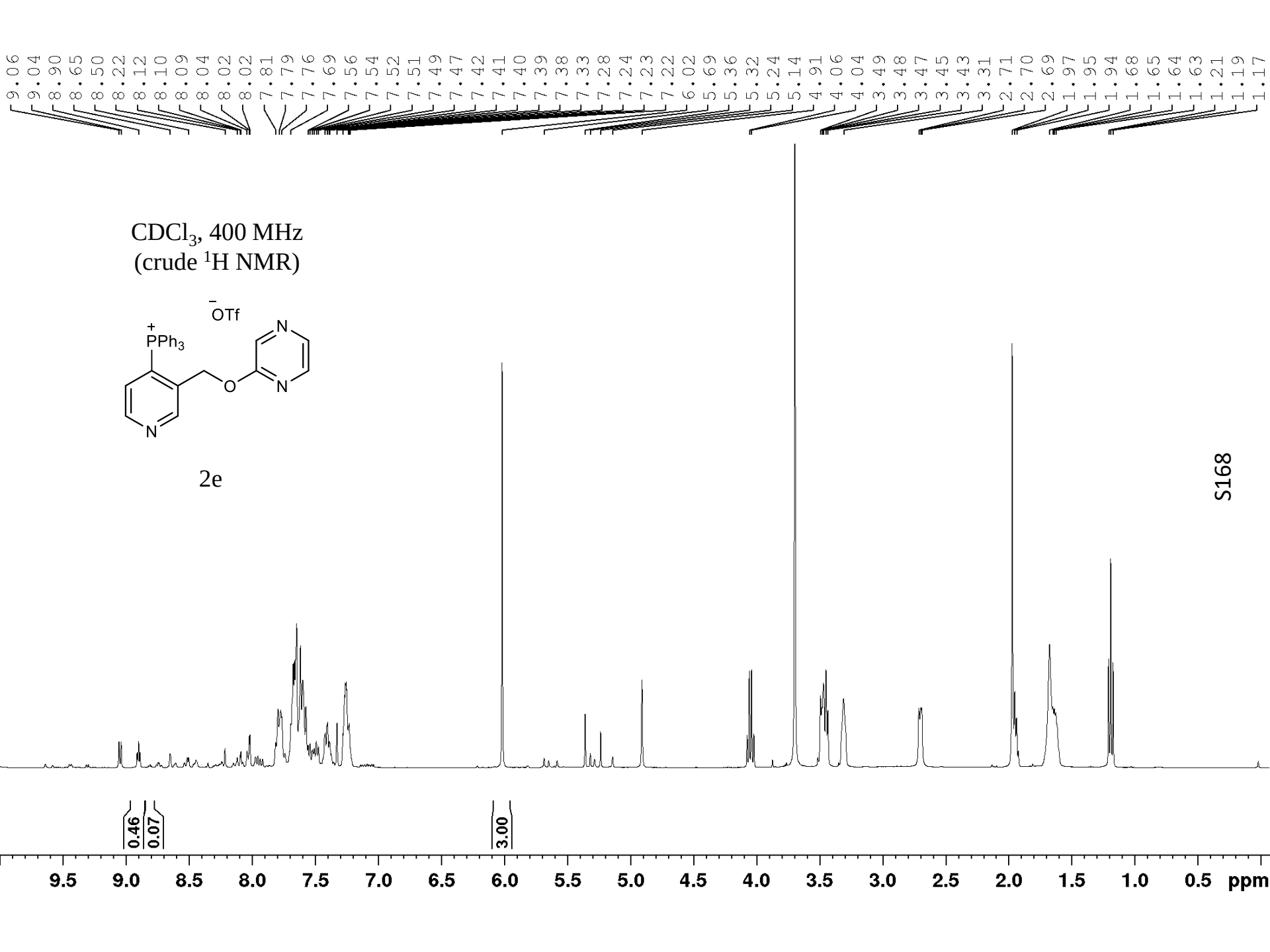
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

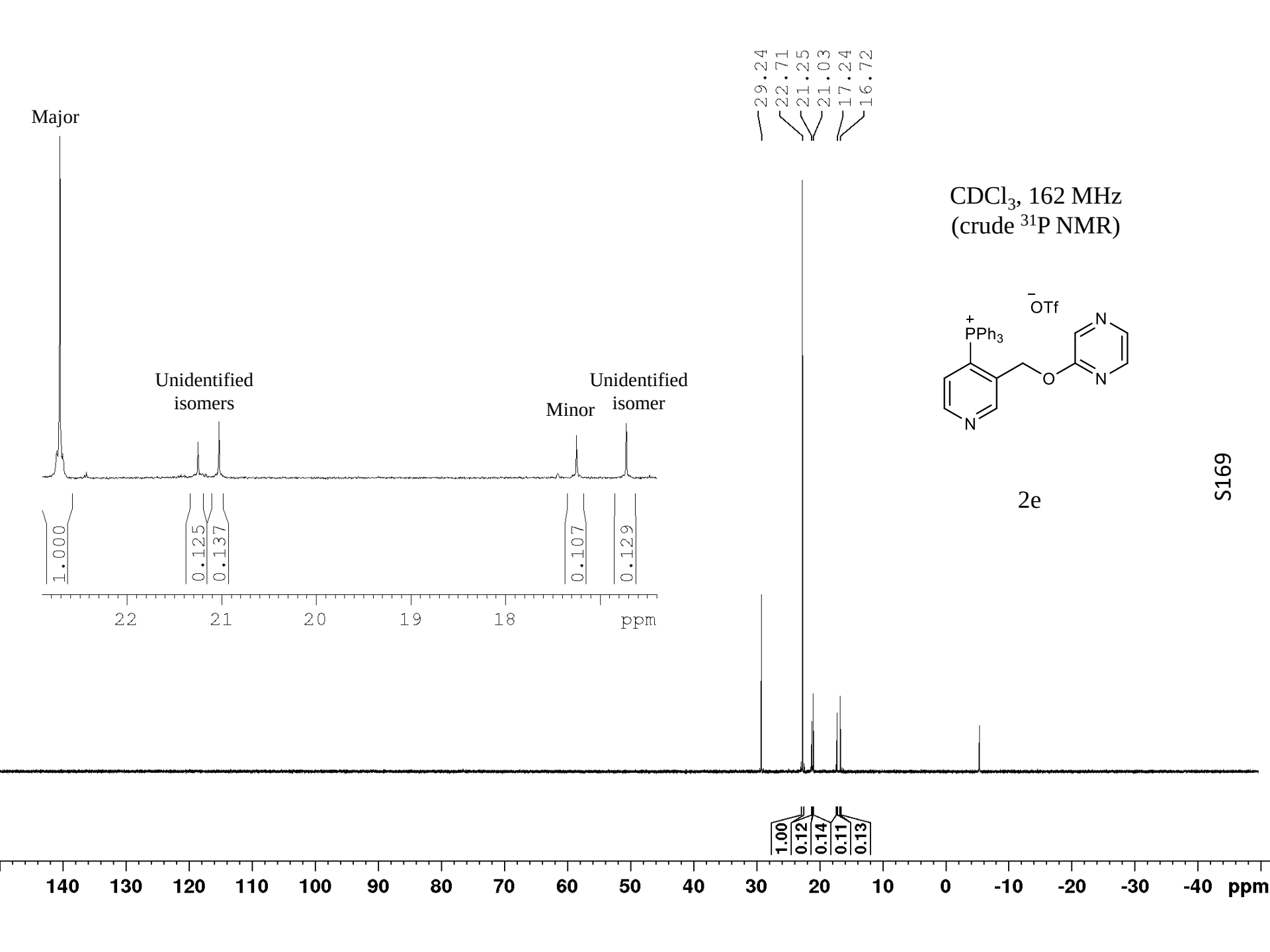


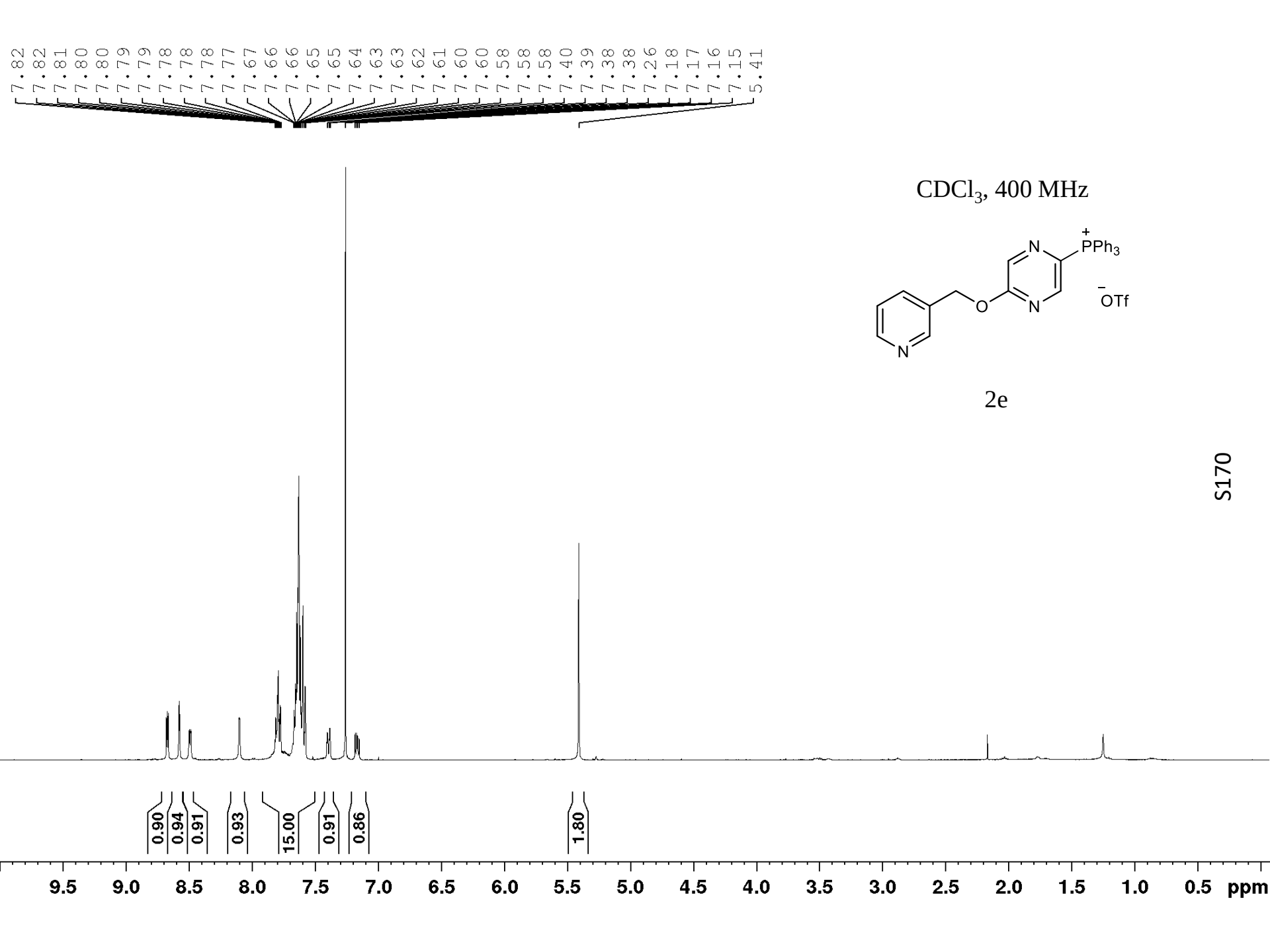
2d

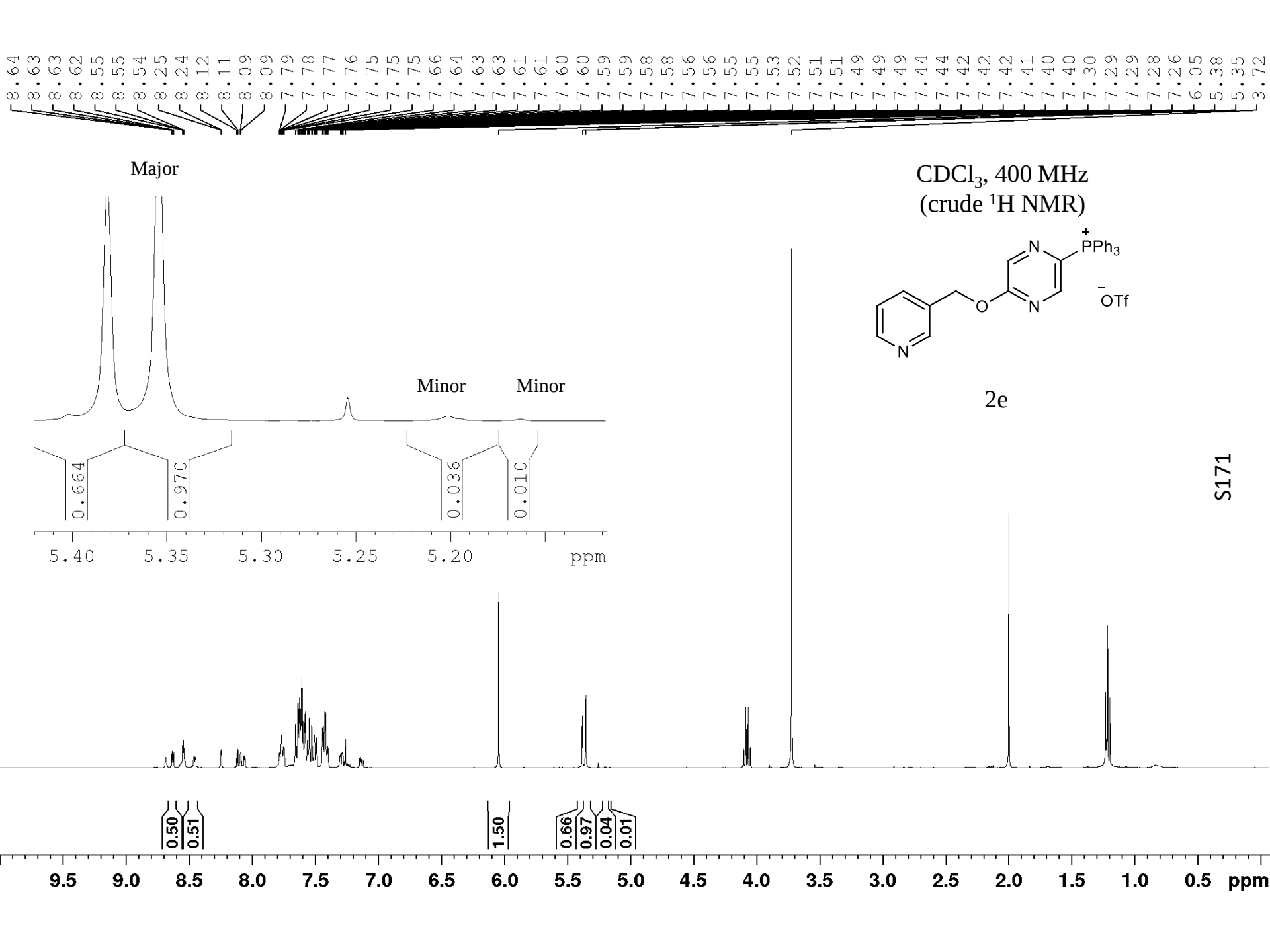
1.00
0.03

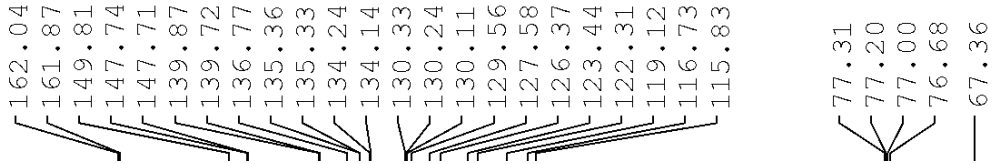
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


9.06
9.04
8.90
8.65
8.50
8.22
8.12
8.10
8.09
8.04
8.02
8.02
7.81
7.79
7.76
7.69
7.56
7.54
7.52
7.51
7.49
7.47
7.42
7.41
7.40
7.39
7.38
7.33
7.28
7.24
7.23
7.22
6.02
5.69
5.36
5.32
5.24
5.14
4.91
4.06
4.04
3.49
3.48
3.47
3.45
3.43
3.31
2.71
2.70
2.69
1.97
1.95
1.94
1.68
1.65
1.64
1.63
1.21
1.19
1.17
CDCl3, 400 MHz
(crude 1H NMR)
OTf
PPh3
N
O
N
N
2e
S168
0.46
0.07
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
0.5
ppm

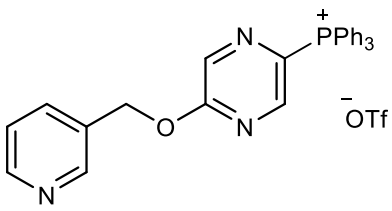

29.24
22.71
21.25
21.03
17.24
16.72
Major
Unidentified isomers
Minor
Unidentified isomer
1.000
0.125
0.137
0.107
0.129
22
21
20
19
18
ppm
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
N
O
N
N
2e
1.00
0.12
0.14
0.11
0.13
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


7.82
7.82
7.81
7.80
7.80
7.79
7.79
7.78
7.78
7.78
7.77
7.67
7.66
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.61
7.60
7.60
7.58
7.58
7.58
7.40
7.39
7.38
7.38
7.26
7.18
7.17
7.16
7.15
5.41
CDCl3, 400 MHz
PPh3
OTf
N
O
2e
S170
0.90
0.94
0.91
0.93
15.00
0.91
0.86
1.80
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
ppm

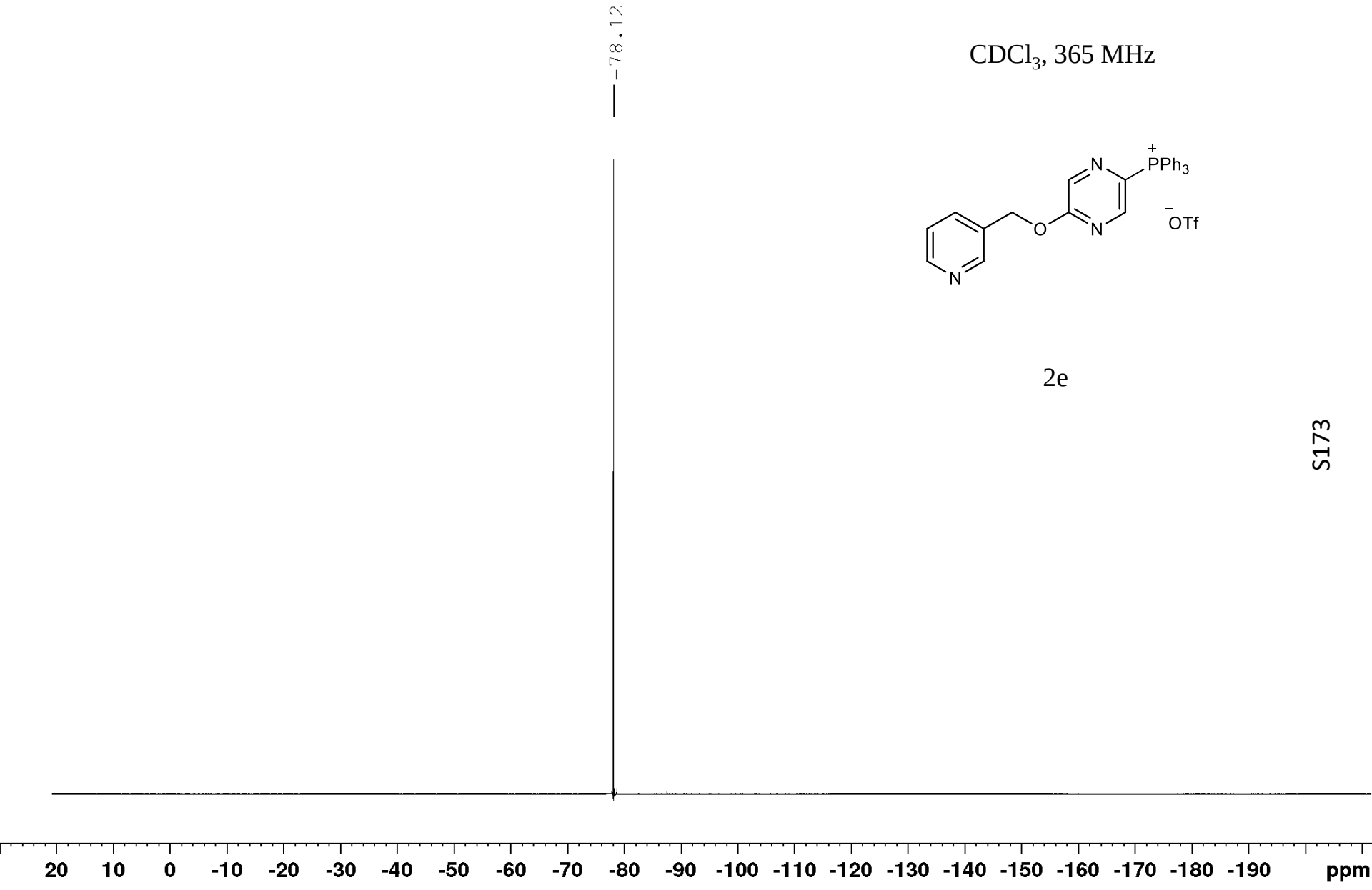

8.64 8.63 8.63 8.62 8.55 8.55 8.54 8.25 8.24 8.12 8.11 8.09 8.09 7.79 7.78 7.77 7.76 7.75 7.75 7.75 7.66 7.64 7.63 7.63 7.61 7.61 7.60 7.60 7.59 7.59 7.58 7.58 7.56 7.56 7.55 7.55 7.53 7.52 7.51 7.51 7.49 7.49 7.49 7.44 7.44 7.42 7.42 7.42 7.41 7.40 7.40 7.30 7.29 7.29 7.28 7.26 6.05 5.38 5.35 3.72
Major
Minor
Minor
0.664
0.970
0.036
0.010
5.40
5.35
5.30
5.25
5.20
ppm
CDCl3, 400 MHz
(crude 1H NMR)
PPh3
OTf
2e
S171
0.50
0.51
1.50
0.66
0.97
0.04
0.01
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
0.5
ppm



$CDCl_3$, 100 MHz

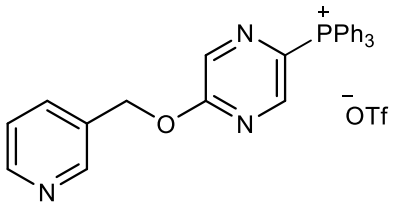


2e


-78.12
CDCl3, 365 MHz
PPh3
OTf
2e
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

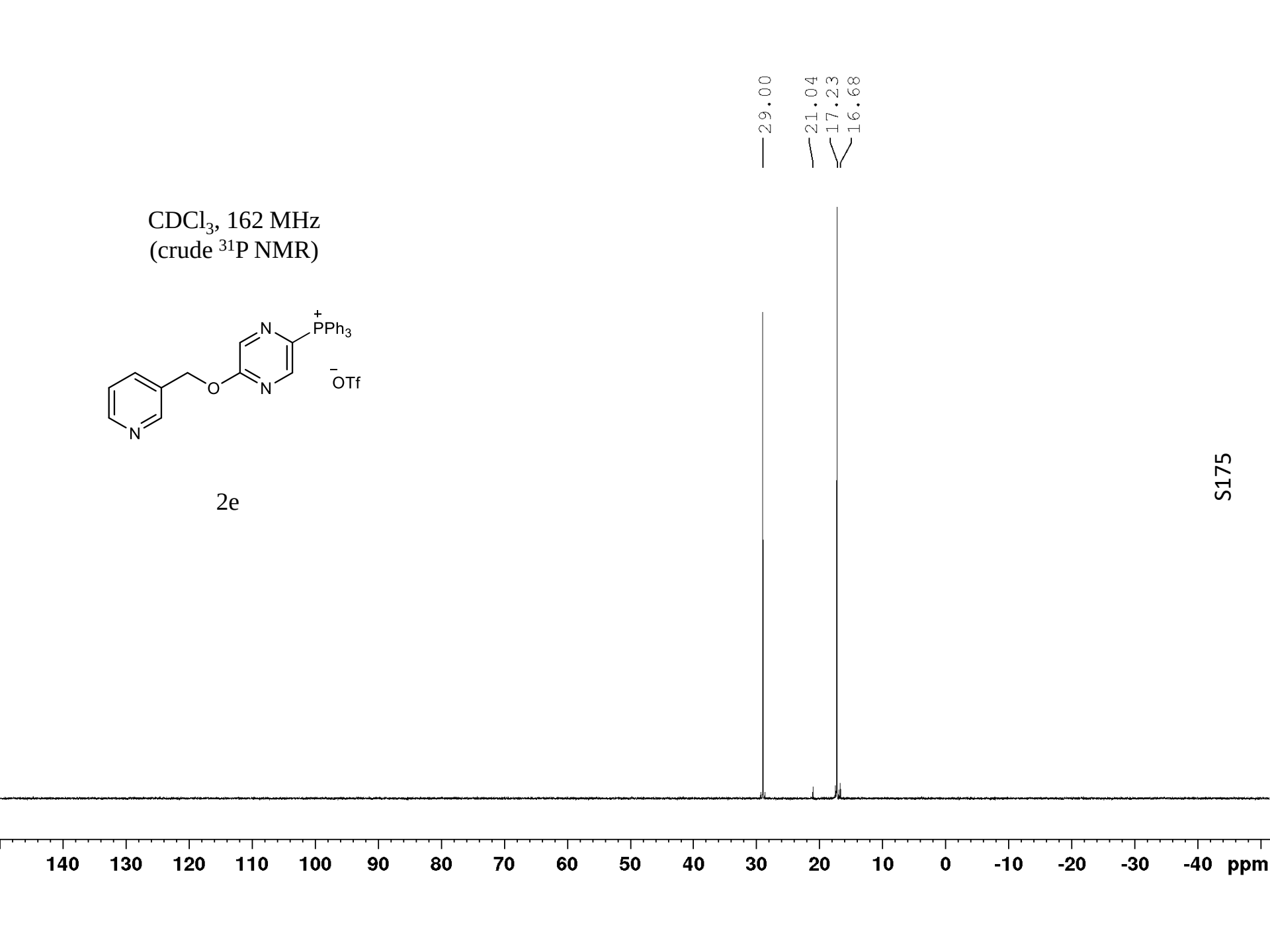
21.07
17.23
16.71

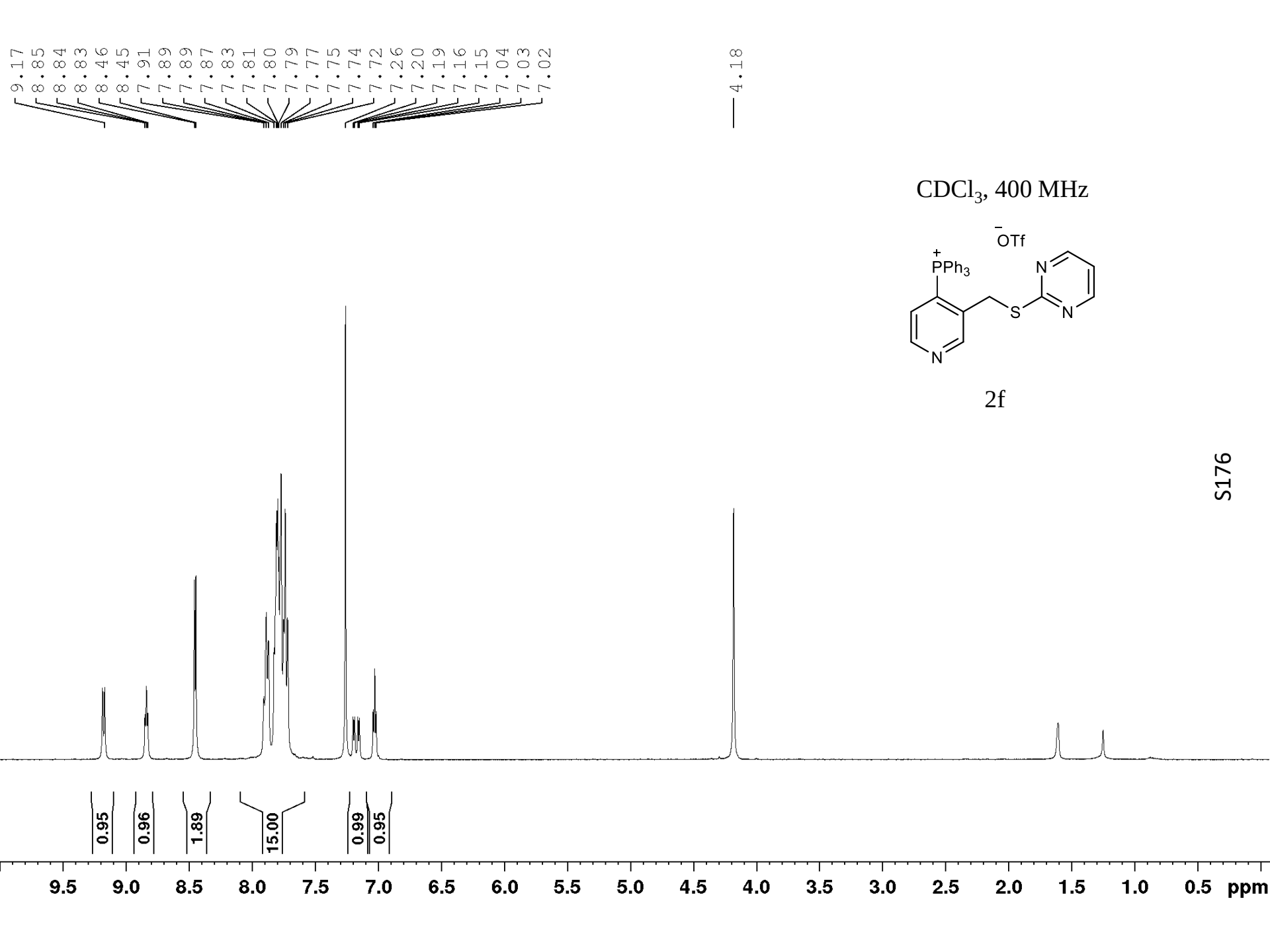
$CDCl_3$, 162 MHz

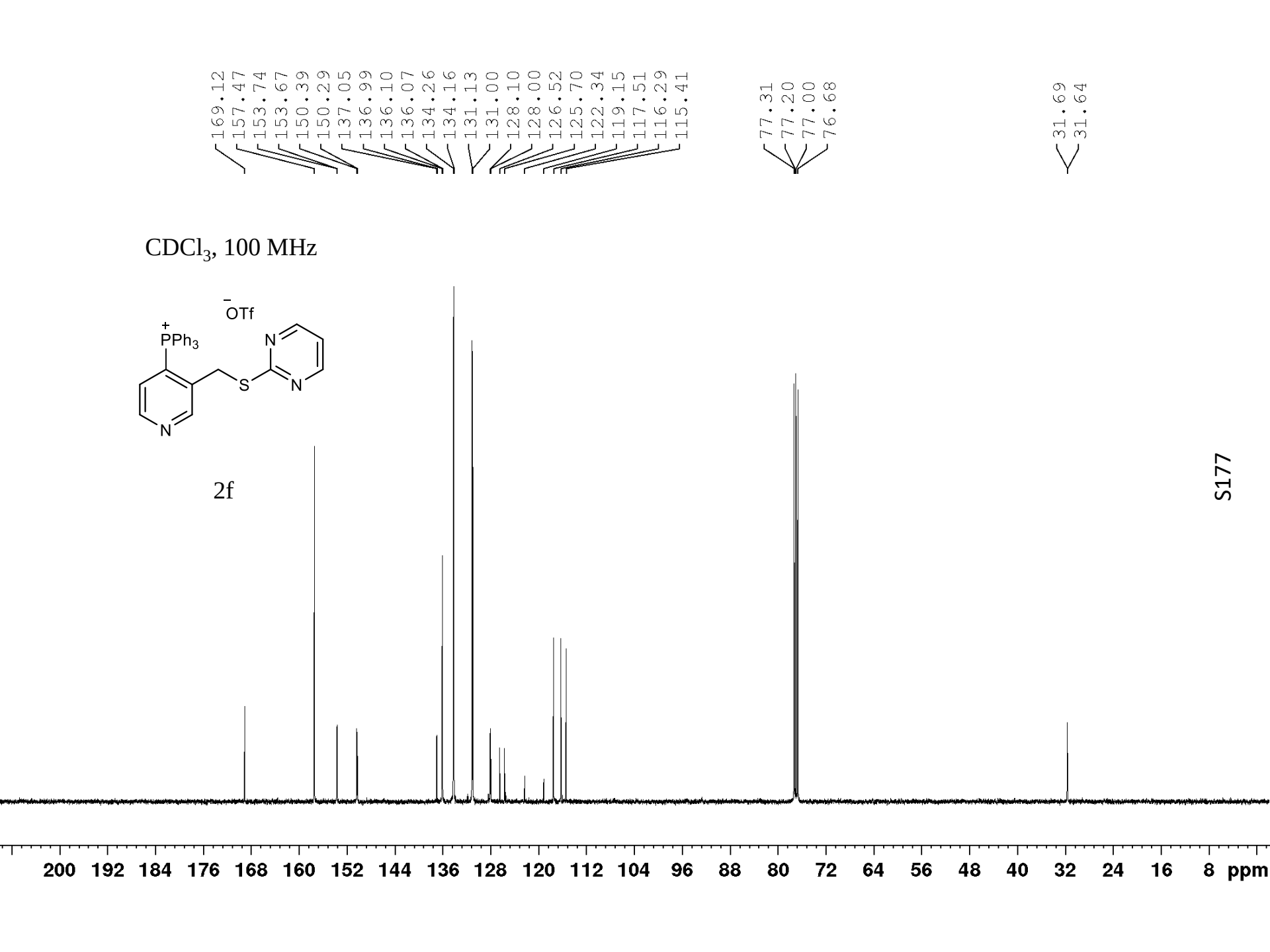


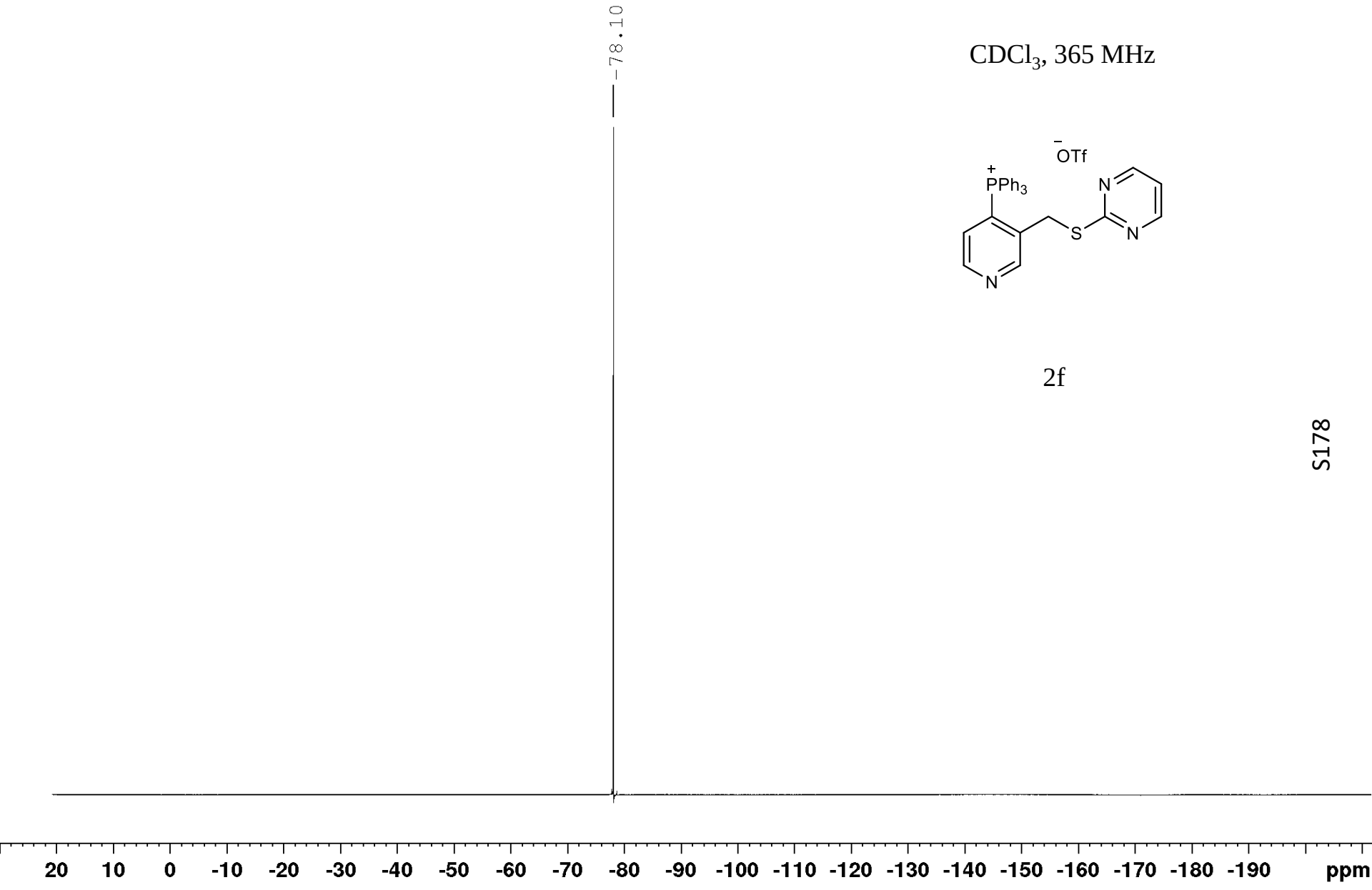
2e

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


29.00
21.04
17.23
16.68
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
OTf
2e
S175
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

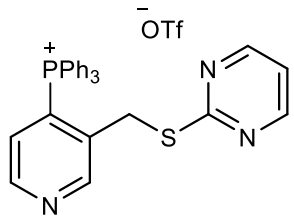

9.17
8.85
8.84
8.83
8.46
8.45
7.91
7.89
7.89
7.87
7.83
7.81
7.80
7.79
7.77
7.75
7.74
7.72
7.26
7.20
7.19
7.16
7.15
7.04
7.03
7.02
4.18
CDCl3, 400 MHz
OTf
PPh3
N
S
N
N
2f
S176
0.95
0.96
1.89
15.00
0.99
0.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


169.12
157.47
153.74
153.67
150.39
150.29
137.05
136.99
136.10
136.07
134.26
134.16
131.13
131.00
128.10
128.00
126.52
125.70
122.34
119.15
117.51
116.29
115.41
77.31
77.20
77.00
76.68
31.69
31.64
CDCl3, 100 MHz
OTf
PPh3
N
S
N
N
2f
S177
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 ppm

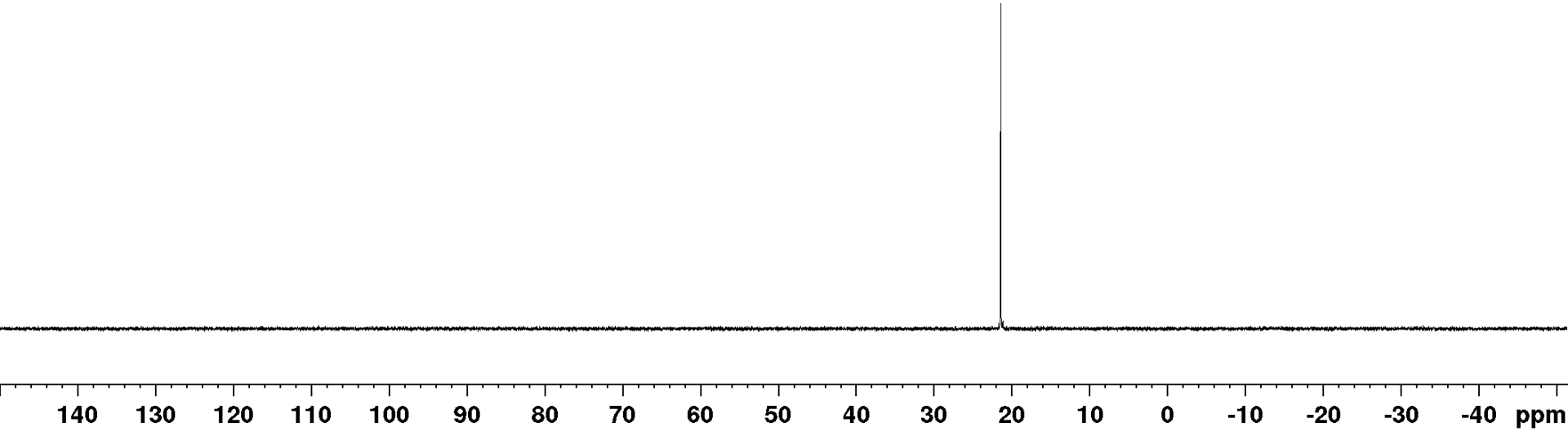

-78.10
CDCl3, 365 MHz
OTf
PPh3
N
S
N
N
2f
S178
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

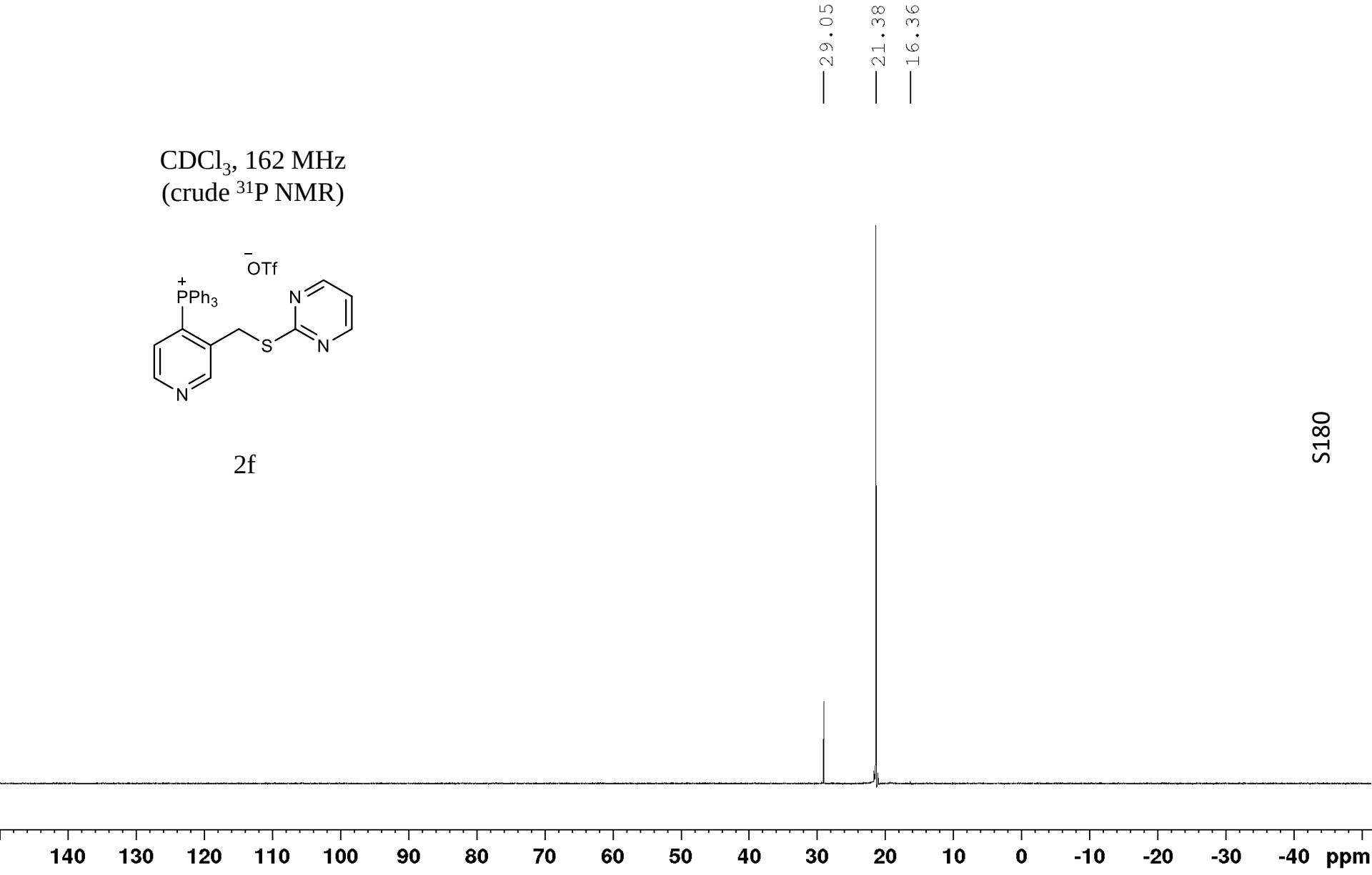
21.42

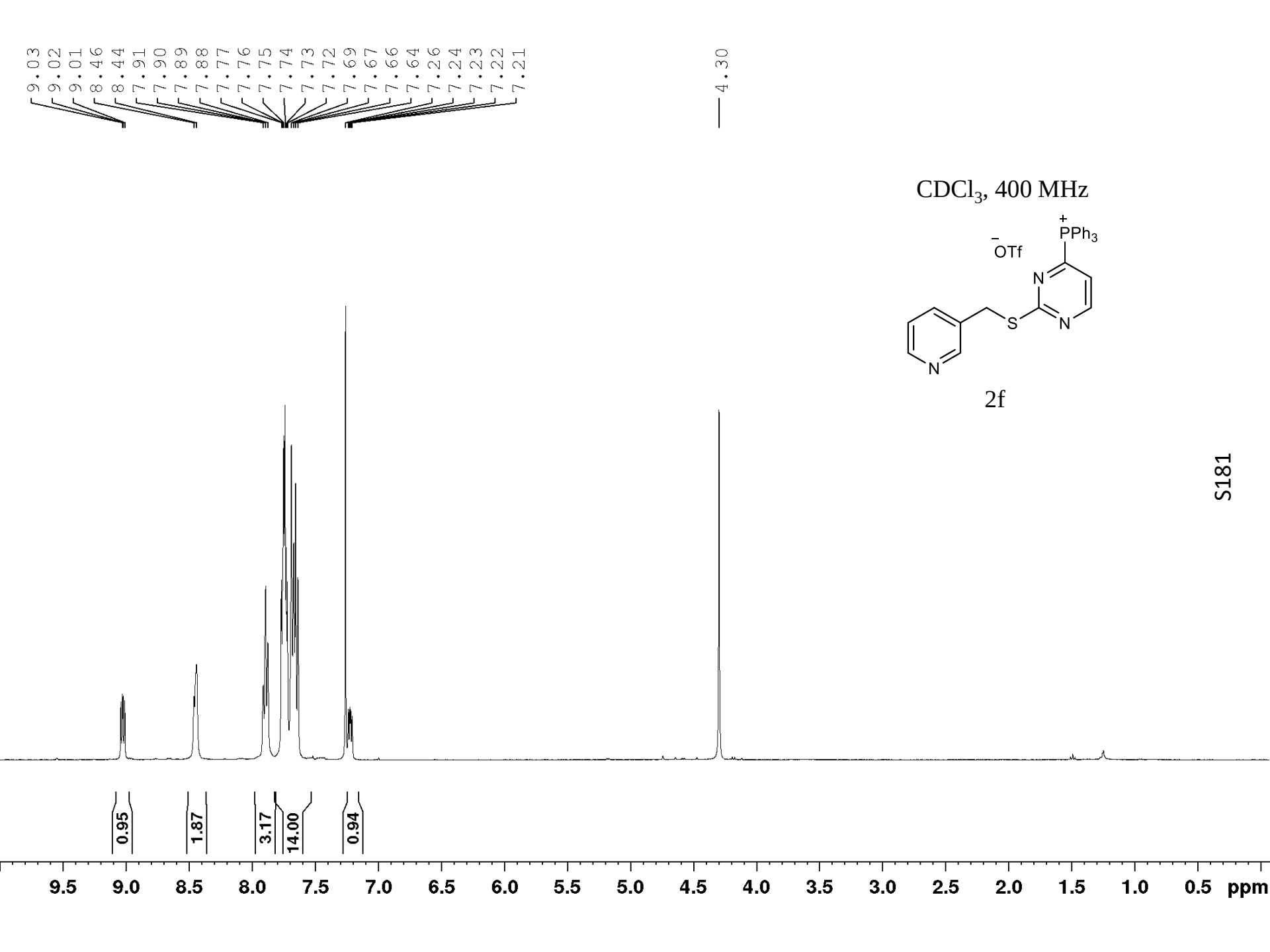
$CDCl_3$, 162 MHz

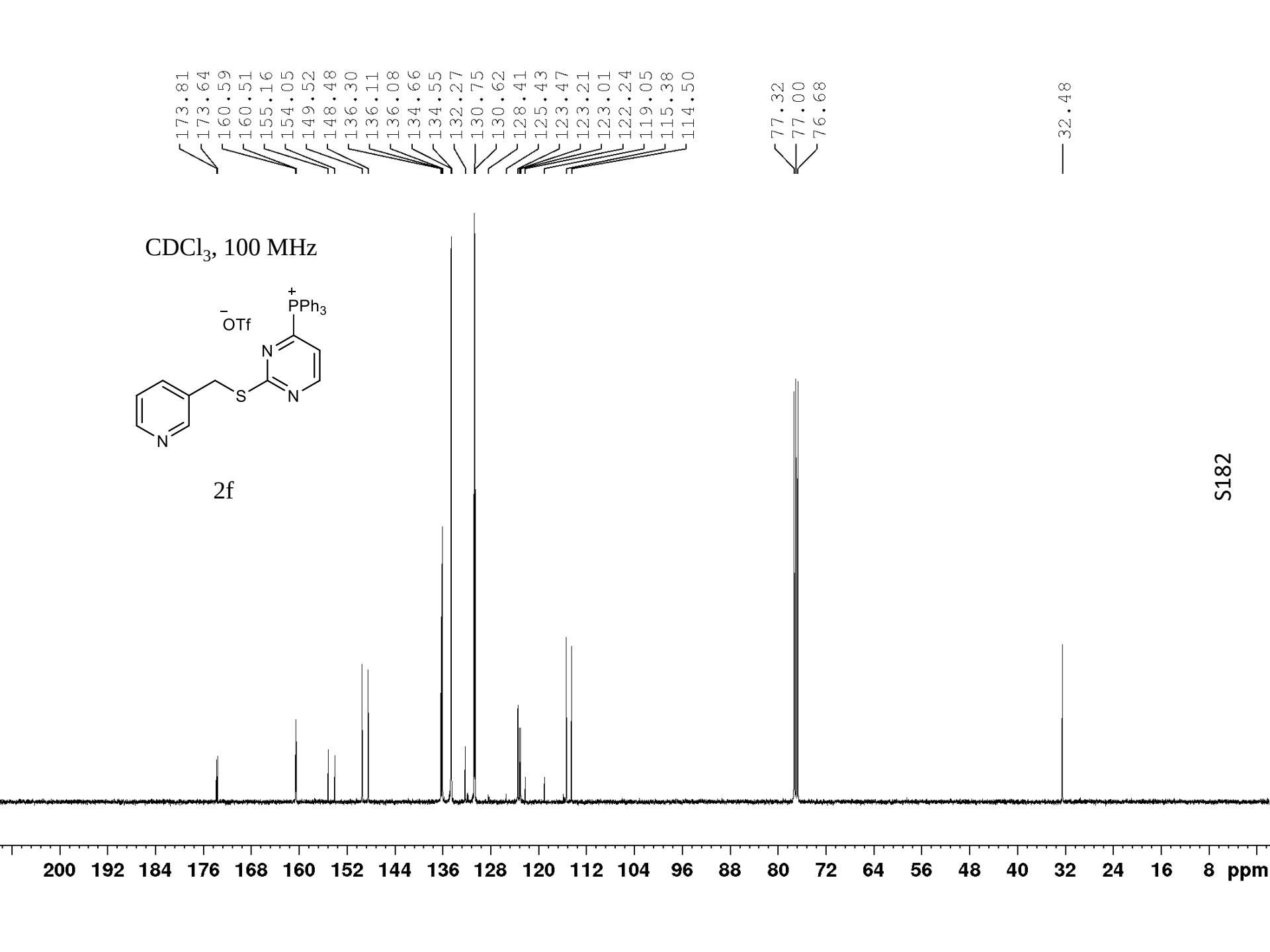


2f

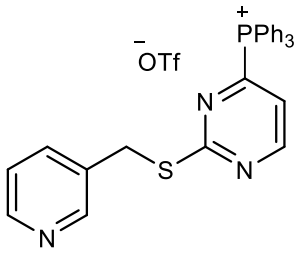



29.05
21.38
16.36
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
N
S
N
N
2f
S180
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

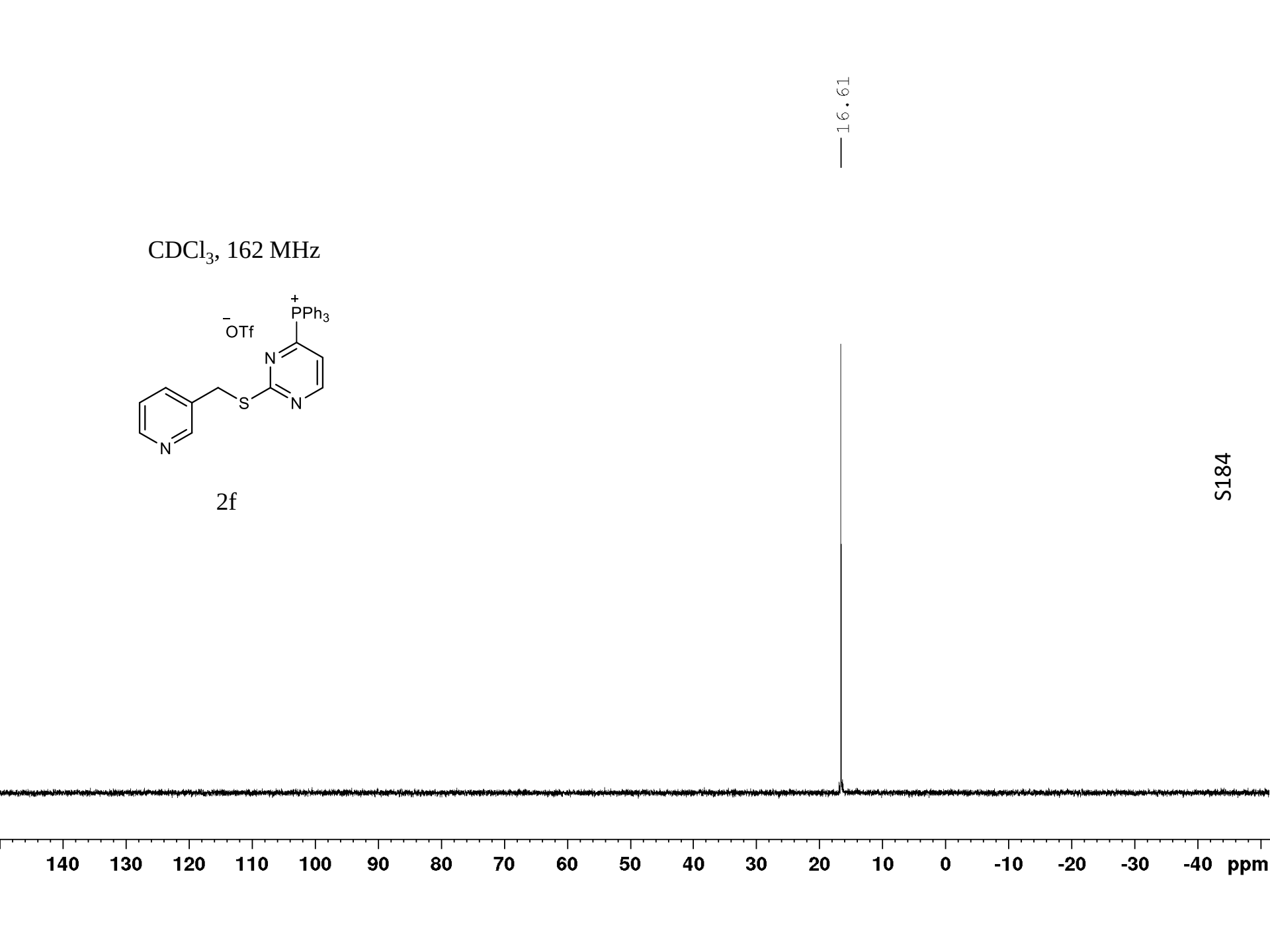

9.03
9.02
9.01
8.46
8.44
7.91
7.90
7.89
7.88
7.77
7.76
7.75
7.74
7.73
7.72
7.69
7.67
7.66
7.64
7.26
7.24
7.23
7.22
7.21
4.30
CDCl3, 400 MHz
PPh3
OTf
N
S
N
N
2f
S181
0.95
1.87
3.17
14.00
0.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


173.81
173.64
160.59
160.51
155.16
154.05
149.52
148.48
136.30
136.11
136.08
134.66
134.55
132.27
130.75
130.62
128.41
125.43
123.47
123.21
123.01
122.24
119.05
115.38
114.50
77.32
77.00
76.68
32.48
CDCl3, 100 MHz
PPh3
OTf
N
S
N
N
2f
S182
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 ppm

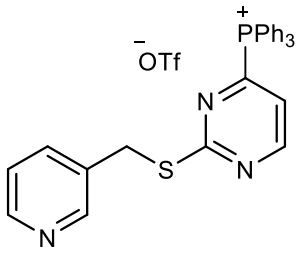
$CDCl_3$, 365 MHz



2f


16.61
CDCl3, 162 MHz
OTf
PPh3
N
S
N
N
2f
S184
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

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

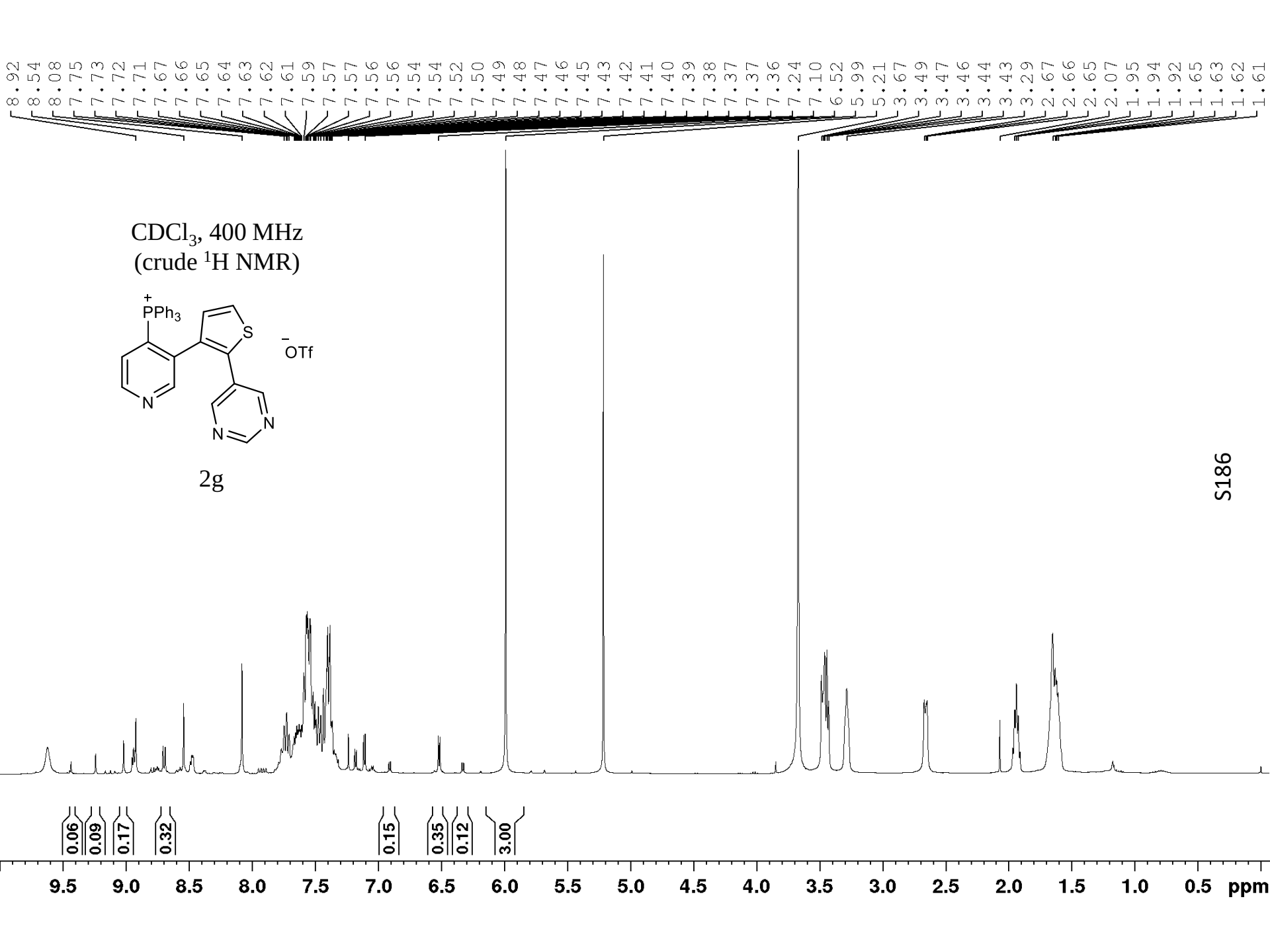


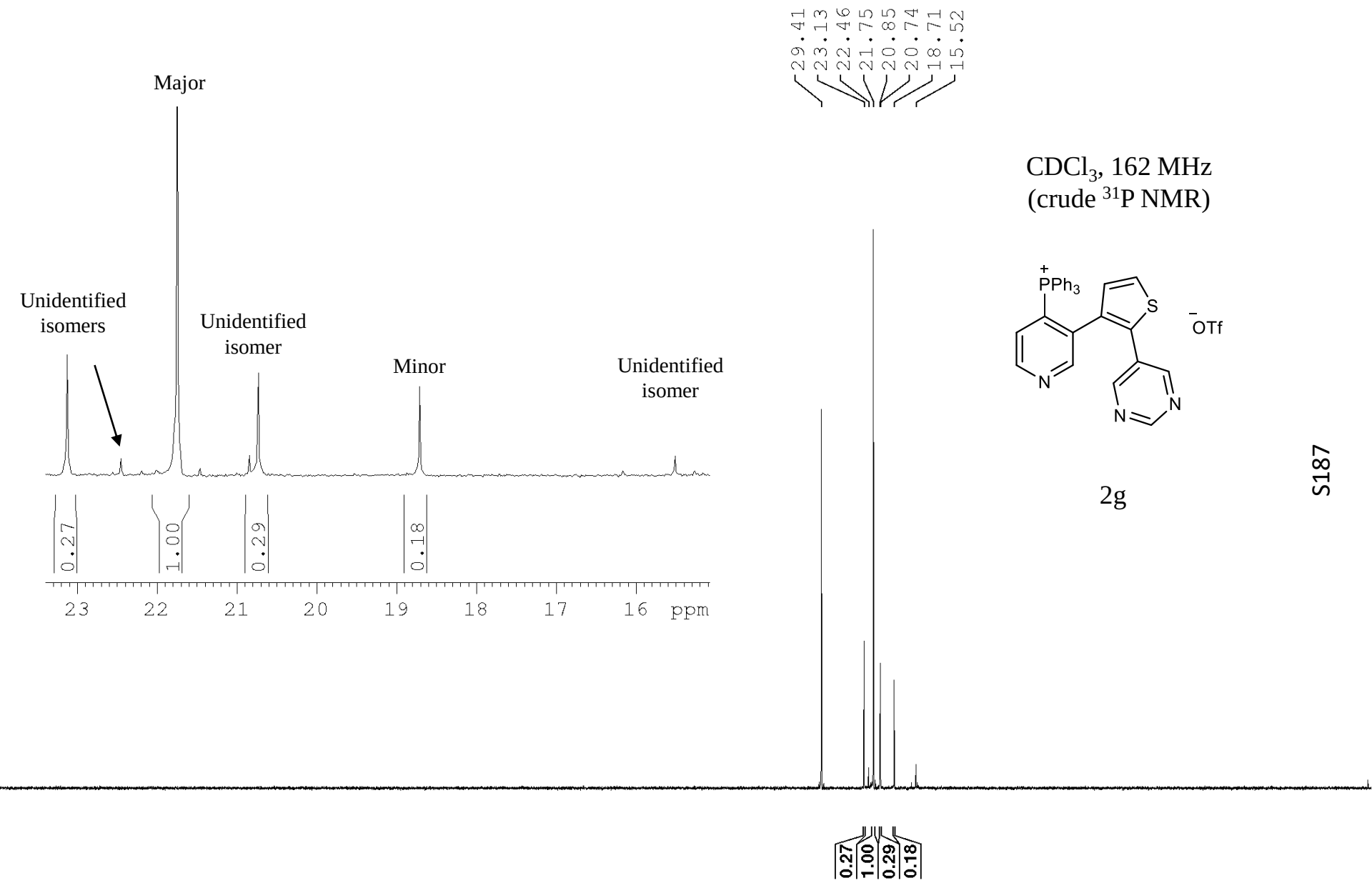
2f

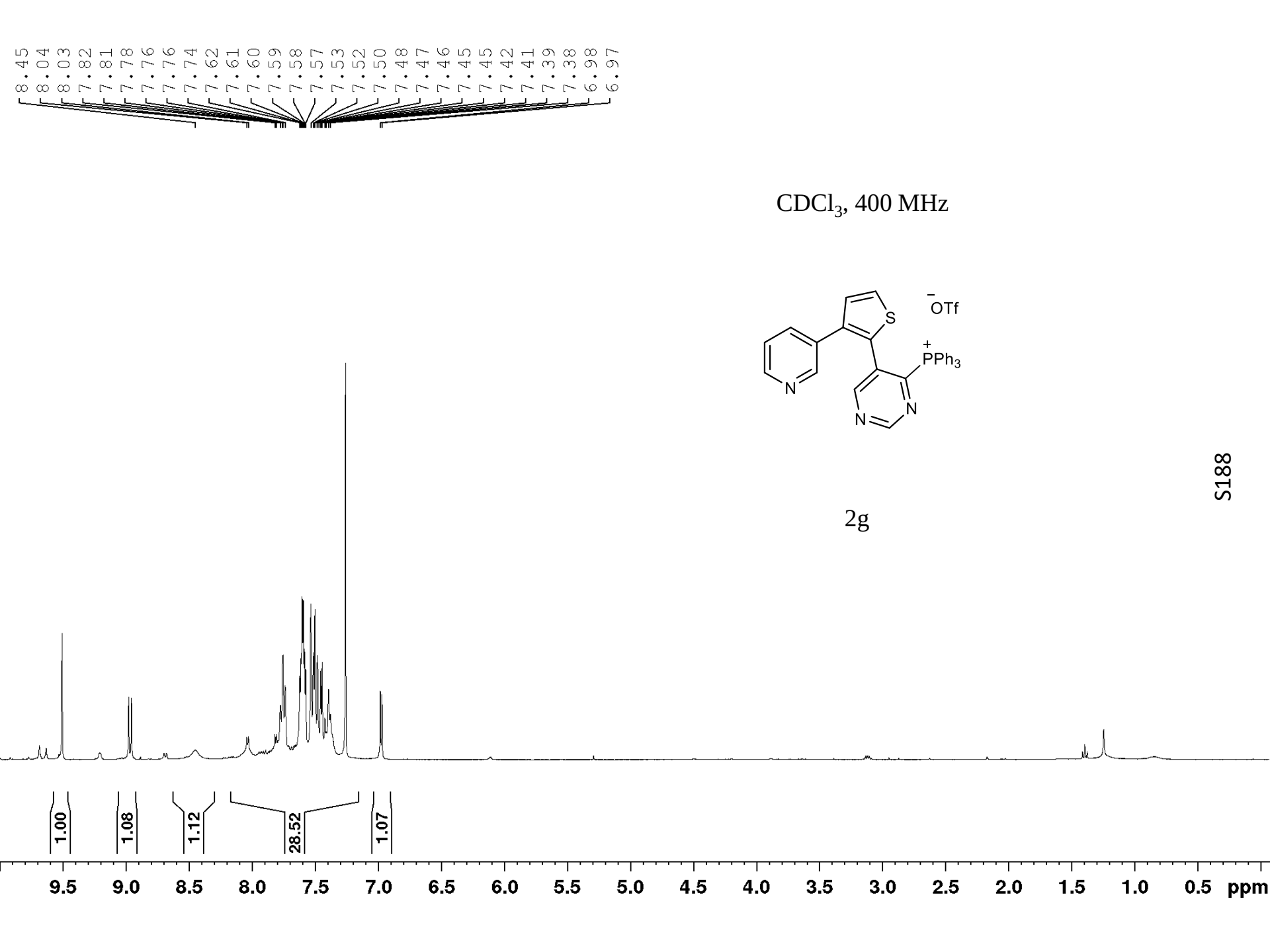
29.03
16.77

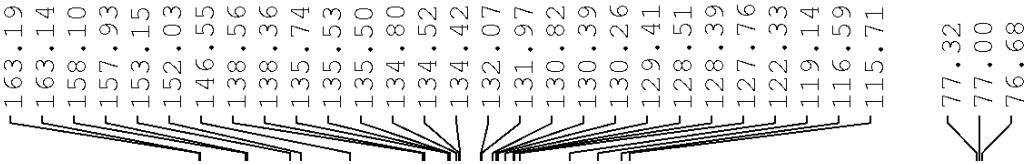
S185

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

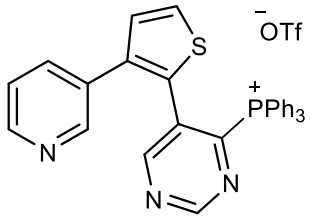

8.92
8.54
8.08
7.75
7.73
7.72
7.71
7.67
7.66
7.65
7.64
7.63
7.62
7.61
7.59
7.57
7.57
7.56
7.56
7.54
7.54
7.52
7.50
7.49
7.48
7.47
7.46
7.45
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.24
7.10
6.52
5.99
5.21
3.67
3.49
3.47
3.46
3.44
3.43
3.29
2.67
2.66
2.65
2.07
1.95
1.94
1.92
1.65
1.63
1.62
1.61
CDCl3, 400 MHz
(crude 1H NMR)
PPh3
S
OTf
N
N
N
2g
S186
0.06
0.09
0.17
0.32
0.15
0.35
0.12
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
0.5
ppm


29.41
23.13
22.46
21.75
20.85
20.74
18.71
15.52
Major
Unidentified isomers
Unidentified isomer
Minor
Unidentified isomer
0.27
1.00
0.29
0.18
23
22
21
20
19
18
17
16
ppm
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
S
OTf
N
N
N
2g
S187
0.27
1.00
0.29
0.18
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

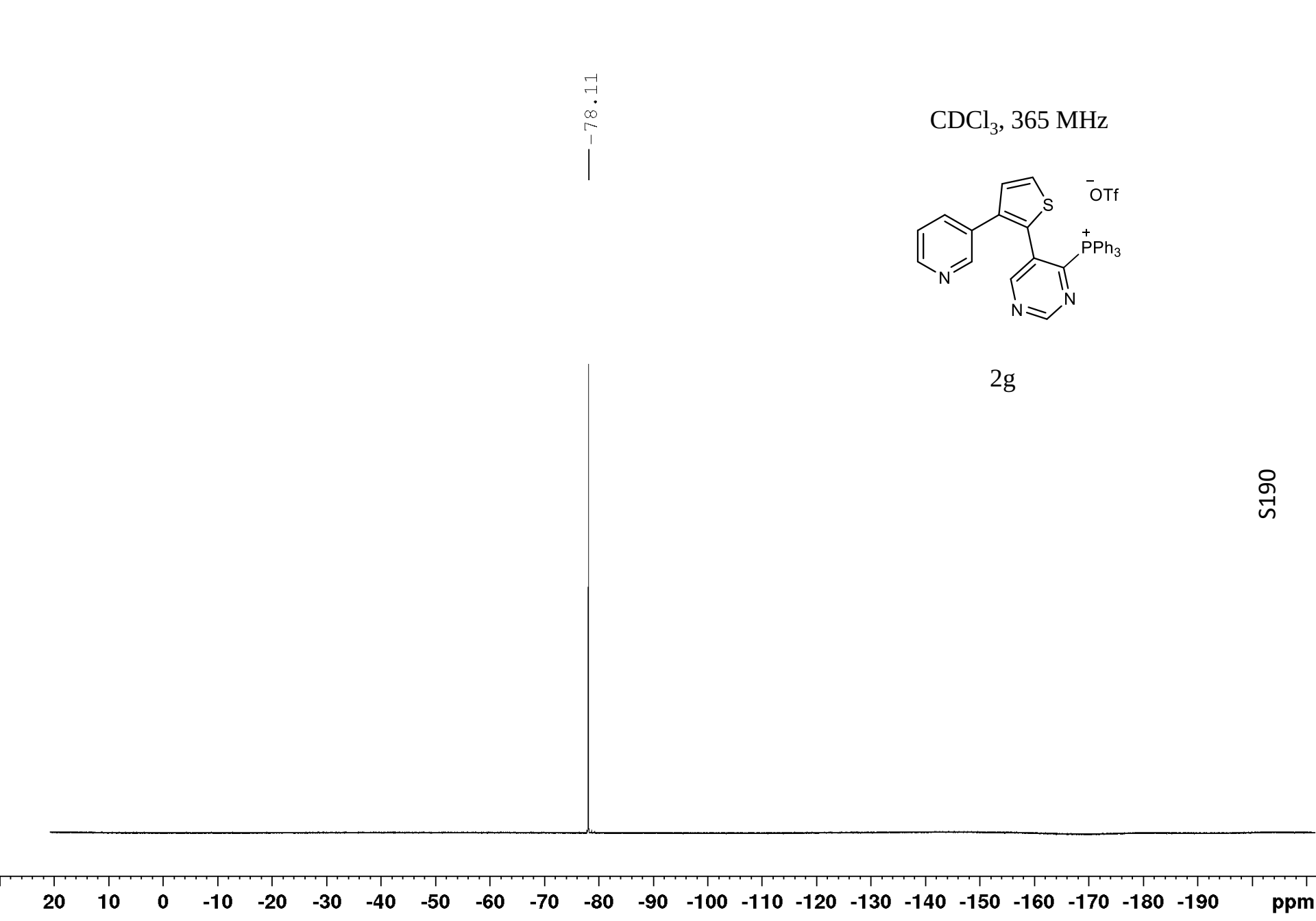

8.45
8.04
8.03
7.82
7.81
7.78
7.76
7.76
7.74
7.62
7.61
7.60
7.59
7.58
7.57
7.53
7.52
7.50
7.48
7.47
7.46
7.45
7.45
7.42
7.41
7.39
7.38
6.98
6.97
CDCl3, 400 MHz
OTf
PPh3
S
N
N
N
2g
S188
1.00
1.08
1.12
28.52
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



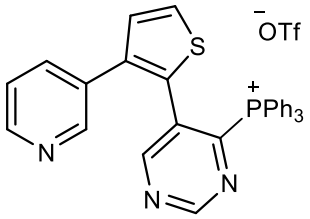
$CDCl_3$, 100 MHz



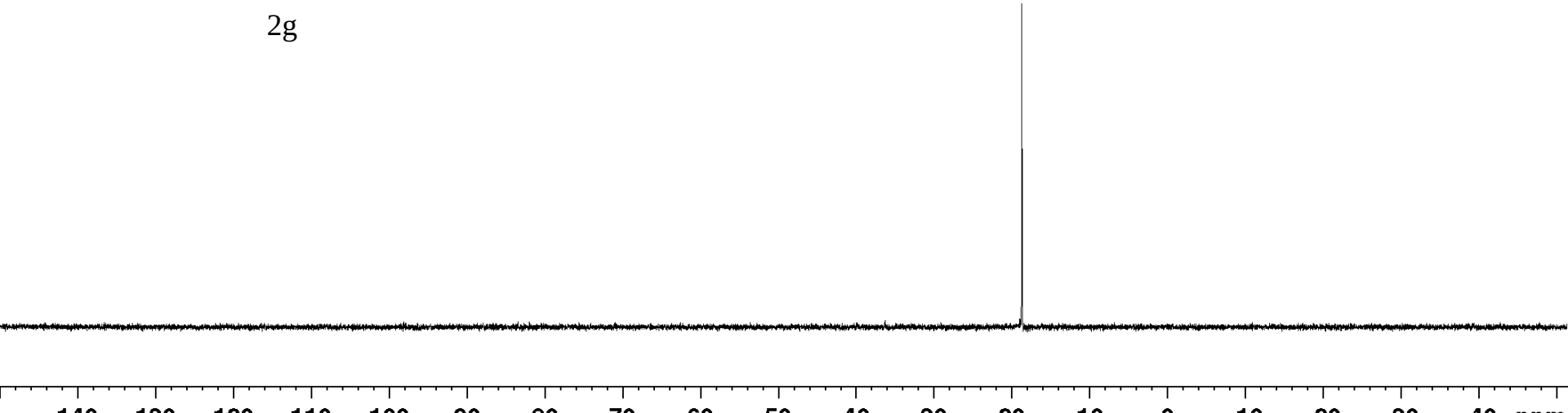
2g

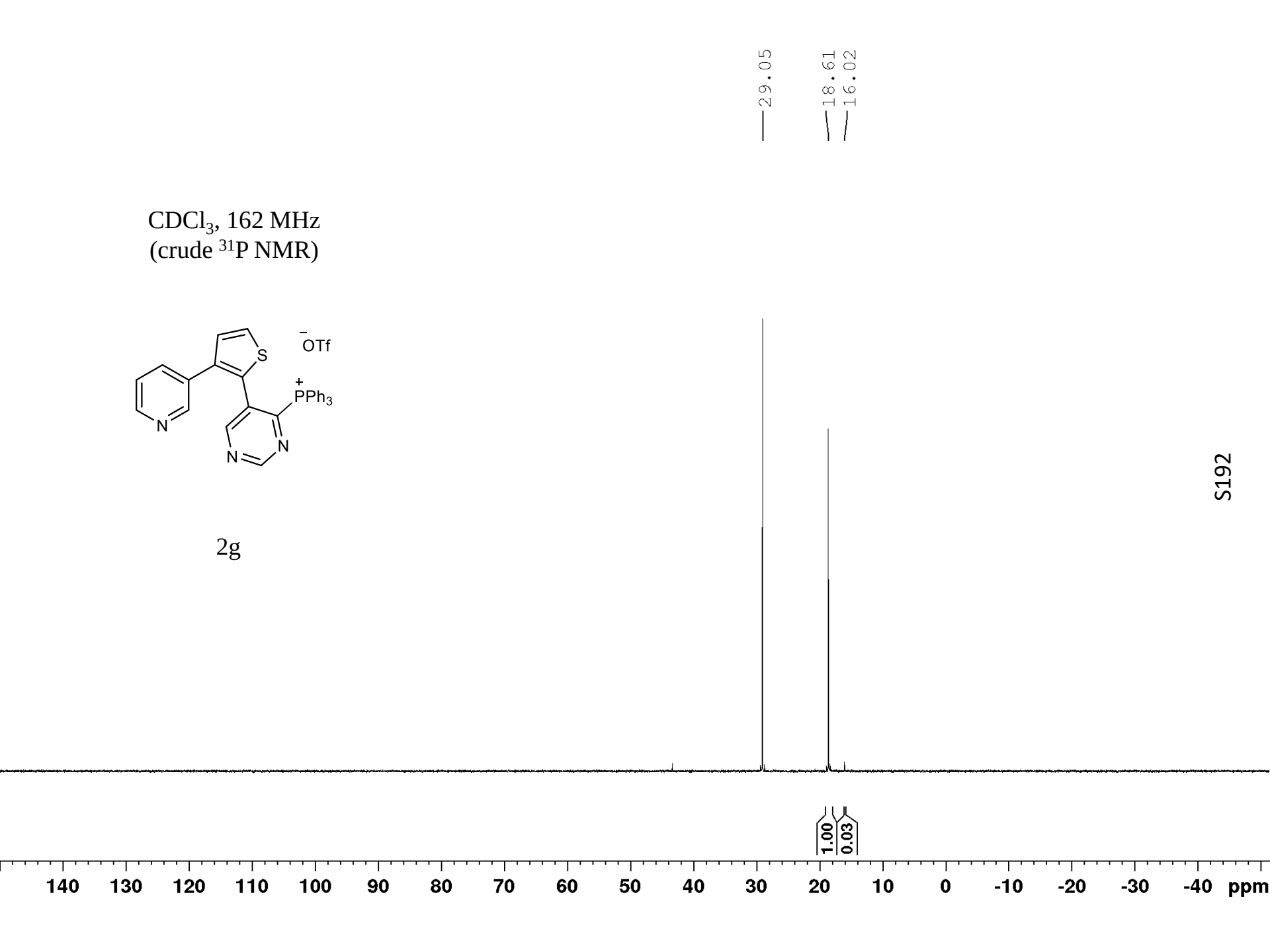

-78.11
CDCl3, 365 MHz
OTf
PPh3
S
N
N
N
2g
S190
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

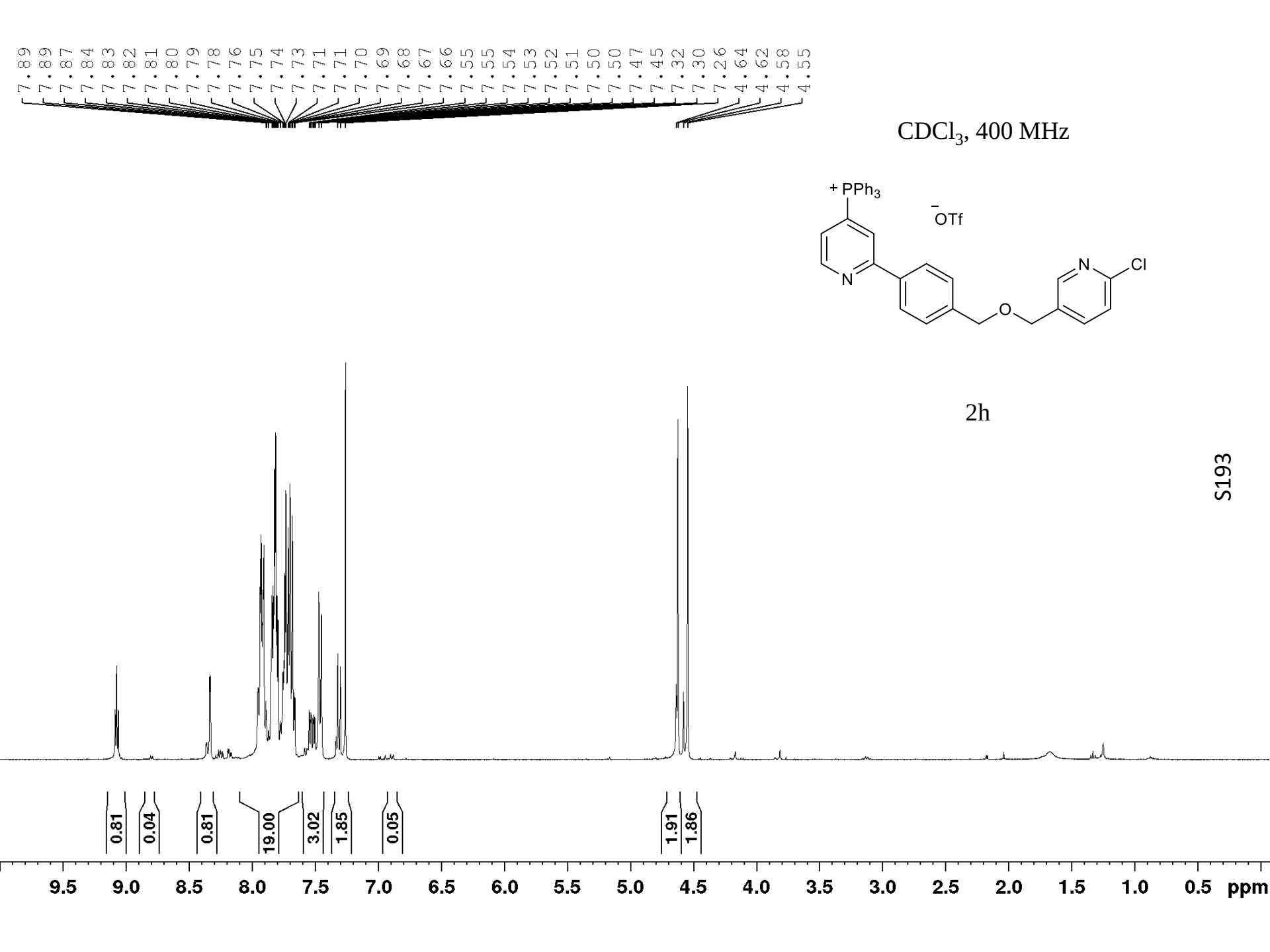
$CDCl_3$, 162 MHz

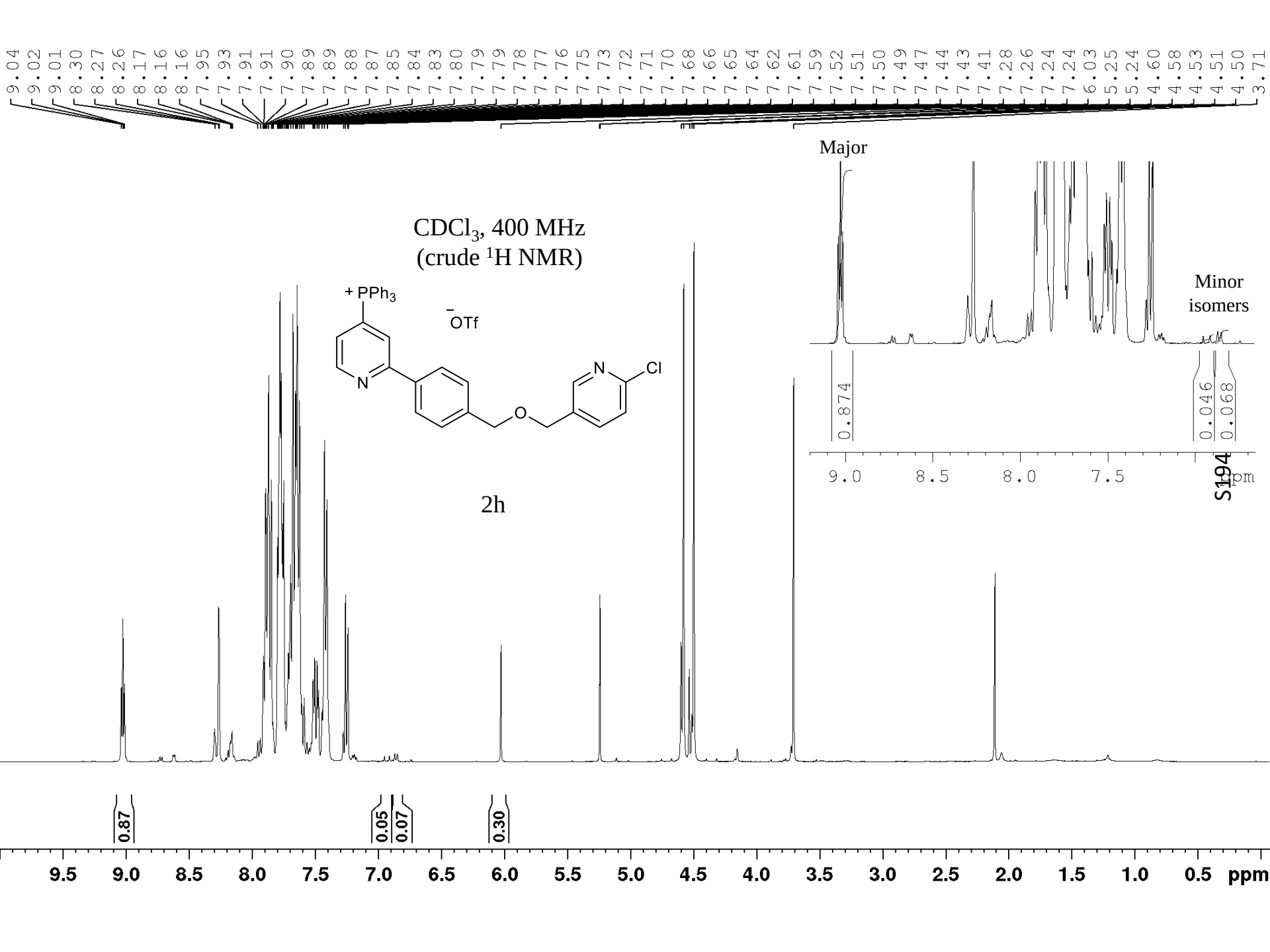


2g



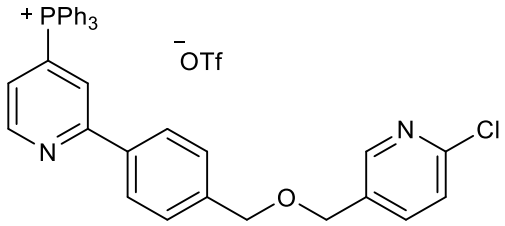

29.05
18.61
16.02
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
2g
S192
1.00
0.03
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


