Supporting Online Material for

A Unified Approach to Couple Aromatic Heteronucleophiles to Azines and Pharmaceuticals

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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) or $(CD_3)_2SO$ (39.5 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}).

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 basic potassium permanganate solution as appropriate.

Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods.[1] Ethyl acetate, Dimethoxyethane (DME), 1,4-dioxane, N,N-Dimethylformamide (DMF), chloroform, 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.

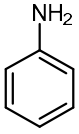
PPh_3 (99%) was purchased from Oakwood Chemical and is most effective when crushed to a powder before use. Tf_2O (99%) was purchased from Oakwood Chemical and used without further purification but was routinely stored in a –20 ºC fridge. NEt_3 and DBU were distilled before use. NaH (60% in mineral oil) was purchased from Sigma Aldrich and was typically distributed into vials and stored in a desiccator. KH (36.3% in Paraffin) was purchased from Sigma Aldrich and was kept in a Glovebox. *n*-BuLi (1.6M in Hexanes) was purchased from Sigma Aldrich and routinely stored in a -20 ºC fridge. 15-Crown-5 was purchased from Oakwood Chemical Company and distilled before use and stored in a -20 ºC fridge. 18-Crown-6 was purchased from Sigma Aldrich and routinely stored in a -20 ºC fridge.

2. Challenging Substrates & Limitations

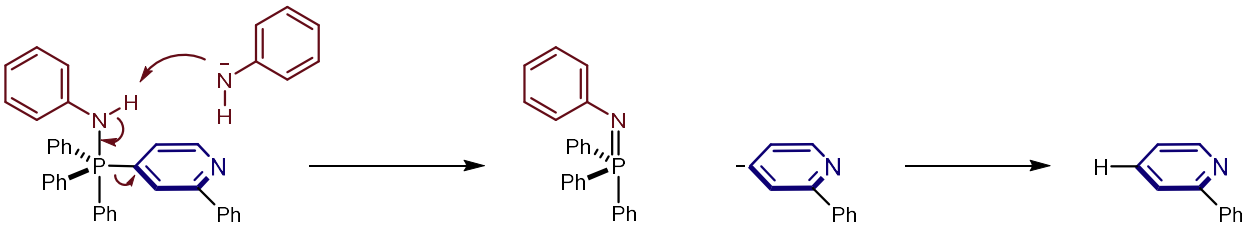
Some nucleophiles and heterocyclic phosphonium salts were unsuccessful for the coupling protocol disclosed in this communication. These cases are stated below along with hypothesized rationales of their unfavorable outcomes.

Nucleophiles:

All these nucleophiles were subjected to deprotonation conditions followed by the addition of Triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (1a).

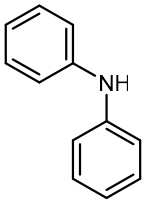


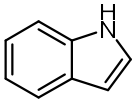
Primary anilines do not form coupled products and we believe that the mechanism below is operative. An intermediate iminophosphorane is detected by LCMS and gives credibility to the mechanistic proposal.

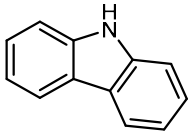


detected by LCMS

m/z LRMS (ESI + APCI) found $[M + H]^+$ 354.2, $C_{14}H_9F_3NS^+$ requires 354.1

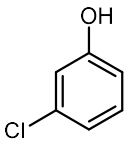




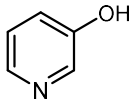


- Diphenyl amine showed no desired product formation. We believe that there is an unfavorable steric interaction from the phenyl rings in the P(V) intermediate that disfavors ligand-coupling to from the C–N bond. Indole and carbazole are also unfavorable as coupling partners and again, our hypothesis is that unfavorable steric interactions from the C–H bonds on the aryl groups disfavor ligand-coupling.

- Only trace product was detected by LCMS for this 1,2,4-triazole when KH, 18-crown-6 & THF were used. All other reaction conditions didn't show any evidence of the desired coupled product. A trend in this coupling process is that nucleophiles that are too electron-deficient can be unsuitable as coupling partners.

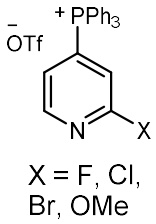


- 3-chlorophenol only produced 8% by of the desired product by crude ^{1}H NMR when ran at 60 °C using NaH, 15-crown-5 and THF. This trend of low yields was consistent among all other mono-halogenated phenols other than iodine (**2c**) and again indicates that nucleophiles that contain electron-withdrawing groups are less effective as coupling partners.

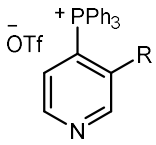


- Both 2- and 3-hydroxypyridine did not form coupled products. As above, the withdrawing effect of the deficient heterocycle renders the intermediate oxyanion unsuitable for ligand coupling. The precise reasons for this effect are not completely clear at this point and are under investigation in our laboratory.

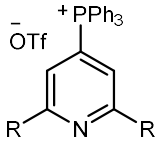
Limitations of Heterocyclic Phosphonium Salts:



-Halogens at the 2-position on the pyridine ring were unfavorable as coupling partners. We observed that an S_NAr pathway was competitive with the desired coupling at the 4-position and resulted in mixtures of products in poor yields. 2-Methoxy pyridine phosphonium salts also resulted in low yields of coupled products.



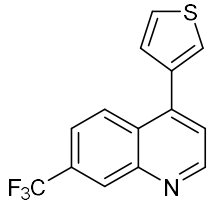
-3-position substituted salts were poor coupling partners for aniline nucleophiles resulting in little or no desired product. Cyano groups were the only 3-substituent that underwent coupling with aniline (**2ah**, **2av**).



- 2,6-disubstituted pyridines do not undergo phosphonium salt formation. Unfavorable steric interactions disfavor reaction with Tf_2O meaning the required N–Tf pyridinium salt is not properly formed. Yield for 2,6-disubstiuted salts are consequently low (<5%).

3. Preparation of Heterocyclic Phosphonium Salt and Aromatic Heteronucleophile Precursors

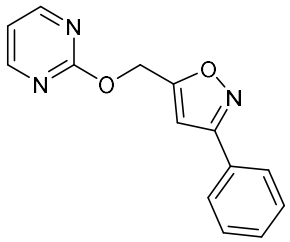
4-(Thiophen-3-yl)-7-(trifluoromethyl)quinoline



An oven dried 100 mL round bottom flask under N_2 was charged with 4-chloro-7-(trifluoromethyl)quinoline (973 mg, 4.20 mmol), thiophen-3-ylboronic acid (699 mg, 5.46 mmol),

$Pd(PPh_3)_4$ (97 mg, 0.08 mmol), K_2CO_3 (1.74 g, 12.6 mmol), 12 mL of H_2O and 36 mL of 1,4-dioxane. After 12 hours of stirring the reaction mixture under reflux was quenched with H_2O (20 mL), organic layer separated, and aqueous layer extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 16% EtOAc in hexanes) to provide the title compound as brown solid (1.147 g, 4.12 mmol, 98% yield). mp 91–93 °C; IR υ_{max}/cm^{-1} (film): 3104, 3064, 1584, 1566, 1506, 1459, 1373, 1325, 1290, 1244, 1219, 1207, 1191, 1156, 1059, 902, 884, 853, 833, 815, 794, 784, 767, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (1H, d, *J* = 4.4 Hz), 8.47 (1H, s), 8.21 (1H, d, *J* = 8.8 Hz), 7.70 (1H, dd, *J* = 1.2, 8.8 Hz), 7.56–7.54 (2H, m), 7.50 (1H, d, *J* = 4.4 Hz), 7.34 (1H, dd, *J* = 1.4, 4.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.3, 147.8, 143.3, 137.6, 131.1 (q, *J* = 32.6 Hz), 128.6, 128.3, 127.7 (q, *J* = 4.3 Hz), 127.1, 126.8, 125.4, 123.9 (q, *J* = 271.1 Hz), 122.6, 122.2 (q, *J* = 3.1 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: -62.76; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 280.1, $C_{14}H_9F_3NS^+$ requires 280.0.

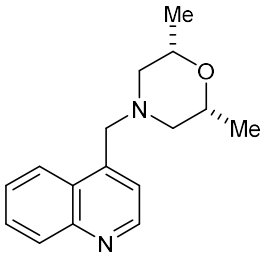
3-Phenyl-5-((pyrimidin-2-yloxy)methyl)isoxazole



An oven dried 100 mL round bottom flask was charged with sodium hydride (60% dispersion in mineral oil, 1.5 equiv.). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of THF (14 mL). The mixture was cooled to 0 °C and a mixture of (3-phenylisoxazol-5-yl)methanol (1.31 g, 7.50 mmol) in THF (7 mL) was added dropwise over 5 minutes, then allowed to stir for 30 mins at 0 °C. A solution of 2-chloropyrimidine (568 mg, 5 mmol) in THF (7 mL) was then added dropwise to the reaction mixture over 5 minutes. The reaction stirred at 0 °C for 5 minutes then was warmed to room temperature and allowed to stir for 14 hours. The mixture was 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 brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (silica gel: 5% EtOAc in CH_2Cl_2) to provide the title compound as a white solid (993 mg, 3.92 mmol, 78% yield). mp 98-105 ºC; IR ν_{max}/cm^{-1} (film): 3129, 3088, 3052, 2986, 1948, 2249, 2162, 1965, 1815, 1607, 1578, 1567, 1471, 1401, 1375, 1323, 1290, 1044, 688; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.57 (2H, d, J = 4.8 Hz), 7.83-7.76 (2H, m), 7.48-7.42 (3H, m), 7.02 (1H, t, J = 4.8 Hz), 6.70 (1H, s), 5.59 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 164.3, 162.5, 159.5, 130.0, 128.9, 128.8, 126.8, 115.8, 101.6, 59.9; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 254.2, $C_{14}H_{12}N_3O_2^+$ requires 254.1.

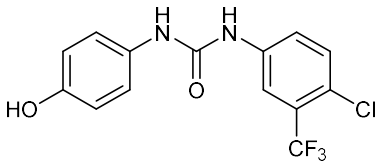
(2R,6S)-2,6-Dimethyl-4-(quinolin-4-ylmethyl)morpholine



An oven-dried 200 mL round bottom flask was charged with 4-quinolinecarboxaldehyde (2.36 g, 15.0 mmol), *cis*-2,6,-dimethylmorpholine (2.03 mL, 16.5 mmol), and sodium triacetoxyhydroborate (6.36 g, 30.0 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill. CH_2Cl_2 (75 mL) was added to the reaction flask along with glacial AcOH (1.73 mL). After 1 hour stirring at room temperature, the reaction was quenched with a saturated aqeuous solution of NH_4Cl (30 mL), diluted with CH_2Cl_2, and the organic layer was separated. The aqueous layer was basified with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were 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 (2.98 g, 11.6 mmol, 77% yield). IR ν_{max}/cm^{-1} (film): 3035, 2971, 2868, 2813, 2774, 980, 815, 662, 645, 591; ^1H NMR

(400 MHz, $CDCl_3$) δ: 8.84 (1H, d, *J* = 4.3 Hz), 8.23 (1H, d, *J* = 8.4 Hz), 8.11 (1H, d, *J* = 8.4 Hz), 7.70 (1H, m), 7.54 (1H, m), 7.40 (1H, d, *J* = 4.3 Hz), 3.87 (2H, s), 3.69 (2H, m), 2.72 (2H, d, *J* = 10.4 Hz), 1.87 (2H, t, *J* = 10.7 Hz), 1.13 (6H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 148.3, 143.6, 129.9, 129.1, 127.6, 126.3, 124.2, 121.4, 71.7 (2C), 59.6, 19.0; *m/z* LRMS (ESI+ APCI) found $[M+H]^+$ 257.2, $C_{16}H_{20}N_2O^+$ requires 257.2.

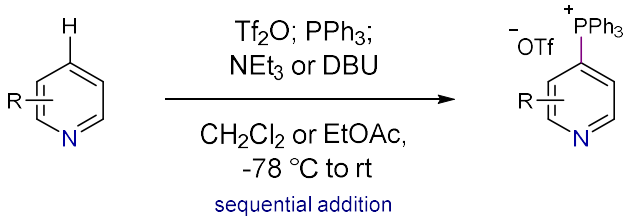
1-(4-Chloro-3-(trifluoromethyl)phenyl)-3-(4-hydroxyphenyl)urea (3)



An oven dried 200 mL round bottom flask was charged with 4-aminophenol (546 mg, 5.00 mmol). The flask was subjected to three cycles of vacuum/nitrogen backfill before addition of CH_2Cl_2 (25 mL). A 0.2 M solution of 1-chloro-4-isocyanato-2-(trifluoromethyl)benzene in THF (25 mL) was added dropwise to the reaction flask and stirred at room temperature for 16 hrs. The reaction mixture was then filtered and rinsed with CH_2Cl_2 and H_2O. The material was then further purified by flash chromatography (silica gel: 35% EtOAc in Toluene) to provide the title compound as a white solid (1.11 g, 3.36 mmol, 84% yield). mp 185-195 ºC; IR ν_{max}/cm^{-1} (film): 3293, 3109, 2359, 1896, 1672, 1623, 1557, 1480, 1326, 1261, 1180, 1145, 1124, 1031, 831; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ: 9.12 (1H, s), 9.03 (1H, s), 8.48 (1H, s), 8.10 (1H, d, *J* = 1.6 Hz), 7.64-7.56 (2H, m), 7.23 (2H, d, *J* = 8.6 Hz), 6.70 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 153.9, 152.6, 139.7, 131.9, 130.5, 126.6 (q, *J* = 30.7 Hz), 122.9 (q, *J* = 273.4 Hz), 122.8 (q, *J* = 4.1 Hz), 121.8, 121.0, 116.5 (q, *J* = 5.8 Hz), 115.2; ^{19}F NMR (365 MHz, $(CD_3)_2SO$) δ: -61.46; *m/z* LRMS (ESI + APCI) found $[M + H]^+$ 331.1, $C_{14}H_{11}ClF_3N_2O_2^+$ requires 331.0.

4. Preparation of Heterocyclic Phosphonium Salts

General Procedure A



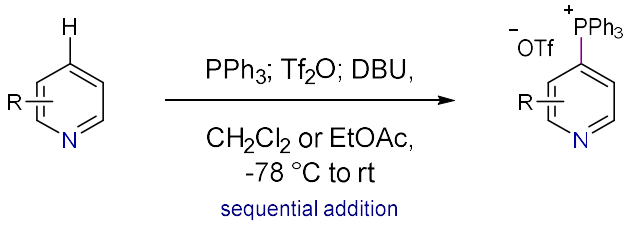
An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 ºC and Tf_2O (1.0 equiv) was added dropwise 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



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 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.

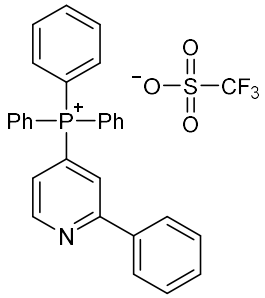
Notes.

1) PPh_3 was crushed into a powder prior to use.

* 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.

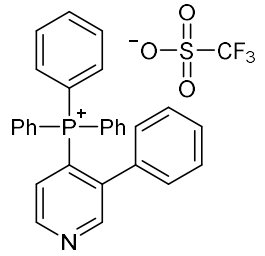
2) Certain substrates require longer periods for the precipitation step and specific cases are indicated below.
3) In a small number of cases, residual CH_2Cl_2 can become trapped in the phosphonium salt products. In these cases, heating the salts under vacuum (50-100 ºC) removed the solvent.
4) In order to evaluate regioselectivity from the crude reaction mixtures, a duplicate reaction was performed, and aliquots taken after addition of the organic base and warming to room temperature. These aliquots were concentrated *in vacuo* and analyzed by ^{1}H and ^{31}P NMR

Triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (1a)



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (1H, app t, *J* = 5.1 Hz), 7.93-7.54 (18H, m), 7.50 (1H, ddd, *J* = 17.8, 5.1, 1.1 Hz), 7.42-7.36 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ:159.1 (d, *J* = 9.9 Hz), 151.6 (d, *J* = 10.7 Hz), 136.7 (d, *J* = 1.5 Hz), 136.1 (d, J = 3.2 Hz), 134.3 (d, *J* = 9.8 Hz), 130.9 (d, *J* = 13.0 Hz), 130.4, 129.23 (d, *J* = 84.1 Hz), 129.0, 127.0, 125.3 (d, *J* = 7.8 Hz), 123.1, (d, *J* = 8.4 Hz), 120.7 (q, *J* = 321.1 Hz), 115.5 (d, *J* = 89.1 Hz). The spectroscopic data is in agreement with our previous synthesis.[2]

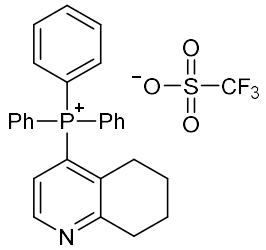
Triphenyl(3-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (1H, app t, *J* = 4.7 Hz), 8.74 (1H, d, *J* = 6.8 Hz), 7.85-7.73 (3H, m), 7.73-7.40 (13H, m), 7.11 (1H, t, *J* = 7.6 Hz),

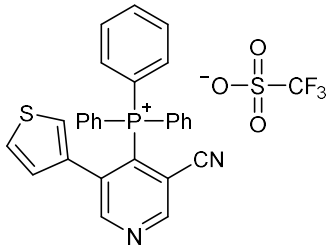
6.91 (2H, app t, J = 7.6 Hz), 6.71 (2H, d, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6 (d, J = 8.0 Hz), 150.0 (d, J = 10.4 Hz), 141.7 (d, J = 7.3 Hz), 135.4 (d, J = 3.0 Hz), 134.4 (d, J = 4.5 Hz), 134.2 (d, J = 10.3 Hz), 130.6 (d, J = 13.0 Hz), 129.2, 128.9, 128.3, 128.2, 126.4 (d, J = 83.4 Hz), 120.8 (q, J = 321.2 Hz), 116.9 (d, J = 89.2 Hz). The spectroscopic data is in agreement with our previous synthesis.[2]

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



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.74 (1H, app t, J = 5.1 Hz), 8.07-7.93 (3H, m), 7.92-7.71 (12H, m), 6.94 (1H, dd, J = 15.3, 5.1 Hz), 3.12-2.97 (2H, m), 2.21-2.04 (2H, m), 1.84-1.71(2H, m), 1.60-1.44 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3 (d, J = 8.4 Hz), 148.2 (d, J = 11.4 Hz), 135.5 (d, J = 7.6 Hz), 135.3 (d, J = 3.1 Hz), 134.1 (d, J = 10.7 Hz), 130.5 (d, J = 13.0 Hz), 126.2 (d, J = 9.9 Hz), 125.5 (d, J = 82.4 Hz), 120.4 (q, J = 322.0 Hz), 116.3 (d, J = 87.7 Hz), 32.0 (d, J = 2.3 Hz), 29.7 (d, J = 5.3 Hz), 21.0, 20.5. The spectroscopic data is in agreement with our previous synthesis.[2]

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

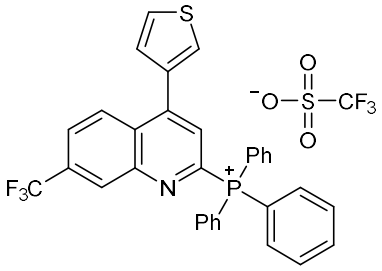


Major
11.4:1 Mixture of Regioisomers

Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.45 (1H, d, J = 5.0 Hz), 9.07 (1H, d, J = 5.5 Hz), 7.98-7.84 (9H, m), 7.77-7.67 (6H, m), 7.21-7.16 (1H, m), 7.13 (1H,

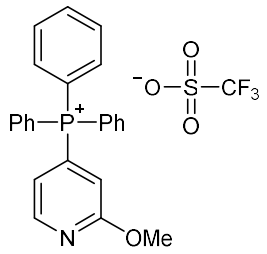
br s), 6.57 (1H, d, J = 4.9 Hz); Major isomer, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.0 (d, J = 6.9 Hz), 154.7 (d, J = 5.8 Hz), 140.2 (d, J = 5.5 Hz), 135.3 (d, J = 3.0 Hz), 134.5 (d, J = 10.8 Hz), 130.4 (d, J = 13.3 Hz), 128.5, 128.3 (d, J = 84.5 Hz), 128.3, 127.8, 120.7 (q, J = 322.4 Hz), 117.0 (d, J = 88.5 Hz), 113.9 (d, J = 6.0 Hz), 113.2 (d, J = 4.4 Hz).

Triphenyl(4-(thiophen-3-yl)-7-(trifluoromethyl)quinolin-2-yl)phosphonium trifluoromethanesulfonate



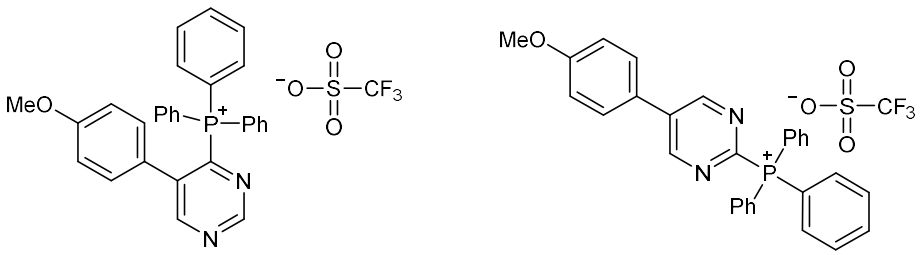
Prepared according to general procedure B (except the reaction was cooled to –50 ºC for the Tf_2O addition, then cooled to –78 ºC for the DBU addition) using 4-(thiophen-3-yl)-7-(trifluoromethyl)quinoline (805 mg, 2.88 mmol), PPh_3 (831 mg, 3.17 mmol), Tf_2O (484 μL, 2.88 mmol) and CH_2Cl_2 (29 mL). After the purification procedure the pure phosphonium salt was isolated as an off-white solid (1.68 g, 2.33 mmol, 81% yield). mp 234-237 °C; IR υ_{max}/cm^{-1} (film): 3064, 1739, 1575, 1540, 1501, 1484, 1439, 1421, 1378, 1335, 1224, 1167, 1140, 1108, 1065, 1030, 997, 918, 835, 797, 785, 748, 728, 701, 689, 663, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (1H, s), 8.40 (1H, d, J = 8.9 Hz), 7.92–7.87 (4H, m), 7.82–7.75 (14H, m), 7.55 (1H, dd, J = 3.0, 4.7 Hz), 7.34 (1H, J = 4.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 148.3, 147.5, 146.5 (d, J = 10.5 Hz), 146.4, 135.9 (d, J = 2.9 Hz), 135.5 (d, J = 1.5 Hz), 134.7 (d, J = 10.1 Hz), 133.2 (q, J = 33.2 Hz), 130.7 (d, J = 12.9 Hz), 128.6 (d, J = 2.4 Hz), 128.3, 128.1, 128.0, 127.8, 125.9–125.6 (m), 123.2 (q, J = 271.7 Hz), 120.7 (q, J = 319.6 Hz), 116.7 (d, J = 88.0 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –63.08, –78.20; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.62; *m*/*z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 540.2, $C_{32}H_{22}F_3NPS^+$ requires 540.1.

Triphenyl(2-methoxypyridin-4-yl)phosphonium trifluoromethanesulfonate



Prepared according to general procedure A using 2-methoxypyridine (52.5 µL, 0.50 mmol), PPh_3 (144 mg, 0.55 mmol), Tf_2O (84 µL, 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 (174 mg, 0.34 mmol, 67% yield). mp 149-154 °C; IR υ_{max}/cm^{-1} (film): 3063, 2956, 2360, 1980, 1583, 1438, 1380, 1264, 1143, 1107, 1031, 722, 635; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.57 (1H, t, J = 5.3 Hz), 7.97-7.87 (3H, m), 7.85-7.74 (6H, m), 7.71-7.59 (6H, m), 7.12 (1H, dd, J = 11.5 Hz, 5.0 Hz), 6.84 (1H, d, J = 15.0 Hz), 4.01 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5 (d, J = 15.7 Hz), 149.8 (d, J = 10.5 Hz), 136.1 (d, J = 2.9 Hz), 134.2 (d, J = 10.5 Hz), 130.9 (d, J = 13.5 Hz), 130.5 (d, J = 85.2 Hz), 120.7 (q, J = 321.2 Hz), 118.8 (d, J = 8.3 Hz), 116.2 (d, J = 10.0 Hz), 115.6 (d, J = 89.6 Hz), 54.3; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.17; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.37; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 519.1, $C_{24}H_{21}NOP^+$ requires 519.1.

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



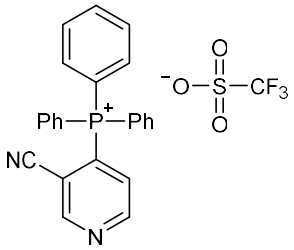
Major Minor

24:1 Mixture of Regioisomers

Prepared according to our previous report.[2] Major isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.44 (1H, s), 8.98 (1H, d, J = 9.0 Hz), 7.80-7.70 (3H, m), 7.67-7.56 (12H, m), 6.91 (2H, d, J = 8.7 Hz), 6.55 (2H, d, J = 8.7 Hz), 3.72 (3H, s); Minor isomer, ^1H NMR (400 MHz, $CDCl_3$) δ: 9.23 (2H, s),

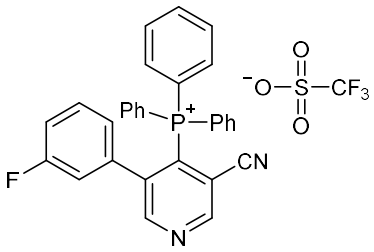
7.80-7.70 (3H, m), 7.70 (2H, d, *J* = 8.7 Hz), 7.67-7.56 (12H, m), 7.09 (2H, d, *J* = 8.6 Hz), 3.88 (3H, s); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8 (d, *J* = 5.3 Hz), 160.5, 157.0 (d, *J* = 16.8 Hz), 149.7 (d, *J* = 114.5 Hz), 142.7 (d, *J* = 19.2 Hz), 135.2 (d, *J* = 3.1 Hz), 134.7 (d, *J* = 10.2 Hz), 130.6, 130.3 (d, *J* = 13.1 Hz), 123.6, 120.8 (q, *J* = 321.3 Hz), 117.1 (d, *J* = 88.6 Hz), 114.4, 55.4.

(3-Cyanopyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



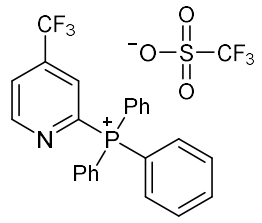
Prepared according to our previous report.[4] ^{1}H NMR (400 MHz, CDCl3) δ: 9.21 (1H, dd, J = 4.2, 4.1), 9.16 (1H, d, J = 5.5 Hz), 7.95–7.91 (3H, m), 7.83–7.71 (13H, m); ^{13}C NMR (100 MHz, CDCl3) δ: 155.5 (d, J = 9.2 Hz), 154.9 (d, J = 5.5 Hz), 136.4 (d, J = 3.1 Hz), 134.7 (d, J = 10.7 Hz), 131.0 (d, J = 13.3 Hz), 130.9 (d, J = 82.7 Hz), 130.2 (d, J = 7.4 Hz), 120.6 (q, J = 319.6 Hz), 114.4 (d, J = 89.5 Hz), 113.6 (d, J = 5.1 Hz), 111.8.

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



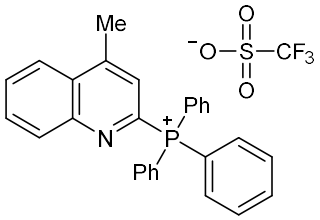
Prepared according to our previous report.[5] ^{1}H NMR (400 MHz, CDCl3) δ: 9.10 (1H, dd, *J* = 4.9, 1.2 Hz), 8.83 (1H, dd, *J* = 5.5, 1.1 Hz), 7.92-7.44 (15H, m), 7.02-6.92 (1H, m), 6.84-6.73 (2H, m), 6.70 (1H, d, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, CDCl3) δ: 162.6 (d, *J* = 247.8 Hz), 152.8, 147.3, 140.1, 137.6 (d, *J* = 7.9 Hz), 135.6, 130.3 (d, *J* = 8.4 Hz), 129.0, 128.7, 127.9, 125.4 (d, *J* = 3.1 Hz), 116.7 (d, *J*, 22.5 Hz), 116.0 (d, *J* = 21.0 Hz), 115.1.

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



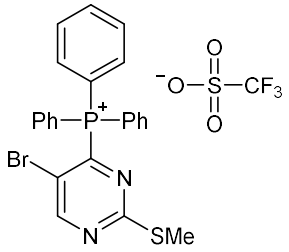
Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, CDCl3) δ: 9.33 (1H, d, *J* = 2.8 Hz), 8.02 (1H, m), 7.92 (3H, m), 7.82–7.69 (13H, m); ^{13}C NMR (100 MHz, CDCl3) δ: 154.2 (d, *J* = 19.9 Hz), 147.0 (d, *J* = 121.0 Hz), 139.9 (qd, *J* = 35.8 Hz, 11.3 Hz), 136.0 (d, *J* = 2.9 Hz), 134.5 (d, *J* = 10.2 Hz), 130.7 (d, *J* = 13.1 Hz), 126.1 (dq, *J* = 25.9, 3.6 Hz), 124.4 (m), 121.5 (qd, *J* = 274.1, 3.0 Hz), 120.7 (q, *J* = 320.5 Hz), 115.9 (d, *J* = 90.0 Hz). The spectroscopic data is in agreement with our reported synthesis.[2]

(4-Methylquinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate



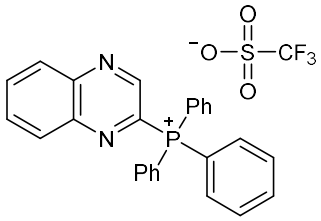
Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.12 (2H, m), 7.94-7.65 (17H, m), 7.53, (1H, d, *J* = 4.6 Hz), 2.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5 (d, *J* = 10.6 Hz), 148.5 (d, *J* = 22.6 Hz), 144.4 (d, *J* = 117.2 Hz), 135.6 (d, *J* = 3.1 Hz), 134.6 (d, *J* = 10.1 Hz), 131.6, 130.6 (d, *J* = 1.2 Hz), 130.5 (d, *J* = 12.9 Hz), 130.4, 128.8, 125.1 (d, *J* = 26.4 Hz), 124.4 (d, *J* = 1.3 Hz), 120.8 (q, *J* = 321.2 Hz), 117.3 (d, *J* = 88.2 Hz), 19.2 (d, *J* = 1.5 Hz).

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



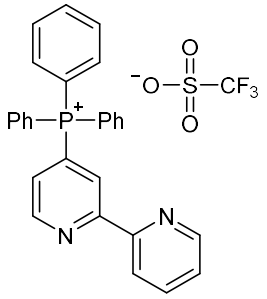
Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (1H, d, *J* = 7.9 Hz), 7.97-7.85 (3H, m), 7.83-7.66 (12H, m), 2.15 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9 (d, *J* = 17.2 Hz), 162.0 (d, *J* = 4.1 Hz), 151.4 (d, *J* = 118.7 Hz), 136.1 (d, *J* = 3.1 Hz), 134.8 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 13.3 Hz), 120.9 (q, *J* = 321.2 Hz), 120.9 (d, *J* = 17.1 Hz), 115.0 (d, *J* = 89.9 Hz), 14.4.

Triphenyl(quinoxalin-2-yl)phosphonium trifluoromethanesulfonate



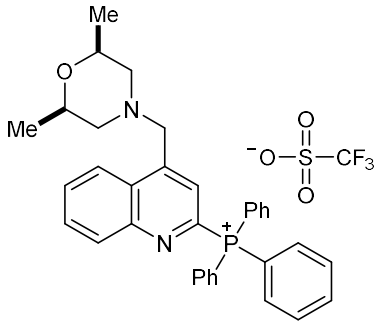
Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, s), 8.27-8.22 (2H, m), 8.09-8.01 (2H, m), 7.93-7.90 (3H, m), 7.79-7.72 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9 (d, *J* = 25.4 Hz), 143.4 (d, *J* = 2.8 Hz), 142.7 (d, *J* = 17.3 Hz), 140.8 (d, *J* = 111.6 Hz), 136.2 (d, *J* = 3.1 Hz), 135.0, 134.7 (d, *J* = 10.5 Hz), 133.1, 130.9 (d, *J* = 13.0 Hz), 130.2 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 2.3 Hz), 120.8 (q, *J* = 319.5 Hz), 116.0 (d, *J* = 88.1 Hz).

[2,2'-Bipyridin]-4-yltriphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.06 (1H, app t, *J* = 5.1 Hz), 8.65 (1H, d, *J* = 13.8 Hz), 8.55 (1H, d, *J* = 4.4 Hz), 8.46 (1H, d, *J* = 7.9 Hz), 7.96-7.88 (3H, m), 7.87-7.74 (7H, m), 7.72-7.55 (7H, m), 7.35 (1H, dd, *J* = 7.7, 4.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8 (d, *J* = 9.9 Hz), 153.4 (d, *J* = 2.3 Hz), 151.4 (d, *J* = 10.7 Hz), 149.3, 137.3, 136.2 (d, *J* = 3.1 Hz), 134.4 (d, *J* = 9.9 Hz), 131.0 (d, *J* = 13.0 Hz), 129.3 (d, *J* = 83.9 Hz), 126.9 (d, *J* = 8.4 Hz), 125.1, 123.9 (d, *J* = 9.2 Hz), 121.7, 120.8 (q, *J* = 321.2 Hz), 115.8 (d, *J* = 89.3 Hz).

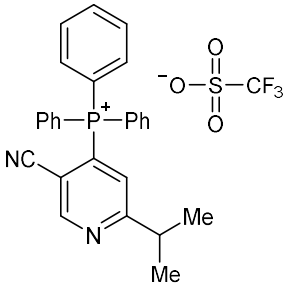
(4-(((2R,6S)-2,6-Dimethylmorpholino)methyl)quinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to general procedure B (except the reaction was cooled to -50 ºC for the Tf_2O addition, then cooled to -78 ºC for the DBU addition) using (2R,6S)-2,6-dimethyl-4-(quinolin-4-ylmethyl)morpholine (558 mg, 2.18 mmol), PPh_3 (629.3 mg, 2.39 mmol), Tf_2O (340 µL, 2.18 mmol), DBU (325 µL, 2.18 mmol) and CH_2Cl_2 (22 mL). After the purification procedure, the title compound was isolated as a white solid (994 mg, 1.49 mmol, 68% yield). mp 188-195 °C; IR ν_{max}/cm^{-1} (film): 3072, 2972, 2937, 2825, 1576, 1439, 1267, 1144, 1110, 1027, 727, 633; ^{1}H NMR

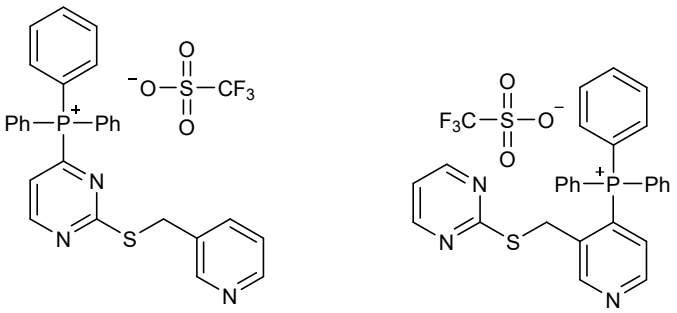
(400 MHz, $CDCl_3$) δ: 8.26 (2H, dd, *J* = 8.4, 16.5 Hz), 7.96-7.70 (18H, m), 4.02 (2H, s), 3.50-3.38 (2H, m), 2.60 (2H, d, *J* = 10.7 Hz), 1.92 (2H, t, *J* = 10.5 Hz), 1.10 (6H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0 (d, *J* = 22.2 Hz), 148.2 (d, *J* = 10.1 Hz), 144.7 (d, *J* = 117.6 Hz), 135.7 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 10.0 Hz), 131.7, 130.9, 130.6, 130.6 (d, *J* = 12.9 Hz), 127.9 (d, *J* = 3.1 Hz), 124.0, 123.6 (d, *J* = 27.4 Hz), 120.9 (q, *J* = 321.1 Hz), 117.4 (d, *J* = 88.2 Hz), 71.6, 59.3, 58.1, 18.9 ; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.09; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 14.47; *m/z* LRMS (ESI + APCI) found 517.3 $[M\text{-}OTf]^+$, $C_{34}H_{34}N_2OP^+$ requires 517.2.

(5-Cyano-2-isopropylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to general procedure A using 6-isopropylnicotinonitrile (438.6 mg, 3.0 mmol), Tf_2O (500 µL, 3.0 mmol), PPh_3 (866 mg, 3.3 mmol), DBU (450 µL, 3.0 mmol) and CH_2Cl_2 (30 mL). After the purification procedure, the title compound was isolated as an off-white solid (1.02 g, 1.83 mmol, 61% yield). mp 59-66 °C; IR ν_{max}/cm^{-1} (film): 3063, 2970, 2933, 2873, 2228, 1571, 1481, 1439, 1259, 1147, 1106, 1029; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.10 (1H, d, *J* = 5.8 Hz), 7.96-7.90 (3H, m), 7.86-7.73 (12H, m), 7.34 (1H, d, *J* = 15.3 Hz), 3.20 (1H, sp, *J* = 6.9 Hz), 1.27 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5 (d, *J* = 8.9 Hz), 154.8 (d, *J* = 6.1 Hz), 136.3 (d, *J* = 3.0 Hz), 134.6 (d, *J* = 10.8 Hz), 131.0 (d, *J* = 82.5 Hz), 131.0 (d, *J* = 13.4 Hz), 127.6 (d, *J* = 7.5 Hz), 120.6 (q, *J* = 321.2 Hz), 114.4 (d, *J* = 89.8 Hz), 113.9 (d, *J* = 5.2 Hz), 108.9 (d, *J* = 3.7 Hz), 36.9, 21.5; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.22; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 23.07; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 407.2, $C_{27}H_{24}N_2P^+$ requires 407.2.

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

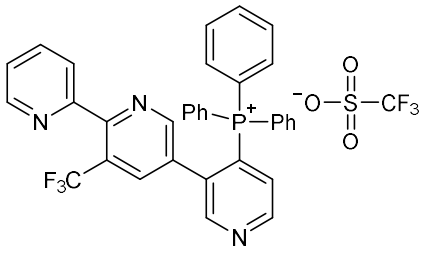


Major Minor

>20:1 Mixture of Regioisomers

Prepared according to our previous report.[7] 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.

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

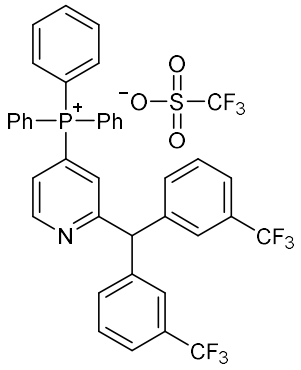


13.4:1:1 Mixture of Regioisomers

Prepared according to our previous report.[3] Major Isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (1H, app t, *J* = 4.7 Hz), 8.79 (1H, d, *J* = 6.8 Hz), 8.70 (1H, d, *J* = 4.7 Hz), 8.27 (1H, d, *J* = 1.7 Hz), 7.87-7.58 (18H, m), 7.55 (1H, d, *J* = 7.8 Hz), 7.39 (1H, dd, *J* = 7.8, 4.7 Hz); Major Isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 155.3, 153.1 (d, *J* = 7.3 Hz), 151.3 (d, *J* = 9.9 Hz), 151.0, 150.6,

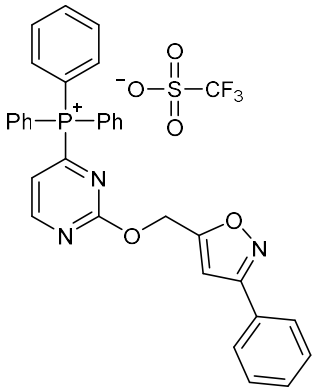
148.8, 136.4, 136.2-136.1(m), 135.7 (d, J = 6.5 Hz), 135.7 (d, J = 2.8 Hz), 134.2 (d, J = 10.3 Hz), 130.7 (d, J = 13.0 Hz), 128.7 (d, J = 9.0 Hz), 127.5 (d, J = 83.1 Hz), 123.9 (q, J = 33.8 Hz), 123.8, 123.4, 122.2 (q, J = 273.7 Hz), 120.6 (q, J = 321.3 Hz), 116.2 (d, J = 88.6 Hz).

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



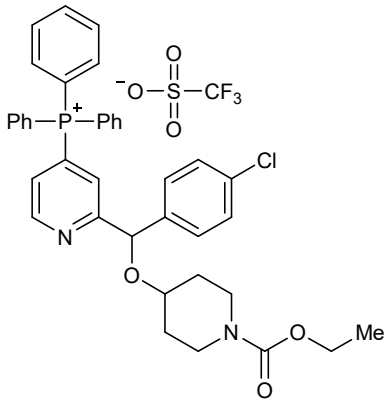
Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, app t, J = 5.1 Hz), 7.91-7.80 (3H, m), 7.78-7.66 (6H, m), 7.63-7.37 (15H, m), 7.29 (1H, d, J = 13.8 Hz), 5.97 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0 (d, J = 9.8 Hz), 151.6 (d, J = 10.4 Hz), 141.7, 136.1 (d, J = 3.1 Hz), 134.3 (d, J = 10.5 Hz), 132.9 (d, J = 1.1 Hz), 130.9 (d, J = 13.1 Hz), 130.7 (q, J = 32.2 Hz), 130.0, 129.6 (d, J = 83.7 Hz), 127.0 (d, J = 8.7 Hz), 125.7-125.4 (2C, m), 124.0 (q, J = 3.8 Hz), 123.8 (q, J = 272.5 Hz), 120.8 (q, J = 321.2 Hz), 115.4 (d, J = 89.5 Hz), 57.8.

Triphenyl(2-((3-phenylisoxazol-5-yl)methoxy)pyrimidin-4-yl)phosphonium trifluoromethanesulfonate



Prepared according to general procedure B (except the reaction was cooled to -50 ºC for the Tf_2O addition, then cooled to -78 ºC for the DBU addition and EtOAc was used instead of CH_2Cl_2) using 3-phenyl-5-((pyrimidin-2-yloxy)methyl)isoxazole (253.3 mg, 3.0 mmol), PPh_3 (865.6 mg, 3.3 mmol), Tf_2O (0.50 mL, 3.0 mmol), DBU (0.45 mL, 3.0 mmol) and EtOAc (15 mL). After the purification procedure, the title compound was isolated as an off-white solid (798.6 mg, 1.20 mmol, 40% yield). mp 49-55 ºC; IR ν_{max}/cm^{-1} (film): 3500, 3064, 2162, 1980, 1613, 1587, 1547, 1439, 1352, 1259, 1223, 1149, 1109, 1029, 688, 635, 529; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (1H, t, *J* = 6.8 Hz), 7.90-7.83 (3H, m), 7.82-7.67 (15H, m), 7.49-7.43 (3H, m), 6.69 (1H, s), 5.58 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 164.4 (d, *J* = 19.5 Hz), 163.8 (d, *J* = 8.4 Hz), 162.5, 156.0 (d, *J* = 112.4 Hz), 136.1 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 13.1 Hz), 130.2, 128.9, 128.4, 126.8, 122.5 (d, *J* = 20.2 Hz), 120.7 (q, *J* = 320.2 Hz), 115.1 (d, *J* = 89.1 Hz), 102.4, 60.6; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.20; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 16.36; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 513.2, $C_{33}H_{26}N_2O_2P^+$ requires 513.2.

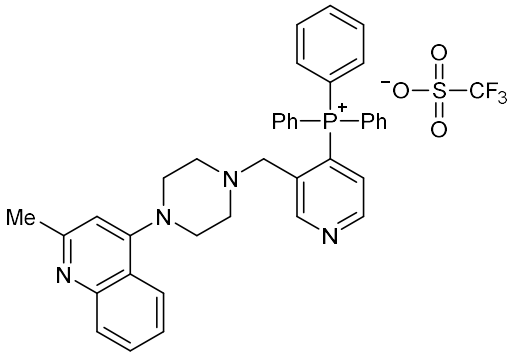
(2-((4-Chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (1H, t, *J* = 5.1 Hz), 7.94-7.86 (3H, m), 7.82-7.73 (6H, m), 7.71-7.59 (7H, m), 7.49 (1H, ddd, *J* = 12.6, 5.0, 1.1 Hz), 7.34-7.25 (4H, m), 5.71 (1H, s), 4.11 (2H, q, *J* = 7.1 Hz), 3.70-3.60 (1H, m), 3.55-3.42 (2H, m), 3.25-3.12 (2H, m), 1.79-1.56 (2H, m), 1.54-1.37 (2H, m), 1.25 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4 (d, *J* = 9.6 Hz), 155.4, 151.1 (d, *J* =10.5 Hz), 138.7, 136.2 (d, *J* = 3.1 Hz), 134.5 (d, *J* = 10.5 Hz), 134.0, 131.0 (d, *J* = 13.1 Hz), 129.3 (d, *J* = 84.1 Hz), 128.8, 128.5,

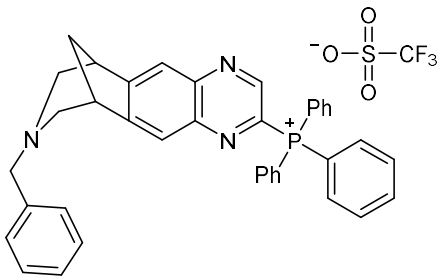
125.9 (d, J = 8.4 Hz), 123.9 (d, J = 9.1 Hz), 120.8 (q, J = 321.2 Hz), 115.8 (d, J = 89.4 Hz), 79.9, 72.8, 61.3, 40.7 (rot), 40.7, 31.3, 30.4 (rot), 14.7.

(3-((4-(2-Methylquinolin-4-yl)piperazin-1-yl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (1H, d, J = 6.8 Hz), 8.84 (1H, app t, J = 4.6 Hz), 7.91-7.70 (17H, m), 7.54 (1H, dd, J = 7.4, 7.8 Hz), 7.33 (1H, dd, J = 7.6, 7.5 Hz), 7.20 (1H, dd, J = 5.0, 15.6 Hz), 6.59 (1H, s), 3.26 (2H, s), 2.81 (4H, s), 2.62 (3H, s), 2.16 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 156.4, 153.5 (d, J = 8.3 Hz), 150.8 (d, J = 10.6 Hz), 148.4, 137.0 (d, J = 5.7 Hz), 135.7 (d, J = 2.9 Hz), 134.0 (d, J = 10.2 Hz), 131.0 (d, J = 13.0 Hz), 129.3, 129.1 (d, J = 9.8 Hz), 128.5, 126.7 (d, J = 81.7 Hz), 124.6, 123.2, 121.3, 120.8 (q, J = 319.4 Hz), 117.0 (d, J = 88.9 Hz), 109.2, 59.1 (d, J = 3.3 Hz), 52.7, 51.2, 25.1.

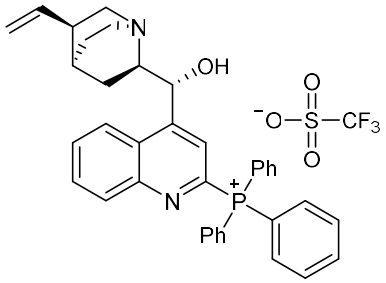
((6R,10S)-8-Benzyl-7,8,9,10-tetrahydro-6H-6,10-methanoazepino[4,5-g]quinoxalin-2-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (1H, s), 8.10-7.72 (17H, m), 7.20-7.05 (3H, m), 6.92-6.80 (2H, m), 3.55-3.27 (4H, m), 3.03-2.87 (2H, m),

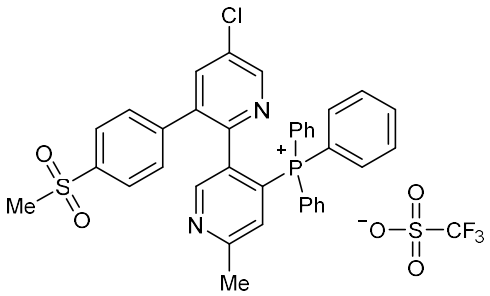
2.66-2.42 (2H, m), 2.29-2.15 (1H, m), 1.87 (1H, d, J = 10.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 144.9 (d, J = 23.5 Hz), 144.2, 143.5 (d, J = 16.9 Hz), 137.5 (br s), 136.0 (d, J = 2.9 Hz), 134.6 (d, J = 10.9 Hz), 130.7 (d, J = 13.0 Hz), 129.2-126.2 (3C, m,), 120.7 (br s), 120.7 (q, J = 321.5 Hz), 116.4 (d, J = 88.3 Hz), 61.3, 57.9-56.1 (2C, m), 43.1-40.4 (3C, m).

(4-((R)-(Benzyloxy)((1S,2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate



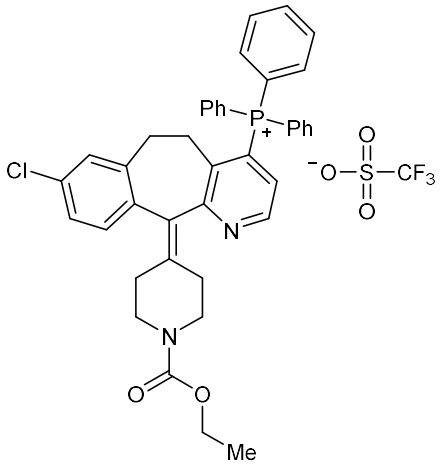
Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, J = 8.1 Hz), 8.26 (1H, d, J = 8.6 Hz), 7.94 (1H, t, J = 7.2 Hz), 7.91-7.60 (17H, m), 7.29-7.02 (3H, m), 7.14-7.02 (2H, m), 5.83-5.45 (2H, m), 5.07-4.89 (2H, m), 4.60 (1H, d, J = 11.4 Hz), 4.33 (1H, d, J = 11.4 Hz), 3.52-3.06 (3H, m), 2.84-2.62 (2H, m), 2.49-2.33 (1H, br s), 2.06-1.47 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2 (d, J = 22.1 Hz), 148.5, 145.1, 143.9, 139.5, 136.6, 135.7 (d, J = 3.0 Hz), 134.5 (d, J = 10.0 Hz), 132.0-131.8 (3C, m), 131.2, 130.4 (d, J = 13.2 Hz), 128.4, 127.9, 127.2, 126.7 (d, J = 3.1 Hz), 126.1, 123.8, 120.6 (q, J = 320.3 Hz), 117.0 (d, J = 87.7 Hz), 115.6, 71.8, 60.7, 55.6, 43.0, 38.3, 26.9, 25.8.

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



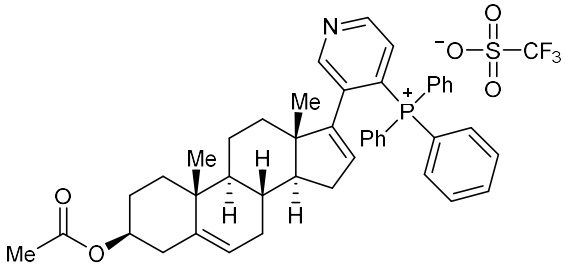
Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (1H, d, *J* = 7.1 Hz), 8.10 (2H, d, *J* = 8.2 Hz), 7.86-7.62 (16H, m), 7.51-7.45 (3H, m), 7.20 (1H, d, *J* = 16.5 Hz), 3.14 (3H, s), 2.54 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8 (d, *J* = 11.2 Hz), 152.4 (d, *J* = 7.3 Hz), 147.5 (d, *J* = 2.2 Hz), 146.1, 141.5, 141.0, 138.9, 135.6, 134.8 (d, *J* = 2.9 Hz), 134.1 (d, *J* = 10.0 Hz), 133.3 (d, *J* = 3.6 Hz), 132.1, 130.8 (d, *J* = 10.2 Hz), 130.0 (d, *J* = 13.1 Hz), 129.8, 128.5, 128.2 (d, *J* = 86.2 Hz), 120.8 (q, *J* = 321.1 Hz), 119.3 (d, *J* = 91.8 Hz), 43.9, 24.6. The spectroscopic data is in agreement with our reported synthesis.[6]

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



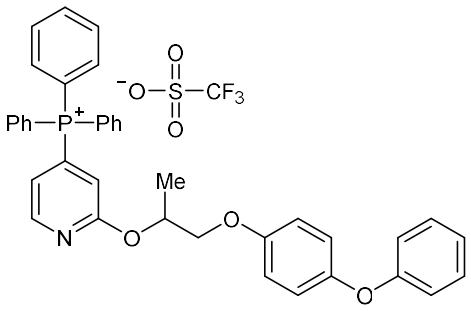
Prepared according to our previous report.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, app t, *J* = 5.0 Hz), 7.97-7.87 (3H, m), 7.86-7.74 (6H, m), 7.73-7.60 (6H, m), 7.16-7.01 (3H, m), 6.71 (1H, s), 4.14 (2H, q, *J* = 7.0 Hz), 3.84-3.61 (2H, m), 3.45- 3.20 (3H, m), 2.75 (1H, dt, *J* = 17.4, 4.7 Hz), 2.58 (1H, dt, *J* = 14.9, 4.7 Hz), 2.53-2.30 (3H, m), 2.26-2.09 (1H, m), 1.60-1.43 (1H, m), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6 (d, *J* = 8.3 Hz), 155.4, 149.1 (d, *J* = 11.4 Hz), 139.2, 136.8, 136.7 (d, *J* = 6.8 Hz), 136.0 (d, *J* = 3.1 Hz), 134.2 (d, *J* = 10.7 Hz), 133.9, 133.6, 132.4, 131.6, 131.1 (d, *J* = 13.0 Hz), 129.9, 127.2 (d, *J* = 10.0 Hz), 127.0 (d, *J* = 82.2 Hz), 126.4, 120.8 (q, *J* = 321.3 Hz), 116.4 (d, *J* = 88.5 Hz), 61.4, 44.6, 44.4, 30.7, 30.4, 30.4, 29.4, 14.6. The spectroscopic data is in agreement with our reported synthesis.[2]

(3-((3S,8R,9S,10R,13S,14S)-3-Acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (1H, d, *J* = 7.2 Hz), 8.72 (1H, app t, *J* = 4.1 Hz), 7.88-7.59 (15H, m), 7.27 (1H, dd, *J* = 15.7, 5.2 Hz), 5.55 (1H, s), 5.28 (1H, d, *J* = 3.4 Hz), 4.58 (1H, m), 2.33-2.18 (2H, m), 1.99 (3H, s), 1.87-1.30 (10H, m), 1.24-1.01 (5H, m), 0.94 (3H, s), 0.79 (1H, td, *J* = 12.1, 3.7 Hz), 0.57 (1H, td, *J* = 11.2, 3.9 Hz), –0.22 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 150.6 (d, *J* = 7.5 Hz), 149.0 (d, *J* = 4.2 Hz), 148.7 (d, *J* = 10.8 Hz), 139.9, 139.1, 137.4 (d, *J* = 6.1 Hz), 135.5 (d, *J* = 2.9 Hz), 134.2 (d, *J* = 9.9 Hz), 130.8 (d, *J* = 13.0 Hz), 130.0 (d, *J* = 10.5 Hz), 125.2 (d, *J* = 83.7 Hz), 121.6, 120.7 (q, *J* = 321.2 Hz), 118.0 (d, *J* = 89.6 Hz), 73.5, 55.3, 49.7, 48.7, 37.9, 36.8, 36.4, 33.5, 32.4, 31.0, 29.7, 27.5, 21.3, 20.3, 19.0, 18.6. The spectroscopic data is in agreement with our reported synthesis.[6]

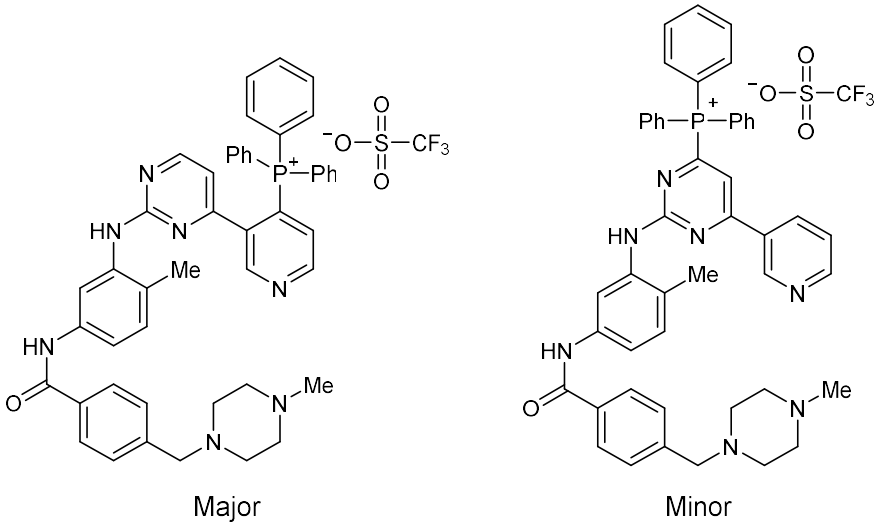
(2-((1-(4-Phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, app t, *J* = 5.3 Hz), 7.93-7.87 (3H, m), 7.82-7.74 (6H, m), 7.67-7.59 (6H, m), 7.30-7.23 (2H, m), 7.13 (1H,

ddd, J = 11.7, 5.3, 1.2 Hz), 7.02 (1H, t, J = 7.4 Hz), 6.94-6.77 (7H, m), 5.66 (1H, sext, J = 5.3 Hz), 4.18-4.07 (2H, m), 1.48 (3H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, J = 15.9 Hz), 158.1, 154.7, 150.3, 149.8 (d, J = 12.1 Hz), 136.1 (d, J = 3.0 Hz), 134.3 (d, J = 10.6 Hz), 130.9 (d, J = 13.0 Hz), 130.8 (d, J = 84.2 Hz), 129.5, 122.4, 120.8 (q, J = 321.2 Hz), 120.6, 119.1 (d, J = 8.1 Hz), 117.5, 116.6 (d, J = 10.0 Hz), 115.6 (d, J = 89.4 Hz), 115.6, 71.5, 70.5, 16.4.

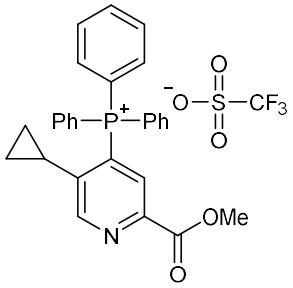
(3-(2-((2-Methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



20:1 Mixture of Regioisomers

Prepared according to our previous report.[6] Major isomer, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.14 (1H, s), 9.55 (1H, d, J = 6.7 Hz), 9.09 (1H, app t, J = 4.6 Hz), 8.31 (1H, d, J = 5.1 Hz), 8.00-7.55 (18H, m), 7.52-7.20 (5H, m), 7.08 (1H, d, J = 8.3 Hz), 6.10 (1H, br), 3.55 (2H, s), 2.70-2.13 (11H, m), 1.74 (3H, s); Major isomer, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.2, 159.8, 159.7 (d, J = 2.0 Hz), 158.3, 152.7 (d, J = 11.4 Hz), 151.8 (d, J = 6.8 Hz), 141.1 (br), 137.3, 136.2, 135.8 (d, J = 3.8 Hz), 134.7 (d, J = 2.3 Hz), 133.9 (d, J = 10.0 Hz), 130.8 (d, J = 10.2 Hz), 130.0, 129.9 (d, J = 13.4 Hz), 128.7, 127.7, 125.6 (d, J = 86.2 Hz), 125.5, 120.7 (q, J = 322.8 Hz), 119.5 (d, J = 92.3 Hz), 117.0, 117.0, 115.6, 110.3, 60.6, 53.2, 50.1, 43.1, 17.0. The spectroscopic data is in agreement with our reported synthesis.[6]

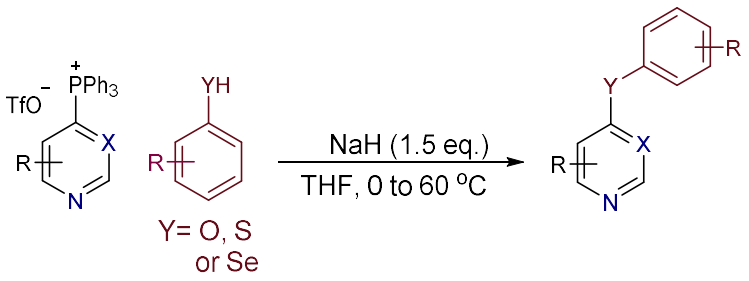
(5-Cyclopropyl-2-(methoxycarbonyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate



Prepared according to general procedure A (except the reaction was cooled to -50 ºC for the PPh_3 addition) using methyl 5-cyclopropylpicolinate (200 mg, 1.12 mmol), Tf_2O (190 µL, 1.12 mmol), PPh_3 (323 mg, 1.23 mmol), DBU (170 µL, 1.12 mmol) and CH_2Cl_2 (11.2 mL). After the purification procedure, the title compound was isolated as a white solid (276 mg, 0.469 mmol, 42% yield). mp: 173-200 °C; IR ν_{max}/cm^{-1} (film): 3069, 2953, 1745, 1577, 1439, 1263, 1133, 1030, 721, 635; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, d, J = 6.4 Hz), 7.96-7.88 (3H, m), 7.87-7.78 (6H, m), 7.78-7.68 (7H, m), 3.94 (3H, s), 1.44 (1H, sp, J = 4.7 Hz), 1.08-1.00 (2H, m), 0.92-0.84 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9 (d, J = 2.4 Hz), 147.8 (d, J = 6.3 Hz), 146.9 (d, J = 7.6 Hz), 146.4 (d, J = 10.7 Hz), 136.2 (d, J = 3.0 Hz), 134.2 (d, J = 10.6 Hz), 131.2 (d, J = 13.2 Hz), 129.0 (d, J = 11.1 Hz), 127.5 (d, J = 84.2 Hz), 120.8 (q, J = 321.1 Hz), 115.9 (d, J = 89.0 Hz), 53.3, 16.4 (d, J = 6.5 Hz), 13.9; ^{19}F NMR (365 MHz, $CDCl_3$) δ: -78.17; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.15; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 438.2, $C_{28}H_{25}NO_2P^+$ requires 438.2.

5. Preparation of Derivatized Azaarenes

General Procedure C

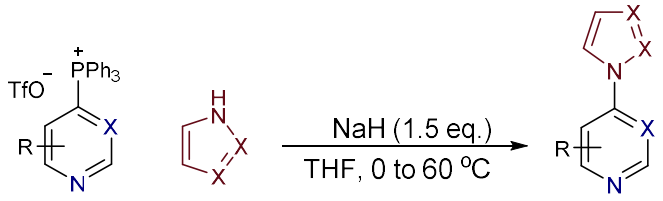


An oven dried 8 mL vial equipped with a septa cap was charged with sodium hydride (60% dispersion in mineral oil, 1.5 equiv) and placed under a nitrogen atmosphere. THF (0.5 M) was added and the suspension was cooled to 0 ºC while stirring. The phenol or thiophenol (1.5 equiv) was added dropwise over 5 min and allowed to stir for 30 min at 0 ºC. The septa cap was briefly removed and the phosphonium salt (1.0 equiv) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and was warmed to 60 ºC and stirred for 2 h. The reaction was quenched with H_2O, the aqueous layer was separated and extracted with CH_2Cl_2 (3x). 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 under the stated conditions to provide the heteroaryl ether/thioether.

Notes.

1) If the phenol/thiophenol was a solid or viscous liquid, it was added dropwise as a 1.5 M solution to an equivalent volume 1.5 M solution of NaH in THF.
2) Certain substrates required longer reaction times. Specific cases are indicated below.
3) Certain substrates showed improved yields when ran in DME at 80 ºC. Specific cases are indicated below.
4) Certain substrates showed improved yields with the addition of 15-crown-5 right before the salt addition. Specific cases are indicated below (Phenol nucleophiles typically require this addition for tolerable yields).

General Procedure D



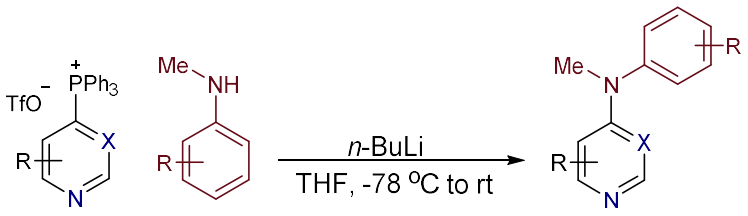
An oven dried 8 mL vial equipped with a septa cap was charged with sodium hydride (60% dispersion in mineral oil, 1.5 equiv) and placed under a nitrogen atmosphere. THF (0.5 M) was added and the suspension was cooled to 0 ºC while stirring. The pyrrole/pyrazole/imidazole (1.5 equiv) was added dropwise over 5 min and allowed to stir for 30 min at 0 ºC. The septa cap

was briefly removed and the phosphonium salt (1.0 equiv) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and was warmed to 60 ºC and stirred for 1 h. The reaction was quenched with H_2O, the aqueous layer was separated and extracted with CH_2Cl_2 (3x). 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 under the stated conditions to provide the coupled azaarene product.

Notes.

1) If the pyrrole/pyrazole/imidazole was a solid or viscous liquid, it was added dropwise as a 1.5 M solution to an equivalent volume 1.5 M solution of NaH in THF.
2) Certain substrates required longer reaction times. Specific cases are indicated below.
3) Certain substrates showed improved yields when ran in DME at 80 ºC. Specific cases are indicated below.
4) Certain substrates showed improved yields with the addition of 15-crown-5 right before the salt addition. Specific cases are indicated below.
5) Certain substrates showed improved yields when KH was used as the base in place of NaH. Specific cases are indicated below.

General Procedure E



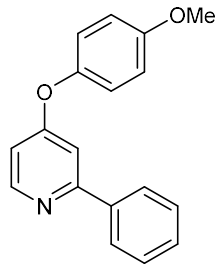
An oven dried 8 mL vial equipped with a septa cap was charged with the aniline (1.5 equiv) and placed under a nitrogen atmosphere. THF (0.25 M) was added and the suspension was cooled to -78 ºC while stirring. *n*-BuLi (1.5 equiv) was added dropwise over 5 min and allowed to stir for 30 min at -78 ºC. The reaction was then allowed to warm to room temp before the septa cap was briefly removed and the phosphonium salt (1.0 equiv) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and stirred for 30 min at room temp. The reaction was quenched with H_2O, the aqueous layer was separated and extracted

with CH_2Cl_2 (3x). 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 under the stated conditions to provide the heteroaryl ether/thioether.

Notes.

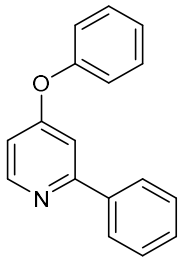
1) Certain substrates required longer reaction times. Specific cases are indicated below.

4-(4-Methoxyphenoxy)-2-phenylpyridine (2a)



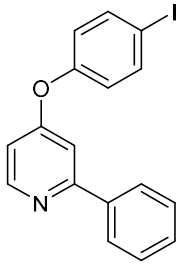
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.5 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2a) as a clear oil (107 mg, 0.39 mmol, 77% yield). IR ν_{max}/cm^{-1} (film): 3066, 3002, 2947, 2842, 2214, 2042, 1612, 1564, 1499, 1470, 1259, 1208, 1112, 908, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (1H, d, J = 5.6 Hz), 7.94-7.88 (2H, m), 7.48-7.37 (3H, m), 7.23 (1H, d, J = 2.3 Hz), 7.10-7.04 (2H, m), 6.99-6.93 (2H, m), 6.74 (1H, dd, J = 5.7, 2.4 Hz), 3.85 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 159.5, 157.1, 151.1, 147.4, 139.2, 129.1, 128.7, 126.9, 122.0, 115.2, 110.2, 108.5, 55.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 278.1, $C_{18}H_{16}NO_2^+$ requires 278.1.

4-Phenoxy-2-phenylpyridine (2b)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), phenol (71 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 4% EtOAc & 1% AcOH in hexanes) afforded the *title compound* (2b) as a yellow amorphous solid (87 mg, 0.35 mmol, 70% yield). IR ν_{max}/cm^{-1} (film): 3062, 2923, 2851, 2215, 1721, 1579, 1562, 1489, 1470, 1305, 1214, 912, 774, 731, 692; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, *J* = 5.6 Hz), 7.95-7.88 (2H, m), 7.49-7.38 (5H, m), 7.30-7.24 (2H, m), 7.17-7.12 (2H, m), 6.78 (1H, dd, *J* = 5.6, 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 159.7, 154.2, 151.2, 139.1, 130.2, 129.1, 128.7, 126.9, 125.3, 120.7, 110.7, 109.1 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 248.1, $C_{17}H_{14}NO^+$ requires 248.1.

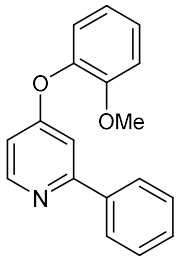
4-(4-Iodophenoxy)-2-phenylpyridine (2c)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-iodophenol (165 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50

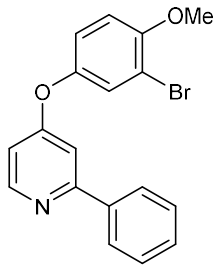
mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2c) as a pink solid (112 mg, 0.30 mmol, 60% yield). mp: 50-57 °C; IR ν_{max}/cm^{-1} (film): 3084, 3045, 2925, 2503, 2208, 1879, 1594, 1556, 1477, 1408, 1214, 1023, 844, 694; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.56 (1H, d, *J* = 5.6 Hz), 7.95-7.89 (2H, m), 7.77-7.71 (2H, m), 7.50-7.38 (3H, m), 7.27 (1H, d, *J* = 2.3 Hz), 6.94-6.88 (2H, m), 6.78 (1H, dd, *J* = 5.6, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 159.8, 154.3, 151.3, 139.2, 138.9, 129.3, 128.7, 126.9, 122.8, 110.8, 109.2, 88.8; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 374.0, $C_{17}H_{13}INO^+$ requires 374.0.

4-(2-Methoxyphenoxy)-2-phenylpyridine (2d)



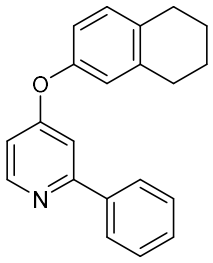
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 2-methoxyphenol (82 μL, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and DME (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2d) as a clear oil (79 mg, 0.28 mmol, 57% yield). IR ν_{max}/cm^{-1} (film): 3066, 3008, 2927, 2839, 2214, 2043, 1580, 1563, 1498, 1470, 1258, 1208, 1112, 907, 728; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.50 (1H, d, *J* = 5.7 Hz), 7.94-7.88 (2H, m), 7.48-7.37 (3H, m), 7.30-7.22 (2H, m), 7.14 (1H, dd, *J* = 7.9, 1.6 Hz), 7.08-6.99 (2H, m), 6.70 (1H, dd, *J* = 5.7, 2.4 Hz), 3.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 159.4, 151.7, 150.9, 142.2, 139.3, 129.0, 128.6, 126.9, 126.7, 122.7, 121.3, 113.0, 109.6, 108.2, 55.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 278.2, $C_{18}H_{16}NO_2^+$ requires 278.1.

4-(3-Bromo-4-methoxyphenoxy)-2-phenylpyridine (2e)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 3-bromo-4-methoxyphenol (152 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and DME (1.0 mL). Flash column chromatography (basic alumina: 20% EtOAc in hexanes) afforded the *title compound* (2e) as a white solid (92 mg, 0.26 mmol, 52% yield). mp: 88-95 °C; IR ν_{max}/cm^{-1} (film): 3061, 2979, 2947, 2846, 2497, 2161, 2042, 1848, 1584, 1561, 1486, 1468, 1437, 1409, 1257, 1205, 1043, 875, 776, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, J = 5.6 Hz), 7.98-7.88 (2H, m), 7.50-7.36 (4H, m), 7.24 (1H, d, J = 2.3 Hz), 7.08 (1H, dd, J = 8.9, 2.9 Hz), 6.95 (1H, d, J = 9.0 Hz), 6.75 (1H, dd, J = 5.6, 2.3 Hz), 3.93 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 159.7, 153.7, 151.2, 147.6, 139.0, 129.2, 128.7, 127.0, 126.2, 120.8, 112.5, 112.2, 110.2, 108.6, 56.7 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 356.1, $C_{18}H_{15}BrNO_2^+$ requires 356.0.

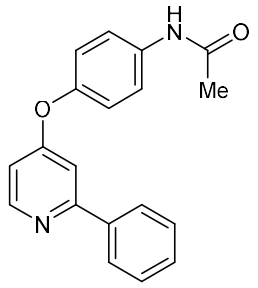
2-Phenyl-4-((5,6,7,8-tetrahydronaphthalen-2-yl)oxy)pyridine (2f)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 5,6,7,8-tetrahydronaphthalen-2-ol (111.2 mg, 0.75 mmol), 15-crown-

5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (basic alumina: 2% EtOAc in hexanes) afforded the *title compound* (2f) as a white solid (122 mg, 0.41 mmol, 81% yield). mp: 57-61 °C; IR ν_{max}/cm^{-1} (film): 3061, 2925, 2835, 2162, 1579, 1561, 1492, 1469, 1238, 1195, 865, 773, 691; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.51 (1H, d, *J* = 5.7 Hz), 7.94-7.89 (2H, m), 7.49-7.37 (3H, m), 7.27 (1H, d, *J* = 2.3 Hz), 7.11 (1H, d, *J* = 8.2 Hz), 6.88-6.82 (2H, m), 6.77 (1H, dd, *J* = 5.6, 2.4 Hz), 2.82-2.74 (4H, m), 1.88-1.77 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 159.5, 151.7, 151.1, 139.3 (2C), 134.3, 130.6, 129.1, 128.7, 127.0, 120.9, 117.9, 110.5, 109.0, 29.5, 28.9, 23.1, 22.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 302.2, $C_{21}H_{20}NO^+$ requires 302.2.

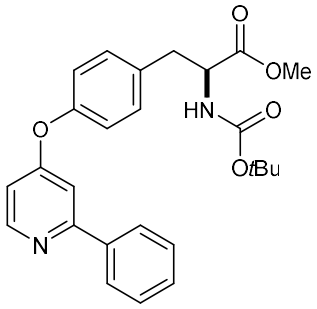
N-(4-((2-Phenylpyridin-4-yl)oxy)phenyl)acetamide (2g)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), N-(4-hydroxyphenyl)acetamide (151.2 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and DME (1.0 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 1% MeOH in DCM) afforded the *title compound* (2g) as a white solid (111 mg, 0.36 mmol, 73% yield). mp: 129-139 °C; IR ν_{max}/cm^{-1} (film): 3297, 3206, 3064, 2923, 2852, 1659, 1546, 1501, 1469, 1405, 1302, 1211, 1016, 911, 849, 776, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.53 (1H, d, *J* = 5.6 Hz), 7.93-7.87 (2H, m), 7.60-7.54 (2H, m), 7.48-7.37 (3H, m), 7.32 (1H, br), 7.25 (1H, d, *J* = 2.2 Hz)

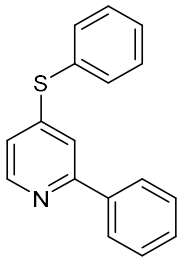
7.13-7.07 (2H, m), 6.77 (1H, dd, J = 5.7, 2.4 Hz), 2.20 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 165.7, 159.7, 151.2, 150.3, 139.0, 135.3, 129.2, 128.7, 127.0, 121.7, 121.4, 110.5, 108.9, 24.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 305.2, $C_{19}H_{17}N_2O_2^+$ requires 305.1.

Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-((2-phenylpyridin-4-yl)oxy)phenyl)propanoate (2h)



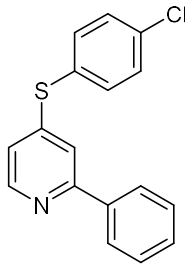
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), methyl (tert-butoxycarbonyl)-L-tyrosinate (222 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel, gradient elution: 30% EtOAc in hexanes to 80% EtOAc in hexanes) afforded the *title compound* (2h) as a white solid (133.1 mg, 0.297 mmol, 59% yield). mp: 29-40 °C; IR ν_{max}/cm^{-1} (film): 3435, 3033, 2979, 2932, 2251, 1979, 1742, 1706, 1586, 1504, 1471, 1219, 1163, 908, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (1H, d, J = 5.6 Hz), 7.95-7.90 (2H, m), 7.48-7.37 (3H, m), 7.27 (1H, d, J = 2.2 Hz), 7.23-7.18 (2H, m), 7.09-7.04 (2H, m), 6.75 (1H, dd, J = 5.6, 2.4 Hz), 5.04 (1H, d, J = 7.7 Hz), 4.66-4.56 (1H, m), 3.74 (3H, s), 3.21-3.00 (2H, m), 1.43 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 165.4, 159.6, 155.0, 153.2, 151.1, 139.0, 133.3, 131.0, 129.1, 128.6, 126.9, 120.7, 110.6, 109.1, 79.9, 54.4, 52.2, 37.9, 28.2; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 449.3, $C_{26}H_{29}N_2O_5^+$ requires 449.2.

2-Phenyl-4-(phenylthio)pyridine (2i)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 2.5% EtOAc in hexanes) afforded the *title compound* (2i) as a clear oil (109 mg, 0.42 mmol, 83% yield). IR ν_{max}/cm^{-1} (film): 3689, 3064, 3040, 2997, 2921, 2850, 2612, 2459, 2162, 1977, 1814, 1764, 1699, 1567, 1534, 1462, 1379, 757, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (1H, d, J = 5.3 Hz), 7.89-7.84 (2H, m), 7.63-7.56 (2H, m), 7.50-7.36 (7H, m), 6.88 (1H, dd, J = 5.3, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 150.8, 149.4, 139.0, 135.0, 129.9, 129.7, 129.6, 129.1, 128.7, 126.9, 119.4, 117.8; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 264.1, $C_{17}H_{14}NS^+$ requires 264.1.

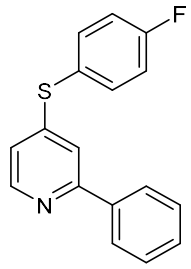
4-((4-Chlorophenyl)thio)-2-phenylpyridine (2j)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-chlorobenzenethiol (109 mg, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF

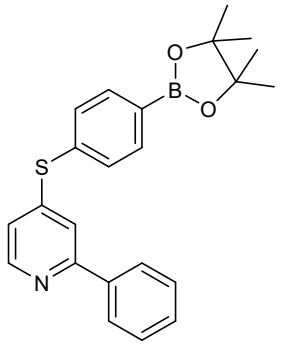
(1.0 mL). Flash column chromatography (silica gel: 2.5% EtOAc in Toluene) afforded the *title compound* (2j) as a white chrystalline solid (109 mg, 0.37 mmol, 73% yield). mp: 86-90 °C IR ν_{max}/cm^{-1} (film): 3076, 3044, 3012, 2924, 2771, 2464, 1980, 1812, 1585, 1536, 1461, 1378, 1089, 836.8, 797, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46 (1H, d, *J* = 5.3 Hz), 7.89-7.85 (2H, m), 7.54-7.49 (2H, m), 7.48-7.38 (6H, m), 6.87 (1H, dd, *J* = 5.3, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 150.0, 149.5, 138.9, 136.1, 136.0, 130.2, 129.2, 128.8, 128.4, 126.9, 119.4, 117.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 298.1, $C_{17}H_{13}ClNS^+$ requires 298.0.

4-((4-Fluorophenyl)thio)-2-phenylpyridine (2k)



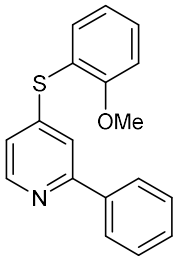
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-fluorobenzenethiol (80 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 2.5% EtOAc in Toluene) afforded the *title compound* (2k) as a white solid (110 mg, 0.39 mmol, 78% yield). mp: 75-79 °C; IR ν_{max}/cm^{-1} (film): 3090, 3067, 3037, 2923, 2853, 2466, 2040, 1813, 1702, 1585, 1570, 1537, 1489, 1223, 776; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (1H, d, *J* = 5.3 Hz), 7.92-7.83 (2H, m), 7.65-7.55 (2H, m), 7.48-7.35 (4H, m), 7.22-7.13 (2H, m), 6.83 (1H, dd, *J* = 5.3, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, *J* = 251 Hz), 157.5, 150.9, 149.4, 138.9, 137.5 (d, *J* = 8.5 Hz), 129.2, 128.7, 126.9, 124.8 (d, *J* = 3.5 Hz), 118.96, 117.43, 117.23 (d, *J* = 21.9 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –110.25 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 282.1, $C_{17}H_{13}FNS^+$ requires 282.1.

2-Phenyl-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)thio)pyridine (2l)



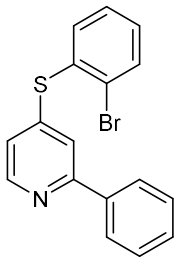
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenethiol (177 mg, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 8% EtOAc in hexanes) afforded the *title compound* (2l) as a yellow oil (119.4 mg, 0.307 mmol, 61% yield). IR ν_{max}/cm^{-1} (film): 2979, 2928, 2247, 2216, 1715, 1569, 1358, 1142, 907, 729; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.44 (1H, d, *J* = 5.3 Hz), 7.90-7.85 (4H, m), 7.60-7.53 (2H, m), 7.50-7.36 (4H, m), 6.90 (1H, dd, *J* = 5.3, 1.7 Hz), 1.37 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 150.1, 149.4, 139.0, 136.0, 133.6, 133.5, 129.1, 128.7, 127.0, 119.9, 118.4, 84.2, 24.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 390.2, $C_{23}H_{25}BNO_2S^+$ requires 390.2.

4-((2-Methoxyphenyl)thio)-2-phenylpyridine (2m)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 2-methoxybenzenethiol (91 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2m) as a clear oil (115 mg, 0.39 mmol, 79% yield). IR ν_{max}/cm^{-1} (film): 3062, 2936, 2835, 2167, 1567, 1476, 1462, 1274, 1247, 1022, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (1H, d, *J* = 5.3 Hz), 7.89-7.84 (2H, m), 7.60-7.54 (1H, m), 7.52-7.36 (5H, m), 7.08-7.00 (2H, m), 6.83 (1H, dd, *J* = 5.3, 1.8 Hz), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 157.2, 150.1, 149.1, 139.2, 137.2, 131.9, 129.0, 128.7, 126.9, 121.6, 119.1, 117.6, 117.0, 111.7, 56.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 294.2, $C_{18}H_{16}NOS^+$ requires 294.1.

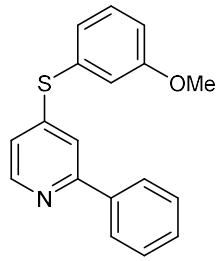
4-((2-Bromophenyl)thio)-2-phenylpyridine (2n)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 2-bromobenzenethiol (90 μL, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel, gradient elution: 10% EtOAc in hexanes to 20% EtOAc in hexanes) afforded the *title compound* (2n) as a brown oil (144 mg, 0.42 mmol, 84% yield). IR ν_{max}/cm^{-1} (film): 3056, 2925, 2456, 2162, 1979, 1567, 1536, 1444, 1379, 752, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (1H, d, *J* = 5.3 Hz), 7.91-7.86 (2H, m), 7.77 (1H, dd, *J* = 7.8, 1.2 Hz), 7.64 (1H, dd, *J* = 7.8, 1.7 Hz), 7.50-7.35 (5H, m), 7.35-7.29 (1H, m), 6.88 (1H, dd, *J* = 5.3, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$)

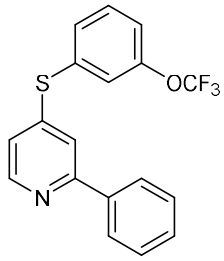
δ: 157.7, 149.6, 148.4, 138.9, 136.5, 134.1, 131.7, 131.0, 129.6, 129.2, 128.7, 128.6, 127.0, 119.9, 118.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 342.1, $C_{17}H_{13}BrNS^+$ requires 342.0.

4-((3-Methoxyphenyl)thio)-2-phenylpyridine (2o)



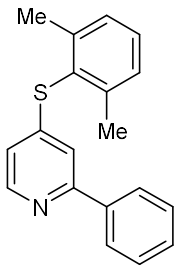
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 3-methoxybenzenethiol (93 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2o) as a yellow oil (118 mg, 0.40 mmol, 80% yield). IR ν_{max}/cm^{-1} (film): 3001, 2933, 2834, 1566, 1479, 1231, 772, 690; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.44 (1H, d, J = 5.3 Hz), 7.90-7.85 (2H, m), 7.47-7.34 (5H, m), 7.17 (1H, d, J = 7.6 Hz), 7.13-7.10 (1H, m), 7.00 (1H, dd, J = 8.3, 2.6 Hz), 6.90 (1H, dd, J = 5.3, 1.7 Hz), 3.83 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 157.5, 150.6, 149.4, 139.0, 130.8, 130.7, 129.1, 128.7, 127.1, 126.9, 119.8, 119.5, 118.0, 115.7, 55.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 294.1, $C_{18}H_{16}NOS^+$ requires 294.1.

2-Phenyl-4-((3-(trifluoromethoxy)phenyl)thio)pyridine (2p)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 3-(trifluoromethoxy)benzenethiol (146 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.5 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 15% EtOAc in hexanes) afforded the *title compound* (2p) as a clear oil (81.8 mg, 0.235 mmol, 47% yield). IR ν_{max}/cm^{-1} (film): 2925, 2853, 2218, 1568, 1251, 1219, 1205, 1165, 907, 730, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (1H, dd, *J* = 5.3, 0.5 Hz), 7.90-7.85 (2H, m), 7.52-7.38 (7H, m), 7.34-7.28 (1H, m), 6.93 (1H, dd, *J* = 5.3, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 149.8, 149.7, 149.0, 138.8, 132.6, 132.5, 131.0, 129.3, 128.8, 126.9, 126.6, 121.8, 120.4 (q, J = 258.2 Hz), 119.9, 118.5; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.88; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 348.1, $C_{18}H_{13}F_3NOS^+$ requires 348.1.

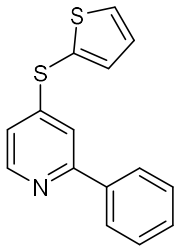
4-((2,6-Dimethylphenyl)thio)-2-phenylpyridine (2q)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 2,6-dimethylbenzenethiol (100 μL, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 2% EtOAc in toluene) afforded the *title compound* (2q) as a clear oil (108 mg, 0.37 mmol, 74% yield). IR ν_{max}/cm^{-1} (film): 3054, 2958, 2922, 2459, 2161, 1948, 1727, 1567, 1535, 1460, 1375, 1103, 770, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (1H, d, *J* = 5.3 Hz), 7.84-7.79 (2H, m), 7.44-7.32 (3H, m), 7.30-7.17 (4H, m), 6.63 (1H, dd, *J* = 5.3, 1.8 Hz), 2.41 (6H, s); ^{13}C NMR (100 MHz,

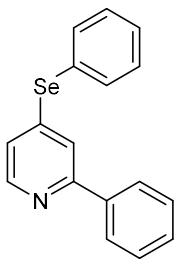
$CDCl_3$)δ: 157.3, 150.3, 149.3, 144.1, 139.1, 130.2, 129.0, 128.8, 128.7, 127.6, 126.9, 118.0, 116. 6, 21.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 292.2, $C_{19}H_{18}NS^+$ requires 292.1.

2-Phenyl-4-(thiophen-2-ylthio)pyridine (2r)



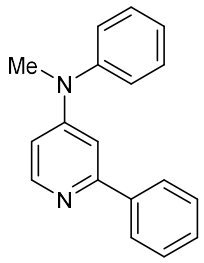
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), thiophene-2-thiol (70 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 2.5% EtOAc in toluene) afforded the *title compound* (2r) as a tan oil (93 mg, 0.35 mmol, 69% yield). IR ν_{max}/cm^{-1} (film): 3062, 3036, 2993, 2923, 2360, 2162, 1952, 1567, 1379, 1072, 771, 691; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.46 (1H, d, J = 5.3 Hz), 7.90-7.85 (2H, m), 7.63 (1H, dd, J = 5.3, 1.2 Hz), 7.48-7.37 (5H, m), 7.19 (1H, dd, J = 5.3, 3.5 Hz), 6.89 (1H, dd, J = 5.3, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 151.5, 149.4, 139.0, 137.9, 132.9, 129.1, 128.7, 128.5, 127.0, 126.5, 118.2, 116.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 270.1, $C_{15}H_{12}NS_2^+$ requires 270.0.

2-Phenyl-4-(phenylselanyl)pyridine (2s)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzeneselenol (80 μL, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 5% EtOAc in hexanes) afforded the *title compound* (2s) as a white solid (141 mg, 0.45 mmol, 91% yield). mp: 43-47 °C; IR ν_{max}/cm^{-1} (film): 3064, 3033, 2923, 2452, 2163, 1961, 1891, 1753, 1562, 1534, 1438, 1379, 1019, 825, 774, 738, 698, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (1H, d, *J* = 5.2 Hz), 7.90-7.84 (2H, m), 7.71-7.65 (2H, m), 7.58 (1H, d, *J* = 1.1 Hz), 7.50-7.36 (6H, m), 7.04 (1H, dd, *J* = 5.3, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 149.4, 146.2, 138.9, 136.1, 129.9, 129.3, 129.1, 128.7, 126.9, 126.5, 122.4, 120.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 312.2, $C_{17}H_{14}NSe^+$ requires 312.0.

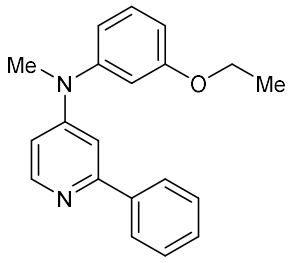
N-Methyl-N,2-diphenylpyridin-4-amine (2u)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 470 μL, 0.75 mmol), *N*-methylaniline (81 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (2.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2u) as a tan powder (117 mg, 0.45 mmol, 90% yield). mp: 77-82 °C; IR ν_{max}/cm^{-1} (film): 3061, 3045, 3038, 2917, 2852, 2818, 2592, 2501, 2161, 2050, 1953, 1842, 1603, 1597, 1536, 1480, 1445, 1360, 1235, 1135, 983, 825, 760, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (1H, d, *J* = 5.8 Hz), 7.88-7.83 (2H, m), 7.52-7.33 (5H, m), 7.31-7.24 (3H, m), 6.99 (1H, d, *J* = 2.4 Hz), 6.54 (1H, dd, *J* = 8.4, 3.4 Hz), 3.39 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$)

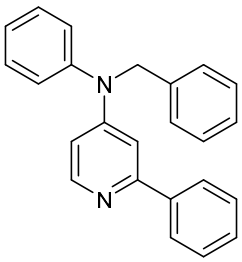
δ: 158.0, 154.6, 149.8, 146.4, 140.4, 130.0, 128.5, 128.5, 127.0, 126.6, 126.3, 107.2, 105.4, 39.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 261.1, $C_{18}H_{17}N_2^+$ requires 261.1.

N-(3-Ethoxyphenyl)-N-methyl-2-phenylpyridin-4-amine (2v)



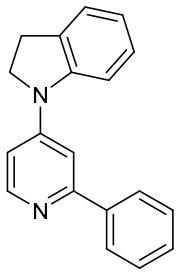
Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 234 μL, 0.38 mmol), 3-ethoxy-*N*-methylaniline (57 mg, 0.38 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (141 mg, 0.25 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 60% EtOAc in hexanes) afforded the *title compound* (2v) as an orange oil (63 mg, 0.20 mmol, 81% yield). IR ν_{max}/cm^{-1} (film): 2978, 2928, 2162, 1574, 1543, 1478, 1446,. 1245, 1203, 1046, 984, 773, 695; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.32 (1H, d, *J* = 5.8 Hz), 7.90-7.84 (2H, m), 7.46-7.30 (4H, m), 7.01 (1H, d, *J* = 2.4 Hz), 6.86-6.77 (3H, m), 6.56 (1H, dd, *J* = 5.9, 2.5 Hz), 4.04 (2H, q, *J* = 6.9 Hz), 3.37 (3H, s), 1.42 (3H, t, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 158.0, 154.5, 149.8, 147.5, 140.4, 130.6, 128.5, 128.5, 127.0, 118.6, 112.8, 112.4, 107.4, 105.6, 63.6, 39.5, 14.8; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 305.2, $C_{20}H_{21}N_2O^+$ requires 305.2.

N-Benzyl-N,2-diphenylpyridin-4-amine (2w)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 234 μL, 0.38 mmol), *N*-benzylaniline (65 μL, 0.38 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (141 mg, 0.25 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2w) as an orange amorphous solid (52 mg, 0.15 mmol, 62% yield). IR ν_{max}/cm^{-1} (film): 3062, 2961, 2930, 2860, 2253, 1715, 1588, 1496, 1385, 1271, 1120, 904, 725, 649; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (1H, d, *J* = 5.9 Hz), 7.79-7.74 (2H, m), 7.46-7.31 (11H, m), 7.30-7.26 (2H, m), 7.01 (1H, d, *J* = 2.4 Hz), 6.55 (1H, dd, *J* = 5.9, 2.5 Hz), 5.03 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 154.1, 149.9, 145.7, 140.3, 137.5, 130.0, 128.8, 128.5, 128.5, 127.3, 126.9, 126.8, 126.5, 126.4, 107.8, 106.0, 56.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 337.2, $C_{24}H_{21}N_2^+$ requires 337.2.

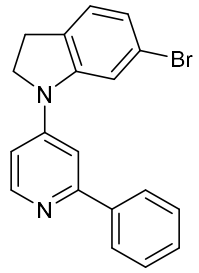
1-(2-Phenylpyridin-4-yl)indoline (2x)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 0.47 mL, 0.75 mmol), indoline (84.1 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (282.5 mg, 0.5 mmol) and THF (2.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2x) as a brown oil (92.3 mg, 0.339 mmol, 68% yield). IR ν_{max}/cm^{-1} (film): 2978, 2928, 2162, 1574, 1543, 1478, 1446, 1245, 1203, 1046, 984, 773, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (1H, d, *J* = 5.8 Hz), 7.99-7.94 (2H, m), 7.51-7.45 (3H, m), 7.45-7.37 (2H, m), 7.26-7.16 (2H, m), 7.02 (1H, dd, *J* = 5.8, 2.3 Hz), 6.94-6.88 (1H, m), 4.07 (2H, t, *J* = 8.3 Hz), 3.21 (2H, t, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$)

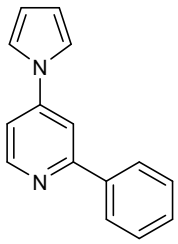
δ: 158.5, 150.3, 150.2, 144.6, 140.1, 132.2, 128.8, 128.6, 127.2, 127.0, 125.5, 121.0, 110.6, 108.9, 107.2, 51.2, 27.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 273.1, $C_{19}H_{17}N_2^+$ requires 273.1.

6-Bromo-1-(2-phenylpyridin-4-yl)indoline (2y)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 234 μL, 0.375 mmol), 6-bromoindoline (74 mg, 0.38 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (141 mg, 0.25 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 30% EtOAc in hexanes) afforded the *title compound* (2y) as a white solid (36 mg, 0.10 mmol, 41% yield). mp: 75-80°C; IR ν_{max}/cm^{-1} (film): 3298, 3035, 2956, 2162, 1608, 1574, 1478, 1431, 1270, 988, 769.5, 691.4; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, d, *J* = 5.8 Hz), 7.99-7.94 (2H, m), 7.52-7.38 (5H, m), 7.10-7.06 (1H, m), 7.05-6.99 (2H, m), 4.09 (2H, t, *J* = 8.4 Hz), 3.15 (2H, t, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 150.4, 149.8, 146.1, 139.8, 131.2, 129.0, 128.7, 127.0, 126.4, 123.6, 120.8, 113.5, 109.2, 107.5, 51.7, 27.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 351.1, $C_{19}H_{16}BrN_2^+$ requires 351.0.

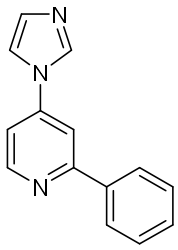
2-Phenyl-4-(1H-pyrrol-1-yl)pyridine (2z)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), pyrrole (52 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-

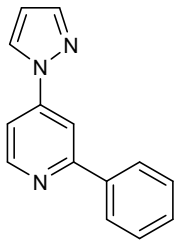
yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2z) as a clear oil (81 mg, 0.37 mmol, 74% yield). IR ν_{max}/cm^{-1} (film): 3063, 2925, 2852, 2360, 2340, 2246, 2218, 1718, 1594, 1494, 1351, 1256, 1066, 1176, 905, 723; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.66 (1H, d, *J* = 5.2 Hz), 8.00 (2H, d, *J* = 7.3 Hz), 7.69 (1H, d, *J* = 1.6 Hz), 7.53-7.41(3H, m), 7.29-7.20 (3H, m), 6.42 (2H, t, *J* = 1.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 151.1, 147.3, 139.0, 129.4, 128.8, 127.0, 118.4, 112.2, 112.1, 110.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 221.1, $C_{15}H_{13}N_2^+$ requires 221.1.

4-(1H-Imidazol-1-yl)-2-phenylpyridine (2ab)



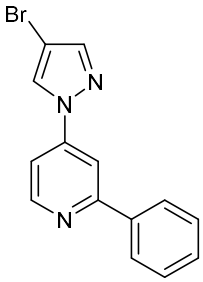
Prepared according to general procedure D using potassium hydride (36.3% dispersion in mineral oil, 41 mg, 0.38 mmol), 18-crown-6 (99 mg, 0.38 mmol) was added at the start with potassium hydride, 1*H*-imidazole (26 mg, 0.38 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (141 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3, gradient elution: 60% EtOAc in hexanes to 80% EtOAc in hexanes) afforded the *title compound* (2ab) as a clear oil (28 mg, 0.13 mmol, 51% yield). IR ν_{max}/cm^{-1} (film): 3123, 3062, 2924, 2851, 2222, 1979, 1595, 1568, 1496, 1240, 1054, 905, 725, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.78 (1H, d, *J* = 5.4 Hz); 8.08 (1H, s), 8.05-8.00 (2H, m), 7.73 (1H, d, *J* = 1.9 Hz), 7.55-7.44 (4H, m), 7.31-7.26 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 160.0, 151.5, 144.5, 138.3, 135.0, 131.6, 129.8, 129.0, 127.0, 117.0, 113.1, 111.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 222.1, $C_{14}H_{12}N_3^+$ requires 222.1.

2-Phenyl-4-(1H-pyrazol-1-yl)pyridine (2ac)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 1H-pyrazole (51 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 15% EtOAc in hexanes) afforded the *title compound* (2ac) as a clear oil (80 mg, 0.36 mmol, 72% yield). IR ν_{max}/cm^{-1} (film): 3032, 1591, 1568, 1521, 1482, 1442, 1395, 1381, 1041, 774, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (1H, d, *J* = 5.4 Hz); 8.20-8.00 (4H, m), 7.80 (1H, d, *J* = 1.4 Hz), 7.59-7.40 (4H, m), 6.58-6.53 (1H, dd, *J* = 2.4, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 151.0, 146.8, 142.4, 138.8, 129.4, 128.8, 127.1, 126.7, 110.9, 109.5, 109.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 222.1, $C_{14}H_{12}N_3^+$ requires 222.1.

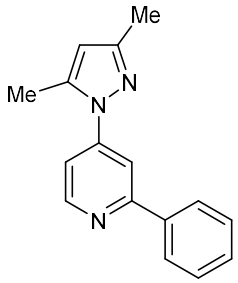
4-(4-Bromo-1H-pyrazol-1-yl)-2-phenylpyridine (2ad)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-bromo-1H-pyrazole (110 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry

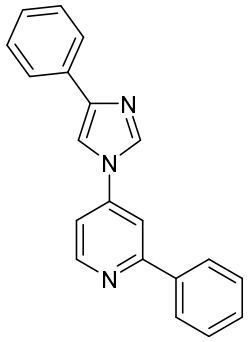
loading (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2ad) as a white solid (97 mg, 0.32 mmol, 64% yield). mp: 140-143 °C; IR ν_{max}/cm^{-1} (film): 3142, 3116, 3029, 2921, 1928, 1694, 1593, 1569, 1478, 1447, 1414, 1406, 1339, 1251, 1148, 954, 777, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (1H, d, *J* = 5.4 Hz); 8.12 (1H, s), 8.10-8.02 (3H, m), 7.76 (1H, s), 7.56-7.43 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 151.1, 146.2, 142.9, 138.6, 129.6, 128.9, 127.0, 126.8, 110.5, 109.1, 97.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 300.1, $C_{14}H_{11}BrN_3^+$ requires 300.0.

4-(3,5-Dimethyl-1H-pyrazol-1-yl)-2-phenylpyridine (2ae)



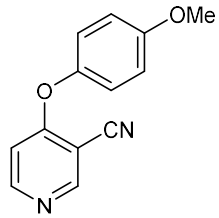
Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 3,5-dimethyl-1H-pyrazole (72 mg, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 30% EtOAc in hexanes) afforded the *title compound* (2ae) as a clear oil (47 mg, 0.19 mmol, 37% yield). IR ν_{max}/cm^{-1} (film): 2925, 2225, 1710, 1593, 1573, 905, 727; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (1H, d, *J* = 5.4 Hz), 8.06-8.01 (2H, m), 7.92 (1H, d, *J* = 1.7 Hz), 7.51-7.40 (3H, m), 7.38 (1H, dd, *J* = 5.4, 2.0 Hz), 6.08 (1H, m), 2.50 (3H, s), 2.32 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 159.0, 150.6, 150.6, 147.5, 139.9, 138.9, 129.3, 128.8, 127.0, 115.4, 114.1, 109.3, 13.6, 13.3; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 250.2, $C_{16}H_{16}N_3^+$ requires 250.1.

2-Phenyl-4-(4-phenyl-1H-imidazol-1-yl)pyridine (2af)



Prepared according to general procedure D using potassium hydride (36.3% dispersion in mineral oil, 83 mg, 0.75 mmol), 4-phenylimidazole (108 mg, 0.75 mmol), 18-Crown-6 (198 mg, 0.75 mmol), triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.5 mmol) and THF (1.0 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 40% EtOAc in hexanes) afforded the *title compound* (2af) as a yellow oil (38 mg, 0.13 mmol, 25% yield). IR ν_{max}/cm^{-1} (film): 3058, 2924, 2360, 2341, 2217, 1592, 1568, 1493, 1445, 1238, 1056, 726, 692, 906; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.78 (1H, d, J = 5.4 Hz), 8.11 (1H, s), 8.04 (2H, d, J = 6.9 Hz), 7.86 (2H, d, J = 7.3 Hz), 7.76 (1H, d, J = 1.6 Hz), 7.71 (1H, s), 7.56-7.39 (5H, m), 7.35-7.28 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 151.5, 144.3 (2C), 138.3, 135.1, 133.0, 129.8, 128.9, 128.7, 127.6, 127.0, 125.1, 112.8, 112.1, 111.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 298.2, $C_{20}H_{16}N_3^+$ requires 298.1.

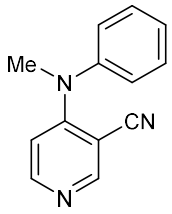
4-(4-Methoxyphenoxy)nicotinonitrile (2ag)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75

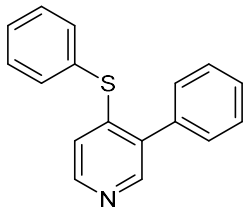
mmol), (3-cyanopyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (257 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 50% EtOAc in hexanes) afforded the *title compound* (2ag) as a colorless amorphous solid (90.9 mg, 0.402 mmol, 80% yield). IR ν_{max}/cm^{-1} (film): 3062, 2973, 2936, 2839, 2232, 1585, 1567, 1502, 1481, 1277, 1242, 1195, 1179, 1027, 889, 838; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (1H, s), 8.51 (1H, d, J = 5.9 Hz), 7.95-7.10-7.03 (2H, m), 7.00-6.95 (2H, m), 6.64 (1H, d, J = 5.9 Hz), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 158.0, 154.6, 154.4, 145.9, 122.0, 115.4, 114.0, 109.5, 100.5, 55.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 227.1, $C_{13}H_{11}N_2O_2^+$ requires 227.1.

4-(Methyl(phenyl)amino)nicotinonitrile (2ah)



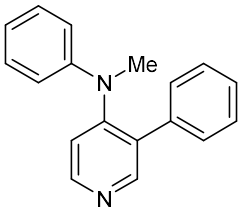
Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 470 μL, 0.75 mmol), *N*-methylaniline (81 μL, 0.75 mmol), (3-cyanopyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (257 mg, 0.50 mmol) and THF (2.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2ah) as an orange amorphous solid (86 mg, 0.41 mmol, 82% yield). IR ν_{max}/cm^{-1} (film): 3018, 2920, 2855, 2208, 1600, 1582, 1495, 1405, 1203, 1051, 809, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, s), 8.31 (1H, d, J = 6.2 Hz), 7.50-7.42 (2H, m), 7.42-7.33 (1H, m), 7.25-7.20 (2H, m), 6.65 (1H, d, J = 6.2 Hz), 3.52 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3, 155.0, 152.1, 145.9, 130.3, 127.8, 126.6, 116.8, 110.4, 95.9, 41.8; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 210.1, $C_{13}H_{12}N_3^+$ requires 210.1.

3-Phenyl-4-(phenylthio)pyridine (2ai)



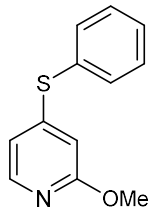
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), triphenyl(3-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 10% EtOAc in toluene) afforded the *title compound* (2ai) as a clear oil (101.2 mg, 0.384 mmol, 77% yield). IR ν_{max}/cm^{-1} (film): 3066, 3035, 2997, 2923, 2950, 2612, 1980, 1815, 1763, 1699, 1567, 1462, 1379, 757, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (1H, s), 8.25 (1H, d, *J* = 5.4 Hz), 7.54-7.38 (10H, m), 6.68 (1H, d, *J* = 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3, 149.2, 148.3, 136.7, 135.6, 134.8, 130.0, 129.9, 129.7, 129.4, 128.5, 128.4, 120.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 264.1, $C_{17}H_{14}NS^+$ requires 264.1.

N-Methyl-N,3-diphenylpyridin-4-amine (2aj)



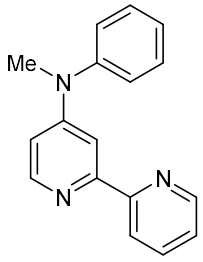
Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 0.468 mL, 0.75 mmol), *N*-methylaniline (81.2 μL, 0.75 mmol), triphenyl(3-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (282.6 mg, 0.5 mmol) and THF (2.0 mL).

2-Methoxy-4-(phenylthio)pyridine (2ak)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), triphenyl(2-methoxypyridin-4-yl)phosphonium trifluoromethanesulfonate (260 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 5% EtOAc in hexanes) followed by filtration through a plug of silica eluting with 100% DCM afforded the *title compound* (2ak) as a clear oil (49 mg, 0.22 mmol, 45% yield). IR ν_{max}/cm^{-1} (film): 3060, 2981, 2947, 2857, 2226, 1588, 1542, 1473, 1385, 1035, 905, 728; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.94 (1H, d, *J* = 5.5 Hz), 7.57-7.51 (2H, m), 7.46-7.40 (3H, m), 6.60 (1H, dd, *J* = 5.5, 1.6 Hz) 6.33 (1H, d, *J* = 1.4 Hz), 3.87 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5, 152.3, 146.4, 135.2, 129.8, 129.6, 129.5, 114.8, 107.2, 53.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 218.1, $C_{12}H_{12}NOS^+$ requires 218.1.