7.89
7.89
7.87
7.84
7.83
7.82
7.81
7.80
7.79
7.78
7.76
7.75
7.74
7.73
7.71
7.71
7.70
7.69
7.68
7.67
7.66
7.55
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.47
7.45
7.32
7.30
7.26
4.64
4.62
4.58
4.55
CDCl3, 400 MHz
+ PPh3
OTf
N
N
Cl
O
2h
S193
0.81
0.04
0.81
19.00
3.02
1.85
0.05
1.91
1.86
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
ppm


9.04 9.02 9.01 8.30 8.27 8.26 8.17 8.16 8.16 7.95 7.93 7.91 7.91 7.90 7.89 7.89 7.88 7.87 7.85 7.84 7.83 7.80 7.79 7.79 7.78 7.77 7.76 7.75 7.73 7.72 7.71 7.70 7.68 7.66 7.65 7.64 7.62 7.61 7.59 7.52 7.51 7.50 7.49 7.47 7.44 7.43 7.41 7.28 7.26 7.24 7.24 6.03 5.25 5.24 4.60 4.58 4.53 4.51 4.50 3.71
Major
Minor isomers
0.874
0.046
0.068
9.0
8.5
8.0
7.5
ppm
CDCl3, 400 MHz
(crude 1H NMR)
+ PPh3
OTf
N
N
Cl
O
2h
0.87
0.05
0.07
0.30
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
ppm

158.93
158.83
151.72
151.61
150.53
150.48
148.68
140.32
140.20
138.35
136.37
136.23
136.20
136.10
135.68
135.66
134.56
134.44
134.34
132.54
131.04
130.91
130.53
130.40
129.74
128.90
128.26
127.28
127.13
125.32
125.24
124.01
123.22
123.14
122.34
119.15
117.43
116.54
116.02
115.13
77.31
77.20
76.99
76.68
71.93
68.88
68.72

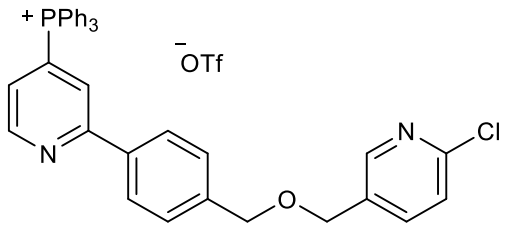
$CDCl_3$, 100 MHz



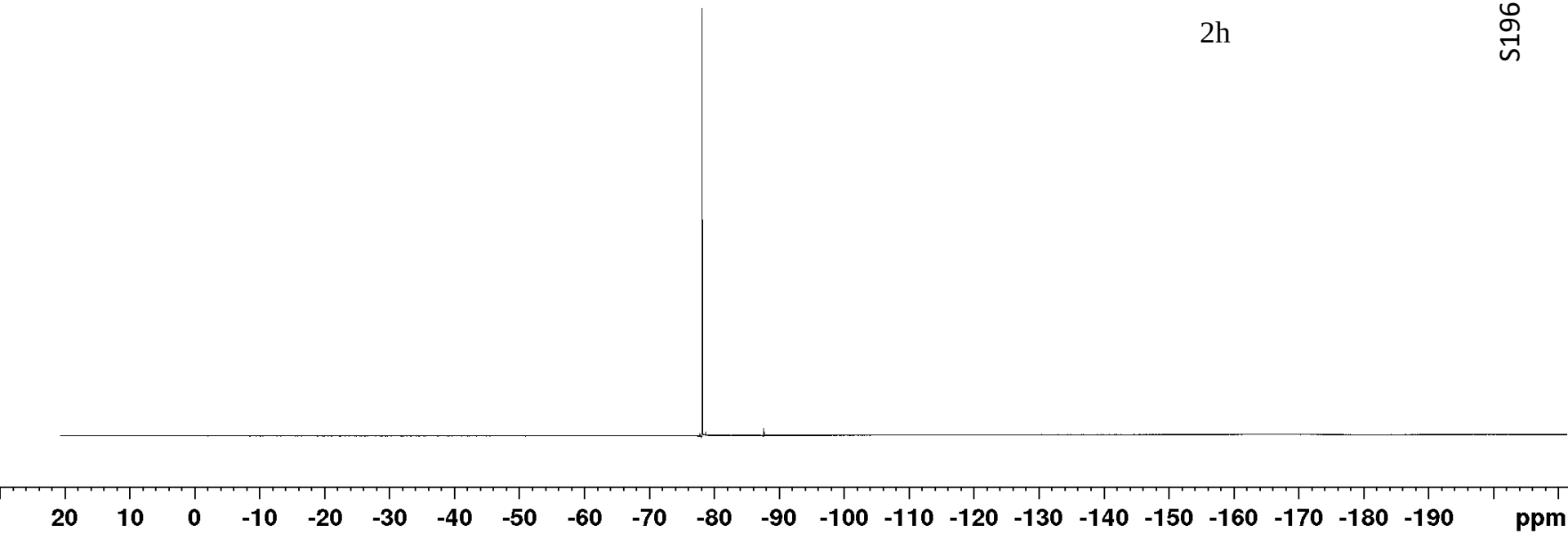
2h

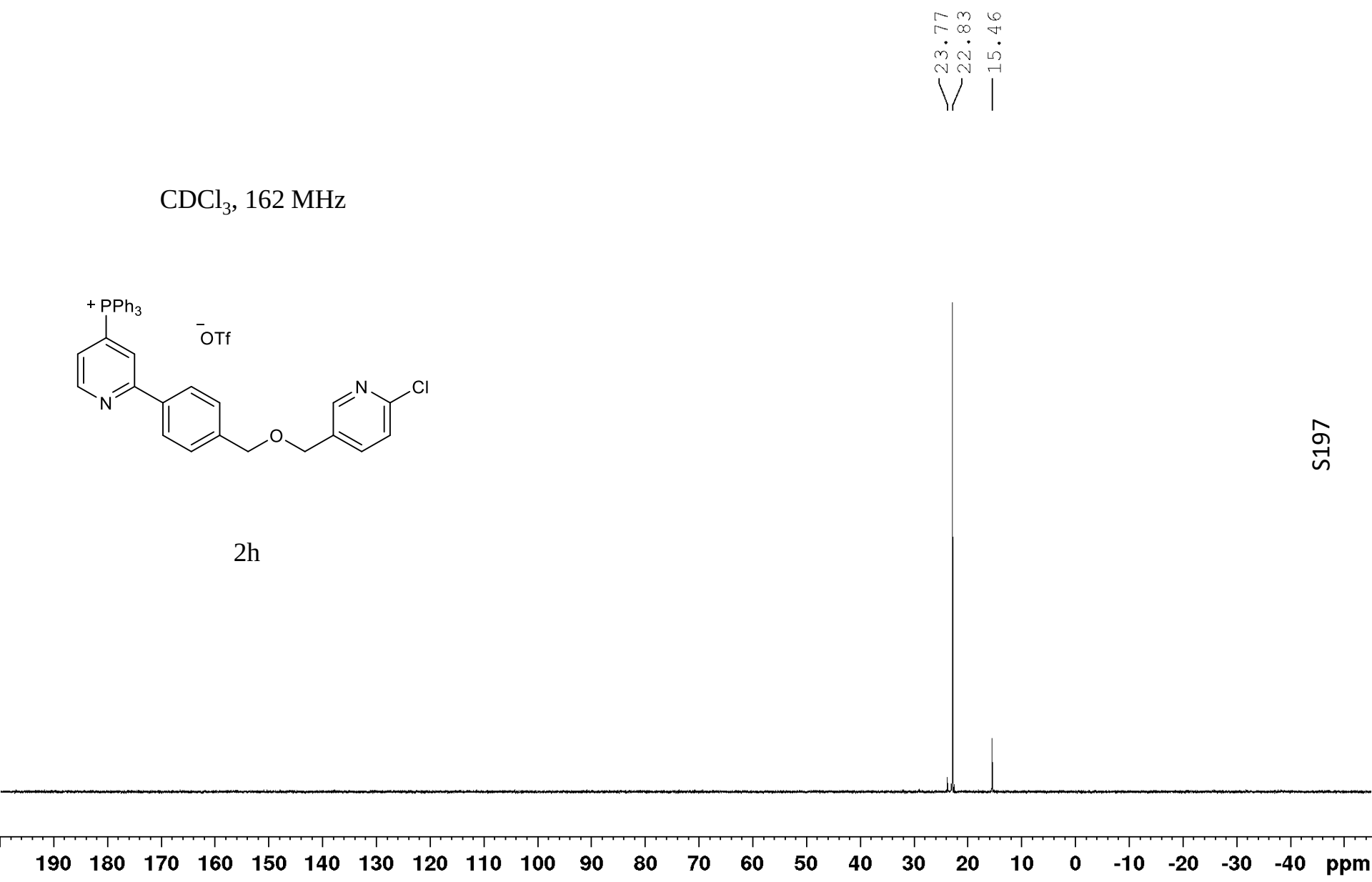
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



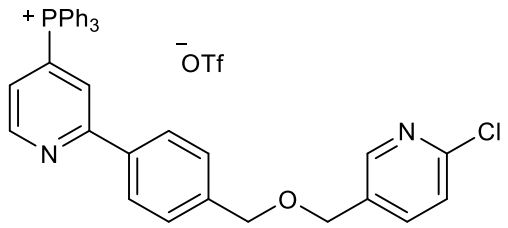
2h




23.77
22.83
15.46
CDCl3, 162 MHz
+ PPh3
OTf
N
O
N
Cl
2h
S197
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

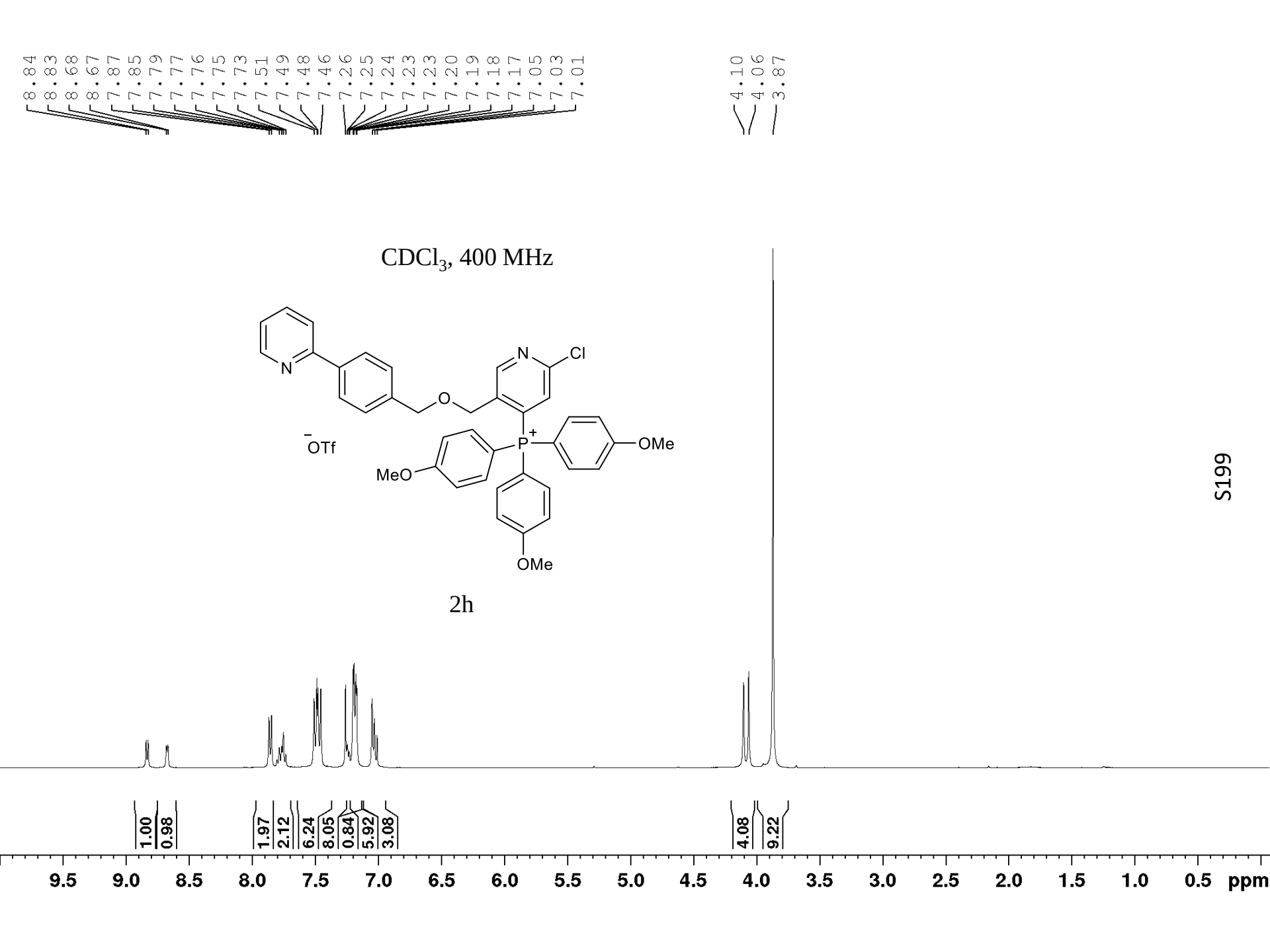
29.10
23.79
22.74
15.38

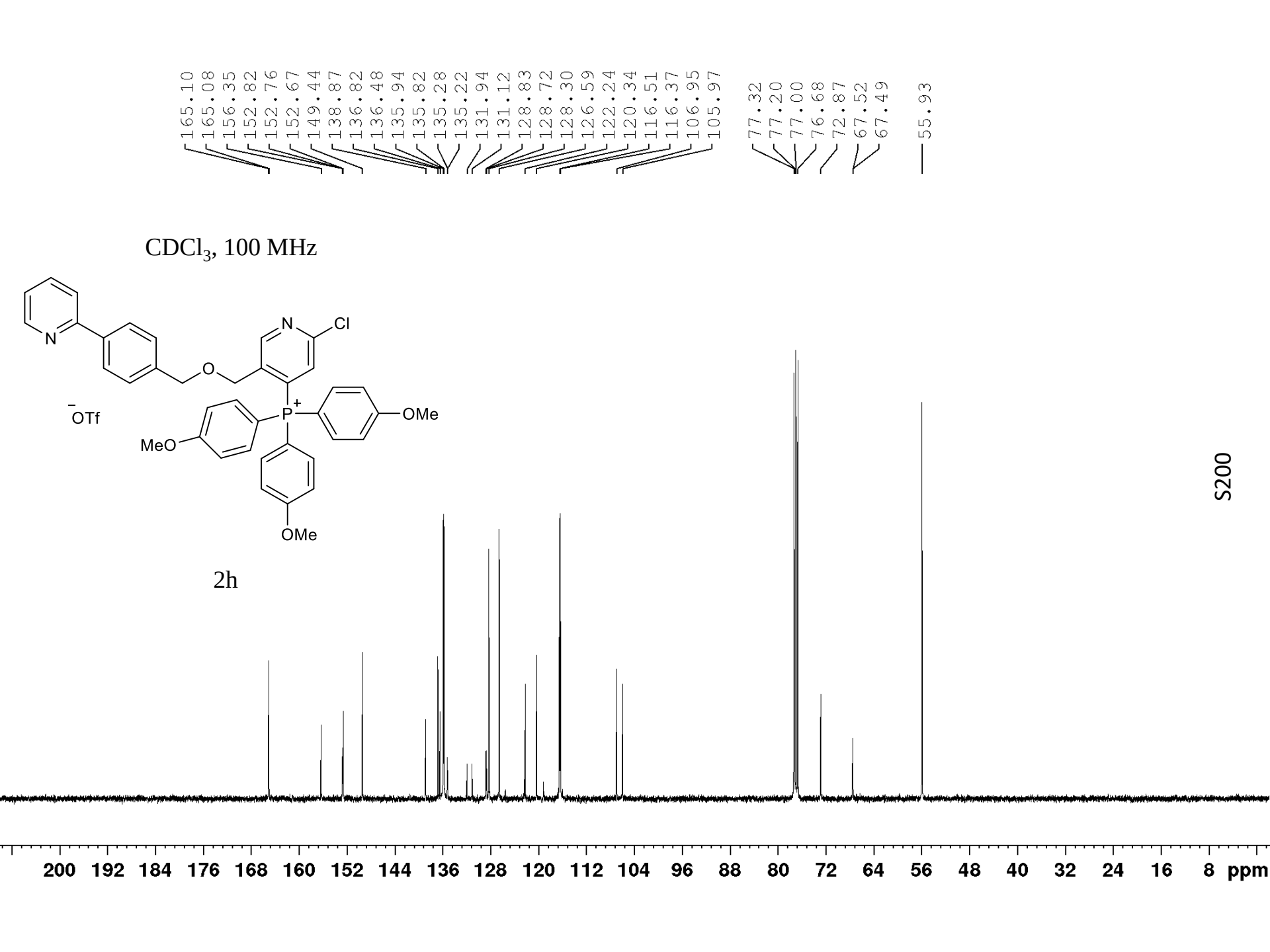
$CDCl_3$, 162 MHz (crude ^{31}P NMR)

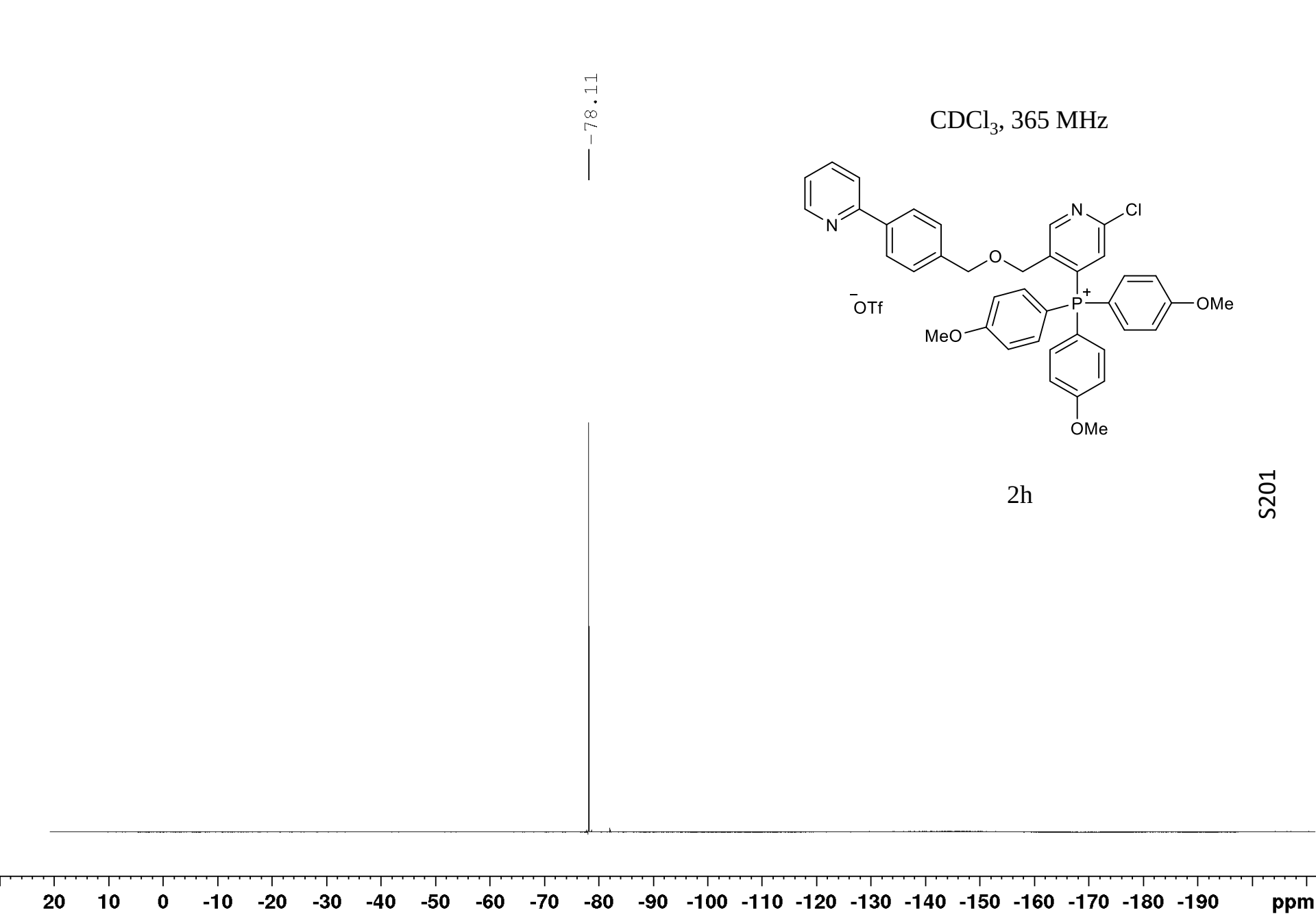


2h

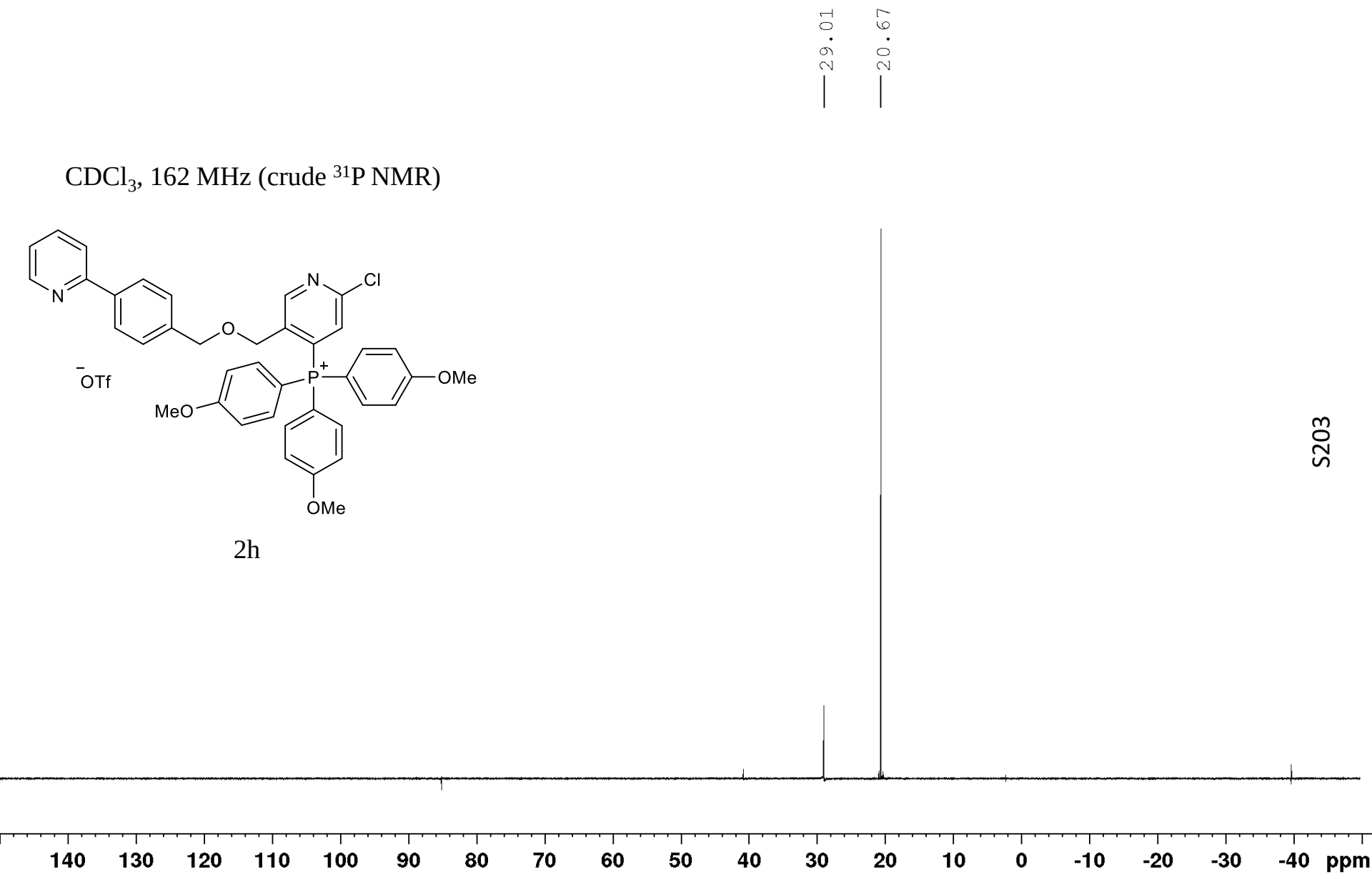
S198

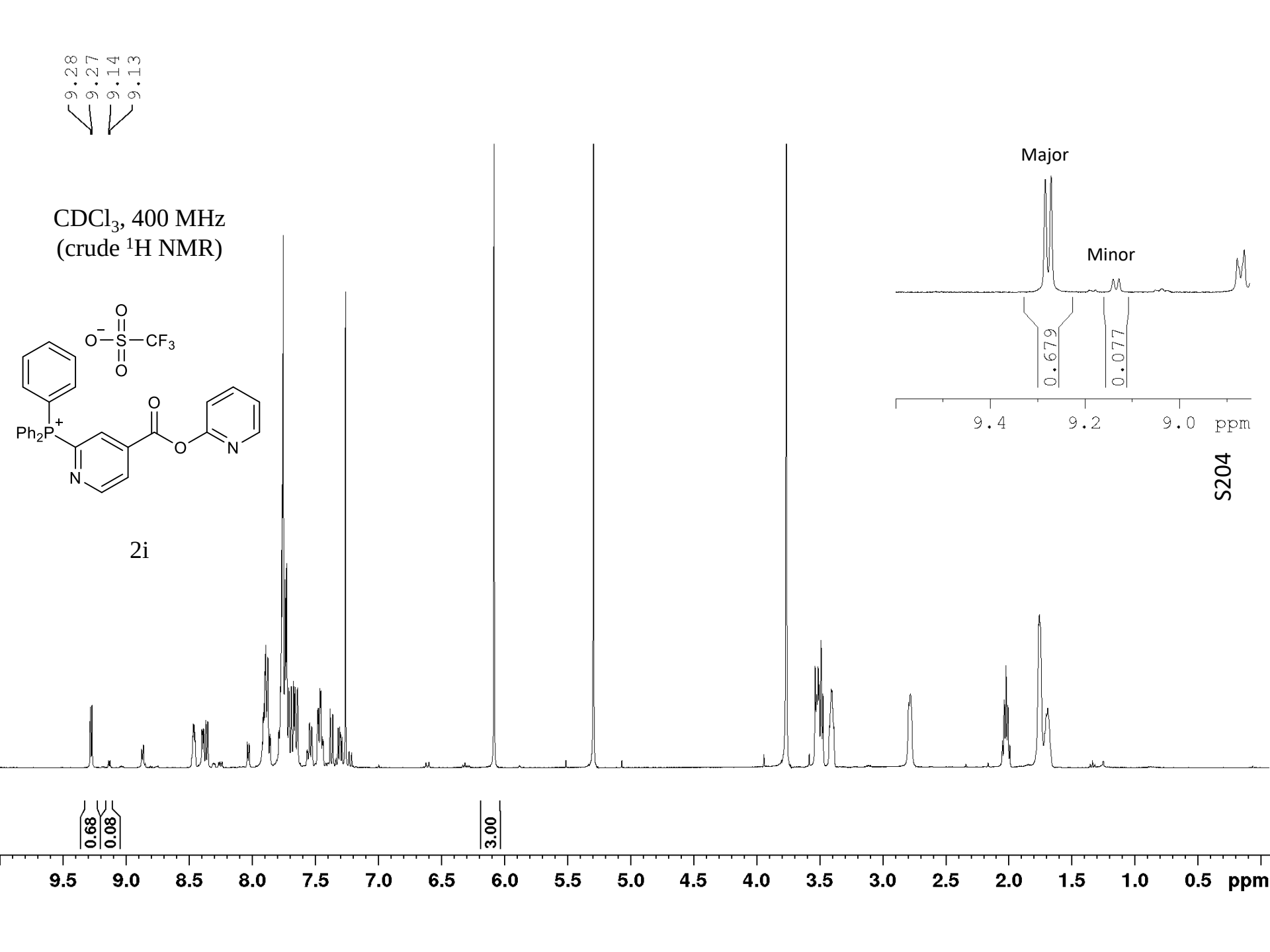

8.84
8.83
8.68
8.67
7.87
7.85
7.79
7.77
7.76
7.75
7.73
7.51
7.49
7.48
7.46
7.26
7.25
7.24
7.23
7.23
7.20
7.19
7.18
7.17
7.05
7.03
7.01
4.10
4.06
3.87
CDCl3, 400 MHz
N
Cl
O
OTf
P+
OMe
MeO
OMe
2h
S199
1.00
0.98
1.97
2.12
6.24
8.05
0.84
5.92
3.08
4.08
9.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


165.10
165.08
156.35
152.82
152.76
152.67
149.44
138.87
136.82
136.48
135.94
135.82
135.28
135.22
131.94
131.12
128.83
128.72
128.30
126.59
122.24
120.34
116.51
116.37
106.95
105.97
77.32
77.20
77.00
76.68
72.87
67.52
67.49
55.93
CDCl3, 100 MHz
N
Cl
O
OTf
P
OMe
MeO
OMe
2h
S200
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 ppm

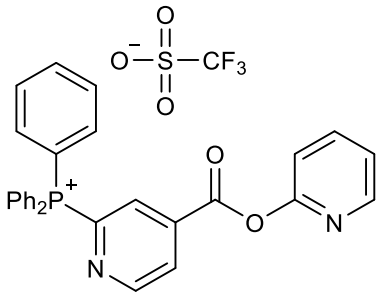

-78.11
CDCl3, 365 MHz
N
N
Cl
O
OTf
P
MeO
OMe
OMe
2h
S201
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


20.60
CDCl3, 162 MHz
N
Cl
O
P+
OMe
MeO
OMe
OTf
2h
S202
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

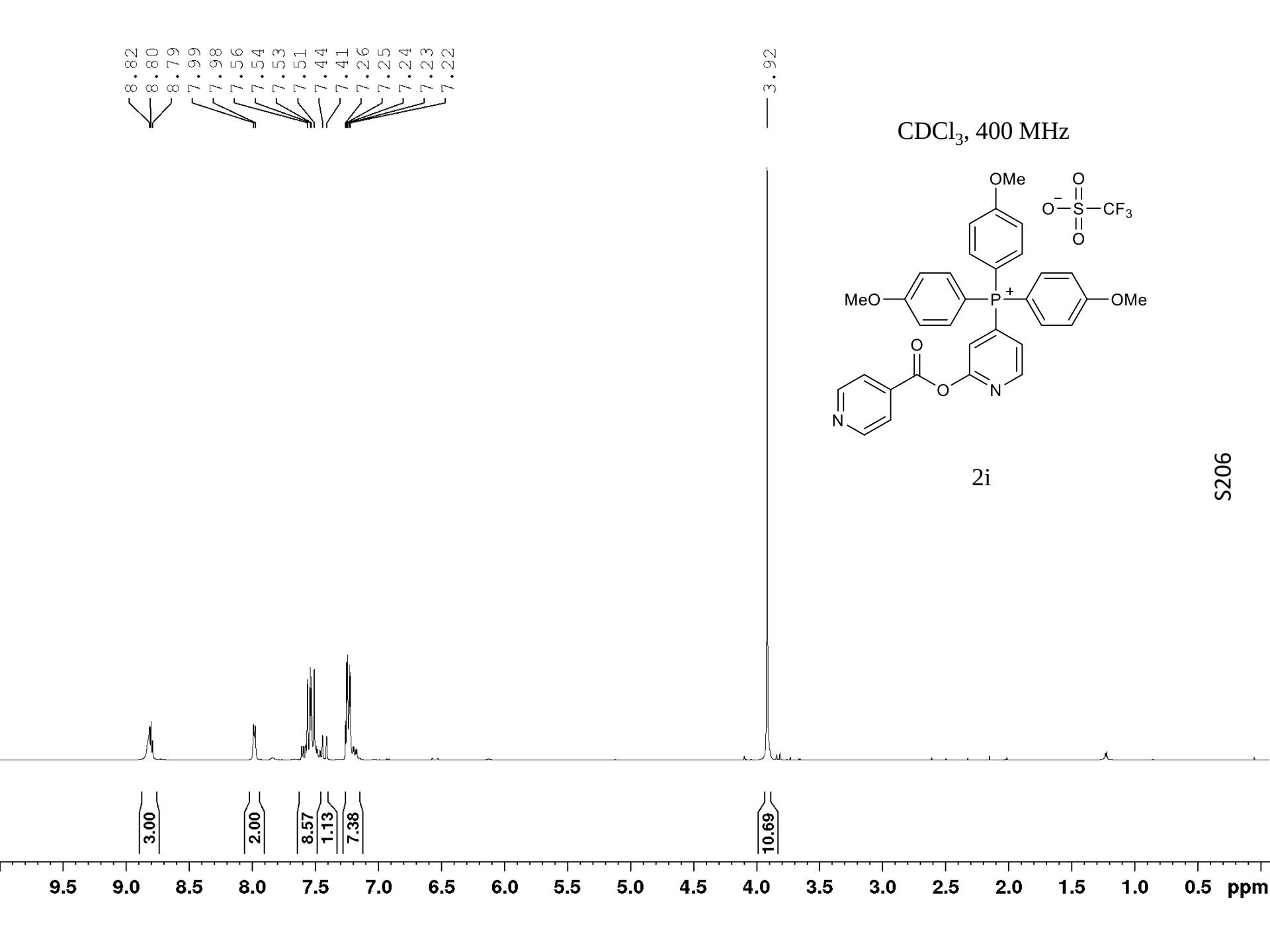

29.01
20.67
CDCl3, 162 MHz (crude 31P NMR)
N
Cl
O
OTf
P+
MeO
OMe
OMe
2h
S203
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

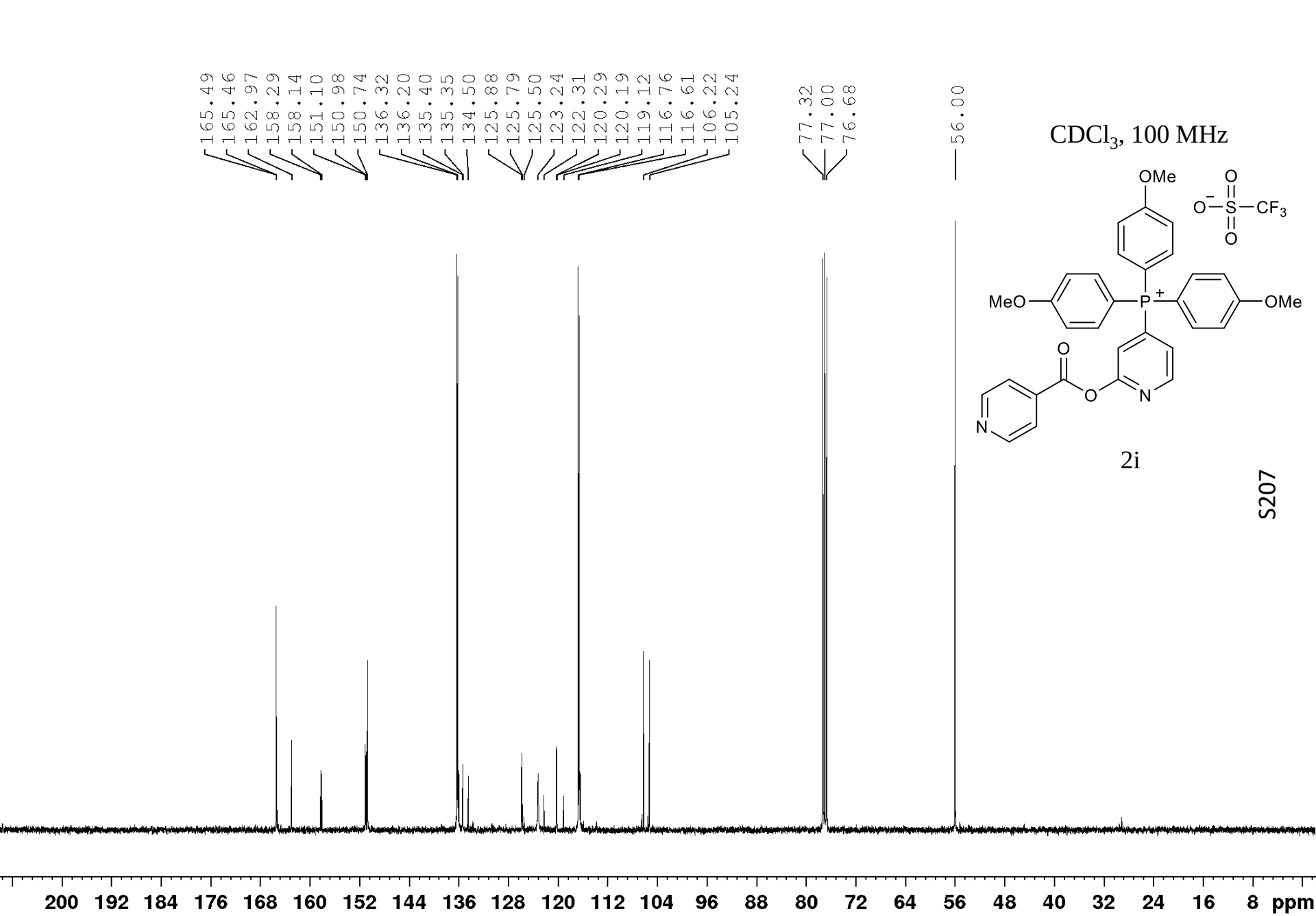

9.28
9.27
9.14
9.13
CDCl3, 400 MHz
(crude 1H NMR)
2i
Major
Minor
0.679
0.077
9.4
9.2
9.0 ppm
S204
0.68
0.08
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

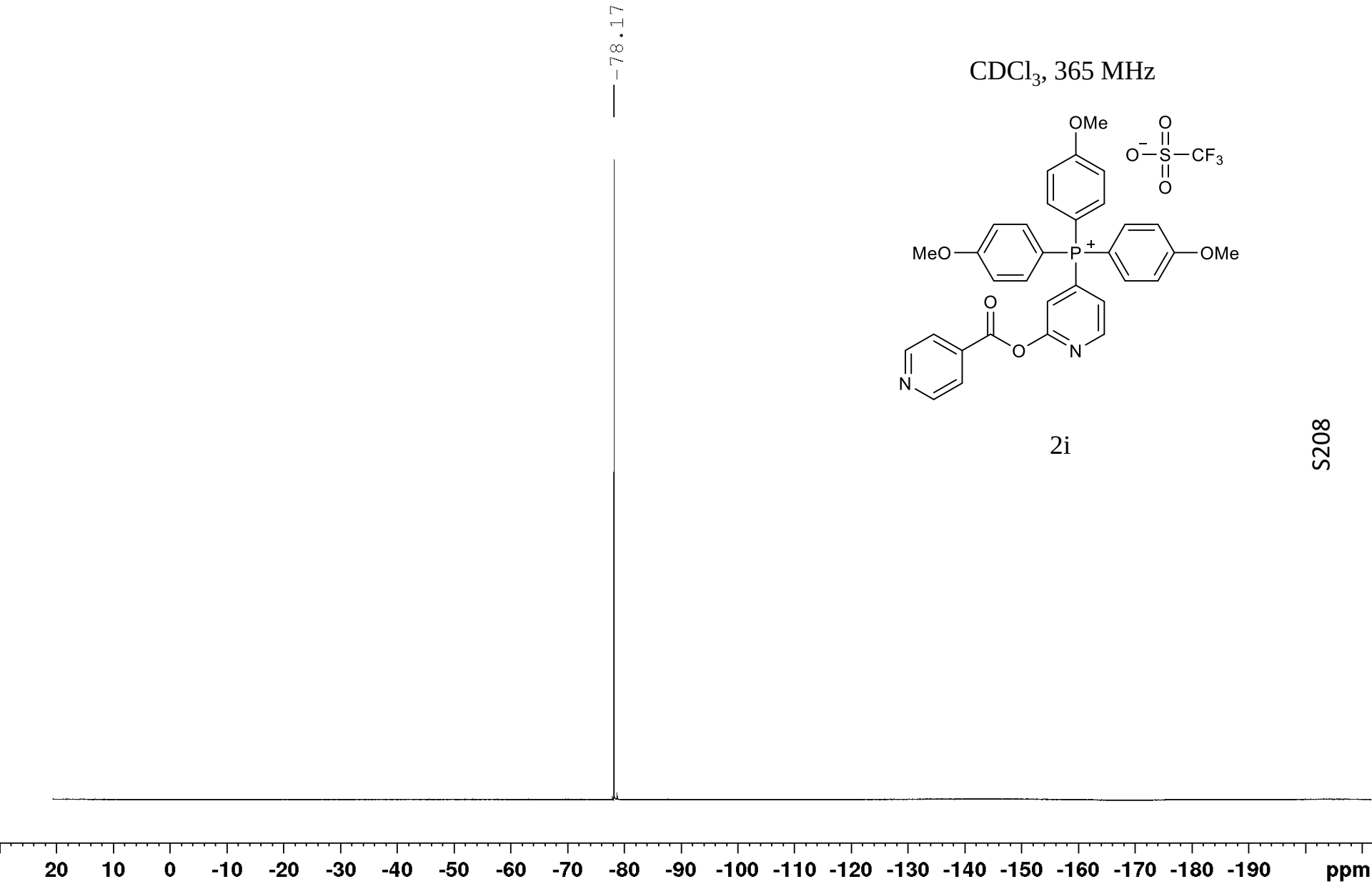
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

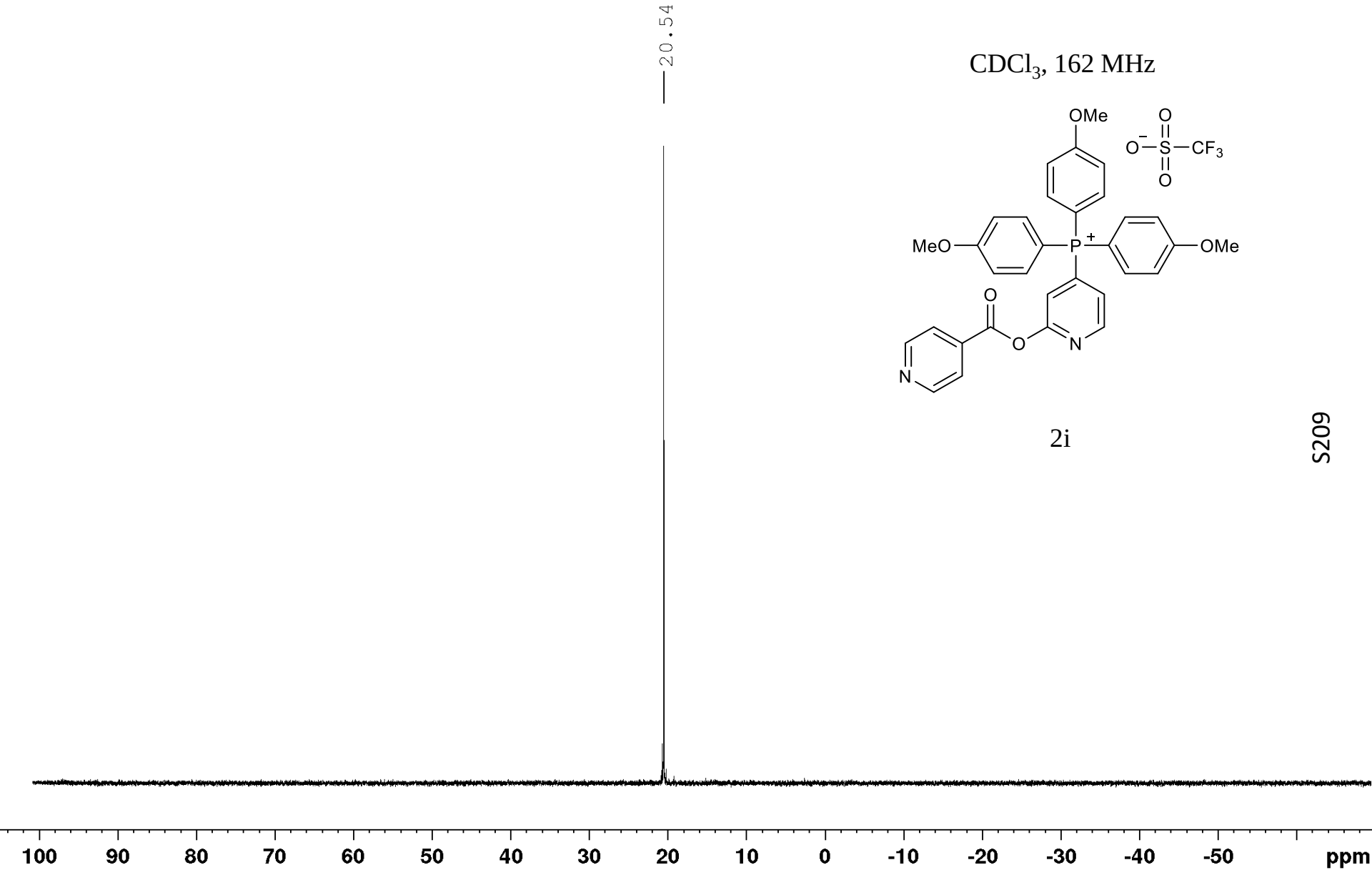


2i

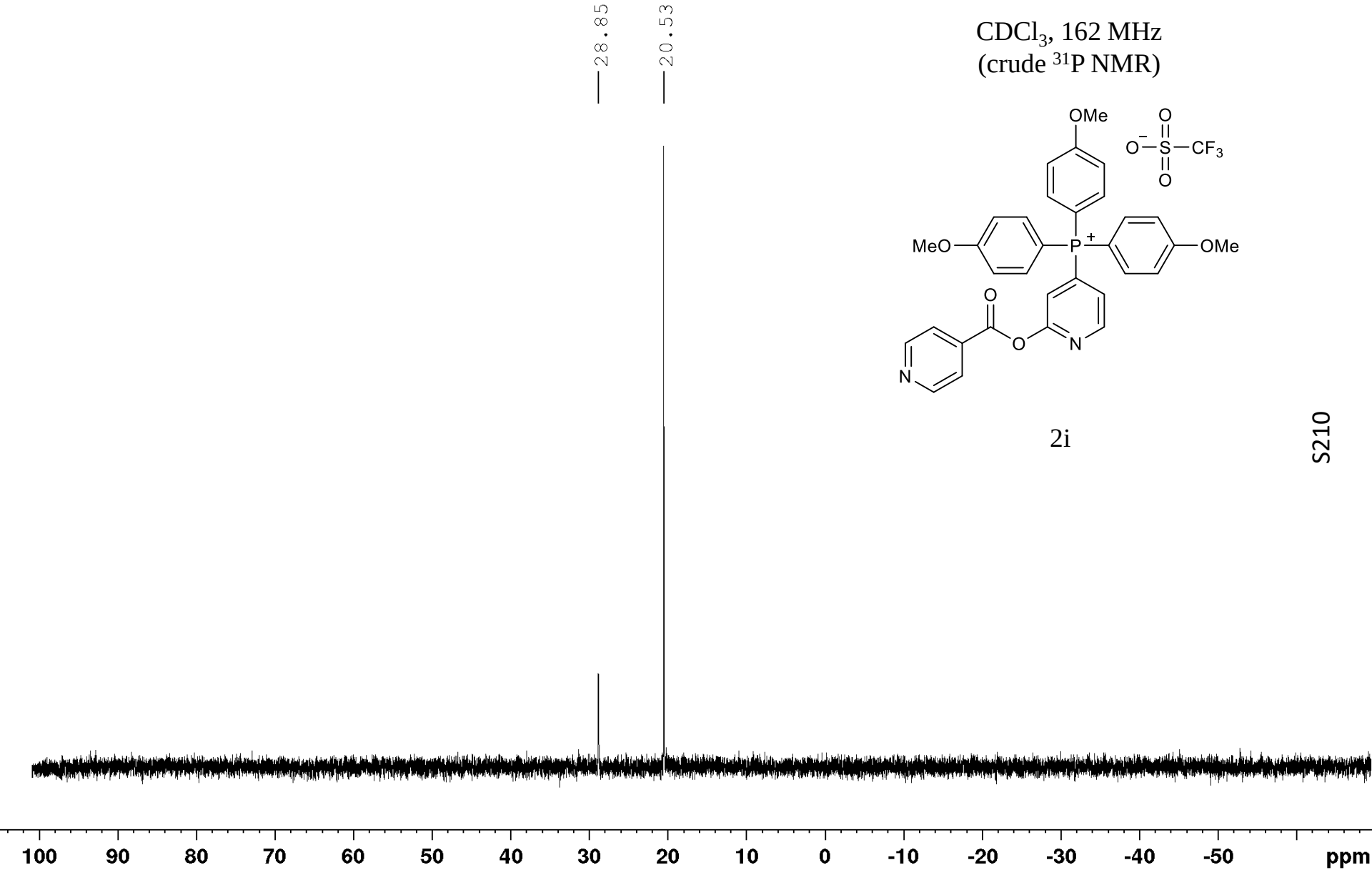

8.82
8.80
8.79
7.99
7.98
7.56
7.54
7.53
7.51
7.44
7.41
7.26
7.25
7.24
7.23
7.22
3.92
CDCl3, 400 MHz
OMe
O
O
S
CF3
MeO
P
+
OMe
O
O
N
N
2i
S206
3.00
2.00
8.57
1.13
7.38
10.69
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

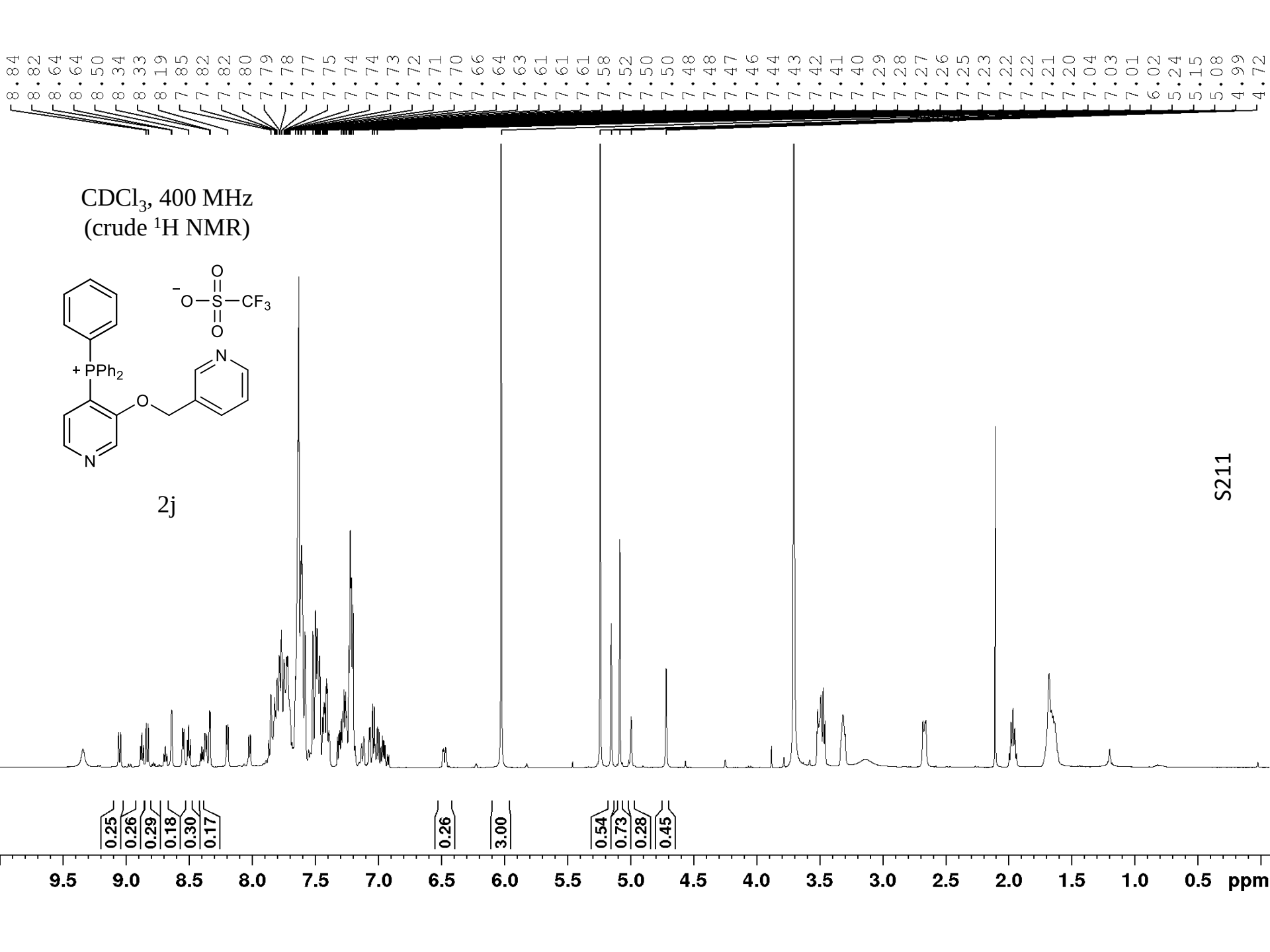

165.49
165.46
162.97
158.29
158.14
151.10
150.98
150.74
136.32
136.20
135.40
135.35
134.50
125.88
125.79
125.50
123.24
122.31
120.29
120.19
119.12
116.76
116.61
106.22
105.24
77.32
77.00
76.68
56.00
CDCl3, 100 MHz
OMe
MeO
OMe
P+
O
O
S
CF3
O
O
O
N
N
2i
S207
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

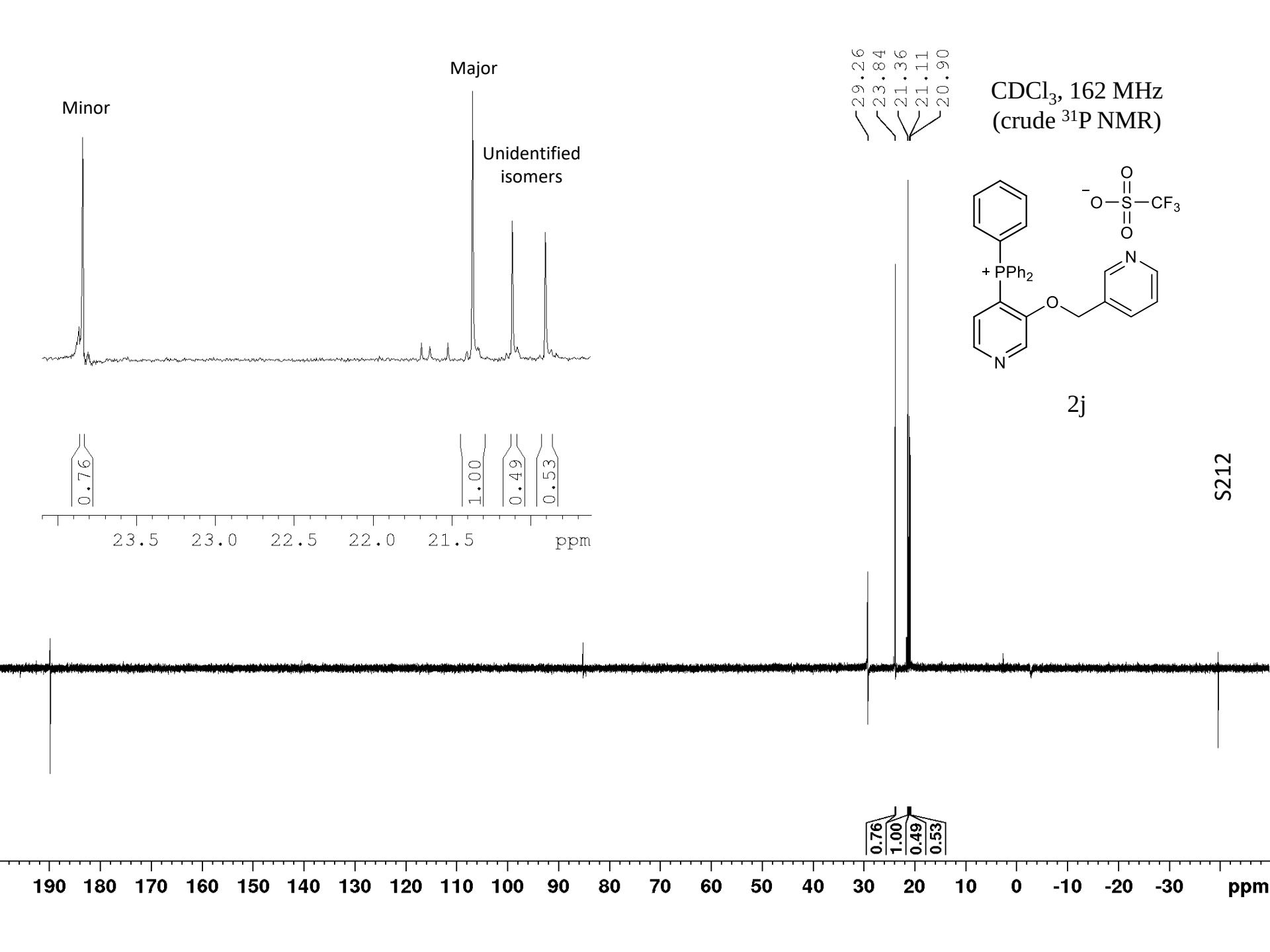

-78.17
CDCl3, 365 MHz
OMe
O
O
S
CF3
O
MeO
P
+
OMe
O
O
N
N
2i
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

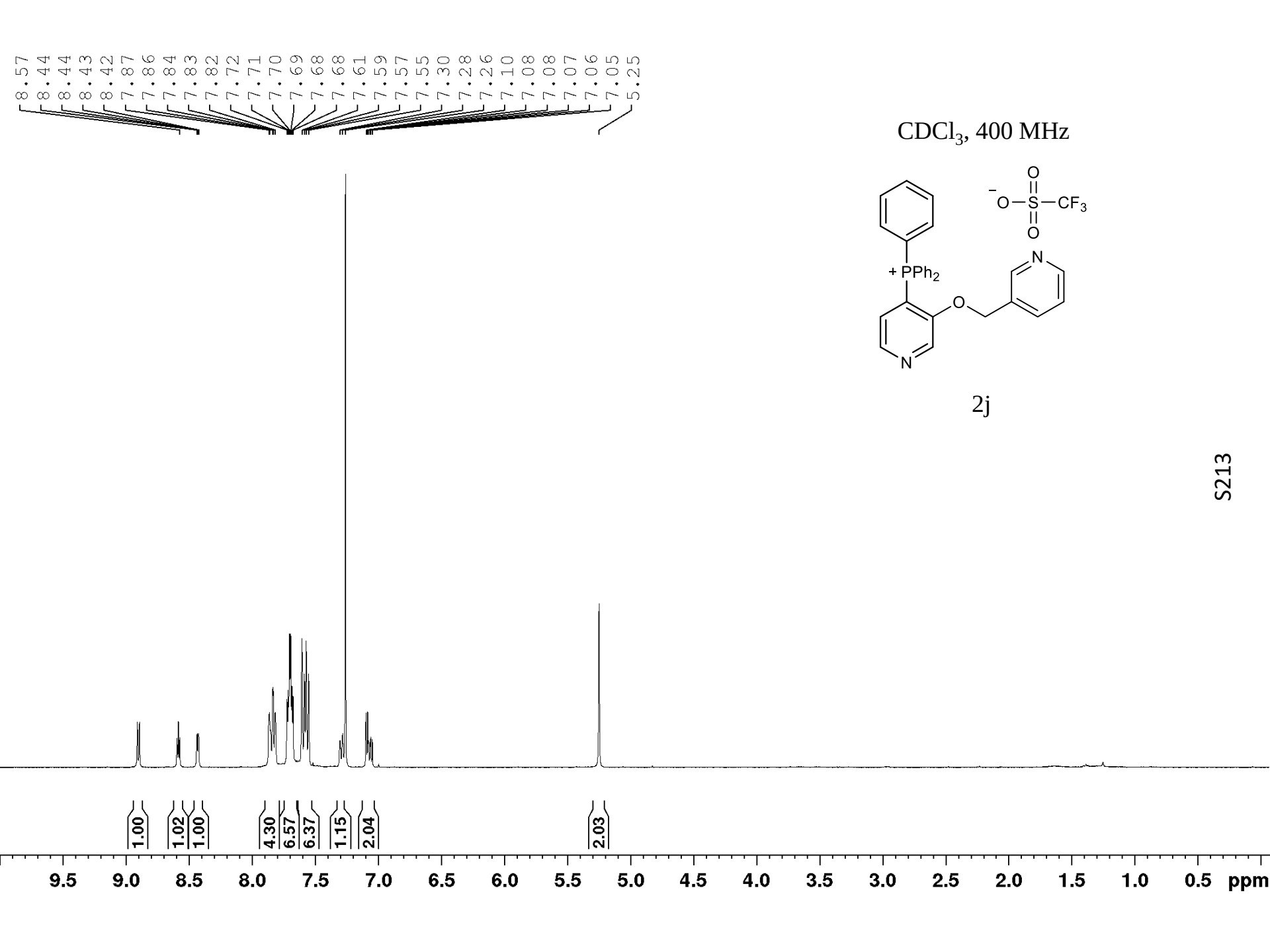

20.54
CDCl3, 162 MHz
OMe
O
O
S
CF3
O
MeO
P
+
OMe
O
O
N
N
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

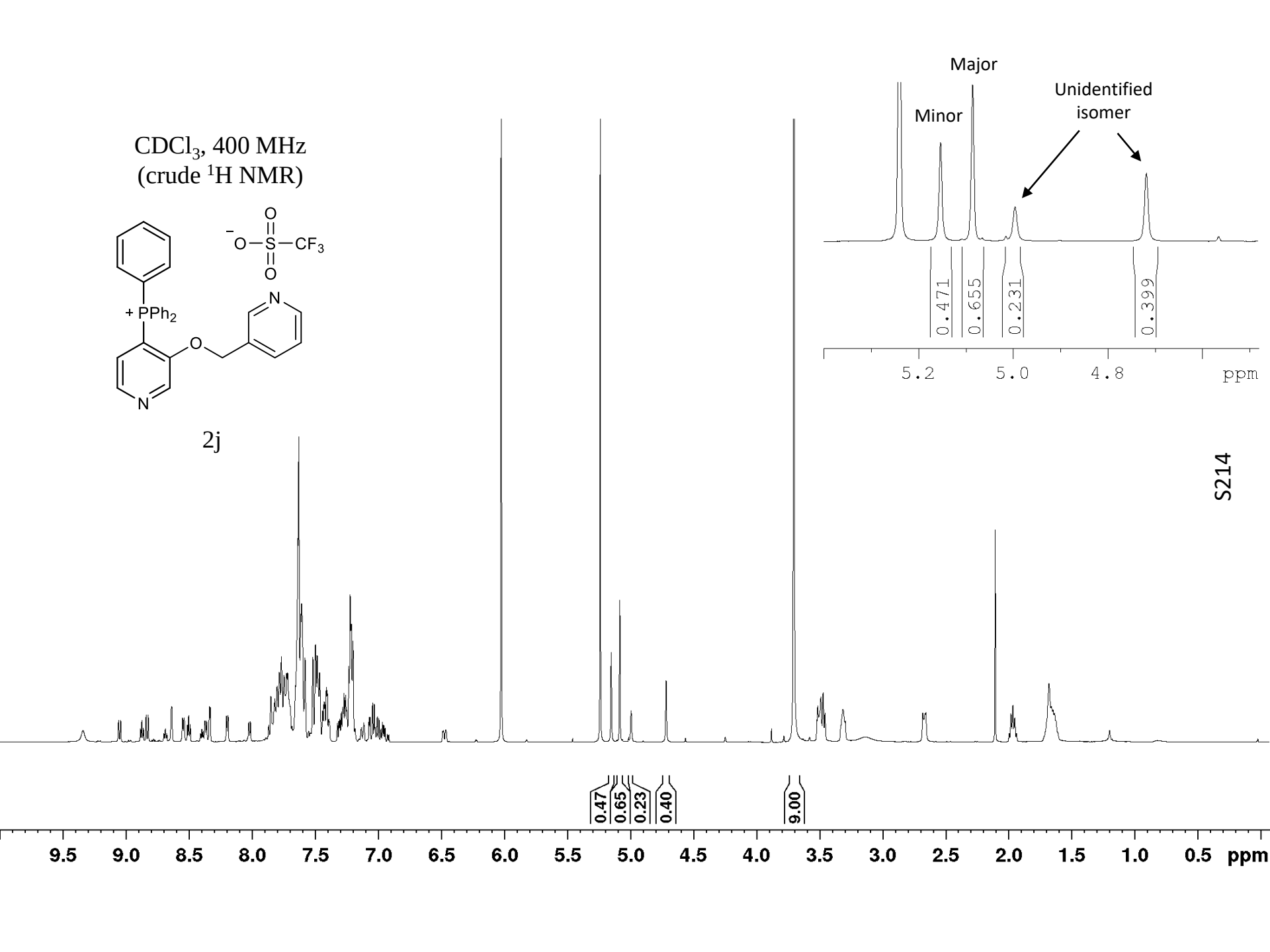
2i

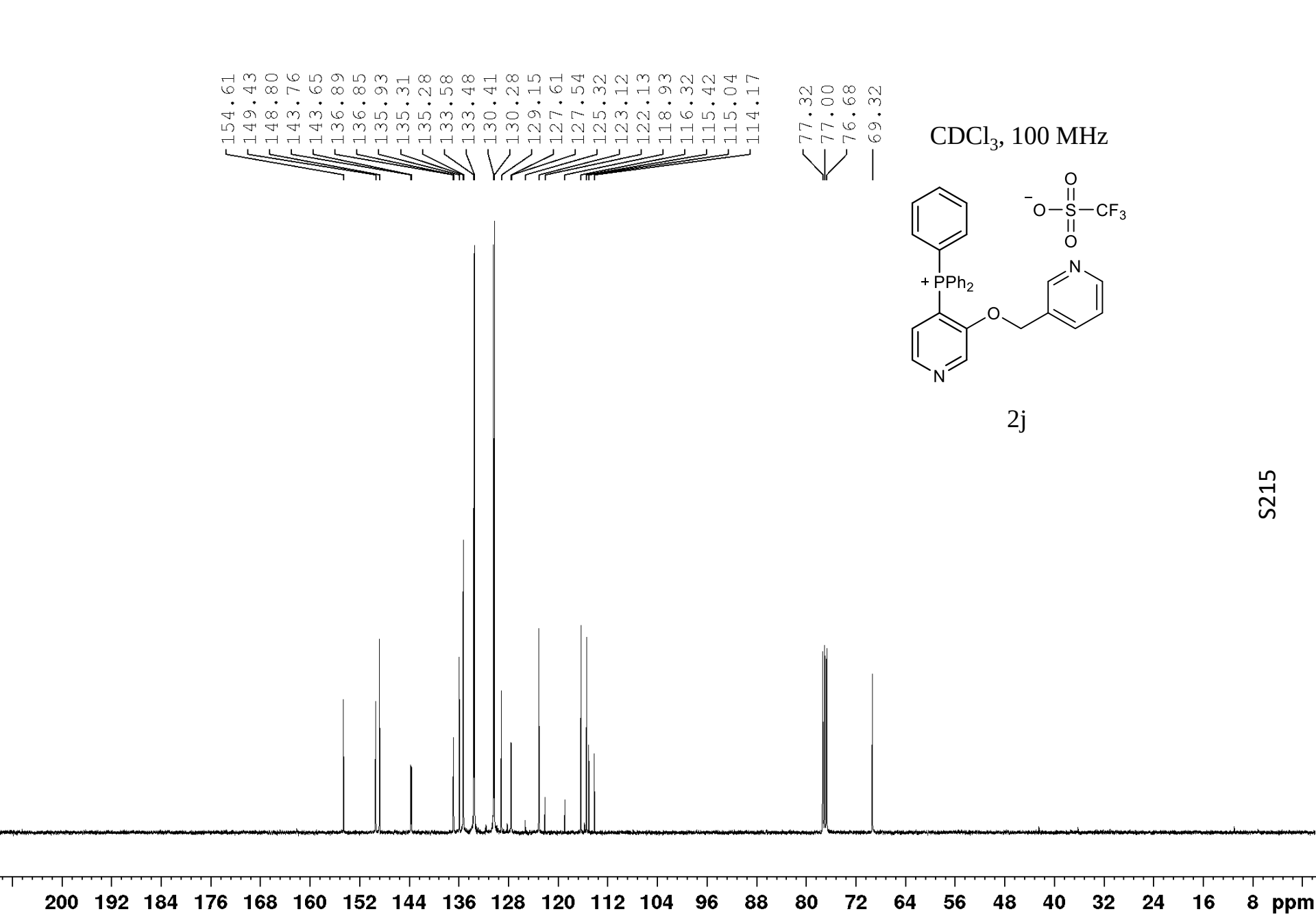

28.85
20.53
CDCl3, 162 MHz
(crude 31P NMR)
OMe
O
O
S
CF3
O
MeO
P
+
OMe
O
O
N
N
2i
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm


8.84 8.82 8.64 8.64 8.50 8.34 8.33 8.19 7.85 7.82 7.82 7.80 7.79 7.78 7.77 7.75 7.74 7.74 7.73 7.72 7.71 7.70 7.66 7.64 7.63 7.61 7.61 7.61 7.58 7.52 7.50 7.50 7.48 7.48 7.47 7.46 7.44 7.43 7.42 7.41 7.40 7.29 7.28 7.27 7.26 7.25 7.23 7.22 7.22 7.21 7.20 7.04 7.03 7.01 6.02 5.24 5.15 5.08 4.99 4.72
CDCl3, 400 MHz
(crude 1H NMR)
2j
S211
0.25 0.26 0.29 0.18 0.30 0.17 0.26 3.00 0.54 0.73 0.28 0.45
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 ppm

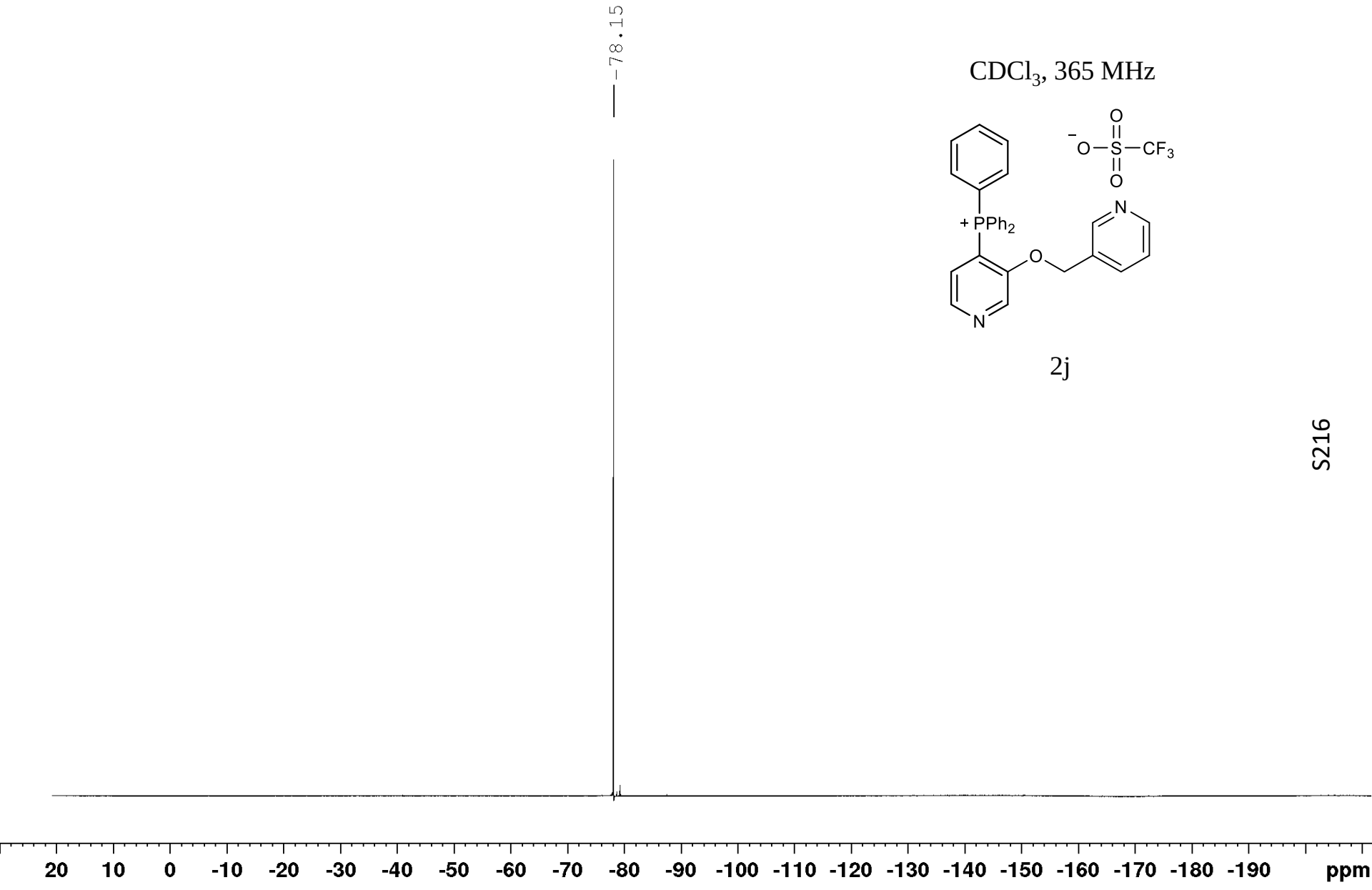

Major
Minor
Unidentified
isomers
29.26
23.84
21.36
21.11
20.90
CDCl3, 162 MHz
(crude 31P NMR)
+ PPh2
O
N
O
O
S
O
CF3
2j
S212
0.76
1.00
0.49
0.53
23.5
23.0
22.5
22.0
21.5
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

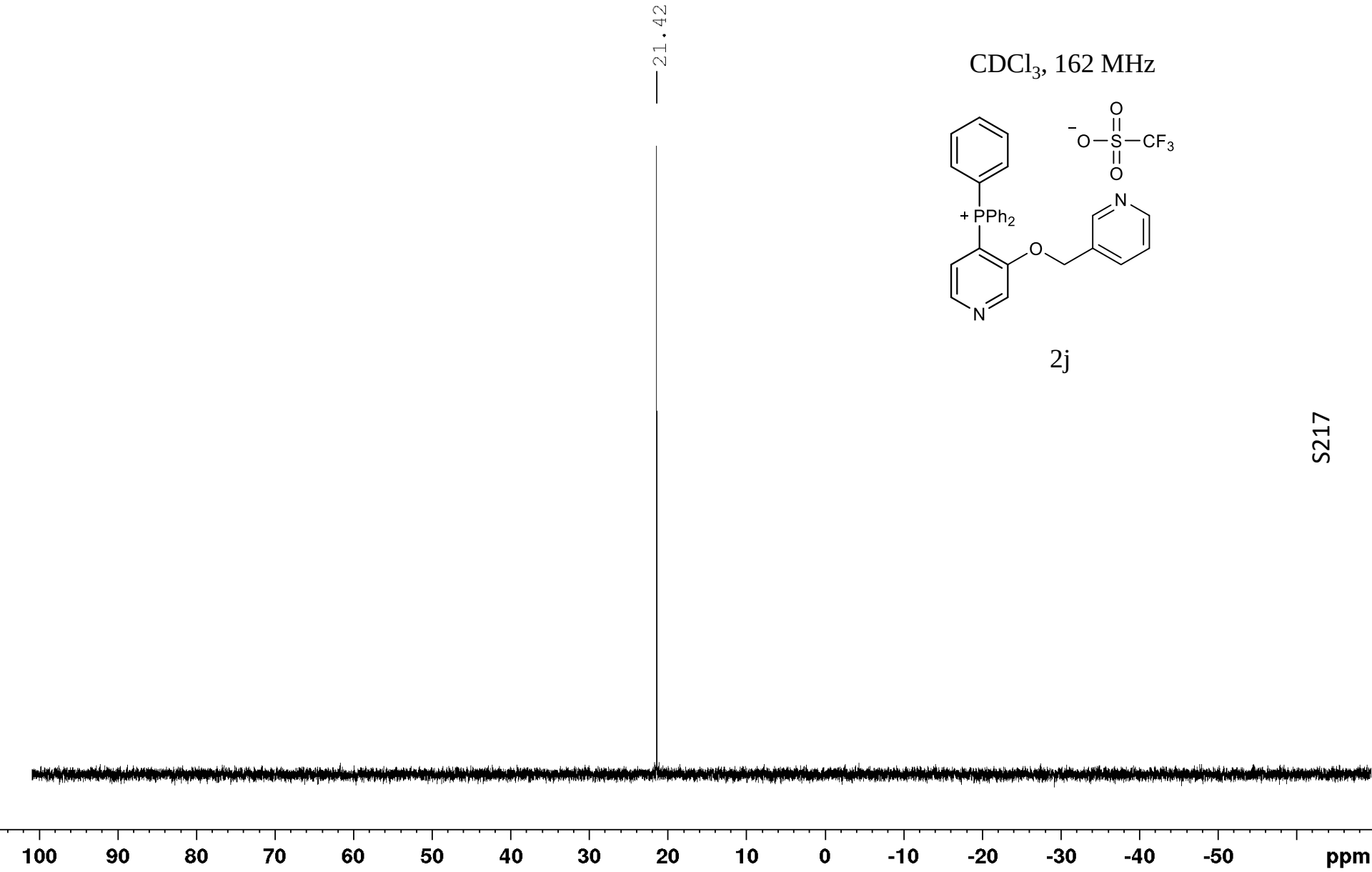

8.57
8.44
8.44
8.43
8.42
7.87
7.86
7.84
7.83
7.82
7.72
7.71
7.70
7.69
7.68
7.68
7.61
7.59
7.57
7.55
7.30
7.28
7.26
7.10
7.08
7.08
7.07
7.06
7.05
5.25
CDCl3, 400 MHz
+ PPh2
O
S
CF3
N
N
2j
1.00
1.02
1.00
4.30
6.57
6.37
1.15
2.04
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

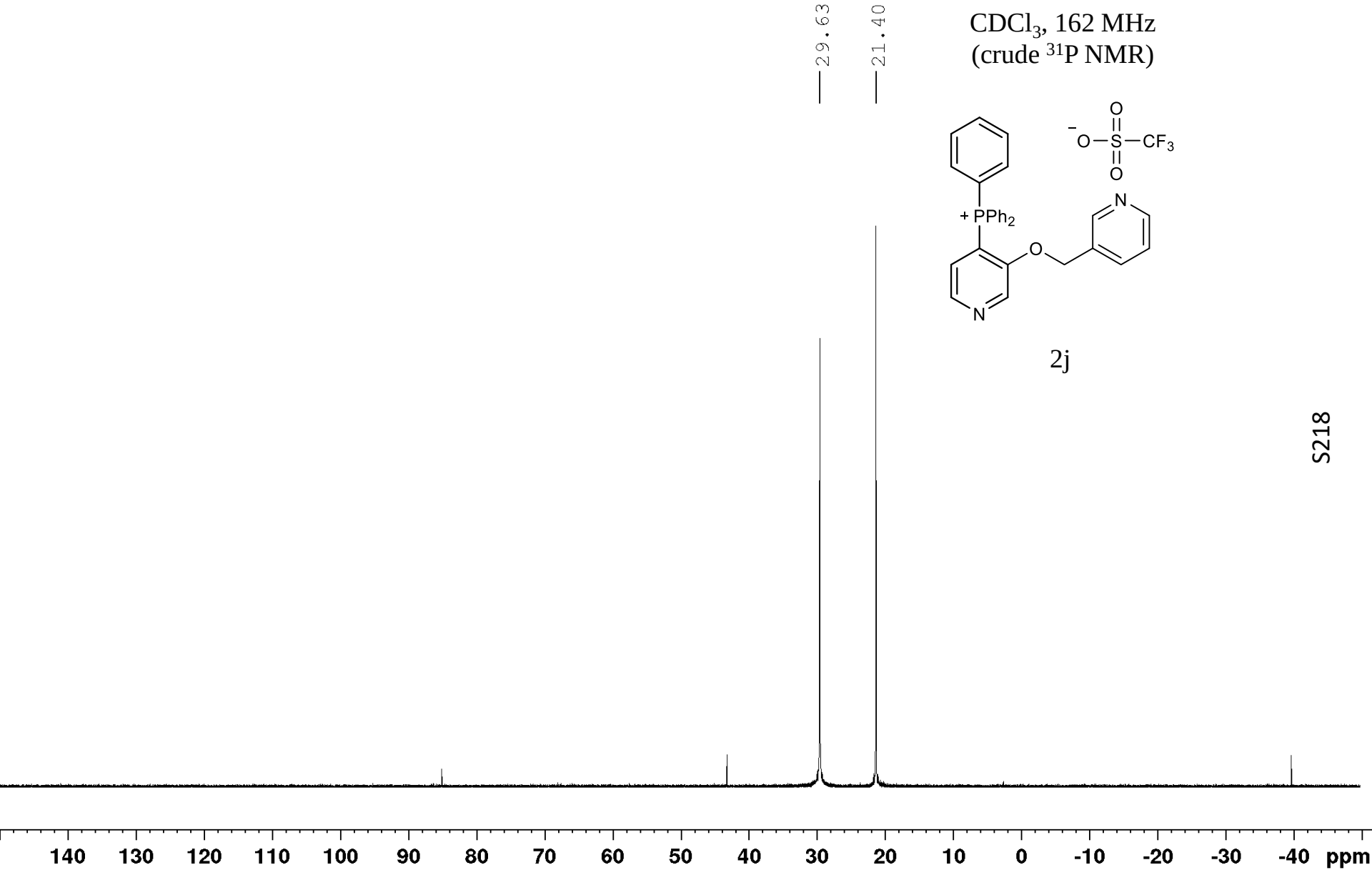

CDCl3, 400 MHz
(crude 1H NMR)
2j
Major
Minor
Unidentified
isomer
0.471
0.655
0.231
0.399
5.2
5.0
4.8
ppm
S214
0.47
0.65
0.23
0.40
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

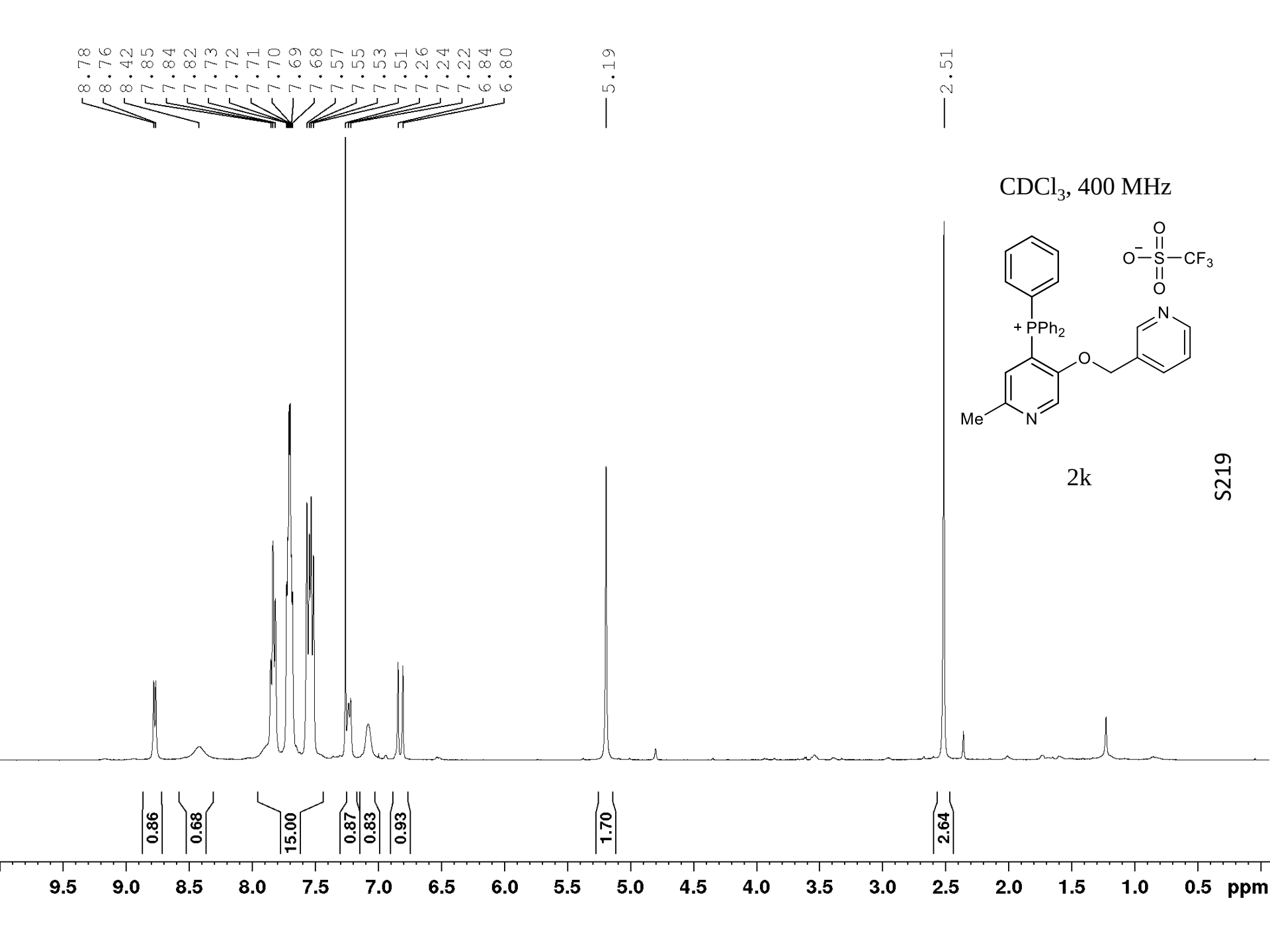

154.61
149.43
148.80
143.76
143.65
136.89
136.85
135.93
135.31
135.28
133.58
133.48
130.41
130.28
129.15
127.61
127.54
125.32
123.12
122.13
118.93
116.32
115.42
115.04
114.17
77.32
77.00
76.68
69.32
CDCl3, 100 MHz
+ PPh2
O
S
CF3
N
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

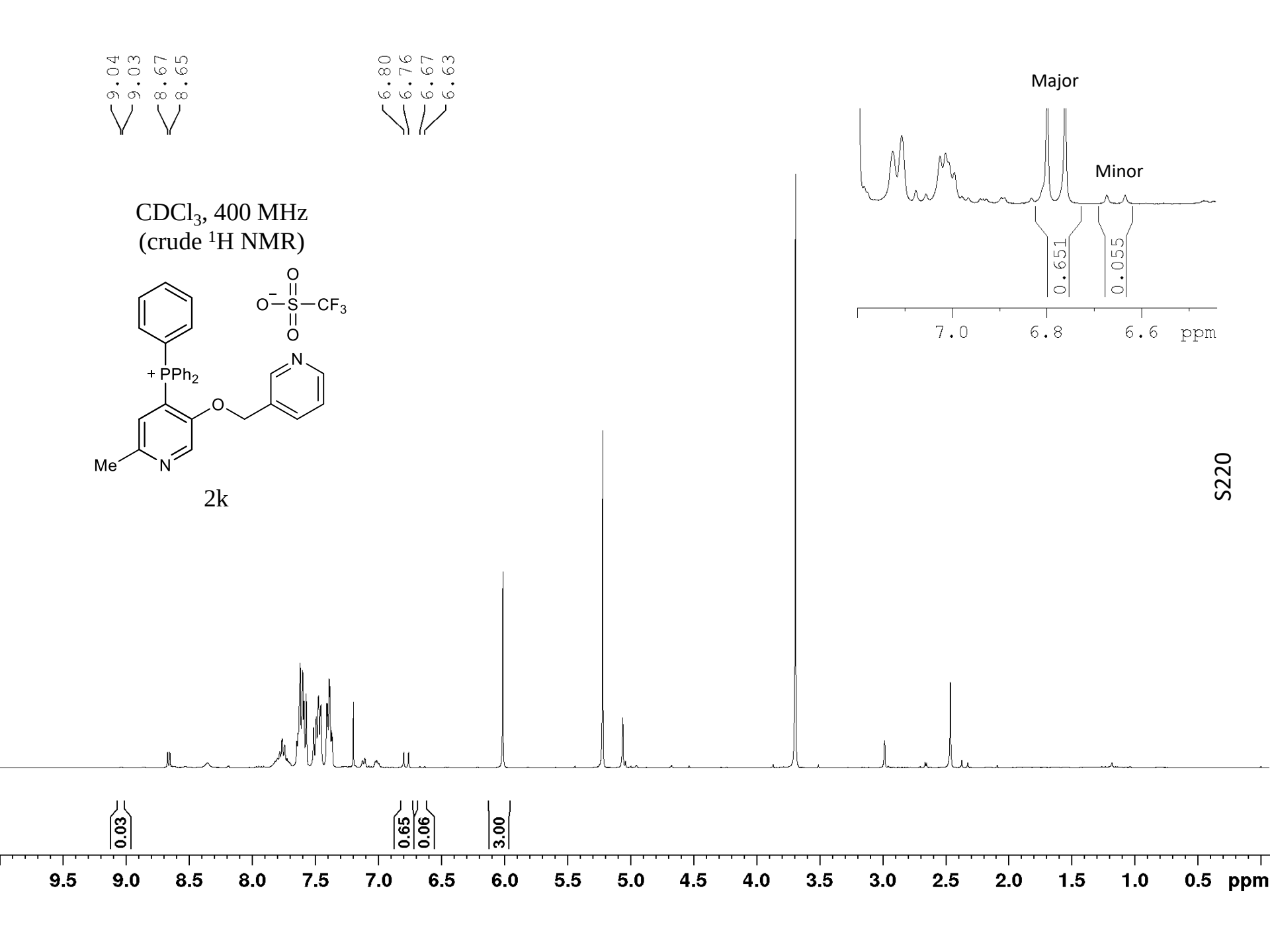
2j

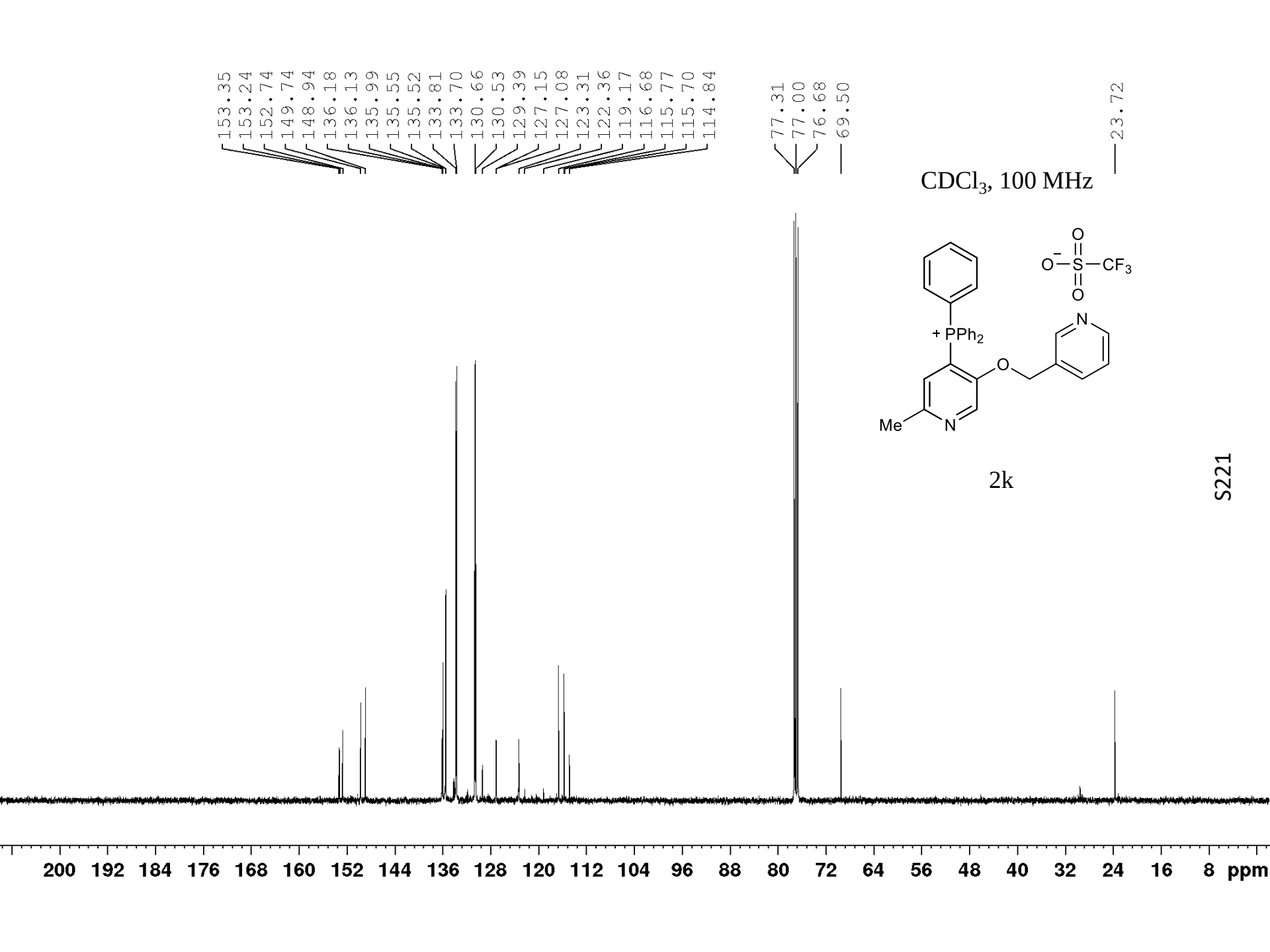

-78.15
CDCl3, 365 MHz
+ PPh2
O
S
CF3
N
N
2j
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


21.42
CDCl3, 162 MHz
2j
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

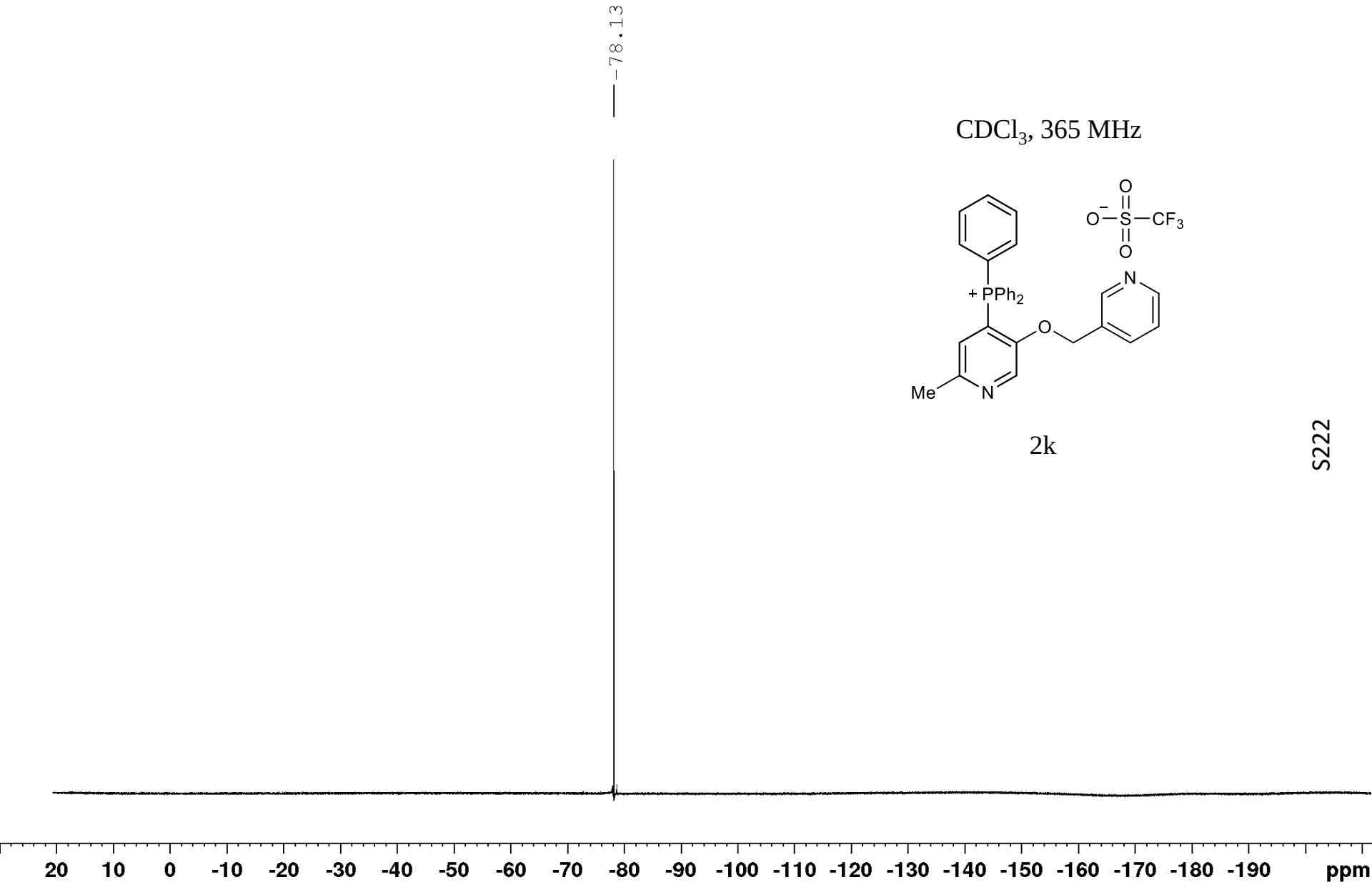

29.63
21.40
CDCl3, 162 MHz
(crude 31P NMR)
+ PPh2
O
O
S
CF3
N
N
2j
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

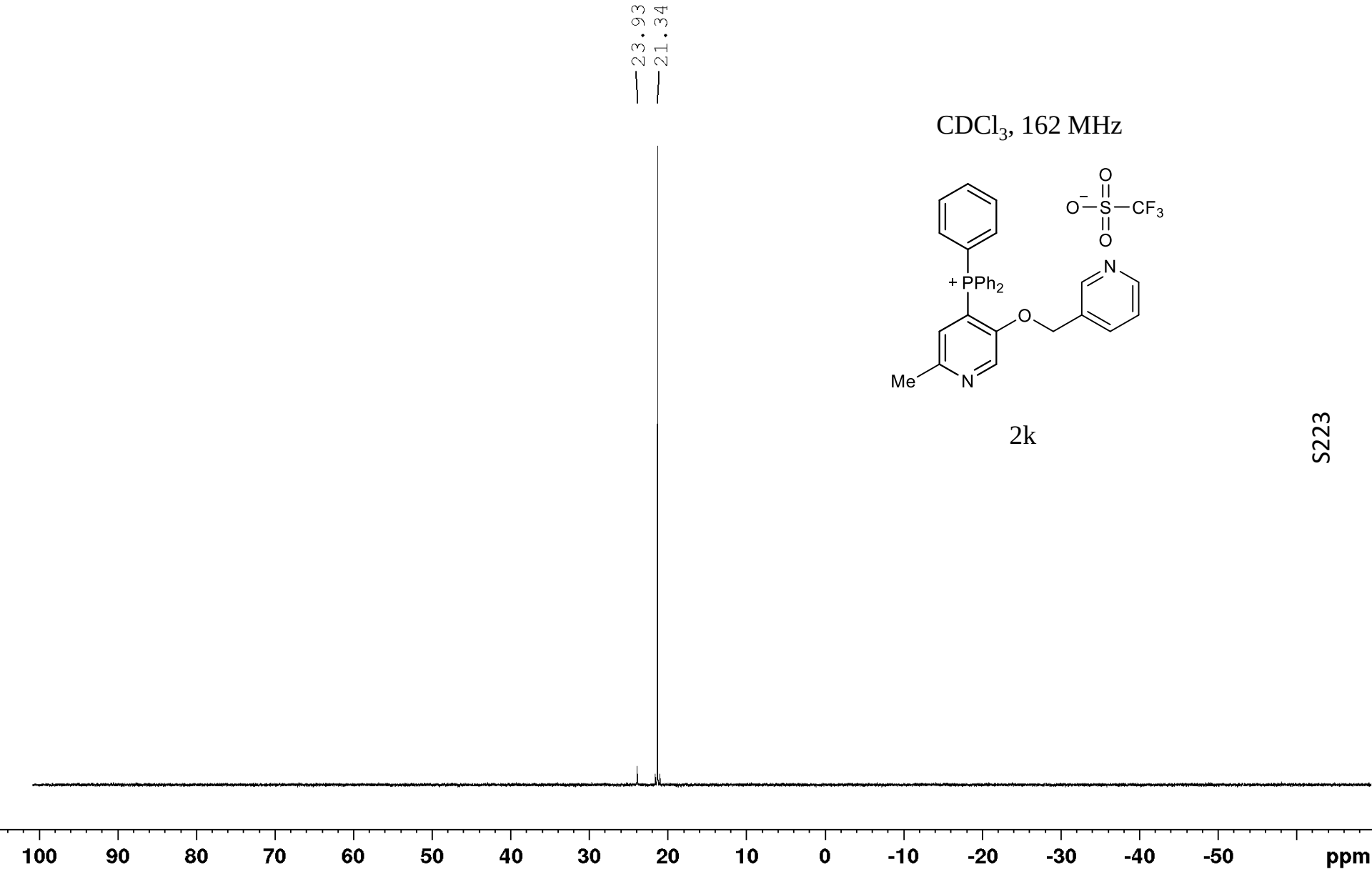

8.78
8.76
8.42
7.85
7.84
7.82
7.73
7.72
7.71
7.70
7.69
7.68
7.57
7.55
7.53
7.51
7.26
7.24
7.22
6.84
6.80
5.19
2.51
CDCl3, 400 MHz
+ PPh2
O
N
Me
N
O
O
S
CF3
O
2k
S219
0.86
0.68
15.00
0.87
0.83
0.93
1.70
2.64
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


9.04
9.03
8.67
8.65
6.80
6.76
6.67
6.63
Major
Minor
0.651
0.055
7.0
6.8
6.6
ppm
CDCl3, 400 MHz
(crude 1H NMR)
+ PPh2
O
N
Me
2k
S220
0.03
0.65
0.06
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
0.5
ppm

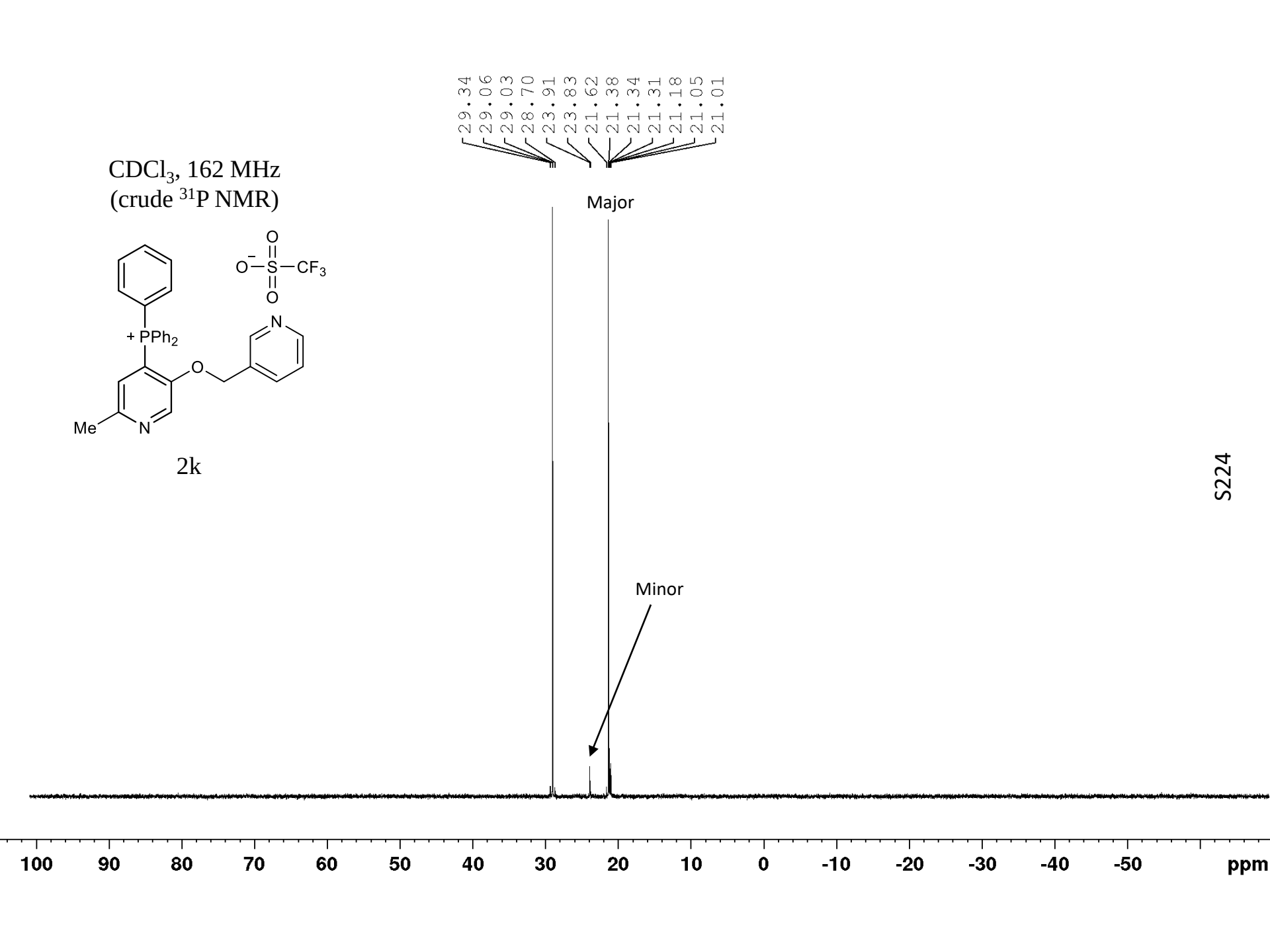

153.35
153.24
152.74
149.74
148.94
136.18
136.13
135.99
135.55
135.52
133.81
133.70
130.66
130.53
129.39
127.15
127.08
123.31
122.36
119.17
116.68
115.77
115.70
114.84
77.31
77.00
76.68
69.50
23.72
CDCl3, 100 MHz
+ PPh2
O
N
Me
N
O
O
S
CF3
O
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

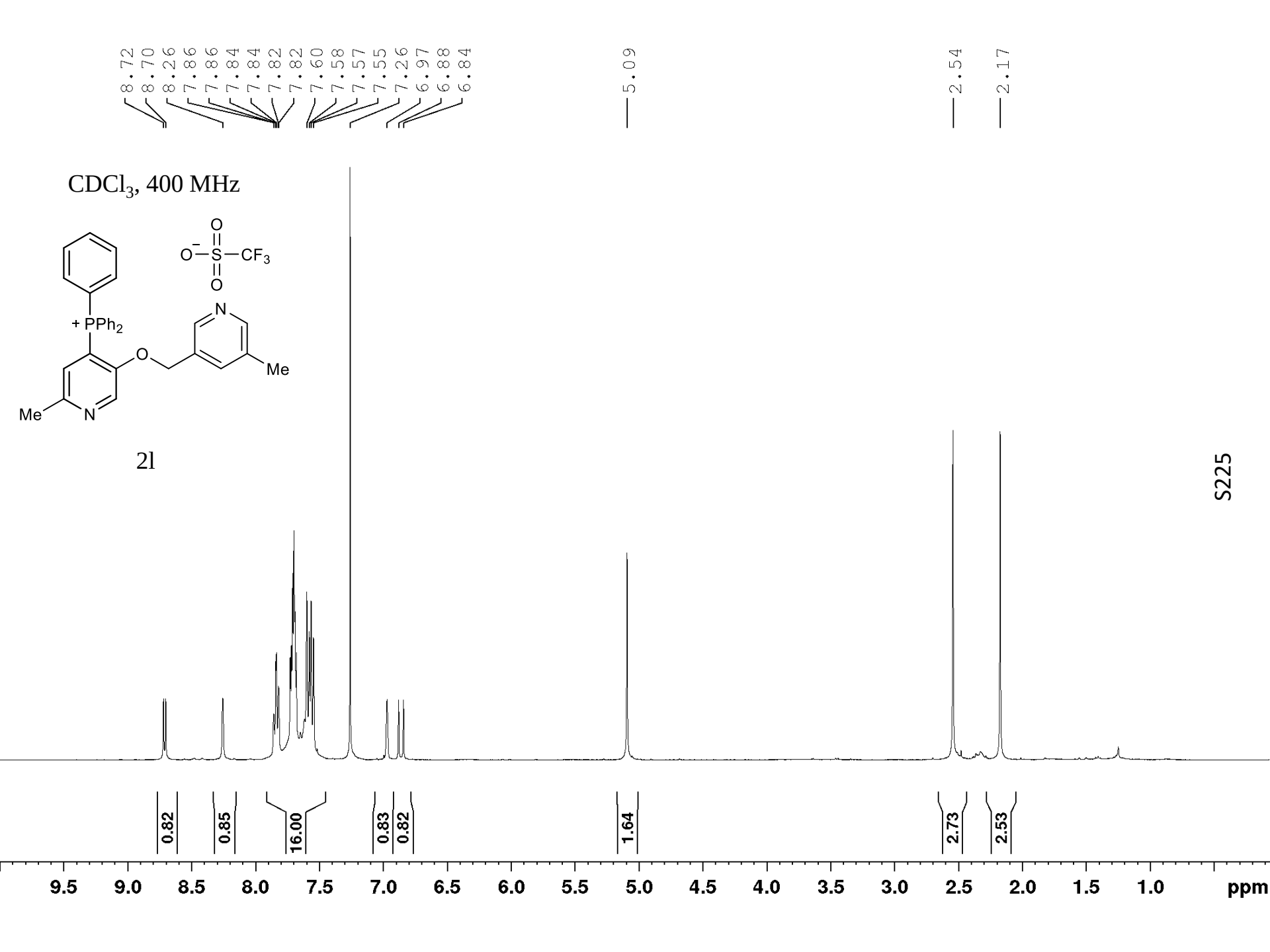
2k

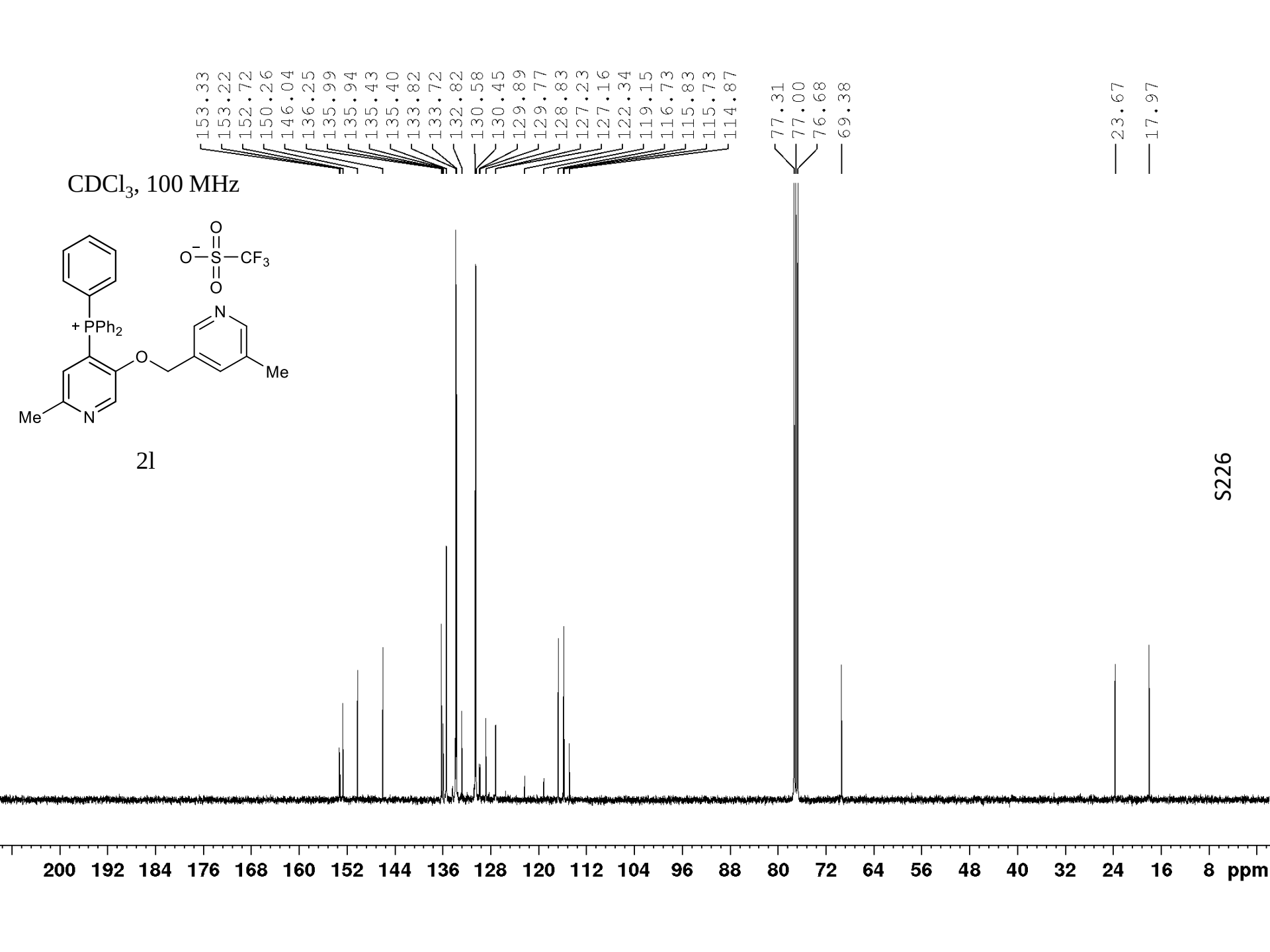

-78.13
CDCl3, 365 MHz
+PPh2
Me
N
O
O
O
S
CF3
2k
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


23.93
21.34
CDCl3, 162 MHz
+PPh2
O
N
Me
N
O
O
S
CF3
O
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

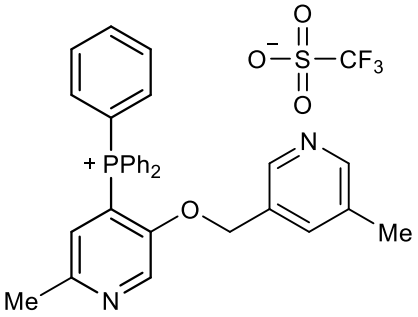
2k


29.34
29.06
29.03
28.70
23.91
23.83
21.62
21.38
21.34
21.31
21.18
21.05
21.01
CDCl3, 162 MHz
(crude 31P NMR)
Major
Minor
2k
S224
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm


8.72
8.70
8.26
7.86
7.86
7.84
7.84
7.82
7.82
7.60
7.58
7.57
7.55
7.26
6.97
6.88
6.84
5.09
2.54
2.17
CDCl3, 400 MHz
+ PPh2
O
O
S
CF3
N
Me
Me
N
2l
S225
0.82
0.85
16.00
0.83
0.82
1.64
2.73
2.53
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

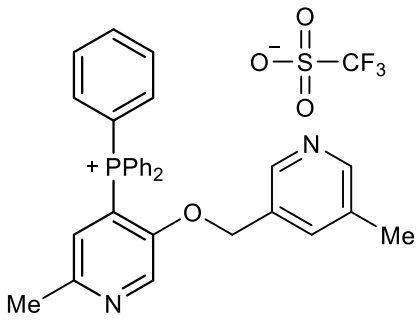

153.33
153.22
152.72
150.26
146.04
136.25
135.99
135.94
135.43
135.40
133.82
133.72
132.82
130.58
130.45
129.89
129.77
128.83
127.23
127.16
122.34
119.15
116.73
115.83
115.73
114.87
77.31
77.00
76.68
69.38
23.67
17.97
CDCl3, 100 MHz
O
O
S
CF3
+ PPh2
N
O
Me
Me
N
2l
S226
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



2l

$CDCl_3$, 162 MHz

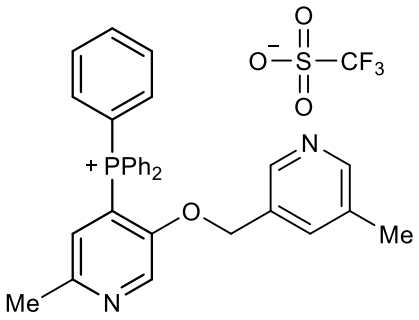


2l

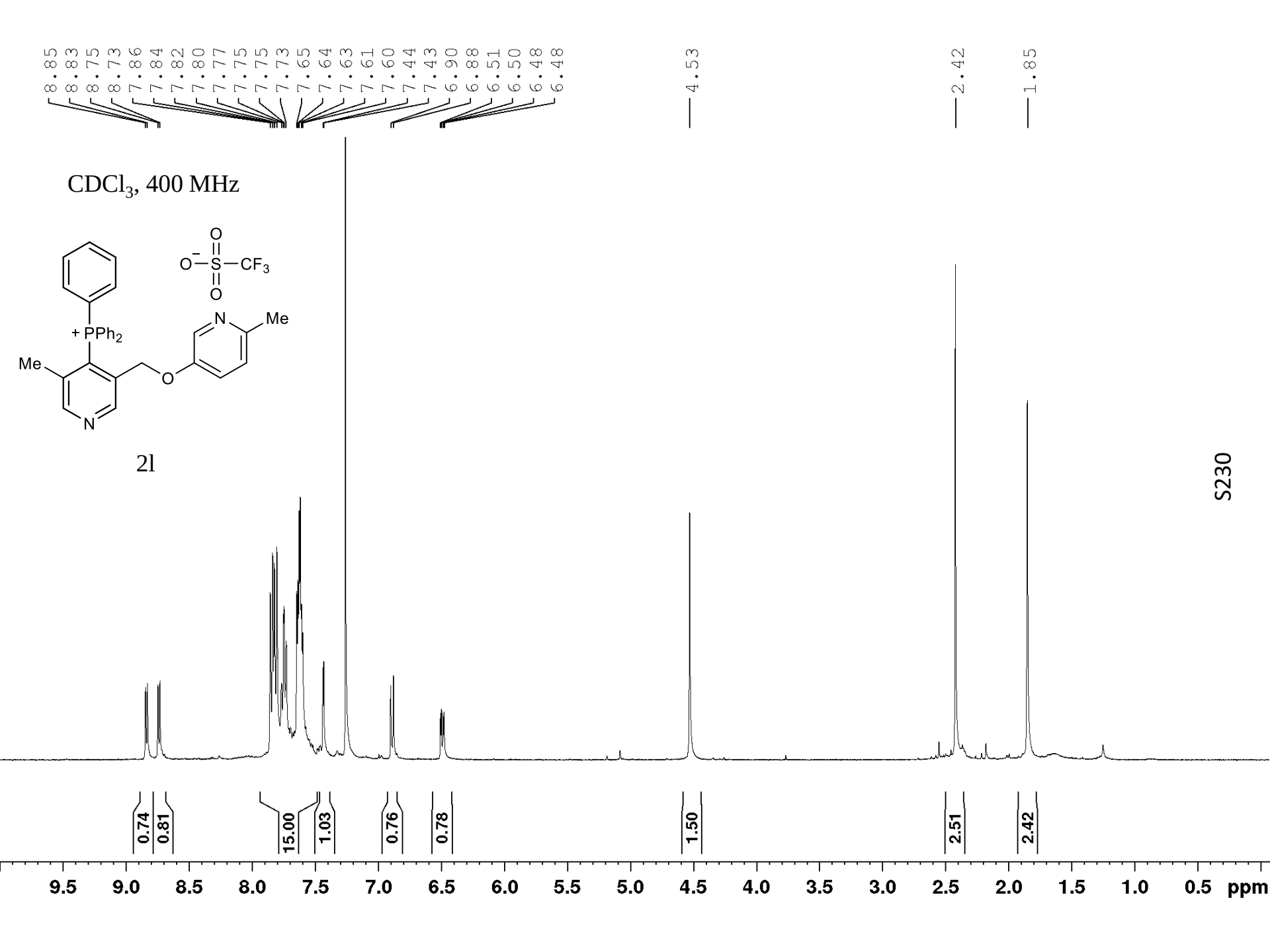
21.28

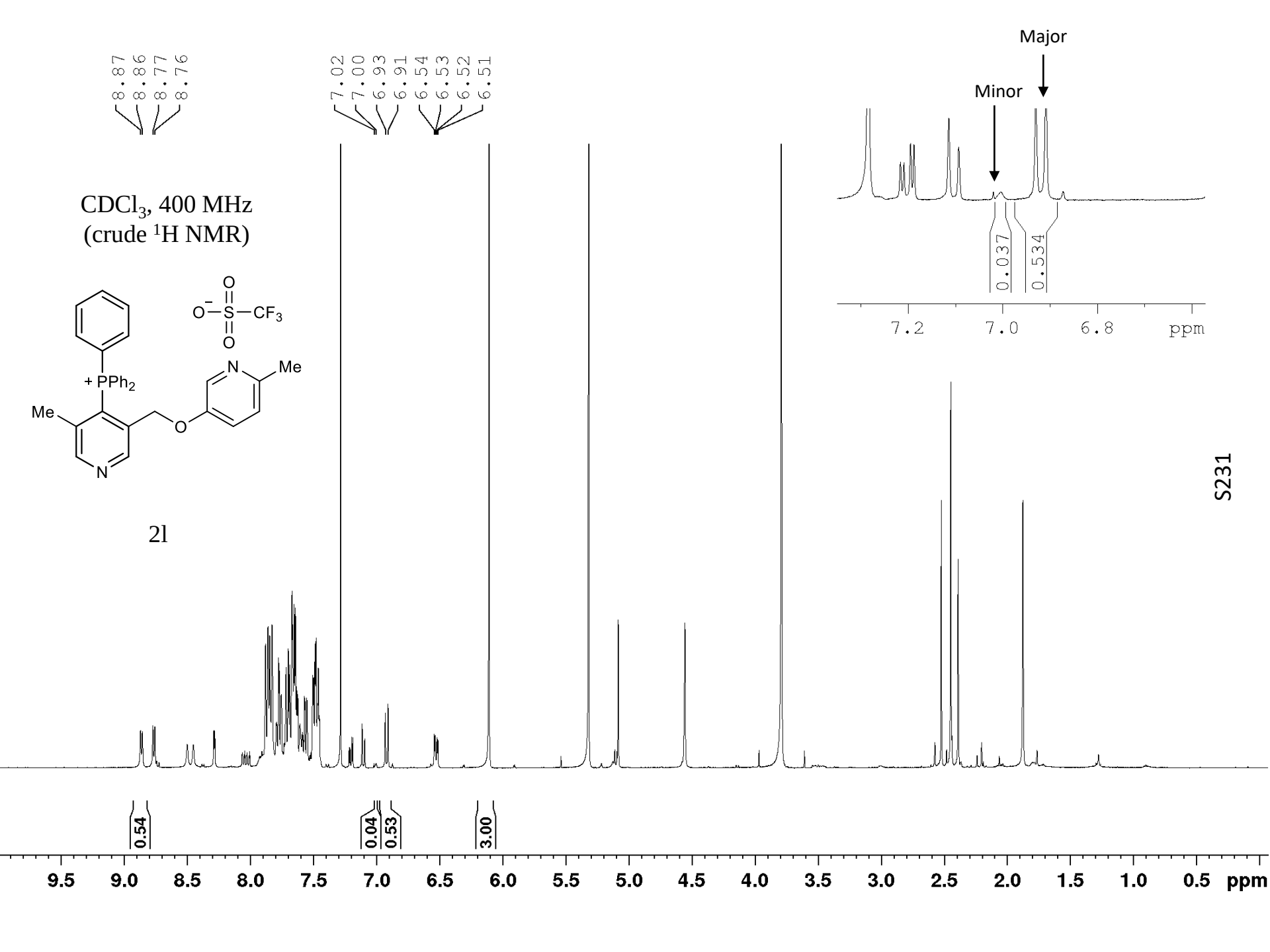
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm

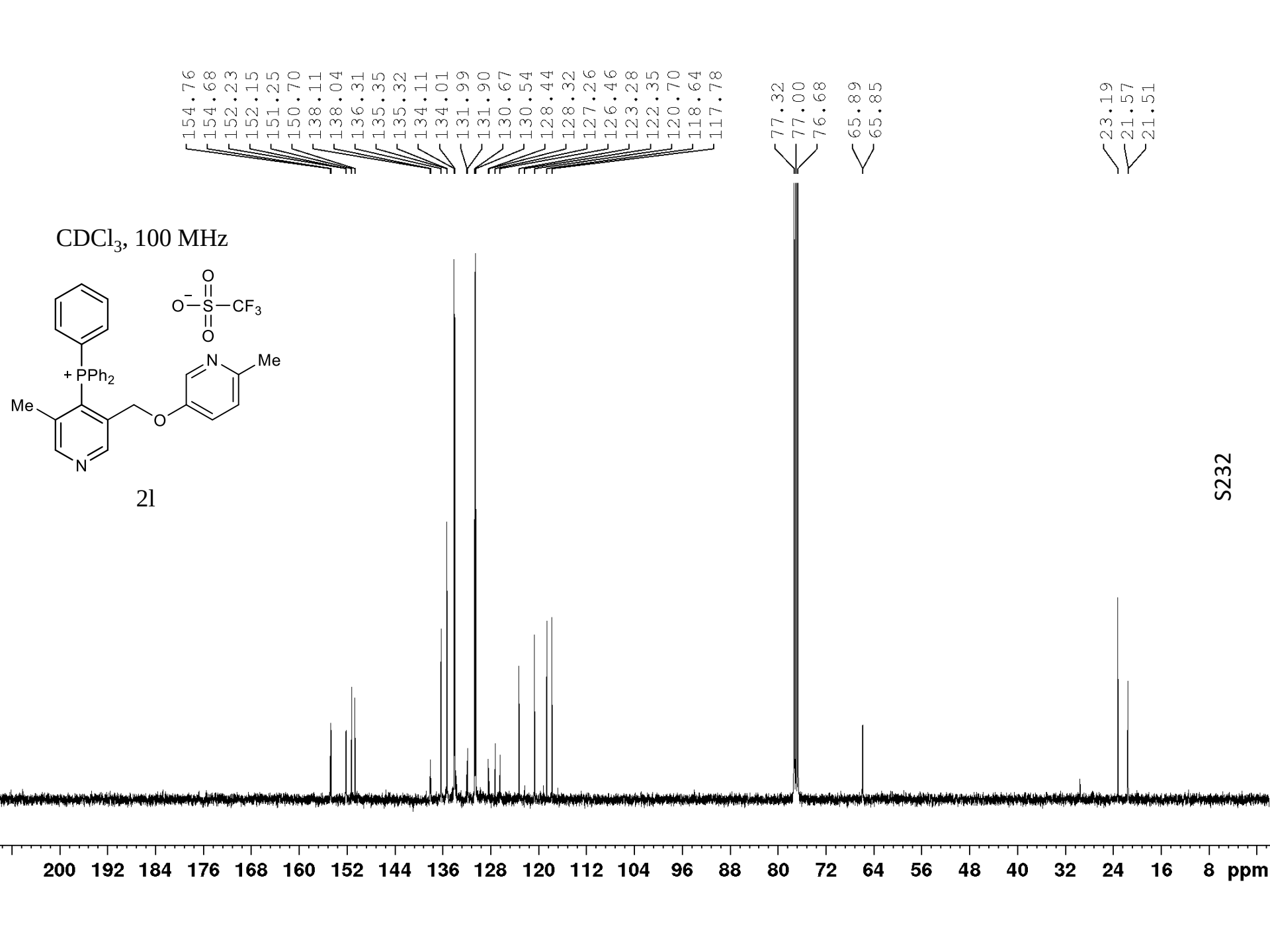
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)



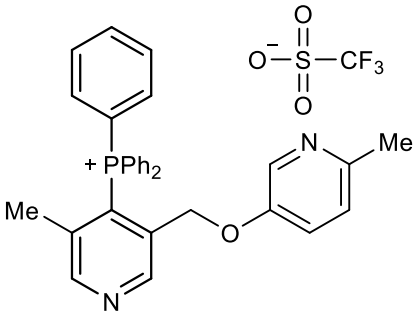
2l


8.85
8.83
8.75
8.73
7.86
7.84
7.82
7.80
7.77
7.75
7.75
7.73
7.65
7.64
7.63
7.61
7.60
7.44
7.43
6.90
6.88
6.51
6.50
6.48
6.48
4.53
2.42
1.85
CDCl3, 400 MHz
2l
S230
0.74
0.81
15.00
1.03
0.76
0.78
1.50
2.51
2.42
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
ppm


8.87
8.86
8.77
8.76
7.02
7.00
6.93
6.91
6.54
6.53
6.52
6.51
CDCl3, 400 MHz
(crude 1H NMR)
2l
Major
Minor
0.037
0.534
7.2
7.0
6.8
ppm
S231
0.54
0.04
0.53
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
0.5
ppm

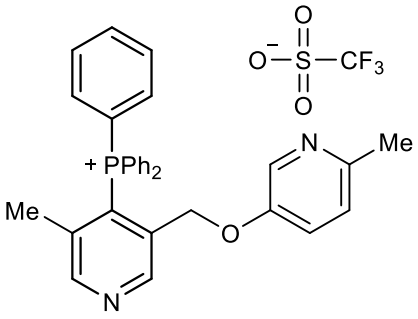

154.76
154.68
152.23
152.15
151.25
150.70
138.11
138.04
136.31
135.35
135.32
134.11
134.01
131.99
131.90
130.67
130.54
128.44
128.32
127.26
126.46
123.28
122.35
120.70
118.64
117.78
77.32
77.00
76.68
65.89
65.85
23.19
21.57
21.51
CDCl3, 100 MHz
2l
S232
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



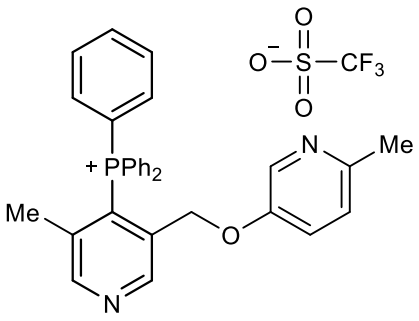
2l

$CDCl_3$, 162 MHz

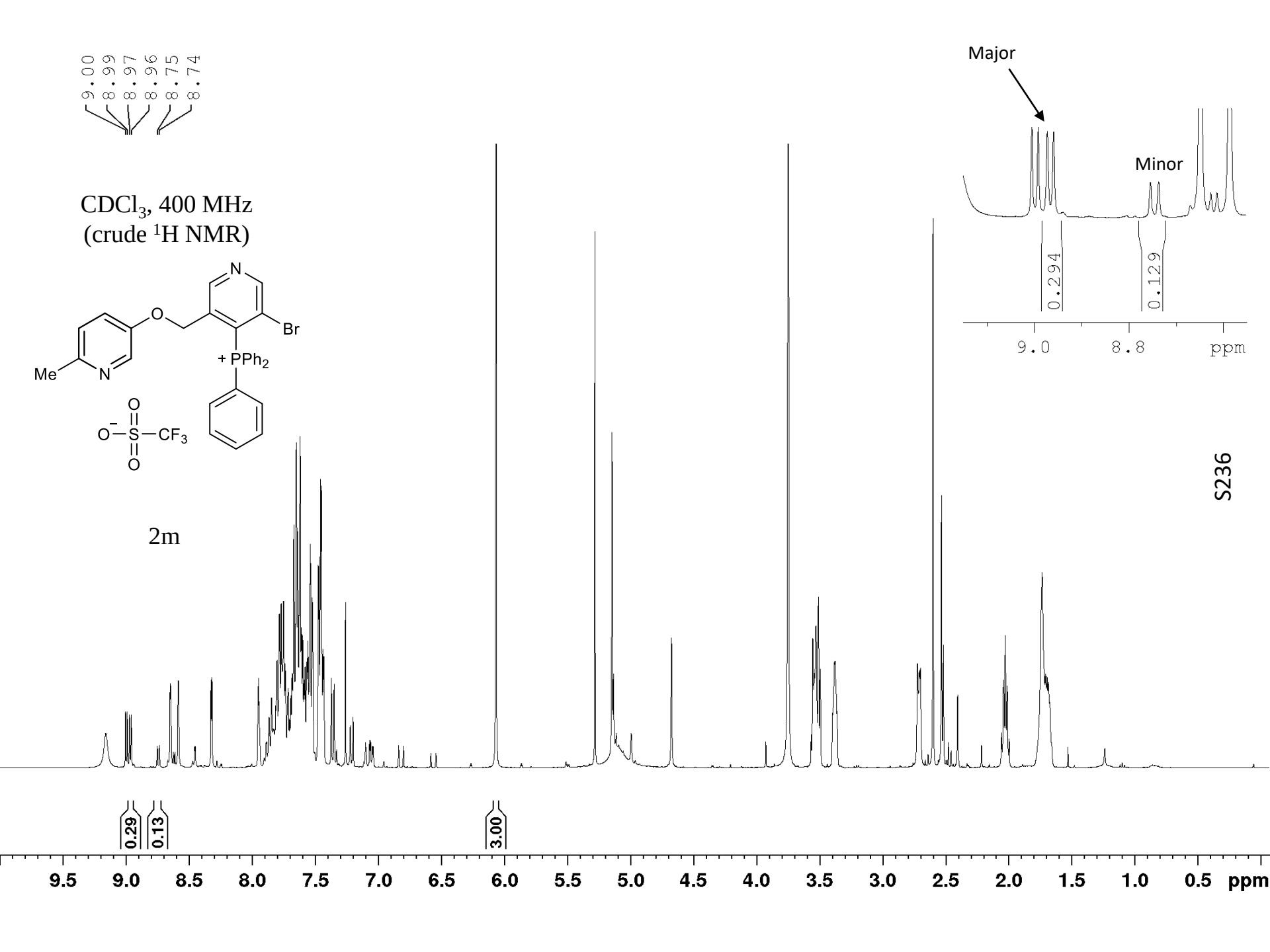


2l

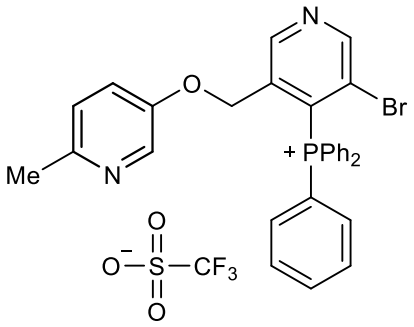
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)



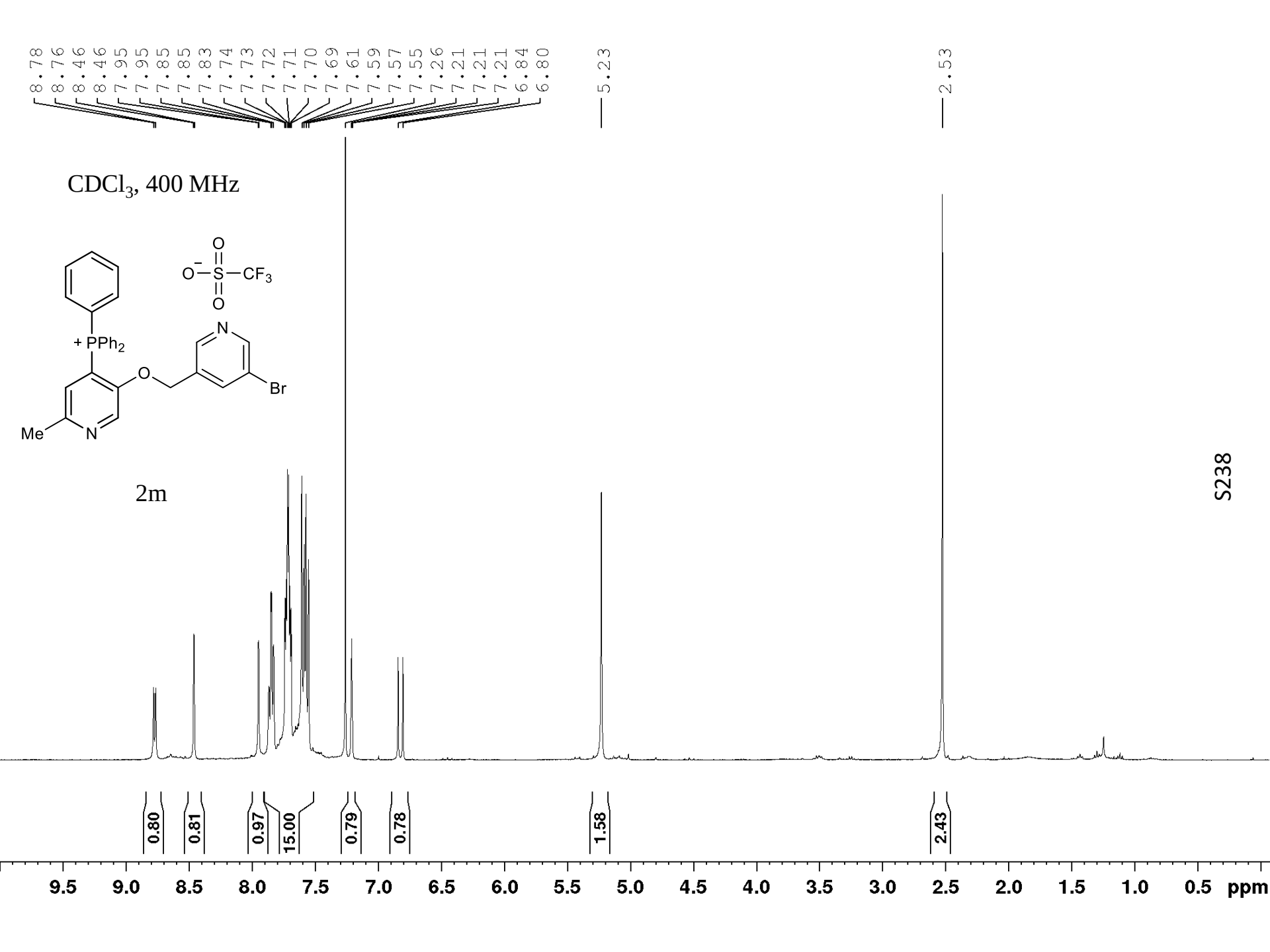
2l


9.00
8.99
8.97
8.96
8.75
8.74
CDCl3, 400 MHz
(crude 1H NMR)
Me
N
O
Br
+ PPh2
O
O
S
CF3
2m
Major
Minor
0.294
0.129
9.0
8.8
ppm
S236
0.29
0.13
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
0.5
ppm

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

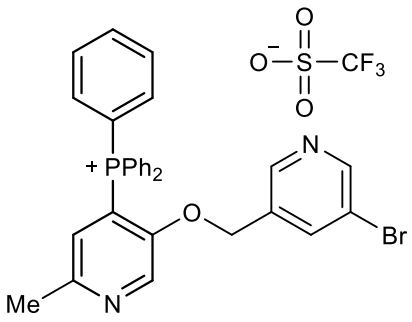


2m


8.78
8.76
8.46
8.46
7.95
7.95
7.85
7.85
7.83
7.74
7.73
7.72
7.71
7.70
7.69
7.61
7.59
7.57
7.55
7.26
7.21
7.21
7.21
6.84
6.80
5.23
2.53
CDCl3, 400 MHz
+ PPh2
O
O
S
CF3
O
O
N
O
Br
Me
N
2m
S238
0.80
0.81
0.97
15.00
0.79
0.78
1.58
2.43
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
ppm

153.26
153.15
152.42
150.48
146.99
138.02
136.26
136.21
135.43
135.40
133.68
133.57
131.30
130.54
130.41
126.96
126.89
122.19
120.05
119.00
116.54
115.64
115.43
114.58
77.32
76.68
68.35
23.57

$CDCl_3$, 100 MHz

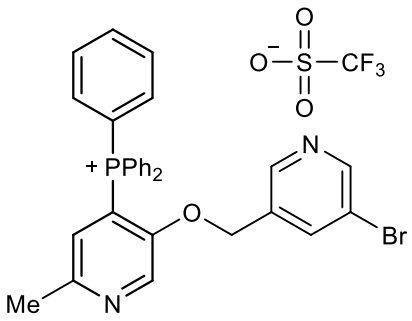


2m

S239

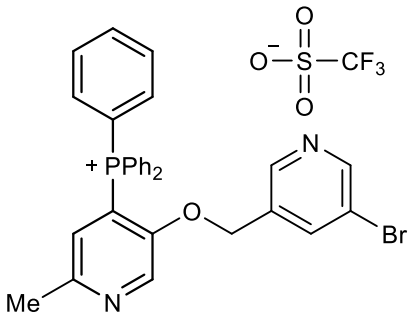
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



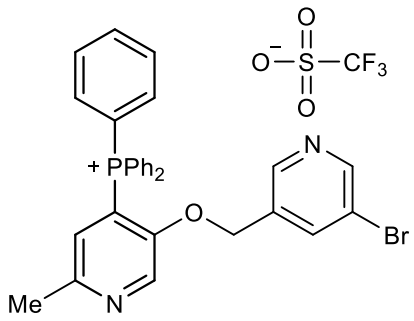
2m

$CDCl_3$, 162 MHz

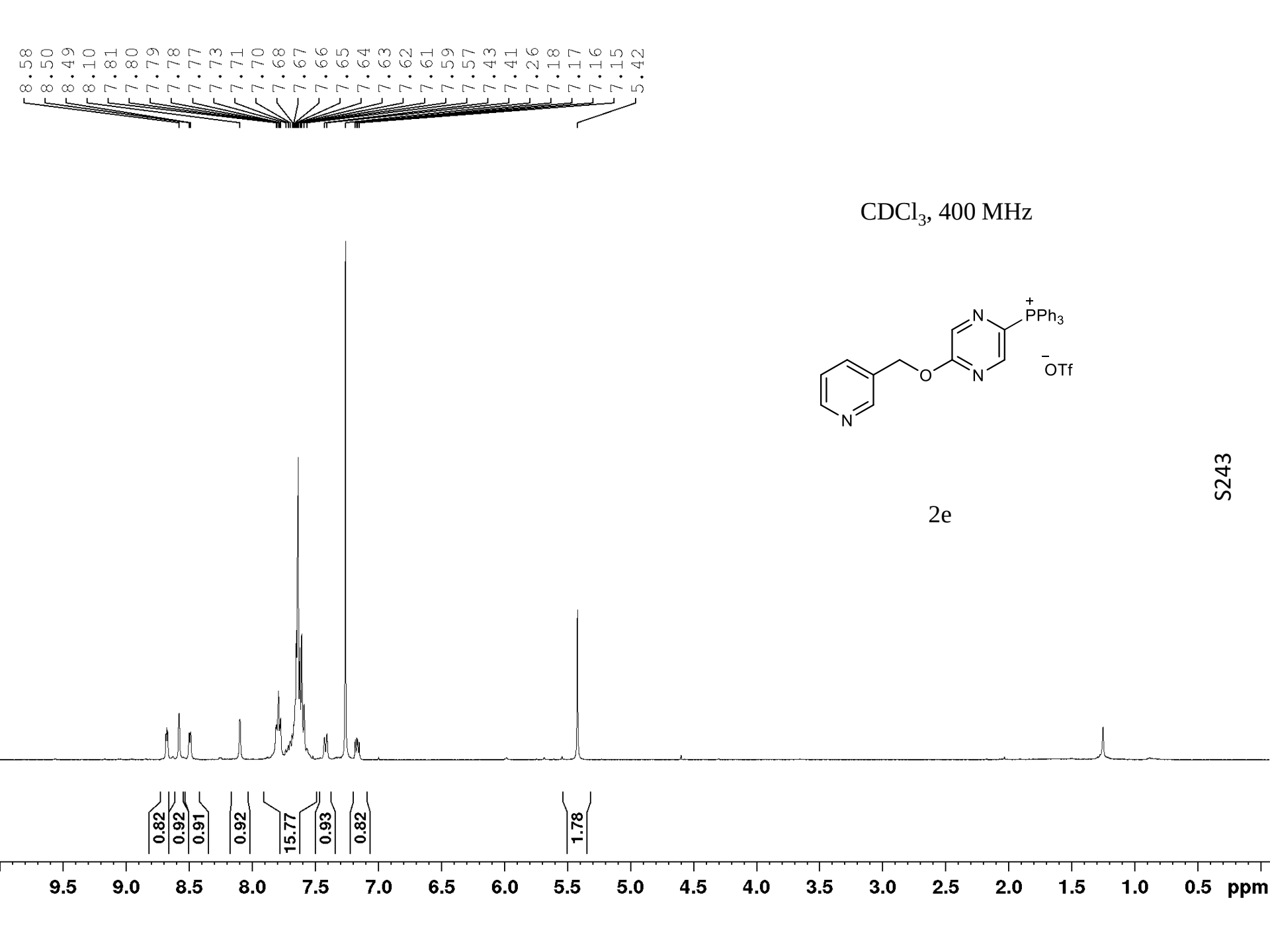


2m

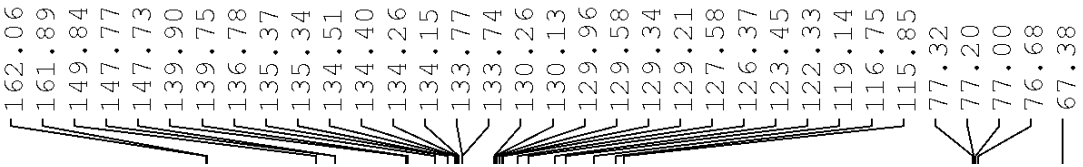
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)



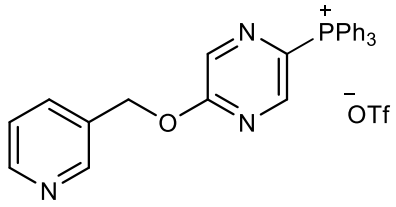
2m


8.58
8.50
8.49
8.10
7.81
7.80
7.79
7.78
7.77
7.73
7.71
7.70
7.68
7.67
7.66
7.65
7.64
7.63
7.62
7.61
7.59
7.57
7.43
7.41
7.26
7.18
7.17
7.16
7.15
5.42
CDCl3, 400 MHz
PPh3
OTf
N
O
0.82
0.92
0.91
0.92
15.77
0.93
0.82
1.78
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
ppm

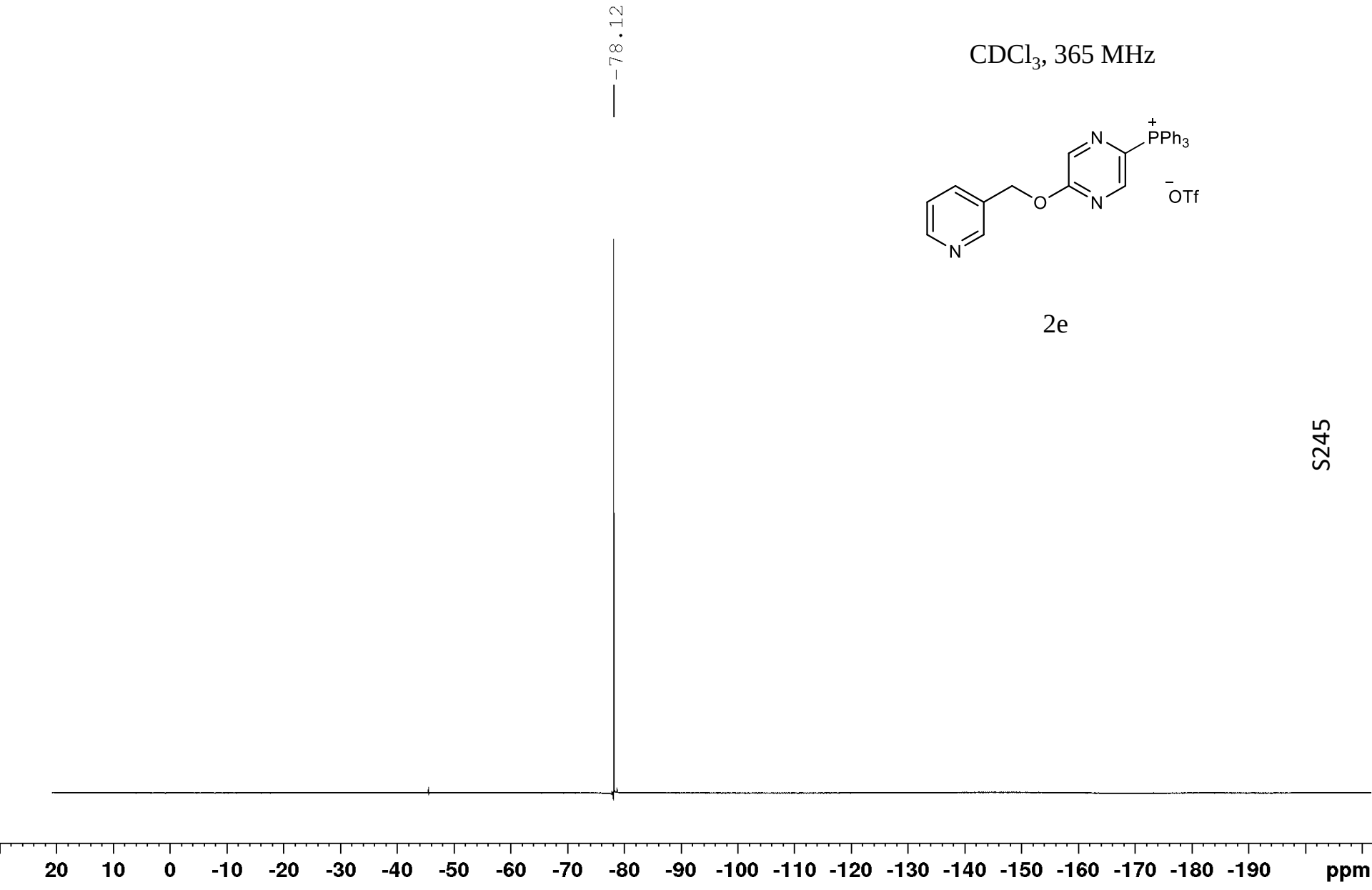
2e



$CDCl_3$, 100 MHz

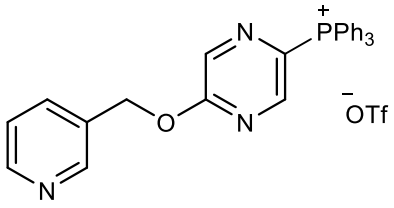


2e

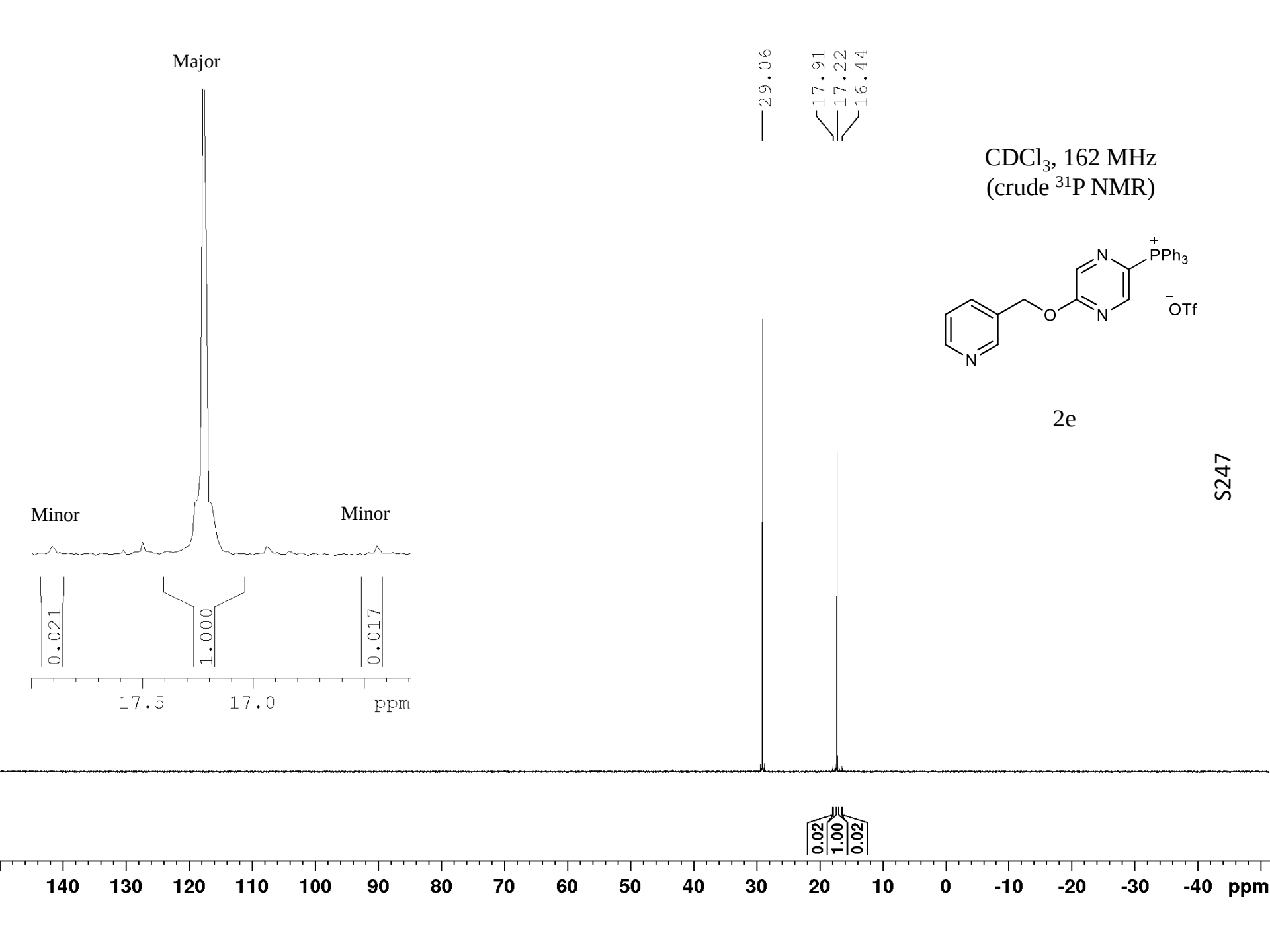

-78.12
CDCl3, 365 MHz
PPh3
OTf
N
O
N
N
2e
S245
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

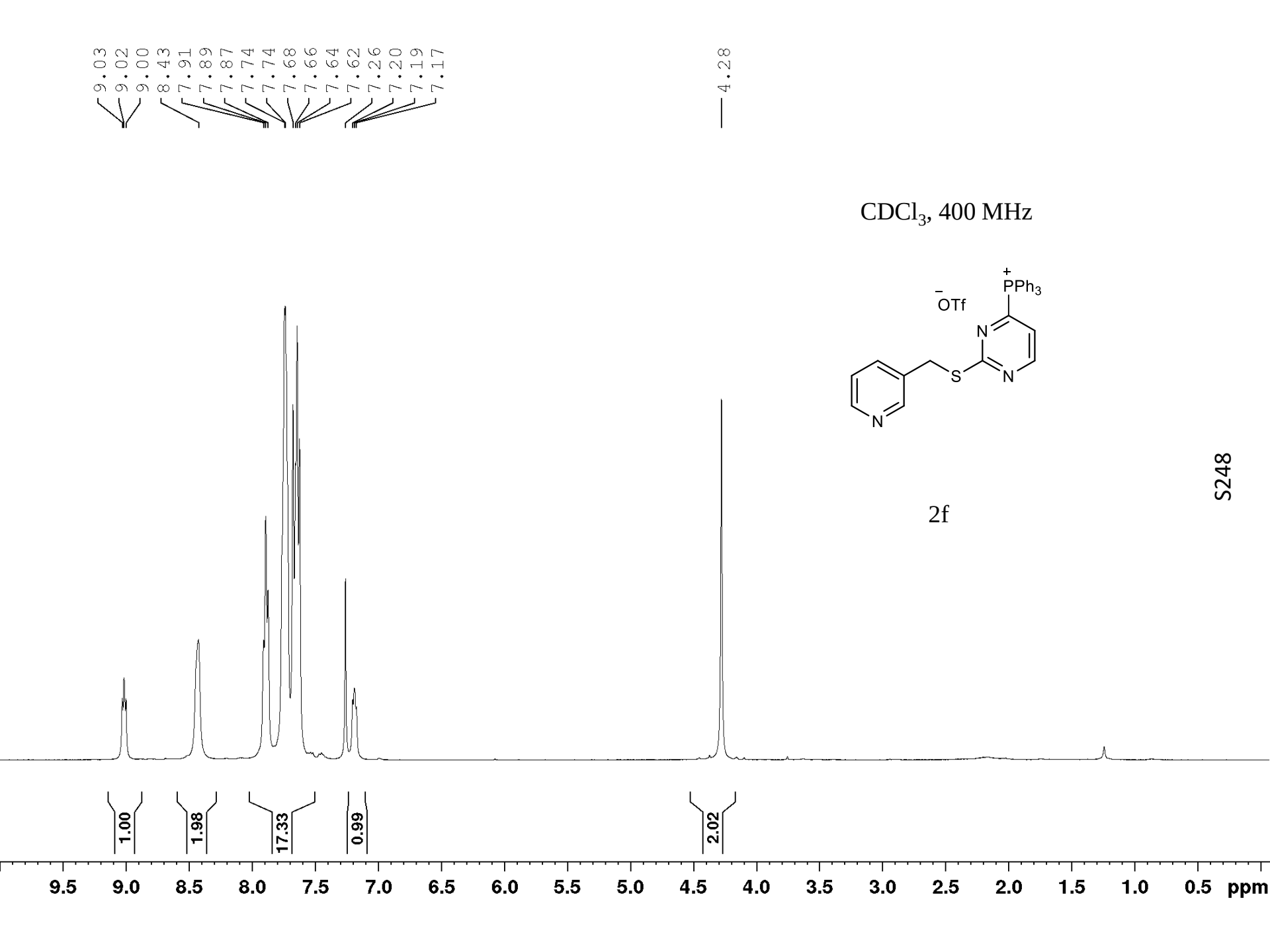
19.43
17.19
16.74

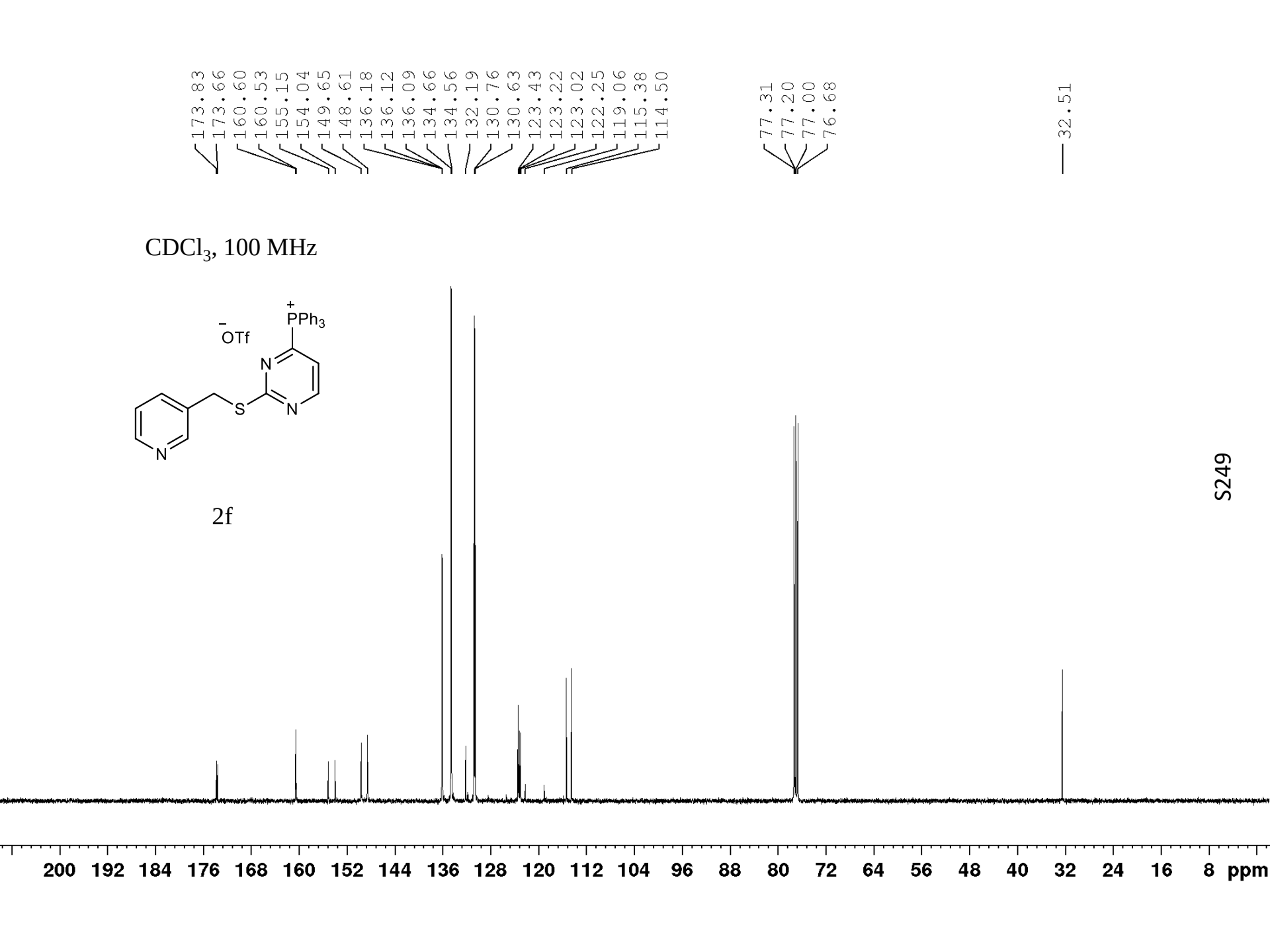
$CDCl_3$, 162 MHz

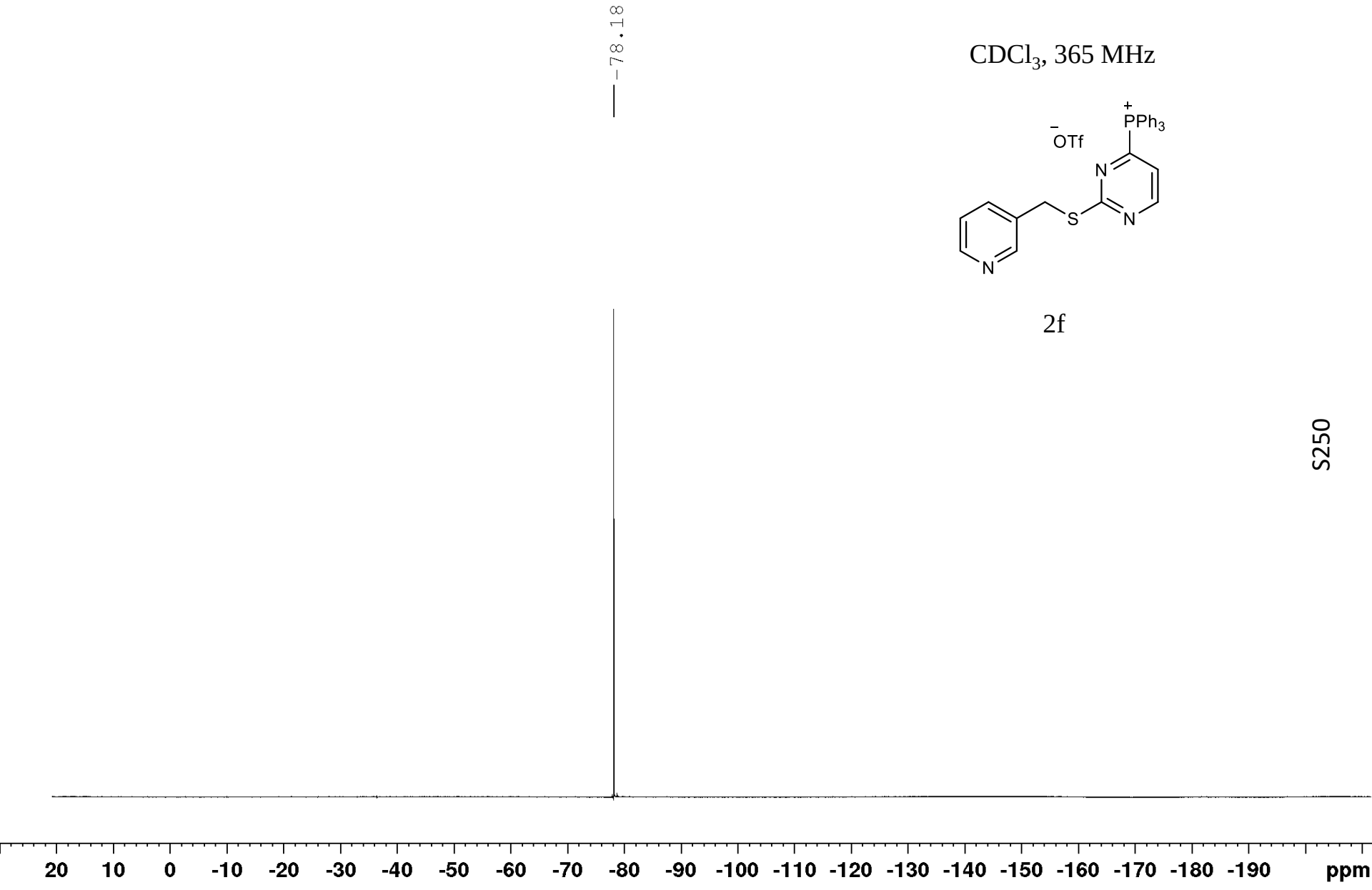


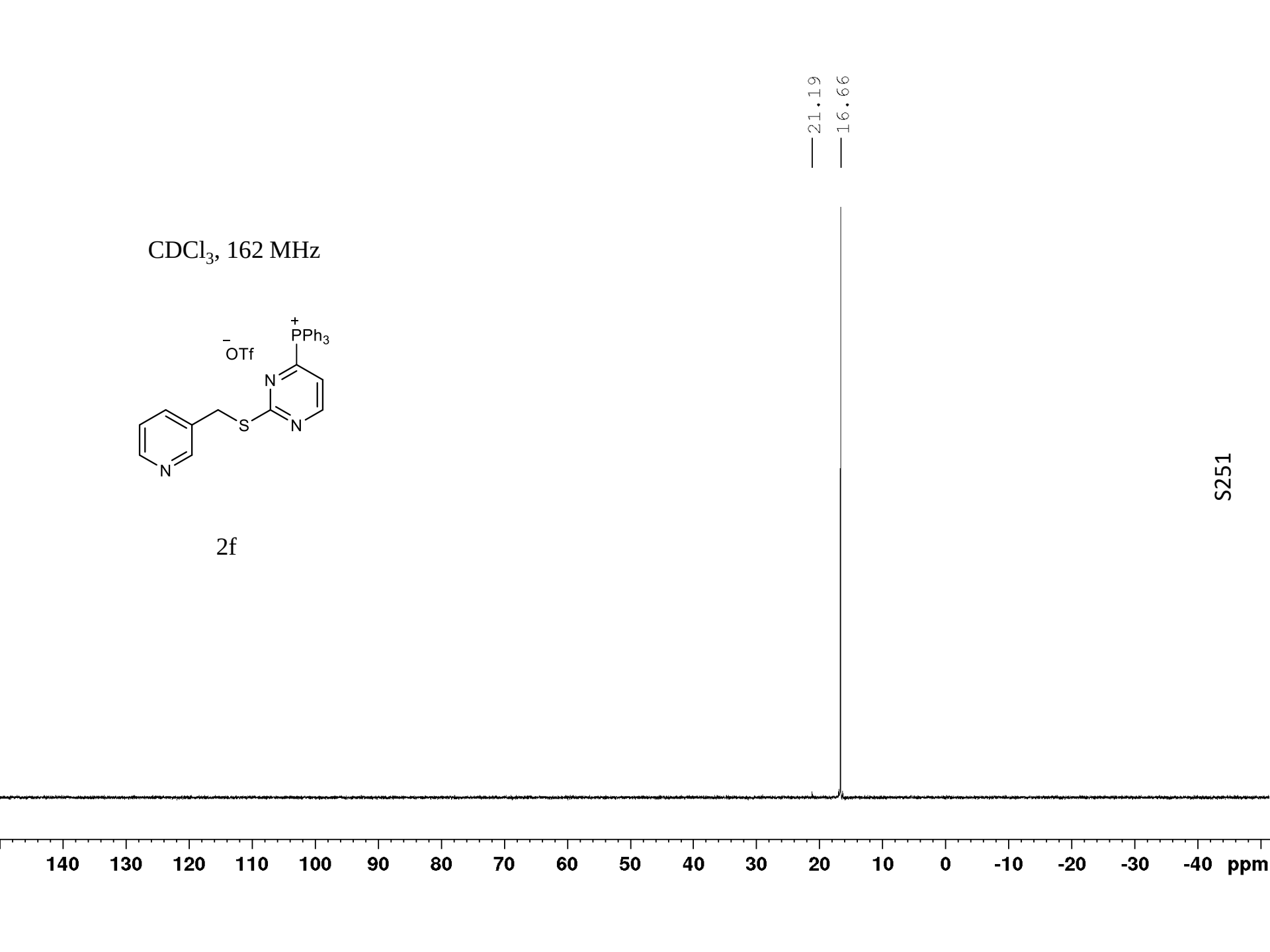
2e

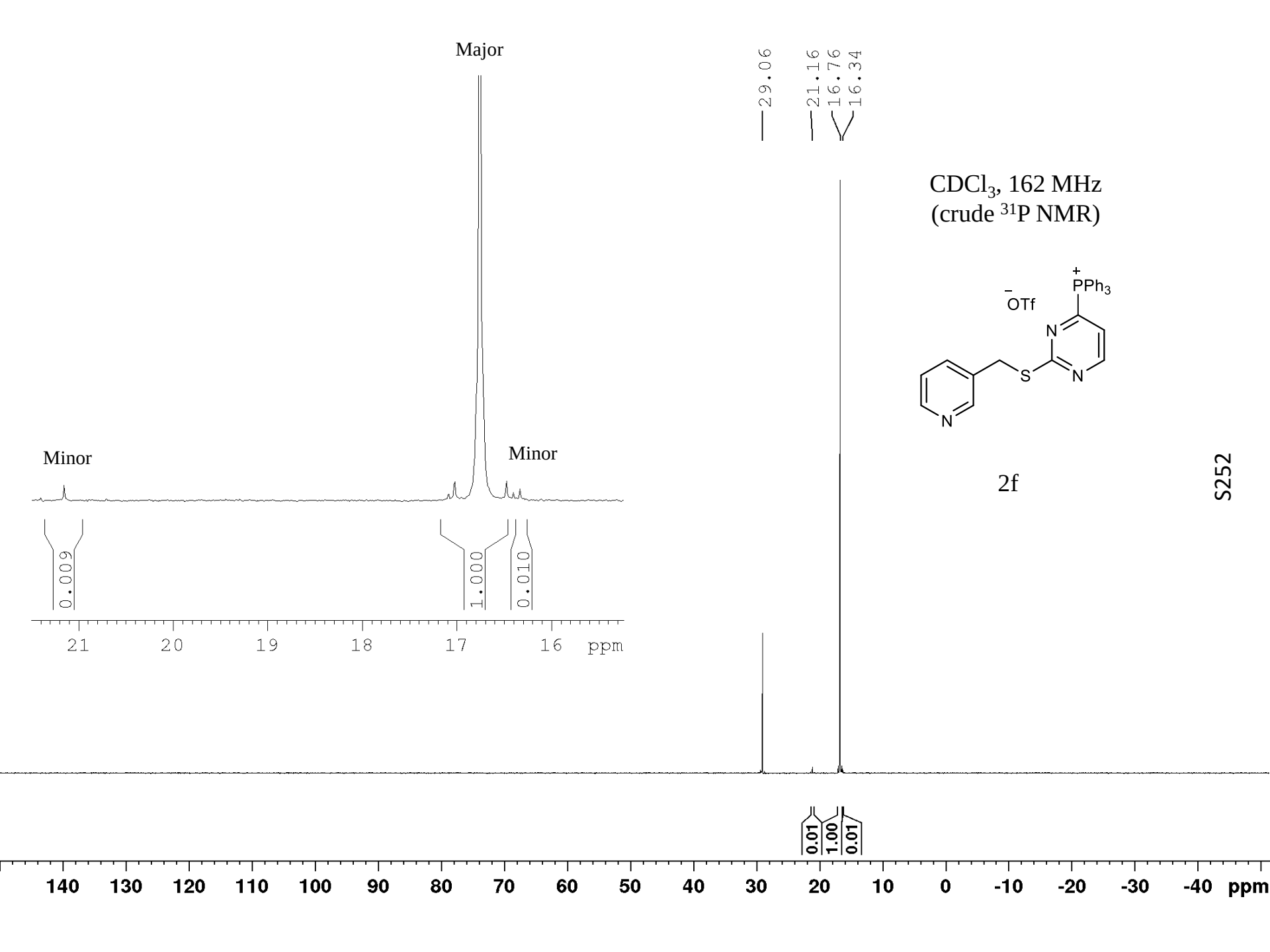

Major
Minor
Minor
29.06
17.91
17.22
16.44
0.021
1.000
0.017
17.5
17.0
ppm
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
OTf
2e
S247
0.02
1.00
0.02
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

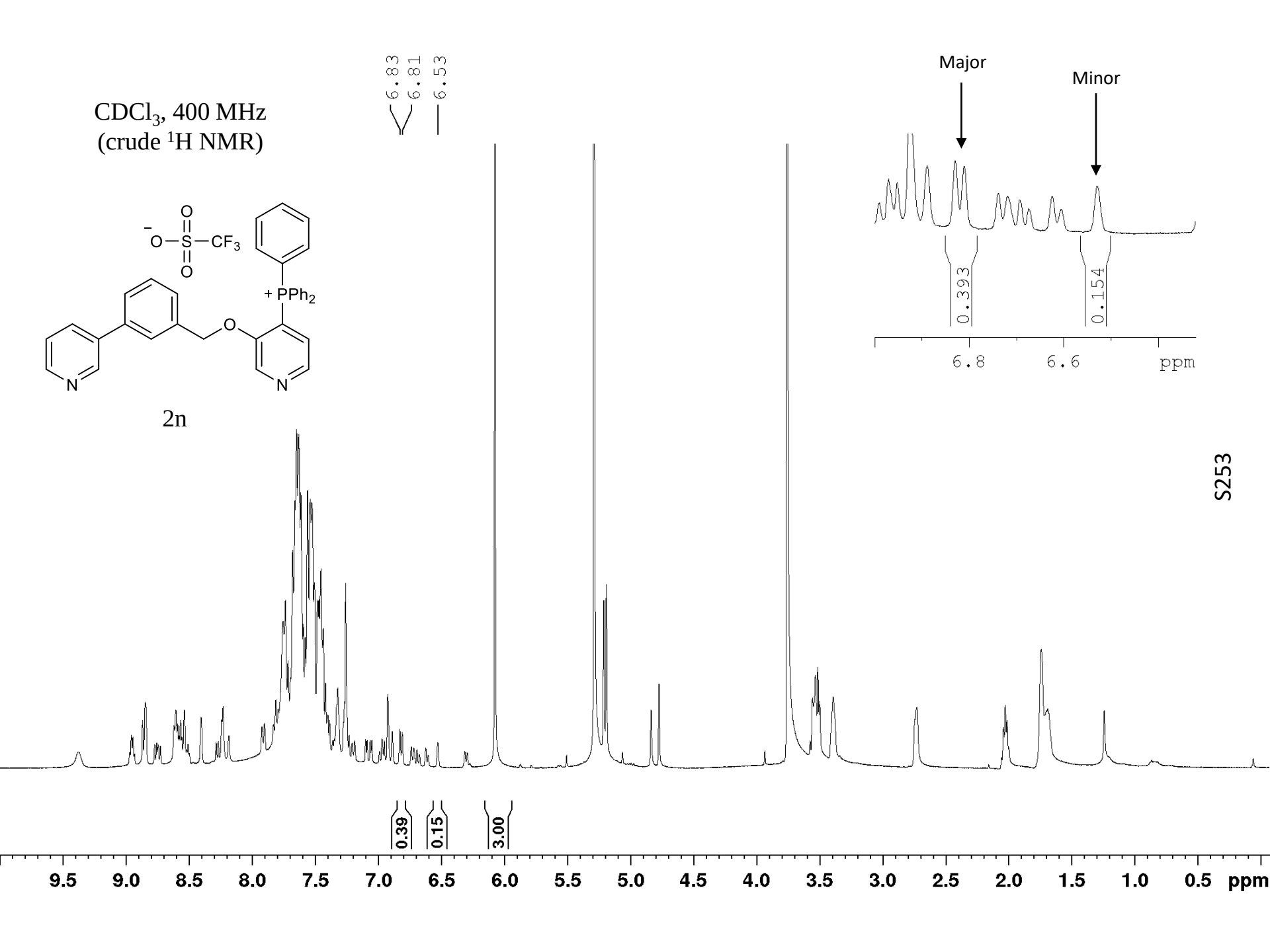

9.03
9.02
9.00
8.43
7.91
7.89
7.87
7.74
7.74
7.68
7.66
7.64
7.62
7.26
7.20
7.19
7.17
4.28
CDCl3, 400 MHz
PPh3
OTf
N
S
N
N
2f
S248
1.00
1.98
17.33
0.99
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