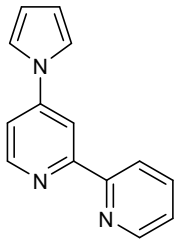
N-Methyl-N-phenyl-[2,2'-bipyridin]-4-amine (2al)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 0.47 mL, 0.75 mmol), *N*-methylaniline (81 μL, 0.75 mmol), [2,2'-bipyridin]-4-yltriphenylphosphoniumtrifluoromethanesulfonate (283 mg, 0.50 mmol) and THF (2.0 mL). Flash column chromatography (silica gel: 20% EtOAc, 2.5% NEt_3 in hexanes) afforded the *title*

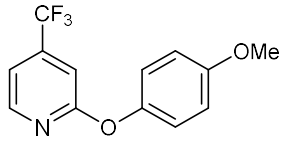
compound (2al) as a tan solid (107 mg, 0.41 mmol, 82% yield). mp: 107-110 °C; IR ν_{max}/cm^{-1} (film): 3061, 3002, 2907, 2821, 2538, 2162, 1979, 1604, 1578, 1567, 1542, 1490, 1468, 1456, 1370, 953, 786, 774, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (1H, d, *J* = 4.1 Hz), 8.32 (1H, d, *J* = 8.0 Hz), 8.22 (1H, d, *J* = 5.8 Hz), 7.80-7.70 (2H, m), 7.45-7.35 (2H, m), 7.25-7.15 (4H, m), 6.52 (1H, dd, *J* = 5.8, 2.6 Hz), 3.41 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.8, 156.7, 154.8, 149.2, 148.9, 146.5, 136.7, 129.9, 126.6, 126.2, 123.4, 121.2, 108.9, 105.3, 39.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 262.1, $C_{17}H_{16}N_3^+$ requires 262.1.

4-(1H-Pyrrol-1-yl)-2,2'-bipyridine (2am)



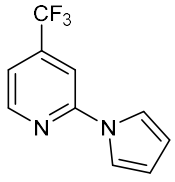
Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), 1H-pyrrole (26 μL, 0.38 mmol), [2,2'-bipyridin]-4-yltriphenylphosphonium trifluoromethanesulfonate (142 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (basic alumina: 5% EtOAc in hexanes) afforded the *title compound* (2am) as a tan amorphous solid (36 mg, 0.16 mmol, 64% yield). IR ν_{max}/cm^{-1} (film): 3060, 2922, 2851, 2222, 1723, 1598, 1584, 1563, 1496, 1350, 1062, 907, 723, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72-8.69 (1H, m), 8.66 (1H, d, *J* = 5.4 Hz), 8.50 (1H, d, *J* = 2.2 Hz), 8.47-8.43 (1H, m), 7.85 (1H, td, *J* = 7.8, 1.7 Hz), 7.39-7.30 (4H, m), 6.42 (2H, t, *J* = 2.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 155.5, 150.6, 149.2, 147.4, 137.0, 124.1, 121.3, 118.5, 113.2, 112.1, 110.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 222.1, $C_{14}H_{12}N_3^+$ requires 222.1.

2-(4-Methoxyphenoxy)-4-(trifluoromethyl)pyridine (2an)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), 4-methoxyphenol (47 mg, 0.38 mmol), 15-crown-5 (75 μL, 0.38 mmol), triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (139 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2an) as a white solid (54 mg, 0.20 mmol, 80% yield). mp: 76-79 °C; IR ν_{max}/cm^{-1} (film): 3073, 3028, 2979, 2921, 2849, 2050, 1758, 1615, 1569, 1503, 1402, 1330, 1294, 1225, 1171, 1137, 1075, 836; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (1H, d, *J* = 5.2 Hz), 7.16 (1H, dd, *J* = 5.2, 0.8 Hz), 7.11 (1H, t, *J* = 1.4 Hz), 7.10-7.05 (2H, m), 6.97-6.92 (2H, m), 3.83 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.7, 157.0, 149.0, 146.6, 141.6 (q, J = 34.1 Hz), 122.5 (q, J = 273.1 Hz), 122.4, 114.9, 113.7 (q, J = 3.3 Hz), 107.6 (q, J = 4.0 Hz), 55.6; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –64.92; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 270.1, $C_{13}H_{11}F_3NO_2^+$ requires 270.1.

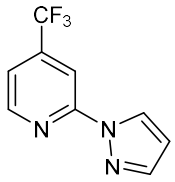
2-(1H-Pyrrol-1-yl)-4-(trifluoromethyl)pyridine (2ao)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 1H-pyrrole (52 μL, 0.75 mmol), triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (279 mg, 0.50 mmol), and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 2% EtOAc in hexanes) afforded the *title compound* (2ao) as a white solid (70 mg, 0.33 mmol, 66% yield).

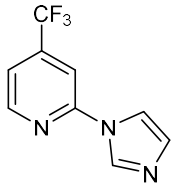
mp: 73-77 °C; IR ν_{max}/cm^{-1} (film): 3160, 3119, 3048, 2922, 1724, 1615, 1575, 1492, 1437, 1352, 1330, 1300, 1276, 1172, 1128, 1059, 935, 839, 735, 675; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (1H, d, *J* = 5.1 Hz), 7.55 (2H, t, *J* = 2.3 Hz), 7.48 (1H, s), 7.30 (1H, dd, *J* = 0.7, 5.1 Hz), 6.39 (2H, t, *J* = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 150.0, 140.8 (q, J = 34.2 Hz), 122.5 (q, J = 273.9 Hz), 118.2, 115.5 (q, J = 3.4 Hz), 112.3, 107.1 (q, J = 3.8 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –64.98 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 213.1, $C_{10}H_8F_3N_2^+$ requires 213.1.

2-(1H-Pyrazol-1-yl)-4-(trifluoromethyl)pyridine (2ap)



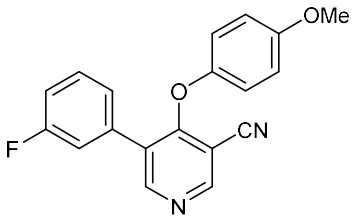
Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 1*H*-pyrazole (51 mg, 0.75 mmol), triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (279 mg, 0.50 mmol), and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 3% EtOAc in hexanes) afforded the *title compound* (2ap), as a volatile clear oil (31 mg, 0.14 mmol, 29% iso. yield, 76% ^{1}H NMR yield). Note that the product evaporates during solvent evaporation. IR ν_{max}/cm^{-1} (film): 2926, 2253, 1577, 1463, 1398, 1345, 1318, 1179, 1149, 1040, 903, 726, 649; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60-8.55 (2H, m); 8.25 (1H, s), 7.78 (1H, d, *J* = 1.0 Hz), 7.39 (1H, d, *J* = 4.4 Hz), 6.50 (1H, t, *J* = 2.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 149.3, 142.8, 141.0 (q, *J* = 34.2 Hz), 127.3, 122.5 (q, *J* = 273.3 Hz), 116.8 (q, *J* = 3.4 Hz), 108.8 (q, *J* = 4.0 Hz), 108.5; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –64.96 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 214.1, $C_9H_7F_3N_3^+$ requires 214.1.

2-(1H-Imidazol-1-yl)-4-(trifluoromethyl)pyridine (2aq)



Prepared according to general procedure D using potassium hydride (36.3% dispersion in parafin, 83 mg, 0.75 mmol), 1H-imidazole (51 mg, 0.75 mmol), triphenyl(4-(trifluoromethyl)pyridin-2-yl)phosphonium trifluoromethanesulfonate (279 mg, 0.50 mmol), and THF (1.0 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 40% EtOAc in hexanes) afforded the *title compound* (2aq) as a white solid (78 mg, 0.37 mmol, 73% yield). mp: 61-66 °C; IR ν_{max}/cm^{-1} (film): 3119, 3053, 2916, 2848, 2225, 1980, 1673, 1615, 1577, 1481, 1438, 1326, 1176, 1141, 1051, 906, 841, 652; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.68 (1H, d, J = 5.1 Hz), 8.42 (1H, s), 7.68 (1H, t, J = 1.4 Hz), 7.54 (1H, s), 7.47 (1H, dd, J = 0.6, 5.1 Hz), 7.25 (1H, t, J = 1.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 149.9, 141.4 (q, J = 34.3 Hz), 135.1, 131.4, 122.3 (q, J = 275.2 Hz), 117.5 (q, J = 3.4 Hz), 116.0, 108.1 (q, J = 3.8 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –64.90 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 214.1, $C_9H_7F_3N_3^+$ requires 214.1.

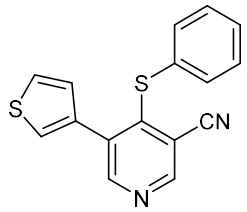
5-(3-Fluorophenyl)-4-(4-methoxyphenoxy)nicotinonitrile (2ar)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), (3-cyano-5-(3-fluorophenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (304 mg, 0.50 mmol) and THF (1.0 mL). Flash column

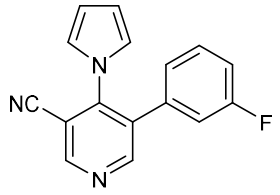
chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 25% EtOAc in hexanes) afforded the *title compound* (2ar) as a yellow solid (117 mg, 0.37 mmol, 73% yield). mp: 93-97 °C; IR ν_{max}/cm^{-1} (film): 3048, 3011, 2954, 2919, 2847, 2235, 1967, 1871, 1583, 1501, 1446, 1432, 1241, 1183, 1031, 878, 794, 696; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.79 (1H, s), 8.75 (1H, s), 7.40-7.33 (1H, m), 7.24-7.20 (1H, m), 7.19-7.15 (1H, m), 7.10-7.04 (1H, m), 6.84-6.76 (4H, m), 3.76 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.6 (d, J = 246.2 Hz), 161.8, 156.7, 155.2, 154.7, 149.6, 134.4 (d, J = 8.1 Hz), 130.3 (d, J = 8.4 Hz), 129.5, 124.9 (d, J = 3.1 Hz), 119.0, 116.3 (d, J = 22.7 Hz), 115.8 (d, J = 21.0 Hz), 114.8, 113.3, 103.5, 55.6; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −112.18; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 321.2, $C_{19}H_{14}FN_2O_2^+$ requires 321.1.

4-(Phenylthio)-5-(thiophen-3-yl)nicotinonitrile (2as)



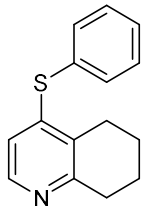
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), (3-cyano-5-(thiophen-3-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (298 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2as) as white solid (121 mg, 0.31 mmol, 63% yield). mp: 129-133 °C; IR ν_{max}/cm^{-1} (film): 3734, 3111, 3054, 2924, 2498, 2232, 1968, 1867, 1725, 1543, 1438, 1077, 842, 787, 736, 656; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.74 (1H, s), 8.67 (1H, s), 7.39-7.34 (1H, m), 7.34-7.29 (1H, m), 7.26-7.18 (4H, m), 7.18-7.12 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.1, 152.9, 148.0, 135.5, 135.4, 132.3, 131.7, 129.4, 128.4, 128.3, 126.1, 125.7, 115.1, 114.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 295.1, $C_{16}H_{11}N_2S_2^+$ requires 295.0.

5-(3-Fluorophenyl)-4-(1H-pyrrol-1-yl)nicotinonitrile (2at)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), 1H-pyrrole (26 μL, 0.38 mmol), (3-cyano-5-(3-fluorophenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (152 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2at) as a brown oil (17 mg, 0.063 mmol, 25% yield). IR ν_{max}/cm^{-1} (film): 3019, 2927, 2236, 1613, 1587, 1496, 1485, 1324, 1215, 1063, 907, 729, 696, 668; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.95 (1H, s); 8.84 (1H, s), 7.37-7.30 (1H, m), 7.09 (1H, td, *J* = 8.4, 2.6 Hz), 6.85 (1H, d, J = 7.7 Hz), 6.75 (1H, dt, *J* = 9.3, 1.8 Hz), 6.64 (2H, t, *J* = 2.1 Hz), 6.30 (2H, t, *J* = 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.9 (d, *J* = 248.0 Hz), 155.1, 153.8, 147.2, 135.4 (d, *J* = 8.1 Hz), 132.3, 130.7 (d, *J* = 8.4 Hz), 124.0 (d, *J* = 3.1 Hz), 121.5, 116.1 (d, *J* = 21.0 Hz), 115.3 (d, *J* = 22.9 Hz), 114.6, 112.0, 107.3; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –111.30; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 264.1, $C_{16}H_{11}FN_3^+$ requires 264.1.

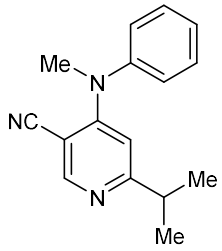
4-(Phenylthio)-5,6,7,8-tetrahydroquinoline (2au)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (76.5 μL, 0.75 mmol), triphenyl(5,6,7,8-tetrahydroquinolin-4-yl)phosphonium trifluoromethanesulfonate (272mg, 0.50 mmol) and DME (1.0 mL). Flash column chromatography (silica gel: 30% EtOAc in toluene) afforded the

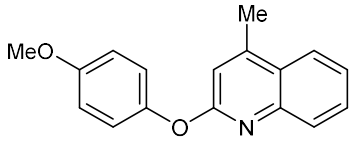
title compound (2au) as a white solid (93 mg, 0.39 mmol, 77% yield). mp: 93-98 °C, IR ν_{max}/cm^{-1} (film): 3034, 2861, 2658, 2535, 2184, 1981, 1880, 1724, 1555, 1433, 1402, 1064, 815, 755, 704, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (1H, d, *J* = 5.3 Hz), 7.55-7.42 (5H, m), 6.41 (1H, d, *J* = 5.3 Hz), 2.91 (2H, t, *J* = 8.0 Hz), 2.73 (2H, t, *J* = 8.0 Hz), 1.94-1.84 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 149.1, 146.1, 135.4, 130.0, 129.9, 129.4, 128.6, 117.7, 32.9, 26.1, 22.8, 22.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 242.1, $C_{15}H_{16}NS^+$ requires 242.1.

6-Isopropyl-4-(methyl(phenyl)amino)nicotinonitrile (2av)



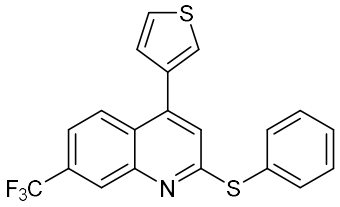
Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 468 μL, 0.75 mmol), *N*-methylaniline (81 μL, 0.75 mmol), (5-cyano-2-isopropylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (278 mg, 0.50 mmol) and THF (2.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2av) as an off-white powder (87 mg, 0.35 mmol, 69% yield). mp: 108-114 °C; IR ν_{max}/cm^{-1} (film): 3060, 3007, 2963, 2921, 2868, 2214, 1863, 1752, 1581, 1534, 1492, 1410, 1310, 1051, 877, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (1H, s), 7.48-7.42 (2H, m), 7.37-7.31 (1H, m), 7.24-7.19 (2H, m), 6.54 (1H, s), 3.49 (3H, s), 2.93 (1H, sp, *J* = 6.8 Hz), 1.26 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.1, 155.8, 155.6, 146.2, 130.1, 127.3, 126.4, 117.1, 107.2, 94.2, 41.7, 36.7, 22.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 252.2, $C_{16}H_{18}N_3^+$ requires 252.1.

2-(4-Methoxyphenoxy)-4-methylquinoline (2aw)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), (4-methylquinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate (277 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (basic alumina: 5% EtOAc in hexanes) afforded the *title compound* (2aw) as a white solid (90 mg, 0.34 mmol, 68% yield). mp: 96-100 °C; IR ν_{max}/cm^{-1} (film): 3067, 2952, 2920, 2835, 2163, 1615, 1575, 1503, 1463, 1442, 1384, 1336, 1201, 1177, 1022, 828, 756; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.90 (1H, dd, *J* = 8.3, 1.2 Hz), 7.79 (1H, dd, *J* = 8.4, 0.7 Hz), 7.62-7.57 (1H, m), 7.45-7.40 (1H, m), 7.19-7.14 (2H, m), 6.97-6.92 (2H, m), 6.89 (1H, d, J = 0.8 Hz), 3.84 (3H, s), 2.66 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9, 156.5, 148.0, 147.3, 146.5, 129.5, 128.4, 125.8, 124.4, 123.6, 122.4, 114.6, 112.4, 55.6, 18.9; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 266.1, $C_{17}H_{16}NO_2^+$ requires 266.1.

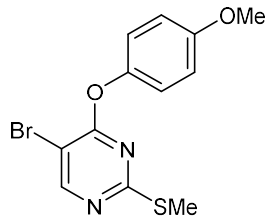
2-(Phenylthio)-4-(thiophen-3-yl)-7-(trifluoromethyl)quinoline (2ax)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), benzenethiol (38 μL, 0.38 mmol), triphenyl(4-(thiophen-3-yl)-7-(trifluoromethyl)quinolin-2-yl)phosphonium trifluoromethanesulfonate (172 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel: 40% DCM in hexanes) afforded the *title compound* (2ax) as a white powder (71 mg, 0.18 mmol, 74% yield). mp: 89-93 °C; IR

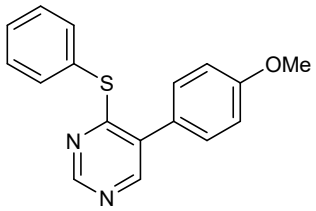
ν_{max}/cm^{-1} (film): 3103, 2923, 2852, 2161, 1792, 1586, 1334, 1288, 1156, 1116, 1097, 1062, 829, 769; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (1H, s), 8.05 (1H, d, *J* = 8.7 Hz), 7.71-7.66 (2H, m), 7.58 (1H, dd, *J* = 8.8, 1.8 Hz), 7.51-7.45 (4H, m), 7.42 (1H, dd, *J* = 2.9, 1.2 Hz), 7.21 (1H, dd, *J* = 5.0, 1.2 Hz), 7.12 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.9, 147.8, 143.4, 137.4, 135.2, 131.6 (q, *J* = 33.1 Hz), 129.9, 129.7, 129.5, 128.5, 126.9, 126.7, 126.5 (q, *J* = 4.4 Hz), 126.4, 125.5, 123.9(q, *J* = 272.1 Hz), 121.3 (q, *J* = 3.2 Hz), 120.8; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.79; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 388.1, $C_{20}H_{13}F_3NS_2^+$ requires 388.0.

5-bromo-4-(4-methoxyphenoxy)-2-(methylthio)pyrimidine (2ay)



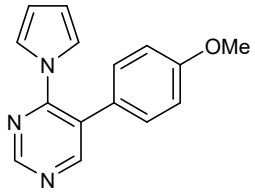
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), (5-bromo-2-(methylthio)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (307 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 5% EtOAc in hexanes) afforded the *title compound* (2ay) as a white solid (142 mg, 0.44 mmol, 87% yield). mp: 86-88 °C; IR ν_{max}/cm^{-1} (film): 3024, 3006, 2926, 2836, 1554, 1537, 1501, 1407, 1332, 1288, 1256, 1221, 1176, 1031, 957, 822, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (1H, s), 7.11-7.06 (2H, m), 6.94-6.89 (2H, m), 3.83 (3H, s), 2.26 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 164.6, 159.4, 157.3, 145.5, 122.5, 114.3, 100.8, 55.6, 14.3; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 327.0, $C_{12}H_{12}BrN_2O_2S^+$ requires 327.0.

5-(4-Methoxyphenyl)-4-(phenylthio)pyrimidine (2az)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), (5-(4-methoxyphenyl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (298 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2az) as a white powder (98 mg, 0.33 mmol, 66% yield). mp: 98-101 °C; IR ν_{max}/cm^{-1} (film): 3074, 3009, 2936, 2835, 2545, 2162, 2061, 1575, 1522, 1509, 1379, 1293, 1252, 1176, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (1H, s); 8.31 (1H, s), 7.56-7.50 (2H, m), 7.49-7.41 (5H, m), 7.09-7.03 (2H, m), 3.90 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 160.2, 156.7, 154.2, 135.6, 132.5, 130.4, 129.5, 129.2, 128.3, 126.6, 114.3, 55.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 295.1, $C_{17}H_{15}N_2OS^+$ requires 295.1.

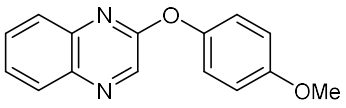
5-(4-Methoxyphenyl)-4-(1H-pyrrol-1-yl)pyrimidine (2ba)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), 1H-pyrrole (26 μL, 0.38 mmol), (5-(4-methoxyphenyl)pyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (149 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the *title compound* (2ba) as a white powder (52 mg, 0.21 mmol, 82% yield). mp: 100-105 °C; IR ν_{max}/cm^{-1} (film): 3158, 3121, 3058, 2924, 2840, 1610, 1578, 1551, 1442, 1393, 1349, 1248, 1178, 1059, 931, 835,

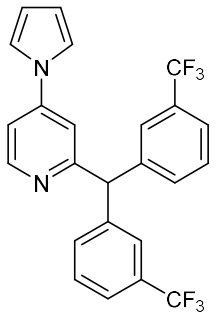
731; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (1H, d, s), 8.60 (1H, s), 7.24-7.19 (2H, m), 7.04(2H, t, *J* = 2.3 Hz), 7.00-6.95 (2H, m), 6.18 (2H, t, *J* = 2.3 Hz), 3.87 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0 (2C), 157.1, 154.6, 130.0, 126.8, 124.4, 120.7, 114.7, 111.4, 55.3; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 252.1, $C_{15}H_{14}N_3O^+$ requires 252.1.

2-(4-Methoxyphenoxy)quinoxaline (2bb)



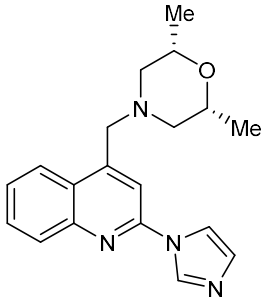
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), 4-methoxyphenol (93 mg, 0.75 mmol), 15-crown-5 (150 μL, 0.75 mmol), triphenyl(quinoxalin-2-yl)phosphonium trifluoromethanesulfonate (270 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography by dissolving in CH_2Cl_2 and dry loading (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2bb) as a white amorphous solid (100 mg, 0.40 mmol, 79% yield). IR ν_{max}/cm^{-1} (film): 3060, 3022, 2953, 2931, 2836, 2599, 2042, 1887, 1830, 1641, 1574, 1499, 1401, 1306, 1251, 1205, 1182, 993, 917, 829, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (1H, s), 8.05 (1H, dd, *J* = 8.0, 1.7 Hz), 7.78-7.74 (1H, m), 7.68-7.57 (2H, m), 7.23-7.18 (2H, m), 7.00-6.95 (2H, m), 3.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 157.2, 156.9, 146.1, 140.0, 139.5, 139.1, 130.2, 128.8, 127.7, 127.2, 122.3, 114.6, 55.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 253.2, $C_{15}H_{13}N_2O_2^+$ requires 253.1.

2-(Bis(3-(trifluoromethyl)phenyl)methyl)-4-(1H-pyrrol-1-yl)pyridine (2bc)



Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.375 mmol), 1*H*-pyrrole (26 μL, 0.38 mmol), (2-(bis(3-(trifluoromethyl)phenyl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (198 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel, gradient elution: 10% EtOAc in hexanes to 20% EtOAc in hexanes) afforded the *title compound* (2bc) as a yellow oil (52 mg, 0.12 mmol, 46% yield). IR ν_{max}/cm^{-1} (film): 2927, 2251, 1980, 1722, 1595, 1497, 1328, 1165, 1127, 1075, 904, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (1H, d, *J* = 5.5 Hz), 7.60-7.35 (8H, m), 7.21 (1H, dd, *J* = 5.5, 2.2 Hz), 7.16-7.08 (3H, m), 6.38 (2H, t, *J* = 2.1 Hz), 5.75 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.0, 151.4, 147.3, 142.5, 132.6, 131.0 (q, *J* = 32.2 Hz), 129.2, 125.9 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.8 Hz), 118.3, 113.5, 112.4, 111.9, 58.7; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –62.57 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 447.1, $C_{24}H_{17}F_6N_2^+$ requires 447.1.

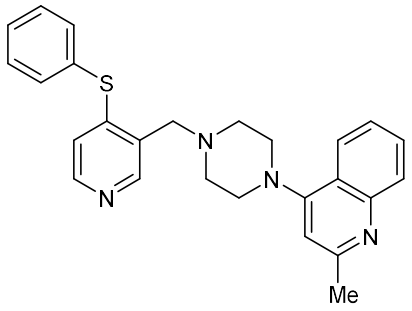
(2R,6S)-4-((2-(1H-Imidazol-1-yl)quinolin-4-yl)methyl)-2,6-dimethylmorpholine (2bd)



Prepared according to general procedure D using potassium hydride (36.3% dispersion in mineral oil, 41 mg, 0.38 mmol), 1*H*-imidazole (26 mg, 0.38 mmol), (4-(((2R,6S)-2,6-dimethylmorpholino)methyl)quinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate (167 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel: 4% MeOH in DCM) afforded the *title compound* (2bd) as a white amorphous solid (52 mg, 0.16 mmol, 64% yield). IR ν_{max}/cm^{-1} (film): 3150, 3127, 2974, 2931, 2877, 2811, 2773, 2205, 1660, 1599, 1432, 1325, 1084, 1058, 931, 721, 651; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (1H, s), 8.19 (1H, dd, *J* = 8.4, 0.7 Hz), 8.04 (1H, dd, *J* = 8.4 Hz, 0.5 Hz), 7.86 (1H,

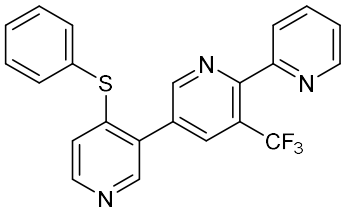
m), 7.77-7.71 (1H, m), 7.61 (1H, s), 7.57-7.51 (1H, m), 7.25 (1H, m), 3.94 (2H, s), 3.78-3.69 (2H, m), 2.75 (2H, d, J = 10.3 Hz), 1.94 (2H, t, J = 10.5 Hz), 1.16 (6H, d, J = 6.3 Hz); ^{13}C NMR (100 MHz,$CDCl_3$)δ: 148.1, 147.4, 147.3, 135.3, 130.7, 130.5, 129.3, 126.3, 126.2, 124.0, 116.5, 111.5 , 71.7, 59.7, 59.4, 19.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 323.2, $C_{19}H_{23}N_4O^+$ requires 323.2.

2-Methyl-4-(4-((4-(phenylthio)pyridin-3-yl)methyl)piperazin-1-yl)quinoline (2be)



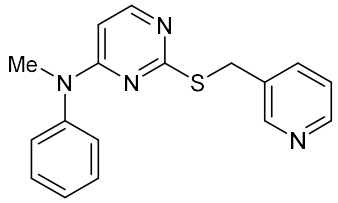
Prepared according to general procedure C sodium hydride (60% dispersion in mineral oil, 6 mg, 0.15 mmol), benzenethiol (16 μL, 0.15 mmol), (3-((4-(2-methylquinolin-4-yl)piperazin-1-yl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (73 mg, 0.10 mmol) and DME (0.4 mL). Flash column chromatography (silica gel, gradient elution: 100% EtOAc to 1% NEt_3 in EtOAc) afforded the *title compound* (2be) as an orange oil (15 mg, 0.034 mmol, 34% yield). IR ν_{max}/cm^{-1} (film): 3061, 2933, 2825, 2361, 2340, 2205, 1589, 1574, 1416, 1283, 1192, 1136, 1006, 905, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (1H, s), 8.22 (1H, d, J = 5.4 Hz), 7.98 (2H, t, J = 7.7 Hz), 7.65-7.58 (1H, m), 7.56-7.51 (2H, m), 7.48-7.39 (4H, m), 6.75 (1H, s), 6.71 (1H, d, J = 5.4 Hz), 3.75 (2H, s), 3.33-3.17 (4H, m), 3.87-3.78 (4H, m), 2.68 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 157.0, 151.0, 149.6, 149.2, 148.6, 135.1, 131.2, 130.5, 129.9, 129.4, 129.2, 129.0, 124. 5, 123.5, 121.9, 121.4, 109.5, 58.4, 52.7, 52.1, 25.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 427.4, $C_{26}H_{27}N_4S^+$ requires 427.2.

4''-(Phenylthio)-3'-(trifluoromethyl)-2,2':5',3''-terpyridine (2bf)



Prepared according to general procedure C sodium hydride (60% dispersion in mineral oil, 30 mg, 0.75 mmol), benzenethiol (77 μL, 0.75 mmol), triphenyl(3'-(trifluoromethyl)-[2,2':5',3''-terpyridin]-4''-yl)phosphonium trifluoromethanesulfonate (356 mg, 0.50 mmol) and THF (1.0 mL). Flash column chromatography (silica gel: 100% EtOAc) followed by a second flash column (20% EtOAc, 10% NEt_3 in hexanes) afforded the *title compound* (2bf) as a yellow amorphous solid (132 mg, 0.32 mmol, 65% yield). IR ν_{max}/cm^{-1} (film): 3060, 2925, 2227, 1569, 1448, 1429, 1331, 1285, 1162, 1138, 1019, 906, 727, 689; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.98 (1H, d, *J* = 1.9 Hz), 8.76 (1H, d, *J* = 4.8 Hz), 8.40 (1H, s), 8.37 (1H, d, *J* = 5.5 Hz), 8.28 (1H, d, *J* = 2.0 Hz), 7.88 (1H, td, *J* = 7.8, 1.8 Hz), 7.80-7.76 (1H, m), 7.55-7.39 (6H, m), 6.80 (1H, d, *J* = 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 156.1, 151.8, 149.8, 149.8, 149.4, 149.1, 136.5, 136.2 (q, J = 5.0 Hz), 135.4, 132.0, 130.2, 130.0, 129.8, 128.9, 125.0 (q, J = 33.0 Hz), 123.4 (q, J = 273.1 Hz), 123.8, 123.7, 120.7; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –57.64 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 410.2, $C_{22}H_{15}F_3N_3S^+$ requires 410.1.

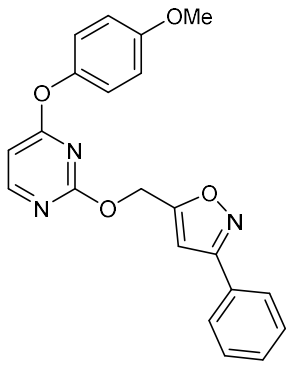
N-Methyl-N-phenyl-2-((pyridin-3-ylmethyl)thio)pyrimidin-4-amine (2bg)



Prepared according to general procedure E using n-butyl lithium (1.6 M in hexanes, 234 μL, 0.38 mmol), *N*-methylaniline (40.6 μL, 0.38 mmol), triphenyl(2-((pyridin-3-

ylmethyl)thio)pyrimidin-4-yl)phosphonium trifluoromethanesulfonate (153 mg, 0.25 mmol) and THF (1.0 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 15% EtOAc in toluene) afforded the *title compound* (2bg) as a yellow oil (29 mg, 0.093 mmol, 37% yield). IR ν_{max}/cm^{-1} (film): 3035, 2927, 2224, 1710, 1600, 1568, 1498, 1348, 1200, 975, 904, 726, 647; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.64 (1H, d, *J* = 1.8 Hz), 8.47 (1H, dd, *J* = 1.5, 4.9 Hz), 7.87 (1H, d, *J* = 6.1 Hz), 7.77-7.72 (1H, m), 7.48-7.41 (2H, m), 7.35-7.30 (1H, m), 7.25-7.19 (3H, m), 5.99 (1H, d, *J* = 6.0 Hz), 4.36 (2H, s), 3.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 161.7, 154.9, 150.2, 148.3, 144.1, 136.3, 134.5, 130.0, 127.3, 126.9, 123.3, 100.9, 37.9, 32.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 309.2, $C_{17}H_{17}N_4S^+$ requires 309.1.

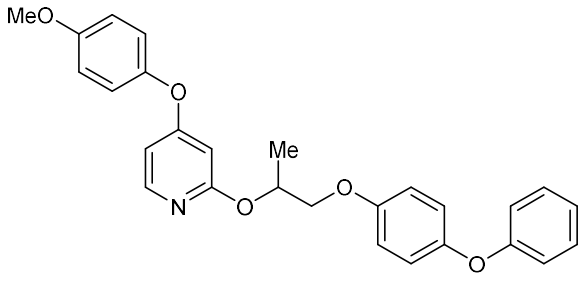
5-(((4-(4-Methoxyphenoxy)pyrimidin-2-yl)oxy)methyl)-3-phenylisoxazole (2bh)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.375 mmol), 4-methoxyphenol (47 mg, 0.38 mmol), 15-crown-5 (74 μL, 0.38 mmol), triphenyl(2-((3-phenylisoxazol-5-yl)methoxy)pyrimidin-4-yl)phosphonium trifluoromethanesulfonate (166 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel, gradient elution: 4% EtOAc in toluene to 8% EtOAc in toluene) afforded the *title compound* (2bh) as a clear oil (52 mg, 0.14 mmol, 55% yield). IR ν_{max}/cm^{-1} (film): 3053, 2917, 2848, 2247, 1610, 1574, 1504, 1441, 1272, 1244, 1193, 1080, 905, 726, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.36 (1H, d, *J* = 5.6 Hz), 7.80-7.74 (2H, m), 7.47-7.42 (3H, m), 7.10-7.04 (2H, m), 6.96-6.90 (2H, m), 6.53 (1H, d, *J* = 5.6 Hz), 6.51 (1H, s), 5.42 (2H, s), 3.82

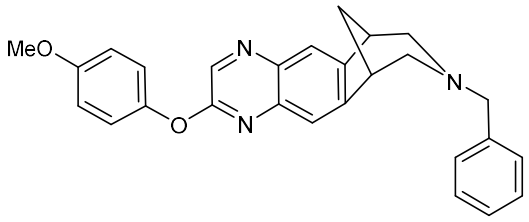
(3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.6, 167.9, 164.2, 162.4, 160.3, 157.4, 145.5, 130.0, 128.9, 126.8, 122.4, 114.8, 102.3, 102.2, 101.8, 59.7, 55.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 376.2, $C_{21}H_{18}N_3O_4^+$ requires 376.1.

4-(4-Methoxyphenoxy)-2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridine (2bi)



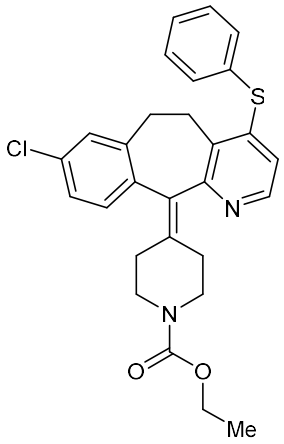
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.375 mmol), 4-methoxyphenol (47 mg, 0.38 mmol), 15-crown-5 (74 μL, 0.38 mmol), (2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (183 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel: 10% EtOAc in hexanes) afforded the *title compound* (2bi) as a clear oil (56 mg, 0.13 mmol, 50% yield). IR ν_{max}/cm^{-1} (film): 3042, 2932, 2836, 2578, 2250, 2050, 1594, 1502, 1488, 1472, 1218, 1203, 1147, 906, 839, 728; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (1H, d, *J* = 5.9 Hz), 7.34-7.27 (2H, m), 7.08-6.99 (3H, m), 6.99-6.88 (8H, m), 6.52 (1H, dd, *J* = 5.9, 2.2 Hz), 6.12 (1H, d, *J* = 2.2 Hz), 5.56 (1H, m), 4.18-4.10 (1H, m), 4.08-4.01 (1H, m), 3.82 (3H, m), 1.45 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 165.0, 158.5, 157.1, 155.2, 150.3, 147.8, 147.3, 129.6, 122.4, 122.1, 120.7, 117.6, 115.8, 115.1, 107.0, 97.4, 71.0, 69.6, 55.6, 17.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 444.2, $C_{27}H_{26}NO_5^+$ requires 444.2.

(6R,10S)-8-Benzyl-2-(4-methoxyphenoxy)-7,8,9,10-tetrahydro-6H-6,10-methanoazepino[4,5-g]quinoxaline (2bj)



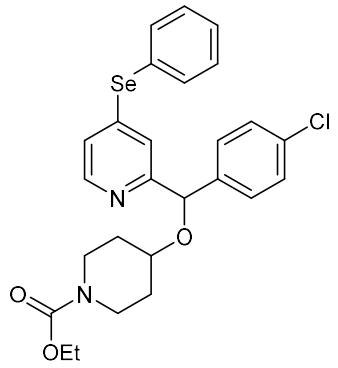
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 6 mg, 0.15 mmol), 4-methoxyphenol (19 mg, 0.15 mmol), 15-crown-5 (30 μL, 0.15 mmol), ((6R,10S)-8-benzyl-7,8,9,10-tetrahydro-6H-6,10-methanoazepino[4,5-g]quinoxalin-2-yl)triphenylphosphonium trifluoromethanesulfonate (71 mg, 0.10 mmol) and THF (0.2 mL). Flash column chromatography (silica gel: 30% EtOAc in hexanes) afforded the *title compound* (2bj) as a yellow oil (24 mg, 0.057 mmol, 57% yield). IR ν_{max}/cm^{-1} (film): 3016, 2950, 1836, 2791, 2162, 2049, 1568, 1503, 1347, 1290, 1202, 907, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (1H, s), 7.73 (1H, s), 7.50 (1H, s), 7.24-7.19 (2H, m), 7.14-7.09 (3H, m), 7.00-6.94 (2H, m), 6.88-6.81 (2H, m), 3.85 (3H, s), 3.46 (2H, s), 3.33-3.21 (2H, m), 2.98-2.87 (2H, m), 2.52 (2H, t, J = 8.3 Hz), 2.34-2.25 (1H, m), 1.81 (1H, d, J = 10.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 156.8, 151.1, 147.8, 146.6, 140.1, 139.6, 138.3, 136.6, 128.3, 128.0, 126.6, 122.3, 120.2, 119.3, 114.6, 61.6, 57.3, 57.2, 55.6, 43.4, 41.4, 41.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 424.2, $C_{27}H_{26}N_3O_2^+$ requires 424.2.

Ethyl 4-(8-chloro-4-(phenylthio)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (2bk)



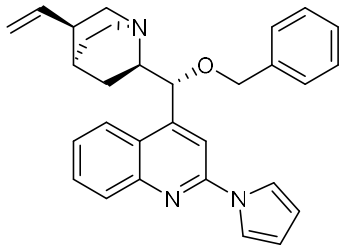
Prepared according to general procedure C sodium hydride (60% dispersion in mineral oil, 12 mg, 0.30 mmol), benzenethiol (31 μL, 0.30 mmol), (8-chloro-11-(1-(ethoxycarbonyl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (159 mg, 0.20 mmol) and THF (0.40 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3, gradient elution: 60% CH_2Cl_2 in hexanes to 70% CH_2Cl_2 in hexanes to 10 % MeOH in CH_2Cl_2) followed by a second flash column (silica gel was packed with hexanes and neutralized with NEt_3, gradient elution: 9.5% CH_2Cl_2, 0.5% NEt_3 in toluene to 8% CH_2Cl_2, 2% NEt_3 in toluene) afforded the *title compound* (2bk) as a white solid (82 mg, 0.17 mmol, 83% yield). 198-201 °C; IR ν_{max}/cm^{-1} (film): 3055, 2977, 2918, 2862, 2360, 2339, 2049, 1693, 1546, 1430, 1222, 1109, 748; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.08 (1H, d, J = 5.4 Hz), 7.54-7.42 (5H, m), 7.21 (1H, d, J = 1.9 Hz), 7.18-7.09 (2H, m), 6.44 (1H, d, J = 5.4 Hz), 4.14 (2H, q, J = 7.2 Hz), 3.90-3.70 (2H, br), 3.50-3.40 (1H, m), 3.28-3.10 (3H, m), 3.04-2.83 (2H, m), 2.54-2.43 (1H, m), 2.40-2.27 (3H, m), 1.25 (3H, t, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 159.2, 155.5, 150.4, 146.1, 139.7, 137.9, 137.7, 135.6, 134.1, 133.0, 130.2, 130.0, 129.8, 129.5, 129.1, 128.7, 126.2, 118.8, 61.3, 44.7, 30.9, 30.6, 28.9, 14.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 491.2, $C_{28}H_{28}ClN_2O_2S^+$ requires 491.2.

Ethyl 4-((4-chlorophenyl)(4-(phenylselanyl)pyridin-2-yl)methoxy)piperidine-1-carboxylate (2bl)



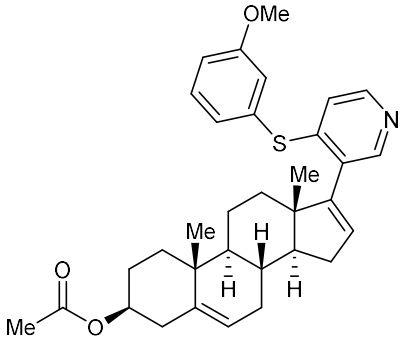
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), benzeneselenol (40 μL, 0.38 mmol), (2-((4-chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (196 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel: 30% EtOAc in toluene) afforded the *title compound* (2bl) as a clear oil (93 mg, 0.18 mmol, 70% yield). IR ν_{max}/cm^{-1} (film): 3289, 3049, 2927, 2667, 2349, 2245, 1690, 1567, 1226, 1085, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (1H, d, *J* = 5.2 Hz), 7.65-7.60 (2H, m), 7.48-7.36 (3H, m), 7.32 (1H, d, *J* = 1.5 Hz), 7.30-7.23 (4H, m), 6.96 (1H, dd, *J* = 5.3, 1.7 Hz), 5.47 (1H, s), 4.13 (2H, q, *J* = 7.2 Hz), 3.65-3.50 (3H, m), 3.25-3.14 (2H, m), 1.80-1.70 (1H, m), 1.70-1.46 (3H, m), 1.26 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7, 155.5, 148.7, 147.2, 139.8, 136.5, 133.5, 129.9, 129.5, 128.6, 128.2, 126.1, 122.5, 120.3, 80.6, 73.3, 61.3, 40.8 (rot), 31.0 (rot), 30.7, 14.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 531.2, $C_{26}H_{28}ClN_2O_3Se^+$ requires 531.1.

(1S,2R,4S,5R)-2-((R)-(2-(1H-Pyrrol-1-yl)quinolin-4-yl)(benzyloxy)methyl)-5-vinylquinuclidine (2bm)



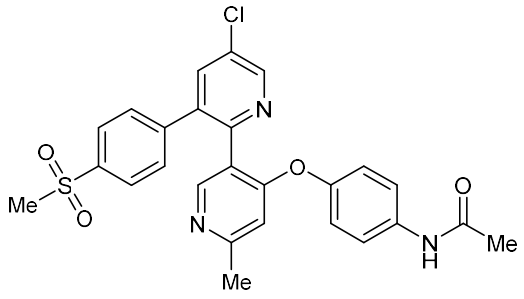
Prepared according to general procedure D using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.38 mmol), 1*H*-pyrrole (26 μL, 0.38 mmol), (4-((R)-(benzyloxy)((1S,2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-2-yl)triphenylphosphonium trifluoromethanesulfonate (199 mg, 0.25 mmol) and THF (0.5 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 80% EtOAc in hexanes) followed by another flash column (silica gel, gradient elution: 100% EtOAc to 5% NEt_3 in EtOAc) afforded the *title compound* (2bm) as white solid (61 mg, 0.14 mmol, 54% yield). mp: 70-76 °C; IR ν_{max}/cm^{-1} (film): 3149, 3064, 3030, 2932, 2862, 1635, 1599, 1479, 1357, 1256, 1066, 959, 731, 695; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09-8.02 (2H, m), 7.75-7.63 (4H, m), 7.54-7.47 (1H, m), 7.41-7.30 (5H, m), 6.40 (2H, t, J = 2.2 Hz), 5.80-5.66 (1H, m), 5.32 (1H, br), 4.99-4.85 (2H, m), 4.48 (2H, s), 3.48-3.34 (1H, m), 3.20-3.05 (2H, m), 2.77-2.58 (2H, m), 2.32-2.22 (1H, m), 1.86-1.46 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 149.7, 147.8, 141.9, 137.7, 130.0, 129.5, 128.6, 127.9, 127.8, 127.6, 125.6, 124.6, 123.1 (br), 118.5, 114.3, 111.6, 108.8 (br), 71.6, 60.8, 57.1, 43.3, 40.0, 27.9, 27.8, 22.7 (br); *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 450.3, $C_{30}H_{32}N_3O^+$ requires 450.3.

(3S,8R,9S,10R,13S,14S)-17-(4-((3-Methoxyphenyl)thio)pyridin-3-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (2bn)



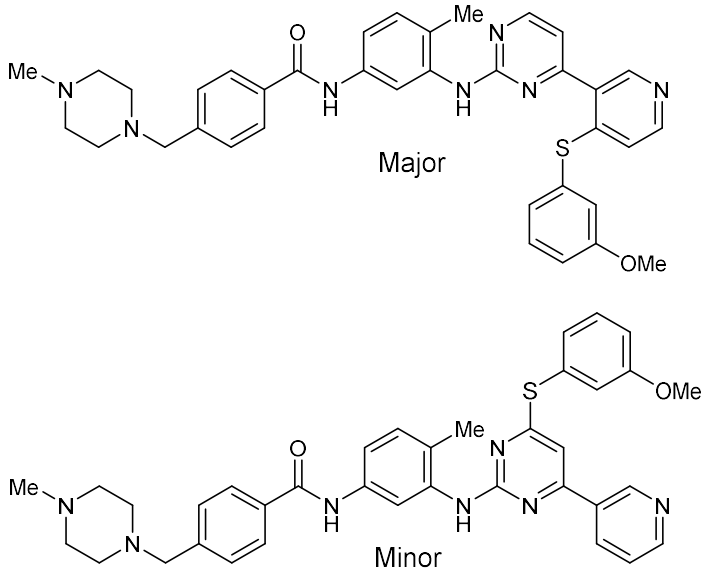
Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 11 mg, 0.28 mmol), 3-methoxybenzenethiol (34 μL, 0.28 mmol), (3-((3S,8R,9S,10R,13S,14S)-3-acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (120 mg, 0.15 mmol) and THF (0.3 mL). Flash column chromatography (basic alumina, gradient elution: 20% EtOAc in hexanes to 30% EtOAc in hexanes) afforded the *title compound* (2bn) as a clear oil (49 mg, 0.092 mmol, 61% yield). IR ν_{max}/cm^{-1} (film): 3246, 3032, 2935, 2797, 2361, 2341, 2162, 1655, 1571, 1446, 1402, 1282, 1162, 1010, 814, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (1H, s), 8.14 (1H, d, *J* = 5.0 Hz), 7.35 (1H, t, *J* = 8.0 Hz), 7.11-7.07 (1H, m), 7.05-7.02 (1H, m), 7.00-6.95 (1H, m), 6.65 (1H, d, *J* = 5.3 Hz), 5.97-5.93 (1H, m), 5.43 (1H, d, *J* = 4.9 Hz), 4.68-4.57 (1H, m), 3.82 (3H, s), 2.42-2.31 (3H, m), 2.20-2.00 (6H, m), 1.92-1.81 (2H, m), 1.77-1.52 (7H, m), 1.15-1.00 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 160.4, 157.5, 155.0, 150.3, 149.6, 148.2, 147.7, 140.0, 132.9, 131.8, 130.7, 127.5, 122.3, 120.3, 115.4, 73.9, 56.9, 55.4, 50.4, 49.7, 38.1, 36.9, 36.8, 34.7, 32.3, 31.6, 30.7, 27.7, 21.4, 20.7, 19.3, 16.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 530.3, $C_{33}H_{40}NO_3S^+$ requires 530.3.

N-(4-((5-Chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)oxy)phenyl)acetamide (2bo)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 15 mg, 0.375 mmol), N-(4-hydroxyphenyl)acetamide (57 mg, 0.38 mmol), 15-crown-5 (74 μL, 0.38 mmol), (5-chloro-6'-methyl-3-(4-(methylsulfonyl)phenyl)-[2,3'-bipyridin]-4'-yl)triphenylphosphonium trifluoromethanesulfonate (192 mg, 0.25 mmol) and DME (0.5 mL). Flash column chromatography (silica gel, gradient elution: 3% MeOH in DCM to 5% MeOH in DCM) afforded the *title compound* (2bo) as a clear oil (49 mg, 0.12 mmol, 48% yield). IR ν_{max}/cm^{-1} (film): 3317, 3062, 2929, 2252, 1980, 1676, 1599, 1504, 1313, 1151, 904, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (1H, d, *J* = 2.3 Hz), 8.66 (1H, s), 7.84-7.79 (2H, m), 7.72 (1H, d, *J* = 2.3 Hz), 7.41-7.33 (4H, m), 7.20-7.14 (1H, br), 6.24-6.18 (3H, m), 3.09 (3H, s), 2.43 (3H, s), 2.17 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.8, 162.6, 160.0, 150.0, 148.7, 148.4, 148.0, 144.1, 140.2, 137.3, 136.2, 132.0, 129.6, 127.7, 123.1, 121.6, 120.4, 109.5, 69.1, 44.3, 24.3, 23.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 508.1, $C_{26}H_{23}ClN_3O_4S^+$ requires 508.1.

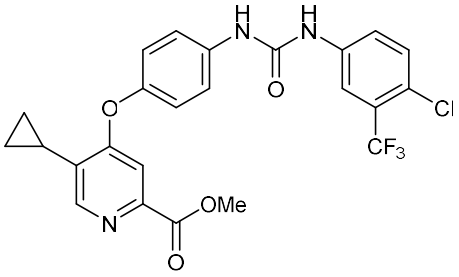
N-(3-((4-(4-((3-Methoxyphenyl)thio)pyridin-3-yl)pyrimidin-2-yl)amino)-4-methylphenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide (2bp)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 6 mg, 0.15 mmol), 3-methoxybenzenethiol (19 μL, 0.15 mmol), (3-(2-((2-methyl-5-(4-((4-methylpiperazin-1-yl)methyl)benzamido)phenyl)amino)pyrimidin-4-yl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (90 mg, 0.10 mmol) and THF (0.2 mL). Flash column chromatography (silica gel was packed with hexanes and neutralized with NEt_3: 4% MeOH in DCM) afforded the *title compound* (2bp) as a yellow solid (40 mg, 0.063 mmol, 57% yield, 6% regioisomer) mp: 78-84 °C; IR ν_{max}/cm^{-1} (film): 3246, 3032, 2935, 2797, 2361, 2341, 2162, 1655, 1571, 1446, 1402, 1282, 1162, 1010, 814, 726; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, s), 8.56 (1H, d, *J* = 5.1 Hz), 8.35 (1H, d, *J* = 2.1 Hz), 8.29 (1H, d, *J* = 5.5 Hz), 7.86 (1H, s), 7.77 (2H, d, *J* = 8.2 Hz), 7.58 (1H, dd, *J* = 8.1, 1.6 Hz), 7.41 (2H, d, *J* = 8.2 Hz), 7.31-7.19 (3H, m), 7.09 (1H, d, *J* = 5.1 Hz), 7.07-7.04 (1H, m), 7.02-7.00 (1H, m), 6.95 (1H, dd, *J* = 8.3, 2.4 Hz), 6.78 (1H, d, *J* = 5.5 Hz), 3.75 (3H, s), 3.56 (2H, s), 2.60-2.41 (8H, br), 2.35 (3H, s), 2.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 163.6, 160.5, 160.0, 158.8, 150.2, 149.8, 149.5, 142.5, 137.4, 136.6, 133.8, 131.4, 131.0, 130.9, 130.8, 129.2, 127.6, 127.0, 124.5, 121.3, 120.2, 116.0, 115.8, 113.6, 111.4, 62.5, 55.4,

55.1, 53.1, 46.0, 17.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 632.4, $C_{36}H_{38}N_7O_2S^+$ requires 632.3.

Methyl 4-(4-(3-(4-chloro-3-(trifluoromethyl)phenyl)ureido)phenoxy)-5-cyclopropylpicolinate (2bq)



Prepared according to general procedure C using sodium hydride (60% dispersion in mineral oil, 11 mg, 0.275 mmol), 1-(4-Chloro-3-(trifluoromethyl)phenyl)-3-(4-hydroxyphenyl)urea (67.1 mg, 0.203 mmol), 15-Crown-5 (40.3 μL, 0.203 mmol), (5-cyclopropyl-2-(methoxycarbonyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (79.3 mg, 0.14 mmol) and DME (0.27 mL). Flash column chromatography (silica: 70% EtOAc in hexanes) followed by a second flash column (silica, gradient elution: 85% EtOAc, 5% NEt_3 in hexanes to 100% EtOAc) afforded the *title compound* (2bq) as an off-white amorphous solid (28 mg, 0.055 mmol, 40% yield). IR ν_{max}/cm^{-1} (film): 3350, 3310, 3125, 3082, 2957, 1731, 1710, 1599, 1552, 1504, 1482, 1418, 1301, 1229, 1203, 1173, 1110, 984, 831, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.24 (1H, s), 9.00 (1H, s), 8.28 (1H, s), 8.12 (1H, d, *J* = 2.2 Hz), 7.69-7.55 (4H, m), 7.20-7.13 (3H, m), 3.78 (3H, s), 2.27-2.18 (1H, m), 1.12-1.05 (2H, m), 1.00-0.94 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 164.8, 163.6, 152.5, 148.4, 147.7, 146.3, 139.3, 136.8, 132.0, 131.8, 126.7 (q, *J* = 30.2 Hz), 123.1, 122.8 (q, *J* = 272.2 Hz), 122.3 (q, *J* = 1.8 Hz), 121.2, 120.6, 116.8 (q, *J* = 5.4 Hz), 110.0, 52.3, 8.3, 8.0; ^{19}F NMR (365 MHz, $(CD_3)_2SO$) δ: –62.76 ; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 506.1, $C_{24}H_{20}ClF_3N_3O_4^+$ requires 506.1.

8. References

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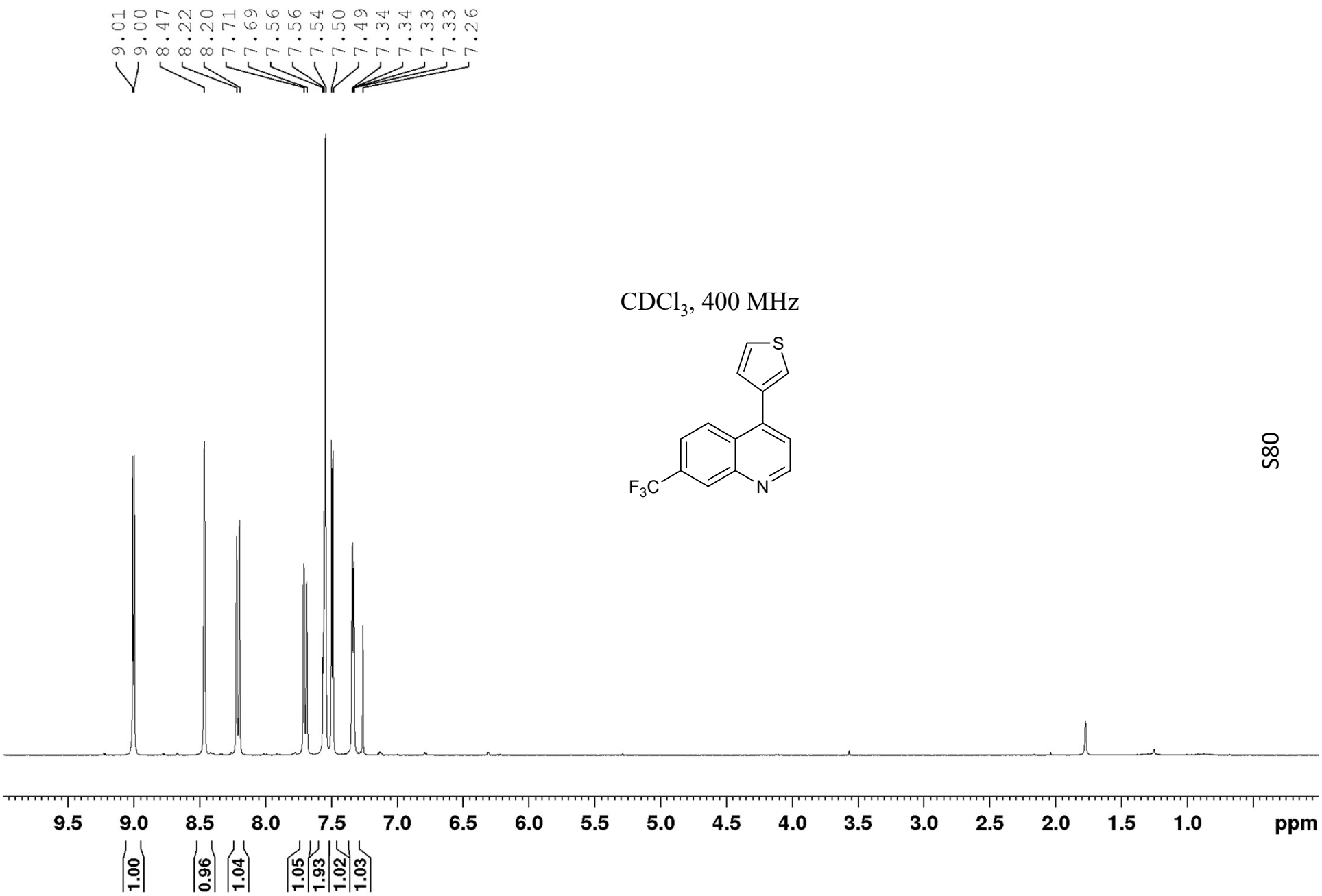
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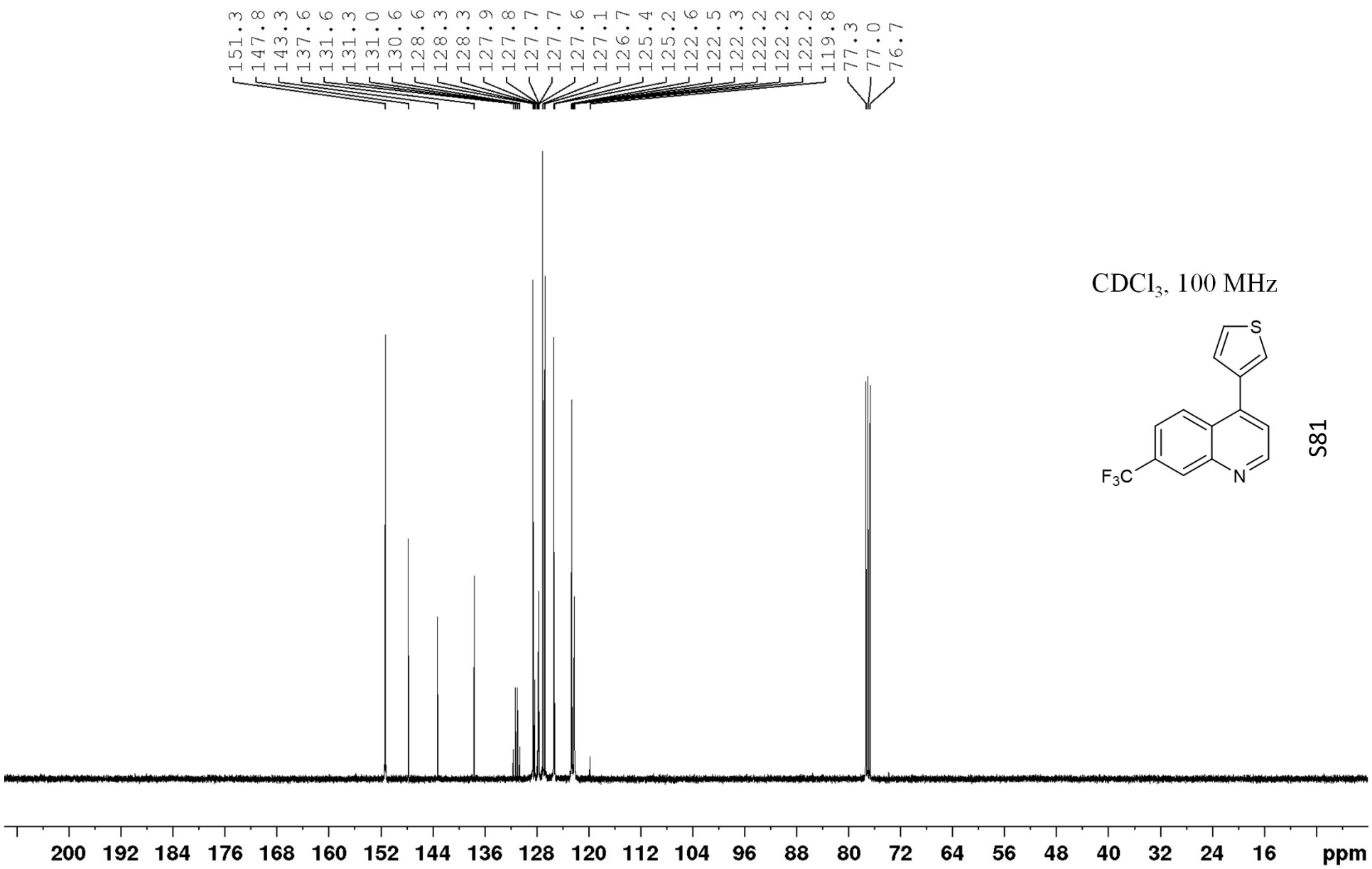
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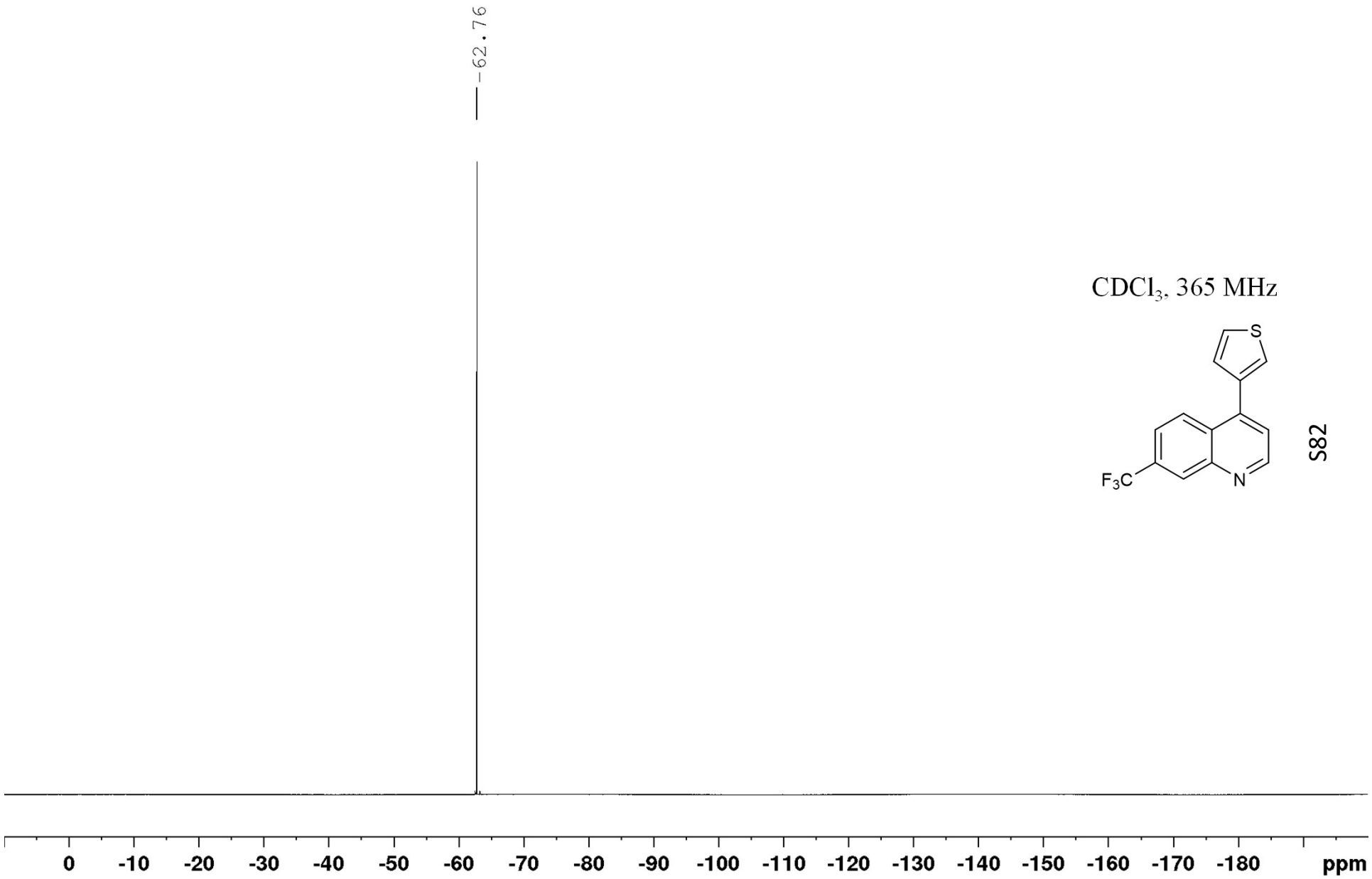
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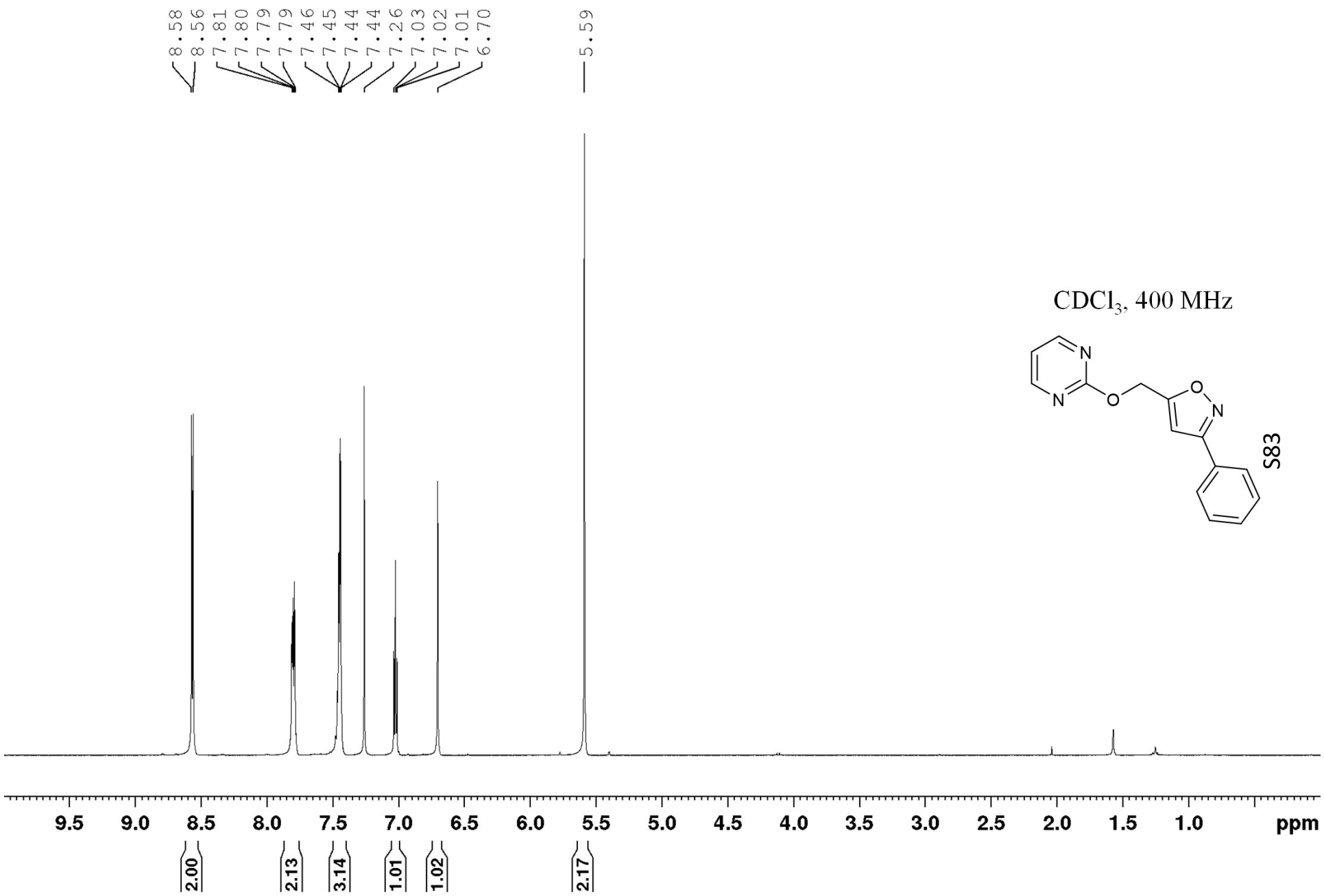
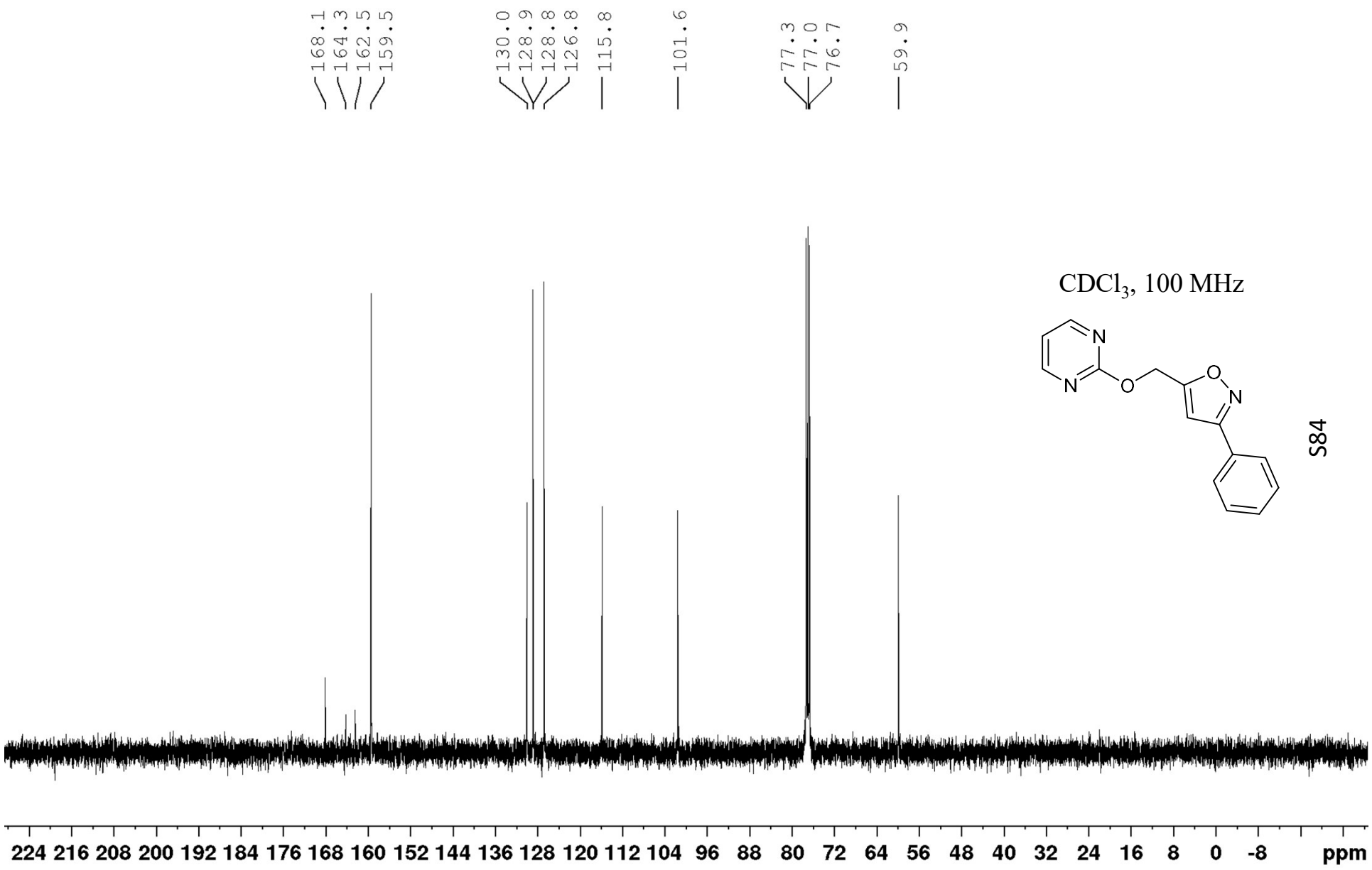
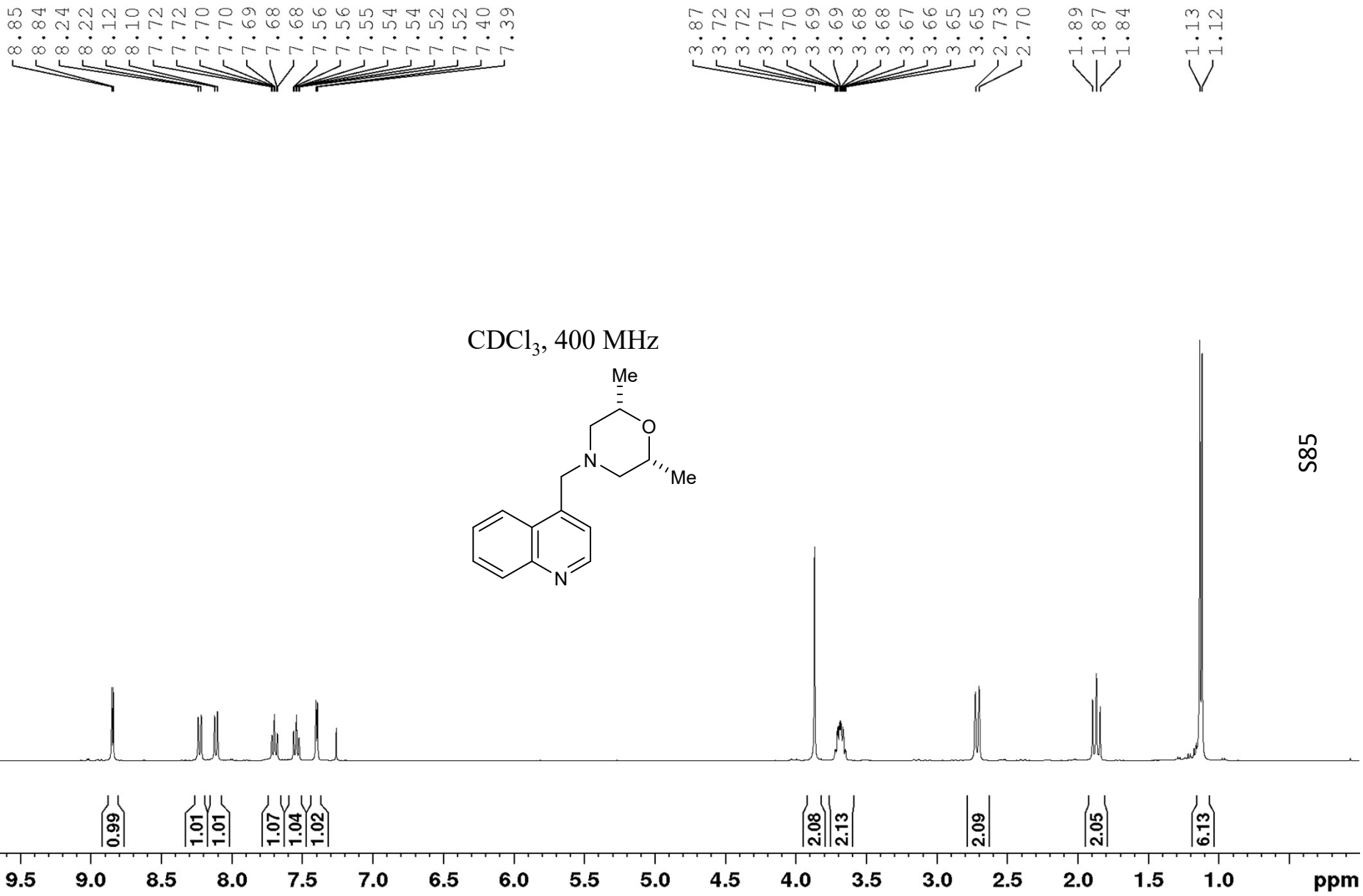
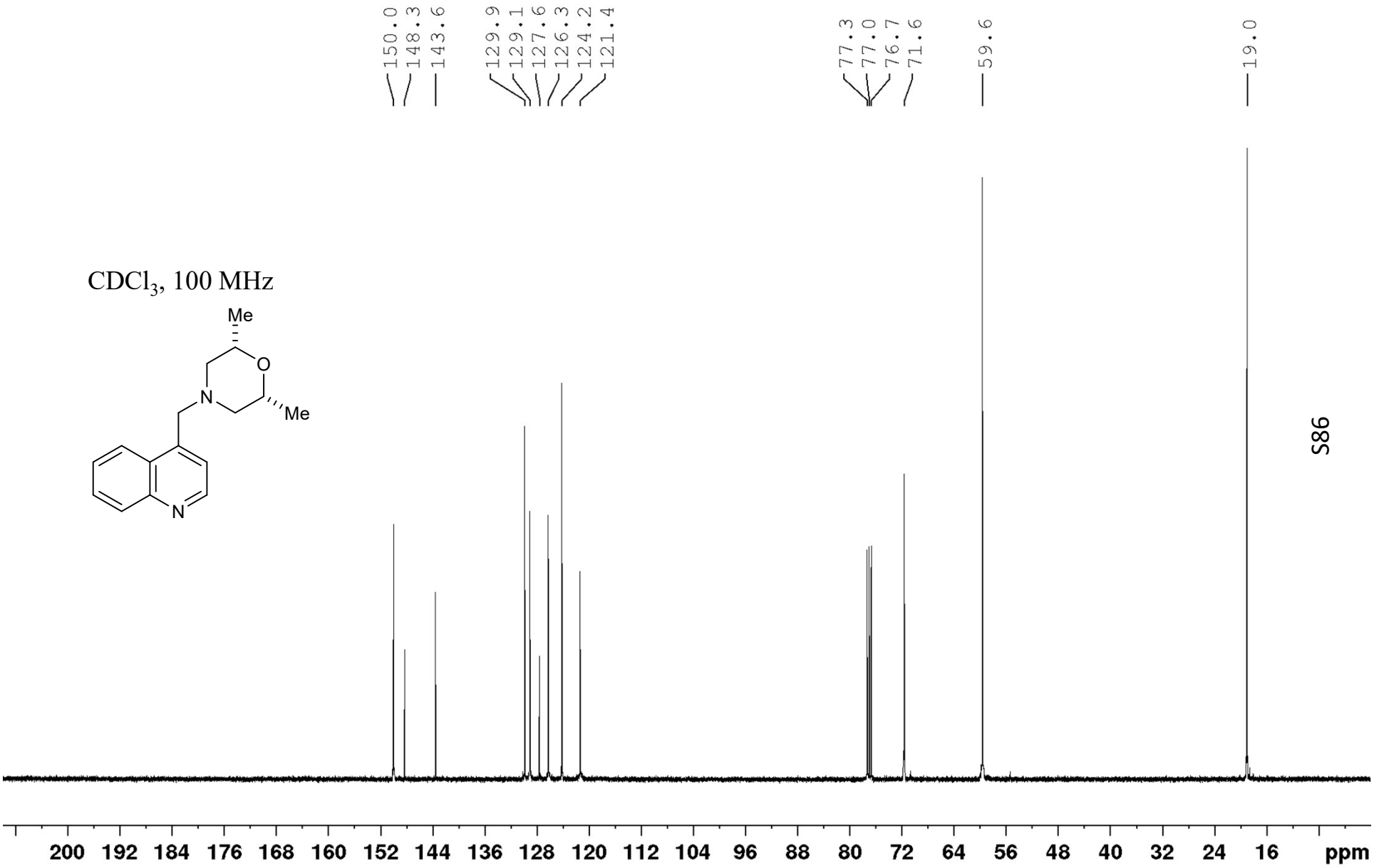
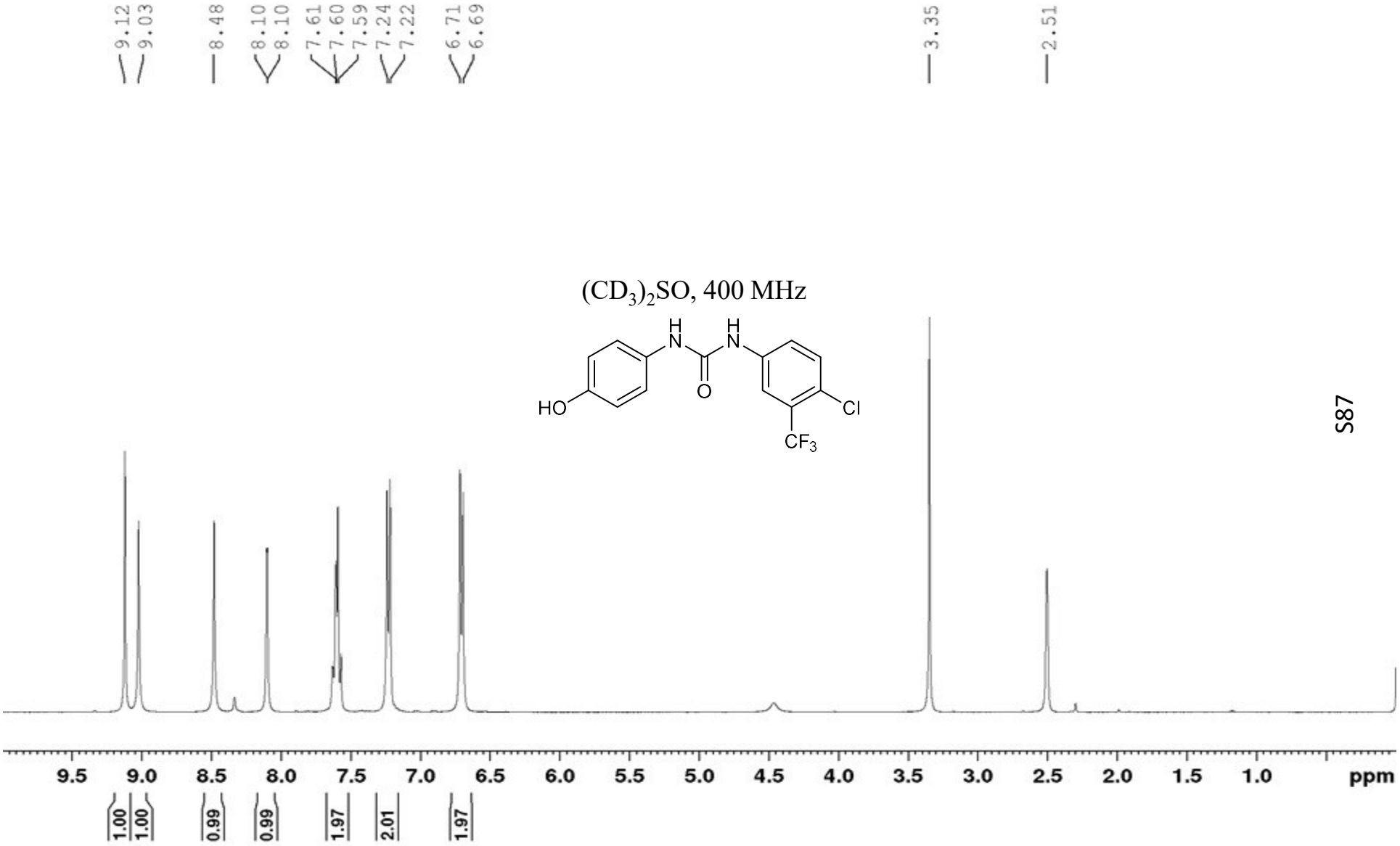
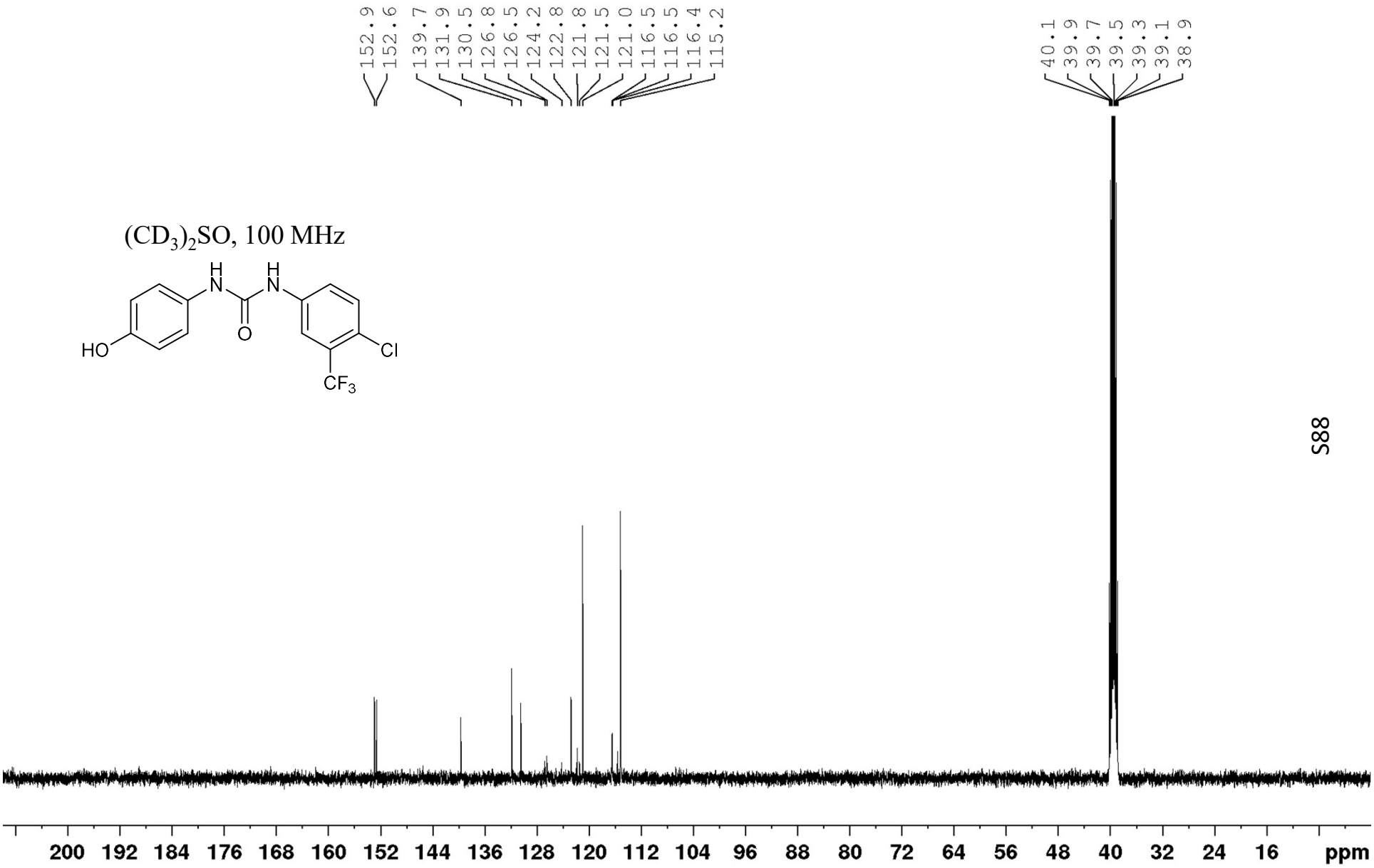

8.58
8.56
7.81
7.80
7.79
7.79
7.46
7.45
7.44
7.44
7.26
7.03
7.02
7.01
6.70
5.59
CDCl3, 400 MHz
N
N
O
O
N
S83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.13
3.14
1.01
1.02
2.17

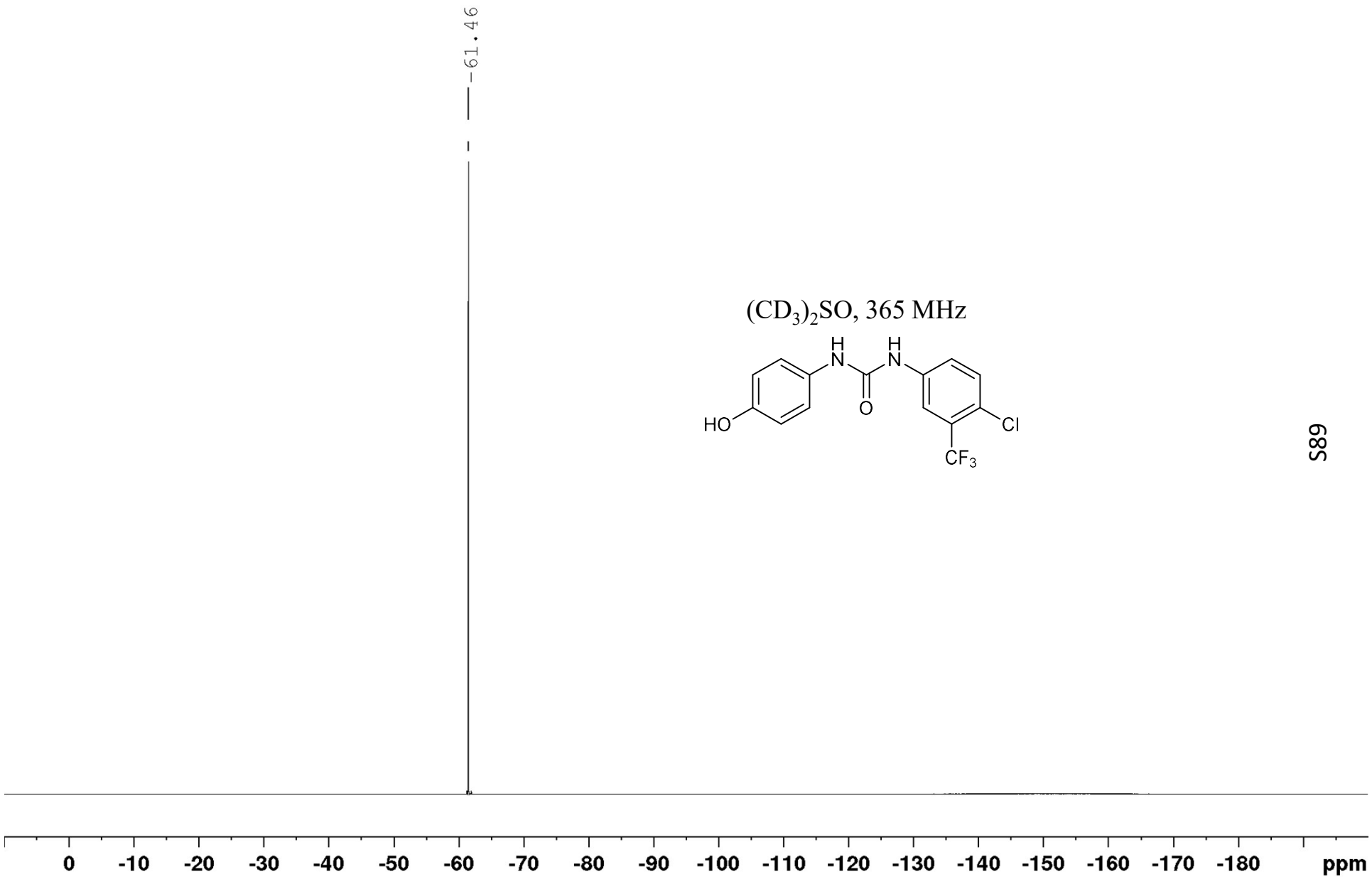

168.1
164.3
162.5
159.5
130.0
128.9
128.8
126.8
115.8
101.6
77.3
77.0
76.7
59.9
CDCl3, 100 MHz
N
N
O
O
N
224 216 208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8 ppm

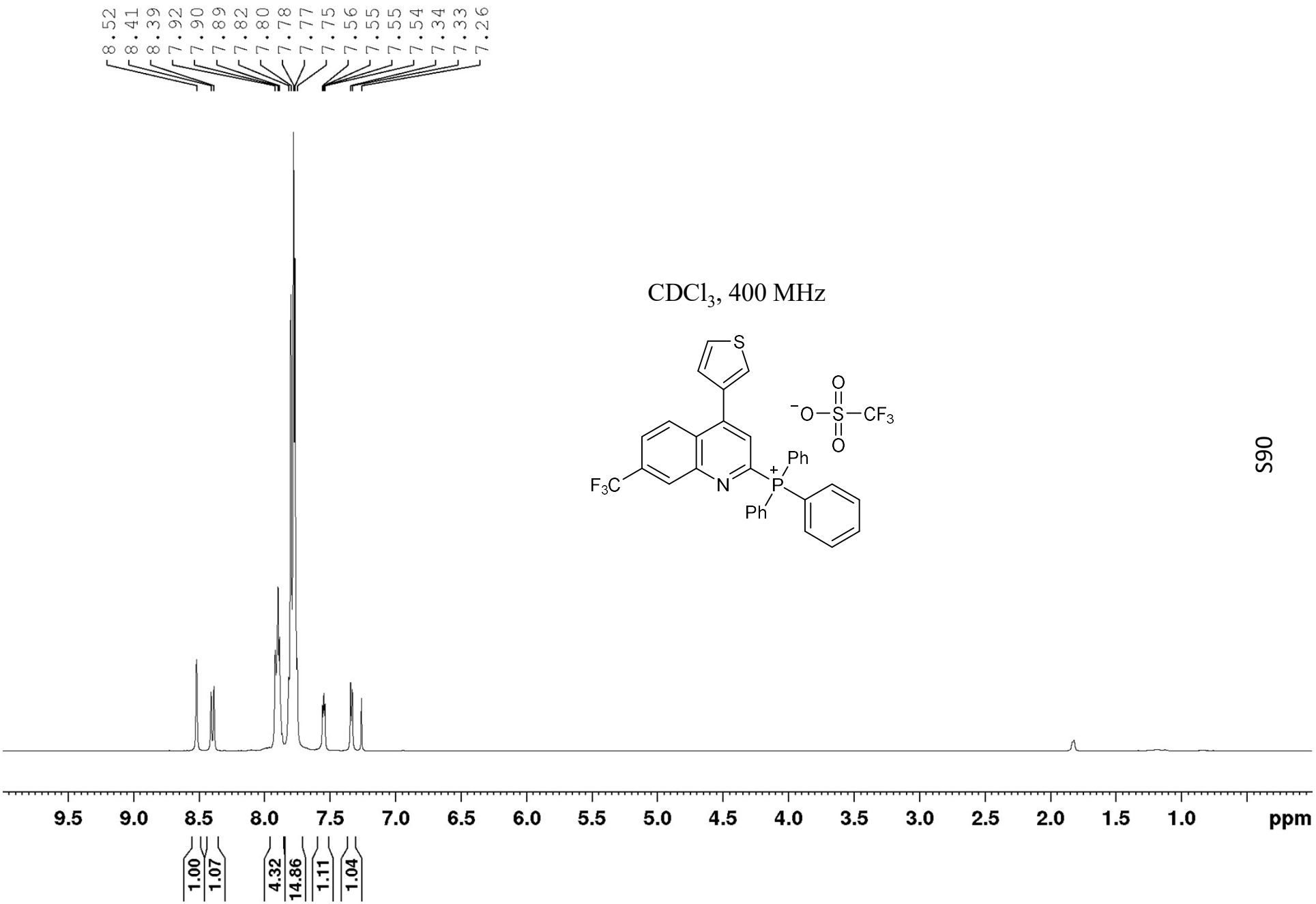

8.85
8.84
8.24
8.22
8.12
8.10
7.72
7.72
7.70
7.70
7.69
7.68
7.68
7.56
7.56
7.55
7.54
7.54
7.52
7.52
7.40
7.39
3.87
3.72
3.72
3.71
3.70
3.69
3.69
3.68
3.68
3.67
3.66
3.65
3.65
2.73
2.70
1.89
1.87
1.84
1.13
1.12
CDCl3, 400 MHz
Me
O
N
Me
N
S85
0.99
1.01
1.01
1.07
1.04
1.02
2.08
2.13
2.09
2.05
6.13
9.5
9.0
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
ppm

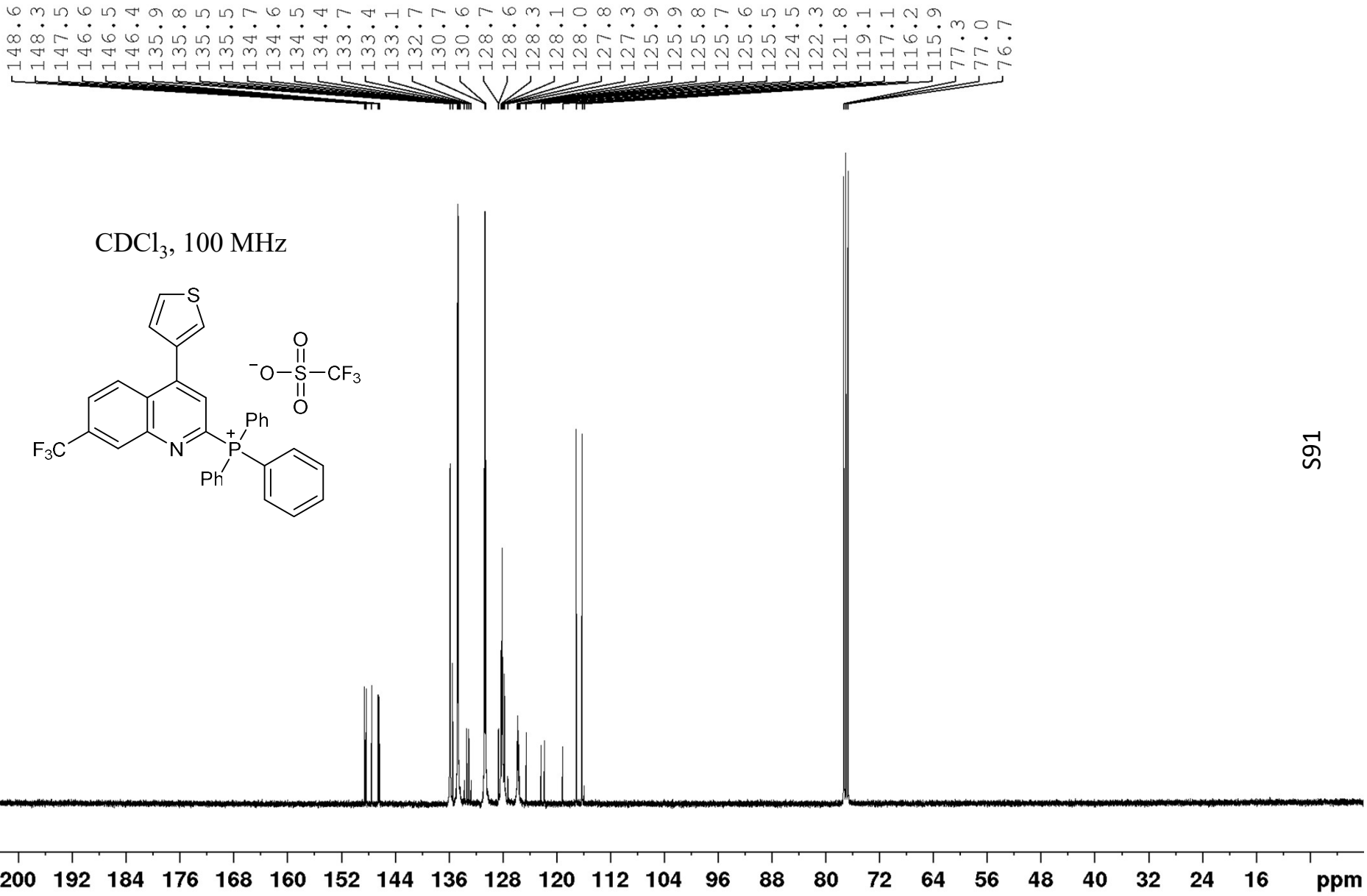

150.0
148.3
143.6
129.9
129.1
127.6
126.3
124.2
121.4
77.3
77.0
76.7
71.6
59.6
19.0
CDCl3, 100 MHz
Me
O
N
Me
N
S86
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

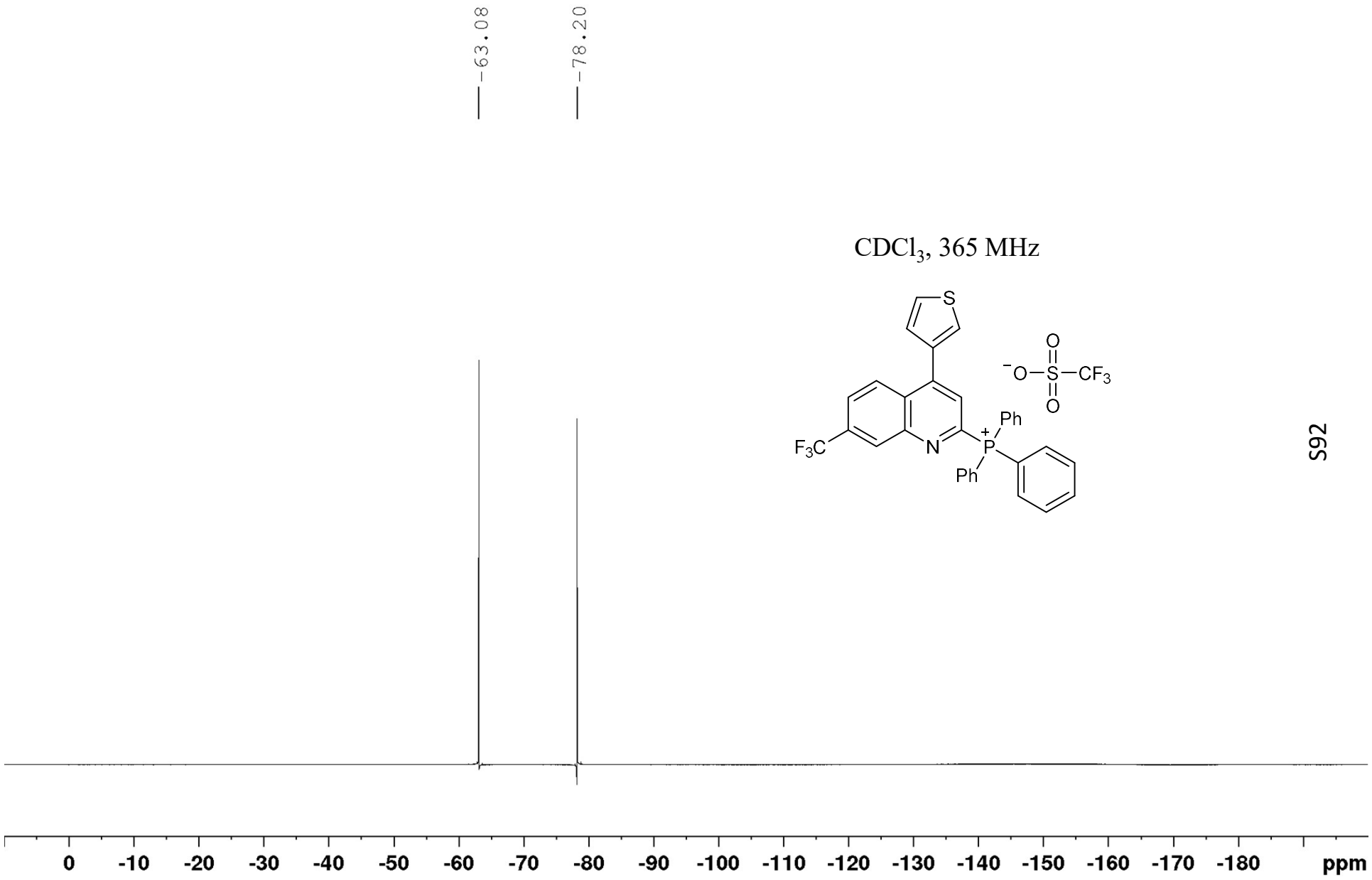

9.12
9.03
8.48
8.10
8.10
7.61
7.60
7.59
7.24
7.22
6.71
6.69
3.35
2.51
(CD3)2SO, 400 MHz
HO
H
N
O
H
N
Cl
CF3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
0.99
0.99
1.97
2.01
1.97


152.9
152.6
139.7
131.9
130.5
126.8
126.5
124.2
122.8
121.8
121.5
121.0
116.5
116.5
116.4
115.2
40.1
39.9
39.7
39.5
39.3
39.1
38.9
(CD3)2SO, 100 MHz
HO
H
N
O
H
N
Cl
CF3
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

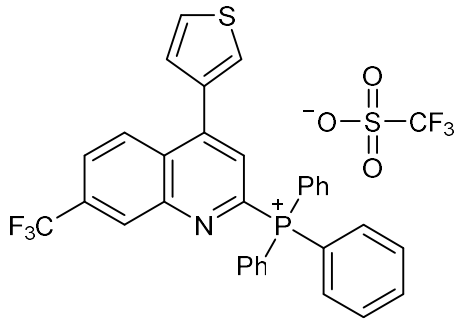

-61.46
(CD3)2SO, 365 MHz
HO
H
N
O
H
N
Cl
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


8.52
8.41
8.39
7.92
7.90
7.89
7.82
7.80
7.78
7.77
7.75
7.56
7.55
7.55
7.54
7.34
7.33
7.26
CDCl3, 400 MHz
S
O
O
O
CF3
Ph
Ph
F3C
N
P
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
1.00
1.07
4.32
14.86
1.11
1.04


148.6
148.3
147.5
146.6
146.5
146.4
135.9
135.8
135.5
135.5
134.7
134.6
134.5
134.4
133.7
133.4
133.1
132.7
130.7
130.6
128.7
128.6
128.3
128.1
128.0
127.8
127.3
125.9
125.9
125.8
125.7
125.6
125.5
124.5
122.3
121.8
119.1
117.1
116.2
115.9
77.3
77.0
76.7
CDCl3, 100 MHz
S
O
O
S
CF3
Ph
Ph
F3C
N
P
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-63.08
-78.20
CDCl3, 365 MHz
S
O
O
O
S
CF3
Ph
P
Ph
N
F3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

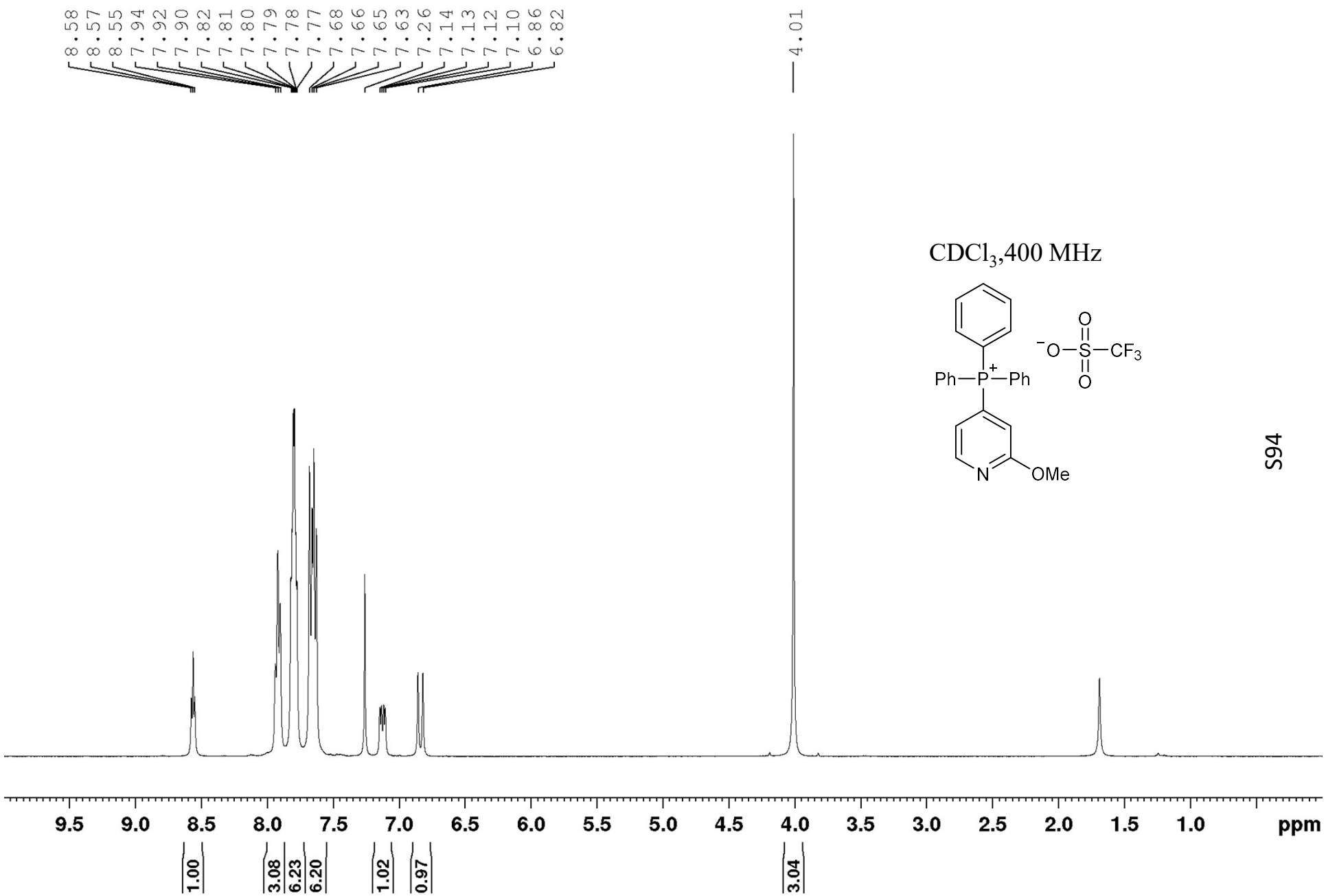
$CDCl_3$, 162 MHz

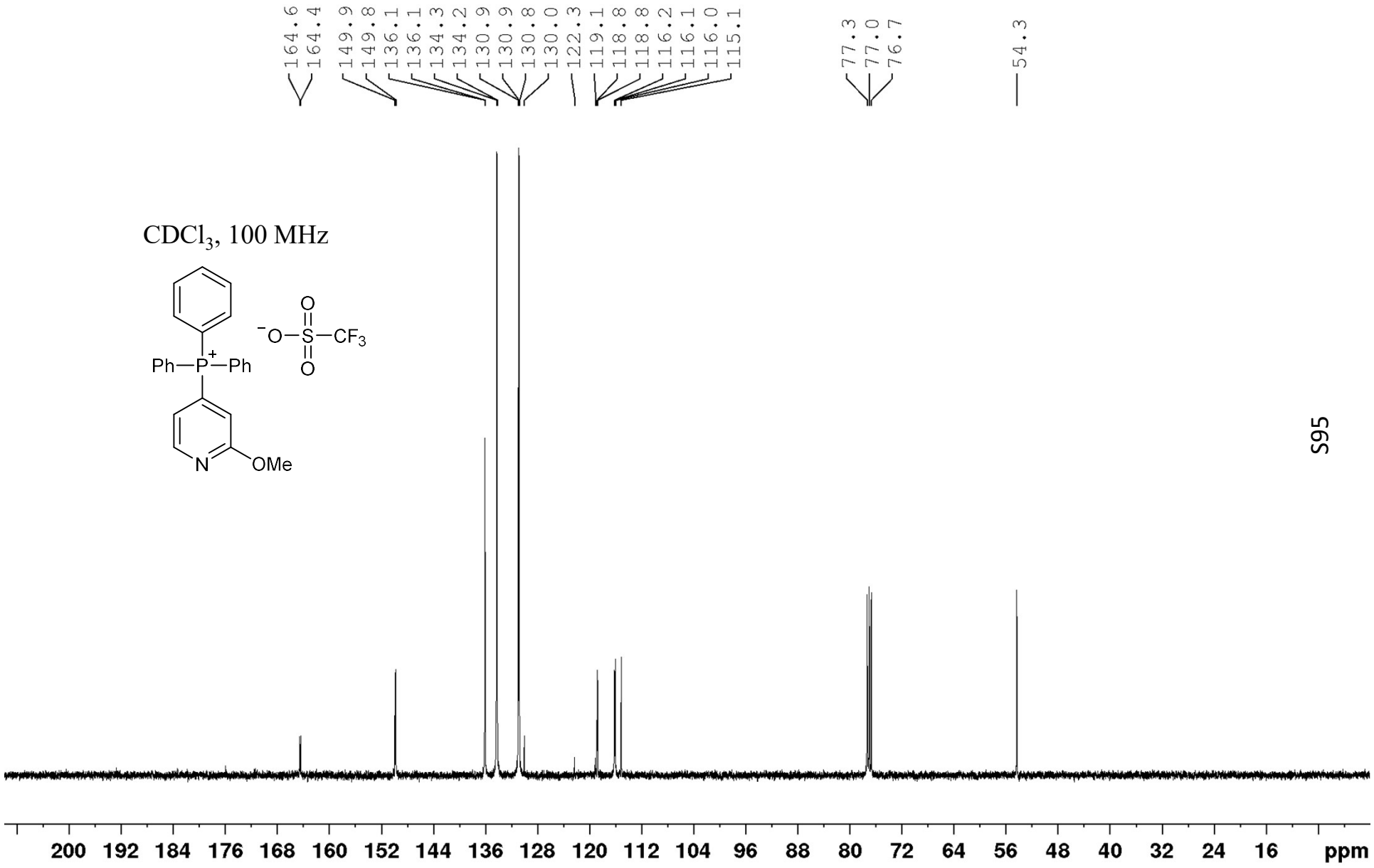


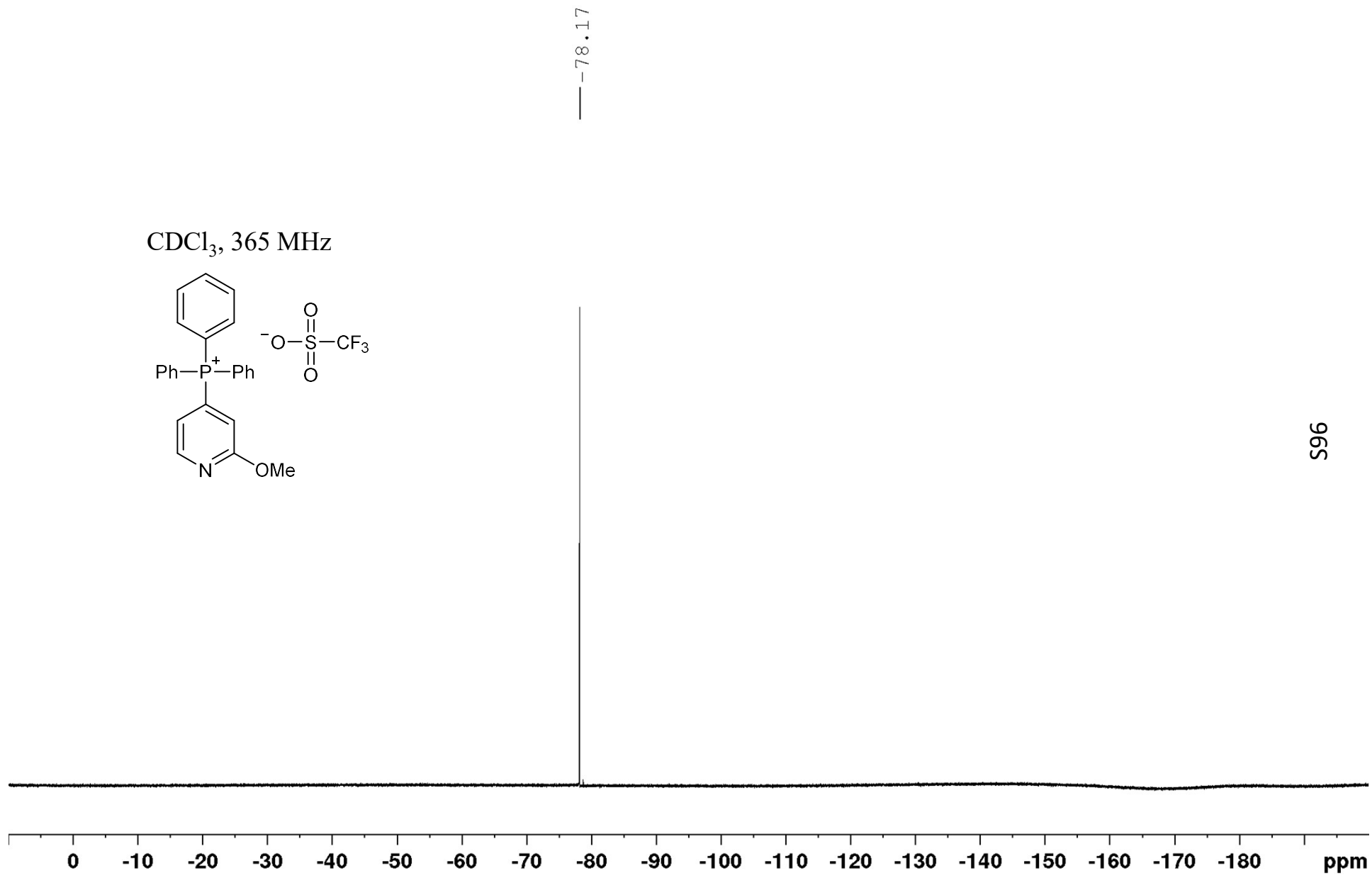
15.62

S93

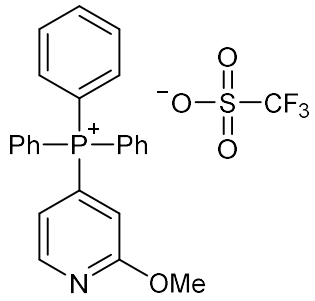
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.58
8.57
8.55
7.94
7.92
7.90
7.82
7.81
7.80
7.79
7.78
7.77
7.68
7.66
7.65
7.63
7.26
7.14
7.13
7.12
7.10
6.86
6.82
4.01
CDCl3,400 MHz
Ph—P+—Ph
O
O—S—CF3
O
N
OMe
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
1.00
3.08
6.23
6.20
1.02
0.97
3.04


164.6
164.4
149.9
149.8
136.1
136.1
134.3
134.2
130.9
130.9
130.8
130.0
122.3
119.1
118.8
118.8
116.2
116.1
116.0
115.1
77.3
77.0
76.7
54.3
CDCl3, 100 MHz
Ph—P+—Ph
−O—S—CF3
N
OMe
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

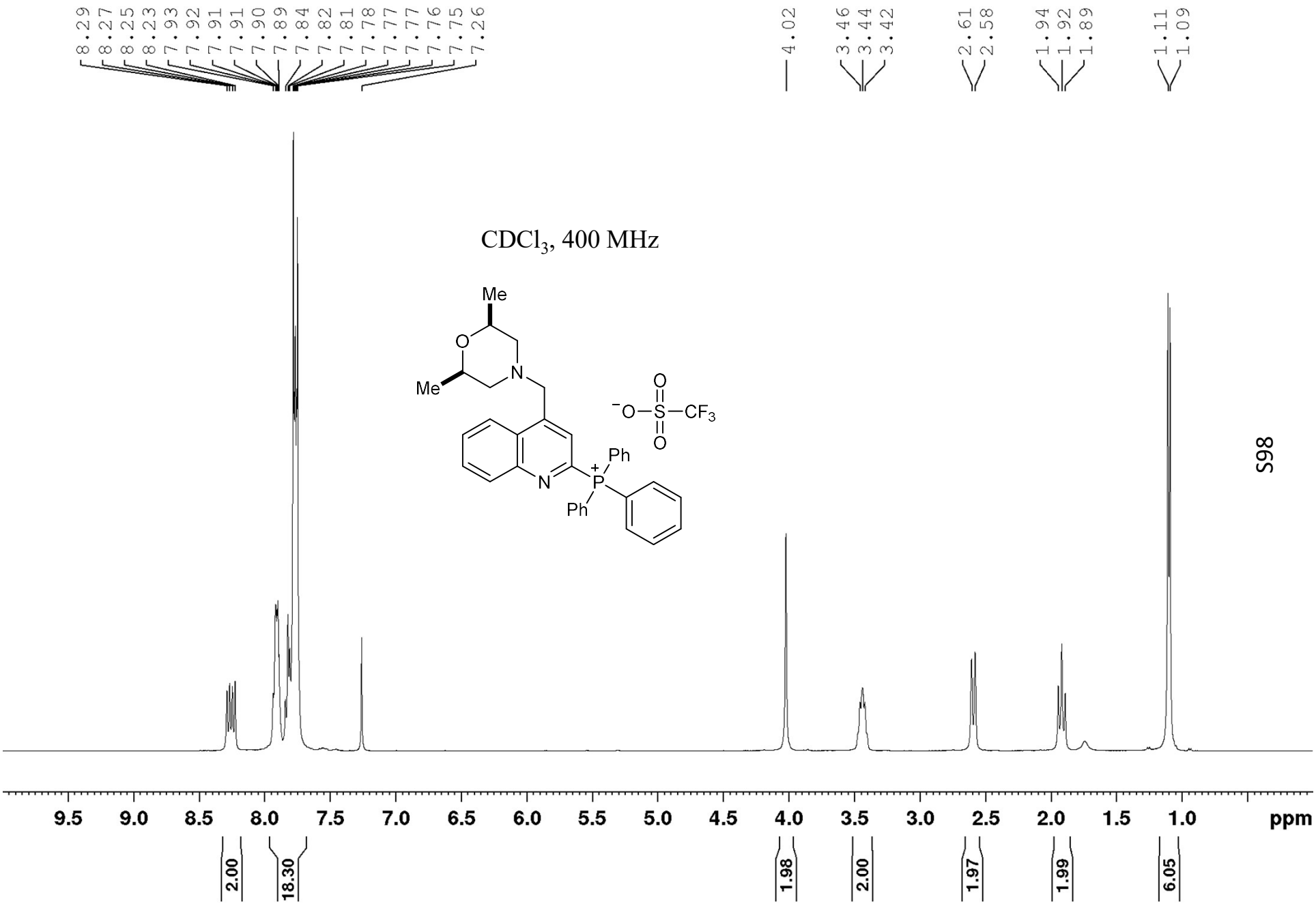

-78.17
CDCl3, 365 MHz
Ph—P+—Ph
O
O—S—CF3
O
N
OMe
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

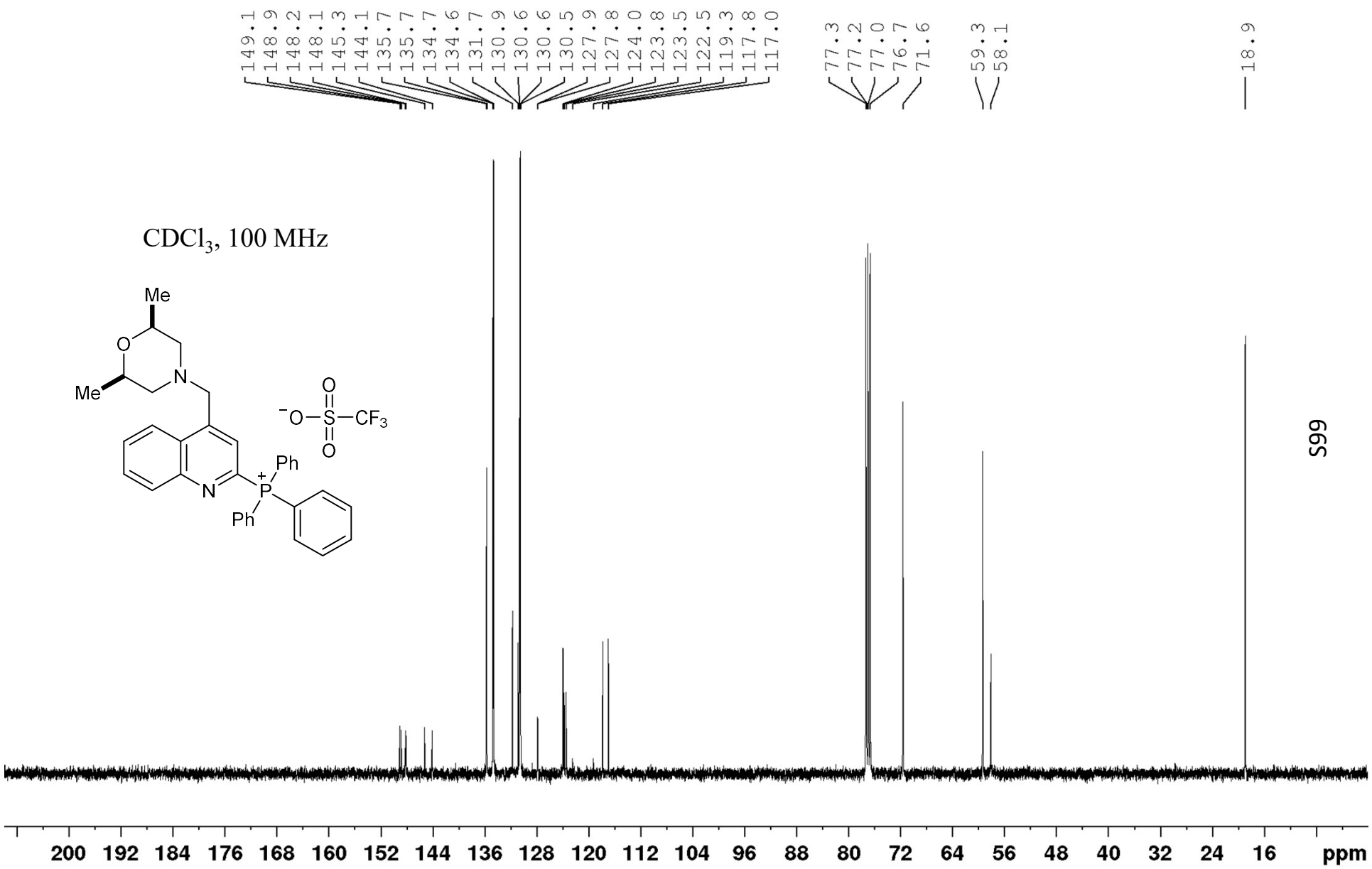
$CDCl_3$, 162 MHz

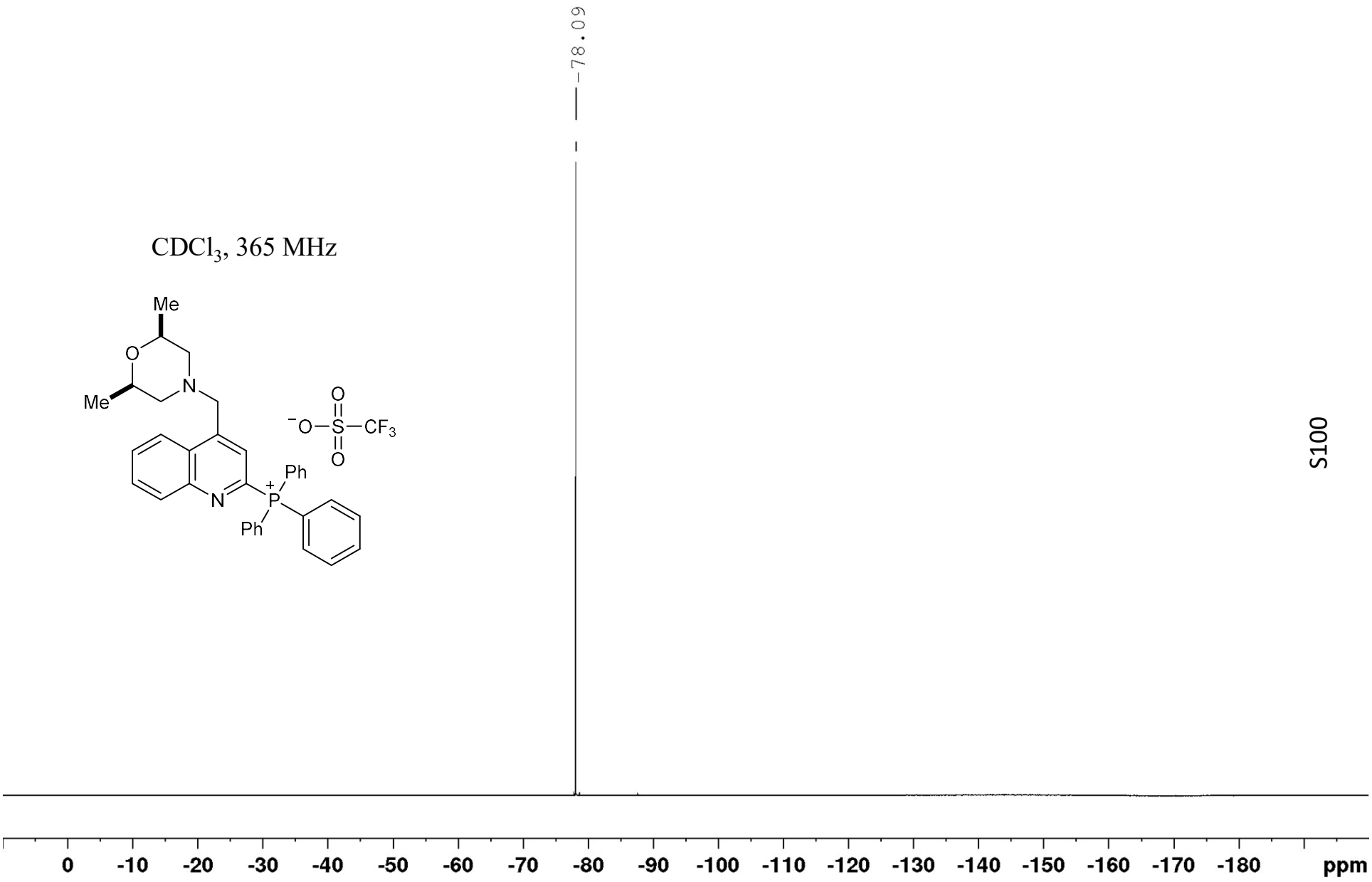


22.37

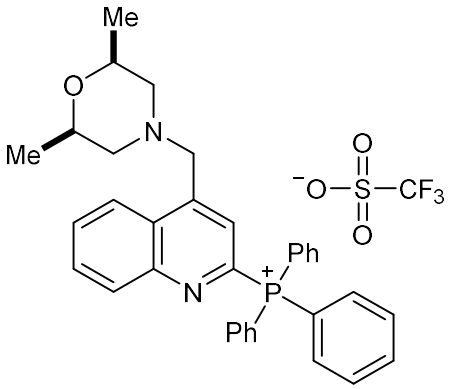
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


8.29
8.27
8.25
8.23
7.93
7.92
7.91
7.91
7.90
7.89
7.84
7.82
7.81
7.78
7.77
7.77
7.76
7.75
7.26
4.02
3.46
3.44
3.42
2.61
2.58
1.94
1.92
1.89
1.11
1.09
CDCl3, 400 MHz
Me
O
N
Me
O
O
−O−S−CF3
O
Ph
+
P
N
Ph
S98
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
2.00
18.30
1.98
2.00
1.97
1.99
6.05

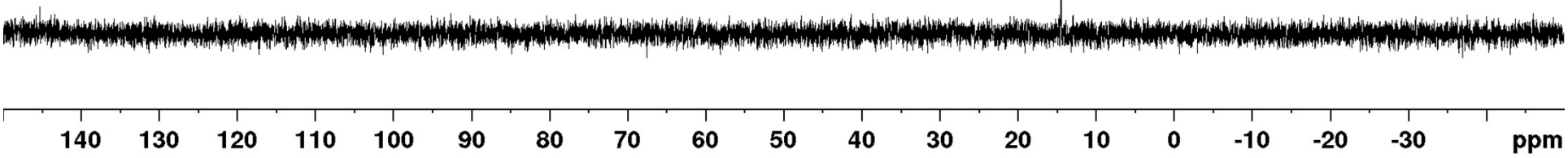

149.1
148.9
148.2
148.1
145.3
144.1
135.7
135.7
134.7
134.6
131.7
130.9
130.6
130.6
130.5
127.9
127.8
124.0
123.8
123.5
122.5
119.3
117.8
117.0
77.3
77.2
77.0
76.7
71.6
59.3
58.1
18.9
CDCl3, 100 MHz
Me
O
N
Me
O
O
−O−S−CF3
O
Ph
N
P+
Ph
Ph
S99
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

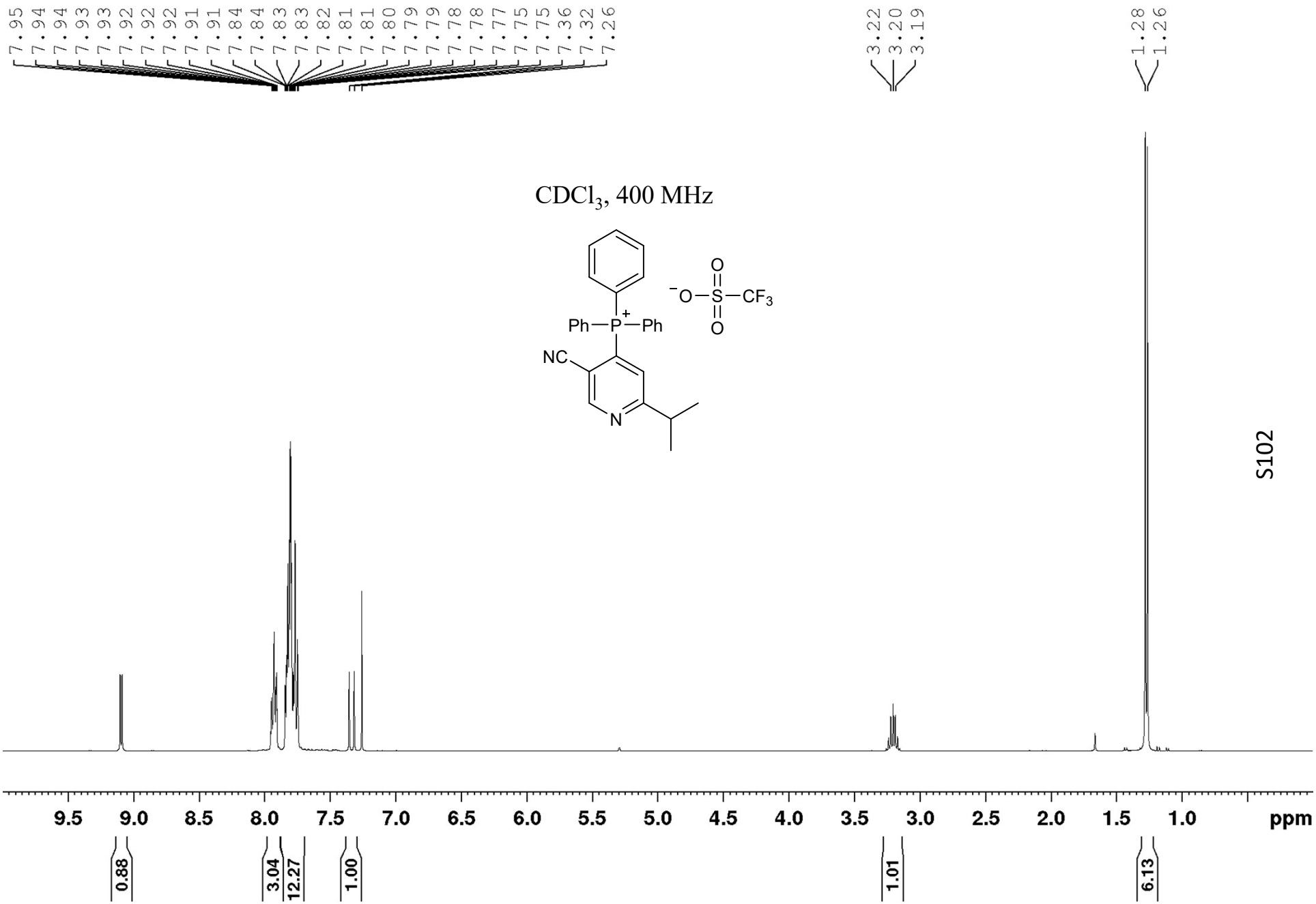

-78.09
CDCl3, 365 MHz
Me
O
Me
N
O
O
S
CF3
O
Ph
N
P
Ph
Ph
S100
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

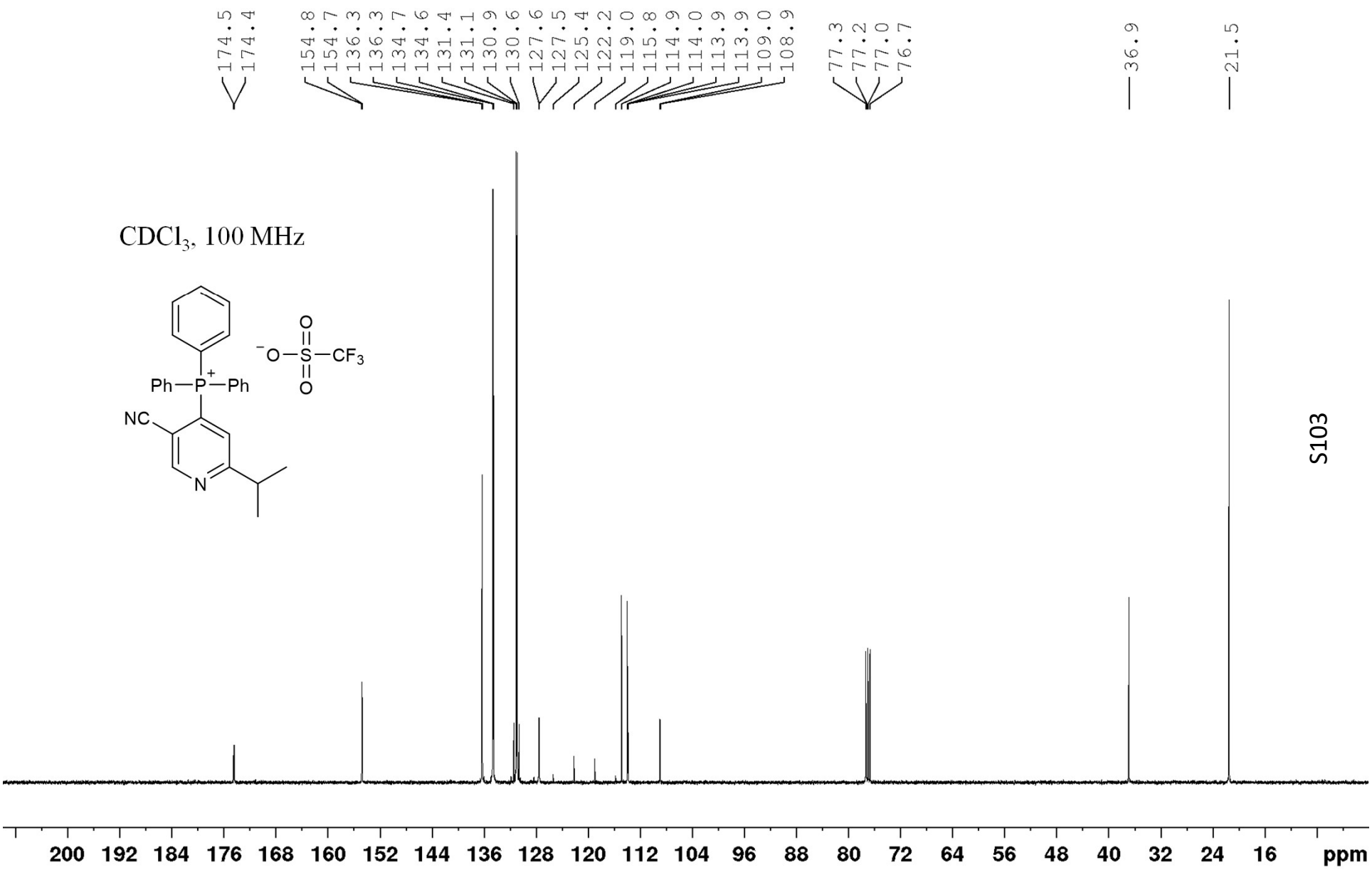
$CDCl_3$, 162 MHz

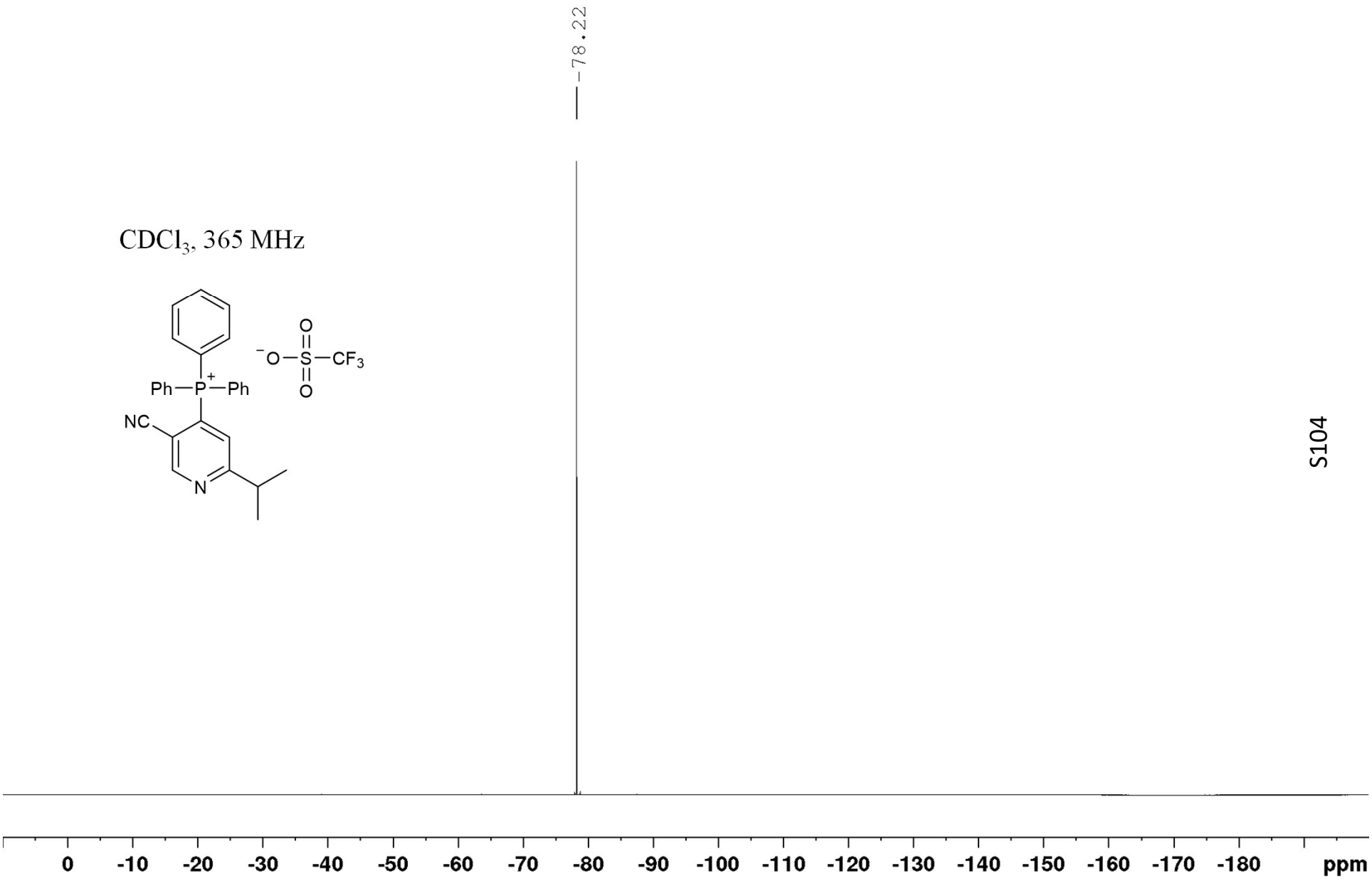


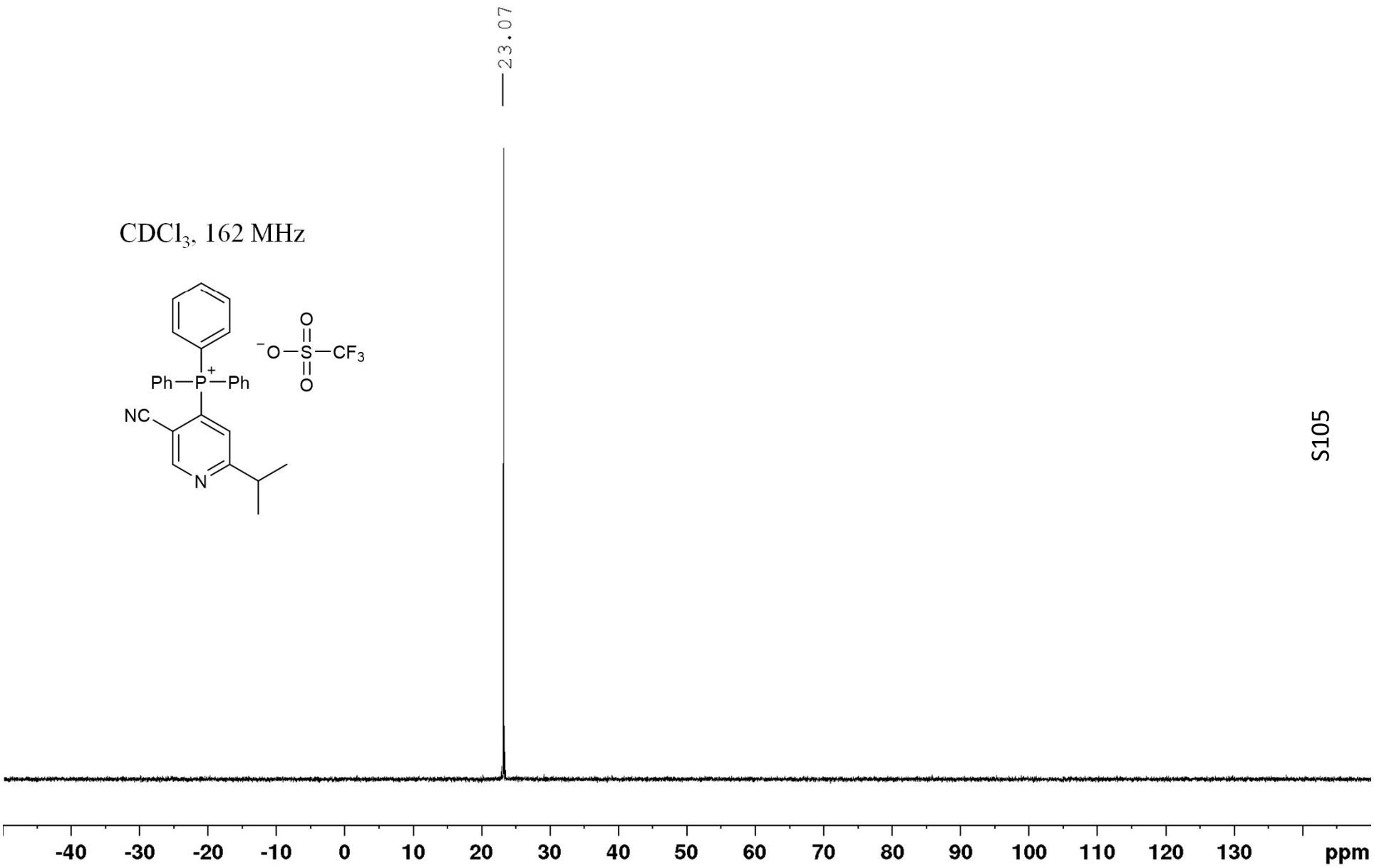
14.47

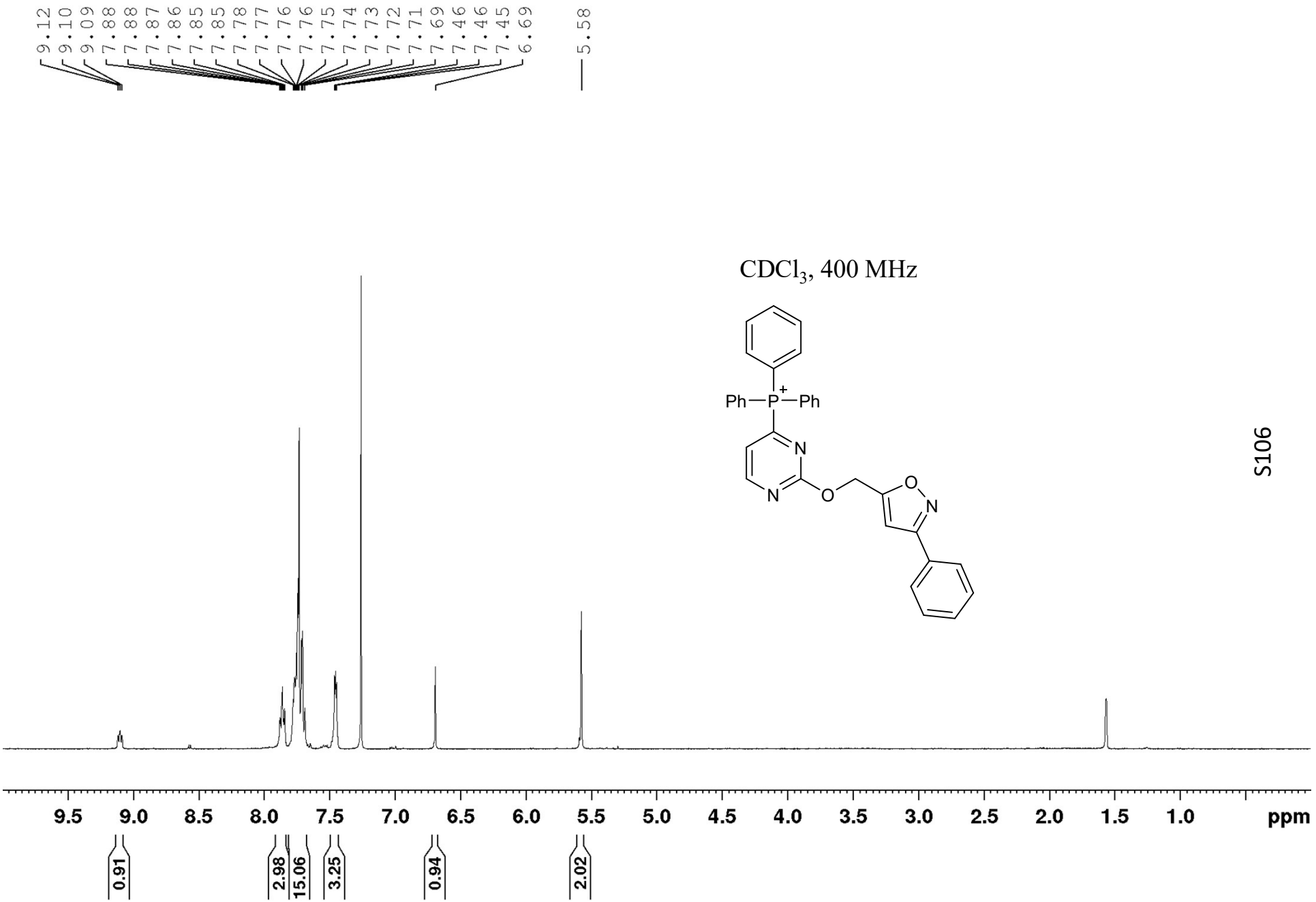


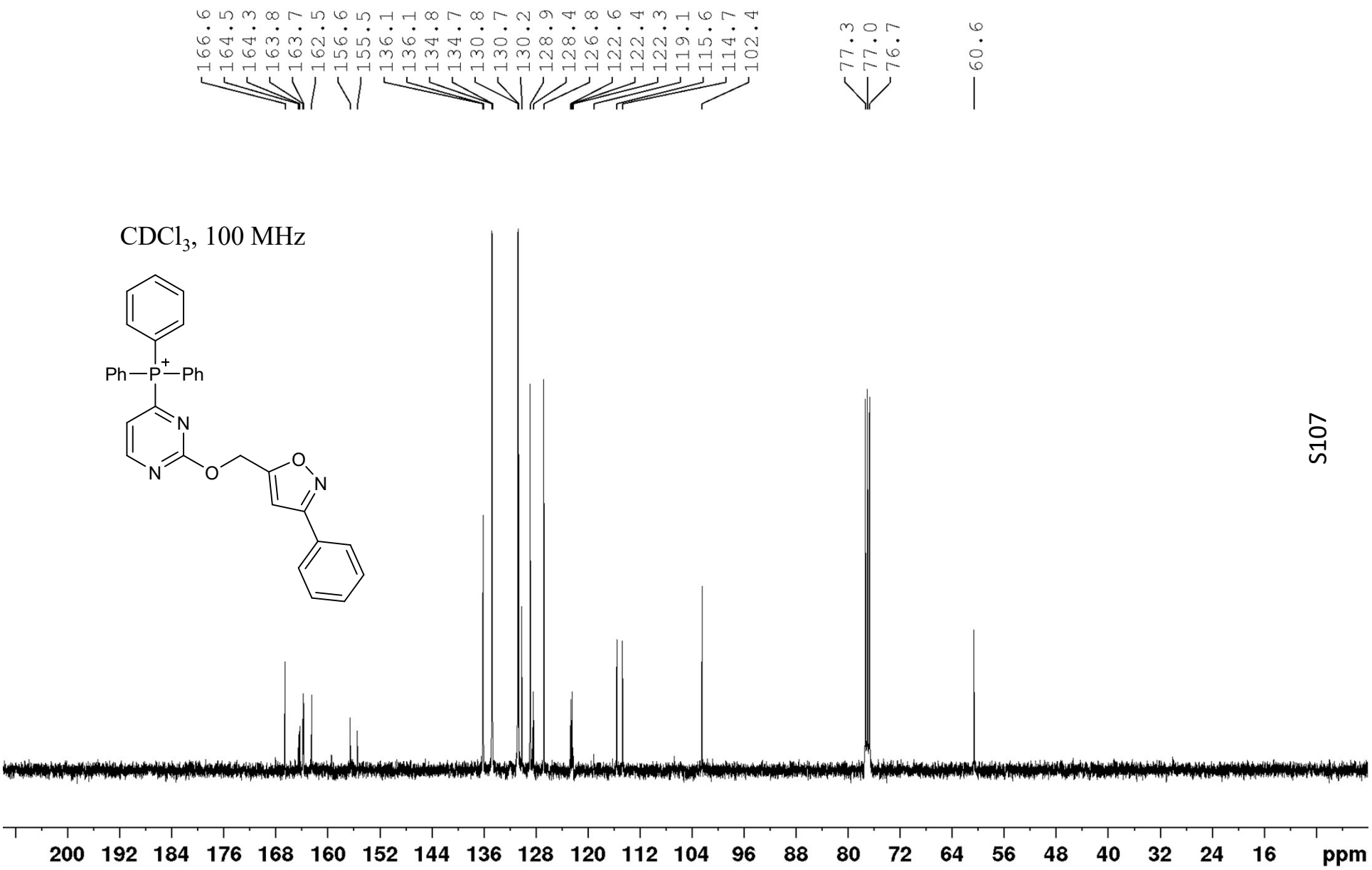

7.95
7.94
7.94
7.93
7.93
7.92
7.92
7.92
7.91
7.91
7.84
7.84
7.83
7.83
7.82
7.81
7.81
7.80
7.79
7.79
7.78
7.78
7.77
7.75
7.75
7.36
7.32
7.26
3.22
3.20
3.19
1.28
1.26
CDCl3, 400 MHz
Ph—P—Ph
NC
N
O
O—S—CF3
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.88
3.04
12.27
1.00
1.01
6.13

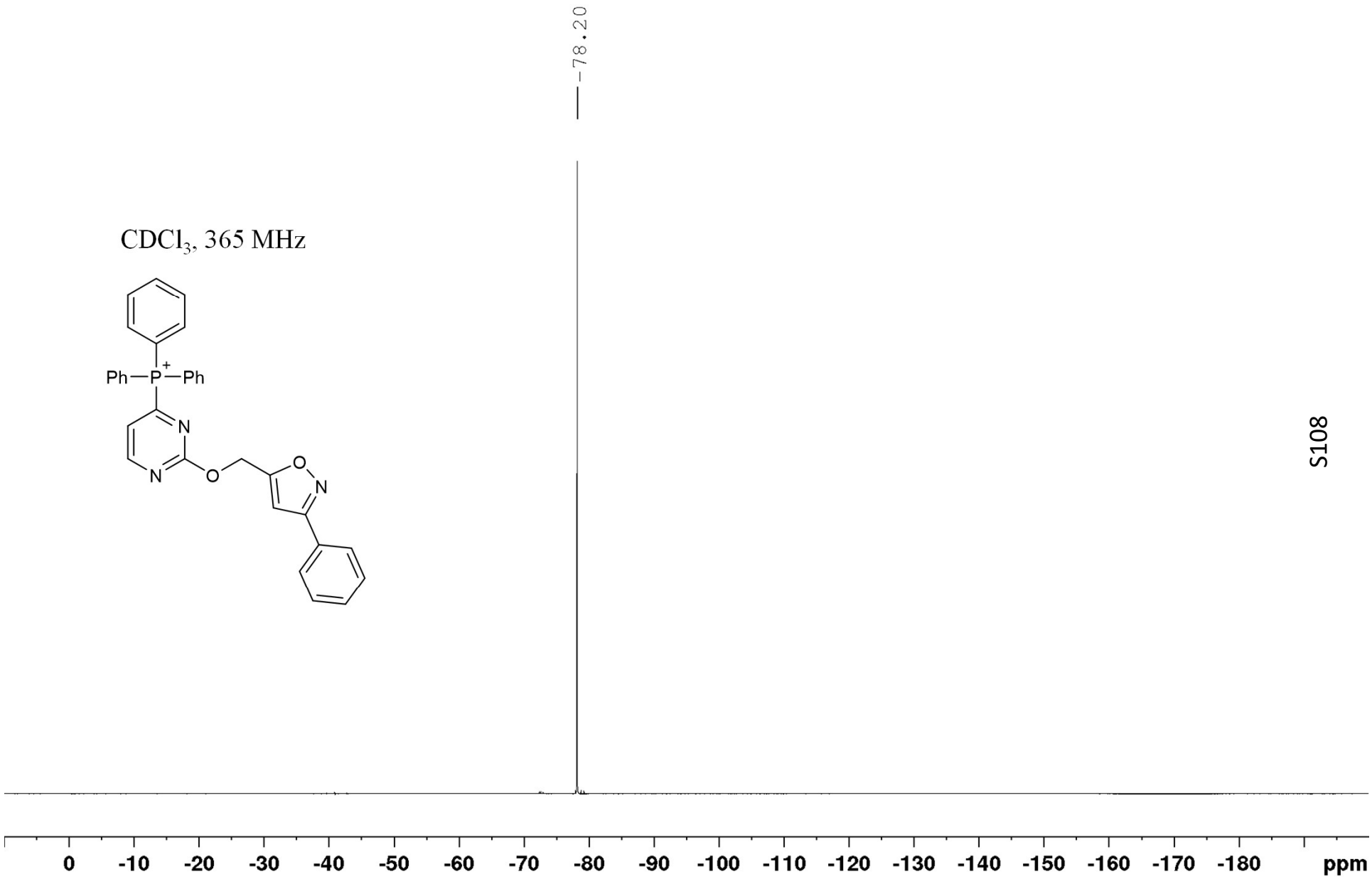

174.5
174.4
154.8
154.7
136.3
136.3
134.7
134.6
131.4
131.1
130.9
130.6
127.6
127.5
125.4
122.2
119.0
115.8
114.9
114.0
113.9
113.9
109.0
108.9
77.3
77.2
77.0
76.7
36.9
21.5
CDCl3, 100 MHz
Ph—P+—Ph
NC
N
O
O—S—CF3
O
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

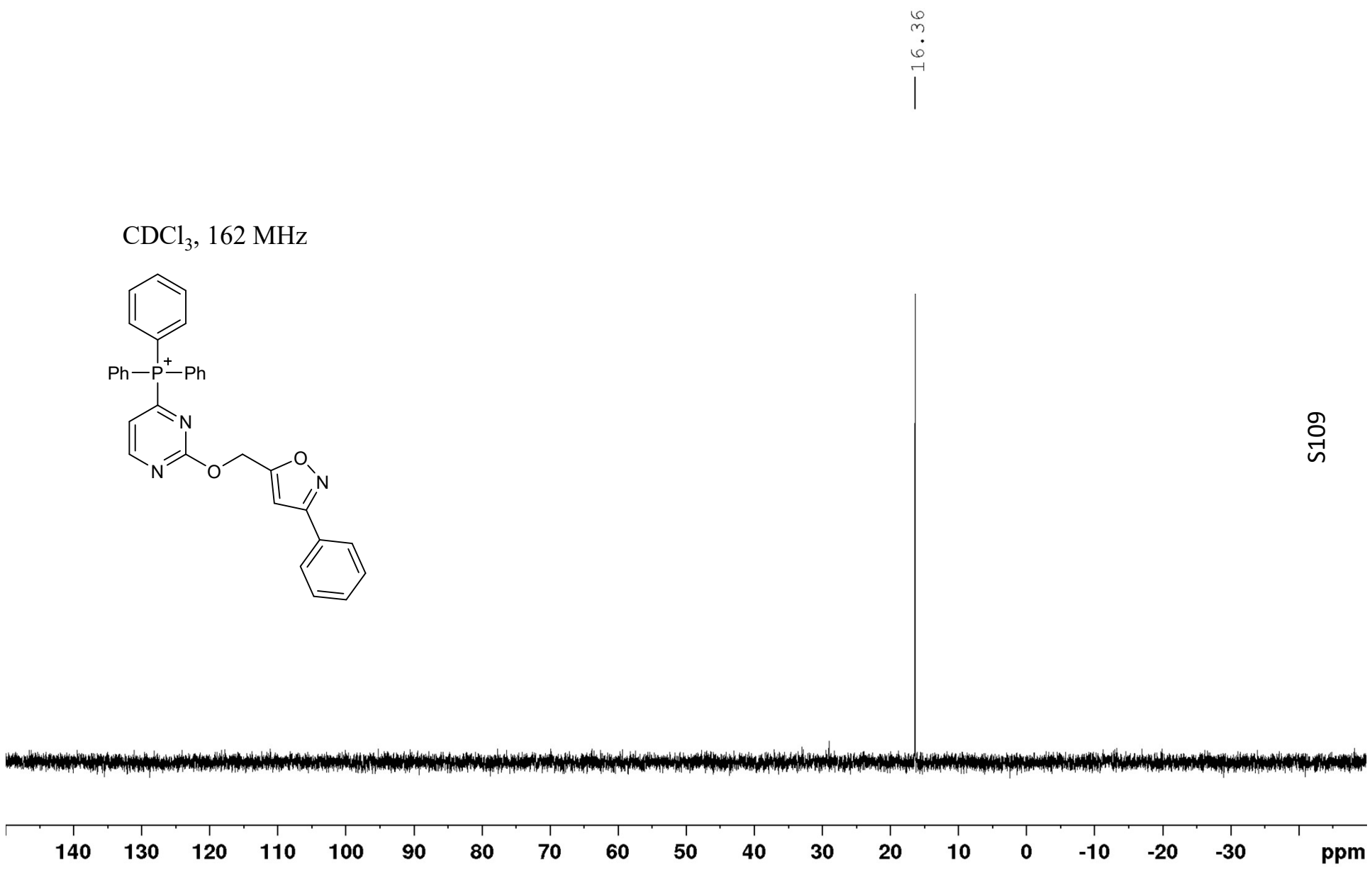

-78.22
CDCl3, 365 MHz
Ph—P—Ph
NC
N
O
S
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

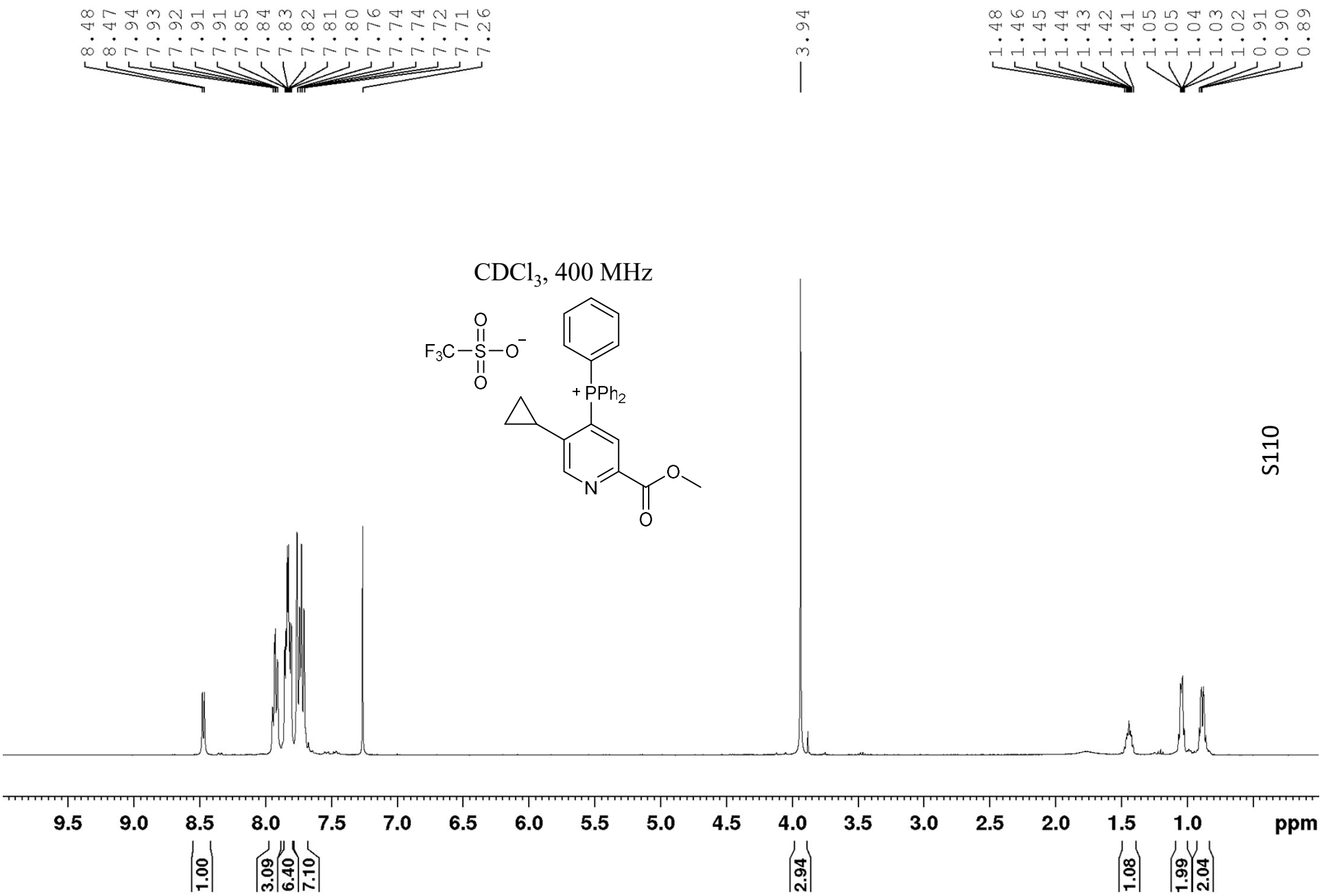

23.07
CDCl3, 162 MHz
Ph—P—Ph
NC
N
O
S
CF3
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
ppm

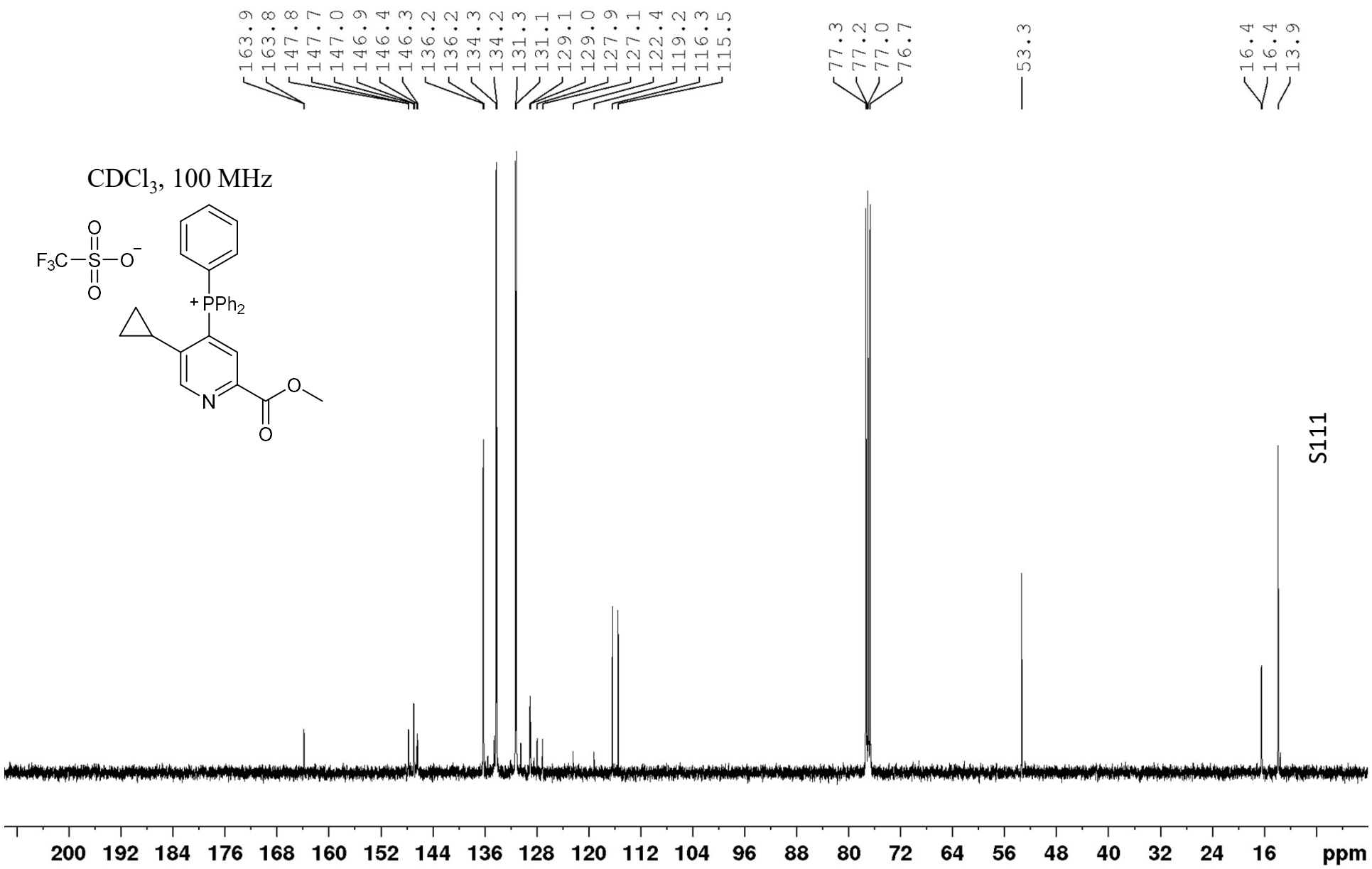

9.12
9.10
9.09
7.88
7.88
7.87
7.86
7.85
7.85
7.78
7.77
7.76
7.76
7.75
7.74
7.73
7.72
7.71
7.69
7.46
7.46
7.45
6.69
5.58
CDCl3, 400 MHz
Ph—P+—Ph
N
N
O
O
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.91
2.98
15.06
3.25
0.94
2.02

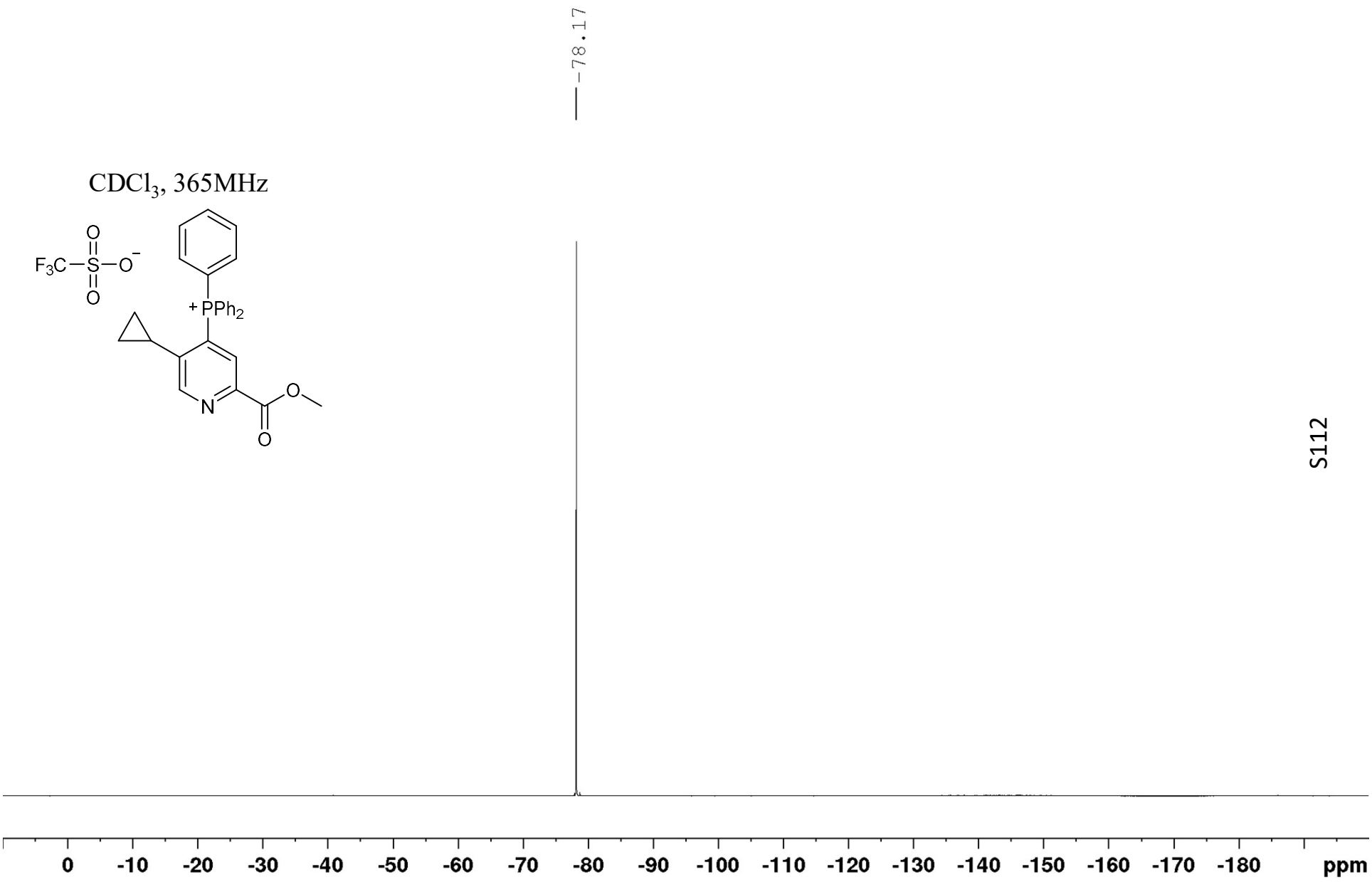

166.6
164.5
164.3
163.8
163.7
162.5
156.6
155.5
136.1
136.1
134.8
134.7
130.8
130.7
130.2
128.9
128.4
126.8
122.6
122.4
122.3
119.1
115.6
114.7
102.4
77.3
77.0
76.7
60.6
CDCl3, 100 MHz
Ph
P
Ph
N
N
O
O
N
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-78.20
CDCl3, 365 MHz
Ph—P+—Ph
N
N
O
O
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

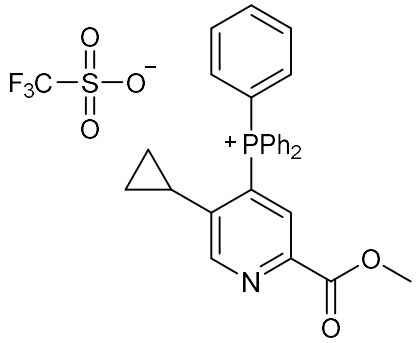

16.36
CDCl3, 162 MHz
Ph
P
Ph
N
N
O
O
N
S109
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm


8.48
8.47
7.94
7.93
7.92
7.91
7.91
7.85
7.84
7.83
7.82
7.81
7.80
7.76
7.74
7.74
7.72
7.71
7.26
3.94
1.48
1.46
1.45
1.44
1.43
1.42
1.41
1.05
1.05
1.04
1.03
1.02
0.91
0.90
0.89
CDCl3, 400 MHz
F3C
S
O
O
O
O
+PPh2
N
O
O
S110
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
1.00
3.09
6.40
7.10
2.94
1.08
1.99
2.04

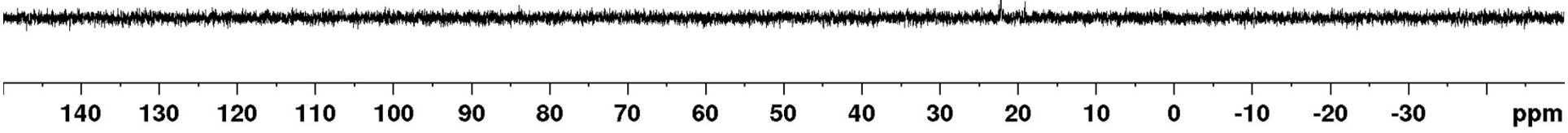

163.9
163.8
147.8
147.7
147.0
146.9
146.4
146.3
136.2
136.2
134.3
134.2
131.3
131.1
129.1
129.0
127.9
127.1
122.4
119.2
116.3
115.5
77.3
77.2
77.0
76.7
53.3
16.4
16.4
13.9
CDCl3, 100 MHz
F3C—S—O⁻
+PPh2
N
O
O
O
S111
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

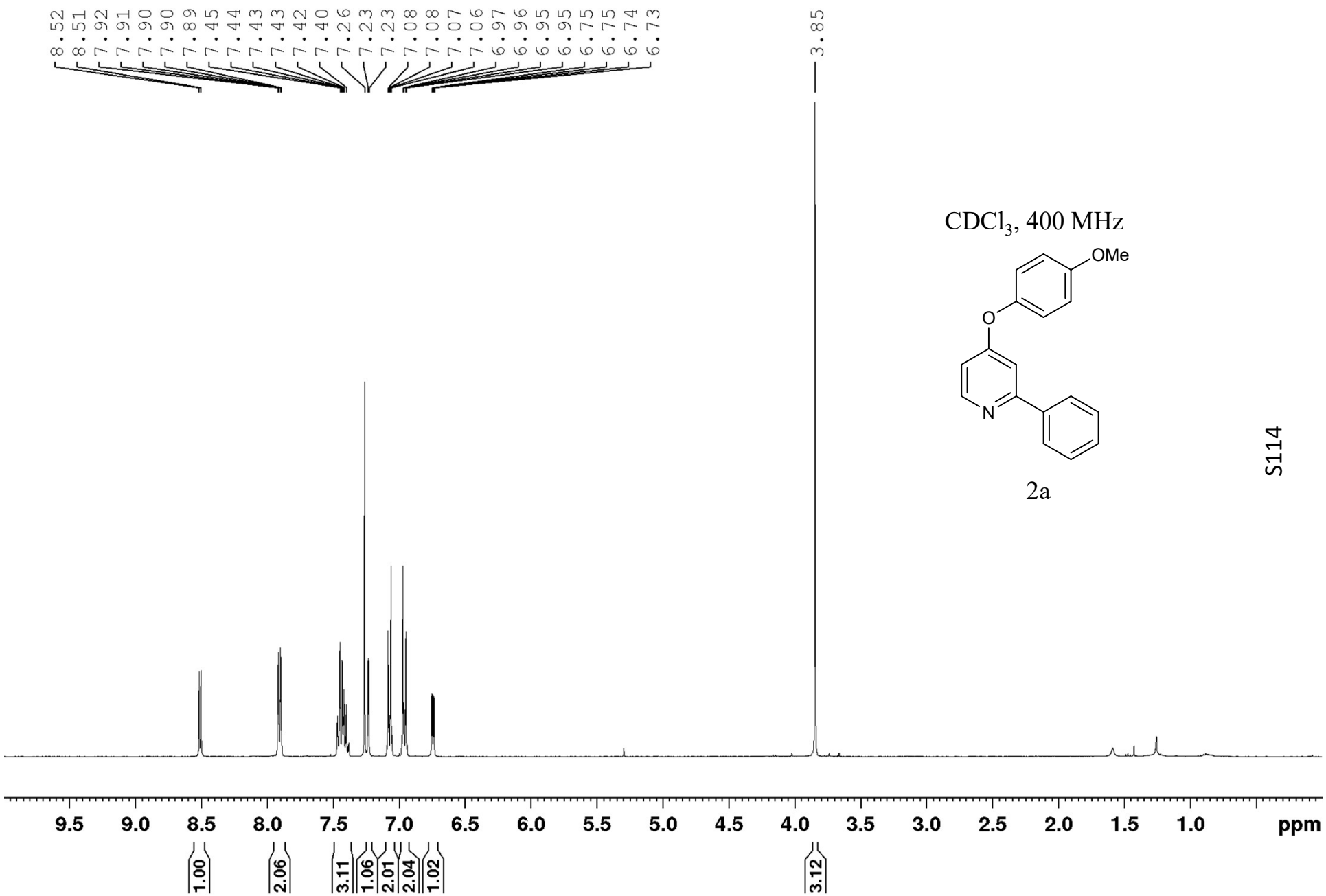

-78.17
CDCl3, 365MHz
F3C—S—O⁻
+PPh2
N
O
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

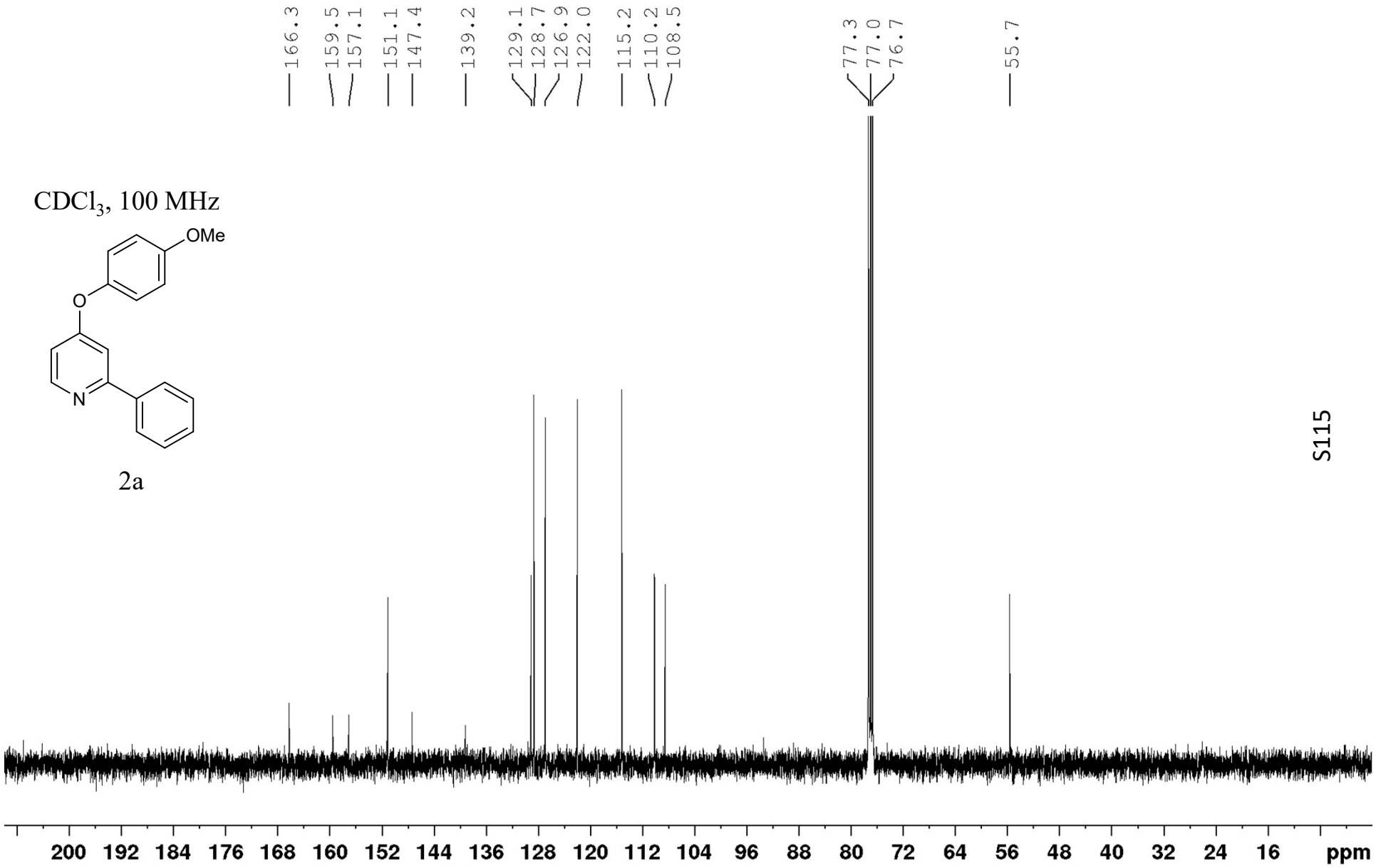
$CDCl_3$, 162 MHz



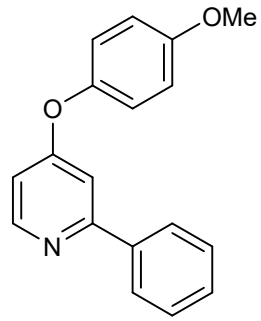
22.15



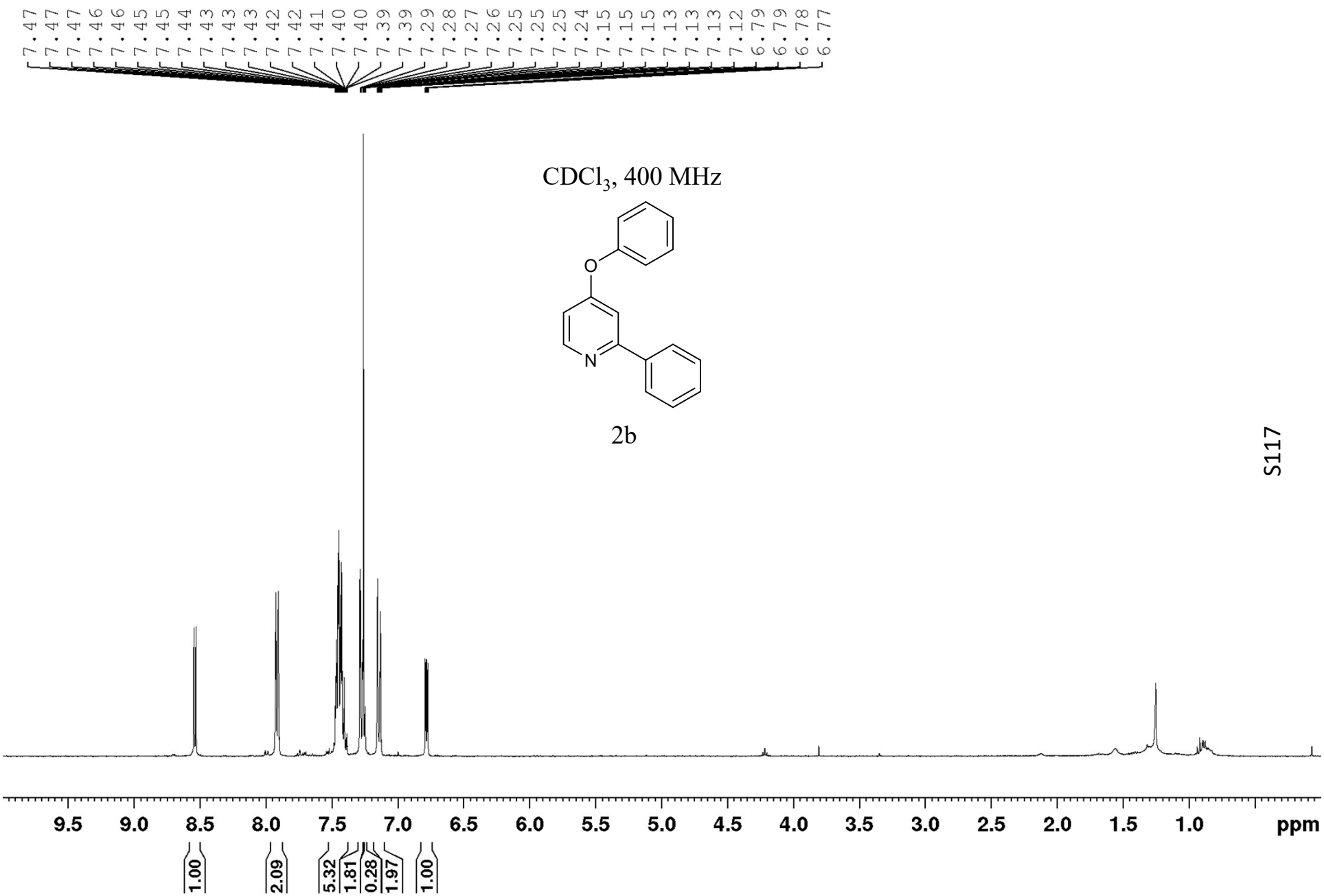

8.52
8.51
7.92
7.91
7.90
7.90
7.89
7.45
7.44
7.43
7.43
7.42
7.40
7.26
7.23
7.23
7.08
7.08
7.07
7.06
6.97
6.96
6.95
6.95
6.75
6.75
6.74
6.73
3.85
CDCl3, 400 MHz
OMe
O
N
2a
S114
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
3.11
1.06
2.01
2.04
1.02
3.12

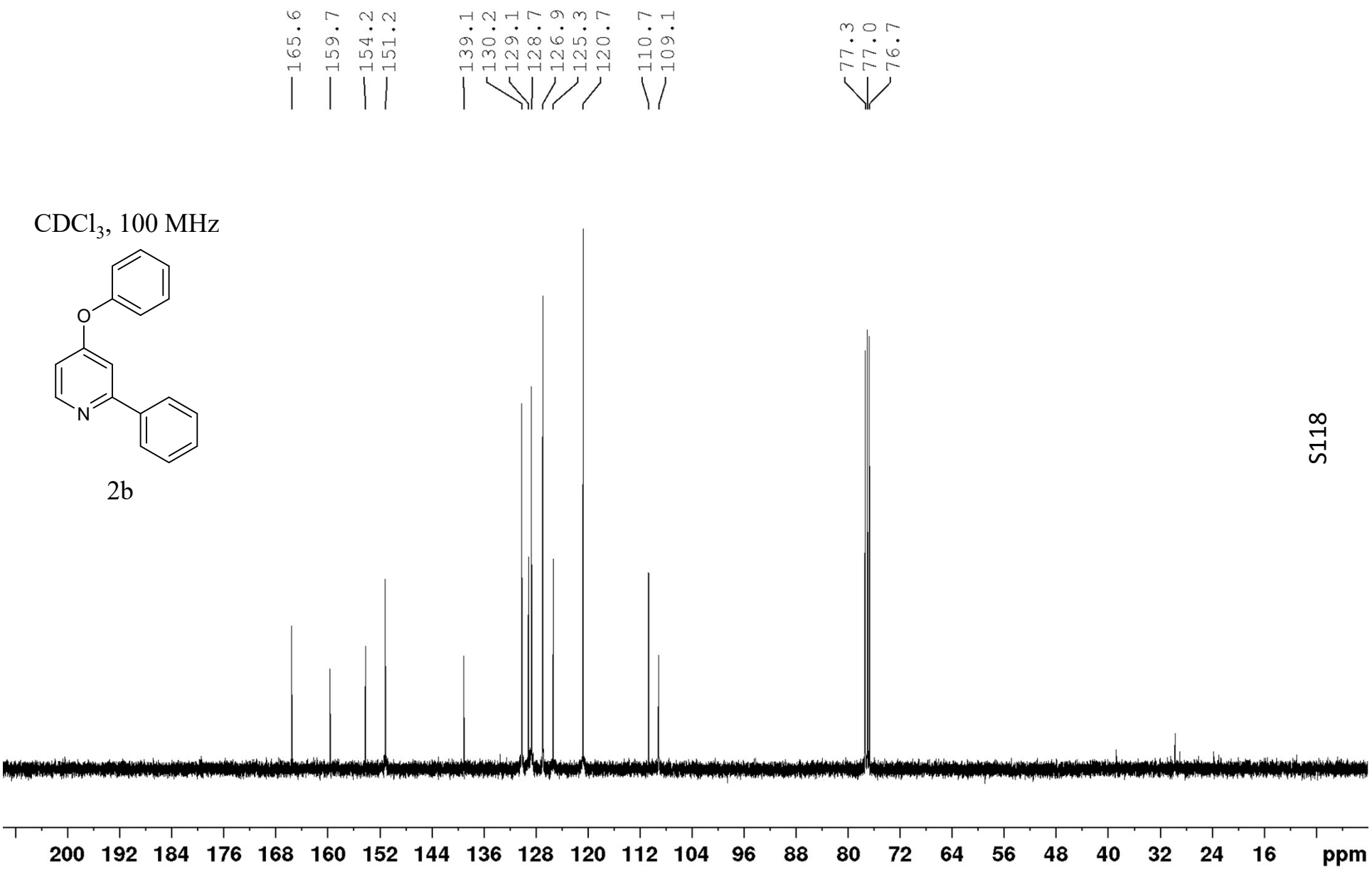

166.3
159.5
157.1
151.1
147.4
139.2
129.1
128.7
126.9
122.0
115.2
110.2
108.5
77.3
77.0
76.7
55.7
CDCl3, 100 MHz
OMe
O
N
2a
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

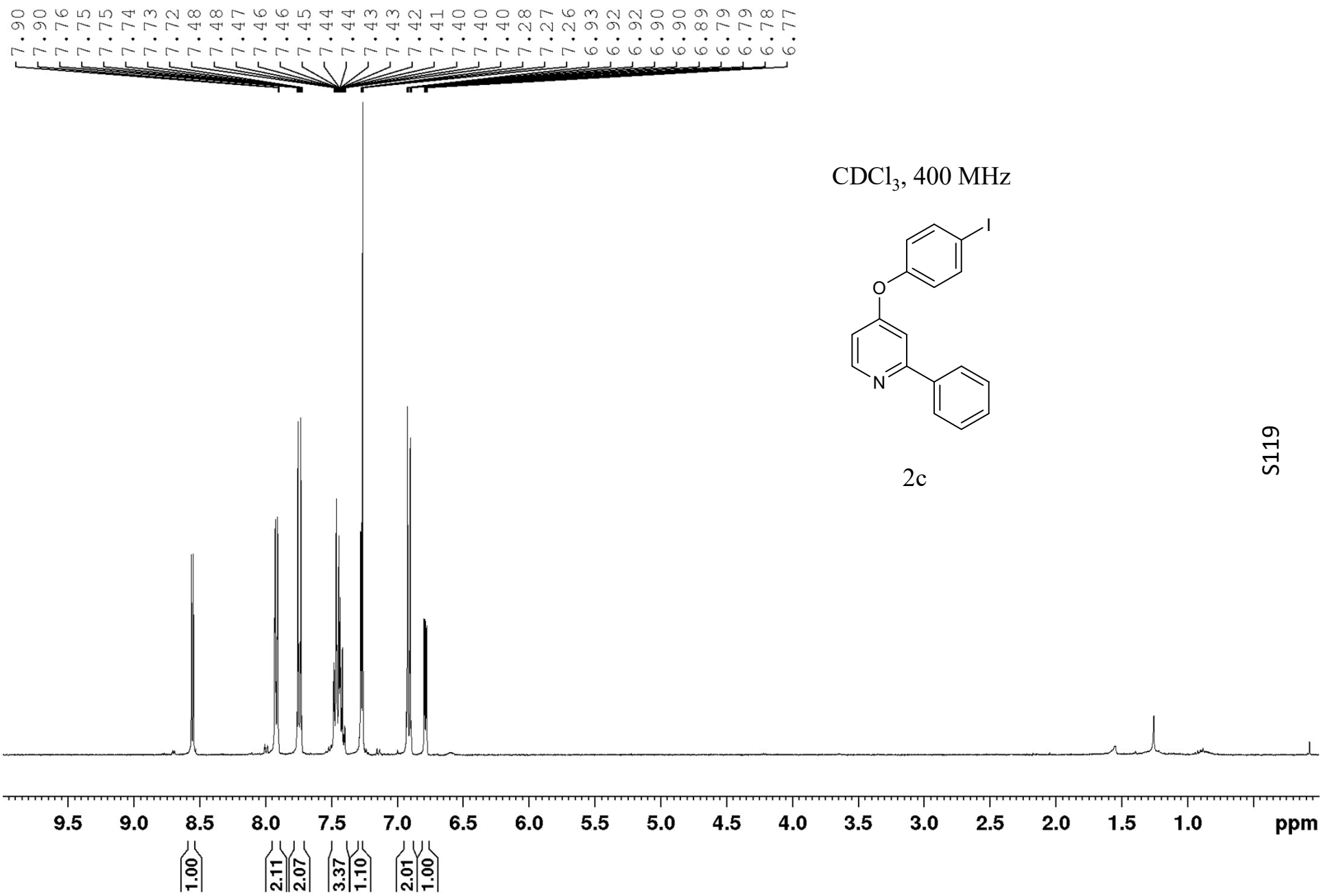
Crude ^{31}P NMR
$CDCl_3$, 365 MHz

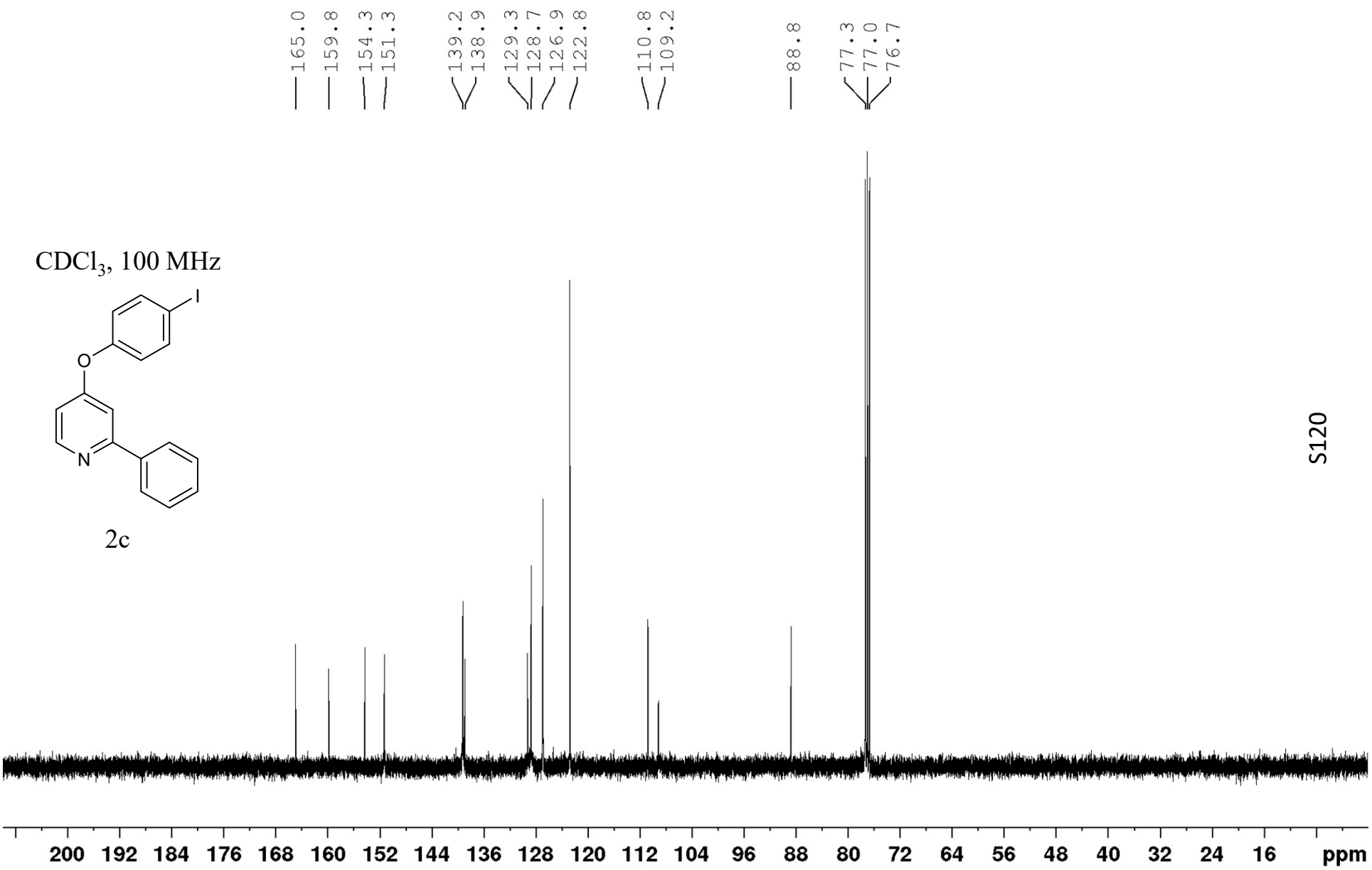


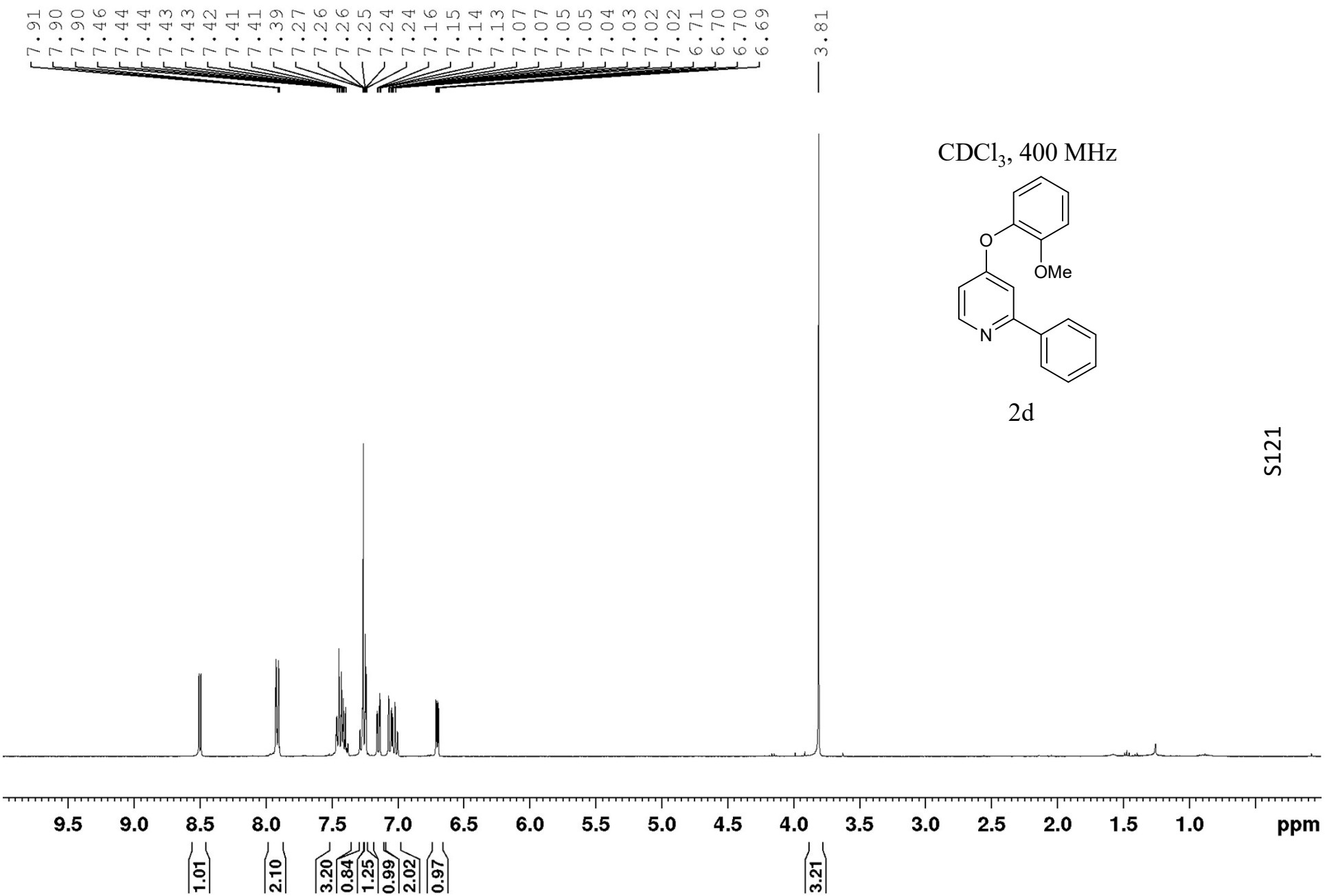
2a

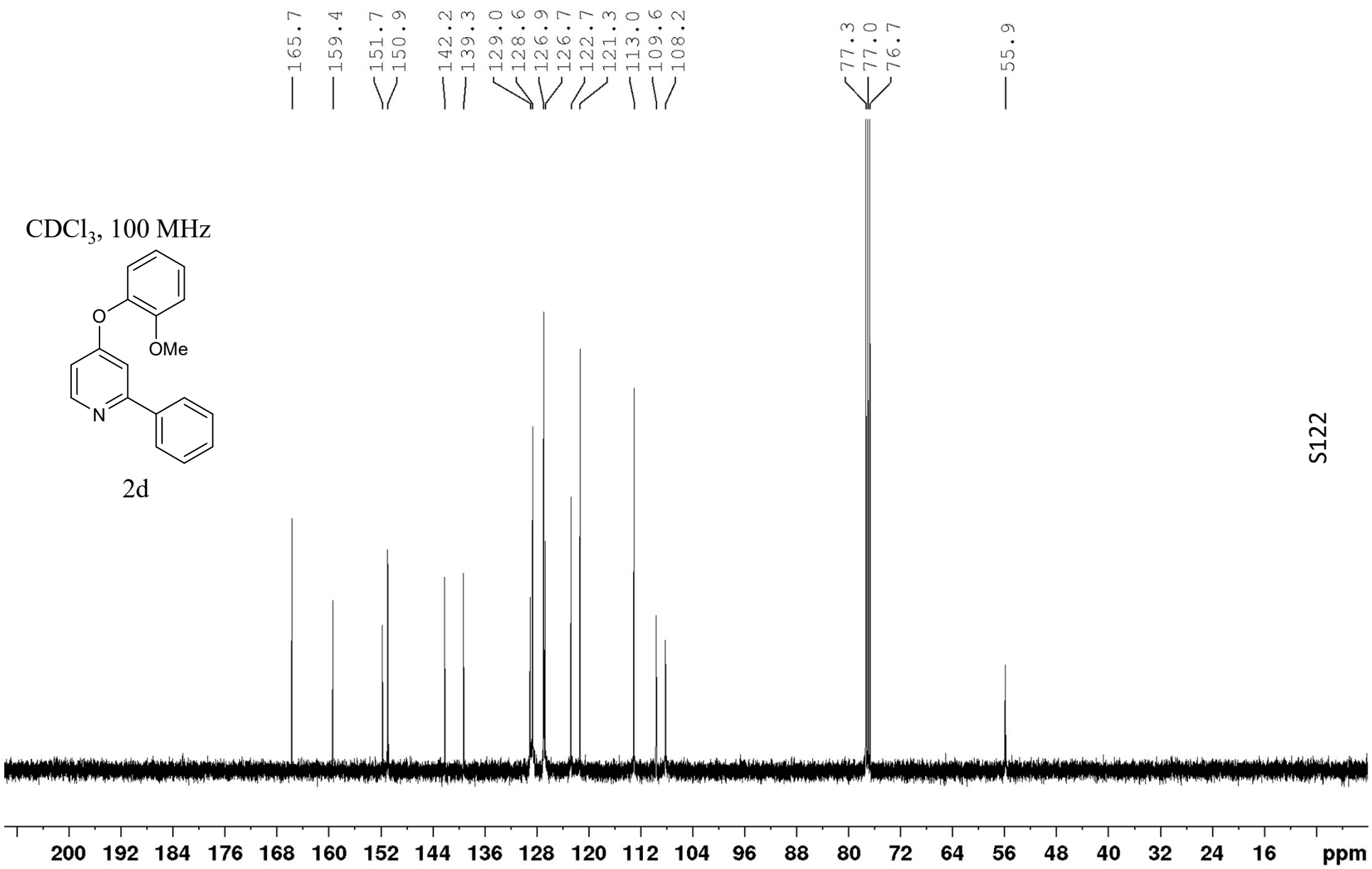

7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.29
7.28
7.27
7.26
7.25
7.25
7.25
7.24
7.15
7.15
7.15
7.13
7.13
7.13
7.12
6.79
6.79
6.78
6.77
CDCl3, 400 MHz
O
N
2b
S117
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.09
5.32
1.81
0.28
1.97
1.00

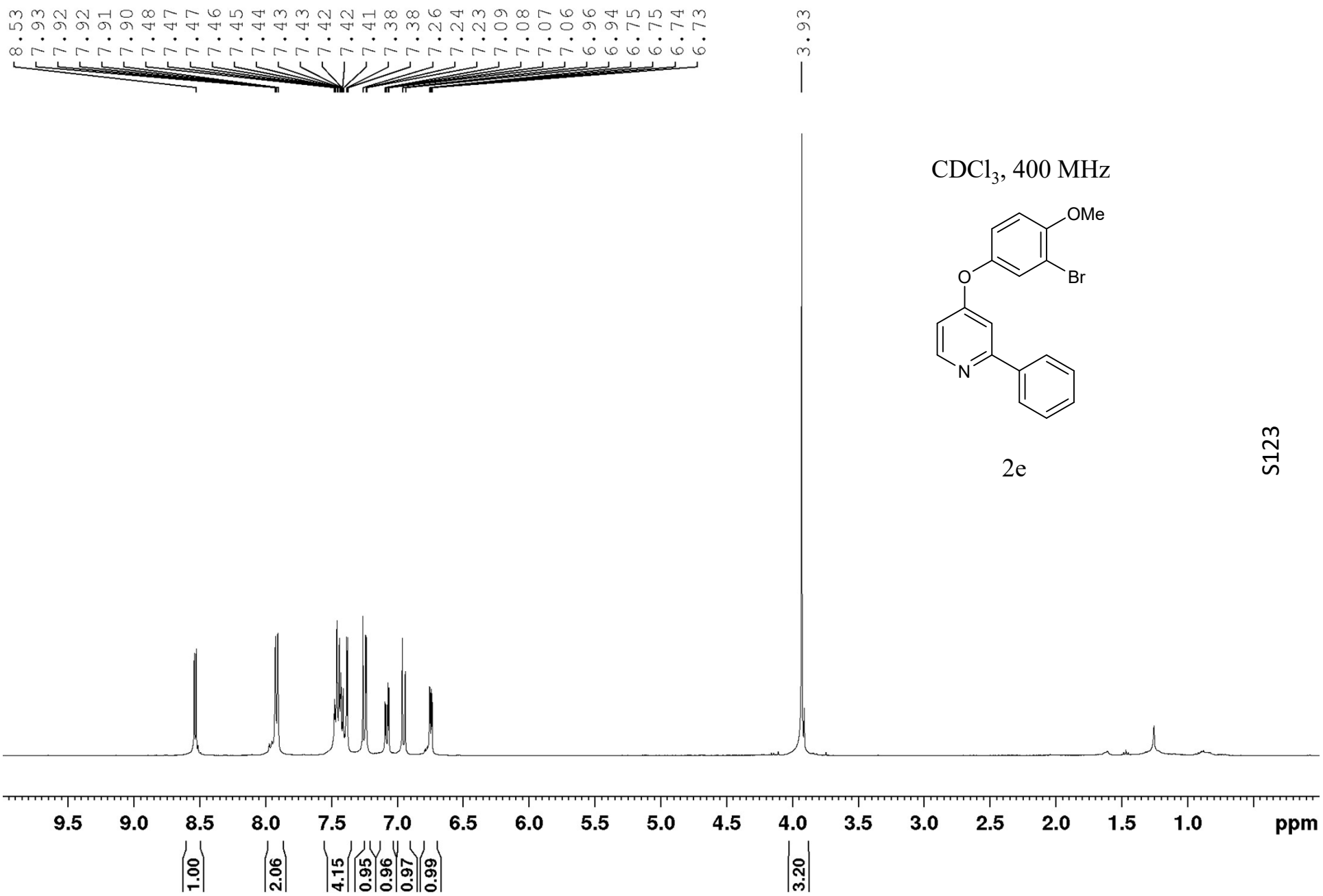

165.6
159.7
154.2
151.2
139.1
130.2
129.1
128.7
126.9
125.3
120.7
110.7
109.1
77.3
77.0
76.7
CDCl3, 100 MHz
O
N
2b
S118
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