173.83
173.66
160.60
160.53
155.15
154.04
149.65
148.61
136.18
136.12
136.09
134.66
134.56
132.19
130.76
130.63
123.43
123.22
123.02
122.25
119.06
115.38
114.50
77.31
77.20
77.00
76.68
32.51
CDCl3, 100 MHz
PPh3
OTf
N
S
N
N
2f
S249
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 ppm

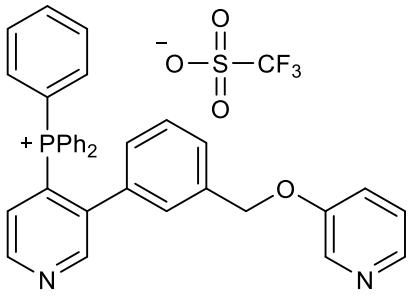

-78.18
CDCl3, 365 MHz
PPh3
OTf
N
S
N
N
2f
S250
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


21.19
16.66
CDCl3, 162 MHz
OTf
PPh3
N
S
N
N
2f
S251
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


Major
29.06
21.16
16.76
16.34
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
OTf
N
S
N
N
2f
Minor
Minor
0.009
1.000
0.010
21
20
19
18
17
16
ppm
0.01
1.00
0.01
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


CDCl3, 400 MHz
(crude 1H NMR)
6.83
6.81
6.53
Major
Minor
0.393
0.154
6.8
6.6
ppm
2n
S253
0.39
0.15
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
0.5
ppm

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

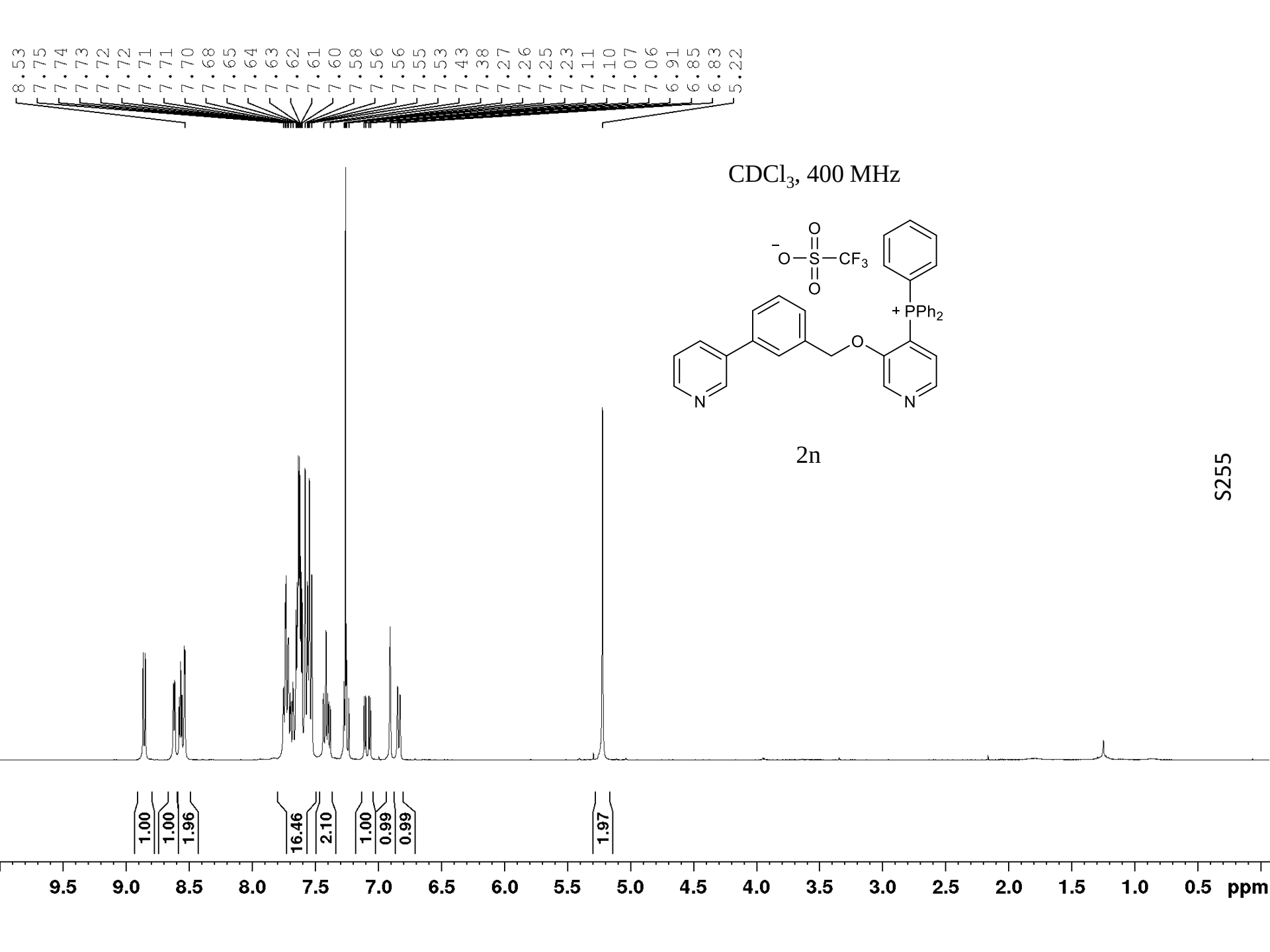


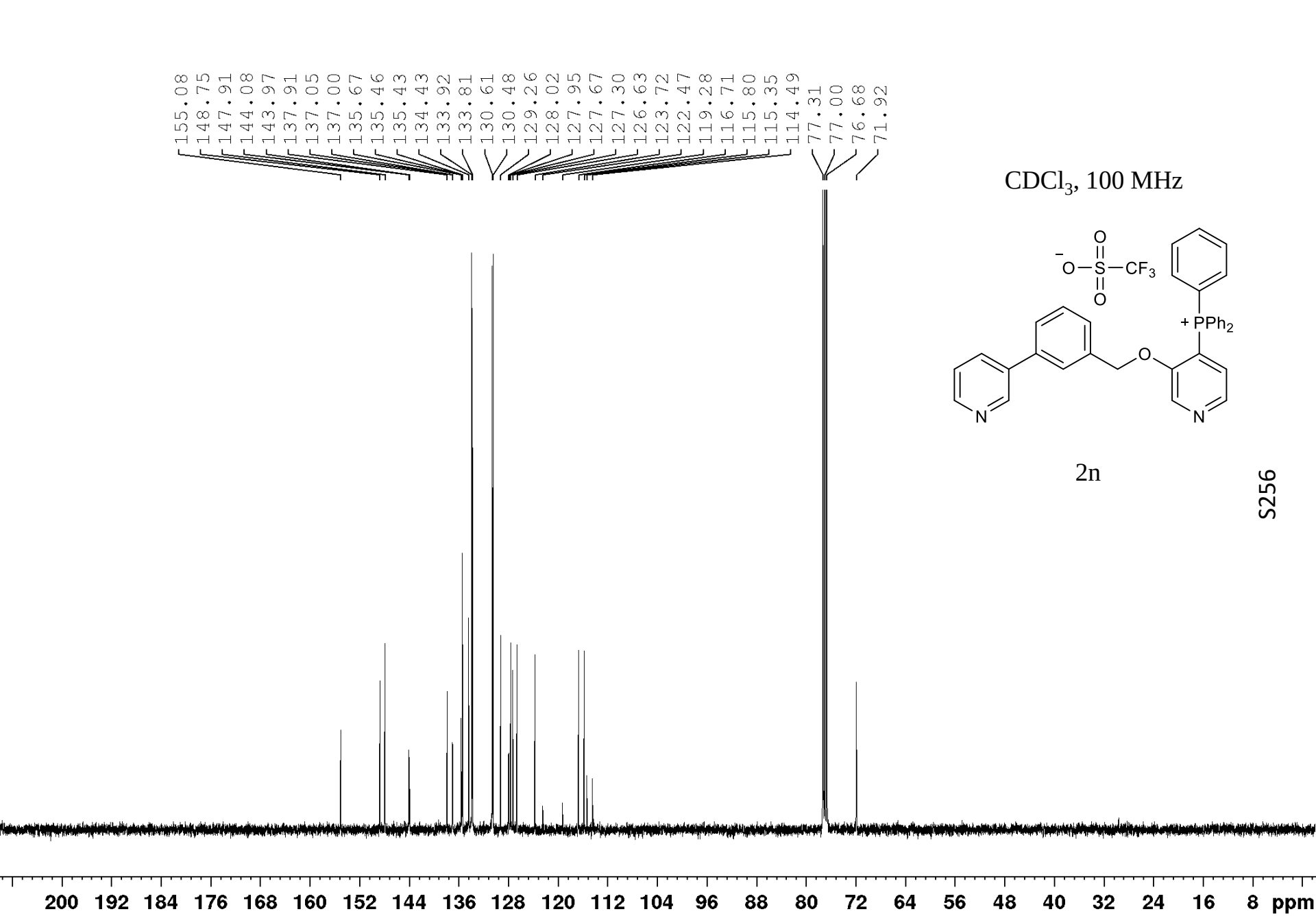
2n

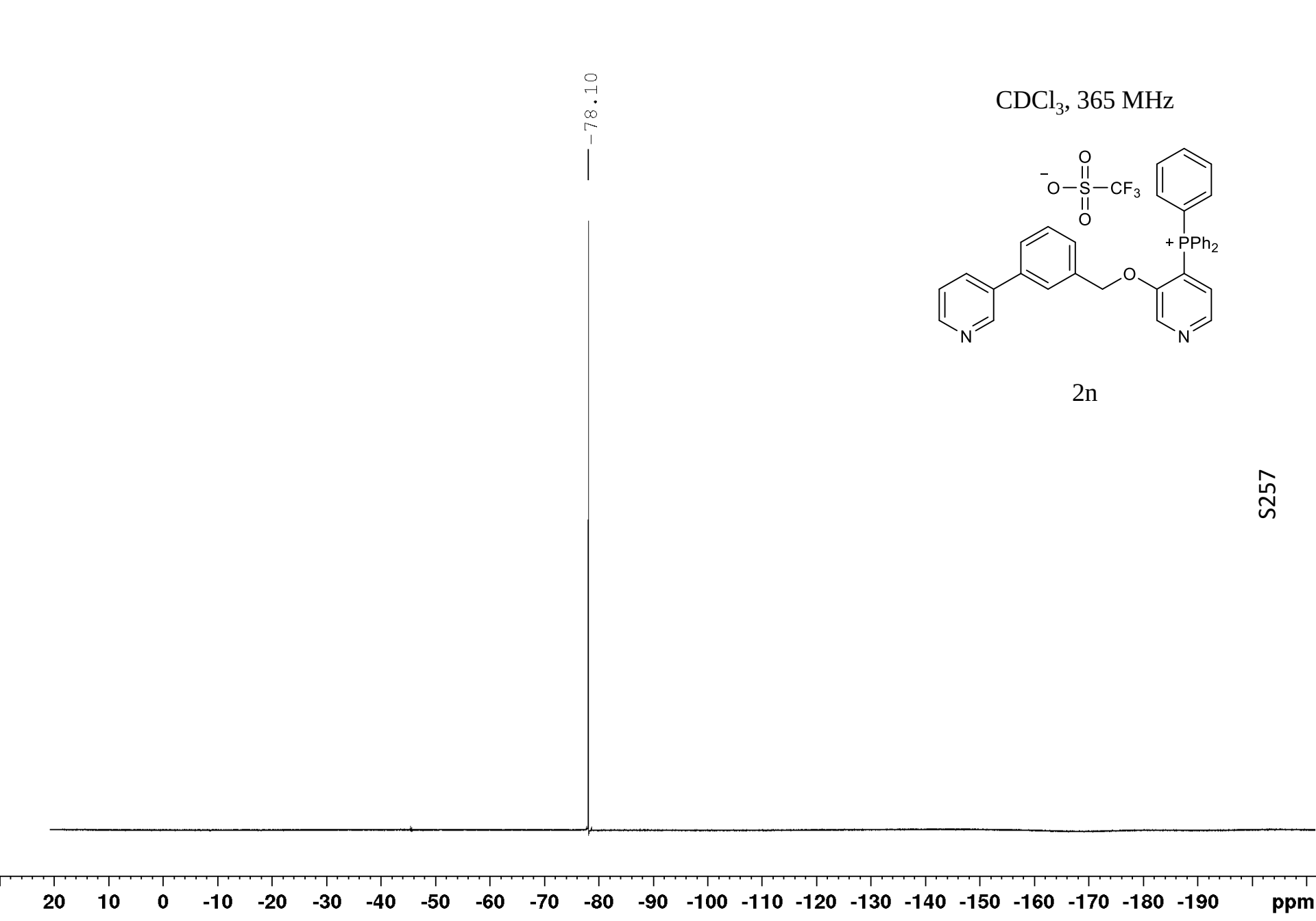
29.16
21.46
21.44
21.35

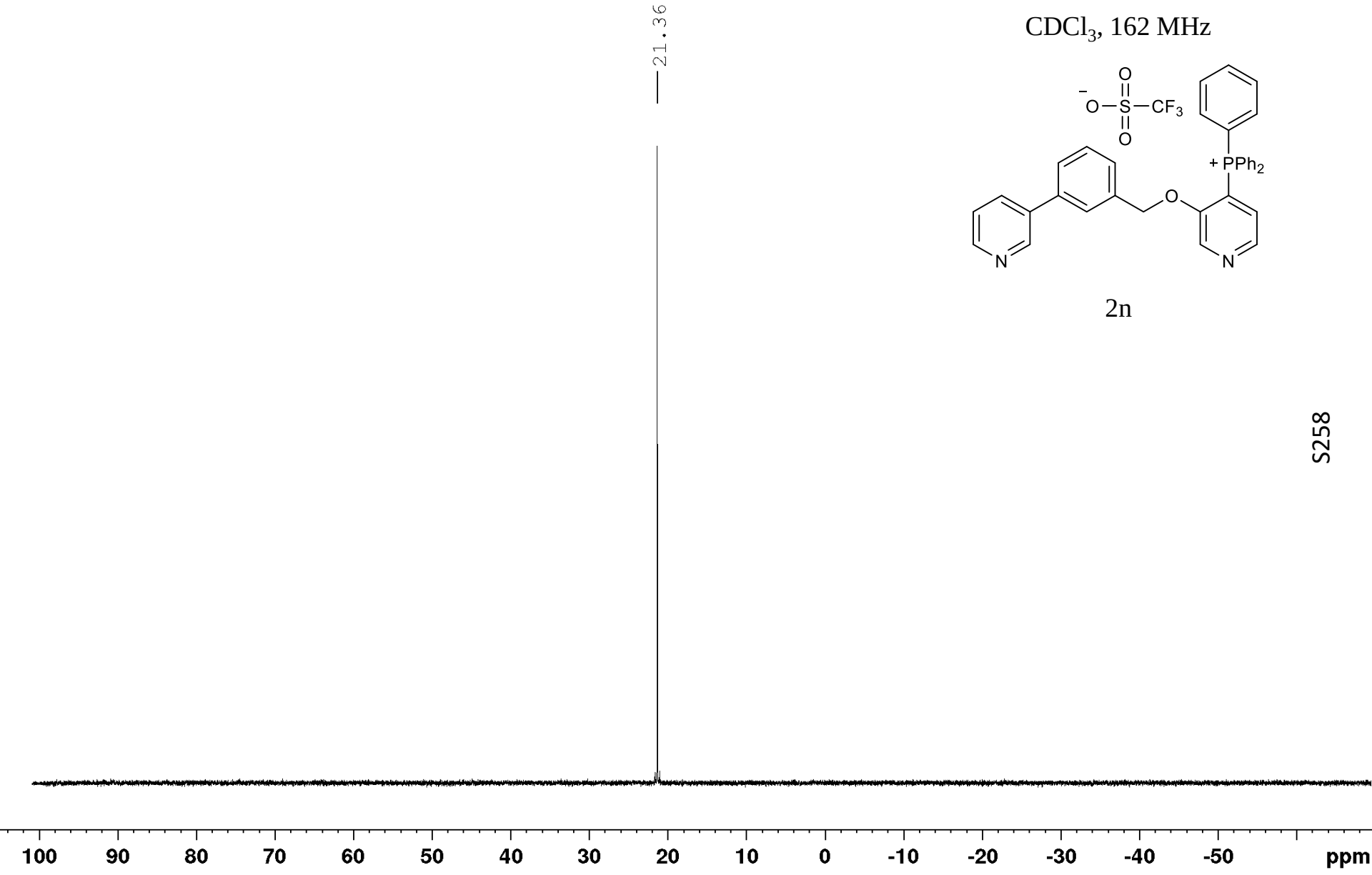
S254

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

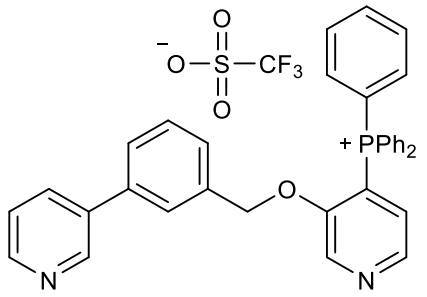

8.53
7.75
7.74
7.73
7.72
7.72
7.71
7.71
7.70
7.68
7.65
7.64
7.63
7.62
7.61
7.60
7.58
7.56
7.56
7.55
7.53
7.43
7.38
7.27
7.26
7.25
7.23
7.11
7.10
7.07
7.06
6.91
6.85
6.83
5.22
CDCl3, 400 MHz
2n
S255
1.00
1.00
1.96
16.46
2.10
1.00
0.99
0.99
1.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


155.08
148.75
147.91
144.08
143.97
137.91
137.05
137.00
135.67
135.46
135.43
134.43
133.92
133.81
130.61
130.48
129.26
128.02
127.95
127.67
127.30
126.63
123.72
122.47
119.28
116.71
115.80
115.35
114.49
77.31
77.00
76.68
71.92
CDCl3, 100 MHz
2n
S256
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 ppm

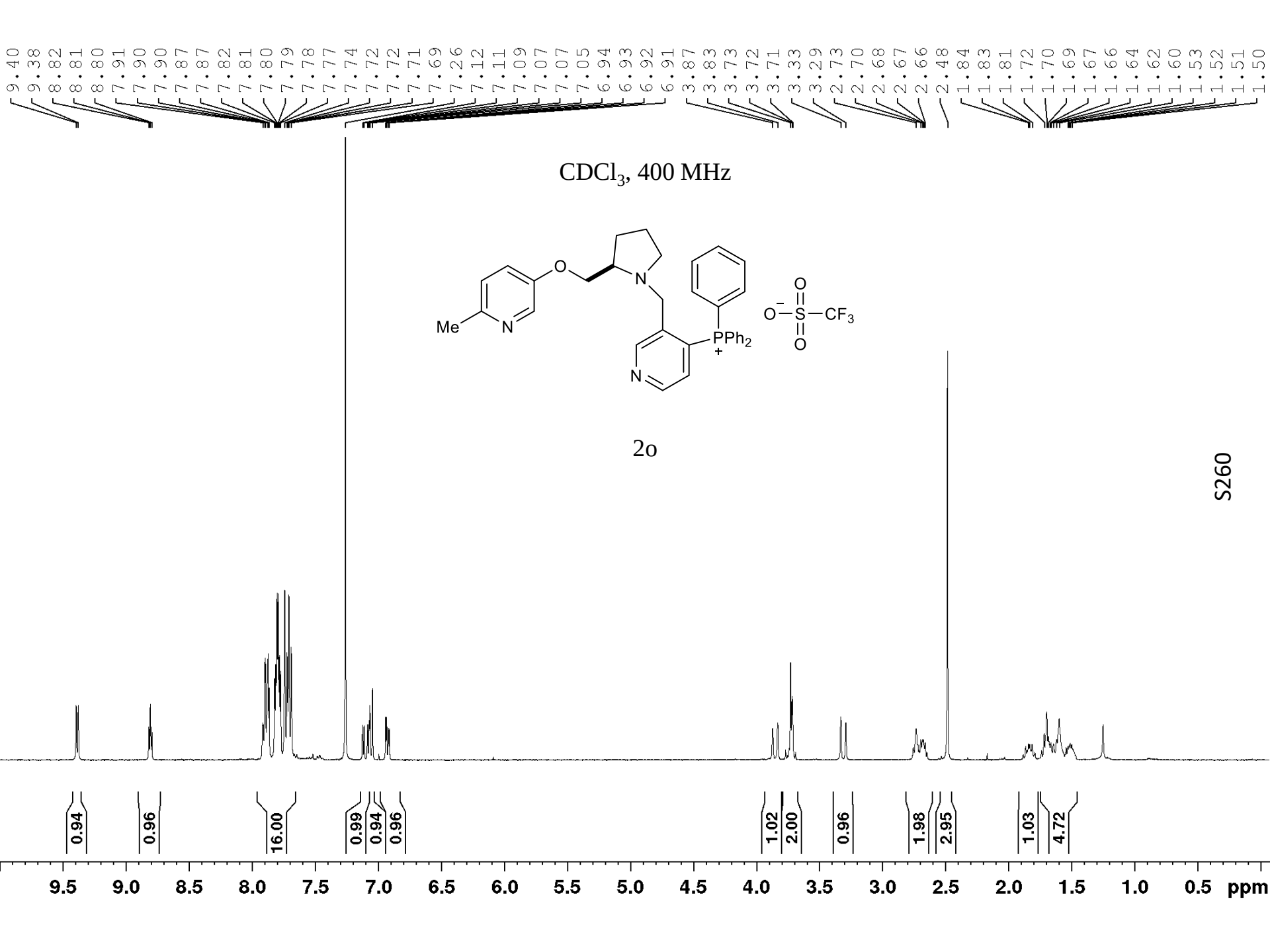

-78.10
CDCl3, 365 MHz
+ PPh2
2n
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

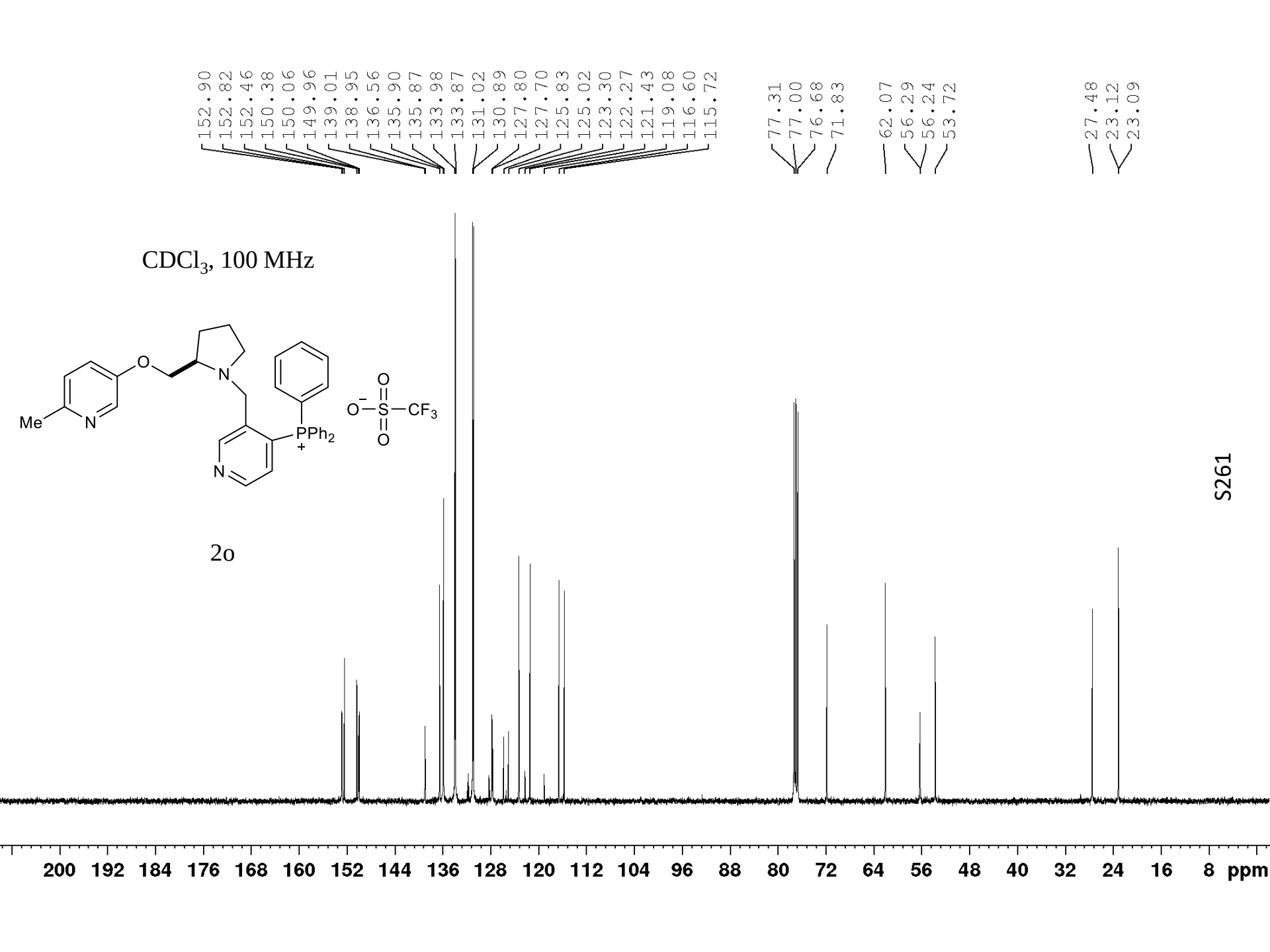

21.36
CDCl3, 162 MHz
2n
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

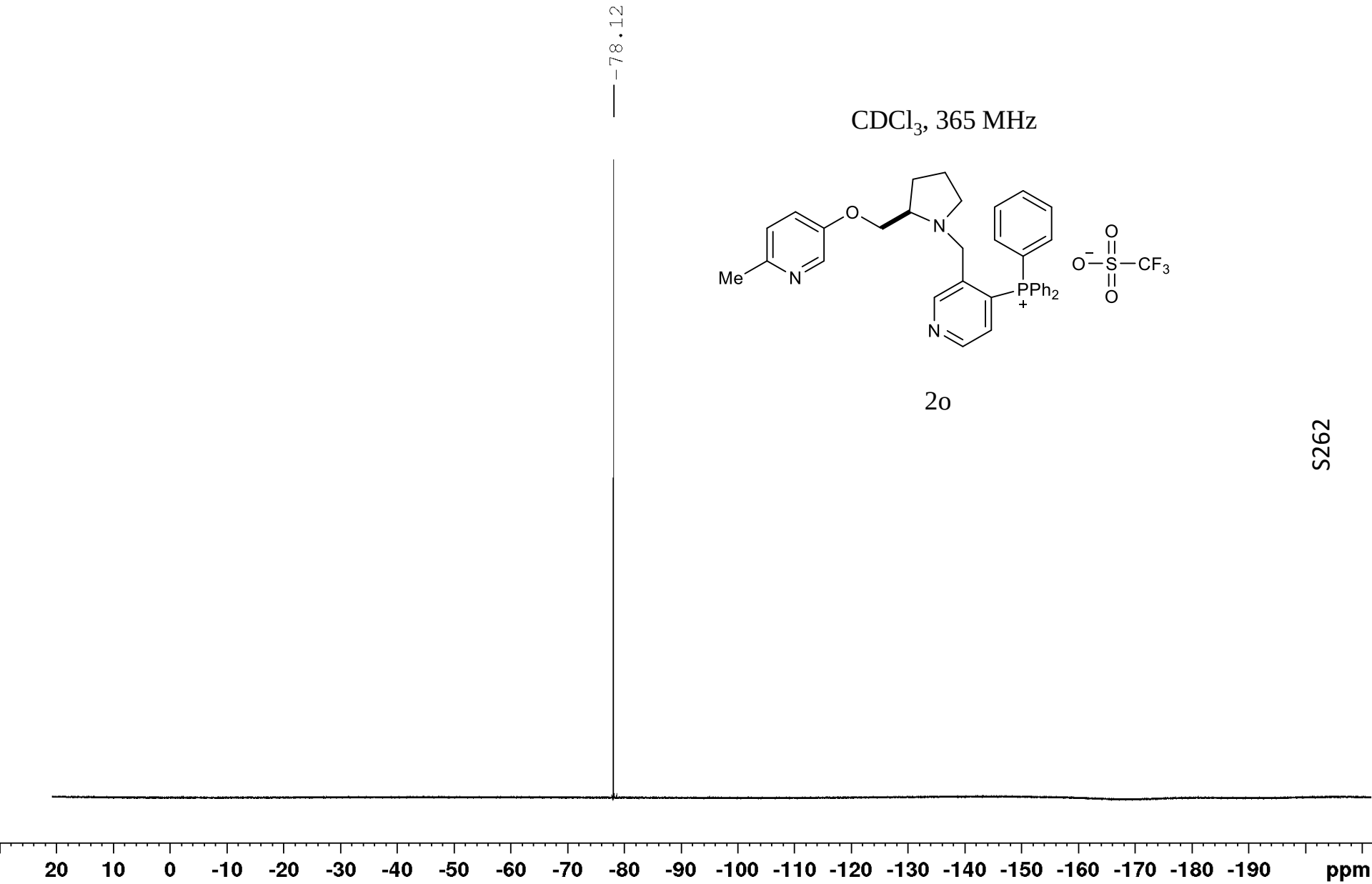
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

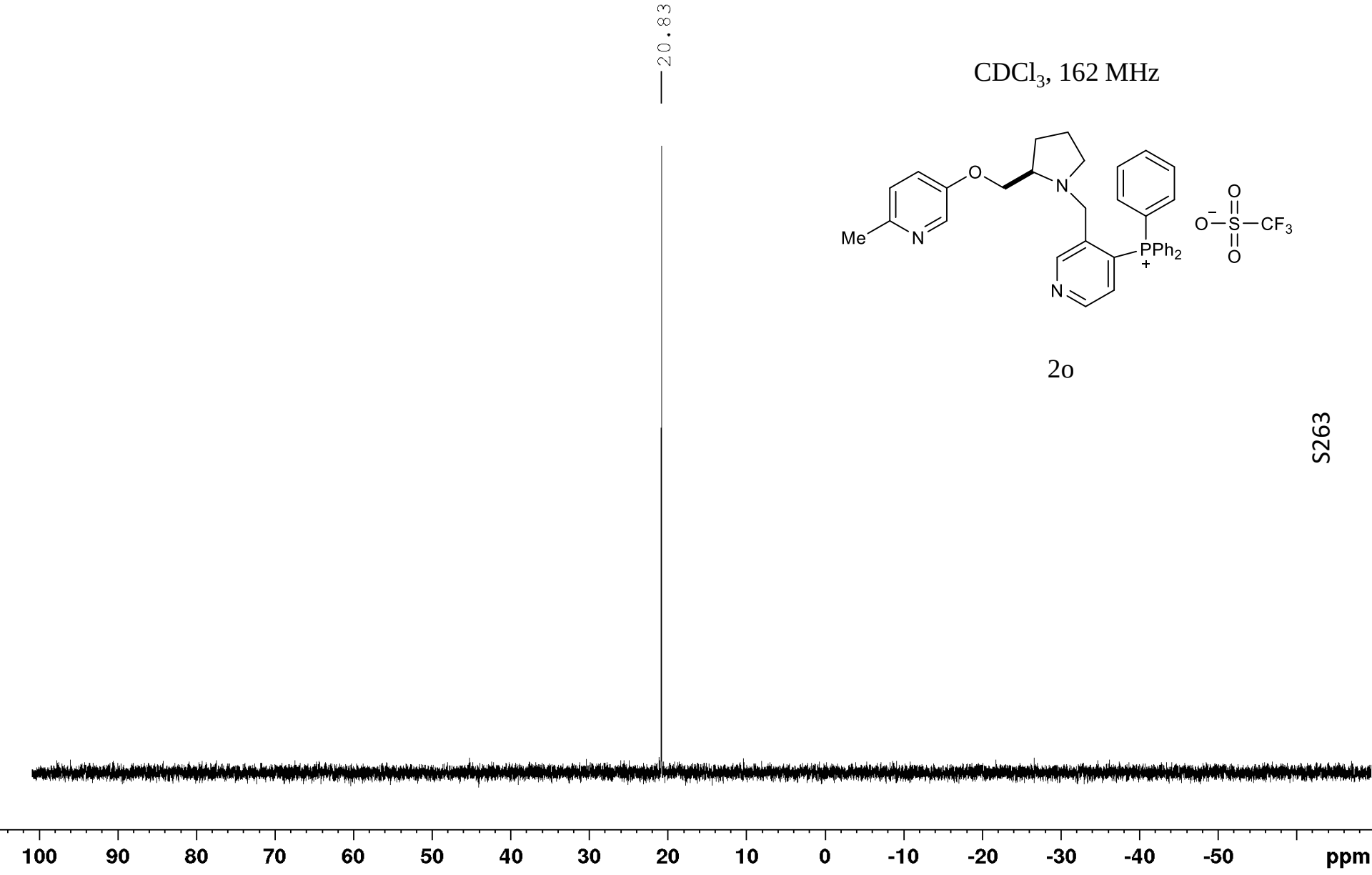


2n

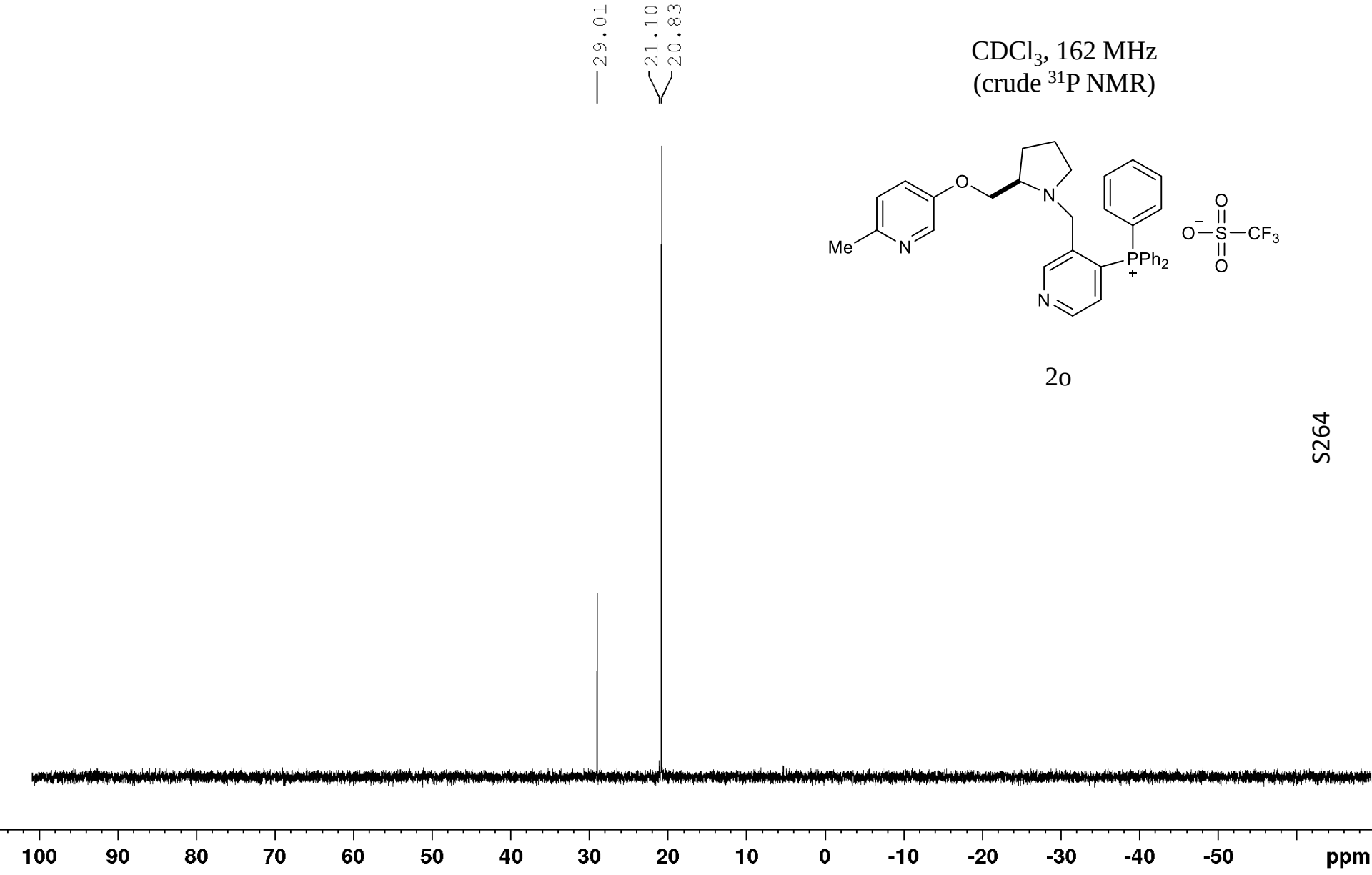

9.40 9.38 8.82 8.81 8.80 7.91 7.90 7.90 7.87 7.87 7.82 7.81 7.80 7.79 7.78 7.77 7.74 7.72 7.72 7.71 7.69 7.26 7.12 7.11 7.09 7.07 7.07 7.05 6.94 6.93 6.92 6.91 3.87 3.83 3.73 3.72 3.71 3.33 3.29 2.73 2.70 2.68 2.67 2.66 2.48 1.84 1.83 1.81 1.72 1.70 1.69 1.67 1.66 1.64 1.62 1.60 1.53 1.52 1.51 1.50
CDCl3, 400 MHz
Me
N
O
N
PPh2
+
N
O
O
S
CF3
O
2o
S260
0.94
0.96
16.00
0.99
0.94
0.96
1.02
2.00
0.96
1.98
2.95
1.03
4.72
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 ppm

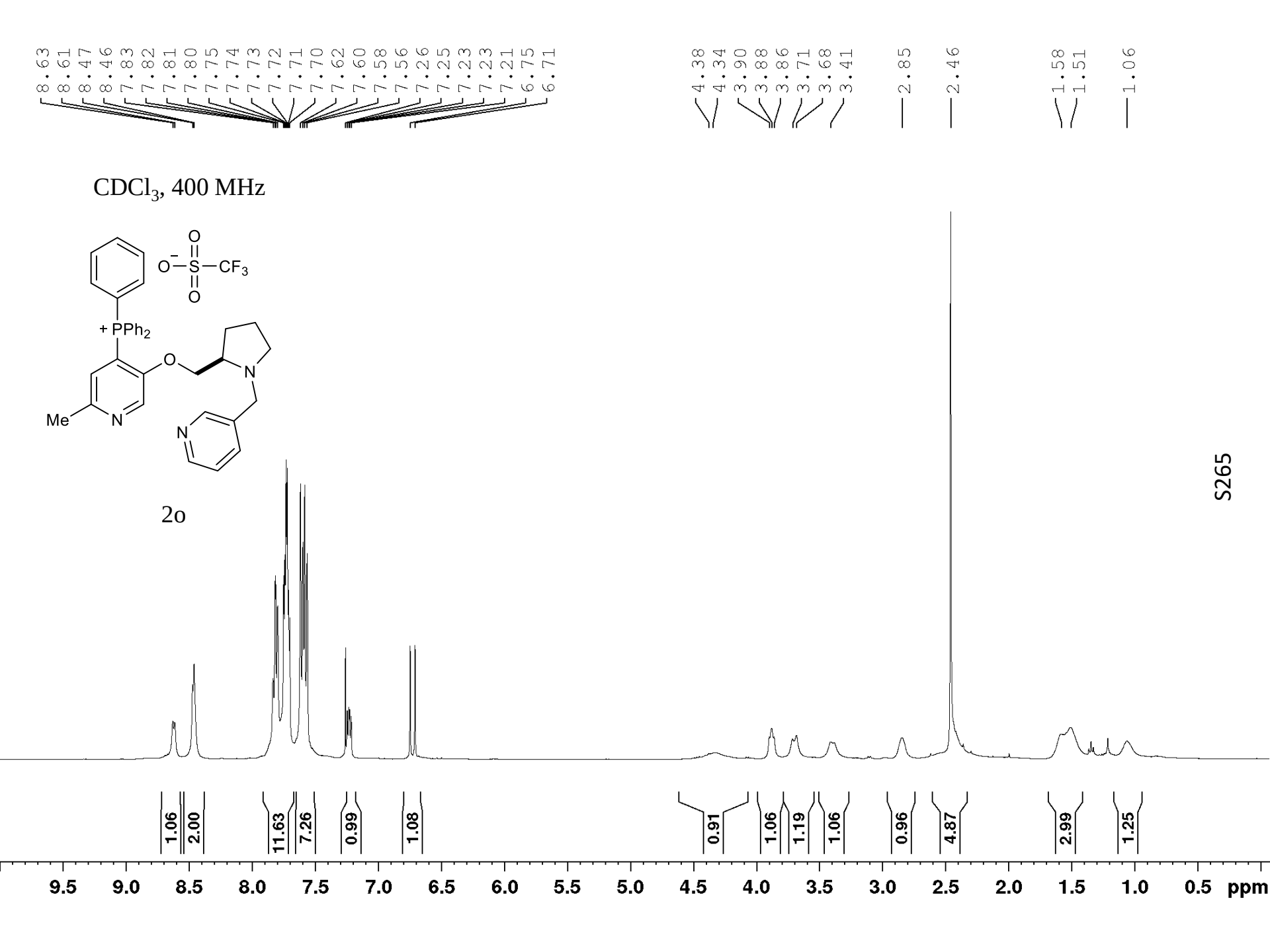

152.90
152.82
152.46
150.38
150.06
149.96
139.01
138.95
136.56
135.90
135.87
133.98
133.87
131.02
130.89
127.80
127.70
125.83
125.02
123.30
122.27
121.43
119.08
116.60
115.72
77.31
77.00
76.68
71.83
62.07
56.29
56.24
53.72
27.48
23.12
23.09
CDCl3, 100 MHz
Me
N
O
N
PPh2
+
N
O
O
S
CF3
O
2o
S261
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

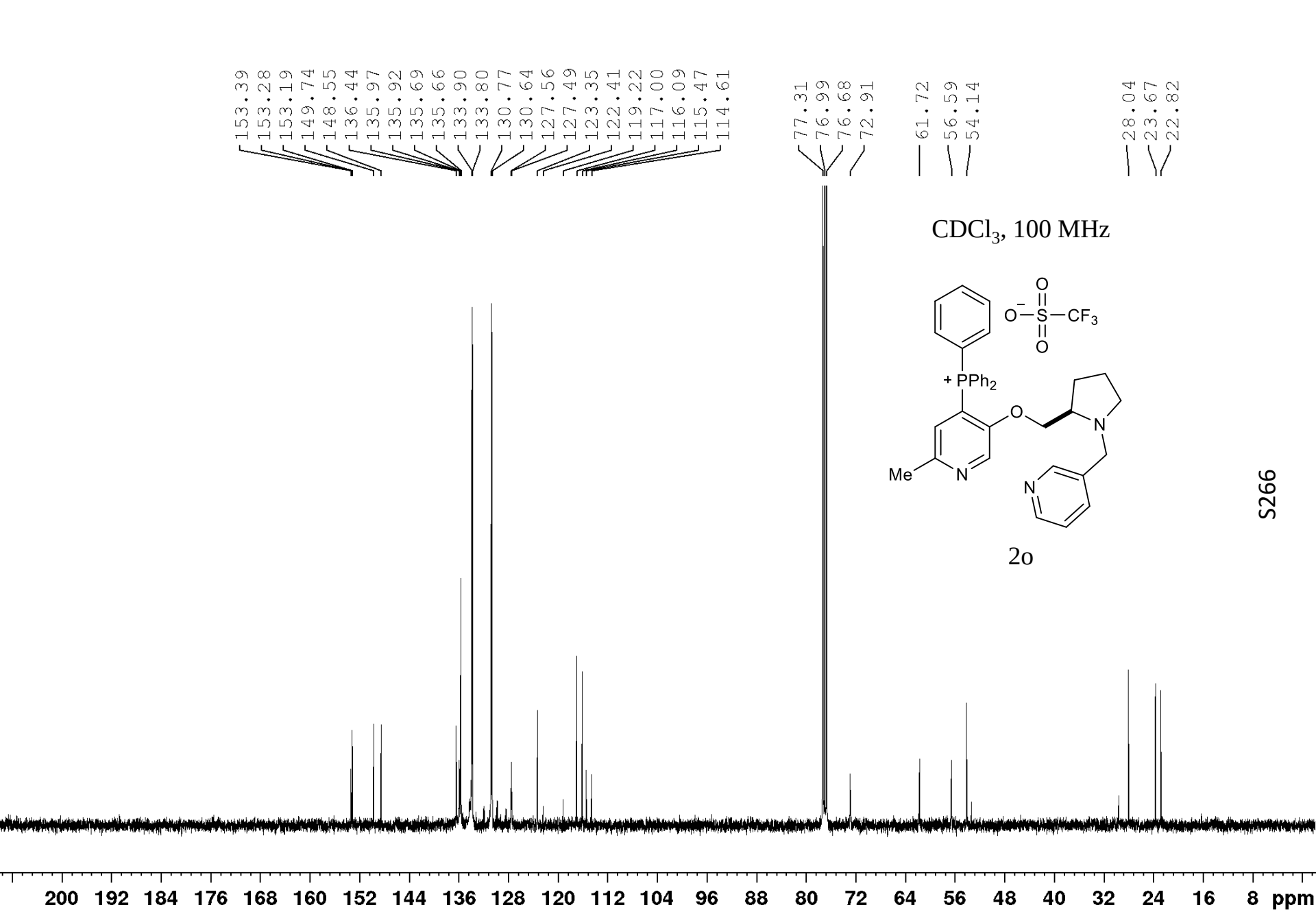

-78.12
CDCl3, 365 MHz
Me
N
O
N
PPh2
+
N
O
O
S
CF3
O
2o
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm


20.83
CDCl3, 162 MHz
Me
N
O
N
PPh2
+
N
O
O
S
CF3
O
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

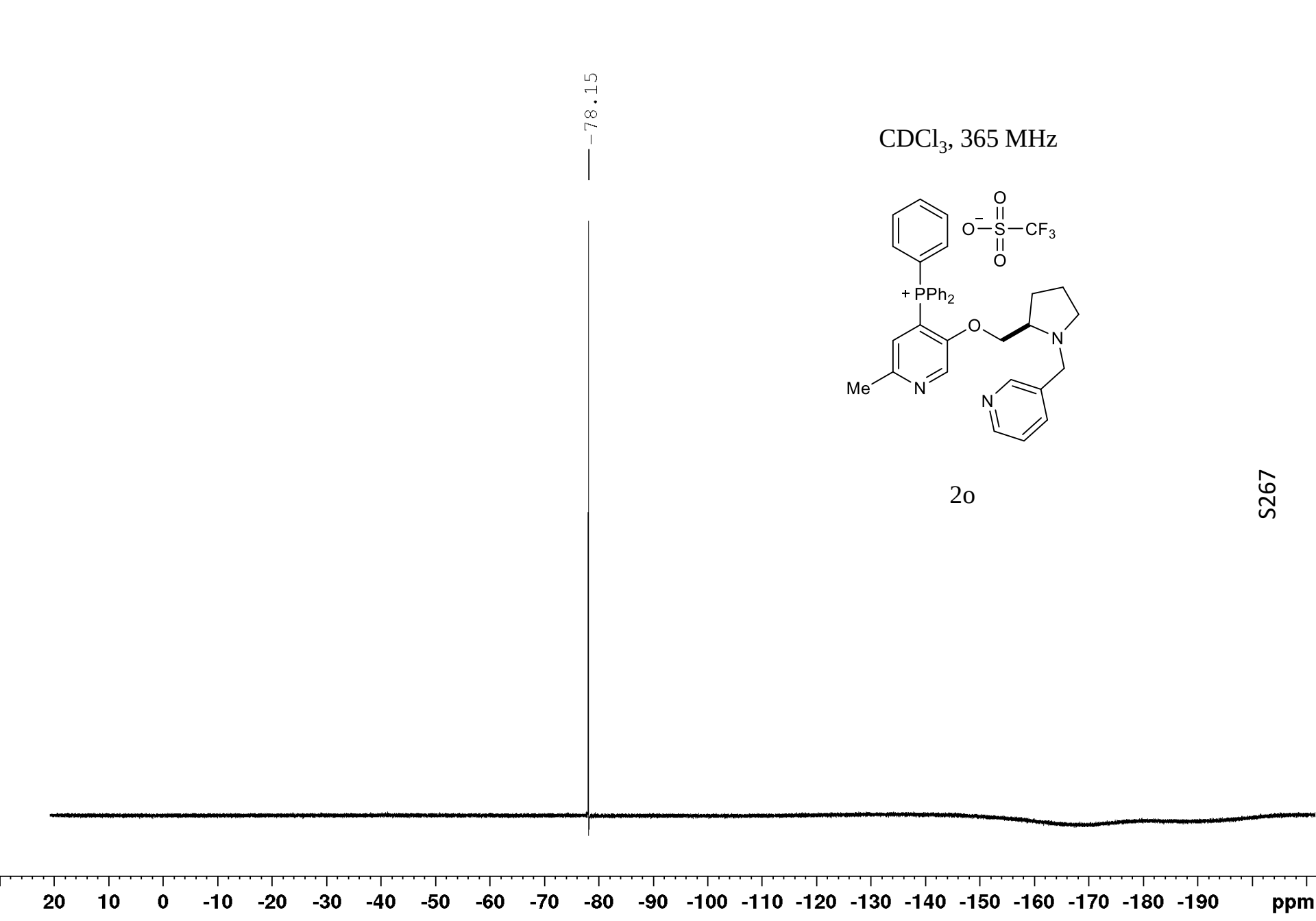
2o


29.01
21.10
20.83
CDCl3, 162 MHz
(crude 31P NMR)
Me
N
O
N
PPh2
+
N
O
O
S
CF3
O
2o
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

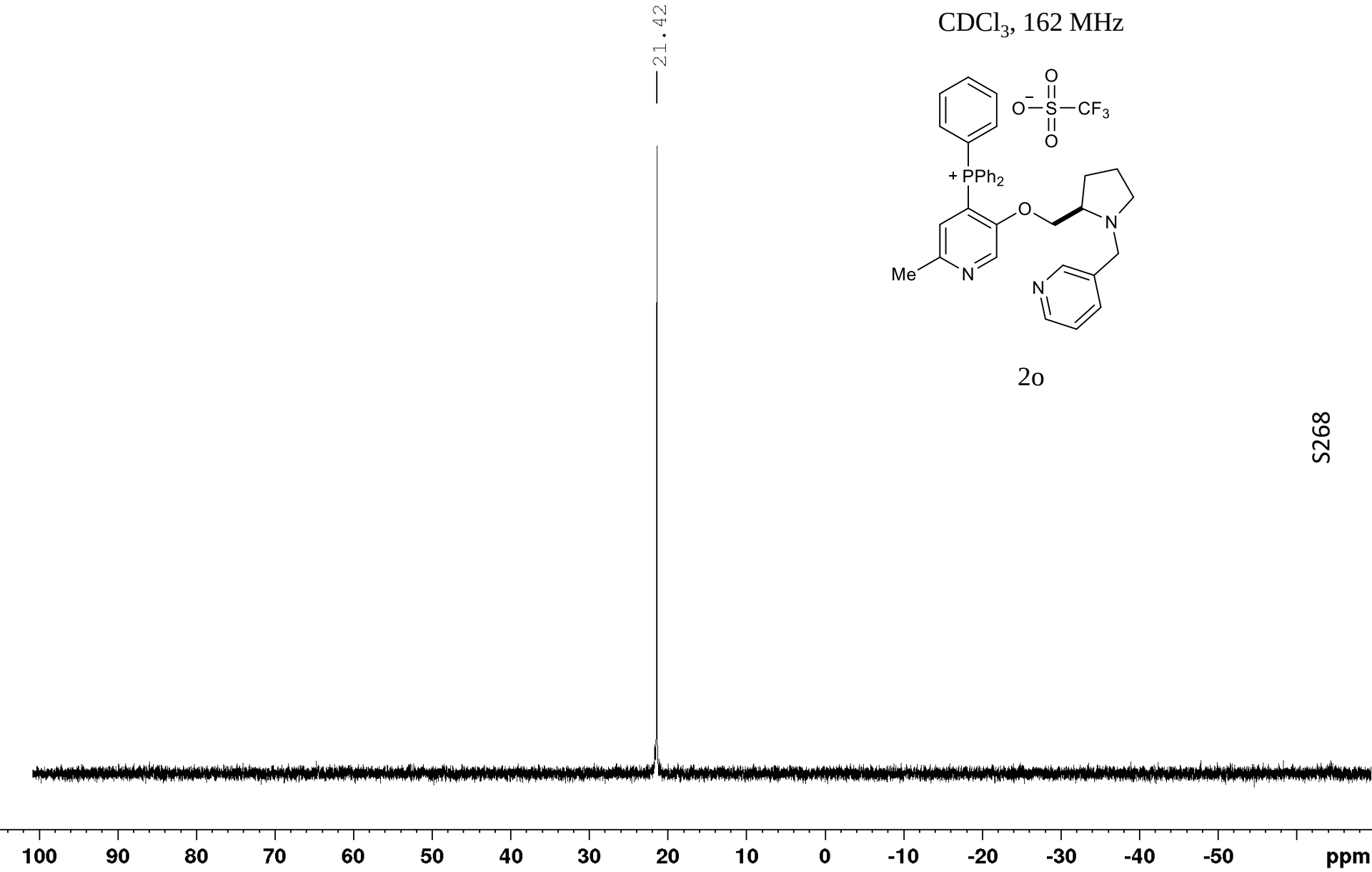

8.63
8.61
8.47
8.46
7.83
7.82
7.81
7.80
7.75
7.74
7.73
7.72
7.71
7.70
7.62
7.60
7.58
7.56
7.26
7.25
7.23
7.23
7.21
6.75
6.71
4.38
4.34
3.90
3.88
3.86
3.71
3.68
3.41
2.85
2.46
1.58
1.51
1.06
CDCl3, 400 MHz
2o
S265
1.06
2.00
11.63
7.26
0.99
1.08
0.91
1.06
1.19
1.06
0.96
4.87
2.99
1.25
9.5
9.0
8.5
8.0
7.5
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
0.5
ppm


153.39
153.28
153.19
149.74
148.55
136.44
135.97
135.92
135.69
135.66
133.90
133.80
130.77
130.64
127.56
127.49
123.35
122.41
119.22
117.00
116.09
115.47
114.61
77.31
76.99
76.68
72.91
61.72
56.59
54.14
28.04
23.67
22.82
CDCl3, 100 MHz
+ PPh2
O
S
CF3
Me
N
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 ppm

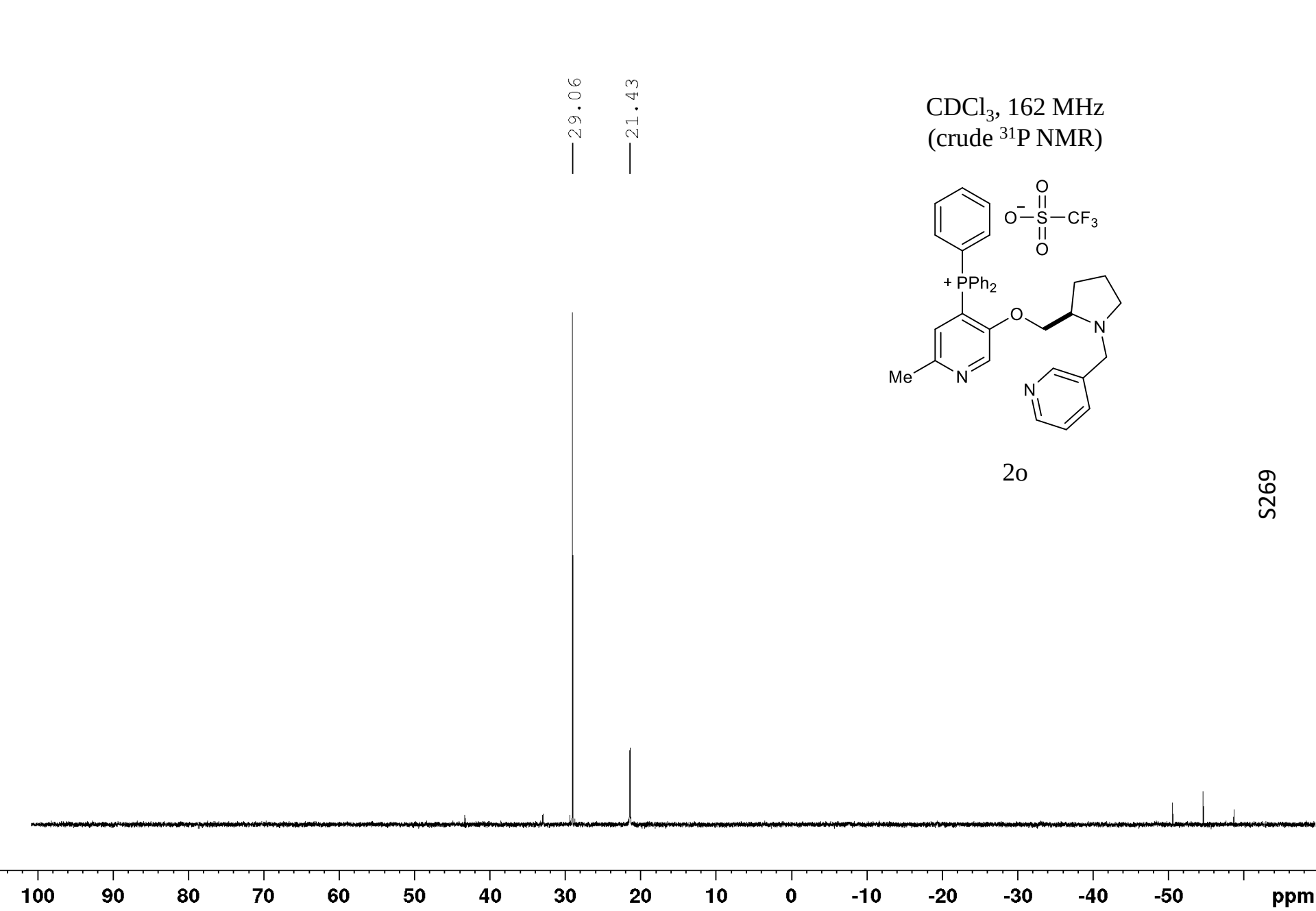
2o


-78.15
CDCl3, 365 MHz
+ PPh2
O
O
S
CF3
O
O
Me
N
N
N
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

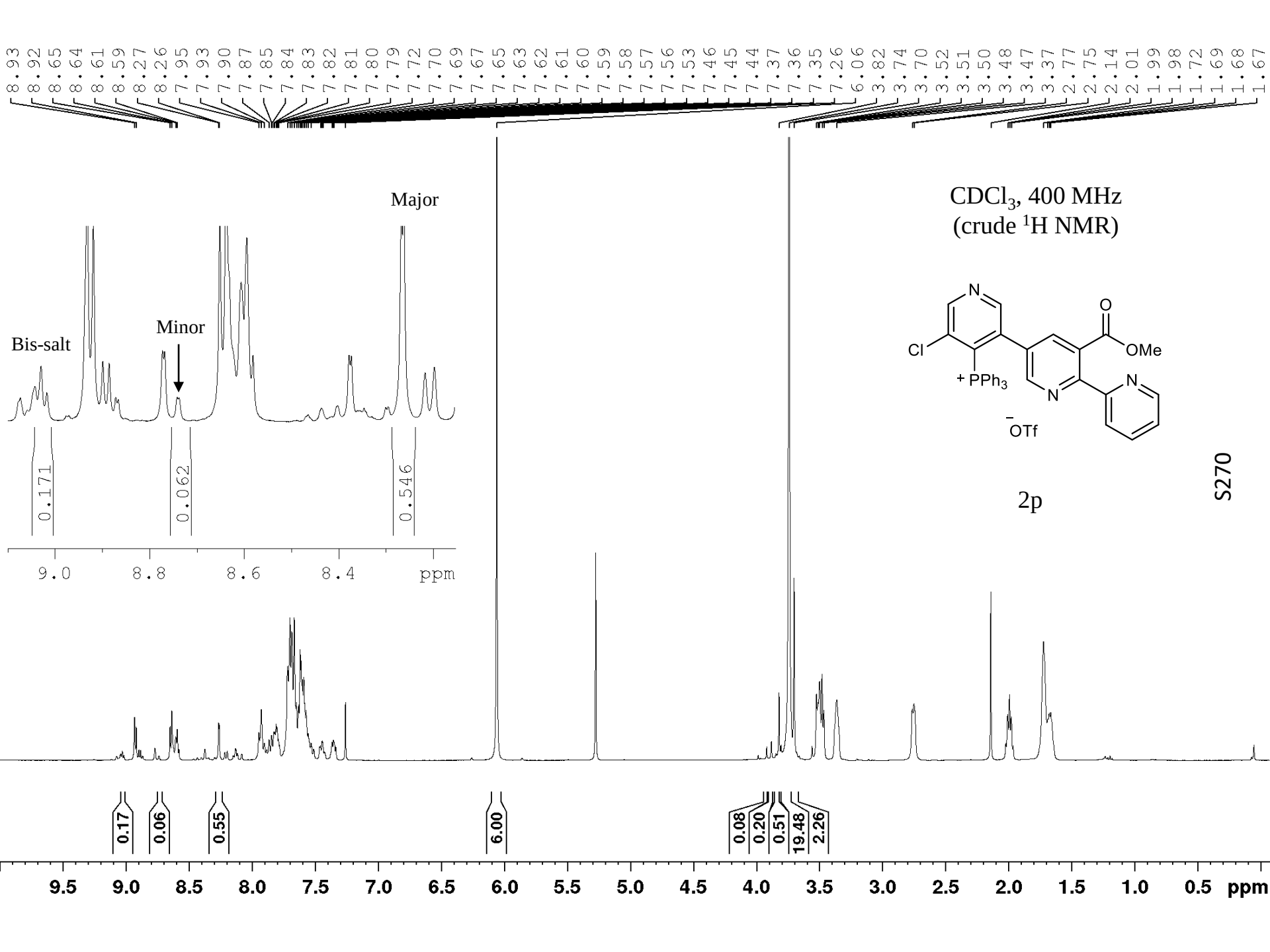
2o

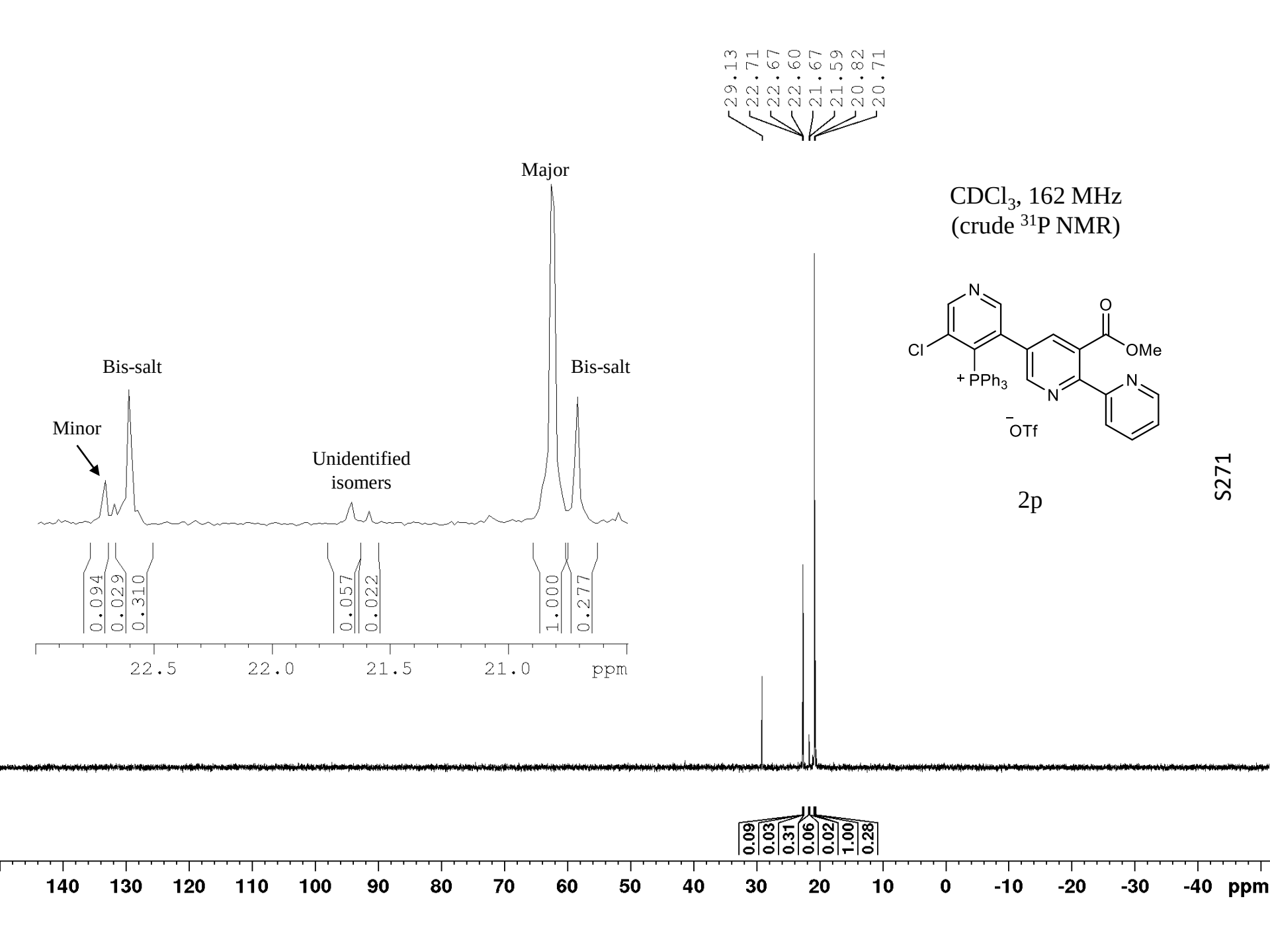

21.42
CDCl3, 162 MHz
+ PPh2
O
N
Me
N
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

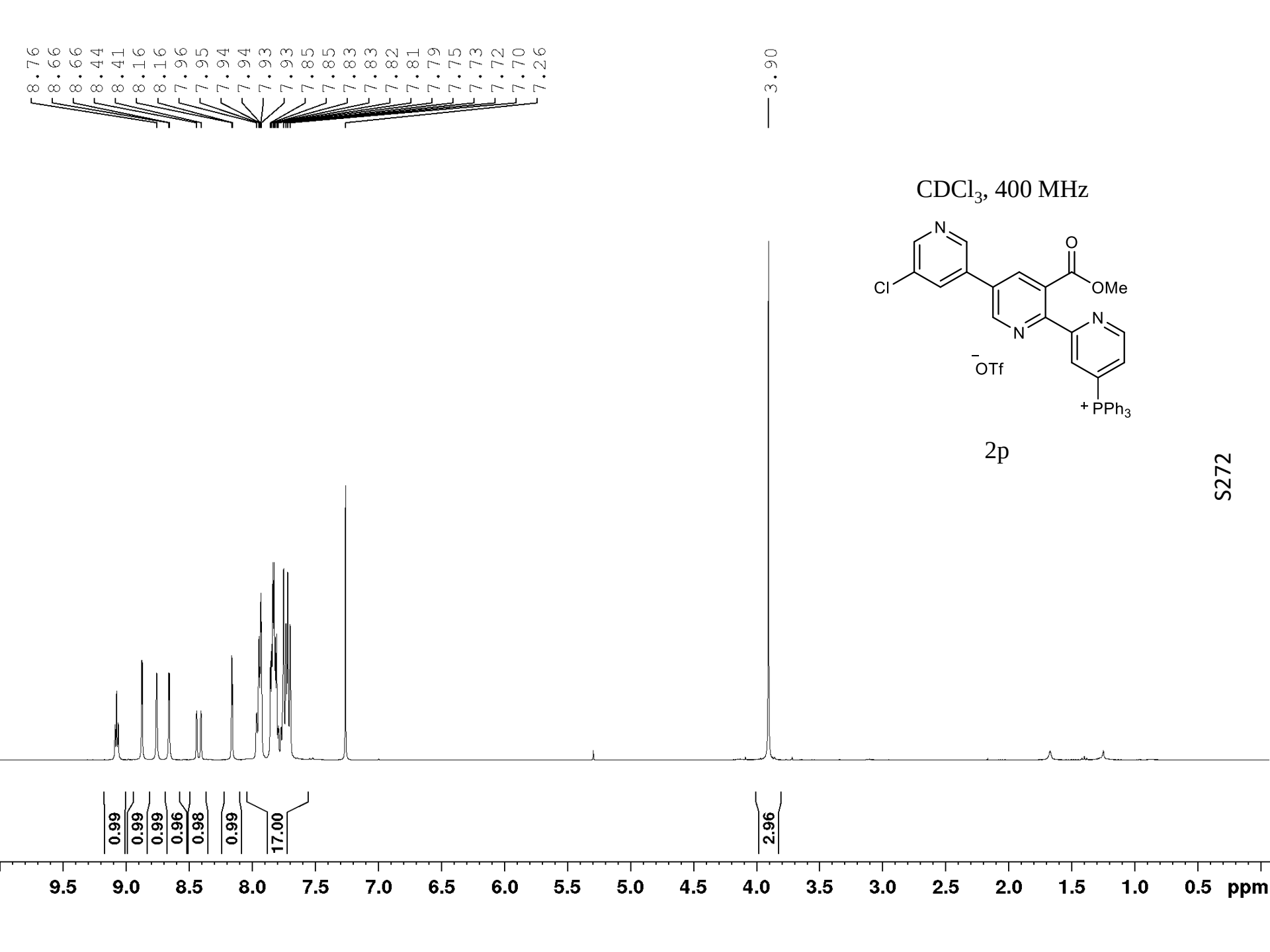
2o

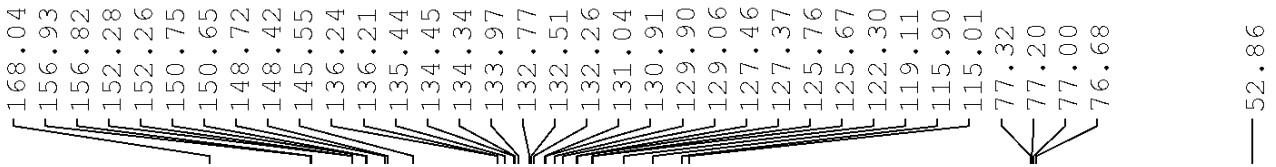

29.06
21.43
CDCl3, 162 MHz
(crude 31P NMR)
O
O⁻–S–CF3
O
+ PPh2
O
N
Me
N
N
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

2o

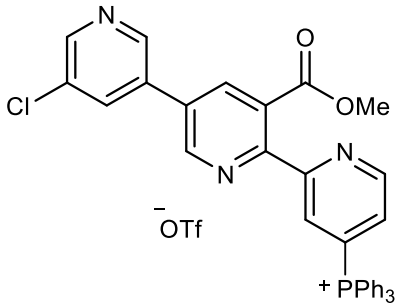

8.93 8.92 8.65 8.64 8.61 8.59 8.27 8.26 7.95 7.93 7.90 7.87 7.85 7.84 7.83 7.82 7.81 7.80 7.79 7.72 7.70 7.69 7.67 7.65 7.63 7.62 7.61 7.60 7.59 7.58 7.57 7.56 7.53 7.46 7.45 7.44 7.37 7.36 7.35 7.26 6.06 3.82 3.74 3.70 3.52 3.51 3.50 3.48 3.47 3.37 2.77 2.75 2.14 2.01 1.99 1.98 1.72 1.69 1.68 1.67
Major
Minor
Bis-salt
0.171
0.062
0.546
9.0 8.8 8.6 8.4 ppm
CDCl3, 400 MHz
(crude 1H NMR)
Cl
N
O
OMe
+ PPh3
N
N
OTf
2p
S270
0.17 0.06 0.55 6.00 0.08 0.20 0.51 19.48 2.26
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 ppm


29.13
22.71
22.67
22.60
21.67
21.59
20.82
20.71
Major
Bis-salt
Bis-salt
Minor
Unidentified
isomers
0.094
0.029
0.310
0.057
0.022
1.000
0.277
22.5
22.0
21.5
21.0
ppm
CDCl3, 162 MHz
(crude 31P NMR)
Cl
N
+ PPh3
OTf
O
OMe
N
N
2p
S271
0.09
0.03
0.31
0.06
0.02
1.00
0.28
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

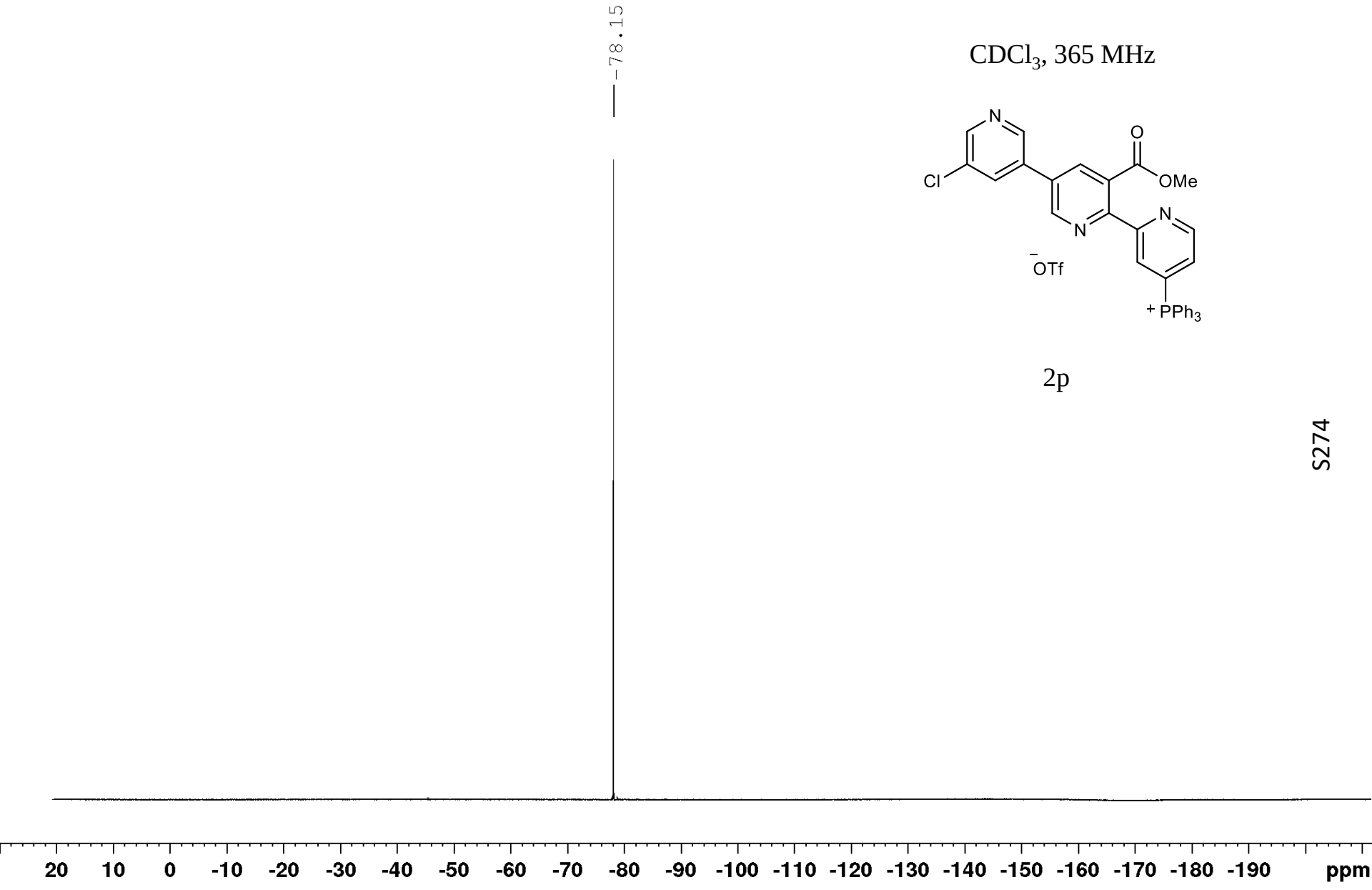

8.76
8.66
8.66
8.44
8.41
8.16
8.16
7.96
7.95
7.94
7.94
7.93
7.93
7.85
7.85
7.83
7.83
7.82
7.81
7.79
7.75
7.73
7.72
7.70
7.26
3.90
CDCl3, 400 MHz
N
Cl
O
OMe
N
N
OTf
+ PPh3
2p
S272
0.99
0.99
0.99
0.96
0.98
0.99
17.00
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



$CDCl_3$, 100 MHz



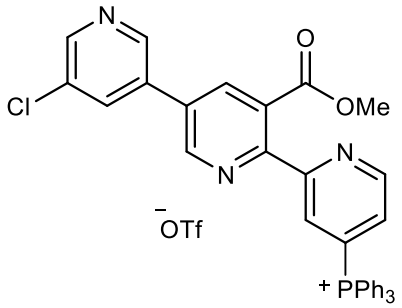
2p


-78.15
CDCl3, 365 MHz
N
O
Cl
OMe
N
N
OTf
+ PPh3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

2p

22.69
22.66

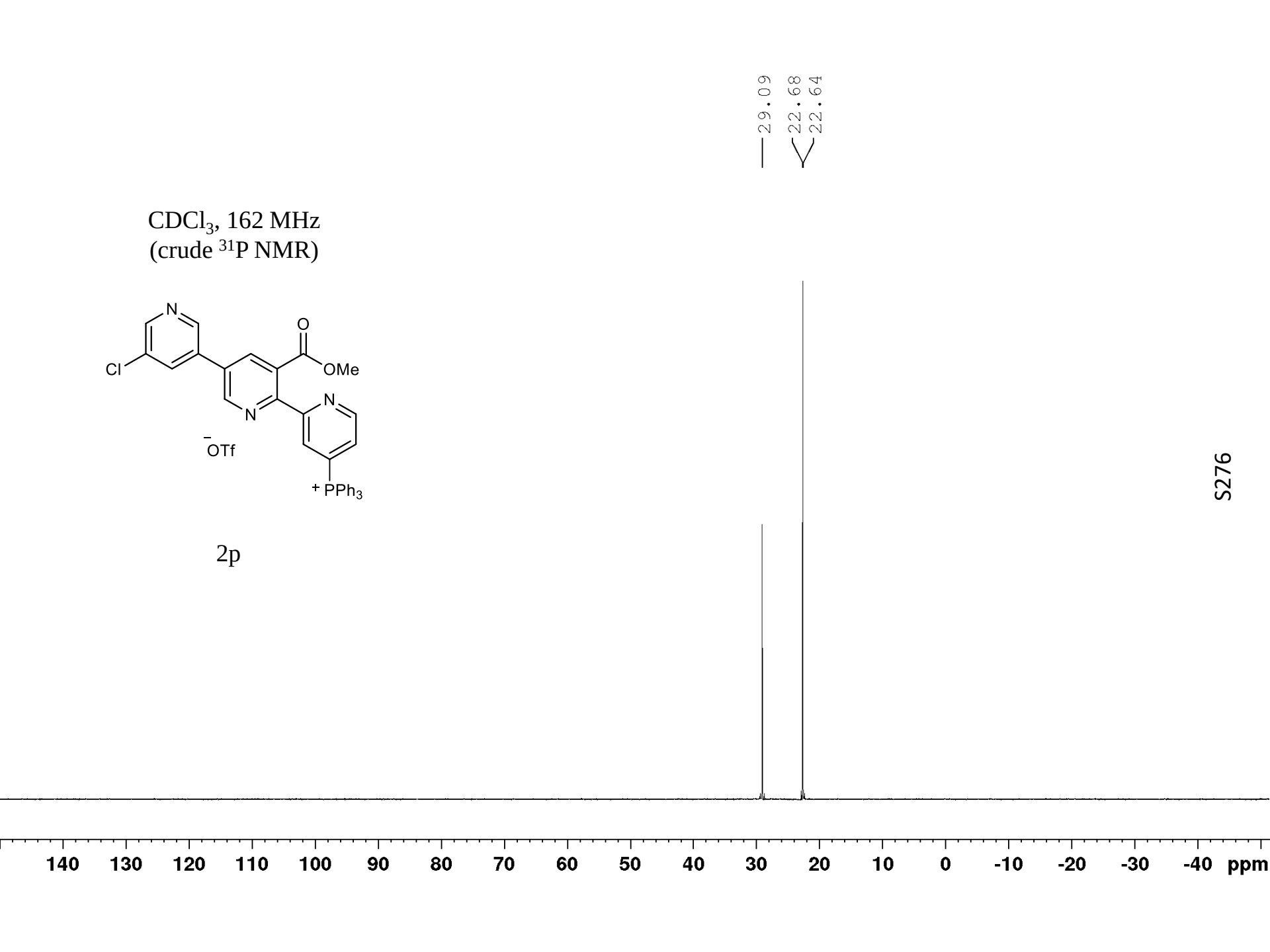
$CDCl_3$, 162 MHz

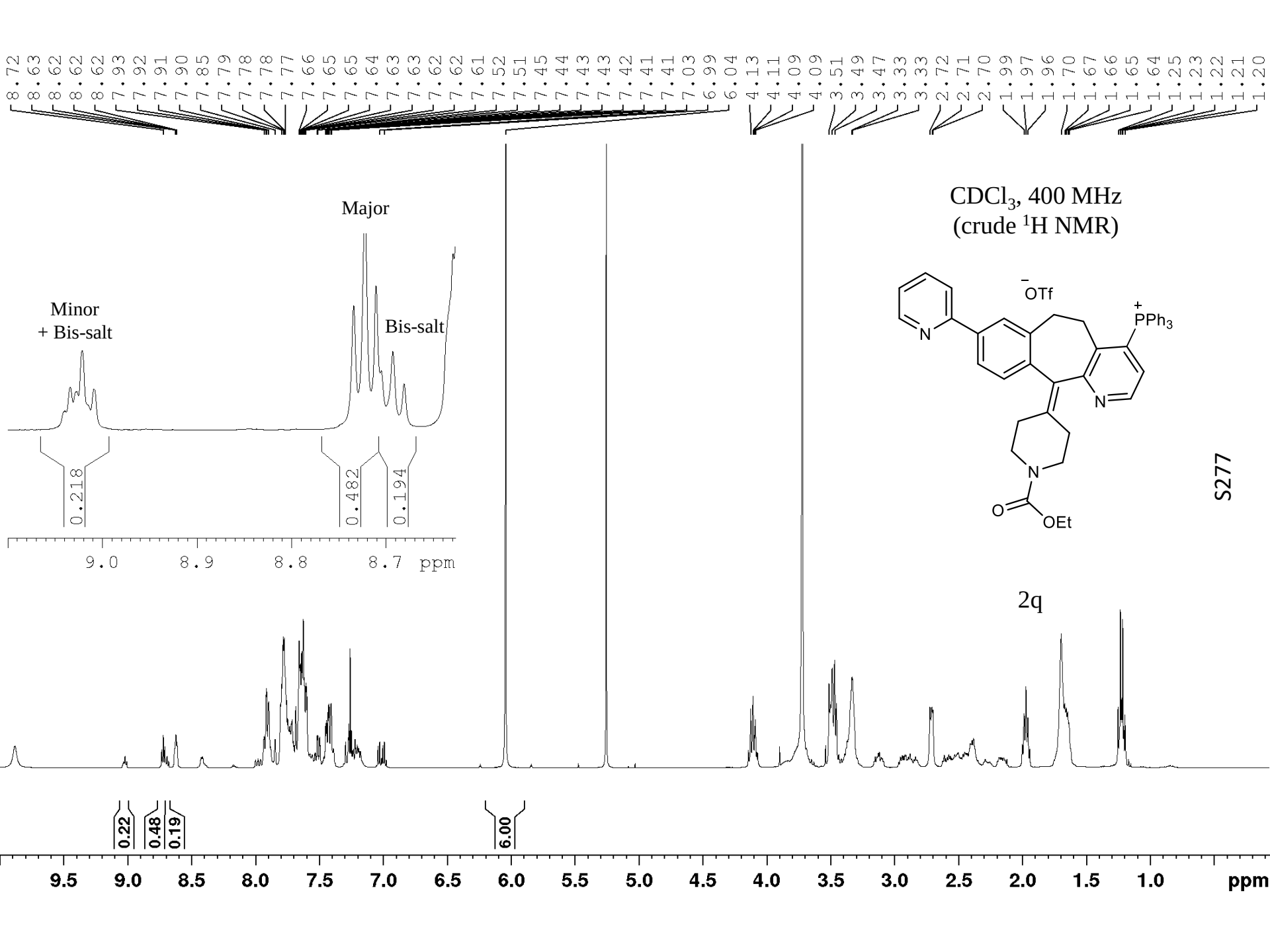


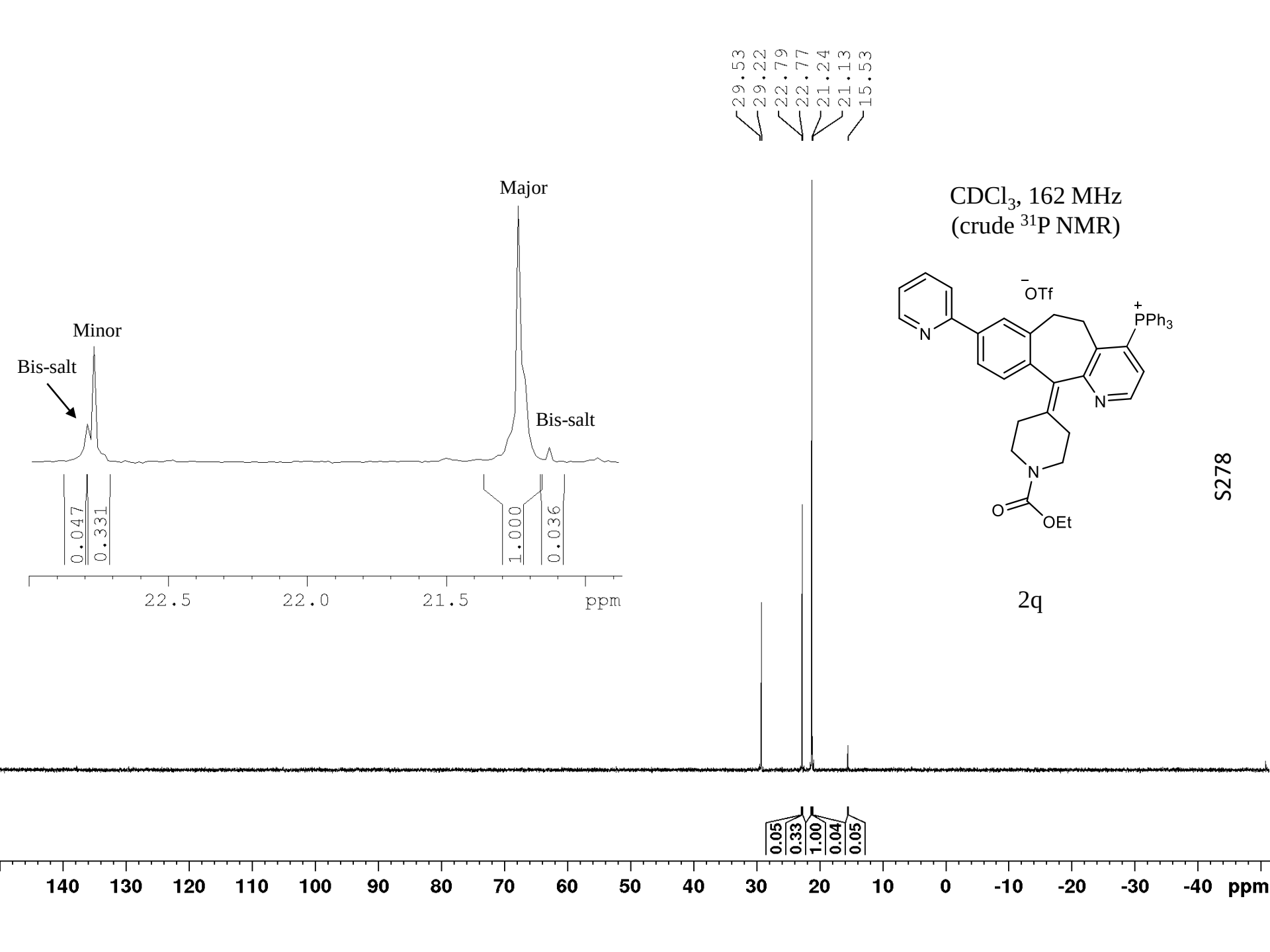
2p

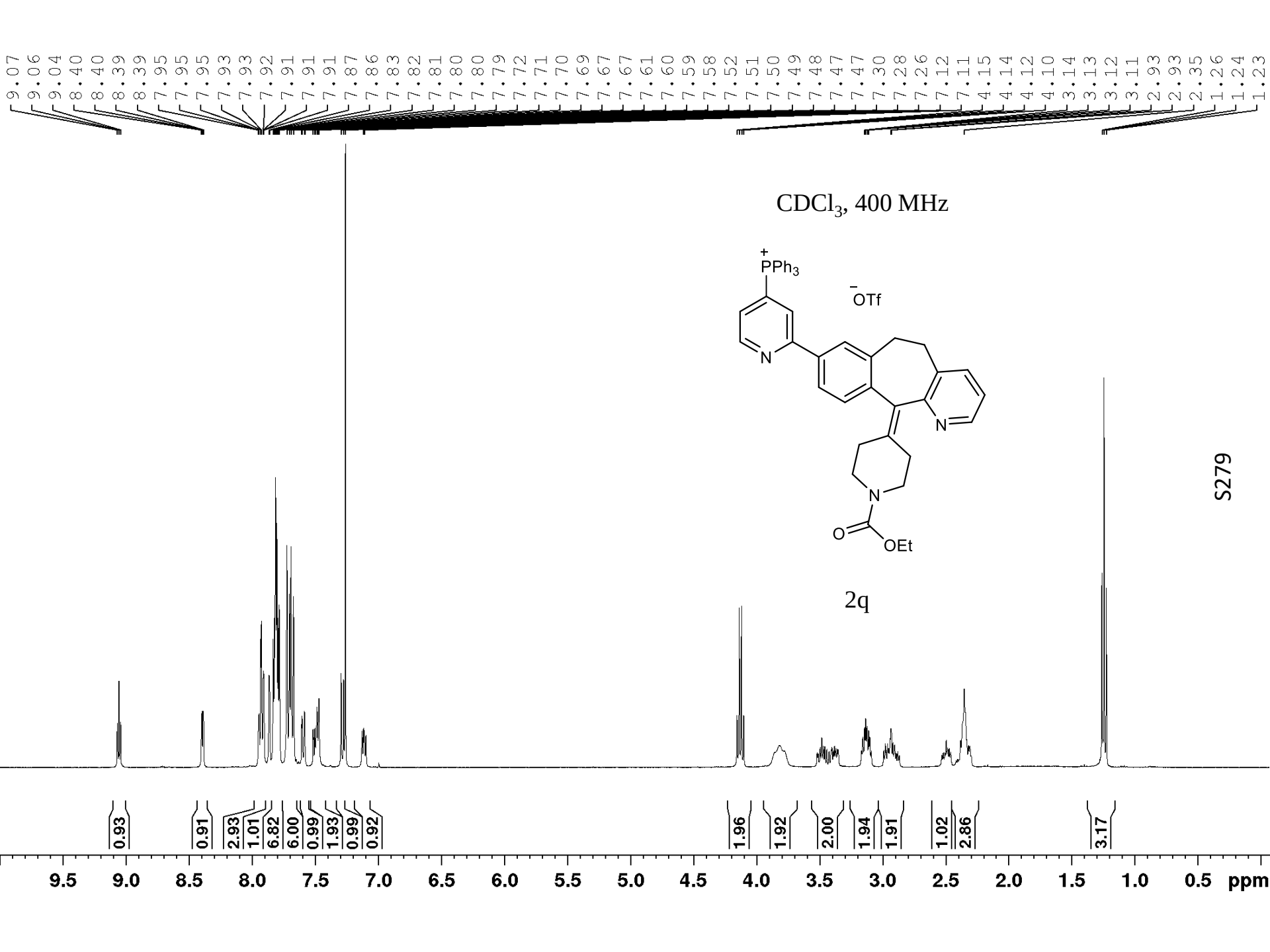
S275

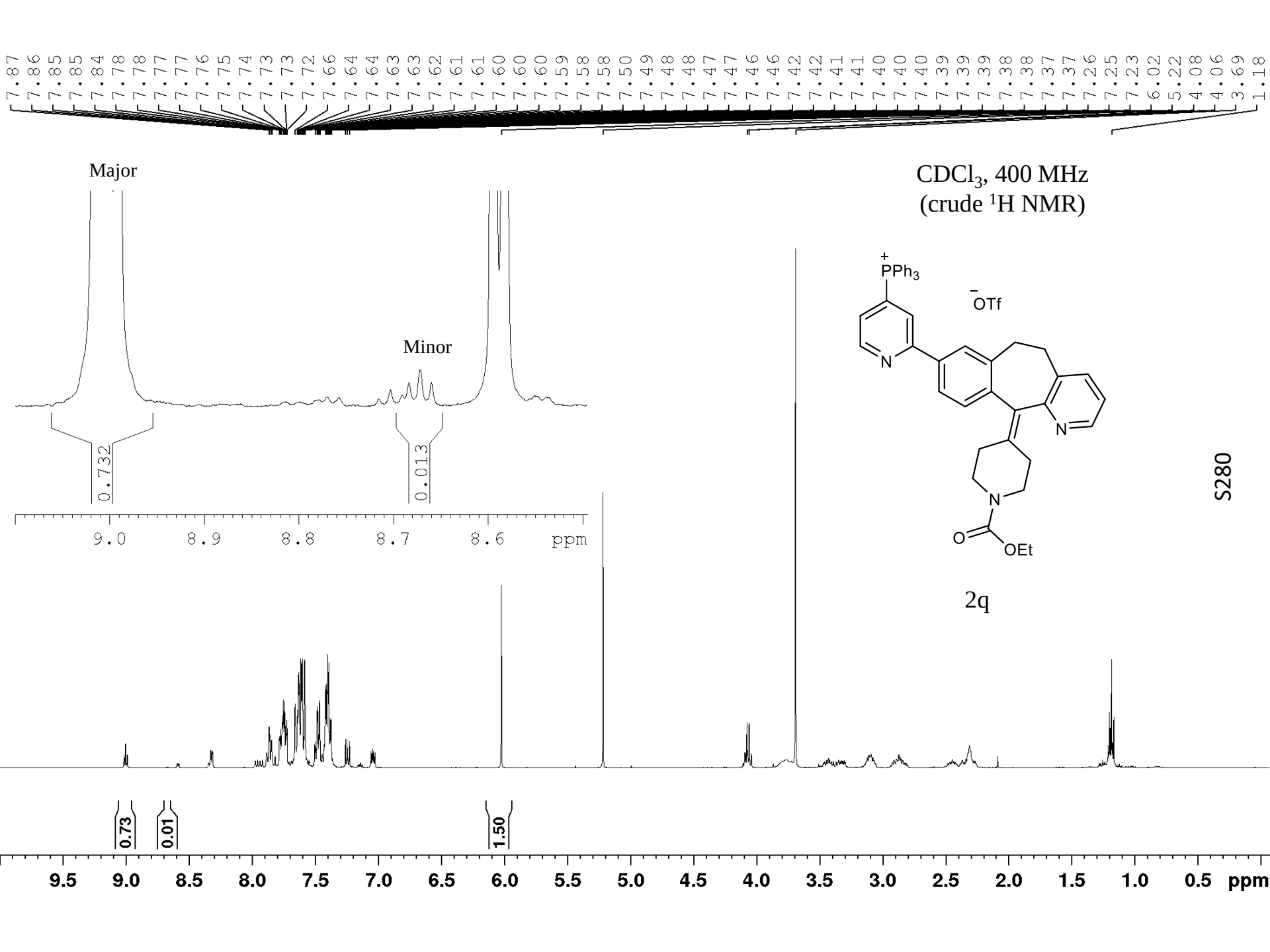
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

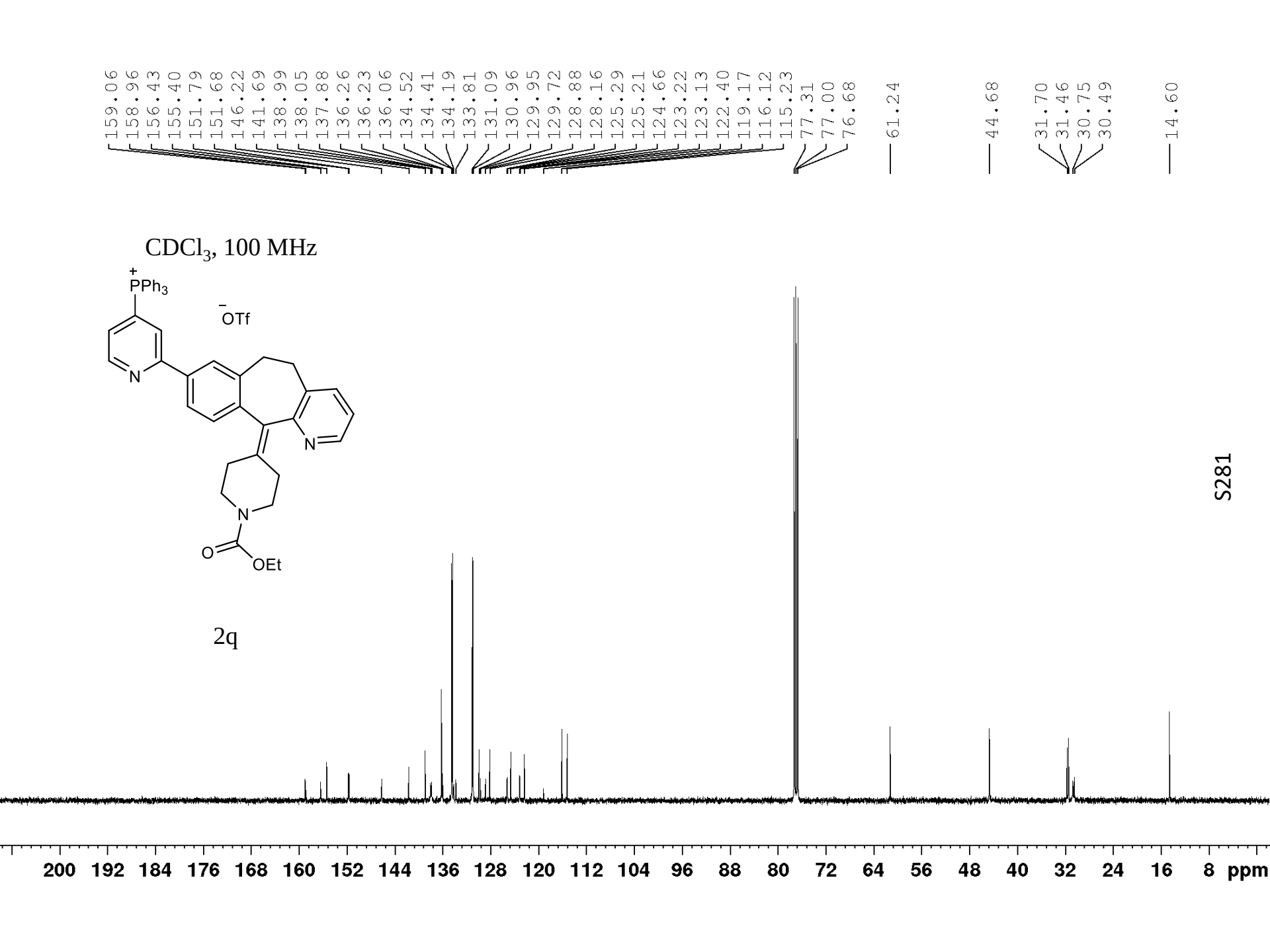

29.09
22.68
22.64
CDCl3, 162 MHz
(crude 31P NMR)
N
Cl
O
OMe
N
N
OTf
+ PPh3
2p
S276
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

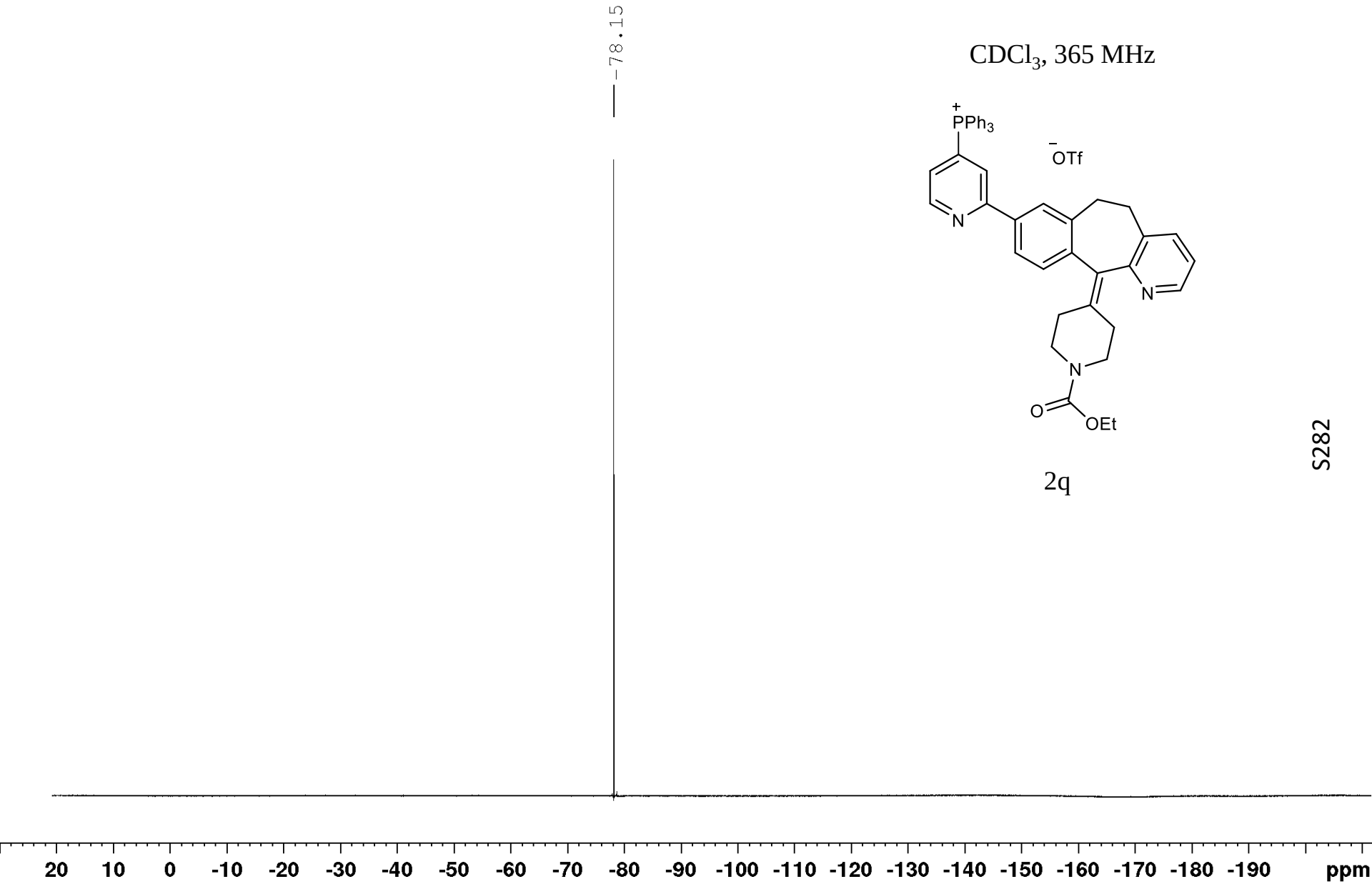

8.72 8.63 8.62 8.62 8.62 7.93 7.92 7.91 7.90 7.85 7.79 7.78 7.78 7.77 7.66 7.65 7.65 7.64 7.63 7.63 7.62 7.62 7.61 7.52 7.51 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.03 6.99 6.04 4.13 4.11 4.09 4.09 3.51 3.49 3.47 3.33 3.33 2.72 2.71 2.70 1.99 1.97 1.96 1.70 1.67 1.66 1.65 1.64 1.25 1.23 1.22 1.21 1.20
Major
Minor
+ Bis-salt
Bis-salt
0.218
0.482
0.194
9.0 8.9 8.8 8.7 ppm
CDCl3, 400 MHz
(crude 1H NMR)
OTf
PPh3
N
N
N
O
OEt
S277
2q
0.22
0.48
0.19
6.00
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

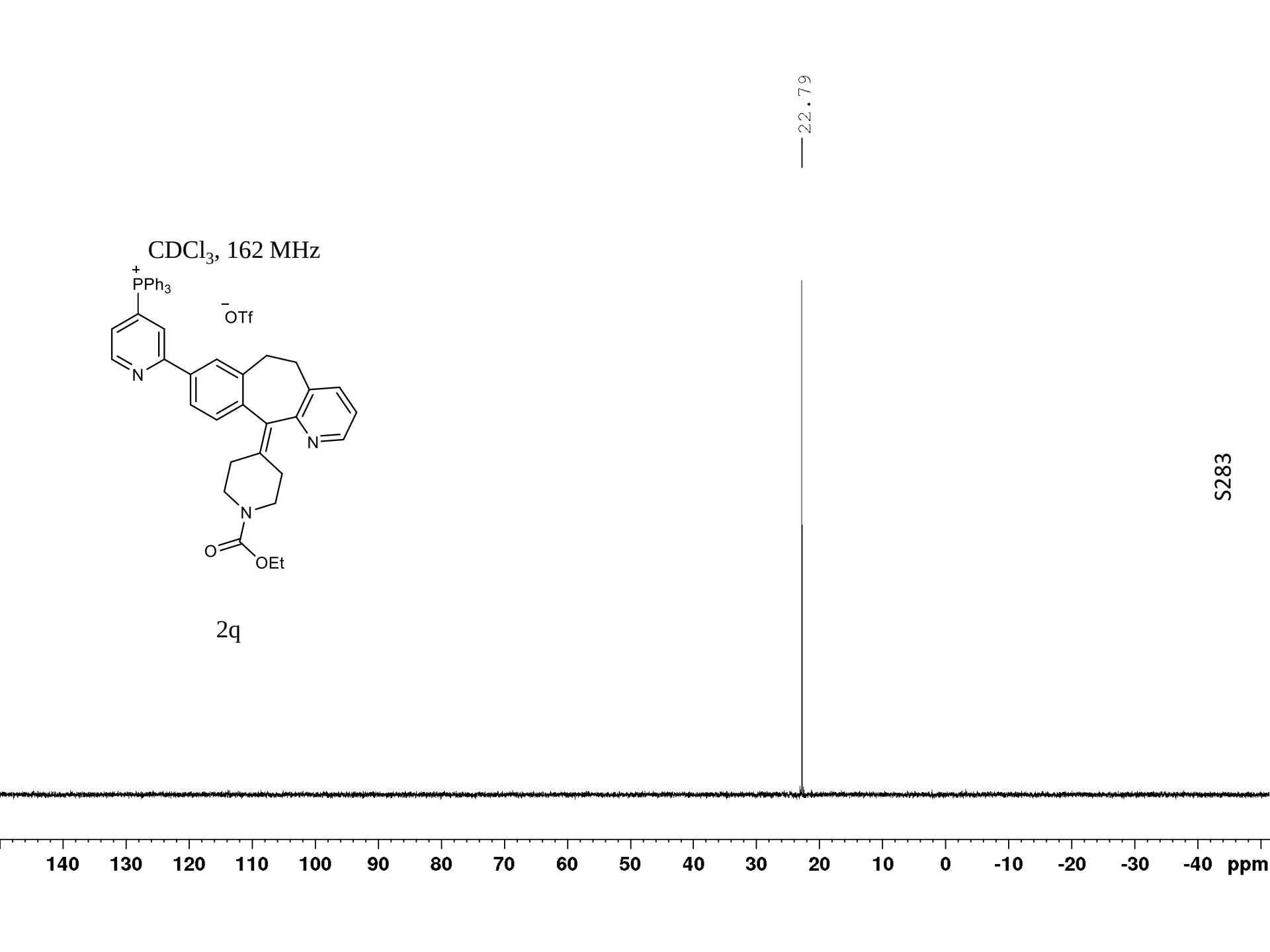

29.53
29.22
22.79
22.77
21.24
21.13
15.53
Major
Minor
Bis-salt
Bis-salt
0.047
0.331
1.000
0.036
22.5
22.0
21.5
ppm
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
N
N
N
O
OEt
2q
S278
0.05
0.33
1.00
0.04
0.05
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

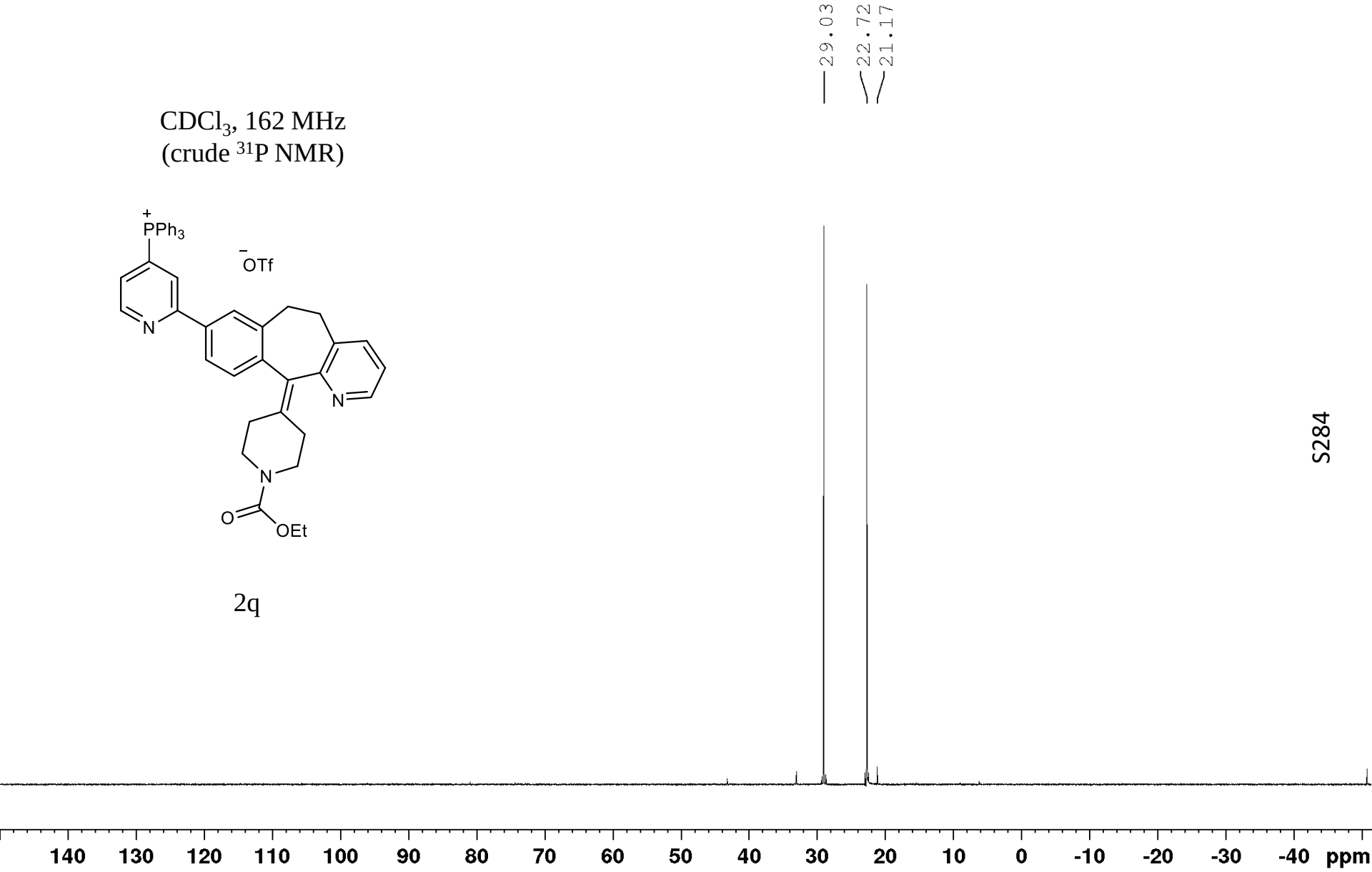

9.07 9.06 9.04 8.40 8.40 8.39 8.39 7.95 7.95 7.95 7.93 7.93 7.92 7.91 7.91 7.91 7.87 7.86 7.83 7.82 7.81 7.80 7.80 7.79 7.72 7.71 7.70 7.69 7.67 7.67 7.61 7.60 7.59 7.58 7.52 7.51 7.50 7.49 7.48 7.47 7.47 7.30 7.28 7.26 7.12 7.11 4.15 4.14 4.12 4.10 3.14 3.13 3.12 3.11 2.93 2.93 2.35 1.26 1.24 1.23
CDCl3, 400 MHz
PPh3
OTf
N
N
N
O
OEt
2q
S279
0.93 0.91 2.93 1.01 6.82 6.00 0.99 1.93 0.99 0.92 1.96 1.92 2.00 1.94 1.91 1.02 2.86 3.17
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 ppm

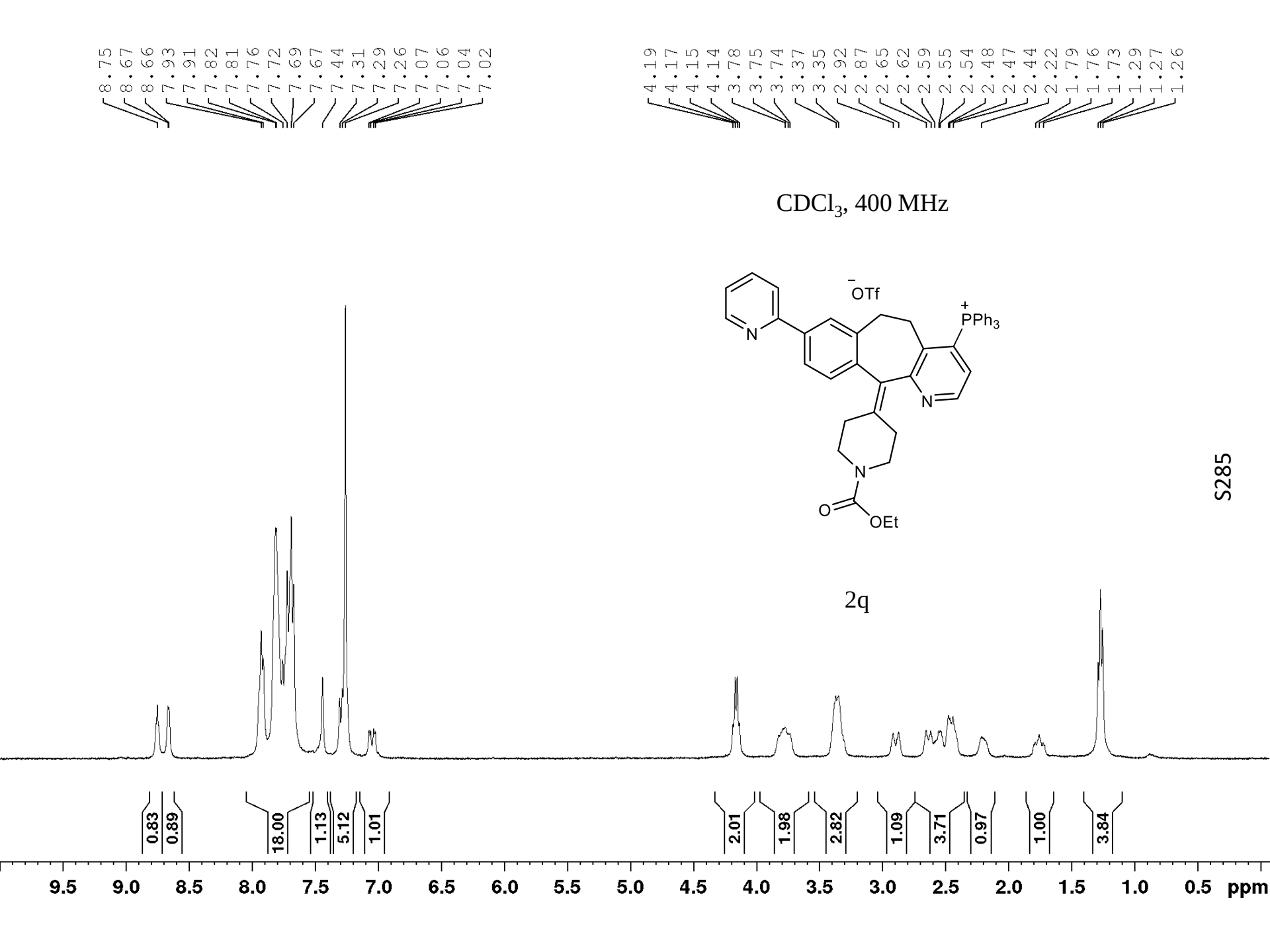

Major
Minor
0.732
0.013
9.0
8.9
8.8
8.7
8.6
ppm
CDCl3, 400 MHz
(crude 1H NMR)
PPh3
OTf
N
N
N
O
OEt
2q
S280
0.73
0.01
1.50
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

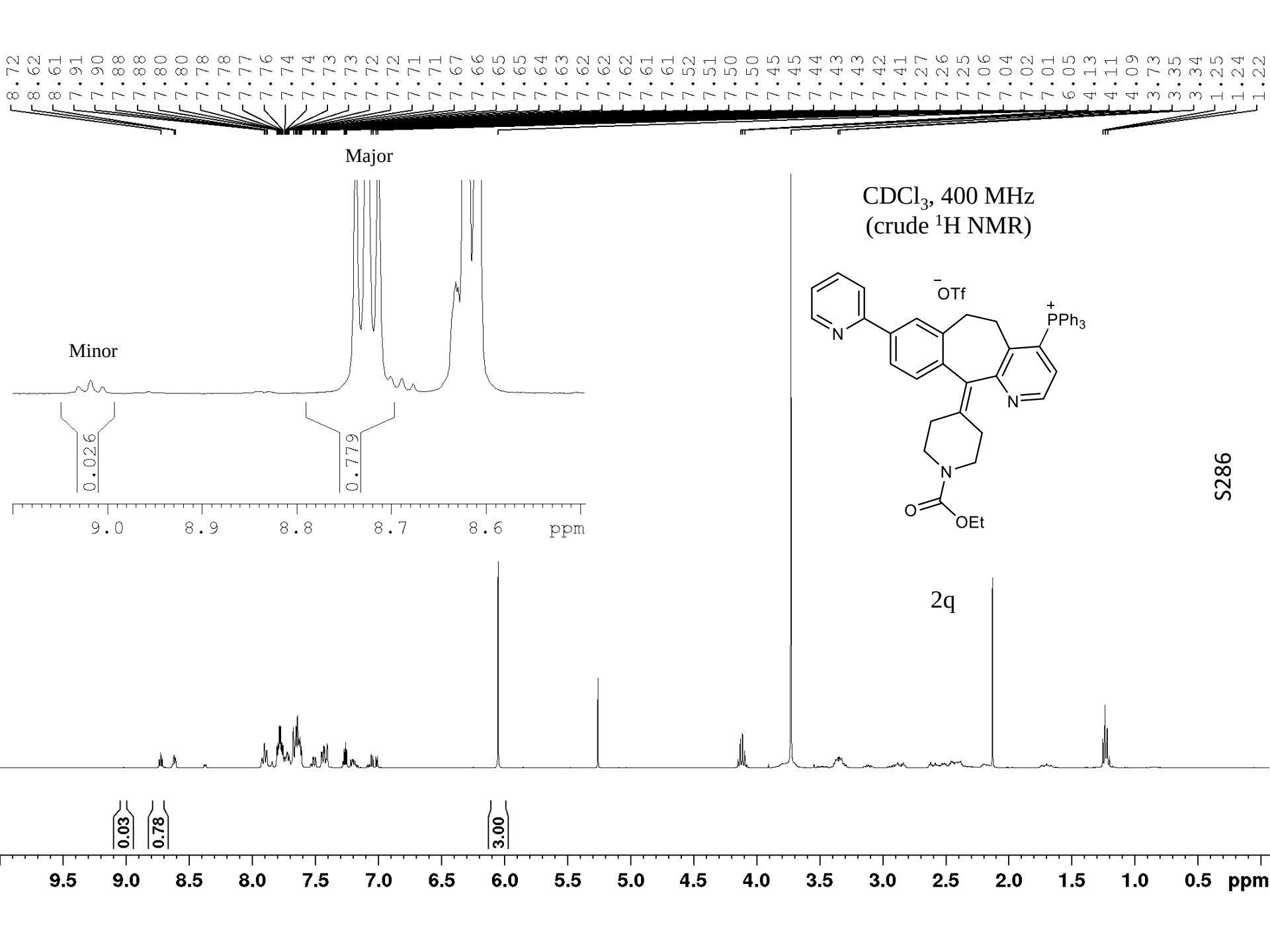

159.06
158.96
156.43
155.40
151.79
151.68
146.22
141.69
138.99
138.05
137.88
136.26
136.23
136.06
134.52
134.41
134.19
133.81
131.09
130.96
129.95
129.72
128.88
128.16
125.29
125.21
124.66
123.22
123.13
122.40
119.17
116.12
115.23
77.31
77.00
76.68
61.24
44.68
31.70
31.46
30.75
30.49
14.60
CDCl3, 100 MHz
PPh3
OTf
N
N
N
O
OEt
2q
S281
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 ppm

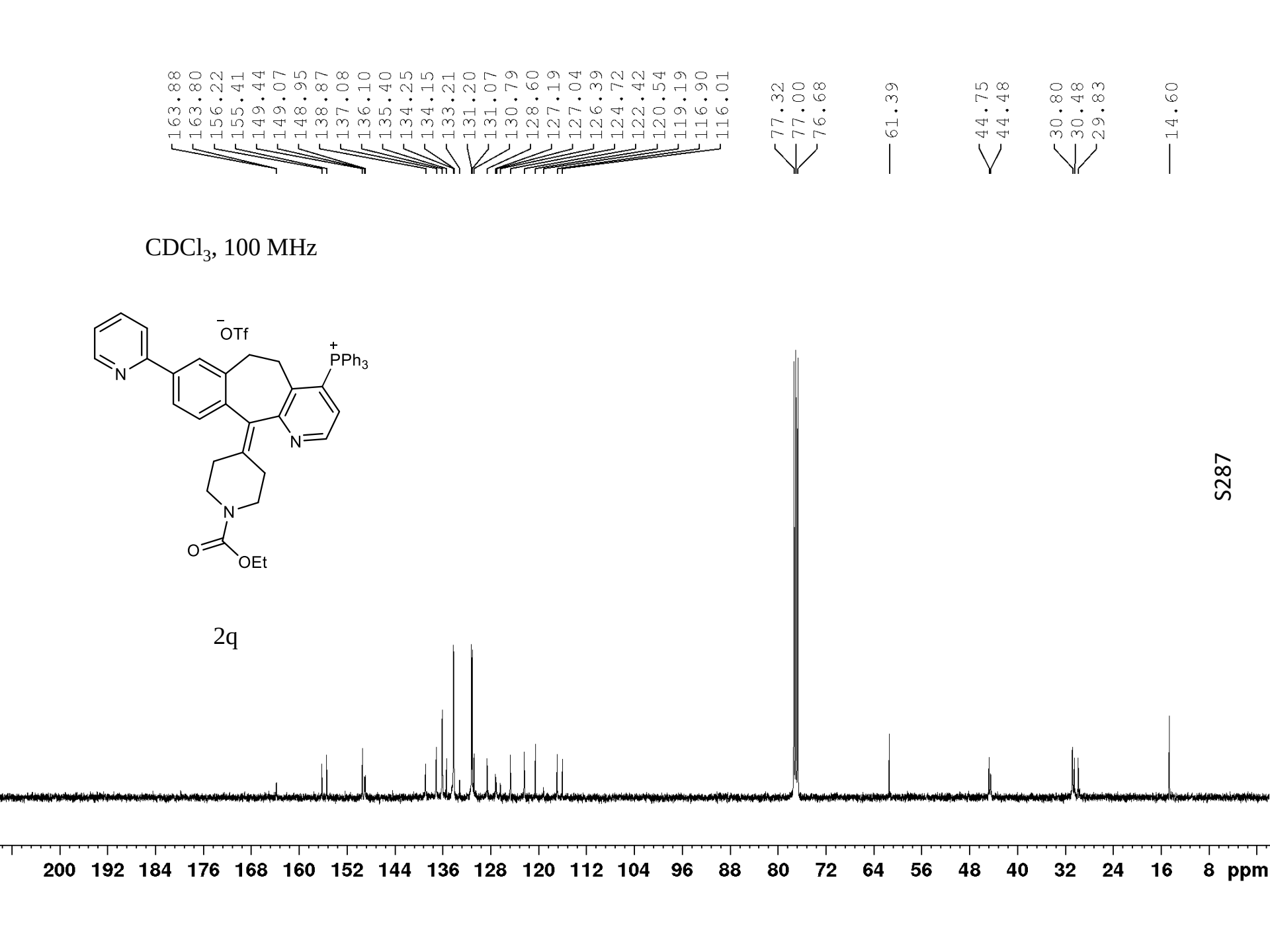

-78.15
CDCl3, 365 MHz
PPh3
OTf
N
N
N
O
OEt
2q
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


22.79
CDCl3, 162 MHz
PPh3
OTf
N
N
N
O
OEt
2q
S283
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

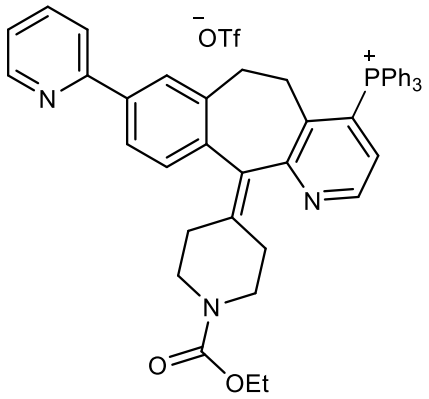

29.03
22.72
21.17
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
OTf
N
N
N
O
OEt
2q
S284
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


8.75
8.67
8.66
7.93
7.91
7.82
7.81
7.76
7.72
7.69
7.67
7.44
7.31
7.29
7.26
7.07
7.06
7.04
7.02
4.19
4.17
4.15
4.14
3.78
3.75
3.74
3.37
3.35
2.92
2.87
2.65
2.62
2.59
2.55
2.54
2.48
2.47
2.44
2.22
1.79
1.76
1.73
1.29
1.27
1.26
CDCl3, 400 MHz
OTf
PPh3
N
N
N
O
OEt
2q
S285
0.83
0.89
18.00
1.13
5.12
1.01
2.01
1.98
2.82
1.09
3.71
0.97
1.00
3.84
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
ppm

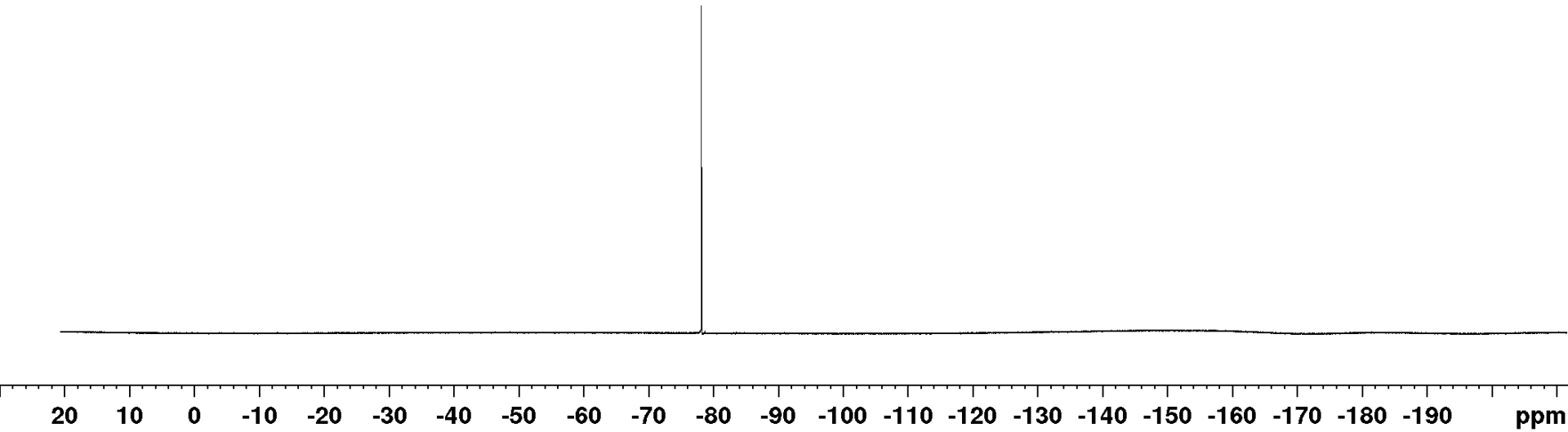

8.72 8.62 8.61 7.91 7.90 7.88 7.88 7.80 7.80 7.78 7.78 7.77 7.76 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.71 7.67 7.66 7.65 7.65 7.64 7.63 7.62 7.62 7.62 7.61 7.61 7.52 7.51 7.50 7.50 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.27 7.26 7.25 7.06 7.04 7.02 7.01 6.05 4.13 4.11 4.09 3.73 3.35 3.34 1.25 1.24 1.22
Major
Minor
0.026
0.779
9.0 8.9 8.8 8.7 8.6 ppm
CDCl3, 400 MHz
(crude 1H NMR)
OTf
PPh3
N
N
N
O
OEt
S286
2q
0.03
0.78
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 0.5 ppm


163.88
163.80
156.22
155.41
149.44
149.07
148.95
138.87
137.08
136.10
135.40
134.25
134.15
133.21
131.20
131.07
130.79
128.60
127.19
127.04
126.39
124.72
122.42
120.54
119.19
116.90
116.01
77.32
77.00
76.68
61.39
44.75
44.48
30.80
30.48
29.83
14.60
CDCl3, 100 MHz
OTf
PPh3
N
N
N
O
OEt
2q
S287
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 ppm

$CDCl_3$, 365 MHz

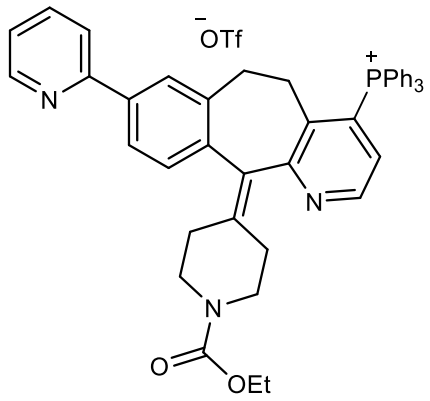


2q



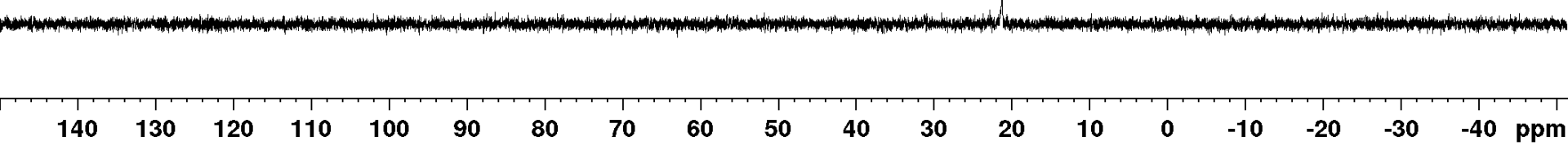
21.24

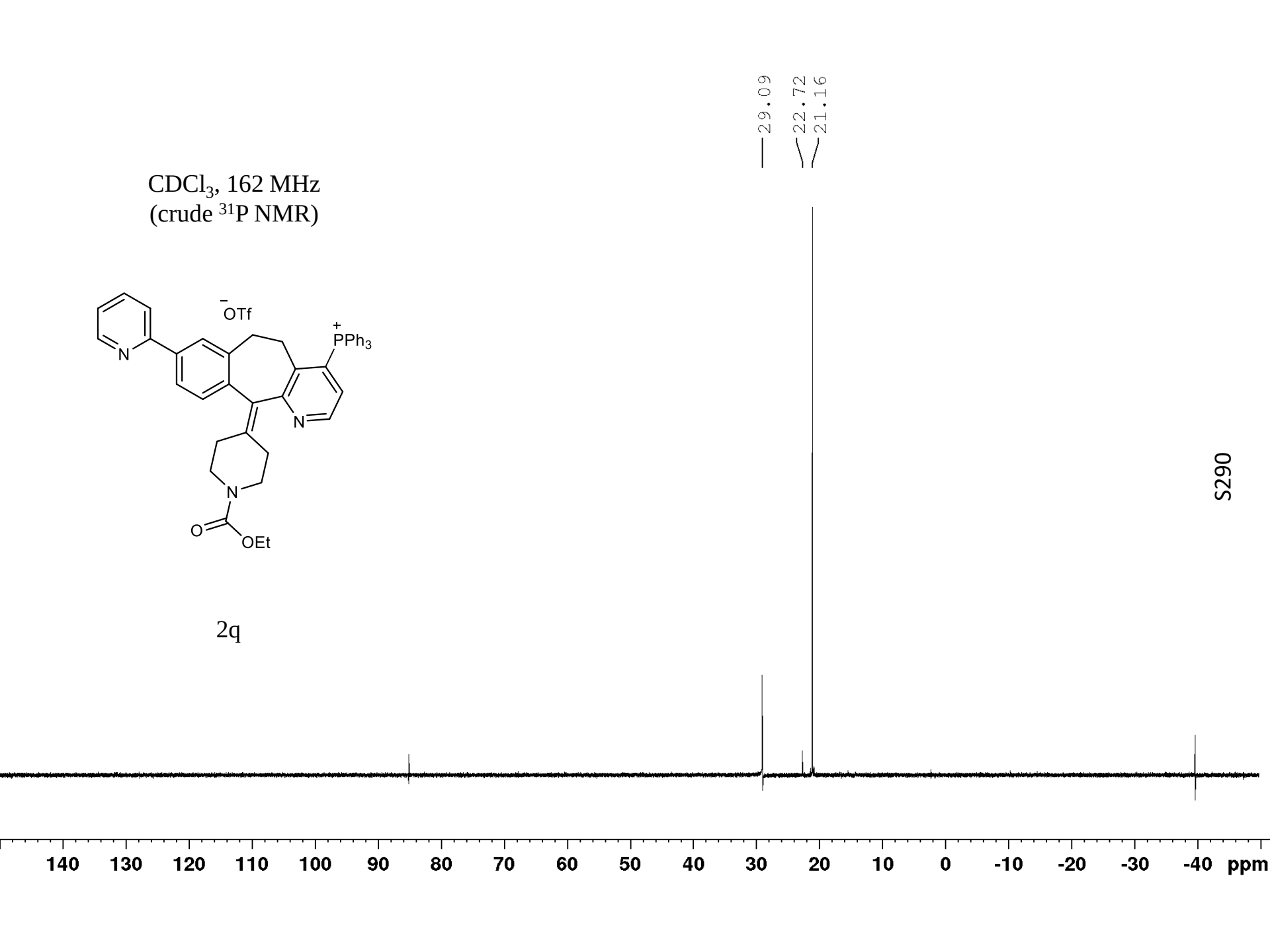
$CDCl_3$, 162 MHz

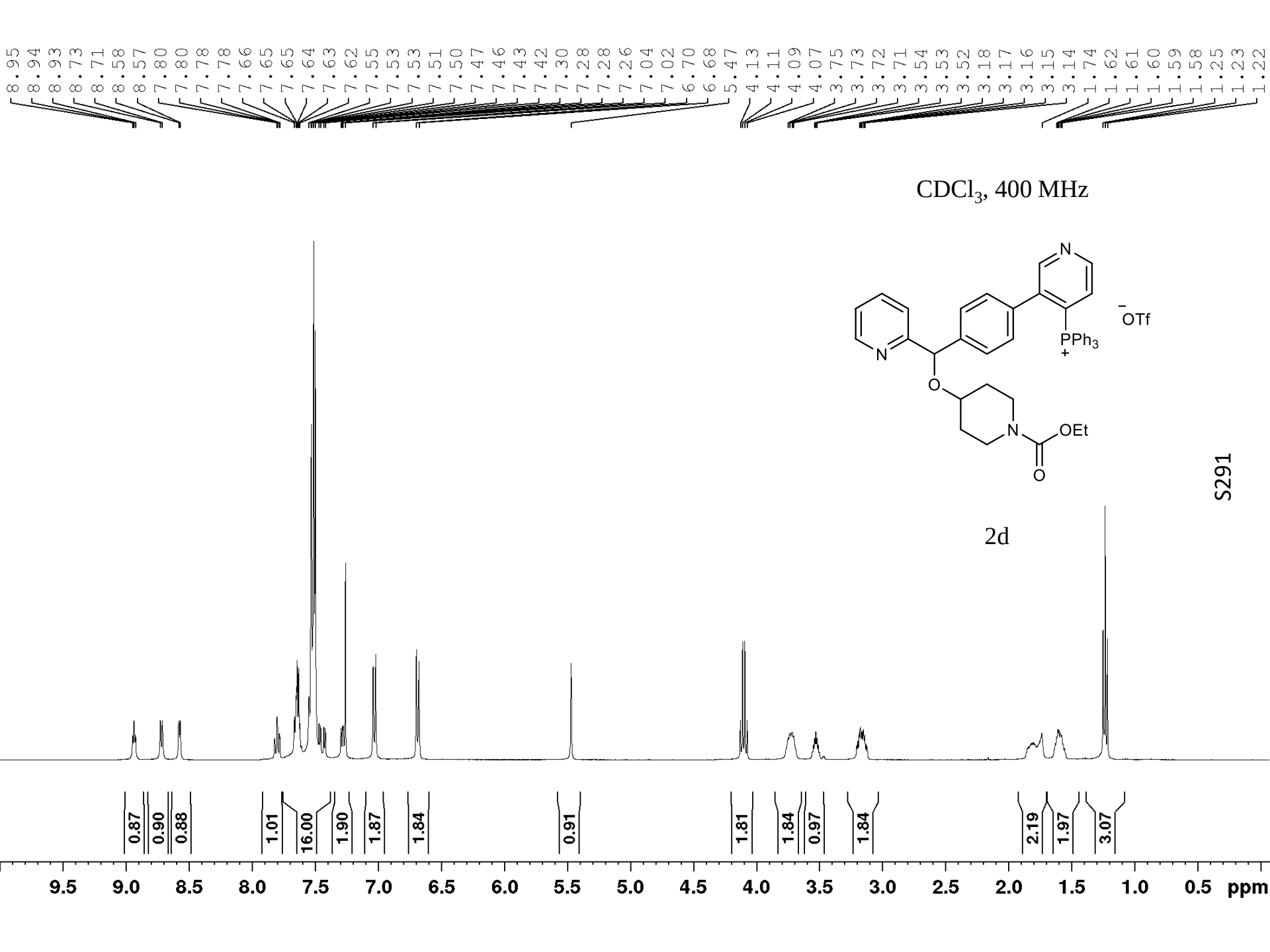


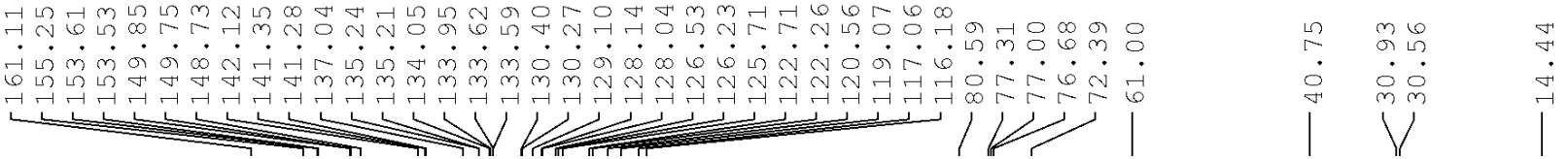
2q

S289

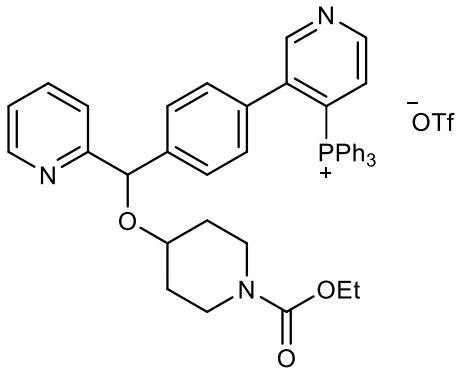



29.09
22.72
21.16
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
N
N
N
O
OEt
2q
S290
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

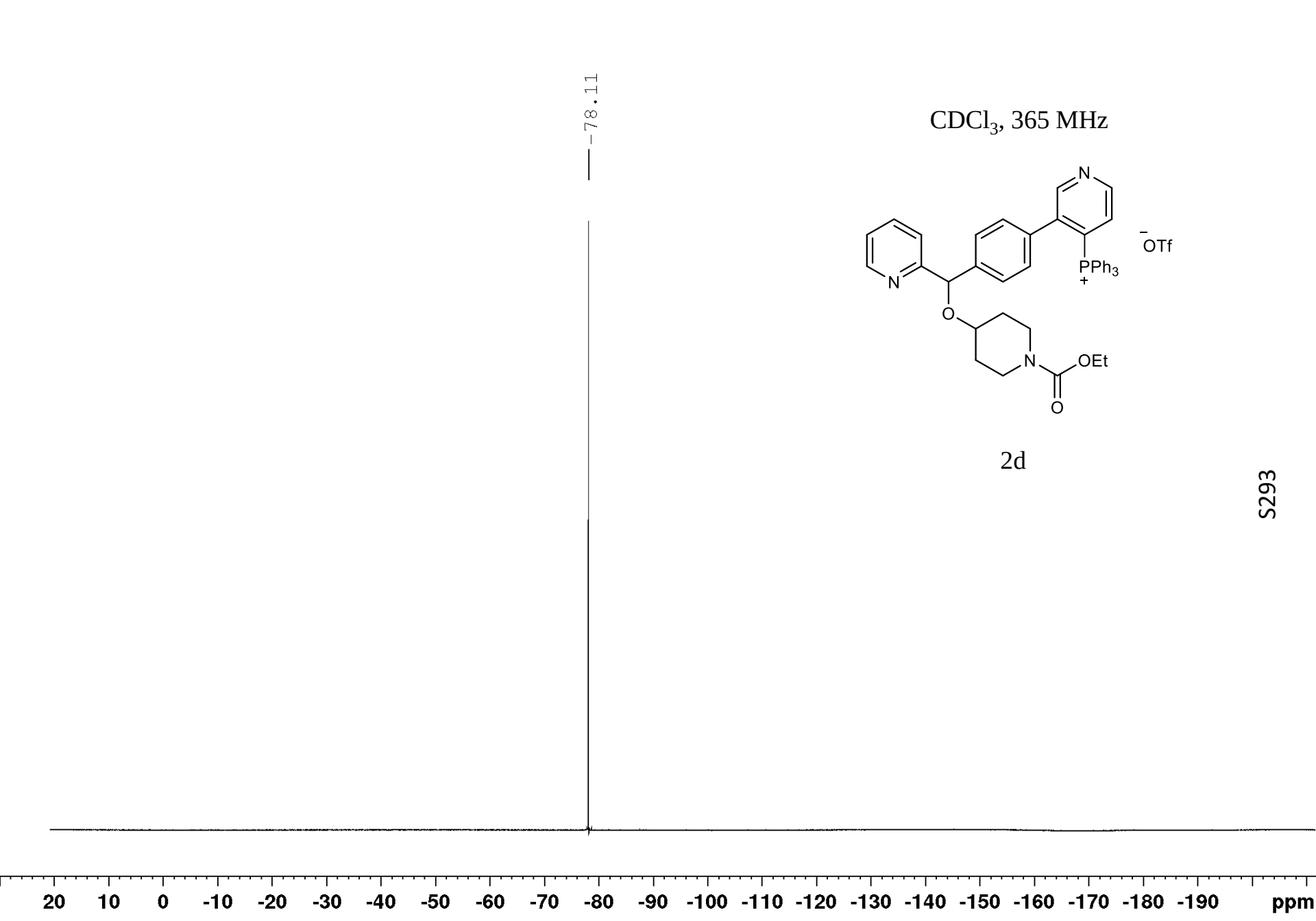

8.95
8.94
8.93
8.73
8.71
8.58
8.57
7.80
7.80
7.78
7.78
7.66
7.65
7.65
7.64
7.63
7.62
7.55
7.53
7.53
7.51
7.50
7.47
7.46
7.43
7.42
7.30
7.28
7.28
7.26
7.04
7.02
6.70
6.68
5.47
4.13
4.11
4.09
4.07
3.75
3.73
3.72
3.71
3.54
3.53
3.52
3.18
3.17
3.16
3.15
3.14
1.74
1.62
1.61
1.60
1.59
1.58
1.25
1.23
1.22
CDCl3, 400 MHz
N
OTf
PPh3
+
N
O
N
OEt
O
S291
2d
0.87
0.90
0.88
1.01
16.00
1.90
1.87
1.84
0.91
1.81
1.84
0.97
1.84
2.19
1.97
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
0.5
ppm



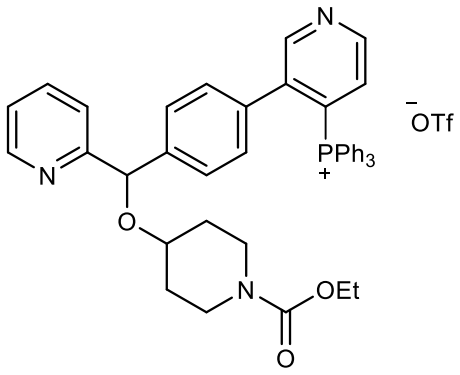
$CDCl_3$, 100 MHz



2d

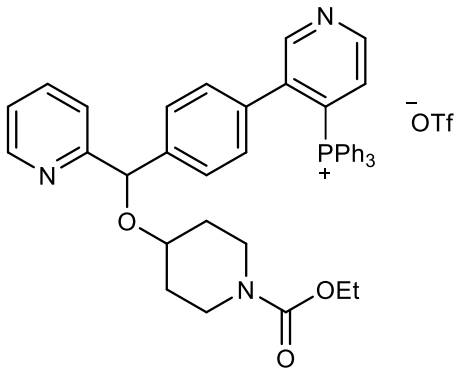

-78.11
CDCl3, 365 MHz
N
PPh3
+
OTf
N
O
N
OEt
O
2d
S293
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

$CDCl_3$, 162 MHz



2d

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

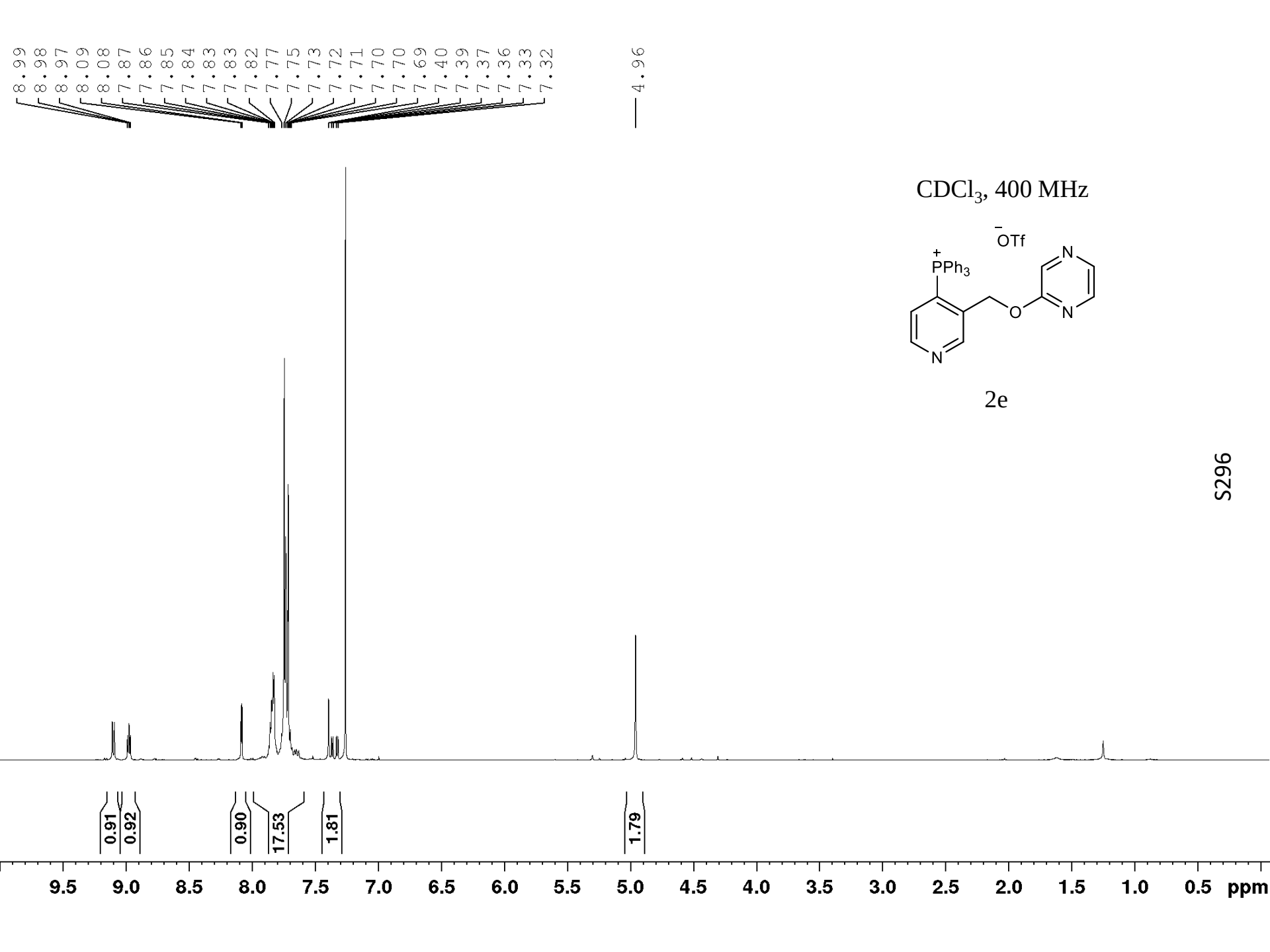


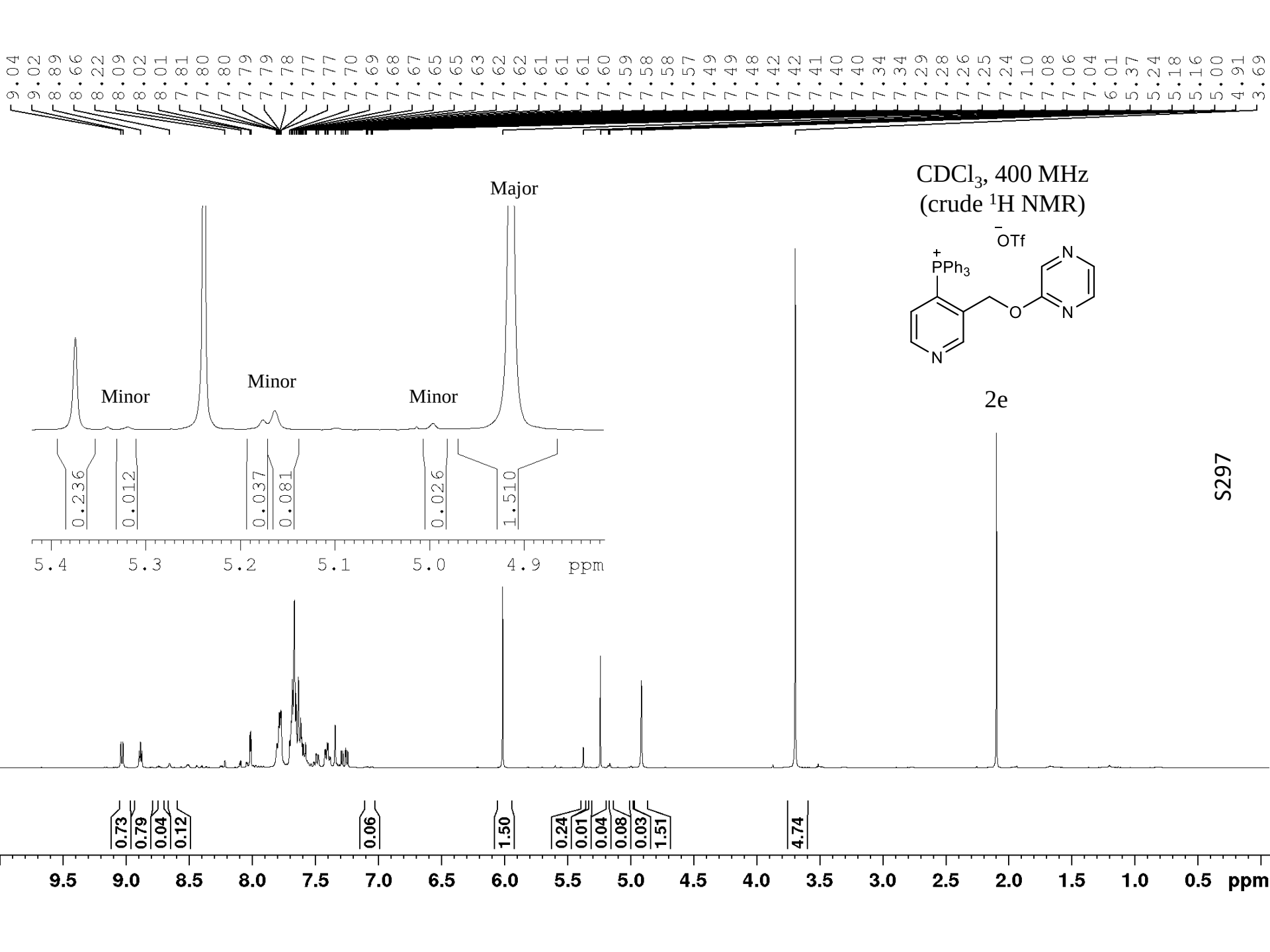
2d

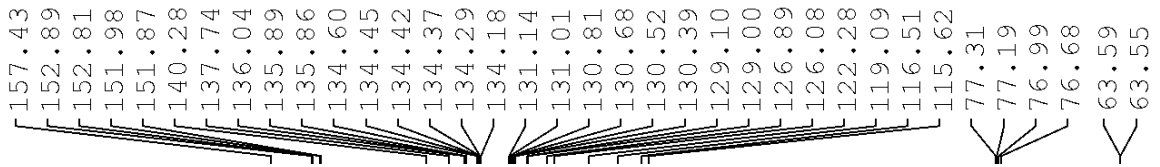
28.95
22.49
21.39

S295

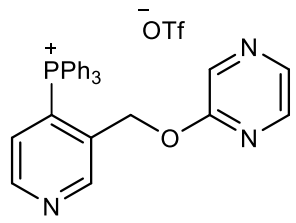
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


8.99
8.98
8.97
8.09
8.08
7.87
7.86
7.85
7.84
7.83
7.83
7.82
7.77
7.75
7.73
7.72
7.71
7.70
7.70
7.69
7.40
7.39
7.37
7.36
7.33
7.32
4.96
CDCl3, 400 MHz
OTf
PPh3
N
O
N
N
2e
S296
0.91
0.92
0.90
17.53
1.81
1.79
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
ppm


9.04 9.02 8.89 8.66 8.22 8.09 8.02 8.01 7.81 7.80 7.80 7.79 7.79 7.78 7.77 7.77 7.70 7.69 7.68 7.67 7.65 7.65 7.63 7.62 7.62 7.61 7.61 7.61 7.60 7.59 7.58 7.58 7.57 7.49 7.49 7.48 7.42 7.42 7.41 7.40 7.40 7.34 7.34 7.29 7.28 7.26 7.25 7.24 7.10 7.08 7.06 7.04 6.01 5.37 5.24 5.18 5.16 5.00 4.91 3.69
CDCl3, 400 MHz
(crude 1H NMR)
OTf
PPh3
2e
Major
Minor
Minor
Minor
0.236
0.012
0.037
0.081
0.026
1.510
5.4 5.3 5.2 5.1 5.0 4.9 ppm
0.73 0.79 0.04 0.12 0.06 1.50 0.24 0.01 0.04 0.08 0.03 1.51 4.74
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 ppm
S297



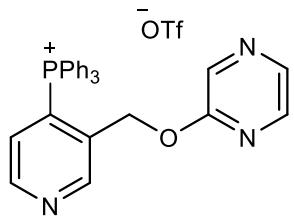
$CDCl_3$, 100 MHz



2e

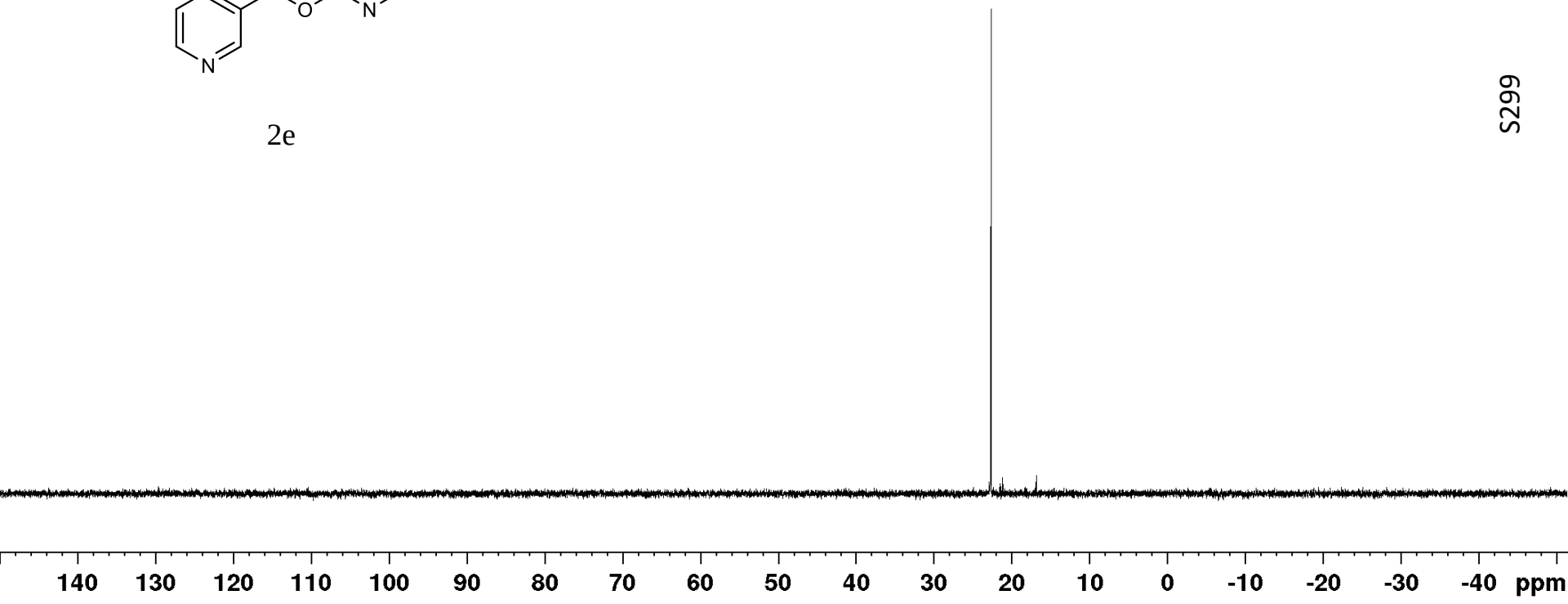
22.66
21.16
16.80

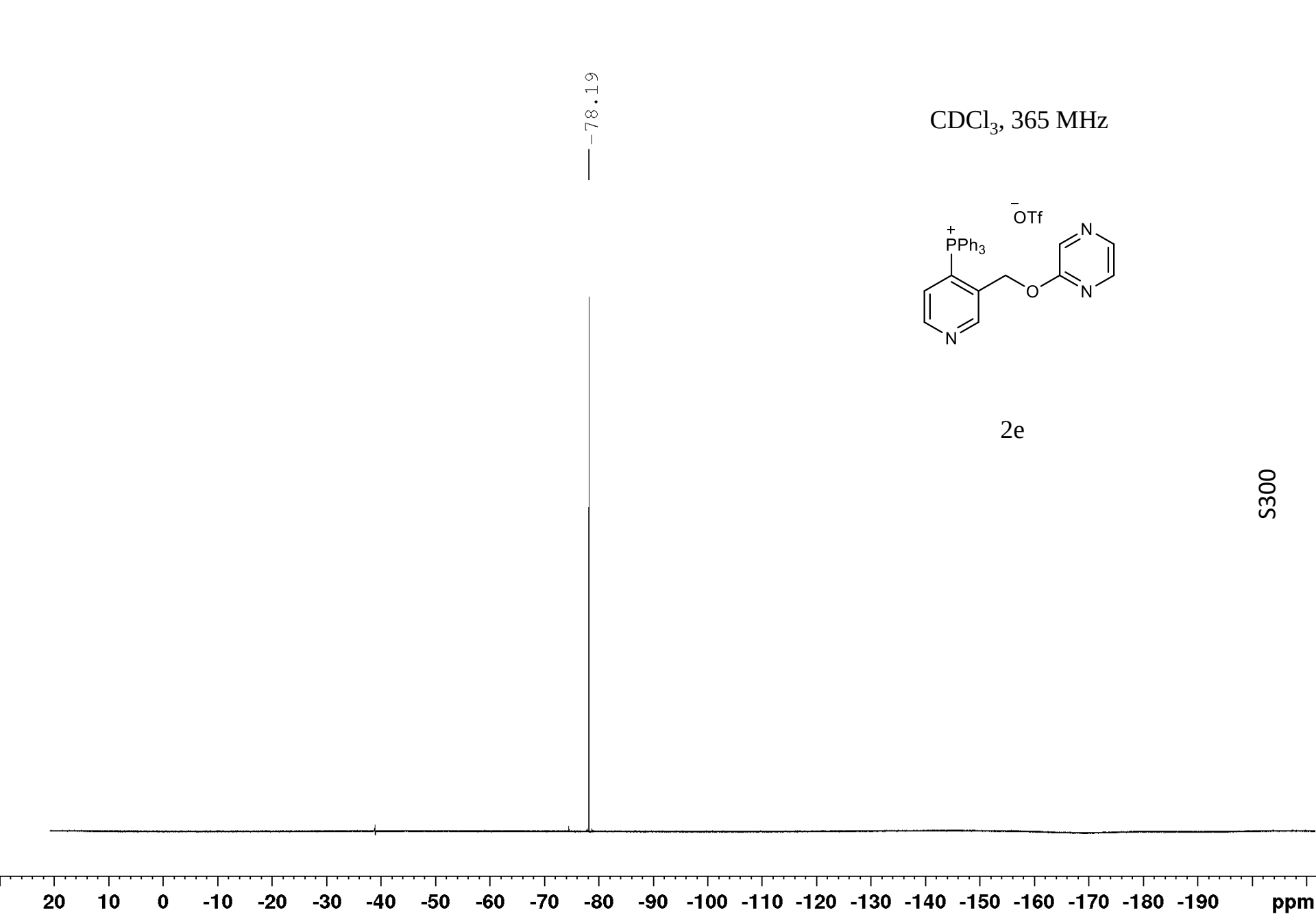
$CDCl_3$, 162 MHz



2e

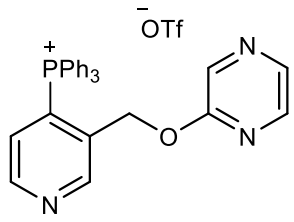
S299




-78.19
CDCl3, 365 MHz
OTf
PPh3
N
O
N
N
2e
S300
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

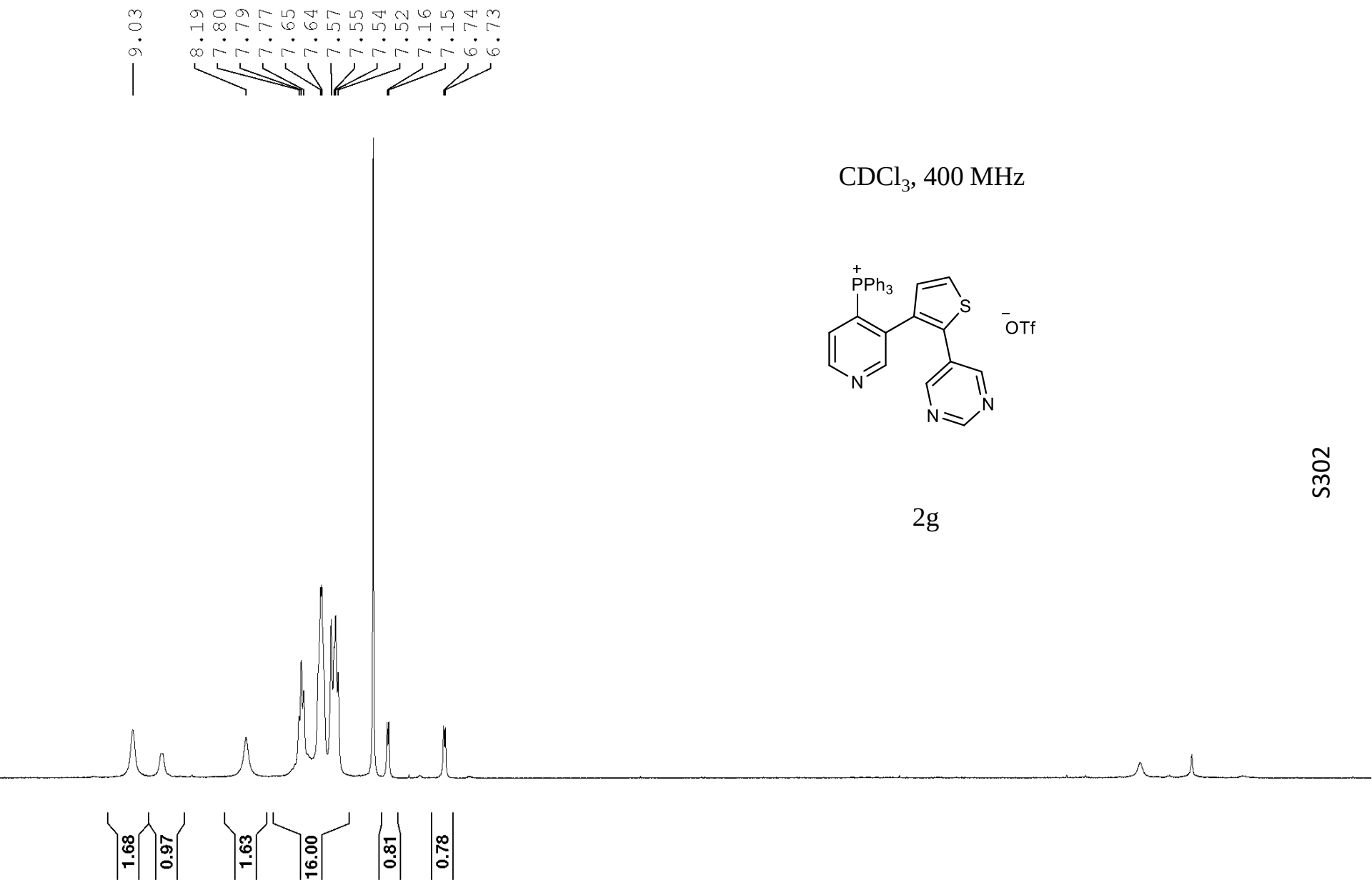
29.16
22.61
21.39
21.33
21.01
16.64

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

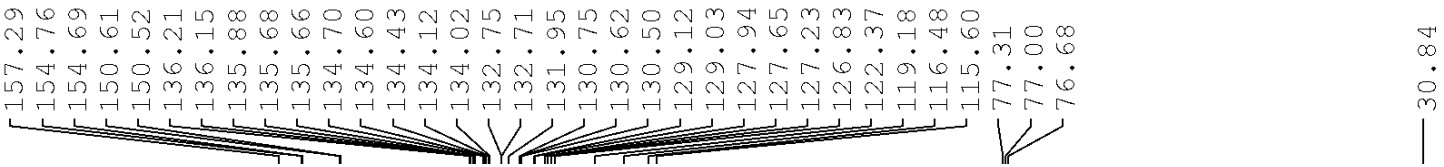


2e

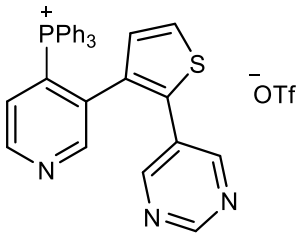
S301


9.03
8.19
7.80
7.79
7.77
7.65
7.64
7.57
7.55
7.54
7.52
7.16
7.15
6.74
6.73
CDCl3, 400 MHz
PPh3
S
OTf
N
N
N
1.68
0.97
1.63
16.00
0.81
0.78
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
ppm

2g

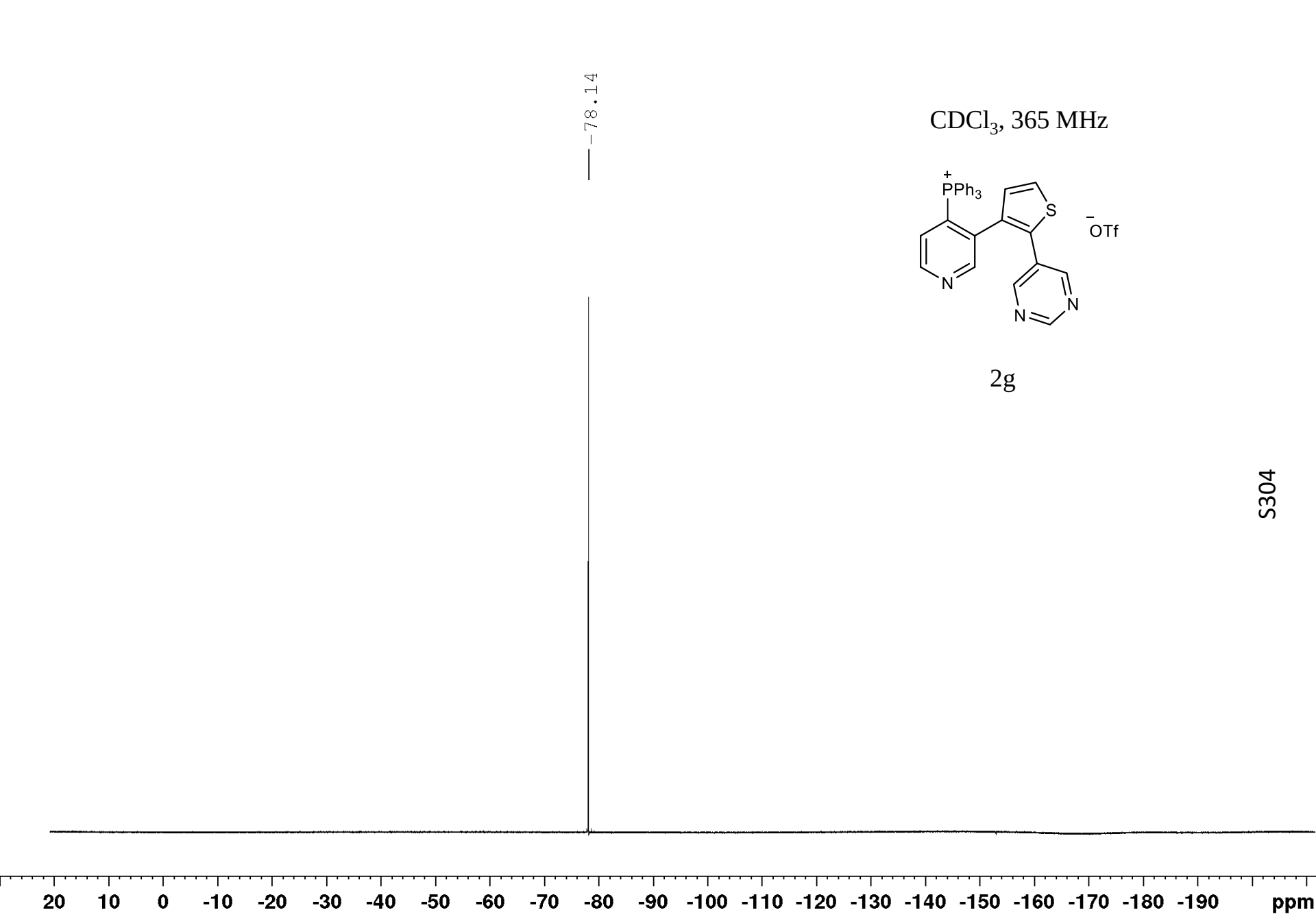


$CDCl_3$, 100 MHz

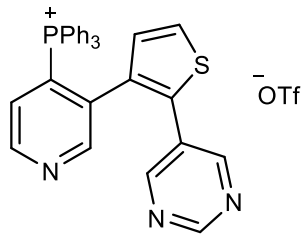


2g

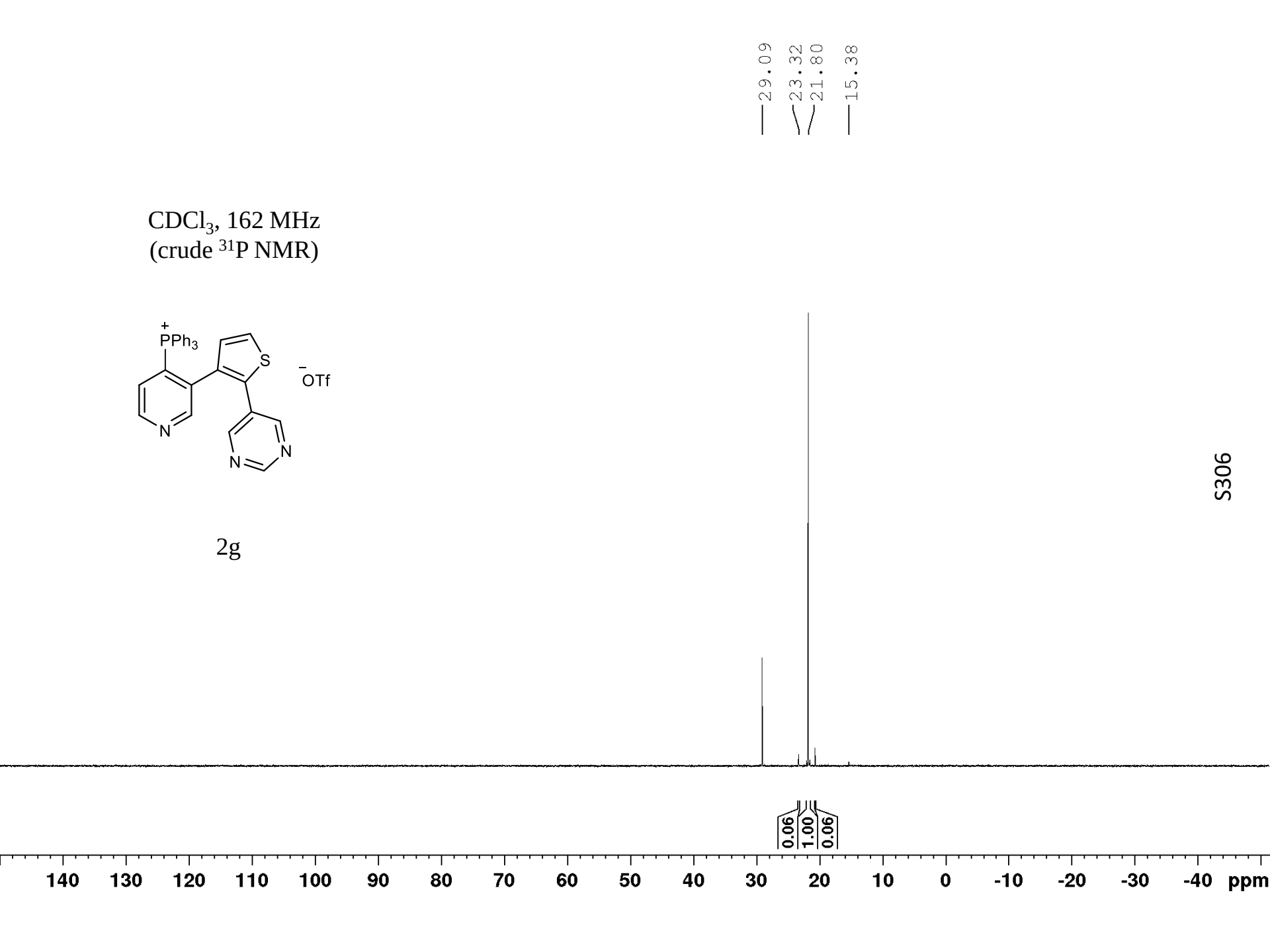
S303

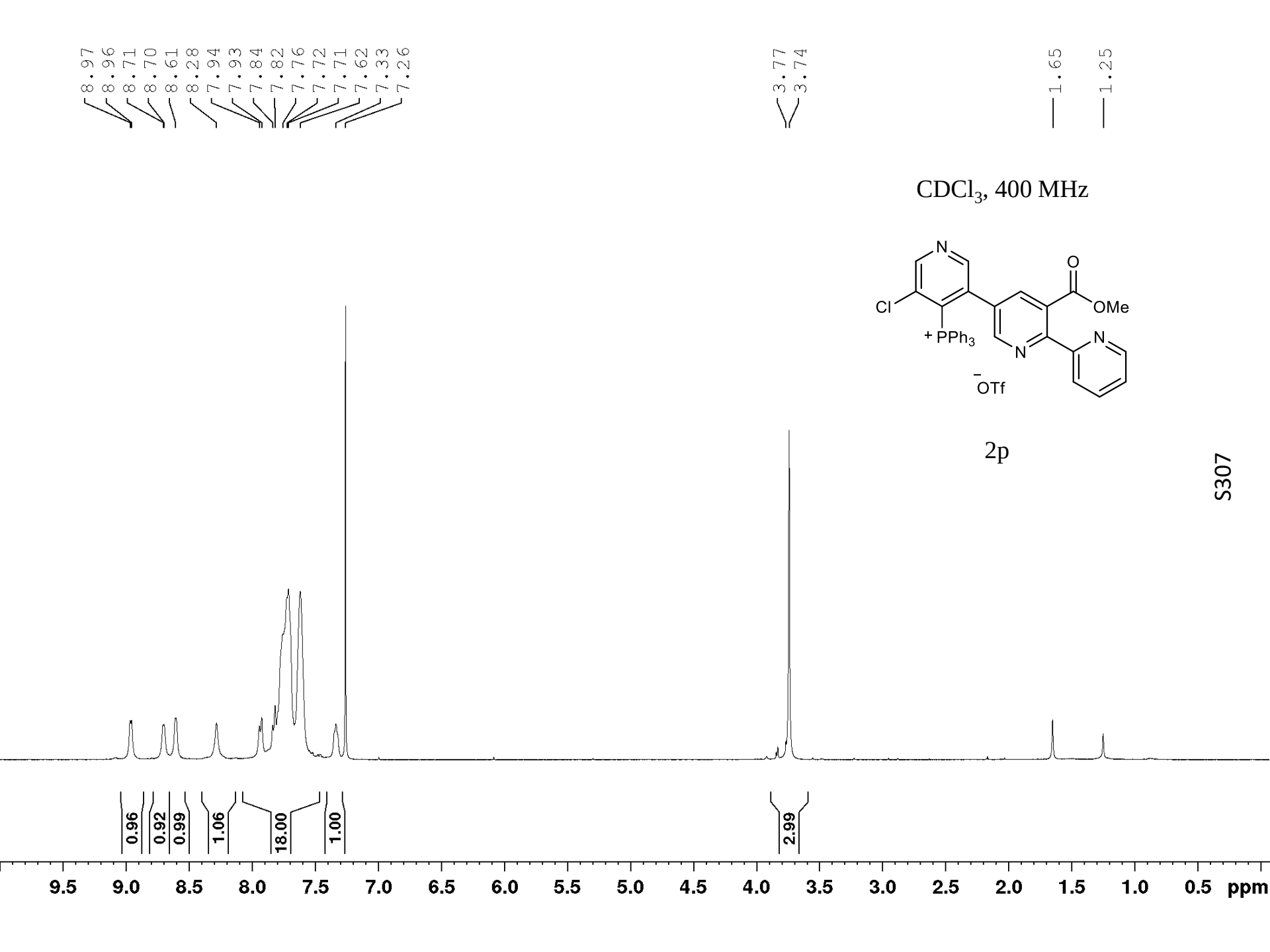

-78.14
CDCl3, 365 MHz
PPh3
S
OTf
N
N
N
2g
S304
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