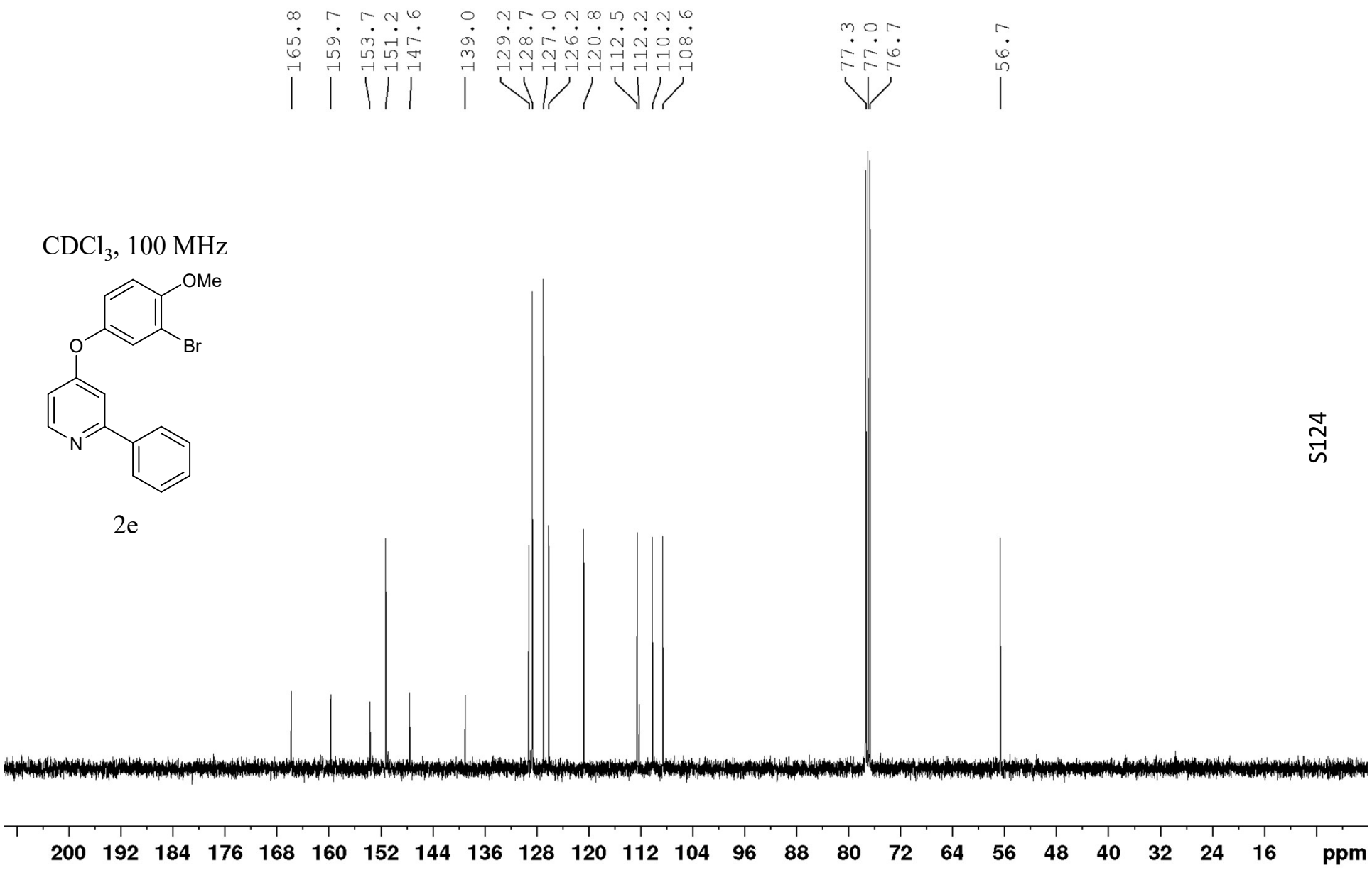

7.90
7.90
7.76
7.75
7.75
7.74
7.73
7.72
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.40
7.28
7.27
7.26
6.93
6.92
6.92
6.90
6.90
6.89
6.79
6.79
6.78
6.77
CDCl3, 400 MHz
I
O
N
2c
S119
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.11
2.07
3.37
1.10
2.01
1.00

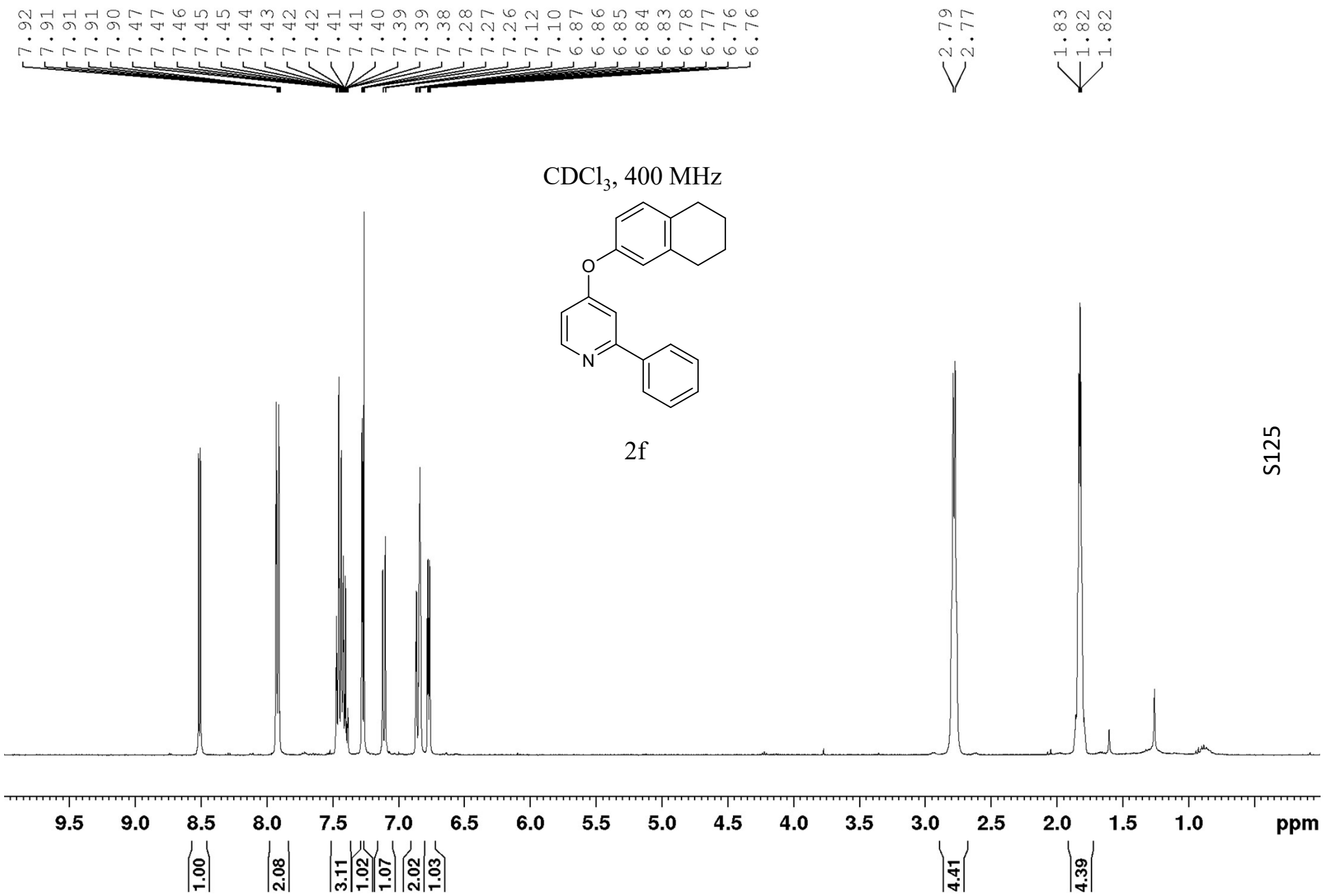

165.0
159.8
154.3
151.3
139.2
138.9
129.3
128.7
126.9
122.8
110.8
109.2
88.8
77.3
77.0
76.7
CDCl3, 100 MHz
I
O
N
2c
S120
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

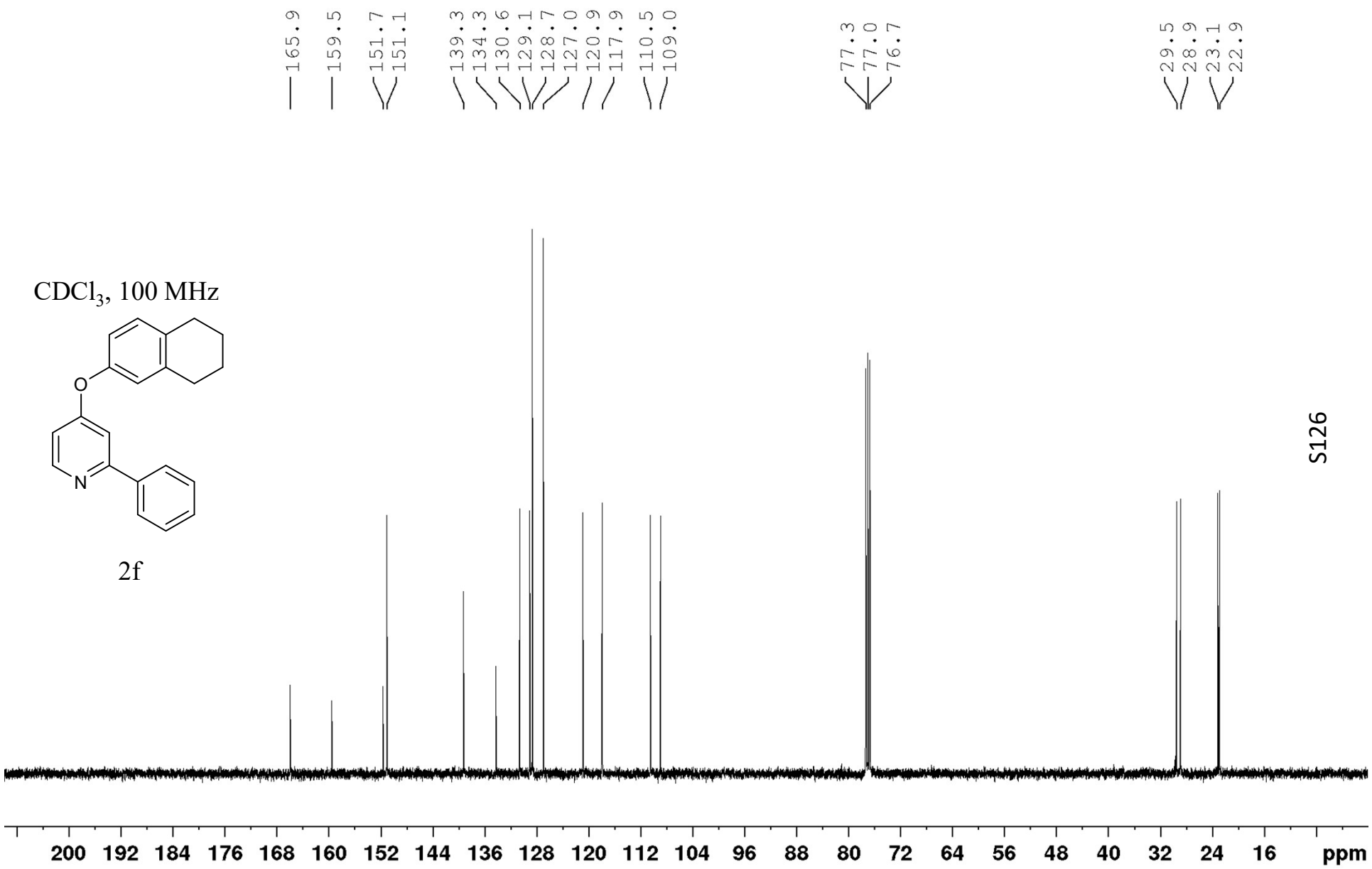

7.91
7.90
7.90
7.46
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.39
7.27
7.26
7.26
7.25
7.24
7.24
7.16
7.15
7.14
7.13
7.07
7.07
7.05
7.05
7.04
7.03
7.02
7.02
6.71
6.70
6.70
6.69
3.81
CDCl3, 400 MHz
O
OMe
N
2d
S121
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.01
2.10
3.20
0.84
1.25
0.99
2.02
0.97
3.21

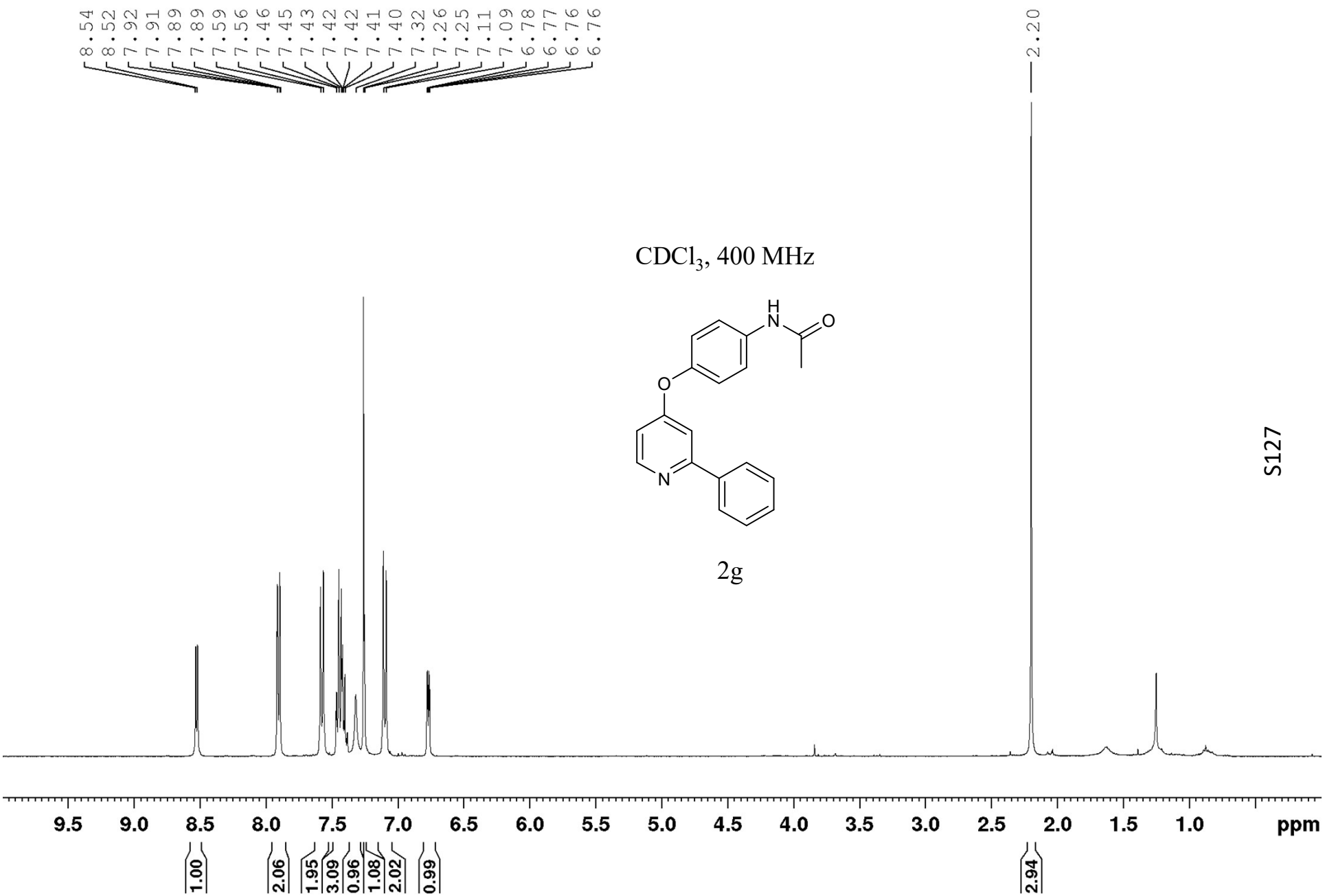

165.7
159.4
151.7
150.9
142.2
139.3
129.0
128.6
126.9
126.7
122.7
121.3
113.0
109.6
108.2
77.3
77.0
76.7
55.9
CDCl3, 100 MHz
O
OMe
N
2d
S122
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

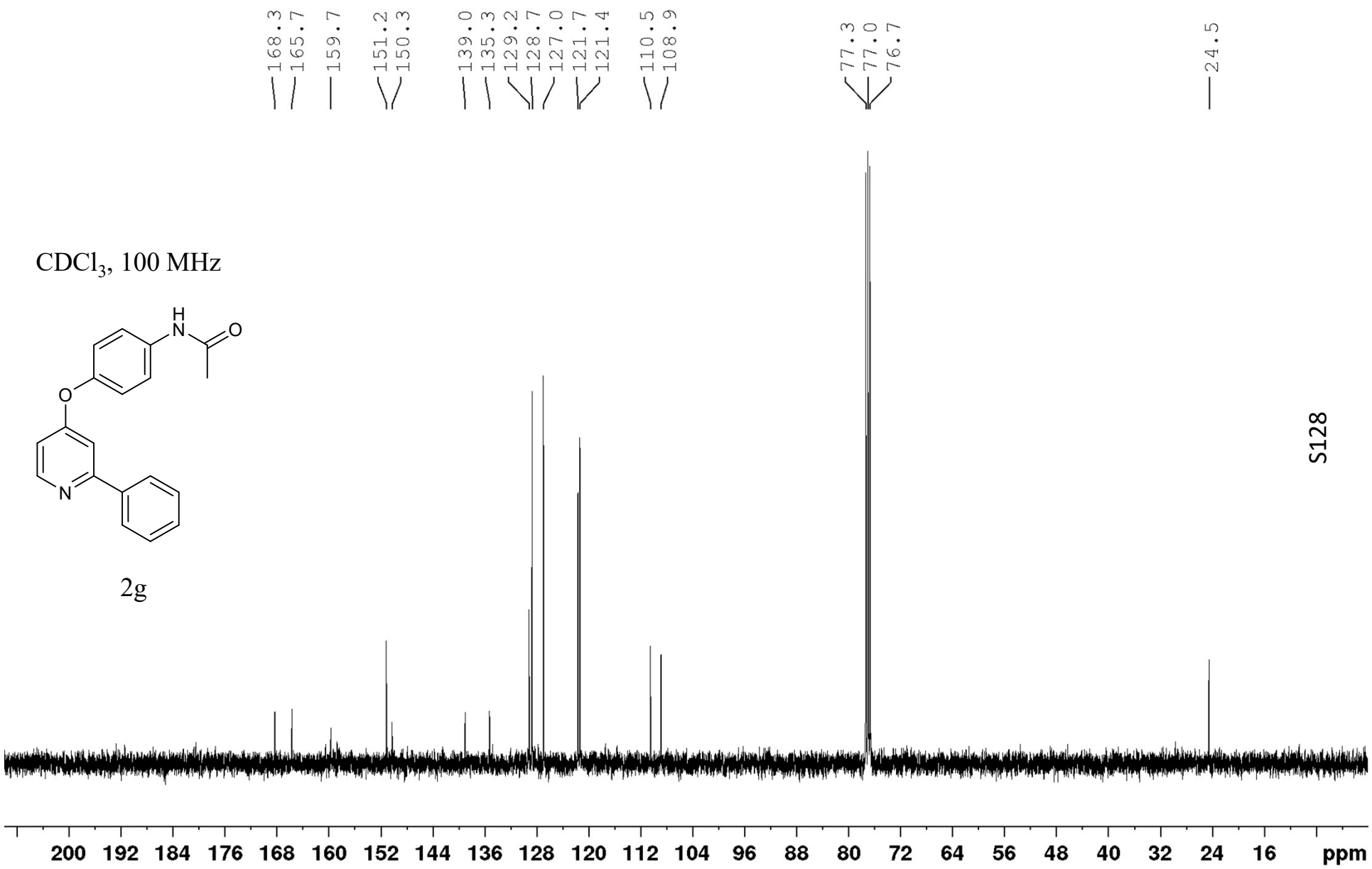

8.53
7.93
7.92
7.92
7.91
7.90
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.38
7.38
7.26
7.24
7.23
7.09
7.08
7.07
7.06
6.96
6.94
6.75
6.75
6.74
6.73
3.93
CDCl3, 400 MHz
OMe
Br
O
N
2e
S123
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
4.15
0.95
0.96
0.97
0.99
3.20

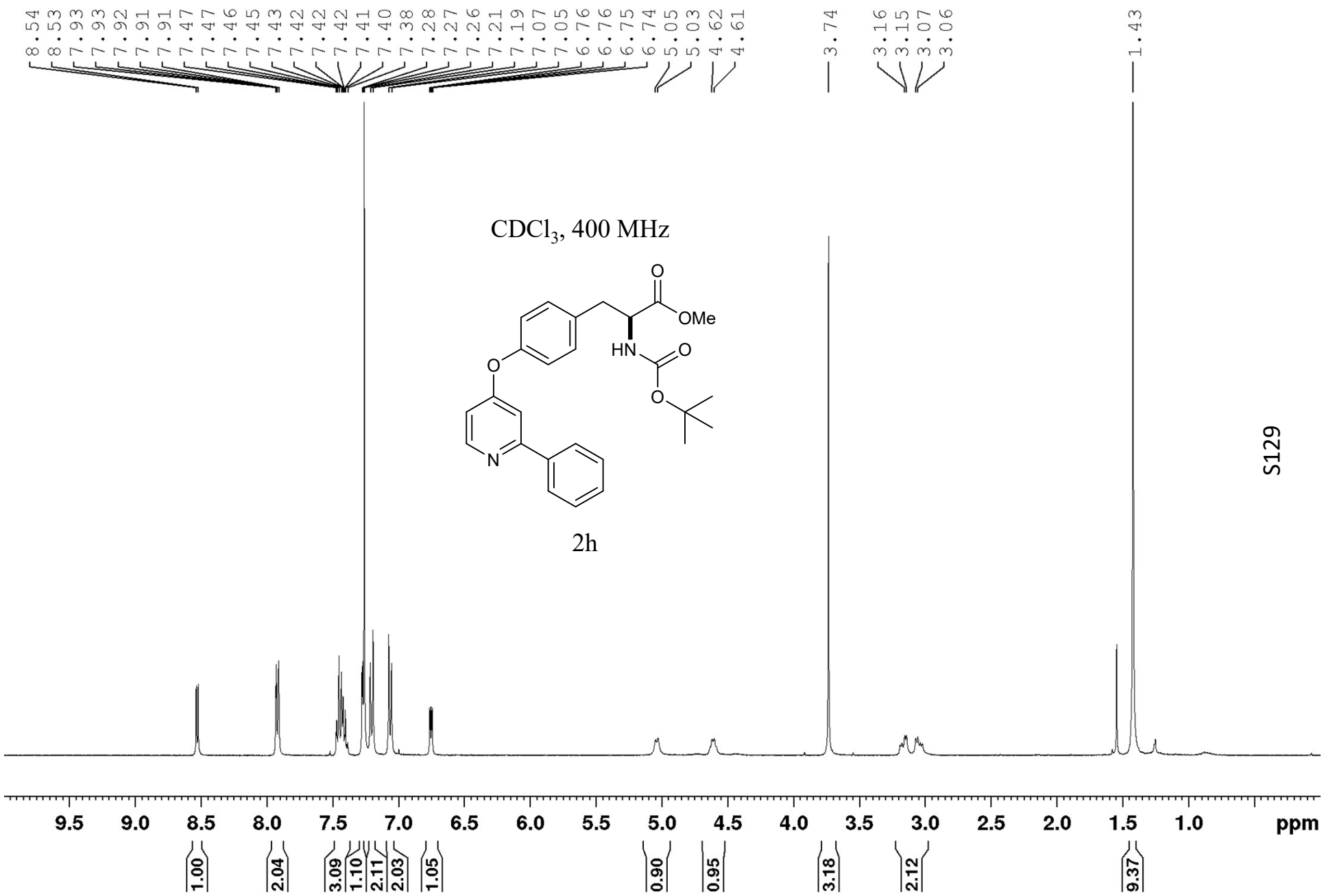

165.8
159.7
153.7
151.2
147.6
139.0
129.2
128.7
127.0
126.2
120.8
112.5
112.2
110.2
108.6
77.3
77.0
76.7
56.7
CDCl3, 100 MHz
OMe
Br
O
N
2e
S124
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

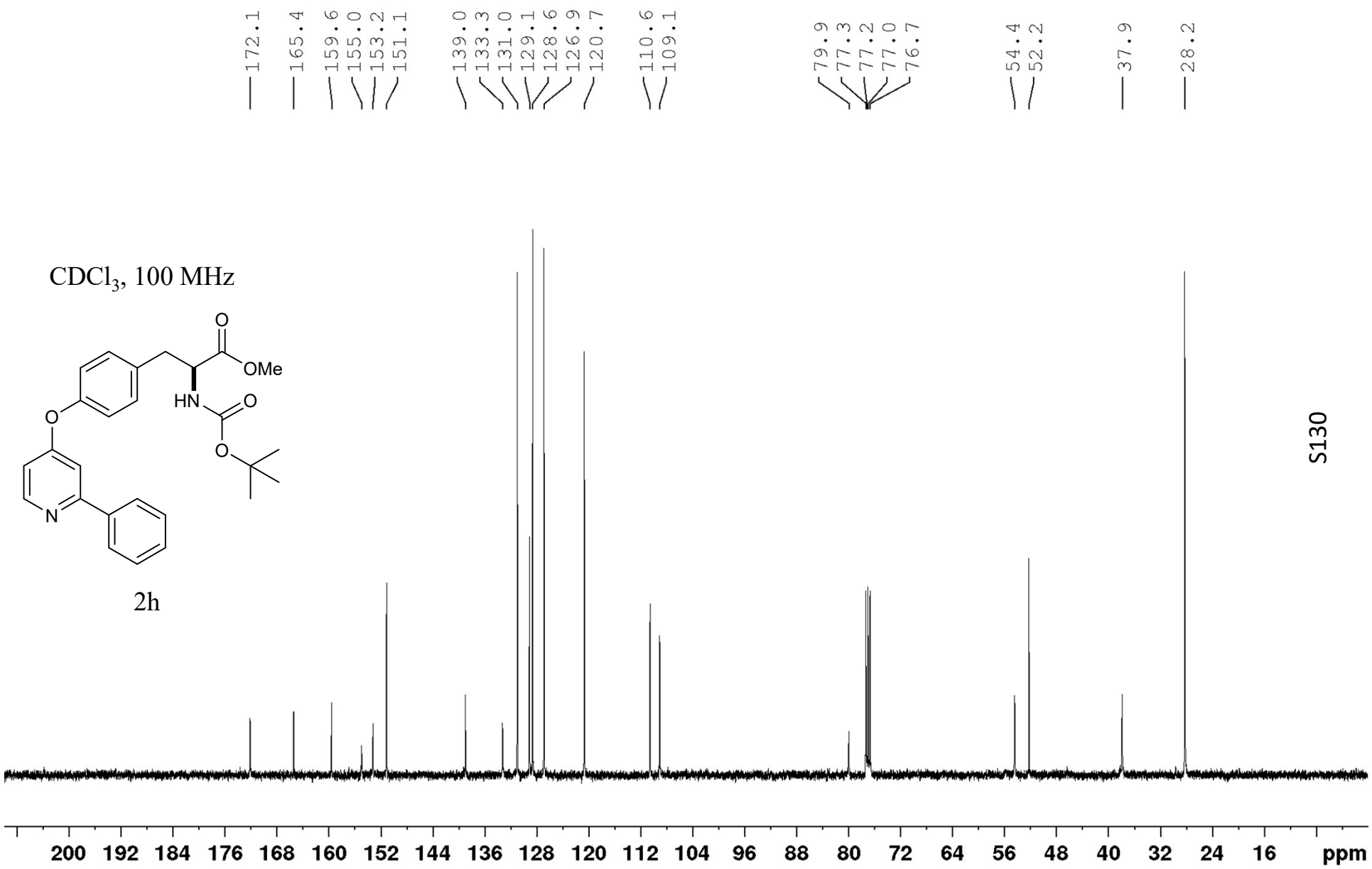

7.92
7.91
7.91
7.91
7.90
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.28
7.27
7.26
7.12
7.10
6.87
6.86
6.85
6.84
6.83
6.78
6.77
6.76
6.76
2.79
2.77
1.83
1.82
1.82
CDCl3, 400 MHz
O
N
2f
S125
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.08
3.11
1.02
1.07
2.02
1.03
4.41
4.39

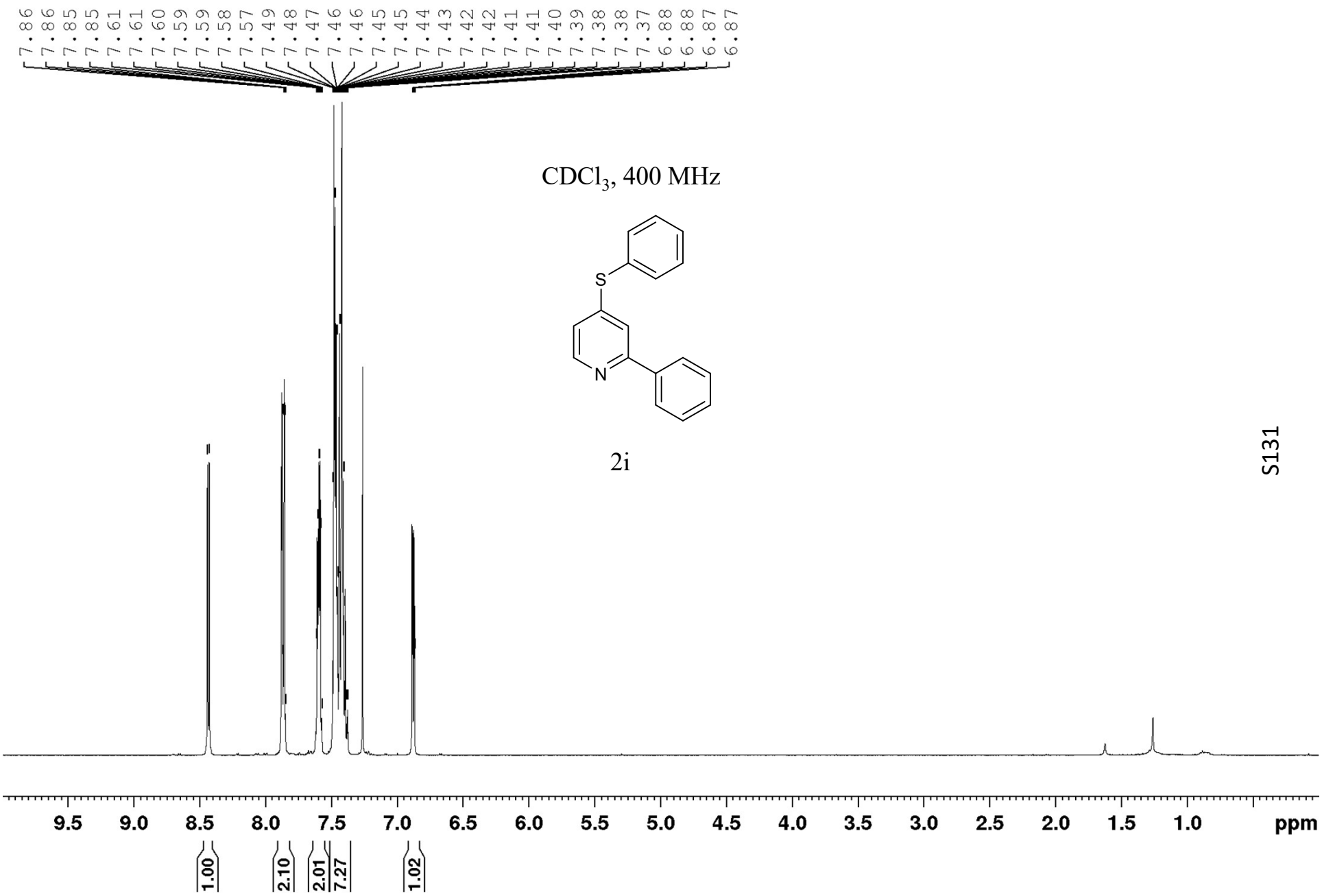

165.9
159.5
151.7
151.1
139.3
134.3
130.6
129.1
128.7
127.0
120.9
117.9
110.5
109.0
77.3
77.0
76.7
29.5
28.9
23.1
22.9
CDCl3, 100 MHz
O
N
2f
S126
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

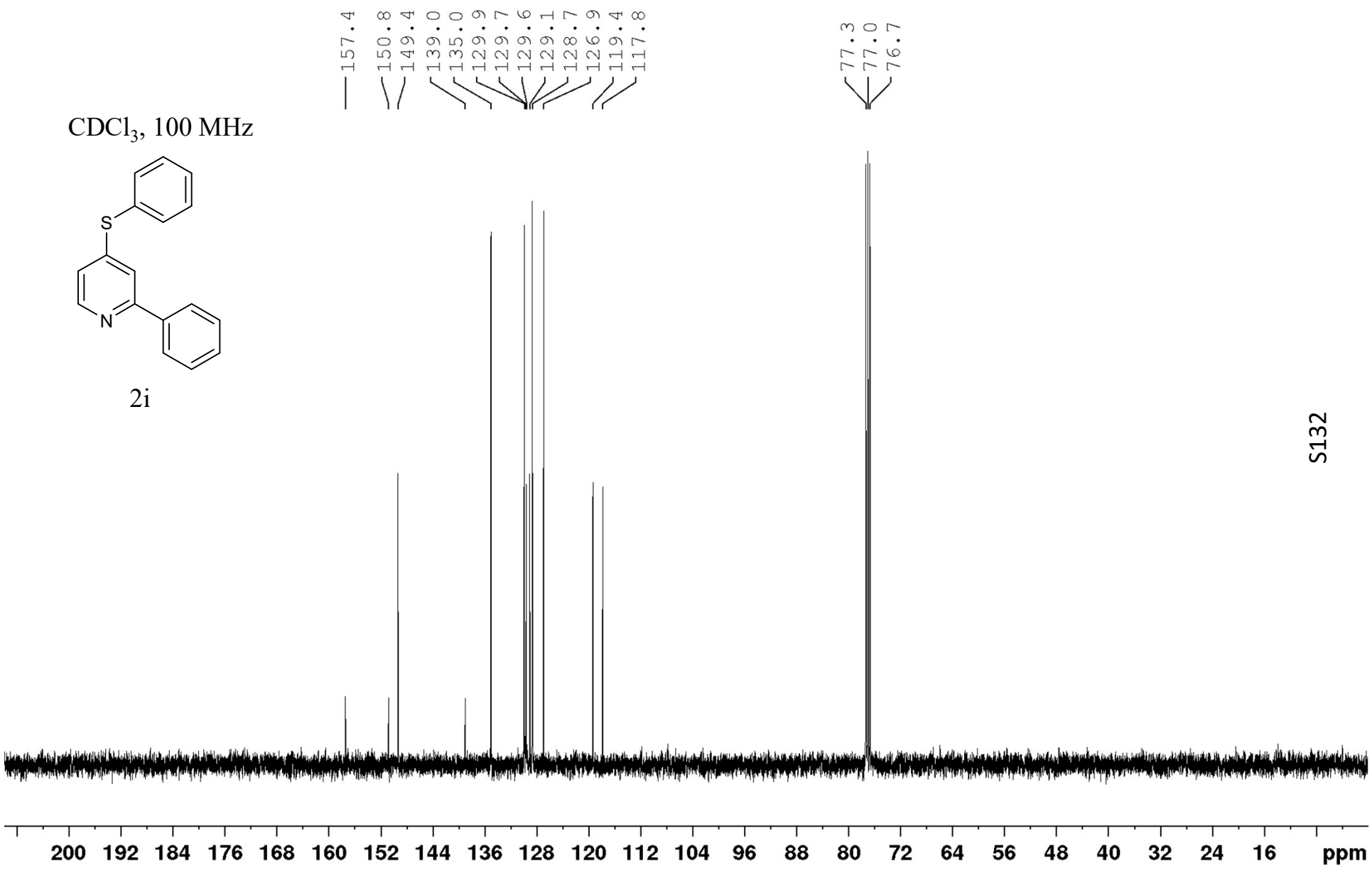

8.54
8.52
7.92
7.91
7.89
7.89
7.59
7.56
7.46
7.45
7.43
7.42
7.42
7.41
7.40
7.32
7.26
7.25
7.11
7.09
6.78
6.77
6.76
6.76
2.20
CDCl3, 400 MHz
H
N
O
O
N
2g
S127
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
1.95
3.09
0.96
1.08
2.02
0.99
2.94

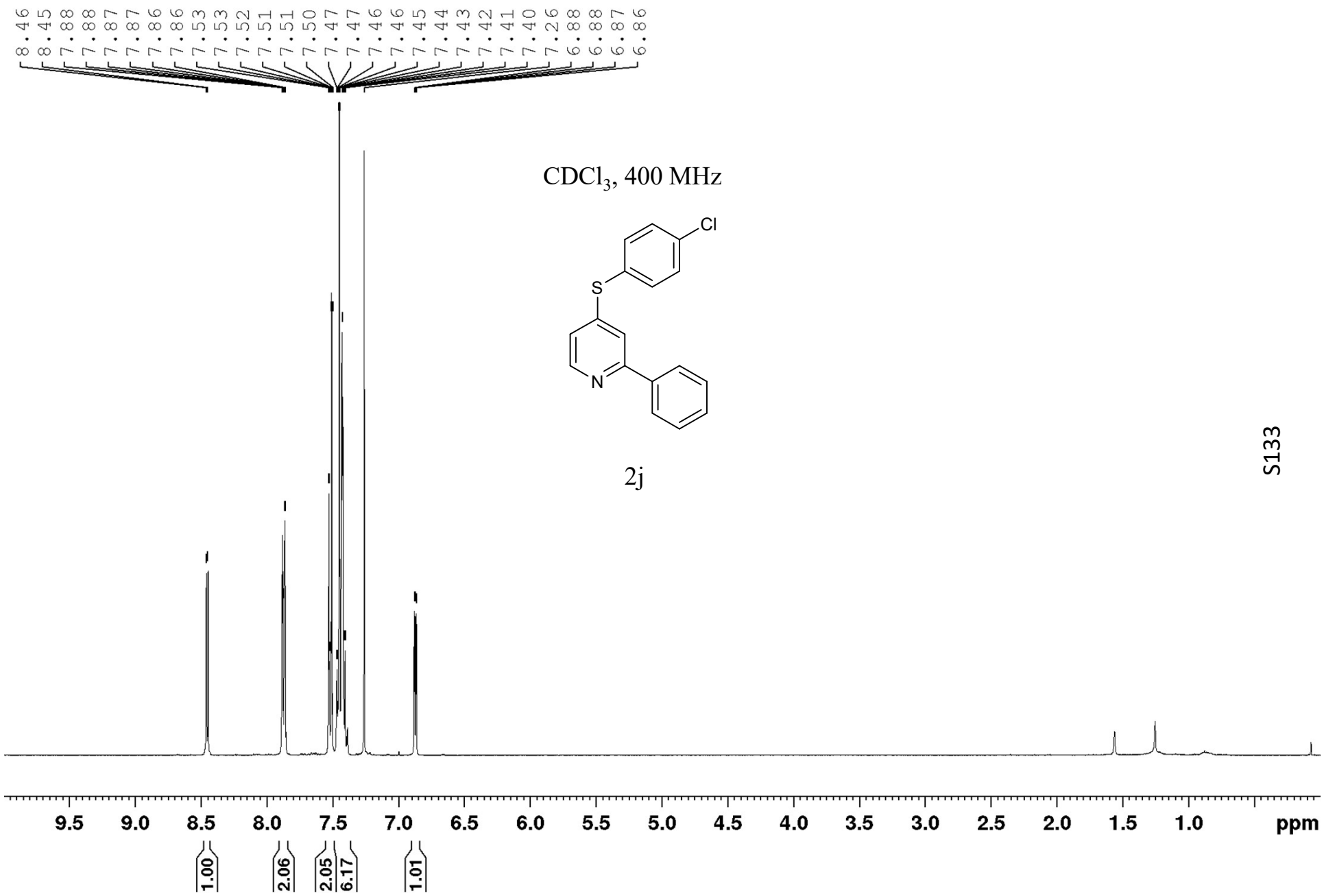

168.3
165.7
159.7
151.2
150.3
139.0
135.3
129.2
128.7
127.0
121.7
121.4
110.5
108.9
77.3
77.0
76.7
24.5
CDCl3, 100 MHz
H
N
O
O
N
2g
S128
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

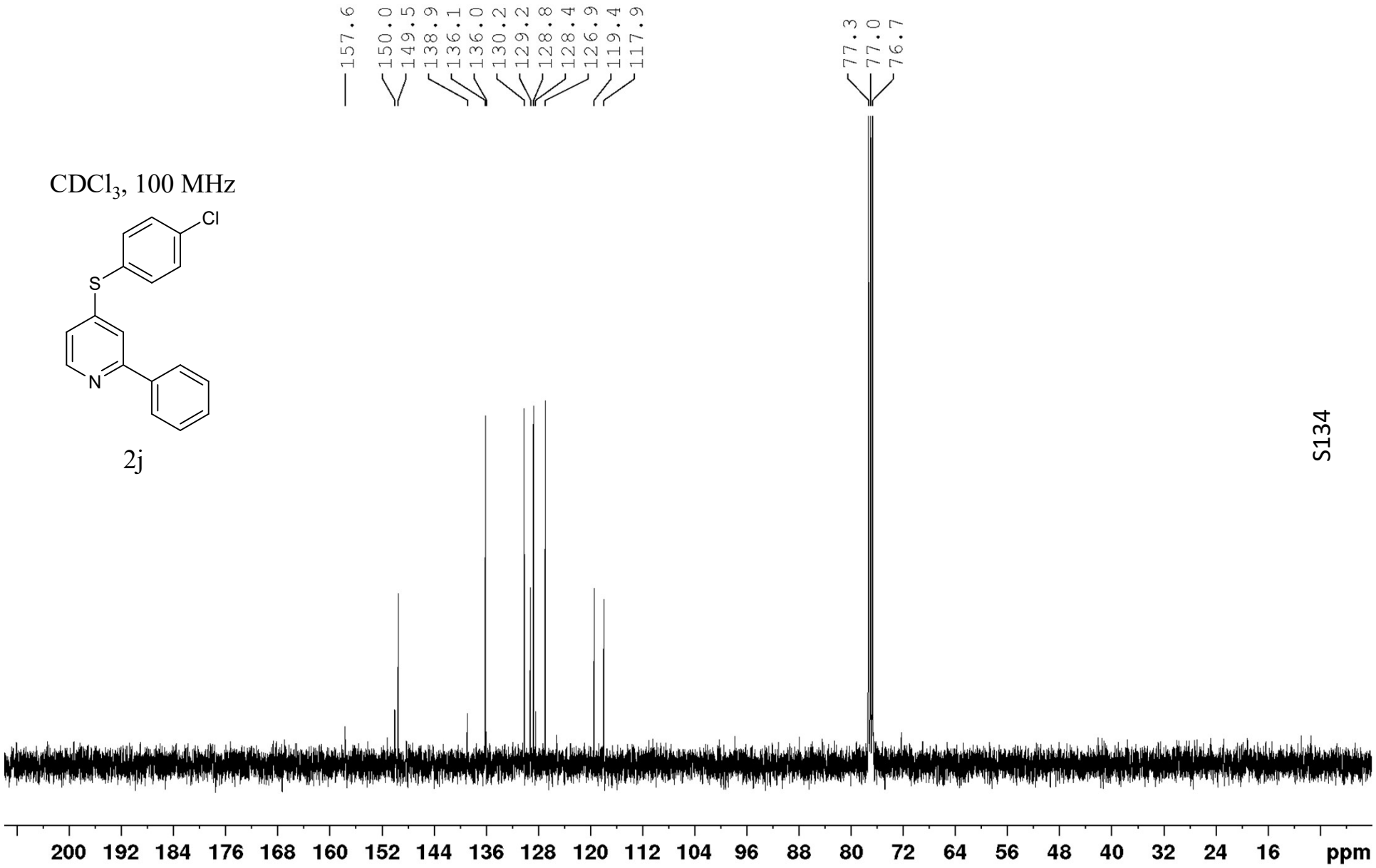

8.54
8.53
7.93
7.93
7.92
7.91
7.91
7.47
7.47
7.46
7.45
7.43
7.42
7.42
7.42
7.41
7.40
7.38
7.28
7.27
7.26
7.21
7.19
7.07
7.05
6.76
6.76
6.75
6.74
5.05
5.03
4.62
4.61
3.74
3.16
3.15
3.07
3.06
1.43
CDCl3, 400 MHz
O
OMe
HN
O
O
O
O
N
2h
S129
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.04
3.09
1.10
2.11
2.03
1.05
0.90
0.95
3.18
2.12
9.37

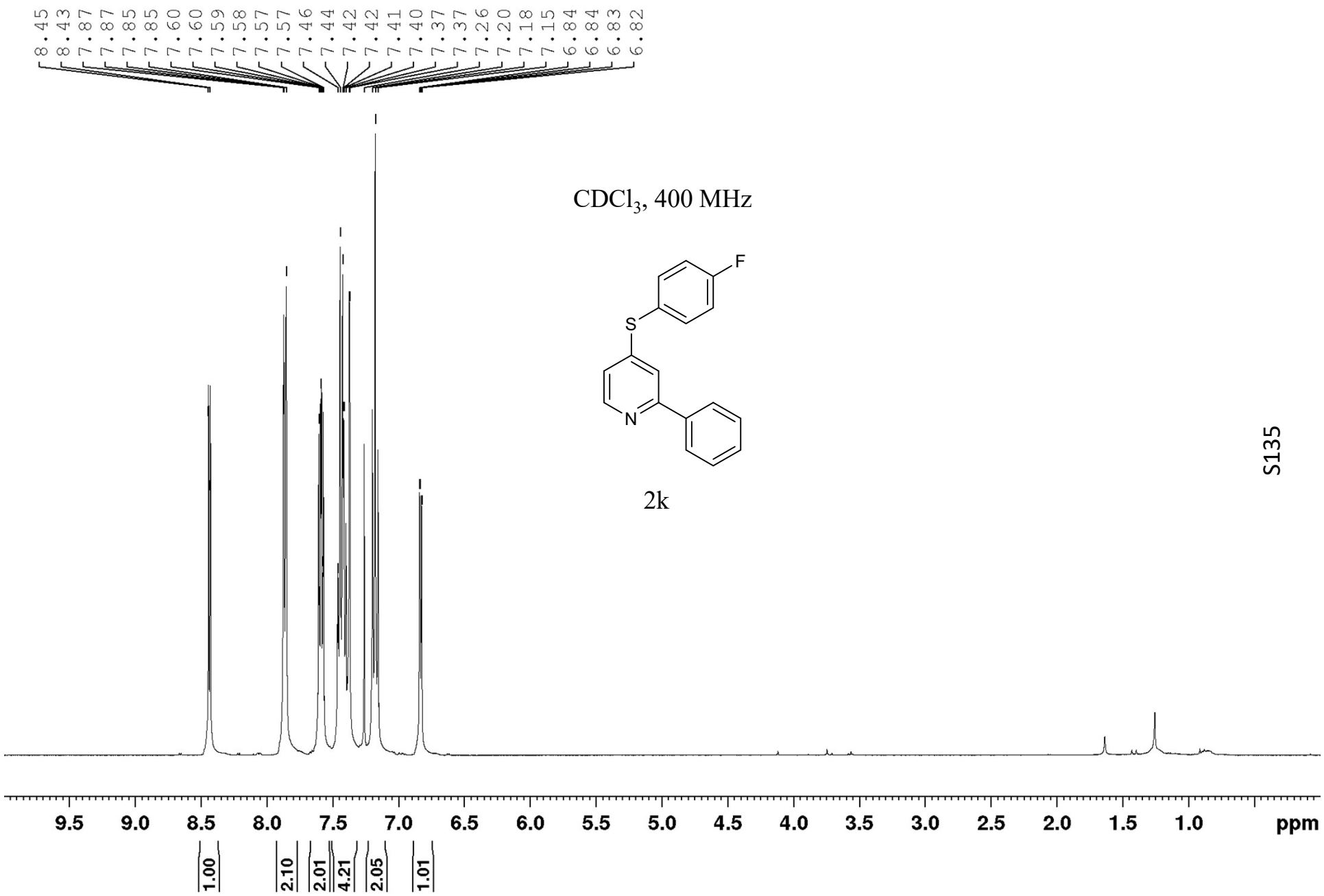

172.1
165.4
159.6
155.0
153.2
151.1
139.0
133.3
131.0
129.1
128.6
126.9
120.7
110.6
109.1
79.9
77.3
77.2
77.0
76.7
54.4
52.2
37.9
28.2
CDCl3, 100 MHz
O
OMe
HN
O
O
O
O
N
2h
S130
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

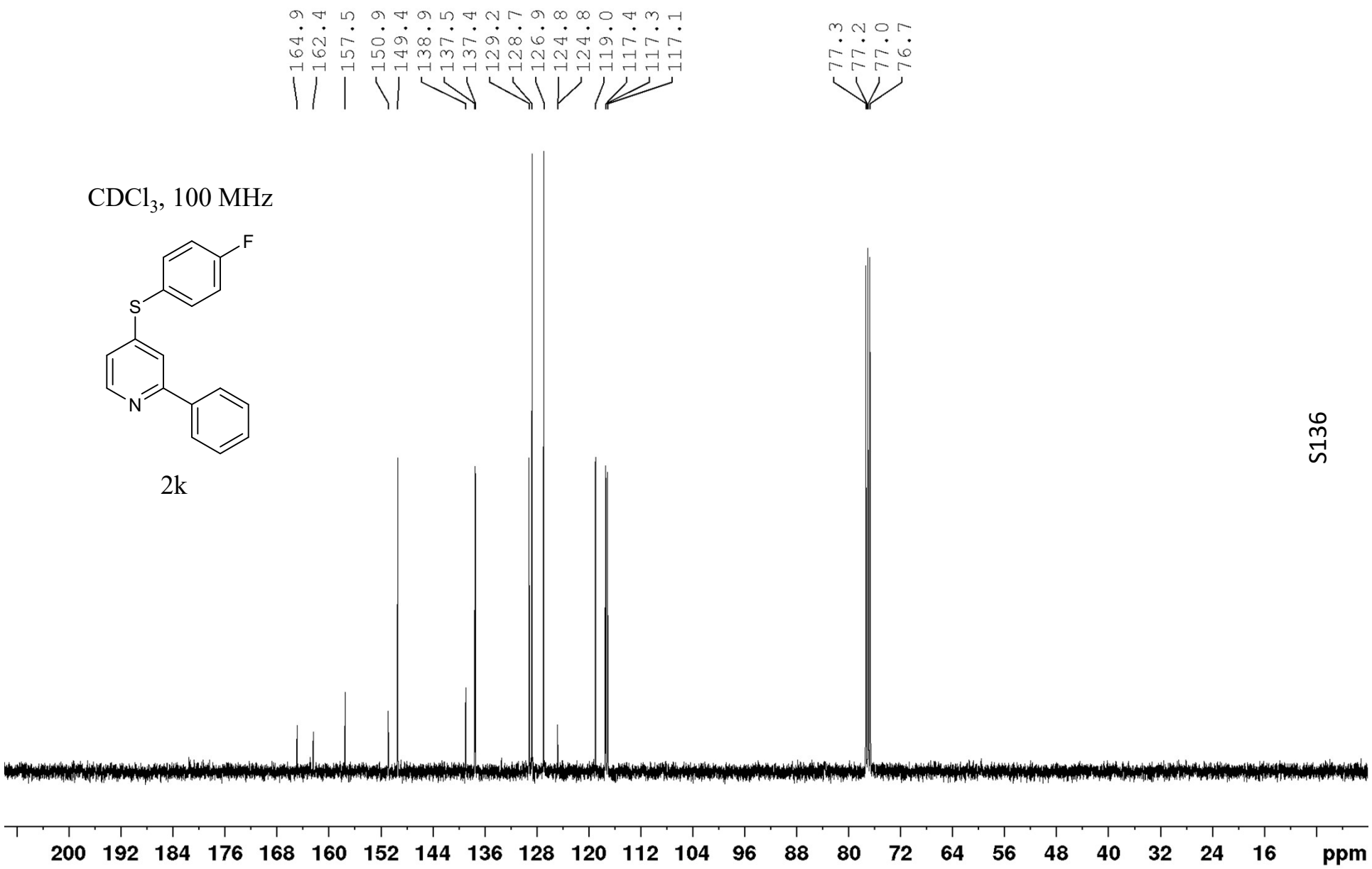

7.86
7.86
7.85
7.85
7.61
7.61
7.60
7.59
7.59
7.58
7.57
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
6.88
6.88
6.87
6.87
CDCl3, 400 MHz
S
N
2i
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.10
2.01
7.27
1.02

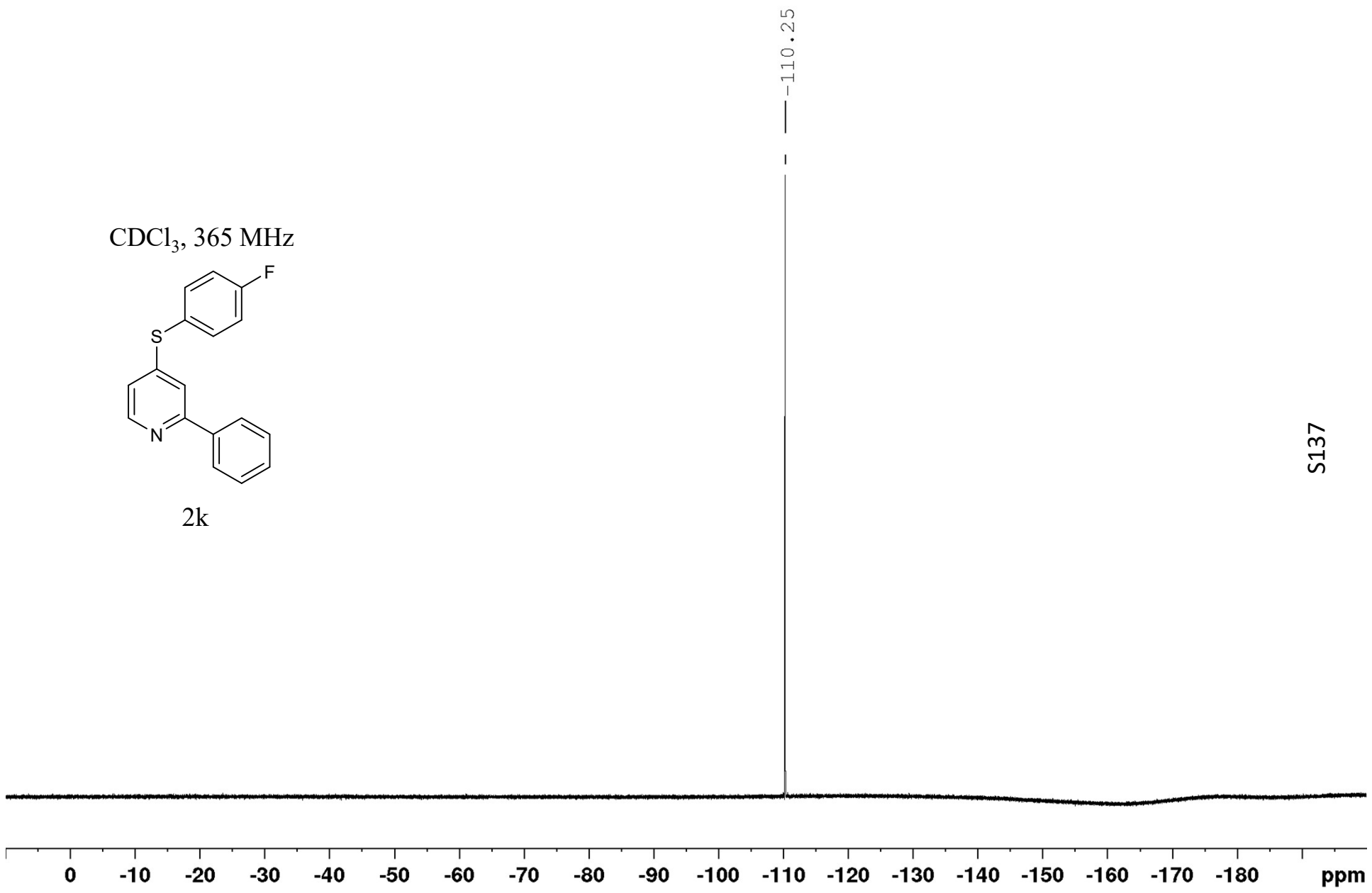

157.4
150.8
149.4
139.0
135.0
129.9
129.7
129.6
129.1
128.7
126.9
119.4
117.8
77.3
77.0
76.7
CDCl3, 100 MHz
S
N
2i
S132
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

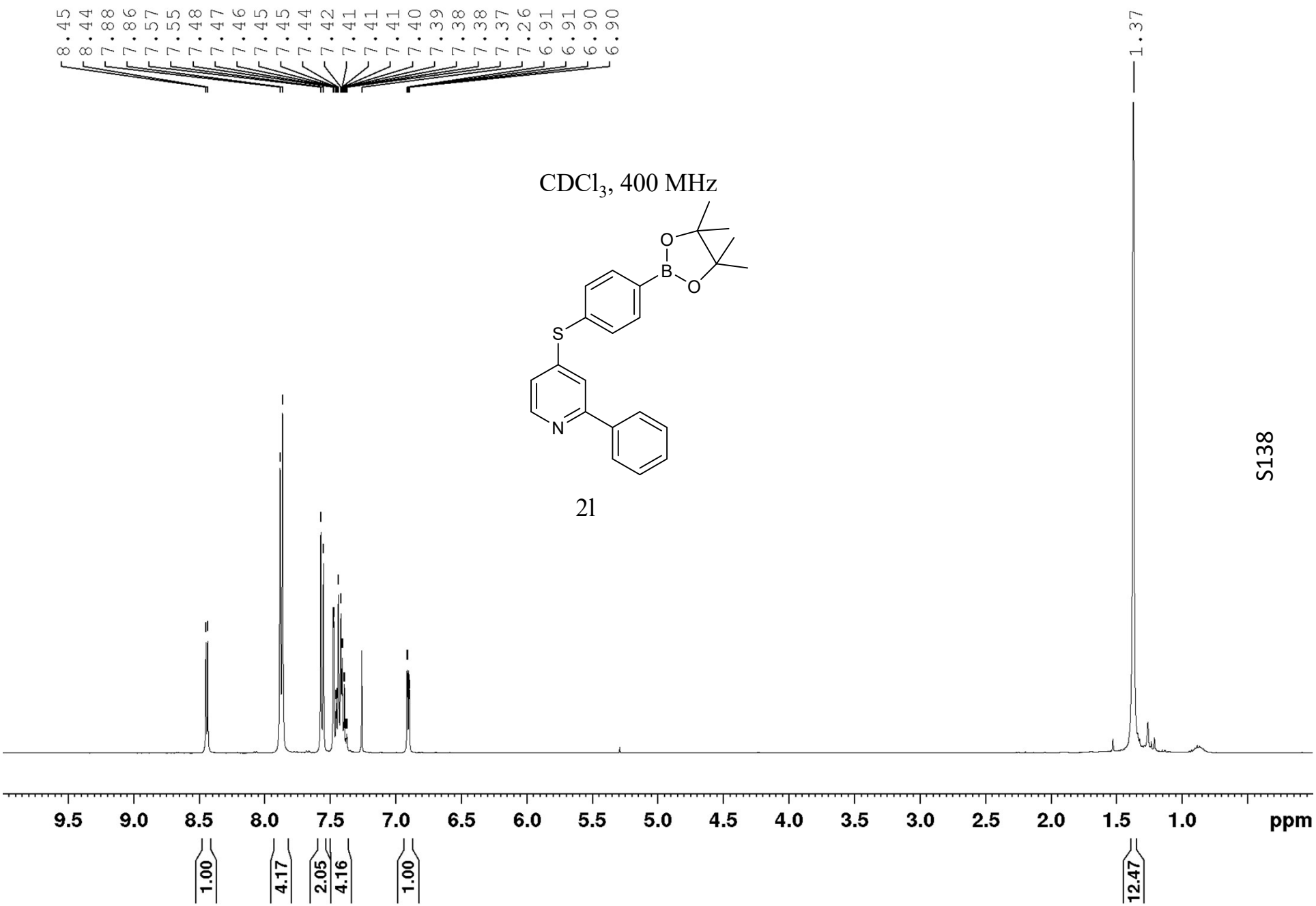

8.46
8.45
7.88
7.88
7.87
7.87
7.86
7.86
7.53
7.53
7.52
7.51
7.51
7.50
7.47
7.47
7.46
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.26
6.88
6.88
6.87
6.86
CDCl3, 400 MHz
Cl
S
N
2j
S133
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
2.05
6.17
1.01

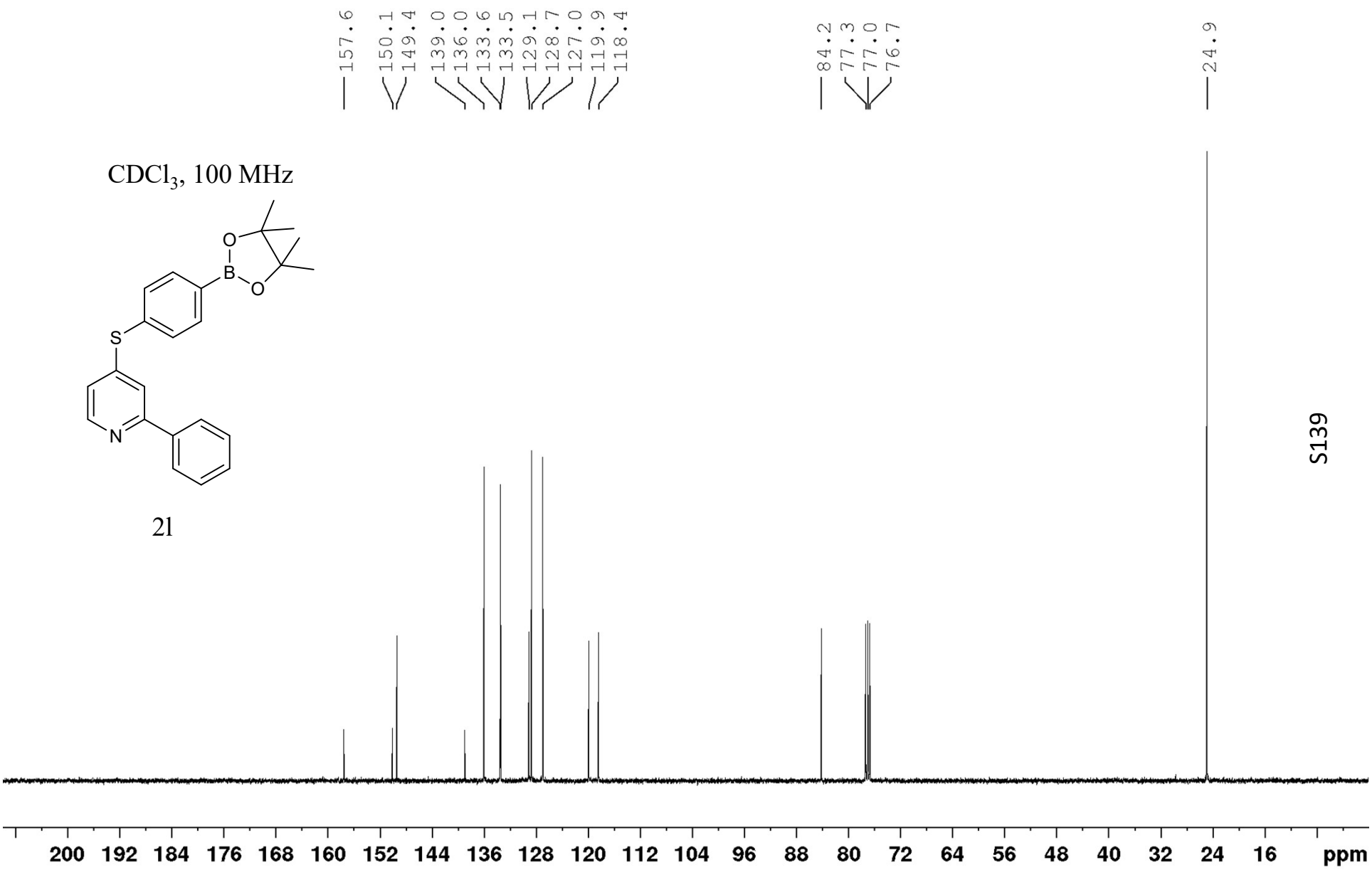

157.6
150.0
149.5
138.9
136.1
136.0
130.2
129.2
128.8
128.4
126.9
119.4
117.9
77.3
77.0
76.7
CDCl3, 100 MHz
Cl
S
N
2j
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

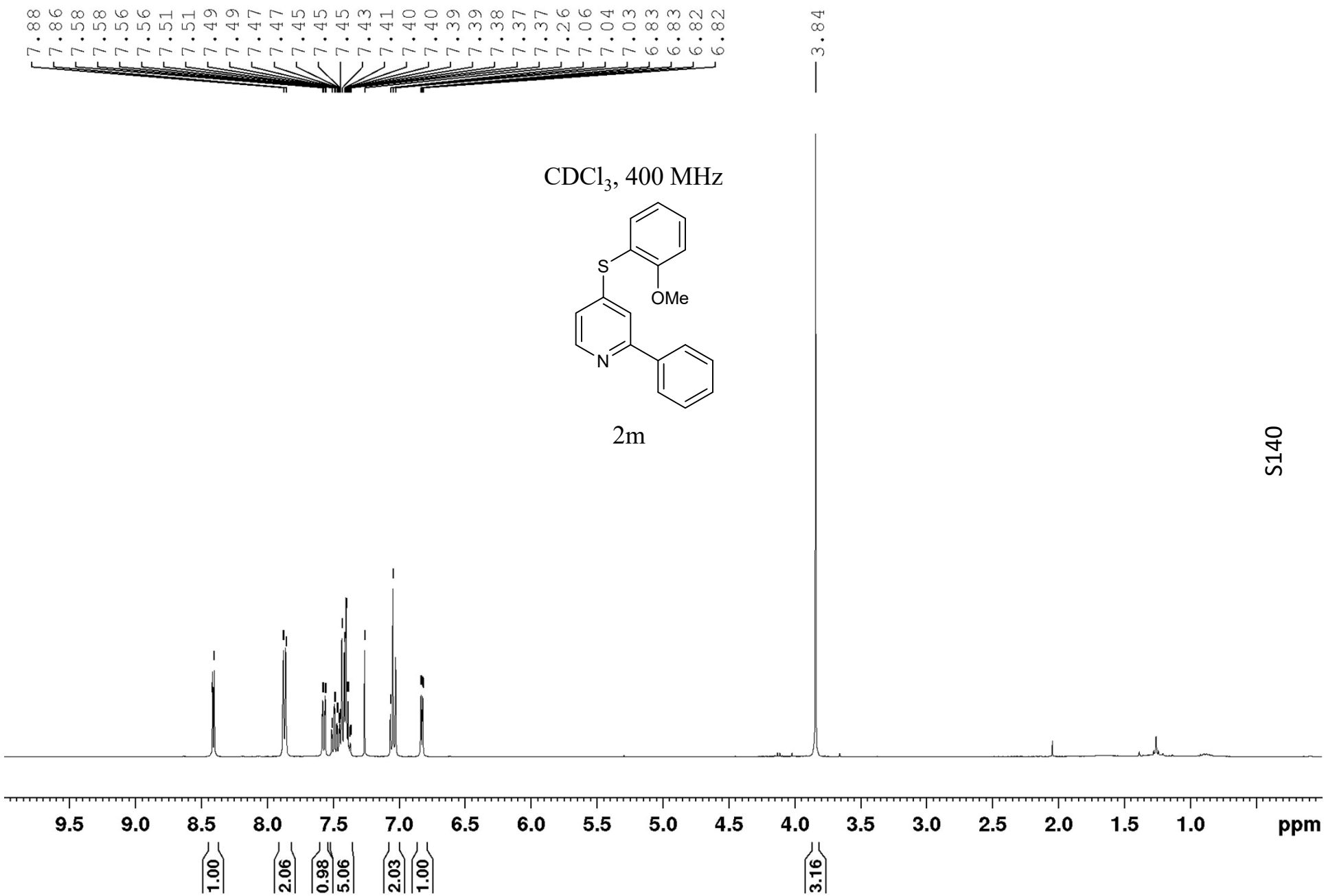

8.45
8.43
7.87
7.87
7.85
7.85
7.60
7.60
7.59
7.58
7.57
7.57
7.46
7.44
7.42
7.42
7.41
7.40
7.37
7.37
7.26
7.20
7.18
7.15
6.84
6.84
6.83
6.82
CDCl3, 400 MHz
F
S
N
2k
S135
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.10
2.01
4.21
2.05
1.01

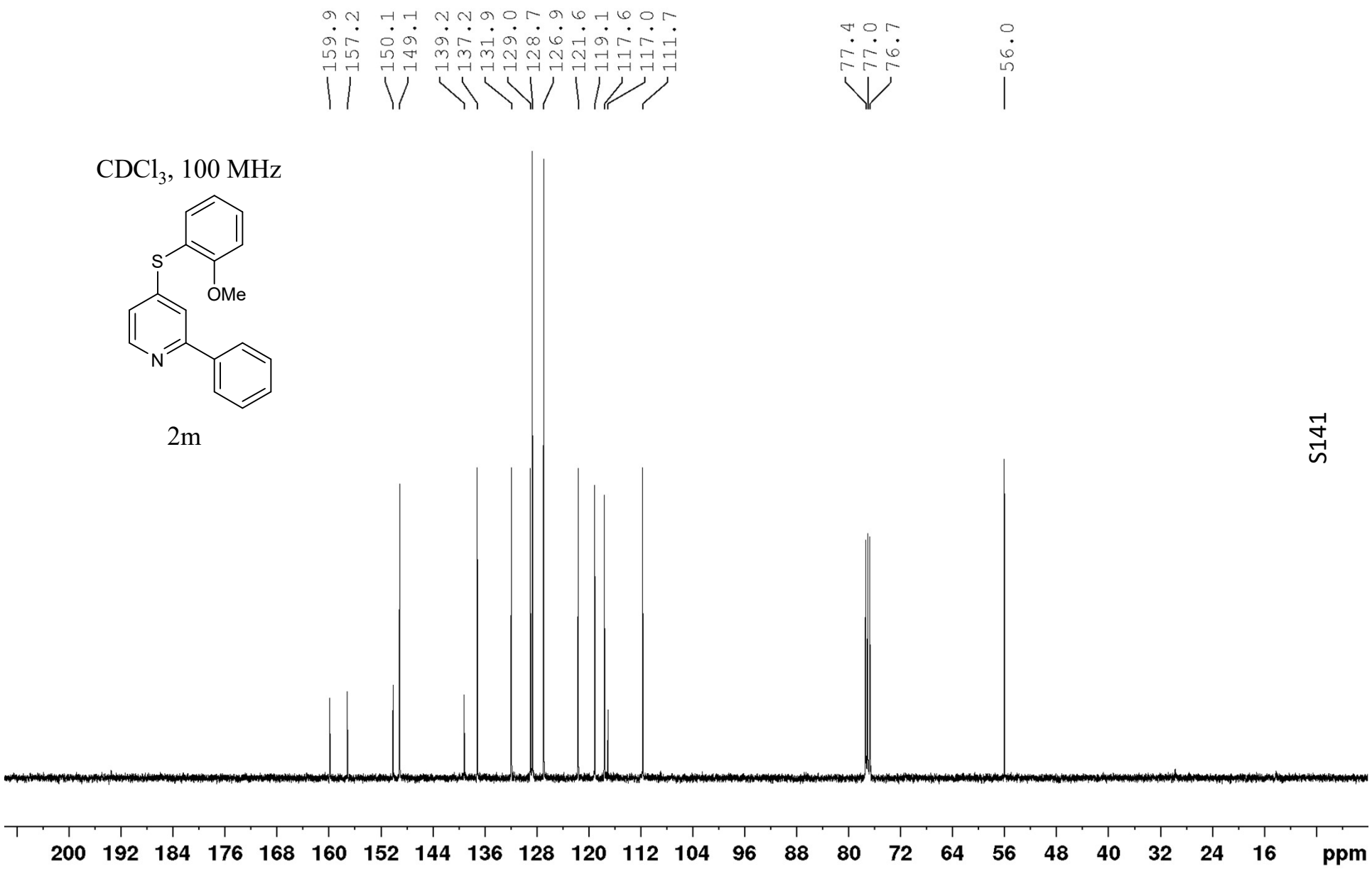

164.9
162.4
157.5
150.9
149.4
138.9
137.5
137.4
129.2
128.7
126.9
124.8
124.8
119.0
117.4
117.3
117.1
77.3
77.2
77.0
76.7
CDCl3, 100 MHz
F
S
N
2k
S136
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

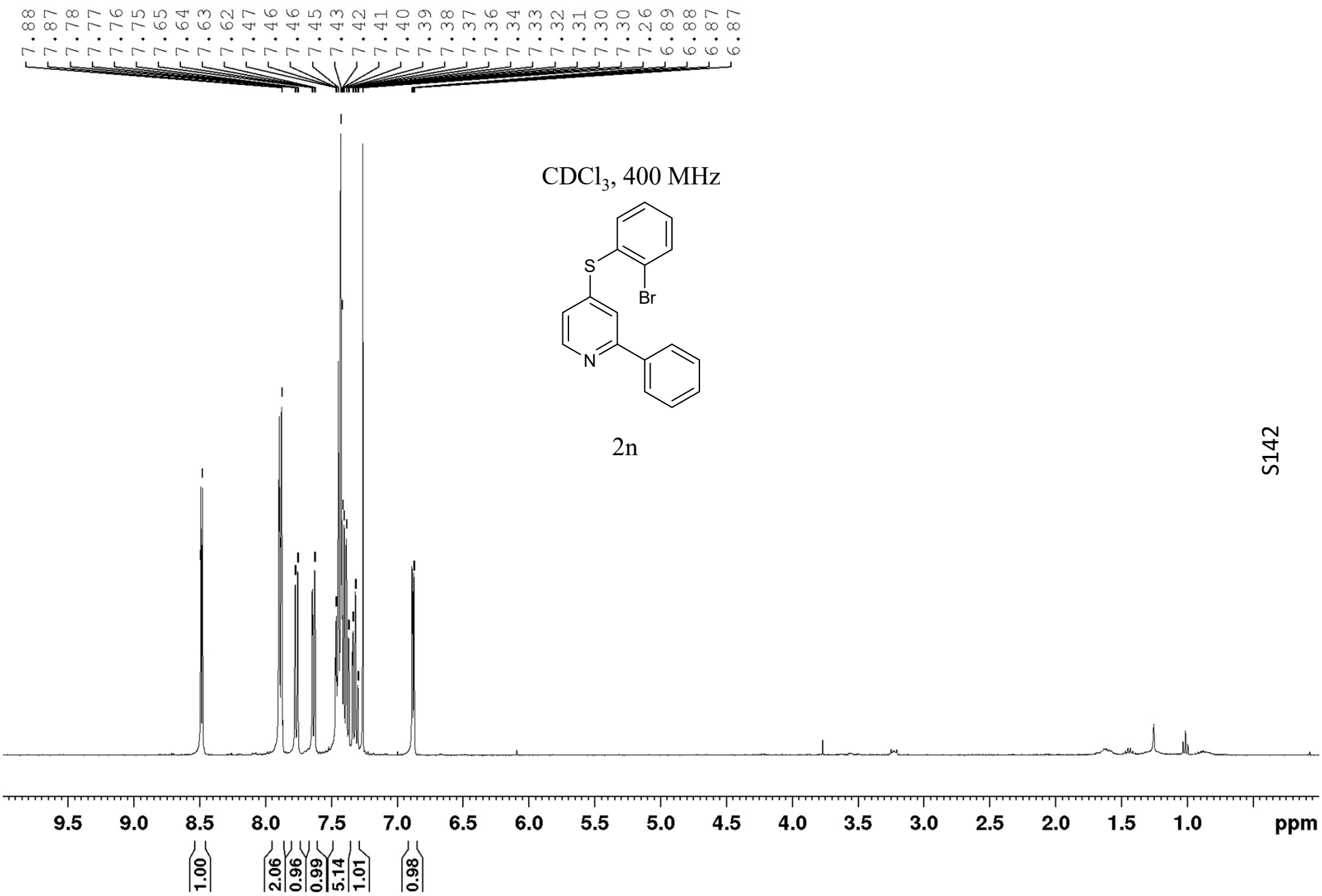

-110.25
CDCl3, 365 MHz
F
S
N
2k
S137
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

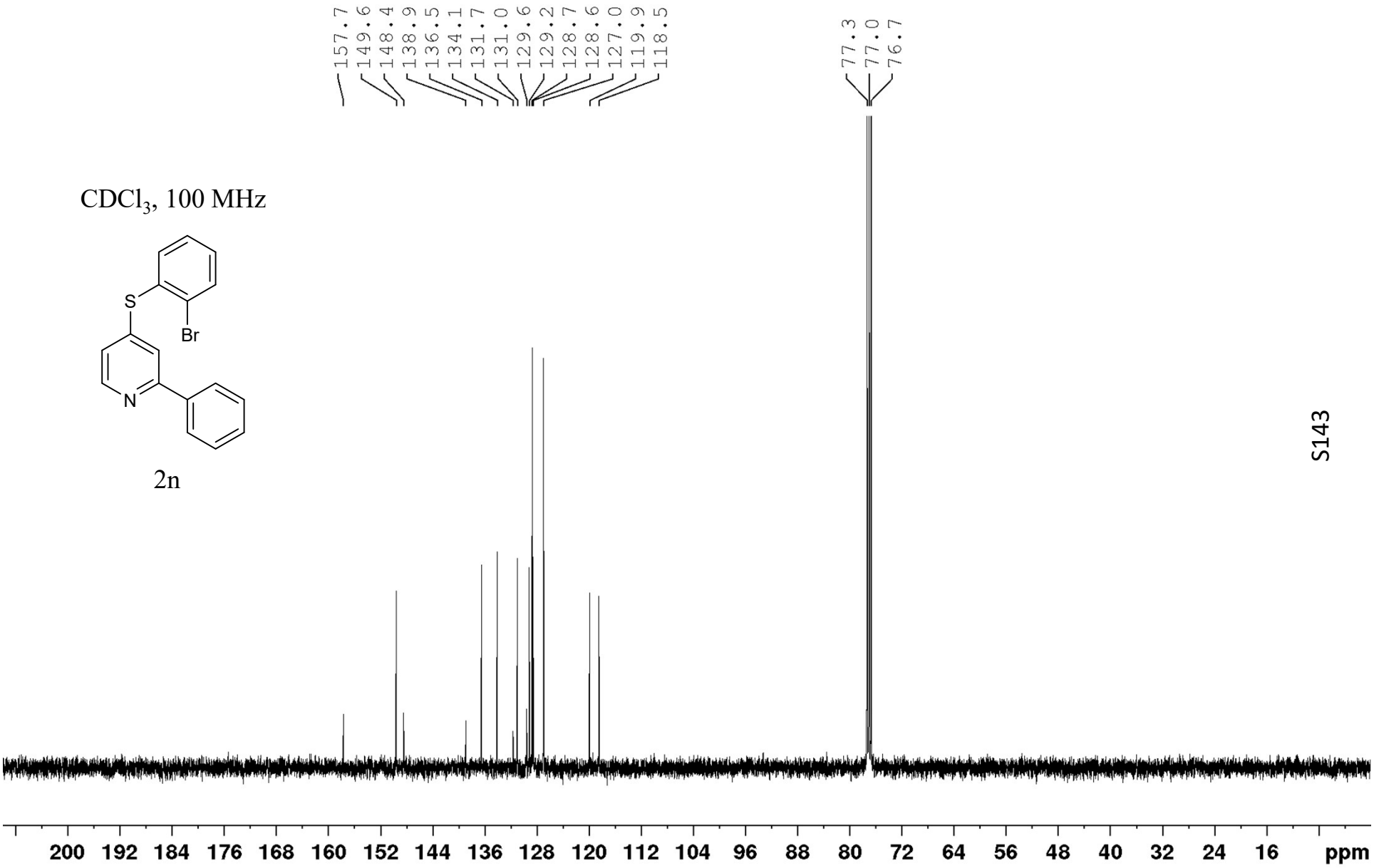

8.45
8.44
7.88
7.86
7.57
7.55
7.48
7.47
7.46
7.45
7.45
7.44
7.42
7.41
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.26
6.91
6.91
6.90
6.90
1.37
CDCl3, 400 MHz
O
B
O
S
N
21
S138
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
4.17
2.05
4.16
1.00
12.47

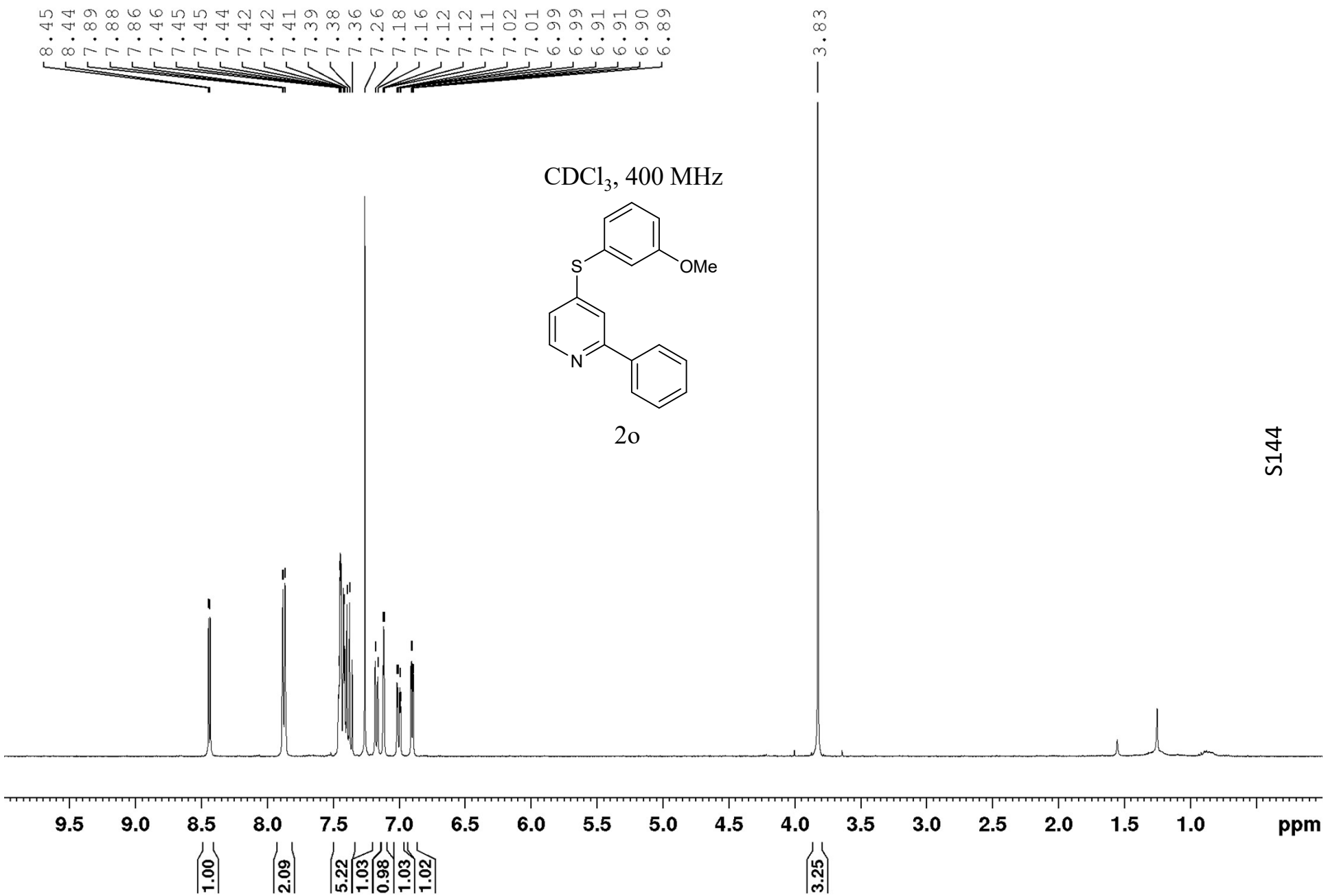

157.6
150.1
149.4
139.0
136.0
133.6
133.5
129.1
128.7
127.0
119.9
118.4
84.2
77.3
77.0
76.7
24.9
CDCl3, 100 MHz
O
B
O
S
N
21
S139
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

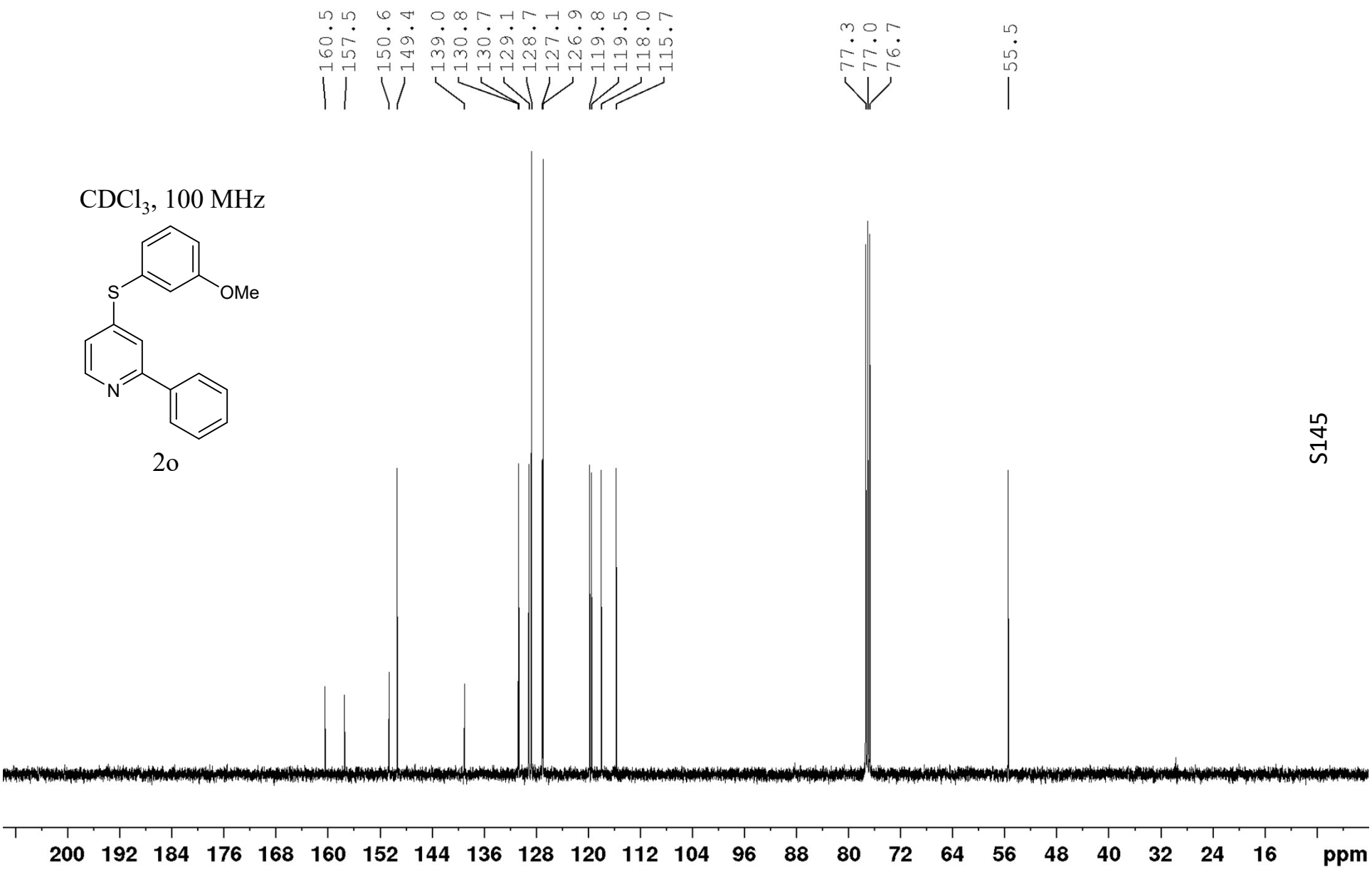

7.88
7.86
7.58
7.58
7.56
7.56
7.51
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.45
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.26
7.06
7.04
7.03
6.83
6.83
6.82
6.82
3.84
CDCl3, 400 MHz
S
OMe
N
2m
S140
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
0.98
5.06
2.03
1.00
3.16

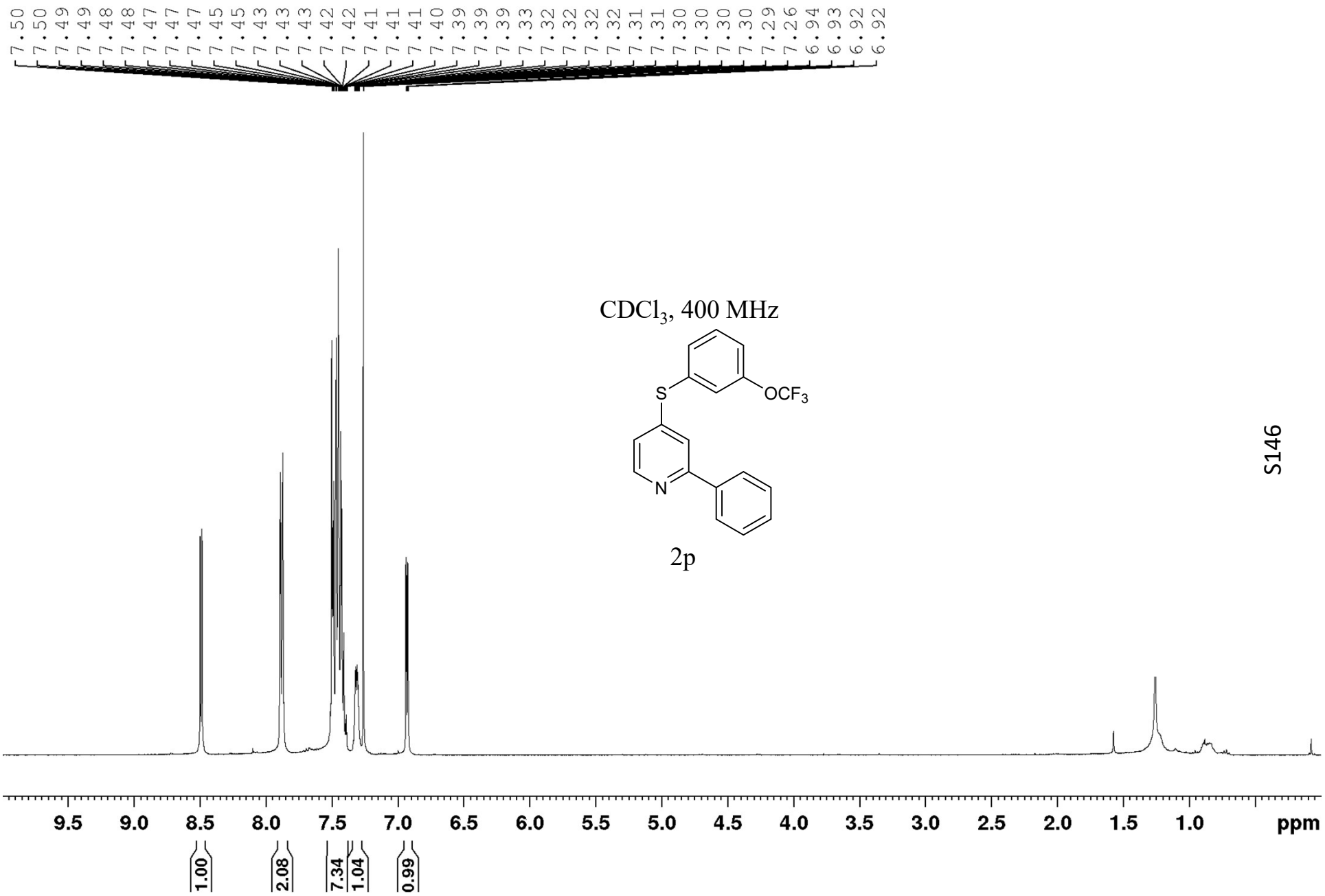

159.9
157.2
150.1
149.1
139.2
137.2
131.9
129.0
128.7
126.9
121.6
119.1
117.6
117.0
111.7
77.4
77.0
76.7
56.0
CDCl3, 100 MHz
S
OMe
N
2m
S141
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

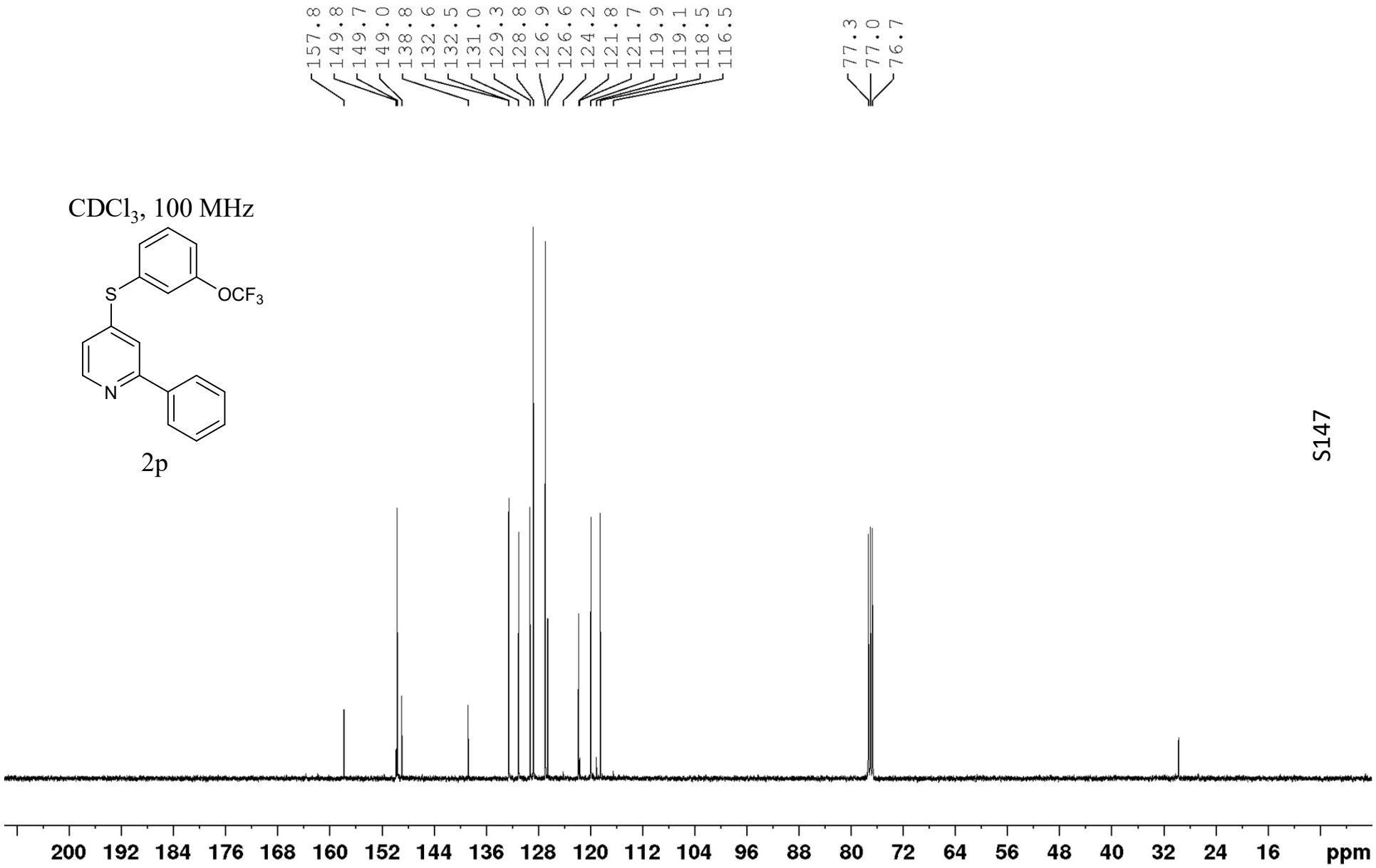

7.88
7.87
7.78
7.77
7.76
7.75
7.65
7.64
7.63
7.62
7.47
7.46
7.46
7.45
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.26
6.89
6.88
6.87
6.87
CDCl3, 400 MHz
S
Br
N
2n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
0.96
0.99
5.14
1.01
0.98

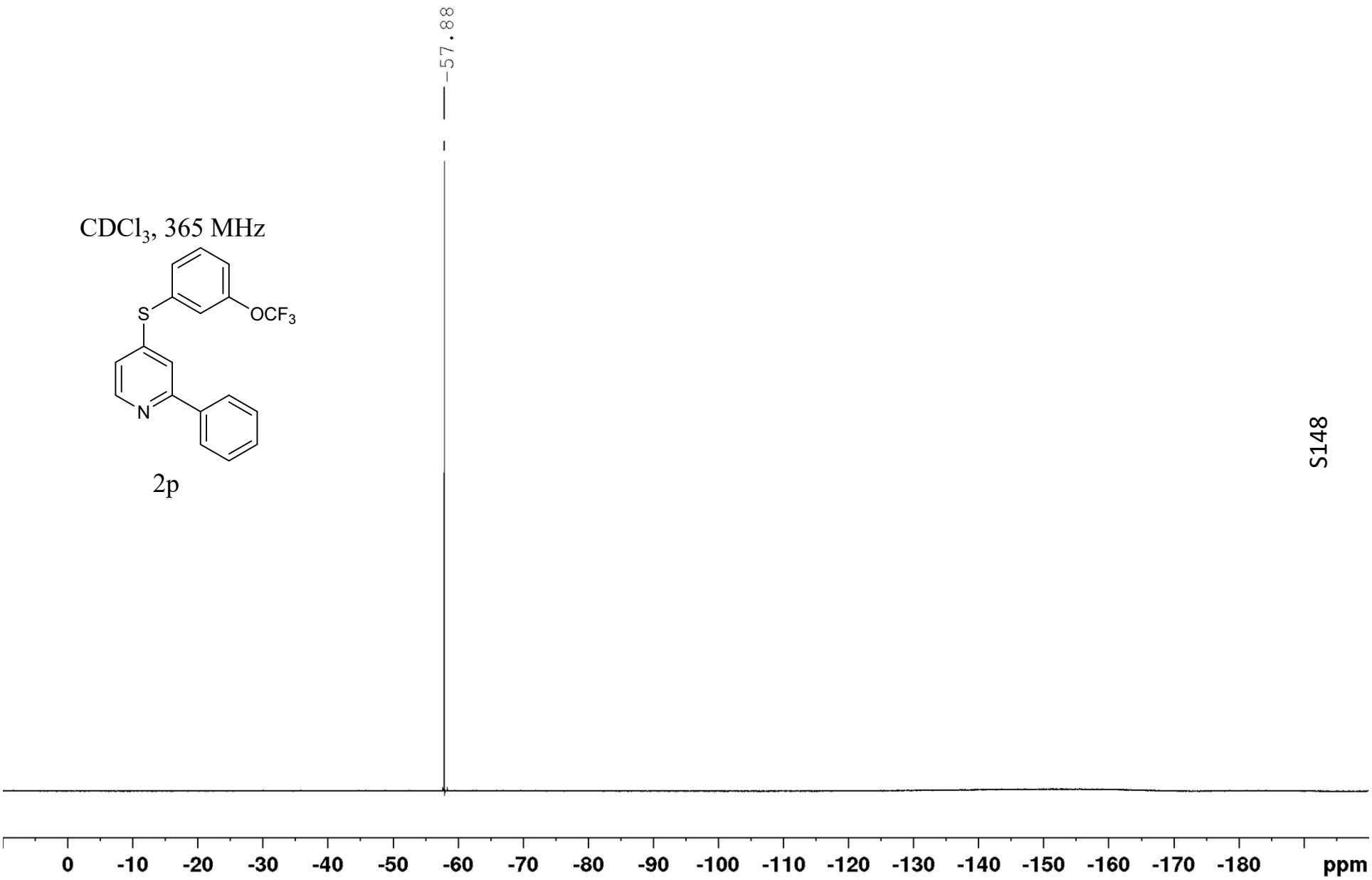

157.7
149.6
148.4
138.9
136.5
134.1
131.7
131.0
129.6
129.2
128.7
128.6
127.0
119.9
118.5
77.3
77.0
76.7
CDCl3, 100 MHz
S
Br
N
2n
S143
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

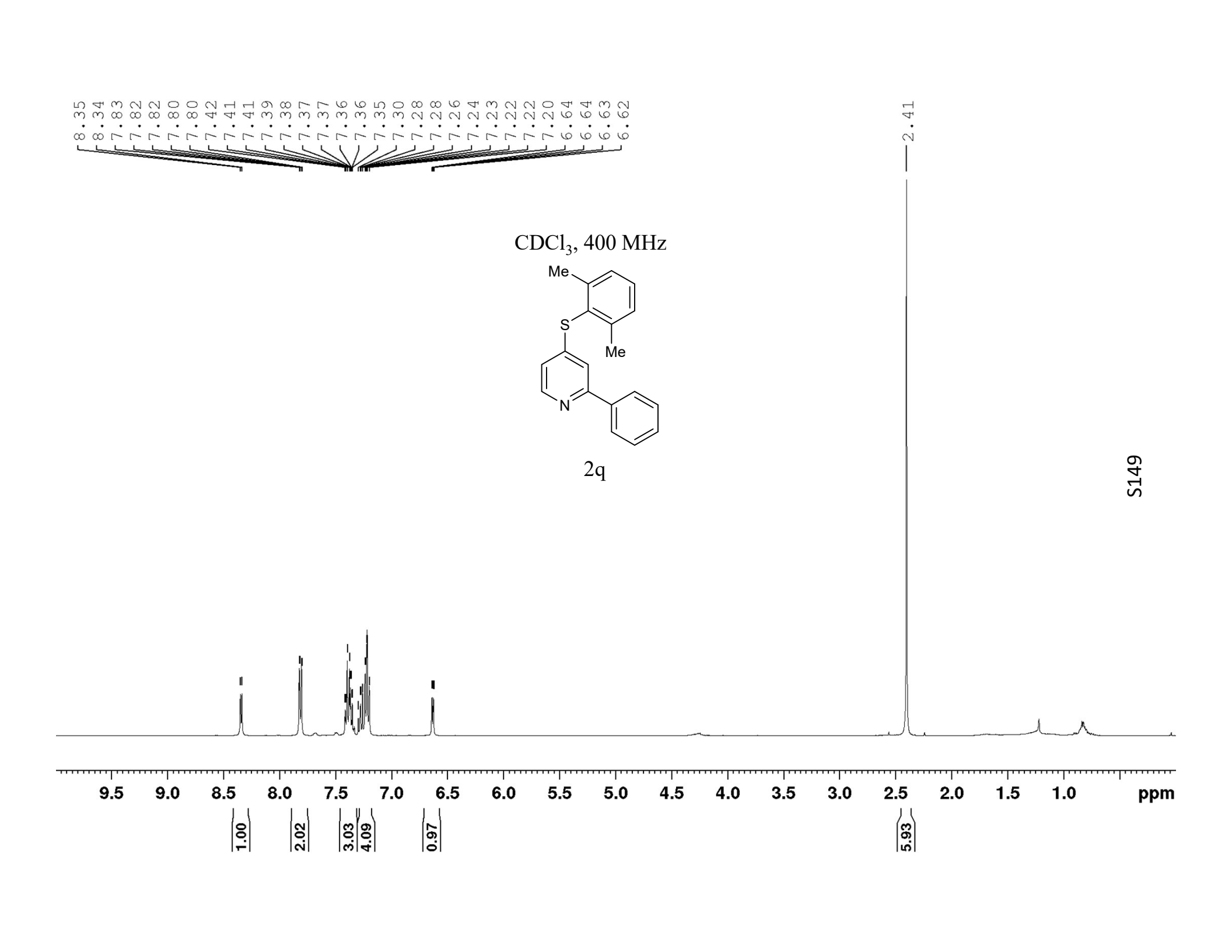

8.45
8.44
7.89
7.88
7.86
7.46
7.45
7.45
7.44
7.42
7.42
7.41
7.39
7.38
7.36
7.26
7.18
7.16
7.12
7.12
7.11
7.02
7.01
6.99
6.99
6.91
6.91
6.90
6.89
3.83
CDCl3, 400 MHz
S
OMe
N
2o
S144
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.09
5.22
1.03
0.98
1.03
1.02
3.25

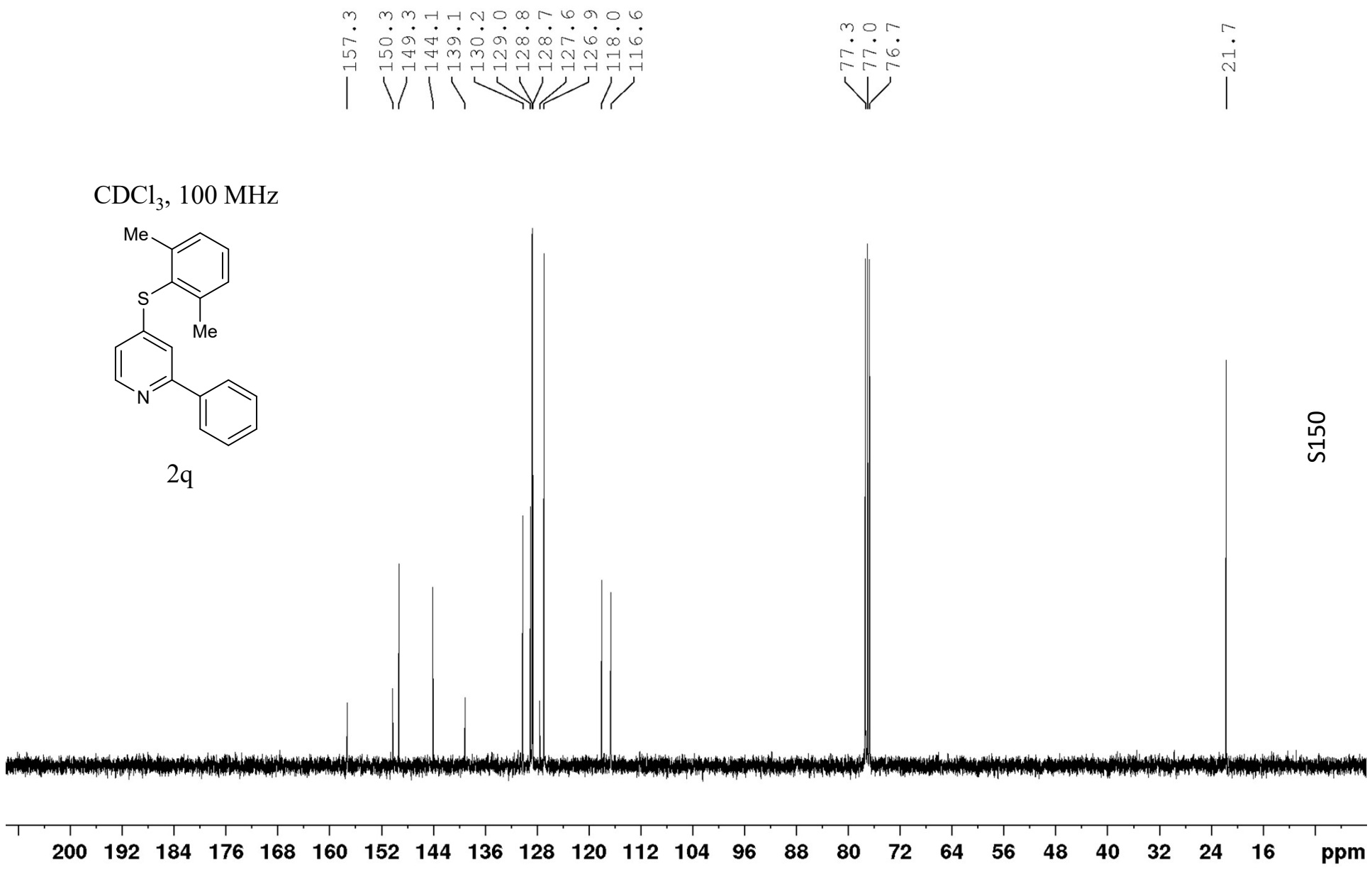

160.5
157.5
150.6
149.4
139.0
130.8
130.7
129.1
128.7
127.1
126.9
119.8
119.5
118.0
115.7
77.3
77.0
76.7
55.5
CDCl3, 100 MHz
S
OMe
N
2o
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