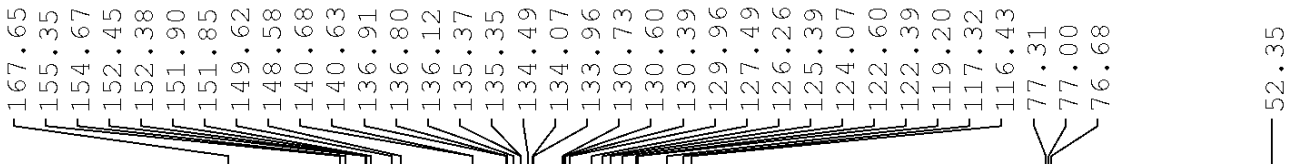
$CDCl_3$, 162 MHz



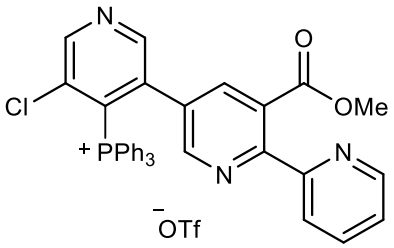
2g


29.09
23.32
21.80
15.38
CDCl3, 162 MHz
(crude 31P NMR)
PPh3
S
OTf
N
N
N
2g
S306
0.06
1.00
0.06
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

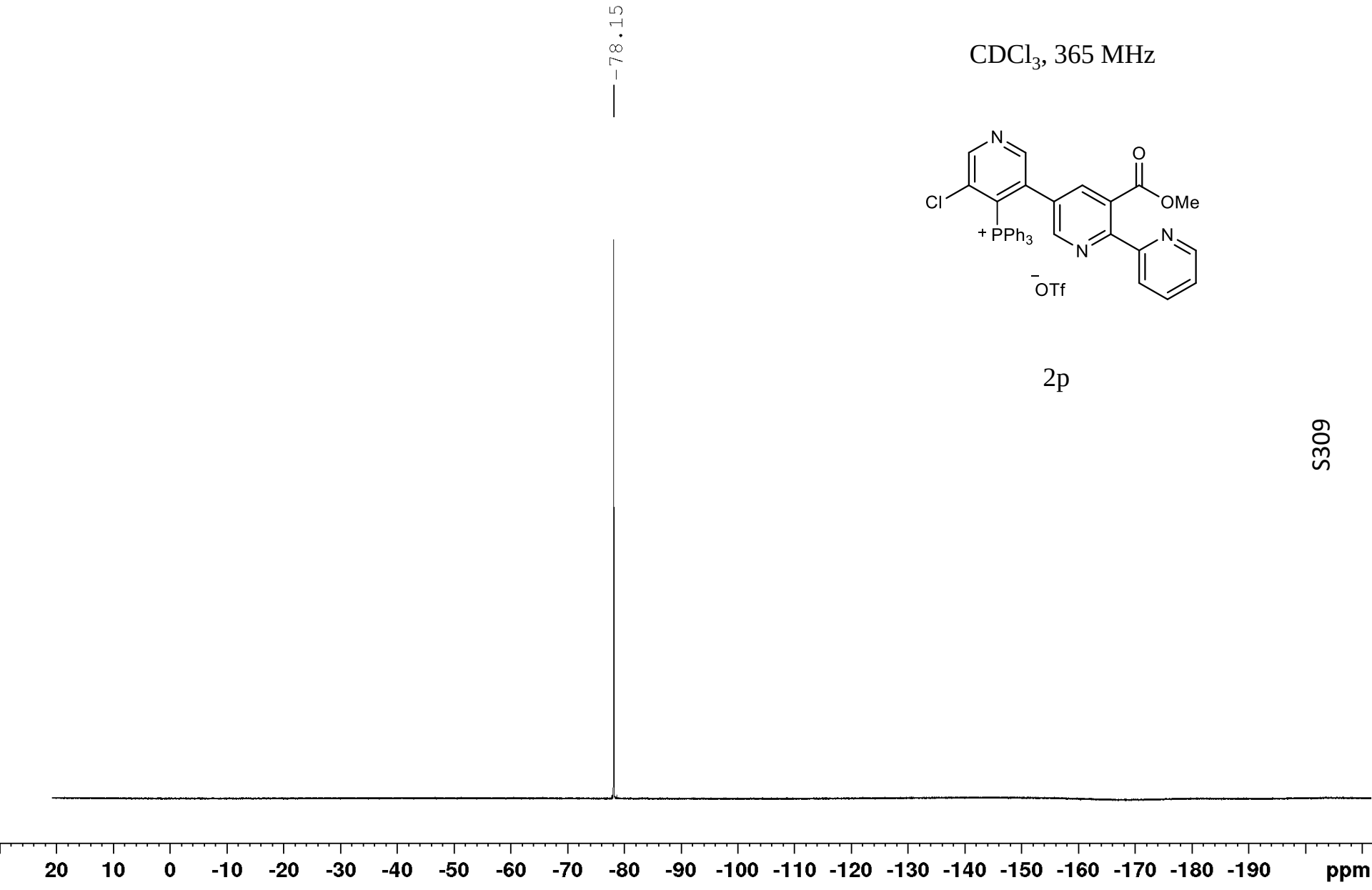

8.97
8.96
8.71
8.70
8.61
8.28
7.94
7.93
7.84
7.82
7.76
7.72
7.71
7.62
7.33
7.26
3.77
3.74
1.65
1.25
CDCl3, 400 MHz
N
O
Cl
OMe
+ PPh3
N
N
OTf
2p
S307
0.96
0.92
0.99
1.06
18.00
1.00
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



$CDCl_3$, 100 MHz

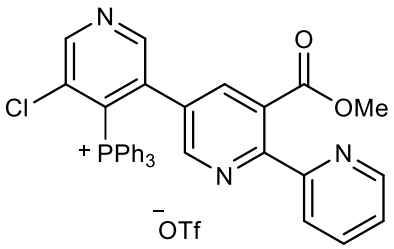


2p


-78.15
CDCl3, 365 MHz
N
O
Cl
OMe
+ PPh3
N
N
OTf
2p
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

21.64
20.78

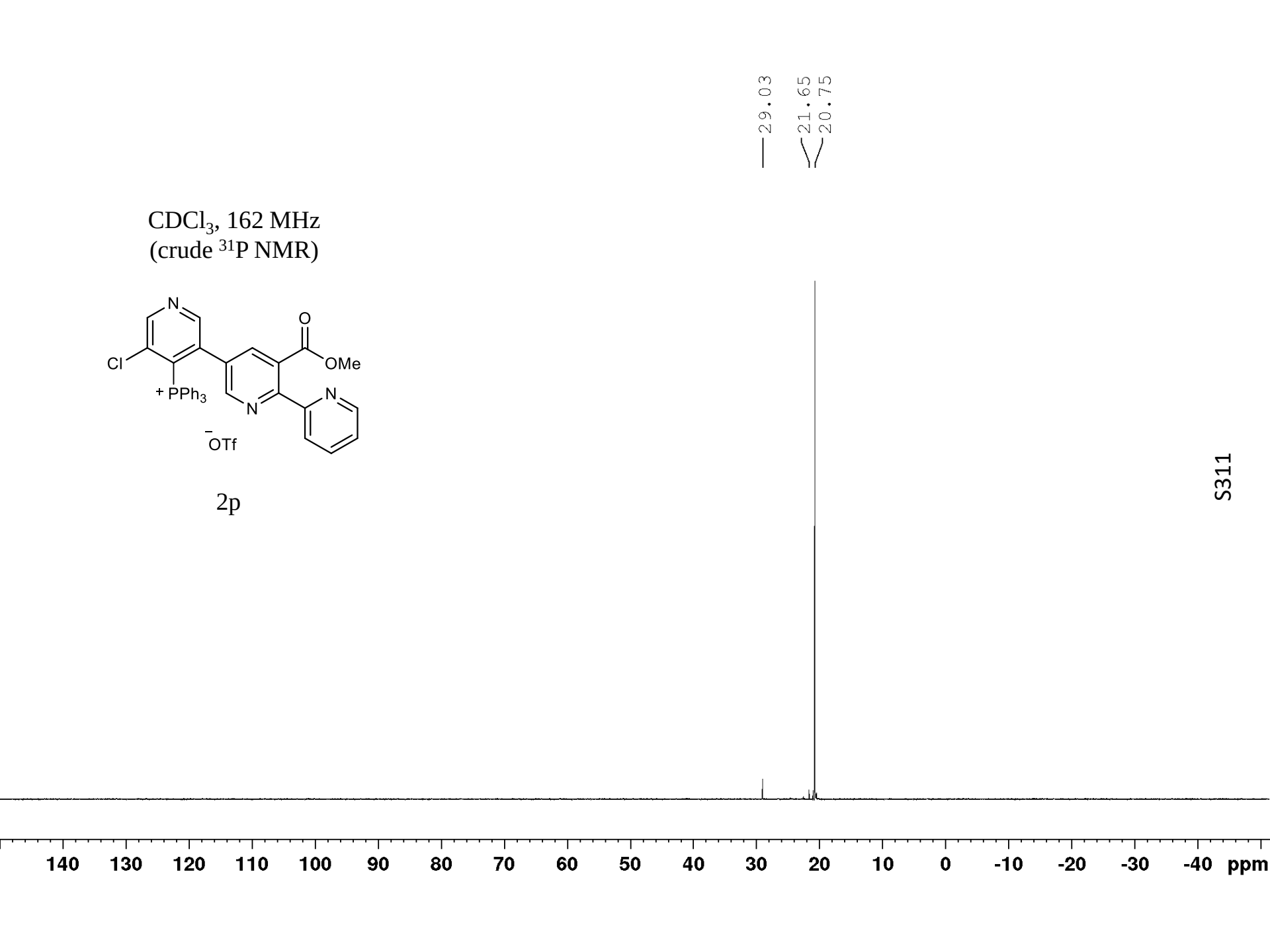
$CDCl_3$, 162 MHz

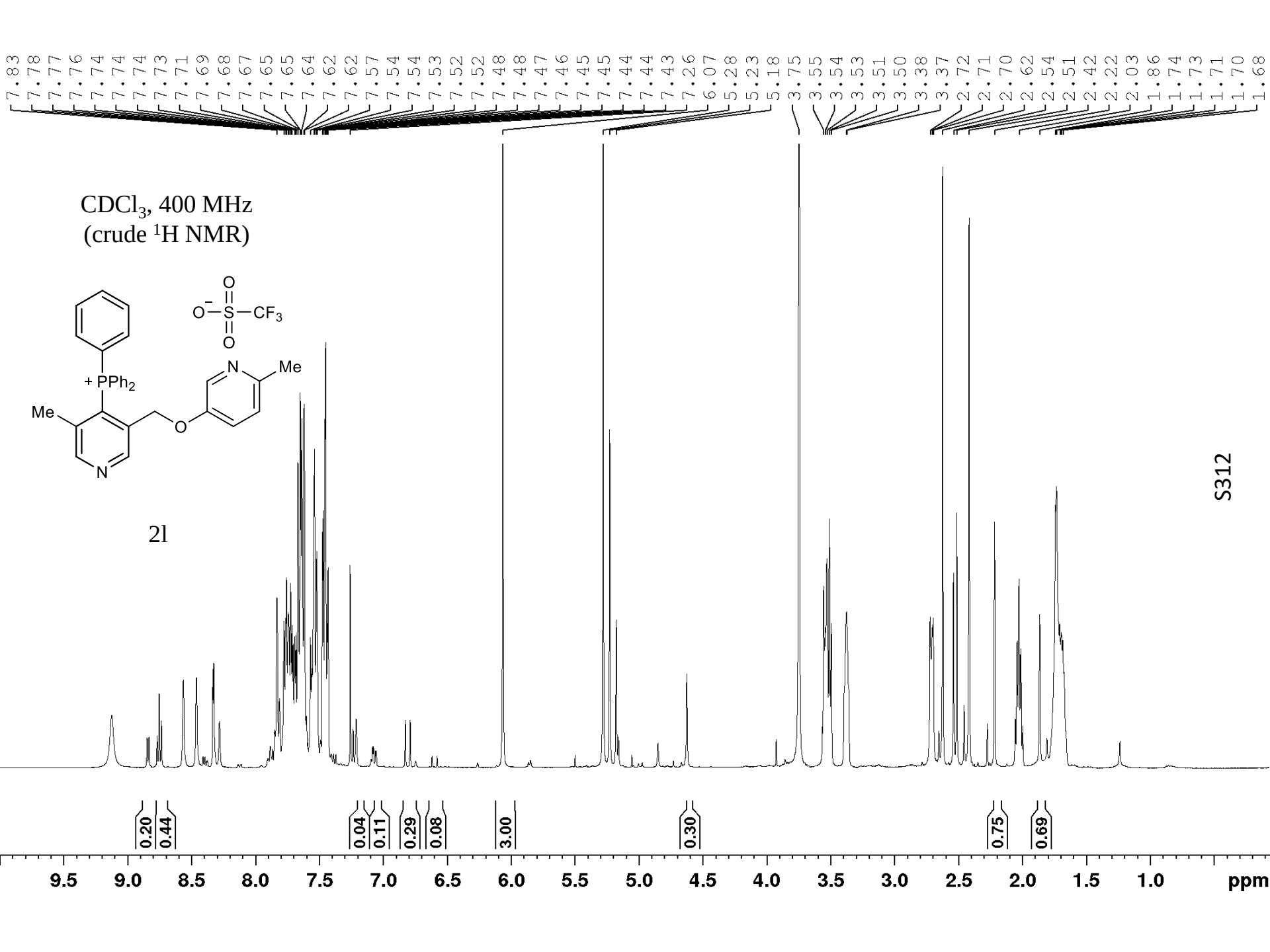


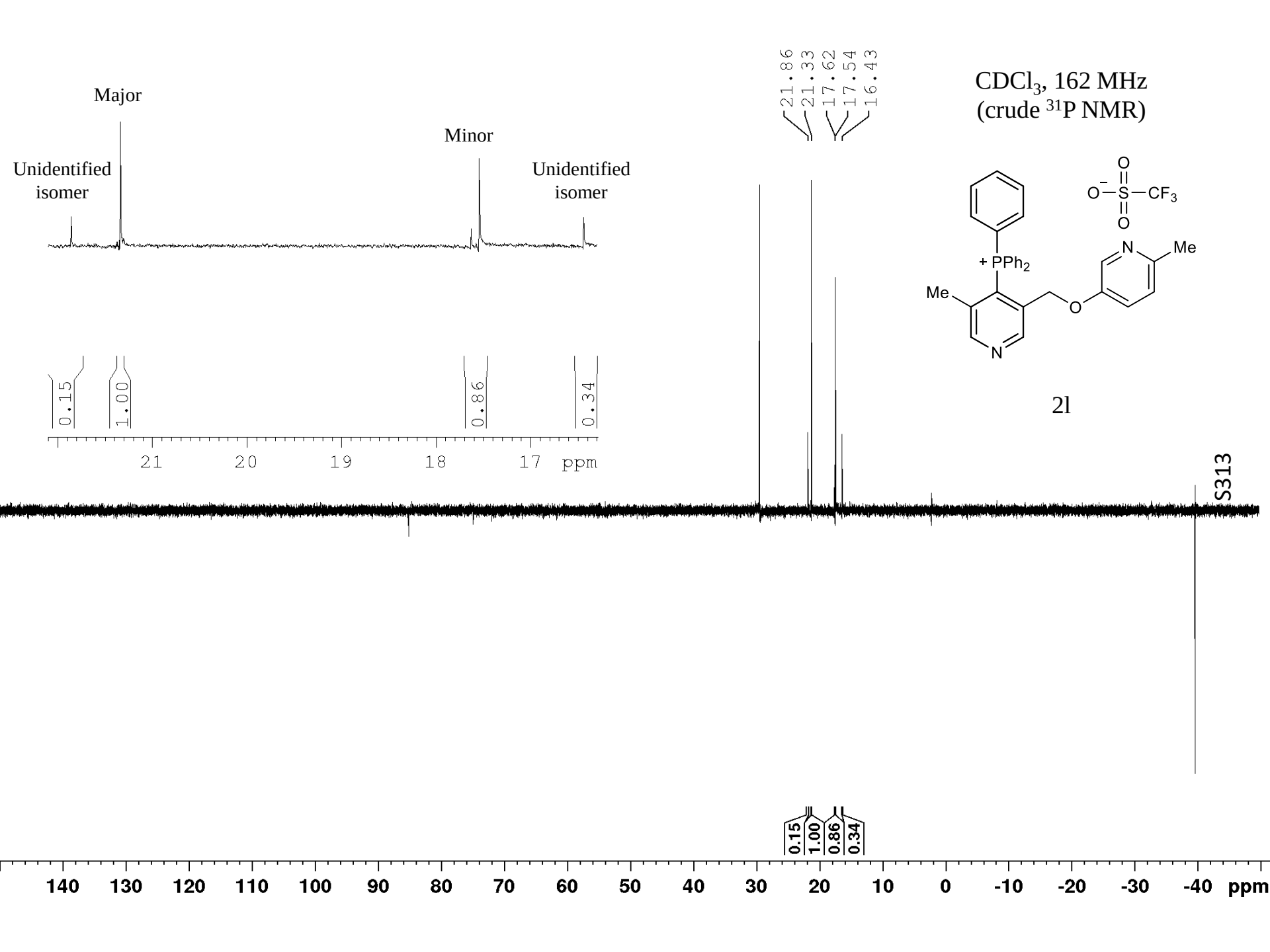
2p

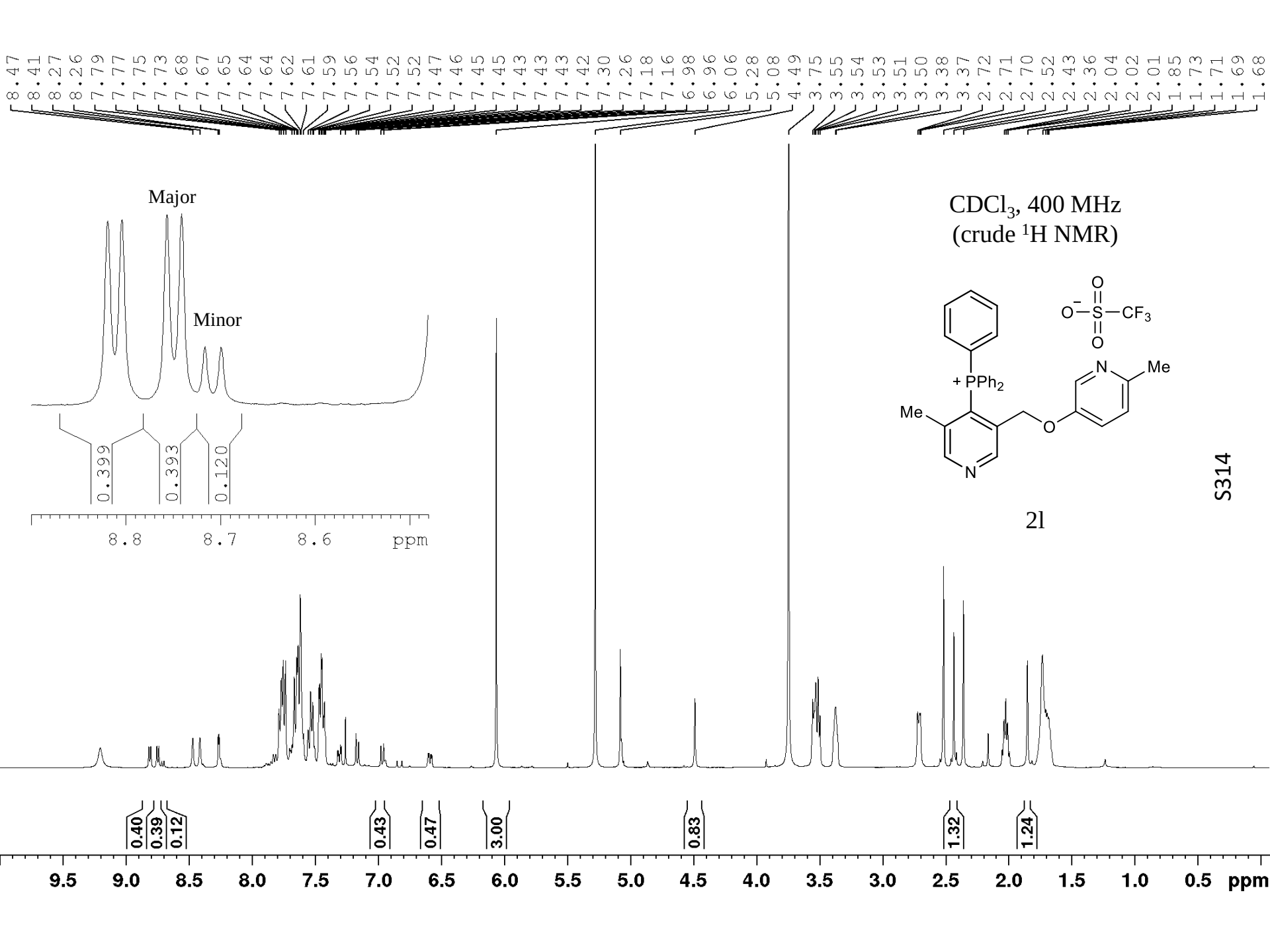
S310

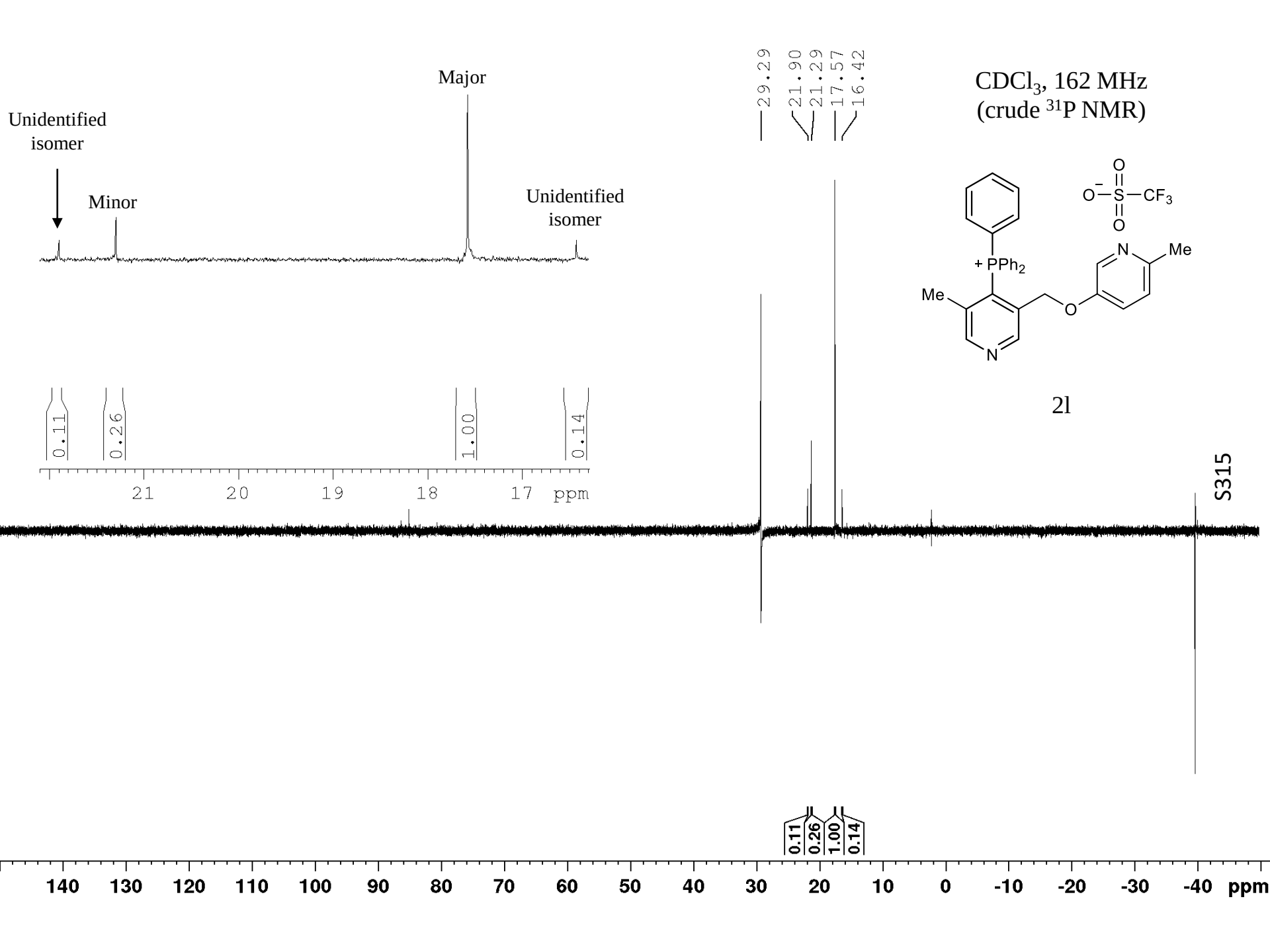
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

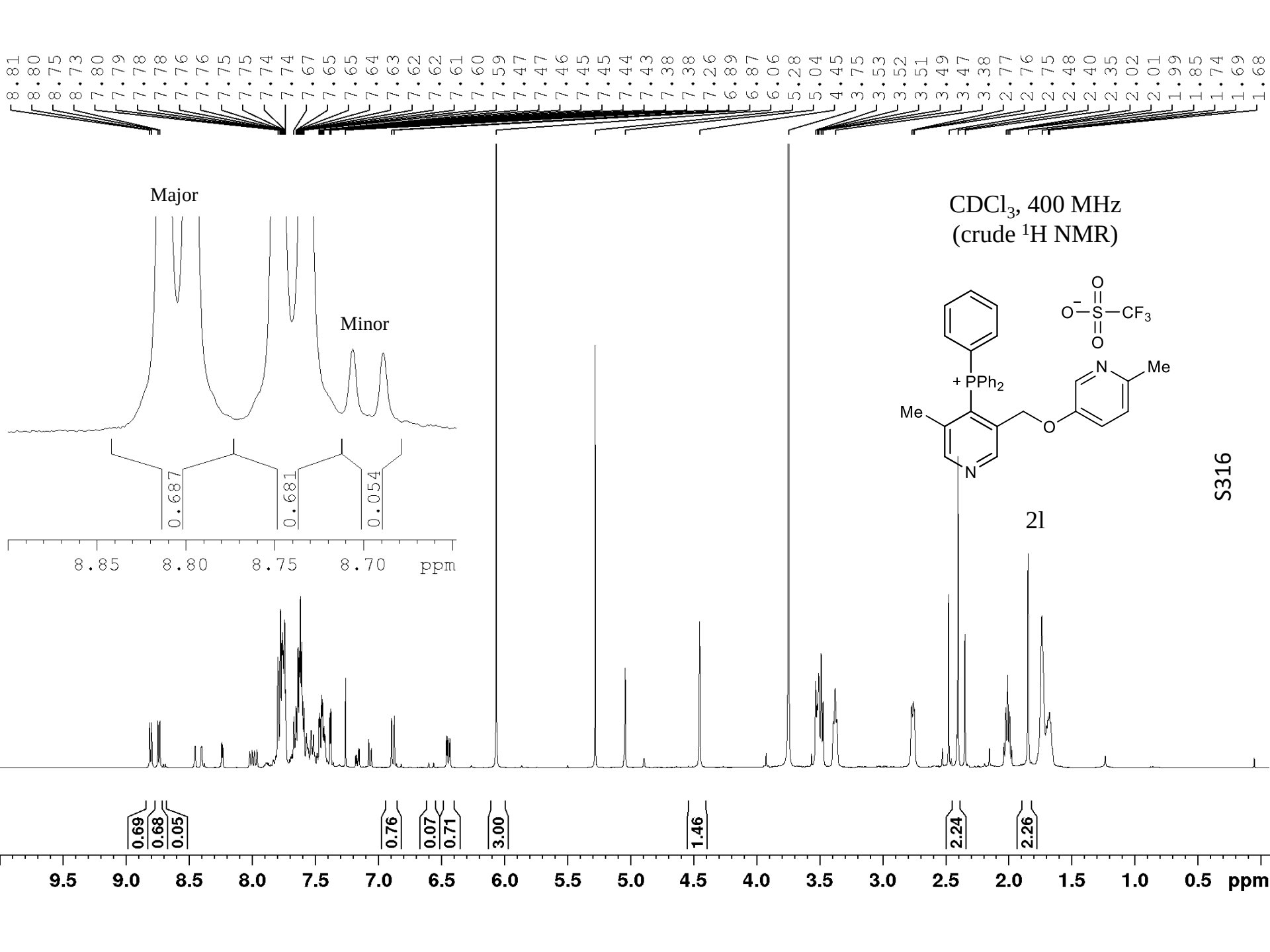

29.03
21.65
20.75
CDCl3, 162 MHz
(crude 31P NMR)
N
Cl
+ PPh3
OTf
O
OMe
N
N
2p
S311
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

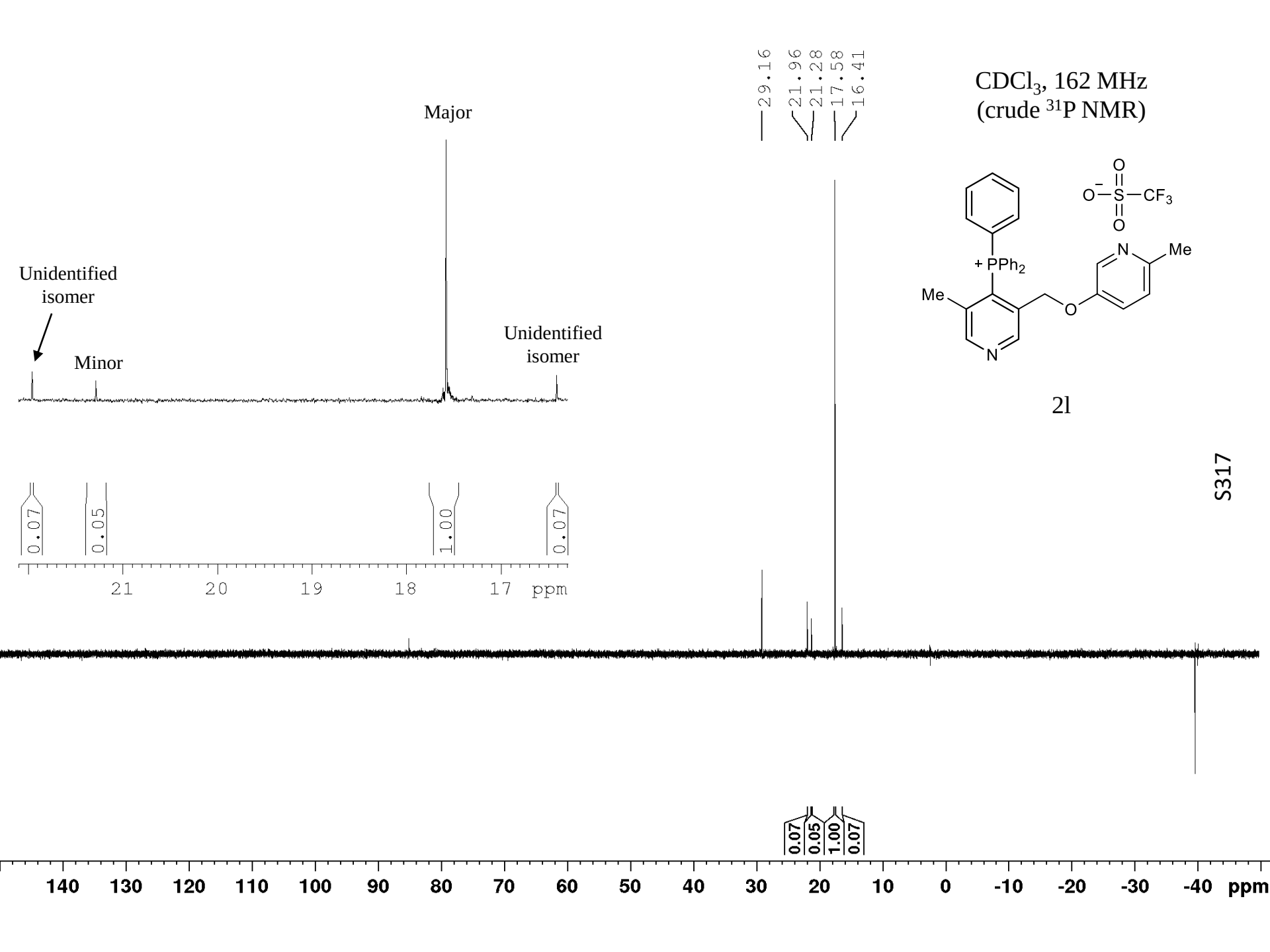

7.83 7.78 7.77 7.76 7.74 7.74 7.74 7.73 7.71 7.69 7.68 7.67 7.65 7.65 7.64 7.62 7.62 7.57 7.54 7.54 7.53 7.52 7.52 7.48 7.48 7.47 7.46 7.45 7.45 7.44 7.44 7.43 7.26 6.07 5.28 5.23 5.18 3.75 3.55 3.54 3.53 3.51 3.50 3.38 3.37 2.72 2.71 2.70 2.62 2.54 2.51 2.42 2.22 2.03 1.86 1.74 1.73 1.71 1.70 1.68
CDCl3, 400 MHz
(crude 1H NMR)
2l
S312
0.20
0.44
0.04
0.11
0.29
0.08
3.00
0.30
0.75
0.69
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

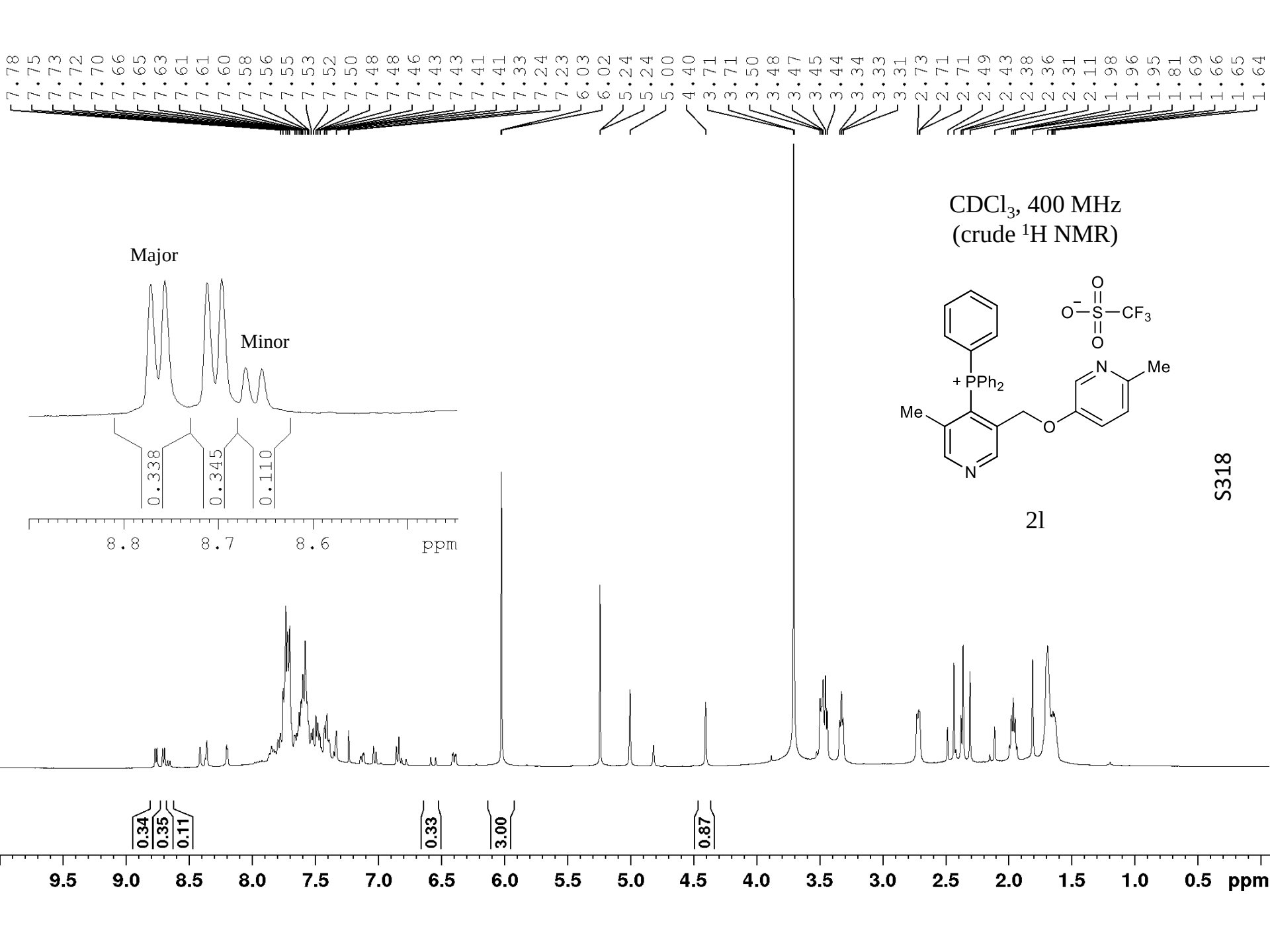

Major
Minor
Unidentified isomer
Unidentified isomer
21.86
21.33
17.62
17.54
16.43
CDCl3, 162 MHz
(crude 31P NMR)
+ PPh2
Me
N
Me
O
O
O
O
S
CF3
2l
0.15
1.00
0.86
0.34
21
20
19
18
17
ppm
S313
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

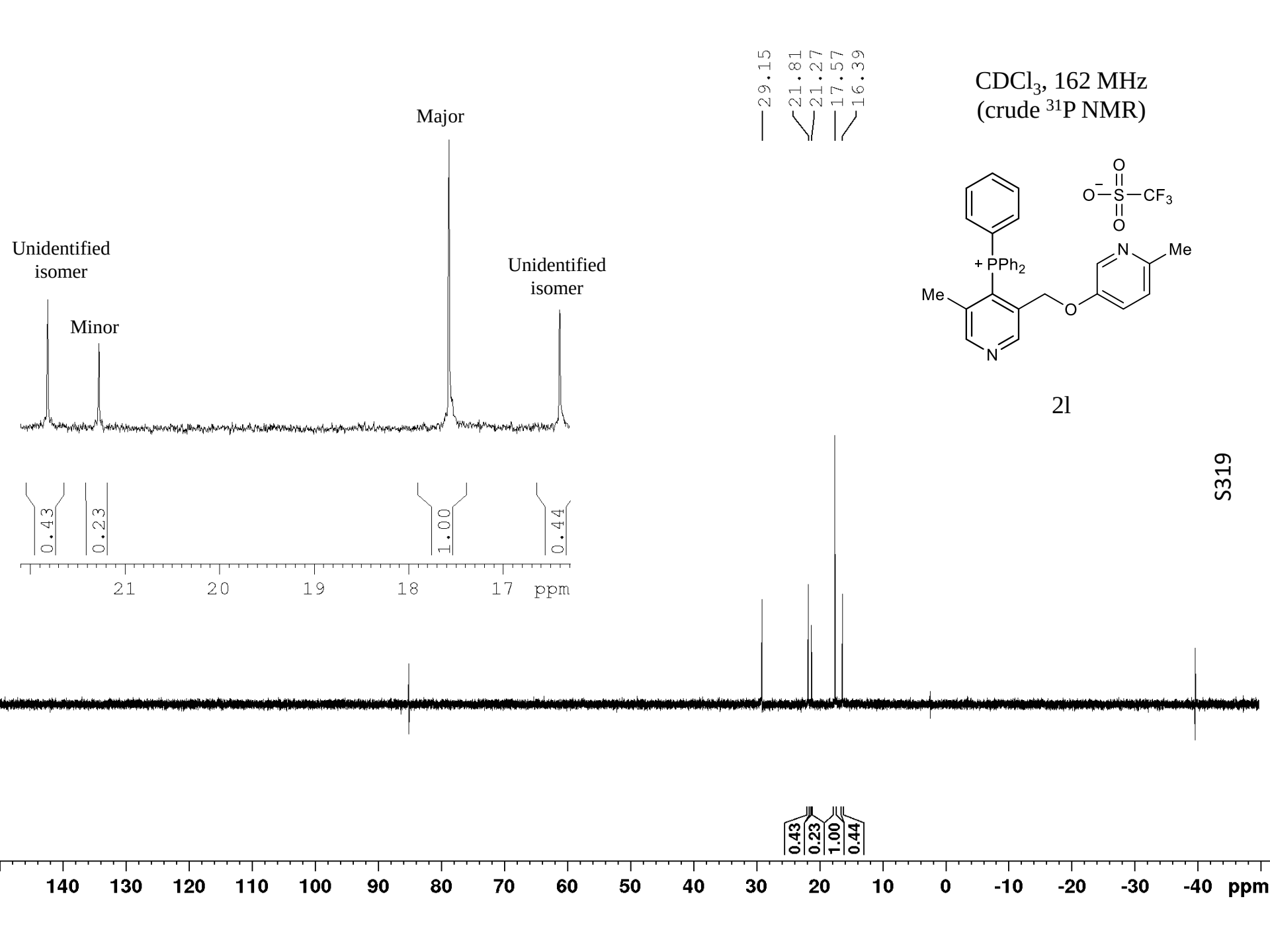

Major
Minor
0.399
0.393
0.120
8.8
8.7
8.6
ppm
CDCl3, 400 MHz
(crude 1H NMR)
+ PPh2
Me
O
N
Me
O
O
O
S
CF3
2l
S314
0.40
0.39
0.12
0.43
0.47
3.00
0.83
1.32
1.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

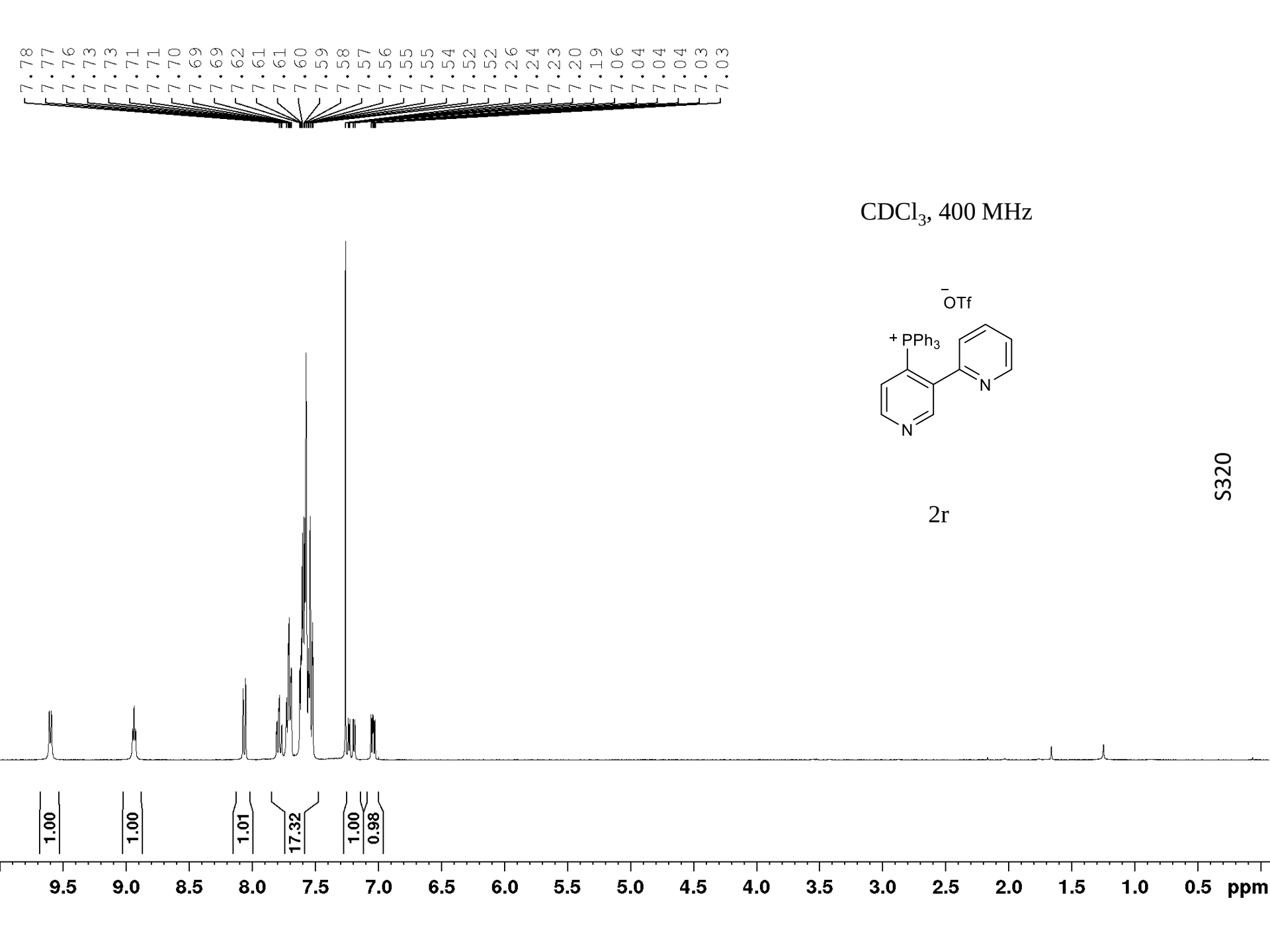

Major
Unidentified isomer
Minor
Unidentified isomer
29.29
21.90
21.29
17.57
16.42
CDCl3, 162 MHz
(crude 31P NMR)
+ PPh2
Me
N
Me
O
O
O
O
S
CF3
2l
0.11
0.26
1.00
0.14
21
20
19
18
17
ppm
S315
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

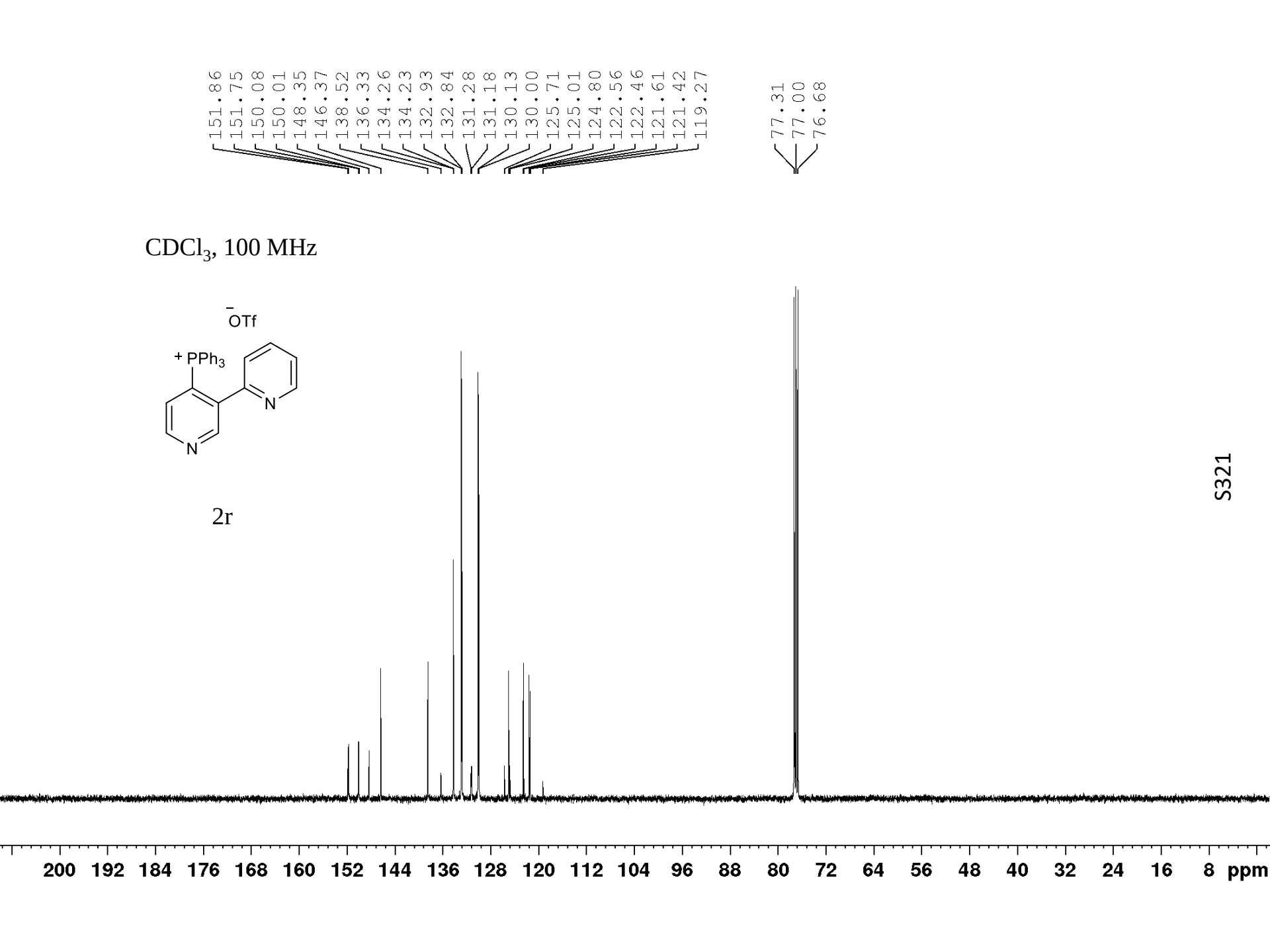

Major
Minor
0.687
0.681
0.054
8.85
8.80
8.75
8.70
ppm
CDCl3, 400 MHz
(crude 1H NMR)
+ PPh2
Me
N
Me
O
O
O
O
S
CF3
2l
S316
0.69
0.68
0.05
0.76
0.07
0.71
3.00
1.46
2.24
2.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

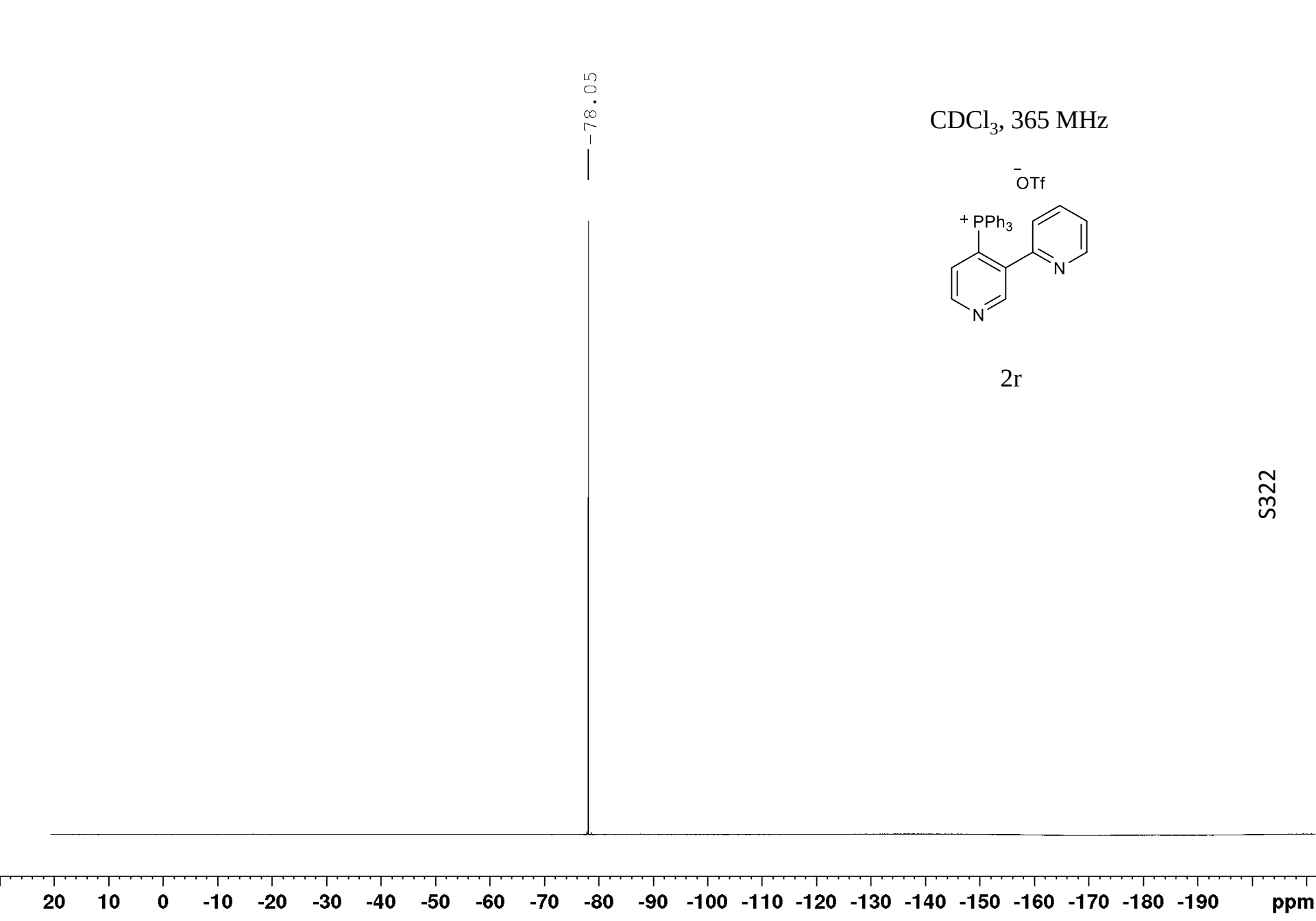

29.16
21.96
21.28
17.58
16.41
CDCl3, 162 MHz
(crude 31P NMR)
Major
Unidentified
isomer
Minor
Unidentified
isomer
0.07
0.05
1.00
0.07
21
20
19
18
17
ppm
2l
S317
0.07
0.05
1.00
0.07
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

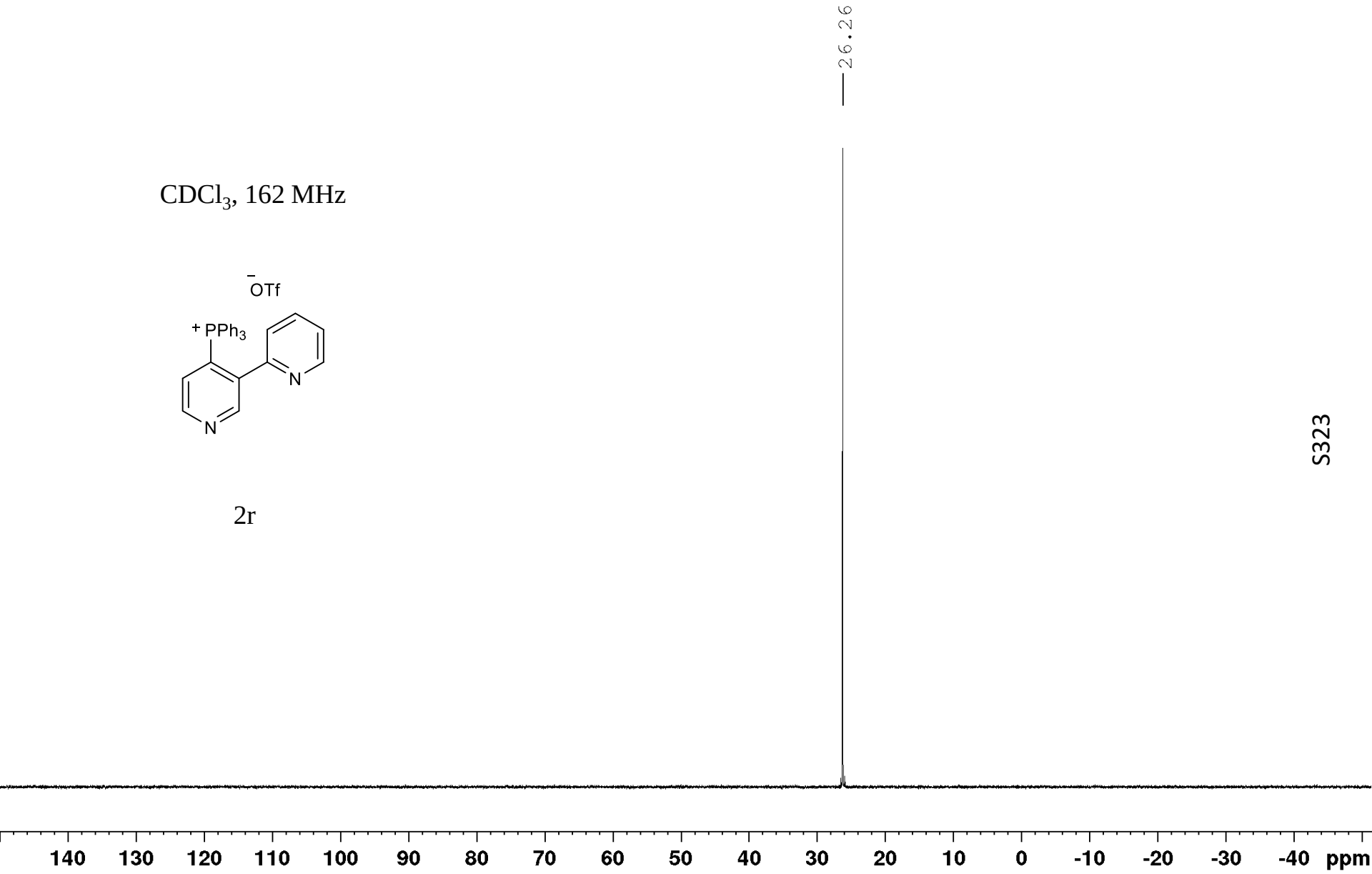

7.78 7.75 7.73 7.72 7.70 7.66 7.65 7.63 7.61 7.61 7.60 7.58 7.56 7.55 7.53 7.52 7.50 7.48 7.48 7.46 7.43 7.43 7.41 7.41 7.33 7.24 7.23 6.03 6.02 5.24 5.24 5.00 4.40 3.71 3.71 3.50 3.48 3.47 3.45 3.44 3.34 3.33 3.31 2.73 2.71 2.71 2.49 2.43 2.38 2.36 2.31 2.11 1.98 1.96 1.95 1.81 1.69 1.66 1.65 1.64
CDCl3, 400 MHz
(crude 1H NMR)
Major
Minor
0.338
0.345
0.110
8.8
8.7
8.6
ppm
+ PPh2
Me
N
Me
O
N
O
O
O
S
CF3
2l
S318
0.34
0.35
0.11
0.33
3.00
0.87
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 ppm

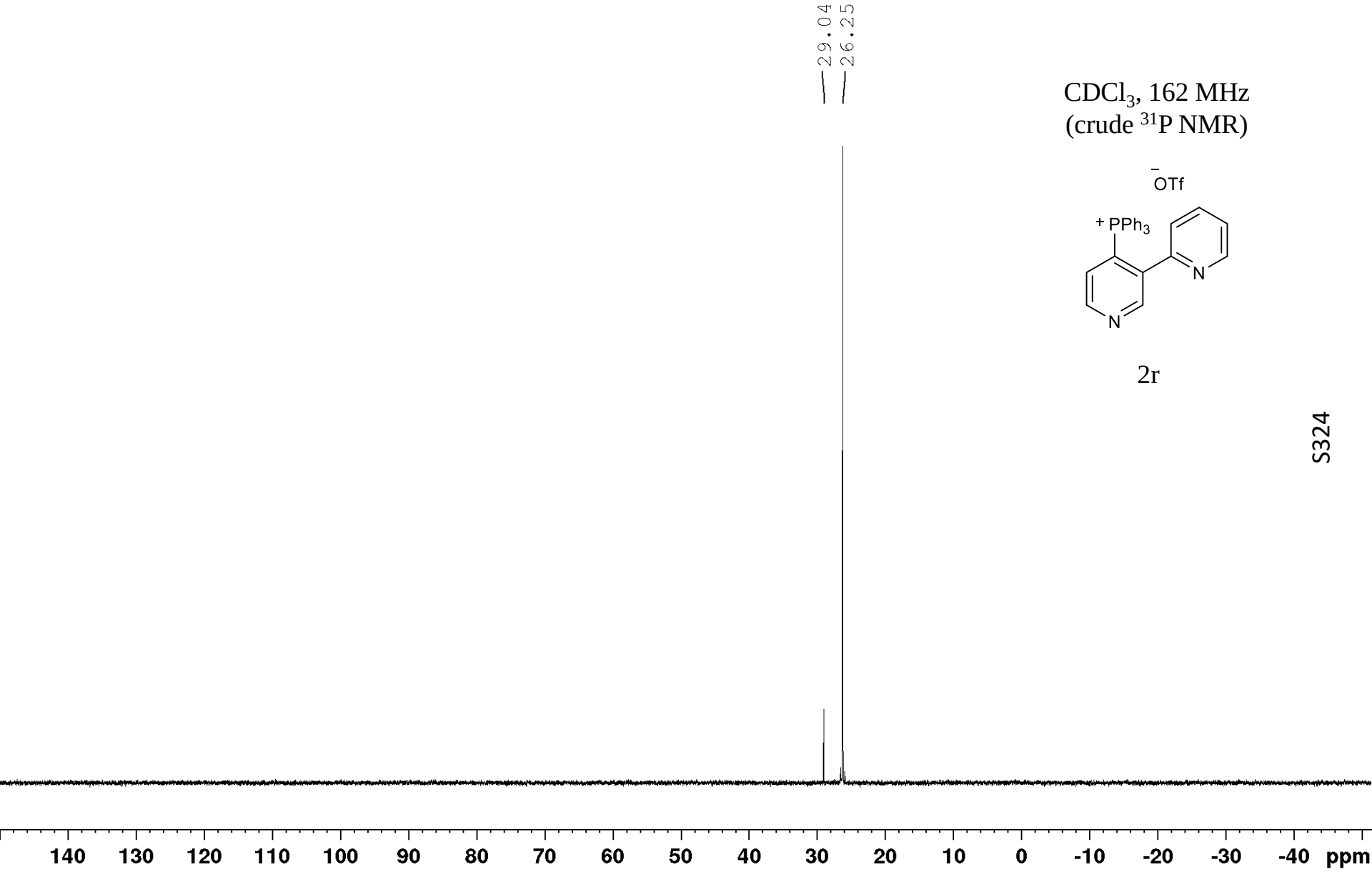

29.15
21.81
21.27
17.57
16.39
CDCl3, 162 MHz
(crude 31P NMR)
Major
Unidentified isomer
Minor
Unidentified isomer
2l
S319
0.43
0.23
1.00
0.44
21
20
19
18
17
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

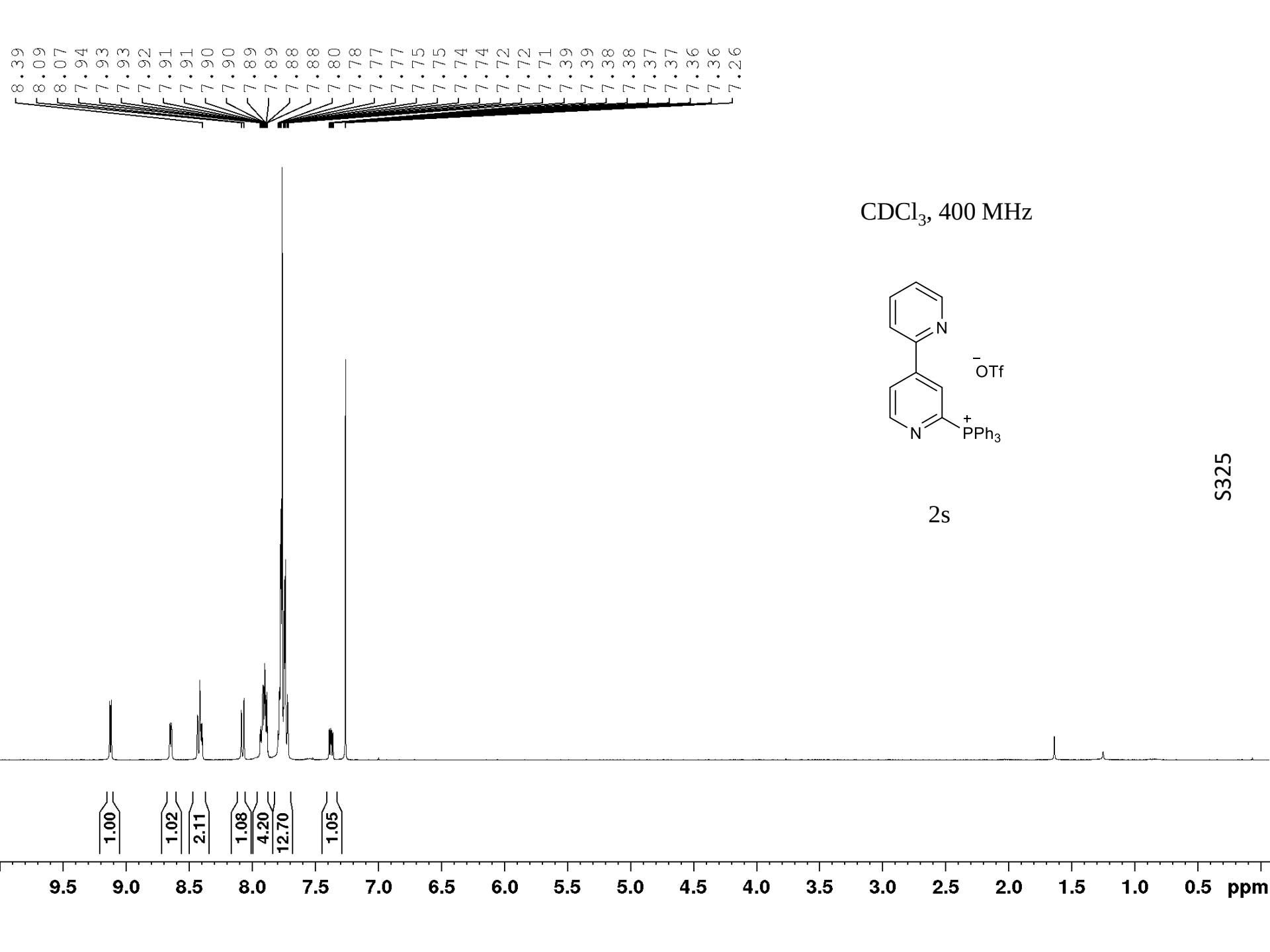

7.78
7.77
7.76
7.73
7.73
7.71
7.71
7.70
7.69
7.69
7.62
7.61
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.55
7.54
7.52
7.52
7.26
7.24
7.23
7.20
7.19
7.06
7.04
7.04
7.04
7.03
7.03
CDCl3, 400 MHz
OTf
+ PPh3
N
N
S320
2r
1.00
1.00
1.01
17.32
1.00
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

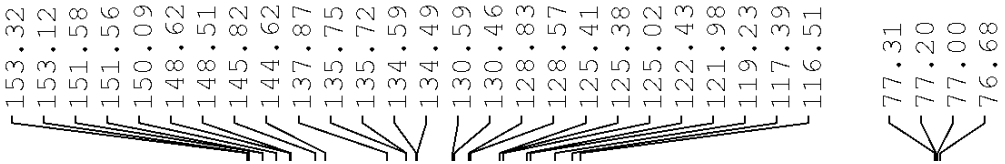

151.86
151.75
150.08
150.01
148.35
146.37
138.52
136.33
134.26
134.23
132.93
132.84
131.28
131.18
130.13
130.00
125.71
125.01
124.80
122.56
122.46
121.61
121.42
119.27
77.31
77.00
76.68
CDCl3, 100 MHz
OTf
+ PPh3
N
N
2r
S321
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


-78.05
CDCl3, 365 MHz
OTf
+ PPh3
N
N
2r
S322
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

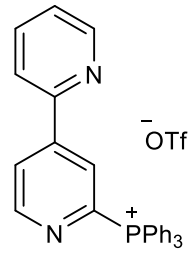

26.26
CDCl3, 162 MHz
OTf
+ PPh3
N
N
2r
S323
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


29.04
26.25
CDCl3, 162 MHz
(crude 31P NMR)
OTf
+ PPh3
N
N
2r
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

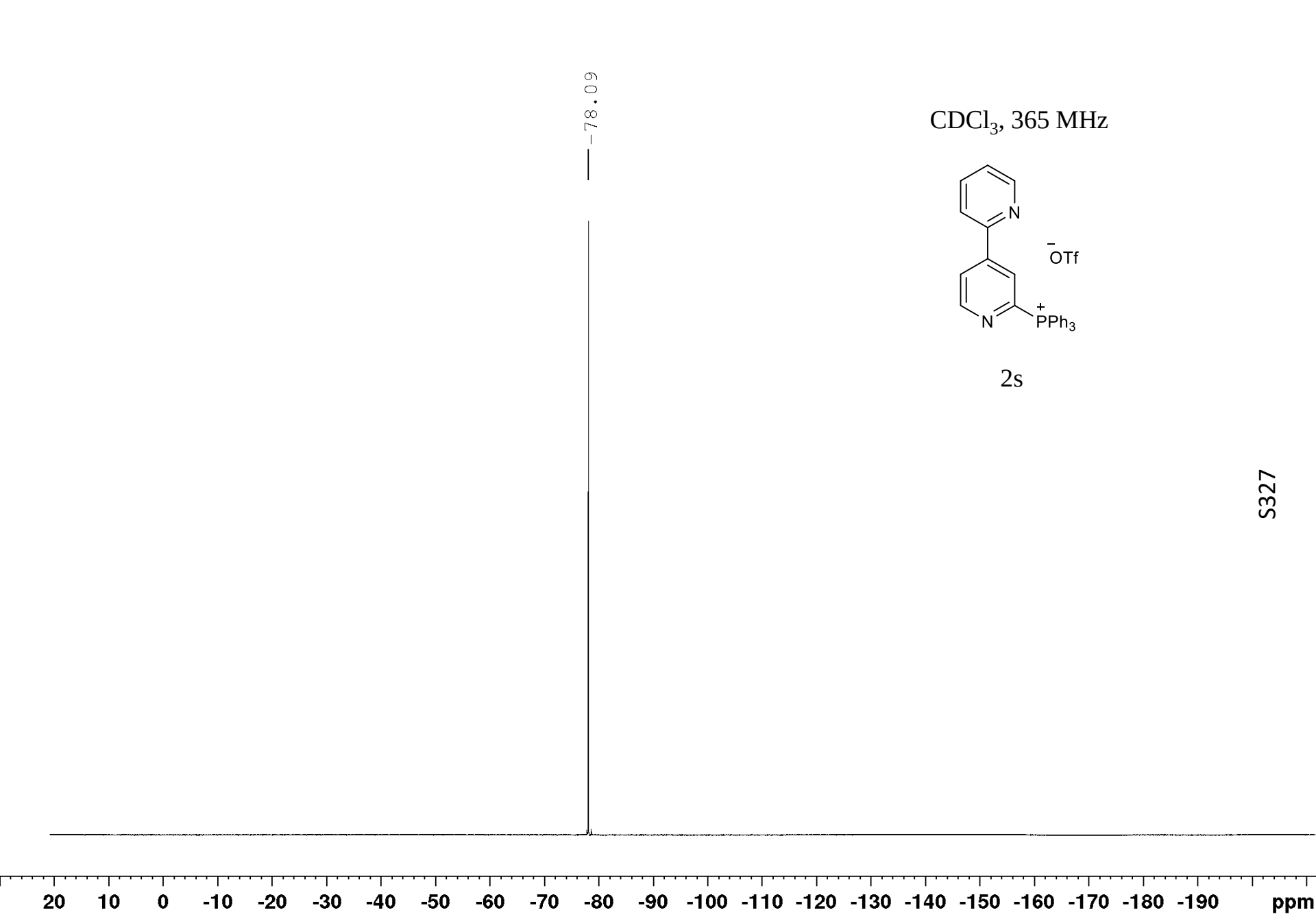

8.39
8.09
8.07
7.94
7.93
7.93
7.92
7.91
7.91
7.90
7.90
7.89
7.89
7.88
7.88
7.80
7.78
7.77
7.77
7.75
7.75
7.74
7.74
7.72
7.72
7.71
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.26
CDCl3, 400 MHz
N
OTf
N
PPh3
2s
S325
1.00
1.02
2.11
1.08
4.20
12.70
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



$CDCl_3$, 100 MHz

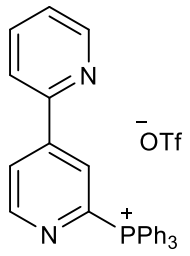


2s


-78.09
CDCl3, 365 MHz
N
OTf
N
PPh3
2s
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

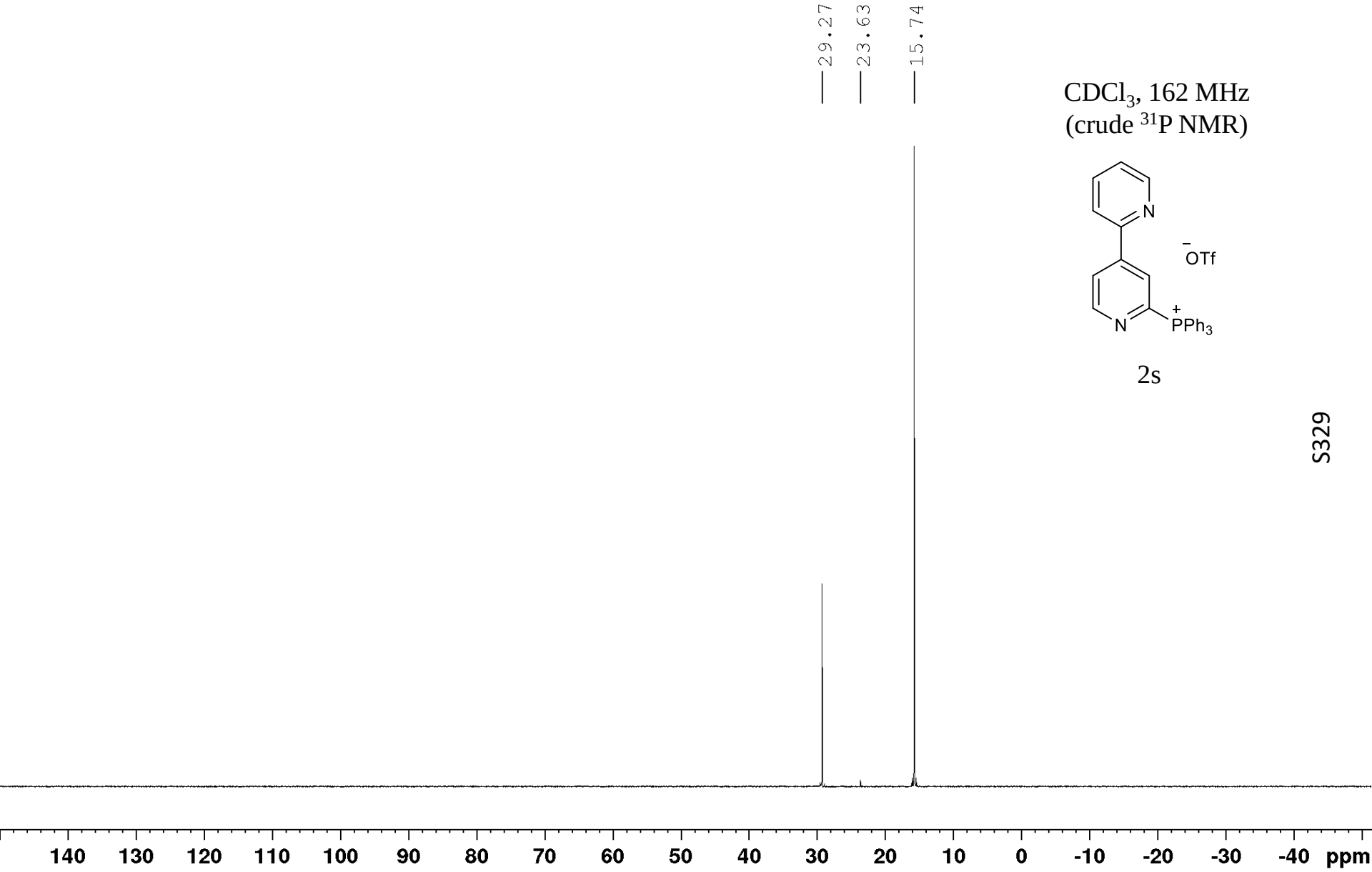
16.06
15.79
15.51

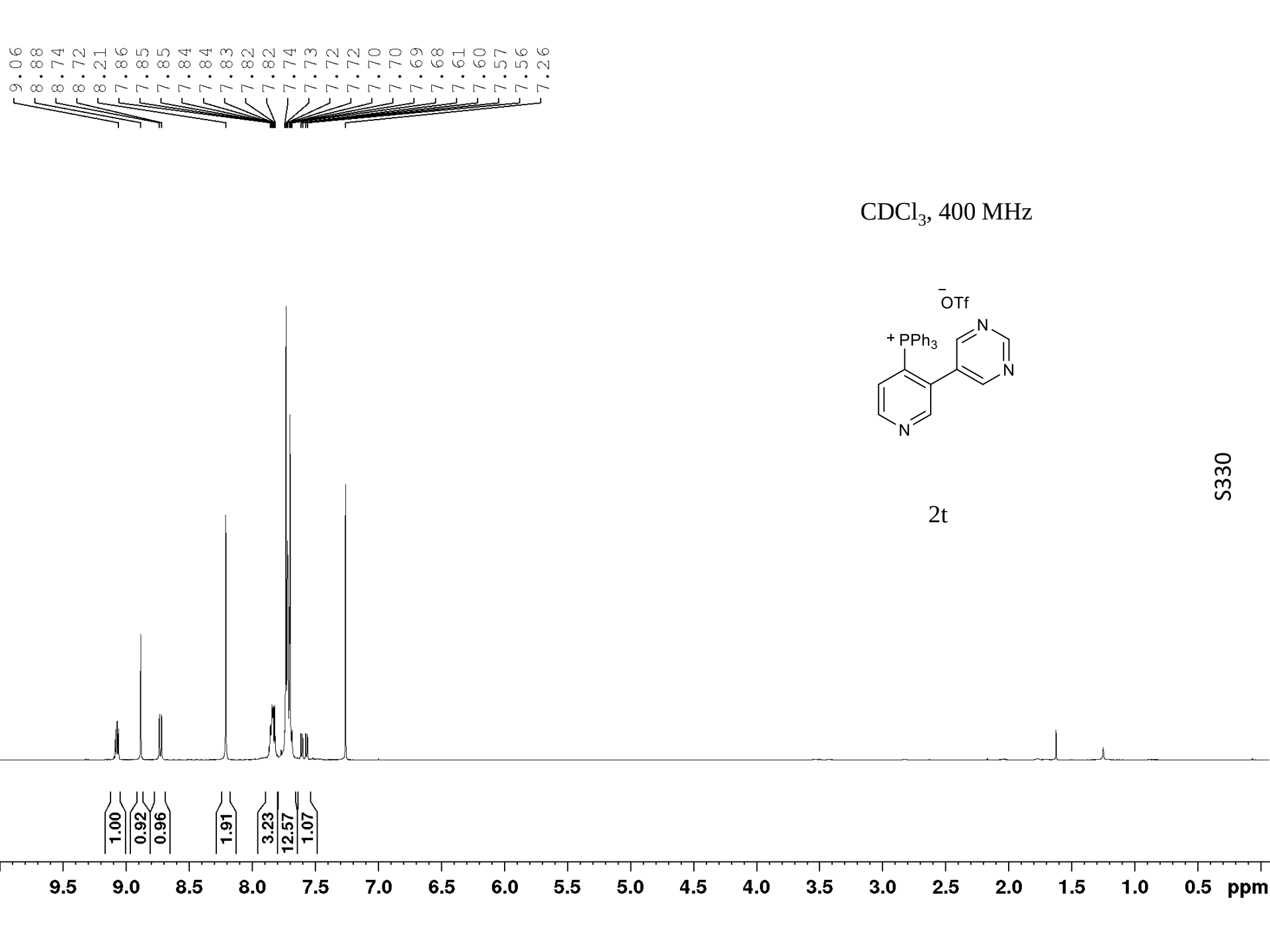
$CDCl_3$, 162 MHz



2s

S328

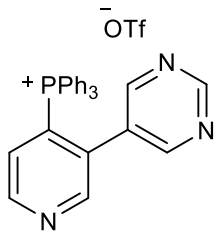

29.27
23.63
15.74
CDCl3, 162 MHz
(crude 31P NMR)
N
OTf
N
PPh3
2s
S329
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm


9.06
8.88
8.74
8.72
8.21
7.86
7.85
7.85
7.84
7.84
7.83
7.82
7.82
7.74
7.73
7.72
7.72
7.70
7.70
7.69
7.68
7.61
7.60
7.57
7.56
7.26
CDCl3, 400 MHz
OTf
+ PPh3
N
N
N
2t
S330
1.00
0.92
0.96
1.91
3.23
12.57
1.07
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
0.5
ppm

158.02
156.05
153.37
153.29
151.66
151.56
135.90
135.87
134.43
134.32
134.16
134.10
130.96
130.83
129.67
129.63
128.92
128.83
127.74
126.92
122.23
119.04
116.74
115.85

77.32
77.00
76.68

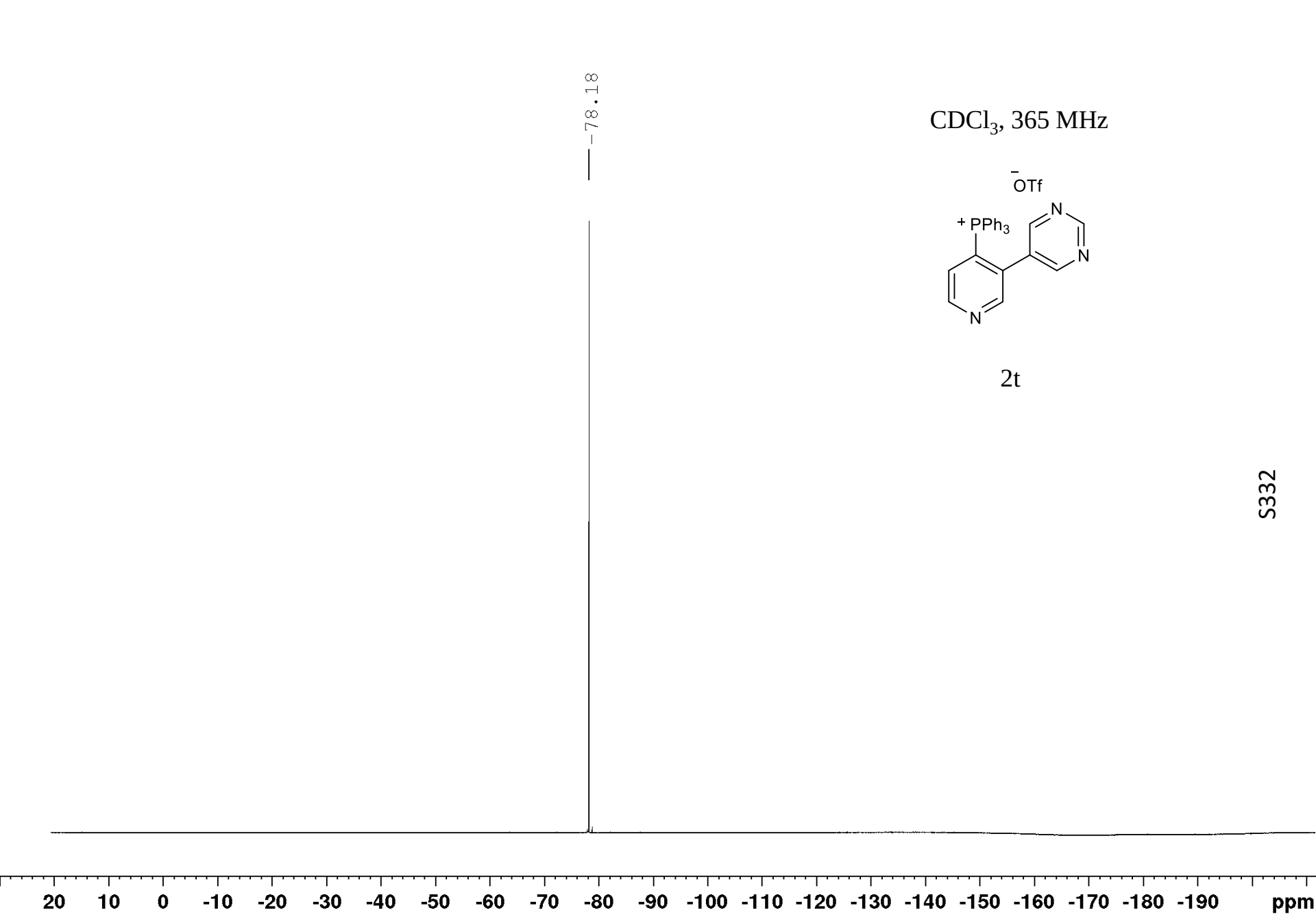
$CDCl_3$, 100 MHz



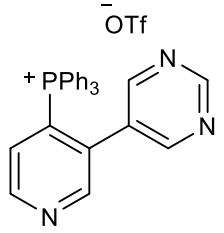
2t

S331

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 ppm

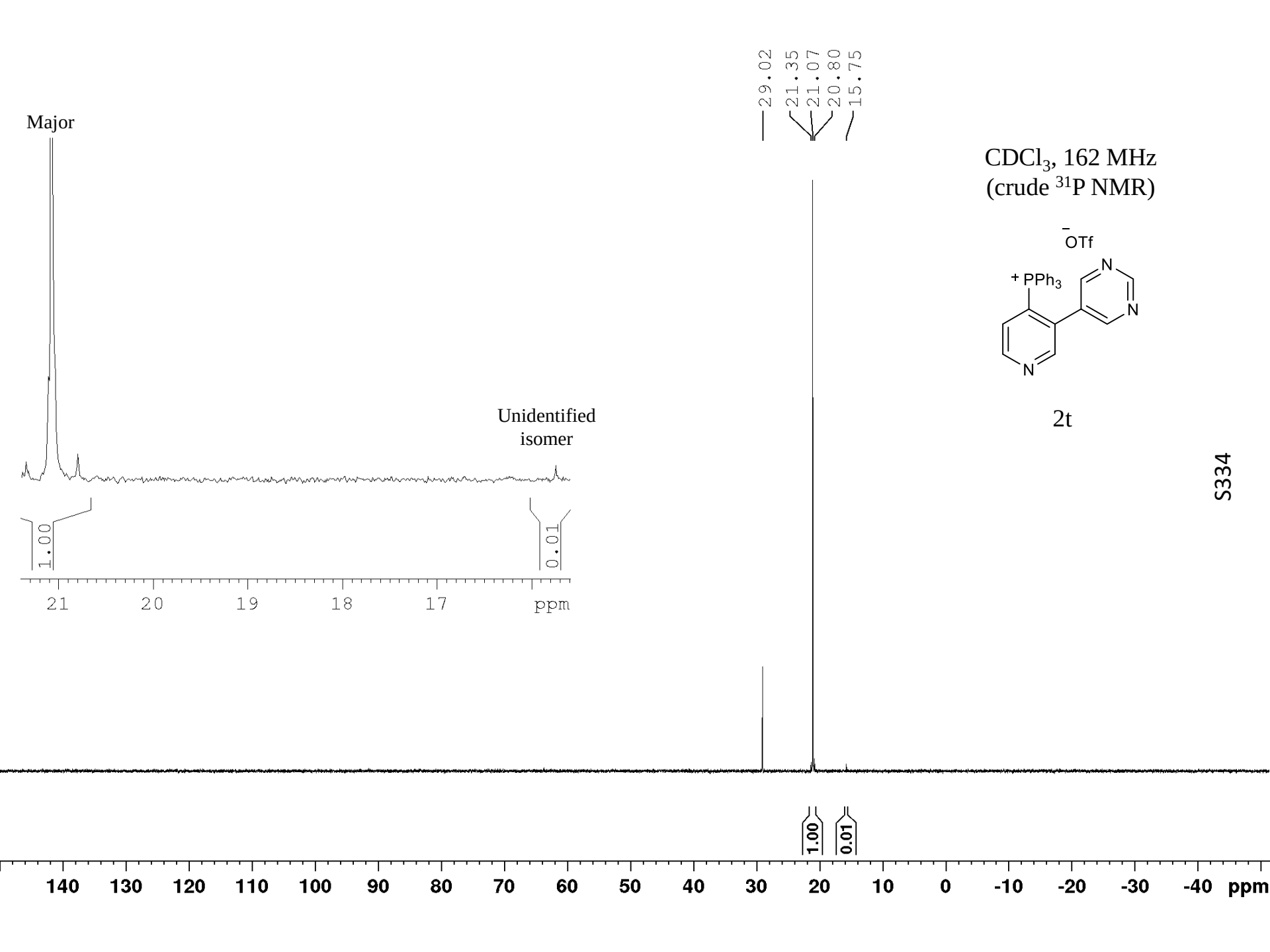

-78.18
CDCl3, 365 MHz
OTf
+ PPh3
N
N
N
2t
S332
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

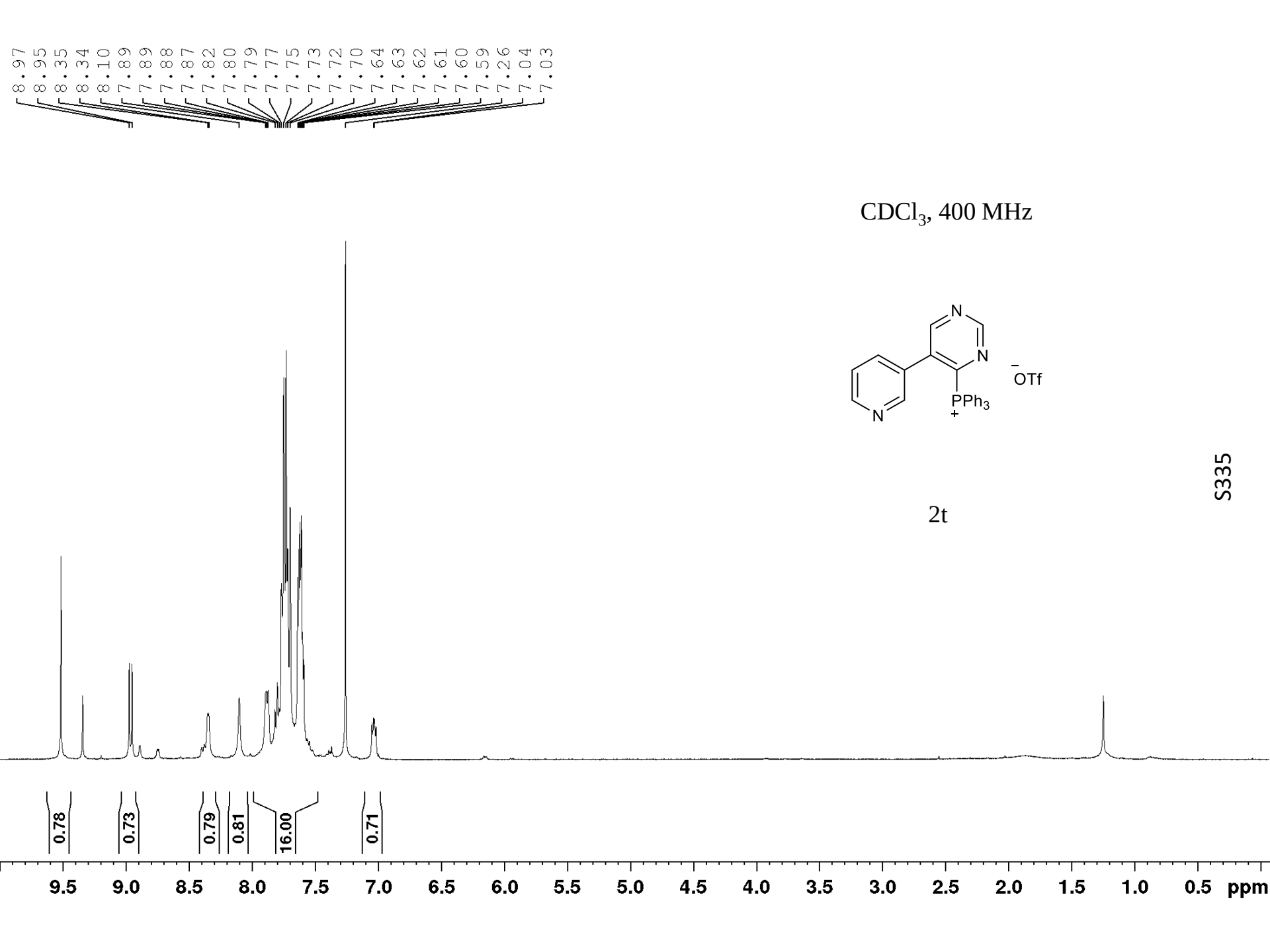
$CDCl_3$, 162 MHz

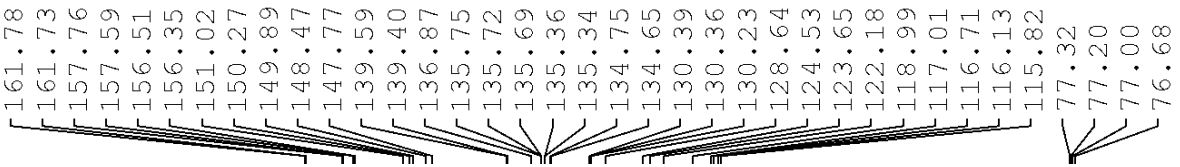


2t

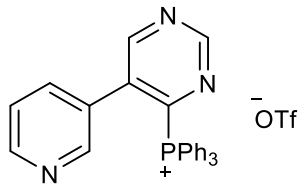
S333


29.02
21.35
21.07
20.80
15.75
Major
Unidentified isomer
1.00
0.01
21
20
19
18
17
ppm
CDCl3, 162 MHz
(crude 31P NMR)
OTf
PPh3
2t
S334
1.00
0.01
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

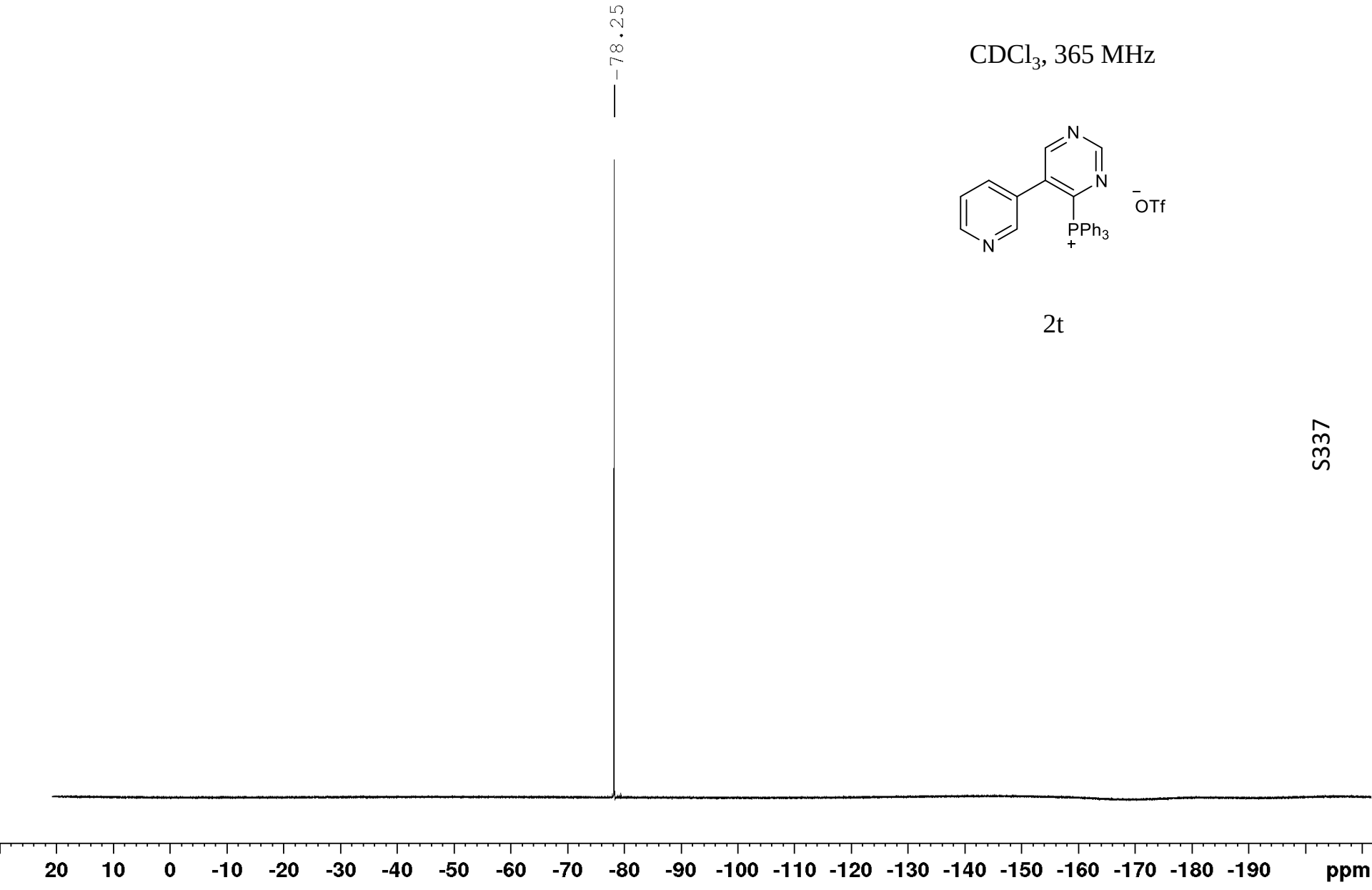

8.97
8.95
8.35
8.34
8.10
7.89
7.89
7.88
7.87
7.82
7.80
7.79
7.77
7.75
7.73
7.72
7.70
7.64
7.63
7.62
7.61
7.60
7.59
7.26
7.04
7.03
CDCl3, 400 MHz
N
N
N
PPh3
+
OTf
2t
S335
0.78
0.73
0.79
0.81
16.00
0.71
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



$CDCl_3$, 100 MHz

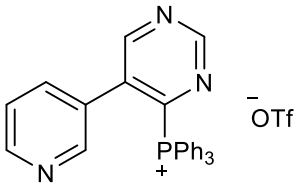


2t


−78.25
CDCl3, 365 MHz
N
N
PPh3
+
N
−
OTf
2t
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

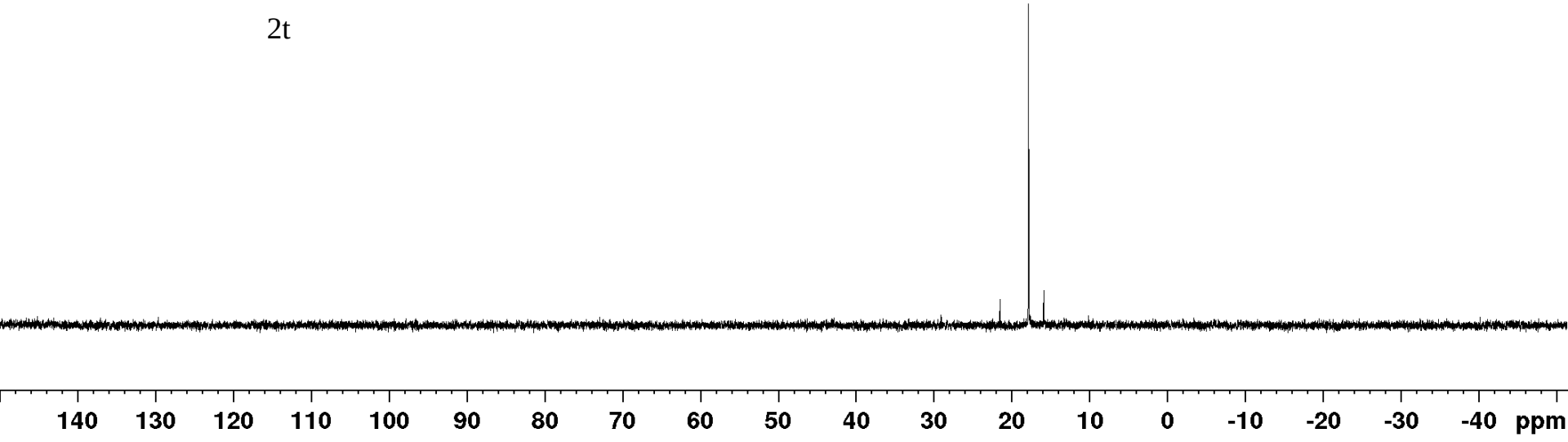
21.51
17.86
15.89

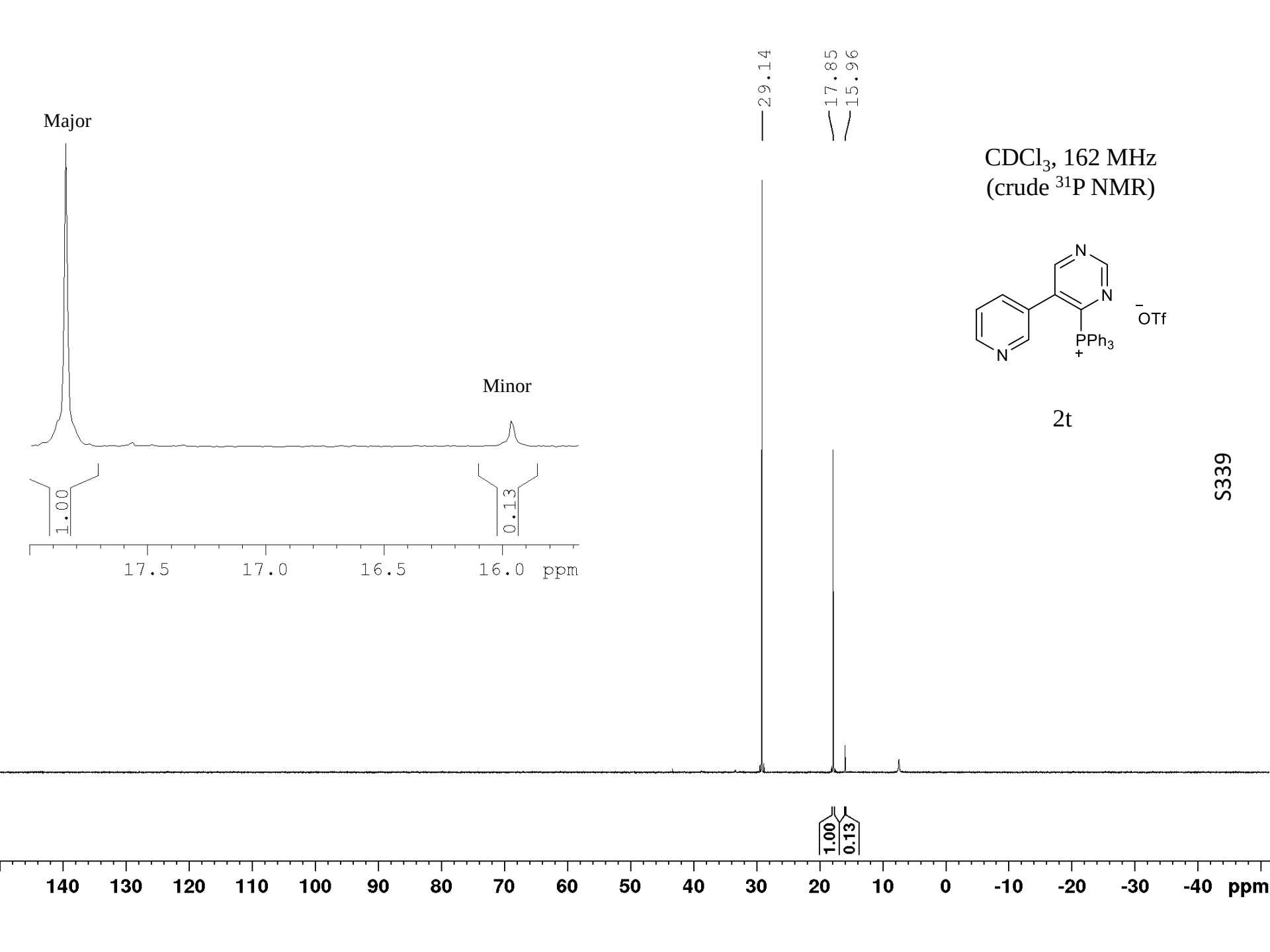
$CDCl_3$, 162 MHz

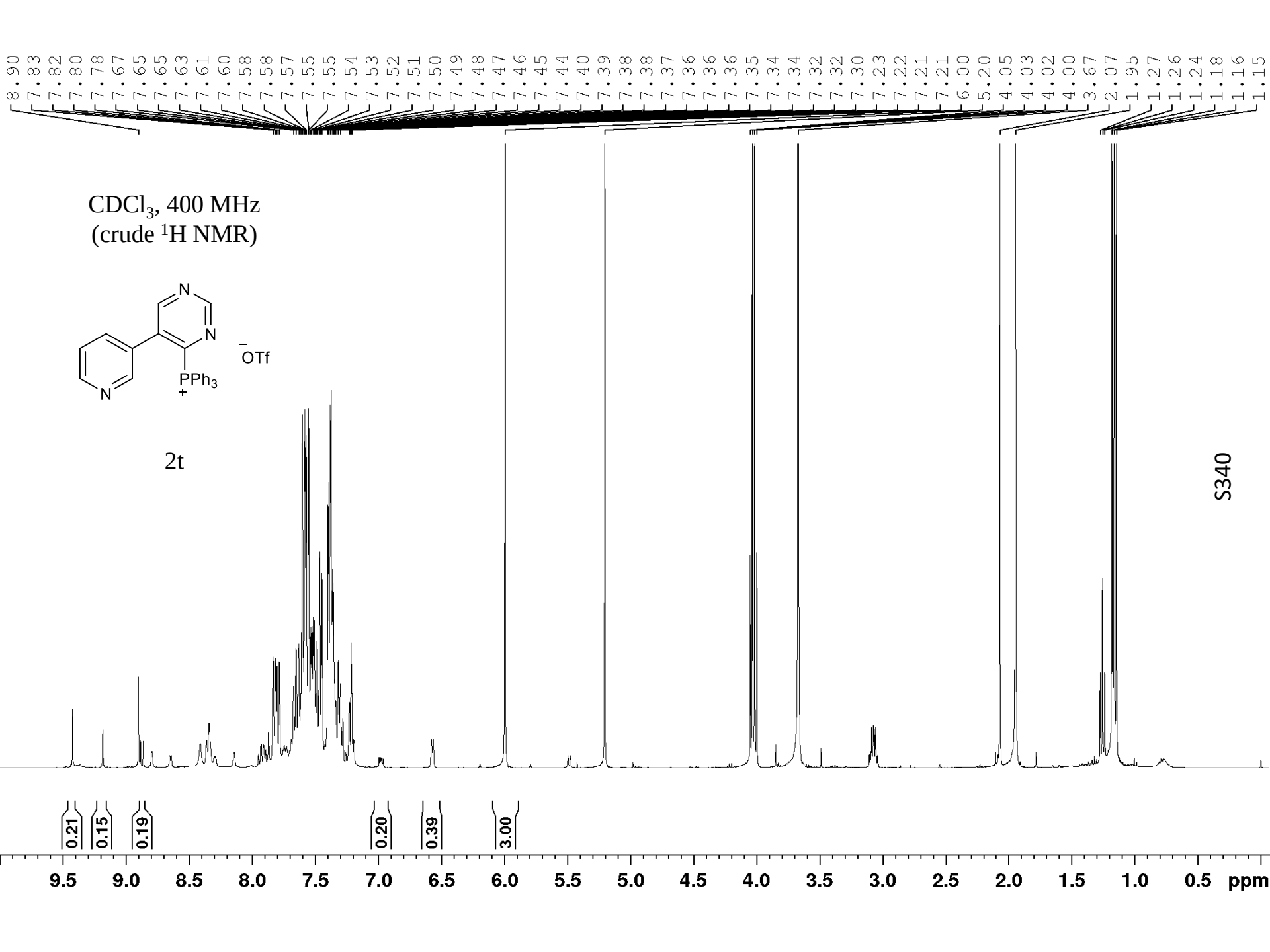


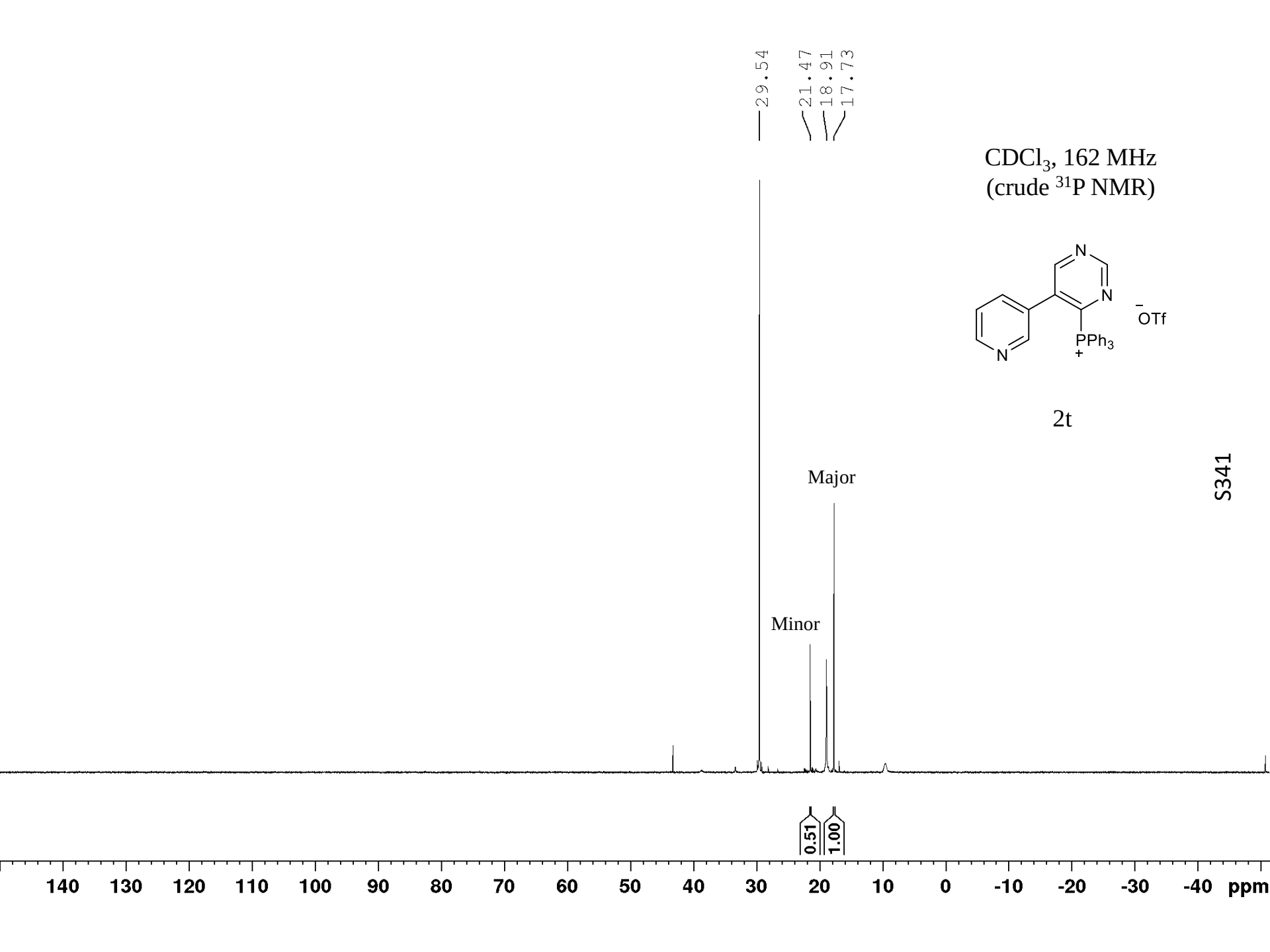
S338

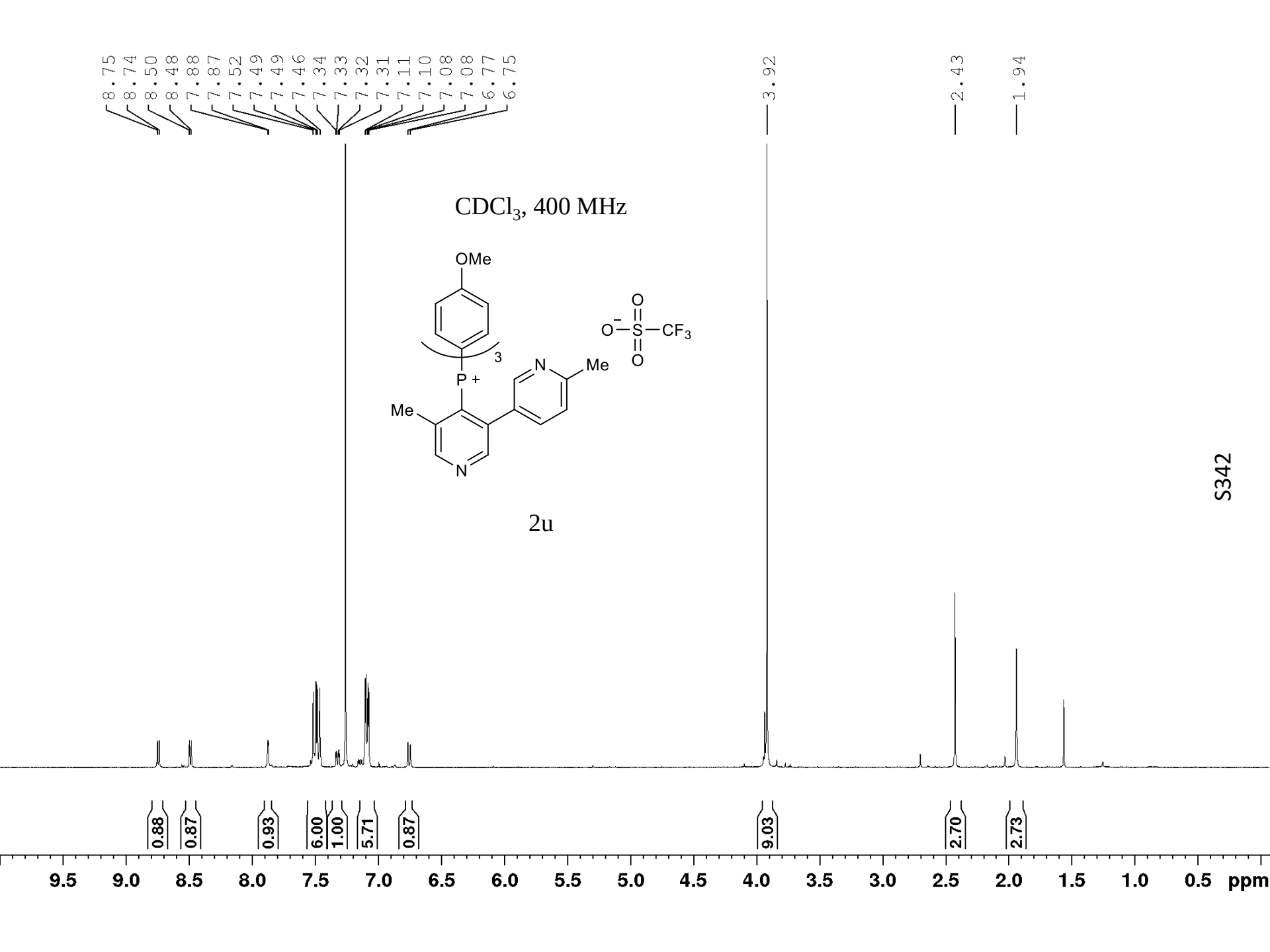
2t

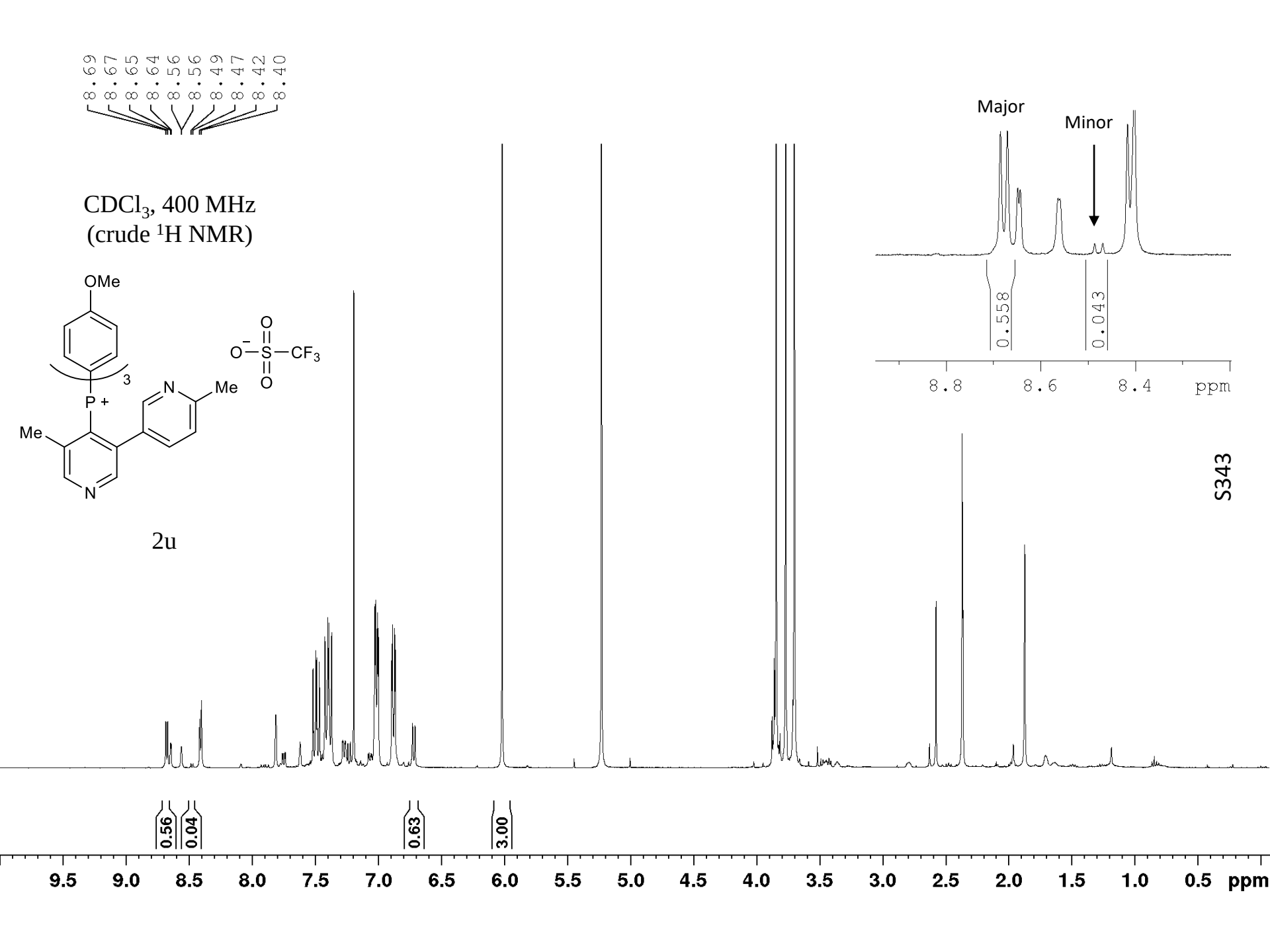


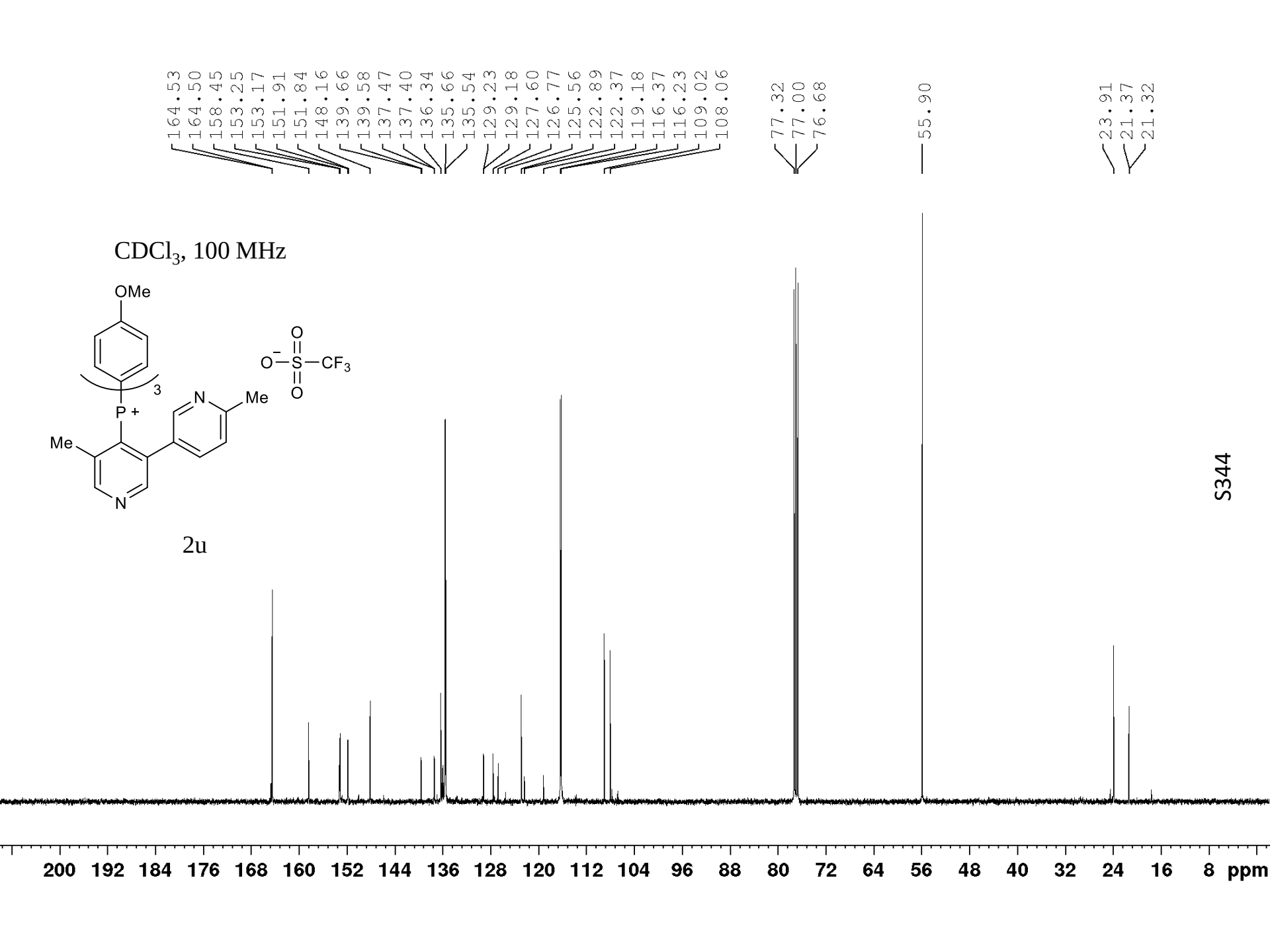

Major
Minor
29.14
17.85
15.96
1.00
0.13
17.5
17.0
16.5
16.0 ppm
CDCl3, 162 MHz
(crude 31P NMR)
N
N
N
PPh3
+
OTf
2t
S339
1.00
0.13
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

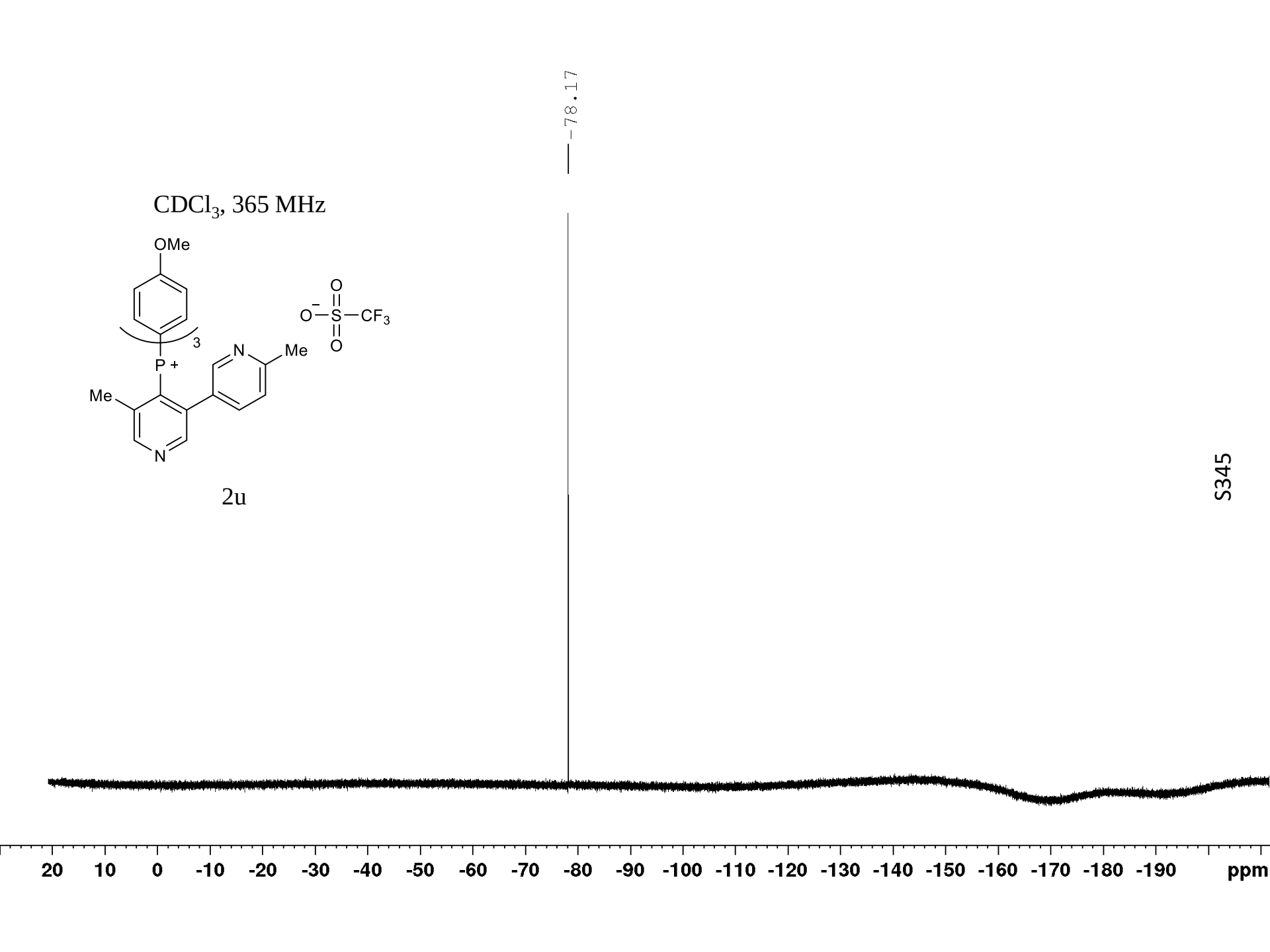

8.90 7.83 7.82 7.80 7.78 7.67 7.65 7.65 7.63 7.61 7.60 7.58 7.58 7.57 7.55 7.55 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.32 7.32 7.30 7.23 7.22 7.21 7.21 6.00 5.20 4.05 4.03 4.02 4.00 3.67 2.07 1.95 1.27 1.26 1.24 1.18 1.16 1.15
CDCl3, 400 MHz
(crude 1H NMR)
N
N
PPh3
+
N
OTf
2t
S340
0.21
0.15
0.19
0.20
0.39
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 0.5 ppm


29.54
21.47
18.91
17.73
CDCl3, 162 MHz
(crude 31P NMR)
N
N
N
PPh3
+
OTf
2t
S341
Major
Minor
0.51
1.00
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 ppm

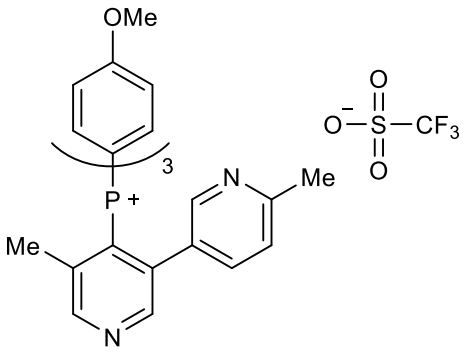

8.75
8.74
8.50
8.48
7.88
7.87
7.52
7.49
7.49
7.46
7.34
7.33
7.32
7.31
7.11
7.10
7.08
7.08
6.77
6.75
3.92
2.43
1.94
CDCl3, 400 MHz
OMe
3
P +
Me
N
Me
O
O
S
CF3
N
2u
S342
0.88
0.87
0.93
6.00
1.00
5.71
0.87
9.03
2.70
2.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


8.69
8.67
8.65
8.64
8.56
8.56
8.49
8.47
8.42
8.40
CDCl3, 400 MHz
(crude 1H NMR)
OMe
O
O
S
CF3
3
P +
N
Me
Me
N
2u
Major
Minor
0.558
0.043
8.8
8.6
8.4
ppm
S343
0.56
0.04
0.63
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
0.5
ppm

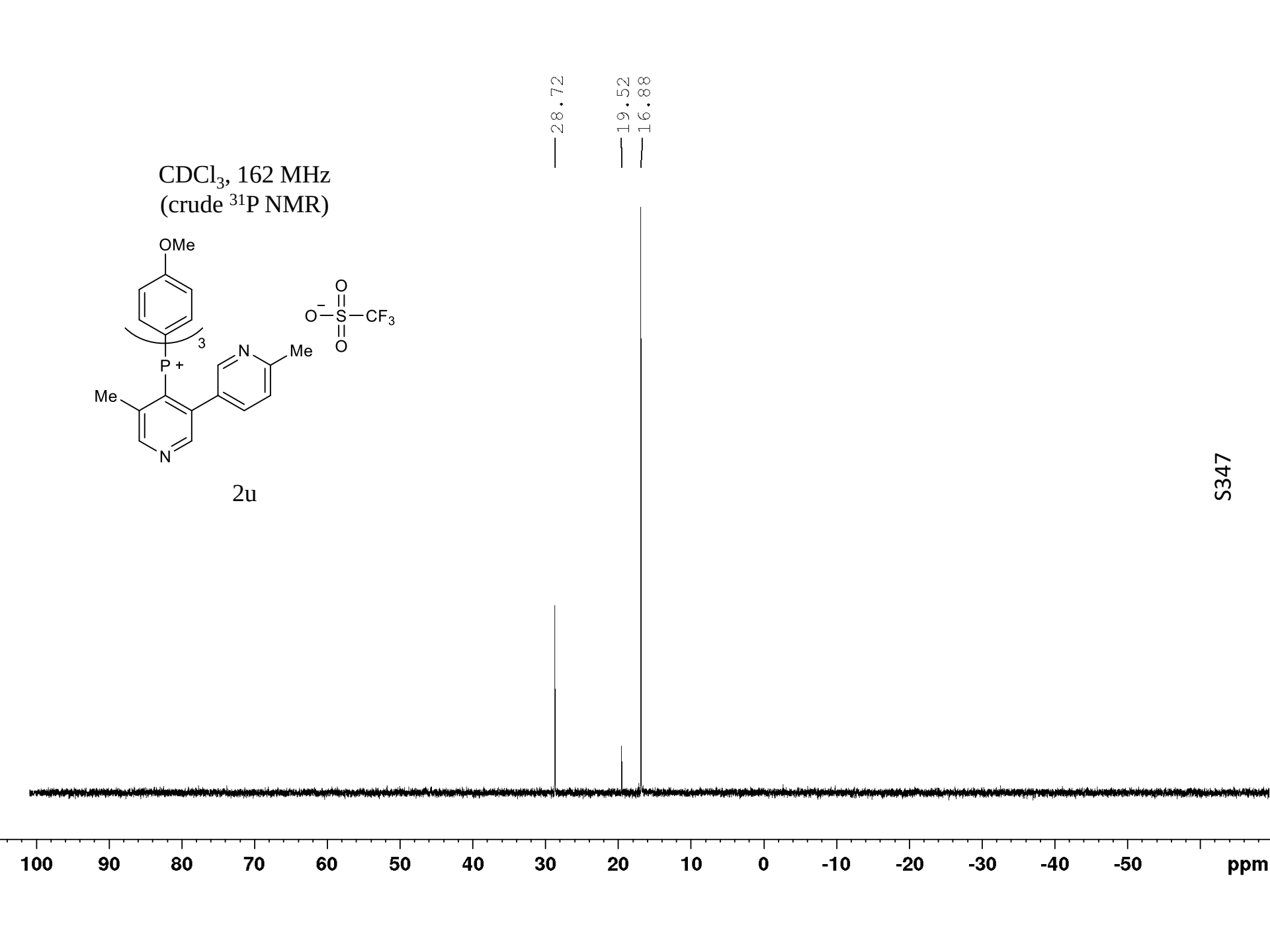

164.53
164.50
158.45
153.25
153.17
151.91
151.84
148.16
139.66
139.58
137.47
137.40
136.34
135.66
135.54
129.23
129.18
127.60
126.77
125.56
122.89
122.37
119.18
116.37
116.23
109.02
108.06
77.32
77.00
76.68
55.90
23.91
21.37
21.32
CDCl3, 100 MHz
OMe
O
O
S
CF3
3
P +
N
Me
Me
N
2u
S344
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

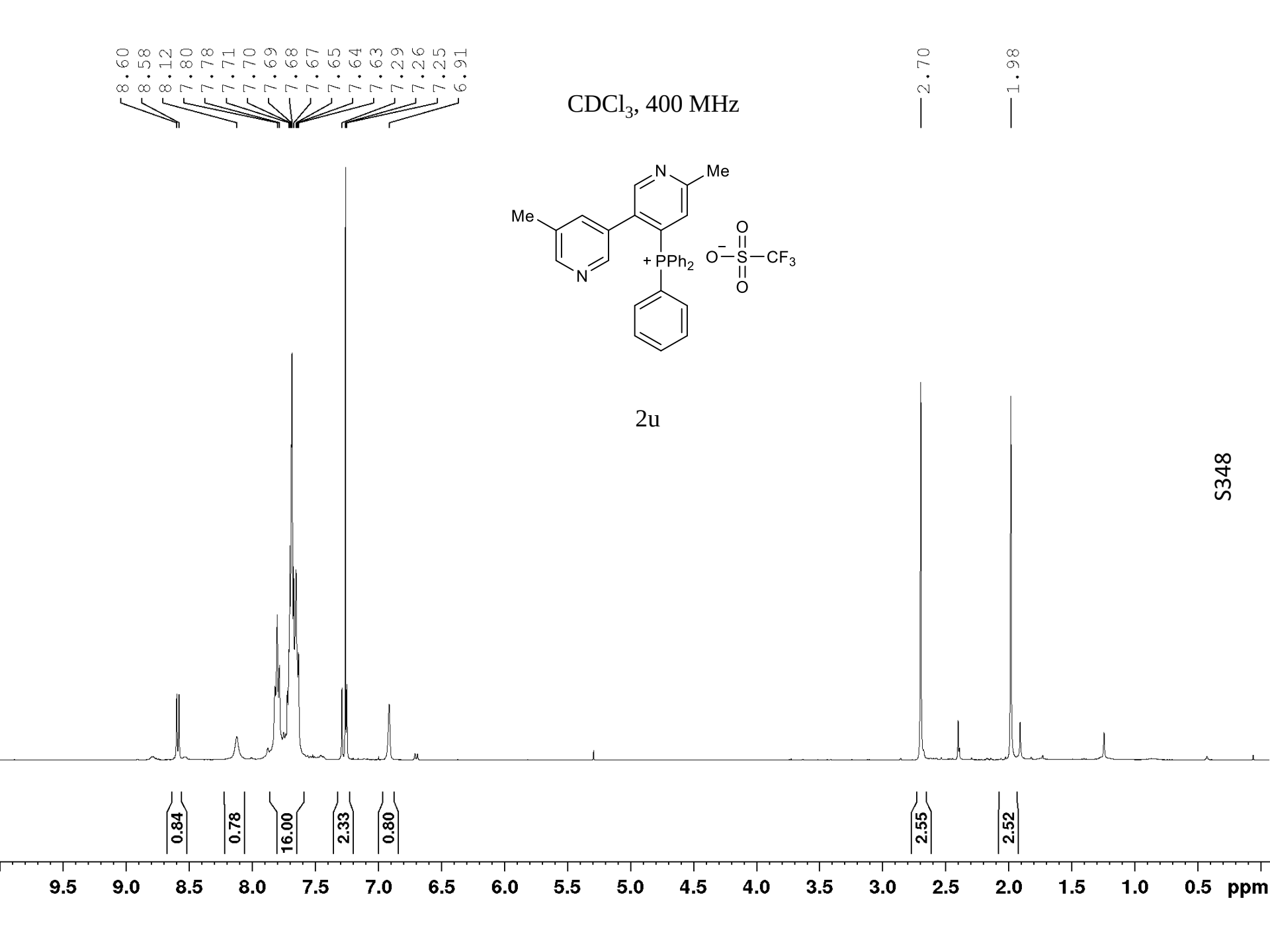

-78.17
CDCl3, 365 MHz
OMe
O
O
S
CF3
3
N
Me
P +
Me
N
2u
S345
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

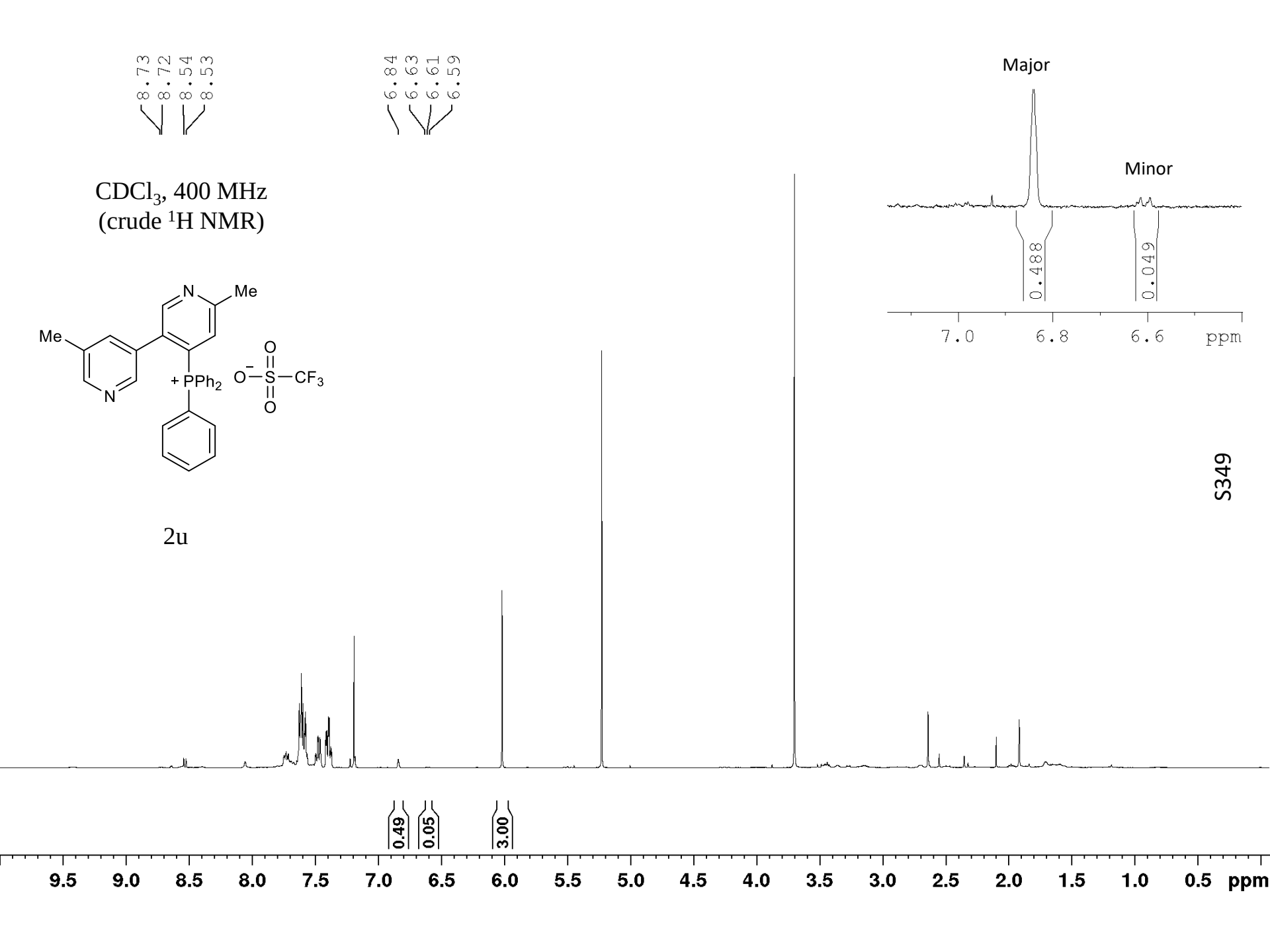
$CDCl_3$, 162 MHz

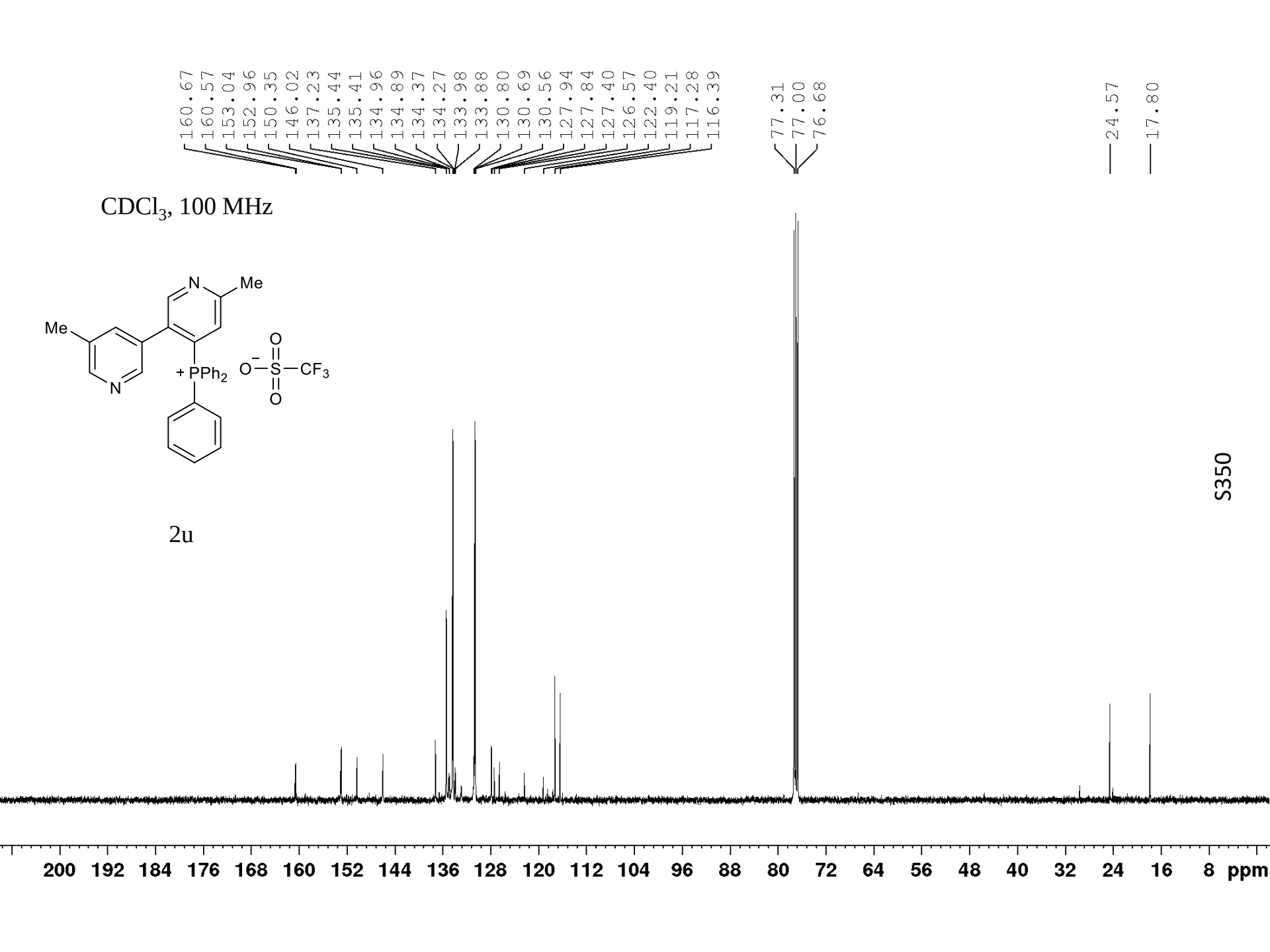


2u

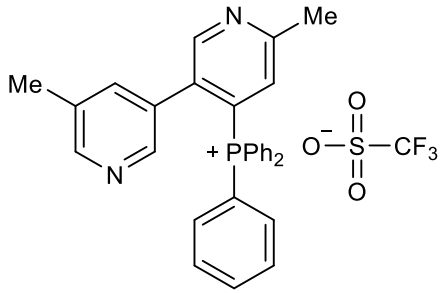

28.72
19.52
16.88
CDCl3, 162 MHz
(crude 31P NMR)
OMe
O
O
S
CF3
3
P +
N
Me
Me
N
2u
S347
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm


8.60
8.58
8.12
7.80
7.78
7.71
7.70
7.69
7.68
7.67
7.65
7.64
7.63
7.29
7.26
7.25
6.91
2.70
1.98
CDCl3, 400 MHz
Me
N
Me
+ PPh2
O
O
S
CF3
O
2u
S348
0.84
0.78
16.00
2.33
0.80
2.55
2.52
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
ppm


8.73
8.72
8.54
8.53
6.84
6.63
6.61
6.59
CDCl3, 400 MHz
(crude 1H NMR)
Me
N
Me
Me
N
+ PPh2
O
O−S−CF3
O
2u
Major
Minor
0.488
0.049
7.0
6.8
6.6
ppm
S349
0.49
0.05
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
0.5
ppm

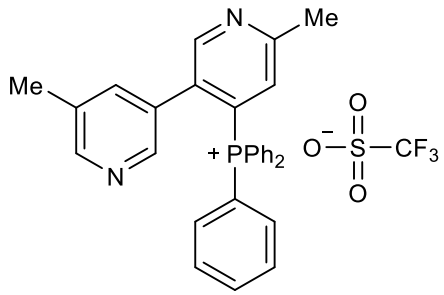

160.67
160.57
153.04
152.96
150.35
146.02
137.23
135.44
135.41
134.96
134.89
134.37
134.27
133.98
133.88
130.80
130.69
130.56
127.94
127.84
127.40
126.57
122.40
119.21
117.28
116.39
77.31
77.00
76.68
24.57
17.80
CDCl3, 100 MHz
Me
N
Me
Me
N
+ PPh2
O
O
S
CF3
O
2u
S350
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



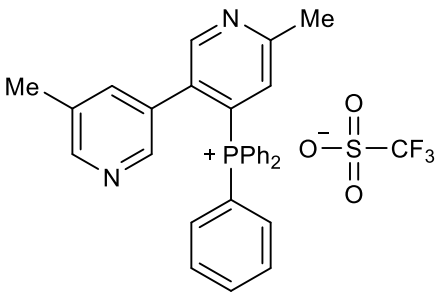
2u

$CDCl_3$, 162 MHz

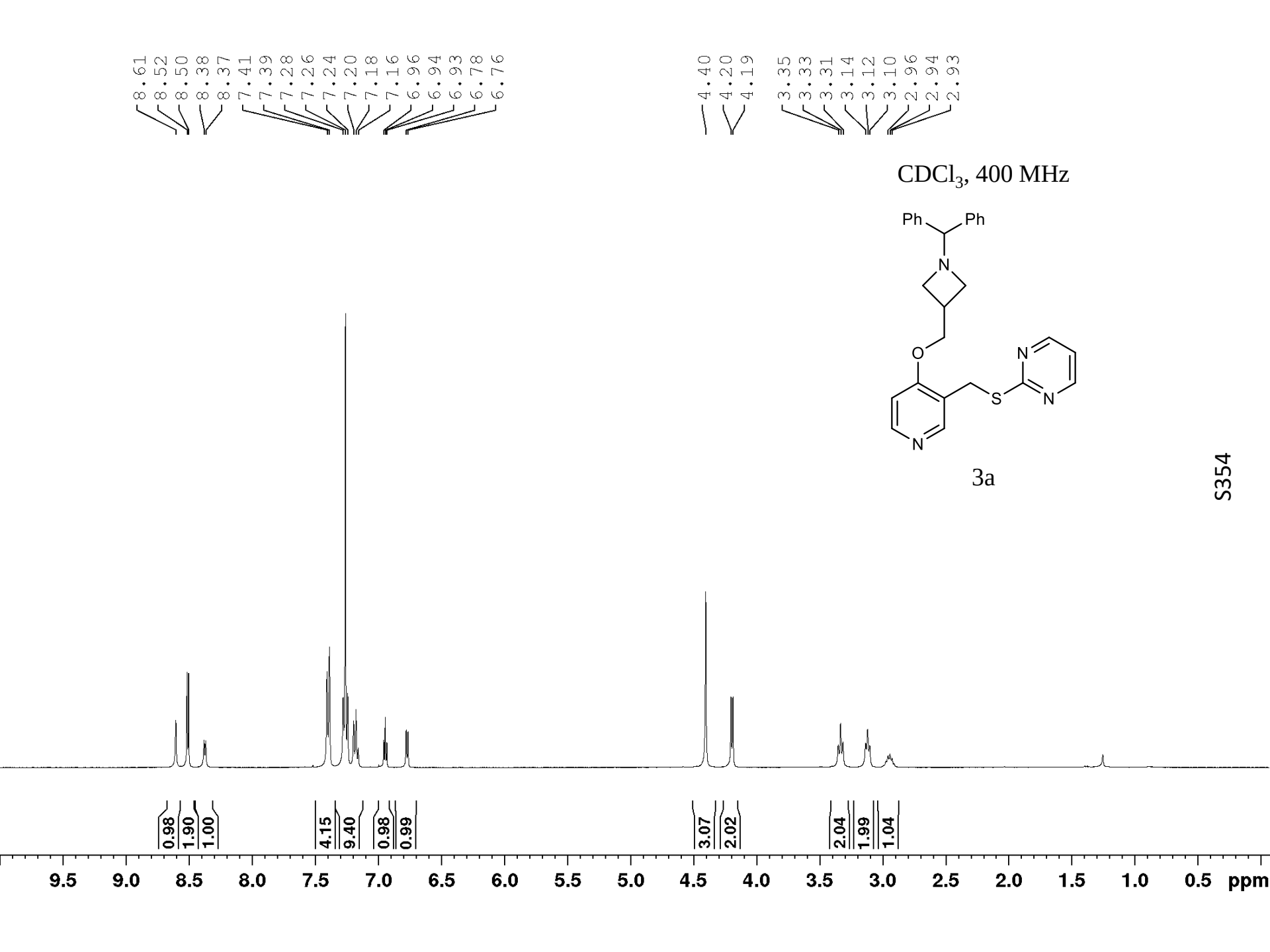


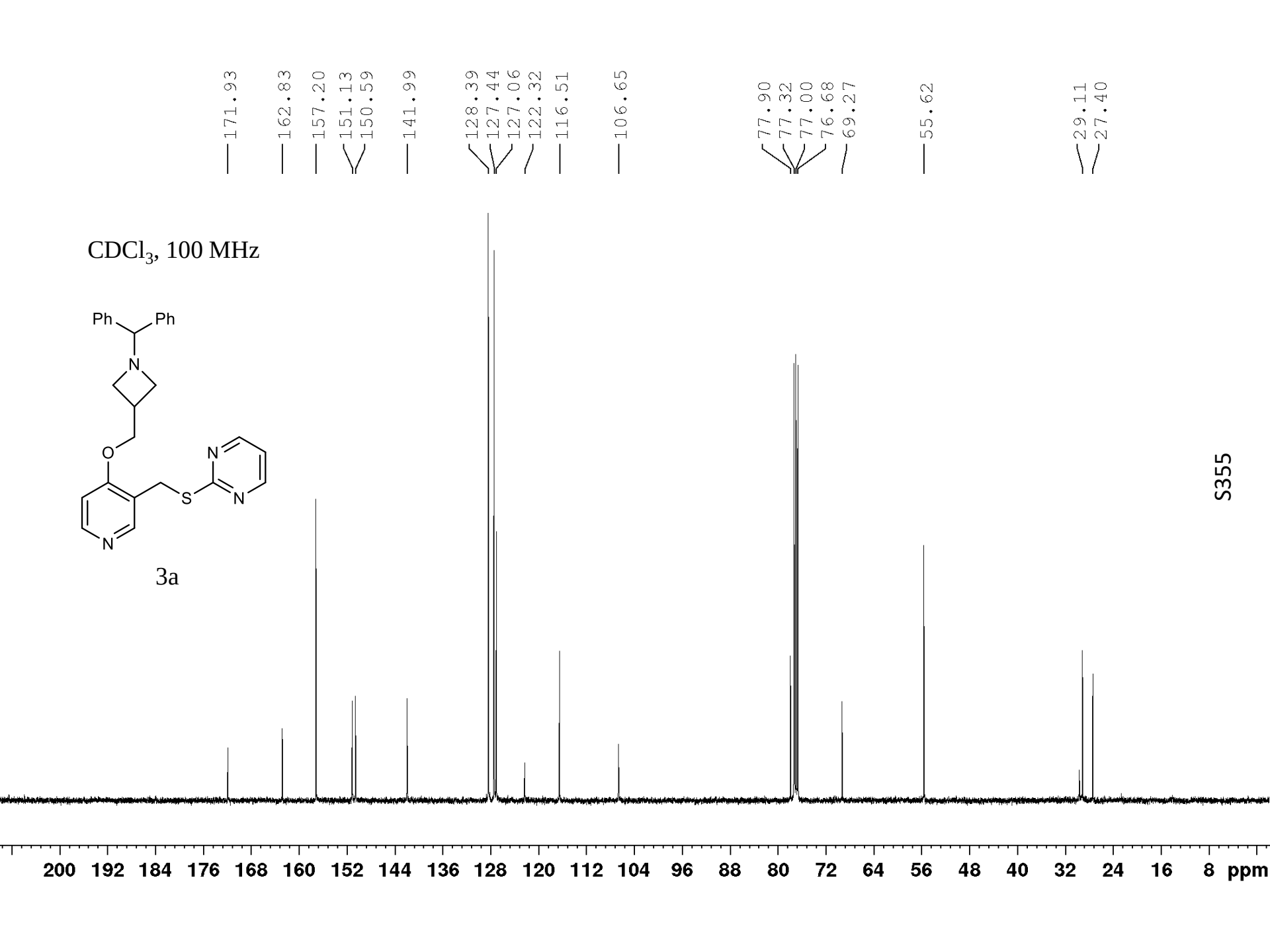
2u

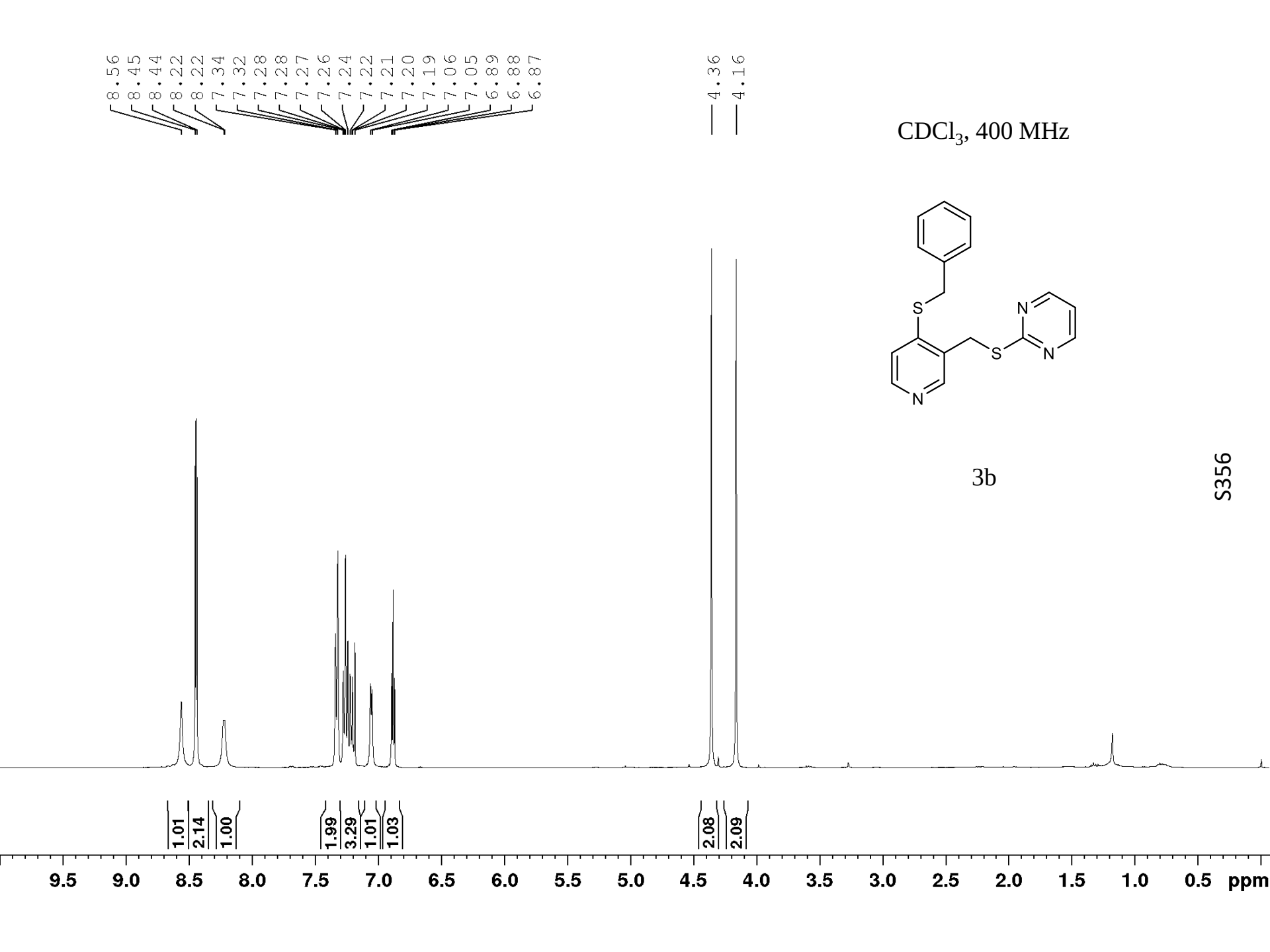
$CDCl_3$, 162 MHz
(crude ^{31}P NMR)

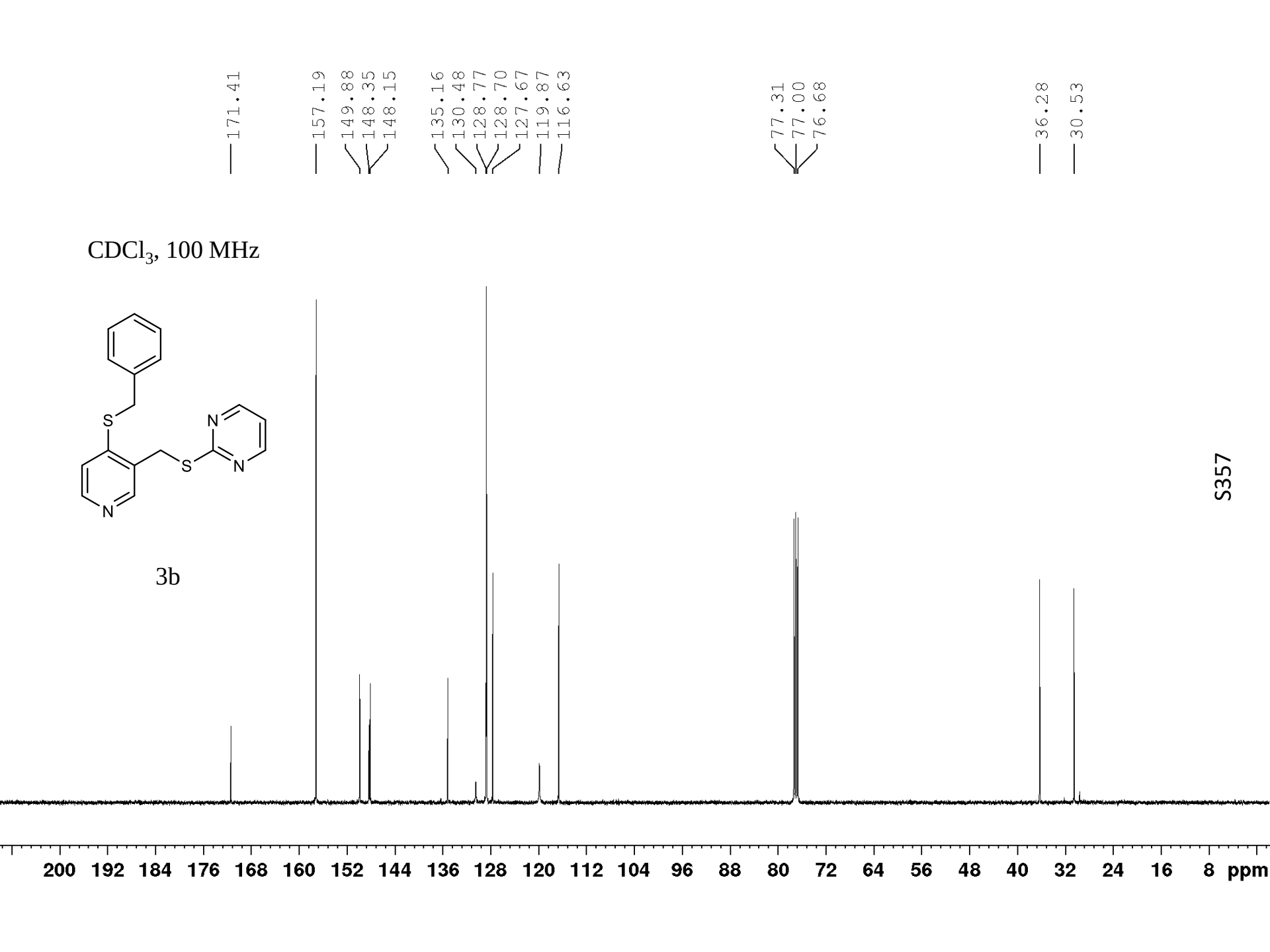


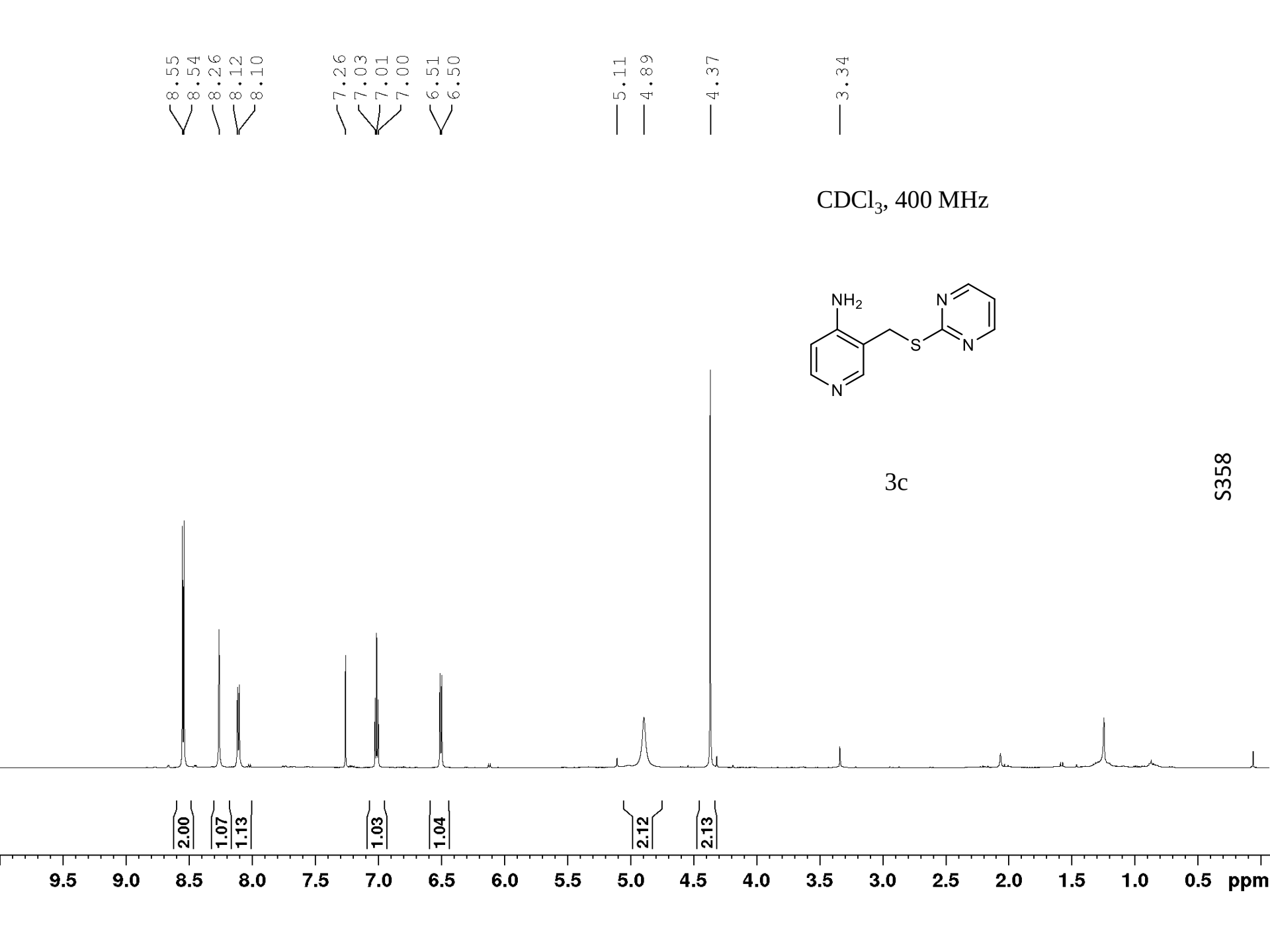
2u

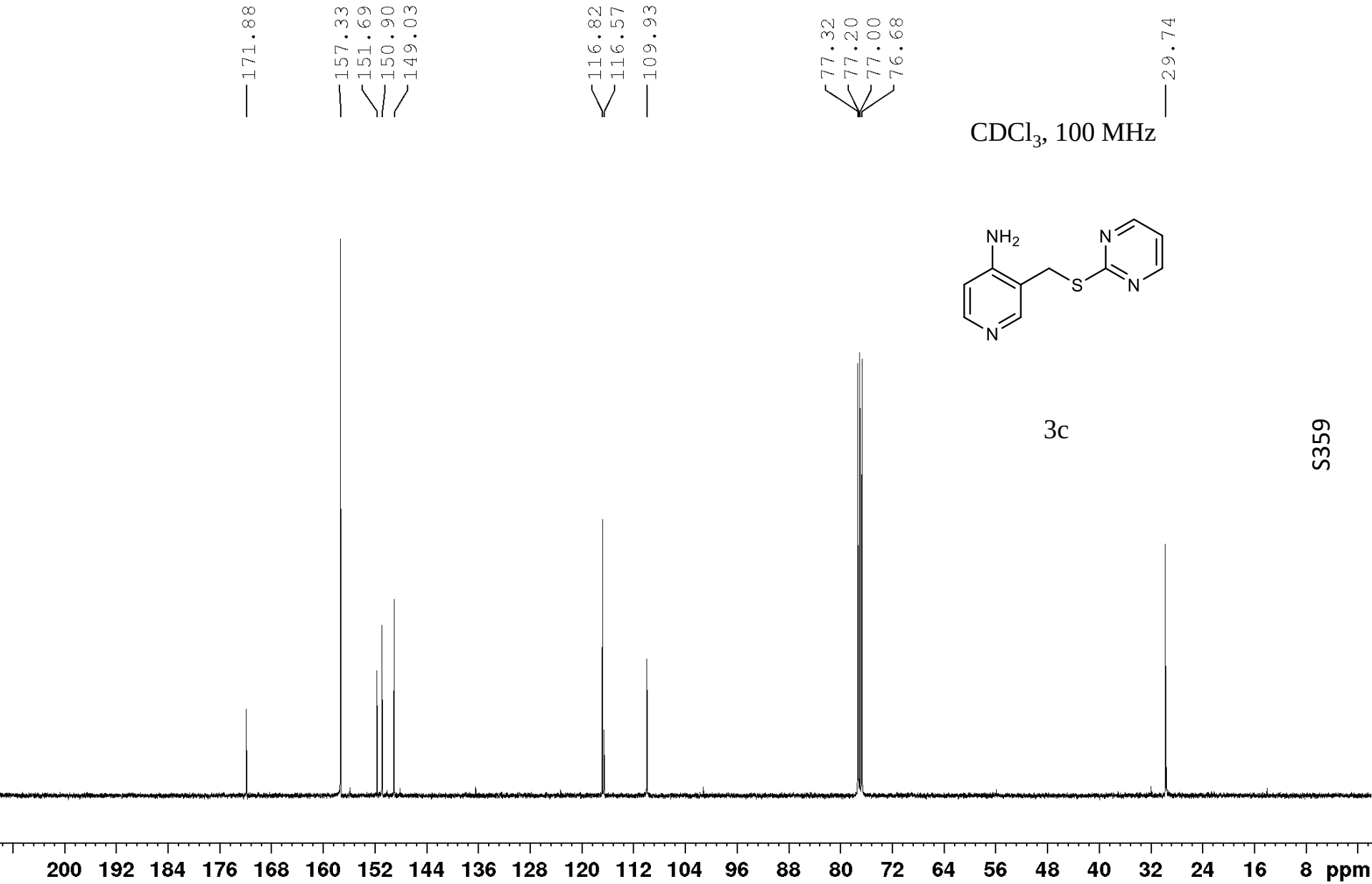

8.61
8.52
8.50
8.38
8.37
7.41
7.39
7.28
7.26
7.24
7.20
7.18
7.16
6.96
6.94
6.93
6.78
6.76
4.40
4.20
4.19
3.35
3.33
3.31
3.14
3.12
3.10
2.96
2.94
2.93
CDCl3, 400 MHz
Ph
Ph
N
O
N
S
N
N
3a
S354
0.98
1.90
1.00
4.15
9.40
0.98
0.99
3.07
2.02
2.04
1.99
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

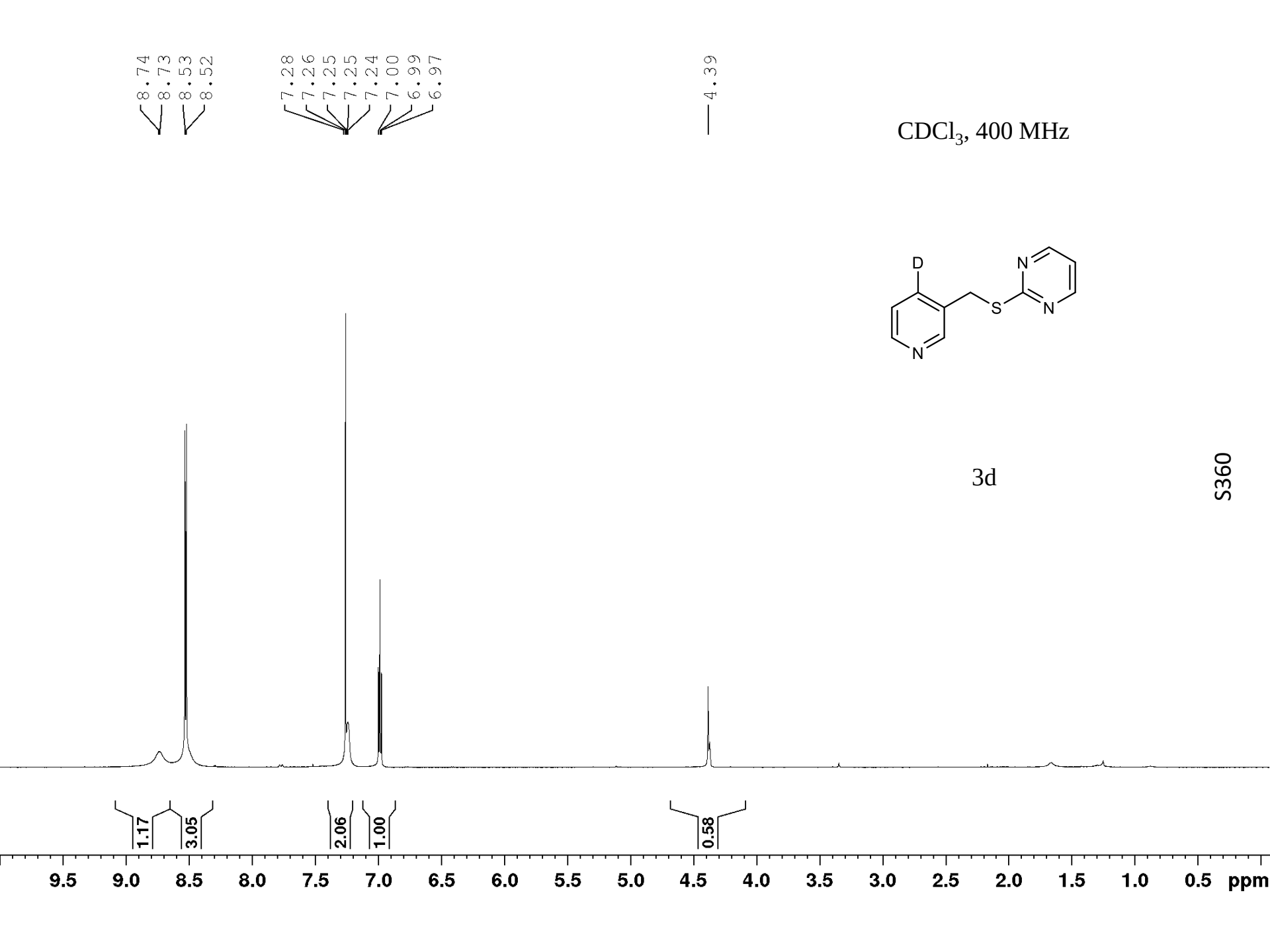

171.93
162.83
157.20
151.13
150.59
141.99
128.39
127.44
127.06
122.32
116.51
106.65
77.90
77.32
77.00
76.68
69.27
55.62
29.11
27.40
CDCl3, 100 MHz
Ph
Ph
N
O
N
S
N
N
3a
S355
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