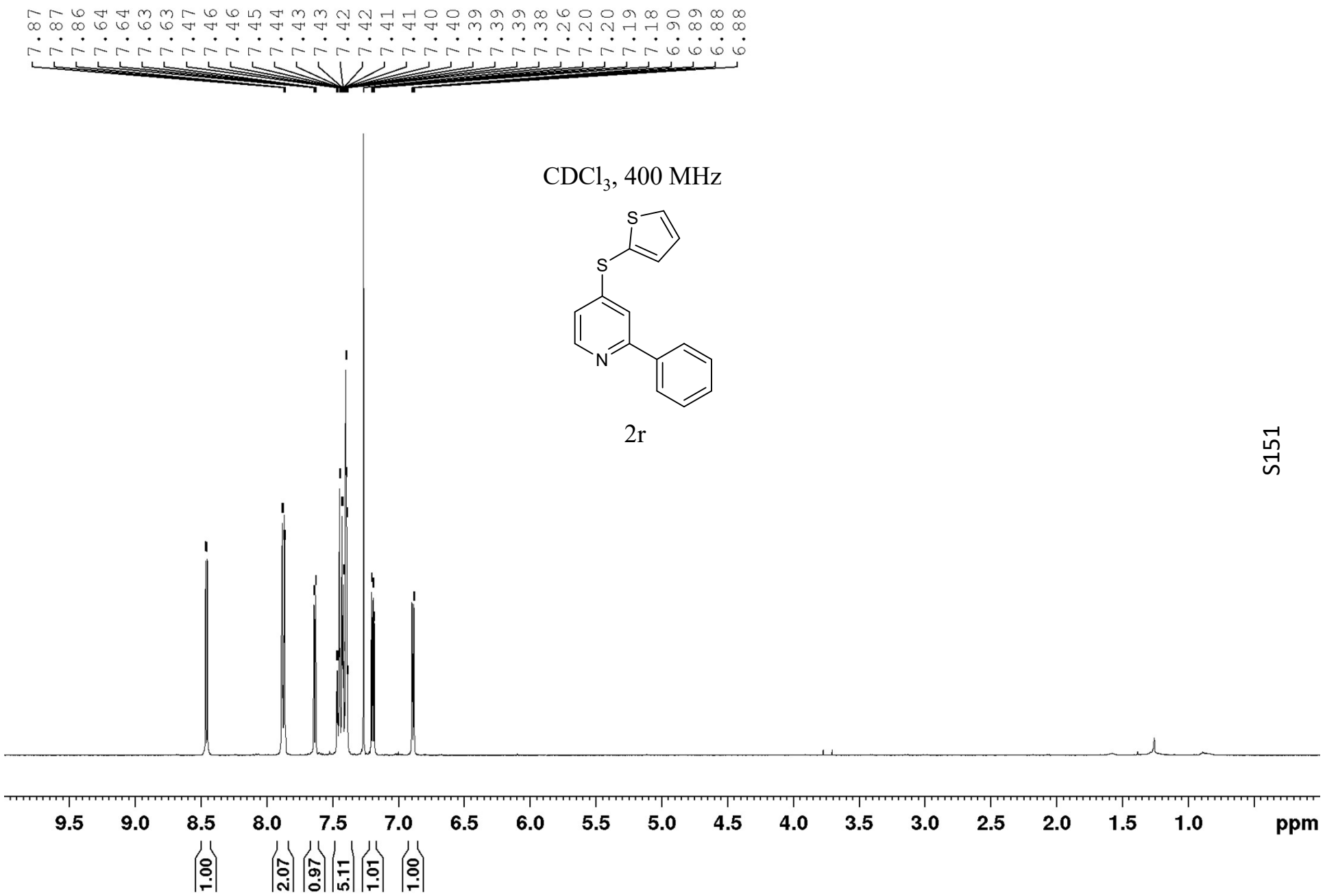

7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.45
7.45
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.39
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.30
7.29
7.26
6.94
6.93
6.92
6.92
CDCl3, 400 MHz
S
OCF3
N
2p
S146
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.08
7.34
1.04
0.99


157.8
149.8
149.7
149.0
138.8
132.6
132.5
131.0
129.3
128.8
126.9
126.6
124.2
121.8
121.7
119.9
119.1
118.5
116.5
77.3
77.0
76.7
CDCl3, 100 MHz
S
OCF3
N
2p
S147
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

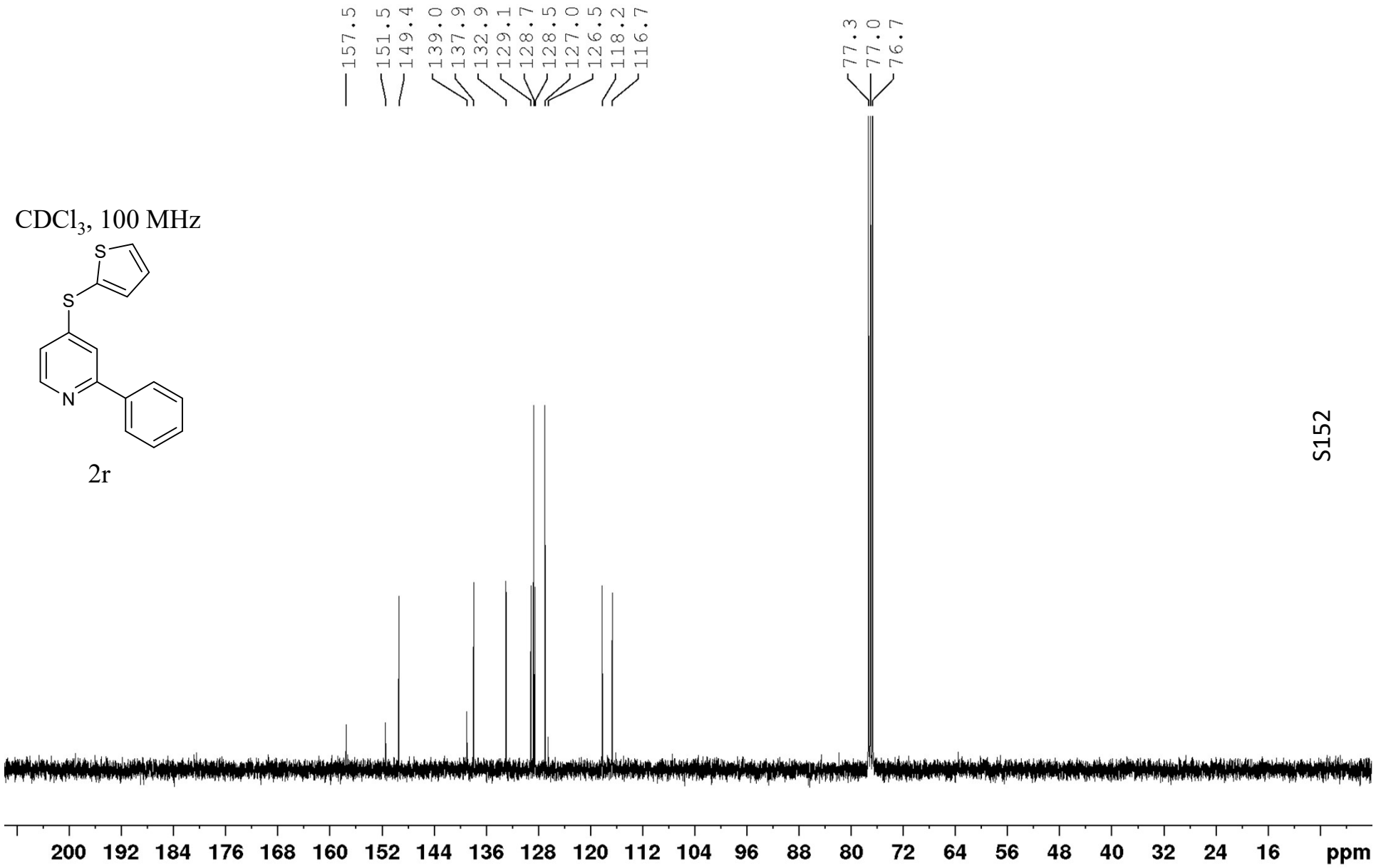

-57.88
CDCl3, 365 MHz
S
OCF3
N
2p
S148
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

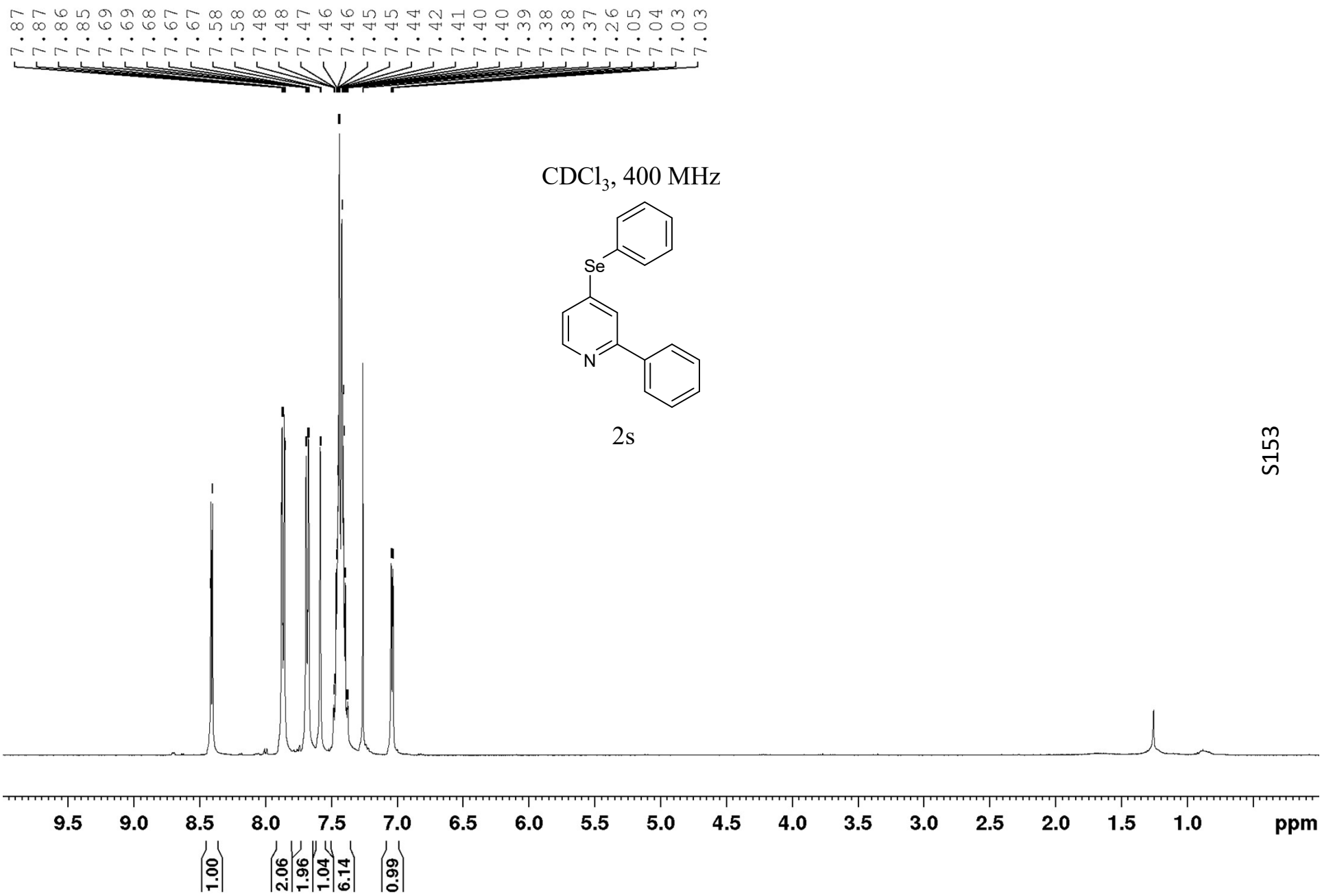

8.35
8.34
7.83
7.82
7.82
7.80
7.80
7.42
7.41
7.41
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.30
7.28
7.28
7.26
7.24
7.23
7.22
7.22
7.20
6.64
6.64
6.63
6.62
2.41
CDCl3, 400 MHz
Me
S
Me
N
2q
S149
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.02
3.03
4.09
0.97
5.93

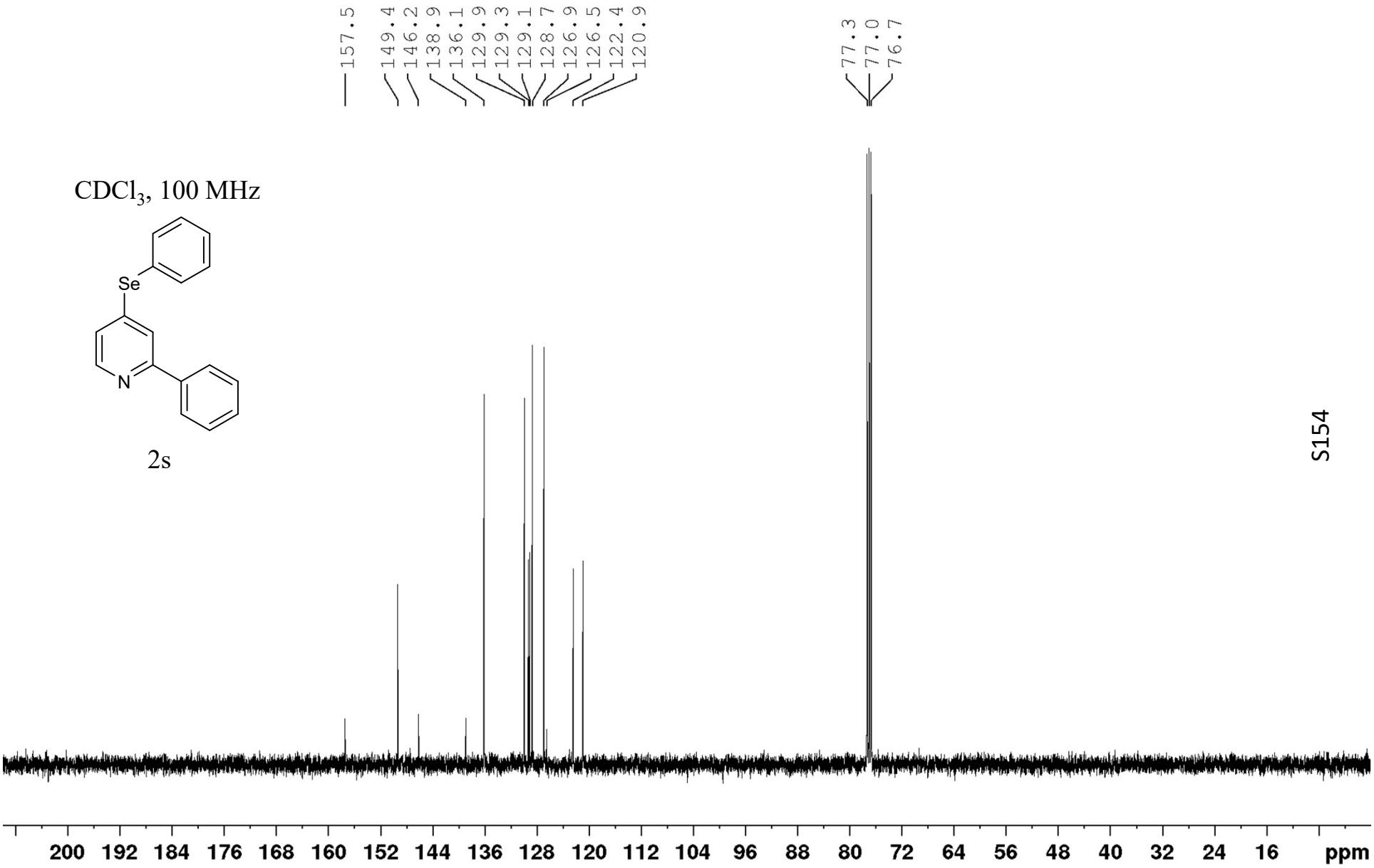

157.3
150.3
149.3
144.1
139.1
130.2
129.0
128.8
128.7
127.6
126.9
118.0
116.6
77.3
77.0
76.7
21.7
CDCl3, 100 MHz
Me
S
Me
N
2q
S150
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

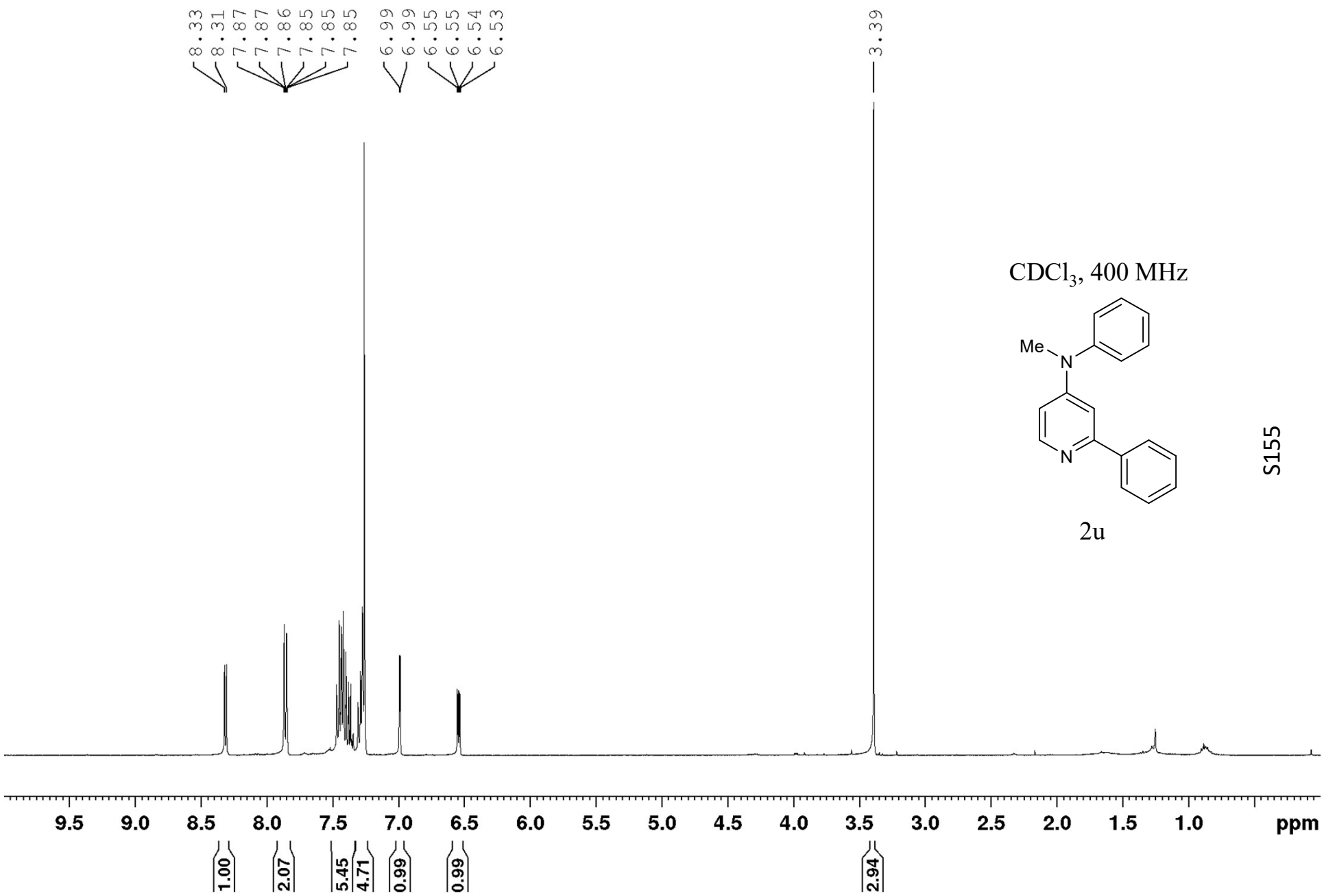

7.87
7.87
7.86
7.64
7.64
7.63
7.63
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.26
7.20
7.20
7.19
7.18
6.90
6.89
6.88
6.88
CDCl3, 400 MHz
S
S
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.07
0.97
5.11
1.01
1.00

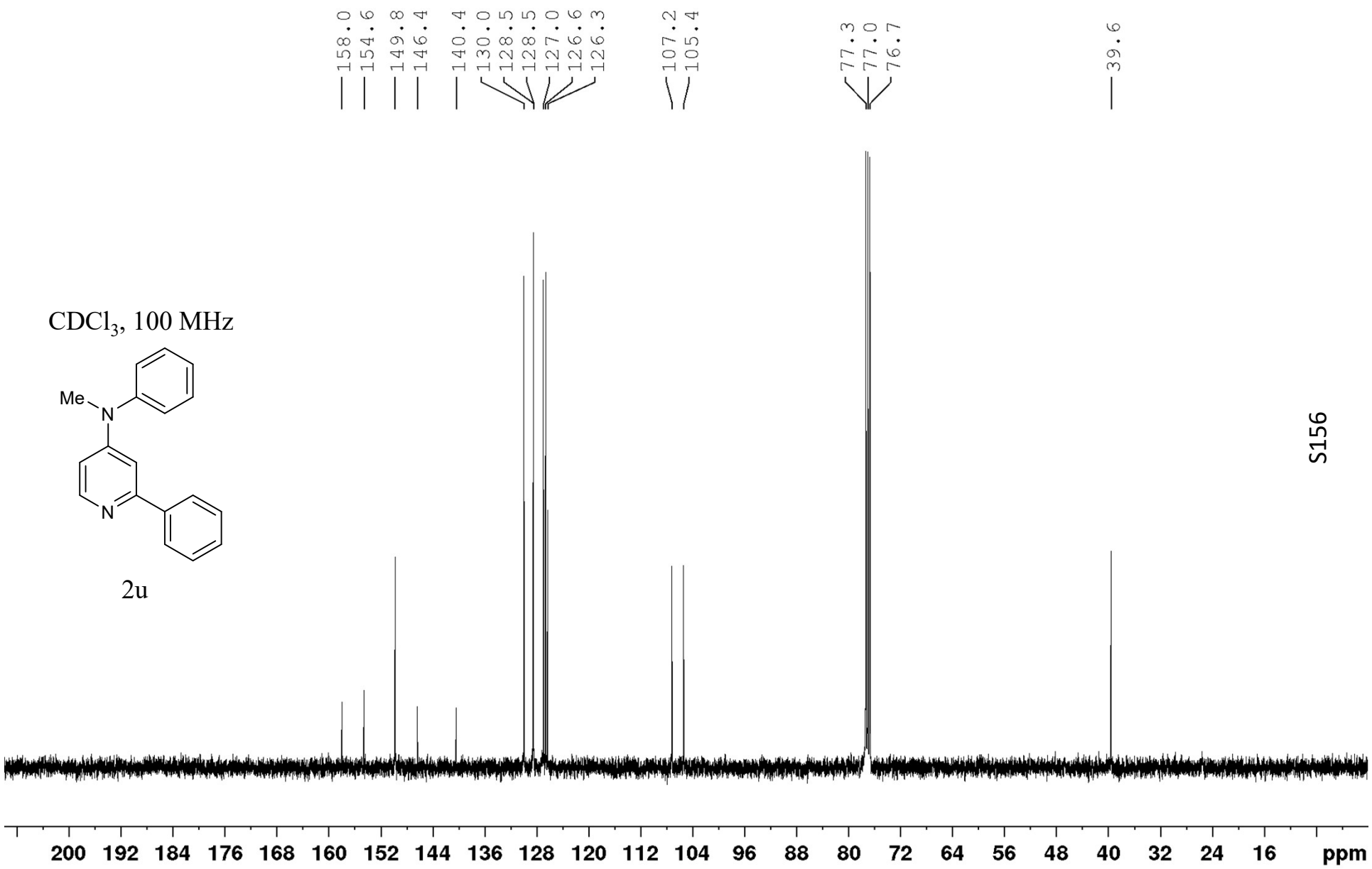
2r

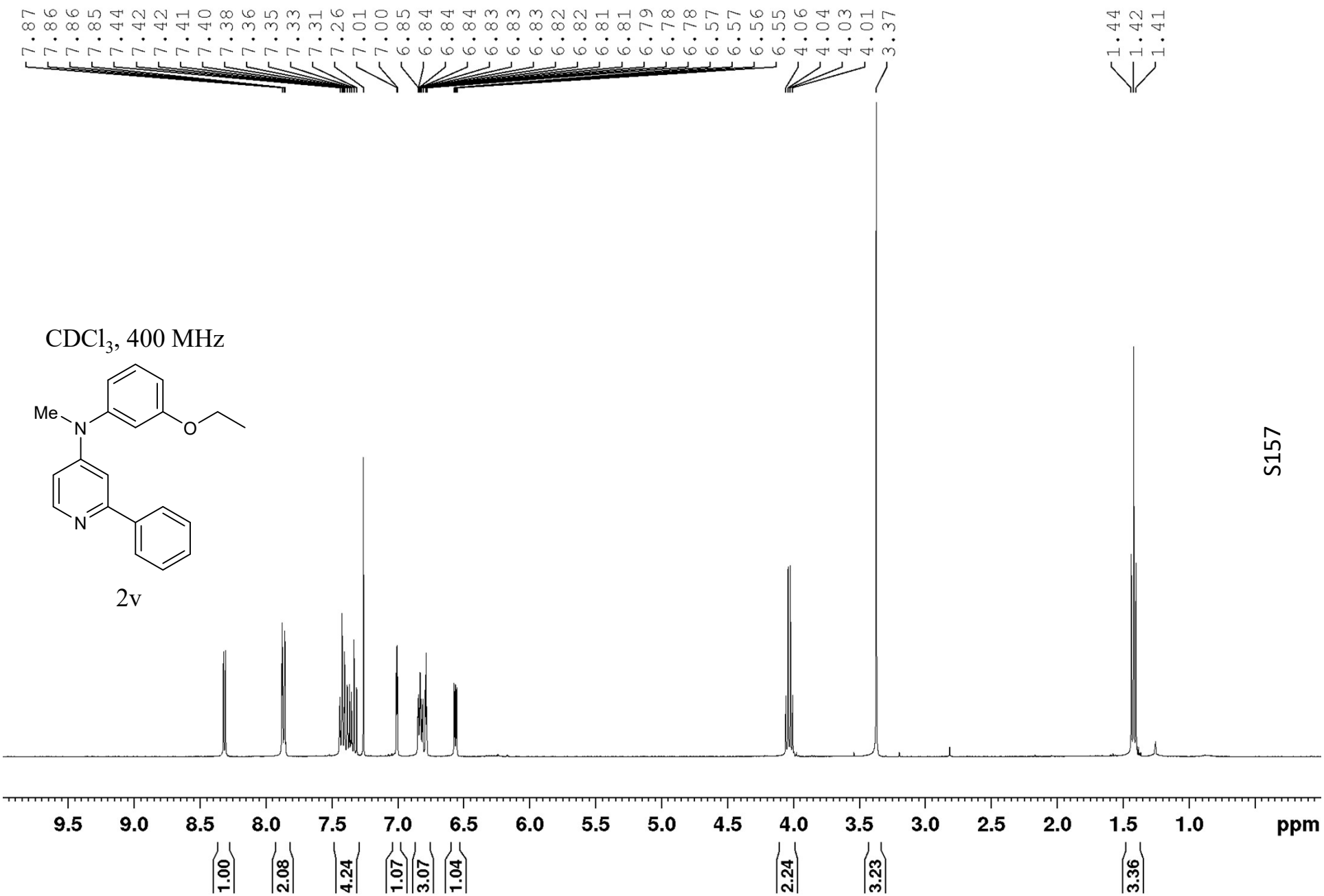

157.5
151.5
149.4
139.0
137.9
132.9
129.1
128.7
128.5
127.0
126.5
118.2
116.7
77.3
77.0
76.7
CDCl3, 100 MHz
S
S
N
2r
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

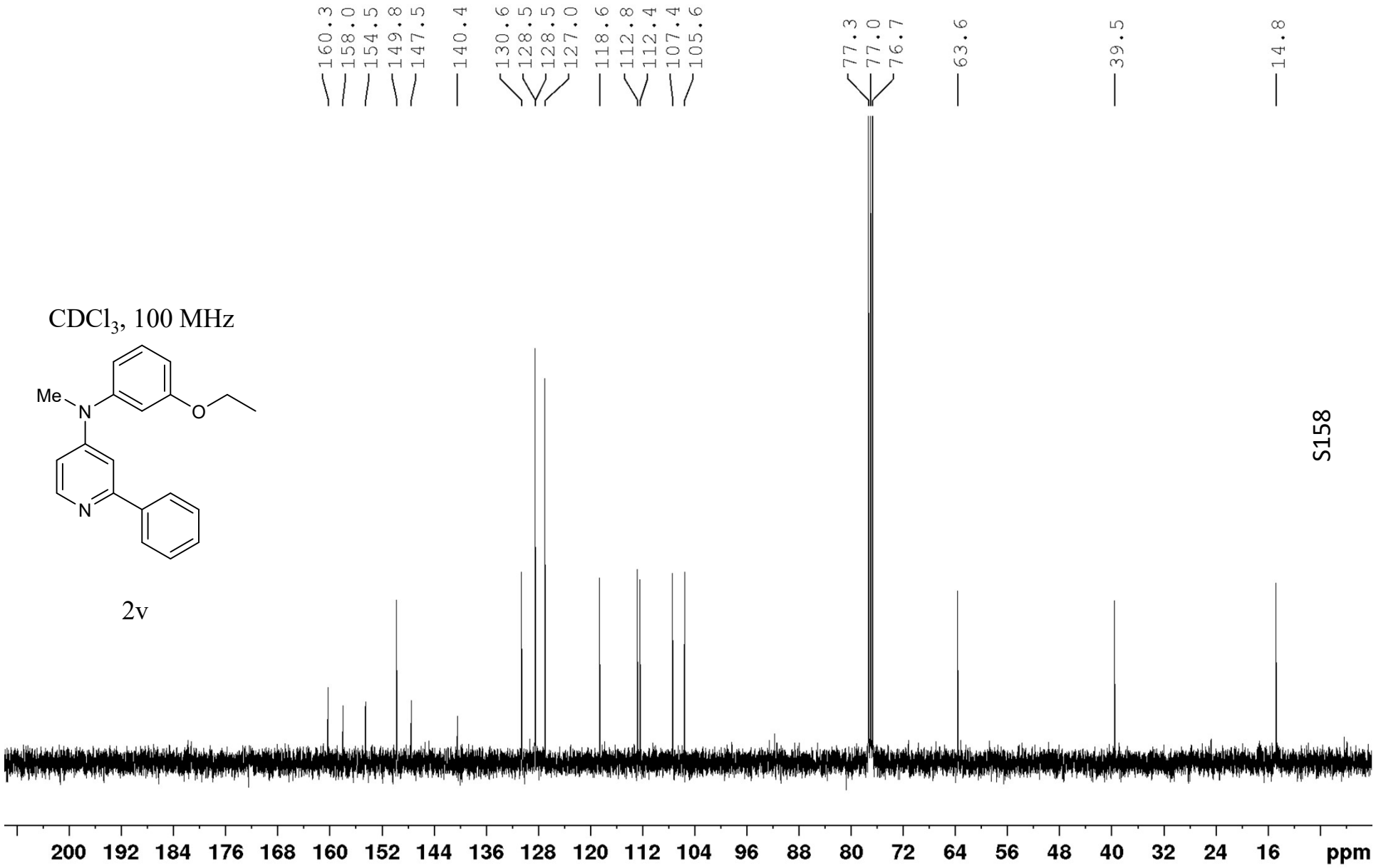

7.87
7.87
7.86
7.85
7.69
7.69
7.68
7.67
7.67
7.58
7.58
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.26
7.05
7.04
7.03
7.03
CDCl3, 400 MHz
Se
N
2s
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.06
1.96
1.04
6.14
0.99

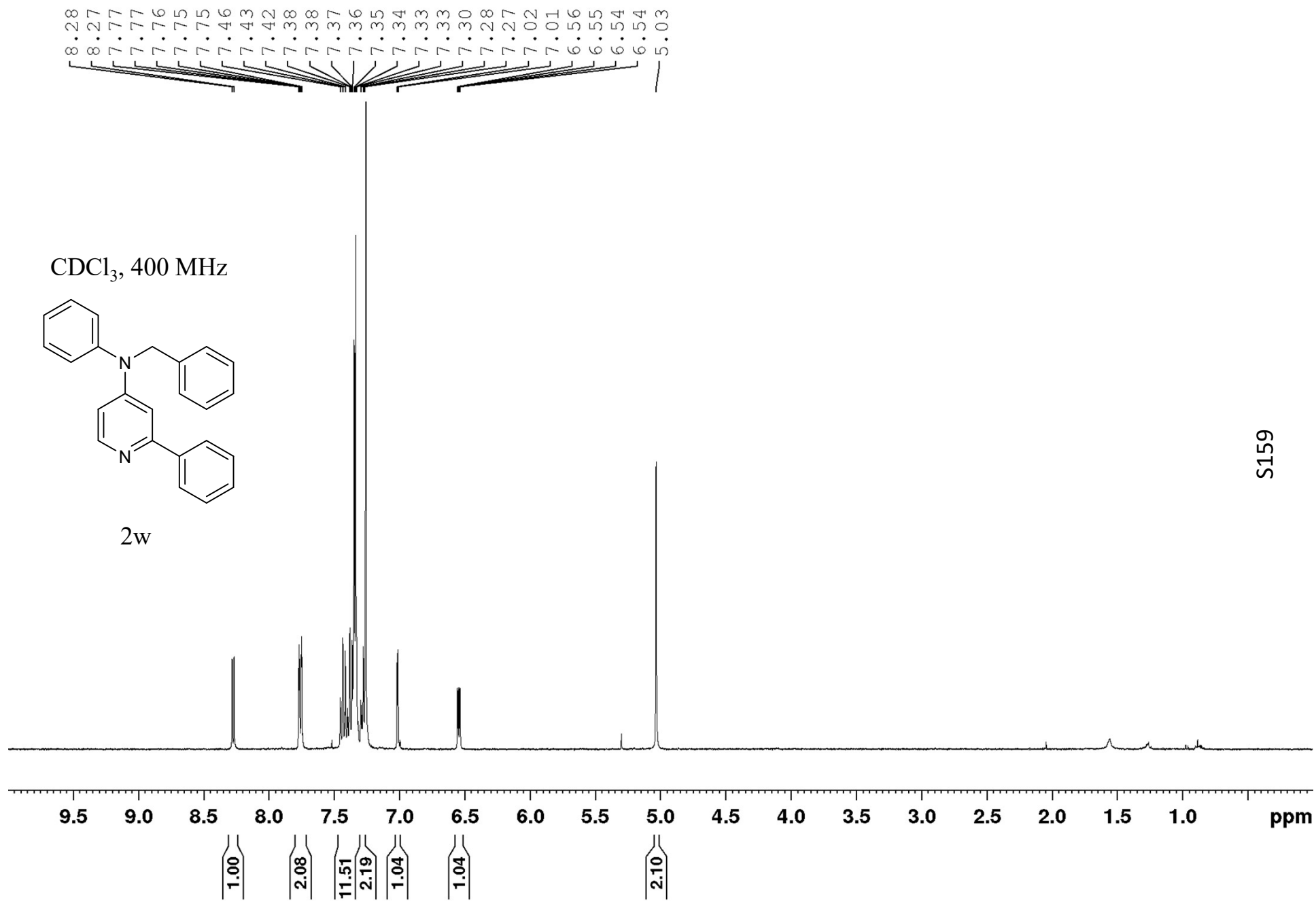

157.5
149.4
146.2
138.9
136.1
129.9
129.3
129.1
128.7
126.9
126.5
122.4
120.9
77.3
77.0
76.7
CDCl3, 100 MHz
Se
N
2s
S154
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

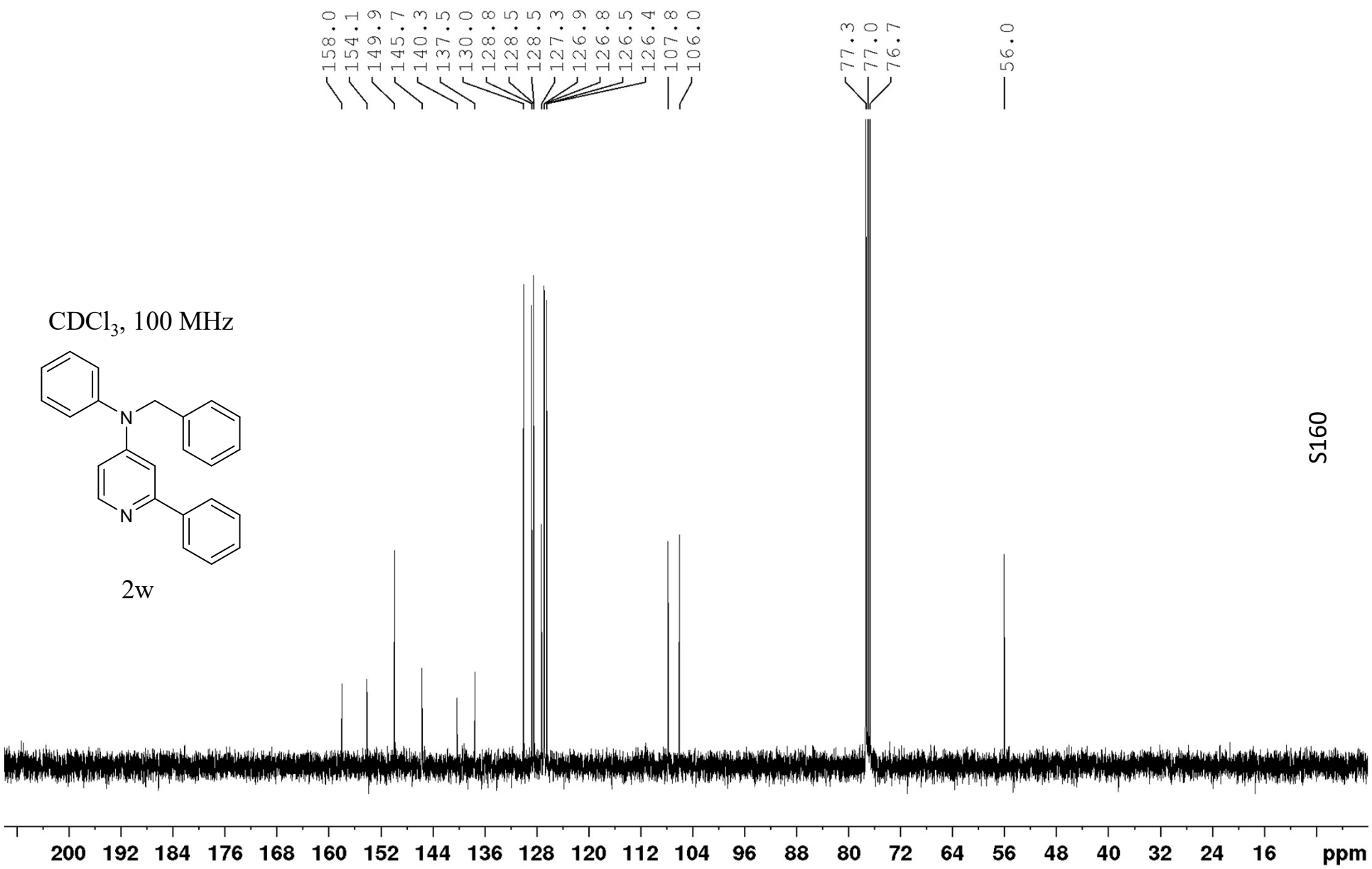

8.33
8.31
7.87
7.87
7.86
7.85
7.85
7.85
6.99
6.99
6.55
6.55
6.54
6.53
3.39
CDCl3, 400 MHz
Me
N
N
2u
S155
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.07
5.45
4.71
0.99
0.99
2.94

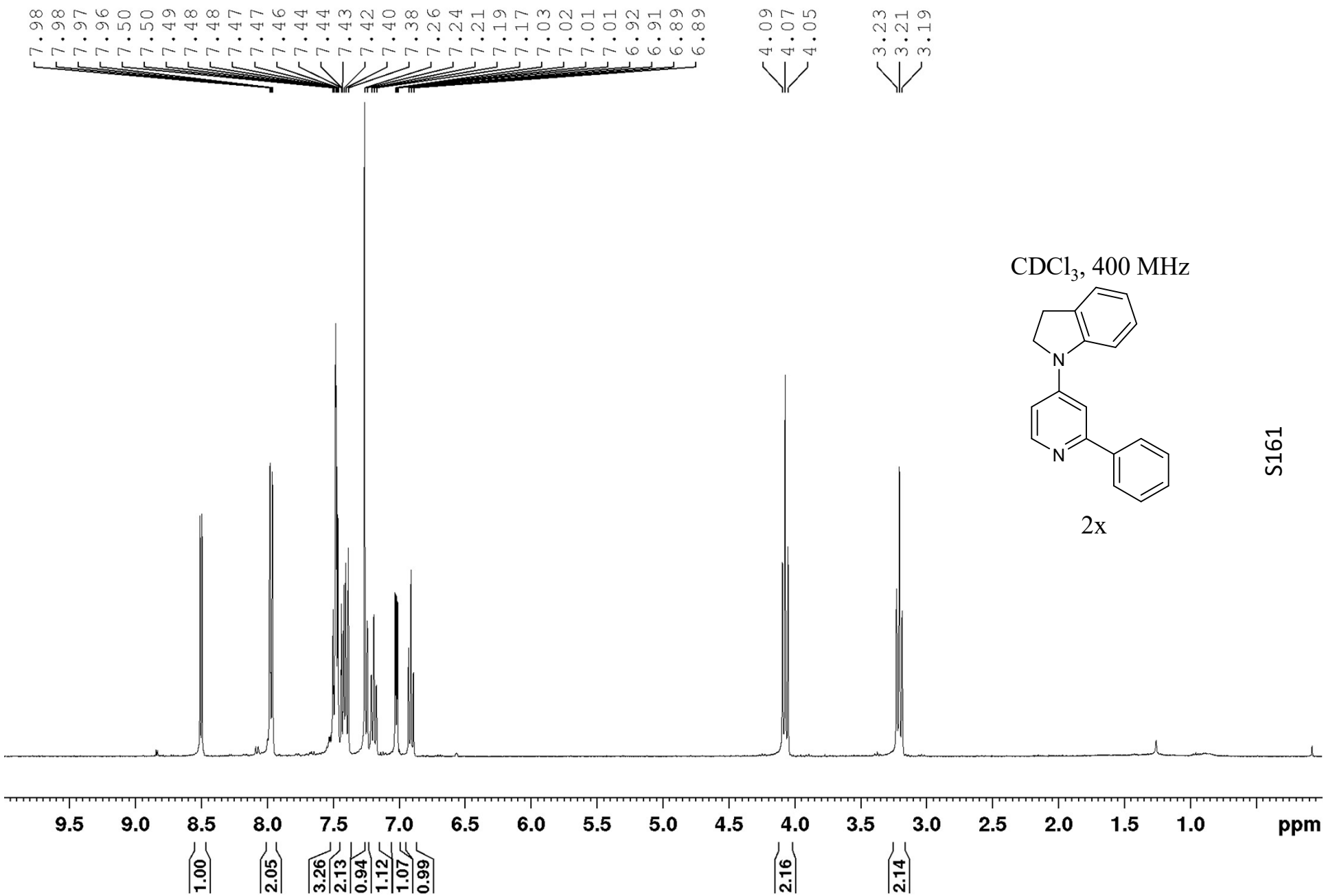

158.0
154.6
149.8
146.4
140.4
130.0
128.5
128.5
127.0
126.6
126.3
107.2
105.4
77.3
77.0
76.7
39.6
CDCl3, 100 MHz
Me
N
N
2u
S156
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

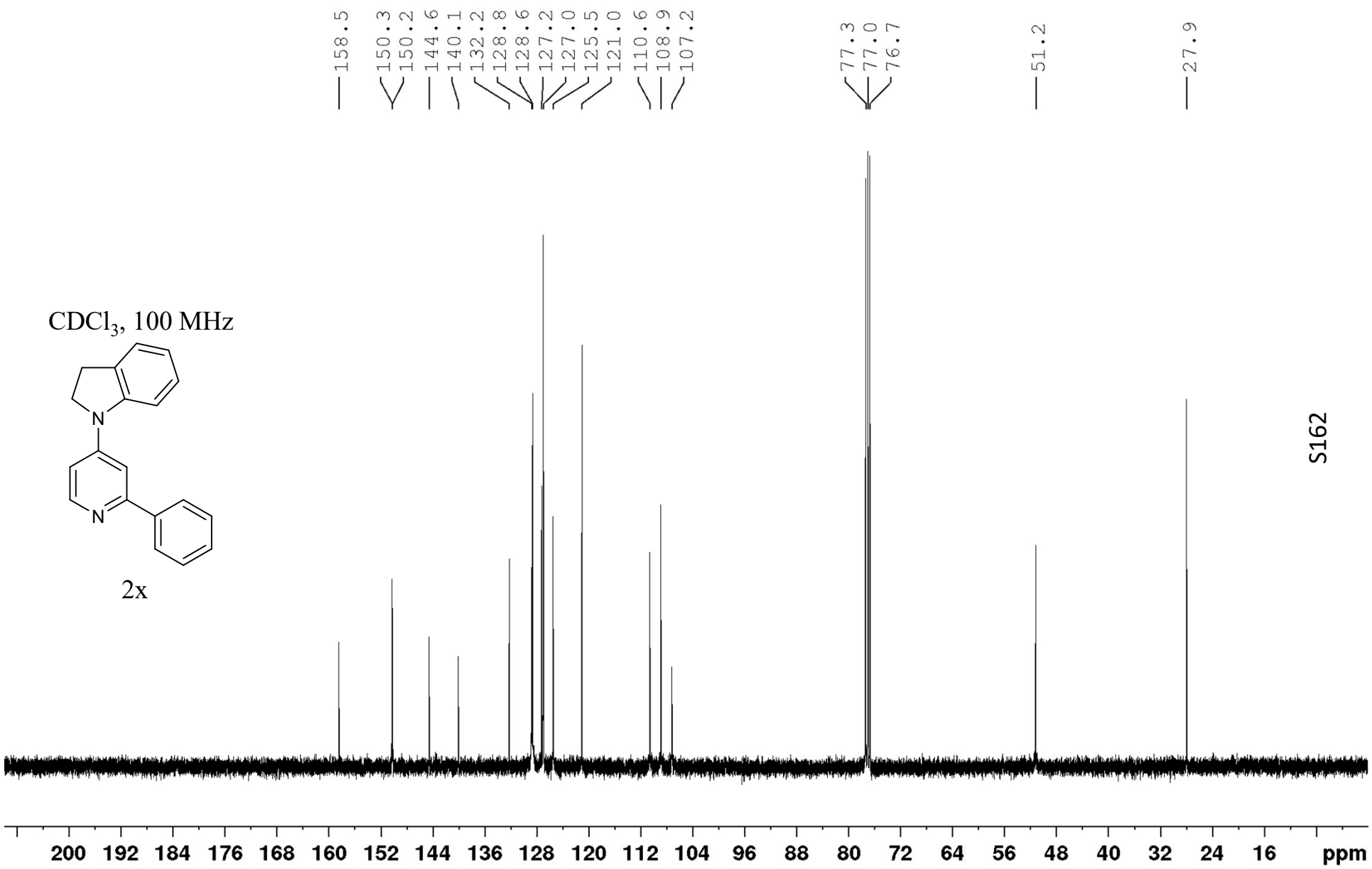

7.87
7.86
7.86
7.85
7.44
7.42
7.42
7.41
7.40
7.38
7.36
7.35
7.33
7.31
7.26
7.01
7.00
6.85
6.84
6.84
6.84
6.83
6.83
6.83
6.82
6.82
6.81
6.81
6.79
6.78
6.78
6.57
6.57
6.56
6.55
4.06
4.04
4.03
4.01
3.37
1.44
1.42
1.41
CDCl3, 400 MHz
Me
N
O
N
2v
S157
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.08
4.24
1.07
3.07
1.04
2.24
3.23
3.36

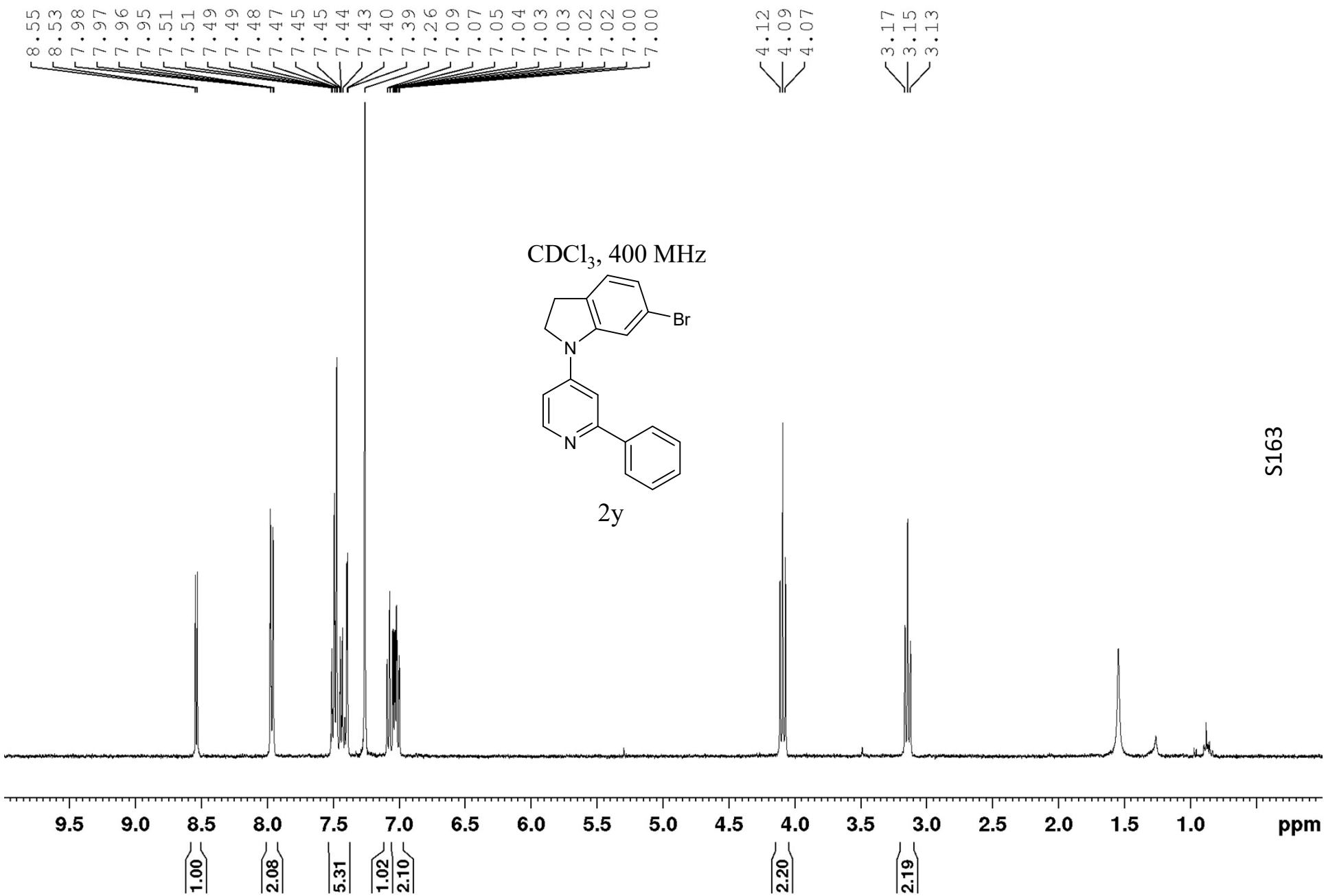

160.3
158.0
154.5
149.8
147.5
140.4
130.6
128.5
128.5
127.0
118.6
112.8
112.4
107.4
105.6
77.3
77.0
76.7
63.6
39.5
14.8
CDCl3, 100 MHz
Me
N
O
N
2v
S158
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

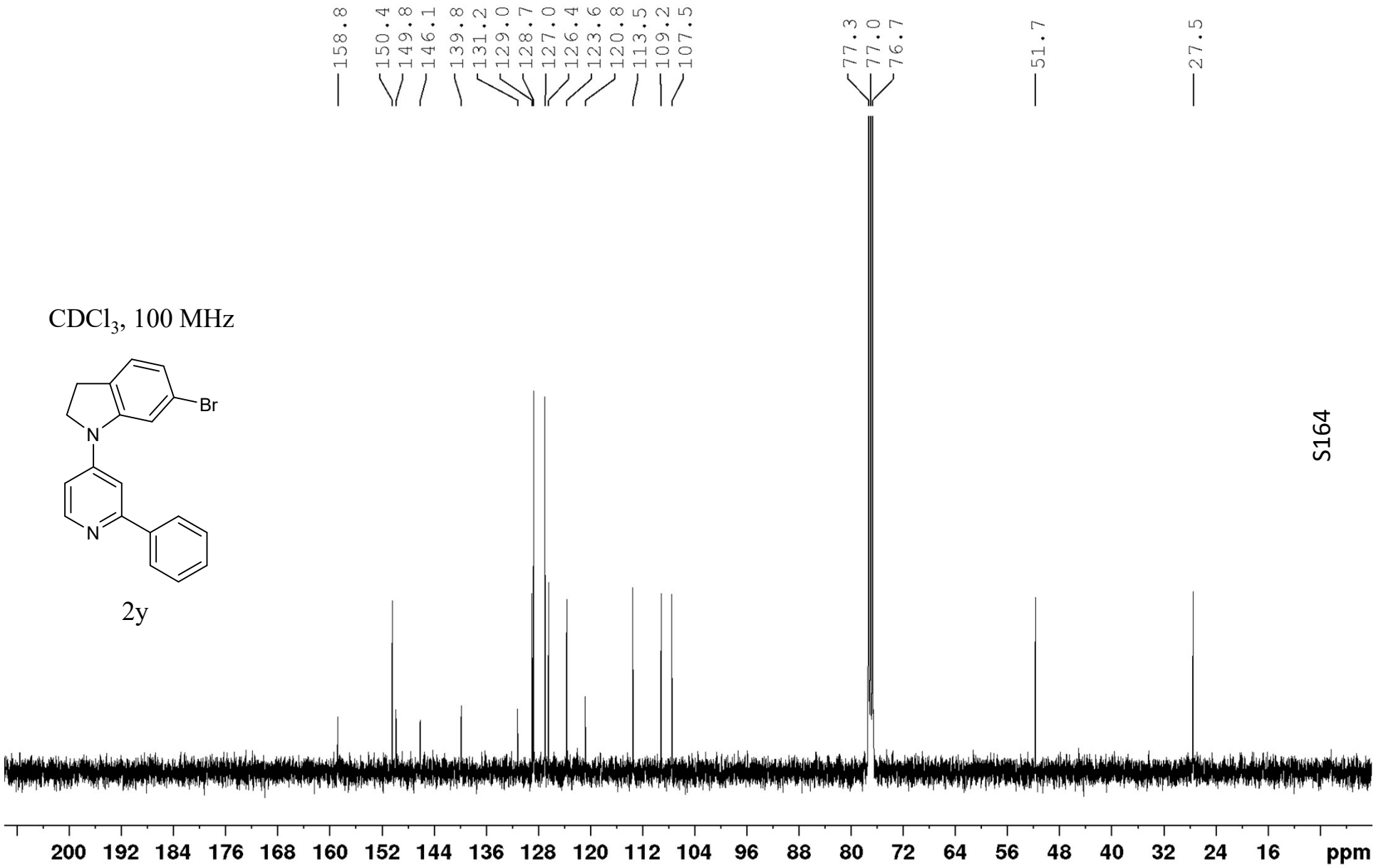

8.28
8.27
7.77
7.77
7.76
7.75
7.75
7.46
7.43
7.42
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.30
7.28
7.27
7.02
7.01
6.56
6.55
6.54
6.54
5.03
CDCl3, 400 MHz
N
N
2w
S159
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.08
11.51
2.19
1.04
1.04
2.10

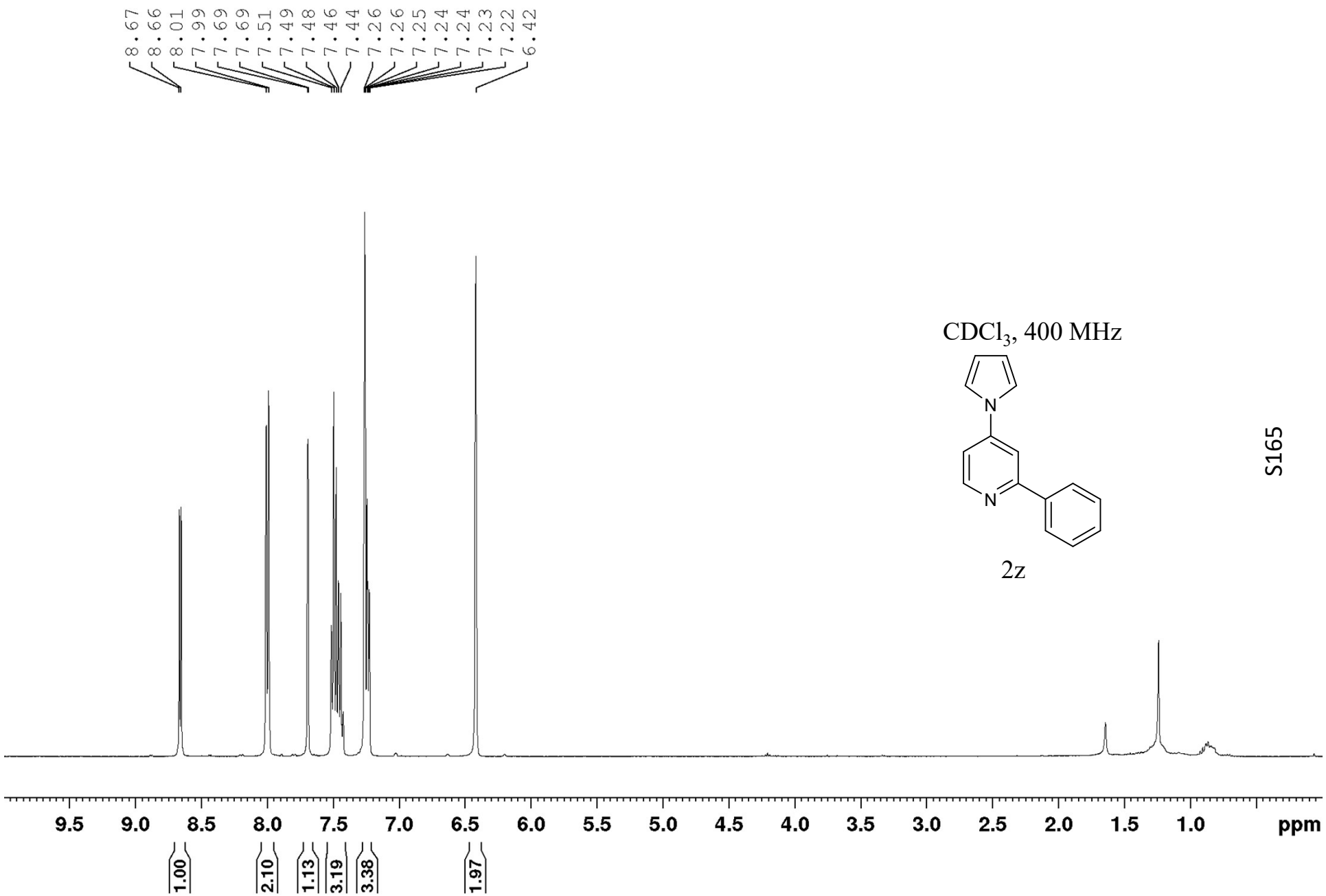

158.0
154.1
149.9
145.7
140.3
137.5
130.0
128.8
128.5
128.5
127.3
126.9
126.8
126.5
126.4
107.8
106.0
77.3
77.0
76.7
56.0
CDCl3, 100 MHz
N
N
2w
S160
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

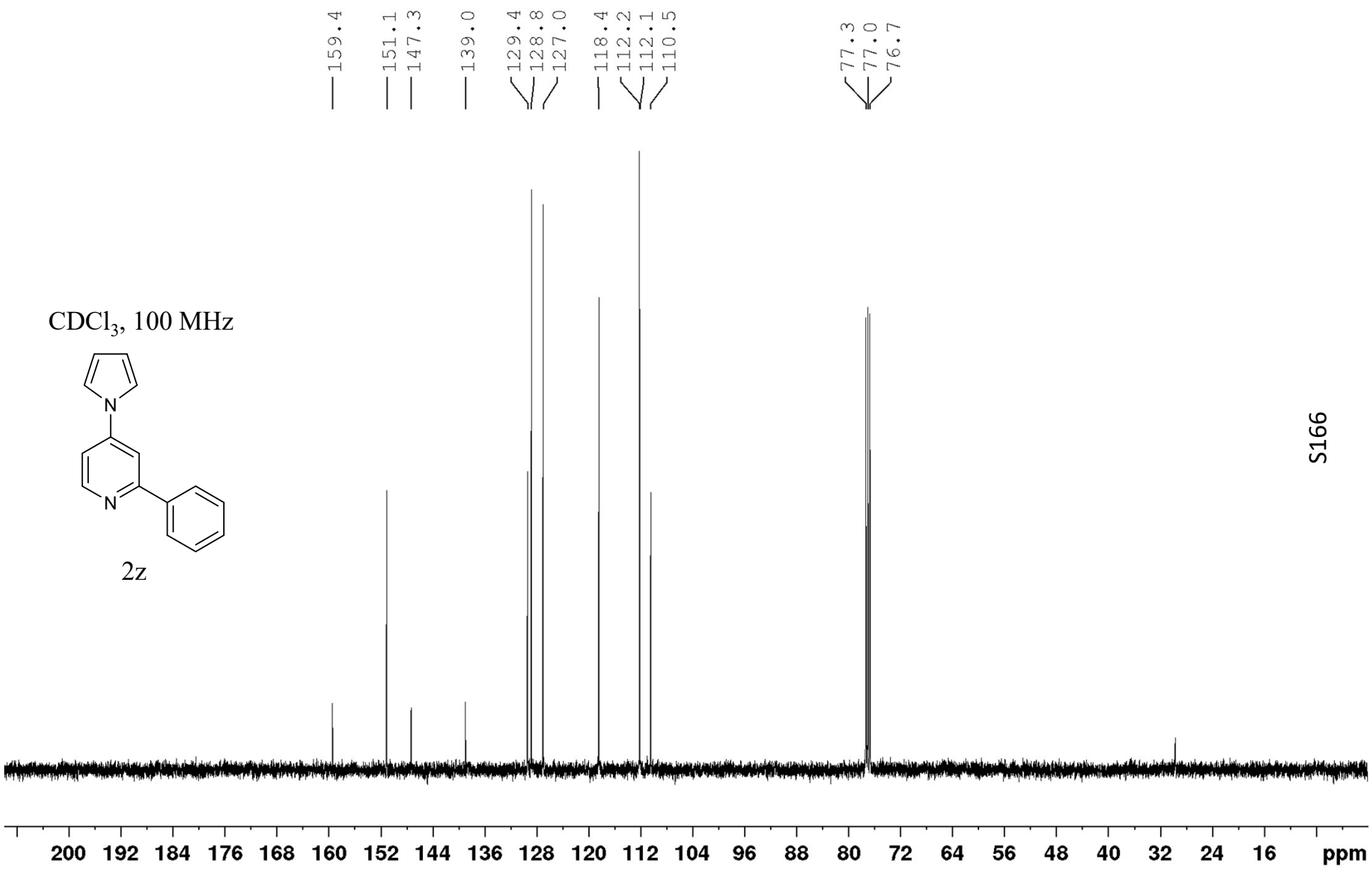

7.98
7.98
7.97
7.96
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.44
7.44
7.43
7.42
7.40
7.38
7.26
7.24
7.21
7.19
7.17
7.03
7.02
7.01
7.01
6.92
6.91
6.89
6.89
4.09
4.07
4.05
3.23
3.21
3.19
CDCl3, 400 MHz
N
N
2x
S161
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.05
3.26
2.13
0.94
1.12
1.07
0.99
2.16
2.14

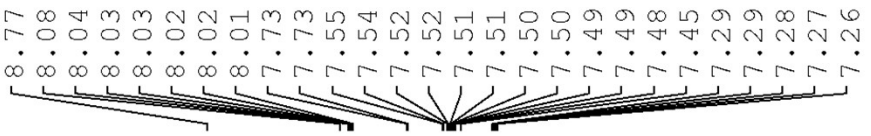

158.5
150.3
150.2
144.6
140.1
132.2
128.8
128.6
127.2
127.0
125.5
121.0
110.6
108.9
107.2
77.3
77.0
76.7
51.2
27.9
CDCl3, 100 MHz
2x
S162
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.55
8.53
7.98
7.97
7.96
7.95
7.51
7.51
7.49
7.49
7.48
7.47
7.45
7.45
7.44
7.43
7.40
7.39
7.26
7.09
7.07
7.05
7.04
7.03
7.03
7.02
7.02
7.00
7.00
4.12
4.09
4.07
3.17
3.15
3.13
CDCl3, 400 MHz
Br
N
N
2y
S163
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
1.00
2.08
5.31
1.02
2.10
2.20
2.19

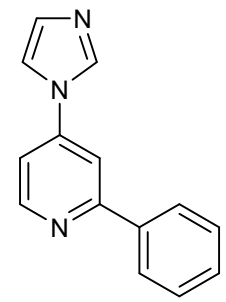

158.8
150.4
149.8
146.1
139.8
131.2
129.0
128.7
127.0
126.4
123.6
120.8
113.5
109.2
107.5
77.3
77.0
76.7
51.7
27.5
CDCl3, 100 MHz
Br
N
N
2y
S164
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.67
8.66
8.01
7.99
7.69
7.69
7.51
7.49
7.48
7.46
7.44
7.26
7.26
7.25
7.24
7.24
7.23
7.22
6.42
CDCl3, 400 MHz
N
N
2z
S165
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
1.00
2.10
1.13
3.19
3.38
1.97

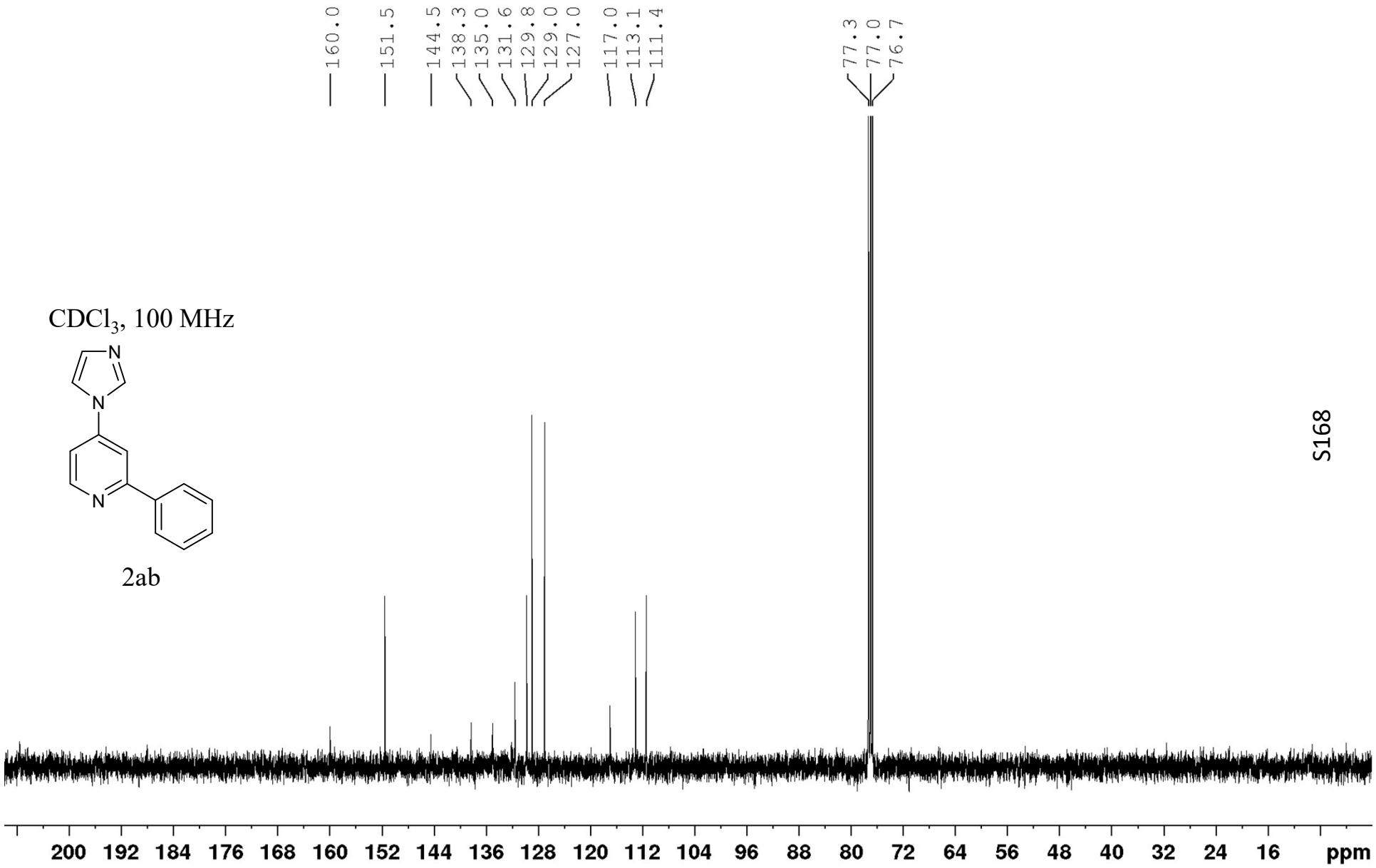

159.4
151.1
147.3
139.0
129.4
128.8
127.0
118.4
112.2
112.1
110.5
77.3
77.0
76.7
CDCl3, 100 MHz
N
N
2z
S166
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

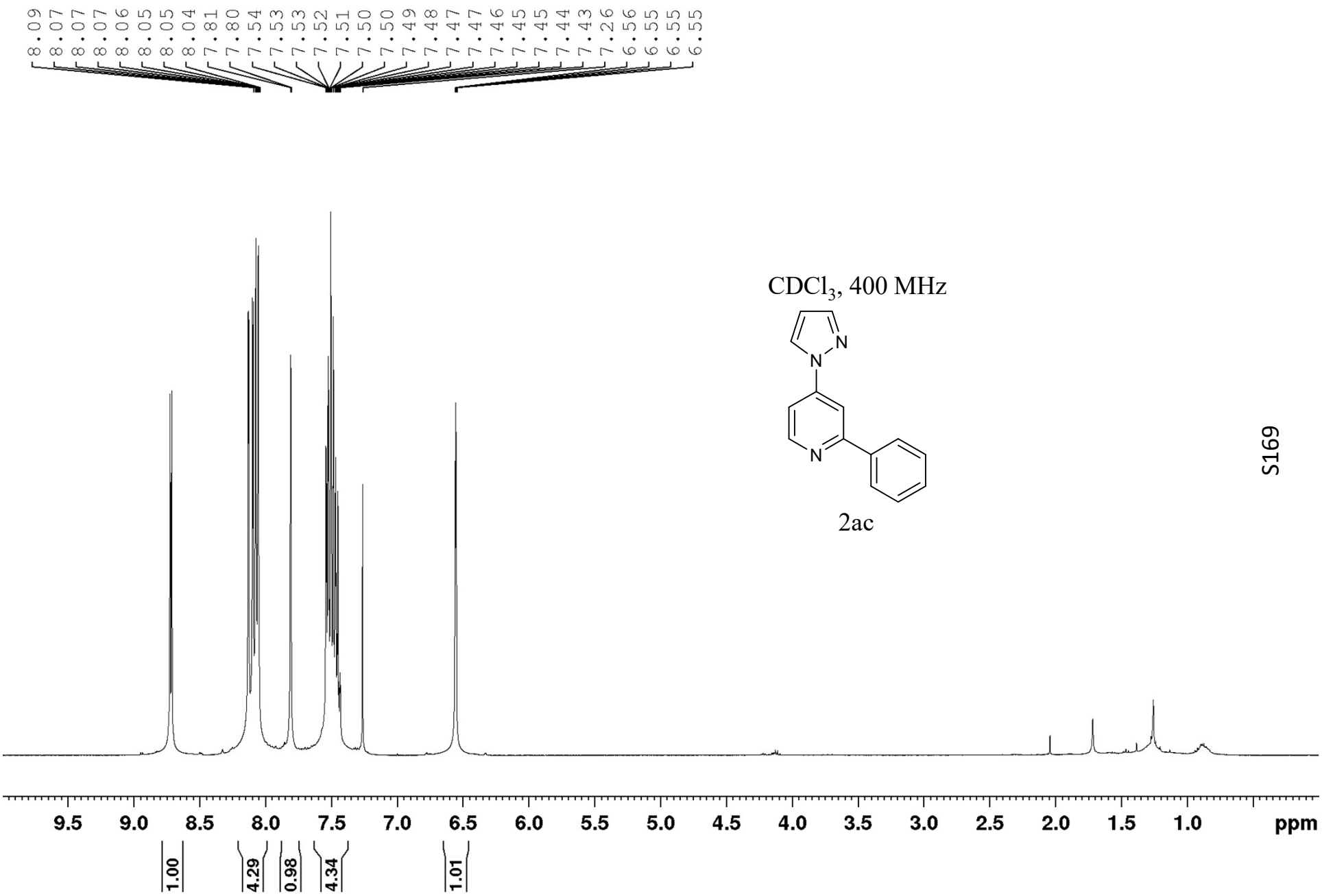


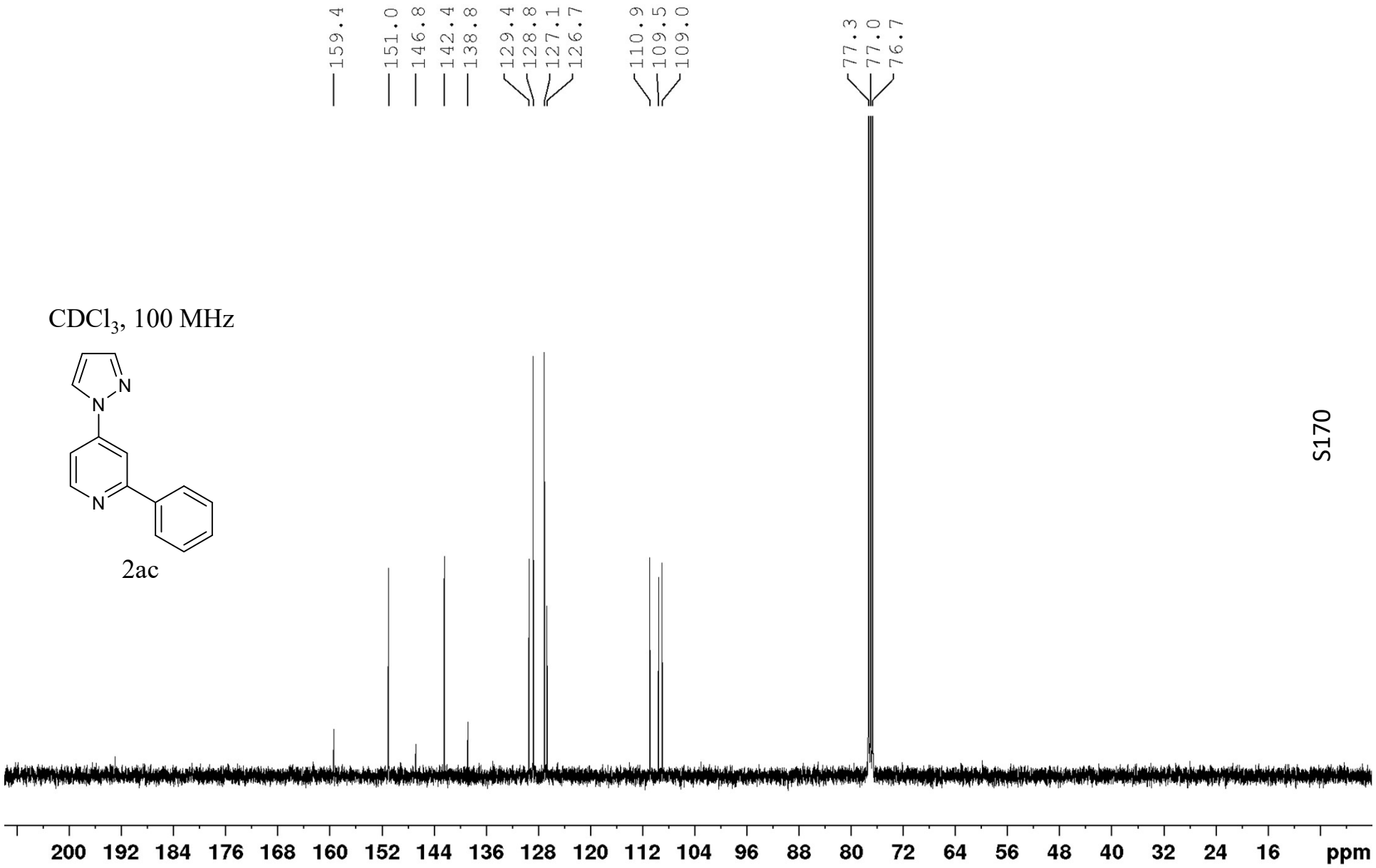
$CDCl_3$, 400 MHz

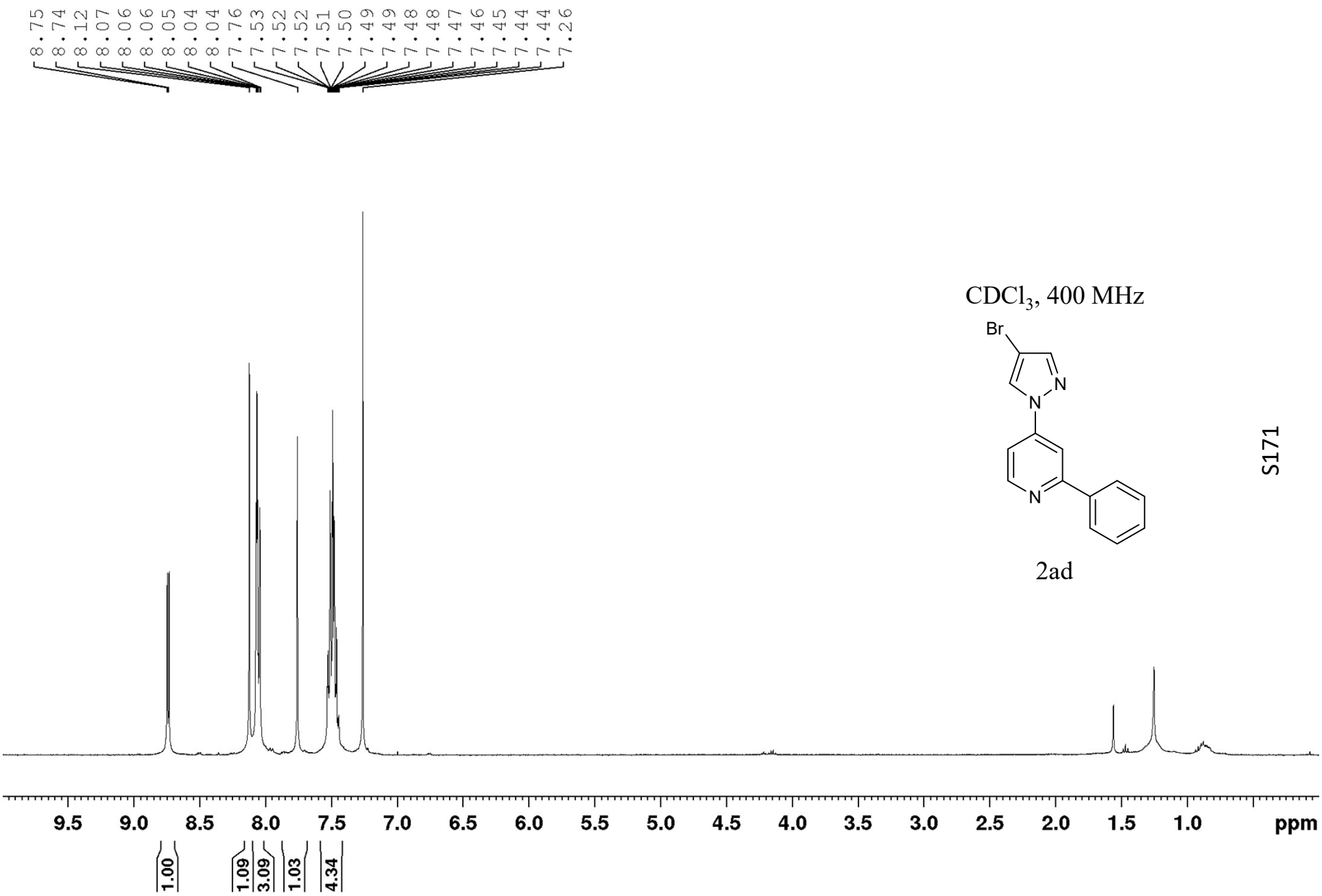


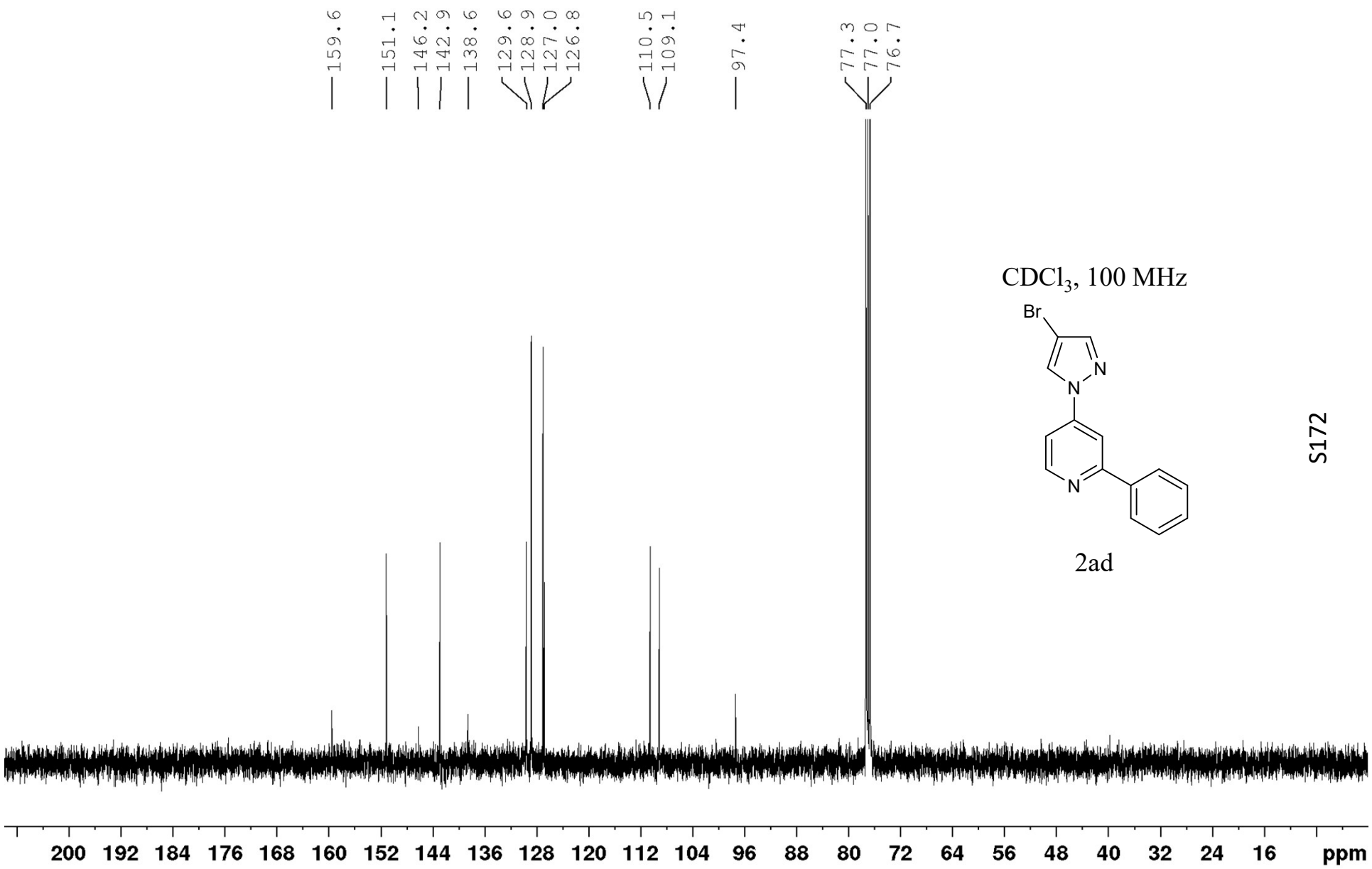
2ab

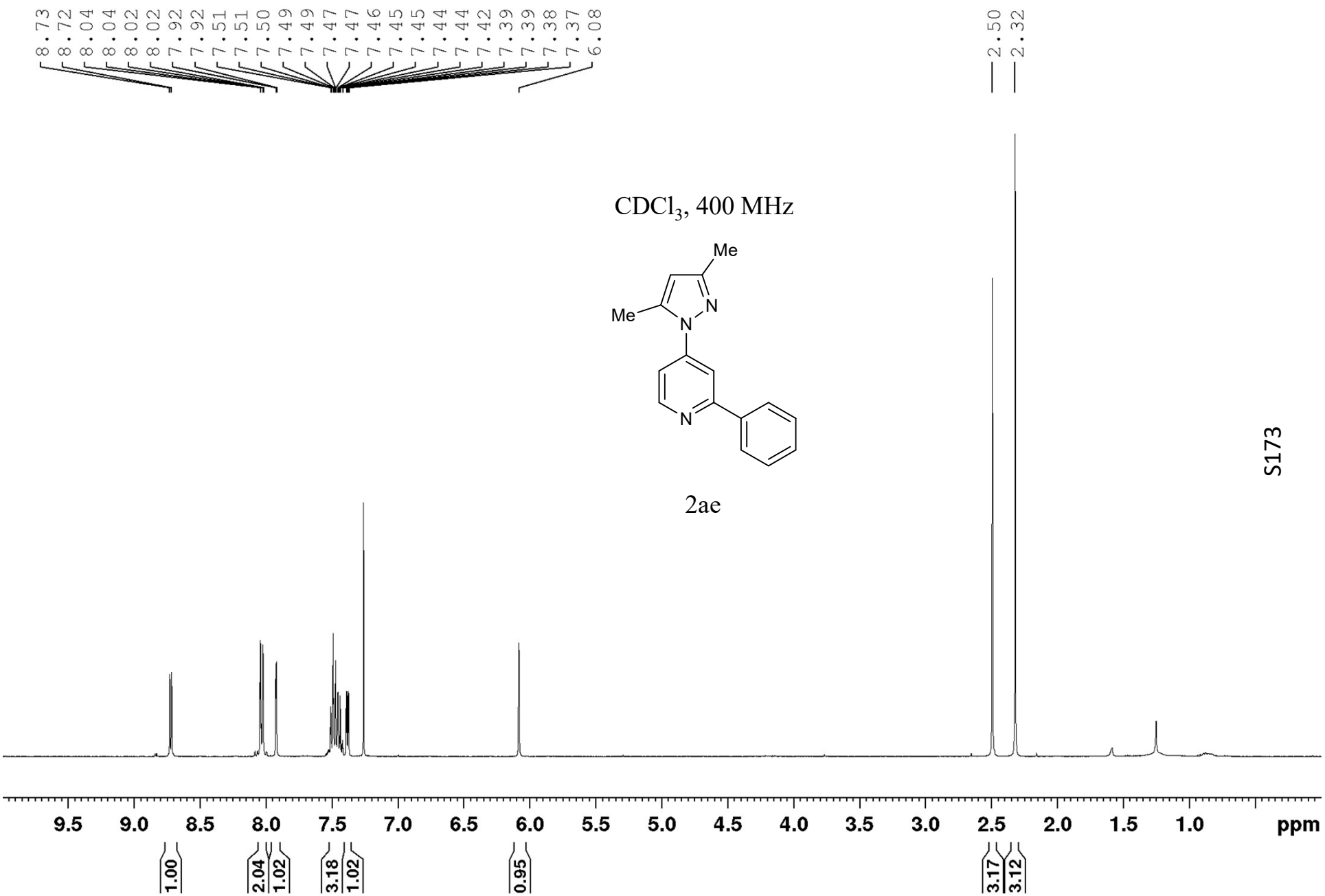

160.0
151.5
144.5
138.3
135.0
131.6
129.8
129.0
127.0
117.0
113.1
111.4
77.3
77.0
76.7
CDCl3, 100 MHz
N
N
N
2ab
S168
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

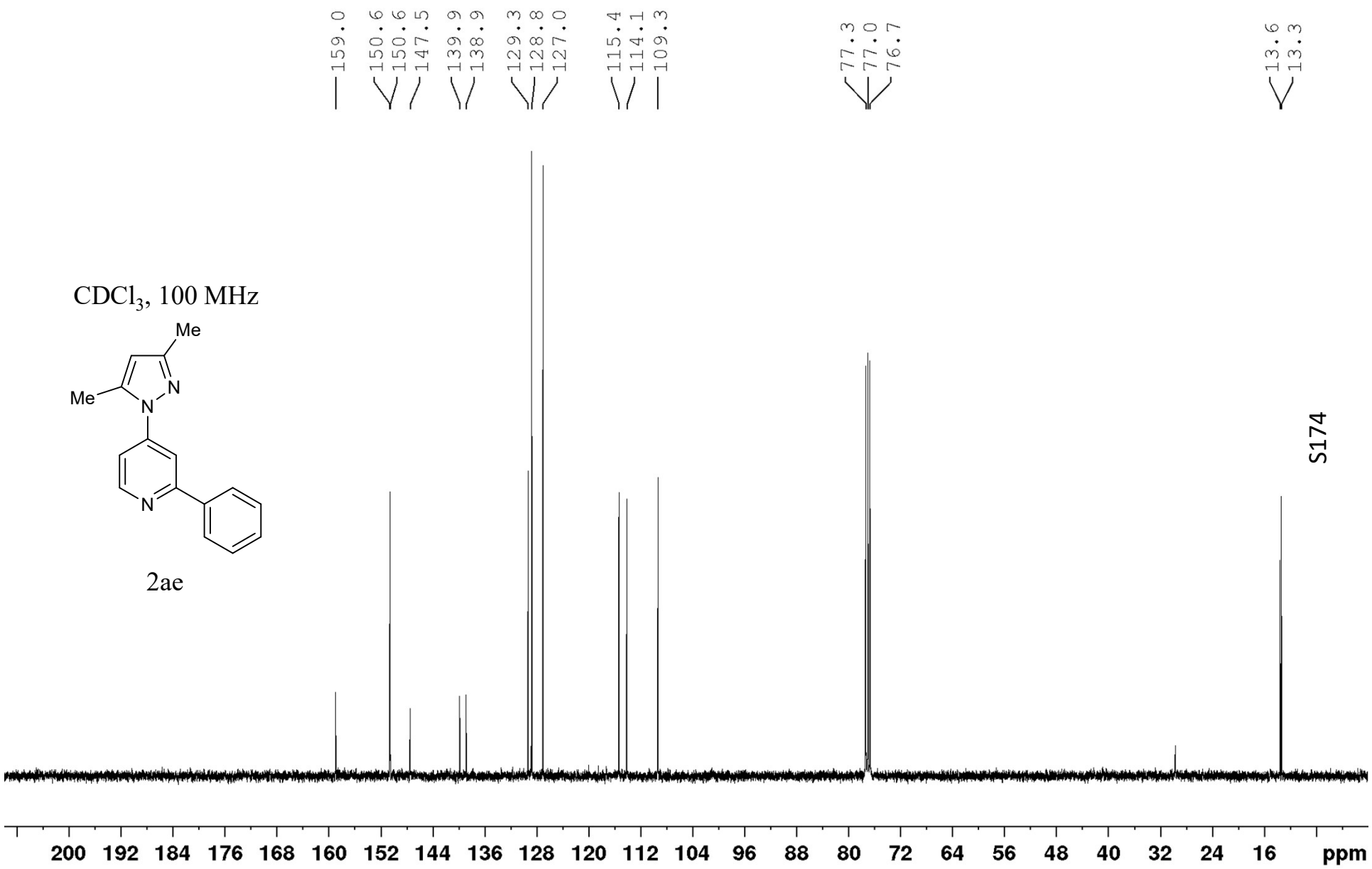

8.09
8.07
8.07
8.07
8.06
8.05
8.05
8.04
7.81
7.80
7.54
7.53
7.53
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.26
6.56
6.55
6.55
6.55
CDCl3, 400 MHz
N
N
N
2ac
S169
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
4.29
0.98
4.34
1.01

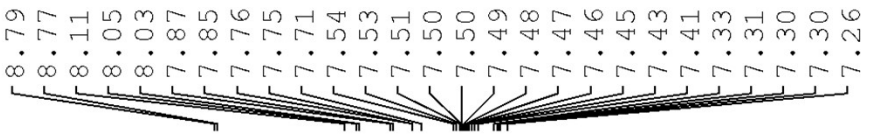

159.4
151.0
146.8
142.4
138.8
129.4
128.8
127.1
126.7
110.9
109.5
109.0
77.3
77.0
76.7
CDCl3, 100 MHz
2ac
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.75
8.74
8.12
8.07
8.06
8.06
8.05
8.04
8.04
7.76
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.26
CDCl3, 400 MHz
Br
N
N
N
2ad
S171
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
1.00
1.09
3.09
1.03
4.34

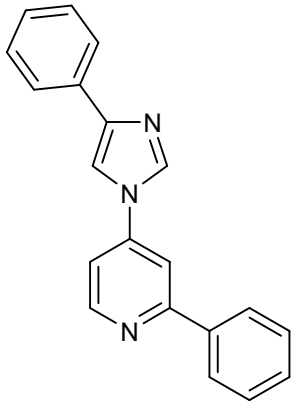

159.6
151.1
146.2
142.9
138.6
129.6
128.9
127.0
126.8
110.5
109.1
97.4
77.3
77.0
76.7
CDCl3, 100 MHz
Br
N
N
N
2ad
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.73
8.72
8.04
8.04
8.02
8.02
7.92
7.92
7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.42
7.39
7.39
7.38
7.37
6.08
2.50
2.32
CDCl3, 400 MHz
Me
Me
N
N
N
2ae
S173
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
1.00
2.04
1.02
3.18
1.02
0.95
3.17
3.12

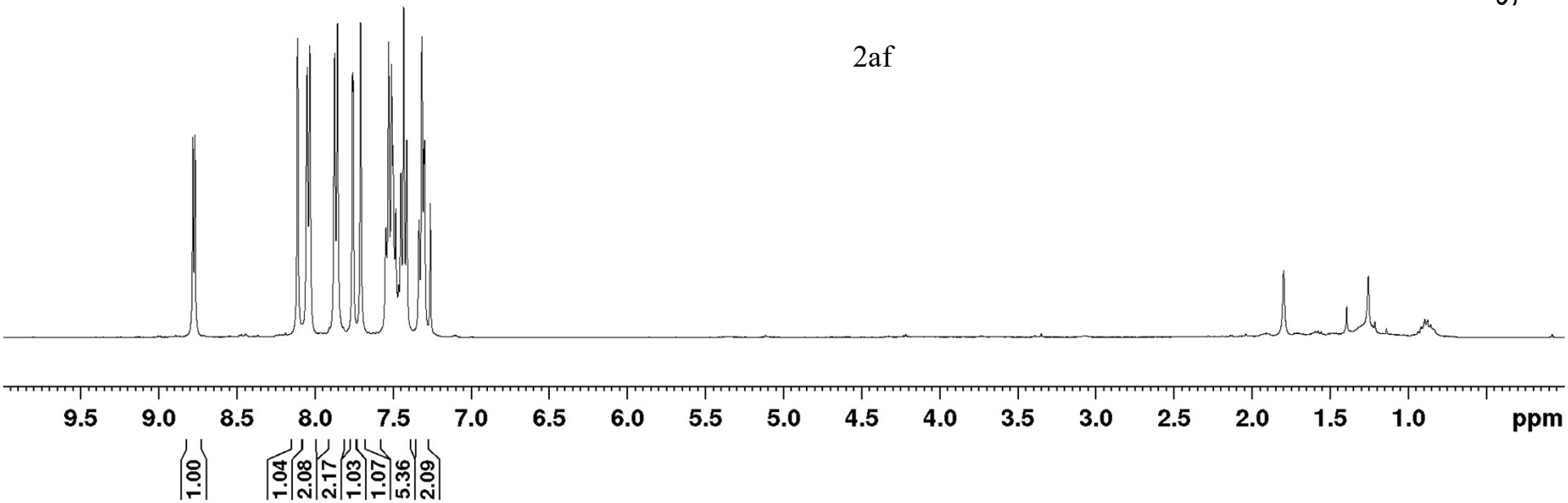

159.0
150.6
150.6
147.5
139.9
138.9
129.3
128.8
127.0
115.4
114.1
109.3
77.3
77.0
76.7
13.6
13.3
CDCl3, 100 MHz
Me
Me
N
N
N
2ae
S174
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm



$CDCl_3$, 400 MHz

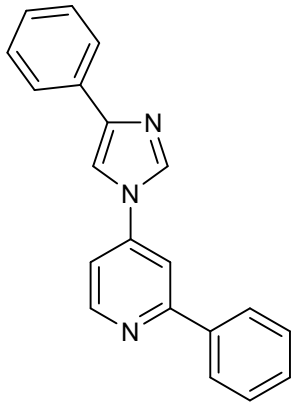


2af

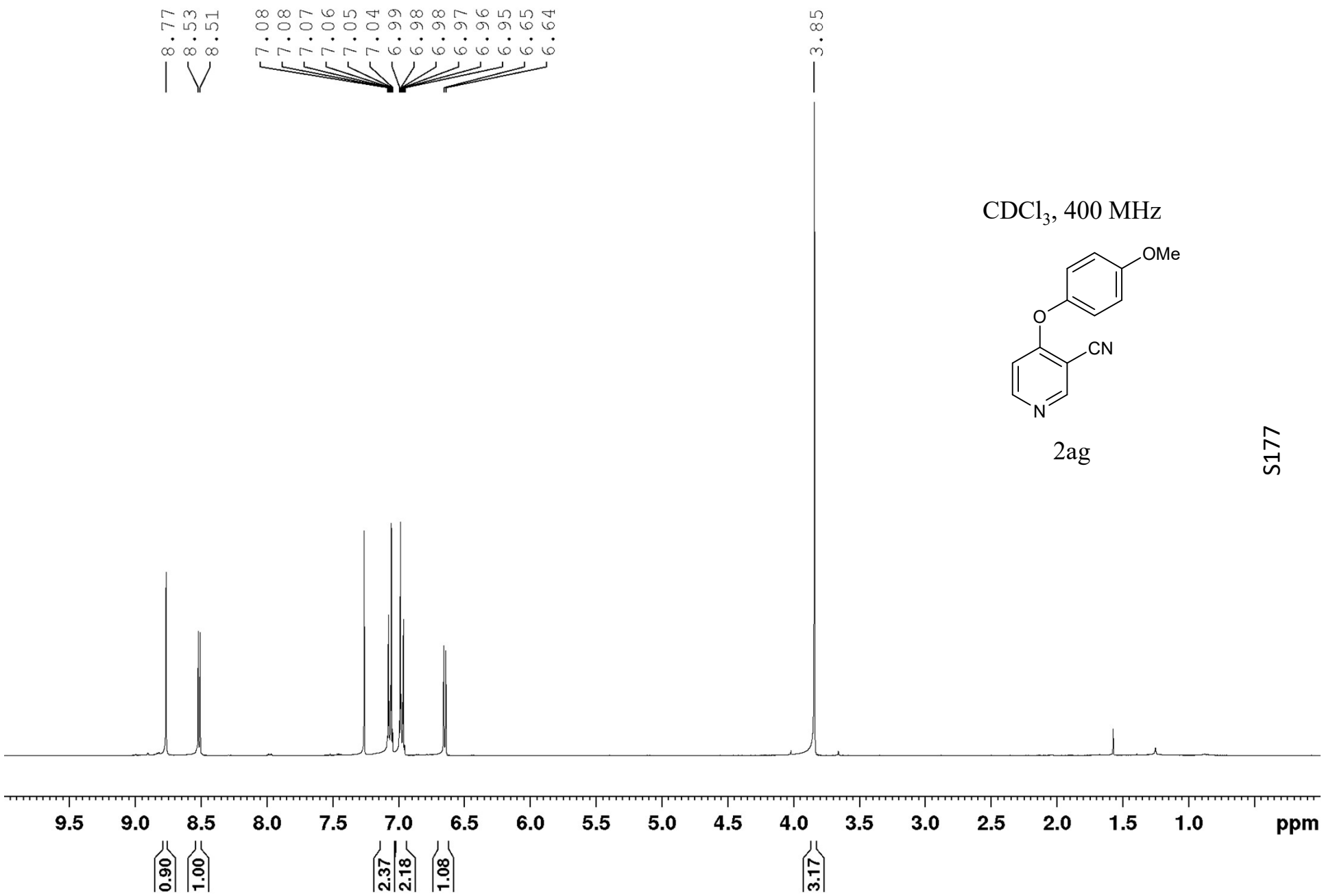


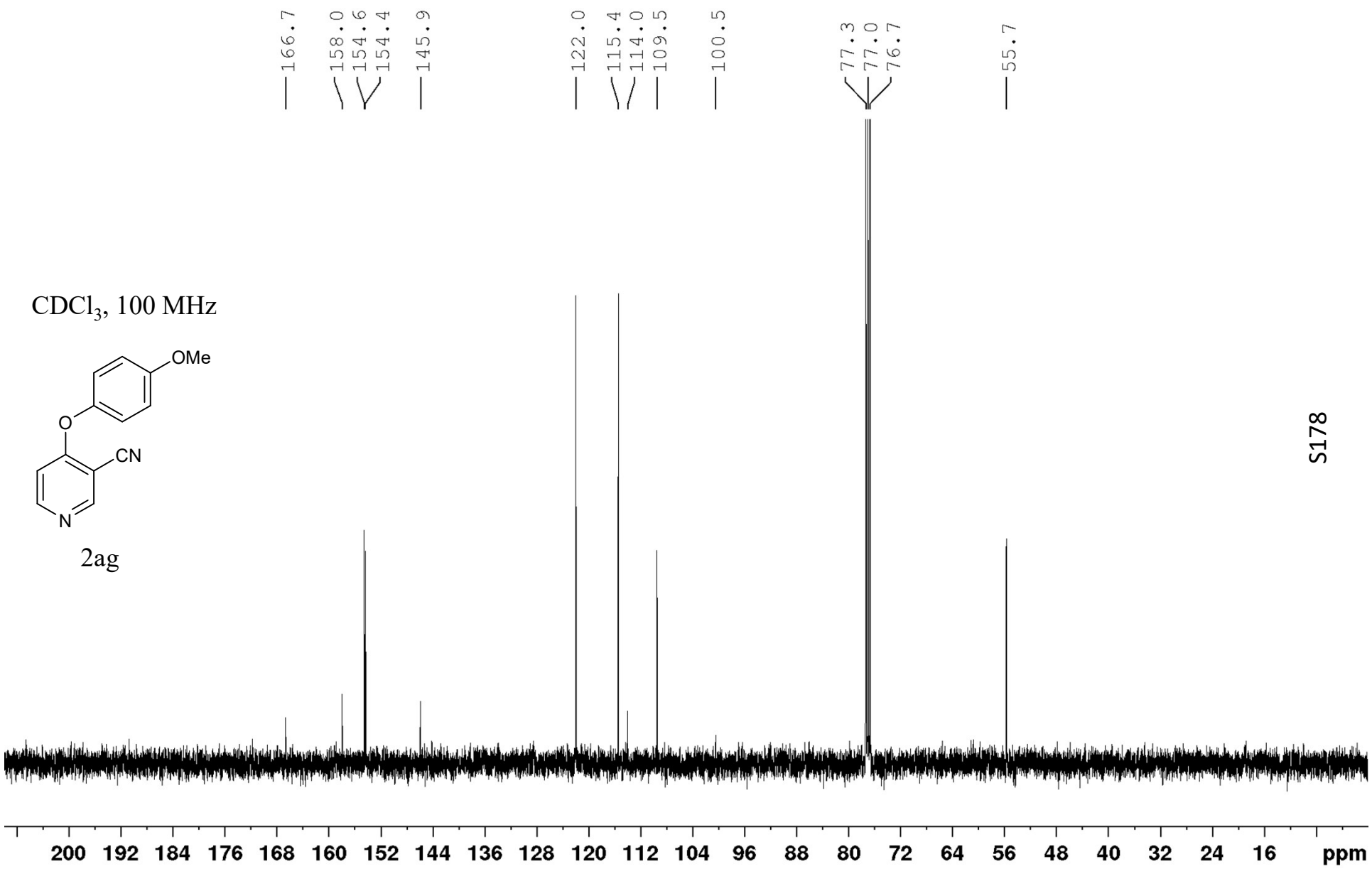
160.0
151.5
144.3
138.3
135.1
133.0
129.8
128.9
128.7
127.6
127.0
125.1
112.8
112.1
111.1
77.3
77.0
76.7

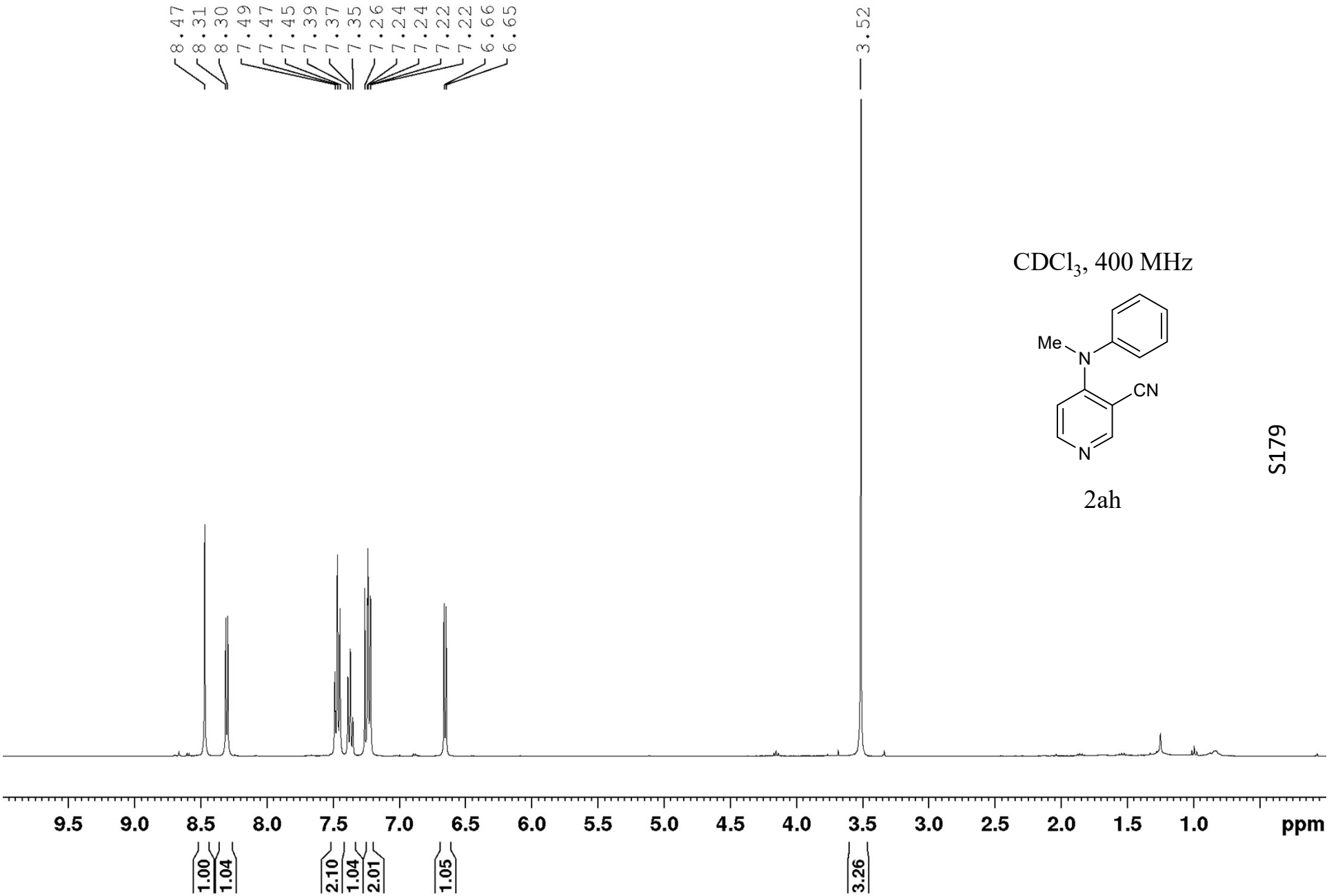
$CDCl_3$, 100 MHz

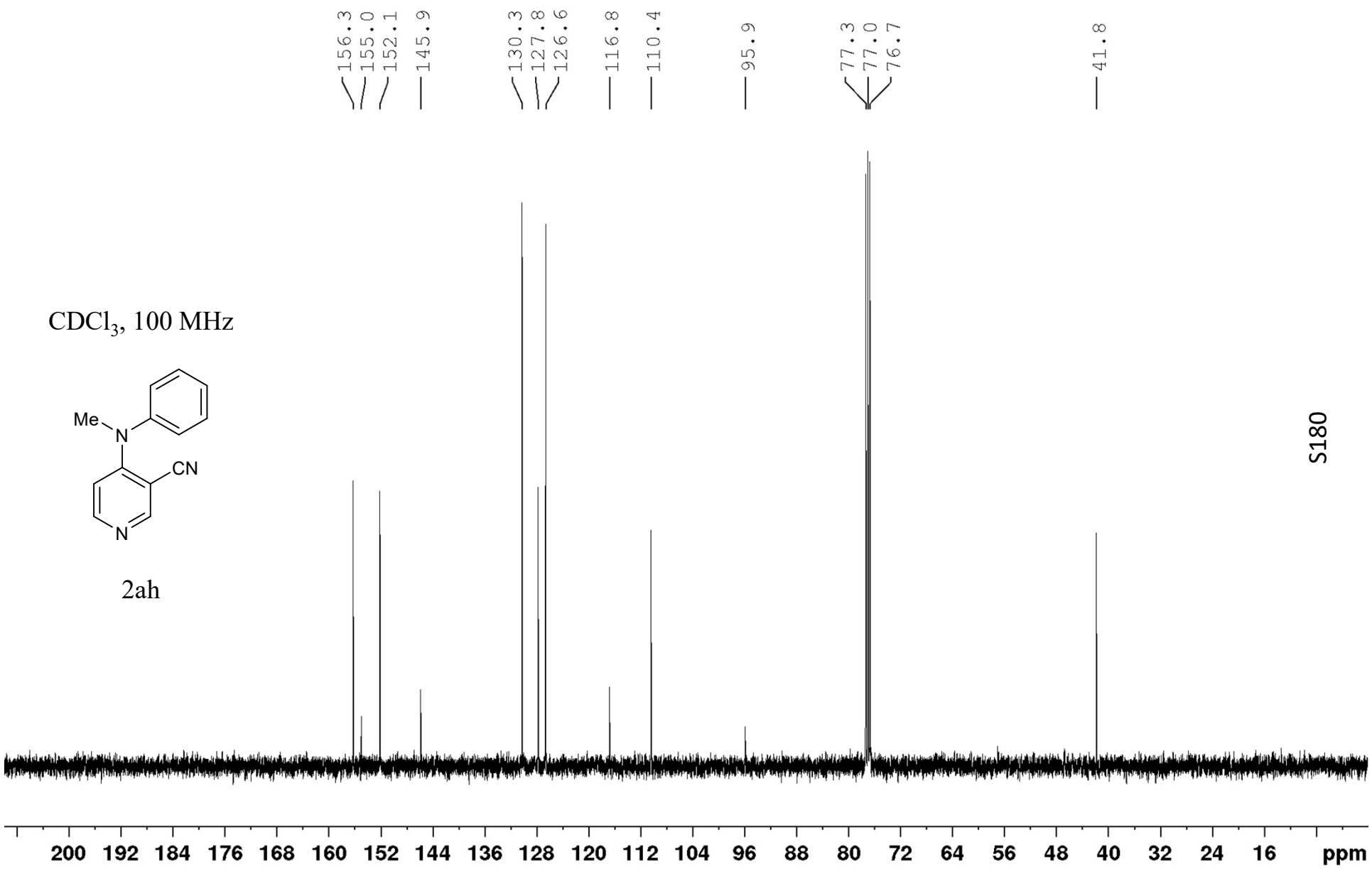


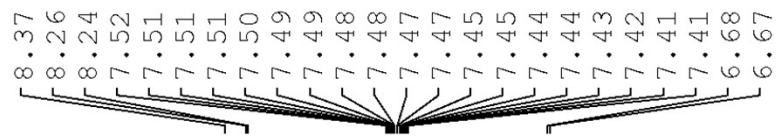
2af


8.77
8.53
8.51
7.08
7.08
7.07
7.06
7.05
7.04
6.99
6.98
6.98
6.97
6.96
6.95
6.65
6.64
3.85
CDCl3, 400 MHz
OMe
O
CN
N
2ag
S177
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
0.90
1.00
2.37
2.18
1.08
3.17

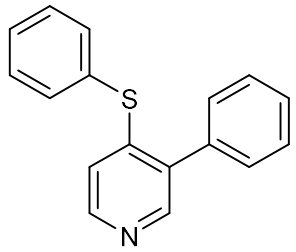

166.7
158.0
154.6
154.4
145.9
122.0
115.4
114.0
109.5
100.5
77.3
77.0
76.7
55.7
CDCl3, 100 MHz
OMe
O
CN
N
2ag
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.47
8.31
8.30
7.49
7.47
7.45
7.39
7.37
7.35
7.26
7.24
7.24
7.22
7.22
6.66
6.65
3.52
CDCl3, 400 MHz
Me
N
CN
N
2ah
S179
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
1.00
1.04
2.10
1.04
2.01
1.05
3.26

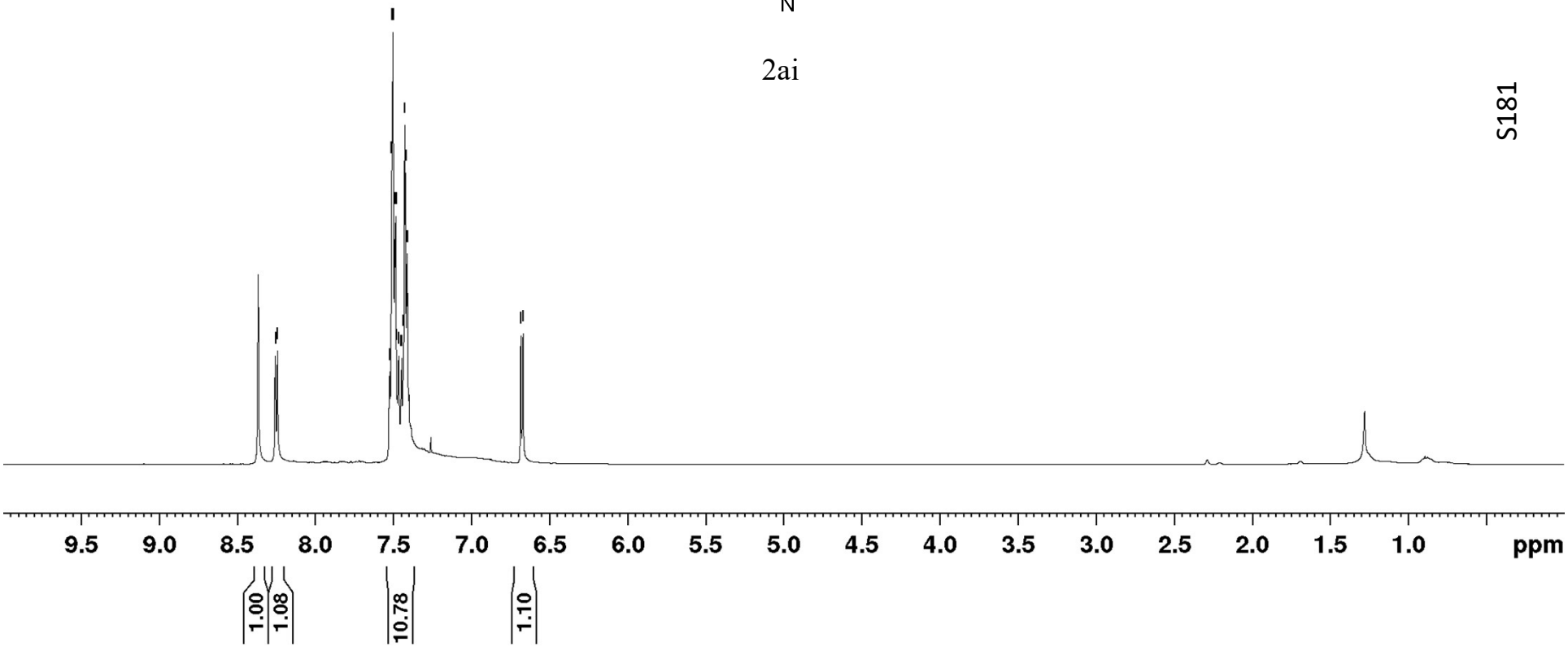

156.3
155.0
152.1
145.9
130.3
127.8
126.6
116.8
110.4
95.9
77.3
77.0
76.7
41.8
CDCl3, 100 MHz
Me
N
CN
N
2ah
S180
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

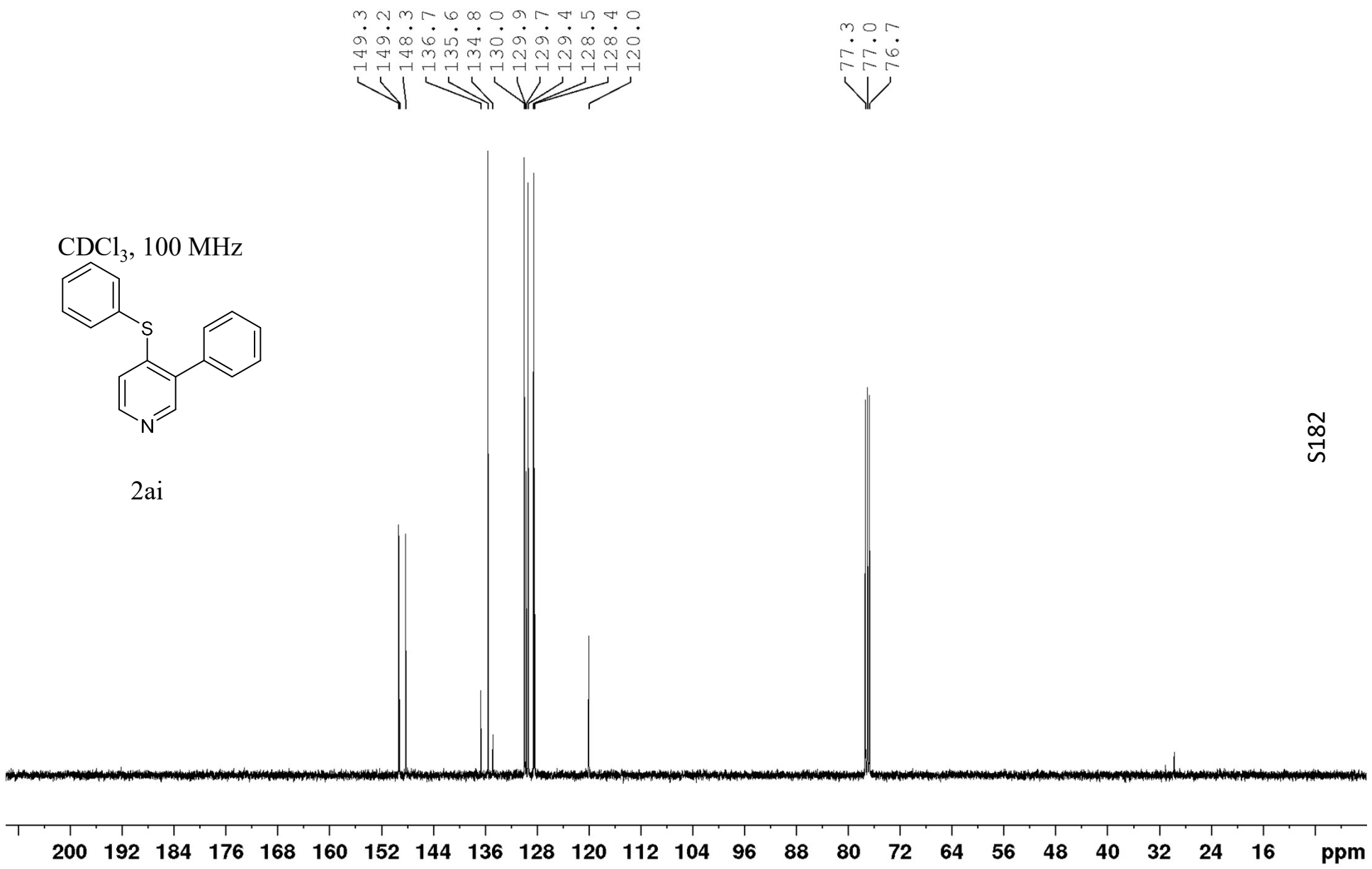


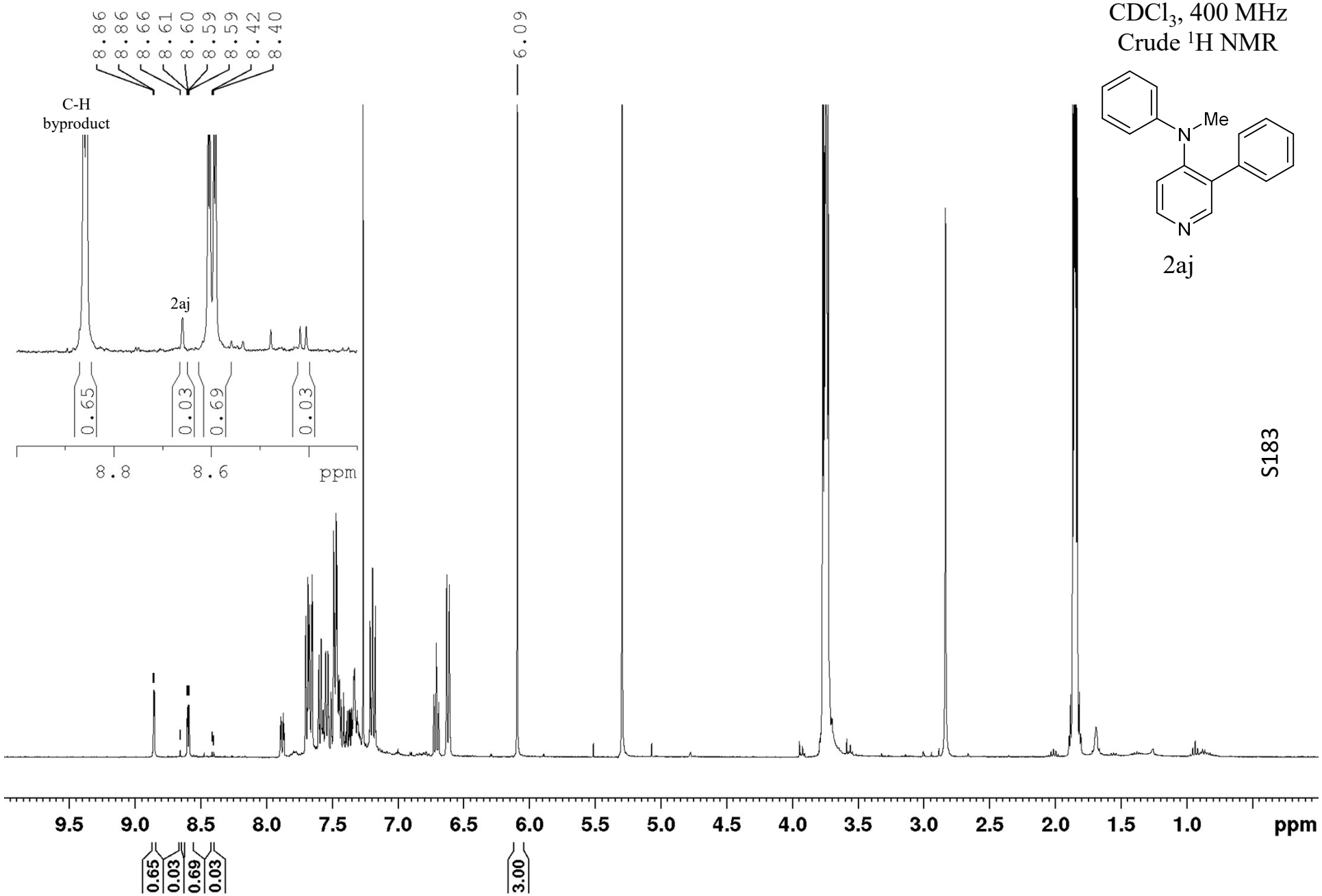
$CDCl_3$, 400 MHz

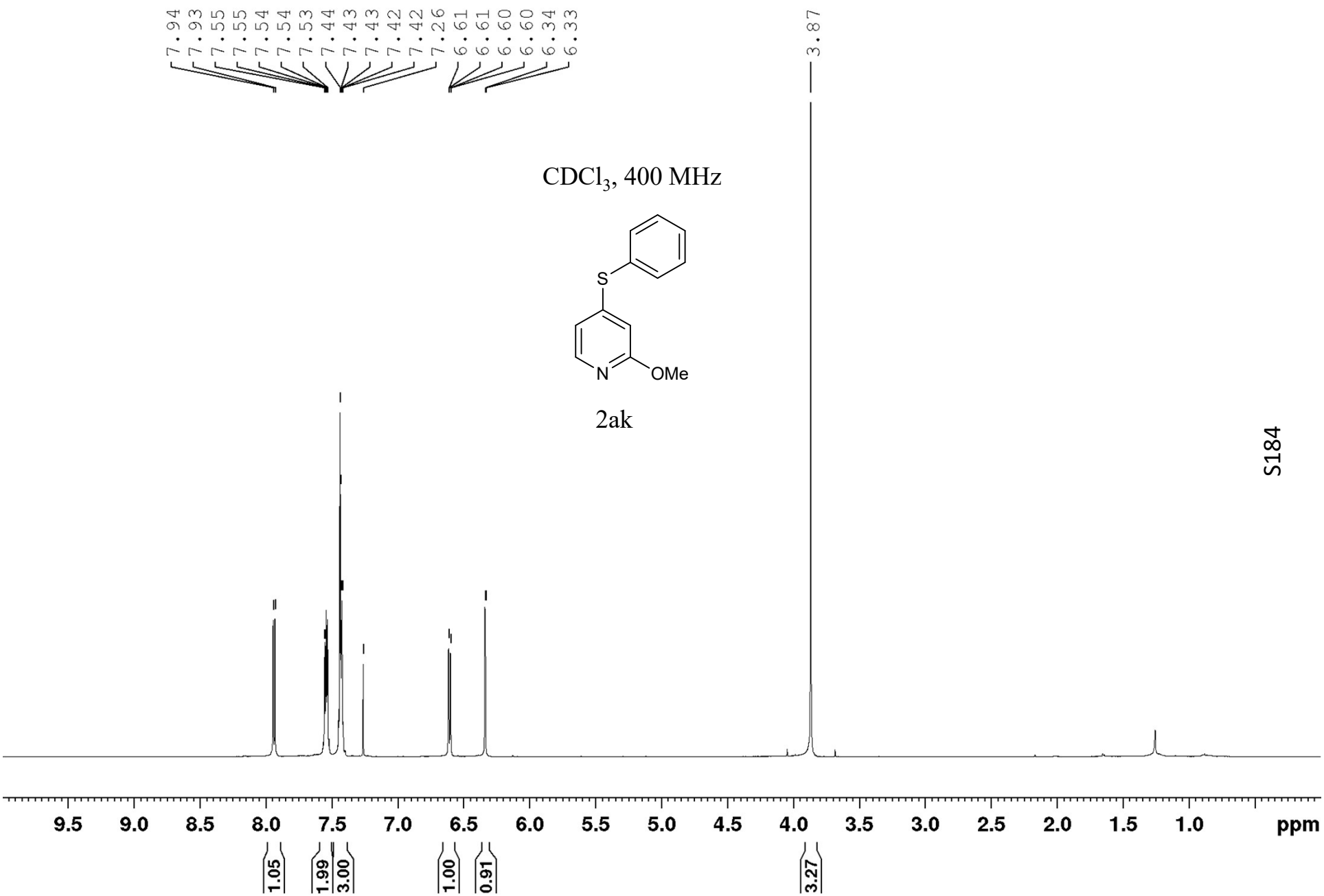


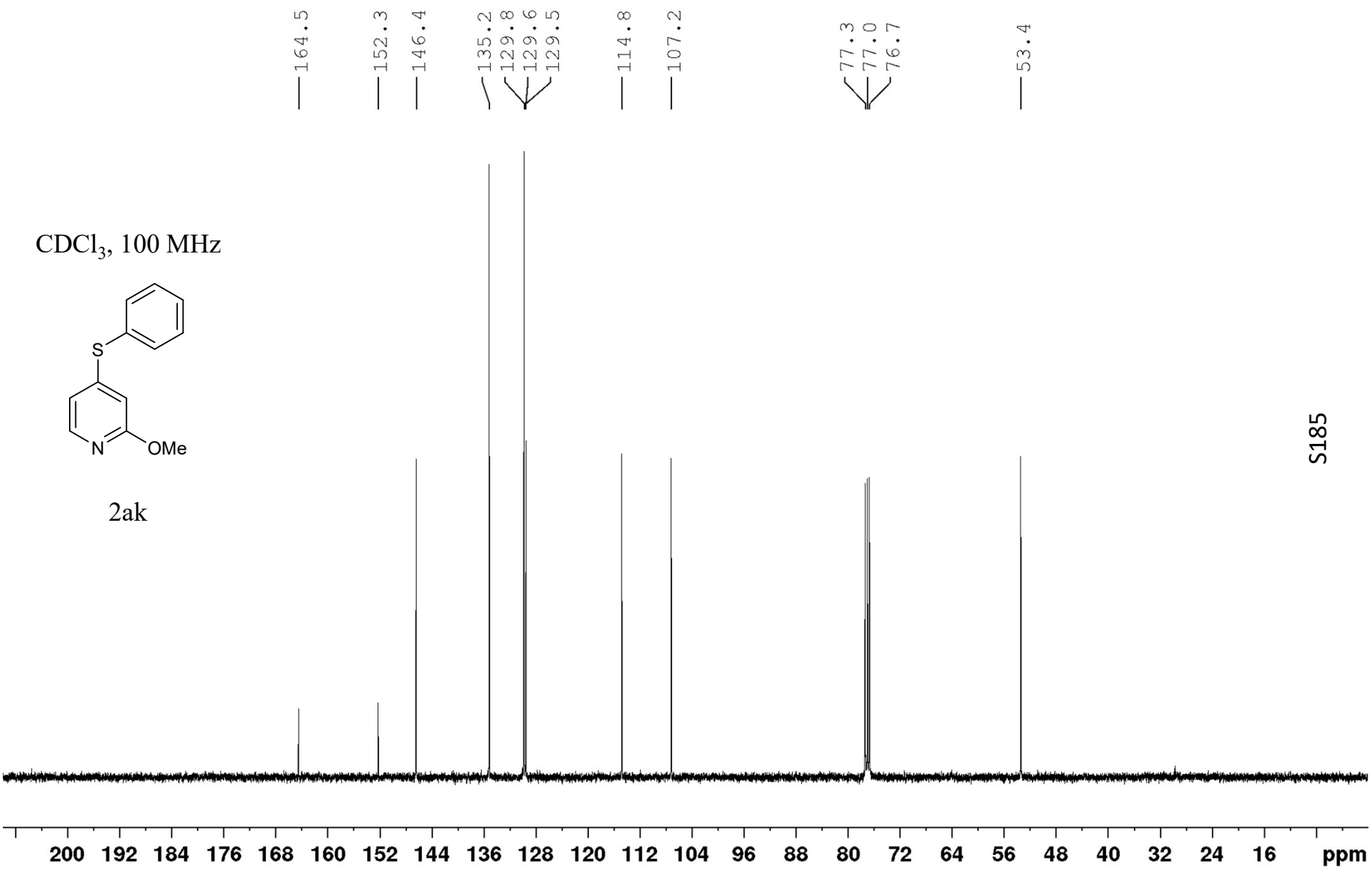
2ai

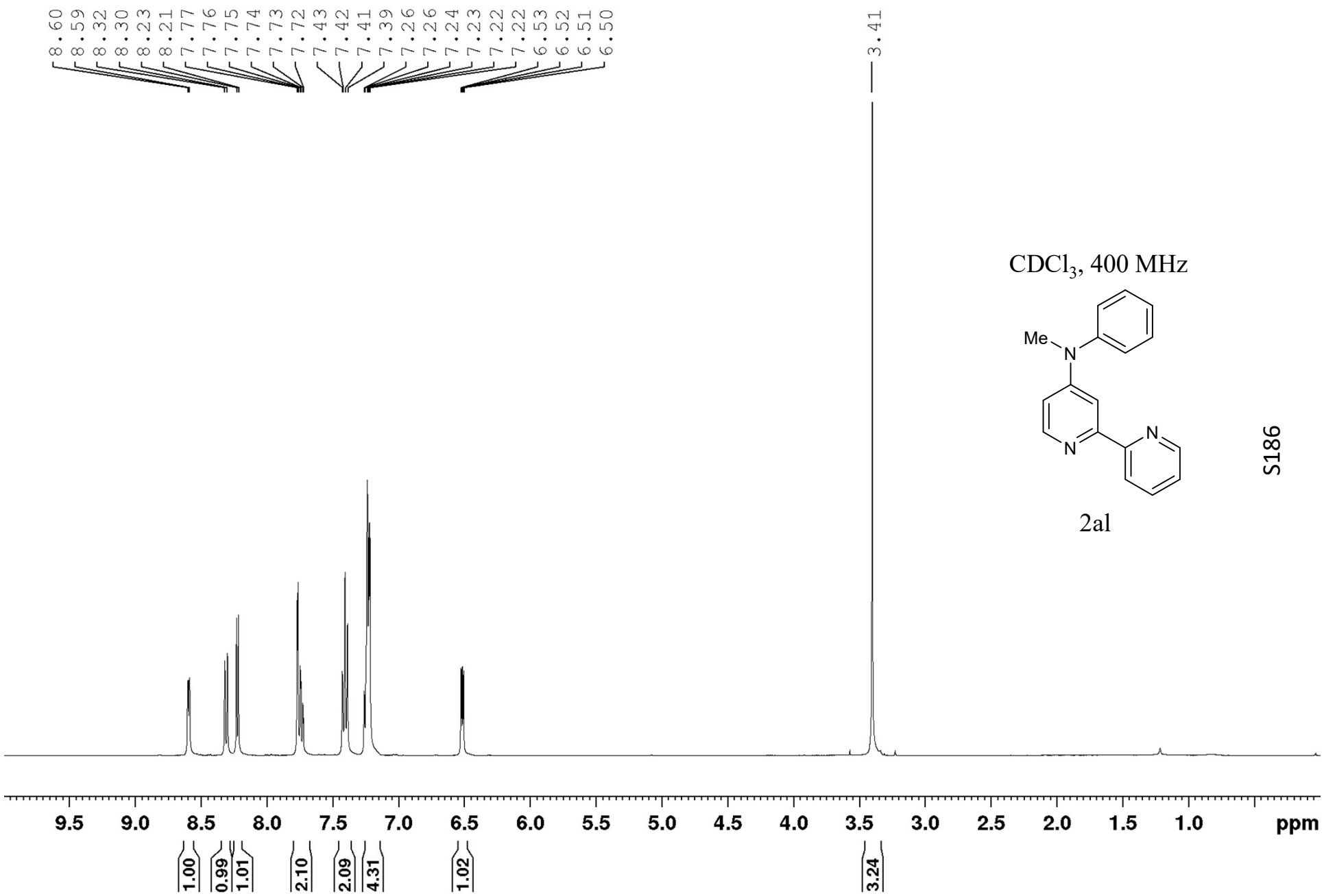


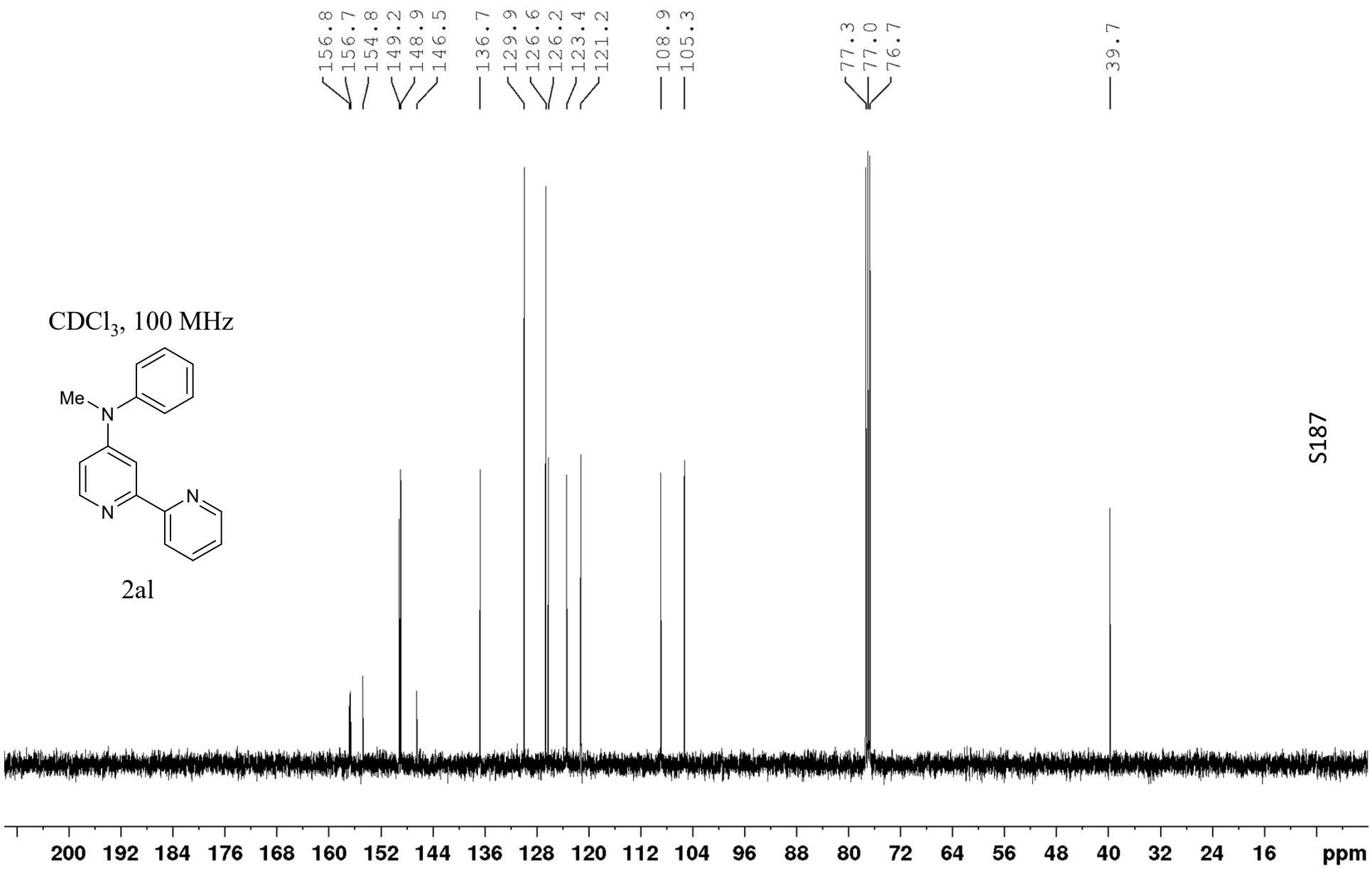

149.3
149.2
148.3
136.7
135.6
134.8
130.0
129.9
129.7
129.4
128.5
128.4
120.0
77.3
77.0
76.7
CDCl3, 100 MHz
S
N
2ai
S182
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

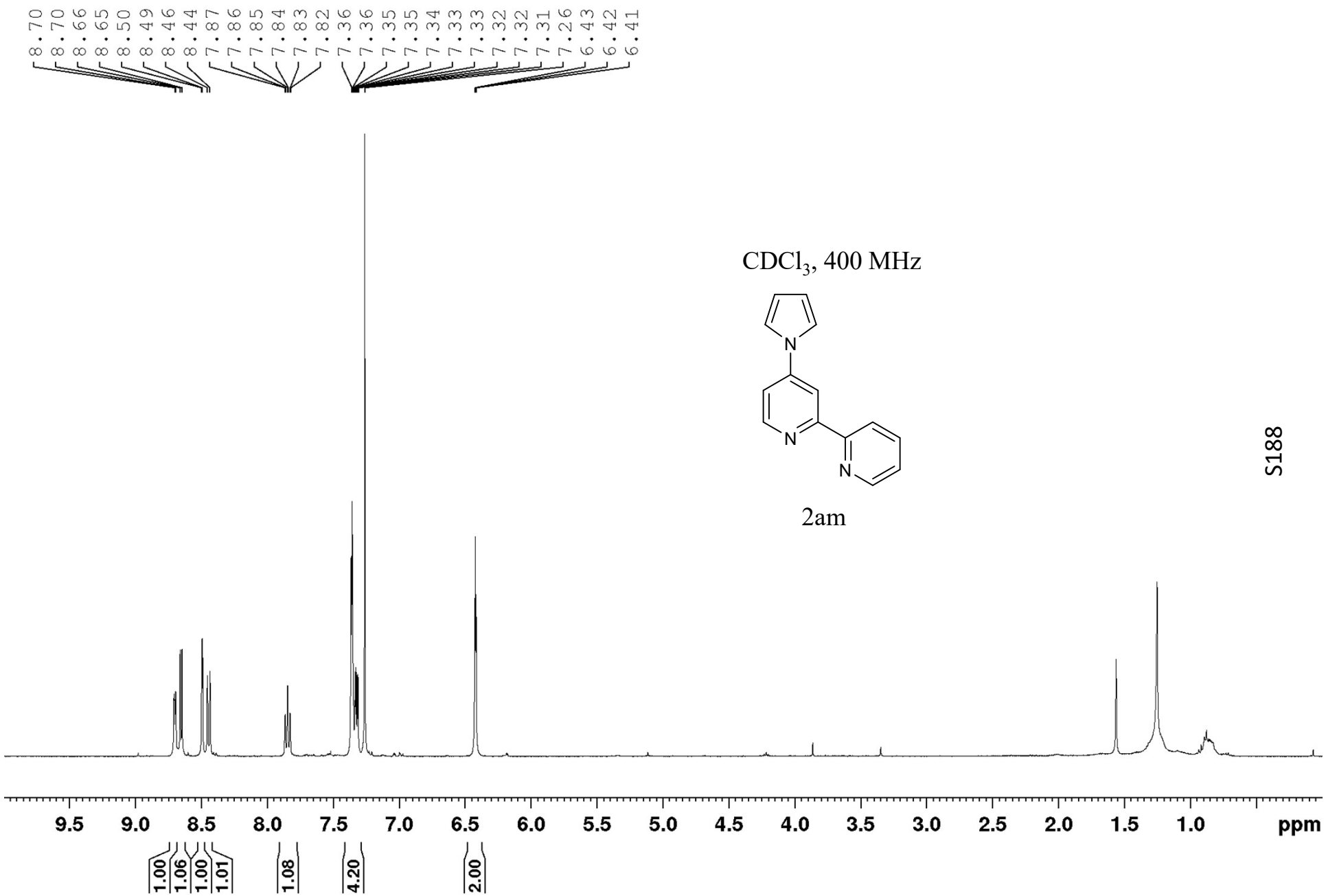

CDCl3, 400 MHz
Crude 1H NMR
Me
N
N
2aj
S183
C-H
byproduct
2aj
8.86
8.86
8.66
8.61
8.60
8.59
8.59
8.42
8.40
6.09
0.65
0.03
0.69
0.03
8.8
8.6
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.65
0.03
0.69
0.03
3.00

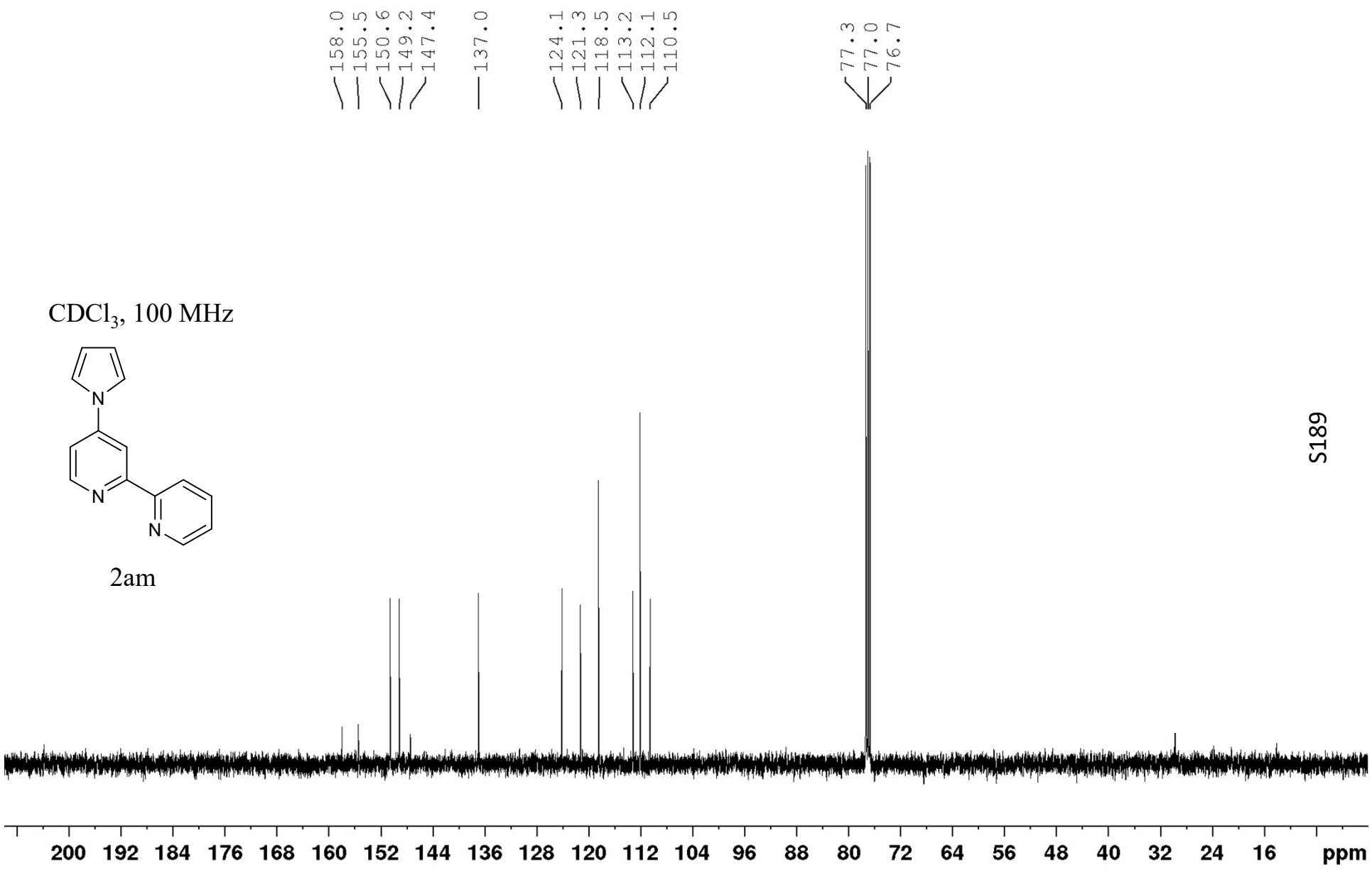

7.94
7.93
7.55
7.55
7.54
7.54
7.53
7.44
7.43
7.43
7.42
7.42
7.26
6.61
6.61
6.60
6.60
6.34
6.33
3.87
CDCl3, 400 MHz
S
N
OMe
2ak
S184
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.05
1.99
3.00
1.00
0.91
3.27

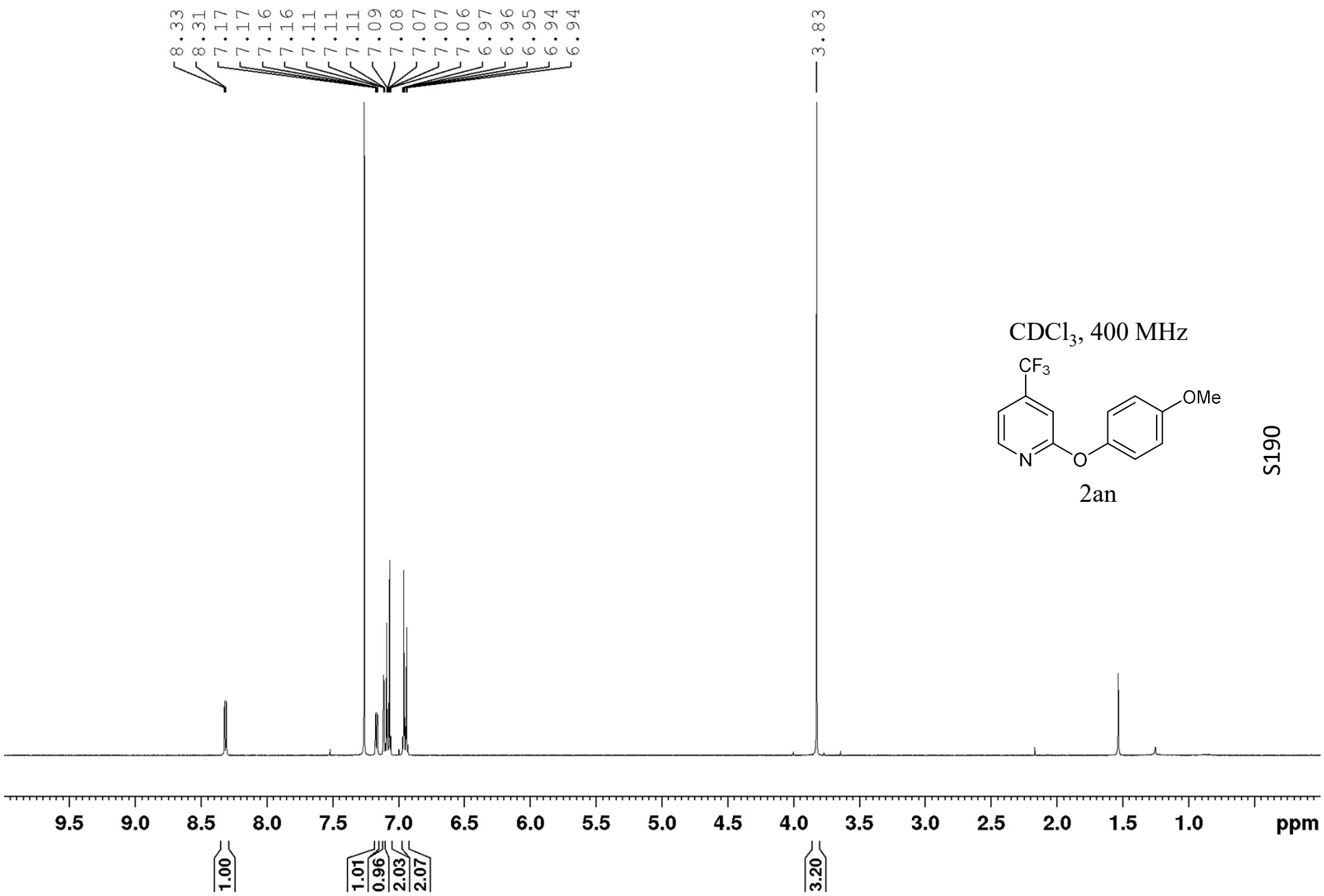

164.5
152.3
146.4
135.2
129.8
129.6
129.5
114.8
107.2
77.3
77.0
76.7
53.4
CDCl3, 100 MHz
S
N
OMe
2ak
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

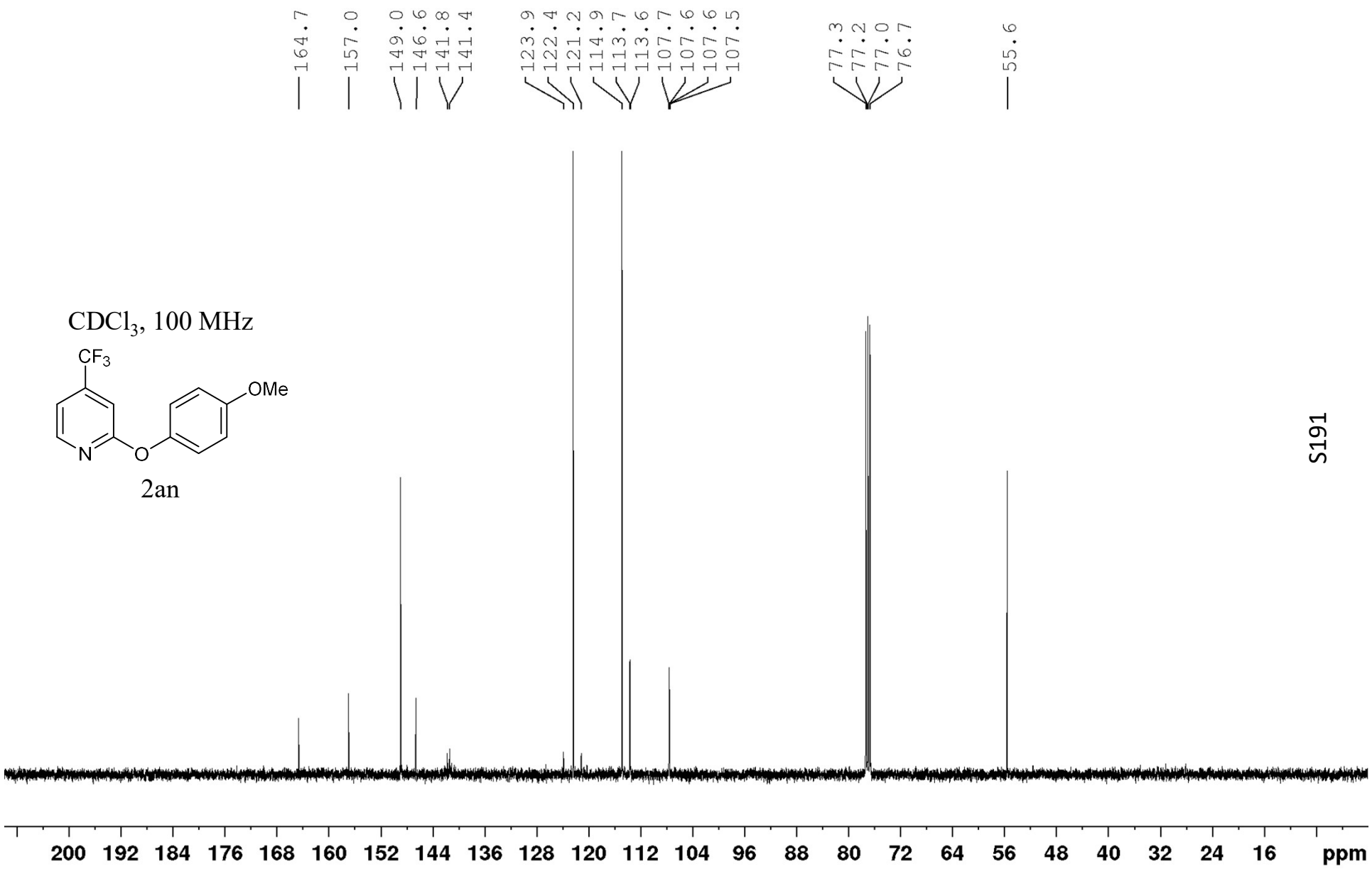

8.60
8.59
8.32
8.30
8.23
8.21
7.77
7.76
7.75
7.74
7.73
7.72
7.43
7.42
7.41
7.39
7.26
7.26
7.24
7.23
7.22
7.22
6.53
6.52
6.51
6.50
3.41
CDCl3, 400 MHz
Me
N
N
N
2al
S186
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
1.01
2.10
2.09
4.31
1.02
3.24

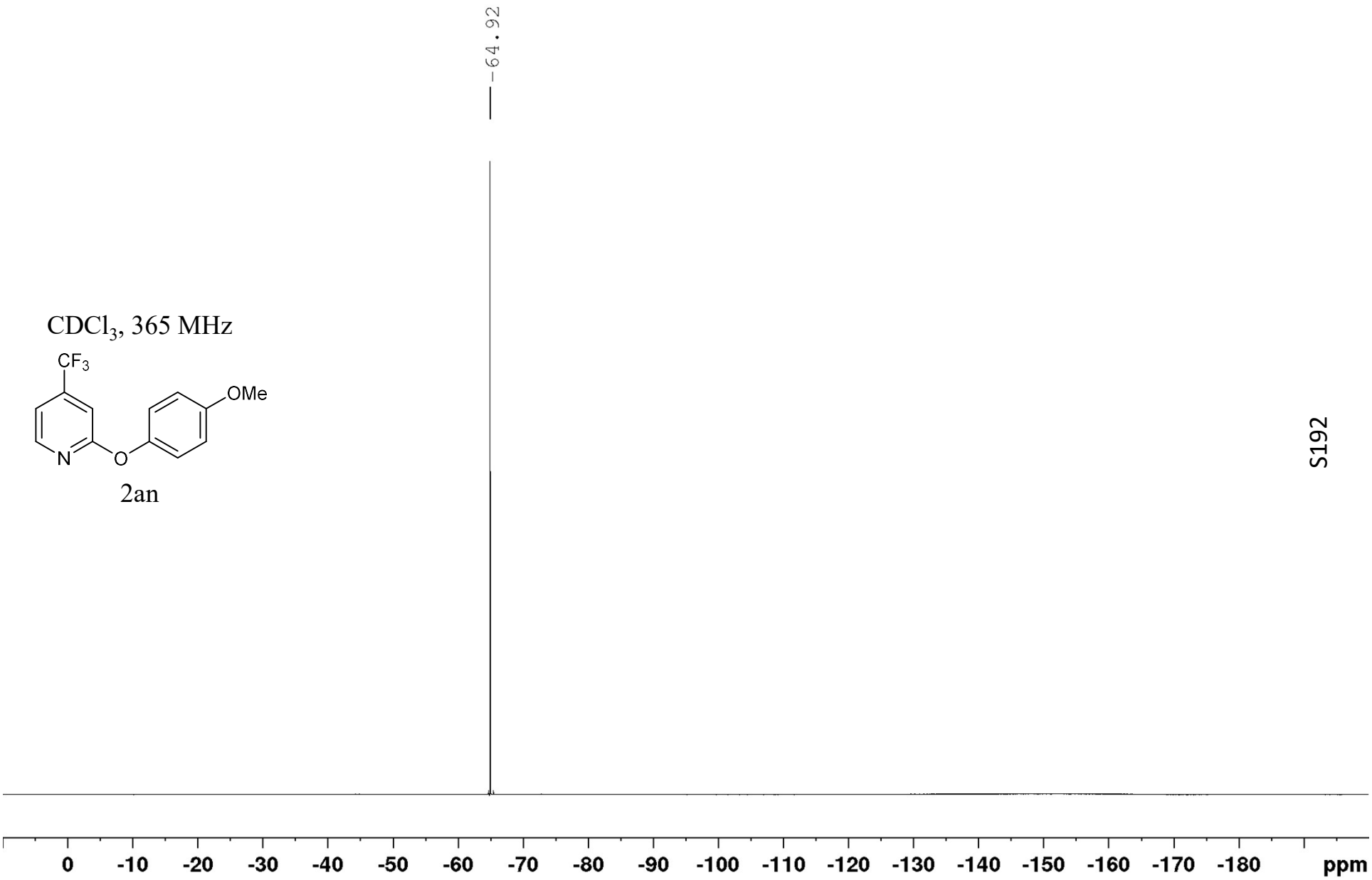

156.8
156.7
154.8
149.2
148.9
146.5
136.7
129.9
126.6
126.2
123.4
121.2
108.9
105.3
77.3
77.0
76.7
39.7
CDCl3, 100 MHz
Me
N
N
N
2al
S187
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

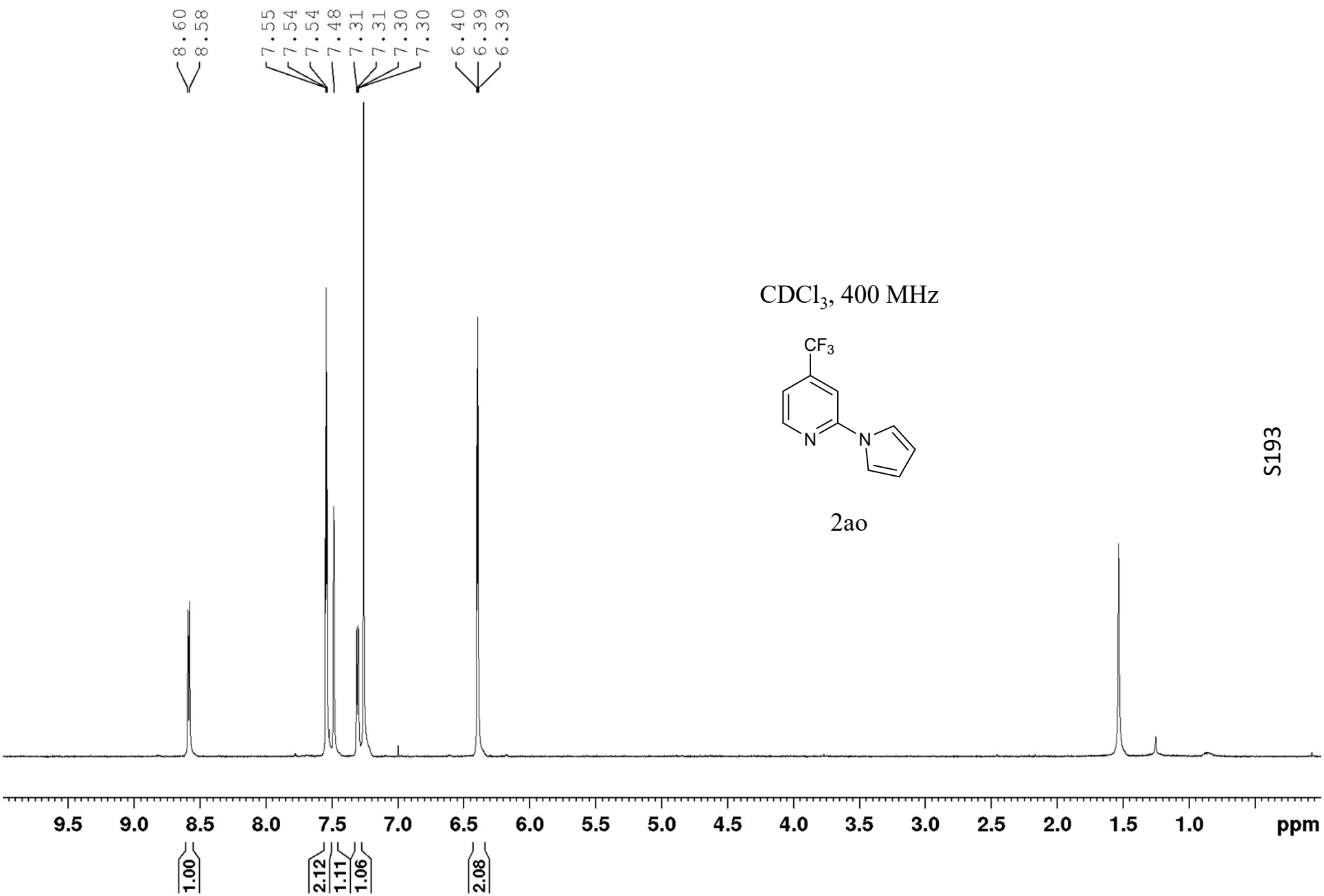

8.70
8.70
8.66
8.65
8.50
8.49
8.46
8.44
7.87
7.86
7.85
7.84
7.83
7.82
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.26
6.43
6.42
6.41
CDCl3, 400 MHz
N
N
N
2am
S188
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.06
1.00
1.01
1.08
4.20
2.00

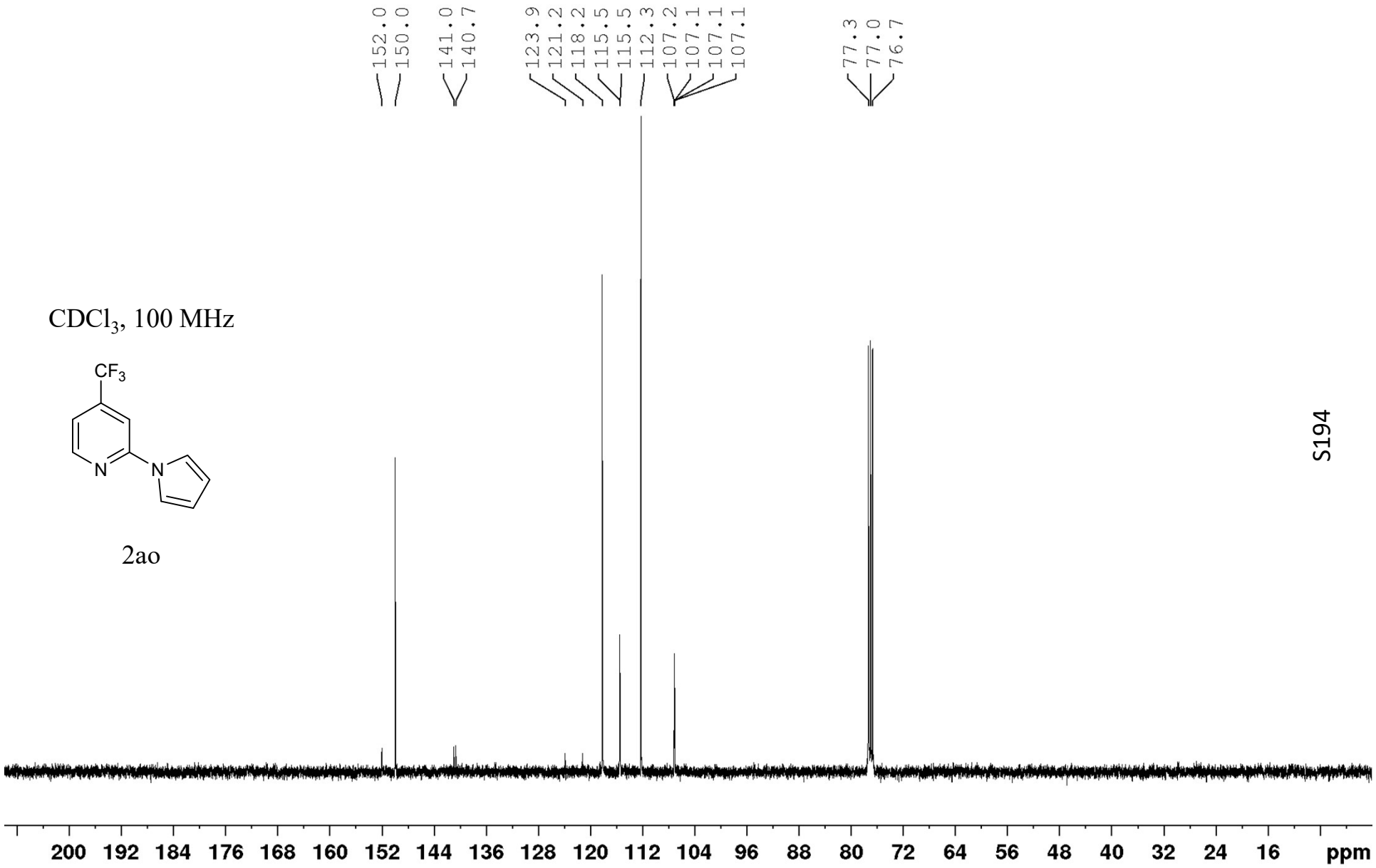

158.0
155.5
150.6
149.2
147.4
137.0
124.1
121.3
118.5
113.2
112.1
110.5
77.3
77.0
76.7
CDCl3, 100 MHz
2am
S189
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

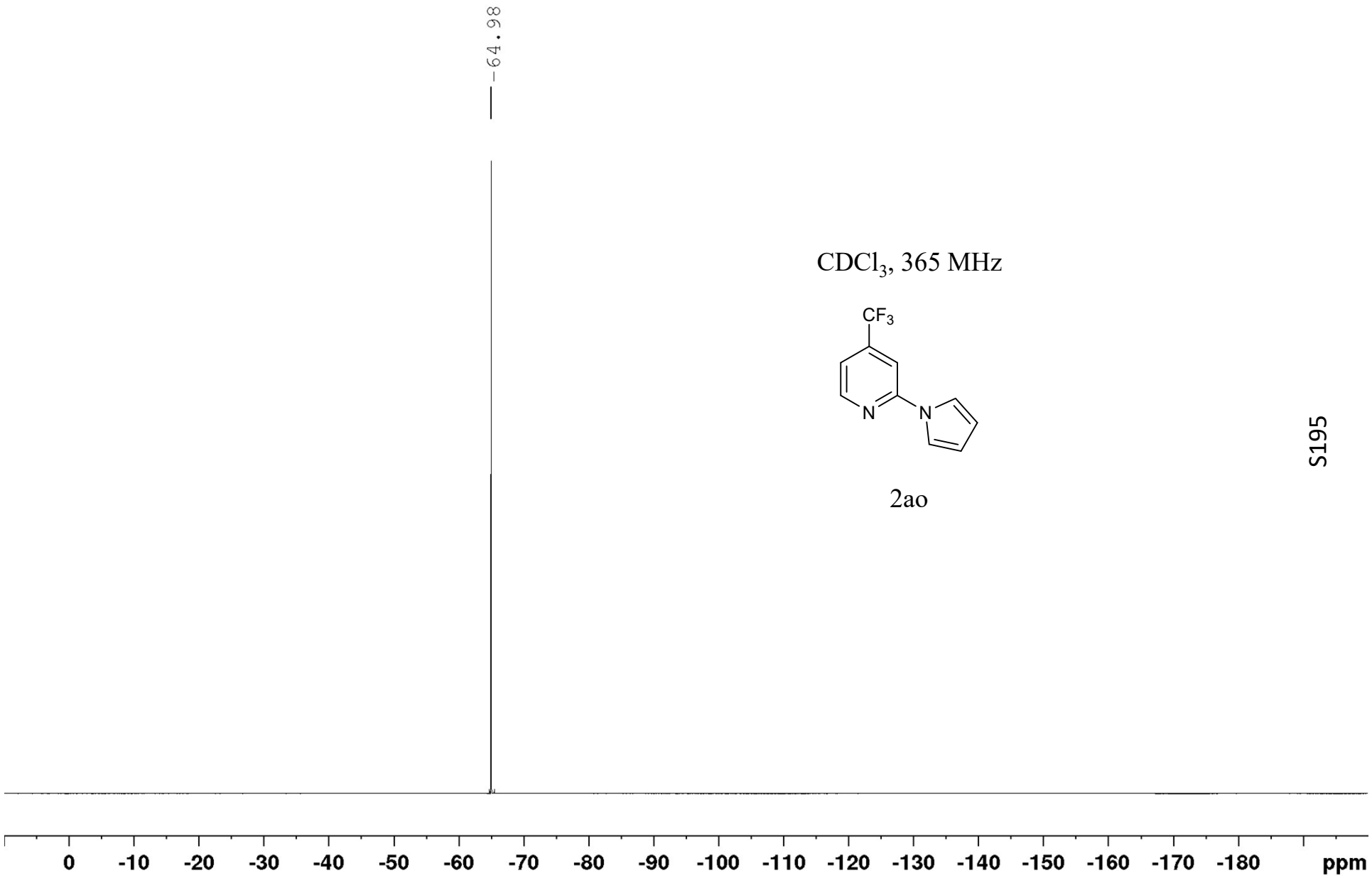

8.33
8.31
7.17
7.17
7.16
7.16
7.11
7.11
7.11
7.09
7.08
7.07
7.07
7.06
6.97
6.96
6.95
6.94
6.94
3.83
CDCl3, 400 MHz
CF3
OMe
N
O
2an
S190
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
0.96
2.03
2.07
3.20

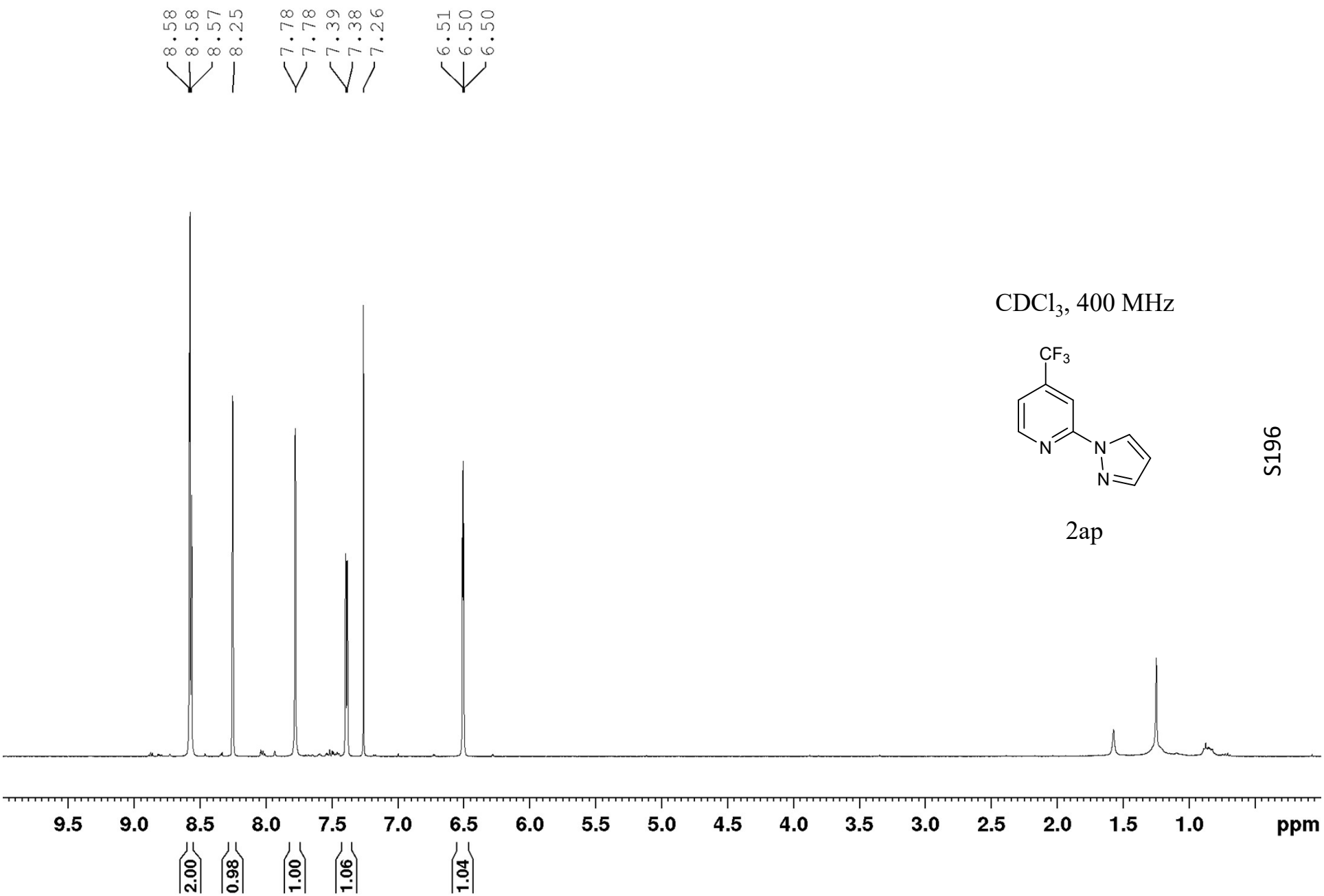

164.7
157.0
149.0
146.6
141.8
141.4
123.9
122.4
121.2
114.9
113.7
113.6
107.7
107.6
107.6
107.5
77.3
77.2
77.0
76.7
55.6
CDCl3, 100 MHz
CF3
OMe
N
O
2an
S191
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

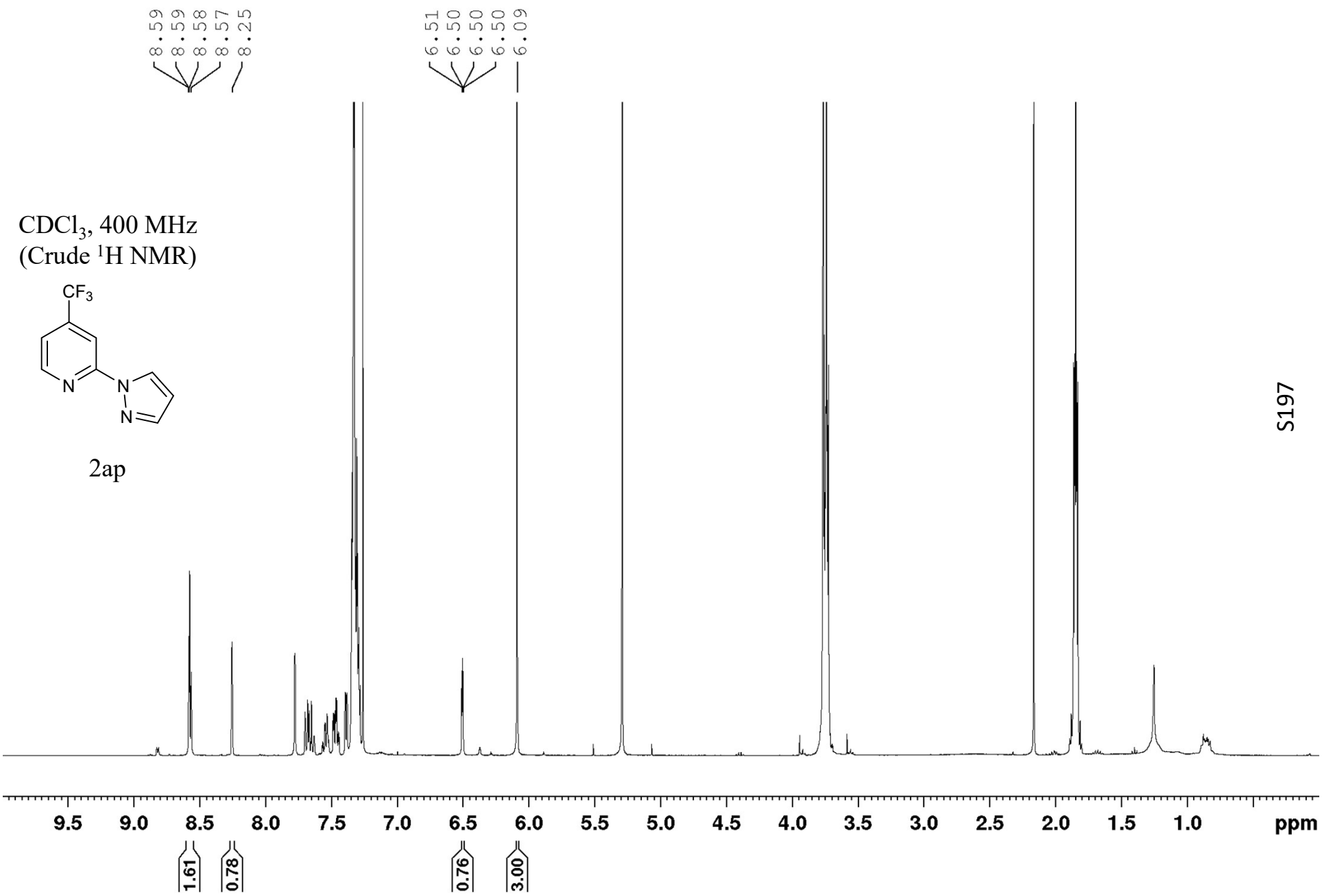

-64.92
CDCl3, 365 MHz
CF3
OMe
N
O
2an
S192
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

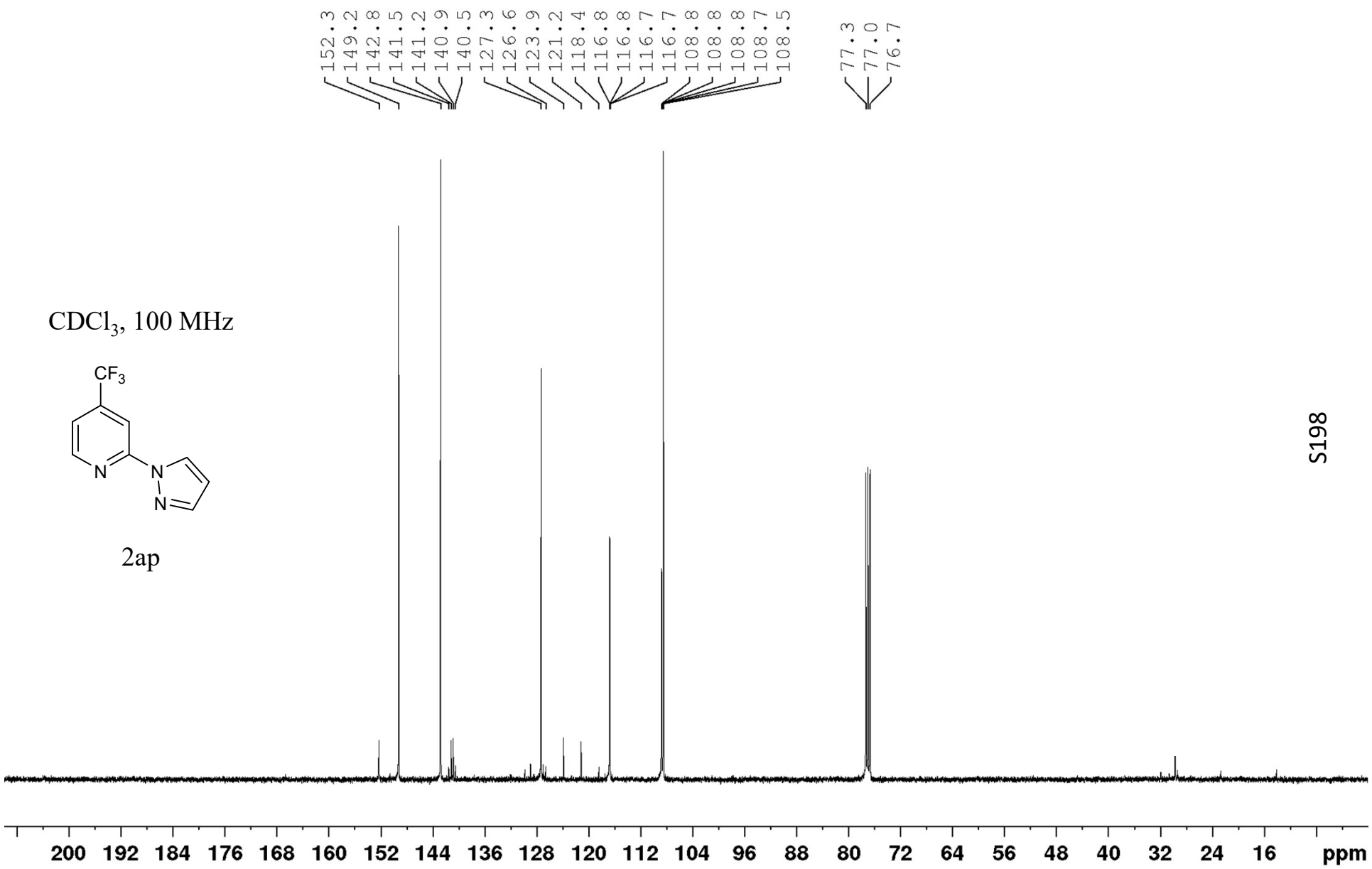

8.60
8.58
7.55
7.54
7.54
7.48
7.31
7.31
7.30
7.30
6.40
6.39
6.39
CDCl3, 400 MHz
CF3
N
N
2ao
S193
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.12
1.11
1.06
2.08

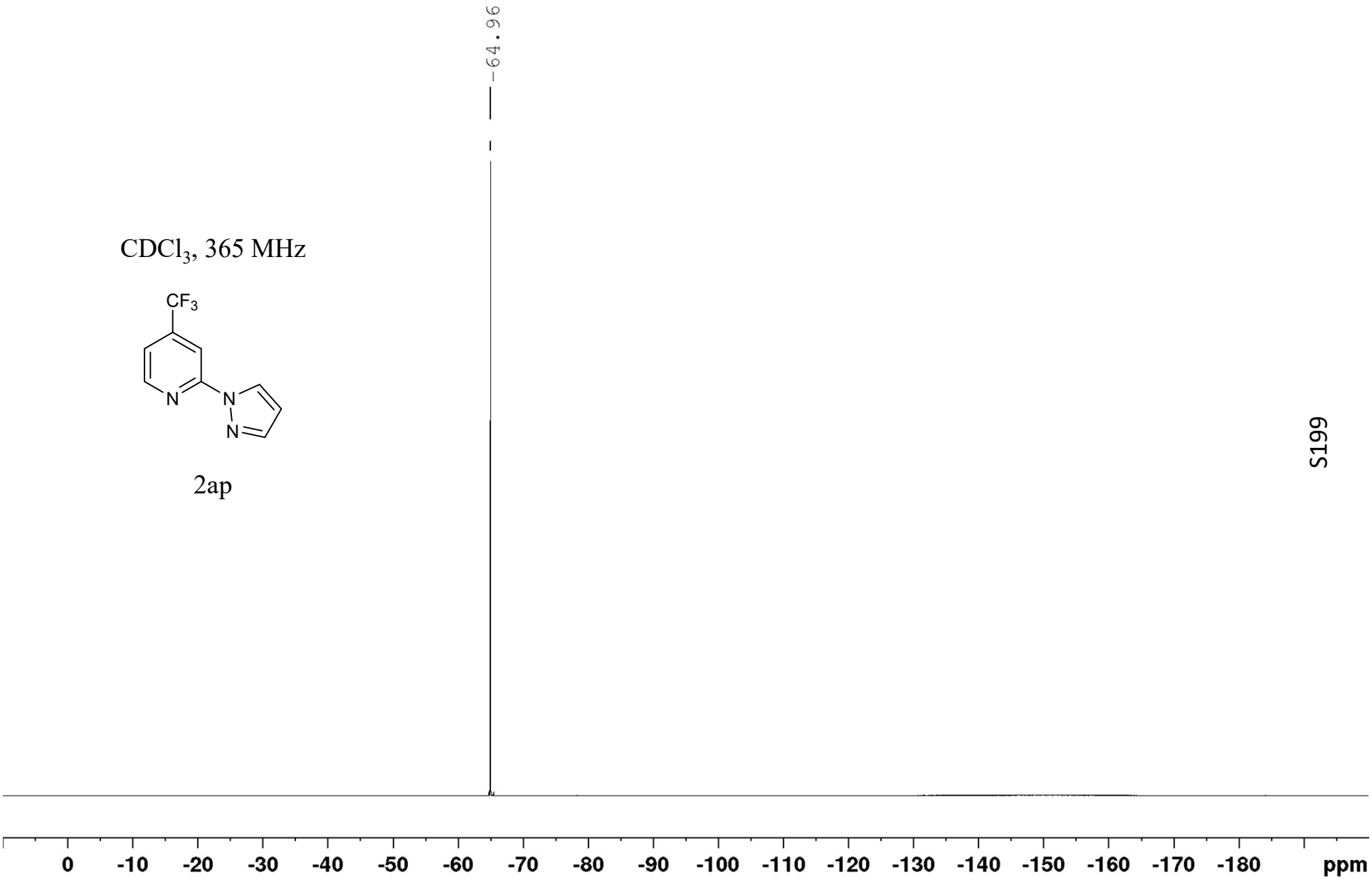

152.0
150.0
141.0
140.7
123.9
121.2
118.2
115.5
115.5
112.3
107.2
107.1
107.1
107.1
77.3
77.0
76.7
CDCl3, 100 MHz
CF3
N
N
2ao
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

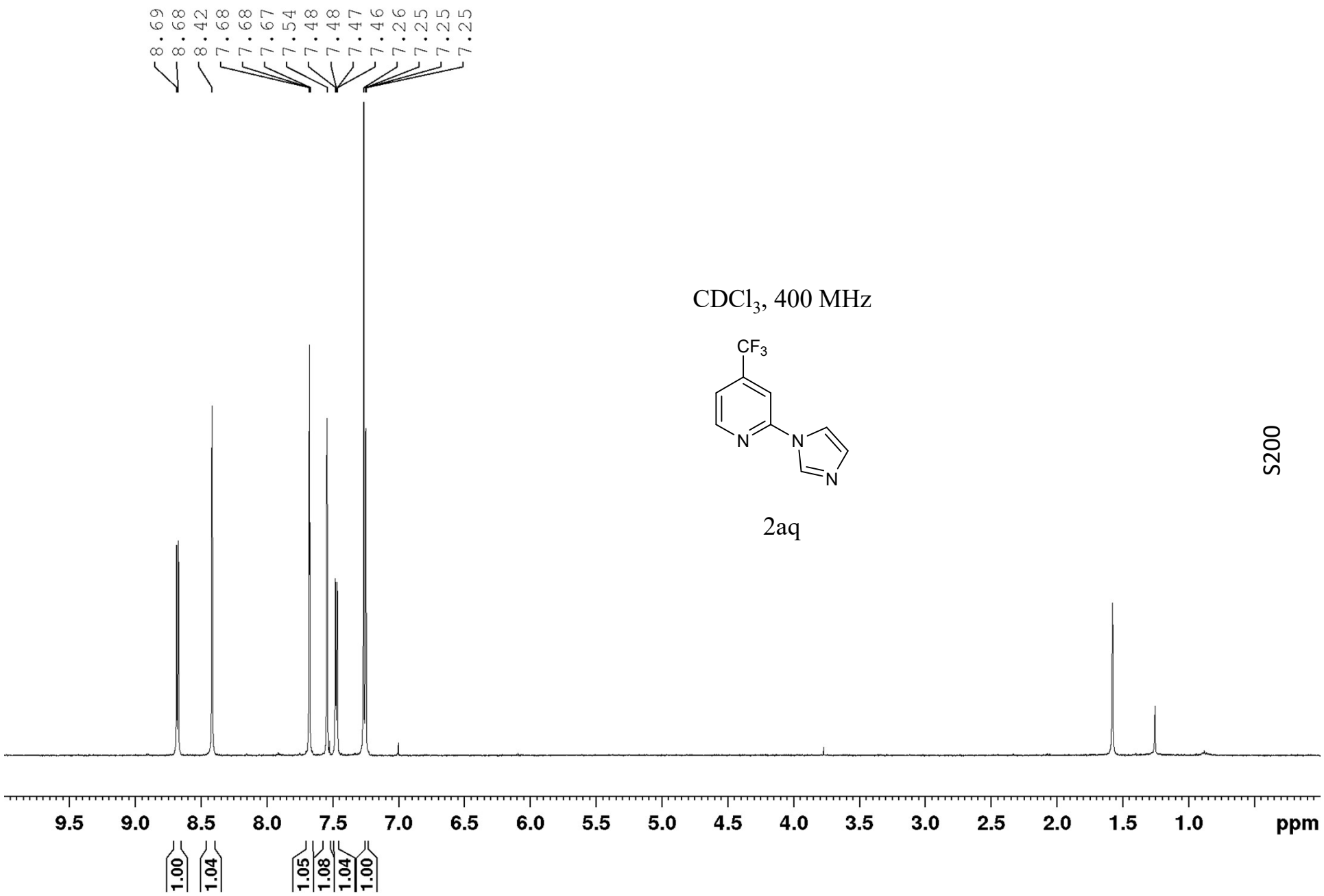

-64.98
CDCl3, 365 MHz
CF3
N
N
2ao
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

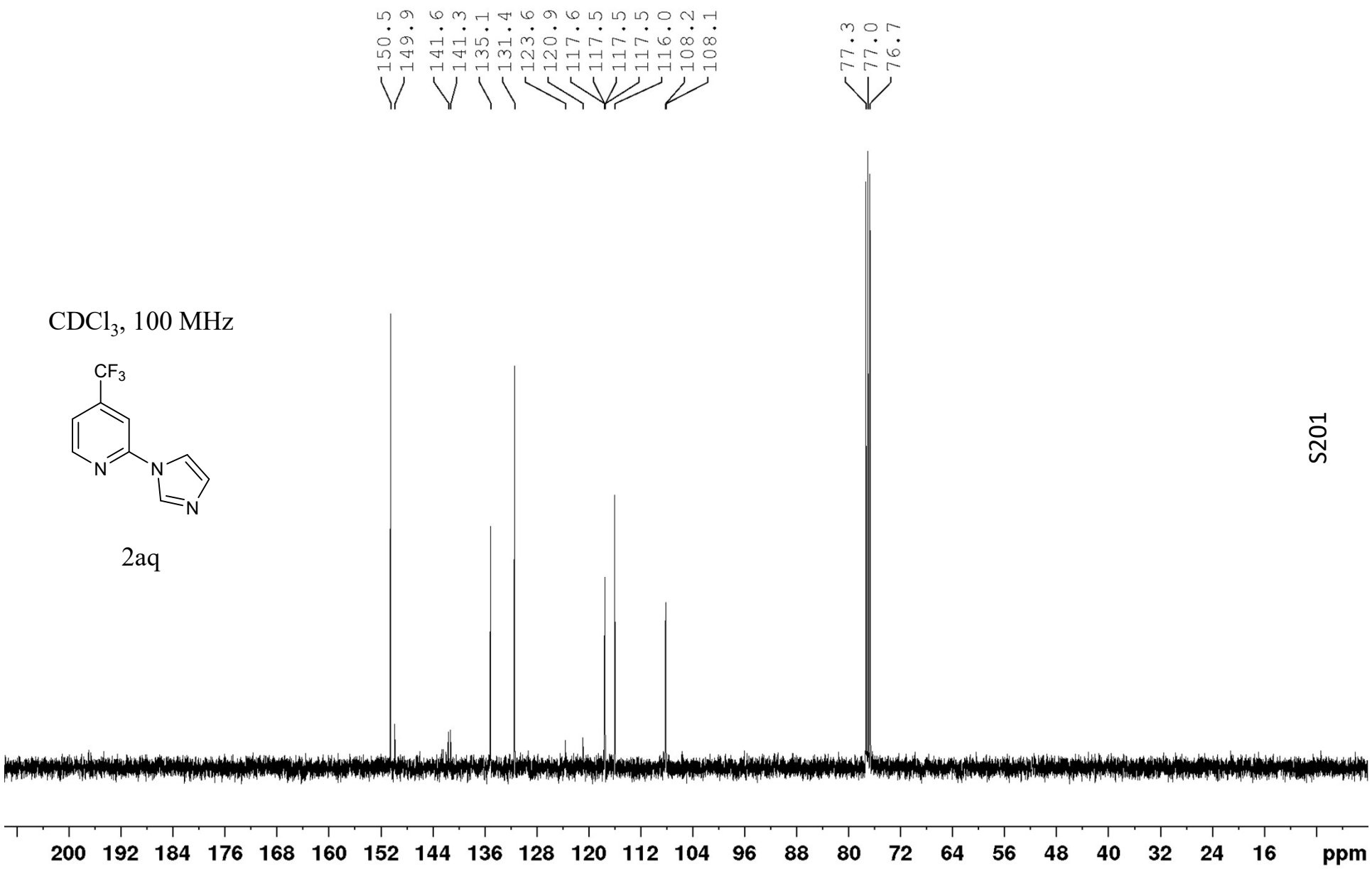

8.58
8.58
8.57
8.25
7.78
7.78
7.39
7.38
7.26
6.51
6.50
6.50
CDCl3, 400 MHz
CF3
N
N
N
2ap
S196
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
0.98
1.00
1.06
1.04

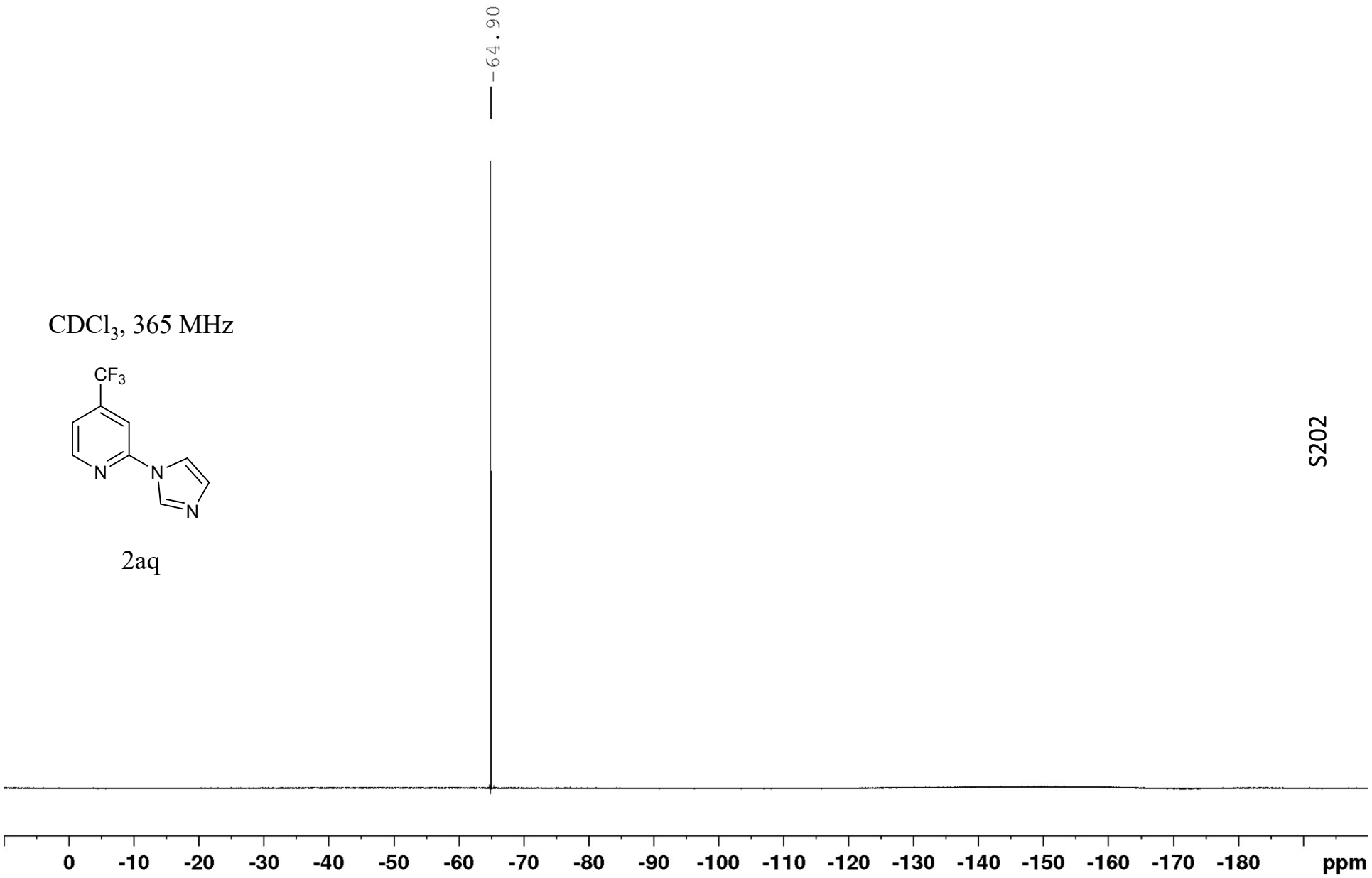

8.59
8.59
8.58
8.57
8.25
6.51
6.50
6.50
6.50
6.09
CDCl3, 400 MHz
(Crude 1H NMR)
CF3
N
N
N
2ap
S197
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.61
0.78
0.76
3.00

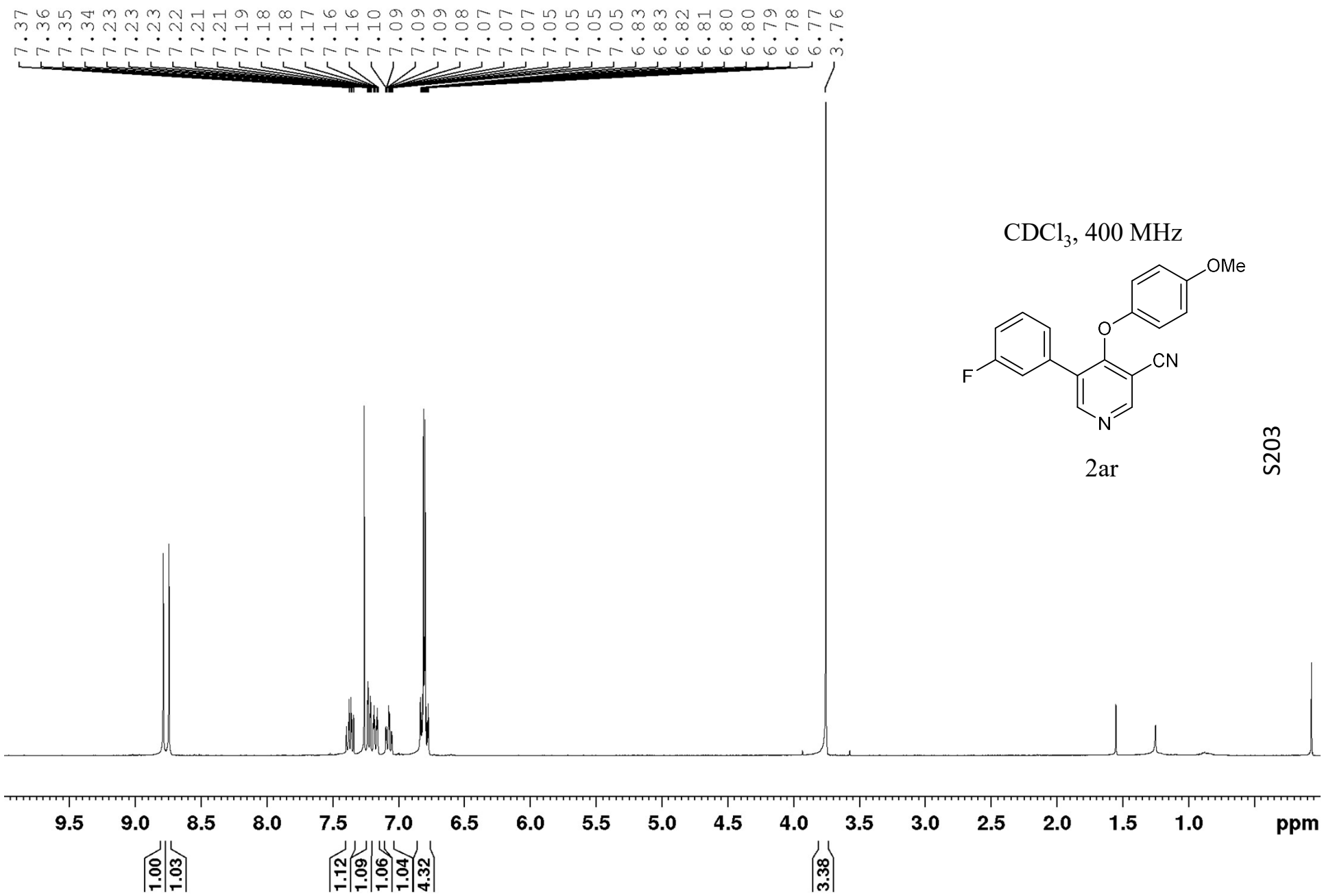

152.3
149.2
142.8
141.5
141.2
140.9
140.5
127.3
126.6
123.9
121.2
118.4
116.8
116.8
116.7
116.7
108.8
108.8
108.8
108.7
108.5
77.3
77.0
76.7
CDCl3, 100 MHz
CF3
N
N
N
2ap
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

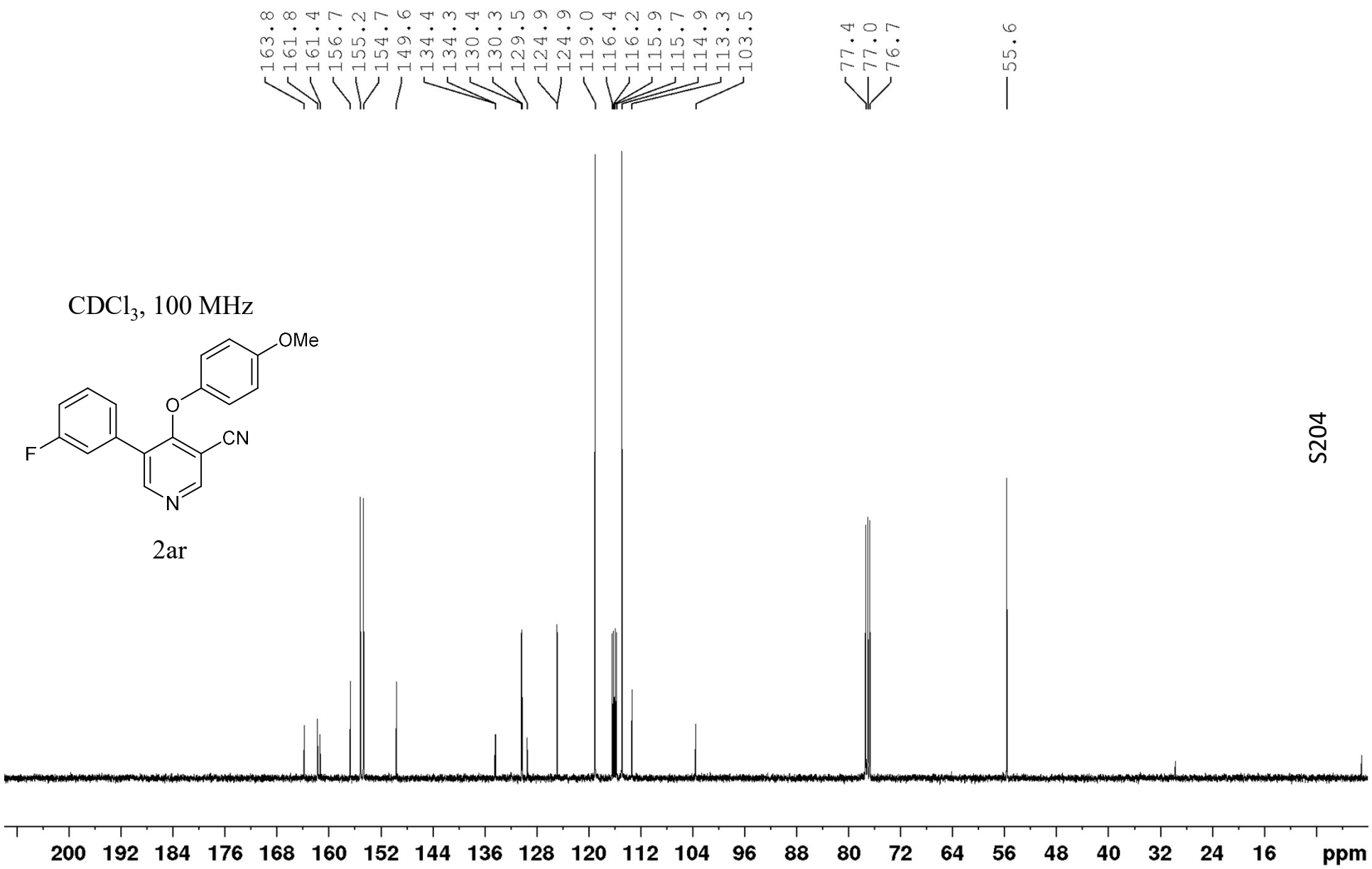

-64.96
CDCl3, 365 MHz
CF3
N
N
N
2ap
S199
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


8.69
8.68
8.42
7.68
7.68
7.67
7.54
7.48
7.48
7.47
7.46
7.26
7.25
7.25
7.25
CDCl3, 400 MHz
CF3
N
N
N
2aq
S200
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
1.00
1.04
1.05
1.08
1.04
1.00

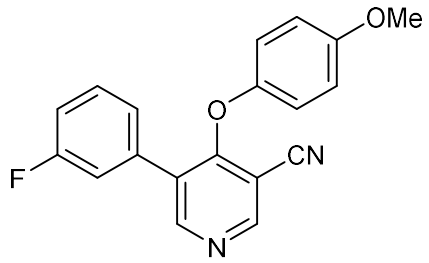

150.5
149.9
141.6
141.3
135.1
131.4
123.6
120.9
117.6
117.5
117.5
117.5
116.0
108.2
108.1
77.3
77.0
76.7
CDCl3, 100 MHz
CF3
N
N
N
2aq
S201
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


-64.90
CDCl3, 365 MHz
CF3
N
N
N
2aq
S202
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

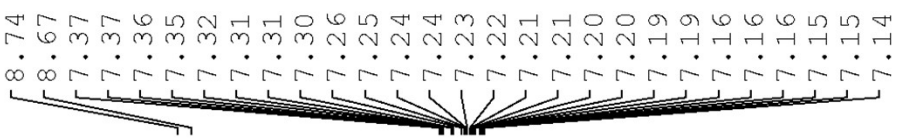

7.37
7.36
7.35
7.34
7.23
7.23
7.23
7.22
7.21
7.21
7.19
7.18
7.18
7.17
7.16
7.16
7.10
7.09
7.09
7.09
7.08
7.07
7.07
7.07
7.05
7.05
7.05
7.05
6.83
6.83
6.82
6.81
6.80
6.80
6.79
6.78
6.77
3.76
CDCl3, 400 MHz
OMe
O
CN
F
N
2ar
S203
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.03
1.12
1.09
1.06
1.04
4.32
3.38


163.8
161.8
161.4
156.7
155.2
154.7
149.6
134.4
134.3
130.4
130.3
129.5
124.9
124.9
119.0
116.4
116.2
115.9
115.7
114.9
113.3
103.5
77.4
77.0
76.7
55.6
CDCl3, 100 MHz
OMe
O
CN
F
N
2ar
S204
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