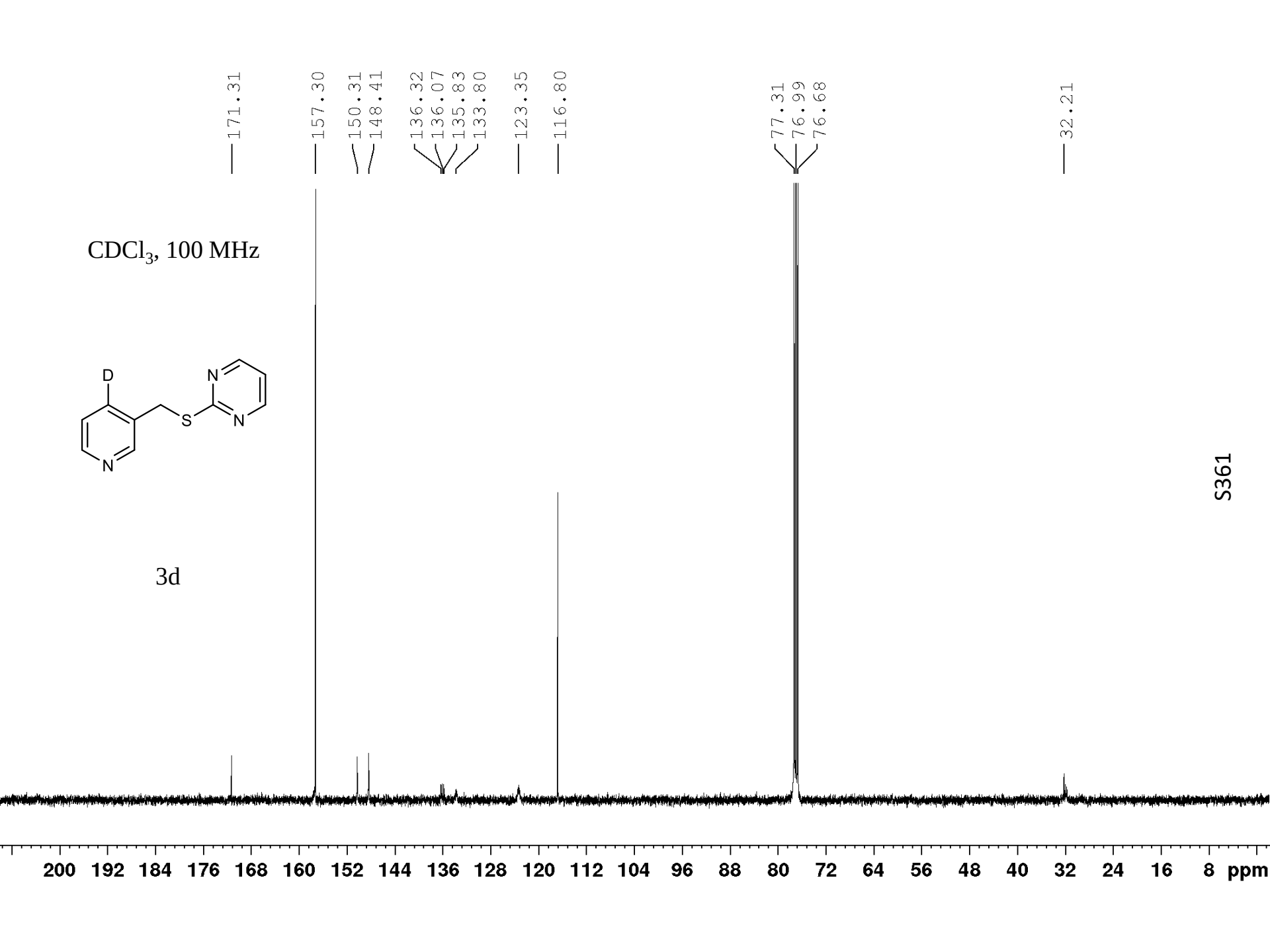

8.56
8.45
8.44
8.22
8.22
7.34
7.32
7.28
7.28
7.27
7.26
7.24
7.22
7.21
7.20
7.19
7.06
7.05
6.89
6.88
6.87
4.36
4.16
CDCl3, 400 MHz
S
N
S
N
N
3b
S356
1.01
2.14
1.00
1.99
3.29
1.01
1.03
2.08
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

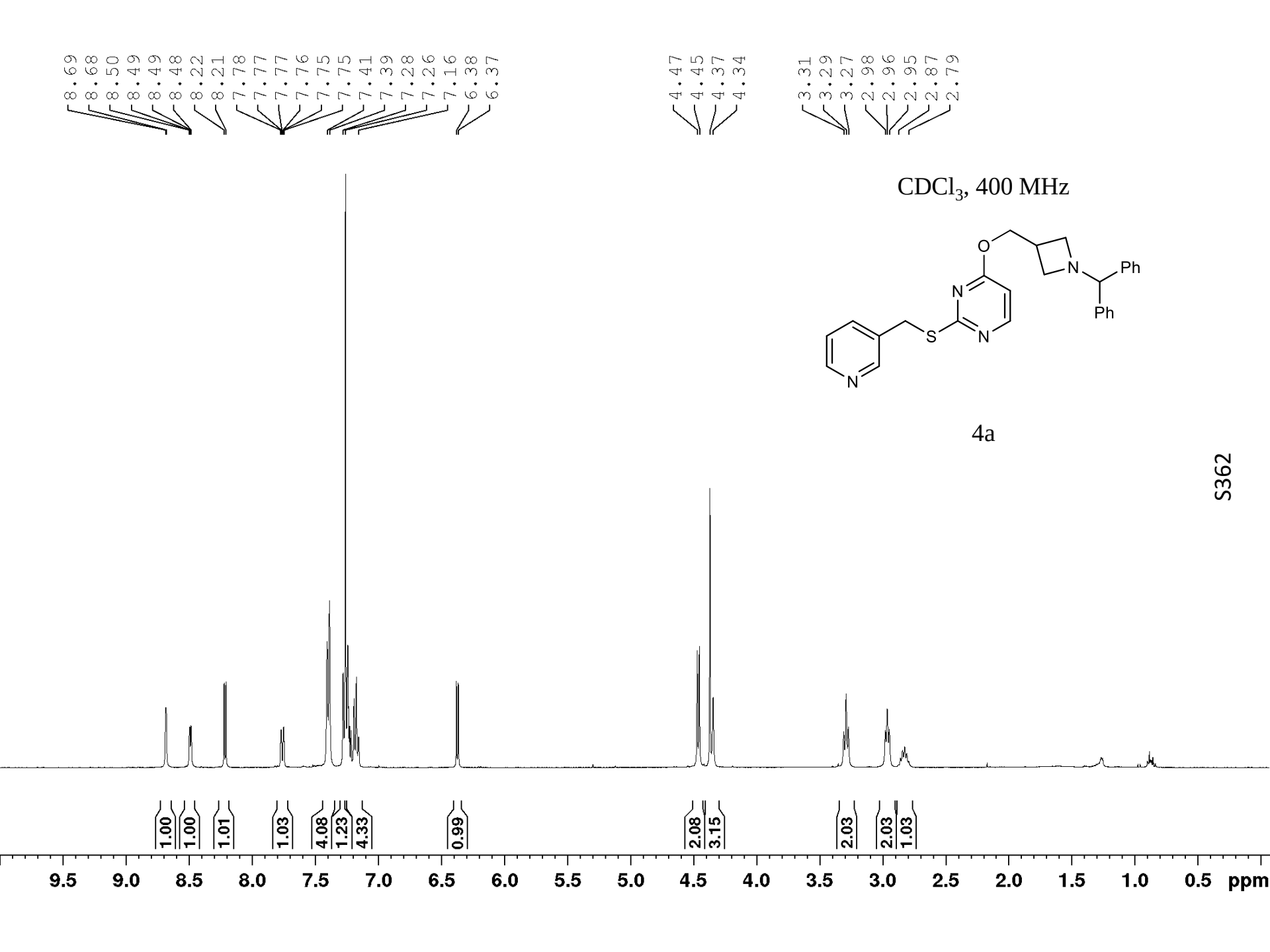

171.41
157.19
149.88
148.35
148.15
135.16
130.48
128.77
128.70
127.67
119.87
116.63
77.31
77.00
76.68
36.28
30.53
CDCl3, 100 MHz
S
N
S
N
N
3b
S357
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

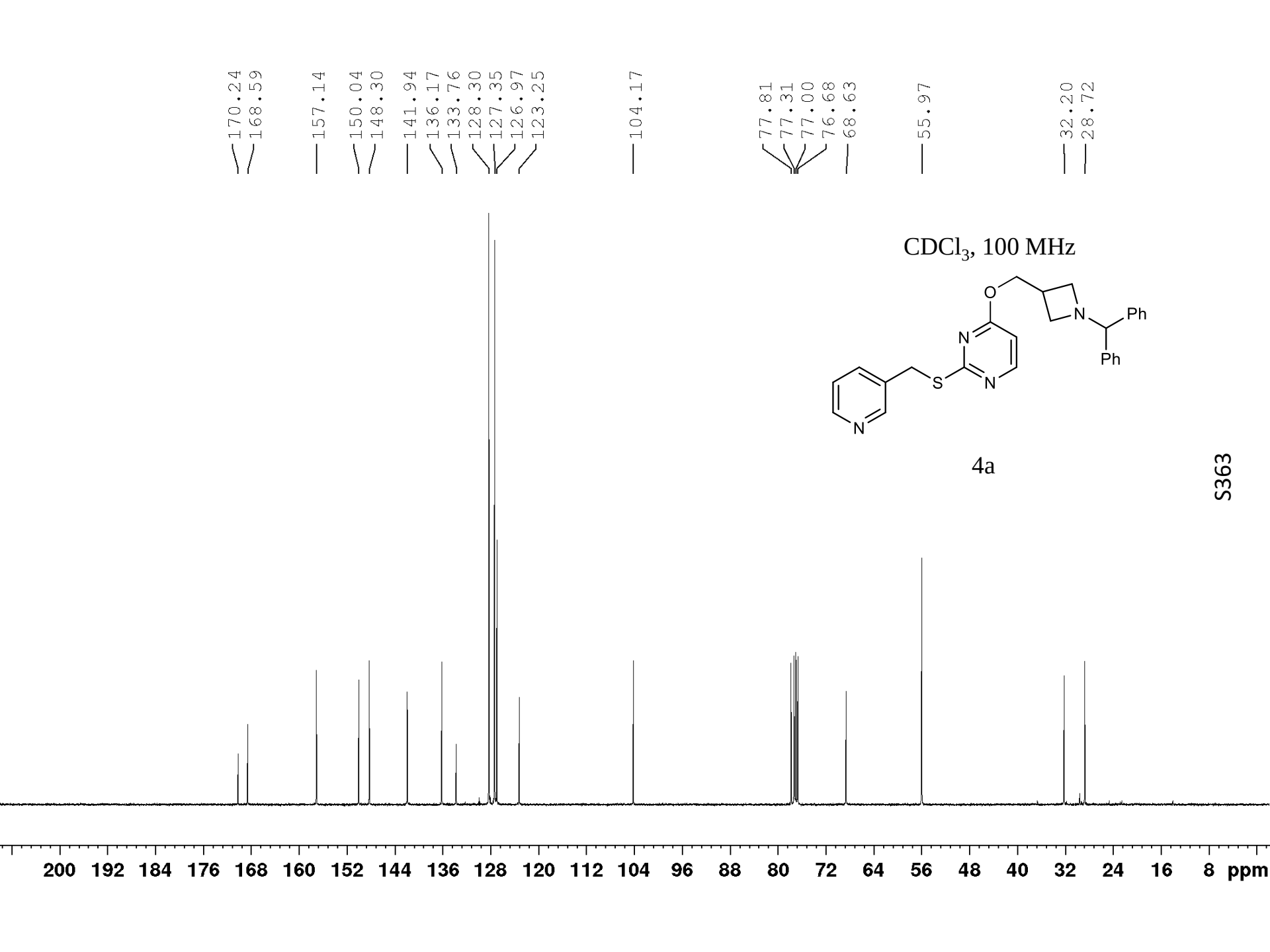

8.55
8.54
8.26
8.12
8.10
7.26
7.03
7.01
7.00
6.51
6.50
5.11
4.89
4.37
3.34
CDCl3, 400 MHz
NH2
N
S
N
N
3c
S358
2.00
1.07
1.13
1.03
1.04
2.12
2.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

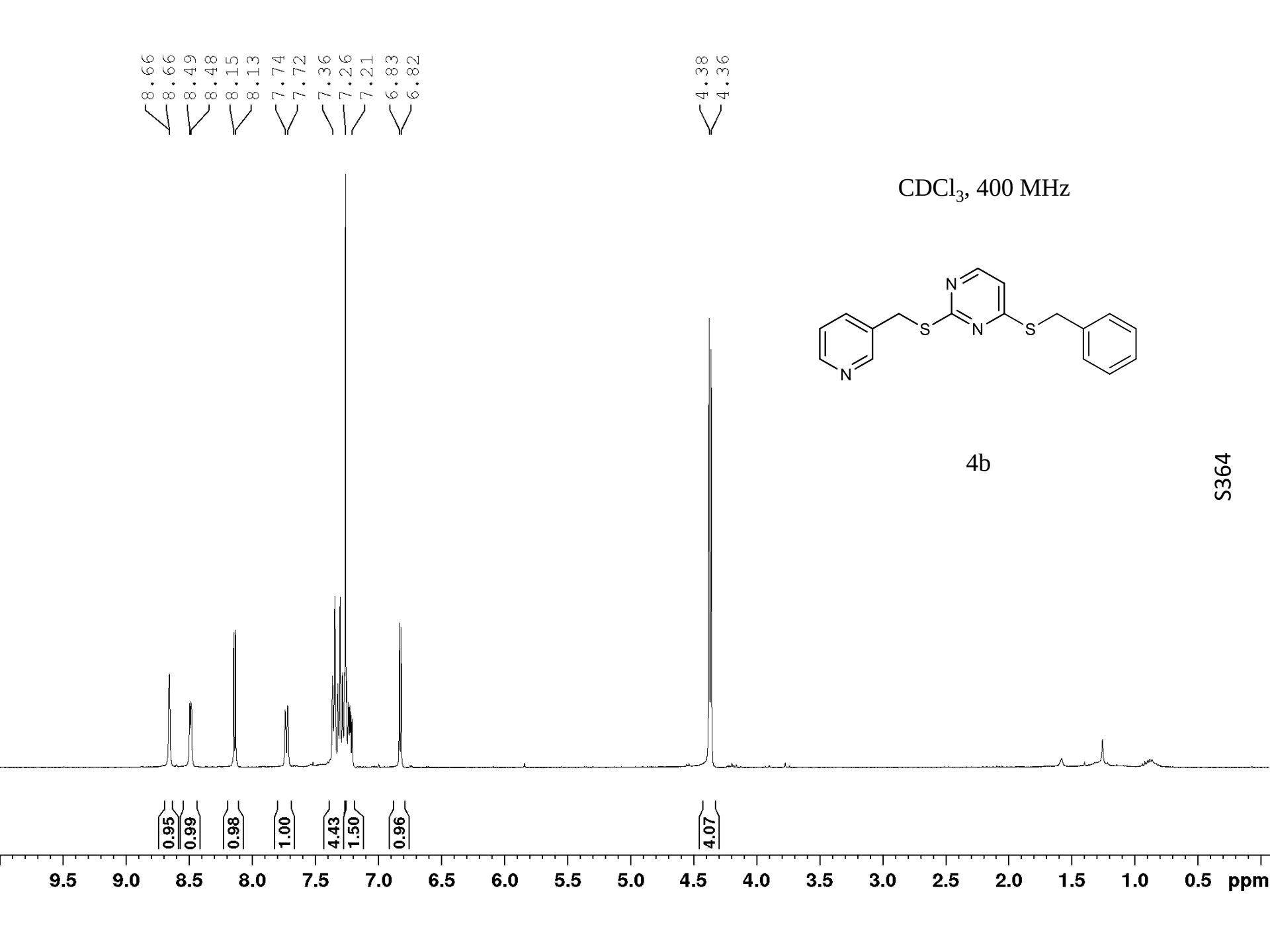

171.88
157.33
151.69
150.90
149.03
116.82
116.57
109.93
77.32
77.20
77.00
76.68
29.74
CDCl3, 100 MHz
NH2
N
S
N
N
3c
S359
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

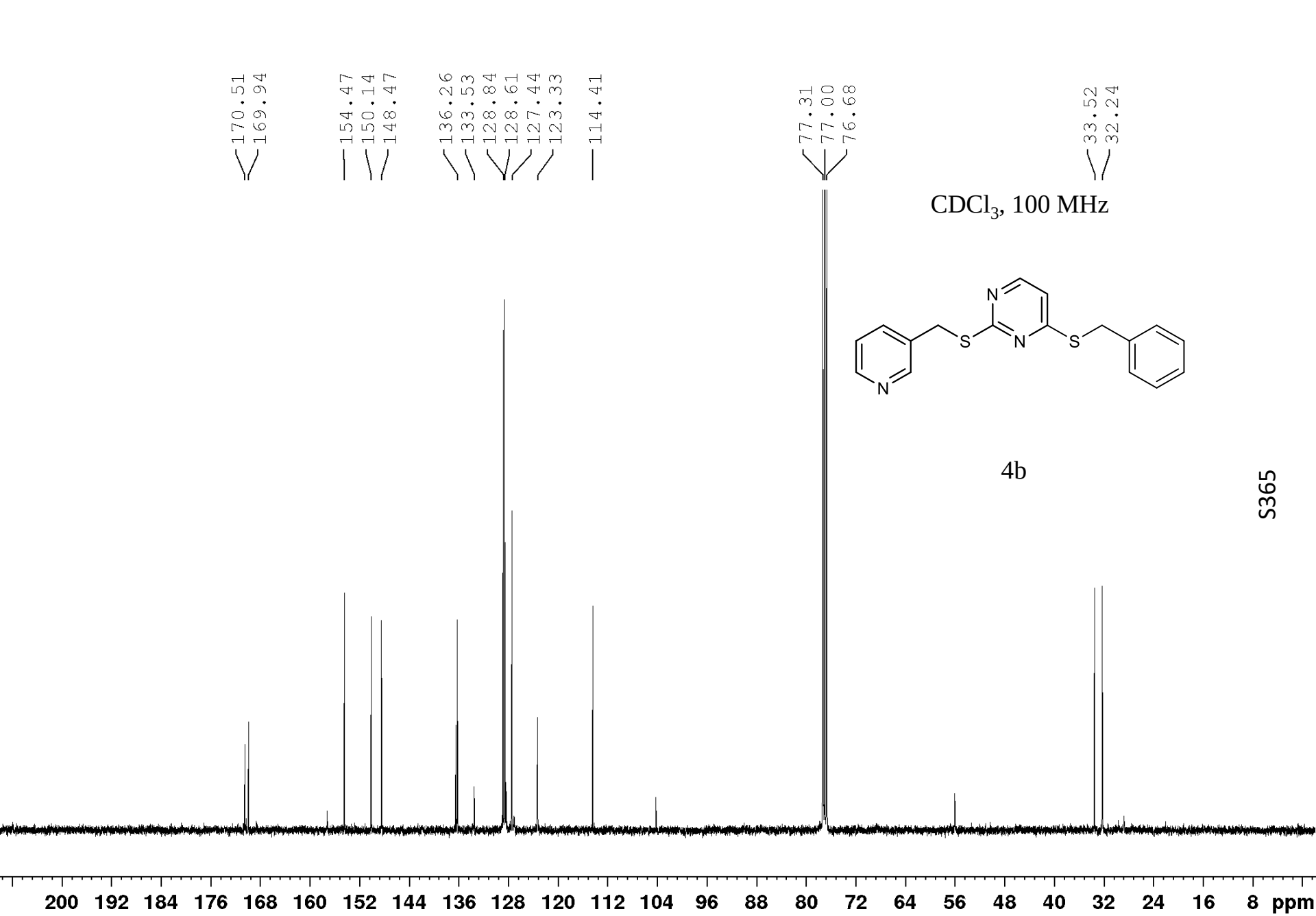

8.74
8.73
8.53
8.52
7.28
7.26
7.25
7.25
7.24
7.00
6.99
6.97
4.39
CDCl3, 400 MHz
D
N
S
N
N
3d
S360
1.17
3.05
2.06
1.00
0.58
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

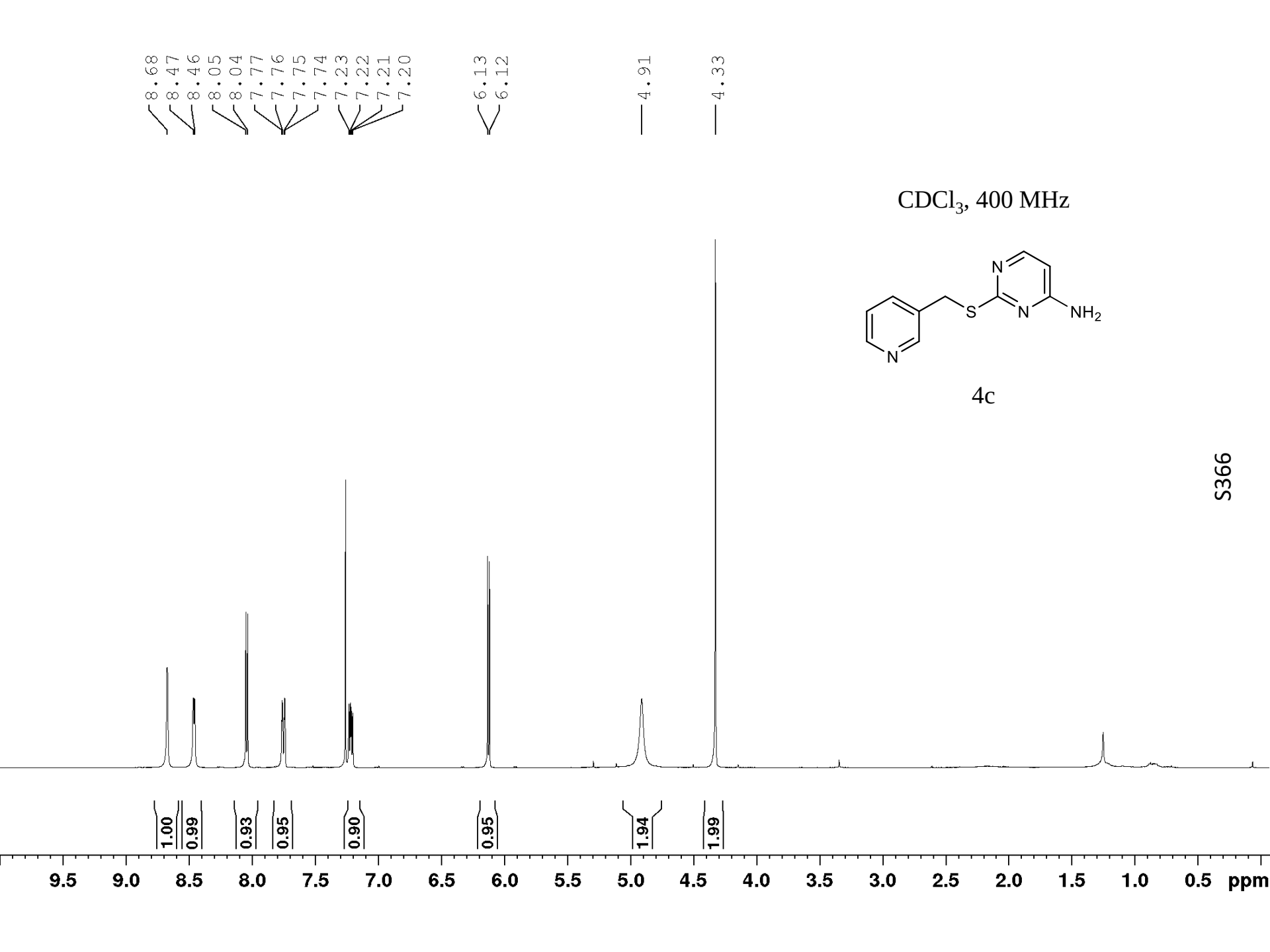

171.31
157.30
150.31
148.41
136.32
136.07
135.83
133.80
123.35
116.80
77.31
76.99
76.68
32.21
CDCl3, 100 MHz
D
N
S
N
N
3d
S361
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

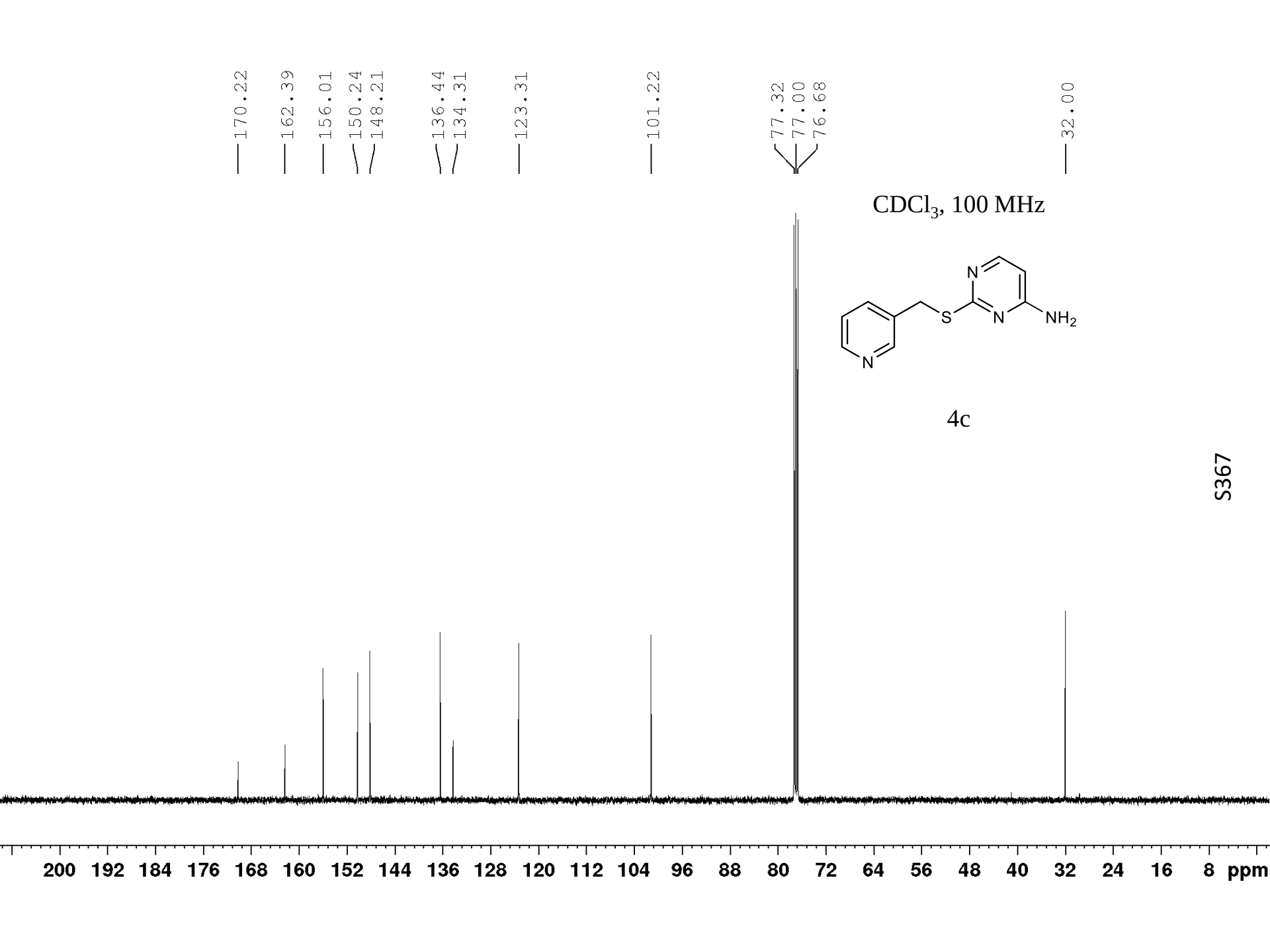

8.69
8.68
8.50
8.49
8.49
8.48
8.22
8.21
7.78
7.77
7.77
7.76
7.75
7.75
7.41
7.39
7.28
7.26
7.16
6.38
6.37
4.47
4.45
4.37
4.34
3.31
3.29
3.27
2.98
2.96
2.95
2.87
2.79
CDCl3, 400 MHz
O
N
Ph
Ph
N
S
N
N
4a
S362
1.00
1.00
1.01
1.03
4.08
1.23
4.33
0.99
2.08
3.15
2.03
2.03
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

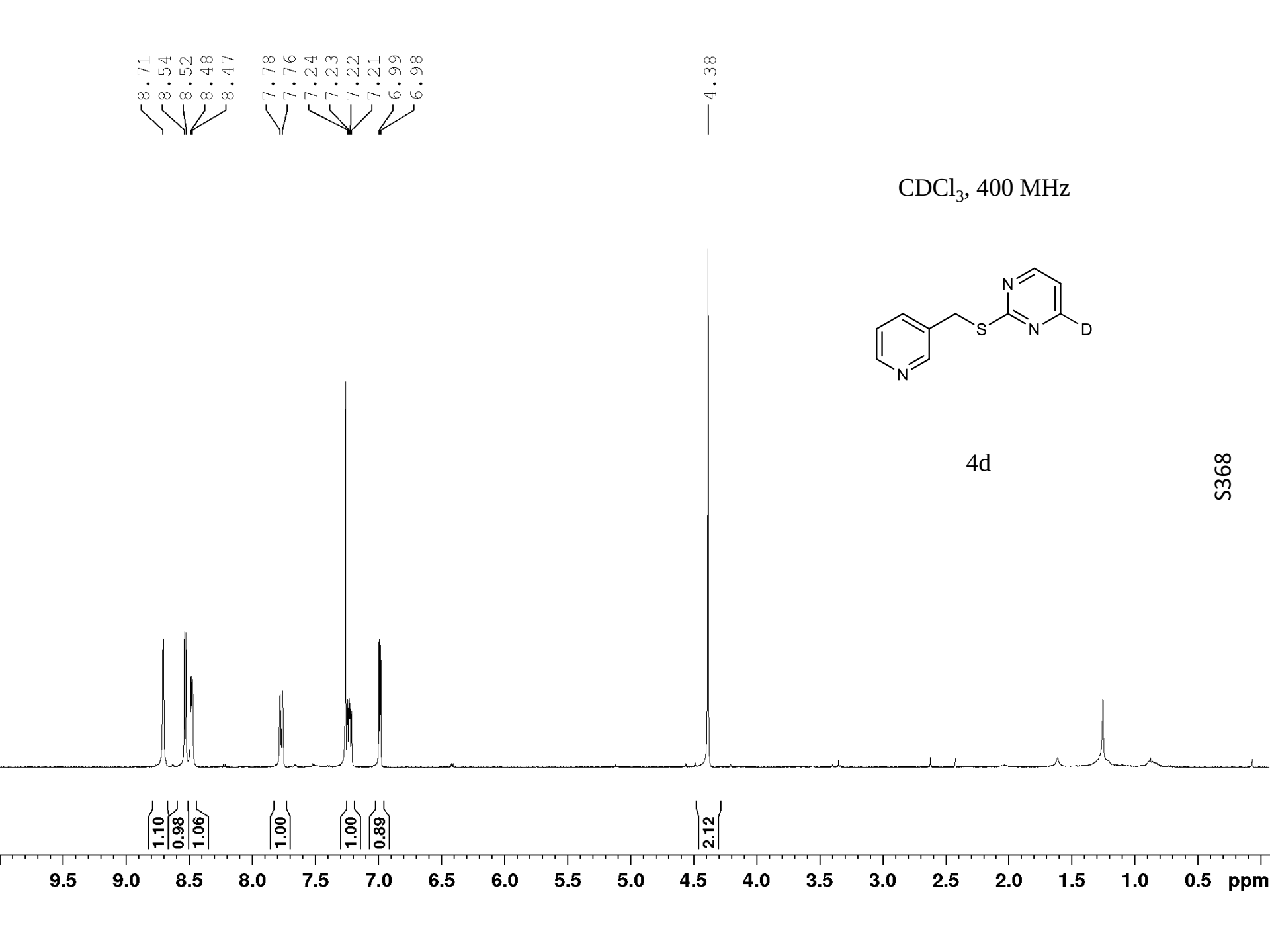

170.24
168.59
157.14
150.04
148.30
141.94
136.17
133.76
128.30
127.35
126.97
123.25
104.17
77.81
77.31
77.00
76.68
68.63
55.97
32.20
28.72
CDCl3, 100 MHz
O
N
Ph
Ph
N
S
N
N
4a
S363
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

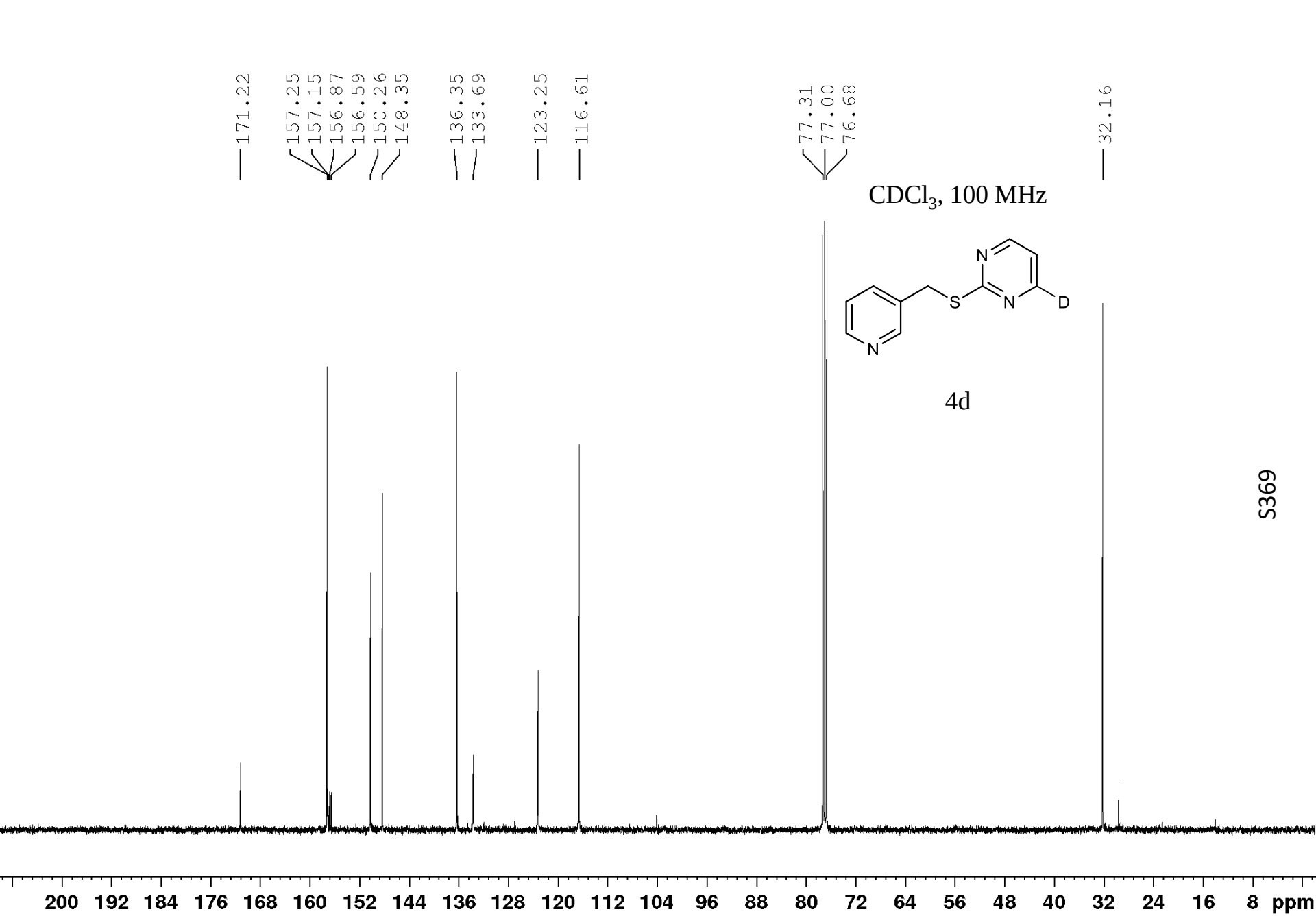

8.66
8.66
8.49
8.48
8.15
8.13
7.74
7.72
7.36
7.26
7.21
6.83
6.82
4.38
4.36
CDCl3, 400 MHz
N
S
N
S
N
4b
S364
0.95
0.99
0.98
1.00
4.43
1.50
0.96
4.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

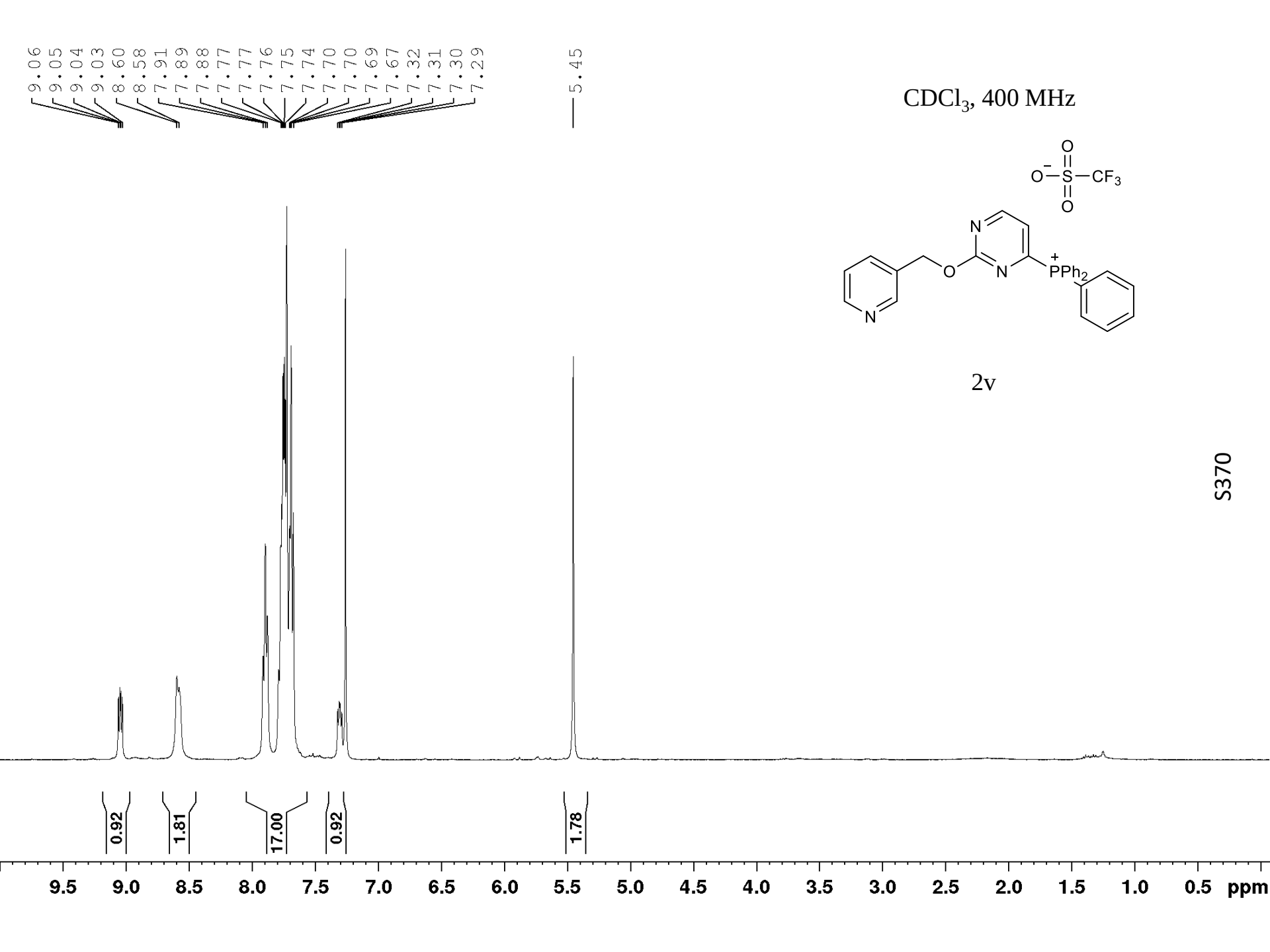

170.51
169.94
154.47
150.14
148.47
136.26
133.53
128.84
128.61
127.44
123.33
114.41
77.31
77.00
76.68
33.52
32.24
CDCl3, 100 MHz
N
S
N
S
N
4b
S365
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

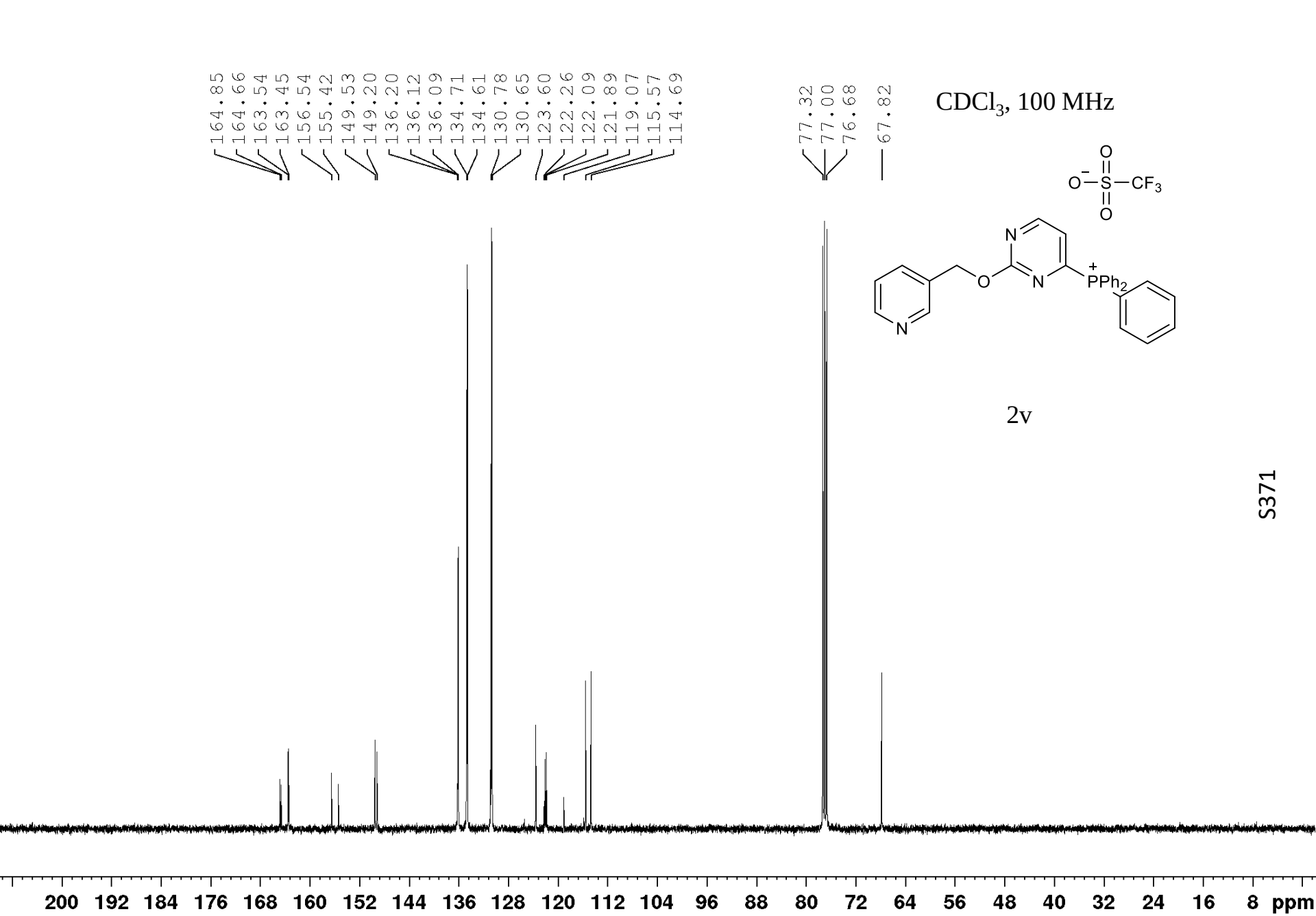

8.68
8.47
8.46
8.05
8.04
7.77
7.76
7.75
7.74
7.23
7.22
7.21
7.20
6.13
6.12
4.91
4.33
CDCl3, 400 MHz
N
S
N
NH2
N
4c
S366
1.00
0.99
0.93
0.95
0.90
0.95
1.94
1.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

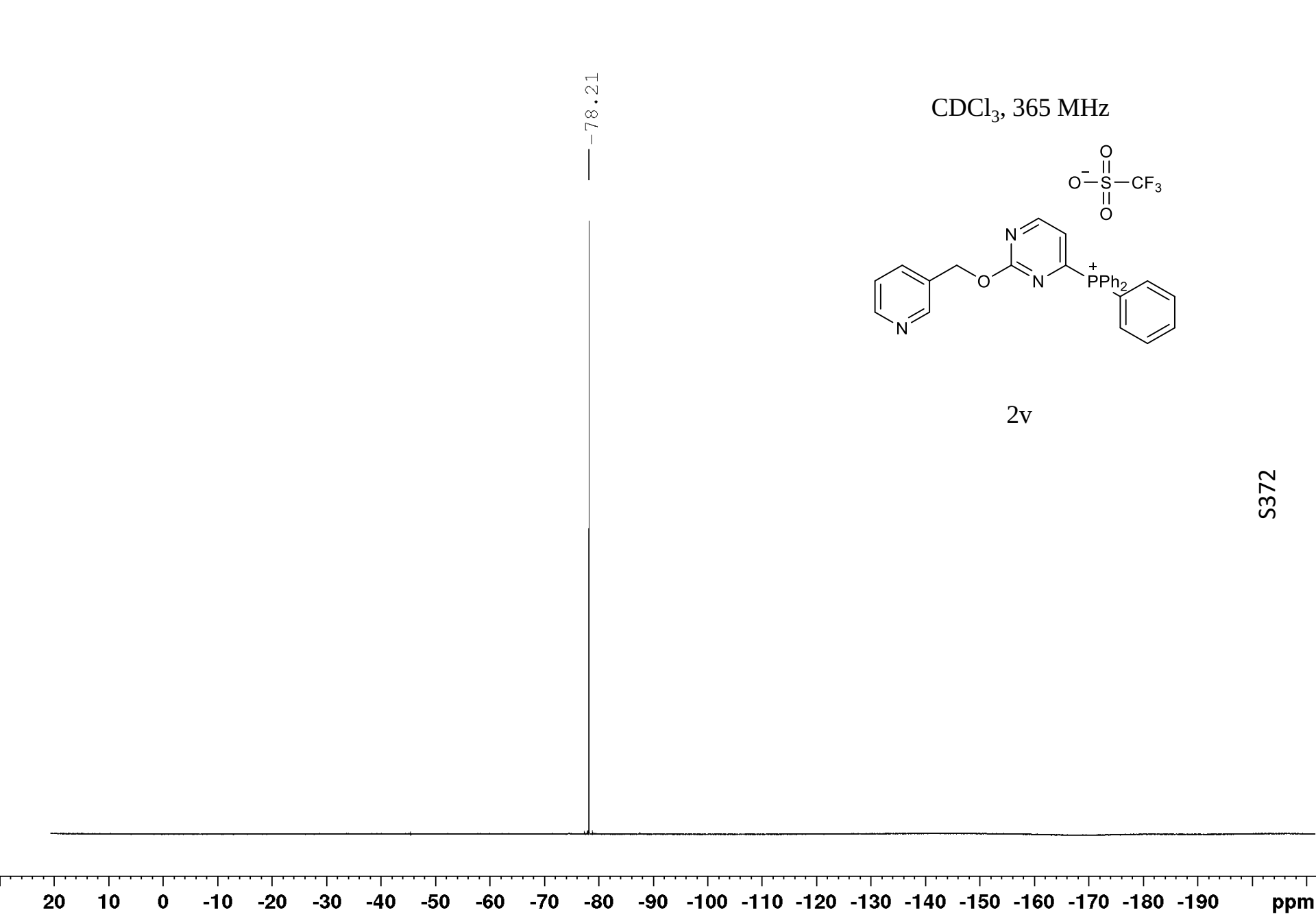

170.22
162.39
156.01
150.24
148.21
136.44
134.31
123.31
101.22
77.32
77.00
76.68
32.00
CDCl3, 100 MHz
N
S
N
NH2
N
4c
S367
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

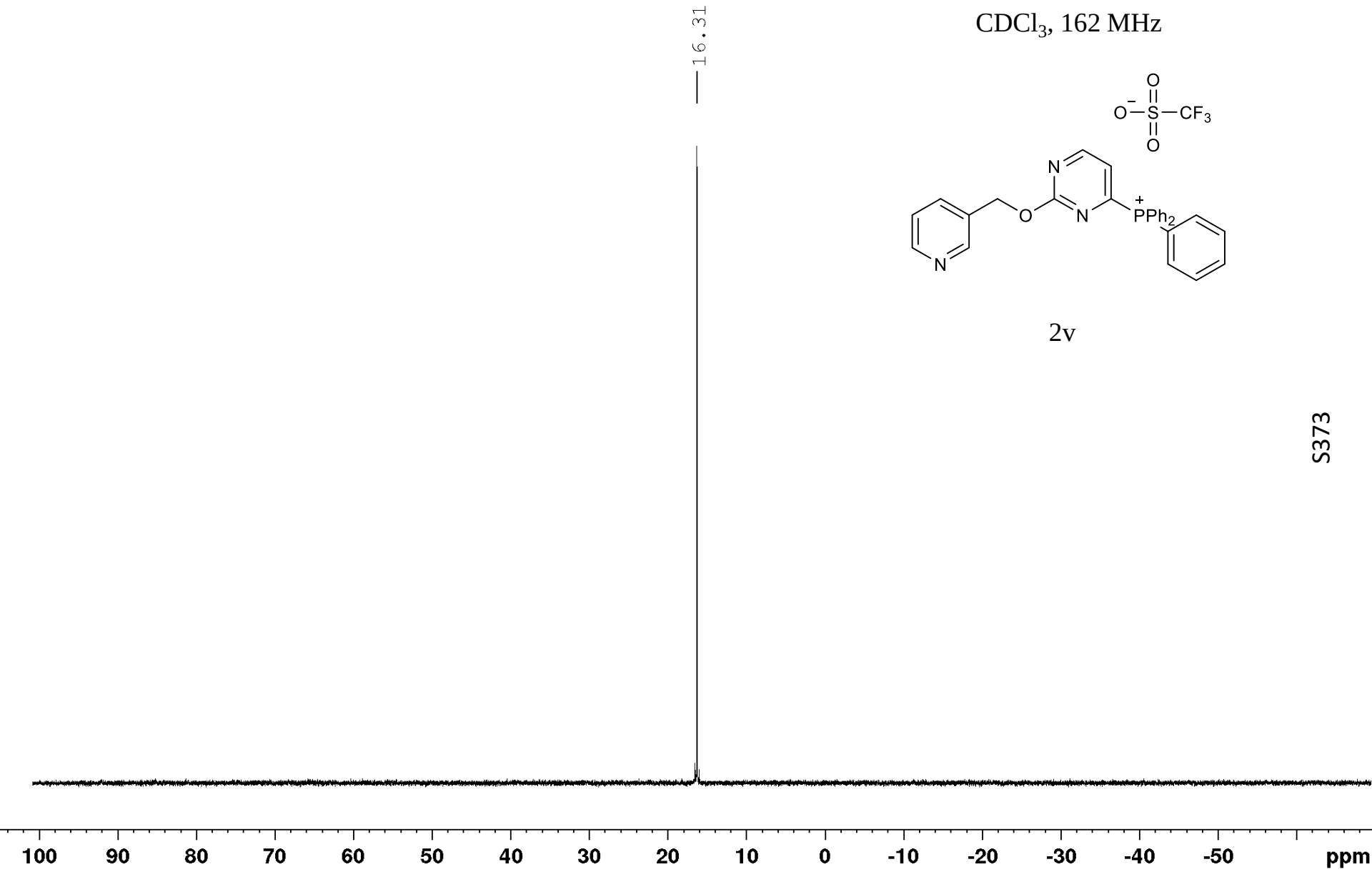

8.71
8.54
8.52
8.48
8.47
7.78
7.76
7.24
7.23
7.22
7.21
6.99
6.98
4.38
CDCl3, 400 MHz
N
S
N
D
N
4d
S368
1.10
0.98
1.06
1.00
1.00
0.89
2.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

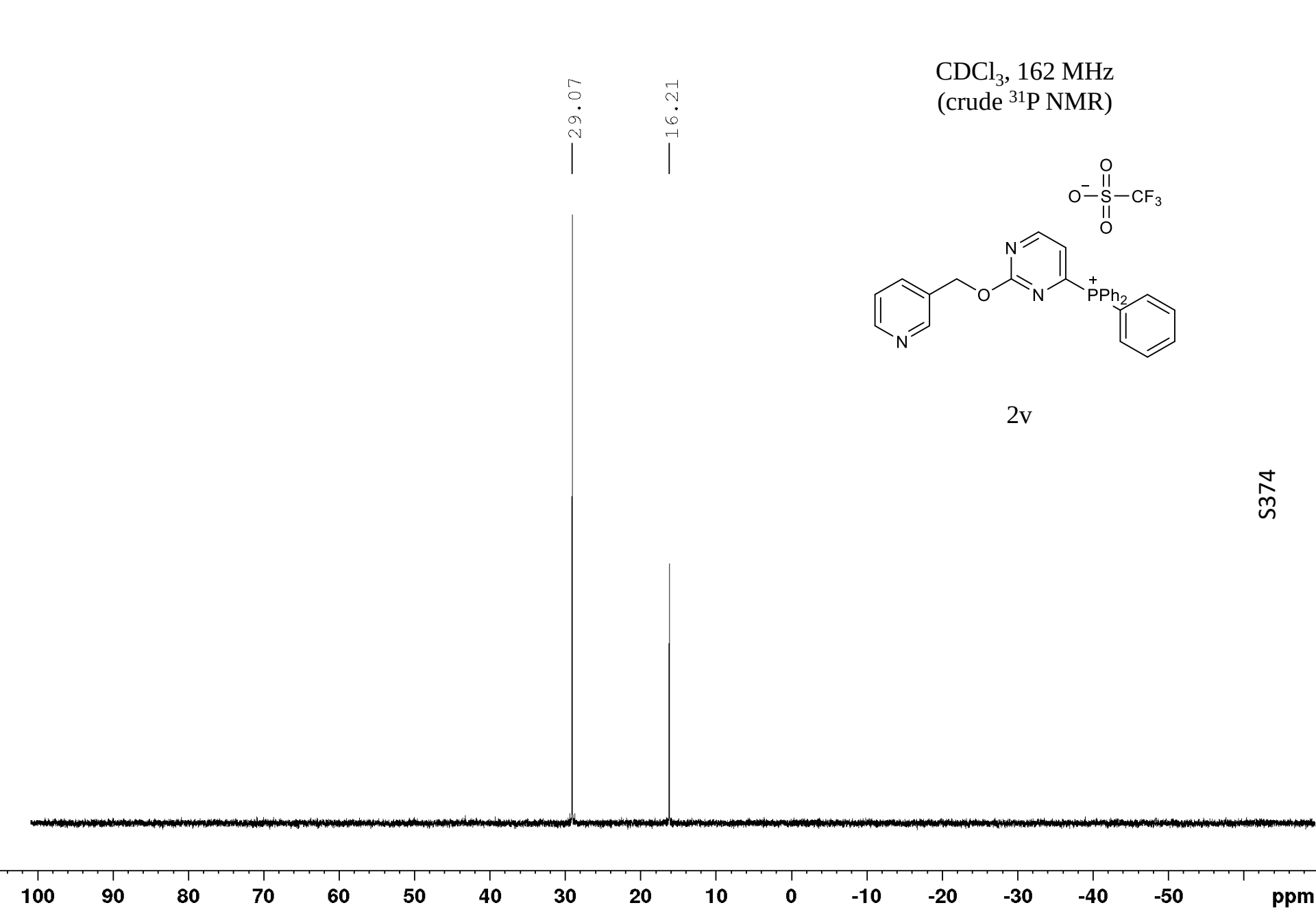

171.22
157.25
157.15
156.87
156.59
150.26
148.35
136.35
133.69
123.25
116.61
77.31
77.00
76.68
32.16
CDCl3, 100 MHz
N
S
N
D
N
4d
S369
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

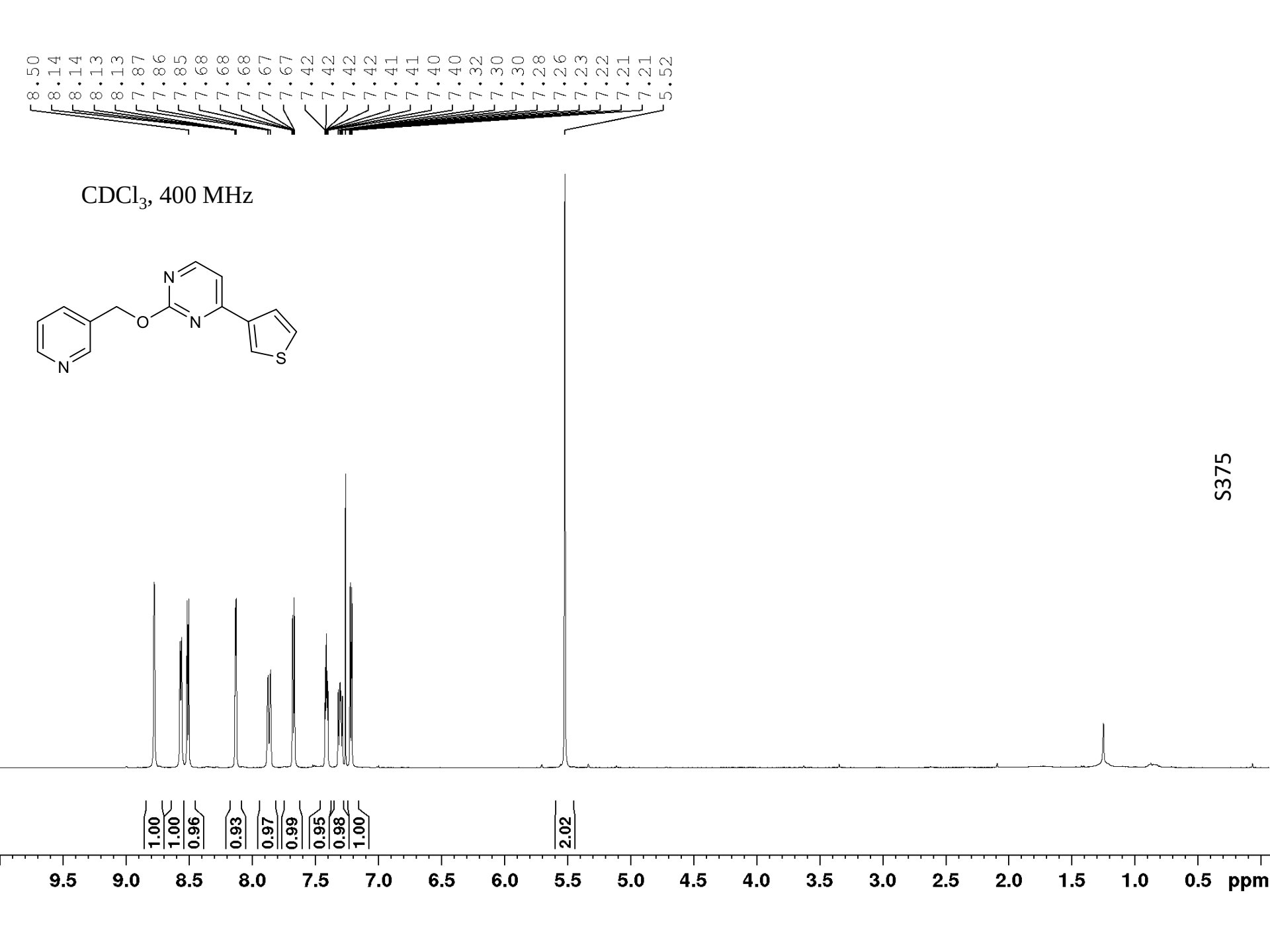

9.06
9.05
9.04
9.03
8.60
8.58
7.91
7.89
7.88
7.77
7.77
7.76
7.75
7.74
7.70
7.70
7.69
7.67
7.32
7.31
7.30
7.29
5.45
CDCl3, 400 MHz
2v
S370
0.92
1.81
17.00
0.92
1.78
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

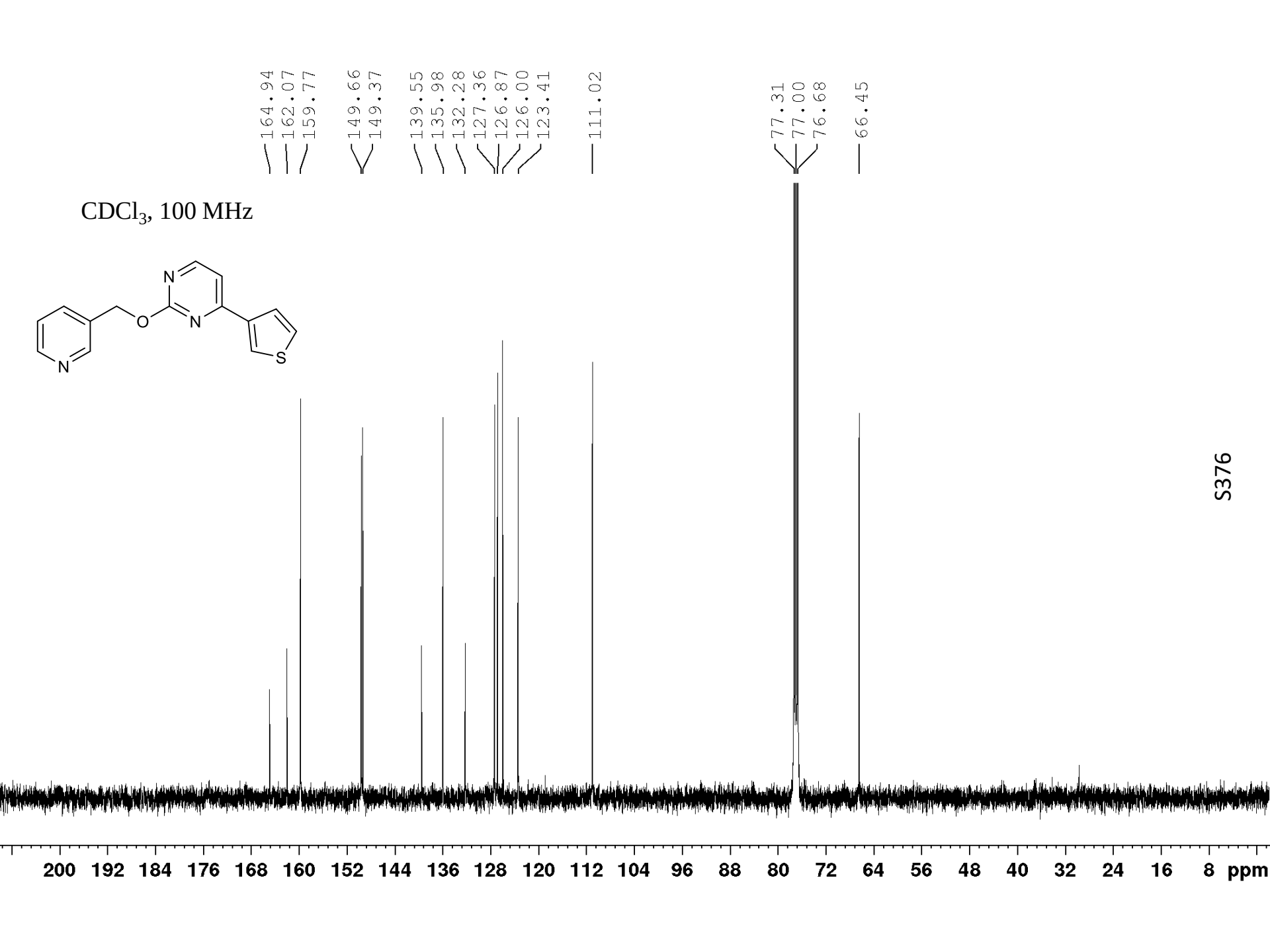

164.85
164.66
163.54
163.45
156.54
155.42
149.53
149.20
136.20
136.12
136.09
134.71
134.61
130.78
130.65
123.60
122.26
122.09
121.89
119.07
115.57
114.69
77.32
77.00
76.68
67.82
CDCl3, 100 MHz
2v
S371
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

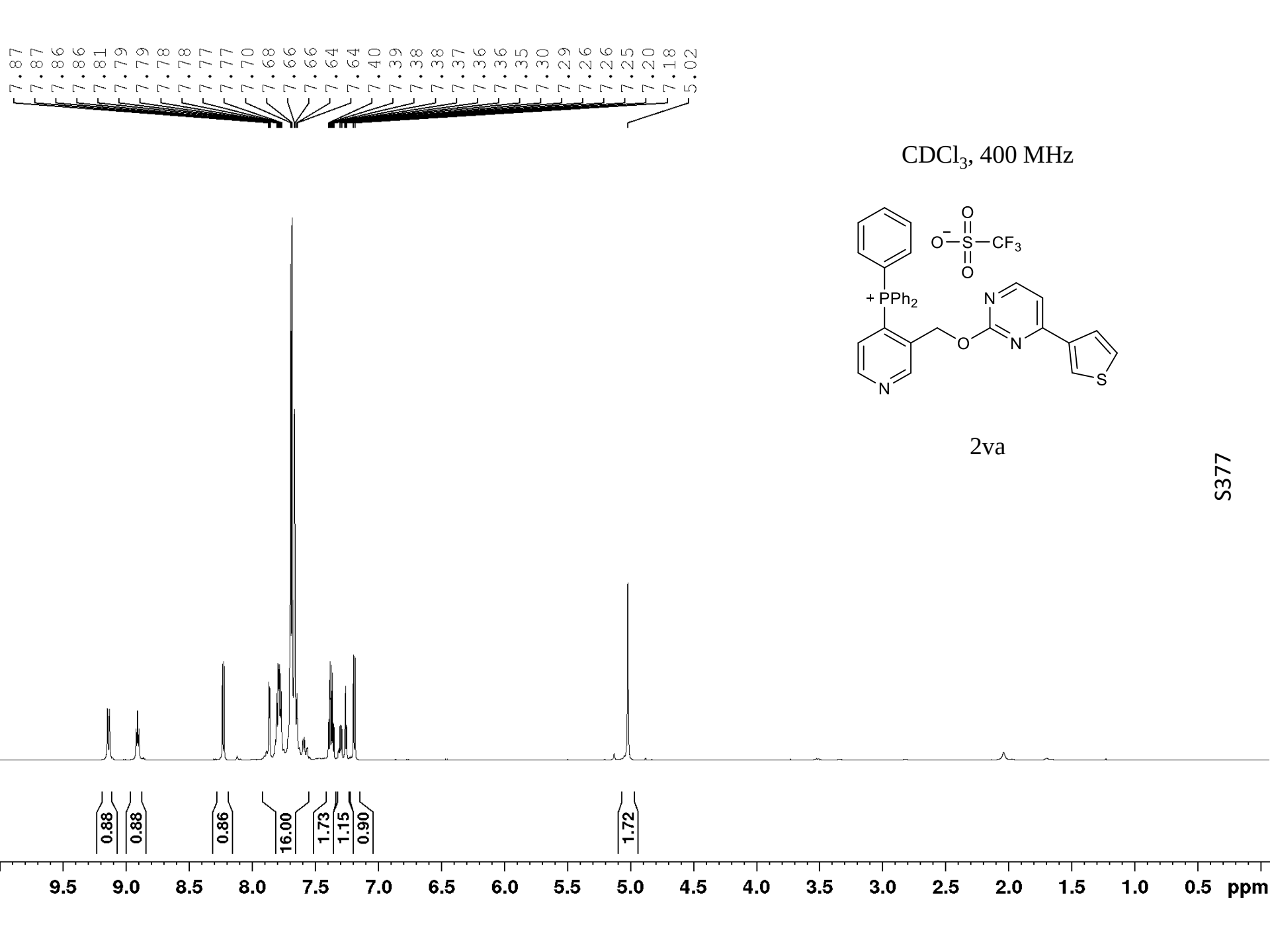

-78.21
CDCl3, 365 MHz
2v
S372
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm

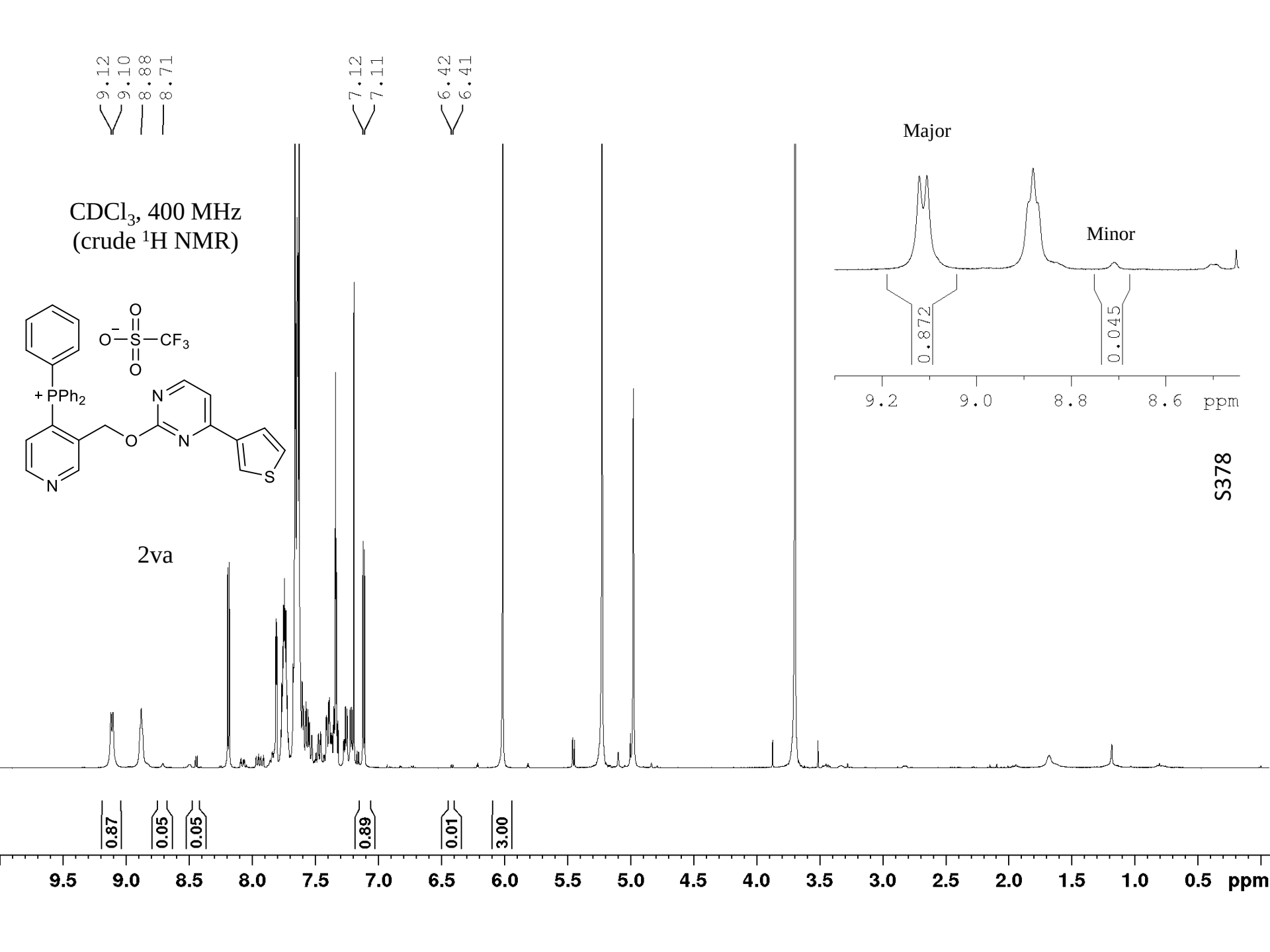

16.31
CDCl3, 162 MHz
2v
S373
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm

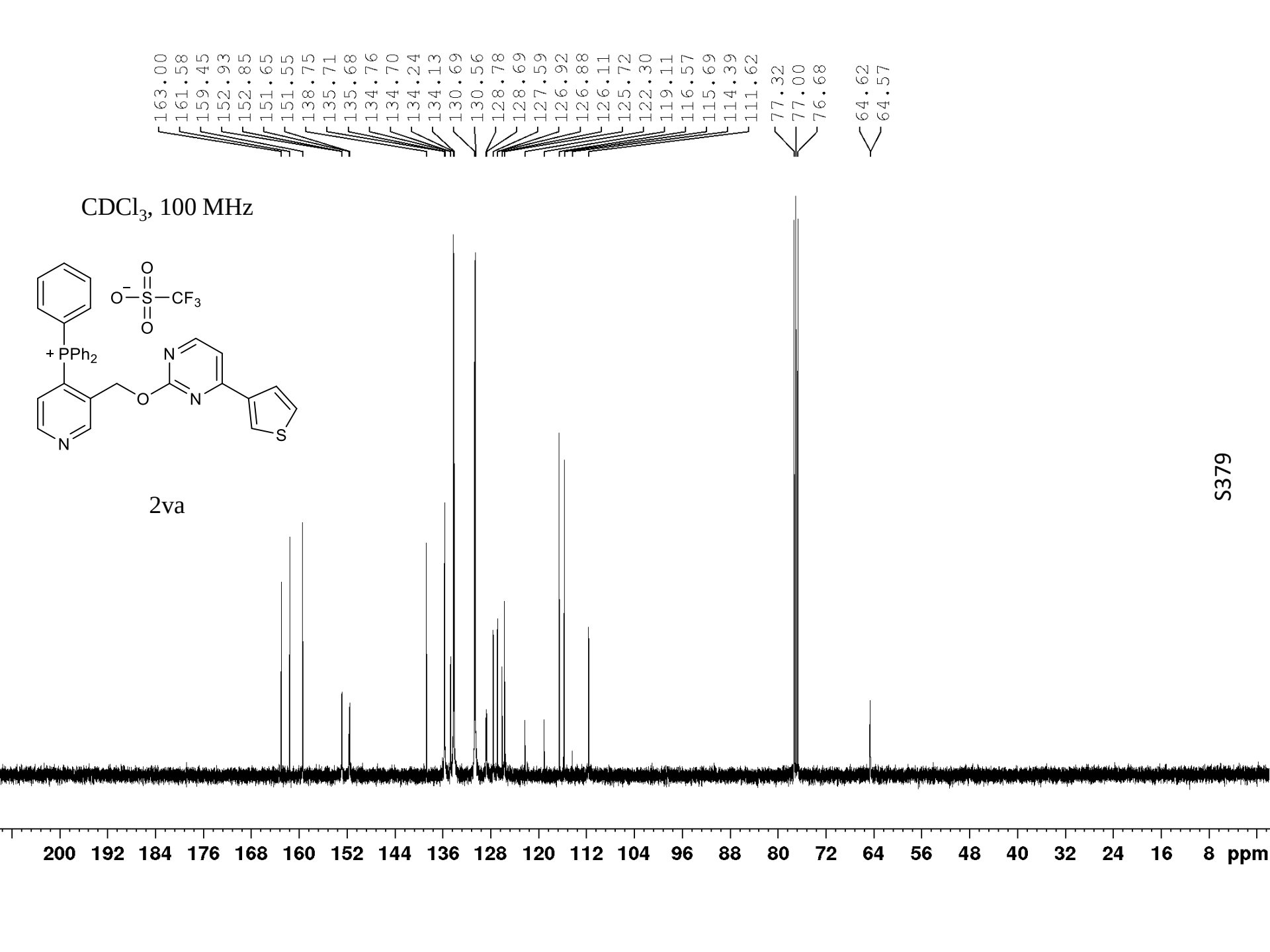

29.07
16.21
CDCl3, 162 MHz
(crude 31P NMR)
2v
S374
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ppm


8.50
8.14
8.14
8.13
8.13
7.87
7.86
7.85
7.68
7.68
7.68
7.67
7.67
7.42
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.32
7.30
7.30
7.28
7.26
7.23
7.22
7.21
7.21
5.52
CDCl3, 400 MHz
N
O
N
N
S
S375
1.00
1.00
0.96
0.93
0.97
0.99
0.95
0.98
1.00
2.02
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
0.5
ppm

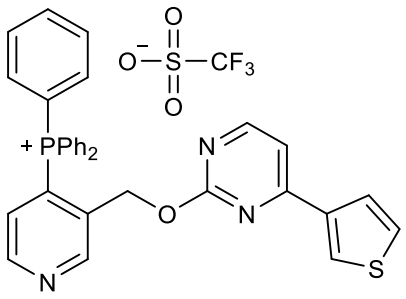

164.94
162.07
159.77
149.66
149.37
139.55
135.98
132.28
127.36
126.87
126.00
123.41
111.02
77.31
77.00
76.68
66.45
CDCl3, 100 MHz
N
O
N
N
S
S376
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm


7.87
7.87
7.86
7.86
7.81
7.79
7.79
7.78
7.78
7.77
7.77
7.70
7.68
7.66
7.66
7.64
7.64
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.30
7.29
7.26
7.26
7.25
7.20
7.18
5.02
CDCl3, 400 MHz
+ PPh2
O
O
S
CF3
N
O
N
N
S
2va
S377
0.88
0.88
0.86
16.00
1.73
1.15
0.90
1.72
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
ppm


9.12
9.10
8.88
8.71
7.12
7.11
6.42
6.41
CDCl3, 400 MHz
(crude 1H NMR)
2va
Major
Minor
0.872
0.045
9.2
9.0
8.8
8.6
ppm
S378
0.87
0.05
0.05
0.89
0.01
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
0.5
ppm

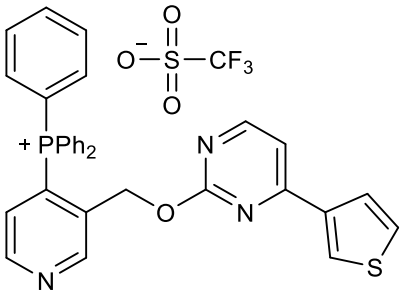

163.00
161.58
159.45
152.93
152.85
151.65
151.55
138.75
135.71
135.68
134.76
134.70
134.24
134.13
130.69
130.56
128.78
128.69
127.59
126.92
126.88
126.11
125.72
122.30
119.11
116.57
115.69
114.39
111.62
77.32
77.00
76.68
64.62
64.57
CDCl3, 100 MHz
+ PPh2
O
O
S
CF3
N
O
N
N
S
2va
S379
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 ppm

$CDCl_3$, 365 MHz



2va

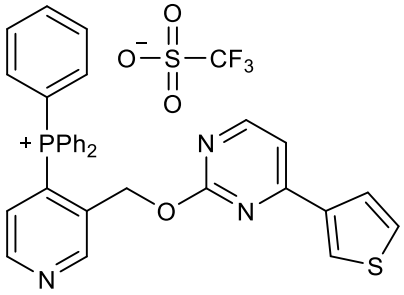
$CDCl_3$, 162 MHz



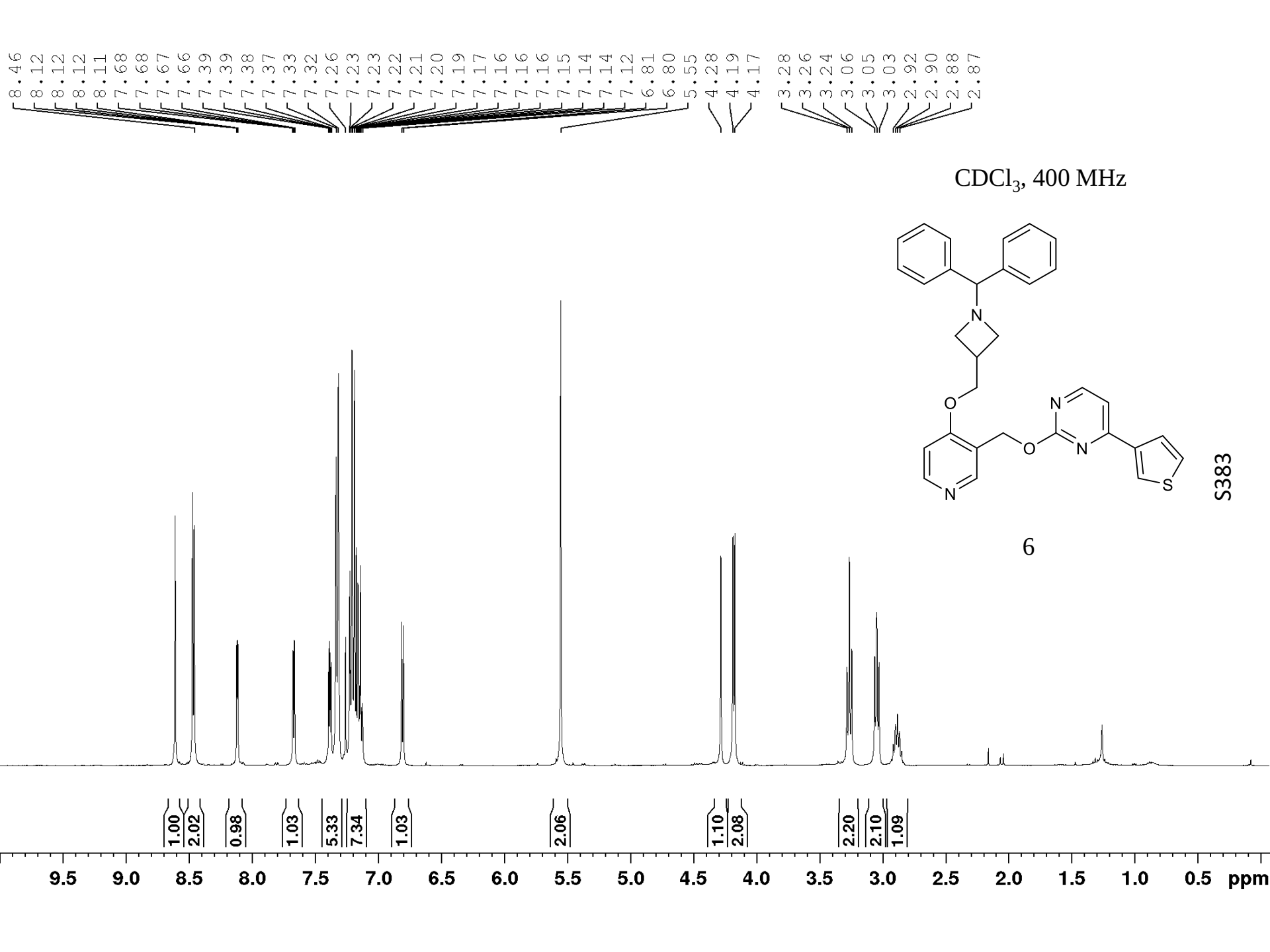
2va

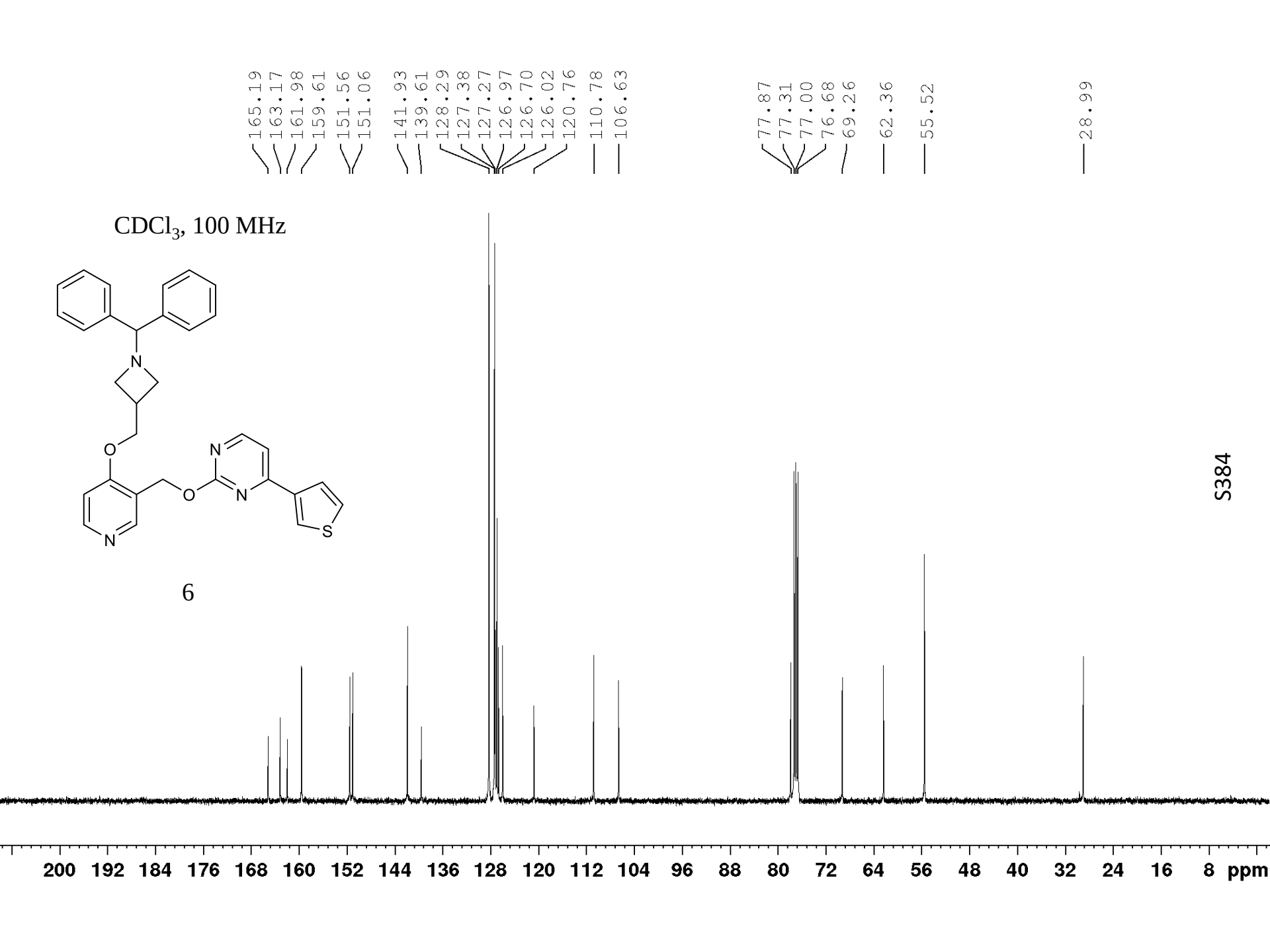
S381

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



2va


8.46
8.12
8.12
8.12
8.11
7.68
7.68
7.67
7.66
7.39
7.39
7.38
7.37
7.33
7.32
7.26
7.23
7.23
7.22
7.21
7.20
7.19
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.12
6.81
6.80
5.55
4.28
4.19
4.17
3.28
3.26
3.24
3.06
3.05
3.03
2.92
2.90
2.88
2.87
CDCl3, 400 MHz
S383
6
1.00
2.02
0.98
1.03
5.33
7.34
1.03
2.06
1.10
2.08
2.20
2.10
1.09
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
ppm


165.19
163.17
161.98
159.61
151.56
151.06
141.93
139.61
128.29
127.38
127.27
126.97
126.70
126.02
120.76
110.78
106.63
77.87
77.31
77.00
76.68
69.26
62.36
55.52
28.99
CDCl3, 100 MHz
N
O
N
O
N
N
S
6
S384
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 ppm