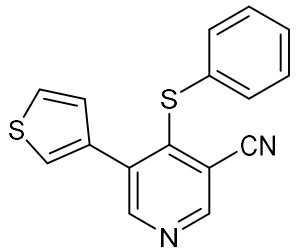
$CDCl_3$, 365 MHz



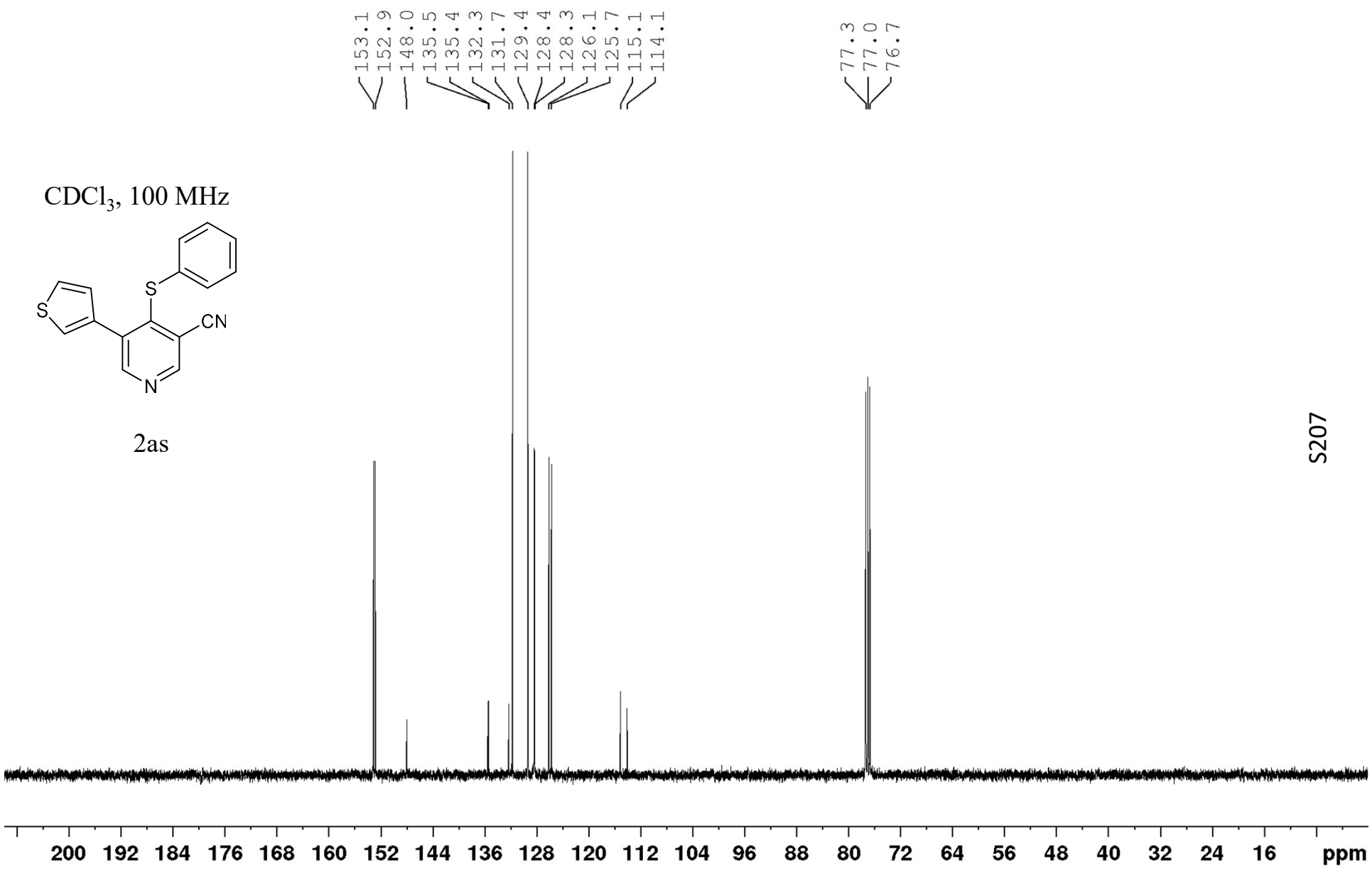
2ar

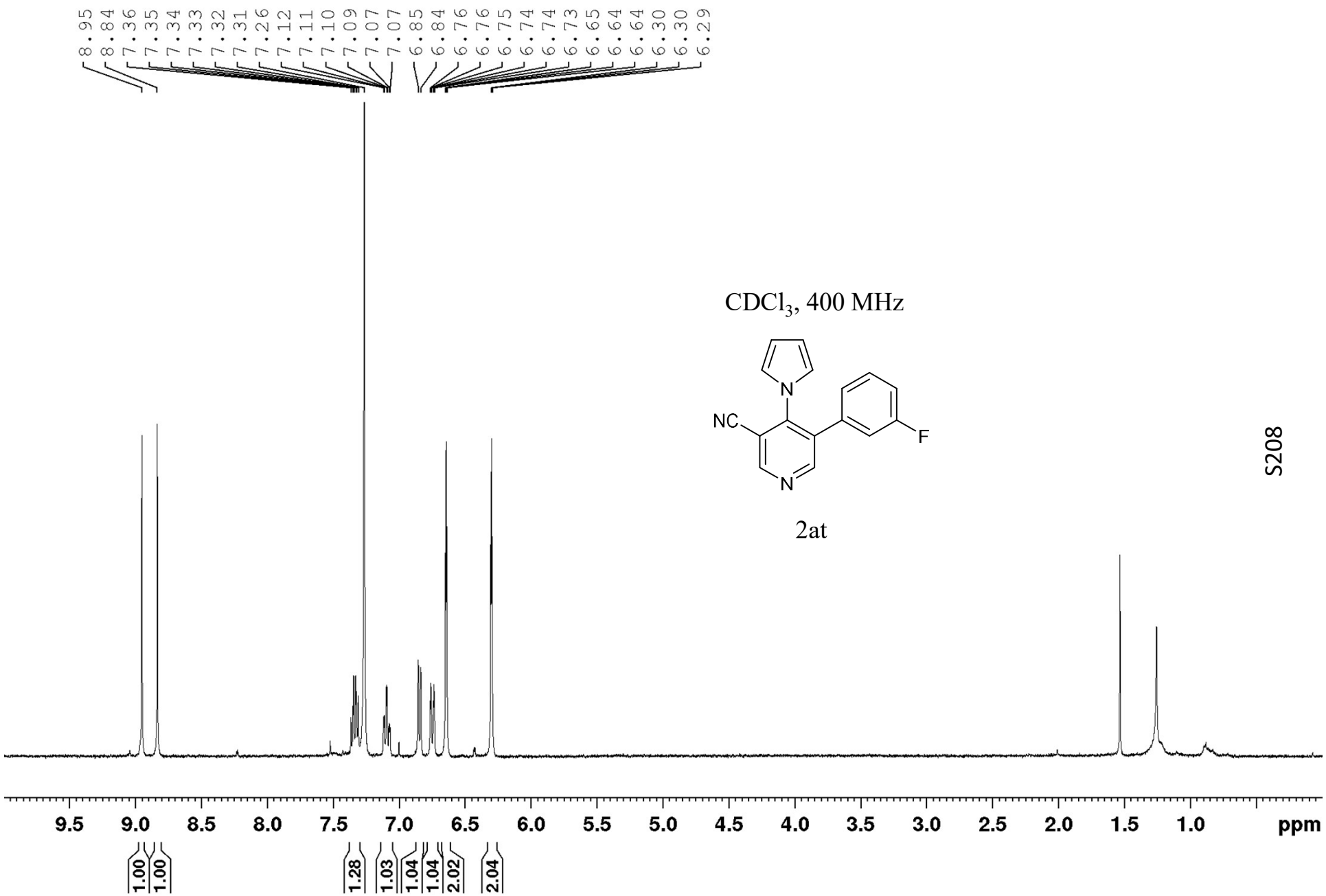


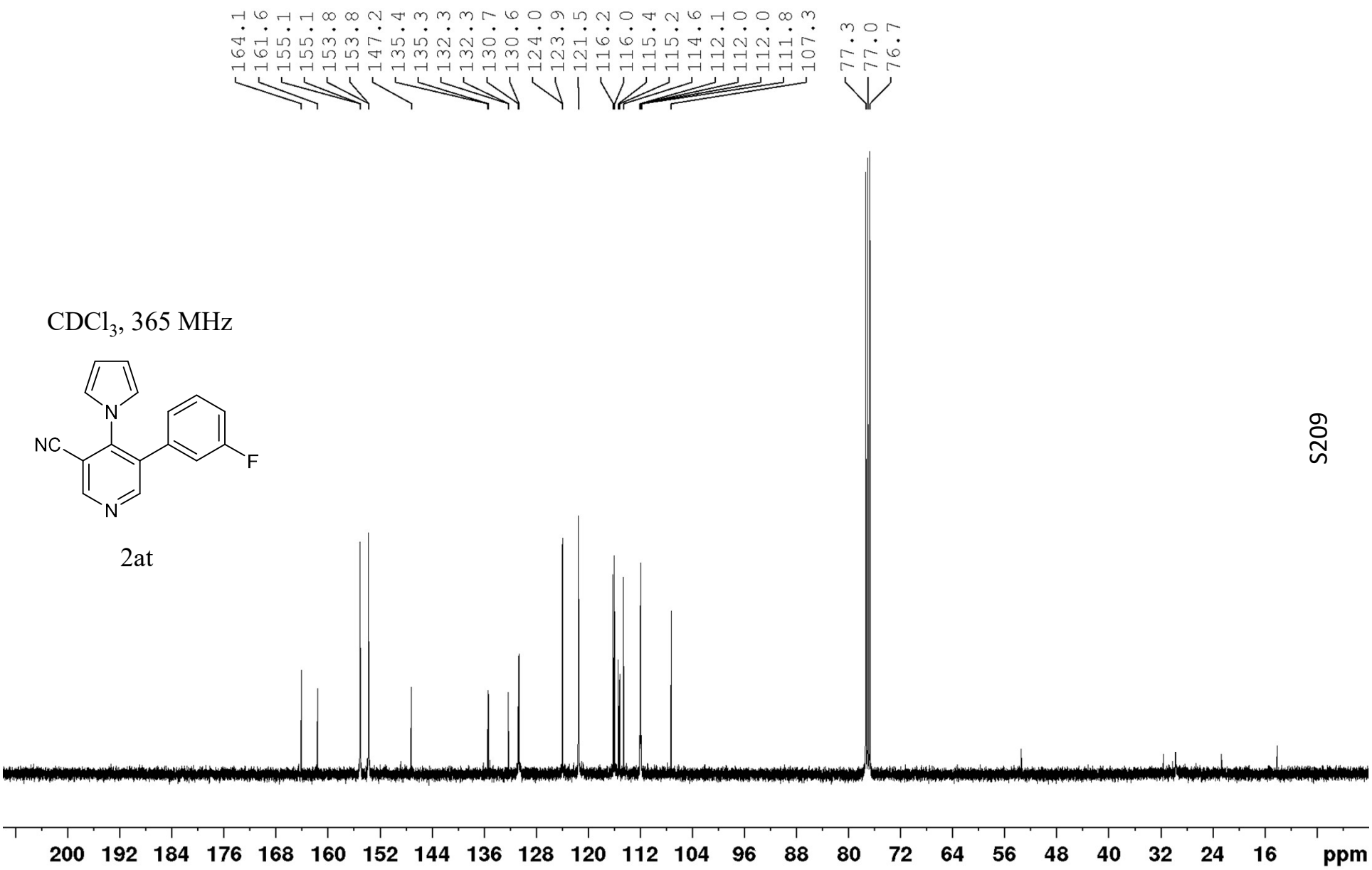
$CDCl_3$, 400 MHz

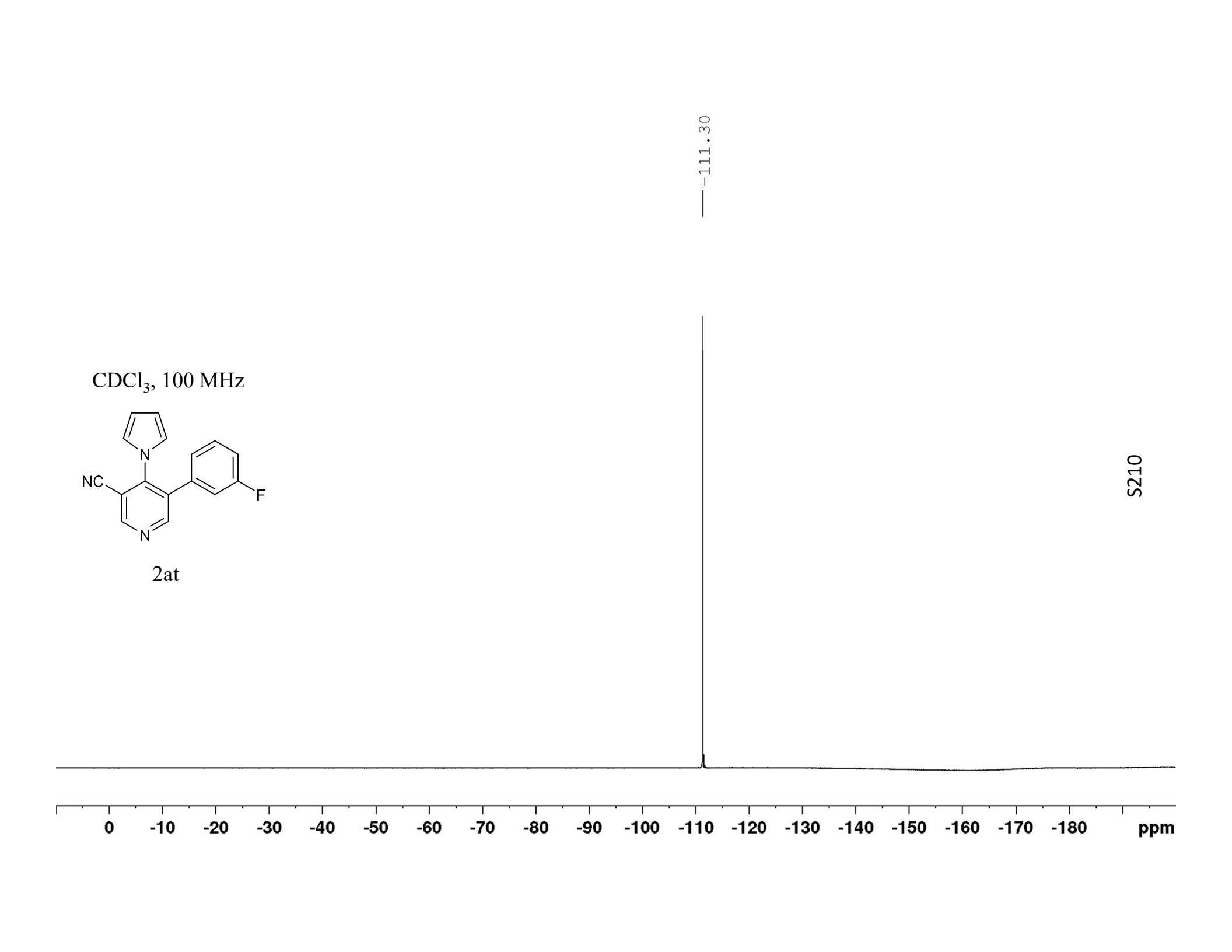


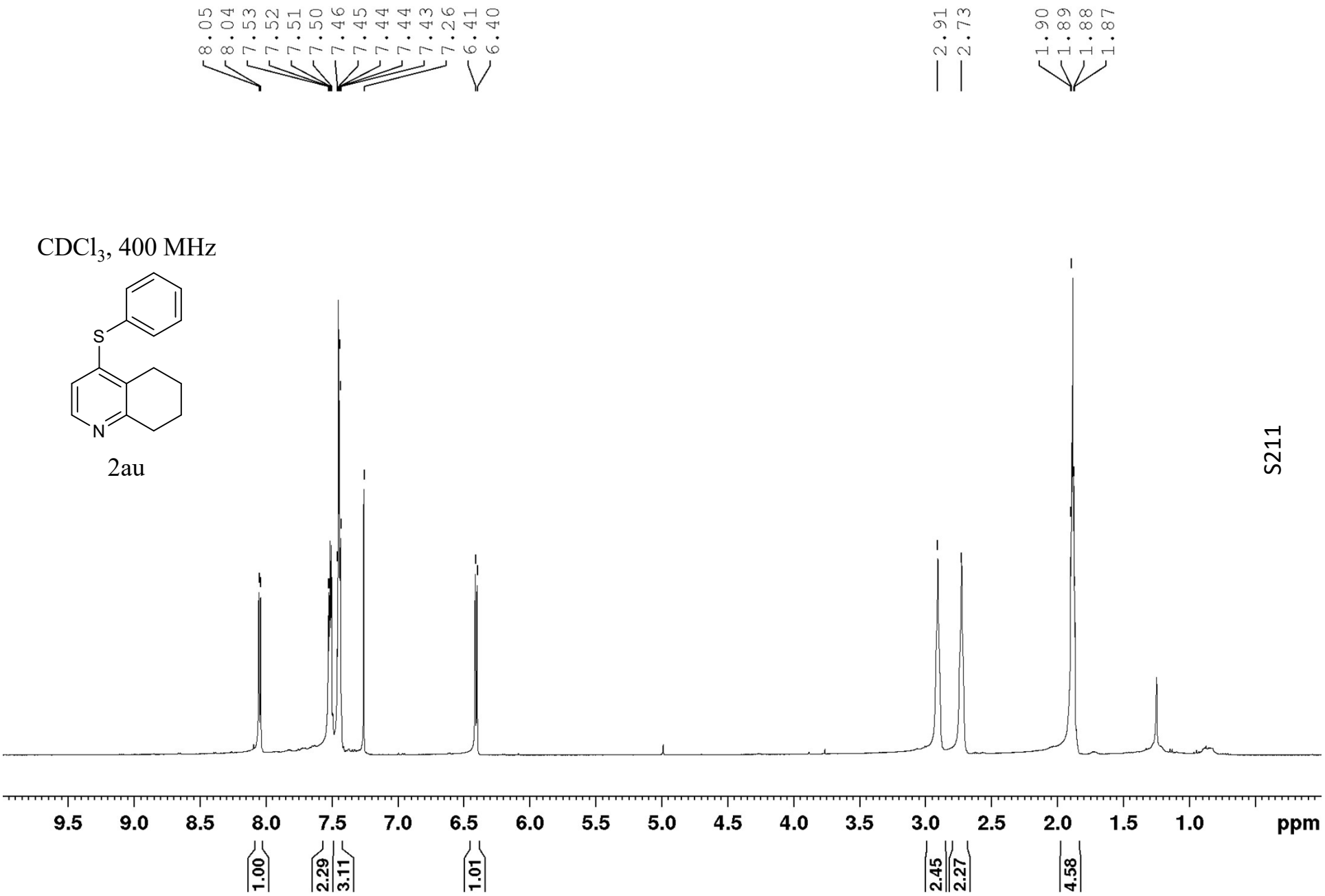
2as

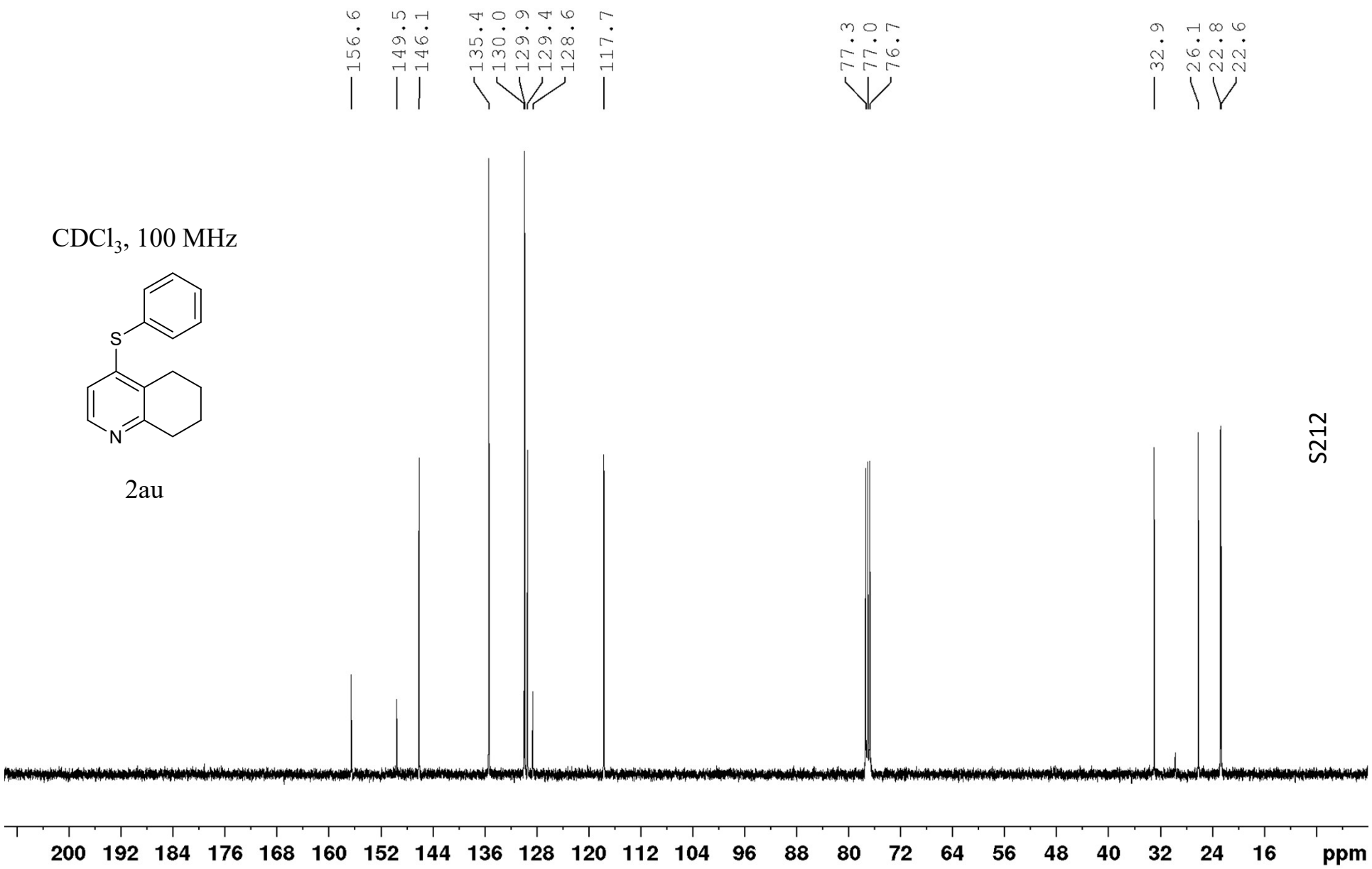

153.1
152.9
148.0
135.5
135.4
132.3
131.7
129.4
128.4
128.3
126.1
125.7
115.1
114.1
77.3
77.0
76.7
CDCl3, 100 MHz
S
S
CN
N
2as
S207
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

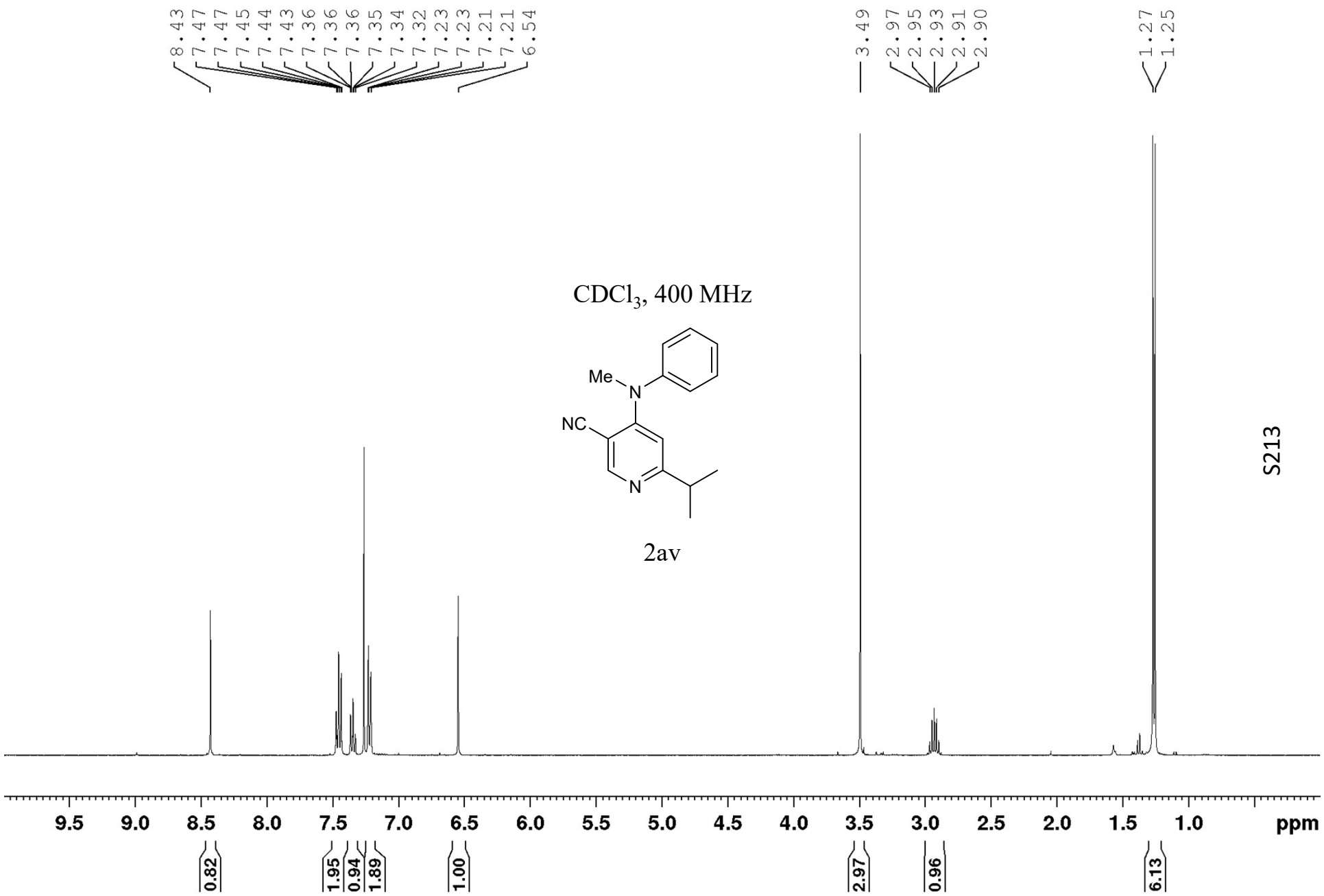

8.95
8.84
7.36
7.35
7.34
7.33
7.32
7.31
7.26
7.12
7.11
7.10
7.09
7.07
7.07
6.85
6.84
6.76
6.76
6.75
6.74
6.74
6.73
6.65
6.64
6.64
6.30
6.30
6.29
CDCl3, 400 MHz
NC
F
N
N
2at
S208
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
1.28
1.03
1.04
1.04
2.02
2.04

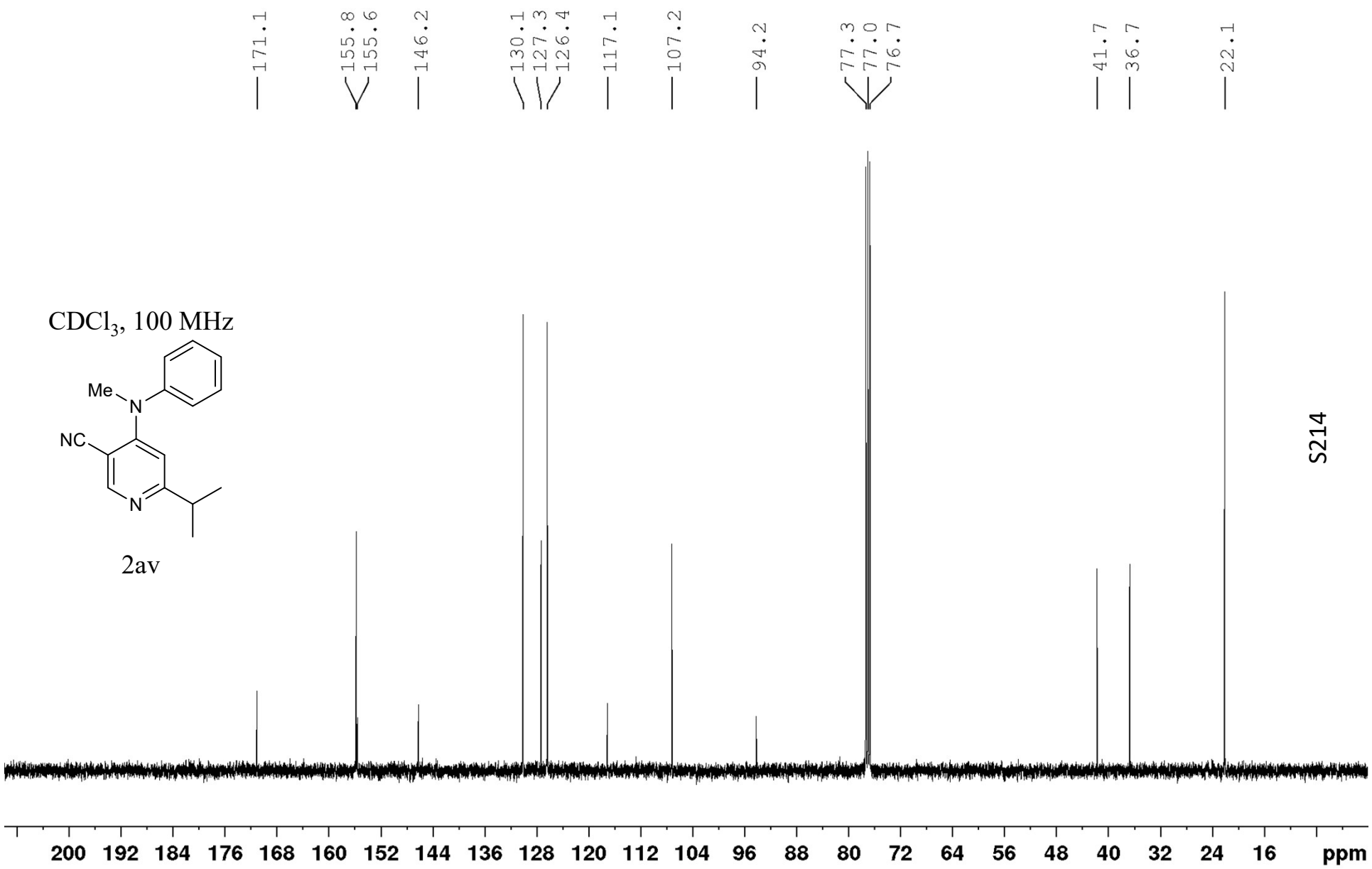

164.1
161.6
155.1
155.1
153.8
153.8
147.2
135.4
135.3
132.3
132.3
130.7
130.6
124.0
123.9
121.5
116.2
116.0
115.4
115.2
114.6
112.1
112.0
112.0
111.8
107.3
77.3
77.0
76.7
CDCl3, 365 MHz
NC
F
N
N
2at
S209
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

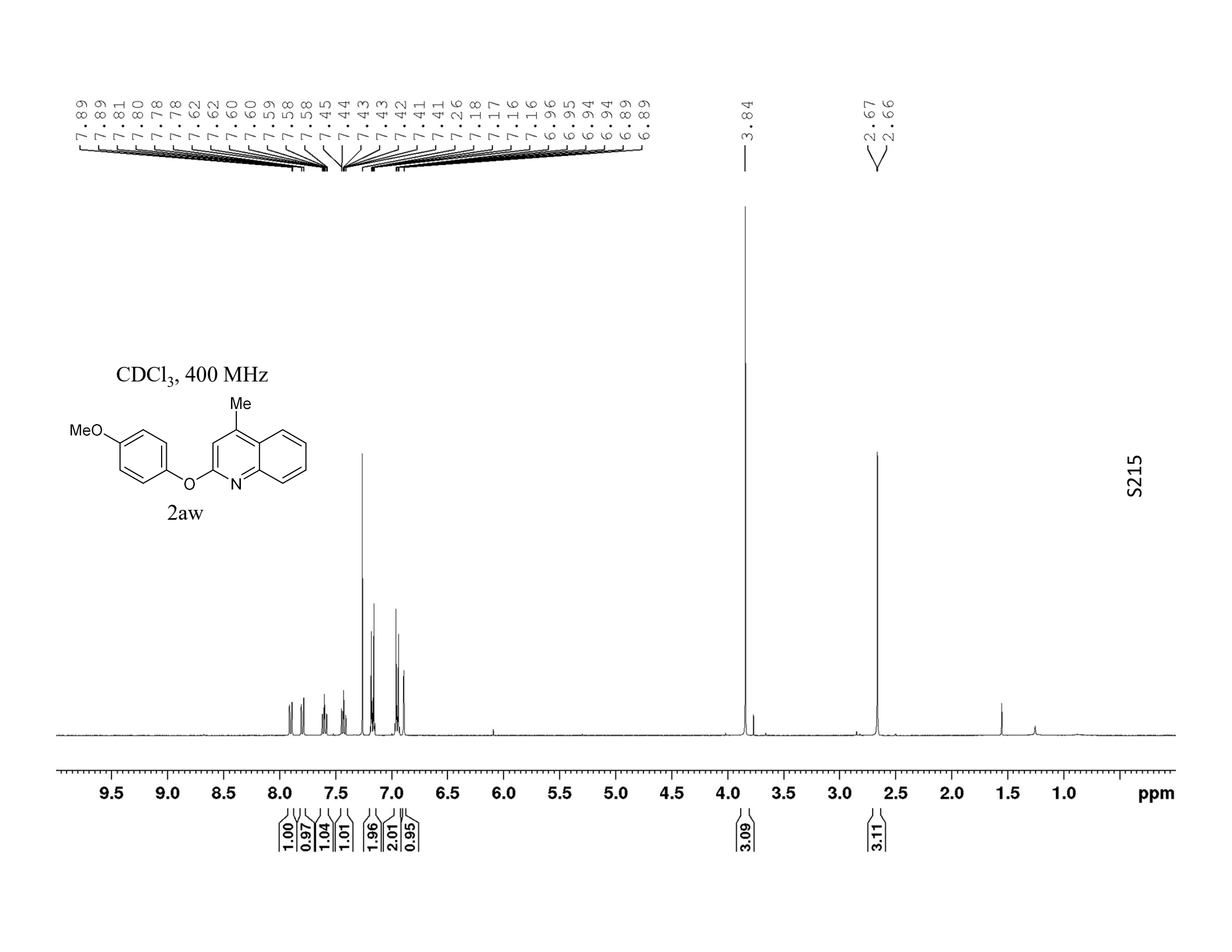

-111.30
CDCl3, 100 MHz
NC
N
F
N
2at
S210
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

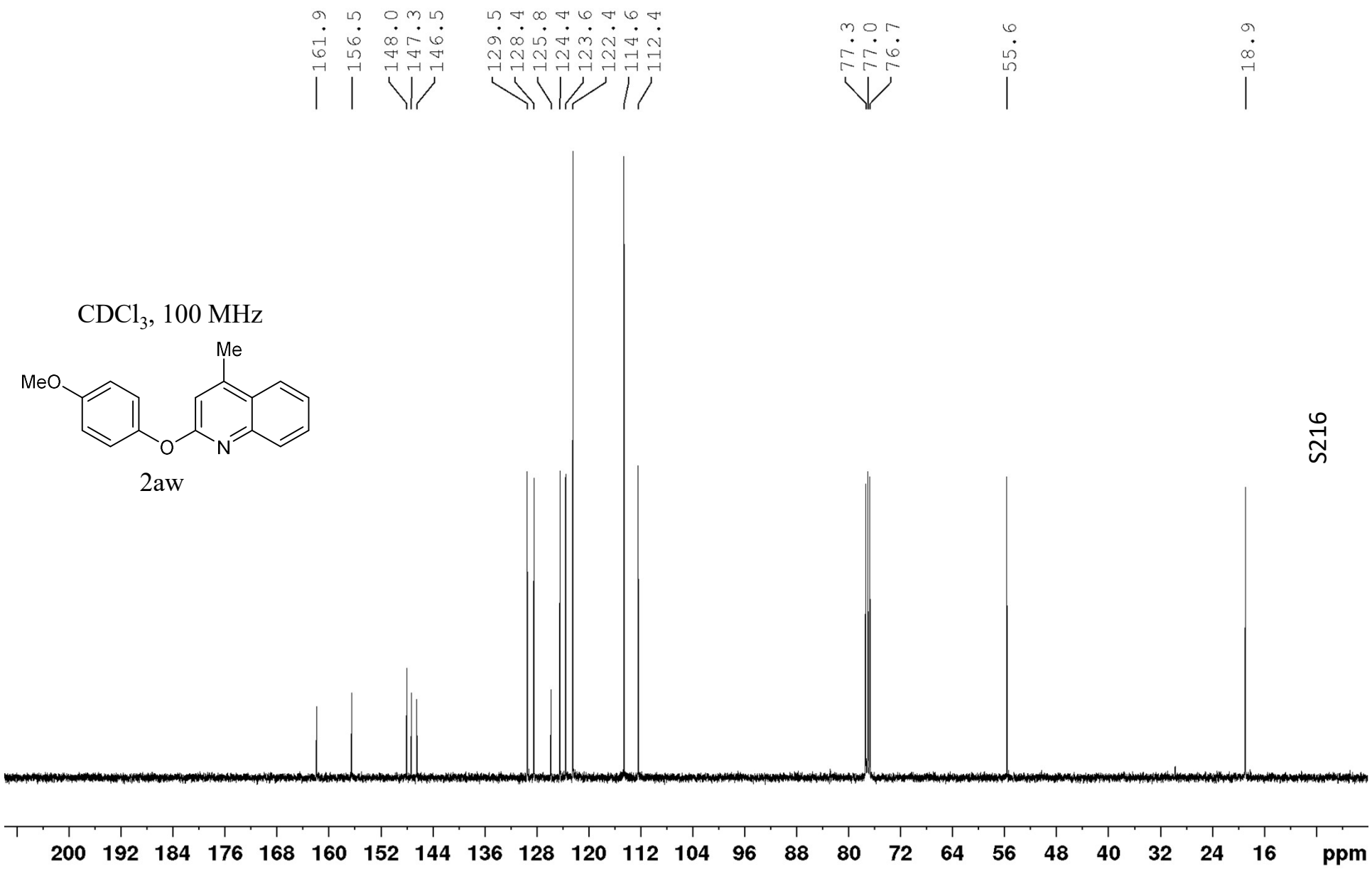

8.05
8.04
7.53
7.52
7.51
7.50
7.46
7.45
7.44
7.44
7.43
7.26
6.41
6.40
2.91
2.73
1.90
1.89
1.88
1.87
CDCl3, 400 MHz
S
N
2au
S211
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.29
3.11
1.01
2.45
2.27
4.58

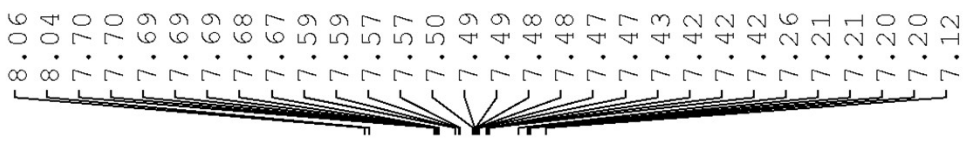

156.6
149.5
146.1
135.4
130.0
129.9
129.4
128.6
117.7
77.3
77.0
76.7
32.9
26.1
22.8
22.6
CDCl3, 100 MHz
S
N
2au
S212
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.43
7.47
7.47
7.45
7.44
7.43
7.36
7.36
7.36
7.35
7.34
7.32
7.23
7.23
7.21
7.21
6.54
3.49
2.97
2.95
2.93
2.91
2.90
1.27
1.25
CDCl3, 400 MHz
Me
N
NC
N
2av
S213
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
0.82
1.95
0.94
1.89
1.00
2.97
0.96
6.13

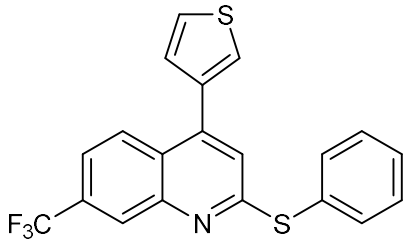

171.1
155.8
155.6
146.2
130.1
127.3
126.4
117.1
107.2
94.2
77.3
77.0
76.7
41.7
36.7
22.1
CDCl3, 100 MHz
Me
N
NC
N
2av
S214
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


7.89
7.89
7.81
7.80
7.78
7.78
7.62
7.62
7.60
7.60
7.59
7.58
7.58
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.26
7.18
7.17
7.16
7.16
6.96
6.95
6.94
6.94
6.89
6.89
3.84
2.67
2.66
CDCl3, 400 MHz
Me
MeO
O
N
2aw
S215
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
1.00
0.97
1.04
1.01
1.96
2.01
0.95
3.09
3.11

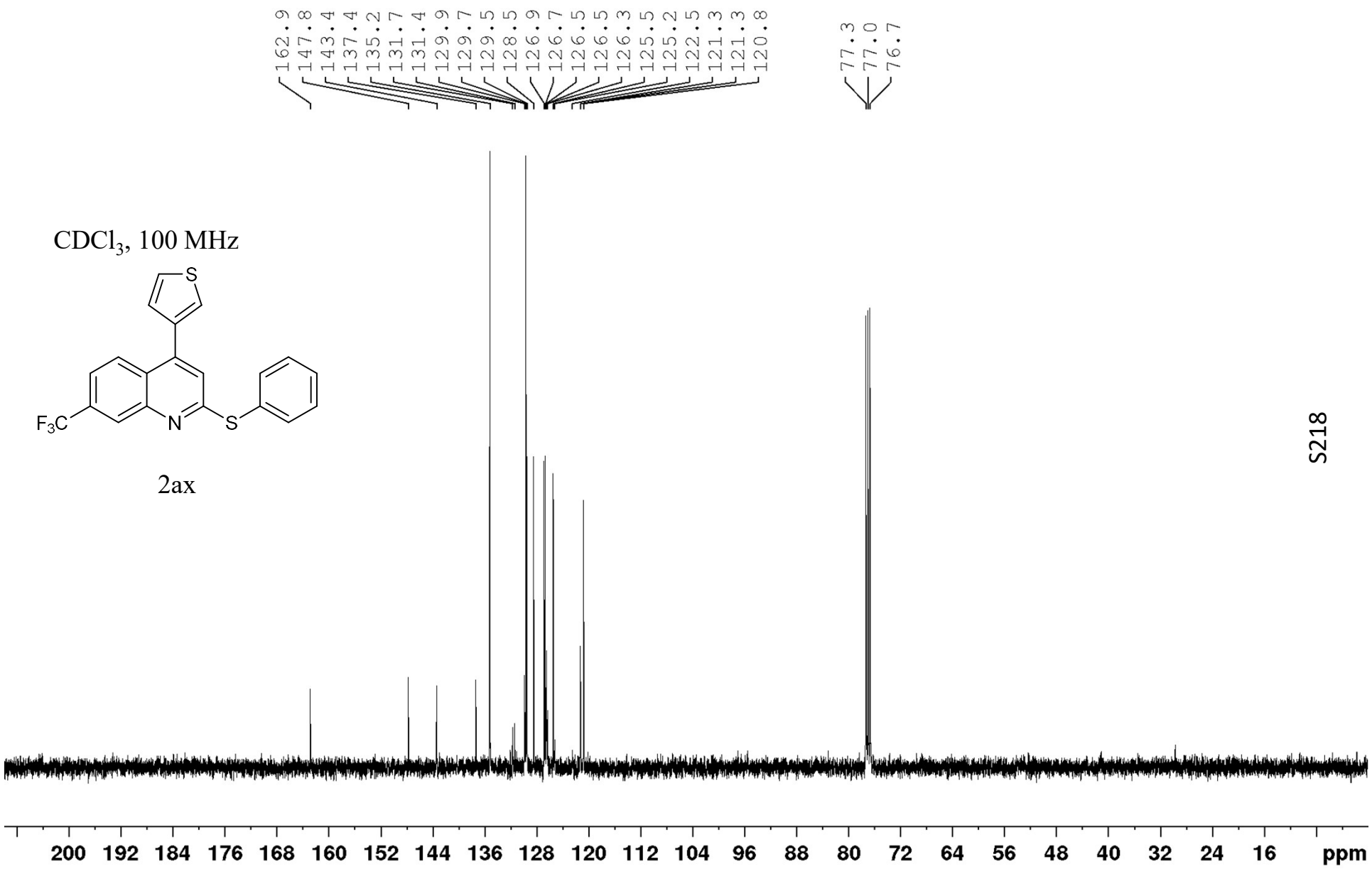

161.9
156.5
148.0
147.3
146.5
129.5
128.4
125.8
124.4
123.6
122.4
114.6
112.4
77.3
77.0
76.7
55.6
18.9
CDCl3, 100 MHz
Me
MeO
O
N
2aw
S216
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

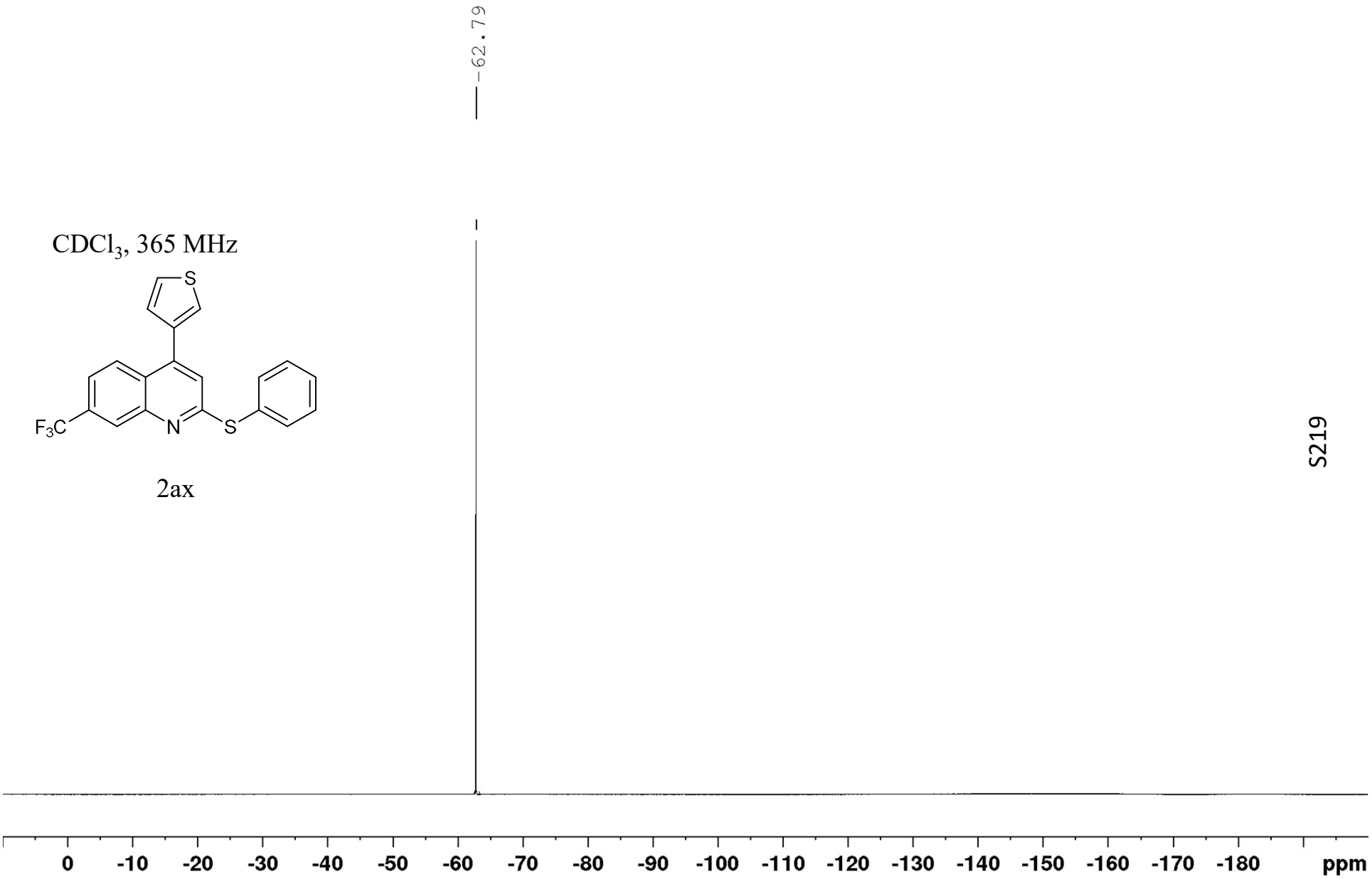


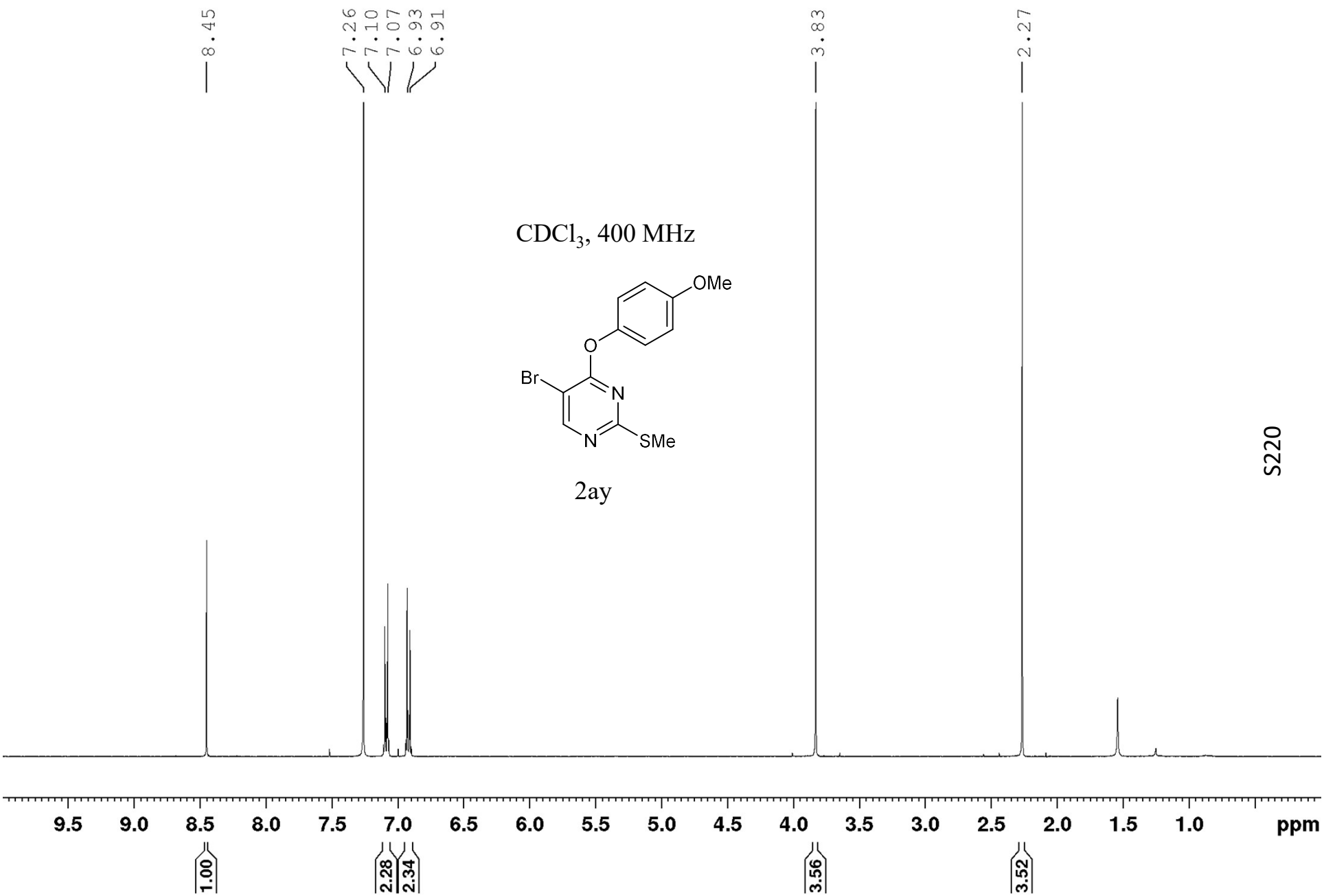
$CDCl_3$, 400 MHz

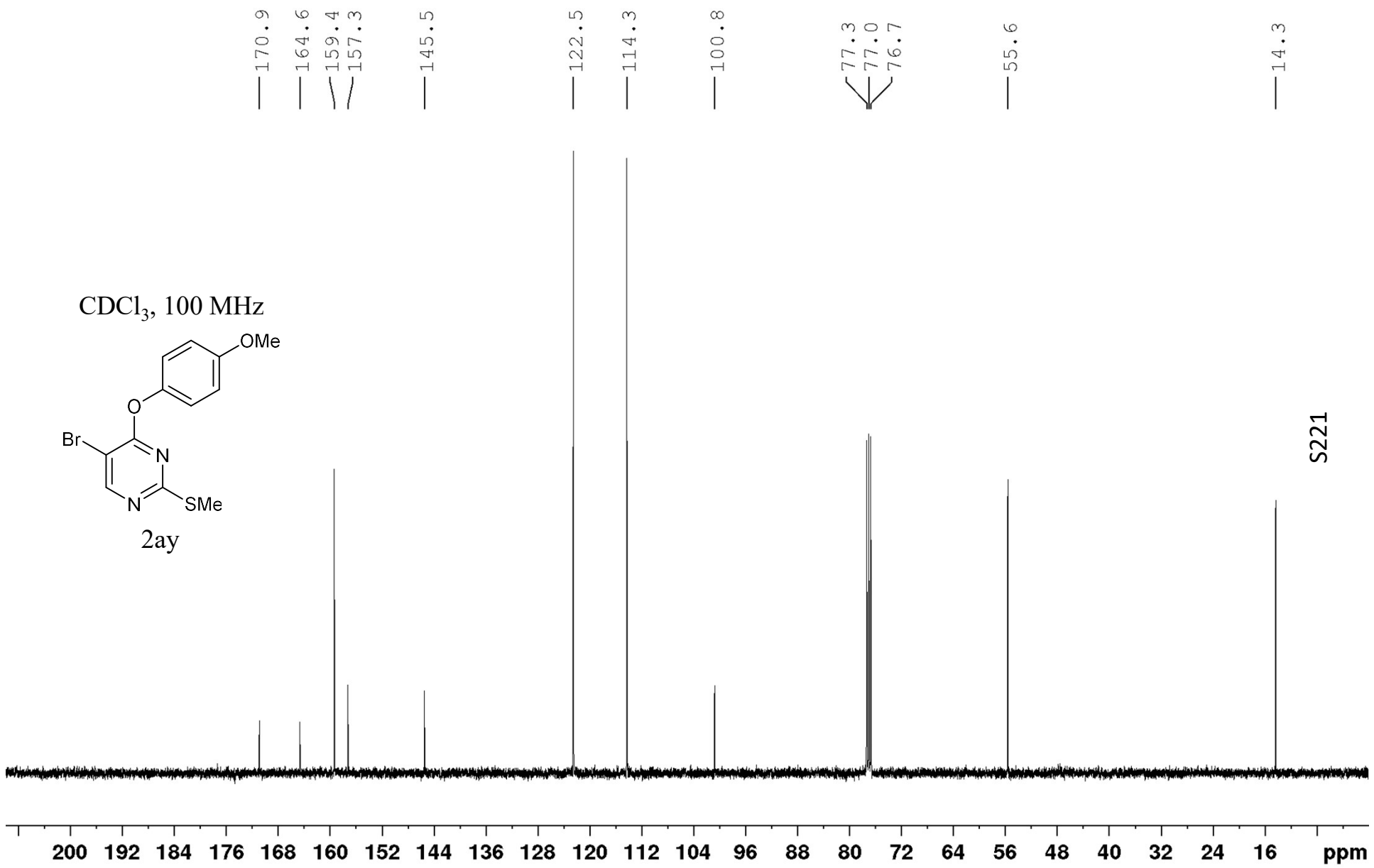


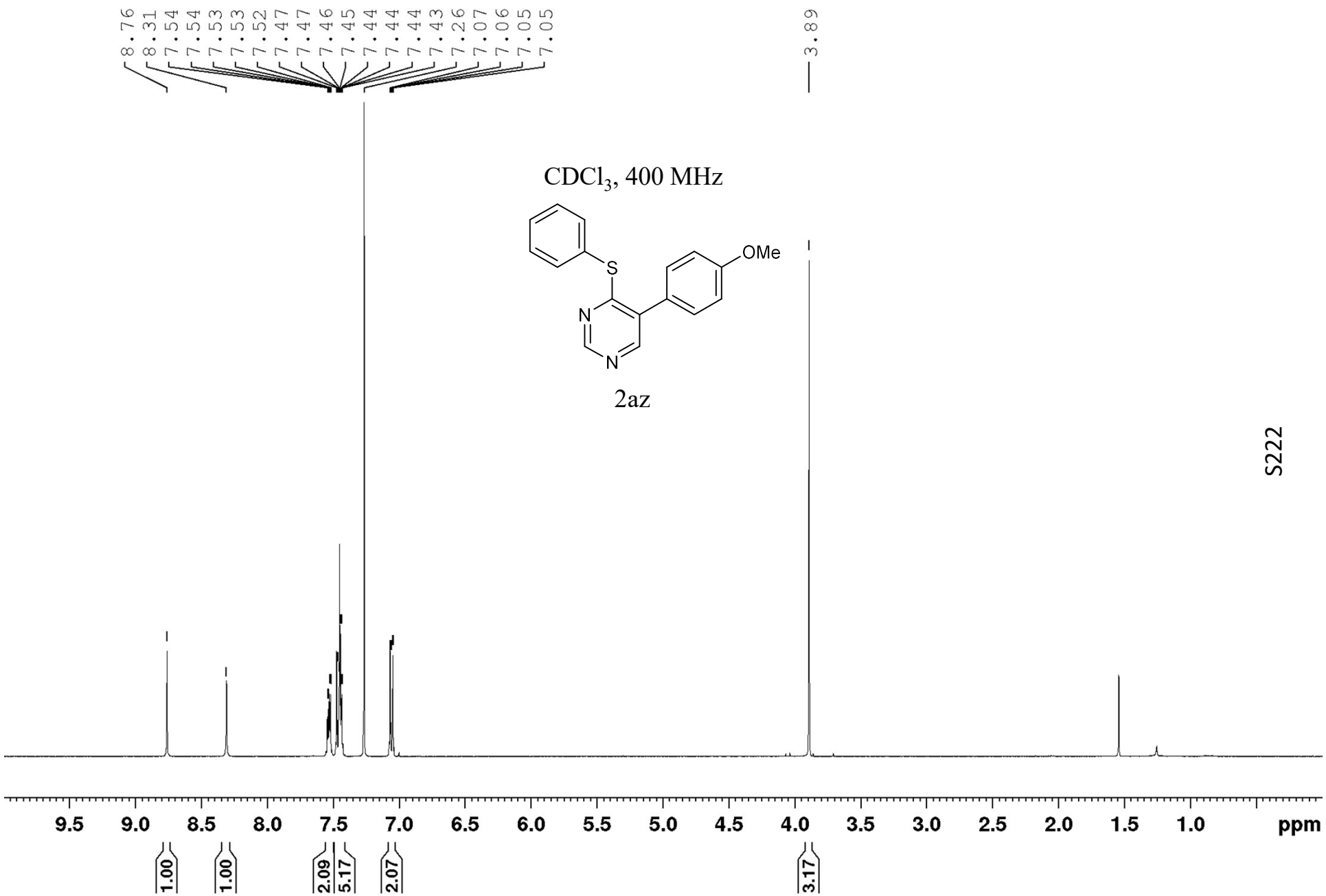
2ax

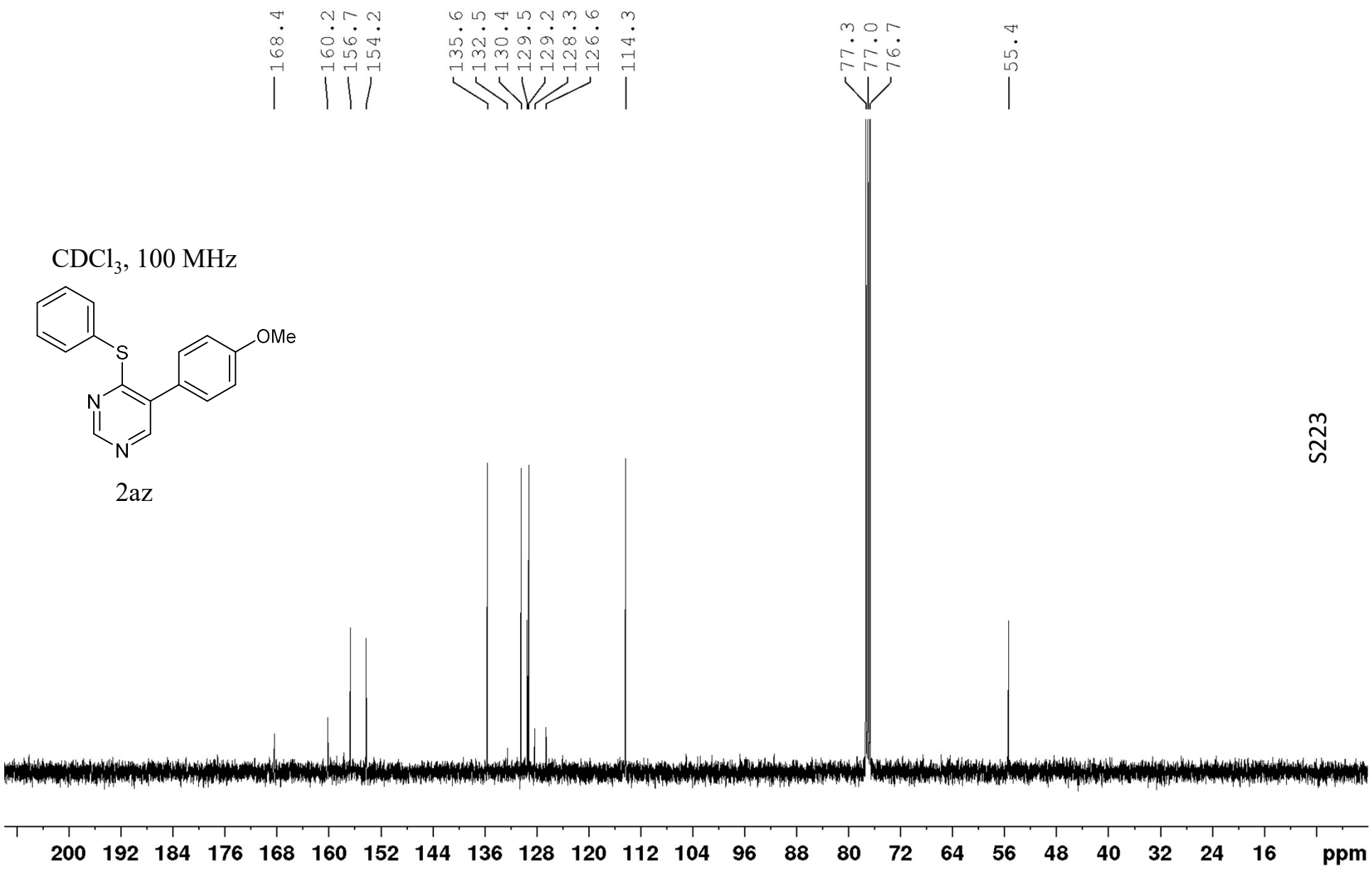

162.9
147.8
143.4
137.4
135.2
131.7
131.4
129.9
129.7
129.5
128.5
126.9
126.7
126.5
126.5
126.3
125.5
125.2
122.5
121.3
121.3
120.8
77.3
77.0
76.7
CDCl3, 100 MHz
S
F3C
N
S
2ax
S218
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

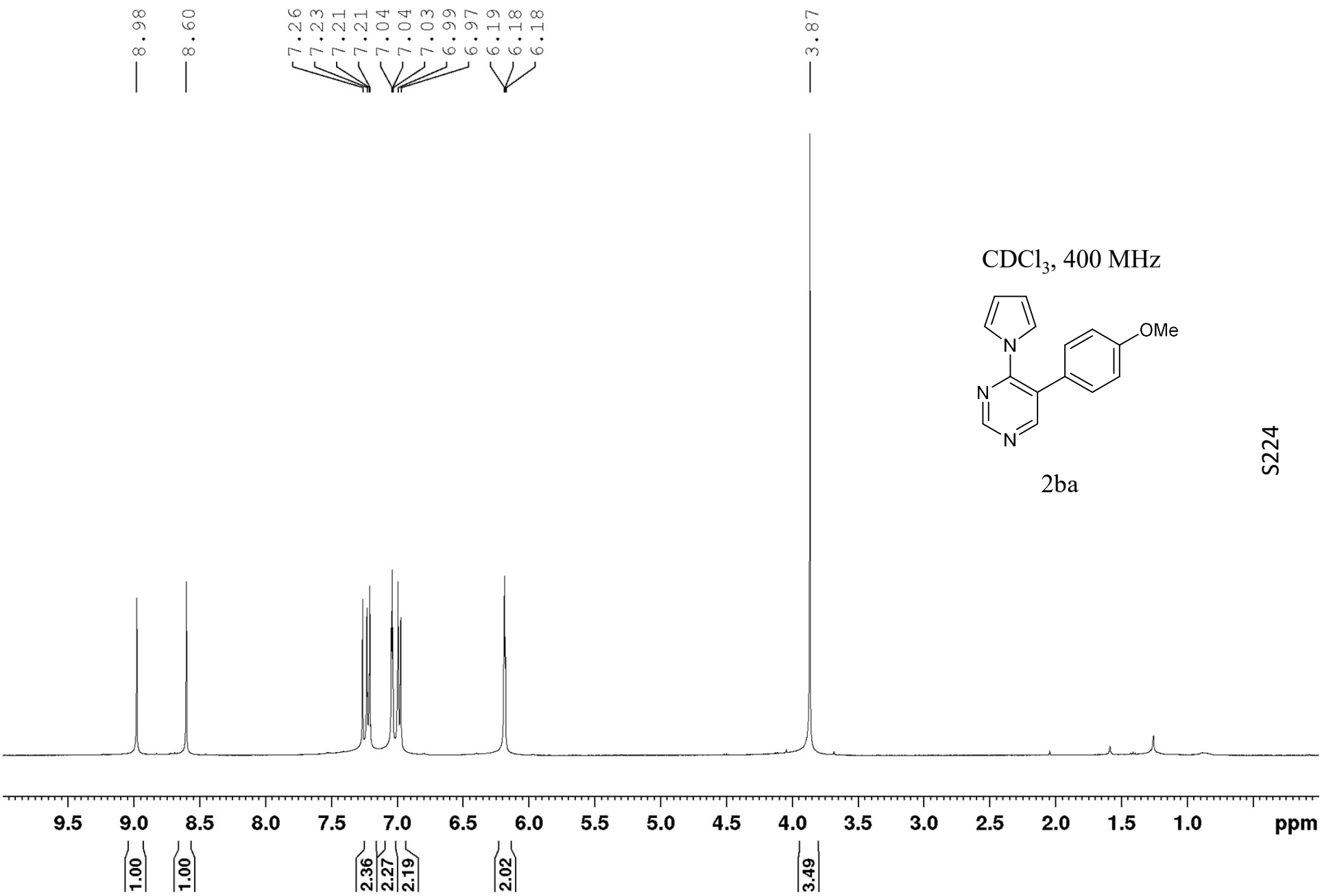

-62.79
CDCl3, 365 MHz
S
F3C
N
S
2ax
S219
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

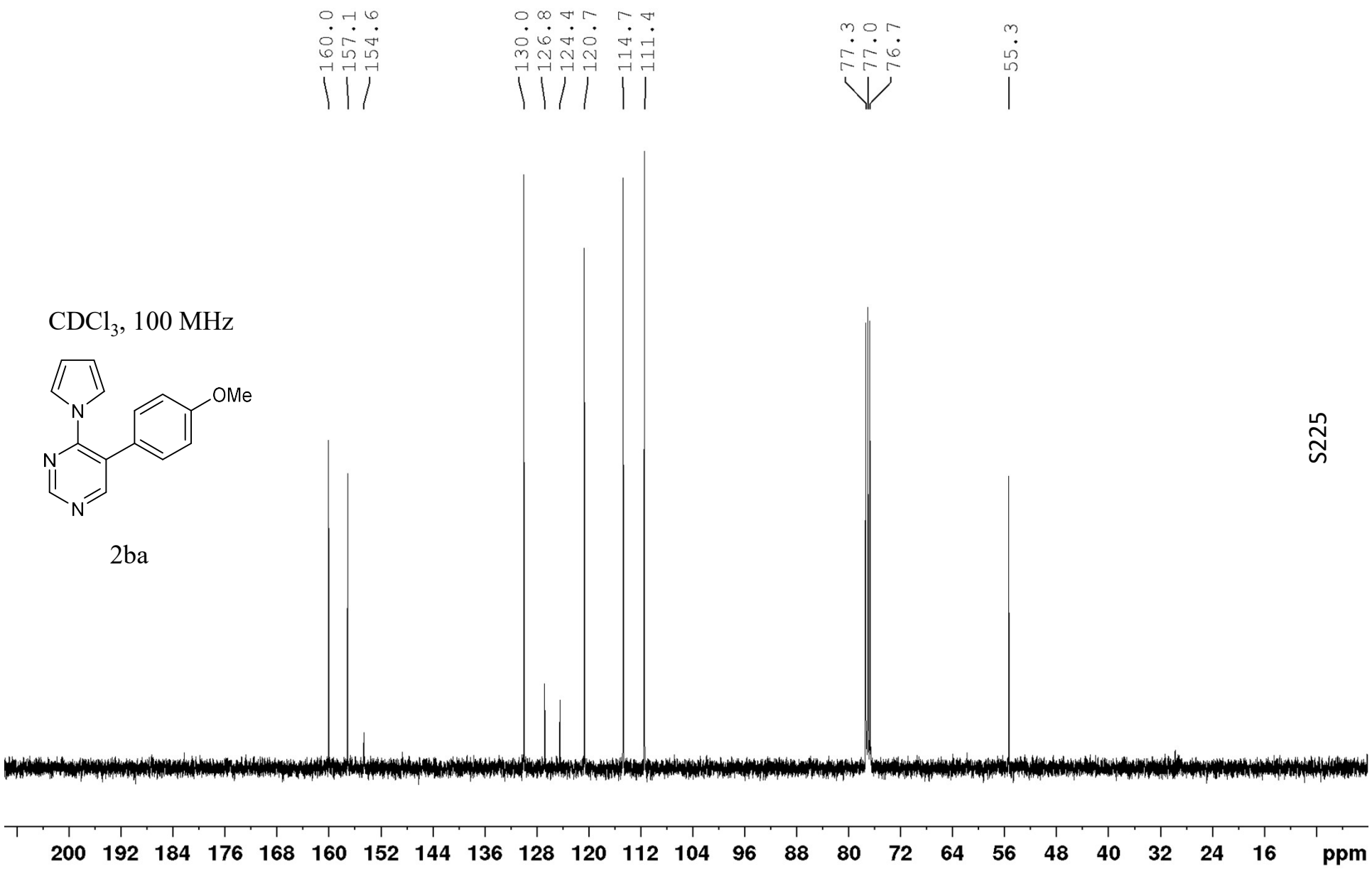

8.45
7.26
7.10
7.07
6.93
6.91
3.83
2.27
CDCl3, 400 MHz
OMe
O
Br
N
N
SMe
2ay
S220
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.28
2.34
3.56
3.52

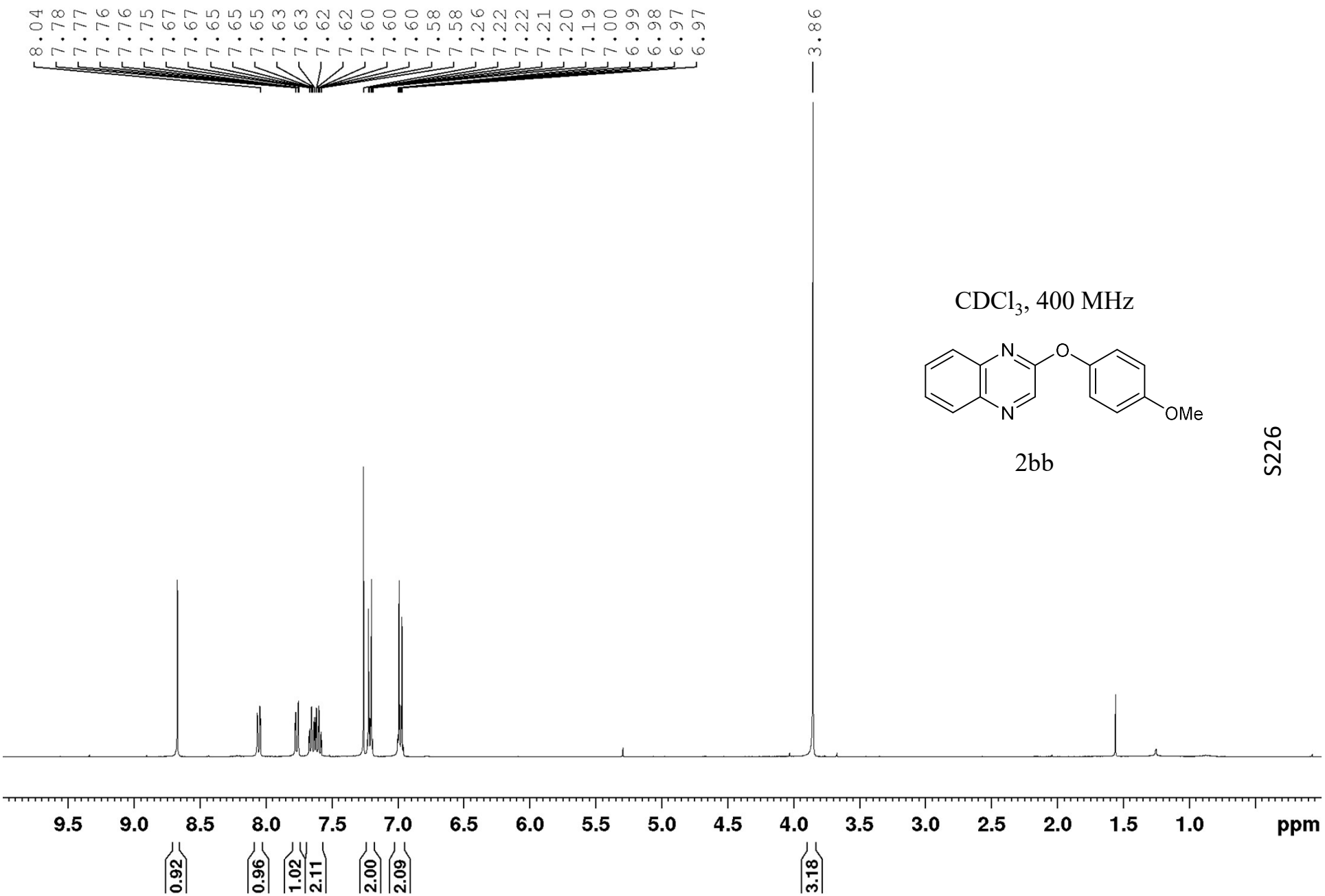

170.9
164.6
159.4
157.3
145.5
122.5
114.3
100.8
77.3
77.0
76.7
55.6
14.3
CDCl3, 100 MHz
OMe
O
Br
N
N
SMe
2ay
S221
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

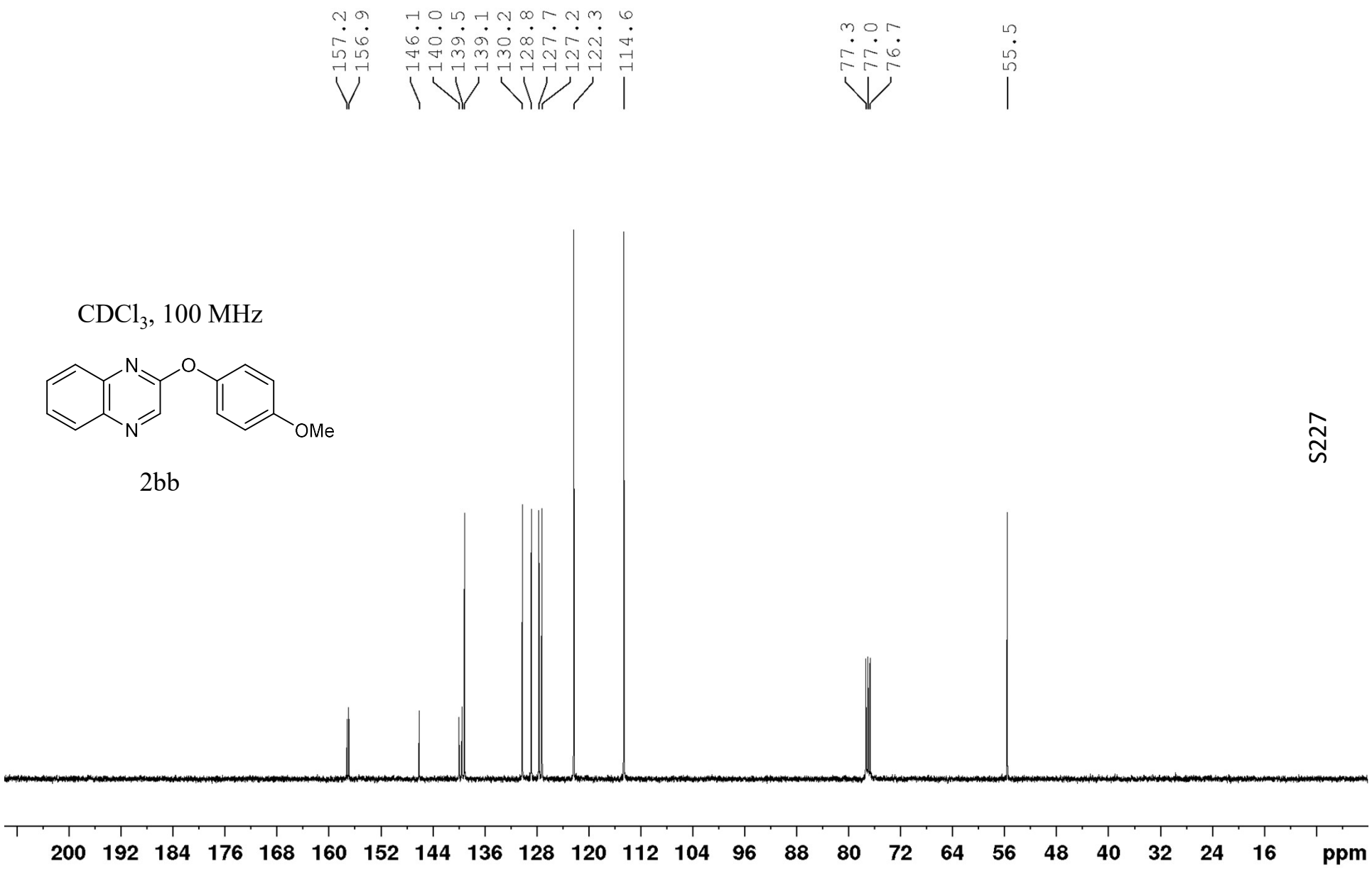

8.76
8.31
7.54
7.54
7.53
7.53
7.52
7.47
7.47
7.46
7.45
7.44
7.44
7.44
7.43
7.26
7.07
7.06
7.05
7.05
3.89
CDCl3, 400 MHz
S
N
N
OMe
2az
S222
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
2.09
5.17
2.07
3.17

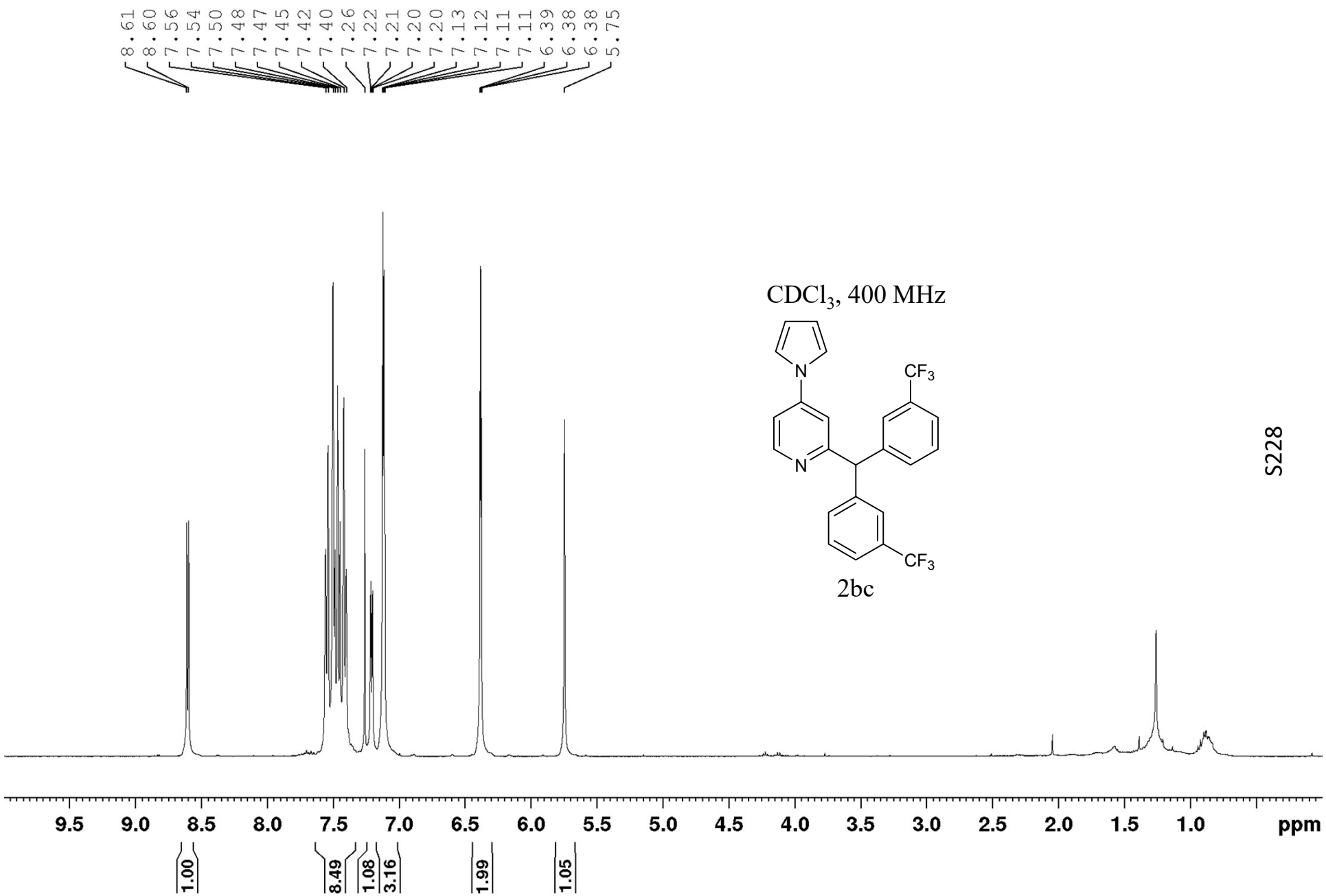

168.4
160.2
156.7
154.2
135.6
132.5
130.4
129.5
129.2
128.3
126.6
114.3
77.3
77.0
76.7
55.4
CDCl3, 100 MHz
S
N
N
OMe
2az
S223
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

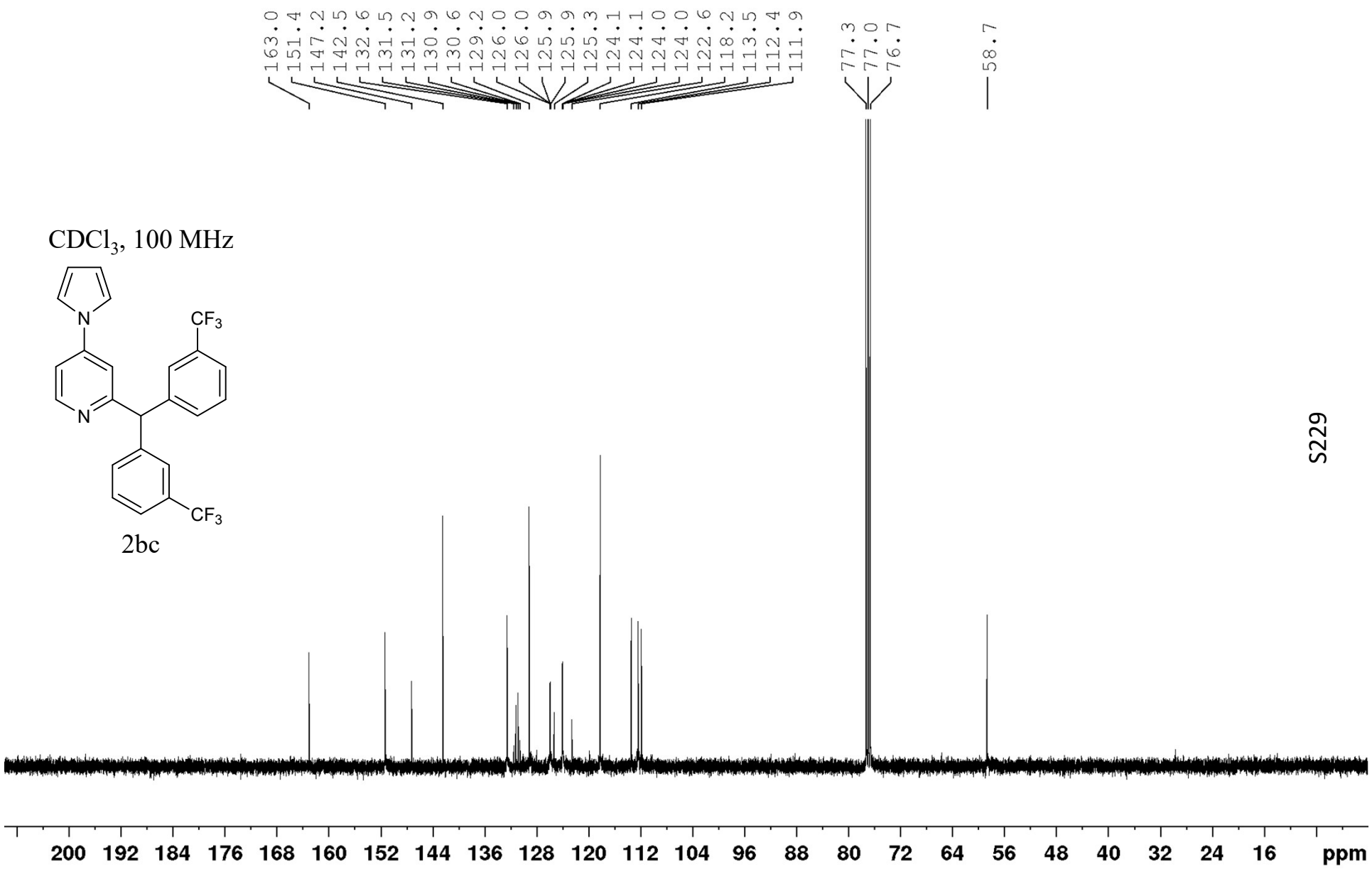

8.98
8.60
7.26
7.23
7.21
7.21
7.04
7.04
7.03
6.99
6.97
6.19
6.18
6.18
3.87
CDCl3, 400 MHz
OMe
N
N
N
2ba
S224
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
2.36
2.27
2.19
2.02
3.49

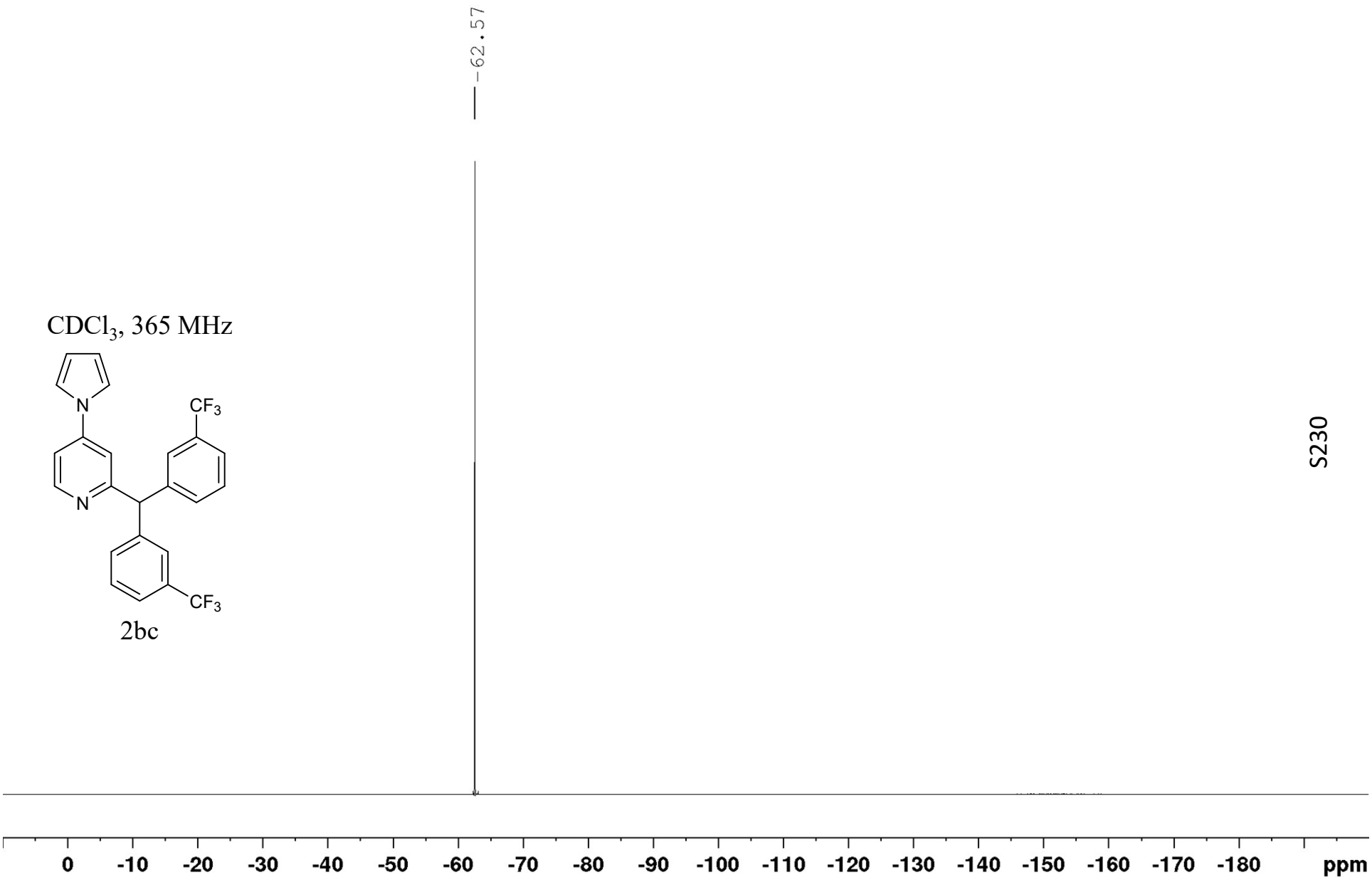

160.0
157.1
154.6
130.0
126.8
124.4
120.7
114.7
111.4
77.3
77.0
76.7
55.3
CDCl3, 100 MHz
OMe
N
N
N
2ba
S225
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

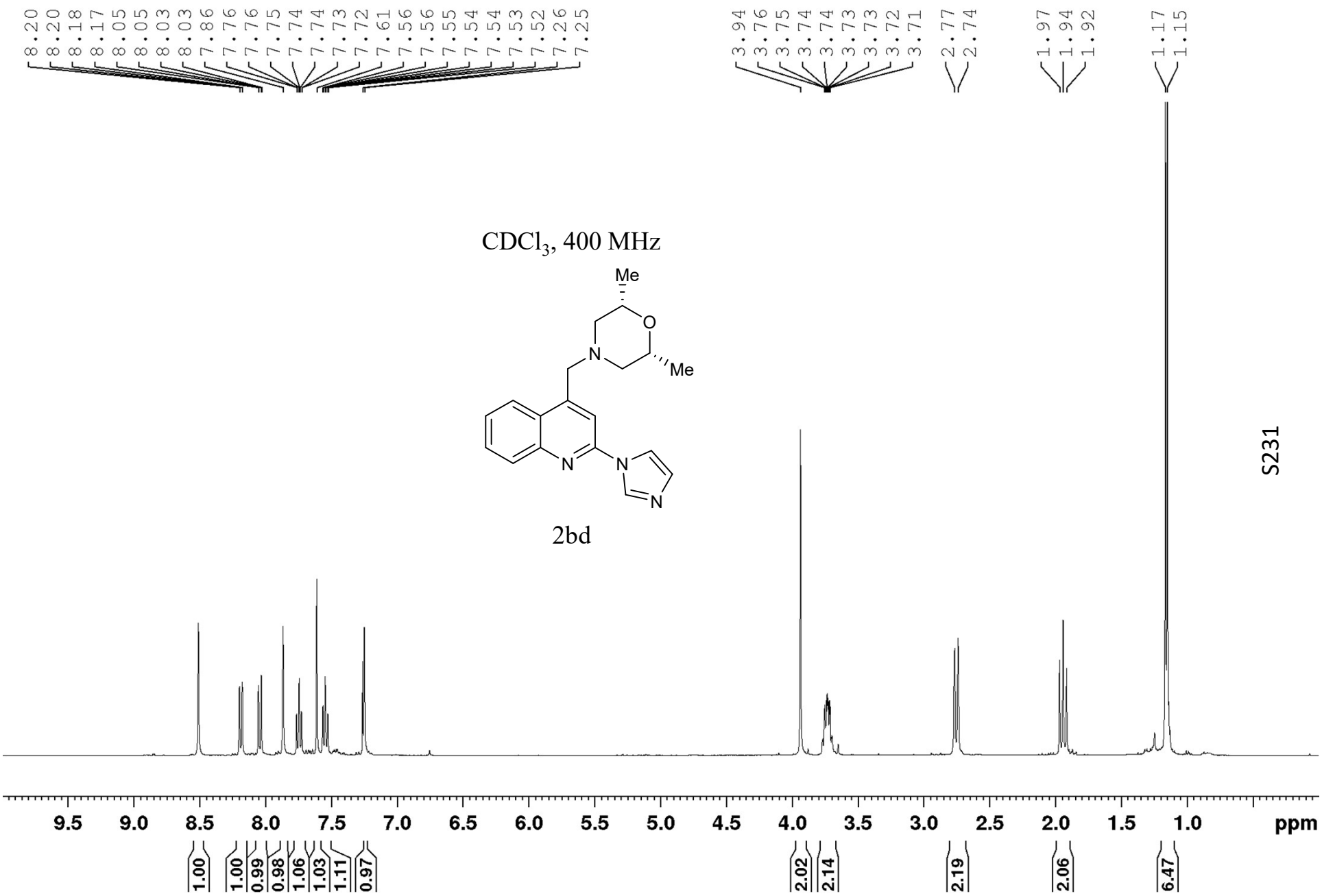

8.04
7.78
7.77
7.76
7.76
7.75
7.67
7.67
7.65
7.65
7.65
7.63
7.63
7.62
7.62
7.60
7.60
7.60
7.58
7.58
7.26
7.22
7.22
7.21
7.20
7.19
7.00
6.99
6.98
6.97
6.97
3.86
CDCl3, 400 MHz
N
O
N
OMe
2bb
S226
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.92
0.96
1.02
2.11
2.00
2.09
3.18

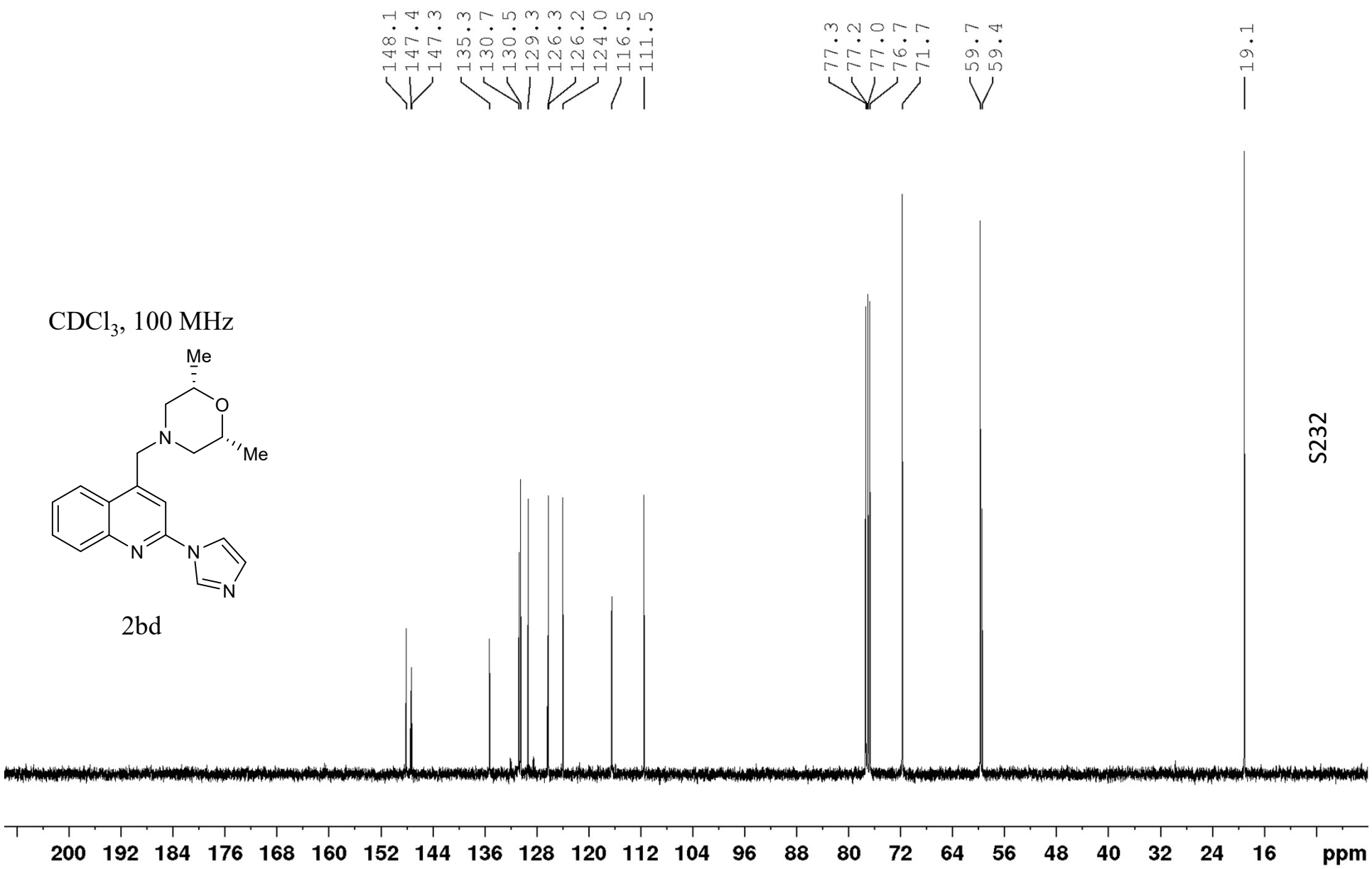

157.2
156.9
146.1
140.0
139.5
139.1
130.2
128.8
127.7
127.2
122.3
114.6
77.3
77.0
76.7
55.5
CDCl3, 100 MHz
N
O
N
OMe
2bb
S227
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

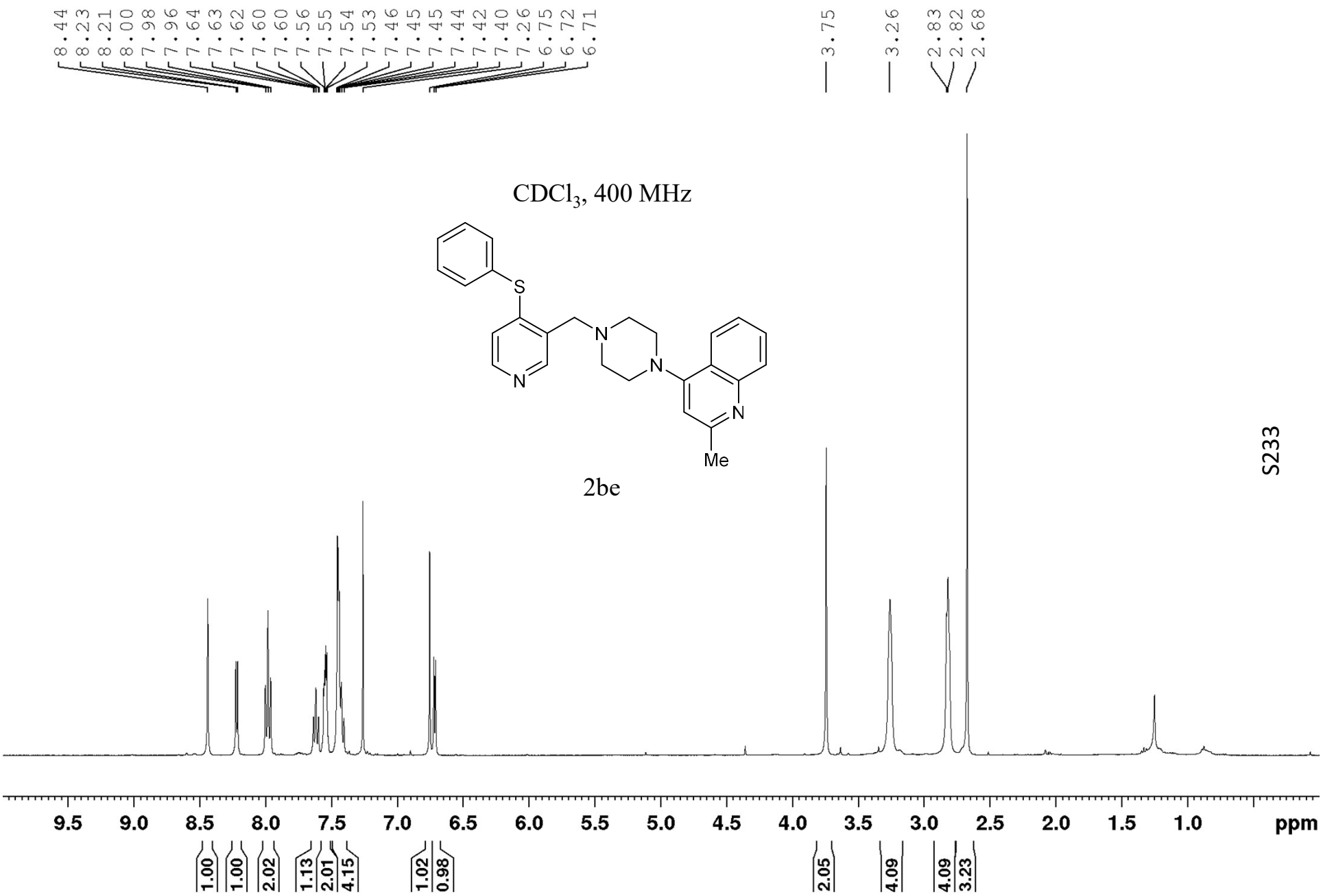

8.61
8.60
7.56
7.54
7.50
7.48
7.47
7.45
7.42
7.40
7.26
7.22
7.21
7.20
7.20
7.13
7.12
7.11
7.11
6.39
6.38
6.38
5.75
CDCl3, 400 MHz
N
CF3
N
CF3
2bc
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
8.49
1.08
3.16
1.99
1.05

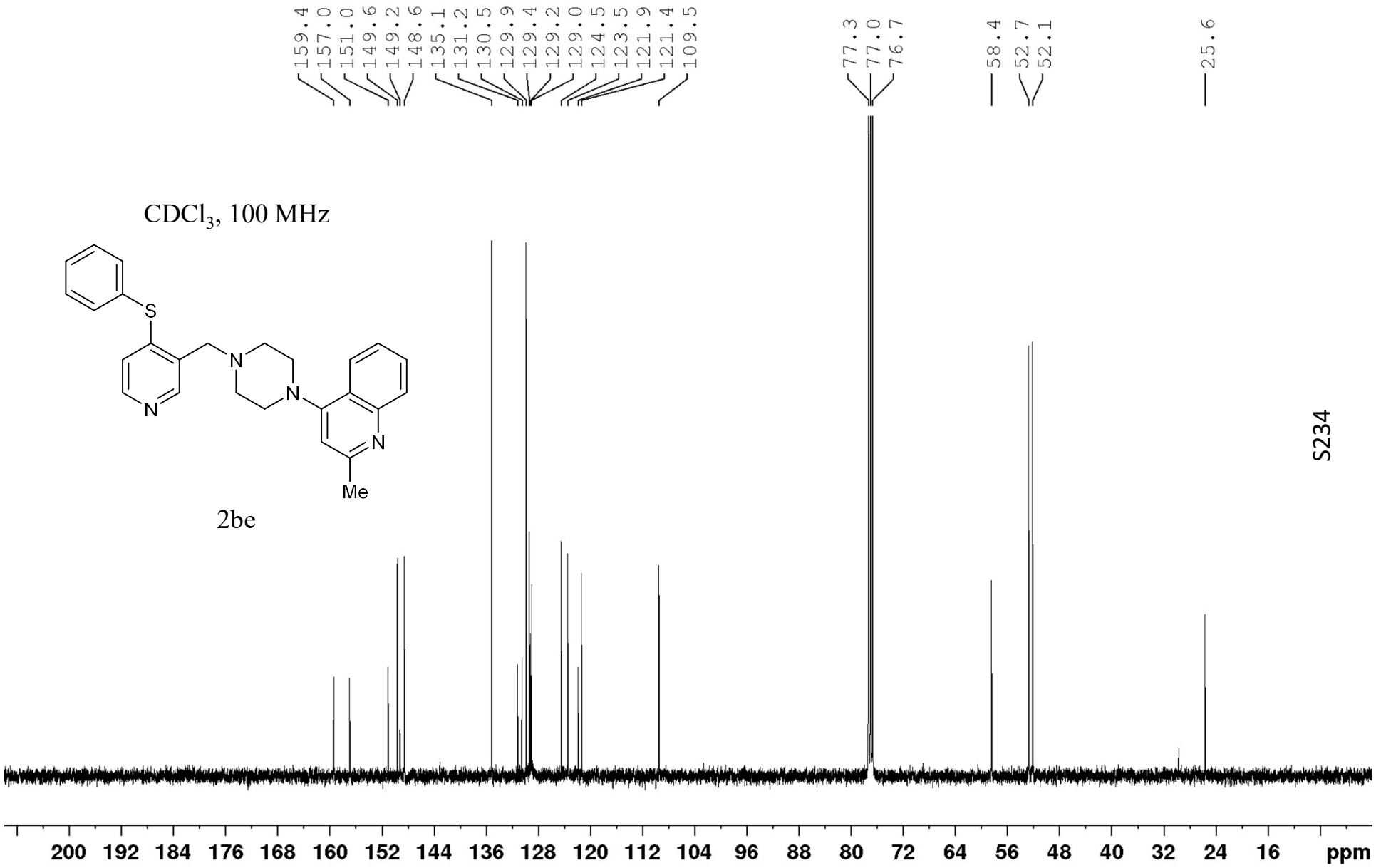

163.0
151.4
147.2
142.5
132.6
131.5
131.2
130.9
130.6
129.2
126.0
126.0
125.9
125.9
125.3
124.1
124.1
124.0
124.0
122.6
118.2
113.5
112.4
111.9
77.3
77.0
76.7
58.7
CDCl3, 100 MHz
N
CF3
N
CF3
2bc
S229
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

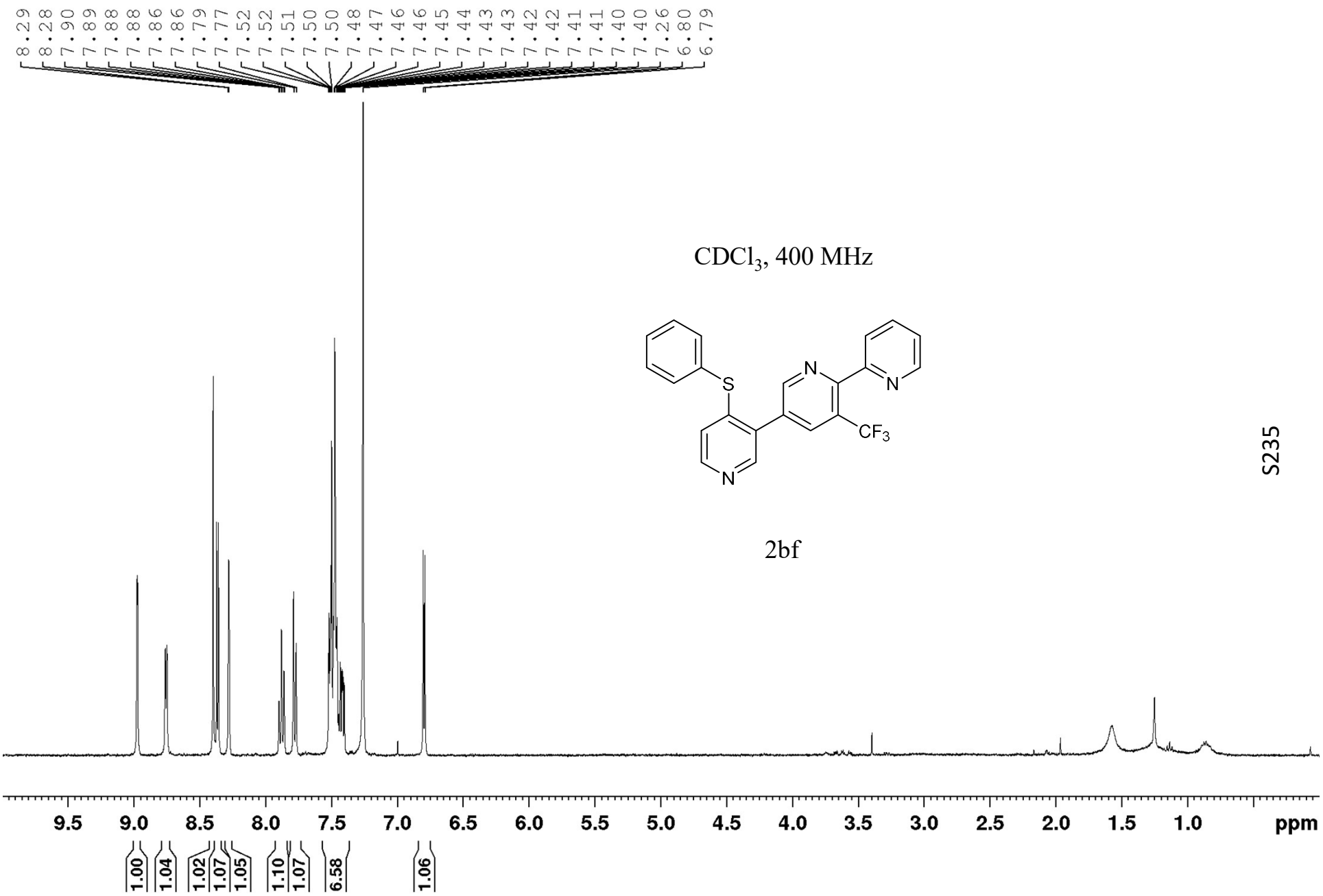

-62.57
CDCl3, 365 MHz
N
CF3
N
CF3
2bc
S230
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

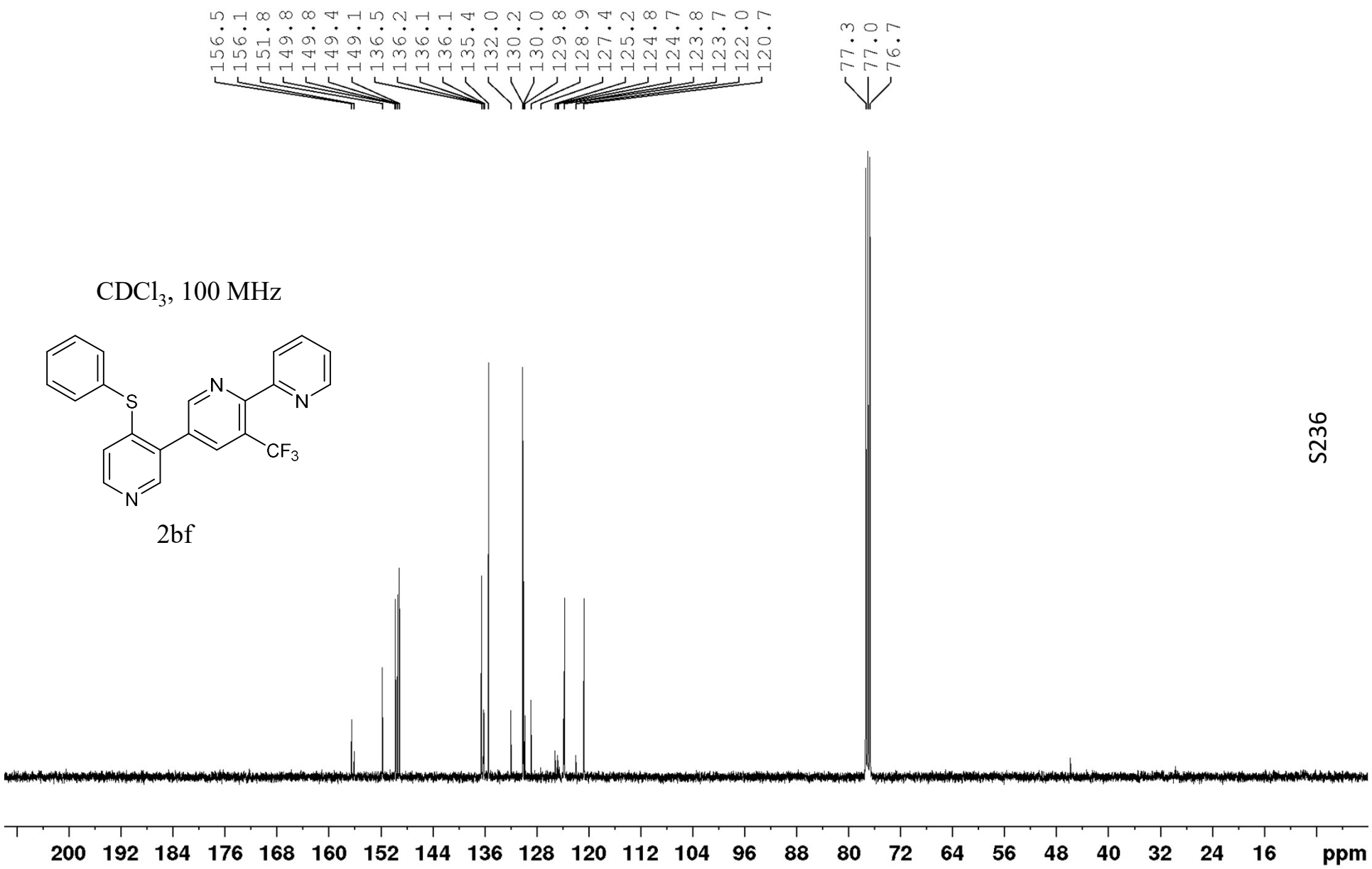

8.20
8.20
8.18
8.17
8.05
8.05
8.03
8.03
7.86
7.76
7.76
7.75
7.74
7.74
7.73
7.72
7.61
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.26
7.25
3.94
3.76
3.75
3.74
3.74
3.73
3.73
3.72
3.71
2.77
2.74
1.97
1.94
1.92
1.17
1.15
CDCl3, 400 MHz
Me
O
N
Me
N
N
N
2bd
S231
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
0.99
0.98
1.06
1.03
1.11
0.97
2.02
2.14
2.19
2.06
6.47

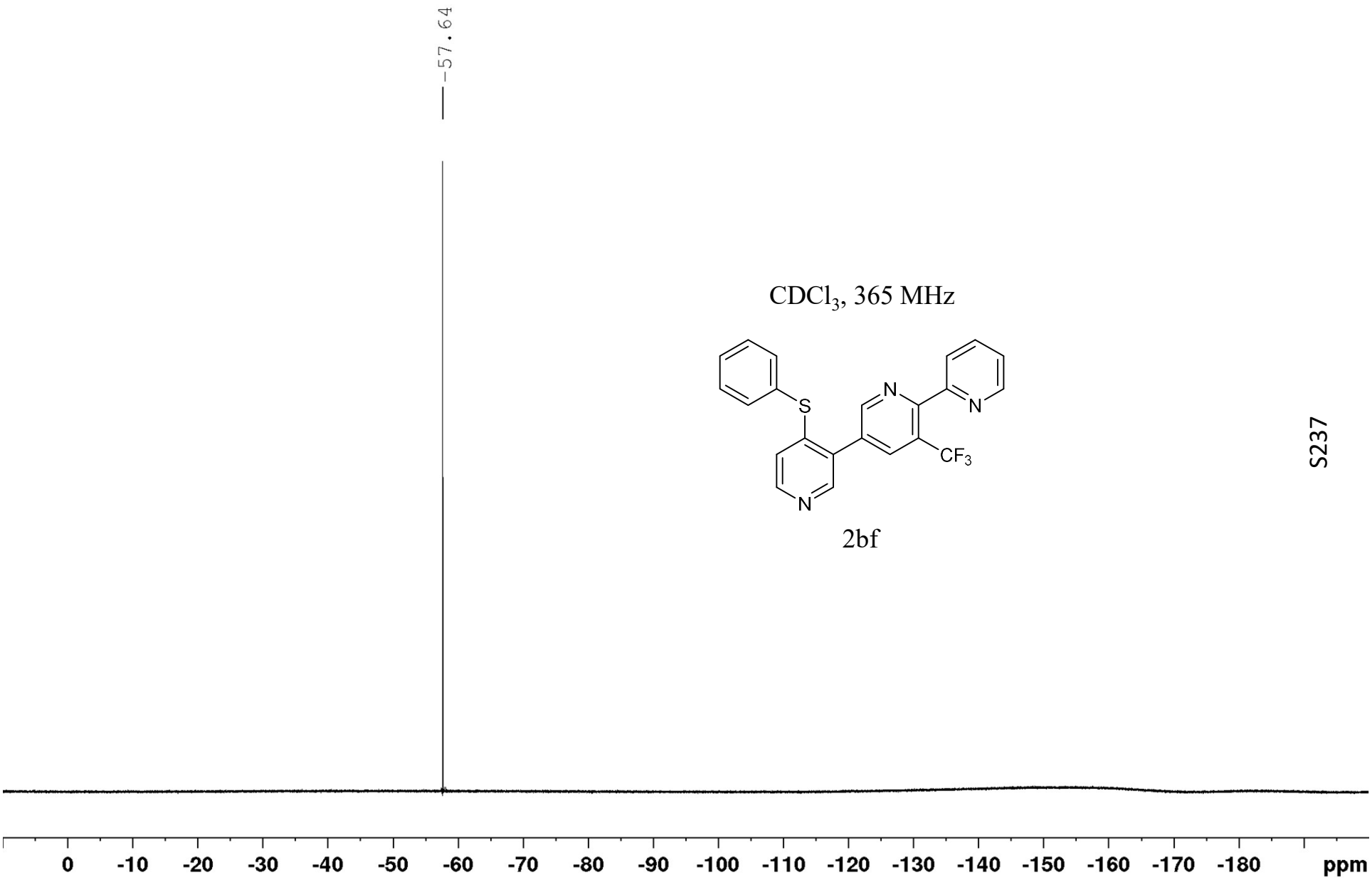

148.1
147.4
147.3
135.3
130.7
130.5
129.3
126.3
126.2
124.0
116.5
111.5
77.3
77.2
77.0
76.7
71.7
59.7
59.4
19.1
CDCl3, 100 MHz
Me
O
N
Me
N
N
N
2bd
S232
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

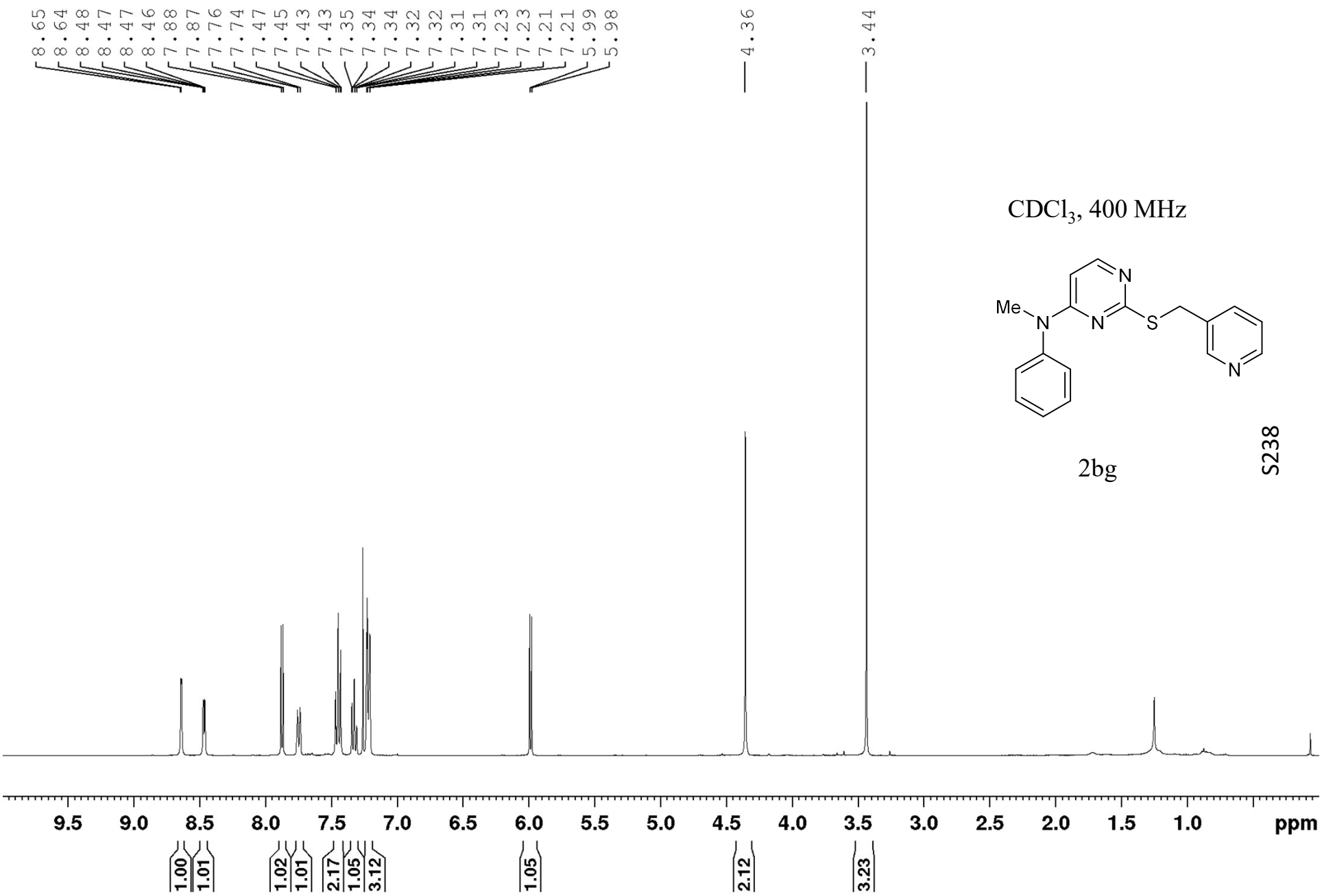

8.44
8.23
8.21
8.00
7.98
7.96
7.64
7.63
7.62
7.60
7.60
7.56
7.55
7.54
7.53
7.46
7.45
7.45
7.44
7.42
7.40
7.26
6.75
6.72
6.71
3.75
3.26
2.83
2.82
2.68
CDCl3, 400 MHz
S
N
N
N
N
Me
2be
S233
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
2.02
1.13
2.01
4.15
1.02
0.98
2.05
4.09
4.09
3.23

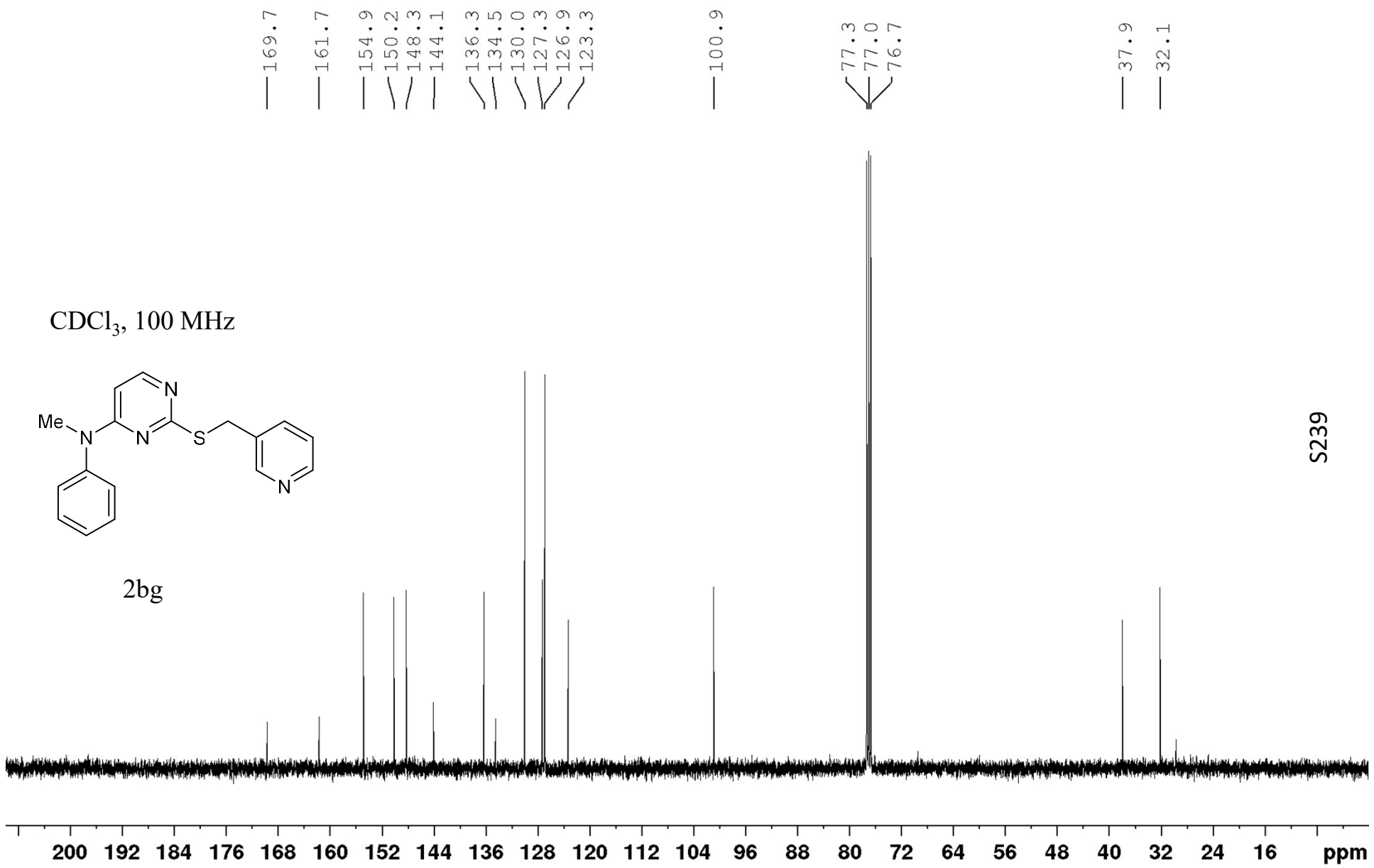

159.4
157.0
151.0
149.6
149.2
148.6
135.1
131.2
130.5
129.9
129.4
129.2
129.0
124.5
123.5
121.9
121.4
109.5
77.3
77.0
76.7
58.4
52.7
52.1
25.6
CDCl3, 100 MHz
S
N
N
N
N
Me
2be
S234
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

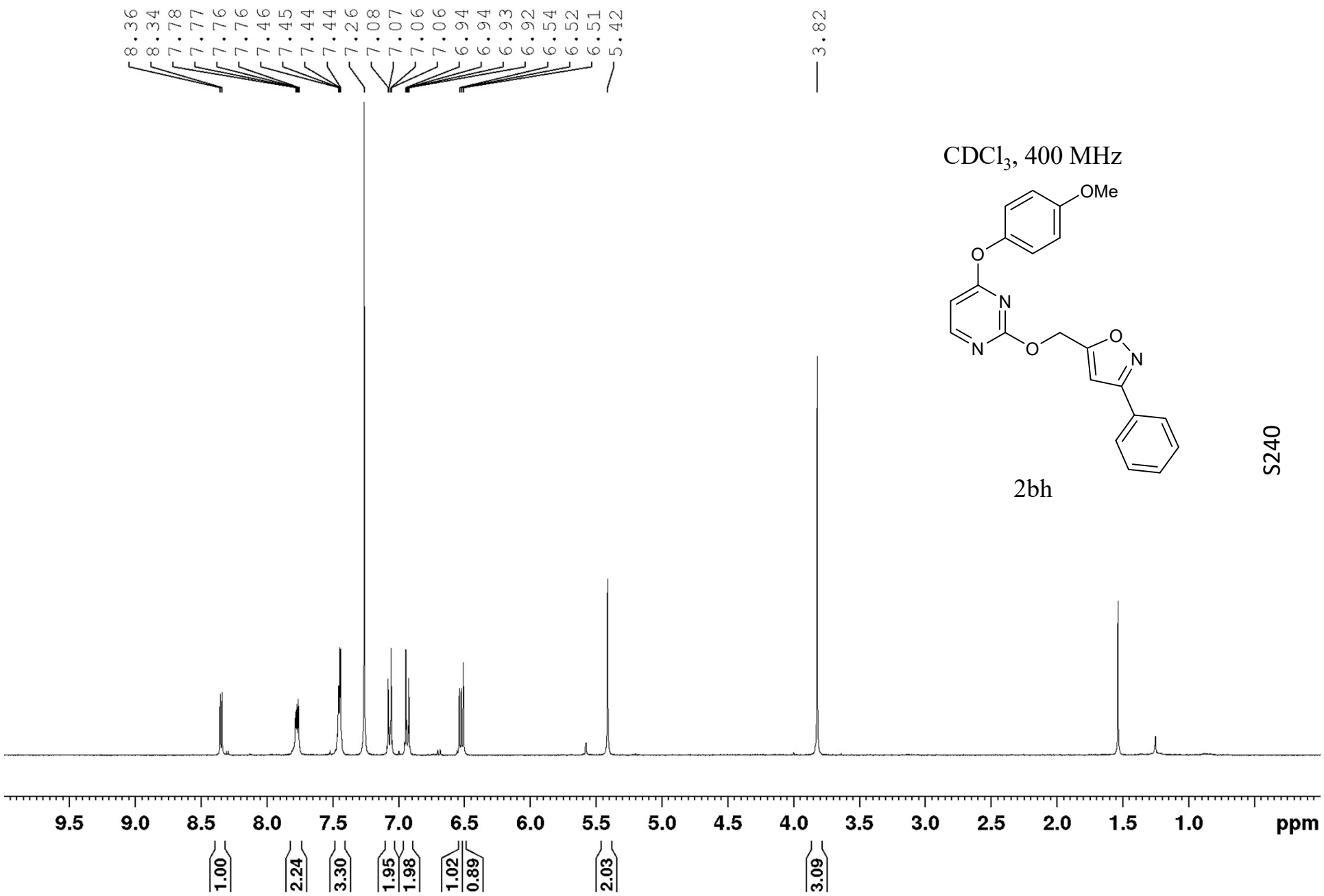

8.29
8.28
7.90
7.89
7.88
7.88
7.86
7.86
7.79
7.77
7.52
7.52
7.51
7.50
7.50
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.26
6.80
6.79
CDCl3, 400 MHz
S
N
N
N
CF3
2bf
S235
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.04
1.02
1.07
1.05
1.10
1.07
6.58
1.06

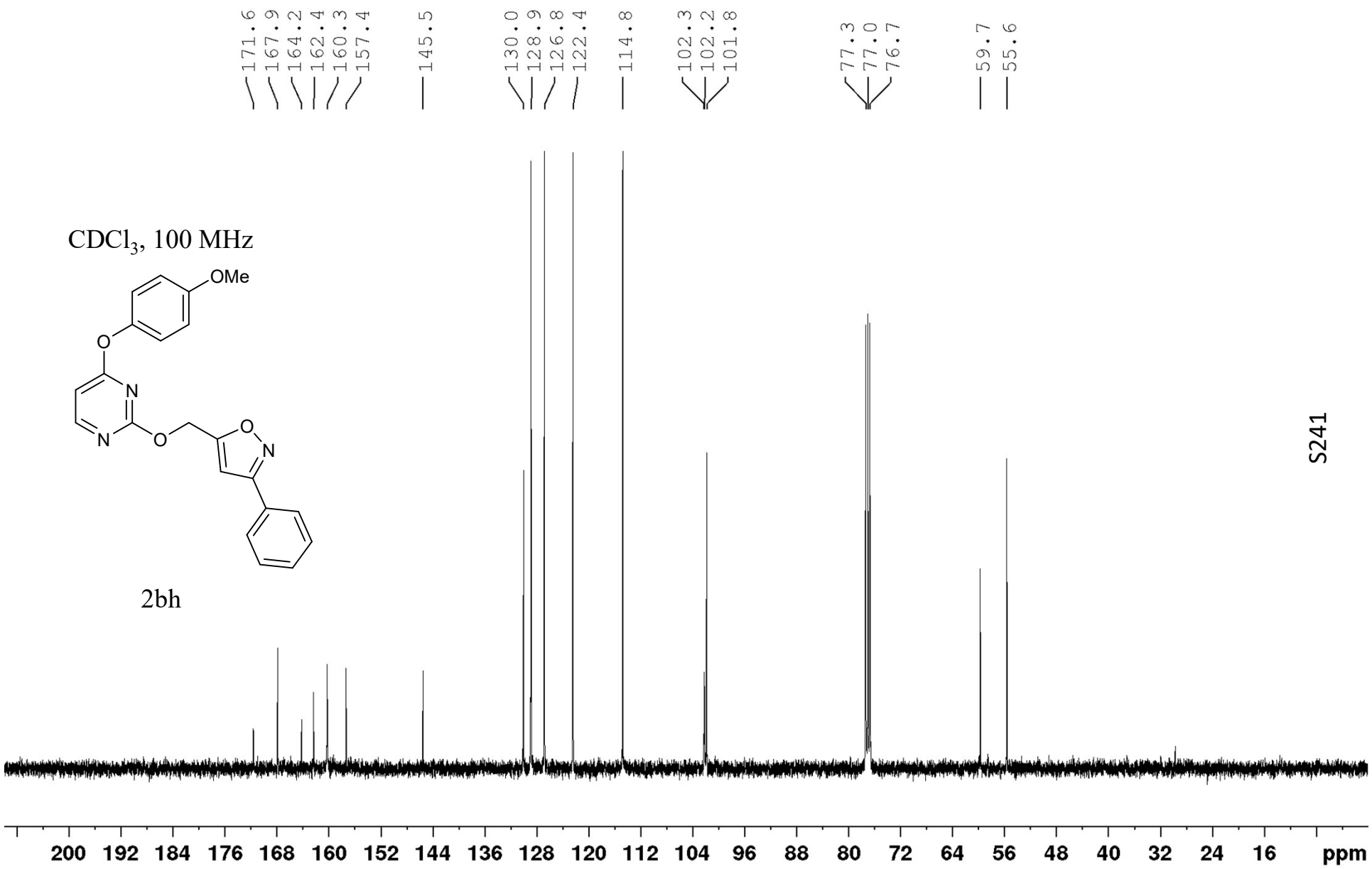

156.5
156.1
151.8
149.8
149.8
149.4
149.1
136.5
136.2
136.1
136.1
135.4
132.0
130.2
130.0
129.8
128.9
127.4
125.2
124.8
124.7
123.8
123.7
122.0
120.7
77.3
77.0
76.7
CDCl3, 100 MHz
S
N
N
N
CF3
2bf
S236
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

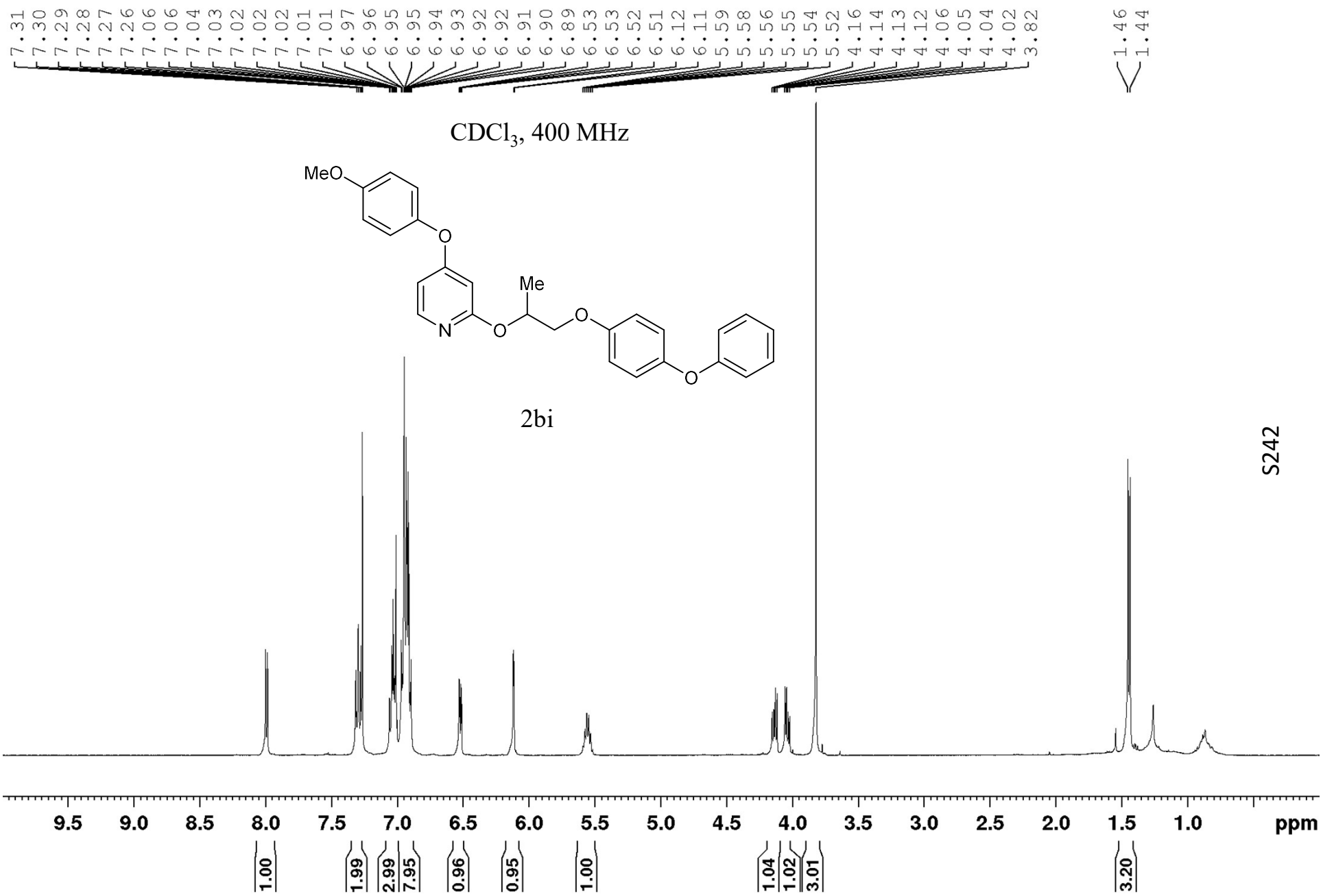

-57.64
CDCl3, 365 MHz
S
N
N
N
CF3
2bf
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

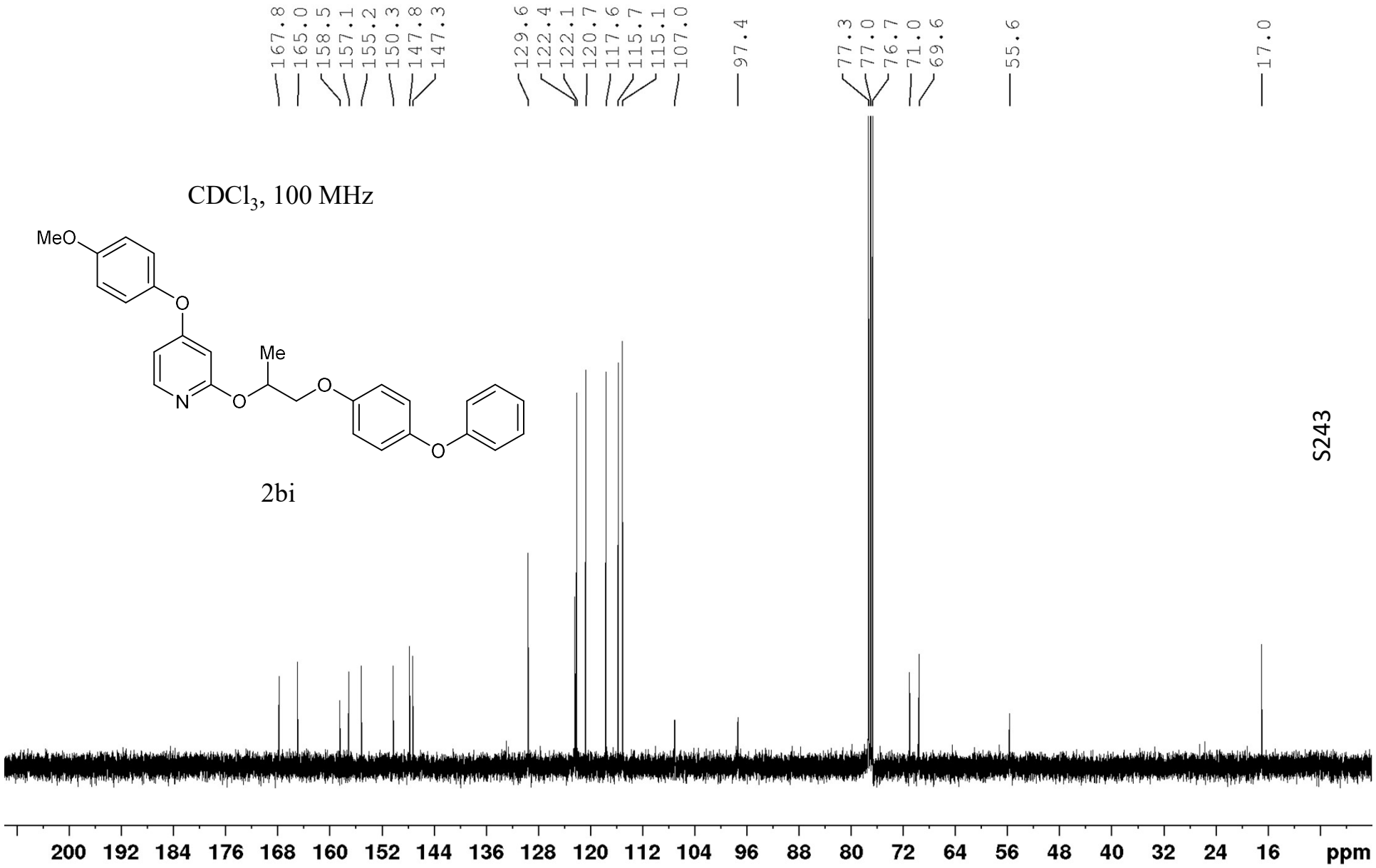

8.65
8.64
8.48
8.47
8.47
8.46
7.88
7.87
7.76
7.74
7.47
7.45
7.43
7.43
7.35
7.34
7.34
7.32
7.32
7.31
7.31
7.23
7.23
7.21
7.21
5.99
5.98
4.36
3.44
CDCl3, 400 MHz
Me
N
N
N
S
N
2bg
S238
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
1.02
1.01
2.17
1.05
3.12
1.05
2.12
3.23

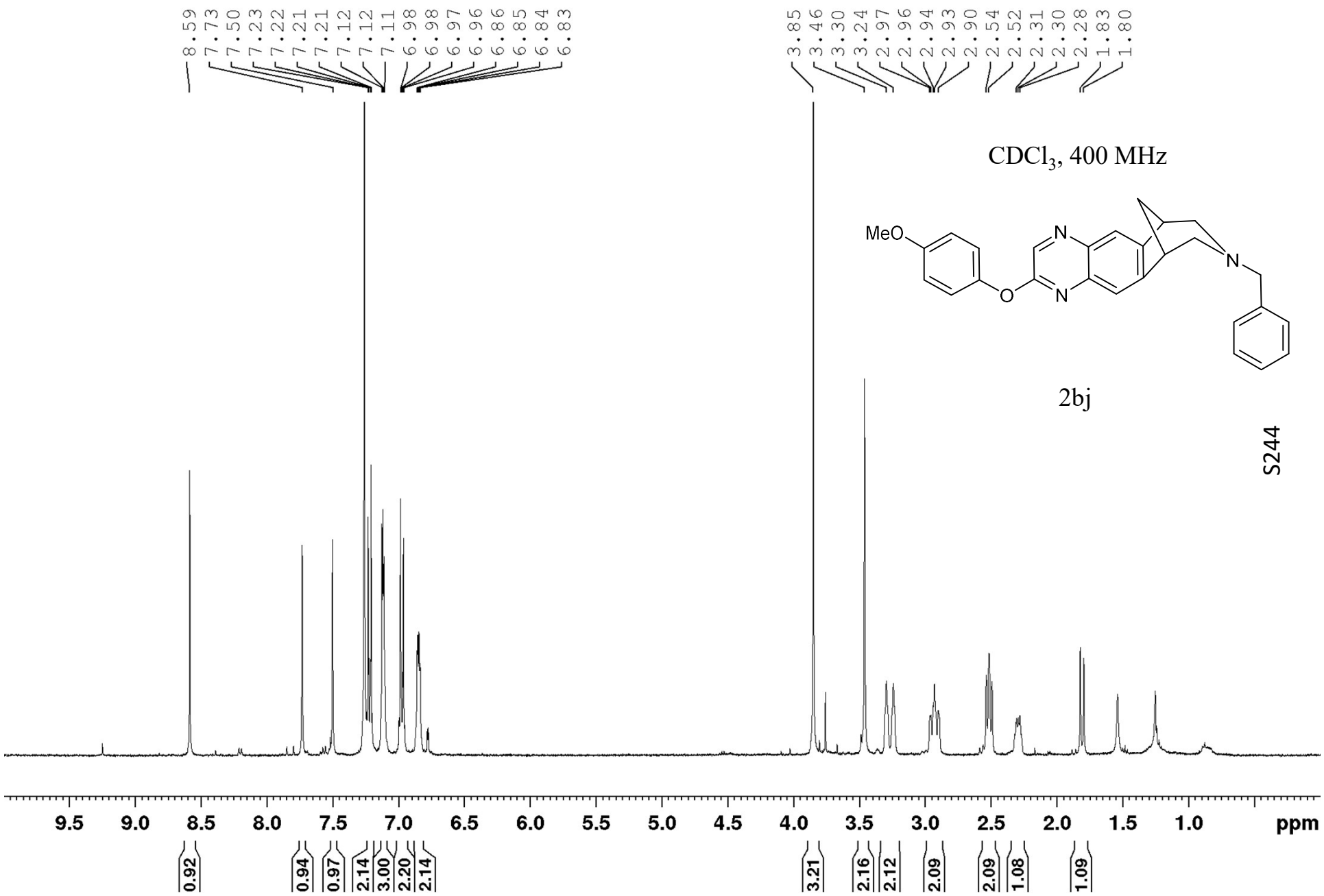

169.7
161.7
154.9
150.2
148.3
144.1
136.3
134.5
130.0
127.3
126.9
123.3
100.9
77.3
77.0
76.7
37.9
32.1
CDCl3, 100 MHz
Me
N
N
N
S
N
2bg
S239
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

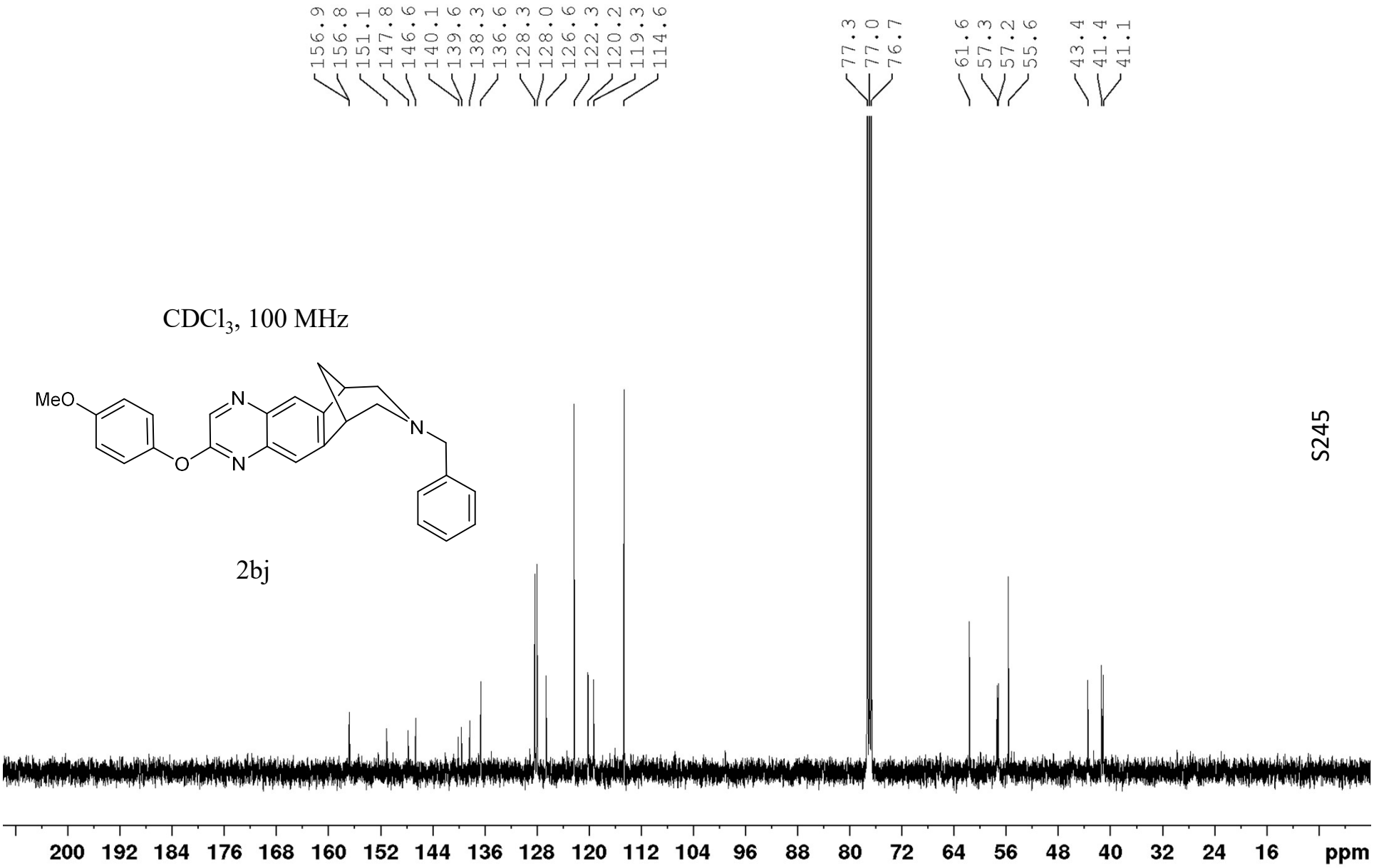

8.36
8.34
7.78
7.77
7.76
7.76
7.46
7.45
7.44
7.44
7.26
7.08
7.07
7.06
7.06
6.94
6.94
6.93
6.92
6.54
6.52
6.51
5.42
3.82
CDCl3, 400 MHz
OMe
O
N
N
O
O
N
2bh
S240
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.24
3.30
1.95
1.98
1.02
0.89
2.03
3.09

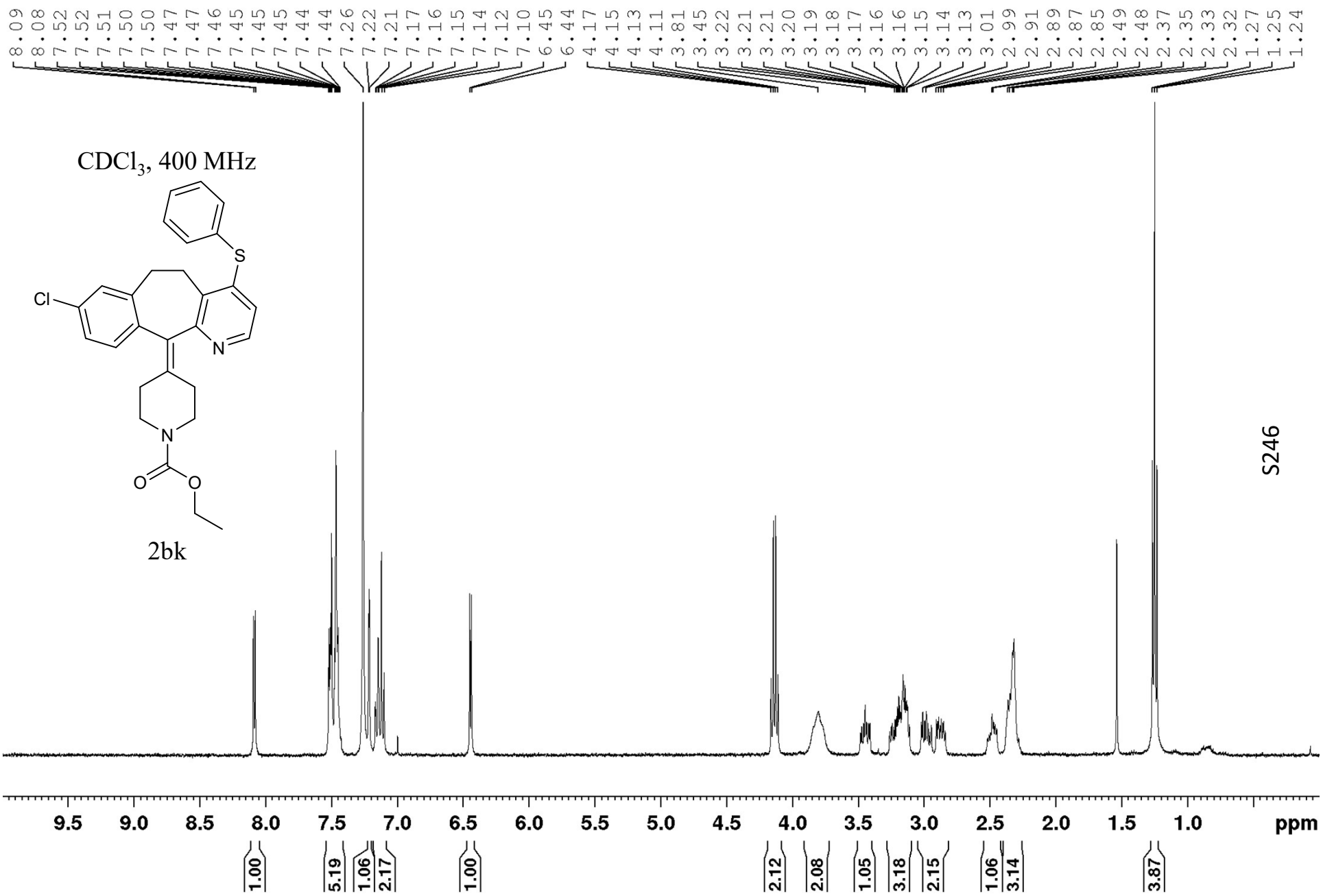

171.6
167.9
164.2
162.4
160.3
157.4
145.5
130.0
128.9
126.8
122.4
114.8
102.3
102.2
101.8
77.3
77.0
76.7
59.7
55.6
CDCl3, 100 MHz
OMe
O
N
N
O
O
N
2bh
S241
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

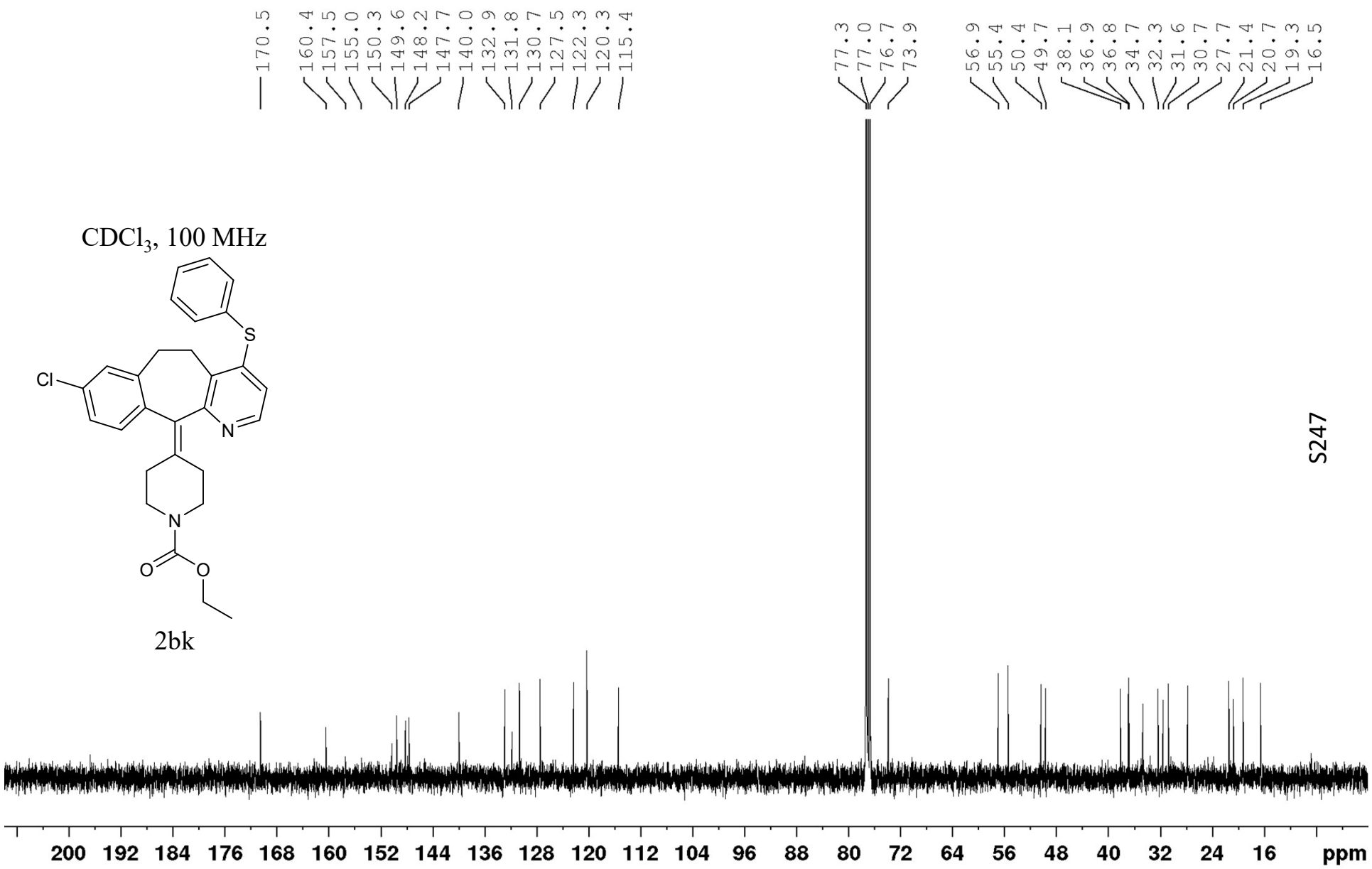

7.31
7.30
7.29
7.28
7.27
7.26
7.06
7.06
7.04
7.03
7.02
7.02
7.02
7.01
7.01
6.97
6.96
6.95
6.95
6.94
6.93
6.92
6.92
6.91
6.90
6.89
6.53
6.53
6.52
6.51
6.12
6.11
5.59
5.58
5.56
5.55
5.54
5.52
4.16
4.14
4.13
4.12
4.06
4.05
4.04
4.02
3.82
1.46
1.44
CDCl3, 400 MHz
MeO
O
Me
N
O
O
O
2bi
S242
9.5
9.0
8.5
8.0
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
1.00
1.99
2.99
7.95
0.96
0.95
1.00
1.04
1.02
3.01
3.20

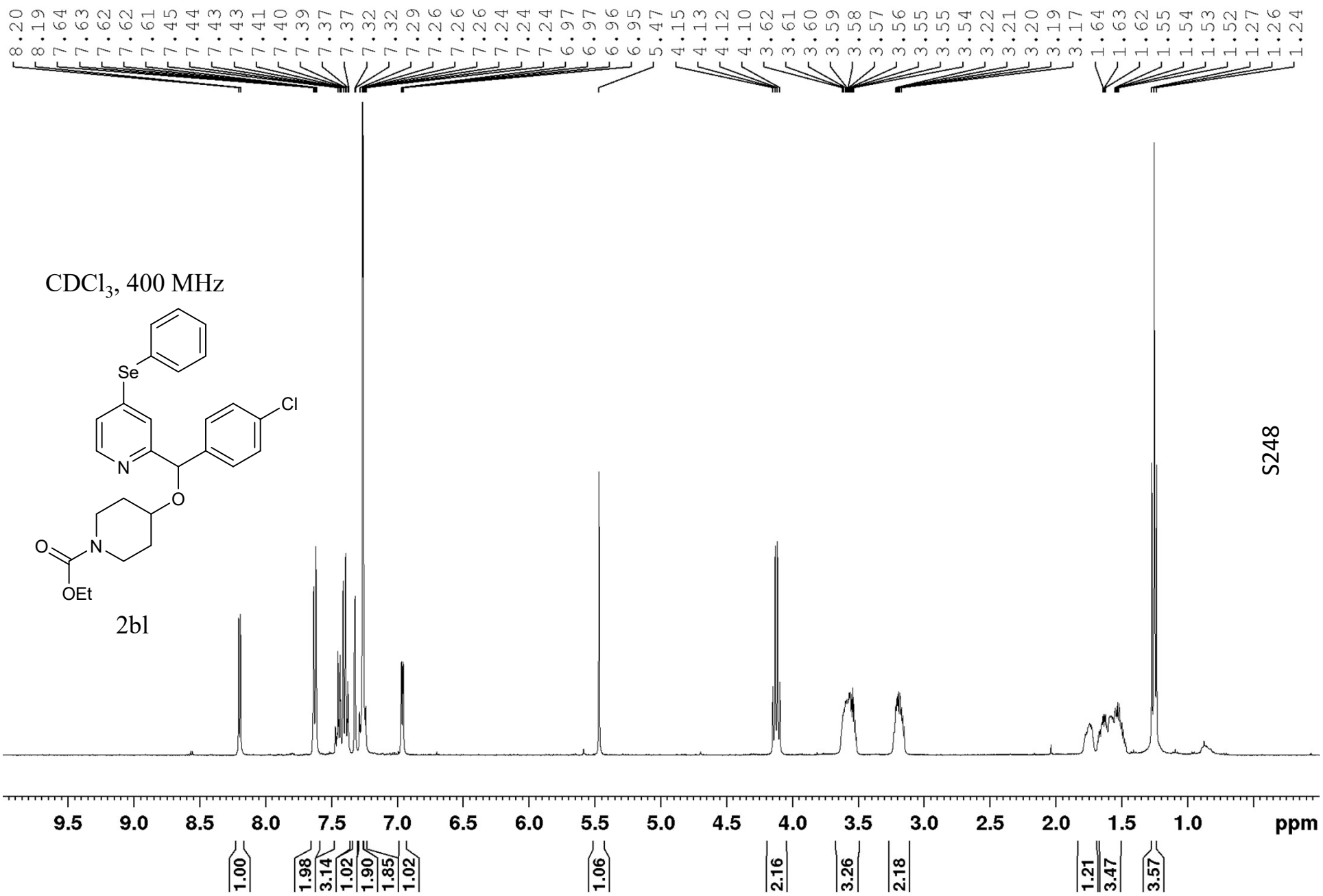

167.8
165.0
158.5
157.1
155.2
150.3
147.8
147.3
129.6
122.4
122.1
120.7
117.6
115.7
115.1
107.0
97.4
77.3
77.0
76.7
71.0
69.6
55.6
17.0
CDCl3, 100 MHz
MeO
O
Me
N
O
O
O
2bi
S243
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

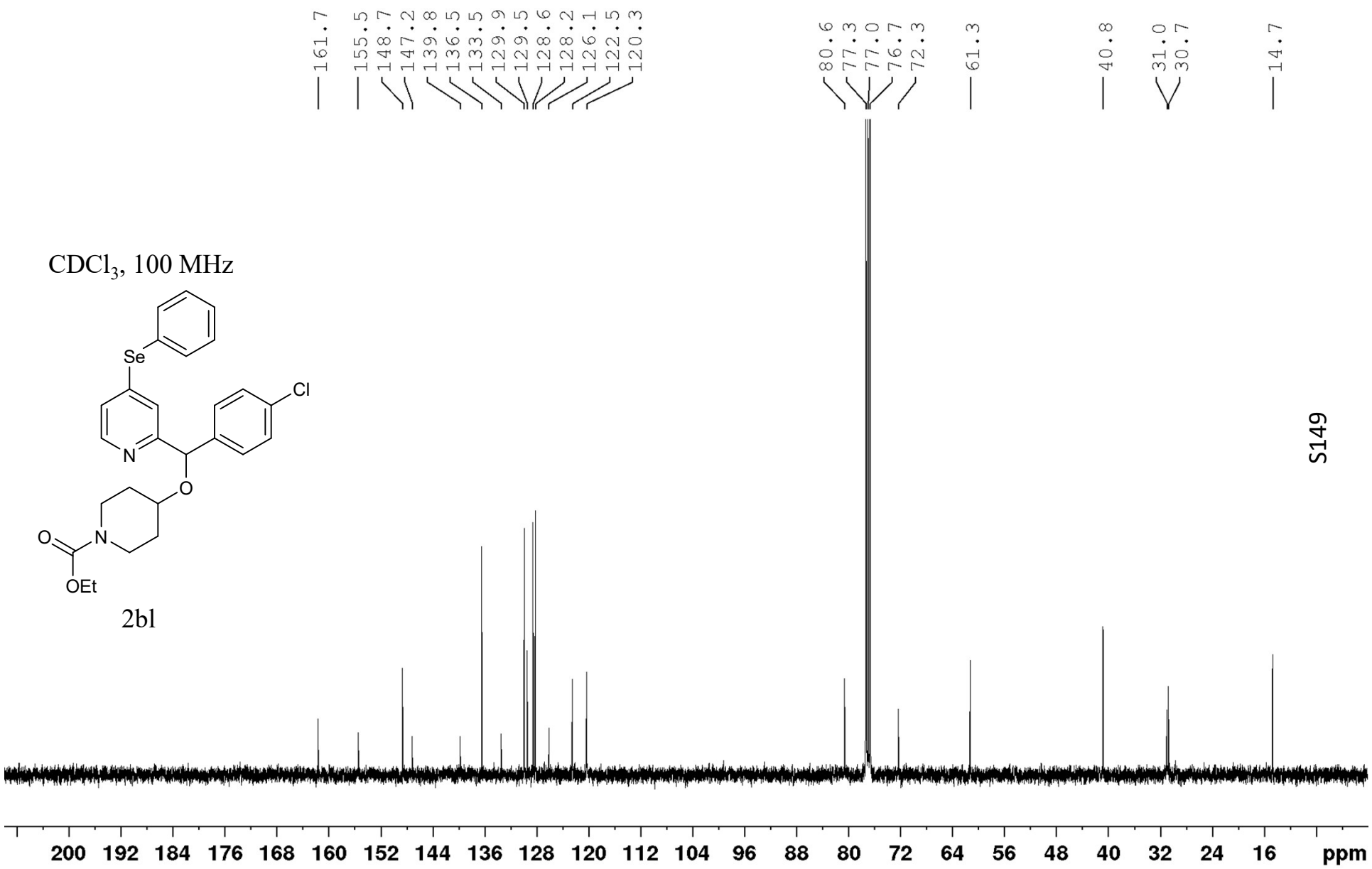

8.59
7.73
7.50
7.23
7.22
7.21
7.21
7.12
7.12
7.11
6.98
6.98
6.97
6.96
6.86
6.85
6.84
6.83
3.85
3.46
3.30
3.24
2.97
2.96
2.94
2.93
2.90
2.54
2.52
2.31
2.30
2.28
1.83
1.80
CDCl3, 400 MHz
MeO
N
N
O
N
2bj
S244
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.92
0.94
0.97
2.14
3.00
2.20
2.14
3.21
2.16
2.12
2.09
2.09
1.08
1.09

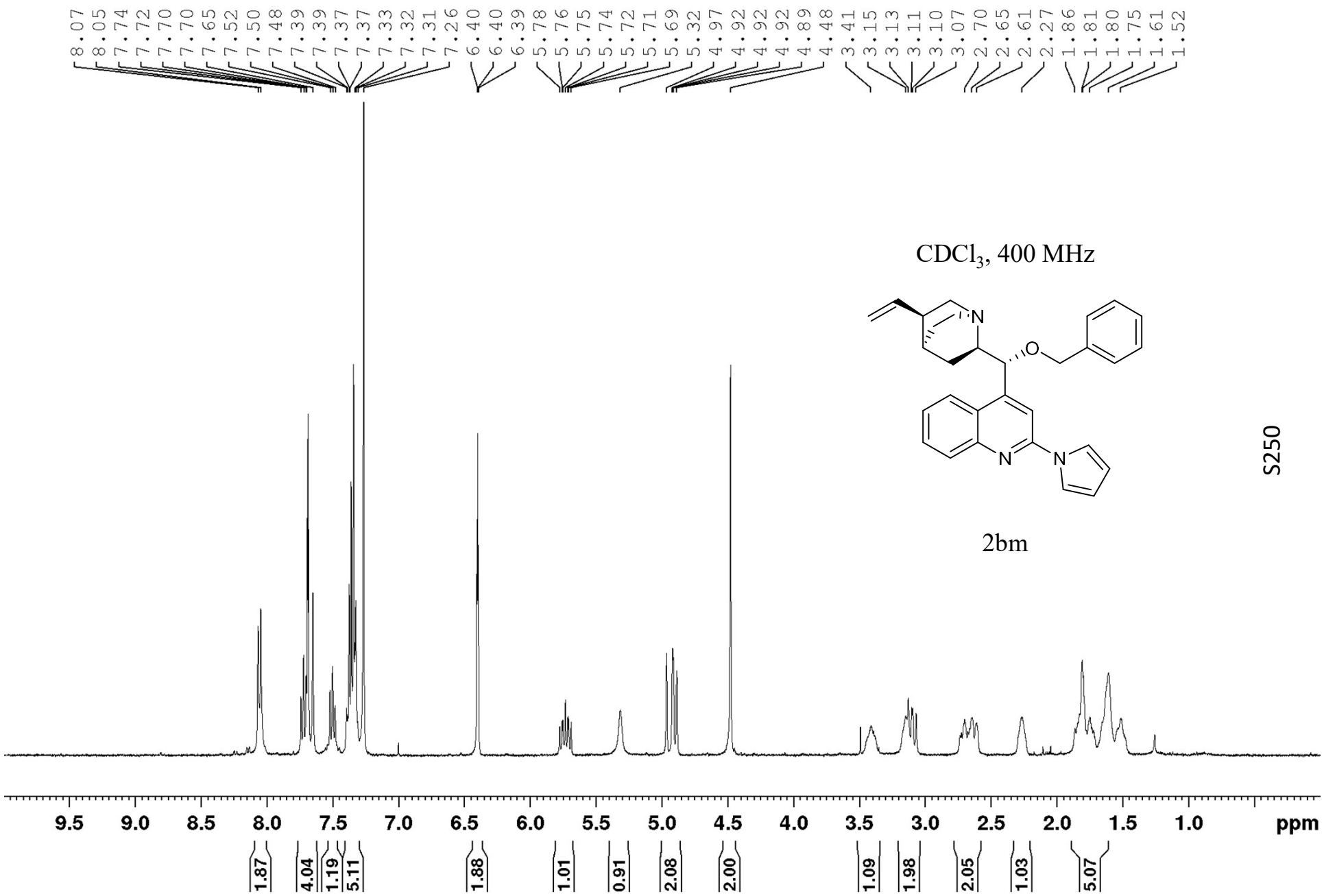

156.9
156.8
151.1
147.8
146.6
140.1
139.6
138.3
136.6
128.3
128.0
126.6
122.3
120.2
119.3
114.6
77.3
77.0
76.7
61.6
57.3
57.2
55.6
43.4
41.4
41.1
CDCl3, 100 MHz
MeO
N
N
O
N
2bj
S245
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

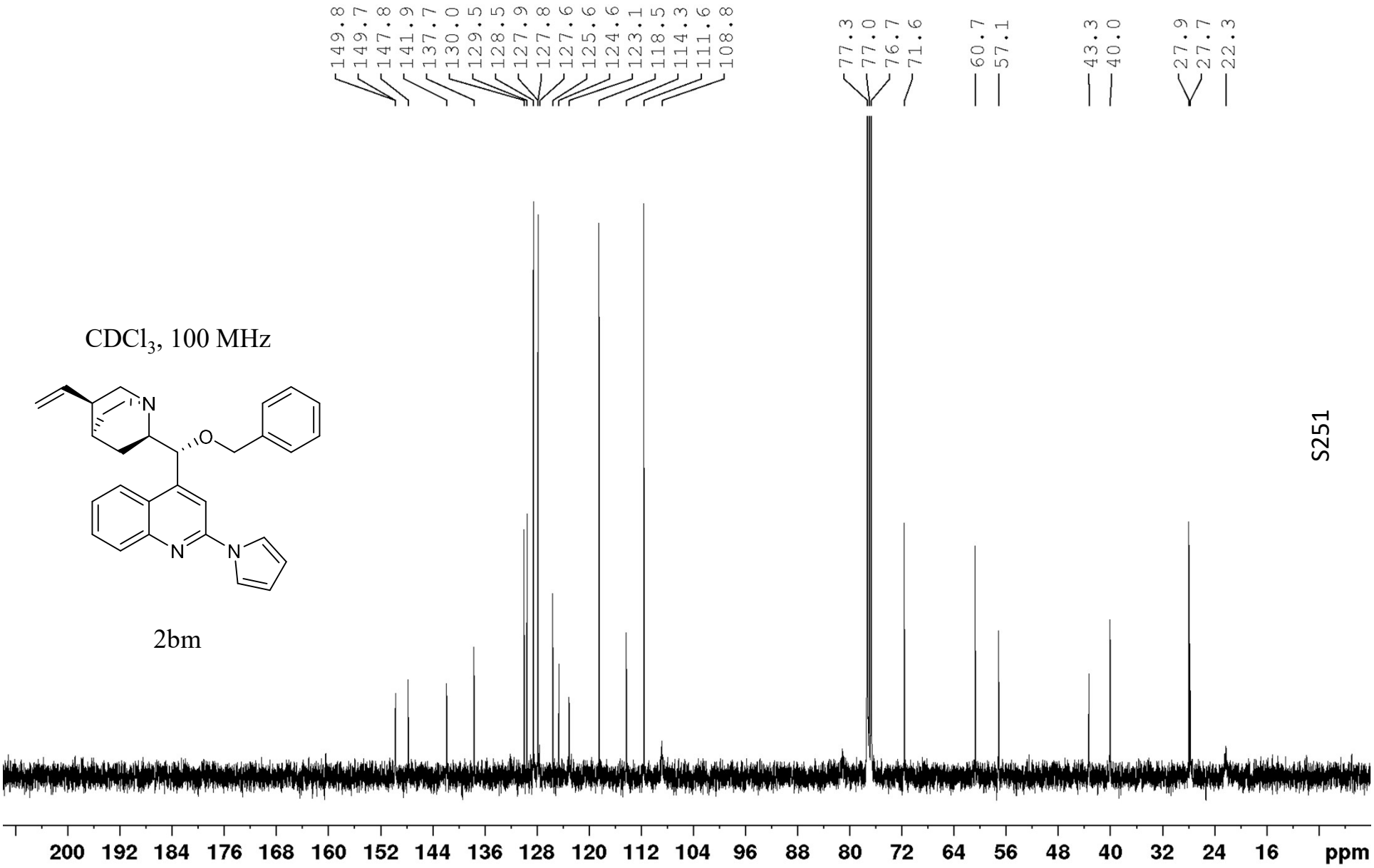

8.09
8.08
7.52
7.52
7.51
7.50
7.50
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.44
7.26
7.22
7.21
7.17
7.16
7.15
7.14
7.12
7.10
6.45
6.44
4.17
4.15
4.13
4.11
3.81
3.45
3.22
3.21
3.21
3.20
3.19
3.18
3.17
3.16
3.16
3.15
3.14
3.13
3.01
2.99
2.91
2.89
2.87
2.85
2.49
2.48
2.37
2.35
2.33
2.32
1.27
1.25
1.24
CDCl3, 400 MHz
S
Cl
N
N
O
O
2bk
S246
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
1.00
5.19
1.06
2.17
1.00
2.12
2.08
1.05
3.18
2.15
1.06
3.14
3.87

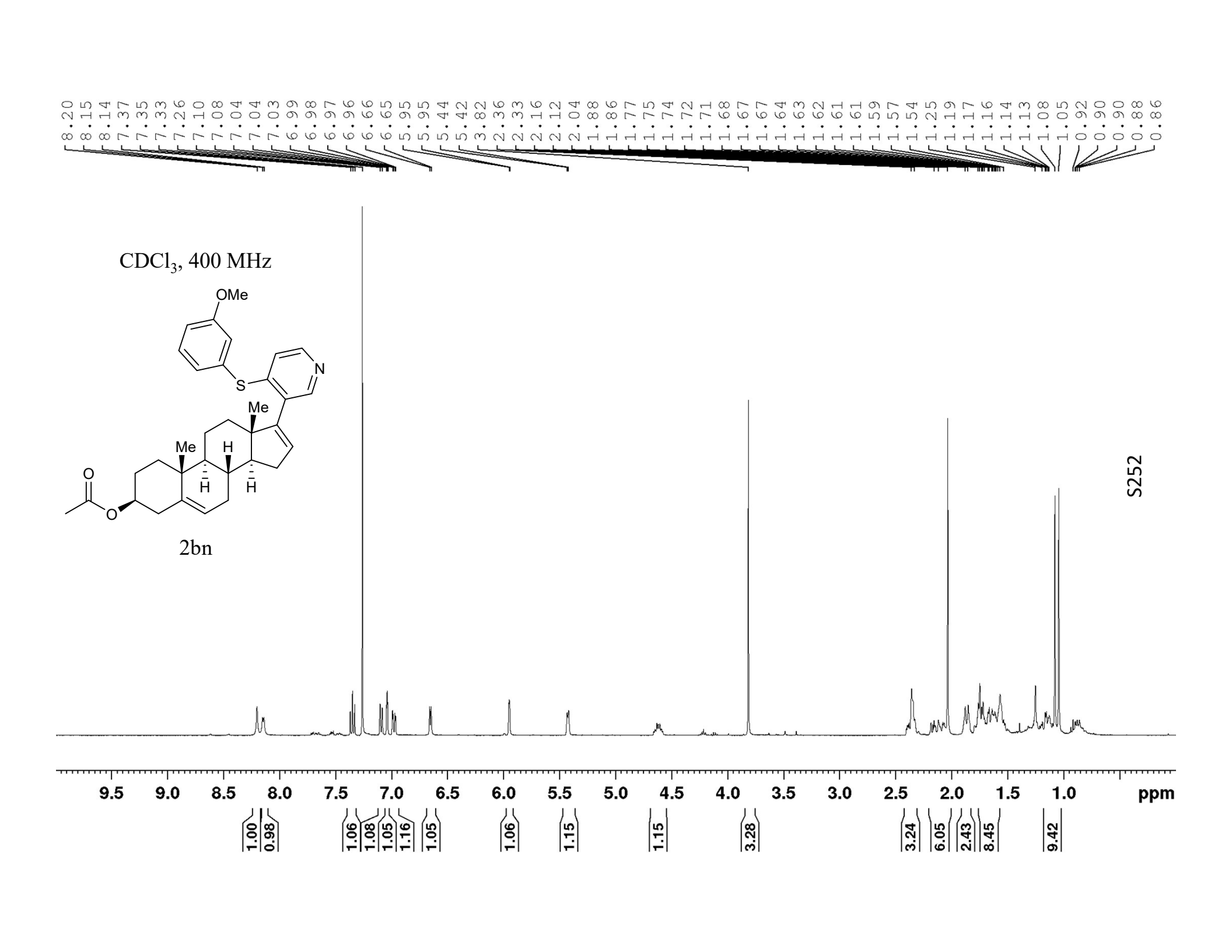

170.5
160.4
157.5
155.0
150.3
149.6
148.2
147.7
140.0
132.9
131.8
130.7
127.5
122.3
120.3
115.4
77.3
77.0
76.7
73.9
56.9
55.4
50.4
49.7
38.1
36.9
36.8
34.7
32.3
31.6
30.7
27.7
21.4
20.7
19.3
16.5
CDCl3, 100 MHz
S
Cl
N
N
O
O
2bk
S247
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

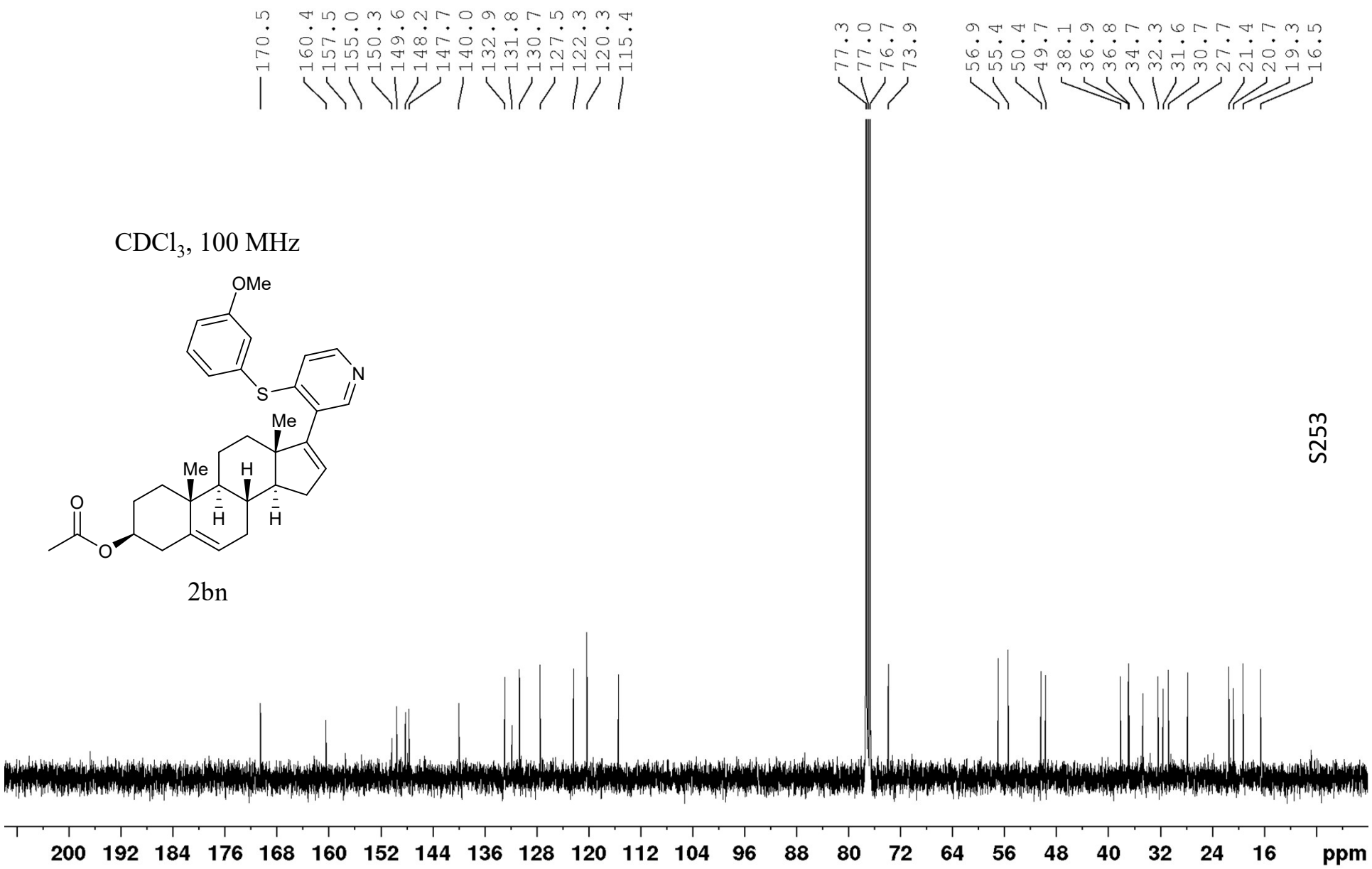

8.20
8.19
7.64
7.63
7.62
7.62
7.61
7.45
7.44
7.43
7.43
7.41
7.40
7.39
7.37
7.37
7.32
7.32
7.29
7.26
7.26
7.26
7.24
7.24
7.24
6.97
6.97
6.96
6.95
5.47
4.15
4.13
4.12
4.10
3.62
3.61
3.60
3.59
3.58
3.57
3.56
3.55
3.55
3.54
3.22
3.21
3.20
3.19
3.17
1.64
1.63
1.62
1.55
1.54
1.53
1.52
1.27
1.26
1.24
CDCl3, 400 MHz
Se
Cl
N
O
O
N
OEt
2bl
S248
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
1.00
1.98
3.14
1.02
1.90
1.85
1.02
1.06
2.16
3.26
2.18
1.21
3.47
3.57

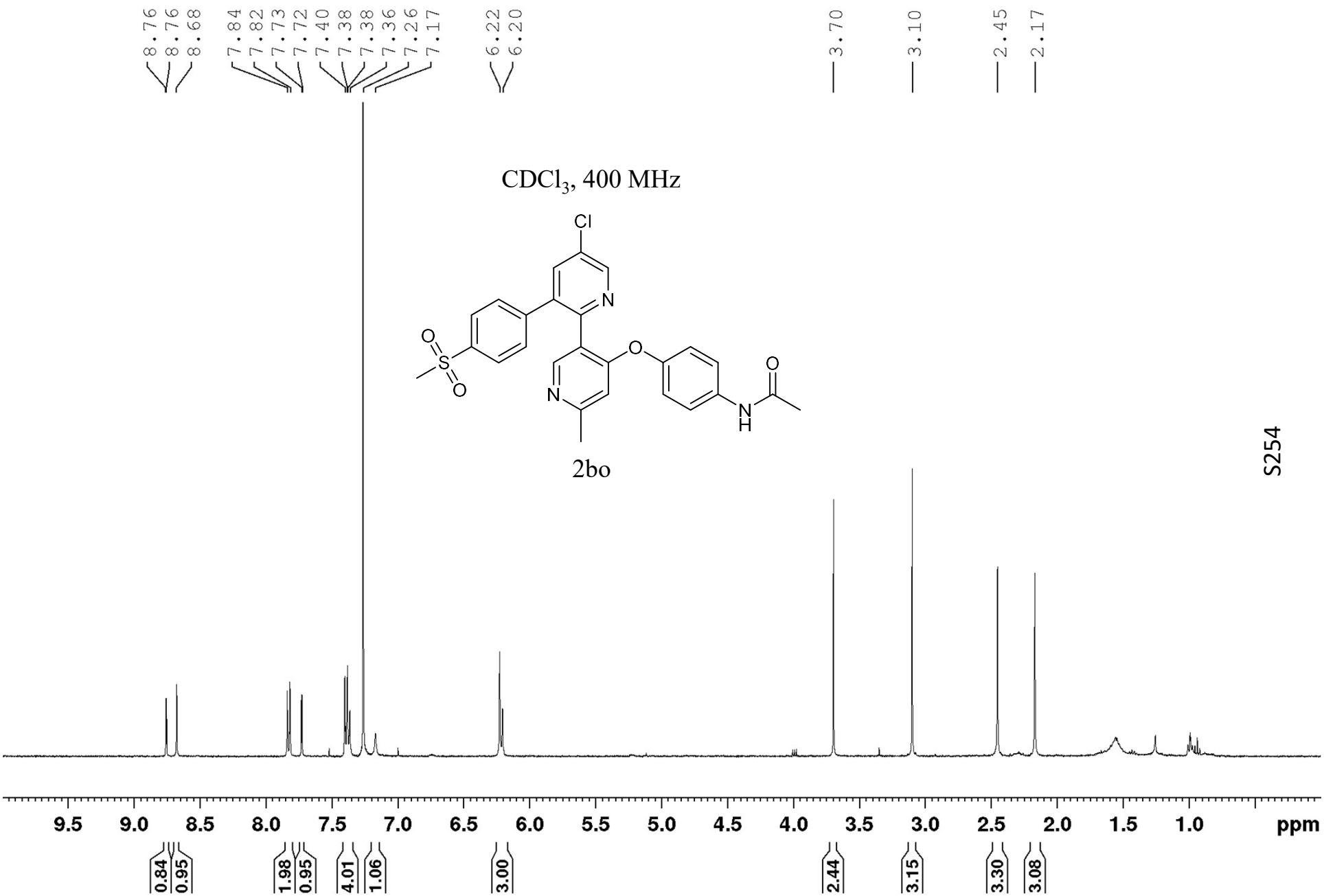

161.7
155.5
148.7
147.2
139.8
136.5
133.5
129.9
129.5
128.6
128.2
126.1
122.5
120.3
80.6
77.3
77.0
76.7
72.3
61.3
40.8
31.0
30.7
14.7
CDCl3, 100 MHz
Se
Cl
N
O
O
N
OEt
2bl
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

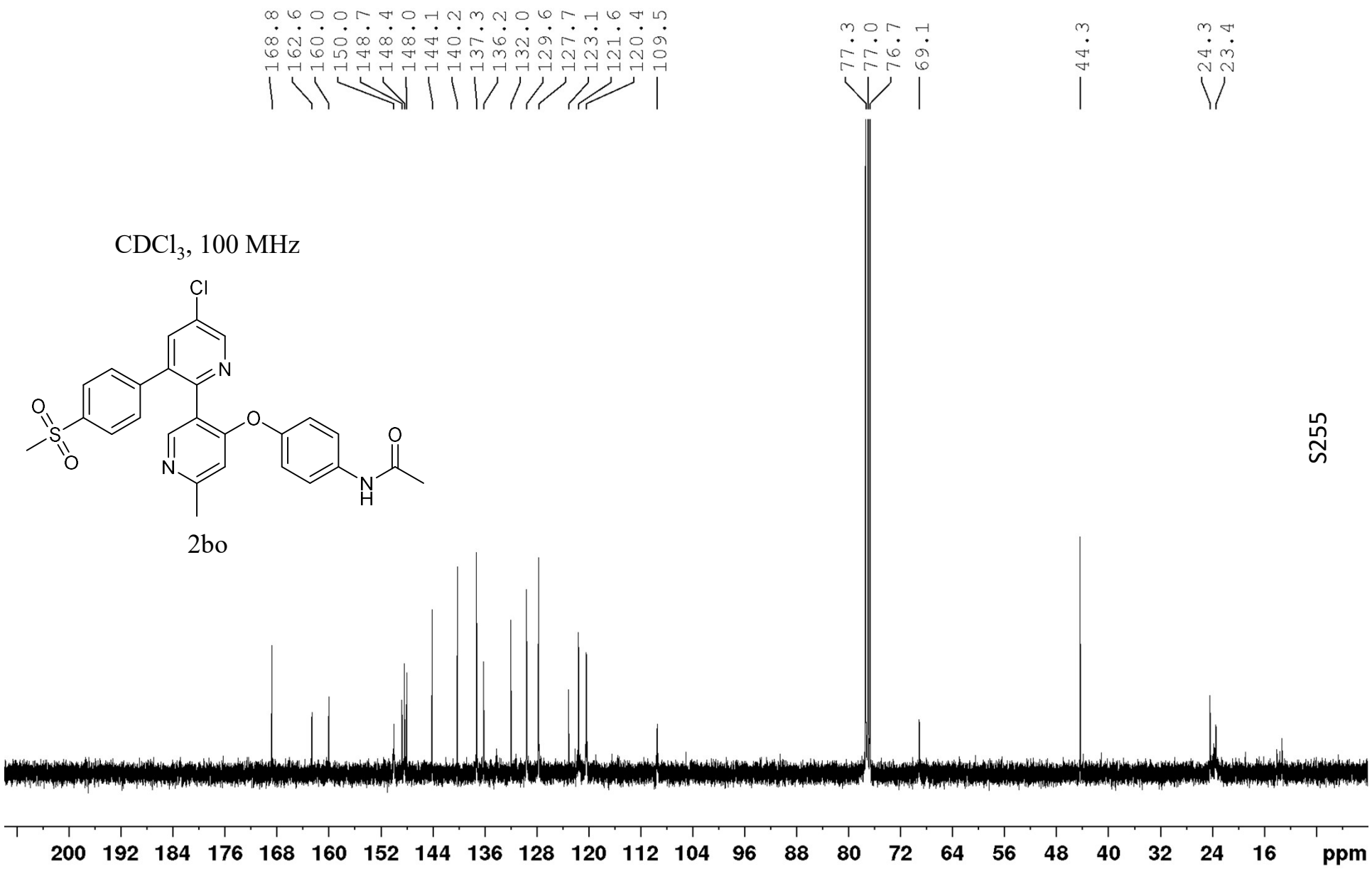

8.07
8.05
7.74
7.72
7.70
7.70
7.65
7.52
7.50
7.48
7.39
7.39
7.37
7.37
7.33
7.32
7.31
7.26
6.40
6.40
6.39
5.78
5.76
5.75
5.74
5.72
5.71
5.69
5.32
4.97
4.92
4.92
4.92
4.89
4.48
3.41
3.15
3.13
3.11
3.10
3.07
2.70
2.65
2.61
2.27
1.86
1.81
1.80
1.75
1.61
1.52
CDCl3, 400 MHz
N
O
N
N
2bm
S250
9.5
9.0
8.5
8.0
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
1.87
4.04
1.19
5.11
1.88
1.01
0.91
2.08
2.00
1.09
1.98
2.05
1.03
5.07

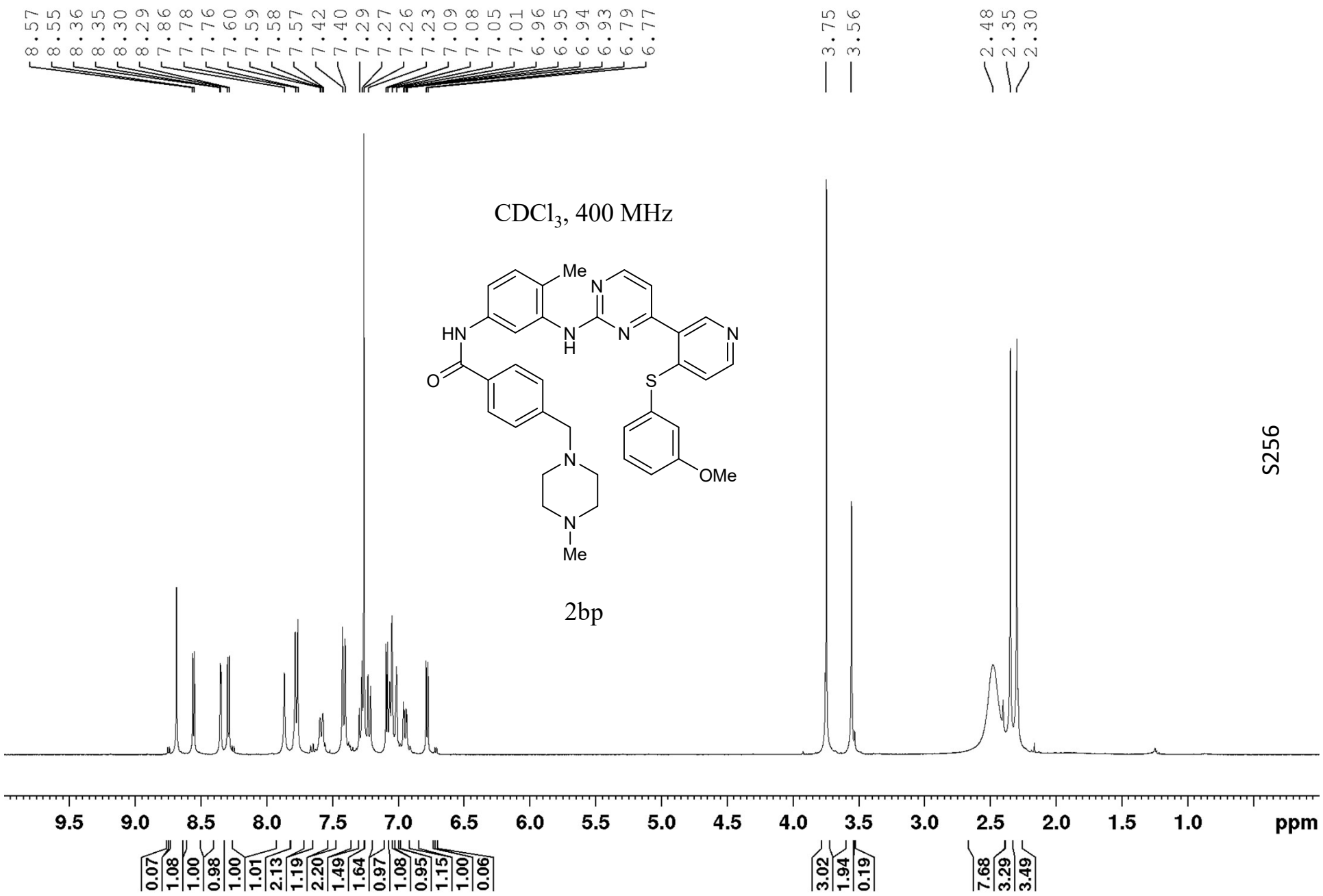

149.8
149.7
147.8
141.9
137.7
130.0
129.5
128.5
127.9
127.8
127.6
125.6
124.6
123.1
118.5
114.3
111.6
108.8
77.3
77.0
76.7
71.6
60.7
57.1
43.3
40.0
27.9
27.7
22.3
CDCl3, 100 MHz
N
O
N
N
2bm
S251
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

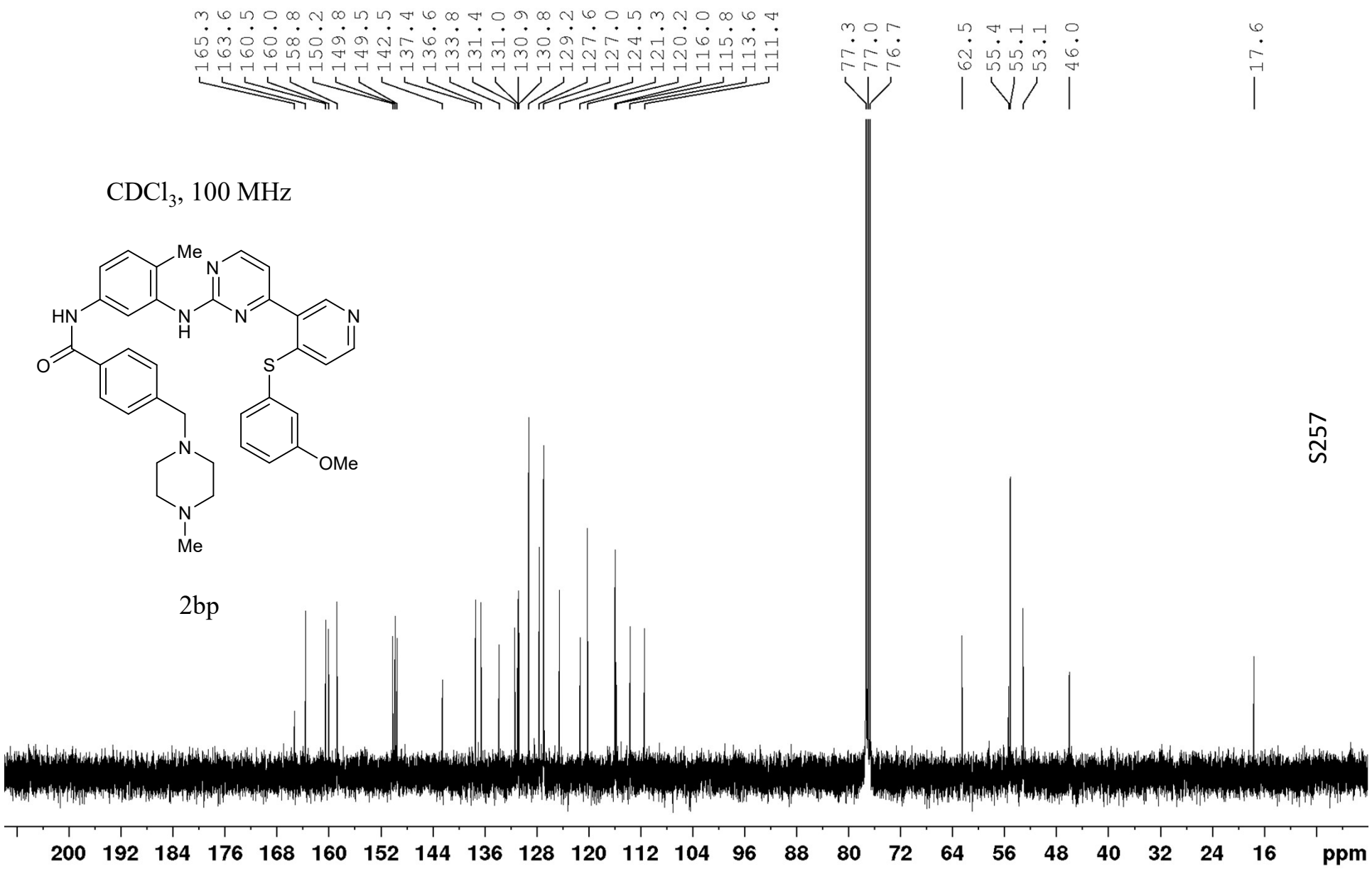

8.20
8.15
8.14
7.37
7.35
7.33
7.26
7.10
7.08
7.04
7.04
7.03
6.99
6.98
6.97
6.96
6.66
6.65
5.95
5.95
5.44
5.42
3.82
2.36
2.33
2.16
2.12
2.04
1.88
1.86
1.77
1.75
1.74
1.72
1.71
1.68
1.67
1.67
1.64
1.63
1.62
1.61
1.61
1.59
1.57
1.54
1.25
1.19
1.17
1.16
1.14
1.13
1.08
1.05
0.92
0.90
0.90
0.88
0.86
CDCl3, 400 MHz
OMe
N
S
Me
Me
H
H
H
O
O
2bn
S252
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
1.00
0.98
1.06
1.08
1.05
1.16
1.05
1.06
1.15
1.15
3.28
3.24
6.05
2.43
8.45
9.42

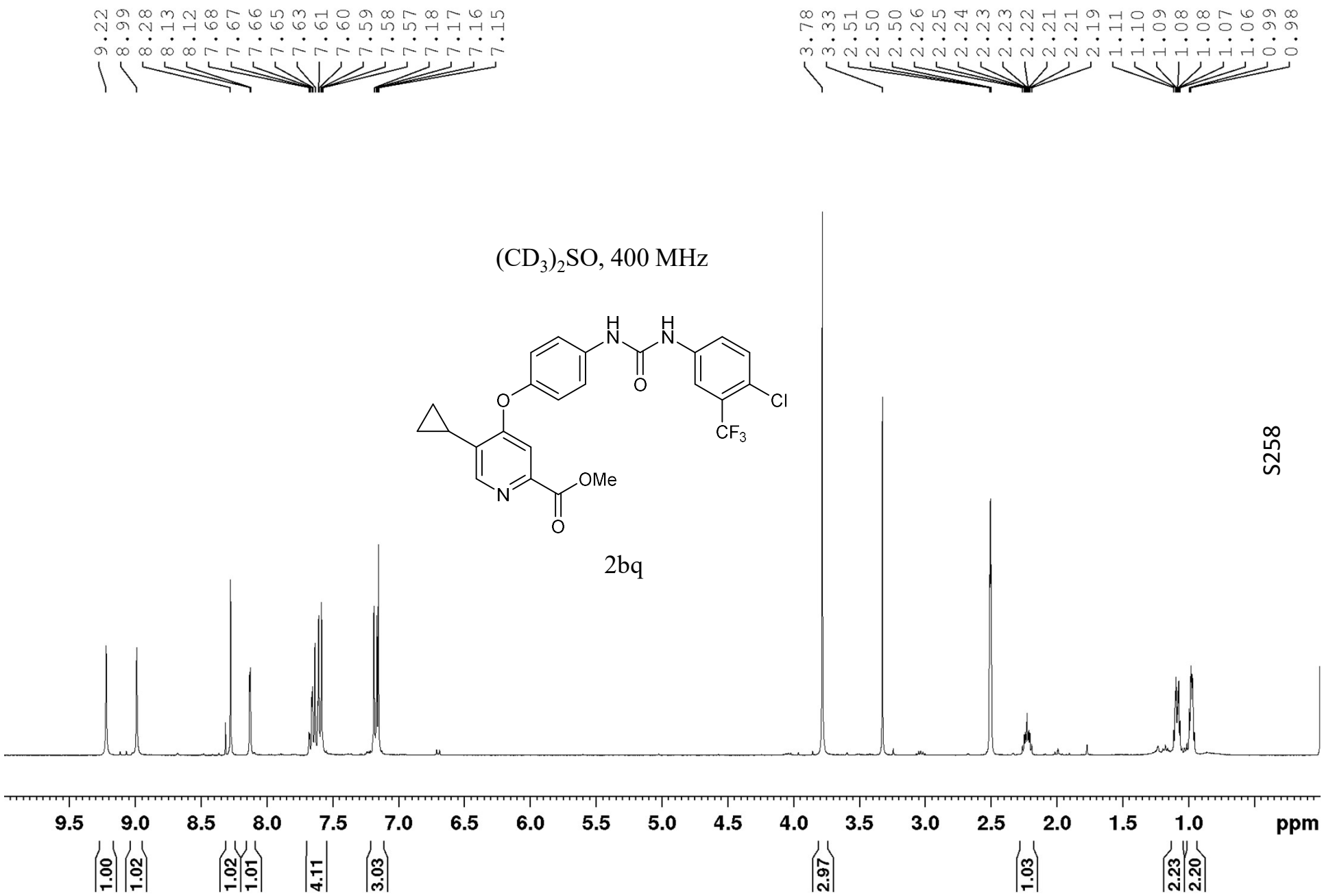

170.5
160.4
157.5
155.0
150.3
149.6
148.2
147.7
140.0
132.9
131.8
130.7
127.5
122.3
120.3
115.4
77.3
77.0
76.7
73.9
56.9
55.4
50.4
49.7
38.1
36.9
36.8
34.7
32.3
31.6
30.7
27.7
21.4
20.7
19.3
16.5
CDCl3, 100 MHz
OMe
S
N
Me
Me
H
H
H
O
O
2bn
S253
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm

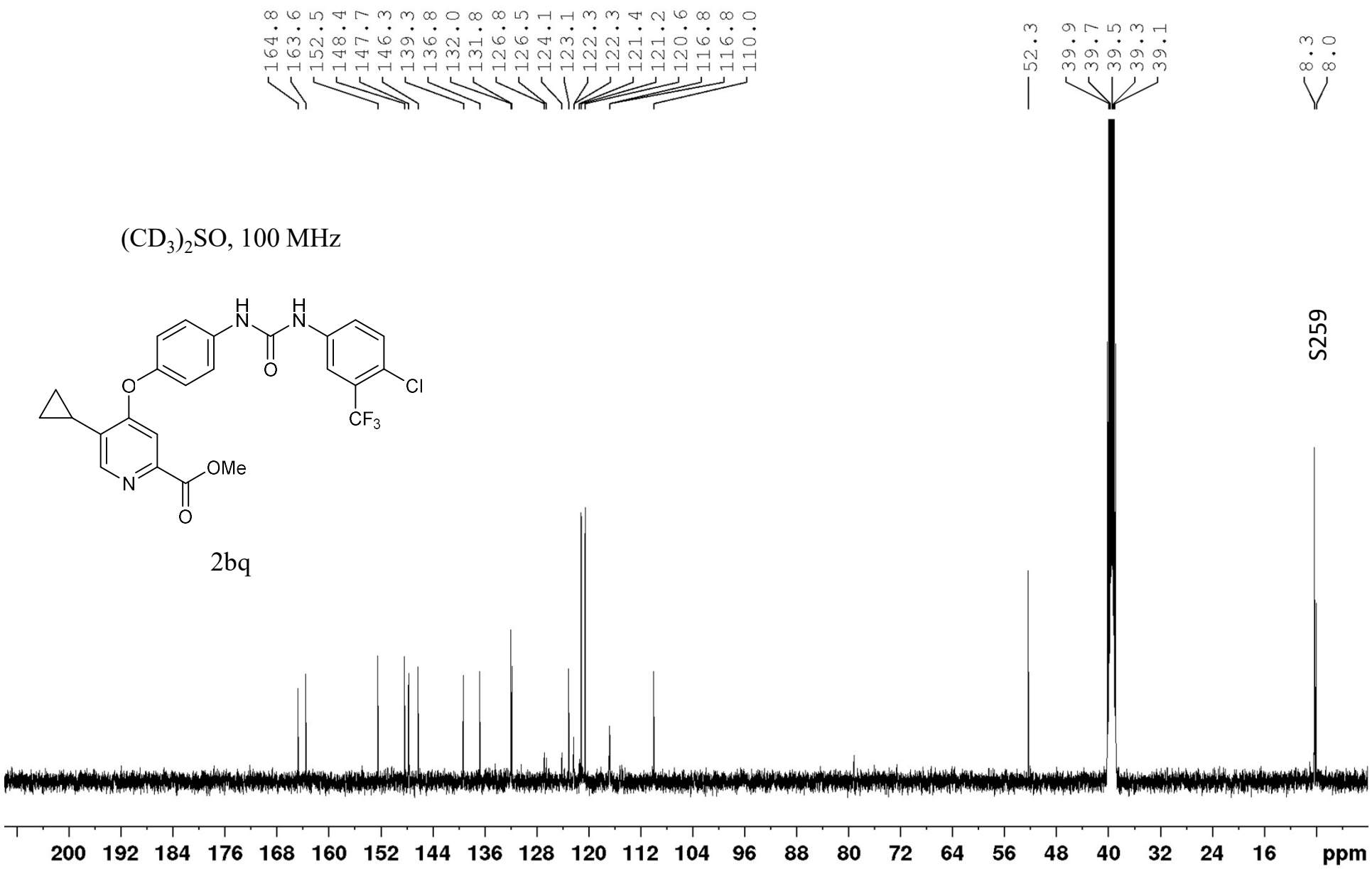

8.76
8.76
8.68
7.84
7.82
7.73
7.72
7.40
7.38
7.38
7.36
7.26
7.17
6.22
6.20
3.70
3.10
2.45
2.17
CDCl3, 400 MHz
Cl
N
O
S
O
O
N
O
N
H
2bo
S254
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.84
0.95
1.98
0.95
4.01
1.06
3.00
2.44
3.15
3.30
3.08

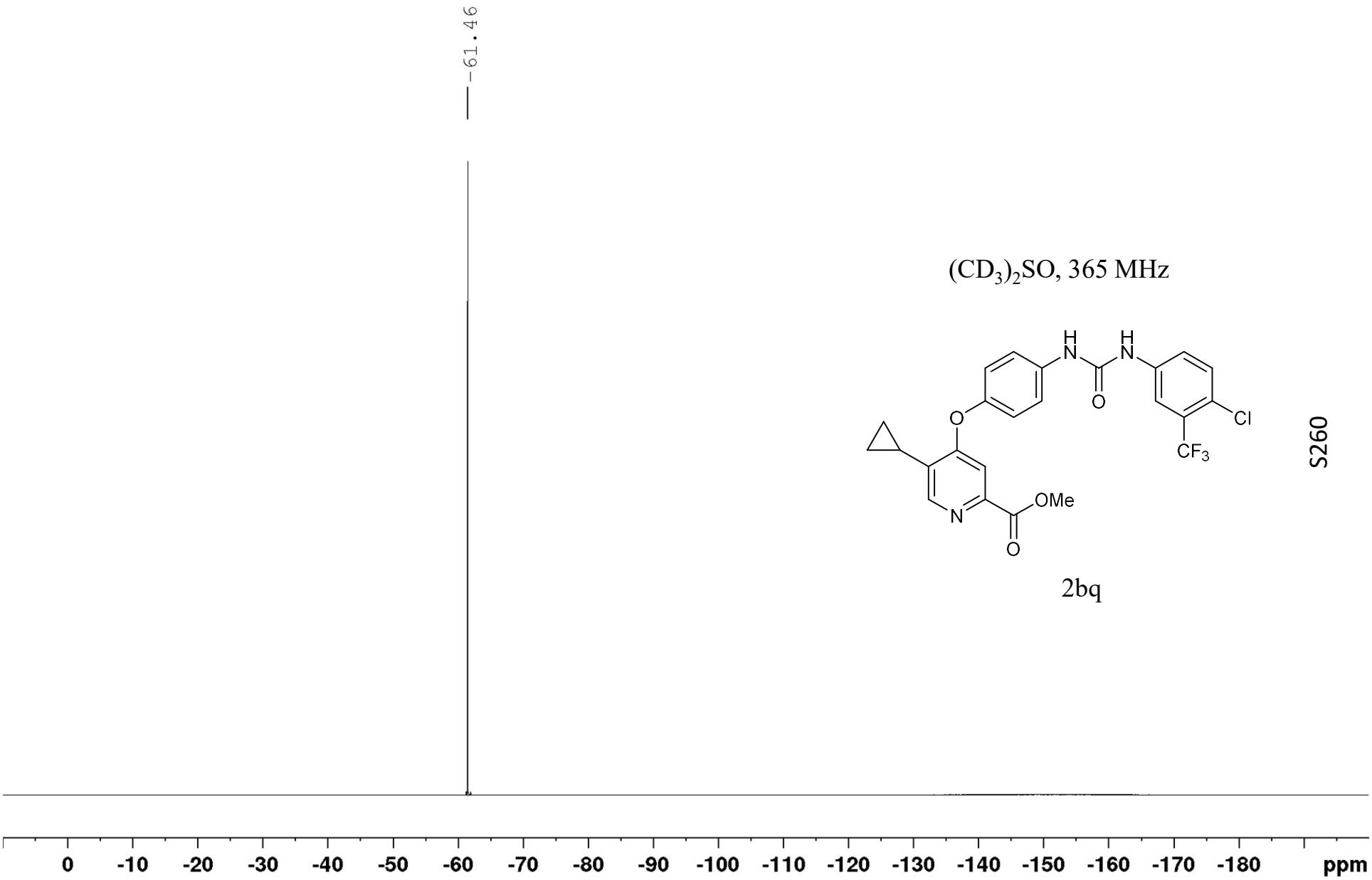

168.8
162.6
160.0
150.0
148.7
148.4
148.0
144.1
140.2
137.3
136.2
132.0
129.6
127.7
123.1
121.6
120.4
109.5
77.3
77.0
76.7
69.1
44.3
24.3
23.4
CDCl3, 100 MHz
Cl
N
O
S
O
O
N
O
N
H
2bo
S255
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


8.57
8.55
8.36
8.35
8.30
8.29
7.86
7.78
7.76
7.60
7.59
7.58
7.57
7.42
7.40
7.29
7.27
7.26
7.23
7.09
7.08
7.05
7.01
6.96
6.95
6.94
6.93
6.79
6.77
3.75
3.56
2.48
2.35
2.30
CDCl3, 400 MHz
Me
N
HN
N
H
N
N
O
S
N
OMe
N
Me
2bp
S256
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
0.07
1.08
1.00
0.98
1.00
1.01
2.13
1.19
2.20
1.49
1.64
0.97
1.08
0.95
1.15
1.00
0.06
3.02
1.94
0.19
7.68
3.29
3.49


165.3
163.6
160.5
160.0
158.8
150.2
149.8
149.5
142.5
137.4
136.6
133.8
131.4
131.0
130.9
130.8
129.2
127.6
127.0
124.5
121.3
120.2
116.0
115.8
113.6
111.4
77.3
77.0
76.7
62.5
55.4
55.1
53.1
46.0
17.6
CDCl3, 100 MHz
Me
N
HN
N
H
N
N
O
S
N
OMe
N
Me
2bp
S257
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm


9.22
8.99
8.28
8.13
8.12
7.68
7.67
7.66
7.65
7.63
7.61
7.60
7.59
7.58
7.57
7.18
7.17
7.16
7.15
3.78
3.33
2.51
2.50
2.50
2.26
2.25
2.24
2.23
2.23
2.22
2.21
2.21
2.19
1.11
1.10
1.09
1.08
1.08
1.07
1.06
0.99
0.98
(CD3)2SO, 400 MHz
H
N
H
N
O
O
Cl
CF3
OMe
N
O
2bq
S258
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
1.00
1.02
1.02
1.01
4.11
3.03
2.97
1.03
2.23
2.20


164.8
163.6
152.5
148.4
147.7
146.3
139.3
136.8
132.0
131.8
126.8
126.5
124.1
123.1
122.3
122.3
121.4
121.2
120.6
116.8
116.8
110.0
52.3
39.9
39.7
39.5
39.3
39.1
8.3
8.0
S259
(CD3)2SO, 100 MHz
H
N
H
N
O
O
Cl
CF3
OMe
N
O
2bq
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 ppm



$(CD_3)_2SO$, 365 MHz

2bq